# Effect of Structure on Excited-State Intramolecular Proton Transfer-Based Sensors for Phosphonofluoridate G-Series Nerve Agent Vapour Detection

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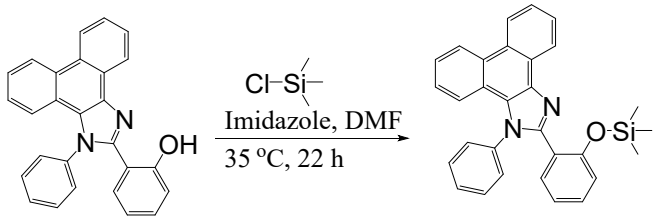
## Experimental

### Synthesis and Characterisation of Materials.

All reagents were purchased from commercial sources and were used as received unless otherwise stated. Dichloromethane was distilled before use. Silica gel (230-400 mesh) used for column chromatography was purchased from Merck. Thin-layer chromatography (TLC) was performed using aluminium backed silica gel 60 F254 plates from Merck. NMR spectra were taken using either a Bruker Avance 500 MHz or Ascend 500 MHz spectrometer with chemical shifts (δ) reported in parts per million (ppm) and referenced to the residual solvent peak. $^{1}$H and $^{13}$C NMR were performed in deuterated chloroform referenced to 7.26 ppm for $^{1}$H and 77.0 ppm for $^{13}$C, or in deuterated dimethyl sulfoxide referenced to 2.50 ppm for $^{1}$H and 39.5 ppm for $^{13}$C. The following symbols indicate peak assignments, TMSH = trimethylsilyl proton, $TESCH_3$ = methyl proton on triethylsilyl, $TESCH_2$ = methylene proton on triethylsilyl, TBDMS-MeH = methyl proton on *tert*-butyl dimethylsilyl, TBDMS-*t*BuH = *tert*-butyl proton on *tert*-butyl dimethylsilyl, $TIPSCH_3$ = methyl proton of triisopropylsilyl, TIPSCH = methine proton of triisopropylsilyl, TBDPS-PhH = phenyl proton on *tert*-butyl diphenylsilyl, TBDPS-*t*BuH = *tert*-butyl proton on *tert*-butyl diphenylsilyl, , PhenH = phenanthranyl proton, NPhH = proton of N-phenyl, SiOPhH = proton on silyl ether protected phenol, PhH = phenyl proton, OPhH = proton on phenol, $BuCH_3$ = *n*-butyl methyl proton, $BuCH_2$ = *n*-butyl methylene proton, $EtHxCH_3$ = ethylhexyl methyl proton, $EtHxCH_2$ = *n*-hexyl methylene proton, EtHxCH = ethylhexyl methine proton, $EtHxCH_2O$ = ethylhexyl proton on the $CH_2$ next to oxygen, Gly-$CH_3$ = methyl proton of glycol, Gly-$CH_2$ = methylene proton of glycol ether, G1-BPH = first generation dendron branching phenyl H; G1-SPhH = first generation dendron surface phenyl H. Coupling constants (*J*) are given in Hertz (Hz) and are quoted to the nearest 0.5 Hz. High-resolution mass spectrum (HRMS) measurements were performed using Bruker micrOTOF-Q (quadrupole – Time of Flight) instrument with a Bruker ESI source (ESI-micrOTOF-Q). Melting points (MPs) were measured in a glass capillary on a Büchi B-545 melting point apparatus and are uncorrected. The UV-visible spectra of the samples were performed using a Cary 5000 UV–Vis spectrophotometer. PL spectra of the samples were measured using either an Edinburgh Instruments FS5 spectrofluorometer in dichloromethane or an OceanOptics Flame spectrometer on thin films on quartz substrates using an LED lamp (365 nm) as the excitation source. The film PLQYs were measured using the absolute method described by Greenham *et. al.*[1] The samples were excited using a Kimmon 325 nm HeCd laser CW laser. During the measurement, the samples were kept in a SphereOptics

integrating sphere under a nitrogen rich environment. A Newport 818-UV photodetector mounted to the integrating sphere was used to detect the photoluminescence intensity, which was quantified using a KEITHLEY 2401 source meter. The reflectance and transmittance of the thin films were quantified using a Newport 1918-C optical power meter. Di-*iso*-propyl fluorophosphate (DFP) was synthesized following a reported procedure using di-*iso*-propylphosphite, cupric chloride, and cesium fluoride.[2] DFP undergoes hydrolysis during storage, resulting in the formation of di-*iso*-propylphosphoric acid and hydrogen fluoride in a 1:1 ratio. Therefore, the purity of the DFP was determined using $^{31}$P NMR spectra by the integration of the signals corresponding to the DFP and di-*iso*-propylphosphoric acid.

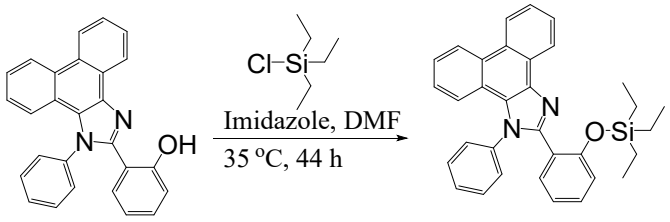
**1-Phenyl-2-(2-((trimethylsilyl)oxy)phenyl)-1H-phenanthro[9,10-d]imidazole (PhIm-TMS)**




**PhIm-OH** **PhIm-TMS**

A mixture of 2-[1-phenyl-1*H*-phenanthro[9,10-d]imidazol-2-yl]phenol (**PhIm-OH**)[3] (580 mg, 1.50 mmol), trimethylsilyl chloride (0.30 mL, 2.3 mmol), imidazole (337 mg, 4.95 mmol), and anhydrous *N*,*N*-dimethylformamide (10 mL) was stirred under argon in an oil bath held in an oil bath held at 35 °C for 22 h. The mixture was allowed to cool to room temperature and then water (50 mL) and ethylacetate (50 mL) were added. The organic phase was separated and washed with water (5 × 50 mL), dried over anhydrous magnesium sulfate, and filtered. The filtrate was collected and the solvent removed. The residue was purified using column chromatography over Bio-Beads S-X1 support with toluene as eluent to give **PhIm-TMS** as a white solid (460 mg, 67%). mp 183-184 °C. $\lambda_{max}$(dichloromethane)/nm: 260 (log$\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$ 4.82), 284 (4.27), 295 sh (4.11), 308 (4.05), 342 (3.39), 358 (3.43). $\lambda_{max}$(fluorescence) (dichloromethane)/nm: 367, 375, 403 sh. $^1$H NMR ($\delta$, 500 MHz, $CD_2Cl_2$): 0.09 (9 H, s, TMSH), 6.77 (1 H, dd, $J$ = 1.0, $J$ = 8.0, SiOPhH), 6.98 (1 H, ddd, $J$ = 1.0, $J$ = 7.5, $J$ = 7.5, SiOPhH), 7.25-7.30 (3 H, m, PhenH and SiOPhH), 7.41-7.51 (6 H, m, NPhH and SiOPhH), 7.52 (1 H, ddd, $J$ = 2.0, $J$ = 6.5, $J$ = 8.5, PhenH), 7.66 (1 H, ddd, $J$ = 1.5, $J$ = 7.0, $J$ = 8.5, PhenH), 7.73 (1 H, ddd, $J$ = 1.0, $J$ = 7.0, $J$ = 8.0, PhenH), 8.73-8.77 (2 H, m, PhenH), 8.78-8.81 (1 H, m, PhenH). $^{13}$C NMR ($\delta$, 125 MHz, $CD_2Cl_2$): -0.31, 120.0, 121.3, 121.4, 122.8, 123.5, 123.9, 124.3, 125.1, 125.6, 126.6, 127.5(7), 127.6(1), 127.9, 128.4, 129.0, 129.3, 129.4, 129.5, 131.1, 132.7, 137.6, 138.5, 150.4, 154.6. *m*/*z* [HRMS-ESI$^+$] $C_{30}H_{26}N_2OSi$: expected 459.1887 ([M+H]$^+$), found: 459.1895 ([M+H]$^+$).

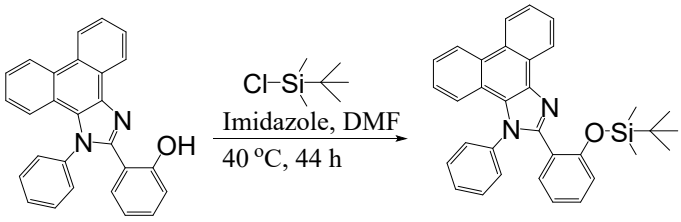
**1-Phenyl-2-(2-((triethylsilyl)oxy)phenyl)-1H-phenanthro[9,10-d]imidazole (PhIm-TES)**




**PhIm-OH** **PhIm-TES**

A mixture of **PhIm-OH**[2] (580 mg, 1.5 mmol), triethylsilyl chloride (0.40 mL, 2.3 mmol), imidazole (337 mg, 4.95 mmol), and anhydrous *N*,*N*-dimethylformamide (10 mL) was stirred under argon in an oil bath held in an oil bath held at 35 °C for 44 h. The mixture was allowed to cool to room temperature and then water (50 mL) and ethylacetate (50 mL) were added. The organic phase was separated and washed with water (5 × 50 mL), dried over anhydrous magnesium sulfate, and filtered. The filtrate was collected and the solvent removed. The residue was purified using column chromatography over Bio-Beads S-X1 support with toluene as eluent to give **PhIm-TES** as a white solid (447 mg, 60%). mp 111-112 °C. $\lambda_{max}$(dichloromethane)/nm: 260 (log$\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$ 4.87), 284 (4.31), 295 sh (4.14), 308 (4.09), 342 (3.39), 358 (3.46). $\lambda_{max}$(fluorescence) (dichloromethane)/nm: 366, 374, 401 sh. $^1$H NMR ($\delta$, 500 MHz, $CDCl_3$): 0.61 (6 H, q, *J* = 8.0, $TESCH_2$), 0.77 (9 H, t, *J* = 8.0, $TESCH_3$), 6.73 (1 H, brdd, *J* = 0.5, *J* = 8.0, SiOPhH), 6.92 (1 H, ddd, *J* = 1.0, *J* = 7.5, *J* = 7.5, SiOPhH), 7.19-7.29 (3 H, m, PhenH and SiOPhH), 7.38 (1 H, dd, *J* = 2.0, *J* = 7.5, SiOPhH), 7.41-7.47 (5 H, m, NPhH), 7.51 (1 H, ddd, *J* = 2.0, *J* = 6.5, *J* = 8.5, PhenH), 7.64 (1 H, ddd, *J* = 1.5, *J* = 7.0, *J* = 8.5, PhenH), 7.72 (1 H, ddd, *J* = 1.0, *J* = 7.0, *J* = 8.0, PhenH), 8.72 (1 H, brd, *J* = 8.5, PhenH), 8.78 (1 H, brd, *J* = 8.5, PhenH), 8.82-8.85 (1 H, m, PhenH). $^{13}$C NMR ($\delta$, 125 MHz, $CDCl_3$): 5.0, 6.4, 119.1, 120.7, 120.9, 122.7, 123.0(1), 123.0(5), 124.0, 124.6, 125.2, 126.1, 127.1, 127.5, 128.1, 128.5, 129.0(0), 129.0(4), 129.1, 130.7, 132.3, 137.3, 138.1, 150.1, 154.5. *m*/*z* [HRMS-ESI$^+$] $C_{33}H_{32}N_2OSi$: expected 501.2357 ([M+H]$^+$), found: 501.2372 ([M+H]$^+$).

