Metal-free TEMPO-Catalyzed Oxidative C-C Bond Formation from Csp³-H Bonds Using Molecular Oxygen as The Oxidant

Bo Zhang, a Yuxin Cui, a and Ning Jiao*a,b

a State Key Laboratory of Natural and Biomimetic Drugs, School of Pharmaceutical Sciences, Peking University, Xue Yuan Rd. 38, Beijing 100191, China,
b Shanghai Key Laboratory of Green Chemistry and Chemical Processes, Department of Chemistry, East China Normal University, Shanghai 200062, China

E-mail: jiaoning@bjmu.edu.cn
Fax: (+86)10-82805297

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1. General Remarks
All manipulations were conducted with a standard Schlenk tube under dioxygen atmosphere, $^1$H-NMR spectra were recorded on Bruker AVIII-400 spectrometer. Chemical shifts (in ppm) were referenced to tetramethylsilane ($\delta = 0$ ppm) in CDCl$_3$ as an internal standard. $^{13}$C-NMR spectra were obtained by the same NMR spectrometer and were calibrated with CDCl$_3$ ($\delta = 77.00$ ppm). Mass spectra were recorded by PE SCLEX QSTAR spectrometer. HR-MS were obtained using electrospray ionization (ESI) mass spectrometer. Unless otherwise noted, materials and solvents obtained from commercial suppliers were used without further purification.

2. The substrates investigated in this reaction

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<tr>
<td>2</td>
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<td>11</td>
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<tr>
<td>12</td>
<td>L</td>
<td>Starting materials</td>
</tr>
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$^a$ Reaction conditions: substrate (0.2 mmol), 2a (0.5 mL), TEMPO (0.02 mmol), stirred at 60 °C under O$_2$ (1 atm) for 24 h. $^b$ The reaction was carried out at 100 °C for 3 days. $^c$ The reaction was carried out at 100 °C for 59h.
3. The proposed Mechanism

The plausible mechanism of this transformation is proposed in the following Scheme 2. Initially, TEMPO abstracts a hydrogen atom from the benzyl C-H bonds of 9,10-dihydroacridine 1 to produce the benzyl radical A and TEMPOH. Subsequently, the intermediates D and/or D' are generated in the presence of molecular oxygen via B and C as previously reported process.\(^1\) The conversion from the intermediates D and/or D' with the nucleophile 2 to the product 3 is unknown yet. The radical coupling with nucleophiles maybe involved in this step.\(^2\) In the absence of any nucleophile, the hydroperoxyl D and/or D' can be oxidized to ketone 5.\(^1\) We have tried to synthesize some intermediates such as hydroperoxyl or hydroxyl intermediate, but failed due to the unstability of these compounds. More detailed studies are needed to understand the mechanism.

![Proposed mechanism for the transformation](image_url)
4. Preparation of substrates

9,10-Dihydroacridine 1a, 1b, 1d, 1i and 1m were prepared according to reported methods.3

9,10-Dihydroacridine 1c was synthesised according to the synthetic method of 1b.

10-Propyl-9,10-dihydroacridine (1c)4

The reaction was carried out on 2.0 mmol and the product 1c was obtained in 54% yield as a white solid. IR:(KBr) $\nu_{\text{max}}$ 2961, 1596, 1480, 1374, 1260, 748 cm$^{-1}$; $^1$H-NMR (400 MHz, CDCl$_3$, ppm) $\delta$ 7.17 (t, $J$ = 7.8 Hz, 2H), 7.11 (d, $J$ = 7.6 Hz, 2H), 6.89-6.86 (m, 4H), 3.95 (s, 2H), 3.80 (t, $J$ = 7.6 Hz, 2H), 1.88-1.79 (m, 2H), 1.03 (t, $J$ = 7.4 Hz, 3H); $^{13}$C-NMR (100 MHz, CDCl$_3$, ppm) $\delta$ 142.1, 128.0, 126.8, 123.5, 120.2, 112.3, 47.5, 32.9, 19.0, 11.2; MS (70 eV): m/z (%): 223.2 (7) [M$^+$], 179.9 (100).

9,10-Dihydroacridine 1e-1h were prepared according to the synthetic method of 1d.

10-(4-Methoxybenzyl)-9,10-dihydroacridine (1e)

The reaction was carried out on 10.0 mmol and the product 1e was obtained in 57% total yield in two steps as a white solid. IR:(KBr) $\nu_{\text{max}}$ 2912, 1595, 1513, 1481, 1376, 1251, 750 cm$^{-1}$; $^1$H-NMR (400 MHz, CDCl$_3$, ppm) $\delta$ 7.17-7.04 (m, 6H), 6.91-6.85 (m, 4H), 6.70 (d, $J$ = 7.6 Hz, 2H), 5.09 (s, 2H), 4.09 (m, 2H), 3.79 (s, 3H); $^{13}$C-NMR (100 MHz, CDCl$_3$, ppm) $\delta$ 142.2, 128.7, 127.9, 127.3, 127.0, 123.2, 120.5, 114.1, 113.1, 55.2, 50.2, 32.6; MS (70 eV): m/z (%): 301.2 (5) [M$^+$], 121.1 (100); HRMS m/z (ESI): Calcd. for C$_{21}$H$_{18}$NO [M-H$^-$] 300.1388, Found: 300.1393.

10-(4-(Tert-butyl)benzyl)-9,10-dihydroacridine (1f)
The reaction was carried out on 10.0 mmol and the product 1f was obtained in 60% total yield in two steps as a white solid. IR:(KBr) $\nu_{\text{max}}$ 2962, 1595, 1480, 1370, 1265, 750 cm$^{-1}$; $^1$H-NMR (400 MHz, CDCl$_3$, ppm) $\delta$ 7.31 (d, $J = 8.4$ Hz, 2H), 7.13 (t, $J = 8.4$ Hz, 4H), 7.04 (t, $J = 7.4$ Hz, 2H), 6.87 (t, $J = 7.2$ Hz, 2H), 6.69 (d, $J = 8.0$ Hz, 2H), 5.09 (s, 2H), 4.08 (d, 2H), 1.30 (s, 9H); $^{13}$C-NMR (100 MHz, CDCl$_3$, ppm) $\delta$ 149.6, 142.2, 133.8, 127.9, 127.0, 125.8, 125.6, 123.1, 120.5, 113.2, 50.6, 34.4, 32.6, 31.4; MS (70 eV): m/z (%): 327.2 (33) [M]$^+$, 147.2 (100); HRMS m/z (ESI): Calcd. for C$_{24}$H$_{24}$N [M-H]$^+$ 326.1907, Found: 326.1909.

