

**Perylenequinone Natural Products: Enantioselective Synthesis of the Oxidized Pentacyclic Core**

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*Supporting Information, Part 1*

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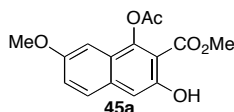
## ***General Considerations***

**Materials:** Purchased reagents were used without further purification unless otherwise stated. Unless otherwise noted, all non-aqueous reactions were carried out under an atmosphere of dry argon in oven-dried glassware (85 °C). If anhydrous conditions were required, reactions were carried out under an atmosphere of argon in flame-dried glassware with magnetic stirring. Tetrahydrofuran, dichloromethane, toluene, and ether were degassed with argon and passed through a neutral alumina (Al<sub>2</sub>O<sub>3</sub>) column solvent purification system. If anhydrous solvents were needed, they were further dried by distillation from sodium or CaH<sub>2</sub> under argon. Flash chromatography was performed with EM Science silica gel 60 (230-400 mesh) using a forced flow of the indicated solvent system.

**Analytical Methods:** Thin layer chromatography (TLC) was carried out with 0.25 mm silica-gel plates 60-F plates. Visualization was accomplished with ceric ammonium molybdate or a 250 nm UV light. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on 300, 360, and 500 MHz spectrometers at ambient temperature. Data are reported as follows: chemical shift in parts per million (δ, ppm) from the solvent resonance of deuterated chloroform (CDCl<sub>3</sub>) 7.27 ppm. Multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), integration, and coupling constant (Hz). Mass spectra were with an ionization mode of either CI or ESI. IR spectra were acquired as film or solutions using a Si-Comp probe. Melting points are uncorrected. Optical rotations were measured with a sodium lamp and are reported as follows:  $[\alpha]_D^{20}$  (c = g/100 mL, solvent). Enantiomeric excess was determined using an HPLC equipped with Chiralpak AD or OD columns (0.46 cm × 25 cm) from Daicel or using a gas chromatograph (GC) with a Supelco β-DEX<sup>TM</sup> 120 column (12 m × 0.25 mm). Circular dichroism (CD) and UV

spectroscopy measurements were carried out on a Jasco J-720 Spectropolarimeter integrated with a refrigerated circulator digital temperature controller.

### ***Synthetic Procedures***



**Methyl 1-acetoxy-3-hydroxy-7-methoxy-2-naphthoate (45a).** 4-Methoxyphenylacetic acid (6.65 g, 40 mmol) was heated at reflux in  $\text{SOCl}_2$  (10 mL) for 1 h. Excess  $\text{SOCl}_2$  was removed *in vacuo* to afford the acid chloride as a brown oil. To a stirred suspension of NaH (3.2 g, 60% in oil) in THF (40 mL) was added dimethylmalonate (4.6 mL, 40 mmol) dropwise. The mixture was heated at reflux for 1 h. After cooling to room temperature, the acid chloride in THF (20 mL) was added slowly to this malonate solution. After stirring overnight, the mixture was quenched with 12 N HCl and extracted with  $\text{CH}_2\text{Cl}_2$ . Filtration and concentration yielded a residue which was dissolved in  $\text{CH}_2\text{Cl}_2$  and loaded onto a  $\text{SiO}_2$  pad. The pad was washed with hexanes to remove mineral oil and then with 15% EtOAc/hexanes to provide methyl 4-(4-methoxyphenyl)-2-methoxycarbonyl-3-oxobutyrate as a slightly impure oil in 63% yield (7.1 g) which was used without further purification: IR (thin film) 2957, 2926, 1733, 1613, 1218, 1177  $\text{cm}^{-1}$ ; HRMS (ES) calcd for  $\text{C}_{14}\text{H}_{16}\text{O}_6$  ( $\text{MH}^+$ ) 280.0947, found 280.0945.

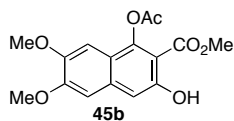
Methyl 4-(4-methoxyphenyl)-2-methoxycarbonyl-3-oxobutyrate (6.7 g, 24 mmol) was dissolved in  $\text{CH}_3\text{SO}_3\text{H}$  (60 g) along with  $\text{P}_2\text{O}_5$  (6.0 g).<sup>1</sup> The mixture was stirred at room temperature vigorously under  $\text{N}_2$  for 6 h, and then the mixture was poured onto ice and water. The resultant yellow solid precipitate was collected by filtration, washed with water, and dried overnight to provide the product (5.0 g, 84% yield): IR (thin film) 3362 (br), 3011, 1652, 1278

<sup>1</sup> For a description of  $\text{P}_2\text{O}_5/\text{CH}_3\text{SO}_3\text{H}$  as an alternative to polyphosphoric acid see: Eaton, P. E.; Carlson, G. R.; Lee, J. T. *J. Org. Chem.* **1973**, 38, 4071-4073.

cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 11.3 (s, OH), 8.7 (s, OH), 7.5 (s, 1H), 7.46 (d, *J* = 8.8 Hz, 1H), 7.18 (d, *J* = 8.5 Hz, 1H), 6.73 (s, 1H), 4.11 (s, 3H), 3.9 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 170.5, 160.1, 155.8, 152.0, 133.3, 127.5, 123.4, 119.9, 102.4, 101.9, 97.6, 55.3, 52.9; HRMS (ES) calcd for CHO (M<sup>+</sup>) 248.0685, found 248.0684.

Bisphenol (10 g, 40 mmol) was dissolved in Ac<sub>2</sub>O (30 mL) and pyridine (25 mL). After 1 h, the mixture was poured onto ice and water and was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined extracts were washed further with 1 N HCl and dried over Na<sub>2</sub>SO<sub>4</sub>. After filtration and concentration, the residue was purified by chromatography (1% MeOH/CH<sub>2</sub>Cl<sub>2</sub>) to provide methyl 2,4-diacetoxy-6-methoxy-3-naphthoate as a white solid (12.8 g, 96% yield): IR (thin film) 3393 (br), 3011, 1768, 1725, 1613, 1258, 1235, 1181 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.46 (d, *J* = 8.9 Hz, 1H), 7.18 (dd, *J* = 8.9, 2.2 Hz, 1H), 7.06 (s, 1H), 6.97 (d, *J* = 1.7 Hz, 1H), 3.94 (s, 3H), 3.92 (s, 3H), 3.87 (s, 3H), 2.41 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 169.4, 168.6, 164, 158.5, 146.0, 143.4, 130.0, 129.1, 126.5, 121.7, 118.6, 117.3, 100.6, 55.3, 52.4, 20.7, 20.6; HRMS (ESI) calcd for C<sub>17</sub>H<sub>16</sub>O<sub>7</sub>Na (MNa<sup>+</sup>) 355.0794, found 355.0786.

To methyl 2,4-diacetoxy-6-methoxy-3-naphthoate (12.8 g, 38.6 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (200 mL) was slowly added NaOMe (2.1 g, 38.9 mmol) in MeOH (200 mL). After 30 min, the mixture was treated with 1 N HCl, extracted with CH<sub>2</sub>Cl<sub>2</sub>, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated. The residue was purified by chromatography (1% MeOH/ CH<sub>2</sub>Cl<sub>2</sub>) to provide the product as a white solid in 48% yield (5.4 g, 18.6 mmol): IR (thin film) 3300, 2957, 1768, 1675, 1224, 1197 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 10.4 (s, OH), 7.53 (d, *J* = 8.7 Hz, 1H), 7.19 (s, 1H), 7.16 (d, *J* = 8.5 Hz, 1H), 6.96 (s, 1H), 3.95 (s, 3H), 3.84 (s, 3H), 2.43 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 169.2, 169.0, 156.6, 154.6, 147.4, 133.2, 127.9, 123.1, 122.4, 110.2, 107.8, 100.2, 55.1, 52.9, 20.7; HRMS (ES) calcd for C<sub>15</sub>H<sub>14</sub>O<sub>6</sub> (MH<sup>+</sup>) 290.0790, found 290.0786.



**Methyl 1-acetoxy-3-hydroxy-6,7-dimethoxy-2-naphthoate (45b).** 3,4-

Dimethoxyphenylacetic acid (19.6 g, 100 mmol) was heated at reflux in  $\text{SOCl}_2$  (30 mL) for 2 h. Excess  $\text{SOCl}_2$  was removed *in vacuo* to afford the acid chloride as a brown oil. To a stirred suspension of NaH (16.0 g, 60% in oil) in THF (600 mL) was added dimethylmalonate (46 mL, 400 mmol) dropwise. The mixture was heated at reflux for 1 h. After cooling to room temperature, the acid chloride in THF (200 mL) was added slowly to this malonate solution. After stirring overnight, the mixture was quenched with 12 N HCl and extracted with  $\text{CH}_2\text{Cl}_2$ . Filtration and concentration yielded a residue, which was dissolved in  $\text{CH}_2\text{Cl}_2$  and loaded onto a  $\text{SiO}_2$  pad. The pad was washed with 50%  $\text{CH}_2\text{Cl}_2$ /hexanes to remove mineral oil and then with  $\text{CH}_2\text{Cl}_2$  to provide methyl 4-(3,4-dimethoxyphenyl)-2-methoxycarbonyl-3-oxobutyrates as an oil (45.0 g) which was used without further purification.

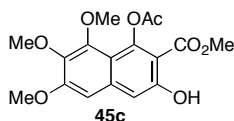
The above methyl 4-(3,4-dimethoxyphenyl)-2-methoxycarbonyl-3-oxobutyrates was dissolved in  $\text{CH}_3\text{SO}_3\text{H}$  (300 g) along with  $\text{P}_2\text{O}_5$  (30.0 g).<sup>1</sup> The mixture was stirred at room temperature vigorously under  $\text{N}_2$  for 4 h, and then the mixture was poured onto ice and water. The resultant yellow solid precipitate was collected by filtration, washed with water and MeOH, and dried overnight to yield the product (23.0 g, 83% yield over two steps). This material was found to have the spectral data identical to that previously reported.<sup>2</sup>

To bisphenol (18.0 g, 65 mmol) was added  $\text{Ac}_2\text{O}$  (100 mL, 1.06 mol) and pyridine (100 mL, 1.24 mol). The mixture was stirred at room temperature overnight and poured onto ice and water. The resultant mixture was extracted with  $\text{CH}_2\text{Cl}_2$ . After filtration and concentration, the

<sup>2</sup> Weisgraber, K. H.; Weiss, U. *J. Chem. Soc., Perkin Trans. 1* **1972**, 83-88.

residue was purified by chromatography (0.5% MeOH/CH<sub>2</sub>Cl<sub>2</sub>) to provide methyl 2,4-diacetoxy-6,7-dimethoxy-3-naphthoate as a solid in 95% yield (22.3 g).

