**Supporting Information**

**Experimental Section**

**General Methods:** All melting points were uncorrected. The progression of all the reaction was monitored by TLC using hexanes/ethyl acetate mixture as eluent. Column chromatography was carried out on Silica gel by using increasing polarity. 1H, 13C and DEPT-135 spectra were recorded in CDCl3 using TMS as an internal standard on a Bruker 300 MHz spectrometer at room temperature. Chemical shift values are quoted in parts per million (ppm) and coupling constants (J) are quoted in Hertz (Hz). Mass spectra were recorded on JEOL GC mate mass spectrometer. The X-ray diffraction measurements were carried out at 298 K on a Bruker (2008) SMART APEX 2 area detector diffractometer.

**General procedure for the synthesis of Baylis –Hillman adducts (2a,b, 3)**

A mixture of 4-oxoazetidine-2-carbaldehyde 1a, b (25 mmol, 2.653 g), methyl acrylate (37.5 mmol, 3.228 g) and DABCO (3.75 mmol, 0.420 g) was kept at room temperature for 12-15 days. After completion of the reaction as evidenced by TLC analysis, the reaction mixture was diluted with ethylacetate (20 mL) and washed successively with 2N HCl solution, water and aqueous NaHCO3 solution. Organic layer was dried over anhydrous Na2SO4. Solvent was evaporated under reduced pressure and residue was purified by column chromatography using hexane: EtOAc (8:2) as eluent to afford Baylis –Hillman adducts (2a,b, 3) in good yield.

**Compound 2a:** White solid (75 %), Mp: 96-98 ºC; IR (KBr): 3472, 1744, 1705 cm-1; 1H NMR (300 MHz, CDCl3): δ 2.61 (br s, 1H, -OH), 3.77 (s, 3H), 3.79 (s, 3H), 4.33-4.34 (t, J = 2.1, 1.8 Hz, 1H), 4.49-4.50 (d, J = 2.1 Hz, 1H), 5.23 (s, 1H), 6.21 (s, 1H), 6.46 (s, 1H), 6.90-6.93 (d, J = 9.0 Hz, 2H), 7.17-7.32 (m, 5H), 7.47-7.50 (d, J = 9.0 Hz, 2H). 13C-NMR (75 MHz, CDCl3): δ 52.2, 53.3, 55.5, 62.3, 65.4, 114.6, 118.8, 127.2, 127.4, 127.6, 128.8, 130.4, 135.0, 138.8, 156.3, 165.3, 166.1. HRMS (ESI-TOF): Calcd. for C21H22NO6 [M + H]+ 384.1447, Found 384.1449.

**Compound 3:** White solid (72 %), Mp: 117-119 ºC; IR (KBr): 3225, 2361, 1720 cm-1; 1H NMR (300 MHz, CDCl3): δ 3.43-3.45 (d, J = 4.2 Hz, 1H,), 3.78 (s, 3H), 4.30 (s, 1H), 4.45 (s, 1H), 4.84 (s, 1H), 6.10 (s, 1H), 6.25 (s, 1H), 6.87-6.90 (d, J = 8.7 Hz, 2H), 7.22-7.25 (d, J = 7.5 Hz, 2H), 7.28-7.35 (m, 4H). 13C-NMR (75 MHz, CDCl3): δ 55.5, 56.4, 62.7, 72.7, 114.3, 120.5, 122.7, 127.5, 128.0, 129.1, 130.2, 133.0, 133.8, 156.9, 165.3. HRMS (ESI-TOF): Calcd for C20H19N2O3 [M + H]+ 335.1396, Found 335.1392.

**General Procedure for the Synthesis of Fused Pyrrolidine/Pyrrolizidine Derivatives**

Sarcosine**5**or proline**8** (1.0 mmol) and isatin4/acenapthequinone10/ninhydrin 14(1.0 mmol) were added to a solution of BHA azetidin-2-yl methyl acrylate 2a,b/ azetidin-2-yl acrylonitrile 3(1.0 mmol) and the mixture was heated at reflux in methanol (20 ml). After completion of the reaction was indicated by TLC analysis, methanol was evaporated under reduced pressure and the residue diluted with dichloromethane and washed with brine and water. The organic layer was separated and removed and the residue was subjected to column chromatography by using ethyl acetate/hexane as eluent [14].

