**Supporting Information Available**.

***General synthetic procedure for 7a-b***.

Compound 5 (6.28 mmol) dissolved in 10 mL of acetonitrile was added dropwise to a solution of the crude 4a (8.97 mmol) in 30 mL of acetonitrile containing $K_2CO_3$ (2.47 g, 17.9 mmol) at rt. The resultant suspension was refluxed for 24-30 h. The reaction mixture was cooled, filtered, diluted with EtOAc, washed with water, brine and dried over $Na_2SO_4$. The organic layer was evaporated under vacuum and the brownish oily residue was purified over silica gel column chromatography using hexane / EtOAc (8: 2) as eluent.

**Ethyl 6–[2,5–di(trimethylsilyl)tetrahydro–1H–1-pyrrolyl]–(E)–2-hexenoate (7a)**.

Pale yellow oil. Yield 65 %. IR (neat): 2952, 1723, 1367, 1249 $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 200 MHz): δ 0.05 (s, 18H), 1.27 (t, *J* = 7.3 Hz, 3H), 1.35- 2.03 (m, 6H), 2.05- 2.62 (m, 6H), 4.18 (q, *J* = 7.3 Hz, 2H), 5.83 (dt, *J* = 15.2, 1.4 Hz, 1H), 6.97 (dt, *J* = 15.2, 6.9 Hz, 1H). MS (*m/z*, relative intensity): 355($M^+$, 1), 340 (9), 282 (100), 73 (12).

**Ethyl 7–[2,5–di(trimethylsilyl)tetrahydro–1H–1-pyrrolyl]–(E)–2-heptenoate (7b)**.

Yellow viscous oil. Yield 67 %. IR (neat): 3429, 2952, 1717, 1368 $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 200 MHz): δ 0.05 (s, 18H), 1.27 (t, *J* = 7.2 Hz, 3H), 1.35- 1.73 (m, 5H), 1.76- 1.98 (m, 3H), 2.11- 2.59 (m, 6H), 4.18 (q, *J* = 7.2 Hz, 2H), 5.83 (dt, *J* = 15.6, 1.4 Hz, 1H), 6.95 (dt, *J* = 15.6, 6.9 Hz, 1H). $^{13}C$ NMR ($CDCl_3$, 50 MHz): δ - 2.12, 13.88, 25.60, 26.36, 29.66, 31.88, 55.29, 55.57, 59.38, 121.18, 148.32, 165.80. MS (*m/z*, relative intensity): 369 ($M^+$,1), 354 (6), 296 (100), 73 (53).

***General synthetic procedure for 7c-d***.

To a stirring solution of amine 4b (6.55 mmol) in 50 mL of ethanol at rt was added 6a (4.6 mmol) dissolved in 10 mL of ethanol. After stirring for 3 h, $NaBH_3CN$ (0.29 g, 4.6 mmol) followed by glacial acetic acid (1.0 mL) was added. The reaction mixture was basified by slow addition of concentrated $NH_4OH$ solutions. The reaction mixture was diluted with water (10 mL), extracted with chloroform (3 X 25 mL), washed with brine and dried over $Na_2SO_4$. The organic layer was concentrated and the crude residue was purified over silica gel chromatography using hexane / EtOAc (9: 1) as eluent.

**Ethyl 6–[2,6–di(trimethylsilyl)hexahydro–1–pyridinyl]–(E)–2-hexenoate (7c)**.

Pale yellow oil. Yield 73 %. IR (neat): 2951, 1723, 1402 $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 200 MHz): δ 0.05 (s, 18H), 1.30 (t, *J* = 7.3 Hz, 3H), 1.35- 1.70 (m, 8H), 2.03- 2.42 (m, 5H), 2.83- 2.95 (m, 1H), 4.17 (q, *J* = 7.3 Hz, 2H), 5.78 (dt, *J* = 15.4, 1.4, Hz, 1H), 6.97 (dt, *J* = 15.4, 6.9 Hz, 1H). $^{13}C$ NMR ($CDCl_3$, 50 MHz): δ - 1.45, 14.12, 19.65, 25.06, 28.25, 29.85, 50.34, 51.53, 59.82, 121.25, 149.06, 166.36. MS (*m/z*, relative intensity): 369 ($M^+$, 1), 354 (4), 296 (100), 73 (81).

