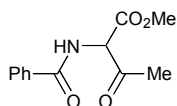


## The rhodium carbene route to oxazoles: a remarkable catalyst effect

Baolu Shi, Alexander J. Blake, Ian B. Campbell, Brian D. Judkins,  
and Christopher J. Moody

### ELECTRONIC SUPPLEMENTARY INFORMATION

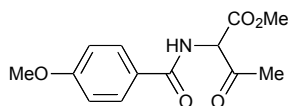
#### Methyl 2-benzoylamino-3-oxobutanoate 3a



Colourless oil (90 mg, 60%); (lit.,<sup>1</sup> mp 93 – 94 °C); (Found: M+Na<sup>+</sup>, 258.0742.

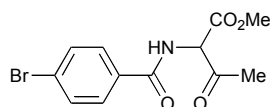
C<sub>12</sub>H<sub>13</sub>NO<sub>4</sub>+Na<sup>+</sup> requires 258.0742);  $\nu_{\max}$  (CHCl<sub>3</sub>)/cm<sup>-1</sup> 1727, 1606, 1256;  $\delta_{\text{H}}$  (300 MHz; CDCl<sub>3</sub>) 7.84 – 7.80 (2H, m, ArH), 7.51 – 7.40 (4H, m, ArH, NH), 5.44 (1H, d, *J* 6.3, NHCH), 3.82 (3H, s, OMe), 2.32 (3H, s, Me);  $\delta_{\text{C}}$  (75 MHz; CDCl<sub>3</sub>) 198.6, 166.9, 166.8, 133.0, 132.2 (CH), 128.7 (CH), 127.4 (CH), 63.5 (CH), 53.5 (Me), 28.1 (Me).

#### Methyl 2-(4-methoxybenzoylamino)-3-oxobutanoate 3b



Colourless oil (93 mg, 55%); (Found: M+Na<sup>+</sup>, 288.0833. C<sub>13</sub>H<sub>15</sub>NO<sub>5</sub>+Na<sup>+</sup> requires 288.0848);  $\nu_{\max}$  (CHCl<sub>3</sub>)/cm<sup>-1</sup> 1732, 1606, 1492, 1256;  $\delta_{\text{H}}$  (300 MHz; CDCl<sub>3</sub>) 7.81 – 7.76 (2H, m, ArH), 7.25 (1H, d, *J* 6.3, NHCH), 6.93 – 6.89 (2H, m, ArH), 5.41 (1H, d, *J* 6.3, NHCH), 3.83 (3H, s, OMe), 3.81 (3H, s, OMe), 2.41 (3H, s, Me);  $\delta_{\text{C}}$  (75 MHz; CDCl<sub>3</sub>) 198.9, 166.9, 166.3, 162.8, 129.3 (CH), 125.2, 113.9 (CH), 63.4 (CH), 55.5 (Me), 53.4 (Me), 28.1 (Me).

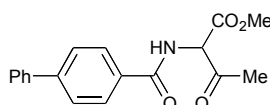
### Methyl 2-(4-bromobenzoylamino)-3-oxobutanoate 3c



Colourless solid (154 mg, 77%); mp 87 – 89 °C; (Found:  $M+Na^+$ , 335.9836).

$C_{12}H_{12}^{79}BrNO_4+Na^+$  requires 335.9847);  $\nu_{max}$  ( $CHCl_3$ )/ $cm^{-1}$  1754, 1728, 1661, 1477, 1216;  $\delta_H$  (400 MHz;  $CDCl_3$ ) 7.68 (2H, d,  $J$  8.4, ArH), 7.54 (2H, d,  $J$  8.4, ArH), 7.35 (1H, d,  $J$  6.0,  $NHCH$ ), 5.41 (1H, d,  $J$  6.4,  $NHCH$ ), 3.81 (3H, s, OMe), 2.41 (3H, s, Me);  $\delta_C$  (100 MHz;  $CDCl_3$ ) 198.2, 166.4, 165.8, 131.8 (CH), 131.6, 128.8 (CH), 126.8, 63.2 (CH), 53.4 (Me), 28.0 (Me).

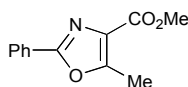
### Methyl 2-(4-phenylbenzoylamino)-3-oxobutanoate 3d



Colourless solid (59 mg, 30%); mp 115 – 117 °C; (Found:  $M+Na^+$ , 334.1039).

