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Supporting Information

Integration of Benzo[*h*]quinoline and π-Extended Dibenzo[*b,f*]silepins on Pentacoordinate Silicon

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Experimental Section

Measurements. ^{1}H (400 MHz), ^{13}C (100 MHz), and ^{29}Si (80 MHz) NMR spectra were recorded on a JEOL JNM-EX400 spectrometer. ^{1}H and ^{13}C NMR spectra used tetramethylsilane (TMS) as an internal standard. ^{29}Si NMR spectra were referenced externally to TMS in $CDCl_3$. UV–vis spectra were recorded on a Shimadzu UV-3600 spectrophotometer. Fluorescence emission spectra were recorded on a HORIBA JOBIN YVON Fluoromax-4 spectrofluorometer. Elemental analysis was performed at the Microanalytical Center of Kyoto University. All reactions were performed under nitrogen or argon atmosphere.

Materials. Tetrahydrofuran (THF) and diethyl ether were purified using a two-column solid-state purification system (Glasscontour System, Joerg Meyer, Irvine, CA). 10-Bromobenzo[*h*]quinoline,[1] (*Z*)-1,2-bis(2-bromo-4-chlorophenyl)ethene[2] and (*Z*)-1,2-bis(2-bromo-5-chlorophenyl)ethene[2] were prepared according to the literature. Other reagents were commercially available and used as received.

5-(10-Benzo[*h*]quinolyl)-2,8-dichloro-5-methyldibenzo[*b*,*f*]silepin (2pC). To a solution of (*Z*)-1,2-bis(2-bromo-5-chlorophenyl)ethene (3.26 g, 8.00 mmol) in diethyl ether (320 mL), a solution of *n*-butyllithium in hexane (1.6 M, 10.0 mL, 16 mmol) was added dropwise at –78 °C, and the resulting mixture was held at –78 °C for 10 min, followed by the addition of TMEDA (2.38 mL, 16.0 mmol). After the mixture was stirred for 2 h at –78 °C, trichloro(methyl)silane (0.94 mL, 8.00 mmol) was added. The resulting mixture was allowed to warm to room temperature and left to stir for 18 h. The solvent was removed at 65 °C under argon, and then at room temperature

under reduced pressure at ambient temperature. The obtained solid was dissolved in THF (40 mL), and the solution and TMEDA (1.19 mL, 8.00 mmol) were added to a solution of 10-benzo[*h*]quinolyllithium in THF (generated by treating 10-bromobenzo[*h*]quinoline (2.06 g, 8.00 mmol) with *n*-butyllithium (1.6 M in hexane, 5.0 mL, 8.0 mmol) in THF (48 mL) for 30 min at –78 °C). After stirring at room temperature for 22 h, NH_4Cl (aq) was added, followed by extraction with cyclopentyl methyl ether, drying over $MgSO_4$, and removal of the solvent under vacuum. The solid was dissolved in chloroform again and filtered through a short plug of silica gel. Recrystallization from chloroform/ethanol gave a pale yellow solid in 54% yield (2.02 g, 4.32 mmol). ^{1}H NMR (400 M Hz, $CDCl_3$): δ = 8.58 (br, 1H, Ar*H*), 8.06 (dd, *J* = 8.0, 1.6 Hz, 1H, Ar*H*), 7.91 (d, *J* = 7.6 Hz, 1H, Ar*H*), .7.79 (m, 3H, Ar*H*), 7.64 (d, *J* = 8.8 Hz, 1H, Ar*H*), 7.50 (br, 2H, Ar*H*), 7.37 (m, 1H, Ar*H*), 7.32 (br, 2H, Ar*H*) 7.21 (s, 2H, Ar*H*), 6.59 (s, 2H, -C*H*=C*H*-), 1.12 (s, 3H, -CH_3) ppm. ^{13}C NMR (100 M Hz, $CDCl_3$): δ = 145.6, 141.7, 140.1, 137.6, 136.2, 135.4, 134.4, 133.8, 132.5, 131.4, 130.1, 128.7, 128.4, 127.2, 127.0, 126.4, 124.9, 121.6, –3.1 ppm. ^{29}Si NMR (80 M Hz, $CDCl_3$): δ = –21.1 ppm. HRMS (ESI+): m/z: calcd for $C_{28}H_{20}NSiCl_2$ ($M+H^+$): 468.0737; found: 468.0738.

5-(10-Benzo[*h*]quinolyl)-2,8-dichloro-5-(2-(2-ethoxyethoxy)ethoxy)-dibenzo[*b*,*f*]silepin (2pO). To a solution of (*Z*)-1,2-bis(2-bromo-5-chlorophenyl)ethene (3.26 g, 8.00 mmol) in diethyl ether (320 mL), a solution of *n*-butyllithium in hexane (1.6 M, 10.0 mL, 16 mmol) was added dropwise at –78 °C and the resulting mixture was held at –78 °C for 10 min followed by the addition of TMEDA (2.38 mL, 16.0 mmol). After the mixture was stirred for 2 h at –78 °C, trichloro((2-ethoxyethoxy)ethoxy)silane (2.14 g, 8.00 mmol) in diethyl ether (8.0 mL) was added. The resulting mixture was allowed to warm to room temperature and left to stir for 5 h at ambient temperature. The solvent was removed at room temperature under reduced pressure. The

obtained solid was dissolved in THF (40 mL), and the solution and TMEDA (1.19 mL, 8.00 mmol) were added to a solution of 10-benzo[*h*]quinolyllithium in THF (generated by treating 10-bromobenzo[*h*]quinoline (2.06 g, 8.00 mmol) with *n*-butyllithium (1.6 M in hexane, 5.0 mL, 8.0 mmol) in THF (48 mL) for 30 min at –78 °C). After stirring at room temperature for 11 h, NH_4Cl (aq) was added, followed by extraction with cyclopentyl methyl ether, drying over $MgSO_4$, and removal of the solvent under vacuum. The crude product was purified by silica gel column chromatography eluted with hexane/ethyl acetate (4/1), followed by precipitation in hexane to give a yellow solid in 40% yield (1.87 g, 3.19 mmol). The product was used without further purification. HRMS (ESI+): m/z: calcd for $C_{33}H_{30}NO_3SiCl_2$ ($M+H^+$): 586.1371; found: 586.1367.

5-(10-Benzo[*h*]quinolyl)-3,7-dichloro-5-methyldibenzo[*b*,*f*]silepin (2mC). Similarly to the preparation of **2pC**, **2mC** was synthesized from (*Z*)-1,2-bis(2-bromo-4-chlorophenyl)ethene (3.26 g, 8.00 mmol) in 63% yield as a white solid (2.37 g, 5.05 mmol). ^{1}H NMR (400 M Hz, $CDCl_3$): δ = 8.64 (br,1H, Ar*H*), 8.07 (d, *J* = 6.8 Hz, 1H, Ar*H*), 7.91 (m, 3H, Ar*H*), .7.79 (d, *J* = 8.8 Hz, 1H, Ar*H*), 7.64 (d, *J* = 8.8 Hz, 1H, Ar*H*), 7.48–7.41 (m,3H, Ar*H*), 7.26–7.23 (m, 2H, Ar*H*), 7.15 (s, 2H, Ar*H*), 6.59 (s, 2H, -C*H*=C*H*-), 0.88 (s, 3H, -CH_3) ppm. ^{13}C NMR (100 M Hz, $CDCl_3$): δ = 145.6, 143.8, 138.6, 137.5, 136.1, 135.5, 135.4, 133.8, 133.5, 132.7, 132.2, 131.9, 130.8, 130.1, 128.7, 127.7, 127.2, 126.5, 124.8, 121.8, –3.3 ppm. ^{29}Si NMR (80 M Hz, $CDCl_3$): δ = –21.9 ppm. HRMS (ESI+): m/z: calcd for $C_{28}H_{20}NSiCl_2$ ($M+H^+$): 468.0737; found: 468.0739.

5-(10-Benzo[*h*]quinolyl)-3,7-dichloro-5-(2-(2-ethoxyethoxy)ethoxy)-dibenzo[*b*,*f*]silepin (2mO). Similarly to the preparation of **2pO**, **2mO** was synthesized from (*Z*)-1,2-bis(2-bromo-4-chlorophenyl)ethene (3.26 g, 8.00 mmol) in 25% yield as a yellow solid (1.19 g, 2.03 mmol).

The product was used without further purification. HRMS (ESI+): m/z: calcd for $C_{33}H_{30}NO_3SiCl_2$ ($M+H^+$): 586.1372; found: 586.1367.

5-(10-Benzo[*h*]quinolyl)-2,8-dichloro-5-fluorodibenzo[*b*,*f*]silepin (2pF). Boron trifluoride diethyl etherate (0.754 mL, 6.00 mmol) was added to a solution of **2pO** (1.76 g, 3.00 mmol) in dichloromethane (15 mL) at room temperature. After the solution was stirred at room temperature for 2 h, sodium bicarbonate (saturated aqueous) was added. The organic layer was separated, dried over $MgSO_4$, filtered, and concentrated under vacuum. The crude product was purified by silica gel column chromatography eluted with hexane/chloroform (3/2) to give a colorless solid in 56% yield (0.800 g, 1.69 mmol). ^{1}H NMR (400 M Hz, $CDCl_3$): δ = 8.57 (d, J = 6.8 Hz, 1H, Ar*H*), 8.19 (m, 2H, Ar*H*), 8.03 (d, J = 8.8 Hz, 1H, Ar*H*), 7.97 (m, 1H, Ar*H*), 7.81 (m, 2H, Ar*H*), 7.40 (s, 2H, Ar*H*), 7.28 (m, 1H, Ar*H*), 6.84 (s, 2H, -C*H*=C*H*-) 6.77 (d, J = 7.6 Hz, 2H, Ar*H*), 6.64 (d, J = 8.0 Hz, 2H, Ar*H*) ppm. ^{29}Si NMR (80 M Hz, $CDCl_3$): δ = –42.2 (d, J = 270 Hz) ppm. HRMS (ESI+): m/z: calcd for $C_{27}H_{17}NFSiCl_2$ ($M+H^+$): 472.0491; found: 472.0486. Elemental analysis: calcd for $C_{27}H_{16}NFSiCl_2$: C 68.65, H 3.41, N 2.96; found: C 68.61, H 3.31, N 3.17.

