Supplementary Information

Catalyst-free synthesis of α-thioacrylic acids via cascade thiolation and 1,4-aryl migration of aryl alkynoates at room temperature

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Contents

1. General information .................................................................S2

2. General procedure for the catalyst-free cascade thiolation and 1,4-aryl migration of aryl alkynoates leading to α-thioacrylic acids..................................................S3

3. Preliminary mechanistic studies ........................................S3-S6

4. Characterization data of products 3aa–3qa.................................S6-S16

5. Copies of NMR spectra for 3aa–3qa...........................................S17-S57
1. General information

All commercially available reagent grade chemicals were purchased from Aldrich, Acros, Alfa Aesar and Energy Chemical Company and used as received without further purification unless otherwise stated. \(^1\)H NMR, \(^{13}\)C NMR and \(^{19}\)F NMR were recorded in CDCl\(_3\) on a Bruker Avance III 400 spectrometer with TMS as internal standard (500 MHz \(^1\)H, 125 MHz \(^{13}\)C) at room temperature, the chemical shifts (\(\delta\)) were expressed in ppm and \(J\) values were given in Hz. The following abbreviations are used to indicate the multiplicity: singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), doublet of triplets (dt), and multiplet (m). All first order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted were designated as multiplet (m). Mass analyses and HRMS were obtained on a Finnigan-LCQDECA mass spectrometer and a Bruker Daltonics Bio-TOF-Q mass spectrometer by the ESI method, respectively. Column chromatography was performed on silica gel (200-300 mesh).
2. General procedure for the cascade thiolation and 1,4-aryl migration of aryl alkynoates leading to α-thioacrylic acids.

![Chemical Reaction Diagram]

To a solution of aryl alkynoates 1 (0.2 mmol) in EtOH 2 mL was added thiols 2 (0.4 mmol). The reaction mixture was stirred at room temperature under air for 6h. After completion of the reaction, the solution was concentrated in vacuum. The residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product 3.

3. Preliminary mechanistic studies

3.1 The addition of TEMPO in the model reaction system.

To a solution of 3-phenylpropiolate 1a (0.2 mmol) and 4-methylbenzenethiol 2a (0.4 mmol) in EtOH 2 mL was added TEMPO (0.4 mmol). The reaction mixture was stirred at room temperature under air for 6h. After completion of the reaction, the solution was concentrated in vacuum, only a trace amount of desired product 3aa was detected. In addition, TEMPO-trapped complex (p-MePhS-TEMPO) was also detected by LC-MS analysis.
3.2 The reaction of 3-phenylpropiolate 1a and PhSSPh 4d.

To a solution of 3-phenylpropiolate 1a (0.2 mmol) in EtOH 2 mL was added PhSSPh (0.4 mmol). The reaction mixture was stirred at room temperature under air for 6h. After completion of the reaction, the solution was concentrated in vacuum, none of the desired product 3ad was detected.

3.3 DFT study.
Computational methods:
DFT study was performed by using Gaussian09 program\(^1\). Geometry optimization was conducted with B3LYP method\(^2\) and 6-31G(d) basis set. At the same level of theory, frequency analysis was performed to identify the optimized structures as intermediates or transition states, and to obtain thermodynamic corrections at 298.15 K and 1 atm. Based on the optimized structures, solution-phase single-point energies
were calculated with B3LYP-D3 method\textsuperscript{3}, 6-311+G(d,p) basis set and SMD solvation model (solvent=ethanol).\textsuperscript{4} The Gibbs free energies of each species were obtained by adding the thermodynamic corrections to the solution-phase single-point energies.

References:

\textbf{Figure S1}. Calculated energy profile for competitive hydrogen atom transfer and
cyclization. Relative Gibbs free energies are given in kcal/mol.

**Table S1.** Calculated energies of every species (in Hartree).

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**4. Characterization data of products**

_3,3-diphenyl-2-(p-tolylthio)acrylic acid_

Compound 3aa was obtained in 73% yield according to the general procedure. $^1$H NMR (DMSO-d6, 500 MHz, ppm): $\delta$ 12.76 (s, 1H), 7.39 (t, $J$ = 5.0 Hz, 2H), 7.34-7.28 (m, 8H), 7.21 (d, $J$ = 6.5 Hz, 2H), 7.17 (d, $J$ = 8.0 Hz, 2H), 2.28 (s, 3H); $^{13}$C NMR (DMSO-d6, 125MHz, ppm): $\delta$ 167.8, 148.0, 141.4, 141.1, 137.3, 130.7, 130.4, 130.2, 129.4, 128.9, 128.8, 128.7, 128.6, 128.4, 128.0, 21.1; HRMS calc. for C$_{22}$H$_{18}$O$_2$SNa (M+Na)$^+$, 369.0925; found, 369.0923.

