

SUPPORTING INFORMATION

NaI-Mediated Acetamidophilic Phenylation of Alkenes with Nitriles as the Nucleophiles: A Direct Access to Acetamidophilic Sulphides

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General Information

General experimental: All reactions were carried out under air condition. Solvents were dried and degassed by standard methods. And alkenes, disulfide, aryl-thiols, nitriles, sodium iodide and the oxidants used in the reaction were obtained from commercial sources and used without further purification. Flash column chromatography was performed using silica gel (300-400 mesh). Analytical thin-layer chromatography was performed using glass plates pre-coated with 200-300 mesh silica gel impregnated with a fluorescent indicator (254 nm). NMR spectra were recorded in CDCl₃ on a Varian Inova-400 NMR spectrometer (400 MHz); chemical shifts were reported in ppm with the solvent or internal TMS signals as reference, and coupling constants (J) were given in Hertz. The peak information was described as: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, comp = composite. Products were characterized by comparison of ¹H NMR, ¹³C NMR and TOF-MS data in the literatures.

General procedure for the acetamidophilenylation reaction of alkenes (1) with phenyl disulfide (2) or aryl thiols and nitriles (3).

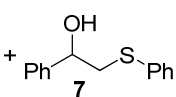
To an oven-dried hermetic tube containing a magnetic stirring bar was added alkenes (1, 0.6 mmol), disulfide (2, 0.15 mmol) or aryl-thiols (0.3 mmol), nitriles (2.0 mL), sodium iodide (0.06 mmol, 9.0 mg), ammonium persulfate (0.6 mmol, 136.9 mg), H₂O (0.6 mmol, 11 μL). The reaction mixture was stirred at 100 °C for 12 hours in a sealed tube. At the end of the reaction, the reaction mixture was cooled to room temperature. After removal of the solvent, the residue was purified by column chromatography on silica gel (eluent: Hexanes:EtOAc = 6:1 to 3:1) to afford the pure products.

Table S1. Optimization of Reaction Conditions for Acetamidosulphenylation^a

entry	cat.	oxidant	T (°C)	yield (%) ^b
1	TBAI	(NH ₄) ₂ S ₂ O ₈	80	48
2	-	(NH ₄) ₂ S ₂ O ₈	80	NR
3	TBAI	-	80	NR
4	TBAF	(NH ₄) ₂ S ₂ O ₈	80	43
5	TBAC	(NH ₄) ₂ S ₂ O ₈	80	trace
6	TBAB	(NH ₄) ₂ S ₂ O ₈	80	trace
7	TMAI	(NH ₄) ₂ S ₂ O ₈	80	46
8	NH ₄ I	(NH ₄) ₂ S ₂ O ₈	80	57
9	NaI	(NH ₄) ₂ S ₂ O ₈	80	61
10	I ₂	(NH ₄) ₂ S ₂ O ₈	80	55
11	NIS	(NH ₄) ₂ S ₂ O ₈	80	60
12	PhI(OAc) ₂	(NH ₄) ₂ S ₂ O ₈	80	NR
13	NaI	K ₂ S ₂ O ₈	80	51
14	NaI	Na ₂ S ₂ O ₈	80	59
15	NaI	TBHP	80	NR
16	NaI	PhI(OAc) ₂	80	NR
17	NaI	BQ	80	NR
18	NaI	PhI(OAc) ₂	80	NR
19	NaI	AgOAc	80	NR
20	NaI	(NH ₄) ₂ S ₂ O ₈	90	76
21	NaI	(NH ₄) ₂ S ₂ O ₈	100	88
22	NaI	(NH ₄) ₂ S ₂ O ₈	110	83
23^c	NaI	(NH₄)₂S₂O₈	100	92 (89)^d

^a Reaction conditions: Styrene (**1a**, 0.6 mmol), diphenyl disulfide (**2a**, 0.15 mmol), acetonitrile (**3a**, 2.0 mL), catalyst (0.06 mmol) and oxidant (0.6 mmol) at indicated temperature for 12 h. ^b Isolated yield based on 0.3 mmol scale. ^c H₂O (0.6 mmol, 11 μL) was added. ^d Thiophenol (0.3 mmol) instead of diphenyl disulfide was used. TBAI = Tetrabutyl ammonium iodide, TBAC = Tetrabutyl ammonium chloride, TBAB = Tetrabutyl ammonium bromide, TMAI = tetramethyl ammonium iodide.