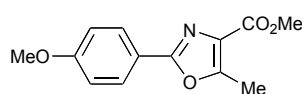
$C_{18}H_{17}NO_4+Na^+$  requires 334.1055);  $\delta_H$  (400 MHz;  $CDCl_3$ ) 7.92 (2H, d,  $J$  8.4, ArH), 7.67 (2H, d,  $J$  8.4, ArH), 7.61 (2H, d,  $J$  8.4, ArH), 7.47 (2H, t,  $J$  8.8, ArH), 7.42 – 7.38 (2H, m, ArH,  $NHCH$ ), 5.48 (1H, d,  $J$  6.4,  $CHNH$ ), 3.86 (3H, s, OMe), 2.48 (3H, s, Me);  $\delta_C$  (100 MHz;  $CDCl_3$ ) 198.6, 166.8, 166.6, 145.1, 140.0, 131.6, 129.1 (CH), 128.2 (CH), 127.9 (CH), 127.4 (CH), 127.3 (CH), 63.5 (CH), 53.5 (Me), 28.2 (Me).

### Methyl 5-methyl-2-phenyloxazole-4-carboxylate 4a



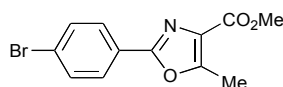
Pale yellow solid (61 mg, 83%); mp 89 – 91 °C (lit.,<sup>2</sup> mp 88 – 89 °C); (Found: M+Na<sup>+</sup>, 240.0624. C<sub>12</sub>H<sub>11</sub>NO<sub>3</sub>+Na<sup>+</sup> requires 240.0637);  $\nu_{\max}$  (CHCl<sub>3</sub>)/cm<sup>-1</sup> 1715, 1615, 1440, 1351;  $\delta_{\text{H}}$  (400 MHz; CDCl<sub>3</sub>) 8.06 – 8.03 (2H, m, ArH), 7.45 – 7.41 (3H, m, ArH), 3.92 (3H, s, OMe), 2.69 (3H, s, Me);  $\delta_{\text{C}}$  (100 MHz; CDCl<sub>3</sub>) 162.8, 159.6, 156.3, 130.7, 128.7 (CH), 128.5, 126.5 (CH), 51.9 (Me), 12.0 (Me); one carbon unobserved.

### Methyl 2-(4-methoxyphenyl)-5-methyloxazole-4-carboxylate 4b



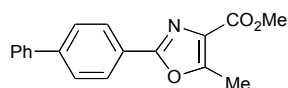
Colourless solid (60 mg, 81%); mp 108 – 109 °C (lit.,<sup>2</sup> mp 105 – 106 °C); (Found: C, 62.89; H, 5.21; N, 5.44. C<sub>13</sub>H<sub>13</sub>NO<sub>4</sub> requires C, 63.15; H, 5.30; N, 5.67%); (Found: M+H<sup>+</sup>, 248.0915. C<sub>13</sub>H<sub>13</sub>NO<sub>4</sub>+H<sup>+</sup> requires 248.0923);  $\nu_{\max}$  (solid)/cm<sup>-1</sup> 1709, 1614, 1501, 1433, 1345, 1254;  $\delta_{\text{H}}$  (300 MHz; CDCl<sub>3</sub>) 7.97 (2H, d, *J* 9.0, ArH), 6.93 (2H, d, *J* 9.0, ArH), 3.92 (3H, s, OMe), 3.83 (3H, s, OMe), 2.67 (3H, s, Me);  $\delta_{\text{C}}$  (75 MHz; CDCl<sub>3</sub>) 162.9, 161.6, 159.7, 155.8, 128.2 (CH), 119.2, 114.1 (CH), 55.3 (Me), 51.9 (Me), 12.2 (Me); one carbon unobserved.