**Ethyl 7–[2,6–di(trimethylsilyl)hexahydro–1–pyridinyl]–(E)–2-heptenoate (7d**).

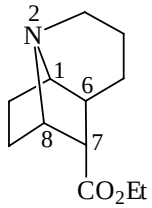
Thick yellow oil. Yield 75 %. IR (neat): 2949, 1723, 1655, 1368$cm^{-1}$. $^1H$ NMR ($CDCl_3$, 200 MHz): δ 0.05 (s, 18H), 1.29 (t, *J* = 7.3 Hz, 3H),1.33- 1.72 (m, 10H), 2.12- 2.43 (m, 5H), 2.76- 2.95 (m, 1H), 4.19 (q, *J* = 7.3 Hz, 2H), 5.83 (dt, *J* = 15.2, 1.4 Hz, 1H), 6.97 (dt, *J* = 15.2, 6.9 Hz, 1H). $^{13}C$ NMR ($CDCl_3$, 50 MHz): δ - 1.49, 14.05, 19.62, 25.06, 25.74, 29.25, 32.10, 50.57, 51.45, 59.69, 121.33, 148.65, 166.22. MS (*m/z*, relative intensity): 383 ($M^+$, 1), 310 (58), 156 (49), 73 (100).

***General Intramolecular [3 + 2] - Cycloaddition Procedure***.

A solution of 7 (2.8 mmol) in 10 mL of dry $CH_2Cl_2$ was introduced dropwise to an argon flushed 50 mL two neck flask containing a suspension of vacuum dried Ag(I)F (0.89 g, 7.02 mmol) in $CH_2Cl_2$ (30 mL).

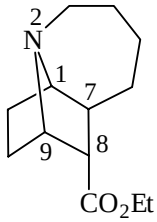
The color of the reaction mixture gradually turned to dark brown with concomitant deposition of silver on the surface of the flask in the form of mirror. The reaction mixture was periodically monitored through TLC. After stirring for 4- 6 h, the reaction mixture was filtered through a small plug of celite and the solvent was evaporated to give a crude brown residue. The crude residues were purified by silica gel column chromatography using ($CHCl_3$: MeOH: $NH_3$ = 97: 2: 1) as eluent.

**Ethyl 2–azatricyclo[4.4.0.0$^{2,8}$]decane–7–carboxylate (8a)**.



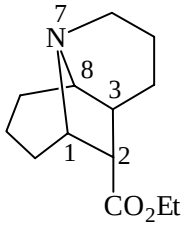

Thick yellow oil. Yield 61 %. IR (neat): 3145, 2927, 1723, 1395 cm$^{-1}$. $^1$H NMR ($CDCl_3$, 500 MHz): δ 1.22- 1.25 (m, 1H), 1.27 (t, *J* = 7.3 Hz, 3H), 1.31- 1.43 (m, 2H), 1.51- 1.64 (m, 3H), 1.65- 1.78 (m, 2H), 2.53 (m, 1H, $H_{6endo}$), 2.95 (d, *J* = 5.7 Hz, 1H, $H_{7exo}$), 3.05- 3.17 (m, 3H, $H_{3exo}$, $H_{3endo}$, $H_1$), 3.73 (t, *J* = 4.6 Hz, 1H, $H_8$), 4.15 (q, *J* = 7.3 Hz, 2H). $^{13}$C NMR ($CDCl_3$, 125 MHz): δ 14.06, 17.45, 25.49, 26.73, 28.07, 39.79, 46.17, 48.69, 60.42, 64.22, 65.31, 172.77. MS (*m/z*, relative intensity): 209 ($M^+$, 56), 180 (26), 164 (28), 136 (100), 83 (68). HRMS: calcd for $C_{12}H_{19}NO_2$ 209.1415 found 209.1411.

**Ethyl 2–azatricyclo[5.4.0.0$^{2,9}$]undecane–8–carboxylate (8b).**



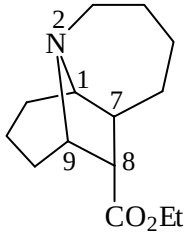

Yellow oil. Yield 41 %. IR (neat): 2937, 1729, 1385 cm$^{-1}$. $^1$H NMR ($CDCl_3$, 200 MHz): δ 1.27 (t, *J* = 7.3 Hz, 3H), 1.32- 1.87 (m, 10H), 2.53- 2.62 (m, 1H, $H_{7endo}$), 2.62- 2.68 (m, 1H, $H_{3endo}$), 2.88 (t, *J* = 5.1 Hz, 1H, $H_{8exo}$), 3.23- 3.37 (m, 1H, $H_{3exo}$), 3.40 (d, *J* = 3.6 Hz, 1H, $H_1$), 3.55 (t, *J* = 4.3 Hz, 1H, $H_9$), 4.15 (q, *J* = 7.3 Hz, 2H). $^{13}$C NMR ($CDCl_3$, 50 MHz): δ 14.11, 24.59, 25.82, 27.39, 29.26, 29.52, 45.52, 49.56, 50.29, 60.52, 63.72, 66.54, 172.89.