Table S2. TEMPO-Mediated Control Experiments^a

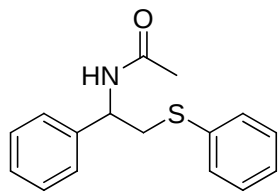
$$\text{1a} + \text{2a} + \text{3a} \xrightarrow[\text{TEMPO}]{\text{NaI, (NH}_4)_2\text{S}_2\text{O}_8, \text{H}_2\text{O, 100 }^\circ\text{C, 12 h}} \text{4a} + \text{7}$$


entry	TEMPO (equiv)	atmosphere	yield of 4a (%)	yield of 7 (%)
1	2.0	air	<5	56
2	2.0	O ₂	<5	58
3	2.0	Ar	20	<5
4 ^b	6.0	air	<5	trace

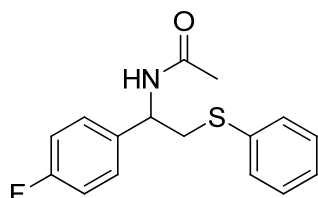
^aReaction conditions: Styrene (**1a**, 0.6 mmol), diphenyl disulfide (**2a**, 0.15 mmol), acetonitrile (**3a**, 2.0 mL), sodium iodide (0.06 mmol, 9.0 mg), ammonium persulfate (0.6 mmol, 136.9 mg), H₂O (0.6 mmol, 11 μ L), 100 $^\circ$ C, 12 h. ^b diphenyl disulfide **2a** was recovered.

To further verify the above proposed mechanism, TEMPO-mediated control experiments were conducted (Table S2). Only trace of **4a** was detected in the presence of 2.0 equivalent of TEMPO under open air condition combined with another product **7** in 56% yield (Table S2, entry 1), which suggested that the radical intermediate should be involved in this transformation. Further investigation indicated that O₂ participated in the formation of **7** (Table S2, entries 1-3), which is consistent with the reported literatures.¹ This result also indicated the existence of radical intermediate **E**, which was generated by the certain excess of ammonium sulfate radical anions **A** and preferred to react with O₂ since **E** could not be further oxidized to **F** with limited amount of **A**.^{1a-d} And the reaction was totally inhibited with 6.0 equivalent of TEMPO with all **2a** was recovered (entry 4), which confirmed that the reaction initiated with the radical intermediate.

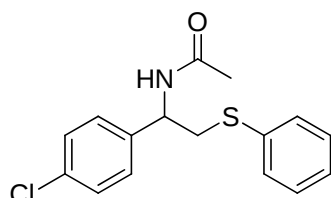
Characterization Data of the Products



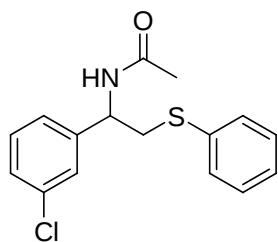
***N*-(1-Phenyl-2-(phenylthio)ethyl)acetamide (4a).**² Yellow Oil; 74.9 mg, 92% yield. ¹H NMR (400 MHz, CDCl₃) (δ, ppm) 7.36-7.33 (m, 2H), 7.32-7.23 (m, 7H), 7.19-7.15 (m, 1H), 6.44 (d, *J* = 7.2 Hz, 1H), 5.18-5.13 (q, *J* = 7.2 Hz, 1H), 3.37-3.32 (m, 1H), 3.28-3.23 (m, 1H), 1.90 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) (δ, ppm) 169.8, 140.5, 135.7, 129.8, 129.1, 128.8, 127.8, 126.7, 126.5, 53.0, 39.8, 23.2. HRMS (TOF MS CI⁺) calculated for C₁₆H₁₈NOS [M+H]⁺: 272.1109, found 272.1112.



