

SUPPORTING INFORMATION

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**Metal-free hydroalkoxylation of ynesulfonamides with ester**

authored by

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## GENERAL EXPERIMENTAL INFORMATION

Unless otherwise indicated, all starting materials were obtained from commercial supplies and used as received. Solvents were distilled prior to use. Ynamides (**1a**, **1i**, **1j**, **1o**, **1p**)<sup>1</sup>, (**1b**, **1d**)<sup>2</sup>, (**1c**, **1h**)<sup>3</sup>, **1e**<sup>4</sup>, **1f**<sup>5</sup>, **1g**<sup>6</sup>, **1k**<sup>7</sup>, **1l**<sup>8</sup>, **1m**<sup>9</sup> and **1n**<sup>11</sup> were synthesized to the literatures. All reactions were performed in oven-dried glassware under nitrogen atmosphere. Chromatographic separations were performed using 200~300 mesh silica gel. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were obtained on a Bruker's Ascend™ 400 NMR spectrometer using CDCl<sub>3</sub> as solvent with TMS or residual solvent as standard unless otherwise noted. <sup>13</sup>C NMR (100 MHz) spectra were reported in ppm with the internal chloroform signal at 77.2 ppm as a standard. Infrared spectra was obtained on a PerkinElmer FT/IR spectrophotometer and relative intensities are expressed qualitatively as s (strong), m (medium), and w (weak). TLC analysis was performed using 254 nm polyester-backed plates and visualized using UV and KMnO<sub>4</sub> stain. High-resolution mass spectra (HRMS) were performed on a Bruker MicrOTOF-Q II mass spectrometer. All spectral data obtained for new compounds are reported here.

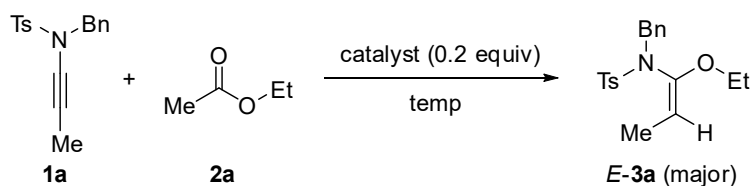
### General Procedure for the Condition Optimization (Table 1).

To an oven-dried sealed tube were added ynesulfonamide **1a**<sup>1</sup> (61.1 mg, 0.20 mmol) and EtOAc **2a** (1.0 mL, ynesulfonamide *concn* = 0.20 M) at rt. The reaction vessel was then cooled to the specified reaction temperature and the specified catalyst (0.04 mmol) was added to the tube. When the reaction was judged to be completed by TLC after stirring at the specified reaction temperature for the corresponding reaction time, the reaction mixture was filtered through a pad of silica gel and concentrated *in vacuo*. After the *E/Z* ratio of the crude product was confirmed by <sup>1</sup>H NMR spectroscopy, the mixture was purified by flash silica gel column chromatography [gradient eluent: 30:1-8:1 petroleum ether/EtOAc] to afford separable enamides *E*-**3a** and *Z*-**3a**.

**E-3a**: *R<sub>f</sub>* = 0.27 [10:1 petroleum ether/EtOAc]; white solid; mp = 88–89 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.07 (t, 3H, *J* = 7.0 Hz), 1.43 (d, 3H, *J* = 6.7 Hz), 2.43 (s, 3H), 3.49 (q, 2H, *J* = 6.9 Hz), 4.31 (s, 2H), 4.49 (q, 1H, *J* = 6.7 Hz), 7.25 (s, 5H), 7.29 (d, 2H, *J* = 8.1 Hz), 7.79 (d, 2H, *J* = 8.3 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 12.1, 14.3, 21.7, 51.6, 63.2, 98.4, 127.9, 128.2, 128.3, 129.3, 129.6, 135.5, 136.9, 143.5, 145.7; IR (neat) (cm<sup>-1</sup>) 1676w, 1348s, 1192m, 1164s, 1108m, 1088m; HRMS (ESI): *m/z* calcd for C<sub>19</sub>H<sub>24</sub>NO<sub>3</sub>S [M+H]<sup>+</sup>: 346.1471; found 346.1471.

**Z-3a**: *R<sub>f</sub>* = 0.28 [10:1 petroleum ether/EtOAc]; white solid; mp = 64–65 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.04 (t, 3H, *J* = 7.0 Hz), 1.53 (d, 3H, *J* = 6.9 Hz), 2.43 (s, 3H), 3.55 (q, 2H, *J* = 7.0 Hz), 4.40 (q, 1H, *J* = 6.9 Hz), 4.45 (s, 2H), 7.24-7.31 (m, 7H), 7.68 (d, 2H, *J* = 8.3 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 11.0, 14.9, 21.7, 52.9, 64.4, 106.2, 127.97, 128.02, 128.5, 129.3, 129.5, 136.2, 136.7,

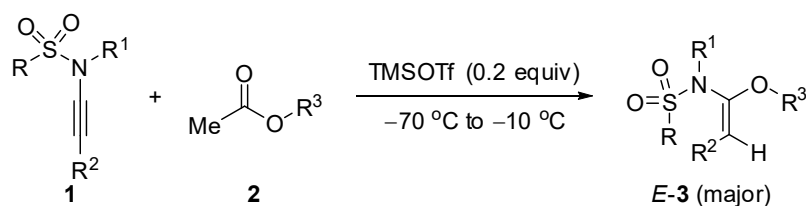
143.7, 145.2; IR (neat) (cm<sup>-1</sup>) 1672w, 1349s, 1182m, 1163s, 1108m, 1077m; HRMS (ESI): m/z calcd for C<sub>19</sub>H<sub>23</sub>NO<sub>3</sub>S [M+H]<sup>+</sup>: 346.1471; found 346.1468.



Entry <sup>a</sup>	Catalyst	Temp (°C)	Time (min)	Yield (%) <sup>b</sup>	E/Z <sup>c</sup>
1	ZnI <sub>2</sub>	rt	240	0	—
2	Zn(OTf) <sub>2</sub>	rt	180	35	≥25:1
3	Cu(OTf) <sub>2</sub>	rt	30	59	11:1
4	AlCl <sub>3</sub>	rt	240	18	≥25:1
5	TfOH	rt	20	40	≥25:1
6	Tf <sub>2</sub> O	rt	20	45	≥25:1
7	TMSOTf	rt	20	50	≥25:1
8	Tf <sub>2</sub> NH	rt	20	68	18:1
9	CSA	rt	280	trace	≥25:1
10	Cu(OTf) <sub>2</sub>	0	330	29 <sup>d</sup>	9:1
11	Tf <sub>2</sub> NH	0	20	71	≥25:1
12	Tf <sub>2</sub> NH	-40	20	90	6:1
13	Tf <sub>2</sub> NH	-70	60	17 <sup>e</sup>	5:1
14	TfOH	0	20	72	≥25:1
15	TfOH	-40	20	91	8:1
16	TfOH	-70	20	82	8:1
17	Tf <sub>2</sub> O	0	20	72	≥25:1
18	Tf <sub>2</sub> O	-40	20	89	8:1
19	Tf <sub>2</sub> O	-70	20	72	8:1
20	TMSOTf	0	20	55	≥25:1
21	TMSOTf	-20	20	65	≥25:1
22	TMSOTf	-40	20	80	14:1
23	TMSOTf	-60	20	86	14:1
24	TMSOTf	-70	20	91	14:1

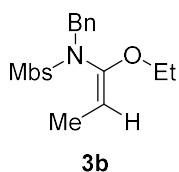
<sup>a</sup> Unless otherwise noted, reactions were carried out using **1a** (0.20 mmol) with catalyst (0.04 mmol) in EtOAc (1.0 mL) under N<sub>2</sub>. <sup>b</sup> Isolated yields. <sup>c</sup> Determined by <sup>1</sup>H NMR spectroscopy of unpurified reaction mixture. <sup>d</sup> 57% of **1a** was recovered. <sup>e</sup> 77% of **1a** was recovered.