### Methyl 2-(4-bromophenyl)-5-methyloxazole-4-carboxylate 4c



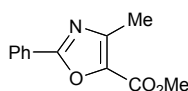
Yellow solid (66 mg, 70%); mp 125 – 127 °C; (Found: M+Na<sup>+</sup>, 317.9722. C<sub>12</sub>H<sub>10</sub><sup>79</sup>BrNO<sub>3</sub>+Na<sup>+</sup> requires 317.9712);  $\nu_{\max}$  (CHCl<sub>3</sub>)/cm<sup>-1</sup> 1715, 1614, 1482, 1350, 1240;  $\delta_{\text{H}}$  (400 MHz; CDCl<sub>3</sub>) 7.89 (2H, d, *J* 8.8, ArH), 7.55 (2H, d, *J* 8.8, ArH), 3.92 (3H, s, OMe), 2.67 (3H, s, Me);  $\delta_{\text{C}}$  (100 MHz; CDCl<sub>3</sub>) 162.7, 158.9, 156.7, 132.1 (CH), 128.8, 128.1 (CH), 125.5, 125.4, 52.2 (Me), 12.2 (Me).

### Methyl 2-biphenyl-5-methyloxazole-4-carboxylate 4d



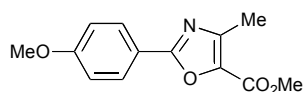
Yellow solid (43 mg, 91%); mp 128 – 129 °C; (Found:  $M+Na^+$ , 316.0931.  $C_{18}H_{15}NO_3+Na^+$  requires 316.0950);  $\delta_H$  (300 MHz;  $CDCl_3$ ) 8.13 (2H, d,  $J$  8.7, ArH), 7.68 (2H, d,  $J$  8.7, ArH), 7.65 – 7.61 (2H, m, ArH), 7.46 (2H, m, ArH), 7.37 (1H, m, ArH), 3.95 (3H, s, OMe), 2.72 (3H, s, Me);  $\delta_C$  (75 MHz;  $CDCl_3$ ) 163.0, 159.7, 156.6, 143.6, 140.1, 129.0 (CH), 128.7, 128.1 (CH), 127.5 (CH), 127.2 (CH), 127.1 (CH), 125.5, 52.2 (Me), 12.3 (Me).

### Methyl 4-methyl-2-phenyloxazole-5-carboxylate 5a



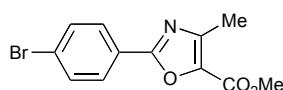
Colourless solid (40 mg, 18%); mp 54 – 55 °C (lit.,<sup>3</sup> mp 45-47 °C); (Found:  $M+H^+$ , 218.0894.  $C_{12}H_{11}NO_3+H^+$  requires 218.0817);  $\nu_{max}$  ( $CHCl_3$ )/ $cm^{-1}$  1713, 1542;  $\delta_H$  (400 MHz;  $CDCl_3$ ) 8.13 – 8.11 (2H, m, ArH), 7.50 – 7.47 (3H, m, ArH), 3.94 (3H, s, OMe), 2.55 (3H, s, Me);  $\delta_C$  (100 MHz;  $CDCl_3$ ) 162.5, 159.4, 147.5, 137.4, 131.7 (CH), 129.0 (CH), 127.4 (CH), 126.5, 52.1 (Me), 13.6 (Me).

### Methyl 2-(4-methoxyphenyl)-4-methyloxazole-5-carboxylate 5b



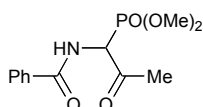
Colourless solid (19 mg, 24%); mp 68 – 70 °C (lit.,<sup>4</sup> white solid, mp not given); (Found:  $M+H^+$ , 248.0913.  $C_{13}H_{13}NO_4+H^+$  requires 248.0923);  $\nu_{max}$  (solid)/ $cm^{-1}$  1707, 1608, 1254, 1108;  $\delta_H$  (400 MHz;  $CDCl_3$ ) 8.05 (2H, d,  $J$  8.0, ArH), 6.97 (2H, d,  $J$  8.0, ArH), 3.93 (3H, s, OMe), 3.86 (3H, s, OMe), 2.52 (3H, s, Me);  $\delta_C$  (100 MHz;  $CDCl_3$ ) 162.7, 162.5, 159.6, 147.5, 136.9, 129.2 (CH), 119.1, 114.5 (CH), 55.6 (Me), 52.0 (Me), 13.6 (Me).

