

Supporting Information

for

Silica sulfuric acid: a reusable solid catalyst for one pot synthesis of densely substituted pyrrole-fused isocoumarins under solvent-free conditions

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Detailed analytical data

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Preparation of silica sulfuric acid:

15.0 g of silica gel (60–120 mesh) was washed with 1 mol/L HCl, followed by deionized water, 30% H₂O₂, and then again with deionized water. After thorough washing, the silica was dried overnight at 373 K in vacuum to get preconditioned silica gel. A 100-mL round-bottomed flask was charged with silica gel and fitted with a magnetic stirrer. Then chlorosulfonic acid (5.83 g, 50.0 mmol) was added dropwise to the silica gel at r.t. for a period of 0.5 h. Immediately HCl gas started to emerge from the reaction vessel. After addition of chlorosulfonic acid, the resulting mixture was stirred until there was no more HCl outgassing from the vessel. A white solid (silica sulfuric acid) of 19.0 g was obtained [1].

Thermal gravimetric analysis (TGA) of silica sulfuric acid (SSA):

The weight change of catalyst precursor was measured by using a TGA thermal analyzer apparatus under a flow of dry air. The temperature was raised from room temperature to 700 °C by using a linear programmer at a heating rate of 10 °C/min. The sample weight was 18.7 mg. The TGA curve for the catalyst is illustrated in Figure S1. The weight losses found from TGA measurements agree fairly well with those expected for the decomposition of silica sulfuric acid to silica. For the catalyst, the thermo gravimetric curve seems to indicate a decomposition that is considered to be due to the removal of silica sulfuric acid (130–360 °C). It goes along with a total overall weight loss 29.29%, which solely represents the decomposition of the silica sulfuric acid to silica.²

References

1. Zolfigol, M. A. *Tetrahedron* **2001**, *57*, 9509.
2. Shaterian, H. R.; Ghashang, M.; Feyzi, M. *Applied Catalysis A: General* **2008**, *345*, 128.

