Supporting Information

Metal Free Biomimetic Deaminative Direct C-C Coupling of Unprotected Primary Amines with Active Methylene Compounds

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Experimental:

General: All reactions involving air- or moisture-sensitive reagents or intermediates were carried out in oven-dried glassware under an argon atmosphere. Dichloromethane (CH₂Cl₂) was freshly distilled from phosphorus (V) oxide (P₂O₅). Commercial grade xylene, benzene and toluene were distilled over CaH₂ before use. All other solvents and reagents were purified according to standard procedures or were used as received from Aldrich, Acros, Merck and Spectrochem. ¹H, ¹³C NMR spectroscopy: Varian Mercury plus 400 MHz, Bruker 600 MHz (at 298 K), Bruker 400 MHz (at 298 K). Chemical shifts, δ (in ppm), are reported relative to TMS δ (¹H) 0.0 ppm, δ (¹³C) 0.0 ppm which was used as the inner reference. Otherwise the solvents residual proton resonance and carbon resonance (CDCl₃, δ (¹H) 7.26 ppm, δ (¹³C) 77.2 ppm; DMSO-d₆, (¹H) 2.50 ppm, δ (¹³C) 39.6 ppm) were used for calibration. Column chromatography: Merck or Spectrochem silica gel 60-120 under gravity. MS (ESI-HRMS): Mass spectra were recorded on an Agilent Accurate-Mass Q-TOF LC/MS 6520, and peaks are given in m/z (% of basis peak).
Scheme s1: Gram scale synthesis

The major byproduct of the reaction, 9-Fluorenone, which was isolated easily, can be recycled after its conversion to 9-Fluorenone imine.

Table s1: Optimization of the reaction conditions for the synthesis of dihydropyridines.

<table>
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<tr>
<th>entry</th>
<th>conditions</th>
<th>yield$^b$</th>
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<tr>
<td>1</td>
<td>toluene, rt, 12 h</td>
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<tr>
<td>2</td>
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<td>6</td>
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<td>neat, close tube, 60 h</td>
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<td>toluene, reflux, 48 h, NH$_4$OAc (1 eq)</td>
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<td>9</td>
<td>toluene, reflux, 48 h, NH$_4$OAc (2 eq)</td>
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<td>toluene, reflux, 60 h, NH$_4$OAc (2 eq)</td>
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<td></td>
<td>Solvent, Reaction Conditions, Yield (%)</td>
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<td>12</td>
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<td>26</td>
<td>THF, reflux, 48 h, NH$_4$OAc (2 eq)</td>
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*a* 1eq (0.56 mmol) benzyl amine, 1eq 9-fluorenone imine (0.56 mmol), and 2 eq ethylacetoacetate (1.12 mmol) were reacted in 2 mL solvent. *b* Isolated yield.

Kinetic experiments:
In a NMR tube, benzylamine (30 mg, 0.28 mmol) was added to a solution of 9-fluorenone imine 2 (50 mg, 0.28 mmol) and triphenylmethane (13.8 mg, 0.056 mmol) in benzene-d$_6$ (0.75 mL) and the solution was kept 12 h in room temperature. The yield of the imine 11 was calculated to be 80-90% form the $^1$H NMR experiment. Then the mixture was heated and the time dependent concentrations of 11 was calculated using $^1$H-NMR experiments.
Figure s1: Identification of 12.

General procedure for the synthesis of olefin (GP I): Amine (0.56 mmol) was added to a solution of 9-fluorenone imine (0.56 mmol) in toluene (2 mL) and the mixture was stirred at room temperature for 1 h. Active methylene compound (0.56 mmol) was then added to the mixture and the reaction mixture was refluxed for 48 h under argon atmosphere (placing argon balloon). After disappearance of starting materials (indicated by TLC) solvent was evaporated under reduced pressure. The crude mixture was subjected to column chromatography (silica) to afford analytically pure products.
Diethyl 2-benzylidemalonate (3a): According to GP I, benzylamine (60 mg, 0.56 mmol), 9-fluorenone imine 2 (0.10 g, 0.56 mmol) and diethylmalonate (85 μL, 0.56 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:20) of crude product gave 3a as a colorless oil (97 mg, 70%).

$^1$H NMR (600 MHz, CDCl$_3$) δ = 7.73 (s, 1H), 7.46 - 7.33 (m, 2H), 7.39 - 7.34 (m, 3H), 4.35 - 4.27 (m, 4H), 1.32 (t, $J = 7.2$ Hz, 3H), 1.28 (t, $J = 7.2$ Hz, 3H) ppm.

$^{13}$C NMR (151 MHz, CDCl$_3$) δ = 166.9, 164.3, 142.3, 133.1, 130.7, 129.6, 129.0, 126.5, 61.9, 61.8, 14.3, 14.1 ppm.

Diethyl 2-(4-methylbenzylidene)malonate (3b): According to GP I, 4-methylbenzylamine (68 mg, 0.56 mmol), 9-fluorenone imine 2 (0.10 g, 0.56 mmol) and diethylmalonate (85 μL, 0.56 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:20) of crude product gave 3b as a colorless oil (99 mg, 67%).

$^1$H NMR (400 MHz, CDCl$_3$) δ = 7.70 (s, 1H), 7.35 - 7.32 (d, $J = 8.0$ Hz, 2H), 7.18 (d, $J = 8.0$ Hz, 2H), 4.37 - 4.27 (m, 4H), 2.36 (s, 3H), 1.34 - 1.29 (m, 6H) ppm. $^{13}$C NMR (151 MHz, CDCl$_3$) δ = 167.2, 164.5, 142.4, 141.4, 130.3, 129.8, 129.8, 125.4, 61.9, 61.6, 21.7, 14.4, 14.1 ppm.

Diethyl 2-(4-methoxybenzylidene)malonate (3c): According to GP I, 4-methoxybenzylamine (77 mg, 0.56 mmol), 9-fluorenone imine 2 (0.10 g, 0.56 mmol) and diethylmalonate (85 μL, 0.56 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:20) of crude product gave 3c as a colorless oil (0.10 g, 64%).

$^1$H NMR (600 MHz, CDCl$_3$) δ = 7.68 (s, 1H), 7.43 - 7.39 (m, 2H), 6.89 - 6.82 (d, $J = 8.8$ Hz, 2H), 4.36 (q, $J = 7.1$ Hz, 2H), 4.30 (q, $J = 7.1$ Hz, 2H), 3.83 (s, 3H), 1.34 - 1.31 (m, 6H) ppm. $^{13}$C NMR (151 MHz, CDCl$_3$) δ = 167.4, 164.6, 161.7, 141.9, 131.7, 125.5, 123.7, 114.4, 61.8, 61.6, 55.5, 14.3, 14.1 ppm.
Diethyl 2-(4-chlorobenzylidene)malonate (3d): According to GP I, 4-chlorobenzylamine (79 mg, 0.56 mmol), 9-fluorenone imine 2 (0.10 g, 0.56 mmol) and diethylmalonate (85 μL, 0.56 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:20) of crude product gave 3d as a colorless oil (0.11 g, 69%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.67 (s, 1H), 7.40 - 7.34 (m, 4H), 4.36 - 4.28 (m, 4H), 1.35 - 1.28 (m, 6H) ppm. $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ = 166.6, 164.1, 140.9, 136.8, 131.6, 130.8, 129.3, 127.1, 62.1, 62.0, 14.3, 14.1 ppm.

