Autoinductive Thiolation/Oxygenation of Alkenes at Room Temperature

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General information

All reactions were run under a dry air atmosphere with a dry air balloon fitted on a Schlenk tube. All glassware was oven dried at 110 °C for hours and cooled down under vacuum. All the solvents were purified according to the solvents handbook. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. α-Bromostyrene derivatives and α-chlorostyrene derivatives were all prepared following literature procedures. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (bp. 60-90 °C). GC-MS spectra were recorded on a Varian GC-MS 3900-2100T or a Varian GCMS-QP2010SE. EPR spectra were recorded on a Bruker A-200 spectrometer. GC yields were recorded with a Varian GC 3900 gas chromatography instrument with a FID detector. IR spectra were recorded on a Mettler Toledo React IR TM 15 spectrometer using a diamond comb. All new compounds were characterized by ¹H NMR, ¹³C NMR and HRMS. The known compounds were characterized by ¹H NMR, ¹³C NMR. ¹H and ¹³C NMR data were recorded with ADVANCE III 400 MHz with tetramethylsilane as an internal standard. High resolution mass spectra (HRMS) were measured with a Waters Micromass GCT instrument. All chemical shifts (δ) were reported in ppm and coupling constants (J) in Hz. All chemical shifts were reported relative to tetramethylsilane (0 ppm for ¹H), CD₃OD (3.31 ppm for ¹H), and CDCl₃ (77.16 ppm for ¹³C), respectively.

Experimental section

1) Impact of reaction parameters

Table S1. Impact of Reaction Parameters

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<tr>
<td>2</td>
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<tr>
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<td>4</td>
<td>MeCN</td>
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<tr>
<td>5</td>
<td>Toluene</td>
<td>1 atm of air</td>
<td>71</td>
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<tr>
<td>6</td>
<td>DMSO</td>
<td>1 atm of air</td>
<td>87</td>
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</tbody>
</table>
7  NMP       1 atm of air     74
8  H₂O       1 atm of air     69
9  DMF/H₂O (1:1) 1 atm of air     58
10 DMF       1 atm of air     89
11 DMF       1 atm of air     26d
12 DMF       1 atm of O₂     93
13 DMF       1 atm of N₂     trace
14 DMF       1 atm of air     93 (83)\

*Unless otherwise specified, all reactions were carried out using 1a (0.2 mmol), 2a (0.6 mmol), in solvent (4.0 mL) at room temperature for 1 h. b Yield was determined by 1H NMR analysis using diphenylmethane as internal standard, isolated yield in parenthesis. c 2a (0.4 mmol). d 2a (0.2 mmol). DMF (2.0 mL).

2) Procedure and analytical data of compounds 3aa-3ga.

1-phenyl-2-(p-tolythio)ethan-1-one (3aa)[2a] Typical procedure: To an oven-dried Schlenk tube equipped with a stir bar was added p-toluenethiol (2a, 0.60 mmol), and a balloon filled with dry air was connected to the Schlenk tube through the side arm and purged one time. Then, α-bromostyrene (0.20 mmol), and DMF (2.0 mL) were successively injected in the reaction tube with magnetic stirring. The reaction mixture was allowed to stir vigorously at room temperature in a warm room for 1 h. Thereafter, water was added and the mixture was extracted with ethyl acetate (x 4). The combined organic layers were dried on Na₂SO₄ and concentrated under reduced pressure. The resulting crude product was separated on a silica gel column with petroleum ether and ethyl acetate as eluent to afford the desired product. 1H NMR (400 MHz, CDCl₃) δ 7.92-7.94 (m, 2H), 7.57 (dt, J = 8.8, 1.2 Hz, 1H), 7.45 (t, J = 8.0 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 7.09 (t, J = 7.6 Hz, 2H), 4.21 (s, 2H) 2.31 (s, 3H). 13C NMR (101 MHz, CDCl₃) δ 194.3, 137.7, 135.5, 133.5, 131.7, 130.9, 130.0, 128.8, 128.7, 42.0, 21.2.

