

## Supporting Information

### Bismuth-based Cyclic Synthesis of 3,5-Di-*tert*-butyl-4-hydroxybenzoic Acid via the Oxyarylcarboxy Dianion, $(\text{O}_2\text{CC}_6\text{H}_2^t\text{Bu}_2\text{O})^{2-}$

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#### EXPERIMENTAL:

All manipulations and syntheses described below were conducted with the rigorous exclusion of air and water using standard Schlenk line and glovebox techniques under an argon or dinitrogen atmosphere. Solvents were sparged with UHP argon and dried by passage through columns containing Q-5 and molecular sieves prior to use. Deuterated NMR solvents were dried over NaK alloy, degassed by three freeze-pump-thaw cycles, and vacuum transferred before use.  $^1\text{H}$  NMR spectra were recorded on Bruker DR400, GN500, or CRYO500 MHz spectrometers ( $^{13}\text{C}$  NMR spectra on the 500 MHz spectrometer operating at 125 MHz) at 298 K unless otherwise stated and referenced internally to residual protio-solvent resonances. IR samples were prepared neat on KBr salt plates on a Varian 1000 FT-IR system. GC-MS spectra were collected on a ThermoTrace MS and GC-MS instrument. High-resolution mass spectra (HRMS) were obtained from the UC Irvine Mass Spectrometry Facility. potassium 2,6-di-*tert*-butylphenolate was synthesized via an adaptation of a literature procedure by treatment of the parent phenol with one equiv of  $\text{KN}(\text{SiMe}_3)_2$  in toluene, followed by filtration of the resulting white solid, and washing with hexane.<sup>1</sup>  $\text{CO}_2$  (99.98%) and  $^{13}\text{CO}_2$  (99%) were purchased from Airgas and Cambridge Isotope Laboratories, respectively. Phenol reagents were sublimed prior

to use.  $[\text{Et}_3\text{NH}][\text{Cl}]$  ( $\geq 99\%$ ) was purchased from Sigma-Aldrich.  $\text{Ar}'\text{Bi}(\text{C}_6\text{H}_2^t\text{Bu}_2\text{-3,5-O-4})$  and  $\text{Ar}'\text{Bi}[\text{O}_2\text{C}(\text{C}_6\text{H}_2^t\text{Bu}_2\text{-3-5-O-4})\text{-}\kappa^2\text{O},\text{O}']$  were prepared according to the literature.<sup>2,3</sup>

**3,5-di-*tert*-butyl-4-hydroxybenzoic acid, 4.**  $[\text{Et}_3\text{NH}][\text{Cl}]$  (23 mg, 0.17 mmol) was added as a solid to a stirred yellow suspension of **2** (50 mg, 0.08 mmol) in THF (8 mL). After stirring for 30 min, the reaction mixture became clear and colorless. After stirring overnight, the solvent was removed under vacuum to yield an off-white solid which was stirred in hexane (10 mL) for 1 h. The insoluble material was collected by centrifugation and identified as  $\text{Ar}'\text{BiCl}_2$  by  $^1\text{H}$  and  $^{13}\text{C}$  NMR.<sup>4</sup> Solvent was removed to yield the hexane soluble carboxylic acid, **4** (17 mg, 88%), identified by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy and GC-MS.<sup>5</sup>

**Dipotassium 3,5-di-*tert*-butyl-4-oxidobenzoate, 5.** Solid KI (77 mg, 0.46 mmol) was added to a stirring yellow mixture of **2** (100 mg, 0.15 mmol) in THF (10 mL). After stirring overnight, the solvent was removed by vacuum and the yellow solids washed with hexane (10 mL). The yellow solids were extracted with minimum THF and these extractions dried under vacuum to give **5** as an off-white solid (35 mg, 70%).  $^1\text{H}$  NMR (500 MHz, acetonitrile- $d_3$ ):  $\delta$  7.76 [s, 2H,  $\text{KOC}_6\text{H}_2^t\text{Bu}_2\text{CO}_2\text{K}$ ], 1.38 [s, 18H,  $\text{KOC}_6\text{H}_2^t\text{Bu}_2\text{CO}_2\text{K}$ ]. **5** was protonated with 2 equiv of  $[\text{Et}_3\text{NH}][\text{Cl}]$  to yield **4**, identified by GC-MS and  $^1\text{H}$  NMR spectroscopy,<sup>5</sup> and KCl.

