Visible Light Mediated Photocatalytic N-Radical Cascade Reactivity of γ,δ-Unsaturated N-Arylsulfonylhydrazones: A General Approach to Structurally Diverse Tetrahydropyridazines

Visible Light Mediated Photocatalytic *N*-Radical Cascade Reactivity of γ,δ-Unsaturated *N*-Arylsulfonylhydrazones: a General Approach to Structurally Diverse Tetrahydropyridazines

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KEYWORDS: photocatalysis, ruthenium, unsaturated arylsulfonylhydrazones, dearomatization, Smiles rearrangement, cyclization, tetrahydropyridazines.

ABSTRACT

Tetrahydropyridazines are of particular interest for their versatility as intermediates in organic synthesis and display pharmacological activity in several domains. Here, we describe the photocatalytic synthesis of different tetrahydropyridazines starting from γ,δ-unsaturated N-arylsulfonylhydrazones. Simple structural changes of substrates result into three different pathways beginning from a common *N*-hydrazonyl radical which evolvesthrough a dominocarboamination/dearomatization, a HAT process, or a photoinduced radical Smiles rearrangementto afford diverse tetrahydropyridazines. All reactions are carried out in very mild conditions and quite inexpensive $[Ru(bpy)_3]Cl_2$is used as the catalyst. Preliminary mechanism studies are presented, among them luminescence and electrochemical characterization of the involved species. Computational studies allow to rationalize the mechanism in accord with the experimental findings.

Introduction

The synthesis of nitrogen-containing heterocycles represents one of the major focus in organic synthesis.[1, 2] Among them, tetrahydropyridazines are of particular interest since they are frequently found in natural products and pharmacologically active compounds. Their activity as lipoxygenase inhibitors,[3, 4] cardiotonics,[5, 6] antibacterials,[7] cannabinoid receptor antagonists,[8] influenza neuraminidase inhibitors[9] has been reported (Figure 1), in addition to studies correlated to their herbicidal properties.[10] Moreover, they are versatile intermediates in organic synthesis.[11]

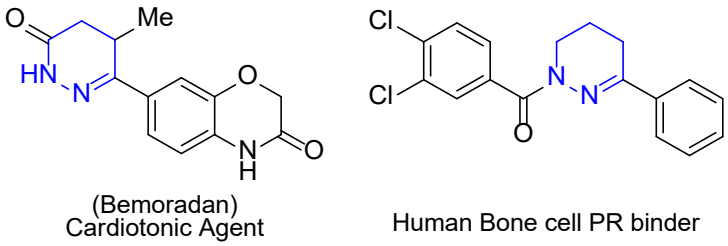
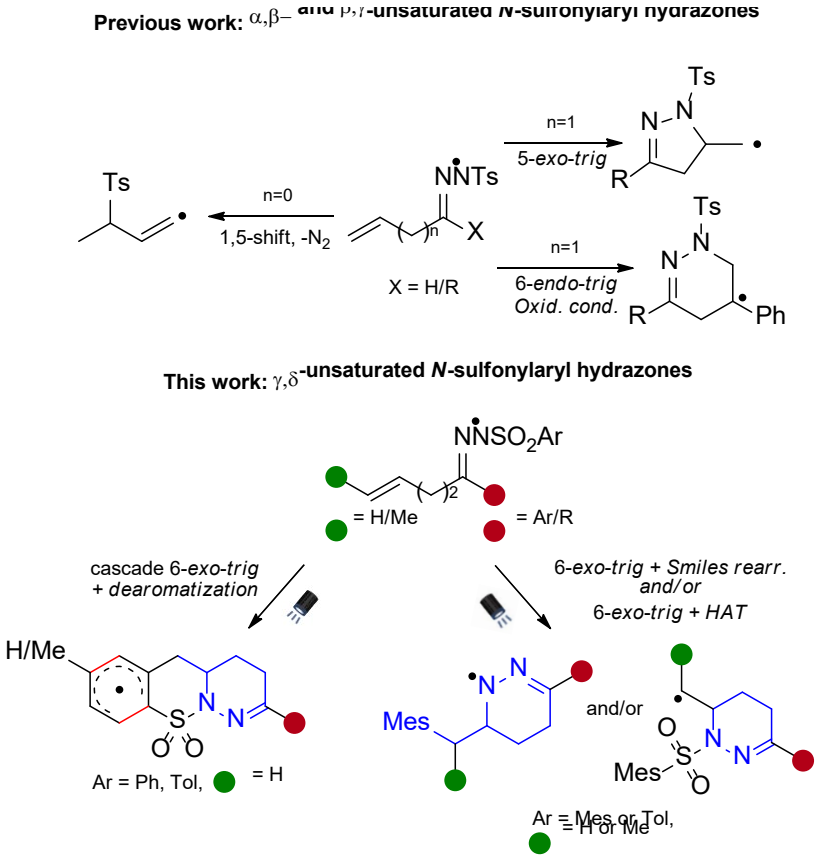


Figure 1 Biologically active 1,4,5,6-tetrahydropyridazines

As a consequence, many efforts have been dedicated to new strategies for the construction of these nitrogen heterocycles: among those, [4 + 2] cycloaddition of azoalkenes,[12-15] 1,2-diaza-1,3-dienes,[9, 16]or diazenes,[17] and [3 + 3] formal cycloadditions[18] exploiting cyclopropyl derivatives and hydrazones.[19, 20] Nevertheless, the need for available starting materials and a good compatibility of reaction conditions with several functional groups has been the driving force for the use of other cyclization strategies. In this context, hydrazones represent an appealing alternative,[21-24] being easy to prepare and displaying a very peculiar reactivity.[25-30] Many synthetic approaches exploiting them have been reported, like Palladium [31, 32] and Copper mediated cyclizations,[33, 34] but especially, visible light-mediated processes. Photocatalytic transformations have, indeed, attracted huge interest in the last years, disclosing alternative routes to functionalized molecules under mild reaction conditions and with high functional group tolerance.[35-39] In particular, visible light-mediated generation of *N*-centered radicals[40, 41] has rapidly became one of the most efficient approach in the synthesis of *N*-heterocycles (Scheme 1).[42-44]Thus far, the pioneering work by Xiao and co-workers has emerged as a milestone, giving access to 4,5-dihydropyrazoles in good yields from β,γ-unsaturated hydrazones through a photocatalytic *N*-radical hydroamination.[45] Similar strategies afforded pyrazolines, pyridazines and isoxazolines under oxidative conditions,[46, 47] or by a radical mediated cyclization/allylation.[48] Moreover, the light-induced *N*-radical 5-

*exo*cyclization/addition/aromatization cascade by dual Ru/Co co-catalysis was reported, affording various dihydropyrazole-fused benzosultams from β,γ-unsaturated hydrazones.[49]Dihydropyrazoles were also obtained starting from aldehyde hydrazones with halo-1,3-dicarbonyls[44] or α-halohydrazones with β-ketocarbonyls.[50] In 2017 our research group reported the first example of a visible light driven transformation of α,β-unsaturated sulfonylhydrazones to allylic sulfones by the generation of highly delocalized radicals, crucial in promoting nitrogen loss instead of the commonly observed intramolecular hydroamination.[51] A 1,5-rearrangement of the sulfonyl group with loss of nitrogen was hypothesized *via* a six member ring transition state, moreover the formation of a vinyl radical was demonstrated (Scheme 1). To our knowledge, no studies on visible-light mediated reactivity of γ,δ-unsaturated derivatives are reported in literature, so we decided to explore such substrates as possible precursors for tetrahydropyridazines synthesis and compare them to α,β and β,γ-analogues (Scheme 1).

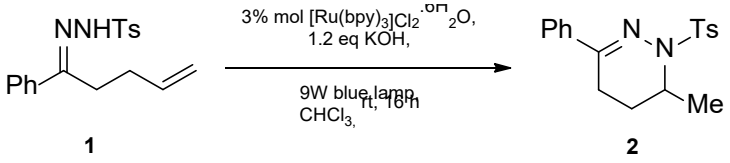


Scheme 1*N*-radical-centred reactivity of unsaturated aryl hydrazones to afford different N-tetrahydropyridazine scaffolds.

Results and discussion

Reaction Optimisation and Scope

First attempts were carried out using phenylbut-3-enyl-*N*-tosylhydrazone (**1**). The effect of the light source, solvent, photocatalyst and base was studied and the complete optimization is reported in supporting information (table 1 in ESI). Under the best reaction conditions, KOH was used as the base, $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ as the catalyst in $CHCl_3$, a 9W blue lamp as the light source, to afford **2** in 24% yield (Scheme 2).



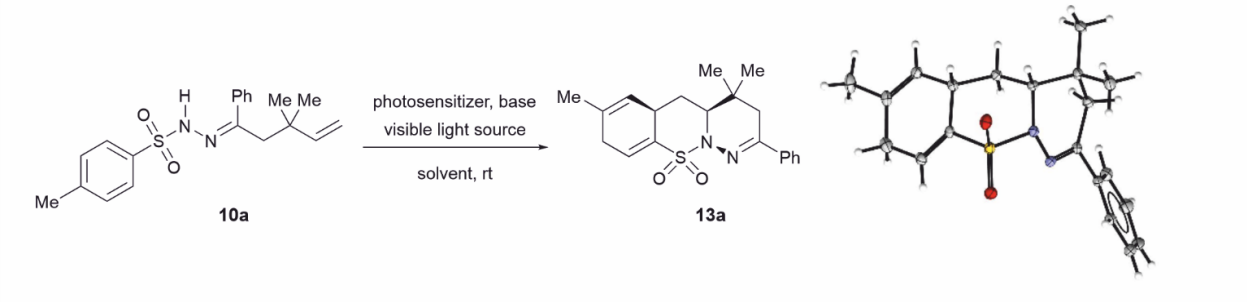
1 **2**

Scheme 2 Photocatalyzed cyclization of phenylbut-3-enyl-*N*-tosylhydrazone (**1**)

Despite the reaction selectively afforded product **2** deriving from the originally designed 6-*exo-trig* cyclization (Scheme 2), any attempt to enhance the yield was unsuccessful, even when a more powerful light source was used (40W). In the light of these results, we speculated a competition between the desired cyclization and the formation of a stable allylic radical which could be further involved in alternative reaction pathways leading to byproducts or product degradation. Therefore, we turned our attention to phenyl-2,2-dimethylbut-3-enyl-*N*-tosylhydrazone (**10a**), where the presence of two geminal CH_3 at the β-C avoids the undesired 1,5-HAT. When **10a** was reacted under the optimized reaction conditions for **1** (entry 1,Table 1), we witnessed the total conversion of the reagent yielding an unexpectedly different product. NMR analysis suggested structure **13a** containing a 1,4-dienic moiety corroborated by a broad singlet at 5.35 and a multiplet at 6.75 ppm pertinent to alkenyl sp_2 protons and three signals related to methylenes in the DEPT-135 spectrum (31.4, 31.5 and 34.6 ppm). This structure was eventually confirmed by Single Crystal X-ray Diffraction (Table 1, top right). Most importantly, we observed the formation of a single diastereoisomer. This new outcome delighted us, mostly because the introduction of two geminal methyl groups afforded, with complete diastereoselectivity, a tricyclic structure containing a 1,4-diene moiety as result of an arene dearomatization. This was probably the consequence of a cascade process involving two consecutive *exo-trig*-cyclizations, a very different result from the cyclization/addition/aromatization cascade of β,γ-unsaturated-*N*-tosylhydrazones reported by Xiao *et al.* where the dienic portion spontaneously evolved to an aromatic ring.[49]1,4-(Skipped)

dienes are ubiquitous structural units in natural products such as polyenic macrolides,[52-54] macrolactames,[55]and alkaloids[56] and also in functional materials.[57-59] Their synthesis is not trivial and in the last years the dearomatization approach has emerged as a powerful strategy to access this motif.[60]Optimization of reaction conditions for **10a** is reported in Table 1. When a 40W blue light was utilized (entry 2), the yield of **13a** increased to 52%. The use of K_2CO_3 in $CHCl_3$ afforded the product in 40% yield (entry 3) and 73% yield was obtained switching the solvent to CH_3CN (entry 10). A mixture of degradation products was recovered using both KOH and NaOH as the bases in CH_3CN (entries 4, 5 and 6), whereas Cs_2CO_3 demonstrated a complete inefficacy, in fact starting material **10a** was fully recovered (entry 7). The base was essential for the success of the reaction as demonstrated by entry 17. 1.5 eq. of the base respect to **10a** resulted optimal for the reaction. The effect of the light source power was evident as well, since the reaction carried out using a 9W blue lamp did not reach completion after 72h (85% conversion, 50% yield, entry 9). Different photocatalysts were also tested: 3% mol $[Ru(bpy)_3]Cl_2·6H_2O$ resulted optimal (entry 10), since lower loadings gave a total conversion but lower yields (58 and 55% respectively, entries 11 and 12). Anyway, its performances were superior to $[Ir(ppy)_2(dtbpy)][PF_6]$ and $[Ir\{dFCF_3ppy_2(bpy)]PF_6$ (entries 14 and 15) and Eosin Y, the latter being completely inefficient (entry 13). Experiments in the absence of photosensitizer (entry 18) or light (entry 19) afforded no product, confirming the photocatalytic nature of the process.

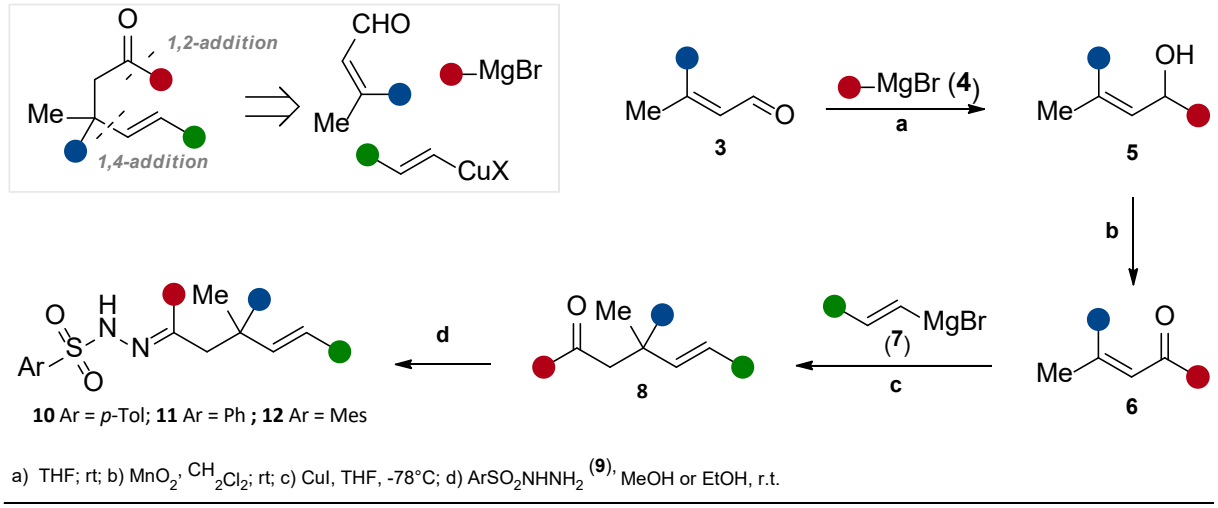
Table 1 Optimization for photocatalyzed cyclization of phenylprop-3-enyl-*N*-tosylhydrazone (**10a**)

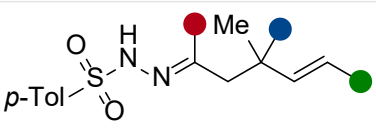


Entry	Base	Photosensitizer	Solvent	Time [h]	Conversion [%]	Yield[a] [%]
1[c]	KOH (1.2 eq.)	$[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (3%)	$CHCl_3$	16	100	35 (22)[b]
2[f]	KOH (1.2 eq.)	$[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (3%)	$CHCl_3$	16	100	52 (45)[b]
3[f]	K_2CO_3 (1.5 eq.)	$[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (3%)	$CHCl_3$	16	100	40 (35)[b]
4[f]	KOH (1.2 eq.)	$[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (3%)	CH_3CN	16	100	0[g]
5[f]	KOH (1.5 eq.)	$[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (3%)	CH_3CN	16	100	0[g]
6 [c]	NaOH (1.5 eq.)	$[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (3%)	CH_3CN	16	100	0
7[c]	Cs_2CO_3 (1.5 eq.)	$[Ru(bpy)_3]Cl_2 \cdot 6H_2O$(3%)	CH_3CN	16	0	0
8[c]	K_2CO_3 (1.5 eq.)	$[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (3%)	CH_3CN	16	45	43
9[c]	K_2CO_3 (1.5 eq.)	$[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (3%)	CH_3CN	72	85	50
10[f]	**K_2CO_3 (1.5 eq.)**	**$[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (3%)**	**CH_3CN**	**16**	**100**	**73 (70)[b]**
11[f]	K_2CO_3 (1.5 eq.)	$[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (2%)	CH_3CN	16	100	58
12[f]	K_2CO_3 (1.5 eq.)	$[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (1%)	CH_3CN	16	100	55
13[d]	K_2CO_3 (1.5 eq.)	Eosyn Y	CH_3CN	72	0	0
14[e]	K_2CO_3 (1.5 eq.)	$[Ir(ppy)_2(dtbpy)][PF_6]$ (3%)	CH_3CN	16	100	37
15[e]	K_2CO_3 (1.5 eq.)	$[Ir\{dFCF_3ppy\}_2(bpy)]PF_6$ (3%)	CH_3CN	16	100	42 (36)[b]
16[f]	K_2CO_3 (1.5 eq.)	$[Ru(bpz)_3][PF_6]_2 \cdot 6H_2O$ (3%)	CH_3CN	16	0	0
17[f]	-	$[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (3%)	CH_3CN	16	0	0
18[f]	K_2CO_3 (1.5 eq.)	-	CH_3CN	16	0	0
19[h]	K_2CO_3 (1.5 eq.)	$[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (3%)	CH_3CN	16 h	Traces	Traces

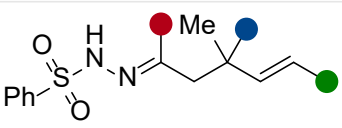
Reactions conditions: tosylhydrazone**10a** (0.3 mmol), anhydrous solvent (5 mL) [reagent concentration: 0.06 M], base, catalyst. [a] Determined by NMR spectroscopy using nitromethane as internal standard; [b] Yields determined on isolated product; [c] 450 nm light source – blue light. 9W, [d] 550 nm light source – green light; [e] 365 nm light source – purple light; [f] 450 nm light source – blue light, 40W, [g] a mixture of degradation products was recovered; [h]reaction performed in the dark.

Conditions listed in entry 10 resulted to be the best, so we extended the scope of the reaction to the β-hindered-γ,δ-unsaturated hydrazones listed in Scheme 3. Tosyl, phenylsulfonyl (**10** and **11**) and mesytylsulfonyl-hydrazones (**12**) were prepared in order to evaluate the influence of the substituent on the hydrazonyl moiety (Scheme 3) starting from the suitable α,β-unsaturated aldehyde **3** which was reacted with a Grignard reagent **4**. The so-formed alcohol **5**, after oxidation with MnO_2, afforded the γ,δ-unsaturated ketone **8** and, after reaction with the arylsulfonyl hydrazide, the corresponding hydrazone (**10**,**11** or **12**). Acetone and acetophenone derivatives were used as starting materials for the preparation of both terminal and internal γ,δ-unsaturated hydrazones. Moreover, natural terpene pulegone was exploited (**10l and 12g**). As reported in Table 2, best results were obtained with tosylhydrazones **10a** and **10i** and afforded hexahydrobenzo[e]pyridazino[1,6-b][1,2]thiazine-10,10-dioxide **13a** and **13i** in 70% and 73% yields respectively, thus demonstrating that an aromatic group is not compulsory and the reaction can be successfully applied to aliphatic arylsulfonylhydrazones. The reaction demonstrated to be totally diastereoselective, X-ray diffraction-derived molecular structure of **13a** are reported in Table 1 (see ESI Table 5,6 and 7). In the case of methyl derivative **10i** the reaction was scaled up to 2 mmoles and product **13i** was obtained in 51% yield after 72 h. When phenylsulfonylhydrazones **11a** and **11b** were subjected to irradiation, products **13j** and **13k** were recovered in lower yields with respect to those obtained with tosylhydrazones **10a** and **10i** (40% and 55% yield respectively). Electron-rich aromatic rings can also be introduced: 2-naphthyl (**13b**, 43%), 3-methoxyphenyl (**13f**, 50%) and tolyl substituents. In the last case *meta*, *para* and *ortho* derivatives (**10c**, **10d** and **10e**) were used in order to evaluate both electronic and steric effects. *O*-tolyl derivative afforded the product **13e** in lower yield respect to *meta* **13c** and *para* **13d**, which are comparable, thus demonstrating an influence of steric effects. The electron-poor 2-pyridinyl derivative **10g** afforded product **13g** in 37% yield, slightly worse than electron rich substrates. The reaction was also successfully extended to the unsaturated hydrazone **10l** deriving from pulegone, a monoterpene ketone found in the leaves and flowering tops of several members of the mint family *Lamiaceae*, affording the corresponding tetrahydropyridazine **13l** in 35% yield.



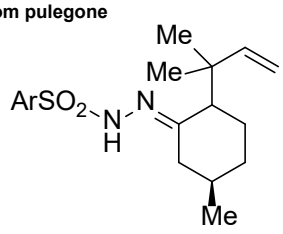


10a	Ph	Me	H
10b	2-Napht	Me	H
10c	*m*-Tol	Me	H
10d	*p*-Tol	Me	H
10e	*o*-Tol	Me	H
10f	*m*-MeOPh	Me	H
10g	2-Pyr	Me	H
10h	Ph	Ph	H
10i	Me	Me	H
10j	Ph	Me	Me
10k	Me	Me	Me

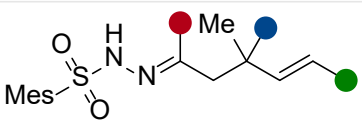


11a	Ph	Me	H
11b	Me	Me	H

From pulegone

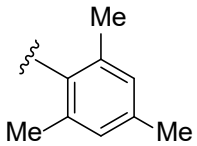


10l Ar: *p*-Tol; **12g** Ar: Mes



12a	Ph	Me	H
12b	2-Napht	Me	H
12c	*p*-Tol	Me	H
12d	*o*-Tol	Me	H
12e	Me	Me	H
12f	Ph	Me	Me

Mes (mesityl) =



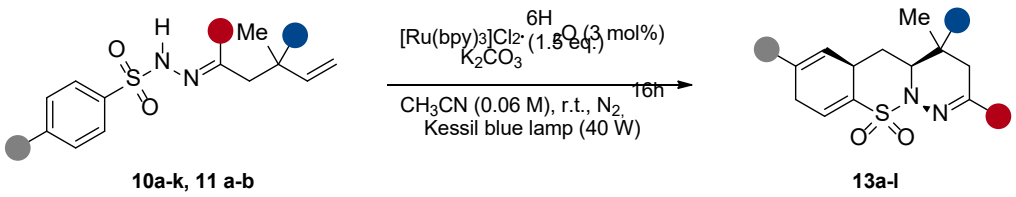
Scheme 3 Synthesis and list of the β-hinderedγ,δ-unsaturated hydrazones

Finally, also the geminal substituents in the bridge were changed and the tosylhydrazone **10j**, where a phenyl group was introduced in place of one of the two methyl groups, successfully afforded the cyclization product **13h** in 34% yield.

Furthermore, we tested the reactivity of mesitylhydrazones (mesityl=2,4,6-trimethylphenyl) **12a-12g** and a completely different outcome was observed (Table 3). Two products were recovered in high yields: the first, (**14a**), derived from the photocatalyzed cyclization of the *N*-hydrazonyl radical and the second due to a photoradical promoted carboamination/Smiles rearrangement (**15a**).[61-64] Best results were obtained with 2,2-dimethylbut-3-enylphenylmesitylhydrazone (**12a**) and 2,2-dimethylbut-3-enylmethylmesitylhydrazone (**12e**)

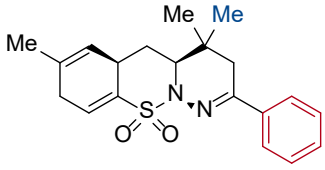
with a total yield of 95% and a ratio of 53 : 47and 61 : 39 between products **14a**/**15a** and **14e**/**15e** respectively, again demonstrating no difference between aromatic and aliphatic derivatives (Table 3). When 2-naphthyl (**12b**) was introduced as the substituent, 72% yield was obtained and a ratio of 58 :42 between the cyclization product **14b**and the Smiles rearrangement **15b.** Also in this case, steric hindrance of *o*-tolyl derivative **12d** decreased the efficiency of the process compared to *p*-substituted **12c** (87% versus 62% yield;Table 3). Pulegone hydrazone **12g** was subjected to irradiation, as well. In such case only product **14f** was recovered in 35 % yield, while only traces of the corresponding Smiles rearrangement product were observed. We reasoned that the steric hindrance and the rigidity of the pulegone cyclic structure make the attack of the so-formed alkyl radical to the aromatic ring more difficult.

Table 2 Scope of the synthesis of tetrahydropyridazines by photocatalyzed cyclization of γ,δ-unsaturated-*N*-arylsulfonylhydrazones (**10a-l**, **11a-b**)[a,b,c]

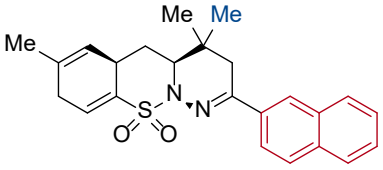


10a-k, 11 a-b **13a-l**

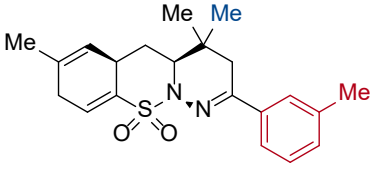
From *N*-tosylhydrazones



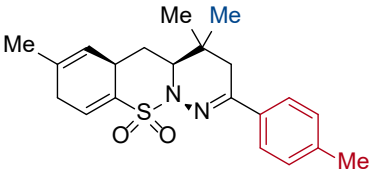
13a: 70%



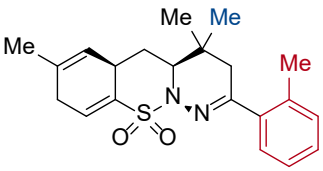
13b: 43%



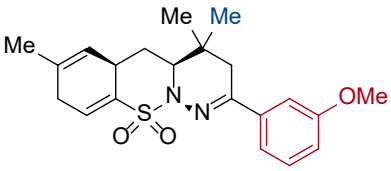
13c: 60%



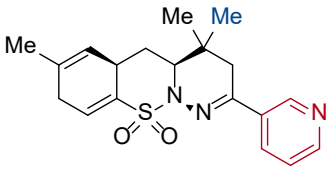
13d: 62%



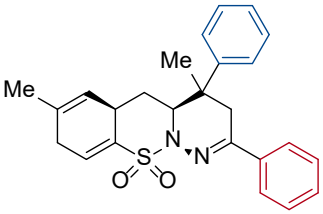
13e: 52%



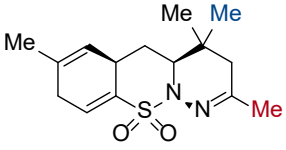
13f: 50%



13g: 37%

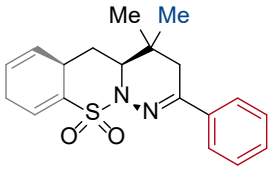


13h: 34%

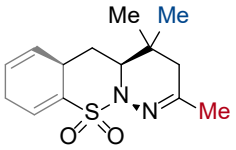


13i: 73%(51%)[d]

From *N*-benzenesulfonylhydrazones

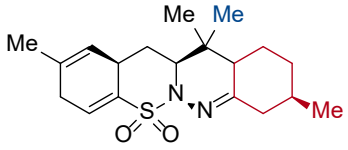


13j: 40%



13k: 55%

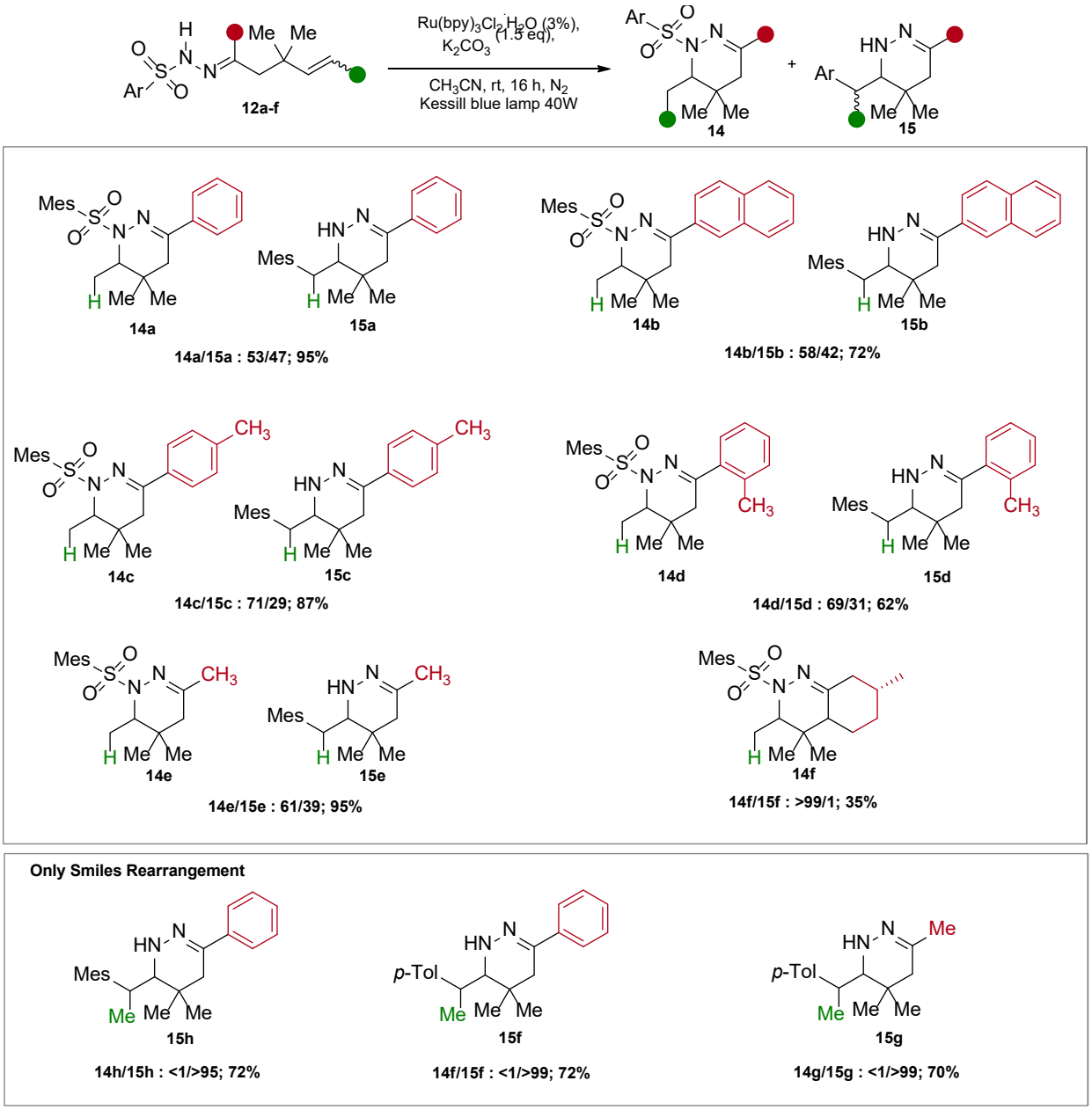
From pulegone



13l: 35%

[a] Reaction conditions: arylsulfonylhydrazone **10a-l**and **11a-b** 0.3 mmol, K_2CO_3 0.45 mmol, anhydrous CH_3CN 5 mL, $[Ru(bpy)_3]Cl_2·6H_2O$ 0.09 mmol (3%), Kessil blue lamp 40W, 16 h, inert atm.; [b] yields determined on isolated product; [c] relative configurations of products were assigned by analogy to **13a**. [d] reaction scaled to 2 mmol of **13i** (51%, 72h).

