

**Supporting Information**  
**for**  
**Synthesis of  $\beta$ -triazolylenones via metal-free desulfonylative alkylation of**  
***N*-tosyl-1,2,3-triazoles**

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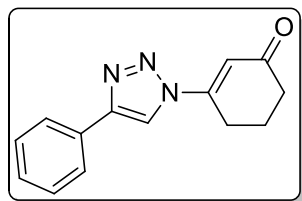
**General Experimental Details.** Buchi-M-560 apparatus was used to record melting points of the solid compounds and are uncorrected. IR spectra were recorded on Perkin Elmer Spectrum One FT spectrometer. Bruker 400 and 500 MHz spectrometers were used to record NMR spectra (<sup>1</sup>H, <sup>13</sup>C, APT and <sup>19</sup>F) by using TMS as the internal standard. Coupling constants (*J*) are reported in Hz. Micromass Q-TOF mass spectrometer was used to record High Resolution Mass Spectra at 60-70 eV in ESI mode. X-ray data were collected on a Rigaku Saturn 724+ diffractometer that was equipped with graphite using monochromatic (Cu and Mo-K $\alpha$ ) radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The structures were solved by using direct methods (SHELXS97) and refined by full-matrix least-squares against F2 by using SHELXL97 software. *N*-Tosyl and *N*-mesyl triazoles were prepared by literature methods.<sup>1</sup> All the 1,3-dicarbonyl compounds were commercially available (Sigma/Alfa Aesar/Spectrochem).

### General Procedure

*N*-Tosyl phenyl triazole (59 mg, 0.2 mmol) and 1,3-dicarbonyl compound (0.2 mmol) were stirred in anhydrous chloroform (3 mL) under inert atmosphere at room temperature. After completion of the reaction (as observed by TLC) the solvent was removed and the residue was directly subjected to silica-gel column chromatography (20% EA-PE) to afford the product as a white solid in 78% yield.

### Experimental Data

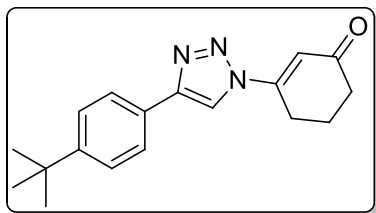
#### 3-(4-Phenyl-1*H*-1,2,3-triazol-1-yl)cyclohex-2-enone (3a)



White solid; Yield 38 mg, 78%; mp 116-118 °C; IR (neat, cm<sup>-1</sup>) 3137 (w), 3114 (w), 3055 (vw), 2927 (m), 2854 (w), 1668 (vs), 1622 (vs), 1455 (m), 1435 (m), 1229 (m), 1020 (m), 764 (m), 738 (s), 705 (m); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  2.27 (quint, *J* = 6.4 Hz, 2H), 2.57 (t, *J* = 6.4 Hz, 2H), 3.25 (t, *J* = 6.4 Hz, 2H), 6.44 (s, 1H), 7.40 (t, *J* = 7.7 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.87 (d, *J* = 7.7 Hz, 2H), 8.12 (s, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  21.5, 26.0, 37.2, 115.5, 116.6, 126.2, 129.1, 129.2, 129.5, 149.0, 153.0, 198.5; HRMS

(ES<sup>+</sup>) calcd for C<sub>14</sub>H<sub>14</sub>N<sub>3</sub>O (MH<sup>+</sup>) 240.1131, found 240.1134.