**Compound 6a:** White solid. (85%), Mp: 239-242 ºC; IR (KBr): 3140, 1765, 1759, 1711 cm-1; 1H NMR (300 MHz, CDCl3): δ 2.39-2.47 (m, 1H), 2.54 (s, -NCH3, 3H), 2.58-2.64 (m, 1H), 2.67-2.77 (dd, J = 7.8, 8.7 Hz, 1H), 3.05-3.11 (dd, J = 8.7, 9.3 Hz, 1H), 3.71 (s, -OCH3, 3H), 4.71 (s, 1H), 4.92-4.93 (d, J = 1.2 Hz, 1H), 5.54-5.55 (d, J = 0.9 Hz, 1H), 6.79-6.82 (d, J = 8.7 Hz, 2H), 6.95-6.97 (d, J = 7.8 Hz, 1H), 7.07-7.18 (m, 4H), 7.24-7.27 (m, 2H), 7.34-7.41 (m, 3H), 7.72-7.75 (d, J = 7.5 Hz, 1H), 8.86 (s, 1H, N-H). 13C NMR (75 MHz, CDCl3): δ 28.1, 34.0, 52.9, 55.4, 56.3, 59.1, 71.7, 73.8, 80.0, 114.1, 114.8, 116.5, 120.0, 123.0, 124.2, 127.9, 129.8, 131.0, 135.9, 157.2, 157.3, 162.1, 170.3, 172.4. DEPT-135 NMR (75 MHz, CDCl3): δ 28.1, 34.0, 52.9, 55.4, 59.1, 73.8, 80.0, 114.8, 116.5, 116.6, 120.0, 123.0, 124.2, 129.8, 131.0. Mass: m/z 525.60 (M+). Anal.Calcd. For C30H27N3O6: C, 68.56, H, 5.18, N, 8.00 %; Found: C, 68.65, H, 5.12, N, 7.91%.

CCDC-882505 (for 6a) contains the supplementary crystallographicdata for this paper. These data can be obtained free of chargefrom The Cambridge Crystallographic Data Centre via[www.ccdc.cam.ac.uk/data\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif)

**Compound 6b:** White solid. (81%), Mp: 278-281 ºC; IR (KBr): 3107, 1759, 1744, 1707 cm-1; 1H NMR (300 MHz, CDCl3+ DMSO-d6): δ 1.93-2.04 (m, 1H), 2.48 (s, 3H), 2.64-2.72 (m, 2H), 2.97-3.06 (m, 1H), 3.77 (s, 3H), 4.33-4.36 (dd, J = 2.4 Hz, 1H), 4.49-4.52 (d, J = 7.8 Hz, 1H), 4.76-4.77 (d, J = 2.4 Hz, 1H), 6.85-6.88 (d, J = 9.0 Hz, 2H), 7.05-7.12 (m, 2H), 7.32-7.41 (m, 4H), 7.48-7.57 (m, 5H), 10.57 (s, 1H, NH). 13C NMR (75 MHz, CDCl3+ DMSO-d6): δ 32.9, 39.0, 57.7, 59.8, 60.2, 60.8, 63.5, 76.5, 79.4, 118.4, 118.8, 119.6, 121.6, 124.2, 125.3, 127.8, 132.7, 134.0, 135.4, 138.4, 142.1, 161.5, 173.9, 177.6. DEPT-135 NMR (75 MHz, CDCl3+ DMSO-d6): δ 32.9, 39.0, 57.7, 59.8, 60.2, 63.4, 79.4, 118.8, 119.6, 121.6, 124.2, 125.3, 127.8, 132.7, 134.0, 135.4. Mass: m/z 509.62 (M+). Anal.Calcd. For C30H27N3O5: C, 70.71; H, 5.34; N, 8.25 %; Found: C, 70.65, H, 5.42, N, 8.33%.

**Compound 7:** Brown solid. (83%), Mp: 217-220 ºC; IR (KBr): 3212, 1762, 1744, 1690 cm-1; 1H NMR (300 MHz, CDCl3): δ 2.40-2.47 (m, 1H), 2.56 (s, -NCH3, 3H), 3.04-3.11 (m, 1H), 3.73 (s, 3H), 4.69 (s, 1H), 4.92-4.93 (d, J = 1.5 Hz, 1H), 5.53-5.54 (d, J = 1.2 Hz, 1H), 6.81-6.84 (dd, J = 2.4, 2.1 Hz, 2H), 6.90-6.95 (m, 1H), 7.07-7.13 (m, 2H), 7.14-7.15 (m, 1H), 7.17-7.18 (m, 1H), 7.24 (s, 1H), 7.26 (s, 1H), 7.32-7.39 (m, 2H), 7.46-7.50 (dd, J = 2.7 Hz, 1H), 8.70 (s, 1H, N-H). 13C NMR (75 MHz, CDCl3): δ 28.2, 34.0, 53.0, 55.4, 56.0, 59.0, 71.5, 73.8, 79.9, 114.9, 115.7-115.8 (J = 29.7 Hz), 116.4, 116.6-116.9 (J = 97.2 Hz), 117.5-117.6 (J = 31.5 Hz), 117.9-118.2 (J = 92.7 Hz), 120.1, 123.0, 127.9, 129.8, 132.13-132.16 (J = 8.1 Hz), 157.3, 160.4, 162.0, 169.5, 172.0. DEPT 135 NMR (75 MHz, CDCl3): δ 28.2, 34.0, 53.0, 55.4, 59.0, 73.8, 79.9, 114.9, 116.4, 116.6-116.9 (J = 97.2 Hz), 117.5-117.6 (J = 31.5 Hz), 117.9-118.2 (J = 92.7 Hz), 120.1, 123.0, 129.8. Mass: m/z 527.48 (M+). Anal.Calcd. For C30H26FN3O5: C, 68.30, H, 4.97, N, 7.97 %; Found: C, 68.37, H, 4.90, N, 8.03%.