### General Procedure for Synthesis of Enamides **3**.



To an oven-dried sealed tube were added ynesulfonamide **1a**<sup>1</sup> (61.1 mg, 0.20 mmol) and EtOAc

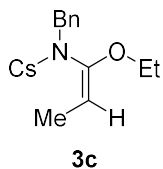
**2a** (1.0 mL, ynesulfonamide *concn* = 0.20 M) at rt. The reaction vessel was then cooled to  $-70\text{ }^{\circ}\text{C}$  and TMSOTf (7.2  $\mu\text{L}$ , 0.04 mmol) was added to the tube. When the reaction was judged to be completed by TLC after stirring at  $-70\text{ }^{\circ}\text{C}$  for 20 min, the reaction mixture was filtered through a pad of silica gel and concentrated *in vacuo*. After the *E/Z* ratio of the crude product was confirmed by  $^1\text{H}$  NMR spectroscopy, the mixture was purified by flash silica gel column chromatography [gradient eluent: 30:1-8:1 petroleum ether/EtOAc] to afford a separable 14:1 mixture of enamides *E-3a* (58.6 mg, 0.17 mmol) and *Z-3a* (4.2 mg, 0.01 mmol) in 91% yield.



A separable 19:1 mixture of enamides *E-3b* (66.4 mg, 0.18 mmol) and *Z-3b* (3.5 mg, 0.01 mmol) were prepared from ynesulfonamide **1b**<sup>2</sup> (63.9 mg, 0.20 mmol) and EtOAc **2a** (1.0 mL, ynesulfonamide *concn* = 0.20 M) in 95% yield after stirring at  $-70\text{ }^{\circ}\text{C}$  for 10 min.

***E-3b***:  $R_f$  = 0.39 [4:1 petroleum ether/EtOAc]; white solid; mp = 95–96  $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.10 (t, 3H,  $J$  = 7.0 Hz), 1.44 (d, 3H,  $J$  = 6.7 Hz), 3.51 (q, 2H,  $J$  = 6.9 Hz), 3.89 (s, 3H), 4.14-4.43 (m, 2H), 4.49 (q, 1H,  $J$  = 6.7 Hz), 6.97 (d, 2H,  $J$  = 9.0 Hz), 7.26 (s, 5H), 7.85 (d, 2H,  $J$  = 9.0 Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  12.1, 14.4, 51.6, 55.8, 63.2, 98.4, 113.9, 127.9, 128.2, 129.6, 130.4, 131.6, 135.5, 145.8, 163.0; IR (neat) ( $\text{cm}^{-1}$ ) 1674w, 1593w, 1495w, 1347s, 1254s, 1162s; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{19}\text{H}_{24}\text{NO}_4\text{S}$  [ $\text{M}+\text{H}$ ]<sup>+</sup>: 362.1421; found 362.1422.

***Z-3b***:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.04 (t, 3H,  $J$  = 7.0 Hz), 1.53 (d, 3H,  $J$  = 6.8 Hz), 3.56 (q, 2H,  $J$  = 7.0 Hz), 3.88 (s, 3H), 4.40 (q, 1H,  $J$  = 6.9 Hz), 4.44 (s, 2H), 6.94 (d, 2H,  $J$  = 9.0 Hz), 7.26-7.28 (m, 7H), 7.72 (d, 2H,  $J$  = 9.0 Hz).

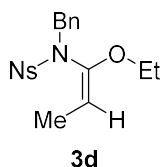


A separable 13:1 mixture of enamides *E-3c* (55.9 mg, 0.15 mmol) and *Z-3c* (4.3 mg, 0.01 mmol) were prepared from ynesulfonamide **1c**<sup>3</sup> (64.4 mg, 0.20 mmol) and EtOAc **2a** (1.0 mL, ynesulfonamide *concn* = 0.20 M) in 82% yield after stirring at  $-50\text{ }^{\circ}\text{C}$  for 30 min.

***E-3c***:  $R_f$  = 0.33 [10:1 petroleum ether/EtOAc]; white solid; mp = 78–79  $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.09 (t, 3H,  $J$  = 7.0 Hz), 1.42 (d, 3H,  $J$  = 6.7 Hz), 3.51 (q, 2H,  $J$  = 6.9 Hz), 4.12-4.44 (m, 2H), 4.51 (q, 1H,  $J$  = 6.7 Hz), 7.24-7.28 (m, 5H), 7.47 (d, 2H,  $J$  = 8.6 Hz), 7.84 (d, 2H,  $J$  = 8.7 Hz);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  12.1, 14.3, 51.9, 63.3, 98.7, 128.1, 128.3, 129.0, 129.6, 129.7, 135.0, 138.4, 139.2, 145.5; IR (neat) ( $\text{cm}^{-1}$ ) 1680w, 1469w, 1348s, 1191m, 1166s, 1083s; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{18}\text{H}_{21}\text{ClNO}_3\text{S}$   $[\text{M}+\text{H}]^+$ : 366.0925; found 366.0926.

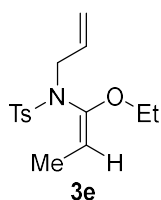
**Z-3c**:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.07 (t, 3H,  $J = 7.0$  Hz), 1.54 (d, 3H,  $J = 6.9$  Hz), 3.58 (q, 2H,  $J = 7.0$  Hz), 4.38 (q, 1H,  $J = 6.9$  Hz), 4.47 (s, 2H), 7.24-7.30 (m, 5H), 7.43 (d, 2H,  $J = 8.7$  Hz), 7.68 (d, 2H,  $J = 8.7$  Hz).



A separable 9:1 mixture of enamides *E*-**3d** (50.4 mg, 0.13 mmol) and *Z*-**3d** (5.6 mg, 0.01 mmol) were prepared from ynesulfonamide **1d**<sup>2</sup> (66.5 mg, 0.20 mmol) and EtOAc **2a** (1.0 mL, ynesulfonamide *concn* = 0.20 M) in 74% yield after stirring at  $-20$  °C for 20 min.

**E-3d**:  $R_f = 0.52$  [4:1 petroleum ether/EtOAc]; white solid; mp = 123–124 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.08 (t, 3H,  $J = 7.0$  Hz), 1.43 (d, 3H,  $J = 6.8$  Hz), 3.54 (q, 2H,  $J = 6.9$  Hz), 4.20-4.50 (m, 2H), 4.57 (q, 1H,  $J = 6.8$  Hz), 7.25-7.29 (m, 5H), 8.07 (d, 2H,  $J = 8.8$  Hz), 8.33 (d, 2H,  $J = 8.8$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  12.1, 14.3, 52.3, 63.5, 99.1, 123.9, 128.3, 128.4, 129.4, 129.6, 134.6, 145.2, 145.8, 150.1; IR (neat) ( $\text{cm}^{-1}$ ) 1680w, 1532s, 1352s, 1301w, 1164s, 1108m; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{18}\text{H}_{21}\text{N}_2\text{O}_5\text{S}$   $[\text{M}+\text{H}]^+$ : 377.1166; found 377.1168.

**Z-3d**:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.11 (t, 3H,  $J = 7.0$  Hz), 1.56 (d, 3H,  $J = 6.9$  Hz), 3.63 (q, 2H,  $J = 7.0$  Hz), 4.37 (q, 1H,  $J = 6.9$  Hz), 4.53 (s, 2H), 7.26-7.31 (m, 5H), 7.87 (d, 2H,  $J = 8.9$  Hz), 8.27 (d, 2H,  $J = 8.9$  Hz).