5-(10-Benzo[*h*]quinolyl)-3,7-dichloro-5-fluoro-dibenzo[*b*,*f*]silepin (2mF). Similarly to the preparation of **2pF**, **2mF** was synthesized from **2mO** (1.05 g, 1.80 mmol) in 48% yield as a colorless solid (0.405 g, 0.858 mmol). ^{1}H NMR (400 M Hz, $CDCl_3$): δ = 8.58 (d, J = 6.8 Hz, 1H, Ar*H*), 8.21 (d, 2H, Ar*H*), 8.05 (d, J = 8.8 Hz, 1H, Ar*H*), 7.97 (m, 2H, Ar*H*), 7.82 (d, J = 9.2 Hz, 1H, Ar*H*), 7.35–7.29 (m, 3H, Ar*H*), 7.19 (d, J = 6.8 Hz, 2H, Ar*H*), 6.83 (s, 2H, -C*H*=C*H*-) 6.67 (s, 2H, Ar*H*) ppm. ^{29}Si NMR (80 M Hz, $CDCl_3$): δ = –45.3 (d, J = 270 Hz) ppm. Elemental analysis: calcd for $C_{27}H_{16}NFSiCl_2$: C 68.65, H 3.41, N 2.96; found: C 67.98, H 3.39, N 2.95.

5-(10-Benzo[*h*]quinolyl)-2,8-bis(4-methoxyphenyl)-5-methyldibenzo[*b*,*f*]silepin (3pCO). A mixture of **2pC** (0.187 g, 0.400 mmol), 4-methoxyphenylboronic acid (0.182 g, 1.20 mmol), tripotassium phosphate (0.340 g, 0.016 mmol), and chloro(2-dicyclohexylphosphino-2′,4′,6′-triisopropyl-1,1′-biphenyl)[2-(2′-amino-1,1′-biphenyl)]palladium(II) (12.6 mg, 0.016 mmol) was heated at 55 °C in THF (2.0 mL) and water (0.4 mL) with stirring for 12 h. Then, water was poured into the solution. After extraction with cyclopentyl methyl ether, drying over $MgSO_4$, and condensation under vacuum, the crude product was purified by silica gel column chromatography eluted with hexane/ethyl acetate (9/1 to 4/1) to give a colorless solid in 55% yield (0.135 g, 0.220 mmol). ^{1}H NMR (400 M Hz, $CDCl_3$): δ = 8.72 (br, 1H, Ar*H*), 8.01 (m, 3H, Ar*H*), 7.89 (d, *J* = 7.6 Hz, 1H, Ar*H*), .7.77 (d, *J* = 8.8 Hz, 1H, Ar*H*), 7.60 (d, *J* = 8.8 Hz, 2H, Ar*H*), 7.51 (m, 7H, Ar*H*), 7.43 (s, 2H, Ar*H*), 7.33 (dd, *J* = 8.0, 4.4 Hz, 1H, Ar*H*) 6.94 (d, *J* = 8.8 Hz, 4H, Ar*H*), 6.77 (s, 2H, -C*H*=C*H*-), 3.82 (s, 6H, -OCH_3), 1.20 (s, 3H, -CH_3) ppm. ^{13}C NMR (100 M Hz, $CDCl_3$): δ = 159.1, 145.8, 140.9, 139.9, 137.9, 136.4, 135.2, 135.1, 133.8, 133.7, 133.1, 132.5, 129.8, 128.6, 128.1, 128.0, 127.1, 126.9, 126.4, 125.1, 124.7, 121.5, 121.4, 114.1, 55.3, –3.04 ppm. ^{29}Si NMR (80 M Hz, $CDCl_3$): δ = –20.6 ppm. HRMS (ESI+): m/z: calcd for $C_{42}H_{34}NO_2Si$ ($M+H^+$): 612.2353; found: 612.2340.

5-(10-Benzo[*h*]quinolyl)-5-fluoro-2,8-bis(4-methoxyphenyl)dibenzo[*b*,*f*]silepin (3pFO). A mixture of **2pF** (0.189 g, 0.400 mmol), 4-methoxyphenylboronic acid (0.182 g, 1.20 mmol), tripotassium phosphate (0.340 g, 0.016 mmol), and chloro(2-dicyclohexylphosphino-2′,4′,6′-triisopropyl-1,1′-biphenyl)[2-(2′-amino-1,1′-biphenyl)]palladium(II) (12.6 mg, 0.016 mmol) was heated at 55 °C in THF (2.0 mL) and water (0.4 mL) with stirring for 12 h. Then, water was poured into the solution. After extraction with cyclopentyl methyl ether, drying over $MgSO_4$, and

condensation under vacuum, the crude product was purified by silica gel column chromatography eluted with hexane/ethyl acetate (3/1) to give a colorless solid in 51% yield (0.126 g, 0.204 mmol). ^{1}H NMR (400 M Hz, $CDCl_3$): δ = 8.64 (d, J = 6.8 Hz, 1H, Ar*H*), 8.17 (m, 2H, Ar*H*), 8.05–7.96 (m, 3H, Ar*H*), 7.79 (d, J = 8.8 Hz, 1H, Ar*H*), 7.62 (d, J = 1.2 Hz, 2H, Ar*H*), 7.46 (d, J = 8.0 Hz, 4H, Ar*H*), 7.26 (d, J = 8.0 Hz, 1H, Ar*H*), 7.01 (m, 4H, Ar*H*, -C*H*=C*H*-), 6.92 (d, J = 9.2 Hz, 4H, Ar*H*), 6.82 (d, J = 8.0 Hz, 2H, Ar*H*), 3.81 (s, 6H, -OCH_3) ppm. ^{29}Si NMR (80 M Hz, $CDCl_3$): δ = –40.4 (d, J = 270 Hz) ppm. HRMS (ESI+): m/z: calcd for $C_{41}H_{31}FNO_2Si$ ($M+H^+$): 616.2103; found: 616.2088. Elemental analysis: calcd for $C_{41}H_{30}FNO_2Si$: C 79.97, H 4.91, N 2.27; found: C 79.33, H 5.12, N 2.29.

5-(10-Benzo[*h*]quinolyl)-3,7-bis(4-methoxyphenyl)-5-methyldibenzo[*b*,*f*]silepin (3mCO). A mixture of **2mC** (0.187 g, 0.400 mmol), 4-methoxyphenylboronic acid (0.182 g, 1.20 mmol), tripotassium phosphate (0.340 g, 0.016 mmol), and chloro(2-dicyclohexylphosphino-2′,4′,6′-triisopropyl-1,1′-biphenyl)[2-(2′-amino-1,1′-biphenyl)]palladium(II) (12.6 mg, 0.016 mmol) was heated at 55 °C in THF (2.0 mL) and water (0.4 mL) with stirring for 6 h. Then, water was poured into the solution. After extraction with cyclopentyl methyl ether, drying over $MgSO_4$, and condensation under vacuum, the crude product was purified by silica gel column chromatography eluted with hexane/ethyl acetate (4/1). Recrystallization from dichloromethane/hexane gave a pale yellow solid in 60% yield (0.146 g, 0.239 mmol). ^{1}H NMR (400 M Hz, $CDCl_3$): δ = 8.51 (br, 1H, Ar*H*), 8.12 (br, 2H, Ar*H*), 7.99 (d, J = 8.0 Hz, 1H, Ar*H*), .7.88 (d, J = 7.6 Hz, 1H, Ar*H*), 7.77 (d, J = 8.8 Hz, 1H, Ar*H*), 7.60 (m, 5H, Ar*H*), 7.47 (m, 3H, Ar*H*), 7.35–7.29 (m, 4H, Ar*H*) 6.99 (d, J = 8.4 Hz, 4H, Ar*H*), 6.70 (s, 2H, -C*H*=C*H*-), 3.85 (s, 6H, -OCH_3), 1.25 (s, 3H, -CH_3) ppm. ^{13}C NMR (100 M Hz, $CDCl_3$): δ = 159.0, 145.8, 145.6, 141.9, 139.3, 138.8, 137.8, 136.4, 135.1, 134.0, 133.7, 132.4, 132.3, 131.3, 129.8, 129.2, 128.7,

128.0, 127.2, 126.4, 126.0, 124.7, 121.4, 55.3, –3.1 ppm. ^{29}Si NMR (80 M Hz, $CDCl_3$): δ = –20.0 ppm. HRMS (ESI+): m/z: calcd for $C_{42}H_{34}NO_2Si$ ($M+H^+$): 612.2353; found: 612.2340.

5-(10-Benzo[*h*]quinolyl)-5-fluoro-3,7-bis(4-methoxyphenyl)dibenzo[*b*,*f*]silepin (3mFO). A mixture of **2mF** (0.189 g, 0.400 mmol), 4-methoxyphenylboronic acid (0.182 g, 1.20 mmol), tripotassium phosphate (0.340 g, 0.016 mmol), and chloro(2-dicyclohexylphosphino-2′,4′,6′-triisopropyl-1,1′-biphenyl)[2-(2′-amino-1,1′-biphenyl)]palladium(II) (12.6 mg, 0.016 mmol) was heated at 55 °C in THF (2.0 mL) and water (0.4 mL) with stirring for 6 h. Then, water was poured into the solution. After extraction with cyclopentyl methyl ether, drying over $MgSO_4$, and condensation under vacuum, the crude product was purified by silica gel column chromatography eluted with hexane/ethyl acetate (7/3) to give a pale yellow solid in 91% yield (0.225 g, 0.365 mmol). ^{1}H NMR (400 M Hz, $CDCl_3$): δ = 8.66 (d, J = 6.8 Hz, 1H, Ar*H*), 8.14 (m, 3H, Ar*H*), 7.96 (m, *2*H, Ar*H*), 7.76 (d, J = 8.8 Hz, 1H, Ar*H*), 7.43 (m, 2H, Ar*H*), 7.41 (m, 2H, Ar*H*), 7.23 (m, 1H, Ar*H*), 7.01–6.93 (m, 8H, Ar*H*), 6.99 (d, J = 8.4 Hz, 4H, Ar*H*), 6.70 (s, 2H, -C*H*=C*H*-), 6.68 (s, 2H, Ar*H*), 3.69 (s, 6H, -OCH_3) ppm. HRMS (ESI+): m/z: calcd for $C_{41}H_{31}FNO_2Si$ ($M+H^+$): 616.2103; found: 616.2084. Elemental analysis: calcd for $C_{41}H_{30}FNO_2Si$: C 79.97, H 4.91, N 2.27; found: C 79.33, H 5.12, N 2.29.

