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3-(Hetero)aryl-4-indolylamino-α-tetralones by Diastereoselective Internal Redox Cyclization: An "Azaenamine" Conjugate Addition

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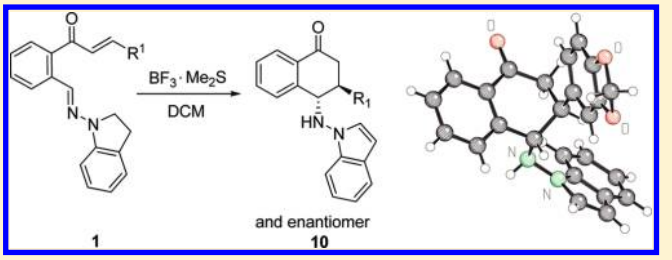
Supporting Information

ABSTRACT: (*E*)-3-(Hetero)aryl-1-(2-((*E*)-(indolin-1-ylimino)methyl)phenyl)prop-2-en-1-ones **1** undergo 6-*exo*-*trig* cyclization reactions upon treatment with $BF_3 \cdot Me_2S$ in dichloromethane at low temperature to give the tetralones **10** in good yield. This cyclization process can be considered to be an intramolecular Michael-type addition which is accompanied by an internal redox reaction as the indoline fragment is oxidized to indole with simultaneous hydrogen shift to nitrogen atom N1 and the α-carbon atom of the Michael system. The reactions at the iminic centers take place via umpolung of the classical carbonyl reactivity. The reaction is diastereoselective and affords exclusivly 3,4-disubstituted α-tetralones **10** as *trans*-diastereomers. According to quantum chemical calculations the reactions take place under kinetic control with the *trans*-diastereomer being the kinetically favored product as it has the lower activation barrier compared to the *cis*-diastereomer.



INTRODUCTION

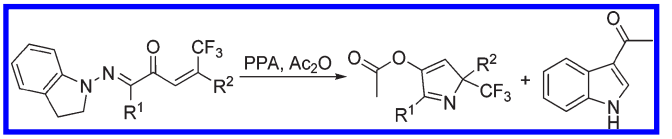
Polyunsaturated *N*-aminoindoline-derived hydrazones exhibit chemical properties different from other hydrazone derivatives, as we have learned from our previous studies.[1] Although these investigations were mainly focused on electrophilic cyclization reactions[2] we could demonstrate that in the case of aza-Nazarov cyclization reactions[3] the indoline fragment as part of *N*-aminoindoline-derived hydrazones might be used as precursor of the indole leaving group, which is formed in the N−N-bond fission step (Scheme 1).[1] The formation of 2*H*-pyrroles from azadienones and silver nitrate mediated cyclizations of alkyne hydrazones to give annulated pyridine derivatives are the first examples of the application of aminoindoline-derived hydrazones in the synthesis of nitrogen-containing heterocycles.[1] The strong tendency toward aromatization of the indoline fragment upon oxidation giving the indole is a key factor which explains the unique behavior of *N*-aminoindoline-derived hydrazones.

We designed the system **1**, which could be considered as a precursor for the vinylogous aza-Nazarov ring-closure process.[4] Here, a phenylene unit is introduced between the iminic and the carbonyl carbon atoms in comparison to our previous system **2**. We were interested to learn about the chemical reactivity of this system under electrophilic conditions, e.g., in the presence of Brønsted or Lewis acids (Scheme 2).

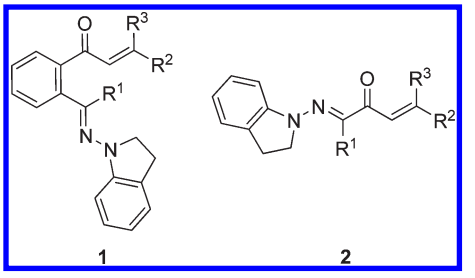
RESULTS AND DISCUSSION

The cyclization precursor **1** was synthesized by a straightforward route starting with the esterification of 2-formylbenzoic acid **3** to give **4**, which was conducted in DMF using MeI in the presence of K_2CO_3 under reflux.[5] The ester **4** was then

Scheme 1. Aza-Nazarov synthesis of 2*H*-pyrroles



Scheme 2



transformed into hydrazone **5** by reacting it with *N*-aminoindoline in methanol. *N*-Aminoindoline was prepared from commercially available indoline via a nitrosation−reduction sequence.[6] In the next step, the ester group of **5** was converted into the corresponding phosphonate by reacting it with deprotonated methyl dimethylphosphonate in THF at −78 °C.[7] The resulting phosphonate **6** was used in Horner−Wadsworth−Emmons reactions[8] (HWE reaction) employing various aldehydes to afford

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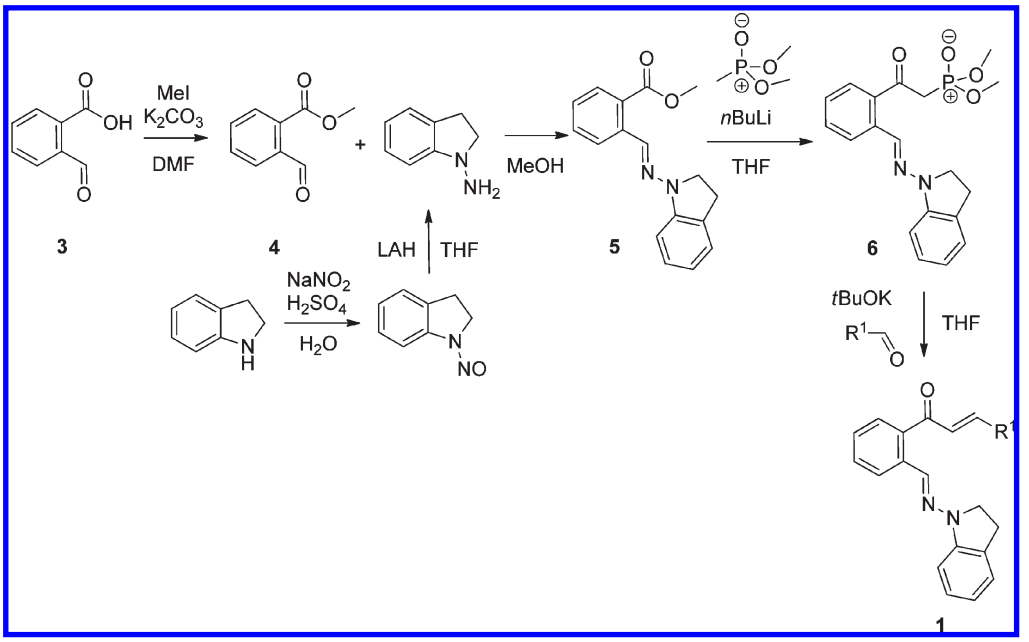
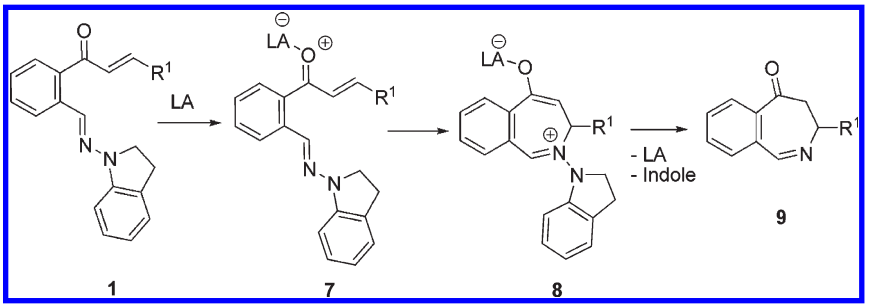
Scheme 3. Synthesis of (*E*)-3-(Hetero)aryl-1-(2-((*E*)-(indolin-1-ylimino)methyl)phenyl)prop-2-en-1-ones 1a−k



Scheme 4. Expected Reactivity of Compounds 1 upon Treatment with Lewis Acids (LA)



the *E*-olefination products **1a**−**k** in moderate to excellent yield. The HWE reactions were carried out at rt in THF applying *t*-BuOK as base (Scheme 3).

Constitution, configuration, and conformation in the solid state of the olefination product **1e** were elucidated by X-ray diffraction (Figure 1).[9] The structures of the precursors **1a**−**k** with isolated yields of the olefination step are given in Table 1.

In order to induce a cyclization process,[10] our aim was the selective electrophilic activation of compounds **1** at the carbonyl oxygen in the presence of the hydrazone unit by using oxophilic Lewis acids.[11] We were expecting 3-substituted benzazepinones **9** as cyclic products (Scheme 4).[12]

In the course of these studies, we noticed that the $BF_3 \cdot Et_2O$ and $BF_3 \cdot Me_2S$ complexes were the best choice for promoting the cyclization. Other tested Lewis acids like $TiCl_4$ gave no reaction at low temperature (−78 °C) but gave complex mixtures at −15 to +10 °C. Thus, in the following experiments the hydrazones were treated with $BF_3 \cdot Me_2S$ in dry DCM in the temperature range of −10 to 0 °C. In contrast to our expectations, the products obtained were six-membered α-tetralone derivatives **10** containing a hydrazine fragment in the side chain and no seven membered heterocycles as analyzed by NMR spectroscopy and X-ray diffraction (Scheme 5).

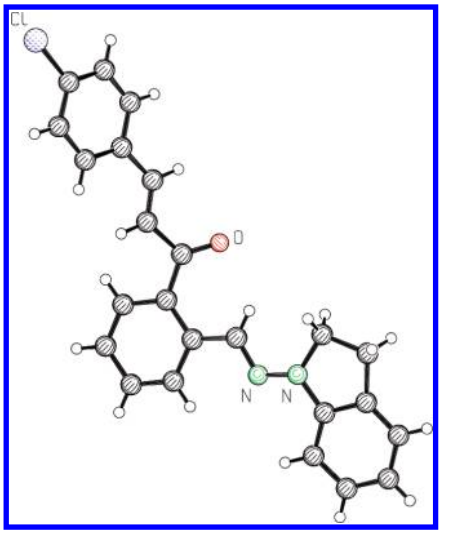


Figure 1. Molecular structure of compound **1e** in the solid state (X-ray diffraction).[9]

This new reaction is quite versatile with respect to the substitution pattern. Thus, the R^1 substituents might be aryl moieties

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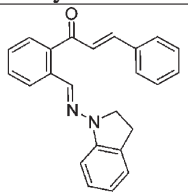
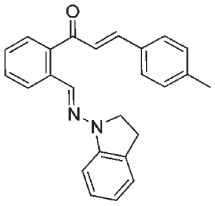
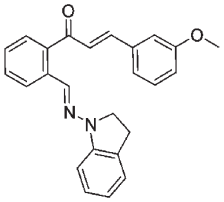
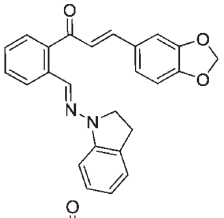
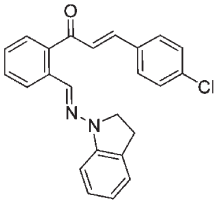
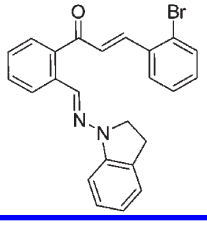
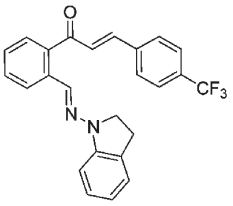
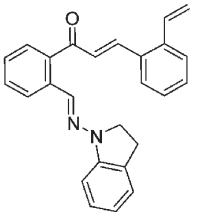
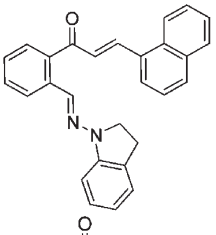
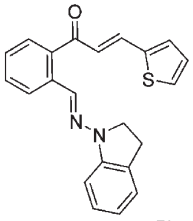
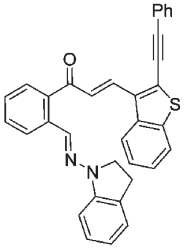
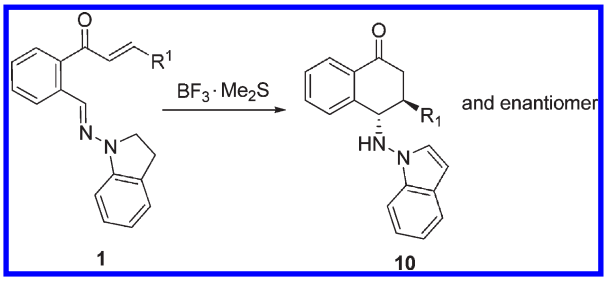
Table 1. Structures and Yields of (*E*)-3-(Hetero)aryl-1-(2-((*E*)-(indolin-1-ylimino)methyl)phenyl)prop-2-en-1-ones 1

No.	Hydrazone	Reaction time [h]	Yield [%]
1a		2	85
1b		24	73
1c		16	87
1d		24	55
1e		5	58
1f		2	93
1g		4	67
1h		24	57
1i		24	64
1j		20	87
1k		24	49

Scheme 5. Synthesis of 3-(Hetero)aryl-4-indolylamino-α-tetralones 10 from (*E*)-3-(Hetero)aryl-1-(2-((*E*)-(indolin-1-ylimino)methyl)phenyl)prop-2-en-1-ones 1



bearing electron-donating or -withdrawing groups at different positions of the aryl ring. Even aryl groups containing additional olefinic and alkyne substituents could be introduced. Among the tested heterocyclic groups we were successful with thiophene and benzothiophene groups as R^1 substituent. The structures and the isolated yields of the products **10** obtained are given in Table 2.

