Supporting Information
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Stereoselective Synthesis of Geometrically Strained, Oxindole Appended Vinyl Cyclopropane and Highly Substituted Cyclopentenes via Sulphur Ylide Cyclopropanation and Vinyl Cyclopropane Rearrangement

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1. General considerations

All the reactions were carried out in oven-dried glassware. Analytical TLC was performed on a pre-coated aluminum sheet of silica gel G/UV-254 of 0.2 mm thickness (Merck, Germany) and was visualized on exposure to either UV-lamp or in an iodine chamber. Column chromatography was performed on silica gel (100-200 mesh, Merck, India) as adsorbent. NMR spectra were recorded at 500 MHz (for $^1$H) and 125 MHz (for $^{13}$C) respectively, either on a JEOL ECA 500 MHz or Brucker Avance DPX-500 MHz spectrometer. Chemical shifts are reported in δ (ppm) relative to TMS ($^1$H) or CDCl$_3$ ($^{13}$C) as internal standard. Mass spectra were recorded using JEOL JMS 600H mass spectrometer. FTIR spectra were recorded on Bruker Alpha FT-IR spectrometer. Absorbencies are reported in cm$^{-1}$. Yields refer to quantities obtained after chromatography. All the solvents used were reagent grade and were purified before use.

2. General experimental procedures

2.1 Synthesis of vinyl cyclopropanes-2-oxindoles (3a-k) and (5a-g)

To a mixture of bromo isomerized MBH adducts 1a (100mg, 0.323 mmol), activated styrene/isatilidines (1.2 equiv.) in dry CH$_3$CN (2.0 mL) at 0 °C was added dimethyl sulfide (1.0 equiv., 0.028 mmol), K$_2$CO$_3$ (1.2 equiv., 53 mg). The mixture was allowed to warm to RT and the progress of reaction was monitored by TLC. After completion of the reaction, solvent was removed under vacuum and then Water (5.0 mL) was added and extracted with ethyl acetate (3×5 mL). The combined organic layer was dried over anhydrous Na$_2$SO$_4$ and solvent was removed \textit{in vacuo}. The crude product obtained was then purified by silica gel column
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chromatography using EtOAc: hexane (20: 80) as eluent to afford vinyl cyclopropanes-2-oxindoles 3 and 5 in good yields (60-85\%).

2.2 Synthesis of (dispirocyclopentene)bisoxindole 6

Spirovinylicyclopropane-2-oxindoles 5a (60mg, 0.130mmol) and MgI₂ (0.2 equiv., 0.007 mg) were taken in a two necked RB flask, septum sealed with reflux setup, evacuated and filled with N₂ gas. Dry THF (3mL) was added via syringe at RT, and then the mixture was set to reflux. After completion of the reaction (monitored by TLC), the solvent was removed under vacuum. The crude product obtained was purified by silica gel column chromatography using EtOAc: hexane (40:60) as eluent to afford (dispirocyclopentene) bisoxindole 6a in good yields (91\% yield).

2.3 Synthesis of bis (spiro-2-oxindoles) 8

Spirovinylicyclopropane-2-oxindoles 5a (60mg, 0.130mmol) and ethyl 2, 3-butadienoate (1.2 equiv., 0.152mmol) 7 were taken in a two neck RB flask, evacuated, filled with nitrogen gas. Toluene (1.5 ml) and tributylphosphine (20 mol %) was added and the mixture was stirred at RT. After completion of the reaction (monitored by TLC), solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography using EtOAc: hexane (30:70) to furnish the corresponding bis (spiro-2-oxindoles) 8a in good yields (79\% yield).