5-(10-Benzo[*h*]quinolyl)-5-methyl-2,8-bis[(4-trifluoromethyl)phenyl]-dibenzo[*b*,*f*]silepin (3pCF). A mixture of **2pC** (0.187 g, 0.400 mmol), 4-(trifluoromethyl)phenylboronic acid (0.228 g, 1.20 mmol), tripotassium phosphate (0.340 g, 0.016 mmol), and chloro(2-dicyclohexylphosphino-2′,4′,6′-triisopropyl-1,1′-biphenyl)[2-(2′-amino-1,1′-biphenyl)]palladium(II) (12.6 mg, 0.016 mmol) was heated at 55 °C in THF (2.0 mL) and water (0.4 mL) with stirring for 12 h. Then, water was poured into the solution. After extraction with

cyclopentyl methyl ether, drying over $MgSO_4$, and condensation under vacuum, the crude product was purified by silica gel column chromatography eluted with hexane/ethyl acetate (95/5) to give a colorless solid in 54% yield (0.148 g, 0.215 mmol). ^{1}H NMR (400 M Hz, $CDCl_3$): δ = 8.70 (br, 1H, Ar*H*), 8.06 (m, 3H, Ar*H*), 7.93 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.81 (d, *J* = 8.8 Hz, 1H, Ar*H*), 7.67 (m, 10H, Ar*H*), 7.60 (m, 2H, Ar*H*), 7.53 (d, *J* = 7.6 Hz, 1H, Ar*H*), 7.48 (s, 2H, Ar*H*), 7.37 (m, 1H, Ar*H*), 6.81 (s, 2H, -C*H*=C*H*-), 1.23 (s, 3H, -CH_3) ppm. ^{29}Si NMR (80 M Hz, $CDCl_3$): δ = –21.0 ppm. HRMS (ESI+): m/z: calcd for $C_{42}H_{28}F_6NSi$ ($M+H^+$): 688.1890; found: 688.1877. Elemental analysis: calcd for $C_{42}H_{27}F_6NSi$: C 73.35, H 3.96, N 2.04; found: C 72.81, H 4.13, N 1.96.

5-(10-Benzo[*h*]quinolyl)-5-fluoro-2,8-bis[(4-trifluoromethyl)phenyl]-dibenzo[*b*,*f*]silepin (3pFF). A mixture of **2pF** (0.189 g, 0.400 mmol), 4-(trifluoromethyl)phenylboronic acid (0.228 g, 1.20 mmol), tripotassium phosphate (0.340 g, 0.016 mmol), and chloro(2-dicyclohexylphosphino-2′,4′,6′-triisopropyl-1,1′-biphenyl)[2-(2′-amino-1,1′-biphenyl)]palladium(II) (12.6 mg, 0.016 mmol) was heated at 55 °C in THF (2.0 mL) and water (0.4 mL) with stirring for 12 h. Then, water was poured into the solution. After extraction with cyclopentyl methyl ether, drying over $MgSO_4$, and condensation under vacuum, the crude product was purified by silica gel column chromatography eluted with hexane/ethyl acetate (4/1). Recrystallization from dichloromethane/hexane gave a colorless solid in 44% yield (0.121 g, 0.174 mmol). ^{1}H NMR (400 M Hz, $CDCl_3$): δ = 8.65 (d, *J* = 6.8 Hz, 1H, Ar*H*), 8.20 (m, 2H, Ar*H*), 8.05 (d, *J* = 8.8 Hz, 1H, Ar*H*), 7.99 (m, 2H, Ar*H*), 7.82 (d, *J* = 9.2 Hz, 1H, Ar*H*), 7.67–7.59 (m, 10H, Ar*H*), 7.27 (dd, *J* = 8.0, 4.8 Hz, 1H, Ar*H*), 7.05 (m, 4H, Ar*H*, -C*H*=C*H*-), 6.87 (d, *J* = 7,6 Hz, 4H, Ar*H*) ppm. HRMS (ESI+): m/z: calcd for $C_{41}H_{25}F_7NSi$ ($M+H^+$):

692.1639; found: 692.1622. Elemental analysis: calcd for $C_{41}H_{24}F_7NSi$: C 71.19, H 3.50, N 2.02; found: C 71.25, H 3.75, N 2.02.

5-(10-Benzo[*h*]quinolyl)-5-methyl-3,7-bis[(4-trifluoromethyl)phenyl]-dibenzo[*b*,*f*]silepin (3mCF). A mixture of **2mC** (0.187 g, 0.400 mmol), 4-(trifluoromethyl)phenylboronic acid (0.228 g, 1.20 mmol), tripotassium phosphate (0.340 g, 0.016 mmol), and chloro(2-dicyclohexylphosphino-2′,4′,6′-triisopropyl-1,1′-biphenyl)[2-(2′-amino-1,1′-biphenyl)]palladium(II) (12.6 mg, 0.016 mmol) was heated at 55 °C in THF (2.0 mL) and water (0.4 mL) with stirring for 12 h. Then, water was poured into the solution. After extraction with cyclopentyl methyl ether, drying over $MgSO_4$, and condensation under vacuum, the crude product was purified by silica gel column chromatography eluted with hexane/ethyl acetate (95/5). Recrystallization from dichloromethane/hexane gave a colorless solid in 56% yield (0.155 g, 0.225 mmol). ^{1}H NMR (400 M Hz, $CDCl_3$): δ = 8.45 (br, 1H, Ar*H*), 8.15 (br, 2H, Ar*H*), 8.03 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.92 (d, *J* = 7.6 Hz, 1H, Ar*H*), 7.81 (d, *J* = 8.8 Hz, 1H, Ar*H*), 7.71 (br, 8H, Ar*H*), 7.64 (d, *J* = 8.8 Hz, 1H, Ar*H*), 7.52 (d, *J* = 7.6 Hz, 4H, Ar*H*), 7.35 (d, *J* = 7.6 Hz, 2H, Ar*H*), 7.28 (d, *J* = 8.0 Hz, 1H, Ar*H*), 6.75 (s, 2H, -C*H*=C*H*-), 1.26 (s, 3H, -CH_3) ppm. ^{29}Si NMR (80 M Hz, $CDCl_3$): δ = –21.0 ppm. HRMS (ESI+): m/z: calcd for $C_{42}H_{28}F_6NSi$ ($M+H^+$): 688.1890; found: 688.1872. Elemental analysis: calcd for $C_{42}H_{27}F_6NSi$: C 73.35, H 3.96, N 2.04; found: C 73.37, H 4.08, N 2.06.

5-(10-Benzo[*h*]quinolyl)-5-fluoro-3,7-bis[(4-trifluoromethyl)phenyl]-dibenzo[*b*,*f*]silepin (3mFF). A mixture of **2mF** (0.189 g, 0.400 mmol), 4-(trifluoromethyl)phenylboronic acid (0.228 g, 1.20 mmol), tripotassium phosphate (0.340 g, 0.016 mmol), and chloro(2-dicyclohexylphosphino-2′,4′,6′-triisopropyl-1,1′-biphenyl)[2-(2′-amino-1,1′-

biphenyl)]palladium(II) (12.6 mg, 0.016 mmol) was heated at 55 °C in THF (2.0 mL) and water (0.4 mL) with stirring for 12 h. Then, water was poured into the solution. After extraction with cyclopentyl methyl ether, drying over $MgSO_4$, and condensation under vacuum, the crude product was purified by silica gel column chromatography eluted with hexane/ethyl acetate (4/1). Recrystallization from dichloromethane/hexane gave a colorless solid in 29% yield (79.3 mg, 0.115 mmol). ^{1}H NMR (400 M Hz, $CDCl_3$): δ = 8.66 (br, 1H, Ar*H*), 8.12 (m, 2H, Ar*H*), 7.99 (m, 2H, Ar*H*), 7.85 (m, 2H, Ar*H*), 7.68–7.61 (m, 8H, Ar*H*), 7.53 (dd, *J* = 8.0, 1.0 Hz, 1H, Ar*H*), 7.40 (m, 3H, Ar*H*), 7.13 (m, 2H, Ar*H*), 6.87 (s, 2H, -C*H*=C*H*-) ppm. ^{13}C NMR (100 M Hz, $CDCl_3$): δ = 146.3, 144.5, 140.3, 139.6, 138.7, 136.5, 136.0, 133.9, 132.8, 132.6, 130.7, 130.1, 129.6, 129.3, 129.2, 129.0, 128.4, 127.7, 127.3, 127.2, 126.8, 126.6, 126.2, 126.0, 125.6, 124.7, 123.0, 122.0 ppm. HRMS (ESI+): m/z: calcd for $C_{41}H_{24}F_6NSi$ ($M–F^+$): 672.1577; found: 672.1599. Elemental analysis: calcd for $C_{41}H_{24}F_7NSi$: C 71.19, H 3.50, N 2.02; found: C 71.03, H 3.76, N 1.96.

Computational details. All calculations were carried out with ORCA 2.9.[3] The geometry of the singlet ground state was optimized by the TPSS functional[4] and the def2-TZVP basis set.[5] On the basis of the optimized structure, the absorption properties were calculated by TD-DFT within the Tamm-Dancoff approximation.[6] The TD-DFT calculations were performed at the PBE0 hybrid functional level[7] with the def2-TZVP basis set. The resolution of the identity (RI) approximation[8] was applied for the TPSS functional, and RI and chain of spheres approximation (RIJCOSX)[9] were also applied for the hybrid functionalization. The auxiliary basis function for coulomb fitting[10] was used as the fitting basis in the RI and RIJCOSX treatments. In all cases, the empirical London dispersion correction (DFT-D3(bj))[11] was applied.

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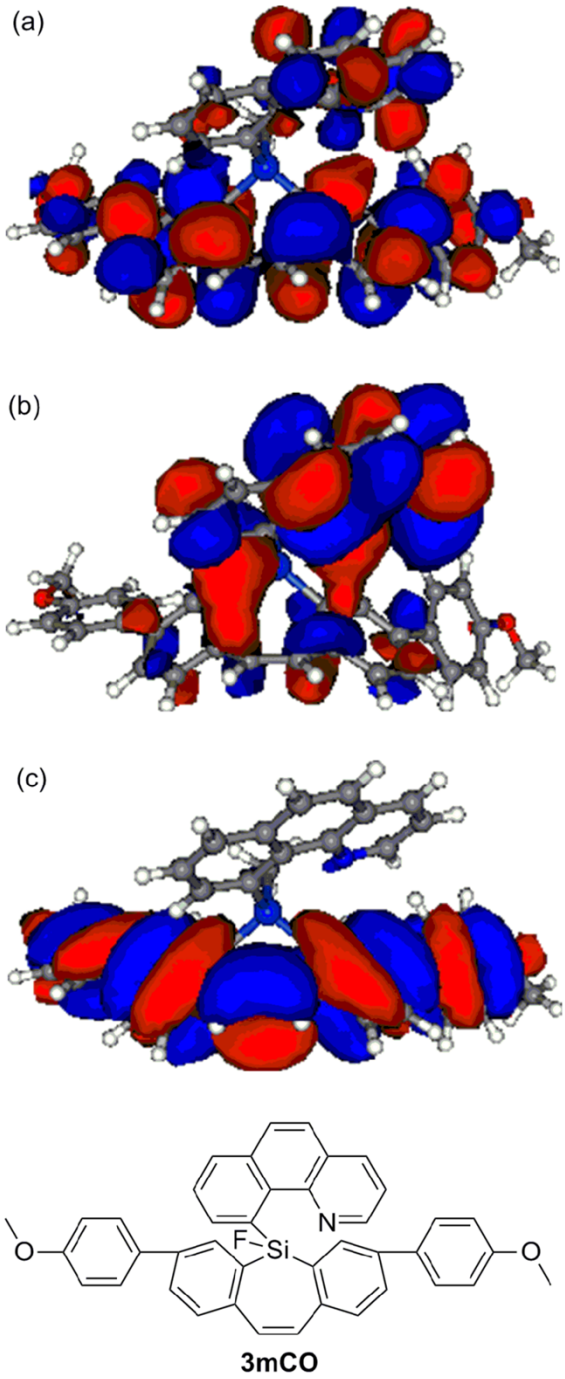


Figure S1. Kohn-Sham orbital diagrams of **3mCO** (PBE0-D3(bj)/def2-TZVP//TPSS-D3(bj)/def2-TZVP): (a) LUMO+2, (b) LUMO, (c) HOMO.

