Supporting Information

Direct α-Acyloxylation of Organic Sulfides with the Hypervalent (Diacyloxyiodo)benzene/Tetra-n-Butylammonium Bromide (TBAB) Reagent Combination

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1. General information

Unless otherwise noted, all reagents were purchased from commercial sources and used without further purification. The reaction solvent, DCM was dried by refluxing over CaH₂, and freshly distilled prior to use. All reactions were monitored by TLC and visualized by UV lamp (254 nm)/or by staining with a solution of 10 g phosphomolybdic acid and 100 mL EtOH followed by heating. Flash column chromatography was performed using 230-400 mesh silica gel. ¹H NMR (400 MHz) and ¹³C NMR (150 MHz) spectra were obtained on Bruker AV-400 instrument. Chemical shifts for ¹H NMR spectra were reported in δ ppm referenced to an internal SiMe₄ standard. The abbreviations s, brs, d, t, q and m stand for the resonance multiplicity singlet, broad singlet, doublet, triplet, quartet and multiplet, respectively. HR-ESI-MS spectra were recorded on a Bruker Esquire LC mass spectrometer using electrospray ionization. GC-MS (EI) spectra were recorded on an Agilent Technologies 7890A GC-MS system.

2. Preparation of Substrates

2.1 General procedure for the preparation of Hypervalent Iodine(III) Reagents

To a round-bottom flask, PhI(OAc)₂ (3.22g, 10 mmol, 1.0 eq.) and R₃COOH (22 mmol, 2.2 eq.) were dissolved in m-xylene (50 mL) and the flask was heated in 65 ºC under reduced pressure (about 30-50 Torr.) using a diaphragm pump. When the xylene was removed, petroleum ether (PE) was used to wash the solid for 3 times and the white solid was filtered and dried in vacuum. Product PhI(O₂CR₃)₂ was obtained and could be used directly in the following reaction.

2.1.1 Characterization of Hypervalent Iodine(III) Reagents

**Iodobenzene dipropionate(3a)***

Following the general procedure. White solid, 63% yield; ¹H NMR (600 MHz, CDCl₃): δ 8.07 (d, J = 7.8 Hz, 2H; HAr), 7.57 (t, J = 7.2 Hz, 1H; HAr), 7.48 (t, J = 7.2 Hz, 2H; HAr), 2.26 (q, J = 7.2 Hz, 4H; CH₂), 1.06 (t, J = 7.8 Hz, 6H; CH₃); ¹³C NMR (150 MHz, CDCl₃): δ179.6 (CO), 134.9 (C₆H₄), 131.7 (C₆H₄), 121.8 (C₆H₄), 27.6 (CH₂), 10.0 (CH₃).

**Iodobenzene Dipivalate(3b)***

Following the general procedure. White solid, 63% yield; ¹H NMR (600 MHz, CDCl₃): δ 8.07 (d, J = 7.8 Hz, 2H; HAr), 7.57 (t, J = 7.2 Hz, 1H; HAr), 7.48 (t, J = 7.2 Hz, 2H; HAr), 2.26 (q, J = 7.2 Hz, 4H; CH₂), 1.06 (t, J = 7.8 Hz, 6H; CH₃); ¹³C NMR (150 MHz, CDCl₃): δ179.6 (CO), 134.9 (C₆H₄), 131.7 (C₆H₄), 121.8 (C₆H₄), 27.6 (CH₂), 10.0 (CH₃).
Following the general procedure. White solid, 65% yield; \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) 8.00 (d, \(J = 8.4\) Hz, 2H; H\(_{Ar}\)), 7.54 (t, \(J = 7.2\) Hz, 1H; H\(_{Ar}\)), 7.46 (t, \(J = 7.8\) Hz, 2H; H\(_{Ar}\)), 1.10 (s, 18H; CH\(_3\)); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): δ183.7 (CO), 134.3 (C\(_{Ar}\)), 131.4 (C\(_{Ar}\)), 130.7 (C\(_{Ar}\)), 122.1 (C\(_{Ar}\)), 39.1 (C), 27.8 (CH\(_3\)).

