

# Electron Transfer Triggered by Optical Excitation of Phenothiazine- *Tris(Meta-Phenylene-Ethynylene)-(Tricarbonyl)(bpy)(py)Rhenium(I)*

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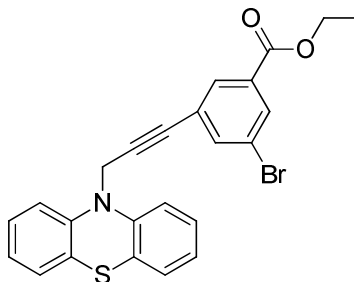
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## Synthesis and Characterization of Compounds.

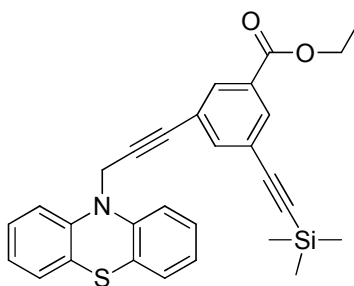
**Synthesis of 10-(prop-2-yn-1-yl)-10H-phenothiazine (1).** 10-(prop-2-yn-1-yl)-10H-phenothiazine was prepared according to literature procedure.<sup>1</sup>

**Synthesis of ethyl 3-bromo-5-iodobenzoate (2).** Ethyl 3-bromo-5-iodobenzoate was synthesized according to literature procedure.<sup>2</sup>



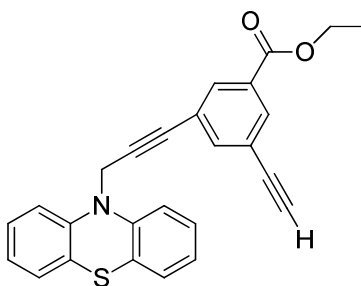
**Synthesis of ethyl 3-(3-(10H-phenothiazin-10-yl)prop-1-yn-1-yl)-5-bromobenzoate (3).** A microwave flask was charged with **2** (1.55 g, 4.3 mmol), **1** (1.16 g, 4.89 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.102 mg, 0.14 mmol), zinc chloride (1.108 g, 8.1 mmol) and transferred to the glovebox. Degassed triethylamine (4.86 mL) and tetrahydrofuran (24.36

mL) were added to the mixture in a glovebox and the flask was sealed. The mixture was stirred at 100 °C in the microwave for 2 hours. Purification with flash chromatography using hexane/ethyl acetate (9:0.5) afforded 0.89 g product (Yield: 35%). <sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 8.12 (t, *J* = 1.7, 1H), 8.02 (t, *J* = 1.5, 1H), 7.76 (t, *J* = 1.7, 1H), 7.28-7.20 (m, 4H), 7.14 (dd, *J* = 7.6, 1.4, 2H), 6.97 (td, *J* = 7.5, 1.3, 2H), 4.77 (s, 2H), 4.35 (q, *J* = 7.1, 2H), 1.37 (t, *J* = 7.1, 3H). <sup>13</sup>C NMR (151 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 165.10, 144.89, 138.96, 133.37, 133.19, 132.06, 128.33, 127.76, 125.46, 124.09, 123.75, 122.86, 115.60, 87.81, 84.33, 62.48, 39.85, 14.84. HRMS-ES (*m/z*) [*M*<sup>+</sup>] measured 465.0228 Calculated: 465.0221.

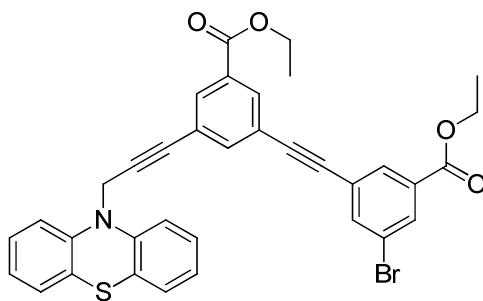


**Synthesis of ethyl 3-(3-(10H-phenothiazin-10-yl)prop-1-yn-1-yl)-5-(trimethylsilyl)-**

**ethynyl)benzoate.** A microwave flask was charged with **3** (1.04 g, 2.2 mmol), bis(triphenylphosphine)palladium(II) dichloride (51 mg, 0.072 mmol), zinc chloride (0.45 g, 3.3 mmol) and transferred to the glovebox. Degassed triethylamine (2.46 mL), degassed trimethylsilylacetylene (0.35 mL, 2.46 mmol), and tetrahydrofuran (11 mL) were added to the mixture in the glovebox and the flask was sealed. The mixture was stirred at 100 °C in the microwave for 2 hours. Purification with flash chromatography using hexane/ethyl acetate (9:0.5) afforded 0.78 g product (Yield: 73%). <sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 8.04 (t, *J* = 1.6, 1H), 8.02 (t, *J* = 1.6, 1H), 7.68 (t, *J* = 1.6, 1H), 7.30 – 7.20 (m, 4H), 7.14 (dd, *J* = 7.6, 1.5, 2H), 6.98 (td, *J* = 7.4, 1.2, 2H), 4.76 (s, 2H), 4.35 (q, *J* = 7.1, 2H), 1.37 (t, *J* = 7.1, 3H), 0.24 (s, 9H). <sup>13</sup>C NMR (151 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 165.64, 144.94, 139.29, 133.38, 133.10, 132.09, 128.34, 127.75, 124.76, 124.12, 124.04, 123.73, 115.64, 103.61, 87.04, 84.95, 62.27, 47.14, 39.92, 14.90, 0.34. HRMS-ES (*m/z*) [*M*<sup>+</sup>] measured 481.15 Calculated: 481.15.