3. Spectroscopic data of new compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>FTIR (KBr):</th>
<th>¹H NMR (500 MHz, CDCl₃/TMS): δ</th>
<th>¹³C NMR (125 MHz, CDCl₃/TMS): δ</th>
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<tr>
<td>3a</td>
<td>3321, 2999, 2250, 1722, 1605, 1514 cm⁻¹</td>
<td>7.42-7.39 (m, 2H), 7.37-7.32 (m, 2H), 7.04 (t, J = 7.5 Hz, 1H), 7.03-6.94 (m, 2H), 6.87 (d, J = 8.0 Hz, 1H), 4.22 (d, J = 9.2 Hz, 1H), 3.96 (s, 3H), 3.82 (s, 3H), 3.45 (d, J = 9.5 Hz, 1H), 3.29 (s, 3H); ¹³C NMR (125 MHz, CDCl₃/TMS): δ 166.2, 165.7, 160.5, 144.5, 132.4, 132.1, 129.7, 129.5, 124.2, 122.7, 122.5, 119.3, 114.6, 113.2, 113.0, 108.7, 55.3, 55.0, 40.2, 33.1, 26.2, 16.6; FAB Mass: Calcd. for C₂₅H₁₉N₃O₅is m/z = 441.43, Found(M+1): m/z = 442.45</td>
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<tr>
<td>3b</td>
<td>3443, 2948, 2248, 1728, 1605, 1530, 1468 cm⁻¹</td>
<td>8.32 (bs, 1H), 8.25 (d, J = 7.6 Hz, 1H), 7.77 (d, J = 7.6 Hz, 1H), 7.64-7.60 (m, 2H), 7.37 (t, J = 7.6 Hz, 1H), 7.03 (t, J = 7.6 Hz, 1H), 6.84 (d, J = 7.6 Hz, 1H), 4.24 (q, J = 6.8 Hz, 2H), 3.97 (s, 3H), 3.85 (d, J = 8.9 Hz, 1H), 3.55 (d, J = 9.2 Hz, 1H), 3.26 (s, 3H), 1.26 (t, J = 6.8 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃/TMS): δ 166.6, 165.4, 164.7, 148.6, 135.5, 134.6, 132.0, 131.4, 130.1,</td>
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125.1, 124.2, 123.8, 122.7, 119.4, 115.9, 63.6, 53.0, 40.0, 35.6, 32.2, 26.3, 14.1;  
FAB Mass: Calcd. for C$_{26}$H$_{21}$N$_3$O$_5$ is m/z = 455.46, Found(M+1): m/z = 456.44

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<th>Compound</th>
<th>FTIR (KBr):</th>
<th>$^1$H NMR (500 MHz, CDCl$_3$/TMS): δ</th>
<th>$^{13}$C NMR (125 MHz, CDCl$_3$/TMS): δ</th>
<th>FAB Mass: Calcd. for C$<em>{24}$H$</em>{19}$N$_3$O$_7$ is m/z = 461.42, Found(M+): m/z = 461.69</th>
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<td>3c</td>
<td>3442, 2931, 2247, 2202, 1720, 1599, 1437 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$<em>3$/TMS): δ 7.41-7.38 (m, 2H), 7.33 (d, J = 8.4 Hz, 2H), 7.03 (t, J = 7.6 Hz, 1H), 6.95 (d, J = 8.4 Hz, 2H), 6.87 (d, J = 7.6 Hz, 1H), 4.22 (d, J = 9.9 Hz, 1H), 3.96 (s, 3H), 3.82 (s, 3H), 3.46 (d, J = 9.2 Hz, 1H), 3.29 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$<em>3$/TMS): δ 166.3, 165.8, 160.5, 144.6, 132.5, 129.9, 126.6, 124.3, 122.8, 122.5, 119.2, 114.7, 113.3, 113.2, 108.9, 55.8, 53.2, 40.3, 33.2, 26.4, 16.7; FAB Mass: Calcd. for C$</em>{24}$H$</em>{19}$N$_3$O$_7$ is m/z = 461.42, Found(M+): m/z = 461.69</td>
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<td>3d</td>
<td>3433, 3005, 2943, 2244, 1709, 1600, 1466 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$<em>3$/TMS): δ 7.41-7.38 (m, 2H), 7.29-7.23 (m, 4H), 7.03 (t, J = 7.6 Hz, 1H), 6.87 (d, J = 7.6 Hz, 1H), 4.21 (d, J = 9.2 Hz, 1H), 3.96 (s, 3H), 3.29 (s, 3H), 3.47 (d, J = 9.9 Hz, 1H), 2.37 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$<em>3$/TMS): δ 166.3, 165.8, 144.6, 139.7, 132.5, 132.3, 130.0, 129.5, 128.4, 127.7, 124.3, 122.8, 119.2, 113.3, 113.1, 108.9, 53.2, 40.5, 33.1, 26.4, 21.4, 16.7; FAB Mass: Calcd. for C$</em>{24}$H$</em>{19}$N$_3$O$_7$ is m/z = 461.42, Found(M+): m/z = 461.69</td>
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<td>3e</td>
<td>3305, 2946, 2355, 1706, 1599, 1466 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$<em>3$/TMS): δ 7.56 (d, J = 7.6 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 7.31-7.29 (m, 2H), 7.21-7.19 (m, 2H), 7.00 (t, J = 7.6 Hz, 1H), 6.81 (d, J = 7.6 Hz, 1H), 4.20 (q, J = 6.8 Hz, 2H), 4.13 (q, J = 9.2 Hz, 2H), 3.59 (s, 3H), 3.41 (d, J = 9.9 Hz, 1H), 3.41 (d, J = 9.9 Hz, 1H), 3.24 (s, 3H), 2.35 (s, 3H), 1.22 (t, J = 6.8 Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$<em>3$/TMS): δ 166.7, 164.6, 163.5, 144.4, 144.3, 132.2, 131.9, 131.4, 130.1, 130.0, 129.7, 28.5, 124.6, 122.5, 119.6, 116.4, 108.4, 63.1, 52.8, 40.2, 35.5, 32.5, 26.2, 21.3, 14.3; FAB Mass: Calcd. for C$</em>{24}$H$</em>{22}$N$_3$O$_6$ is m/z = 444.47, Found(M+1): m/z = 445.47</td>
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<tr>
<td>3e'</td>
<td>3266, 2889, 1710, 1610, 1585 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$<em>3$/TMS): δ 7.38-7.34 (m, 2H), 7.23 (d, J = 7.6 Hz, 2H), 7.14 (d, J = 7.6 Hz, 2H), 7.01 (t, J = 7.6 Hz, 1H), 6.83 (d, J = 7.6 Hz, 1H), 4.29 (d, J = 6.8 Hz, 1H), 4.13 (q, J = 9.2 Hz, 2H), 3.59 (s, 3H), 3.45 (d, J = 9.9 Hz, 1H), 3.25 (s, 3H), 2.33 (s, 3H), 1.12 (t, J = 6.9 Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$<em>3$/TMS): δ 171.9, 163.5, 161.5, 146.0, 137.2, 132.3, 131.8, 130.0, 129.8, 129.1, 128.4, 122.9, 119.6, 115.7, 108.3, 62.2, 58.7, 52.4, 45.1, 39.8, 26.2, 21.1, 14.1; FAB Mass: Calcd. for C$</em>{26}$H$</em>{24}$N$_3$O$_5$ is m/z = 444.48, Found(M+1): m/z = 445.47</td>
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### Supporting Information