10-(4-Chlorobenzyl)-9,10-dihydroacridine (1g)

The reaction was carried out on 10.0 mmol and the product 1g was obtained in 53% total yield in two steps as a white solid. IR:(KBr) $\nu_{\text{max}}$ 2911, 1594, 1477, 1371, 1266, 1232, 746 cm$^{-1}$; $^1$H-NMR (400 MHz, CDCl$_3$, ppm) $\delta$ 7.26 (d, $J = 8.4$ Hz, 2H), 7.14 (t, $J = 8.6$ Hz, 4H), 7.04 (t, $J = 7.8$ Hz, 2H), 6.89 (t, $J = 7.4$ Hz, 2H), 6.61 (d, $J = 8.4$ Hz, 2H), 5.08 (s, 2H), 4.07 (d, 2H); $^{13}$C-NMR (100 MHz, CDCl$_3$, ppm) $\delta$ 141.9, 135.5, 132.6, 128.9, 128.1, 127.7, 127.0, 123.3, 120.8, 112.9, 50.2, 32.5; MS (70 eV): m/z (%): 305.1 (10) [M]$^+$, 179.9 (100); HRMS m/z (ESI): Calcd. for C$_{20}$H$_{15}$NCl [M-H]$^+$ 304.0893, Found: 304.0900.

10-(2-Bromobenzyl)-9,10-dihydroacridine (1h)

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The reaction was carried out on 10.0 mmol and the product 1h was obtained in 57% total yield in two steps as a white solid. IR:(KBr) νmax 2935, 1594, 1480, 1267, 1229, 747 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃, ppm) δ 7.65 (d, J = 7.2 Hz, 1H), 7.16-7.08 (m, 4H), 7.04 (t, J = 7.6 Hz, 2H), 6.93-6.87 (m, 3H), 6.54 (d, J = 8.0 Hz, 2H), 5.06 (s, 2H), 4.10 (s, 2H); ¹³C-NMR (100 MHz, CDCl₃, ppm) δ 141.6, 134.9, 133.0, 128.6, 128.3, 128.1, 127.5, 127.1, 132.1, 122.4, 120.8, 112.9, 52.0, 32.4; MS (70 eV): m/z (%): 349.0 (10) [M]⁺, 179.9 (100); HRMS m/z (ESI): Calcd. for C₂₀H₁₅NBr [M-H]⁺ 348.0388, Found: 348.0384.

9,10-Dihydroacridine 1j-1l were prepared according to the synthetic method of 1i.

**10-(p-Tolyl)-9,10-dihydroacridine (1j)**

The reaction was carried out on 1.5 mmol and the product 1j was obtained in 57% yield as a white solid. IR:(KBr) νmax 2917, 1595, 1478, 1315, 1275, 749 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃, ppm) δ 7.39 (d, J = 7.6 Hz, 2H), 7.19 (d, J = 7.6 Hz, 2H), 7.12 (d, J = 7.2 Hz, 2H), 6.92 (t, J = 7.4 Hz, 2H), 6.83 (t, J = 7.2 Hz, 2H), 6.21 (d, J = 8.4 Hz, 2H), 4.21 (s, 2H), 2.46 (s, 3H); ¹³C-NMR (100 MHz, CDCl₃, ppm) δ 142.8, 138.3, 138.0, 131.4, 130.9, 128.3, 126.6, 120.7, 120.4, 114.0, 31.9, 21.3; MS (70 eV): m/z (%): 271.3 [M]⁺; HRMS m/z (ESI): Calcd. for C₂₀H₁₆N [M-H]⁺ 270.1283, Found: 270.1284.

**10-(4-Methoxyphenyl)-9,10-dihydroacridine (1k)**

The reaction was carried out on 2.0 mmol and the product 1k was obtained in 55% yield as a white solid. IR:(KBr) νmax 2931, 1593, 1479, 1315, 1246, 749 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃, ppm) δ 7.23 (d, J = 8.4 Hz, 2H), 7.12 (t, J = 7.6 Hz, 4H), 6.94 (t, J = 7.6 Hz, 2H), 6.84 (t, J = 7.2 Hz, 2H), 6.23 (d, J = 8.4 Hz, 2H), 4.21 (s, 2H), 3.90 (s, 3H); ¹³C-NMR (100 MHz, CDCl₃, ppm) δ 159.1, 143.0, 133.6, 132.2, 128.3, 126.6, 120.8, 120.4, 115.9, 113.9, 55.5, 31.9; MS (70 eV): m/z (%): 287.3 [M]⁺; HRMS m/z (ESI): Calcd. for C₂₀H₁₆NO [M-H]⁺ 286.1232, Found: 286.1231.

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10-([1,1'-Biphenyl]-4-yl)-9,10-dihydroacridine (1l)

The reaction was carried out on 1.5 mmol and the product 1l was obtained in 52% yield as a white solid. IR:(KBr) $\nu_{\text{max}}$ 2919, 1597, 1481, 1317, 1268, 751 cm$^{-1}$; $^1$H-NMR (400 MHz, CDCl$_3$, ppm) $\delta$ 7.83 (d, $J = 8.0$ Hz, 2H), 7.69 (d, $J = 7.6$ Hz, 2H), 7.50 (t, $J = 7.6$ Hz, 2H), 7.42-7.38 (m, 3H), 7.42 (d, $J = 7.2$ Hz, 2H), 6.97 (t, $J = 7.6$ Hz, 2H), 6.86 (t, $J = 7.2$ Hz, 2H), 6.29 (d, $J = 8.0$ Hz, 2H), 4.24 (s, 2H); $^{13}$C-NMR (100 MHz, CDCl$_3$, ppm) $\delta$ 142.7, 141.0, 140.3, 131.6, 129.5, 128.9, 128.4, 127.7, 127.2, 126.7, 120.8, 120.5, 114.0, 31.9; MS (70 eV): m/z (%): 333.3 [M]$^+$, 77.0 (100); HRMS m/z (ESI): Calcd. for C$_{25}$H$_{18}$N [M-H]$^-$ 332.1439, Found: 332.1436.