Diethyl 2-(4-(trifluoromethoxy)benzylidene)malonate (3e): According to GP I, 4-trifluoromethoxybenzylamine (0.11 g, 0.56 mmol), 9-fluorenone imine 2 (0.10 g, 0.56 mmol) and diethylmalonate (85 μL, 0.56 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:20) of crude product gave 3e as a colorless oil (0.13 g, 68%). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ = 7.70 (s, 1H), 7.49 (d, $J$ = 8.4 Hz, 2H), 7.22 (d, $J$ = 8.4 Hz, 2H), 4.36 - 4.29 (m, 4H), 1.34 (t, $J$ = 7.1 Hz, 3H), 1.29 (t, $J$ = 7.1 Hz, 3H) ppm. $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ = 166.5, 164.1, 150.7 (4 peaks, CF$_3$), 140.5, 131.7, 131.2, 127.4, 121.1, 62.1, 62.1, 14.3, 14.1 ppm. HRMS: Exact mass calculated for C$_{15}$H$_{15}$F$_3$O$_5$ ([M+H]$^+$): 333.0944, Found: 333.0961.

Diethyl 2-(4-fluorobenzylidene)malonate (3f): According to GP I, 4-Fluorobenzylamine (70 mg, 0.56 mmol), 9-fluorenone imine 2 (0.10 g, 0.56 mmol) and diethylmalonate (85 μL, 0.03 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:20) of crude product gave 3f as a colorless oil (0.10 g, 68%). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ = 7.68 (s, 1H), 7.47 - 7.44 (m, 2H), 7.06 (t, $J$ = 8.4 Hz, 2H), 4.35 - 4.28 (m, 4H), 1.34 - 1.28 (m, 6H) ppm. $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ = 166.8, 164.9 (a), 164.2, 163.2 (a), 141.0, 131.8, 131.6, 129.6, 129.3, 129.0, 126.3, 126.3, 116.3, 116.2, 62.0, 61.9, 14.3, 14.1 ppm.
Diethyl 2-(2-fluorobenzylidene)malonate (3g): According to GP I, 2-fluorobenzylamine (70 mg, 0.56 mmol), 9-fluorenone imine 2 (0.10 g, 0.56 mmol) and diethylmalonate (85 μL, 0.56 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:20) of crude product gave 3g as a colorless oil (89 mg, 60%). $^1$H NMR (600 MHz, CDCl$_3$) δ = 7.89 (s, 1H), 7.43 (t, $J$ = 7.6 Hz, 1H), 7.39 - 7.34 (m, 1H), 7.13 - 7.06 (m, 2H), 4.33 - 4.26 (m, 4H), 1.32 (t, $J$ = 7.1 Hz, 3H), 1.24 (t, $J$ = 7.2 Hz, 3H) ppm. $^{13}$C NMR (151 MHz, CDCl$_3$) δ = 166.1, 163.8, 162.1 (a), 159.6 (a), 134.8, 134.6, 132.4, 132.3, 129.4, 129.4, 128.2, 128.2, 124.3, 124.3, 121.4, 121.2, 116.0, 115.8, 61.8, 61.7, 14.1, 13.9 ppm.

Diethyl 2-(2-chlorobenzylidene)malonate (3h): According to GP I, 2-chlorobenzylamine (79 mg, 0.56 mmol), 9-fluorenone imine 2 (0.10 g, 0.56 mmol) and diethylmalonate (85 μL, 0.56 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:20) of crude product gave 3h as a colorless oil (0.10 g, 65%). $^1$H NMR (600 MHz, CDCl$_3$) δ = 8.03 (s, 1H), 7.44 - 7.42 (m, 2H), 7.33 - 7.30 (m, 1H), 7.23 (t, $J$ = 7.5 Hz, 1H), 4.32 (q, $J$ = 7.2 Hz, 2H), 4.23 (q, $J$ = 7.2 Hz, 2H), 1.34 (t, $J$ = 7.2 Hz, 3H), 1.18 (t, $J$ = 7.2 Hz, 3H) ppm. $^{13}$C NMR (151 MHz, CDCl$_3$) δ = 166.1, 163.9, 139.5, 134.9, 132.2, 131.4, 130.1, 129.5, 129.0, 127.0, 62.1, 61.9, 14.3, 14.0 ppm.

Diethyl 2-(2-methoxybenzylidene)malonate (3i): According to GP I, 2-methoxybenzylamine (77 mg, 0.56 mmol), 9-fluorenone imine 2 (0.10 g, 0.56 mmol) and diethylmalonate (85 μL, 0.56 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:20) of crude product gave 3i as a colorless oil (0.11 g, 70%). $^1$H NMR (600 MHz, CDCl$_3$) δ = 8.07 (s, 1H), 7.38 - 7.33 (m, 2H), 6.90 - 6.87 (m, 2H), 4.30 - 4.24 (m, 4H), 3.83 (s, 3H), 1.31 (t, $J$ = 7.2 Hz, 3H), 1.22 (t, $J$ = 7.2 Hz, 3H) ppm. $^{13}$C NMR (151 MHz, CDCl$_3$) δ = 166.9, 164.5, 158.1, 138.4, 132.1, 129.3, 126.3, 122.4, 120.6, 110.9, 61.6, 61.5, 55.6, 14.3, 14.0 ppm.
Diethyl 2-(3,4-dichlorobenzylidene)malonate (3j)[1d]: According to GP I, 3,4-dichlorobenzylamine (98 mg, 0.56 mmol), 9-fluorenone imine 2 (0.10 g, 0.56 mmol) and diethylmalonate (85 μL, 0.56 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:20) of crude product gave 3j as a colorless oil (0.12 g, 65%). $^1$H NMR (600 MHz, CDCl$_3$) δ = 7.61 (s, 1H), 7.55 (d, $J = 2.0$ Hz, 1H), 7.45 (d, $J = 8.4$ Hz, 1H), 7.28 (dd, $J = 8.4, 2.1$ Hz, 1H), 4.38 - 4.29 (m, 4H), 1.33 (q, $J = 7.2$ Hz, 6H) ppm. $^{13}$C NMR (151 MHz, CDCl$_3$) δ = 166.2, 163.8, 139.4, 134.9, 133.4, 133.1, 131.2, 131.0, 128.6, 128.3, 62.2, 62.2, 14.3, 14.2 ppm.

Diethyl 2-(3-methoxybenzylidene)malonate (3k)[1f]: According to GP I, 3-methoxybenzylamine (77 mg, 0.56 mmol), 9-fluorenone imine 2 (0.10 g, 0.56 mmol) and diethylmalonate (85 μL, 0.56 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:20) of crude product gave 3k as a colorless oil (0.1 g, 64%). $^1$H NMR (600 MHz, CDCl$_3$) δ = 7.73 (s, 1H), 7.32 - 7.29 (m, 1H), 7.08 - 7.06 (m, 1H), 7.02 - 7.01 (m, 1H), 6.97-6.96 (m, 1H), 4.38 - 4.31 (m, 4H), 3.82 (s, 3H), 1.36 (t, $J = 7.2$ Hz, 3H), 1.32 (t, $J = 7.2$ Hz, 3H) ppm. $^{13}$C NMR (151 MHz, CDCl$_3$) δ = 166.9, 164.3, 159.9, 142.2, 134.4, 130.0, 126.8, 122.2, 116.7, 114.5, 61.9, 61.9, 55.5, 14.4, 14.1 ppm.

