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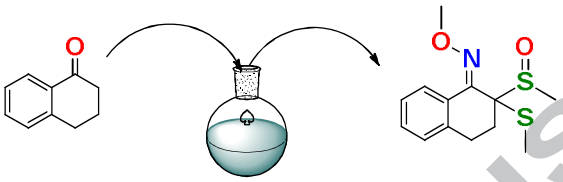

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Insights for diastereoselective synthesis of cyclic α-sulfinyl and sulfanyl oximes

Gislaine Aparecida Honorato[a], Ricardo Vieira de Lima[a], Bhaskar Reddy Manda[b], Derisvaldo Rosa Paiva[c], Tairine Pimentel[b] and Roberto da Silva Gomes[a,b]*

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ABSTRACT

The comparison in several reaction conditions for synthesis of nonracemic α-methylsulfinylation of 3,4-dihydronaphthalen-1(2*H*)-one was achieved. The sulfanylation reactions of 3,4-dihydronaphthalen-1(2*H*)-one-*O*-methyloxime and 2-(methylsulfinyl)-3,4-dihydronaphthalen-1(2*H*)-one-*O*-methyloxime by homogenous reaction medium are reported. The products were obtained in good yields and de. The yields, diastereoselectivity and theoretical calculations to all obtained compounds to support the experimental data are compared and discussed.

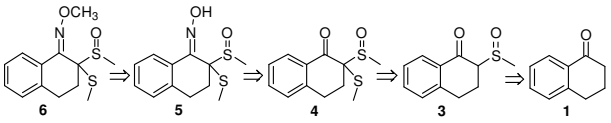
Introduction of sulfur functionality into organic molecules is an important process for the drug development[1-5] and fine chemical synthesis[6-8]. The sulfanylation of β-ketosulfoxides have shown to be important intermediates owing to fact that the obtained sulfoxides can be used as chiral auxiliaries in asymmetric synthesis[9-11], as efficient stereoselective inductors[12-14], in Diels-Alder reaction[15-17] in the C-C bond formation reactions,[18-21] and drug candidates[22,23].

Literature reports of both homogeneous and heterogeneous transfer sulfanylation methods are comparable in terms of yield and diastereoselectivity[24-26]. Generally, the β-ketosulfoxides can be achieved by the reaction between a chiral sufinyl anion and an ester,[24b] however when a cyclic ketone is used, the β-ketosulfoxides are not accessible.

In a previous communication, we reported the sulfanylation of 2-(methylsulfinyl)-2,3-dihydro-1*H*-inden-1-one by phase transfer catalysis using benzyltriethylammonium chloride (TEBAC) as catalyst as well as in homogeneous conditions furnish the products in good yield and in high disatereoisomeric excess (de).[27]

As part of our general program of exploring the scope of sulfanylation by the utilization of either PTC or homogeneous method led us to investigate the sulfanylation of 3,4-dihydronaphthalen-1(2*H*)-one as well as 3,4-dihydronaphthalen-1(2*H*)-one-*O*-methyl oxime. In this context, an efficient nonracemic synthetic route for 2-(methylsulfinyl)-2-(methylsulfanyl)-3,4-dihydronaphthalen-1(2*H*)–one-*O*-methyl oxime is reported.

In contribution to synthetically useful building blocks, Scheme 1 illustrates the retrosynthetic analysis of 2-(methylsulfinyl)-2-(methylsulfanyl)-3,4-dihydronaphthalen-1(2*H*)-one-*O*-methyl oxime **6**. The target compound was planned to be obtained by the below disconnection, starting from a simpler and inexpensive starting material.

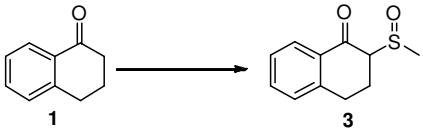


Scheme 1. Retrosynthesis of novel 2-(methylsulfinyl)-2-(methylsulfanyl)-3,4-dihydronaphthalen-1(2*H*)-one-*O*-methyl oxime **6**.