***N*-(1-(4-Fluorophenyl)-2-(phenylthio)ethyl)acetamide (4b).** Yellow Solid; m.p. 53-55 °C. 79.7 mg, 92% yield. ¹H NMR (400 MHz, CDCl₃) (δ, ppm) 7.35-7.32 (m, 2H), 7.28-7.24 (m, 2H), 7.23-7.17 (m, 3H), 6.97 (t, *J* = 8.7 Hz, 2H), 6.42 (d, *J* = 7.2 Hz, 1H), 5.13 (q, *J* = 7.1 Hz, 1H), 3.35-3.30 (m, 1H), 3.25-3.20 (m, 1H), 1.92 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) (δ, ppm) 169.3, 161.7 (d, *J* = 244.8 Hz), 135.8 (d, *J* = 3.2 Hz), 134.8, 129.4, 128.7, 127.9 (d, *J* = 8.1 Hz), 126.2, 115.1 (d, *J* = 21.4 Hz), 51.9, 39.4, 22.7; HRMS (TOF MS CI⁺) calculated for C₁₆H₁₇FNOS [M+H]⁺: 290.1015, found 290.1018.

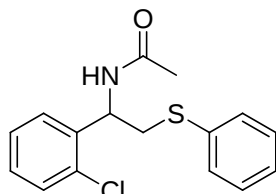


***N*-(1-(4-Chlorophenyl)-2-(phenylthio)ethyl)acetamide (4c).** Yellow Solid; m.p. 94.2-96.4 °C; 86.0 mg, 94% yield. ¹H NMR (400 MHz, CDCl₃) (δ, ppm) 7.35-7.32 (m, 2H), 7.29-7.24 (m, 4H), 7.22-7.19 (m, 1H), 7.18-7.15 (m, 2H), 6.39 (d, *J* = 7.6 Hz, 1H), 5.11 (q, *J* = 7.2 Hz, 1H), 3.33-3.28 (m, 1H), 3.25-3.20 (m, 1H), 1.92 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) (δ, ppm) 169.3, 138.5, 134.7, 133.1, 129.6, 128.7, 128.4, 127.5, 126.3, 52.0, 39.3, 22.7. HRMS (TOF MS CI⁺) calculated for C₁₆H₁₇ClNOS [M+H]⁺: 306.0719, found 306.0723.

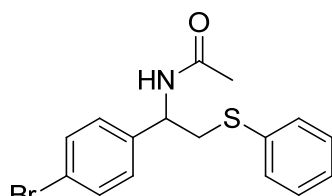


***N*-(1-(3-Chlorophenyl)-2-(phenylthio)ethyl)acetamide (4d).** Yellow Oil. 70.6 mg, 77% yield. ¹H NMR (400 MHz, CDCl₃) (δ, ppm) 7.36-7.33 (m, 2H), 7.29-7.26 (m, 2H),

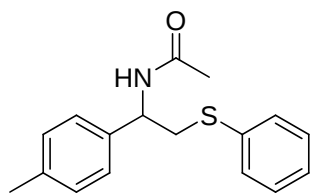
7.23-7.17 (m, 4H), 7.13-7.10 (m, 1H), 6.39 (d, $J = 7.2$ Hz, 1H), 5.12 (q, $J = 7.2$ Hz, 1H), 3.32-3.21 (m, 2H), 1.94 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 169.3, 142.1, 134.6, 134.1, 129.7, 129.5, 128.7, 127.5, 126.4, 126.2, 124.5, 52.1, 39.4, 22.7. HRMS (TOF MS CI^+) calculated for $\text{C}_{16}\text{H}_{17}\text{ClNOS}$ $[\text{M}+\text{H}]^+$: 306.0719, found 306.0731.