**Iodobenzene ditetradecanoate(3c)**

![Iodobenzene ditetradecanoate](image)

Following the general procedure. White solid, 65% yield; \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) 8.07 (d, \(J = 8.4\) Hz, 2H; H\(_{Ar}\)), 7.57 (t, \(J = 7.2\) Hz, 1H; H\(_{Ar}\)), 7.48 (t, \(J = 7.8\) Hz, 2H; H\(_{Ar}\)), 2.24 (t, \(J = 7.5\) Hz, 4H; CH\(_2\)), 1.55–1.51 (m, 4H; CH\(_2\)), 1.25–1.22 (m, 40H; CH\(_2\)), 0.88 (t, \(J = 7.2\) Hz, 6H; CH\(_3\)); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): δ179.1 (CO), 135.0 (C\(_{Ar}\)), 131.7 (C\(_{Ar}\)), 131.0 (C\(_{Ar}\)), 121.9 (C\(_{Ar}\)), 130.2 (C\(_{Ar}\)), 34.2 (CH\(_2\)), 32.1 (CH\(_2\)), 29.8 (CH\(_2\)), 29.78 (2CH\(_2\)), 29.7 (CH\(_2\)), 29.6 (CH\(_2\)), 29.5 (CH\(_2\)), 29.4 (CH\(_2\)), 29.36 (CH\(_2\)), 25.8 (CH\(_2\)), 22.8 (CH\(_2\)), 14.3 (CH\(_3\)).

**Iodobenzene Dibenzoate(3d)**

![Iodobenzene Dibenzoate](image)

Following the general procedure. White solid, 77% yield; \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) 8.24 (d, \(J = 7.8\) Hz, 2H; H\(_{Ar}\)), 7.94 (d, \(J = 8.4\) Hz, 4H; H\(_{Ar}\)), 7.62 (t, \(J = 7.2\) Hz, 1H; H\(_{Ar}\)), 7.55 (t, \(J = 7.8\) Hz, 2H; H\(_{Ar}\)), 7.50 (t, \(J = 7.2\) Hz, 2H; H\(_{Ar}\)), 7.37 (t, \(J = 7.8\) Hz, 4H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): δ171.4 (CO), 135.0 (C\(_{Ar}\)), 132.6 (C\(_{Ar}\)), 131.8 (C\(_{Ar}\)), 131.1 (C\(_{Ar}\)), 130.2 (C\(_{Ar}\)), 130.2 (C\(_{Ar}\)), 128.3 (C\(_{Ar}\)), 122.4 (C\(_{Ar}\)).

### 2.2 General procedure for preparation of organic thioether

![General procedure for preparation of organic thioether](image)

2-bromo-1-arylethanone (10 mmol) was added in portions to a solution of NaSCH\(_3\) (12 mmol, 1.2 eq.) in methanol (50 mL). Within a few minutes the solution turned orange. After the addition was completed, the mixture was stirred at room temperature for 15 min and water was then added to the mixture. The product was extracted with dichloromethane, the organic layer was dried over Na\(_2\)SO\(_4\), filtered and evaporated in vacuo. The residue was purified by flash chromatography (petroleum ether : CH\(_2\)Cl\(_2\) = 5:1) to afford the desired product.

### 2.2.1 Characterization of organic thioether

**2-(methylthio)-1-phenylethan-1-one(1t)**
Colorless oil, 73% yield; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.97 (d, $J = 8.0$ Hz, 2H; H$_{Ar}$), 7.57 (t, $J = 8.0$ Hz, 1H; H$_{Ar}$), 7.46 (t, $J = 8.0$ Hz, 2H; H$_{Ar}$), 3.76 (s, 2H; CH$_2$), 2.13 (s, 3H; CH$_3$); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 194.1 (CO), 135.3 (C$_{Ar}$), 133.4 (C$_{Ar}$), 128.8 (C$_{Ar}$), 128.2 (C$_{Ar}$), 39.1 (CH$_2$), 16.0 (CH$_3$);

3. General procedure for $\alpha$-oxyalkylation of thioether

A solution of thioether 1a (0.5 mmol), tetrabutylammonium bromide (TBABr, 1.5 mmol, 3.0 equiv) and PhI(OAc)$_2$ (1.75 equiv) in dichloromethane (2 mL) was stirred in sealed tube at room temperature for 6 h under nitrogen atmosphere. The reaction was then concentrated in vacuum and purified by column chromatography using petroleum ether/ethyl acetate to afford corresponding products.