**Compound 9:** White solid. (79%), M.p: 205-207 ºC; IR (KBr): 3231, 1759, 1746, 1720 cm-1; 1H NMR (300 MHz, CDCl3+ DMSO-d6): δ 1.39-1.49 (m, 1H), 1.63-1.78 (m, 2H), 2.04-2.14 (m, 2H), 2.56-2.58 (m, 2H), 2.64-2.70 (m, 2H), 3.75 (s, 3H), 4.46-4.48 (d, J = 6.6 Hz, 1H), 4.56-4.58 (d, J = 7.8 Hz, 1H), 5.70 (s, 1H), 6.84-6.86 (d, J = 6.9 Hz, 2H), 7.02-7.11 (m, 3H), 7.25-7.34 (m, 5H), 7.43-7.46 (d, J = 7.5 Hz, 2H), 7.65-7.67 (d, J = 7.2 Hz, 1H), 10.68 (s, 1H, NH). 13C NMR (75 MHz, CDCl3+ DMSO-d6): δ 29.9, 37.0, 38.7, 54.1, 60.1, 61.6, 67.1, 68.6, 80.9, 84.9, 85.0, 118.8, 118.9, 121.1, 121.4, 125.4, 127.3, 128.7, 133.3, 134.0, 134.2, 135.6, 142.6, 161.7, 162.3, 167.9, 173.2, 179.6. DEPT 135 NMR (75 MHz, CDCl3+ DMSO-d6): δ 30.0, 37.1, 38.7, 54.1, 60.1, 67.1, 68.6, 84.9, 84.9, 118.9, 121.1, 121.3, 125.4, 127.2, 128.7, 133.3, 134.2, 135.6. Mass: m/z 551.65 (M+). Anal.Calcd. For C32H29N3O6: C, 69.68, H, 5.30, N, 7.62%; Found: C, 69.75, H, 5.38, N, 7.55%.

**Compound 11a:** Pale yellow solid. (85%), M.p: 181-183 ºC; IR (KBr): 3136, 1759, 1728 cm-1; 1H NMR (300 MHz, CDCl3): δ 2.08-2.18 (m, 1H), 2.22-2.27 (m, 1H), 2.31 (s, 3H), 3.46-3.51 (dd, J = 7.8, 8.1 Hz, 1H), 3.57 (s, 3H), 3.70 (s, 3H), 4.23 (s, 1H), 4.27 (s, 1H), 5.70-5.71 (d, J = 1.2 Hz, 1H), 6.25 (s, 1H), 6.70-6.73 (d, J = 9.0 Hz, 2H), 7.04-7.08 (t, J = 6.9, 7.2 Hz, 1H), 7. 16-7.23 (m, 4H), 7.32-7.37 (t, J = 7.8, 7.5 Hz, 2H), 7.48-7.60 (m, 3H), 7.70-7.79 (t, J = 8.7, 9.0 Hz, 2H). 13C NMR (75 MHz, CDCl3): δ 28.7, 38.5, 52.1, 55.3, 58.1, 59.7, 66.1, 71.2, 80.4, 87.9, 108.8, 114.3, 116.3, 120.1, 120.5, 122.5, 122.6, 125.7, 125.9, 127.2, 128.8, 129.0, 129.6, 130.8, 134.2, 137.4, 138.8, 156.7, 157.7, 163.4, 172.0. DEPT-135 NMR (75 MHz, CDCl3): δ 28.6, 38.5, 52.2, 55.3, 58.1, 59.7, 71.2, 80.3, 113.9, 114.3, 116.3, 116.6, 120.1, 120.5, 122.5, 122.6, 125.7, 125.9, 127.2, 128.8, 129.6. Mass: m/z 592.59 (M+). Anal.Calcd. For C35H32N2O7: C, 70.93, H, 5.44, N, 4.73%; Found: C, 71.05, H, 5.37, N, 4.80 %.

