

Supporting Information

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2. General experimental procedure and characterization data (S2-S9).
3. ^1H and ^{13}C NMR spectra of compounds **3**, **4**, **5**, **7** and **9** (S10-S49).

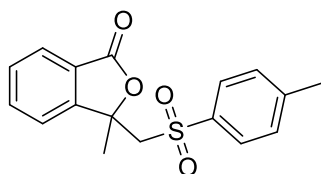
General experimental methods:

Unless otherwise stated, all commercial reagents were used as received. All solvents were dried and distilled according to standard procedures. Flash column chromatography was performed using silica gel (60-Å pore size, 32–63µm, standard grade). Analytical thin-layer chromatography was performed using glass plates pre-coated with 0.25 mm 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light. Organic solutions were concentrated on rotary evaporators at ~20 Torr at 25–35°C. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the δ scale. ^1H and ^{13}C NMR spectra were recorded in CDCl_3 on a Bruker DRX-400 spectrometer operating at 400 MHz and 100 MHz, respectively. All chemical shift values are quoted in ppm and coupling constants quoted in Hz. High resolution mass spectrometry (HRMS) spectra were obtained on a microTOF II Instrument.

*General experimental procedure for the reaction of 2-vinylbenzoic acid **1**, sulfur dioxide, and aryldiazonium tetrafluoroborates **2**.*

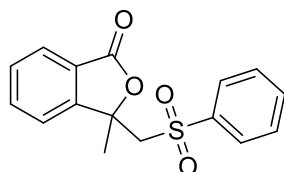


2-Vinylbenzoic acid **1** (0.2 mmol) was added to a mixture of aryldiazonium tetrafluoroborate **2** (0.3 mmol), $\text{DABCO}\cdot(\text{SO}_2)_2$ (0.16 mmol) and $\text{Ir}(\text{ppy})_3$ (2 mol %) in DCE under N_2 atmosphere. The mixture was stirred under blue LED irradiation for 12 h. After completion as indicated by TLC, the solvent was evaporated and the residue was purified directly by flash column chromatography (n -hexane/ethyl acetate/ CH_2Cl_2 = 5:1:1) to give the corresponding product **3**.



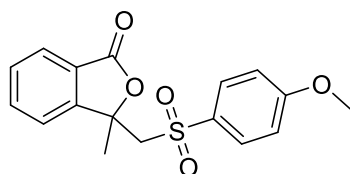
3-methyl-3-(tosylmethyl)isobenzofuran-1(3H)-one (**3a**); white solid

^1H NMR (400 MHz, CDCl_3): δ 7.86 (d, J = 7.6 Hz, 1H), 7.65 (td, J = 7.6, 0.9 Hz, 1H), 7.61 (d, J = 8.3 Hz, 2H), 7.58 – 7.49 (m, 2H), 7.30 (d, J = 8.1 Hz, 2H), 3.84-3.71 (m, 2H), 2.44 (s, 3H), 1.81 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 168.4, 150.8, 145.0, 137.0, 134.3, 129.8, 129.7, 127.9, 125.7, 125.5, 122.1, 82.9, 62.9, 26.9, 21.6. HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{17}\text{O}_4\text{S}^+$: 317.0842 ($\text{M}+\text{H}^+$), found: 317.0858.



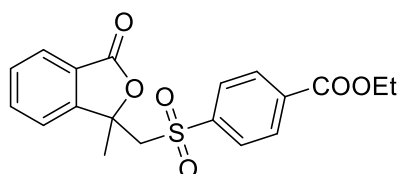
3-methyl-3-((phenylsulfonyl)methyl)isobenzofuran-1(3H)-one (**3b**); white solid

^1H NMR (400 MHz, CDCl_3): δ 7.86 (d, J = 7.5 Hz, 1H), 7.73 (d, J = 7.7 Hz, 2H), 7.64 (t, J = 7.2 Hz, 2H), 7.58 – 7.45 (m, 4H), 3.89-3.75 (m, 2H), 1.81 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 168.3, 150.6, 139.9, 134.3, 133.9, 129.7, 129.2, 127.8, 125.7, 125.5, 122.0, 82.8, 62.8, 26.9. HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{15}\text{O}_4\text{S}^+$: 303.0686 ($\text{M}+\text{H}^+$), found: 303.0681.



