Electric Supplementary Information

Controllable Intramolecular Interaction of 3D Arranged π-Conjugated Luminophores Based on a POSS Scaffold, Leading to Highly Thermally-Stable and Emissive Materials

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General

^{1}H, ^{13}C and ^{29}Si NMR spectra were recorded on JEOL EX400 and AL400 instruments at 400, 100 and 80 MHz, respectively. Samples were analyzed in $CDCl_3$, and the chemical shift values were expressed relative to Me_4Si as an internal standard. Analytical thin layer chromatography (TLC) was performed with silica gel 60 Merck F254 plates. Column chromatography was performed with Wakogel C-300 silica gel. Automated flash chromatography was carried out on a YAMAZEN CORPORATION, YFLC Al-580 (Hi-Flash^{TM} Column 2L). High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-MS700 spectrometer for electron ionization (EI), a Thermo Fisher Scientific EXACTIVE spectrometer for atmospheric pressure chemical ionization (APCI) and Thermo Fisher Scientific OrbitrapXL spectrometers for matrix assisted laser desorption/ionization (MALDI) using 1,8-dihydroxy-9,10-dihydroanthracen-9-one (DIT) as a matrix. Recyclable preparative high-performance liquid chromatography (HPLC) was carried out on a Japan Analytical Industry Co. Ltd., Model LC918R (JAIGEL-1H and 2H columns) and LC9204 (JAIGEL-2.5H and 3H columns) using $CHCl_3$ as an eluent. UV−vis absorption spectra were recorded on a SHIMADZU UV-3600 spectrophotometer, and samples were analyzed in $CHCl_3$ at room temperature. Fluorescence emission spectra were recorded on a HORIBA JOBIN YVON Fluoromax-4 spectrofluorometer, and samples were analyzed at room temperature. The PL lifetime measurement was recorded on a Horiba FluoroCube spectrofluorometer system; excitation was carried out using a UV diode laser (NanoLED 292 nm). Thermogravimetric analysis (TGA) was recorded on a Seiko instrument inc. EXSTAR TG/DTA6000. Differential scanning calorimetry (DSC) was recorded on a Seiko instrument inc. EXSTAR DSC6220. Elemental analyses were performed at the Microanalytical Center of Kyoto University.

Materials

Compounds **1**[1], **2**[2], **5**[3], **8**[4] were synthesized according to the literatures. Trimethylsilylacetylene, ethynylbenzene, 1-bromo-4-(trimethylsilyl)benzene, bis(triphenylphosphine)palladium(II) dichloride ($PdCl_2(PPh_3)_2$), tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$), 1,1'-bis(diphenylphosphino)ferrocene (dppf) and NBu_4F were purchased from Tokyo Chemical Industry Co., Ltd. and used without further purification. PPh_3, CuI, Sodium nitrite, KI, CH_3CN, MeOH, concentrated H_2SO_4 and K_2CO_3 were purchased from Wako Pure Chemical Industries and used without further purification. THF and Et_3N were purchased from Wako Pure Chemical Industries and Kanto Chemical Co., Inc. and were purified using a two-column solid-state purification system (Glasscontour System, Joerg Meyer, Irvine, CA) under Ar pressure.

Synthetic Procedures and Characterization

Synthesis of octa(4-((4-(phenylethynyl)phenyl)ethynyl)phenyl)POSS

- 3, Ph3POSS -

A mixture of **1** (496 mg, 2.45 mmol), **2** (500 mg, 0.245 mmol), $Pd_2(dba)_3$ (26.9 mg, 0.0294 mmol), dppf (32.6 mg, 0.0588 mmol), CuI (11.2 mg, 0.0588 mmol), THF (40 mL) and Et_3N (40 mL) was placed in a round-bottom flask equipped with a magnetic stirring bar. After degassing the reaction mixture several times, the reaction was carried out at 70 °C for 24 h with stirring. After the reaction mixture was cooled to room temperature, precipitates were removed by filtration, and the solvent was removed with a rotary evaporator. The crude was dissolved again in THF, then precipitated into cold MeOH. The residue was purified by automated flash chromatography on SiO_2 ($CHCl_3$/hexane = 1/4 v/v, then $CHCl_3$ as an eluent) to afford **3** (127 mg, 0.0481 mmol, 20%) as a yellow solid.

$R_f = 1.00$ ($CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.78 (d, $J = 7.6$ Hz, 16H), 7.58 (d, $J = 8.0$ Hz, 16H), 7.55−7.48 (m, 48H), 7.35−7.31 (m, 24H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 134.2, 134.1, 131.7, 131.6, 131.6, 131.1, 129.7, 128.4, 126.0, 123.5, 123.1, 122.8, 91.5, 90.9, 90.9, 89.1 ppm; ^{29}Si NMR ($CDCl_3$, 80 MHz) δ −78.2 ppm. HRMS (APCI) calcd. for $C_{176}H_{105}O_{12}Si_8$ $[M+H]^+$: 2633.5755, found 2633.5822. Elemental analysis calcd. for $C_{176}H_{104}O_{12}Si_8$: C 80.21 H 3.98 found: C 79.40 H 3.98.

Synthesis of trimethyl(4-((4-(phenylethynyl)phenyl)ethynyl)phenyl)silane

- 4, Ph3TMS -

A mixture of **2** (122 mg, 0.600 mmol), 1-bromo-4-(trimethylsilyl)benzene (138 mg, 0.111 mL, 0.600 mmol), $Pd_2(dba)_3$ (11.0 mg, 0.0120 mmol), dppf (13.3 mg, 0.0240 mmol), CuI (4.57 mg, 0.0240 mmol), THF (15 mL) and Et_3N (15 mL) was placed in a round-bottom flask equipped with a magnetic stirring bar. After degassing the reaction mixture several times, the reaction was carried out at 70 °C for 20 h with stirring. After the reaction mixture was cooled to room temperature, precipitates were removed by filtration, and the solvent was removed with a rotary evaporator. The residue was purified by column chromatography on SiO_2 (hexane as an eluent). Further purification was carried out by recrystallization with $CHCl_3$ and MeOH (good and poor solvent, respectively) to afford **4** (49.7 mg, 0.142 mmol, 24%) as a white solid.

R_f = 0.17 ($CHCl_3$/hexane = 1/1 v/v). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.56–7.47 (m, 10H), 7.38–7.32 (m, 3H), 0.28 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 141.4, 133.3, 131.7, 131.6, 131.5, 130.7, 128.4, 128.4, 123.3, 123.2, 123.2, 101.2, 91.5, 91.3, 89.5, 89.2, −1.3 ppm. HRMS (EI) calcd. for $C_{25}H_{22}Si$ $[M]^+$: 350.1491, found 350.1487. Elemental analysis calcd. for $C_{25}H_{22}Si$: C 85.66 H 6.33 found: C 85.55 H 6.36.

Synthesis of octa(4-((4-((4-(*tert*-butyl)phenyl)ethynyl)phenyl)ethynyl)phenyl)POSS

- 6, *t*-BuPOSS -

A mixture of 1-(*tert*-butyl)-4-((4-ethynylphenyl)ethynyl)benzene, **5** (673 mg, 2.60 mmol), **2** (530 mg, 0.260 mmol), $Pd_2(dba)_3$ (28.6 mg, 0.0312 mmol), dppf (34.6 mg, 0.0624 mmol), CuI (11.9 mg, 0.0624 mmol), THF (40 mL) and Et_3N (40 mL) was placed in a round-bottom flask equipped with a magnetic stirring bar. After degassing the reaction mixture several times, the reaction was carried out at 70 °C for 15 h with stirring. After the reaction mixture was cooled to room temperature, precipitates were removed by filtration, and the solvent was removed with a rotary evaporator. The crude was dissolved again in THF, then precipitated into cold MeOH. The residue was purified by automated flash chromatography on SiO_2 ($CHCl_3$/hexane = 1/3 v/v as an eluent). Further purification was carried out by recrystallization with $CHCl_3$ and MeOH (good and poor solvent, respectively) to afford **6** (150 mg, 0.0486 mmol, 19%) as an orange solid.

R_f = 0.33 ($CHCl_3$/hexane = 1/3 v/v). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.78 (d, J = 7.0 Hz, 16H), 7.58 (d, J = 6.8 Hz, 16H), 7.52–7.49 (m, 32H), 7.47 (d, J = 6.4 Hz, 16H), 7.37 (d, J = 8.4 Hz, 16H), 1.32 (s, 72H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.8, 134.1, 131.6, 131.5, 131.4, 131.1, 129.7, 126.0, 125.4, 123.8, 122.6, 120.0, 91.7, 90.9, 90.8, 88.5, 34.8, 31.2 ppm; ^{29}Si NMR ($CDCl_3$, 80 MHz) δ −78.1 ppm. HRMS (MALDI) calcd. for $C_{208}H_{168}O_{12}Si_8$ $[M]^+$: 3081.0690, found: 3081.0724. Elemental analysis calcd. for $C_{208}H_{168}O_{12}Si_8$: C 81.00 H 5.49 found: C 79.99 H 5.36.

Synthesis of (4-((4-((4-(*tert*-butyl)phenyl)ethynyl)phenyl)ethynyl)phenyl)trimethylsilane

- 7, *t*-BuTMS -

A mixture of **5** (152 mg, 0.586 mmol), 1-bromo-4-(trimethylsilyl)benzene (148 mg, 0.121 mL, 0.645 mmol), $Pd_2(dba)_3$ (16.1 mg, 0.0176 mmol), dppf (19.5 mg, 0.0352 mmol), CuI (6.70 mg, 0.0352 mmol), THF (15 mL) and Et_3N (15 mL) was placed in a round-bottom flask equipped with a magnetic stirring bar. After degassing the reaction mixture several times, the reaction was carried out at 70 °C for 19 h with stirring. After the reaction mixture was cooled to room temperature, precipitates were removed by filtration, and the solvent was removed with a rotary evaporator. The residue was purified by column chromatography on SiO_2 ($CHCl_3$/hexane = 1/2 v/v as an eluent) to afford **7** (105 mg, 0.258 mmol, 44%) as a yellow solid.