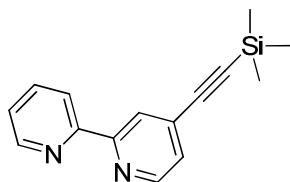


**Synthesis of ethyl 3-(3-(10H-phenothiazin-10-yl)prop-1-yn-1-yl)-5-ethynylbenzoate (4).** Ethyl 3-(3-(10H-phenothiazin-10-yl)prop-1-yn-1-yl)-5-trimethylsilyl-ethynylbenzoate (0.25 g, 0.53 mmol) was reacted with potassium carbonate (6.25 mg, 0.045 mmol) in a mixture of dichloromethane (1.25 mL) and methanol (3.12 mL). The reaction was allowed to react until the starting material was completely consumed. The reaction was monitored *via* thin layer chromatography. Purification with flash chromatography using hexane/ethyl acetate (9:0.5) afforded 93.3 mg product (Yield: 43%). <sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 8.00 (t, *J* = 1.6, 1H), 7.97 (t, *J* = 1.6, 1H), 7.63 (t, *J* = 1.7, 1H), 7.31 – 7.08 (m, 6H), 6.96 (td, *J* = 7.5, 1.2, 2H), 4.68 (s, 2H), 4.35 (q, *J* = 7.1, 2H), 3.20 (s, 1H), 1.37 (t, *J* = 7.1, 3H). <sup>13</sup>C NMR (151 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 165.42, 144.80, 139.41, 133.46, 133.34, 132.03, 128.19, 127.61, 123.99, 123.95, 123.59, 123.51, 115.50, 87.05, 84.65, 82.23, 79.42, 62.19, 39.77, 14.71. HRMS-ES (m/z) [M<sup>+</sup>] measured 409.11 Calculated: 409.11.

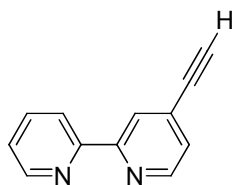


**Synthesis of ethyl 3-(3-(10H-phenothiazin-10-yl)prop-1-yn-1-yl)-5-((3-bromo-5-ethoxycarbonyl)phenyl)ethynylbenzoate (5).** A microwave flask was charged with **2** (0.22 g, 0.62 mmol), **4** (0.26, 0.65 mmol), bis(triphenylphosphine)palladium(II) dichloride (1.36 mg, 0.002 mmol), zinc chloride (0.126 g, 0.93 mmol) and transferred to a glovebox. Degassed triethylamine (0.65 mL)

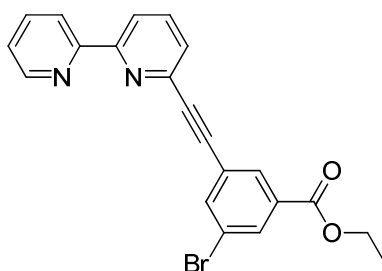
and tetrahydrofuran (3.1 mL) were added to the mixture in the glovebox and the flask was sealed. The mixture was stirred at 100 °C in the microwave for 2 hours. Purification with flash chromatography using hexane/ethyl acetate (18/1) afforded 0.2 g product (Yield: 51%). <sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 8.07 (t, *J* = 1.7, 1H), 8.05 (t, *J* = 1.6, 1H), 8.04 (t, *J* = 1.5, 1H), 7.99 (t, *J* = 1.6, 1H), 7.77 (t, *J* = 1.7, 1H), 7.69 (t, *J* = 1.6, 1H), 7.23-7.04 (m, 6H), 6.89 (td, *J* = 7.5, 1.2, 2H), 4.69 (s, 2H), 4.29 (m, 4H), 1.31 (td, *J* = 7.1, 3.2, 6H). <sup>13</sup>C NMR (151 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 165.38, 164.81, 144.64, 138.73, 138.46, 133.20, 133.08, 133.00, 132.89, 131.98, 131.76, 128.01, 127.42, 125.25, 123.94, 123.77, 123.66, 123.41, 122.67, 115.33, 89.81, 88.71, 86.90, 84.50, 62.19, 62.05, 39.62, 14.51, 14.50. HRMS-ES (*m/z*) [*M*<sup>+</sup>] measured: 637.0718, calculated 637.0745 error: 4.3 ppm.



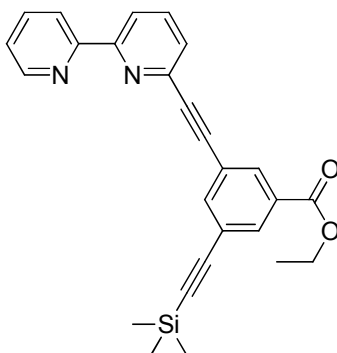
**Synthesis of 6-((trimethylsilyl)ethynyl)-2,2'-bipyridine (7).** A microwave flask was charged with 6-bromo-2,2'-bipyridine (0.375 g, 1.59 mmol), bis(triphenylphosphine)-palladium(II) dichloride (66 mg, 0.094 mmol), zinc chloride (0.32 g, 2.34 mmol) and transferred to a glovebox. Degassed triethylamine (3.18 mL), degassed trimethylsilylacetylene (0.45 mL, 3.18 mmol) and tetrahydrofuran (7.95 mL) were added to the mixture in the glovebox and the flask was sealed. The mixture was stirred at 100 °C in the microwave for 3 hours. Purification with flash chromatography using CH<sub>2</sub>Cl<sub>2</sub>/MeOH (99/1) afforded 0.32 g product (Yield: 79%). <sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 8.35 (ddd, *J* = 4.8, 1.8, 0.9, 1H), 8.12 (dt, *J* = 8.0, 1.1, 1H), 8.08 (dd, *J* = 8.0, 1.1, 1H), 7.53 (ddd, *J* = 8.0, 7.5, 1.8, 1H), 7.48 (t, *J* = 7.8, 1H), 7.17 (dd, *J* = 7.7, 1.0, 1H), 7.03 (ddd, *J* = 7.5, 4.8, 1.2, 1H), 0.00 (s, 9H). <sup>13</sup>C NMR (151 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 156.85, 155.89, 149.76, 142.87, 137.64, 137.48, 128.01, 124.25, 121.60, 121.04, 104.55, 45.62, 0.00. HRMS-ES (*m/z*) [*M*+*H*] observed 252.1160, calculated 253.1161, error 0.4.