### Methyl 2-(4-bromophenyl)-4-methyloxazole-5-carboxylate 5c



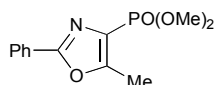
Pink solid (36 mg, 38%); mp 109 – 111 °C; (Found:  $M+H^+$ , 295.9919.  $C_{12}H_{10}^{79}BrNO_3+H^+$  requires 295.9922);  $\nu_{max}$  (solid)/ $cm^{-1}$  1714, 1610, 1599, 1436, 1100;  $\delta_H$  (400 MHz;  $CDCl_3$ ) 7.97 (2H, d,  $J$  8.4, ArH), 7.61 (2H, d,  $J$  8.4, ArH), 3.94 (3H, s, OMe), 2.53 (3H, s, Me);  $\delta_C$  (100 MHz;  $CDCl_3$ ) 161.6, 159.3, 147.5, 137.6, 132.2, 128.8, 126.5 (CH), 125.4 (CH), 52.2 (Me), 13.5 (Me).

### Dimethyl (1-benzoylamino-2-oxopropyl)phosphonate 7



Colourless solid (83 mg, 62%); mp 64 – 66 °C; (Found: C, 50.18; H, 5.54; N, 4.73.  $C_{12}H_{16}NO_5P$  requires C, 50.53; H, 5.65; N, 4.91%); (Found:  $M+Na^+$ , 308.0657.  $C_{12}H_{16}NO_5P+Na^+$  requires 308.0664);  $\nu_{max}$  ( $CHCl_3$ )/ $cm^{-1}$  3606, 3425, 1723, 1665, 1509, 1482, 1264, 1037;  $\delta_H$  (400 MHz;  $CDCl_3$ ) 7.82 (2H, d,  $J$  8.2, ArH), 7.51 (1H, t,  $J$  8.2, ArH), 7.43 (2H, t,  $J$  8.2, ArH), 7.21 (1H, br d,  $J$  7.6,  $NHCH$ ), 5.54 (1H, dd,  $J$  24.0, 7.6,  $CHNH$ ), 3.85 (3H, d,  $J$  11.0, OMe), 3.76 (3H, d,  $J$  11.0, OMe), 2.47 (3H, d,  $J$  0.8, Me);  $\delta_C$  (100 MHz;  $CDCl_3$ ) 199.8 (d,  $J$  2.0), 166.8 (d,  $J$  4.0), 133.2, 132.2 (CH), 128.8 (CH), 127.3 (CH), 57.9 (CH, d,  $J$  141.0), 54.3 (Me, d,  $J$  5.0), 53.9 (Me, d,  $J$  7.0), 29.1 (Me).

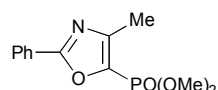
### Dimethyl 5-methyl-2-phenyloxazole-4-phosphonate 8



Pale yellow solid (34 mg, 44%); mp 39 – 40 °C; (Found:  $M+Na^+$ , 290.0549.  $C_{12}H_{14}NO_4P+Na^+$  requires 290.0558);  $\nu_{max}$  ( $CHCl_3$ )/ $cm^{-1}$  1246, 1036;  $\delta_H$  (500 MHz;  $CDCl_3$ )

8.03 (2H, m, ArH), 7.44 (3H, m, ArH), 3.84 (6H, d,  $J$  11.5, OMe), 2.66 (3H, d,  $J$  2.0, Me);  $\delta_C$  (125 MHz; CDCl<sub>3</sub>) 161.4 (d,  $J$  21.0), 159.2 (d,  $J$  38.0), 130.9 (CH), 128.9 (CH), 126.7 (CH), 124.3 (d,  $J$  242.0), 53.2 (Me, d,  $J$  5.0), 11.7 (Me).; one carbon unobserved.

### Dimethyl 4-methyl-2-phenyloxazole-5-phosphonate 9a



Colourless solid (61 mg, 49%); mp 29 – 30 °C; (Found: C, 53.99; H, 5.30; N, 5.05.

C<sub>12</sub>H<sub>14</sub>NO<sub>4</sub>P requires C, 53.94; H, 5.28; N, 5.24%); (Found: M+H<sup>+</sup>, 268.0716.

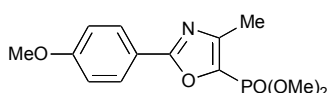
C<sub>12</sub>H<sub>14</sub>NO<sub>4</sub>P+H<sup>+</sup> requires 268.0739);  $\nu_{\max}$  (CHCl<sub>3</sub>)/cm<sup>-1</sup> 1260, 1034;  $\delta_H$  (500 MHz; CDCl<sub>3</sub>)

8.07 (2H, m, ArH), 7.51 – 7.45 (3H, m, ArH), 3.83 (6H, d,  $J$  11.5, OMe), 2.49 (3H, d,  $J$  2.0,

Me);  $\delta_C$  (125 MHz; CDCl<sub>3</sub>) 164.6 (d,  $J$  14.0), 151.3 (d,  $J$  28.0), 134.3 (d,  $J$  240.0), 131.5

(CH), 129.0 (CH), 127.2 (CH), 126.5, 53.3 (Me, d,  $J$  5.0), 12.9 (Me).