3.1 Characterization of $\alpha$-Acetoxy sulfide

(phenylthio)methyl acetate (2a)

Light yellow oil, 60 mg (66% yield); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.37 (d, $J = 8.0$ Hz, 2H; H$_{Ar}$), 7.24-7.18 (m, 3H; H$_{Ar}$), 5.33 (s, 2H; CH$_2$), 2.02 (s, 3H; CH$_3$); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 170.4 (CO), 134.8 (C$_{Ar}$), 130.4 (C$_{Ar}$), 129.2 (C$_{Ar}$), 127.5 (C$_{Ar}$), 68.1 (CH$_2$), 21.2 (CH$_3$); GC-MS (EI): m/z (%): 182, 152, 123, 110, 77, 65, 43 (100), 28.

((4-fluorophenyl)thio)methyl acetate (2b)

Colorless oil, 80 mg (80% yield); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.46 (d, $J = 8.0$ Hz, 2H; H$_{Ar}$), 7.02 (t, $J = 8.0$ Hz, 2H; H$_{Ar}$), 5.33 (s, 2H; CH$_2$), 2.09 (s, 3H; CH$_3$); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 170.3 (CO), 162.7 (d, $J = 246.3$ Hz; C$_{Ar}$), 133.6 (d, $J = 8.2$ Hz; C$_{Ar}$), 129.6 (d, $J = 3.4$ Hz; C$_{Ar}$), 116.3 (d, $J = 21.9$ Hz; C$_{Ar}$), 68.9 (CH$_2$), 21.1 (CH$_3$); GC-MS (EI): m/z (%): 200, 170, 141, 128, 83.1, 43 (100); HRMS (ES+) exact mass calculated for [M+Na]$^+$ (C$_4$H$_4$FO$_2$S) requires m/z 223.0205, found m/z 223.0204.
((4-chlorophenyl)thio)methyl acetate(2c)

Light yellow oil, 79 mg (73% yield); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.37 (d, $J$ = 8.0 Hz, 2H; H$_{Ar}$), 7.28 (d, $J$ = 8.0 Hz, 2H; H$_{Ar}$), 5.37 (s, 2H; CH$_2$), 2.09 (s, 3H; CH$_3$); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 170.3 (CO), 133.7 (C$_{Ar}$), 133.3 (C$_{Ar}$), 131.8 (C$_{Ar}$), 129.3 (C$_{Ar}$), 68.0 (CH$_2$), 21.1 (CH$_3$); GC-MS (EI): m/z (%): 216, 186, 157, 144, 108, 73, 43 (100), 28.

((4-bromophenyl)thio)methyl acetate(2d)

Light yellow oil, 74 mg (55% yield); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.43 (d, $J$ = 8.0 Hz, 2H; H$_{Ar}$), 7.30 (d, $J$ = 8.0 Hz, 2H; H$_{Ar}$), 5.37 (s, 2H; CH$_2$), 2.09 (s, 3H; CH$_3$); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 170.2 (CO), 134.0 (C$_{Ar}$), 132.2 (C$_{Ar}$), 131.9 (C$_{Ar}$), 121.6 (C$_{Ar}$), 67.8 (CH$_2$), 21.1 (CH$_3$); GC-MS (EI): m/z (%): 260, 230, 188, 122, 108, 43 (100), 28.

((4-cyanophenyl)thio)methyl acetate(2e)

White solid, 33 mg (32% yield); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.57 (d, $J$ = 8.0 Hz, 2H; H$_{Ar}$), 7.47 (d, $J$ = 8.0 Hz, 2H; H$_{Ar}$), 5.48 (s, 2H; CH$_2$), 2.10 (s, 3H; CH$_3$); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 170.1 (CO), 142.4 (C$_{Ar}$), 132.6 (C$_{Ar}$), 128.3 (C$_{Ar}$), 118.6 (C$_{Ar}$), 110.0 (CN), 65.7 (CH$_2$), 21.0 (CH$_3$); GC-MS (EI): m/z (%): 207, 177, 148, 134, 90, 73, 43 (100), 28.