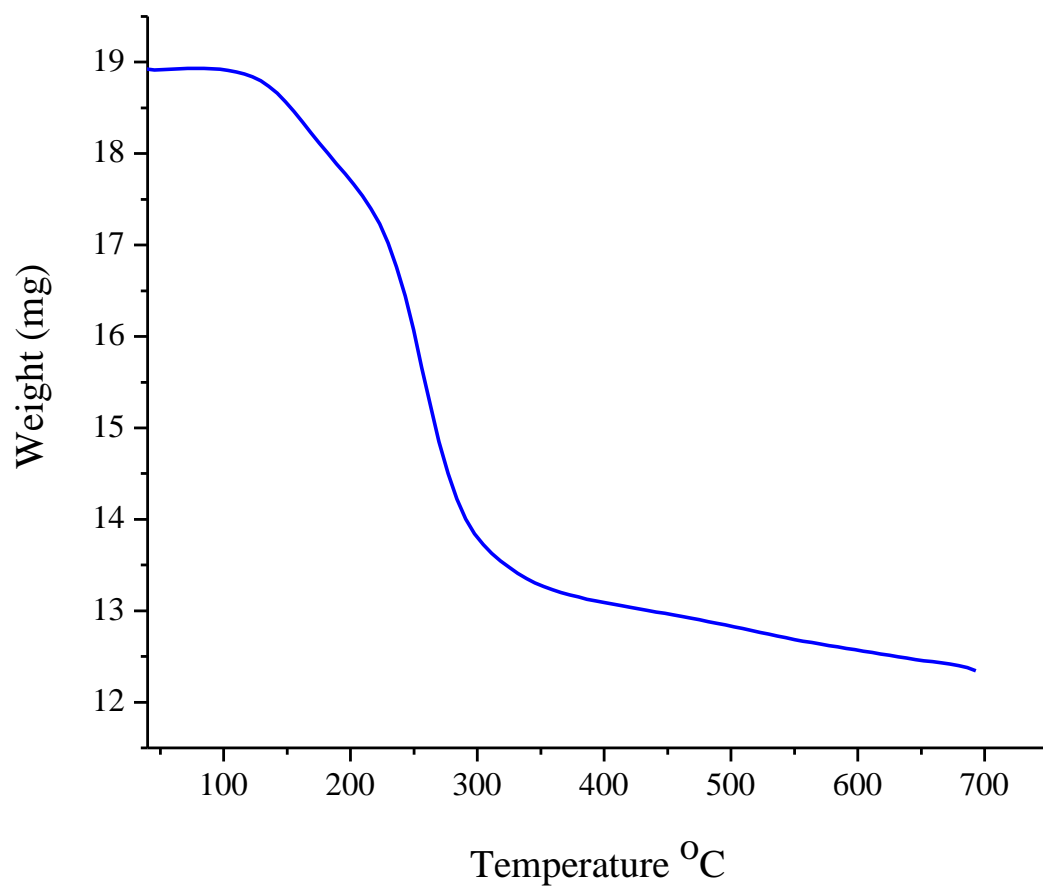


Figure S1 TGA curve of the silica sulfuric acid.

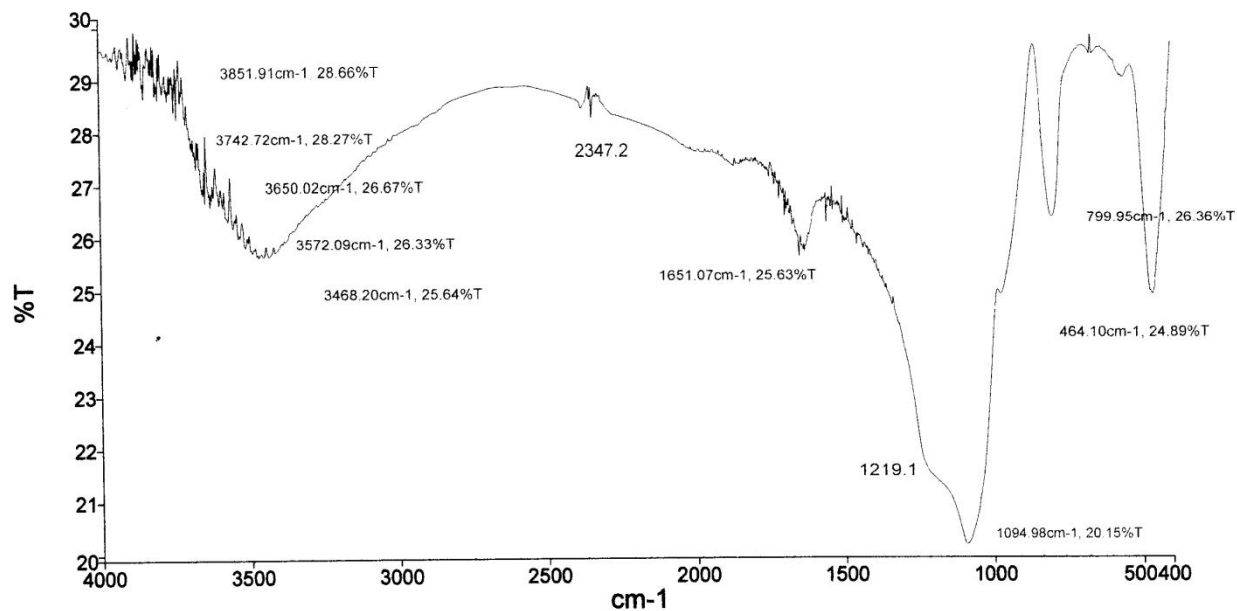


Figure S2: IR spectrum of Silica.