5. Experimental procedures and characterization of products

10-Methyl-9-(nitromethyl)-9,10-dihydroacridine (3aa)

**Typical procedure:** 10-methyl-9,10-dihydroacridine 1a (39.5 mg, 0.2 mmol) and TEMPO (3.2 mg, 0.02 mmol) were placed in a 25 mL Schlenk tube. Then CH$_3$NO$_2$ 2a 0.5 mL was added. The reaction mixture was stirred at 60 °C under O$_2$ (1 atm) for 18 h as monitored by TLC. The solvent was removed and the residue was purified by silica gel column chromatography (PE/Et$_2$O = 10/1) to afford 46.9 mg (92 % yield) of 3aa. 3aa: white solid; IR:(KBr) $\nu_{\text{max}}$ 2913, 1594, 1472, 1334, 1265, 761 cm$^{-1}$; $^1$H-NMR (400 MHz, CDCl$_3$, ppm) $\delta$ 7.28 (t, $J = 7.8$ Hz, 2H), 7.21 (d, $J = 6.8$ Hz, 2H), 6.99-6.95 (m, 4H), 4.79 (t, $J = 8.0$ Hz, 1H), 4.33 (d, $J = 8.0$ Hz, 2H), 3.40 (s, 3H); $^{13}$C-NMR (100 MHz, CDCl$_3$, ppm) $\delta$ 142.4, 128.5, 128.2, 121.33, 121.31, 112.6, 78.9, 43.1, 33.0; MS (70 eV): m/z (%): 254.2 (7) [M]$^+$, 194.1 (100); HRMS m/z (ESI): Calcd. for C$_{15}$H$_{15}$N$_2$O$_2$ [M+H]$^+$ 255.1128, Found: 255.1126.

10-Methyl-9-(1-nitroethyl)-9,10-dihydroacridine (3ab)
The reaction of 10-methyl-9,10-dihydroacridine 1a (39.3 mg, 0.2 mmol), TEMPO (3.5 mg, 0.02 mmol) in nitroethane 2b (0.5 mL) at 60 °C under dioxygen for 18 h afforded 51.9 mg (97%) of 3ab. 3ab: white solid; IR:(KBr) νmax 2909, 1595, 1547, 1474, 1337, 1270, 756 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃, ppm) δ 7.31-7.25 (m, 2H), 7.18 (d, J = 7.2 Hz, 1H), 7.14 (d, J = 7.6 Hz, 1H), 7.01-6.93 (m, 4H), 4.58-4.51 (m, 1H), 4.43 (d, J = 8.8 Hz, 1H), 3.40 (s, 3H), 1.33 (d, J = 6.4 Hz, 3H); ¹³C-NMR (100 MHz, CDCl₃, ppm) δ 142.9, 142.3, 129.4, 128.4, 128.3, 122.2, 121.3, 120.9, 120.6, 112.6, 112.4, 85.6, 48.9, 33.0, 16.6; MS (70 eV): m/z (%): 268.2 (5) [M⁺], 194.1 (100); HRMS m/z (ESI): Calcd. for C₁₆H₁₇N₂O₂ [M+H⁺] 269.1285, Found: 269.1286.

10-Methyl-9-(1-nitropropyl)-9,10-dihydroacridine (3ac)

The reaction of 10-methyl-9,10-dihydroacridine 1a (39.5 mg, 0.2 mmol), TEMPO (3.2 mg, 0.02 mmol) in 1-nitropropane 2c (0.5 mL) at 60 °C under dioxygen for 27 h afforded 54.9 mg (97%) of 3ac. 3ac: white solid; IR:(KBr) νmax 2975, 2931, 1594, 1550, 1474, 1370, 1339, 1269, 1132, 749 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃, ppm) δ 7.32-7.20 (m, 3H), 7.11 (d, J = 7.6 Hz, 1H), 7.02-6.93 (m, 4H), 4.40-4.35 (m, 2H), 3.41 (s, 3H), 2.02-1.92 (m, 1H), 1.59-1.50 (m, 1H), 0.77 (t, J = 7.4 Hz, 3H); ¹³C-NMR (100 MHz, CDCl₃, ppm) δ 142.9, 142.2, 129.5, 128.3, 128.2, 128.1, 122.2, 121.3, 121.1, 120.9, 121.1, 122.3, 92.0, 48.4, 33.0, 24.6, 10.2; MS (70 eV): m/z (%): 282.2 (4) [M⁺], 194.1 (100); HRMS m/z (ESI): Calcd. for C₁₇H₁₉N₂O₂ [M+H⁺] 283.1441, Found: 283.1441.

2-(10-Methyl-9,10-dihydroacridin-9-yl)cyclopentanone (3ad)

The reaction of 10-methyl-9,10-dihydroacridine 1a (39.3 mg, 0.2 mmol), TEMPO (3.5 mg, 0.02 mmol) in cyclopentanone 2d (0.5 mL) at 80 °C under dioxygen for 36 h afforded 44.7 mg (81%) of 3ad. 3ad: white solid; IR:(KBr) νmax 2965, 2888, 1734,
1593, 1478, 1346, 1269, 1146, 1130, 757 cm\(^{-1}\); \(^1\)H-NMR (400 MHz, CDCl\(_3\), ppm) \(\delta\) 7.25-7.18 (m, 3H), 7.09 (d, \(J = 7.2\) Hz, 1H), 7.95 (t, \(J = 7.4\) Hz, 1H), 6.89-6.85 (m, 3H), 4.69 (d, \(J = 2.8\) Hz, 1H), 3.37 (s, 3H), 2.31-2.16 (m, 2H), 1.83-1.63 (m, 3H), 1.55-1.35 (m, 2H); \(^{13}\)C-NMR (100 MHz, CDCl\(_3\), ppm) \(\delta\) 219.1, 143.5, 142.7, 129.1, 128.0, 127.3, 126.3, 123.5, 120.8, 120.6, 111.9, 111.8, 59.4, 41.8, 38.7, 32.9, 24.5, 20.3; MS (70 eV): m/z (%): 277.1 (3) \([M]^+\), 194.2 (100); HRMS m/z (ESI): Calcd. for C\(_{19}\)H\(_{19}\)NNaO \([M+Na]^+\) 300.1359, Found: 300.1360.

2-(10-Methyl-9,10-dihydroacridin-9-yl)cyclohexanone (3ae)

\[
\begin{align*}
\text{N} & \quad \text{Me} \\
& \quad \text{O}
\end{align*}
\]

The reaction of 10-methyl-9,10-dihydroacridine 1a (39.5 mg, 0.2 mmol), TEMPO (3.2 mg, 0.02 mmol) in cyclohexanone 2e (0.5 mL) at 80 °C under dioxygen for 36 h afforded 51.5 mg (88 %) of 3ae. 3ae: white solid; IR:(KBr) \(\nu_{\text{max}}\) 2921, 1707, 1593, 1475, 1339, 1269, 757 cm\(^{-1}\); \(^1\)H-NMR (400 MHz, CDCl\(_3\), ppm) \(\delta\) 7.34 (d, \(J = 7.6\) Hz, 1H), 7.24-7.17 (m, 3H), 6.95-6.89 (m, 4H), 4.66 (d, \(J = 6.8\) Hz, 1H), 3.36 (s, 3H), 2.55-2.50 (m, 1H), 2.40-2.31 (m, 1H), 2.30-2.15 (m, 1H), 1.91-1.88 (m, 1H), 1.73-1.69 (m, 1H), 1.64-1.55 (m, 2H), 1.49-1.38 (m, 1H), 1.29-1.19 (m, 1H); \(^{13}\)C-NMR (100 MHz, CDCl\(_3\), ppm) \(\delta\) 212.0, 143.5, 142.9, 129.7, 129.0, 127.3, 127.0, 126.8, 124.7, 120.6, 120.3, 112.0, 111.9, 56.6, 42.5, 41.5, 32.9, 30.4, 27.9, 24.6; MS (70 eV): m/z (%): 291.2 (3) \([M]^+\), 194.3 (100); HRMS m/z (ESI): Calcd. for C\(_{20}\)H\(_{21}\)NNaO \([M+Na]^+\) 314.1515, Found: 314.1516.

