Electronic Supplementary Information:

Efficient Bromination of Olefins, Alkynes, and Ketones with Dimethyl Sulfoxide and Hydrobromic Acid

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(A) General Remarks

All commercially available compounds were purchased from Sigma-Aldrich, Alfa-Aesar, Acros, Beijing Ouhe and Beijing Chemical Works, Ltd. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Analysis of crude reaction mixture was done on an Agilent 7890 GC System with an Agilent 5975 Mass Selective Detector. Products were purified by flash chromatography on silica gel. $^1$H-NMR spectra were recorded on Bruker AVANCE III-400 spectrometers. Chemical shifts (in ppm) were referenced TMS in CDCl$_3$ (0 ppm). $^{13}$C-NMR spectra were obtained by using the same NMR spectrometers and were calibrated with CDCl$_3$ ($\delta = 77.00$ ppm). Mass spectra were recorded using a PE SCLEX QSTAR spectrometer. High resolution mass spectra were obtained with a Bruker APEX IV Fourier transform ion cyclotron resonance mass spectrometer.

(B) Experimental Procedure and Characterization Data of Products

Typical procedure for dibromination of olefins and alkynes: Olefin 1 or alkyne 6 (0.5 mmol) and DMSO (43 $\mu$L, 0.6 mmol) were dissolved in EA (2 mL). Aqueous hydrobromic acid (48%, 202 mg, 1.2 mmol) was added to the solution at 60 $^\circ$C and the mixture were stirred for 0.5 h under air at that temperature. After cooling down to room temperature and concentrating in vacuum, the residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate) to afford the dibrominated product 3 or 7.

2-(1,2-Dibromoethyl)naphthalene (3a)$^{[1]}$

The reaction of 2-vinyl naphthalene 1a (77.1 mg, 0.5 mmol), DMSO (43 $\mu$L, 0.6 mmol), and aqueous hydrobromic acid (48%, 202 mg, 1.2 mmol) in EA (2 mL) at 60 $^\circ$C for 0.5 h, affords 125.4 mg (80%) of 3a as a white solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.89–7.83 (m, 4H), 7.53–7.50 (m, 3H), 5.33 (dd, $J = 8.8$, 7.2 Hz, 1H), 4.16–4.13 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 135.7, 133.5, 132.9, 129.1, 128.2, 127.8, 127.4, 126.9, 126.7, 124.4, 51.3, 34.8.

(1,2-Dibromoethyl)benzene (3b)$^{[2]}$

The reaction of styrene 1b (52.1 mg, 0.5 mmol), DMSO (43 $\mu$L, 0.6 mmol), and aqueous hydrobromic acid (48%, 202 mg, 1.2 mmol) in
EA (2 mL) at 60 °C for 0.5 h, affords 93.6 mg (71%) of 3b as a white solid. 1H NMR (400 MHz, CDCl3) δ 7.38–7.31 (m, 5H), 5.13 (dd, J = 10.4, 5.6 Hz, 1H), 4.08–3.98 (m, 2H). 13C NMR (100 MHz, CDCl3) δ 138.6, 129.1, 128.8, 127.6, 50.9, 35.0.

1-Bromo-4-(1,2-dibromoethyl)benzene (3c)[3]

The reaction of 1-bromo-4-vinylbenzene 1c (91.5 mg, 0.5 mmol), DMSO (43 μL, 0.6 mmol), and aqueous hydrobromic acid (48%, 202 mg, 1.2 mmol) in EA (2 mL) at 60 °C for 0.5 h, affords 130.1 mg (76%) of 3c as a white solid. 1H NMR (CDCl3, 400 MHz): δ 7.52 (d, J = 8.8 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 5.09 (dd, J = 11.2, 5.2 Hz, 1H), 4.06 (dd, J = 10.2, 5.0 Hz, 1H), 3.99–3.94 (m, 1H). 13C NMR (CDCl3, 100 MHz): δ 137.7, 132.1, 129.3, 123.2, 49.5, 34.6.