**Trimethylsilyl 3,5-di-*tert*-butyl-4-((trimethylsilyl)oxy)benzoate, 6.** To a stirring yellow mixture of **2** (97 mg, 0.15 mmol) in THF (10 mL) was added excess  $\text{Me}_3\text{SiCl}$  (0.1 mL, 0.8 mmol) inducing a rapid fading of color, with the reaction mixture becoming clear and colorless after 20 min. After stirring overnight, the solvent was removed by vacuum and the white solids were stirred in hexane (10 mL). White insoluble material was collected and identified as  $\text{Ar}'\text{BiCl}_2$  by NMR spectroscopy.<sup>4</sup> Hexane was removed under vacuum to yield **6** as a white solid (43 mg, 73%).  $^1\text{H}$  NMR (500 MHz, benzene- $d_6$ ):  $\delta$  8.42 [s, 2H,

$\text{Me}_3\text{SiOC}_6\text{H}_2^t\text{Bu}_2\text{CO}_2\text{SiMe}_3$ , 1.30 [s, 18H,  $\text{Me}_3\text{SiOC}_6\text{H}_2^t\text{Bu}_2\text{CO}_2\text{SiMe}_3$ ], 0.37 [s, 9H,  $\text{Me}_3\text{SiOC}_6\text{H}_2^t\text{Bu}_2\text{CO}_2\text{SiMe}_3$ ], 0.30 [s, 9H,  $\text{Me}_3\text{SiOC}_6\text{H}_2^t\text{Bu}_2\text{CO}_2\text{SiMe}_3$ ].  $^{13}\text{C}$  NMR (125 MHz, benzene- $d_6$ ):  $\delta$  167.6 [ $\text{Me}_3\text{SiOC}_6\text{H}_2^t\text{Bu}_2\text{CO}_2\text{SiMe}_3$ ], 158.3 [ $\text{Me}_3\text{SiOC}_6\text{H}_2^t\text{Bu}_2\text{CO}_2\text{SiMe}_3$ ], 141.7 [ $\text{Me}_3\text{SiOC}_6\text{H}_2^t\text{Bu}_2\text{CO}_2\text{SiMe}_3$ ], 124.5 [ $\text{Me}_3\text{SiOC}_6\text{H}_2^t\text{Bu}_2\text{CO}_2\text{SiMe}_3$ ], 35.7 [ $\text{Me}_3\text{SiOC}_6\text{H}_2(\text{CMe}_3)_2\text{CO}_2\text{SiMe}_3$ ], 31.6 [ $\text{Me}_3\text{SiOC}_6\text{H}_2(\text{CMe}_3)_2\text{CO}_2\text{SiMe}_3$ ], 4.1 [ $\text{Me}_3\text{SiOC}_6\text{H}_2^t\text{Bu}_2\text{CO}_2\text{SiMe}_3$ ], 0.3 [ $\text{Me}_3\text{SiOC}_6\text{H}_2^t\text{Bu}_2\text{CO}_2\text{SiMe}_3$ ]. IR: 3036w, 2958m, 1692s, 1601w, 1418m, 1364w, 1310s, 1250s, 1151m, 1124m, 906s, 851s, 780m, 639w  $\text{cm}^{-1}$ . HRMS (CI+)  $m/z$  calcd for  $\text{C}_{21}\text{H}_{38}\text{O}_3\text{Si}_2$  (M+H) $^+$  395.2438, found 395.2439.