R_f = 0.53 ($CHCl_3$/hexane = 1/2 v/v). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.51−7.44 (m, 10H), 7.40−7.34 (m, 2H), 1.33 (s, 9H), 0.28 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.8, 141.3, 133.2, 131.5, 131.5, 131.4, 130.7, 125.4, 123.4, 123.4, 123.0, 120.0, 91.5, 91.3, 89.6, 88.5, 34.8, 31.2, −1.2 ppm. HRMS (EI) calcd. for $C_{29}H_{30}Si$ $[M]^+$: 406.2117, found 406.2113.

Synthesis of 2,6-diisopropyl-4-(phenylethynyl)aniline - 9 -

A mixture of 4-iodo-2,6-diisopropylaniline, **8** (11.0 g, 36.3 mmol), ethynylbenzene (4.08 g, 4.39 mL, 39.9 mmol), $PdCl_2(PPh_3)_2$ (765 mg, 1.09 mmol), PPh_3 (571 mg, 2.18 mmol), CuI (208 mg, 1.09 mmol), THF (50 mL) and Et_3N (50 mL) was placed in a round-bottom flask equipped with a magnetic stirring bar. After degassing the reaction mixture several times, the reaction was carried out at 50 °C for 12 h with stirring. After the reaction mixture was cooled to room temperature, precipitates were removed by filtration, and the solvent was removed with a rotary evaporator. The residue was purified by column chromatography on SiO_2 ($CHCl_3$/hexane = 1/1 v/v as an eluent) to afford **9** (8.85 g, 31.9 mmol, 87%) as a dark red solid.

R_f = 0.24 ($CHCl_3$/hexane = 1/1 v/v). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.53−7.51 (m, 2H), 7.34−7.28 (m, 3H), 7.23 (s, 2H), 3.91 (s, 2H), 2.89 (sep, J = 6.8 Hz, 2H), 1.29 (d, J = 6.8 Hz, 12H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.9, 132.2, 131.4, 128.2, 127.5, 126.6, 124.1, 112.3, 91.2, 86.8, 27.9, 22.3 ppm. HRMS (APCI) calcd. for $C_{20}H_{24}N$ $[M+H]^+$: 278.1903, found 278.1898.

Synthesis of 2-iodo-1,3-diisopropyl-5-(phenylethynyl)benzene - 10 -

A mixture of **9** (6.75 g, 24.3 mmol), CH_3CN (300 mL), H_2O (200 mL) and concentrated H_2SO_4 (30 mL) was placed in an Erlenmeyer flask at 0 °C, equipped with a magnetic stirring bar. To the reaction mixture, $NaNO_2$ (2.18 g, 31.6 mmol) in H_2O (4 mL) was slowly added at 0 °C. After stirring for 20 min, the mixture was added into a solution of KI (25.1 g, 151 mmol) in CH_3CN (100 mL) and H_2O (100 mL) at 0 °C. The reaction mixture was stirred at room temperature for 36 h, then at 60 °C for 1 h. The mixture was quenched by the addition of aqueous $NaHSO_3$ solution, and the organic layer was extracted three times with $CHCl_3$. The combined organic layer was washed with brine and dried over $MgSO_4$. $MgSO_4$ was removed by filtration, and the solvent was evaporated. The residue was purified by column chromatography on SiO_2 ($CHCl_3$/hexane = 1/1 v/v as an eluent) to afford **10** (8.12 g, 0.0209 mmol, 66%) as an orange liquid.

R_f = 0.78 ($CHCl_3$/hexane = 1/1 v/v). ^1H NMR ($CDCl_3$, 400 MHz) δ 7.56−7.54 (m, 2H), 7.37−7.34 (m, 3H), 7.23 (s, 2H), 3.40 (sep, J = 6.8 Hz, 2H), 1.25 (d, J = 6.8 Hz, 12H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.3, 131.6, 128.3, 128.3, 126.8, 123.3, 123.1, 109.3, 89.7, 89.1, 39.3, 23.2 ppm. HRMS (APCI) calcd. for $C_{20}H_{22}I$ $[M+H]^+$: 389.0761, found 389.0751.

Synthesis of ((2,6-diisopropyl-4-(phenylethynyl)phenyl)ethynyl)trimethylsilane - 11 -

A mixture of **10** (3.81 g, 9.81 mmol), trimethylsilylacetylene (1.45 g, 2.04 mL, 14.7 mmol), $PdCl_2(PPh_3)_2$ (207 mg, 0.294 mmol), PPh_3 (154 mg, 0.588 mmol), CuI (56.0 mg, 0.294 mmol), THF (20 mL) and Et_3N (20 mL) was placed in a round-bottom flask equipped with a magnetic stirring bar. After degassing the reaction mixture several times, the reaction was carried out at 70 °C for 2 days with stirring. After the reaction mixture was cooled to room temperature, precipitates were removed by filtration, and the solvent was removed with a rotary evaporator. The residue was purified by column chromatography on SiO_2 (Hexane as an eluent) to afford **11** (2.11 g, 5.86 mmol, 60%) as a yellow solid.

R_f = 0.40 (hexane). ^1H NMR ($CDCl_3$, 400 MHz) δ 7.59−7.57 (m, 2H), 7.37−7.35 (m, 3H), 7.31 (s, 2H), 3.54 (sep, J = 6.8 Hz, 2H), 1.30 (d, J = 6.8 Hz, 12H), 0.30 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ

151.3, 131.6, 128.3, 128.3, 125.5, 123.3, 123.0, 121.3, 104.5, 101.9, 90.1, 90.1, 31.7, 22.9, −0.1 ppm. HRMS (APCI) calcd. for $C_{25}H_{31}Si$ $[M+H]^+$: 359.2190, found 359.2180. Elemental analysis calcd. for $C_{25}H_{30}Si$: C 83.74 H 8.43 found: C 83.54 H 8.48.

Synthesis of 2-ethynyl-1,3-diisopropyl-5-(phenylethynyl)benzene - 12 -

11 (200 mg, 0.588 mmol) in THF (15 mL) was placed in a round-bottom flask equipped with a magnetic stirring bar. After degassing several times, NBu_4F (1 M in THF, 0.667 mL, 0.667 mmol) was added to the solution at room temperature for 15 min with stirring. The mixture was quenched by the addition of H_2O, and the organic layer was extracted three times with $CHCl_3$. The combined organic layer was washed with brine and dried over $MgSO_4$. $MgSO_4$ was removed by filtration, and the solvent was removed with a rotary evaporator. The residue was purified by column chromatography on SiO_2 (hexane as an eluent) to afford **12** (146 mg, 0.510 mmol, 90%) as a transparent liquid.

$R_f = 0.55$ (hexane). ^1H NMR ($CDCl_3$, 400 MHz) δ 7.56−7.54 (m, 2H), 7.32−7.30 (m, 5H), 3.55 (sep, J = 6.8 Hz, 2H), 3.51 (s, 1H), 1.26 (d, J = 6.8 Hz, 12H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.6, 131.6, 128.3, 128.3, 125.5, 123.4, 123.2, 120.0, 90.3, 89.9, 86.5, 80.2, 31.5, 23.1 ppm. HRMS (APCI) calcd. for $C_{22}H_{23}$ $[M+H]^+$: 287.1794, found 287.1790. Elemental analytical data were not obtained because **12** is unstable.

Synthesis of octa(4-((2,6-diisopropyl-4-(phenylethynyl)phenyl)ethynyl)phenyl)POSS
- 13, *i*-PrPOSS -

A mixture of **12** (626 mg, 2.18 mmol), **2** (445 mg, 0.218 mmol), $Pd_2(dba)_3$ (24.0 mg, 0.0262 mmol), dppf (29.1 mg, 0.0524 mmol), CuI (10.0 mg, 0.0524 mmol), THF (40 mL) and Et_3N (40 mL) was placed in a round-bottom flask equipped with a magnetic stirring bar. After degassing the reaction mixture several times, the reaction was carried out at 70 °C for 20 h with stirring. After the reaction mixture was cooled to room temperature, precipitates were removed by filtration, and the solvent was removed with a rotary evaporator. The crude was dissolved again in THF, then precipitated into cold MeOH. The residue was purified by automated flash chromatography on SiO_2 ($CHCl_3$/hexane = 1/3 v/v as an eluent). Further purification was carried out by recrystallization with $CHCl_3$ and MeOH (good and poor solvent, respectively) to afford **13** (162 mg, 0.0490 mmol, 22%) as a white solid.

R_f = 0.33 ($CHCl_3$/hexane = 1/3 v/v). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.84–7.82 (m, 16H), 7.62–7.56 (m, 32H), 7.36–7.31 (m, 40H), 3.61 (sep, J = 6.8 Hz, 16H), 1.34 (d, J = 6.8 Hz, 96H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.0, 134.1, 131.6, 130.8, 129.5, 128.3, 128.3, 126.5, 125.7, 123.3, 123.2, 120.8, 98.4, 90.3, 90.1, 88.2, 31.9, 23.1 ppm; ^{29}Si NMR ($CDCl_3$, 80 MHz) δ −78.2 ppm. HRMS (MALDI) calcd. for $C_{224}H_{200}O_{12}Si_8$ $[M]^+$: 3305.3194, found: 3305.3179. Elemental analysis calcd. for $C_{224}H_{200}O_{12}Si_8$: C 81.31 H 6.09 found: C 80.60 H 6.09.

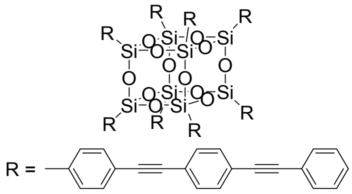
Synthesis of (4-((2,6-diisopropyl-4-(phenylethynyl)phenyl)ethynyl)phenyl)trimethylsilane

- 14, *i*-PrTMS -

A mixture of **12** (146 mg, 0.510 mmol), 1-bromo-4-(trimethylsilyl)benzene (129 mg, 0.105 mL, 0.561 mmol), $Pd_2(dba)_3$ (14.0 mg, 0.0153 mmol), dppf (17.0 mg, 0.0306 mmol), CuI (5.8 mg, 0.0306 mmol), THF (15 mL) and Et_3N (15 mL) was placed in a round-bottom flask equipped with a magnetic stirring bar. After degassing the reaction mixture several times, the reaction was carried out at 70 °C for 12 h with stirring. After the reaction mixture was cooled to room temperature, precipitates were removed by filtration, and the solvent was removed with a rotary evaporator. The residue was purified by column chromatography on SiO_2 ($CHCl_3$/hexane = 1/2 v/v as an eluent) to afford **14** (34.0 mg, 0.0782 mmol, 15%) as a white solid.