((4-nitrophenyl)thio)methyl acetate(2f)

Yellow solid, 39 mg (34% yield); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.15 (d, $J$ = 8.0 Hz, 2H; H$_{Ar}$), 7.51 (d, $J$ = 8.0 Hz, 2H; H$_{Ar}$), 5.52 (s, 2H; CH$_2$), 2.12 (s, 3H; CH$_3$); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 170.1 (CO), 146.2 (C$_{Ar}$), 144.9 (C$_{Ar}$), 127.8 (C$_{Ar}$), 124.2 (C$_{Ar}$), 65.5 (CH$_2$), 21.0 (CH$_3$); GC-MS (EI): m/z (%): 227, 297, 168, 121, 108, 96, 58, 43 (100), 28.

((4-formylphenyl)thio)methyl acetate(2g)
Colorless oil, 35 mg (33% yield); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.95 (s, 1H; CHO), 7.80 (d, $J = 8.0$ Hz, 2H; H$_A$), 7.52 (d, $J = 8.0$ Hz, 2H; H$_B$), 5.51 (s, 2H; CH$_2$), 2.11 (s, 3H; CH$_3$); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 191.3 (CHO), 170.2 (CO), 143.9 (CA$_B$), 134.5 (CA$_A$), 130.3 (CA$_B$), 127.9 (CA$_A$), 65.8 (CH$_2$), 21.1 (CH$_3$); GC-MS (EI): m/z (%): 210, 180, 138, 109, 73, 65, 51, 43 (100), 28.

($p$-tolylthio)methyl acetate (2h)

Light yellow oil, 74 mg (55% yield); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.36 (d, $J = 8.0$ Hz, 2H; H$_A$), 7.11 (d, $J = 8.0$ Hz, 2H; H$_B$), 5.36 (s, 2H; CH$_2$), 2.34 (s, 3H; CH$_3$), 2.09 (s, 3H; CH$_3$); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 170.4 (CO), 137.7 (CA$_B$), 131.2 (CA$_A$), 131.0 (CA$_B$), 130.0 (CA$_A$), 68.8 (CH$_2$), 21.2 (2CH$_3$); GC-MS (EI): m/z (%): 196, 166, 137, 124 (100), 91, 77, 65, 43.

((4-methoxyphenyl)thio)methyl acetate (2i)

Colorless oil, 49 mg (46% yield); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.42 (d, $J = 8.0$ Hz, 2H; H$_A$), 6.86 (d, $J = 8.0$ Hz, 2H; H$_B$), 5.28 (s, 2H; CH$_2$), 3.79 (s, 3H; OCH$_3$), 2.08 (s, 3H; CH$_3$); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 170.4 (CO), 159.9 (CA$_A$), 134.1 (CA$_B$), 124.8 (CA$_A$), 114.8 (CA$_B$), 69.7 (CH$_2$), 55.4 (OCH$_3$), 21.1 (CH$_3$); GC-MS (EI): m/z (%): 212, 182, 140 (100), 125, 77, 43, 28; HRMS (ES$^+$) exact mass calculated for [M+Na]$^+$ (C$_{10}$H$_{12}$O$_3$S) requires $m/z$ 235.0405, found $m/z$ 235.0397.

((2-fluorophenyl)thio)methyl acetate (2j)

Light yellow oil, 78 mg (78% yield); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.65 (t, $J = 8.0$ Hz, 1H; H$_A$), 7.45-7.42 (m, 1H; H$_B$), 7.29-7.22 (m, 2H; H$_C$), 5.52 (s, 2H; CH$_2$), 2.23 (s, 3H; CH$_3$); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 170.3 (CO), 161.6 (d, $J = 244.9$ Hz; CA$_B$), 133.6 (CA$_A$), 130.0 (d, $J = 8.0$ Hz; CA$_B$), 124.8 (d, $J = 3.7$ Hz; CA$_A$), 121.2 (d, $J = 17.7$ Hz; CA$_B$), 116.0 (d, $J = 22.5$ Hz; CA$_A$), 67.1 (d, $J = 2.3$ Hz; CH$_2$), 21.0 (CH$_3$); GC-MS (EI): m/z (%): 200, 170, 128, 83, 57, 43 (100), 28; HRMS (ES$^+$) exact mass calculated for [M+Na]$^+$ (C$_9$H$_9$FO$_2$S) requires $m/z$ 223.0205, found $m/z$ 223.0198.