This bisacetate (22.3 g, 61.6 mmol) was then treated with NaOMe (3.33 g, 61.6 mmol) in MeOH/CH<sub>2</sub>Cl<sub>2</sub> (100 mL/100 mL) at room temperature. After 3 h, the mixture was poured onto ice and 1 N HCl and the resultant mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>. After filtration and concentration, the residue was purified by chromatography (1% MeOH/CH<sub>2</sub>Cl<sub>2</sub>). The product **45b** was isolated as yellow solid (11.2 g, 57% yield): IR (thin film) 2957, 1768, 1675, 1235, 1204, 1170 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 10.6 (s, OH), 7.11 (s, 1H), 6.95 (s, 1H), 6.9 (s, 1H), 3.98 (s, 6H), 3.94 (s, 3H), 2.45 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 169.4, 169.1, 155.9, 153.1, 148.9, 147.3, 134.6, 117.0, 110.6, 109.0, 105.8, 105.4, 104.6, 103.0, 100.8, 55.96, 55.93, 55.74, 52.82, 52.61, 20.91, 20.83; HRMS (ES) calcd for C<sub>16</sub>H<sub>17</sub>O<sub>7</sub> (MH<sup>+</sup>) 321.0974, found 321.1039.



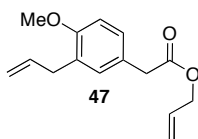
**Methyl 1-acetoxy-3-hydroxy-6,7,8-trimethoxy-2-naphthoate (45c).** 3,4,5-Trimethoxyphenylacetic acid (2.26 g, 10 mmol) was heated at reflux with oxalyl chloride (10 mL) and DMF (1.0 mL) in benzene (100 mL) for 1 h. Excess oxalyl chloride was removed *in vacuo* to afford the acid chloride<sup>6</sup> as a brown oil. To a stirred suspension of NaH (2 g, 60% in oil) in THF (60 mL) was added dimethylmalonate (1.71 mL, 15 mmol) dropwise. The mixture was heated at reflux for 1 h. The acid chloride in THF (20 mL) was then slowly added to this malonate solution. After stirring overnight, the mixture was quenched with 12 N HCl and extracted with CH<sub>2</sub>Cl<sub>2</sub>. Filtration and concentration yielded a residue which was purified by chromatography (1% MeOH/CH<sub>2</sub>Cl<sub>2</sub>). The resultant methyl 4-(3,4,5-trimethoxyphenyl)-2-

methoxycarbonyl-3-oxobutyrate was obtained in slightly impure form as an oil (2.75 g, 81% yield) which was used without further purification: HRMS (ES) calcd for  $C_{16}H_{20}O_8Na$  ( $MNa^+$ ) 363.1045, found 363.1056.

Methyl 4-(3,4,5-trimethoxyphenyl)-2-methoxycarbonyl-3-oxobutyrate (2.2 g, 6.5 mmol) was dissolved in  $CH_3SO_3H$  (35 g) along with  $P_2O_5$  (3.5 g).<sup>1</sup> The mixture was stirred at room temperature vigorously under  $N_2$ . After 3 h, the mixture was poured onto ice and water. The precipitate was collected by filtration and dried overnight to yield the product as a white solid (1.0 g, 75% yield): IR (thin film) 3451, 3223, 2945, 1668, 1625, 1243, 1119  $cm^{-1}$ ;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  11.5 (s, OH), 10.4 (br s, OH), 6.66 (s, 1H), 6.62 (s, 1H), 4.06 (s, 3H), 4.00 (s, 3H), 3.90 (s, 3H), 3.85 (s, 3H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  171.2, 160.3, 156.4, 155.9, 150.2, 138.6, 136.3, 107.5, 101.8, 101.6, 97.9, 62.3, 61.2, 55.8, 52.8; HRMS (ES) calcd for  $C_{15}H_{16}O_7Na$  ( $MNa^+$ ) 331.0794, found 331.0808.

Bisphenol (616 mg, 2 mmol) was dissolved in  $Ac_2O$  (5 mL) and pyridine (4 mL). After 1 h, the mixture was poured onto ice and water and was extracted with  $CH_2Cl_2$ . The combined extracts were washed further with 1 N HCl and dried over  $Na_2SO_4$ . After filtration and concentration, the residue was purified by chromatography (1% MeOH/  $CH_2Cl_2$ ) to provide methyl 2,4-diacetoxy-5,6,7-trimethoxy-3-naphthoate as a solid (820 mg, >99% yield): IR (thin film) 3389 (br), 2945, 1768, 1729, 1625, 1258, 1189, 1112  $cm^{-1}$ ;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  7.33 (s, 1H), 6.90 (s, 1H), 3.95 (s, 3H), 3.93 (s, 3H), 3.91 (s, 3H), 3.89 (s, 3H), 2.35 (s, 3H), 2.30 (s, 3H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  169.1, 168.9, 164.2, 155.0, 148.8, 146.1, 144.9, 143.1, 133.0, 117.7, 116.5, 115.9, 103.0, 61.9, 61.2, 55.9, 52.4, 20.8, 20.5; HRMS (ES) calcd for  $C_{19}H_{20}O_9Na$  ( $MNa^+$ ) 415.0991, found 415.1005.

Methyl 2,4-diacetoxy-5,6,7-trimethoxy-3-naphthoate (300 mg, 0.75 mmol) was dissolved in  $\text{CH}_2\text{Cl}_2$  (8 mL) and NaOMe (46 mg, 0.85 mmol) in MeOH (8 mL) was slowly added. After 30 min, the reaction was quenched with 1 N HCl. After extraction with  $\text{CH}_2\text{Cl}_2$ , drying over  $\text{Na}_2\text{SO}_4$ , and concentration, the residue was purified by chromatography (1% MeOH/  $\text{CH}_2\text{Cl}_2$ ) to provide the product as a solid in 67% yield (180 mg, 0.5 mmol): IR (thin film) 3366 (br), 2945, 1671, 1625, 1239, 1200, 1116  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  10.7 (s, OH), 7.08 (s, 1 H), 6.73 (s, 1 H), 3.99 (s, 3H), 3.95 (s, 3H), 3.93 (s, 3H), 3.89 (s, 3H), 2.39 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  169.8, 169.4, 156.3, 156.0, 149.3, 148.6, 141.2, 136.3, 112.4, 109.3, 106.5, 101.3, 61.7, 61.2, 55.9, 53.0, 20.8; HRMS (ES) calcd for  $\text{C}_{17}\text{H}_{18}\text{O}_8\text{Na}$  ( $\text{MNa}^+$ ) 373.0899, found 373.0883.

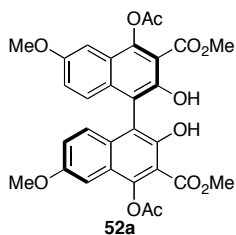


**Allyl 2-(3-allyl-4-methoxyphenyl)acetate (47).** To a solution of 2-(4-hydroxyphenyl)acetic acid (5.0 g, 32.9 mmol) in DMF (85 mL) under Ar was added  $\text{K}_2\text{CO}_3$  (13.6 g, 98.4 mmol) then allyl bromide (6.3 mL, 72.8 mmol). The mixture was stirred for 2 d, then was poured over ice- $\text{H}_2\text{O}$ . The aqueous phase was extracted with  $\text{Et}_2\text{O}$ , and the organics were washed with  $\text{H}_2\text{O}$  and brine, dried over  $\text{Na}_2\text{SO}_4$ , and the solvent was evaporated. The residue was purified via  $\text{SiO}_2$  chromatography (0%-10% EtOAc/hexanes) to yield product as an oil (7.5 g, 98%):  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ )  $\delta$  3.59 (s, 2H), 4.51-4.60 (m, 4H), 5.19-5.44 (m, 4H), 5.85-6.04 (m, 2H), 6.87 (d,  $J = 8.7$  Hz, 2H), 7.20 (d,  $J = 8.7$  Hz, 2H);  $^{13}\text{C}$  NMR: (200 MHz,  $\text{CDCl}_3$ )  $\delta$  171.8, 158.0, 133.6, 132.4, 130.6, 126.4, 118.4, 117.9, 115.1, 69.0, 65.7, 40.7; HRMS (ESI): [ $\text{MNa}^+$ ] calcd for  $\text{C}_{14}\text{H}_{16}\text{O}_3\text{Na}$ , 255.0997; found, 255.1005.



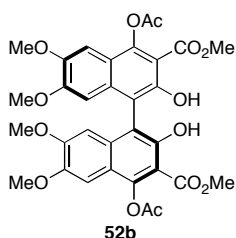
A solution of this allyl ether (3.0 g, 12.9 mmol) in Ph<sub>2</sub>O (65 mL) was heated to reflux under Ar for 2 h. The reaction was cooled, then filtered through SiO<sub>2</sub>, rinsing with hexanes, then 20% EtOAc/hexanes. The solvent was evaporated to yield the product as an oil (2.9 g, 95%): IR (thin film) 3435, 3078, 2940, 1719, 1267, 1150 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 3.38 (d, *J* = 6.3 Hz, 2H), 3.57 (s, 2H), 4.60 (d, *J* = 5.6 Hz, 2H), 5.13-5.30 (m, 4H), 5.86-6.03 (m, 2H), 6.72 (d, *J* = 8.7 Hz, 1H), 7.02-7.03 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 153.7, 136.7, 132.4, 131.7, 129.0, 126.5, 126.0, 118.7, 116.9 (2), 116.3, 65.9, 40.8, 35.4; HRMS (ESI): [MNa<sup>+</sup>] calcd for C<sub>14</sub>H<sub>16</sub>O<sub>3</sub>Na, 255.0997; found, 255.0997.