The compound **6** could be obtained from oxime **5**. The oxime **5** can be prepared from 2-sulfinyl-2-sulfanyl ketone **4**, which could be formed from α-sulfinyl ketone **3** which in turn could be prepared from the commercially available 3,4-dihydronaphthalen-1(2*H*)-one **1** as an inexpensive starting material.

Asymmetric oxidation of sulphides[29,30] by using of Sharpless reagent [titanium tetraisopropoxide (TTIP)], (*R,R*) diethyl tartrate (DET) and *tert*-butyl hydrogen peroxide (TBHP) was carried out, achieving **3** (Scheme 2, conditions a) with 50 % yield, 10% of ee and 50 % of de, calculated by ^{1}H NMR shifts of methylsulfinyl hydrogens by using Kagan's reagent between 3.85-3.87 ppm[31].

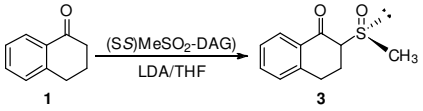
To improve the preparation of optically active **3**, a direct condensation of 3,4-dihydronaphthalen-1(2*H*)-one **1** with methylsulfinyl chloride as methysulfinyl donor with LDA as bulky base was performed (Scheme 2, conditions b).



Scheme 2: Synthetic method for the compound **3:** a) 1) $CH_3SSO_2CH_3$, LDA; 2) Ti[O(i-pr)]$_4$, (*R*,*R*)-DET, CH_2Cl_2, TBHP; b) CH_3SOCl, LDA, THF.

Our approach was diastereoselective and the yield was 67%, 10% ee and 71% de which was calculated from the relative integration of ^{1}H NMR signals corresponding to methylsulfinyl groups at δ 2.72 ppm and 2.96 ppm for the majority and minority, respectively, using Kagan´s reagent and this route showed to be better in comparison to that one described in the literature[26].

To obtain the diastereomerically enriched **3**, the reaction was performed employing 1,2:5,6-di-*O*-isopropylidene-α-*D*-glucofuranosyl-(-)-(S*S*)-methane-sulfinate ((S*S*)-MeSO$_2$-DAG) (Scheme 3) as chiral sulfinylating agent[10,11]. In this approach we obtained 72% yield, 11% of ee and 76% of de of (S*S*)-**3** as a mixture of epimers (7:3) providing a new stereogenic center of known absolute configuration (Scheme 3).



Scheme 3. New methylsulfinylation approach using ((S*S*)-MeSO$_2$-DAG) to obtain optically active **3**.

The influence of steric and electronic effects on the conformational properties are essential to rationalize the stereocontrol of this reaction considering both possibilities (S*S*-C2*R* or S*S*-C2*S*)-**3** for nucleophilic attack of **1**. Furthermore, aiming to confirm our stereochemical assignment of ^{1}H NMR spectra, a density functional theory (DFT) calculation was performed. Theoretical calculations for compound **3** indicates that the more stable (S*S*-C2*R*)-**3** (E_{rel}=0.00 kcal mol^{-1}; μ=2.77 *D*) *R*-configuration C2 displays the S=O (α= -77.1°) substituent in a *syn-periplanar* geometry with respect to the carbonyl group (Figure 1). This geometry allows the following short intramolecular contacts between the oppositely charged $O^{\delta-}(1)_{[CO]}\cdots S^{\delta+}(4)$; $O^{\delta-}(1)_{[CO]}\cdots H^{\delta+}$(both 15,16,17); $O^{\delta-}(1)_{[CO]}\cdots H^{\delta+}(26)$ and $O^{\delta-}(5)_{[SO]}\cdots H^{\delta+}(21)$ atoms, which are shorter than the sum of the van der Waals radii (ΣvdW) by Δl≅-0.01 Å, Δl≅-0.29 Å, Δl≅-0.27 Å and Δ≅-0.27 Å, respectively.