R_f = 0.57 ($CHCl_3$/hexane = 1/2 v/v). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.67–7.62 (m, 6H), 7.45–7.41 (m, 6H), 3.71 (sep, J = 6.8 Hz, 2H), 1.43 (d, J = 6.8 Hz, 12H), 0.38 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.8, 141.1, 133.3, 131.6, 130.4, 128.3, 128.2, 125.6, 124.0, 123.3, 123.0, 121.2, 99.1, 90.2, 90.2, 86.9, 31.8, 23.1, 0.4 ppm. HRMS (APCI) calcd. for $C_{31}H_{35}Si$ $[M+H]^+$: 435.2503, found 435.2497. Elemental analysis calcd. for $C_{31}H_{34}Si$: C 85.66 H 7.88 found: C 85.48 H 7.90.

NMR spectra



3, **Ph3POSS**

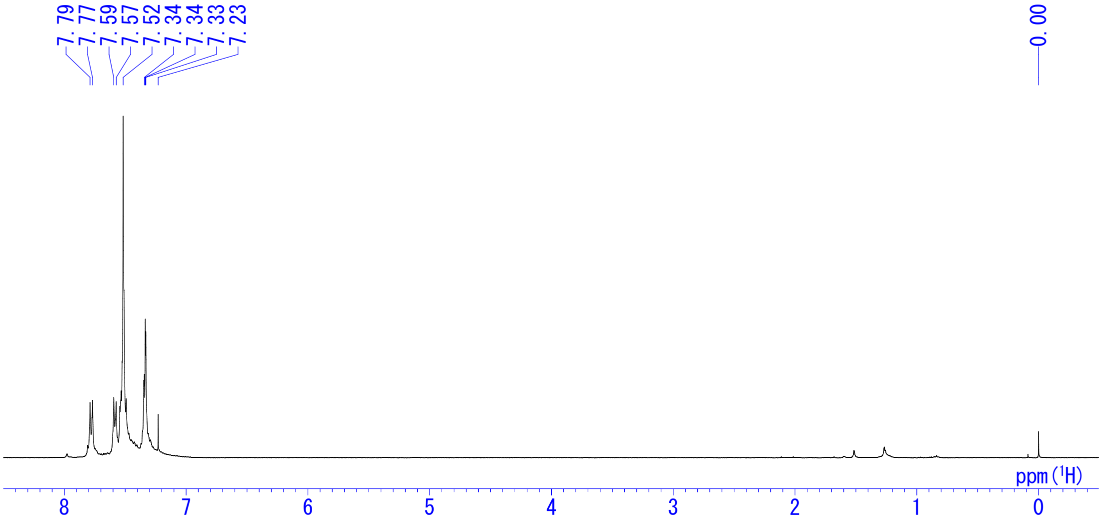


Figure S1. ^{1}H NMR spectrum of **3** in $CDCl_3$.

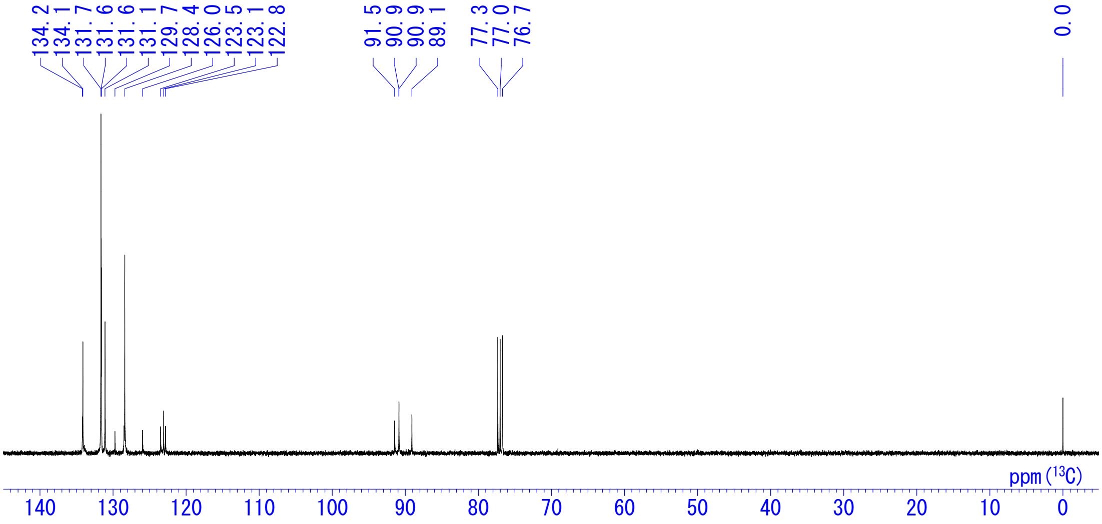


Figure S2. ^{13}C NMR spectrum of **3** in $CDCl_3$.

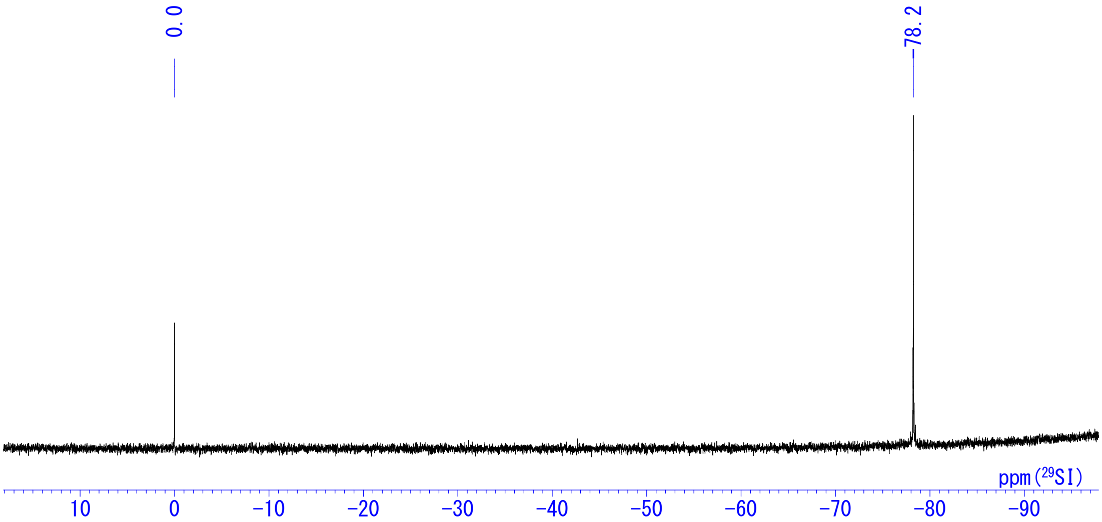
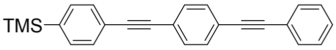


Figure S3. ^{29}Si NMR spectrum of **3** in CDCl$_3$.



4, **Ph3TMS**

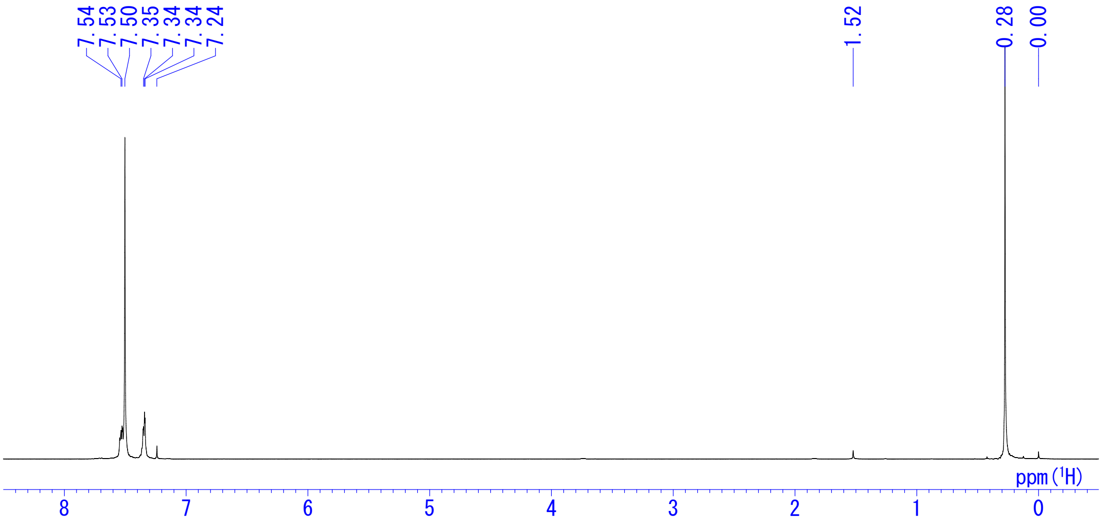


Figure S4. ^{1}H NMR spectrum of **4** in $CDCl_3$.

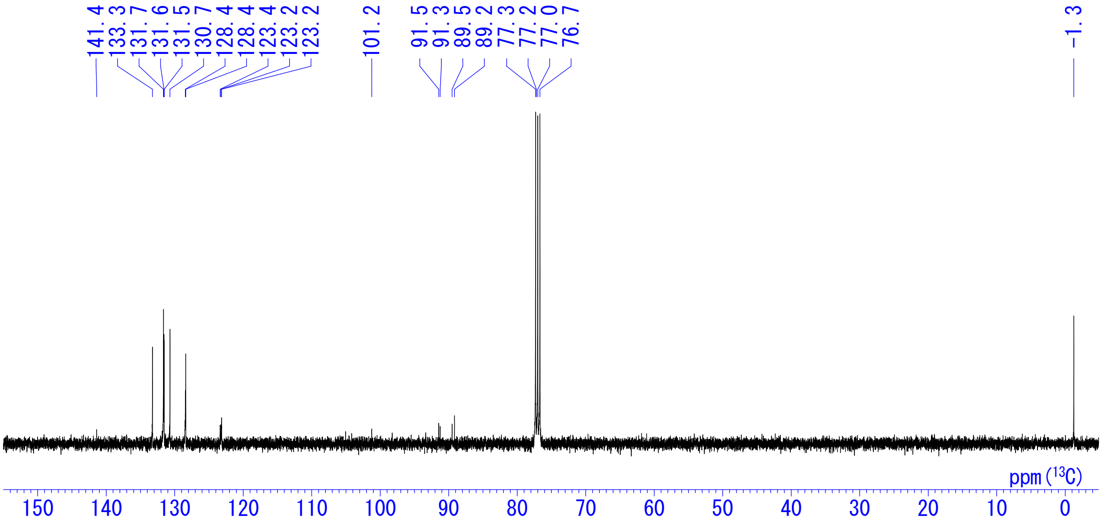
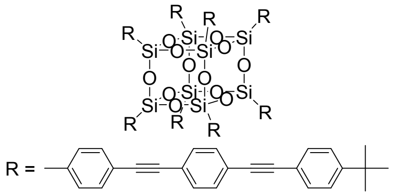


Figure S5. ^{13}C NMR spectrum of **4** in $CDCl_3$.