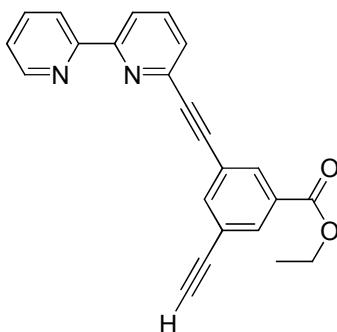
**Synthesis of 6-ethynyl-2,2'-bipyridine (8).** To a solution of **7** (0.1 g, 0.40 mmol) in tetrahydrofuran (3.5 mL) was added a solution of tetrabutylammonium fluoride in tetrahydrofuran (0.43 mL, 1.0 M). The solution was allowed to react for 5 min then was concentrated *in vacuo*. The crude product was purified by silica gel column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 99/1) to give 70 mg product (Yield: 97%). <sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 8.67 (ddd, *J* = 4.7, 1.7, 0.9, 1H), 8.46 – 8.43 (m, 2H), 7.87-7.78 (m, 2H), 7.52 (dd, *J* = 7.6, 1.0, 1H), 7.34 (ddd, *J* = 7.5, 4.8, 1.2, 1H), 3.26 (s, 1H). <sup>13</sup>C NMR (151 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 157.30, 155.95, 149.94, 142.28, 137.94, 137.68, 128.29, 124.88, 121.78, 121.59, 83.74, 77.25. HRMS-ES (*m/z*) [*M*<sup>+</sup>] *M*+*H* measured 181.0772, calculated 181.0766, error: 3.5.



**Synthesis of ethyl 3-(2,2'-bipyridin-6-ylethynyl)-5-bromobenzoate (9).** A microwave flask was charged with **2** (0.114 g, 0.32 mmol), **8** (0.07 g, 0.39 mmol), *bis*(triphenylphosphine)-palladium(II) dichloride (8.4 mg, 0.012 mmol), zinc chloride (66 mg, 0.48 mmol) and transferred to a glovebox. Degassed triethylamine (0.38 mL), degassed and tetrahydrofuran (1.61 mL) were added to the mixture in the glovebox and the flask was sealed. The mixture was stirred at 100 °C in the microwave for 3 hours and then it was concentrated *in vacuo*. The crude product was purified by silica gel column chromatography (dichloromethane/methanol, 99/1) to give 70 mg product (Yield: 54%). <sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 8.62-8.57 (m, 1H), 8.43 – 8.29 (m, 2H), 8.16 (t, *J* = 1.5, 1H), 8.13 – 8.07 (m, 1H), 7.89 (t, *J* = 1.7, 1H), 7.80 – 7.76 (m, 2H), 7.51 (dd, *J* = 7.6, 1.0, 1H), 7.27 (ddd, *J* = 7.5, 4.8, 1.1, 1H), 4.31 (q, *J* = 7.1, 2H), 1.33 (t, *J* = 7.1, 3H). <sup>13</sup>C NMR (151 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 165.09, 155.96, 149.98, 139.07, 138.00, 137.70, 135.85, 134.08, 133.55, 132.39, 128.26, 125.41, 125.30, 124.90, 123.00, 121.81, 121.51, 91.42, 87.02, 62.52, 14.81. HRMS-ES (*m/z*) [*M*+*H*] measured 409.0358, calculated 409.0275, error: 4.1

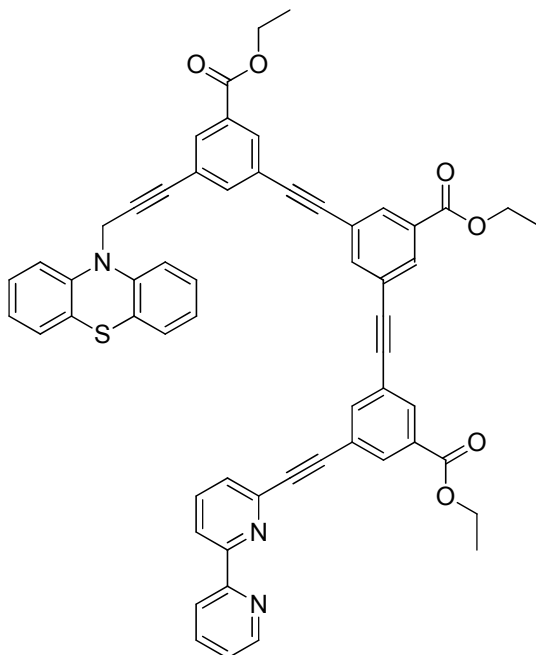


**Synthesis of ethyl 3-(2,2'-bipyridin-6-ylethynyl)-5-((trimethylsilyl)ethynyl)benzoate (9a).** A microwave flask was charged with **9** (59 mg, 0.144 mmol), *bis*(triphenylphosphine)-palladium(II) dichloride (5.6 mg, 0.0079 mmol), zinc chloride (30 mg, 0.22 mmol) and transferred to the glovebox. Degassed triethylamine (0.22 mL), degassed trimethylsilylacetylene (30  $\mu$ L, 0.217 mmol) and tetrahydrofuran (0.72 mL) were added to the mixture in the glovebox and the flask was sealed. The mixture was stirred at 100 °C in the microwave for 3 hours and then it was concentrated *in vacuo*. The crude product was purified by silica gel column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 99/1) to give 20 mg product (Yield: 33%). <sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  8.44-8.38 (m, 1H), 8.27 – 8.07 (m, 2H), 7.96 (t, *J* = 1.6, 1H), 7.84 (t, *J* = 1.6, 1H), 7.68 – 7.50 (m, 3H), 7.31 (dd, *J* = 7.6, 1.0, 1H), 7.17 – 6.98 (m, 1H), 4.11 (q, *J* = 7.1, 2H), 1.13 (t, *J* = 7.1, 3H), 0.00 (s, 9H). HRMS-ES (*m/z*) [M+H] measured 425.1682 calculated 425.1685 error - 0.8 ppm.