1-phenyl-2-(phenylthio)ethan-1-one (3ab):[2a] The synthesis procedure is the same as for 3aa. 1H NMR (400 MHz, CDCl₃) δ 7.93 (d, J = 7.6 Hz, 2H), 7.56 (t, J = 7.2 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 7.38 (d, J = 7.6 Hz, 2H), 7.27 (t, J = 7.4 Hz, 2H), 7.21 (t, J = 7.2 Hz, 1H), 4.27 (s, 2H). 13C NMR (101 MHz, CDCl₃) δ 194.1, 135.4, 134.8, 133.6, 130.5, 129.1, 128.8, 127.2, 41.3.
1-phenyl-2-(m-tolylthio)ethan-1-one (3ac): The synthesis procedure is the same as for 3aa. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.93 (m, 2H), 7.57 (t, $J$ = 7.4 Hz, 1H), 7.45 (t, $J$ = 7.6 Hz, 2H), 7.14-7.20 (m, 3H), 7.02 (d, $J$ = 6.0 Hz, 1H), 4.26 (s, 2H) 2.29 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 194.2, 138.9, 135.5, 134.6, 133.5, 131.2, 129.0, 128.7 (7), 128.7 (5), 128.1, 127.5, 41.3, 21.4. HRMS (ESI+) calculated for C$_{15}$H$_{15}$OS (M+H): 243.0844; found: 243.0842.

![Image of 1-phenyl-2-(m-tolylthio)ethan-1-one (3ac)]

2-((2-methoxyphenyl)thio)-1-phenylethan-1-one (3ad): The synthesis procedure is the same as for 3aa. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.94 (d, $J$ = 7.6 Hz, 2H), 7.56 (t, $J$ = 7.6 Hz, 1H), 7.44 (t, $J$ = 7.2 Hz, 2H), 7.34 (dd, $J$ = 7.6, 0.9 Hz, 1H), 7.25 (t, $J$ = 7.8 Hz, 1H), 6.84-6.89 (m, 2H), 4.22 (s, 2H) 3.83 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 194.6, 158.4, 135.7, 133.4, 132.7, 129.2, 128.7, 128.6 (7), 122.1, 121.1, 110.8, 55.8, 39.6. HRMS (ESI+) calculated for C$_{15}$H$_{15}$O$_2$S (M+H): 259.0793; found: 259.0785.

![Image of 2-((2-methoxyphenyl)thio)-1-phenylethan-1-one (3ad)]

2-((3-methoxyphenyl)thio)-1-phenylethan-1-one (3ae): The synthesis procedure is the same as for 3aa. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.94-7.96 (m, 2H), 7.58 (t, $J$ = 7.4 Hz, 1H), 7.46 (t, $J$ = 7.6 Hz, 2H), 7.19 (t, $J$ = 8.0 Hz, 1H), 6.96 (ddd, $J$ = 7.8, 1.6, 0.6 Hz, 1H), 6.93 (t, $J$ = 2.0 Hz, 1H), 6.76 (ddd, $J$ = 8.0, 2.4, 0.6 Hz, 1H), 4.29 (s, 2H) 3.77 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 194.2, 159.9, 136.2, 135.5, 133.6, 130.0, 128.8 (1), 128.8 (0), 122.4, 115.5, 113.0, 55.4, 41.2. HRMS (ESI+) calculated for C$_{15}$H$_{15}$O$_2$S (M+H): 259.0793; found: 259.0788.

![Image of 2-((3-methoxyphenyl)thio)-1-phenylethan-1-one (3ae)]

2-((4-methoxyphenyl)thio)-1-phenylethanone (3af).$^{2b}$ The synthesis procedure is the same as for 3aa. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.93-7.90 (m, 2H), 7.57 (t, $J$ = 7.4 Hz, 1H), 7.45 (t, $J$ = 7.6 Hz, 2H), 7.35 (d, $J$ = 8.8 Hz, 2H), 6.82 (d, $J$ = 8.8 Hz, 2H), 4.13 (s, 2H) 3.78 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 194.4, 159.8, 135.6, 134.8, 133.4, 128.8, 128.7, 124.6, 114.8, 55.4, 42.9.
2-((4-bromophenyl)thio)-1-phenylethan-1-one (3ag).

