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PAPER

Base Catalysed Domino and Self-domino Michael-Aldol Reactions: One-pot Synthesis of Dispirocyclopentaneoxindoles Containing Multiple Chiral Stereocenters

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Abstract: A one-pot method for the construction of three classes of densely functionalized dispirocyclopentaneoxindoles containing multiple chiral stereocenters is developed. Base promoted self-domino and domino reactions with and without the participation of solvents, alcohol, is accomplished. Piperidine catalyzed self-domino reaction involves the participation of the nucleophilic solvent, alcohol, resulting in complex dispiro compounds containing four and five diastereoisomeric centers. Triethylamine promotes the self-domino reaction between two molecules of 3-phenacylideneoxindoles with added nucleophiles, and not with the solvent nucleophile. Diisopropylethylamine facilitates the domino reaction between 3-phenacylidineoxindole and phenacylacenaphthylenone allowing the construction of novel dispirocyclopentaneoxindoles with high yields and diastereoselectivity. A plausible mechanism is tentatively proposed to account for the diastereoselectivity of the domino Michael-Aldol reaction.

The development of simple and efficient methods for the construction of synthetically and biologically important spirocyclic oxindoles has gained considerable importance.[1] We report, herein, the efficient one-pot synthesis of densely functionalized spirocyclopentaneoxindoles containing five-carbon and four-carbon chiral stereocenters including two non-contiguous dispirostereocenters. Spirooxindole structural motif is commonly present in a number of natural and unnatural biologically active alkaloids.[2-4] The 3,3'-spirooxindoles are the most privileged structural motifs playing a vital role in biological activities,[5] even though the biological importance of five or six membered spirocyclicoxindoles are not uncommon. Considering the biological significance of spirocyclopentaneoxindoles embodied in natural alkaloid derivatives[6] such as marcfortine A, cirinalins A, citrinadin B, and cyclopiamine B (Figure 1), efficient synthesis of these structural motifs containing multiple

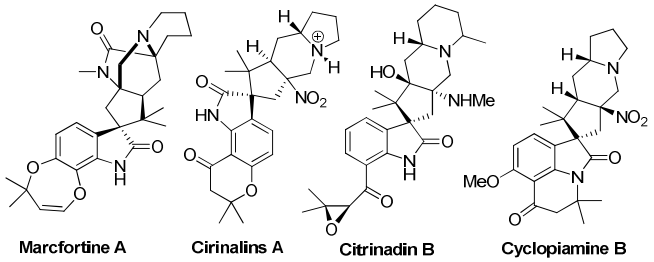
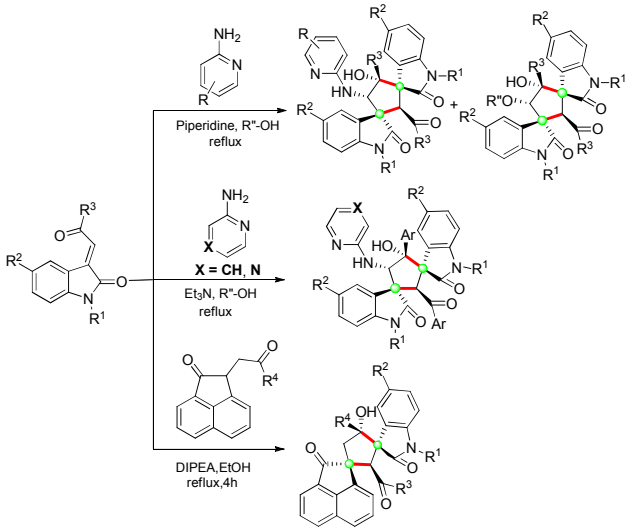


Fig 1 Natural products containing spirocyclopentaneoxindole scaffold

chiral stereocenters is both important and challenging to synthetic chemists.

In recent years, organocatalytic phosphine-catalyzed reactions have been explored for the synthesis of spirocyclopentaneoxindoles.[7, 8] However, there are only a few reports available in literature for the efficient synthesis of spirocyclopentaneoxindoles,[9] and very few methods are available for the construction of bispirooxindoles containing all carbon chiral stereocenters with multiple quaternary dispirostereocenters. Recently, Barbas III *et al* have reported an organocatalytic asymmetric synthesis of dispirocyclopentaneoxindoles.[3f] Yan *et al* have reported a base catalyzed diastereoselective domino synthesis of dispirocyclooxindoles.[10] Several metal or organocatalyzed enantioselective syntheses of spirocyclopentaneoxindoles have also been successfully explored.[4c,7a,c,8,11] The recent report on the facile construction of novel bisspirocyclopentanebisoxindoles by self-domino reaction between two molecules of 3-phenacylideneoxindoles is particularly encouraging.[12] Literature survey shows that 3-phenacylideneoxindoles have long been used as active electron-deficient alkenes in many synthetic procedures such as 1,3-dipolar cycloaddition, Diels−Alder reaction, Michael addition, and versatile multicomponent reactions for the design of fused cyclic and spirocyclic frameworks.[13-15] However, there are only very few examples of the synthesis of dispirocyclopentanebisoxindoles involving 3-

phenacylidineoxindoles. As a part of our interest in the development of methodologies for single-step construction of densely functionalized dispirooxindoles containing multiple chiral stereocenters,[16] herein, we report organocatalytic domino Michael addition/Aldol reaction involving 3-phenacylideneoxindoles for the synthesis of three classes of spirocyclic oxindole derivatives.

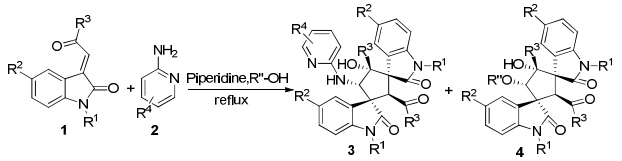


Scheme 1 Synthetic cascade approach to spirocyclicoxindoles

Results and Discussion

Encouraged by the self-domino reaction reported[12] by Yan *et al*., and our interest in one-pot multicomponent reactions,[16] we set out to explore base–catalysed Michael-Aldol reaction (Scheme 1). When ethanol was used as the reaction medium and 5 mol % piperidine (pKa 11.22) as base-catalyst, both the alcohol (solvent) and 2-aminopyridine acted as nucleophiles, leading to the formation of spirooxindoles **3a** and **4a** (Table 1). The ethoxy group in the dispirocyclopentanebisoxindole **4a** apparently stems from the nucleophilic substitution of the solvent, ethanol. Although two products were formed, isolation of **3a** and **4a** could be easily achieved owing to the difference in their R_f values. The generality of this reaction to yield two classes of spirooxindoles was

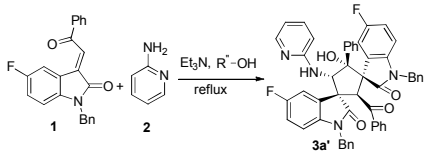
Table 1 Substrate Scope[a]



Entry	R^1	R^2	R^3	R^4	R"-OH	3/4	Yield (%)[b]
1	Bn	H	Ph	H	EtOH	**3a**/**4a**	48/45
2	Bn	Cl	4-MeC_6H_4	H	EtOH	**3b**/**4b**	43/47
3	Bn	H	Ph	H	EtOH	**3c**/**4c**	45/46
4	Bn	F	Ph	H	MeOH	**3d**/**4d**	47/42

[a] All reactions were carried out with 1.0 mmol 3-phenacylidineoxindole **1**, 0.5 mmol aminopyridines **2**, and 5 mol % piperidine in 10 mL alcohol. [b] Isolated yield

Table 2 Optimisation of reaction conditions[a]



Entry	base	solvent	Temp (°C)	Time (hr)	Yield (%)[b]
1	DABCO	EtOH	rt	8.0	-
2	DABCO	EtOH	70	7.2	25
3	Et_3N	EtOH	rt	5.0	-
4	Et_3N	EtOH	80	0.5	42
5	**Et_3N**	**EtOH**	**80**	**4.0**	**95**
6	Et_3N	MeOH	80	5.0	80
7	Et_3N	CAN	80	6.0	-
8	Et_3N	THF	80	6.2	-

[a] Reaction conditions: 3-phenacylidineoxindole (1.0 mmol), 2-aminopyridine (0.5 mmol) and base catalyst (5 mol %) in different solvents (10 mL). [b] Isolated yield.

established by synthesizing a series of dispirooxindloes of the types **3** and **4** (Table 1). All the compounds were characterized using IR, NMR and mass analytical methods, and found to be a single diastereoisomer.

Although the piperidine-catalyzed Michael-Aldol reaction gave the desired products **3** and **4** (Table 1) with excellent diastereoselectivity, the overall yield was poor with respect to **3** or **4**. We envisioned that only 2-aminopyridine substituted products **3** would be formed in excellent yield if a weaker base, instead of piperidine, is used for catalysis. Thus, when 5 mol % triethylamine (pKa 10.7) was used as the catalyst in ethanol medium neither **3a** nor **4a** was formed at room temperature. However, when the reaction mixture was heated under reflux for 30 min, only the 2-aminopyridine substituted spirooxindole **3a'** formed in 42% yield (Table 2), and the ethanol substituted product **4a'** could not be detected. Thus, triethylamine, being a weaker base than piperidine, doesn't

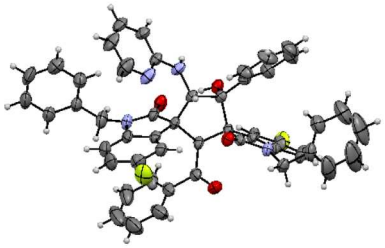
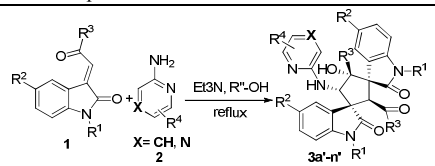


Fig 2 Ortep-diagram of compound **3a'**

seem to promote the participation of alcohol (a weaker nucleophile than 2-aminopyridine) in this self-domino reaction. The reaction was optimized with respect to the reaction temperature, time, solvent and amount of base needed for catalysis, so as to improve the yield of spirooxindole **3a'** (Table 2). The best result was obtained by refluxing the ethanolic solution of 1.0 mmol of (*E*)-1-benzyl-3-(2-oxo-2-phenyl ethylidene) indolin-2-one and 0.5 mmol of 2-aminopyridine in the presence of 5 mol % trimethylamine for 4 h, that resulted in the formation of the

desired spirooxindole **3a'** in 95% yield. Interestingly, the structurally related tertiary amine DABCO also yielded the spirooxindole **3a'** *albeit* at a relatively lower yield. Further, nucleophilic substitution of solvent was not observed when methanol was used as the reaction medium. Single crystal

Table 3 Substrate Scope[a]



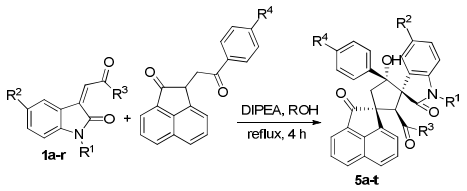
Entry	R^1	R^2	R^3	R^4/X	3	Yield(%)[b]
1	Bn	F	Ph	H/CH	**3a′**	95
2	Bn	Cl	Ph	H/CH	**3b′**	89
3	Bn	Br	Ph	H/CH	**3c′**	87
4	Bn	H	4-BrC_6H_4	H/CH	**3d′**	82
5	Bn	H	4-biphenyl	H/CH	**3e′**	78
6	Me	H	Ph	H/CH	**3f′**	87
7	Me	H	4-ClC_6H_4	H/CH	**3g′**	83
8	Bn	F	Ph	6-Me/CH	**3h′**	84
9	Bn	F	Ph	5-Br/CH	**3i′**	86
10	Bn	F	Ph	4-Me/CH	**3j′**	91
11	Bn	F	Ph	5-Cl/CH	**3k′**	88
12	Bn	F	Ph	H/N	**3l′**	93
13	Bn	H	4-$OMeC_6H_4$	H/N	**3m'**	90
14	Bn	H	Ph	2-aminobenzthiazole	**3n′**	80

[a] All reactions were carried out with 1.0 mmol 3-phenacylidineoxindole **1**, 0.5 mmol aminopyridines **2**, and 5 mol % Et_3N in 10 mL ethanol. [b] Isolated yield.

XRD data of spirocyclicoxindole **3a'** revealed the stereochemical disposition of various moieties in the newly formed five-member ring (Figure 2). Notably, the stereochemical preferences adopted by **3a'** (Figure 2) are similar to those of the spirooxindole derivatives synthesized using chiral[3f] and achiral[12] organocataysts. This observation reveals the strong influence of the transition state on the stereochemical outcome of the spirooxindole derivatives.

To investigate the generality of this reaction under the optimized conditions, we used various nucleophiles and substituted phenacylidineindolinones (Table 3). Though the reaction was carried out in alcoholic solution containing a non-chiral catalyst, the reaction proceeded smoothly and resulted in the diastereoselective formation of densely functionalized bispirooxindoles as a single isomer containing an all chiral cyclopentyl ring with two non-contiguous dispiro quaternary chiral stereocenters. In almost all the cases the products were obtained in good yields (Table 3). When 2-aminobenzthiazole (Table 3, entry 14) was used as the nucleophile, the reaction took a slightly longer time, and resulted in a lower yield, which may be ascribed to the bulkiness of the 2-aminobenzthiazole moiety. ^1H and ^{13}C NMR spectra of the prepared bispirooxindoles clearly showed the existence of a single diastereoisomer in all the preparations, and the other possible diastereoisomer was not observed. The spectroscopic and X-ray diffraction analyses revealed that the isolated diastereoisomer contained two oxindole moieties in 1,3-*trans* orientation, while the 2- benzoyl group and the 5-aryl group were in *cis* orientation with

Table 4 Substrate Scope[a]



Entry	R^1	R^2	R^3	R^4	5	Yield (%)[b]
1	Bn	H	Ph	Ph	**5a**	92
2	Bn	H	4-MeC_6H_4	Ph	**5b**	83
3	Bn	H	4-$OMeC_6H_4$	Ph	**5c**	86
4	Bn	H	Ph	Ph	**5d**	72
5	Bn	F	Ph	Ph	**5e**	76
6	Bn	Cl	Ph	Ph	**5f**	74
7	Bn	Cl	4-MeC_6H_4	Ph	**5g**	80
8	Me	H	Ph	Ph	**5h**	71
9	3-Me-Bn	H	Ph	Ph	**5i**	65
10	H	H	Ph	Br	**5j**	70
11	Bn	H	Ph	Br	**5k**	76
12	3-Me-Bn	H	Ph	Br	**5l**	81
13	Bn	H	4-$OMeC_6H_4$	Br	**5m**	68
14	C_3H_3	H	Ph	Br	**5n**	78
15	Bn	H	OMe	Ph	**5o**	86
16	Bn	H	OEt	Ph	**5p**	83
17	C_3H_3	H	OMe	Ph	**5q**	74
18	C_3H_3	H	OEt	Ph	**5r**	72
19	C_3H_3	H	OEt	Br	**5s**	68
20	Bn	H	OEt	Br	**5t**	76

