Supporting Information

Phosphine-Catalyzed One-Pot Isomerization of 3-Alkynoates and [2+3]-Cycloaddition with Imines: Formal Synthesis of Securinega alkaloid (±)-Allosecurinine

General:

Phosphine includes PPh$_3$, BINAP, (2S, 3S)-CHIRAPHOS, (S, S)-Et-DUPHOS, (R, R)-Et-DUPHOS, (R, R)-Et-BPE (+)-DIOP, (S)-(−)-2-[2-(Di phenylphosphino)-phenyl]-4-isopropyl-2-oxazoline and (R, R)-DIPAMP were purchased from commercial suppliers. Alkynes, Ethyl-diazo-acetate, Copper iodide, Aldehydes and Sulphonamides were purchased from commercial suppliers. All alkynoates and imines were synthesized using the previous reports. All reactions were carried out under nitrogen atmosphere unless otherwise stated. Commercial solvents and reagents were used without further purification with following exceptions: toluene and dichloromethane was distilled from calcium hydride prior to use. Reactions were monitored through thin layer chromatography [Merck 60 F254 pre-coated silica gel plate (0.2 mm thickness)]. Subsequent to elution, spots were visualized using UV radiation (254 nm) on Spectroline Model ENF-24061/F 254 nm. Further visualization was possible using basic solution of potassium permanganate or acidic solution of ceric molybdate as stain, followed by heating on a hot plate. Flash chromatography was performed using Merck silica gel 60 with distilled solvents. All HPLC chromatograms were recorded using Agilent 1100 and 1200 series. Infrared spectra were recorded on a Shimadzu IR Prestige-21 FT-IR. Liquid samples were examined as film between NaCl salt plates. HRMS spectra were recorded on a Waters Q–Tof Permier Spectrometer. $^1$H NMR and $^{13}$C NMR spectra were recorded using Bruker Avance 300, 400 and 500 MHz spectrometers. Chemical shifts for $^1$H NMR spectra are reported as δ in units of parts per million (ppm) downfield from SiMe$_4$ (δ 0.0) and relative to the signal of chloroform-d (δ 7.260, singlet). Multiplicities were given as: s (singlet); brs (broad singlet); d (doublet); t (triplet); q (quartet); dd (doublets of doublet); ddd (doublets of doublets of doublet); td (triplet of doublet); m (multiplets); ddt (doublet of doublet of triplet) and etc. Coupling constants are reported as a J value in Hz. Carbon nuclear magnetic resonance spectra ($^{13}$C NMR) are reported as δ in units of parts per million (ppm) downfield from SiMe$_4$ (δ 0.0) and relative to the signal of chloroform-d (δ 77.00, triplet).
General procedure for aliphatic aldimines:

A mixture of aldehyde (1 mmol), p-toluenesulfonamide (1 mmol) and benzenesulfinic acid sodium salt (1.1 mmol) in formic acid and H$_2$O was stirred at room temperature. The resulting white precipitate was filtered off, washed with H$_2$O, then pentane. The resulting solid was dissolved in CH$_2$Cl$_2$, then Sat. aq. NaHCO$_3$ was added and the solution was well stirred for 2 h at r.t. The organic phase was decanted, the aqueous phase extracted with CH$_2$Cl$_2$ and the combined organic layers dried over anhydrous NaHCO$_3$, filtered off and the solvent removed under vacuum to yield the corresponding aldimines. All the imines were taken as such to next step without further purification.

N-(5-(benzyloxy)pentylidene)-4-methylbenzenesulfonamide (6a):
The product was prepared by using above general procedure, employing 5-(benzyloxy)pentanal (1.0 g, 5.20 mmol), p-toluenesulfonamide (890 mg, 5.20 mmol) and benzenesulfinic acid sodium salt (940 mg, 5.72 mmol). After 24 h, the resulting white precipitate was filtered off, washed with H$_2$O (2 x 10 mL), then pentane (2 x 10 mL). The solid was dissolved in CH$_2$Cl$_2$ (50 mL), then sat. aq. NaHCO$_3$ (40 mL) was added and the solution was well stirred for 2 h at r.t. The organic phase was decanted, the aqueous phase extracted with CH$_2$Cl$_2$ (50 mL) and the combined organic layers dried over anhydrous NaHCO$_3$, filtered off and the solvent removed under vacuum to yield the aldimines 6a (1.15 g, 64% yield); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$= 8.59 (t, $J$=4.3 Hz; 1H), 7.78-7.82 (m, 2H), 7.25-7.35 (m, 7H), 4.45 (s, 2H), 3.45 (t, $J$=5.9 Hz, 2H), 2.25-2.35 (m, 2H), 2.42 (s, 3H), 1.55-1.75 (m, 4H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$); $\delta$= 178.1, 144.7, 138.4, 134.6, 129.8 (2), 128.4 (2), 128.1 (2), 127.63 (2), 127.6, 72.9, 69.5, 35.6, 29.0, 21.6, 21.5 ppm.

4-methyl-N-(2-phenylethylidene)benzenesulfonamide (6b):
The product was prepared by using above general procedure, employing 2-phenylacetaldehyde (1.0 g, 8.33 mmol), p-toluenesulfonamide (1.42 g, 8.33 mmol) and benzenesulfinic acid sodium salt (1.50 g, 9.16 mmol). After 48 h, the resulting white precipitate was filtered off, washed with H$_2$O (2 x 10 mL), then pentane (2 x 10 mL). The solid was dissolved in CH$_2$Cl$_2$ (50 mL), then sat. aq NaHCO$_3$ (40 mL) was added and the solution was well stirred for 2 h at r.t. The organic phase was decanted, the aqueous phase extracted with CH$_2$Cl$_2$ (50 mL) and the combined organic layers dried
over anhydrous NaHCO₃, filtered off and the solvent removed under vacuum to yield the aldimines 6b (840 g, 37% yield); **NMR (400 MHz, CDCl₃):** δ = 8.60 (t, J=5.3 Hz; 1H), 7.78-7.82 (m, 2H), 7.25-7.35 (m, 7H), 3.79 (d, J=5.3 Hz; 2H), 2.44 (s, 3H) ppm.

### 4-methyl-N-(2-methylpropylidene)benzenesulfonamide (6c):

The product was prepared by using above general procedure, employing isobutyraldehyde (1.0 g, 13.9 mmol), p-toluenesulfonamide (2.38 g, 13.9 mmol) and benzenesulfonic acid sodium salt (2.50 g, 15.2 mmol). After 12 h, the resulting white precipitate was filtered off, washed with H₂O (2 x 10 mL), then pentane (2 x 10 mL). The solid was dissolved in CH₂Cl₂ (50 mL), then sat. aq NaHCO₃ (40 mL) was added and the solution was well stirred for 2 h at r.t. The organic phase was decanted, the aqueous phase extracted with CH₂Cl₂ (50 mL) and the combined organic layers dried over anhydrous NaHCO₃, filtered off and the solvent removed under vacuum to yield the aldimines 6c (2.22 g, 71% yield); **¹H NMR (400 MHz, CDCl₃):** δ = 8.47 (d, J=4.2 Hz; 1H), 7.77 (d, J= 8.2 Hz; 2H), 7.30 (d, J= 8.1 Hz; 2H), 2.63-2.67 (m, 1H), 2.42 (s, 3H), 1.12 (d, J=6.9 Hz; 6H) ppm. **¹³C NMR (100 MHz, CDCl₃):** δ = 181.8, 144.6, 134.7, 129.8 (2), 128.0 (2), 34.6, 21.6, 17.9 (2) ppm.

### N-(cyclohexylmethylene)-4-methylbenzenesulfonamide (6d):

The product was prepared by using above general procedure, employing cyclohexanecarbaldehyde (1.0 g, 8.9 mmol), p-toluenesulfonamide (1.52 g, 8.9 mmol) and benzenesulfonic acid sodium salt (1.60 g, 9.8 mmol). After 12 h, the resulting white precipitate was filtered off, washed with H₂O (2 x 10 mL), then pentane (2 x 10 mL). The solid was dissolved in CH₂Cl₂ (50 mL), then sat. aq NaHCO₃ (40 mL) was added and the solution was well stirred for 2 h at r.t. The organic phase was decanted, the aqueous phase extracted with CH₂Cl₂ (50 mL) and the combined organic layers dried over anhydrous NaHCO₃, filtered off and the solvent removed under vacuum to yield the aldimines 6d (1.75 g, 74% yield); **¹H NMR (500 MHz, CDCl₃):** δ = 8.47 (d, J=4.4 Hz; 1H), 7.79 (d, J= 8.2 Hz; 2H), 7.33 (d, J= 8.0 Hz; 2H), 2.44 (brs, 4H), 1.60-1.90 (m, 5H), 1.10-1.40 (m, 5H) ppm. **¹³C NMR (125 MHz, CDCl₃):** δ = 181.0, 144.6, 134.8, 129.7 (2), 128.0 (2), 43.6, 28.3 (2), 25.6, 25.0 (2), 21.6 ppm.

### N-butylidene-4-methylbenzenesulfonamide (6e):

The product was prepared by using above general procedure, employing
isobutyraldehyde (1.0 g, 13.9 mmol), p-toluenesulfonamide (2.38 g, 13.9 mmol) and benzenesulfinic acid sodium salt (2.50 g, 15.2 mmol). After 16 h, the resulting white precipitate was filtered off, washed with H₂O (2 x 10 mL), then pentane (2 x 10 mL). The solid was dissolved in CH₂Cl₂ (50 mL), then sat. aq NaHCO₃ (40 mL) was added and the solution was well stirred for 2 h at r.t. The organic phase was decanted, the aqueous phase extracted with CH₂Cl₂ (50 mL) and the combined organic layers dried over anhydrous NaHCO₃, filtered off and the solvent removed under vacuum to yield the aldimines 6e (2.12 g, 68% yield); ¹H NMR (400 MHz, CDCl₃): δ= 8.60 (t, J=4.4 Hz; 1H), 7.80 (d, J= 8.0 Hz; 2H), 7.32 (d, J= 7.9 Hz; 2H), 2.48-2.52(m, 2H), 2.43(s, 3H), 1.60-1.69 (m, 2H), 0.94 (t, J=7.4 Hz; 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ= 178.3, 144.7, 134.7, 129.8 (2), 128.1 (2), 37.7, 21.6, 18.1, 13.6 ppm.

4-methyl-N-octylidenebenzenesulfonamide (6f):

![NTs](image) The product was prepared by using above general procedure, employing isobutyraldehyde (1.0 g, 7.8 mmol), p-toluenesulfonamide (1.33 g, 7.8 mmol) and benzenesulfinic acid sodium salt (1.40 g, 8.58 mmol). After 24 h, the resulting white precipitate was filtered off, washed with H₂O (2 x 10 mL), then pentane (2 x 10 mL). The solid was dissolved in CH₂Cl₂ (50 mL), then sat. aq NaHCO₃ (40 mL) was added and the solution was well stirred for 2 h at r.t. The organic phase was decanted, the aqueous phase extracted with CH₂Cl₂ (50 mL) and the combined organic layers dried over anhydrous NaHCO₃, filtered off and the solvent removed under vacuum to yield the aldimines 6f (1.34 g, 61% yield); ¹H NMR (500 MHz, CDCl₃): δ= 8.60 (t, J=4.6 Hz; 1H), 7.80 (d, J= 8.3 Hz; 2H), 7.34 (d, J= 7.9 Hz; 2H), 2.48-2.52(m, 2H), 2.43(s, 3H), 1.57-1.67 (m, 2H), 1.20-1.35 (m, 8H), 0.84 (t, J=7.1 Hz; 3H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ= 178.6, 144.6, 134.7, 129.8 (2), 128.1 (2), 35.9, 31.5, 28.9, 28.8, 24.6, 22.5, 21.6, 14.0 ppm.