The synthesis procedure is the same as for 3aa. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.99-7.89 (m, 2H), 7.58 (t, $J = 7.2$ Hz, 1H), 7.46 (t, $J = 7.6$ Hz, 2H), 7.38 (d, $J = 8.6$ Hz, 2H), 7.24 (d, $J = 8.6$ Hz, 2H), 4.25 (s, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 193.8, 135.3, 133.7, 133.4, 133.3, 130.4, 128.9, 128.8, 41.3.

2-((4-chlorophenyl)thio)-1-phenylethan-1-one (3ah).

The synthesis procedure is the same as for 3aa. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.92-7.95 (m, 2H), 7.59 (t, $J = 7.4$ Hz, 1H), 7.47 (t, $J = 7.6$ Hz, 2H), 7.32 (d, $J = 8.4$ Hz, 2H), 7.24 (d, $J = 8.4$ Hz, 2H), 4.25 (s, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 193.9, 135.3, 133.7, 133.4, 133.3, 132.1, 129.3, 128.9, 128.8, 41.3.

2-((2-fluorophenyl)thio)-1-phenylethan-1-one (3ai).

The synthesis procedure is the same as for 3aa. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.93 (m, 2H), 7.58 (tt, $J = 7.4$, 1.2 Hz, 1H), 7.45 (t, $J = 7.0$ Hz, 2H), 7.40 (dt, $J = 7.6$, 1.2 Hz, 1H), 7.23-7.29 (m, 1H), 7.04-7.09 (m, 2H), 4.25 (s, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 193.9, 162.1 (d, $^1$J$_{CF}$ = 247.2 Hz), 135.4, 133.9 (d, $^4$J$_{CF}$ = 1.3 Hz), 133.6, 129.9 (d, $^3$J$_{CF}$ = 3.7 Hz), 121.3 (d, $^2$J$_{CF}$ = 17.1 Hz), 115.0 (d, $^2$J$_{CF}$ = 22.5 Hz), 40.5 (d, $^4$J$_{CF}$ = 2.7 Hz). HRMS (ESI+) calculated for C$_{14}$H$_{12}$OSF (M+H): 246.0593; found: 247.0591.

2-((3-fluorophenyl)thio)-1-phenylethan-1-one (3aj).

The synthesis procedure is the same as for 3aa. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.96 (d, $J = 8.4$ Hz, 2H), 7.60 (tt, $J = 7.4$, 1.2 Hz, 1H), 7.48 (t, $J = 6.8$ Hz, 2H), 7.24 (ddd, $J = 8.0$, 8.0, 2.0 Hz, 1H), 7.14 (ddd, $J = 7.6$, 1.6, 0.8 Hz, 1H), 7.14 (dt, $J = 6.8$ Hz, 2H).
$J = 9.2, 2.4$ Hz, 1H), 6.90 (ddt, $J = 8.4, 2.4, 0.8$ Hz, 1H), 4.32 (s, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 193.7, 162.8 (d, $^1J_{CF} = 249.4$ Hz), 137.4 (d, $^2J_{CF} = 7.9$ Hz), 135.3, 133.8, 130.4 (d, $^3J_{CF} = 8.6$ Hz), 128.9, 128.8, 125.3 (d, $^4J_{CF} = 3.0$ Hz), 116.6 (d, $^5J_{CF} = 23.2$ Hz), 113.9 (d, $^6J_{CF} = 21.3$ Hz), 40.8. HRMS (ESI+) calculated for C$_{14}$H$_{12}$OSF (M+H): 246.0593; found: 247.0587.

2-((4-fluorophenyl)thio)-1-phenylethan-1-one (3ak). The synthesis procedure is the same as for 3aa. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.91-7.93 (m, 2H), 7.59 (tt, $J = 7.2, 0.9$ Hz, 1H), 7.46 (t, $J = 7.6$ Hz, 2H), 7.36-7.41 (m, 2H), 6.98 (tt, $J = 8.6, 2.0$ Hz, 2H), 4.20 (s, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 194.1, 162.6 (d, $^1J_{CF} = 248.9$ Hz), 135.4, 134.1 (d, $^2J_{CF} = 8.3$ Hz), 133.7, 129.5 (d, $^3J_{CF} = 3.4$ Hz), 128.8, 116.4 (d, $^4J_{CF} = 22.0$ Hz), 42.2.