**2-(2-((tert-Butyldimethylsilyl)oxy)phenyl)-1-phenyl-1H-phenanthro[9,10-d]imidazole (PhIm-TBDMS)**

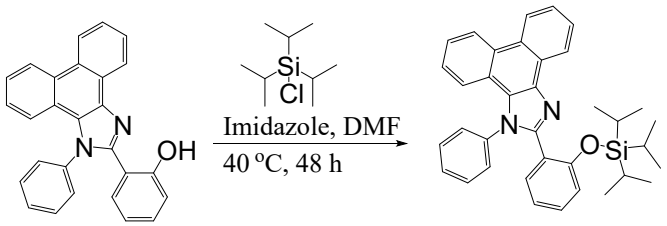



**PhIm-OH** **PhIm-TBDMS**

A mixture of **PhIm-OH**[3] (773 mg, 2.00 mmol), *tert*-butyldimethylsilyl chloride (452 mg, 3.00 mmol), imidazole (450 mg, 6.60 mmol), and anhydrous *N*,*N*-dimethylformamide (10 mL) was stirred under argon in an oil bath held at 40 °C for 44 h. The mixture was allowed to cool to room temperature and then water (50 mL) and ethylacetate (50 mL) were added. The organic phase was separated and washed with water (5 × 50 mL), dried over anhydrous magnesium sulfate, and filtered. The filtrate was collected and the solvent removed. The residue was purified using column chromatography over silica with dichloromethane:hexane

(1:1) and then dichloromethane:ethylacetate (1:0 to 4:1) mixtures as eluent. The product was further purified by recrystallization using dichloromethane and methanol to give **PhIm-TBDMS** as a white solid (772 mg, 77%). mp 169-170 °C. $\lambda_{max}$(dichloromethane)/nm: 259 (log$\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$ 4.86), 284 (4.29), 295 sh (4.13), 308 (4.06), 340 (3.37), 357 (3.43). $\lambda_{max}$(fluorescence) (dichloromethane)/nm: 365, 374, 400 sh. $^1$H NMR ($\delta$, 500 MHz, $CD_2Cl_2$): 0.10 (6 H, s, TBDMS-MeH), 0.71 (9 H, s, TBDMS-tBuH), 6.83 (1 H, ddd, *J* = 0.5, *J* = 1.0, *J* = 8.0, SiOPhH), 6.93 (1 H, ddd, *J* = 1.0, *J* = 7.5, *J* = 7.5, SiOPhH), 7.22 (1 H, ddd, *J* = 0.5, *J* = 1.5, *J* = 8.5, PhenH), 7.25-7.29 (2 H, m, PhenH and SiOPhH), 7.32 (1 H, dd, *J* = 2.0, *J* = 7.5, SiOPhH), 7.44-7.49 (5 H, m, NPhH), 7.52 (1 H, ddd, *J* = 1.5, *J* = 7.0, *J* = 8.5, PhenH), 7.65 (1 H, ddd, *J* = 1.5, *J* = 7.0, *J* = 8.5, PhenH), 7.72 (1 H, ddd, *J* = 1.0, *J* = 7.0, *J* = 8.0, PhenH), 8.73-8.76 (2 H, m, PhenH), 8.78-8.81 (1 H, m, PhenH). $^{13}$C NMR ($\delta$, 125 MHz, $CD_2Cl_2$): -4.4, 18.2, 25.5, 120.1, 121.1, 121.3, 122.9, 123.4, 123.5, 123.9, 124.3, 125.1, 125.6, 126.6, 127.5, 127.7, 127.9, 128.4, 128.9, 129.3, 129.5, 129.7, 131.1, 132.4, 137.5, 138.5, 150.1, 155.2. *m/z* [HRMS-ESI$^+$] $C_{33}H_{32}N_2OSi$: expected 501.2357 ([M+H]$^+$), found: 501.2355 ([M+H]$^+$).

**1-Phenyl-2-(2-((triisopropylsilyl)oxy)phenyl)-1H-phenanthro[9,10-d]imidazole (PhIm-TIPS)**

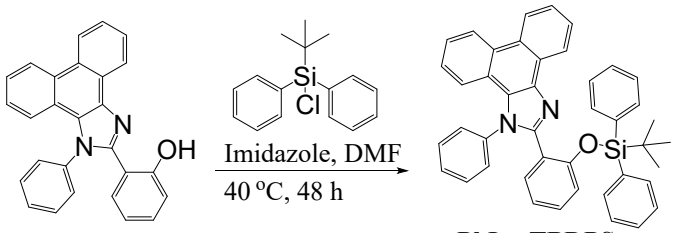



**PhIm-OH** **PhIm-TIPS**

A mixture of **PhIm-OH**[3] (580 mg, 1.50 mmol), tri-*iso*-propylsilyl chloride (0.50 mL, 2.3 mmol), imidazole (337 mg, 4.95 mmol), and anhydrous *N*,*N*-dimethylformamide (10 mL) was stirred under argon in an oil bath held at 40 °C for 48 h. The mixture was allowed to cool to room temperature and then water (50 mL) and ethylacetate (50 mL) were added. The organic phase was separated and washed with water (5 × 50 mL), dried over anhydrous magnesium sulfate, and filtered. The filtrate was collected and the solvent removed. The residue was purified by recrystallization using dichloromethane and methanol to give **PhIm-TIPS** as a white solid (534 mg, 65%). mp 179-180 °C. $\lambda_{max}$(dichloromethane)/nm: 259 (log$\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$ 4.86), 284 (4.31), 295 sh (4.13), 308 (4.07), 340 (3.41), 358 (3.47). $\lambda_{max}$(fluorescence) (dichloromethane)/nm: 365, 374, 401 sh. $^1$H NMR ($\delta$, 500 MHz, $CDCl_3$): 0.92 (18 H, d, *J* = 7.5, TIPSC$H_3$), 1.19 (3 H, septet, *J* = 7.5, TIPSCH), 6.79 (1 H, dd, *J* = 1.0, *J* = 8.5, SiOPhH), 6.86 (1 H, ddd, *J* = 1.0, *J* = 7.5, *J* = 7.5, SiOPhH), 7.19 (1 H, ddd, *J* = 1.5, *J* = 7.5, *J* = 8.5, SiOPhH), 7.23 (1 H, ddd, *J* = 0.5, *J* = 1.5, *J* = 8.5, PhenH), 7.26 (1 H, ddd, *J* = 1.0, *J* = 7.0, *J* = 8.5, PhenH), 7.30 (1 H, dd, *J* = 1.5, *J* = 7.5, SiOPhH), 7.39-7.47 (5 H, m, NPhH), 7.51 (1 H, ddd, *J* = 1.5, *J* = 7.0, *J* = 8.5, PhenH), 7.64 (1 H, ddd, *J* = 1.5, *J* = 7.0, *J* = 8.5, PhenH), 7.71 (1 H, ddd, *J* = 1.0, *J* = 7.0, *J* = 8.0, PhenH), 8.70-8.73 (1 H, m, PhenH), 8.77-8.80 (1 H, m, PhenH), 8.79-8.82 (1 H, m, PhenH). $^{13}$C NMR ($\delta$, 125 MHz, $CDCl_3$): 12.6, 17.7, 118.7, 120.2, 120.9, 122.6, 122.7, 122.9, 123.0, 124.0, 124.6, 125.1, 126.0, 127.0, 127.1, 127.5, 128.0, 128.4, 129.0(0),

129.0(1), 129.2, 130.6, 132.2, 137.2, 138.1, 150.0, 155.0. *m/z* [HRMS-ESI$^+$] $C_{36}H_{38}N_2OSi$: expected 543.2826 ([M+H]$^+$), found: 543.2842 ([M+H]$^+$).

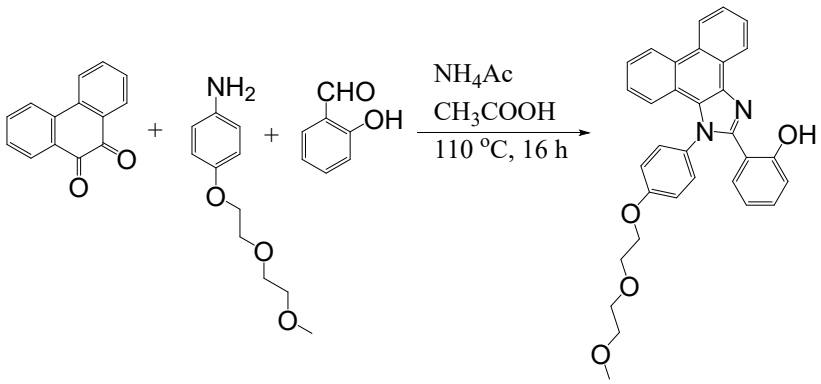
**2-(2-((tert-Butyldiphenylsilyl)oxy)phenyl)-1-phenyl-1H-phenanthro[9,10-d]imidazole (PhIm-TBDPS)**