1-Chloro-4-(1,2-dibromoethyl)benzene (3d)[4]

The reaction of 1-chloro-4-vinylbenzene 1d (69.3 mg, 0.5 mmol), DMSO (43 μL, 0.6 mmol), and aqueous hydrobromic acid (48%, 202 mg, 1.2 mmol) in EA (2 mL) at 60 °C for 0.5 h, affords 110.5 mg (74%) of 3d as a white solid. 1H NMR (CDCl3, 400 MHz): δ 7.38–7.33 (m, 4H), 5.10 (dd, J = 11.0, 5.0 Hz, 1H), 4.06 (dd, J = 10.4, 5.2 Hz, 1H), 3.99–3.94 (m, 1H). 13C NMR (CDCl3, 100 MHz): δ 137.1, 135.0, 129.1, 129.0, 49.5, 34.6.

1-(1,2-Dibromoethyl)-4-methylbenzene (3e)[4]

The reaction of 1-methyl-4-vinylbenzene 1e (59.1 mg, 0.5 mmol), DMSO (43 μL, 0.6 mmol), and aqueous hydrobromic acid (48%, 202 mg, 1.2 mmol) in EA (2 mL) at 60 °C for 0.5 h, affords 109.7 mg (79%) of 3e as a white solid. 1H NMR (CDCl3, 400 MHz): δ 7.38–7.33 (m, 4H), 5.14 (dd, J = 10.6, 5.2 Hz, 1H), 4.07 (dd, J = 10.4, 5.6 Hz, 1H), 4.05–3.99 (m, 1H), 2.36 (s, 3H). 13C NMR (CDCl3, 100 MHz): δ 139.2, 135.6, 129.6, 127.5, 51.0, 35.0, 21.3.

4-(1,2-Dibromoethyl)-1,1'-biphenyl (3f)[5]

The reaction of 4-vinyl-1,1'-biphenyl 1f (90.1 mg, 0.5 mmol), DMSO (43 μL, 0.6 mmol), and aqueous hydrobromic acid (48%, 202 mg, 1.2 mmol) in EA (2 mL) at 60 °C for 0.5 h, affords 137.7 mg (81%) of 3f as a white solid. 1H NMR (400 MHz, CDCl3) δ 7.65–7.63 (m, 4H), 7.52–7.41 (m, 5H), 5.25 (dd, J = 8.7, 5.9 Hz, 1H), 4.16–4.07 (m, 2H). 13C NMR (100 MHz, CDCl3) δ 142.0, 140.1, 137.4, 128.8, 128.0, 127.6, 127.5, 127.1, 50.7, 34.8.

1-(1,2-Dibromoethyl)-3-nitrobenzene (3g)[6]
The reaction of 1-nitro-3-vinylbenzene 1g (74.6 mg, 0.5 mmol), DMSO (43 μL, 0.6 mmol), and aqueous hydrobromic acid (48%, 202 mg, 1.2 mmol) in EA (2 mL) at 60 °C for 0.5 h, affords 117.4 mg (76%) of 3g as a yellow solid. \(^1\)H NMR (CDCl\(_3\), 400 MHz): δ 8.29 (t, \(J = 1.8\) Hz, 1H), 8.23–8.21 (m, 1H), 7.75 (d, \(J = 7.6\) Hz, 1H), 7.59 (t, \(J = 8.0\) Hz, 1H), 5.19 (dd, \(J = 11.2, 4.8\) Hz, 1H), 4.11 (dd, \(J = 10.6, 5.0\) Hz, 1H), 4.04–3.98 (m, 1H). \(^1\)C NMR (CDCl\(_3\), 100 MHz): δ 148.4, 140.8, 133.7, 129.9, 124.0, 122.8, 48.0, 34.1.

