**Electronic Supplementary Information**

**Double Heteroannulation of S,N-Acetals: A Facile Access of Quinolone Derivatives**

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General Procedure for the Synthesis of $\alpha$-(2-Haloaroyl)-$\alpha$-(2-haloaryl)-ketene $S,N$-acetals 3

Scheme S1: Synthesis of $\alpha$-(2-Haloaroyl)-$\alpha$-(2-haloaryl)-ketene $S,N$-acetals 3

To a stirring suspension of NaH (60% suspension in mineral oil) (0.240 g, 6.0 mmol) in DMF (4.0 mL) at 0 °C was added drop wise the corresponding deoxybenzoin 1 (3.0 mmol) in DMF (3.0 mL). After being further stirred for 1 h at room temperature, a solution of isothiocyanate 2 (3.0 mmol) in DMF (2.0 mL) was added to the reaction mixture at 0 °C and followed by further stirring for 1 h at room temperature. To this reaction mixture MeI (3.6 mmol) in DMF (1.0 mL) was added at 0 °C and further stirred for 2-6 h. After complete consumption of the starting materials (monitored by TLC), the reaction mixture was quenched with saturated NH$_4$Cl solution and extracted with EtOAc. The combined organic layer washed with water (3 x 20 mL) & brine (20 mL), dried over anhyd. Na$_2$SO$_4$ and concentrated under reduced pressure. The crude products were purified by flash chromatography using EtOAc/hexanes as eluent.

1,2-Bis(2-bromophenyl)-3-(methylthio)-3-(phenylamino)prop-2-en-1-one (3a)

Reaction time: 8 h
Yield: 93%, as a yellow colour solid.
Melting point: 116 – 118 °C
R$_f$: 0.37 in 10% ethyl acetate in hexane
IR (KBr): ν (cm$^{-1}$) = 3448, 3050, 3002, 2924, 2852, 1578, 1545, 1425, 1370, 1316, 1247, 1195, 1089, 1051, 1024, 976, 905, 850, 749, 734.
$^1$H NMR (400 MHz, CDCl$_3$) δ = 13.54 (s, 1H), 7.52 (d, $J = 7.6$ Hz, 2H), 7.47 (dd, $J = 8.0$, 1.2 Hz, 1H), 7.42 – 7.37 (m, 4H), 7.24 – 7.22 (m, 1H), 7.19 (dd, $J = 7.6$, 1.6 Hz, 1H), 7.08 (td, $J = 7.6$, 1.2 Hz, 1H), 7.05 – 6.94 (m, 3H), 1.91 (s, 3H).
$^{13}$C NMR (100 MHz, CDCl$_3$) δ = 190.0, 165.5, 142.8, 139.8, 138.9, 134.0, 132.4, 132.2, 129.5, 129.4, 129.1, 128.7, 127.2, 126.9, 126.5, 125.8, 124.1, 119.2, 114.7, 17.2.
HR-MS (ESI): Calcd. for C$_{22}$H$_{17}$Br$_2$NOS [M+H]: 501.9470, Found: 501.9491.
1,2-Bis(2-bromophenyl)-3-((4-methoxyphenyl)amino)-3-(methylthio)prop-2-en-1-one (3b)

Reaction time: 4 h  
Yield: 64%, as a pale yellow colour solid.  
Melting point: 128 – 130 °C  
Rf: 0.43 in 10% ethyl acetate in hexane  
IR (KBr): ν (cm⁻¹) = 3428, 3072, 2989, 2958, 2927, 2830, 1550, 1509, 1375, 1314, 1245, 1179, 1025, 871, 829, 763, 746.

1H NMR (400 MHz, CDCl₃) δ = 13.60 (s, 1H), 7.46 (dd, J = 8.0, 1.2 Hz, 1H), 7.44 – 7.37 (m, 4H), 7.18 (dd, J = 7.6, 2.0 Hz, 1H), 7.06 (td, J = 7.4, 1.2 Hz, 1H), 7.02 (td, J = 7.2, 1.2 Hz, 1H), 6.99 – 6.90 (m, 4H), 3.83 (s, 3H), 1.89 (s, 3H).

