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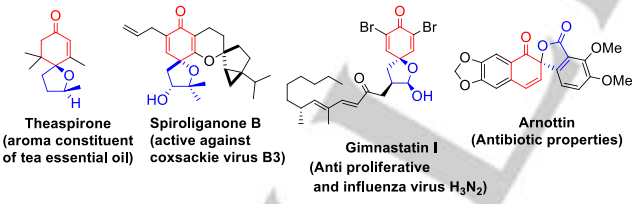
Controlling Stereoselectivity in Tribromide Mediated Oxidative Dearomatisations – Synthesis of Selective Spirofurano-naphthalones

Debayan Sarkar*[a], Puspendu Kuila[a], Devashish Sood[a]

Abstract: A series of ammonium tribromides were screened for exploring the role of ammonium counterpart attached to tribromides on generation of stereoselective spiro-furans via oxidative dearomatisation of naphthols. The proposition enlightens a suitable combination of the ammonium tribromide and solvent employed, deliver the best achieved diastereoselectivities. This in turn, has also envisioned the mechanistic aspects related to these category of reactions. The mentioned dearomative spiro-furano naphthalones has also been successfully achieved on a large-scale

Introduction

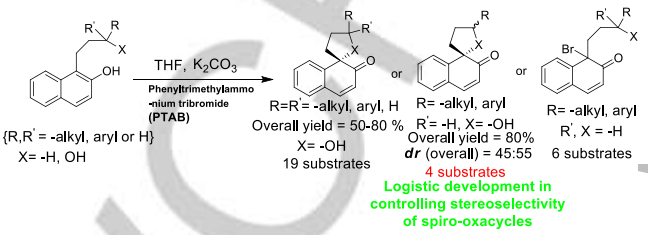
Oxidative dearomatisation of easily available phenols and naphthols have been a lucrative ladder of exploring molecular complexity[1] as they furnish cyclo-hexadieneones which can easily be functionalised with appropriate nucleophiles to access many natural products of biological relevance.[2] (Figure 1) Dearomative spiro-oxacyclisation of arenols is a facile route towards generation of the spiro-furans since many natural products like Theaspirone, Spiroliganone B and Gimnastatin I contain a spiro-furan core and exhibit a wide range of bioactivity. Thus, the emphasized biological activity and notable stereochemistry related to spiro-furans has delivered an important synthetic status to them.[3] Undoubtedly, oxidative dearomatisation reactions has been explored well and a recent review from the Quideau group[4] has been an enchanting resource. Recently a tutorial from You[5] group delineates the mechanistic insight of this reaction, nevertheless it requires an urgent attention.[6]



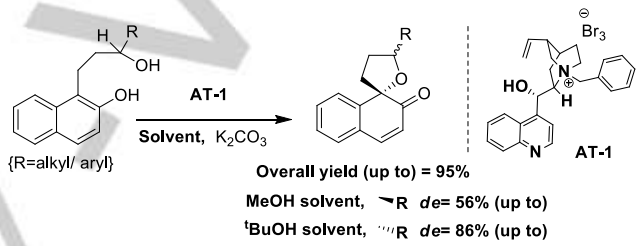
. **Figure 1.** Biologically active spirocyclic natural products

The last decade has witnessed a rigorous application of hypervalent iodine reagents into dearomative spiro-oxacyclisation of phenols and naphthols towards generation of the spiro-furans,[7] however as Harned[8] mentions, the problem retains with the development of a generalised arene-iodine catalyst which can be applied to a wide variety of substrate. Some notable reports in this direction comes from the groups of Ciufolini,[9] Kita,[10] Ishihara,[11] Ibrahim,[12] where hypervalent iodine reagents have been suitably employed to achieve varied spiro-oxacycles. Preparation of hypervalent iodine reagents require presence of oxidative additives and are synthesized in multiple steps. There has been less successful attempts to develop metal free protocols towards such transformations.

(a) Our previous work: Phenyltrimethylammonium tribromide (PTAB) mediated synthesis of spiro-oxacycles[13]



(b) This work: Quaternary Ammonium Tribromide (**QATB**) mediated synthesis of selective spiro-oxacycles



Scheme 1. Synthesis of spiro-furano naphthalone

Our group has been focusing on oxidative dearomatisation reactions. Recently, we have developed an ammonium tribromide mediated spiro-cyclisation of phenols and naphthols[13] (Scheme 1a). Hitherto, the achieved diastereoselectivity in substituted spirofurans was unsatisfactory. The presence of ammonium counterpart in the reactive intermediate, mentioned in our previous report,[13] insisted us to study the possible aspects of tuning the ammonium counterpart and see the desired effect on the aforesaid diastereoselectivity. Interestingly, it was found that not only changing the ammonium counterpart of tribromides but also altering the solvents had an impact on diastereoselectivity. Hence, this has delivered a newer outlook towards the mechanistic aspects of the tribromide mediated oxidative dearomatisation. Thus, as an advancement of our continuous efforts towards oxidative dearomatisation reactions, we report the fine controlling of diastereoselectivity in quaternary ammonium tribromide mediated genereration of spirofurans (Scheme 1b).

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†Electronic supplementary information (ESI) available: Detailed experimental procedures, spectral data for all compounds, including copies of ^1H, ^{13}C NMR spectra, HPLC data. See DOI: 10.1039/x0xx00000x

Results and Discussion

The tribromides (1-7) were synthesised as per the synthetic routes available in literature.[14] (+)-N-benzylcinchonine ammonium tribromide (**AT-1**) was developed from (+)-N-benzylcinchonine ammonium bromide using potassium bromide and oxone in aqueous medium. The outlook behind the synthesis was to penetrate into a sterical diversified variance (Figure 2). With our previous experience, we found moderate diastereoselectivity with varied substitution in the hydroxy- naphthols (when R= -Me the ***dr*** was 1.2:1) where (1'S, 5R) -spiro-furano-naphthalone was the major diastereomer in all cases. This delivered an apprehension that a less encumbered *exo*-face attack in the partially planar reactive intermediate (**R1**) is more accessible to a bulkier alcohol with minimal stereo-electronic interactions (Figure 3). Herein, we look through a planned perception of subsequently increasing bulkiness on tribromides and look into the changes or rather improvements in the diastereoselectivities during generation of dearomative spiro-furan. To start with, 1-(3-hydroxy-3-phenylpropyl) naphthalene-2-ol (**g**) was chosen as the model substrate and the quaternary ammonium tribromides (Table 1) and solvents (Table 4) were varied to check the effects on the induced diastereoselectivity. (Supporting Information)

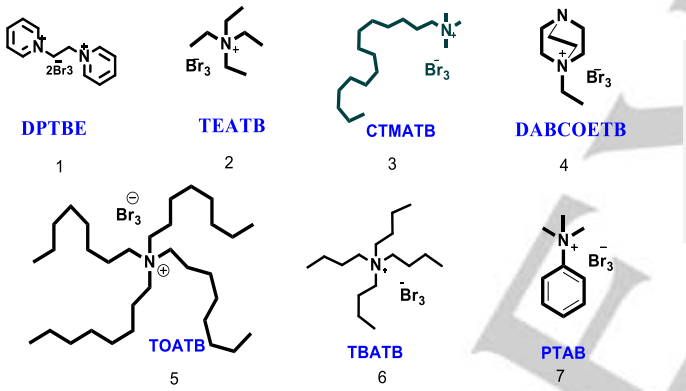


Figure 2. Synthesized Tribromides: 1,2-Dipyridinium ditribromide-ethane (DPTBE, 1), Tetraethylammonium tribromide (TEATB, 2), Cetyltrimethylammonium tribromide (CTMATB, 3), 1-benzyl-4-aza-1-azonia-bicyclo [2.2.2] octane tribromide (DABCOETB, 4), Tetraoctylammonium tribromide (TOATB, 5), Tetrabutylammonium tribromide (TBATB, 6), Phenyltrimethylammonium tribromide (PTAB, 7)

To our projected aspirations, we were overwhelmed to find that an appropriate tuning of the ammonium counterpart of the tribromide, posed an accelerative effect on the stereoselectivity of the synthesised spiro-furans. When 1-(3-hydroxy-3-phenylpropyl) naphthalene-2-ol was chosen as substrate, in presence of DABCOETB (Table 1, entry 1.6) the achieved ***dr*** was 27.1:72.9 (g1:g2), whereas the ***dr*** was found to be 45.9:54.1 (g1:g2) (Table 1, entry 1.1) when tetraethylammonium tribromide (TEATB) was employed. Not only the 1-(3-hydroxy-3-phenylpropyl) naphthalene-2-ol (**g**), but also other substitutions like 1-(3-hydroxy-4-phenylbutyl)naphthalen-2-ol (**h**) delivered almost similar observations (Table 2) using varied tribromide salts. Thus when 1-(3-hydroxy-4-phenylbutyl)naphthalen-2-ol (**h**) was reacted in presence of DPTBE (Table 2, entry 1.1) the ***dr*** obtained was 51.3:48.7 (h1:h2), whereas the ***dr*** was found to be 30.3:69.7 (h1:h2) when DPTBE was replaced by TBATB (Table 2, entry 2.7). TBATB exemplified a better result (yield as well as ***dr***) as compared to PTAB in all cases (Table 1 & Table 2).

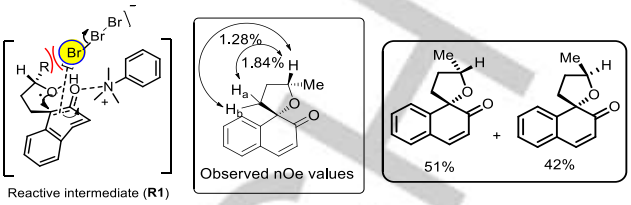
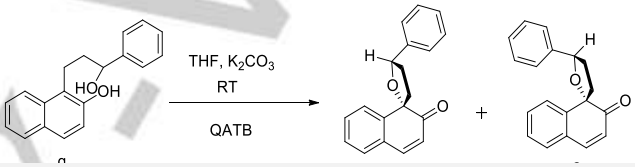


Figure 3. Reactive intermediate (R1) & previous report on diastereoselectivity employing PTAB-salt[13]

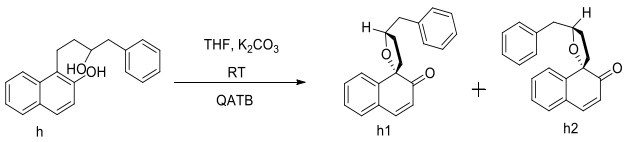
Table 1. Optimisation of diastereoselectivity using different QATB-salts in spiro-furano-naphthalone synthesis from 1-(3-hydroxy-3-phenylpropyl)naphthalene-2-ol[a]



Entry No.	QATBs (equiv)	Overall yield[c] (g1 + g2) in %	Time (h)	Diastereomeric ratio[d]	
				g1	g2
1.1	TEATB	97	10	45.9	54.1
1.2	CTMATB	92	12	37.1	62.9
1.3	PTAB	82	12	35.7	64.3
1.4	DPTBE[b]	90	9	34.5	65.5
1.5	TOATB	88	18	34.5	65.5
1.6	DABCOETB	93	12	27.1	72.9
1.7	**TBATB**	**95**	**12**	**26.3**	**73.7**

[a]Conditions: reaction performed on a 0.04 mmol scale, with 1-(3-hydroxy-3-phenyl)naphthalene-2-ol (1 equiv), QATB (1 equiv), K_2CO_3 (1 equiv), THF, rt. [b]DPTBE (0.5 equiv) was used. [c]isolated yields. [d]Determined by ^1H NMR spectroscopy.

