Chapter 3

Visible Light Photoredox Catalysis: Investigation of Distal sp$^3$ C-H Activation of $t$-Amines
3.1 Introduction / Background of our concept:

Recently, C-H functionalization using visible light photoredox catalysis\(^1\) have emerged as a novel concept in organic synthesis mainly due to environmental concern. As discussed in Chapter 1 (Section 1.4.3) and 2, in the context of \(\alpha\)-sp\(^3\) C-H functionalization of \(t\)-amines (an important synthetic transformation in the synthesis of many biologically active compounds), chemistry from both \(\alpha\)-amino alkyl radical\(^2,3\) and iminium ion\(^2,4\) have been explored mainly employing Ru(bpy)\(_3\)Cl\(_2\) or [Ir(ppy)\(_2\)(dtb-bpy)]PF\(_6\) complex as visible light absorbing photocatalyst, (Figure 1), though such transformations were reported earlier via oxidative photoinduced electron transfer (PET) processes\(^5\) utilizing electron deficient aromatics as an electron acceptors.

![Figure 1. Photoredox oxidation of \(t\)-amines.](image)

Importantly, although \(\alpha\)-sp\(^3\) C-H functionalization of \(t\)-amines by photoredox catalyses abound, distal sp\(^3\) C-H functionalization of \(t\)-amines is an infrequent observation.\(^6,7\) Continuing with our interest to investigate new synthetic methodologies by photoredox catalysis in general\(^8\) and \(t\)-amines in particular,\(^5a,9,10\) we got interested to explore visible light (blue LED) mediated photoredox catalyzed one electron oxidation of \(t\)-amines where two possible sp\(^3\) C-H sites are available for deprotonation (Figure 2). In this context, we selected 10-methyl-9,10-dihydroacridine (AcrH\(_2\), \(1\)) and 4-alkyl-\(N,N\) dimethyl anilines (\(2-3\)) for our study and disclose herein a mechanistically interesting and synthetically useful chemistry.

![Figure 2. \(t\)-Amines having two possible deprotonation sites.](image)
However, in order to put our work in proper perspective, it would be appropriate to highlight few important literature methodologies pertaining to distal (β/C3 or γ/C4) sp³ C-H activation of t-amines for C-C bond formation reactions.

3.2 Earlier reports:

3.2.1 Non-photochemical approaches:

Liang and co-workers have reported a mild platinum-catalyzed oxidative dehydrogenation of α,β-C(sp³)-H bonds of t-amines for in situ generation of enamine intermediate, which reacted with various nitroolefins to produce corresponding addition product (Scheme 1).\textsuperscript{11}

**Scheme 1:** Platinum-catalyzed reaction of t-amines with nitroolefins.

Mechanistically, platinum catalyst [Pt] coordinates to nitrogen, which upon oxidation produces an iminium ion intermediate 9 through the activation of α sp³ C-H bond. Subsequent β-hydrogen elimination produces enamine 10, which undergoes
Michael addition with nitroolefins 5 and 7 to give the Michael adduct intermediates 11 (path A) and 12 (path B), respectively. Afterward, hydrogen elimination from 11 produces 6 readily. In contrast, 12 reacts intramolecularly by the nucleophilic hydroxyl group giving rise to a structurally different product 8.\(^\text{11}\)

Similar reaction as mentioned above by using more ubiquitous Fe metal catalyst in presence of di-tert-butyl peroxide (TBP) as an oxidant (Scheme 2) is also reported.\(^\text{12}\)

**Scheme 2:** Iron-catalyzed reaction of t-amines with nitroolefins.

Bruneau and co-workers have reported ruthenium catalysed regioselective C(3) alkylation of 15 via dehydrogenation (under nonoxidative conditions), C-C bond formation followed by transfer hydrogenation reaction sequence as shown in Scheme 3.\(^\text{13}\)

**Scheme 3:** C3 alkylation of t-amines with aldehyde.

In the context of direct γ sp\(^3\) C-H bond activation of t-amines, Klussmann and co-workers have reported an oxidative cross-coupling reaction of N-substituted acridanes (18) with ketones (19) in presence of catalytic amount of triflic acid and elemental oxygen.\(^\text{14}\) Mechanistically this reaction involved a radical pathway intermediated-autoxidative formation of N-substituted acridane hydroperoxide (21), which through H\(^+\) catalysis generated carbocationic intermediate 22 and reaction of this intermediate with the enolate produced 20 (Scheme 4).
Scheme 4: Acid catalyzed aerobic coupling of N-substituted acridane with ketone.

Similar type of reaction is also reported by TEMPO-catalysed coupling of N-substituted acridanes 18 with various nucleophiles, such as nitromethane, malonate and malononitrile (Scheme 5). 15 Although in this report, on the basis of kinetic isotopic effect (K_H/K_D = 4.0), the cleavage of benzylic C-H bond (γ sp^3 C-H) was involved as the rate-determining step, more detailed mechanistic studies were suggested in order to unravel this hypothesis.

Scheme 5: TEMPO catalyzed aerobic coupling of N-substituted acridanes with various nucleophiles.
3.2.2 Photochemical approaches:

Photoinduced electron-proton-electron loss reaction sequence of NADH\(^{16}\) and their analogues such as 10-methyl-9,10-dihydroacridine\(^{17}\)(AcrH\(_2\), 1) and 1-benzyl-1,4-dihydronicotinamide (BNAH, 27)\(^{6a}\) have been extensively studied to understand the mechanistic pathways involved in biological oxidation-reduction reactions and for the reduction of various organic substrates. However, in rare transformations Pac and co-workers reported the Ru(bpy)\(_3\)Cl\(_2\) photocatalysed reaction of BNAH (27) with several aromatic carbonyl compounds to obtain 1:1 coupling adducts of kind 29 in moderate to good yields along with corresponding less efficient or no reduction products of carbonyl compounds. The mechanism of this reaction is shown in Scheme 6.

![Scheme 6: Coupling reactions of BNAH with carbonyl compounds.](image)

However, it is important to note that Pac and co-workers in their earlier report demonstrated that the Ru(bpy)\(_3\)Cl\(_2\) photocatalysed reaction of BNAH (27) with electron deficient olefin 34 mainly gave reduced product 35 along with some minor coupling adduct 36 in exceptional cases (Scheme 7).\(^{6a}\) Furthermore, in an elaborate mechanistic study, it was pointed out that 34 which possessed one aryl substituent with no extra electron-withdrawing group at \(\beta\) position gave coupling adduct 36 in low to moderate yield (4-37\%) along with traces of dimers of 27 and 34.\(^{6b}\)
Scheme 7: Photochemical reactions of BNAH with electron deficient alkenes

It may be worthy of mention that Mak and co-workers reported the direct irradiation between \(1\) and more activated 9-fluorenylidene-malononitrile (38) in deaerated acetonitrile, using high-pressure Hg lamp produced coupling product (41), as shown in Scheme 8.18

Scheme 8: Photochemical coupling of 1 with 9-fluorenylidene-malononitrile (38).

From above discussion, it is evident that compared to \(\alpha/C2\) sp\(^3\) C-H activation of \(t\)-amines (Chapter 1, 2), very limited studies are available for distal sp\(^3\) C-H activation of \(t\)-amines. Considering the demand for further exploration in this field and our interest in developing photoinduced electron processes, we decided to take this challenge of investigating distal sp\(^3\) C-H functionalization of \(t\)-amines for alkylation reaction by visible light photoredox catalysis.
3.3 Results and discussion:

3.3.1 γ sp3 C-H activation reaction of t-amines with electron deficient alkenes:

We began our investigation by irradiating a mixture of 1 (AcrH2, 1 equiv.), methyl vinyl ketone (42, 3 equiv.) and catalytic amount of Ru(bpy)₃Cl₂·6H₂O (5 mol%) in degassed acetonitrile utilizing a blue LED (light emitting diode) (eq 1). Progress of reaction was monitored by following the disappearance of 1 on TLC. After 20 h of photoirradiation, when almost all of the 1 was consumed, solvent was removed and the product was purified by column chromatography to obtain 43 in 70% yield. In order to study the effect of solvent on this reaction, irradiations were carried out in different solvents and the results are summarized in Table 1. It was observed that there is no reaction either in dry toluene or dry THF (entries 2-3) and comparatively low yield was observed in dry CH₂Cl₂, MeOH, DMSO and DMF (entries 4-7). Almost similar results were observed employing [Ir(ppy)₂(dtb-bpy)]PF₆ (5 mol%) as a photoredox catalyst (entry 8). ¹⁹

Table 1: Photocatalyzed γ sp³ C-H alkylation of 1 with MVK (42).[^a]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Yield [%]</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>MeCN</td>
<td>70</td>
</tr>
<tr>
<td>2</td>
<td>Toluene</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>THF</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>CH₂Cl₂</td>
<td>09</td>
</tr>
<tr>
<td>5</td>
<td>MeOH</td>
<td>12</td>
</tr>
<tr>
<td>6</td>
<td>DMSO</td>
<td>26</td>
</tr>
<tr>
<td>7</td>
<td>DMF</td>
<td>40</td>
</tr>
<tr>
<td>8</td>
<td>MeCN</td>
<td>72[^b]</td>
</tr>
</tbody>
</table>

[^a] Reaction condition: 1 (0.51 mmol), 42 (1.53 mmol), Ru(bpy)₃Cl₂ catalyst (5 mol%), Blue LED light irradiation, Solvent (2 mL), 20 h.[^b] Reaction using [Ir(ppy)₂(dtb-bpy)]PF₆ catalyst (5 mol%).
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Control experiments:

When photoirradiation between 1 (1 equiv.) and MVK (42, 3 equiv.) was carried out in the absence of Ru(bpy)$_3$Cl$_2$ catalyst in degassed acetonitrile with blue LED, there was no observable product even after prolonged irradiation (48 h). Similarly, when the mixture of I(1 equiv.), MVK (42, 3 equiv.) and Ru(bpy)$_3$Cl$_2$ (5 mol%) in degassed acetonitrile was kept for 48 h in dark at room temperature, there was no reaction observed. These two appropriate control experiments showed that both Ru(bpy)$_3$Cl$_2$ catalyst and visible light (blue LED) were needed for the formation of 43.