13C NMR (100 MHz, CDCl₃) δ = 189.6, 166.2, 157.8, 142.9, 139.1, 134.1, 132.6, 132.4, 132.2, 129.3, 129.0, 128.9, 127.2, 126.9, 125.8, 119.3, 114.6, 113.9, 55.6, 17.1.


1,2-Bis(2-chlorophenyl)-3-(methylthio)-3-((4-nitrophenyl)amino)prop-2-en-1-one (3c)

Reaction time: 4 h  
Yield: 71%, as a yellow colour solid.  
Melting point: 122 – 124 °C  
Rf: 0.40 in 10% ethyl acetate in hexane  
IR (KBr): ν (cm⁻¹) = 3447, 3050, 2925, 2843, 1587, 1560, 1514, 1423, 1364, 1338, 1312, 1266, 1250, 1112, 1091, 1062, 1032, 869, 854, 751.

1H NMR (400 MHz, CDCl₃) δ = 13.17 (s, 1H), 8.27 (d, J = 8.8 Hz, 2H), 7.64 (d, J = 9.2 Hz, 2H), 7.33 (dd, J = 7.6, 1.6 Hz, 1H), 7.29 – 7.27 (m, 1H), 7.19 (d, J = 8.0 Hz, 1H), 7.15 – 7.06 (m, 4H), 7.02 – 6.98 (m, 1H), 2.02 (s, 3H).

13C NMR (100 MHz, CDCl₃) δ = 191.6, 162.1, 146.2, 144.1, 140.1, 136.2, 136.0, 133.6, 130.1, 129.9, 129.6, 129.5, 129.2, 127.0, 126.7, 126.0, 125.4, 122.0, 116.4, 17.1.

1,2-Bis(2-bromophenyl)-3-(cyclopropylamino)-3-(methylthio)prop-2-en-1-one (3d)

Reaction time: 4 h

Yield: 70%, as a brown colour solid.

Melting point: 146 – 148 °C

Rf: 0.28 in 5% ethyl acetate in hexane

IR (KBr): ν (cm⁻¹) = 3431, 3063, 3046, 2993, 2925, 2848, 1542, 1559, 1423, 1390, 1280, 1251, 1155, 1050, 930, 805,764, 751, 733.

¹H NMR (400 MHz, CDCl₃) δ = 12.63 (s, 1H), 7.43 (d, J = 7.6 Hz, 1H), 7.35 (d, J = 7.6 Hz, 1H), 7.29 (dd, J = 7.6, 1.2 Hz, 1H), 7.06 (d, J = 7.2 Hz, 1H), 7.02 – 6.90 (m, 4H), 3.14 – 3.09 (m, 1H), 2.32 (s, 3H), 0.99 – 0.95 (m, 4H).

¹³C NMR (100 MHz, CDCl₃) δ = 188.8, 169.7, 143.1, 139.6, 134.4, 132.3, 132.1, 129.1, 129.0, 128.6, 127.0, 126.9, 126.4, 119.4, 111.4, 28.6, 17.5, 9.2, 8.6.


2-(6-Bromobenzod[2][1,3]dioxol-5-yl)-1-(2-bromophenyl)-3-((4-chlorophenyl)amino)-3-(methylthio)prop-2-en-1-one (3e)

Reaction time: 6 h

Yield: 59%, as a yellow colour solid.

Melting point: 155 – 157 °C

Rf: 0.28 in 5% ethyl acetate in hexane

IR (KBr): ν (cm⁻¹) = 3448, 3090, 3054, 2918, 2887, 1557, 1551, 1481, 1419, 1368, 1314, 1233, 1198, 1130, 1080, 1036, 935, 859, 819, 751, 732.