1-(1,2-Dibromoethyl)-3-methylbenzene (3h)[7]

The reaction of 1-methyl-3-vinylbenzene 1h (59.1 mg, 0.5 mmol), DMSO (43 μL, 0.6 mmol), and aqueous hydrobromic acid (48%, 202 mg, 1.2 mmol) in EA (2 mL) at 60 °C for 0.5 h, affords 104.0 mg (75%) of 3h as a white solid. \(^1\)H NMR (CDCl\(_3\), 400 MHz): δ 7.29–7.25 (m, 1H), 7.20–7.19 (m, 2H), 7.15 (d, \(J = 7.2\) Hz, 1H), 5.11 (dd, \(J = 10.4, 5.6\) Hz, 1H), 4.08–3.99 (m, 2H), 2.37 (s, 3H). \(^1\)C NMR (CDCl\(_3\), 100 MHz): δ 138.6, 138.5, 130.0, 128.7, 128.3, 124.7, 51.1, 35.0, 21.4.

1-Chloro-2-(1,2-dibromoethyl)benzene (3i)

The reaction of 1-chloro-2-vinylbenzene 1i (69.3 mg, 0.5 mmol), DMSO (43 μL, 0.6 mmol), and aqueous hydrobromic acid (48%, 202 mg, 1.2 mmol) in EA (2 mL) at 60 °C for 0.5 h, affords 110.3 mg (74%) of 3i as a white solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 7.52 (d, \(J = 7.6\) Hz, 1H), 7.39 (d, \(J = 7.8\) Hz, 1H), 7.33 (t, \(J = 8.2\) Hz, 1H), 5.70 (t, \(J = 7.7\) Hz, 1H), 4.12–4.07 (m, 2H). \(^1\)C NMR (100 MHz, CDCl\(_3\)) δ 136.0, 133.9, 130.1, 130.0, 128.3, 127.5, 45.5, 33.6.

(1,2-Dibromopropan-2-yl)benzene (3j)[8]

The reaction of \(\alpha\)-methylstyr ene 1j (59.1 mg, 0.5 mmol), DMSO (43 μL, 0.6 mmol), and aqueous hydrobromic acid (48%, 202 mg, 1.2 mmol) in EA (2 mL) at 60 °C for 0.5 h, affords 101.0 mg (73%) of 3j as colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 7.56–7.54 (m, 2H), 7.38–7.30 (m, 3H), 4.35 (d, \(J = 10.2\) Hz, 1H), 4.13 (d, \(J = 10.2\) Hz, 1H), 2.31 (s, 3H). \(^1\)C NMR (100 MHz, CDCl\(_3\)) δ 141.9, 128.5, 128.4, 126.5, 63.7, 43.5, 29.9.

(1,2-Dibromopropyl)benzene (3k)[8]

The reaction of \((E)\)-\(\beta\)-methylstyr ene 1k (59.1 mg, 0.5 mmol), DMSO (43 μL, 0.6 mmol), and aqueous hydrobromic acid (48%, 202 mg, 1.2 mmol) in EA (2 mL) at 60 °C for 0.5 h, affords 108.4 mg (78%) of 3k as a white solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 7.41–7.32 (m, 5H), 5.05 (d, \(J = 10.4\) Hz, 1H), 4.63–4.59 (m, 1H), 2.05 (d, \(J = 6.4\) Hz, 3H). \(^1\)C NMR (100 MHz, CDCl\(_3\)) δ 140.6, 128.8, 126.6, 127.7, 59.1, 51.1, 25.8.

1,2-Dibromo-2,3-dihydro-1\(H\)-indene (3l)[9]
The reaction of indene \(1l\) (58.1 mg, 0.5 mmol), DMSO (43 \(\mu\)L, 0.6 mmol), and aqueous hydrobromic acid (48\%, 202 mg, 1.2 mmol) in EA (2 mL) at 60 °C for 0.5 h, affords 101.2 mg (73\%) of \(3l\) as colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.46–7.44 (m, 1H), 7.34–7.27 (m, 3H), 5.62 (s, 1H), 4.86 (dt, \(J = 5.2, 1.2\) Hz, 1H), 3.79 (dd, \(J = 17.5, 5.2\) Hz, 1H), 3.25 (d, \(J = 17.5\) Hz, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 140.5, 140.5, 129.7, 127.9, 125.7, 125.4, 57.7, 54.4, 41.4.