Dimethyl 2-benzylimidemalonate (3l)[1e]: According to GP I, benzylamine (60 mg, 0.36 mmol), 9-fluorenone imine 2 (0.10 g, 0.56 mmol) and dimethylmalonate (64 μL, 0.56 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:15) of crude product gave 3l as a colorless oil (77 mg, 62%). $^1$H NMR (400 MHz, CDCl$_3$) δ = 7.78 (s, 1H), 7.43 - 7.37 (m, 5H), 3.84 (s, 6H) ppm. $^{13}$C NMR (151 MHz, CDCl$_3$) δ = 167.4, 164.7, 143.2, 132.9, 130.9, 129.6, 129.1, 125.6, 53.0, 52.9 ppm.
Dimethyl 2-(2-methoxybenzylidene)malonate (3m)<sup>(Ig)</sup>: According to GP I, 2-methoxybenzylamine (77, 0.56 mmol), 9-fluorenone imine 2 (0.10 g, 0.56 mmol) and dimethylmalonate (64 μL, 0.56 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:15) of crude product gave 3m as a colorless oil (88 mg, 63%).<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 8.11 (s, 1H), 7.38 - 7.32 (m, 2H), 6.93 - 6.89 (m, 2H), 3.84 (s, 3H), 3.83 (s, 3H), 3.77 (s, 3H) ppm. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ = 167.4, 164.9, 158.2, 139.3, 132.4, 129.2, 125.4, 122.3, 120.7, 111.1, 55.7, 52.7, 52.6 ppm.

Dibenzyl 2-benzylidenemalonate (3n)<sup>(Ie)</sup>: According to GP I, benzylamine (60 mg, 0.56 mmol), 9-fluorenone imine 2 (0.10 g, 0.56 mmol) and dibenzylmalonate (0.14 mL, 0.56 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:10) of crude product gave 3n as a colorless oil (0.13 g, 64%).<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 7.82 (s, 1H), 7.39 - 7.28 (m, 15H), 5.313 (s, 2H), 5.309 (s, 2H) ppm. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ = 166.5, 164.1, 143.4, 135.7, 135.0, 132.8, 130.8, 129.7, 129.0, 128.97, 128.78, 128.73, 128.65, 128.48, 128.22, 125.8, 67.8, 67.4 ppm.

Dibenzyl 2-(2-methoxybenzylidene)malonate (3o): According to GP I, 2-methoxybenzylamine (77 mg, 0.56 mmol), 9-fluorenone imine 2 (0.10 g, 0.56 mmol) and dibenzylmalonate (0.14 mL, 0.56 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:10) of crude product gave 3o as a colorless oil (0.16 g, 72%).<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 8.17 (s, 1H), 7.37 - 7.23 (m, 12H), 6.89 - 6.75 (m, 2H), 5.29 (s, 2H), 5.24 (s, 2H), 3.82 (s, 3H) ppm. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ = 166.6, 164.3, 158.2, 139.7, 135.8, 135.2, 132.3, 129.4, 128.8, 128.7, 128.6, 128.5, 128.3, 128.2, 125.6, 122.2, 120.7, 111.0, 67.5, 67.2, 55.6 ppm. HRMS: Exact mass calculated for C<sub>25</sub>H<sub>22</sub>O<sub>2</sub> ([M+H]<sup>+</sup>): 403.1540, Found: 403.1555.

Diethyl 2-((furan-2-yl)methylene)malonate (3p)<sup>(Ia)</sup>: According to GP I, furfurylamine (54 mg, 0.56 mmol), 9-fluorenone imine 2 (0.10 g, 0.56 mmol) and diethylmalonate (85 μL, 0.56 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:20) of crude product gave 3p as a colorless oil (80 mg,
Diethyl 2-butyldenemalonate (3q): According to GP I, butylamine (40 mg, 0.56 mmol), 9-fluorenone imine 2 (0.10 g, 0.56 mmol) and diethylmalonate (85 μL, 0.56 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:20) of crude product gave 3q as a colourless oil (61 mg, 51%). \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta = 6.99\) (t, \(J = 7.8\) Hz, 1H), 4.31 - 4.28 (m, 2H), 2.29 - 2.25 (m, 2H), 1.55 - 1.48 (m, 2H), 1.33 (t, \(J = 7.2\) Hz, 3H), 1.27 (t, \(J = 7.2\) Hz, 3H) ppm. \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta = 165.7, 164.0, 149.3, 128.8, 61.3, 61.2, 31.7, 21.7, 14.2, 14.1, 13.8\) ppm.

\((E/Z)\)-ethyl 2-benzylidene-3-oxobutanoate (3r): According to GP I, benzylamine (60 mg, 0.56 mmol), 9-fluorenone imine 2 (0.10 g, 0.56 mmol) and Ethyl acetoacetate (71 μL, 0.56 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:20) of crude product gave a mixture of E/Z (1.3:1) isomer of 3r as a colorless oil (76 mg, 62%). \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta = 7.67\) (s, 1H), 7.57 (s, 1H), 7.46 - 7.44 (m, 1H), 7.41 - 7.37 (m, 8H), 4.35 - 4.28 (m, 4H), 2.43 (s, 2H), 2.35 (s, 3H), 1.33 (t, \(J = 7.2\) Hz, 3H), 1.27 (t, \(J = 7.2\) Hz, 3H) ppm. \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta = 203.8, 194.9, 168.0, 164.6, 141.5, 140.7, 134.8, 134.2, 133.1, 133.06, 130.9, 130.6, 129.9, 129.7, 129.1, 129.1, 62.0, 61.8, 31.5, 26.8, 14.4, 14.1 ppm.

\((E/Z)\)-ethyl 2-(2-chlorobenzylidene)-3-oxobutanoate (3s): According to GP I, 2-Chlorobenzylamine (79 mg, 0.56 mmol), 9-fluorenone imine 2 (0.10 g, 0.56 mmol) and Ethyl acetoacetate (71 μL, 0.56 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:20) of crude product gave a mixture of E/Z (1.5:1) isomer of 3s as a colorless oil (91 mg, 64%). \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta = 7.85\) (s, 1H), 7.78 (s, 1H), 7.36 - 7.32 (m, 4H), 7.25
- 7.20 (m, 3H), 7.17 - 7.11 (m, 2H), 4.25 - 4.19 (m, 2H), 4.16 - 4.11 (m, 2H), 2.36 (s, 2H), 2.14 (s, 3H), 1.24 (t, J = 7.2 Hz, 4H), 1.07 (t, J = 7.2 Hz, 2H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 202.0, 194.6, 166.8, 164.1, 138.3, 137.5, 136.8, 136.5, 134.7, 134.4, 132.1, 131.9, 131.4, 131.2, 130.2, 129.9, 129.9, 129.3, 127.1, 127.0, 61.8, 6.7, 31.3, 26.8, 14.2, 13.9 ppm.

Cinnamic acid (3t)$^{(3b)}$: According to GP I: Benzylamine (60 mg, 0.56 mmol), 9-fluorenone imine 2 (0.10 g, 0.56 mmol) and malonic acid (58 mg, 0.56 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:1) of crude product gave 3t as a white solid (58 mg, 70%). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ = 7.81 (d, J = 16.0 Hz, 1H), 7.58 - 7.56 (m, 2H), 7.42 - 7.41 (m, 3H), 6.47 (d, J = 16.0 Hz, 1H) ppm. $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ = 172.9, 147.3, 134.2, 131.0, 129.2, 128.6, 117.5 ppm.