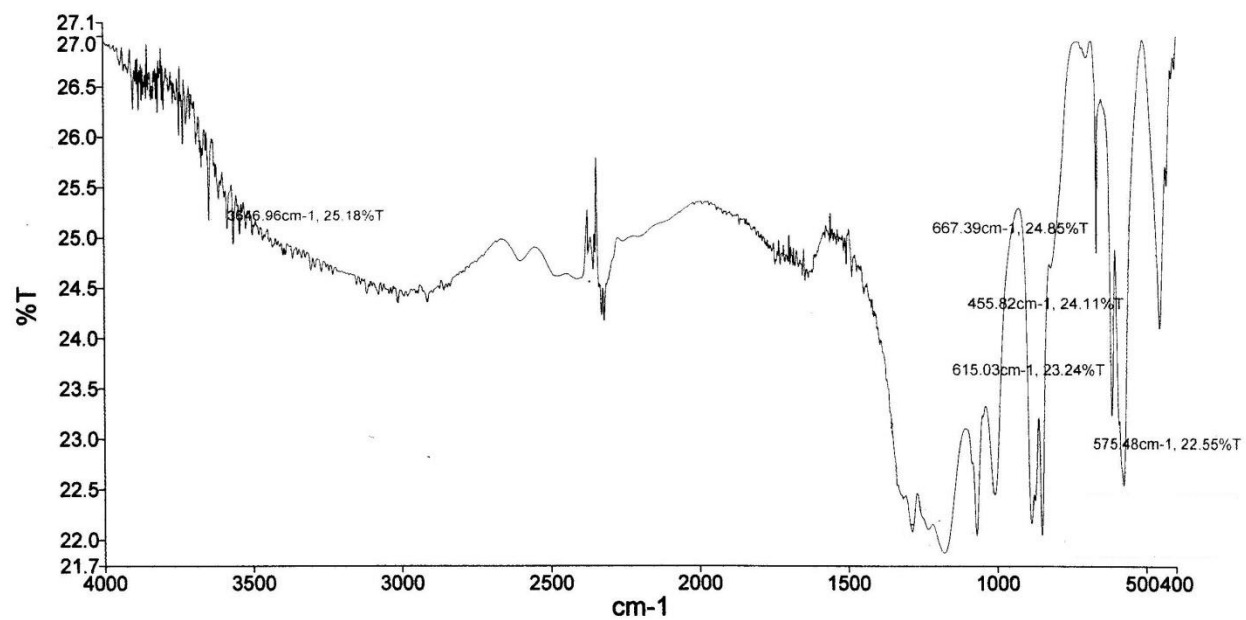


Figure S3: IR spectrum of silica sulfuric acid.