¹H NMR (400 MHz, CDCl₃) δ = 13.37 (s, 1H), 7.44 – 7.41 (m, 3H), 7.37 – 7.34 (m, 2H), 7.22 (dd, J = 7.6, 1.6 Hz, 1H), 7.09 (td, J = 7.6, 1.2 Hz, 1H), 7.03 (td, J = 7.6, 1.2 Hz, 1H), 6.92 (s, 1H), 6.88 (s, 1H), 5.89 (d, J = 7.6 Hz, 2H), 1.94 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ = 190.6, 165.5, 148.0, 147.1, 142.6, 138.5, 132.5, 131.6, 131.1, 129.6 (2C), 126.8, 126.7, 125.1, 119.4, 119.1, 115.1, 112.8, 112.2, 101.9, 17.1.


[ESI-4]
1,2-Bis(2-bromo-4,5-dimethoxyphenyl)-3-(methylthio)-3-(phenylamino)prop-2-en-1-one (3f)

Reaction time: 8 h
Yield: 62%, as a yellow colour solid.
Melting point: 79 – 81°C
Rf: 0.38 in ethyl acetate/hexane (1:2)
IR (KBr): ν (cm\(^{-1}\)) = 3448, 2997, 2929, 2838, 1594, 1542, 1507, 1459, 1381, 1356, 1327, 1256, 1206, 1168, 1098, 1026, 863, 831, 778.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) δ = 13.46 (s, 1H), 7.50 (d, J = 7.6 Hz, 2H), 7.39 (t, J = 7.6 Hz, 2H), 7.21 (t, J = 7.6 Hz, 1H), 6.92 (s, 1H), 6.88 (s, 1H), 6.82 (s, 1H), 6.77 (s, 1H), 3.81 (s, 3H), 3.79 (s, 3H), 3.78 (s, 3H), 3.74 (s, 3H), 1.92 (s, 3H).

\(^13\)C NMR (100 MHz, CDCl\(_3\)) δ = 190.1, 165.9, 149.1, 148.9, 148.0, 147.5, 139.9, 135.4, 131.2, 129.5, 125.7, 123.9, 118.7, 116.0, 115.0, 114.6, 114.3, 110.1, 109.5, 56.10, 56.07, 56.065, 55.98, 17.1.

HR-MS (ESI): Calcd. for C\(_{26}\)H\(_{25}\)Br\(_2\)NO\(_5\)S [M+H]: 621.9916, Found: 621.9893.
[M+H]: 625.9853, Found: 625.9877.

1,2-Bis(6-bromobenzod[\(d\)][1,3]dioxol-5-yl)-3-(methylthio)-3-(phenylamino)prop-2-en-1-one (3g)

Reaction time: 6.5 h
Yield: 67%, as a yellow colour solid.
Melting point: 197 – 199 °C
Rf: 0.40 in 10% ethyl acetate in hexane
IR (KBr): ν (cm\(^{-1}\)) = 3428, 3081, 2923, 2848, 1563, 1540, 1497, 1476, 1410, 1391, 1360, 1340, 1311, 1241, 1117, 1069, 1033, 928, 881, 866, 765.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) δ = 13.43 (s, 1H), 7.47 (d, J = 7.6 Hz, 2H), 7.38 (t, J = 7.6 Hz, 2H), 7.20 (t, J = 7.6 Hz, 1H), 6.96 (s, 1H), 6.92 (s, 1H), 6.86 (s, 1H), 6.76 (s, 1H), 5.94 (d, J = 6.8 Hz, 2H), 5.90 (d, J = 11.2 Hz, 2H), 1.90 (s, 3H).

\(^13\)C NMR (100 MHz, CDCl\(_3\)) δ = 189.5, 166.1, 148.1, 148.0, 147.1, 146.6, 139.9, 136.5, 131.8, 129.5, 125.7, 124.0, 119.5, 114.4, 112.9, 112.7, 112.2, 110.3, 107.0, 101.9, 101.8, 17.1.