**PhIm-OH** **PhIm-TBDPS**

A mixture of **PhIm-OH**[3] (580 mg, 1.50 mmol), *tert*-butyldiphenylsilyl chloride (0.58, 2.3 mmol), imidazole (337 mg, 4.95 mmol), and anhydrous *N*,*N*-dimethylformamide (10 mL) was stirred under argon in an oil bath held at 40 °C for 48 h. The mixture was allowed to cool to room temperature and then water (50 mL) and ethylacetate (50 mL) were added. The organic phase was separated and washed with water (5 × 50 mL), dried over anhydrous magnesium sulfate, and filtered. The filtrate was collected and the solvent removed. The residue was purified using column chromatography over silica with dichloromethane:hexane (1:1) and then dichloromethane:ethylacetate (4:1) mixtures as eluent to give a white solid (541 mg, 57%). mp 217-218 °C. $\lambda_{max}$(dichloromethane)/nm: 259 (log$\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$ 4.87), 284 (4.31), 295 sh (4.13), 308 (4.07), 339 (3.36), 357 (3.44). $\lambda_{max}$(fluorescence) (dichloromethane)/nm: 364, 373, 401 sh. $^1$H NMR ($\delta$, 500 MHz, $CDCl_3$): 0.82 (9 H, s, TBDPS-tBuH), 6.43 (1 H, ddd, *J* = 0.5, *J* = 1.0, *J* = 8.0, SiOPhH), 6.82 (1 H, ddd, *J* = 1.0, *J* = 7.5, *J* = 7.5, SiOPhH), 6.93 (1 H, ddd, *J* = 2.0, *J* = 7.5, *J* = 8.5, SiOPhH), 7.19-7.24 (5 H, m, TBDPS-PhH and PhenH), 7.26 (1 H, ddd, *J* = 1.0, *J* = 7.0, *J* = 8.5, PhenH), 7.32-7.37 (3 H, m, TBDPS-PhH and SiOPhH), 7.39-7.42 (4 H, m, NPhH), 7.45-7.49 (1 H, m, NPhH), 7.52 (1 H, ddd, *J* = 1.5, *J* = 7.0, *J* = 8.5, PhenH), 7.55-7.57 (4 H, m, TBDPS-PhH), 7.66 (1 H, ddd, *J* = 1.5, *J* = 7.0, *J* = 8.5, PhenH), 7.73 (1 H, ddd, *J* = 1.0, *J* = 7.0, *J* = 8.0, PhenH), 8.75 (1 H, ddd, *J* = 0.5, *J* = 0.5, *J* = 8.5, PhenH), 8.81 (1 H, ddd, *J* = 0.5, *J* = 0.5, *J* = 8.5, PhenH), 8.87 (1 H, ddd, *J* = 0.5, *J* = 1.5, *J* = 8.0, PhenH). $^{13}$C NMR ($\delta$, 125 MHz, $CDCl_3$): 19.4, 26.3, 119.2, 120.4, 120.9, 122.4, 122.8, 123.0(1), 123.0(4), 124.0, 124.7, 125.3, 126.1, 127.2, 127.3, 127.5, 127.7, 128.1, 128.6, 129.0(6), 129.1(3), 129.3, 129.8, 130.3, 132.1, 132.6, 135.4, 137.2, 138.1, 149.8, 154.4. *m/z* [HRMS-ESI$^+$] $C_{43}H_{36}N_2OSi$: expected 625.2670 ([M+H]$^+$), found: 625.2679 ([M+H]$^+$).

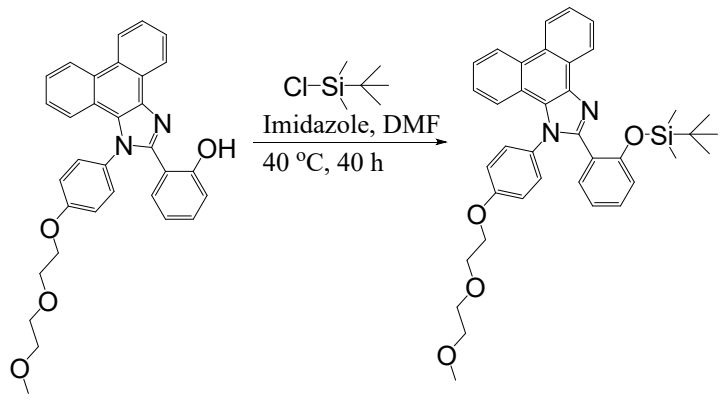
**2-[1-(4-{2-[2-Methoxyethoxy]ethoxy}phenyl)-1*H*-phenanthro[9,10-d]imidazol-2-yl]phenol (GLPhIm-OH)**




**GLPhIm-OH**

A mixture of 9,10-phenanthrenequinone (1.04 g, 5.00 mmol), 4-[2-(2-methoxyethoxy)ethoxy]phenylamine[4] (1.58 g, 7.50 mmol), salicylaldehyde (0.52 mL, 5.0 mmol), ammonium acetate (1.90 g, 25.0 mmol), and glacial acetic acid (20 mL) was stirred under argon in an oil bath held at 110 °C for 16 h. The mixture was allowed to cool to room temperature and then saturated potassium carbonate aqueous solution was added dropwise until pH = 6. The mixture was then extracted with dichloromethane (3 × 50 mL). The combined organic portions were washed with brine (50 mL), dried over anhydrous magnesium sulfate, and filtered. The filtrate was collected and the solvent removed. The residue was purified using column chromatography over silica with dichloromethane:hexane (1:1–1:0) and then dichloromethane:ethyl acetate (20:1) mixtures as eluent to give **GLPhIm-OH** as a yellowish solid (1.02 g, 40%). mp 123-124 ºC. $\lambda_{max}$(dichloromethane)/nm: 256 sh (log$\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$ 4.63), 264 (4.78), 271 sh (4.63), 286 sh (4.26), 304 (4.16), 322 sh (4.27), 334 (4.39), 347 (4.29), 365 (4.33). $\lambda_{max}$(fluorescence) (dichloromethane)/nm: 469. $^1$H NMR ($\delta$, 500 MHz, $CD_2Cl_2$): 3.39 (3 H, s, Gly-$CH_3$), 3.59-3.61 (2 H, m, Gly-$CH_2$), 3.73-3.75 (2 H, m, Gly-$CH_2$), 3.93-3.95 (2 H, m, Gly-$CH_2$), 4.30-4.32 (2 H, m, Gly-$CH_2$), 6.57 (1 H, ddd, *J* = 1.5, *J* = 7.0, *J* = 8.5, OPhH), 6.89 (1 H, dd, *J* = 1.5, *J* = 8.0, OPhH), 7.08 (1 H, dd, *J* = 1.5, *J* = 8.5, OPhH), 7.19-7.27 (4 H, m, OPhH, PhenH, NPhH), 7.33 (1 H, ddd, *J* = 1.0, *J* = 7.0, *J* = 8.5, PhenH), 7.52-7.57 (3 H, m, PhenH, NPhH), 7.70 (1 H, ddd, *J* = 1.5, *J* = 7.0, *J* = 8.5, PhenH), 7.77 (1 H, ddd, *J* = 1.0, *J* = 7.0, *J* = 8.0, PhenH), 8.69 (1 H, brd, *J* = 8.0, PhenH), 8.74 (1 H, brd, *J* = 8.0, PhenH), 8.79 (1 H, brd, *J* = 8.5, PhenH), 13.77 (1 H, brs, OH). $^{13}$C NMR ($\delta$, 125 MHz, $CD_2Cl_2$): 59.1, 68.4, 69.9, 71.1, 72.3, 113.6, 116.8, 118.1, 118.4, 121.4, 122.7, 123.1, 123.6, 124.4, 125.6, 126.1, 126.3, 126.6, 127.0, 127.7, 127.8, 128.7, 129.7, 130.4, 131.0, 131.8, 134.5, 149.2, 159.6, 160.7. *m*/*z* [HRMS-ESI$^+$] $C_{32}H_{28}N_2O_4$: expected 505.2122 ([M+H]$^+$), found: 505.2102 ([M+H]$^+$).

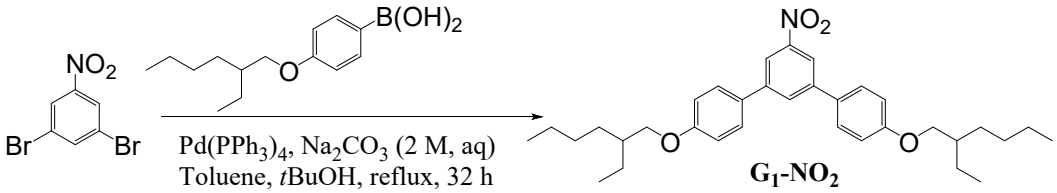
2-[2-({*tert*-Butyldimethylsilyl}oxy)phenyl]-1-[4-(2-{2-methoxyethoxy}ethoxy)phenyl]-1*H*-phenanthro[9,10-d]imidazole (**GLPhIm-TBDMS**)




**GLPhIm-OH** **GLPhIm-TBDMS**

A mixture of **GLPhIm-OH** (504 mg, 1.00 mmol), *tert*-butyldimethylsilyl chloride (226 mg, 1.50 mmol), imidazole (224 mg, 3.29 mmol), and anhydrous *N*,*N*-dimethylformamide (10 mL) was stirred under argon in an oil bath held at 40 °C for 40 h. Water (50 mL) and ethylacetate (50 mL) were added, and the organic phase was separated, washed with water (5 × 50 mL), dried over anhydrous magnesium sulfate, and filtered. The filtrate was collected and the solvent removed. The residue was purified using column chromatography over BioBeads with toluene as eluent to give **GLPhIm-TBDMS** as a white solid (418 mg, 68%). mp 102-103 ºC. $\lambda_{max}$(dichloromethane)/nm: 254 sh (log$\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$ 4.77), 260 (4.86), 284 (4.31), 296 sh (4.12), 309 (4.04), 340 (3.33), 358 (3.50). $\lambda_{max}$(fluorescence) (dichloromethane)/nm: 340, 368, 402. $^1$H NMR ($\delta$, 500 MHz, $CD_2Cl_2$): 0.09 (6 H, s, TBDMS-MeH), 0.71 (9 H, s, TBDMS-tBuH), 3.35 (3 H, s, Gly-$CH_3$), 3.54-3.55 (2 H, m, Gly-$CH_2$), 3.67-3.69 (2 H, m, Gly-$CH_2$), 3.82-3.85 (2 H, m, Gly-$CH_2$), 4.14-4.16 (2 H, m, Gly-$CH_2$), 6.84 (1 H, dd, *J* = 1.0, *J* = 8.5, SiOPhH), 6.93-6.98 (3 H, m, SiOPhH, NPhH), 7.25-7.33 (4 H, m, SiOPhH, PhenH), 7.35 (2 H, 1/2AA′BB′, NPhH), 7.52 (1 H, ddd, *J* = 2.0, *J* = 6.0, *J* = 8.5, PhenH), 7.64 (1 H, ddd, *J* = 1.5, *J* = 7.0, *J* = 8.0, PhenH), 7.71 (1 H, ddd, *J* = 1.0, *J* = 7.0, *J* = 8.0, PhenH), 8.72-8.74 (2 H, brm, PhenH), 8.79 (1 H, brd, *J* = 8.5, PhenH). $^{13}$C NMR ($\delta$, 125 MHz, $CD_2Cl_2$): -4.4, 18.2, 25.5, 59.1, 68.1, 69.9, 71.1, 72.3, 115.2, 120.1, 121.1, 121.3, 122.8, 123.4(6), 123.5(4), 124.0, 124.3, 125.0, 125.5, 126.6, 127.5, 127.8, 128.0, 128.3, 129.2, 129.9, 131.0, 131.2, 132.4, 137.4, 150.4, 155.1, 159.5. *m*/*z* [HRMS-ESI$^+$] $C_{38}H_{42}N_2O_4Si$: expected 619.2987 ([M+H]$^+$), found: 619.2960 ([M+H]$^+$).