**Reaction of 2 with Iodine.** In an argon-filled glovebox, a brown THF (3 mL) solution of  $\text{I}_2$  (33 mg, 0.13 mmol) was added to a stirred yellow mixture of **2** (85 mg, 0.13 mmol) in THF (8 mL). The reaction mixture quickly turned clear and red/brown. After stirring for 4 h, the solvent was removed under vacuum. The resulting yellow solids were extracted with hexane (10 mL) leaving off-white insoluble material identified by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy as  $\text{Ar}^t\text{BiI}_2$ .<sup>4</sup> The red hexane extract was dried to yield red solids identified by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy and GC-MS as the coupled product (3,3',5,5'-tetra-*tert*-butyl-4,4'-diphenquinone).<sup>6,7</sup>

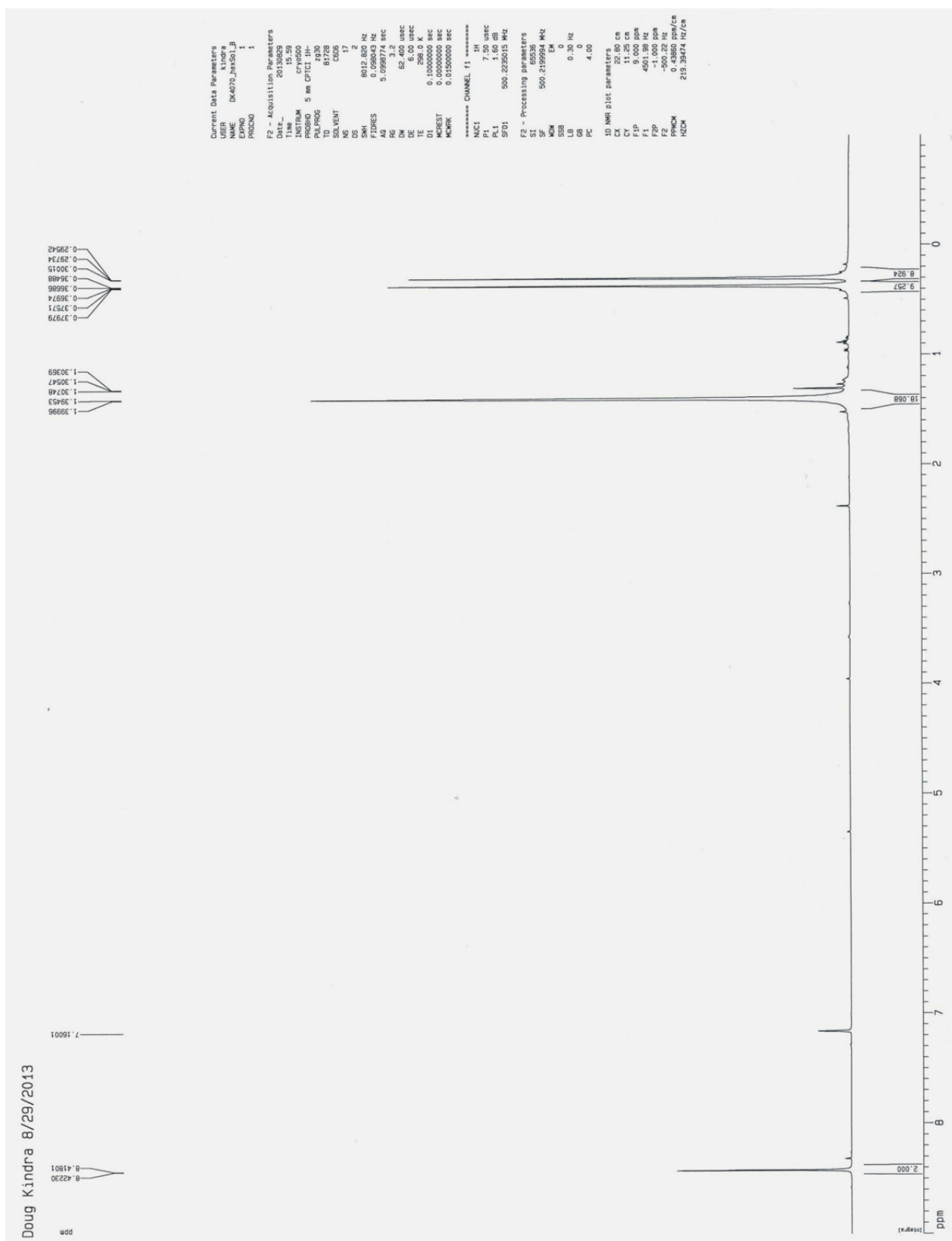


Figure S1. <sup>1</sup>H NMR spectrum of compound **6** in benzene-*d*<sub>6</sub>.