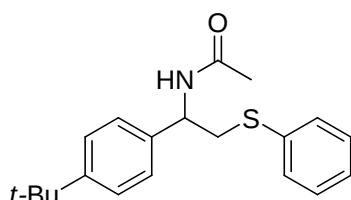
***N*-(1-(2-Chlorophenyl)-2-(phenylthio)ethyl)acetamide (4e).** Yellow Oil. 68.8 mg, 75% yield. ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.38-7.35 (m, 2H), 7.32-7.28 (m, 2H), 7.26-7.25 (m, 2H), 7.22-7.16 (m, 3H), 6.31 (d, $J = 7.2$ Hz, 1H), 5.50-5.45 (m, 1H), 3.42-3.30 (m, 2H), 1.97 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 169.5, 137.6, 134.9, 132.8, 130.2, 130.1, 129.1, 129.0, 128.3, 127.0, 126.8, 51.1, 38.1, 23.2. HRMS (TOF MS CI^+) calculated for $\text{C}_{16}\text{H}_{17}\text{ClNOS}$ $[\text{M}+\text{H}]^+$: 306.0719, found 306.0716.



***N*-(1-(4-Bromophenyl)-2-(phenylthio)ethyl)acetamide (4f).** Yellow Solid; m.p. 96.0-98.4 °C. 90.0 mg, 86% yield. ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.42-7.38 (m, 2H), 7.34-7.31 (m, 2H), 7.28-7.25 (m, 2H), 7.22-7.18 (m, 1H), 7.10 (d, $J = 8.4$ Hz, 2H), 6.42 (d, $J = 7.6$ Hz, 1H), 5.09 (q, $J = 7.2$ Hz, 1H), 3.32-3.19 (m, 2H), 1.92 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 169.3, 139.1, 134.6, 131.3, 129.6, 128.7, 127.9, 126.3, 121.2, 52.0, 39.3, 22.7. HRMS (TOF MS CI^+) calculated for $\text{C}_{16}\text{H}_{17}\text{BrNOS}$ $[\text{M}+\text{H}]^+$: 350.0214, found 350.0221.

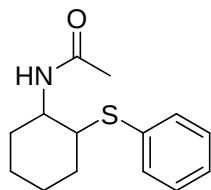


***N*-(2-(Phenylthio)-1-(p-tolyl)ethyl)acetamide (4g).** Yellow Oil. 69.3 mg, 81% yield. ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.37-7.34 (m, 2H), 7.28-7.24 (m, 2H), 7.19-7.15 (m, 1H), 7.15-7.10 (m, 4H), 6.26 (d, $J = 7.2$ Hz, 1H), 5.13 (q, $J = 7.0$ Hz, 1H), 3.40-3.22 (m, 2H), 2.31 (s, 3H), 1.91 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 169.2, 137.1, 136.9, 135.3, 129.2, 129.0, 128.6, 126.1, 125.9, 52.3, 39.1, 22.8, 20.6. HRMS (TOF MS CI^+) calculated for $\text{C}_{17}\text{H}_{20}\text{NOS}$ $[\text{M}+\text{H}]^+$: 286.1266, found 286.1270.

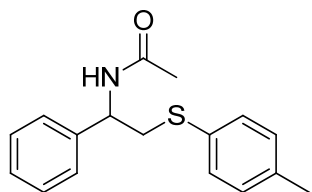


***N*-(1-(4-(tert-Butyl)phenyl)-2-(phenylthio)ethyl)acetamide (4h).** Yellow Oil. 81.5 mg, 83% yield. ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.36-7.31 (m, 4H), 7.27-7.23

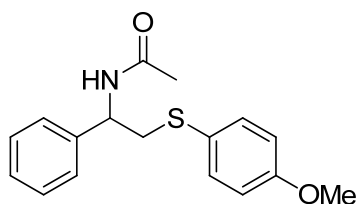
(m, 2H), 7.21-7.14 (m, 3H), 6.18 (d, $J = 7.6$ Hz, 1H), 5.17 (q, $J = 6.9$ Hz, 1H), 3.41-3.27 (m, 2H), 1.92 (s, 3H), 1.29 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 169.1, 150.3, 136.8, 135.3, 129.2, 128.6, 125.9, 125.2, 52.2, 39.1, 34.0, 30.8, 22.8. HRMS (TOF MS CI^+) calculated for $\text{C}_{20}\text{H}_{26}\text{NOS}$ $[\text{M}+\text{H}]^+$: 328.1735, found 328.1741.