HR-MS (ESI): Calcd. for C\(_{24}\)H\(_{17}\)Br\(_2\)NO\(_3\)S [M+H]: 589.9267, Found: 589.9247.
[M+H]: 591.9248, Found: 591.9226.
[M+H]: 593.9227, Found: 593.9202.
1,2-Bis(6-bromobenzod[1,3]dioxol-5-yl)-3-(methylthio)-3-((2-trifluoromethyl)phenyl)amino)prop-2-en-1-one (3h)

Reaction time: 4.5 h
Yield: 63%, as a yellow colour solid.
Melting point: 106 – 108 °C
Rf: 0.33 in 20% ethyl acetate in hexane
IR (KBr): ν (cm⁻¹) = 3448, 3010, 2917, 2848, 1555, 1543, 1506, 1478, 1412, 1391, 1361, 1340, 1315, 1281, 1243, 1167, 1124, 1057, 1035, 931, 874, 841, 786, 765.

^1^H NMR (400 MHz, CDCl₃) δ = 13.28 (s, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.70 (d, J = 7.6 Hz, 1H), 7.56 (t, J = 7.6 Hz, 1H), 7.30 (t, J = 7.6 Hz, 1H), 6.97 (s, 1H), 6.95 (s, 1H), 6.85 (s, 1H), 6.76 (s, 1H), 5.95 (dd, J = 7.4 Hz, 1.2 Hz, 2H), 5.91 (dd, J = 8.4 Hz, 1.2 Hz, 2H), 1.85 (s, 3H).

^13^C NMR (100 MHz, CDCl₃) δ = 190.1, 165.1, 148.23, 148.18, 147.2, 146.7, 138.7 (d, J = 2 Hz), 136.0, 132.9, 131.3, 126.7 (q, J = 5.2 Hz), 125.8, 125.3, 123.8 (q, J = 271 Hz), 123.5 (q, J = 30 Hz), 119.1, 116.5, 112.7, 112.6, 112.3, 110.2, 107.0, 102.0, 101.9, 16.4.


General Procedure for the Synthesis of S,N-Acetals 5a-h

To a stirring suspension of NaH (60% suspension in mineral oil) (0.240 g, 6.0 mmol) in DMF (4.0 mL) at 0 °C was added drop wise the corresponding ketone (3.0 mmol) in DMF (3.0 mL). After being further stirred for 1 h at room temperature, a solution of isothiocyanate 2 (3.0 mmol) in DMF (2.0 mL) was added to the reaction mixture at 0 °C and followed by further stirring for 1 h at room temperature. To this reaction mixture MeI (3.6 mmol) in DMF (1.0 mL) was added at 0 °C and further stirred for 2-6 h. After complete consumption of the starting materials (monitored by TLC), the reaction mixture was quenched with saturated NH₄Cl solution and extracted with EtOAc. The combined organic layer washed with water (3
x 20 mL) & brine (20 mL), dried over anhyd. Na₂SO₄ and concentrated under reduced pressure. The crude products were purified by flash chromatography using EtOAc/hexanes as eluent.

1-(2-Bromophenyl)-3-(methylthio)-3-(phenylamino)prop-2-en-1-one (5a)

Reaction time: 6.5 h

Yield: 74%, as a yellow colour solid.

Melting point: 118 – 120 °C

R_f: 0.30 in 10% ethyl acetate in hexane

IR (KBr): ν (cm⁻¹) = 3437, 3054, 3025, 2923, 1594, 1565, 1476, 1429, 1301, 1246, 1157, 1023, 835, 748.

¹H NMR (400 MHz, CDCl₃) δ = 13.16 (s, 1H), 7.61 (dd, J = 8.0, 0.8 Hz, 1H), 7.51 (dd, J = 7.6, 1.6 Hz, 1H), 7.41 – 7.33 (m, 5H), 7.29 – 7.21 (m, 2H), 5.53 (s, 1H), 2.38 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ = 187.8, 168.1, 143.3, 138.0, 133.5, 130.1, 129.3, 129.2, 127.4, 126.8, 125.6, 119.6, 92.5, 14.9.