**3f**

FTIR (KBr): 3437, 3011, 2947, 2245, 1712, 1604, 1465 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)/TMS): δ 7.43-7.38 (m, 2H), 7.33-7.31 (m, 2H), 7.26-7.25 (m, 2H), 7.04 (t, J = 7.6 Hz, 1H), 6.87 (d, J = 7.6 Hz, 1H), 4.23 (d, J = 9.1 Hz, 1H), 3.96 (s, 3H), 3.39 (d, J = 9.9 Hz, 1H), 3.30 (s, 3H), 2.49 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)/TMS): δ 166.3, 165.9, 144.7, 138.6, 132.4, 131.6, 130.9, 129.8, 129.7, 128.1, 126.8, 125.5, 124.4, 122.8, 119.2, 113.0, 108.9, 53.3, 53.3, 39.7, 33.4, 26.4, 19.6, 16.2; FAB Mass: Calcd. for C\(_{24}\)H\(_{19}\)N\(_3\)O\(_3\) is m/z = 397.43, Found(M+1): m/z = 398.77

**3g**

FTIR (KBr): 3429, 3272, 3055, 2243, 1708, 1607, 1468 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)/TMS): δ 7.46-7.42 (m, 2H), 7.34-7.30 (m, 2H), 7.25 (s, 2H), 7.11-7.07 (m, 2H), 4.74 (d, J = 17.5 Hz, 1H), 4.50 (d, J = 17.5 Hz, 1H), 4.23 (d, J = 9.1 Hz, 1H), 3.96 (s, 3H), 3.40 (d, J = 9.9 Hz, 1H), 2.49 (s, 3H), 2.27 (t, 1H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)/TMS): δ 165.8, 165.4, 142.7, 138.6, 132.4, 132.2, 130.9, 130.2, 129.9, 129.6, 128.1, 126.8, 124.5, 123.2, 119.3, 113.2, 112.9, 109.9, 76.4, 72.9, 53.3, 39.8, 33.5, 29.4, 19.6, 16.2; FAB Mass: Calcd. for C\(_{26}\)H\(_{19}\)N\(_3\)O\(_3\) is m/z = 421.45, Found(M+1): m/z = 422.89

**3h**

FTIR (KBr): 3443, 3281, 2947, 2205, 1716, 1607, 1469 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)/TMS): δ 7.44-7.41 (m, 2H), 7.29-7.24 (m, 4H), 7.10-7.07 (m, 2H), 4.75-4.70 (dd, J = 3.0, 17.5 Hz, 1H), 4.52 (dd, J = 3.0, 17.5 Hz, 1H), 4.21 (d, J = 9.9 Hz, 1H), 3.96 (s, 3H), 3.47 (d, J = 9.1 Hz, 1H), 2.37 (s, 3H), 2.27 (t, J = 2.2 Hz, 1H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)/TMS): δ 165.7, 165.4, 142.7, 138.6, 132.4, 132.2, 130.9, 130.2, 130.0, 128.4, 127.5, 124.4, 123.2, 119.3, 133.2, 133.0, 109.9, 76.4, 72.9, 53.3, 40.5, 33.2, 29.4, 21.4, 16.7; FAB Mass: Calcd. for C\(_{26}\)H\(_{19}\)N\(_3\)O\(_3\) is m/z = 421.45, Found(M+1): m/z = 422.60