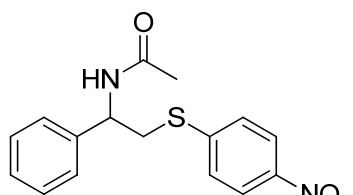
***N*-(2-(Phenylthio)cyclohexyl)acetamide (4i).** White Solid; m.p. 133.2-135.0 °C. 22.4 mg, 30% yield. ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.50-7.47 (m, 2H), 7.36-7.27 (m, 3H), 5.67 (d, $J = 7.0$ Hz, 1H), 3.84-3.76 (m, 1H), 3.00-2.94 (m, 1H), 2.24-2.10 (m, 2H), 1.96 (s, 3H), 1.78-1.70 (m, 2H), 1.51-1.34 (m, 2H), 1.32-1.20 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 169.1, 133.4, 132.5, 128.5, 126.9, 52.3, 51.1, 33.0, 32.5, 25.3, 23.9, 23.0. HRMS (TOF MS CI^+) calculated for $\text{C}_{14}\text{H}_{20}\text{NOS}$ $[\text{M}+\text{H}]^+$: 250.1266, found 250.1269.



***N*-(1-Phenyl-2-(*p*-tolylthio)ethyl)acetamide (5a).** Yellow Solid; m.p. 71.5-74.0 °C. 77.0 mg, 90% yield. ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.32-7.26 (m, 4H), 7.25-7.22 (m, 3H), 7.09-7.07 (m, 2H), 6.27 (d, $J = 7.6$ Hz, 1H), 5.13 (q, $J = 7.2$ Hz, 1H), 3.32-3.20 (m, 2H), 2.30 (s, 3H), 1.92 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 169.7, 140.6, 136.8, 131.7, 130.7, 129.9, 128.7, 127.8, 126.6, 52.9, 40.6, 23.2, 21.1. HRMS (TOF MS CI^+) calculated for $\text{C}_{17}\text{H}_{20}\text{NOS}$ $[\text{M}+\text{H}]^+$: 286.1266, found 286.1280.

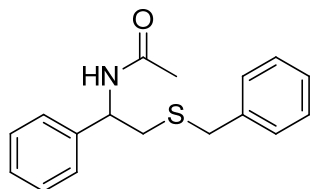


***N*-((2-[(4-Methoxyphenyl)thio]-1-phenylethyl)acetamide (5b).** Yellow Solid; m.p. 92.4-94.0 °C. 77.7 mg, 86% yield. ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.35-7.21 (m, 7H), 6.82 (d, $J = 8.8$ Hz, 2H), 6.30 (d, $J = 7.6$ Hz, 1H), 5.08 (q, $J = 7.4$ Hz, 1H), 3.77 (s, 3H), 3.24-3.14 (m, 2H), 1.94 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 169.2, 158.8, 140.2, 133.2, 128.2, 127.2, 126.1, 125.0, 114.3, 54.9, 52.5, 41.4, 22.8. HRMS (TOF MS CI^+) calculated for $\text{C}_{17}\text{H}_{20}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$: 302.1215, found 302.1221.

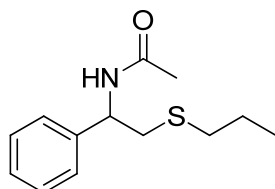


***N*-((2-[(4-Nitrophenyl)thio]-1-phenylethyl)acetamide (5c).**

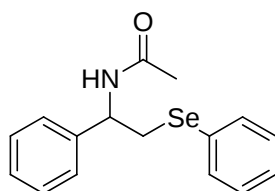
Yellow Oil. 52.1mg, 55% yield. ^1H NMR (400 MHz, d-DMSO) (δ , ppm) 8.54 (d, J = 8.4 Hz, 1H), 8.17 (d, J = 9.0 Hz, 2H), 7.60 (d, J = 9.0 Hz, 2H), 7.45-7.37 (m, 4H), 7.34-7.30 (m, 1H), 5.12-5.06 (m, 1H), 3.55-3.44 (m, 2H), 1.90 (s, 3H). ^{13}C NMR (100 MHz, d-DMSO) (δ , ppm) 168.8, 147.1, 144.5, 141.2, 128.4, 127.5, 126.9, 126.5, 123.9, 51.4, 36.8, 22.6. HRMS (TOF MS Cl^+) calculated for $\text{C}_{16}\text{H}_{17}\text{N}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$: 317.0960, found 317.0961.