Table 2. Optimisation of diastereoselectivity using different QATB-salts in spiro-furano-naphthalone synthesis from 1-(3-hydroxy-4-phenylbutyl)naphthalene-2-ol[a]

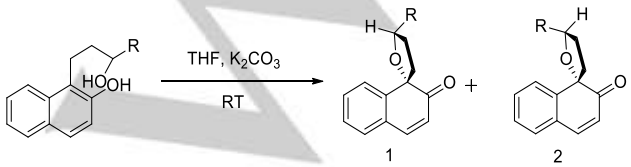


Entry No.	QATBs (equiv)	Overall yield[c] (h1 + h2) in %	Time (h)	Diastereomeric ratio[d] h1	h2
2.1	DPTBE[b]	90	8	51.3	48.7
2.2	TEATB	93	8	52.4	47.6
2.3	DABCOETB	90	14	44.2	55.8
2.4	TOATB	85	18	40.6	59.4
2.5	CTMATB	85	14	38.5	61.5
2.6	PTAB	87	12	38.5	61.5
2.7	**TBATB**	**90**	**12**	**29**	**71**

[a]Conditions: reaction performed on a 0.03 mmol scale, with 1-(3-hydroxy-3-benzyl) naphthalene-2-ol (1 equiv), QATB (1 equiv), K_2CO_3 (1 equiv), THF, rt. [b]DPTBE (0.5 equiv) was used. [c]isolated yields. [d]Determined by ^{1}H NMR spectroscopy.

Thus, it is observed (Table 1 and Table 2) that formation of **g2** and **h2** isomers were increased with increased bulkiness on QATBs up to a certain extent; Though TOATB is bulkier than TBATB but TOATB delivered less selectivity over TBATB. Interestingly, the change in the substitution of the 3-substituted hydroxyl-naphthols delivered a recognized pattern of diastereoselectivity. For example 1-(3-hydroxyoctyl)naphthalene-2-ol (**e**) delivered 61.5% of the **e2**-diastereomer in presence of PTAB whereas the same delivered a higher diastereoselectivity (73.3%) of the **e2**-diastereomer in presence of TBATB (Table 3, entry 3.5), whilst R= octyl (**l**) did not show such extent of change in stereoselectivity (Table 3, entry 3.12). When differently substituted 1-(3-hydroxy-3-alkyl/aryl)naphthalen-2-ols were screened with two tribromides PTAB and TBATB, we found tetrabutylammonium tribromide (TBATB) fitted as the best one. Thus, it implies that the reactive intermediate resembles an asymmetric pocket comprising of the properly oriented tribromide and substrate which delivers such stereoselectivity. At the same instant, it was also noteworthy that a compatible combination of the alkyl substituent in the chain and ammonium tribromide (which means bulkiness on both the substrate and ammonium counterpart affects upto a certain limit but beyond that it is abortive, i.e. effective steric crowding is the determining factor) was to be hand-picked to get the best stereo-selectivity. The relative stereochemistry has been denoted on the basis of nOe experiments.[13] (Figure 4)

Table 3. Relative diastereoselectivity with varied 3-alkyl substituents using anhydrous THF solvent[a]



Entry No.	-R	Diastereomeric ratio[b] using PTAB: Overall yield[c] (1+2)%	Time (h)	1	2	Diastereomeric ratio[b] using TBATB: Overall yield[c] (1+2)%	Time (h)	1	2
3.1	-methyl **(a)**	85	8	44.5 (a1)	54.5 (a2)	89	14	23.8 (a1)	76.2 (a2)
3.2	-ethyl **(b)**	76	10	40.0 (b1)	60.0 (b2)	81	16	29.4 (b1)	70.6 (b2)
3.3	-propyl **(c)**	70	8	35.7 (c1)	64.3 (c2)	79	12	27.8 (c1)	72.2 (c2)
3.4	-butyl **(d)**	72	8	39.4 (d1)	60.6 (d2)	86	12	26.6 (d1)	73.4 (d2)
3.5	-pentyl **(e)**	70	14	38.5 (e1)	61.5 (e2)	76	21	26.7 (e1)	73.3 (e2)
3.6	-isopropyl **(f)**	75	14	42.2 (f1)	57.8 (f2)	81	16	30.3 (f1)	69.7 (f2)
3.7	-phenyl **(g)**	81	10	35.7 (g1)	64.3 (g2)	95	12	26.3 (g1)	73.7 (g2)
3.8	-benzyl **(h)**	80	8	38 (h1)	62 (h2)	90	14	27.4 (h1)	72.6 (h2)
3.9	-4-fluorobenzyl **(i)**	78	10	38.7 (i1)	61.3 (i2)	90	10	23.5 (i1)	76.5 (i2)
3.10	-cyclohexyl **(j)**	75	16	42.6 (j1)	57.4 (j2)	83	19	38.1 (j1)	61.9 (j2)
3.11	-homobenzyl **(k)**	80	10	41.6 (k1)	58.4 (k2)	85	16	31.2 (k1)	68.8 (k2)
3.12	-octyl **(l)**	72	16	27.8 (l1)	72.2 (l2)	75	24	24 (l1)	76 (l2)
3.13	-4-methylbenzene **(m)**	82	10	28 (m1)	72 (m2)	93	11	25.7 (m1)	74.3 (m2)
3.14	-4-fluorobenzene **(n)**	80	8	33.7 (n1)	66.3 (n2)	96	10	30.3 (n1)	69.7 (n2)

[a]Conditions: 1-(3-hydroxy-3-alkyl/-aryl)naphthalene-2-ol (1 equiv), QATB (1 equiv), K_2CO_3 (1 equiv), THF, rt. [b]Determined by ^{1}H NMR spectroscopy. [c]isolated yields. *(details in Supporting Information)*

In order to assign the relative stereochemistry, multiple nuclear Overhauser effect (**nOe**) experiments (Figure 4) were performed with the spiro-furano naphthalones (Table 3), **'2'** was the major diastereomer in all cases. (*details in Supporting Information*)

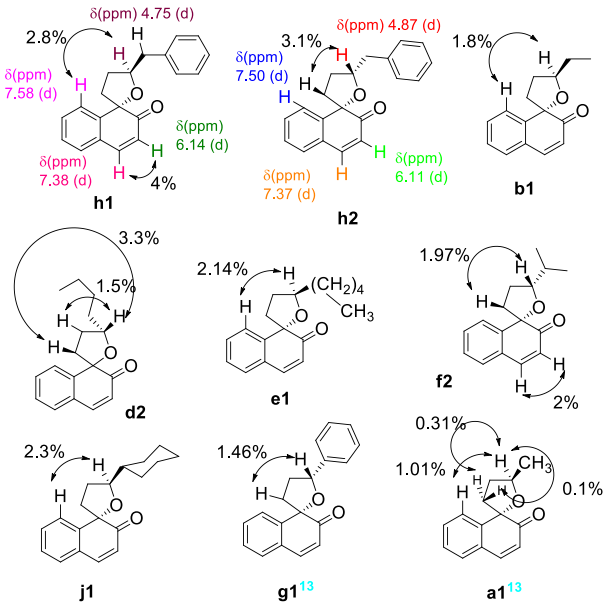
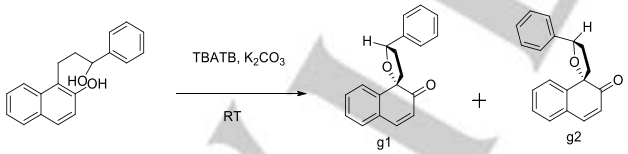


Figure 4. nOe studies

It was further interesting to note, that the solvent chosen for the reaction also plays a dominant role (Table 4). The ***dr*** is completely reversed in MeOH and THF, when 1-(3-hydroxy-3-phenylpropyl)naphthalene-2-ol undergoes the respective cyclisation to deliver the spiro-furano naphthalone. Different solvents display a wider variety of diastereoselectivity which also puts forward the proposal of a necessary combination of appropriate tribromide-salt, alkyl substituent and the solvent for achieving the best diastereoselectivity.

Table 4. Solvent effects on diastereoselective oxidative spiro cyclization of 1-(3-hydroxy-3-phenyl)naphthalene-2-ol using TBATB-salt[a]

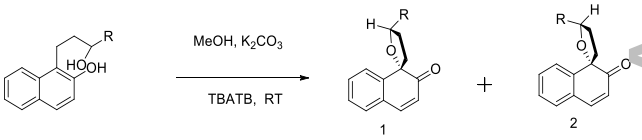


Entry. No.	Solvent	Overall yield[b] (g1 + g2) in %	Time (h)	Diastereomeric ratio[c]	
				g1	g2
4.1	THF	95	12	26.3	73.7
4.2	**MeOH**	**96**	**5**	**75.3**	**24.7**
4.3	Trifluoro ethanol	90	8	32.2	67.8
4.4	Hexafluoro propan 2-ol	86	10	60	40
4.5	Toluene	85	24	33.8	66.2
4.6	Ethanol	92	10	75	25
4.7	Acetonitrile	88	16	39.3	60.7
4.8	**^{t}Butanol**	**95**	**20**	**15.6**	**84.4**
4.9	DCM	90	10	39.6	60.4
4.10	Hexane	85	24	50	50

[a]Conditions: 1-(3-hydroxy-3-phenyl)naphthalene-2-ol (1 equiv), TBATB (1 equiv), K_2CO_3 (1 equiv), solvent, rt. [b]Isolated yield [c]Determined by 1H NMR spectroscopy.

Polar solvents delivered better selectivity than non-polar solvents. Among the polar solvents, in general, polar protic solvent delivered reversed diastereoselectivity than that of polar aprotic solvent (Table 4). When 3-phenyl substituted naphthol (**g**) was reacted with the best optimised QATB-salt (TBATB), we observed 73% **g2** isomer was generated in THF (Table 4, entry 3.1), albeit, 75% **g1** isomer was developed in MeOH solvent (Table 4, entry 3.2). To generalise the perception, we examined a series of substrates in methanol solvent (Table 5). With *tert*-butanol, a series of substrates was varied and found that *tert*-butanol afforded the same major diastereomer as in case of THF with better diastereoselectivity and yields. (discussed in Table 6).

Table 5. Relative diastereoselectivity with variant 3-alkyl substituents using methanol solvent[a]



Entry No.	-R	Overall yield[b] (1 + 2) in %	Time (h)	Diastereomeric ratio[c]	
				1	2
5.1	-ethyl (b)	93	8	78.2 (b1)	21.8 (b2)
5.2	-propyl (c)	86	8	77.4 (c1)	22.6 (c2)
5.3	-butyl (d)	91	8	79.4 (d1)	20.6 (d2)
5.4	-octyl (l)	85	9	80.8 (l1)	19.2 (l2)
5.5	-phenyl (g)	96	5	75.2 (g1)	24.8 (g2)
5.6	-4-fluoro benzene (n)	95	5	77.5 (n1)	22.5 (n2)
5.7	-cyclohexyl (j)	89	6	76.5 (j1)	23.5 (j2)

[a]Conditions: 1-(3-hydroxy-3-alkyl/-aryl)naphthalene-2-ol (1 equiv), TBATB (1 equiv), K_2CO_3 (1 equiv), MeOH, rt. [b]Isolated yield. [c]Determined by ^1H NMR spectroscopy.

In case of MeOH, we presume that the reaction proceeds with the formation of MeOBr[14a] (scheme 2). The generated alkoxy naphthalen-2yl-hypobromide coordinates with the quaternary ammonium bromide which further increases the steric bulkiness to the reverse side (shown in reactive intermediate R3).