**Compound 11b:** Pale yellow solid. (81%), Mp: 172-174 ºC; IR (KBr): 3148, 1755, 1728 cm-1; 1H NMR (300 MHz, CDCl3): δ 1.94-2.00 (m, 1H), 2.15-2.25 (m, 1H), 2.33 (s, 3H), 3.31 (s, 3H), 3.48-3.53 (m, 1H), 3.57-3.65 (m, 1H), 3.71 (s, 3H), 4.11-4.13 (t, J = 2.7 Hz, 1H), 4.17-4.18 (d, J = 3.0 Hz, 1H), 4.69-4.70 (d, J = 2.1 Hz, 1H), 6.29 (br s, 1H), 6.72-6.75 (dd, J = 2.1 Hz, 2H), 7.10-7.12 (d, J = 6.9 Hz, 1H), 7.19-7.22 (dd, J = 2.1 Hz, 2H), 7.31-7.35 (m, 5H), 7.45-7.50 (dd, J = 7.2 Hz, 1H), 7.54-7.59 (dd, J = 6.9 Hz 1H), 7.65-7.67 (d, J = 6.3 Hz, 1H), 7.75-7.78 (dd, J = 1.8, 2.1 Hz, 2H). 13C NMR (75 MHz, CDCl3): δ 29.1, 38.6, 51.9, 55.4, 56.4, 58.1, 59.8, 66.2, 73.76, 88.4, 108.38, 114.3, 119.9, 120.5, 122.4, 125.7, 125.8, 127.1, 127.7, 127.9, 128.8, 128.9, 129.8, 130.8, 134.4, 134.7, 137.4, 139.0, 156.4, 165.6, 171.9. DEPT-135 NMR (75 MHz, CDCl3): δ 29.1, 38.6, 51.9, 55.4, 56.3, 58.1, 59.8, 73.7, 114.3, 119.9, 120.5, 122.4, 125.7, 125.8, 127.1, 127.7, 127.9, 128.8, 128.9. Mass: m/z 576.70 (M+). Anal.Calcd. For C35H32N2O6: C, 72.90; H, 5.59; N, 4.86 %; Found: C, 72.82, H, 5.67, N, 4.95 %.

**Compound 12:** Pale yellow solid. (84%), Mp: 248-250 ºC; IR (KBr): 3163, 2361, 1728 cm-1; 1H NMR (300 MHz, CDCl3): δ 2.08 (s, 3H), 2.43-2.51 (m, 1H), 2.96-3.06 (dt, J = 4.8, 5.4 Hz, 1H), 3.36-3.44 (dt, J = 5.1 Hz, 1H), 3.50-3.58 (dt, J = 4.2 Hz, 1H), 3.76 (s, 3H), 4.48-4.49 (d, J = 2.1 Hz, 1H), 4.79 (s, 1H), 4.95-4.96 (d, J = 1.8 Hz, 1H), 6.62 (br s, 1H), 6.78-6.81 (d, J = 8.7 Hz, 2H), 7.22-7.25 (d, J = 9.0 Hz, 2H), 7.32-7.39 (m, 5H), 7.60-7.65 (t, J = 7.8 Hz 1H), 7.75-7.82 (m, 2H), 7.96-8.01 (t, J = 8.4, 7.2 Hz 2H), 8.18-8.21 (d, J = 8.1 Hz, 1H). 13C NMR (75 MHz, CDCl3): δ 27.7, 35.2, 47.4, 51.3, 54.5, 55.5, 61.6, 69.0, 77.2, 81.3, 114.5, 118.6, 119.5, 122.0, 123.7, 127.1, 127.9, 128.0, 128.7, 129.2, 129.6, 130.6, 130.9, 131.1, 132.6, 134.1, 143.6, 156.4, 165.4. Mass: m/z 543.57 (M+). Anal.Calcd. For C34H29N3O4: C, 75.12; H, 5.38; N, 7.73 %; Found: C, 75.19, H, 5.30, N, 7.81 %.