The ^{1}H NMR spectra of the compounds **10** gave clear evidence that exclusively the diastereomers in which substituents at position 3 and 4 are *trans* located to each other were generated in the ring-forming step. The selective formation of the *trans*-product was further confirmed by X-ray diffraction (Figure 2).

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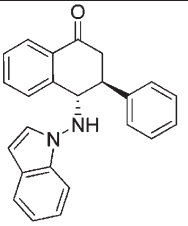
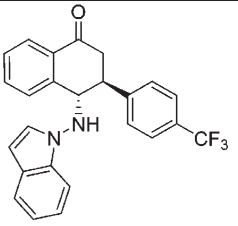
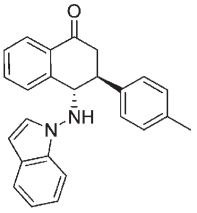
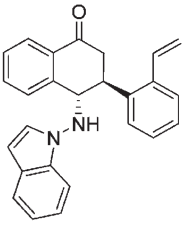
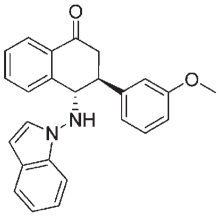
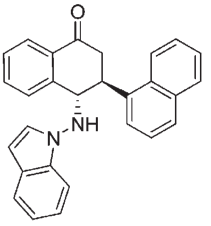
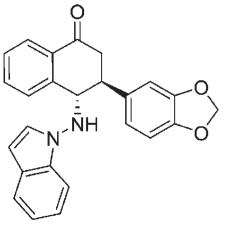
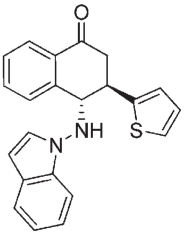
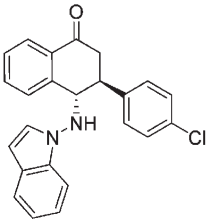
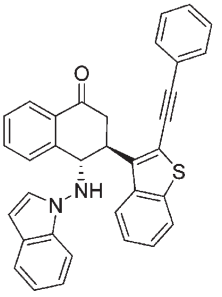
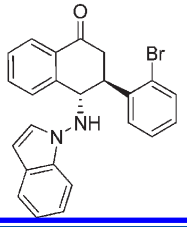
Table 2. Structures and Yields of 3-(Hetero)aryl-4-indolylamino-α-tetralones 10

No	Product	Yield %	No	Product	Yield %
10a		57	**10g**		55
10b		77	**10h**		61
10c		84	**10i**		60
10d		67	**10j**		75
10e		56	**10k**		57
10f		85			

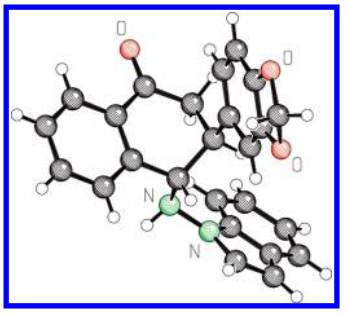


Figure 2. Molecular structure of compound **10d** in the solid state (X-ray diffraction).[9]

In most cases, 1.2 equiv of the Lewis acid was sufficient to complete the reaction, but for **10d**, **10j**, and **10k** we used 2 equiv of $BF_3 \cdot Me_2S$.

We propose the following mechanism for the observed transformation (Scheme 6).

The key step of the reaction is the Lewis acid induced intramolecular conjugate addition of the imine carbon atom of the hydrazone unit to the β-carbon atom of the α,β-unsaturated carbonyl subunit of the activated substrate **11**. As a result a 6-*exo*-*trig* cyclization affords cyclic species **12** containing the diazenium cation fragment. Tautomerization of the diazenium cation **12** into an iminium cation **13**[2d,13] followed by deprotonation from the 3-position of the indoline, further proton−BF_3 exchange and

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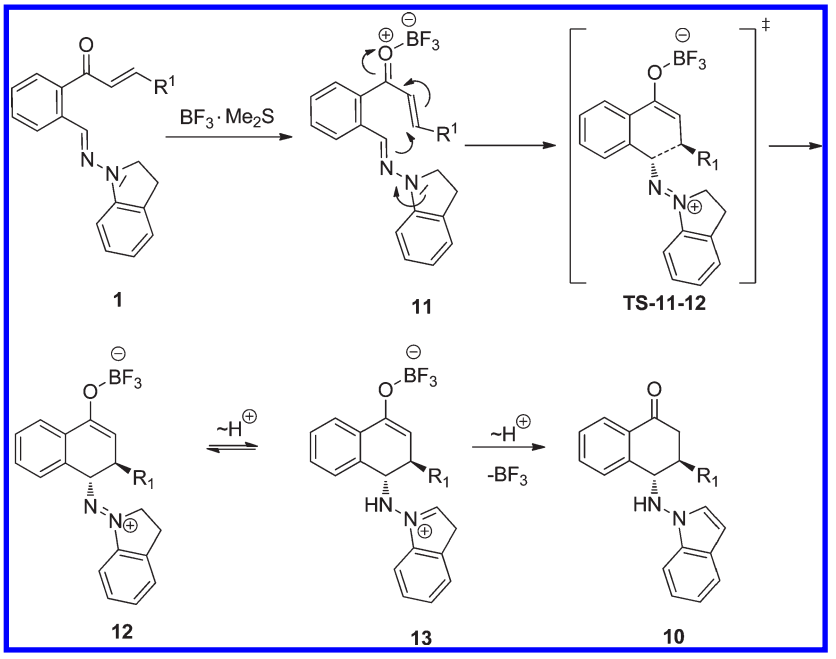
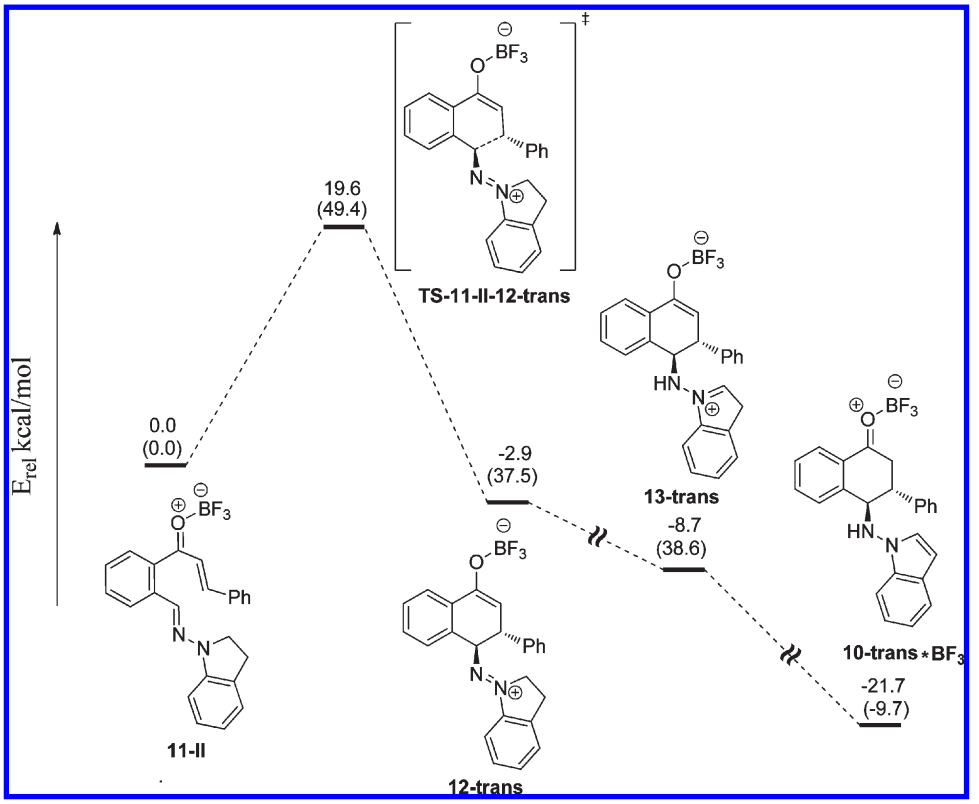
Scheme 6. Proposed Mechanism of the $BF_3 \cdot Me_2S$-Assisted Cyclization Reaction of (*E*)-3-(Hetero)aryl-1-(2-((*E*)-(indolin-1-ylimino)methyl)phenyl)prop-2-en-1-ones 1 To Give Compounds 10



Scheme 7. Calculated Relative Energies for the Complete Cyclization Pathway of Compound 11 To Give 10-trans Product (CPCM(UAKS)-HF/def2-QZVPP//HF/6-311G(d,p) and HF/def2-QZVPP//HF/6-311G(d,p) (in Parentheses) Including Zero-Point Correction (ZPE)) (kcal/mol)



keto−enol tautomerism leads to the formation of the observed products **10** without cleavage of the N−N bond. Quite interesting in this reaction sequence is the function of the hydrazone carbon atom as a nucleophile,[14] illustrating once more

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the reactivity of hydrazones in the sense of an "azaenamine" featuring "Umpolung reactivity" of the C═N−NR_2 subunit. Furthermore, this transformation illustrates the value of indoline substituents as internal reduction partners, which are able to transfer hydrogen to other parts of the molecule, while being oxidized to the much more stable aromatic indole moieties. Thus, this reaction may be considered as an internal redox cyclization process.[15] Recently, Pan et al. and Seidel et al. have reported on redox isomerizations of indolines to give indoles via azomethine ylide intermediates.[16]

Interestingly, the computational gas-phase modeling[17] by HF/6-311G(d,p) geometry optimizations of the complete cyclization pathway starting with one of the conformer of the BF_3 complex **11-II** (R^1 = Ph)[18] to give the product complex **10-trans**·BF_3 (Scheme 7) gave quite positive reaction energies. To our surprise, B3LYP/6-311G(d,p) gas-phase calculations of the products **12** completely failed to give the expected cyclic structures and transition states but led back to the open-chain BF_3 complexes **11** of the starting materials. However, reasonable reaction energies could be obtained from CPCM(UAKS)-HF/def2-QZVPP//HF/6-311G(d,p)-(single point) calculations with a dichloromethane solvent sphere[19] on the HF structures.[20] The failure of the gas phase calculations without solvent sphere might be traced back to the change of a well delocalized zwitterionic system (like **11**) into a system with distinct charge separation (like **12**). According to the solvent sphere single-point calculations, the ring-closing step includes an activation barrier of approximately 20 kcal/mol, which is in agreement with the experimental conditions (1 h of stirring at −10 to 0 °C). The importance of the formation of the aromatic indole moiety as driving force for this ring-closure process is nicely seen form the relative energies of the last two tautomerisation steps.

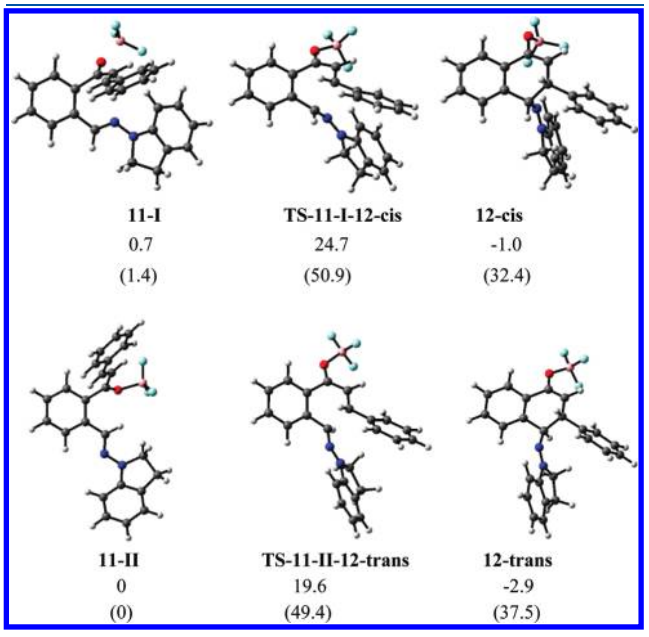

Figure 3. Calculated relative energies for the 1,6-cyclization pathway starting from different conformations of **11** (as obtained from IRC calculations) to give **12-cis** (upper line) and **12-trans** (lower line) via the corresponding transition states **TS-11-I-12-cis** and **TS-11-II-12-trans** (CPCM(UAKS)-HF/def2-QZVPP//HF/6-311G(d,p) and HF/def2-QZVPP//HF/6-311G(d,p) (in parentheses) including zero-point correction (ZPE)) (kcal/mol).