**3i**

FTIR (KBr): 3417, 3097, 2347, 1706, 1608, 1532 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)/TMS): δ 8.33 (s, 1H), 8.31 (d, J = 7.6 Hz, 1H), 7.79 (d, J = 7.6 Hz, 1H), 7.68 (t, J = 7.6 Hz, 1H), 7.49 (d, J = 7.6 Hz, 1H), 7.42 (t, J = 7.6 Hz, 1H), 7.06 (t, J = 7.6 Hz, 1H), 6.88 (d, J = 7.6 Hz, 1H), 4.30 (d, J = 9.2 Hz, 1H), 3.99 (s, 3H), 3.60 (d, J = 9.9 Hz, 1H), 3.30 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)/TMS): δ 166.3, 165.7, 148.7, 144.8, 134.5, 133.5, 133.1, 132.7, 130.6, 128.1, 124.9, 124.6, 124.0, 122.9, 119.1, 112.6, 108.9, 53.4, 39.6, 33.4, 26.4, 16.8; FAB Mass: Calcd. for C\(_{23}\)H\(_{16}\)N\(_4\)O\(_2\) is m/z = 428.40, Found(M+1): m/z = 429.77

FTIR (KBr): 3445, 3259, 2250, 1710, 1602, 1466 cm\(^{-1}\); \(^1\)H NMR (500 MHz,
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<th>Compound</th>
<th>1H NMR (500 MHz, CDCl₃/TMS)</th>
<th>13C NMR (125 MHz, CDCl₃/TMS)</th>
<th>FAB Mass</th>
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<td>3j</td>
<td>δ 7.46-7.42 (m, 3H), 7.33 (t, J = 7.6 Hz, 1H), 7.26-7.17 (m, 2H), 7.10-7.07 (m, 2H), 4.74-4.70 (dd, J = 3.3, 17.6 Hz, 1H), 4.47-4.51 (dd, J = 3.0, 17.0 Hz, 1H), 4.17 (d, J = 9.9 Hz, 1H), 3.98 (s, 3H), 3.54 (d, J = 9.1 Hz, 1H), 2.27 (t, J = 2.3 Hz, 1H); δ 165.6, 165.4, 142.8, 132.4, 131.1, 131.7, 129.6, 129.2, 124.9, 125.6, 123.3, 119.3, 118.8, 116.2, 116.1, 112.8, 112.8, 109.9, 76.4, 72.9, 53.3, 34.8, 33.0, 29.4, 16.1;</td>
<td>Calcd. for C₂₅H₁₆FN₃O₃m/z = 425.41, Found(M+1): m/z = 426.89</td>
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<tr>
<td>3k</td>
<td>FTIR (KBr): 3430, 3273, 3053, 2244, 1708, 1606, 1461 cm⁻¹; δ 7.46-7.40 (m, 7H), 7.10-7.05 (m, 2H), 4.75-4.71 (dd, J = 2.3, 18.3 Hz, 1H), 4.47-4.51 (dd, J = 2.3, 18.3 Hz, 1H), 4.25 (d, J = 9.9 Hz, 1H), 3.97 (s, 3H), 3.51 (d, J = 9.9 Hz, 1H), 2.27 (t, J = 2.3 Hz, 1H); δ 165.7, 165.4, 142.7, 132.4, 132.2, 130.6, 130.0, 129.72, 129.4, 128.6, 124.4, 123.2, 119.3, 113.1, 112.9, 109.9, 76.4, 72.9, 53.3, 40.5, 33.2, 29.4, 16.6;</td>
<td>FAB Mass: Calcd. for C₂₅H₁₇N₃O₃m/z = 407.42, Found(M+): m/z = 407.56</td>
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<tr>
<td>5a</td>
<td>FTIR (KBr): 3061, 2931, 1721, 1608, 1469, 1236 cm⁻¹; δ 7.58 (d, J = 7.6 Hz, 1H), 7.54 (d, J = 7.6 Hz, 1H), 7.33-7.26 (m, 2H), 7.10 (t, J = 7.6 Hz, 1H), 6.96 (t, J = 7.6 Hz, 1H), 6.88 (d, J = 7.6 Hz, 1H), 6.73 (d, J = 7.6 Hz, 1H), 4.22-4.15 (m, 3H), 3.93 (s, 3H), 3.21 (s, 3H), 3.10 (s, 3H), 3.08 (d, J = 8.4 Hz, 1H), 1.23 (t, J = 6.8 Hz, 3H); δ 172.5, 170.0, 168.1, 166.6, 144.2, 144.1, 134.9, 131.0, 130.7, 127.9, 126.0, 124.6, 123.1, 122.6, 122.2, 120.1, 108.1, 61.5, 52.5, 42.3, 39.2, 33.8, 26.7, 26.1, 14.2; FAB Mass: Calcd. for C₂₆H₂₄N₂O₆m/z = 460.48, Found(M+1): m/z = 461.91</td>
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<td>5b</td>
<td>FTIR (KBr): 3340, 2980, 2234, 1726, 1608, 1511, 1367 cm⁻¹; δ 7.56 (t, J = 8.4 Hz, 2H), 7.34-7.29 (m, 2H), 7.11 (t, J = 7.6 Hz, 1H), 7.00 (t, J = 7.6 Hz, 1H), 6.96 (d, J = 7.6 Hz, 1H), 6.89 (d, J = 7.6 Hz, 1H), 4.22-4.13 (m, 3H), 4.40 (d, J = 2.2, 2H), 3.94 (s, 3H), 3.21 (s, 3H), 3.08 (d, J = 8.4 Hz, 1H), 1.23 (t, J = 6.9 Hz, 3H); δ 172.4, 168.1, 166.9, 144.2, 142.1, 135.6, 130.9, 128.0, 125.9, 124.7, 123.1, 122.6, 122.2, 109.1, 108.1, 72.3, 61.6, 52.6, 42.4, 39.0, 34.0, 29.0, 26.7, 14.2, 13.5; FAB Mass: Calcd. for C₂₈H₂₄N₂O₆m/z = 484.50, Found(M+1): m/z = 485.55</td>
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5c