Table 3 Alternative reactivity with γ,δ-unsaturated mesitylsulfonylhydrazones (**12a-12f**) and 2.2-dimethylpent-3-enone arylhydrazones (**10j-k**)[a,b,c]



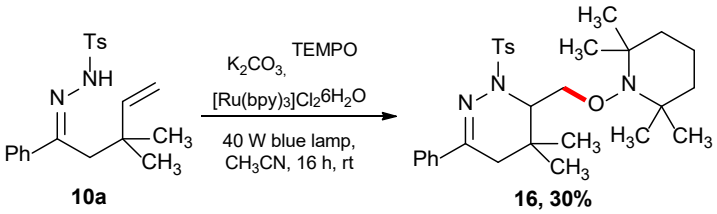
[a] Reaction conditions: arylsulfonylhydrazone 0.3 mmol, K_2CO_3 0.45 mmol, anhydrous CH_3CN 5 mL, $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ 0.09 mmol (3%), Kessil blue lamp 40W, 16 h, inert atm.; [b] determined on isolated product; [c] Mes (mesityl) = 2,4,6-trimethylphenyl

Then we moved on testing tosylhydrazones **10j**, **10k** and **12f** where an internal double bond was introduced. Again, this modification imposed a different reaction outcome because only the Smiles rearrangement product was recovered in all cases. Not only with mesitylsulfonyl hydrazone **12f**(product **15h**, 72%), but also when tosyl derivatives **10j** and **10k** were involved (72 and 70% for **15h** and **15g** respectively). We supposed that the presence of the methyl makes difficult the

interaction with the *ortho* H of the aromatic ring. Finally, the reaction demonstrated to be diastereoselective, in fact only a diastereoisomer was recovered.

Reaction mechanism studies

To verify if a *C*-centered radical is involved as a key intermediate during the process, a trapping experiment with TEMPO was realized. The model reaction was carried out in the presence of TEMPO (2.0 equiv) affording 1-phenyl-*N*-tosyl-6-(2,2,6,6-tetramethyl-*N*-methylenoxy)1,4,5,6-tetrahydropyridazine **16** in 30% yield (Scheme 4). The structure of TEMPO adduct was confirmed by HRMS, NMR spectroscopy and Single Crystal X-ray diffraction (Figure 2).



Scheme 4TEMPO trapping experiment

To exclude the possibility of a chain radical mechanism, experiments with **10a** were also carried out in the presence of radical initiators: no reaction was induced when AIBN was used, whereas the more reactive benzoyl peroxide produced a mixture of degradation by-products (see ESI).

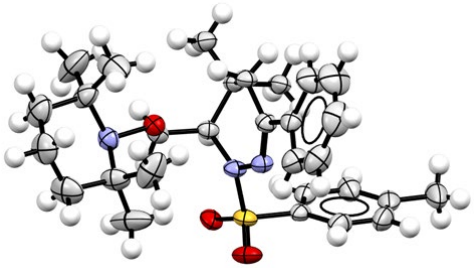


Figure 2 ORTEP plot of the asymmetric unit of TEMPO adduct **16** in the crystal structure (Color Code: grey, carbon; navy blue, nitrogen; red, oxygen; yellow, sulfur; 50 % of probability represented)

Then, the Stern –Volmer luminescence quenching studies were performed (Figure 3,left). The interaction mechanism between the K^+ salt of the model substrate **K^+-10a** and $[Ru(bpy)_3]^{2+}$ was investigated (see details in ESI). The non-linearity of the trend is due to both static and dynamic quenching, in agreement with the formation of an ion pair between the tosylhydrazone anion **K^+-10a** and the $[Ru(bpy)_3]^{2+}$, as already observed in previous studies.[51, 65] The model reaction has

been also studied from an electrochemical point of view. The cyclovoltammetries (CVs) of 2,2-dimethylbut-3-enylphenone-*N*-tosylhydrazone-K+ salt (**K$^+$-10a**) and the corresponding isolated reaction product (**13a**) show that **K$^+$-10a** can be irreversibly oxidized, affording **13a** that, conversely, is stable in the employed reaction conditions. Given the electrochemical characterization of these species, we followed by CV the whole reaction. Therefore, a 0.1 mM $Ru(bpy)_3Cl_2.6H_2O$ and 3mM **K$^+$-10a** solution in acetonitrile was irradiated for 20 hours, under nitrogen atmosphere**.** In Figure 3 right, we observed, immediately after the begin of the irradiation, only the peak of **K$^+$-10a** (+ 0.52 V). The low concentration of the catalyst does not allow to detect it as its peaks are covered by those of the substrate **K$^+$-10a**. After 4 hours under irradiation, as the reaction proceeds, the peak of the substrate **K$^+$-10a** located at + 0.52 V begins to decrease in intensity while the signal of product **13a**, at + 1.23 V, grows (red line). Finally, after 20 hours of irradiation, the reaction goes to completeness showing an intense peak at + 1.23 V due to the complete conversion of the substrate **K$^+$-10a** and the signal of tosylhydrazone salt disappeared **K$^+$-10a** (blue line).

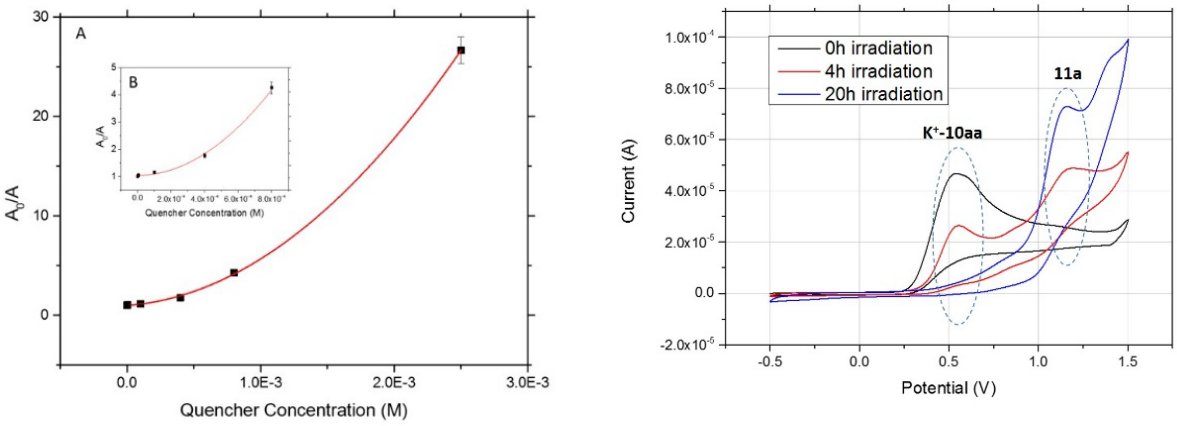


Figure 3 Left: Stern-Volmer plot for the $[Ru(bpy)_3]^{2+}$ luminescence quenching in the presence of 2,2-dimethylbut-3-enylphenone-*N*-tosylhydrazone-K$^+$ salt (**K$^+$-10a**). Right: electrochemical characterization of the reaction. The CVs were carried at three different time during the reaction: 1) t = 0h (black); 2) t = 4h (red); 3) t = 20h of irradiation (blue).

Computational studies

The experimental results have been flanked by the computational DFT study of the reaction mechanism in CH_3CN (the details on the method and the full data are reported in the ESI). Given the experimental results and the computational data recovered so far, a general reaction mechanism is hypothesized in Scheme 5. Here we only focus on the key steps of the reaction mechanism; the complete scheme, discussion and energy profiles are reported in the ESI. The computational study is focused on the fate of the radicals **A** and performed for the reaction of tosylhydrazones **10i** ($R^{'}$, $R^{''}$ = H) and **10k** ($R^{'}$= Me, $R^{''}$ = H)and mesitylsulfonylhydrazone **12e** ($R^{'}$ = H, $R^{''}$ = Me).The energy values commented here are Gibbs free energies at room temperature (ΔG, in kcal mol^{-1}). The experimental data and the comparison with the previous study[51] allow us to deduce that the deprotonation of arylhydrazones **10** occurs under basic conditions to afford the anions **10'** in accordance with electrochemical measurements on $\mathbf{K^+}$**-10a**. Their single-electron oxidation by the excited state of the photocatalyst ($*[Ru(bpy)_3]^{2+}$) gives the *N*-centered radicals **A** and,[51] following an *exo*-closure, the radicals **B**. Actually, this step takes place through several conformations of $\mathbf{TS^A}$ yielding the same number of radical intermediates **B**. The lowest activation energies are quite similar for the three hydrazones:$\Delta G^{\ddagger}$ = 10.8 and 9.2 kcal mol^{-1} for the tolyl derivatives **10i** and **10k** and 12.2 kcal mol^{-1} for the mesityl derivative **12e**. This step is monomolecular, so we can easily apply the Eyring equation that furnishes (taking into account all conformations) an estimation of the rate constants which are $2 \bullet 10^5$ (**10i**), $1 \bullet 10^6$ (**10k**) and $1 \bullet 10^4$ (**12e**) sec^{-1}. This fast formation of radicals **B** is irreversible, being exoergic in all cases (ΔG = -9.7, -11.1, and -7.6 kcal mol^{-1}) giving rise to three possible pathways:

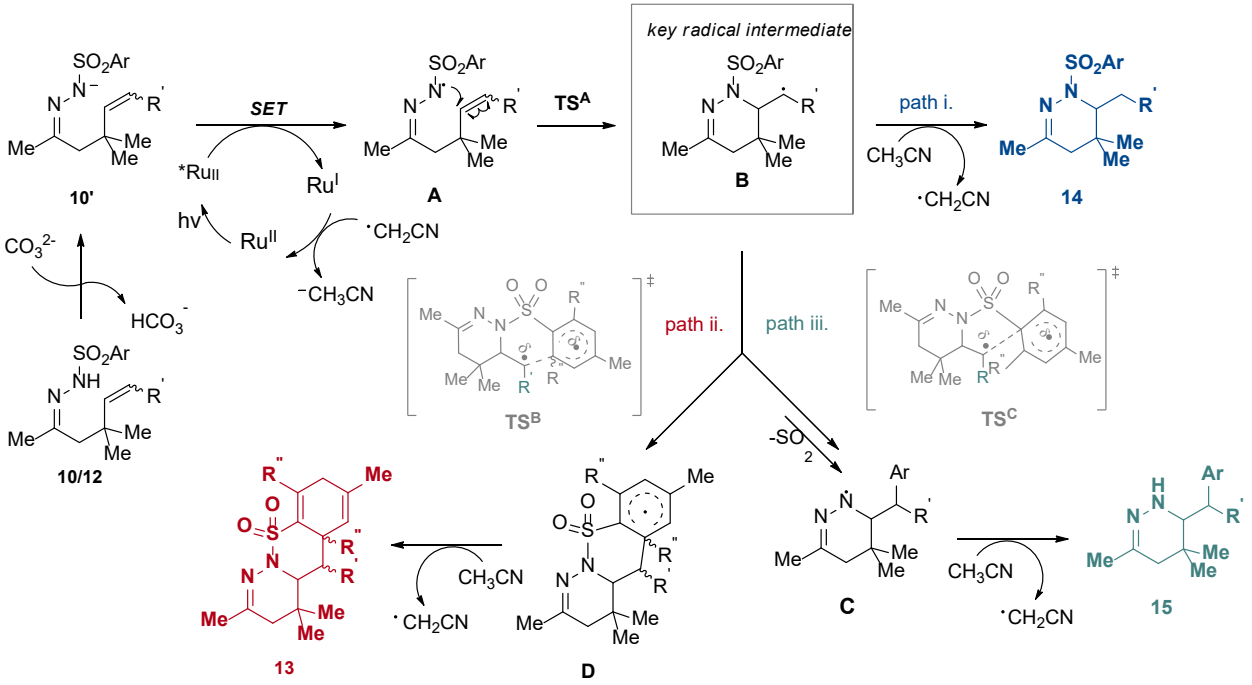
i. the hydrogen atom transfer (HAT) from the solvent CH_3CN generating products **14;**
ii. the intramolecular attack of the radical centers to the *ortho* (with respect to the sulfur) position of the aromatic yielding, after the HAT from CH_3CN, products **13**;
iii. the intramolecular attack of the primary radical centers to the *ipso* positions of the aromatic yielding, (a sort of radical *Smiles* rearrangement) and the final HAT from the solvent, products **15**.

Process **i** is bimolecular and involves a molecule taken from the solvent while pathways **ii** and **iii** are monomolecular. Therefore, we cannot confidentially compare the rate constant calculated for pathway **i** with those calculated for the other two pathways. However, the rate constant for the HAT of triplet benzophenone with CH_3CN reaction has been measured,[66] the value is 10^2 sec^{-1}.

The pathway **ii**, passing through **TS^{B}**, requires to overcome a barrier of 14.4, 17.2 and 17.1 kcal mol^{-1} (lowest values of all conformations for each TS) for the tolyl **10i** and **10m** and for the mesityl **12e**, respectively. For pathway **iii**, passing through **TS^{C}**, the $\Delta G^{\ddagger}$ are, respectively, 16.0, 15.8, and 14.7 kcal mol^{-1} for the tolyl **10i** and **10m** and for the mesityl **12e**. We first focus on the different outcomes when, in the γ,δ-unsaturated hydrazones containing the terminal double bond, the aryl is the tolyl (**10i**) or the mesityl (**12e**). Comparing the last two pathways, we can observe that for the tolyl derivative **10i,** the attack to the *ortho* positions (**TS^{B}**, Figure 4, left) is favored. The rate constant that we can estimate by the Eyring equation is $4 \bullet 10^{2}$ sec^{-1}, twenty times larger than that for **TS^{C}** ($2 \bullet 10^{1}$ sec^{-1}). For the mesityl derivative **12e**, it is the attack to the *ipso* positions (**TS^{C}**, Figure 4, right) to be favored. The rate constant is $2 \bullet 10^{2}$ sec^{-1}, and has to be compared to 3 sec^{-1} for **TS^{B}**. Therefore, our calculations indicate that for the tolyl derivative **10i**, the formation of the condensed three-rings **13** (*i.e.***13i**), is preferred. While, for the mesityl derivative **12e**, the formation of the radical Smiles rearrangement product **15** (i.e. **15e**) is preferred. As said above, here we are not confident in using the calculated rate constant for pathway **I**but we have an indication that it can be around 10^{2} sec^{-1}. This value is just of the same order that one calculated for the other two pathways. We can also observe that the reaction constant for the formation of product **13** (*i.e.***13i**) from **10i** is twice the one of product **15** (*i.e.***15e**) from **12e**. This is in a semi-quantitative agreement with the experimental finding: **13i** is the only product obtained from the tolyl derivative **10i** while in the reaction of the mesityl derivative **12e**, **15e** (39%), being its rate constant lower, is generated along with **14** (*i.e.***14e**, 61%).

The reason why the intramolecular attack of the primary radical centers to the *ortho* positions of the aromatics (**TS^{B}**) in the mesityl derivative ($\Delta G^{\ddagger}$ = 17.1 kcal mol^{-1}) is more difficult than that in the tolyl case ($\Delta G^{\ddagger}$ = 14.4 kcal mol^{-1}) is presumably the steric hindrance of the *ortho* methyl groups in the first case. This effect is absent in the cases of the attack to the *ipso* positions. By contrast, the same methyl groups in the mesityl derivative concur to stabilize the incipient delocalized aromatic radicals formed in **TS^{C}**, which, in fact, presents a lower barrier ($\Delta G^{\ddagger}$ = 14.7 kcal mol^{-1}) that in the case of the tolyl derivative ($\Delta G^{\ddagger}$ = 16.0 kcal mol^{-1}). These results are qualitatively applicable to all other cases with the terminal γ,δ-unsaturated hydrazone. When Ar is a phenyl or a tolyl (see Table 3), the lack of the *para*-methyl does not change the choice between pathways **ii** and **iii**: all arylhydrazones follow the same pathway as **10i** yielding **13a-n**. The presence of an aryl or alkyl group linked to C=N is also irrelevant: the choice between pathways **ii** and **iii** is uniquely

due to the nature of the Ar as the comparison between Tables 2 and 3 confirms. For the tolyl derivatives, when the γ,δ-unsaturated hydrazone contains an internal double bond instead of a terminal one as in **10k**, the main product is **15**. The calculations are in qualitative agreement with the experiments: the Smiles rearrangement (pathway **iii**) is favored over the second cyclization (pathway **ii** yielding **13**) by almost 2 kcal mol^{-1} ($\Delta G^{\ddagger}$ = 15.8 kcal mol^{-1} for **TS^{C}** and $\Delta G^{\ddagger}$ = 17.5 kcal mol^{-1} for **TS^{B}**). Therefore, the competition is between pathways **i** (the HAT yielding **14**) and **iii**. As discussed above, we are not confident in comparing rate constants calculated for mono and bimolecular processes but we can do it for homogenous process as HAT for different radicals. The calculated rate constants for the HAT reaction for the primary radicals **B** generated from the terminally double bonded **10i** and **12e** are in the order of 10^{2} sec^{-1} while that for the more stable secondary radical **B**, generated from the internally double bonded **10k** is 10^{-1} sec^{-1}. This can explain why in the latter case, pathway **iii.** is preferred over all the others.



Scheme 5 General reaction mechanism.

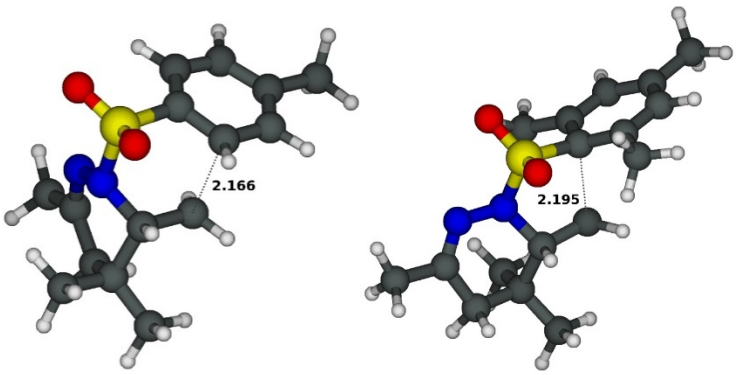


Figure 4 Key transition structures (TS^B, left and TS^C, right) for the formation of products **13i** and **15e.**

Conclusions

In summary, we have reported the synthesis of diverse tetrahydropyridazines following three different patterns simply changing the structural features of the starting γ,δ-unsaturated tosylhydrazones. All reactive pathways exploit a common *N*-centred radical which can undergo, in one case, a totally diastereoselective double cyclization affording 1,4-cyclohexadiene-fused tetrahydropyridazinylthiazines as a result of a dearomatization process. On the other cases, depending on the presence of an internal double bond or a mesitylsulfonylhydrazone, tetrahydropyridazines are obtained by a hydrogen atom transfer from the solvent CH_3CN after the first *exo*-cyclization or a photocatalyzed Smiles rearrangement. Experimental data are supported by computational study of the mechanism which is coherent with the experimental findings and some explanation of the outcomes is put forward.

Experimental Section

Flasks and all equipment used for the generation and reaction of moisture-sensitive compounds were dried by electric heat gun under N_2. All commercially available reagents and solvents were used as received. Anhydrous solvents were purchased by Sigma Aldrich, or distilled as indicated by Armarego.[67] Products were purified by preparative column chromatography on Sigma Aldrich silica-gel for flash chromatography, 0,04-0,063 mm/ 230-400 mesh. Reactions were monitored by TLC using silica-gel on TLC-PET foils Sigma Aldrich, 2-25 μm, layer thickness 0.2 mm, medium pore diameter 60 Å.

^1H and ^{19}F NMR spectra were recorded at NMR Jeol ECZR 600 MHz, ^{13}C NMR spectra at 150 MHz, in $CDCl_3$ or d^6- DMSO.[68] Data were reported as follows: chemical shifts in ppm from Me_4Si as an internal standard, integration, multiplicity, coupling constants (Hz); and assignment. ^{13}C

NMR spectra were measured with complete proton decoupling. DEPT experiments were carried out with a DEPT 135 sequence. Chemical shifts were reported in ppm from the residual pick solvent as an internal standard.GC-MS spectra were obtained on a mass selective detector Agilent 5970 B operating at an ionizing voltage of 70 eV connected to a HP 5890 GC equipped with a HP-1 MS capillary column (25 m length, 0.25 mm I.D., 0.33 µm film thickness.High-resolution mass spectra (HRMS) were determined with a Bruker Daltonics microTOF Mass Spectrometer using electrospray ionization source (ESI).IR spectra were recorded on a BrukerVertex 70 FT-IR.Fluorescence emission spectra were collected with a Cary Eclipse Fluorescence Spectrophotometer, with excitation at 452 nm. Excitation and emission slits set both at 5 nm. Spectra were taken in a fluorescence fused silica cuvette with 1 cm optical path length. Crystal of compounds **13a** and **16** were obtained by slow precipitation from $CHCl_3$ at room temperature. Data of single crystals of compound have been collected on a Gemini R Ultra diffractometer (Agilent Technologies UK Ltd., Oxford, U.K). All the data were collected using graphite monochromated Mo Kα radiation (k= 0.71073 Å) with the x-scan method. Cell parameters were retrieved using CrysAlisPro (Agilent Technologies CrysAlisProSoftare system, version 1.171.35.11 Agilent Technologies U K Ltd., Oxford, U.K (2012)) software, and the same program has been used for performing data reduction, with corrections for Lorenz and polarizing effects. Scaling and absorption corrections were applied by the CrysAlisPro (Agilent Technologies CrysAlisProSoftare system, version 1.171.35.11 Agilent Technologies U K Ltd., Oxford, U.K (2012)) multi-scan technique. All the structures were solved by direct methods using SHELXS-14[69] and refined with full-matrix least-squares method on F^2 inserted in SHELXL-14[70] using the program Olex^2.[71] All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were located in the final Fourier-difference maps and refined with coordinates and U^{iso} calculated and riding on the corresponding atom. Structural illustrations have been drawn with Mercury.[72]

Photochemical reactions were carried out in a cylinder-shaped photochemical reactor (40 mm as ID and 25 mm height for general procedures and reactions, 40 mm as ID and 25 mm height for gram-scale reaction).A Kessil Blue Lamp was used as irradiation source, which emits a band centered at 450 nm and of about 55 nm width t half height. The irradiation source is located at 4 cm from the reaction solution surface.

Computational Method. The structures of reactants, intermediate adducts and transition states were optimized using the density functional method (DFT),[73] with the functional M06-2X[74, 75] and

the basis sets 6-311+G(d,p) for H, C, N, and O atoms and 6-311+G(2df) for S atoms.[76]The nature of the critical points was characterized by using vibrational analysis[77, 78] which also furnished the Zero Point Energies (ZPE) and entropies for the calculations of the Free Energies. These have been converted from the gas phase to the 1M standard state at 1 atm and 298 and 338 K[79] and used to calculate the rate constant with the Eyring equation.[80] Solvent effects were introduced in all calculations using the universal solvation model density method (SMD).[81, 82]Calculations were performed by the quantum package Gaussian 16-A.03.[83] Figures were obtained using the graphical program Molden.[84]

General Procedure for the synthesis of 1-phenyl-4-penten-1-one *N*-tosylhydrazone (1) Under a nitrogen atmosphere in a dried Schlenk bottle, acetophenone *N*-tosylhydrazone (1.44 gr, 5.0 mmol) was dissolved in 10 ml of THF. The resulting mixture was vigorously stirred for 5 minutes, cooled to -78° C, then *n*-BuLi (2.5 M solution, 4.4 mL, 11.0 mmol) was added dropwise over 30 minutes. Turning of the solution from yellow to orange (after addition of 1 eq.) then from orange to red (after addition of 2 eq of *n*-BuLi) was observed. The reaction was stirred at -78°C for 45 minutes. Subsequently allyl bromide was added (0.73 gr, 6.0 mmol), temperature allowed to raise and stirring maintained until complete consumption of the reactant (monitored by TLC). The reaction was then quenched with a NH_4Cl saturated solution (20 mL) and diluted with Et_2O (30 mL). The aqueous phase was extracted with CH_2Cl_2 (3 x 15 mL) then the organic phase reunited, washed with brine (30 mL), dried over Na_2SO_4 and filtered. The obtained crude was then purified by flash chromatography on silica gel (PE/EE 65/35) and subsequently crystalized from methanol to obtain 1.42 gr of 1-phenyl-4-penten-1-one *N*-tosylhydrazone **1** as cubic-shaped colorless crystals (yield 86%). A mixture of isomers was found. Spectral data are coherent with those previously reported in literature.[85, 86] ^{1}H NMR (600 MHz, $CDCl_3$, Me_4Si):δ mixture of isomers (51:49): 7.96 (s, 1H, N-*H*, isomer A), 7.95 (s, 1H, N-*H*, isomer B), 7.89 (d, *J* = 8.0 Hz, 2H, Ar-*H,* isomer A),7.78 (d, *J* = 8.0 Hz, 2H, Ar-*H,* isomer B), 7.44 (m, 4H, Ar-*H*both isomers), 7.32 (m, 8H, Ar-*H,* both isomers), 7.06 (m, 2H, Ar-*H,* both isomers), 5.67 (*J* = 16.9, 10.2, 6.5 Hz, 1H, C*H*=CH_2 , both isomers), 4.96 (dd, *J* = 17.4, 1.1 Hz, 1H, CH=CH_2, *H trans,* both isomers); 4.92 (dd, *J* = 10.7, 1.1 Hz, 1H, CH=CH_2, *H cis*, both isomers), 2.66 (t, *J* = 7.6 Hz, 2H, N=C(Ph)-CH_2isomer A),2.57 (t, *J* = 7.6 Hz, 2H, N=C(Ph)-CH_2isomer B), 2.42 (s, 3H, Ar-CH_3isomer A), 2.41 (s, 3H, Ar-CH_3isomer B), 2.21 (m, 4H, N=C(Ph)-CH_2-CH_2both isomers).

General Procedure for the Synthesis of 6-Methyl-3-phenyl-1-tosyl-1,4,5,6-tetrahydropyridazine (2) In a sealed photochemical reactor, 6.8 mg of $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (0.009 mmol) were dissolved in 5 mL of anhydrous $CHCl_3$ and the solution was degassed with $N_2$for 15 min. Then phenylprop-3-enyl-N-tosylhydrazone (1) (98.5 mg, 0.300 mmol) and KOH (20.0 mg, 0.360 mmol) were added in one portion and the solution degassed for additional 10 min. The mixture was then stirred at 4 cm from the irradiation source at room temperature until reaction completion. The solution was then filtered on a short pad of silica gel using CH_2Cl_2 as eluent and Et_2O to wash the column. The crude product was purified by flash chromatography on silica gel (PE/EE 65/35) to obtain 24.1 mg of a greenish solid **2** (24%). ^{1}H NMR (600 MHz, $CDCl_3$, Me_4Si): δ 7.88 (d, *J* = 8.3 Hz, 2H, Ar-*H*), 7.71 (dd, *J* = 8.1, 1.7 Hz, 2H, Ar-*H*), 7.38 – 7.31 (m, 3H, Ar-*H*), 7.27 (d, *J* = 8.1 Hz, 2H, Ar-*H*), 4.59 (m, 1H, N-C*H*-CH_3), 2.61 (dt, *J* = 18.2, 3.4 Hz, 1H, N=C(Ph)-C(H)*H*), 2.42 (dt, *J* = 18.3, 10.2 Hz, 1H, N=C(Ph)-C(H)*H*), 2.38 (s, 3H, Ar-CH_3), 1.88 (dt, *J* = 9.3, 2.9 Hz, 2H, CH_2-CH_2-CH), 1.14 (d, *J* = 6.8 Hz, 3H, N-CH-CH_3). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$,Me_4Si): δ 147.3 (Cq), 143.6 (Cq), 137.1 (Cq), 135.4 (Cq), 129.5 (2 x CH), 129.2 (CH), 128.4 (2 x CH), 128.2 (2 x CH), 125.3 (2 X CH), 47.4 (CH), 24.4 (CH_2), 21.7 (CH_3), 18.3 (CH_2), 17.5 (CH_3). Mp: 142-145°C. ν_{max} (neat)/cm^{-1}: 3060, 2926, 2866, 1603, 1444, 1238, 907, 839, 762, 690. HRMS (ESI) m/z:$[M + H]^+$ Calcd. For $C_{18}H_{21}N_2O_2S$329.1318;found 329.1320.

General Procedure for the synthesis of α,β-unsaturated ketones(6). A dried three-necked round bottom flask connected with a drip funnel and a reflux condenser was dried under nitrogen atmosphere. Magnesium (290 mg, 12.0 mmol) and a small crystal of double sublimed Iodine was added to the flask, covered with anhydrous THF and vigorously stirred. A small aliquot of the solution of the appropriate arylbromide **4** (10.0 mmol, 1M in THF) was added, and the resulting orange mixture was stirred until a turning to grey or colorless was observed. At this point, the rest of the arylbromide solution was added dropwise through funnel and heated to reflux for 6 hours. The solution was then cooled to rt and 3-methylbut-2-enal **3** (930 mgr, 11.0 mmol, 1 M in THF) was added dropwise. Stirring was maintained till complete consumption of the aldehyde **3** (about 2 hours) then the reaction was cooled to 0° C and quenched diluting with NH_4Cl saturated solution (30 mL) and Et_2O (30 mL). The aqueous layer was extracted with Et_2O (2 x 30 mL) and the collected organic phases were washed with brine (30 mL); and finally dried over Na_2SO_4. Filtration of the solids and removal of the volatiles under reduced pressure afforded an oil corresponding to α,β-unsaturated alcohol **5** that was then poured in a 250 mL round bottom flask and dissolved in

150 mL of CH_2Cl_2. MnO_2 (7.00 gr, 80.0 mmol) was added to the mixture in small portions every hour until complete oxidation of the alcohol **5**. The resulting mixture was filtered over a thin pad of celite that was then washed with CH_2Cl_2 and AcOEt. The solvents were removed under reduced pressure to give an orange oil, whose purification by flash chromatography (PE/AcOEt 97.5/2.5, 1% Et_3N) afforded the desired α- β unsaturated ketone **6** as a yellowish oil.