_3,3-diphenyl-2-(o-tolylthio)acrylic acid_

Compound 3ab was obtained in 71% yield according to the general procedure. $^1$H NMR (DMSO-d6, 500 MHz, ppm): $\delta$ 12.75 (s, 1H), 7.48-7.47 (m, 1H), 7.39 (t, $J$ = 7.2 Hz, 2H), 7.35-7.32(m, 4H), 7.30-7.28(m, 2H), 7.24-7.22(m, 3H), 7.20-7.18 (m, 2H), 2.30 (s, 3H); $^{13}$C NMR (DMSO-d6, 125MHz, ppm): $\delta$ 167.7, 148.2, 141.4, 141.1, 138.7, 133.2, 131.3, 130.8, 129.2, 128.9, 128.9, 128.7, 128.6, 128.5, 127.9, 127.7, 127.1, 20.6; HRMS calc. for C$_{22}$H$_{18}$O$_2$SNa (M+Na)$^+$, 369.0925; found, 369.0926.
3,3-diphenyl-2-(m-tolylthio)acrylic acid
Compound 3ac was obtained in 72% yield according to the general procedure. $^1$H NMR (DMSO-d$_6$, 500 MHz, ppm): $\delta$ 12.80 (s, 1H), 7.38-7.34 (m, 2H), 7.33-7.27 (m, 6H), 7.23-7.19 (m, 5H), 7.06 (d, $J$ = 7.3 Hz, 1H), 2.27 (s, 3H); $^{13}$C NMR (DMSO-d$_6$, 125 MHz, ppm): $\delta$ 168.0, 149.5, 141.5, 141.2, 139.0, 134.3, 130.2, 129.5, 129.3, 129.0, 128.8, 128.7, 128.5, 128.1, 127.2, 126.9, 21.3; HRMS calc. for C$_{22}$H$_{18}$O$_2$Na (M+Na)$^+$, 369.0925; found, 369.0927.

3,3-diphenyl-2-(phenylthio)acrylic acid
Compound 3ad was obtained in 64% yield according to the general procedure. $^1$H NMR (DMSO-d$_6$, 500 MHz, ppm): $\delta$ 12.81 (s, 1H), 7.40-7.35 (m, 6H), 7.34-7.31 (m, 4H), 7.29-7.25 (m, 3H), 7.23-7.22 (m, 2H); $^{13}$C NMR (DMSO-d$_6$, 125 MHz, ppm): $\delta$ 168.0, 149.9, 141.4, 141.1, 134.5, 129.8, 129.6, 129.3, 128.9, 128.8, 128.7, 128.6, 127.4, 127.0; HRMS calc. for C$_{21}$H$_{16}$O$_2$Na (M+Na)$^+$, 355.0769; found, 355.0765.

2-(3,4-dimethoxyphenylthio)-3,3-diphenylacrylic acid
Compound 3ae was obtained in 51% yield according to the general procedure. $^1$H NMR (DMSO-d$_6$, 500 MHz, ppm): $\delta$ 12.75 (s, 1H), 7.40 (t, $J$=7.2 Hz, 2H), 7.35-7.29 (m, 6H), 7.22-7.20 (m, 2H), 6.99-6.94 (m, 3H), 3.74 (s, 6H); $^{13}$C NMR (DMSO-d$_6$, 125 MHz, ppm): $\delta$ 167.8, 149.2, 145.6, 141.4, 141.0, 129.5, 129.2, 129.1, 128.9, 128.8, 128.7, 128.5, 128.4, 124.5, 123.9, 115.3, 112.7, 56.0, 56.0; HRMS calc. for C$_{23}$H$_{20}$O$_4$Na (M+Na)$^+$, 415.0980; found, 415.0983.

2-(4-fluorophenylthio)-3,3-diphenylacrylic acid

2-(3,4-dimethoxyphenylthio)-3,3-diphenylacrylic acid

2-(4-fluorophenylthio)-3,3-diphenylacrylic acid
Compound 3af was obtained in 68% yield according to the general procedure. $^1$H NMR (DMSO-d$_6$, 500 MHz, ppm): $\delta$ 12.85 (s, 1H), 7.47-7.44 (m, 2H), 7.39 (t, $J$ = 7.1 Hz, 2H), 7.35-7.29 (m, 6H), 7.24-7.20 (m, 4H); $^{13}$C NMR (DMSO-d$_6$, 125 MHz, ppm): $\delta$ 167.7, 162.1 (d, $J$ = 243.4 Hz), 148.2, 141.3, 140.9, 133.2 (d, $J$=8.3 Hz), 129.4 (d, $J$=3.0 Hz), 129.3, 128.9, 128.9, 128.7, 128.7, 128.5, 127.8, 116.8 (d, $J$ = 22.0 Hz); $^{19}$F NMR(DMSO-d$_6$): 114.05; HRMS calc. for C$_{21}$H$_{15}$FO$_2$SNa (M+Na)$^+$, 373.0674; found, 373.0677.