[a] All reactions were carried out with 0.5 mmol **1**, 0.5 mmol phenacylacenapthylenone, and 5 mol % DIPEA in 10 mL ethanol. [b] Isolated yield.

respect to the newly formed five membered ring. As the oxindole moiety and the benzoyl group exist in the *trans* position in the starting 3-phenacylideneindolinone, only a multistep reaction process must have resulted in the observed thermodynamically most stable diastereoisomer in this domino reaction. Thus, the reaction proceeds following probably a similar mechanistic pathway as suggested by Yan *et al*.[12]

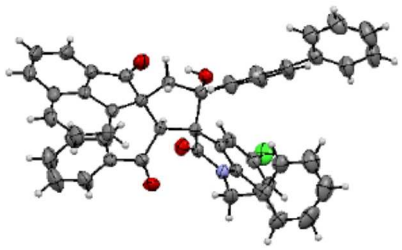
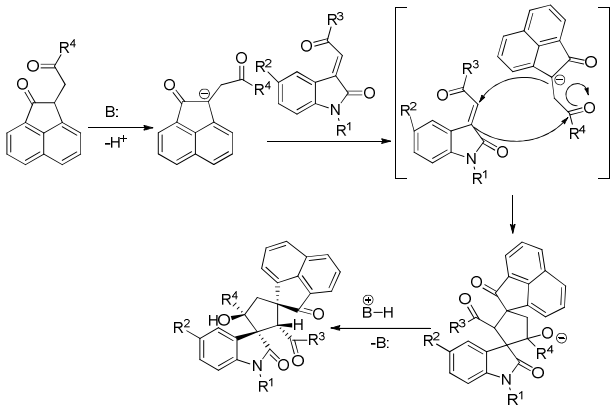


Fig 3 Ortep-diagram of compound **5f**

Base catalyzed Michael addition of *in situ* generated 3-phenacylindolinone with 3-phenacylideneoxindole and subsequent intramolecular aldol condensation has yielded dispirocyclopentanebisoxindoles.[3f, 10] Variously substituted dispirocyclopentanebisoxindoles has also been achieved

through organocatalytic domino reaction between 3-substituted oxindole and 3-phenacylideneindolinone.[12] To probe base promoted synthesis of dispirocyclopentanebisoxindoles having only four chiral stereocenters and shed more light on domino Michael-Aldol reactions, we used DIPEA, a tertiary amine stronger than TEA, in the anticipated domino reaction involving 3-phenacylideneoxindole and phenacylacenaphthylenone. To our delight, the reaction in alcohol medium completed in about 4 h, yielding only a single diastereoisomer of the dispiro compound **5a**. Further experiments were carried out to explore the generality of this domino reaction and the results are summarized in Table 3. The dispiro



Scheme 2 Plausible mechanism

compounds **5a−t** resulted from the domino reaction were thoroughly characterized using ^{1}H and ^{13}C NMR, HRMS, and IR spectral data. Single-crystal X-ray diffraction data of **5f** (Figure 3) was used to confirm the structures of the diastereoisomers isolated from the domino reaction. Single-crystal structure of **5f** and ^{1}H NMR spectra of **5a−t** suggested that the dispiro compounds **5a−t** existed as a single diastereoisomer. A comparison of single-crystal X-ray diffraction data of **5f** and **3a'** revealed that the two aromatic moieties at the 1,3-positions are in trans orientation, while the 2-benzoyl group and the 5-aryl group are in *cis* orientation.[17] Thus, both the self-domino reaction (Table 3) and the domino reaction (Table 4) seem to be highly diastereoselective reactions. There is one methylene unit in the newly formed cyclopentane moiety of **5a−t**. Similar observations have been reported from organocatalytic domino reaction[3f] and self-domino reactions.[12] These observations were useful for us to understand the reaction mechanism of the present study. Accordingly, a possible mechanism for this DIPEA promoted domino Michael-Aldol reaction is provided in Scheme 2.

Conclusions

In summary, we have reported base promoted domino and self-domino reactions for the efficient synthesis of densely functionalized dispirocyclopentane oxindole derivatives. The unique advantages are: 1) Piperidine catalyzed one-pot synthesis of densely functionalized dispirocyclopentanebisoxindoles using amine and alcohol nucleophiles, 2) Triethylamine promoted selective synthesis of all five carbon chiral dispirocyclopentanebisoxindoles without interference from alcohol nucleophiles, and 3) Diisopropylethylamine mediated domino synthesis of dispirocyclopentane derivatives containing only four chiral stereocenters including two non-contiguous quaternary dispiro chiral stereocenetrs. The reactions of 3-phenacylideneoxindoles with substituted **1a−r** also proceeded smoothly to give the expected dispirocylopentane compounds in moderate yields. Use of readily available starting materials, simple reaction conditions, operational simplicity (non-requirement of chromatographic separation) are the other advantages.

Experimental section

General methods

All the reagents were purchased from Sigma-Aldrich and used without further purification. Pre-coated plates (Merck, silica gel 60 GF254, 0.25 mm) were used for TLC analysis. The ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Avance 400 MHz Spectrometer. The ^{13}C NMR, DEPT experiments were carried out on Bruker Avance 100 MHz Spectrometer. The chemical shifts (δ) for ^{1}H and ^{13}C are given in ppm with reference to TMS (zero ppm). Coupling constants are given in Hertz.

General procedure for the preparation of compounds 3a-d and 4a-d:

Procedure 1: In an oven dried 50-mL round-bottom flask 2 mmol 3-phenacylidineoxindole, 1 mmol substituted 2-aminopyridine, 10 mL ethanol and 5 mol % piperidine were taken and the contents of the flask were heated under reflux ~80 °C until the starting materials were consumed. The reaction mixture was allowed to cool to room temperature and then diluted with ethylacetate and water. The organic layer was separated, dried using anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The crude products obtained were purified using column chromatography (silica gel 60-120 mesh).

(2'S, 3R, 3'R, 4'R, 5'S)-2'-benzoyl-1,1''-dibenzyl-4'-hydroxy-4'-phenyl-5'-[(pyridin-2-yl)amino]-1,1'',2,2''-tetrahydrodispiro[indole-3,1'-cyclopentane-3',3''-indole]-2,2''-dione (3a):

White solid, Mp: 260 – 262 ºC; IR (KBr): 3368, 3208, 3070, 2923, 2851, 1719, 1601, 1483, 1352, 1179, 1074, 1008, 976, 815, 773, 733, 691, 540, 455, 409 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.28 (s, 1H), 7.91 (s, 1H), 7.77 (s, 1H), 7.25 - 7.06 (m, 16H), 6.96 (t, *J* = 7.6 Hz, 4H), 6.89 (d, *J* = 6.0 Hz, 2H), 6.53 (d, *J* = 6.8 Hz, 2H), 6.42 (t, *J* = 5.6 Hz, 1H), 6.37 (d, *J* = 8.4 Hz, 1H), 6.05 (d, *J* = 7.6 Hz, 2H), 5.30 (d, *J* = 16.0 Hz, 2H), 5.17 (s, 1H), 5.13 (d, *J* = 15.6 Hz, 1H), 4.44 (d, *J* = 16.0 Hz, 1H), 4.27 (d, *J* = 15.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 194.6, 180.3, 176.0, 156.2, 147.9, 142.5, 140.4, 137.3, 135.5, 134.9, 134.8, 133.6, 131.3, 131.1, 131.0, 129.7,

129.2, 129.0, 128.8, 128.6, 128.5, 128.4, 127.9, 127.8, 127.7, 127.5, 127.3, 127.1, 127.0, 126.3, 125.8, 122.6, 113.8, 110.1, 109.7, 107.3, 85.7, 64.0, 62.6, 62.5, 59.6, 44.6, 44.2; HRMS (EI) Calcd for $[C_{51}H_{40}N_4O_4]^+$: 772.3050; found : 772.3048.

(2'S, 3R, 3'R, 4'R, 5'S)-2'-benzoyl-1,1''-dibenzyl-5'-ethoxy-4'-hydroxy-4'-phenyl-1,1'',2,2''-tetrahydrodispiro[indole-3,1'-cyclopentane-3',3''-indole]-2,2''-dione (4a): White solid, Mp: 260 – 262 ºC; IR (KBr): 3362, 3201, 3060, 2920, 2789, 1720, 1615, 1475, 1350, 1180, 1065, 982, 975, 819, 775, 690, 545, 450, 408 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.19 (s, 1H), 7.95 (s, 1H), 7.36 – 7.33 (m, 6H), 7.29 – 7.22 (m, 6H), 7.19 – 7.09 (m, 5H), 7.07 - 6.99 (m, 5H), 6.59 (d, *J* = 6.8 Hz, 2H), 6.52 (s, 1H), 6.34 (d, *J* = 8.4 Hz, 1H), 6.30 (d, *J* = 8.4 Hz, 1H), 6.06 (s, 1H), 5.27 - 5.21 (m, 3H), 4.47 (d, *J* = 16.4 Hz, 1H), 4.27 (d, *J* = 15.2 Hz, 1H), 3.28 - 3.21 (m, 1H), 3.10 - 3.02 (m, 3H), 0.79 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 195.0, 179.2, 176.4, 142.2, 140.7, 136.2, 135.5, 134.8, 134.3, 131.6, 131.2, 130.8, 129.5, 129.0, 128.7, 128.6, 128.5, 128.3, 128.0, 127.7, 127.6, 127.5, 127.3, 126.7, 126.3, 122.3, 109.9, 109.4, 88.1, 83.9, 68.5, 64.7, 62.7, 58.8, 44.8, 44.1, 15.2; HRMS (EI) Calcd for $[C_{48}H_{40}N_2O_5]^+$: 724.2937; found : 724.2936.

(2'S, 3R, 3'R, 4'R, 5'S)-1,1''-dibenzyl-5,5''-dichloro-4'-hydroxy-2'-(4-methylbenzoyl)-4'-(4-methylphenyl)-5'-[(pyridin-2-yl)amino]-1,1'',2,2''-tetrahydrodispiro[indole-3,1'-cyclopentane-3',3''-indole]-2,2''-dione (3b):

White solid, Mp: 276 - 278 ºC; IR (KBr) : 3380, 3364, 3066, 2928, 2842, 1716, 1604, 1489, 1458, 1337, 1276, 1176, 1031, 984, 890, 802, 775, 732, 695, 617, 532, 450 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.31 (s, 1H), 7.93 (s, 1H), 7.77 (d, *J* = 4.0 Hz, 1H), 7.16 - 7.09 (m, 12H), 6.97 (d, *J* = 7.6 Hz, 2H), 6.90 – 6.82 (m, 8H), 6.49 (d, *J* = 7.2 Hz, 2H), 6.39 (t, *J* = 6.0 Hz, 1H), 6.32 (d, *J* = 8.0 Hz, 1H), 6.04 (d, *J* = 8.4 Hz, 1H), 5.93 (d, *J* = 8.4 Hz, 1H), 5.32 (d, *J* = 16.4 Hz, 1H), 5.21 (d, *J* = 16.8 Hz, 1H), 4.41 (d, *J* = 16.0 Hz, 1H), 4.16 (d, *J* = 15.6 Hz, 1H), 2.28 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 195.1, 181.0, 176.4, 143.4, 142.6, 140.5, 137.6, 137.1, 135.2, 134.2, 133.8, 133.0, 131.6, 129.5, 128.8, 128.6, 128.4, 128.0, 127.6, 127.3, 127.2, 127.1, 127.0, 126.8, 126.6, 126.4, 125.8, 113.5, 109.8, 109.5, 107.1, 86.0, 64.3, 62.5, 59.9, 44.5, 44.1, 21.5, 21.2; HRMS (EI) Calcd for $[C_{53}H_{42}Cl_2N_4O_4]^+$: 868.2583; found : 868.2582.

(2'S, 3R, 3'R, 4'R, 5'S)-1,1''-dibenzyl-5,5''-dichloro-5'-ethoxy-4'-hydroxy-2'-(4-methylbenzoyl)-4'-(4-methylphenyl)-1,1'',2,2''-tetrahydrodispiro[indole-3,1'-cyclopentane-3',3''-indole]-2,2''-dione (4b):

White solid, Mp: 284 - 286 ºC; IR (KBr) : 3299, 3072, 2922, 2852, 1705, 1682, 1609, 1482, 1428, 1343, 1177, 1096, 973, 811, 785, 734, 700, 577, 534, 457 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.23 (s, 1H), 7.97 (s, 1H), 7.32 (t, *J* = 7.2 Hz, 5H), 7.19 – 7.11 (m, 7H), 7.05 (d, *J* = 8.8 Hz, 1H), 6.98 – 6.93 (m, 3H), 6.86 (d, *J* = 7.6 Hz, 2H), 6.54 (d, *J* = 7.2 Hz, 2H), 6.48 (s, 1H), 6.23 (d, *J* = 8.4 Hz, 2H), 6.12 (s, 1H), 5.33 (d, *J* = 15.2 Hz, 1H), 5.26 (d, *J* = 16.4 Hz, 2H), 4.44 (d, *J* = 16.0 Hz, 1H), 4.16 (d, *J* = 15.6 Hz, 1H), 3.33 – 3.25 (m, 1H), 3.12 - 3.05 (m, 1H), 2.33 (s, 3H), 2.26 (s, 3H), 0.79 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 195.6, 179.5, 176.8, 143.3, 142.3, 140.8, 137.2, 135.1, 134.6, 134.3, 134.2, 132.1, 129.3, 128.8, 128.6, 128.5, 128.4, 128.0, 127.9, 127.4, 127.3, 127.0, 126.7, 126.5, 126.4, 109.6, 109.1, 88.2, 84.3, 68.3, 64.9, 62.6, 59.1, 44.7, 44.0, 29.7, 21.2, 15.2; HRMS (EI) Calcd for $[C_{50}H_{42}Cl_2N_2O_5]^+$: 820.2471; found : 820.2470.

(2'S, 3R, 3'R, 4'R, 5'S)-2'-benzoyl-1,1''-dibenzyl-5'-[(5-bromopyridin-2-yl)amino]-4'-hydroxy-4'-phenyl-1,1'',2,2''-tetrahydrodispiro[indole-3,1'-cyclopentane-3',3''-indole]-2,2''-dione (3c):

White solid, Mp: 278 - 280 ºC; IR (KBr) : 3419, 3311, 2924, 2849, 1705, 1616, 1580, 1491, 1396, 1354, 1223, 1180, 1098, 1072, 1016, 970, 918, 885, 803, 750, 727, 691, 577, 531, 508, 455, 400 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.28 (d, *J* = 7.6 Hz, 1H), 7.96 (d, *J* = 7.2 Hz, 1H), 7.77 (s, 1H), 7.30 - 7.15 (m, 6H), 7.13 - 7.05 (m, 15H), 6.93 (s, 1H), 6.87 (t, *J* = 8.0 Hz, 3H), 6.52 (d, *J* = 7.2 Hz, 2H), 6.41 (d, *J* = 7.6 Hz, 1H), 6.02 (d, *J* = 8.0 Hz, 1H), 5.87 (d, *J* = 8.8 Hz, 1H), 5.38 (d, *J* = 14.0 Hz, 2H), 5.26 (d, *J* = 15.6 Hz, 1H), 5.18 (d, *J* = 16.4 Hz, 1H), 4.48 (d, *J* = 16.0 Hz, 1H), 4.11 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 195.8, 181.2, 176.6, 155.4, 148.5, 143.8, 141.9, 139.3, 137.0, 136.0, 135.5, 134.1, 132.4, 129.5, 128.9, 128.8, 128.5, 128.3, 127.8, 127.6, 127.1, 126.7, 126.4, 125.5, 124.2, 122.1, 109.0, 108.8, 108.3, 107.5, 86.1, 64.0, 62.9, 62.5, 59.5, 44.3, 43.9; HRMS (EI) Calcd for $[C_{51}H_{39}BrN_4O_4]^+$: 850.2155; found : 815.2153.