1-(2-Bromophenyl)-3-(methylthio)-3-(p-tolylamino)prop-2-en-1-one (5b)

Reaction time: 4 h

Yield: 72%, as a yellow colour solid.

Melting point: 88 – 90 °C

R_f: 0.35 in 10% ethyl acetate in hexane

IR (KBr): ν (cm⁻¹) = 3449, 3032, 2998, 2905, 2848, 1591, 1551, 1476, 1456, 1432, 1289, 1222, 1152, 1095, 1023, 986, 817, 773, 752.

¹H NMR (400 MHz, CDCl₃) δ = 13.10 (s, 1H), 7.57 (d, J = 7.6 Hz, 1H), 7.49 (d, J = 7.6 Hz, 1H), 7.32 (t, J = 7.6 Hz, 1H), 7.21 – 7.15 (m, 5H), 5.49 (s, 1H), 2.34 (s, 3H), 2.31 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ = 187.3, 168.2, 143.1, 136.5, 135.0, 133.2, 130.1, 129.5, 129.1, 127.1, 125.2, 119.3, 91.9, 20.9, 14.5.


[M+H]: 364.0189, Found: 364.0205.
1-(2-Bromophenyl)-3-((4-methoxyphenyl)amino)-3-(methylthio)prop-2-en-1-one (5c)

Reaction time: 4 h
Yield: 76%, as a brown colour solid.
Melting point: 80 – 82 °C
Rf: 0.33 in 20% ethyl acetate in hexane

IR (KBr): ν (cm⁻¹) = 3448, 3032, 3003, 2956, 2930, 2837, 1598, 1570, 1512, 1478, 1456, 1296, 1246, 1180, 1091, 1035, 1026, 843, 787, 746, 723.

¹H NMR (400 MHz, CDCl₃) δ = 12.91 (s, 1H), 7.60 (dd, J = 8.0, 0.8 Hz, 1H), 7.50 (dd, J = 7.6, 1.6 Hz, 1H), 7.35 (td, J = 7.6, 0.8 Hz, 1H), 7.27 – 7.26 (m, 1H), 7.24 – 7.20 (m, 2H), 6.93 – 6.89 (m, 2H), 5.47 (s, 1H), 3.83 (s, 3H), 2.35 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ = 187.7, 169.2, 158.7, 143.5, 133.5, 130.7, 130.3, 129.3, 127.6, 127.4, 119.6, 114.4, 91.9, 55.6, 14.8.


1-(2-Bromophenyl)-3-((4-chlorophenyl)amino)-3-(methylthio)prop-2-en-1-one (5d)

Reaction time: 4.5 h
Yield: 74%, as a yellow colour solid.
Melting point: 130 – 132 °C
Rf: 0.35 in 10% ethyl acetate in hexane

IR (KBr): ν (cm⁻¹) = 3432, 3050, 2996, 2923, 1573, 1556, 1491, 1474, 1455, 1434, 1296, 1253, 1218, 1156, 1105, 1090, 1023, 1012, 984, 933, 845, 745.

¹H NMR (400 MHz, CDCl₃) δ = 13.13 (s, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.49 (dd, J = 7.6, 1.6 Hz, 1H), 7.37 – 7.34 (m, 3H), 7.28 (d, J = 8.8 Hz, 2H), 7.26 – 7.22 (m, 1H), 5.54 (s, 1H), 2.39 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ = 188.1, 167.9, 143.1, 136.6, 133.6, 132.4, 130.5, 129.38, 129.36, 127.4, 126.8, 119.6, 93.0, 14.9.

HR-MS (ESI): Calcd. for C₁₆H₁₃BrClNOS [M+H]: 381.9663, Found: 381.9614.