**Synthesis of ethyl 3-(2,2'-bipyridin-6-ylethynyl)-5-ethynylbenzoate (10).** To a solution of **9a** (0.1 g, 0.23 mmol) in tetrahydrofuran (2.12 mL) was added a solution of tetrabutylammonium fluoride in tetrahydrofuran (0.26 mL, 1.0 M). The solution was allowed to react for 5 min then was concentrated *in vacuo*. The crude product was purified by silica gel column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 99/1) to give 0.78 g product (Yield: 96%). <sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  8.69 (ddd, *J* = 4.8, 1.8, 0.9, 1H),

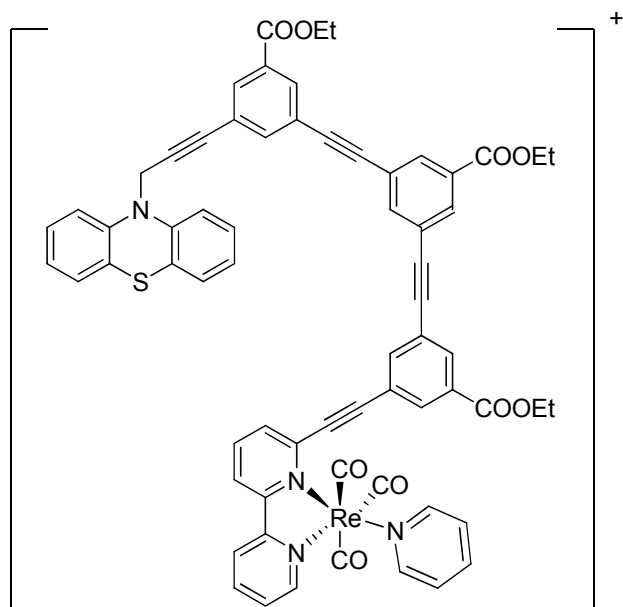
8.48 (dt,  $J = 8.0, 1.1$ , 1H), 8.47 – 8.44 (m, 1H), 8.29 (t,  $J = 1.6$ , 1H), 8.17 (t,  $J = 1.6$ , 1H), 7.93 (t,  $J = 1.6$ , 1H), 7.89-7.87 (m, 2H), 7.60 (dd,  $J = 7.6, 1.1$ , 1H), 7.37 (ddd,  $J = 7.5, 4.8, 1.2$ , 1H), 4.40 (q,  $J = 7.1$ , 2H), 3.26 (s, 1H), 1.42 (t,  $J = 7.1$ , 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  164.83, 156.73, 155.35, 149.26, 142.10, 138.92, 137.26, 136.98, 133.24, 133.10, 131.61, 127.53, 124.17, 123.29, 123.12, 121.11, 120.71, 90.28, 86.39, 81.63, 78.92, 61.66, 14.12. HRMS-ES ( $m/z$ )  $[\text{M}+\text{H}]$  measured 353.1289, calculated 353.1290, error: 0.3 ppm.



**Synthesis of ethyl 3-(3-(10H-phenothiazin-10-yl)prop-1-ynyl)-5-((3-((3-(2,2'-bipyridin-6-ylethynyl)-5-(ethoxycarbonyl)phenyl)ethynyl)-5-ethoxycarbonyl)phenyl)ethynyl)-benzoate (11).**

A microwave flask was charged with **5** (0.116 g, 0.18 mmol), **10** (0.89 g, 0.25 mmol) bis(triphenylphosphine)-palladium(II) dichloride (5.06 mg, 0.0072 mmol), zinc chloride (36.57 mg, 0.27 mmol) and transferred to the glovebox. Degassed triethylamine (0.26 mL), and tetrahydrofuran (1.8 mL) were added to the mixture in the glovebox and the flask was sealed. The mixture was stirred at 100 °C in the microwave for 3 hours and then it was concentrated *in vacuo*. The crude product was purified by silica gel column chromatography ( $\text{CH}_2\text{Cl}_2/\text{MeOH}$ , 99/1) to give 82 mg product (Yield: 50%).  $^1\text{H}$  NMR (600 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  8.69 (ddd,  $J = 4.8, 1.8, 0.9$ , 1H), 8.49 (dt,  $J = 8.0, 1.1$ , 1H), 8.46

(dd,  $J = 8.0, 1.1$ , 1H), 8.29 (t,  $J = 1.6$ , 1H), 8.23 (t,  $J = 1.6$ , 1H), 8.21 (t,  $J = 1.6$ , 1H), 8.19 (t,  $J = 1.6$ , 1H), 8.17 (t,  $J = 1.6$ , 1H), 8.08 (t,  $J = 1.6$ , 1H), 7.99 (t,  $J = 1.6$ , 1H), 7.90 (t,  $J = 1.6$ , 1H), 7.89-7.84 (m, 2H), 7.80 (t,  $J = 1.6$ , 1H), 7.61 (dd,  $J = 7.6, 1.1$ , 1H), 7.36 (ddd,  $J = 7.5, 4.7, 1.2, 1$  H), 7.33 – 6.94 (m, 8H), 4.79 (s, 2H), 4.47 – 4.35 (m, 6H), 1.57 – 1.30 (m, 9H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  164.80, 156.63, 155.41, 149.16, 144.13, 142.02, 138.30, 138.23, 138.02, 137.16, 136.87, 132.85, 132.77, 132.56, 132.54, 132.47, 132.39, 131.60, 131.57, 131.45, 127.51, 127.44, 126.91, 124.06, 123.55, 123.52, 123.51, 123.40, 123.37, 123.30, 123.26, 122.90, 121.01, 120.60, 114.83, 90.23, 88.90, 88.86, 88.84, 88.81, 86.38, 86.36, 84.01, 61.58, 61.57, 61.53, 39.16, 14.04, 14.036, 14.02. HRMS-ES ( $m/z$ ) [M+H] measured 908.2791, calculated 908.2794, error 0.4.