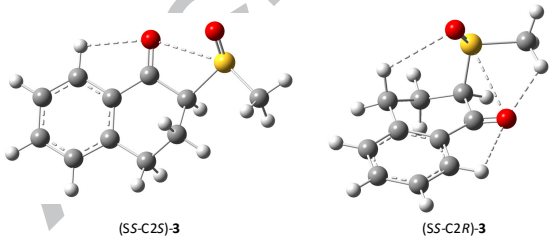
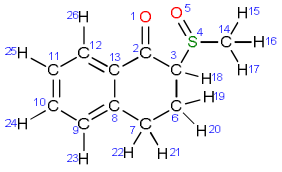


Figure 1. Selected minimum energy conformations and intramolecular contacts for **3** (for atom labelling, see Scheme 4) at the B3LYP/6-311+G(d,p) level of theory.



α = O(1)-C(2)-C(3)-S(4)
β = C(2)-C(3)-S(4)-O(5)
γ = O(1)-C(2)-C(3)-C(6)
δ = O(1)-C(2)-C(13)-C(12)
ω = C(2)-C(3)-C(6)-C(7)

Scheme 4. Atoms labelling and definition of relevant dihedral angles of **3**.

Table 1: Comparison between relative energy (Kcal mol^{-1}), population (*P*), dipole moment (μ, *D*) and selected dihedral (°) for the minimum energy conformations of **3** at the B3LYP/6-311+G(d,p) level of theory.

Comp.	E[a]	μ	Dihedral Angle[b]				
			α	β	γ	δ	ω
(S*S*-C2*R*)-**3**	0.00	2.77	-77.1	-40.4	161.9	-5.2	46.9
(S*S*-C2*S*)-**3**	6.42	6.71	16.1	30.7	145.5	5.2	57.8

[a]Relative energy;
[b]See Scheme 4

The less stable one (S*S*-C2*S*)-**3** (E_{rel}= 6.42 kcal mol^{-1}; μ=6.71 *D*) which *S*-configuration for C2 displays the S=O (α= 16.1°) substituent in a *syn-clinal* geometry with respect to carbonyl group which allows two short intramolecular contacts less than the ΣvdW between the oppositely charged $O^{\delta-}(1)_{[CO]}\cdots S^{\delta+}(4)$, Δl≅-0.48 Å and $O^{\delta-}(1)_{[CO]}\cdots H^{\delta+}(26)$, Δl≅-0.26 Å. These short contacts in S*S*-C2*R*-**3** contribute three attractive electrostatic interactions (hydrogen bond) for the referred compound in comparison to less stable S*S*-C2*S*-**3** which in turn possesses only two hydrogen bonds.

These results prompted us to affirm that the attack of enolate to ((SS)-MeSO$_2$-DAG) favors the more thermodynamically stable (S*S*-C2*R*)-**3** and is due to the diastereoselectivity imposed by the asymmetric induction of the MeSO- group present in ((S*S*)-MeSO$_2$-DAG), increasing the formation of (S*S*-C2*R*)-**3** in comparison to (S*S*-C2*S*)-**3** (Figure 2).

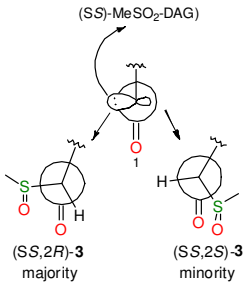
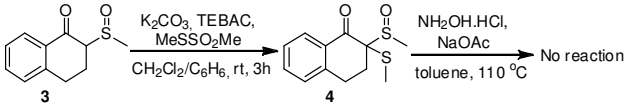


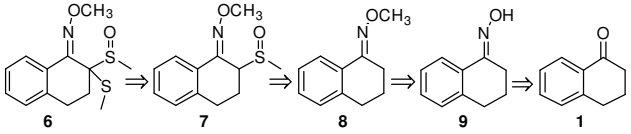
Figure 2. Staggered representation of sulfanylation of **1** via nucleophilic attack.

The *α*-methylsulfanylation reaction of S*S*-C2*R*-**3** was conducted by reaction in phase transfer catalysis (PTC) conditions using *S*-methyl methanesulfonothioate, K_2CO_3 and TEBAC in CH_2Cl_2/C_6H_6 medium at room temperature to achieve the 2-(methylsulfinyl)-2-(methylsulfanyl)-3,4-dihydronaphthalen-1(2*H*)-one **4** in 38% yield with 90% de. The major diastereomer of **4** was isolated by chromatographic separation in 38% yield. The reaction of **4** with hydroxylamine hydrochloride in presence of NaOAc in toluene at reflux[28] was conducted to prepare the targeted compound (Scheme 5). However, this reaction did not occur, possibly due to the lack of *α*-proton for enolization.