**4,4''-Bis[(2-ethylhexyl)oxy]-5'-nitro-1,1':3',1''-terphenyl ($G_1$-$NO_2$)**

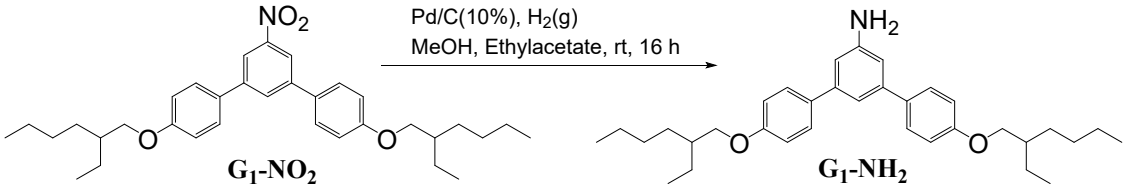



**$G_1$-$NO_2$**

A mixture of 1,3-dibromo-5-nitrobenzene (0.630 g, 2.25 mmol), [4-({2-ethylhexyl}oxy)phenyl]boronic acid[5] (1.69 g, 6.75 mmol), and sodium carbonate (1.06 g, 10.0 mmol) in *tert*-butanol (5 mL), toluene (15 mL), and water (5 mL) was placed under vacuum and backfilled with argon six times. Tetrakis[triphenylphosphine]palladium(0) (260 mg, 0.10 mmol) was added, and the mixture placed under

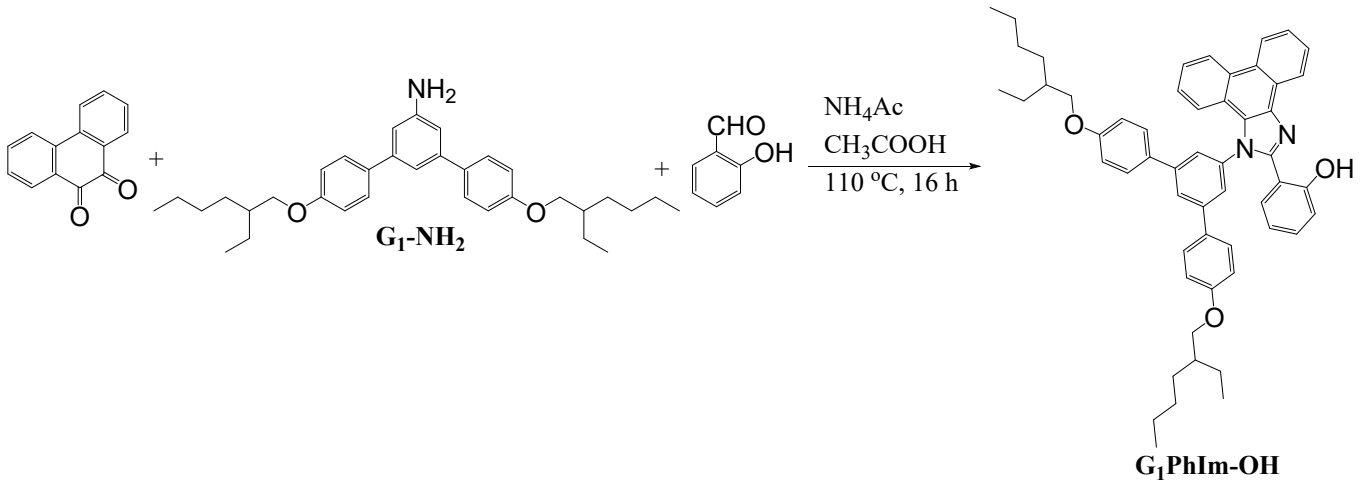
vacuum and backfilled with argon for a further six times. The mixture was stirred in an oil bath held at 100 °C for 32 h. The solution was allowed to cool to room temperature, and diethyl ether (50 mL) and water (50 mL) were added. The layers were separated, and the aqueous layer was extracted with diethyl ether (2 × 50 mL). The organic portions were combined, washed with brine (50 mL), dried over anhydrous magnesium sulfate, and filtered. The filtrate was collected, and the solvent removed. The residue was purified using column chromatography over silica with dichloromethane:*n*-hexane mixtures (0:1 to 1:9) as eluent to give **$G_1$-$NO_2$** as a slightly yellowish oil (1.03 g, 86%). $\lambda_{max}$(dichloromethane)/nm: 260 (log$\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$ 4.52), 279 (4.57), 343 (3.30). $^1$H NMR (δ 500 MHz, $CDCl_3$): 0.91-0.97 (12 H, m, EtHxC$H_3$), 1.31-1.55 (16 H, m, EtHxC$H_2$), 1.73-1.80 (2 H, m, EtHxCH), 3.89-3.93 (4 H, m, EtHxC$H_2$O), 7.02 and 7.60 (8 H, AA′BB′, G1-SPhH), 8.01 (1 H, t, *J* = 1.5, G1-BPH), 8.31 (2 H, d, *J* = 1.5, G1-BPH). $^{13}$C NMR(δ 125 MHz, $CDCl_3$): 11.1, 14.1, 23.0, 23.9, 29.1, 30.5, 39.4, 70.7, 115.1, 119.3, 128.3, 130.6, 131.0, 142.9, 149.2, 159.9.

**4,4''-Bis[(2-ethylhexyl)oxy]-[1,1':3',1''-terphenyl]-5'-amine ($G_1$-$NH_2$)**




A mixture of **$G_1$-$NO_2$** (531 mg, 1.00 mmol), methanol (50 mL) and ethylacetate (50 mL) was placed under vacuum and then backfilled with argon for six times. Then palladium on carbon (10%, 50 mg) was added and the resulting mixture was placed under vacuum and then backfilled with hydrogen three times. After being stirred at room temperature under hydrogen for 16 h, the mixture was placed under vacuum and backfilled with nitrogen for three times to remove the hydrogen before been filtered through a plug of celite, which was then washed with ethyl acetate (100 mL). The filtrate was collected, and the solvent removed. The residue was purified using column chromatography over silica with ethylacetate:*n*-hexane mixtures (0:1 to 1:9) as eluent to give the product as a colorless oil (490 mg, 98%). IR $\nu_{max}$/cm$^{-1}$ 3376 and 3463 ($NH_2$). $\lambda_{max}$(dichloromethane)/nm: 261 (log$\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$ 4.67), 320 (3.72). $^1$H NMR (δ 500 MHz, $CDCl_3$): 0.90-0.96 (12 H, m, EtHxC$H_3$), 1.32-1.55 (16 H, m, EtHxC$H_2$), 1.71-1.78 (2 H, m, EtHxCH), 3.78 (2 H, brs, -$NH_2$), 3.86-3.91 (4 H, m, EtHxC$H_2$O), 6.82 (2 H, d, *J* = 1.5, G1-BPH), 6.96 and 7.53 (8 H, AA′BB′, G1-SPhH), 7.13 (1 H, t, *J* = 1.5, G1-BPH). $^{13}$C NMR(δ 125 MHz, $CDCl_3$): 11.1, 14.1, 23.1, 23.9, 29.1, 30.5, 39.4, 70.6, 112.0, 114.7, 116.3, 128.1, 133.7, 142.6, 146.9, 159.0.

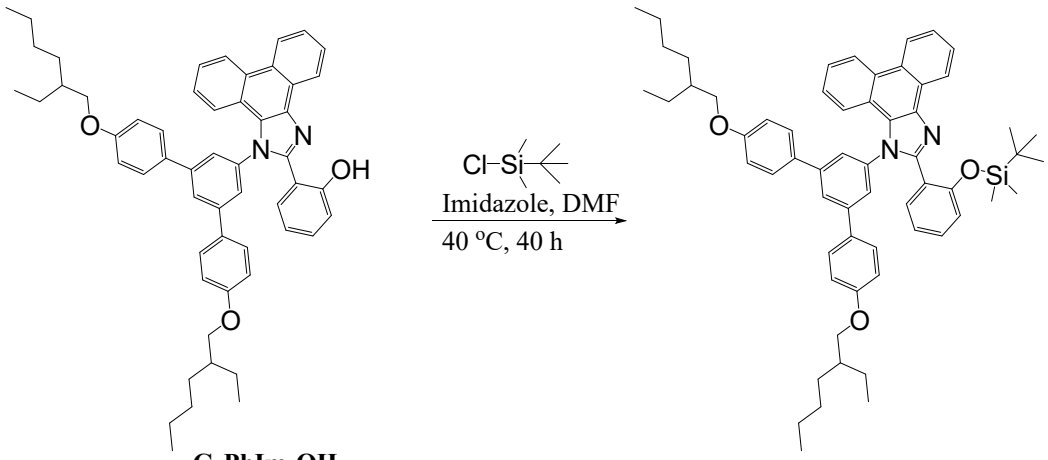
**2-[1-(4,4''-Bis{[2-ethylhexyl]oxy}-{1,1':3',1''-terphenyl}-5'-yl)-1*H*-phenanthro[9,10-d]imidazol-2-yl]phenol (G$_1$PhIm-OH)**