1,2-Dibromo-1,2,3,4-tetrahydronaphthalene (3m)\[^{10}\]

The reaction of 1,2-dihydronaphthalene \(1m\) (65.1 mg, 0.5 mmol), DMSO (43 \(\mu\)L, 0.6 mmol), and aqueous hydrobromic acid (48\%, 202 mg, 1.2 mmol) in EA (2 mL) at 60 °C for 0.5 h, affords 112.4 mg (78\%) of \(3m\) as colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.29 (dd, \(J = 7.5, 1.4\) Hz, 1H), 7.25–7.16 (m, 2H), 7.11 (d, \(J = 7.5\) Hz, 1H), 5.64–5.63 (m, 1H), 4.93–4.90 (m, 1H), 3.25 (d, \(J = 17.7, 11.9\), 6.2 Hz, 1H), 2.91 (dd, \(J = 17.4, 6.0\) Hz, 1H), 2.84–2.76 (m, 1H), 2.20–2.13 (m, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 134.4, 132.8, 131.2, 129.2, 128.9, 126.6, 51.52, 51.49, 25.1, 24.4.

5,6-Dibromo-6,7,8,9-tetrahydro-5\(\text{H}\)-benzo[7]annulene (3n)\[^{11}\]

The reaction of 6,7-dihydro-5\(\text{H}\)-benzo[7]annulene \(1n\) (72.1 mg, 0.5 mmol), DMSO (43 \(\mu\)L, 0.6 mmol), and aqueous hydrobromic acid (48\%, 202 mg, 1.2 mmol) in EA (2 mL) at 60 °C for 0.5 h, affords 129.2 mg (85\%) of \(3n\) as colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.25–7.12 (m, 4H), 5.49 (d, \(J = 5.3\) Hz, 1H), 4.88–4.85 (m, 1H), 3.31–3.23 (m, 1H), 3.00–2.92 (m, 1H), 2.80–2.74 (m, 1H), 2.27–2.21 (m, 1H), 1.98–1.91 (m, 2H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 142.9, 136.3, 131.3, 130.9, 129.3, 126.1, 58.4, 54.7, 35.3, 34.6, 22.8.

1,2-Dibromodecane (3o)\[^{8}\]

The reaction of 1-decene \(1o\) (70.1 mg, 0.5 mmol), DMSO (43 \(\mu\)L, 0.6 mmol), and aqueous hydrobromic acid (48\%, 202 mg, 1.2 mmol) in EA (2 mL) at 60 °C for 0.5 h, affords 141.0 mg (94\%) of \(3o\) as colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 4.20–4.13 (m, 1H), 3.85 (dd, \(J = 10.2, 4.4\) Hz, 1H), 3.63 (t, \(J = 10.0\) Hz, 1H), 2.18–2.09 (m, 1H), 1.83–1.73 (m, 1H), 1.60–1.53 (m, 1H), 1.45–1.28 (m, 11H), 0.89 (t, \(J = 6.5\) Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 53.1, 36.3, 36.0, 31.8, 29.3, 29.1, 28.8, 26.7, 22.6, 14.1.

(2,3-Dibromopropoxy)benzene (3p)\[^{12}\]

The reaction of (allyloxy)benzene \(1p\) (67.1 mg, 0.5 mmol), DMSO (43 \(\mu\)L, 0.6 mmol), and aqueous hydrobromic acid (48\%, 202 mg, 1.2 mmol) in EA (2 mL) at 60 °C for 0.5 h, affords 119.1 mg (81\%) of \(3p\) as colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.32–7.28 (m, 2H), 7.00 (t, \(J = 7.4\) Hz, 1H),
6.95–6.92 (m, 2H), 4.44–4.33 (m, 3H), 3.95–3.86 (m, 2H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 157.9, 129.6, 121.6, 114.8, 69.0, 47.7, 32.7.