((3-fluorophenyl)thio)methyl acetate (2k)
phenyl(phenylthio)methyl acetate (2l)

Light yellow oil, 64 mg (64% yield); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.34-7.30 (m, 1H; H$_{Ar}$), 7.24-7.20 (m, 2H; H$_{Ar}$), 7.00 (t, $J$ = 8.0 Hz, 1H; H$_{Ar}$), 5.47 (s, 2H; CH$_2$), 2.16 (s, 3H; CH$_3$); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 170.3 (CO), 162.8 (d, $J$ = 250.2 Hz; C$_{Ar}$), 137.2 (d, $J$ = 7.8 Hz; C$_{Ar}$), 130.5 (d, $J$ = 8.4 Hz; C$_{Ar}$), 125.3 (d, $J$ = 3.0 Hz; C$_{Ar}$), 114.2 (d, $J$ = 21.0 Hz; C$_{Ar}$), 67.4 (CH$_2$), 21.1 (CH$_3$); GC-MS (EI): $m/z$ (%): 200, 170, 128, 83, 57, 43 (100), 28; HRMS (ES+) exact mass calculated for [M+Na]$^+$ (C$_9$H$_9$FO$_2$S) requires $m/z$ 223.0205, found $m/z$ 223.0199.

1-(phenylthio)allyl acetate (2m)

Light yellow oil, 55 mg (43% yield); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.45-7.29 (m, 10H; H$_{Ar}$), 7.15 (s, 1H; CH), 2.08 (s, 3H; CH$_3$); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 169.6 (CO), 137.3 (C$_{Ar}$), 134.1 (C$_{Ar}$), 132.0 (C$_{Ar}$), 129.0 (C$_{Ar}$), 128.8 (C$_{Ar}$), 128.7 (C$_{Ar}$), 128.6 (C$_{Ar}$), 126.6 (C$_{Ar}$), 81.3 (CH), 21.2 (CH$_3$); GC-MS (EI): $m/z$ (%): 258, 199, 165, 149, 110 (100), 77, 43, 28; HRMS (ES+) exact mass calculated for [M+Na]$^+$ (C$_{15}$H$_{14}$O$_2$S) requires $m/z$ 281.0612, found $m/z$ 281.0606.

1-(phenylthio)prop-2-yn-1-yl acetate (2n)

Light yellow oil, 34 mg (33% yield); $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.31 (d, $J$ = 7.8 Hz, 2H; H$_{Ar}$), 7.26 (t, $J$ = 7.8 Hz, 2H; H$_{Ar}$), 7.19 (t, $J$ = 7.6 Hz, 1H; H$_{Ar}$), 6.45 (d, $J$ = 15.0 Hz, 1H; CH), 5.78-5.74 (m, 1H; =CH), 4.52 (d, $J$ = 6.6 Hz, 2H; =CH$_2$), 1.99 (s, 3H; CH$_3$); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 170.8 (CO), 134.1 (C$_{Ar}$), 130.7 (C$_{Ar}$), 129.8 (C$_{Ar}$), 129.4 (C$_{Ar}$), 127.5 (C$_{Ar}$), 124.8 (C$_{Ar}$), 64.5 (CH), 21.1 (CH$_3$); GC-MS (EI): $m/z$ (%): 208, 165, 147, 110 (100), 77, 59, 43, 28.
methyl 2-acetoxy-2-(phenylthio)acetate(2o)

Light yellow oil, 42 mg (35% yield); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.53 (d, $J$ = 8.0 Hz, 2H; H$_{Ar}$), 7.35-7.33 (m, 3H; H$_{Ar}$), 6.21 (s, 1H; CH), 3.67 (s, 3H; OCH$_3$), 2.17 (s, 3H; CH$_3$); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 169.8 (CO), 166.5 (CO), 134.4 (C$_{Ar}$), 130.0 (C$_{Ar}$), 129.5 (C$_{Ar}$), 129.2 (C$_{Ar}$), 76.8 (CH), 52.9 (CH$_3$), 20.9 (CH$_3$); GC-MS (EI): m/z (%): 240, 181, 152, 139, 121, 110, 77, 65, 43 (100), 28.