**$G_1$-$NH_2$** **$G_1$PhIm-OH**

A mixture of 9,10-phenanthrenequinone (375 mg, 1.80 mmol), 4,4"-bis[(2-ethylhexyl)oxy]-[1,1':3',1"-terphenyl]-5'-amine (**$G_1$-$NH_2$**) (1.03 g, 2.05 mmol), salicylaldehyde (220 mg, 1.80 mmol), ammonium acetate (694 mg, 9.00 mmol), and glacial acetic acid (10 mL) was stirred under argon in an oil bath held at 110 °C for 16 h. The mixture was allowed to cool to room temperature and then water (50 mL) was added. Saturated aqueous potassium carbonate solution was added dropwise until the pH = 6. The mixture was then extracted using dichloromethane (3 × 50 mL). The organic portions were combined, washed with brine (50 mL), dried over anhydrous magnesium sulfate, and filtered. The filtrate was collected and the solvent removed. The residue was purified using column chromatography over silica with dichloromethane:hexane (1:1) as eluent and then precipitation from dichloromethane and methanol to give **$G_1$PhIm-OH** as a slightly yellowish solid (507 mg, 35%). mp 85-86 °C. $\lambda_{max}$(dichloromethane)/nm: 257 sh (log$\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$ 4.80), 265 (4.95), 271 sh (4.92), 334 (4.39), 346 (4.31), 364 (4.33). $\lambda_{max}$(fluorescence) (dichloromethane)/nm: 453. $^1$H NMR ($\delta$, 500 MHz, $CD_2Cl_2$): 0.88-0.94 (12 H, m, EtHxC$H_3$), 1.26-1.55 (16 H, m, EtHxC$H_2$), 1.69-1.77 (2 H, m, EtHxCH), 3.86-3.91 (4 H, m, OC$H_2$), 6.55 (1 H, ddd, *J* = 1.5, *J* = 7.5, *J* = 8.5, OPhH), 7.00 and 7.66 (8 H, AA′BB′, G1-SPhH), 7.06 (1 H, dd, *J* = 1.5, *J* = 8.0, OPhH), 7.10 (1 H, dd, *J* = 1.5, *J* = 8.0, OPhH), 7.21 (1 H, ddd, *J* = 1.5, *J* = 7.0, *J* = 8.5, OPhH), 7.31 (1 H, ddd, *J* = 1.0, *J* = 7.0, *J* = 8.0, PhenH), 7.40 (1 H, dd, *J* = 1.0, *J* = 8.5, PhenH), 7.54 (1 H, ddd, *J* = 1.5, *J* = 7.0, *J* = 8.5, PhenH), 7.71 (1 H, ddd, *J* = 1.5, *J* = 7.0, *J* = 8.5, PhenH), 7.77 (2 H, d, *J* = 1.5, G1-BPH), 7.79 (1 H, ddd, *J* = 1.0, *J* = 7.0, *J* = 8.0, PhenH), 8.18 (1 H, dd, *J* = 1.5, *J* = 1.5, G1-BPH), 8.73 (1 H, dd, *J* = 1.5, *J* = 8.0, PhenH), 8.76 (1 H, brd, *J* = 8.5, PhenH), 8.81 (1 H, brd, *J* = 8.0, PhenH), 13.75 (1 H, brs, OH). $^{13}$C NMR ($\delta$, 125 MHz, $CD_2Cl_2$): 11.2, 14.2, 23.4, 24.2, 29.4, 30.8, 39.7, 71.0, 113.5, 115.4, 118.2, 118.5, 121.6, 122.8, 123.1, 123.7, 124.5, 124.9, 125.7, 126.2, 126.4, 126.8, 126.9, 127.2, 127.5, 127.9, 128.6, 128.8, 129.7, 131.1, 131.7, 134.7, 140.2, 144.3, 149.0, 159.6, 160.3. *m*/*z* [HRMS-ESI$^+$] $C_{55}H_{58}N_2O_3$: expected 795.4520 (100%), 796.4554 (60%), 797.4587 (17%) ([M+H]$^+$), found: 795.4521 (100%), 796.4558 (70%), 797.4600 (20%) ([M+H]$^+$).

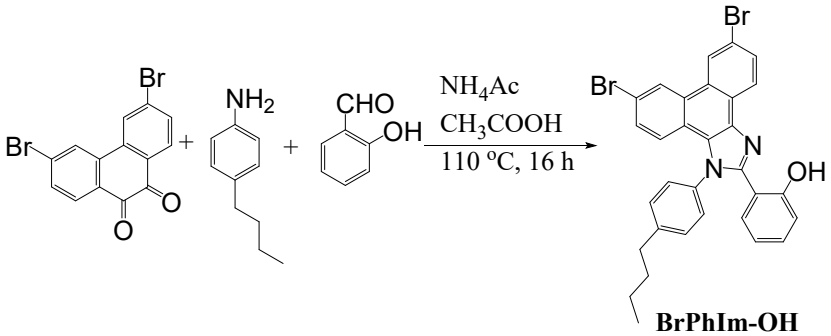
**1-[4,4''-Bis({2-ethylhexyl}oxy)-(1,1':3',1''-terphenyl)-5'-yl]-2-[2-({tert-butyldimethylsilyl}oxy)phenyl]-1*H*-phenanthro[9,10-d]imidazole ($G_1$PhIm-TBDMS)**




**$G_1$PhIm-OH** **G1PhIm-TBDMS**

A mixture of **$G_1$PhIm-OH** (270 mg, 0.34 mmol), *tert*-butyldimethylsilyl chloride (201 mg, 1.30 mmol), imidazole (198 mg, 2.90 mmol), and anhydrous *N*,*N*-dimethylformamide (15 mL) was stirred under argon in an oil bath held at 40 °C for 44 h. Then water (50 mL) and ethylacetate (100 mL) were added and the mixture was separated. The organic layer was washed with water (6 × 50 mL), dried over anhydrous magnesium sulfate, and filtered. The filtrate was collected and the solvent removed. The residue was purified using column chromatography over silica with dichloromethane:hexane (1:1–1:0) mixtures as eluent to give **$G_1$PhIm-TBDMS** as a white solid (160 mg, 52%). mp 82-83 °C. $\lambda_{max}$(dichloromethane)/nm: 260 (log$\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$ 5.00), 280 sh (4.82), 307 sh (4.30), 340 (3.38), 357 (3.43). $\lambda_{max}$(fluorescence) (dichloromethane)/nm: 365, 381, 399 sh. $^1$H NMR ($\delta$, 500 MHz, $CD_2Cl_2$): 0.11 (6 H, s, TBDMS-MeH), 0.71 (9 H, s, TBDMS-tBuH), 0.90-0.95 (12 H, m, EtHx$CH_3$), 1.30-1.56 (16 H, m, EtHx$CH_2$), 1.70-1.77 (2 H, m, EtHxCH), 3.86-3.91 (4 H, m, $CH_2O$), 6.92 (1 H, dd, *J* = 1.0, *J* = 8.5, SiOPhH), 6.95 and 7.50 (8 H, AA′BB′, G1-SPhH), 6.99 (1 H, dd, *J* = 1.0, *J* = 7.5, SiOPhH), 7.28-7.35 (2 H, m, SiOPhH, PhenH), 7.40 (1 H, dd, *J* = 2.0, *J* = 7.5, SiOPhH), 7.54 (1 H, ddd, *J* = 1.5, *J* = 7.0, *J* = 8.5, PhenH), 7.58 (1 H, brdd, *J* = 1.0, *J* = 8.5, PhenH), 7.61 (2 H, d, *J* = 1.5, G1-BPH), 7.67 (1 H, ddd, *J* = 1.5, *J* = 7.0, *J* = 8.5, PhenH), 7.74 (1 H, ddd, *J* = 1.0, *J* = 7.0, *J* = 8.0, PhenH), 7.84 (1 H, dd, *J* = 1.5, *J* = 1.5, G1-BPH), 8.75-8.79 (2 H, m, PhenH), 8.82 (1 H, brd, *J* = 8.5, PhenH). $^{13}$C NMR ($\delta$, 125 MHz, $CD_2Cl_2$): -4.4, 11.2, 14.2, 18.2, 23.4, 24.2, 25.5, 29.4, 30.9, 39.8, 71.0, 115.2, 120.2, 121.4, 121.6, 122.9, 123.5, 124.2, 124.4, 124.6, 125.2, 125.5, 125.6, 126.7, 127.5(1), 127.5(4), 128.0, 128.5, 129.3, 131.2, 132.2, 132.4, 137.6, 139.3, 142.7, 150.3, 155.3, 160.0. *m*/*z* [HRMS-ESI$^+$] $C_{61}H_{72}N_2O_3Si$: expected 909.5385 (100%), 910.5419 (66%), 911.5452 (21%), 912.5486 (4%) ([M+H]$^+$), found: 909.5393 (100%), 910.5419 (71%), 911.5443 (29%), 912.5462 (7%) ([M+H]$^+$).

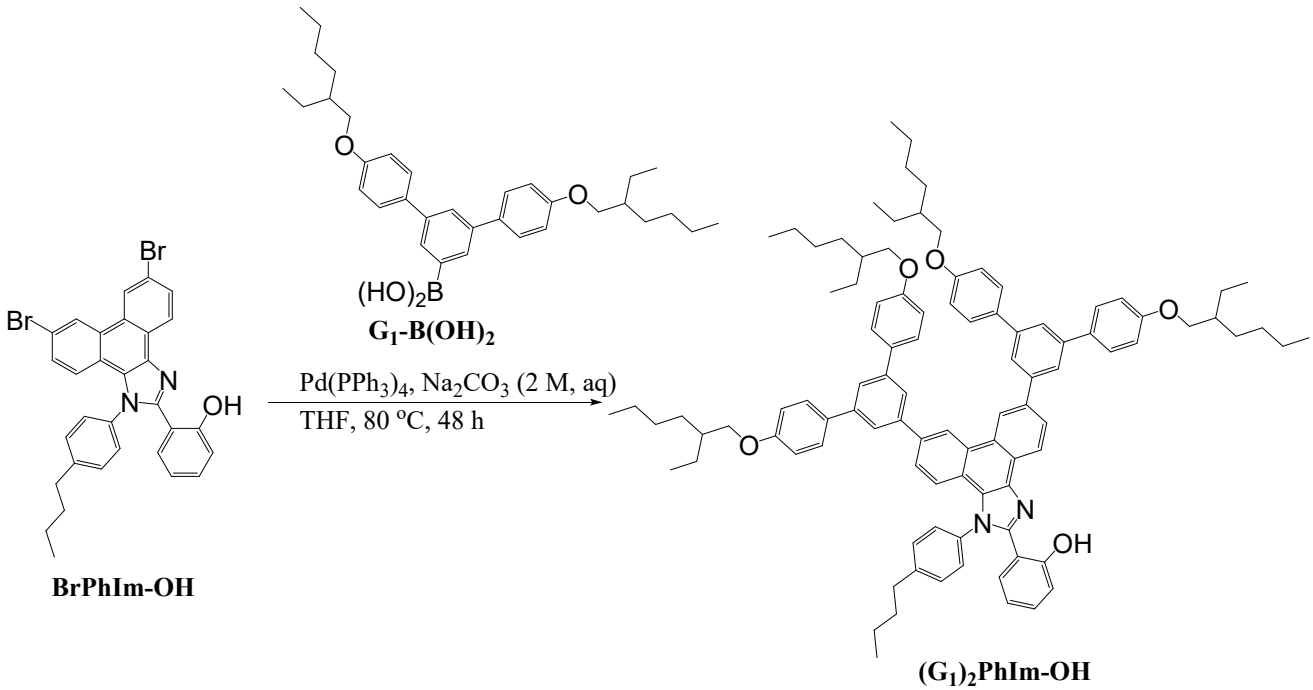
**2-[6,9-Dibromo-1-(4-*n*-butylphenyl)-1*H*-phenanthro[9,10-d]imidazol-2-yl]phenol (2BrPhIm-OH)**