(2'S, 3R, 3'R, 4'R, 5'S)-2'-benzoyl-1,1''-dibenzyl-5'-ethoxy-4'-hydroxy-4'-phenyl-1,1'',2,2''-tetrahydrodispiro[indole-3,1'-cyclopentane-3',3''-indole]-2,2''-dione (4c):

White solid, Mp: 260 – 262 ºC; IR (KBr) : 3362, 3201, 3060, 2920, 2789, 1720, 1615, 1475, 1350, 1180, 1065, 982, 975, 819, 775, 690, 545, 450, 408 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.19 (s, 1H), 7.95 (s, 1H), 7.36 – 7.33 (m, 6H), 7.29 – 7.22 (m, 6H), 7.19 – 7.09 (m, 5H), 7.07 - 6.99 (m, 5H), 6.59 (d, *J* = 6.8 Hz, 2H), 6.52 (s, 1H), 6.34 (d, *J* = 8.4 Hz, 1H), 6.30 (d, *J* = 8.4 Hz, 1H), 6.06 (s, 1H), 5.27 - 5.21 (m, 3H), 4.47 (d, *J* = 16.4 Hz, 1H), 4.27 (d, *J* = 15.2 Hz, 1H), 3.28 - 3.21 (m, 1H), 3.10 - 3.02 (m, 3H), 0.79 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 195.0, 179.2, 176.4, 142.2, 140.7, 136.2, 135.5, 134.8, 134.3, 131.6, 131.2, 130.8, 129.5, 129.0, 128.7, 128.6, 128.5, 128.3, 128.0, 127.7, 127.6, 127.5, 127.3, 126.7, 126.3, 122.3, 109.9, 109.4, 88.1, 83.9, 68.5, 64.7, 62.7, 58.8, 44.8, 44.1, 15.2; HRMS (EI) Calcd for $[C_{48}H_{40}N_2O_5]^+$: 724.2937; found : 724.2936.

(2'S, 3R, 3'R, 4'R, 5'S)-2'-benzoyl-1,1''-dibenzyl-5,5''-difluoro-4'-hydroxy-4'-phenyl-5'-[(pyridin-2-yl)amino]-1,1'',2,2''-tetrahydrodispiro[indole-3,1'-cyclopentane-

3',3''-indole]-2,2''-dione (3d):

White solid, Mp: 285 - 287 ºC; IR (KBr) : 3684, 3384, 3064, 2918, 2852, 1709, 1601, 1489, 1451, 1347, 1266, 1177, 1031, 981, 892, 804, 777, 742, 692, 607, 534, 453 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.18 (d, *J* = 8.4 Hz, 1H), 7.77 - 7.73 (m, 2H), 7.31 - 7.22 (m, 4H), 7.15 - 7.04 (m, 14H), 6.94 (s, 1H), 6.85 (d, *J* = 7.2 Hz, 3H), 6.55 - 6.49 (m, 3H), 6.39 (t, *J* = 6.0 Hz, 1H), 6.31 (dd, *J* = 4.0 Hz. 4.0Hz, 1H), 6.05 (d, *J* = 8.4 Hz, 1H), 5.89 (dd, *J* = 4.0 Hz, 4.0 Hz, 1H), 5.28 (t, *J* = 7.2 Hz, 3H), 5.18 (d, *J* = 16.4 Hz, 1H), 4.46 (d, *J* = 16.0 Hz, 1H), 4.07 (d, *J* =16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 195.6, 181.1, 176.4, 161.2, 158.8, 157.6, 156.4, 147.9, 139.8, 137.9, 137.1, 136.9, 135.8, 135.2, 133.8, 132.6, 131.5, 128.8, 128.6, 128.2, 128.1, 128.0, 127.8, 127.6, 127.2, 127.0, 126.7, 126.6, 126.4, 115.3, 115.2, 115.1, 114.9, 114.6, 114.4, 113.7, 113.5, 109.5, 109.4, 109.3, 109.2, 107.2, 86.2, 64.4, 62.6, 60.0, 53.4, 44.4, 44.1; HRMS (EI) Calcd for $[C_{51}H_{38}F_2N_4O_4]^+$: 808.2861; found : 808.2560.

(2'S, 3R, 3'R, 4'R, 5'S)-2'-benzoyl-1,1''-dibenzyl-5,5''-difluoro-4'-hydroxy-5'-methoxy-4'-phenyl-1,1'',2,2''-tetrahydrodispiro[indole-3,1'-cyclopentane-3',3''-indole]-2,2''-dione (4d):

White solid, Mp: 217 - 219 ºC; IR (KBr): 3346, 3069, 2919, 2846, 2330, 1965, 1830, 1700, 1607, 1492, 1345, 1261, 1177, 1103, 980, 811, 692, 603, 550, 457 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.07 (d, *J* = 8.4 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.36 - 7.25 (m, 11H), 7.19 - 7.08 (m, 7H), 6.81 (d, *J* = 9.2 Hz, 1H), 6.77 (s, 1H), 6.65 (t, *J* = 8.4 Hz, 1H), 6.55 (d, *J* = 7.2 Hz, 2H), 6.26 - 6.20 (m, 2H), 6.10 (s, 1H), 5.45 (d, *J* = 15.2 Hz, 1H), 5.34 (s, 1H), 5.13 (d, *J* = 16.4 Hz, 1H), 4.48 (d, *J* = 16.0 Hz, 1H), 4.08 (d, *J* = 15.2 Hz, 1H), 3.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 195.9, 179.6, 176.8, 159.9, 158.7, 157.6, 139.6, 138.0, 136.8, 135.2, 134.7, 132.6, 132.1, 132.0, 128.9, 128.6, 128.1, 128.0, 127.8, 127.3, 127.0, 126.5, 126.3, 115.2, 115.0, 114.9, 114.8, 114.7, 114.4, 114.2, 113.9, 109.3, 109.2, 109.1, 109.0, 89.5, 84.6, 64.9, 62.5, 60.2, 58.9, 44.7, 44.0; HRMS (EI) Calcd for $[C_{47}H_{37}F_2N_2O_5]^+$: 747.2671; found : 747.2670.

General procedure for the preparation of compounds 3a'-n':

Procedure 2: With slight modification of procedure **1** and using 1 mmol 3-phenacylidineoxindole, 0.5 mmol substituted 2-aminopyridine, 10 mL ethanol and 5 mol % triethylamine only a single crude product was obtained. The crude product was separated by filtration, washed with 10-15 mL of ethanol to obtain pure white solid that did not require further purification.

(2'S, 3R, 3'R, 4'R, 5'S)-2'-benzoyl-1,1''-dibenzyl-5,5''-difluoro-4'-hydroxy-4'-phenyl-5'-[(pyridin-2-yl)amino]-1,1'',2,2''-tetrahydrodispiro[indole-3,1'-cyclopentane-3',3''-indole]-2,2''-dione (3a'):

White solid, Mp: 238 - 240 ºC; IR (KBr): 3383, 3316, 3063, 2922, 2856, 1712, 1602, 1493, 1450, 1384, 1356, 1270, 1177, 1075, 1032, 895, 845, 809, 774, 747, 692, 606, 564, 532 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.17 (d, *J* = 8.8 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.32 – 7.23 (m, 5H), 7.18 – 7.04 (m, 13H), 6.95 (s, 1H), 6.85 (d, *J* = 7.6 Hz, 3H), 6.54 (t, *J* = 8.8 Hz, 1H), 6.49 (d, *J* = 7.2 Hz, 2H), 6.40 (t, *J* = 6.0 Hz, 1H), 6.31 (dd, *J* = 4.0 Hz, 4.0 Hz, 1H), 6.06 (d, *J* = 8.0 Hz, 1H), 5.88 (dd, *J* = 3.6 Hz, 3.6 Hz, 1H), 5.29 (t, *J* = 7.6 Hz, 3H), 5.20 (d, *J* = 16.0 Hz, 1H), 4.46 (d, *J* = 16.0 Hz, 1H), 4.07 (d, *J* = 15.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 195.7, 181.1, 176.4, 160.1 (d, *J* = 240.45 Hz), 158.7 (d, *J* = 238.21 Hz), 156.5, 148.1, 139.9, 137.9, 137.0, 136.9, 135.9, 135.2, 133.8, 132.6, 131.5, 128.8, 128.6, 128.1, 128.0, 127.9, 127.6, 127.2, 127.0, 126.7, 126.6, 126.4, 115.3 (d, *J* = 15.82 Hz), 115.0 (d, *J* = 18.83 Hz), 114.5 (d, *J* = 24.03 Hz), 113.6 (d, *J* = 21.76 Hz), 109.32 (d, *J* = 8.37 Hz), 109.4 (d, *J* = 8.03 Hz), 107.2, 86.2, 64.5, 62.7, 60.1, 58.4, 44.5, 44.1; HRMS (EI) Calcd for $[C_{51}H_{38}F_2N_4O_4]^+$: 808.2861; found : 808.2860.

(2'S, 3R, 3'R, 4'R, 5'S)-2'-benzoyl-1,1''-dibenzyl-5,5''-dichloro-4'-hydroxy-4'-phenyl-5'-[(pyridin-2-yl)amino]-1,1'',2,2''-tetrahydrodispiro[indole-3,1'-cyclopentane-3',3''-indole]-2,2''-dione (3b′):

White solid, Mp: 243 - 245 ºC; IR (KBr): 3387, 3258, 3070, 3031, 2938, 2856, 1958, 1708, 1692, 1657, 1598, 1481, 1434, 1376, 1333, 1302, 1239, 1165, 1075, 962, 899, 809, 755, 692, 630, 587, 552, 501, 532, 462 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.34 (s, 1H), 7.95 (s, 1H), 7.77 (d, *J* = 4.8 Hz, 1H), 7.29 - 7.23 (m, 5H), 7.19 - 7.04 (m, 14H), 6.90 (s, 1H), 6.85 - 6.80 (m, 3H), 6.45 (d, *J* = 7.2 Hz, 2H), 6.40 (t, *J* = 6.0 Hz, 1H), 6.32 (d, *J* = 8.4 Hz, 1H), 6.06 (d, *J* = 8.4 Hz, 1H), 5.88 (d, *J* = 8.0 Hz, 1H), 5.31 - 5.23 (m, 4H), 4.44 (d, *J* = 16.4 Hz, 1H), 4.7 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ (ppm) 195.8, 181.2, 176.3, 156.5, 148.2, 142.6, 140.6, 137.2, 137.1, 135.9, 135.2, 133.8, 132.7, 131.6, 129.7, 129.0, 128.9, 128.7, 128.4, 128.2, 128.1, 128.0, 127.8, 127.4, 127.3, 127.2, 126.8, 126.7, 126.4, 125.9, 113.7, 110.0, 109.7, 107.4, 86.3, 64.4, 62.9, 62.7, 59.9, 44.5, 44.2; HRMS (EI) Calcd for $[C_{51}H_{38}Cl_2N_4O_4]^+$: 840.2270; found : 840.2270.

(2'S, 3R, 3'R, 4'R, 5'S)-2'-benzoyl-1,1''-dibenzyl-5,5''-dibromo-4'-hydroxy-4'-phenyl-5'-[(pyridin-2-yl)amino]-1,1'',2,2''-tetrahydrodispiro[indole-3,1'-cyclopentane-3',3''-indole]-2,2''-dione (3c'):

White solid, Mp: 249 - 251 ºC; IR (KBr): 3387, 3254, 3066, 3031, 2930, 1708, 1692, 1653, 1606, 1477, 1426, 1376, 1337, 1239, 1173, 1079, 970, 806, 747, 696, 634, 583, 540, 466 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.46 (d, *J* = 1.8 Hz, 1H), 8.08 (d, *J* = 1.7 Hz, 1H), 7.77 (d, *J* = 3.9 Hz, 1H), 7.30 – 7.22 (m, 6H), 7.19 – 7.11 (m, 5H), 7.12 – 7.03 (m, 9H), 6.96 (dd, *J* = 8.3, 1.9 Hz, 1H), 6.88 (s, 1H), 6.85 (d, *J* = 7.5 Hz, 2H), 6.45 (d, *J* = 7.1 Hz, 2H), 6.42 – 6.37 (m, 1H), 6.27 (d, *J* = 8.3 Hz, 1H), 6.05 (d, *J* = 8.4 Hz, 1H), 5.83 (d, *J* = 8.3 Hz, 1H), 5.28 (t, *J* = 7.4 Hz, 2H), 5.24 (d, *J* = 15.2 Hz, 1H), 4.44 (d, *J* = 16.2 Hz, 1H), 4.07 (d, *J* = 15.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 195.7, 180.9, 176.1, 156.3, 147.9, 143.0, 141.0,

137.1, 136.9, 135.8, 135.0, 133.6, 132.5, 131.8, 131.8, 131.0, 129.8, 129.7, 128.8, 128.6, 128.6, 128.5, 128.1, 127.9, 127.9, 127.6, 127.2, 127.0, 126.7, 126.6, 126.3, 118.8, 116.9, 114.7, 114.0, 113.6, 110.4, 110.1, 107.2, 86.1, 64.2, 62.8, 62.6, 59.7, 44.4, 44.0. HRMS (EI) Calcd for $[C_{51}H_{38}Br_2N_4O_4]^+$: 928.1260; found : 928.1258.