**Compound 13a:** Yellow solid. (80%), M.p: δ 185-187 ºC; IR (KBr): 3148, 1751, 1720 cm-1; 1H NMR (300 MHz, CDCl3): δ 1.78-1.93 (m, 2H), 2.08-2.15 (m, 2H), 2.37-2.44 (dd, J = 7.5, 7.8 Hz, 1H), 2.49-2.56 (dd, J = 8.7, 9.0 Hz, 1H), 3.00-3.05 (t, J = 6.6 Hz, 1H), 3.38 (s, 3H), 3.57-3.65 (m, 1H), 3.71 (s, 3H), 3.78-3.84 (m, 1H), 4.28 (s, 1H), 4.37 (s, 1H), 5.69 (s, 1H), 6.70-6.73 (d, J = 8.7 Hz, 2H), 7.04-7.09 (t, J = 7.2, 6.9 Hz, 1H), 7.16-7.19 (d, J = 8.7 Hz, 2H), 7.23-7.25 (m, 2H), 7.32-7.37 (t, J = 6.0, 7.2 Hz, 3H), 7.46-7.51 (m, 3H), 7.71-7.78 (dd, J = 8.1, 6.6 Hz, 2H). 13 C NMR (75 MHz, CDCl3): δ 26.8, 31.0, 36.6, 49.5, 52.2, 55.3, 60.0, 66.6, 68.2, 73.1, 80.6, 89.6, 109.2, 114.3, 116.5, 119.8, 120.1, 122.6, 123.4, 125.6, 126.1, 127.2, 128.7, 129.0, 129.6, 130.7, 135.0, 137.1, 139.4, 156.7, 157.8, 163.2, 172.9. DEPT-135 NMR (75 MHz, CDCl3): δ 26.9, 31.0, 36.6, 49.5, 52.3, 55.3, 60.0, 66.6, 73.1, 80.6, 114.3, 116.5, 119.8, 120.1, 122.6, 123.4, 125.6, 126.1, 127.2, 128.7, 129.6. Mass: m/z 618.61 (M+). Anal.Calcd. For C37H34N2O7: C, 71.83, H, 5.54, N, 4.53%; Found: C, 71.92, H, 5.62, N, 4.46%

**Compound 13b:** Pale yellow solid. (83%), M.p: 256-258ºC; IR (KBr): 3194, 1759, 1721 cm-1; 1H NMR (300 MHz, CDCl3): δ 1.87-2.00 (m, 2H), 2.10-2.20 (m, 1H), 2.18-2.25 (m, 2H), 2.35-2.42 (dd, J = 7.8 Hz, 1H), 2.99-3.40 (m, 1H), 3.11 (s, 3H), 3.52-3.60 (dd, J = 8.7, 9.0 Hz, 1H), 3.72 (s, 3H), 3.96-4.03 (dd, J = 7.5, 6.9 Hz, 1H), 4.12 (s, 1H), 4.28-4.29 (d, J = 3.0 Hz, 1H), 4.67 (s, 1H), 6.72-6.75 (d, J = 8.7 Hz, 2H), 7.16-7.19 (d, J = 8.7 Hz, 2H), 7.25-7.36 (m, 6H), 7.44-7.49 (t, J = 7.5, 7.8 Hz, 1H), 7.53-7.58 (m, 2H), 7.73-7.78 (m, 2H). 13C NMR (75 MHz, CDCl3): δ 26.9, 31.2, 36.4, 49.5, 51.9, 55.4, 56.7, 60.2, 66.7, 68.3, 75.6, 90.3, 108.8, 114.3, 119.8, 123.1, 125.6, 126.0, 127.1, 127.8, 127.9, 128.8, 129.0, 129.7, 130.8, 134.8, 135.1, 137.1, 139.6, 156.4, 165.4, 172.9. DEPT-135 NMR (75 MHz, CDCl3): δ 26.9, 31.2, 36.4, 49.5, 51.9, 55.4, 56.7, 60.2, 66.7, 75.6, 114.2, 119.8, 119.9, 123.1, 125.6, 126.1, 127.1, 127.8, 127.9, 128.8, 129.0. Mass: m/z 602.62 (M+). Anal.Calcd. For C37H34N2O6: C, 73.74; H, 5.69; N, 4.65 %; Found: C, 73.83, H, 5.60, N, 4.74%.