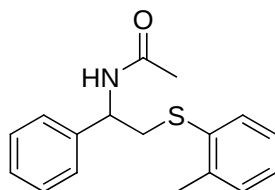
***N*-[2-(Benzylthio)-1-phenylethyl]acetamide (5d).** Yellow Solid; m.p. 105.2-106.8 °C. 81.2 mg, 95% yield. ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.32-7.27 (m, 4H), 7.25-7.20 (m, 6H), 6.33 (d, J = 8.0 Hz, 1H), 5.14 (q, J = 7.0 Hz, 1H), 3.60-3.52 (m, 2H), 2.83-2.73 (m, 2H), 1.93 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 169.2, 140.4, 137.5, 128.5, 128.2, 128.1, 127.2, 126.7, 126.1, 51.7, 36.7, 35.9, 22.8. HRMS (TOF MS Cl^+) calculated for $\text{C}_{17}\text{H}_{20}\text{NOS}$ $[\text{M}+\text{H}]^+$: 286.1266, found 286.1267.



***N*-[1-Phenyl-2-(propylthio)ethyl]acetamide (5e).** Yellow Solid; m.p. 69.0-71.0 °C. 65.4 mg, 92% yield. ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.35-7.24 (m, 5H), 6.38 (d, J = 7.6 Hz, 1H), 5.15 (q, J = 6.7 Hz, 1H), 2.96-2.87 (m, 2H), 2.38 (t, J = 7.4 Hz, 2H), 2.00 (s, 3H), 1.59-1.50 (m, 2H), 0.93 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 169.2, 140.4, 128.2, 127.2, 126.0, 52.1, 37.5, 34.0, 22.8, 22.3, 12.9. HRMS (TOF MS Cl^+) calculated for $\text{C}_{13}\text{H}_{20}\text{NOS}$ $[\text{M}+\text{H}]^+$: 238.1266, found 238.1268.

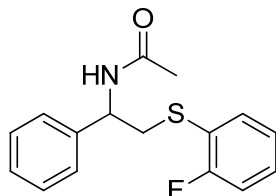


***N*-[1-Phenyl-2-(phenylselanyl)ethyl]acetamide (5f).** Yellow Oil. 58.0 mg, 61% yield. ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.49-7.47 (m, 2H), 7.33-7.27 (m, 3H), 7.25-7.22 (m, 5H), 6.19 (d, J = 7.2 Hz, 1H), 5.24 (q, J = 6.9 Hz, 1H), 3.39-3.25 (m, 2H), 1.90 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 169.1, 140.3, 132.4, 129.3, 128.8, 128.3, 127.3, 126.8, 126.0, 52.8, 33.4, 22.8. HRMS (TOF MS Cl^+) calculated for $\text{C}_{16}\text{H}_{18}\text{NOSe}$ $[\text{M}+\text{H}]^+$: 320.0544, found 320.0557.

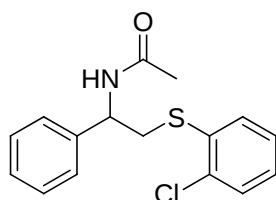


***N*-[1-Phenyl-2-(o-tolylthio)ethyl]acetamide (5g).** Yellow Solid; m.p. 97.6-99.6 °C. 81.2 mg, 95% yield. ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.37-7.35 (m, 1H), 7.33-7.24

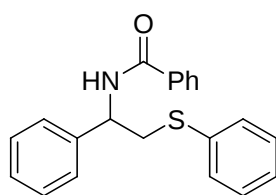
(m, 5H), 7.16-7.08 (m, 3H), 6.26 (d, $J = 7.6$ Hz, 1H), 5.16 (q, $J = 7.2$ Hz, 1H), 3.36-3.21 (m, 2H), 2.33 (s, 3H), 1.93 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 169.2, 140.0, 137.7, 134.3, 129.8, 128.7, 128.3, 127.4, 126.17, 126.15, 126.0, 52.5, 38.6, 22.8, 20.0. HRMS (TOF MS Cl^+) calculated for $\text{C}_{17}\text{H}_{20}\text{NOS}$ $[\text{M}+\text{H}]^+$: 286.1266, found 286.1271.