(E)-3-(4-methoxyphenyl)acrylic acid (3u)$^{(3b)}$: According to GP I: 4-Methoxybenzylamine (77 mg, 0.56 mmol), 9-fluorenone imine 2 (0.10 g, 0.56 mmol) and malonic acid (58 mg, 0.56 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:1) of crude product gave 3u as a white solid (68 mg, 68%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.75 (d, J = 15.9 Hz, 1H), 7.51 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H), 6.32 (d, J = 15.9 Hz, 1H), 3.85 (s, 3H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 172.1, 162.0, 146.9, 130.3, 127.1, 114.8, 114.6, 55.6 ppm.

General procedure for the synthesis of dihydropyridine (GP II): Amine (0.56 mmol) was added to a solution of 9-fluorenone imine (0.56 mmol) in toluene (2 mL) and the mixture was stirred at room temperature for 1 h. Active methylene compound (1.12 mmol) and ammonium acetate (1.12 mmol) was then added to the mixture and the reaction mixture was refluxed for 48 h under argon atmosphere (placing argon balloon). After disappearance of starting materials (indicated by TLC) solvent was evaporated under reduced pressure. The crude mixture was subjected to column chromatography (silica) to afford analytically pure products.
Diethyl-1,4-dihydro-2,6-dimethyl-4-phenylpyridine-3,5-dicarboxylate (6a)\(^{2a}\): According to GP II, benzylamine (60 mg, 0.56 mmol), 9-fluorenone imine 2 (0.10 g, 0.56 mmol), ethyl acetoacetate (1.4 mL, 1.12 mmol) and ammonium acetate (86 mg, 1.12 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:4) of crude product gave 6a as a yellow gum (0.13 g, 68%). \(^1\)H NMR (600 MHz, CDCl\(_3\)) δ = 7.29 - 7.26 (m, \(J = 7.8\) Hz, 2H), 7.20 (t, \(J = 7.2\) Hz, 2H), 7.11 (t, \(J = 7.2\) Hz, 1H), 5.96 (s, 1H), 4.99 (s, 1H), 4.14 - 4.02 (m, 4H), 2.30 (s, 6H), 1.22 (t, \(J = 7.2\) Hz, 6H) ppm. \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) δ = 167.7, 147.8, 144.1, 128.0, 127.8, 126.1, 104.0, 59.7, 39.7, 19.5, 14.3 ppm.

Diethyl-1,4-dihydro-2,6-dimethyl-4-p-tolylpyridine-3,5-dicarboxylate (6b)\(^{2a}\): According to GP II, 4-methylbenzylamine (68 mg, 0.56 mmol), 9-fluorenone imine 2 (0.10 g, 0.56 mmol), ethyl acetoacetate (1.4 mL, 1.12 mmol) and ammonium acetate (86 mg, 1.12 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:4) of crude product gave 6b as a yellow gum (0.13 g, 69%). \(^1\)H NMR (600 MHz, CDCl\(_3\)) δ = 7.17 (d, \(J = 8.4\) Hz, 2H), 7.01 (d, \(J = 7.8\) Hz, 2H), 5.73 (s, 1H), 4.94 (s, 1H), 4.11 - 4.05 (m, 4H), 2.31 (s, 6H), 2.27 (s, 3H), 1.23 (t, \(J = 7.2\) Hz, 6H) ppm. \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) δ = 167.9, 145.1, 144.0, 135.7, 128.7, 128.0, 104.4, 59.9, 39.3, 21.3, 19.8, 14.5 ppm.

Diethyl-4-(4-chlorophenyl)-1,4-dihydro-2,6-dimethylypyridine-3,5-dicarboxylate (6c)\(^{2a}\): According to GP II, 4-chlorobenzylamine (79 mg, 0.56 mmol), 9-fluorenone imine 2 (0.10 g, 0.56 mmol), ethyl acetoacetate (1.4 mL, 1.12 mmol) and ammonium acetate (86 mg, 1.12 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:4) of crude product gave 6c as a yellow gum (0.13 g, 65%). \(^1\)H NMR (600 MHz, CDCl\(_3\)) δ = 7.22 - 7.20 (m, 2H), 7.17 - 7.15 (m, 2H), 5.66 (s, 1H), 4.95 (s, 1H), 4.123 - 4.04 (m, 4H), 2.32 (s, 6H), 1.21 (t, \(J = 7.2\) Hz, 6H) ppm. \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) δ = 167.6, 146.5, 144.2, 131.9, 129.6, 128.1, 104.1, 60.0, 39.5, 19.8, 14.5 ppm.
Diethyl-4-(4-fluorophenyl)-1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylate (6d)²c:

According to GP II, 4-fluorobenzylamine (0.70 g, 0.56 mmol), 9-fluorenone imine 2 (0.10 g, 0.56 mmol), ethyl acetoacetate (1.4 mL, 1.12 mmol) and ammonium acetate (86 mg, 1.12 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:4) of crude product gave 6d as a yellow gum (0.12 g, 64%). ¹H NMR (600 MHz, CDCl₃) δ = 7.24 - 7.22 (m, 2H), 6.90 - 6.86 (m, 2H), 5.67 (s, 1H), 4.95 (s, 1H), 4.14 - 4.03 (m, 4H), 2.32 (s, 6H), 1.21 (t, J = 7.2 Hz, 6H) ppm. ¹³C NMR (151 MHz, CDCl₃) δ = 167.7, 162.3 (a), 160.7 (a), 144.0, 143.9, 143.8, 129.7, 129.6, 114.8, 114.6, 104.4, 60.0, 39.2, 19.8, 14.5 ppm.


Diethyl-1,4-dihydro-2,6-dimethyl-4-(4-(trifluoromethoxy)phenyl)pyridine-3,5dicarboxylate (6e): According to GP II, 4-trifluoromethoxybenzylamine (107 mg, 0.56 mmol), 9-fluorenone imine 2 (0.10 g, 0.56 mmol), ethyl acetoacetate (1.4 mL, 1.12 mmol) and ammonium acetate (86 mg, 1.12 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:4) of crude product gave 6e as a yellow gum (0.16 g, 68%). ¹H NMR (600 MHz, CDCl₃) δ = 7.28 (d, J = 9.0 Hz, 2H), 7.03 (d, J = 8.4 Hz, 2H), 5.82 (s, 1H), 4.99 (s, 1H), 4.13 - 4.03 (m, 4H), 2.32 (s, 6H), 1.20 (t, J = 7.2 Hz, 6H) ppm. ¹³C NMR (151 MHz, CDCl₃) δ = 167.3, 151.6, 144.3, 128.4, 128.3, 124.89 (CF₃), 124.86 (CF₃), 124.82 (CF₃), 124.78 (CF₃), 103.6, 59.9, 19.7, 19.6, 14.3 ppm. HRMS: Exact mass calculated for C₂₀H₂₂F₃NO₅ ([M+H]⁺): 414.1523, Found: 414.1514.