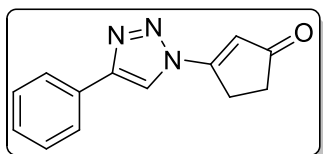
### 3-(4-(4-*tert*-butyl)Phenyl-1*H*-1,2,3-triazol-1-yl)cyclohex-2-enone (3d)



White solid; Yield 42 mg, 70%; mp 148-150 °C; IR (neat,  $\text{cm}^{-1}$ ) 3121 (w), 2953 (m), 1669 (vs), 1621 (s), 1442 (s), 1228 (s);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  1.36 (s, 9H), 2.26 (quint,  $J = 6.5$  Hz, 2H), 2.56 (t,  $J = 6.5$  Hz, 2H), 3.25 (td,  $J = 6.5, 1.3$  Hz, 2H), 6.43 (t,  $J = 1.3$  Hz, 1H), 7.49 (d,  $J = 8.5$  Hz, 2H), 7.80 (d,  $J = 8.5$  Hz, 2H), 8.08 (s, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  21.5, 25.9, 31.4, 34.9, 37.1, 115.3, 116.2, 125.9, 126.1, 126.6, 149.0, 152.4, 153.0, 198.6; HRMS (ES+) calcd for  $\text{C}_{18}\text{H}_{21}\text{N}_3\text{O}$

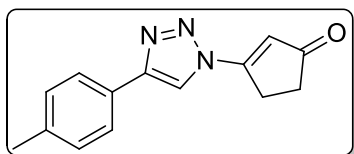
( $\text{MK}^+$ ) 334.1316, found 334.1314.

### 3-(4-Phenyl-1*H*-1,2,3-triazol-1-yl)cyclopent-2-enone (3e)



White solid; Yield 24 mg, 55%; mp 168-170 °C; IR (neat,  $\text{cm}^{-1}$ ) 3133 (vw), 2929 (w), 1664 (vs), 1622 (vs), 1579 (vs), 1462 (m), 1432 (m), 1188 (m), 1023 (m), 852 (m), 765 (s), 693 (m);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.71-2.74 (m, 2H), 3.39-3.42 (m, 2H), 6.42 (s, 1H), 7.42 (t,  $J = 7.4$  Hz, 1H), 7.48 (t,  $J = 7.4$  Hz, 2H), 7.90 (d,  $J = 7.4$  Hz, 2H), 8.13 (s, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  27.1, 34.6, 117.5, 117.7, 126.3, 129.2, 129.3, 129.4, 149.5, 164.6, 205.0; HRMS (ES+) calcd for  $\text{C}_{13}\text{H}_{12}\text{N}_3\text{O}$  ( $\text{MNa}^+$ ) 226.0975, found 226.0975; Selected X-ray data (CCDC 2044636):  $\text{C}_{13}\text{H}_{11}\text{N}_3\text{O}$ ,  $M = 225.25$ , Monoclinic, space group  $P2_1/n$ ,  $a = 5.890$ ,  $\text{\AA}$ ,  $b = 24.263$ ,  $\text{\AA}$ ,  $c = 7.661$ ,  $\text{\AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 99.67^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 1079.3$   $\text{\AA}^3$ ,  $D_x = 1.386$   $\text{Mg m}^{-3}$ ,  $Z = 4$ ,  $F(000) = 472.0$ ,  $\lambda = 0.71073$   $\text{\AA}$ ,  $\mu = 0.092$   $\text{cm}^{-1}$ , total/unique = 1881/1881 [ $R(\text{int}) = 0.0876$ ],  $T = 293(2)$  K,  $\theta$  range =  $\theta_{\text{max}} = 24.996^\circ$ ,  $\theta_{\text{min}} = 3.117^\circ$ , final  $R[I > 2\sigma(I)]$ :  $R_1 = 0.0511$ ,  $wR_2 = 0.1082$ ,  $R(\text{all data})$ :  $R_1 = 0.1056$ ,  $wR_2 = 0.1493$ .