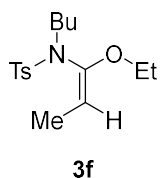


A separable 10:1 mixture of enamides *E*-**3e** (48.5 mg, 0.16 mmol) and *Z*-**3e** (4.8 mg, 0.02 mmol) were prepared from ynesulfonamide **1e**<sup>4</sup> (50.8 mg, 0.20 mmol) and EtOAc **2a** (1.0 mL, ynesulfonamide *concn* = 0.20 M) in 90% yield after stirring at  $-50$  °C for 60 min.

**E-3e**:  $R_f = 0.30$  [10:1 petroleum ether/EtOAc]; white solid; mp = 63–64 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.09 (t, 3H,  $J = 7.0$  Hz), 1.73 (d, 3H,  $J = 6.7$  Hz), 2.42 (s, 3H), 3.61 (q, 2H,  $J = 7.0$  Hz), 3.80 (d, 2H,  $J = 6.4$  Hz), 4.68 (q, 1H,  $J = 6.7$  Hz), 5.06-5.12 (m, 2H), 5.73 (ddt, 1H,  $J = 17.0, 10.1, 6.8$  Hz), 7.27 (d, 2H,  $J = 8.2$  Hz), 7.76 (d, 2H,  $J = 8.3$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  12.4, 14.4,

21.7, 51.0, 63.3, 97.9, 118.8, 128.3, 129.3, 132.8, 137.0, 143.4, 146.5; IR (neat) (cm<sup>-1</sup>) 1677w, 1344s, 1194m, 1162s, 1110m, 1089m; HRMS (ESI): m/z calcd for C<sub>15</sub>H<sub>22</sub>NO<sub>3</sub>S [M+H]<sup>+</sup>: 296.1315; found 296.1312.

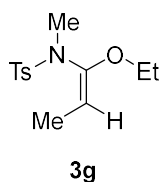
**Z-3e**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.22 (t, 3H, *J* = 7.0 Hz), 1.58 (d, 3H, *J* = 6.9 Hz), 2.43 (s, 3H), 3.78 (q, 2H, *J* = 7.0 Hz), 3.94 (d, 2H, *J* = 6.5 Hz), 4.41 (q, 1H, *J* = 6.8 Hz), 5.12-5.17 (m, 2H), 5.74 (ddt, 1H, *J* = 16.8, 10.0, 6.6 Hz), 7.30 (d, 2H, *J* = 8.2 Hz), 7.73 (d, 2H, *J* = 8.2 Hz).



A separable 10:1 mixture of enamides *E*-**3f** (51.7 mg, 0.17 mmol) and *Z*-**3f** (5.2 mg, 0.02 mmol) were prepared from ynesulfonamide **1f**<sup>5</sup> (54.1 mg, 0.20 mmol) and EtOAc **2a** (1.0 mL, ynesulfonamide *concn* = 0.20 M) in 91% yield after stirring at -70 °C for 10 min.

*E*-**3f**: *R<sub>f</sub>* = 0.33 [10:1 petroleum ether/EtOAc]; white solid; mp = 29–30 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.87 (t, 3H, *J* = 7.3 Hz), 1.09 (t, 3H, *J* = 7.0 Hz), 1.26-1.35 (m, 2H), 1.40-1.47 (m, 2H), 1.75 (d, 3H, *J* = 6.7 Hz), 2.42 (s, 3H), 3.15 (t, 2H, *J* = 6.6 Hz), 3.63 (q, 2H, *J* = 7.0 Hz), 4.71 (q, 1H, *J* = 6.7 Hz), 7.26 (d, 2H, *J* = 8.0 Hz), 7.74 (d, 2H, *J* = 8.2 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 12.5, 13.9, 14.3, 20.1, 21.7, 30.1, 47.4, 63.3, 97.9, 128.2, 129.2, 137.0, 143.2, 146.4; IR (neat) (cm<sup>-1</sup>) 1676m, 1349s, 1193m, 1153s, 1090s, 1022m; HRMS (ESI): m/z calcd for C<sub>16</sub>H<sub>26</sub>NO<sub>3</sub>S [M+H]<sup>+</sup>: 312.1628; found 312.1627.

*Z*-**3f**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.87 (t, 3H, *J* = 7.3 Hz), 1.22 (t, 3H, *J* = 7.0 Hz), 1.26-1.29 (m, 2H), 1.46-1.53 (m, 2H), 1.61 (d, 3H, *J* = 6.9 Hz), 2.43 (s, 3H), 3.27 (t, 2H, *J* = 7.7 Hz), 3.76 (q, 2H, *J* = 7.0 Hz), 4.46 (q, 1H, *J* = 6.9 Hz), 7.29 (d, 2H, *J* = 8.0 Hz), 7.73 (d, 2H, *J* = 8.2 Hz).

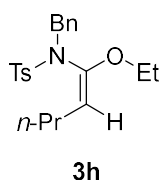


*E*-**3g** (9.6 mg, 0.04 mmol), and a mixture of enamides *E*-**3g** and *Z*-**3g** (33.6 mg, 0.12 mmol; *E/Z* = 6:1) were prepared from ynesulfonamide **1g**<sup>6</sup> (45.2 mg, 0.20 mmol) and EtOAc **2a** (1.0 mL, ynesulfonamide *concn* = 0.20 M) in 80% yield after stirring at -70 °C for 20 min.

*E*-**3g**: *R<sub>f</sub>* = 0.27 [10:1 petroleum ether/EtOAc]; white solid; mp = 79–80 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.11 (t, 3H, *J* = 7.0 Hz), 1.74 (d, 3H, *J* = 6.7 Hz), 2.42 (s, 3H), 2.89 (s, 3H), 3.64 (q, 2H, *J* = 7.0 Hz), 4.57 (q, 1H, *J* = 6.7 Hz), 7.28 (d, 2H, *J* = 8.1 Hz), 7.76 (d, 2H, *J* = 8.2 Hz); <sup>13</sup>C NMR (100

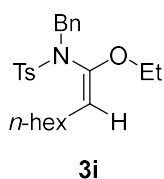
MHz, CDCl<sub>3</sub>)  $\delta$  12.1, 14.3, 21.7, 35.8, 63.4, 95.7, 128.3, 129.3, 136.2, 143.4, 149.0; IR (neat) (cm<sup>-1</sup>) 1679w, 1345s, 1230w, 1152s, 1086m, 1043w; HRMS (ESI): m/z calcd for C<sub>13</sub>H<sub>20</sub>NO<sub>3</sub>S [M+H]<sup>+</sup>: 270.1158; found 270.1159.

**Z-3g**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.24 (t, 3H, *J* = 7.0 Hz), 1.57 (d, 3H, *J* = 6.8 Hz), 2.44 (s, 3H), 2.96 (s, 3H), 3.85 (q, 2H, *J* = 7.0 Hz), 4.29 (q, 1H, *J* = 6.8 Hz), 7.31 (d, 2H, *J* = 8.1 Hz), 7.72 (d, 2H, *J* = 8.3 Hz).



Enamide **E-3h** (68.0 mg, 0.18 mmol; *E/Z*  $\geq$  25:1) was prepared from ynesulfonamide **1h**<sup>3</sup> (66.2 mg, 0.20 mmol) and EtOAc **2a** (1.0 mL, ynesulfonamide *concn* = 0.20 *M*) in 91% yield after stirring at -70 °C for 15 min.