CDCl$_3$/TMS:  δ 7.96 (d, $J = 8.4$ Hz, 1H), 7.56 (d, $J = 6.9$ Hz, 1H), 7.51 (d, $J = 7.6$ Hz, 1H), 7.36 (t, $J = 8.4$ Hz, 1H), 7.29 (t, $J = 7.6$ Hz, 1H), 7.22 (t, $J = 7.6$ Hz, 1H), 6.97 (t, $J = 7.6$ Hz, 1H), 6.74 (d, $J = 8.4$ Hz, 1H), 4.42 (q, $J = 7.6$ Hz, 2H), 4.20 (q, $J = 6.9$ Hz, 1H), 3.99 (d, $J = 8.4$ Hz, 1H), 3.93 (s, 3H), 3.09 (d, $J = 9.9$ Hz, 3H), 1.40 (t, $J = 6.9$ Hz, 3H), 1.22 (t, $J = 7.6$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$/TMS):  δ 170.9, 167.4, 167.0, 166.4, 150.8, 144.2, 139.9, 133.2, 131.2, 131.0, 128.3, 125.2, 124.7, 124.6, 122.6, 122.3, 120.0, 114.9, 108.5, 63.5, 61.7, 52.6, 42.5, 40.8, 34.7, 26.1, 14.4, 14.2; FAB Mass: Calcd. for C$_{28}$H$_{26}$N$_{2}$O$_{8}$ is m/z = 518.51, Found(M+): m/z = 518.91

5d

FTIR (KBr): 3321, 3010, 1716, 1599, 1489, 1391 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$/TMS):  δ 7.58 (d, $J = 7.6$ Hz, 1H), 7.53 (d, $J = 7.6$ Hz, 1H), 7.31 (t, $J = 8.4$ Hz, 1H), 7.25 (t, $J = 7.6$ Hz, 1H), 7.10 (t, $J = 7.6$ Hz, 1H), 6.95 (t, $J = 7.6$ Hz, 1H), 6.88 (d, $J = 7.6$ Hz, 1H), 6.73 (d, $J = 7.6$ Hz, 1H), 5.74-5.69 (m, 1H), 5.16-5.11 (m, 2H), 4.24-4.10 (m, 6H), 3.94 (s, 3H), 3.09 (d, $J = 8.4$ Hz, 1H), 1.23 (t, $J = 6.9$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$/TMS):  δ 172.4, 168.1, 167.1, 166.2, 144.2, 143.2, 134.9, 131.4, 127.9, 125.9, 124.6, 123.1, 122.6, 122.2, 120.1, 117.4, 109.1, 108.1, 61.6, 52.6, 42.3, 42.0, 39.1, 33.7, 26.7, 14.3; FAB Mass: Calcd. for C$_{28}$H$_{26}$N$_{2}$O$_{6}$ is m/z = 486.52, Found(M+1): m/z = 487.70