2-Methylprop-1-enylphenone (6a) Following the described procedure, 1.59 gr (10.0 mmol) of bromobenzene were reacted with magnesium and 3-methylbut-2-enal, then subsequently with MnO_2 to afford 1.04 gr (6.5 mmol) of 2-methylprop-1-enylphenone(**6a**) as a yellowish oil (yield 65%). Spectral data are coherent with those reported in literature.[87] ^{1}HNMR (600 MHz, $CDCl_3$, Me_4Si): δ 7.96-7.90 (m, 2H, Ar*H*); 7.41-7.56 (m, 3H, Ar*H*); 6.75 (sept, *J* = 1.3 Hz, 1H, CO-C*H*); 2.21 (d, *J* = 1.3 Hz, 3H, CH=C-(C*H*$_3$)$_2$); 2.03 (d, *J* = 1.3 Hz, 3H, CH=C-(C*H*$_3$)$_2$).

2-Methylprop-1-enylnaphtone (6b) Following the described procedure, 2.05 gr (10.0 mmol) of 2-bromonaphtalene were reacted with magnesium and 3-methylbut-2-enal **3**, then subsequently with MnO_2 to afford 1.22 gr (5.8 mmol) of 3-methyl-1-(naphthalen-2-yl)but-2-en-1-one **6b** (58%). Spectral data are coherent with those reported in literature.[88] ^{1}HNMR (600 MHz, $CDCl_3$, Me_4Si: δ 8.43-8.40 (m, 1H, Ar-*H*); 8.03 (dd, *J* = 8.7, 1.8 Hz, 1H, Ar-*H*); 7.95 (d, *J* =8.3 Hz, 1H, Ar-*H*); 7.87 (ddt, *J* = 7.5, 5.4, 0.7 Hz, 2H, Ar-*H*); 7.57 (t, *J* =7.5 Hz, 1H, Ar-*H*); 7.53 (t, *J* =7.5 Hz, 1H, Ar-*H*); 6.90 (bs, 1H, CO-C*H*); 2.26 (d, *J* = 1.3 Hz, 3H, CH=C-(C*H*$_3$)$_2$); 2.05 (d, *J* = 1.3 Hz, 3H, CH=C-(C*H*$_3$)$_2$).

2-Methylprop-1-enyl-*m*-tolylketone (6c)Following the described procedure, 1,70 gr (10.0 mmol) of *m*-tolylbromide were reacted with magnesium and 3-methylbut-2-enal **3**, then subsequently with MnO_2 to afford 0.71 gr of 2-methylprop-1-enyl-*m*-tolylketone **6c** as yellowish oil (41%). ^{1}HNMR (600 MHz, $CDCl_3$, Me_4Si):δ 7.73 (s, 1H, Ar*H*); 7.70 (m, 1H, Ar*H*) 7.34 (d, *J*=1.1 Hz, 1H, Ar*H*); 7.32 (m, 1H, Ar*H*); 6.72 (quint, *J* = 1.3 Hz, 1H, CO-C*H*); 2.40 (s, 3H, Ar-C*H*$_3$); 2.19 (d, *J* = 1.3 Hz, 3H, CH=C-(C*H*$_3$)$_2$); 2.01 (d, *J* = 1.3 Hz, 3H, CH=C-(C*H*$_3$)$_2$). ^{13}C{^{1}H}NMR (151 MHz; $CDCl_3$, Me_4Si):δ 191.9 (Cq); 156.4(Cq); 139.4 (Cq); 138.3 (Cq); 133.1 (CH); 128.9 (CH); 128.4 (CH); 125.5 (CH); 121.5 (CH); 28.0 (CH_3); 21.58 (CH_3); 21.2 (CH_3). HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{12}H_{14}O$ 175.1045;found 175.1039.IR ν_{max} (neat)/ cm^{-1}: 3019, 2942, 1659, 1610, 1495, 899 cm^{-1}

2-Methylprop-1-enyl-*p*-tolylketone (6d)Following the described procedure, 1.70 gr (10.0 mmol) of *p*-tolylbromide were reacted with magnesium and 3-methylbut-2-enal **3**, then

subsequently with MnO_2 to afford 1.01 gr of 2-methylprop-1-enyl-*m*-tolylketone **6d** as yellowish oil (59%).[891]HNMR (600 MHz, $CDCl_3$, Me_4Si):δ 7.26 (d, J = 7.8, 2H, Ar*H*); 7.15 (d, J = 7.8, 2H, Ar*H*); 5.41 (m, CO-C*H*); 2.32 (s, 3H, Ar-CH_3); 1.78 (s, 3H, CH=C-(CH_3)$_2$); 1.73 (s, 3H, CH=C-(CH_3)$_2$).

2-Methylprop-1-enyl-*o*-tolylketone (6e)Following the described procedure, 1,70 gr (10.0 mmol) of *o*-tolylbromide were reacted with magnesium and 3-methylbut-2-enal **3**, then subsequently with MnO_2 to afford 0.96 gr of 2-methylprop-1-enyl-*o*-tolylketone **6e** as yellowish oil (55%).[901]HNMR (600 MHz, $CDCl_3$, Me_4Si):δ 7.49 (dm, *J* = 9 Hz, 1H, Ar*H*); 7.31 (td, *J* = 7.2, 1.2 Hz, 1H, Ar*H*) 7.22 (t, *J*=7.0 Hz, 2H, Ar*H*); 7.32 (m, 1H, Ar*H*); 6.42 (m, 1H, CO-C*H*); 2.45 (s, 3H, Ar-CH_3); 2.16 (s, 3H, CH=C-(CH_3)$_2$); 1.96 (s, 3H, CH=C-(CH_3)$_2$).

2-Methylprop-1-enyl-*m*-methoxyphenone (6f)Following the described procedure, 1.86 gr (10.0 mmol) of *m*-bromoanisole were reacted with magnesium and 3-methylbut-2-enal **3**, then subsequently with of MnO_2 to afford 1.05 gr of 2-methylprop-1-enyl-*m*-methoxyphenylketone **6f**as a yellowish oil (55%).[1]HNMR (600 MHz, $CDCl_3$, Me_4Si):δ 7.49 (ddd, *J* = 7.7, 1.5, 0.9 Hz, 1H, Ar-*H*); 7.46 (dd, *J* = 2.7, 1.5 Hz, 1H, Ar-*H*); 7.34 (t, *J* = 7.9 Hz, 1H, Ar-*H*); 7.06 (ddd, *J* = 8.2, 2.7, 1.0 Hz, 1H, Ar-*H*); 6.72 (sept, *J* = 1.3 Hz, 1H, CO-C*H*); 3.85 (s, 3H, O-CH_3); 2.20 (d, *J* = 1.3 Hz, 3H, CH=C-(CH_3)$_2$); 2.01 (d, *J* = 1.4 Hz, 3H, CH=C-(CH_3)$_2$). $^{13}C\{^1H\}$NMR (151 MHz; $CDCl_3$, Me_4Si):δ 191.3 (Cq); 159.9 (Cq); 156.9 (Cq); 140.8 (Cq); 129.5 (CH); 121.3 (CH); 120.9 (CH); 118.9 (CH); 112.6 (CH); 55.5 (CH_3); 28.1 (CH_3); 21.3 (CH_3). HRMS (ESI) m/z: $[M + H]^+$ Calcd. for$C_{12}H_{14}O_2$191.1072; found 191.1075.IR ν_{max} (neat)/ cm^{-1}: 3022, 2899, 1658, 1612, 1495, 1249, 1043, 899 cm^{-1}

2-Methylprop-1-enyl-2-pyridylketone (6g). According to the described procedure, 1,57 gr (10.0 mmol) of 2-bromopyridine were reacted with magnesium. Differently from the general procedure, turning from yellow to black was observed. After complete formation of the Grignard reagent, 3-methylbut-2-enal **3** was added and the obtained crude was subsequently reacted with MnO_2 to afford 0.61 gr of 2-methylprop-1-enyl-2-pyridylketone(**6g**) as a brown oil (38%).[1]HNMR (600 MHz, $CDCl_3$, Me_4Si):δ 8.66 (ddd, *J* = 4.8, 1.8, 1.0 Hz, 1H. Ar-*H*); 8.08 (dt, *J* = 7.9, 1.1 Hz, 1H, Ar-*H*); 7.83 (tt, *J* = 7.7, 1.4 Hz, 1H, Ar-*H*); 7.45 (sept, *J* = 1.3 Hz, 1H, CO-C*H*); 7.42 (ddt, *J* = 7.4, 4.8, 1.2 Hz, 1H, Ar-*H*); 2.30 (d, *J* = 1.3 Hz, 3H, CH=C-(CH_3)$_2$); 2.06 (d, *J* = 1.3 Hz, 3H, CH=C-(CH_3)$_2$). $^{13}C\{^1H\}$NMR (151 MHz; $CDCl_3$, Me_4Si):δ 190.22 (Cq); 159.71 (Cq); 155.35 (Cq); 148.63 (CH); 137.13 (CH); 126.46 (CH); 122.65 (CH); 119.74 (CH); 28.57 (CH_3)., 21.51

(CH_3). HRMS (ESI) m/z: $[M + H]^+$ Calcd. for$C_{10}H_{11}NO$162.0919;found 162.0922. IR ν_{max} (neat)/ cm^{-1}: 3082, 2960, 1688, 1639 1583, 1353, 994.

General Procedure for the synthesis of 2-phenylprop-1-enylphenone (6h). Following a modified procedure to that reported by Luo,[91] acetophenone (2.4 g, 20 mmol) and ethyl orthotitanate (2.4 g, 10 mmol) in 100 ml of heptane were heated to reflux in a bottomed flask equipped with a Dean–Stark trap which was filled with 5 ml of sulfuric acid (96% solution) to absorb the liberating alcohol. When the reaction was complete, the mixture was cooled to room temperature, then 30 mL of acetonitrile were added, and the resulting mixture stirred for 1 hour. The mixture was then transferred to a separatory funnel and the bottom layer was separated and moved to a 50 mL round bottomed flask where it was further treated with 4 mL of hydrochloric acid 37% solution. This mixture was stirred for 10 minutes then heated to reflux and cooled to rt. A precipitate formed which was separated from the filtrated solution. The accumulated precipitate was washed with cold acetonitrile and the resulting organic phase was united with the filtrated solution and the solvent evaporated. The obtained residue was purified on silica gel column chromatography to afford the desired product **6h** as a yellow solid (63% yield).^{1}HNMR (600 MHz, $CDCl_3$, Me_4Si):δ 7.98(dm, *J* = 6.0 Hz, 2H. Ar-*H*), 7.54-7.58 (m, 3H, Ar-*H*), 7.47 (tm, *J* = 7.8 Hz, 2H, Ar-*H*), 7.39-7.42 (ddt, *J* = 7.4, 4.8, 1.2 Hz, 3H, Ar-*H*), 2.16 (s, 3H, CH=C-C*H*$_3$).

General procedure for the synthesis of γ,δ-unsaturated ketones(8) According to the procedure reported by Von Fraunberg[92] with slight modifications, under a nitrogen atmosphere in a dried Schlenk bottle, copper iodide (190 mgr, 0.5 mmol) was added at -40°C to vinylmagnesium bromide **7a** (11.0 mL, commercial 1.0 M solution in THF) or propenylmagnesium bromide **7b** (22.0 mL, commercial 0.5 M solution in THF). The resulting mixture was vigorously stirred for 15 minutes, then a cooled 0.5 M solution of the appropriate α,β-unsaturated ketone **6** (10.0 mmol) in THF was added dropwise over 30 minutes keeping temperature of the bath below -40°C. Once the addition was completed, temperature was allowed to raise up to rt and stirring was maintained until complete consumption of the reactant. The reaction was then quenched with a NH_4Cl/NH_4OH 9/1 solution (30 mL) and diluted with Et_2O (30 mL). The organic phase was washed with NH_4Cl (10 mL aliquots) until the aqueous phase stopped turning blue. It was then washed with brine (30 mL); dried over Na_2SO_4 and filtered. The volatiles were removed under reduced pressure to give a colorless oil, that was used without any further purification.

2,2-Dimethylbut-3-enylphenone (8a) Following the described procedure, 1.60 gr (10.0 mmol) of 2-methylprop-1-enylphenone (**6a)** were reacted with CuI and vinylmagnesiumbromide **7a** to afford 1.64 gr (8.7 mmol) of 2,2-dimethylbut-3-enylphenone **8a** (87%) as a colorless oil.^{1}HNMR (600 MHz, $CDCl_3$, Me_4Si):δ 7.93 – 7.89 (m, 2H, Ar-*H*); 7.53 (ddt, *J* = 7.9, 6.9, 1.3 Hz, 1H, Ar-*H*); 7.46 – 7.40 (m, 2H, Ar-*H*); 5.95 (dd, *J* = 17.4, 10.7 Hz, 1H, C*H*=CH_2); 4.95 (dd, *J* = 17.5, 1.1 Hz, 1H, CH=C*H*$_2$); 4.90 (dd, *J* = 10.7, 1.1 Hz, 1H, CH=C*H*$_2$); 2.96 (s, 2H, CO-C*H*$_2$); 1.17 (s, 6H, CH_2-(C*H*$_3$)$_2$-CH). ^{13}C{^{1}H}NMR (151 MHz; $CDCl_3$, Me_4Si): 199.6 (Cq); 147.5 (CH); 138.4 (Cq); 132.9 (CH); 128.6 (2 x CH); 128.3 (2 x CH); 110.7 (CH_2); 49.2 (CH_2); 36.8 (Cq); 27.4 (2 x CH_3). HRMS (ESI) m/z: $[M + H]^+$ Calcd. for$C_{13}H_{16}O$189.1279;found 189.1275. IR ν_{max} (neat)/ cm^{-1}: 3082, 2960, 1676, 1618, 1240.

2,2-Dimethylbut-3-enylnaphtone (8b) Following the described procedure, 2.10 gr (10.0 mmol) of 2-methylprop-1-enylnaphtone(**6b**) were reacted with CuI and vinylmagnesiumbromide **7a** to afford 1.48 gr 2,2-dimethylbut-3-enylnaphtone **8b** (62%) as a colorless oil which crystallize as a white-yellowish solid after cooling.^{1}HNMR (600 MHz, $CDCl_3$, Me_4Si):δ 8.43 – 8.40 (m, 1H, Ar-*H*); 8.00 (dd, *J* = 8.7, 1.8 Hz, 1H, Ar-*H*); 7.95 (ddq, *J* = 8.2, 1.4, 0.7 Hz, 1H, Ar-*H*); 7.89 – 7.84 (m, 2H, Ar-*H*); 7.58 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1H, Ar-*H*); 7.54 (ddd, *J* = 8.1, 6.9, 1.3 Hz, 1H, Ar-*H*); 6.00 (dd, *J* = 17.4, 10.7 Hz, 1H, C*H*=CH_2); 4.98 (dd, *J* = 17.4, 1.1 Hz, 1H, CH=C*H*$_2$); 4.92 (dd, *J* = 10.7, 1.1 Hz, 1H, CH=C*H*$_2$); 3.09 (s, 2H, CO-C*H*$_2$); 1.22 – 1.20 (s, 6H, CH_2-(C*H*$_3$)$_2$-CH). ^{13}C{H}NMR (151 MHz; $CDCl_3$, Me_4Si): δ 199.6 (Cq); 147.6 (CH); 135.8 (Cq); 135.5 (Cq); 132.6 (Cq); 130.1 (CH); 129.7 (CH); 128.5 (CH); 128.4 (CH); 127.8 (CH); 126.8 (CH); 124.2 (CH); 110.7 (CH_2); 49.3 (CH_2); 37.0 (Cq); 27.4 (2 x CH_3). HRMS (ESI) m/z: $[M + H]^+$ Calcd. for$C_{17}H_{18}O$239.1436; found 239.1440.IR ν_{max} (neat)/ cm^{-1}: 3226, 1639, 1381, 1305, 1164. Mp: 53-56°C.

2,2-Dimethylbut-3-enyl-*m*-tolyl ketone (8c)Following the described procedure, 1.74 gr (10.0 mmol) of 2-methylprop-1-enyl-*m*-tolylketone**(6c)**were reacted with CuI and vinylmagnesiumbromide **7a** to afford 1.69 gr (8.4 mmol) of 2,2-dimethylbut-3-enyl-*m*-tolyl ketone **8c** (84%) as a colorless oil. ^{1}HNMR (600 MHz, $CDCl_3$, Me_4Si):δ 7.7 (dq, *J* = 1.8, 0.9 Hz, 1H, Ar-*H*); 7.69 (dt, *J* = 7.4, 1.7 Hz, 1H, Ar-*H*); 7.34 (ddq, *J* = 7.7, 1.8, 0.8 Hz, 1H, Ar-*H*); 7.33 – 7.29 (m, 1H, Ar-*H*); 5.95 (dd, *J* = 17.4, 10.7 Hz, 1H, C*H*=CH_2); 4.95 (dd, *J* = 17.4, 1.1 Hz, 1H, CH=C*H*$_2$); 4.90 (dd, *J* = 10.7, 1.1 Hz, 1H, CH=C*H*$_2$); 2.94 (s, 2H, CO-C*H*$_2$); 2.39 (d, *J* = 0.8 Hz, 3H, Ar-C*H*$_3$); 1.16 (s, 6H, CH_2-(C*H*$_3$)$_2$-CH). ^{13}C{^{1}H}NMR (151 MHz; $CDCl_3$, Me_4Si): δ 199.8

(Cq); 147.6 (CH); 138.5 (Cq); 138.3 (Cq); 133.6 (CH); 128.8 (CH); 128.4 (CH); 125.6 (CH); 110.6 (CH_2); 49.3 (CH_2); 36.8 (Cq); 27.4 (CH_3); 21.5 (2 x CH_3).HRMS (ESI) m/z: $[M + H]^+$ Calcd. for$C_{14}H_{18}O$203.1436;found 203.1434.IR ν_{max} (neat)/ cm^{-1}: 3082, 2961, 2871, 1673, 1603, 1249.

2,2-Dimethylbut-3-enyl-*p*-tolyl ketone (8d). Following the described procedure, 1.74 gr (10.0 mmol) of 2-methylprop-1-enyl-*p*-tolylketone (**6d**) were reacted with CuI and vinylmagnesiumbromide **7a** to afford 1.71 gr (8.4 mmol) of 2,2-dimethylbut-3-enyl-*p*-tolyl ketone **8d** (85%) as a colorless oil.{Duan, 2015 #80}^{1}HNMR (600 MHz, $CDCl_3$, Me_4Si):δ 7.82 (d, *J* = 7.8 Hz, 2H, Ar-*H*); 7.22 (d, *J* = 7.8 Hz, 2H, Ar-*H*); 5.97 (dd, *J* = 17.4, 10.8 Hz, 1H, C*H*=CH_2); 4.94 (d, *J* = 17.4 Hz, 1H, CH=CH_{2a}); 4.89 (d, *J* = 10.8 Hz, 1H, CH=CH_{2b}); 2.94 (s, 2H, CO-CH_2); 2.39 (s, 3H, Ar-CH_3); 1.16 (s, 6H, CH_2-(CH_3)$_2$-CH).

2,2-Dimethylbut-3-enyl-*o*-tolyl ketone (8e)Following the described procedure, 1.74 gr (10.0 mmol) of 2-methylprop-1-enyl-*o*-tolylketone**(6e)**were reacted with CuI and vinylmagnesiumbromide **7a** to afford 1.09 gr (8.4 mmol) of 2,2-dimethylbut-3-enyl-*o*-tolyl ketone **8e** (54%) as a colorless oil. ^{1}HNMR (600 MHz, $CDCl_3$, Me_4Si):δ 7.52 (d, *J* = 7.2 Hz, 1H, Ar-*H*); 7.52 (td, *J* = 7.2, 1.2 Hz, 1H, Ar-*H*); 7.22 (t, *J* = 7.8 Hz, 2H, Ar-*H*); 5.91 (dd, *J* = 17.4, 11.4 Hz, 1H, C*H*=CH_2); 4.93 (dd, *J* = 17.4, 0.6 Hz, 1H, CH=CH_{2a}); 4.89 (d, *J* = 11.4, 0.6 Hz, 1H, CH=CH_{2b}); 2.89 (s, 2H, CO-CH_2); 2.43 (s, 3H, Ar-CH_3); 1.14 (s, 6H, CH_2-(CH_3)$_2$-CH). ^{13}C{^{1}H}NMR (151 MHz; $CDCl_3$, Me_4Si): δ204.4 (Cq); 147.4 (CH); 140.0 (Cq); 137.4 (Cq); 131.9 (CH); 130.8 (CH); 128.3 (CH); 125.6 (CH); 110.6 (CH_2); 52.9 (CH_2); 37.2 (Cq); 27.4 (CH_3); 21.0 (2 x CH_3).HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{14}H_{18}O$203.1436;found 203.1432.IR ν_{max} (neat)/ cm^{-1}: 3082, 2962, 1678, 1640, 1456, 1346, 1235.

2,2-Dimethylbut-3-enyl-*m*-methoxyphenone (8f)Following the described procedure, 1.90 gr (10.0 mmol) of 2-methylprop-1-enyl-*m*-methoxyphenone (**6f**) were reacted with CuI and vinylmagnesiumbromide **7a** to afford 1.57 gr of 2,2-dimethylbut-3-enyl-*m*-methoxyphenone **8f** (72%) as a colorless oil. ^{1}HNMR (600 MHz, $CDCl_3$, Me_4Si): δ 7.52 (dm, *J* = 7.8 Hz, 1H, Ar-*H*); 7.44 (dd, *J* = 3.0, 1.2 Hz, 1H, Ar-*H*); 7.34 (t, *J* = 7.8 Hz, 2H, Ar-*H*); 7.07 (ddd, *J* = 7.8, 3.0, 1.2 Hz, 2H, Ar-*H*); 5.91 (dd, *J* = 17.4, 10.8 Hz, 1H, C*H*=CH_2); 4.95 (dd, *J* = 17.4, 1.2 Hz, 1H, CH=CH_{2a}); 4.89 (d, *J* = 10.8, 1.2 Hz, 1H, CH=CH_{2b}); 4.08 (s, 3H, Ar-OCH_3); 2.94 (s, 2H, CO-CH_2); 1.16 (s, 6H, CH_2-(CH_3)$_2$-CH). ^{13}C{^{1}H}NMR (151 MHz; $CDCl_3$, Me_4Si): δ199.3 (Cq); 159.8 (Cq); 147.5 (CH); 139.8 (Cq); 129.5 (CH); 121.0 (CH); 119.4 (CH); 112.5 (CH); 110.7 (CH_2);

55.5 (CH_3); 49.4 (CH_2); 36.8 (Cq); 27.4 (CH_3). HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{14}H_{18}O_2$219.1385; found219.1388. IR ν_{max} (neat)/ cm^{-1}: 3073, 2937, 1614, 1593, 1260.

2,2-Dimethylbut-3-enyl-pyridyl ketone (8g) Following the described procedure, 1.61 gr (10.0 mmol) of 2-methylprop-1-enyl-2-pyridylketone (**6g**)were reacted with CuI and vinylmagnesiumbromide **7a** to afford 1.66 gr of 2,2-dimethylbut-3-enyl-pyridyl ketone (**8g**) (88%) as a colorless oil. ^{1}HNMR (600 MHz, $CDCl_3$, Me_4Si): δ 8.64 (ddq, *J* = 4.4, 1.7, 0.9 Hz, 1H, Ar-*H*); 7.97 (dq, *J* = 7.9, 1.2 Hz, 1H, Ar-*H*); 7.81 – 7.75 (m, 1H, Ar-*H*); 7.41 (ddt, *J* = 7.5, 4.8, 1.4 Hz, 1H, Ar-*H*); 5.97 (ddd, *J* = 17.4, 10.7, 1.2 Hz, 1H, C*H*=CH_2); 4.92 (dt, *J* = 17.4, 1.3 Hz, 1H, CH=CH_2); 4.85 (dt, *J* = 10.7, 1.3 Hz, 1H, CH=CH_2); 3.26 (s, 2H, CO-CH_2); 1.15 (d, *J* = 1.4 Hz, 6H, CH_2-(CH_3)$_2$-CH).^{13}C{^{1}H}NMR (151 MHz; $CDCl_3$, Me_4Si): δ 201.1 (Cq); 154.4 (Cq); 148.7 (CH); 147.6 (CH); 136.9 (CH); 126.9 (CH); 121.8 (CH); 110.4 (CH_2); 47.6 (CH_2); 36.80 (Cq); 27.34 (2 x CH_3). HRMS (ESI) m/z: $[M + H]^+$ Calcd. for$C_{12}H_{15}NO$190.1232; found 190.1229.IR ν_{max} (neat)/ cm^{-1}: 3038, 2961, 1689, 1583, 1328, 1013.

2-Phenyl-2-methylbut-3-enylphenone (8h) Following the described procedure, 2.08 gr (10.0 mmol) of 2-phenylprop-1-enylphenone **6h** were reacted with CuI and vinylmagnesium bromide **7a** to afford 2.07 gr of 2-phenyl-2-methylbut-3-enylphenone (**8h**). (83%) as colorless oil. ^{1}HNMR (600 MHz, $CDCl_3$, Me_4Si), δ 7.85 (dm, J = 8.4 Hz, 2H, Ar-*H*); 7.51 (tm, 1H, J = 9.0 Hz, Ar-*H*); 7.39tm, 2H, J = 7.8 Hz, Ar-*H*); 7.33 (dm, J = 8.4 Hz, 2H, Ar-*H*); 7.23 (tm, 2H, J = 9.0 Hz, Ar-*H*); 7.16 (tm, 1H, J = 7.8 Hz, Ar-*H*); 6.26 (dd, *J* = 17.4, 10.2 Hz, 1H, C*H*=CH_2); 5.13 (dd, *J* = 10.2, 1.8 Hz, 1H, CH=CH_{2a}); 5.06 (dd, *J* = 17.4, 1.8 Hz, 1H, CH=CH_{2b}); 3.48 (s, 2H, CO-CH_2); 1.58 (s, 3H, CH_3). ^{13}C{^{1}H}NMR (151 MHz; $CDCl_3$, Me_4Si):δ198.4 (Cq); 146.0 (CH); 132.8 (CH); 129.2 (Cq);128.7 (2 X CH) ; 128.5 (2 X CH); 128.4 (Cq); 128.3 (2 X CH); 128.1 (2 X CH); 126.3 (2 X CH);112.4 (CH_2); 48.4 (CH_2); 43.8 (Cq); 26.0 (CH_3). HRMS (ESI) m/z: $[M + H]^+$ Calcd. for$C_{18}H_{18}O$251.1436; found251.14.40.IR ν_{max} (neat)/ cm^{-1}: 2829, 2667, 2554, 1678, 1452, 1288, 1154, 925.

4,4-Dimethylhex-5-en-2-one (8i) Following the described procedure, 0.98 gr (10.0 mmol) of mesityl oxide **6i** (4-methylpent-3-en-2-one) were reacted with CuI and vinylmagnesium bromide **7a** to afford 1.12 gr of 4,4-dimethylhex-5-en-2-one **8i** (89%) as a colorless oil.[931]HNMR (600 MHz, $CDCl_3$, Me_4Si): δ5.90 (dd, J = 18.0, 10.81H, C*H*=CH_2); 4.94 (dd, *J* = 18.0, 1.1 Hz, 1H, CH=CH_2 (*H trans*)); 4.93 (dd, *J* = 10.8, 1.1 Hz, 1H, CH=CH_2 (*H cis*)); 2.41 (s, 2H, CO-CH_2); 2.09 (s, 3H, CH_3-CO); 1.10 (s, 6H, CH_2-(CH_3)$_2$-CH).

2,2-dimethylpent-3-enylphenone (8j) Following the described procedure, 1.60 gr (10.0 mmol) of 2-methylprop-1-enylphenone **6a** (4-methylpent-3-en-2-one) were reacted with CuI and propenylmagnesium bromide **7b** to afford 1.75 gr of 2,2-dimethylpent-3-enylphenone (**8j**) (87%) as a colorless oil.^{1}HNMR (600 MHz, $CDCl_3$, Me_4Si), mixture of isomers (75:25): δ 7.91(dm, J = 7.2 Hz, 2H, Ar-*H*, *Z* isomer); 7.88(dm, J = 7.2 Hz, 2H, Ar-*H*, *E* isomer); 7.50 (m, 3H, Ar-*H,* both isomers); 7.41 (m, 3H, Ar-*H*, both isomers); 5.52 (dq, *J* = 15.6, 1.8 Hz, 1H, C*H*=CHCH$_3$, *E* isomer); 5.42 (dq, *J* = 12.0, 1.8 Hz, 1H, C*H*=CHCH$_3$, *Z* isomer); 5.33 (dq, *J* = 15.6, 6.0 Hz, 1H, CH=C*H*CH$_3$, *E* isomer); 5.31 (dq, *J* = 12.0, 7.2 Hz, 1H, CH=C*H*CH$_3$, *Z* isomer);3.08 (s, 2H, CO-CH_2, *Z* isomer); 2.91 (s, 2H, CO-CH_2, *E* isomer); 1.68 (dd, *J* = 7.2, 1.8 Hz, 1H, CH=C*H*CH$_3$, *Z* isomer); 1.57 (dd, *J* = 6.0, 1.8 Hz, 1H, CH=C*H*CH$_3$, *E* isomer); 1.27 (s, 6H, CH$_2$-(CH_3)$_2$-CH, *Z* isomer), 1.13 (s, 6H, CH$_2$-(CH_3)$_2$-CH, *E* isomer).^{13}C{^{1}H}NMR (151 MHz; $CDCl_3$, Me_4Si), mixture of isomers (75:25)**:** 199.9 (Cq, *E* isomer); 199.5 (Cq, *Z* isomer); 140.4 (CH, *E* isomer); 138.9 (CH, *Z* isomer); 138.6 (Cq,*E* isomer); 138.4 (Cq, *Z* isomer); 132.8 (2 x CH, *Z* isomer); 132.7 (2 x CH, *E* isomer); 128.5 (2 x CH, *Z* isomer); 128.5 (2 x CH,*E* isomer);128.4 (CH, *E* isomer); 128.2 (CH, *Z* isomer); 123.0 (CH, *Z* isomer); 121.0 (CH, *E* isomer); 50.2 (CH$_2$, *Z* isomer); 50.0 (CH$_2$, *E* isomer); 36.1 (Cq, *Z* isomer); 36.1 (Cq, *E* isomer); 29.3 (CH$_3$,*Z* isomer), 27.9 (CH$_3$, *E* isomer), 18.0 (2 x CH$_3$,*E* isomer), 14.4 (2 x CH$_3$, *Z* isomer).