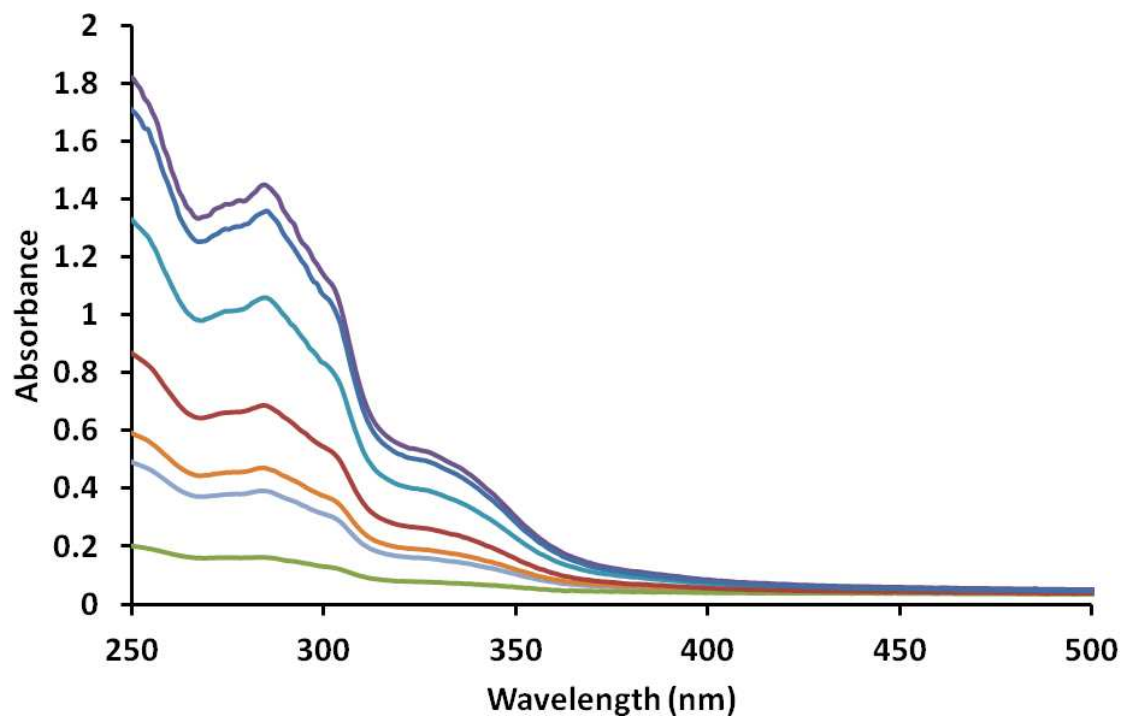


**Synthesis of PTZ-bridge-Re (12).** **13** (40 mg, 0.044 mmol) was reacted with rhenium pentacarbonyl chloride in toluene (1.78 mL). After refluxing the reaction mixtures overnight under argon, the reaction mixture was concentrated in vacuo. The crude product (32 mg, 0.032 mmol) was reacted with silver perchlorate (8.16 mg, 0.0494 mmol) in methanol/toluene (4:1) mixture for 1 day at room temperature in dark. Pyridine (76 mg, 0.96 mmol) was added to the reaction mixture and the resulting reaction mixture was stirred at 50 °C for 5 days. Excess pyridine was removed *in vacuo*. The crude product was purified by silica gel column chromatography ( $\text{CH}_2\text{Cl}_2/\text{MeOH}$ , 95/5) to give 20 mg product (Yield: 36%).  $^1\text{H}$  NMR (600 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  9.16 (dd,  $J = 5.5, 0.8$ , 1H), 8.46 (d,  $J = 8.3$ , 1H),

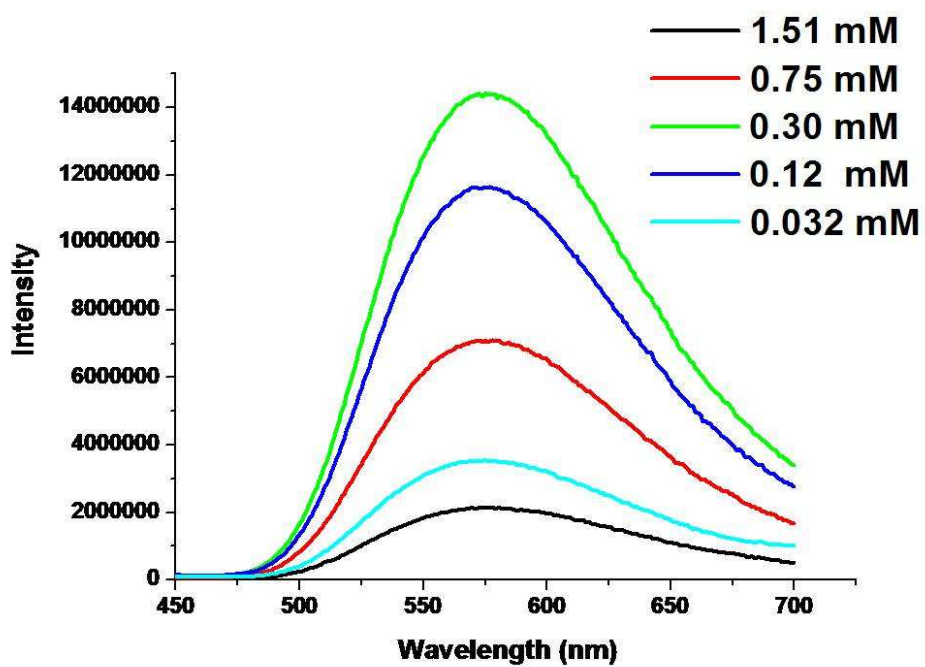


8.42 (dd,  $J = 8.3, 1.1$ , 1H), 8.30 – 8.27 (m, 1H), 8.27 – 8.19 (m, 3H), 8.14 (t,  $J = 1.6$ , 1H), 8.12-8.09 (m,  $J = 3H$ ), 8.08 (t,  $J = 1.6$ , 1H), 8.02 (dd,  $J = 7.9, 1.2$ , 1H), 8.00 – 7.97 (m, 2H), 7.83 (t,  $J = 1.6$ , 1H), 7.81 – 7.69 (m, 3H), 7.31 – 7.24 (m, 2H), 7.24 – 6.85 (m, 8H), 4.70 (s, 2H), 4.49 – 4.19 (m, 6H), 1.33 (m, 9H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  165.42, 165.40, 165.11, 156.96, 156.66, 153.43, 152.38, 147.08, 144.74, 142.09, 141.73, 141.03, 140.48, 139.32, 139.07, 138.83, 138.63, 134.93, 133.79, 133.76, 133.60, 133.33, 133.19, 133.12, 133.00, 132.53, 132.25, 132.09, 131.42, 129.51, 128.11, 127.70, 127.52, 126.47, 125.04, 124.58, 124.20, 123.88, 123.51, 123.08, 122.07, 115.44, 100.35, 90.08, 89.49, 89.30, 89.23, 88.95, 86.99, 84.62, 62.44, 62.23, 62.16, 39.73, 14.64, 14.62. HRMS-FAB (m/z) [M+] measured 1257.2554, calculated 1257.2543.