2-(10-Methyl-9,10-dihydroacridin-9-yl)cycloheptanone (3af)

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\begin{align*}
\text{N} & \quad \text{Me} \\
& \quad \text{O}
\end{align*}
\]

The reaction of 10-methyl-9,10-dihydroacridine 1a (39.3 mg, 0.2 mmol), TEMPO (3.3 mg, 0.02 mmol) in cycloheptanone 2f (0.5 mL) at 80 °C under dioxygen for 36 h afforded 22.6 mg (37 %) of 3af. 3af: white solid; IR:(KBr) \(\nu_{\text{max}}\) 2923, 1699, 1593, 1476, 1339, 1268, 749 cm\(^{-1}\); \(^1\)H-NMR (400 MHz, CDCl\(_3\), ppm) \(\delta\) 7.22-7.16 (m, 3H), 7.07 (d, \(J = 6.8\) Hz, 1H), 6.93-6.89 (m, 4H), 4.39 (d, \(J = 6.8\) Hz, 1H), 3.37 (s, 3H), 2.65-2.59 (m, 1H), 2.13-2.10 (m, 2H), 1.73-1.71 (m, 3H), 1.60-1.56 (m, 1H), 1.33-1.11 (m, 3H), 1.03-0.97 (m, 1H); \(^{13}\)C-NMR (100 MHz, CDCl\(_3\), ppm) \(\delta\) 215.8, 143.3, 142.9, 129.1, 128.8, 127.3, 127.1, 125.6, 123.9, 120.7, 120.4, 112.2, 112.0,
59.5, 46.2, 43.7, 32.9, 28.0, 26.8, 24.9; MS (70 eV): m/z (%): 305.3 (3) [M]+, 194.0 (100); HRMS m/z (ESI): Calcd. for C_{21}H_{23}NNaO [M+Na]+ 328.1672, Found: 328.1673.

2-(10-Methyl-9,10-dihydroacridin-9-yl)pentan-3-one (3ag)

The reaction of 10-methyl-9,10-dihydroacridine 1a (39.7 mg, 0.2 mmol), TEMPO (3.4 mg, 0.02 mmol) in pentan-3-one 2g (0.5 mL) at 80 °C under dioxygen for 36 h afforded 11.7 mg (21 %) of 3ag. 3ag: white solid; IR:(KBr) \( \nu_{\text{max}} \) 2929, 1712, 1595, 1476, 1340, 1273, 1129, 759 cm\(^{-1}\); \(^1\)H-NMR (400 MHz, CDCl\(_3\), ppm) \( \delta \) 7.26-7.16 (m, 3H), 7.03-6.87 (m, 5H), 4.02 (d, \( J = 10.0 \) Hz, 1H), 3.42 (s, 3H), 2.86-2.78 (m, 1H), 2.12-2.02 (m, 1H), 1.60-1.52 (m, 1H), 0.87 (d, \( J = 6.8 \) Hz, 3H), 0.73 (t, \( J = 7.2 \) Hz, 3H); \(^13\)C-NMR (100 MHz, CDCl\(_3\), ppm) \( \delta \) 215.4, 142.7, 142.6, 129.4, 128.5, 127.2, 127.1, 125.7, 124.9, 120.7, 120.4, 112.1, 112.0, 48.5, 47.4, 37.7, 32.9, 15.1, 7.1; MS (70 eV): m/z (%): 279.2 (2) [M]+, 194.0 (100); HRMS m/z (ESI): Calcd. for C\(_{19}\)H\(_{22}\)NO [M+H]+ 280.1696, Found: 280.1698.

Dimethyl 2-(10-methyl-9,10-dihydroacridin-9-yl)malonate (3ah)

The reaction of 10-methyl-9,10-dihydroacridine 1a (39.5 mg, 0.2 mmol), TEMPO (3.4 mg, 0.02 mmol) in dimethyl malonate 2h (0.5 mL) at 80 °C under dioxygen for 36 h afforded 58.8 mg (90 %) of 3ah. 3ah: white solid; IR:(KBr) \( \nu_{\text{max}} \) 2956, 1758, 1594, 1475, 1341, 1260, 1134, 924, 763, 556 cm\(^{-1}\); \(^1\)H-NMR (400 MHz, CDCl\(_3\), ppm) \( \delta \) 7.27-7.22 (m, 4H), 6.96-6.91 (m, 4H), 4.77 (d, \( J = 10.6 \) Hz, 1H), 3.63 (d, \( J = 10.6 \) Hz, 1H), 3.50 (s, 6H), 3.42 (s, 3H); \(^13\)C-NMR (100 MHz, CDCl\(_3\), ppm) \( \delta \) 167.8, 142.8, 128.5, 127.7, 123.2, 120.7, 112.2, 55.6, 52.2, 44.1, 33.0; MS (70 eV): m/z (%): 325.2 (5) [M]+, 194.3 (100); HRMS m/z (ESI): Calcd. for C\(_{19}\)H\(_{20}\)NO\(_4\) [M+H]+ 326.1387, Found: 326.1391.

