

Supporting Information

for

Visible-light photoredox catalysis enabled bromination of phenols and alkenes

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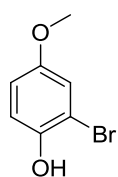
^1H and ^{13}C NMR spectra for products.

General Information

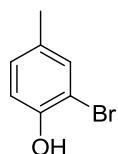
All reagents were purchased from commercial sources unless otherwise noted. Solvents were dried according to standard procedures prior to use. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker AV-400 spectrometer in CDCl_3 . For ^1H NMR (400 MHz), tetramethylsilane (TMS) served as an internal standard ($\delta = 0$ ppm), and data are reported as follows: chemical shift (in ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br =

broad), coupling constant (in Hz), and integration. For ^{13}C NMR (100 MHz), CDCl_3 was used as an internal standard ($\delta = 77.23$ ppm) and spectra were obtained with complete proton decoupling. HRMS spectra were recorded on a Bruker Esquire LC mass spectrometer by using electrospray ionization (ESI, TOF).

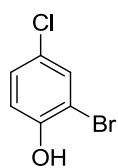
Characterization data of all products



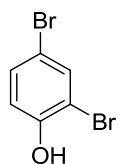
2-Bromo-4-methoxyphenol (2a): ^1H NMR (400 MHz, CDCl_3): δ 7.01 (d, $J = 2.88$ Hz, 1H), 6.94 (d, $J = 8.91$ Hz, 1H), 6.78 (dd, $J = 2.91, 2.88$ Hz, 1H), 5.23 (s, 1H), 3.75 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 153.83, 146.53, 116.85, 116.33, 115.35, 109.92, 55.99.



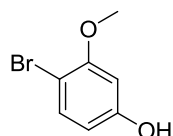
2-Bromo-4-methylphenol (2c): ^1H NMR (400 MHz, CDCl_3): δ 7.27 (s, 1H), 7.01 (d, $J = 8.25$ Hz, 1H), 6.90 (d, $J = 8.24$ Hz, 1H), 5.37 (s, 1H), 2.27 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 150.03, 132.12, 131.41, 129.77, 115.74, 109.83, 20.19.



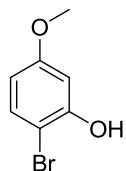
2-Bromo-4-chlorophenol (2d): ^1H NMR (400 MHz, CDCl_3): δ 7.46 (d, $J = 2.06$ Hz, 1H), 7.19 (dd, $J = 2.44, 2.43$ Hz, 1H), 6.95 (d, $J = 8.71$ Hz, 1H), 5.58 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 151.20, 131.59, 131.35, 129.23, 116.89, 116.05.



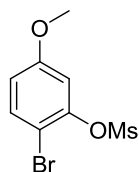
2,4-Bibromophenol (2e): ^1H NMR (400 MHz, CDCl_3): δ 7.59 (d, $J = 2.25$ Hz, 1H), 7.32 (dd, $J = 2.25, 2.24$ Hz, 1H), 6.91 (d, $J = 8.69$ Hz, 1H), 5.89 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 151.83, 134.12, 132.06, 117.48, 112.52, 110.87.



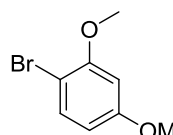
4-Bromo-3-methoxyphenol (2b): ^1H NMR (400 MHz, CDCl_3): δ 7.34 (d, J = 8.52 Hz, 1H), 6.60 (d, J = 2.85 Hz, 1H), 6.42 (dd, J = 2.88, 2.85 Hz, 1H), 5.49 (s, 1H), 3.77 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 156.76, 156.13, 133.36, 108.51, 102.27, 100.46, 56.19.



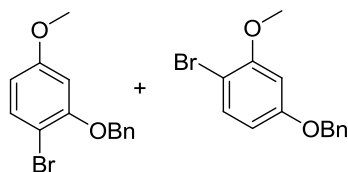
2-Bromo-5-methoxyphenol (2b'): ^1H NMR (400 MHz, CDCl_3): δ 7.32 (d, J = 8.85 Hz, 1H), 6.45 (d, J = 2.68 Hz, 1H), 6.34 (dd, J = 2.71, 2.71 Hz, 1H), 4.94 (s, 1H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 160.61, 153.00, 131.95, 108.45, 101.67, 100.89, 55.55.



2-Bromo-5-methoxyphenyl methanesulfonate (2f): ^1H NMR (400 MHz, CDCl_3): δ 7.49 (d, J = 8.12 Hz, 1H), 7.02 (d, J = 2.82 Hz, 1H), 6.77 (dd, J = 2.84, 2.84 Hz, 1H), 3.81 (s, 3H), 3.26 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 159.90, 146.95, 133.75, 114.98, 110.08, 105.82, 55.87, 38.86.