To a solution of the phenol in DMF (50 mL) under Ar was added NaH (60% in mineral oil, 520 mg, 13 mmol). After stirring 20 min, Me<sub>2</sub>SO<sub>4</sub> (1.1 mL, 12 mmol) was added. After stirring for 2 h, the mixture was diluted with EtOAc and H<sub>2</sub>O, the phases were separated, and the organic phase was extracted with H<sub>2</sub>O and brine, dried (Na<sub>2</sub>SO<sub>4</sub>), and the solvent was evaporated. Purification was accomplished via chromatography (0-10% EtOAc/hexanes) to yield **47** as an oil (2.33 g, 86%): IR (thin film) 3080, 2945, 1733, 1251, 1135 cm<sup>-1</sup>; <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>) δ 3.37 (d, *J* = 6.5 Hz, 2H), 3.57 (s, 2H), 3.81 (s, 3H), 4.59 (d, *J* = 5.5 Hz, 2H), 5.02-5.06 (m, 2H), 5.20-5.29 (m, 2H), 5.87-6.02 (m, 2H), 6.81 (d, *J* = 8.3 Hz, 1H), 7.05 (s, 1H), 7.10 (d, *J* = 8.3 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 172.0, 156.8, 137.2, 132.5, 131.1, 129.2, 128.4, 126.2, 118.5, 115.9, 110.9, 65.8, 55.9, 40.9, 34.6; HRMS (CI): calcd for C<sub>15</sub>H<sub>18</sub>O<sub>3</sub>, (M<sup>+</sup>) 246.1256; found, 246.1257.

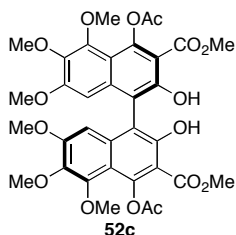


**(M)-Dimethyl 4,4'-diacetoxy-2,2'-dihydroxy-6,6'-dimethoxy-1,1'-binaphthyl-3,3'-**

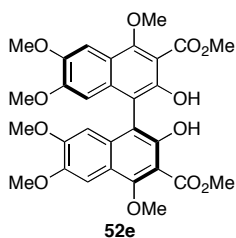
**dicarboxylate (52a).** Asymmetric biaryl coupling was carried out according to the General Procedure with 5 mol% CuI-[(*S,S*)-**51**] and 2 mmol substrate in ClCH<sub>2</sub>CH<sub>2</sub>Cl (2 mL) at 40 °C for 48 h in the presence of powdered 4 Å molecular sieves (0.2 g) to give the product as a yellow solid in 71% yield (0.41 g, 1.42 mmol): [ $\alpha$ ]<sub>D</sub><sup>20</sup> +112.5, (c 1.0, 86% ee, CH<sub>2</sub>Cl<sub>2</sub>); IR (thin film) 3160, 2956, 1773, 1674, 1237, 1178 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  10.6 (s, 2OH), 7.13–7.05 (m, 6H), 4.0 (s, 6H), 3.88 (s, 6H), 2.52 (s, 6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  169.5, 169.1, 156.8, 152.3, 147.7, 132.6, 126.7, 123.1, 122.8, 115.5, 108, 100.9, 55.3, 53.1, 20.9; HRMS (ES) calcd for C<sub>30</sub>H<sub>26</sub>O<sub>12</sub> (MH<sup>+</sup>) 578.1424, found 578.1415; CSP HPLC (Chiralpak AD; 1.0 mL/min, 85:15 hexanes:*i*PrOH)  $t_R(S)$  = 18.7 min,  $t_R(R)$  = 31.8 min.



**(*P*)-Dimethyl 4,4'-diacetoxy-2,2'-dihydroxy-6,6',7,7'-tetramethoxy-1,1'-binaphthyl-3,3'-dicarboxylate (52b).** Asymmetric biaryl coupling was carried out according to the General Procedure with 10 mol% CuI-[(*R,R*)-**51**] and 0.1 mmol substrate in ClCH<sub>2</sub>CH<sub>2</sub>Cl (1 mL) at room temperature for 24 h to give the product as a yellow solid in 72% yield (0.023 g, 0.072 mmol): [ $\alpha$ ]<sub>D</sub><sup>20</sup> –55.2 (c 1.05, 90% ee, CH<sub>2</sub>Cl<sub>2</sub>); IR (thin film) 3426, 2954, 1771, 1669, 1500, 1239, 1207, 1168 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  10.9 (s, 2OH), 7.1 (s, 2H), 6.44 (s, 2H), 4.00 (s, 6H), 3.98 (s, 6H), 3.96 (s, 6H), 3.59 (s, 6H), 2.52 (s, 6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  169.7, 169.1, 153.6, 153.3, 148.8, 147.5, 133.9, 117.2, 114.2, 105.4, 103.2, 101.3, 55.76, 55.71, 52.9, 20.9; HRMS (ES) calcd for C<sub>32</sub>H<sub>30</sub>O<sub>14</sub>Na (MNa<sup>+</sup>) 661.1533, found 661.1543; CSP HPLC: Chiralpak AD, 1.0 mL/min, 80:20 hexanes:*i*PrOH,  $t_R(S)$  = 33.6 min,  $t_R(R)$  = 51.0 min.

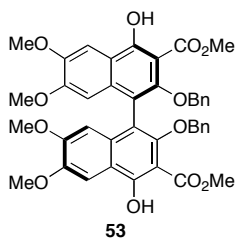


**(M)-Dimethyl 4,4'-diacetoxy-2,2'-dihydroxy-5,5',6,6',7,7'-hexamethoxy-1,1'-binaphthyl-3,3'-dicarboxylate (52c).** Asymmetric biaryl coupling was carried out according to the General Procedure with 10 mol% CuI-[(*S,S*)-**51**] and 0.18 mmol substrate in ClCH<sub>2</sub>CH<sub>2</sub>Cl (2 mL) at room temperature for 24 h to give the product as a yellow solid in 41% yield (0.026 g, 0.074 mmol): [ $\alpha$ ]<sub>D</sub><sup>20</sup> +15.8 (c 1.24, 27% ee, CH<sub>2</sub>Cl<sub>2</sub>); IR (thin film) 2938, 1771, 1668, 1613, 1360, 1200 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  10.9 (s, 2OH), 6.27 (s, 2H), 4.0 (s, 6H), 3.98 (s, 6H), 3.89 (s, 6H), 3.58 (s, 6H), 2.44 (s, 6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  170.0, 169.4, 156.3, 153.9, 149.6, 148.9, 141.3, 135.3, 114.3, 112.7, 106.6, 99.7, 61.8, 61.0, 55.7, 53.1, 22.6, 20.9; HRMS (ES) calcd for C<sub>34</sub>H<sub>34</sub>O<sub>16</sub>Na (MNa<sup>+</sup>) 721.1746, found 721.1744. CSP HPLC (Chiralpak AD; 1.0 mL/min, 90:10 hexanes:*i*PrOH) t<sub>R</sub>(*S*) = 19.08 min, t<sub>R</sub>(*R*) = 24.06 min.



**(P)-Dimethyl 2,2'-dihydroxy-4,4',6,6',7,7'-hexamethoxy-1,1'-binaphthyl-3,3'-dicarboxylate (52e).** Asymmetric biaryl coupling was carried out according to the General Procedure with 10 mol% CuI-[(*S,S*)-**51**] and 0.05 mmol substrate in ClCH<sub>2</sub>CH<sub>2</sub>Cl (1 mL) at room temperature for 24 h to give the product as a yellow solid in 81% yield (0.012 g, 0.041 mmol): [ $\alpha$ ]<sub>D</sub><sup>20</sup> -25.5 (c 0.55, 35% ee, CH<sub>2</sub>Cl<sub>2</sub>); IR (thin film) 3445, 2951, 1661, 1238, 1203 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  10.8 (s, 2H), 7.47 (s, 2H), 6.42 (s, 2H), 4.077 (s, 6H), 4.075 (s,

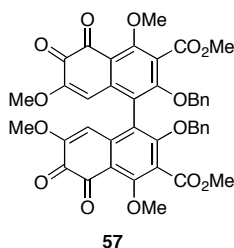
6H), 4.0 (s, 6H), 3.58 (s, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  170.8, 158.3, 153.4, 152.9, 148.3, 134.1, 118.2, 112.2, 105.6, 103.5, 102.3, 63.2, 55.8, 55.7, 52.8; HRMS (ES) calcd for  $\text{C}_{30}\text{H}_{30}\text{O}_{12}\text{Na}$  ( $\text{MNa}^+$ ) 605.1635, found 605.1640; CSP HPLC (Chiralpak AD; 1.0 mL/min, 80:20 hexanes:*i*PrOH)  $t_{\text{R}}(S) = 29.7$  min,  $t_{\text{R}}(R) = 43.4$  min.



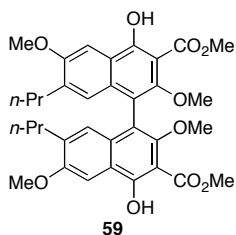
**(*M*)-Dimethyl 2,2'-bis(benzyloxy)-4,4'-dihydroxy-6,6',7,7'-tetramethoxy-1,1'-binaphthyl-3,3'-dicarboxylate (53).** The coupling product **52b** (38 mg, 0.06 mmol) was suspended in THF (1 mL) with BnOH (26 mg, 0.24 mmol) and  $\text{PPh}_3$  (63 mg, 0.24 mmol). DIAD (49 mg, 0.24 mmol) was added and the resultant mixture was kept at room temperature for 48 h. The yellow solution was diluted with EtOAc and washed with water. Concentration afforded an oil which was purified by  $\text{SiO}_2$  chromatography (50-70% EtOAc/hexanes) to provide the bisacetate as a colorless oil (44 mg, 90%):  $[\alpha]_{\text{D}}^{20} -67.4$  (c 1.3, 74% ee,  $\text{CH}_2\text{Cl}_2$ ); IR (thin film) 2953, 1781, 1732, 1242, 1209, 1169  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  2.49 (s, 6H), 3.52 (s, 6H), 3.86 (s, 6H), 3.98 (s, 6H), 4.41 (d,  $J = 10.3$  Hz, 2H), 4.79 (d,  $J = 10.2$  Hz, 2H), 6.5 (s, 2H), 6.79 (d,  $J = 2.4$  Hz, 4 H), 7.11 (m, 8H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  168.6, 165.9, 151.7, 151.4, 149.7, 145.3, 136.4, 130.9, 128.3, 128.1, 127.7, 127.0, 122.3, 120.0, 118.7, 104.7, 100.9, 76.7, 55.8, 52.5, 20.7; HRMS (ESI) calcd for  $\text{C}_{46}\text{H}_{42}\text{O}_{14}\text{Na}$  ( $\text{MNa}^+$ ) 841.2440, found 841.2472.