Dimethyl 2-(10-benzyl-9,10-dihydroacridin-9-yl)malonate (3dh)
The reaction of 10-benzyl-9,10-dihydroacridine 1d (54.5 mg, 0.2 mmol), TEMPO (3.3 mg, 0.02 mmol) in dimethyl malonate 2h (0.5 mL) at 80 °C under dioxygen for 24 h afforded 68.5 mg (85 %) of 3dh. **3dh**: white solid; IR:(KBr) $\nu_{\text{max}}$ 2951, 2924, 1731, 1571, 1471, 1371, 1242, 1160, 1027, 758 cm$^{-1}$; $^1$H-NMR (400 MHz, CDCl$_3$, ppm) $\delta$ 7.31-7.24 (m, 5H), 7.15 (d, $J = 7.2$ Hz, 2H), 7.09 (t, $J = 7.6$ Hz, 2H), 6.91 (t, $J = 7.4$ Hz, 2H), 6.79 (d, $J = 8.0$ Hz, 2H), 5.25 (s, 2H), 4.85 (d, $J = 10.5$ Hz, 1H), 3.63 (d, $J = 10.5$ Hz, 1H), 3.51 (s, 6H); $^{13}$C-NMR (100 MHz, CDCl$_3$, ppm) $\delta$ 167.8, 141.4, 136.4, 128.7, 128.6, 127.8, 126.9, 126.3, 122.8, 120.8, 113.6, 57.3, 52.3, 50.4, 43.9; MS (70 eV): m/z (%): 401.1 (9) [M$^+$], 270.1 (100); HRMS m/z (ESI): Calcd. for C$_{25}$H$_{23}$NNaO$_4$ [M$+$Na$^+$] 424.1519, Found: 424.1518.

**Dimethyl 2-(10-phenyl-9,10-dihydroacridin-9-yl)malonate (3ih)**

The reaction of 10-phenyl-9,10-dihydroacridine 1i (51.9 mg, 0.2 mmol), TEMPO (3.2 mg, 0.02 mmol) in dimethyl malonate 2h (0.5 mL) at 80 °C under dioxygen for 24 h afforded 59.6 mg (77 %) of 3ih. **3ih**: white solid; IR:(KBr) $\nu_{\text{max}}$ 2950, 1755, 1734, 1593, 1475, 1315, 1277, 1256, 1147, 756 cm$^{-1}$; $^1$H-NMR (400 MHz, CDCl$_3$, ppm) $\delta$ 7.63 (t, $J = 7.6$ Hz, 2H), 7.52 (t, $J = 7.2$ Hz, 1H), 7.39 (d, $J = 7.6$ Hz, 2H), 7.29 (d, $J = 7.2$ Hz, 2H), 7.03 (t, $J = 7.6$ Hz, 2H), 6.90 (t, $J = 7.2$ Hz, 2H), 6.39 (d, $J = 8.0$ Hz, 2H), 4.92 (d, $J = 10.0$ Hz, 1H), 3.73 (d, $J = 10.0$ Hz, 1H), 3.51 (s, 6H); $^{13}$C-NMR (100 MHz, CDCl$_3$, ppm) $\delta$ 167.8, 142.3, 140.3, 131.1, 130.6, 128.6, 127.8, 127.4, 121.1, 120.9, 114.2, 58.1, 52.4, 43.6; MS (70 eV): m/z (%): 387.1 (3) [M$^+$], 256.1 (100); HRMS m/z (ESI): Calcd. for C$_{24}$H$_{21}$NNaO$_4$ [M$+$Na$^+$] 410.1363, Found: 410.1363.

**2-(10-Methyl-9,10-dihydroacridin-9-yl)malononitrile (3ai)**

The reaction of 10-methyl-9,10-dihydroacridine 1a (39.7 mg, 0.2 mmol), TEMPO (3.4 mg, 0.02 mmol) and malononitrile 2i (70.0 mg, 1.0 mmol) in DCE (0.3 mL) at...
80 °C under dioxygen for 16 h afforded 39.5 mg (76 %) of 3ai. 3ai: yellowish solid; IR:(KBr) νmax 2890, 2252, 1595, 1475, 1337, 1273, 1129, 891, 758 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃, ppm) δ 7.41-7.36 (m, 4H), 7.10-7.02 (m, 4H), 4.57 (d, J = 8.4 Hz, 1H), 3.70 (d, J = 8.4 Hz, 1H), 3.44 (s, 3H); ¹³C-NMR (100 MHz, CDCl₃, ppm) δ 142.2, 129.5, 129.3, 121.6, 119.1, 113.0, 111.9, 46.1, 33.2, 28.6; MS (70 eV): m/z (%): 259.3 (3) [M]+, 194.3 (100); HRMS m/z (ESI): Calcd. for C₁₇H₁₂N₃ [M-H]⁻ 258.1037, Found: 258.1030.

2-(10-Benzyl-9,10-dihydroacridin-9-yl)malononitrile (3di)

The reaction of 10-benzyl-9,10-dihydroacridine 1d (54.5 mg, 0.2 mmol), TEMPO (3.4 mg, 0.02 mmol) and malononitrile 2i (66.8 mg, 1.0 mmol) in DCE (0.3 mL) at 80 °C under dioxygen for 16 h afforded 65.9 mg (98 %) of 3ai. 3ai: yellowish solid; IR:(KBr) νmax 2892, 2251, 1596, 1542, 1477, 1376, 1268, 1221, 753 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃, ppm) δ 7.42 (d, J = 7.6 Hz, 2H), 7.35-7.23 (m, 5H), 7.14 (d, J = 7.2 Hz, 2H), 7.07 (t, J = 7.4 Hz, 2H), 6.86 (d, J = 8.4 Hz, 2H), 5.19 (s, 2H), 4.71 (d, J = 6.4 Hz, 1H), 3.73 (d, J = 6.8 Hz, 1H); ¹³C-NMR (100 MHz, CDCl₃, ppm) δ 141.3, 136.1, 129.8, 129.2, 128.9, 127.2, 125.9, 121.7, 118.3, 114.3, 111.8, 51.5, 45.7, 31.3; MS (70 eV): m/z (%): 91.1 (100); HRMS m/z (ESI): Calcd. for C₂₃H₁₆N₃ [M-H]⁻ 334.1350, Found: 334.1341.

10-Ethyl-9-(nitromethyl)-9,10-dihydroacridine (3ba)

The reaction of 10-ethyl-9,10-dihydroacridine 1b (42.1 mg, 0.2 mmol), TEMPO (3.4 mg, 0.02 mmol) in CH₃NO₂ 2a (0.5 mL) at 60 °C under dioxygen for 18 h afforded 47.2 mg (88 %) of 3ba. 3ba: white solid; IR:(KBr) νmax 2982, 2914, 1594, 1542, 1477, 1372, 1258, 753 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃, ppm) δ 7.27 (t, J = 7.9 Hz, 2H), 7.19 (d, J = 7.3 Hz, 2H), 7.03 (d, J = 7.9 Hz, 2H), 6.94 (t, J = 7.3 Hz, 2H), 4.78 (t, J = 7.7 Hz, 1H), 4.28 (d, J = 7.7 Hz, 2H), 4.03 (q, J = 7.0 Hz, 2H), 1.39 (t, J = 7.0 Hz, 3H); ¹³C-NMR (100 MHz, CDCl₃, ppm) δ 140.6, 128.6, 128.5, 121.1, 120.8, 112.8, 80.0, 42.9, 40.0, 11.3; MS (70 eV): m/z (%): 268.2 (7) [M]+, 208.2 (100); HRMS m/z (ESI): Calcd. for C₁₆H₁₇N₂O₂ [M+H]⁺ 269.1284, Found: 269.1284.