(1'R, 2'S, 3R, 4'R, 5'S)-1,1''-dibenzyl-2'-(4-bromobenzoyl)-4'-(4-bromophenyl)-4'-hydroxy-5'-[(pyridin-2-yl)amino]-1,1'',2,2''-tetrahydrodispiro[indole-3,3'-cyclopentane-1',3''-indole]-2,2''-dione (3d'):

White solid, Mp: 264 - 266 ºC; IR (KBr): 3371, 3055, 1719, 1676, 1614, 1583, 1485, 1466, 1395, 1364, 1231, 1177, 1063, 1013, 817, 751, 743, 692, 673, 552, 517, 454 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.25 (d, *J* = 6.8 Hz, 1H), 7.93 (d, *J* = 6.4 Hz, 1H), 7.79 (s, 1H), 7. 92 – 6. 24 (m, 23H), 6.58 (d, *J* = 6.0 Hz, 2H), 6.46 (d, *J* = 6.8 Hz, 1H), 6.39 (s, 1H), 6.13 (d, *J* = 7.2 Hz, 1H), 5.95 (d, *J* = 7.6 Hz, 1H), 5.27 (d, *J* = 7.6 Hz, 2H), 5.14 (d, *J* = 14.8 Hz, 1H), 4.47 (d, *J* = 15.6 Hz, 1H), 4.23 (d, *J* = 15.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 194.9, 181.2, 178.5, 156.6, 148.0, 143.8, 141.9, 137.2, 135.6, 135.4, 135.3, 134.0, 131.1, 130.8, 129.3, 129.1, 128.9, 128.7, 128.5, 127.7, 127.4, 127.2, 127.0, 126.8, 126.4, 126.1, 125.5, 124.2, 122.3, 122.2, 113.6, 109.1, 108.8, 106.8, 85.8, 63.9, 63.0, 62.3, 59.5, 44.5, 44.1; HRMS (EI) Calcd for $[C_{51}H_{38}Br_2N_4O_4]^+$: 928.1260; found : 928.1260.

(1'R, 2'S, 3R, 4'R, 5'S)-1,1''-dibenzyl-4'-hydroxy-2'-(4-phenylbenzoyl)-4'-(4-phenylphenyl)-5'-[(pyridin-2-yl)amino]-1,1'',2,2''-tetrahydrodispiro[indole-3,3'-cyclopentane-1',3''-indole]-2,2''-dione (3e'):

White solid, Mp: 206 - 208 ºC; IR (KBr): 3031, 1704, 1684, 1610, 1493, 1466, 1387, 1352, 1231, 1177, 1009, 845, 751, 692, 645, 552, 517 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.25 (d, *J* = 7.3 Hz, 1H), 8.02 (d, *J* = 6.2 Hz, 1H), 7.57 (d, *J* = 6.7 Hz, 2H), 7.48 – 7.33 (m, 11H), 7.26 (s, 10H), 7.20 (s, 3H), 7.13 (d, *J* = 7.6 Hz, 3H), 7.05 (s, 2H), 6.96 (s, 4H), 6.59 (d, *J* = 5.9 Hz, 2H), 6.43 (d, *J* = 6.8 Hz, 1H), 6.34 (d, *J* = 7.5 Hz, 1H), 5.42 (s, 1H), 5.26 (d, *J* = 16.7 Hz, 1H), 5.20 (d, *J* = 15.9 Hz, 1H), 4.56 (d, *J* = 14.4 Hz, 1H), 4.47 (d, *J* = 16.2 Hz, 1H), 4.36 (d, *J* = 14.8 Hz, 1H), 2.61 (d, *J* = 14.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 195.9, 183.9, 176.9, 144.8, 143.8, 141.6, 140.5, 140.2, 139.5, 137.5, 135.7, 135.6, 134.8, 130.4, 128.9, 128.9, 128.7, 128.5, 128.4, 128.3, 128.1, 127.8, 127.6, 127.3, 127.1, 127.0, 126.8, 126.6, 126.3, 126.2, 125.8, 124.3, 121.9, 108.8, 108.5, 84.4, 66.6, 65.4, 54.3, 46.9, 44.6, 43.9. HRMS (EI) Calcd for $[C_{63}H_{48}N_4O_4]^+$: 924.3676; found : 924.3674.

(2'S, 3R, 3'R, 4'R, 5'S)-2'-benzoyl-4'-hydroxy-1,1''-dimethyl-4'-phenyl-5'-[(pyridin-2-yl)amino]-1,1'',2,2''-tetrahydrodispiro[indole-3,1'-cyclopentane-3',3''-indole]-2,2''-dione (3f'):

White solid, Mp: 228 - 230 ºC; IR (KBr): 3375, 3285, 3070, 1715, 1684, 1602, 1489, 1430, 1376, 1329, 1286, 1235, 1181, 1149, 1067, 1009, 973, 927, 813, 770, 731, 657, 599, 536, 474 cm^{-1}; ^1H NMR (400 MHZ, $CDCl_3$): δ (ppm) 8.36 (d, *J* = 4.4 Hz, 1H), 7.87 (d, *J* = 7.2 Hz, 1H), 7.28 - 7.22 (m, 4H), 7.13 – 6.92 (m, 1H), 6.64 (d, *J* = 7.2 Hz, 2H), 6.35 (d, *J* = 7.2 Hz, 2H), 6.25 (d, *J* = 6.8 Hz, 1H), 6.13 (s, 1H), 5.57 (d, *J* = 10.8 Hz, 1H), 5.04 (s, 1H), 2.78 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$,): δ (ppm) 196.9, 176.7, 174.6, 157.0, 144.8, 138.5, 137.3, 136.8, 131.9, 131.5, 128.4, 128.3, 127.6, 127.5, 127.3, 126.9, 126.2, 125.9, 122.4, 120.8, 111.7, 107.3, 106.7, 102.9, 84.9, 65.0, 36.1, 62.2, 58.0, 25.5, 25.0; HRMS (EI) Calcd for $[C_{39}H_{32}N_4O_4]^+$: 620.2424; found : 620.2424.

(2'S, 3R, 3'R, 4'R, 5'S)-2'-(4-chlorobenzoyl)-4'-(4-chlorophenyl)-4'-hydroxy-1,1''-dimethyl-5'-[(pyridin-2-yl)amino]-1,1'',2,2''-tetrahydrodispiro[indole-3,1'-cyclopentane-3',3''-indole]-2,2''-dione (3g'):

White solid, Mp: 258 - 262 ºC; IR (KBr): 3370, 3278, 3072, 1709, 1686, 1608, 1478, 1435, 1366, 1320, 1284, 1232, 1171, 1141, 1005, 968, 921, 813, 770, 735, 650, 595, 526, 472 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.23 (d, *J* = 6.8 Hz, 1H), 7.85 (d, *J* = 7.6 Hz, 1H), 7.71 (s, 1H), 7.66 (s, 1H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.14 (t, *J* = 7.2 Hz, 1H), 7.12 - 6.98 (m, 9H), 6.92 (b s, 5H), 6.70 (d, *J* = 7.6 Hz, 1H), 6.35 (d, *J* = 6.4 Hz, 1H), 6.27 (d, *J* = 18.4 Hz, 1H), 6.11 (d, *J* = 8.0 Hz, 1H), 5.44 (d, *J* = 10.0 Hz, 1H), 5.16 (s, 1H), 3.04 (s, 3H), 2.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$,): δ (ppm) 194.8, 180.3, 175.9, 156.8, 147.4, 144.1, 142.6, 138.4, 136.8, 1351, 134.8, 133.1, 129.2, 128.9, 128.4, 128.2, 127.9, 127.8, 126.9, 125.9, 125.3, 123.7, 121.8, 113.3, 107.7, 107.6, 107.3, 85.5, 64.0, 61.6, 61.2, 59.1, 26.6, 25.8; HRMS (EI) Calcd for $[C_{39}H_{30}Cl_2N_4O_4]^+$: 688.1644; found : 688.1643.

(2'S, 3R, 3'R, 4'R, 5'S)-2'-benzoyl-1,1''-dibenzyl-5,5''-difluoro-4'-hydroxy-5'-[(6-methylpyridin-2-yl)amino]-4'-phenyl-1,1'',2,2''-tetrahydrodispiro[indole-3,1'-cyclopentane-3',3''-indole]-2,2''-dione (3h'):

White solid, Mp: 234 - 236 ºC; IR (KBr): 3371, 3332, 1712, 1665, 1606, 1575, 1485, 1450, 1384, 1341, 1270, 1227, 1165, 1036, 973, 841, 806, 782, 739, 696, 610, 587, 536, 462 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.20 (d, *J* = 7.7 Hz, 1H), 7.74 (d, *J* = 7.1 Hz, 1H), 7.27 (d, *J* = 19.6 Hz, 5H), 7.06 (d, *J* = 22.7 Hz, 11H), 7.02 (d, *J* = 7.1 Hz, 2H), 6.86 (dd, *J* = 17.8, 8.8 Hz, 2H), 6.74 (d, *J* = 6.6 Hz, 2H), 6.56 – 6.43 (m, 3H), 6.31 (d, *J* = 4.6 Hz, 1H), 6.27 (d, *J* = 6.7 Hz, 1H), 5.91 (d, *J* = 7.7 Hz, 1H), 5.83 (d, *J* = 4.0 Hz, 1H), 5.37 – 5.15 (m, 4H), 4.46 (d, *J* = 16.2 Hz, 1H), 4.00 (d, *J* = 15.9 Hz, 1H), 1.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 195.7, 181.1, 176.3, 160.1 (d, *J* = 240.0 Hz), 158.7 (d, *J* = 238.1 Hz), 156.9, 155.8, 139.9, 137.9, 137.3, 136.9, 135.9, 135.2, 133.8, 132.5, 132.1, 132.1, 128.7, 128.6, 128.0, 127.9, 127.9, 127.4, 127.2, 126.9, 126.7, 126.3, 126.3, 115.2 (d, *J* = 24.0 Hz), 114.1 (d, *J* = 23.8 Hz), 113.6 (d, *J* = 25.1 Hz), 112.5, 109.3 (*J* = 7.9 Hz), 109.1 (d, *J* = 8.4 Hz), 104.2, 86.2, 64.4, 63.0, 62.7, 60.1, 44.4, 44.1, 23.8; HRMS (EI) Calcd for $[C_{52}H_{40}F_2N_4O_4]^+$: 822.3018; found : 822.3016.

(2'S, 3R, 3'R, 4'R, 5'S)-2'-benzoyl-1,1''-dibenzyl-5'-[(5-

bromopyridin-2-yl)amino]-5,5''-difluoro-4'-hydroxy-4'-phenyl-1,1'',2,2''-tetrahydrodispiro[indole-3,1'-cyclopentane-3',3''-indole]-2,2''-dione (3i'):

White solid, Mp: 266 - 268 ºC; IR (KBr): 3375, 3066, 3027, 2863, 2793, 2254, 2204, 1692, 1590, 1497, 1352, 1278, 1188, 1141, 1067, 1013, 966, 696, 532 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.15 (d, *J* = 8.4 Hz, 1H), 7.75 (s, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.32 - 7.08 (m, 20H), 6.91 (s, 1H), 6.84 (d, *J* = 7.6 Hz, 2H), 6.57 (t, *J* = 8.4 Hz, 1H), 6.48 (d, *J* = 7.2 Hz, 2H), 6.33 - 6.30 (m, 1H), 5.97 (d, *J* = 8.8 Hz, 1H), 5.94 - 5.91 (m, 1H), 5.29 (d, *J* = 16.4 Hz, 2H), 5.19 (d, *J* = 16.4 Hz, 1H), 4.46 (d, *J* = 16.0 Hz, 1H), 4.05 (d, *J* = 15.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 195.5, 180.9, 176.3, 160.1 (d, *J* = 240.63 Hz), 158.7 (d, *J* = 238.35 Hz), 155.1, 148.4, 139.9, 139.4, 137.8, 136.8, 135.7, 135.2, 133.8, 132.7, 131.5, 131.4, 128.8, 128.6, 128.2, 128.0, 127.9, 127.2, 127.1, 126.6, 126.4, 115.3 (d, *J* = 23.60 Hz), 115.1 (d, *J* = 26.47 Hz), 114.6 (d, *J* = 24.1 Hz), 113.6 (d, *J* = 25.12 Hz), 109.5 (d, *J* = 7.93 Hz), 109.4 (d, *J* = 8.30 Hz), 108.9, 107.8, 86.1, 64.4, 62.72, 62.5, 59.8, 44.5, 44.1; HRMS (EI) Calcd for $[C_{51}H_{37}BrF_2N_4O_4]^+$: 886.1966; found : 886.1964.

(2'S, 3R, 3'R, 4'R, 5'S)-2'-benzoyl-1,1''-dibenzyl-5,5''-difluoro-4'-hydroxy-5'-[(4-methylpyridin-2-yl)amino]-4'-phenyl-1,1'',2,2''-tetrahydrodispiro[indole-3,1'-cyclopentane-3',3''-indole]-2,2''-dione (3j'):

White solid, Mp: 216 - 218 ºC; IR (KBr): 3382, 3089, 3065, 2970, 2914, 1708, 1692, 1622, 1493, 1450, 1372, 1348, 1263, 1181, 1141 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.19 (dd, *J* = 8.6, 2.5 Hz, 1H), 7.74 (dd, *J* = 8.3, 2.5 Hz, 1H), 7.66 (d, *J* = 5.1 Hz, 1H), 7.37 – 7.21 (m, 5H), 7.22 – 6.99 (m, 13H), 6.90 (s, 1H), 6.89 – 6.81 (m, 3H), 6.59 – 6.53 (m, 1H), 6.50 (d, *J* = 6.9 Hz, 2H), 6.32 (dd, *J* = 8.5, 4.2 Hz, 1H), 6.25 (d, *J* = 5.0 Hz, 1H), 5.90 (dd, *J* = 8.6, 4.1 Hz, 1H), 5.82 (s, 1H), 5.31 (s, 1H), 5.27 (d, *J* = 15.9 Hz, 1H), 5.19 (d, *J* = 16.2 Hz, 1H), 4.47 (d, *J* = 16.2 Hz, 1H), 4.09 (d, *J* = 15.9 Hz, 1H), 1.97 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 195.6, 191.7, 181.0, 176.5, 159.4 (d, *J* = 367.0 Hz), 158.3 (d, *J* = 338.4 Hz), 139.88, 138.1, 136.8, 135.8, 135.2, 133.8, 132.6, 131.7, 128.7, 128.6, 128.0, 128.0, 127.8, 127.6, 127.2, 127.0, 126.7, 126.3, 115.2 (d, *J* = 22.8 Hz), 114.9 (d, *J* = 22.1 Hz), 114.5 (d, *J* = 23.6 Hz), 113.6 (d, *J* = 24.9 Hz), 109.4 (d, *J* = 7.9 Hz), 109.4 (d, *J* = 8.2 Hz) 86.2, 64.5, 63.0, 62.6, 60.1, 44.5, 44.1, 20.9; HRMS (EI) Calcd for $[C_{52}H_{40}F_2N_4O_4]^+$: 822.3018; found : 822.3016.