**BrPhIm-OH**

A mixture of 3,6-dibromophenanthrene-9,10-dione[6] (1.10 g, 3.00 mmol), 4-*n*-butylaniline (0.71 mL, 4.5 mmol), salicylaldehyde (0.32 mL, 3.0 mmol), ammonium acetate (1.16 g, 15.0 mmol), and glacial acetic acid (10 mL) was stirred under argon in an oil bath held at 110 °C for 16 h. The mixture was allowed to cool to room temperature and then saturated aqueous potassium carbonate solution was added dropwise until the pH = 6. The mixture was then extracted using dichloromethane (3 × 50 mL). The organic portions were combined, washed with brine (50 mL), dried over anhydrous magnesium sulfate, and filtered. The filtrate was collected and the solvent removed. The residue was purified using column chromatography over silica with dichloromethane:hexane (1:10–1:1) mixtures as eluent to give **2BrPhIm-OH** as a yellow solid (0.57 g, 32%). mp 227-228 °C. $\lambda_{max}$(dichloromethane)/nm: 260 sh (log$\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$ 4.68), 267 (4.77), 276 sh (4.63), 295 (4.30), 304 (4.25), 326 sh (4.40), 339 (4.44), 359 sh (4.14), 378 (4.02). $\lambda_{max}$(fluorescence) (dichloromethane)/nm: 392, 408, 472. $^1$H NMR ($\delta$, 500 MHz, DMSO-d6): 0.94 (3 H, t, *J* = 7.5, BuCH$_3$), 1.34 (2 H, tquart, *J* = 7.5, *J* = 7.5, BuCH$_2$), 1.66 (2 H, tt, *J* = 7.5, *J* = 7.5, BuCH$_2$), 2.74 (2 H, t, *J* = 7.5, BuCH$_2$), 6.64 (1 H, ddd, *J* = 1.0, *J* = 7.5, *J* = 8.0, OPhH), 6.91 (1 H, d, *J* = 9.0, PhenH), 6.92 (1 H, dd, *J* = 1.0, *J* = 8.0, OPhH), 7.00 (1 H, dd, *J* = 1.5, *J* = 8.0, OPhH), 7.23 (1 H, ddd, *J* = 1.5, *J* = 7.5, *J* = 8.0, OPhH), 7.45 and 7.54 (4 H, AA′BB′, NPhH), 7.48 (1 H, dd, *J* = 2.0, *J* = 9.0, PhenH), 7.92 (1 H, dd, *J* = 2.0, *J* = 8.5, PhenH), 8.49 (1 H, d, *J* = 8.5, PhenH), 9.13 (1 H, d, *J* = 1.5, PhenH), 9.15 (1 H, d, *J* = 2.0, PhenH), 11.50 (1 H, brs, OH). $^{13}$C NMR ($\delta$, 125 MHz, DMSO-d6): 13.8, 21.5, 32.7, 34.4, 115.1, 116.5, 118.2, 119.2, 119.6, 121.3, 121.9, 123.9, 125.0, 126.6, 126.7, 127.4, 128.2(9), 128.3(2), 129.0, 129.2, 130.0(8), 130.1, 131.0(6), 131.1(2), 134.7, 135.1, 144.8, 149.8, 157.2. *m/z* [HRMS-ESI$^+$] $C_{31}H_{24}Br_2N_2O$: expected 599.0328 (51%), 601.0308 (100%), 603.0287 (49%) ([M+H]$^+$), found: 599.0318 (50%), 601.0297 (100%), 603.0286 (51%) ([M+H]$^+$).

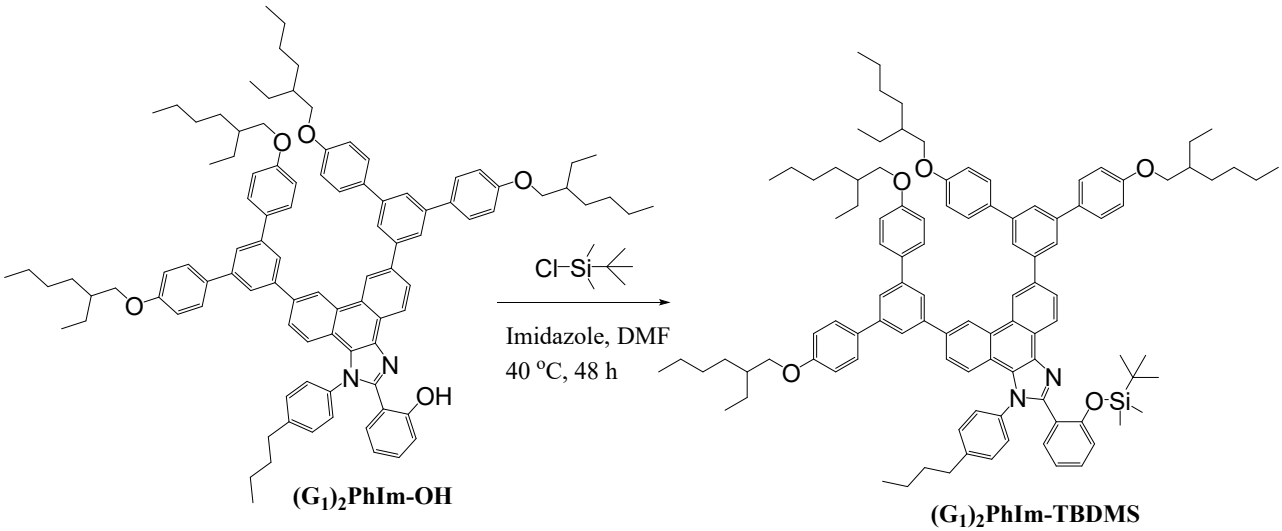
**2-[6,9-Bis(4,4''-bis{[2-ethylhexyl]oxy}-{1,1':3',1''-terphenyl}-5'-yl)-1-(4-*n*-butylphenyl)-1*H*-phenanthro[9,10-d]imidazol-2-yl]phenol [$(G_1)_2$PhIm-OH]**




A mixture of **BrPhIm-OH** (200 mg, 0.33 mmol), **$G_1$-B(OH)$_2$**[7] (530 mg, 1.00 mmol), aqueous sodium carbonate (2 M, 5 mL), and tetrahydrofuran (15 mL) was placed under vacuum and backfilled with argon for six times. Then tetrakis(triphenylphosphine)palladium(0) (38 mg, 0.03 mmol) was added and the resulting mixture was placed under vacuum and backfilled with argon a further six times. The mixture was stirred under argon in an oil bath held at 80 °C for 48 h. After being allowed to cool to room temperature, dichloromethane (50 mL) and water (50 mL) were added and the layers were separated. The aqueous phase was extracted with dichloromethane (2 × 50 mL), and the combined organic phases were washed with brine (2 × 50 mL), dried over anhydrous magnesium sulfate, and filtered. The filtrate was collected and the solvent removed. The residue was purified using column chromatography over silica using a dichloromethane:hexane (1:1) mixture as eluent to give **$(G_1)_2$PhIm-OH** as a white solid (332 mg, 71%). mp 102-103 °C. $\lambda_{max}$(dichloromethane)/nm: 279 (log$\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$ 5.15), 334 sh (4.64), 344 (4.66), 359 sh (4.54), 378 (4.40). $\lambda_{max}$(fluorescence) (dichloromethane)/nm: 388, 408, 471. $^1$H NMR ($\delta$, 500 MHz, $CD_2Cl_2$): 0.89-0.97 (24 H, m, EtHxC$H_3$), 1.05 (3 H, t, $J$ = 7.5, BuC$H_3$), 1.31-1.56 (34 H, m, EtHxC$H_2$, BuC$H_2$), 1.71-1.79 (4 H, m, EtHxCH), 1.79-1.82 (2 H, m, BuC$H_2$), 2.91 (2 H, t, $J$ = 7.5, BuC$H_2$), 3.85-3.93 (8 H, m, C$H_2$O), 6.54 (1 H, ddd, $J$ = 1.5, $J$ = 7.0, $J$ = 8.5, OPhH), 6.87 (1 H, dd, $J$ = 1.5, $J$ = 8.0, OPhH), 6.97 (4 H, 1/2AA′BB′, G1-SPhH), 7.00 and 7.70 (8H, AA′BB′, G1-SPhH), 7.11 (1 H, dd, $J$ = 1.5, $J$ = 8.0, OPhH), 7.24 (1 H, ddd, $J$ = 1.5, $J$ = 7.0, $J$ = 8.5, OPhH), 7.26 (1 H, d, $J$ = 8.5, PhenH), 7.60 (4 H, brs, NPhH), 7.63-7.67 (5 H, PhenH, G1-SPhH), 7.76 (1 H, t, $J$ = 1.5, G1-BPH), 7.80 (1 H, dd, $J$ = 1.5, $J$ = 1.5, G1-BP-H), 7.83 (2 H, dd, $J$ = 1.5, $J$ = 1.5, G1-BPH), 7.95 (2 H, d, $J$ = 1.5, G1-BPH), 8.15 (1 H, brd, $J$ = 8.0, PhenH), 8.83 (1 H, d, $J$ = 8.5, PhenH), 9.14 (1 H, brs, PhenH), 9.20 (1 H, brd, $J$ = 2.0, PhenH), 13.75 (1 H, brs, OH). $^{13}$C NMR ($\delta$, 125 MHz, $CD_2Cl_2$): 11.3, 14.1(8), 14.2(5), 22.6, 23.5, 24.2, 29.5, 30.9, 33.9, 35.8, 39.8, 71.0, 113.6, 115.2(0), 115.2(2), 118.2, 118.3, 122.0, 122.4(8), 122.5(1), 123.1, 123.4, 124.5, 124.6, 124.8, 125.6, 126.5, 126.7, 127.6, 127.8, 128.5, 128.6, 129.1, 129.2, 130.2, 131.1, 131.3, 133.4, 133.6, 134.7, 136.7, 138.6, 139.5, 142.3(4), 142.3(9), 142.4(1), 142.9, 146.6, 149.3, 159.6(7), 159.7(1). *m*/*z*

[HRMS-ESI$^+$] $C_{99}H_{114}N_2O_5$: expected 1411.8801(93%), 1412.8834(100%), 1413.8868(53%) ([M+H]$^+$), found: 1411.8784(75%), 1412.8825(100%), 1413.8850(50%) ([M+H]$^+$).