9-(Nitromethyl)-10-propyl-9,10-dihydroacridine (3ca)
The reaction of 10-propyl-9,10-dihydroacridine 1c (45.0 mg, 0.2 mmol), TEMPO (3.3 mg, 0.02 mmol) in CH$_3$NO$_2$ (0.5 mL) at 60 °C under dioxygen for 18 h afforded 45.6 mg (81 %) of 3ca. 3ca: white solid; IR:(KBr) $\nu_{\text{max}}$ 2957, 2891, 1594, 1541, 1477, 1376, 1277, 745 cm$^{-1}$; $^1$H-NMR (400 MHz, CDCl$_3$, ppm) $\delta$ 7.27 (t, $J = 7.7$ Hz, 2H), 7.19 (d, $J = 7.2$ Hz, 2H), 6.96 (m, 4H), 4.79 (t, $J = 7.7$ Hz, 1H), 4.30 (d, $J = 7.7$ Hz, 2H), 3.87 (t, $J = 7.6$ Hz, 2H), 1.90-1.80 (m, 2H), 1.06 (t, $J = 7.6$ Hz, 3H); $^{13}$C-NMR (100 MHz, CDCl$_3$, ppm) $\delta$ 140.9, 128.5, 128.4, 121.0, 120.8, 113.0, 79.9, 47.2, 42.9, 18.8, 11.2; MS (70 eV): m/z (%): 282.2 (10) [M$^+$], 222.2 (100); HRMS m/z (ESI): Calcd. for C$_{17}$H$_{19}$N$_2$O$_2$ [M+H]$^+$ 283.1441, Found: 283.1442.

10-Benzyl-9-(nitromethyl)-9,10-dihydroacridine (3da)

The reaction of 10-benzyl-9,10-dihydroacridine 1d (54.7 mg, 0.2 mmol), TEMPO (3.3 mg, 0.02 mmol) in CH$_3$NO$_2$ 2a (0.5 mL) at 60 °C under dioxygen for 18 h afforded 48.5 mg (73 %) of 3da. 3da: yellowish solid; IR:(KBr) $\nu_{\text{max}}$ 2918, 1594, 1553, 1478, 1374, 1266, 749 cm$^{-1}$; $^1$H-NMR (400 MHz, CDCl$_3$, ppm) $\delta$ 7.32-7.22 (m, 5H), 7.16-7.12 (m, 4H), 6.95 (t, $J = 7.2$ Hz, 2H), 6.79 (d, $J = 8.0$ Hz, 2H), 5.21 (s, 2H), 4.89 (t, $J = 7.6$ Hz, 1H), 4.39 (d, $J = 7.6$ Hz, 2H); $^{13}$C-NMR (100 MHz, CDCl$_3$, ppm) $\delta$ 141.0, 136.1, 128.8, 128.5, 128.3, 127.0, 126.1, 121.4, 120.7, 113.8, 80.4, 50.4, 42.7; MS (70 eV): m/z (%): 330.2 (6) [M$^+$], 91.1 (100); HRMS m/z (ESI): Calcd. for C$_{21}$H$_{19}$N$_2$O$_2$ [M+H]$^+$ 331.1441, Found: 331.1439.

10-(4-Methoxybenzyl)-9-(nitromethyl)-9,10-dihydroacridine (3ea)

The reaction of 10-(4-methoxybenzyl)-9,10-dihydroacridine 1e (60.5 mg, 0.2 mmol), TEMPO (3.3 mg, 0.02 mmol) in CH$_3$NO$_2$ 2a (0.5 mL) at 60 °C under dioxygen for 18 h afforded 53.1 mg (74 %) of 3ea. 3ea: yellowish solid; IR:(KBr) $\nu_{\text{max}}$ 2918, 2891,
1595, 1544, 1511, 1481, 1376, 1251, 750 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃, ppm) δ 7.22 (d, J = 8.0 Hz, 2H), 7.15 (t, J = 7.2 Hz, 2H), 7.04 (d, J = 8.4 Hz, 2H), 6.95 (t, J = 7.4 Hz, 2H), 6.82 (t, J = 8.0 Hz, 4H), 5.15 (s, 2H), 4.88 (t, J = 7.7 Hz, 1H), 4.38 (d, J = 7.7 Hz, 2H), 3.76 (s, 3H); ¹³C-NMR (100 MHz, CDCl₃, ppm) δ 158.6, 141.1, 128.6, 128.3, 127.7, 121.4, 120.7, 114.2, 113.8, 80.4, 55.2, 49.8, 42.7; MS (70 eV): m/z (%): 360.2 (3) [M⁺], 121.1 (100); HRMS m/z (ESI): Calcd. for C₂₂H₂₀N₂NaO₃ [M+Na⁺] 383.1369, Found: 383.1366.

10-(4-Tert-butylbenzyl)-9-(nitromethyl)-9,10-dihydroacridine (3fa)

![Chemical structure](image)

The reaction of 10-(4-tert-butylbenzyl)-9,10-dihydroacridine 1f (65.8 mg, 0.2 mmol), TEMPO (3.2 mg, 0.02 mmol) in CH₃NO₂ 2a (0.5 mL) at 60 °C under dioxygen for 18 h afforded 63.3 mg (82 %) of 3fa. 3fa: yellowish solid; IR:(KBr) ν max 2961, 1595, 1551, 1478, 1374, 1268, 754 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃, ppm) δ 7.30 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 7.2 Hz, 2H), 7.14 (t, J = 8.4 Hz, 2H), 7.05 (d, J = 8.0 Hz, 2H), 6.95 (t, J = 7.4 Hz, 2H), 6.81 (d, J = 8.4 Hz, 2H), 5.17 (s, 2H), 4.89 (t, J = 7.7 Hz, 1H), 4.38 (d, J = 7.7 Hz, 2H), 1.29 (s, 9H); ¹³C-NMR (100 MHz, CDCl₃, ppm) δ 149.9, 141.1, 132.9, 128.6, 128.3, 125.7, 125.6, 121.4, 120.7, 113.9, 80.5, 50.2, 42.7, 34.4, 31.3; MS (70 eV): m/z (%): 386.2 (1) [M⁺], 117.0 (100); HRMS m/z (ESI): Calcd. for C₂₅H₂₆N₂NaO₂ [M+Na⁺] 409.1891, Found: 409.1891.