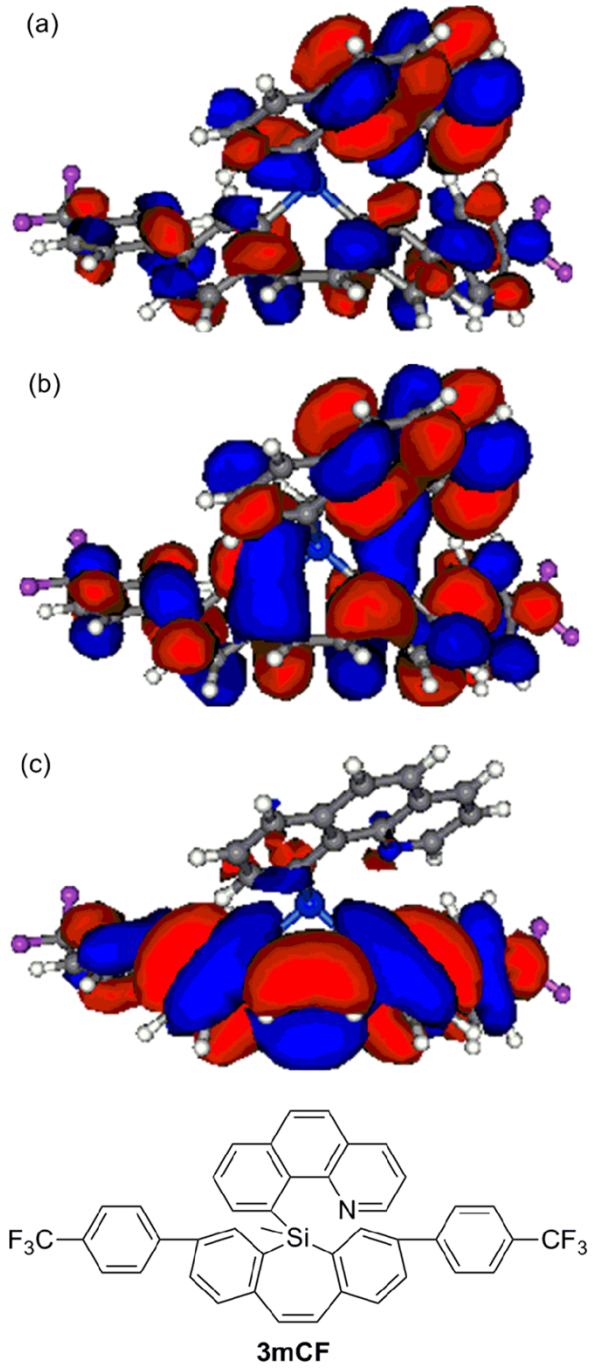


Figure S2. Kohn-Sham orbital diagrams of **3mCF** (PBE0-D3(bj)/def2-TZVP//TPSS-D3(bj)/def2-TZVP): (a) LUMO+1, (b) LUMO, (c) HOMO.

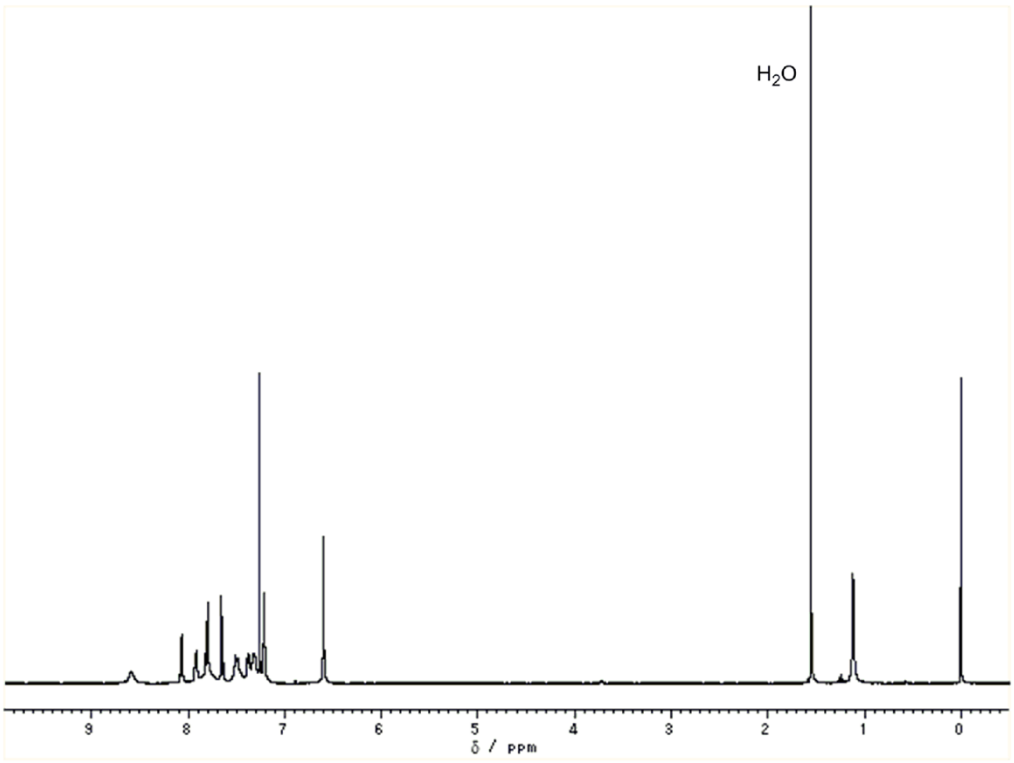


Figure S3. ^{1}H NMR spectrum of **2pC**.

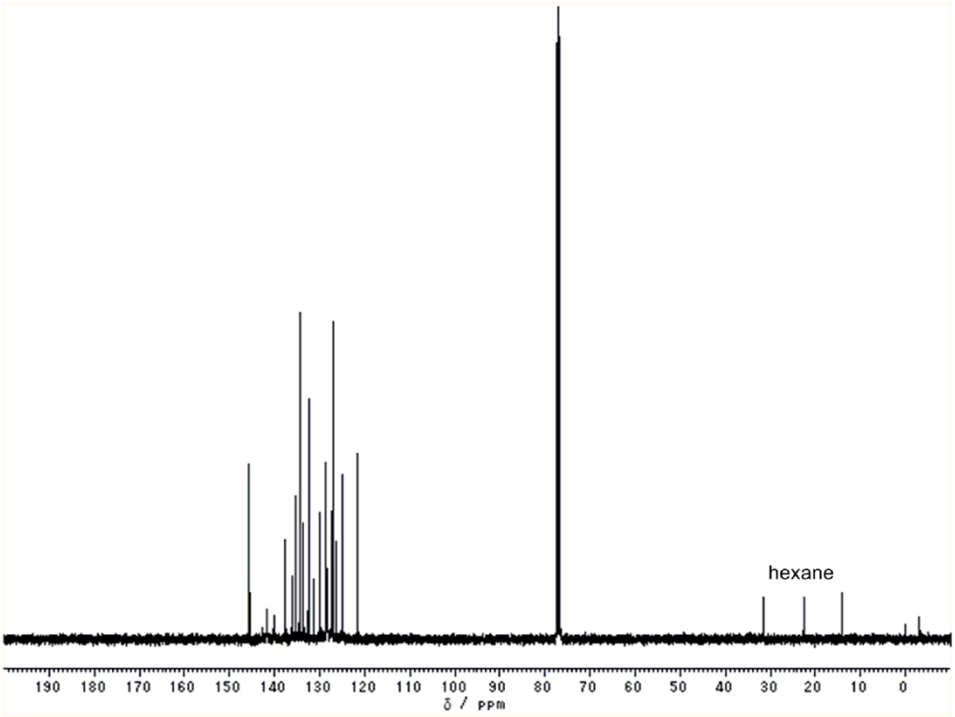


Figure S4. ^{13}C NMR spectrum of **2pC**.

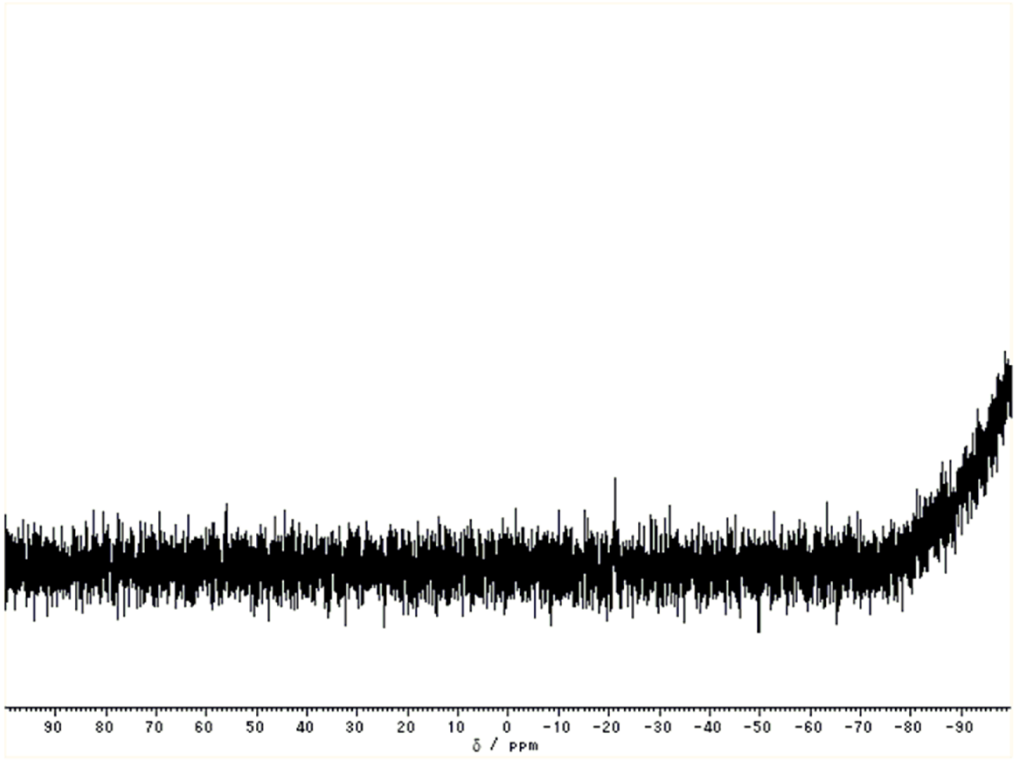


Figure S5. ^{29}Si NMR spectrum of **2pC**.