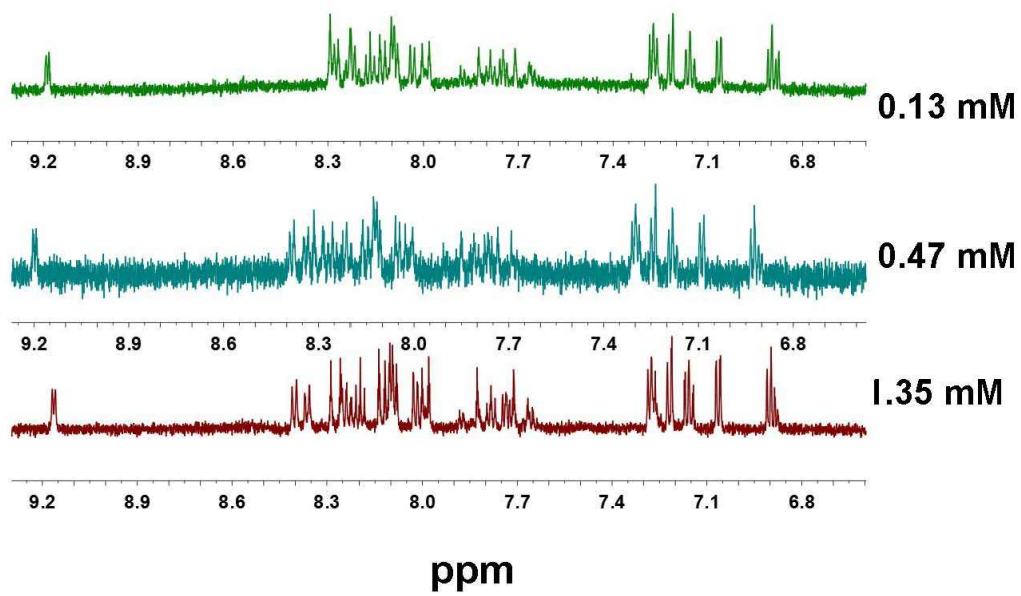
**Aggregation studies.** Donor-bridge-acceptor complexes containing *meta*-phenylene ethynylene linkages have been shown to aggregate under certain conditions.<sup>3</sup> Self-association often leads to enhanced quenching, due to the formation of aggregates with short intermolecular donor-acceptor distances. To verify that no aggregation is occurring in PTZ-bridge-Re, a combination of UV-vis, steady-state fluorescence, and NMR spectroscopies were employed. NMR spectra of PTZ-bridge-Re in dichloromethane solution of concentrations ranging from 0.13 mM to 1.35 mM did not exhibit significant change in the position of resonances, and no additional resonances were observed as concentration was varied. Absorption and emission spectra of PTZ-bridge-Re at concentrations varying from 32  $\mu\text{M}$  to 1.51 mM did not exhibit significant change in peak position, and increasing concentration did not produce additional spectral features. These results suggest that there is no aggregation under our experimental conditions.