To diacetate (26 mg, 0.032 mmol) in  $\text{CH}_2\text{Cl}_2$  (3 mL) was added NaOMe (54 mg, 1.0 mmol) in MeOH (3 mL). After 30 min at room temperature, the yellow solution was diluted with  $\text{CH}_2\text{Cl}_2$  and washed with 1 M HCl. Concentration afforded an oil which was purified by  $\text{SiO}_2$  chromatography (0.5-1% MeOH/  $\text{CH}_2\text{Cl}_2$ ) to provide **53** as a light yellow oil (22 mg, 96%):

$[\alpha]_{\text{D}}^{20}$   $-62.3$  (c 1.1, 74% ee,  $\text{CH}_2\text{Cl}_2$ ); IR (thin film) 2950, 1646, 1506, 1257, 1209, 1172  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  3.54 (s, 6H), 3.86 (s, 6H), 4.03 (s, 6H), 4.41 (d,  $J = 10.3$  Hz, 2H), 4.79 (d,  $J = 10.2$  Hz, 2H), 6.45 (s, 2H), 6.76 (d,  $J = 7.0$  Hz, 4 H), 7.09 (m, 6H), 7.73 (s, 2H), 12.8 (s, 2OH);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  172.1, 161.1, 152.6, 152.6, 148.3, 137.4, 133.1, 127.8, 127.4, 127.3, 117.0, 116.5, 104.6, 103.0, 101.8, 75.9, 55.9, 55.7, 52.4; HRMS (ESI) calcd for  $\text{C}_{42}\text{H}_{38}\text{O}_{12}\text{Na}$  ( $\text{MNa}^+$ ) 757.2261, found 757.2248.

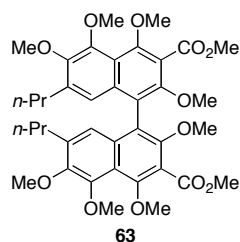


**Dimethyl 2,2'-bis(benzyloxy)-4,4',7,7'-tetramethoxy-5,5',6,6'-tetraoxo-5,5',6,6'-tetrahydro-1,1'-binaphthyl-3,3'-dicarboxylate (57).** *Ortho*-quinone **54** (15 mg, 0.02 mmol) was dissolved in THF (1 mL). TBAF (1.0 mL, 1 M in THF) and MeI (1.0 mL, 16 mmol) were added. After 2 h at room temperature, the deep brown solution was diluted with  $\text{CH}_2\text{Cl}_2$  and washed with  $\text{H}_2\text{O}$ . Concentration afforded an oil which was purified by  $\text{SiO}_2$  chromatography (3% MeOH/  $\text{CH}_2\text{Cl}_2$ ) to provide **x** as an orange solid (13 mg, 86%): IR (thin film) 2940, 1734, 1679, 1550, 1325, 1222, 1112  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2/d_6$ -DMSO)  $\delta$  3.58 (s, 6H), 3.96 (s, 12H), 4.83 (d,  $J = 11.0$  Hz, 2H), 4.92 (d,  $J = 11.0$  Hz, 2H), 5.87 (s, 2OH), 6.98 (m, 4H), 7.20 (m, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_2\text{Cl}_2/d_6$ -DMSO)  $\delta$  175.3, 175.1, 165.1, 163.5, 160.8, 152.3, 138.3, 135.3, 128.8, 128.5, 127.3, 122.6, 122.6, 116.8, 110.9, 76.0, 63.3, 55.9, 53.1; HRMS (ESI) calcd for  $\text{C}_{42}\text{H}_{34}\text{O}_{14}\text{Na}$  ( $\text{MNa}^+$ ) 785.1846, found 785.1858.



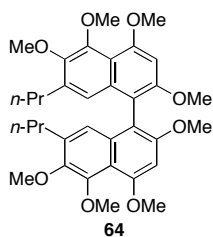
**Dimethyl 4,4'-dihydroxy-2,2',6,6'-tetramethoxy-7,7'-dipropyl-1,1'-binaphthyl-3,3'-dicarboxylate (59).** To a solution of racemic **52d** (102 mg, 0.154 mmol) in dry DMF (2.0 mL) under Ar was added NaH (60% in oil, 12.1 mg, 0.305 mmol) followed by CH<sub>3</sub>I (37 μL, 0.59 mmol). The mixture was stirred for 2 h, then quenched with 1 N HCl and diluted with EtOAc. The phases were separated, the aqueous phase was washed with EtOAc and the combined organic phases were washed with H<sub>2</sub>O and brine, dried (Na<sub>2</sub>SO<sub>4</sub>) and the solvent evaporated. Purification was accomplished with chromatography (10-30% EtOAc/hexanes) to yield 85 mg (80%) of a resin: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.05 (s, 2H), 6.95 (s, 2H), 3.93 (s, 6H), 3.92 (s, 6H), 3.32 (s, 6H), 2.53-2.42 (m, 10H), 1.41-1.35 (m, 4H), 0.75 (t, *J* = 7.2 Hz, 6H).

To a solution of the methyl ether (85 mg, 0.12 mmol) in MeOH (5 mL) and CH<sub>2</sub>Cl<sub>2</sub> (1 mL) was added NaOMe (25 mg, 0.46 mmol). The reaction was stirred for 2 h, then quenched with 1 N HCl. The aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub>, the resultant organic phase washed with H<sub>2</sub>O and brine, dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated in vacuo to yield product (74 mg, 80% from **52d**): IR (thin film) 3358, 2957, 1644, 1251, 1224, cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 0.72 (t, *J* = 7.4 Hz, 6H), 1.34-1.40 (m, 4H), 2.43-2.51 (m, 4H), 3.28 (s, 6H), 3.97 (s, 6H), 3.99 (s, 6H), 6.83 (s, 2H), 7.69 (s, 2H), 12.8 (s, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 172.8, 161.7, 156.3, 153.2, 137.6, 132.5, 126.7, 122.1, 117.1, 102.8, 101.8, 61.9, 55.9, 53.0, 33.3, 23.1, 14.1; HRMS (ESI) calcd for C<sub>34</sub>H<sub>38</sub>O<sub>10</sub>Na (MNa<sup>+</sup>) 629.2363, found 629.2376.



**Dimethyl 2,2',4,4',5,5',6,6'-octamethoxy-7,7'-dipropyl-1,1'-binaphthyl-3,3'-dicarboxylate (63).** To a solution of *o*-quinone **61** (79 mg, 0.12 mmol) in THF (4 mL) and H<sub>2</sub>O (2 mL) was added Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> (329 mg, 1.89 mmol). The red color immediately faded to yellow, and the reaction was stirred under an Ar atmosphere for 10 min. The mixture was then diluted with Et<sub>2</sub>O and H<sub>2</sub>O, the phases were partitioned and the aqueous phase was washed with Et<sub>2</sub>O. The combined organics were washed with H<sub>2</sub>O, brine, dried (Na<sub>2</sub>SO<sub>4</sub>), and the solvent was evaporated to yield a yellow resin as a mixture of products. This mixture was used immediately (storing resulted in decomposition) for the subsequent methylation (**63**) and re-oxidation (**62**) reactions.

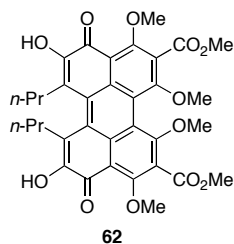
The unpurified mixture (0.076 mmol) was dissolved in THF (6 mL), and MeI (0.45 mL) was added followed by TBAF (1.0 M in THF, 1.5 mL, 1.5 mmol). The reaction was stirred under an Ar atmosphere for 16 h. EtOAc and H<sub>2</sub>O were added to the reaction mixture, the phases were partitioned, and the aqueous phase was washed with EtOAc. The combined organics were washed with H<sub>2</sub>O and brine, dried (Na<sub>2</sub>SO<sub>4</sub>), and the solvent was evaporated to yield a resin. Purification via SiO<sub>2</sub> chromatography (20% EtOAc/hexanes) yielded 46 mg (46%) of product **63** as a resin: IR (thin film) 2941, 1737, 1336, 1258, 1089 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 0.74 (t, *J* = 7.4 Hz, 6H), 1.35-1.39 (m, 4H), 2.43-2.50 (m, 4H), 3.36 (s, 6H), 3.96 (s, 6H), 3.97 (s, 6H), 3.98 (s, 6H), 4.03 (s, 6H), 6.69 (s, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 167.8, 154.2, 152.4, 150.0, 148.0, 138.7, 133.7, 123.0, 122.7, 120.7, 120.0, 64.5, 62.2, 62.1, 61.3, 52.9, 33.1, 23.9, 14.1; HRMS (ESI) calcd for C<sub>38</sub>H<sub>46</sub>O<sub>12</sub>Na (MNa<sup>+</sup>) 717.2887, found 717.2895.



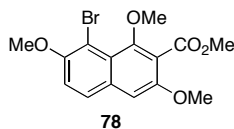
**2,2',4,4',5,5',6,6'-Octamethoxy-7,7'-dipropyl-1,1'-binaphthyl (64).** A mixture of octamethyl ether **63** (77 mg, 0.11 mmol), sat. aq. LiOH (3 mL), and dioxane (5 mL) was heated to reflux for 16 h. The mixture was cooled, acidified with 1 N HCl, and extracted into CH<sub>2</sub>Cl<sub>2</sub>. The organic phase was washed with H<sub>2</sub>O and brine, dried (Na<sub>2</sub>SO<sub>4</sub>), and the solvent was evaporated to yield 50 mg (68%) of dicarboxylic acid: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 0.74 (t, *J* = 7.4 Hz, 6H), 1.36-1.39 (m, 4H), 2.44-2.50 (m, 4H), 3.41 (s, 6H), 3.97 (s, 12H), 4.10 (s, 6H), 6.71 (s, 2H), 10.2 (br s, 2H).