4,4-Dimethylhept-5-en-2-one (8k) Following the described procedure, 0.98 gr (10.0 mmol) of mesityl oxide **6i** (4-methylpent-3-en-2-one) were reacted with CuI and propenylmagnesium bromide **7b** to afford 0.97 gr of 4,4-dimethylhept-5-en-2-one **8k** (69%) as a colorless oil. ^{1}HNMR (600 MHz, $CDCl_3$, Me_4Si), mixture of isomers (60:40): δ 5.52 (dq, *J* = 15.6, 1.8 Hz, 1H, C*H*=CHCH$_3$, *E* isomer); 5.34-5.38 (m, 3H, C*H*=CHCH$_3$, *Z* isomer, CH=C*H*CH$_3$, *E* and *Z* isomer); 2.53 (s, 2H, CO-CH_2, *Z* isomer); 2.37 (s, 2H, CO-CH_2, *E* isomer); 2.11 (s, 2H, CO-CH_3, *Z* isomer); 2.07 (s, 2H, CO-CH_3, *E* isomer); 1.71 (dd, *J* = 6.0, 3.0 Hz, 1H, CH=C*H*CH$_3$, *Z* isomer); 1.65 (dd, *J* = 6.6, 1.2 Hz, 1H, CH=C*H*CH$_3$, *E* isomer); 1.20 (s, 6H, CH$_2$-(CH_3)$_2$-CH, *Z* isomer), 1.07 (s, 6H, CH$_2$-(CH_3)$_2$-CH, *E* isomer). ^{13}C{^{1}H} NMR (151 MHz; $CDCl_3$, Me_4Si), mixture of isomers (75:25):208.8 (Cq, *E* isomer); 208.5 (Cq, *Z* isomer); 140.0 (CH, *E* isomer); 138.5 (CH, *Z* isomer); 123.6 (CH, *Z* isomer); 121.4 (CH, *E* isomer); 56.0 (CH$_2$, *Z* isomer); 55.8 (CH$_2$, *E* isomer); 35.8 (Cq, *Z* isomer); 35.4 (Cq, *E* isomer); 32.4 (CH$_3$, *Z* isomer), 32.0 (CH$_3$, *E* isomer), 29.2 (CH$_3$, *Z* isomer), 27.7 (CH$_3$, *E* isomer), 18.1 (2 x CH$_3$, *E* isomer), 14.4 (2 x CH$_3$, *Z* isomer).

(2S,5R) and(2R,5R)-5-Methyl-2-(2,2-dimethylprop-2-enyl)cyclohexanone (8l) Following the described procedure, 1.52 gr (10.0 mmol) of commercially available *R*-pulegone (4-methylpent-3-en-2-one) were reacted with CuI and vinylmagnesium bromide **7a** to afford 1.49 gr of (2S,5R) and(2R,5R)-5-methyl-2-(2,2-dimethylprop-2-enyl)cyclohexanone **8l** (83%) as a colorless oil. ^{1}HNMR (600 MHz, $CDCl_3$, Me_4Si):(isomer A) δ 5.95 (ddd, *J* = 16.3, 10.8, 1.1 Hz, 1H, C*H*=CH_2), 4.98 – 4.88 (m, 2H, CH=C*H*$_2$), 2.45 (dd, *J* = 13.0, 5.5 Hz, 1H, CH-C(H)*H*-CO), 2.25 (m, 2H, CO-C*H,* CO-CH-C(H)*H*), 2.00 (m, *J* = 2H, CH-C(H)*H*-CO with CO-CH-C(H)*H*), 1.88 – 1.83 (m, 2H, CH-C*H*$_2$-CH_2-CH), 1.56 (m, 1H, CH_3-C*H*), 0.98 (d, *J* = 6.2 Hz, 6H, CH-C-(C*H*$_3$)$_2$), 0.92 (d, *J* = 7.0 Hz, 3H, CH-C*H*$_3$). (isomer B)δ 5.94 (ddd, *J* = 16.3, 10.8, 1.1 Hz, 1H, C*H*-CH_2), 4.98 – 4.88 (m, 2H, CH=C*H*$_2$), 2.18 (m, 1H, CH-C(H)*H*-CO), 2.10 – 2.02 (m, 2H, CH-C(H)*H*-CO), 1.86 (m, 2H, CH-C*H*$_2$-CH_2-CH), 1.80 – 1.70 (m, 1H, CH_3-C*H*), 1.40 (qdd, *J* = 12.9, 3.0, 1.1 Hz, 1H, CH-C(H)*H*-CH_2), 1.30 (qd, *J* = 13.2, 12.8, 2.7 Hz, 1H, CH-C(H)*H*-CH_2), 1.16 – 1.04 (m, 9H, CH-C*H*$_3$ with CH-C-(C*H*$_3$)$_2$). ^{13}C{^{1}H}NMR (151 MHz; $CDCl_3$, Me_4Si): (mixture of isomers):δ 212.6 (Cq), 211.6 (Cq), 147.4 (CH), 147.2 (CH), 111.3 (CH_2), 111.0 (CH_2), 58.9 (CH), 58.8 (CH), 52.5 (CH_2), 50.4 (CH_2), 38.4 (CH), 37.9 (Cq), 36.4 (Cq), 34.7 (CH2), 32.7 (CH), 31.3 (CH_2), 29.0 (CH_2), 25.9 (CH), 25.4 (CH), 25.0 (CH2), 24.3 (CH_3), 23.7 (CH_3), 22.4 (CH_3), 19.8 (CH_3).

General Procedures for the Synthesis of γ,δ-unsaturated *N*-arylsulfonylhydrazones (10, 11, 12)To a vigorously stirred suspension of arylsulfonylhydrazide **9** (5.6 mmol, 1.12eq) in MeOH (3.0 mL); the appropriate ketone or aldehyde **8** (5.0 mmol, 1.0 eq) was added dropwise. The mixture was reacted to completion (about 18 h); then cooled to 0 °C. When the product precipitated it was removed by filtration and used without any further purification, otherwise the solvent was removed under reduced pressure and the crude purified by flash chromatography on deactivated silica gel (PE/AcOEt 90/10) to afford in both case the *N*-arylsulfonylhydrazone (**10** when tosylhydrazone, **11** when phenylsulfonylhydrazone, **12** when mesitylsulfonylhydrazone) as a mixture of isomers (precipitation usually afforded one single stereoisomer or a mixture clearly enriched in only one of the possible stereoisomer).

2,2-Dimethylbut-3-enylphenone-*N*-tosylhydrazone(10a)Following the described procedure 2,2-dimethylbut-3-enylphenone **8a**, (0.95 g, 5.0 mmol) was reacted with *N*-tosylhydrazide **9a** (1.00. g, 5.4 mmol) in methanol (3.0 mL) to obtain 1.03 g (2.9 mmol) of 2,2-dimethylbut-3-enylphenone-*N*-tosylhydrazone(**10a**) (mixture of isomers) as a white powder (58%). ^{1}HNMR (600 MHz, $CDCl_3$, Me_4Si):*(major isomer)* δ 7.89 (d, *J* = 8.3 Hz, 2H, Ar-*H*), 7.87 (s, 1H, N-*H*), 7.49

(dm, *J* = 6.3, 1H, Ar-*H*), 7.35-7.29 (m, 5H, Ar-*H*), 5.58 (dd, *J* = 17.5, 10.6 Hz, 1H, C*H*=CH_2), 4.97 (dd, *J* = 17.5, 0.9 Hz, 1H, CH=CH_2*H trans*), 4.88 (dd, *J* = 10.6, 0.9 Hz, 1H, CH=CH_2*H cis*), 2.67 (s, 2H, N=C(Ar)-CH_2), 2.44 (s, 3H, Ar-CH_3), 0.91 (s, 6H, C(CH_3)$_2$). (minor isomer) δ 7.78 (d, *J* = 8.3 Hz, 2H, Ar-*H*), 7.54 (s, 1H, N-*H*), 7.42-7.36 (m, 5H, Ar-*H),* 7.04 – 7.00 (m, 2H, Ar-*H*), 5.54 (dd, *J* = 17.5, 10.7 Hz, 1H, C*H*=CH_2), 4.67 (dd, *J* = 17.4, 1.3 Hz, 1H, CH=CH_2*H trans*), 4.60 (dd, *J* = 10.7, 1.2 Hz, 1H, CH=CH_2*H cis*), 2.53 (s, 2H, s, 2H, N=C(Ar)-CH_2), 2.43 (s, 3H, Ar-CH_3), 0.85 (s, 6H, C(CH_3)$_2$).^{13}C{^{1}H}NMR (151 MHz; $CDCl_3$, Me_4Si):*(major isomer)* δ 155.2 (Cq), 146.8 (CH), 144.2 (Cq), 138.6 (Cq), 135.5 (Cq), 129.6 (CH)129.6 (2 x CH), 128.4 (2 x CH), 128.2 (2 x CH), 127.0 (2 x CH), 113.4 (CH_2), 39.6 (CH_2), 38.0 (Cq), 27.9 (CH_3), 21.8 (2 x CH_3). (*minor isomer)*156.8 (Cq), 147.2 (CH), 144.0 (Cq), 139.2 (Cq), 136.7 (Cq), 129.8 (CH), 129.5 (2 x CH), 128.3 (2 x CH), 128.0 (2 x CH), 127.2 (2 x CH), 110.5 (CH_2), 50.4(CH_2), 37.4 (Cq) 27.2 (CH_3), 21.7(2 x CH_3). HRMS (ESI) m/z: $[M + H]^+$ Calcd. for$C_{20}H_{24}N_2O_2S$357.1637; found357.1640.

2,2-Dimethylbut-3-enylnaphtone-*N*-tosylhydrazone (10b)Following the described procedure 2,2-dimethylbut-3-enylnaphtone **8b** (1.02 g, 4.3 mmol) was reacted with *N*-tosylhydrazide **9a** (0.87g, 4.7 mmol) in methanol (6.0 mL) refluxed at 50°C overnight. The reaction was then cooled to rt to obtain 1.01 g (2.5 mmol) of 2,2-dimethylbut-3-enylnaphtone-*N*-tosylhydrazone (**10b**) (only one isomer found) as a white powder (58%, PE/EE 7/3). ^{1}HNMR (600 MHz, $CDCl_3$, Me_4Si): δ 7.99 (s, 1H, N-*H*), 7.93 (dt, *J* = 8.3, 1.7 Hz, 2H, Ar-*H*), 7.90 (d, *J* = 1.3 Hz, 1H, Ar-*H*), 7.83 – 7.80 (m, 2H, Ar-*H*), 7.78 (d, *J* = 8.7 Hz, 1H, Ar-*H*), 7.74 (dd, *J* = 8.6, 1.8 Hz, 1H, Ar-*H*), 7.51-7.46 (m, 2H), 7.36 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 5.64 (dd, *J* = 17.5, 10.6 Hz, 1H, C*H*=CH_2), 5.00 (dd, *J* = 17.5, 0.7 Hz, 1H, CH=CH_2*H trans*), 4.90 (dd, *J* = 10.7, 0.8 Hz, 1H, CH=CH_2*H cis*), 2.79 (s, 2H, N=C(Ar)-CH_2), 2.45 (s, 3H, Ar-CH_3), 0.95 (s, 6H, C(CH_3)$_2$).^{13}C{^{1}H}NMR (151 MHz; $CDCl_3$, Me_4Si): δ 154.7 (Cq), 146.9 (CH), 144.3 (Cq), 136.0 (Cq), 135.5 (Cq), 133.9 (Cq), 132.9 (Cq), 129.6 (2 x CH), 128.7 (CH), 128.3 (2 x CH), 128.2 (CH), 127.7 (CH), 126.9 (CH), 126.9 (CH), 126.7 (CH), 124.4 (CH), 113.4 (CH_2), 39.4 (CH_2), 38.1 (Cq), 28.0 (CH_3), 21.8 (2 x CH_3).HRMS (ESI) m/z: $[M + H]^+$ Calcd. for$C_{24}H_{26}N_2O_2S$407.1793; found407.1799.IR ν_{max} (neat)/ cm^{-1}: 3057, 2958, 1599, 1445, 1179.

2,2-Dimethylbut-3-enyl-*m*-tolyl ketone-*N*-tosylhydrazone (10c)Following the described procedure 2,2-dimethylbut-3-enyl-*m*-tolyl ketone **8c** (0.46 g, 2.3 mmol) was reacted with *N*-tosylhydrazide **9a** (0.47 g, 2.5 mmol) in methanol (2 mL) to obtain 0.366 g (1.0 mmol) of 2,2-dimethylbut-3-enyl-*m*-tolyl ketone-*N*-tosylhydrazone **10c** (only one isomer found) as a white

powder (43%, PE/EE 7/3). ^{1}HNMR (600 MHz, $CDCl_3$, Me_4Si): δ 7.90 (dt, *J* = 8.4, 1.8 Hz, 2H, Ar-*H*), 7.85 (s, 1H, N-*H*), 7.34 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 7.28 (m, 2H, Ar-*H*), 7.19 (t, *J* = 7.8 Hz, 1H, Ar-*H*), 7.15 (bd, *J* = 7.8 Hz, 1H, Ar-*H*), 5.58 (dd, *J* = 17.4, 10.8 Hz, 1H, C*H*=CH_2), 4.99 (dd, *J* = 17.4, 0.6 Hz, 1H, CH=CH_2*H trans*), 4.90 (dd, *J* = 10.8, 0.6 Hz, 1H, CH=CH_2*H cis*), 2.65 (s, 2H, N=C(Ar)-CH_2), 2.44 (s, 3H, Ar-CH_3), 2.34 (s, 3H, Ar-CH_3), 0.89 (s, 6H, C(CH_3)$_2$).^{13}C{^{1}H}NMR (151 MHz; $CDCl_3$, Me_4Si): δ 155.3 (Cq), 146.9 (CH), 144.2 (Cq), 138.6 (Cq), 137.9 (Cq), 135.5 (Cq), 130.3 (CH), 129.5 (CH), 128.3 (2 x CH), 128.2 (CH), 127.7 (CH), 124.2 (CH), 113.4 (CH_2), 39.7 (CH_2), 37.9 (Cq), 27.9 (CH_3), 21.7 (CH_3), 21.6 (2 x CH_3). Mp: 120-123°C. IR ν_{max} (neat)/ cm^{-1}: 3284, 3186, 2961, 1641, 1597, 1341, 1164, 792. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for$C_{21}H_{26}N_2O_2S$371.1793; found371.1789.

2,2-Dimethylbut-3-enyl-*p*-tolyl ketone-*N*-tosylhydrazone (10d)Following the described procedure 2,2-dimethylbut-3-enyl-*p*-tolyl ketone **8d** (1.01 g, 5.0 mmol) was reacted with *N*-tosylhydrazide **9a** (1.04 g, 5.6 mmol) in methanol (2 mL) to obtain 1.48 g (4.0 mmol) of 2,2-dimethylbut-3-enyl-*p*-tolyl ketone-*N*-tosylhydrazone **10d** as a white powder (80%, PE/EE 7/3). ^{1}HNMR (600 MHz, $CDCl_3$, Me_4Si): (mixture of isomers)δ 59 : 41*)* 7.87 (d, *J* = 7.8 Hz, 2H, Ar-*H*, major isomer), 7.78 (d, *J* = 8.4 Hz, 2H, Ar-*H*, minor isomer), 7.52 (bs, 1H, N-*H*), 7.40 (d, *J* = 8.4 Hz, 2H, Ar-*H*, major isomer), 7.33 (d, *J* = 8.4 Hz, 2H, Ar-*H*, minor isomer), 7.31 (d, *J* = 7.8 Hz, 2H, Ar-*H*, minor isomer),7.22 (d, *J* = 7.8 Hz, 2H, Ar-*H*, minor isomer), 7.19 (d, *J* = 7.8 Hz, 2H, Ar-*H*, major isomer), 7.11 (d, *J* = 7.8 Hz, 2H, Ar-*H*, major isomer), 6.91 (d, *J* = 8.4 Hz, 2H, Ar-*H*, major isomer), 5.58 (dd, *J* = 14.4, 10.8 Hz, 1H, C*H*=CH_2, major isomer), 5.56 (dd, *J* = 15.0, 10.8 Hz, 1H, CH=CH_2, minor isomer), 4.97 (d, *J* = 16.8 Hz, 1H, CH=CH_2 , *H trans,* major isomer), 4.88 (dd, *J* = 10.8, 1.2 Hz, 1H, CH=CH_2 , *H cis,* major isomer), 4.68 (dd, *J* = 17.4, 1.2 Hz, 1H, CH=CH_2 , *H trans,* minor isomer), 4.61 (dd, *J* = 10.8, 1.2 Hz, 1H, CH=CH_2 , *H cis,* minor isomer), 2.92 (s, 2H, N=C-CH_2, minor isomer), 2.64 (s, 2H, N=C-CH_2, major isomer), 2.44 (s,3H Ar-CH_3, major isomer), 2.43 (s,3H Ar-CH_3, minor isomer), 2.36 (s, 3H Ar-CH_3, minor isomer), 2.33 (s,3H Ar-CH_3, major isomer), 0.91 (s, 6H, C(CH_3)$_2$, major isomer), 0.84 (s, 6H, C(CH_3)$_2$, minor isomer).^{13}C{^{1}H}NMR (151 MHz; $CDCl_3$, Me_4Si): (mixture of isomers 59 : 41) δ 156.4 (Cq), 156.1 (Cq), 147.3 (CH), 146.9 (CH), 144.2 (Cq), 143.9 (Cq), 139.9 (Cq), 139.7 (Cq), 135. 8 (Cq), 135. 5 (Cq), 130.6 (2 x CH), 130.2 (2 x CH), 129.6 (2 x CH), 129.6 (2 x CH), 129.2 (2 x CH), 129.1 (2 x CH), 128.5 (2 X CH), 128.2 (2 X CH), 128.0 (2 X CH), 127.1 (Cq), 126.9 (Cq), 113.4 (CH_2), 110.4 (CH_2), 50.3 (CH_2), 39.5 (CH_2), 37.9 (Cq), 37.3 (Cq), 28.0 (CH_3), 27.4 (CH_3), 27.2 (CH_3),

21.8 (2 x CH_3), 21.7 (2 x CH_3).HRMS (ESI) m/z: $[M + H]^+$ Calcd. for$C_{21}H_{27}N_2O_2S$371.1793; found 371.1796.

2,2-Dimethylbut-3-enyl-*o*-tolyl ketone-*N*-tosylhydrazone (10e)Following the described procedure 2,2-dimethylbut-3-enyl-*o*-tolyl ketone **8e** (1.01 g, 5.0 mmol) was reacted with *N*-tosylhydrazide **9a** (1.04 g, 5.6 mmol) in methanol (2 mL) to obtain 1.48 g (4.0 mmol) of 2,2-dimethylbut-3-enyl-*o*-tolyl ketone-*N*-tosylhydrazone **10e** as a white powder (56%, PE/EE 7/3).^{1}HNMR (600 MHz, $CDCl_3$, Me_4Si): δ 7.89 (bs, 1H, N-*H*), 7.83 (d, *J* = 8.3 Hz, 2H, Ar-*H*), 7.31 (d, *J* = 7.8 Hz, 2H, Ar-*H*), 7.17 (dt, *J* = 7.8, 1.6 Hz, 2H, Ar-*H*), 7.10 (m, 3H, Ar-*H*), 5.68 (dd, *J* = 17.4, 10.8 Hz, 1H, C*H*=CH_2), 5.01 (dd, *J* = 17.4, 0.6 Hz, 1H, CH=CH_2*H trans*), 4.92 (dd, *J* = 10.8, 0.6 Hz, 1H, CH=CH_2*H cis*), 2.64 (s, 2H, N=C(Ar)-CH_2), 2.44 (s, 3H, Ar-CH_3), 2.03 (s, 3H, Ar-CH_3), 0.88 (s, 6H, C(CH_3)$_2$). ^{13}C{^{1}H}NMR (151 MHz; $CDCl_3$, Me_4Si): 156.7 (Cq), 146.7 (CH), 144.2 (Cq), 139.1 (Cq), 136.0 (Cq), 135.8 (Cq), 131.3 (CH), 129.6 (2 x CH), 128.5 (CH), 128.4 (2 x CH), 125.5 (CH), 113.2 (CH_2), 43.3 (CH_2), 38.5 (Cq), 27.7 (CH_3), 21.7 (2 x CH_3), 20.5 (CH_3). Mp: 98-102 °C. IR ν_{max} (neat)/ cm^{-1}: 3280, 3179, 2960, 1645, 1598, 1340, 1167, 768. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for$C_{21}H_{26}N_2O_2S$371.1793; found 371.1797.

2,2-Dimethylbut-3-enyl-*m*-methoxyphenone-*N*-tosylhydrazone (10f)Following the described procedure, 2,2-dimethylbut-3-enyl-*m*-methoxyphenone **8f** (0.48 g, 2.2 mmol) was reacted with *N*-tosylhydrazide **9a** in methanol (0,45 g, 2.4 mmol) to obtain (0.64 g, 1.5 mmol) of 2,2-dimethylbut-3-enyl-*m*-methoxyphenone-*N*-tosylhydrazone **10f** as a white powder (70%,). ^{1}HNMR (600 MHz, $CDCl_3$, Me_4Si: *(*mixture of isomers 66 : 33*)* δ 7.95 (bs, 1H, N-*H,* major isomer), 7.89 (d, *J* = 8.4, Hz, 2H, Ar-*H*, major isomer), 7.78 (d, *J* = 8.4 Hz, 2H, Ar-*H*, minor isomer), 7.61 (bs, 1H, N-*H,* minor isomer), 7.29 (m, 2H, Ar-*H*, both isomers), 7.20 (t, *J* = 7.8 Hz, 1H, Ar-*H*, major isomer), 7.07 (dm, J = 7.8 Hz, 1H, Ar-H, major isomer), 7.03 (m, 1H, Ar-H, major isomer), 6.57 (dt, J = 7.2, 0.6 Hz, 1H, Ar-H, minor isomer), 6.52 (m, 1H, Ar-*H*, minor isomer), 5.58 (dd, *J* = 17.4, 10.8 Hz, 1H, C*H*=CH_2, major isomer), 5.52 (dd, *J* = 17.4, 10.2 Hz, 1H, CH=CH_2, major isomer), 4.98 (d, *J* = 17.4 Hz, 1H, CH=CH_2 , *H trans,* major isomer), 4.86 (d, *J* = 10.2 Hz, 1H, CH=CH_2 , *H cis,* major isomer), 4.67 (dd, *J* = 17.4, 1.8 Hz, 1H, CH=CH_2 , *H trans,* minor isomer), 4.61 (dd, *J* = 10.8, 1.2 Hz, 1H, CH=CH_2 , *H cis,* minor isomer), 3.78 (s, 3H, OCH_3, minor isomer), 3.77 (s, 3H, OCH_3, minor isomer), 2.64 (s, 2H, N=C-CH_2, major isomer), 2.51 (s, 2H, N=C-CH_2, minor isomer), 2.42 (s, 3H Ar-CH_3, both isomers), 0.90 (s, 6H, C(CH_3)$_2$, major

isomer), 0.85 (s, 6H, C(CH_3)$_2$, minor isomer). $^{13}C\{^1H\}$NMR (151 MHz; $CDCl_3$, Me_4Si): *(*mixture of isomers) δ 160.3 (Cq), 159.4 (Cq), 156.0 (Cq), 154.9 (Cq), 147.2 (CH), 146.8 (CH), 144.2 (Cq), 144.0 (Cq), 140.0 (Cq), 135.7 (Cq), 135.5 (Cq), 134.9 (Cq), 130.8 (CH), 129.6 (2 X CH), 129.5 (2 x CH), 128.2 (2 x CH), 128.0 (2 x CH), 119.6 (CH), 119.1 (CH), 115.2 (CH), 115.0 (CH), 113.3 (CH_2), 112.9 (CH), 112.5 (CH), 110.5 (CH_2), 55.4 (CH_3), 55.3 (CH_3), 50.3 (CH_2), 39.6 (CH_2), 38.1 (Cq), 38.0 (Cq), 27.9 (CH_3), 27.2 (CH_3), 21.7 (2 x CH_3), 21.7 (2 x CH_3).HRMS (ESI) m/z: [M + H]$^+$ Calcd. for$C_{20}H_{24}N_2O_2S$387.1742;found387.1739.

2,2-Dimethylbut-3-enyl-pyridyl ketone-*N*-tosylhydrazone (10g)Following the described procedure 2,2-dimethylbut-3-enyl-pyridyl ketone **8g** (0.57 g, 3.0 mmol) were reacted with *N*-tosylhydrazide **9a** (0.61 g, 3.3 mmol) in methanol (5.0 mL) refluxed at 50°C for 16h. The reaction was cooled to rt to obtain 0.450 g (1.26 mmol) of 2,2-dimethylbut-3-enyl-pyridyl ketone-*N*-tosylhydrazone **10g** as a white powder (42%, PE/AcOEt 98/2). ^{1}HNMR (600 MHz, $CDCl_3$, Me_4Si): (isomer A) δ 8.60 (dm, *J* = 4.9 Hz, 1H, Ar-*H*), 8.19 – 8.09 (bs, 1H, N-*H*), 7.87 (dd, *J* = 8.4, 1.9 Hz, 1H, Ar-*H*), 7.88-7.85 (m, 2H, Ar-*H*), 7.43 (d, *J* = 8.1 Hz, 1.1 Hz,1H, Ar-*H*), 7.43 (dt, *J* = 8.1, 1.1 Hz, 1H, Ar-*H*), 7.31 – 7.26 (m, 2H, Ar-*H*), 5.52 (dd, *J* = 17.5, 10.7 Hz, 1H, C*H*=CH_2), 4.62 (dd, *J* = 17.5, 1.2 Hz, 1H, CH=CH_2 , *H trans*), 4.52 (dd, *J* = 10.7, 1.2 Hz, 1H, CH=CH_2 , *H cis*), 2.65 (s, 2H, N=C-CH_2), 2.42 (s,3H Ar-CH_3), 0.77 (s, 6H, C(CH_3)$_2$).(isomer B) δ 8.49 (dd, *J* = 4.9, 1.8, 0.9 Hz, 1H, Ar-*H*), 8.19 – 8.09 (bs, 1H, N-*H*), 7.90 (dd, *J* = 8.4, 1.9 Hz, 1H, Ar-*H*), 7.64 (td, *J* = 7.7, 1.8 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 2H, Ar-*H*), 7.31 – 7.26 (m, 2H, Ar-*H*), 7.21 (ddd, *J* = 7.5, 4.8, 1.2 Hz, 1H, Ar-*H*), 5.66 (dd, *J* = 17.5, 10.6 Hz, 1H, C*H*=CH_2), 4.93 (dt, *J* = 17.4, 1.1 Hz, 1H, CH=CH_2 , *H trans*), 4.87 (dt, *J* = 10.7, 1.4 Hz, 1H, CH=CH_2 , *H cis*), 2.98 (2H, N=C-CH_2), 2.40 (s, 3H, Ar-CH_3), 0.92 (s, 6H, C(CH_3)$_2$). $^{13}C\{^1H\}$NMR (151 MHz; $CDCl_3$, Me_4Si):(mixture of isomers) δ 155.6 (Cq), 155.0 (Cq), 153.6 (Cq), 148.2 (CH), 147.8 (CH), 147.6 (CH), 147.5 (CH), 144.9 (Cq), 144.3 (Cq), 143.5 (Cq),137.4 (CH), 136.6 (Cq), 136.5 (Cq), 135.5 (Cq), 129.7 (2 x CH), 129.5 (2 x CH), 128.1 (2 x CH), 128.1 (2 x CH), 124.0 (CH), 124.0 (CH), 123.9 (CH), 121.3 (CH), 112.9 (CH_2), 110.4 (CH_2), 46.6 (CH_2), 38.15 (Cq), 37.6 (Cq), 37.3 (CH_2), 27.6 (CH_3), 26.9 (CH_3), 21.7 (2 x CH_3), 21.6 (2 x CH_3).HRMS (ESI) m/z: [M + H]$^+$ Calcd. for$C_{19}H_{24}N_3O_2S$358.1589;found 358.1586.

2-Phenyl-2-methylbut-3-enylphenone *N*-tosylhydrazone (10h)Following the described procedure 2-phenyl-2-methylbut-3-enylphenone, **8h** (1.27 gr, 5.1 mmol) was reacted with *N*-tosylhydrazide **9a** (1.05 gr, 5.6 mmol) in methanol (3.0 mL) to obtain 1.07 g (3.3 mmol) 2-phenyl-

2-methylbut-3-enylphenone *N*-tosylhydrazone **10h** (mixture of isomers) as a white powder (64%).^{1}HNMR (600 MHz, $CDCl_3$, Me_4Si), (mixture of isomers):δ 7.75 (d, *J* = 7.8 Hz, 1H, Ar-*H*), 7.69 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 7.47 (m, 1H, Ar-*H*), 7.33 (m, 4H, Ar-*H*), 7.18-7.26 (m, 4H, Ar-*H*), 7.08 (m, 3H, Ar-*H*), 6.73 (bs, 1H, N-*H,* isomer 1), 6.47 (bs, 1H, N-*H,* isomer 2), 6.00 (dd, *J* = 17.4, 10.8, 1H, C*H*=CH_2, isomer 1),5.97 (dd, *J* = 17.4, 10.2, 1H, C*H*=CH_2, isomer 2), 5.15 (d, *J* = 17.4, 1H, CH=CH_2, isomer 1), 5.13 (d, *J* = 10.8, 1H, CH=CH_2, isomer 1),4.90 (d, *J* = 17.4, 1H, CH=CH_2, isomer 2), 4.88 (d, *J* = 10.2, 1H, CH=CH_2, isomer 2), 3.18 (d, *J* = 13.2, 1H, N=C(Me)-CH_{2a}, isomer 1), 3.12 (d, *J* = 13.2, 1H, N=C(Me)-CH_{2b}, isomer 1), 3.07 (d, *J* = 13.8, 1H, N=C(Me)-CH_{2a}, isomer 2), 2.98 (d, *J* = 13.8, 1H, N=C(Me)-CH_{2b}, isomer 2), 2.46 (m, 3H, Ar-CH_3, both isomers), 1.27 (s,3H, CH_3, isomer 1), 1.16 (s, 3H, CH_3, isomer 2). ^{13}C{^{1}H}NMR (151 MHz; $CDCl_3$, Me_4Si),*(*mixture of isomers*)*: δ 156.2 (Cq), 155.5 (Cq), 146.1 (CH), 146.1 (Cq), 146.0 (Cq), 145.5 (Cq), 144.0 (Cq), 144.0 (Cq), 139.0 (Cq), 135.7 (Cq), 135.0 (Cq), 133.5 (Cq), 129.7 (2 x CH), 129.6 (2 x CH), 129.4 (2 x CH), 129.1 (2 x CH), 128.6 (2 X CH), 128.4 (2 X CH), 128.1 (2 X CH), 128.0 (2 X CH), 128.0 (2 X CH), 127.7 (CH), 127.5 (CH), 127.1 (CH), 126.9 (CH), 126.6 (CH), 126.3 (CH), 126.0 (CH), 126.0 (CH), 113.0 (CH_2), 112.3(CH_2), 49.1 (CH_2), 44.7 (Cq),44.3 (Cq), 39.4 (CH_2), 25.9 (CH_3), 25.3 (CH_3), 21.8 (CH_3), 21.8 (CH_3).HRMS (ESI) m/z: $[M + H]^+$ Calcd. for$C_{25}H_{27}N_2O_2S$419.1793; found419.1793.