Experimental set-up:

Identical experimental set-up, as portrayed in chapter 2, section 2.3.3 was utilized to perform these photolytic reactions.

3.3.2 Evaluation of the generality of the reaction:

After our initial successful results, in order to broaden the substrate scope of the reaction (eq. 1), a wide variety of electron deficient alkenes bearing non-aromatic as well as aromatic groups particularly at β-position were investigated under optimized reaction conditions and results are shown in Table 2. The yields are based on the consumption of 1, after column chromatography.

It was observed that compared to the reaction of MVK (42) (entry 1), acrolein (44) gave slightly low yield for corresponding product 52 (47%) (entry 2). However, it is significant to note that compared to simple β-unsubstituted alkenes 42, 44 (entry 1, 2), reactions with corresponding β-phenyl electron deficient alkenes 45, 46 proceeded smoothly to gave the improved yields for the coupled product 53 (87%) and 54 (60%) respectively (entry 3, 4). The scope of this reaction was also evaluated with β-(2-furyl)alkene framework (47) (entry 5), however, the corresponding coupling product 55 was formed in low yield (41%).

It may be significant to note that coupling of 1 with various kind of acyclic, cyclic and differently functionalized electron deficient alkenes, such as chalcone (48), nitrostyrene (49), cyclohexenone (50) and coumarin (51) proceeded with poor to moderate yield (30 - 58%, entries 6-9). In some cases (42, 44, 46 and 50), an excess of electron deficient alkene (3 equiv.) was used due to their competing self-polymerization reactions. Reaction with β-aromatic substituted alkenes (45-49 and 51) also produced small amounts of uncharacterized side products (5-10%).
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\[
1 + \begin{array}{c}
\text{R} - \text{C} - \text{X} \\
\text{42, 44-51 (1 or 3 equiv.)}
\end{array}
\xrightarrow{\text{Ru(bpy)}_2\text{Cl}_2\text{(5 mol%)} \\
\text{MeCN, Blue LED}}
\begin{array}{c}
\text{43, 52-59}
\end{array}
\]

Table 2. Photocatalyzed $\gamma$-sp$^3$ C-H alkylation of 1 with electron deficient alkenes $^{[a]}$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Alkene</th>
<th>Equiv.</th>
<th>Product</th>
<th>Time(h)</th>
<th>Yield %$^{[b]}$</th>
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<tr>
<td>1</td>
<td>O</td>
<td>3</td>
<td><img src="image" alt="Product 43" /></td>
<td>20</td>
<td>70</td>
</tr>
<tr>
<td>2</td>
<td>O</td>
<td>3</td>
<td><img src="image" alt="Product 52" /></td>
<td>18</td>
<td>47</td>
</tr>
<tr>
<td>3</td>
<td>Ph-O</td>
<td>1</td>
<td><img src="image" alt="Product 53" /></td>
<td>27</td>
<td>87</td>
</tr>
<tr>
<td>4</td>
<td>Ph-O</td>
<td>3</td>
<td><img src="image" alt="Product 54" /></td>
<td>22</td>
<td>60</td>
</tr>
<tr>
<td>5</td>
<td>O</td>
<td>1</td>
<td><img src="image" alt="Product 55" /></td>
<td>27</td>
<td>41</td>
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</table>

continued....
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<table>
<thead>
<tr>
<th>Entry</th>
<th>Alkene</th>
<th>Equiv.</th>
<th>Product</th>
<th>Time(h)</th>
<th>Yield [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>Ph=C=Ph</td>
<td>1</td>
<td><img src="image" alt="Product 56" /></td>
<td>20</td>
<td>56</td>
</tr>
<tr>
<td>7</td>
<td>Ph=C=NO2</td>
<td>1</td>
<td><img src="image" alt="Product 57" /></td>
<td>21</td>
<td>40</td>
</tr>
<tr>
<td>8</td>
<td>O</td>
<td>3</td>
<td><img src="image" alt="Product 58" /></td>
<td>21</td>
<td>58</td>
</tr>
<tr>
<td>9</td>
<td>Ph=O=Ph</td>
<td>1</td>
<td><img src="image" alt="Product 59" /></td>
<td>20</td>
<td>30</td>
</tr>
</tbody>
</table>

[a] Reaction condition: 1 (0.51 mmol), 42, 44-51 (0.51 or 1.53 mmol), Ru(bpy)_3Cl_2 catalyst (5 mol %), Blue LED light irradiation, MeCN (2 mL) [b] Yield based on consumption of 1 after column chromatography. [c] Predominantly cis (95%).

It was interesting to note that reaction with 45-51 produced only trans-isomers, which was confirmed by NMR analyses and by single X-ray crystal structures of 56 and 57 (Figure 3).\(^{19}\)

\[\text{Figure 3: X-ray structure of 56 and 57.}\]
3.3.3 Proposed reaction mechanism:

In order to rationalize this photoreaction, a plausible reaction mechanism is proposed as shown in Figure 4. The excited Ru(bpy)$_3^{2+}$ is quenched by single electron transfer from 1 (AcrH$_2$)$_2^{20}$ producing 60 (AcrH$_2$)$^+$ and a Ru(bpy)$_3^{+}$. The (AcrH$_2$)$^+$ undergoes deprotonation to generate $\gamma$-amino alkyl radical (61) (AcrH) which upon addition to activated alkenes forms 62. Reduction of 62 by Ru(bpy)$_3^{+}$ followed by protonation completes the reaction cycle with regeneration of the catalyst.$^{19}$

![Figure 4: Proposed mechanism for photocatalytic $\gamma$ C-H alkylation of 1.](image)

3.3.4 Synthesis of acridone:

Acridone and its derivatives show a wide range of biological and pharmacological activities$^{21}$ including anti-HIV,$^{21a}$ antiviral$^{21f}$ and therefore, their syntheses has attracted the attention of synthetic chemists. However, in most of the reported syntheses the requirement of stringent reaction conditions and tedious work-up, demands development of simpler strategy.$^{22}$

The proposed intermediacy of $\gamma$-amino alkyl radical (61) (AcrH) in the above reaction led us to envisage its application in the synthesis of acridone directly by the reaction of oxygen without using any consumable reagent. In this context, we found that identical photoirradiation of 1 in the presence of Ru(bpy)$_3$Cl$_2$ (5 mol%) in an open atmosphere produced 63 quantitatively (Scheme 9). The formation of 63 may be explained by the reaction of 61 [(AcrH)$^\prime$, Scheme 9] either with ground state
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oxygen\(^{[23a]}\) or by reaction with \(\text{O}_2^{-}\), formed through regeneration of \(\text{Ru(bpy)}_3^{2+}\) via an electron transfer by \(\text{Ru(bpy)}_3^{3+}\) to dissolved oxygen in the solvent.\(^{[23b]}\)

![Scheme 9: Photocatalyzed \(\gamma\) sp\(^3\) C-H oxygenation of 1.](image)

3.3.5 Intramolecular coupling reaction:

After having successfully demonstrated that \(\gamma\)-aminoalkyl radical, generated by visible light photoredox reaction between a \(t\)-amine and \(\text{Ru(bpy)}_3\text{Cl}_2\), undergoes alkylation reactions with activated olefins and oxygenation with air, further encouraged us to evaluate the scope of this work for the synthesis of important heterocyclic scaffold containing challenging all carbon quaternary centre by carrying

![Scheme 10: Photocatalyzed sequential addition reaction of 1 with dienone (64).](image)
out intramolecular reaction. In this regard, identical sequential photoredox catalysed alkylation reaction of 1 with 64 was carried out to produce spirocyclic product 66 (42% yield, based on consumption of 65) whose structure was confirmed by X-ray analysis beside NMR and mass spectral analyses (Scheme 10).

3.4 Investigation of substrate scope of this reaction for various other \( t \)-amines:

3.4.1 Initial results:

After successful demonstration of distal C-H functionalization of 1 by visible light photoredox catalysis, we proceeded to explore its further scope with other \( t \)-amines of type 2-3 having fairly acidic benzylic sp\(^3\) C-H bond. Under identical reaction condition as described earlier for 1, initially 2 (1 equiv.) was irradiated with 48 (1 equiv) in degassed CH\(_2\)CN in the presence of Ru(bpy)\(_3\)Cl\(_2\) (5 mol%), however, there was no indication of any observable reaction (monitored by TLC) even after prolonged irradiation (48 h).\(^{19}\) Identical reaction of 3 also did not result in the formation of any observable product (Scheme 11, eq 2).

\[
\text{Scheme 11: Photocatalytic reaction of } t \text{-anilines with 48.}
\]

Ultimately, after some experimentation with different solvent systems, we found that irradiation (24 h) of 2 (1 equiv.) with 48 (1 equiv) in degassed dry pyridine-MeOH (3:1) by using Ru(bpy)\(_3\)Cl\(_2\) (5 mol%) produced unexpectedly tetrahydroisoquinoline framework (67) in 29% yield (calculated on the basis of the consumption of 2, after column chromatographic purification) (Scheme 11, eq. 3). It is important to note that a careful LCMS analysis of the photolysate indicated complete consumption of 48 with appreciable amount of un-reacted 2 left and the formation of reduced chalcone. Furthermore, appropriate control experiments showed that both catalyst and visible light (blue LED) were needed for the formation of 67. It
is also important to point that use of another photoredox catalyst [Ir(ppy)$_2$(dtb-bpy)]PF$_6$ (5 mol%), did not help in improving the yield of 67.