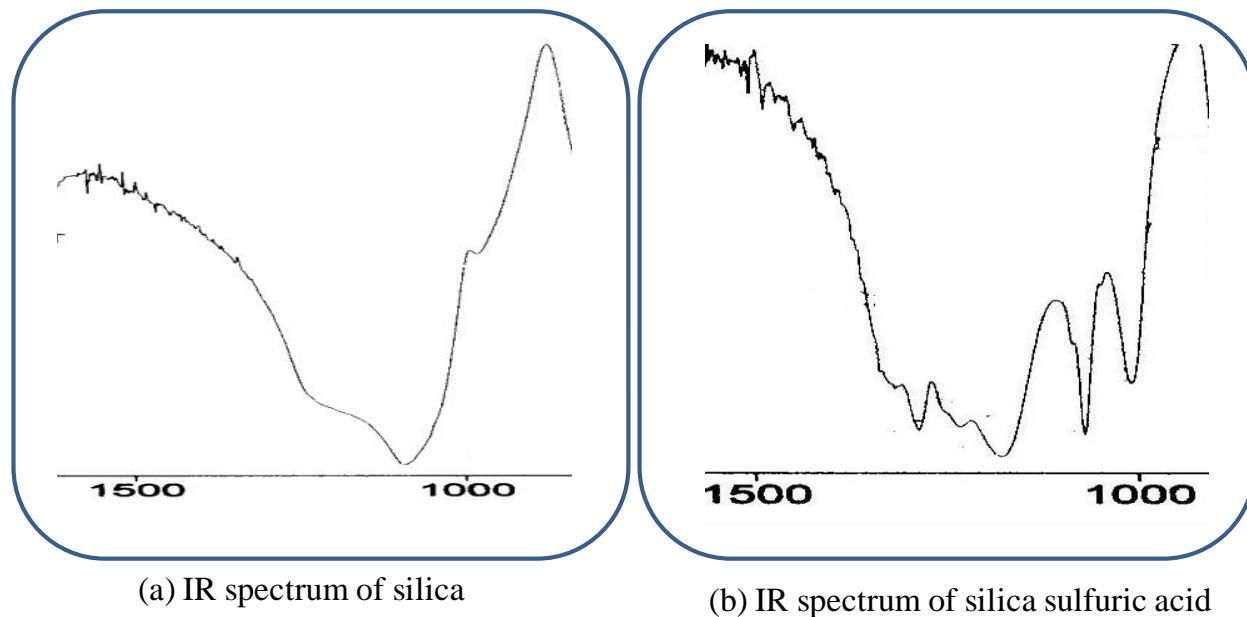


Figure S4: Comparison of IR spectrums of silica gel and silica sulfuric acid

Analysis of IR spectrum: The FT-IR spectrums of the catalyst were shown in Figure S2, S3 and S4. The catalyst is solid and solid state IR spectrum was recorded using the KBr disk technique. For silica (SiO_2), the major peaks are broad band Si–O–Si stretching from 1100 to 1000 cm^{-1} . For sulfonic acid functional group, the FT-IR absorption range of the O=S=O peaks lies in 1180–1250 cm^{-1} .

Spectral data of the compounds

2-Methyl-5-oxo-1-phenyl-1,5-dihydro-4-oxa-1-azacyclopenta[*a*]naphthalene-3-carboxylic acidethylester (8a). Yellow solid; mp 208-210 °C; ^1H NMR (CDCl_3 , 300MHz) δ 8.29 (d, $J = 7.8$ Hz, 1H), 7.65-7.62 (m, 3H), 7.42-7.39 (m, 1H), 7.32-7.30 (m, 1H), 7.27-7.20 (m, 2H), 6.36 (d, $J = 7.8$ Hz, 1H), 4.39 (q, $J = 6.9$ Hz, 2H), 2.38 (s, 3H), 1.43 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 163.6, 162.1, 139.7, 137.3, 134.2, 131.7, 130.3, 130.2, 130.2, 130.0, 128.5, 125.4,

118.4, 118.0, 112.9, 102.1, 60.1, 14.5, 12.0; IR(KBr): 1722 cm^{-1} ; Anal calcd for $\text{C}_{21}\text{H}_{17}\text{NO}_4$: C, 72.61; H, 4.93; N, 4.03 % Found C, 72.50; H, 4.87; N, 3.98%.

1-(4-Fluorophenyl)-2-methyl-5-oxo-1,5-dihydro-4-oxa-1-azacyclopenta[*a*]naphthalene-3-carboxylic acid ethylester (8b). Yellow solid; mp 252-254 $^{\circ}\text{C}$; ^1H NMR (CDCl_3 , 300MHz) δ 8.23 (d, $J = 7.8$ Hz, 1H), 7.50-7.46 (m, 2H), 7.37-7.31 (m, 3H), 7.21 (t, $J = 8.1$ Hz, 1H), 6.38 (d, $J = 8.1$ Hz, 1H), 4.32 (q, $J = 6.9$ Hz, 2H), 2.36 (s, 3H), 1.41 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz, F coupled ^{13}C spectra) δ 164.8, 163.3, 161.9, 161.5, 140.7, 139.8, 134.3, 133.2, 131.7, 130.6, 130.5, 130.1, 125.5, 118.2, 118.2, 117.5, 117.1, 112.9, 102.2, 60.1, 14.4, 11.9; IR(KBr): 1725 cm^{-1} ; Anal calcd for $\text{C}_{21}\text{H}_{16}\text{FNO}_4$: C, 69.04; H, 4.41; N, 3.83 % Found 68.96; H, 4.36; N, 3.80 %.