5e

FTIR (KBr): 3456, 3030, 1731, 1616, 1486 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$/TMS):  δ 7.58 (d, $J = 7.6$ Hz, 1H), 7.53 (d, $J = 7.6$ Hz, 1H), 7.31 (t, $J = 7.6$ Hz, 1H), 7.26-7.22 (t, $J = 7.6$ Hz, 1H), 7.10 (t, $J = 7.6$ Hz, 1H), 6.95 (t, $J = 7.6$ Hz, 1H), 6.88 (d, $J = 7.6$ Hz, 1H), 6.73 (d, $J = 7.6$ Hz, 1H), 5.72-5.69 (m, 1H), 5.16-5.11 (m, 2H), 4.24-4.14 (m, 6H), 4.10 (d, $J = 10.7$ Hz, 1H), 3.94 (s, 3H), 3.09 (d, $J = 8.4$ Hz, 1H), 1.38 (t, $J = 7.6$ Hz, 3H), 1.20 (t, $J = 7.6$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$/TMS):  δ 170.9, 167.4, 167.1, 166.0, 143.4, 140.0, 133.2, 131.4, 131.1, 130.7, 128.3, 125.1, 124.7, 124.5, 122.6, 122.3, 121.8, 120.0, 117.5, 114.9, 109.2, 63.5, 61.8, 52.7, 42.4, 42.1, 40.7, 34.6, 14.4, 14.2; FAB Mass: Calcd. for C$_{30}$H$_{28}$N$_{2}$O$_{8}$ is m/z = 544.55, Found(M+1): m/z = 545.89

5f

FTIR (KBr): 3401, 2991, 1719, 1609, 1479, 1299 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$/TMS):  δ 7.72 (d, $J = 1.7$ Hz, 1H), 7.58 (d, $J = 8.0$ Hz, 1H), 7.41 (dd, $J = 2.3$, 8.0 Hz, 1H), 7.32 (t, $J = 7.4$ Hz, 1H), 7.11 (t, $J = 8.0$ Hz, 1H), 6.89 (d, $J = 7.4$ Hz, 1H), 6.62 (d, $J = 8.5$ Hz, 1H), 4.25-4.21 (q, $J = 6.9$ Hz, 2H), 4.14(d, $J = 8.6$ Hz, 1H), 3.94 (s, 3H), 3.21 (s, 3H), 3.09 (s, 3H), 3.06 (d, $J = 8.5$ Hz, 1H), 1.24 (t, $J = 6.8$ Hz,
Supporting Information

3H); $^1$H NMR (125 MHz, CDCl$_3$/TMS): $\delta$ 172.4, 168.0, 166.5, 166.1, 144.2, 142.9, 136.7, 133.5, 129.8, 128.0, 125.8, 123.1, 122.7, 121.6, 114.9, 109.4, 108.1, 61.6, 52.6, 42.4, 39.3, 33.7, 26.7, 26.2, 14.2; FAB Mass: Calcd. for C$_{26}$H$_{23}$BrN$_2$O$_6$ is m/z = 539.37, Found(M+): m/z = 540.61

FTIR (KBr): 3399, 3091, 1721, 1607, 1401 cm$^{-1}$. $^1$H NMR (500 MHz, CDCl$_3$/TMS): $\delta$ 7.58 (d, $J = 7.5$ Hz, 1H), 7.53 (d, $J = 7.6$ Hz, 1H), 7.31-7.21 (m, 4H), 7.16-7.14 (m, 3H), 7.10 (t, $J = 7.6$ Hz, 1H), 6.93 (t, $J = 16.0$ Hz, 1H), 4.86 (d, $J = 16.0$ Hz, 1H), 4.76 (d, $J = 16.0$ Hz, 1H), 4.23-4.21 (m, 3H), 3.94 (s, 3H), 3.18 (s, 3H), 3.10 (d, $J = 8.5$ Hz, 1H), 1.23 (t, $J = 7.5$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$/TMS): $\delta$ 172.3, 168.1, 170.0, 166.5, 144.2, 143.1, 135.6, 134.8, 130.8, 130.3, 128.7, 127.8, 127.5, 127.0, 126.0, 124.5, 123.0, 122.5, 122.2, 120.1, 109.0, 107.9, 61.4, 52.5, 43.3, 42.2, 38.9, 33.7, 26.5, 14.2. FAB Mass: Calcd. for C$_{32}$H$_{28}$N$_2$O$_6$ is m/z = 536.57, Found(M+): m/z = 536.70