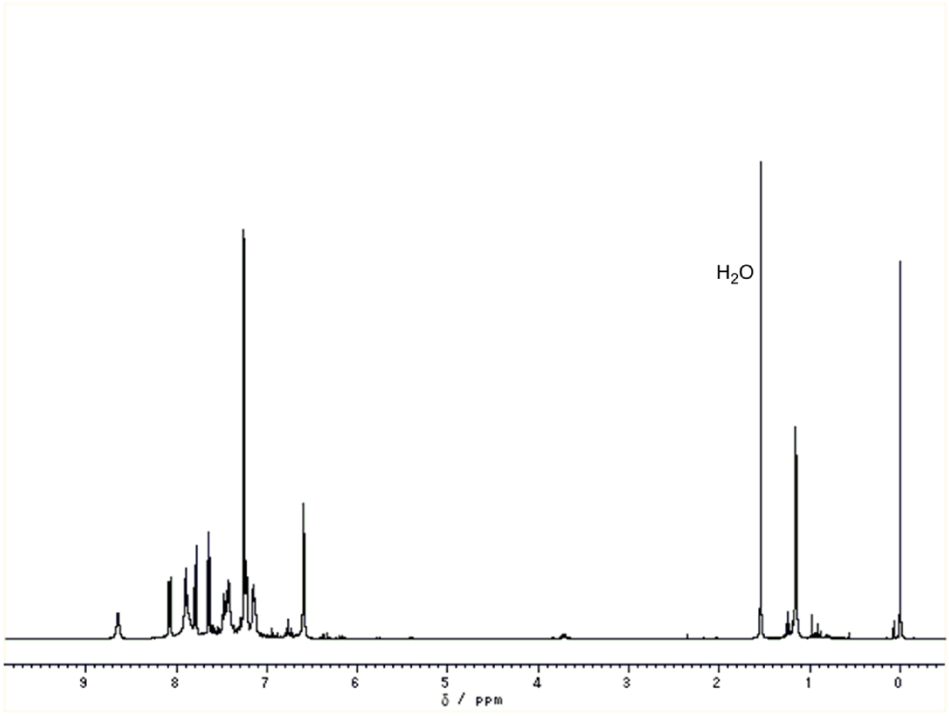


Figure S6. ^{1}H NMR spectrum of **2mC**.

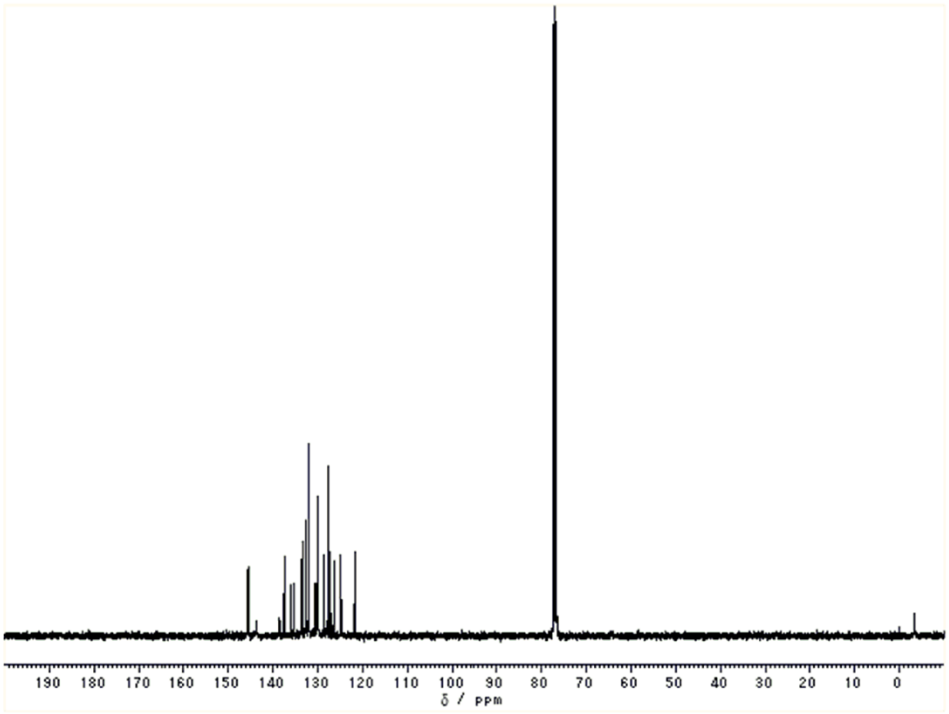


Figure S7. ^{13}C NMR spectrum of **2mC**.

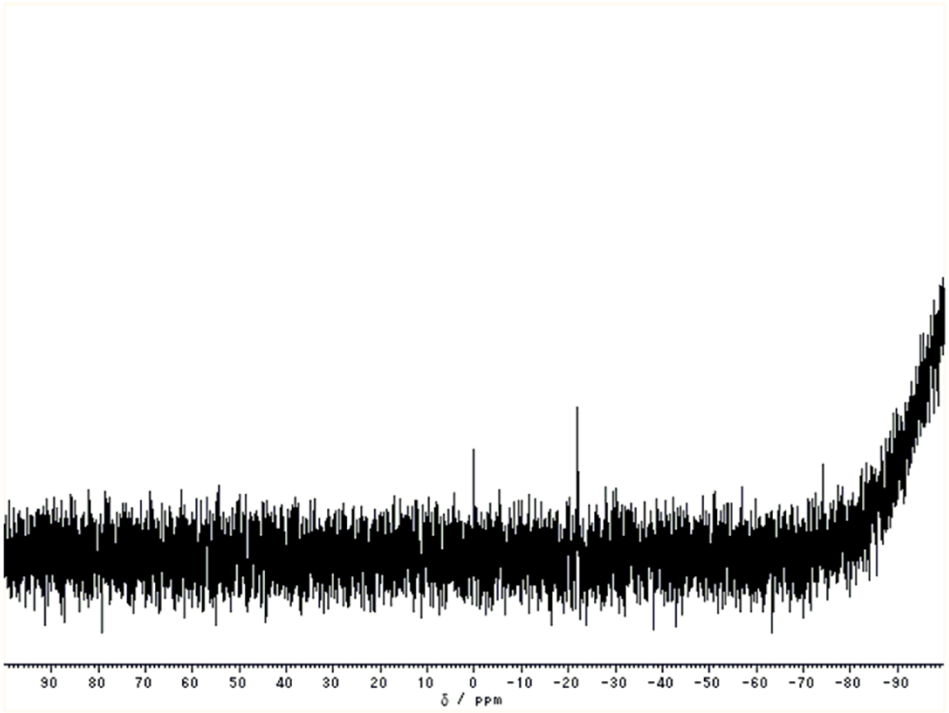


Figure S8. ^{29}Si NMR spectrum of **2mC**.

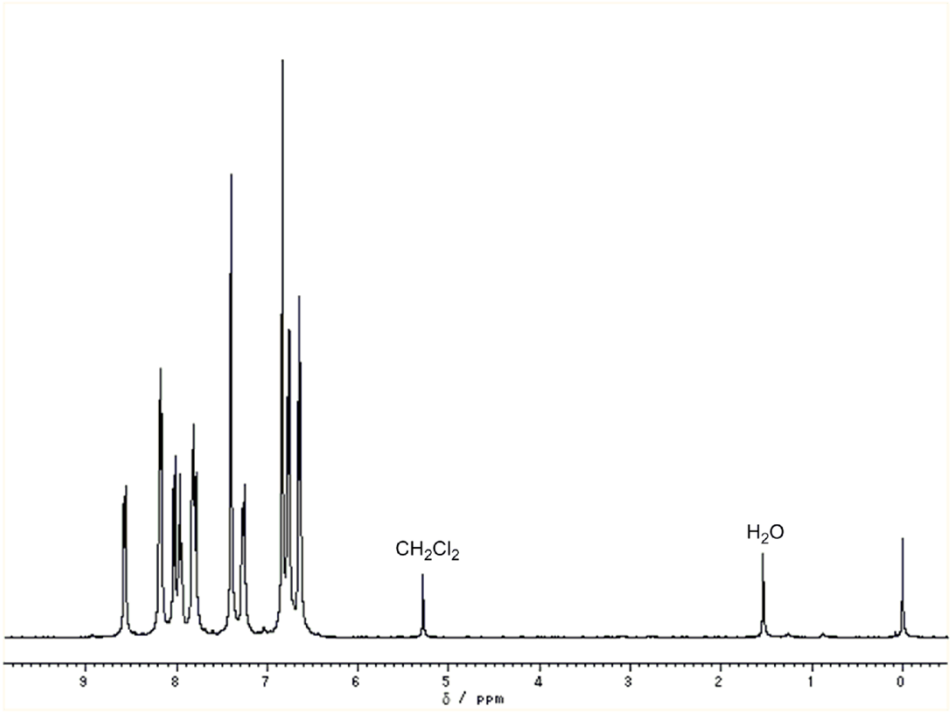


Figure S9. ^{1}H NMR spectrum of **2pF**.

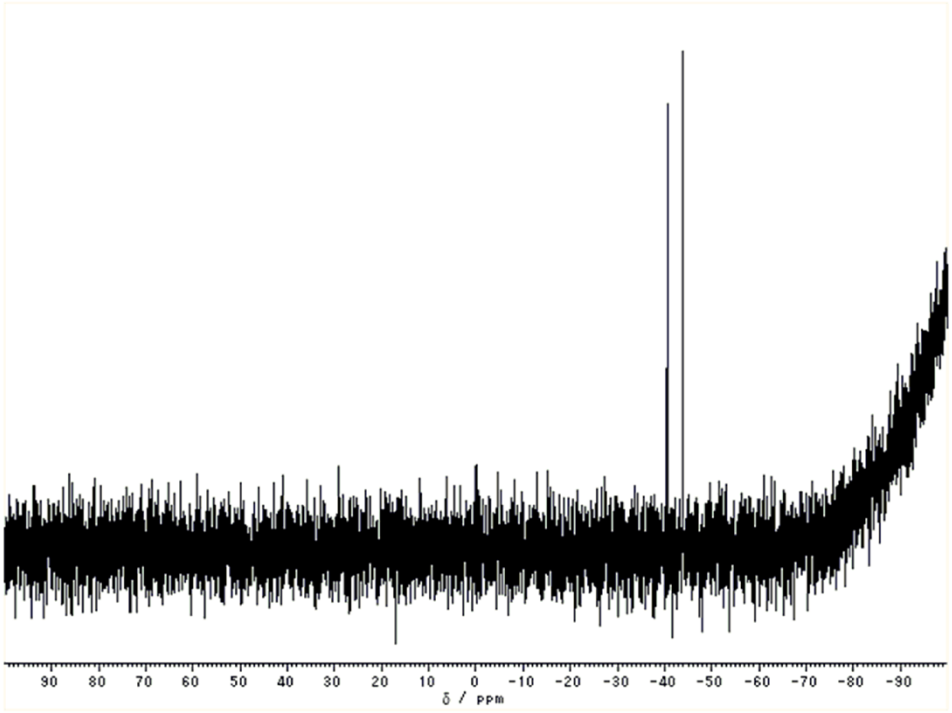


Figure S10. ^{29}Si NMR spectrum of **2pF**.