A mixture of the diacid (50 mg, 0.075 mmol), Cu powder (4 mg), and quinoline (1.0 mL) was heated under Ar in a 180 °C oil bath for 3 h. The black mixture was cooled to room temperature and diluted with EtOAc and 1 N HCl. The aqueous phase was washed with EtOAc, the combined organics were washed with 1 N HCl and brine, dried (Na<sub>2</sub>SO<sub>4</sub>), and filtered through a SiO<sub>2</sub> plug. The solvent was evaporated to yield 19 mg (44%) of the product as a resin: IR (thin film) 2961, 2937, 1590, 1339 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 0.75 (t, *J* = 7.4 Hz, 6H), 1.34-1.40 (m, 4H), 2.40-2.48 (m, 4H), 3.72 (s, 6H), 3.92 (s, 6H), 3.95 (s, 6H), 4.11 (s, 6H), 6.63 (s, 2H), 6.76 (s, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 157.2, 155.0, 148.6 (2), 137.1, 133.7, 122.1, 116.4, 112.5, 95.9, 61.9, 61.3, 57.6, 56.5, 33.0, 23.9, 14.2; HRMS (ESI) calcd for C<sub>34</sub>H<sub>42</sub>O<sub>8</sub>Na (MNa<sup>+</sup>) 601.2777, found 601.2781.





**Dimethyl 5,8-dihydroxy-1,3,10,12-tetramethoxy-4,9-dioxo-6,7-dipropyl-4,9-dihydroperylene-2,11-dicarboxylate (62).** The unpurified mixture from the reduction of **61** (40 mg, 0.063 mmol) was dissolved in dry MeCN (3 mL) under an Ar atmosphere. A solution of FeCl<sub>3</sub> (44 mg, 0.27 mmol) in MeCN (2 mL) was added dropwise, and the reaction mixture was stirred under Ar for 24 h. The mixture was diluted with H<sub>2</sub>O-1 N HCl and the aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic phase was washed with H<sub>2</sub>O and brine, dried (Na<sub>2</sub>SO<sub>4</sub>), and the solvent was evaporated to yield 35 mg of a mixture of products including **61** (major product) and **62**. Purification of a portion of this product was accomplished via a Zorbax Rx-C18 semi-prep HPLC column (9.2 mm x 25 cm) (50-100% MeCN/H<sub>2</sub>O) to yield pure **62** as a purple oil: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 0.62 (t, *J* = 7.35 Hz, 6H), 1.02-1.15 (m, 2H), 1.45-1.53 (m, 2H), 2.60-2.62 (m, 2H), 3.10-3.14 (m, 2H), 3.69 (s, 6H), 4.02 (s, 6H), 4.10 (s, 6H), 7.72 (s, 2H); C18 HPLC (Zorbax Rx-C18, 5.0 mL/min, 50-100% MeCN/H<sub>2</sub>O *t<sub>R</sub>*(**61**) = 12 min, *t<sub>R</sub>*(**62**) = 14 min.



**Methyl 8-bromo-1,3,7-trimethoxy-2-naphthoate (78).** To a solution of diacetate **77** (1.0 g, 3.0 mmol) in AcOH (40 mL) was added NBS (1.1 g, 6.0 mmol). The reaction was stirred for 16 h, then the reaction was poured over ice and the solid was filtered, rinsing with H<sub>2</sub>O. The solid was air dried to yield 1.2 g (97%) of a yellow powder that was used in the next step without

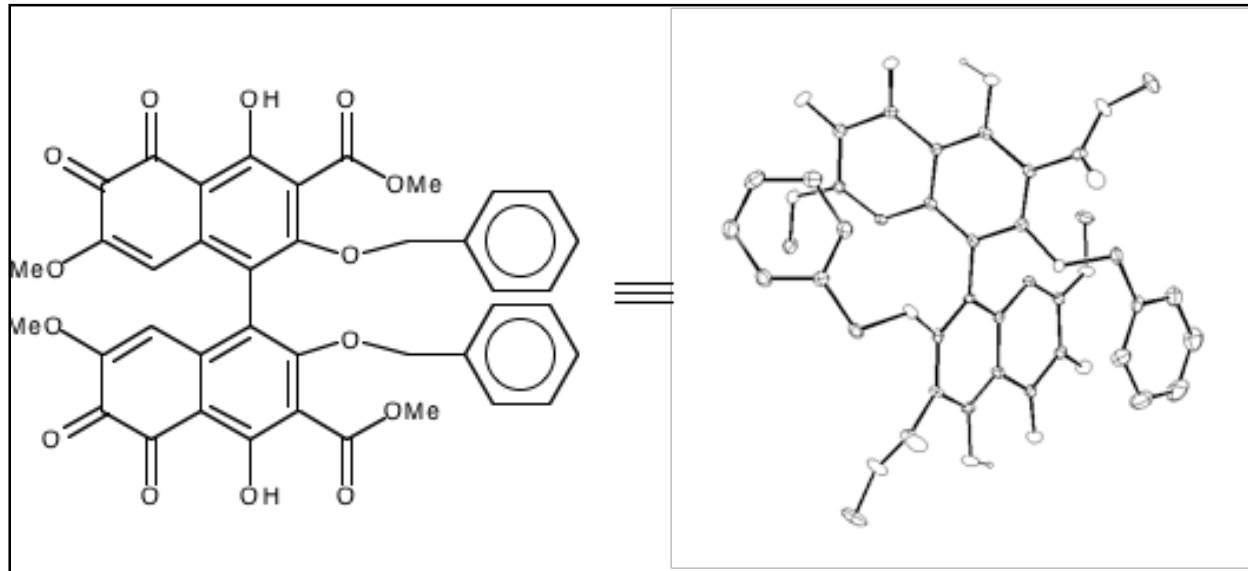
further purification:  $^1\text{H}$  NMR (360 MHz,  $\text{CDCl}_3$ )  $\delta$  2.31 (s, 3H), 2.41 (s, 3H), 3.92 (s, 3H), 4.00 (s, 3H), 7.34 (d,  $J = 9.2$  Hz, 1H), 7.54 (s, 1H), 7.79 (d,  $J = 9.2$  Hz, 1H). To a solution of this bromonaphthalene (1.2 g, 2.9 mmol) in MeOH (30 mL) and  $\text{CH}_2\text{Cl}_2$  (20 mL) under an Ar atmosphere was added NaOMe (0.80 g, 15 mmol), and the reaction was stirred for 16 h. The reaction was acidified with 1 N HCl, diluted with  $\text{CH}_2\text{Cl}_2$ , and the aqueous phase was extracted with  $\text{CH}_2\text{Cl}_2$ . The organic phase was washed with  $\text{H}_2\text{O}$  and brine, dried ( $\text{Na}_2\text{SO}_4$ ), and the solvent was evaporated to yield a yellow solid whose spectra indicated a mono-acetate structure:  $^1\text{H}$  NMR (360 MHz,  $\text{CDCl}_3$ )  $\delta$  2.47 (s, 3H), 3.98 (s, 3H), 4.02 (s, 3H), 7.27 (s, 1H), 7.31 (d,  $J = 9.15$  Hz, 1H), 7.65 (d,  $J = 9.15$  Hz, 1H), 10.37 (s, 1H).

To a solution of the monoacetate (65.1 mg, 0.176 mmol) in acetone (1.8 mL) was added  $\text{K}_2\text{CO}_3$  (209 mg, 1.51 mmol) and  $\text{Me}_2\text{SO}_4$  (33  $\mu\text{L}$ , 0.35 mmol). The reaction mixture was heated to reflux for 18 h, then cooled and poured into  $\text{H}_2\text{O}$ . The aqueous phase was extracted with EtOAc, and the organic phase was washed with  $\text{H}_2\text{O}$  and brine, dried ( $\text{Na}_2\text{SO}_4$ ), and the solvent was evaporated. The residue was dissolved in MeOH (2 mL) and NaOMe (97 mg, 1.8 mmol) was added. The mixture was heated to reflux under Ar for 4 h. The reaction mixture was cooled and acidified with 1 N HCl. The aqueous phase was extracted with EtOAc, the organic phase was washed with  $\text{H}_2\text{O}$  and brine, and dried over  $\text{Na}_2\text{SO}_4$ . The solvent was evaporated to yield 31 mg (52%) of the dimethyl ether monoacetate.

This solid was dissolved in DMF (1 mL), and under an Ar atmosphere NaH (60% in oil, 26.5 mg, 0.663 mmol) was added. After 10 min, MeI (0.10 mL, 1.6 mmol) was added and the reaction mixture was stirred for 16 h. The mixture was poured over ice- $\text{H}_2\text{O}$ , and the solid was filtered and air-dried, followed by drying under high vacuum to yield 26.8 mg (83%) of the trimethyl ether **78** as a tan solid: mp 174-176  $^\circ\text{C}$ ; IR (thin film) 2939, 1730, 1245, 1109, 857  $\text{cm}^{-1}$



**(M)-Dimethyl 3,10-dihydroxy-1,5,8,12-tetramethoxy-4,9-dioxo-6,7-dipropyl-4,9-dihydroperylene-2,11-dicarboxylate (89).** A 0.093 M solution of  $\text{MgI}_2$  was prepared by stirring Mg turnings (10.2 mg, 0.420 mmol) and  $\text{I}_2$  (52.2 mg, 0.206 mmol) in dry  $\text{Et}_2\text{O}$  (2.2 mL) in a flame-dried round bottom for 3 h. To a solution of perylenequinone **88** (10 mg, 0.015 mmol) in dry THF (1.0 mL) under an Ar atmosphere was added a solution of  $\text{MgI}_2$  in  $\text{Et}_2\text{O}$  (0.4 mL, 0.093 M, 0.037 mmol). The dark blue mixture was stirred for 30 min, diluted with  $\text{CH}_2\text{Cl}_2$ , washed with 1 N HCl and brine, dried ( $\text{Na}_2\text{SO}_4$ ), and the solvent was evaporated to yield product **89** as a purple resin that was not stable to further purification (5 mg, 55%, >70% ee):  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  0.52 (t,  $J = 7.3$  Hz, 6H), 0.94-10.2 (m, 2H), 1.26-1.35 (m, 2H), 2.66-2.68 (m, 2H), 3.33 (m, 2H), 3.87 (s, 6H), 4.04 (s, 6H), 4.16 (s, 6H), 15.44 (s, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  14.5, 24.7, 35.4, 53.4, 61.7, 62.0, 106.7, 116.4, 117.2, 127.4, 129.5, 141.3, 151.9, 163.8, 166.0, 172.0, 176.5; IR (film) 3236, 2927, 2858, 1738, 1599, 1460, 1413, 1259, 1220  $\text{cm}^{-1}$ ; HRMS (ES) calcd for  $\text{C}_{34}\text{H}_{33}\text{O}_{12}$  ( $\text{MH}^-$ ) 633.1972, found 633.1974; CSP HPLC (Chiralpak AD, 1.0 mL/min, 97:3 hexanes:*i*-PrOH)  $t_{\text{R}}(\text{S}) = 11.4$  min,  $t_{\text{R}}(\text{R}) = 16.6$  min.