(2'S, 3R, 3'R, 4'R, 5'S)-2'-benzoyl-1,1''-dibenzyl-5'-[(5-chloropyridin-2-yl)amino]-5,5''-difluoro-4'-hydroxy-4'-phenyl-1,1'',2,2''-tetrahydrodispiro[indole-3,1'-cyclopentane-3',3''-indole]-2,2''-dione (3k'):

White solid, Mp: 252 - 254 ºC; IR (KBr): 3383, 3063, 3027, 1708, 1594, 1497, 1450, 1387, 1348, 1266, 1220, 1173, 1032, 970, 899, 841, 806, 751, 696, 610 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.15 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.67 (s, 1H), 7.32 - 7.24 (m, 5H), 7.21 - 7.08 (m, 14H), 6.91 (s, 1H), 6.84 (d, *J* = 8.0 Hz, 3H), 6.57 (t, *J* = 8.8 Hz, 1H), 6.49 (d, *J* = 7.6 Hz, 2H), 6.31 (dd, *J* = 4.0 Hz, 4.0Hz, 1H), 6.00 (d, *J* = 8.8 Hz, 1H), 5.92 (dd, *J* = 4.0 Hz, 4.0 Hz, 1H), 5.30 (d, *J* = 4.8 Hz, 1H), 5.27 (d, *J* = 5.6 Hz, 1H), 5.17 (d, *J* = 16.4 Hz, 1H), 4.46 (d, *J* = 16.4 Hz, 1H), 4.06 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 195.5, 181.0, 176.3, 160.1 (d, *J* = 240.6 Hz), 158.7 (d, *J* = 238.28 Hz), 154.8, 146.2, 139.9, 137.8, 136.8, 135.7, 135.2, 133.8, 132.7, 128.2, 128.0, 127.8, 127.2, 127.0, 126.6, 126.4, 120.3, 115.3 (d, *J* = 23.4 Hz), 115.1 (d, *J* = 26.44 Hz), 114.6 (d, *J* = 17.1 Hz), 113.6 (d, *J* = 25.13 Hz), 109.5 (d, *J* = 8.05 Hz), 109.4 (d, *J* = 8.22 Hz), 108.3, 86.2, 64.4, 62.7, 62.5, 58.9, 44.5, 44.1; HRMS (EI) Calcd for $[C_{51}H_{37}ClF_2N_4O_4]^+$: 842.2471; found : 842.2470.

(2'S, 3R, 3'R, 4'R, 5'S)-2'-benzoyl-1,1''-dibenzyl-5,5''-difluoro-4'-hydroxy-4'-phenyl-5'-[(pyrazin-2-yl)amino]-1,1'',2,2''-tetrahydrodispiro[indole-3,1'-cyclopentane-3',3''-indole]-2,2''-dione (3l'):

White solid, Mp: 288 - 290 ºC; IR (KBr): 3371, 3066, 1704, 1692, 1657, 1583, 1540, 1493, 1446, 1354, 1333, 1270, 1177, 1075, 1001, 977, 899, 806, 751, 692, 610, 560, 540, 458, 423 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.18 (dd, *J* = 8.6, 2.5 Hz, 1H), 7.73 (dd, *J* = 8.3, 2.5 Hz, 1H), 7.65 – 7.60 (m, 2H), 7.59 (s, 1H), 7.36 – 7.22 (m, 5H), 7.19 – 7.06 (m, 12H), 6.97 (s, 1H), 6.84 (d, *J* = 7.7 Hz, 3H), 6.60 – 6.53 (m, 1H), 6.50 (d, *J* = 7.0 Hz, 2H), 6.32 (dd, *J* = 8.6, 4.2 Hz, 1H), 5.95 (dd, *J* = 8.6, 4.1 Hz, 1H), 5.44 (d, *J* = 8.9 Hz, 1H), 5.29 (s, 1H), 5.27 (d, *J* = 18.1 Hz, 1H), 5.18 (d, *J* = 16.2 Hz, 1H), 4.47 (d, *J* = 16.2 Hz, 1H), 4.08 (d, *J* = 15.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 195.4, 180.9, 176.2, 160.1 (d, *J* = 241.4 Hz), 158.7 (d, *J* = 238.4 Hz), 152.7, 141.7, 139.8, 137.7, 136.8, 135.5, 135.1, 133.8, 133.6, 132.7, 132.2, 131.2, 131.1, 128.9, 128.6, 128.2, 127.9, 127.9, 127.9, 127.8, 127.1, 127.0, 126.6, 126.4, 126.3, 115.3 (d, *J* = 23.1 Hz), 114.9 (d, *J* = 41.5 Hz), 114.3 (d, *J* = 44.6 Hz), 113.6 (d, *J* = 25.0 Hz), 109.5 (d, *J* = 8.0 Hz), 109.1 (d, *J* = 8.3 Hz) 86.1, 64.4, 62.6, 61.3, 59.7, 44.4, 44.0; HRMS (EI) Calcd for $[C_{50}H_{37}F_2N_5O_4]^+$: 809.2814; found : 808.2812.

(1'R, 2'S, 3R, 4'R, 5'S)-1,1''-dibenzyl-4'-hydroxy-2'-(4-methoxybenzoyl)-4'-(4-methoxyphenyl)-5'-[(pyrazin-2-yl)amino]-1,1'',2,2''-tetrahydrodispiro[indole-3,3'-cyclopentane-1',3''-indole]-2,2''-dione (3m'):

White solid, Mp: 288 - 290 ºC: IR (KBr): 3375, 3281, 3063, 2938, 2840, 1708, 1676, 1610, 1602, 1516, 1497, 1466, 1387, 1368, 1259, 1181, 1106, 1028, 841, 806, 751, 700, 509, 474 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.28 (d, *J* = 7.6 Hz, 1H), 7.93 (d, *J* = 7.2 Hz, 1H), 7.61 (s, 2H), 7.51 (s, 1H), 7.31 - 7.04 (m, 13H), 6.95 (t, *J* = 8.4 Hz, 4H), 6.88 (b s, 2H), 6.57 (d, *J* = 8.4 Hz, 2H), 6.52 (d, *J* = 8.0 Hz, 4H), 6.43 (d, *J* = 7.2 Hz, 1H), 6.13 (d, *J* = 7.6 Hz, 1H), 5.35 (d, *J* = 14.0 Hz, 1H), 5.29 (s, 1H), 5.22 (d, *J* = 16.0 Hz, 1H), 4.45 (d, *J* = 16.0 Hz, 1H), 4.27 (d, *J* = 15.6 Hz, 1H), 3.72 (s, 3H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 193.8, 181.3, 176.7, 163.0, 159.3, 153.0, 143.9, 141.7, 135.5, 134.3, 133.5, 131.9, 129.8, 129.5,

128.8, 128.3, 127.9, 127.8, 127.2, 126.9, 126.7, 126.5, 125.5, 124.2, 121.9, 113.1, 108.9, 108.5, 85.8, 64.2, 62.0, 59.7, 55.4, 54.9, 44.3, 43.8; HRMS (EI) Calcd for $[C_{52}H_{43}N_5O_6]^+$: 833.3213; found : 833.3212.

(2'S, 3R, 3'R, 4'R, 5'S)-2'-benzoyl-5'-[(1,3-benzothiazol-2-yl)amino]-1,1''-dibenzyl-4'-hydroxy-4'-phenyl-1,1'',2,2''-tetrahydrodispiro[indole-3,1'-cyclopentane-3',3''-indole]-2,2''-dione (3n'):

White solid, Mp: 240 - 242 ºC; IR (KBr): 2914, 1708, 1692, 1622, 1493, 1450, 1372, 1348, 1263, 1181, 1141, 981, 895, 845, 802, 747, 692, 610, 560, 462 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.35 (d, *J* = 7.5 Hz, 1H), 7.96 (d, *J* = 6.7 Hz, 1H), 7.39 (d, *J* = 7.8 Hz, 1H), 7.30 – 7.25 (m, 2H), 7.20 (t, *J* = 7.0 Hz, 5H), 7.17 – 7.06 (m, 10H), 7.06 – 7.00 (m, 3H), 6.98 (d, *J* = 7.9 Hz, 1H), 6.95 (s, 1H), 6.89 (q, *J* = 8.7 Hz, 5H), 6.82 (s, 1H), 6.53 (d, *J* = 6.9 Hz, 2H), 6.41 (d, *J* = 7.3 Hz, 1H), 6.01 (d, *J* = 7.8 Hz, 1H), 5.38 (s, 1H), 5.27 (d, *J* = 15.8 Hz, 1H), 5.18 (d, *J* = 16.2 Hz, 1H), 4.50 (d, *J* = 16.2 Hz, 1H), 4.15 (d, *J* = 15.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 195.6, 180.7, 176.5, 165.7, 152.0, 143.8, 142.1, 136.9, 135.4, 133.8, 132.4, 131.0, 129.5, 129.0, 128.7, 128.6, 128.5, 128.1, 127.9, 127.8, 127.5, 127.1, 127.1, 126.9, 126.6, 126.3, 126.1, 125.7, 125.4, 124.3, 122.1, 121.6, 120.6, 119.3, 109.0, 109.0, 86.0, 66.8, 63.9, 62.5, 59.3, 44.5, 43.9; HRMS (EI) Calcd for $[C_{53}H_{40}N_4O_4S]^+$: 828.2770; found : 828.2768.

General procedure for the preparation of compounds 5a-t

Procedure 3: With slight modification of procedure **2** and using 0.5 mmol 3-phenacylidineoxindole, 0.5 mmol phenacylacenaphthylenone, 10 mL ethanol and 5 mol % DIPEA only a single product was obtained. The crude product was separated by filtration, washed with 10-15 mL of ethanol to obtain pure white solid that did not require further purification.

(1R, 2'S, 3'R, 4'R)-2'-benzoyl-1''-benzyl-4'-hydroxy-4'-(4-phenylphenyl)-1'',2''-dihydro-2H-dispiro[acenaphthylene-1,1'-cyclopentane-3',3''-indole]-2,2''-dione (5a):

White solid, Mp: 254 – 256 °C; IR (KBr): 3397, 3057, 2930, 1713, 1694, 1601, 1489, 1462, 1423, 1365, 1234, 1180, 1103, 1079, 1037, 1002, 956, 832, 790, 732, 751, 701, 654, 608, 573, 519, 461 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.51 (s, 1H), 8.01 (d, *J* = 6.9 Hz, 2H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 3H), 7.57 (d, *J* = 7.7 Hz, 2H), 7.43 (d, *J* = 6.9 Hz, 4H), 7.37 – 7.31 (m, 1H), 7.27 (d, *J* = 8.1 Hz, 3H), 7.18 – 7.09 (m, 2H), 6.96 (dd, *J* = 18.3, 8.3 Hz, 5H), 6.82 (t, *J* = 7.2 Hz, 1H), 6.65 (dd, *J* = 14.0, 6.4 Hz, 2H), 6.61 (s, 2H), 6.44 (d, *J* = 7.2 Hz, 1H), 5.40 (s, 1H), 5.27 (d, *J* = 16.1 Hz, 1H), 4.65 (d, *J* = 14.1 Hz, 1H), 4.49 (d, *J* = 15.9 Hz, 1H), 2.60 (d, *J* = 14.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 213.0, 197.0, 177.1, 143.9, 142.1, 140.5, 140.3, 139.8, 137.5, 136.5, 135.7, 133.0, 131.5, 131.3, 129.9, 129.6, 128.7, 128.7, 128.5, 127.7, 127.3, 127.2, 127.0, 126.8, 126.8, 126.7, 126.5, 126.4, 126.2, 125.7, 124.9, 124.4, 122.7, 121.9, 108.9, 84.4, 67.0, 66.2, 59.4, 46.8, 43.9; HRMS (EI) Calcd for $[C_{49}H_{34}NO_4]^+$: 701.2566; found : 701.2564.

(1R, 2'S, 3'R, 4'R)-1''-benzyl-4'-hydroxy-2'-(4-methylbenzoyl)-4'-(4-phenylphenyl)-1'',2''-dihydro-2H-dispiro[acenaphthylene-1,1'-cyclopentane-3',3''-indole]-2,2''-dione (5b):

White solid, Mp: 240 – 242 °C; IR (KBr): 3369, 3023, 1711, 1688, 1596, 1488, 1423, 1350, 1273, 1230, 1207, 1173, 1103, 1003, 961, 819, 784, 750, 696, 638, 573, 519, 461, 423 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.46 (d, *J* = 5.8 Hz, 1H), 8.03 (d, *J* = 7.0 Hz, 1H), 7.99 (s, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.67 – 7.55 (m, 5H), 7.44 (dd, *J* = 11.8, 7.8 Hz, 4H), 7.36 (d, *J* = 7.3 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 3H), 7.10 (d, *J* = 8.2 Hz, 1H), 6.97 (dt, *J* = 14.3, 7.2 Hz, 3H), 6.83 (d, *J* = 7.7 Hz, 2H), 6.65 (s, 1H), 6.57 (d, *J* = 7.2 Hz, 2H), 6.45 (d, *J* = 7.7 Hz, 2H), 6.32 (d, *J* = 8.3 Hz, 1H), 5.30 (s, 1H), 5.26 (d, *J* = 16.3 Hz, 1H), 4.62 (d, *J* = 14.2 Hz, 1H), 4.45 (d, *J* = 16.1 Hz, 1H), 2.59 (d, *J* = 14.2 Hz, 1H), 1.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 212.9, 196.5, 176.7, 142.5, 142.5, 142.1, 140.4, 140.4, 139.6, 137.3, 135.2, 133.7, 132.9, 131.3, 129.9, 129.5, 128.7, 128.7, 128.6, 127.9, 127.6, 127.4, 127.2, 127.0, 126.7, 126.7, 126.3, 126.1, 124.7, 124.4, 122.8, 109.7, 84.4, 67.2, 66.5, 59.4, 46.7, 44.0, 21.1; HRMS (EI) Calcd for $[C_{50}H_{37}NO_4]^+$: 715.2723; found : 715.2721.

(1R, 2'S, 3'R, 4'R)-1''-benzyl-4'-hydroxy-2'-(4-methoxybenzoyl)-4'-(4-phenylphenyl)-1'',2''-dihydro-2H-dispiro[acenaphthylene-1,1'-cyclopentane-3',3''-indole]-2,2''-dione (5c):

White solid, Mp: 246 – 248 °C; IR (KBr): 3380, 3057, 2923, 2842, 1946, 1696, 1600, 1492, 1350, 1261, 1230, 1173, 1034, 1007, 842, 753, 696, 646, 553, 515, 492, 450 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.49 (d, *J* = 3.8 Hz, 1H), 8.04 (d, *J* = 6.8 Hz, 1H), 7.99 (d, *J* = 6.8 Hz, 1H), 7.94 (d, *J* = 7.9 Hz, 1H), 7.63 (d, *J* = 13.2 Hz, 3H), 7.56 (d, *J* = 7.3 Hz, 2H), 7.41 (d, *J* = 3.9 Hz, 4H), 7.34 (d, *J* = 7.0 Hz, 1H), 7.26 (d, *J* = 8.3 Hz, 2H), 7.18 – 7.04 (m, 2H), 6.96 (d, *J* = 6.7 Hz, 5H), 6.59 (s, 3H), 6.43 (d, *J* = 7.0 Hz, 1H), 6.15 (d, *J* = 8.2 Hz, 2H), 5.36 (s, 1H), 5.29 (d, *J* = 16.0 Hz, 1H), 4.66 (d, *J* = 14.1 Hz, 1H), 4.47 (d, *J* = 16.0 Hz, 1H), 3.50 (s, 3H), 2.60 (d, *J* = 14.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 213.3, 195.1, 177.2, 162.2, 143.9, 142.1, 140.5, 140.2, 139.9, 137.6, 135.7, 133.0, 131.3, 129.9, 129.6, 129.4, 128.8, 128.7, 128.6, 128.5, 127.6, 127.3, 127.0, 126.8, 126.8, 126.7, 126.3, 126.2, 125.7, 124.9, 124.3, 122.7, 121.8, 112.5, 108.8, 84.4, 67.0, 66.0, 59.6, 55.1, 46.8, 43.9; HRMS (EI) Calcd for $[C_{50}H_{37}NO_5]^+$: 731.2672; found : 731.2670.