1-(2-Chlorophenyl)-2-methyl-5-oxo-1,5-dihydro-4-oxa-1-azacyclopenta[*a*]naphthalene-3-carboxylic acid ethylester (8c). Yellow solid; mp 233-235 $^{\circ}\text{C}$; ^1H NMR (CDCl_3 , 300MHz) δ 8.32 (d, $J = 7.8$ Hz, 1H), 7.69-7.55 (m, 4H), 7.35-7.26 (m, 2H), 6.31 (d, $J = 7.8$ Hz, 1H), 4.42 (q, $J = 7.2$ Hz, 2H), 2.37 (s, 3H), 1.45 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 163.5, 162.0, 140.9, 139.5, 135.1, 134.6, 133.9, 131.8, 131.0, 130.7, 130.6, 130.2, 128.5, 125.6, 118.1, 117.5, 112.4, 102.7, 60.2, 14.5, 11.6; IR(KBr): 1724 cm^{-1} ; Anal calcd for $\text{C}_{21}\text{H}_{16}\text{ClNO}_4$: C, 66.06; H, 4.22; N, 3.67 % Found C, 66.17; H, 4.15; N, 3.61 %.

1-(3-Chlorophenyl)-2-methyl-5-oxo-1,5-dihydro-4-oxa-1-azacyclopenta[*a*]naphthalene-3-carboxylic acid ethylester (8d). Yellow solid; mp 230-232 $^{\circ}\text{C}$; ^1H NMR (CDCl_3 , 300MHz) δ 8.20 (d, $J = 7.8$ Hz, 1H), 7.59-7.49 (m, 2H), 7.39 (d, $J = 7.8$ Hz, 1H), 7.32-7.25 (m, 2H), 7.20-7.15 (m, 1H), 6.33 (d, $J = 8.1$ Hz, 1H), 4.28 (q, $J = 6.9$ Hz, 2H), 2.31 (s, 3H), 1.34 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 163.3, 161.8, 140.9, 139.6, 138.4, 135.9, 134.4, 131.8, 131.2,

130.4, 130.0, 128.9, 127.0, 125.7, 118.2, 118.1, 112.8, 102.5, 60.1, 14.4, 12.0; IR(KBr): 1721 cm^{-1} ; Anal calcd for $\text{C}_{21}\text{H}_{16}\text{ClNO}_4$: C, 66.06; H, 4.22; N, 3.67 % Found C, 66.16; H, 4.18; N, 3.63 %.

1-(4-Chlorophenyl)-2-methyl-5-oxo-1,5-dihydro-4-oxa-1-azacyclopenta[*a*]naphthalene-3-carboxylic acid ethylester (8e). Yellow solid; mp 218-220 °C; ^1H NMR (CDCl_3 , 300MHz) δ 8.23 (d, $J = 7.8$ Hz, 1H), 7.63 (d, $J = 6.9$ Hz, 2H), 7.43 (d, $J = 8.4$ Hz, 2H), 7.32 (t, $J = 7.2$ Hz, 1H), 7.24 (t, $J = 7.2$ Hz, 1H), 6.42 (d, $J = 8.1$ Hz, 1H), 4.32 (q, $J = 6.9$ Hz, 2H), 2.36 (s, 3H), 1.40 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 163.2, 161.8, 140.8, 139.6, 136.1, 135.8, 134.3, 131.7, 131.7, 130.5, 130.0, 125.5, 118.2, 117.9, 112.7, 102.3, 60.1, 14.4, 11.9; IR(KBr): 1719 cm^{-1} ; Anal calcd for $\text{C}_{21}\text{H}_{16}\text{ClNO}_4$: C, 66.06; H, 4.22; N, 3.67 % Found C, 65.93; H, 4.15; N, 3.60 %.