Furthermore, the varied projections of spiro-furans in Figure 5 strongly suggest that the conformation 'g1' suffers from minimal stereo-electronic interaction and thus is more thermodynamically stable than 'g2'; generally in polar aprotic solvent we got 'g2' as a major product which proceeds via reactive intermediate **R2** (scheme 3) as quaternary ammonium counterpart coordinates with naphthoxide oxygen and makes this side more sterically bound, but in polar protic solvent bromonium cation co-ordinates with naphthoxide oxygen (scheme 2) and hence won't provide such extent of steric hindrance. As a result, formation of spirofuran is controlled by thermodynamic stability. Thus, a planned combination of QATB and solvent would deliver the desired spiro-furan.

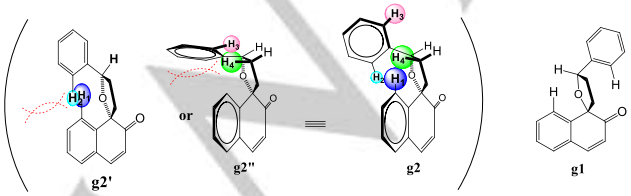
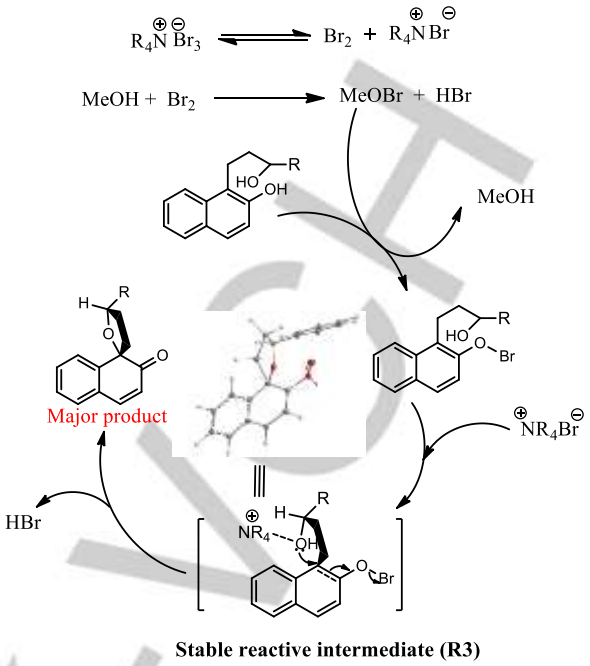
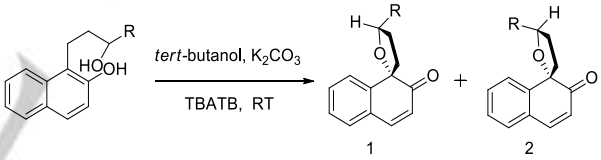


Figure 5. Steric congestion and relative stability



Scheme 2. Plausible reaction mechanism

Table 6. Relative diastereoselectivity with 3-alkyl substituents in *tert*-butanol solvent[a]



Entry No.	-R	QATBs	Overall yield[b] (1+2) in %	Time (h)	Diastereomeric ratio[c]	
					2	1
6.1	-ethyl (b)	TEATB	84	10	59 (b2)	41 (b1)
6.2	-ethyl (b)	PTAB	90	12	69 (b2)	31 (b1)
6.3	-ethyl (b)	TBATB	96	12	82.6 (b2)	17.4 (b1)

The planned variation of the quaternary ammonium counterpart in tert-butanol also exhibited similar accelerating effect on the tuning of specific diastereomers.

Entry No.	-R	QATBs	Overall yield[b] (1 + 2) in %	Time (h)	Diastereomeric ratio[c] 2	1
6.4	-isopropyl (f)	TBATB	96	16	77.5 (f1)	22.5 (f2)
6.5	-propyl (c)	TBATB	93	16	82.0 (c1)	18.0 (c2)
6.6	-butyl (d)	TBATB	89	14	70.5 (d1)	29.5 (d2)
6.7	-octyl (l)	TBATB	85	18	77.0 (l1)	23 (l2)
6.8	-4-fluoro benzyl (i)	TBATB	96	10	75.2 (i1)	24.8 (i2)
6.8	-phenyl (g)	TBATB	92	12	84.4 (g1)	15.6 (g2)
6.9	-cyclohexyl (j)	TBATB	85	16	67 (j1)	33 (j2)
6.10	-4-fluoro benzene (n)	TBATB	95	12	72.5 (n1)	27.5 (n2)

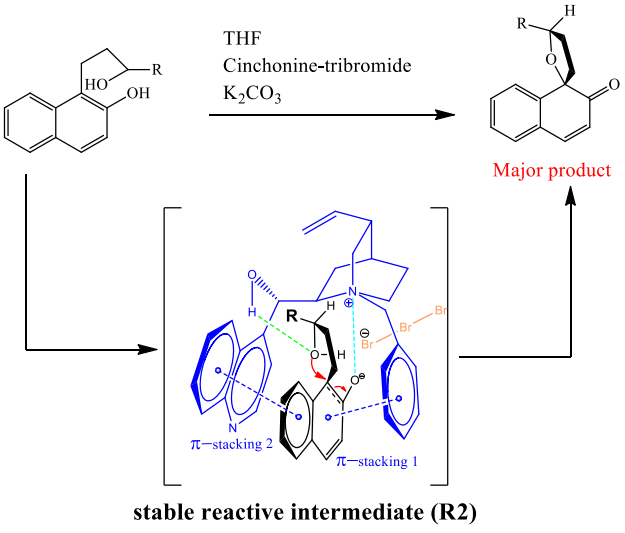
[a]Conditions: 1-(3-hydroxy-3-alkyl/-aryl)naphthalene-2-ol (1 equiv), QATB (1 equiv), K_2CO_3 (1 equiv), *tert*-butanol, rt. [b]Isolated yield. [c]Determined by ^{1}H NMR spectroscopy.

Table 7. Relative diastereoselectivity with cinchonine based tribromide[a]

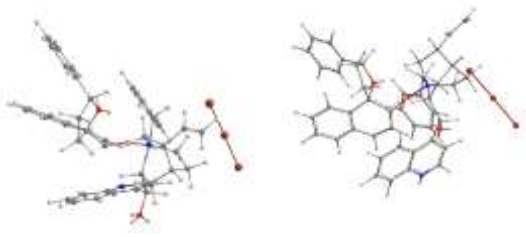
Entry. No.	-R	Solvent	Overall yield[b] (g1 + g2) in %	Time (h)	Diastereomeric ratio[c] 1	2
7.1	-Ph	THF	98	12	19.8	80.2
7.2	-Ph	^{t}BuOH	93	18	13.1	86.9
7.3	-Ph	MeOH	96/ 91[d]	10	77.8/ 73.0[d]	22.2/ 27.0[d]
7.4[d]	-Ph	THF	99	22	7.5	92.5
7.5[d]	-Et	THF	98	28	7.2	92.8

[a]Conditions: 1-(3-hydroxy-3-phenylpropyl)naphthalene-2-ol (1 equiv), AT-1 (1 equiv), K_2CO_3 (1 equiv), solvent, rt. [b]Isolated yield. [c]Determined by ^{1}H NMR spectroscopy. [d](+)-cinchonine (0.5 eqv.) was added as an additive.

The diastereoselectivity arises due to the intimate ion pair arrangement of the cationic counterpart of QATB and the less sterically arranged naphthoxide ion, which attacks the *exo*-face of **R2** maintaining minimal stereoelectronic repulsion (Scheme 3). It is perceived that the reactive intermediate R2 is a concoction of multiple ion-ion interactions; like ion-pair, dipole-dipole, H-bonding, van der Waals, **π**-stacking interactions shown in scheme 3 (which is also visible from minimum energy calculated reactive intermediate **R2**: top view A and side view B). Further oxidative tendencies of Br_3^- ion accelerate the dearomatisation. Also, the tribromide ion is believed to reside out of the reaction cavity which adds to the ion-pair interaction in the reactive intermediate (**R2**). It is further understood that the solvent plays a dominant role to maintain a feasible ion-pair attachment inside the cavity to deliver such tangible outcome (scheme 3).



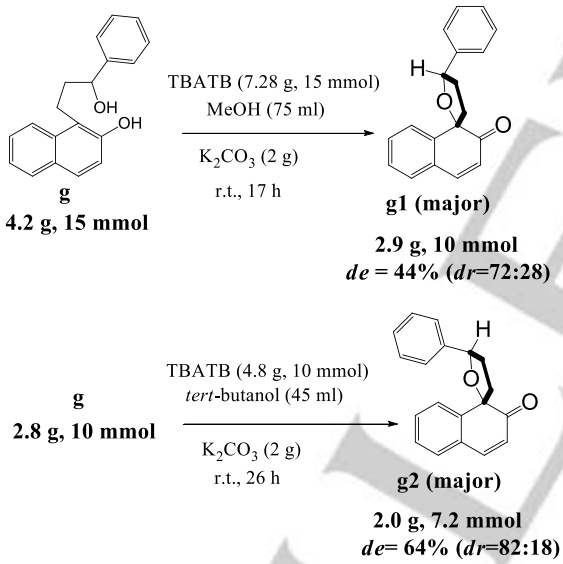
stable reactive intermediate (R2)



top view of R2 (**A**) side view of R2 (**B**)

Scheme 3. A plausible reactive intermediate

The reaction was encountered with our developed (+)-N-benzylcinchonine ammonium tribromide (**AT-1**) in *tert*-butanol as the solvent where the achieved diastereoselectivity was 87% (major isomer). As it is already perceived that naphthol-anion is activated in the process by the ammonium part of **AT-1** whereas the counterpart anion Br_3^- maintains an electrophilic perpendicular approach towards the partially planar ring of reactive intermediate **R2** (scheme 3) with minimal stereo electronic interaction. This generates a reaction cavity and also enhances the non-planarity in the aromatic ring. In an another concurrent trial, the diastereoselectivity increased further when (+)-cinchonine was added as an additive in an ongoing reaction mixture (***dr*** 93:7).



Scheme 4. Scaling-up of the spiro-furano naphthalone

Under the optimised reaction condition, the reaction was conducted on a larger-scale. For the scale-up synthesis of spiro-furano naphthalone, we started with 4.2 g (15 mmol) of 1-(3-hydroxy-3-phenylpropyl)naphthalen-2-ol (**g**) and tetrabutyl ammonium tribromide (7.28 g, 1 eq) in methanol solvent (75 ml) afforded an overall yield of 95%. On choosing of *tert*-butanol as the solvent, the spiro-furano naphthalone was achieved in 90%. The diastereoselectivity accomplished was 72% of **g1** isomer in methanol whereas it was 82% **g2** isomer in *tert*-butanol. (scheme 4)

Initial experiment with a focus on the enantioselectivity variant were performed with 1-(3-hydroxy-3-phenylpropyl)naphthalen-2-ol (**g**) and chiral (+) (2R,4S,5R)-1-benzyl-2-[(S-hydroxy(quinolone-4-yl)-methyl]-5-vinylquinuclidin-1-ium tribromide (**AT-1**) under the same reaction conditions (Table 7, entry 7.1) that produced 25% ee of (+) (1'S, 5S)-5-phenyl-4, 5-dihydro-2'H, 3H-spiro [furan-2, 1'-naphthalen]-2'-one **(g1)**. In order to improve the enantioselectivity, different chiral cinchonine based tribromides are being screened in our laboratory.

