

KI-Mediated Radical Multi-functionalization of Vinyl Azides: A one-pot and efficient approach to β -keto sulfones and α -halo- β -keto sulfones

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Supporting Information

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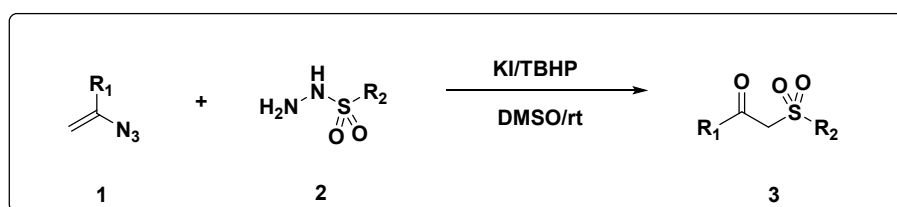
General Information:

All solvents were purified according to standard methods prior to use. Purifications of reaction products were carried out by chromatography using silica gel (200-300 mesh). Melting points were recorded on a BÜCHI B-540 melting point apparatus. NMR spectra were recorded for ^1H NMR at 500 MHz and for ^{13}C NMR at 125 MHz. For ^1H NMR, tetramethylsilane (TMS) served as internal standard ($\delta=0$) and data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), and coupling constant(s) in Hz. For ^{13}C NMR, TMS ($\delta=0$) or CDCl_3 ($\delta=77.26$) was used as internal standard and spectra were obtained with complete proton decoupling. HPLC analysis and the HRMS of all final products were confirmed on a Agilent 1290 HPLC-6224 Time of Flight Mass Spectrometer using PhenomenexLuna 5μ C18, 100 Å, 150 X 4.60 mm 5 micron column at a flow rate of 0.5 mL/min using liner gradients buffer B in A (B: CH_3OH containing 0.1 % formic acid, A: H_2O containing 0.1% formic acid). Mobile phase B was increased linearly from 5% to 95% over 7 min and 95% over the next 2 min, after which the column was equilibrated to 5% for 1 min. Vinyl azides **1** were readily prepared from the corresponding olefins by successive reaction with bromine then with sodium azide. ^[1]

Reference:

1. T. L. Gilchrist, R. Mendonca, *ARKIVOC* **2000**, 769.

General Procedure for the Synthesis of **3**:

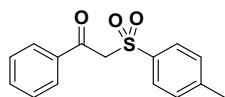


A mixture of vinyl azide **1** (1.0 mmol), sulfonohydrazide **2** (2.0 mmol, 2.0 equiv.) KI (0.4 mmol, 0.4 equiv.) and TBHP (4.0 mmol, 70% in water) was stirred in DMSO (2.0 mL) at room temperature (25 °C) for 6.0-8.0 h. The reaction mixture was quenched with water (10 mL), and then extracted three times with EtOAc. The

combined organic extracts were washed with brine, dried over MgSO_4 and concentrated. Purification of the crude product by chromatography to afford **3a-3k**.

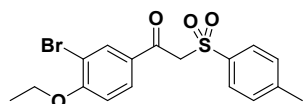
Characterization data of compound 3

1-Phenyl-2-tosylethan-1-one (**3a**)



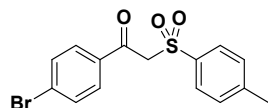
Light yellow solid, m.p. 98.1-99.2 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.98 (d, $J = 7.5$ Hz, 2H), 7.79 (d, $J = 8.5$ Hz, 2H), 7.65 (t, $J = 7.5$ Hz, 1H), 7.51 (t, $J = 7.5$ Hz, 2H), 7.36 (d, $J = 8.0$ Hz, 2H), 4.74 (s, 2H), 2.47 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 188.3, 145.5, 136.0, 134.5, 130.0, 129.5, 129.0, 128.8, 63.8, 21.8. HRMS (ESI): m/z calcd for $(\text{C}_{15}\text{H}_{14}\text{O}_3\text{S}+\text{H})^+$: 275.0736; found: 275.0740.