Diethyl-1,4-dihydro-4-(4-methoxyphenyl)-2,6-dimethylpyridine-3,5-dicarboxylate (6f)²b:

According to GP II, 4-methoxybenzylamine (77 mg, 0.56 mmol), 9-fluorenone imine 2 (0.10 g, 0.56 mmol), ethyl acetoacetate (1.4 mL, 1.12 mmol) and ammonium acetate (86 mg, 1.12 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:4) of crude product gave 6f as a yellow gum (0.14 g, 65%). ¹H NMR (600 MHz, CDCl₃) δ = 7.19 (d, J = 8.8 Hz, 2H), 6.74 (d, J = 8.4 Hz, 2H), 5.97 (br. s, 1H), 4.93 (s, 1H), 4.13 - 4.04 (m, 4H), 3.74 (s, 3H), 2.29 (s, 6H), 1.22 (t, J = 7.2 Hz, 6H) ppm. ¹³C NMR (151 MHz, CDCl₃) δ = 167.9, 158.0, 143.9, 140.5, 129.1, 113.3, 104.5, 59.9, 55.3, 38.9, 19.7, 14.5 ppm.
Diethyl-1,4-dihydro-4-(2-methoxyphenyl)-2,6-dimethylpyridine-3,5-dicarboxylate (6g): According to GP II, 2-methoxybenzylamine (77 mg, 0.56 mmol), 9-fluorenone imine 2 (0.10 g, 0.56 mmol), ethyl acetoacetate (1.4 mL, 1.12 mmol) and ammonium acetate (86 mg, 1.12 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:4) of crude product gave 6g as a yellow gum (0.14 g, 67%). ¹H NMR (600 MHz, CDCl₃) δ = 7.21 - 7.19 (m, 1H), 7.11 - 7.07 (m, 1H), 6.82 - 6.77 (m, 2H), 5.74 (br. s, 1H), 5.27 (s, 1H), 4.04 (q, J = 7.2 Hz, 4H), 3.77 (s, 3H), 2.27 (s, 6H), 1.18 (t, J = 7.2 Hz, 6H) ppm. ¹³C NMR (151 MHz, CDCl₃) δ = 168.3, 157.3, 143.9, 135.5, 130.8, 127.5, 120.2, 110.8, 103.3, 59.7, 55.5, 35.5, 19.7, 14.4 ppm.

Diethyl-4-(2-fluorophenyl)-1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylate (6h): According to GP II, 2-fluorobenzylamine (70 mg, 0.56 mmol), 9-fluorenone imine 2 (0.10 g, 0.56 mmol), ethyl acetoacetate (1.4 mL, 1.12 mmol) and ammonium acetate (86 mg, 1.12 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:4) of crude product gave 6h as a yellow gum (0.12 g, 62%). ¹H NMR (600 MHz, CDCl₃) δ = 7.31 - 7.28 (m, 1H), 7.10 - 7.07 (m, 1H), 7.00 - 6.97 (m, 1H), 6.91 - 6.88 (m, 1H), 5.77 (s, 1H), 5.23 (s, 1H), 4.09 - 4.00 (m, 4H), 2.30 (s, 6H), 1.19 (t, J = 7.2 Hz, 6H) ppm. ¹³C NMR (151 MHz, CDCl₃) δ = 167.8, 160.8 (a), 159.1 (a), 144.5, 135.2, 135.1, 131.3, 131.3, 127.90, 127.9, 123.8, 123.8, 115.2, 115.0, 103.2, 59.9, 34.3, 19.7, 14.2 ppm.

Diethyl-4-(2-chlorophenyl)-1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylate (6i): According to GP II, 2-chlorobenzylamine (79 mg, 0.56 mmol), 9-fluorenone imine 2 (0.10 g, 0.56 mmol), ethyl acetoacetate (1.4 mL, 1.12 mmol) and ammonium acetate (86 mg, 1.12 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:4) of crude product gave 6i as a yellow gum (0.13 g, 65%). ¹H NMR (600 MHz, CDCl₃) δ = 7.36 (dd, J = 7.8, 1.8 Hz, 1H), 7.21 (dd, J = 7.8, 1.4 Hz, 1H), 7.10 (td, J = 7.6, 1.4 Hz, 1H), 7.01 (td, J = 7.6, 1.7 Hz, 1H), 6.25 (s, 1H), 5.38 (s, 1H), 4.08-4.04 (m, 4H), 2.24 (s, 6H), 1.18
(t, J = 7.2 Hz, 6H) ppm. $^{13}$C NMR (151 MHz, CDCl$_3$) δ = 168.0, 145.8, 144.5, 132.5, 131.7, 129.4, 127.4, 126.8, 103.7, 59.9, 37.6, 19.4, 14.4 ppm.

**Diethyl-1,4-dihydro-4-(3-methoxyphenyl)-2,6-dimethylpyridine-3,5-dicarboxylate (6j)$^{(2h)}$:**

According to GP II, 3-methoxybenzylamine (77 mg, 0.56 mmol), 9-fluorenone imine 2 (0.10 g, 0.56 mmol), ethyl acetoacetate (1.4 mL, 1.12 mmol) and ammonium acetate (86 mg, 1.12 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:4) of crude product gave 6j as a yellow gum (0.14 g, 71%). $^1$H NMR (600 MHz, CDCl$_3$) δ = 7.11 (t, J = 8.0 Hz, 1H), 6.88 (d, J = 7.6 Hz, 1H), 6.84 - 6.83 (m, 1H), 6.68 - 6.65 (m, 1H), 6.03 (s, 1H), 4.98 (s, 1H), 4.12 - 4.05 (m, 4H), 3.75 (s, 3H), 2.29 (s, 6H), 1.22 (t, J = 7.2 Hz, 6H) ppm. $^{13}$C NMR (151 MHz, CDCl$_3$) δ = 167.8, 159.4, 149.5, 144.2, 128.9, 120.7, 114.4, 111.0, 104.2, 60.0, 55.3, 39.7, 19.8, 14.5 ppm.

**Diethyl-1,4-dihydro-2,6-dimethyl-4-(3-nitrophenyl)pyridine-3,5-dicarboxylate (6k)$^{(2d)}$:**

According to GP II, 3-Nitrobenzylamine (85 mg, 0.56 mmol), 9-fluorenone imine 2 (0.10 g, 0.56 mmol), ethyl acetoacetate (1.4 mL, 1.12 mmol) and ammonium acetate (86 mg, 1.12 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:4) of crude product gave 6k as a yellow gum (0.13 g, 63%). $^1$H NMR (400 MHz, CDCl$_3$) δ = 8.06 (s, 1H), 7.93 (d, J = 8 Hz, 1H), 7.57 (d, J = 7.6 Hz, 1H), 7.30 (t, J = 8 Hz, 1H), 5.69 (s, 1H), 5.02 (s, 1H), 4.02-3.97 (m, 4H), 2.29 (s, 6H), 1.15 (t, J = 7.2 Hz, 6H) ppm. $^{13}$C NMR (151 MHz, CDCl$_3$) δ = 167.3, 150.1, 148.3, 144.9, 134.7, 128.8, 123.3, 121.5, 103.6, 60.2, 40.2, 19.9, 14.4 ppm.

**Diethyl 1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylate (6l)$^{(2e)}$:** According to GP II, methylamine hydrochloride (38 mg, 0.56 mmol), 9-fluorenone imine 2 (0.10 g, 0.56 mmol), ethyl acetoacetate (1.4 mL, 1.12 mmol) and ammonium acetate (86 mg, 1.12 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:2) of crude product gave 6l as a yellow solid (22 mg, 15%). $^1$H NMR (600 MHz, CDCl$_3$) δ = 5.40 (s, 1H), 4.14 (q, J = 7.2 Hz, 4H), 3.24 (s,
2H), 2.17 (s, 6H), 1.26 (t, J = 7.2 Hz, 6H) ppm. $^{13}$C NMR (151 MHz, CDCl$_3$) δ = 168.3, 145.2, 99.6, 59.9, 25.0, 19.3, 14.7 ppm.