2-(4-chlorophenylthio)-3,3-diphenylacrylic acid

Compound 3ag was obtained in 72% yield according to the general procedure. $^1$H NMR (DMSO-d$_6$, 500 MHz, ppm): $\delta$ 12.89 (s, 1H), 7.43-7.39 (m, 4H), 7.37 (d, $J$ = 7.7 Hz, 2H), 7.34-7.30 (m, 4H), 7.27 (d, $J$ = 8.0 Hz, 2H), 7.23-7.21 (m, 2H); $^{13}$C NMR (DMSO-d$_6$, 125 MHz, ppm): $\delta$ 167.8, 150.4, 141.2, 140.9, 133.6, 132.2, 131.6, 129.6, 129.2, 128.9, 128.8, 128.7, 128.6, 126.5; HRMS calc. for C$_{21}$H$_{15}$ClO$_2$SNa (M+Na)$^+$, 389.0379; found, 389.0381.

2-(3-chlorophenylthio)-3,3-diphenylacrylic acid

Compound 3ah was obtained in 67% yield according to the general procedure. $^1$H NMR (DMSO-d$_6$, 500 MHz, ppm): $\delta$ 13.00 (s, 1H), 7.41-7.30 (m, 10H), 7.27-7.22 (m, 4H); $^{13}$C NMR (DMSO-d$_6$, 125 MHz, ppm): $\delta$ 167.8, 151.6, 141.2, 140.9, 137.4, 134.1, 131.3, 129.2, 129.0, 128.9, 128.8, 128.7, 128.4, 127.9, 127.2, 125.8; HRMS calc. for C$_{21}$H$_{15}$ClO$_2$SNa (M+Na)$^+$, 366.0481; found, 389.0383.

2-(2-chlorophenylthio)-3,3-diphenylacrylic acid

Compound 3ai was obtained in 63% yield according to the general procedure. $^1$H NMR (DMSO-d$_6$, 500 MHz, ppm): $\delta$ 12.95 (s, 1H), 755 (d, $J$ = 7.9 Hz, 1H), 7.47-7.46 (m, 1H), 7.40-7.32 (m, 7H), 7.27-7.24 (m, 5H); $^{13}$C NMR (DMSO-d$_6$, 125 MHz, ppm): $\delta$ 168.0, 153.7, 141.3, 140.9, 134.7, 131.9, 130.2, 129.7, 129.1, 129.0, 129.0, 128.9, 128.8, 128.7, 128.4, 128.3, 124.5; HRMS calc. for C$_{21}$H$_{15}$ClO$_2$SNa (M+Na)$^+$, 366.0481; found, 366.0484.
2-(4-bromophenylthio)-3,3-diphenylacrylic acid
Compound 3aj was obtained in 65% yield according to the general procedure. $^1$H NMR (DMSO-d$_6$, 500 MHz, ppm): $\delta$ 12.91 (s, 1H), 7.54 (d, $J$=8.6 Hz, 2H), 7.38 (t, $J$ = 6.9 Hz, 2H), 7.35-7.32 (m, 6H), 7.26 (d, $J$ = 6.9 Hz, 2H), 7.21 (d, $J$ = 7.9 Hz, 2H); $^{13}$C NMR (DMSO-d$_6$, 125 MHz, ppm): $\delta$ 167.8, 150.6, 141.2, 140.9, 134.2, 132.5, 131.8, 129.2, 128.9, 128.9, 128.8, 128.7, 128.7, 126.3, 120.6; HRMS calc. for C$_{21}$H$_{15}$BrO$_2$SNa (M+Na)$^+$, 432.9874; found, 432.9875.

2-(2,4-dichlorophenylthio)-3,3-diphenylacrylic acid
Compound 3ak was obtained in 58% yield according to the general procedure. $^1$H NMR (DMSO-d$_6$, 500 MHz, ppm): $\delta$ 13.07 (s, 1H), 7.65 (d, $J$=1.85 Hz, 1H), 7.63 (d, $J$ = 8.5 Hz, 1H), 7.50-7.48 (m, 1H), 7.38-7.34 (m, 6H), 7.25-7.24 (m, 4H); $^{13}$C NMR (DMSO-d$_6$, 125 MHz, ppm): $\delta$ 167.8, 153.8, 141.1, 140.8, 133.9, 133.0, 133.9, 133.0, 132.2, 131.1, 129.6, 129.1, 129.0, 128.9, 128.8, 128.7, 128.5, 127.6, 124.2; HRMS calc. for C$_{21}$H$_{14}$Cl$_2$O$_2$SNa (M+Na)$^+$, 422.9989; found, 422.9991.