In addition, photo irradiation of 2 (1 equiv.) with 48 (1 equiv.) using Ru(bpy)$_3$Cl$_2$ (5 mol%) in an open atmosphere in CH$_3$CN did not show the formation of tetrahydroquinoline$^{24}$ (67) at all, however, it was formed in <5% yield in pyridine:MeOH (3:1) after prolonged irradiation (48 h). It is important to mention that in both of these last two reactions, a small amount N-demethylated product of 2 was observed (4-5% yield).$^{25}$

3.4.2 Evaluation of the generality of the reaction:

In order to evaluate the generality of the above mentioned reaction (eq. 3), photo irradiation of various $t$-anilines with representative examples of electron deficient alkenes were investigated under identical experimental conditions and results are shown in Table 3. The yields are based on the consumption of $t$-anilines, after column chromatographic purification.

It was observed that irradiation of 2 with 45 gave corresponding tetrahydroquinoline 68 in slightly high yield (48%, entry 2). However, irradiation of 2 with 42 resulted in low yield of 69 (19%, entry 3), along with small amount of 5-((4-benzylphenyl)(methyl)amino)pentan-2-one (<5%) product. Analogous reaction pattern was observed for the reaction of 3 with 42, 45 and 48 giving rise corresponding tetrahydroquinolines (13- 30%), (entries 4-6). To demonstrate further that this reaction is not limited to only $t$-amines of type 2-3, identical reaction with 73-74 (entries 7-8) were also carried out with 48 which gave corresponding tetrahydroquinoline 75-76 (18-21%), respectively, albeit in low yields. Furthermore, the relative trans stereochemistry of tetrahydroquinolines were established by 2D NMR analyses and by MD simulation study of 71.$^{19}$
**Table 3:** Photocatalytic reaction of *t*-anilines with electron deficient alkenes.\textsuperscript{[a]}

<table>
<thead>
<tr>
<th>Entry</th>
<th><em>t</em>-Aniline</th>
<th>Alkene</th>
<th>Product</th>
<th>Yield\textsuperscript{[b]}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image1" alt="Structure" /></td>
<td><img src="image2" alt="Structure" /></td>
<td><img src="image3" alt="Structure" /></td>
<td>29(45)\textsuperscript{[c]}</td>
</tr>
<tr>
<td>2</td>
<td><img src="image4" alt="Structure" /></td>
<td><img src="image5" alt="Structure" /></td>
<td><img src="image6" alt="Structure" /></td>
<td>48</td>
</tr>
<tr>
<td>3</td>
<td><img src="image7" alt="Structure" /></td>
<td><img src="image8" alt="Structure" /></td>
<td><img src="image9" alt="Structure" /></td>
<td>19</td>
</tr>
<tr>
<td>4</td>
<td><img src="image10" alt="Structure" /></td>
<td><img src="image11" alt="Structure" /></td>
<td><img src="image12" alt="Structure" /></td>
<td>23</td>
</tr>
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<td><img src="image17" alt="Structure" /></td>
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<td><img src="image19" alt="Structure" /></td>
<td><img src="image20" alt="Structure" /></td>
<td><img src="image21" alt="Structure" /></td>
<td>2\textsuperscript{[c]}</td>
</tr>
<tr>
<td>8</td>
<td><img src="image22" alt="Structure" /></td>
<td><img src="image23" alt="Structure" /></td>
<td><img src="image24" alt="Structure" /></td>
<td>18\textsuperscript{[c]}</td>
</tr>
</tbody>
</table>

\textsuperscript{[a]} Reaction condition: *t*-aniline (1 mmol), alkene (1 mmol), catalyst (5 mol%), blue LED light irradiation, pyridine : MeOH (3 : 1 mL), 24 h. \textsuperscript{[b]} Yield based on consumption of *t*-aniline. \textsuperscript{[c]} Yield based on consumption of 2 using 48 (2.5 mmol).
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It should be noted that under the optimized reaction condition, identical activation of 77 or 78 (1 equiv.) with 48 (1 equiv.), either in degassed CH$_3$CN or pyridine:MeOH (3:1) did not show any observable reaction.

3.4.3 Proposed reaction mechanism:

On the basis of observed results, a plausible reaction mechanism is proposed as shown in Figure-5. The support to this proposed mechanism discerns from the formation of 86 and improvement in yields of corresponding tetrahydroquinolines when photoreaction was carried out using 2.5 equivalents of enones (Table 3, entry 1).

Figure 5: Proposed mechanism for the photocatalytic reaction of t-anilines with electron deficient alkenes.
3.5 Proposed rationale for different deprotonation site of \( t \)-amines:

Although, at this stage we do not comprehend exactly the contrasting behavior in the observed deprotonation site between \( 60 \) and \( 79 \), it appears that amine radical cation \( 60 \) (AcrH\(_2\))^+ undergoes \( \gamma \) C-H deprotonation rather than \( \alpha \) C-H deprotonation owing to its higher acidity generating thermodynamically stable \( 61 \) (AcrH) rather than \( 87 \)^20,26 (Figure 6). In contrast, \( \alpha \) C-H deprotonation from \( 79 \) could be mainly due to localization of charge on nitrogen contributing to low reaction barriers^27 for generating \( 80 \) compared to the formation of \( 88 \) by distal C-H deprotonation. Further mechanistic study in this regard is under progress.19

![Figure 6: Possible deprotonation pathways of \( 60 \) and \( 79 \).](image)

It is important to mention that, while this work (Section 3.4) was in progress, two independent publications appeared simultaneously from the groups of Yu and Bian^24a and Rueping^24b reporting formation of tetrahydroquinoline frameworks from the reaction of \( t \)-anilines with various differently substituted olefins, by using visible light photoredox catalysis. Yu and Bian co-workers reported the formation of tetrahydroquinolines from \( t \)-anilines and N-aryl or N-benzyl maleimides using Ru(bpy)\(_3\)Cl\(_2\) or \([\text{Ir}(ppy)_2(\text{dtb-bpy})]\text{PF}_6\) as catalyst and air as a terminal oxidant (Scheme 12, eq 4). The mechanism of this reaction is shown in Scheme 12.24a
Scheme 12: Photocatalytic reactions of t-anilines with 90.

Rueping and co-workers have reported the formation of cyclic and acyclic products from the photoreaction between N,N-dimethyl anilines and benzylidene malononitrile by using [Ir(ppy)$_2$(dtb-bpy)]PF$_6$ as a catalyst in the presence and absence of oxygen respectively (Scheme 13, eq. 5-6).$^{24b}$

Scheme 13: Photocatalytic reactions of t-anilines with 96.
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3.6 Summary:

In conclusion, we disclose an unprecedented, mechanistically interesting and synthetically useful one electron oxidative chemistry of $t$-amines having two possible sites for deprotonation through visible light photoredox catalysis. It has been found that deprotonation occurs either from $\gamma$ sp$^3$ C-H or $\alpha$ sp$^3$ C-H site, from their corresponding radical cations, depending on the structure of the amines. The activation of 10-methyl-9,10-dihydroacridine in the presence of electron deficient alkenes leads to $\gamma$ sp$^3$ C-H alkylation whereas 4-alkyl-$N$, $N$-dimethylanilines produces synthetically useful substituted tetrahydroquinolines through $\alpha$ sp$^3$ C-H alkylation/cyclization sequence. Further, application of the methodology is demonstrated by the synthesis of 10-methylacridin-9(10H)-one without using any consumable reagent. This strategy may lead to an easy, economic and eco-friendly protocol for the syntheses of biologically active and pharmacologically important acridone derivatives.
3.7 Experimental section:

3.7.1 Preparation of substrates:

10-methyl-9,10-dihydroacridine 1(AcrH$_2$)$_{28}$:

To a solution of acridine (1g, 5.58 mmol) in dry acetone (12 mL) was added methyl iodide (1.04 mL, 16.74 mmol) and the resulting reaction mixture refluxed under argon atmosphere for 24 h. The precipitated orange colored crystalline 10-methylacridin-10-ium iodide (A) was separated by filtration, dried and used as such for the next step without any purification.

A solution of 10-methylacridin-10-ium iodide (1.25 g, 3.89 mmol) in CH$_3$OH:H$_2$O (4:2, 60 mL) was charged in a 100 mL round bottom flask and stirred at 0 ºC. NaBH$_4$ (0.294 g, 7.78 mmol) was slowly introduced into the flask while stirring. After further stirring for another 1 h at 10 ºC, solid separated from the solution was filtered, dried and crystallized [EtOH: H$_2$O (95:5)] to obtain pure 10-methyl-9,10-dihydroacridine 1 (AcrH$_2$) (0.505 g, 2.59 mmol) as a white solid.

$R_f$ (49:1 Hexanes : EtOAc) = 0.65.