1-phenyl-2-((4-(trifluoromethyl)phenyl)thio)ethan-1-one (3al). The synthesis procedure is the same as for 3aa. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.97 (d, $J = 7.2$ Hz, 2H), 7.61 (tt, $J = 7.2, 0.9$ Hz, 1H), 7.47-7.53 (m, 4H), 7.43 (d, $J = 8.4$ Hz, 2H), 4.37 (s, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 193.5, 140.5, 135.2, 134.0, 129.0, 128.9, 128.6, 128.5 (q, $^2J_{CF} = 32.8$ Hz), 125.9 (q, $^3J_{CF} = 3.8$ Hz), 124.1 (q, $^4J_{CF} = 272.9$ Hz), 39.9. HRMS (ESI+) calculated for C$_{14}$H$_{12}$SOF (M+H): 297.0561; found: 297.0554.

1-phenyl-2-(thiophen-2-ythio)ethan-1-one (3am). The synthesis procedure is the same as for 3aa. $^1$H NMR (400 MHz, CD3OD) δ 7.92-7.94 (m, 2H), 7.58-7.63 (m, 1H), 7.45-7.50 (m, 3H), 7.08 (dd, $J = 3.6, 0.8$ Hz, 1H), 6.96 (dd, $J = 5.2, 3.6$ Hz, 1H), 4.22 (s, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 194.0, 135.5, 133.6, 132.2, 130.8, 128.8, 128.7, 127.8, 45.5. HRMS (ESI+) calculated for C$_{12}$H$_{13}$S$_2$O (M+H): 235.0251; found: 235.0238.
1-phenyl-2-(thiophen-2-ylthio)ethan-1-one (3ba). The synthesis procedure is the same as for 3aa. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.68 (dd, \(J = 4.0, 1.2\) Hz, 1H), 7.65 (dd, \(J = 5.0, 1.0\) Hz, 1H), 7.32 (d, \(J = 8.0\) Hz, 2H), 7.08-7.12 (m, 3H), 4.09 (s, 2H), 2.31 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 187.6, 142.6, 137.8, 134.4, 133.0, 131.7, 130.9, 130.0, 128.3, 42.5, 21.2.

1-(2-methoxyphenyl)-2-(p-tolylthio)ethan-1-one (3ca). The synthesis procedure is the same as for 3aa. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.71 (dd, \(J = 7.6, 1.2\) Hz, 1H), 7.45 (ddd, \(J = 8.4, 7.6, 2.0\) Hz, 1H), 7.22 (d, \(J = 8.4\) Hz, 2H), 7.04 (d, \(J = 8.0\) Hz, 2H), 7.00 (dt, \(J = 7.6, 0.8\) Hz, 1H), 6.93 (d, \(J = 8.4\) Hz, 1H), 4.26 (s, 2H), 3.86 (s, 3H), 2.28 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 196.2, 158.6, 136.8, 134.1, 131.8, 131.3, 130.7, 129.7, 126.3, 120.9, 111.5, 55.6, 46.4, 21.1. HRMS (ESI+) calculated for C\(_{16}\)H\(_{17}\)SO\(_2\) (M+H): 273.0949; found: 273.0946.

1-[(1,1'-biphenyl)-4-yl]-2-(p-tolylthio)ethan-1-one (3da). The synthesis procedure is the same as for 3aa. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.00 (d, \(J = 8.4\) Hz, 2H), 7.66 (d, \(J = 8.4\) Hz, 2H), 7.61 (d, \(J = 7.2\) Hz, 2H), 7.47 (t, \(J = 7.2\) Hz, 2H), 7.40 (tt, \(J = 7.2, 0.9\) Hz, 1H), 7.31 (d, \(J = 8.0\) Hz, 2H), 7.09 (d, \(J = 8.0\) Hz, 2H), 4.22 (s, 2H), 2.31 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 193.9, 146.1, 139.8, 137.6, 134.1, 131.6, 130.9, 130.0, 129.4, 129.1, 128.4, 127.4, 41.9, 21.2. HRMS (ESI+) calculated for C\(_{21}\)H\(_{19}\)SO (M+H): 319.1157; found: 319.1150.