3,3-diphenyl-2-(2-(trifluoromethyl)phenylthio)acrylic acid
Compound 3al was obtained in 74% yield according to the general procedure. $^1$H NMR (DMSO-d$_6$, 500 MHz, ppm): $\delta$ 12.90 (s, 1H), 7.73 (d, $J$=7.6 Hz, 2H), 7.68 (t, $J$ = 7.4 Hz, 1H), 7.44 (t, $J$ = 7.6 Hz, 1H), 7.40-7.32 (m, 6H), 7.27 (d, $J$ = 8.1 Hz, 2H), 7.26-7.23 (m, 2H); $^{13}$C NMR (DMSO-d$_6$, 125 MHz, ppm): $\delta$ 167.6, 153.2, 141.2, 140.8, 134.6, 133.4, 131.5, 129.0, 128.9, 128.9, 128.8, 128.7, 127.7, 127.4, 127.3, 125.1, 124.1 (d, $J$ = 272.2Hz), 120.9; $^{19}$F NMR(DMSO-d$_6$): 59.72; HRMS calc. for C$_{22}$H$_{15}$F$_3$O$_2$SNa (M+Na)$^+$, 423.0643; found, 423.0641.

2-(4-hydroxyphenylthio)-3,3-diphenylacrylic acid
Compound 3am was obtained in 65% yield according to the general procedure. $^1$H NMR (DMSO-d$_6$, 500 MHz, ppm): $\delta$ 12.65 (s, 1H), 9.72 (s, 1H), 7.40 (t, $J$ = 7.3 Hz, 2H), 7.34-7.26 (m, 8H), 7.19 (d, $J$ = 8.1 Hz, 2H), 6.75 (d, $J$ = 8.6 Hz, 2H); $^{13}$C NMR (DMSO-d$_6$, 125 MHz, ppm): $\delta$ 167.4, 158.3, 143.6, 141.5, 141.0, 134.8, 130.4, 129.6, 128.9, 128.8, 128.6, 128.3, 128.2, 120.7, 116.6; HRMS calc. for C$_{21}$H$_{16}$O$_3$SNa (M+Na)$^+$, 371.0718; found, 371.0715.

2-(3-methylfuran-2-ylthio)-3,3-diphenylacrylic acid

Compound 3an was obtained in 71% yield according to the general procedure. $^1$H NMR (DMSO-d$_6$, 500 MHz, ppm): $\delta$ 12.79 (s, 1H), 7.55 (d, $J$=1.9Hz, 1H), 7.42 (t, $J$ = 7.5 Hz, 2H), 7.35-7.31 (m, 3H), 7.30-7.25 (m, 3H), 7.18 (d, $J$ = 8.2 Hz, 2H), 6.47 (d, $J$ = 1.9 Hz, 1H), 2.27 (s, 3H); $^{13}$C NMR (DMSO-d$_6$, 125 MHz, ppm): $\delta$ 172.0, 161.5, 146.7, 146.5, 145.9, 145.7, 145.3, 135.2, 134.4, 133.7, 133.6, 133.4, 133.0, 120.7, 111.8, 16.9; HRMS calc. for C$_{20}$H$_{16}$O$_3$SNa (M+Na)$^+$, 359.0718; found, 359.0719.

2-(4-tert-butylbenzylthio)-3,3-diphenylacrylic acid

Compound 3ao was obtained in 24% yield according to the general procedure. $^1$H NMR (DMSO-d$_6$, 500 MHz, ppm): $\delta$ 13.19 (s, 1H), 7.36 (d, $J$=8.3 Hz, 2H), 7.32-7.26 (m, 3H), 7.21 (d, $J$ = 7 Hz, 2H), 7.18 (d, $J$ = 8.0 Hz, 2H), 6.91-6.89 (m, 2H), 3.93 (s, 2H), 1.31 (s, 9H); $^{13}$C NMR (DMSO-d$_6$, 125 MHz, ppm): $\delta$ 168.5, 150.1, 141.4, 140.7, 134.6, 129.5, 129.2, 128.9, 128.8, 128.7, 128.6, 128.4, 128.2, 128.0, 125.6, 37.1, 34.7, 31.6; HRMS calc. for C$_{26}$H$_{26}$O$_2$SNa (M+Na)$^+$, 425.1551; found, 425.1553.

2-(butylthio)-3,3-diphenylacrylic acid

Compound 3ap was obtained in 36% yield according to the general procedure. $^1$H NMR (DMSO-d$_6$, 500 MHz, ppm): $\delta$ 13.08 (s, 1H), 7.38 (t, $J$=7.3 Hz, 2H), 7.32-7.26 (m, 4H), 7.21 (d, $J$ = 7 Hz, 2H), 7.18 (d, $J$ = 8.0 Hz, 2H), 2.67 (t, $J$ = 7.3 Hz, 2H), 1.56-1.50 (m, 2H), 1.33-1.24 (m, 2H), 0.85 (t, $J$ = 7.4 Hz, 3H); $^{13}$C NMR (DMSO-d$_6$, 125 MHz, ppm): $\delta$ 172.0, 161.5, 146.7, 146.5, 145.9, 145.7, 145.3, 135.2, 134.4, 133.7, 133.6, 133.4, 133.0, 120.7, 111.8, 16.9; HRMS calc. for C$_{26}$H$_{26}$O$_2$SNa (M+Na)$^+$, 425.1551; found, 425.1553.
125 MHz, ppm): δ 172.9, 147.5, 146.2, 145.6, 134.0, 133.7, 133.4, 133.3, 132.9, 132.8, 37.1, 36.5, 26.4, 18.6; HRMS calc. for C_{19}H_{20}O_{2}SNa (M+Na)^{+}, 335.1082; found, 335.1086.