**Figure S1.** UV-vis absorption spectra of PTZ-bridge-Re in CH<sub>2</sub>Cl<sub>2</sub> at various concentrations.

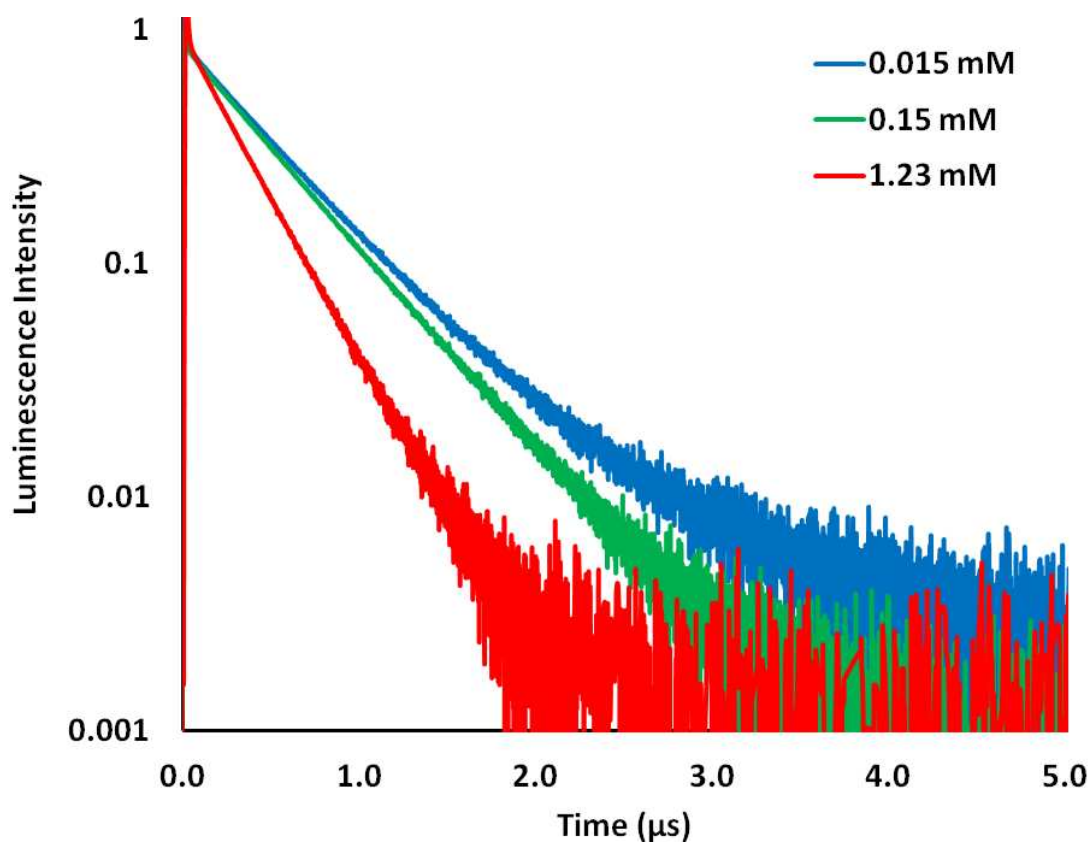


**Figure S2.** Steady-state emission spectra of PTZ-bridge-Re in CH<sub>2</sub>Cl<sub>2</sub> at various concentrations.



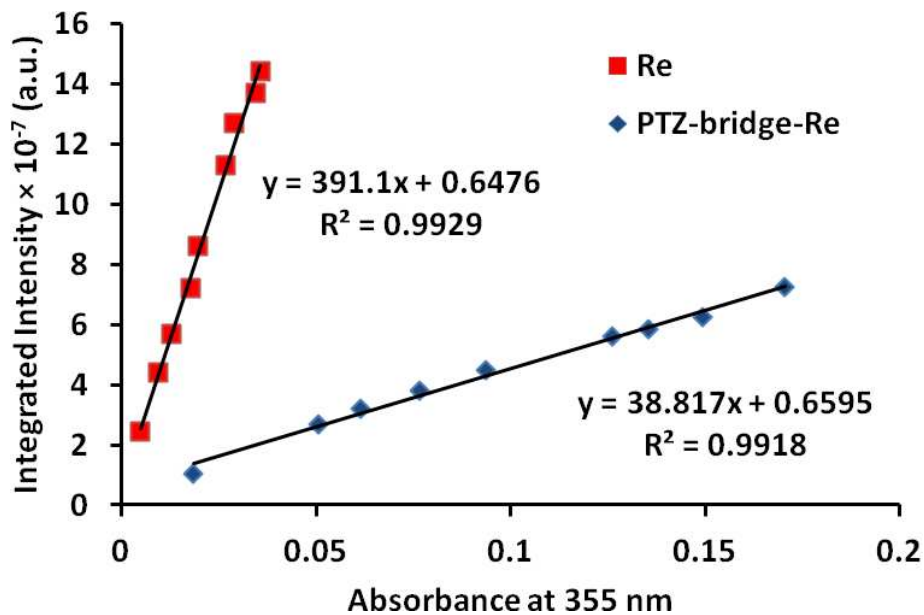
**Figure S3.** <sup>1</sup>H-NMR spectra of PTZ-bridge-Re complex in CD<sub>2</sub>Cl<sub>2</sub> at various concentrations.

**Bimolecular Quenching.** The excited-state lifetime and steady-state intensity were found to depend on the concentration of PTZ-bridge-Re in solution. Analysis of the longer component of the excited-state lifetime at a series of concentrations allowed a bimolecular quenching rate constant of  $1.1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  to be determined. When the lifetime is extrapolated to zero concentration, a natural lifetime of 530 ns is obtained. This value is close to that of the  $[\text{Re}(\text{CO})_3(\text{bpy})(\text{py})]^+$  model compound (560 ns in degassed  $\text{CH}_2\text{Cl}_2$ ).



**Figure S4.** Concentration-dependent luminescence of PTZ-bridge-Re in  $\text{CH}_2\text{Cl}_2$ .

**Quantum yield measurements of PTZ-bridge-Re.** Quantum yield measurements were performed in CH<sub>2</sub>Cl<sub>2</sub> using [Re(CO)<sub>3</sub>(bpy)(py)]<sup>+</sup> as a standard. The quantum yield of PTZ-bridge-Re was found to be approximately 10% that of the standard. Higher concentrations of PTZ-bridge-Re did not exhibit linear behavior as a result of intermolecular self-quenching.



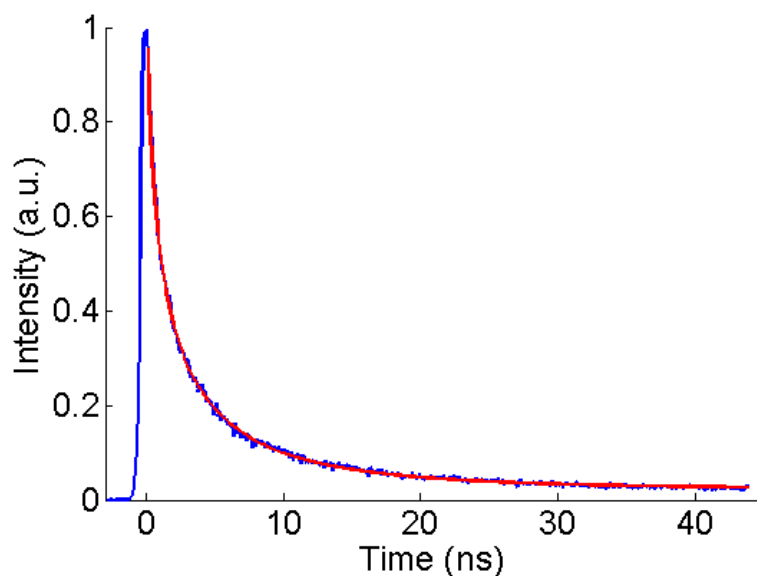
**Figure S5.** Quantum yield measurements of PTZ-bridge-Re relative to Re.

**Fitting of the fast component of PTZ-bridge-Re luminescence decay.** All photophysical measurements were collected at concentrations below 0.1 mM, unless otherwise stated. The data collected over the first 50 ns were used to determine the kinetics of the more rapid decay component. Single and double exponential fitting are incapable of adequately representing the data, even when an additional 530 ns decay component is added. A three-exponential equation (plus a fixed 530 ns component) models the data well, with lifetimes,  $\tau = 10.0 \pm 0.8$ ;  $2.7 \pm 0.2$ ;  $0.56 \pm 0.02$  ns and an average lifetime,  $\langle\tau\rangle = 3.2$  ns.