**Ethyl 7–azatricyclo[5.4.0.0$^{3,8}$]undecane–2–carboxylate (8c).**




Thick yellow oil. Yield 69 %. IR (neat): 3147, 2930, 1723, 1400 cm$^{-1}$. $^1$H NMR ($CDCl_3$, 200 MHz): δ 1.27 (t, *J* = 7.3 Hz, 3H), 1.35- 1.48 (m, 2H), 1.53- 1.84 (m, 6H), 1.85- 2.13 (m, 2H), 2.78 (m, 1H, $H_{3endo}$), 2.87 (bs, 1H, $H_8$), 2.93- 3.07 (m, 2H, $H_{6endo}$, $H_{6exo}$), 3.07- 3.14 (d, *J* = 6.3 Hz, 1H, $H_{2exo}$), 3.58- 3.69 (m, 1H, $H_1$), 4.04- 4.32 (m, 2H). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ 14.11, 15.97, 18.47, 29.41, 29.74, 32.04, 39.51, 50.32, 53.96, 60.19, 64.08, 67.80, 173.53. MS (*m/z*, relative intensity): 223 ($M^+$, 77), 194 (55), 178 (38), 150 (78), 136 (43), 97 (100). HRMS: calcd for $C_{13}H_{21}O_2N$ 223.1572 found 223.1563.

**Ethyl 2–azatricyclo[5.5.0.0$^{2,9}$]dodecane–8–carboxylate (8d).**




Thick yellow oil. Yield 64 %. IR (neat): 2929, 1716, 1398 cm$^{-1}$. $^{1}$H NMR ($CDCl_3$, 200 MHz): δ 1.28 (t, *J* = 7.2 Hz, 3H), 1.33- 1.92 (m, 12H), 2.61 (dt, *J* = 14.8, 5.4 Hz, 1H, $H_{3endo}$), 2.81- 2.94 (m, 1H, $H_{7endo}$), 2.95- 3.06 (t, *J* = 7.2 Hz, 1H, $H_{8exo}$), 3.06- 3.16 (m, 1H, $H_{3exo}$), 3.22 (bs, 1H, $H_1$), 3.32- 3.45 (m, 1H, $H_9$), 4.04- 4.31 (m, 2H). $^{13}$C NMR ($CDCl_3$, 50 MHz): δ 14.08, 16.75, 25.49, 27.53, 29.50, 30.43, 32.0, 43.95, 54.98, 55.97, 59.99, 62.43, 66.06, 173.0. MS (*m/z*, relative intensity): 237 ($M^+$, 27), 208 (42), 164 (54), 123 (87), 97 (100). HRMS: calcd for $C_{14}H_{23}O_2N$ 237.1728 found 237.1747.

***General synthetic procedure for 10a-b***.

Compound 9 (5.22 mmol) dissolved in 10 mL of acetonitrile was added dropwise to a solution of the amine 4 (6.97 mmol) in acetonitrile (15 mL) containing $K_2CO_3$ (1.93 g, 13.96 mmol). The resultant suspension was refluxed for 6- 8 h. The reaction mixture was cooled, filtered, diluted with EtOAc, washed with water, brine and dried over $Na_2SO_4$. The organic layer was evaporated and the brownish oil residue was purified over silica gel column chromatography using hexane / EtOAc (9: 1) as eluent.

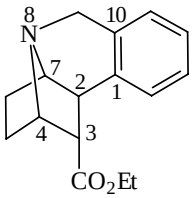
**Ethyl 3–{2-[2,5–di(trimethylsilyl)tetrahydro–1H–pyrrolyl methyl]phenyl}–(E)–2–propenoate (10a).**

Pale yellow oil. Yield 81 %. IR (neat): 2935, 1695, 1428 cm$^{-1}$. $^{1}$H NMR ($CDCl_3$, 200 MHz): δ -0.1 (s, 18H), 1.35 (t, *J* = 7.3 Hz, 3H), 1.55- 1.77 (m, 2H), 1.83- 2.04 (m, 2H), 2.33 (t, *J* = 4.8 Hz, 2H), 3.43 (d, *J* = 13.7 Hz, 1H), 3.98 (d, *J* = 13.7 Hz, 1H), 4.14- 4.35 (m, 2H), 6.33 (d, *J* = 15.6 Hz, 1H), 7.17- 7.36 (m, 3H), 7.48- 7.72 (m, 1H), 8.48 (d, *J* = 15.6 Hz, 1H). $^{13}$C NMR ($CDCl_3$, 50 MHz): δ -2.26, 14.06, 26.36, 55.38, 57.48, 59.84, 119.19, 126.2, 127.19, 129.14, 131.15, 134.7, 138.99, 142.77, 166.43. MS (*m/z*, relative intensity): 403 ($M^+$, 2), 330 (100), 117 (35), 73 (39).