3,3-dip-tolyl-2-(p-tolylthio)acrylic acid

Compound 3ba was obtained in 74% yield according to the general procedure. $^1$H NMR (DMSO-d6, 500 MHz, ppm): δ 12.63 (s, 1H), 7.28 (d, $J = 8.2$ Hz, 2H), 7.18-7.12 (m, 8H), 7.07 (d, $J = 8.1$ Hz, 2H), 2.30 (s, 3H), 2.29 (s, 3H), 2.28 (s, 3H); $^{13}$C NMR (DMSO-d6, 125 MHz, ppm): δ 168.1, 148.8, 138.8, 138.4, 138.2, 137.9, 137.0, 130.9, 130.3, 130.2, 129.4, 129.3, 129.2, 129.0, 126.5, 21.3, 21.2, 21.1; HRMS calc. for C_{24}H_{22}O_{2}SNa (M+Na)^{+}, 397.1238; found, 397.1239.

2-(4-chlorophenylthio)-3,3-dip-tolylacrylic acid

Compound 3bh was obtained in 74% yield according to the general procedure. $^1$H NMR (DMSO-d6, 500 MHz, ppm): δ 12.81 (s, 1H), 7.43-7.38 (m, 4H), 7.18-7.14 (m, 6H), 7.10-7.08 (m, 2H), 2.30 (s, 3H), 2.29 (s, 3H); $^{13}$C NMR (DMSO-d6, 125 MHz, ppm): δ 168.1, 151.1, 138.6, 138.5, 138.2, 138.2, 134.1, 131.2, 131.1, 129.6, 129.3, 129.2, 129.0, 125.0, 21.3, 21.3; HRMS calc. for C_{23}H_{19}ClO_{2}SNa (M+Na)^{+}, 417.0692; found, 417.0691.

3,3-dim-tolyl-2-(p-tolylthio)acrylic acid

Compound 3ca was obtained in 73% yield according to the general procedure. $^1$H NMR (DMSO-d6, 500 MHz, ppm): δ 12.70 (s, 1H), 7.29 (d, $J = 8.2$ Hz, 2H), 7.26 (d, $J = 7.7$ Hz, 1H), 7.21 (t, $J = 7.5$Hz, 1H), 7.17 (d, $J = 8.0$ Hz, 2H), 7.12 (t, $J = 7.9$ Hz, 3H), 7.03 (d, $J = 12.5$ Hz, 3H), 2.28 (s, 3H), 2.26 (s, 3H), 2.25 (s, 3H); $^{13}$C NMR (DMSO-d6, 125 MHz, ppm): δ 167.8, 148.3, 141.5, 141.1, 137.9, 137.7, 137.2, 130.7, 130.6, 130.2, 129.7, 129.3, 129.1, 128.7, 128.5, 127.7, 126.3, 126.1, 21.5, 21.4, 21.1; HRMS calc. for C_{24}H_{22}O_{2}SNa (M+Na)^{+}, 397.1238; found, 397.1240.
3,3-bis(4-fluorophenyl)-2-(p-tolylthio)acrylic acid

Compound 3da was obtained in 74% yield according to the general procedure. $^1$H NMR (DMSO-d$_6$, 500 MHz, ppm): $\delta$ 12.85 (s, 1H), 7.36-7.33 (m, 2H), 7.31-7.29 (m, 2H), 7.25-7.22 (m, 3H), 7.21-7.16 (m, 5H), 2.28 (s, 3H); $^{13}$C NMR (DMSO-d$_6$, 125 MHz, ppm): $\delta$ 167.6, 162.3 ($d$, $J$ = 275.1 Hz), 162.2 ($d$, $J$ = 244.2 Hz), 145.8, 137.7 ($d$, $J$ = 3.2 Hz), 137.5, 137.2 ($d$, $J$ = 3.2 Hz), 131.7 ($d$, $J$ = 8.3 Hz), 131.2 ($d$, $J$ = 8.3 Hz), 130.8, 130.3, 130.1, 128.7, 115.8 ($d$, $J$ = 20.2 Hz), 115.6 ($d$, $J$ = 20.4 Hz), 20.1; $^{19}$F NMR (DMSO-d$_6$): 113.23; HRMS calc. for C$_{22}$H$_{16}$F$_2$O$_2$SNa (M+Na)$^+$, 405.0737; found, 405.0739.