1-(3-Bromo-4-ethoxyphenyl)-2-tosylethan-1-one (**3b**)



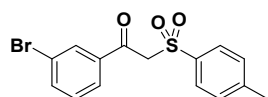
Light yellow solid, m.p. 97.2-98.2 °C, ^1H NMR (500 MHz, CDCl_3) δ 8.09 (d, $J = 2.5$ Hz, 1H), 7.93 (dd, $J = 8.5, 2.5$ Hz, 1H), 7.76-7.72 (m, 2H), 7.34 (d, $J = 8.0$ Hz, 2H), 6.92 (d, $J = 8.5$ Hz, 1H), 4.63 (s, 2H), 4.20 (q, $J = 7.0$ Hz, 2H), 2.45 (s, 3H), 1.52 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 185.6, 160.3, 145.6, 135.8, 134.8, 131.2, 130.0, 129.7, 128.7, 112.8, 112.0, 65.4, 63.7, 21.8, 14.6. HRMS (ESI): m/z calcd for $(\text{C}_{17}\text{H}_{17}\text{BrO}_4\text{S}+\text{H})^+$: 397.0104; found: 397.0108.

1-(4-Bromophenyl)-2-tosylethan-1-one (**3c**)



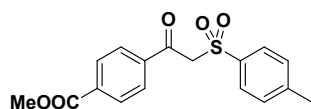
White solid, m.p. 141.2-141.8 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.98 (d, $J = 7.5$ Hz, 2H), 7.79 (d, $J = 8.5$ Hz, 2H), 7.65 (t, $J = 7.5$ Hz, 1H), 7.51 (t, $J = 7.5$ Hz, 2H), 7.36 (d, $J = 8.0$ Hz, 2H), 4.67 (s, 2H), 2.45 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 187.4, 145.7, 135.7, 134.6, 132.4, 131.0, 130.1, 130.0, 128.7, 63.9, 21.9. HRMS (ESI): m/z calcd for $(\text{C}_{15}\text{H}_{13}\text{BrO}_3\text{S}+\text{H})^+$: 352.9842; found: 352.9847.

1-(3-Bromophenyl)-2-tosylethan-1-one (**3d**)



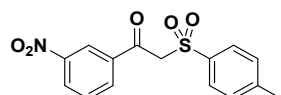
White solid, m.p. 140.2-141.3 °C, ¹H NMR (500 MHz, CDCl₃) δ 8.02 (s, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.77-7.76 (m, 3H), 7.41-7.36 (m, 3H), 4.69 (s, 2H), 2.47 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 187.1, 145.8, 137.5, 137.3, 135.6, 132.2, 130.5, 130.1, 128.7, 128.2, 123.3, 63.8, 21.9. HRMS (ESI): *m/z* calcd for (C₁₅H₁₄BrO₃S+H)⁺: 352.9842; found: 352.9850.

Methyl 4-(2-tosylacetyl) benzoate (**3e**)



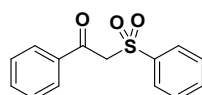
White solid, m.p. 95.2-95.5 °C, ¹H NMR (500 MHz, CDCl₃) δ 8.14-8.12 (m, 2H), 8.02-8.00 (m, 2H), 7.75 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 4.74 (s, 2H), 3.96 (s, 3H), 2.45 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 188.0, 166.0, 145.7, 138.9, 135.8, 135.0, 130.1, 130.0, 129.4, 128.7, 64.0, 62.7, 21.8. HRMS (ESI): *m/z* calcd for (C₁₇H₁₇O₅S+H)⁺: 333.0791; found: 333.0795.