1-(2-Bromophenyl)-3-(methylthio)-3-(pyridin-3-ylamino)prop-2-en-1-one (5e)

Reaction time: 5 h
Yield: 72%, as a yellow colour solid.

IR (KBr): ν (cm\(^{-1}\)) = 3420, 2921, 1580, 1555, 1482, 1451, 1422, 1293, 1253, 1158, 1020, 746.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) [obtained as a (7.7:1 inseparable mixture of E/Z isomers] \(\delta = 13.17\) (s, 1H) [4.66 (s, 1H)], 8.66 (d, \(J = 2.4\) Hz, 1H) [8.38 – 8.37 (m, 1H)], 8.51 – 8.50 (m, 1H) [8.34 – 8.32 (m, 1H)], 7.72 – 7.70 (m, 1H) [7.76 – 7.74 (m, 1H)], 7.61 (d, \(J = 7.6\) Hz, 1H), 7.49 (dd, \(J = 7.4, 1.6\) Hz, 1H) [7.56 – 7.54 (m, 2H)], 7.36 – 7.32 (m, 2H) [7.38 (br s, 2H)], 7.24 – 7.21 (m, 1H) [7.264 (br s, 1H)], 5.60 (s, 1H) [6.82 (s, 1H)], 2.41 (s, 3H) [2.38 (s, 3H)].

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 188.4\) [199.6], 167.8 [170.0], 147.4 [145.1], 146.6 [144.5], 142.8 [140.5], 134.9 [134.2], 133.5 [132.1], 132.7 [131.8], 130.6 [131.5], 129.3 [130.0], 127.4 [127.5], 123.6 [123.83], 119.4 [123.79], 93.6 [118.6], 14.8 [16.6].

HR-MS (ESI): Calcd. for C\(_{15}\)H\(_{13}\)BrN\(_2\)OS [M+H]: 349.0005, Found: 349.0000.

1-(2-Bromophenyl)-3-(isopropylamino)-3-(methylthio)prop-2-en-1-one (5f)

Reaction time: 4 h
Yield: 75%, as a pale yellow colour solid.

IR (KBr): ν (cm\(^{-1}\)) = 3420, 2921, 1580, 1555, 1482, 1451, 1422, 1293, 1253, 1158, 1020, 746.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 11.65\) (s, 1H), 7.57 (dd, \(J = 7.8, 1.2\) Hz, 1H), 7.49 – 7.47 (m, 1H), 7.31 (td, \(J = 7.4, 0.8\) Hz, 1H), 7.19 (td, \(J = 7.4, 1.6\) Hz, 1H), 3.98 – 3.89 (m, 1H), 2.41 (s, 3H), 1.35 (d, \(J = 6.4\) Hz, 6H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 186.5, 168.4, 143.7, 133.3, 129.9, 129.3, 127.2, 119.5, 89.7, 46.4, 23.2, 14.4.

[M+H]: 316.0188, Found: 316.0214.
1-(2-Bromophenyl)-2-methyl-3-(methylthio)-3-(phenylamino)prop-2-en-1-one (5g)

Yield: 60%, as a yellow colour viscous liquid.

R_f: 0.38 in 5% ethyl acetate in hexane

IR (KBr): ν (cm\(^{-1}\)) = 3463, 3054, 2983, 2926, 1709, 1555, 1428, 1385, 1314, 1265, 1243, 1164, 1051, 1025, 993, 961, 902, 857, 761, 744.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) [obtained as a (2:1) inseparable mixture of E/Z isomers] δ = 12.95 (s, 1H) [4.69 (s, 1H)], 7.57 (d, \(J = 8.0\) Hz, 1H) [7.519 – 7.511 (m, 1H)], 7.37 – 7.34 (m, 4H) [7.39 – 7.38 (m, 1H), 7.323 – 7.321 (m, 1H), 7.31 – 7.29 (m, 2H)], 7.23 – 7.21 (m, 2H) [7.20 (br s, 1H), 7.18 – 7.16 (m, 1H)], 7.15 – 7.13 (m, 1H) [7.06 (t, \(J = 7.3\) Hz, 1H)], 6.36 (m, 1H) [6.63 (br s, 1H)], 2.05 (s, 3H) [2.38 (s, 3H)], 1.90 (s, 3H) [1.48 (s, 3H)].