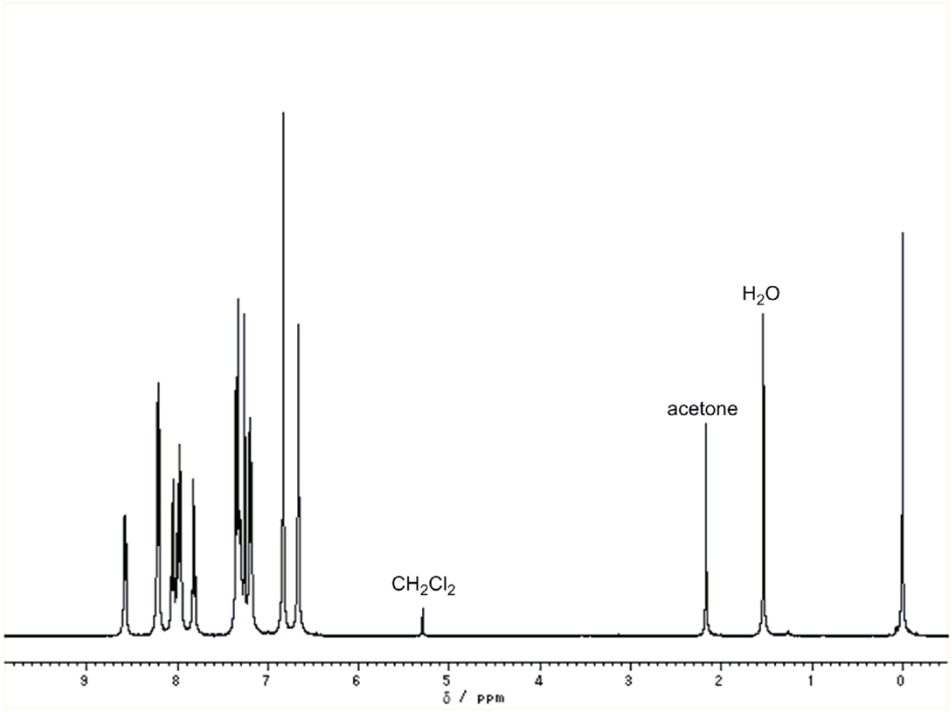


Figure S11. ^{1}H NMR spectrum of **2mF**.

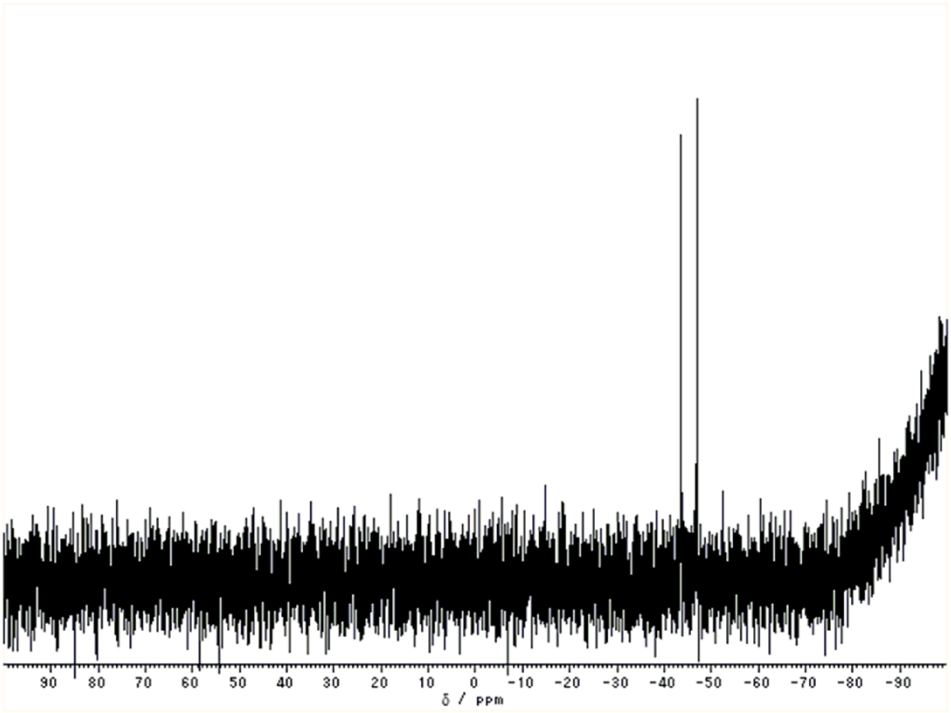


Figure S12. ^{29}Si NMR spectrum of **2mF**.

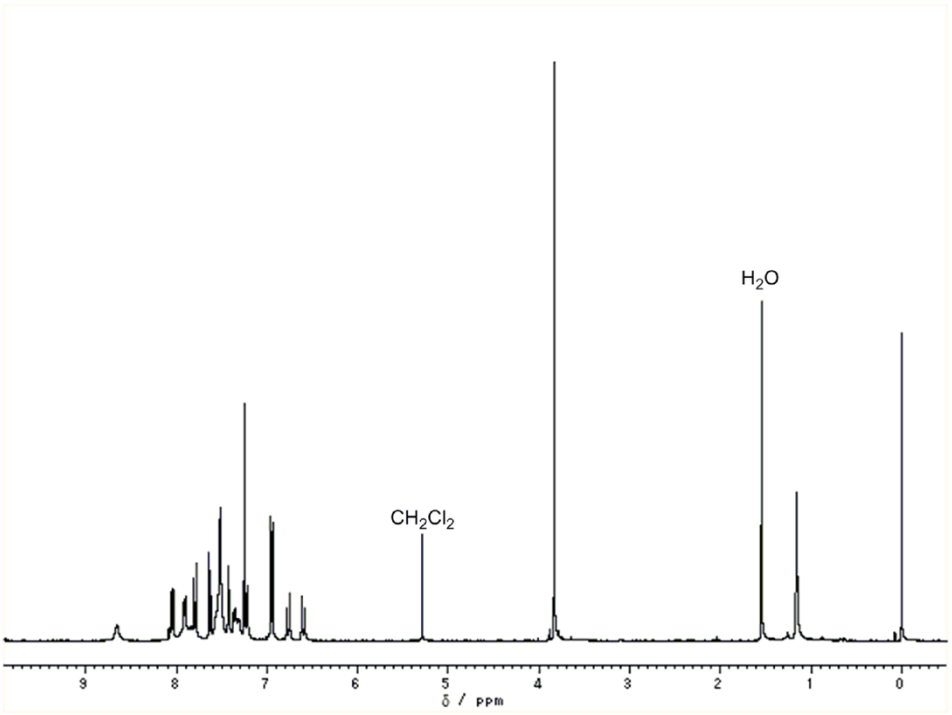


Figure S13. ^{1}H NMR spectrum of **3pCO**.

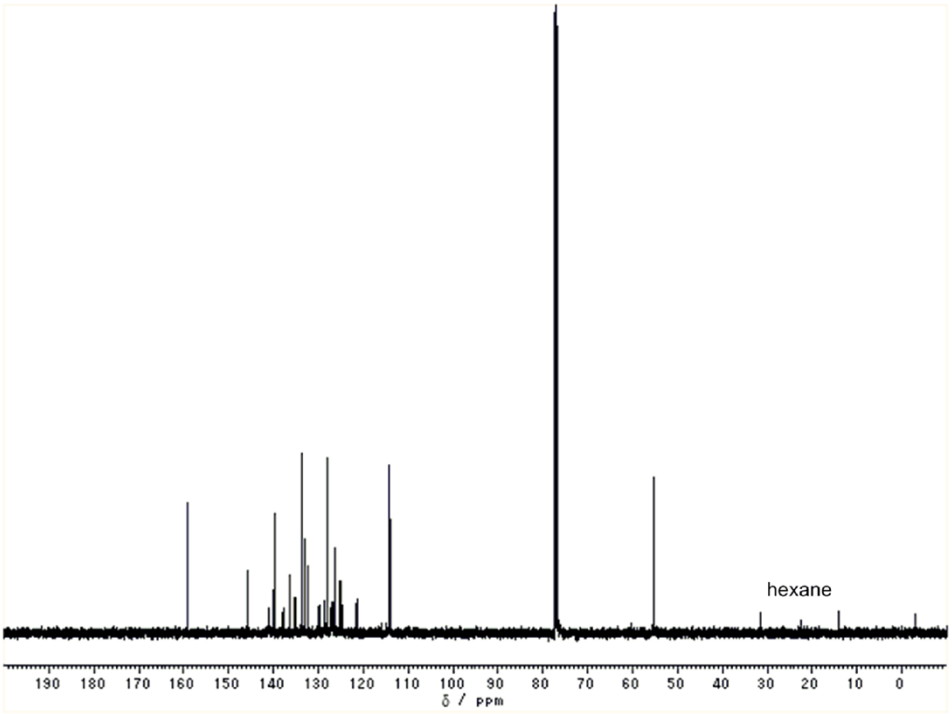


Figure S14. ^{13}C NMR spectrum of **3pCO**.