1-(3-Nitrophenyl)-2-tosylethan-1-one (**3f**)



Light yellow solid, m.p. 127.1-127.8 °C, ¹H NMR (500 MHz, CDCl₃) δ 8.73 (t, *J* = 2.0 Hz, 1H), 8.48-8.46 (m, 1H), 8.35-8.33 (m, 1H), 7.76-7.72 (m, 3H), 7.36 (d, *J* = 8.0 Hz, 2H), 4.77 (s, 2H), 2.46 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 186.5, 148.6, 146.0, 137.0, 135.5, 135.0, 130.3, 130.2, 128.6, 128.5, 124.3, 64.0, 21.8. HRMS (ESI): *m/z* calcd for (C₁₅H₁₄NO₅S+H)⁺: 320.0587; found: 320.0594.

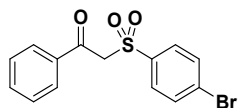
1-Phenyl-2-(phenylsulfonyl) ethan-1-one (**3g**)



White solid, m.p. 121.5-123.1 °C, ¹H NMR (500 MHz, CDCl₃) δ 7.94 (d, *J* = 7.5 Hz, 2H), 7.90 (d, *J* = 7.5 Hz, 2H), 7.68-7.65 (m, 1H), 7.64-7.61 (m, 1H), 7.55 (t, *J* = 8.0 Hz, 2H), 7.48 (t, *J* = 8.0 Hz, 2H), 4.74 (s, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 188.1,

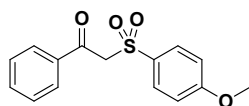
138.9, 135.9, 134.5, 134.4, 129.4, 129.3, 129.0, 128.7, 63.6, 29.8. HRMS (ESI): m/z calcd for $(C_{14}H_{13}O_3S+H)^+$: 261.0580; found: 261.0587.

2-((4-Bromophenyl) sulfonyl)-1-phenylethan-1-one (**3h**)



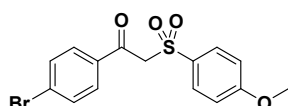
Light yellow solid, m.p. 113.2-114.2 °C, 1H NMR (500 MHz, $CDCl_3$) δ 7.95-7.93 (m, 2H), 7.77-7.75(m, 2H), 7.71-7.69 (m, 2H), 7.66-7.63 (m, 1H), 7.52-7.49 (m, 2H), 4.74 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.0, 137.9, 135.8, 134.7, 132.7, 130.4, 129.9, 129.4, 129.1, 63.5. HRMS (ESI): m/z calcd for $(C_{14}H_{12}BrO_3S+H)^+$: 338.9685; found: 338.9690.

2-((4-Methoxyphenyl) sulfonyl)-1-phenylethan-1-one (**3i**)



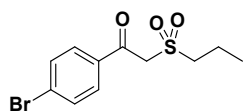
White solid, m.p. 105.2-106.3 °C, 1H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, $J = 7.5$ Hz, 2H), 7.80 (d, $J = 8.5$ Hz, 2H), 7.62 (t, $J = 7.5$ Hz, 1H), 7.48 (t, $J = 7.5$ Hz, 2H), 6.98 (d, $J = 8.5$ Hz, 2H), 4.71 (s, 2H), 3.87 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.4, 164.3, 136.0, 134.4, 131.0, 130.4, 129.5, 128.9, 114.5, 63.9, 55.8. HRMS (ESI): m/z calcd for $(C_{15}H_{15}O_4S+H)^+$: 291.0686; found: 291.0687.

1-(4-Bromophenyl)-2-((4-methoxyphenyl) sulfonyl) ethan-1-one (**3j**)



Light yellow solid, m.p. 135.2-136.7 °C, 1H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, $J = 8.5$ Hz, 2H), 7.77 (d, $J = 8.5$ Hz, 2H), 7.63 (d, $J = 8.5$ Hz, 2H), 6.99 (d, $J = 8.5$ Hz, 2H), 4.67 (s, 2H), 3.88 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 187.6, 164.4, 134.7, 132.4, 131.0, 130.1, 130.0, 114.6, 64.1, 55.9. HRMS (ESI): m/z calcd for $(C_{15}H_{14}BrO_4S+H)^+$: 368.9791; found: 368.9797.