IR (neat): 2805, 1586, 1454, 1327, 1258, 1160, 1118, 1029, 917, 858, 740 cm$^{-1}$.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.24 - 7.17 (m, 4 H), 6.95 (t, $J$ = 7.4 Hz, 2 H), 6.90 (d, $J$ = 8.0 Hz, 2 H), 3.91 (s, 2 H), 3.40 (s, 3 H)

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 143.6, 127.5, 126.8, 124.2, 120.5, 111.8, 33.2, 33.1

HRMS: (ESI-MS) $m/z$ calculated for C$_{14}$H$_{14}$N [M+H]$^+$: 196.1121, found: 196.1118.
4-Benzyl-N,N-dimethylaniline (2)

To a mixture of AlCl₃ (2.1 g, 15.74 mmol) and dry dichloromethane (50 mL) in 250 mL two neck round bottom flask was slowly added benzoyl chloride (2.21 g, 15.72 mmol) and N,N-dimethylaniline (2 g, 16.50 mmol) at 0°C under argon atmosphere. The reaction mixture was stirred for 4 h at 0°C and further 3 h at room temperature. Afterwards the reaction mixture was diluted with dichloromethane (50 mL), water (15 mL) and stirred for another 15 min. The separated organic layer was washed with water (2 x 20 mL), saturated aqueous NaHCO₃ solution (2 x 20 mL), dried over Na₂SO₄, concentrated under reduced pressure and chromatographed to obtain pure (4-(dimethylamino)phenyl)(phenyl)methanone (A) (2.3 g, 10.2 mmol) as a yellow solid.

A mixture of (4-(dimethylamino)phenyl)(phenyl)-methanone (A) (2.3 g, 10.21 mmol), hydrazine-hydrate (2.56 g, 51.05 mmol), NaOH (2.04 g, 51.05 mmol) and diethylene glycol (65 mL) contained in a 250 mL round bottom flask, was heated at 155 °C for 5 h. The reaction mixture was allowed to come to rt and diluted with ethyl acetate (100 mL) and water (100 mL). The organic layer was separated and the aqueous layer was extracted with ethyl acetate (2 x 100 mL). The combined organic layers were dried over Na₂SO₄, concentrated under reduced pressure and purified by column chromatography to obtain 4-benzyl-N,N-dimethylaniline (2) (1.8 g, 8.51 mmol) as a yellow liquid.

Rf (19:1 Hexanes : EtOAc) = 0.8

IR (neat): 2900, 1615, 1520, 1493, 1346, 1218, 1162, 754 cm⁻¹

¹H NMR (500 MHz, CDCl₃) δ 7.38 - 7.32 (m, 2 H), 7.30 - 7.23 (m, 3 H), 7.15 (d, J = 8.5 Hz, 2 H), 6.78 (d, J = 8.5 Hz, 2 H), 3.98 (s, 2 H), 2.99 (s, 6 H)

¹³C NMR (125 MHz, CDCl₃) δ 149.1, 142.0, 129.5, 129.3, 128.8, 128.3, 125.7, 113.0, 40.9, 40.8

HRMS: (ESI-MS) m/z calculated for C₁₅H₁₈N [M + H]⁺: 212.1434, found: 212.1434.
Methyl 2-(4-(dimethylamino)phenyl)acetate (3)^30:

A 50 mL single neck round bottom flask containing mixture of 2-(4-aminophenyl)acetic acid (1 g, 6.62 mmol) and dry MeOH (20 mL) was charged with SOCl₂ (0.53 mL, 7.28 mmol) drop-wise at 0 °C under argon atmosphere. After stirring at 0 °C for 30 min. and additionally 30 min. at rt, it was refluxed for 3 h. Excess of SOCl₂ along with MeOH was distilled off under reduced pressure. The crude methyl 2-(4-aminophenyl)acetate (A) (1.04 g, 6.30 mmol) was used as such for the next step without any purification.

To a stirring mixture of crude methyl 2-(4-aminophenyl)acetate (A) (1.04 g, 6.30 mmol) and K₂CO₃ (4.35 g, 31.48 mmol) in CH₃CN (20 mL), MeI (1.18 mL, 18.90 mmol) was introduced and refluxed for 8 h. Excess of MeI along with CH₃CN was evaporated off to obtain a solid mass which was treated with dichloromethane (50 mL) and water (50 mL). The organic layer was separated and the aqueous layer was extracted with dichloromethane (2 x 50 mL). The combined organic layer was washed with brine (20 mL), dried over Na₂SO₄, concentrated under reduced pressure and purified by column chromatography to obtain pure methyl 2-(4-(dimethylamino)phenyl)acetate (3) (0.8 g, 4.14 mmol) as a yellow liquid.

RF (9:1 Hexanes : EtOAc) = 0.4

IR (neat): 2951, 1733, 1615, 1523, 1436, 1347, 1259, 1154, 808 cm⁻¹

¹H NMR (400 MHz, CDCl₃) δ 7.15 (d, J = 8.8 Hz, 2 H), 6.71 (d, J = 8.5 Hz, 2 H), 3.67 (s, 3 H), 3.53 (s, 2 H), 2.93 (s, 6 H)

¹³C NMR (100 MHz, CDCl₃) δ 172.7, 149.6, 129.8, 121.9, 112.8, 51.9, 40.7, 40.2

HRMS: (ESI-MS) m/z calculated for C₁₁H₁₆NO₂ [M + H]⁺: 194.1176, found: 194.1171
3.7.2. General photoredox reaction for $\gamma$ sp$^3$ C-H alkylation of 10-methyl-9,10-dihydroacridine (1) with electron deficient alkenes:\(^1\)

A dry 25 mL Schlenk or round bottom flask equipped with a magnetic stir bar was charged with a 10-methyl-9,10-dihydroacridine (1) (0.1 g, 0.51 mmol), electron deficient alkenes (0.51 mmol or 1.53 mmol), Ru(bpy)$_3$Cl$_2$•6H$_2$O (0.019 g, 25.5 μmol, 5 mol%) and HPLC grade acetonitrile (2 mL). The solution was degassed using three freeze-pump-thaw cycles and stirred at room temperature at a distance of approximately 3 cm from a blue light emitting diode. The photochemical reaction was monitored by TLC analysis. After completion, the solvent was removed under reduced pressure and residue purified by silica gel column chromatography using hexanes: ethyl acetate to obtain corresponding $\gamma$ sp$^3$ C-H alkylation products. (The details of reaction conditions are summarized in Table 2).

![Reaction Diagram](image)

4-(10-methyl-9,10-dihydroacridin-9-yl)butan-2-one (43):

Yield: 70% (yellow oil).

$R_f$ (19:1 Hexanes : EtOAc) = 0.3.

IR (neat): 2924, 2857, 1712, 1596, 1473, 1349, 1275, 1132, 1047, 754 cm$^{-1}$.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.26 - 7.22 (m, 2 H), 7.14 (dd, $J$ = 1.2, 7.3 Hz, 2 H), 6.98 - 6.93 (m, 4 H), 3.89 (t, $J$ = 7.3 Hz, 1 H), 3.40 (s, 3 H), 2.34 (t, $J$ = 7.6 Hz, 2 H), 2.06 (s, 3 H), 1.82 (q, $J$ = 7.3 Hz, 2 H).
Chapter 3:

\(^{13}\text{C NMR}\) (125 MHz, CDCl\(_3\)) \(\delta\) 208.8, 142.4, 128.1, 127.0, 126.9, 120.5, 112.1, 43.0, 40.6, 32.9, 31.3, 29.9.

HRMS: (ESI-MS) \(m/z\) calculated for \(\text{C}_{18}\text{H}_{20}\text{NO} [\text{M + H}]^+\): 266.1539, found: 266.1538.

3-(10-methyl-9,10-dihydroacridin-9-yl)propanal (52):

\[
\begin{array}{c}
\text{H}\\
\text{O}\\
\text{C}\\
\text{H}\\
\text{C}\\
\text{C}\\
\text{N}\\
\text{52}
\end{array}
\]

**Yield:** 47% (yellow viscous oil)

**R_f** (19:1 Hexanes : EtOAc) = 0.7

**IR** (neat): 2920, 2851, 1719, 1593, 1472, 1345, 1273, 1131, 1042, 748 cm\(^{-1}\)

\(^1\text{H NMR}\) (500 MHz, CDCl\(_3\)) \(\delta\) 9.61 (t, \(J = 1.5\) Hz, 1 H), 7.25 (dt, \(J = 1.5, 7.8\) Hz, 2 H), 7.15 (dd, \(J = 1.5, 7.3\) Hz, 2 H), 6.99 - 6.93 (m, 4 H), 3.93 (t, \(J = 7.2\) Hz, 1 H), 3.40 (s, 3 H), 2.35 (dt, \(J = 1.5, 7.5\) Hz, 2 H), 1.89 (q, \(J = 7.3\) Hz, 2 H)

\(^{13}\text{C NMR}\) (125 MHz, CDCl\(_3\)) \(\delta\) 202.4, 142.4, 128.2, 127.2, 126.5, 120.6, 112.2, 43.0, 40.9, 32.9, 29.9

HRMS: (ESI-MS) \(m/z\) calculated for \(\text{C}_{17}\text{H}_{18}\text{NO} [\text{M + H}]^+\): 252.1383, found: 252.1382.

