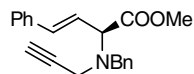


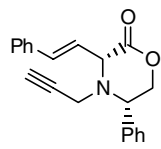
## Supporting Information

### Compound 4a:



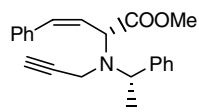
IR (KBr) 3269, 2925, 2844, 1739,  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  7.28 - 7.45 (m, 10H), 6.81 (d,  $J = 15.9$  Hz, 1H), 6.33 (dd,  $J = 15.9$  Hz, 8.4 Hz, 1H), 4.24 (d,  $J = 8.4$  Hz, 1H), 3.83 (d,  $J = 13.3$  Hz, 1H), 3.80 (s, 3H), 3.78 (d,  $J = 13.3$  Hz, 1H), 3.49 (dd,  $J = 17.6$ , 2.3 Hz, 1H), 3.38 (dd,  $J = 17.6$ , 2.3 Hz, 1H), 2.31 (m, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  172.3, 138.2, 136.3, 135.7, 129.4, 128.9, 128.6, 128.4, 127.6, 126.9, 124.6, 78.67, 74.08, 68.30, 55.05, 52.34, 39.33; EIMS  $m/z$  (%) 319 ( $\text{M}^+$ , 1), 260 (100); Anal. calcd for  $\text{C}_{21}\text{H}_{21}\text{NO}_2$ : C, 78.97; H, 6.63; N 4.39. Found: C, 79.17; H, 6.83; N, 4.17.

### Compound 4d:



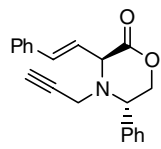
$[\alpha]_{\text{D}}^{20} = -141.1$  (c 1.01,  $\text{CHCl}_3$ ); IR (KBr) 3278, 2926, 1746  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  7.47 - 7.26 (m, 10H), 6.89 (d,  $J = 15.8$  Hz, 1H), 6.25 (dd,  $J = 15.8$ , 7.4 Hz, 1H), 4.16 (dd,  $J = 0.7$ , 3.3 Hz, 1H), 3.44 (dd,  $J = 17.8$ , 2.3 Hz, 1H), 3.23 (dd,  $J = 17.8$ , 2.3 Hz, 1H), 2.29 (m, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  168.9, 135.9, 135.2, 129.0, 128.9, 128.5, 128.2, 128.1, 126.7, 124.4, 76.59, 74.71, 71.83, 64.04, 57.75, 40.11; EIMS  $m/z$  (%) 317 ( $\text{M}^+$ , 3), 168 (100); Anal. calcd for  $\text{C}_{21}\text{H}_{19}\text{NO}_2$ : C, 79.47; H, 6.03; N, 4.41. Found: C, 79.15; H, 5.94; N, 4.15.

### Compound 4e:



$^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 300 MHz)  $\delta$  7.38 - 7.01 (m, 10H), 6.56 (d,  $J = 11.6$  Hz, 1H), 5.98 (dd,  $J = 11.6$ , 10.0 Hz, 1H), 4.90 (d,  $J = 10.0$  Hz, 1H), 4.29 (q,  $J = 6.8$  Hz, 1H), 3.60 (dd,  $J = 4.2$ , 2.4 Hz, 1H), 3.34 (s, 3H), 1.83 (m, 1H), 1.22 (d,  $J = 9.8$  Hz, 3H); EIMS  $m/z$  (%) 274 ( $\text{M}^+ - \text{COOMe}$ , 100).