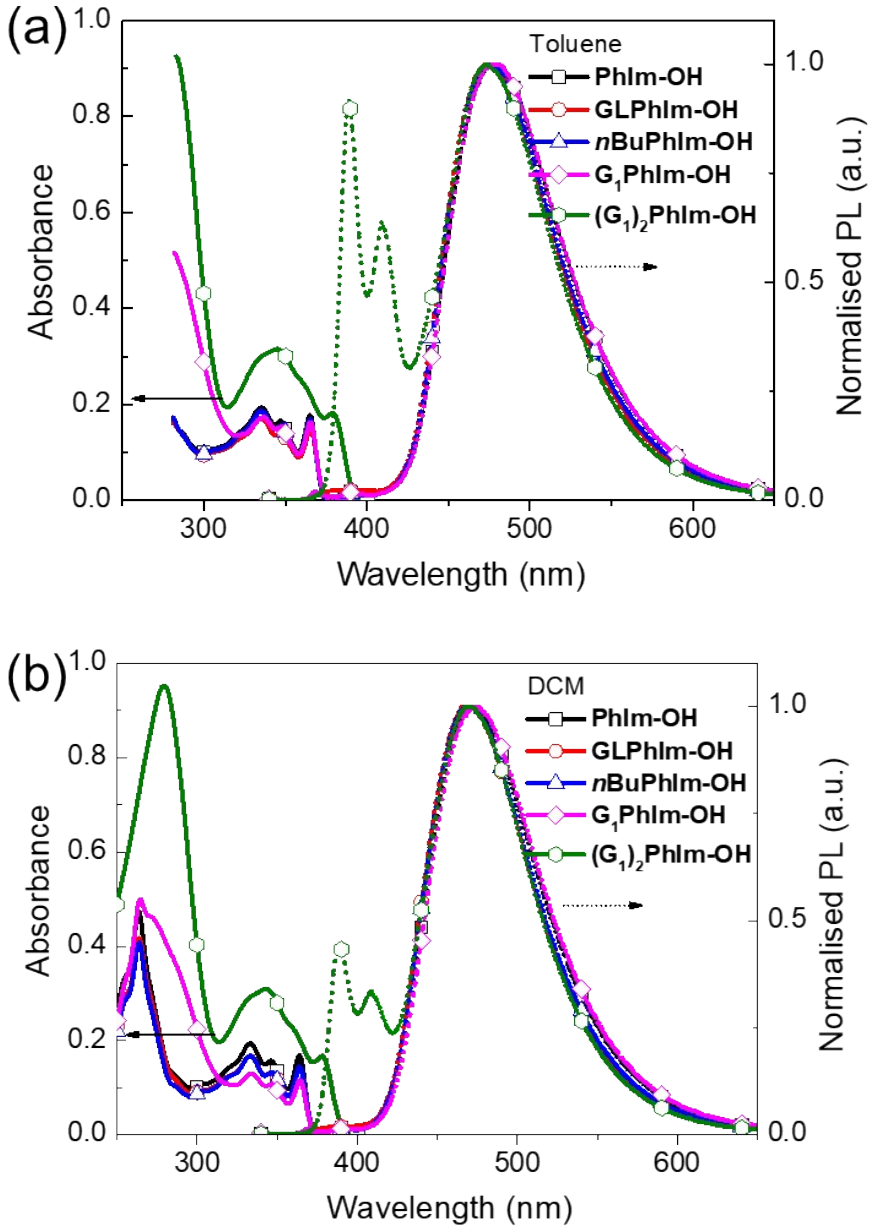
**6,9-Bis[4,4''-bis({2-ethylhexyl}oxy)-(1,1':3',1''-terphenyl)-5'-yl]-2-[2-({*tert*-butyldimethylsilyl}oxy)phenyl]-1-[4-*n*-butylphenyl]-1*H*-phenanthro[9,10-d]imidazole [$(G_1)_2$PhIm-TBDMS]**




$(G_1)_2$PhIm-OH $(G_1)_2$PhIm-TBDMS

A mixture of **$(G_1)_2$PhIm-OH** (200 mg, 0.14 mmol), *tert*-butyldimethylsilyl chloride (201 mg, 1.30 mmol), imidazole (198 mg, 2.90 mmol), and anhydrous *N*,*N*-dimethylformamide (15 mL) was stirred under argon in an oil bath held at 40 °C for 48 h. Then water (50 mL) and ethylacetate (100 mL) were added and the mixture was separated. Then the organic layer was washed with water (5 × 50 mL), dried over anhydrous magnesium sulfate, and filtered. The filtrate was collected and the solvent removed. The residue was purified using column chromatography over silica with dichloromethane:hexane (1:1–1:0) mixtures as eluent and then precipitation from dichloromethane and methanol to give **$(G_1)_2$PhIm-TBDMS** as a white solid (177 mg, 82%). mp 101-102 °C. $\lambda_{max}$(dichloromethane)/nm: 279 (log$\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$ 5.21), 324 sh (4.47), 370 sh (3.70). $\lambda_{max}$(fluorescence) (dichloromethane)/nm: 384, 401, 428 sh. $^1$H NMR ($\delta$, 500 MHz, $CD_2Cl_2$): 0.14 (6 H, s, TBDMS-MeH), 0.75 (9 H, s, TBDMS-tBuH), 0.89-0.98 (27 H, m, EtHx$CH_3$, Bu$CH_3$), 1.30-1.58 (34 H, m, EtHx$CH_2$, Bu$CH_2$), 1.65-1.70 (2 H, m, Bu$CH_2$), 1.71-1.78 (4 H, m, EtHxCH), 2.72 (2 H, t, $J$ = 7.5, Bu$CH_2$), 3.85-3.93 (8 H, m, $CH_2O$), 6.86 (1 H, dd, $J$ = 1.0, $J$ = 8.5, SiOPhH), 6.94-7.02 (9 H, m, SiOPhH, G1-SPhH), 7.27-7.32 (3 H, m, SiOPhH, NPhH), 7.36 (1 H, d, $J$ = 8.5, PhenH), 7.37 (1 H, dd, $J$ = 2.0, $J$ = 7.5, SiOPhH), 7.40 (2 H, 1/2AA′BB′, NPhH), 7.63-7.67 (5 H, m, PhenH, G1-SPhH), 7.71 (4 H, 1/2AA′BB′, G1-SPhH), 7.76 (1 H, dd, $J$ = 1.5, $J$ = 1.5, G1-BPH), 7.79 (1 H, dd, $J$ = 1.5, $J$ = 1.5, G1-BPH), 7.83 (2 H, d, $J$ = 1.5, G1-BPH), 7.96 (2 H, d, $J$ = 1.5, G1-BPH), 8.10 (1 H, dd, $J$ = 1.5, $J$ = 8.5, PhenH), 8.88 (1 H, d, $J$ = 8.5, PhenH), 9.15 (1 H, d, $J$ = 1.5, PhenH), 9.19 (1 H, d, $J$ = 1.5, PhenH). $^{13}$C NMR ($\delta$, 125 MHz, $CD_2Cl_2$): -4.3, 11.3, 14.1, 14.3, 18.3, 22.7, 23.5, 24.2, 25.6, 29.5, 30.9, 33.7, 35.7, 39.8, 71.0, 115.2, 120.1, 121.1, 122.0, 122.3, 122.9(7), 123.0(2), 123.5, 123.9, 124.4, 124.5, 124.6, 124.8, 126.2, 127.4, 127.5, 128.0, 128.5(6), 128.6(2), 128.8, 129.7, 131.1, 132.5, 133.5, 133.6, 135.9, 137.6, 138.1, 138.7, 142.4, 142.7, 143.2, 144.8, 150.6, 155.2, 159.7. *m*/*z* [HRMS-ESI$^+$] $C_{105}H_{128}N_2O_5Si$: expected 1525.9665

(88%), 1526.9699 (100%), 1527.9732 (56%) ([M+H]$^+$), found: 1525.9689 (40%), 1526.9751 (100%), 1527.9733 (55%) ([M+H]$^+$).



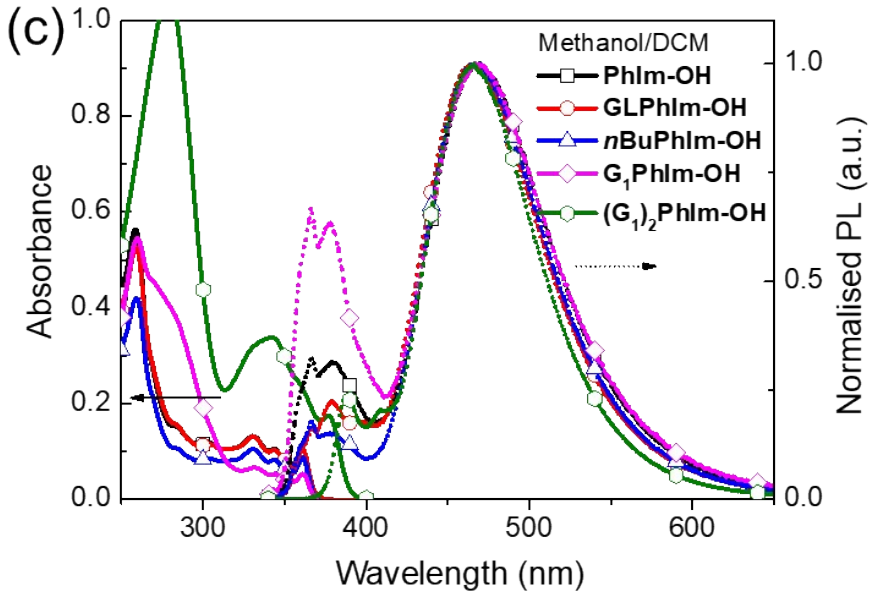
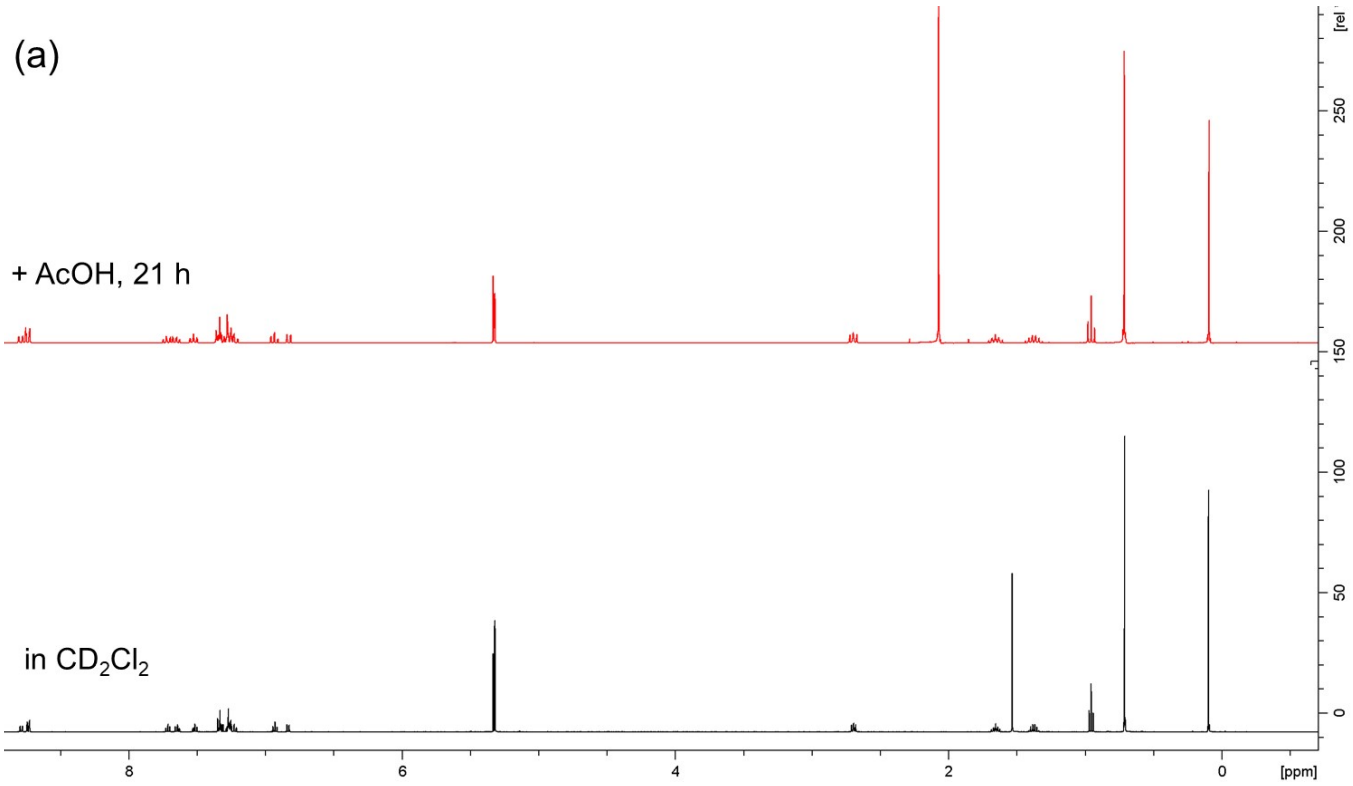