4-(10-methyl-9,10-dihydroacridin-9-yl)-4-phenylbutan-2-one (53):

\[
\begin{array}{c}
\text{O}\\
\text{C}\\
\text{Ph}\\
\text{C}\\
\text{C}\\
\text{N}\\
\text{53}
\end{array}
\]

**Yield:** 87% (white solid)
Chapter 3:

**Rf** (9:1 Hexanes : EtOAc) = 0.5.

**IR** (neat): 3026, 2909, 1700, 1592, 1475, 1340, 1269, 1131, 756, 700 cm$^{-1}$.

**$^1$H NMR** (400 MHz, CDCl$_3$) $\delta$ 7.31 - 7.16 (m, 3 H), 7.15 - 7.05 (m, 3 H), 6.98 (t, $J$ = 7.3 Hz, 1 H), 6.86 - 6.77 (m, 3 H), 6.74 (d, $J$ = 6.8 Hz, 1 H), 6.64 (d, $J$ = 5.3 Hz, 2 H), 4.07 (d, $J$ = 6.5 Hz, 1 H), 3.37 (q, $J$ = 7.1 Hz, 1 H), 3.09 (s, 3 H), 2.87 - 2.74 (m, 2 H), 1.96 (s, 3 H)

**$^{13}$C NMR** (100 MHz, CDCl$_3$) $\delta$ 207.5, 142.9, 142.8, 141.1, 128.9, 128.9, 128.2, 127.3, 127.2, 127.0, 126.3, 125.2, 124.0, 120.2, 119.7, 112.0, 111.9, 49.7, 47.4, 46.3, 32.8, 30.4

**HRMS**: (ESI-MS) $m/z$ calculated for C$_{24}$H$_{24}$NO $[M + H]^+$: 342.1852, found: 342.1851.

3-(10-methyl-9,10-dihydroacridin-9-yl)-3-phenylpropanal (54):

![Image](image.png)

**Yield**: 60% (white crystalline solid).

**Rf** (19:1 Hexanes : EtOAc) = 0.4

**IR** (neat): 2875, 1709, 1590, 1465, 1338, 1267, 1126, 747, 694 cm$^{-1}$.

**$^1$H NMR** (500 MHz, CDCl$_3$) $\delta$ 9.40 (t, $J$ = 2.0 Hz, 1 H), 7.30 - 7.24 (m, 1 H), 7.24 - 7.19 (m, 1 H), 7.17 - 7.11 (m, 3 H), 7.10 (dd, $J$ = 1.4, 7.5 Hz, 1 H), 6.98 (dt, $J$ = 0.9, 7.3 Hz, 1 H), 6.86 (dd, $J$ = 2.0, 8.1 Hz, 2 H), 6.83 - 6.79 (m, 1 H), 6.77 - 6.74 (m, 1 H), 6.73 - 6.67 (m, 2 H), 4.08 (d, $J$ = 6.7 Hz, 1 H), 3.46 - 3.37 (m, 1 H), 3.17 (s, 3 H), 2.79 - 2.74 (m, 2 H)

**$^{13}$C NMR** (125 MHz, CDCl$_3$) $\delta$ 201.8, 142.9, 142.8, 140.6, 129.1, 129.0, 128.3, 127.6, 127.4, 127.2, 126.6, 124.5, 124.0, 120.3, 120.0, 112.1, 112.0, 50.2, 46.3, 46.0, 32.8.
Chapter 3:

HRMS: (ESI-MS) $m/z$ calculated for $C_{23}H_{22}NO \ [M + H]^+$: 328.1696, found: 328.1694.

4-(furan-2-yl)-4-(10-methyl-9,10-dihydroacridin-9-yl)butan-2-one (55):

\[
\text{Yield: (yellow oil):}
\]

\[
R_f (19:1 \text{ Hexanes : EtOAc}) = 0.4
\]

\[
\text{IR (neat): 2922, 1715, 1593, 1475, 1345, 1271, 1130, 751 cm}^{-1}
\]

\[
\text{H NMR (500 MHz, CDCl}_3) \ \delta \ 7.27 (bs, 1 \ H), \ 7.26 - 7.15 (m, 2 \ H), \ 6.96 (d, \ J = 7.0 \ Hz, \ 1 \ H), \ 6.93 - 6.86 (m, 3 \ H), \ 6.85 - 6.79 (m, 2 \ H), \ 6.14 (dd, \ J = 1.8, 2.7 Hz, 1 \ H), \ 5.58 (d, \ J = 2.7 Hz, 1 \ H), \ 4.18 (d, \ J = 7.6 Hz, 1 \ H), \ 3.44 (ddd, \ J = 5.5, 7.6, 9.5 Hz, 1 \ H), \ 3.33 (s, 3 \ H), \ 2.74 (dd, \ J = 9.5, 16.5 Hz, 1 \ H), \ 2.58 (dd, \ J = 5.2, 16.5 Hz, 1 \ H), \ 1.89 (s, 3 \ H)
\]

\[
\text{C NMR (125 MHz, CDCl}_3) \ \delta \ 207.2, \ 154.9, \ 143.0, \ 142.5, \ 140.8, \ 129.1, \ 128.5, \ 127.4, \ 127.1, \ 124.9, \ 124.1, \ 120.1, \ 112.1, \ 111.9, \ 110.0, \ 107.0, \ 48.0, \ 43.9, \ 40.8, \ 33.0, \ 30.1
\]

HRMS: (ESI-MS) $m/z$ calculated for $C_{22}H_{22}NO_2 \ [M + H]^+$: 332.1645, found: 332.1643.

3-(10-methyl-9,10-dihydroacridin-9-y1)-1,3-diphenylpropan-1-one (56):

\[
\text{Yield: 56% (white crystalline soild).}
\]
Chapter 3:

\[ R_f (19:1 \text{ Hexanes} : \text{EtOAc}) = 0.4 \]

**IR** (neat): 2885, 1677, 1589, 1466, 1338, 1272, 1126, 1036, 747, 690 cm\(^{-1}\)

\( ^1\text{H NMR} \) (400 MHz, CDCl\(_3\)) \( \delta \) 7.84 (d, \( J = 7.3 \) Hz, 2 H), 7.56 (t, \( J = 7.3 \) Hz, 1 H), 7.44 (t, \( J = 7.6 \) Hz, 2 H), 7.29 - 7.19 (m, 3 H), 7.10 - 7.06 (m, 3 H), 6.98 (t, \( J = 7.4 \) Hz, 1 H), 6.84 - 6.79 (m, 4 H), 6.67 - 6.65 (m, 2 H), 4.23 (d, \( J = 6.3 \) Hz, 1 H), 3.60 (q, \( J = 6.9 \) Hz, 1 H), 3.46 (dd, \( J = 6.5, 16.8 \) Hz, 1 H), 3.29 (dd, \( J = 7.6, 16.9 \) Hz, 1 H), 3.04 (s, 3 H)

\( ^{13}\text{C NMR} \) (100 MHz, CDCl\(_3\)) \( \delta \) 198.8, 143.0, 142.8, 141.3, 137.2, 132.8, 129.1, 129.0, 128.4, 128.3, 127.9, 127.2, 127.0, 126.2, 125.4, 124.1, 120.3, 119.8, 111.9, 49.2, 47.7, 40.8, 32.8

**HRMS:** (ESI-MS) \( m/z \) calculated for C\(_{29}\)H\(_{26}\)NO \([M + H]^+\): 404.2009, found: 404.2008.

CCDC-963947 contains the supplementary crystallographic data for 56.

10-methyl-9-(2-nitro-1-phenylethyl)-9,10-dihydroacridine (57):  

![Chemical Structure](image)

**Yield:** 40% (white crystalline solid)

\[ R_f (19:1 \text{ Hexanes} : \text{EtOAc}) = 0.5 \]

**IR** (neat): 2912, 1591, 1549, 1465, 1378, 1339, 1267, 1126, 1038, 740, 693, 639 cm\(^{-1}\)

\( ^1\text{H NMR} \) (400MHz, CDCl\(_3\)) \( \delta \) 7.59 - 7.37 (m, 6 H), 7.30 - 7.27 (m, 1 H), 7.15 - 7.12 (m, 4 H), 6.94 (d, \( J = 6.8 \) Hz, 2 H), 4.96 - 4.92 (m, 2 H), 4.48 (d, \( J = 6.5 \) Hz, 1 H), 3.98 (td, \( J = 6.8, 8.9 \) Hz, 1 H), 3.40 (s, 3 H)

\( ^{13}\text{C NMR} \) (100 MHz, CDCl\(_3\)) \( \delta \) 142.8, 142.7, 136.7, 128.9, 128.7, 128.1, 127.8, 127.7, 127.6, 127.4, 123.3, 122.7, 120.6, 120.3, 112.4, 112.2, 77.1, 50.1, 47.8, 32.8
Chapter 3:

**HRMS**: (ESI-MS) \( m/z \) calculated for \( \text{C}_{22}\text{H}_{21}\text{N}_{2}\text{O}_{2} [\text{M} + \text{H}]^{+} \): 345.1598, found: 345.1597.