\(^13\)C NMR (100 MHz, CDCl\(_3\)) δ = 192.4 [200.3], 162.7 [167.6], 143.5 [150.0], 133.5 [128.7], 132.8 [140.7], 129.3 [129.7 (2C)], 127.60 [131.6], 127.56 [129.2], 124.9 [127.3], 123.3 [118.9], 119.7 [123.7], 106.9 [119.1], 16.8 [14.9], 16.5 [13.1].


[\(\text{M}+\text{H}\): 364.0189, Found: 364.0213.]

1-(2-Bromophenyl)-3-((2-methoxyphenyl)amino)-2-methyl-3-(methylthio)prop-2-en-1-one (5h)

Yield: 60%, as a yellow colour solid.

Melting point: 88 – 90 °C

R_f: 0.40 in 20% ethyl acetate in hexane

IR (KBr): ν (cm\(^{-1}\)) = 3447, 3002, 2962, 2933, 1592, 1582, 1553, 1495, 1458, 1383, 1312, 1254, 1177, 1112, 1026, 989, 862, 751.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) [obtained as a (2.7:1) inseparable mixture of E/Z isomers] δ = 12.34 (s, 1H) [4.54 (br s, 1H)], 7.59 (d, \(J = 7.6\) Hz, 1H) [7.48 – 7.46 (m, 1H)], 7.54 (d, \(J = 8.0\) Hz, 1H), 7.32 (d, \(J = 7.6\) Hz, 1H) [7.29 – 7.28 (m, 2H)], 7.24 – 7.21 (m, 1H) [7.16 – 7.15 (m, 1H)], 7.19 – 7.17 (m, 1H) [7.03 (t, \(J = 7.8\) Hz, 1H)], 7.11 – 7.07 (m, 1H) [6.85 (d, \(J = 8.1\), 1H)], 6.94 – 6.88 (m, 2H) [6.79 – 6.77 (m, 1H), 6.13 (br s, 1H)], 3.89 (s, 3H) [3.67 (s, 3H)], 2.09 (s, 3H) [2.41 (s, 3H)], 1.93 (s, 3H) [1.47 (s, 3H)].

\(^13\)C NMR (100 MHz, CDCl\(_3\)) δ = 192.3 [200.7], 151.6 [161.4], 143.8 [148.7], 133.3 [140.9], 132.7 [128.9], 131.4 [138.6], 129.8, 129.6 [127.2 (2C)], 127.7 [124.7], 127.5 [122.4], 125.1
[121.4], 122.4 [121.6], 120.7 [121.1], 118.9 [111.5], 111.0 [108.0], 55.9 [55.5], 16.57 [14.3], 16.47 [13.2].

HR-MS (ESI): Calcd. for C_{18}H_{18}BrNO_{2}S [M+H]: 392.0314, Found: 392.0319.


Table S1: Controlled Experiments\textsuperscript{c}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Metal salt</th>
<th>Ligand</th>
<th>Base</th>
<th>Solvent</th>
<th>Additive</th>
<th>8a (Yield)</th>
<th>7a (Yield)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CuI</td>
<td>1,10-phen</td>
<td>KO’Bu</td>
<td>DMF</td>
<td>-</td>
<td>no reaction</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>CuI</td>
<td>1,10-phen</td>
<td>KO’Bu</td>
<td>DMF</td>
<td>benzylamine</td>
<td>45%\textsuperscript{b}</td>
<td>5%\textsuperscript{b}</td>
</tr>
<tr>
<td>3</td>
<td>CuI</td>
<td>1,10-phen</td>
<td>KO’Bu</td>
<td>DMF</td>
<td>benzylamine/H_{2}O</td>
<td>no reaction</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a) Reaction conditions: 4a (10 mol \%), 1, 10-phen (12 mol\%), KO’Bu (3 equiv), BnNH\textsubscript{2} (1.5 equiv), DMF (2.0 mL). \textsuperscript{b) Isolated yield. c) Standard vial technique.}