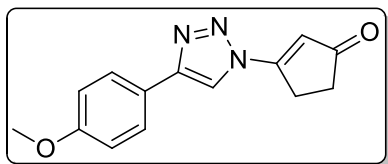
### 3-(4-(*p*-tolyl-1*H*-1,2,3-triazol-1-yl)cyclopent-2-enone (3f)



White solid; Yield 34 mg, 71%; mp 183-185 °C; IR (neat,  $\text{cm}^{-1}$ ) 2922 (w), 2854 (vw), 1717 (s), 1697 (m), 1621 (m), 1219 (w), 1049 (m), 750 (vs);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.41 (s, 3H), 2.70-2.73 (m, 2H), 3.39-3.41 (m, 2H), 6.40 (s, 1H), 7.28 (d,  $J = 7.9$  Hz, 2H), 7.79 (d,  $J = 7.9$  Hz, 2H), 8.08 (s, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  21.5, 27.1, 34.6, 117.3, 117.4,

126.2, 126.3, 129.9, 139.4, 149.5, 164.6, 205.0; HRMS (ES+) calcd for  $\text{C}_{14}\text{H}_{13}\text{NONa}$  ( $[\text{M}-\text{N}_2]\text{Na}^+$ ) 234.0889, found 234.0884.

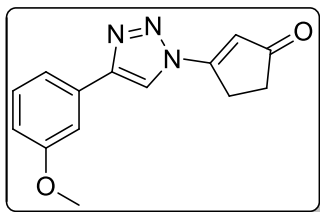
### 3-(4-Methoxy phenyl-1*H*-1,2,3-triazol-1-yl)cyclopent-2-enone (3g)



Whitesolid; Yield 32 mg, 61%; mp 168-170 °C; IR (neat,  $\text{cm}^{-1}$ ) 2922 (m), 2855 (w), 1716 (w), 1624 (vvs), 1262 (w), 1030 (m), 849 (w), 765 (w);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  2.70-2.72 (m, 2H), 3.38-3.40 (m, 2H), 3.86 (s, 3H), 6.39 (s, 1H), 6.99 (d,  $J = 8.8$  Hz, 2H), 7.82 (d,  $J = 8.8$  Hz, 2H), 8.03 (s, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  27.1, 34.6, 55.6, 114.7, 116.7, 117.3, 121.8, 127.7, 149.4, 160.6, 164.7, 205.1; HRMS

(ES+) calcd for  $\text{C}_{14}\text{H}_{14}\text{NO}_2$  ( $[\text{M}-\text{N}_2]\text{H}^+$ ) 228.1019, found 228.1015.

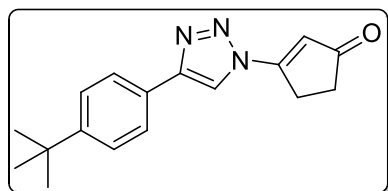
### 3-(3-Methoxy phenyl-1H-1,2,3-triazol-1-yl)cyclopent-2-enone (3h)



White solid; Yield 20 mg, 38%; mp 168-170 °C; IR (neat,  $\text{cm}^{-1}$ ) 3131 (w), 2931(w), 1710 (vs), 1623 (s), 1584 (m), 1436 (m), 1256 (m), 1044 (m), 1017 (s), 787 (m);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  2.70-2.72 (m, 2H), 3.37-3.39 (m, 2H), 3.88 (s, 3H), 6.42 (s, 1H), 6.95 (dd,  $J = 7.9, 2.1$  Hz, 1H), 7.37 (t,  $J = 7.9$  Hz, 1H), 7.42 (d,  $J = 7.9$  Hz, 1H), 7.40 (d,  $J = 2.1$  Hz, 1H), 8.12 (s, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  27.1, 34.6, 55.6, 111.5, 115.2, 117.6, 117.9, 118.6, 130.3, 130.4, 149.3, 160.3, 164.5, 205.0; HRMS (ES<sup>+</sup>)

calcd for  $\text{C}_{14}\text{H}_{14}\text{N}_3\text{O}_2$  ( $\text{MH}^+$ ) 256.1081, found 256.1085.