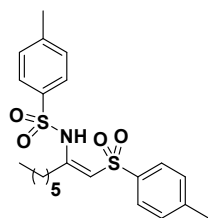
1-(4-Bromophenyl)-2-(propylsulfonyl) ethan-1-one (**3k**)



Light yellow solid, m.p.: 83.2-84.4 °C, ¹H NMR (500 MHz, CDCl₃) δ 7.88 (d, *J* = 9.0 Hz, 2H), 7.67 (d, *J* = 9.0 Hz, 2H), 4.52 (s, 2H), 3.22-3.19 (m, 2H), 1.99-1.88 (m, 2H), 1.11 (t, *J* = 7.5 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 188.5, 134.6, 132.5, 130.9, 130.5, 59.8, 55.4, 15.9, 13.2. HRMS (ESI): *m/z* calcd for (C₁₁H₁₄BrO₃S+H)⁺: 304.9842; found: 304.9838.

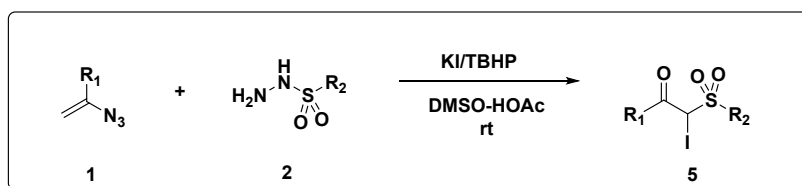
Characterization data of compound 4

(*Z*)-4-methyl-N-(1-tosyloct-1-en-2-yl)benzenesulfonamide (**4**)



Light yellow solid, m.p.: 93.2-94.6 °C, ¹H NMR (500 MHz, CDCl₃) δ 8.98 (s, 1H), 7.93 (d, *J* = 8.0 Hz, 2H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.31-7.26 (m, 4H), 5.48 (s, 1H), 2.67- 2.64 (m, 2H), 2.41 (d, *J* = 7.0 Hz, 6H), 1.40-1.35 (m, 2H), 1.25-1.12 (m, 6H), 0.85 (t, *J* = 7.0 Hz, 3H).

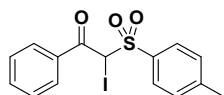
General Procedure for the Synthesis of 5:



A mixture of vinyl azide **1** (1.0 mmol), sulfonohydrazide **2** (2.0 mmol, 2.0 equiv.) KI (1.5 mmol, 1.5 equiv.) and TBHP (4.0 mmol, 70% in water) was stirred in DMSO-HOAc (2.0 mL, V: V=1:1) at room temperature (25 °C) for 8.0 h. The reaction mixture was quenched with water (10 mL), and then extracted three times with EtOAc. The combined organic extracts were washed with brine, dried over MgSO₄ and concentrated. Purification of the crude product by chromatography to afford **5a-5j**.

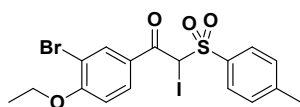
Characterization data of compound 5

2-Iodo-1-phenyl-2-tosylethan-1-one (**5a**)



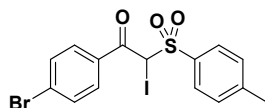
White solid, m.p. 168.2-169.3 °C, ¹H NMR (500 MHz, CDCl₃) δ 7.90 (dd, *J* = 12.5, 8.0 Hz, 4H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 6.52 (s, 1H), 2.45 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 188.4, 146.3, 134.6, 133.8, 132.3, 131.1, 129.7, 129.3, 129.1, 38.0, 21.9. HRMS (ESI): *m/z* calcd for (C₁₅H₁₃IO₃S+H)⁺: 400.9703; found: 400.9703.