6, ***t*-BuPOSS**

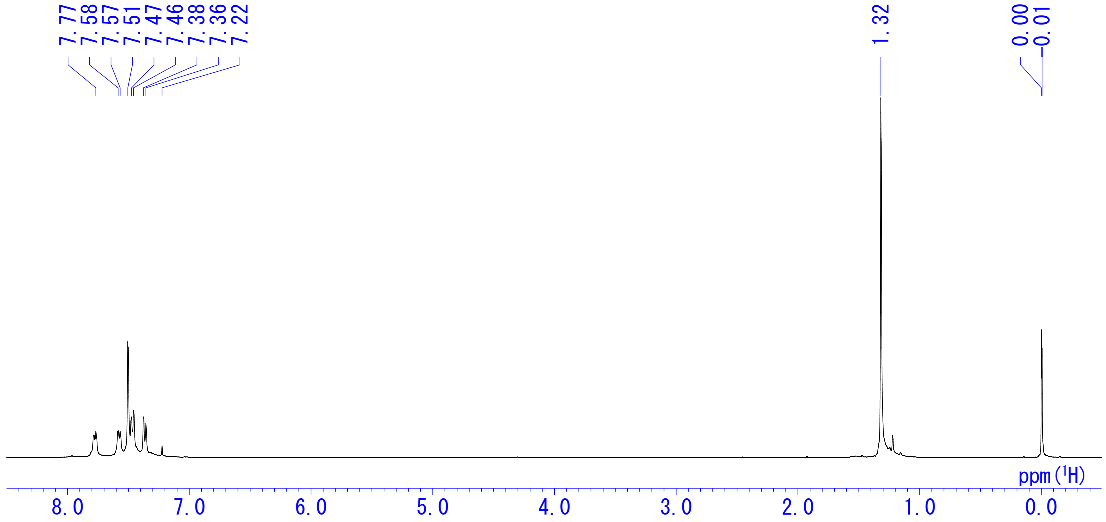


Figure S6. ^{1}H NMR spectrum of **6** in CDCl$_3$.

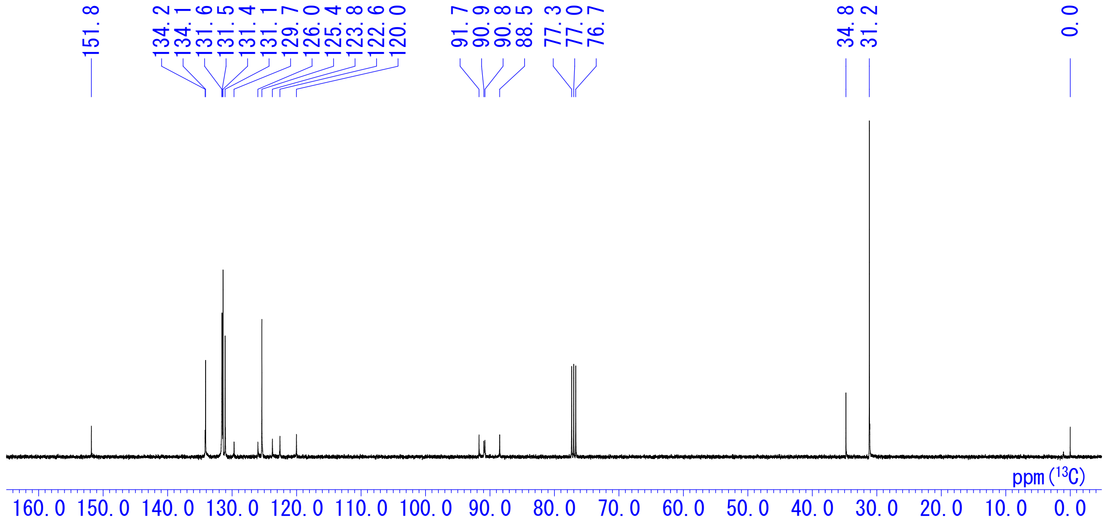


Figure S7. ^{13}C NMR spectrum of **6** in CDCl$_3$.

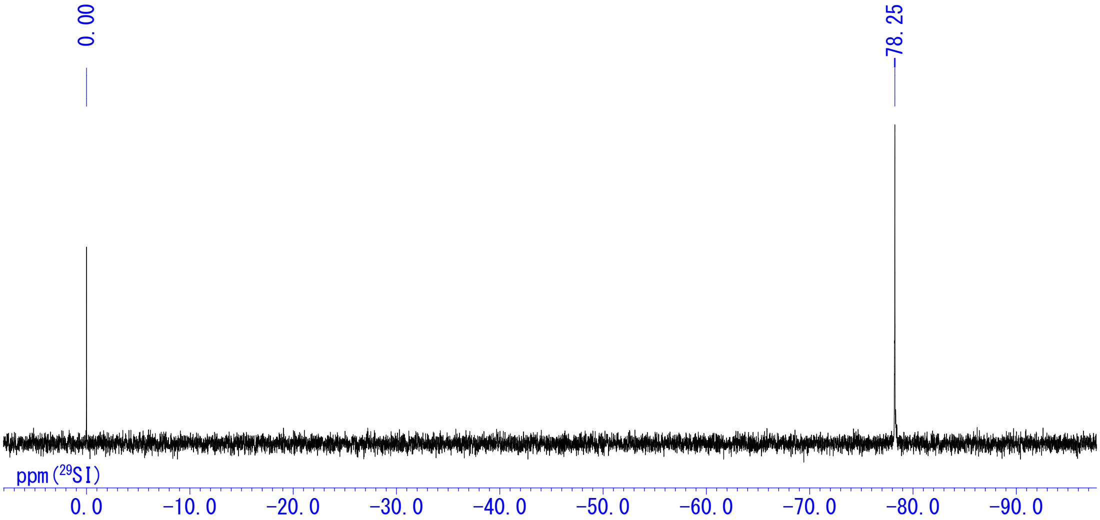
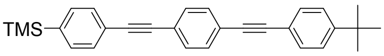


Figure S8. ^{29}Si NMR spectrum of **6** in $CDCl_3$.



7, ***t*-BuTMS**

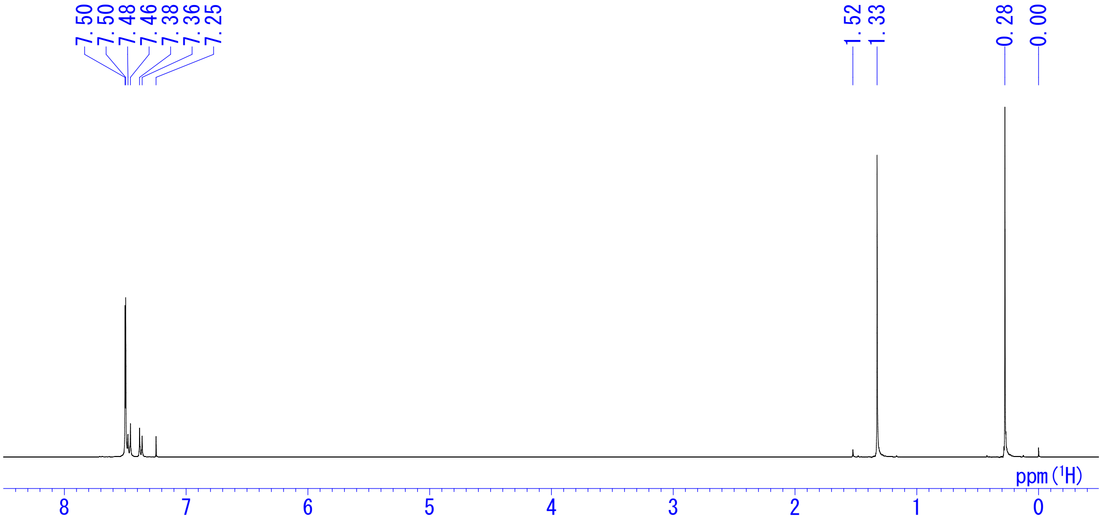


Figure S9. ^{1}H NMR spectrum of **7** in $CDCl_3$.

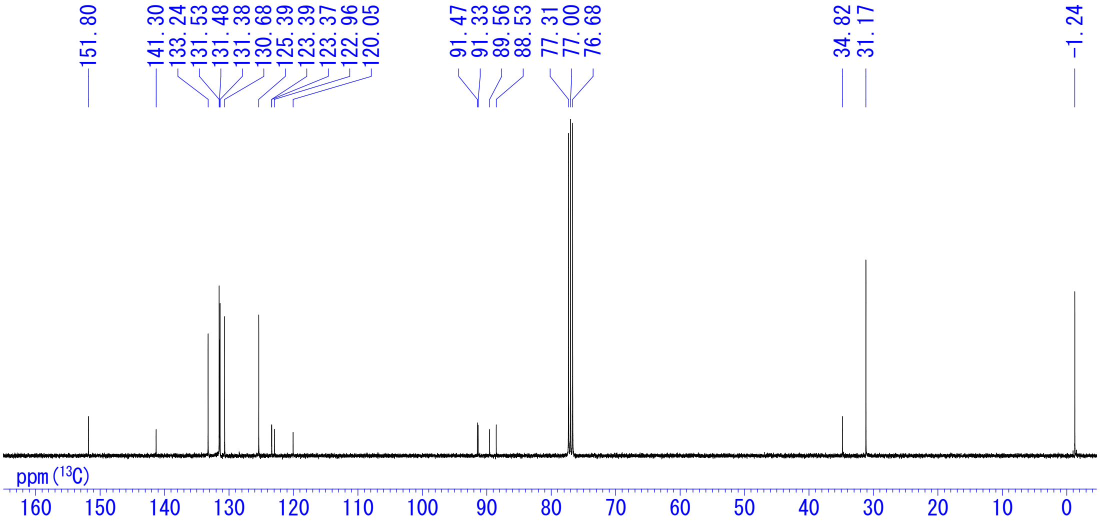
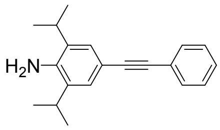


Figure S10. ^{13}C NMR spectrum of **7** in $CDCl_3$.