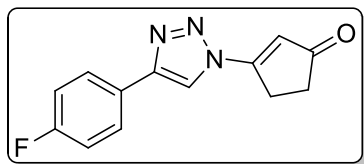
### 3-(4-(4-*tert*-butyl)Phenyl)-1H-1,2,3-triazol-1-yl)cyclopent-2-enone (3i)



White solid; Yield 30 mg, 53%; mp 233-235 °C; IR (neat,  $\text{cm}^{-1}$ ) 3115 (m), 3086 (w), 2959 (s), 1715 (s), 1697 (m), 1621 (vs), 1434 (s), 1028 (m), 809 (w);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  1.36 (s, 9H), 2.70-2.72 (m, 2H), 3.39-3.41 (m, 2H), 6.41 (s, 1H), 7.50 (d,  $J = 8.3$  Hz, 2H), 7.82 (d,  $J = 8.3$  Hz, 2H), 8.09 (s, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  27.1, 31.4, 34.6, 35.0, 117.3, 117.4, 126.1, 126.2, 126.3, 149.5, 152.7, 164.6, 205.1;

HRMS (ES<sup>+</sup>) calcd for  $\text{C}_{17}\text{H}_{19}\text{N}_3\text{O}$  ( $[\text{M}-\text{N}_2]\text{Na}^+$ ) 276.1359, found 276.1358.

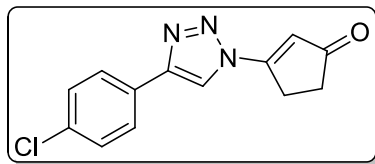
### 3-(4-(4-Fluorophenyl)-1H-1,2,3-triazol-1-yl)cyclopent-2-enone (3j)



White solid; Yield 32 mg, 67%; mp 173-175 °C; IR (neat,  $\text{cm}^{-1}$ ) 3114 (w), 1713 (vs), 1698 (vs), 1620 (vs), 1459 (m), 1444 (m), 1239 (s), 1218 (s), 859 (s), 838 (s), 807 (s);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.69-2.72 (m, 2H), 3.37-3.39 (m, 2H), 6.41 (s, 1H), 7.15 (t,  $J = 8.6$  Hz, 2H), 7.86 (dd,  $J = 8.6, 5.3$  Hz, 2H), 8.12 (s, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  27.1,

34.6, 116.3 (d,  $J = 22.5$  Hz), 117.5, 117.6, 125.4, 128.1 (d,  $J = 7.5$  Hz), 148.5, 163.4 (d,  $J = 248.8$  Hz), 164.5, 205.0;  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -111.7; HRMS (ES<sup>+</sup>) calcd for  $\text{C}_{13}\text{H}_{11}\text{FN}_3\text{O}$  ( $\text{MH}^+$ ) 244.0881, found 244.0883.

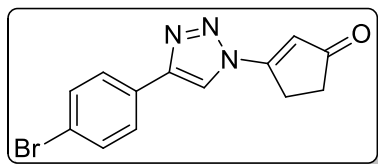
### 3-(4-(4-Chlorophenyl)-1H-1,2,3-triazol-1-yl)cyclopent-2-enone (3k)



White solid; Yield 38 mg, 52%; mp 184-186 °C; IR (neat,  $\text{cm}^{-1}$ ) 2933 (w), 1713 (m), 1689 (w), 1616 (vs), 1455 (m), 1431 (m), 1236 (m), 1216 (m), 1022 (s), 812 (m), 742 (vs);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  2.71-2.73 (m, 2H), 3.38-3.40 (m, 2H), 6.42 (t,  $J = 1.6$  Hz, 1H), 7.45 (d,  $J = 8.5$  Hz, 2H), 7.83 (d,  $J = 8.5$  Hz, 2H), 8.12 (s, 1H);  $^{13}\text{C}$  NMR (125 MHz,

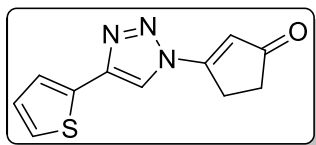
$\text{CDCl}_3$ )  $\delta$  27.1, 34.6, 117.7, 117.8, 127.5, 127.7, 129.5, 135.3, 148.4, 164.4, 204.9; HRMS (ES<sup>+</sup>) calcd for  $\text{C}_{13}\text{H}_{10}\text{ClN}_3\text{O}$  ( $\text{MNa}^+$ ) 282.0405, found 282.0399.