1-(naphthalen-2-yl)-2-(p-tolylthio)ethan-1-one (3ea). The synthesis procedure is the same as for 3aa. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.38 (s, 1H), 7.99 (dd, \(J = 8.6, 1.8\) Hz, 1H), 7.89 (t, \(J = 6.8\) Hz,
2H), 7.86 (d, J = 5.6 Hz, 1H), 7.60 (ddd, J = 8.0, 6.8, 0.9 Hz, 1H), 7.54 (ddd, J = 8.0, 6.8, 0.9 Hz, 1H), 7.31 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 4.32 (s, 2H), 2.30 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 194.3, 137.7, 135.7, 132.8, 132.5, 131.8, 131.0, 130.7, 130.0, 129.7, 128.8, 128.6, 127.9, 126.9, 124.3, 42.1, 21.2. HRMS (ESI+) calculated for C19H17SO (M+H): 293.1000; found: 293.0997.

1-phenyl-2-(p-tolylthio)propan-1-one (3fa). The synthesis procedure is the same as for 3aa. 1H NMR (400 MHz, CDCl3) δ 7.95-7.97 (m, 2H), 7.55 (d, J = 7.4 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 4.55 (q, J = 6.8 Hz, 2H), 2.32 (s, 3H). 1H NMR (101 MHz, CDCl3) δ 196.2, 139.1, 135.8, 135.3, 133.1, 129.8, 128.7, 128.6, 127.7, 46.2, 21.3, 16.9.

2-(p-tolylthio)-3,4-dihydronaphthalen-1(2H)-one (3ga). The synthesis procedure is the same as for 3aa. 1H NMR (400 MHz, CDCl3) δ 8.05 (dd, J = 8.0, 0.8 Hz, 1H), 7.48 (dt, J = 7.4, 0.9 Hz, 1H), 7.38 (d, J = 8.0 Hz, 2H), 7.32 (t, J = 7.6 Hz, 1H), 7.23 (d, J = 7.6 Hz, 1H), 7.12 (d, J = 7.6 Hz, 2H), 4.02 (dd, J = 6.2, 4.2 Hz, 1H), 3.26 (ddd, J = 16.8, 9.6, 4.4 Hz, 1H), 2.89 (dt, J = 17.2, 5.0 Hz, 1H), 2.43-2.52 (m, 1H), 2.29-2.36 (m, 4H). 13C NMR (101 MHz, CDCl3) δ 193.4, 143.1, 138.3, 133.8, 133.7, 131.5, 130.0, 129.2, 128.8, 128.3, 127.0, 54.0, 29.2, 26.6, 21.3. HRMS (ESI+) calculated for C19H17SO (M+H): 269.0922; found: 269.1001.

1-(p-tolyl)-2-(p-tolylthio)ethan-1-one (3ha). Typical procedure: To an oven-dried Schlenk tube equipped with a stir bar was added p-toluenethiol (2a, 0.80 mmol), and a balloon filled with dry air was connected to the Schlenk tube through the side arm and purged one time. Then, 1-(1-chlorovinyl)-4-methylbenzene (0.20 mmol), and DMF (2.0 mL) were successively injected in
the reaction tube with magnetic stirring. The reaction mixture was allowed to stir vigorously at room temperature in a warm room for 1 h. Thereafter, water was added and the mixture was extracted with ethyl acetate (x 4). The combined organic layers were dried on Na₂SO₄ and concentrated under reduced pressure. The resulting crude product was separated on a silica gel column with petroleum ether and ethyl acetate as eluent to afford the desired product. ¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H), 4.19 (s, 2H), 2.41 (s, 3H), 2.31 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 194.0, 144.4, 137.5, 133.0, 131.0, 130.0, 129.5, 128.9, 41.9, 21.8, 21.2. HRMS (ESI+) calculated for C₁₆H₁₇SO (M+H): 257.1000; found: 257.1000.

1-(4-bromophenyl)-2-(p-tolylthio)ethan-1-one (3ia). The synthesis procedure is the same as for 3ha. ¹H NMR (400 MHz, CDCl₃) δ 7.78 (d, J = 8.4 Hz, 2H), 7.59 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H), 7.09 (d, J = 8.4 Hz, 2H), 4.14 (s, 2H), 2.31 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 193.3, 137.9, 134.2, 132.1, 131.9, 130.4, 130.3, 130.0, 128.7, 41.8, 21.2. HRMS (ESI+) calculated for C₁₅H₁₄OSBr (M+H): 320.9949; found: 320.9944.