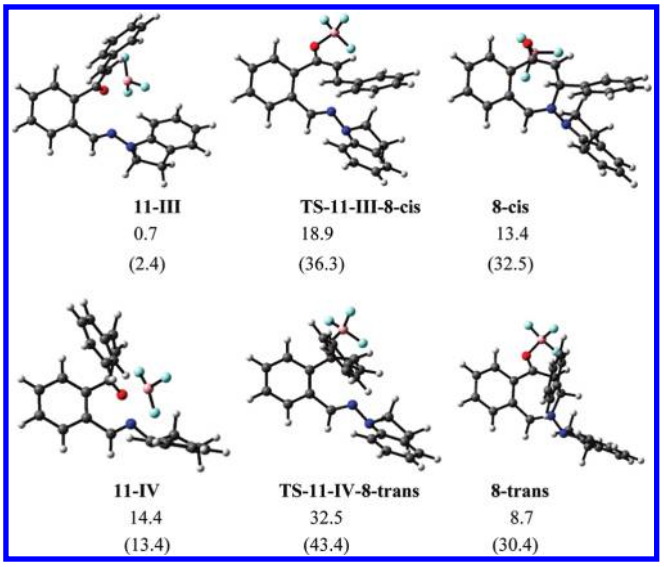

Figure 4. Calculated relative energies for the 1,7-cyclization pathway starting from different conformations **11-III, 11-IV** (as obtained from IRC calculations) to give **8-cis** (upper line) and **8-trans** (lower line) via the corresponding transition states **TS-11-III-8-cis** and **TS-11-IV-8-trans** (CPCM(UAKS)-HF/def2-QZVPP//HF/6-311G(d,p) and HF/def2-QZVPP//HF/6-311G(d,p) (in parentheses) including zero-point correction (ZPE)) (kcal/mol).

These single-point calculations also explain the exclusive formation of the *trans* diastereomer by kinetic reaction control. Thus, the transition structure **TS-11-II-12-trans** for the formation of the *trans*-6-membered ring product **12-trans** is 5.1 kcal/mol lower in energy compared to the transition structure **TS-11-I-12-cis** which leads to the *cis*-6-membered ring product **12-cis**. Both *cis*- and *trans*-pathways have similar thermochemistry (Figure 3). The calculated (gas phase) transition structure **TS-11-II-12-trans** is nonplanar and is characterized by a relatively short C−C distance (1.92 Å) of the forming bond. This is in accord with a Michael-type addition with small charge separation (NBO −0.076 for the "azaenamine" carbon and 0.026 for the β-carbon atom).[21]

As discussed above, experimentally, the formation of a 7-membered ring structure is not observed. The calculations show that the cyclization reaction path starting from conformer **11-III** leading to the *cis*-7-membered ring structure **8-cis** is endothermic by 12.7 kcal/mol and the one from **11-IV** to the *trans*-7-membered ring **8-trans** requires a high energy conformation for the cyclization of the open-chain species (**11-IV**), while the activation barrier is also very high (32.5 kcal/mol) (Figure 4). IRC calculations prove the mutual relationship of these structures on the energy hypersurface.

CONCLUSIONS

In conclusion, we have shown that upon treatment with BF_3·Me_2S, aminoindoline-derived unsaturated hydrazones **1** undergo 6-*exo*-*trig* cyclization reactions to form the tetralone derivatives **10**. This intramolecular Michael type cyclization reactions are accompanied by an internal redox process as the indoline fragment is oxidized into an indole with simultaneous hydrogen shift to the H_2**C**-CHRR′ and RHC-**N**H subunits, respectively. The reaction at the iminic center takes place via umpolung of the classical carbonyl reactivity, underlining the

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"azaenamine" character of such species. The reaction products, *trans*-3,4-disubstituted α-tetralones **10**, were obtained as single diastereomers. Quantum chemical calculations suggest that the cyclization reaction takes place under kinetic control, thus explaining the observed diastereoselectivity.

α-Tetralones are reported to have significant medicinal importance.[22] As both tetralone and indole moieties are biologically active entities these novel products might be interesting for pharmaceutical and medicinal purposes.

EXPERIMENTAL SECTION

Melting points are uncorrected. ^{1}H, ^{13}C, ^{19}F, ^{31}P, GCOSY, GHSQC, GHMBC and 1D-NOE NMR spectroscopy: TMS (^{1}H) (0.00 ppm) and $CDCl_3$ (^{13}C) (77.0 ppm) were used as internal references, and $CFCl_3$ (^{19}F) (0.0 ppm) and 85% H_3PO_4 (^{31}P) (0.0 ppm) were used as external references. When necessary, the experiments were carried out with complete exclusion of moisture.

(*E*)-Methyl 2-((Indolin-1-ylimino)methyl)benzoate (5). This compound was prepared from the 2-methoxycarbonylbenzaldezyde **4** and *N*-aminoindoline. 2-Methoxycarbonylbenzaldehyde **4** 0.164 g (1 mmol) was dissolved in methanol (4 mL), and *N*-aminoindoline (1.1 mmol) in ethanol (1 mL) was added slowly at 0 °C. The reaction mixture was stirred at rt for 30 min. The resulting product was separated by filtration and washed with water and cold methanol. **5**. Yellow solid, 0.194 g (0.69 mmol, 69%). Mp: 105−106 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.25 (t, *J* = 8.2 Hz, 2H, CH_2), 3.91 (s, 1H, CH_3O), 3.94 (t, *J* = 8.2 Hz, 2H, CH_2N), 6.83 (td, *J* = 7.2, 1.3 Hz, 1H, *H*-arom), 7.13−7.31 (m, 4H, *H*-arom), 7.51 (t, *J* = 7.6 Hz, 1H, *H*-arom), 7.91 (dd, *J* = 7.9, 1.1 Hz, 1H, *H*-arom), 8.23 (d, *J* = 8.0 Hz, 1H, *H*-arom), 8.30 (s, 1H, C*H*N). ^{13}C NMR (75 MHz, $CDCl_3$): δ 27.0 (CH_2), 48.2 (CH_2N), 52.1 (CH_3O), 109.0 (CH), 120.5 (CH), 124.9 (CH), 126.0 (CH), 126.9 (CH), 127.0, 127.7, 127.8 (CH), 130.6 (CH), 131.8 (CH), 132.0 (CH), 137.6, 147.8, 167.9 (COO). IR (neat) $\tilde{\nu}$ 3057 (w), 3024 (w), 2988 (w), 2945 (w), 1709 (m), 1609 (w), 1572 (m), 1543 (m), 1477 (m), 1431 (m), 1398 (m), 1352 (w), 1300 (m), 1240 (s), 1188 (m), 1161 (m), 1074 (m), 1047 (w), 1036 (w), 970 (w), 897 (m), 841 (w), 764 (w), 754 (m), 743 (s), 702 (m), 660 (w) cm^{-1}. HRMS (ESI): calcd for $C_{17}H_{16}N_2O_2Na$ 303.1109, found 303.1127. Anal. Calcd for $C_{17}H_{16}N_2O_2$ (280.32): C, 72.84; H, 5.75; N, 9.99. Found: C, 72.89; H, 5.67; N, 10.05.

(*E*)-Dimethyl 2-(2-((Indolin-1-ylimino)methyl)phenyl)-2-oxoethylphosphonate (6). Dimethyl methylphosphonate 0.14 mL (1.3 mmol, *d* = 1.161) was dissolved in abs THF (1 mmol of the compound in 1.5 mL of solvent) and cooled to −78 °C, and 0.81 mL of *n*-BuLi (1.6 M in hexane, 1.3 mmol) was added slowly. The reaction mixture was stirred for 1 h at −78 °C. Then the hydrazone **5** 0.280 g (1 mmol) in abs THF (1 mmol of the compound in 0.5 mL) was added. The reaction mixture was stirred for 4 h at −78 °C and then quenched with AcOH (1 equiv) and water (ca. 10 equiv). After evaporation of most of the liquid phase, the residue was dissolved in dichloromethane and washed with water and then with saturated aqueous $NaHCO_3$ solution and again with water. The residue was dried with $MgSO_4$ and purified by column chromatography. **6**. Yellow oil, 0.310 g (0.83 mmol, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.24 (t, *J* = 8.3 Hz, 2H, CH_2), 3.58 (d, *J* = 22.1 Hz, 2H, CH_2P), 3.72 (d, *J* = 11.2 Hz, 6H, CH_3O), 3.88 (t, *J* = 8.2 Hz, 2H, CH_2N), 6.83 (td, *J* = 7.2, 1.6 Hz, 1H, *H*-arom), 7.13−7.20 (m, 3H, *H*-arom), 7.32 (td, *J* = 7.6, 1.1 Hz, 1H, *H*-arom), 7.47 (td, *J* = 7.9, 1.1 Hz, 1H, *H*-arom), 7.60 (dd, *J* = 7.7, 0.9 Hz, 1H, *H*-arom), 7.73 (s, 1H, C*H*N), 7.88 (d, *J* = 7.8 Hz, 1H, *H*-arom). ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.0 (CH_2), 40.8 (d, *J* = 128.4 Hz, CH_2P), 48.0 (CH_2N), 52.9 (d, *J* = 6.4 Hz, CH_3O), 108.8 (CH), 120.8 (CH), 124.9 (CH), 126.9 (CH), 127.0 (CH), 127.5, 128.0 (CH), 129.1 (CH),130.6 (CH), 131.4 (CH), 135.3, 136.2 (d, *J* = 2.0 Hz), 147.3, 196.3 (CO). ^{31}P NMR (162 MHz, $CDCl_3$): δ 23.2. IR (neat) $\tilde{\nu}$: 3509 (w), 3030 (w), 2957 (w), 2928 (w), 2853 (w), 1688 (w), 1666 (m), 1606 (w), 1562 (w), 1531 (m), 1487(m), 1476 (s), 1462 (m), 1402 (s), 1302 (m), 1254 (s), 1194 (s), 1167 (m), 1130 (w), 1117 (w), 1045 (s), 1022 (s), 986 (s), 891 (m), 876 (m), 835 (m), 804 (m), 760 (s), 750 (s), 725 (m), 667 (w) cm^{-1}. HRMS (ESI): calcd for $C_{19}H_{21}N_2O_4PNa$ 395.1131, found 395.1130. Anal. Calcd for $C_{19}H_{21}N_2O_4P$ (372.35): C, 61.29; H, 5.68; N, 7.52. Found: C, 60.62; H, 5.73; N, 7.24.

General Procedure for the Preparation of (*E*)-3-(Hetero)-aryl-1-(2-((*E*)-(indolin-1-ylimino)methyl)phenyl)prop-2-en-1-ones (1). *t*-BuOK (1.2 equiv) was dissolved in abs THF (1 mmol of the base in 10 mL of solvent), and the ketophosphonate **3** (1 equiv) in THF (1 mmol of the compound in 2 mL of the solvent) was added. The reaction mixture was stirred for 1 h at rt, and the aromatic aldehyde (1 equiv) in THF was added. The reaction mixture was stirred for the time indicated in Table 1 at rt, and then the solvent was evaporated. The residue was dissolved in dichloromethane, washed with brine, dried with $MgSO_4$, concentrated, and purified by column chromatography. In all cases, the *E*-product is observed in crude NMR.