### 3-(4-(4-Bromophenyl)-1H-1,2,3-triazol-1-yl)cyclopent-2-enone (3l)



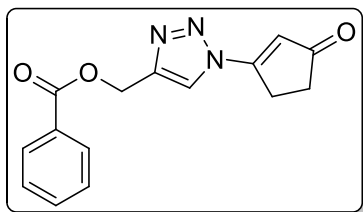
White solid; Yield 34mg, 54%; mp 205-207 °C; IR (neat,  $\text{cm}^{-1}$ ) 2930 (vw), 1708 (vvs), 1693 (vvs), 1622 (vs), 1451 (vs), 1430 (vs), 1237 (m), 1215 (m), 1184 (m), 1072 (vw), 1024 (s), 1015 (s), 807 (m);  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-d}_6$ )  $\delta$  2.59-2.61 (unresolved m, 2H), 3.26-3.28 (unresolved m, 2H), 6.61 (s, 1H), 7.70 (d,  $J = 6.4$  Hz, 2H), 7.85 (d,  $J = 6.4$  Hz, 2H), 9.31 (s, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO}$ )  $\delta$  26.5, 34.3, 117.4, 120.8, 121.8, 127.5, 128.6, 132.1, 146.7, 164.9, 205.2; HRMS ( $\text{ES}^+$ ) calcd for  $\text{C}_{13}\text{H}_{11}\text{BrN}_3\text{O}$  ( $\text{MH}^+$ ) 304.0080, found 304.0083.

### 3-(4-(Thiophen-2-yl)-1H-1,2,3-triazol-1-yl)cyclopent-2-enone (3m)



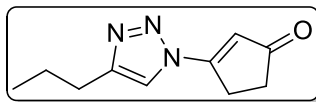
White solid; Yield 34 mg, 75%; mp 205-207 °C; IR (neat,  $\text{cm}^{-1}$ ) 3150 (w), 3044 (w), 2936 (w), 1718 (s), 1692 (vs), 1618 (vs), 1454 (s), 1430 (s), 1265 (m), 1205 (m), 1183 (m), 1040 (s), 860 (m), 801 (s), 743 (vvs);  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-d}_6$ )  $\delta$  1.74-1.76 (m, 2H), 2.43-2.45 (m, 2H), 5.80 (s, 1H), 6.36 (dd,  $J = 4.5, 3.0$  Hz, 1H), 6.70 (d,  $J = 3.0$  Hz, 1H), 6.81 (d,  $J = 4.5$  Hz, 1H), 8.36 (s, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO}$ )  $\delta$  26.5, 34.3, 117.4, 119.5, 125.3, 126.7, 128.2, 131.3, 143.2, 164.9, 205.3; HRMS ( $\text{ES}^+$ ) calcd for  $\text{C}_{11}\text{H}_{10}\text{N}_3\text{OS}$  ( $\text{MH}^+$ ) 232.0539.

### (1-(3-Oxocyclopent-1-en-1-yl)-1H-1,2,3-triazol-4-yl)methyl benzoate (3n)



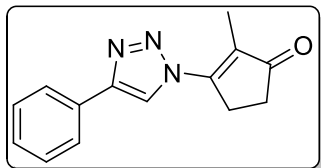
White solid; Yield 46 mg, 82%; mp 128-130 °C; IR (neat,  $\text{cm}^{-1}$ ) 3107 (w), 3085 (w), 2929 (w), 1709 (vs), 1620 (m), 1599 (m), 1453 (m), 1267 (s), 1243 (m), 716 (s);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  2.68-2.70 (m, 2H), 3.32-3.35 (m, 2H), 5.54 (s, 2H), 6.42 (t,  $J = 1.6$  Hz, 1H), 7.44 (t,  $J = 7.8$  Hz, 2H), 7.58 (t,  $J = 7.8$  Hz, 1H), 8.05 (d,  $J = 7.8$  Hz, 2H), 8.09 (s, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  27.1, 34.6, 57.7, 118.1, 122.9, 128.7, 129.5, 129.9, 133.6, 144.8, 164.3, 166.6, 204.8; HRMS ( $\text{ES}^+$ ) calcd for  $\text{C}_{15}\text{H}_{13}\text{N}_3\text{O}_3\text{Na}$  ( $\text{MNa}^+$ ) 306.0849, found 306.0849.