1-(4-chlorophenyl)-2-(p-tolylthio)ethan-1-one (3ja). The synthesis procedure is the same as for 3ha. ¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 7.6 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 4.15 (s, 2H), 2.32 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 193.1, 140.0, 138.0, 133.8, 131.9, 130.5, 130.3, 130.1, 129.1, 41.8, 21.3. HRMS (ESI+) calculated for C₁₅H₁₄OSOCl (M+H): 277.0454; found: 277.0454.

2-(p-tolylthio)-1-(4-(trifluoromethyl)phenyl)ethan-1-one (3ka). The synthesis procedure is the same as for 3ha. ¹H NMR (400 MHz, CDCl₃) δ 8.02 (d, J = 8.4 Hz, 2H), 7.71 (d, J = 8.4 Hz, 2H),
7.27 (d, $J = 8.0$ Hz, 2H), 7.10 (d, $J = 8.0$ Hz, 2H), 4.18 (s, 2H), 2.32 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 193.3, 138.2, 134.7 (q, $^{2}J_{CF} = 32.7$ Hz), 132.1, 130.1, 129.2, 125.8 (q, $^{3}J_{CF} = 3.7$ Hz), 123.7 (q, $^{1}J_{CF} = 273.6$ Hz), 42.0, 21.3. HRMS (ESI+) calculated for C$_{16}$H$_{14}$SO$_{3}$ (M+H): 311.0717; found: 311.0709.

3) Labeling experiments.

Typical procedure for labeling experiment: An oven-dried Schlenk tube equipped with a stir bar were capped by septa for injections and a three way cock which was connected to a nitrogen line and a balloon filled with $^{18}$O$_2$ respectively. After evacuation under vacuum and flushing with N$_2$ for one time, p-toluenethiol (2a, 0.60 mmol) and DMF (2.0 mL) was quickly added under N$_2$, and the reaction mixture was degassed the air by the method of freeze-pump-thaw cycle for 4 times. Then, $^{18}$O$_2$ was purged one time, $\alpha$-Bromostyrene (0.20 mmol) was further injected into the reaction tube with magnetic stirring. The reaction mixture was vigorous stirred at RT (warm room) for 1 h. Thereafter, the reaction mixture was analyzed by GC-MS and was further separated on a silica gel column with petroleum ether and ethyl acetate as eluent to afford the desired product in 80% yield.

The EI-MS spectral of 3aa'
The relative intensity of m/z 244 and m/z 242 are 45120 and 31729 respectively.

Typical procedure for labeling experiment: To an oven-dried Schlenk tube equipped with a stir bar was added p-toluenethiol (2a, 0.60 mmol), and a balloon filled with dry air was connected to the Schlenk tube through the side arm and purged one time. Then, α-bromostyrene (0.20 mmol), and DMF (2.0 mL) were successively injected in the reaction tube with magnetic stirring. The reaction mixture was allowed to stir vigorously at RT in a warm room for 1 h. Thereafter, H$_2$O$_{18}$ (20 eq.) was added and the mixture was allowed to stir for another 1 h. After completion, the reaction mixture was analyzed by GC-MS and was further separated on a silica gel column with petroleum ether and ethyl acetate as eluent to afford the desired product in 79% yield.

The EI-MS spectral of 3aa'

4) EPR experiments.

EPR spectra was recorded at 298 K on EPR spectrometer operated at 9.4158 GHz. Typical spectrometer parameters are shown as follows, scan range: 100 G; center field set: 3359.8 G; time constant: 163.84 ms; scan time: 30.72 s; modulation amplitude: 1.0 G; modulation frequency: 100 kHz; receiver gain: 1.00x105; microwave power: 19.05 mW.