### Dimethyl 2-(4-methoxyphenyl)-4-methyloxazole-5-phosphonate 9b



Pale yellow solid (75 mg, 54%); mp 70 – 72 °C; (Found: M+Na<sup>+</sup>, 320.0650.

C<sub>13</sub>H<sub>16</sub>NO<sub>5</sub>P+Na<sup>+</sup> requires 320.0664);  $\nu_{\max}$  (CHCl<sub>3</sub>)/cm<sup>-1</sup> 1258, 1032;  $\delta_H$  (400 MHz; CDCl<sub>3</sub>)

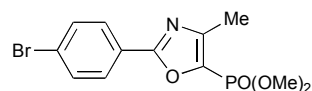
7.99 (2H, d,  $J$  8.8, ArH), 6.94 (2H, d,  $J$  8.8, ArH), 3.84 (3H, s, OMe), 3.80 (6H, d,  $J$  11.6,

OMe), 2.45 (3H, d,  $J$  2.4, Me);  $\delta_C$  (100 MHz; CDCl<sub>3</sub>) 164.7 (d,  $J$  15.0), 162.3, 151.4 (d,  $J$

27.0), 133.6 (d,  $J$  242.0), 129.0 (CH), 119.2, 114.4 (CH), 55.5 (Me), 53.2 (Me, d,  $J$  6.0), 12.9

(Me).

### Dimethyl 2-(4-bromophenyl)-4-methyloxazole-5-phosphonate 9c

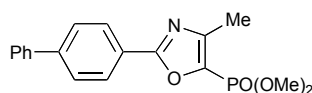


Colourless solid (75 mg, 46%); mp 74 – 75 °C; (Found: C, 41.34; H, 3.72; N, 3.74.

$C_{12}H_{13}BrNO_4P$  requires C, 41.64; H, 3.79; N, 4.05%); (Found:  $M+Na^+$ , 369.9634.

$C_{12}H_{13}^{79}BrNO_4P+Na^+$  requires 369.9663);  $\nu_{max}$  ( $CHCl_3$ )/ $cm^{-1}$  1261, 1035;  $\delta_H$  (500 MHz;  $CDCl_3$ ) 7.94 (2H, d,  $J$  8.5, ArH), 7.61 (2H, d,  $J$  8.5, ArH), 3.85 (6H, d,  $J$  11.5, OMe), 2.48 (3H, d,  $J$  2.0, Me);  $\delta_C$  (125 MHz;  $CDCl_3$ ) 163.7 (d,  $J$  14.0), 151.4 (d,  $J$  28.0), 134.8 (d,  $J$  240.0), 132.3, 128.7, 126.3 (CH), 125.5 (CH), 53.3 (Me, d,  $J$  6.0), 12.9 (Me).

### Dimethyl 2-(4-biphenyl)-4-methyloxazole-5-phosphonate 9d

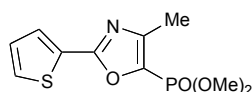


Colourless solid (79 mg, 49%); mp 78 – 80 °C; (Found: C, 62.67; H, 5.37; N, 3.85.

$C_{18}H_{18}NO_4P$  requires C, 62.97; H, 5.28; N, 4.08%); (Found:  $M+Na^+$ , 366.0881.

$C_{18}H_{18}NO_4P+Na^+$  requires 366.0871);  $\nu_{max}$  ( $CHCl_3$ )/ $cm^{-1}$  1602, 1261, 1035;  $\delta_H$  (500 MHz;  $CDCl_3$ ) 8.15 (2H, m, ArH), 7.70 (2H, m, ArH), 7.63 (2H, d,  $J$  7.5, ArH), 7.47 (2H, d,  $J$  7.5, ArH), 7.39 (1H, m, ArH), 3.85 (6H, d,  $J$  11.5, OMe), 2.51 (3H, d,  $J$  2.0, Me);  $\delta_C$  (125 MHz;  $CDCl_3$ ) 164.5 (d,  $J$  14.0), 151.5 (d,  $J$  26.0), 144.3, 140.0, 134.4 (d,  $J$  241.0), 129.1 (CH), 128.2 (CH), 127.8 (CH), 127.6 (CH), 127.3 (CH), 125.3, 53.3 (Me, d,  $J$  5.0), 12.9 (Me).