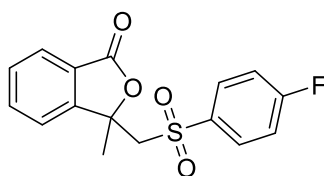
3-(((4-methoxyphenyl)sulfonyl)methyl)-3-methylisobenzofuran-1(3H)-one (**3c**); white solid

^1H NMR (400 MHz, CDCl_3): δ 7.86 (d, J = 7.6 Hz, 1H), 7.68-7.64 (m, 3H), 7.54 (dd, J = 17.6, 7.6 Hz, 2H), 6.95 (d, J = 8.5 Hz, 2H), 3.87 (s, 3H), 3.84-3.71 (m, 2H), 1.80 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 168.5, 166.7, 150.8, 134.3, 131.4, 130.1, 129.7, 125.7, 125.5, 122.1, 114.4, 83.0, 63.0, 55.7, 26.9. HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{17}\text{O}_5\text{S}^+$: 333.0791 ($\text{M}+\text{H}^+$), found: 333.0778.



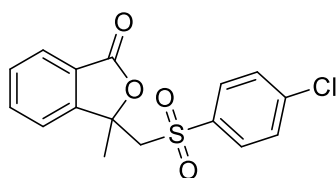
ethyl 4-(((1-methyl-3-oxo-1,3-dihydroisobenzofuran-1-yl)methyl)sulfonyl)benzoate (**3d**); white solid

^1H NMR (400 MHz, CDCl_3): δ 8.16 (d, $J = 7.9$ Hz, 2H), 7.88 (d, $J = 7.4$ Hz, 1H), 7.81 (d, $J = 8.0$ Hz, 2H), 7.64 (t, $J = 7.3$ Hz, 1H), 7.57 (t, $J = 7.4$ Hz, 1H), 7.47 (d, $J = 7.5$ Hz, 1H), 4.42 (q, $J = 6.9$ Hz, 2H), 3.94-3.77 (m, 2H), 1.81 (s, 3H), 1.42 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 168.2, 164.8, 150.5, 143.5, 135.2, 134.4, 130.3, 129.8, 127.9, 125.9, 125.5, 121.8, 82.6, 62.7, 61.8, 26.9, 14.2. HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{19}\text{O}_6\text{S}^+$: 375.0897 ($\text{M}+\text{H}^+$), found: 375.0899.



3-(((4-fluorophenyl)sulfonyl)methyl)-3-methylisobenzofuran-1(3H)-one (**3e**); white solid

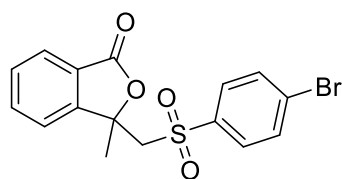
^1H NMR (400 MHz, CDCl_3): δ 7.87 (d, $J = 7.6$ Hz, 1H), 7.75 (dd, $J = 7.5, 5.2$ Hz, 2H), 7.67 (t, $J = 7.4$ Hz, 1H), 7.57 (t, $J = 7.4$ Hz, 1H), 7.48 (d, $J = 7.6$ Hz, 1H), 7.18 (t, $J = 8.1$ Hz, 2H), 3.90-3.73 (m, 2H), 1.81 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 168.3, 165.9 (d, $^1J_{\text{CF}} = 256.3$ Hz), 150.6, 135.9, 134.4, 130.9 (d, $^3J_{\text{CF}} = 9.7$ Hz), 129.8, 125.8, 125.5, 121.8, 116.6 (d, $^2J_{\text{CF}} = 22.7$ Hz), 82.7, 62.9, 26.9. ^{19}F NMR (276 MHz, CDCl_3): δ 102.59-102.65 (m). HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{14}\text{FO}_4\text{S}^+$: 321.0591 ($\text{M}+\text{H}^+$), found: 321.0596.



3-(((4-chlorophenyl)sulfonyl)methyl)-3-methylisobenzofuran-1(3H)-one (**3f**); white solid

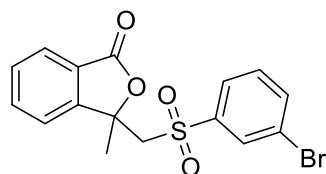
^1H NMR (400 MHz, CDCl_3): δ 7.87 (d, $J = 7.5$ Hz, 1H), 7.68-7.64 (m, 3H), 7.56 (t, $J = 7.4$ Hz, 1H), 7.51 – 7.43 (m, 3H), 3.90-3.73 (m, 2H), 1.80 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 168.3, 150.6, 140.8, 138.4, 134.4, 129.9, 129.6, 129.4, 125.9, 125.5, 121.8,

82.7, 62.9, 26.9. HRMS (ESI) calcd for $C_{16}H_{14}ClO_4S^+$: 337.0296 ($M+H^+$), found: 337.0311.