10-(4-Chlorobenzyl)-9-(nitromethyl)-9,10-dihydroacridine (3ga)

![Chemical structure](image)

The reaction of 10-(4-chlorobenzyl)-9,10-dihydroacridine 1g (61.5 mg, 0.2 mmol), TEMPO (3.3 mg, 0.02 mmol) in CH₃NO₂ 2a (0.5 mL) at 60 °C under dioxygen for 18 h afforded 64.5 mg (88 %) of 3ga. 3ga: yellowish solid; IR:(KBr) ν max 2917, 1595, 1553, 1478, 1375, 1270, 755 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃, ppm) δ 7.25 (m, 4H), 7.16 (t, J = 7.8 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H), 6.97 (t, J = 7.4 Hz, 2H), 6.74 (d, J = 8.0 Hz, 2H), 5.17 (s, 2H), 4.89 (t, J = 7.6 Hz, 1H), 4.39 (d, J = 7.6 Hz, 2H); ¹³C-NMR (100 MHz, CDCl₃, ppm) δ 140.8, 134.5, 132.8, 129.0, 128.6, 128.4, 127.5, 121.7, 120.8, 113.6, 80.4, 49.8, 42.6; MS (70 eV): m/z (%): 364.2 (1) [M⁺], 125.0 (100);
HRMS m/z (ESI): Calcd. for C_{21}H_{18}ClN_{2}O_{2} [M+H]^+ 365.1051, Found: 365.1054.

10-(2-Bromobenzyl)-9-(nitromethyl)-9,10-dihydroacridine (3ha)

![Chemical structure of 3ha](image)

The reaction of 10-(2-bromobenzyl)-9,10-dihydroacridine 1h (70.4 mg, 0.2 mmol), TEMPO (3.4 mg, 0.02 mmol) in CH_{3}NO_{2} 2a (0.5 mL) at 60 °C under dioxygen for 18 h afforded 74.6 mg (91 %) of 3ha. 3ha: yellowish solid; IR (KBr) \( \nu_{\text{max}} \) 2961, 1594, 1548, 1477, 1372, 1266, 1027, 758, 742 cm\(^{-1}\); \(^1\)H-NMR (400 MHz, CDCl\(_3\), ppm) \( \delta \) 7.68 (d, \( J = 7.6 \) Hz, 1H), 7.25 (d, \( J = 6.8 \) Hz, 2H), 7.16 (t, \( J = 7.4 \) Hz, 3H), 7.09 (t, \( J = 7.2 \) Hz, 1H), 6.98 (t, \( J = 7.4 \) Hz, 2H), 6.76 (d, \( J = 7.6 \) Hz, 1H), 6.67 (d, \( J = 8.9 \) Hz, 2H), 5.16 (s, 2H), 4.92 (t, \( J = 7.7 \) Hz, 1H), 4.41 (d, \( J = 7.7 \) Hz, 2H); \(^{13}\)C-NMR (100 MHz, CDCl\(_3\), ppm) \( \delta \) 140.6, 134.1, 133.2, 128.8, 128.7, 128.4, 128.1, 127.4, 122.3, 121.7, 120.7, 113.6, 80.6, 51.7, 42.6; MS (70 eV): m/z (%): 410.1 (1) [M]\(^+\), 169.1 (100); HRMS m/z (ESI): Calcd. for C_{21}H_{18}BrN_{2}O_{2} [M+H]^+ 409.0546, Found: 409.0551.

9-(Nitromethyl)-10-phenyl-9,10-dihydroacridine (3ia)

![Chemical structure of 3ia](image)

The reaction of 10-phenyl-9,10-dihydroacridine 1i (51.8 mg, 0.2 mmol), TEMPO (3.3 mg, 0.02 mmol) in CH_{3}NO_{2} 2a (0.5 mL) at 60 °C under dioxygen for 18 h afforded 55.3 mg (85 %) of 3ia. 3ia: yellowish solid; IR (KBr) \( \nu_{\text{max}} \) 2912, 1594, 1548, 1474, 1375, 1312, 1270, 746, 702 cm\(^{-1}\); \(^1\)H-NMR (400 MHz, CDCl\(_3\), ppm) \( \delta \) 7.63 (t, \( J = 7.6 \) Hz, 2H), 7.52 (t, \( J = 7.4 \) Hz, 1H), 7.32 (d, \( J = 7.6 \) Hz, 2H), 7.24 (d, \( J = 7.6 \) Hz, 2H), 7.06 (t, \( J = 7.2 \) Hz, 2H), 6.93 (t, \( J = 7.4 \) Hz, 2H), 6.36 (d, \( J = 8.0 \) Hz, 2H), 4.97 (t, \( J = 7.5 \) Hz, 1H), 4.48 (d, \( J = 7.5 \) Hz, 2H); \(^{13}\)C-NMR (100 MHz, CDCl\(_3\), ppm) \( \delta \) 141.9, 140.1, 130.9, 130.8, 128.6, 128.3, 128.2, 121.4, 118.8, 114.5, 81.2, 42.3; MS (70 eV): m/z (%): 316.2 (1) [M]\(^+\), 77.0 (100); HRMS m/z (ESI): Calcd. for C_{20}H_{17}N_{2}O_{2} [M+H]^+ 317.1285, Found: 317.1289.

9-(Nitromethyl)-10-p-tolyl-9,10-dihydroacridine (3ja)
The reaction of 10-p-tolyl-9,10-dihydroacridine 1j (54.7 mg, 0.2 mmol), TEMPO (3.4 mg, 0.02 mmol) in CH$_3$NO$_2$ 2a (0.5 mL) at 60 °C under dioxygen for 18 h afforded 57.1 mg (86 %) of 3ja. 3ja: yellowish solid; IR:(KBr) $\nu_{\text{max}}$ 3026, 2923, 1594, 1548, 1511, 1475, 1374, 1314, 1270, 747 cm$^{-1}$; $^1$H-NMR (400 MHz, CDCl$_3$, ppm) $\delta$ 7.36 (d, $J = 8.0$ Hz, 2H), 7.24-7.18 (m, 4H), 7.05 (t, $J = 7.6$ Hz, 2H), 6.38 (d, $J = 8.0$ Hz, 2H), 4.96 (t, $J = 7.3$ Hz, 1H), 4.47 (d, $J = 7.3$ Hz, 2H), 6.38 (d, $J = 8.0$ Hz, 2H), 4.96 (t, $J = 7.3$ Hz, 1H), 4.47 (d, $J = 7.3$ Hz, 2H), 2.48 (s, 3H); $^{13}$C-NMR (100 MHz, CDCl$_3$, ppm) $\delta$ 142.1, 138.5, 137.3, 131.5, 130.5, 128.3, 128.2, 121.4, 118.8, 114.6, 81.2, 42.3, 21.3; MS (70 eV): m/z (%): 330.2 (7) [M]$^+$, 270.2 (100); HRMS m/z (ESI): Calcd. for C$_{21}$H$_{19}$N$_2$O$_2$ [M+H]$^+$ 331.1441, Found: 331.1442.