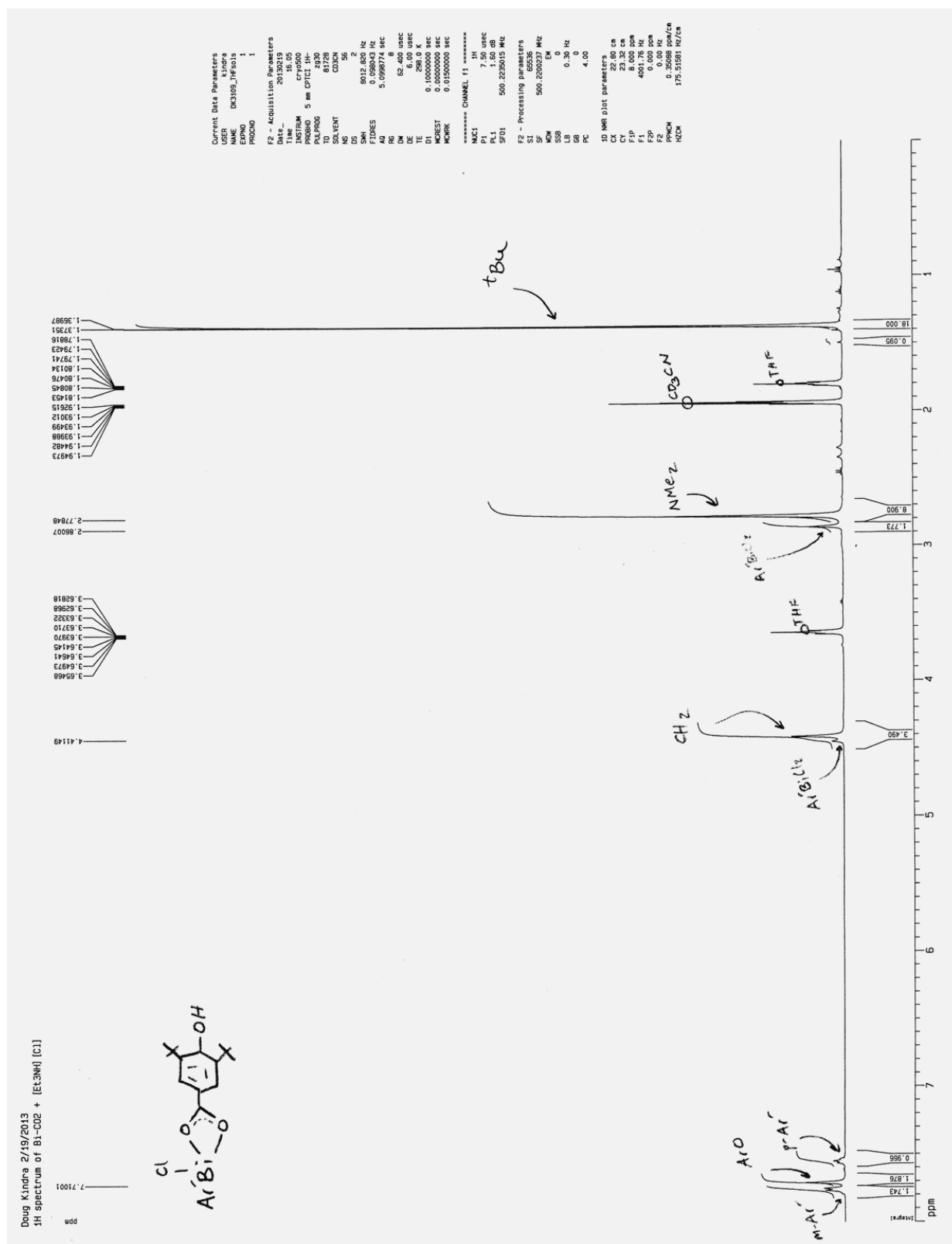


Figure S3. <sup>1</sup>H NMR spectrum of compound 2 and 1 equiv of [Et<sub>3</sub>NH][Cl] in benzene-d<sub>6</sub>.

## REFERENCES

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