(1R, 2'S, 3'R, 4'R)-1''-benzyl-2'-(4-bromobenzoyl)-4'-hydroxy-4'-(4-phenylphenyl)-1'',2''-dihydro-2H-dispiro[acenaphthylene-1,1'-cyclopentane-3',3''-indole]-2,2''-dione (5d):

White solid, Mp: 250 – 252 °C; IR (KBr): 3387, 3056, 3033, 1701, 1605, 1578, 1489, 1462, 1416, 1362, 1235, 1177, 1070, 996, 958, 835, 785, 754, 696, 642, 515, 465

cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.51 (d, *J* = 6.6 Hz, 1H), 8.04 (d, *J* = 7.0 Hz, 1H), 7.98 (t, *J* = 7.0 Hz, 2H), 7.74 – 7.59 (m, 3H), 7.56 (d, *J* = 7.5 Hz, 2H), 7.43 (d, *J* = 6.7 Hz, 4H), 7.34 (t, *J* = 6.5 Hz, 1H), 7.26 (d, *J* = 7.7 Hz, 2H), 7.12 (dd, *J* = 15.7, 7.7 Hz, 2H), 7.04 – 6.90 (m, 3H), 6.85 – 6.68 (m, 4H), 6.61 (d, *J* = 7.0 Hz, 2H), 6.57 (s, 1H), 6.44 (d, *J* = 7.2 Hz, 1H), 5.29 (s, 1H), 5.24 (d, *J* = 16.0 Hz, 1H), 4.64 (d, *J* = 14.1 Hz, 1H), 4.49 (d, *J* = 16.0 Hz, 1H), 2.60 (d, *J* = 14.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 212.9, 196.1, 176.9, 143.9, 142.1, 140.4, 140.3, 139.6, 137.4, 135.5, 135.3, 133.4, 131.1, 130.4, 129.9, 129.6, 128.8, 128.7, 128.5, 127.9, 127.8, 127.3, 127.0, 126.8, 126.6, 126.6, 126.4, 126.3, 126.2, 125.7, 124.8, 124.6, 122.9, 121.9, 108.9, 84.4, 66.9, 66.4, 59.4, 46.5, 43.9; HRMS (EI) Calcd for $[C_{49}H_{34}BrNO_4]^+$: 779.1671; found : 779.1671.

(1R, 2'S, 3'R, 4'R)-2'-benzoyl-1''-benzyl-5''-fluoro-4'-hydroxy-4'-(4-phenylphenyl)-1'',2''-dihydro-2H-dispiro[acenaphthylene-1,1'-cyclopentane-3',3''-indole]-2,2''-dione (5e):

White solid, Mp: 240 – 242 °C; IR (KBr): 3557, 3369, 3061, 2927, 1711, 1688, 1600, 1488, 1446, 1419, 1350, 1273, 1234, 1173, 1134, 1100, 1000, 961, 788, 765, 696, 519 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.50 (t, *J* = 3.8 Hz, 1H), 8.02 (d, *J* = 7.0 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.3 Hz, 1H), 7.68 – 7.55 (m, 5H), 7.44 (t, *J* = 9.3 Hz, 4H), 7.33 (dd, *J* = 17.8, 7.7 Hz, 3H), 7.08 – 6.89 (m, 5H), 6.82 (d, *J* = 7.7 Hz, 2H), 6.72 – 6.62 (m, 3H), 6.59 (d, *J* = 7.3 Hz, 2H), 6.32 (dd, *J* = 8.5, 4.2 Hz, 1H), 5.32 (s, 1H), 5.26 (d, *J* = 16.1 Hz, 1H), 4.63 (d, *J* = 14.3 Hz, 1H), 4.47 (d, *J* = 16.1 Hz, 1H), 2.60 (d, *J* = 14.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 212.9, 196.9, 176.8, 157.5, 142.1, 140.4, 140.4, 139.8, 139.6, 137.3, 136.3, 135.3, 133.1, 131.6, 131.2, 129.9, 129.5, 128.7, 128.5, 127.7, 127.4, 127.3, 127.0, 126.9, 126.7, 126.5, 126.3, 126.3, 124.8, 124.5, 122.8, 115.0, 114.8, 114.0, 113.7, 109.3, 109.2, 84.4, 67.4, 66.4, 59.4, 46.7, 44.0, 29.7; HRMS (EI) Calcd for $[C_{49}H_{34}FNO_4]^+$: 719.2472; found : 719.2470.

(1R, 2'S, 3'R, 4'R)-2'-benzoyl-1''-benzyl-5''-chloro-4'-hydroxy-4'-(4-phenylphenyl)-1'',2''-dihydro-2H-dispiro[acenaphthylene-1,1'-cyclopentane-3',3''-indole]-2,2''-dione (5f):

White solid, Mp: 258 - 260 °C; IR (KBr): 3396, 3057, 2934, 1711, 1677, 1627, 1600, 1492, 1465, 1434, 1369, 1350, 1238, 1130, 1011, 930, 857, 830, 784, 669, 600, 534, 480 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.48 (s, 1H), 8.09 – 7.97 (m, 2H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.68 – 7.54 (m, 6H), 7.44 (dd, *J* = 11.7, 7.8 Hz, 5H), 7.34 (dd, *J* = 18.1, 7.6 Hz, 4H), 7.11 (d, *J* = 8.1 Hz, 1H), 7.05 – 6.90 (m, 6H), 6.83 (t, *J* = 7.3 Hz, 1H), 6.73 – 6.63 (m, 4H), 6.58 (d, *J* = 7.1 Hz, 2H), 6.33 (d, *J* = 8.2 Hz, 1H), 5.32 (s, 1H), 5.25 (d, *J* = 16.1 Hz, 1H), 4.62 (d, *J* = 14.3 Hz, 1H), 4.47 (d, *J* = 16.1 Hz, 1H), 2.60 (d, *J* = 14.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 212.8, 196.9, 176.7, 142.5, 142.1, 140.4, 140.4, 139.6, 137.2, 136.2, 135.2, 133.1, 131.7, 131.2, 129.9, 129.5, 128.7, 128.6, 127.7, 127.4, 127.3, 127.0, 126.7, 126.5, 126.3, 126.1, 124.7, 124.5, 122.9, 109.8, 84.4, 67.2, 66.4, 59.3, 46.7, 44.0; HRMS (EI) Calcd for $[C_{49}H_{34}ClNO_4]^+$: 735.2176; found : 735.2175.

(1R, 2'S, 3'R, 4'R)-1''-benzyl-5''-chloro-4'-hydroxy-2'-(4-methylbenzoyl)-4'-(4-phenylphenyl)-1'',2''-dihydro-2H-dispiro[acenaphthylene-1,1'-cyclopentane-3',3''-indole]-2,2''-dione (5g):

White solid, Mp: 254 - 256 °C; IR (KBr): 3553, 3373, 3034, 2927, 1711, 1684, 1603, 1488, 1423, 1346, 1234, 1177, 1119, 1003, 967, 919, 830, 784, 765, 700, 646, 596, 569, 523, 465, 419 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.47 (d, *J* = 5.9 Hz, 1H), 8.03 (d, *J* = 6.9 Hz, 1H), 7.99 (s, 1H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.68 – 7.53 (m, 5H), 7.44 (dd, *J* = 11.6, 7.5 Hz, 4H), 7.36 (d, *J* = 7.0 Hz, 1H), 7.31 (d, *J* = 7.7 Hz, 2H), 7.10 (d, *J* = 8.3 Hz, 1H), 6.98 (dt, *J* = 14.5, 7.8 Hz, 3H), 6.83 (d, *J* = 7.3 Hz, 2H), 6.65 (s, 1H), 6.57 (d, *J* = 7.3 Hz, 2H), 6.45 (d, *J* = 7.5 Hz, 2H), 6.32 (d, *J* = 8.2 Hz, 1H), 4.62 (d, *J* = 14.2 Hz, 1H), 4.45 (d, *J* = 16.1 Hz, 1H), 2.59 (d, *J* = 14.2 Hz, 1H), 1.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 212.9, 196.5, 176.7, 142.5, 142.5, 142.1, 140.4, 140.4, 139.6, 137.3, 135.2, 133.7, 132.9, 131.3, 129.9, 129.5, 128.7, 128.7, 128.6, 127.9, 127.6, 127.4, 127.2, 127.0, 127.0, 126.7, 126.3, 126.1, 124.7, 124.4, 122.8, 109.7, 84.4, 67.2, 66.5, 59.5, 46.7, 44.0, 21.1; HRMS (EI) Calcd for $[C_{50}H_{36}ClNO_4]^+$: 749.2333; found : 749.2333.

(1R, 2'S, 3'R, 4'R)-2'-benzoyl-4'-hydroxy-1''-methyl-4'-(4-phenylphenyl)-1'',2''-dihydro-2H-dispiro[acenaphthylene-1,1'-cyclopentane-3',3''-indole]-2,2''-dione (5h):

White solid, Mp: 244 – 246 °C; IR (KBr): 3334, 3053, 2927, 2857, 1703, 1688, 1607, 1492, 1469, 1430, 1346, 1234, 1123, 1096, 1007, 965, 923, 830, 780, 757, 696, 646, 600 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.57 (d, *J* = 5.8 Hz, 1H), 8.05 (d, *J* = 7.0 Hz, 1H), 7.94 (d, *J* = 7.1 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.60 (t, *J* = 6.1 Hz, 2H), 7.53 (d, *J* = 7.4 Hz, 1H), 7.43 – 7.28 (m, 7H), 7.18 (d, *J* = 9.4 Hz, 5H), 6.96 (d, *J* = 7.7 Hz, 2H), 6.82 (d, *J* = 7.8 Hz, 2H), 6.66 (d, *J* = 7.5 Hz, 1H), 6.57 (s, 1H), 5.33 (s, 1H), 4.57 (d, *J* = 14.1 Hz, 1H), 2.96 (s, 3H), 2.58 (d, *J* = 14.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 213.2, 196.5, 176.8, 144.5, 144.2, 142.2, 140.6, 140.1, 139.9, 139.6, 137.0, 135.3, 133.1, 131.4, 129.9, 129.6, 128.7, 127.9, 127.6, 127.2, 126.9, 126.9, 126.7, 126.2, 125.8, 125.8, 125.6, 124.9, 124.4, 122.7, 121.8, 107.5, 84.5, 67.5, 65.3, 59.6, 46.2, 25.9; HRMS (EI) Calcd for $[C_{43}H_{31}NO_4]^+$: 625.2253; found : 625.2253.

(1R, 2'S, 3'R, 4'R)-2'-benzoyl-4'-hydroxy-1''-[(3-methylphenyl)methyl]-4'-(4-phenylphenyl)-1'',2''-dihydro-2H-dispiro[acenaphthylene-1,1'-cyclopentane-3',3''-indole]-2,2''-dione (5i):

White solid, Mp: 256 - 258 °C; IR (KBr): 3394, 3052, 2931, 1715, 1674, 1623, 1600, 1497, 1455, 1424, 1360, 1352, 1248, 1130, 1021, 934, 852, 828, 774, 670, 602, 536, 482 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.46 (d, *J*

= 6.4 Hz, 1H), 8.25 (d, *J* = 7.2 Hz, 1H), 8.08 (d, *J* = 6.9 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.89 – 7.83 (m, 2H), 7.80 (d, *J* = 7.0 Hz, 1H), 7.77 – 7.71 (m, 1H), 7.60 (td, *J* = 16.4, 8.0 Hz, 5H), 7.42 – 7.29 (m, 8H), 7.13 (d, *J* = 6.8 Hz, 3H), 7.06 (d, *J* = 7.6 Hz, 2H), 6.94 (d, *J* = 8.1 Hz, 2H), 6.81 (d, *J* = 7.4 Hz, 2H), 6.73 (s, 1H), 5.63 (s, 1H), 4.61 (d, *J* = 13.9 Hz, 1H), 2.73 (d, *J* = 13.7 Hz, 1H), 2.18 (s, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$): δ (ppm) 212.9, 196.5, 176.7, 142.5, 142.4, 142.1, 140.4, 140.4, 139.6, 137.3, 135.2, 133.7, 132.9, 131.3, 129.9, 129.5, 128.7, 128.7, 128.6, 127.9, 127.6, 127.4, 127.2, 127.0, 127.0, 126.7, 126.6, 126.3, 126.1, 124.7, 124.4, 122.8, 109.7, 84.4, 77.3, 77.0, 76.7, 67.2, 66.5, 59.4, 46.7, 44.0, 21.0; HRMS (EI) Calcd for $[C_{50}H_{37}NO_4]^+$: 715.2723; found : 715.2723.

(1R, 2'S, 3'R, 4'R)-2'-benzoyl-4'-(4-bromophenyl)-4'-hydroxy-1'',2''-dihydro-2H-dispiro[acenaphthylene-1,1'-cyclopentane-3',3''-indole]-2,2''-dione (5j):

White solid, Mp: 250 - 252 °C; IR (KBr, cm^{-1}): 3513, 3455, 2928, 2848, 1702, 1615, 1352, 1262, 1144, 901, 720, 617, 467 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.39 (d, *J* = 6.7 Hz, 1H), 8.17 (d, *J* = 6.9 Hz, 1H), 8.06 (d, *J* = 7.0 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 2H), 7.83 (dd, *J* = 11.1, 7.9 Hz, 2H), 7.70 (dd, *J* = 11.5, 4.7 Hz, 2H), 7.66 (s, 1H), 7.61 (dd, *J* = 11.7, 7.2 Hz, 2H), 7.01 (d, *J* = 8.2 Hz, 2H), 6.88 (d, *J* = 8.2 Hz, 2H), 6.71 (q, *J* = 8.3 Hz, 3H), 6.66 (s, 1H), 5.47 (s, 1H), 4.48 (d, *J* = 14.2 Hz, 1H), 2.64 (d, *J* = 14.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 212.7, 204.3, 196.4, 142.1, 141.6, 139.5, 137.9, 137.4, 137.2, 134.8, 134.1, 133.4, 131.1, 131.0, 130.4, 130.3, 130.2, 130.0, 129.5, 128.1, 127.9, 127.9, 126.6, 125.0, 124.8, 124.4, 124.3, 123.0, 122.8, 121.6, 120.9, 84.2, 71.6, 67.70, 59.6, 47.0; HRMS (EI) Calcd for $[C_{36}H_{24}BrNO_4]^+$: 613.0889; found : 613.0889.