FTIR (KBr): 3440, 3339, 2951, 1734, 1711, 1568, 1334 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$/TMS): $\delta$ 7.65-7.63 (m, 2H), 7.50 (d, $J = 7.6$ Hz, 2H), 7.27-7.26 (m, 2H), 7.11 (t, $J = 8.4$ Hz, 2H), 7.02 (t, $J = 7.6$ Hz, 2H), 6.70 (t, $J = 6.1$ Hz, 2H), 6.62 (t, $J = 6.8$ Hz, 2H), 6.52 (t, $J = 7.6$ Hz, 2H), 6.19 (t, $J = 7.6$ Hz, 2H), 5.10 (d, $J = 10.7$ Hz, 2H), 3.99-3.63 (m, 4H), 3.56 (s, 3H), 3.50 (s, 3H), 3.26 (s, 3H), 3.22 (s, 3H), 2.97 (s, 3H), 2.96 (s, 3H), 0.95 (t, $J = 7.6$ Hz, 3H), 0.68 (t, $J = 6.9$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$/TMS): $\delta$ 172.3, 168.1, 170.0, 166.5, 144.2, 143.1, 135.6, 134.8, 130.8, 130.3, 128.7, 127.8, 127.5, 127.0, 126.0, 124.5, 123.0, 122.5, 122.2, 120.1, 109.0, 107.9, 61.4, 52.5, 43.3, 42.2, 38.9, 33.7, 26.5, 14.2. HRMS: Calcd. for C$_{26}$H$_{23}$N$_2$O$_6$ is m/z = 460.48, Found(M+): m/z = 461.17

FTIR (KBr): 3398, 2980, 1731, 1714, 1578 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$/TMS): $\delta$ 7.66 (s, 1H), 7.47 (d, $J = 7.4$ Hz, 1H), 7.34 (t, $J = 8.0$ Hz, 2H), 7.23 (dd, $J = 1.7$, 8.0 Hz, 2H), 7.06 (t, $J = 7.4$ Hz, 1H), 6.67 (d, $J = 7.4$ Hz, 1H), 6.59(d, $J = 8.6$ Hz, 1H), 6.23 (d, $J = 1.7$ Hz, 1H), 5.06 (d, $J = 1.7$ Hz, 1H), 4.01 (m, 1H), 3.83 (m, 1H), 3.69-3.65 (m, 2H), 3.61 (s, 3H), 3.02 (s, 3H), 2.97 (s, 3H), 0.98 (t, $J = 6.8$ Hz, 1H), 0.68 (t, $J = 6.9$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$/TMS): $\delta$ 172.7, 170.9, 168.4, 162.7, 146.1, 144.2, 143.6, 137.1, 131.8, 131.5, 130.2, 129.2, 128.5, 126.9, 126.8, 125.2, 124.0, 122.0, 121.7, 114.1, 109.0, 108.5, 63.9, 61.4, 55.0, 45.9, 51.9, 26.9, 26.6, 26.5, 13.8, 13.6.
<table>
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<tr>
<th>Compound</th>
<th>FTIR (KBr):</th>
<th>¹H NMR (500 MHz, CDCl₃/TMS):</th>
<th>¹³C NMR (125 MHz, CDCl₃/TMS):</th>
<th>FAB Mass:</th>
</tr>
</thead>
<tbody>
<tr>
<td>8a</td>
<td>3427, 2945, 1717, 1612, 1470, 1345 cm⁻¹;</td>
<td>δ 7.66 (d, J = 7.4 Hz, 1H), 7.28-7.17 (m, 2H), 6.92-6.87 (m, 2H), 6.84 (d, J = 7.4 Hz, 1H), 6.75 (d, J = 7.4 Hz, 1H), 4.27-4.24 (m, 1H), 4.08-4.05 (m, 1H), 3.93 (q, J = 6.9 Hz, 2H), 3.65 (d, J = 6.8 Hz, 1H), 3.59 (d, J = 8.4 Hz, 1H), 3.24-3.23 (m, 4H), 3.22 (s, 3H), 3.10 (s, 3H), 2.58-2.54 (dd, J = 6.8 Hz, 1H), 1.27 (t, J = 6.8 Hz, 3H), 1.02 (t, J = 6.8 Hz, 3H);</td>
<td>δ 174.5, 137.1, 169.4, 168.5, 162.4, 145.2, 144.3, 143.8, 136.0, 129.2, 127.7, 124.3, 124.0, 122.3, 121.7, 107.8, 107.5, 64.8, 61.8, 60.9, 60.7, 51.9, 41.7, 40.8, 40.1, 38.9, 26.9, 26.3, 14.3, 13.9;</td>
<td>Calcd. for C₂₆H₂₃N₂O₆Br is m/z = 539.37, Found(M+1): m/z = 540.41</td>
</tr>
<tr>
<td>8b</td>
<td>3440, 2931, 1711, 1608, 1469, 1337cm⁻¹;</td>
<td>δ 7.26-7.23 (m, 1H), 7.15-7.11 (m, 2H), 6.99 (t, J = 6.9 Hz, 2H), 6.95 (t, J = 7.6 Hz, 2H), 6.80 (d, J = 8.4 Hz, 1H), 6.70 (t, J = 7.6 Hz, 1H), 4.72-4.68 (dd, J = 2.3, 17.5 Hz, 1H), 4.26-4.23 (dd, J = 2.3, 17.6 Hz, 1H), 4.06-3.78 (m, 4H), 3.73 (s, 3H), 3.67-3.62 (dd, J = 2.3, 19.1 Hz, 1H), 3.20 (s, 3H), 3.03 (d, J = 9.2 Hz, 1H), 2.95 (dd, J = 9.2 Hz, 1H), 2.92-2.88 (dd, J = 3.1, 19.1 Hz, 1H), 2.28 (t, J = 1.5 Hz, 1H), 1.12 (t, J = 7.6 Hz, 3H), 0.89 (t, J = 7.6 Hz, 3H);</td>
<td>δ 174.7, 172.4, 170.6, 168.0, 163.0, 147.8, 143.6, 142.9, 128.9, 127.9, 125.1, 123.3, 122.3, 122.0, 108.9, 108.0, 72.3, 66.9, 62.0, 61.3, 60.5, 51.9, 41.3, 40.09, 39.2, 38.9, 29.5, 29.9, 14.3, 14.1, 13.8;</td>
<td>Calcd. for C₃₂H₃₂N₂O₈ is m/z = 572.61, Found(M+1): m/z = 573.95</td>
</tr>
</tbody>
</table>
4. Scanned copies of original spectra