4,4-Dimethylhex-5-en-2-one-*N*-tosylhydrazone (10i)Following the described procedure 4,4-dimethylhex-5-en-2-one, **8i** (0.640 gr, 5.1 mmol) was reacted with *N*-tosylhydrazide **9a** (1.05 gr, 5.6 mmol) in methanol (3.0 mL) to obtain 0.720 g (2.45 mmol) of 4,4-dimethylhex-5-en-2-one-*N*-tosylhydrazone **10i** (mixture of isomers) as a white powder (48%).^{1}HNMR (600 MHz, $CDCl_3$, Me_4Si):(major isomer) δ 7.82 (d, *J* = 8.3 Hz, 2H, Ar-*H*), 7.79 (bs, 1H, N-*H*), 7.29 (d, *J* = 7.9 Hz, 2H, Ar-*H*), 5.69 (dd, *J* = 17,3, 10.8 Hz, 1H, C*H*=CH_2),), 4.76 (dd, *J* = 10.8, 1.6 Hz, 1H, CH=CH_2 (*H cis)*), 4.73 (dd, *J* = 17.3, 1.2 Hz, 1H, CH=CH_2 (*H trans)*), 2.42 (s, 3H, Ar-CH_3), 2.21 (s, 2H, CH_2), 1.71 (s, 3H, N=C-CH_3), 0.84 (s, 6H, C(CH_3)$_2$). (minor isomer)δ 7.79 (d, *J* = 8.3 Hz, 2H, Ar-*H*), 7.5 (s, 1H, N-*H*), 7.34 (d, *J* = 7.9 Hz, 2H, Ar-*H*), 5.90 (dd, *J* = 17.3, 10.8 Hz, 1H, C*H*=CH_2), 4.98 (bd, *J* = 10.8 Hz, 1H, CH=CH_2 (*H cis)*), 4.94 (bd, *J* = 17.4 Hz, 1H, CH=CH_2 (*H trans)*), 2.41 (s, 3H, Ar-CH_3), 2.19 (s, 2H, CH_2), 1.91 (s, 3H, N=C-CH_3), 1.04 (s, 6H, C(CH_3)$_2$). ^{13}C{^{1}H}NMR (151 MHz; $CDCl_3$, Me_4Si): (mixture of isomers) δ 147.5 (CH), 144.0 (Cq), 135.5 (Cq), 130.1 (2 x CH), 129.5 (2 x CH), 128.4 (2 x CH), 128.2 (2 X CH), 128.1 (Cq), 110.9 (CH_2), 51.4 (CH_2), 37.2

(Cq), 27.8 (CH_3), 27.1 (CH_3), 26.9 (CH_3), 21.7 (CH_3), 18.0 (2 x CH_3).HRMS (ESI) m/z: $[M + H]^+$ Calcd. for$C_{15}H_{23}N_2O_2S$295.1480; found 295.1478.

2,2-dimethylpent-3-enylphenone-*N*-tosylhydrazone (10j)Following the described procedure 2,2-dimethylpent-3-enylphenone **8j** (1.01 g, 5.0 mmol) was reacted with *N*-tosylhydrazide **9a** (1.00. g, 5.4 mmol) in methanol (3.0 mL) to obtain 1.07 g (2.9 mmol) of 2,2-dimethylbut-3-enylphenone-*N*-tosylhydrazone(**10j**) (mixture of isomers) as a white powder (58%). ^{1}HNMR (600 MHz, d_6-DMSO, Me_4Si), (mixture of isomers)*:* δ 10.58 (s, 1H, NH, isomer 1), 10.56 (s, 1H, NH, isomer 2), 9.90 (s, 1H, NH, isomer 3), 9.89 (s, 1H, NH, isomer 4), 7.70-7.72m, 4H, Ar-*H*), 7.47 (m, 2H, Ar-*H*), 7.45 (m, 1H, Ar-*H*), 7.32-7.39 (m, 4H, Ar-*H*), 7.23-7.28 (m, 6H, Ar-*H*), 5.23 (dq, *J* = 15.6, 1.8 Hz, 1H, C*H*=CH-CH_3, isomer 1), 5.23 (dq, *J* = 12.0, 1.8 Hz, 1H, C*H*=CH-CH_3, isomer 2), 4.93-5.03 (bm, 2H, CH=C*H*CH_3*all isomers,* C*H*=CH-CH_3, isomer 3 and 4), 2.85 (s, 2H, N=C(Ar)-CH_2, isomers 1 and 2), 2.75 (s, 2H, N=C(Ar)-CH_2),isomers 3 and 4), 2.30 (s, 3H, Ar-CH_3, isomer 1 and 2), 2.29 (s, 3H, Ar-CH_3, isomer 3 and 4), 1.49 (dd, J = 6.6, 1.2 Hz, 1H, CH=CHCH_3, isomer 3), 1.47 (dd, J = 7.2, 1.8 Hz, 1H, CH=CHCH_3, isomer 1), 1.28 (m, 1H, CH=CHCH_3, isomer 2 and 4), 0.91 (s, 6H, C(CH_3)$_2$, isomer 1), 0.89 (s, 6H, C(CH_3)$_2$, isomer 4), 0.80 (s, 6H, C(CH_3)$_2$, isomer 2), 0.77 (s, 6H, C(CH_3)$_2$, isomer 3). ^{13}C{^{1}H}NMR (151 MHz; d_6-DMSO, Me_4Si):(mixture of isomers) δ 154.9 (Cq), 154.5 (Cq), 143.5 (CH), 143.4 (Cq), 143.2 (Cq), 140.9 (CH), 139.7 (Cq), 139.6 (CH), 138.8 (CH), 138.6 (CH), 136.8 (Cq), 136.6 (Cq), 136.5 (Cq),129.7 (CH), 129.5 (2 x CH), 129.2 (2 x CH), 129.0 (2 x CH), 128.8 (2 x CH), 128.6 (2 x CH), 128.5 (2 x CH), 128.3 (2 x CH), 128.2 (2 x CH), 128.0 (2 x CH), 127.6 (2 x CH), 127.6 (2 x CH), 127.2 (2 x CH), 127.1 (2 x CH), 122.8 (2 x CH), 120.1 (CH), 120.0 (CH), 50.7 (CH_2), 46.0 (CH_2), 38.3 (CH_2), 38.3 (CH_2), 38.0 (Cq), 37.6 (Cq), 29.2 (CH_3), 29.2 (CH_3), 27.7 (CH_3), 21.3 (CH_3), 17.9 (2 x CH_3), 17.8 (2 x CH_3), 14.3 (2 x CH_3), 14.2 (2 x CH_3).HRMS (ESI) m/z: $[M + H]^+$ Calcd. for$C_{21}H_{27}N_2O_2S$371.1793; found 371.1795.

4,4-Dimethylhept-5-enone-*N*-tosylhydrazone (10k)Following the described procedure 4,4-dimethylhept-5-en-2-one, **8k** (0.71 gr, 5.1 mmol) was reacted with *N*-tosylhydrazide **9a** (1.05 gr, 5.6 mmol) in methanol (3.0 mL) to obtain 1.01 g (3.3 mmol) of 4,4-dimethylhex-5-en-2-one-*N*-tosylhydrazone **10k** (mixture of isomers) as a white powder (64%).^{1}HNMR (600 MHz, d_6-DMSO, Me_4Si), (mixture of isomers):δ 9.90 (bs, 1H, N-*H,* isomer 1), 9.88 (bs, 1H, N-*H,* isomer 2), 7.62 (d, *J* = 8.4 Hz, 2H, Ar-*H,* both isomers), 7.33 (d, *J* = 8.4 Hz, 2H, Ar-*H*, isomer 1), 7.31 (d, *J* = 8.4 Hz, 2H, Ar-*H*, isomer 1), 5.29 (dq, *J* = 13,8, 1.8 Hz, 1H, C*H*=CHCH_3, isomer 1),), 5.10 (m, 3H,

C*H*=CHCH$_3$, isomer 2 and CH=C*H*CH$_3$, both isomers), 2.46 (m, 3H, Ar-C*H$_3$*, isomer 2), 2.33 (m, 3H, Ar-C*H$_3$*, isomer 1), 2.12 (s, 2H, N=C(Me)-C*H*$_2$, isomer 1), 2.02 (s, 2H, N=C(Me)-C*H*$_2$, isomer 2), 1.73 (s, 3H, N=C-C*H*$_3$, isomer 1), 1.69 (s, 3H, N=C-C*H*$_3$, isomer 2), 1.50 (m, 1H, CH=CHC*H*$_3$, isomer 1),), 1.45 (m, 3H, CH=CHC*H*$_3$, isomer 2),0.88 (s, 6H, C(C*H*$_3$)$_2$, isomer 1), 0.72 (s, 6H, C(C*H*$_3$)$_2$, isomer 2). ^{13}C{^{1}H}NMR (151 MHz; d$_6$-DMSO, Me$_4$Si), *(*mixture of isomers*)*: δ 157.8 (Cq), 157.6 (Cq), 143.4 (Cq), 141.1 (CH), 139.0 (CH), 136.9 (Cq), 129.7 (2 x CH), 129.7 (2 x CH), 128.1 (2 X CH), 128.1 (2 X CH), 123.3 (CH), 120.5 (CH), 51.4 (CH$_2$), 51.3 (CH$_2$),39.6 (Cq), 36.7 (Cq), 29.1 (CH$_3$), 27.7 (CH$_3$), 21.5 (CH$_3$), 19.5 (CH$_3$), 19.2 (CH$_3$), 18.2 (2 x CH$_3$), 14.5 (2 x CH$_3$).HRMS (ESI) m/z: [M + H]$^+$ Calcd. for$C_{16}H_{25}N_2O_2S$309.1637; found 309.1640.

(5*R*)-5-Methyl-2-(1,1-dimethylprop-2-enyl)cyclohexanone *N*-tosylhydrazone (10l)Following the described procedure pulegone derivative **8l**, (1.2g, 6.7 mmol) was reacted with *N*-tosylhydrazide **9a** (1.4 g, 7.5 mmol) in methanol (5.0 mL) to obtain 1.3 g (3.8 mmol) upon precipitation with water of pulegone tosylhydrazone **10l** as a white powder (57%). Only 2 isomer observed.^{1}HNMR (600 MHz, CDCl$_3$, Me$_4$Si): (mixture of 2 isomers 85/15), (major isomer) δ 7.84 (d, *J* = 8.2 Hz, 2H, Ar-*H*), 7.46 (s, 1H, N-*H*), 7.29 (d, *J* = 8.2 Hz, 2H, Ar-*H*), 5.83 (dd, *J* = 17.6, 10.8 Hz, 1H, C*H*=CH$_2$), 4.79 (dd, *J* = 17.6, 1.5 Hz, 1H, CH-C*H$_2$H trans*), 4.76 (dd, *J* = 10.8, 1.5 Hz, 1H, CH-C*H$_2$H cis*), 2.56 (dd, 1H, *J* = 13.5, 4.0 Hz, N=C-C(H)*H*-C(Me)H), 2.41 (s, 3H, Ar-C*H*$_3$),1.91-1.85 (m, 2H, CH-C*H*$_2$-CH$_2$-C(Me)H), 1.76 – 1.71 (m, 1H, C*H*-CH$_2$-CH$_2$-C(Me)H), 1.59 – 1.53 (m, 1H, CH$_2$-C(Me)*H*-CH$_2$), 1.41 (dd, 1H, *J* = 13.5, 11.5 Hz, N=C-C(H)*H*-C(Me)H), 1.22 (ddd, *J* = 14.5, 12.8, 4.0 Hz, 1H, CH-CH$_2$-C(H)*H*-C(Me)H), 1.03 (ddm, *J* = 13.5, 11.5, 1H, CH-CH$_2$-C(H)*H*-C(Me)H), 0.98 (s, 3H, C(CH$_3$) C*H*$_3$), 0.97 (s, 3H, C(CH$_3$) C*H*$_3$), 0.91 (d, *J* = 6.5 Hz, 3H, CH$_2$-CH-C*H*$_3$). (minor isomer)δ 7.79 (d, *J* = 8.2 Hz, 2H, Ar-*H*), 7.35 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 5.75 (dd, *J* = 17.3, 11.0 Hz, 1H, C*H*=CH$_2$), 5.60 (s, 1H, N-*H*), 4.76 (dd, 1H, *J* = 17.5, 1.5 Hz, CH-C*H$_2$H trans*), 4.75 (dd, 1H, *J* = 10.8, 1.5 Hz, CH-C*H$_2$H cis*), 2.44 (s, 3H, Ar-C*H*$_3$), 2.35 – 2.29 (m, 1H, N=C-C(H)*H*-C(Me)H), 2.15 (t, 1H, *J* = 5.8 Hz, N=C-C(H)*H*-C(Me)H), 1.95 – 1.83 (m, 2H, CH-C*H*$_2$-CH$_2$-C(Me)H), 1.78 – 1.67 (m, 2H, CH$_2$-C(Me)*H*-CH$_2$ with C*H*-CH$_2$-CH$_2$-C(Me)H), 1.36 – 1.27 (m, 1H, CH-CH$_2$-C(H)*H*-C(Me)H), 1.10 (d, 1H, *J* = 12.2 Hz, CH-CH$_2$-C(H)*H*-C(Me)H), 0.90 (s, 3H, C(CH$_3$)-C*H*$_3$), 0.89 (s, 3H, C(CH$_3$)-C*H*$_3$), 0.87 (d, *J* = 6.2 Hz, 3H, CH$_2$-CH-C*H*$_3$).^{13}C{^{1}H}NMR (151 MHz; CDCl$_3$, Me$_4$Si): (mixture of isomers), δ 162.1 (Cq), 148.0 (CH), 144.0 (Cq), 135.6 (Cq), 130.0 (CH), 129.5 (2 x CH), 128.5 (2 x CH), 128.4 (2 x CH), 110.9 (CH$_2$), 110.5 (CH$_2$), 53.9 (CH), 51.8 (CH), 39.7 (Cq), 38.8 (Cq), 36.2 (CH$_2$), 34.4 (CH$_2$), 34.0

(CH), 32.1 (Cq), 31.2 (Cq), 28.9 (CH_2), 27.0 (CH_2), 25.8 (CH_3), 25.4 (CH_3), 23.9 (CH_3), 22.2 (CH_3), 21.4 (CH_3),21.7 (CH_3).HRMS (ESI) m/z: $[M + H]^+$ Calcd. for$C_{19}H_{29}N_2O_2S$349.1950; found 349.1952.

2,2-Dimethylbut-3-enylphenone-*N*-phenylsulfonylhydrazone (11a)Following the described procedure 2,2-dimethylbut-3-enylphenone **8a** (0.38 g, 2.0 mmol) was reacted with phenylsulfonylhydrazide **9b** (0.38 g, 2.2 mmol) in methanol (2 mL) to obtain 1.13 g (3.5 mmol) of 2,2-dimethylbut-3-enylphenone-*N*-phenylsulfonylhydrazone **11a** (only one isomer found) as a white powder (50%). ^{1}HNMR (600 MHz, $CDCl_3$, Me_4Si):δ 8.04 – 7.99 (m, 2H, Ar-*H*), 7.88 (s, 1H, N-*H*), 7.63 (tt, *J* = 7.4, 1.8 Hz, 1H, Ar-*H*), 7.57 (ddt, *J* = 8.2, 6.7, 1.1 Hz, 2H, Ar-*H*), 7.48 (dt, *J* = 6.6, 1.7, 1.3 Hz, 2H, Ar-*H*), 7.37 – 7.28 (m, 3H, Ar-*H*), 5.57 (dd, *J* = 17.5, 10.6 Hz, 1H, C*H*=CH_2), 4.96 (dd, *J* = 17.5, 0.9 Hz, 1H, CH=CH_2*H trans*), 4.87 (dd, *J* = 10.6, 0.9 Hz, 1H, CH=CH_2,*H cis*), 2.70 – 2.64 (m, 2H, N=C(Ph)-CH_2), 0.91 – 0.88 (bs, 6H, C-(CH_3)$_2$).^{13}C{^{1}H}NMR (151 MHz; $CDCl_3$, Me_4Si): δ 155.4 (Cq), 146.8 (CH), 138.6 (Cq), 138.4 (Cq), 133.4 (CH), 129.7 (CH), 129.0 (2 x CH), 128.4 (2 x CH), 128.2 (2 x CH), 128.0 (2 x CH), 113.5 (CH_2), 39.7 (CH_2), 37.9 (Cq), 27.9 (2 x CH_3). HRMS (ESI) m/z: $[M + H]^+$ Calcd. for$C_{19}H_{22}N_2O_2S$ 343.1480; found 343.1481. IR ν_{max} (neat)/ cm^{-1}: 3059, 2956, 1641, 1445, 1349, 1160. m.p.: 104-107 °C.

4,4-Dimethylhex-5-en-2-one-*N*-phenylsulfonylhydrazone (11b)Following the described procedure 4,4-dimethylhex-5-en-2-one, **8i** (0.50 gr, 4.0 mmol) was reacted with *N*-phenylsulfonylhydrazide **9b** (0.770 gr, 4.5 mmol) in methanol (2.5 mL) to obtain 0.762 g (2.72 mmol) of 4,4-dimethylhex-5-en-2-one-*N*-phenylsulfonylhydrazone **11b** (mixture of isomers) as a white powder (68%).^{1}HNMR (600 MHz, $CDCl_3$, Me_4Si): (major isomer)δ 7.96 (d, *J* = 1.2 Hz, 2H, Ar-*H*), 7.95 (t, *J* = 1.7 Hz, 1H, Ar-*H*), 7.74 (bs, 1H, N-*H*), 7.57 (tt, *J* = 7.4, 1.2 Hz, 2H, Ar-*H*), 5.66 (dd, *J* = 17.4, 10.8 Hz, 1H, C*H*=CH_2), 4.73 (dd, *J* = 10.8 1.2 Hz, 1H, CH=CH_2, *H cis*), 4.71 (dd, *J* = 17.4, 1.3 Hz, 1H, CH=CH_2, *H trans*), 2.19 (s, 2H, N=C(Me)-CH_2), 1.72 (s, 3H, N=C-CH_3), 0.81 (s, 6H, C(CH_3)$_2$). (minor isomer)δ 7.96 (d, *J* = 1.2 Hz, 2H, Ar-*H*), 7.92 (t, *J* = 1.7 Hz, 1H, Ar-*H*), 7.74 (s, 1H, N-*H*), 7.59 (tt, *J* = 7.4, 1.2 Hz, 2H, Ar-*H*), 5.67 (dd, *J* = 17.4, 10.8 Hz, 1H, C*H*=CH_2), 4.96-4.81 (m, 2H, CH=CH_2), 2.19 (s, 2H, N=C(Me)-CH_2), 1.91 (s, 3H, N=C-CH_3), 1.02 (s, 6H, C(CH_3)$_2$). ^{13}C{^{1}H}NMR (151 MHz; $CDCl_3$, Me_4Si): (mixture of isomers) δ 156.9 (Cq), 156.8 (Cq), 147.4 (CH), (147.1 (CH), 138.5 (Cq), 133.1 (CH), 129.4 (2 x CH), 129.0 (2 x CH), 128.3 (CH), 128.2 (2 x CH), 128.0 (2 x CH), 112.9 (CH_2), 110.9 (CH_2), 51.4(CH_2), 43.8 (CH_2), 37.7

(Cq), 37.2 (Cq), 27.7 CH_3), 26.8 (CH_3), 26.3 (2 x CH_3), 18.2 (2 x CH_3).HRMS (ESI) m/z: $[M + H]^+$ Calcd. for$C_{14}H_{21}N_2O_2S$ 281.1324; found281.1322.

2,2-Dimethylbut-3-enylphenone-*N*-mesitylsulfonylhydrazone (12a)Following the described procedure 2,2-dimethylbut-3-enylphenone **8a** (0.75 g, 4.0 mmol) was reacted with *N*-mesitylsulfonylhydrazide **9c** (0.96 g, 4.5 mmol) in methanol (2.5 mL) to obtain 0.81 g (2.1 mmol) of 2,2-dimethylbut-3-enylphenone-*N*-2,4,6-mesitylsulfonylhydrazone **12a** (only one isomer found) as a white powder (53%, PE/EE 9/1). ^{1}HNMR (600 MHz, $CDCl_3$, Me_4Si): δ 7.93-7.96 (bs, 1H, N-*H*), 7.47 (dd, *J* = 8.0, 1.6 Hz, 2H, Ar-*H*), 7.34 – 7.25 (m, 3H, Ar-*H*), 6.97 (s, 2H, Ar-*H*), 5.78 (dd, *J* = 17.5, 10.6 Hz, 1H, C*H*=CH_2), 5.01 (d, *J* = 17.4 Hz, 1H, C*H*=CH_2*H trans*), 4.95 (dd, *J* = 10.8, 0.7 Hz, 1H, C*H*=CH_2 *H cis*), 2.71 (s, 6H, *orto* Ar-*CH_3*), 2.68 (s, 2H, N=C-C*H_2*), 2.30 (s, 3H, *para* Ar-*CH_3*), 0.97 (s, 6H, C(C*H_3*)$_2$). ^{13}C{^{1}H}NMR (151 MHz; $CDCl_3$, Me_4Si): δ 154.2 (Cq), 146.8 (CH), 143.0 (Cq), 140.6 (2 x Cq), 138.8 (Cq), 132.5 (Cq), 131.9 (2 x CH), 129.3 (CH), 128.3 (2 x CH), 127.0 (2 x CH), 113.0 (CH_2), 39.0 (CH_2), 38.1(Cq), 28.0 (CH_3), 23.6 (2 x CH_3), 21.1 (2 x CH_3).Mp: 76-82°C. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for$C_{22}H_{28}N_2O_2S$385.1950; found 385.1954. IR ν_{max} (neat)/ cm^{-1}: 3201, 2962, 1602, 1444, 1377, 1159.

2,2-Dimethylbut-3-enylnaphtone-*N*-mesitylsulfonylhydrazone (12b)Following the described procedure 2,2-dimethylbut-3-enylnaphtone **8b**, (0.480 g, 2.0 mmol) was reacted with *N*-mesitylsulfonylhydrazide **9c** (0.47 g, 2.2 mmol) in methanol (2 mL) at rt to obtain 0.312 g of 2,2-dimethylbut-3-enylnaphtone-*N*-2,4,6-mesitylsulfonylhydrazone (**12b**) (0.72 mmol) as a white powder (36%, PE/AcOEt 99/1). ^{1}HNMR (600 MHz, $CDCl_3$, Me_4Si): δ 8.02 (s, 1H, N-*H*), 7.89 (m, 1H, Ar-*H*), 7.87 (m, 1H, Ar-*H*), 7.80 (m, 2H, Ar-*H*), 7.75 (dd, *J* = 8.7, 3.3 Hz, 1H, Ar-*H*), 7.66 (m, 1H, Ar-*H*) 7.47 (m, 1H, Ar-*H*), 6.99 (s, 2H, Ar-*H*), 5.83 (dd, *J* = 17.4, 10.6 Hz, 1H, C*H*=CH_2), 5.07 (d, *J* = 17.4 Hz, 1H, C*H*=CH_2*H trans*), 4.99 (dd, *J* = 10.8, 0.7 Hz, 1H, C*H*=CH_2 *H cis*), 2.80 (s, 2H, N=C-C*H_2*), 2.75 (s, 6H, *orto* Ar-*CH_3*), 2.31 (s, 3H, *para* Ar-*CH_3*), 1.01 (s, 6H, C(C*H_3*)$_2$). ^{13}C{^{1}H}NMR (151 MHz; $CDCl_3$, Me_4Si): 153.9 (Cq), 146.9 (CH), 143.1 (Cq), 140.6 (2 x Cq), 136.2 (Cq), 133.8 (Cq), 132.9 (Cq), 132.5 (Cq), 132.0 (2 x CH), 128.6 (CH), 128.0 (CH), 127.7 (CH), 126.8 (CH), 126.7 (Cq), 126.4 (CH), 124.5 (CH), 113.2 (CH_2), 39.0 (CH_2), 38.2 (Cq), 28.1 (CH_3), 23.5 (CH_3), 21.2 (2 x CH_3). Mp: 59-65°C. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for$C_{26}H_{30}N_2O_2S$435.2106; found 435,2110 .IR ν_{max} (neat)/ cm^{-1}: 3228, 2960, 1602, 1467, 1376, 1331, 1187, 1161, 1052.

2,2-Dimethylbut-3-enyl-*p*-tolyl ketone-*N*-mesitylsulfonylhydrazone (12c)Following the described procedure 2,2-dimethylbut-3-enyl-*p*-tolyl ketone **8d**, (0.85 g, 4.0 mmol) was reacted with *N*-mesitylsulfonylhydrazide **9c** (0.95 g, 4.5 mmol) in methanol (2 mL) to obtain 0.98 g (2.5 mmol) of 2,2-dimethylbut-3-enyl-p-tolyl ketone-*N*-mesitylsulfonylhydrazone **12c** as a white powder (62%, PE/AcOEt 98/2). ^{1}HNMR (600 MHz, $CDCl_3$, Me_4Si): (mixture of isomers 83 : 17).^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.93 (s, 1H, N-*H,* major isomer), 7.63 (bs, 1H, N-*H* minor isomer), 7.37 (d, *J* = 8.3 Hz, , 2H, Ar-*H*, minor isomer), 7.34 (d, *J* = 8.1 Hz, 2H, Ar-*H* major isomer), 7.22 (d, *J* = 7.8 Hz, 2H, Ar-*H*, both isomers), 7.09 (m, 4H, Ar-*H,* both isomers), 6.96 (d, *J* = 4.0 Hz, 2H, Mes-*H*, both isomers), 5.79 (dd, *J* = 17.4, 10.2 Hz, 1H, C*H*=CH_2 major isomer), 5.54 (dd, *J* = 17.4, 10.2 Hz, 1H, C*H*=CH_2 minor isomer), 5.02 (dd, *J* = 17.4, 0.6 Hz, 1H, CH=C*H*$_2$, *H trans* major isomer), 4.96 (dd, *J* = 10.2, 1.2 Hz, 1H, CH=C*H*$_2$, *H cis* major isomer) 4.66 (dd, *J* = 17.4, 1.2 Hz, 1H, CH=C*H*$_2$, *H trans,* minor isomer), 4.59 (dd, *J* = 10.8, 1.2 Hz, 1H, CH=C*H*$_2$, *H cis,* minor isomer), 2.70 (m, 12H Ar-CH_3, both isomers), 2.59 (s, 2H, N=C-C*H*$_2$, major isomer), 2.45 (s, 2H, N=C-C*H*$_2$, major isomer), 2.31 (s, 3H, *p*-tolyl C*H*$_3$ major isomer), 2.30 (s, 3H, *p*-tolyl C*H*$_3$, minor isomer), 2.29 (s, 3H Ar-CH_3 major isomer), 2.29 (s, 3H Ar-CH_3,minor isomer), 0.97 (s, 6H, C(C*H*$_3$)$_2$, minor isomer), 0.76 (s, 6H, C(C*H*$_3$)$_2$ major isomer). ^{13}C{^{1}H}NMR (151 MHz; $CDCl_3$, Me_4Si): *(*mixture of isomers) δ154.7 (Cq), 154.3 (Cq), 147.0 (CH), 142.9 (CH), 140.6 (Cq), 140.5 (Cq), 139.4 (CH), 136.1 (CH), 132.6 (CH), 131.9 (2 x CH), 130.2 (2 x CH), 129.0 (2 x CH), 126.9 (2 x CH), 126.8 (2 x CH), 113.0 (CH_2), 110.4 (CH_2), 39.0 (CH_2), 38.1 (Cq), 37.7 (Cq), 36.2 (CH_2); 35.9 (CH); 28.0 (CH_3), 27.4 (CH_3), 23.6 (CH_3), 23.5 (CH_3), 21.3 (2 x CH_3) 21.1 (2 x CH_3).HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{23}H_{31}N_2O_2S$399.2106; found 399.2109.

2,2-Dimethylbut-3-enyl-*o*-tolyl ketone-*N*-mesitylsulfonylhydrazone (12d)Following the described procedure 2,2-dimethylbut-3-enyl-*o*-tolyl ketone **8e**, (0.40 g, 2.0 mmol) was reacted with *N*-mesitylsulfonylhydrazide **9c** (0.45 g, 2.2 mmol) in methanol (2 mL) to obtain 139 mg (0.35) of 2,2-dimethylbut-3-enyl-*o*-tolyl ketone-*N*-mesitylsulfonylhydrazone **12d** as a white powder that was immediately subjected to irradiation (15%, PE/AcOEt 98/2).^{941}H NMR (600 MHz, $CDCl_3$-*d*);δ 7.30 (m, 1H, Ar-*H*), 7.27 (m, 2H, Ar-*H*), 7.20 (m, 1H, Ar-*H*), 6.96 (s, 2H, Ar-*H*), 5.62 (dd, *J* = 17.5, 10.7 Hz, 1H, C*H*=CH_2), 4.70 (dd, *J* = 17.5, 1.3 H, 1H, CH=C*H*$_2$ *H trans*), 4.64 (dd, *J* = 10.7, 1.3 Hz, 1H, CH=C*H*$_2$ *H cis*), 2.57 (s, 2H, N=C(Ar)-C*H*$_2$),2.56 (s, 6H, 2 x Ar-C*H*$_3$), 2.31 (s, 3H, *o*-tolyl C*H*$_3$), 2.30 (s, 3H, Ar-C*H*$_3$), 0.90 (s, 6H, C(C*H*$_3$)$_2$).