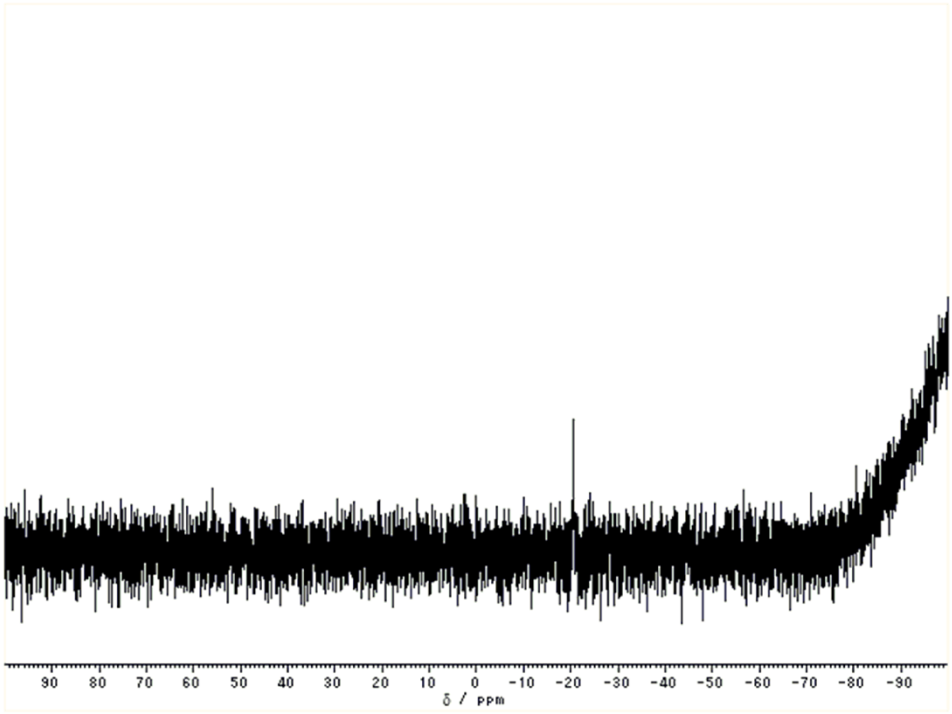


Figure S15. ^{29}Si NMR spectrum of **3pCO**.

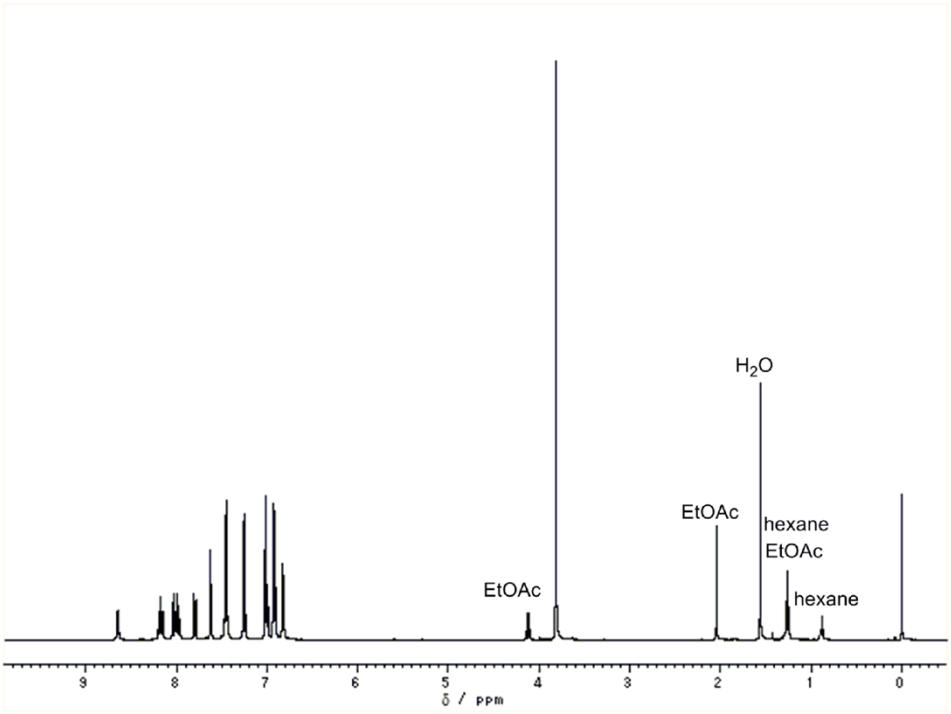


Figure S16. ^{1}H NMR spectrum of **3pFO**.

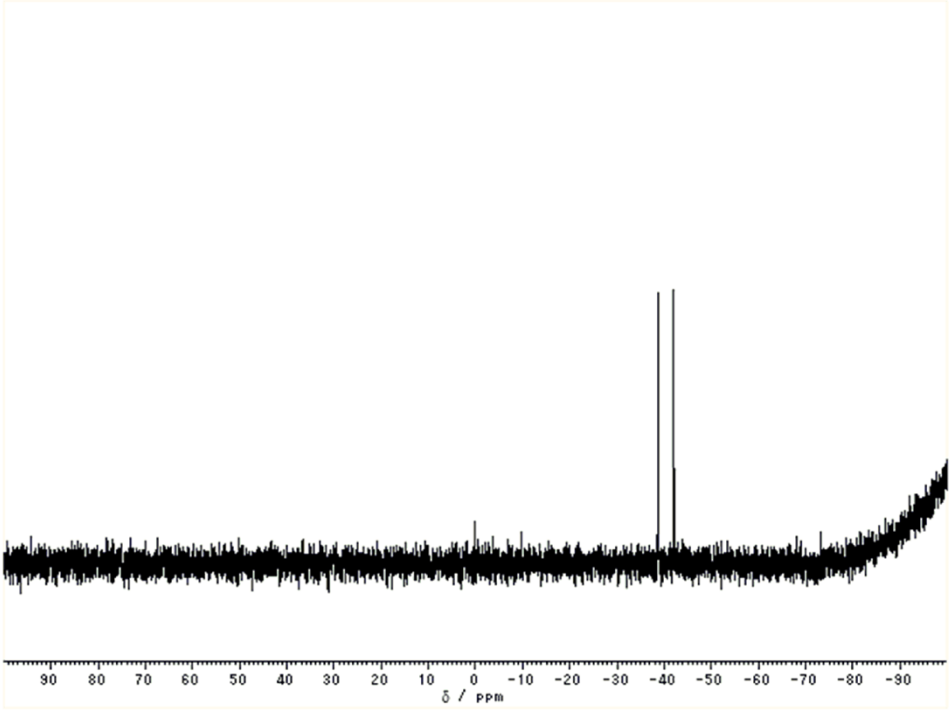


Figure S17. ^{29}Si NMR spectrum of **3pFO**.

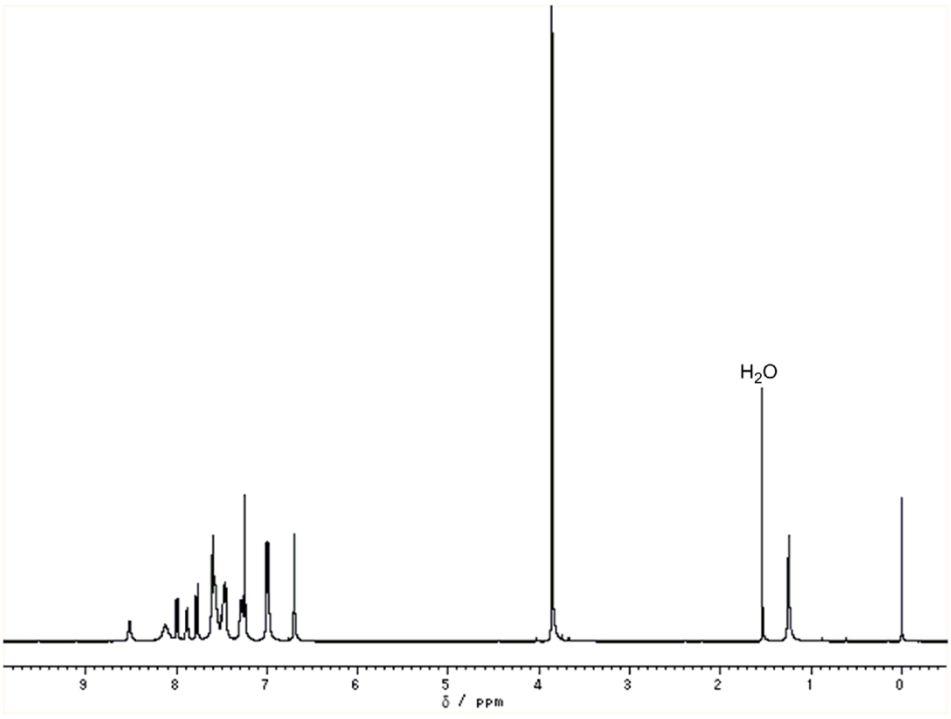


Figure S18. ^{1}H NMR spectrum of **3mCO**.

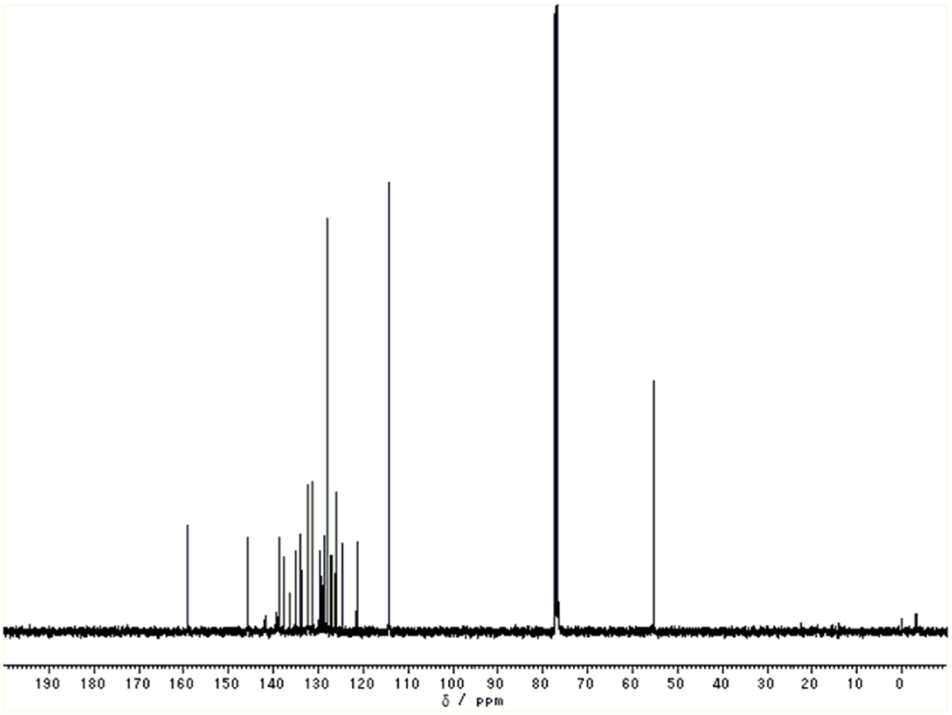


Figure S19. ^{13}C NMR spectrum of **3mCO**.