**Diethyl 4-(furan-2-yl)-1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylate (6m)**

According to GP II, furfurylamine (54 mg, 0.56 mmol), 9-fluorenone imine 2 (0.10 g, 0.56 mmol), ethyl acetoacetate (1.4 mL, 1.12 mmol) and ammonium acetate (86 mg, 1.12 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:4) of crude product gave 6m as a yellow gum (0.12 g, 67%). $^1$H NMR (600 MHz, CDCl$_3$) δ = 7.20 (s, 1H), 6.20 - 6.19 (m, 1H), 6.01 (s, 1H), 5.93 (d, J = 3.0 Hz, 1H), 5.19 (s, 1H), 4.20 - 4.09 (m, 4H), 2.31 (s, 6H), 1.25 (t, J = 7.2 Hz, 6H) ppm. $^{13}$C NMR (151 MHz, CDCl$_3$) δ = 167.7, 158.8, 145.4, 141.0, 110.2, 104.6, 100.8, 60.0, 33.5, 19.7, 14.5 ppm.

**Diethyl-4-(3,4-dichlorophenyl)-1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylate (6n)**

According to GP II, 3,4-dichlorobenzylamine (98 mg, 0.56 mmol), 9-fluorenone imine 2 (0.10 g, 0.56 mmol), ethyl acetoacetate (1.4 mL, 1.12 mmol) and ammonium acetate (86 mg, 1.12 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:4) of crude product gave 6n as a yellow gum (0.14 g, 63%). $^1$H NMR (600 MHz, CDCl$_3$) δ = 7.32 (d, J = 1.8 Hz, 1H), 7.25 (d, J = 3.6 Hz, 1H), 7.11 (dd, J = 8.4, 2.4 Hz, 1H), 5.70 (s, 1H), 4.92 (s, 1H), 4.14 - 4.03 (m, 4H), 2.32 (s, 6H), 1.23 (t, J = 7.2 Hz, 6H) ppm. $^{13}$C NMR (151 MHz, CDCl$_3$) δ = 167.4, 148.2, 144.5, 131.8, 130.3, 130.0, 129.9, 127.8, 103.6, 60.2, 39.5, 19.9, 14.5 ppm.

**Dimethyl 1,4-dihydro-2,6-dimethyl-4-phenylpyridine-3,5-dicarboxylate (6o)**

According to GP II, benzylamine (60 mg, 0.56 mmol), 9-fluorenone imine 2 (0.10 g, 0.56 mmol), methyl acetoacetate (1.2 mL, 1.12 mmol) and ammonium acetate (86 mg, 1.12 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:4) of crude product gave 6o as a yellow gum (0.12 g, 70%). $^1$H NMR (400 MHz, CDCl$_3$) δ = 7.20 - 7.17 (m, 2H), 7.16 - 7.12 (m, 2H), 7.08-7.04 (m, 1H), 5.60 (s, 1H), 4.93 (s, 1H), 3.57 (s, 6H),
2.27 (s, 6H) ppm. $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ = 168.2, 147.6, 144.4, 128.2, 127.8, 126.4, 104.1, 51.2, 39.4, 19.9 ppm.

**Dibenzyl 1,4-dihydro-2,6-dimethyl-4-phenylpyridine-3,5-dicarboxylate (6p)**: According to GP II, benzylamine (60 mg, 0.56 mmol), 9-fluorenone imine 2 (0.10 g, 0.56 mmol), benzyl acetoacetate (1.9 mL, 1.12 mmol) and ammonium acetate (86 mg, 1.12 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:4) of crude product gave 6p as a yellow gum (0.18 g, 70%). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ = 7.29 - 7.28 (m, 5H), 7.20 - 7.19 (m, 6H), 7.17 - 7.11 (m, 4H), 5.77 (s, 1H), 5.11 - 5.04 (m, 5H), 2.33 (s, 6H) ppm. $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ = 167.5, 147.6, 144.6, 144.6, 136.7, 128.5, 128.0, 127.9, 126.4, 104.1, 65.8, 39.7, 19.9 ppm.

**Dibenzyl 1,4-dihydro-4-(3-methoxyphenyl)-2,6-dimethylpyridine-3,5-dicarboxylate (6q)**: According to GP I: According to GP II, 3-methoxybenzylamine (77 mg, 0.56 mmol), 9-fluorenone imine 2 (0.10 g, 0.56 mmol), benzyl acetoacetate (1.9 mL, 1.12 mmol) and ammonium acetate (86 mg, 1.12 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:4) of crude product gave 6q as a yellow gum (0.18 g, 65%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.28 - 7.20 (m, 10H), 7.07 (t, $J$ = 8 Hz, 1H), 6.81 (d, $J$ = 7.6 Hz, 1H), 6.76 - 6.75 (m, 1H), 6.68 - 6.65 (m, 1H), 5.73 (s, 1H), 5.12 - 5.04 (m, 5H), 3.57 (s, 3H), 2.32 (s, 6H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 167.5, 159.5, 149.2, 144.8, 136.7, 129.0, 128.5, 128.0, 127.9, 120.7, 114.1, 111.7, 103.9, 65.8, 55.1, 39.7, 19.8 ppm. HRMS: Exact mass calculated for C$_{30}$H$_{29}$NO$_5$ ([M+H]$^+$): 484.2118, Found: 484.2130.
10-(4-Methylbenzyl)-9-(p-tolyl)decahydroacridine-1,8(2H,5H)-dione (6r)<sup>(2e)</sup>: According to GP I, 4-methylbenzylamine (0.135 g, 1.12 mmol), 9-fluorenone imine 2 (0.10 g, 0.56 mmol) and 1,2-cyclohexanedione (0.13 g, 1.12 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:1) of crude product gave 6r as a white solid (0.14 g, 62%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 7.20 - 7.18 (m, 4H), 7.04 (d, <i>J</i> = 7.8 Hz, 2H), 7.00 (d, <i>J</i> = 7.8 Hz, 2H), 5.35 (s, 1H), 4.89 (s, 2H), 2.68 - 2.64 (m, 2H), 2.50 - 2.45 (m, 2H), 2.37 (s, 3H), 2.37 - 2.34 (m, 2H), 2.31 - 2.28 (m, 2H), 2.26 (s, 3H), 1.98 - 1.94 (m, 2H), 1.91 - 1.87 (m, 2H) ppm. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ = 196.12, 152.43, 143.50, 137.84, 135.49, 133.99, 130.09, 128.92, 127.88, 125.41, 116.49, 48.83, 36.68, 31.48, 26.87, 21.64, 21.27, 21.25 ppm.

10-Benzyl-decahydro-9-phenylacridine-1,8(5H,8aH)-dione(6s)<sup>(2e)</sup>: According to GP I, benzylamine (0.12 g, 1.12 mmol), 9-fluorenone imine 2 (0.10 g, 0.56 mmol) and cyclohexanedione (0.13 g, 1.12 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:1) of crude product gave 6s as a white solid (0.13 g, 60%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 7.40 (t, <i>J</i> = 7.4 Hz, 2H), 7.35 (t, <i>J</i> = 7.3 Hz, 1H), 7.31 - 7.30 (m, 2H), 7.22 (t, <i>J</i> = 7.8 Hz, 2H), 7.16 (d, <i>J</i> = 7.2 Hz, 2H), 7.14 - 7.11 (m, 1H), 5.44 (s, 1H), 4.96 (s, 2H), 2.72 - 2.67 (m, 2H), 2.53-2.48 (m, 2H), 2.44 - 2.40 (m, 2H), 2.35 - 2.30 (m, 2H), 2.03 - 1.98 (m, 2H), 1.96 - 1.89 (m, 2H) ppm. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ = 196.1, 152.5, 146.3, 137.1, 129.5, 128.3, 128.1, 128.0, 126.2, 125.5, 116.5, 49.1, 36.7, 31.8, 26.9, 21.7 ppm.