1-(3-Bromo-4-ethoxyphenyl)-2-iodo-2-tosylethan-1-one (**5b**)



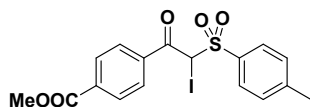
Pale white solid, m.p. 172.2-173.4 °C, ¹H NMR (500 MHz, CDCl₃) δ 8.08 (d, *J* = 2.0 Hz, 1H), 7.90 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 8.5 Hz, 1H), 6.42 (s, 1H), 4.19 (q, *J* = 7.0 Hz, 2H), 2.45 (s, 3H), 1.51 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 185.7, 160.4, 146.3, 134.8, 132.2, 131.0, 130.9, 129.7, 128.7, 127.1, 112.9, 112.1, 65.5, 38.2, 21.9, 14.6. HRMS (ESI): *m/z* calcd for (C₁₇H₁₆BrIO₄S+H)⁺: 522.9070; found: 522.9074.

1-(3-Bromo-4-ethoxyphenyl)-2-iodo-2-tosylethan-1-one (**5c**)



Pale white solid, m.p. 147.3-148.2 °C, ¹H NMR (500 MHz, DMSO) δ 7.89-7.88 (m, 2H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.73-7.71 (m, 2H), 7.45 (s, 1H), 7.41 (d, *J* = 8.0 Hz, 2H), 2.38 (s, 2H). ¹³C NMR (125 MHz, DMSO) δ 189.0, 145.2, 133.1, 132.5, 132.0, 130.8, 129.6, 129.5, 128.8, 39.2, 21.2. HRMS (ESI): *m/z* calcd for (C₁₅H₁₂BrIO₃S+H)⁺: 478.8808; found: 478.8809.

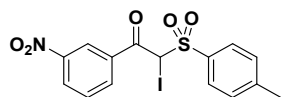
Methyl 4-(2-iodo-2-tosylacetyl) benzoate (**5d**)



Pale white solid, m.p. 125.2-126.3 °C, ¹H NMR (500 MHz, CDCl₃) δ 8.12 (d, *J* = 8.0 Hz, 2H), 7.97 (d, *J* = 8.5 Hz, 2H), 7.88 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 2H),

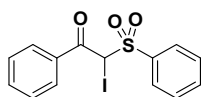
6.48 (s, 1H), 3.96 (s, 3H), 2.46 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 188.1, 165.9, 146.5, 137.0, 135.2, 132.2, 131.1, 130.2, 129.7, 129.3, 52.8, 38.1, 21.9. HRMS (ESI): m/z calcd for (C₁₇H₁₅IO₅S+H)⁺: 458.9758; found: 458.9760.

2-Iodo-1-(3-nitrophenyl)-2-tosylethan-1-one (**5e**)



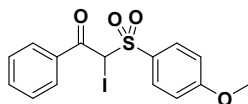
Yellow solid, m.p. 148.2-149.3 °C, ¹H NMR (500 MHz, CDCl₃) δ 8.73 (s, 1H), 8.48 (d, *J* = 8.0 Hz, 2H), 8.32 (d, *J* = 8.0 Hz, 2H), 7.88 (d, *J* = 8.0 Hz, 2H), 7.72 (t, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 6.48 (s, 1H), 2.47 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 186.6, 148.7, 146.8, 135.1, 134.9, 132.2, 131.0, 130.4, 129.9, 128.6, 124.3, 38.1, 21.9. HRMS (ESI): m/z calcd for (C₁₅H₁₂INO₅S+H)⁺: 445.9554; found: 445.9558.

2-Iodo-1-phenyl-2-(phenylsulfonyl) ethan-1-one (**5f**)



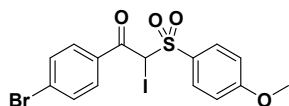
White solid, m.p. 136.2-137.4 °C, ¹H NMR (500 MHz, CDCl₃) δ 8.02 (d, *J* = 8.0 Hz, 2H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.68 (t, *J* = 2.5 Hz, 1H), 7.62 (d, *J* = 2.5 Hz, 1H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 8.0 Hz, 1H), 6.53 (s, 1H). ¹³C NMR (125 MHz, CDCl₃) δ 188.3, 135.3, 135.0, 134.8, 133.6, 131.0, 129.3, 129.2, 129.0, 37.6. HRMS (ESI): m/z calcd for (C₁₄H₁₂IO₃S+H)⁺: 386.9546; found: 386.9553.