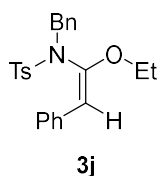
**E-3h**: *R<sub>f</sub>* = 0.33 [10:1 petroleum ether/EtOAc]; white solid; mp = 45–46 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  0.68 (t, 3H, *J* = 7.3 Hz), 0.83-1.00 (m, 2H), 1.09 (t, 3H, *J* = 7.0 Hz), 1.90 (q, 2H, *J* = 7.4 Hz), 2.44 (s, 3H), 3.52 (q, 2H, *J* = 6.8 Hz), 4.04-4.38 (m, 2H), 4.43 (t, 1H, *J* = 7.1 Hz), 7.25 (s, 5H), 7.29 (d, 2H, *J* = 8.0 Hz), 7.80 (d, 2H, *J* = 8.3 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  13.9, 14.3, 21.7, 23.1, 29.2, 51.6, 63.2, 104.4, 127.9, 128.27, 128.30, 129.3, 129.7, 135.5, 136.9, 143.4, 144.7; IR (neat) (cm<sup>-1</sup>) 1673w, 1348s, 1182m, 1163s, 1113m, 1089m; HRMS (ESI): m/z calcd for C<sub>21</sub>H<sub>28</sub>NO<sub>3</sub>S [M+H]<sup>+</sup>: 374.1784; found 374.1782.



Enamide **E-3i** (75.6 mg, 0.18 mmol; *E/Z*  $\geq$  25:1) was prepared from ynesulfonamide **1i**<sup>1</sup> (74.1 mg, 0.20 mmol) and EtOAc **2a** (1.0 mL, ynesulfonamide *concn* = 0.20 *M*) in 91% yield after stirring at -70 °C for 20 min.

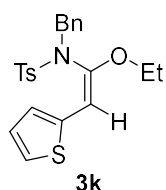
**E-3i**: *R<sub>f</sub>* = 0.33 [10:1 petroleum ether/EtOAc]; white solid; mp = 64–65 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  0.85 (t, 3H, *J* = 7.2 Hz), 1.09 (t, 3H, *J* = 7.0 Hz), 1.00-1.14 (m, 5H), 1.16-1.27 (m, 3H), 1.91 (q, 2H, *J* = 7.4 Hz), 2.44 (s, 3H), 3.52 (q, 2H, *J* = 6.9 Hz), 3.97-4.38 (m, 2H), 4.42 (t, 1H, *J* = 7.1 Hz), 7.25 (s, 5H), 7.29 (d, 2H, *J* = 8.1 Hz), 7.80 (d, 2H, *J* = 8.2 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  14.29, 14.30, 21.7, 22.8, 27.2, 29.2, 30.0, 31.9, 51.5, 63.2, 104.7, 127.9, 128.3, 129.3, 129.7, 135.5, 136.9, 143.4, 144.5, one carbon missing due to overlap; IR (neat) (cm<sup>-1</sup>) 1678w, 1342s, 1199w,

1161s, 1116m, 1092m; HRMS (ESI):  $m/z$  calcd for  $C_{24}H_{34}NO_3S$   $[M+H]^+$ : 416.2254; found 416.2252.



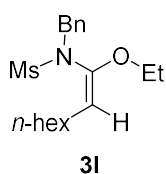
Enamide *E-3j* (72.4 mg, 0.18 mmol;  $E/Z \geq 25:1$ ) was prepared from ynesulfonamide **1j**<sup>1</sup> (73.0 mg, 0.20 mmol) and EtOAc **2a** (1.0 mL, ynesulfonamide *concn* = 0.20 M) in 88% yield after stirring at  $-70$  °C for 50 min.

*E-3j*:  $R_f$  = 0.33 [6:1 petroleum ether/EtOAc]; white solid; mp = 113–114 °C;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  1.21 (t, 3H,  $J$  = 7.0 Hz), 2.44 (s, 3H), 3.75 (q, 2H,  $J$  = 6.9 Hz), 4.31 (s, 2H), 5.45 (s, 1H), 6.90 (d, 2H,  $J$  = 7.2 Hz), 7.05 (t, 2H,  $J$  = 7.3 Hz), 7.10–7.16 (m, 2H), 7.23–7.27 (m, 4H), 7.35 (d, 2H,  $J$  = 7.4 Hz), 7.79 (d, 2H,  $J$  = 8.3 Hz);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  14.3, 21.7, 52.4, 64.2, 103.1, 126.3, 127.8, 128.0, 128.3, 128.6, 129.2, 129.4, 134.4, 134.7, 137.1, 143.7, 147.3, one carbon missing due to overlap; IR (neat) ( $cm^{-1}$ ) 1651m, 1596w, 1446w, 1357w, 1343m, 1165s; HRMS (ESI):  $m/z$  calcd for  $C_{24}H_{26}NO_3S$   $[M+H]^+$ : 408.1628; found 408.1626.



Enamide *E-3k* (73.5 mg, 0.18 mmol;  $E/Z \geq 25:1$ ) was prepared from ynesulfonamide **1k**<sup>7</sup> (74.4 mg, 0.20 mmol) and EtOAc **2a** (1.0 mL, ynesulfonamide *concn* = 0.20 M) in 89% yield after stirring at  $-30$  °C for 50 min.

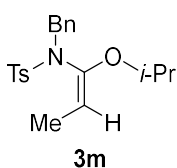
*E-3k*:  $R_f$  = 0.39 [4:1 petroleum ether/EtOAc]; white solid; mp = 148–149 °C;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  1.14 (t, 3H,  $J$  = 7.0 Hz), 2.45 (s, 3H), 3.65 (q, 2H,  $J$  = 6.6 Hz), 4.32–4.51 (m, 2H), 5.72 (s, 1H), 6.87–6.92 (m, 2H), 7.07–7.17 (m, 6H), 7.29 (d, 2H,  $J$  = 8.1 Hz), 7.82 (d, 2H,  $J$  = 8.2 Hz);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  14.2, 21.8, 52.5, 64.0, 99.6, 124.4, 126.0, 126.2, 128.0, 128.1, 128.9, 129.2, 130.1, 134.0, 136.4, 137.3, 143.8, 145.7; IR (neat) ( $cm^{-1}$ ) 1651m, 1361w, 1346m, 1227m, 1164s, 1078m; HRMS (ESI):  $m/z$  calcd for  $C_{22}H_{24}NO_3S_2$   $[M+H]^+$ : 414.1192; found 414.1189.





Enamide **E-31** (59.9 mg, 0.18 mmol; *E/Z*  $\geq$  25:1) was prepared from ynesulfonamide **11**<sup>8</sup> (59.2 mg, 0.20 mmol) and EtOAc **2a** (1.0 mL, ynesulfonamide *concn* = 0.20 M) in 88% yield after stirring at  $-70$  °C for 20 min.

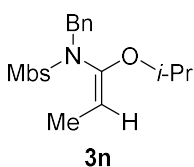
**E-31**:  $R_f$  = 0.52 [4:1 petroleum ether/EtOAc]; white solid; mp = 36–37 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  0.85 (t, 3H,  $J$  = 7.2 Hz), 1.01–1.15 (m, 5H), 1.17–1.26 (m, 3H), 1.30 (t, 3H,  $J$  = 7.0 Hz), 1.82 (q, 2H,  $J$  = 7.5 Hz), 2.96 (s, 3H), 3.66 (q, 2H,  $J$  = 6.8 Hz), 4.45 (t, 1H,  $J$  = 7.2 Hz), 4.39–4.59 (m, 2H), 7.28–7.35 (m, 5H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  14.3, 14.6, 22.8, 27.0, 29.1, 29.9, 31.9, 39.4, 52.3, 63.6, 104.4, 128.1, 128.4, 129.7, 135.5, 145.0; IR (neat) (cm<sup>-1</sup>) 1675m, 1334s, 1145s, 1115s, 1045m; HRMS (ESI):  $m/z$  calcd for C<sub>18</sub>H<sub>30</sub>NO<sub>3</sub>S [M+H]<sup>+</sup>: 340.1941; found 340.1940.