Decahydro-9-(4-methoxyphenyl)-3,3,6,6-tetramethylacridine-1,8(5H,8aH)-dione(6t)<sup>(2e)</sup>: According to GP I, 4-methoxybenzylamine (77 mg, 0.56 mmol), 9-fluorenone imine 2 (0.10 g, 0.56 mmol) and 5,5-dimethyl-1,3-cyclohexanedione (0.16 g, 1.12 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:1) of crude product gave 6t as a white solid (0.115 g, 54%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 8.85 (s, 1H), 7.23 (d, <i>J</i> = 8.4 Hz, 2H), 6.69 (d, <i>J</i> = 8.4 Hz, 2H), 5.02 (s, 1H), 3.63 (s, 3H), 2.24 - 2.09 (m, 8H), 1.03 (s, 6H), 0.92 (s, 6H) ppm. <sup>13</sup>C NMR
(151 MHz, CDCl$_3$) $\delta$ = 196.5, 157.7, 150.2, 139.4, 129.0, 113.3, 113.1, 55.1, 51.0, 40.4, 32.9, 32.7, 29.7, 27.1 ppm.

**Decahydro-3,3,6,6-tetramethyl-9-phenylacridine-1,8(5H,8aH)-dione (6u)**: According to GP I, benzylamine (60 mg, 0.56 mmol), 9-fluorenone imine 2 (0.10 g, 0.56 mmol) and 5,5-dimethyl-1,3-cyclohexanedione (0.16 g, 1.12 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:1) of crude product gave 6u as a white solid (97 mg, 50%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 8.66 (s, 1H), 7.34 (d, $J$ = 6.8 Hz, 2H), 7.18 (t, $J$ = 7.6 Hz, 1H), 7.06 (t, $J$ = 7.3 Hz, 1H), 5.10 (s, 1H), 2.28 - 2.11 (m, 8H), 1.05 (s, 6H), 0.94 (s, 6H) ppm. $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ = 195.5, 147.5, 146.5, 128.3, 128.2, 126.2, 114.1, 50.9, 41.5, 33.8, 32.9, 29.7, 27.4 ppm.

**Diethyl-4-heptadecyl-1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylate (7a)**: According to GP II, octadecylamine (0.151 g, 0.56 mmol), 9-fluorenone imine 2 (0.10 g, 0.56 mmol), ethyl acetoacetate (1.4 mL, 1.12 mmol) and ammonium acetate (86 mg, 1.12 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:5) of crude product gave 7a as a yellow gum (0.16 g, 58%). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ = 5.54 (s, 1H), 4.23 - 4.11 (m, 4H), 3.91 (t, $J$ = 6 Hz, 1H), 2.27 (s, 6H), 1.30 - 1.21 (m, 38H), 0.87 (t, $J$ = 7.2 Hz, 3H) ppm. $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ = 168.4, 144.8, 103.6, 59.8, 37.1, 33.1, 32.1, 30.2, 30.0, 29.97, 29.93, 29.88, 29.58, 25.1, 22.9, 19.7, 14.6, 14.4 ppm (Less no carbon observed due to overlapping in aliphatic region). HRMS: Exact mass calculated for C$_{30}$H$_{53}$NO$_4$ ([M+H]$^+$): 492.4047, Found: 492.4031.

**Diethyl-1,4-dihydro-2,6-dimethyl-4-tridecylpyridine-3,5-dicarboxylate (7b)**: According to GP II, tetradecylamine (0.119 g, 0.56 mmol), 9-fluorenone imine 2 (0.10 g, 0.56 mmol), ethyl acetoacetate (1.4 mL, 1.12 mmol) and ammonium acetate (86 mg, 1.12 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:5) of crude product gave 7b as a yellow gum (0.15 g, 60%). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ = 5.51 (s, 1H), 4.24 - 4.12 (m, 4H), 3.91 (t, $J$ = 6 Hz, 1H), 2.28 (s, 6H), 1.30 - 1.18 (m, 30H), 0.87 (t, $J$ =
7.2 Hz, 3H) ppm. $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ = 168.4, 144.7, 103.6, 59.8, 37.1, 33.1, 32.1, 30.2, 30.01, 29.96, 29.93, 29.92, 29.88, 29.58, 25.1, 22.9, 19.7, 14.6, 14.4 ppm (Less no carbon observed due to overlapping in aliphatic region). HRMS: Exact mass calculated for C$_{26}$H$_{43}$NO$_4$ ([M+H]$^+$): 436.3421, Found: 436.3434.

**Diethyl-1,4-dihydro-2,6-dimethyl-4-nonylpyridine-3,5-dicarboxylate (7c)**: According to GP II, decylamine (88 mg, 0.56 mmol), 9-fluorenone imine 2 (0.10 g, 0.56 mmol), ethyl acetoacetate (1.4 mL, 1.12 mmol) and ammonium acetate (86 mg, 1.12 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:5) of crude product gave 7c as a yellow gum (0.131 g, 63%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 5.60 (s, 1H), 4.23 - 4.18 (m, 2H), 4.16 - 4.11 (m, 2H), 3.91 (t, $J$ = 6.4 Hz, 1H), 2.27 (s, 6H), 1.30 - 1.18 (m, 22H), 0.87 (t, $J$ = 7.2 Hz, 3H) ppm. $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ = 168.4, 144.8, 103.6, 59.8, 37.1, 33.1, 32.1, 30.2, 30.0, 29.9, 29.6, 25.1, 22.9, 19.7, 14.6, 14.4 ppm.

**Diethyl-4-hexyl-1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylate (7d)**: According to GP II, heptylamine (64 mg, 0.56 mmol), 9-fluorenone imine 2 (0.10 g, 0.56 mmol), ethyl acetoacetate (1.4 mL, 1.12 mmol) and ammonium acetate (86 mg, 1.12 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:4) of crude product gave 7d as a yellow gum (0.116 g, 56%). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ = 5.51 (s, 1H), 4.24 - 4.11 (m, 4H), 3.91 (t, $J$ = 6.0 Hz, 1H), 2.28 (s, 6H), 1.30 - 1.19 (m, 16H), 0.85 (t, $J$ = 7.2 Hz, 3H) ppm. $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ = 168.4, 144.8, 103.6, 59.8, 37.1, 33.1, 32.2, 29.8, 25.1, 23.0, 19.7, 14.6, 14.4 ppm.

**Diethyl-1,4-dihydro-2,6-dimethyl-4-propylpyridine-3,5-dicarboxylate (7e)**: According to GP II, butylamine (41 mg, 0.56 mmol), 9-fluorenone imine 2 (0.10 g, 0.56 mmol), ethyl acetoacetate (1.4 mL, 1.12 mmol) and ammonium acetate (86 mg, 1.12 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:4) of crude product gave 7e as a yellow gum (89 mg, 54%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 5.50 (s, 1H), 4.23 - 4.12 (m,
4H), 3.93 (t, J = 5.6 Hz, 1H), 2.28 (s, 6H), 1.30 - 1.18 (m, 10H), 0.84 (t, J = 7.2 Hz, 3H) ppm. $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ = 168.4, 144.8, 103.6, 59.8, 39.4, 32.9, 19.7, 18.2, 14.6, 14.5 ppm.