4,4-Dimethylhex-5-en-2-one-*N*-mesitylsulfonylhydrazone (12e)Following the described procedure 4,4-dimethylhex-5-en-2-one, **8i** (0.630 g, 5.0 mmol) was reacted with *N*-mesitylsulfonylhydrazide **9c** (1.070 g, 5.00 mmol) in methanol (3.1 mL) to obtain 1,13 g (3.5 mmol) 4,4-dimethylhex-5-en-2-one-*N*-mesitylhydrazone **12e** (mixture of isomers) as a white powder (70%, PE/EE 95/5).^{1}HNMR (600 MHz, $CDCl_3$, Me_4Si): (major isomer)δ 7.37 (bs, 1H, N-*H*), 6.94 (s, 2H, Ar-*H*), 5.64 (dd, *J* = 17.4, 10.7 Hz, 1H, C*H*=CH_2), 4.74 (bd, *J* = 10.7, 1H, CH=CH_2, *H cis*), 4.70 (dd, *J* = 17.5, 1.2 Hz, 1H, CH=CH_2 *H trans*), 2.64 (s, 6H, *orto* Ar-CH_3), 2.28 (s, 3H, *para* Ar-CH_3), 2.13 (s, 2H, N=C(Me)-CH_2), 1.71 (s, 3H, N=C-CH_3), 0.79 (s, 6H, C(CH_3)$_2$). (minor isomer)δ 7.37 (bs, 1H, N-*H*), 6.97 (s, 2H, Ar-*H*), 5.82 (dd, *J* = 17.5, 10.7 Hz, 1H, C*H*=CH_2), 5.04 (d, *J* = 10.7, 1H, CH=CH_2, *H cis*), 5.02 (d, *J* = 17.5, 1H, CH=CH_2 *H trans*), 2.66 (s, 6H, *orto* Ar-CH_3), 2.29 (s, 3H, *para* Ar-CH_3), 1.89 (s, 2H, N=C(Me)-CH_2), 1.78 (s, 3H, N=C-CH_3), 1.09 (s, 6H, C(CH_3)$_2$). ^{13}C{^{1}H}NMR (151 MHz; $CDCl_3$, Me_4Si): (mixture of isomers) δ 154.6 (Cq), 147.5 (CH), 142.8 (Cq), 140.4 (2 x Cq), 140.2 (2 x Cq), 132.6 (Cq), 131.8 (2 x CH), 131.8 (2 x CH), 110.8 (CH_2), 51.3 (CH_2), 37.2 (Cq), 27.9 (Cq), 27.0 (2 x CH_3), 26.7 (2 x CH_3), 23.2 (CH_3), 21.0 (CH_3), 17.8 (2 x CH_3). HRMS (ESI) m/z: $[M + H]^+$ Calcd. for$C_{17}H_{27}N_2O_2S$323.1793; found 323.1794.

2,2-dimethylpent-3-enylphenone-*N*-mesitylsulfonylhydrazone (12f)Following the described procedure 2,2-dimethylpent-3-enylphenone **8j**, (1.01 g, 5.0 mmol) was reacted with *N*-mesitylsulfonylhydrazide **9c** (1.00. g, 5.4 mmol) in methanol (3.0 mL) to obtain 1.43 g (2.9 mmol) of 2,2-dimethylbut-3-enylphenone-*N*-tosylhydrazone(**12f**) (mixture of 4 isomers) as a white powder (72%). ^{1}HNMR (600 MHz, $CDCl_3$, Me_4Si), (mixture of isomers)*:* δ 7.93 (s, 1H, NH, isomer 1), 7.93 (s, 1H, NH, isomer 2), 7.92 (s, 1H, NH, isomer 3), 7.91 (s, 1H, NH, isomer 4), 7.50 (m, 4H, Ar-*H*), 7.41-7.43 (m, 3H, Ar-*H*), 7.29 (m, 3H, Ar-*H*), 7.13 (dm, J = 7.2 Hz, 2H, Ar-*H,* isomer 1), 7.06 (dm, J = 6.6 Hz, 2H, Ar-*H,* isomer 1 and 2), 7.03 (dm, J = 6.6 Hz, 2H, Ar-*H,* isomer 1 and 2), 6.93-6.96(m, 2H, Mes-*H,* all isomers), 4.97-5.00 (bm, 1H, C*H*=CH-CH_3, all isomers), 4.93-5.03 (bm, 2H, CH=C*H*CH_3,all isomers), 2.71 (s, 2H, N=C(Ar)-CH_2, isomers 1 and 2), 2.60 (s, 2H, N=C(Ar)-CH_2), isomers 3 and 4), 2.30 (s, 3H, Ar-CH_3, isomer 1 and 2), 2.29 (s, 3H, Ar-CH_3, isomer 3 and 4), 1.70 (dd, J = 6.6, 1.2 Hz, 1H, CH=CHCH_3, isomer 3), 1.68 (dd, J = 7.2, 1.8 Hz, 1H, CH=CHCH_3, isomer 1), 1.66 (bd, J = 7.2 Hz, 1H, CH=CHCH_3, isomer 12), 1.58 (dd, J = 6.0, 1.8 Hz, 1H, CH=CHCH_3, isomer 4), 1.07 (s, 6H, C(CH_3)$_2$, isomer 1), 0.98 (s, 6H, C(CH_3)$_2$, isomer 4), 0.93 (s, 6H, C(CH_3)$_2$, isomer 2), 0.66 (s, 6H, C(CH_3)$_2$, isomer 3). ^{13}C{^{1}H}NMR (151

MHz; $CDCl_3$, Me_4Si):(mixture of isomers) δ 155.6 (Cq), 155.0 (Cq), 154.0 (Cq), 142.9 (CH), 142.9 (Cq), 142.7 (Cq), 140.7 (Cq), 140.5 (Cq), 140.3 (CH), 140.1 (Cq), 140.0 (CH), 139.2 (Cq), 139.0 (CH), 138.2 (CH), 134.0 (Cq), 132.7 (Cq), 131.9 (CH), 131.8 (2 x CH), 129.6 (2 x CH), 129.6 (2 x CH), 129.5 (2 x CH), 129.5 (2 x CH), 129.4 (2 x CH), 129.3 (2 x CH), 128.3 (2 x CH), 128.2 (2 x CH), 127.2 (2 x CH), 127.0 (2 x CH), 124.0 (CH), 123.4 (2 x CH), 120.8 (2 x CH), 51.0 (CH_2), 50.7 (CH_2), 44.7 (CH_2), 39.7 (CH_2), 39.4 (CH_2), 37.8 (Cq), 37.3 (Cq), 36.7 (Cq), 36.6 (Cq), 30.6 (CH_3), 29.3 (CH_3), 28.6 (CH_3), 27.7 (CH_3), 23.6 (CH_3), 23.2 (CH_3), 21.1 (2 X CH_3), 18.0 (2 x CH_3), 17.8 (2 x CH_3), 17.1 (2 x CH_3), 14.7 (2 x CH_3), 14.3 (2 x CH_3).HRMS (ESI) m/z: $[M + H]^+$ Calcd. for$C_{23}H_{31}N_2O_2S$399.5694; found 399.5694.

(5*R*)-5-Methyl-2-(1,1-dimethylprop-2-enyl)cyclohexanone *N*-mesitylsulfonylhydrazone (12g)Following the described procedure, pulegone derivative **8l** (0.61 g, 3.4 mmol) was reacted with *N*-mesitylsulfonylhydrazide **9c** (0.79 g, 3.7 mmol) in methanol (2.5 mL) to obtain 0.68 g (1.8 mmol) of (5*R*)-5-methyl-2-(1,1-dimethylprop-2-enyl)cyclohexanone *N*-mesitylsulfonylhydrazone **12g** after column chromatography, affording a white solid product as a mixture of the 4 isomer (54%, PE/EE 9/1). ^{1}HNMR (600 MHz, $CDCl_3$, Me_4Si): (mixture of 4 isomers): 6.97 (s, 2H, Ar-*H*, isomers 1), 6.93 (s, 2H, Ar-*H* isomer 2 and 3), 6.83 (s, 2H, Ar-*H* isomer 4), 5.95 (dd, *J* = 17.4, 10.9 Hz, 1H, C*H*=CH_2 isomer 1), 5.81 (dd, *J* = 17.5, 10.6 Hz, 1H, C*H*=CH_2 isomer 2 and 3), 5.70 (dd, *J* = 17.6, 10.7 Hz, H, C*H*=CH_2 isomer 4), 4.94 (bm, 2H, CH=CH_2 isomer 1 and 4), 4.70 (bm, 2H, CH=CH_2 isomer 2 and 3), 2.64 (s, 6H, *orto* Ar-CH_3 all isomers), 2.56 (dd, *J* = 13.4, 4.3, 1.7 Hz, 1H, N=C-C(H)*H*-C(Me)H, isomer 2), 2.53 (m, 1 H, isomer 3), 2.33 (m, 1H,) 1.41 (dd, 1H, *J* = 13.4, 11.5 Hz, N=C-C(H)*H*-C(Me)H, isomer 2), 2.27 (s, 6H, *para* Ar-CH_3 all isomers), 2.56 ((dd, 1H, *J* = 13.5, 4.0 Hz, isomer 2), 2.35 – 2.31 (m, 1H, N=C-C(H)*H*-C(Me)H isomer 3), 2.29 (d, *J* = 14.8 Hz, 2H N=C-C(H)*H*-C(Me)H, isomer 2), 2.17 (ddd, *J* = 13.0, 4.9, 1.3 Hz, 2H, CH-CH_2-CH_2-C(Me)H isomer 2), 2.07 (t, 1H, *J* = 5.8 Hz, N=C-C(H)*H*-C(Me)H isomer 3), 1.99 (dd, *J* = 12.5, 1.3 Hz, CH-CH_2-CH_2-C(Me)H isomer 2), 1.95 – 1.83 (m, 2H, CH-CH_2-CH_2-C(Me)H isomer 3), 1.80-1.72 (m, 6H, CH_2-C(Me)*H*-CH_2 with C*H*-CH_2-CH_2-C(Me)H with C*H*-CH_2-CH_2-C(Me)H all isomers), 1.59 (ddt, *J* = 10.9, 8.7, 3.2 Hz, 1H, isomer 2), 1.55 – 1.49 (m, 0H), 1.43 (dm, *J* =11.5, 1H, CH-CH_2-C(H)*H*-C(Me)H isomer 2), 1.41 (d, *J* = 11.4 Hz, 1H, CH-CH_2-C(H)*H*-C(Me)H, isomer 1) 1.34-1.29 (m, 1H, CH-CH_2-C(H)*H*-C(Me)H), isomer 3), 1.24 – 1.15 (m, 2H, CH-CH_2-C(H)*H*-C(Me)H, all isomers), 1.19 (ddd, *J* = 14.5, 12.8, 4.0 Hz, 1H, CH-CH_2-C(H)*H*-C(Me)H isomer 2), 1.10 (d, 1H, *J* = 12.2 Hz, CH-CH_2-C(H)*H*-C(Me)H isomer 3), 1.05 (dt, *J* =

8.0, 2.0 Hz, 2H, CH-CH_2-C(H)*H*-C(Me)H, isomer 2), 0.98 (d, *J* = 6.5 Hz, 3H, CH_2-CH-CH_3, isomer 1), 0.94 (d, *J* = 6.5 Hz, 3H, CH_2-CH-CH_3, isomer 2 and 3), 0.91 ((d, *J* = 6.5 Hz, 3H, CH_2-CH-CH_3), 0.87 (s, 3H, C(CH_3) CH_3 isomer 1), 0.86 (s, 3H, C(CH_3) CH_3 isomer 2 and 3), 0.84 (s, 3H, C(CH_3) CH_3 isomer 4), 0.73 (s, 3H, C(CH_3) CH_3isomer 1), 0.71 (s, 3H, C(CH_3) CH_3isomer 2), 0.70 (s, 3H, C(CH_3) CH_3isomer 3), 0.69 (s, 3H, C(CH_3) CH_3isomer 4).$^{13}C\{^1H\}$NMR (151 MHz; $CDCl_3$, Me_4Si): *(mixture of 4 isomers),*δ 159.8 (Cq), 159.8 (Cq), 147.9 (CH), 147.7 (CH), 147.4 (CH), 147.2 (CH), 142.7 (Cq), 142.7 (Cq), 140.1 (2xCq), 140.0 (2x Cq), 137.5 (Cq), 132.7 (CH), 132.2 (CH), 131.9 (2XCH), 131.8 (2XCH), 130.7 (CH_2), 112.8(CH_2), 111.0(CH_2), 110.9(CH_2), 110.0(CH_2), 58.8 (CH),53.8 (CH), 52.1 (CH), 51.8 (CH), 39.6 (Cq), 38.7 (Cq), 36.4 (CH), 35.7 (CH_2), 35.6 (CH_2), 34.7 (CH_2), 34.4 (CH_2), 34.3 (CH) 34.1 (CH) 33.6 (CH_2),31.8 (CH), 31.2 (CH_2), 29.0 (CH_2), 28.9 (CH_2), 26.8 (CH_3), 25.6(CH_2), 25.5(CH_3), 25.4(CH_3), 25.0 (CH_3), 23.7 (CH_3), 23.5, (CH_3), 23.2 (CH_3), 23.1 (CH_3), 23.0 (CH_3), 22.4 (CH_3), 22.3 (CH_3), 21.4 (CH_3), 21.2 (2xCH_3), 21.1 (2xCH_3), 21.0 (2xCH_3), 19.1 (2xCH_3). HRMS (ESI) m/z: $[M + H]^+$ Calcd. for$C_{22}H_{35}N_2O_2S$391.2419; found391.2421.

Synthesis of 2,2-dimethylbut-3-enylphenone-*N*-tosylhydrazone-K^+ salt (K^+-10a)According to our previously reported procedure,[51] 2,2-dimethylbut-3-enylphenone-*N*-tosylhydrazone **10a** (1 mmol, 0.360 gr) was dissolved in the minimal amount of anhydrous MeOH at 0°C and under nitrogen atmosphere, then sublimed *tert*-BuO-K^+ (1 mmol, 0.112 g) was added, and the solution was stirred in the dark for 30 minutes. Solvent evaporation afforded 0.39 gr of 2,2-dimethylbut-3-enylphenone-*N*-tosylhydrazone-K^+ salt (**K^+-10a**) (>99%). ^1H NMR (600 MHz, Methanol-d_4) δ 7.75 (d, *J* = 8.2 Hz, 2H, Ar-*H*), 7.39 – 7.35 (m, 2H, Ar-*H*), 7.21 (d, *J* = 7.9 Hz, 3H, Ar-*H*), 7.18 (t, *J* = 7.4 Hz, 2H, Ar-*H*), 7.14 (d, *J* = 7.0 Hz, 1H, Ar-*H*), 5.73 (dd, *J* = 17.4, 10.7 Hz, 1H, C*H*=CH_2), 4.63 (dd, *J* = 17.5, 1.7 Hz, 1H, CH=CH_2*H trans*), 4.49 (dd, *J* = 10.7, 1.6 Hz, 1H, CH=CH_2*H cis*), 2.88 (s, 2H, N=C(Ph)-CH_2), 2.34 (s, 3H, Ar-CH_3), 0.80 (s, 6H, C(CH_3)$_2$). $^{13}C\{^1H\}$ NMR (151 MHz, Methanol-d_4)δ 150.3 (Cq),149.0 (CH), 142.1 (Cq), 141.9 (Cq), 140.3 (Cq), 128.3 (2 x CH), 127.4 (2 x CH), 126.9 (2 x CH), 126.8 (2 x CH), 126.6 (CH), 108.1 (CH_2), 37.9 (Cq), 37.2 (CH_2), 29.9 (CH_3), 26.71 (2 x CH_3). HRMS (ESI) m/z: $[M + H]^+$ Calcd. for$C_{20}H_{23}N_2O_2S$355.1486found 355.1483. IR ν_{max} (neat)/ cm^{-1}: 2957, 2923, 2053, 1636, 1441, 1279, 1078

General procedure for the photocatalytic synthesis of dearomatizon products (13) In a sealed photochemical reactor, 6.75 mg of $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (0.009 mmol) were dissolved in 5

mL of anhydrous CH_3CN, the solution was degassed with N_2 for 15 min then the suitable tosylhydrazone **10** or phenylsulfonylhydrazone **11** (0.30 mmol) and 62.2 mg of K_2CO_3 (0.45 mmol) were added. The solution was then stirred at 4 cm from the irradiation source (see above) at room temperature until the reaction was completed as monitored by TLC analysis. The solution was then filtered on a short pad of silica gel using CH_2Cl_2 as eluent. The crude product was purified by flash chromatography on silica gel (hexane/acetone 92/8) to obtain the dearomatized product **13**.

4,4,7-Trimethyl-2-phenyl-3,4,4a,5,5a,8-hexahydrobenzo[e]pyridazino[1,6-b][1,2]thiazine 10,10-dioxide (13a) Following the general procedure A, 107 mg (0.30 mmol) of 2,2-dimethylbut-3-enylphenone-*N*-tosylhydrazone (**10a**) were reacted with K_2CO_3 and $[Ru(bpy)_3]Cl_2{\cdot}6H_2O$ for 16 h under blue light irradiation to obtain 75 mg (0.210 mmol) of 4,4,7-trimethyl-2-phenyl-3,4,4a,5,5a,8-hexahydrobenzo[e]pyridazino[1,6-b][1,2]thiazine 10,10-dioxide **13a** (70%) as a white solid.^{1}H NMR (600 MHz, $CDCl_3$, Me_4Si): δ 7.80 – 7.75 (m, 2H, Ar-*H*), 7.38 – 7.32 (m, 3H, Ar-*H*), 6.74 (tm, *J* = 3.5, Hz, 1H, CH_2-C*H*=C), 5.25 (dq, *J* = 3.1, 1.6 Hz, 1H, CH_3CH=C*H*), 4.01 (dd, *J* = 12.6, 2.4 Hz, 1H, N-C*H*), 3.48 (bs,CH_2-C*H*-CH=), 2.75 (m, 2H, CH-C*H*$_2$-C(CH_3)$_2$), 2.38 (d, *J* = 18.4 Hz, 1H, CH-C(H)*H*-C(CH_3)), 2.28 (d, *J* = 18.3 Hz, 1H, CH-C(H)*H*-C(CH_3)), 1.78 (ddd, *J* = 13.5, 4.0, 1.8 Hz, 1H, CH-C(H)*H*-CH), 1.64 (t, *J* = 1.5 Hz, 3H, C*H*$_3$CH=CH), 1.23 (q, *J* = 12.7 Hz, 1H, CH-C(H)*H*-CH), 1.11 (s, 6H, CH_2-C(C*H*$_3$)$_2$). ^{13}C{^{1}H}NMR (151 MHz, $CDCl_3$,Me_4Si): δ 149.1 (Cq), 137.0 (Cq), 135.5 (Cq), 131.9 (CH), 130.5 (Cq), 129.5 (CH), 128.4 (2 x CH), 125.6 (2 x CH), 121.2 (CH), 62.5 (CH), 35.4 (CH), 34.6 (CH_2), 31.5 (CH_2), 31.4 (CH_2), 31.0 (Cq), 28.3 (CH_3), 27.0 (CH_3), 22.7 (CH_3). Mp: 169.2-170.5 °C, degradation. ν_{max} (neat)/cm^{-1}: 2966, 2921, 2908, 1448, 1345, 1159, 1060, 1021.HRMS (ESI) m/z: $[M + Na]^+$ Calcd. for$C_{20}H_{24}N_2O_2S$379.1451; found379.1451.

4,4,7-Trimethyl-2-(naphthalen-2-yl)-3,4,4a,5,5a,8-hexahydrobenzo[e]pyridazino[1,6-b][1,2]thiazine 10,10-dioxide (13b) Following the general procedure A, 122 mg (0.30 mmol) of 2,2-dimethylbut-3-enylnaphtone-*N*-tosylhydrazone (**10b**) were reacted with K_2CO_3 and $[Ru(bpy)_3]Cl_2{\cdot}6H_2O$ under blue light irradiation for 16 h to obtain 52.5 mg (0.13 mmol) of 2,4,4-trimethyl-3,4,4a,5,5a,8-hexahydrobenzo[e]pyridazino[1,6-b][1,2]thiazine 10,10-dioxide **13b** (43%) as a white solid.^{1}H NMR (600 MHz, $CDCl_3$, Me_4Si): δ 8.11 (dd, *J* = 8.7, 1.8 Hz, 1H, Ar-*H*), 8.01 (s, 1H, Ar-*H*), 7.82 (ddd, *J* = 9.0, 5.6, 3.4 Hz, 2H Ar-*H*), 7.79 (d, *J* = 9.0 Hz, 1H, Ar-*H*), 7.47 (tt, *J* = 5.8, 4.7 Hz, 2H, Ar-*H*), 6.78 (m, 1H, CH_2-C*H*=C), 5.26 (m, 1H, CH_3CH=C*H*), 4.06

(dd, *J* = 12.7, 2.4 Hz, 1H, N-C*H*), 3.51 (bs, 1H, CH_2-C*H*-CH), 2.75 (m, 2H, CH-C*H*$_2$-C(CH_3)$_2$), 2.54 ((d, *J* = 18.0 Hz, 1H, CH-C(H)*H*-C(CH_3)), 2.42 (d, *J* = 18.2 Hz, 1H, CH-C(H)*H*-C(CH_3)), 1.81 (ddd, *J* = 13.3, 4.2, 2.4 Hz, 1H, CH-C(H)*H*-CH), 1.64 (s, 3H, C*H*$_3$CH=CH) 1.29 (q, *J* = 12.7 Hz, 1H, CH-C(H)*H*-CH), 1.16 (s, 6H, CH_2-C(C*H*$_3$)$_2$). $^{13}C\{^1H\}$NMR (151 MHz, $CDCl_3$,Me_4Si): δ 148.9 (Cq), 135.5 (Cq), 134.5 (Cq), 133.9 (Cq), 133.0 (Cq), 132.0 (CH), 130.5 (Cq), 128.5 (CH), 128.0 (CH), 127.8 (CH), 126.8 (CH), 126.4 (CH), 125.0 (CH), 123.4 (CH), 121.2 (CH), 62.7 (CH), 35.4 (CH), 34.5 (CH_2), 31.6 (CH_2), 31.4 (CH_2), 31.1 (Cq), 28.4 (CH_3), 27.0 (CH_3), 22.7 (CH_3). Mp: 63.4-67.2 °C. ν_{max}(neat)/cm^{-1}: 3057, 2958, 2923, 1599, 1445, 1349, 1349, 1179, 1158, 1018. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for$C_{24}H_{26}N_2O_2S$407.1793; found407.17.92.

4,4,7-Trimethyl-2-(m-tolyl)-3,4,4a,5,5a,8-hexahydrobenzo[e]pyridazino[1,6-b][1,2]thiazine 10,10-dioxide (13c) Following the general procedure A, 111 mg (0.30 mmol) of 2,2-dimethylbut-3-enyl-m-tolyl ketone-*N*-tosylhydrazone (**10c**) were reacted with K_2CO_3 and $[Ru(bpy)_3]Cl_2·6H_2O$ under blue light irradiation for 16 h to obtain 66.6 mg (0.18 mmol) of 4,4,7-trimethyl-2-(m-tolyl)-3,4,4a,5,5a,8-hexahydrobenzo[e]pyridazino[1,6-b][1,2]thiazine 10,10-dioxide **13c** (60%) as a white solid. ^1H NMR (600 MHz, $CDCl_3$, Me_4Si): δ 7.58 (s, 1H, Ar-*H*), 7.55 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 7.25 (dd, *J* = 7.8, 7.2 Hz, 1H, Ar-*H*), 7.18 (d, *J* = 7.2 Hz, 1H, Ar-*H*), 6.76 (bs, 1H, CH_2-C*H*=C), 5.26 (m, 1H, CH_3CH=C*H*), 4.02 (dd, *J* = 12.5, 2.4 Hz, 1H, N-C*H*), 3.49 (m, 1H, CH_2-C*H*-CH), 2.76 (m, 1H, CH-C*H*$_2$-C(CH_3)$_2$), 2.37 (s, 3H, Ar-C*H*$_3$), 2.36 (s, 1H, CH-C(H)*H*-C(CH_3)), 2.29 (d, *J* = 18.2 Hz, 1H, CH-C(H)*H*-C(CH_3)), 1.78 (ddd, *J* = 13.3, 4.2, 2.5 Hz, 1H, CH-C(H)*H*-CH), 1.65 (s, 3H, C*H*$_3$CH=CH), 1.24 (q, *J* = 12.7 Hz, 1H, CH-C(H)*H*-CH), 1.12 (s, 6H, CH_2-C(C*H*$_3$)$_2$). $^{13}C\{^1H\}$NMR (151 MHz, $CDCl_3$,Me_4Si): δ 149.2 (Cq), 138.1 (Cq), 137.0 (Cq), 135.4 (Cq), 131.9 (CH), 130.5 (Cq), 130.3 (CH), 128.3 (CH), 126.2 (CH), 122.8 (CH), 121.2 (CH), 62.5 (CH), 35.4 (CH), 34.7 (CH_2), 31.5 (CH_2), 31.4 (CH_2), 31.0 (Cq), 28.3 (CH_3), 27.0 (CH_3), 22.7 (CH_3), 21.6 (CH_3). Mp: 73.0-75.2 °C. ν_{max} (neat)/cm^{-1}: 2957, 2921, 2854, 1604, 1446, 1349, 1159, 1157, 1021. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for$C_{21}H_{26}N_2O_2S$371.1793; found371.1797.

4,4,7-Trimethyl-2-(*p*-tolyl)-3,4,4a,5,5a,8-hexahydrobenzo[e]pyridazino[1,6-b][1,2]thiazine 10,10-dioxide (13d)Following the general procedure A, 111 mg (0.30 mmol) of 2,2-dimethylbut-3-enyl-p-tolyl ketone-*N*-tosylhydrazone (**10d**) were reacted with K_2CO_3 and $[Ru(bpy)_3]Cl_2·6H_2O$ under blue light irradiation for 16 h to obtain 68.8 mg (0.18 mmol) of 4,4,7-trimethyl-2-(*p*-tolyl)-3,4,4a,5,5a,8-hexahydrobenzo[e]pyridazino[1,6-b][1,2]thiazine 10,10-dioxide **13d** (62%) as a

white solid.^{1}H NMR (600 MHz, $CDCl_3$, Me_4Si): δ 7.66 (dd, *J* = 8.4, 1.8 Hz, 2H, Ar-*H*), 7.26 (bd, *J* = 8.4 Hz, 2H, Ar-*H*), 6.74 (td, *J* = 3.6, 1.8 Hz, 1H, CH_2-C*H*=C), 5.26 (dd, *J* = 12.6, 1.8 Hz, 1H, CH_3CH=C*H*), 3.47 (m, 1H, CH_2-C*H*-CH), 2.76 (m, 1H, C*H*$_2$-C(CH_3)$_2$), 2.37 (dd, *J* = 18.0, 0.6 Hz, 1H, CH-C(H)*H*-C(CH_3), 2.34 (s, 3H, Ar-C*H*$_3$), 2.25 (bd, *J* = 18.0, 1H, CH-C(H)*H*-C(CH_3), 1.76 (ddd, *J* = 13.2, 4.2, 2.4 Hz, 1H, CH-C(H)*H*-CH), 1.63 (s, 3H, C*H*$_3$CH=CH), 1.24 (d, *J* = 12.0 Hz, 1H, CH-C(H)*H*-CH), 1.20 (d, *J* = 12.0 Hz, 1H, CH-C(H)*H*-CH), 1.11 (s, 3H, CH_2-C(C*H*$_3$)$_2$), 1.10 (s, 3H, CH_2-C(C*H*$_3$)$_2$).^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$,Me_4Si): δ 149.1 (Cq), 139.6 (Cq), 135.4 (Cq), 134.2 (Cq), 131.8 (CH), 130.5 (Cq), 129.1 (2 X CH), 125.5 (2 X CH), 121.2 (CH), 62.5 (CH), 35.4 (CH), 34.6 (CH_2), 31.4 (2 X CH_2), 31.0 (Cq), 28.3 (CH_3), 27.0 (CH_3), 22.7 (CH_3), 21.3 (CH_3). Mp: degradation 172.5-180°C. ν_{max} (neat)/cm^{-1}: 2971, 2916, 2862, 1449, 1344, 1177, 1159. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for$C_{21}H_{26}N_2O_2S$371.1793; found 371.1791.

4,4,7-Trimethyl-2-(*o*-tolyl)-3,4,4a,5,5a,8-hexahydrobenzo[e]pyridazino[1,6-b][1,2]thiazine 10,10-dioxide (13e)Following the general procedure A, 111 mg (0.30 mmol) of 2,2-dimethylbut-3-enyl-*o*-tolyl ketone-*N*-tosylhydrazone (**10e**) were reacted with K_2CO_3 and $[Ru(bpy)_3]Cl_2·6H_2O$ under blue light irradiation for 16 h to obtain 57.7 mg (0.16 mmol) of 4,4,7-trimethyl-2-(*o*-tolyl)-3,4,4a,5,5a,8-hexahydrobenzo[e]pyridazino[1,6-b][1,2]thiazine 10,10-dioxide **13e** (52%) as a white solid.^{1}H NMR (600 MHz, $CDCl_3$, Me_4Si): δ 7.17-7.21 (m, 4H, Ar-*H*), 6.74 (td, *J* = 3.6, 1.8 Hz, 1H, CH_2-C*H*=C), 5.26 (m, 1H, CH_3CH=C*H*), 3.99 (dd, J = 12.6, 1.8 Hz, 1H, C=CHC*H*), 3.51 (m, 1H, C*H*$_2$-C(CH_3)$_2$), 2.77 (dm, *J* = 6.6 Hz, 2H, C*H*$_2$-CH=C), 2.34 (s, 3H, Ar-C*H*$_3$), 2.22 (dd, *J* = 19.0 1.2 Hz, 1H, CH-C(H)*H*-C(CH_3), 2.15 (d, *J* = 18.7 Hz, 1H, CH-C(H)*H*- C(CH_3), 2.15 (ddd, *J* = 13.2, 4.8, 3.0 Hz, 1H, CH-C(H)*H*-CH), 1.69 (s, 3H, C*H*$_3$CH=CH), 1.37 (d, *J* = 12.6 Hz, 1H, CH-C(H)*H*-CH), 1.33 (d, *J* = 12.6 Hz, 1H, CH-C(H)*H*-CH), 1.17 (s, 3H, CH_2-C(C*H*$_3$)$_2$), 1.06 (s, 3H, CH_2-C(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$,Me_4Si): δ 153.2 (Cq), 137.8 (Cq), 136.1 (Cq), 135.5 (Cq), 132.1 (CH), 131.1 (CH), 128.6 (CH), 127.8 (CH), 125.8 (CH), 121.3 (CH), 62.0 (CH), 38.3 (CH_2), 35.4 (CH), 31.6 (CH_2), 31.4 (CH_2), 31.2 (Cq), 28.3 (CH_3), 26.7 (CH_3), 22.8 (CH_3), 20.8 (CH_3).Mp: degradation 165.0-169.2 °C. ν_{max} (neat)/cm^{-1}: 2961, 2942, 2871, 2114, 1734, 1346, 1156, 1176.HRMS (ESI) m/z: $[M + H]^+$ Calcd. for$C_{21}H_{26}N_2O_2S$371.1793found371.1793.