A separable 8:1 mixture of enamides **E-3m** (55.5 mg, 0.15 mmol) and **Z-3m** (6.9 mg, 0.02 mmol) were prepared from ynesulfonamide **1a** (60.2 mg, 0.20 mmol) and isopropyl acetate **2b** (1.0 mL, ynesulfonamide *concn* = 0.20 M) in 87% yield after stirring at  $-40$  °C for 15 min.

**E-3m**:  $R_f$  = 0.34 [10:1 petroleum ether/EtOAc]; white solid; mp = 52–53 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.04 (d, 6H,  $J$  = 6.0 Hz), 1.44 (d, 3H,  $J$  = 6.8 Hz), 2.44 (s, 3H), 3.99 (hept, 1H,  $J$  = 6.0 Hz), 4.07–4.45 (m, 2H), 4.48 (q, 1H,  $J$  = 6.7 Hz), 7.24–7.30 (m, 7H), 7.80 (d, 2H,  $J$  = 8.3 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  12.3, 21.4, 21.7, 51.4, 68.9, 98.5, 127.9, 128.2, 128.4, 129.3, 129.6, 135.6, 137.0, 143.4, 144.0; IR (neat) (cm<sup>-1</sup>) 1676w, 1346s, 1196m, 1162s, 1090s, 1039w; HRMS (ESI):  $m/z$  calcd for C<sub>20</sub>H<sub>26</sub>NO<sub>3</sub>S [M+H]<sup>+</sup>: 360.1628; found 360.1627.

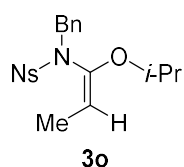
**Z-3m**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  0.99 (d, 6H,  $J$  = 6.1 Hz), 1.51 (d, 3H,  $J$  = 6.8 Hz), 2.43 (s, 3H), 4.05 (hept, 1H,  $J$  = 6.1 Hz), 4.44 (q, 1H,  $J$  = 6.8 Hz), 4.46 (s, 2H), 7.27–7.35 (m, 7H), 7.67 (d, 2H,  $J$  = 8.3 Hz).



A separable 9:1 mixture of enamides **E-3n** (58.5 mg, 0.16 mmol) and **Z-3n** (6.5 mg, 0.02 mmol) were prepared from ynesulfonamide **1b** (63.8 mg, 0.20 mmol) and isopropyl acetate **2b** (1.0 mL, ynesulfonamide *concn* = 0.20 M) in 87% yield after stirring at  $-40$  °C for 15 min.

**E-3n**:  $R_f$  = 0.50 [4:1 petroleum ether/EtOAc]; white solid; mp = 53–54 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.05 (d, 6H,  $J$  = 6.0 Hz), 1.45 (d, 3H,  $J$  = 6.7 Hz), 3.89 (s, 3H), 4.00 (hept, 1H,  $J$  = 6.0 Hz), 4.11–4.44 (m, 2H), 4.48 (q, 1H,  $J$  = 6.8 Hz), 6.96 (d, 2H,  $J$  = 9.0 Hz), 7.24–7.29 (m, 5H), 7.85 (d, 2H,  $J$  = 9.0 Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  12.3, 21.5, 51.4, 55.8, 68.9, 98.5, 113.8, 127.9, 128.2, 129.6, 130.5, 131.7, 135.7, 144.1, 163.0; IR (neat) ( $\text{cm}^{-1}$ ) 1675w, 1597w, 1331s, 1263s, 1155s, 1093s; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{20}\text{H}_{26}\text{NO}_4\text{S}$  [ $\text{M}+\text{H}$ ] $^+$ : 376.1577; found 376.1576.

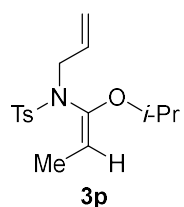
**Z-3n**:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.99 (d, 6H,  $J$  = 6.2 Hz), 1.52 (d, 3H,  $J$  = 6.8 Hz), 3.87 (s, 3H), 4.06 (hept, 1H,  $J$  = 6.2 Hz), 4.447 (q, 1H,  $J$  = 6.8 Hz), 4.449 (s, 2H), 6.93 (d, 2H,  $J$  = 8.9 Hz), 7.26–7.35 (m, 5H), 7.71 (d, 2H,  $J$  = 8.9 Hz).



A separable 6:1 mixture of enamides **E-3o** (56.6 mg, 0.14 mmol) and **Z-3o** (9.4 mg, 0.02 mmol) were prepared from ynesulfonamide **1d** (66.4 mg, 0.20 mmol) and isopropyl acetate **2b** (1.0 mL, ynesulfonamide *concn* = 0.20 M) in 85% yield after stirring at –10 °C for 1.6 h.

**E-3o**:  $R_f$  = 0.53 [4:1 petroleum ether/EtOAc]; white solid; mp = 139–140 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.05 (d, 6H,  $J$  = 6.0 Hz), 1.44 (d, 3H,  $J$  = 6.8 Hz), 4.03 (hept, 1H,  $J$  = 6.0 Hz), 4.23–4.50 (m, 2H), 4.55 (q, 1H,  $J$  = 6.8 Hz), 7.28 (s, 5H), 8.08 (d, 2H,  $J$  = 9.0 Hz), 8.33 (d, 2H,  $J$  = 9.0 Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  12.2, 21.4, 52.1, 69.4, 99.1, 123.9, 128.3, 128.4, 129.5, 129.6, 134.7, 143.5, 145.8, 150.1; IR (neat) ( $\text{cm}^{-1}$ ) 1678w, 1529s, 1354s, 1305w, 1171s, 1089m; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_5\text{SNa}$  [ $\text{M}+\text{Na}$ ] $^+$ : 413.1142; found 413.1140.

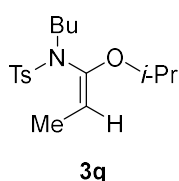
**Z-3o**:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.07 (d, 6H,  $J$  = 6.2 Hz), 1.55 (d, 3H,  $J$  = 6.7 Hz), 4.11 (hept, 1H,  $J$  = 6.2 Hz), 4.35 (q, 1H,  $J$  = 6.8 Hz), 4.54 (s, 2H), 7.28–7.30 (m, 5H), 7.85 (d, 2H,  $J$  = 9.0 Hz), 8.26 (d, 2H,  $J$  = 8.9 Hz).



A separable 7:1 mixture of enamides **E-3p** (50.0 mg, 0.16 mmol) and **Z-3p** (7.1 mg, 0.02 mmol) were prepared from ynesulfonamide **1e** (51.0 mg, 0.20 mmol) and isopropyl acetate **2b** (1.0 mL, ynesulfonamide *concn* = 0.20 M) in 92% yield after stirring at –40 °C for 20 min.

**E-3p**:  $R_f = 0.40$  [10:1 petroleum ether/EtOAc]; colorless oil;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.08 (d, 6H,  $J = 6.0$  Hz), 1.74 (d, 3H,  $J = 6.7$  Hz), 2.42 (s, 3H), 3.78-3.79 (m, 2H), 4.08 (hept, 1H,  $J = 6.1$  Hz), 4.66 (q, 1H,  $J = 6.7$  Hz), 5.06-5.12 (m, 2H), 5.74 (ddt, 1H,  $J = 16.9, 10.1, 6.8$  Hz), 7.26 (d, 2H,  $J = 8.3$  Hz), 7.76 (d, 2H,  $J = 8.4$  Hz);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  12.5, 21.4, 21.7, 50.8, 69.1, 98.1, 118.8, 128.3, 129.2, 132.8, 136.9, 143.3, 144.6; IR (neat) ( $\text{cm}^{-1}$ ) 1675m, 1350s, 1194m, 1164s, 1104s, 1090s; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{16}\text{H}_{23}\text{NO}_3\text{SNa}$   $[\text{M}+\text{Na}]^+$ : 332.1291; found 332.1294.