(3,4-Dibromobutyl)benzene (3q)[13]

The reaction of (allyloxy)benzene 1q (66.1 mg, 0.5 mmol), DMSO (43 \(\mu\)L, 0.6 mmol), and aqueous hydrobromic acid (48%, 202 mg, 1.2 mmol) in EA (2 mL) at 60 °C for 0.5 h, affords 131.5 mg (90%) of 3q as colorless oil. \(^{1}\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.29–7.21 (m, 5H), 4.09 (m, 1H), 3.83–3.81 (m, 1H), 3.64–3.59 (m, 1H), 2.92–2.90 (m, 1H), 2.75–2.73 (m, 1H), 2.46–2.45 (m, 1H), 2.07–2.06 (m, 1H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 140.2, 128.51, 128.47, 126.2, 52.0, 37.6, 36.2, 32.9.

(2,3-Dibromo-2-methylpropyl)benzene (3r)[14]

The reaction of (2-methylallyl)benzene 1r (66.1 mg, 0.5 mmol), DMSO (43 \(\mu\)L, 0.6 mmol), and aqueous hydrobromic acid (48%, 202 mg, 1.2 mmol) in EA (2 mL) at 60 °C for 0.5 h, affords 121.7 mg (83%) of 3r as colorless oil. \(^{1}\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.40–7.31 (m, 5H), 3.81 (d, \(J = 10.2\) Hz, 1H), 3.74 (d, \(J = 10.2\) Hz, 1H), 3.33–3.21 (m, 2H), 1.91 (s, 3H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 136.0, 130.9, 128.0, 127.3, 66.6, 47.1, 42.2, 30.7.

1,2-Dibromocyclohexane (3s)[15]

The reaction of cyclohexene 1s (41.1 mg, 0.5 mmol), DMSO (43 \(\mu\)L, 0.6 mmol), and aqueous hydrobromic acid (48%, 202 mg, 1.2 mmol) in EA (2 mL) at 60 °C for 0.5 h, affords 100.5 mg (83%) of 3s as colorless oil. \(^{1}\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 4.46 (s, 2H), 2.49–2.43 (m, 2H), 1.91–1.79 (m, 4H), 1.55–1.50 (m, 2H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 55.2, 31.9, 22.4.

6,7-Dibromodecahydro-1,4-methanonaphthalene (3t)[16]

The reaction of octahydro-1,4-methanonaphthalene 1t (74.1 mg, 0.5 mmol), DMSO (43 \(\mu\)L, 0.6 mmol), and aqueous hydrobromic acid (48%, 202 mg, 1.2 mmol) in EA (2 mL) at 60 °C for 0.5 h, affords 135.5 mg (88%) of 3t as a white solid. \(^{1}\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 4.70 (dt, \(J = 6.3, 3.1\) Hz, 1H), 4.34–4.27 (m, 1H), 2.02 (dt, \(J = 12.9, 5.0\) Hz, 1H), 1.96–1.87 (m, 5H), 1.72–1.66 (m, 1H), 1.60–1.50 (m, 4H), 1.29–1.19 (m, 2H), 1.12 (d, \(J = 10.4\) Hz, 1H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 56.8, 54.8, 42.8, 41.9, 41.3, 36.4, 36.1, 33.5, 33.2, 29.3, 29.2.

1,2-Dibromocyclooctane (3u)[17]

The reaction of \((Z)\)-cyclooctene 1u (55.1 mg, 0.5 mmol), DMSO (43 \(\mu\)L, 0.6 mmol), and aqueous hydrobromic acid (48%, 202 mg, 1.2 mmol) in EA (2 mL) at 60 °C for 0.5 h, affords 109.3 mg (81%) of 3u as colorless oil. \(^{1}\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 4.61–4.56 (m, 2H), 2.45–2.38 (m, 2H),
2.14–2.05 (m, 2H), 1.89–1.82 (m, 2H), 1.71–1.55 (m, 4H), 1.52–1.45 (m, 2H). $^{13}$C NMR (CDCl$_3$, 100 MHz): δ 61.5, 33.2, 25.9, 25.4.