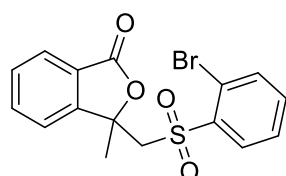
3-(((4-bromophenyl)sulfonyl)methyl)-3-methylisobenzofuran-1(3*H*)-one (**3g**); white solid

1H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, J = 7.5 Hz, 1H), 7.68 – 7.55 (m, 6H), 7.46 (d, J = 7.6 Hz, 1H), 3.89-3.72 (m, 2H), 1.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.3, 150.6, 138.9, 134.4, 132.6, 129.9, 129.5, 129.4, 125.9, 125.5, 121.8, 82.7, 62.9, 26.9. HRMS (ESI) calcd for $C_{16}H_{14}BrO_4S^+$: 380.9791 ($M+H^+$), found: 380.9792.



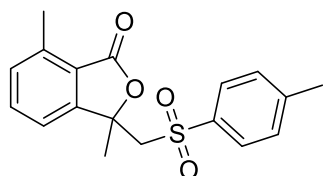
3-(((3-bromophenyl)sulfonyl)methyl)-3-methylisobenzofuran-1(3*H*)-one (**3h**); white solid

1H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, J = 7.5 Hz, 1H), 7.76-7.74 (m, 2H), 7.71 – 7.61 (m, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.45-7.38 (m, 2H), 3.91-3.75 (m, 2H), 1.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.2, 150.1, 141.5, 137.0, 134.3, 130.8, 130.8, 130.0, 126.5, 125.9, 125.6, 123.2, 121.9, 82.6, 62.8, 27.1. HRMS (ESI) calcd for $C_{16}H_{14}BrO_4S^+$: 380.9791 ($M+H^+$), found: 380.9793.



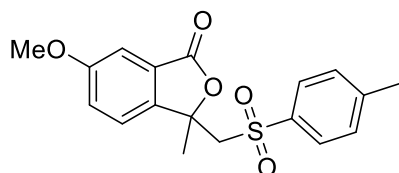
3-(((2-bromophenyl)sulfonyl)methyl)-3-methylisobenzofuran-1(3*H*)-one (**3i**); white solid

^1H NMR (400 MHz, CDCl_3): δ 7.83 (d, J = 7.5 Hz, 1H), 7.74 (d, J = 7.8 Hz, 1H), 7.70 (d, J = 7.8 Hz, 1H), 7.58 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 7.4 Hz, 1H), 7.47 – 7.40 (m, 2H), 7.37 (t, J = 7.6 Hz, 1H), 4.23 – 4.14 (m, 2H), 1.79 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 168.1, 150.3, 138.7, 135.3, 134.9, 134.2, 131.6, 129.8, 128.1, 125.7, 125.6, 121.8, 120.6, 82.6, 60.0, 27.1. HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{14}\text{BrO}_4\text{S}^+$: 380.9791 ($\text{M}+\text{H}^+$), found: 380.9776.



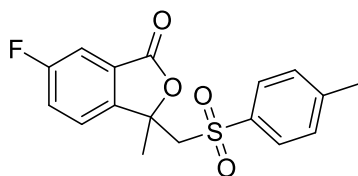
3,7-dimethyl-3-(tosylmethyl)isobenzofuran-1(3H)-one (**3j**); white solid

^1H NMR (400 MHz, CDCl_3): δ 7.61 (d, J = 7.8 Hz, 2H), 7.50 (t, J = 7.5 Hz, 1H), 7.37 – 7.10 (m, 4H), 3.84-3.68 (m, 2H), 2.65 (s, 3H), 2.43 (s, 3H), 1.77 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 168.6, 151.2, 145.0, 139.8, 137.0, 133.9, 131.3, 129.8, 128.0, 123.0, 119.3, 81.8, 63.2, 27.0, 21.6, 17.3. HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{19}\text{O}_4\text{S}^+$: 331.0999 ($\text{M}+\text{H}^+$), found: 331.0998.