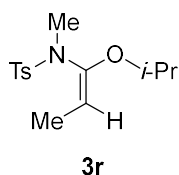
**Z-3p**:  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.19 (d, 6H,  $J = 6.2$  Hz), 1.57 (d, 3H,  $J = 6.8$  Hz), 2.43 (s, 3H), 3.95 (d, 2H,  $J = 6.6$  Hz), 4.21 (hept, 1H,  $J = 6.1$  Hz), 4.48 (q, 1H,  $J = 6.8$  Hz), 5.11-5.18 (m, 2H), 5.74 (ddt, 1H,  $J = 16.7, 10.1, 6.6$  Hz), 7.30 (d, 2H,  $J = 8.1$  Hz), 7.74 (d, 2H,  $J = 8.2$  Hz).



A separable 8:1 mixture of enamides **E-3q** (50.0 mg, 0.15 mmol) and **Z-3q** (6.3 mg, 0.02 mmol) were prepared from ynesulfonamide **1f** (54.3 mg, 0.20 mmol) and isopropyl acetate **2b** (1.0 mL, ynesulfonamide *concn* = 0.20 M) in 86% yield after stirring at  $-40$  °C for 15 min.

**E-3q**:  $R_f = 0.42$  [10:1 petroleum ether/EtOAc]; colorless oil;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.88 (t, 3H,  $J = 7.3$  Hz), 1.10 (d, 6H,  $J = 6.1$  Hz), 1.26-1.35 (m, 2H), 1.40-1.48 (m, 2H), 1.76 (d, 3H,  $J = 6.7$  Hz), 2.41 (s, 3H), 3.13 (s, 2H), 4.11 (hept, 1H,  $J = 6.1$  Hz), 4.70 (q, 1H,  $J = 6.8$  Hz), 7.24-7.27 (m, 2H), 7.75 (d, 2H,  $J = 8.3$  Hz);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  12.6, 13.9, 20.1, 21.4, 21.7, 30.0, 47.2, 69.0, 98.3, 128.3, 129.1, 137.0, 143.1, 144.6; IR (neat) ( $\text{cm}^{-1}$ ) 1674m, 1349s, 1192m, 1152s, 1104s, 1090s; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{17}\text{H}_{27}\text{NO}_3\text{SNa}$   $[\text{M}+\text{Na}]^+$ : 348.1604; found 348.1606.

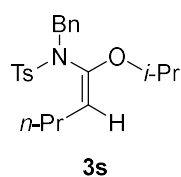
**Z-3q**:  $\delta$  0.86 (t, 3H,  $J = 7.3$  Hz), 1.18 (d, 6H,  $J = 6.1$  Hz), 1.22-1.26 (m, 2H), 1.45-1.53 (m, 2H), 1.59 (d, 3H,  $J = 6.8$  Hz), 2.43 (s, 3H), 3.28 (t, 2H,  $J = 7.7$  Hz), 4.16 (hept, 1H,  $J = 6.1$  Hz), 4.56 (q, 1H,  $J = 6.8$  Hz), 7.29 (d, 2H,  $J = 8.0$  Hz), 7.73 (d, 2H,  $J = 8.3$  Hz).



A separable 5:1 mixture of enamides **E-3r** (38.4 mg, 0.14 mmol) and **Z-3r** (7.7 mg, 0.03 mmol) were prepared from ynesulfonamide **1g** (45.3 mg, 0.20 mmol) and isopropyl acetate **2b** (1.0 mL, ynesulfonamide *concn* = 0.20 M) in 81% yield after stirring at  $-40$  °C for 15 min.

**E-3r**:  $R_f = 0.33$  [10:1 petroleum ether/EtOAc]; white solid; mp = 53–54 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.11 (d, 6H,  $J = 6.0$  Hz), 1.73 (d, 3H,  $J = 6.7$  Hz), 2.42 (s, 3H), 2.87 (s, 3H), 4.09 (hept, 1H,  $J = 6.0$  Hz), 4.57 (q, 1H,  $J = 6.7$  Hz), 7.27 (d, 2H,  $J = 8.0$  Hz), 7.76 (d, 2H,  $J = 8.3$  Hz);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  12.2, 21.4, 21.7, 35.7, 69.3, 96.6, 128.4, 129.2, 136.2, 143.3, 147.3; IR (neat) ( $\text{cm}^{-1}$ ) 1676m, 1342s, 1225m, 1152s, 1105s, 1087s; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{14}\text{H}_{21}\text{NO}_3\text{SNa}$   $[\text{M}+\text{Na}]^+$ : 306.1134; found 306.1137.

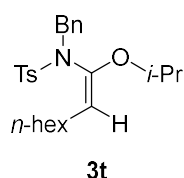
**Z-3r**:  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.22 (d, 6H,  $J = 6.2$  Hz), 1.56 (d, 3H,  $J = 6.8$  Hz), 2.44 (s, 3H), 2.95 (s, 3H), 4.28–4.36 (m, 2H), 7.31 (d, 2H,  $J = 8.0$  Hz), 7.73 (d, 2H,  $J = 8.3$  Hz).



A separable 16:1 mixture of enamides **E-3s** (62.1 mg, 0.16 mmol) and **Z-3s** (3.9 mg, 0.01 mmol) were prepared from ynesulfonamide **1h** (66.6 mg, 0.20 mmol) and isopropyl acetate **2b** (1.0 mL, ynesulfonamide *concn* = 0.20 M) in 86% yield after stirring at –40 °C for 15 min.

**E-3s**:  $R_f = 0.37$  [10:1 petroleum ether/EtOAc]; white solid; mp = 37–38 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.67 (t, 3H,  $J = 7.3$  Hz), 0.84–0.97 (m, 2H), 1.06 (d, 6H,  $J = 6.0$  Hz), 1.92 (q, 2H,  $J = 7.1$  Hz), 2.43 (s, 3H), 4.01 (hept, 1H,  $J = 6.0$  Hz), 4.06–4.61 (m, 2H), 4.41 (t, 1H,  $J = 7.1$  Hz), 7.21–7.30 (m, 7H), 7.80 (d, 2H,  $J = 8.3$  Hz);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  13.9, 21.3, 21.7, 23.1, 29.3, 51.4, 68.8, 104.5, 127.9, 128.2, 128.3, 129.2, 129.6, 135.6, 137.0, 142.8, 143.4; IR (neat) ( $\text{cm}^{-1}$ ) 1670w, 1348s, 1162s, 1110s, 1090s, 1043m; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{22}\text{H}_{30}\text{NO}_3\text{S}$   $[\text{M}+\text{H}]^+$ : 388.1941; found 388.1939.

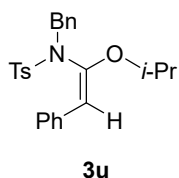
**Z-3s**:  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.79 (t, 3H,  $J = 7.4$  Hz), 0.97 (d, 6H,  $J = 6.1$  Hz), 1.18–1.28 (m, 2H), 1.95 (q, 2H,  $J = 7.4$  Hz), 2.43 (s, 3H), 4.06 (hept, 1H,  $J = 6.1$  Hz), 4.31 (t, 1H,  $J = 7.4$  Hz); 4.46 (s, 2H), , 7.26–7.27 (m, 7H), 7.68 (d, 2H,  $J = 8.3$  Hz).