1,2-Dibromo-1-methylcyclohexane (3v)$^{[18]}$

The reaction of 1-methylcyclohexene 1v (48.1 mg, 0.5 mmol), DMSO (43 μL, 0.6 mmol), and aqueous hydrobromic acid (48%, 202 mg, 1.2 mmol) in EA (2 mL) at 60 °C for 0.5 h, affords 107.7 mg (84%) of 3v as colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 4.65 (s, 1H), 2.58–2.50 (m, 1H), 2.12–2.05 (m, 1H), 2.02–1.93 (m, 5H), 1.86–1.75 (m, 2H), 1.68–1.53 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 70.7, 61.9, 37.6, 34.0, 32.5, 22.7, 20.7.

3-(Bromomethyl)-3-methylisobenzofuran-1(3H)-one (5a)

The reaction of 2-(prop-1-en-2-yl)benzoic acid 4a (81.1 mg, 0.5 mmol), DMSO (43 μL, 0.6 mmol), and aqueous hydrobromic acid (48%, 202 mg, 1.2 mmol) in EA (2 mL) at 60 °C for 1 h, affords 105.4 mg (87%) of 5a as a white solid. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.82 (d, $J = 7.6$ Hz, 1H), 7.64–7.62 (m, 1H), 7.50 (t, $J = 7.4$ Hz, 1H), 7.45 (d, $J = 7.6$ Hz, 1H), 3.68 (d, $J = 11.1$ Hz, 1H), 3.65 (d, $J = 11.1$ Hz, 1H), 1.75 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 168.9, 151.1, 134.3, 129.8, 126.2, 125.8, 121.4, 84.5, 37.8, 24.2. HRMS (ESI) Calcd for [C$_{10}$H$_{10}$BrO$_2$, M + H]$^+$: 240.9859, Found: 240.9863.

3-(Bromomethyl)-3-phenylisobenzofuran-1(3H)-one (5b)

The reaction of 2-(1-phenylvinyl)benzoic acid 4b (112.1 mg, 0.5 mmol), DMSO (43 μL, 0.6 mmol), and aqueous hydrobromic acid (48%, 202 mg, 1.2 mmol) in EA (2 mL) at 60 °C for 1 h, affords 148.2 mg (98%) of 5b as a white solid. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.93 (d, $J = 7.6$ Hz, 1H), 7.76–7.72 (m, 1H), 7.67 (d, $J = 7.7$ Hz, 1H), 7.61–7.56 (m, 3H), 7.42–7.36 (m, 3H), 4.15 (d, $J = 11.4$ Hz, 1H), 4.09 (d, $J = 11.4$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 168.8, 149.8, 137.5, 134.3, 129.9, 129.1, 129.0, 126.5, 126.0, 125.4, 122.5, 87.2, 37.9. HRMS (ESI) Calcd for [C$_{15}$H$_{12}$BrO$_2$, M + H]$^+$: 303.0015, Found: 303.0018.

(E)-(1,2-Dibromoprop-1-en-1-yl)benzene (7a)$^{[14]}$

The reaction of 1-phenyl-1-propyne 6a (58.1 mg, 0.5 mmol), DMSO (43 μL, 0.6 mmol), and aqueous hydrobromic acid (48%, 202 mg, 1.2 mmol) in EA (2 mL) at 60 °C for 8 h, affords 118.7 mg (86%) of 7a as colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.38–7.32 (m, 5H), 2.62 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 140.8, 129.1, 128.6, 128.2, 117.2, 116.8, 29.3.