### Dimethyl 4-methyl-2-(2-thienyl)oxazol-5-phosphonate 9e

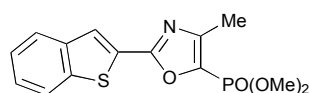


Colourless solid (66 mg, 51%); mp 67 – 68 °C; (Found: C, 43.95; H, 4.43; N, 4.86.

$C_{10}H_{12}NO_4PS$  requires C, 43.96; H, 4.43; N, 5.13%); (Found:  $M+H^+$ , 274.0312.

$C_{10}H_{12}NO_4PS+H^+$  requires 274.0303);  $\nu_{max}$  ( $CHCl_3$ )/ $cm^{-1}$  1591, 1259, 1033;  $\delta_H$  (400 MHz;  $CDCl_3$ ) 7.74 (1H, dd,  $J$  4.5, 1.5, thiophene-5-H), 7.48 (1H, dd,  $J$  6.5, 1.5, thiophene-3-H), 7.11 (1H, dd,  $J$  6.5, 4.5, thiophene-4-H), 3.81 (6H, d,  $J$  14.0, OMe), 2.44 (3H, d,  $J$  3.0, Me);  $\delta_C$  (100 MHz;  $CDCl_3$ ) 160.6 (d,  $J$  15.0), 151.4 (d,  $J$  27.0), 133.8 (d,  $J$  241.0), 130.1 (CH), 129.7 (CH), 128.8, 128.3 (CH), 53.3 (Me, d,  $J$  5.0), 12.8 (Me).

### Dimethyl 2-(benzo[*b*]thiophen-2-yl)-4-methyloxazole-5-phosphonate 9f

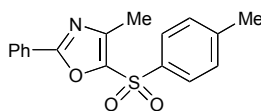


Colourless solid (77 mg, 52%); mp 144 – 145 °C; (Found: C, 51.73; H, 4.31; N, 4.04.

$C_{14}H_{14}NO_4PS$  requires C, 52.01; H, 4.36; N, 4.33%); (Found:  $M+Na^+$ , 346.0276.

$C_{14}H_{14}NO_4PS+Na^+$  requires 346.0279);  $\nu_{max}$  ( $CHCl_3$ )/ $cm^{-1}$  1596, 1261, 1036;  $\delta_H$  (500 MHz;  $CDCl_3$ ) 8.01 (1H, s, thiophene-3-H), 7.86 (2H, m, ArH), 7.42 (2H, m, ArH), 3.85 (6H, d,  $J$  11.5, OMe), 2.50 (3H, d,  $J$  2.5, Me);  $\delta_C$  (125 MHz;  $CDCl_3$ ) 160.6 (d,  $J$  15.0), 151.6 (d,  $J$  26.0), 141.1, 139.4, 134.7 (d,  $J$  240.0), 128.4, 126.6 (CH), 126.5 (CH), 125.3 (CH), 125.0 (CH), 122.7 (CH), 53.5 (Me, d,  $J$  5.0), 12.9 (Me).

### 4-Methyl-2-phenyl-5-(toluene-4-sulfonyl)oxazole 11a



Colourless solid (91 mg, 77%); mp 146 – 148 °C; (Found: C, 65.05; H, 4.75; N, 4.42.

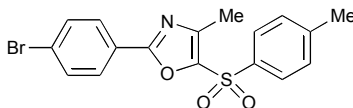
$C_{17}H_{15}NO_3S$  requires C, 65.16; H, 4.82; N, 4.47%); (Found:  $M+H^+$ , 314.0849.

$C_{17}H_{15}NO_3S+H^+$  requires 314.0851);  $\nu_{max}$  ( $CHCl_3$ )/ $cm^{-1}$  1580, 1338, 1147;  $\delta_H$  (400 MHz;  $CDCl_3$ ) 8.00 (2H, m, ArH), 7.92 (2H, d,  $J$  8.4, ArH), 7.51 – 7.42 (3H, m, ArH), 7.36 (2H, d,  $J$  8.4, ArH), 2.58 (3H, s, Me), 2.43 (3H, s, Me);  $\delta_C$  (100 MHz;  $CDCl_3$ ) 162.8, 145.3, 144.9,



142.2, 137.7, 132.0 (CH), 130.2 (CH), 129.0 (CH), 127.7 (CH), 127.3 (CH), 125.9, 21.8 (Me),  
13.0 (Me).