2-Iodo-2-((4-methoxyphenyl) sulfonyl)-1-phenylethan-1-one (**5g**)



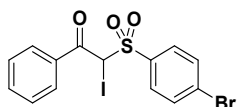
White solid, m.p. 132.1-133.3 °C, ¹H NMR (500 MHz, DMSO) δ 7.96 (d, *J* = 7.5 Hz, 2H), 7.88 (d, *J* = 8.5 Hz, 2H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.42 (s, 1H), 7.12-7.11 (m, 2H), 3.82 (s, 3H). ¹³C NMR (125 MHz, DMSO) δ 189.6, 163.7, 134.3, 133.5, 132.1, 128.9, 128.8, 127.3, 114.2, 55.8, 39.3. HRMS (ESI): m/z calcd for (C₁₅H₁₄IO₄S+H)⁺: 416.9652; found: 416.9659.

1-(4-Bromophenyl)-2-iodo-2-((4-methoxyphenyl) sulfonyl) ethan-1-one (**5h**)



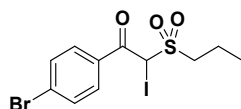
Yellow solid, m.p. 156.2-157.4 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.95-7.89 (m, 2H), 7.80 (d, $J = 8.5$ Hz, 2H), 7.64-7.61 (m, 2H), 7.05 -6.98 (m, 2H), 6.44 (s, 1H), 3.89 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 187.7, 164.9, 133.4, 132.5, 132.4, 130.8, 130.3, 126.3, 114.3, 55.9, 38.2. HRMS (ESI): m/z calcd for $(\text{C}_{15}\text{H}_{13}\text{BrIO}_4\text{S}+\text{H})^+$: 494.8757; found: 494.8763.

2-((4-Bromophenyl) sulfonyl)-2-iodo-1-phenylethan-1-one (**5i**)



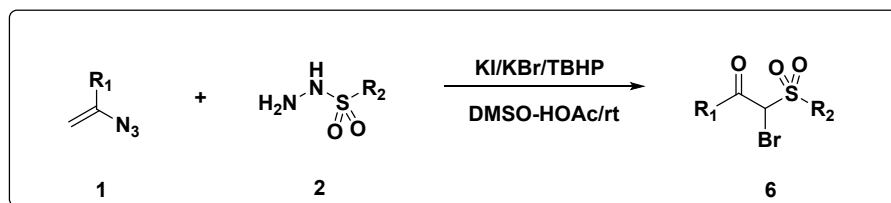
Light yellow solid, m.p. 131.2-132.4 °C, ^1H NMR (500 MHz, DMSO) δ 7.96 (d, $J = 7.5$ Hz, 2H), 7.90-7.85 (m, 4H), 7.66 (t, $J = 7.5$ Hz, 1H), 7.53 (s, 1H), 7.49 (d, $J = 7.5$ Hz, 2H). ^{13}C NMR (125 MHz, DMSO) δ 189.1, 138.8, 135.6, 134.3, 132.3, 130.2, 129.0, 128.8, 128.2, 39.4. HRMS (ESI): m/z calcd for $(\text{C}_{14}\text{H}_{11}\text{BrIO}_3\text{S}+\text{H})^+$: 464.8651; found: 464.8655.

1-(4-Bromophenyl)-2-iodo-2-(propylsulfonyl) ethan-1-one (**5j**)



White solid, 118.2-119.3 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.84 (d, $J = 8.5$ Hz, 2H), 7.66 (d, $J = 8.5$ Hz, 2H), 6.31 (s, 1H), 3.72-3.50 (m, 2H), 2.04-1.89 (m, 2H), 1.14 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 188.5, 132.7, 132.0, 130.8, 130.7, 52.3, 33.6, 15.2, 13.3. HRMS (ESI): m/z calcd for $(\text{C}_{11}\text{H}_{12}\text{BrIO}_3\text{S}+\text{H})^+$: 430.8808; found: 430.8809.