(*E*)-1-(2-((*E*)-(Indolin-1-ylimino)methyl)phenyl)-3-phenyl-prop-2-en-1-one (1a). This compound was obtained from (*E*)-dimethyl 2-(2-((indolin-1-ylimino)methyl)phenyl)-2-oxoethylphosphonate **6** (0.225 g, 0.6 mmol) and benzaldehyde (0.064 g, 0.6 mmol) according to the general procedure. The subsequent chromatographic purification (Et_2O/pentane, 1:4) gave 0.180 g (0.51 mmol, 85%) of **1a** as a yellow solid. Mp: 113−114 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.04 (t, *J* = 8.2 Hz, 2H, CH_2), 3.67 (t, *J* = 8.2 Hz, 2H, CH_2N), 6.70 (td, *J* = 7.2, 1.1 Hz, 1H, *H*-arom), 6.98 (d, *J* = 7.3 Hz, 1H, *H*-arom), 7.04−7.13 (m, 3H), 7.21 (td, *J* = 7.5, 0.9 Hz, 1H, *H*-arom), 7.25−7.27 (m, 3H), 7.36−7.43 (m, 5H), 7.54 (s, 1H, C*H*N), 7.97 (d, *J* = 7.9 Hz, 1H, *H*-arom). ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.9 (CH_2), 47.9 (CH_2N), 109.0 (CH), 120.4 (CH), 124.7 (CH), 126.2 (CH), 126.8 (CH), 126.9 (CH), 127.4, 127.8 (CH), 128.3 (CH), 128.4 (CH), 128.9 (CH), 130.4 (CH), 130.5 (CH), 130.6 (CH), 134.5, 135.2, 137.2, 145.1 (CH), 147.6, 196.0 (CO). IR (neat) $\tilde{\nu}$: 3051 (w), 3030 (w), 2953 (w), 2926 (w), 2897 (w), 2872 (w), 2853 (w), 1659 (m), 1607 (m), 1570 (m), 1547 (m), 1485 (m), 1435 (m), 1396 (m), 1329 (m), 1298 (m), 1265 (m), 1252 (m), 1204 (m), 1192 (m), 1161 (m), 1113 (m), 999 (m), 988 (m), 978 (m), 955 (m), 918 (w), 891 (w), 843 (w), 797 (w), 775 (w), 754 (s), 739 (s), 689 (m), 679 (m), 650 (m), 619 (w) cm^{-1}. HRMS (ESI): calcd for $C_{24}H_{20}N_2OH$ 353.1648, found 353.1655. Anal. Calcd for $C_{24}H_{20}N_2O$ (352.43): C, 81.79; H, 5.72; N, 7.95. Found: C, 81.22; H, 5.68; N, 7.69.

(*E*)-1-(2-((*E*)-(Indolin-1-ylimino)methyl)phenyl)-3-*p*-tolyl-prop-2-en-1-one (1b). This compound was obtained from (*E*)-dimethyl 2-(2-((indolin-1-ylimino)methyl)phenyl)-2-oxoethylphosphonate **6** (0.225 g, 0.6 mmol) and 4-methylbenzaldehyde (0.072 g, 0.6 mmol) according to the general procedure. The subsequent chromatographic purification (Et_2O/pentane, 1:5) gave 0.160 g (0.44 mmol, 73%) of **1b** as an orange solid. Mp: 134−135 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.26 (s, 3H, CH_3), 3.06 (t, *J* = 8.3 Hz, 2H, CH_2), 3.69 (t, *J* = 8.3 Hz, 2H, CH_2N), 6.71 (td, *J* = 7.2, 1.3 Hz, 1H, *H*-arom), 6.99 (d, *J* = 7.4 Hz, 1H, *H*-arom), 7.03 (d, *J* = 16.0 Hz, 1H, *H*-olef), 7.07−7.14 (m, 4H), 7.22 (td, *J* = 7.5, 1.1 Hz, 1H, *H*-arom), 7.32−7.43 (m, 5H), 7.56 (s, 1H, C*H*N), 8.00 (d, *J* = 7.9 Hz, 1H, *H*-arom). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.5 (CH_3), 26.9 (CH_2), 47.9 (CH_2N), 109.0 (CH), 120.4 (CH), 124.7 (CH), 126.0 (CH), 126.1 (CH), 126.8 (CH), 127.4, 127.8 (CH), 128.38 (CH), 128.43 (CH), 129.7 (CH), 130.5 (CH), 131.8, 135.2, 137.4, 141.1, 145.5 (CH), 147.6, 196.1 (CO). IR (neat) $\tilde{\nu}$: 3049 (w), 3026 (w), 2914 (w), 2855 (w), 1659 (m), 1597 (m), 1568 (m), 1545 (m), 1487 (m), 1476 (m), 1439 (m), 1400 (m), 1325 (m), 1300 (m), 1256 (s), 1217 (w), 1198 (s), 1163 (m), 1115 (w), 1059 (w), 1015 (m), 991 (m), 970 (w), 878 (w), 812 (s), 773 (m), 743 (s), 716 (w), 650 (w), 633 (w) cm^{-1}. HRMS (ESI): calcd for $C_{25}H_{22}N_2OH$ 367.1805, found 367.1817. Anal. Calcd for $C_{25}H_{22}N_2O$ (366.45): C, 81.94; H, 6.05; N, 7.64. Found: C, 81.81; H, 6.00; N, 7.42.

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(*E*)-1-(2-((*E*)-(Indolin-1-ylimino)methyl)phenyl)-3-(3-methoxyphenyl)prop-2-en-1-one (1c). This compound was obtained from (*E*)-dimethyl 2-(2-((indolin-1-ylimino)methyl)phenyl)-2-oxoethylphosphonate **6** (0.225 g, 0.6 mmol) and 3-methoxybenzaldehyde (0.082 g, 0.6 mmol) according to the general procedure. The subsequent chromatographic purification (Et_2O/pentane, 1:4) gave 0.200 g (0.52 mmol, 87%) of **1c** as an orange solid. Mp: 100−101 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.05 (t, J = 8.2 Hz, 2H, CH_2), 3.69 (m, 5H, CH_2N, CH_3O), 6.71 (td, J = 7.1, 1.5 Hz, 1H, *H*-arom), 6.83 (dd, J = 8.2, 2.5 Hz, 1H, *H*-arom), 6.94−7.25 (m, 8H), 7.34−7.44 (m, 3H), 7.55 (s, 1H, C*H*N), 7−97 (d, J = 7.9 Hz, 1H, *H*-arom). ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.9 (CH_2), 47.9 (CH_2N), 55.2 (CH_3O), 109.0 (*C*H), 113.1 (*C*H), 116.4 (*C*H), 120.5 (*C*H), 121.0 (*C*H), 124.7 (*C*H), 126.2 (*C*H), 126.8 (*C*H), 127.2 (*C*H), 127.4, 127.8 (*C*H), 128.5 (*C*H), 129.9 (*C*H), 130.4 (*C*H), 130.6 (*C*H), 135.2, 135.9, 137.2, 145.0 (*C*H), 147.6, 159.8, 196.0 (CO). IR (neat) ν(tilde): 3055 (w), 3030 (w), 3005 (w), 2936 (w), 2853 (w), 2835 (w), 1645 (m), 1597 (s), 1578 (s), 1551 (m), 1477 (s), 1464 (s), 1435 (m), 1402 (s), 1321 (m), 1298 (m), 1258 (s), 1231 (s), 1192 (s), 1157 (s), 1117 (w), 1042 (m), 1015 (m), 982 (m), 883 (m), 853 (m), 789 (m), 743 (s), 708 (m), 677 (m), 654 (w), 636 (w), 606 (w) cm^{-1}. HRMS (ESI): calcd for $C_{25}H_{22}N_2O_2H$ 383.1754, found 383.1753. Anal. Calcd for $C_{25}H_{22}N_2O_2$ (382.45): C, 78.51; H, 5.80; N, 7.32. Found: C, 78.36; H, 5.97; N, 6.87.

(*E*)-3-(Benzo[*d*][1,3]dioxol-5-yl)-1-(2-((*E*)-(indolin-1-ylimino)methyl)phenyl)prop-2-en-1-one (1d). This compound was obtained from (*E*)-dimethyl 2-(2-((indolin-1-ylimino)methyl)phenyl)-2-oxoethylphosphonate **6** (0.225 g, 0.6 mmol) and piperonal (0.090 g, 0.6 mmol) according to the general procedure. The subsequent chromatographic purification (Et_2O/pentane, 1:4) gave 0.130 g (0.33 mmol, 55%) of **1d** as a red solid. Mp: 169−170 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.09 (t, J = 8.2 Hz, 2H, CH_2), 3.72 (t, J = 8.3 Hz, 2H, CH_2N), 5.92 (s, 2H, OCH_2O), 6.70−6.75 (m, 2H), 6.88−7.13 (m, 6H), 7.23 (td, J = 7.5, 1.1 Hz, 1H, *H*-arom), 7.31−7.43 (m, 3H), 7.57 (s, 1H, C*H*N), 8.01 (d, J = 7.9 Hz, 1H, *H*-arom). ^{13}C NMR (75 MHz, $CDCl_3$): δ 27.0 (CH_2), 47.9 (CH_2N), 101.6 (OCH_2O), 106.6 (*C*H), 108.6 (*C*H), 109.0 (*C*H), 120.4 (*C*H), 124.7 (*C*H), 125.0 (*C*H), 125.1 (*C*H), 126.1 (*C*H), 126.8 (*C*H), 127.4, 127.8 (*C*H), 128.4 (*C*H), 129.0, 130.50 (*C*H), 130.54 (*C*H), 135.1, 137.5, 145.2 (*C*H), 147.7, 148.4, 149.9, 195.9 (CO). IR (neat) $\tilde{\nu}$: 3055 (w), 3024 (w), 2928 (w), 2911 (w), 2853 (w), 1655 (m), 1607 (m), 1587 (m), 1564 (m), 1539 (m), 1487 (s), 1446 (s), 1402 (s), 1368 (m), 1269 (s), 1261 (s), 1248 (s), 1196 (s), 1159 (s), 1111 (w), 1103 (m), 1028 (s), 982 (s), 918 (m), 864 (m), 847 (m), 818 (m), 768 (s), 750 (s), 735 (s), 702 (w), 656 (m) cm^{-1}. HRMS (ESI): calcd for $C_{25}H_{20}N_2O_3H$ 397.1547, found 397.1552. Anal. Calcd for $C_{25}H_{20}N_2O_3$ (396.44): C, 75.74; H, 5.08; N, 7.07. Found: C, 75.13; H, 5.11; N, 6.92.

(*E*)-3-(4-Chlorophenyl)-1-(2-((*E*)-(indolin-1-ylimino)methyl)phenyl)prop-2-en-1-one (1e). This compound was obtained from (*E*)-dimethyl 2-(2-((indolin-1-ylimino)methyl)phenyl)-2-oxoethylphosphonate **6** (0.225 g, 0.6 mmol) and 4-chlorobenzaldehyde (0.085 g, 0.6 mmol) according to the general procedure. The subsequent chromatographic purification (Et_2O/pentane, 1:4) gave 0.135 g (0.35 mmol, 58%) of **1e** as an orange solid. Mp: 165−166 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.09 (t, J = 8.3 Hz, 2H, CH_2), 3.72 (t, J = 8.3 Hz, 2H, CH_2N), 6.73 (td, J = 7.1, 1.6 Hz, 1H, *H*-arom), 7.00−7.12 (m, 4H), 7.22−7.27 (m, 3H), 7.34−7.44 (m, 5H, *H*-arom), 7.56 (s, 1H, C*H*N), 7.96 (dd, J = 7.9, 0.5 Hz, 1H, *H*-arom). ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.0 (CH_2), 47.9 (CH_2N), 109.0 (*C*H), 120.6 (*C*H), 124.8 (*C*H), 126.4 (*C*H), 126.9 (*C*H), 127.38 (*C*H), 127.43, 127.8 (*C*H), 128.5 (*C*H), 129.2 (*C*H), 129.5 (*C*H), 130.4 (*C*H), 130.7 (*C*H), 133.1, 135.3, 136.4, 137.1, 143.4 (*C*H), 147.6, 195.7 (CO). IR (neat) $\tilde{\nu}$: 3049 (w), 3028 (w), 2914 (w), 2853 (w), 1665 (m), 1605(m), 1566 (m), 1543 (m), 1487 (s), 1477 (s), 1467 (m), 1436 (m), 1400 (s), 1350 (w), 1298 (m), 1263 (s), 1254 (s), 1202 (s), 1194 (s), 1163 (m), 1115 (w), 1088 (m), 1011 (m), 986 (m), 970 (w), 874 (w), 820 (s), 800 (w), 760 (m), 746 (s), 716 (w), 662 (w), 637 (w) cm^{-1}. HRMS (ESI): calcd for $C_{24}H_{19}ClN_2ONa$ 409.1078, found 409.1070.