9

Figure S11. ^{1}H NMR spectrum of **9** in CDCl$_3$.

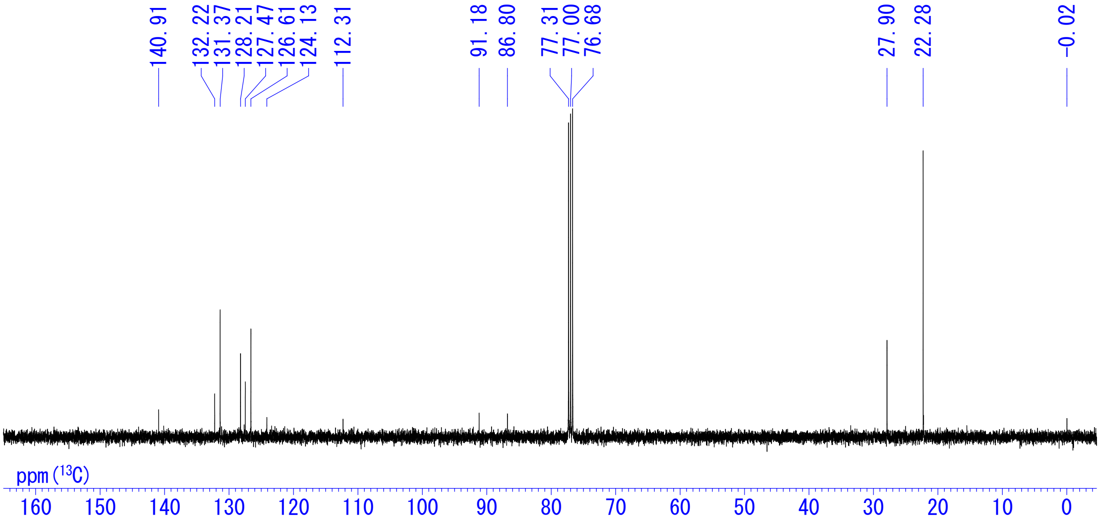
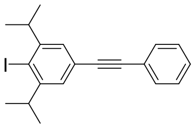


Figure S12. ^{13}C NMR spectrum of **9** in CDCl$_3$.



10

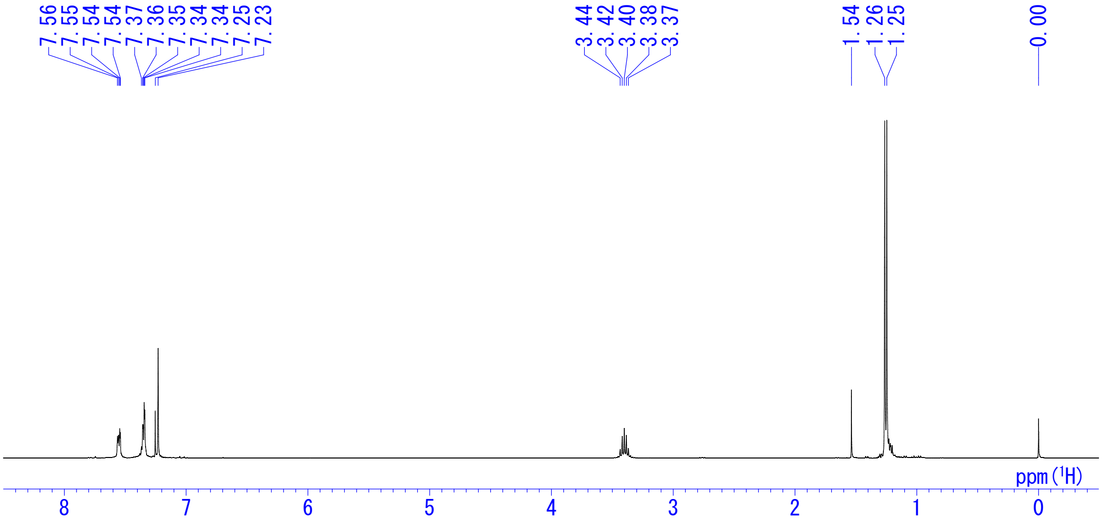


Figure S13. ^{1}H NMR spectrum of **10** in CDCl$_3$.

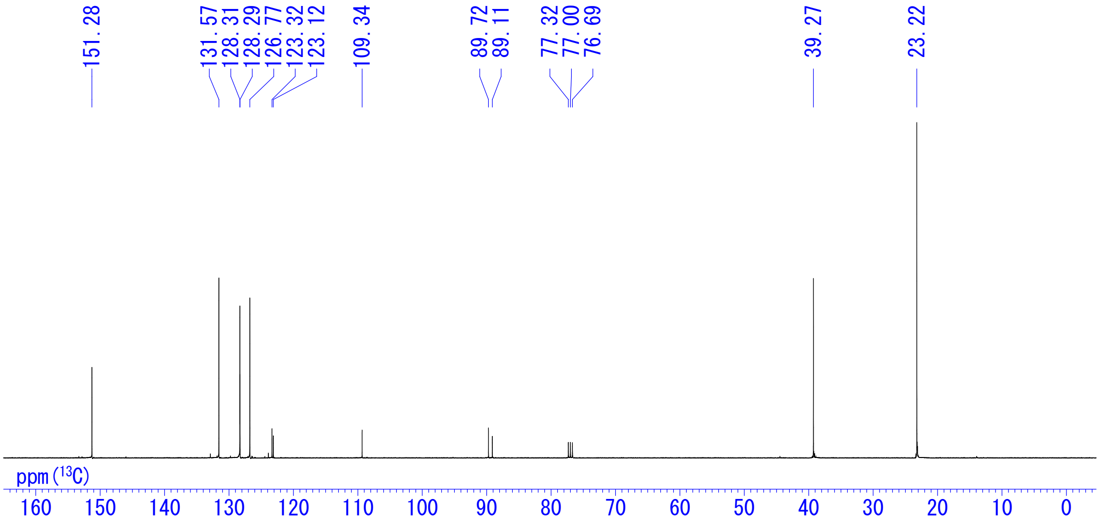
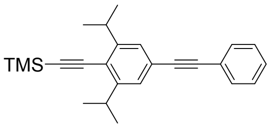


Figure S14. ^{13}C NMR spectrum of **10** in CDCl$_3$.



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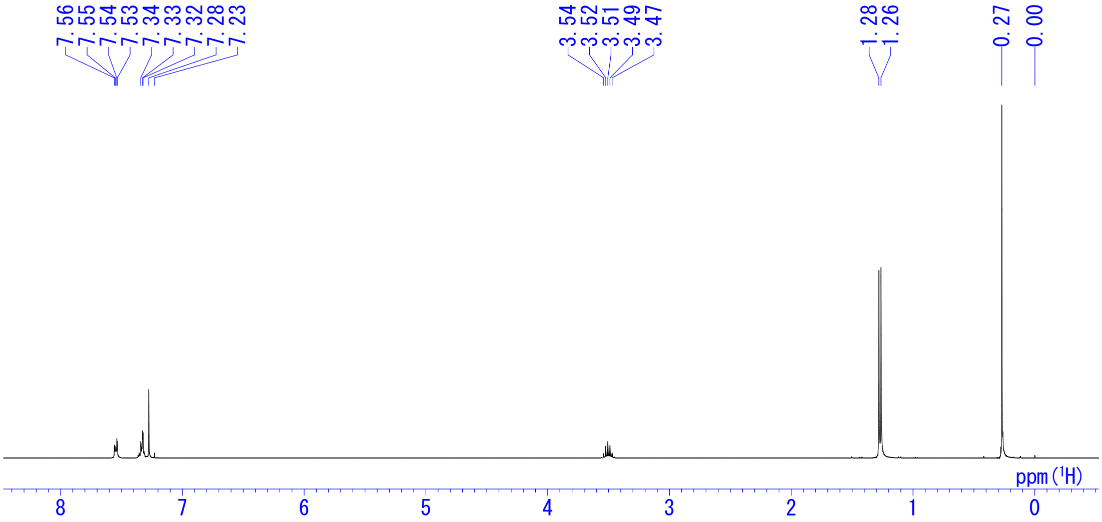


Figure S15. ^{1}H NMR spectrum of **11** in $CDCl_3$.

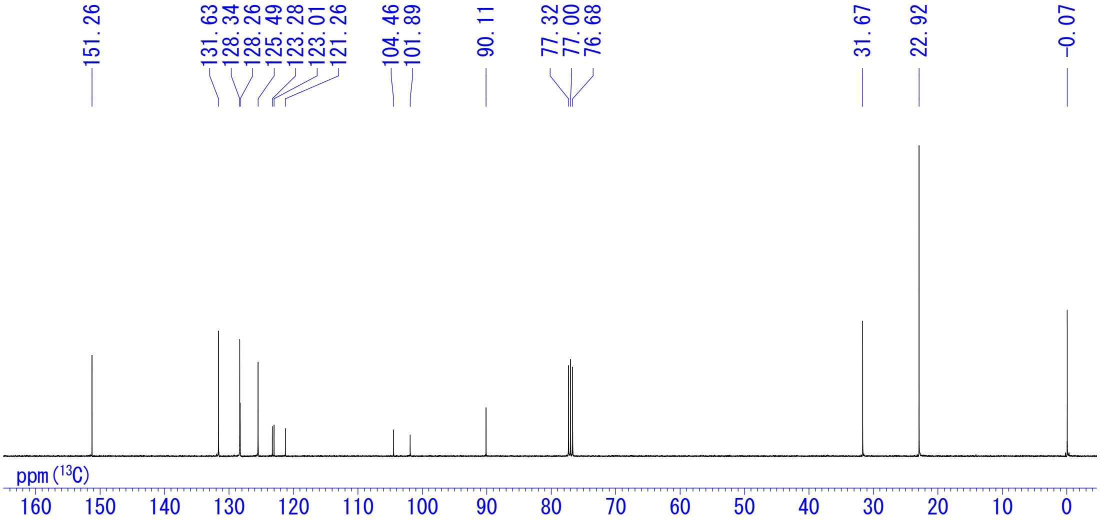
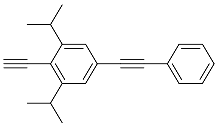


Figure S16. ^{13}C NMR spectrum of **11** in $CDCl_3$.