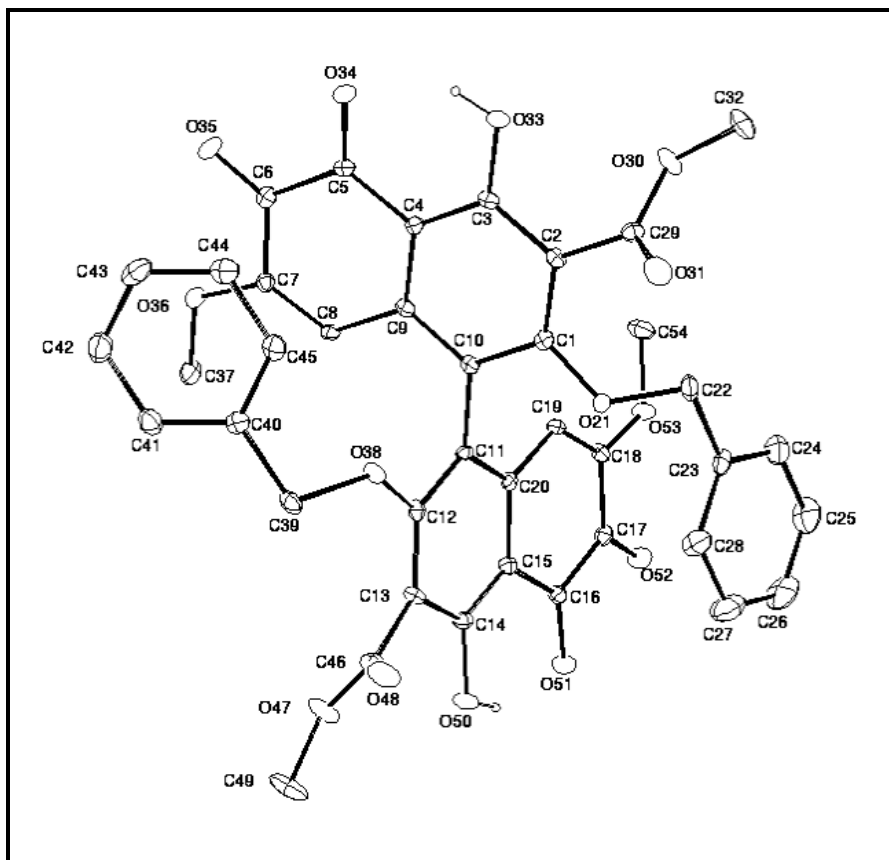
*X-ray Structure Determination of Compound 54*

Compound **54**,  $C_{42}H_{32}O_{14}Cl_6$ , crystallizes in the triclinic space group  $P\bar{1}$  with  $a=12.104(4)\text{\AA}$ ,  $b=12.965(3)\text{\AA}$ ,  $c=15.309(4)\text{\AA}$ ,  $\alpha=76.681(2)^\circ$ ,  $\beta=104.981(7)^\circ$ ,  $\gamma=114.121(7)^\circ$ ,  $V=2096.9(10)\text{\AA}^3$ ,  $Z=2$  and  $d_{\text{calc}}=1.542\text{ g/cm}^3$ . X-ray intensity data were collected on a Rigaku Mercury CCD area detector employing graphite-monochromated Mo- $K_\alpha$  radiation ( $\lambda=0.71069\text{ \AA}$ ) at a temperature of  $143^\circ\text{K}$ . Indexing was performed from a series of four  $0.5^\circ$  oscillation images with exposures of 30 seconds per frame. A hemisphere of data was collected using 30 second exposures and a crystal-to-detector distance of 35 mm. A total of 440 images were collected: one sweep was performed using  $\phi$ -scans from  $-90^\circ$  to  $+90^\circ$  in  $0.5^\circ$  steps at  $\omega = 0^\circ$  and  $\chi = 0^\circ$  with a detector swing angle of  $-10^\circ$ ; a second sweep was done using  $\omega$ -scans from  $-20^\circ$  to  $+20^\circ$  in  $0.5^\circ$  steps at  $\chi = -90^\circ$  and  $\phi = 0^\circ$  with a detector swing angle of  $-10^\circ$ . Oscillation images were processed using CrystalClear<sup>1</sup>, producing a listing of unaveraged  $F^2$  and  $\sigma(F^2)$  values which were then passed to the teXsan<sup>2</sup> program package for further processing and structure solution on a Silicon Graphics

O2 computer. A total of 12995 reflections were measured over the ranges  $5.06 \leq 2\theta \leq 50.7^\circ$ ,  $-11 \leq h \leq 14$ ,  $-15 \leq k \leq 12$ ,  $-18 \leq l \leq 15$  yielding 7308 unique reflections ( $R_{\text{int}} = 0.0326$ ). The intensity data were corrected for Lorentz and polarization effects but not for absorption.

The structure was solved by direct methods (SIR92<sup>3</sup>). Refinement was by full-matrix least squares based on  $F^2$  using SHELXL-93<sup>4</sup>. All reflections were used during refinement ( $F^2$ 's that were experimentally negative were replaced by  $F^2 = 0$ ). The weighting scheme used was  $w=1/[\sigma^2(F_o^2) + 0.0216P^2 + 3.5407P]$  where  $P = (F_o^2 + 2F_c^2)/3$ . Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a "riding" model. Refinement converged to  $R_1=0.0678$  and  $wR_2=0.1079$  for 5526 reflections for which  $F > 4\sigma(F)$  and  $R_1=0.0999$ ,  $wR_2=0.1171$  and  $\text{GOF} = 1.142$  for all 7307 unique, non-zero reflections and 565 variables<sup>5</sup>. The maximum  $\Delta/\sigma$  in the final cycle of least squares was 0.000 and the two most prominent peaks in the final difference Fourier were  $+0.314$  and  $-0.350 \text{ e}/\text{\AA}^3$ .

**Table S54.1** lists cell information, data collection parameters, and refinement data. Final positional and equivalent isotropic thermal parameters are given in **Table S54.2**. Anisotropic thermal parameters are in **Table S54.3**. **Tables S55.4** and **S54.5** list bond distances and bond angles. **Figure S54.1** is an ORTEP<sup>6</sup> representation of the molecule with 30% probability thermal ellipsoids displayed.



**Figure S54.1** ORTEP drawing of the title compound with 30% probability thermal ellipsoids.

**Table S54.1** Summary of Structure Determination of Compound **54**

Formula:	$C_{42}H_{32}O_{14}Cl_6$
Formula weight:	973.38
Crystal class:	triclinic
Space group:	$P\bar{1}$ (#2)
Z	2
Cell constants:	
a	12.104(4) Å
b	12.965(3) Å
c	15.309(4) Å
$\alpha$	76.681(2)°
$\beta$	104.981(7)°
$\gamma$	114.121(7)°
V	2096.9(10) Å <sup>3</sup>
$\mu$	4.79 cm <sup>-1</sup>
crystal size, mm	0.48 x 0.06 x 0.01
$D_{calc}$	1.542 g/cm <sup>3</sup>
F(000)	996
Radiation:	Mo-K $\alpha$ ( $\lambda=0.71069$ Å)
2 $\theta$ range	5.06 – 50.7 °
hkl collected:	-11 ≤ h ≤ 14; -15 ≤ k ≤ 12; -18 ≤ l ≤ 15
No. reflections measured:	12995
No. unique reflections:	7308 ( $R_{int}=0.0326$ )
No. observed reflections	5526 ( $F>4\sigma$ )
No. reflections used in refinement	7307
No. parameters	565
R indices ( $F>4\sigma$ )	$R_1=0.0678$ $wR_2=0.1079$
R indices (all data)	$R_1=0.0999$ $wR_2=0.1171$
GOF:	1.142
Final Difference Peaks, e/Å <sup>3</sup>	+0.314, -0.350