Conclusions

In conclusion, we feel enthusiastic to report the way out of controlling stereoselectivity in tribromide mediated oxidative dearomatisation of naphthols, thus generating stereoselective spiro-furano naphthalones. A fine tuning of the tribromide salt used, the alkyl substituent and the choice of appropriate solvent can achieve the best possible diastereoselectivities in the oxidative spiro-oxacylisations of naphthols. The present protocol has been generalised and economic. The mechanistic outlook associated with oxidative dearomatisation reactions is also taken into account to a fair extent. Presently, the asymmetric version of the reaction is being carried out in our laboratories which would further clarify the best possible outcomes along with a clear mechanistic optimization.

Experimental Section

All the reactions were performed under nitrogen atmosphere using oven dried glassware. All solvents are used in dried condition. THF was first dried over potassium carbonate then by metallic sodium with benzophenone. ^{t}BuOH, MeOH, Hexane, Toluene, EtOH were also dried over sodium metal. AcN and DCM were dried over P_2O_5. Potassium carbonate, 1,1,1-trifluoro ethanol and 1,1,1,3,3,3-Hexafluoropropan2-ol was purchased from HIMEDIA and used without further purification. Anhydrous sodium sulphate was used for drying reaction mixture after aqueous workup.

TLC was performed with .25mm coated commercial silica gel plates (E-Merck, DC-kiesel gel 60 F_{254}) and stain by Iodine, vanillin solution. Chromatographic separation was done by using (100-200mesh) silica gel.^{1}H & ^{13}C NMR were recorded on a Bruker (400MHz). NMR chemical shift value are reported in (δ ppm). TMS is taken as internal slandered for ^{1}H the residual signal for $CDCl_3$ taken as 7.28 ppm & for ^{13}C 77.00ppm. ^{1}H spectral data reported as δ (multiplicity, Coupling constant, integration). Multiplicity was reported as follows, s=singlet, d=doublet, t=triplet, q=quartet, m=multiplate, dd=doublet of a doublet. HRMS (High resolution Mass Spectra) was measured in a QTOF I (quadrupolehexapole-TOF) mass spectrometer with an orthogonal Z-spray-electrospray interface on micro (YA-263) mass spectrometer. IR spectra were recorded by using Perkin-Elmer spectrum-2 spectrometer using thin film deposit on KBr & absorption frequency reported in cm^{-1}. All the reactions are carried out in room temperature (25ºC). HPLC data [Chiral HPLC was performed by using Chiral-AM (5µm, 250 X 4.6 mm), Chiral OM (5µm, 250 X 4.6 mm), or Chiral-AM (10µm, 250 X 4.6 mm) columns].

General Experimental Procedure (A) for Preparation of Ammonium Tribromides (1-7, AT-1). To prepare the different quaternary ammonium tribromides we followed those procedures which was referred in reference number 14. To a well stirred trisubstituated amine (1 mmol) in dry acetonitrile solution, alkyl bromides (1.3 mmol) was added. The mixture was then allowed to stir at room temperature for 24 hours. Then the solvent was evaporated in vacuum at 50ºC and the resultant solid was dissolved in 5ml of water, Potassium bromide (2.5 mmol) was added and left it for 3mins. Then to

the mixture, aqueous solution of Oxone (1.25 mmol) was added dropwise and allowed it to stir at room temperature for 30mins. After that the solid was filtered off and washed with water and kept it for drying in desiccator for few days.

General Experimental procedure (B) for Oxidative Dearomatisation of Naphthols & synthesis of Spiro-furano-naphthalones. To a well stirred mixture of alkylated 3-hydroxy 2-naphthols (1mmol) in dry solvent (4ml) with potassium carbonate (1 mmol), quaternary ammonium tribromide (1 mmol) was added. The mixture was then allowed to stir at room temperature for overall 5-24 hours mentioned in the table (5). The reaction mixture was quenched with distilled water and extracted with Ethyl acetate. The organic part was washed with brine solution and dried over anhydrous sodium sulphate. Then the solvent was evaporated by reduced pressure. The mass was then purified by column chromatography using silica-gel (getting the data of mixture of diastereomers, performed flash chromatography) in appropriate solvents to deliver the desired compounds.

5-phenyl-4, 5-dihydro-2'H, 3H-spiro[furan-2, 1'-naphthalen]-2'-one (g). Was synthesized according to the general procedure B with 1-(3-hydroxy-3-phenylpropyl)naphthalen-2-ol (20 mg, 0.072 mmol) and TBATB salt using THF as a solvent at room temperature (30°C). Total reaction time was 12 hrs. The product was obtained as a yellow liquid (19 mg, 0.068 mmol, 95%) after elution with 10% ethyl acetate in petroleum ether of the crude reaction mixture. (R_f= 0.5, 15% ethyl acetate in petroleum ether) ^{1}H NMR (400 MHz, $CDCl_3$) for the diastereomeric mixture (g2:g1 = 2.8:1) δ 7.88 – 7.86 (m, 1H), 7.71 (t, *J* = 8.3 Hz, 1H), 7.57 (d, *J* = 7.5 Hz, 1H), 7.50 – 7.28 (m, 4H), 6.22 – 6.10 (m, 1H), 5.66 (dd, *J* = 8.3, 5.9 Hz, 1H), 5.49 (dd, *J* = 10.0, 5.5 Hz, 1H), 2.71-2.52 (m, 2H), 2.36 – 2.27 (m, 1H), 2.18 – 2.04 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.7, 202.4, 146.1, 144.9, 144.4, 141.5, 130.4, 129.5, 129.2, 129.1, 128.5, 128.4, 127.9, 127.9, 127.6, 126.9, 126.1, 125.7, 125.6, 124.1, 124.0, 88.2, 85.7, 83.6, 41.5, 40.7, 33.5, 32.9.

(1'S, 5S)-5-phenyl-4, 5-dihydro-2'H, 3H-spiro [furan-2, 1'-naphthalen]-2'-one (g1). Elution with 3% ethyl acetate in petroleum ether afforded yellow liquid (5 mg, 0.018 mmol, 26.3%). R_f= 0.5 (15% ethyl acetate in petroleum ether). IR (Neat Film, KBr) 2975.63, 1686.85, 1070.22, 756.11;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.7 Hz, 2H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.47 – 7.28 (m, 7H), 6.16 (d, *J* = 10.0 Hz, 1H), 5.49 (dd, *J* = 9.8, 5.5 Hz, 1H), 2.74 – 2.66 (m, 1H), 2.38-2.33 (m, 2H), 2.30 – 2.05 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.6, 146.1, 144.4, 141.5, 130.4, 129.6, 129.1, 128.4, 127.9, 126.9, 125.6, 124.1, 87.8, 85.7, 41.5, 33.5; HRMS (ESI) calc'd for $C_{19}H_{16}O_2$ [M]+: 276.1150, Found: 276.1152. ee 25% [Chiral AM, (10µm, 250 X 4.6 mm) column hexane/iPrOH 99.5:0.5, flow rate 0.5 mL/min, 25ºC, λ = 250 nm; t_R (major) = 21.7 min and t_R (minor) = 33.7 min].

(1'S, 5R)-5-phenyl-4, 5-dihydro-2'H, 3H-spiro[furan-2,1'-naphthalen]-2'-one (g2). Elution with 4% ethyl acetate in petroleum ether afforded yellow liquid (14 mg, 0.05 mmol, 73.7%). R_f= 0.5 (15% ethyl acetate in petroleum ether). IR (Neat Film, KBr) 2975.73, 1686.02, 1070.72, 755.17; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.5 Hz, 1H), 7.57 (d, *J* = 7.5 Hz, 2H), 7.47 – 7.39 (m, 3H), 7.37 – 7.26 (m, 4H), 6.17 (d, *J* = 10.0 Hz, 1H), 5.66 (dd, *J* = 8.3, 5.9 Hz, 1H), 2.65-2.50 (m, 2H), 2.20 – 2.05 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.0, 145.0, 144.9, 141.7, 130.3, 129.5, 129.3, 128.5, 127.9, 127.5, 126.0, 125.7, 124.0, 87.6, 83.6, 40.7, 32.9; HRMS (ESI) calc'd for $C_{19}H_{16}O_2$ [M]+: 276.1150, Found: 276.1153.

5-benzyl-4, 5-dihydro-2'H, 3H-spiro[furan-2,1'-naphthalen]-2'-one (h). Was synthesized according to the general procedure B with 1-(3-hydroxy-4-phenylbutyl)naphthalen-2-ol (20 mg, 0.068 mmol) and TBATB salt using THF as a solvent at room temperature (30°C). Total reaction time was 14 hrs. The product was obtained as a yellow liquid (18 mg, 0.058 mmol, 90%) after elution with 10% ethyl acetate in petroleum ether of the crude reaction mixture. (R_f= 0.6, 15% ethyl acetate in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) for the diastereomeric mixture (h2:h1 = 2.3:1) δ 7.59 (d, *J* = 7.5 Hz, 1H), 7.54 – 7.46 (m, 1H), 7.44 – 7.22 (m, 3H), 7.20 – 7.16 (m, 1H), 6.13 (d, *J* = 9.9 Hz, 1H), 4.87 (m, 1H), 4.81 – 4.64 (m, 1H), 3.49-3.43 (m, 1H), 3.34 (dt, *J* = 8.7, 4.2 Hz, 1H), 3.12 – 2.99 (m, 1H), 2.55-2.50 (m, 2H), 2.45 – 2.37 (m, 1H), 2.13 – 1.80 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.1, 202.9, 145.9, 145.2, 144.7, 144.3, 139.0, 138.0, 130.3, 130.1, 129.6, 129.5, 129.3, 129.1, 128.4, 128.4, 127.8, 127.7, 126.4, 126.2, 125.5, 124.0, 124.0, 88.8, 88.2, 84.6, 83.1, 42.0, 41.6, 40.8, 40.1, 29.6, 29.4.

(1'S, 5S)-5-benzyl-4, 5-dihydro-2'H, 3H-spiro[furan-2,1'-naphthalen]-2'-one (h1). Elution with 3% ethyl acetate in petroleum ether afforded yellow liquid (5 mg, 0.017 mmol, 29.5%). R_f= 0.6 (15% ethyl acetate in petroleum ether). IR (Neat Film, KBr) 2959.92, 1684.03, 1053.01, 755.14; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.3 Hz, 1H), 7.42 – 7.24 (m, 8H), 6.14 (d, *J* = 9.8 Hz, 1H), 4.79 – 4.72 (m, 1H), 3.45 (dd, *J* = 13.4, 6.4 Hz, 1H), 3.08 (dd, *J* = 13.4, 7.4 Hz, 1H), 2.54-2.49 (m, 1H), 2.03-1.87 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.0, 144.3, 139.0, 130.3, 129.3, 129.0, 128.4, 127.7, 126.2, 125.5, 124.0, 88.8, 84.6, 42.0, 40.8, 29.6; HRMS (ESI) calc'd for $C_{20}H_{18}O_2$ [M]+ : 290.1306, Found: 290.1295.

(**1'S, 5R)-5-benzyl-4, 5-dihydro-2'H, 3H-spiro[furan-2,1'-naphthalen]-2'-one (h2).** Elution with 4% ethyl acetate in petroleum ether afforded yellow liquid (13 mg, 0.04 mmol, 70.5%). R_f= 0.6 (15% ethyl acetate in petroleum ether). IR (Neat Film, KBr) 2959.92, 1684.33, 1052.83, 668.38; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.49 (m, 1H), 7.39 – 7.32 (m, 6H), 7.32 – 7.25 (m, 3H), 6.11 (d, *J* = 9.8 Hz, 1H), 4.86 (m, 1H), 3.33 (dd, *J* = 13.4, 5.4 Hz, 1H), 3.01 (dd, *J* = 13.3, 7.8 Hz, 1H), 2.40 (dt, *J* = 11.8, 7.3 Hz, 1H), 2.13 – 2.05 (m, 1H), 1.95 – 1.80 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.1, 145.2, 144.7 138.0, 130.1, 129.5, 129.1, 128.4, 127.8, 126.4, 125.5, 124.0, 88.1, 83.2, 41.6, 40.1, 29.3; HRMS (ESI) calc'd for $C_{20}H_{18}O_2$ [M]+ : 290.1306, Found: 290.1301.