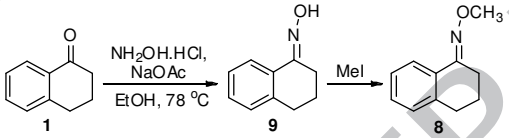
Scheme 5. Attempting for the synthesis of compound **6**.

To overcome this synthetic problem, different chemical conditions and synthetic strategies have tested. Scheme 6 describes the retrosynthetic analysis leading to the key intermediates for the synthesis of targeted molecule. The required compound **6** could be obtained by α-methylsulfanylation of α-methylsulfinyl naphthone **7** which in turn can be prepared by the α-methylsulfanylation of compound **8**. This corresponds to a decision that thiolated groups can be added late. Then, the compound **8** can be prepared by methylation of **9** prepared by the corresponding naphthone **1** which can be chosen again as a starting material.



Scheme 6. New retrosynthetic proposal of 2-(methylsulfinyl)-2-(methylsulfanyl)-*O*-methyl oxime.

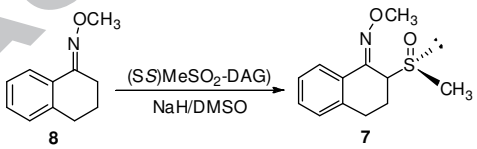
The reaction of commercially available tetralone **1** with hydroxylamine hydrochloride in ethanol in presence of NaOAc under reflux achieved the oxime **9** in quantitative yield[32]. The obtained oxime was subjected to *O*-methylation with MeI and afforded the 3,4-dihydronaphthalen-1(2*H*)-one-*O*-methyloxime in 92% yield[33] (Scheme 7).



Scheme 7. Synthesis of methyloxime **8**.

The methylsulfinylation was performed using the same methodology of compound **3** synthesis (Scheme 3). However, the use of oxime **8** in LDA/THF leads to ketone **3**, then, the system base/solvent was changed by NaH as small base in DMSO[26] (Scheme 8) and the 2-methylsulfinyl-*O*-methyl-oxime **7** with known stereogenic center was obtained after chromatographic purification in 69% yield, 12% ee and 75% de.

The ^{1}H NMR spectral analysis of the crude product allowed to conclude that the formation of a diastereomeric mixture (90:10), confirmed by the presence of one signal related to the $SOCH_3$ at 2.66 ppm and a triplet at δ 4.77 ppm (J = 4 Hz) corresponding to methine hydrogen.



Scheme 8. Synthesis of methylsulfinyl oxime **7**.

To understand this diastereoselectivity, theoretical calculations using density functional theory (DFT) calculation was performed for **7** (Figure 3, Scheme 9, Table 2).

Theoretical calculations for **7** indicate the more stable conformer (S*S*, C2*S*-**7**) (E_{rel}=0.00 kcal mol^{-1}; μ=3.71 *D*) present the S=O (α= 66.0°) substituent in a *syn-clinal* geometry with respect to the oximic group and configuration (*S*) for C2. This conformation allows the attractive intramolecular contacts (hydrogen bond) between the oppositely charged $N^{\delta-}(1)_{[CN]}\cdots H^{\delta+}(26)$; $O^{\delta-}(30)_{[NO]}\cdots H^{\delta+}(18)$; $O^{\delta-}(5)_{[SO]}\cdots H^{\delta+}(19)$ and $O^{\delta-}(5)_{[SO]}\cdots H^{\delta+}(20)$ atoms, whose are shorter than the ΣvdW radii by Δl≅-0.15 Å, Δl≅-0.28 Å, Δl≅-0.26 Å and Δl≅-0.28 Å, respectively, the oppositely charged short intramolecular contact between $O^{\delta-}(30)_{[NO]}\cdots S^{\delta+}(4)$ atoms, Δl≅-0.25 Å and one repulsive short contact between $S^{\delta+}(4)\cdots H^{\delta+}(20)$ atoms, Δl≅-0.17 Å.