X-ray crystal structure analysis of **1e**:[9] formula $C_{24}H_{19}ClN_2O$, M = 386.86, orange crystal 0.25 × 0.10 × 0.05 mm, a = 6.0519(2) Å, b = 10.2844(8) Å, c = 16.9410(8) Å, α = 74.927(5)°, β = 88.001(4)°, γ = 77.262(5)°, V = 992.79(10) Å^3, ρ_{calc} = 1.294 g cm^{-3}, μ = 1.825 mm^{-1}, empirical absorption correction (0.658 ≤ T ≤ 0.914), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 11836 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/λ] = 0.60 Å^{-1}, 3302 independent (R_{int} = 0.039) and 2883 observed reflections [$I \geq 2\sigma(I)$], 253 refined parameters, R = 0.071, wR^2 = 0.195, max (min) residual electron density 1.27 (−0.39) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

(*E*)-3-(2-Bromophenyl)-1-(2-((*E*)-(indolin-1-ylimino)methyl)phenyl)prop-2-en-1-one (1f). This compound was obtained from (*E*)-dimethyl 2-(2-((indolin-1-ylimino)methyl)phenyl)-2-oxoethylphosphonate **6** (0.225 g, 0.6 mmol) and 2-bromobenzaldehyde (0.111 g, 0.6 mmol) according to the general procedure. The subsequent chromatographic purification (Et_2O/pentane, 1:4) gave 0.240 g (0.56 mmol, 93%) of **1f** as a red oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.12 (t, J = 8.3 Hz, 2H, CH_2), 3.76 (t, J = 8.3 Hz, 2H, CH_2N), 6.73 (td, J = 7.0, 1.8 Hz, 1H, *H*-arom), 6.98 (d, J = 16 Hz, 1H, *H*-olef), 7.02 (d, J = 7.3 Hz, 1H, *H*-arom), 7.07−7.28 (m, 5H, *H*-arom), 7.40−7.54 (m, 4H, *H*-arom), 7.59 (s, 1H, C*H*N), 7.78 (d, J = 16 Hz, 1H, *H*-olef), 7.94 (d, J = 7.8 Hz, 1H, *H*-arom). ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.0 (CH_2), 48.0 (CH_2N), 109.1 (*C*H), 120.5 (*C*H), 124.8 (*C*H), 125.7, 126.5 (*C*H), 126.9 (*C*H), 127.4, 127.7 (*C*H), 127.8 (*C*H), 127.9 (*C*H), 128.7 (*C*H), 129.7 (*C*H), 130.5 (*C*H), 130.8 (*C*H), 131.2 (*C*H), 133.4 (*C*H), 134.9, 135.4, 136.9, 143.1 (*C*H), 147.6, 195.8 (CO). IR (neat) $\tilde{\nu}$: 3040 (w), 3030 (w), 2924 (w), 2853 (w), 1657 (m), 1607 (m), 1595 (m), 1545 (m), 1477 (s), 1464 (s), 1439 (m), 1400 (s), 1352 (w), 1319 (m), 1300 (m), 1260 (s), 1202 (s), 1194 (s), 1161 (m), 1113 (m), 1047 (m), 1024 (m), 1012 (m), 976 (m), 926 (w), 883 (w), 860 (w), 804 (w), 743 (s), 667 (m), 646 (m), 604 (w) cm^{-1}. HRMS (ESI): calcd for $C_{24}H_{19}BrN_2$-OH 431.0754/433.0734, found 431.0753/433.0734.

(*E*)-1-(2-((*E*)-(Indolin-1-ylimino)methyl)phenyl)-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (1g). This compound was obtained from (*E*)-dimethyl 2-(2-((indolin-1-ylimino)methyl)phenyl)-2-oxoethylphosphonate **6** (0.225 g, 0.6 mmol) and 4-trifluoromethylbenzaldehyde (0.105 g, 0.6 mmol) according to the general procedure. The subsequent chromatographic purification (Et_2O/pentane, 1:4) gave 0.170 g (0.40 mmol, 67%) of **1g** as a red solid. Mp: 142−143 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.06 (t, J = 8.3 Hz, 2H, CH_2), 3.69 (t, J = 8.3 Hz, 2H, CH_2N), 6.71 (td, J = 7.1, 1.7 Hz, 1H, *H*-arom), 6.98 (d, J = 7.3 Hz, 1H, *H*-arom), 7.03−7.14 (m, 3H), 7.23 (td, J = 7.5, 1.1 Hz, 1H, *H*-arom), 7.37−7.44 (m, 3H), 7.47−7.52 (m, 4H, *H*-arom), 7.54 (s, 1H, C*H*N), 7.90 (d, J = 7.6 Hz, 1H, *H*-arom). ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.9 (CH_2), 47.9 (CH_2N), 109.0 (*C*H), 120.6 (*C*H), 123.8 (q, J = 272.3 Hz, CF_3), 124.8 (*C*H), 125.8 (q, J = 3.8 Hz, $CHCCF_3$), 126.6 (*C*H), 126.9 (*C*H), 127.4, 127.8 (*C*H), 128.3 (*C*H), 128.5 (*C*H), 129.1 (*C*H), 130.3 (*C*H), 130.9 (*C*H), 131.2, 131.7 (q, J = 32.6 Hz, CCF_3), 135.4, 136.8, 138.1, 142.3 (*C*H), 147.5, 195.5 (CO). ^{19}F NMR (282.5 MHz, $CDCl_3$): δ −62.8. IR (neat) $\tilde{\nu}$: 3057 (w), 3028 (w), 2920 (w), 2876 (w), 2859 (w), 1668 (m), 1631 (m), 1607 (m), 1566 (w), 1543 (m), 1485 (m), 1477 (s), 1439 (m), 1400 (m), 1321 (s), 1300 (m), 1263 (m), 1206 (m), 1163 (s), 1126 (s), 1109 (s), 1067 (s), 1040 (w), 1011 (m), 989 (m), 968 (w), 959 (w), 895 (w), 829 (s), 760 (m), 745 (s), 685 (w), 656 (m), 617 (w) cm^{-1}. HRMS (ESI): calcd for $C_{25}H_{19}F_3N_2OH$ 421.1522, found 421.1523. Anal. Calcd for $C_{25}H_{19}$-F_3N_2O (420.43): C, 71.42; H, 4.56; N, 6.66. Found: C, 71.28; H, 4.58; N, 6.51.

(*E*)-1-(2-((*E*)-(Indolin-1-ylimino)methyl)phenyl)-3-(2-vinylphenyl)prop-2-en-1-one (1h). This compound was obtained from

(*E*)-dimethyl 2-(2-((indolin-1-ylimino)methyl)phenyl)-2-oxoethylphosphonate **6** (0.225 g, 0.6 mmol) and 2-vinylbenzaldehyde (0.080 g, 0.6 mmol) according to the general procedure. The subsequent chromatographic purification (Et_2O/pentane, 1:5) gave 0.130 g (0.34 mmol, 57%) of **1h** as a red oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.10 (t, J = 8.3 Hz, 2H, CH_2), 3.74 (t, J = 8.3 Hz, 2H, CH_2N), 5.26 (dd, J = 11.0, 1.1 Hz, 1H, CH_2-olef), 5.50 (dd, J = 17.3, 1.1 Hz, 1H, CH_2-olef), 6.73 (td, J = 7.2, 1.3 Hz, 1H, *H*-arom), 6.88 (dd, J = 17.3, 11.0 Hz, 1H, C*H*-olef), 6.98 (d, J = 15.9 Hz, 1H, *H*-olef), 7.02 (d, J = 7.3 Hz, 1H, *H*-arom), 7.07−7.29 (m, 5H), 7.38−7.48 (m, 4H), 7.59 (s, 1H, C*H*N), 7.79 (d, J = 15.9 Hz, 1H, *H*-olef), 7.96 (d, J = 7.7 Hz, 1H, *H*-arom). ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.0 (CH_2), 48.0 (CH_2N), 109.1 (*C*H), 118.1 (CH_2), 120.5 (*C*H), 124.8 (*C*H), 126.4 (*C*H), 126.9 (*C*H), 127.0 (*C*H), 127.1 (*C*H), 127.4, 127.88 (*C*H), 127.91 (*C*H), 128.6 (*C*H), 129.0 (*C*H), 130.1 (*C*H), 130.5 (*C*H), 130.7 (*C*H), 132.8, 134.1 (*C*H), 135.3, 137.3, 138.4, 142.6 (*C*H), 147.6, 195.9 (CO). IR (neat) $\tilde{\nu}$: 3084 (w), 3057 (w), 3028 (w), 2928 (w), 2855 (w), 1657 (m), 1589 (m), 1545 (m), 1477 (s), 1464 (s), 1441 (m), 1400 (m), 1321 (m), 1300 (m), 1260 (s), 1194 (s), 1161 (m), 1113 (w), 1061 (w), 1013 (m), 978 (m), 920 (m), 883 (w), 858 (w), 820 (w), 743 (s), 708 (w), 691 (w), 652 (w) cm^{-1}. HRMS (ESI): calcd for $C_{26}H_{22}N_2OH$ 379.1805, found 379.1798. Anal. Calcd for $C_{26}H_{22}N_2O$ (378.47): C, 82.51; H, 5.86; N, 7.40. Found: C, 82.24; H, 5.91; N, 7.35.

(*E*)-1-(2-((*E*)-(Indolin-1-ylimino)methyl)phenyl)-3-(naphthalen-1-yl)prop-2-en-1-one (1i). This compound was obtained from (*E*)-dimethyl 2-(2-((indolin-1-ylimino)methyl)phenyl)-2-oxoethylphosphonate **6** (0.225 g, 0.6 mmol) and 1-naphthaldehyde (0.094 g, 0.6 mmol) according to the general procedure. The subsequent chromatographic purification (Et_2O/pentane, 1:4) gave 0.155 g (0.39 mmol, 64%) of **1i** as an orange solid. Mp: 107−108 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.05 (t, J = 8.2 Hz, 2H, CH_2), 3.72 (t, J = 8.2 Hz, 2H, CH_2N), 6.72 (t, J = 7.3 Hz, 1H, *H*-arom), 7.00 (d, J = 7.3 Hz, 1H, *H*-arom), 7.06−7.17 (m, 3H), 7.27 (td, J = 7.5, 1.0 Hz, 1H, *H*-arom), 7.35−7.45 (m, 4H), 7.52 (d, J = 7.6 Hz, 1H, *H*-arom), 7.62 (s, 1H, C*H*N), 7.68 (d, J = 7.2 Hz, 1H, *H*-arom), 7.74−7.80 (m, 2H), 7.95−8.00 (m, 2H, *H*-arom), 8.28 (d, J = 15.8 Hz, 1H, *H*-olef). ^{13}C NMR (75 MHz, $CDCl_3$): δ 27.0 (CH_2), 48.0 (CH_2N), 109.1 (*C*H), 120.5 (*C*H), 123.3 (*C*H), 124.8 (*C*H), 125.1 (*C*H), 125.4 (*C*H), 126.2 (*C*H), 126.4 (*C*H), 126.9 (*C*H), 127.0 (*C*H), 127.4, 127.9 (*C*H), 128.6 (*C*H), 128.7 (*C*H), 129.6 (*C*H), 130.5 (*C*H), 130.70 (*C*H), 130.72 (*C*H), 131.5, 132.1, 133.6, 135.4, 137.4, 141.8 (*C*H), 147.6, 195.9 (CO). IR (neat) $\tilde{\nu}$: 3053 (w), 2924 (w), 2851 (w), 1657 (m), 1638 (m), 1595 (m), 1570 (m), 1543 (m), 1477 (s), 1464 (m), 1441 (m), 1400 (s), 1346 (m), 1300 (m), 1252 (s), 1198 (s), 1161 (m), 1115 (w), 1020 (w), 1007 (m), 976 (m), 885 (w), 853 (w), 799 (m), 777 (s), 746 (s), 698 (m), 683 (w) cm^{-1}. HRMS (ESI): calcd for $C_{28}H_{22}N_2OH$ 403.1805, found 403.1813.

(*E*)-1-(2-((*E*)-(Indolin-1-ylimino)methyl)phenyl)-3-(thiophene-2-yl)prop-2-en-1-one (1j). This compound was obtained from (*E*)-dimethyl 2-(2-((indolin-1-ylimino)methyl)phenyl)-2-oxoethylphosphonate **6** (0.225 g, 0.6 mmol) and thiophene-2-carbaldehyde (0.068 g, 0.6 mmol) according to the general procedure. The subsequent chromatographic purification (Et_2O/pentane, 1:5) gave 0.186 g (0.52 mmol, 87%) of **1j** as a red solid. Mp: 132−133 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.08 (t, J = 8.3 Hz, 2H, CH_2), 3.72 (t, J = 8.3 Hz, 2H, CH_2N), 6.72 (td, J = 7.2, 1.4 Hz, 1H, *H*-arom), 6.88 (d, J = 15.7 Hz, 1H, *H*-olef), 6.96 (dd, J = 5.1, 3.7 Hz, 1H, *H*-arom), 7.01 (d, J = 7.3 Hz, 1H, *H*-arom), 7.07−7.13 (m, 2H, *H*-arom), 7.16 (m, 1H, *H*-arom), 7.23 (td, J = 7.5, 1.2 Hz, 1H, *H*-arom), 7.30 (d, J = 5.1 Hz, 1H, *H*-arom), 7.37−7.44 (m, 2H, *H*-arom), 7.55 (d, J = 15.7 Hz, 1H, *H*-olef), 7.57 (s, 1H, C*H*N), 8.00 (dd, J = 7.9, 0.5 Hz, 1H, *H*-arom). ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.0 (CH_2), 47.9 (CH_2N), 109.0 (*C*H), 120.5 (*C*H), 124.7 (*C*H), 125.7 (*C*H), 126.1 (*C*H), 126.8 (*C*H), 127.5, 127.8 (*C*H), 128.3 (*C*H), 128.4 (*C*H), 129.1 (*C*H), 130.4 (*C*H), 130.6 (*C*H), 131.9 (*C*H), 135.2, 137.2, 137.6 (*C*H), 140.0, 147.6, 195.3 (CO). IR (neat) $\tilde{\nu}$: 3100 (w), 3084 (w), 3049 (w), 3028 (w), 2936 (w), 2920 (w), 2899 (w), 2859 (w), 1654 (m), 1607 (m), 1582 (s), 1545 (s), 1485 (s), 1477 (s), 1462 (m), 1443 (w), 1404 (s), 1364 (m), 1300 (m), 1267 (m), 1256 (s), 1231 (m), 1206 (s), 1194 (s), 1163 (m), 1115 (w), 1086 (w), 1044 (w), 1013 (s), 964 (s), 880 (w), 870 (m), 847 (m), 827 (m), 768 (m), 745 (s), 729 (s), 700 (m), 690 (m), 656 (m), 626 (w) cm^{-1}. HRMS (ESI): calcd for $C_{22}H_{18}N_2OSH$ 359.1213, found 359.1213.