5-(4-fluorobenzyl)-4, 5-dihydro-2'H, 3H-spiro[furan-2,1'-naphthalen]-2'-one (i). Was synthesized according to the general procedure B with 1-(4-(4-fluorophenyl)-3-hydroxybutyl)naphthalen-2-ol (20 mg, 0.064 mmol) and TBATB salt using THF as a solvent at room temperature (30°C). Total reaction time was 10 hrs. The product was obtained as a yellow liquid (18 mg, 0.068 mmol, 90%) after elution with 10% ethyl acetate in petroleum ether of the crude reaction mixture. (R_f= 0.6, 15% ethyl acetate in petroleum ether) ^{1}H NMR (400 MHz, $CDCl_3$) for the diastereomeric mixture (i2:i1 = 3.2:1) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.5 Hz, 1H), 7.54 (d, *J* = 7.5 Hz, 1H), 7.50 – 7.30 (m, 11H), 7.16 – 7.01 (m, 4H), 6.19 (dd, *J* = 12.6, 9.9 Hz, 2H), 4.97 – 4.84 (m, 1H), 4.84 – 4.71 (m, 1H), 3.47 (dd, *J* = 13.5, 7.0 Hz, 1H), 3.33 (dd, *J* = 13.8, 5.5 Hz, 1H), 3.09 (td, *J* = 13.0, 7.0 Hz, 2H), 2.66 – 2.52 (m, 1H), 2.48 (dt, *J* = 12.1, 7.5 Hz, 1H), 2.23 – 1.78 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.0, 202.7, 163.0, 160.5, 144.7, 144.4, 131.0, 130.9, 130.1, 129.2, 127.8, 125.4, 124.0, 115.3, 115.2, 115.08, 114.99, 89.0, 88.0, 84.5, 83.0, 41.2, 40.8, 40.7, 40.1, 29.6 29.4.

(1'S, 5S)-5-(4-fluorobenzyl)-4, 5-dihydro-2'H, 3H-spiro[furan-2,1'-naphthalen]-2'-one (i1). Elution with 3% ethyl acetate in petroleum ether afforded yellow liquid (4.2 mg, 0.014 mmol, 23.5%). R_f= 0.5 (15% ethyl acetate in petroleum ether). IR (Neat Film, KBr) 2938.92, 1680.93, 1056.01, 755.11; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.3 Hz, 1H), 7.50 – 7.32 (m, 6H), 7.12 – 7.04 (m, 2H), 6.21 (d, *J* = 9.8 Hz, 1H), 4.81-4.75 (m, 1H), 3.33 (dd, *J* = 13.8, 5.5 Hz, 1H), 3.07 (dd, *J* = 13.8, 6.8 Hz, 1H), 2.67 – 2.47 (m, 1H), 2.18 – 1.85 (m, 3H); ^{13}C

NMR (100 MHz, $CDCl_3$) δ 202.9, 162.6, 145.8, 144.4, 130.8, 130.7, 130.3, 129.6, 129.0, 127.8, 125.5, 124.0, 115.2, 115.0, 88.9, 84.5, 41.2, 40.8, 29.6; HRMS (ESI) calc'd for $C_{20}H_{17}F NaO_2$ [M+Na]+ : 331.1105, Found: 331.1102.

(1'S, 5R)-5-(4-fluorobenzyl)-4, 5-dihydro-2'H, 3H-spiro[furan-2,1'-naphthalen]-2'-one (i2). Elution with 4% ethyl acetate in petroleum ether afforded yellow liquid (13.7 mg, 0.04 mmol, 76.5%). R_f= 0.5 (15% ethyl acetate in petroleum ether). IR (Neat Film, KBr) 2968.15, 1682.07, 1057.00, 756.17; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.5 Hz, 1H), 7.45-7.35 (m, 6H), 7.10 (m, 2H), 6.18 (d, *J* = 9.8 Hz, 1H), 5.03 – 4.78 (m, 1H), 3.33 (dd, *J* = 13.8, 5.5 Hz, 1H), 3.07 (dd, *J* = 13.8, 7.3 Hz, 1H), 2.48 (dt, *J* = 12.3, 7.5 Hz, 1H), 2.16 (m, 1H), 2.03 – 1.81 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.0, 162.7, 144.7, 131.0, 130.9, 130.1, 129.5, 129.2, 127.8, 125.4, 124.0, 115.3, 115.1, 88.0, 83.0, 40.7, 40.1, 29.4; HRMS (ESI) calc'd for $C_{20}H_{17}F NaO_2$ [M+Na]+ : 331.1105, Found: 331.1104.

5-phenethyl-4, 5-dihydro-2'H, 3H-spiro[furan-2,1'-naphthalen]-2'-one (k). Was synthesized according to the general procedure B with 1-(3-hydroxy-5-phenylpentyl)naphthalen-2-ol (20 mg, 0.065 mmol) and TBATB salt using THF as a solvent at room temperature (30°C). Total reaction time was 16 hrs. The product was obtained as a yellow liquid (17 mg, 0.056 mmol, 85%) after elution with 10% ethyl acetate in petroleum ether of the crude reaction mixture (R_f= 0.6, 15% ethyl acetate in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) for the diastereomeric mixture (k2:k1 = 2.2:1) δ 7.59 (dd, *J* = 20.6, 7.7 Hz, 1H), 7.42 – 7.16 (m, 10H), 6.10 (dd, *J* = 9.8, 3.5 Hz, 1H), 4.68 – 4.60 (m, 1H), 4.51 – 4.44 (m, 1H), 2.96 – 2.77 (m, 2H), 2.49 – 2.32 (m, 1H), 2.27-2.16 (qd, 2H), 2.09-1.70 (m, 4H).

(1'S, 5R)-5-phenethyl-4, 5-dihydro-2'H, 3H-spiro[furan-2,1'-naphthalen]-2'-one (k1). Elution with 3% ethyl acetate in petroleum ether afforded colourless liquid (5.3 mg, 0.017 mmol, 31.2%). R_f= 0.6 (15% ethyl acetate in petroleum ether). IR (Neat Film, KBr) 2963.98, 1682.93, 1062.01, 755.12; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.5 Hz, 1H), 7.51 – 7.29 (m, 10H including CDCl3), 6.19 (d, *J* = 9.8 Hz, 1H), 4.59 – 4.55 (m, 1H), 3.04-2.86 (m, 2H), 2.58 – 2.55 (m, 1H), 2.48 – 2.45 (m, 1H), 2.18 – 2.10 (m, 2H), 2.02 – 1.92 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.8, 146.1, 144.3, 142.2, 130.3, 129.7, 129.0, 128.6, 128.3, 127.7, 125.7, 125.5, 124.1, 88.4, 82.8, 41.0, 37.0, 32.7, 29.7; HRMS (ESI) calc'd for $C_{21}H_{20}NaO_2$ [M+Na]+ : 327.1356, Found: 327.1353.

(1'S, 5S)-5-phenethyl-4, 5-dihydro-2'H, 3H-spiro[furan-2,1'-naphthalen]-2'-one (k2). Elution with 4% ethyl acetate in petroleum ether afforded yellow liquid (11.7 mg, 0.038 mmol, 68.9%). R_f= 0.6 (15% ethyl acetate in petroleum ether). IR (Neat Film, KBr) 2987.73, 1681.65, 1066.06, 755.12; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.5 Hz, 1H), 7.53 – 7.29 (m, 9H), 6.19 (d, *J* = 9.8 Hz, 1H), 4.75 – 4.68 (m, 1H), 3.04 – 2.98 (m, 1H), 2.93 – 2.85 (m, 1H), 2.54-2.47 (m, 1H), 2.33 – 2.26 (m, 2H), 2.12 – 2.09 (m, 1H), 2.01-1.96 (m, 1H), 1.88 – 1.81 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.1, 145.3, 144.6, 142.0, 130.2, 129.1, 129.0, 128.6, 128.5, 128.3, 127.8, 125.9, 125.7, 125.4, 124.0, 88.0, 82.2, 40.1, 37.8, 32.7, 30.1; HRMS (ESI) calc'd for $C_{21}H_{20}NaO_2$ [M+Na]+ : 327.1356, Found: 327.1355.

5-methyl-4, 5-dihydro-2'H, 3H-spiro[furan-2,1'-naphthalen]-2'-one (a). Was synthesized according to the general procedure B with 1-(3-hydroxybutyl)naphthalen-2-ol (20 mg, 0.093 mmol) and TBATB salt using THF as a solvent at room temperature (30°C). Total reaction time was 14 hrs. The product was obtained as a yellow liquid (17 mg, 0.079 mmol, 89%) after elution with 10% ethyl acetate in petroleum ether of the crude reaction mixture (R_f= 0.7, 15% ethyl acetate in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) for the diastereomeric mixture (a2:a1 = 3.2:1) δ 7.68-7.59 (m, 1H), 7.43 – 7.25 (m, 4H), 6.11 (d, *J* = 9.8 Hz, 1H), 4.75 – 4.66 (m, 2H), 2.53 – 2.39 (m, 1H), 2.22-2.17 (m, 1H), 2.09-1.90 (m, 1H), 1.97 – 1.89 (m, 2H), 1.88 – 1.80 (m, 1H), 1.73-1.65(m, 1H), 1.57-1.56 (m, 2H)1.51 (d, *J* = 6.0 Hz, 3H).

(1'S, 5R)-5-methyl-4, 5-dihydro-2'H, 3H-spiro[furan-2,1'-naphthalen]-2'-one (a2). Elution with 2% ethyl acetate in petroleum ether afforded yellow liquid (11.7 mg, 0.055 mmol, 69.1%). R_f= 0.7 (15% ethyl acetate in petroleum ether). IR (Neat Film, KBr) 2893.15, 1682.11,1045.57,700.4; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.6 Hz, 1H), 7.41-7.26 (m, 5H including CDCl3), 6.09 (d, *J* = 9.9 Hz, 1H), 4.74 – 4.66 (m, 1H), 2.41 (dt, *J* = 12.6, 7.8 Hz, 1H), 2.20 – 2.14 (m, 1H), 1.95-1.89 (m, 1H), 1.73-1.64 (m, 1H), 1.49 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.3, 145.5, 144.6, 130.1, 129.5, 129.1, 127.7, 125.5, 124.1, 88.1, 78.8, 40.6, 32.0, 21.0; HRMS (ESI) calc'd for $C_{14}H_{14}O_2$ [M]+: 214.0994, Found: 214.0996.

(1'S, 5S)-5-methyl-4, 5-dihydro-2'H, 3H-spiro[furan-2,1'-naphthalen]-2'-one (a1). Elution with 1% ethyl acetate in petroleum ether afforded yellow liquid (5.2 mg, 0.024mmol, 20.9%). R_f= 0.7 (15% ethyl acetate in petroleum ether). IR (Neat Film, KBr) 2965.17,1683.08, 1048.08, 700.14; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.0 Hz, 1H), 7.45 – 7.25 (m, 5H including CDCl3), 6.09 (d, *J* = 9.9 Hz, 1H), 4.71 – 4.63 (m, 1H), 2.51-2.47 (m, 1H), 2.07 – 1.79 (m, 3H), 1.54 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.9, 146.1, 144.2, 130.3, 129.6, 129.0, 127.7, 125.4, 124.0, 88.6, 79.8, 41.3, 31.4, 20.8; HRMS (ESI) calc'd for $C_{14}H_{14}O_2$ [M]+: 214.0994, Found: 214.0995.