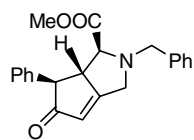
Compound **5d**:



$[\alpha]_D^{20} = +229.3$  (c 1.39,  $\text{CHCl}_3$ ); IR(KBr) 3304, 1749  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  7.47 - 7.26 (m, 10H), 6.85 (d,  $J = 15.8$  Hz, 1H), 6.50 (dd,  $J = 15.8, 8.1$  Hz, 1H), 4.62 - 4.38 (m, 4H), 3.40 (dd,  $J = 17.0, 2.4$  Hz, 1H), 3.16 (dd,  $J = 17.0, 2.4$  Hz, 1H), 2.30 (m, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  168.9, 136.9, 136.0, 128.9, 128.6, 128.5, 128.2, 128.1, 126.7, 121.1, 79.31, 73.69, 72.10, 63.14, 57.23, 39.18; EIMS  $m/z$  (%) 317 ( $\text{M}^+$ , 1); Anal. calcd for  $\text{C}_{21}\text{H}_{19}\text{NO}_2$ : C, 79.49; H, 5.99; N, 4.42. Found: C, 79.06; H, 6.30; N, 4.29.

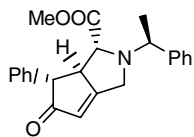
**General procedure for Pauson-Khand reaction of 1, 6- enyne amino esters:** to a solution of 1, 6- enyne amino ester **1a** (160 mg, 0.5 mmol),  $\text{Co}_2(\text{CO})_8$  (18 mg, 0.05 mmol) in dry benzene (3.6 mL), was added tributylphosphane (94 mg, 0.3 mmol) at room temperature, then the reaction mixture was heated at  $70^\circ\text{C}$  under 1 atm of carbon monoxide until the substrate was consumed (monitored by TLC). The residue was concentrated, purified by flash chromatography to afford **1b** (114 mg, 65%) as colorless solid.

Compound **6**:



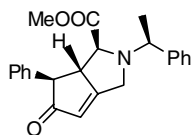
IR (KBr) 3063, 1749, 1714  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  7.37 - 7.10 (m, 10H), 6.02 (q,  $J = 1.9$  Hz, 1H), 4.16 - 4.19 (m, 2H), 3.60 - 3.51 (m, 6H), 3.38 (d,  $J = 17.8$  Hz, 1H), 3.26 (d,  $J = 9.8$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  207.5, 180.1, 171.9, 137.5, 137.3, 129.3, 128.8, 128.7, 128.6, 128.5, 127.8, 127.4, 124.0, 69.4, 58.7, 58.4, 58.3, 52.9, 52.1; EIMS  $m/z$  (%) 347 ( $\text{M}^+$ , 3), 91 (100). Anal. calcd for  $\text{C}_{22}\text{H}_{21}\text{NO}_3$ : C, 76.08; H, 6.05; N, 4.03. Found: C, 75.98; H, 6.30; N, 3.99.

**Compound 7:**



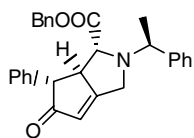
IR (KBr) 3029, 2975, 1746, 1710, 1643  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  7.33 -6.96 (m, 10H), 5.96 (q,  $J = 1.97$  Hz, 1H), 4.03 (dd,  $J = 17.6$ , 1.7Hz, 1H) 3.85 (q,  $J = 6.7$  Hz, 1H), 3.52 (d,  $J = 17.6$  Hz, 1H), 3.48 -3.42 (m, 1H), 3.39 (d,  $J = 4.15$  Hz, 1H), 3.23 (d,  $J = 9.66$  Hz, 1H), 3.19 (s, 3H), 1.38 (d,  $J = 6.7$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  207.3, 179.5, 173.1, 140.7, 136.9, 128.6, 128.5, 128.2, 127.7, 127.6, 127.2, 123.4, 67.6, 61.7, 58.8, 58.1, 52.1, 49.9, 20.6; EIMS  $m/z$  (%) 361 ( $\text{M}^+$ , 0.8), 274(100).