A separable 16:1 mixture of enamides **E-3t** (74.5 mg, 0.17 mmol) and **Z-3t** (4.7 mg, 0.01 mmol) were prepared from ynesulfonamide **1i** (75.0 mg, 0.20 mmol) and isopropyl acetate **2b** (1.0 mL, ynesulfonamide *concn* = 0.20 M) in 92% yield after stirring at –40 °C for 15 min.

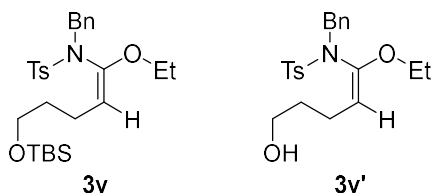
*E*-**3t**:  $R_f = 0.46$  [10:1 petroleum ether/EtOAc]; colorless oil;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.85 (t, 3H,  $J = 7.2$  Hz), 1.06 (d, 6H,  $J = 6.1$  Hz), 0.94-1.16 (m, 5H), 1.18-1.32 (m, 3H), 1.92 (q, 2H,  $J = 7.1$  Hz), 2.44 (s, 3H), 4.01 (hept, 1H,  $J = 6.0$  Hz), 4.07-4.64 (m, 2H), 4.40 (t, 1H,  $J = 7.2$  Hz), 7.21-7.33 (m, 7H), 7.80 (d, 2H,  $J = 8.3$  Hz);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  14.3, 21.4, 21.7, 22.8, 27.4, 29.2, 30.1, 31.9, 51.4, 68.8, 104.9, 127.9, 128.3, 128.4, 129.3, 129.7, 135.7, 137.0, 142.7, 143.4; IR (neat) ( $\text{cm}^{-1}$ ) 1670w, 1372w, 1348s, 1161s, 1107s, 1092s; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{25}\text{H}_{36}\text{NO}_3\text{S}$   $[\text{M}+\text{H}]^+$ : 430.2410; found 430.2409.

*Z*-**3t**:  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.87 (t, 3H,  $J = 7.0$  Hz), 0.97 (d, 6H,  $J = 6.1$  Hz), 1.66-1.29 (m, 8H), 1.93-1.97 (m, 2H), 2.43 (s, 3H), 4.06 (hept, 1H,  $J = 6.1$  Hz), 4.30 (t, 1H,  $J = 7.4$  Hz), 4.45 (s, 2H), 7.26-7.27 (m, 7H), 7.67 (d, 2H,  $J = 8.3$  Hz).



Enamide *E*-**3u** (72.0 mg, 0.17 mmol;  $E/Z \geq 25:1$ ) was prepared from ynesulfonamide **1j** (73.4 mg, 0.20 mmol) and isopropyl acetate **2b** (1.0 mL, ynesulfonamide *concn* = 0.20 M) in 86% yield after stirring at  $-40$  °C for 2 h.

*E*-**3u**:  $R_f = 0.32$  [10:1 petroleum ether/EtOAc]; white solid; mp = 109–110 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.17 (d, 6H,  $J = 6.0$  Hz), 2.45 (s, 3H), 4.26 (hept, 1H,  $J = 6.1$  Hz), 4.29 (s, 2H), 5.42 (s, 1H), 6.87-6.89 (m, 2H), 7.02-7.06 (m, 2H), 7.09-7.17 (m, 2H), 7.23-7.28 (m, 4H), 7.34-7.37 (m, 2H), 7.81 (d, 2H,  $J = 8.3$  Hz);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  21.4, 21.8, 52.3, 70.2, 102.9, 126.2, 127.8, 127.9, 128.25, 128.31, 128.7, 129.2, 129.4, 134.7, 134.8, 137.2, 143.6, 145.7; IR (neat) ( $\text{cm}^{-1}$ ) 1652m, 1341s, 1158s, 1110s, 1083s; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{25}\text{H}_{28}\text{NO}_3\text{S}$   $[\text{M}+\text{H}]^+$ : 422.1784; found 422.1782.

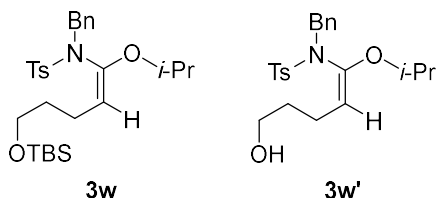


Enamides *E*-**3v** (60.2 mg, 0.12 mmol;  $E/Z \geq 25:1$ ) and *E*-**3v'** (15.8 mg, 0.04 mmol;  $E/Z \geq 25:1$ ) were prepared from ynesulfonamide **1m**<sup>9</sup> (92.5 mg, 0.20 mmol) and EtOAc **2a** (1.0 mL, ynesulfonamide *concn* = 0.20 M) in 60% yield after stirring at  $-70$  °C for 20 min.

*E*-**3v**:  $R_f = 0.45$  [6:1 petroleum ether/EtOAc]; white solid; mp = 35–36 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.03 (s, 6H), 0.89 (s, 9H), 1.09 (t, 3H,  $J = 7.0$  Hz), 1.18 (s, 2H), 1.96 (q, 2H,  $J = 7.3$  Hz),

2.44 (s, 3H), 3.39 (t, 2H,  $J = 6.7$  Hz), 3.51 (q, 2H,  $J = 6.8$  Hz), 4.03-4.40 (m, 2H), 4.44 (t, 1H,  $J = 7.2$  Hz), 7.25 (s, 5H), 7.30 (d, 2H,  $J = 8.1$  Hz), 7.79 (d, 2H,  $J = 8.2$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  -5.1, 14.3, 18.5, 21.7, 23.6, 26.2, 33.1, 51.5, 63.1, 63.2, 104.0, 128.0, 128.29, 128.32, 129.3, 129.6, 135.5, 136.9, 143.4, 144.8; IR (neat) ( $\text{cm}^{-1}$ ) 1676w, 1346s, 1257m, 1165s, 1095s, 1040m; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{27}\text{H}_{42}\text{NO}_4\text{Si}$   $[\text{M}+\text{H}]^+$ : 504.2598; found 504.2599.

*E-3v'*:  $R_f = 0.27$  [2:1 petroleum ether/EtOAc]; white solid; mp = 88–89 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.09 (t, 3H,  $J = 7.0$  Hz), 1.28-1.32 (m, 2H), 1.78 (s, 1H), 1.86-2.09 (m, 2H), 2.45 (s, 3H), 3.46 (t, 2H,  $J = 5.9$  Hz), 3.53 (q, 2H,  $J = 6.5$  Hz), 4.08-4.58 (m, 2H), 4.39 (t, 1H,  $J = 7.1$  Hz), 7.27 (s, 5H), 7.30 (d, 2H,  $J = 8.2$  Hz), 7.79 (d, 2H,  $J = 8.2$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  14.3, 21.7, 23.2, 32.6, 51.7, 62.1, 63.3, 104.0, 128.1, 128.3, 128.4, 129.4, 129.8, 135.4, 136.6, 143.7, 145.1; IR (neat) ( $\text{cm}^{-1}$ ) 3572br, 1675m, 1346s, 1163s, 1092m, 1070m; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{21}\text{H}_{28}\text{NO}_4\text{S}$   $[\text{M}+\text{H}]^+$ : 390.1734; found 390.1733.