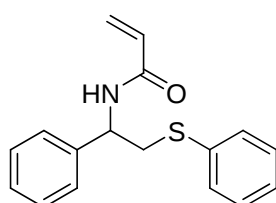
***N*-{2-[(2-Fluorophenyl)thio]-1-phenylethyl}acetamide (5h).** Yellow Oil. 81.5 mg, 94% yield. ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.42-7.38 (m, 1H), 7.31-7.23 (m, 5H), 7.22-7.18 (m, 1H), 7.07-7.00 (m, 2H), 6.46 (d, $J = 7.6$ Hz, 1H), 5.13 (q, $J = 7.2$ Hz, 1H), 3.35-3.23 (m, 2H), 1.93 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 169.3, 161.1 (d, $J_{\text{C-F}} = 243.7$ Hz), 139.7, 132.6 (d, $J = 1.6$ Hz), 128.6 (d, $J_{\text{C-F}} = 7.8$ Hz), 128.2, 127.4, 126.1, 124.2 (d, $J = 3.7$ Hz), 121.7 (d, $J = 16.7$ Hz), 115.3 (d, $J = 22.4$ Hz), 52.4, 38.8, 22.7. HRMS (TOF MS Cl^+) calculated for $\text{C}_{16}\text{H}_{17}\text{FNOS}$ $[\text{M}+\text{H}]^+$: 290.1015, found 290.1027.



***N*-{2-[(2-Chlorophenyl)thio]-1-phenylethyl}acetamide (5i).** Yellow Solid; m.p. 79.4-81.6 °C. 76.9 mg, 84% yield. ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.44-7.42 (m, 1H), 7.35-7.31 (m, 2H), 7.30-7.24 (m, 4H), 7.21-7.17 (m, 1H), 7.13-7.09 (m, 1H), 6.38 (d, $J = 7.2$ Hz, 1H), 5.18 (q, $J = 6.9$ Hz, 1H), 3.44-3.27 (m, 2H), 1.95 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 169.4, 139.6, 134.2, 133.8, 129.6, 129.3, 128.3, 127.5, 126.89, 126.86, 126.2, 52.3, 38.1, 22.8. HRMS (TOF MS Cl^+) calculated for $\text{C}_{16}\text{H}_{17}\text{ClNOS}$ $[\text{M}+\text{H}]^+$: 306.0719, found 306.0719.

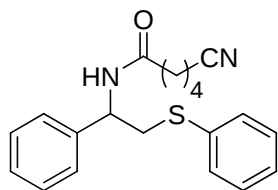


***N*-[1-Phenyl-2-(phenylthio)ethyl]benzamide (6a).** White Solid; m.p. 65.0-66.8 °C. 67.0 mg, 67% yield. ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.69-7.67 (m, 2H), 7.47 (t, $J = 7.4$ Hz, 1H), 7.41-7.35 (m, 4H), 7.33-7.32 (m, 4H), 7.30-7.23 (m, 2H), 7.22-7.17 (m, 2H), 6.77 (d, $J = 6.8$ Hz, 1H), 5.37 (q, $J = 7.1$ Hz, 1H), 3.53-3.39 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 166.9, 140.4, 135.4, 134.2, 131.6, 130.0, 129.2, 128.8, 128.6, 127.9, 127.0, 126.7, 126.6, 53.5, 40.0. HRMS (TOF MS Cl^+) calculated for $\text{C}_{21}\text{H}_{20}\text{NOS}$ $[\text{M}+\text{H}]^+$: 334.1266, found 334.1271.