5-ethyl-4, 5-dihydro-2'H, 3H-spiro[furan-2,1'-naphthalen]-2'-one (b). Was synthesized according to the general procedure B with 1-(3-hydroxypentyl)naphthalen-2-ol (20 mg, 0.086 mmol) and TBATB salt using THF as a solvent at room temperature (30°C). Total reaction time was 16 hrs. The product was obtained as a yellow liquid (16.5 mg, 0.072 mmol, 81%) after elution with 10% ethyl acetate in petroleum ether of the crude reaction mixture. (R_f= 0.6, 15% ethyl acetate in petroleum ether) ^{1}H NMR (400 MHz, $CDCl_3$) for the diastereomeric mixture (b2:b1 = 2.4:1) δ 7.62 (t, *J* = 8.5 Hz, 1H), 7.43 – 7.25 (m, 4H), 6.10 (dd, *J* = 9.9, 2.2 Hz, 1H), 4.56 – 4.49 (m, 1H), 4.48-4.41 (m, 1H), 2.52 – 2.39 (m, 1H), 2.22 – 2.17 (m, 1H), 2.08 – 1.68 (m, 4H), 1.13-1.05 (m, 3H), 0.91-0.84 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.3, 203.0, 146.2, 145.4, 144.6, 144.2, 130.3, 130.1, 129.6, 129.1, 128.9, 127.7, 127.6, 125.5, 125.4, 124.1, 124.0, 88.0, 85.5, 84.2, 41.0, 40.1, 29.6, 29.4, 28.8, 28.4, 10.7, 10.5.

(1'S, 5R)-5-ethyl-4, 5-dihydro-2'H, 3H-spiro[furan-2,1'-naphthalen]-2'-one (b1). Elution with 1% ethyl acetate in petroleum ether afforded yellow liquid (5 mg, 0.022 mmol, 29.4%). R_f= 0.6 (15% ethyl acetate in petroleum ether). IR (Neat Film, KBr) 2955.58, 1686.92, 1063.69, 755.15; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.8 Hz, 1H), 7.41-7.23 (m, 4H), 6.08 (d, *J* = 9.9 Hz, 1H), 4.46-4.39(m, 1H), 2.50 – 2.45 (m, 1H), 2.08 – 1.77 (m, 4H), 1.04 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.9, 146.1, 144.1, 130.2, 129.3, 128.8, 127.5, 125.4, 124.0, 88.0, 85.4, 40.9, 29.3, 28.3, 10.6; HRMS (ESI) calc'd for $C_{15}H_{16}O_2$ [M]+: 228.1150, Found: 228.1146.

(1'S, 5S)-5-ethyl-4, 5-dihydro-2'H, 3H-spiro [furan-2, 1'-naphthalen]-2'-one (b2). Elution with 2% ethyl acetate in petroleum ether afforded yellow liquid (11.5 mg, 0.05 mmol, 70.5%). R_f= 0.6 (15% ethyl acetate in petroleum ether). IR (Neat Film, KBr) IR 2956.68, 2875.28, 1687.9, 1064.58, 755.14; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.8 Hz, 1H) 7.39 – 7.24 (m, 4H), 6.08 (d, *J* = 9.9 Hz, 1H), 4.50 (p, *J* = 6.7 Hz, 1H), 2.43-2.36 (m,1H), 2.21-2.13 (m, 1H), 1.96-1.83 (m, 2H), 1.78 – 1.64 (m, 2H), 1.07 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.3, 145.3, 144.5, 144.1, 130.0, 129.5, 129.0, 128.8, 127.6, 125.3, 123.9, 87.9, 84.1, 40.0, 29.5, 28.7, 10.4; HRMS (ESI) calc'd for $C_{15}H_{16}O_2$ [M]+: 228.1150, Found: 228.1148.

5-propyl-4, 5-dihydro-2'H, 3H-spiro[furan-2,1'-naphthalen]-2'-one (c). Was synthesized according to the general procedure B with 1-(4-(4-fluorophenyl)-3-

hydroxybutyl)naphthalen-2-ol (20 mg, 0.082 mmol) and TBATB salt using THF as a solvent at room temperature (30°C). Total reaction time was 12 hrs. The product was obtained as a yellow liquid (16 mg, 0.066 mmol, 79%) after elution with 10% ethyl acetate in petroleum ether of the crude reaction mixture. (R_f= 0.6, 15% ethyl acetate in petroleum ether) ^{1}H NMR (400 MHz, $CDCl_3$) for the diastereomeric mixture (c2:c1 = 2.6:1) δ 7.70 (t, *J* = 7.9 Hz, 1H), 7.50 – 7.33 (m, 4H), 6.08 (dd, *J* = 9.9, 1.8 Hz, 1H), 4.70-4.62 (m, 1H), 4.61 – 4.55 (m, 1H), 2.59 – 2.45 (m, 1H), 2.31 – 2.23 (m, 1H), 2.14– 1.52, 4H) 1.13- 1.08 (m, 3H), 0.98-0.8(m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.3, 202.6, 144.4, 144.0, 137.0, 130.2, 130.0, 129.5, 129.0, 128.8, 127.6, 127.5, 125.5, 125.3, 124.3, 124.0, 123.9, 88.3, 87.8, 83.7, 82.6, 40.9, 40.1, 38.0, 37.5, 31,8, 30.0, 29.7, 29.6, 22.6, 19.6, 19.4, 14.2, 14.1.

(1'S, 5R)-5-propyl-4, 5-dihydro-2'H, 3H-spiro [furan-2, 1'-naphthalen]-2'-one (c1). Elution with 1% ethyl acetate in petroleum ether afforded yellow liquid (4.4 mg, 0.018mmol, 27.8%). R_f= 0.6 (15% ethyl acetate in petroleum ether). IR (Neat Film, KBr) 2961.09, 1682.93, 1060.69, 755.15; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.7 Hz, 1H), 7.41 – 7.23 (m, 5H including $CDCl_3$), 6.08 (d, *J* = 9.9 Hz, 1H), 4.53-4.45 (m, 1H), 2.50 – 2.46 (m, 1H), 2.09 – 1.71 (m, 4H), 1.61 – 1.41 (m, 1H), 1.05 – 0.96 (m, 3H), 0.90-0.83 (m,1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.7, 146.5, 144.1, 130.2, 129.4, 128.9, 127.6, 125.5, 124.1, 88.1, 83.8, 41.0, 37.6, 29.8, 19.7, 14.2; HRMS (ESI) calc'd for $C_{16}H_{18}NaO_2$ [M+Na]+ : 265.1199, Found: 265.1197.

(1'S, 5S)-5-propyl-4, 5-dihydro-2'H, 3H-spiro[furan-2,1'-naphthalen]-2'-one (c2). Elution with 2% ethyl acetate in petroleum ether afforded yellow liquid (11.6 mg, 0.047 mmol, 72.2%). R_f= 0.7 (15% ethyl acetate in petroleum ether). IR (Neat Film, KBr) 2963.01, 1683.43, 1066.17, 755.14; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.57 (m, 1H), 7.41 – 7.25 (m, 5H including $CDCl_3$), 6.08 (d, *J* = 9.9 Hz, 1H), 4.61 – 4.5 (m, 1H), 2.44– 2.36 (m, 1H), 2.22-2.14 (m, 1H), 1.95 – 1.85 (m, 2H), 1.74 – 1.44 (m, 3H), 1.05 – 0.99 (m, 3H), 0.90-0.83 (m,1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.3, 145.5, 144.6, 130.1, 129.6, 129.1, 127.7, 125.4, 124.0, 87.9, 82.7, 40.2, 38.1, 30.1, 19.5, 14.3; HRMS (ESI) calc'd for $C_{16}H_{18}NaO_2$ [M+Na]+ : 265.1199, Found: 265.1196.

5-isopropyl-4, 5-dihydro-2'H, 3H-spiro[furan-2,1'-naphthalen]-2'-one (f). Was synthesized according to the general procedure B with 1-(3-hydroxy-4-methylpentyl)naphthalen-2-ol (20 mg, 0.082 mmol) and TBATB salt using THF as a solvent at room temperature (30°C). Total reaction time was 16 hrs. The product was obtained as a yellow liquid (16 mg, 0.066 mmol, 81%) after elution with 10% ethyl ace-tate in petroleum ether of the crude reaction mixture. (R_f= 0.6, 15% ethyl acetate in petroleum ether) ^{1}H NMR (400 MHz, $CDCl_3$) for the diastereomeric mixture (f2:f1 = 2.2:1) δ 7.65 (d, *J* = 7.8 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.44 – 7.24 (m, 5H), 6.10 (dd, *J* = 10.0, 3.2 Hz, 2H), 4.38– 4.27 (m, 1H), 4.14-4.09 (m, 1H), 2.53 – 2.37 (m, 2H), 2.20-2.09 (m, 1H), 2.03 – 1.78 (m, 3H), 1.17-1.14(m, 3H), 1.05-1.02(m, 2H) 0.98(d, J=6.8 Hz, 2H).

(1'S, 5S)-5-isopropyl-4, 5-dihydro-2'H, 3H-spiro[furan-2,1'-naphthalen]-2'-one (f1). Elution with 1% ethyl acetate in petroleum ether afforded yellow liquid (4.9 mg, 0.02mmol, 30.5%). R_f= 0.6 (15% ethyl acetate in petroleum ether). IR (Neat Film, KBr) 2957.89, 1680.99, 1059.0, 755.14; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58-7.56 (m, 1H), 7.41 – 7.37 (m, 1H), 7.30 – 7.29 (d, *J*=9.8 Hz, 1H), 7.29-7.22 (m, 2H), 6.07(d, *J*=9.9 Hz, 1H) 4.12-4.06 (m, 1H), 2.51 – 2.43 (m, 1H), 2.17 – 2.09 (m, 1H), 2.03-1.81 (m, 1H), 1.12 (d, *J* = 6.7 Hz, 3H), 0.96 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.0, 146.5, 144.1, 130.3, 129.6, 128.9, 127.6, 125.5, 124.1, 89.9, 88.0, 41.1, 33.3, 28.1, 20.4, 18.8; HRMS (ESI) calc'd for $C_{16}H_{18}NaO_2$ [M+Na]+ : 265.1199, Found: 265.1198.

(1'S, 5R)-5-isopropyl-4, 5-dihydro-2'H, 3H-spiro[furan-2,1'-naphthalen]-2'-one (f2). Elution with 2% ethyl acetate in petroleum ether afforded yellow liquid (11.1 mg, 0.046 mmol, 69.8%). R_f= 0.6 (15% ethyl acetate in petroleum ether). IR (Neat Film, KBr) 2958.85, 1683.89, 1065.69, 756.11; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64-7.62 (m, 1H), 7.39-7.24 (m, 4H), 6.09 (d, *J*=9.9 Hz, 1H), 4.32 – 4.26 (m, 1H), 2.42 – 2.34 (m, 1H), 2.15 – 2.06 (m, 1H), 1.99-1.91(m, 1H), 1.87-1.74(m, 2H), 1.13 (d, *J* = 6.7 Hz, 3H), 1.00 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.3, 145.3, 144.4, 130.0, 129.5, 129.0, 127.6, 125.3, 123.9, 89.8, 88.0, 40.7, 33.3, 27.6, 19.6, 18.8; HRMS (ESI) calc'd for $C_{16}H_{18}NaO_2$ [M+Na]+ : 265.1199, Found: 265.1196.