### 2-(4-Bromophenyl)-4-methyl-5-(toluene-4-sulfonyl)oxazole 11b

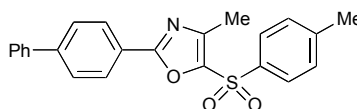


Colourless solid (109 mg, 73%); mp 175 – 176 °C; (Found: C, 51.91; H, 3.47; N, 3.44.

$C_{17}H_{14}BrNO_3S$  requires C, 52.05; H, 3.60; N, 3.57%); (Found:  $M+H^+$ , 391.9947.

$C_{17}H_{14}^{79}BrNO_3S+H^+$  requires 391.9956);  $\nu_{max}$  ( $CHCl_3$ )/ $cm^{-1}$  1601, 1336, 1148;  $\delta_H$  (500 MHz;  $CDCl_3$ ) 7.91 (2H, d,  $J$  9.0, ArH), 7.85 (2H, d,  $J$  8.0, ArH), 7.57 (2H, dt,  $J$  9.0, ArH), 7.36 (2H, d,  $J$  8.0, ArH), 2.56 (3H, s, Me), 2.42 (3H, s, Me);  $\delta_C$  (125 MHz;  $CDCl_3$ ) 161.9, 145.4, 145.0, 142.5, 137.6, 132.4 (CH), 130.3 (CH), 128.7 (CH), 127.8 (CH), 126.8, 124.8, 21.8 (Me), 13.0 (Me).

### 2-(4-Biphenyl)-4-methyl-5-(toluene-4-sulfonyl)oxazole 11c

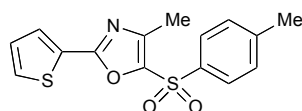


Colourless solid (95 mg, 64%); mp 174 – 176 °C; (Found: C, 70.33; H, 4.85; N, 3.55.

$C_{23}H_{19}NO_3S$  requires C, 70.93; H, 4.92; N, 3.60%); (Found:  $M+H^+$ , 390.1156.

$C_{23}H_{19}NO_3S+H^+$  requires 390.1164);  $\nu_{max}$  ( $CHCl_3$ )/ $cm^{-1}$  1336, 1178;  $\delta_H$  (500 MHz;  $CDCl_3$ ) 8.07 (2H, d,  $J$  8.5, ArH), 7.94 (2H, d,  $J$  7.5, ArH), 7.67 (2H, d,  $J$  8.5, ArH), 7.61 (2H, d,  $J$  7.5, ArH), 7.46 (2H, m, ArH), 7.38 (3H, m, ArH), 2.60 (3H, s, Me), 2.43 (3H, s, Me);  $\delta_C$  (125 MHz;  $CDCl_3$ ) 162.6, 145.1, 144.9, 144.5, 142.1, 139.6, 137.6, 130.1 (CH), 128.9 (CH), 128.2 (CH), 127.6 (2 x CH), 127.5 (CH), 127.1 (CH), 124.5, 21.6 (Me), 12.8 (Me).

#### 4-Methyl-2-(2-thienyl)-5-(toluene-4-sulfonyl)oxazole 11d



Colourless solid (94 mg, 77%); mp 158 – 159 °C; (Found: C, 56.45; H, 4.07; N, 4.22.

$C_{15}H_{13}NO_3S_2$  requires C, 56.41; H, 4.10; N, 4.39%); (Found:  $M+Na^+$ , 342.0214.

$C_{15}H_{13}NO_3S_2+Na^+$  requires 342.0234);  $\nu_{max}$  ( $CHCl_3$ )/ $cm^{-1}$  1587, 1337, 1145;  $\delta_H$  (500 MHz;  $CDCl_3$ ) 7.89 (2H, d,  $J$  8.0, ArH), 7.71 (1H, dd,  $J$  4.0, 1.5, thiophene-5-H), 7.49 (1H, dd,  $J$  5.0, 1.5, thiophene-3-H), 7.35 (2H, d,  $J$  8.0, ArH), 7.10 (1H, dd,  $J$  5.0, 4.0, thiophene-4-H), 2.54 (3H, s, Me), 2.42 (3H, s, Me);  $\delta_C$  (125 MHz;  $CDCl_3$ ) 158.9, 145.3, 145.1, 141.6, 137.6, 130.8 (CH), 130.3 (CH), 130.2 (CH), 128.4 (CH), 128.2, 127.7 (CH), 21.8 (Me), 12.9 (Me).