2-(3-methoxyphenyl)-4,4,7-trimethyl-3,4,4a,5,5a,8-hexahydrobenzo[e]pyridazino[1,6-b][1,2]thiazine 10,10-dioxide (13f) Following the general procedure A, 116 mg (0.30 mmol) of 2,2-dimethylbut-3-enyl-m-methoxyphenone-*N*-tosylhydrazone (**10f**) were reacted with K_2CO_3

and $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ under blue light irradiation for 16 h to obtain 58 mg (0.15 mmol) of 2-(3-methoxyphenyl)-4,4,7-trimethyl-3,4,4a,5,5a,8-hexahydrobenzo[e]pyridazino[1,6-b][1,2]thiazi ne 10,10-dioxide **13f** (50%) as a white solid.^{1}H NMR (600 MHz, $CDCl_3$, Me_4Si): δ 7.34 (d, 1H, J = 1,8 Hz, Ar-H), 7.32 (dm, 1H, J = 6.6 Hz, Ar-*H*), 7.28 (d, 1H, J = 8.4 Hz, Ar-*H*), 7.24 (t, 1H, J = 7.8 Hz, Ar-*H*), 6.90 (dd, J = 7.8, 2.0, 1H, Ar-*H*), 6.74 (td, *J* = 3.6, 1.5 Hz, 1H, CH_2-C*H*=C), 5.25 (q, *J* = 1.8 Hz, 1H, CH_3CH=C*H*), 4.01 (dd, *J* = 13.0, 2.4 Hz, 1H, N-C*H*), 3.82 (s, 3H, O-CH_3), 3.48 (m, 1H, CH_2-C*H*-CH=), 2.75 (m, 2H, CH_2-C$(CH_3)_2$), 2.35 (d, *J* = 18.3 Hz, 1H, CH-C(H)*H*-C(CH_3)), 2.26 (d, *J* = 18.5 Hz, 1H, CH-C(H)*H*-C(CH_3)), 1.77 (ddd, *J* = 13.4, 4.3, 2.5 Hz, 1H, CH-C(H)*H*-CH), 1.64 (s, 3H, CH_3CH=CH), 1.22 (m, 1H, CH-C(H)*H*-CH), 1.11 (d, *J* = 3.0 Hz, 6H, CH_2-C(CH_3)$_2$).^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$,Me_4Si): δ 159.7 (Cq), 148.9 (Cq), 138.5 (Cq), 135.5 (Cq), 131.9 (CH), 130.5 (Cq), 129.4 (CH), 121.2 (CH), 118.1 (CH), 115.1 (CH), 111.1 (CH), 62.5 (CH), 55.5 (CH_3), 35.4 (CH), 34.7 (CH_2), 31.5 (CH_2), 31.4 (CH_2), 31.0 (Cq), 28.3 (CH_3), 26.9 (CH_3), 22.7 (CH_3).Mp: 85.0-89.5 °C ν_{max} (neat)/cm^{-1}: 3030, 2961, 1598, 1449, 1349, 1287.HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{21}H_{26}N_2O_3S$387.1742; found 387.1740.

4,4,7-Trimethyl-2-(pyridin-2-yl)-3,4,4a,5,5a,8-hexahydrobenzo[e]pyridazino[1,6-b][1,2]thiazine 10,10-dioxide (13g) Following the general procedure A, 107 mg (0.30 mmol) of 2,2-dimethylbut-3-enyl-pyridyl ketone-*N*-tosylhydrazone (**10g**) were reacted with K_2CO_3 and $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ under blue light irradiation for 16 h to obtain 40 mg (0.11mmol) of 4,4,7-trimethyl-2-(pyridin-2-yl)-3,4,4a,5,5a,8-hexahydrobenzo[e]pyridazino[1,6-b][1,2]thiazine 10,10-dioxide **13g** (37%) as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$, Me_4Si): δ 8.52 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H, Ar-*H*), 8.11 (dt, *J* = 8.1, 1.1 Hz, 1H, Ar-*H*), 7.66 (ddd, *J* = 8.1, 7.4, 1.8 Hz, 1H, Ar-*H*), 7.24 (ddd, *J* = 7.4, 4.8, 1.2 Hz, 1H, Ar-*H*), 6.74 (td, *J* = 3.5, 1.5 Hz, 1H, CH_2-C*H*=C), 5.26 (dq, *J* = 3.2, 1.6 Hz, 1H, CH_3CH=C*H*), 4.02 (ddd, *J* = 12.7, 2.5, 1.2 Hz, 1H, N-C*H*), 3.52 – 3.45 (m, 1H, CH_2-C*H*-CH), 2.73 (dd, *J* = 19.3, 1.3 Hz, 1H, CH-CH_2-C$(CH_3)_2$), 2.38 (dd, *J* = 19.3, 1.0 Hz, 1H, CH-C(H)*H*-C(CH_3)), 1.81 (ddd, *J* = 13.4, 4.2, 2.5 Hz, 1H, CH-C(H)*H*-CH), 1.64 (dd, *J* = 1.9, 1.0 Hz, 3H, CH_3CH=CH), 1.26 (dt, *J* = 13.4, 12.5 Hz, 1H, CH-C(H)*H*-CH), 1.11 (s, 3H, CH_2-CH_3(CH_3)), 1.09 (s, 3H, CH_2-CH_3(CH_3)). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$,Me_4Si): δ 154.8 (Cq), 150.6 (Cq), 148.4 (CH), 136.3 (CH), 135.7 (Cq), 131.8 (CH), 130.4 (Cq), 124.0 (CH), 121.2 (CH), 120.6 (CH), 63.0 (CH), 35.4 (CH), 33.6 (CH_2), 31.7 (CH_2), 31.4 (CH_2), 30.7 (Cq), 28.3 (CH_3), 26.8 (CH_3), 22.7 (CH_3). Mp: 55.0-58.7 °C. ν_{max} (neat)/cm^{-1}: 3053, 2964, 1581, 1434, 1349, 1179. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{19}H_{23}N_3O_2S$358.1589; found 358.1590.

4,7-Dimethyl-2,4-diphenyl-3,4,4a,5,5a,8-hexahydrobenzo[e]pyridazino[1,6-b][1,2]thiazine 10,10-dioxide (13h) Following the general procedure A, 125 mg (0.30 mmol) of 2-phenyl-2-methylbut-3-enylphenone *N*-tosylhydrazone(**10h**)were reacted with K_2CO_3 and $[Ru(bpy)_3]Cl_2·6H_2O$ for 16 h under blue light irradiation to obtain 43 mg (0.10 mmol) of 4,4,7-trimethyl-2-phenyl-3,4,4a,5,5a,8-hexahydrobenzo[e]pyridazino[1,6-b][1,2]thiazine 10,10-dioxide **13h** (34%) as a white solid.^{1}H NMR (600 MHz, $CDCl_3$, Me_4Si): δ 7.85 (m, 2H, Ar-*H*), 7.40 (m, 3H, Ar-*H*),7.30 (m, 2H, Ar-*H*),7.25 (m, 3H, Ar-*H*), 6.76 (tm, *J* = 3.0, Hz, 1H, CH_2-C*H*=C), 5.23 (q, *J* = 1.2 Hz, 1H, CH_3CH=C*H*), 4.47 (dd, *J* = 12.6, 1.8 Hz, 1H, N-C*H*), 3.51 (bs, 1 H, CH_2-C*H*-CH=), 3.21 (d, *J* = 18.4 Hz, 1H, CPhMe-CH_{2a}),2.78 (m, 2H, CH-CH_2-C(CH_3Ph), 2.54 (d, *J* = 18.4 Hz, 1H, CPhMe-CH_{2b}), 1.88 (ddd, *J* = 13.8, 4.2, 3.0 Hz, 1H, CH-C(H)*H*-CH), 1.67 (s, 3H, CH_3CH=CH), 1.43 (q, *J* = 13.0 Hz, 1H, CH-C(H)*H*-CH).^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$,Me_4Si): δ 149.3 (Cq), 145.2 (Cq), 135.6 (Cq), 135.5 (Cq), 132.0 (CH), 130.7 (Cq), 129.7 (CH), 128.8 (2 x CH), 128.5 (2 x CH), 127.1 (CH), 125.7 (2 x CH), 125.4 (2 x CH), 121.1 (CH), 62.6 (CH), 35.3 (CH), 34.0 (CH_2), 32.2 (CH_2), 31.4 (CH_2), 29.8 (Cq), 26.5 (CH_3), 22.7 (CH_3). Mp: 113.0-117.0 °C.ν_{max} (neat)/cm^{-1}:2964, 2929, 2256, 1498, 1412, 1338, 1180, 1157. HRMS (ESI) m/z: $[M + Na]^+$ Calcd. for$C_{25}H_{26}N_2O_2S$441.1607;found441.1614.

2,4,4,7-Tetramethyl-3,4,4a,5,5a,8-hexahydrobenzo[e]pyridazino[1,6-b][1,2]thiazine 10,10-dioxide (13i) Following the general procedure A,88 mg (0.30 mmol) of 4,4-dimethylhex-5-en-2-one-*N*-tosylhydrazone (**10i**) were reacted with K_2CO_3 and $[Ru(bpy)_3]Cl_2·6H_2O$ for 16 h under blue light irradiation to obtain 65 mg (0.22 mmol) of 2,4,4,7-tetramethyl-3,4,4a,5,5a,8-hexahydrobenzo[e]pyridazino[1,6-b][1,2]thiazine 10,10-dioxide **13i** (73 %) as a white solid.^{1}H NMR (600 MHz, $CDCl_3$, Me_4Si): δ6.74 (t, *J*=3.8 Hz, 1H, CH_2-C*H*=C);5.26 (q, *J*=2.1 Hz 1H, CH_3CH=C*H*);3.87 (dd, *J*=12.8, 2.3 Hz, 1H, N-C*H*);3.43 (bs, 1H, CH_2-C*H*-CH);2.83 (ddd, *J* = 23.3, 7.8, 3.5 Hz, 1H, CH-C(H)*H*-C(CH_3));2.75 (dd, *J* = 22.7, 8.6, 1H, CH-C(H)*H*-C(CH_3)), 1.95 (s, 3H, CH_3-C=N);1.88 (d, *J* = 18.9 Hz, 1H, CH-C(H)*H*-C(CH_3)$_2$); 1.84 (d, *J* = 19.0 Hz, 1H, CH-C(H)*H*-C(CH_3)$_2$), 1.72 (ddd, *J* = 13.5, 4.5, 2.3 Hz, 1H, CH-C(H)*H*-CH), 1.69 (s, 3H, CH_3CH=CH);1.59 (d, J = 3.6, 1H, C*H*(CH_3)=CH), 1.17 (q, *J* = 12.9 Hz, 1H, CH-C(H)*H*-CH); 1.05 (s, 3H, CH_2-C(CH_3)CH_3); 1.00 (s, 3H, CH_2-C(CH_3) (CH_3)).^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$,Me_4Si): δ 152.7 (Cq);135.1 (Cq);131.8 (CH); 130.6 (Cq); 121.4 (CH); 62.0 (CH); 38.6 (CH_2); 35.41 (CH); 31.5(CH_2); 31.01 (Cq); 30.9 (CH_2); 28.3(CH_3); 26.7(CH_3); 24.3(CH_3);

22.9(CH_3).Mp: degradation 192.0-195° C. ν_{max} (neat)/cm^{-1}: 2962, 1637, 1343, 1177, 1155. HRMS (ESI) m/z: $[M + Na]^+$ Calcd. for$C_{15}H_{22}N_2O_2S$317.1294; found317.1294.

4,4-Dimethyl-2-phenyl-3,4,4a,5,5a,8-hexahydrobenzo[e]pyridazino[1,6-b][1,2]thiazine 10,10-dioxide (13j) Following the general procedure A, 103 mg (0.30 mmol) of 2,2-dimethylbut-3-enylphenone-*N*-phenylsulfonylhydrazone (**11a**) were reacted with K_2CO_3 and $[Ru(bpy)_3]Cl_2·6H_2O$ for 16 h under blue light irradiation to obtain 41 mg (0.120 mmol) of 4,4-dimethyl-2-phenyl-3,4,4a,5,5a,8-hexahydrobenzo[e]pyridazino[1,6-b][1,2]thiazine 10,10-dioxide **13j** (40%) as a white solid.^{1}H NMR (600 MHz, $CDCl_3$, Me_4Si): δ 7.80 – 7.74 (m, 2H, Ar-*H*), 7.38 – 7.33 (m, 3H, Ar-*H*), 6.76 (bm, 1H, CH_2-C*H*=C), 5.63 (dm, *J* = 10.1, 1H, CH-C*H*=CH-CH_2, 1H,), 5.54 (dm, *J* = 10.2, 3.3, 2.0 Hz, 1H, CH_3CH=C*H*), 4.03 (dd, *J* = 12.7, 2.5 Hz, 1H, N-C*H*), 3.52 (m, 1H, CH_2-C*H*-CH), 2.87 (tm, *J* = 8.6 Hz, 2H), 2.39 (dd, *J* = 18.3, 1.1 Hz, 1H, CH-C(H)*H*-C(CH_3 2.29 (dd, *J* = 18.4, 0.9 Hz, 1H, CH-C(H)*H*-C(CH_3), 1.79 (ddd, *J* = 13.3, 4.2, 2.5 Hz, 1H, CH-C(H)*H*-CH), 1.29 (q, *J* = 12.8 Hz, 1H, CH-C(H)*H*-CH), 1.12 (d, *J* = 1.8 Hz, 6H, CH_2-C(C*H*$_3$)$_2$). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$,Me_4Si): δ 149.1 (Cq), 136.9 (Cq), 135.5 (Cq), 131.8 (CH), 129.5 (CH), 128.4 (2 x CH), 126.6 (CH), 125.6 (2 x CH), 123.0 (CH), 62.5 (CH), 34.6 (CH_2), 34.4 (CH), 31.2 (CH_2), 31.0 (Cq), 28.3 (CH_3), 27.0 (CH_3), 26.8 (CH_2).Mp: 141.9 -144.5 °C. ν_{max} (neat)/cm^{-1}: 3059, 2956, 2922, 2868, 1445, 1349, 1169, 1019, 955. HRMS (ESI) m/z: $[M + Na]^+$ Calcd. for$C_{19}H_{22}N_2O_2S$365.1294;found 365.1285.

2,4,4-Trimethyl-3,4,4a,5,5a,8-hexahydrobenzo[e]pyridazino[1,6-b][1,2]thiazine 10,10-dioxide (13k) Following the general procedure A, 84 mg (0.30 mmol) of 4,4-dimethylhex-5-en-2-one-*N*-phenylsulfonylhydrazone (**11b**) were reacted with K_2CO_3 and $[Ru(bpy)_3]Cl_2·6H_2O$ under blue light irradiation for 16 h to obtain 46 mg (0.165 mmol) of 2,4,4-trimethyl-3,4,4a,5,5a,8-hexahydrobenzo[e]pyridazino[1,6-b][1,2]thiazine 10,10-dioxide **13k** (55%) as a white solid.^{1}H NMR (600 MHz, $CDCl_3$, Me_4Si):δ 6.74 (bs, 1H, CH_2-C*H*=C), 5.67 (dm, *J* = 10.2 Hz, 1H, CH-C*H*=CH-CH_2), 5.54 (dm, *J* = 10.1Hz, 1H, CH-CH=C*H*-CH_2), 3.87 (dd, *J* = 12.8, 2.3 Hz, 1H, N-C*H*), 3.45 (m, 1H, CH_2-C*H*-CH), 2.94 (dm, *J* = 23.9Hz, 1H, , CH-C(H)*H*-C(CH_3)), 2.85 (ddq, *J* = 23.9, 8.7, 3.3 Hz, 1H, CH-C(H)*H*-C(CH_3)), 1.95 (s, 3H, C*H*$_3$-C=N), 1.87 (d, *J* = 6.5 Hz, 2H, CH-C*H*$_2$-C(CH_3)$_2$), 1.72 (ddd, *J* = 13.3, 4.2, 2.4 Hz, 1H, CH-C(H)*H*-CH), 1.22 (q, *J* = 12.8 Hz, 1H, CH-C(H)*H*-CH), 1.05 (s, 3H, CH_2-C(C*H*$_3$)$_2$), 0.99 (s, 3H, CH_2-C(C*H*$_3$)$_2$). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$,Me_4Si):bδ152.7 (Cq), 135.2 (Cq), 131.7 (CH), 126.7 (CH), 123.0 (CH), 62.0 (CH), 38.5 (CH_2), 34.3 (CH), 30.9 (Cq), 30.6 (CH_2), 28.2 (Cq), 26.8 (CH_2) , 26.6 (CH_3), 24.2 (CH_3).Mp:

degradation 185.0-190.2 °C. **ν_{max}** (neat)/cm^{-1}: 2975, 712, 1639, 1341, 1171.HRMS (ESI) m/z: $[M + H]^+$ Calcd. for$C_{14}H_{20}N_2O_2S$281.1324; found 281.1322.

2,9,12,12-Tetramethyl-3,8,9,10,11,11a,12,12a,13,13a-decahydrobenzo[5,6][1,2]thiazino[2,3-b]cinnoline 5,5-dioxide (13l) Following the general procedure A, 101 mg (0.300 mmol) of pulegone tosylhydrazone(**10l**) were reacted with K_2CO_3 and $[Ru(bpy)_3]Cl_2·6H_2O$ under blue light irradiation for 16 h to obtain 36,5mg (0.105 mmol) of 2,9,12,12-tetramethyl-3,8,9,10,11,11a,12,12a,13,13a-decahydrobenzo[5,6][1,2]thiazino[2,3-b]cinnoline 5,5-dioxide **13l** (35%) as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$, Me_4Si):δ 6.72 (bs, 1H, CH_2-C*H*=C), 5.25 (bs, 1H, CH_3CH=C*H*), 3.90 (dd, *J* = 12.7, 2.3 Hz, 1H, N-C*H*), 3.40 (m, 1H, CH_2-C*H*-C$(CH_3)_2$), 2.81 (dm, *J* = 22.2 Hz, 1H, CH_{2a}-CH- C$(CH_3)_2$), 2.74 (dd, *J* = 22.2 Hz, 7.4 Hz, 1H, CH_{2b}-CH-C$(CH_3)_2$), 2.58 (dt, *J* = 14.5, 2.4 Hz, 1H, CH- CH_{2a}-C(CH_3)), 1.84 (m, 2H, CH(CH_3)-CH_2-C=N), 1.72 (d, *J* = 13.7 Hz, 1H, CH-CH_{2a}-CH_2), 1.68 (m, 1H, CH(CH_3)- CH_2 -C(H)*H*-CH); 1.67 (s, 3H, CH_3CH=CH); 1.59 (bm, 1H, CH_2-C*H*(CH_3)-CH_2), 1.55 (s, 2H, CH_3CH=CH), 1.32 – 1.19 (m, 2H, CH(CH_3)- CH_2 -C(H)*H*-CH with CH_2-C(C*H*)=N), 1.06 (qd, *J* = 12.5, 11.4, Hz, 1H, CH(CH_3)-C(H)*H*-CH_2-CH), 1.00 (s, 3H, (CH_3)$_{2a}$), 0.99 (s, 3H, (CH_3)$_{2b}$), 0.93 (d, *J* = 6.5 Hz, 3H, CH-CH_3).^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$,Me_4Si):δ 158.3 (Cq), 135.1 (Cq), 132.0 (CH), 130.5 (CH), 121.3 (CH), 64.7 (CH), 43.3 (Cq), 42.5 (Cq), 35.5 (CH), 34.1 (CH_2), 33.8 (Cq), 33.2 (CH), 31.4 (CH_2), 30.0 (CH_2), 25.6 (CH_2), 25.1 (CH_3), 24.9 (CH_3), 22.8 (CH_3), 22.1 (CH_3).Mp: degradation 118.0-124.0 °C. ν_{max} (neat)/cm^{-1}: 2949, 1737, 1630, 1453, 1352, 1150. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{19}H_{28}N_2O_2S$349.1950;found 349.1947.**General procedure for the photoirradiation of β-hindered-γ,δ-unsaturated *N*-mesitylsulfonylhydrazones (12) and internal β-hindered-γ,δ-unsaturated *N*-arylsulfonylhydrazones (10 j-k)**In a sealed photochemical reactor, 6,75 mg of $[Ru(bpy)_3]Cl_2·6H_2O$ (0.009 mmol) were dissolved in 5 mL of anhydrous CH_3CN, the solution was degassed with N_2 for 15 min then the suitable arylsulfonylhydrazone (**12a-g, 10j-k)** (0.30 mmol) and 62.2 mg of K_2CO_3 (0.45 mmol) were added. The solution was then stirred at 4 cm from the irradiation source (see above) at room temperature until the reaction was completed as monitored by TLC analysis. Then, it was filtered on a short pad of silica gel using CH_2Cl_2 as eluent and Et_2O to wash the column. The crude product was purified by flash chromatography on silica gel (hexane/Et_2O 9/1).

1-(Mesitylsulfonyl)-4,5,5-trimethyl-3-phenyl-1,4,5,6-tetrahydropyridazine (14a) According to general procedure 115 mg (0.30 mmol) of 2,2-dimethylbut-3-enylphenone-*N*-2,4,6-mesitylsulfonylhydrazone **12a** were reacted with K_2CO_3 and $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ under blue light irradiation for 16 h to obtain 57.5 mg (0.15 mmol) of 1-(mesitylsulfonyl)-4,5,5-trimethyl-3-phenyl-1,4,5,6-tetrahydropyridazine **14a** (50%) as a white solid.^{1}H NMR (600 MHz, $CDCl_3$, Me_4Si): δ 7.56 (d, *J* = 6.8 Hz, 2H, Ar-*H*), 7.30 (m, 3H, Ar-*H*), 6.97 (s, 2H, Ar-*H*), 4.14 (q, *J* = 6.6 Hz, 1H, N-C*H*), 2.74 (s, 6H, *orto* Ar-(CH_3)), 2.40 (d, *J* = 18.0 Hz, 1H, $(CH_3)_2$-CH-C(H)*H*)), 2.30 (s, 3H, *para* Ar-(CH_3)), 2.26 (d, *J* = 18.0, 1H, $(CH_3)_2$-CH-C(H)*H*), 1.30 (d, *J* = 6.6 Hz, 3H,N-CH-CH_3), 1.11 (s, 3H, CH(CH_3)-C(CH_3)$_2$), 0.94 (s, 3H, CH(CH_3)-C(CH_3)$_2$). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$,Me_4Si): δ 145.3 (Cq), 142.7 (Cq), 141.0 (2 x Cq), 137.3 (Cq), 133.1 (Cq), 131.8 (2 xCH), 129.0 (CH), 128.3 (2 x CH), 125.3 (2 x CH), 56.5 (CH), 33.4 (CH_2), 30.9 (Cq), 28.5 (CH_3), 27.0 (CH_3), 23.5 (2 x CH_3), 21.1 (CH_3), 15.1 (CH_3). Mp: 136.5-139.4 °C. ν_{max} (neat)/cm^{-1}: 2964, 2930, 2873, 1598, 1461, 1443, 1327, 1162 HRMS (ESI) m/z: $[M + H]^+$ Calcd. for$C_{22}H_{28}N_2O_2S$ 385.1950; found 385.1952.

1-(Mesitylsulfonyl)-5,5,6-trimethyl-3-(naphthalen-2-yl)-1,4,5,6-tetrahydropyridazine (14b) According to the general procedure, 130 mg (0.30 mmol) of 2,2-dimethylbut-3-enylnaphtone-*N*-2,4,6-mesitylsulfonylhydrazone (**12b**) were reacted with K_2CO_3 and $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ under blue light irradiation for 16 h to obtain 54 mg (0.12 mmol) of 1-(mesitylsulfonyl)-5,5,6-trimethyl-3-(naphthalen-2-yl)-1,4,5,6-tetrahydropyridazine **14b** (42%) as a white solid.^{1}H NMR (600 MHz, $CDCl_3$, Me_4Si): δ 7.90 (s, 1H, Ar-*H*), 7.79 (m, 3H, Ar-*H*), 7.74 (d, *J* = 8.7 Hz, 1H, Ar-*H*), 7.45 (m, 2H, Ar-*H*), 6.99 (s, 2H, Ar-*H*), 4.17 (q, *J* = 6.6 Hz, 1H, N-C*H*), 2.78 (s, 6H, *orto* Ar-(CH_3)), 2.52 (d, *J* = 17.7 Hz, 1H, $(CH_3)_2$-CH-C(H)*H*))), 2.42 (d, *J* = 17.7 Hz, 1H, $(CH_3)_2$-CH-C(H)*H*)), 2.31 (s, 3H, *para* Ar-(CH_3)), 1.34 (d, *J* = 6.6 Hz, 3H, N-CH-CH_3)), 1.16 (s, 3H, CH(CH_3)-C(CH_3)$_2$), 0.98 (s, 3H, , CH(CH_3)-C(CH_3)$_2$). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$,Me_4Si): δ 145.2 (Cq), 142.8 (Cq), 141.0 (2 x Cq), 134.9 (Cq), 133.6 (Cq), 133.1 (Cq),133.0 (Cq), 131.8 (2 x CH), 128.4 (CH), 127.9 (CH), 127.7 (CH), 126.6 (CH), 126.4 (CH), 124.7 (CH), 123.1 (CH), 56.6 (CH), 33.3 (CH_2), 30.9 (Cq), 28.6 (CH_3), 27.1 (CH_3), 23.5 (2 x CH_3), 21.1 (CH_3), 15.1 (CH_3). Mp: 136.2-139.8 °C. ν_{max} (neat)/cm^{-1}: 3052, 2958, 1602, 1503, 1321, 1160. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for$C_{26}H_{30}N_2O_2S$435.2106; found435.21.04.

1-(Mesitylsulfonyl)-5,5,6-trimethyl-3-(*p*-tolyl)-1,4,5,6-tetrahydropyridazine (14c)According to the general procedure, 119 mg (0.30 mmol) of 2,2-dimethylbut-3-enyl-p-tolyl

ketone-*N*-mesitylsulfonylhydrazone (**12c**) were reacted with K_2CO_3 and $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ under blue light irradiation for 16 h to obtain 74 mg (0.19 mmol) of 1-(mesitylsulfonyl)-5,5,6-trimethyl-3-(p-tolyl)-1,4,5,6-tetrahydropyridazine **14c** (62%) as a white solid.^{1}H NMR (600 MHz, $CDCl_3$, Me_4Si): δ 7.46 (d, *J* = 7.8 Hz, 1H, Ar-*H*), 7.10 (d, *J* = 7.8 Hz, 1H, Ar-*H*), 6.95 (s, 2H, Ar-*H*), 4.12 (q, *J* = 6.6 Hz, 1H, N-C*H*), 2.76 (s, 6H, *orto* Ar-(CH_3)$_2$), 2.38 (d, *J* = 18.0 Hz, 1H, (CH$_3$)$_2$-CH-C(H)*H*), 2.32 (s, 3H, *para* Ar-CH_3), 2.29 (s, 3H, Ar-CH_3, tolyl), 2.23 (d, *J* = 18.0 Hz, 1H, (CH$_3$)$_2$-CH-C(H)*H*), 1.29 (d, *J* = 6.6 Hz, 3H, N-CH-CH_3), 1.10 (s, 3H, CH(CH$_3$)-C(CH_3)$_2$), 0.92 (s, 3H, , CH(CH$_3$)-C(CH_3)$_2$). ^{13}C{^{1}H}NMR (151 MHz, $CDCl_3$,Me_4Si): δ 145.4 (Cq), 142.6 (Cq), 141.0 (2 x Cq), 138.9 (Cq), 134.6 (Cq), 133.2 (Cq),131.7 (2 x CH), 129.0 (2 x CH), 125.2 (2 x CH), 54.4 (CH), 33.4 (CH$_2$), 30.9 (Cq), 28.5 (CH$_3$), 27.0 (CH$_3$), 23.5 (2 x CH$_3$), 21.3 (CH$_3$), 21.1 (CH$_3$), 15.0 (CH$_3$). Mp: 142.0-147.0 °C. ν_{max} (neat)/cm^{-1}: 3020, 2958, 1682, 1611, 1511, 1324, 1109. HRMS (ESI) m/z: [M + Na]$^+$ Calcd. for$C_{23}H_{30}N_2O_2S$ 421.1920; found 421.1919.

1-(Mesitylsulfonyl)-5,5,6-trimethyl-3-(*o*-tolyl)-1,4,5,6-tetrahydropyridazine (14d)According to the general procedure, 119 mg (0.30 mmol) of 2,2-dimethylbut-3-enyl-o-tolyl ketone-*N*-mesitylsulfonylhydrazone (**12d**) were reacted with K_2CO_3 and $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ under blue light irradiation for 16 h to obtain 49 mg (0.13 mmol) of 1-(mesitylsulfonyl)-5,5,6-trimethyl-3-(*o*-tolyl)-1,4,5,6-tetrahydropyridazine **14d** (42.5%) as a white solid.^{1}H NMR (600 MHz, $CDCl_3$, Me_4Si): δ 7.13 (m, 4H), 6.89 (s, 2H, Ar-*H*), 4.10 (q, *J* = 6.6 Hz, 1H), 2.76 (s, 6H, *orto* Ar-(CH_3)$_2$), 2.43 (d, *J* = 18.0 Hz, 1H, (CH$_3$)$_2$-CH-C(H)*H*), 2.27 (s, 3H, *para* Ar-CH_3), 2.01 (s, 3H, *orto* tolyl), 1.99 (d, *J* = 18.0 Hz, 1H, (CH$_3$)$_2$-CH-C(H)*H*),), 1.35 (d, *J* = 6.6 Hz, 3H, N-CH-CH_3), 1.06 (s, 3H, CH(CH$_3$)-C(CH_3)$_2$), 0.99 (s, 3H, , CH(CH$_3$)-C(CH_3)$_2$). ^{13}C{^{1}H}NMR (151 MHz, $CDCl_3$, Me_4Si): δ 148.1 (Cq) 141.0 (2 x Cq), 138.3 (Cq), 136.0 (Cq), 133.3 (Cq) 131.7 (2 x CH), 131.0 (CH), 128.1 (CH), 127.7 (CH), 125.5 (CH), 56.1 (CH), 37.0 (CH$_2$), 31.0 (Cq), 29.8 (CH$_3$), 28.4 (CH$_3$), 26.8 (CH$_3$), 23.3 (CH$_3$), 21.0 (CH$_3$), 20.1 (CH$_3$), 15.2 (CH$_3$).Mp: 112.0-116.7°C. ν_{max} (neat)/cm^{-1}: 2992, 2958, 1602, 1456, 1317, 1161, 1032, 776.HRMS (ESI) m/z: [M + Na]$^+$ Calcd. for: $C_{23}H_{30}N_2O_2S$421.1920; found421.1916 .