(*E*)-1-(2-((*E*)-(Indolin-1-ylimino)methyl)phenyl)-3-(2-(phenylethynyl)benzo[*b*]thiophene-3-yl)prop-2-en-1-one (1k). This compound was obtained from (*E*)-dimethyl 2-(2-((indolin-1-ylimino)methyl)phenyl)-2-oxoethylphosphonate **6** (0.225 g, 0.6 mmol) and 2-(phenylethynyl)benzo[*b*]thiophene-3-carbaldehyde (0.157 g, 0.6 mmol) according to the general procedure. The subsequent chromatographic purification (Et_2O/pentane, 1:5) gave 0.150 g (0.30 mmol, 49%) of **1k** as a red solid. Mp: 173−174 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.03 (t, J = 8.2 Hz, 2H, CH_2), 3.70 (t, J = 8.2 Hz, 2H, CH_2N), 6.69 (td, J = 7.3, 1.1 Hz, 1H, *H*-arom), 6.96−7.10 (m, 3H), 7.15−7.35 (m, 8H), 7.41 (td, J = 7.9, 1.0 Hz, 1H, *H*-arom), 7.53 (dd, J = 7.7, 0.9 Hz, 1H, *H*-arom), 7.62 (s, 1H, C*H*N), 7.65−7.67 (m, 1H, *H*-arom), 7.75 (d, J = 16.2 Hz, 1H, *H*-olef), 7.86−7.88 (m, 1H, *H*-arom), 7.91 (d, J = 16.2 Hz, 1H, *H*-olef), 7.98 (d, J = 7.8 Hz, 1H, *H*-arom). ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.9 (CH_2), 47.9 (CH_2N), 82.9 (C-alkyne), 102.4 (C-alkyne), 109.1 (*C*H), 120.5 (*C*H), 121.9, 122.3 (*C*H), 122.4 (*C*H), 124.7 (*C*H), 125.38, 125.43 (*C*H), 126.1 (*C*H), 126.3 (*C*H), 126.9 (*C*H), 127.4, 127.8 (*C*H), 128.4 (*C*H), 128.6 (*C*H), 128.7 (*C*H), 129.3 (*C*H), 130.4 (*C*H), 130.6 (*C*H), 131.6 (*C*H), 133.8, 135.2 (*C*H), 135.4, 137.1, 137.4, 139.1, 147.6, 196.2 (CO). IR (neat) $\tilde{\nu}$: 3051 (w), 3030 (w), 2949 (w), 2926 (w), 2853 (w), 2191 (w), 1657 (m), 1589 (s), 1570 (m), 1547 (m), 1481 (s), 1433 (m), 1404 (m), 1360 (m), 1323 (m), 1269 (s), 1254 (m), 1200 (s), 1188 (m), 1163 (m), 1113 (w), 1028 (m), 1018 (m), 966 (m), 881 (m), 851 (w), 748 (s), 735 (s), 725 (s), 699 (w), 661 (w), 650 (w) cm^{-1}. HRMS (ESI): calcd for $C_{34}H_{24}N_2OSH$ 509.1682, found 509.1677.

General Procedure for the Cyclization of (*E*)-3-(Hetero)-aryl-1-(2-((*E*)-(indolin-1-ylimino)methyl)phenyl)prop-2-en-1-ones Using $BF_3\cdot Me_2S$. A solution of $BF_3\cdot Me_2S$ (1.2 equiv unless otherwise indicated below) in dry dichloromethane (0.1 mL of $BF_3\cdot Me_2S$ in 10 mL of solvent) was cooled to −10 °C. A solution of the (*E*)-3-(hetero)aryl-1-(2-((*E*)-(indolin-1-ylimino)methyl)phenyl)-prop-2-en-1-one **1** (1 equiv) in dry dichloromethane (1 mmol of the compound in 5 mL of solvent) was added dropwise with stirring. After complete addition, stirring was continued for 1 h, while the temperature increased to 0 °C. A saturated solution of sodium hydrogen carbonate was added to neutralize the mixture. The organic layer was washed with a saturated sodium hydrogen carbonate solution. Then the organic layer was washed with water and dried with $MgSO_4$, and the solvent was evaporated. The substances were purified by column chromatography.

(3*R*(*S*),4*R*(*S*))-4-(1*H*-Indol-1-ylamino)-3-phenyl-3,4-dihydronaphthalen-1(2*H*)-one (10a). This compound was obtained from (*E*)-1-(2-((*E*)-(indolin-1-ylimino)methyl)phenyl)-3-phenylprop-2-en-1-one **1a** 0.135 g (0.38 mmol) according to the general procedure. The subsequent chromatographic purification (Et_2O/pentane, 1:4) gave 0.077 g (0.22 mmol, 57%) of **10a** as a yellow solid. Mp: 171−172 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.97 (dd, J = 17.6, 1.5 Hz, 1H, CH_2, axial), 3.46 (m, 1H, C*H*, equatorial), 3.76 (dd, J = 17.6, 6.1 Hz, 1H, CH_2, equatorial), 4.89 (d, J = 2.4 Hz, 1H, C*H*, equatorial), 5.02 (s, 1H, N*H*), 6.49 (dd, J = 3.3, 0.7 Hz, 1H, 3-*H*-indole), 6.87 (m, 2H, *H*-arom), 7.07−7.29 (m, 6H, *H*-arom), 7.43−7.52(m, 3H, *H*-arom), 7.64 (d, J = 7.9 Hz, 1H, *H*-arom), 7.89 (m, 1H, *H*-arom), 8.15 (dd, J = 7.4, 1.7 Hz, 1H, *H*-arom). ^{13}C NMR (100 MHz, $CDCl_3$): δ 38.6 (CH_2), 41.4 (*C*H), 63.8 (*C*HN), 100.5 (*C*H), 109.1 (*C*H), 120.1 (*C*H), 121.4 (*C*H), 122.4 (*C*H), 126.6, 126.8 (*C*H), 127.2 (*C*H), 127.4 (*C*H), 127.6 (*C*H), 128.5 (*C*H), 129.3 (*C*H), 129.7 (*C*H), 132.9, 134.3 (*C*H), 135.9, 138.7, 140.7,

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197.0 (CO). IR (neat) $\tilde{\nu}$: 3273 (w), 3059 (w), 3026 (w), 1903 (w), 1674 (s), 1601 (m), 1495 (w), 1454 (m), 1408 (w), 1337 (w), 1315 (w), 1293 (m), 1246 (m), 1215 (m), 1159 (w), 1090 (w), 1049 (w), 1028 (w), 955 (w), 934 (m), 841 (w), 799 (w), 775 (w), 760 (m), 741 (s), 723 (s), 696 (s), 623 (w) cm^{-1}. HRMS (ESI): calcd for $C_{24}H_{20}N_2ONa$ 375.1468, found 375.1466.

(3*R*(*S*),4*R*(*S*))-4-(1*H*-Indol-1-ylamino)-3-*p*-tolyl-3,4-dihydronaphthalen-1(2*H*)-one (10b). This compound was obtained from (*E*)-1-(2-((*E*)-(indolin-1-ylimino)methyl)phenyl)-3-*p*-tolylprop-2-en-1-one **1b** 0.145 g (0.40 mmol) according to the general procedure. The subsequent chromatographic purification (Et_2O/pentane, 1:4) gave 0.111 g (0.30 mmol, 77%) of **10b** as a yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ 2.17 (s, 3H, CH_3), 2.94 (dd, J = 17.6, 1.8 Hz, 1H, CH_2, axial), 3.41 (m, 1H, *CH*, equatorial), 3.72 (dd, J = 17.6, 6.0 Hz, 1H, CH_2, equatorial), 4.85 (d, J = 2.3 Hz, 1H, *CH*, equatorial), 5.02 (s, 1H, *NH*), 6.47 (d, J = 3.2, Hz, 1H, 3-*H*-indole), 6.75 (d, J = 8.0 Hz, 2H, *H*-arom), 6.90 (d, J = 8.0 Hz, 2H, *H*-arom), 7.12−7.29 (m, 4H, *H*-arom), 7.41−7.50 (m, 3H, *H*-arom), 7.63 (d, J = 7.9 Hz, 1H, *H*-arom), 8.13 (dd, J = 7.1, 1.9 Hz, 1H, *H*-arom). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.8 (CH_3), 38.7 (CH_2), 41.1 (*CH*), 63.8 (*CHN*), 100.4 (CH), 109.1 (*CH*), 120.1 (*CH*), 121.3 (*CH*), 122.3 (*CH*), 126.6, 127.1 (*CH*), 127.4 (*CH*), 127.5 (*CH*), 129.2 (*CH*), 129.7 (*CH*), 132.9, 134.2 (*CH*), 135.9, 136.3, 137.6, 138.8, 197.1 (CO). IR (neat) $\tilde{\nu}$: 3287 (w), 3053 (w), 3026 (w), 2955 (w), 2920 (w), 1680 (s), 1626 (w), 1601 (m), 1514 (m), 1483 (w), 1454 (m), 1414 (w), 1337 (w), 1315 (w), 1290 (m), 1244 (m), 1215 (m), 1190 (w), 1157 (w), 1090 (w), 1049 (w), 1020 (w), 926 (w), 908 (m), 843 (w), 818 (m), 760 (s), 737 (s), 669 (w), 648 (w) cm^{-1}. HRMS (ESI): calcd for $C_{25}H_{22}N_2ONa$ 389.1624, found 389.1631.

(3*R*(*S*),4*R*(*S*))-4-(1*H*-Indol-1-ylamino)-3-(3-methoxyphenyl)-3,4-dihydronaphthalen-1(2*H*)-one (10c). This compound was obtained from (*E*)-1-(2-((*E*)-(indolin-1-ylimino)methyl)phenyl)-3-(3-methoxyphenyl)prop-2-en-1-one **1c** 0.155 g (0.41 mmol) according to the general procedure. The subsequent chromatographic purification (Et_2O/pentane, 1:3) gave 0.130 g (0.34 mmol, 84%) of **10c** as a yellow solid. Mp: 126−127 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 2.94 (ddd, J = 17.6, 1.7, 0.7 Hz, 1H, CH_2, axial), 3.42 (m, 1H, *CH*, equatorial), 3.60 (s, 3H, OCH_3), 3.74 (dd, J = 17.6, 6.0 Hz, 1H, CH_2, equatorial), 4.89 (d, J = 2.5 Hz, 1H, *CH*, equatorial), 5.03 (s, 1H, *NH*), 6.38−6.48 (m, 2H, *H*-arom), 6.49 (dd, J = 3.3, 0.7 Hz, 1H, 3-*H*-indole), 6.61 (dd, J = 8.0, 2.2 Hz, 1H, *H*-arom), 7.02 (m, 1H, *H*-arom), 7.12−7.29 (m, 4H, *H*-arom), 7.42−7.52 (m, 3H, *H*-arom), 7.64 (d, J = 7.9 Hz, 1H, *H*-arom), 8.14 (dd, J = 7.4, 1.8 Hz, 1H, *H*-arom). ^{13}C NMR (75 MHz, $CDCl_3$): δ 38.7 (CH_2), 41.4 (*CH*), 55.0 (CH_3), 63.6 (*CHN*), 100.5 (CH), 109.1 (*CH*), 111.8 (*CH*), 113.8 (*CH*), 119.9 (*CH*), 120.1 (*CH*), 121.4 (*CH*), 122.3 (*CH*), 126.6, 127.2 (*CH*), 127.3 (*CH*), 129.3 (*CH*), 129.5 (*CH*), 129.7 (*CH*), 132.8, 134.3 (*CH*), 135.9, 138.8, 142.3, 159.5, 196.9 (CO). IR (neat) $\tilde{\nu}$: 3271 (w), 3055 (w), 3028 (w), 2959 (w), 2905 (w), 2835 (w), 1676 (s), 1601 (m), 1584 (m), 1510 (w), 1491 (m), 1454 (m), 1435 (m), 1406 (w), 1337 (w), 1317 (w), 1290 (m), 1256 (m), 1242 (m), 1215 (m), 1198 (w), 1180 (m), 1148 (w), 1125 (w), 1047 (m), 1009 (w), 961 (w), 932 (w), 874 (m), 760 (s), 739 (s), 700 (s), 664 (w), 637 (w) cm^{-1}. HRMS (ESI): calcd for $C_{25}H_{22}N_2O_2Na$ 405.1573, found 405.1576.