(E)-(1,2-Dibromohex-1-en-1-yl)benzene (7b)$^{[19]}$

The reaction of hex-1-yn-1-ylbenzene 6b (79.1 mg, 0.5 mmol), DMSO (43 μL, 0.6 mmol), and aqueous hydrobromic acid (48%, 202 mg, 1.2 mmol) in EA (2 mL) at 60 °C for 8 h, affords 108.3 mg (68%) of 7b as colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.38–7.23 (m, 5H), 2.85 (t, $J$
\[ \text{H} \text{NMR (400 MHz, CDCl}_3 \text{)} \delta 7.99-7.97 \text{ (m, 2H), 7.62-7.59} \text{ (m, 1H), 7.50-7.47} \text{ (m, 2H), 4.45} \text{ (s, 2H).}^{13} \text{C NMR (100 MHz, CDCl}_3 \text{)} \delta 191.2, 133.9, 133.9, 128.9, 128.8, 30.9.\]

**2-Bromo-1-phenylbutan-1-one (9b)**

The reaction of acetophenone 8a (60.1 mg, 0.5 mmol), DMSO (43 \( \mu \)L, 0.55 mmol), and aqueous hydrobromic acid (48%, 101 mg, 0.6 mmol) in EA (2 mL) at 60 \( ^\circ\)C for 2 h, affords 72.3 mg (73%) of 9a as a pale yellow solid. \( ^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.99–7.97 (m, 2H), 7.62–7.59 (m, 1H), 7.50–7.47 (m, 2H), 4.45 (s, 2H). \( ^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 191.2, 133.9, 133.9, 128.9, 128.8, 30.9.
The reaction of butyrophenone 8b (74.1 mg, 0.5 mmol), DMSO (43 μL, 0.6 mmol), and aqueous hydrobromic acid (48%, 101 mg, 0.6 mmol) in EA (2 mL) at 60 °C for 6 h, affords 108.0 mg (94%) of 9b as pale yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.02–8.01 (m, 2H), 7.61 (t, $J = 7.6$ Hz, 1H), 7.50 (t, $J = 7.8$ Hz, 1H), 5.08 (dd, $J = 7.6$, 6.4 Hz, 1H), 2.28–2.10 (m, 2H), 1.08 (t, $J = 7.4$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 193.2, 134.5, 133.6, 128.8, 128.7, 49.0, 26.9, 12.1.

2-Bromo-1-phenylbutan-1-one (9c)$^{[24]}$

The reaction of isobutyrophenone 8c (74.1 mg, 0.5 mmol), DMSO (43 μL, 0.6 mmol), and aqueous hydrobromic acid (48%, 101 mg, 0.6 mmol) in EA (2 mL) at 60 °C for 6 h, affords 102.6 mg (90%) of 9c as colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.15–8.12 (m, 2H), 7.54–7.50 (m, 1H), 7.45–7.42 (m, 1H), 2.04 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 196.9, 134.9, 132.3, 130.0, 128.1, 60.3, 31.5.

(1-Bromocyclohexyl)(phenyl)methanone (9d)$^{[25]}$

The reaction of cyclohexyl(phenyl)methanone 8d (94.1 mg, 0.5 mmol), DMSO (43 μL, 0.6 mmol), and aqueous hydrobromic acid (48%, 101 mg, 0.6 mmol) in EA (2 mL) at 60 °C for 6 h, affords 122.9 mg (92%) of 9d as colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.09–8.07 (m, 2H), 7.53 (t, $J = 7.6$ Hz, 1H), 7.43 (t, $J = 7.6$ Hz, 2H), 2.38–2.32 (m, 2H), 2.22–2.17 (m, 2H), 1.83–1.77 (m, 2H), 1.59–1.52 (m, 3H), 1.41–1.38 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 197.4, 135.8, 132.0, 129.7, 128.1, 67.9, 38.2, 24.9, 23.5.
(F) References
(G) $^1$H NMR and $^{13}$C NMR Spectra of Products

![NMR Spectra Image]

$3a$
Cl

Br

Br

3d

4.00

1.00

1.02

1.03

S17
Cl
Br
Br
3d
$3h$