**CCDC-963948** contains the supplementary crystallographic data for 57.

3-(10-methyl-9,10-dihydroacridin-9-yl)cyclohexanone (58):

![Chemical Structure of 58](image)

**Yield**: 58% (white solid).

\( \text{R}_{f} \) (19:1 Hexanes : EtOAc) = 0.5

**IR** (neat): 2896, 1701, 1591, 1467, 1334, 1267, 1225, 1131, 1041, 883, 749 cm\(^{-1}\)

**\(^1\text{H NMR}\)** (500 MHz, CDCl\(_3\)) \( \delta \) 7.29 - 7.25 (m, 2 H), 7.14 (dt, \( J = 1.5, 7.2 \text{ Hz} \), 2 H), 7.00 - 6.95 (m, 4 H), 3.80 (d, \( J = 6.4 \text{ Hz} \), 1 H), 3.39 (s, 3 H), 2.29 - 2.21 (m, 2 H), 2.19 - 2.13 (m, 1 H), 2.05 - 1.91 (m, 3 H), 1.81 - 1.75 (m, 1 H), 1.46 (td, \( J = 4.0, 13.1 \text{ Hz} \), 1 H), 1.37 - 1.29 (m, 1 H)

**\(^1\text{C NMR}\)** (125 MHz, CDCl\(_3\)) \( \delta \) 212.2, 142.8, 129.1, 129.0, 127.3, 127.2, 125.0, 124.5, 120.4, 120.3, 112.2, 49.4, 45.3, 45.2, 41.2, 32.9, 28.3, 25.1

**HRMS**: (ESI-MS) \( m/z \) calculated for \( \text{C}_{20}\text{H}_{22}\text{NO} [\text{M} + \text{H}]^{+} \): 292.1696, found: 292.1695.

4-(10-methyl-9,10-dihydroacridin-9-yl)chroman-2-one (59):

![Chemical Structure of 59](image)

**Yield**: 30% (white solid).
**Chapter 3:**

**Rf** (9:1 Hexanes : EtOAc) = 0.8

**IR** (neat): 2914, 1753, 1591, 1466, 1334, 1258, 1143, 1029, 908, 748 cm⁻¹

**¹H NMR** (400 MHz, CDCl₃) δ 7.33 - 7.22 (m, 3 H), 7.01 - 6.95 (m, 5 H), 6.91 (t, J = 7.5 Hz, 1 H), 6.82 (t, J = 7.3 Hz, 1 H), 6.69 (d, J = 7.6 Hz, 1 H), 6.46 - 6.44 (m, 1 H), 3.95 (d, J = 8.1 Hz, 1 H), 3.40 (s, 3 H), 3.07 (t, J = 7.2 Hz, 1 H), 2.83 (dd, J = 1.5, 16.4 Hz, 1 H), 2.57 (dd, J = 6.6, 16.4 Hz, 1 H)

**¹³C NMR** (100MHz, CDCl₃) δ 168.1, 151.7, 142.8, 142.7, 129.5, 129.2, 129.1, 128.4, 127.9, 127.6, 123.9, 123.6, 122.9, 120.7, 120.4, 116.6, 112.4, 111.9, 48.7, 41.1, 33.0, 31.7

**HRMS**: (ESI-MS) m/z calculated for C₂₃H₂₀NO₂ [M + H]⁺: 342.1489, found: 342.1488.

**10-methylacridin-9(10H)-one (63):**

![Image of 10-methylacridin-9(10H)-one (63)](image)

**Yield**: 90% (white crystalline solid).

**Rf** (6:4 Hexanes : EtOAc) = 0.4

**IR** (neat): 2912, 1588, 1488, 1453, 1362, 1260, 1172, 1030, 799, 747, 667 cm⁻¹

**¹H NMR** (500 MHz, CDCl₃) δ 8.56 (dd, J = 1.5, 7.9 Hz, 2 H), 7.71 (dd, J = 1.7, 7.0, 8.7 Hz, 2 H), 7.49 (d, J = 8.9 Hz, 2 H), 7.32 - 7.25 (m, 2 H), 3.86 (s, 3 H)

**¹³C NMR** (125 MHz, CDCl₃) δ 178.0, 142.4, 133.7, 127.6, 122.4, 121.2, 114.7, 33.5

**HRMS**: (ESI-MS) m/z calculated for C₁₄H₁₂NO [M + H]⁺: 210.0913, found: 210.0913.

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5-(10-methyl-9,10-dihydroacridin-9-yl)pent-1-en-3-one (65):

Yield: 51% (yellow thick oil).

R_f (19:1 Hexanes : EtOAc) = 0.5

IR (neat): 2925, 1678, 1594, 1475, 1344, 1269, 1130, 1043, 755, 504 cm\(^{-1}\)

\(^1\)H NMR (200 MHz, CDCl\(_3\)) \(\delta\) 7.27 - 7.14 (m, 4 H), 7.00 - 6.92 (m, 4 H), 6.30 (dd, \(J = 10.2, 17.7\) Hz, 1 H), 6.09 (dd, \(J = 1.5, 17.7\) Hz, 1 H), 5.77 (dd, \(J = 1.5, 10.2\) Hz, 1 H), 3.93 (t, \(J = 7.2\) Hz, 1 H), 3.40 (s, 3 H), 2.51 (t, \(J = 7.5\) Hz, 2 H), 1.87 (q, \(J = 7.4\) Hz, 2 H)

\(^{13}\)C NMR (50 MHz, CDCl\(_3\)) \(\delta\) 200.6, 142.3, 136.4, 128.1, 128.0, 127.9, 127.0, 126.9, 120.5, 112.1, 42.9, 36.4, 32.9, 31.2

HRMS: (ESI-MS) \(m/z\) calculated for C\(_{19}\)H\(_{20}\)NO \([M + H]^+\): 278.1539, found: 278.1538.

10-methyl-10H-spiro[acridine-9,1'-cyclohexan]-4'-one (66):

Yield: 42% (white crystalline solid):

R_f (9:1 Hexanes : EtOAc) = 0.7

IR (neat): 2923, 1716, 1590, 1465, 1346, 1270, 1130, 848, 750 cm\(^{-1}\)
Chapter 3:

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.50 - 7.48 (m, 2 H), 7.32 - 7.29 (m, 2 H), 7.09 - 7.06 (m, 4 H), 3.52 (s, 3 H), 2.53 - 2.51 (m, 4 H), 2.48 - 2.45 (m, 4 H)

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 212.3, 142.8, 130.2, 126.9, 123.8, 120.9, 112.8, 39.1, 38.2, 33.4, 31.4

HRMS: (ESI-MS) $m/z$ calculated for C$_{19}$H$_{20}$NO $[M + H]^+$: 278.1539, found: 278.1538.

CCDC-963949 contains the supplementary crystallographic data for 66.

3.7.3 General procedure for photoredox reaction of $\tau$-anilines with electron deficient alkenes:

Identical irradiation, as described above (Section 3.7.2), set up was used to photolyze $\tau$-aniline (2-3, 73-74) (1 mmol), $\alpha$, $\beta$-unsaturated carbonyl compound (42 or 45 or 48) (1 or 2.5 mmol), Ru(bpy)$_3$Cl$_2$$\cdot$6H$_2$O (5 mol%) in dry pyridine-MeOH (3:1 mL) for 24 h. 19 (The details of reaction conditions are summarized in Table 3).

(6-benzyl-1-methyl-3-phenyl-1,2,3,4-tetrahydroquinolin-4-yl)(phenyl)methanone (67):

Yield: 29% (using 1 equiv. of 48) and 45% (using 2.5 equiv. of 48), (yellow oil).

R$_f$ (19:1 Hexanes : EtOAc) = 0.4.

IR (neat): 3026, 1681, 1615, 1514, 1494, 1453, 1216, 757, 698 cm$^{-1}$
Chapter 3:

**1H NMR** (500 MHz, CDCl₃) δ 7.81 - 7.80 (m, 2 H), 7.55 - 7.53 (m, 1 H), 7.42 - 7.39 (m, 2 H), 7.29 - 7.26 (m, 2 H), 7.23 - 7.20 (m, 3 H), 7.18 - 7.14 (m, 3 H), 7.07 (d, J = 7.0 Hz, 2 H), 7.01 (dd, J = 1.7, 8.4 Hz, 1 H), 6.74 - 6.72 (m, 2 H), 4.93 (d, J = 8.9 Hz, 1 H), 3.78 (s, 2 H), 3.70 (dt, J = 4.3, 8.9 Hz, 1 H), 3.45 (dd, J = 4.1, 11.4 Hz, 1 H), 3.38 (dd, J = 9.2, 11.3 Hz, 1 H), 2.98 (s, 3 H)

**13C NMR** (125 MHz, CDCl₃) δ 202.1, 144.7, 141.8, 141.7, 137.2, 132.7, 129.4, 129.3, 128.8, 128.6, 128.5, 128.2, 127.6, 127.0, 125.7, 121.2, 112.0, 55.8, 52.9, 42.6, 40.8, 39.4

**HRMS:** (ESI-MS) m/z calculated for C₃₀H₂₈NO [M + H]⁺: 418.2165, found: 418.2165.

1-(6-benzyl-1-methyl-3-phenyl-1,2,3,4-tetrahydroquinolin-4-yl)ethanone (68):

![Chemical Structure](image)

**Yield:** 48% (White solid).

**Rf** (19:1 Hexanes : EtOAc) = 0.6

**IR** (neat): 3020, 2925, 1702, 1615, 1495, 1454, 1216, 757 cm⁻¹

**1H NMR** (400 MHz, CDCl₃) δ 7.37 - 7.28 (m, 5 H), 7.23 - 7.17 (m, 5 H), 7.05 (d, J = 8.3 Hz, 1 H), 6.77 (s, 1 H), 6.71 (d, J = 8.3 Hz, 1 H), 4.07 (d, J = 9.5 Hz, 1 H), 3.88 (s, 2 H), 3.52 (dt, J = 4.0, 9.5 Hz, 1 H), 3.38 (dd, J = 3.3, 11.3 Hz, 1 H), 3.31 - 3.26 (m, 1 H), 2.95 (s, 3 H), 2.04 (s, 3 H)