N-(5-(4-methoxybenzyloxy)pentylidene)-4-methylbenzenesulfonamide (9):

![PMBO](image) The product was prepared by using above general procedure, employing 5-(4-methoxybenzyloxy)pentanal (1.0 g, 4.5 mmol), p-toluenesulfonamide (770 mg, 4.5 mmol) and benzenesulfinic acid sodium salt (812 mg, 4.95 mmol). After 24 h, the resulting white precipitate was filtered off, washed with H₂O (2 x 10 mL), then pentane (2 x 10 mL). The solid was dissolved in CH₂Cl₂ (50 mL), then sat. aq NaHCO₃ (40 mL) was added and the solution
was well stirred for 2 h at r.t. The organic phase was decanted, the aqueous phase extracted with CH₂Cl₂ (50 mL) and the combined organic layers dried over anhydrous NaHCO₃, filtered off and the solvent removed under vacuum to yield the aldimines 9 (1.1 g, 66% yield); ¹H NMR (400 MHz, CDCl₃): δ= 8.59 (t, J= 4.3 Hz; 1H), 7.78 (d, J= 8.2 Hz; 2H), 7.33 (d, J= 8.1Hz; 2H), 7.23 (d, J= 8.5Hz; 2H), 6.87 (d, J=8.5Hz; 2H), 4.40 (s, 2H), 3.80 (s, 3H), 3.42 (t, J= 6.0 Hz; 2H), 2.49-2.55 (m, 2H), 2.42 (s, 3H), 1.59-1.75 (m, 4H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ= 178.1, 159.2, 144.8, 134.7, 130.5 (2), 129.9 (2), 129.3 (2), 128.2 (2), 113.8, 72.6, 69.3, 55.4, 35.7, 29.1, 21.7, 21.6 ppm.

**General procedure for [2+3]-Cycloaddition reaction:**

To a solution of alkynoates and imines in toluene (4 mL) cooled to 0°C, phosphine catalyst in toluene was added dropwise for 10 min. The solution was warmed to room temperature and stirred until then disappearance of alkynoates. Flash column chromatography using hexane and ethyl acetate was done to obtain pyrrolines.

**Table 1: Optimization of reaction condition**

<table>
<thead>
<tr>
<th>S. No</th>
<th>Phosphines</th>
<th>Solvents</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Triphenylphosphine</td>
<td>toluene</td>
<td>0</td>
</tr>
<tr>
<td>2.</td>
<td>Tricyclohexylphosphine</td>
<td>toluene</td>
<td>51</td>
</tr>
<tr>
<td>3.</td>
<td>Trimethoxyphosphine</td>
<td>toluene</td>
<td>27</td>
</tr>
<tr>
<td>4.</td>
<td>Tri-n-butylphosphine</td>
<td>toluene</td>
<td>71</td>
</tr>
<tr>
<td>5.</td>
<td>Tri-t-butylphosphine</td>
<td>toluene</td>
<td>69</td>
</tr>
<tr>
<td>6.</td>
<td><strong>Trimethylphosphine</strong></td>
<td>toluene</td>
<td><strong>84</strong></td>
</tr>
<tr>
<td>7.</td>
<td>Trimethylphosphine</td>
<td>CH₂Cl₂</td>
<td>77</td>
</tr>
<tr>
<td>8.</td>
<td>Trimethylphosphine</td>
<td>Diethyl ether</td>
<td>68</td>
</tr>
<tr>
<td>9.</td>
<td>Trimethylphosphine</td>
<td>Dimethoxymethane</td>
<td>trace</td>
</tr>
<tr>
<td>10.</td>
<td>Trimethylphosphine</td>
<td>THF</td>
<td>81</td>
</tr>
<tr>
<td>11.</td>
<td>Trimethylphosphine</td>
<td>DMF</td>
<td>trace</td>
</tr>
<tr>
<td>12.</td>
<td>Triethylphosphine</td>
<td>toluene</td>
<td>75</td>
</tr>
</tbody>
</table>
13. Ethylenebis(diphenylphosphine) toluene 64
14. 1,3-bis(diphenylphosphino)propane toluene 69
15. 1,5-Bis(diphenylphosphino)pentane toluene 71

Ethyl 2,5-diphenyl-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (3aa):

The product was prepared by above general procedure, employing ethyl-4-phenylbut-3-ynoate (50 mg, 0.265 mmol), (E)-N-benzylidene-4-methylbenzenesulfonamide (82 mg, 0.318 mmol) and PMe₃ (5 mg, 0.053 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (100 mg, 0.223 mmol, 84% yield); 

1H NMR (400 MHz, CDCl₃): δ = 7.25 – 7.30 (m, 10H), 7.19 – 7.21 (m, 2H), 6.99 – 7.01 (m, 2H), 6.75 (t, J = 2.1 Hz, 1H), 5.95 (t, J = 2.5 Hz, 1H), 5.87 (t, J = 2.5 Hz, 1H), 3.93 - 4.13 (m, 2H), 2.31 (s, 3H), 1.07 (t, J = 7.13 Hz, 3H) ppm.

13C NMR (100 MHz, CDCl₃): δ = 162.0, 143.1, 139.3, 139.2, 138.2, 136.0, 133.9, 129.1(2), 128.55(2), 128.50(2), 128.1(2), 128.0, 127.7(2), 127.2(2), 69.8, 69.5, 60.8, 29.6, 21.3, 13.8 ppm.

FTIR (neat): ν = 3053, 2986, 2926, 2304, 1721, 1454, 1421, 1341, 1265, 1165, 1093 cm⁻¹; HRMS (ESI, m/z): calcd for C₂₆H₂₆NO₄S [M+H]⁺ 448.1583, found: 448.1585.

Ethyl 2-(4-ethylphenyl)-5-phenyl-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (3ab):

The product was prepared by above general procedure, employing ethyl-4-phenylbut-3-ynoate (50 mg, 0.265 mmol), (E)-N-(4-ethylbenzylidene)-4-methylbenzenesulfonamide (92 mg, 0.318 mmol) and PMe₃ (5 mg, 0.053 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (96 mg, 0.202 mmol, 76% yield); 

1H NMR (400 MHz, CDCl₃): δ = 7.16 – 7.30 (m, 9H), 6.97 – 7.09 (m, 4H), 6.72 – 6.73 (m, 1H), 5.85 – 5.90 (m, 2H), 3.92 - 4.07 (m, 2H), 2.61 (q, J = 7.60 Hz, 2H), 2.30 (s, 3H), 1.22 (t, J = 7.60 Hz, 3H) ppm.

13C NMR (100 MHz, CDCl₃): δ = 162.2 (1C), 144.1 (1C), 143.1 (1C), 139.1 (1C), 138.4 (1C), 136.6 (1C), 136.2 (1C), 134.1 (1C), 129.1 (2C), 128.6 (2C), 128.5 (2C), 128.2 (2C), 127.8 (2C), 127.7 (2C), 127.3 (2C), 69.8 (1C), 69.4 (1C), 60.8 (1C), 28.6 (1C), 21.4 (1C), 15.7 (1C), 13.9 (1C) ppm. FTIR (neat): ν = 3055, 2984, 2968, 2932, 1721, 1599, 1454, 1421, 1341, 1265, 1165, 1093 cm⁻¹; HRMS (ESI, m/z): calcd for C₂₈H₃₀NO₄S [M+H]⁺ 476.1896, found: 476.1896.

Ethyl 5-phenyl-2-p-tolyl-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (3ac):

The product was prepared by above general procedure, employing ethyl-4-phenylbut-3-ynoate (50 mg, 0.265 mmol), (E)-4-methyl-N-(4-
ethylbenzylidene) benzenesulfonamide (87 mg, 0.318 mmol) and PMe₃ (5 mg, 0.053 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (83 mg, 0.181 mmol, 68% yield); ¹H NMR (400 MHz, CDCl₃): δ = 7.22 – 7.37 (m, 9H), 7.01 – 7.08 (m, 4H), 6.72 – 6.73 (m, 1H), 5.88 – 5.89 (m, 1H), 5.82 – 5.84 (m, 1H), 3.97 - 4.08 (m, 2H), 2.32 (s, 6H), 1.09 (t, J = 7.12 Hz, 3H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 162.2 (1C), 143.2 (1C), 139.1 (1C), 138.4 (1C), 137.8 (1C), 136.5 (1C), 136.0 (1C), 134.0 (1C), 129.2 (2C), 128.9 (2C), 128.6 (2C), 128.4 (2C), 128.1 (1C), 127.7 (2C), 127.4 (2C), 69.9 (1C), 69.4 (1C), 60.9 (1C), 21.4 (1C), 21.2 (1C), 13.9 (1C) ppm. FTIR (neat): ν = 3053, 2986, 2305, 1721, 1454, 1341, 1265, 1165, 1092 cm⁻¹; HRMS (ESI, m/z): calcd for C₂₇H₂₈NO₄S [M+H]⁺ 462.1705, found: 462.1712.

Ethyl 2-(4-methoxyphenyl)-5-phenyl-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (3ad):

The product was prepared by above general procedure, employing ethyl-4-phenylbut-3-ynoate (50 mg, 0.265 mmol), (E)-N-(4-methoxybenzylidene)-4-methylbenzenesulfonamide (92 mg, 0.318 mmol) and PMe₃ (5 mg, 0.053 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (90 mg, 0.189 mmol, 71% yield); ¹H NMR (400 MHz, CDCl₃): δ = 7.21 – 7.36 (m, 9H), 7.00 – 7.03 (m, 2H), 6.79 – 6.81 (m, 2H), 6.72 – 6.73 (m, 1H), 5.89 – 5.90 (m, 1H), 5.82 – 5.83 (m, 1H), 3.98 - 4.09 (m, 2H), 3.79 (s, 3H), 2.31 (s, 3H), 1.09 (t, J = 7.50 Hz, 3H) ppm. ¹³C NMR (100MHz, CDCl₃): δ = 162.4 (1C), 159.6 (1C), 143.3 (1C), 139.3 (1C), 138.6 (1C), 136.3 (1C), 134.1 (1C), 131.8 (1C), 129.9 (2C), 129.4 (2C), 128.8 (2C), 128.3 (1C), 127.8 (2C), 127.5 (2C), 113.8 (2C), 69.9 (1C), 69.3 (1C), 61.0 (1C), 55.4 (1C), 21.7 (1C), 14.1 (1C) ppm. FTIR (neat): ν = 3053, 2986, 2305, 1719, 1512, 1341, 1265, 1165, 1094, 1034 cm⁻¹; HRMS (ESI, m/z): calcd for C₂₇H₂₈NO₅S [M+H]⁺ 482.1688, found: 482.1681.