11-oxo-6,11-dihydrodibenzo[b,e]thiepin-6-yl acetate(2p)

White solid, 103 mg (72% yield); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.11 (d, $J$ = 8.0 Hz, 1H; H$_{Ar}$), 7.59 (d, $J$ = 8.0 Hz, 1H; H$_{Ar}$), 7.50-7.45 (m, 1H; H$_{Ar}$), 7.43-7.36 (m, 2H; H$_{Ar}$), 6.86 (s, 1H; CH), 1.97 (s, 3H; CH$_3$); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 196.1 (CO), 168.8 (CO), 139.9 (C$_{Ar}$), 135.9 (C$_{Ar}$), 135.6 (C$_{Ar}$), 133.8 (C$_{Ar}$), 132.8 (C$_{Ar}$), 131.8 (C$_{Ar}$), 131.6 (C$_{Ar}$), 129.4 (C$_{Ar}$), 129.2 (C$_{Ar}$), 128.5 (C$_{Ar}$), 125.9 (C$_{Ar}$), 124.5 (C$_{Ar}$), 75.9 (CH), 21.0 (CH$_3$); GC-MS (EI): m/z (%): 284, 242, 213 (100), 197, 181, 152, 77, 43; HRMS (ES+) exact mass calculated for [M+Na]$^+$ (C$_{16}$H$_{12}$O$_3$S) requires m/z 307.0405, found m/z 307.0396.

(naphthalen-2-ylthio)methyl acetate(2q)

Light yellow solid, 78 mg (69% yield); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.95 (s, 1H; H$_{Ar}$), 7.83-7.79 (m, 3H; H$_{Ar}$), 7.55-7.47 (m, 3H; H$_{Ar}$), 5.52 (s, 2H; CH$_2$), 2.13 (s, 3H; CH$_3$); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 170.4 (CO), 133.7 (C$_{Ar}$), 132.4 (C$_{Ar}$), 132.0 (C$_{Ar}$), 129.0 (C$_{Ar}$), 128.9 (C$_{Ar}$), 127.8 (C$_{Ar}$), 127.8 (C$_{Ar}$), 127.5 (C$_{Ar}$), 126.8 (C$_{Ar}$), 126.3 (C$_{Ar}$), 68.0 (CH$_2$), 21.2 (2CH$_3$); GC-MS (EI): m/z (%): 232, 173, 160 (100), 128, 115, 43, 28.

(thiophen-2-ylthio)methyl acetate(2r)

Light yellow oil, 50 mg (53% yield); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.26-6.97 (m, 3H; 3CH), 5.17 (s, 2H; CH$_2$), 2.13 (s, 3H; CH$_3$); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 170.2 (CO), 135.6 (CH), 132.9 (CH), 130.8 (CH), 116.0 (CH), 70.4 (CH$_2$), 21.2 (CH$_3$); GC-MS (EI): m/z (%): 188, 158, 116,
(decylthio)methyl acetate\(2s\)

Light yellow oil, 39 mg (32% yield); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 5.14 (s, 2H; CH\(_2\)), 2.66 (t, \(J = 7.6\) Hz, 2H; CH\(_2\)), 2.08 (s, 3H; CH\(_3\)), 1.66-1.58 (m, 2H; CH\(_2\)), 1.26 (m, 14H; CH\(_2\)), 0.87 (t, \(J = 7.2\) Hz, 3H; CH\(_3\)); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): \(\delta\) 170.8 (CO), 66.8 (CH\(_2\)), 32.5 (CH\(_2\)), 32.0 (CH\(_2\)), 29.89 (CH\(_2\)), 29.7 (CH\(_2\)), 29.6 (CH\(_2\)), 29.4 (CH\(_2\)), 28.8 (CH\(_2\)), 22.8 (CH\(_2\)), 21.2 (CH\(_3\)), 14.2 (CH\(_3\)); GC-MS (EI): m/z (%): 246, 216, 185, 171, 157, 143, 129, 115, 101, 87, 73, 65, 43 (100), 29.