12

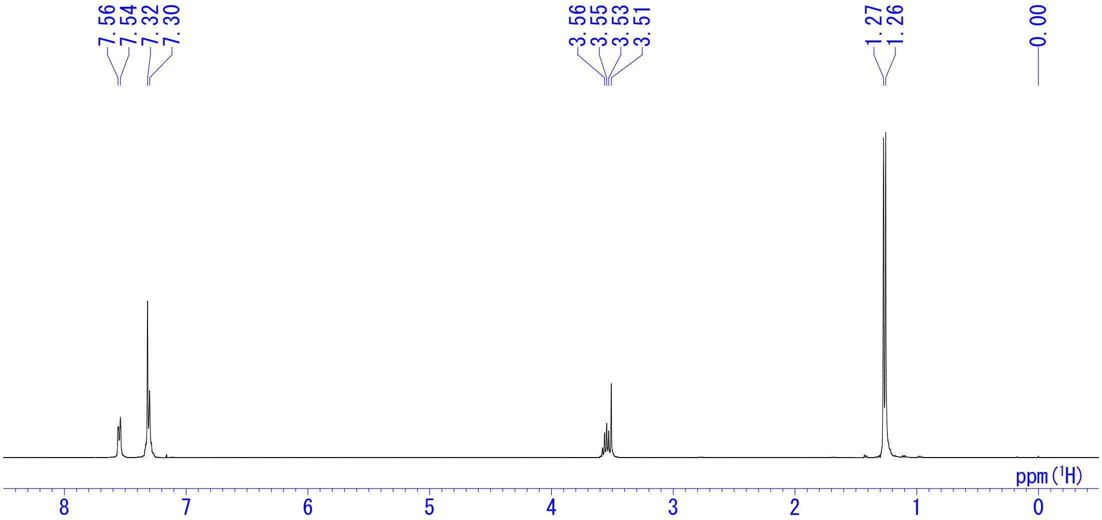


Figure S17. ^{1}H NMR spectrum of **12** in $CDCl_3$.

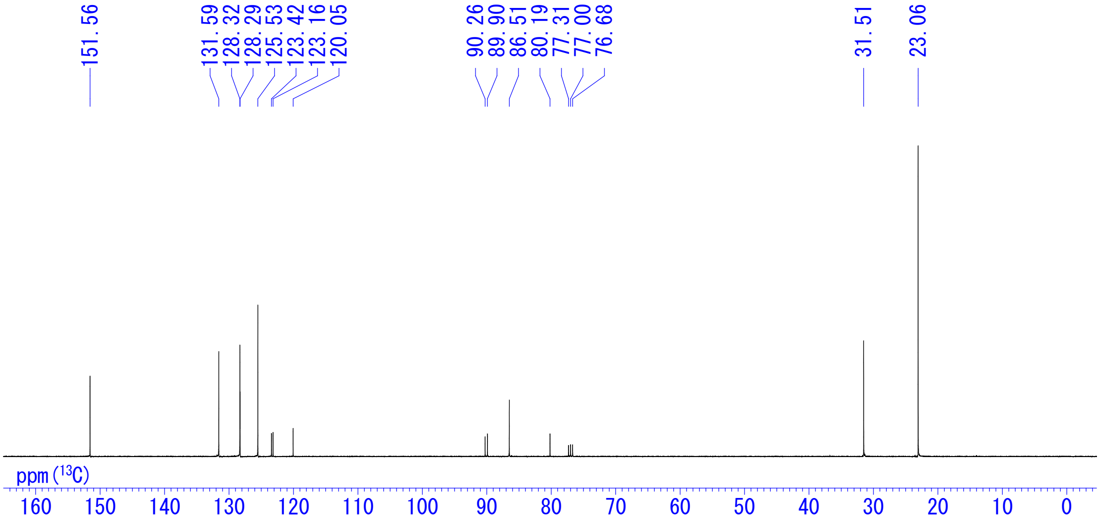
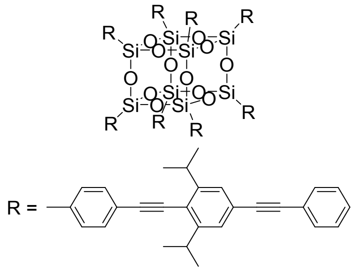


Figure S18. ^{13}C NMR spectrum of **12** in $CDCl_3$.



13, ***i*-PrPOSS**

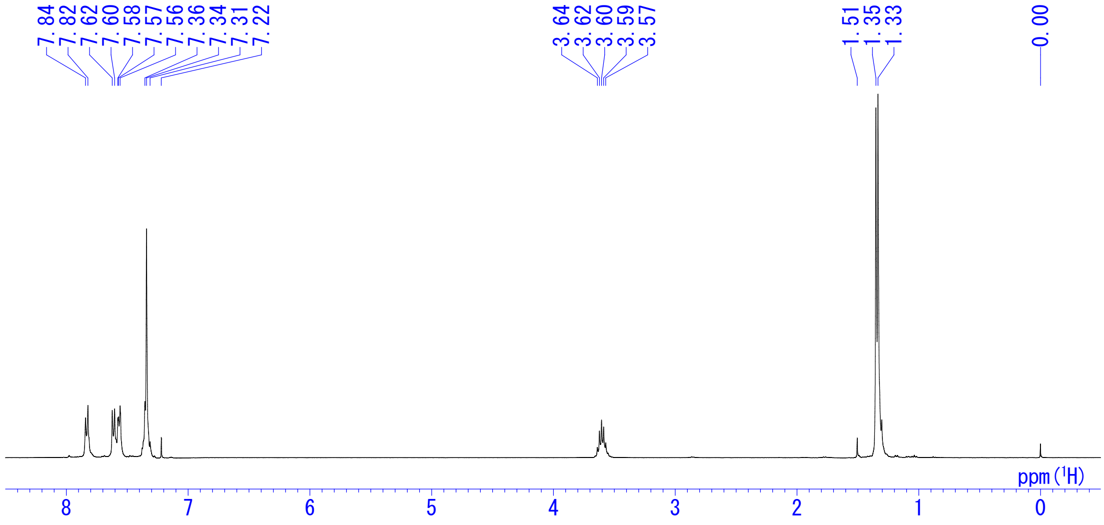


Figure S19. ^{1}H NMR spectrum of **13** in CDCl$_3$.

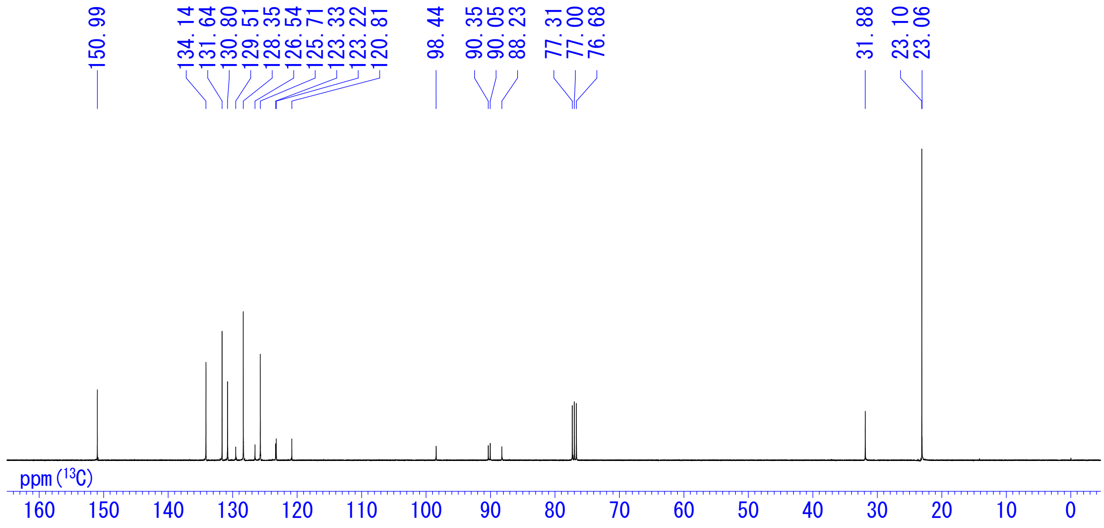


Figure S20. ^{13}C NMR spectrum of **13** in CDCl$_3$.

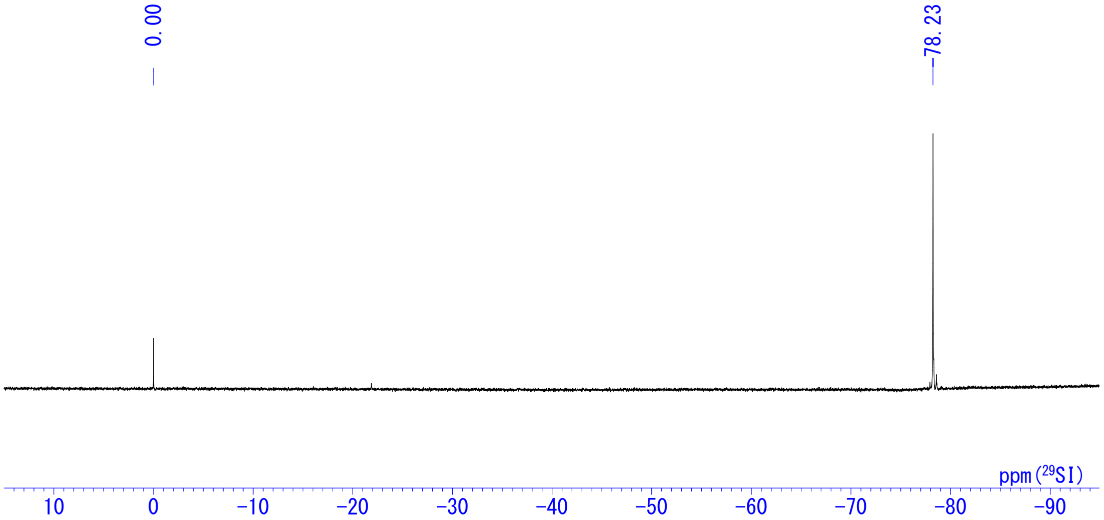
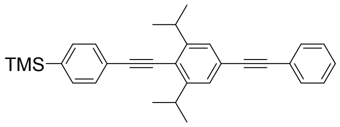


Figure S21. ^{29}Si NMR spectrum of **13** in $CDCl_3$.