Ethyl 2-(2-methoxyphenyl)-5-phenyl-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (3ae):

The product was prepared by above general procedure, employing ethyl-4-phenylbut-3-ynoate (50 mg, 0.265 mmol), (E)-N-(2-methoxybenzylidene)-4-methylbenzenesulfonamide (92 mg, 0.318 mmol) and PMe₃ (5 mg, 0.053 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (89 mg, 0.186 mmol, 70% yield); ¹H NMR (400 MHz, CDCl₃): δ = 7.47 – 7.53 (m, 4H), 7.30 – 7.38 (m, 3H), 7.12 – 7.21 (m, 4H), 6.80 – 6.85 (d, 1H), 6.66 – 6.72 (m, 1H), 5.88 – 5.90 (m, 1H), 5.82 – 5.83 (m, 1H), 3.98 - 4.09 (m, 2H), 3.79 (s, 3H), 2.31 (s, 3H), 1.09 (t, J = 7.50 Hz, 3H) ppm. ¹³C NMR (100MHz, CDCl₃): δ = 162.4 (1C), 159.6 (1C), 143.3 (1C), 139.3 (1C), 138.6 (1C), 136.3 (1C), 134.1 (1C), 131.8 (1C), 129.9 (2C), 129.4 (2C), 128.8 (2C), 128.3 (1C), 127.8 (2C), 127.5 (2C), 113.8 (2C), 69.9 (1C), 69.3 (1C), 61.0 (1C), 55.4 (1C), 21.7 (1C), 14.1 (1C) ppm. FTIR (neat): ν = 3053, 2986, 2305, 1719, 1512, 1341, 1265, 1165, 1094, 1034 cm⁻¹; HRMS (ESI, m/z): calcd for C₂₇H₂₈NO₅S [M+H]⁺ 478.1688, found: 478.1681.
6.83 – 6.85 (m, 2H), 6.71 (m, 1H), 6.33 (m, 1H), 5.82 (m, 1H), 3.89 - 4.09 (m, 2H), 3.85 (s, 3H), 2.34 (s, 3H), 1.01 (t, J = 7.50 Hz, 3H) ppm. $^{13}$C NMR (100MHz, CDCl$_3$): δ = 162.1 (1C), 157.5 (1C), 143.4 (1C), 139.2 (1C), 138.9 (1C), 135.0 (1C), 134.3 (1C), 129.3 (3C), 129.2 (1C), 128.6 (2C), 128.4 (1C), 128.0 (1C), 127.8 (2C), 127.5 (2C), 120.5 (1C), 111.1 (1C), 69.8 (1C), 62.6 (1C), 60.7 (1C), 55.8 (1C), 21.5 (1C), 13.8 (1C) ppm. FTIR (neat): ν = 3055, 2984, 2839, 2305, 1719, 1598, 1493, 1352, 1265, 1167, 1094 cm$^{-1}$; HRMS (ESI, m/z): calcd for C$_{27}$H$_{28}$NO$_5$S [M+H]$^+$ 478.1688, found: 478.1681.

Ethyl 2-(4-bromophenyl)-5-phenyl-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (3af):

The product was prepared by above general procedure, employing ethyl-4-phenylbut-3-ynoate (50 mg, 0.265 mmol), (E)-N-(4-bromobenzylidene)-4-methylbenzenesulfonamide (108 mg, 0.318 mmol) and PMe$_3$ (5 mg, 0.053 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (76 mg, 0.143 mmol, 54% yield); $^1$H NMR (400 MHz, CDCl$_3$): δ = 7.32 – 7.34 (m, 7H), 7.20 – 7.23 (m, 4H), 7.03 – 7.05 (m, 2H), 6.76 (brs, 1H), 5.86 (brs, 2H), 3.99 - 4.10 (m, 2H), 2.34 (s, 3H), 1.11 (t, J = 7.20 Hz, 3H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 162.1 (1C), 143.7 (1C), 139.8 (1C), 138.7 (1C), 138.7 (1C), 135.9 (1C), 133.8 (1C), 131.5 (2C), 130.4 (2C), 129.5 (2C), 128.9 (2C), 128.5 (1C), 127.8 (2C), 127.5 (2C), 122.3 (1C), 70.1 (1C), 69.1 (1C), 61.2 (1C), 21.6 (1C), 14.1 (1C) ppm. FTIR (neat): ν = 3055, 2986, 2305, 1719, 1421, 1341, 1265, 1165, 1092 cm$^{-1}$; HRMS (ESI, m/z): calcd for C$_{26}$H$_{25}$BrNO$_4$S [M+H]$^+$ 526.0688, found: 526.0682.

Ethyl 2-(4-chlorophenyl)-5-phenyl-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (3ag):

The product was prepared by above general procedure, employing ethyl-4-phenylbut-3-ynoate (50 mg, 0.265 mmol), (E)-N-(4-chlorobenzylidene)-4-methylbenzenesulfonamide (94 mg, 0.318 mmol) and PMe$_3$ (5 mg, 0.053 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (114 mg, 0.236 mmol, 89% yield); $^1$H NMR (400 MHz, CDCl$_3$): δ = 7.36 – 7.37 (m, 2H), 7.24 – 7.29 (m, 4H), 7.06 – 7.08 (m, 2H), 6.93 – 6.94 (m, 2H), 6.73 (t, J = 2.18 Hz, 1H), 6.43 – 6.44 (m, 1H), 6.31 – 6.32 (m, 1H), 6.07 (t, J = 2.35 Hz, 1H), 5.79 (t, J = 2.60 Hz, 1H), 4.02 - 4.19 (m, 2H), 2.27 (s, 3H), 1.14 (t, J = 7.13 Hz, 3H) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): δ = 162.0 (1C), 151.6 (1C), 142.9 (1C), 142.4 (2C), 140.5 (2C), 138.1 (1C), 136.8 (1C), 131.1 (1C), 128.3 (4C), 110.6 (2C), 110.0 (2C), 69.8 (2C), 62.3(2C), 61.0 (2C), 21.5 (2C) ppm. FTIR (neat): ν = 3063, 2982, 2928, 2905, 1715, 1655, 1599, 1495, 1456, 1341, 1258, 1161 cm$^{-1}$; HRMS (ESI, m/z): calcd for C$_{26}$H$_{25}$ClNO$_4$S [M+H]$^+$ 482.1193, found: 482.1163.
Ethyl 2-(furan-2-yl)-5-phenyl-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (3ah):

The product was prepared by above general procedure, employing ethyl-4-phenylbut-3-ynoate (50 mg, 0.265 mmol), (E)-N-(furan-2-ylmethylene)-4-methylbenzenesulfonamide (79 mg, 0.318 mmol) and PMe3 (5 mg, 0.053 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (74 mg, 0.170 mmol, 64% yield); 1H NMR (400 MHz, CDCl3): δ= 7.22 – 7.37 (m, 10H), 7.04 – 7.05 (m, 2H), 6.76 – 6.77 (m, 1H), 5.88 – 5.89 (m, 1H), 5.85 – 5.86 (m, 1H), 3.99 – 4.09 (m, 2H), 2.33 (s, 3H), 1.10 (t, J = 7.13 Hz, 3H) ppm. 13C NMR (125 MHz, CDCl3): δ = 161.9, 143.4, 139.6, 138.1, 137.9, 135.7, 133.8, 133.6, 129.8 (2), 129.2 (2), 128.6 (2), 128.3, 128.2, 127.6 (2), 127.2 (2), 69.8, 68.8, 21.4, 13.8 ppm.


Ethyl 2-(furan-2-yl)-5-p-tolyl-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (3bh):

The product was prepared by above general procedure, employing ethyl 4-p-tolylbut-3-ynoate (50 mg, 0.247 mmol), (E)-N-(furan-2-ylmethylene)-4-methylbenzenesulfonamide (74 mg, 0.297 mmol) and PMe3 (5 mg, 0.049 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (86 mg, 0.190 mmol, 77% yield); 1H NMR (300 MHz, CDCl3): δ= 6.90 – 7.30 (m, 9H), 6.76 (t, J=2.1 Hz, 1H), 6.45 – 6.49 (m, 1H), 6.25 – 6.35 (m, 1H), 6.05 (t, J=2.5 Hz, 1H), 5.75 (t, J=2.6 Hz, 1H), 3.99 – 4.09 (m, 2H), 2.33 (s, 3H), 2.28 (s, 3H), 1.14 (t, J = 7.20 Hz, 3H) ppm. 13C NMR (100 MHz, CDCl3): δ= 162.0 (1C), 151.6 (1C), 142.8 (1C), 142.2 (1C), 140.6 (1C), 138.0 (1C), 136.7 (1C), 135.1 (1C), 130.9 (1C), 129.1 (2C), 128.9 (2C), 128.0 (2C), 127.0 (2C), 110.5 (1C), 109.8 (1C), 69.5 (1C), 62.1 (1C), 60.9 (1C), 21.4 (1C), 21.1 (1C), 13.9 (1C) ppm. FTIR (neat): ν = 3053, 2984, 2968, 1721, 1599, 1340, 1265, 1165, 1094 cm⁻¹; HRMS (ESI, m/z): calcd for C25H26NO5S [M+H]+ 452.1524, found: 452.1521.

Ethyl 2-(furan-2-yl)-5-(4-methoxyphenyl)-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (3ch):

The product was prepared by above general procedure, employing ethyl 4-(4-methoxyphenyl)but-3-ynoate (50 mg, 0.229 mmol), (E)-N-(furan-2-ylmethylene)-4-methylbenzenesulfonamide (74 mg, 0.297 mmol) and PMe3 (5 mg, 0.046 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (73 mg, 0.156 mmol, 68% yield); 1H NMR (400 MHz, CDCl3): δ= 7.26 – 7.31 (m, 3H), 7.05 – 7.06 (m, 2H), 6.76 – 6.77 (m, 1H), 5.88 – 5.89 (m, 1H), 5.85 – 5.86 (m, 1H), 3.99 – 4.09 (m, 2H), 2.33 (s, 3H), 1.10 (t, J = 7.13 Hz, 3H) ppm. 13C NMR (125 MHz, CDCl3): δ = 161.9, 143.4, 139.6, 138.1, 137.9, 135.7, 133.8, 133.6, 129.8 (2), 129.2 (2), 128.6 (2), 128.3, 128.2, 127.6 (2), 127.2 (2), 69.8, 68.8, 21.4, 13.8 ppm.

FTIR (neat): ν = 3053, 2984, 2968, 1721, 1599, 1340, 1265, 1165, 1094 cm⁻¹; HRMS (ESI, m/z): calcd for C26H28NO5S [M+H]+ 452.1524, found: 452.1521.
7.04 – 7.06 (m, 2H), 6.93 – 6.95 (m, 2H), 6.77 – 6.79 (m, 2H), 6.71 – 6.72 (m, 1H), 6.41 – 6.42 (m, 1H), 6.30 – 6.32 (m, 1H), 6.04 – 6.05 (m, 1H), 5.75 – 5.77 (m, 1H), 4.04 – 4.17 (m, 2H), 3.78 (s, 3H), 2.28 (s, 3H), 1.15 (t, J = 7.20 Hz, 3H) ppm.

$^{13}$C NMR (125 MHz, CDCl$_3$): \( \delta = 162.0 \) (1C), 159.6 (1C), 151.5 (1C), 142.7 (1C), 142.3 (1C), 140.5 (1C), 136.9 (1C), 130.9 (1C), 130.2 (1C), 129.5 (2C), 128.9 (2C), 127.0 (2C), 113.8 (2C), 110.5 (1C), 109.9 (1C), 69.2 (1C), 62.0 (1C), 60.9 (1C), 55.3 (1C), 21.4 (1C), 14.0 (1C) ppm.

FTIR (neat): \( \nu = 3055, 2984, 2305, 1719, 1512, 1265, 739 \text{ cm}^{-1} \);

HRMS (ESI, m/z): calcd for C$_{25}$H$_{26}$NO$_6$S [M+H]$^+$ 468.1481, found: 468.1480.