**Compound 14:** Pale yellow solid. (80%), M.p: 196-198 ºC; IR (KBr): 3202, 2353, 1721 cm-1; 1H NMR (300 MHz, CDCl3): δ 1.86-2.00 (m, 2H), 2.07-2.12 (m, 2H), 2.18-2.21 (m, 1H), 2.40-2.47 (m, 1H), 2.93-3.02 (m, 1H), 3.06-3.15 (m, 1H), 3.71 (s, 3H), 3.78 (s, 1H), 3.82-3.85 (m, 1H), 4.32 (s, 1H), 4.79 (s, 1H), 6.73-6.77 (m, 2H), 7.18-7.21 (m, 2H), 7.26-7.37 (m, 5H), 7.48-7.51 (m, 1H), 7.57-7.70 (m, 3H), 7.79-7.83 (m, 1H), 7.87-7.90 (m, 1H). 13C NMR (75 MHz, CDCl3): δ 26.5, 31.0, 32.9, 49.3, 53.5, 55.4, 55.8, 59.4, 67.9, 75.3, 89.5, 110.0, 114.5, 120.4, 120.7, 124.4, 126.0, 126.9, 127.8, 127.9, 128.1, 129.0, 129.1, 129.2, 130.8, 132.9, 133.9, 137.3, 137.6, 156.9, 165.3. DEPT-135 NMR (75 MHz, CDCl3): δ 26.5, 31.0, 32.8, 49.3, 55.4, 55.7, 59.3, 67.9, 75.2, 114.5, 120.4, 120.6, 124.4, 126.0, 126.8, 127.8, 127.9, 128.1, 129.1, 129.2. Mass: m/z 569.70 (M+). Anal.Calcd. For C36H31N3O4: C, 75.90; H, 5.49; N, 7.38 %; Found: C, 75.83, H, 5.58, N, 7.45%.

**Compound 16a:** Colorless solid. (85%), M.p: 172-174 ºC; IR (KBr): 3186, 1758, 1751, 1713 cm-1; 1H NMR (300 MHz, CDCl3): δ 1.94-2.02 (m, 1H), 2.30-2.36 (m, 1H), 2.40 (s, 3H), 3.28-3.34 (dd, J = 7.2, 8.1 Hz, 1H), 3.42-3.49 (m, J = 8.7, 7.8 Hz, 1H), 3.71 (s, 6H), 4.18 (s, 1H), 4.31 (s, 1H), 5.61 (s, 1H), 6.75-6.78 (d, J = 8.7 Hz, 2H), 7.03-7.08 (t, J = 7.2, 6.9 Hz, 1H), 7.15-7.17 (d, J = 8.7 Hz, 2H), 7.21-7.25 (m, 2H), 7.31-7.36 (t, J = 7.8, 7.5 Hz, 2H), 7.47-7.51 (t, J = 6.9 Hz, 1H), 7.64-7.70 (m, 3H). 13C NMR (75 MHz, CDCl3): δ 28.4, 37.6, 52.9, 55.4, 58.2, 59.2, 67.0, 72.2, 80.5, 85.3, 103.2, 114.4, 116.3, 120.1, 122.6, 122.7, 125.1, 128.8, 129.6, 130.7, 136.4, 137.1, 149.2, 156.9, 157.6, 161.1, 171.1, 198.2. DEPT-135 NMR (75 MHz, CDCl3): δ 28.4, 37.6, 52.9, 55.4, 58.2, 59.1, 72.2, 80.4, 114.4, 116.3, 120.1, 122.6, 122.7, 125.1, 129.6, 130.7, 137.1. Mass: m/z 570.64 (M+). Anal.Calcd. For C32H30N2O8: C, 67.36, H, 5.30, N, 4.91%; Found: C, 67.43, H, 5.39, N, 4.82 %.

**Compound 16b:** Colorless solid. (79%), M.p: 172-174 ºC; IR (KBr): 3116, 1759, 1752, 1721 cm-1; 1H NMR (300 MHz, CDCl3): δ 2.01-2.06 (m, 1H), 2.47 (s, 3H), 3.33-3.43 (m, 2H), 3.50 (s, 3H), 3.75 (s, 3H), 4.05 (s, 1H), 4.23-4.24 (d, J = 3.3 Hz, 1H), 4.57 (s, 1H), 5.66 (br s, 1H), 6.78-6.80 (d, J = 8.7 Hz, 2H), 7.18-7.21 (d, J = 8.7 Hz, 2H), 7.29-7.37 (m, 5H), 7.50-7.55 (t, J = 7.2, 7.5 Hz ,1H), 7.68-7.76 (m, 2H), 7.80-7.82 (d, J = 7.5 Hz, 1H). 13 C NMR (75 MHz, CDCl3): δ 28.9, 37.7, 52.6, 55.4, 56.6, 58.2, 59.4, 67.1, 75.1, 85.8, 102.8, 114.3, 120.2, 122.7, 125.1, 127.8, 129.0, 129.4, 130.7, 134.3, 136.6, 137.1, 149.3, 156.7, 165.3, 170.8, 198.4. DEPT-135 NMR (75 MHz, CDCl3): δ 28.9, 37.7, 52.6, 55.4, 56.6, 58.2, 59.4, 75.1, 77.2, 114.3, 120.2, 122.7, 125.1, 127.8, 129.0, 130.7, 137.1. Mass: m/z 554.51 (M+). Anal.Calcd. For C32H30N2O7: C, 69.30, H, 5.45, N, 5.05 %; Found: C, 69.37, H, 5.39, N, 4.97 %.