**13C NMR** (100MHz, CDCl₃) δ 209.5, 144.5, 141.8, 141.1, 129.6, 129.1, 128.9, 128.8, 128.6, 128.3, 127.5, 127.2, 125.8, 119.6, 112.0, 58.6, 56.1, 42.0, 40.9, 39.3, 27.5

**HRMS:** (ESI-MS) m/z calculated for C₂₅H₂₆NO [M + H]⁺: 356.2009, found: 356.2008.
Chapter 3:

1-(6-benzyl-1-methyl-1,2,3,4-tetrahydroquinolin-4-yl)ethanone (69):

![Chemical structure of 69](image)

**Yield:** 19% (yellow oil).

**Rf** (19:1 Hexanes : EtOAc) = 0.35

**IR** (neat): 2927, 1706, 1615, 1514, 1494, 1453, 1325, 1210, 702 cm⁻¹

**¹H NMR** (400 MHz, CDCl₃) δ 7.32 - 7.28 (m, 2 H), 7.22 - 7.19 (m, 3 H), 7.02 (dd, J = 2.0, 8.3 Hz, 1 H), 6.83 (d, J = 1.5 Hz, 1 H), 6.63 (d, J = 8.3 Hz, 1 H), 3.90 (s, 2 H), 3.72 (t, J = 5.6 Hz, 1 H), 3.30 - 3.24 (m, 1 H), 3.16 - 3.10 (m, 1 H), 2.89 (s, 3 H), 2.35 - 2.27 (m, 1 H), 2.12 (s, 3 H), 2.07 - 1.99 (m, 1 H)

**¹³C NMR** (100 MHz, CDCl₃) δ 210.3, 144.8, 141.9, 130.1, 129.0, 128.9, 128.7, 128.3, 125.8, 119.7, 111.7, 51.2, 48.3, 40.8, 39.0, 27.9, 24.5

**HRMS:** (ESI-MS) m/z calculated for C₁₉H₂₂NO [M + H]⁺: 280.1696, found: 280.1695.

methyl 2-(4-benzoyl-1-methyl-3-phenyl-1,2,3,4-tetrahydroquinolin-6-yl)acetate (70):

![Chemical structure of 70](image)

**Yield:** 23% (yellow oil).

**Rf** (4:1 Hexanes : EtOAc) = 0.5

**IR** (neat): 3027, 2950, 1736, 1682, 1615, 1517, 1448, 1272, 1216, 1155, 1015, 756, 699 cm⁻¹
Chapter 3:

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.84 (d, $J = 7.3$ Hz, 2 H), 7.54 (t, $J = 7.3$ Hz, 1 H), 7.42 (t, $J = 7.3$ Hz, 2 H), 7.26 - 7.11 (m, 6 H), 6.76 - 6.74 (m, 2 H), 4.95 (d, $J = 8.3$ Hz, 1 H), 3.69 - 3.64 (m, 1 H), 3.61 (s, 3 H), 3.48 - 3.38 (m, 4 H), 2.98 (s, 3 H)

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 202.0, 172.5, 145.5, 141.6, 137.1, 132.9, 129.6, 128.9, 128.7, 128.6, 128.5, 127.5, 127.0, 122.0, 121.2, 111.8, 55.4, 52.4, 51.8, 42.4, 40.1, 39.3

HRMS: (ESI-MS) $m/z$ calculated for C$_{26}$H$_{26}$NO$_3$ [M + H]$^+$: 400.1907, found: 400.1907.

methyl 2-(4-acetyl-1-methyl-3-phenyl-1,2,3,4-tetrahydroquinolin-6-yl)acetate (71):

Yield: 30% (yellow oil).

$R_t$ (4:1 Hexanes : EtOAc) = 0.5

IR (neat): 3025, 2925, 1738, 1705, 1616, 1516, 1454, 1435, 1217, 1159, 1017, 757, 701 cm$^{-1}$

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.32 (t, $J = 7.3$ Hz, 2 H), 7.27 - 7.24 (m, 1 H), 7.22 - 7.19 (m, 2 H), 7.11 (dd, $J = 1.8$, 8.5 Hz, 1 H), 6.80 (s, 1 H), 6.69 (d, $J = 8.2$ Hz, 1 H), 4.06 (d, $J = 9.5$ Hz, 1 H), 3.67 (s, 3 H), 3.49 (s, 2 H), 3.48 - 3.46 (m, 1 H), 3.37(dd, $J = 4.1$, 11.4 Hz, 1 H), 3.28 (dd, $J = 9.5$, 11.6 Hz, 1 H), 2.94 (s, 3 H), 2.06 (s, 3 H)

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 209.5, 172.5, 145.2, 141.1, 129.5, 129.2, 128.9, 127.5, 127.3, 122.2, 119.6, 111.9, 58.4, 55.9, 51.9, 41.8, 40.1, 39.2, 27.7.

HRMS: (ESI-MS) $m/z$ calculated for C$_{21}$H$_{24}$NO$_3$ [M + H]$^+$: 338.1751, found: 338.1750.
methyl 2-(4-acetyl-1-methyl-1,2,3,4-tetrahydroquinolin-6-yl)acetate (72):

Yield: 13% (yellow oil):

R_f (4:1 Hexanes : EtOAc) = 0.4.

IR (neat): 2925, 1738, 1709, 1616, 1517, 1435, 1328, 1262, 1210, 1162, 1015 cm⁻¹

_1H NMR_ (500 MHz, CDCl₃) δ 7.05 (dd, J = 2.1, 8.2 Hz, 1 H), 6.89 (d, J = 1.5 Hz, 1 H), 6.61 (d, J = 8.2 Hz, 1 H), 3.72 (t, J = 5.5 Hz, 1 H), 3.67 (s, 3 H), 3.49 (s, 2 H), 3.25 (ddd, J = 4.3, 9.7, 11.4 Hz, 1 H), 3.15 - 3.10 (m, 1 H), 2.87 (s, 3 H), 2.31 - 2.25 (m, 1 H), 2.14 (s, 3 H), 2.04 - 1.97 (m, 1 H)

_13C NMR_ (125 MHz, CDCl₃) δ 210.0, 172.6, 145.3, 130.4, 129.2, 121.6, 119.7, 111.7, 51.9, 51.0, 48.1, 40.1, 38.9, 28.1, 24.2

HRMS: (ESI-MS) m/z calculated for C_{13}H_{20}NO_{3} [M + H]^+: 262.1438, found: 262.1438.

(1,6-dimethyl-3-phenyl-1,2,3,4-tetrahydroquinolin-4-yl)(phenyl)methanone (75):

Yield: 21% (yellow oil).

R_f (19:1 Hexanes : EtOAc) = 0.4.

IR (neat): 3028, 2920, 1679, 1514, 1449, 1277, 1243, 1002, 804, 759, 698 cm⁻¹

_1H NMR_ (400 MHz, CDCl₃) δ 7.84 (d, J = 8.1 Hz, 2 H), 7.54 (t, J = 7.3 Hz, 1 H), 7.41 (t, J = 7.6 Hz, 2 H), 7.29 - 7.13 (m, 5 H), 7.02 (d, J = 8.3 Hz, 1 H), 6.72 (d, J = 8.3 Hz, 1 H), 6.68 (s, 1 H), 4.93 (d, J = 8.6 Hz, 1 H), 3.66 (dt, J = 4.0, 8.7 Hz, 1 H), 3.46 - 3.28 (m, 2 H), 2.96 (s, 3 H), 2.15 (s, 3 H)
Chapter 3:

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 202.2, 144.3, 141.8, 137.1, 132.8, 129.2, 128.7, 128.7, 128.6, 128.5, 127.5, 126.9, 126.1, 121.3, 111.9, 55.7, 52.7, 42.7, 39.4, 20.2

**HRMS:** (ESI-MS) $m/z$ calculated for C$_{24}$H$_{24}$NO [M + H]$^+$: 342.1852, found: 342.1850

(1-methyl-3-phenyl-1,2,3,4-tetrahydroquinolin-4-yl)(phenyl)methanone (76):

Yield: 18% (yellow oil).

R$_f$ (19:1 Hexanes : EtOAc) = 0.35.

IR (neat): 3028, 2925, 1680, 1600, 1504, 1449, 1325, 1277, 1216, 1001, 745, 697 cm$^{-1}$

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.87 (d, $J = 7.3$ Hz, 2 H), 7.55 (t, $J = 7.3$ Hz, 1 H), 7.42 (t, $J = 7.6$ Hz, 2 H), 7.26 (d, $J = 7.3$ Hz, 2 H), 7.24 - 7.15 (m, 4 H), 6.86 (d, $J = 7.5$ Hz, 1 H), 6.79 (d, $J = 8.1$ Hz, 1 H), 6.63 (t, $J = 7.3$ Hz, 1 H), 5.00 (d, $J = 8.6$ Hz, 1 H), 3.70 (dt, $J = 4.1$, 8.5 Hz, 1 H), 3.49 (dd, $J = 4.2$ Hz, $J = 11.5$ Hz, 1 H) 3. 43 - 3.39 (m, 1 H), 3.00 (s, 3 H)

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 202.0, 146.3, 141.7, 137.2, 132.9, 128.7, 128.7, 128.6, 128.5, 128.1, 127.5, 127.0, 121.1, 116.8, 111.6, 55.6, 52.3, 42.3, 39.3

**HRMS:** (ESI-MS) $m/z$ calculated for C$_{23}$H$_{22}$NO [M + H]$^+$: 328.1696, found: 328.1696
3.8 References:


Chapter 3:


Chapter 3:


Chapter 3:

3.9 Spectra:

[Image of spectra with chemical shifts]
Chapter 3:

Chemical Shift (ppm)

127.47, 126.80, 120.53, 111.82

33.17, 33.06

8.5, 8.0, 7.5, 7.0, 6.5, 6.0, 5.5, 5.0, 4.5, 4.0, 3.5, 3.0, 2.5, 2.0, 1.5, 1.0, 0.5, 0

Chemical Shift (ppm)
Chapter 3:

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Chapter 3:
Chapter 3:

![Chemical Shift (ppm) Graph](image1)

![Chemical Shift (ppm) Graph](image2)

![Chemical Shift (ppm) Graph](image3)
Chapter 3:

COSY

HSQC
Chapter 3:

Chemical Shift (ppm)

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Chapter 3:

![Chemical Shift Spectrum](image1)

![COSY Spectrum](image2)
NOESY

Chemical Shift (ppm)
Chapter 3:

COSY

HSQC
Chapter 3:

HMBC

NOESY
Chapter 3:

COSY

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Chapter 3:
Chapter 3:

COSY

[Graph of COSY spectrum]

HSQC

[Graph of HSQC spectrum]

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Chapter 3:

HMBC

NOESY
Chapter 3:

**MD Simulation**

![MD Simulation Image](image)

**Figure 1.** Stereo view of minimized structures (a, b) and superimposed 20 minimum energy structures (c, d) for compound 71.