**Ethyl 2-(furan-2-yl)-5-(6-methoxynaphthalen-2-yl)-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (3dh):**

The product was prepared by above general procedure, employing ethyl 4-(6-methoxynaphthalen-2-yl)but-3ynoate (50 mg, 0.186 mmol), (E)-N-(furan-2-ylmethylene)-4-methylbenzenesulfonamide (56 mg, 0.224 mmol) and PMe$_3$ (3 mg, 0.037 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (59 mg, 0.114 mmol, 61% yield);

$^1$H NMR (400 MHz, CDCl$_3$): \( \delta = 7.58 – 7.68 \) (m, 3H), 7.34 – 7.45 (m, 2H), 6.98 – 7.14 (m, 4H), 6.76 – 6.80 (m, 3H), 6.47 – 6.48 (m, 1H), 6.35 – 6.36 (m, 1H), 6.13 – 6.14 (m, 1H), 5.93 (t, \( J = 2.3 \text{ Hz} \), 1H), 4.05 – 4.19 (m, 2H), 3.92 (s, 3H), 2.17 (s, 3H), 1.16 (t, J = 7.20 Hz, 3H) ppm.

$^{13}$C NMR (75 MHz, CDCl$_3$): \( \delta = 162.0 \) (1C), 158.0 (1C), 151.7 (1C), 142.7 (1C), 142.2 (1C), 140.5 (1C), 136.8 (1C), 134.4 (1C), 132.9 (1C), 131.0 (1C), 129.6 (1C), 128.8 (2C), 128.5 (1C), 127.4 (1C), 127.1 (1C), 126.9 (2C), 125.9 (1C), 118.9 (1C), 110.6 (1C), 110.0 (1C), 105.5 (1C), 69.8 (1C), 62.2 (1C), 60.9 (1C), 55.3 (1C), 21.3 (1C), 14.0 (1C) ppm. FTIR (neat): \( \nu = 3053, 2986, 2305, 1719, 1512, 1265, 739 \text{ cm}^{-1} \); HRMS (ESI, m/z): calcd for C$_{29}$H$_{27}$NO$_6$S [M+H]$^+$ 518.1637, found: 518.1636.

**Ethyl-2-(furan-2-yl)-1-tosyl-5-(4-(trifluoromethyl) phenyl)-2,5-dihydro-1H-pyrrole-3-carboxylate (3eh):**

The product was prepared by above general procedure, employing ethyl 4-(4-(trifluoromethyl) phenyl)but-3ynoate (50 mg, 0.195 mmol), (E)-N-(furan-2-ylmethylene)-4-methylbenzenesulfonamide (58 mg, 0.234 mmol) and PMe$_3$ (3 mg, 0.039 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (82 mg, 0.162 mmol, 83% yield);

$^1$H NMR (300 MHz, CDCl$_3$): \( \delta = 7.46 \) (brs, 4H), 7.35
(m, 1H), 6.90-7.10 (m, 4H), 6.70 (t, J=2.2Hz, 1H), 6.50 (m, 1H), 6.40(m, 1H), 6.10 (t, J=2.6Hz, 1H), 5.81 (t, J=2.7Hz, 1H), 4.00-4.22 (m, 2H), 2.28 (s, 3H), 1.16 (t, J=7.20 Hz, 3H) ppm. 13C NMR (100MHz, CDCl3): δ = 162.0 (1C), 159.6 (1C), 151.5 (1C), 142.7 (1C), 142.3 (1C), 140.5 (1C), 136.9 (1C), 130.9 (1C), 130.2 (1C), 129.5 (2C), 128.9 (2C), 127.0 (2C), 113.8 (2C), 110.5 (1C), 109.9 (1C), 69.2 (1C), 62.0 (1C), 60.9 (1C), 55.3 (1C), 21.4 (1C), 14.0 (1C) ppm.


Ethyl-2-(furan-2-yl)-5-(thiophen-2-yl)-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate(3fh):

The product was prepared by above general procedure, employing ethyl 4-(thiophen-2-yl)but-3-ynoate (50 mg, 0.257 mmol), (E)-N-(furan-2-ylmethylene)-4-methylbenzenesulfonamide (77 mg, 0.309 mmol) and PMe3 (5 mg, 0.051 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (103 mg, 0.203 mmol, 79% yield); 1H NMR (300 MHz, CDCl3): δ = 7.25 – 7.28 (m, 2H), 7.10 – 7.15 (m, 1H), 7.00 - 7.05 (m, 3H), 6.94 – 6.96 (m, 2H), 6.75 – 6.77 (m, 1H), 6.41 – 6.42 (m, 1H), 6.29 – 6.31 (m, 1H), 6.05 – 6.07 (m, 1H), 5.93 – 5.95 (m, 1H), 3.99 – 4.17 (m, 2H), 2.29 (s, 3H), 1.16 (t, J = 7.20 Hz, 3H) ppm. 13C NMR (75 MHz, CDCl3): δ = 161.9 (1C), 151.4 (1C), 142.7 (1C), 142.3 (1C), 139.7 (1C), 139.1 (1C), 137.0 (1C), 131.3 (1C), 128.9 (2C), 127.1 (1C), 126.8 (2C), 126.0 (1C), 124.3 (1C), 110.5 (1C), 109.9 (1C), 64.7 (1C), 61.9 (1C), 61.0 (1C), 21.4 (1C), 13.9 (1C) ppm. FTIR (neat): ν = 3055, 2984, 1719, 1340, 1265, 1161, 1094, 1013, 737 cm⁻¹; HRMS (ESI, m/z): calcd for C22H22NO5S2 [M+H]^+ 444.0939, found: 444.0938.

Ethyl 2-(furan-2-yl)-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (3gh):

The product was prepared by above general procedure, employing ethyl but-3-ynoate (50 mg, 0.446 mmol), (E)-N-(furan-2-ylmethylene)-4-methylbenzenesulfonamide (77 mg, 0.309 mmol) and PMe3 (7 mg, 0.089 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (158 mg, 0.312 mmol, 70% yield); 1H NMR (300 MHz, CDCl3): δ = 7.45 – 7.48 (m, 2H), 7.15 - 7.20 (m, 3H), 6.82 (q, J=2.01 Hz, 1H), 6.34 – 6.37 (m, 1H), 6.25 – 6.30 (m, 1H), 5.87 (td, J=5.5, 1.7Hz, 1H), 4.25 – 4.55 (m, 2H), 4.00 – 4.20 (m, 2H), 2.38 (s, 3H), 1.59 (t, J=7.12 Hz, 3H) ppm. 13C NMR (75 MHz, CDCl3): δ = 161.6, 151.3, 143.2, 142.1, 136.9, 135.6, 133.0, 129.5 (2), 127.0 (2), 110.4, 109.1, 61.7, 60.8, 54.2, 21.4, 13.9 ppm. FTIR (neat): ν = 3053, 2986, 2305, 1721, 1422, 1265, 1165, 895 cm⁻¹; HRMS (ESI, m/z): calcd for C18H20NO5S [M+H]^+ 362.1062, found: 362.1067.
Triethyl 1-tosyl-2, 5-dihydro-1H-pyrrole-2,3,5-tricarboxylate (3ha):

The product was prepared by above general procedure, employing diethyl pent-2-ynedioate (50 mg, 0.271 mmol), (E)-N-benzylidene-4-methylbenzenesulfonamide (84 mg, 0.326 mmol) and PMe$_3$ (5 mg, 0.054 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product as colorless oil (75 mg, 0.149 mmol, 55% yield); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$= 7.42 – 7.45 (m, 2H), 7.32 – 7.35 (m, 2H), 7.26 (brs, 3H), 7.15 - 7.17 (m, 2H), 6.70 (t, $J$=2.3 Hz, 1H), 5.80 – 5.82 (m, 1H), 5.51 (t, $J$=2.7 Hz, 1H), 4.15 – 4.35 (m, 1H), 3.95 – 4.10 (m, 2H), 2.30 (s, 3H), 1.10 (t, $J$=7.14 Hz, 3H) ppm.

Ethyl 1-(methylsulfonyl)-2,5-diphenyl-2,5-dihydro-1H-pyrrole-3-carboxylate (5aa):

The product was prepared by above general procedure, employing ethyl 4-phenylbut-3-ynoate (50 mg, 0.266 mmol), (E)-N-benzylidene methanesulfonamide (58 mg, 0.319 mmol) and PMe$_3$ (5 mg, 0.053 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (113 mg, 0.223 mmol, 84% yield); $^1$H NMR (300 MHz, CDCl$_3$): $\delta$= 7.30 – 7.51 (m, 10H), 6.83 – 6.84 (m, 1H), 6.03 – 6.04 (m, 1H), 5.96 – 5.98 (m, 1H), 3.99 – 4.17 (m, 2H), 2.04 (s, 3H), 1.10 (t, $J$ = 7.05 Hz, 3H) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$= 162.1 (1C), 139.2 (1C), 139.1 (1C), 138.3 (1C), 134.1 (1C), 129.0 (1C), 128.7 (2C), 128.6 (1C), 128.4 (2C), 128.4 (2C), 128.0 (2C), 69.4 (1C), 68.9 (1C), 60.9 (1C), 42.6 (1C), 13.9 (1C) ppm.

FTIR (neat): $\nu$ = 3055, 2986, 2305, 1719, 1456, 1422, 1334, 1265, 1151 cm$^{-1}$; HRMS (ESI, m/z): calcd for C$_{20}$H$_{22}$NO$_4$S [M+H]$^+$ 372.1270, found: 372.1270.

Ethyl 1-(methylsulfonyl)-5-phenyl-2-(4-(trifluoromethyl)phenyl)-2,5-dihydro-1H-pyrrole-3-carboxylate (5ab):

The product was prepared by above general procedure, employing ethyl 4-phenylbut-3-ynoate (50 mg, 0.266 mmol), (E)-N-(4-(trifluoromethyl)benzylidene)methanesulfonamide (80 mg, 0.319 mmol) and PMe$_3$ (5 mg, 0.053 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (102 mg, 0.202 mmol, 76% yield); $^1$H NMR (300 MHz, CDCl$_3$): $\delta$= 7.59 – 7.66 (m, 4H), 7.38 – 7.50 (m, 5H), 6.88 – 6.90 (m, 1H), 6.08 – 6.09 (m, 1H), 5.97 – 5.99 (m, 1H), 4.03 – 4.16 (m, 2H), 7.42 – 7.45 (m, 2H), 7.32 – 7.35 (m, 2H), 7.26 (brs, 3H), 7.15 - 7.17 (m, 2H), 6.70 (t, $J$=2.3 Hz, 1H), 5.80 – 5.82 (m, 1H), 5.51 (t, $J$=2.7 Hz, 1H), 4.15 – 4.35 (m, 1H), 3.95 – 4.10 (m, 2H), 2.30 (s, 3H), 1.10 (t, $J$=7.14 Hz, 3H) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$= 162.1 (1C), 139.2 (1C), 139.1 (1C), 138.3 (1C), 134.1 (1C), 129.0 (1C), 128.7 (2C), 128.6 (1C), 128.4 (2C), 128.4 (2C), 128.0 (2C), 69.4 (1C), 68.9 (1C), 60.9 (1C), 42.6 (1C), 13.9 (1C) ppm.