2-(p-tolylthio)-3,3-bis(4-(trifluoromethyl)phenyl)acrylic acid

Compound 3ea was obtained in 73% yield according to the general procedure. $^1$H NMR (DMSO-d$_6$, 500 MHz, ppm): $\delta$ 13.09 (s, 1H), 7.78 ($d$, $J$ = 7.9 Hz, 2H), 7.72 ($d$, $J$ = 8.3 Hz, 2H), 7.59 ($d$, $J$ = 8.1 Hz, 2H), 7.45 ($d$, $J$ = 8.2 Hz, 2H), 7.35-7.33 ($m$, 2H), 7.19 ($d$, $J$ = 7.1 Hz, 2H), 2.29 (s, 3H); $^{13}$C NMR (DMSO-d$_6$, 125 MHz, ppm): $\delta$ 166.8, 144.8, 144.5, 143.4, 138.1, 132.3, 131.7, 130.5, 130.3, 129.8, 128.9 ($q$, $J$ = 31.6 Hz), 126.0 ($d$, $J$ = 3.4 Hz), 125.7 ($d$, $J$ = 3.4 Hz), 125.6, 123.4, 121.3; $^{19}$F NMR (DMSO-d$_6$): 61.19, 61.21; HRMS calc. for C$_{24}$H$_{16}$F$_6$O$_2$SNa (M+Na)$^+$, 505.0673; found, 505.0677.

3,3-bis(4-bromophenyl)-2-(p-tolylthio)acrylic acid

Compound 3fa was obtained in 66% yield according to the general procedure. $^1$H NMR (DMSO-d$_6$, 500 MHz, ppm): $\delta$ 12.94 (s, 1H), 7.60 ($d$, $J$ = 8.4 Hz, 2H), 7.54 ($d$, $J$ = 8.5 Hz, 2H), 7.31 ($d$, $J$ = 8.1 Hz, 2H), 7.27 ($d$, $J$ = 8.4 Hz, 2H), 7.18 ($d$, $J$ = 8.1 Hz, 2H), 7.14 ($d$, $J$ = 8.4 Hz, 2H), 2.28 (s, 3H); $^{13}$C NMR (DMSO-d$_6$, 125 MHz, ppm): $\delta$ 172.0, 149.6, 145.0, 144.5, 142.5, 136.7, 136.7, 136.5, 135.9, 135.8, 135.1, 134.6,
134.4, 127.0, 126.8, 25.8; HRMS calc. for C_{22}H_{16}Br_{2}O_{2}SNa (M+Na)^+, 524.9135; found, 524.9133.

(E)-3-phenyl-3-p-tolyl-2-(p-tolylthio)acrylic acid

Compound 3ga was obtained in 71% yield according to the general procedure. $^1$H NMR (DMSO-d6, 500 MHz, ppm): $\delta$ 12.70 (s, 1H), 7.38 (t, $J = 7.0$ Hz, 2H), 7.33-7.33 (m, 1H), 7.29 (t, $J = 8.7$ Hz, 4H), 7.17 (d, $J = 8.1$ Hz, 2H), 7.14 (d, $J = 8.1$ Hz, 2H), 7.09 (d, $J = 8.0$ Hz, 2H), 2.28 (s, 3H), 2.28 (s, 3H); $^{13}$C NMR (DMSO-d6, 125 MHz, ppm): $\delta$ 168.0, 148.3, 141.3, 138.6, 138.2, 137.2, 130.6, 130.6, 130.2, 129.4, 129.2, 128.9, 128.7, 128.4, 127.1, 21.2, 21.1; HRMS calc. for C_{23}H_{20}O_{2}SNa (M+Na)^+, 383.1082; found, 383.1085.

(E)-3-phenyl-3-m-tolyl-2-(p-tolylthio)acrylic acid

Compound 3ha was obtained in 68% yield according to the general procedure. $^1$H NMR (DMSO-d6, 500 MHz, ppm): $\delta$ 12.73 (s, 1H), 7.38 (t, $J = 7.0$ Hz, 2H), 7.33-7.31 (m, 1H), 7.31-7.28 (m, 4H), 7.22 (t, $J = 7.6$ Hz, 1H), 7.17 (d, $J = 8.1$ Hz, 2H), 7.12 (d, $J = 7.6$ Hz, 1H), 7.03 (t, $J = 7.7$ Hz, 1H), 7.01(s, 1H), 2.28 (s, 3H), 2.25 (s, 3H); $^{13}$C NMR (DMSO-d6, 125 MHz, ppm): $\delta$ 167.8, 148.4, 141.5, 141.1, 137.7, 137.2, 130.6, 130.5, 130.2, 129.4, 129.3, 129.3, 128.8, 128.6, 128.4, 127.7, 126.1, 21.4, 21.1; HRMS calc. for C_{23}H_{20}O_{2}SNa (M+Na)^+, 383.1082; found, 383.1081.