5-butyl-4, 5-dihydro-2'H, 3H-spiro[furan-2,1'-naphthalen]-2'-one (d). Was synthesized according to the general procedure B with 1-(3-hydroxyheptyl)naphthalen-2-ol (20 mg, 0.077 mmol) and TBATB salt using THF as a solvent at room temperature (30°C). Total reaction time was 12 hrs. The product was obtained as a yellow liquid (17 mg, 0.066 mmol, 86%) after elution with 10% ethyl ace-tate in petroleum ether of the crude reaction mixture. (R_f= 0.7, 15% ethyl acetate in petroleum ether) ^{1}H NMR (400 MHz, $CDCl_3$) for the diastereomeric mixture (d2:d1 = 2.7:1) δ 7.59 (t, *J*=7.6 Hz, 1H), 7.47 – 7.23 (m, 6H), 6.10-6.07 (m, 2H), 4.59 – 4.52 (m, 1H), 4.51 – 4.44 (m, 1H), 2.48 – 2.36 (m, 1H), 2.20-2.15 (m, 1H), 2.08-1.81 (m, 1H), 1.74-1.60 (m, 1H), 1.52 – 1.37 (m, 2H), 0.97-0.86 (m, 3H).

(1'S, 5R)-5-butyl-4, 5-dihydro-2'H, 3H-spiro[furan-2,1'-naphthalen]-2'-one (d1). Elution with 1% ethyl acetate in petroleum ether afforded yellow liquid (4.5 mg, 0.018 mmol, 26.6%). R_f= 0.7 (15% ethyl acetate in petroleum ether). IR (Neat Film, KBr) 2957.18, 1680.03, 1055.04, 755.16; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.9 Hz, 1H), 7.43 – 7.35 (m, 1H), 7.32 (d, *J* = 9.9 Hz, 1H), 7.29 – 7.23 (m, 3H including CDCl3), 6.08 (d, *J* = 9.9 Hz, 1H), 4.51 – 4.46 (m, 1H), 2.50-2.45 (m, 1H), 2.07 – 1.99 (m, 2H), 1.93 – 1.79 (m, 3H), 1.52 – 1.36 (m, 3H), 0.96-0.92 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.0, 146.3, 144.1, 130.3, 129.6, 128.9, 127.6, 125.5, 124.1, 88.2, 84.1, 41.0, 35.2, 29.8, 28.7, 22.9, 14.2; HRMS (ESI) calc'd for $C_{17}H_{20}NaO_2$ [M+Na]+ : 279.1356, Found: 279.1357.

(1'S, 5S)-5-butyl-4, 5-dihydro-2'H, 3H-spiro[furan-2,1'-naphthalen]-2'-one (d2). Elution with 3% ethyl acetate in petroleum ether afforded yellow liquid (12.5 mg, 0.048 mmol, 73.4%). R_f= 0.7 (15% ethyl acetate in petroleum ether). IR (Neat Film, KBr) 2956.03, 1683.27, 1057.00, 755.17; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 11.3, 4.5 Hz, 1H), 7.41-7.25 (m, 4H), 6.09 (d, *J* = 9.9 Hz, 1H), 4.66 – 4.43 (m, 1H), 2.43-2.36 (m, 1H), 2.21 – 2.14 (m, 1H), 1.93-1.85 (m, 2H), 1.74 – 1.52 (m, 2H), 1.47 – 1.39 (m, 3H), 0.97 – 0.92 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.1, 145.5, 144.6, 130.1, 129.6, 129.1, 127.7, 125.4, 124.0, 87.9, 82.9, 40.2, 35.6, 30.1, 28.5, 22.9, 14.1; HRMS (ESI) calc'd for $C_{17}H_{20}NaO_2$ [M+Na]+ : 279.1356, Found: 279.1354.

5-pentyl-4, 5-dihydro-2'H, 3H-spiro[furan-2,1'-naphthalen]-2'-one (e). Was synthesized according to the general procedure B with 1-(3-hydroxyheptyl)naphthalen-2-ol (20 mg, 0.073 mmol) and TBATB salt using THF as a solvent at room temperature (30°C). Total reaction time was 21 hrs. The product was obtained as a yellow liquid (15 mg, 0.055 mmol, 76%) after elution with 10% ethyl ace-tate in petroleum ether of the crude reaction mixture. (R_f= 0.7, 15% ethyl acetate in petroleum ether) ^{1}H NMR (400 MHz, $CDCl_3$) for the diastereomeric mixture (e2:e1 = 2.7:1) δ 7.60 (t, *J* = 7.4 Hz, 1H), 7.42 – 7.25 (m, 4H), 6.10 (dd, *J* = 9.9, 2.0 Hz, 1H), 4.61 – 4.54 (m, 1H), 4.53-4.47 (m, 1H), 2.52-2.38 (m, 1H), 2.23 – 2.15 (m, 1H), 2.07-2.03 (m, 1H), 1.96 – 1.83 (m, 2H), 1.80 – 1.64 (m, 2H), 1.60 – 1.25 (m, 9H), 0.95 – 0.88 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.3, 203.0, 146.3, 145.5, 144.6, 144.2, 130.3, 130.1, 129.6, 129.6, 129.1, 128.9, 127.7, 127.6, 125.5, 125.4,

124.1, 124.0, 87.9, 84.2, 83.0, 41.0, 40.2, 35.9, 35.5, 32.0, 30.1, 29.8, 29.7, 26.2, 26.0, 22.7, 22.7, 14.1, 14.1.

(1'S, 5R)-5-pentyl-4, 5-dihydro-2'H, 3H-spiro[furan-2,1'-naphthalen]-2'-one (e1). Elution with 1% ethyl acetate in petroleum ether afforded yellow liquid (4 mg, 0.015 mmol, 26.7%). R_f= 0.7 (15% ethyl acetate in petroleum ether). IR (Neat Film, KBr) 2955.00, 1680.03, 1056.04, 755.14; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.5 Hz, 1H), 7.41 (td, *J* = 7.4, 1.8 Hz, 1H), 7.34 (d, *J* = 9.9 Hz, 1H), 7.32 – 7.25 (m, 2H), 6.10 (d, *J* = 9.9 Hz, 1H), 4.52-4.48 (m, 1H), 2.52-2.47 (m, 1H), 2.09 – 1.75 (m, 4H), 1.55 – 1.27 (m, 4H), 0.98-0.90 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.8, 146.3, 144.0, 130.2, 129.7, 128.9, 127.6, 125.5, 124.1, 88.2, 84.1, 41.0, 35.5, 32.0, 29.9, 26.1, 22.6, 14.0; HRMS (ESI) calc'd for $C_{18}H_{22}NaO_2$ [M+Na]+ : 2993.1512, Found: 293.1511.

(1'S, 5S)-5-pentyl-4, 5-dihydro-2'H, 3H-spiro[furan-2, 1'-naphthalen]-2'-one (e2). Elution with 2% ethyl acetate in petroleum ether afforded yellow liquid (11 mg, 0.04 mmol, 73.3%). R_f= 0.7 (15% ethyl acetate in petroleum ether). IR (Neat Film, KBr) 2857.59,1684.03, 1060.87, 755.14; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.8 Hz, 1H), 7.43 – 7.27 (m, 4H), 6.11 (d, *J* = 9.9 Hz, 1H), 4.61 – 4.54 (m, 1H), 2.43-2.40 (m, 1H), 2.22 – 2.17 (m, 1H), 1.95 – 1.88 (m, 2H), 1.74 – 1.66 (m, 3H), 1.42-1.37(m, 3H), 0.97-0.90 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.0, 145.5, 144.6, 130.1, 129.6, 129.1, 127.7, 125.4, 124.0, 87.6, 83.0, 40.2, 35.9, 32.0, 30.1, 26.0, 22.7, 14.1; HRMS (ESI) calc'd for $C_{18}H_{22}NaO_2$ [M+Na]+ : 2993.1512, Found: 293.1514.

5-octyl-4, 5-dihydro-2'H, 3H-spiro[furan-2,1'-naphthalen]-2'-one (l). Was synthesized according to the general procedure B with 1-(3-hydroxyundecyl)naphthalen-2-ol (20 mg, 0.063 mmol) and TBATB salt using THF as a solvent at room temperature (30°C). Total reaction time was 24 hrs. The product was obtained as a yellow liquid (15 mg, 0.048 mmol, 75%) after elution with 10% ethyl ace-tate in petroleum ether of the crude reaction mixture. (R_f= 0.8, 15% ethyl acetate in petroleum ether) ^{1}H NMR (400 MHz, $CDCl_3$) for the diastereomeric mixture (l2:l1 = 2.6:1) δ 7.60 (t, *J* = 7.8 Hz, 1H), 7.42 – 7.24 (m, 2H), 6.10 (d, *J* = 9.9 Hz, 1H), 4.61 – 4.54 (m, 1H), 4.53-4.46 (m, 1H), 2.51-2.47 (m, 1H), 2.44 – 2.37 (m, 1H), 2.23 – 2.15 (m, 1H), 2.08-2.01 (m, 1H), 1.96 – 1.82 (m, 2H), 1.74 – 1.63 (m, 2H), 1.59 – 1.51 (m, 1H), 1.48 – 1.41 (m, 1H), 1.39-1.21 (m, 6H), 0.92-0.84 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.3, 203.0, 146.3, 145.5, 144.6, 144.2, 130.3, 130.1, 129.6, 129.6, 129.1, 128.9, 127.7, 127.6, 125.5, 125.4, 124.1, 124.0, 88.2, 87.9, 84.2, 83.0, 63.1, 41.0, 40.2, 35.9, 35.5, 31.9, 31.8, 30.1, 29.8, 29.7, 29.6, 29.6, 29.3, 29.3, 26.5, 26.3, 22.7, 14.2.

5-cyclohexyl-4, 5-dihydro-2'H, 3H-spiro[furan-2,1'-naphthalen]-2'-one (j). Was synthesized according to the general procedure B with 1-(3-cyclohexyl-3-hydroxypropyl)naphthalen-2-ol (20 mg, 0.07 mmol) and TBATB salt using THF as a solvent at room temperature (30°C). Total reaction time was 19 hrs. The product was obtained as a yellow liquid (17 mg, 0.06 mmol, 83%) after elution with 10% ethyl ace-tate in petroleum ether of the crude reaction mixture. (R_f= 0.7, 15% ethyl acetate in petroleum ether) ^{1}H NMR (400 MHz, $CDCl_3$) for the diastereomeric mixture (j2:j1 = 1.6:1) δ 7.63 (d, *J* = 7.6 Hz, 1H), 7.58(d, *J*=7.7 Hz, 1H), 7.42 – 7.26 (m, 4H), 6.09 (dd, *J* = 9.9, 3.7 Hz, 1H), 4.35-4.29 (dd, *J* = 13.9, 7.4 Hz, 1H), 4.17 – 4.12 (m, 1H), 2.52 – 2.34 (m, 4H), 2.22 – 2.06 (m, 2H), 2.01 – 1.62 (m, 4H), 1.43 – 0.798 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.4, 203.0, 146.5, 145.6, 144.5, 144.1, 138.7, 130.3, 130.1, 129.6, 129.1, 128.9, 127.7, 127.6, 125.5, 125.4, 124.1, 124.1, 88.8, 87.4, 87.2, 43.1, 42.8, 41.0, 40.1, 30.9, 30.0, 29.7, 27.3, 29.1, 27.9, 27.8, 26.6, 26.6, 26.1, 26.0, 26.0, 25.8.