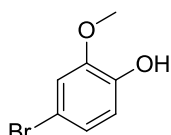


4-Bromo-3-methoxyphenyl methanesulfonate (2g): ^1H NMR (400 MHz, CDCl_3): δ 7.49 (d, J = 8.92 Hz, 1H), 7.01 (d, J = 2.82 Hz, 1H), 6.77 (dd, J = 2.84, 2.85 Hz, 1H), 3.81 (s, 3H), 3.26 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 159.90, 146.94, 133.74, 114.97, 110.08, 105.82, 55.87, 38.86.

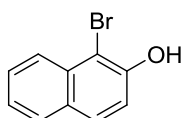


2-(Benzyloxy)-1-bromo-4-methoxybenzene (2h) and 4-(benzyloxy)-1-bromo-2-methoxybenzene (2i): ^1H NMR (400 MHz, CDCl_3): δ 7.49-7.33 (m, 10H), 6.58 (d, J = 2.62 Hz, 1H), 6.54 (d, J = 2.66 Hz, 0.65H), 6.47 (dd, J = 2.68, 2.67 Hz, 1H), 6.42 (dd, J = 2.69, 2.70 Hz, 0.65H), 5.13 (s, 1.30 H), 5.05 (s, 2H), 3.85 (s, 3H), 3.76 (s, 2.56H). ^{13}C NMR (100 MHz, CDCl_3): δ 160.10, 159.41,

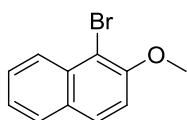
156.62, 155.71, 136.57, 136.46, 133.24, 133.19, 128.69, 128.62, 128.19, 127.98, 127.56, 127.06, 106.90, 106.57, 103.29, 102.78, 101.73, 100.94, 70.81, 70.42, 56.17, 55.56.



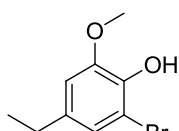
4-Bromo-2-methoxyphenol (2j): ^1H NMR (400 MHz, CDCl_3): δ 7.00-6.97 (m, 2H), 6.80 (d, J = 8.24 Hz, 1H), 5.51 (s, 1H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 147.23, 144.91, 124.19, 115.75, 114.18, 111.57, 56.16.



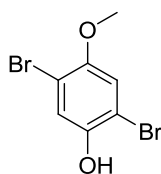
1-Bromonaphthalen-2-ol (2k): ^1H NMR (400 MHz, CDCl_3): δ 8.02 (d, J = 8.48 Hz, 1H), 7.77 (d, J = 8.16 Hz, 1H), 7.73 (d, J = 8.45 Hz, 1H), 7.56 (t, J = 15.40 Hz, 1H), 7.38 (t, J = 15.03 Hz, 1H), 7.26 (d, J = 8.85 Hz, 1H), 5.93 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 150.61, 132.32, 129.71, 129.35, 128.23, 127.86, 125.35, 124.16, 117.18, 106.16.



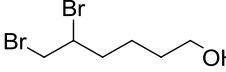
1-Bromo-2-methoxynaphthalene (2l): ^1H NMR (400 MHz, CDCl_3): δ 8.23 (d, J = 8.60 Hz, 1H), 7.84-7.73 (m, 3H), 7.597 (t, J = 15.42 Hz, 1H), 7.40 (t, J = 15.05 Hz, 1H), 7.28 (d, J = 8.99 Hz, 1H), 4.04 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 153.79, 133.16, 129.86, 128.97, 128.05, 127.75, 126.16, 124.34, 113.68, 108.73, 57.09.

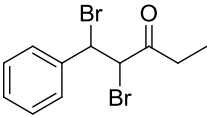


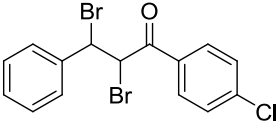
2-Bromo-4-ethyl-6-methoxyphenol (2m): ^1H NMR (400 MHz, CDCl_3): 7.09 (s, 1H), 6.71 (s, 1H), 5.48 (s, 1H), 3.87 (s, 3H), 2.70-2.64 (m, 2H), 1.21-1.17 (t, J = 15.04 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 146.03, 144.27, 134.72, 118.43, 114.36, 111.47, 56.07, 29.11, 14.68.

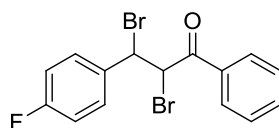


2,5-Dibromo-4-methoxyphenol (2n): ^1H NMR (400 MHz, CDCl_3): δ 7.12 (d, J = 2.95 Hz, 1H), 6.80 (d, J = 2.96 Hz, 1H), 5.65 (s, 1H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 153.73, 143.51, 126.08, 117.76, 116.61, 111.54, 56.02.