FTIR (neat): $\nu$ = 3055, 2986, 2305, 1719, 1456, 1422, 1334, 1265, 1151 cm$^{-1}$; HRMS (ESI, m/z): calcd for C$_{20}$H$_{22}$NO$_4$S [M+H]$^+$ 372.1270, found: 372.1270.
2.25 (s, 3H), 1.13 (t, J = 7.20 Hz, 3H) ppm. \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta= 161.8\) (1C), 143.4 (1C), 139.7 (1C), 138.0 (1C), 133.8 (1C), 129.2 (2C), 129.0 (1C), 128.8 (2C), 128.0 (2C), 125.7 (1C), 125.6 (1C), 125.6 (1C), 69.6 (1C), 68.5 (1C), 61.2 (1C), 42.3 (1C), 13.9 (1C) ppm. FTIR (neat): \(v = 3053, 2986, 2305, 1721, 1422, 1325, 1067, 895\) cm\(^{-1}\).

Ethyl 1-(methylsulfonyl)-2-(4-nitrophenyl)-5-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate (5ac):

The product was prepared by above general procedure, employing ethyl 4-phenylbut-3-ynoate (50 mg, 0.266 mmol), (E)-N-(4-nitrobenzylidene) methanesulfonamide (73 mg, 0.319 mmol) and PMe\(_3\) (5 mg, 0.053 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (63 mg, 0.125 mmol, 47% yield); \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta= 8.23 – 8.26\) (m, 2H), 7.67 – 7.69 (m, 2H), 7.40– 7.47 (m, 5H), 6.91 – 6.93 (m, 1H), 6.11 – 6.12 (m, 1H), 5.98 – 6.00 (m, 1H), 4.05 – 4.17 (m, 2H), 2.29 (s, 3H), 1.16 (t, J = 7.12 Hz, 3H) ppm. \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta= 161.6\) (1C), 147.7 (1C), 146.6 (1C), 139.5 (1C), 138.1 (1C), 138.0 (1C), 134.3 (1C), 133.5 (1C), 129.4 (2C), 129.3 (2C), 129.2 (1C), 127.9 (2C), 123.8 (2C), 69.7 (1C), 68.2 (1C), 61.3 (1C), 42.2 (1C), 13.9 (1C) ppm. FTIR (neat): \(v = 3053, 2986, 2305, 1721, 1491, 1335, 1265, 1152, 1090\) cm\(^{-1}\); HRMS (ESI, m/z): calcd for C\(_{20}\)H\(_{21}\)N\(_2\)O\(_4\)S [M+H]\(^+\) 417.1127, found: 417.1129.

Ethyl 2-(4-chlorophenyl)-1-(methylsulfonyl)-5-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate (5ad):

The product was prepared by above general procedure, employing ethyl 4-phenylbut-3-ynoate (50 mg, 0.266 mmol), (E)-N-(4-chlorobenzylidene) methanesulfonamide (69 mg, 0.319 mmol) and PMe\(_3\) (5 mg, 0.053 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (95 mg, 0.189 mmol, 71% yield); \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta= 7.34– 7.47\) (m, 9H), 6.84 – 6.86 (m, 1H), 6.00 – 6.02 (m, 1H), 5.94 – 5.96 (m, 1H), 4.03 – 4.16 (m, 2H), 2.23 (s, 3H), 1.14 (t, J = 7.05 Hz, 3H) ppm. \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta= 161.9\) (1C), 139.5 (1C), 138.1 (1C), 138.0 (1C), 134.3 (1C), 133.8 (1C), 129.8 (2C), 129.1 (2C), 128.9 (3C), 127.9 (2C), 69.5 (1C), 68.3 (1C), 61.1 (1C), 42.5 (1C), 13.9 (1C) ppm. FTIR (neat): \(v = 3053, 2986, 2305, 1721, 1491, 1335, 1265, 1152, 1090\) cm\(^{-1}\); HRMS (ESI, m/z): calcd for C\(_{20}\)H\(_{21}\)ClNO\(_4\)S [M+H]\(^+\) 406.0880, found: 406.0723.

Ethyl 2-(4-cyanophenyl)-1-(methylsulfonyl)-5-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate (5ae):

The product was prepared by above general procedure, employing ethyl 4-phenylbut-3-ynoate (50 mg, 0.266 mmol), (E)-N-(4-cyanobenzylidene) methanesulfonamide (66 mg, 0.319 mmol) and PMe\(_3\) (5 mg, 0.053 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (95 mg, 0.189 mmol, 71% yield); \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta= 7.34– 7.47\) (m, 9H), 6.84 – 6.86 (m, 1H), 6.00 – 6.02 (m, 1H), 5.94 – 5.96 (m, 1H), 4.03 – 4.16 (m, 2H), 2.23 (s, 3H), 1.14 (t, J = 7.05 Hz, 3H) ppm. \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta= 161.9\) (1C), 139.5 (1C), 138.1 (1C), 138.0 (1C), 134.3 (1C), 133.8 (1C), 129.8 (2C), 129.1 (2C), 128.9 (3C), 127.9 (2C), 69.5 (1C), 68.3 (1C), 61.1 (1C), 42.5 (1C), 13.9 (1C) ppm. FTIR (neat): \(v = 3053, 2986, 2305, 1721, 1491, 1335, 1265, 1152, 1090\) cm\(^{-1}\); HRMS (ESI, m/z): calcd for C\(_{20}\)H\(_{21}\)ClNO\(_4\)S [M+H]\(^+\) 406.0880, found: 406.0723.
(5 mg, 0.053 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (86 mg, 0.170 mmol, 64 % yield); \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.73 – 7.76\) (m, 2H), 7.61 – 7.65 (m, 1H), 7.40–7.52 (m, 6H), 6.90 – 6.91 (m, 1H), 6.03 – 6.05 (m, 1H), 5.95 – 5.97 (m, 1H), 4.04 – 4.18 (m, 2H), 2.27 (s, 3H), 1.16 (t, \(J = 7.20\) Hz, 3H) ppm. \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta = 161.6\) (1C), 141.2 (1C), 139.9 (1C), 137.7 (1C), 133.5 (1C), 133.0 (1C), 132.1 (1C), 131.8 (1C), 129.5 (1C), 129.3 (2C), 129.2 (1C), 127.9 (2C), 118.4 (1C), 112.8 (1C), 69.6 (1C), 68.2 (1C), 61.3 (1C), 42.2 (1C), 13.9 (1C) ppm. FTIR (neat): \(\nu = 3055, 2986, 2305, 1719, 1339, 1265, 1153\) cm\(^{-1}\); HRMS (ESI, m/z): calcd for C\(_{21}\)H\(_{21}\)N\(_2\)O\(_4\)S \([\text{M+H}]^+\) 397.1229, found: 397.1222.

Ethyl 2-(4-methoxyphenyl)-1-(methylsulfonyl)-5-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate

The product was prepared by above general procedure, employing ethyl 4-phenylbut-3-ynoate (50 mg, 0.266 mmol), (E)-N-(4-methoxybenzylidene) methanesulfonamide (68 mg, 0.319 mmol) and PMe\(_3\) (5 mg, 0.053 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (94 mg, 0.186 mmol, 70% yield); \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.33 – 7.49\) (m, 7H), 6.91 – 6.92 (m, 1H), 6.89 – 6.90 (m, 1H), 6.80 – 6.81 (m, 1H), 6.00 – 6.01 (m, 1H), 5.93 – 5.95 (m, 1H), 4.02 – 4.15 (m, 2H), 3.81 (s, 3H), 2.20 (s, 3H), 1.13 (t, \(J = 7.20\) Hz, 3H) ppm. \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta = 162.5\) (1C), 159.8 (1C), 139.1 (1C), 138.7 (1C), 134.3 (1C), 131.5 (1C), 129.8 (2C), 129.1 (2C), 128.8 (1C), 128.1 (2C), 114.2 (2C), 69.5 (1C), 68.6 (1C), 61.2 (1C), 55.5 (1C), 42.9 (1C), 14.2 (1C) ppm. HRMS (ESI, m/z): calcd for C\(_{21}\)H\(_{23}\)NO\(_5\)S \([\text{M+H}]^+\) 402.1368, found: 402.1371.

Ethyl 2-(furan-2-yl)-1-(methylsulfonyl)-5-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate (5ag):

The product was prepared by above general procedure, employing ethyl 4-phenylbut-3-ynoate (50 mg, 0.266 mmol), (E)-N-(furan-2-ylmethylene) methanesulfonamide (55 mg, 0.319 mmol) and PMe\(_3\) (5 mg, 0.053 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (120 mg, 0.236 mmol, 89% yield); \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.53 – 7.56\) (m, 2H), 7.34 – 7.46 (m, 4H), 6.81 – 6.83 (m, 1H), 6.53 – 6.54 (m, 1H), 6.40 – 6.41 (m, 1H), 6.08 – 6.10 (m, 1H), 5.82 – 5.84 (m, 1H), 4.06 – 4.25 (m, 2H), 2.10 (s, 3H), 1.18 (t, \(J = 7.05\) Hz, 3H) ppm. \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta = 161.9\) (1C), 151.0 (1C), 142.7 (1C), 140.2 (1C), 137.8 (1C), 131.3 (1C), 128.9 (2C), 128.8 (1C), 128.4 (2C), 110.8 (1C), 110.2 (1C), 69.3
(1C), 61.7 (1C), 61.0 (1C), 42.1 (1C), 14.0 (1C) ppm. **HRMS (ESI, m/z):** calcld for C$_{18}$H$_{20}$NO$_5$S [M+H]$^+$ 362.1062, found: 362.1061.

**Ethyl 2-(4-(benzyl氧)butyl)-5-phenyl-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (7aa):**

The product was prepared by above general procedure, employing ethyl 4-phenylbut-3-ynoate (50 mg, 0.266 mmol), (E)-N-(5-(benzyl氧)pentylidene)-4-methylbenzenesulfonamide (110 mg, 0.319 mmol) and PMe$_3$ (5 mg, 0.053 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (103 mg, 0.194 mmol, 73% yield); $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.63 – 7.65 (m, 2H), 7.38 – 7.39 (m, 2H), 7.22 – 7.34 (m, 10H), 6.59 – 6.61 (m, 1H), 5.58 (s, 1H), 4.82 – 4.86 (m, 1H), 4.46 (s, 2H), 4.12 – 4.19 (m, 2H), 3.39 – 3.43 (m, 2H), 2.38 (s, 3H), 1.88 – 1.97 (m, 1H), 1.72 – 1.82 (m, 1H), 1.45 – 1.64 (m, 4H), 1.23 (t, $J$ = 7.20 Hz, 3H) ppm. $^{13}$C NMR (500MHz, CDCl$_3$): $\delta$ = 162.5 (1C), 143.8(1C), 139.0 (1C), 138.8 (1C), 138.7 (1C), 135.1 (1C), 134.8 (1C), 129.7 (2C), 128.6 (2C), 128.3 (2C), 128.0 (1C), 127.7 (2C), 127.6 (2C), 127.4 (1C), 127.3 (2C), 72.9 (1C), 70.3 (1C), 69.5 (1C), 66.8 (1C), 60.9 (1C), 34.9 (1C), 29.6 (1C), 22.0 (1C), 21.5 (1C), 14.1 (1C) ppm. **FTIR (neat):** $\nu$ = 3053, 2941, 2866, 1717, 1677, 1647, 1599, 1495, 1454, 1350, 1265, 1165, 1090, 1028 cm$^{-1}$; **HRMS (ESI, m/z):** calcld for C$_{31}$H$_{35}$NO$_6$S [M+H]$^+$ 534.2314, found: 534.2317.