(1'S, 5S)-5-cyclohexyl-4, 5-dihydro-2'H, 3H-spiro [furan-2, 1'-naphthalen]-2'-one (j1). Elution with 1% ethyl acetate in petroleum ether afforded yellow liquid (6.4 mg, 0.023 mmol, 38.1%). R_f= 0.7 (15% ethyl acetate in petroleum ether). IR (Neat Film, KBr) IR 2925.10, 2851.80, 1680.99, 1614.45, 1449.53, 1124.52, 1060.87, 814.94, 755.14 ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 13.3, 7.7 Hz, 1H), 7.43– 7.25 (m, 5H including CDCl3), 6.09 (d, *J* = 9.8 Hz, 1H), 4.18-4.13 (m, 1H), 2.50-2.47 (m, 1H), 2.22-2.18 (m, 1H), 2.01-1.70 (m, 6H), 1.41-1.02 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.0, 146.5, 144.1, 130.3, 129.6, 128.9, 128.8, 127.6, 125.5, 124.1, 88.9, 87.8, 42.8, 41.0, 30.9, 29.1, 27.9, 26.6, 26.0, 25.8; HRMS (ESI) calc'd for $C_{19}H_{22}NaO_2$ [M+Na]+ : 305.1512, Found: 305.1510.

(1'S, 5R)-5-cyclohexyl-4, 5-dihydro-2'H, 3H-spiro [furan-2, 1'-naphthalen]-2'-one (j2). Elution with 2% ethyl acetate in petroleum ether afforded yellow liquid (10.5 mg, 0.037 mmol, 61.9%). R_f= 0.7 (15% ethyl acetate in petroleum ether). IR (Neat Film, KBr) IR 2923.17, 2850.84, 1683.89, 1448.57, 1057.01, 820.77, 755.14^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.7 Hz, 1H), 7.43-7.27(m, 5H including CDCl3), 6.10 (d, *J* = 9.9 Hz, 1H), 4.32 (dd, *J* = 13.9, 7.4 Hz 1H), 2.43-2.38 (m, 1H), 2.15 – 2.09 (m, 2H), 1.89 – 1.65 (m, 6H), 1.35 – 1.13 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.5, 145.6, 144.5, 130.1, 129.6, 129.1, 127.7, 125.4, 124.1, 87.2, 86.6, 43.1, 40.2, 30.0 29.3, 27.8, 26.6, 26.1, 26.0; HRMS (ESI) calc'd for $C_{19}H_{22}NaO_2$ [M+Na]+ : 305.1512, Found: 305.1511.

5-(p-tolyl)-4, 5-dihydro-2'H, 3H-spiro[furan-2,1'-naphthalen]-2'-one (m). Was synthesized according to the general procedure B with 1-(3-hydroxyundecyl)naphthalen-2-ol (20 mg, 0.068 mmol) and TBATB salt using THF as a solvent at room temperature (30°C). Total reaction time was 11 hrs. The product was obtained as a yellow liquid (18 mg, 0.062 mmol, 93%) after elution with 10% ethyl acetate in petroleum ether of the crude reaction mixture. (R_f = 0.5, 15% ethyl acetate in petroleum ether) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 1H), 7.71 (t, *J* = 7.3 Hz, 1H), 7.48 – 7.38 (m, 3H), 7.34 – 7.24 (m, 4H), 6.16 (dd, *J* = 9.9, 2.5 Hz, 1H), 5.64 (t, *J* = 7.0 Hz, 1H), 5.56 – 5.36 (m, 1H), 2.70-2.65 (m 1H), 2.61 – 2.52 (m, 1H), 2.40 (d, *J* = 6.6 Hz, 4H), 2.33 – 2.29 (m, 1H) 2.16 – 2.06 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.72, 146.24, 144.92, 144.39, 138.48, 137.50, 130.43, 130.27, 129.64, 129.27, 129.20, 129.08, 127.92, 127.83, 126.95, 126.95, 126.07, 125.76, 125.61, 124.08, 124.02, 88.09, 85.66, 83.61, 41.52, 40.75, 33.50, 32.81, 21.29, 21.24.

(1'S, 5S)-5-(p-tolyl)-4, 5-dihydro-2'H, 3H-spiro [furan-2, 1'-naphthalen]-2'-one. (m1) Elution with 3% ethyl acetate in petroleum ether afforded yellow liquid (4.6 mg, 0.016 mmol, 25.7%). R_f= 0.5 (15% ethyl acetate in petroleum ether). IR (Neat Film, KBr) 2973.26, 1683.91, 1650.02, 756.13 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.65 (m, 3H), 7.46- 7.36 (m, 2H), 7.32 – 7.19 (m, 4H), 6.15 (d, *J* = 10.0 Hz, 1H), 5.45 (dd, *J* = 14.8, 8.4 Hz, 1H), 2.70-2.62(m, 1H), 2.40- 2.25(m, 5H), 2.14-2.06(m, 1H)**;** ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.38, 144.32, 130.39, 129.05, 127.80, 126.92, 125.61, 124.10, 85.64, 77.19, 41.50, 33.47, 21.24; HRMS (ESI) calc'd for $C_{20}H_{18}O_2Na$ $[M+Na]^+$: 313.1199, Found : 313.1193.

(1'S, 5R)-5-(p-tolyl)-4, 5-dihydro-2'H, 3H-spiro [furan-2, 1'-naphthalen]-2'-one. (m2) Elution with 4% ethyl acetate in petroleum ether afforded yellow liquid (13.4 mg, 0.046 mmol, 74.3%). R_f= 0.5 (15% ethyl acetate in petroleum ether). IR (Neat Film, KBr) 2989.36, 1681.35, 1660.61, 755.14 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.6 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.43 – 7.38 (m, 2H), 7.33 (dd, *J* = 4.2, 1.9 Hz, 2H), 7.29 – 7.24 (m, 2H), 6.16 (d, *J* = 9.9 Hz, 1H), 5.63 (t, *J* = 7.0 Hz, 1H), 2.60 – 2.51 (m, 2H), 2.41 (s, 3H), 2.16-2.06 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.06, 145.12, 144.88, 138.73, 137.22, 130.25, 129.54, 129.24, 129.18, 129.06, 127.90, 126.93, 126.06, 125.77, 124.02, 87.63, 83.60, 40.72, 32.79, 21.21; HRMS (ESI) calc'd for $C_{20}H_{18}O_2Na$ $[M+Na]^+$: 313.1199, Found : 313.1196.

5-(4-fluorophenyl)-4, 5-dihydro-2'H,3H-spiro[furan-2,1'-naphthalen]-2'-one. (n) Was synthesized according to the general procedure B with 1-(3-(4-fluorophenyl)-3-hydroxypropyl)naphthalen-2-ol (20 mg, 0.067 mmol) and TBATB salt using THF as a solvent at room temperature (30°C). Total reaction time was 10 hrs. The product was obtained as a yellow liquid (19 mg, 0.062 mmol, 96%) after elution with 10% ethyl acetate in petroleum ether of the crude reaction mixture. (R_f = 0.4, 15% ethyl acetate in petroleum ether) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75-7.71 (m, 1H), 7.55 (m, 1H), 7.44 – 7.39 (m, 2H), 7.24 – 7.16 (m, 4H), 7.03-6.97 (m, 2H), 6.05-6.02 (m, 1H), 5.52 – 5.49 (m, 1H), 5.34 (m, 2H), 2.49-2.37 (m 1H), 2.19 – 1.94 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.79, 202.59, 163.74,156.40, 145.96, 144.89,144.46, 130.45, 129.13, 128.74, 128.66, 127.92, 125.55, 124.02, 115.43, 115.25, 115.04, 88.17, 85.02, 82.99. 41.46, 40.52, 32.57, 32.09

(1'S,5S)-5-(4-fluorophenyl)-4,5-dihydro-2'H,3H-spiro[furan-2,1'-naphthalen]-2'-one. (n1) Elution with 4% ethyl acetate in petroleum ether afforded yellow liquid (5.7 mg, 0.019 mmol, 30%). R_f= 0.5 (15% ethyl acetate in petroleum ether). IR (Neat Film, KBr) 2938.92, 1680.93, 1057.01, 755.11 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.74 (m, 1H), 7.71 – 7.59 (m, 1H), 7.40 (ddd, *J* = 19.3, 12.2, 6.0 Hz, 1H), 7.33 – 7.21 (m, 1H), 7.07 (tt, *J* = 5.4, 3.1 Hz, 1H), 6.13 (d, *J* = 8.2 Hz, 1H), 5.56 – 5.28 (m, 1H), 2.64 (ddd, *J* = 12.6, 6.0, 1.8 Hz, 1H), 2.37 – 2.14 (m, 1H), 2.15 – 1.98 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.60, 163.74, 144.45, 130.44, 129.12, 128.69, 127.91, 125.54, 124.02, 115.25, 115.04, 88.16, 85.02, 41.45, 33.56.

(1'S,5R)-5-(4-fluorophenyl)-4,5-dihydro-2'H,3H-spiro[furan-2,1'-naphthalen]-2'-one. (n2) Elution with 5% ethyl acetate in petroleum ether afforded yellow liquid (13.3 mg, 0.045 mmol, 30%). R_f= 0.5 (15% ethyl acetate in petroleum ether). IR (Neat Film, KBr) 2938.01, 1683.00, 1055.95, 756.33 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.7, 1H), 7.55 – 7.52 (m, 2H), 7.43 - 7.41 (m, 2H), 7.35 – 7.32 (m, 2H), 7.14 - 7.10 (m, 2H), 6.16 (d, *J* = 8.1 Hz, 1H), 5.65 – 5.62 (m, 1H), 2.65-2.48 (m, 2H), 2.15 – 2.05 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.73, 163.54, 144.88, 130.28, 129.59, 128.31, 128.01, 127.77, 127.69, 125.64, 124.01, 115.46, 115.22, 87.46, 82.99, 40.52, 32.99.

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Keywords: spiro-furano naphthalone, QATBs, diastereoselective, dearomatisation , gram-scale

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Layout 1:

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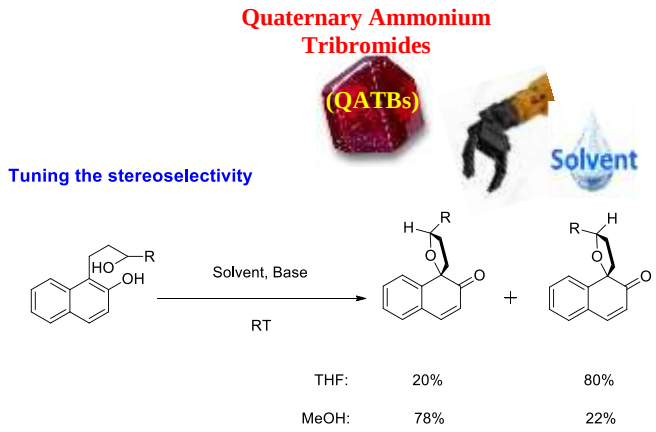

Key Topic* spiro-furano naphthalone, QATBs, diastereoselective, dearomatisation, gram-scale

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Title: Controlling Stereoselectivity in Tribromide Mediated Oxidative Dearomatisations – Tuning The Synthesis of Selective Spirofurano-naphthalones

A mild and highly stereocontrolled tribromide mediated synthesis of spiro-furano naphthalones via oxidative dearomatisation process.