(1R, 2'S, 3'R, 4'R)-2'-benzoyl-1''-benzyl-4'-(4-bromophenyl)-4'-hydroxy-1'',2''-dihydro-2H-dispiro[acenaphthylene-1,1'-cyclopentane-3',3''-indole]-2,2''-dione (5k):

White solid, Mp: 255 - 257 °C; IR (KBr): 3387, 3047, 2946, 2852, 1740, 1686, 1621, 1492, 1469, 1429, 1419, 1362, 1235, 1210, 1178, 1024, 951, 852, 825, 783, 769, 736, 704, 644, 602, 563, 452 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.46 (s, 1H), 8.10 – 7.84 (m, 3H), 7.60 (s, 3H), 7.37 – 7.02 (m, 9H), 6.91 (d, *J* = 6.7 Hz, 2H), 6.81 (s, 1H), 6.62 (s, 5H), 6.47 (d, *J* = 7.0 Hz, 1H), 5.34 (s, 1H), 5.29 (d, *J* = 16.0 Hz, 1H), 4.51 (dd, *J* = 20.8, 15.6 Hz, 2H), 2.54 (d, *J* = 14.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 212.9, 196.8, 176.9, 143.8, 142.1, 139.6, 137.5, 136.4, 135.6, 133.1, 131.6, 131.1, 130.8, 129.9, 129.5, 128.8, 128.6, 128.1, 127.7, 127.2, 127.1, 126.5, 126.4, 125.7, 124.8, 124.5, 122.8, 122.1, 122.0, 108.9, 84.0, 66.8, 66.12, 59.3, 46.5, 43.9; HRMS (EI) Calcd for $[C_{43}H_{30}BrNO_4]^+$: 703.1358; found : 703.1358.

(1R, 2'S, 3'R, 4'R)-2'-benzoyl-4'-(4-bromophenyl)-4'-hydroxy-1''-[(3 methylphenyl)methyl]-1'',2''-dihydro-2H-dispiro[acenaphthylene-1,1'-cyclopentane-3',3''-indole]-2,2''-dione (5l):

White solid, Mp: 238 - 240 °C; IR (KBr): 3503, 3450, 2927, 2850, 1700, 1603, 1350, 1261, 1134, 903, 719, 607 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.74 (d, *J* = 7.2 Hz, 1H), 8.47 (s, 1H), 8.16 (d, *J* = 8.2 Hz, 1H), 8.11 (d, *J* = 7.1 Hz, 1H), 8.04 (d, *J* = 7.3 Hz, 1H), 8.00 (d, *J* = 7.6 Hz, 1H), 7.94 (d, *J* = 7.3 Hz, 1H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.71 (t, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 7.2 Hz, 3H), 7.25 (d, *J* = 7.1 Hz, 2H), 7.15 (d, *J* = 7.0 Hz, 1H), 7.11 (s, 1H), 7.07 (d, *J* = 8.3 Hz, 2H), 7.03 (d, *J* = 10.2 Hz, 2H), 6.91 (d, *J* = 7.6 Hz, 2H), 6.81 (t, *J* = 7.4 Hz, 1H), 6.66 (d, *J* = 7.5 Hz, 1H), 6.62 (d, *J* = 7.0 Hz, 1H), 6.49 (d, *J* = 7.6 Hz, 1H), 6.11 (d, *J* = 7.6 Hz, 1H), 5.34 (s, 1H), 5.15 (d, *J* = 16.0 Hz, 1H), 4.51 (t, *J* = 14.5 Hz, 2H), 2.53 (d, *J* = 14.1 Hz, 1H), 2.33 (s, 3H), 1.25 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 213.0, 196.7, 176.9, 143.9, 142.1, 139.6, 138.0, 137.5, 136.4, 135.6, 133.1, 132.2, 131.9, 131.5, 131.2, 130.7, 130.3, 129.9, 129.5, 128.8, 128.7, 128.4, 128.0, 127.9, 127.7, 127.6, 127.2, 126.5, 126.4, 125.6, 125.5, 124.8, 124.5, 123.2, 122.8, 122.1, 121.9, 108.9, 84.0, 66.8, 66.0, 59.3, 46.6, 44.0, 21.5; HRMS (EI) Calcd for $[C_{44}H_{32}BrNO_4]^+$: 717.1515; found : 717.1511.

(1R, 2'S, 3'R, 4'R)-1''-benzyl-4'-(4-bromophenyl)-4'-hydroxy-2'-(4-methoxybenzoyl)-1'',2''-dihydro-2H-dispiro[acenaphthylene-1,1'-cyclopentane-3',3''-indole]-2,2''-dione (5m):

White solid, Mp: 242 - 244 °C; IR (KBr): 3359, 2926, 2848, 1656, 1604, 1480, 1264, 1169, 1021, 926, 786, 609, 544, 472, 406 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.44 (d, *J* = 6.1 Hz, 1H), 8.03 (d, *J* = 7.1 Hz, 1H), 7.98 – 7.90 (m, 2H), 7.67 – 7.54 (m, 3H), 7.30 – 7.19 (m, 5H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.08 (t, *J* = 6.7 Hz, 3H), 6.94 (d, *J* = 8.4 Hz, 2H), 6.61 (d, *J* = 10.1 Hz, 3H), 6.46 (d, *J* = 7.6 Hz, 1H), 6.14 (d, *J* = 8.4 Hz, 2H), 5.30 (t, *J* = 7.9 Hz, 2H), 4.56 (d, *J* = 14.1 Hz, 1H), 4.47 (d, *J* = 15.9 Hz, 1H), 3.50 (s, 3H), 2.54 (d, *J* = 14.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 213.2, 195.0, 177.0, 162.3, 143.8, 142.1, 139.6, 137.6, 135.6, 133.1, 130.8, 129.9, 129.6, 129.3, 128.8, 128.6, 128.1, 127.6, 127.0, 126.4, 125.7, 124.8, 124.4, 122.7, 122.1, 121.9, 112.5, 108.8, 84.0, 66.8, 65.90, 59.5, 55.1, 46.5, 43.9; HRMS (EI) Calcd for $[C_{44}H_{32}BrNO_5]^+$: 733.1464; found : 733.1464.

(1R, 2'S, 3'R, 4'R)-2'-benzoyl-4'-(4-bromophenyl)-4'-hydroxy-1''-(prop-2-yn-1-yl)-1'',2''-dihydro-2H-dispiro[acenaphthylene-1,1'-cyclopentane-3',3''-indole]-2,2''-dione (5n):

White solid, Mp: 238 - 240 °C; IR (KBr): 3342, 2926, 2857, 2340, 1715, 1666, 1604, 1267, 1123, 1097, 926, 900, 779, 697, 658, 530, 432 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.39 (d, *J* = 6.7 Hz, 1H), 8.17 (d, *J* = 6.9 Hz, 1H), 8.06 (d, *J* = 7.0 Hz, 1H), 7.99 (d, *J* = 7.9 Hz, 2H), 7.87 – 7.78 (m, 2H), 7.69 (d, *J* = 7.6 Hz, 2H), 7.66 (s, 1H), 7.61 (s, 2H), 7.01 (d, *J* = 8.1 Hz, 3H), 6.88 (d, *J* = 8.3 Hz, 3H), 6.71 (dd, *J* = 17.3, 9.4 Hz, 5H), 5.47 (s, 1H), 4.49 (d, *J* = 14.1 Hz, 1H), 2.65 (d, *J* = 14.2 Hz, 1H), 1.25 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 212.8, 204.3, 196.4, 142.1, 139.5, 137.3, 134.7, 134.0, 133.4, 131.0, 130.4,

130.3, 129.9, 129.5, 128.1, 128.0, 127.9, 127.9, 126.6, 125.0, 124.8, 124.4, 123.1, 122.8, 120.9, 84.2, 71.6, 67.7, 59.6, 46.9, 29.7; HRMS (EI) Calcd for $[C_{39}H_{26}BrNO_4]^+$: 651.1045; found : 651.1045.

Methyl (1R,2'S,3'R,4'R)-1''-benzyl-4'-hydroxy-2,2''-dioxo-4'-(4-phenylphenyl)-1'',2''-dihydro-2H-dispiro[acenaphthylene-1,1'-cyclopentane-3',3''-indole]-2'-carboxylate (5o):

White solid, Mp: 266 - 268 °C; IR (KBr): 3557, 3380, 1746, 1711, 1688, 1607, 1492, 1465, 1423, 1365, 1200, 1177, 1138, 1103, 1015, 961, 834, 784, 753, 700, 650, 603, 523 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.60 (d, *J* = 7.0 Hz, 1H), 8.23 (d, *J* = 8.1 Hz, 1H), 8.16 (d, *J* = 7.0 Hz, 1H), 7.94 (d, *J* = 7.0 Hz, 1H), 7.89 (d, *J* = 8.3 Hz, 1H), 7.82 (t, *J* = 7.5 Hz, 1H), 7.75 (t, *J* = 7.7 Hz, 1H), 7.55 (d, *J* = 7.5 Hz, 2H), 7.42 (t, *J* = 7.4 Hz, 3H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.25 (d, *J* = 7.2 Hz, 2H), 7.20 – 7.10 (m, 2H), 6.95 (dt, *J* = 14.2, 7.0 Hz, 2H), 6.55 (d, *J* = 7.2 Hz, 1H), 6.45 (s, 1H), 6.42 (d, *J* = 7.2 Hz, 1H), 5.16 (d, *J* = 16.1 Hz, 1H), 4.59 (d, *J* = 8.8 Hz, 1H), 4.40 (d, *J* = 16.1 Hz, 1H), 2.70 (s, 3H), 2.58 (d, *J* = 14.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 212.0, 176.3, 169.0, 143.7, 142.8, 141.1, 140.4, 140.3, 137.4, 135.4, 133.1, 130.6, 130.3, 129.7, 128.8, 128.7, 128.5, 128.1, 127.3, 127.0, 126.9, 126.5, 126.5, 126.3, 126.3, 126.1, 124.5, 123.3, 122.1, 108.8, 84.8, 67.0, 61.6, 59.5, 51.2, 46.4, 43.7; HRMS (EI) Calcd for $[C_{44}H_{33}NO_5]^+$: 655.2359; found : 655.2359.

Ethyl (1R,2'S,3'R,4'R)-1''-benzyl-4'-hydroxy-2,2''-dioxo-4'-(4-phenylphenyl)-1'',2''-dihydro-2H-dispiro[acenaphthylene-1,1'-cyclopentane-3',3''-indole]-2'-carboxylate (5p):

White solid, Mp: 256 - 258 °C; IR (KBr): 3335, 3057, 2921, 2850, 1705, 169, 1603, 1492, 1425, 1350, 1237, 1175, 1073, 1013, 967, 826, 788, 745, 696, 650, 520, 453 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.82 (d, *J* = 7.0 Hz, 1H), 8.39 (d, *J* = 8.1 Hz, 1H), 8.32 (d, *J* = 7.0 Hz, 1H), 8.11 (d, *J* = 7.0 Hz, 1H), 8.06 (d, *J* = 8.3 Hz, 1H), 7.98 (t, *J* = 7.6 Hz, 1H), 7.92 (t, *J* = 7.7 Hz, 1H), 7.72 (d, *J* = 7.5 Hz, 2H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.51 (d, *J* = 7.3 Hz, 1H), 7.43 (d, *J* = 6.7 Hz, 2H), 7.32 (p, *J* = 7.4 Hz, 2H), 7.11 (dt, *J* = 14.4, 7.1 Hz, 2H), 6.70 (d, *J* = 7.3 Hz, 2H), 6.61 (s, 1H), 6.59 (d, *J* = 7.2 Hz, 1H), 5.35 (d, *J* = 16.0 Hz, 1H), 4.77 (d, *J* = 14.2 Hz, 1H), 4.73 (s, 1H), 4.55 (d, *J* = 16.1 Hz, 1H), 3.41 (dd, *J* = 15.1, 7.3 Hz, 2H), 2.76 (d, *J* = 14.2 Hz, 1H), 0.16 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 212.3, 176.3, 168.4, 143.7, 143.1, 141.19, 140.4, 140.3, 137.5, 135.4, 133.0, 130.8, 130.4, 129.8, 128.7, 128.5, 128.1, 127.3, 127.0, 126.8, 126.6, 126.6, 126.3, 126.1, 124.4, 123.6, 123.2, 122.1, 108.8, 84.7, 66.9, 61.7, 60.3, 59.5, 46.4, 43.8, 12.6; HRMS (EI) Calcd for $[C_{45}H_{35}NO_5]^+$: 669.2515; found : 669.2515.

Methyl (1R,2'S,3'R,4'R)-4'-hydroxy-2,2''-dioxo-4'-(4-phenylphenyl)-1''-(prop-2-yn-1-yl)-1'',2''-dihydro-2H-dispiro[acenaphthylene-1,1'-cyclopentane-3',3''-indole]-2'-carboxylate (5q):

White solid, Mp: 260 – 262 °C; IR (KBr): 3395, 3307, 2925, 1739, 1709, 1609, 1493, 1466, 1424, 1362, 1343, 1212, 1177, 1139, 1104, 1008, 962, 927, 788, 754, 700, 661 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.58 (d, *J* = 7.0 Hz, 1H), 8.24 (d, *J* = 8.2 Hz, 1H), 8.16 (d, *J* = 7.1 Hz, 1H), 7.89 (t, *J* = 6.2 Hz, 2H), 7.83 (t, *J* = 7.5 Hz, 1H), 7.75 (t, *J* = 7.7 Hz, 1H), 7.49 (d, *J* = 7.6 Hz, 2H), 7.36 (dd, *J* = 18.0, 8.4 Hz, 5H), 7.30 (d, *J* = 7.0 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.12 (d, *J* = 7.4 Hz, 2H), 6.83 (d, *J* = 7.7 Hz, 1H), 6.41 (s, 1H), 4.54 (s, 1H), 4.48 (d, *J* = 14.3 Hz, 1H), 4.42 (d, *J* = 17.6 Hz, 1H), 4.07 (d, *J* = 17.7 Hz, 1H), 2.72 (s, 3H), 2.56 (d, *J* = 14.3 Hz, 1H), 1.76 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 212.0, 175.1, 169.1, 142.9, 142.4, 141.0, 140.7, 140.3, 136.7, 133.1, 130.6, 130.3, 129.7, 128.8, 128.7, 128.1, 127.1, 126.8, 126.2, 126.0, 124.5, 123.3, 123.2, 108.3, 85.0, 71.2, 67.5, 60.5, 59.5, 51.3, 45.8, 28.6; HRMS (EI) Calcd for $[C_{40}H_{29}NO_5]^+$: 603.2046; found : 603.2044.