**Compound 17:** White solid. (83%), M.p: 132-134 ºC; IR (KBr): 3163, 2355, 1759, 1720 cm-1; 1H NMR (300 MHz, CDCl3): δ 1.92-2.02 (m, 1H), 2.31-2.36 (dd, J = 4.2, 3.9 Hz, 1H,), 2.41(s, 3H), 3.30-3.35 (t, J = 7.5 Hz, 1H), 3.43-3.48 (m, 1H), 3.73 (s, 3H), 4.17 (s, 1H), 4.31 (s, 1H), 5.61 (s, 1H), 6.76-6.78 (d, J = 8.7 Hz, 2H), 7.04-7.09 (t, J = 6.9 Hz, 1H), 7.15-7.18 (d, J = 8.4 Hz, 2H), 7.21-7.23 (d, J = 7.8 Hz, 2H), 7.32-7.37 (t, J = 7.2, 7.5 Hz, 2H), 7.48-7.52 (m, 1H), 7.64-7.76 (m, 3H). 13C NMR (75 MHz, CDCl3): δ 23.4, 37.6, 52.9, 55.4, 58.2, 59.1, 67.0, 72.2, 80.5, 85.3, 103.2, 114.4, 116.3, 120.1, 122.6, 122.7, 125.1, 128.8, 129.6, 130.7, 136.4, 137.1, 149.2, 156.9, 157.6, 163.1, 171.2, 198.2. DEPT-135 NMR (75 MHz, CDCl3): δ 28.4, 37.6, 52.9, 55.4, 58.2, 59.1, 72.2, 80.5, 114.4, 116.3, 120.1, 122.6, 122.7, 125.1, 129.6, 130.7, 137.1. Mass: m/z 521.61(M+). Anal.Calcd. For C31H27N3O5: C, 71.39; H, 5.22; N, 8.06%; Found: C, 71.46, H, 5.30, N, 7.78%.

**Compound 18a:** Colorless solid. (82%), M.p: 167-169 ºC; IR (KBr): 3163, 1759, 1750, 1720 cm-1; 1H NMR (300 MHz, CDCl3): δ 1.74-1.86 (m, 3H), 1.89-2.01 (m, 1H), 2.04-2.10 (m, 1H), 2.24-2.31 (dd, J = 7.5 Hz, 1H), 2.44-2.51 (dd, J = 7.2, 7.5 Hz, 1H), 2.85-2.90 (m, 1H), 3.46-3.55 (m, 1H), 3.67 (s, 3H), 3.74 (s, 3H), 4.23 (s, 1H), 4.34 (s, 1H), 5.62 (s, 1H), 6.75-6.78 (d, J = 9.0 Hz, 2H), 7.04-7.09 (t, J = 7.2 Hz, 1H), 7.15-7.23 (m, 4H), 7.32-7.37 (m, 2H), 7.45-7.49 (m, 1H), 7.61 (s, 1H), 7.63-7.68 (t, J = 7.5 Hz, 2H). 13C NMR (75 MHz, CDCl3): δ 26.5, 30.3, 34.7, 48.3, 52.9, 55.4, 59.4, 67.8, 73.7, 77.2, 80.5, 86.5, 104.5, 114.4, 116.4, 120.1, 122.7, 122.9, 124.4, 128.7, 129.6, 130.5, 136.4, 137.0, 149.1, 156.8, 157.6, 162.9, 171.8, 197.0. DEPT-135 NMR (75 MHz, CDCl3): δ 26.5, 30.3, 34.7, 48.3, 53.0, 55.4, 59.4, 67.8, 73.7, 80.5, 114.3, 116.4, 120.1, 122.7, 122.9, 124.4, 129.6, 130.6, 137.0. Mass: m/z 596.70 (M+). Anal.Calcd. For C34H32N2O8: C, 68.45, H, 5.41, N, 4.70%; Found: C, 68.58, H, 5.49, N, 4.76 %.