1-(4-Methoxyphenyl)-2-methyl-5-oxo-1,5-dihydro-4-oxa-1-azacyclopenta[*a*]naphthalene-3-carboxylic acid ethylester (8f). Yellow solid; mp 194-196 °C; ^1H NMR (CDCl_3 , 300MHz) δ 8.23 (d, $J = 8.1$ Hz, 1H), 7.28-7.14 (m, 4H), 7.03 (d, $J = 8.7$ Hz, 2H), 6.39 (d, $J = 8.1$ Hz, 1H), 4.32 (q, $J = 6.9$ Hz, 2H), 3.87 (s, 3H), 2.30 (s, 3H), 1.35 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 163.7, 161.9, 160.5, 140.7, 140.1, 134.3, 131.7, 130.5, 129.7, 129.5, 125.4, 118.4, 118.0, 115.3, 113.0, 101.9, 60.1, 55.6, 14.5, 11.9; IR(KBr): 1716 cm^{-1} ; Anal calcd for $\text{C}_{22}\text{H}_{19}\text{NO}_5$: C, 70.02; H, 5.07; N, 3.71 % Found C, 70.14; H, 5.00; N, 3.66 %.

1-(3-Methoxyphenyl)-2-methyl-5-oxo-1,5-dihydro-4-oxa-1-azacyclopenta[*a*]naphthalene-3-carboxylic acid ethylester (8g). Yellow solid; mp 198-200 °C; ^1H NMR (CDCl_3 , 300MHz) δ 8.26 (d, $J = 7.8$ Hz, 1H), 7.52 (t, $J = 8.1$ Hz, 1H), 7.33 (t, $J = 7.8$ Hz, 1H), 7.27-7.15 (m, 2H), 6.99-6.95 (m, 2H), 6.46 (d, $J = 8.1$ Hz, 1H), 4.36 (q, $J = 6.9$ Hz, 2H), 3.88 (s, 3H), 2.39 (s, 3H),

1.41 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 163.5, 162.1, 160.9, 140.7, 139.6, 138.2, 134.3, 131.6, 130.9, 130.3, 125.4, 120.5, 118.5, 117.9, 115.9, 114.0, 112.8, 102.0, 60.1, 55.6, 14.5, 11.9; IR (KBr): 1720 cm^{-1} ; Anal calcd for $\text{C}_{22}\text{H}_{19}\text{NO}_5$: C, 70.02; H, 5.07; N, 3.71 % Found C, 70.15; H, 5.02; N, 3.67 %.

1-(3-Hydroxyphenyl)-2-methyl-5-oxo-1,5-dihydro-4-oxa-1-azacyclopenta[*a*]naphthalene-3-carboxylic acid ethylester (8h). Yellow solid; mp 254-256 °C; ^1H NMR (d_6 -DMSO, 300MHz) δ 10.13 (bs, 1H), 8.13 (d, $J = 7.8$ Hz, 1H), 7.53-7.43 (m, 2H), 7.32 (t, $J = 7.5$ Hz, 1H), 7.08 (d, $J = 8.1$ Hz, 1H), 6.95 (d, $J = 7.5$ Hz, 1H), 6.87 (s, 1H), 6.44 (d, $J = 8.1$ Hz, 1H), 4.24 (q, $J = 6.9$ Hz, 2H), 2.29 (s, 3H), 1.29 (t, $J = 6.6$ Hz, 3H); ^{13}C NMR (d_6 -DMSO, 75 MHz) δ 162.8, 161.5, 159.1, 140.8, 139.5, 137.8, 135.2, 131.5, 131.4, 130.2, 126.2, 119.1, 118.7, 117.7, 117.5, 115.5, 112.5, 101.2, 59.8, 14.7, 12.1; IR (KBr): 3350, 1722 cm^{-1} ; Anal calcd for $\text{C}_{21}\text{H}_{17}\text{NO}_5$: C, 69.41; H, 4.72; N, 3.85 % Found C, 69.29; H, 4.67; N, 3.79 %.