(E)-3-(4-methoxyphenyl)-3-phenyl-2-(p-tolylthio)acrylic acid

Compound 3ia was obtained in 64% yield according to the general procedure. $^1$H NMR (DMSO-d6, 500 MHz, ppm): $\delta$ 12.70 (s, 1H), 7.37 (t, $J = 7.1$ Hz, 2H), 7.33-7.31 (m, 1H), 7.29-7.27 (m, 4H), 7.16 (d, $J = 8.0$ Hz, 2H), 7.13-7.11 (m, 2H), 6.90 (d, $J = 8.8$ Hz, 2H), 3.75 (s, 3H), 2.28 (s, 3H); $^{13}$C NMR (DMSO-d6, 125 MHz, ppm): $\delta$ 168.4, 159.3, 149.1, 141.3, 137.2, 133.6, 130.7, 130.4, 130.3, 130.0, 129.3, 128.8, 128.5, 125.9, 114.1, 55.6, 21.0; HRMS calc. for C_{23}H_{20}O_{3}SNa (M+Na)^+, 399.1031; found, 399.1033.
(E)-3-phenyl-3-o-tolyl-2-(p-tolylthio)acrylic acid

Compound 3ja was obtained in 71% yield according to the general procedure. \(^1\)H NMR (DMSO-d6, 500 MHz, ppm): \(\delta\) 12.56 (s, 1H), 7.37-7.32 (m, 6H), 7.31-7.29 (m, 1H), 7.27-7.25 (m, 1H), 7.22-7.20 (m, 3H), 7.18-7.15 (m, 2H), 2.29 (s, 3H), 2.14 (s, 3H); \(^13\)C NMR (DMSO-d6, 125 MHz, ppm): \(\delta\) 172.2, 153.0, 145.9, 144.0, 141.9, 140.8, 135.5, 135.3, 135.1, 134.2, 134.0, 133.3, 133.2, 133.0, 130.7, 25.8, 24.9; HRMS calc. for C\(_{23}\)H\(_{20}\)O\(_2\)SNa (M+Na): 383.1082; found, 383.1087.

(E)-3-(4-fluorophenyl)-3-phenyl-2-(p-tolylthio)acrylic acid

Compound 3ka was obtained in 76% yield according to the general procedure. \(^1\)H NMR (DMSO-d6, 500 MHz, ppm): \(\delta\) 12.81 (s, 1H), 7.39 (t, \(J = 7.1\) Hz, 2H), 7.34-7.32 (m, 1H), 7.29 (d, \(J = 8.1\) Hz, 4H), 7.25-7.22 (m, 2H), 7.18-7.15 (m, 4H), 2.27 (s, 3H); \(^13\)C NMR (DMSO-d6, 125 MHz, ppm): \(\delta\) 167.7, 162.3(t, \(J = 244.3\) Hz), 146.8, 140.9, 137.9 (d, \(J = 3.1\)Hz), 137.4, 131.1 (d, \(J = 8.4\)Hz), 130.8, 130.3, 129.4, 128.9, 128.6, 128.4, 115.6 (d, \(J = 21.5\)Hz), 21.1; \(^19\)F NMR (DMSO-d6): 113.51; HRMS calc. for C\(_{22}\)H\(_{17}\)FO\(_2\)SNa (M+Na): 387.0831, found, 387.0833.

(E)-3-(4-chlorophenyl)-3-phenyl-2-(p-tolylthio)acrylic acid

Compound 3la was obtained in 77% yield according to the general procedure. \(^1\)H NMR (DMSO-d6, 500 MHz, ppm): \(\delta\) 12.87 (s, 1H), 7.40-7.37 (m, 4H), 7.34-7.32 (m, 1H), 7.30 (d, \(J = 8.2\) Hz, 4H), 7.22-7.20 (m, 2H), 7.17 (d, \(J = 8.1\) Hz, 2H), 2.28 (s, 3H); \(^13\)C NMR (DMSO-d6, 125 MHz, ppm): \(\delta\) 167.5, 146.3, 140.7, 140.3, 137.5, 133.4, 131.0, 130.8, 130.3, 130.1, 129.4, 129.1, 128.9, 128.7, 128.6, 21.1; HRMS calc. for C\(_{22}\)H\(_{17}\)ClO\(_2\)SNa (M+Na): 403.0535; found, 403.0537.