**Compound 8:**



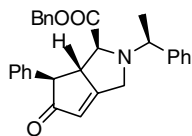
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  7.27 - 7.00 (m, 10H), 5.87 (q,  $J = 1.9$  Hz, 1H), 4.03 (d,  $J = 17.6$  Hz, 1H), 3.83 (q,  $J = 6.8$  Hz, 1H), 3.48 - 3.44 (m, 6H), 3.15 (d,  $J = 9.8$  Hz, 1H), 1.38 (d,  $J = 6.8$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  207.4, 179.6, 172.3, 141.1, 136.8, 128.6, 128.4, 128.2, 128.12, 128.10, 127.7, 127.1, 123.6, 68.5, 61.5, 58.9, 58.1, 51.7, 49.9, 16.8.

**Compound 9:**



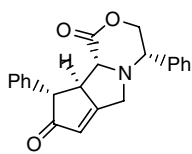
$^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 600 MHz, )  $\delta$  7.43 - 6.87 (m, 15H), 5.58 (m, 1H), 4.68 (d,  $J = 12$  Hz, 1H), 4.60 (d,  $J = 12$  Hz, 1H), 3.91 (q,  $J = 6.6$  Hz, 1H), 3.5 - 3.47 (m, 1H), 3.39 (dt,  $J = 17.4$ , 1.8 Hz, 1H), 3.16 (d,  $J = 3.6$  Hz, 1H), 3.13 (d,  $J = 10.2$  Hz, 1H), 1.11 (d,  $J = 6.6$  Hz, 3H)

**Compound 10:**



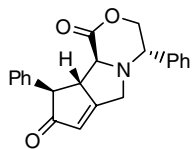
$^1\text{H NMR}$  ( $\text{CDCl}_3$ , 600 MHz)  $\delta$  7.38 - 7.08 (m, 15H), 5.98 (m, 1H), 5.14 (d,  $J = 12.3$  Hz, 1H), 4.82 (d,  $J = 12.3$  Hz, 1H), 4.12 (d,  $J = 17.6$  Hz, 1H), 3.91 (q,  $J = 6.7$  Hz, 1H), 3.63 - 3.60 (m, 1H), 3.48 (d,  $J = 17.6$  Hz, 1H), 3.46 (d,  $J = 4.3$  Hz, 1H), 3.27 (d,  $J = 9.8$  Hz, 1H), 1.43 (d,  $J = 6.4$  Hz, 3H)

**Compound 11:**



$[\alpha]_{\text{D}}^{20} = +227.8$  (c 1.145,  $\text{CHCl}_3$ ); IR(KBr) 2939, 2795, 1750, 1708, 1648  $\text{cm}^{-1}$   
 $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ , 300 MHz)  $\delta$  7.41 - 7.24 (m, 10H), 6.10 (m, 1H), 4.42 (dd,  $J = 11.2, 4.7$  Hz, 1H), 4.30 (dd,  $J = 11.2, 9.2$  Hz, 1H), 4.04 - 3.94 (m, 2H), 3.64 - 3.59 (m, 2H), 3.25 - 3.16 (m, 2H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  208.4, 179.3, 167.5, 137.8, 136.7, 129.4, 129.3, 129.2, 129.1, 128.8, 128.1, 127.4, 125.7, 74.6, 67.3, 63.6, 58.1, 56.2, 51.5 EIMS  $m/z$  (%) 345( $\text{M}^+$ , 17), 104(100);  
 Anal. calcd for  $\text{C}_{22}\text{H}_{19}\text{NO}_3$ : C, 76.52; H, 5.51; N, 4.06. Found: C, 76.29; H, 5.78; N, 3.91.

**Compound 12:**



IR(KBr) 2925, 2795, 1747, 1702, 1657  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ , 300 MHz)  $\delta$  7.35-7.16 (m, 10H), 6.09 (m, 1H), 4.26 - 4.19 (m, 2H), 4.05 - 3.99 (m, 2H), 3.86 (d,  $J = 15.6$  Hz, 1H), 3.66 (m, 1H), 3.55 (d,  $J = 3.6$  Hz, 1H), 3.42 (d,  $J = 15.6$  Hz, 1H); EIMS  $m/z$  (%) 345( $\text{M}^+$ , 11), 104(100);