(3*R*(*S*),4*R*(*S*))-4-(1*H*-Indol-1-ylamino)-3-(benzo[*d*][1,3]dioxol-5-yl)-3,4-dihydronaphthalen-1(2*H*)-one (10d). This compound was obtained from (*E*)-3-(benzo[*d*][1,3]dioxol-5-yl)-1-(2-((*E*)-(indolin-1-ylimino)methyl)phenyl)prop-2-en-1-one **1d** 0.120 g (0.30 mmol) according to the general procedure. The subsequent chromatographic purification (Et_2O/pentane, 1:3) gave 0.080 g (0.20 mmol, 67%) of **10d** as a yellow solid. Mp: 174−175 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 2.91 (dd, J = 17.6, 1.6 Hz, 1H, CH_2, axial), 3.36 (m, 1H, *CH*), 3.74 (dd, J = 17.6, 6.0 Hz, 1H, CH_2, equatorial), 4.84 (d, J = 2.4 Hz, 1H, *CH*, equatorial), 5.02 (s, 1H, *NH*), 5.81 (s, 2H, OCH_2O), 6.30−6.34 (m, 2H, *H*-arom), 6.49 (dd, J = 3.3, 0.6 Hz, 1H, 3-*H*-indole), 6.53 (d, J = 7.9 Hz, 1H, *H*-arom), 7.15 (td, J = 7.1, 0.9 Hz, 1H, *H*-arom), 7.23−7.30 (m, 3H, *H*-arom), 7.44−7.54 (m, 3H, *H*-arom), 7.64 (d, J = 7.9 Hz, 1H, *H*-arom), 8.14 (dd, J = 7.5, 1.7 Hz, 1H, *H*-arom). ^{13}C NMR (75 MHz, $CDCl_3$): δ 38.9 (CH_2), 41.2 (*CH*), 63.9 (*CHN*), 100.6 (CH), 100.9 (OCH_2O), 108.1 (*CH*), 108.2 (*CH*), 109.1 (*CH*), 120.1 (*CH*), 120.7 (*CH*), 121.4 (*CH*), 122.4 (*CH*), 126.6, 127.2 (*CH*), 127.3 (*CH*), 129.3 (*CH*), 129.7 (*CH*), 132.8, 134.4 (*CH*), 134.5, 135.9, 138.7, 146.2, 147.7, 196.9 (CO). IR (neat) $\tilde{\nu}$: 3269 (w), 3071 (w), 3028 (w), 2963 (w), 2893 (w), 1674 (s), 1601 (m), 1503 (m), 1489 (s), 1441 (m), 1335 (w), 1292 (m), 1233 (s), 1173 (w), 1125 (w), 1092 (w), 1036 (s), 932 (m), 903 (m), 864 (w), 810 (m), 760 (s), 735 (s), 704 (s), 667 (w), 644 (w), 610 (w) cm^{-1}. HRMS (ESI): calcd for $C_{25}H_{20}N_2O_3Na$ 419.1366, found 419.1358.

X-ray crystal structure analysis of **10d**:[9] formula $C_{25}H_{20}N_2O_3$, M = 396.43, yellow crystal 0.30 × 0.07 × 0.03 mm, a = 11.8959(7) Å, b = 7.2879(3) Å, c = 22.7295(18) Å, β = 91.218(4)°, V = 1970.1(2) $Å^3$, ρ_{calc} = 1.337 g cm^{-3}, μ = 0.714 mm^{-1}, empirical absorption correction ($0.814 \le T \le 0.979$), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 14105 reflections collected ($\pm h, \pm k, \pm l$), $[(\sin\theta)/\lambda]$ = 0.60 $Å^{-1}$, 3387 independent (R_{int} = 0.042) and 2619 observed reflections [$I \ge 2\sigma(I)$], 274 refined parameters, R = 0.045, wR^2 = 0.123, max. (min.) residual electron density 0.25 (−0.16) e $Å^{-3}$, hydrogen atoms calculated and refined as riding atoms.

(3*R*(*S*),4*R*(*S*))-4-(1*H*-Indol-1-ylamino)-3-(4-chlorophenyl)-3,4-dihydronaphthalen-1(2*H*)-one (10e). This compound was obtained from (*E*)-3-(4-chlorophenyl)-1-(2-((*E*)-(indolin-1-ylimino)-methyl)phenyl)prop-2-en-1-one **1e** 0.115 g (0.30 mmol) according to the general procedure. The subsequent chromatographic purification (Et_2O/pentane, 1:3) gave 0.075 g (0.19 mmol, 65%) of **10e** as a yellow solid. Mp: 140−141 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 2.94 (ddd, J = 17.7, 2.1, 0.9 Hz, 1H, CH_2, axial), 3.41 (m, 1H, *CH*, equatorial), 3.79 (dd, J = 17.7, 6.1 Hz, 1H, CH_2, equatorial), 4.84 (d, J = 2.2 Hz, 1H, *CH*, equatorial), 5.02 (s, 1H, *NH*), 6.51 (dd, J = 3.3, 0.8 Hz, 1H, 3-*H*-indole), 6.77 (d, J = 8.4 Hz, 2H, *H*-arom), 7.16 (ddd, J = 8.0, 7.2, 1.0 Hz, 1H, *H*-arom), 7.24−7.31 (m, 3H, *H*-arom), 7.48−7.54 (m, 3H, *H*-arom), 7.65 (d, J = 7.9 Hz, 1H, *H*-arom), 8.15 (dd, J = 7.1, 1.9 Hz, 1H, *H*-arom). ^{13}C NMR (75 MHz, $CDCl_3$): δ 38.3 (CH_2), 40.7 (*CH*), 63.8 (*CHN*), 100.7 (CH), 109.0 (*CH*), 120.2 (*CH*), 121.5 (*CH*), 122.5 (*CH*), 126.6, 127.3 (*CH*), 128.7 (*CH*), 128.9 (*CH*), 129.5 (*CH*), 129.7 (*CH*), 132.6, 132.8, 134.5 (*CH*), 135.9, 136.3, 138.2, 139.1, 196.7 (CO). IR (neat) $\tilde{\nu}$: 3281 (w), 3055 (w), 3026 (w), 2955 (w), 2891 (w), 1680 (s), 1599 (m), 1512 (w), 1493 (m), 1454 (m), 1412 (w), 1339 (w), 1290 (m), 1244 (m), 1215 (m), 1200 (w), 1159 (w), 1115 (w), 1092 (m), 1049 (w), 1013 (m), 953 (w), 926 (w), 880 (w), 829 (m), 787 (m), 760 (s), 741 (s), 719 (s), 667 (w), 660 (w), 621 (w) cm^{-1}. HRMS (ESI): calcd for $C_{24}H_{19}ClN_2ONa$ 409.1078, found 409.1079.

(3*R*(*S*),4*R*(*S*))-4-(1*H*-Indol-1-ylamino)-3-(2-bromophenyl)-3,4-dihydronaphthalen-1(2*H*)-one (10f). This compound was obtained from (*E*)-3-(2-bromophenyl)-1-(2-((*E*)-(indolin-1-ylimino)-methyl)phenyl)prop-2-en-1-one **1f** 0.220 g (0.51 mmol) according to the general procedure. The subsequent chromatographic purification (Et_2O/pentane, 1:4) gave 0.186 g (0.43 mmol, 85%) of **10f** as a yellow solid. Mp: 116−117 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 2.87 (d, J = 18.2 Hz, 1H, CH_2, axial), 3.71 (dd, J = 18.2, 6.6 Hz, 1H, CH_2, equatorial), 3.96 (d, J = 6.6 Hz, 1H, *CH*, equatorial), 4.80 (dd, J = 1.6, 0.5 Hz, 1H, *CH*, equatorial), 5.08 (s, 1H, *NH*), 6.32 (d, J = 3.3 Hz, 1H, 3-*H*-indole), 6.65 (dd, J = 7.2, 2.2 Hz, 1H, *H*-arom), 6.85−6.92 (m, 3H, *H*-arom), 7.05 (t, J = 7.1 Hz, 1H, *H*-arom), 7.16 (td, J = 7.4, 1.5 Hz, 1H, *H*-arom), 7.29 (td, J = 7.4, 1.5 Hz, 1H, *H*-arom), 7.31−7.38 (m, 2H, *H*-arom), 7.41 (d, J = 8.2 Hz, 1H, *H*-arom), 7.52 (d, J = 7.9 Hz, 1H, *H*-arom), 8.09 (dd, J = 7.7, 1.3 Hz, 1H, *H*-arom). ^{13}C NMR (100 MHz, $CDCl_3$): δ 37.9 (CH_2), 41.6 (*CH*), 61.4 (*CHN*), 99.8 (CH), 108.9 (*CH*), 119.9 (*CH*), 121.3 (*CH*), 122.1 (*CH*), 124.8, 126.8, 127.0 (*CH*), 127.6 (*CH*), 128.3 (*CH*), 128.4 (*CH*), 128.5 (*CH*), 129.4 (*CH*), 130.1 (*CH*), 132.5, 133.3 (*CH*), 134.3 (*CH*), 135.8, 138.4, 139.5, 197.1 (CO).

IR (neat) $\tilde{\nu}$: 3279 (w), 3063 (w), 3026 (w), 2957 (w), 2909 (w), 1680 (s), 1599 (m), 1568 (w), 1512 (w), 1470 (m), 1470 (m), 1454 (m), 1439 (w), 1402 (w), 1337 (w), 1294 (m), 1242 (m), 1217 (w), 1200 (w), 1125 (w), 1047 (w), 1022 (s), 943 (w), 928 (w), 880 (w), 835 (w), 792 (w), 739 (s), 719 (s), 664 (m), 621 (w) cm^{-1}. HRMS (ESI): calcd for $C_{24}H_{19}N_2OBrNa$ 453.0578/455.0558, found 453.0567/455.0557.

(3*R*(*S*),4*R*(*S*))-4-(1*H*-Indol-1-ylamino)-3-(4-(trifluoromethyl)-phenyl)-3,4-dihydronaphthalen-1(2*H*)-one (10g). This compound was obtained from (*E*)-1-(2-((*E*)-(indolin-1-ylimino)methyl)phenyl)-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-one **1g** 0.155 g (0.37 mmol) according to the general procedure. The subsequent chromatographic purification (Et_2O/pentane, 1:4) gave 0.085 g (0.20 mmol, 55%) of **10g** as a yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ 2.95 (dd, J = 17.7, 1.0 Hz, 1H, CH_2, axial), 3.48 (m, 1H, C*H*, equatorial), 3.81 (dd, J = 17.7, 6.1 Hz, 1H, CH_2, equatorial), 4.87 (d, J = 2.0 Hz, 1H, C*H*, equatorial), 5.06 (s, 1H, N*H*), 6.51 (dd, J = 3.3, 0.7 Hz, 1H, 3-*H*-indole), 6.94 (d, J = 8.4 Hz, 2H, *H*-arom), 7.16 (td, J = 7.1, 0.9 Hz, 1H, *H*-arom), 7.26−7.30 (m, 3H, *H*-arom), 7.34 (d, J = 8.2 Hz, 2H, *H*-arom), 7.47−7.56 (m, 3H, *H*-arom), 7.65 (d, J = 7.9 Hz, 1H, *H*-arom), 8.16 (dd, J = 7.6, 1.5 Hz, 1H, *H*-arom). ^{13}C NMR (100 MHz, $CDCl_3$): δ 38.1 (CH_2), 41.3 (CH), 63.6 (CHN), 100.8 (CH), 109.0 (CH), 120.3 (CH), 121.5 (CH), 122.5 (CH), 123.9 (q, J = 271 Hz, CF_3), 125.4 (q, J = 3.7 Hz, $CHCCF_3$), 126.6, 127.2 (CH), 127.3 (CH), 128.0 (CH), 129.1 (q, J = 32.6 Hz, CCF_3), 129.6 (CH), 129.7 (CH), 132.8, 134.6 (CH), 135.9, 138.0, 144.7, 196.4 (CO). ^{19}F NMR (282.5 MHz, $CDCl_3$): δ −62.7 ppm. IR (neat) $\tilde{\nu}$: 3279 (w), 3059 (w), 3028 (w), 2959 (w), 2914 (w), 1680 (s), 1620 (w), 1601 (w), 1514 (w), 1472 (w), 1456 (w), 1418 (w), 1323 (s), 1290 (m), 1244 (w), 1215 (w), 1165 (s), 1115 (s), 1069 (s), 1016 (m), 953 (w), 928 (w), 908 (w), 880 (w), 841 (m), 797 (w), 760 (m), 739 (s), 710 (s), 650 (w) cm^{-1}. HRMS (ESI): calcd for $C_{25}H_{19}F_3N_2ONa$ 443.1342, found 443.1341.