**Table S54.2** Refined Positional Parameters for Compound **54**

Atom	X	y	Z	$U_{eq}, \text{\AA}^2$
C1	0.6907(3)	-0.0528(3)	0.8553(2)	0.0154(7)
C2	0.6853(3)	0.0553(3)	0.8269(2)	0.0149(7)
C3	0.6650(3)	0.1063(3)	0.8900(2)	0.0149(7)
C4	0.6510(3)	0.0496(3)	0.9790(2)	0.0142(7)
C5	0.6421(3)	0.1078(3)	1.0451(2)	0.0148(7)
C6	0.6288(3)	0.0453(3)	1.1416(2)	0.0171(8)
C7	0.6328(3)	-0.0698(3)	1.1634(2)	0.0162(7)
C8	0.6420(3)	-0.1199(3)	1.0993(2)	0.0148(7)
H8	0.6396(3)	-0.1944(3)	1.1145(2)	0.020
C9	0.6558(3)	-0.0617(3)	1.0069(2)	0.0139(7)
C10	0.6751(3)	-0.1128(3)	0.9445(2)	0.0137(7)
C11	0.6911(3)	-0.2259(3)	0.9679(2)	0.0132(7)
C12	0.8060(3)	-0.2271(3)	1.0221(2)	0.0154(7)
C13	0.8370(3)	-0.3235(3)	1.0401(2)	0.0169(8)
C14	0.7504(3)	-0.4203(3)	1.0008(2)	0.0170(8)
C15	0.6367(3)	-0.4221(3)	0.9487(2)	0.0147(7)
C16	0.5547(3)	-0.5201(3)	0.9046(2)	0.0179(8)
C17	0.4308(3)	-0.5191(3)	0.8467(2)	0.0187(8)
C18	0.4063(3)	-0.4146(3)	0.8351(2)	0.0169(8)
C19	0.4873(3)	-0.3238(3)	0.8757(2)	0.0152(7)
H19	0.4675(3)	-0.2597(3)	0.8679(2)	0.020
C20	0.6055(3)	-0.3229(3)	0.9315(2)	0.0143(7)
C22	0.6647(4)	-0.1089(3)	0.7077(2)	0.0279(9)
H22a	0.7234(4)	-0.0514(3)	0.6720(2)	0.037
H22b	0.5903(4)	-0.0923(3)	0.6934(2)	0.037
C23	0.6360(3)	-0.2265(3)	0.6863(2)	0.0221(8)
C24	0.5300(4)	-0.2782(3)	0.6258(3)	0.0350(10)
H24	0.4749(4)	-0.2416(3)	0.5997(3)	0.047
C25	0.5059(4)	-0.3841(4)	0.6041(3)	0.0440(12)
H25	0.4353(4)	-0.4179(4)	0.5627(3)	0.058
C26	0.5858(5)	-0.4393(4)	0.6433(3)	0.0504(13)
H26	0.5693(5)	-0.5105(4)	0.6287(3)	0.067
C27	0.6901(5)	-0.3894(4)	0.7041(4)	0.0519(13)
H27	0.7436(5)	-0.4276(4)	0.7313(4)	0.069
C28	0.7164(4)	-0.2826(3)	0.7252(3)	0.0348(10)
H28	0.7881(4)	-0.2486(3)	0.7656(3)	0.046
C29	0.7187(3)	0.1261(3)	0.7383(2)	0.0184(8)
C32	0.6626(4)	0.2441(4)	0.6081(3)	0.0407(11)
H32a	0.727(2)	0.3143(10)	0.6244(3)	0.061
H32b	0.5910(8)	0.259(2)	0.5735(10)	0.061
H32c	0.690(3)	0.2111(11)	0.5720(10)	0.061
C37	0.6106(4)	-0.2300(3)	1.2790(3)	0.0301(10)
H37a	0.598(2)	-0.2529(7)	1.3412(6)	0.045
H37b	0.6842(10)	-0.2379(5)	1.274(2)	0.045
H37c	0.5413(14)	-0.2775(4)	1.2404(11)	0.045
C39	0.9660(3)	-0.1154(3)	1.1367(2)	0.0224(8)
H39a	1.0482(3)	-0.0980(3)	1.1270(2)	0.030
H39b	0.9421(3)	-0.1864(3)	1.1781(2)	0.030

C40	0.9635(3)	-0.0205(3)	1.1760(2)	0.0195(8)
C41	0.9759(4)	-0.0277(3)	1.2697(3)	0.0274(9)
H41	0.9864(4)	-0.0912(3)	1.3081(3)	0.036
C42	0.9728(4)	0.0591(4)	1.3064(3)	0.0339(10)
H42	0.9820(4)	0.0539(4)	1.3692(3)	0.045
C43	0.9562(4)	0.1532(3)	1.2497(3)	0.0341(10)
H43	0.9522(4)	0.2105(3)	1.2743(3)	0.045
C44	0.9456(3)	0.1626(3)	1.1562(3)	0.0281(9)
H44	0.9356(3)	0.2265(3)	1.1180(3)	0.037
C45	0.9502(3)	0.0761(3)	1.1202(3)	0.0226(8)
H45	0.9443(3)	0.0828(3)	1.0575(3)	0.030
C46	0.9618(3)	-0.3244(3)	1.0856(3)	0.0210(8)
C49	1.0697(4)	-0.4284(4)	1.1926(3)	0.0438(12)
H49a	1.0563(7)	-0.491(2)	1.2416(13)	0.066
H49b	1.1309(9)	-0.3606(9)	1.216(2)	0.066
H49c	1.0977(14)	-0.446(2)	1.1465(6)	0.066
C54	0.2530(4)	-0.3349(3)	0.7700(3)	0.0304(9)
H54a	0.1700(9)	-0.3565(9)	0.736(2)	0.046
H54b	0.305(2)	-0.2681(7)	0.737(2)	0.046
H54c	0.255(2)	-0.319(2)	0.8287(3)	0.046
O21	0.7156(2)	-0.1091(2)	0.8034(2)	0.0197(5)
O30	0.6320(2)	0.1653(2)	0.6905(2)	0.0306(7)
O31	0.8135(2)	0.1462(2)	0.7150(2)	0.0296(6)
O33	0.6634(2)	0.2117(2)	0.8636(2)	0.0194(5)
H33	0.650(4)	0.2324(14)	0.9053(10)	0.029
O34	0.6451(2)	0.2070(2)	1.0279(2)	0.0225(6)
O35	0.6136(2)	0.0911(2)	1.1963(2)	0.0267(6)
O36	0.6221(2)	-0.1134(2)	1.2511(2)	0.0219(6)
O38	0.8800(2)	-0.1258(2)	1.0507(2)	0.0188(5)
O47	0.9558(2)	-0.4102(2)	1.1534(2)	0.0311(7)
O48	1.0558(2)	-0.2575(2)	1.0623(2)	0.0304(6)
O50	0.7836(2)	-0.5105(2)	1.0123(2)	0.0258(6)
H50	0.728(2)	-0.5613(14)	0.986(2)	0.039
O51	0.5775(2)	-0.6067(2)	0.9104(2)	0.0255(6)
O52	0.3578(2)	-0.6037(2)	0.8134(2)	0.0278(6)
O53	0.2953(2)	-0.4265(2)	0.7817(2)	0.0232(6)
C55	0.2547(4)	-0.0292(3)	0.5742(3)	0.0331(10)
H55	0.2590(4)	-0.0345(3)	0.6399(3)	0.044
Cl1	0.22493(12)	0.09334(10)	0.51746(8)	0.0519(3)
Cl2	0.39625(12)	-0.01955(13)	0.55604(10)	0.0616(4)
Cl3	0.13621(12)	-0.15170(10)	0.53455(9)	0.0520(3)
C56	-0.1727(4)	-0.4309(3)	0.3931(3)	0.0316(10)
H56	-0.2385(4)	-0.4410(3)	0.3390(3)	0.042
Cl4	-0.03340(11)	-0.33587(9)	0.35961(8)	0.0457(3)
Cl5	-0.20895(13)	-0.37558(11)	0.47185(9)	0.0579(4)
Cl6	-0.16324(11)	-0.56499(9)	0.44189(8)	0.0433(3)
$U_{eq} = \frac{1}{3}[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha]$				

**Table S54.3** Refined Thermal Parameters (U's) for Compound **54**

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
C1	0.010(2)	0.016(2)	0.018(2)	-0.0058(14)	0.000(2)	0.0033(14)
C2	0.013(2)	0.013(2)	0.016(2)	0.0008(13)	0.002(2)	0.0032(14)
C3	0.009(2)	0.011(2)	0.021(2)	-0.0019(14)	-0.001(2)	0.0027(13)
C4	0.010(2)	0.015(2)	0.017(2)	-0.0060(14)	-0.0014(14)	0.0045(14)
C5	0.010(2)	0.012(2)	0.021(2)	-0.0039(14)	0.001(2)	0.0031(13)
C6	0.013(2)	0.017(2)	0.019(2)	-0.0057(14)	0.003(2)	0.0021(14)
C7	0.017(2)	0.015(2)	0.015(2)	-0.0035(14)	0.001(2)	0.0043(14)
C8	0.017(2)	0.008(2)	0.019(2)	-0.0009(13)	0.003(2)	0.0049(14)
C9	0.009(2)	0.013(2)	0.017(2)	-0.0019(13)	-0.0005(14)	0.0023(13)
C10	0.009(2)	0.011(2)	0.017(2)	-0.0031(13)	-0.0003(14)	0.0007(13)
C11	0.015(2)	0.014(2)	0.014(2)	-0.0004(13)	0.007(2)	0.0073(14)
C12	0.016(2)	0.016(2)	0.012(2)	-0.0001(13)	0.004(2)	0.0029(14)
C13	0.015(2)	0.016(2)	0.019(2)	0.0012(14)	0.002(2)	0.008(2)
C14	0.020(2)	0.013(2)	0.020(2)	0.0001(14)	0.006(2)	0.008(2)
C15	0.015(2)	0.013(2)	0.016(2)	0.0000(13)	0.005(2)	0.0048(14)
C16	0.023(2)	0.016(2)	0.016(2)	0.0009(14)	0.005(2)	0.008(2)
C17	0.020(2)	0.016(2)	0.019(2)	-0.0060(14)	0.004(2)	0.003(2)
C18	0.015(2)	0.014(2)	0.018(2)	-0.0008(14)	0.000(2)	0.0047(14)
C19	0.016(2)	0.014(2)	0.017(2)	-0.0003(14)	0.003(2)	0.008(2)
C20	0.016(2)	0.013(2)	0.013(2)	0.0010(13)	0.006(2)	0.0041(14)
C22	0.044(3)	0.027(2)	0.013(2)	-0.004(2)	0.000(2)	0.015(2)
C23	0.027(2)	0.022(2)	0.016(2)	-0.003(2)	0.009(2)	0.005(2)
C24	0.039(3)	0.033(2)	0.028(2)	-0.005(2)	0.004(2)	0.011(2)
C25	0.046(3)	0.033(3)	0.039(3)	-0.016(2)	0.001(2)	-0.001(2)
C26	0.070(4)	0.025(2)	0.056(3)	-0.017(2)	0.019(3)	0.007(2)
C27	0.063(4)	0.046(3)	0.062(3)	-0.020(2)	0.010(3)	0.031(3)
C28	0.029(2)	0.038(3)	0.042(3)	-0.017(2)	0.003(2)	0.013(2)
C29	0.021(2)	0.012(2)	0.021(2)	-0.0020(14)	0.004(2)	0.005(2)
C32	0.061(3)	0.042(3)	0.021(2)	0.014(2)	0.010(2)	0.030(2)
C37	0.053(3)	0.020(2)	0.019(2)	0.002(2)	0.011(2)	0.014(2)
C39	0.018(2)	0.025(2)	0.021(2)	-0.004(2)	-0.006(2)	0.009(2)
C40	0.011(2)	0.019(2)	0.027(2)	-0.009(2)	0.000(2)	0.0031(14)
C41	0.024(2)	0.035(2)	0.024(2)	-0.003(2)	0.001(2)	0.014(2)
C42	0.034(3)	0.047(3)	0.025(2)	-0.010(2)	0.004(2)	0.017(2)
C43	0.030(2)	0.036(2)	0.045(3)	-0.019(2)	0.007(2)	0.014(2)
C44	0.021(2)	0.023(2)	0.037(3)	-0.008(2)	0.001(2)	0.007(2)
C45	0.016(2)	0.027(2)	0.023(2)	-0.006(2)	0.001(2)	0.006(2)
C46	0.019(2)	0.014(2)	0.029(2)	-0.004(2)	0.001(2)	0.006(2)
C49	0.026(2)	0.036(2)	0.058(3)	0.008(2)	-0.008(2)	0.018(2)
C54	0.028(2)	0.024(2)	0.038(2)	-0.008(2)	-0.009(2)	0.015(2)
O21	0.029(2)	0.0223(13)	0.0128(13)	-0.0021(10)	0.0035(11)	0.0148(11)
O30	0.035(2)	0.040(2)	0.0189(14)	0.0114(12)	0.0062(13)	0.0240(14)
O31	0.026(2)	0.032(2)	0.029(2)	0.0065(12)	0.0135(13)	0.0103(12)
O33	0.026(2)	0.0131(13)	0.0214(14)	0.0016(10)	0.0057(12)	0.0108(10)
O34	0.030(2)	0.0166(14)	0.025(2)	-0.0051(10)	0.0030(12)	0.0123(11)
O35	0.039(2)	0.0188(14)	0.027(2)	-0.0083(11)	0.0112(13)	0.0101(12)
O36	0.034(2)	0.0158(13)	0.0179(14)	-0.0009(10)	0.0086(12)	0.0098(11)
O38	0.0155(13)	0.0143(12)	0.0210(14)	-0.0045(10)	-0.0064(11)	0.0046(10)
O47	0.021(2)	0.0255(14)	0.038(2)	0.0077(12)	-0.0026(13)	0.0105(12)