### 3-(4-Propyl-1H-1,2,3-triazol-1-yl)cyclopent-2-enone (3o)



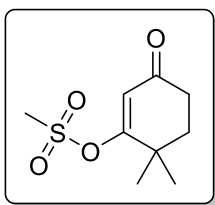
White solid; Yield 20 mg, 52%; mp 101-103 °C; IR (neat,  $\text{cm}^{-1}$ ) 3128 (w), 3077 (w), 2959 (m), 2934 (m), 2874 (w), 1714 (vs), 1698 (vs), 1621 (vs), 1457 (s), 1431 (m), 1189 (s), 1045 (s), 868 (s);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  1.00 (t,  $J = 7.5$  Hz, 3H), 1.74 (sext,  $J = 7.5$  Hz, 2H), 2.66-2.68 (m, 2H), 2.76 (t,  $J = 7.5$  Hz, 2H), 3.32-3.35 (m, 2H), 6.31 (d,  $J = 1.3$  Hz, 1H), 7.67 (s, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  13.9, 22.5, 27.0, 27.6, 34.5, 116.9, 119.4, 150.3, 164.9, 205.2; HRMS ( $\text{ES}^+$ ) calcd for  $\text{C}_{10}\text{H}_{14}\text{N}_3\text{O}$  ( $\text{MH}^+$ ) 192.1131, found 192.1129.

## 2- Methyl-3-(4-phenyl-1*H*-1,2,3-triazol-1-yl)cyclopent-2-enone (3p)



White solid; Yield 26 mg, 55%; mp 179-180 °C; IR (neat,  $\text{cm}^{-1}$ ) 3140 (m), 2929 (m), 1703 (vs), 1645 (vvs), 1455 (m), 1436 (s), 1301 (m), 1240 (m), 1012 (m), 767 (vs), 696 (m);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.18 (t,  $J = 2.0$  Hz, 3H), 2.69-2.72 (m, 2H), 3.23-3.28 (m, 2H), 7.40 (t,  $J = 7.2$  Hz, 1H), 7.48 (t,  $J = 7.2$  Hz, 2H), 7.91 (d,  $J = 7.2$  Hz, 2H), 8.16 (s, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  9.7, 26.6, 33.4, 118.2, 126.1, 127.3, 129.1, 129.2, 129.4, 148.5, 157.1, 206.0; HRMS (ES+) calcd for  $\text{C}_{14}\text{H}_{14}\text{N}_3\text{O}$  ( $\text{MH}^+$ ) 240.1131, found 240.1130.

## 2- Methyl-3-(4-phenyl-1*H*-1,2,3-triazol-1-yl)cyclopent-2-enone (4a)



Colourless liquid; Yield 20 mg, 45%; IR (neat,  $\text{cm}^{-1}$ ) 3019 (w), 2962 (vs), 2873 (m), 1666 (vs), 1614 (vs), 1469 (m), 1371 (vs), 1355 (vs), 1095 (m), 734 (m), 538 (m);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  2.08 (s, 6H), 2.25 (s, 2H), 3.45 (d,  $J = 0.9$  Hz, 2H), 3.19 (s, 3H), 6.02 (br s, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  32.4, 32.6, 38.6, 41.2, 41.9, 50.1, 114.7, 166.1, 198.3; HRMS (ES+) calcd for  $\text{C}_9\text{H}_{14}\text{O}_4\text{S}$  ( $\text{MH}^+$ ) 219.0686, found 219.0684.

## References

1. Raushel, J.; Fokin, V. V. *Org. Lett.* **2010**, *12*, 4952-4955. doi.org/10.1021/ol102087r