2-Methyl-5-oxo-1-*p*-tolyl-1,5-dihydro-4-oxa-1-azacyclopenta[*a*]naphthalene-3-carboxylic acid ethylester (8i). Yellow solid; mp 202-204 °C; ^1H NMR (CDCl_3 , 300MHz) δ 8.23 (d, $J = 8.1$ Hz, 1H), 7.38 (d, $J = 8.1$ Hz, 2H), 7.30-7.15 (m, 4H), 6.39 (d, $J = 8.1$ Hz, 1H), 4.33 (q, $J = 7.2$ Hz, 2H), 2.49 (s, 3H), 2.33 (s, 3H), 1.38 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 163.6, 162.1, 140.7, 140.2, 139.8, 134.6, 134.2, 131.6, 130.8, 130.4, 128.2, 125.3, 118.5, 118.0, 112.8, 101.9, 60.0, 21.3, 14.5, 11.9; IR (KBr): 1720 cm^{-1} ; Anal calcd for $\text{C}_{22}\text{H}_{19}\text{NO}_4$: C, 73.12; H, 5.30; N, 3.88 % Found C, 73.01; H, 5.26; N, 3.82 %.

1-(2,4-Dimethylphenyl)-2-methyl-5-oxo-1,5-dihydro-4-oxa-1-azacyclopenta[*a*]naphthalene-3-carboxylic acid ethylester (8j). Yellow solid; mp 190-192 °C; ^1H NMR (CDCl_3 , 300MHz) δ 8.27 (d, $J = 7.8$ Hz, 1H), 7.29-7.11 (m, 5H), 6.31 (d, $J = 7.8$ Hz, 1H), 4.35 (q, $J = 6.9$, 2H), 2.44

(s, 3H), 2.29 (s, 3H), 1.86 (s, 3H), 1.38 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 163.7, 162.2, 140.7, 140.5, 139.2, 136.4, 134.6, 133.5, 132.3, 131.7, 130.5, 128.4, 128.2, 125.5, 117.9, 117.7, 112.2, 102.2, 60.1, 21.3, 17.0, 14.5, 11.6; IR (KBr): 1717 cm^{-1} ; Anal calcd for $\text{C}_{23}\text{H}_{21}\text{NO}_4$: C, 73.58; H, 5.64; N, 3.73 % Found C, 73.71; H, 5.56; N, 3.69 %.

1-(4-Bromophenyl)-2-methyl-5-oxo-1,5-dihydro-4-oxa-1-azacyclopenta[*a*]naphthalene-3-carboxylic acid ethylester (8k). Yellow solid; mp 212-214 °C; ^1H NMR (CDCl_3 , 300MHz) δ 8.27 (d, $J = 7.5$ Hz, 1H), 7.80 (d, $J = 8.4$ Hz, 2H), 7.38-7.22 (m, 4H), 6.43 (d, $J = 8.1$ Hz, 1H), 4.36 (q, $J = 6.9$ Hz, 2H), 2.36 (s, 3H), 1.41 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 163.3, 161.8, 140.9, 139.6, 136.3, 134.3, 133.5, 131.8, 130.2, 130.0, 125.6, 124.2, 118.2, 118.0, 112.7, 102.5, 60.1, 14.4, 12.0; IR (KBr): 1721 cm^{-1} ; Anal calcd for $\text{C}_{21}\text{H}_{16}\text{BrNO}_4$: C, 59.17; H, 3.78; N, 3.29 % Found 59.05; H, 3.70; N, 3.22 %.

2-Methyl-1-(4-nitrophenyl)-5-oxo-1,5-dihydro-4-oxa-1-azacyclopenta[*a*]naphthalene-3-carboxylic acid ethylester (8l). Yellow solid; mp 260-262 °C; ^1H NMR (CDCl_3 , 300MHz) δ 8.52 (d, $J = 8.1$ Hz, 2H), 8.34 (d, $J = 7.8$, 1H), 7.64 (d, $J = 8.7$ Hz, 2H), 7.39-7.30 (m, 2H), 6.36 (d, $J = 7.5$ Hz, 1H), 4.41 (q, $J = 7.2$ Hz, 2H), 2.41 (s, 3H), 1.44 (t, $J = 7.2$ Hz, 3H); IR (KBr): 1726 cm^{-1} ; Anal calcd for $\text{C}_{21}\text{H}_{16}\text{N}_2\text{O}_6$: C, 64.28; H, 4.11; N, 7.14 % Found C, 64.19; H, 4.05; N, 7.08 %.