14, ***i*-PrTMS**

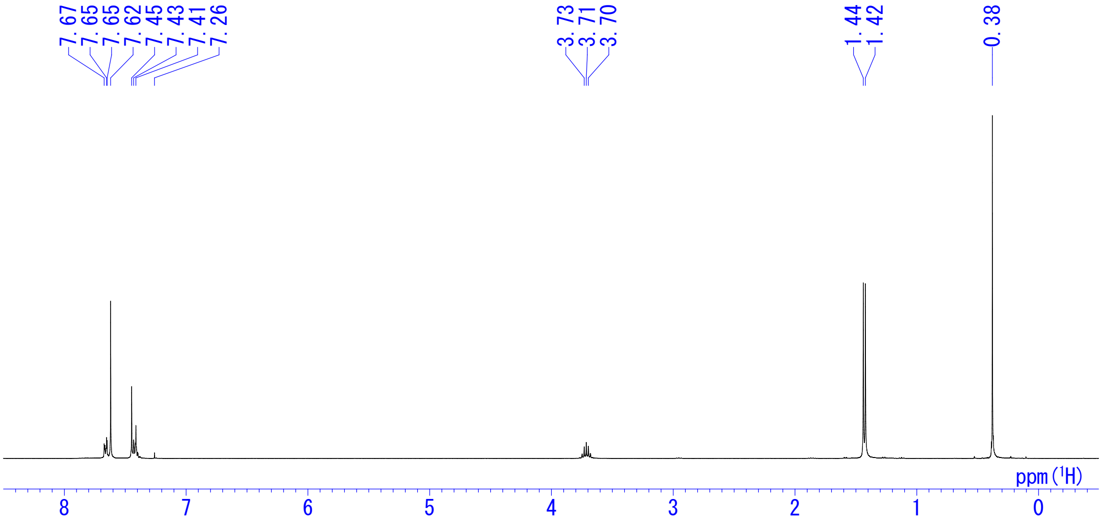


Figure S22. ^{1}H NMR spectrum of **14** in $CDCl_3$.

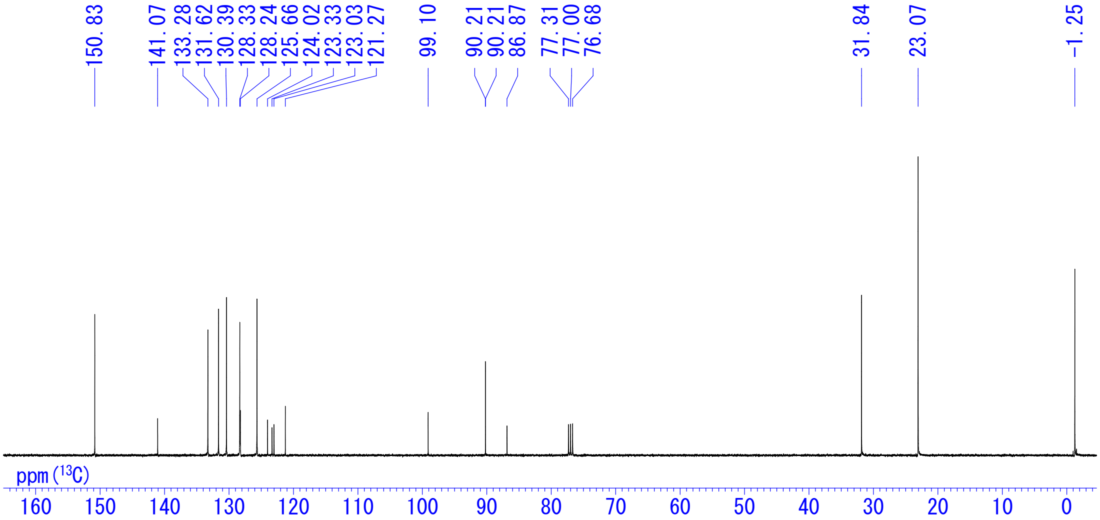


Figure S23. ^{13}C NMR spectrum of **15** in $CDCl_3$.

PL lifetime decay curves

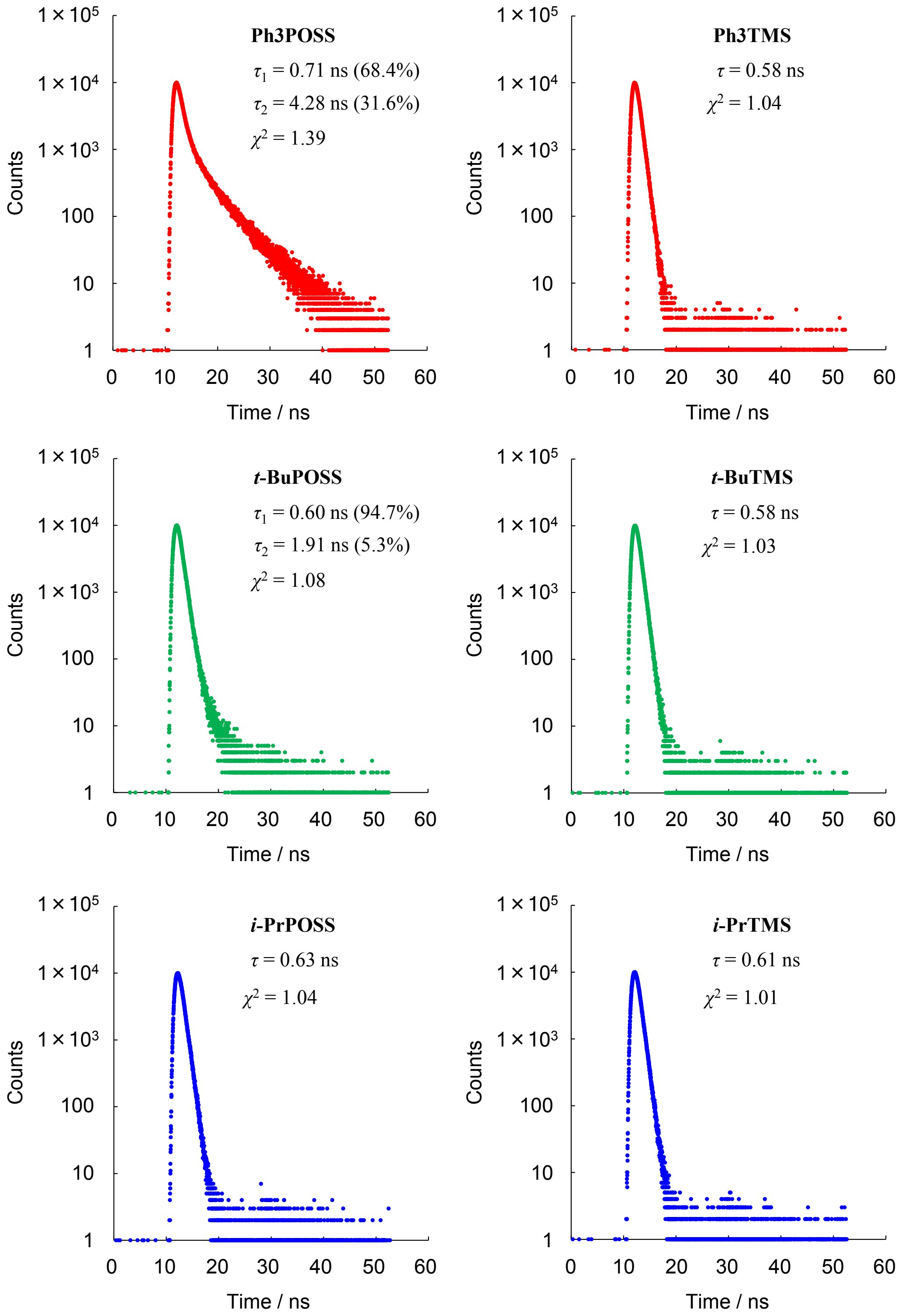


Figure S24. PL lifetime decay curves of **Ph3POSS**, **Ph3TMS**, ***t*-BuPOSS**, ***t*-BuTMS**, ***i*-PrPOSS** and ***i*-PrTMS** in $CHCl_3$ (1.0×10^{-6} M) at room temperature, excited at 292 nm with LED laser. The values at 416 nm were monitored.

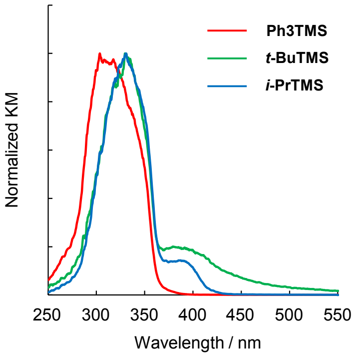


Figure S25. Diffuse reflection (Kubelka-Munk) spectra of **Ph3TMS**, ***t*-BuTMS** and ***i*-PrTMS** in the solid state.

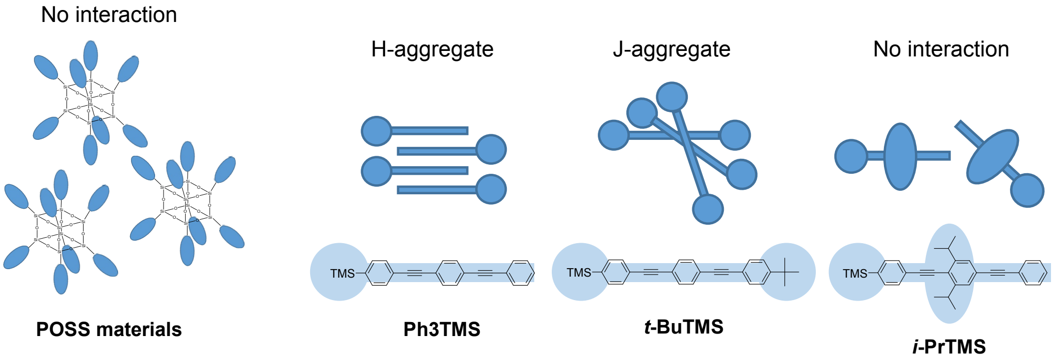


Figure S26. POSS materials and model compounds in a solid state.