O50	0.027(2)	0.0188(14)	0.034(2)	-0.0065(11)	-0.0041(13)	0.0152(12)
O51	0.031(2)	0.0162(14)	0.031(2)	-0.0066(11)	-0.0007(12)	0.0120(11)
O52	0.026(2)	0.0203(14)	0.035(2)	-0.0140(12)	-0.0050(13)	0.0082(12)
O53	0.0211(14)	0.0190(13)	0.030(2)	-0.0094(11)	-0.0053(12)	0.0111(11)
C55	0.037(3)	0.036(2)	0.026(2)	-0.009(2)	0.004(2)	0.012(2)
Cl1	0.0651(9)	0.0432(7)	0.0454(7)	-0.0002(5)	0.0057(6)	0.0241(6)
Cl2	0.0399(8)	0.0898(10)	0.0615(9)	-0.0189(7)	0.0049(7)	0.0288(7)
Cl3	0.0523(8)	0.0439(7)	0.0591(8)	-0.0263(6)	0.0130(6)	0.0055(6)
C56	0.030(2)	0.028(2)	0.028(2)	-0.002(2)	-0.005(2)	0.009(2)
Cl4	0.0453(7)	0.0386(6)	0.0372(7)	0.0089(5)	0.0083(5)	0.0069(5)
Cl5	0.0616(9)	0.0528(8)	0.0650(9)	-0.0242(6)	0.0141(7)	0.0170(6)
Cl6	0.0505(7)	0.0280(6)	0.0421(7)	0.0072(5)	0.0043(6)	0.0142(5)

The form of the anisotropic displacement parameter is:

$$\exp[-2\pi^2(a^{*2}U_{11}h^2+b^{*2}U_{22}k^2+c^{*2}U_{33}l^2+2b^*c^*U_{23}kl+2a^*c^*U_{13}hl+2a^*b^*U_{12}hk)].$$

**Table S54.4** Bond Distances in Compound **54**, Å

C1-O21	1.351(4)	C1-C2	1.392(4)	C1-C10	1.424(5)
C2-C3	1.408(5)	C2-C29	1.500(5)	C3-O33	1.339(4)
C3-C4	1.407(5)	C4-C9	1.428(4)	C4-C5	1.442(4)
C5-O34	1.239(4)	C5-C6	1.526(5)	C6-O35	1.218(4)
C6-C7	1.471(5)	C7-C8	1.343(5)	C7-O36	1.349(4)
C8-C9	1.458(5)	C9-C10	1.394(5)	C10-C11	1.506(4)
C11-C20	1.388(5)	C11-C12	1.427(5)	C12-O38	1.349(4)
C12-C13	1.397(5)	C13-C14	1.407(5)	C13-C46	1.495(5)
C14-O50	1.346(4)	C14-C15	1.396(5)	C15-C20	1.434(4)
C15-C16	1.439(5)	C16-O51	1.241(4)	C16-C17	1.536(5)
C17-O52	1.215(4)	C17-C18	1.465(5)	C18-C19	1.345(5)
C18-O53	1.349(4)	C19-C20	1.461(5)	C22-O21	1.434(4)
C22-C23	1.514(5)	C23-C28	1.382(5)	C23-C24	1.386(5)
C24-C25	1.383(6)	C25-C26	1.369(7)	C26-C27	1.372(7)
C27-C28	1.384(6)	C29-O31	1.199(4)	C29-O30	1.328(4)
C32-O30	1.453(4)	C37-O36	1.431(4)	C39-O38	1.446(4)
C39-C40	1.503(5)	C40-C45	1.387(5)	C40-C41	1.388(5)
C41-C42	1.385(5)	C42-C43	1.380(6)	C43-C44	1.384(6)
C44-C45	1.385(5)	C46-O48	1.197(4)	C46-O47	1.328(4)
C49-O47	1.446(4)	C54-O53	1.434(4)	C55-C11	1.754(4)
C55-C13	1.755(4)	C55-C12	1.757(4)	C56-C14	1.756(4)
C56-C15	1.758(4)	C56-C16	1.764(4)		

**Table S54.5** Bond Angles in Compound **54**, °

O21-C1-C2	124.0(3)	O21-C1-C10	113.5(3)	C2-C1-C10	122.5(3)
C1-C2-C3	117.8(3)	C1-C2-C29	123.0(3)	C3-C2-C29	118.5(3)
O33-C3-C4	121.2(3)	O33-C3-C2	117.9(3)	C4-C3-C2	120.8(3)
C3-C4-C9	120.7(3)	C3-C4-C5	119.8(3)	C9-C4-C5	119.3(3)
O34-C5-C4	123.4(3)	O34-C5-C6	117.6(3)	C4-C5-C6	119.0(3)
O35-C6-C7	123.0(3)	O35-C6-C5	119.5(3)	C7-C6-C5	117.5(3)
C8-C7-O36	128.1(3)	C8-C7-C6	121.0(3)	O36-C7-C6	110.9(3)
C7-C8-C9	122.5(3)	C10-C9-C4	118.7(3)	C10-C9-C8	120.8(3)
C4-C9-C8	120.5(3)	C9-C10-C1	119.4(3)	C9-C10-C11	123.6(3)
C1-C10-C11	116.8(3)	C20-C11-C12	120.1(3)	C20-C11-C10	122.7(3)
C12-C11-C10	116.9(3)	O38-C12-C13	124.9(3)	O38-C12-C11	112.9(3)
C13-C12-C11	122.2(3)	C12-C13-C14	117.1(3)	C12-C13-C46	124.0(3)
C14-C13-C46	118.2(3)	O50-C14-C15	120.8(3)	O50-C14-C13	117.2(3)
C15-C14-C13	121.9(3)	C14-C15-C20	120.5(3)	C14-C15-C16	119.9(3)
C20-C15-C16	119.4(3)	O51-C16-C15	124.0(3)	O51-C16-C17	117.2(3)
C15-C16-C17	118.8(3)	O52-C17-C18	123.1(3)	O52-C17-C16	119.5(3)
C18-C17-C16	117.5(3)	C19-C18-O53	128.1(3)	C19-C18-C17	121.5(3)
O53-C18-C17	110.3(3)	C18-C19-C20	122.0(3)	C11-C20-C15	118.3(3)
C11-C20-C19	121.2(3)	C15-C20-C19	120.6(3)	O21-C22-C23	107.1(3)
C28-C23-C24	119.2(4)	C28-C23-C22	120.4(4)	C24-C23-C22	120.4(3)
C25-C24-C23	120.3(4)	C26-C25-C24	120.1(4)	C25-C26-C27	120.0(4)
C26-C27-C28	120.5(5)	C23-C28-C27	119.9(4)	O31-C29-O30	124.5(3)
O31-C29-C2	123.7(3)	O30-C29-C2	111.8(3)	O38-C39-C40	107.3(3)
C45-C40-C41	118.7(3)	C45-C40-C39	121.1(3)	C41-C40-C39	120.2(3)
C42-C41-C40	120.5(4)	C43-C42-C41	120.1(4)	C42-C43-C44	120.2(4)
C43-C44-C45	119.3(4)	C44-C45-C40	121.2(4)	O48-C46-O47	124.0(3)
O48-C46-C13	124.1(3)	O47-C46-C13	111.8(3)	C1-O21-C22	122.0(3)
C29-O30-C32	115.3(3)	C7-O36-C37	116.9(3)	C12-O38-C39	123.2(2)
C46-O47-C49	115.8(3)	C18-O53-C54	117.2(3)	C11-C55-C13	110.2(2)
C11-C55-C12	109.7(2)	C13-C55-C12	109.9(2)	C14-C56-C15	110.3(2)
C14-C56-C16	110.5(2)	C15-C56-C16	109.8(2)		

1. CrystalClear: Rigaku Corporation, 1999.

2. teXsan: Crystal Structure Analysis Package, Molecular Structure Corporation (1985 & 1992).

3. SIR92: Altomare, A., Burla, M.C., Camalli, M., Cascarano, M., Giacovazzo, C., Guagliardi, A., Polidoro, G. (1994). *J. Appl. Cryst.*, **27**, 435.

4. SHELXL-93: Program for the Refinement of Crystal Structures, Sheldrick, G.M. (1993), University of Göttingen, Germany.

$$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$wR_2 = \{ \sum w (F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2 \}^{1/2}$$

$$GOF = \{ \sum w (F_o^2 - F_c^2)^2 / (n - p) \}^{1/2}$$

where n = the number of reflections and p = the number of parameters refined.

6. "ORTEP-II: A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations". C.K. Johnson (1976) ORNL-5138.