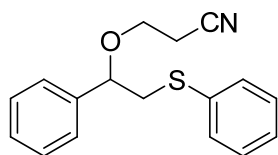
***N*-[1-Phenyl-2-(phenylthio)ethyl]acrylamide (6b).** Yellow Oil. 29.8 mg,

35% yield. ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.38-7.34 (m, 2H), 7.33-7.31 (m, 2H), 7.29-7.26 (m, 4H), 7.21-7.19 (m, 1H), 7.17-7.09 (m, 1H), 6.28-6.24 (m, 1H), 6.19-6.14 (m, 1H), 6.10-6.03 (m, 1H), 5.65-5.62 (m, 1H), 5.25 (q, $J = 7.0$ Hz, 1H), 3.48-3.43 (m, 1H), 3.35-3.30 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 165.0, 140.1, 135.4, 130.5, 129.9, 129.1, 128.8, 128.0, 127.1, 126.7, 126.6, 53.0, 39.7. HRMS (TOF MS CI^+) calculated for $\text{C}_{17}\text{H}_{18}\text{NOS}$ $[\text{M}+\text{H}]^+$: 284.1109, found 284.1105.



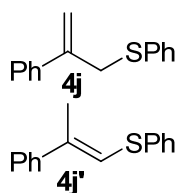
5-Cyano-N-[1-phenyl-2-(phenylthio)ethyl]pentanamide (6c). White

Solid. 81.2 mg, 80% yield. ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.43-7.39 (m, 3H), 7.37-7.30 (m, 6H), 7.27-7.24 (m, 1H), 6.16 (d, $J = 7.4$ Hz, 1H), 5.23 (q, $J = 7.2$ Hz, 1H), 3.45-3.34 (m, 2H), 2.40-2.36 (m, 2H), 2.27-2.23 (m, 2H), 1.84-1.78 (m, 2H), 1.17-1.69 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 170.9, 139.8, 134.9, 129.3, 128.7, 128.4, 127.5, 126.2, 126.1, 119.1, 52.4, 39.3, 34.8, 24.3, 24.0, 16.5. HRMS (TOF MS CI^+) calculated for $\text{C}_{20}\text{H}_{23}\text{N}_2\text{OS}$ $[\text{M}+\text{H}]^+$: 339.1531, found 339.1537.

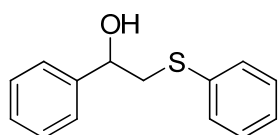


3-[1-Phenyl-2-(phenylthio)ethoxy]propanenitrile (6d). Yellow Oil.

55.3 mg, 65% yield. ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.37-7.27 (m, 8H), 7.24-7.23 (m, 1H), 7.17 (t, $J = 7.2$ Hz, 1H), 4.45-4.39 (m, 1H), 3.59-3.46 (m, 2H), 3.38-3.27 (m, 1H), 3.13-3.08 (m, 1H), 2.62-2.49 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 139.3, 135.8, 129.0, 128.5, 128.3, 128.1, 126.2, 125.7, 117.2, 81.4, 63.2, 40.9, 18.4. HRMS (TOF MS CI^+) calculated for $\text{C}_{17}\text{H}_{18}\text{NOS}$ $[\text{M}+\text{H}]^+$: 284.1109, found 284.1102.



A mixture of Phenyl(2-phenylallyl)sulfane (4j) and (E)-Phenyl(2-phenylprop-1-enyl)sulfane (4j').³ Yellow oil. 61.8 mg, 91% yield. ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.54-7.48 (m, 6H), 7.44-7.36 (m, 8H), 7.34-7.26 (m, 4H), 6.65 (s, 0.75H), 5.47 (s, 1H), 5.26 (s, 1H), 4.05 (s, 2H), 2.33 (s, 2.76H).



1-Phenyl-2-(phenylthio)ethanol (7).⁴ Yellow Oil. ^1H NMR (400 MHz,

CDCl_3) (δ , ppm) 7.49-7.47 (m, 2H), 7.44-7.38 (m, 5H), 7.37-7.33 (m, 2H), 7.31-7.28 (m, 1H), 4.80-4.77 (m, 1H), 3.41-3.36 (m, 1H), 3.19-3.13 (m, 1H), 2.94 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 141.7, 134.4, 129.8, 128.7, 128.1, 127.5, 126.3, 125.4, 71.2, 43.6.

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