General Procedure for the Synthesis of 6:

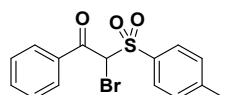


A mixture of vinyl azide **1** (1.0 mmol), sulfonylhydrazide **2** (2.0 mmol, 2.0 equiv.), KI (0.4 mmol, 0.4 equiv.), KBr (1.0 mmol, 1.0 equiv.) and TBHP (4.0 mmol, 70% in

water) was stirred in DMSO (2.0 mL) at room temperature (25 °C) for 6.0-8.0 h. The reaction mixture was quenched with water (10 mL), and then extracted three times with EtOAc. The combined organic extracts were washed with brine, dried over MgSO₄ and concentrated. Purification of the crude product by chromatography to afford **6a-6h**.

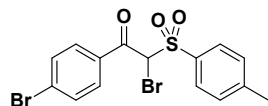
Characterization data of compound 6

2-Bromo-1-phenyl-2-tosylethan-1-one (**6a**)



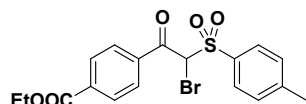
White solid, m.p. 149.2-150.0 °C, ¹H NMR (500 MHz, CDCl₃) δ 8.00 (d, *J* = 7.0 Hz, 2H), 7.84 (d, *J* = 8.5 Hz, 2H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 6.22 (s, 1H), 2.47 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 186.9, 146.6, 134.8, 131.7, 131.1, 130.5, 129.7, 129.6, 129.1, 60.3, 22.0. HRMS (ESI): *m/z* calcd for (C₁₆H₁₃BrO₅S+H)⁺: 351.9769; found: 352.9850.

2-Bromo-1-(4-bromophenyl)-2-tosylethan-1-one (**6d**)



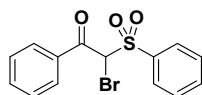
Light yellow solid, m.p. 157.8-159.8 °C, ¹H NMR (500 MHz, CDCl₃) δ 7.91-7.86 (m, 2H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.69-7.64 (m, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 6.13 (s, 1H), 2.48 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 186.0, 146.8, 133.2, 132.5, 131.9, 131.2, 131.0, 130.5, 129.8, 60.7, 22.0. HRMS (ESI): *m/z* calcd for (C₁₅H₁₃Br₂O₃S+H)⁺: 430.8947; found: 430.8954.

Ethyl 4-(2-bromo-2-tosylacetyl)benzoate (**6e**)



White solid, m.p. 127.7-128.7 °C, ¹H NMR (500 MHz, CDCl₃) δ 8.16 (d, *J* = 8.0 Hz, 2H), 8.06 (d, *J* = 8.5 Hz, 2H), 7.83 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 6.20 (s, 1H), 3.96 (s, 3H), 2.47 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 186.6, 165.9, 146.8, 137.6, 135.3, 131.8, 131.0, 130.2, 129.8, 129.6, 60.5, 52.8, 22.0. HRMS (ESI): *m/z* calcd for (C₁₆H₁₃BrO₅S+H)⁺: 409.9824; found: 410.9896.

2-Bromo-1-phenyl-2-(phenylsulfonyl)ethan-1-one (**6f**)



White solid, m.p. 127.2-129.2 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.99 (t, $J = 7.5$ Hz, 4H), 7.73 (t, $J = 7.5$ Hz, 1H), 7.66 (t, $J = 7.5$ Hz, 1H), 7.59 (t, $J = 8.0$ Hz, 2H), 7.52 (t, $J = 8.0$ Hz, 2H), 6.23 (s, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 186.7, 135.2, 134.8, 134.5, 131.1, 129.6, 129.1, 60.1. HRMS (ESI): m/z calcd for $(\text{C}_{16}\text{H}_{13}\text{BrO}_5\text{S}+\text{H})^+$: 337.9612; found: 338.9687.