**General procedure for the synthesis of benzimidazole (GP III):** Amine (0.56 mmol) was added to a solution of 9-fluorenone imine (0.56 mmol) in toluene (2 mL) and the mixture was stirred at room temperature for 1 h. o-Phenylenediamine (1.12 mmol) then added to the mixture and the reaction mixture was refluxed for 48 h under argon atmosphere (placing argon balloon). After disappearance of starting materials (indicated by TLC) solvent was evaporated under reduced pressure. The crude mixture was subjected to column chromatography (silica) to afford analytically pure products.

**2-(4-methylphenyl)-1H-benzo[d]imidazole (9a)$^{(3a)}$:** According to GP III, 4-Chloroenzylamine (79 mg, 0.56 mmol), 9-fluorenone imine 2 (0.10 g, 0.56 mmol) and o-phenylenediamine (60 mg, 0.56 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:3) of crude product gave 9a as a pale yellow solid (84 mg, 66%). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ = 13.03 (s, 1H), 8.23 (d, J = 8.6 Hz, 2H), 7.70 (s, 1H), 7.63 (d, J = 8.6 Hz, 2H), 7.57 (s, 1H), 7.26 - 7.21 (m, 2H) ppm. $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ = 150.3, 143.9, 135.2, 134.6, 129.1, 128.2, 122.8, 121.9, 119.0, 111.5, 99.6 ppm.

**2-(2-chlorophenyl)-1H-benzo[d]imidazole (9b)$^{(3a)}$:** According to GP III, 2-chloroenzylamine (79 mg, 0.56 mmol), 9-fluorenone imine 2 (0.10 g, 0.56 mmol) and o-phenylenediamine (60 mg, 0.56 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:3) of crude product gave 9c as a white solid (80 mg, 63%). $^1$H NMR (400 MHz, DMSO-$D_6$) $\delta$ = 12.78 (s, 1H), 7.93 - 7.90 (m, 1H), 7.72 (s, 1H), 7.67 - 7.65 (m, 1H), 7.64 - 7.51 (m, 3H), 7.28 - 7.25 (m, 2H) ppm. $^{13}$C NMR (101 MHz, DMSO-$D_6$) $\delta$ = 149.6, 143.6, 135.1, 132.5, 132.1, 131.7, 130.8, 130.3, 127.9, 123.3, 122.2, 119.5, 112.2 ppm.
**2-p-tolyl-1H-benzo[d]imidazole (9c)**: According to GP III, 4-methylenzylamine (68 mg, 0.56 mmol), 9-fluorenone imine 2 (0.10 g, 0.56 mmol) and o-phenylenediamine (60 mg, 0.56 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:3) of crude product gave 9b as a white solid (72 mg, 62%). $^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$ = 12.88 (s, 1H), 8.08 (d, $J$ = 8.2 Hz, 2H), 7.66 (s, 1H), 7.66 (s, 1H), 7.54 (d, $J$ = 8.0 Hz, 2H), 7.21 (d, $J$ = 4.4 Hz, 2H), 2.38 (s, 3H) ppm. $^{13}$C NMR (101 MHz, DMSO-d$_6$) $\delta$ = 150.3, 143.9, 135.2, 134.6, 129.1, 128.2, 122.8, 121.9, 119.0, 111.5, 99.6 ppm.

**Diethyl 2-(3-aminobenzylidene) malonate (16)**: According to GP I, 2-aminobenzylamine (0.10 g, 0.82 mmol), 9-fluorenone imine 2 (0.22 g, 1.23 mmol) and diethylmalonate (0.13 mL, 0.82 mmol) were reacted for 48 h and solvent was evaporated after cooling down the reaction mixture. Then crude mixture was dissolved in methanol and 1 (N) aq HCl was added to it. After 3 h stirring at rt, solvent was evaporated and reaction mixture was diluted by NaHCO$_3$ (10 mL) and the mixture was extracted with ethyl acetate (3 X 20 mL). The combined organic layers were washed successively with water (20 mL) and brine (10 mL). The organic layer was dried over sodium sulphate and the solvents were evaporated to get the crude reaction mixture which was subjected to column chromatography (silica gel; EtOAc: hexane, 1:4) to obtain analytically pure product (16) as a pale yellow oil (0.12 g, 54%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.64 (s, 1H), 7.18 (t, $J$ = 7.8 Hz, 1H), 6.91 (d, $J$ = 8.0 Hz, 1H), 6.85 – 6.84 (m, 1H), 6.82 – 6.79 (m, 1H), 4.35 – 4.27 (m, 4H), 2.52 (s, 2H), 1.32 (t, $J$ = 7.2 Hz, 3H), 1.28 (t, $J$ = 7.2 Hz, 3H) ppm. $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ = 167.0, 164.3, 144.6, 142.3, 134.2, 123.0, 126.6, 121.4, 118.6, 116.9, 62.0, 61.9, 14.4, 14.1 ppm.

**References:**


(c) Hajra, S.; Aziz, S. M.; Maji, R. *RSCAdv.*, **2013**, 3, 10185.

(e) A. B. Smith, Z. Liu, *Org. Lett.* **2008**, *10*, 4363


(h) CAS Number 140-10-3


f1 (ppm)
The image contains a spectrum for the compound 3e, which has a molecular structure with CO$_2$Et and OCF$_3$ substituents. The spectrum shows peaks at various ppm values, with annotations indicating specific chemical shifts.

- CO$_2$Et groups at 150.66, 150.68, 150.69, 150.70 ppm.
- OCF$_3$ group at 14.10 ppm.
- CDCl$_3$ resonances at 77.44, 77.23, 77.02 ppm.

The spectrum provides valuable information about the chemical structure and bonding of the compound 3e.
$\text{f}_1$ (ppm)

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$\text{H}_2\text{C} - \text{O}$

$\text{CO}_2\text{Et}$

3k

$\text{CO}_2\text{Et}$
$6g$

Chemical shifts and assignments:
- $7.44$ ppm (CDCl$_3$)
- $7.02$ ppm (CDCl$_3$)
- $77.44$ ppm CDCl$_3$
- $77.23$ ppm CDCl$_3$
- $77.02$ ppm CDCl$_3$
- $103.32$ ppm
- $110.79$ ppm
- $120.16$ ppm
- $127.46$ ppm
- $130.83$ ppm
- $135.53$ ppm
- $143.90$ ppm
- $157.31$ ppm
- $168.29$ ppm
The image contains an NMR spectrum with chemical shifts indicated at various positions on the x-axis labeled in ppm. The spectrum shows peaks at different frequencies, with some labeled features. The molecule structure is also present, labeled as 6h in the image. The chemical structure includes functional groups such as ethoxy (EtO2), carboxylate (CO2Et), and other specific groups.

$\text{f}_1 \text{ (ppm)}$

$\text{EtO}_2\text{C}$

$\text{CO}_2\text{Et}$

$\text{H}_2\text{C}$

$\text{N}$

$\text{CH}_3$

$\text{Cl}$

61
\begin{align*}
\text{Chart Image:}
\end{align*}
[RAW TEXT IS A SCIENTIFIC DOCUMENT]
The image shows an NMR spectrum with peaks at various ppm values. The spectrum includes peaks at 8.073, 7.656, 7.275, 7.203, 2.954, and 2.383 ppm. The compound indicated is 9c.