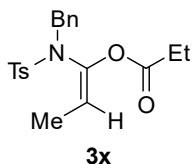
A separable 14:1 mixture of enamides *E-3w* (59.5 mg, 0.11 mmol) and *Z-3w* (4.2 mg, 0.01 mmol), and enamide *E-3w'* (14.0 mg, 0.03 mmol;  $E/Z \geq 25:1$ ) were prepared from ynesulfonamide **1m** (92.3 mg, 0.20 mmol) and isopropyl acetate **2b** (1.0 mL, ynesulfonamide *concn* = 0.20 *M*) in 61% yield after stirring at -40 °C for 30 min.

*E-3w*:  $R_f = 0.33$  [10:1 petroleum ether/EtOAc]; colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.02 (s, 6H), 0.88 (s, 9H), 1.05 (d, 6H,  $J = 6.0$  Hz), 1.11-1.22 (m, 2H), 1.97 (q, 2H,  $J = 6.6$  Hz), 2.44 (s, 3H), 3.38 (t, 2H,  $J = 6.8$  Hz), 4.00 (hept, 1H,  $J = 6.0$  Hz), 4.08-4.64 (m, 2H), 4.41 (t, 1H,  $J = 7.2$  Hz), 7.24-7.30 (m, 7H), 7.80 (d, 2H,  $J = 8.3$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  -5.1, 18.5, 21.3, 21.7, 23.8, 26.2, 33.1, 51.4, 63.2, 68.9, 104.2, 128.0, 128.3, 128.4, 129.3, 129.6, 135.6, 136.9, 143.0, 143.4; IR (neat) ( $\text{cm}^{-1}$ ) 1672w, 1462w, 1353s, 1253m, 1163s, 1092s; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{28}\text{H}_{44}\text{NO}_4\text{Si}$   $[\text{M}+\text{H}]^+$ : 518.2755; found 518.2754.

*Z-3w*:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.01 (s, 6H), 0.87 (s, 9H), 0.97 (d, 6H,  $J = 6.1$  Hz), 1.37-1.44 (m, 2H), 2.01 (q, 2H,  $J = 7.6$  Hz), 2.43 (s, 3H), 3.48 (t, 2H,  $J = 6.5$  Hz), 4.06 (hept, 1H,  $J = 6.1$  Hz), 4.32 (t, 1H,  $J = 7.4$  Hz), 4.45 (s, 2H), 7.26-7.30 (m, 7H), 7.67 (d, 2H,  $J = 8.2$  Hz).

*E-3w'*:  $R_f = 0.26$  [2:1 petroleum ether/EtOAc]; colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.06 (d, 6H,  $J = 5.9$  Hz), 1.29-1.33 (m, 2H), 1.76-2.16 (m, 3H), 2.45 (s, 3H), 3.47 (t, 2H,  $J = 6.1$  Hz), 4.02

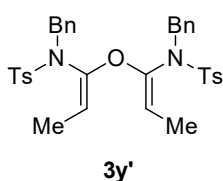
(hept, 1H,  $J = 6.0$  Hz), 4.09-4.75 (m, 2H), 4.36 (t, 1H,  $J = 7.1$  Hz), 7.27-7.32 (m, 7H), 7.80 (d, 2H,  $J = 8.3$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  21.4, 21.8, 23.4, 32.6, 51.6, 62.1, 69.0, 104.1, 128.1, 128.3, 128.4, 129.3, 129.8, 135.5, 136.7, 143.3, 143.6; IR (neat) ( $\text{cm}^{-1}$ ) 3397br, 1671m, 1456w, 1348s, 1160s, 1110s, 1090s; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{22}\text{H}_{30}\text{NO}_4\text{S}$   $[\text{M}+\text{H}]^+$ : 404.1890; found 404.1892.



*E*-**3x** (4.5 mg, 0.01 mmol), and a mixture of enamides *E*-**3x** and *Z*-**3x** (26.8 mg, 0.07 mmol; *E/Z* = 5:1) were prepared from ynesulfonamide **1a** (60.1 mg, 0.20 mmol) and propionic anhydride **2c** (1.0 mL, ynesulfonamide *concn* = 0.20 M) in 42% yield after stirring at  $-40$  °C for 20 min.

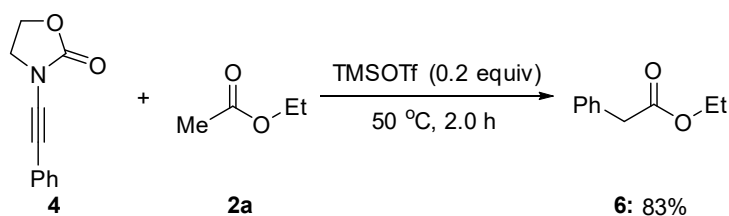
*E*-**3x**:  $R_f$ =0.31 [6:1 petroleum ether/EtOAc]; colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.00 (t, 3H,  $J = 7.5$  Hz), 1.30 (d, 3H,  $J = 7.0$  Hz), 2.14 (q, 2H,  $J = 7.5$  Hz), 2.45 (s, 3H), 4.36 (s, 2H), 5.44 (q, 1H,  $J = 7.1$  Hz), 7.28-7.39 (m, 7H), 7.80 (d, 2H,  $J = 8.3$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  8.9, 12.3, 21.8, 27.5, 51.9, 120.7, 128.1, 128.2, 128.5, 129.6, 129.7, 135.5, 136.8, 137.1, 143.9, 172.2; IR (neat) ( $\text{cm}^{-1}$ ) 3359w, 2919m, 1761m, 1660w, 1632w, 1598w, 1352s, 1164s; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{20}\text{H}_{23}\text{NO}_4\text{SNa}$   $[\text{M}+\text{Na}]^+$ : 396.1240; found 396.1243.

*Z*-**3x**:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.04 (t, 3H,  $J = 7.5$  Hz), 1.39 (d, 3H,  $J = 7.0$  Hz), 2.22 (q, 2H,  $J = 7.5$  Hz), 2.44 (s, 3H), 4.49 (s, 2H), 4.98 (q, 1H,  $J = 7.0$  Hz), 7.28-7.39 (m, 7H), 7.75 (d, 2H,  $J = 8.3$  Hz).



Enamide **3y'** (20.0 mg, 0.03 mmol) was prepared from ynesulfonamide **1a** (61.3 mg, 0.20 mmol) and phenyl acetate **2d** (1.0 mL, ynesulfonamide *concn* = 0.20 M) in 32% yield after stirring at  $0$  °C for 20 min.

**3y'**:  $R_f$ =0.42 [4:1 petroleum ether/EtOAc]; white solid; mp = 166–167 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.50 (d, 6H,  $J = 7.0$  Hz), 2.44 (s, 6H), 2.94-3.74 (m, 2H), 4.16-4.71 (m, 2H), 4.85 (q, 2H,  $J = 7.0$  Hz), 6.82 (d, 4H,  $J = 4.8$  Hz), 7.14-7.23 (m, 6H), 7.29 (d, 4H,  $J = 8.0$  Hz), 7.62 (d, 4H,  $J = 8.2$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  12.6, 21.8, 50.9, 110.3, 128.1, 128.2, 128.3, 129.1, 129.7, 134.9, 136.6, 142.8, 144.1; IR (neat) ( $\text{cm}^{-1}$ ) 2923w, 1695w, 1684w, 1454w, 1350s, 1164s, 1079s; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{34}\text{H}_{36}\text{N}_2\text{O}_5\text{S}_2\text{Na}$   $[\text{M}+\text{Na}]^+$ : 639.1958; found 639.1960.



Ester **6**<sup>10</sup> (27.1 mg, 0.17 mmol) was prepared from ynamide **4**<sup>11</sup> (37.8 mg, 0.20 mmol) and ethyl acetate **2a** (1.0 mL, ynesulfonamide *concn* = 0.20 M) in 83% yield after stirring at 50 °C for 2 h.

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