(E)-3-(4-bromophenyl)-3-phenyl-2-(p-tolylthio)acrylic acid
Compound 3ma was obtained in 74% yield according to the general procedure. $^1$H NMR (DMSO-d6, 500 MHz, ppm): $\delta$ 12.87 (s, 1H), 7.54 (d, $J = 8.5$ Hz, 2H), 7.40 (t, $J = 7.1$ Hz, 2H), 7.35-7.32 (m, 1H), 7.31-7.30 (m, 4H), 7.17 (d, $J = 8.1$ Hz, 2H), 7.15 (d, $J = 8.6$ Hz, 2H), 2.28 (s, 3H); $^{13}$C NMR (DMSO-d6, 125 MHz, ppm): $\delta$ 167.5, 146.3, 140.7, 140.6, 137.5, 131.7, 131.0, 131.0, 130.3, 130.1, 129.4, 129.1, 128.9, 128.6, 122.0, 21.1; HRMS calc. for C$_{22}$H$_{17}$BrO$_2$SNa (M+Na)$^+$, 447.0030; found, 447.0033.

(E)-3-(naphthalen-2-yl)-3-phenyl-2-(p-tolylthio)acrylic acid

Compound 3na was obtained in 54% yield according to the general procedure. $^1$H NMR (DMSO-d6, 500 MHz, ppm): $\delta$ 12.74 (s, 1H), 7.94-7.88 (m, 2H), 7.85 (d, $J = 8.7$ Hz, 1H), 7.80 (s, 1H), 7.55-7.52 (m, 2H), 7.42-7.32 (m, 6H), 7.28-7.26 (m, 1H), 7.19 (d, $J = 8.0$ Hz, 2H), 2.29 (s, 3H); $^{13}$C NMR (DMSO-d6, 125 MHz, ppm): $\delta$ 167.8, 148.3, 140.9, 139.1, 137.3, 132.9, 130.6, 130.5, 130.3, 129.5, 129.1, 128.9, 128.6, 128.4, 128.1, 128.0, 127.9, 127.1, 127.0, 126.9, 21.1; HRMS calc. for C$_{25}$H$_{20}$O$_2$SNa (M+Na)$^+$, 419.1082; found, 419.1087.

(Z)-3-phenyl-3-p-tolyl-2-(p-tolylthio)acrylic acid

Compound 3oa was obtained in 73% yield according to the general procedure. $^1$H NMR (DMSO-d6, 500 MHz, ppm): $\delta$ 12.69 (s, 1H), 7.31-7.27 (m, 5H), 7.19-7.15 (m, 8H), 2.30 (s, 3H), 2.27 (s, 3H); $^{13}$C NMR (DMSO-d6, 125 MHz, ppm): $\delta$ 167.9, 148.4, 141.7, 138.3, 137.9, 137.1, 130.6, 130.5, 130.2, 129.4, 129.4, 129.0, 128.6, 127.4, 21.3, 21.1; HRMS calc. for C$_{23}$H$_{20}$O$_2$SNa (M+Na)$^+$, 383.1082; found,383.1085.

(Z)-3-(4-fluorophenyl)-3-phenyl-2-(p-tolylthio)acrylic acid

Compound 3pa was obtained in 68% yield according to the general procedure. $^1$H NMR (DMSO-d6, 500 MHz, ppm): $\delta$ 12.77 (s, 1H), 7.34-7.29 (m, 7H), 7.23-7.19 (m, 4H), 7.17 (d, $J = 8.1$ Hz, 2H), 2.28 (s, 3H); $^{13}$C NMR (DMSO-d6, 125 MHz, ppm): $\delta$
167.7, 162.1 (d, J = 243.9 Hz), 146.9, 141.3, 137.4, 137.3, 131.7 (d, J = 8.3 Hz), 130.8, 130.3, 130.2, 129.0, 128.7, 128.7, 128.4, 115.8 (d, J = 21.5 Hz), 21.1; \(^{19}\)F NMR (DMSO-d6): 113.46; HRMS calc. for C\(_{22}\)H\(_{17}\)FO\(_2\)SNa (M+Na\(^+\))\(^+\), 387.0831, found, 387.0833.

(Z)-3-(3-bromophenyl)-3-phenyl-2-(p-tolylthio)acrylic acid

Compound 3qa was obtained in 68% yield according to the general procedure. \(^1\)H NMR (DMSO-d6, 500 MHz, ppm): \(\delta\) 12.83 (s, 1H), 7.54-7.49 (m, 1H), 7.43-7.28 (m, 8H), 7.22-7.21 (m, 2H), 7.17 (d, J = 8.0 Hz, 2H), 2.28 (s, 3H); \(^{13}\)C NMR (DMSO-d6, 125 MHz, ppm): \(\delta\) 167.4, 143.3, 140.8, 137.6, 131.8, 131.2, 131.1, 130.3, 129.9, 129.5, 129.4, 129.0, 128.9, 128.8, 128.5, 128.0, 122.0, 21.1; HRMS calc. for C\(_{22}\)H\(_{17}\)BrO\(_2\)SNa (M+Na\(^+\))\(^+\), 447.0030; found, 447.0035.
5. Copies of NMR spectra for 3aa-3qa.
3ae
3ai
3ak
3bh
3da
3ea
3fa
3ga
3ha
3ia
3ja
3ka
3ma
3na
3pa
3qa