4.1 The interaction between 1a (α-bromostyrene) / 2a (p-toluenethiol) was investigated by electron paramagnetic resonance (EPR) (X band, 9.4GHz, RT): (1) To an oven-dried Schlenk tube equipped with a stir bar was added p-toluenethiol (2a, 0.30 mmol), the Schlenk tube through
the side arm and purged one time. Then, DMF (2.0 mL) were successively injected in the reaction tube with magnetic stirring. The reaction mixture was allowed to stir vigorously at room temperature in a warm room for 15 minutes. Thereafter, 10 uL of DMPO (5,5-dimethyl-1-pyrroline N-oxide) was added and well mixed. Afterwards, 20 uL of the mixture was quickly taken out into a small tube and analyzed by EPR. (2) An oven-dried Schlenk tube equipped with a stir bar was evacuated under vacuum and flushed with air through a dry air balloon for one times. Then, 1a (0.1 mmol) and DMF (2.0 mL) were successively injected in the reaction tube with magnetic stirring. The reaction mixture was allowed to stir vigorously at room temperature in a warm room for 15 minutes. Thereafter, 10 uL of DMPO (5,5-dimethyl-1-pyrroline N-oxide) was added and well mixed. Afterwards, 20 uL of the mixture was quickly taken out into a small tube and analyzed by EPR.

Figure S1. DMPO spin trapping of radical formed from  
(a) 2a (0.30 mmol) in DMF (2.0 mL) at RT under 1 atm of air (balloon), (b) 1a (0.10 mmol) in DMF (2.0 mL) at RT was monitored by electron paramagnetic resonance (EPR) (X band, 9.4GHz, RT).

4.2 Comparison of DMPO-radical adduct formed from the interaction between 2a and air with the DMPO-thiyl radical adduct.

4.2.1 The generation of the DMPO-thiyl radical adduct from the reaction between 2a and AIBN under N₂: (1) An oven-dried Schlenk tube equipped with a stir bar were capped by septa for injections and a nitrogen line, after evacuation under vacuum and flushing with N₂ for one time. Then, p-toluenethiol (2a, 0.30 mmol) and DMF (2.0 mL) was quickly added under N₂, and the reaction mixture was degassed the air by the method of freeze-pump-thaw cycle for 2 times. Subsequently, AIBN (azodisobutyronitrile, 0.10 mmol) was added under N₂ and the reaction mixture was degassed the air by the method of freeze-pump-thaw cycle for 3 times. The reaction mixture was allowed to stir vigorously at 70 °C for 15 minutes. Thereafter, 10 uL of DMPO (5,5-dimethyl-1-pyrroline N-oxide) was added and well mixed. Afterwards, 20 uL of the mixture was quickly taken out into a small tube and analyzed by EPR.
Figure S2. Comparison of the DMPO-radical adducts formed from (a) 2a (0.30 mmol) in DMF (2.0 mL) at RT under 1 atm of air (balloon), (b) 2a (0.30 mmol) and AIBN (0.1 mmol) in DMF (2.0 mL) at 70 °C was monitored by electron paramagnetic resonance (EPR) (X band, 9.4GHz, RT).

4.2.2 Blank control experiments.

(1) The interaction between 2a (p-toluenethiol) and DMF under N₂: An oven-dried Schlenk tube equipped with a stir bar were capped by septa for injections and a nitrogen line, after evacuation under vacuum and flushing with N₂ for one time. Then, p-toluenethiol (2a, 0.30 mmol) and DMF (2.0 mL) was quickly added under N₂, and the reaction mixture was degassed the air by the method of freeze-pump-thaw cycle for 4 times. The reaction mixture was allowed to stir vigorously at 70 °C for 15 mintues. Thereafter, 10 uL of DMPO (5,5-dimethyl-1-pyrroline N-oxide) was added and well mixed. Afterwards, 20 uL of the mixture was quickly taken out into a small tube and analyzed by EPR.

Figure S3. DMPO spin trapping of radical formed from 2a (0.30 mmol) in degassed DMF (2.0 mL) at 70 °C under N₂.

(2) The interaction between AIBN and DMF under N₂: An oven-dried Schlenk tube equipped with a stir bar were capped by septa for injections and a nitrogen line, after evacuation under vacuum and flushing with N₂ for one time. Then, AIBN (2a, 0.10 mmol) and DMF (2.0 mL) was quickly added under N₂, and the reaction mixture was degassed the air by the method of freeze-pump-thaw cycle for 4 times. The reaction mixture was allowed to stir vigorously at 70 °C for 15 mintues. Thereafter, 10 uL of DMPO (5,5-dimethyl-1-pyrroline N-oxide) was added and well mixed. Afterwards, 20 uL of the mixture was quickly taken out into a small tube and analyzed by EPR.
5) ReactIR experiments.