1-(methylthio)-2-oxo-2-phenylethyl acetate\(2t\)

Light yellow oil, 65 mg (58% yield); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.00 (d, \(J = 8.0\) Hz, 2H; H\(_{Ar}\)), 7.57 (t, \(J = 8.0\) Hz, 1H; H\(_{Ar}\)), 7.45 (t, \(J = 8.0\) Hz, 2H; H\(_{Ar}\)), 6.83 (s, 1H; CH), 2.19 (s, 3H; CH\(_3\)), 2.08 (s, 3H; CH\(_3\)); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): \(\delta\) 188.8 (CO), 170.2 (CO), 133.8 (C\(_{Ar}\)), 133.8 (C\(_{Ar}\)), 128.7 (C\(_{Ar}\)), 128.7 (C\(_{Ar}\)), 75.2 (CH), 20.8 (CH\(_3\)), 11.6 (CH\(_3\)); GC-MS (EI): m/z (%): 224, 196, 178, 137, 105 (100), 77, 43; HRMS (ES+) exact mass calculated for [M+Na\(^+\)] (C\(_{11}\)H\(_{12}\)O\(_3\)S) requires m/z 247.0405, found m/z 247.0399.

4. Scope of hypervalent iodine (III) reagents derivatives

4.1 Characterization of the product

(phenylthio)methyl propionate\(3a\)a)

Light yellow solid, 54 mg (55% yield); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.38 (d, \(J = 8.0\) Hz, 2H;
HAr), 7.25-7.18 (m, 3H; HAr), 5.35 (s, 2H; CH2), 2.30 (q, J = 8.0 Hz, 2H; CH2), 1.08 (t, J = 8.0 Hz, 3H; CH3); 13C NMR (150 MHz, CDCl3): δ 173.9 (CO), 134.9 (CAr), 130.5 (CAr), 129.2 (CAr), 127.5 (CAr), 68.0 (CH2), 27.8 (CH2), 9.0 (CH3); GC-MS (EI): m/z (%): 196, 166, 123, 110, 77, 57 (100), 29; HRMS (ES+) exact mass calculated for [M+Na]+ (C10H12O2S) requires m/z 219.0456, found m/z 219.0446.

(phenylthio)methyl pivalate(3ab)

Light yellow solid, 90 mg (80% yield); 1H NMR (400 MHz, CDCl3): δ 7.39 (d, J = 8.0 Hz, 2H; HAr), 7.24-7.19 (m, 3H; HAr), 5.33 (s, 2H; CH2), 1.13 (s, 9H; CH3); 13C NMR (150 MHz, CDCl3): δ 177.8 (CO), 135.0 (CAr), 130.7 (CAr), 129.2 (CAr), 127.5 (CAr), 68.3 (CH2), 38.9 (C), 27.1 (CH3); GC-MS (EI): m/z (%): 224, 194, 123, 110, 85, 57 (100), 41, 28; HRMS (ES+) exact mass calculated for [M+Na]+ (C12H16O2S) requires m/z 247.0769, found m/z 247.0760.

(phenylthio)methyl tetradecanoate(3ac)

Light yellow solid, 103 mg (59% yield); 1H NMR (400 MHz, CDCl3): δ 7.47 (d, J = 8.0 Hz, 2H; HAr), 7.36-7.27 (m, 3H; HAr), 5.44 (s, 2H; CH2), 2.36 (t, J = 8.0 Hz, 2H; CH2), 1.66-1.60 (m, 2H; CH2), 1.34-1.27 (m, 20H; CH2), 0.90 (t, J = 8.0 Hz, 3H; CH3); 13C NMR (150 MHz, CDCl3): δ 173.1 (CO), 134.9 (CAr), 130.3 (CAr), 129.1 (CAr), 127.3 (CAr), 67.8 (CH2), 34.4 (CH2), 32.0 (CH2), 29.7 (CH2), 29.72 (2CH2), 29.66 (CH2), 29.5 (CH2), 29.4 (CH2), 29.3 (CH2), 29.1 (CH2), 24.9 (CH2), 22.8 (CH2), 14.2 (CH3); GC-MS (EI): m/z (%): 350, 211 (100), 123, 95, 71, 43, 27.