**Ethyl-2-(4-(benzyl氧)butyl)-S-(2-(tetrahydro-2H-pyran-2-yloxy)ethyl)-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (7oa):**

The product was prepared by above general procedure, employing ethyl 6-(tetrahydro-2H-pyran-2-yloxy)hex-3-ynoate (50 mg, 0.208 mmol), (E)-N-(5-(benzyl氧)pentylidene)-4-methylbenzenesulfonamide (86 mg, 0.250 mmol) and PMe$_3$ (3 mg, 0.042 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (85 mg, 0.146 mmol, 70% yield); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.60 – 7.70 (m, 2H), 7.20 – 7.35 (m, 7H), 6.50 – 6.65 (m, 1H), 4.57 – 4.70 (m, 2H), 4.47 (s, 2H), 4.40 – 4.45 (m, 1H), 4.10 (q, $J$=7.13 Hz, 2H),3.75 – 3.90 (m, 2H), 3.47 – 3.67 (m, 2H), 3.45 (t, $J$=6.6 Hz, 2H), 2.37 (s, 3H), 2.10 – 2.30 (m, 1H), 1.44 – 2.00 (m, 12H), 1.32 – 1.42 (m, 1H), 1.20 (t, $J$=7.1 Hz, 3H) ppm. **FTIR (neat):** $\nu$ = 3053, 2984, 2938, 2864, 1717, 1647, 1599, 1495, 1454, 1350, 1265, 1165, 1090, 1028 cm$^{-1}$; **HRMS (ESI, m/z):** calcld for C$_{27}$H$_{36}$NO$_6$S [M+H]$^+$ 502.2246, found: 502.2263 (THP cleaved mass).

**Ethyl-2-benzyl-5-phenyl-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (7ab):**

![Ethyl 2-benzyl-5-phenyl-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (7ab)](image-url)
The product was prepared by above general procedure, employing ethyl 4-phenylbut-3-ynoate (50 mg, 0.266 mmol), (E)-4-methyl-N-(2-phenylethylidene)benzenesulfonamide (87 mg, 0.319 mmol) and PMe₃ (5 mg, 0.053 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (109 mg, 0.236 mmol, 89% yield); ¹H NMR (300 MHz, CDCl₃): δ = 7.67 – 7.69 (m, 2H), 7.14 – 7.29 (m, 6H), 7.02 – 7.08 (m, 4H), 6.54 – 6.57 (m, 2H), 6.40 – 6.41 (m, 1H), 5.36 – 5.38 (m, 1H), 5.05 – 5.08 (m, 1H), 4.14 – 4.25 (m, 2H), 3.30 – 3.48 (m, 2H), 2.44 (s, 3H), 1.30 (t, *J* = 7.05 Hz, 3H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ = 162.8 (1C), 143.9 (1C), 139.7 (1C), 138.7 (1C), 136.4 (1C), 134.3 (1C), 133.1 (1C), 131.0 (2C), 129.9 (2C), 128.3 (2C), 128.2 (2C), 128.0 (2C), 127.9 (2C), 127.9 (1C), 126.5 (1C), 70.0 (1C), 67.7 (1C), 61.1 (1C), 39.6 (1C), 21.6 (1C), 14.2 (1C) ppm. FTIR (neat): ν = 3055, 2984, 1717, 1599, 1350, 1265, 1165, 1092 cm⁻¹; HRMS (ESI, m/z): calcd for C₂₇H₂₈NO₄S [M+H]+ 462.1739, found: 462.1698.

Ethyl 2-isopropyl-5-phenyl-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (7ac):

The product was prepared by above general procedure, employing ethyl 4-phenylbut-3-ynoate (50 mg, 0.266 mmol), (E)-4-methyl-N-(2-methylpropylidene)benzenesulfonamide (72 mg, 0.319 mmol) and PMe₃ (5 mg, 0.053 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (92 mg, 0.223 mmol, 84% yield); ¹H NMR (300 MHz, CDCl₃): δ = 7.70 – 7.72 (m, 2H), 7.46 – 7.48 (m, 2H), 7.33 – 7.36 (m, 2H), 7.26 – 7.29 (m, 3H), 6.70 – 6.71 (m, 1H), 5.56 – 5.57 (m, 1H), 4.73 (d, *J* = 5.00 Hz, 1H), 4.11 – 4.19 (m, 2H), 2.40 (s, 3H), 1.97 – 2.01 (m, 1H), 1.26 (t, *J* = 7.25 Hz, 3H), 0.93 (d, *J* = 7.00 Hz, 3H), 0.79 (d, *J* = 7.00 Hz, 3H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ = 163.0 (1C), 143.9 (1C), 139.0 (1C), 138.2 (1C), 136.0 (1C), 134.2 (1C), 129.7 (2C), 128.5 (2C), 127.9 (2C), 127.8 (1C), 127.1 (2C), 72.4 (1C), 68.9 (1C), 60.9 (1C), 33.6 (1C), 21.5 (1C), 19.5 (1C), 19.4 (1C), 14.1 (1C) ppm. FTIR (neat): ν = 3057, 2968, 2934, 2907, 1719, 1647, 1599, 1348, 1265, 1165, 1090, 895, 816 cm⁻¹; HRMS (ESI, m/z): calcd for C₂₃H₂₉NO₄S [M+H]+ 414.1739, found: 414.1738.

Ethyl 2-cyclohexyl-5-phenyl-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (7ad):

The product was prepared by above general procedure, employing ethyl 4-phenylbut-3-ynoate (50 mg, 0.266 mmol), (E)-N-(cyclohexylmethylene)-4-methylbenzenesulfonamide (85 mg, 0.319 mmol) and PMe₃ (5 mg, 0.053 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (108 mg, 0.239 mmol, 89% yield); ¹H NMR (300 MHz, CDCl₃): δ = 7.70 – 7.72 (m, 2H), 7.46 – 7.48 (m, 2H), 7.33 – 7.36 (m, 2H), 7.26 – 7.29 (m, 3H), 6.70 – 6.71 (m, 1H), 5.56 – 5.57 (m, 1H), 4.73 (d, *J* = 5.00 Hz, 1H), 4.11 – 4.19 (m, 2H), 2.40 (s, 3H), 1.97 – 2.01 (m, 1H), 1.26 (t, *J* = 7.25 Hz, 3H), 0.93 (d, *J* = 7.00 Hz, 3H), 0.79 (d, *J* = 7.00 Hz, 3H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ = 163.0 (1C), 143.9 (1C), 139.0 (1C), 138.2 (1C), 136.0 (1C), 134.2 (1C), 129.7 (2C), 128.5 (2C), 127.9 (2C), 127.8 (1C), 127.1 (2C), 72.4 (1C), 68.9 (1C), 60.9 (1C), 33.6 (1C), 21.5 (1C), 19.5 (1C), 19.4 (1C), 14.1 (1C) ppm. FTIR (neat): ν = 3057, 2968, 2934, 2907, 1719, 1647, 1599, 1348, 1265, 1165, 1090, 895, 816 cm⁻¹; HRMS (ESI, m/z): calcd for C₂₃H₂₉NO₄S [M+H]+ 414.1739, found: 414.1738.
90% yield); $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.68 – 7.70 (m, 2H), 7.45 – 7.47 (m, 2H), 7.30 – 7.34 (m, 2H), 7.23 – 7.27 (m, 3H), 6.67 (brs, 1H), 5.56 (brs, 1H), 4.70 – 4.71 (m, 1H), 4.12 – 4.17 (m, 2H), 2.37 (s, 3H), 1.61 – 1.69 (m, 6H), 1.26 (t, $J$ = 7.00 Hz, 3H), 0.85 – 1.16 (m, 5H) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ = 163.0 (1C), 143.8 (1C), 139.0 (1C), 138.1 (1C), 136.0 (1C), 134.3 (1C), 129.7 (2C), 128.5 (2C), 127.8 (2C), 127.2 (2C), 71.8 (1C), 68.9 (1C), 60.9 (1C), 43.6 (1C), 29.9 (1C), 29.8 (1C), 26.4 (1C), 26.1 (1C), 21.5 (1C), 14.1 (1C) ppm. FTIR (neat): $\nu$ = 3055, 2984, 2930, 2853, 1719, 1647, 1599, 1495, 1449, 1348, 1265, 1165, 1092 cm$^{-1}$; HRMS (ESI, m/z): calcd for C$_{26}$H$_{32}$NO$_4$S [M+H]$^+$ 454.2018, found: 454.2029.

Ethyl 5-phenyl-2-propyl-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (7ae):

The product was prepared by above general procedure, employing ethyl 4-phenylbut-3-ynoate (50 mg, 0.266 mmol), (E)-N-butylidene-4-methylbenzenesulfonamide (72 mg, 0.319 mmol) and PMe$_3$ (5 mg, 0.053 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (85 mg, 0.205 mmol, 77% yield); $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.60 – 7.70 (m, 2H), 7.20 – 7.40 (m, 7H), 6.55 – 6.60 (m, 1H), 5.55 – 5.60 (m, 1H), 4.80 - 4.85 (m, 1H), 4.10 – 4.25 (m, 2H), 2.40 (s, 3H), 1.65 – 1.75 (m, 2H), 1.35 – 1.50 (m, 2H), 1.25 (t, $J$=7.1 Hz, 3H), 0.87 (t, $J$=7.3 Hz, 3H). 5.96 – 5.98 (m, 1H), 3.99 – 4.17 (m, 2H), 2.04 (s, 3H), 1.10 (t, $J$ = 7.05 Hz, 3H) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ = 162.8 (1C), 144.0 (1C), 139.3 (1C), 138.8 (1C), 135.4 (1C), 135.0 (1C), 129.9 (2C), 128.8 (2C), 128.2 (1C), 127.9 (2C), 127.5 (2C), 69.7 (1C), 67.0 (1C), 61.1 (1C), 37.6 (1C), 21.7 (1C), 18.8 (1C), 14.1 (1C), 14.2 (1C) ppm. FTIR (neat): $\nu$ = 3055, 2982, 2963, 2934, 2872, 1719, 1647, 1599, 1348, 1265, 1165, 1092 cm$^{-1}$; HRMS (ESI, m/z): calcd for C$_{26}$H$_{32}$NO$_4$S [M+H]$^+$ 414.1739, found: 414.1720.

Ethyl 2-heptyl-5-phenyl-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (7af):

The product was prepared by above general procedure, employing ethyl 4-phenylbut-3-ynoate (50 mg, 0.266 mmol), (E)-4-methyl-N-octylidenebenzenesulfonamide (90 mg, 0.319 mmol) and PMe$_3$ (5 mg, 0.053 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (101 mg, 0.215 mmol, 81% yield); $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.61 – 7.64 (m, 2H), 7.41 – 7.43 (m, 2H), 7.28 – 7.36 (m, 3H), 7.24 – 7.26 (m, 2H), 6.60 (brs, 1H), 5.60 (brs, 1H), 4.84 – 4.86 (m, 1H), 4.13 – 4.22 (m, 2H), 2.40
(s, 3H), 1.84 – 1.91 (m, 1H), 1.70 – 1.77 (m, 1H), 1.29 – 1.43 (m, 2H) 1.26 (m, 5H), 1.20 (s, 6H), 0.86 (t, J = 7.20 Hz, 3H) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): δ= 162.6 (1C), 143.7 (1C), 139.0 (1C), 138.7 (1C), 135.2 (1C), 135.0 (1C), 129.7 (2C), 128.6 (2C), 128.0 (1C), 127.7 (2C), 127.4 (2C), 69.4 (1C), 66.9 (1C), 60.9 (1C), 34.9 (1C), 31.7 (1C), 29.4 (1C), 29.0 (1C), 25.1 (1C), 22.7 (1C), 21.5 (1C), 14.1 (2C) ppm.