1-(Mesitylsulfonyl)-3,5,5,6-tetramethyl-1,4,5,6-tetrahydropyridazine (14e) According to the general procedure, 97 mg (0.30 mmol) of 4,4-dimethylhex-5-en-2-one-*N*-mesitylhydrazone **12e** were reacted with K_2CO_3 and $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ under blue light irradiation for 16 h to obtain 53 mg (0.165 mmol) of 1-(mesitylsulfonyl)-3,5,5,6-tetramethyl-1,4,5,6-tetrahydropyridazine **14e** (55%) as a white solid.^{1}H NMR (600 MHz, $CDCl_3$, Me_4Si):δ 6.92 (s, 2H, Ar-*H*), 3.97 (qd, *J* = 6.6,

1.5 Hz, 1H, N-C*H*), 2.68 (s, 6H, *orto* Ar-(CH_3)), 2.28 (s, 3H, *para* Ar-(CH_3)), 2.00 (d, *J* = 18.5 Hz, 1H, $(CH_3)_2$-CH-C(H)*H*)), 1.82 (s, 3H, N=C-CH_3), 1.67 (dd, *J* = 18.5, 1.5 Hz, 1H, $(CH_3)_2$-CH-C(H)*H*)), 1.21 (d, *J* = 6.6 Hz, 3H, N-CH-CH_3)), 0.98 (s, 3H, CH(CH_3)-C(CH_3)$_2$), 0.88 (d, *J* = 0.9 Hz, 3H, CH(CH_3)-C(CH_3)$_2$). $^{13}C\{^1H\}$NMR (151 MHz, $CDCl_3$,Me_4Si):δ 148.3 (Cq), 142.3 (Cq), 141.0 (2 x Cq), 133.6 (Cq), 131.6 (2 x CH), 55.9 (CH), 37.2 (CH_2), 31.0 (Cq), 28.4 (CH_3), 26.8 (CH_3), 24.1 (CH_3), 23.4 (2 x CH_3), 21.1 (CH_3), 14.5(CH_3).Mp: degradation 150-170 °C. ν_{max}(neat)/cm^{-1}: 2967, 1712, 1602, 1314, 1080.HRMS (ESI) m/z: $[M + H]^+$ Calcd. for$C_{17}H_{26}N_2O_2S$323.1793; found 323.1790.

(7*R*)-2-(Mesitylsulfonyl)-3,4,4,7-tetramethyl-2,3,4,4a,5,6,7,8-octahydrocinnoline (14f)According to the general procedure, 105 mg (0.30 mmol) of pulegone derivative *N*-mesitylsulfonylhydrazone (**12g**) were reacted with K_2CO_3 and $[Ru(bpy)_3]Cl_2·6H_2O$ under blue light irradiation for 16 h to obtain 37 mg (0.124 mmol) of (7*R*)-2-(mesitylsulfonyl)-3,4,4,7-tetramethyl-2,3,4,4a,5,6,7,8-octahydrocinnoline **14f** (35%) as a white solid.^{1}H NMR (600 MHz, $CDCl_3$, Me_4Si):δ 6.92 (s, 2H, Ar-*H*), 3.97 (q, *J* = 6.6 Hz, 1H, N-C(CH_3)*H*), 2.68 (s, 6H, *orto* Ar-CH_3), 2.35 (ddd, *J* = 14.7, 4.1, 2.3 Hz, 1H, CH-CH_2-C(CH_3)H), 2.28 (s, 3H, *para* Ar-(CH_3)), 1.86 (dd, J = 12.0, 4.4 Hz, 1H, C(H)*H*-C=N); 1.81-1.77 (m, 2H, CH-C(H)*H*-CH_2-CH), 1.72 (t, *J* = 12.6, 1H, CH-C(H)*H*-C(CH_3)H), 1.49 – 1.42 (m, 1H, CH -CH_2-C(H)*H*-CH), 1.18 (d, *J* = 6.6 Hz, 3H, N-CH-CH_3), 1.17 – 0.98 (m, 2H, CH-C(H)*H*-CH_2-CH with CH -CH_2-C(H)*H*-CH), 0.96 (s, 3H, -C(CH_3)-CH_3), 0.90 (d, *J* = 6.5 Hz, 3H, CH_2-C*H*(CH_3)-CH_2), 0.84 (s, 3H, -C(CH_3)-CH_3). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$, Me_4Si): δ 153.9 (Cq), 142.3 (Cq), 141.1 (2 x Cq), 133.6 (Cq), 131.6 (2 x CH), 58.4 (CH), 42.9 (CH_2), 41.03 (CH), 34.0 (CH_2), 32.8 (CH), 25.3 (CH_3), 25.1 (CH_2), 24.9 (CH_3), 23.4 (2 x CH_3), 22.2 (CH_3), 21.1 (CH_3), 13.2 (CH_3). Mp: degradation 106-115 °C. ν_{max} (neat)/cm^{-1}: 3001, 2937, 1627, 1602, 1379, 1159.HRMS (ESI) m/z: $[M + H]^+$ Calcd. for$C_{21}H_{32}N_2O_2S$ 377.2263; found 377.2265.

5,5-Dimethyl-3-phenyl-6-(2,4,6-trimethylbenzyl)-1,4,5,6-tetrahydropyridazine (15a) According to general procedure 115 mg (0.30 mmol) of 2,2-dimethylbut-3-enylphenone-*N*-2,4,6-mesitylsulfonylhydrazone **12a** were reacted with K_2CO_3 and $[Ru(bpy)_3]Cl_2·6H_2O$ under blue light irradiation for 16 h to obtain 43 mg (0.13 mmol) of 5,5-dimethyl-3-phenyl-6-(2,4,6-trimethylbenzyl)-1,4,5,6-tetrahydropyridazine **15a** (45%) as a greenish oil.^{1}H NMR (600 MHz, $CDCl_3$, Me_4Si):δ 7.62 (d, J = 7.2 Hz, 2H, Ar-*H*), 7.31 (tm, J = 7.5, 2H, Ar-*H*), 7.24 (m, 1H, Ar-*H*), 6.85 (s, 2H, Ar-*H*), 5.39 (bs, 1H, N-*H*), 3.06 (dm, *J* = 11.5Hz, 1H, NH-CH-C(H)*H*-CH), 2.89 (dd,

J = 13.8, 3.5 Hz, 1H, NH-CH-C(H)*H*-CH), 2.77 (tm, *J* = 12.5, 1H, NH-C*H*), 2.43 (d, *J* = 17.6 Hz, 1H, N=C(Ph)-C(H)*H*), 2.38 (d, *J* = 17.7 Hz, 1H, N=C(Ph)-C(H)*H*), 2.33 (s, 6H, *orto* Ar-(C*H*$_3$)), 2.25 (s, 3H, *para* Ar-(C*H*$_3$)), 1.18 (s, 3H C(CH$_3$)-C*H*$_3$), 1.11 (s, 3H, C(CH$_3$)-C*H*$_3$). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$,Me_4Si):δ 141.6 (Cq), 138.8 (Cq), 137.3 (2 x Cq), 136.0 (Cq), 131.5 (Cq), 129.5 (2 x CH), 128.3 (2 x CH), 127.6 (CH), 124.2 (2 x CH), 59.0 (CH), 39.1 (CH_2), 30.6 (Cq), 27.4 (2 x CH_3), 26.8 (CH_2), 22.4 (CH_3), 20.9 (CH_3), 20.6 (CH_3). ν_{max}(neat)/cm^{-1}: 3064, 2978, 1598, 1428, 1379, 1065. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for$C_{22}H_{28}N_2$321.2325; found 321.2330.

5,5-dimethyl-3-(naphthalen-2-yl)-6-(2,4,6-trimethylbenzyl)-1,4,5,6-tetrahydropyridazine (15b) According to general Procedure B, 130 mg (0.30 mmol) of 2,2-dimethylbut-3-enylnaphtone-*N*-2,4,6-mesitylsulfonylhydrazone (**12b**) were reacted with K_2CO_3 and $[Ru(bpy)_3]Cl_2·6H_2O$ under blue light irradiation for 16 h to obtain 35 mg (0.093 mmol) of 5,5-dimethyl-3-(naphthalen-2-yl)-6-(2,4,6-trimethylbenzyl)-1,4,5,6-tetrahydropyridazine**15b** (30%) as a greenish solid. ^1H NMR (600 MHz, $CDCl_3$, Me_4Si): δ 7.94 (dd, *J* = 8.8, 1.8 Hz, 1H, Ar-*H*), 7.86 (s, 1H, Ar-*H*), 7.76 (m, *J* = 15.9, 7.7 Hz, 3H, Ar-*H*), 7.43 (q, J = 6.6 Hz, 2H, Ar-*H*), 6.86 (s, 2H, Ar-*H*), 5.48 (s, 1H, N-*H*), 3.09 (dd, *J* = 11.6, 2.7 Hz, 1H, NH-CH-C(H)*H*-CH), 2.89 (dd, *J* = 13.7, 3.1 Hz, 1H, NH-C*H*), 2.80 (dd, *J* = 13.7, 11.6 Hz, 1H, NH-CH-C(H)*H*-CH), 2.51 (d, *J* = 2.8 Hz, 2H, N=C(Ar)-C*H*$_2$), 2.32 (s, 6H, *orto* Ar-(C*H*$_3$)), 2.23 (s, 3H, *para* Ar-(C*H*$_3$), 1.20 (s, 3H, C(CH$_3$)-C*H*$_3$), 1.13 (s, 3H, C(CH$_3$)-C*H*$_3$). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$,Me_4Si): δ 141.3 (Cq), 137.3 (2 x Cq), 136.3 (Cq), 136.0 (Cq), 133.5 (Cq), 133.0 (Cq), 131.4 (Cq), 129.5 (2 x CH), 128.2 (CH), 127.7 (CH), 127.7 (CH), 126.1 (CH), 125.8 (CH), 122.9 (CH), 122.7 (CH), 59.1 (CH), 39.0 (CH_2), 30.6 (Cq), 27.5 (2 x CH_3), 26.9 (CH_2), 22.4 (CH_3), 20.9 (CH_3), 20.6 (CH_3). Mp: 124.5-128.7 °C. ν_{max}(neat)/cm^{-1}: 3052, 2961, 1606, 1479, 1365, 1260.HRMS (ESI) m/z: $[M + H]^+$ Calcd. for$C_{26}H_{30}N_2$371.2482; found371.2490.

5,5-Dimethyl-3-(*p*-tolyl)-6-(2,4,6-trimethylbenzyl)-1,4,5,6-tetrahydropyridazine (15c)According to the general procedure, 119 mg (0.30 mmol) of 2,2-dimethylbut-3-enyl-p-tolyl ketone-*N*-mesitylsulfonylhydrazone (**12c**) were reacted with K_2CO_3 and $[Ru(bpy)_3]Cl_2·6H_2O$ under blue light irradiation for 16 h to obtain 25 mg (0.075 mmol) of 5,5-dimethyl-3-(p-tolyl)-6-(2,4,6-trimethylbenzyl)-1,4,5,6-tetrahydropyridazine **15c** (25%) as a greenish oil.^1H NMR (600 MHz, $CDCl_3$, Me_4Si): δ 7.52 (dm, *J* = 8.4, 2H, Ar-*H*), 7.13 (d, J = 8.4 Hz, 2H, Ar-*H*), 6.86 (s, 2H, Ar-*H*), 5.34 (bs, 1H, N-*H*), 3.05 (dd, *J* = 11.4, 3.0 Hz, 1H, NH-CH-C(H)*H*-CH), 2.89 (dd, *J* = 13.8, 3.6 Hz, 1H, NH-C*H*), 2.80 (dd, *J* = 13.8, 11.4 Hz, 1H, NH-CH-C(H)*H*-CH), 2.43 (d, *J* = 17.4 Hz,

1H, N=C(Ar)-CH_{2a}), 2.36 (d, *J* = 17.4 Hz, 1H, N=C(Ar)-CH_{2b}), 2.34 (s, 6H, *orto* Ar-CH_3), 2.33 (s, 3H, *para* Ar-(CH_3), 2.25 (s, 3H, *para* Ar-(CH_3), 1.18 (s, 3H, C(CH_3)-CH_3), 1.12 (s, 3H, C(CH_3)-CH_3).^{13}C{^{1}H}NMR (151 MHz, $CDCl_3$,Me_4Si): δ 142.1 (Cq), 137.2 (2 x Cq), 136.0 (2 x Cq), 131.7 (Cq), 131.5 (2 x Cq), 129.5 (2x CH), 129.2 (Cq), 129.0 (2 x CH), 124.3 (2 x CH), 59.0 (CH), 39.2 (CH_2), 30.6 (Cq), 27.4 (2 x CH_3), 26.8 (CH_2), 22.3 (CH_3), 21.2 (CH_3), 20.9 (CH_3), 20.5 (CH_3). ν_{max}(neat)/cm^{-1}: 3372, 2958, 2916, 2885, 1511, 1460, 1366, 1324. HRMS (ESI) m/z: [M + H]$^+$ Calcd. for$C_{23}H_{30}N_2$335.2482; found 335.2481.

5,5-Dimethyl-3-(*o*-tolyl)-6-(2,4,6-trimethylbenzyl)-1,4,5,6-tetrahydropyridazine (15d)According to the general procedure, 119 mg (0.30 mmol) of 2,2-dimethylbut-3-enyl-*o*-tolyl ketone-*N*-mesitylsulfonylhydrazone (**12d**) were reacted with K_2CO_3 and [Ru(bpy)$_3$]Cl_2·6H_2O under blue light irradiation for 16 h to obtain 16 mg (0.06 mmol) of 5,5-dimethyl-3-(o-tolyl)-6-(2,4,6-trimethylbenzyl)-1,4,5,6-tetrahydropyridazine **15d** (19%) as a greenish oil.^{1}H NMR (600 MHz, $CDCl_3$, Me_4Si): δ 7.15 (m, 4H, Ar-*H*), 6.85 (s, 2H, Ar-*H*), 5.04 (bs, 1H, N-*H*), 3.07 (dd, *J* = 11.4, 3.0 Hz, 1H, NH-CH-C(H)*H*-CH), 2.89 (dd, *J* = 13.8, 3.6 Hz, 1H, NH-C*H*), 2.78 (dd, *J* = 13.8, 11.4 Hz, 1H, NH-CH-C(H)*H*-CH), 2.36 (d, *J* = 17.4 Hz, 1H, N=C(Ar)-CH_{2a}), 2.34 (s, 6H, *orto* Ar-CH_3), 2.33 (s, 3H, *orto* tolyl), 2.24 (s, 3H, *para* Ar-(CH_3)), 2.23 (d, *J* = 17.4 Hz, 1H, N=C(Ar)-CH_{2b}), 1.24 (s, 3H, C(CH_3)-CH_3), 1.16 (s, 3H, C(CH_3)-CH_3). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, Me_4Si): δ 141.8 (Cq), 137.3 (Cq), 137.3 (Cq), 137.2 (2 x Cq), 136.0 (2 x Cq), 135.6 (Cq), 130.8 (CH), 129.5 (2 x CH), 127.8 (CH), 125.7 (CH), 59.1 (CH), 42.7 (CH_2), 30.7 (Cq), 27.2 (CH_3), 27.0 (CH_2), 24.2 (CH_3), 22.4(CH_3), 20.9(CH_3), 20.6 (CH_3), 20.4 (CH_3). ν_{max}(neat)/cm^{-1}: 3371, 2975, 2920, 1611, 1484, 1453, 1384, 1319, 1259, 1014. HRMS (ESI) m/z: [M + H]$^+$ Calcd. for$C_{23}H_{30}N_2$335.2487; found 335.2489.

3,5,5-trimethyl-6-(2,4,6-trimethylbenzyl)-1,4,5,6-tetrahydropyridazine (15e) According to the general procedure, 97 mg (0.30 mmol) of 4,4-dimethylhex-5-en-2-one-*N*-mesitylhydrazone **12e** were reacted with K_2CO_3 and [Ru(bpy)$_3$]Cl_2·6H_2O under blue light irradiation for 16 h to obtain 53 mg (0.165 mmol) of 31 mg (0.120 mmol) of 3,5,5-trimethyl-6-(2,4,6-trimethylbenzyl)-1,4,5,6-tetrahydropyridazine **15e** (40%) as a greenish oil.^{1}H NMR (600 MHz, $CDCl_3$, Me_4Si):δ 6.81 (s, 2H, Ar-*H*), 4.80 (s, 1H, N-*H*), 2.84 (dd, *J* = 11.5, 3.3 Hz, 2H, NH-CH-C(H)*H*-CH), 2.80 (dd, *J* = 13.8, 3.3 Hz, 2H, NH-CH-C(H)*H*-CH), 2.66 (dd,*J* = 13.7, 11.5 Hz, 1H, NH-CH-C(H)*H*-CH), 2.30 (s, 6H, *orto* Ar-(CH_3)), 2.22 (s, 3H *para* Ar-(CH_3)), 1.99 (d, *J* = 18.2 Hz, 1H, N=C(Me)-C(H)*H*), 1.83 (d, *J* = 18.3 Hz, 1H, N=C(Me)-C(H)*H*), 1.77 (s, 3H, N=C-C(CH_2)H_3), 1.06 (s, 3H,

C(CH_3)-C*H*$_3$), 1.03 (s, 3H, C(CH_3)-C*H*$_3$).^{13}C{^{1}H}NMR (151 MHz, $CDCl_3$,Me_4Si):δ 145.0 (Cq), 137.2 (2 x Cq), 136.0 (Cq), 131.8 (Cq), 129.4 (2 x CH), 59.0 (CH), 43.2 (CH_2), 30.9 (Cq), 27.2 (2 x CH_3), 26.6 (CH_2), 23.6 (CH_3), 22.0 (CH_3), 20.8 (CH_3), 20.5 (CH_3).ν_{max} (neat)/cm^{-1}: 3377, 2950 2916, 1593, 1480, 1447, 1264, 1127, 1067.HRMS (ESI) m/z: [M + H]$^+$ Calcd. for$C_{17}H_{26}N_2$259.2174;found 259.2173.

5,5-Dimethyl-3-phenyl-6-(1-tolylethyl)-1,4,5,6-tetrahydropyridazine (15f) According to the general procedure, 119 mg (0.30 mmol) of 2,2-dimethylpent-3-en-2-one-*N*-tosylhydrazone **10j** were reacted with K_2CO_3 and [Ru(bpy)$_3$]Cl_2·6H_2O under blue light irradiation for 16 h to obtain 66 mg (0.22 mmol) 5,5-dimethyl-3-phenyl-6-(2,4,6-trimethylbenzyl)-1,4,5,6-tetrahydropyridazine **15f** (72%) as a yellow solid.^{1}H NMR (600 MHz, $CDCl_3$, Me_4Si):δ7.55 (dd, *J* = 8.4 Hz, 2H, Ph*H*), 7.55 (tm, *J* = 7.2 Hz, 2H, Ph*H*), 7.22 (tt, *J* = 7.2 Hz, 1.2, 1H, Ph*H*), 7.15 (dm, J = 6.6 Hz, 2H, Ar-*H*), 7.11 (dm, J = 6.6 Hz, 2H, Ar-*H*), 5.40 (s, 1H, N-*H*), 2.99 (d, *J* = 7.8 Hz, 1H, C*H*-ring), 2.92 (quint, *J* = 7.2 Hz, 1H, Tol-C*H*-CH_3), 2.40 (d,*J* = 18.0 Hz, 1H, C(H)*H*-ring), 2.32 (s, 3H, Ar-C*H*$_3$), 2.20 (d,*J* = 18.0 Hz, 1H, C(H)*H*-ring), 1.41 (d, *J* = 7.2 Hz, 3H, *J* = 7.2 Hz, 1H, Tol-CH-C*H*$_3$), 1.20 (s, 3H, CH_3ring), 0.90 (s, 3H, CH_3ring). ^{13}C{^{1}H}NMR (151 MHz, $CDCl_3$,Me_4Si):δ 141.2 (Cq), 140.9 (Cq), 138.8 (Cq), 136.4 (Cq), 129.5 (2 x CH), 128.2 (2 x CH), 128.0 (2 x CH), 127.4 (CH), 124.2 (2 x CH), 65.4 (CH), 40.3 (CH_2), 40.2 (CH), 31.0 (Cq), 29.4 (CH_3), 22.7 (CH_3), 22.5 (CH_3), 21.1 (CH_3). Mp: 89.0-95.8°C. ν_{max} (neat)/cm^{-1}: 3381, 3010, 2990, 1591, 1514, 1467, 1338, 1324, 1071. HRMS (ESI) m/z: [M + H]$^+$ Calcd. for$C_{21}H_{26}N_2$307.2169; found 307.2175.

3,5,5-Trimethyl-6-(1-tolylethyl)-1,4,5,6-tetrahydropyridazine (15g) According to the general procedure, 92 mg (0.30 mmol) of 4,4-dimethylhept-5-enone-*N*-tosylhydrazone **10k** were reacted with K_2CO_3 and [Ru(bpy)$_3$]Cl_2·6H_2O under blue light irradiation for 16 h to obtain 51.2 mg (0.21 mmol) 5,5-dimethyl-3-phenyl-6-(2,4,6-trimethylbenzyl)-1,4,5,6-tetrahydropyridazine 15g (70%) as a yellowish oil.^{1}H NMR (600 MHz, $CDCl_3$, Me_4Si):δ 7.11 (m, J = 6.6 Hz, 2H, Ar-*H*), 7.06 (dm, J = 6.6 Hz, 2H, Ar-*H*), 5.40 (s, 1H, N-*H*), 2.92 (q, *J* = 7.2 Hz, 1H, Tol-C*H*-CH_3), 2.74 (d, *J* = 7.2 Hz, 1H, C*H*-ring), 2.31 (s, 3H, Ar-C*H*$_3$), 1.98 (d,*J* = 16.8 Hz, 1H, C(H)*H*-ring), 1.73 (s, 3H, N=C-C*H*$_3$), 1.67 (d,*J* = 16.8 Hz, 1H, C(H)*H*-ring), 1.34 (d, *J* = 7.2 Hz, 3H, *J* = 7.2 Hz, 1H, Tol-CH-C*H*$_3$), 1.08 (s, 3H, CH_3ring), 0.88 (s, 3H, CH_3ring). ^{13}C{^{1}H}NMR (151 MHz, $CDCl_3$,Me_4Si):δ 144.8 (Cq), 141.5 (Cq), 136.2 (Cq), 129.3 (2 x CH), 128.0 (2 x CH), 65.3 (CH), 44.4 (CH_2), 40.0 (CH), 31.6 (Cq), 29.2 (CH), 23.2 (CH_3), 22.7 (CH_3), 22.4 (CH_3), 21.1 (CH_3). ν_{max} (neat)/cm^{-1}:

3060, 2964, 1498, 1338, 1260, 1157. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for$C_{16}H_{26}N_2$245.2018; found 245.2015.

5,5-Dimethyl-3-phenyl-6-(1-mesityllethyl)-1,4,5,6-tetrahydropyridazine (15h) According to the general procedure, 119 mg (0.30 mmol) of 2,2-dimethylpent-3-en-2-one-*N*-mesitylsulfonylhydrazone **12f** were reacted with K_2CO_3 and $[Ru(bpy)_3]Cl_2·6H_2O$ under blue light irradiation for 16 h to obtain 66 mg (0.22 mmol) 5,5-dimethyl-3-phenyl-6-(2,4,6-trimethylbenzyl)-1,4,5,6-tetrahydropyridazine **15h** (72%) as a yellow solid.^{1}H NMR (600 MHz, $CDCl_3$, Me_4Si): δ7.58 (dd, *J* = 7.2, 1.8 Hz, 2H, Ph*H*), 7.31 (tm, *J* = 7.2 Hz, 2H, Ph*H*), 7.24 (tm, *J* = 7.2 Hz, 1H, Ph*H,* isomer A), 7.22 (tm, *J* = 7.2 Hz, 1H, Ph*H,* isomer B), 6.83 (s, 2H, Mes-*H,* isomer A), 6.82 (s, 2H, Mes-*H,* isomer B), 5.31 (s, 1H, N-*H*), 3.51 (quint, *J* = 7.2 Hz, 1H, Tol-C*H*-CH_3), 3.32 (d, *J* = 9.0 Hz, 1H, C*H*-ring), 2.52 (d, *J* = 17.4 Hz, 1H, C(H)*H*-ring), 2.39 (s, 3H, Ar-C*H₃*), 2.34 (s, 3H, Ar-C*H₃*), 2.28 (d, *J* = 17.4 Hz, 1H, C(H)*H*-ring), 2.24 (s, 3H, Ar-C*H₃*), 1.45 (d, *J* = 7.2 Hz, 3H, *J* = 7.2 Hz, 1H, Tol-CH-C*H*$_3$), 1.25 (s, 3H, CH_3 ring), 1.10 (s, 3H, CH_3 ring). $^{13}C\{^1H\}$NMR (151 MHz, $CDCl_3$,Me_4Si):(mixture of isomers) δ 140.3 (Cq), 138.8 (Cq), 137.4 (Cq), 136.1 (Cq), 135.9 (Cq), 131.4 (CH), 129.8 (2 x CH), 128.3 (2 x CH), 127.4 (CH), 124.1 (2 x CH), 63.5 (CH), 40.7 (CH_2), 40.2 (Cq), 34.2 (CH), 31.5 (Cq), 29.5 (CH_3), 22.6 (CH_3), 21.9 (CH_3), 21.4 (CH_3), 20.7 (CH_3), 20.2 (CH_3).ν_{max} (neat)/cm^{-1}: 3394, 3010, 2992, 1608, 1572, 1445, 1307, 1131. Mp: 85.4-89.7 °C. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for$C_{23}H_{30}N_2$335.2482; found 335.2482.

TEMPO-trapping experiment: isolation of TEMPO adduct 16 In a sealed photochemical reactor 6.8 mg (0.009 mmol) of $[Ru(bpy)_3]Cl_2·6H_2O$ were dissolved in 5 mL of anhydrous CH_3CN, and the solution was degassed with N_2 for 15 min. Then 2,2-dimethylbut-3-enylphenonetosylhydrazone **10a** (107.0 mg, 0.300 mmol), TEMPO radical (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl) (94.0 mg, 0.600 mmol) and K_2CO_3 (62.5 mg, 0.45 mmol) were added in one portion and the solution degassed for additional 10 min. The mixture was then stirred at 4 cm from the irradiation source (see above) at room temperature for 16 h. The solution was then filtered on a pad of silica gel and celite using CH_2Cl_2 as eluent and Et_2O to wash the column. The crude product was purified by flash chromatography on silica gel (hexane/acetone 92/8) to obtain 46.4 mg (0.009 mmol) of the TEMPO-adduct (5,5-dimethyl-3-phenyl-6-(((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)-1-tosyl-1,4,5,6-tetrahydropyridazine) **16** as light pink crystals (yield=30%). ^{1}H NMR (600 MHz, Methanol-d_4) δ 7.75 (d, *J* = 8.2 Hz, 2H, Ar-*H*), 7.39 – 7.35 (m, 2H, Ar-*H*), 7.21 (d, *J* = 7.9 Hz, 3H, Ar-*H*), 7.18 (t, *J* = 7.4 Hz, 2H, Ar-*H*), 7.14 (d, *J* = 7.0

Hz, 1H, Ar-*H*), 5.73 (dd, *J* = 17.4, 10.7 Hz, 1H, C*H*=CH_2), 4.63 (dd, *J* = 17.5, 1.7 Hz, 1H, CH=CH_2*H trans*), 4.49 (dd, *J* = 10.7, 1.6 Hz, 1H, CH=CH_2*H cis*), 2.88 (s, 2H, N=C(Ph)-CH_2), 2.34 (s, 3H, Ar-CH_3), 0.80 (s, 6H, C(CH_3)$_2$). $^{13}C\{^1H\}$NMR (151 MHz, Methanol-d_4) δ 150.3 (Cq), 149.0 (CH), 142.1 (Cq), 141.9 (Cq), 140.3 (Cq), 128.3 (2 x CH), 127.4 (2 x CH), 126.9 (2 x CH), 126.8 (2 x CH), 126.6 (CH), 108.1 (CH_2), 37.9 (Cq), 37.2 (CH_2), 29.9 (CH_3), 26.71 (2 x CH_3). HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{29}H_{41}N_3O_3S$512.294; found 512.2938. IR ν_{max} (neat)/ cm^{-1}: 3002, 2951, 1733, 1598, 1493, 1344, 1167, 1092. X-RAY: see ESI

Scaled-up procedure for the synthesis of 2,4,4,7-Tetramethyl-3,4,4a,5,5a,8-hexahydrobenzo[e]pyridazino[1,6-b][1,2]thiazine 10,10-dioxide (13i) In a large-sized sealed photochemical reactor (40 mm as ID and 25 mm height), 40 mg of $[Ru(bpy)_3]Cl_2·6H_2O$ (0.06 mmol) were dissolved in 25 mL of anhydrous CH_3CN, and the solution was degassed with N_2 for 15 min. Then 4,4-Dimethylhex-5-en-2-one-N-tosylhydrazone **10i** (0.590 gr, 2.00 mmol) andK_2CO_3 (0.415 g, 3.00 mmol) were added in one portion and the solution degassed for additional 10 min. The mixture was then stirred at 4 cm from the irradiation source (see above) at room temperature until reaction completion, which occurred in 72 h. The solution was then filtered on a pad of silica gel and celite using CH_2Cl_2 as eluent and Et_2O to wash the column. The crude product was purified by flash chromatography on silica gel (hexane/acetone 92/8) to obtain 0.300 g of *2*,4,4,7-Tetramethyl-3,4,4a,5,5a,8-hexahydrobenzo[e]pyridazino[1,6-b][1,2]thiazine 10,10-dioxide **13i**as a white solid (yield=51%).

Conflicts of interest

There are no conflicts to declare.

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ASSOCIATED CONTENT

Supporting Information.

The following files are available free of charge.

ESI experimental (PDF)

ESI computational (PDF)

Spectra (PDF)

CHECKCIF compounds **13a** and **16**

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Author Contributions

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