### X-Ray Crystal data

	<b>Crystal Data for 4b</b>	<b>Crystal Data for 5b</b>	<b>Crystal Data for 7</b>
Empirical Formula	C <sub>13</sub> H <sub>13</sub> NO <sub>4</sub>	C <sub>13</sub> H <sub>13</sub> NO <sub>4</sub>	C <sub>12</sub> H <sub>16</sub> NO <sub>5</sub> P
Formula Weight	247.24	247.24	285.23
Crystal System	triclinic	monoclinic	monoclinic
Unit cell dimensions /Å	<i>a</i> = 6.8926(8)	<i>a</i> = 12.2324(14)	<i>a</i> = 17.2037(9)
/Å	<i>b</i> = 7.4333(9)	<i>b</i> = 7.1119(8)	<i>b</i> = 8.6712(4)
/Å	<i>c</i> = 12.285(2)	<i>c</i> = 13.548(2)	<i>c</i> = 20.5323(11)
/degrees	α = 78.908(2)		
/degrees	β = 85.615(2)	β = 91.188(2)	β = 114.006(2)
/degrees	γ = 72.613(2)		
Volume/ Å <sup>3</sup>	589.3(2)	1178.4(4)	2798.0(4)
Temperature/K	150(2)	150(2)	150(2)
Space Group	<i>P</i> -1	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>C</i> 2/ <i>c</i>
Z value	2	4	8
Reflections total	5217	7364	12210
Reflections unique, <i>R</i> <sub>int</sub>	2643, 0.106	2655, 0.097	3210, 0.058
Final <i>R</i> <sub>1</sub> [ <i>F</i> >4σ( <i>F</i> )]	0.0492	0.0424	0.034
Final <i>wR</i> <sub>2</sub> [all data]	0.132	0.117	0.0988
CCDC deposition no.	721492	721493	721494

	<b>Crystal Data for 9f</b>	<b>Crystal Data for 11a</b>
Empirical Formula	C <sub>14</sub> H <sub>14</sub> NO <sub>4</sub> PS	C <sub>17</sub> H <sub>15</sub> NO <sub>3</sub> S

Formula Weight	323.29	313.36
Crystal System	monoclinic	triclinic
Unit cell dimensions /Å	$a = 20.561(2)$	$a = 8.1096(9)$
/Å	$b = 5.7605(6)$	$b = 10.0737(12)$
/Å	$c = 12.8043(12)$	$c = 10.7607(13)$
/degrees		$\alpha = 66.986(2)$
/degrees	$\beta = 107.171(2)$	$\beta = 70.896(2)$
/degrees		$\gamma = 78.509(2)$
Volume/ Å <sup>3</sup>	1449.0(2)	762.0(3)
Temperature/K	150(2)	150(2)
Space Group	$P2_1/c$	$P-1$
Z value	4	2
Reflections total	12932	6735
Reflections unique, $R_{\text{int}}$	3328, 0.048	3425, 0.023
Final $R_1 [F > 4\sigma(F)]$	0.0370	0.0358
Final $wR_2$ [all data]	0.106	0.101
CCDC deposition no.	721495	721496

## References

1. T. Nemoto, T. Harada, T. Matsumoto and Y. Hamada, *Tetrahedron Lett.*, 2007, **48**, 6304.
2. P. M. T. Ferreira, L. S. Monteiro and G. Pereira, *Eur. J. Org. Chem.*, 2008, 4676.
3. G. Vernin, S. Treppendahl and J. Metzger, *Helv. Chim. Acta*, 1977, **60**, 284.
4. J. Ammann, J. R. Gillig, L. J. Heinz, P. A. Hipskind, M. D. Kinnick, Y. Lai, J. M. Morin, J. A. Nixon, C. Ott, K. A. Savin, T. Schotten, L. J. Sliker, N. J. Snyder and M. A. Robertson, WO2003097047-A1, 2003.