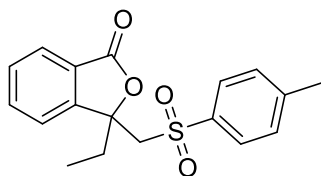
6-methoxy-3-methyl-3-(tosylmethyl)isobenzofuran-1(3H)-one (**3k**); white solid

^1H NMR (400 MHz, CDCl_3): δ 7.75 (d, J = 8.5 Hz, 1H), 7.61 (d, J = 8.0 Hz, 2H), 7.32 – 7.24 (m, 2H), 7.03 (d, J = 8.4 Hz, 1H), 6.87 (s, 1H), 3.86 (s, 3H), 3.81-3.70 (m, 2H), 2.43 (s, 3H), 1.78 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 168.1, 164.8, 153.5, 145.0, 137.1, 129.8, 127.9, 127.2, 117.8, 117.1, 106.0, 82.1, 63.0, 55.8, 26.8, 21.6. HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{19}\text{O}_5\text{S}^+$: 347.0948 ($\text{M}+\text{H}^+$), found: 347.0954.



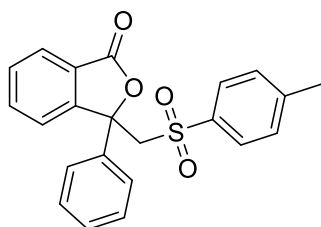
6-fluoro-3-methyl-3-(tosylmethyl)isobenzofuran-1(3H)-one (**3l**); white solid

^1H NMR (400 MHz, CDCl_3): δ 7.62 (d, J = 8.2 Hz, 2H), 7.56-7.49 (m, 2H), 7.39-7.31 (m, 3H), 3.82-3.72 (m, 2H), 2.45 (s, 3H), 1.80 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 167.1, 163.4 (d, $^1J_{\text{CF}}$ = 250.9 Hz), 146.2, 145.2, 137.0, 129.9, 127.9, 124.2 (d, $^3J_{\text{CF}}$ = 8.6 Hz), 122.2, 122.0, 112.1 (d, $^2J_{\text{CF}}$ = 23.8 Hz), 83.0, 62.9, 27.1, 21.6. ^{19}F NMR (276 MHz, CDCl_3): δ 110.29-110.35 (m). HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{16}\text{FO}_4\text{S}^+$: 335.0748 ($\text{M}+\text{H}^+$), found: 335.0747.



3-ethyl-3-(tosylmethyl)isobenzofuran-1(3H)-one (**3m**); white solid

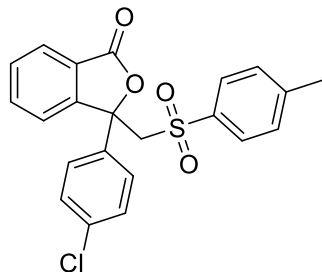
^1H NMR (400 MHz, CDCl_3): δ 7.86 (d, J = 7.5 Hz, 1H), 7.65 (t, J = 7.3 Hz, 1H), 7.57-7.54 (t, 3H), 7.45 (d, J = 7.6 Hz, 1H), 7.28 (d, J = 8.3 Hz, 2H), 3.89-3.75 (m, 2H), 2.43 (s, 3H), 2.29-2.20 (m, 1H), 2.08-1.99 (m, 1H), 0.67 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 168.7, 148.7, 144.9, 137.1, 134.1, 129.8, 129.6, 127.8, 126.7, 125.6, 122.3, 85.5, 62.0, 32.5, 21.6, 6.9. HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{19}\text{O}_4\text{S}^+$: 331.0999 ($\text{M}+\text{H}^+$), found: 331.0998.



3-phenyl-3-(tosylmethyl)isobenzofuran-1(3H)-one (**3n**); white solid

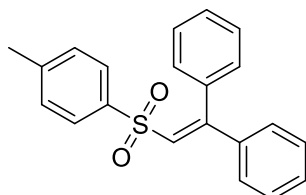
^1H NMR (400 MHz, CDCl_3): δ 7.88 (d, J = 7.6 Hz, 1H), 7.66 – 7.58 (m, 2H), 7.57 – 7.50 (m, 3H), 7.44 (dd, J = 8.0, 1.4 Hz, 2H), 7.36 – 7.28 (m, 3H), 7.25 (d, J = 8.1 Hz, 2H),

4.30-4.18 (m, 2H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 168.5, 149.1, 144.9, 139.0, 137.0, 134.2, 129.8, 129.0, 128.8, 127.9, 125.8, 125.6, 124.6, 123.3, 85.0, 63.0, 21.6. HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{19}\text{O}_4\text{S}^+$: 379.0999 ($\text{M}+\text{H}^+$), found: 379.0981.