The less stable conformer (S*S*-C2*R*-**7**) (E_{rel}=5.84 kcal mol^{-1}; μ=3.38 *D*) present configuration (*R*) for C2 and the S=O (α= -96.3°) substituent is in an *anti-clinal* geometry with respect to the oximic group. Similarly to S*S*-C2*S*-**7**, the geometry of S*S*-C2*R*-**7** allows four oppositely charged short intramolecular contact (hydrogen bond) between $N^{\delta-}(1)_{[CN]}\cdots H^{\delta+}(26)$, Δl≅-0.31 Å; $O^{\delta-}(30)_{[NO]}\cdots H^{\delta+}(18)$, Δl≅-0.43 Å; $O^{\delta-}(5)_{[SO]}\cdots H^{\delta+}(19)$, Δl≅-0.29 Å and $O^{\delta-}(30)_{[NO]}\cdots H^{\delta+}$(both 15,16,17) atoms, but allows one important repulsive short contact between $S^{\delta+}(4)\cdots H^{\delta+}(19)$, Δl≅-0.15 Å atoms and as consequence, a significant Coulombic repulsion of these atoms arises, which act destabilizing this conformer.

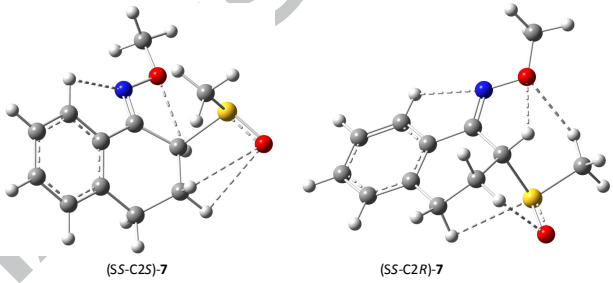
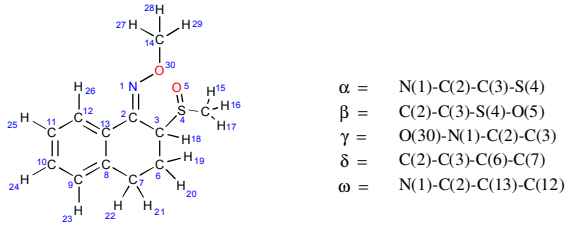


Figure 3. Selected minimum energy conformations and intramolecular contacts for **7** (for atom labelling, see Scheme 9) at the B3LYP/6-311+G(d,p) level of theory.



Scheme 9. Atoms labelling of 2-methylsulfinyl-*O*-methyl-oxime **7** and definition of relevant dihedral angles.

Table 2: Comparison between relative energy (Kcal mol^{-1}), dipole moment (μ, D) and selected dihedral (°) for the minimum energy conformations of **7** at the B3LYP/6-311+G(d,p) level of theory.

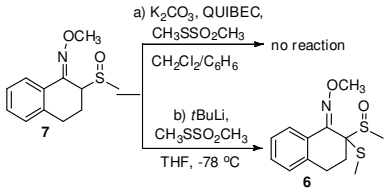
Comp.	E[a]	μ	Dihedral Angle[b]				
			α	β	γ	δ	ω
(S*S*-C2*S*)-**7**	0.00	3.71	66.0	158.0	-3.33	33.9	-29.3
(S*S*-C2*R*)-**7**	5.84	3.38	-96.3	-158.0	1.83	52.1	9.36

[a]Relative energy;
[b]See Scheme 9

In summary, the lowest Coulombic repulsive effect combined with the stabilizing effect of $O^{\delta-}(30)_{[NO]}\cdots S^{\delta+}(4)$ atoms and four hydrogen bonds in (S*S*-C2*S*-**7**) thermodynamically favors the formation of this conformer in comparison to the two Coulombic repulsive effect which destabilizing in a higher intensity in (S*S*-C2*R*-**7**), even with its four hydrogen bonds. These results allowed us to consider that the nucleophilic attack occur in (S*S*, C2*R*)-**7** preferably compared to (S*S*, C2*S*)-**7**.