Ethyl (1R,2'S,3'R,4'R)-4'-hydroxy-2,2''-dioxo-4'-(4-phenylphenyl)-1''-(prop-2-yn-1-yl)-1'',2''-dihydro-2H-dispiro[acenaphthylene-1,1'-cyclopentane-3',3''-indole]-2'-carboxylate (5r):

White solid, Mp: 252 - 254 °C; IR (KBr): 3503, 3450, 2927, 2850, 1700, 1603, 1350, 1261, 1134, 903, 719, 607, 465 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.63 (d, *J* = 7.4 Hz, 1H), 8.23 (d, *J* = 8.2 Hz, 1H), 8.16 (d, *J* = 7.0 Hz, 1H), 7.89 (t, *J* = 7.7 Hz, 1H), 7.85 – 7.80 (m, 1H), 7.76 (d, *J* = 7.2 Hz, 1H), 7.49 (d, *J* = 7.2 Hz, 1H), 7.36 (dd, *J* = 18.7, 7.4 Hz, 4H), 7.19 (s, 1H), 7.12 (d, *J* = 7.3 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 2H), 6.40 (s, 2H), 4.51 (s, 1H), 4.45 (d, *J* = 16.8 Hz, 1H), 4.03 (d, *J* = 18.0 Hz, 2H), 3.24 (dd, *J* = 15.5, 7.8 Hz, 2H), 2.57 (d, *J* = 14.3 Hz, 2H), 2.18 (s, 2H), 1.74 (s, 1H), 0.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 212.1, 174.9, 168.3, 143.1, 142.3, 140.9, 136.7, 133.1, 130.6, 130.5, 130.4, 129.7, 128.9, 128.1, 127.5, 126.0, 125.9, 124.5, 123.5, 123.3, 122.3, 122.1, 108.4, 84.6, 77.3, 77.0, 76.7, 76.4, 71.3, 67.4, 60.4, 59.4, 45.6, 29.7, 28.7, 12.6; HRMS (EI) Calcd for $[C_{41}H_{31}NO_5]^+$: 617.2202; found : 617.2202.

Ethyl (1R,2'S,3'R,4'R)-4'-(4-bromophenyl)-4'-hydroxy-2,2''-dioxo-1''-(prop-2-yn-1-yl)-1'',2''-dihydro-2H-dispiro[acenaphthylene-1,1'-cyclopentane-3',3''-indole]-2'-carboxylate (5s):

White solid, Mp: 255 - 257 °C; IR (KBr): 3312, 3070, 2939, 1696, 1611, 1480, 1431, 1342, 1179, 1080, 989, 910, 815, 746, 697, 576, 550, 458 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.61 (d, *J* = 7.0 Hz, 1H), 8.25 (d, *J* = 8.1 Hz, 1H), 8.16 (s, 1H), 7.92 (d, *J* = 8.3 Hz, 1H), 7.85 (d, *J* = 7.6 Hz, 2H), 7.76 (t, *J* = 7.7 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.29 (s, 1H), 7.22 (t, *J* = 7.4 Hz, 2H), 6.96 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 7.7 Hz, 1H), 6.43 (s, 1H), 4.56 (dd, *J* = 17.7, 2.3 Hz, 1H), 4.49 (s, 1H), 4.41 (d, *J* = 14.2 Hz, 1H), 4.02 (dd, *J* = 17.7, 2.1 Hz, 1H), 3.31 – 3.17 (m, 2H), 2.53 (d, *J* = 14.3 Hz, 1H), 2.06 (s, 1H), 0.04 – 0.01 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 212.1, 174.9, 168.3, 143.1, 142.3, 140.9, 136.7, 133.1, 130.6, 130.5, 130.4, 129.7, 128.9, 128.1, 127.5, 126.0, 125.9, 124.5,

123.5, 123.3, 122.3, 122.1, 108.4, 84.6, 76.4, 71.3, 67.4, 60.4, 59.5, 45.6, 29.7, 28.7, 12.6; HRMS (EI) Calcd for $[C_{35}H_{26}BrNO_5]^+$: 619.0994; found : 619.0994.

Ethyl (1R,2'S,3'R,4'R)-1''-benzyl-4'-(4-bromophenyl)-4'-hydroxy-2,2''-dioxo-1'',2''-dihydro-2H-dispiro[acenaphthylene-1,1'-cyclopentane-3',3''-indole]-2'-carboxylate (5t):

White solid, Mp: 256-258 °C; IR (KBr): 3334, 3057, 2923, 2850, 1707, 1692, 1603, 1492, 1423, 1350, 1234, 1177, 1073, 1011, 967, 826, 788, 746, 696, 650, 523, 457 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.64 (d, *J* = 7.0 Hz, 1H), 8.27 (d, *J* = 8.0 Hz, 1H), 8.19 (d, *J* = 6.8 Hz, 1H), 7.97 – 7.92 (m, 2H), 7.86 (t, *J* = 7.6 Hz, 1H), 7.78 (t, *J* = 7.6 Hz, 1H), 7.33 – 7.25 (m, 5H), 7.20 (d, *J* = 7.5 Hz, 1H), 7.16 (d, *J* = 7.4 Hz, 1H), 7.11 (d, *J* = 7.9 Hz, 2H), 6.59 (d, *J* = 7.1 Hz, 2H), 6.50 (d, *J* = 8.7 Hz, 2H), 5.24 (d, *J* = 16.0 Hz, 1H), 4.54 (d, *J* = 14.5 Hz, 2H), 4.42 (d, *J* = 16.0 Hz, 1H), 3.27 (q, *J* = 7.2 Hz, 2H), 2.57 (d, *J* = 14.2 Hz, 1H), 0.07 – -0.01 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 212.2, 176.1, 168.3, 143.6, 143.1, 140.9, 137.5, 135.3, 133.1, 130.8, 130.7, 130.3, 129.7, 128.9, 128.6, 128.1, 128.0, 127.1, 126.3, 126.2, 126.0, 124.5, 123.6, 123.3, 122.1, 108.8, 84.4, 66.7, 61.6, 60.3, 59.4, 46.2, 43.8, 12.6; HRMS (EI) Calcd for $[C_{39}H_{30}BrNO_5]^+$: 671.1307; found : 671.1305.

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Notes and references

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1 For reviews, see: (a) C. Marti and E. M. Carreira, *Eur. J. Org. Chem*. 2003, 2209; (b) R. M. Williams and R. J. Cox, *Acc. Chem. Res*. 2003, **36**, 127; (c) H. Lin and S. J. Danishefsky, *Angew. Chem*. 2003, **115**, 38; (d) C. V. Galliford and K. A. Scheidt, *Angew. Chem*. 2007, **119**, 8902; (e) F. Zhou, Y.-L. Liu and J. Zhou, *Adv. Synth. Catal*. 2010, **352**, 1381.

2 (a) M. M. C. Lo, C. S. Neumann, S. Nagayama, E. O. Perlstein and S. L. Schreiber, *J. Am. Chem. Soc*. 2004, **126**, 16077; (b) C. Chen, X. Li, C. S. Neumann, M. M. C. Lo and S. L.Schreiber, *Angew. Chem*. 2005, **117**, 2289; (c) A. K. Franz, P. D. Dreyfuss and S. L. Schreiber, *J. Am. Chem. Soc*. 2007, **129**, 1020; (d) S. Shangary, *Proc. Natl. Acad. Sci. USA*. 2008, **105**, 3933; (e) F. Yu, R. Huang, H. Ni, J. Fan, S. Yan and J. Lin, *Green Chem*. 2013, **15**, 453; (f) J. P. MacDonald, B. H. Shupe, J. D. Schreiber and A. K. Franz, *Chem. Commun*. 2014, **50**, 5242.

3 (a) Q. Wei and L. Gong, *Org. Lett*. 2010, **12**, 1008; (b) K. Jiang, Z. Jia, S. Chen, L. Wu and Y. Chen, *Chem. Eur. J*. 2010, **16**, 2852; (c) A. Voituriez, N. Pinto, M. Neel, P. Retailleau and A. Marinetti, *Chem. Eur. J*. 2010, **16**, 12541; (d) X. Zhang, S. Cao, Y. Wei and M. Shi, *Chem. Commun*. 2011, **47**, 1548; (e) F. Zhong, X. Han, Y. Wang and Y. Lu, *Angew. Chem., Int. Ed*. 2011, **50**, 7837; (f) B. Tan, N. R. Candeias and C. F. Barbas III, *Nat. Chem*. 2011, **3**, 473; (g) B. Viswambharan, K. Selvakumar, S. Madhavan and P. Shanmugam, *Org. lett*. 2010, **12**, 2108.

4 For recent examples of the catalytic enantioselective construction of spirooxindoles fused with five-membered carbocycles, see: (a) R. Rios, *Chem. Soc. Rev*. 2012, **41**, 1060; (b) F. R. Zhong, X. Y. Han, Y. Q. Wang and Y. X. Lu, *Angew. Chem*. 2011, **123**, 7983; (c) J. Peng, X. Huang, L. Jiang, H. L. Cui and Y. C. Chen, *Org. Lett*. 2011, **13**, 4584; (d) N. V. Hanhan, N. R. Ball-Jones, N. T. Tran and A. K. Franz, *Angew. Chem*. 2012, **124**, 1013; (e) J. Dugal-Tessier, E. A. O_Bryan, T. B. H. Schroeder, D. T. Cohen and K. A. Scheidt, *Angew. Chem*. 2012, **124**, 5047; (f) S. W. Duan, Y. Li, Y. Y. Liu, Y. Q. Zou, D. Q. Shi and W. J. Xiao, *Chem. Commun*. 2012, **48**, 5160; (g) F. Shi, Z. L. Tao, S. W. Luo, S. J. Tu and L. Z. Gong, *Chem. Eur. J*. 2012, **18**, 6885; (h) A. Awata and T. Arai, *Chem. Eur. J*. 2012, **18**, 8278; (i) B. M. Trost and K. Hirano, *Org. Lett*. 2012, **14**, 2446; (j) Z. Q. Liu, X. Q. Feng and H. F. Du, *Org. Lett*. 2012, **14**, 3154; (k) L-L. Wang, J-F. Bai, L. Peng, L-W. Qi, Li-Na. Jia, Y-L. Guo, X-Y. Luo, X-Y. Xu and L-X. Wang, *Chem. Commun*. 2012, **48**, 5175.

5 (a) C. V. Galliford and K. A. Scheidt, *Angew. Chem., Int. Ed*. 2007, **46**, 8748; (b) X. H. Chen, Q. Wei, S. W. Luo, H. Xiao and L. Z. Gong, *J. Am. Chem. Soc*. 2009, **131**, 13819; (c) B. Tan, X. Zeng, W. Leong, Z. Shi, C. F. Barbas III and G. Zhong, *Chem. Eur. J*. 2012, **18**, 63; (d) B. Trost and M. Brennan, *Org. lett*. 2006, **8**, 2027; (e) P. R. Sebahar and R. M. Williams, *J. Am. Chem. Soc*. 2000, **122**, 5666; (f) T. Onishi, P. R. Sebahar and R. M. Williams, *Org. Lett*. 2003, **5**, 3135; (g) M. V. D. Teresa and Pinho e Melo, *Eur. J. Org. Chem*. 2006, 2873; (h) C. Najera and J. M. Sansano, *Angew. Chem., Int. Ed*. 2005, **44**, 6272; (i) I. Coldham and R. Hufton, *Chem. Rev*. 2005, **105**, 2765.

6 (a) M. Tsuada, Y. Kasai, K. Komatsu, T. Sone, M. Tanaka, Y. Mokami and J. Kobayashi, *Org. Lett*. 2004, **6**, 3087; (b) T. Mugishima, M. Tsuda, Y. Kasai, H. Ishiyama, E. Fukushi, J. Kawabata, M. Watanabe, K. Akao and J. Kobayashi, *J. Org. Chem*. 2005, **70**, 9430; (c) T. J. Greshock, A. W. Grubbs, P. Jiao, D. T. Wicklow, J. B. Gloer and R. M. Williams, *Angew. Chem., Int. Ed*. 2008, **47**, 3573.

7 (a) B. M. Trost, N. Cramer and S. M. Silverman, *J. Am. Chem. Soc*. 2007, **129**, 12396; (b) B. Tan, N. R. Candeias and C. F. Barbas, III. *J. Am. Chem. Soc*. 2011, **133**, 4672; (c) K. Albershofer, B. Tan and C. F. Barbas, III. *Org. Lett*. 2012, **14**, 1834.

8 (a) X. Li, Y. Li, F. Peng, S. Wu, Z. Li, Z. Sun, H. Zhang and Z. Shao, *Org. Lett*. 2011, **13**, 6160; (b) Y. Li, X. Li, F. Peng, Z. Li, S. Wu, Z. Sun, H. Zhang and Z. Shao, *Org. Lett*. 2011, **13**, 6200; (c) Y. Wang, L. Liu, T. Zhang, N. Zhong, D. Wang and Y. Chen, *J. Org. Chem*. 2012, **77**, 4143.

9 (a) D. Basavaiah and K. R. Reddy, *Org. Lett*. 2007, **9**, 57; (b) G. Shanthi and P. T. Perumal, *Tetrahedron Lett*. 2008, **49**, 7139; (c) K. Selvakumar, V. Vaithiyanathan and P. Shanmugam, *Chem. Comm*. 2010, **46**, 2826; (d) K. A. P. Lingam, P. Shanmugam and K. Selvakumar, *Synlett*, 2012, **2**, 278.

10 J. Sun, Y. Sun, H. Gong, Y. J. Xie and C. Yan, *Org. Lett*. 2012, **14**, 5172.

11 A. Voituriez, N. Pinto, M. Neel, P. Retailleau and A. Marinetti, *Chem. Eur. J*. 2010, **16**, 12541.

12 J. Sun, Y-J. Xie and C-G. Yan, *J. Org. Chem*. 2013, **78**, 8354.

13 (a) M. Tsuda, Y. Kasai, K. Komatsu, T. Sone, M., Y. Tanaka, Y. Mokami and J. Kobayashi, *Org. Lett*. 2004, **6**, 3087; (b) T. Mugishima, M. Tsuda, Y. Kasai, H. Ishiyama, E. Fukushi, J. Kawabata, M. Watanabe, K. Akao and J. Kobayashi, *J. Org. Chem*. 2005, **70**, 9430; (c) T. J. Greshock, A. W. Grubbs, P. Jiao, D. T. Wicklow, J. B. Gloer and R. M. Williams, *Angew. Chem., Int. Ed*. 2008, **47**, 3573.

14 (a) J. Liu, H. Sun, X. Liu, L. Ouyang, T. Kang, Y. Xie and X. Wang, *Tetrahedron Lett*. 2012, **53**, 2336. (b) A. B. S. Babu and R. Raghunathan, *Tetrahedron Lett*. 2008, **49**, 4487.

15 (a) B. Tan, G. Hernandez-Torres and C. F. Barbas, III. *J. Am. Chem. Soc*. 2011, **128**, 12354; (b) J. Li, N. Wang, C. Li and X. Jia, *Org. Lett*. 2012, **14**, 4994.

16 (a) K. Suman, S. Lanka and S. Thennarasu, *Org. Lett*. 2014, **16**, 3732; (b) S. Lanka, S. Thennarasu and P. T. Perumal, *RSC Adv*. 2014, **4**, 2263: (c) S. Lanka, S. Thennarasu and P. T. Perumal, *Tetrahedron Lett*. 2014, **55**, 2585. (d) S. Lanka, S. Thennarasu and P. T. Perumal, *Tetrahedron Lett*. 2012, **53**, 7052.

17 CCDC-1041758 (**3a'**) and -1041757 (**5f**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.