Distance constraints used in MD calculations for compound 71 derived from 2D NOESY experiment are given in table 4. MD simulation was done on Schrodinger software by using macro module tool. This calculation has produced 100 minimized structures out of that 20 best superimposed structures are shown in fig c & d. The superimposed structure shows less than 0.1 Å RMSD values.

### Table 4:

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<th>(F2) [ppm]</th>
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<th>Lower Bound</th>
<th>Between</th>
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Chapter 3:

NOESY

**Chemical Shift (ppm)**

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<th>Chemical Shift (ppm)</th>
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<tbody>
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<td>7.85</td>
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LCMS analysis of photoirradiation reaction between 2 and 48 (eq 3):

### Qualitative Compound Report

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<th>Compound Label</th>
<th>RT (min)</th>
<th>Mass (Da)</th>
<th>M/Z</th>
<th>Formula</th>
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<tbody>
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<td>319.070</td>
<td>C14H13NO4</td>
<td>C14H13NO4</td>
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<td>315.070</td>
<td>C14H13NO4</td>
<td>C14H13NO4</td>
</tr>
<tr>
<td>C2H5NO4</td>
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<td>C14H13NO4</td>
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### MS Spectrum Peak List

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<th>M/Z (Da)</th>
<th>RT (min)</th>
<th>Formula</th>
<th>Mass (Da)</th>
</tr>
</thead>
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<td>225.051</td>
<td>1.438</td>
<td>C10H10N2O2</td>
<td>245.069</td>
</tr>
<tr>
<td>234.051</td>
<td>1.438</td>
<td>C10H10N2O2</td>
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<tr>
<td>225.051</td>
<td>1.438</td>
<td>C10H10N2O2</td>
<td>245.069</td>
</tr>
</tbody>
</table>
Chapter 3:

Qualitative Compound Report

MS Zcaled Spectrum

MS Spectrum Peak List

Compound Label

m/z RT Algorithm Mass

Cpt 3: C30 H27 N2 O 440.1880 1.55 Find By Formula 417.2097

Cpt 3: C30 H27 N2 O + ES (E) 438.1265, 438.1266, 419.2199, 440.1885, 441.2108 (Scan Frag=100.0V SID)

MS Zcaled Spectrum

MS Spectrum Peak List

m/z Abundance Formula Ion

418.1273 1 418.1273 [M+H]+
419.2198 1 419.2198 [M+H]+
420.2392 1 420.2392 [M+H]+
421.2586 1 421.2586 [M+H]+
422.2780 1 422.2780 [M+H]+
423.2974 1 423.2974 [M+H]+
424.3169 1 424.3169 [M+H]+
425.3301 1 425.3301 [M+H]+
426.3495 1 426.3495 [M+H]+
427.3689 1 427.3689 [M+H]+
428.3884 1 428.3884 [M+H]+

Agilent Technologies

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Printed at: 8:42 PM on 9/14/2013

Qualitative Compound Report

440.3386 1 440.3386 [M+Na]+

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3.10 Single crystal structure analysis:

Crystal structure of 3-(10-methyl-9,10-dihydroacridin-9-yl)-1,3-diphenylpropan-1-one (56):

Table 5: Crystal data and structural refinement for 56.

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<th>Crystal Data</th>
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<tbody>
<tr>
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Chapter 3:

### Data Collection

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<td>2(\Theta) range for data collection</td>
<td>5.86 to 58.3°</td>
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<tr>
<td>Index ranges</td>
<td>(-60 \leq h \leq 58, -7 \leq k \leq 5, -25 \leq l \leq 25)</td>
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<td>Reflections collected</td>
<td>10408</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>4984[R(int) = 0.0397]</td>
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<tr>
<td>Data/restraints/parameters</td>
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<tr>
<td>Goodness-of-fit on (F^2)</td>
<td>1.049</td>
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<tr>
<td>Final R indexes [(I \geq 2\sigma (I))]</td>
<td>(R_1 = 0.0702, wR_2 = 0.1381)</td>
</tr>
<tr>
<td>Final R indexes [all data]</td>
<td>(R_1 = 0.1430, wR_2 = 0.1763)</td>
</tr>
<tr>
<td>Largest diff. peak/hole / e Å⁻³</td>
<td>0.19/-0.26</td>
</tr>
</tbody>
</table>

### Crystal Structure of 10-methyl-9-(2-nitro-1-phenylethyl)-9,10-dihydroacridine (57):

![Crystal Structure Image](image)

**Table 6**: Crystal data and structural refinement for 57.

<table>
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<th>Crystal Data</th>
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<td>Space group</td>
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<tr>
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</table>

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Chapter 3:

<table>
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<th>Parameter</th>
<th>Value</th>
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</thead>
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<tr>
<td>β°</td>
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<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>ρ_{calc} mg/mm³</td>
<td>1.302</td>
</tr>
<tr>
<td>m/mm⁻¹</td>
<td>0.084</td>
</tr>
<tr>
<td>F(000)</td>
<td>728.0</td>
</tr>
</tbody>
</table>

**Data Collection**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal size/mm³</td>
<td>0.35 x 0.14 x 0.11</td>
</tr>
<tr>
<td>2Θ range for data collection</td>
<td>6.92 to 58.1°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-24 ≤ h ≤ 20, -7 ≤ k ≤ 7, -24 ≤ l ≤ 25</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>7251</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>3975[R(int) = 0.0661]</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>3975/0/236</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>0.935</td>
</tr>
<tr>
<td>Final R indexes [I≥2σ(I)]</td>
<td>R₁ = 0.0765, wR₂ = 0.1691</td>
</tr>
<tr>
<td>Final R indexes [all data]</td>
<td>R₁ = 0.1728, wR₂ = 0.2185</td>
</tr>
<tr>
<td>Largest diff. peak/hole / e Å⁻³</td>
<td>0.28/-0.22</td>
</tr>
</tbody>
</table>

**Crystal Structure of 10-methyl-10H-spiro[acridine-9,1'-cyclohexan]-4'-one (66):**

![Crystal Structure of 10-methyl-10H-spiro[acridine-9,1'-cyclohexan]-4'-one (66)](image)
### Table 7: Crystal data and structural refinement for 66.

<table>
<thead>
<tr>
<th>Crystal Data</th>
<th></th>
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</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C_{19}H_{19}NO</td>
</tr>
<tr>
<td>Formula weight</td>
<td>277.35</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>219.99(10)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P-1</td>
</tr>
<tr>
<td>a/Å</td>
<td>8.6574(8)</td>
</tr>
<tr>
<td>b/Å</td>
<td>9.3517(8)</td>
</tr>
<tr>
<td>c/Å</td>
<td>10.6769(9)</td>
</tr>
<tr>
<td>α°</td>
<td>103.888(7)</td>
</tr>
<tr>
<td>β°</td>
<td>108.883(8)</td>
</tr>
<tr>
<td>γ°</td>
<td>108.807(8)</td>
</tr>
<tr>
<td>Volume/Å³</td>
<td>714.71(11)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>ρ_{calc},mg/mm³</td>
<td>1.289</td>
</tr>
<tr>
<td>m/mm¹</td>
<td>0.079</td>
</tr>
<tr>
<td>F(000)</td>
<td>296.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Data Collection</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal size/mm³</td>
<td>0.28 × 0.21 × 0.15</td>
</tr>
<tr>
<td>2Θ range for data collection</td>
<td>6.8 to 58.38°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-11 ≤ h ≤ 9, -12 ≤ k ≤ 12, -11 ≤ l ≤ 13</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>5158</td>
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<tr>
<td>Independent reflections</td>
<td>3264[R(int) = 0.0250]</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>3264/0/191</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.033</td>
</tr>
<tr>
<td>Final R indexes [I&gt;=2σ (I)]</td>
<td>R₁ = 0.0510, wR₂ = 0.1209</td>
</tr>
<tr>
<td>Final R indexes [all data]</td>
<td>R₁ = 0.0656, wR₂ = 0.1357</td>
</tr>
<tr>
<td>Largest diff. peak/hole / e Å⁻³</td>
<td>0.23/-0.22</td>
</tr>
</tbody>
</table>