(3*R*(*S*),4*R*(*S*))-4-(1*H*-Indol-1-ylamino)-3-(2-vinylphenyl)-3,4-dihydronaphthalen-1(2*H*)-one (10h). This compound was obtained from (*E*)-1-(2-((*E*)-(indolin-1-ylimino)methyl)phenyl)-3-(2-vinylphenyl)prop-2-en-1-one **1h** 0.090 g (0.24 mmol) according to the general procedure. The subsequent chromatographic purification (Et_2O/pentane, 1:4) gave 0.055 g (0.15 mmol, 61%) of **10h** as a yellow solid. Mp: 151−152 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 2.94 (d, 1H, J = 16.9 Hz, CH_2, axial), 3.75−3.84 (m, 2H, C*H*, CH_2), 4.69 (dd, J = 10.9, 1.6 Hz, 1H, CH_2-olefin), 4.73 (s, 1H, C*H*), 5.03 (s, 1H, N*H*), 5.33 (dd, J = 17.1, 1.6 Hz, 1H, CH_2-olefin), 6.00 (dd, J = 17.1, 10.9 Hz, 1H, C*H*-olefin), 6.50 (dd, J = 3.3, 0.8 Hz, 1H, 3-*H*-indole), 6.71 (dd, J = 7.8, 1.1 Hz, 1H, *H*-arom), 6.93 (td, J = 7.6, 1.4 Hz, 1H, *H*-arom), 7.04 (td, J = 7.5, 0.9 Hz, 1H, *H*-arom), 7.16 (ddd, J = 8.0, 7.1, 1.0 Hz, 1H, *H*-arom), 7.21−7.29 (m, 4H, *H*-arom), 7.43−7.52 (m, 3H, *H*-arom), 7.67 (d, J = 7.8 Hz, 1H, *H*-arom), 8.18 (m, 1H, *H*-arom). ^{13}C NMR (100 MHz, $CDCl_3$): δ 37.6 (CH), 37.8 (CH_2), 62.5 (CHN), 100.0 (CH), 109.1 (CH), 116.9 (CH_2-olefin), 120.1 (CH), 121.4 (CH), 122.3 (CH), 126.6 (CH), 126.8 (CH), 126.9, 127.0 (CH), 127.1 (CH), 127.7 (CH), 128.1 (CH), 129.3 (CH), 130.0 (CH), 132.7, 133.4 (CH), 134.4 (CH), 135.7, 136.9, 137.4, 138.3, 197.4 (CO). IR (neat) $\tilde{\nu}$: 3275 (w), 3123 (w), 3103 (w), 3086 (w), 3059 (w), 3028 (w), 2914 (w), 1672 (w), 1599 (m), 1512 (w), 1483 (w), 1456 (m), 1443 (w), 1406 (w), 1314 (w), 1290 (m), 1248 (m), 1215 (m), 1125 (w), 1092 (w), 1026 (w), 989 (w), 951 (w), 924 (m), 851 (w), 839 (m), 806 (w), 762 (s), 748 (s), 735 (s), 725 (s), 704 (m), 667 (w), 625 (w) cm^{-1}. HRMS (ESI): calcd for $C_{26}H_{22}N_2ONa$ 401.1624, found 401.1624.

(1′*R*(*S*),2′*R*(*S*))-1′-(1*H*-Indol-1-ylamino)-2′,3′-dihydro-1,2′-binaphthyl-4′(1′*H*)-one (10i). This compound was obtained from (*E*)-1-(2-((*E*)-(indolin-1-ylimino)methyl)phenyl)-3-(naphthalen-1-yl)-prop-2-en-1-one **1i** 0.125 g (0.31 mmol) according to the general procedure. The subsequent chromatographic purification (Et_2O/pentane, 1:3) gave 0.075 g (0.19 mmol, 60%) of **10i** as a yellow solid. Mp: 195−196 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 3.08 (d, J = 18.0 Hz, 1H, CH_2, axial), 3.99 (dd, J = 18.0, 6.4 Hz, 1H, CH_2, equatorial), 4.33 (d, J = 6.3 Hz, 1H, C*H*, equatorial), 4.98 (s, 1H, C*H*, equatorial), 5.12 (s, 1H, N*H*), 6.63 (dd, J = 3.3, 0.8 Hz, 1H, 3-*H*-indole), 6.84−6.98 (m, 3H, *H*-arom), 7.12 (m, 1H, *H*-arom), 7.19−7.34 (m, 4H, *H*-arom), 7.40 (d, J = 3.3 Hz, 1H, *H*-arom), 7.47−7.51 (m, 2H, *H*-arom), 7.54−7.59 (m, 2H, *H*-arom), 7.70 (d, J = 8.1 Hz, 1H, *H*-arom), 7.76 (d, J = 7.6 Hz, 1H, *H*-arom), 8.23 (m, 1H, *H*-arom). ^{13}C NMR (75 MHz, $CDCl_3$): δ 37.1 (CH), 38.1 (CH_2), 62.8 (CHN), 100.4 (CH), 109.1 (CH), 120.4 (CH), 121.7 (CH), 122.3 (CH), 122.6(CH), 124.9 (CH), 125.1 (CH), 125.5 (CH), 126.2 (CH), 127.0, 127.3 (CH), 127.5 (CH), 128.3 (CH), 128.9 (CH), 129.4 (CH), 130.0 (CH), 130.8, 132.5, 133.7, 134.5 (CH), 135.8, 136.1, 138.6, 197.6 (CO). IR (neat) $\tilde{\nu}$: 3281 (w), 3119 (w), 3096 (w), 3051 (w), 2965 (w), 2909 (w), 1676 (s), 1597 (m), 1510 (w), 1456 (w), 1406 (w), 1398 (w), 1339 (w), 1292 (m), 1244 (m), 1217 (m), 1184 (w), 1128 (w), 1051 (w), 1028 (w), 934 (w), 908 (m), 858 (w), 785 (m), 770 (s), 756 (s), 743 (s), 727 (s), 694 (m), 644 (w), 621 (w) cm^{-1}. HRMS (ESI): calcd for $C_{28}H_{22}N_2ONa$ 425.1624, found 425.1626.

(3*R*(*S*),4*S*(*R*))-4-(1*H*-Indol-1-ylamino)-3-(thiophene-2-yl)-3,4-dihydronaphthalen-1(2*H*)-one (10j). This compound was obtained from (*E*)-1-(2-((*E*)-(indolin-1-ylimino)methyl)phenyl)-3-(thiophene-2-yl)prop-2-en-1-one **1j** 0.120 g (0.34 mmol) according to the general procedure. The subsequent chromatographic purification (Et_2O/pentane, 1:3) gave 0.090 g (0.25 mmol, 75%) of **10j** as a yellow solid. Mp: 65−66 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 2.97 (ddd, J = 17.3, 2.2, 1.0 Hz, 1H, CH_2, axial), 3.72 (m. 1H, C*H*, equatorial), 3.85 (dd, J = 17.3, 5.6 Hz, 1H, CH_2, equatorial), 4.97 (d, J = 2.3 Hz, 1H, C*H*, equatorial), 5.05 (s, 1H, N*H*), 6.48 (dd, J = 3.3, 0.8 Hz, 1H, 3-*H*-indole), 6.56 (dt, J = 3.5, 1.0 Hz, 1H, *H*-arom), 6.72 (dd, J = 5.1, 3.6 Hz, 1H, *H*-arom), 6.98 (dd, J = 5.1, 1.1 Hz, 1H, *H*-arom), 7.15 (td, J = 7.1, 1.0 Hz, 1H, *H*-arom), 7.24−7.31 (m, 3H, *H*-arom), 7.45−7.55 (m, 3H, *H*-arom), 7.63 (d, J = 7.9 Hz, 1H, *H*-arom), 8.12 (dd, J = 7.7, 1.5 Hz, 1H, *H*-arom). ^{13}C NMR (100 MHz, $CDCl_3$): δ 37.8 (CH), 40.0 (CH_2), 63.6 (CHN), 100.6 (CH), 109.0 (CH), 120.2 (CH), 121.4 (CH), 122.4 (CH), 124.1 (CH), 125.2 (CH), 126.6 (CH), 127.2 (CH), 127.4 (CH), 129.5 (CH), 130.0 (CH), 132.8, 134.4 (CH), 135.9, 138.5, 143.9, 196.0 (CO). IR (neat) $\tilde{\nu}$: 3279 (w), 3103 (w), 3071 (w), 3053 (w), 3028 (w), 2957 (w), 2899 (w), 1680 (s), 1614 (m), 1601 (m), 1483 (w), 1466 (w), 1454 (m), 1418 (w), 1335 (m), 1290 (m), 1240 (m), 1213 (m), 1200 (w), 1179 (w), 1159 (w), 1090 (w), 1049 (w), 1028 (w), 1009 (w), 908 (m), 851 (m), 831 (w), 760 (s), 739 (s), 698 (s), 648 (w), 627 (w) cm^{-1}. HRMS (ESI): calcd for $C_{22}H_{18}N_2OSNa$ 381.1032, found 381.1035.

(3*R*(*S*),4*R*(*S*))-4-(1*H*-Indol-1-ylamino)-3-(2-(phenylethynyl)-benzo[*b*]thiophene-3-yl)-3,4-dihydronaphthalen-1(2*H*)-one (10k). This compound was obtained from (*E*)-1-(2-((*E*)-(indolin-1-ylimino)methyl)phenyl)-3-(2-(phenylethynyl)benzo[*b*]thiophene-3-yl)-prop-2-en-1-one **1k** 0.105 g (0.21 mmol) according to the general procedure. The subsequent chromatographic purification (Et_2O/pentane, 1:3) gave 0.060 g (0.12 mmol, 57%) of **10k** as a yellow solid. Mp: 200−201 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 3.60−3.62 (m, 2H, CH_2), 4.04 (m, 1H), 4.98 (s, 1H, N*H*), 5.06 (d, J = 4.0 Hz, 1H), 6.53 (dd, J = 3.3, 0.6 Hz, 1H, 3-*H*-indole), 6.67 (d, J = 8.2 Hz, 1H, *H*-arom), 6.98 (m, 1H, *H*-arom), 7.14−7.30 (m, 5H, *H*-arom), 7.36−7.49 (m, 8H, *H*-arom), 7.63 (d, J = 8.0 Hz, 1H, *H*-arom), 7.69 (d, J = 7.3 Hz, 1H, *H*-arom), 7.97 (dd, J = 7.6, 1.5 Hz, 1H, *H*-arom). ^{13}C NMR (75 MHz, $CDCl_3$): δ 36.4 (CH), 37.3 (CH_2), 61.8 (CHN), 82.3 (C-alkyne), 99.4 (C-alkyne), 100.5 (CH), 109.3 (CH), 120.2, 120.3 (CH), 121.4 (CH), 121.5 (CH), 122.0 (CH), 122.2, 122.5 (CH), 124.6 (CH), 125.6 (CH), 126.8, 127.2 (CH), 127.8 (CH), 128.3 (CH), 129.0 (CH), 129.21 (CH), 129.24 (CH), 131.4 (CH), 133.76 (CH), 133.79, 135.7, 136.8, 138.1, 139.1, 139.6, 196.9 (CO). IR (neat) $\tilde{\nu}$: 3264 (w), 3113 (w), 3061 (w), 3017 (w), 2907 (w), 2859 (w), 2199 (w), 1676 (s), 1597 (m), 1485 (m), 1456 (m), 1441 (m), 1396 (w), 1356 (w), 1312 (w), 1294 (s), 1258 (m), 1242 (m), 1219 (m), 1207 (w), 1196 (w), 1179 (w), 1053 (w), 1024 (m), 1007 (w), 916 (w), 893 (w), 851 (m), 772 (m), 754 (s), 745 (s),

725 (s), 689 (s), 669 (m), 621 (w) cm^{-1}. HRMS (ESI): calcd for $C_{34}H_{24}N_2OSNa$ 531.1502, found 531.1515.

■ ASSOCIATED CONTENT

Supporting Information. ^1H and ^{13}C spectra for the new compounds; Cartesian coordinates (HF/6-311G(d,p)) and CPCM(UAKS)-HF/def2-QZVPP//HF/6-311G(d,p)+ZPE energies for the calculated structures; graphics of the crystal structures showing thermal ellipsoids with 50% probability. This material is available free of charge via the Internet at http://pubs.acs.org.

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