(phenylthio)methyl benzoate(3ad)

Light yellow oil, 89 mg (77% yield); 1H NMR (400 MHz, CDCl3): δ 8.09 (d, J = 7.6 Hz, 2H; HAr), 7.61-7.54 (m, 3H; HAr), 7.46 (t, J = 8.0 Hz, 2H; HAr), 7.38-7.34 (m, 3H; HAr), 5.69 (s, 2H; CH2); 13C NMR (150 MHz, CDCl3): δ 165.9 (CO), 134.8 (CAr), 133.4 (CAr), 130.7 (CAr), 129.8 (CAr), 129.7 (CAr), 129.2 (CAr), 128.5 (CAr), 127.5 (CAr), 68.9 (CH2); GC-MS (EI): m/z (%): 244, 214, 123, 105 (100), 77, 51.

(((4-cyanophenyl)thio)methyl pivalate (3eb)
Light yellow oil, 50 mg (40% yield); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.56 (d, $J$ = 8.0 Hz, 2H; $H_{Ar}$), 7.47 (d, $J$ = 8.0 Hz, 2H; $H_{Ar}$), 5.47 (s, 2H; CH$_2$), 1.17 (s, 9H; 3CH$_3$); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 177.4 (CO), 142.5 (CAr), 132.5 (CAr), 128.2 (CAr), 118.5 (CAr), 109.9 (CN), 65.7 (CH$_2$), 38.9 (C), 26.9 (CH$_3$); GC-MS (EI): $m/z$ (%): 249, 219 204, 191, 176, 163, 148, 134, 85, 75, 57(100), 41, 29.

((4-nitrophenyl)thio)methyl pivalate(3fb)

Light yellow oil, 65 mg (51% yield); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.15 (d, $J$ = 8.0 Hz, 2H; $H_{Ar}$), 7.51 (d, $J$ = 8.0 Hz, 2H; $H_{Ar}$), 5.52 (s, 2H; CH$_2$), 1.19 (s, 9H; 3CH$_3$); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 177.5 (CO), 146.2 (CAr), 145.2 (CAr), 127.8 (CAr), 124.2 (CAr), 65.5 (CH$_2$), 39.0 (C), 27.0 (CH$_3$); GC-MS (EI): $m/z$ (%): 269, 253, 239,168, 121, 85, 77, 69, 57(100), 41, 29.

5. Mechanism detecting experiment

A solution of thioanisole 1a (0.1 mmol), tetrabutylammonium bromide and (TBABr, 0.3 mmol, 3.0 equiv) and Phl(OAc)$_2$ (1.75 equiv) was added in CDCl$_3$ (0.4 mL). From the $^{13}$C NMR, we can clearly observe the existing of the AcOH, which can strongly prove the rationality of the mechanism.

6. References

7. NMR Spectra for all the compounds

Iodobenzene dipropionate(3a)
Iodobenzene Dipivalate(3b)
Iodobenzene ditetradecanoate(3c)
Iodobenzene Dibenzoate(3d)
2-(methylthio)-1-phenylethan-1-one(1v)
(phenylthio)methyl acetate (2a)
((4-fluorophenyl)thio)methyl acetate(2b)
((4-chlorophenyl)thio)methyl acetate(2c)
((4-bromophenyl)thio)methyl acetate (2d)
((4-nitrophenyl)thio)methyl acetate(2f)
((4-formylphenyl)thio)methyl acetate (2g)
(p-tolylthio)methyl acetate(2h)
((4-methoxyphenyl)thio)methyl acetate (2i)
((2-fluorophenylthio)methyl acetate(2j))
((3-fluorophenyl)thio)methyl acetate (2k)
phenyl(phenylthio)methyl acetate (2l)
1-(phenylthio)allyl acetate (2m)
1-(phenylthio)prop-2-yn-1-yl acetate(2n)
methyl 2-acetoxy-2-(phenylthio)acetate(2o)
11-oxo-6,11-dihydrodibenzo[b,e]thiepin-6-yl acetate(2p)
(naphthalen-2-ylthio)methyl acetate (2q)
(thiophen-2-ylthio)methyl acetate (2r)
(decylthio)methyl acetate(2s)
1-(methylthio)-2-oxo-2-phenylethyl acetate(2t)
(phenylthio)methyl propionate (3aa)
(phenylthio)methyl pivalate(3ab)
(phenylthio)methyl tetradecanoate(3ac)
(phenylthio)methyl benzoate (3ad)
((4-nitrophenyl)thio)methyl pivalate(3fb)
$^{13}$C NMR of mechanism detecting experiment

AcOH(CO)