To get the further carbonyl functionality at α-position, it is needed the methylsulfanylation at α-position. The reaction of **7** with *S*-methyl methanesulfonothioate using K_2CO_3 as base and *N*-Benzylquininium chloride (QUIBEC) as catalyst in CH_2Cl_2:C_6H_6 (1:1) was carried out to afford the compound **6** (Scheme 10a). However, this reaction did not occur which can be rationalized due to the *N*-benzylquininium substituent (bulk substituent) present in QUIBEC catalyst which hinders the attack of the sulfinylating agent.

Consequently, the homogeneous conditions using ^{t}BuLi as base with *S*-methyl methanesulfonothioate in THF at -78 ^{o}C was carried out and afforded the 2-(methylsulfinyl)-2-(methylsulfanyl)-*O*-methyl oxime **6**. The product was obtained in 50% yield as a mixture of diastereomers, illustrated by the analysis of ^{1}H NMR of the crude reaction mixture in which two simplets was observed at δ 2.50 ppm and 2.21 ppm, referring to the methyl groups using Kagan´s reagent.



Scheme 10. Synthesis of targeted molecule **6** in (a) PTC and (10b) homogeneous phase.

Conclusions

In conclusion, a single step sulfinylation reaction of 1-tetralone is conceived in good yield. A convenient method for diastereoselective sulfanylation of 3,4-dihydronaphthalen-1(2*H*)-one-*O*-methyl oxime and 2-(methylsulfinyl)-3,4-dihydronaphthalen-1(2*H*)-one-*O*-methyl oxime has also been achieved. We have shown that the homogeneous reaction medium is a viable method over phase transfer catalysis for sulfanylation.