Figures of the thermal stability of luminescence

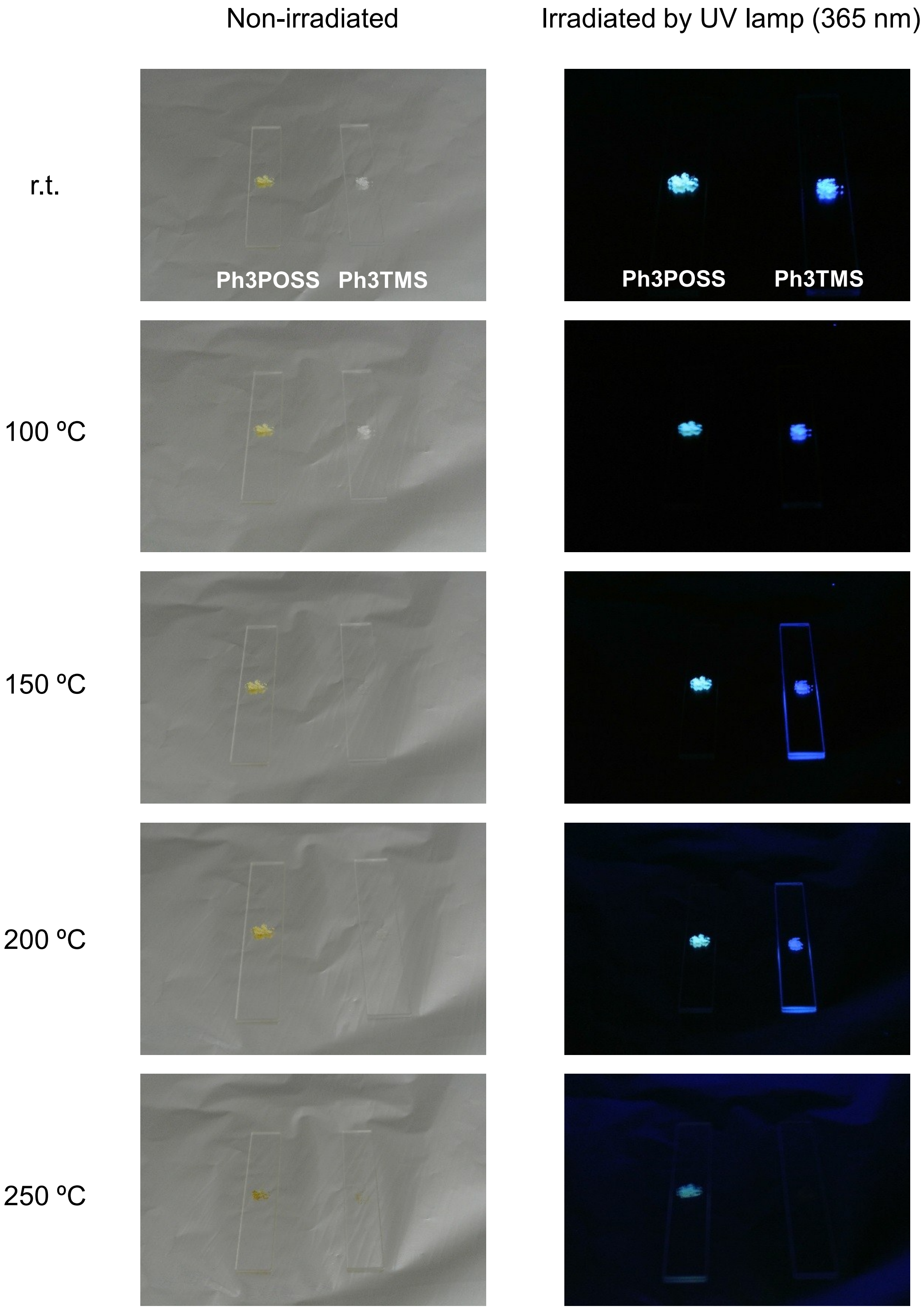


Figure S27. Pictures of **Ph3POSS** and **Ph3TMS** on a hotplate.

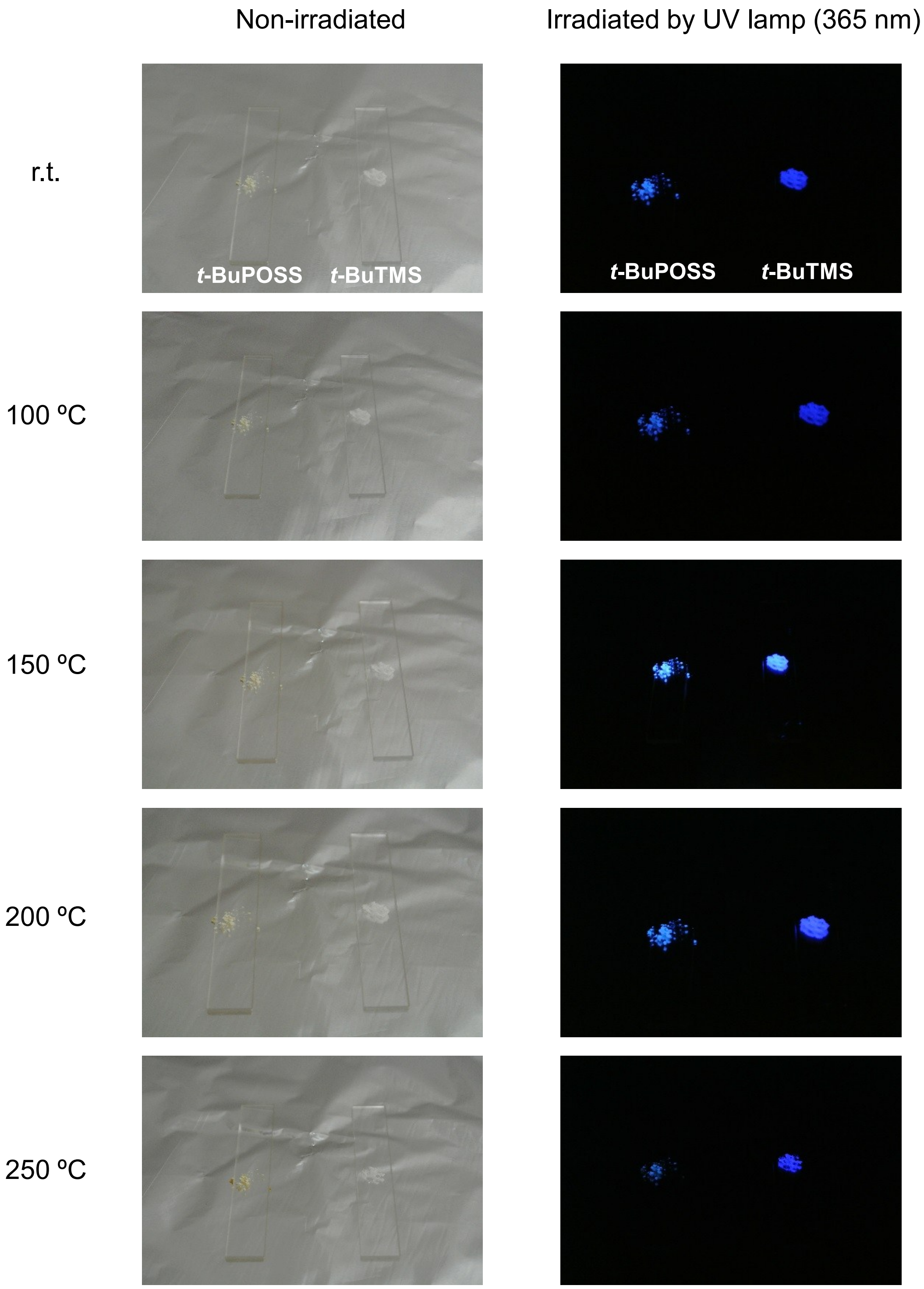


Figure S28. Pictures of ***t*-BuPOSS** and ***t*-BuTMS** on a hotplate.

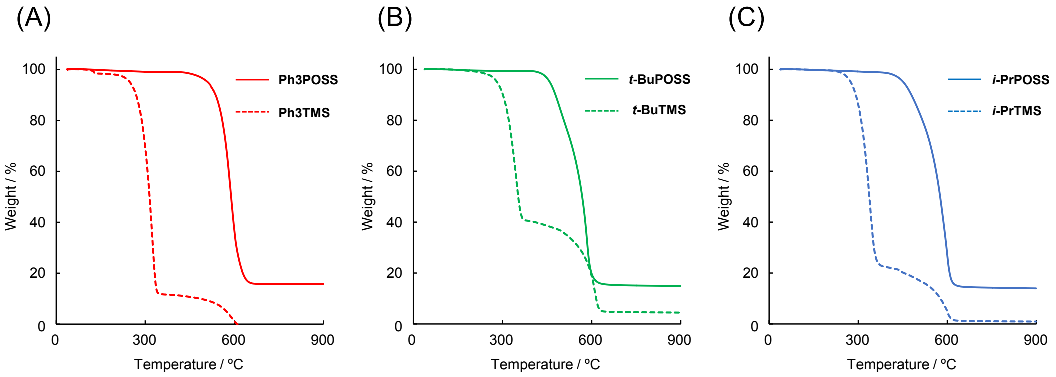


Figure S29. TGA curves of (A) **Ph3POSS** and **Ph3TMS**, (B) ***t*-BuPOSS** and ***t*-BuTMS**, and (C) ***i*-PrPOSS** and ***i*-PrTMS** under air (scan rate, 10 °C min^{-1}).

Table S1. Thermal degradation temperatures of the compounds[a]

Compd.	T_d / °C
Ph3POSS	505
***t*-BuPOSS**	446
***i*-PrPOSS**	444
Ph3TMS	252
***t*-BuTMS**	281
***i*-PrTMS**	272

[a] Determined from TGA profiles at the onset of degradation in the profile with temperature increase rate of 10 °C·min^{-1} in air.

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3. J. E. Rogers, T. M. Cooper, P. A. Fleitz, D. J. Glass and D. G. *J.* McLean, *Phys Chem A*, 2002, **106**, 10108–10115.
4. H. Yang, G. Li, Z. Ma, J. Chao and Z. GuO, *J. Catal.*, 2010, **276**, 123–133.