CCDC-882507 (for 18a) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Compound 18b:** Colorless solid. (84%), M.p: 188-191 ºC; IR (KBr): 3146, 1762, 1755, 1728 cm-1; 1H NMR (300 MHz, CDCl3): δ 1.74-1.89 (m, 2H), 2.01-2.08 (m, 2H), 2.10-2.15 (dd, J = 7.8 Hz, 1H), 2.28-2.35 (dd, J = 6.6 Hz, 1H), 2.84-2.91 (m, 1H), 3.46 (s, 3H), 3.75 (s, 3H), 3.81-3.85 (t, J = 6.9, 6.6 Hz, 1H), 4.07-4.09 (t, J = 2.4, 3.0 Hz 1H), 4.26-4.27 (d, J = 3.3 Hz, 1H), 4.60-4.61 (d, J = 2.1 Hz, 1H), 6.76-6.79 (d, J = 9.0 Hz, 2H), 7.16-7.19 (d, J = 9.0 Hz, 2H), 7.29-7.38 (m, 5H), 7.46-7.51 (m, 1H), 7.65-7.70 (m, 3H). 13C NMR (75 MHz, CDCl3): δ 26.6, 30.5, 34.5, 48.4, 52.6, 55.4, 56.6, 59.6, 67.8, 68.0, 76.3, 87.0, 103.7, 114.3, 120.0, 122.8, 124.5, 127.8, 127.9, 129.0, 129.3, 130.5, 134.4, 136.4, 137.1, 149.3, 156.6, 165.2, 171.6, 197.2. DEPT-135 NMR (75 MHz, CDCl3): δ 26.6, 30.5, 34.5, 48.4, 52.7, 55.4, 56.6, 59.6, 68.0, 76.3, 114.3, 120.0, 122.9, 124.5, 127.8, 127.9, 129.1, 130.6, 137.1. Mass: m/z 580.71 (M+). Anal.Calcd. For C34H32N2O7: C, 70.33; H, 5.56; N, 4.82 %; Found: C, 70.24, H, 5.63, N, 4.75 %.

**Compound 19:** White solid. (81%), M.p: 132-134 ºC; IR (KBr): 3140, 2352, 1758, 1716 cm-1; 1H NMR (300 MHz, CDCl3): δ 1.77-1.91 (m, 2H), 1.96-2.01 (m, 2H), 2.27-2.33 (dd, J = 6.6 Hz, 2H), 2.96-3.04 (m, 1H), 3.10-3.19 (m, 1H), 3.69-3.73 (m, 1H), 3.75 (s, 3H), 3.86 (s, 1H), 4.32 (s, 1H), 4.74-4.75 (d, J = 2.1 Hz, 1H), 6.17 (br s, 1H), 6.78-6.81 (d, J = 9.0 Hz, 2H), 7.21-7.24 (d, J = 9.0 Hz, 2H), 7.26-7.39 (m, 5H), 7.52-7.57 (m, 1H), 7.72-7.74 (m, 2H), 7.79-7.82 (d, J = 7.5 Hz, 1H). 13C NMR (75 MHz, CDCl3): δ 26.4, 30.2, 34.6, 49.5, 52.9, 55.4, 55.7, 58.9, 68.5, 74.9, 86.0, 104.4, 114.6, 119.2, 120.1, 123.6, 124.9, 127.8, 128.3, 128.8, 129.3, 131.0, 133.6, 135.7, 137.8, 148.2, 156.9, 164.9, 195.8. DEPT-135 NMR (75 MHz, CDCl3): δ 26.4, 30.2, 34.5, 49.5, 55.4, 55.7, 58.9, 68.5, 74.9, 114.6, 120.1, 123.6, 124.9, 127.8, 128.3, 129.3, 131.0, 137.8. Mass: m/z 547.66 (M+). Anal.Calcd. For C33H29N3O5: C, 72.38; H, 5.34; N, 7.67%; Found: C, 72.45, H, 5.29, N, 7.73%.

CCDC-885084 (for 19) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Result:**

S1 Fig. X-ray crystal structure of compound 6a

(a) S. Sundaramoorthy, R. Rajesh, R. Raghunathan, D. Velmurugan, *Acta Cryst.* **2012**, *E68*, o2202; (b) CCDC-882505 (for **6a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

S2 Fig. X-ray crystal structure of compound 18a

S. Sundaramoorthy, R. Rajesh, R. Raghunathan, D. Velmurugan, *Acta Cryst.* **2012**, *E68*, o2200- o2201; (b) CCDC-882507 (for **18a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif)

S3 Fig. X-ray crystal structure of compound 19

CCDC-885084 (for **19**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif

S4 Fig. 2D representations of *β*-lactam compounds. A) Ampicillin B) Compound 7 C) Compound 6a and D) Compound 3 to the active site pocket of PBP (PDB ID: 2Z2M.