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References and notes

1. Bi, J.; Wang, J.; Zhou, K.; Wang, Y.; Fang, M.; Du, Y. *ACS Med. Chem. Lett.*, **2015**, *6*, 476-480.
2. Pejin, B.; Iodice, C.; Tommonaro, G.; De Rosa, S. *J. Nat. Prod.*, **2008**, *71*, 1850-1853.
3. Secrist, J.A.; Tiwari, K. N.; Montgomery, J. M. *J. Med. Chem.*, **1991**, *34*, 2361-2366.
4. QingPeng, W.; JingQing, Z.; Guri, L. V. D.; Kun, W.; HuiZhen, Z.; ChengHe, Z. *Sci. China Chem.*, **2012**, *55*, 2134-2153.
5. Rückle, T.; Biamonte, M.; Grippi-Vallotton, T.; Arkinstall, S.; Cambet, Y.; Camps, M.; Chabert, C.; Church, D. J.; Halazy, S.; Jiang, X.; Martinou, I.; Nichols, A.; Sauer, W.; Gotteland, J. *J. Med. Chem.*, **2004**, *47*, 6921-6934.
6. Ulman, A.; Willand, C. S.; Kohler, W.; Robello, D. R.; Williams, D. J.; Handley, L. *J. Am. Chem. Soc.*, **1990**, *112*, 7083-7090.
7. Vittal, J. J.; Ng, M. T. *Acc. Chem. Res.*, **2006**, *39*, 869-877.
8. Tao, X. L.; Boyer, C.; Lowe, A. B.; Davis, T. P. *Macromolecules*, **2010**, *43*, 20-24.
9. Wladislaw, B.; Marzorati, L.; Biaggio, F. C.; Vargas, R. R.; Bjorklund, M. B.; Zukerman-Schpector, J. *Tetrahedron*, **1999**, *55*, 12023-12030.
10. Rodrigues, A.; Wladislaw, B.; Di Vitta, C.; Filho, J. E. P. C.; Marzorati, L.; Bueno M. A.; Olivato, P. R. *Tetrahedron Lett.*, **2010**, *51*, 5344-5348.
11. I. Fernandez, N. Khiar, J.; Llera, M.; Alcudia, F. *J. Org. Chem.*, **1992**, *57*, 6789-6796.
12. Corey, E. J.; Chaykowski, M. J. *J. Am. Chem. Soc.*, **1962**, *84*, 867-868.
13. Kunieda, N.; Nokami, J.; Kinoshita, M. *Chem. Lett.*, **1974**, 369-372.
14. a) Schneider, F.; Simon, R. *Synthesis*, **1986**, 582; b) Carrefio, M. C.; Ruano, J. L. G.; Rubio, A. *Tetrahedron Lett.*, **1987**, *28*, 4861-4864.
15. Mancheño, O. G.; Arrayás, R. G.; Carretero, J. C. *J. Am. Chem. Soc.*, **2004**, *126*, 456-457.
16. Jagt, J. C.; Van Leusen, A. M. *J. Org. Chem.*, **1974**, *39*, 564-566.
17. Han, B.; Li, J.; Ma, C.; Zhang, S.; Chen, Y. *Angew. Chem. Int. Ed.*, **2008**, *120*, 10119-10122.
18. Tsuchihashi, G.; Mitamura, S.; Inoue, S.; Ogura, K. *Tetrahedron Lett.*, **1973**, *14*, 323-326.
19. Posner, G. H.; Mallamo, J. P.; Miura, K. *J. Am. Chem. Soc.*, **1981**, *103*, 2886-2888.
20. Pyne, S. G.; Bloem, P.; Chapman, S. L.; Dixon, C. E.; Griffith, R. *J. Org. Chem.*, **1990**, *55*, 1086-1093.
21. Davis, R.; Kern, J. R.; Kurz, L. J.; Pfister, J. R. *J. Am. Chem. Soc.*, **1988**, *110*, 7873-7874.
22. Parsons, W. J.; Ramkumar, W.; Stiles, G. L. *Mol. Pharmacol.*, **1988**, *33*, 441-448. TIRAR 22 E 23
23. Kutter, E.; Austel, V. *Arzneimittelforschung*, **1981**, *31*, 135-141.
24. a) Ruano, J. L. G.; Barros, D.; Maestro, M. C.; Arava-Maturana, R. Fischer, J. *J. Org. Chem.*, **1996**, *61*, 9462-9470. b) Kunieda, N.; Nokami, J.; Kinoshita, M. *Chem. Lett.*, **1974**, 377-380
25. Ruano, J. L. G.; Barros, D.; Maestro, M. C.; Alcudia, A.; Fernandez, I. *Tetrahedron: Asymmetry*, **1998**, *9*, 3445-3453.
26. Bianchi, T. A.; Cate, L. A. *J. Org. Chem.*, **1977**, *42*, 2031–2032.
27. Paiva, D. R.; Gomes, R. S. *Orbital: The Electronic Journal of Chemistry*, **2013**, *5*, 56-63.
28. Deshmukh, M.; Duñach, E.; Juge, S.; Kagan, H. B. *Tetrahedron Lett.*, **1984**, *25*, 3467-3470
29. Pitchen, P.; Kagan, H. B. *Tetrahedron. Lett.*, **1984**, *25*, 1049–1052.
30. Pitchen, P.; Dunach, E.; Deshmukh, M. N.; Kagan, H. B. *J. Am. Chem. Soc.*, **1984**, *106*, 8188-8193.
31. See suplemmentary information.
32. Wladislaw, B.; Bueno, M. A.; Marzorati, L.; Di Vitta; C.; Zukerman-Schpector, J. *J. Org. Chem.*, **2004**, *69*, 9296-9298.
33. Douglass, I. B.; Norton, R. V. *J. Org. Chem.*, **1968**, *33*, 2104-2106.

Highlights

- A single step sulfinylation reaction of 1-tetralone is conceived in good yield.
- A convenient method for diastereoselective sulfanylation of cyclic ketones and oximes has been achieved.
- The homogeneous reaction medium is a viable method over phase transfer catalysis for sulfanylation.
- Stereoselectivity was discussed and compared using ^{1}H NMR technique.
- Theoretical calculations explain the diastereoselectivity and stereocontrol.