**Ethyl 3–{2-[2,6–di(trimethylsilyl)hexahydro–1–pyridinyl methyl]phenyl}–(E)–2–propenoate (10b).**

Thick yellow oil. Yield 84 %. IR (neat): 2920, 1716, 1441, 1244 cm$^{-1}$. $^{1}$H NMR ($CDCl_3$, 200 MHz): δ 0.05 (s, 18H), 1.32 (t, *J* = 7.3 Hz, 3H), 1.47- 1.77 (m, 6H), 2.22- 2.40 (m, 2H), 3.63 (d, *J* = 13.7 Hz, 1H), 4.28 (q, *J* = 7.3Hz, 2H), 4.34 (d, *J* = 13.7 Hz, 1H), 6.34 (d, *J* = 15.6 Hz, 1H), 7.21- 7.45 (m, 2H), 7.50- 7.67 (m, 2H), 8.27 (d, *J* = 15.6 Hz, 1H). $^{13}$C NMR ($CDCl_3$, 50 MHz): δ -1.23, 14.19, 19.68, 24.76, 50.87, 51.57, 60.06, 119.52, 126.12, 126.85, 129.44, 130.39, 134.08, 139.61, 142.41, 166.58. MS (*m/z*, relative intensity): 417 ($M^+$, 2), 345 (100), 131 (16), 73 (41).

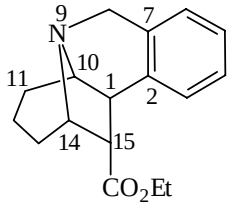
**Ethyl 8-azatetracyclo[8.4.0.0$^{2,7}$.0$^{4,8}$]tetradeca-1(10),11, 13-triene-3-carboxylate (11a).**




Viscous yellow oil. Yield 73 %. IR (neat): 2975, 1729, 1455,1177 cm$^{-1}$. $^{1}$H NMR ($CDCl_3$, 200 MHz): δ 1.27 (t, *J* = 7.3 Hz, 3H), 1.28- 1.43 (m, 1H), 1.55- 1.97 (m, 3H), 2.77 (d, *J* = 6.3 Hz, 1H, $H_{3exo}$), 3.18 (d, *J* =

5.4 Hz, 1H, $H_7$), 3.36 (d, *J* = 1.8 Hz, 1H, $H_{2endo}$), 3.74 (t, *J* = 4.9 Hz, 1H, $H_4$), 4.04 (d, *J* = 18.5 Hz, 1H, $H_{9endo}$), 4.14 (q, *J* = 7.3 Hz, 2H), 4.42 (d, *J* = 18.5 Hz, 1H, $H_{9exo}$), 6.95- 7.20 (m, 4H). $^{13}C$ NMR ($CDCl_3$, 50 MHz): δ 13.93, 25.43, 25.7, 45.33, 50.67, 56.31, 60.1, 62.32, 66.78, 124.63, 125.19, 125.62, 125.98, 132.88, 143.98, 172.03. MS (*m/z*, relative intensity): 257 ($M^+$, 42), 184 (100), 169 (47), 115 (77), 91 (40), 68 (76). HRMS: cald for $C_{16}H_{19}O_2N$ 257.1415, found 257.1426.

**Ethyl 9-azatetracyclo[8.5.0.0$^{2,7}$.0$^{9,14}$]pentadeca-2(7),3,5-triene-15-carboxylate (11b).**




Viscous yellow oil. Yield 75 %. IR (neat): 2937, 1730, 1457, 1190 $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 200 MHz): δ 1.27 (t, *J* = 7.3 Hz, 3H), 1.37- 1.67 (m, 2H), 1.72- 2.0 (m, 4H), 3.03 (dd, *J* = 7.8, 2.0 Hz, 1H, $H_{15exo}$), 3.16 (bs, 1H, $H_{10}$), 3.59 (d, *J* = 2.0 Hz, 1H, $H_{1endo}$), 3.68 (t, *J* = 3.9 Hz, 1H, $H_{14}$), 3.77 (d, *J* = 18.0 Hz, 1H, $H_{8endo}$), 4.05- 4.31 (m, 2H), 4.55 (d, *J* = 18.0 Hz, 1H, $H_{8exo}$), 6.82- 7.20 ( m, 4H). $^{13}C$ NMR ($CDCl_3$, 50 MHz): δ 14.03, 15.79, 29.20, 43.84, 58.40, 58.68, 60.21, 65.27, 67.74, 123.77, 125.17, 125.93, 126.24, 132.8, 147.9, 172.05. MS (*m/z*, relative intensity): 271 ($M^+$, 62), 198 (100), 184 (37), 156 (24), 117 (45), 82 (22). HRMS: cald for $C_{17}H_{21}O_2N$ 271.1572 found 271.1567.