5.1 The interaction between 1a (α-bromostyrene) / 2a (p-toluenethiol) and air was explored by operando IR: an oven-dried three-necked reaction vessel was equipped with a stir bar, the operando IR probe was inserted through an adapter into the middle neck, the other two necks were capped by septa for injections and a nitrogen line, after evacuation under vacuum and flushing with air through a dry air balloon for three times. At room temperature, THF (4.0 mL) was added to the vessel via a springe and the reaction was monitored by operando IR. Afterwards, 1a (0.2 mmol) or 2a (0.6 mmol) was added and the reaction mixture was allowed to stir vigorously at room temperature for 1 h.

The kinetic profiles of the reactions:

Figure S5. (A) The kinetic profile of the reaction of 1a (0.20 mmol) in THF (4.0 mL) at RT for 1 h under 1 atm of air (balloon). (B) The kinetic profile of the reaction of 2a (0.60 mmol) in THF (4.0 mL) at RT for 1 h under 1 atm of air (balloon).
Figure S6. The Characteristic IR band of the different species (in THF).

5.2.1 The model reaction between 1a and 2a under argon was monitored by operando IR: an oven-dried three-necked reaction vessel was equipped with a stir bar, the operando IR probe was inserted through an adapter into the middle neck, the other two necks were capped by septa for injections and a argon line, after evacuation under vacuum and flushing with argon for three times. At room temperature, degassed THF (4.0 mL) was added to the vessel via a springe and the reaction was monitored by operando IR. Afterwards, 1a (0.2 mmol) or 2a (0.6 mmol) was added and the reaction mixture was allowed to stir vigorously at room temperature for 1 h.

5.2.2 The model reaction between 1a and 2a in the presence of dioxygen was monitored by operando IR: an oven-dried three-necked reaction vessel was equipped with a stir bar, the operando IR probe was inserted through an adapter into the middle neck, the other two necks were capped by septa for injections and dry air balloon, after evacuation under vacuum and flushing with air through the dry air balloon for three times. At room temperature, THF (4.0 mL) was added to the vessel via a springe and the reaction was monitored by operando IR. Afterwards, 1a (0.2 mmol) and 2a (0.6 mmol) were added and the reaction mixture was allowed to stir vigorously at room temperature for 1 h. Thereafter, the mixture was analyzed by GC, 3aa was obtained in 85% yield, and the conversions of 1a and 2a were 99% and 97% respectively. Additionally, aryl disulfide 4a was obtained in 0.187 mmol, which is approximately equal to the expected β-keto sulfide 3aa.

The kinetic profiles of the reactions:
Figure S7. The kinetic profile of the reaction of 1a (0.20 mmol) and 2a (0.60 mmol) in THF (4.0 mL) at RT for 1 h. (A) Under argon atmosphere. (B) Under 1 atm of air (balloon).

Figure 8. The Characteristic IR band of the desired product 3aa (in THF).

6) Diaryl disulfide as the starting material.

\[
\begin{align*}
\text{Br} \quad \text{Ph} & \quad \text{S} \quad \text{S} \quad \text{Ph} \\
1a & \quad 4a
\end{align*}
\]

\[
\xymatrix{
Br \quad \text{Ph} & \quad \text{S} \quad \text{S} \quad \text{Ph} \\
1a & \quad 4a
}
\]

Typical procedure: To an oven-dried Schlenk tube equipped with a stir bar was added aryl disulfide (4a, 0.15 mmol), and a balloon filled with dry air was connected to the Schlenk tube through the side arm and purged one time. Then, α-bromostyrene (0.10 mmol) and DMF (1.0 mL) were successively injected in the reaction tube with magnetic stirring. The reaction mixture was allowed to stir vigorously at room temperature in a warm room for 1 h. Thereafter, 3aa was not detected by GC-MS analysis, and 97% of 4a was recovered by GC analysis.

References

NMR Spectra of Products
S22
S30
S39