Figure 1 $^1$H NMR spectrum of compound 3a
**Figure 2** $^{13}$C NMR spectrum of compound 3a

**Figure 3** DEPT-135 spectrum of compound 3a
Supporting Information

Figure 4 HOMOCOSY spectrum of compound 3a

Figure 5 HMQC spectrum of compound 3a

Figure 6 $^1$H NMR spectrum of compound 3b
Figure 7 $^{13}$C NMR spectrum of compound 3b

Figure 8 $^1$H NMR spectrum of compound 3c
Figure 9 $^{13}$C NMR spectrum of compound 3c

Figure 10 $^1$H NMR spectrum of compound 3d
Figure 11 $^{13}$C NMR spectrum of compound 3d

Figure 12 $^1$H NMR spectrum of compound 3e
Figure 13 $^{13}$C NMR spectrum of compound $3e$

Figure 14 $^1$H NMR spectrum of compound $3f$
Figure 15 13C NMR spectrum of compound 3f

Figure 16 1H NMR spectrum of compound 3g
**Figure 17** $^{13}$C NMR spectrum of compound 3g

**Figure 18** $^{1}$H NMR spectrum of compound 3h
Figure 19 $^{13}$C NMR spectrum of compound 3h

Figure 20 $^1$H NMR spectrum of compound 3i
Figure 21 $^{13}$C NMR spectrum of compound 3i

Figure 22 $^1$H NMR spectrum of compound 3j
Figure 23 $^{13}$C NMR spectrum of compound 3j

Figure 24 $^1$H NMR spectrum of compound 3k
Figure 25 $^{13}$C NMR spectrum of compound 3k

Figure 26 $^1$H NMR spectrum of compound 3e'
Figure 27 $^{13}$C NMR spectrum of compound 3e’

Figure 28 $^1$H NMR spectrum of compound 5a
Figure 29 $^{13}$C NMR spectrum of compound 5a

Figure 30 $^1$H NMR spectrum of compound 5b
Figure 31 $^{13}$C NMR spectrum of compound 5b

Figure 32 $^1$H NMR spectrum of compound 5c
Figure 33  $^{13}$C NMR spectrum of compound 5c

Figure 34  $^1$H NMR spectrum of compound 5d
Figure 35 $^{13}$C NMR spectrum of compound 5d

Figure 36 $^1$H NMR spectrum of compound 5e
Figure 37 $^{13}$C NMR spectrum of compound 5e

Figure 38 $^1$H NMR spectrum of compound 3f
Figure 39 $^{13}$C NMR spectrum of compound 5f

Figure 40 $^1$H NMR spectrum of compound 5g
Figure 41 $^{13}$C NMR spectrum of compound 5g

Figure 42 $^1$H NMR spectrum of compound 6a
Figure 43 $^{13}$C NMR spectrum of compound 6a

Figure 44 DEPT-135 spectrum of compound 6a
Figure 45 HRMS spectrum of compound 6a

Figure 46 $^1$H NMR spectrum of compound 6b
Figure 47 $^{13}$C NMR spectrum of compound 6b

Figure 48 $^1$H NMR spectrum of compound 8a
Figure 49 $^{13}$C NMR spectrum of compound 8a

Figure 50 DEPT-135 spectrum of compound 8a
Figure 51 FAB Mass spectrum of compound 10a

Figure 52 $^1$H NMR spectrum of compound 8b
Figure 53 $^{13}$C NMR spectrum of compound 8b