1-Benzyl-2-methyl-5-oxo-1,5-dihydro-4-oxa-1-azacyclopenta[*a*]naphthalene-3-carboxylic acid ethylester (8m). Yellow solid; mp 180-182 °C; ^1H NMR (CDCl_3 , 300MHz) δ 8.27 (d, $J = 7.8$ Hz, 1H), 7.44 (t, $J = 8.4$ Hz, 1H), 7.38-7.21 (m, 5H), 7.02 (d, $J = 6.9$ Hz, 2H), 5.54 (s, 2H), 4.38 (q, $J = 7.2$ Hz, 2H), 2.61 (s, 3H), 1.44 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 163.5, 161.9, 140.9, 139.2, 135.3, 134.7, 131.8, 130.1, 129.3, 128.0, 125.4, 125.3, 118.6, 118.0,

111.9, 101.8, 60.1, 48.7, 14.5, 10.9; IR(KBr): 1720 cm^{-1} ; Anal calcd for $\text{C}_{22}\text{H}_{19}\text{NO}_4$: C, 73.12; H, 5.30; N, 3.88 % Found C, 73.21; H, 5.25; N, 3.84 %.

2-Methyl-5-oxo-1-propyl-1,5-dihydro-4-oxa-1-azacyclopenta[*a*]naphthalene-3-carboxylic acidethylester (8n). Yellow solid; mp 132-134 $^{\circ}\text{C}$; ^1H NMR (CDCl_3 , 300MHz) δ 8.28 (d, $J = 7.8$ Hz, 1H), 7.64 (t, $J = 7.8$ Hz, 1H), 7.54 (d, $J = 8.1$ Hz, 1H), 7.29 (t, $J = 7.2$ Hz, 1H), 4.35 (q, $J = 6.9$ Hz, 2H), 4.17 (t, $J = 7.2$ Hz, 2H), 2.61 (s, 3H), 1.86-1.79 (m, 2H), 1.42 (t, $J = 6.9$ Hz, 3H), 1.03 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 163.5, 161.9, 140.9, 138.5, 134.8, 131.9, 130.3, 125.1, 118.3, 117.8, 110.9, 101.0, 59.8, 46.7, 23.3, 14.5, 11.0, 10.9; IR(KBr): 1720 cm^{-1} ; Anal calcd for $\text{C}_{18}\text{H}_{19}\text{NO}_4$: C, 68.99; H, 6.11; N, 4.47 % Found C, 68.88; H, 6.04; N, 4.41 %.

1-Butyl-2-methyl-5-oxo-1,5-dihydro-4-oxa-1-azacyclopenta[*a*]naphthalene-3-carboxylic acidethylester (8o). Yellow solid; mp 125-127 $^{\circ}\text{C}$; ^1H NMR (CDCl_3 , 300MHz) δ 8.29 (d, $J = 7.8$ Hz, 1H), 7.65 (t, $J = 7.5$ Hz, 1H), 7.56 (d, $J = 8.1$ Hz, 1H), 7.30 (t, $J = 7.8$ Hz, 1H), 4.36 (q, $J = 7.2$ Hz, 2H), 4.20 (t, $J = 7.8$ Hz, 2H), 2.62 (s, 3H), 1.79-1.74 (m, 2H), 1.49-1.40 (m, 5H), 1.00 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 163.5, 161.9, 141.0, 138.4, 134.7, 132.0, 130.4, 125.1, 118.3, 117.8, 110.9, 101.0, 59.8, 45.1, 32.1, 19.8, 14.5, 13.6, 11.0; IR(KBr): 1719 cm^{-1} ; Anal calcd for $\text{C}_{19}\text{H}_{21}\text{NO}_4$: C, 69.71; H, 6.47; N, 4.28 % Found C, 69.61; H, 6.41; N, 4.20 %.