FTIR (neat): ν = 3053, 2986, 2957, 2928, 2857, 1715, 1422, 1350, 1265, 1165, 1092 cm$^{-1}$; HRMS (ESI, m/z): calcd for C$_{27}$H$_{35}$NO$_4$S [M+H]$^+$ 470.2291, found: 470.2302.

Ethyl-5-(2-hydroxyethyl)-2-(4-(4-methoxybenzyl)oxy)butyl)-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (10):

The product was prepared by above general procedure, employing ethyl 6-hydroxyhex-3-ynoate (2 g, 12.0 mmol), (E)-N-(5-(4-methoxybenzyl)oxy) pentylenediy)-4-methylbenzenesulfonylamide (5.76 g, 14.4 mmol) and PMe$_3$ (200 mg, 2.5 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (30% ethyl acetate in hexane) to afford product (5.5 g, 81% yield); $^1$H NMR (300 MHz, CDCl$_3$): δ= 7.66 – 7.69 (m, 2H), 7.24 - 7.27 (m, 4H), 6.85 – 6.88 (m, 2H), 6.48 (brs, 1H), 4.60 – 4.65 (m, 2H), 4.42 (s, 2H), 4.07 – 4.15 (m, 3H), 3.93 – 4.01 (m, 1H), 3.77 (s, 3H), 3.69 – 3.75 (m, 1H), 3.46 (t, J=6.4Hz, 2H), 2.38 (s, 3H), 1.48 - 2.00 (m, 9H), 1.18-1.21 (m, 4H) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): δ= 162.2, 159.0, 144.0, 140.2, 134.5, 133.5, 130.7, 129.8, 127.6, 113.7, 72.5, 69.9, 66.6, 64.2, 60.8, 58.5, 55.2, 39.0, 35.4, 29.5, 21.9, 21.5, 14.0 ppm. FTIR (neat): ν = 3053, 2985, 2304, 1716, 1555, 1344, 1265, 1163, 738 cm$^{-1}$; HRMS (ESI, m/z): calcd for C$_{20}$H$_{30}$NO$_6$S [M+H]$^+$ 412.1794, found: 412.1800 (PMB cleaved mass).

4-(hydroxymethyl)-5-(4-(4-methoxybenzyl)oxy)-butyl)-1-tosyl-2,5-dihydro-1H-pyrrol-2-yl)ethanol (11):

DIBAL-H (1.0 M in THF, 2.7 g, 18.8 mmol) was added dropwise to a solution of ethyl 5-(2-hydroxyethyl)-2-(4-(4-methoxybenzyl)oxy)butyl)-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (5 g, 9.4 mmol) in dry THF (100 mL) at 0 °C. After 2 h, ethanol (2 mL) was added slowly, and then stirred with aq. solution of sodium potassium tartarate for 5 h. Organic layers were evaporated to get crude residue, that was purified through flash column chromatography (50% ethyl acetate in hexane) to afford product (3.4 g, 74% yield); $^1$H NMR (300 MHz, CDCl$_3$): δ= 7.68 (d, J=8.1, 2H), 7.24 – 7.28 (m, 4H), 6.88 (d, J=8.5, 2H), 5.42 (s, 1H), 5.30 (s, 1H), 4.51 (brs, 1H), 4.38 – 4.42 (m, 3H), 3.88 – 4.02 (m, 3H), 3.80 (s, 3H), 3.68 – 3.72 (m, 1H), 3.40 – 3.50 (m, 2H), 2.40 (s, 3H), 1.40-2.00 (m, 11H)
\[ \delta = 159.1, 143.8, 141.9, 133.7, 130.5, 129.2, 127.6, 124.5, 113.7, 72.5, 69.7, 67.1, 64.0, 58.9(2), 55.2, 39.9, 34.5, 29.4, 21.6, 21.5 \text{ ppm.} \]

**FTIR (neat):** \[ \nu = 3055, 2933, 2304, 1512, 1421, 1340, 1265, 1161, 1093, 894, 815, 744 \text{ cm}^{-1} \];

**HRMS (ESI, m/z):** calcd for C\(_{18}\)H\(_{28}\)NO\(_5\)S [M+H]\(^{+}\) 370.1688, found: 370.1689 (PMB cleaved mass).

\[ \text{2-(5-(hydroxymethyl)-4-(4-(4-methoxybenzylxylo)-butyl)-3-tosyl-6-oxa-3-azabicyclo[3.1.0]hexan-2-yl)ethanol (12):} \]

\[ m\text{-CPBA (2.75 g, 61.3 mmol; 77%) was added to a solution of 4-(hydroxymethyl)-5-(4-(4-methoxybenzylxylo)butyl)-1-tosyl-2,5-dihydro-1H-pyrrol-2-yl)ethanol (3 g, 6.1 mmol) in CH}_2Cl_2 (50 mL) at 0 \text{ }^\circ\text{C. After 12 h, saturated NaHCO}_3 \text{ solution was added, extracted with ethyl acetate. Organic layers were evaporated to get crude residue, that was purified through flash column chromatography (40% ethyl acetate in hexane) to afford product (2.5 g, 81% yield);} \]

**\(^1\text{H NMR (300 MHz, CDCl}_3\):** \[ \delta = 7.62 \text{ (d, J=8.1, 2H), 7.25 – 7.29 (m, 4H), 6.88 \text{ (d, J=8.5, 2H), 4.43 (s, 2H), 3.85 – 4.05 (m, 4H), 3.79 (s, 3H), 3.65 – 3.75 (m, 1H), 3.55 – 3.65 (m, 1H), 3.45 – 3.50 (m, 2H), 3.31 (brs, 1H), 2.41 (s, 3H), 1.35 – 1.85 (m, 9H) ppm.} \]

**\(^{13}\text{C NMR (125 MHz, CDCl}_3\):** \[ \delta = 159.0, 143.6, 134.7, 130.4, 129.3, 129.2, 127.9, 72.5, 69.6, 68.2, 61.5, 61.3, 58.5, 58.1, 57.6, 55.1, 35.6, 32.9, 29.3, 23.0, 21.5 \text{ ppm.} \]

**FTIR (neat):** \[ \nu = 3053, 2985, 2303, 1512, 1421, 1342, 1265, 1159, 1093, 894, 740 \text{ cm}^{-1} \];

**HRMS (ESI, m/z):** calcd for C\(_{18}\)H\(_{28}\)NO\(_6\)S [M+H]\(^{+}\) 386.1657, found: 386.1647 (PMB cleaved mass).

\[ \text{5-(2-hydroxyethyl)-3-(hydroxymethyl)-2-(4-(4-methoxybenzylxylo)butyl)-1-tosylpyrrolidin-3-ol (13):} \]

\[ \text{DIBAL-H (1.0 M in THF, 2.24 g, 15.8 mmol) was added dropwise to a solution of 5-(hydroxymethyl)-4-(4-(4-methoxybenzylxylo)butyl)-3-tosyl-6-oxa-3-azabicyclo[3.1.0]hexan-2-yl)ethanol (2 g, 3.9 mmol) in dry THF (100 mL) at -78 \text{ }^\circ\text{C then increased the temperature to -25 }^\circ\text{C. After 24 h, ethanol (2 mL) was added slowly, and then stirred with aq. solution of sodium potassium tartarate for 5 h. Organic layers were evaporated to get crude residue, that was purified through flash column chromatography (80% ethyl acetate in hexane) to afford product (1.28 g, 64% yield);} \]

**\(^1\text{H NMR (300 MHz, CDCl}_3\):** \[ \delta = 7.75 \text{ (d, J=8.2, 2H), 7.24 – 7.28 (m, 4H), 6.88 (d, J=8.5, 2H), 4.41 (s, 2H), 3.95 – 4.05 (m, 1H), 3.79 (s, 3H), 3.65 – 3.75 (m, 1H), 3.55 – 3.65 (m, 1H), 3.45 – 3.50 (m, 2H), 3.31 (brs, 1H), 2.42 - 2.52 (brs, 1H), 2.39 (s, 3H), 2.28 – 2.33 (brs, 1H), 2.05 – 2.10 (m, 1H), 1.95 – 2.03 (m, 1H), 1.70 -1.80 (m, 1H), 1.50 – 1.65 (m, 5H), 1.30 – 1.38 (m, 1H), 1.17 – 1.25 (m, 1H) ppm.} \]

**\(^{13}\text{C NMR (125 MHz, CDCl}_3\):** \[ \delta = 159.1, 143.7, 134.9, 130.5, 129.3, 129.2, 128.3, 113.7, 82.0, \]
72.4, 69.8, 69.3, 64.6, 59.6, 56.4, 55.2, 40.6, 40.5, 33.0, 29.3, 22.6, 21.5 ppm. **FTIR (neat):** \( \nu = 3053, 2981, 2304, 1421, 1265, 1159, 1091, 1033, 894, 738 \text{ cm}^{-1} \); **HRMS (ESI, m/z):** calcd for C\(_{38}\)H\(_{50}\)NO\(_6\)S [M+H]\(^+\) 388.1794, found: 388.1769 (PMB cleaved mass).

6-(4-(4-methoxybenzyloxy)butyl)-2,2-dimethyl-7-tosyl-1,3-dioxa-7-azaspiro[4.4]nonan-8-yl)ethanol (14):

To a solution of 2-2-dimethoxy propane (2.63 g, 25 mmol) and 5-(2-hydroxyethyl)-3-(hydroxymethyl)-2-(4-(4-methoxybenzyloxy)butyl)-1-tosylpyrrolidin-3-ol (1.2 g, 2.5 mmol) in CH\(_2\)Cl\(_2\), camphorsulfonic acid (58 mg, 0.25 mmol) was added and stirred for 1h at 25 °C. Saturated solution of NaHCO\(_3\) (2 mL) was added, extracted with CH\(_2\)Cl\(_2\). Organic layer was concentrated to get crude product that was purified using column chromatography (70% ethyl acetate in hexane) to get pure product (1.0 g, 77% yield); **\(^1\)H NMR (300 MHz, CDCl\(_3\)):** \( \delta = 7.71 \text{ (d, } J=8.2\text{Hz, } 2\text{H}), 7.23 – 7.28 \text{ (m, } 4\text{H}), 6.88 \text{ (d, } J=8.6\text{Hz, } 2\text{H}), 4.44 \text{ (s, } 2\text{H}), 3.80 – 3.85 \text{ (m, } 2\text{H}), 3.79 \text{ (s, } 3\text{H}), 3.77 – 3.78 \text{ (m, } 1\text{H}), 3.62 – 3.70 \text{ (m, } 2\text{H}), 3.57 \text{ (dd, } J=9.7, 3.7\text{Hz, } 1\text{H}), 3.45 - 3.52 \text{ (m, } 2\text{H}), 2.41 \text{ (s, } 3\text{H}), 2.20 – 2.27 \text{ (m, } 1\text{H}), 2.09 \text{ (dd, } J=9.7, 3.7\text{Hz, } 1\text{H}), 1.65 – 1.85 \text{ (m, } 4\text{H}), 1.55 -1.62 \text{ (m, } 2\text{H}), 1.38 – 1.48 \text{ (m, } 1\text{H}), 1.27 – 1.37 \text{ (m, } 1\text{H}), 0.99 \text{ (s, } 3\text{H}), 0.95 \text{ (s, } 3\text{H}) \text{ ppm.} **\(^{13}\)C NMR (125 MHz, CDCl\(_3\)):** \( \delta = 159.0, 142.8, 134.9, 130.5, 129.2, 128.7, 128.5, 113.6, 109.0, 88.0, 72.4, 69.8, 68.7, 67.3, 59.6, 56.9, 55.1, 42.3, 40.3, 33.5, 29.5, 26.7, 25.5, 22.5, 21.3 ppm.** **FTIR (neat):** \( \nu = 3055, 2983, 2968, 1720, 1598, 1454, 1340, 1265, 1165, 1093, 813, 742 \text{ cm}^{-1} \); **HRMS (ESI, m/z):** calcd for C\(_{29}\)H\(_{43}\)NO\(_5\)S [M+H]\(^+\) 548.2682, found: 548.2677.