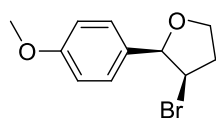

5,6-Dibromohexan-1-ol [1] (4f): ^1H NMR (400 MHz, CDCl_3) : δ 4.22-4.13 (m, 1H), 3.85 (dd, J = 10.3, 4.4 Hz, 1H), 3.65 (dt, J = 20.3, 6.3 Hz, 3H), 2.24-2.10 (m, 1H), 1.89-1.67 (m, 2H), 1.65-1.48 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3) : δ 62.71 (s), 52.97 (s), 36.39 (s), 36.00 (s), 32.03 (s), 23.36 (s).


1,2-Dibromo-1-phenylpentan-3-one (4b): ^1H NMR (400 MHz, CDCl_3) : δ 7.44-7.36 (m, 5H), 5.37 (d, J = 11.6 Hz, 1H), 4.95 (d, J = 11.6 Hz, 1H), 2.87 (q, J = 7.2 Hz, 1H), 2.76 (q, J = 7.2 Hz, 1H), 1.23 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 201.79 (s), 138.09 (s), 129.45 (s), 129.01 (s), 128.29 (s), 51.83 (s), 49.71 (s), 34.00 (s), 8.03 (s).

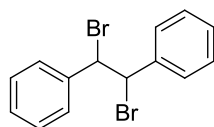

2,3-Dibromo-1-(4-chlorophenyl)-3-phenylpropan-1-one [2] (4c): ^1H NMR (400 MHz, Acetone): δ 8.35-8.25 (m, 2H), 7.79-7.73 (m, 2H), 7.70-7.64 (m, 2H), 7.44 (dt, J = 19.5, 7.0 Hz, 3H), 6.49 (d, J = 11.3 Hz, 1H), 5.74 (d, J = 11.3 Hz, 1H). ^{13}C NMR (100 MHz, Acetone) : δ 206.32 (s), 131.65 (s), 130.15 (d, J = 14.1 Hz), 129.59 (d, J = 6.3 Hz), 51.16 (s), 47.26 (s), 29.84 (s).



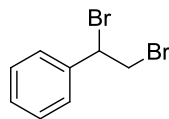
2,3-Dibromo-3-(4-fluorophenyl)-1-phenylpropan-1-one (4d): ^1H NMR (400 MHz, CDCl_3): δ 8.03 (d, J = 8.7 Hz, 2H), 7.57-7.46 (m, 4H), 7.12 (t, J = 8.6 Hz, 2H), 5.70 (d, J = 11.3 Hz, 1H), 5.61 (d, J = 11.3 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 190.03 (s), 164.34 (s), 141.08 (s), 134.23 (s), 132.80 (s), 130.38 (d, J = 10.4 Hz), 129.58 (s), 116.02 (s), 48.91 (s), 47.03 (s).



3-Bromo-2-(4-methoxyphenyl)tetrahydrofuran (8): ^1H NMR (400 MHz, CDCl_3) : δ 7.30 (d, J = 8.5 Hz, 2H), 6.89 (d, J = 8.8 Hz, 2H), 5.05 (d, J = 5.0 Hz, 1H), 4.23 (td, J = 8.2, 4.2 Hz, 1H), 4.14 (ddd, J = 9.9, 9.1, 6.4 Hz, 2H), 3.80 (s, 3H), 2.62-2.51 (m, 1H), 2.31 (ddt, J = 13.6, 7.1, 4.4 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) : δ 159.61 (s), 132.00 (s), 127.15 (s), 114.06 (s), 88.35 (s), 67.47 (s), 55.43 (s), 52.87 (s), 36.38 (s).



1,2-Dibromo-1,2-diphenylethane [3] (4a): ^1H NMR (400 MHz, CDCl_3): δ 7.18 (s, 5H), 5.48 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 137.92 (s), 128.72 (d, J = 2.9 Hz), 128.31 (s), 59.25 (s).



1,2-Dibromo-1-phenylethane [4] (4e): ^1H NMR (400 MHz, CDCl_3): δ 7.44-7.34 (m, 5H), 5.15 (dd, J = 10.6, 5.5 Hz, 1H), 4.13-3.99 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 138.64 (s), 129.21 (s), 128.89 (s), 127.68 (s), 50.89 (s), 35.04 (s).

References:

1. G. I. Nikishin, L. L. Sokova, N. I. Kapustina, *Russian Chemical Bulletin*, **2012**, 61, 459.
2. M. A. Rekhter, G. N. Grushetskaya, A. A. Panasenko, M. Z. Krimer, *Chemistry of Heterocyclic Compounds*, **1995**, 31, 792.
3. Kefeng Ma, Shaw Li, Richard G. Weiss, *Org. Lett.*, **2008**, 10, 4155.
4. Gajanan K. Dewkar, Srinivasarao V. Narina, Arumugam Sudalai, *Org. Lett.*, **2003**, 5, 4501.

^1H NMR and ^{13}C NMR spectra for bromophenols and other bromoproducts