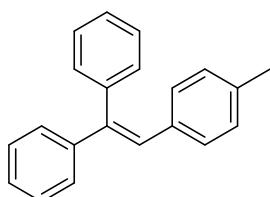
3-(4-chlorophenyl)-3-(tosylmethyl)isobenzofuran-1(3H)-one (**3o**); white solid

^1H NMR (400 MHz, DMSO): δ 7.83 (d, J = 7.5 Hz, 1H), 7.73 (d, J = 7.7 Hz, 1H), 7.64 (t, J = 7.3 Hz, 1H), 7.59 – 7.53 (m, 3H), 7.49 (d, J = 8.1 Hz, 2H), 7.39 (d, J = 8.6 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 4.86-4.75 (m, 2H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, DMSO): δ 168.7, 150.4, 144.5, 138.7, 137.9, 135.1, 133.7, 130.4, 129.9, 129.1, 127.9, 127.1, 125.6, 124.5, 123.9, 85.0, 60.6, 21.5. HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{21}\text{ClNO}_4\text{S}^+$: 430.0874 ($\text{M}+\text{NH}_4^+$), found: 430.0874.



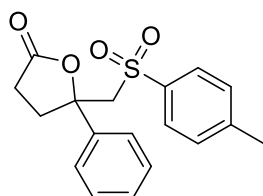
(2-tosylethene-1,1-diyl)dibenzene (**4**) (ref: G. A. Russell, P. Ngoviwatchai, H. Tashtoush and J. Hershberger, *Organometallics* 1987, **6**, 1414.); white solid

^1H NMR (400 MHz, CDCl_3): δ 7.47 (d, J = 7.8 Hz, 2H), 7.36 (dd, J = 12.7, 5.9 Hz, 2H), 7.29 (t, J = 7.4 Hz, 4H), 7.20 (d, J = 8.1 Hz, 2H), 7.14 (d, J = 7.9 Hz, 2H), 7.09 (d, J = 7.8 Hz, 2H), 6.99 (s, 1H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 154.6, 143.7, 139.1, 138.5, 135.5, 130.1, 129.7, 129.2, 128.9, 128.7, 128.5, 128.1, 127.7, 127.6, 21.5.



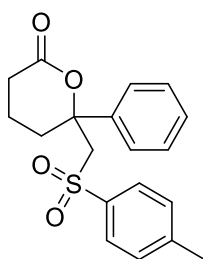
(2-(*p*-tolyl)ethene-1,1-diyl)dibenzene (**5**) (ref: B.-J. Li, Y.-Z. Li, X.-Y. Lu, J. Lu, B.-T. Guan and Z.-J. Shi, *Angew. Chem.* 2008, **120**, 10278.); colorless oil

^1H NMR (400 MHz, CDCl_3): δ 7.31 – 7.20 (m, 10H), 6.94-6.90 (m, 5H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 143.5, 141.6, 140.6, 136.6, 134.5, 130.4, 129.4, 128.7, 128.6, 128.1, 128.1, 127.5, 127.3, 127.3, 21.1.



5-phenyl-5-(tosylmethyl)dihydrofuran-2(3*H*)-one (**7**); white soild

^1H NMR (400 MHz, CDCl_3): δ 7.70 (d, J = 7.9 Hz, 2H), 7.49 – 7.13 (m, 7H), 3.87 – 3.59 (m, 2H), 3.41-3.33 (m, 1H), 2.89-2.81 (m, 1H), 2.69 – 2.58 (m, 1H), 2.55 – 2.44 (m, 1H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 175.3, 144.9, 141.8, 137.4, 129.8, 128.8, 128.4, 127.8, 124.4, 84.6, 64.9, 32.4, 28.1, 21.6. HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{22}\text{NO}_4\text{S}^+$: 348.1264 ($\text{M}+\text{NH}_4^+$), found: 348.1261.



6-phenyl-6-(tosylmethyl)tetrahydro-2*H*-pyran-2-one (**9**); white soild

^1H NMR (400 MHz, CDCl_3): δ 7.73 (d, J = 7.7 Hz, 2H), 7.43 – 7.12 (m, 7H), 3.89 – 3.52 (m, 2H), 2.99-2.91 (m, 1H), 2.55– 2.42 (m, 6H), 1.86 – 1.80 (m, 1H), 1.53 – 1.48 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 169.6, 144.7, 141.4, 137.7, 129.7, 128.9, 128.2, 127.9, 124.8, 84.4, 66.3, 30.2, 29.2, 21.6, 16.1. HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{21}\text{O}_4\text{S}^+$: 345.1155 ($\text{M}+\text{H}^+$), found: 345.1152.