10-(4-Methoxyphenyl)-9-(nitromethyl)-9,10-dihydroacridine (3ka)

The reaction of 10-(4-methoxyphenyl)-9,10-dihydroacridine 1k (57.6 mg, 0.2 mmol), TEMPO (3.3 mg, 0.02 mmol) in CH$_3$NO$_2$ 2a (1.0 mL) at 60 °C under dioxygen for 18 h afforded 62.2 mg (90 %) of 3ka. 3ka: yellowish solid; IR:(KBr) $\nu_{\text{max}}$ 3035, 2913, 1592, 1544, 1513, 1473, 1315, 1249, 1035, 758 cm$^{-1}$; $^1$H-NMR (400 MHz, CDCl$_3$, ppm) $\delta$ 7.23 (d, $J = 8.0$ Hz, 4H), 7.13 (d, $J = 8.4$ Hz, 2H), 7.07 (t, $J = 7.6$ Hz, 2H), 6.93 (t, $J = 7.2$ Hz, 2H), 6.40 (d, $J = 8.0$ Hz, 2H), 4.96 (t, $J = 7.5$ Hz, 1H), 4.47 (d, $J = 7.5$ Hz, 2H), 3.91 (s, 3H); $^{13}$C-NMR (100 MHz, CDCl$_3$, ppm) $\delta$ 159.4, 142.3, 132.5, 131.8, 128.3, 128.2, 121.4, 118.8, 116.0, 114.5, 81.2, 55.5, 42.3; MS (70 eV): m/z (%): 346.2 (3) [M]$^+$, 62.9 (100); HRMS m/z (ESI): Calcd. for C$_{21}$H$_{19}$N$_2$O$_2$ [M+H]$^+$ 347.1390, Found: 347.1395.

10-(Biphenyl-4-yl)-9-(nitromethyl)-9,10-dihydroacridine (3la)
The reaction of 10-(biphenyl-4-yl)-9,10-dihydroacridine 1l (67.0 mg, 0.2 mmol), TEMPO (3.4 mg, 0.02 mmol) in CH₃NO₂ 2a (0.5 mL) at 60 °C under dioxygen for 18h afforded 53.3 mg (68 %) of 3la. 3la: yellowish solid; IR:(KBr) νmax 3031, 2952, 1593, 1543, 1478, 1375, 753, 745 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃, ppm) δ 7.85 (d, J = 7.6 Hz, 2H), 7.70 (d, J = 7.6 Hz, 2H), 7.50 (t, J = 7.4 Hz, 2H), 7.43-7.38 (m, 3H), 7.26 (d, J = 7.2 Hz, 2H), 7.09 (t, J = 7.6 Hz, 2H), 6.96 (t, J = 7.4 Hz, 2H), 6.46 (d, J = 8.4 Hz, 2H), 4.99 (t, J = 7.4 Hz, 1H), 4.50 (d, J = 7.4 Hz, 2H); ¹³C-NMR (100 MHz, CDCl₃, ppm) δ 141.9, 141.5, 140.0, 139.2, 131.2, 129.5, 129.0, 128.3, 127.8, 127.2, 121.5, 118.9, 114.6, 81.2, 42.3; MS (70 eV): m/z (%): 392.2 (7) [M]+, 77.0 (100); HRMS m/z (ESI): Calcd. for C₂₆H₂₁N₂O₂ [M+H]+ 393.1598, Found: 393.1605.

9-(Nitromethyl)-9,10-dihydroacridine (3ma) and acridine (4)

The reaction of 9,10-dihydroacridine 1m (36.5 mg, 0.2 mmol), TEMPO (3.4 mg, 0.02 mmol) in CH₃NO₂ 2a (0.5 mL) at 60 °C under dioxygen for 18h afforded 41.0 mg (43 % 3ma and 57 % 4) of 3ma and 4 (3ma:4 = 1:1); ¹H-NMR (400 MHz, CDCl₃, ppm) 3ma δ 7.19-7.15 (m, 4H), 6.92 (t, J = 7.4 Hz, 2H), 6.79 (d, J = 8.0 Hz, 2H), 6.55 (s, 1H), 4.87 (t, J = 7.6 Hz, 1H), 4.36 (d, J = 7.6 Hz, 2H), 4 δ 8.75 (s, 1H), 8.24 (d, J = 8.6 Hz, 2H), 7.98 (d, J = 8.6 Hz, 2H), 7.77 (t, J = 7.2 Hz, 2H), 7.52 (t, J = 7.2 Hz, 2H); ¹³C-NMR (100 MHz, CDCl₃, ppm) 3ma δ 139.6, 128.4, 121.4, 117.8, 113.9, 80.2, 41.9, 4 δ: 149.0, 136.0, 130.2, 129.2, 128.1, 126.5, 125.6; MS (70 eV): m/z (%):3ma: 240.2 [M]+; 4: 179.2 [M]+.

10-methylacridin-9(10H)-one (5)

The reaction of 10-methyl-9,10-dihydroacridine 1a (39.5 mg, 0.2 mmol), TEMPO
(3.5 mg, 0.02 mmol) in CH₃CN (0.5 mL) at 80 °C under dioxygen for 40 h afforded 42.2 mg (100 %) of 5. 5: white solid; IR:(KBr) ν_max 2925, 1757, 1631, 1595, 1490, 1490, 1368, 1290, 1268, 1180, 755 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃, ppm) δ 8.55 (d, J = 8.0 Hz, 2H), 7.70 (t, J = 7.8 Hz, 2H), 7.49 (d, J = 8.8 Hz, 2H), 7.27 (t, J = 7.4 Hz, 2H), 3.86 (s, 3H); ¹³C-NMR (100 MHz, CDCl₃, ppm) δ 178.1, 142.5, 133.7, 127.7, 122.5, 121.2, 114.7, 33.5; MS (70 eV): m/z (%): 209.2 [M]⁺. HRMS m/z (ESI): Calcd. for C₁₄H₁₂NO [M+H]⁺ 210.0913, Found: 210.0910.

Reference:


6. Mechanistic Studies
6.1 Intermolecular Kinetic Isotopic Effect (KIE) Studies

\[ \text{[D}_2\text{-}1\text{a} \xrightarrow{\text{standard condition}} \text{[D}_1\text{-}3\text{aa}}] \\
\]

17% yield, \( k_H/k_D = 4.0 \)

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acridine standard substance