8-(2-iodoethyl)-6-(4-(4-methoxybenzyloxy)-butyl)-2,2-dimethyl-7-tosyl-1,3-dioxa-7-azaspiro[4.4]nonane (15):

To a solution of 6-(4-(4-methoxybenzyloxy)butyl)-2,2-dimethyl-7-tosyl-1,3-dioxa-7-azaspiro[4.4]nonan-8-yl)ethanol (1 g, 1.8 mmol), imidazole (375 mg, 5.4 mmol) and triphenylphosphine (710 mg, 2.7 mmol) in CH\(_2\)Cl\(_2\), was added I\(_2\) (685 mg, 2.7 mmol) at 25 °C then continued stirring for 12 h. Saturated solution of Na\(_2\)S\(_2\)O\(_3\) (2 mL) and NaHCO\(_3\) (2 mL) was added, extracted with ethyl acetate. Organic layer was concentrated to get crude product that was purified using column chromatography (25% ethyl acetate in hexane) to get pure product (1.0 g, 87% yield); **\(^1\)H NMR (300 MHz, CDCl\(_3\)):** \( \delta = 7.74 \text{ (d, } J=8.2\text{Hz, } 2\text{H}), 7.25 – 7.28 \text{ (m, } 4\text{H}), 6.87-6.89 \text{ (m, } 2\text{H}), 4.44 \text{ (s, } 2\text{H}), 3.81 – 3.83 \text{ (m, } 1\text{H}), 3.80 \text{ (s, } 3\text{H}), 3.62 – 3.72 \text{ (m, } 2\text{H}), 3.59 \text{ (dd, } J= 9.6, 3.4\text{Hz, } 1\text{H}), 3.48 \text{ (t, } J=5.7\text{Hz, } 2\text{H}), 3.21 – 3.31 \text{ (m, } 1\text{H}), 2.98 – 3.05 \text{ (m, } 1\text{H}), 2.69 – 2.79 \text{ (m, } 1\text{H}), 2.42 \text{ (s, } 3\text{H}), 1.95 – 2.10
(m, 2H), 1.50 – 1.70 (m, 6H), 1.38 – 1.48 (m, 1H), 1.02 (s, 3H), 0.98 (s, 3H) ppm. \(^{13}\)C NMR (125 MHz, CDCl\(_3\)); \(\delta= 159.0, 142.9, 134.5, 130.6, 129.2, 128.8, 128.7, 113.7, 109.2, 87.6, 72.5, 69.8, 68.9, 67.2, 59.6, 55.2, 41.0, 90.4, 33.8, 29.5, 26.8, 25.5, 22.6, 21.4, 14.1, 0.92 ppm.

FTIR (neat): \(\nu = 3444, 2983, 2933, 1512, 1454, 1342, 1247, 1159, 1089, 1004, 815, 738 \text{ cm}^{-1}\); HRMS (ESI, m/z): calcd for \(\text{C}_{21}\text{H}_{33}\text{NO}_5\text{S} [\text{M+H}]^+ 538.1124\), found: 538.1116 (PMB cleaved mass).

6-(4-(4-methoxybenzylxy)butyl)-2,2-dimethyl-7-tosyl-8-vinyl-1,3-dioxa-7-azaspiro[4.4]nonane (16):

To a slurry of NaH (120 mg, 3.0 mmol, 60%) and TBAI (55.3 mg, 0.15 mmol) in THF (10 mL) was added 8-(2-iodoethyl)-6-(4-(4-methoxybenzylxy)butyl)-2,2-dimethyl-7-tosyl-1,3-dioxa-7-azaspiro[4.4]nonane (1 g, 1.5 mmol) in THF (10 mL) at 0 \(^{\circ}\)C then refluxed for 12 h. Ice-cold water was added dropwise, extracted with ethyl acetate. Organic layer was concentrated to get crude product that was purified using column chromatography (20% ethyl acetate in hexane) to get pure product (0.7 g, 88% yield); \(^1\)H NMR (300 MHz, CDCl\(_3\)); \(\delta= 7.72 (d, J=8.2\text{Hz}, 2H), 7.22 – 7.28 (m, 4H), 6.89 (d, J=2, 2H), 5.88 – 5.97 (m, 1H), 5.24 (d, J=1, 1H), 5.12 (d, J=1, 1H), 4.43 (s, 2H), 4.00 – 4.07 (m, 1H), 3.83 – 3.87 (m, 1H), 3.78 (s, 3H), 3.68 – 3.71 (m, 1H), 3.63 – 3.73 (m, 1H), 3.47 (t, J=5.7\text{Hz}, 2H), 2.4 (s, 3H), 2.00 – 2.07 (m, 1H), 1.75 -1.81 (m, 1H), 1.30 – 1.70 (m, 6H), 1.00 (s, 3H), 1.03 (s, 3H) ppm. \(^{13}\)C NMR (125 MHz, CDCl\(_3\)); \(\delta= 159.0, 142.7, 139.7, 134.9, 130.5, 129.1, 128.7, 128.4, 115.1, 113.6, 109.1, 87.5, 72.4, 69.7, 68.9, 67.0, 61.0, 55.1, 42.3, 33.7, 29.5, 26.7, 25.6, 22.5, 21.3 ppm. FTIR (neat); \(\nu = 3053, 2985, 2304, 1421, 1265, 1159, 894, 738, 705 \text{ cm}^{-1}\); HRMS (ESI, m/z): calcd for \(\text{C}_{21}\text{H}_{32}\text{NO}_5\text{S} [\text{M+H}]^+ 410.1942\), found: 410.945 (PMB cleaved mass).

6-(4-(4-methoxybenzylxy)butyl)-2,2-dimethyl-8-vinyl-1,3-dioxa-7-azaspiro[4.4]nonane (17):

To a solution of naphthalene (1.69 g, 13.2 mmol) in dry DMSO (2 mL), sodium metal (261 mg, 11.8 mmol) was added then stirred at 25 \(^{\circ}\)C. After 2 h, dark green colour was observed. Above mixture was added dropwise to a pre-dissolved solution of 6-(4-(4-methoxybenzylxy)butyl)-2,2-dimethyl-7-tosyl-8-vinyl-1,3-dioxa-7-azaspiro[4.4]nonane (700 mg; 1.32 mmol) in dry DMSO at -78 \(^{\circ}\)C. After 30 minute, saturated solution of NaHCO\(_3\) (2 mL) was added then stirred with solid K\(_2\)CO\(_3\) (6 g) for 5 h. Extracted with CH\(_2\)Cl\(_2\) (100 mL, 3 times), combined organic layer was concentrated to get crude product that was purified using column chromatography (80% ethyl
acetate in hexane) to get pure product (340 mg, 69% yield); \(^1\)H NMR (300 MHz, CDCl\(_3\)): δ = 7.18 (d, J=8.4 Hz, 2H), 6.80 (d, J=8.4 Hz, 2H), 5.62 – 5.71 (m, 1H), 4.90 – 5.11 (m, 2H), 4.34 (s, 2H), 4.02 (d, J=9.0 Hz, 1H), 3.71 (s, 3H), 3.57 – 3.67 (m, 2H), 3.37 – 3.40 (m, 2H), 2.95 – 2.98 (m, 1H), 2.55 (brs, 1H), 2.13 (dd, J=13.3, 7.0 Hz, 1H), 1.40 – 1.70 (m, 5H), 1.31 (s, 3H), 1.28 (s, 3H), 1.15 – 1.25 (m, 1H) ppm.

\(^13\)C NMR (125 MHz, CDCl\(_3\)): δ = 159.0, 140.3, 130.5, 129.1, 115.1, 113.6, 108.4, 88.0, 72.4, 69.9, 69.8, 66.1, 58.4, 55.1, 44.4, 30.5, 29.7, 26.8, 25.7, 24.2 ppm.

FTIR (neat): ν = 3053, 2985, 2937, 2862, 2304, 1612, 1512, 1265, 1099, 1056, 1035, 738 cm\(^{-1}\);

HRMS (ESI, m/z): calcd for C\(_{14}\)H\(_{26}\)NO\(_3\) [M+H]\(^+\) 256.1913, found: 256.1915 (PMB cleaved mass).

Tert-butyl-3-hydroxy-3-(hydroxymethyl)-2-(4-(4-methoxybenzyloxy)butyl)-5-vinylpyrrolidine-1-carboxylate (18):

To a solution of 6-(4-(4-methoxybenzyloxy)butyl)-2,2-dimethyl-8-vinyl-1,3-dioxa-7-azaspiro[4.4]nonane (300 mg; 0.8 mmol) in THF:H\(_2\)O (1:1, 10 mL), was added 3 M HCl (3.0 mL) at 0°C. After 5 h stirring at 25°C, adjusted the pH to 9.0 using NaHCO\(_3\) then (BOC)_2O (350 mg, 1.6 mmol) in THF was added dropwise at 25°C. After 2 h, extracted with ethyl acetate, combined organic layer was concentrated to get crude product that was purified by column chromatography (90% ethyl acetate in hexane) to get pure product (330 mg; 88% over 2 step); \(^1\)H NMR (300 MHz, DMSO-d\(_6\)): δ = 7.22 (d, J=8.5 Hz, 2H), 6.88 (d, J=8.6 Hz, 2H), 5.75 (brs, 1H), 4.90 – 5.05 (m, 2H), 4.50 – 4.65 (m, 2H), 4.34 (s, 2H), 4.25 (brs, 1H), 3.73 (s, 3H), 3.65 (brs, 1H), 3.35 – 3.40 (m, 4H), 1.85 – 1.90 (m, 1H), 1.40 – 1.60 (m, 6H), 1.35 (s, 9H), 1.00 – 1.10 (brs, 1H) ppm.

\(^13\)C NMR (125 MHz, CDCl\(_3\)): δ = 159.0, 156.4, 140.2, 130.5, 129.1(2), 114.0, 113.6(2), 81.2, 79.6, 72.4, 70.0(2), 66.3, 64.8, 58.8, 55.1(2), 39.6, 32.6, 29.6, 28.3(2) ppm.

FTIR (neat): ν = 3053, 2980, 1683, 1612, 1512, 1392, 1265, 1033, 738 cm\(^{-1}\);

HRMS (ESI, m/z): calcd for C\(_{16}\)H\(_{30}\)NO\(_5\) [M+H]\(^+\) 316.2065, found: 316.2066 (PMB cleaved mass).

References:


1H-1H- Noesy correlation was observed between both Ha and Hb with Hc. Also both Ha and Hb have correlation with Ha' and Hb' respectively.