References:

$^1$H NMR Spectra of 3a

$^{13}$C NMR Spectra of 3a
$^1$H NMR Spectra of 3b

$^{13}$C NMR Spectra of 3b
$^1$H NMR Spectra of 3c

$^{13}$C NMR Spectra of 3c
$^1$H NMR Spectra of 3d

$^{13}$C NMR Spectra of 3d
$^1$H NMR Spectra of $3e$

$^{13}$C NMR Spectra of $3e$
$^{1}$H NMR Spectra of 3f

$^{13}$C NMR Spectra of 3f
$^1$H NMR Spectra of $3g$

$^{13}$C NMR Spectra of $3g$
$^1\text{H NMR Spectra of 3h}$

$^{13}\text{C NMR Spectra of 3h}$
$^1$H NMR Spectra of 4a

$^{13}$C NMR Spectra of 4a
\[ ^1H \text{NMR Spectra of } 4b \]

\[ ^{13}C \text{ NMR Spectra of } 4b \]
$^1$H NMR Spectra of 4c

$^{13}$C NMR Spectra of 4c
$^{1}$H NMR Spectra of 4d

$^{13}$C NMR Spectra of 4d
$^1$H NMR Spectra of 4e

$^{13}$C NMR Spectra of 4e
$^1$H NMR Spectra of 4f

$^{13}$C NMR Spectra of 4f
$^1$H NMR Spectra of 4g

$^{13}$C NMR Spectra of 4g
$^1$H NMR Spectra of 4h

$^{13}$C NMR Spectra of 4h
$^1$H NMR Spectra of 5a

$^{13}$C NMR Spectra of 5a
$^1$H NMR Spectra of 5b

$^{13}$C NMR Spectra of 5b
$^1$H NMR Spectra of 5c

$^{13}$C NMR Spectra of 5c
$^1$H NMR Spectra of 5d

$^{13}$C NMR Spectra of 5d
$^1$H NMR Spectra of 5e

$^{13}$C NMR Spectra of 5e
$^1$H NMR Spectra of 5f

$^{13}$C NMR Spectra of 5f
$^1$H NMR Spectra of 5g

$^{13}$C NMR Spectra of 5g
$^1$H NMR Spectra of 5h

$^{13}$C NMR Spectra of 5h
$^1$H NMR Spectra of 6a

$^{13}$C NMR Spectra of 6a
$^1$H NMR Spectra of 6b

$^{13}$C NMR Spectra of 6b
$^1$H NMR Spectra of 6c

$^{13}$C NMR Spectra of 6c
\[ \text{\textsuperscript{1}H NMR Spectra of } 6d \]

\[ \text{\textsuperscript{13}C NMR Spectra of } 6d \]
$^{1}$H NMR Spectra of 6e

$^{13}$C NMR Spectra of 6e
$^1$H NMR Spectra of $6g$

$^{13}$C NMR Spectra of $6g$
$^1$H NMR Spectra of 6h

$^{13}$C NMR Spectra of 6h
$^1$H NMR Spectra of 7a

$^{13}$C NMR Spectra of 7a
$^1$H NMR Spectra of 7b

$^{13}$C NMR Spectra of 7b
$^1$H NMR Spectra of 7f

$^{13}$C NMR Spectra of 7f
$^1$H NMR Spectra of 8a

$^{13}$C NMR Spectra of 8a
$^1$H NMR Spectra of 8b

$^{13}$C NMR Spectra of 8b
$^1$H NMR Spectra of 8e

$^{13}$C NMR Spectra of 8e
$^1$H NMR Spectra of 7e

$^{13}$C NMR Spectra of 7e