**Figure S1**. UV-vis absorption and PL spectra of **PhIm-OH**, **GLPhIm-OH**, ***n*BuPhIm-OH**, **$G_1$PhIm-OH**, and **$(G_1)_2$PhIm-OH** in toluene (a), dichloromethane (b) and mixed methanol:dichloromethane (1:1 for **$(G_1)_2$PhIm-OH** and 9:1 for other compounds) at a concentration of $1 \times 10^{-5}$ M.



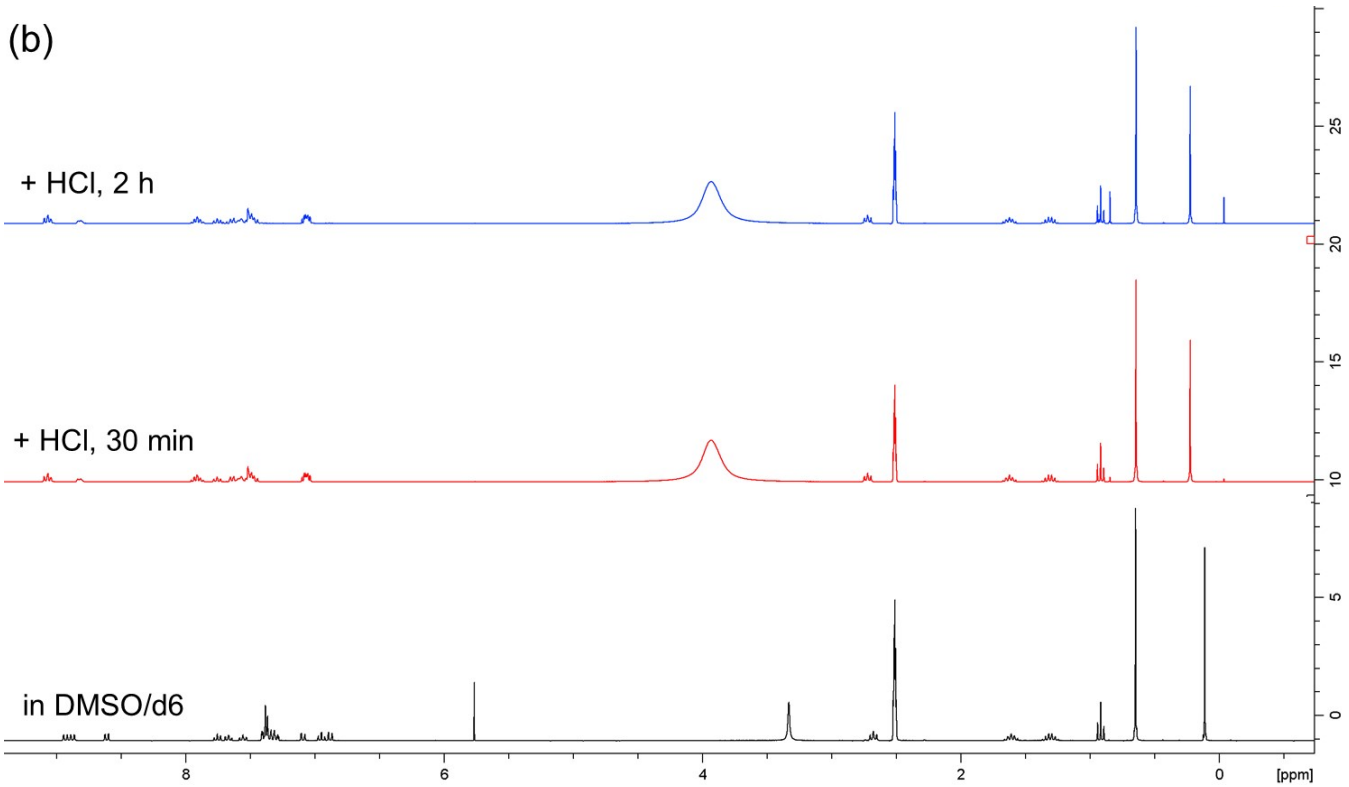
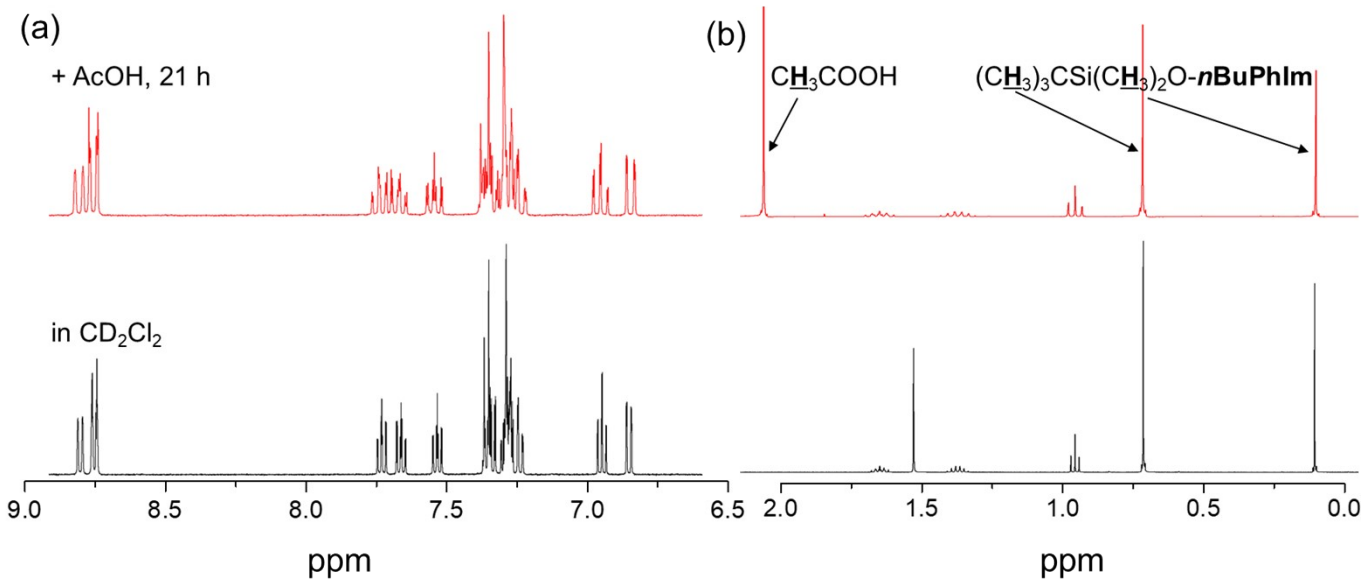



**Figure S2.** [1]NMR spectra of ***n*BuPhIm-TBDMS** before and after adding (a) acetic acid (6 eq.) and (b) HCl (5 eq.).



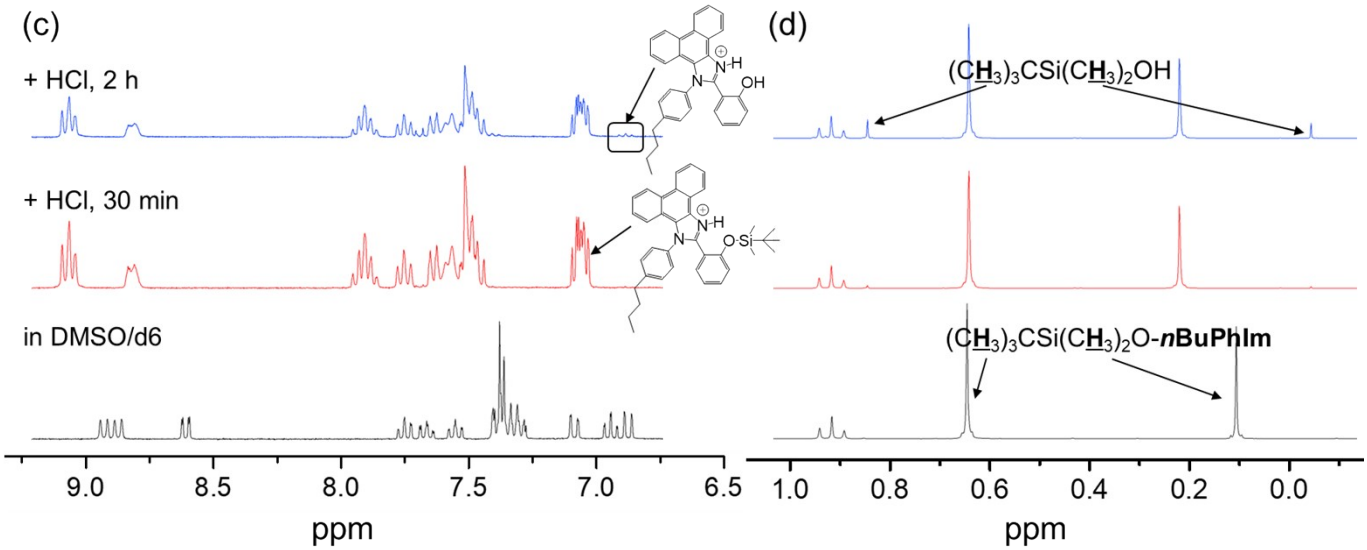



**Figure S3.** [1]NMR spectra of ***n*BuPhIm-TBDMS** before and after adding (a, b) acetic acid (6 eq.) and (c, d) hydrochloric acid (5 eq.). The spectra are zoomed-in in specific regions for clarity with the full spectra shown in Figure S2.

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