A stretched-exponential function plus a fixed 530 ns exponential was applied and produced values of  $\tau = 1.72$ ,  $\beta = 0.574$ ,  $\langle\tau\rangle = 2.7$  ns. These values were relatively unchanged ( $\tau = 1.73$ ,  $\beta = 0.571$ ,  $\langle\tau\rangle = 2.8$  ns) when the 530 ns term was removed.

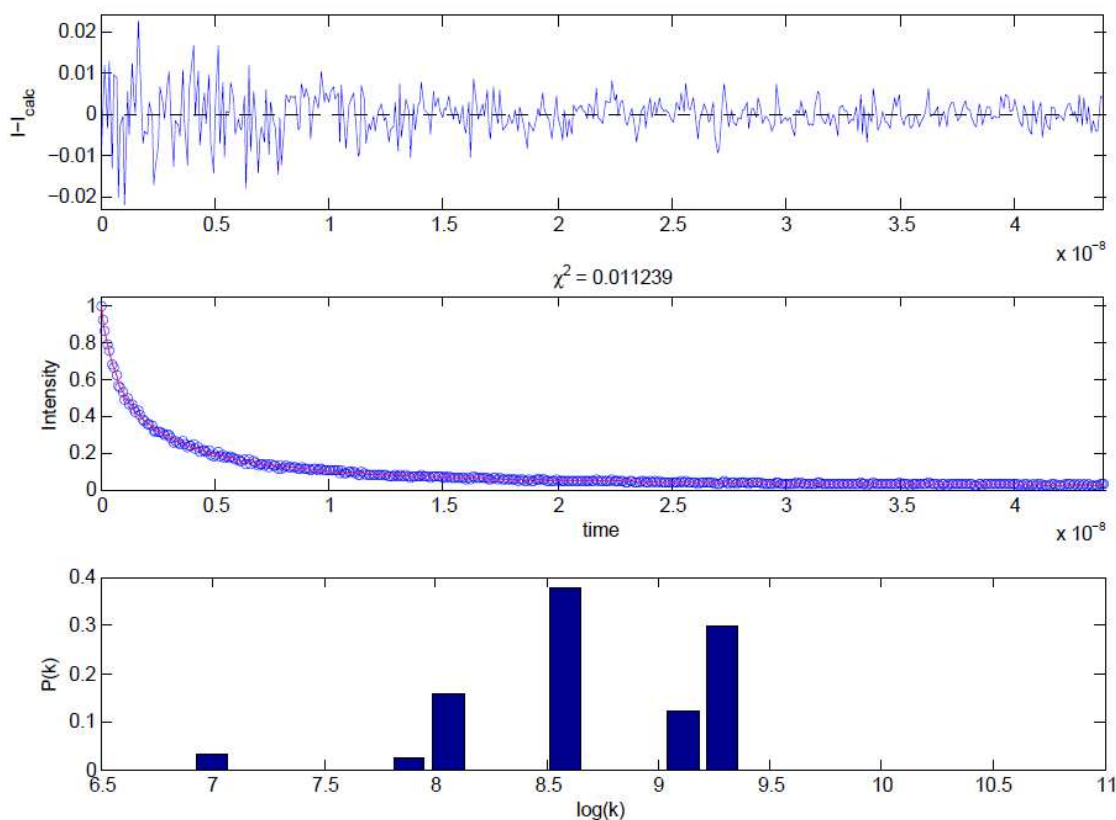
$$y = Ae^{-\left(\frac{t}{\tau}\right)^\beta} + Be^{-\left(\frac{t}{5.3 \times 10^{-7}}\right)}$$

$$\langle\tau\rangle = \frac{t}{\beta} \Gamma(\beta^{-1})$$



**Figure S6.** Stretched-exponential fit of the rapid decay component,  $\tau = 1.72$ ,  $\beta = 0.574$ ,  $\langle\tau\rangle = 2.7$  ns.

In light of the observed non-exponential decay of the faster component (discussed above) we also obtained a rate distribution ( $P(k)$ ) from the numerical inversion of the Laplace transform that describes the time-resolved luminescence intensity  $I(t) = \sum P(k)\exp(-kt)$ . The data was fit using a MATLAB (The Mathworks) algorithm (LSQNONNEG) that minimizes the sum of the squared deviations ( $\chi^2$ ) between the observed and calculated values of  $I(t)$ , subject to the nonnegativity constraint (non-negative least squares analysis). This produced a  $P(k)$  distribution with lifetimes ( $\tau$ ) in the 0.2–6 ns range and an average value of  $\tau = 1.9$  ns, in good agreement with the three exponential and stretched-exponential fits.



**Figure S7.**  $P(k)$  distributions extracted from non-negative least squares analysis of the rapid component of the luminescence decay. Top panel: residual difference between observed and calculated intensity with minimized  $\chi^2$ . Middle panel: luminescence decay data (circles) fit to a sum of exponentials (line). Bottom panel: probability distribution of rates ( $\log(k)$ ) with an average value of  $\tau = 1.9$  ns.



## Computational Modeling.

Density functional theoretical calculations were conducted using the ORCA computational chemistry package (F. Neese, version 2.8.0), applying the generalized gradient approximation density functional PW91.<sup>4</sup> Initial geometry optimizations were performed using a 2 $\zeta$ -quality SV-ZORA basis set,<sup>5</sup> which employs the zeroth order relativistic approximation (ZORA) to the Dirac equation to account for relativistic effects. Additionally, the conductor-like screening model (COSMO)<sup>6</sup> of a continuum solvent was used, with parameters appropriate for CH<sub>2</sub>Cl<sub>2</sub> solvation, and the empirical van der Waals correction of Grimme was applied.<sup>7,8</sup> The initial geometry solutions were then used as input to run more intensive calculations with a 3 $\zeta$ -quality TZV-ZORA basis set. To test the validity of the calculated geometric parameters, numerical frequency calculations were performed. The lack of any negative (imaginary) frequencies appearing in the list of computed frequencies strongly suggests that we found true minima rather than saddle points on the energy surface.

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