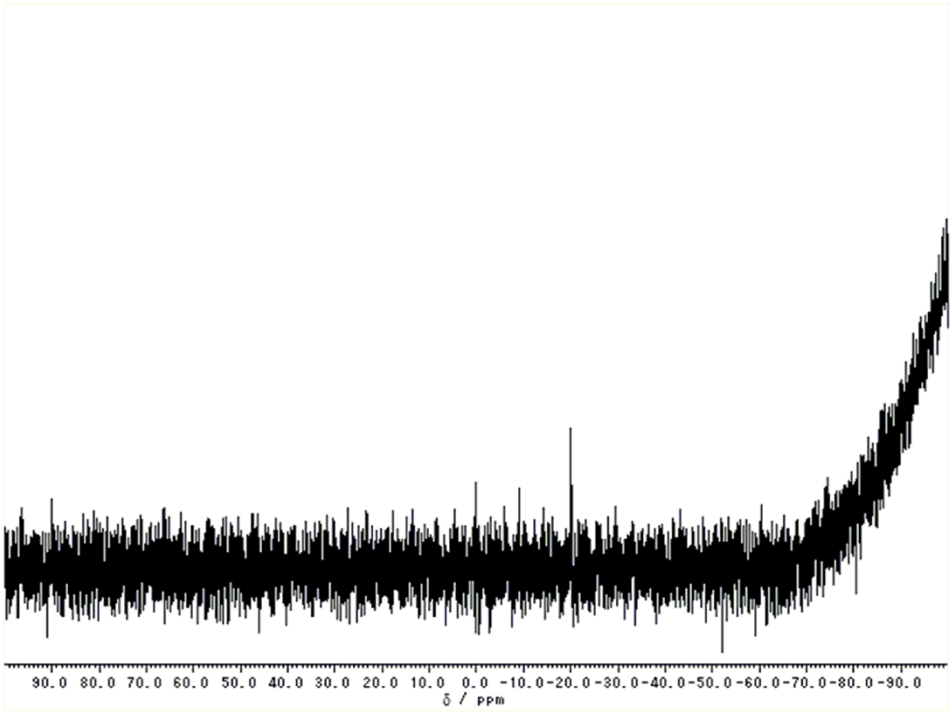


Figure S20. ^{29}Si NMR spectrum of **3mCO**.

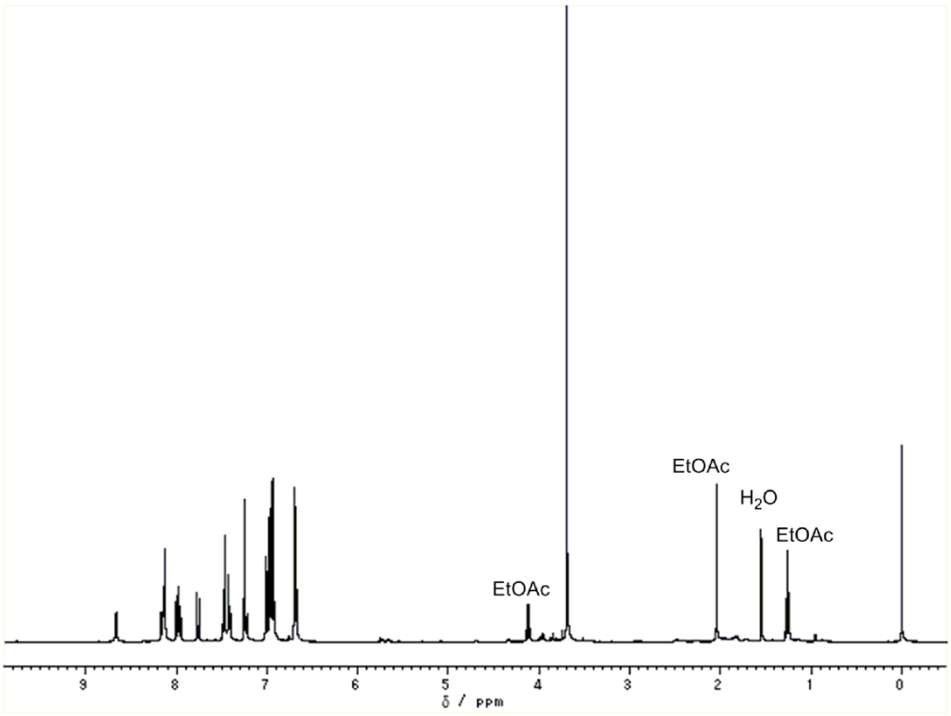


Figure S21. ^{1}H NMR spectrum of **3mFO**.

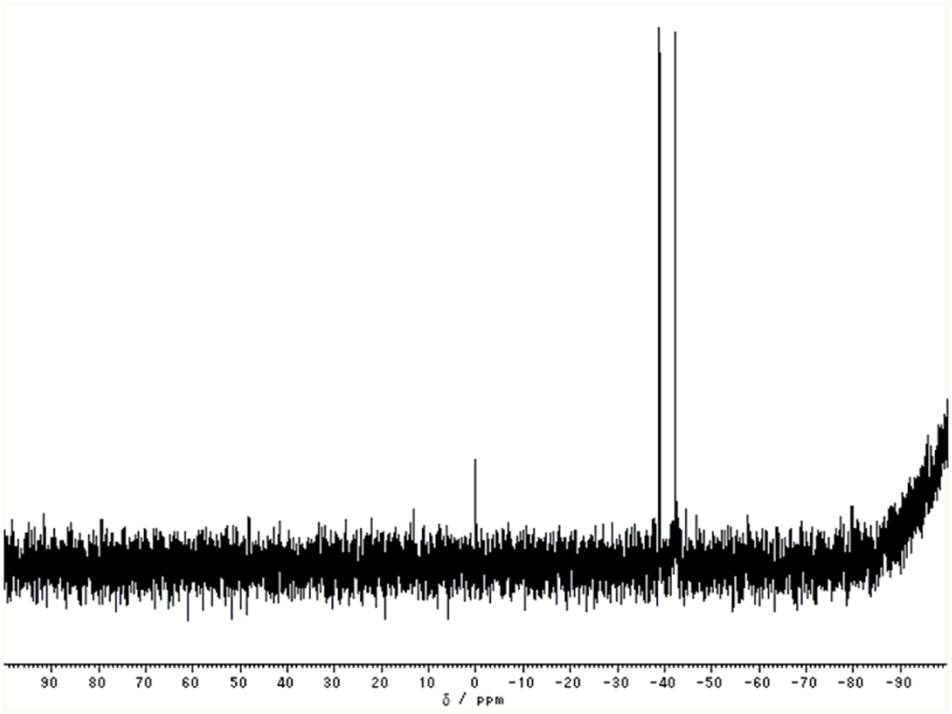


Figure S22. ^{29}Si NMR spectrum of **3mFO**.

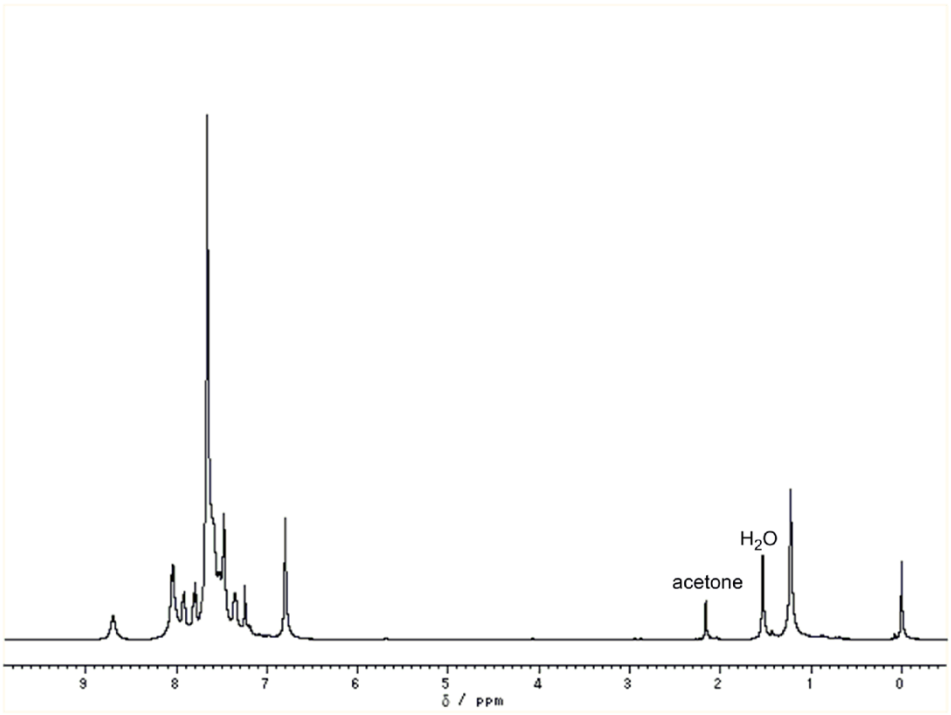


Figure S23. ^{1}H NMR spectrum of **3pCF**.

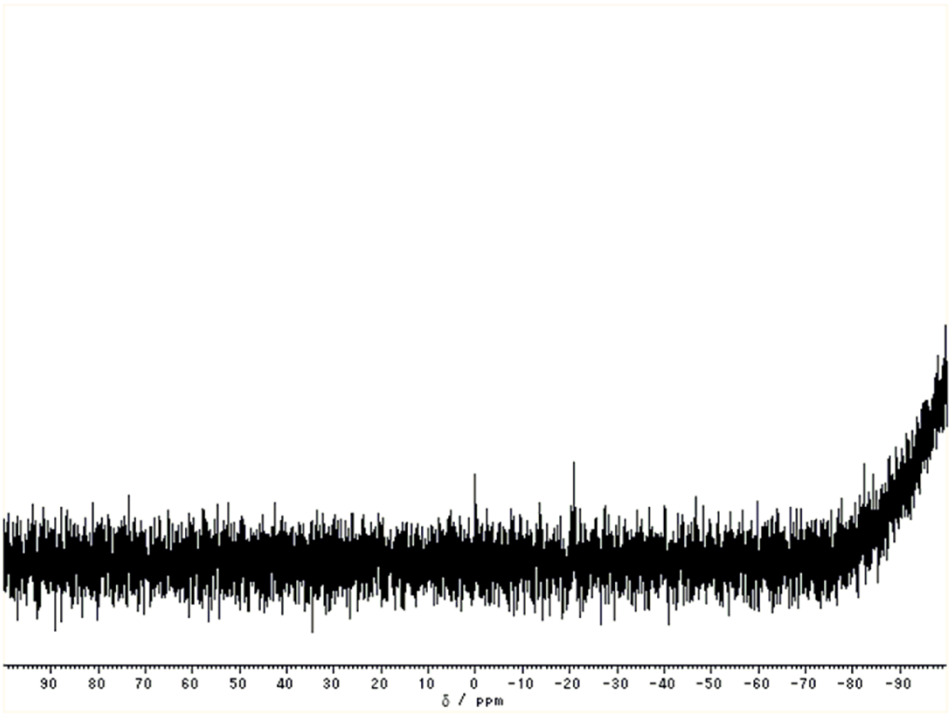


Figure S24. ^{29}Si NMR spectrum of **3pCF**.

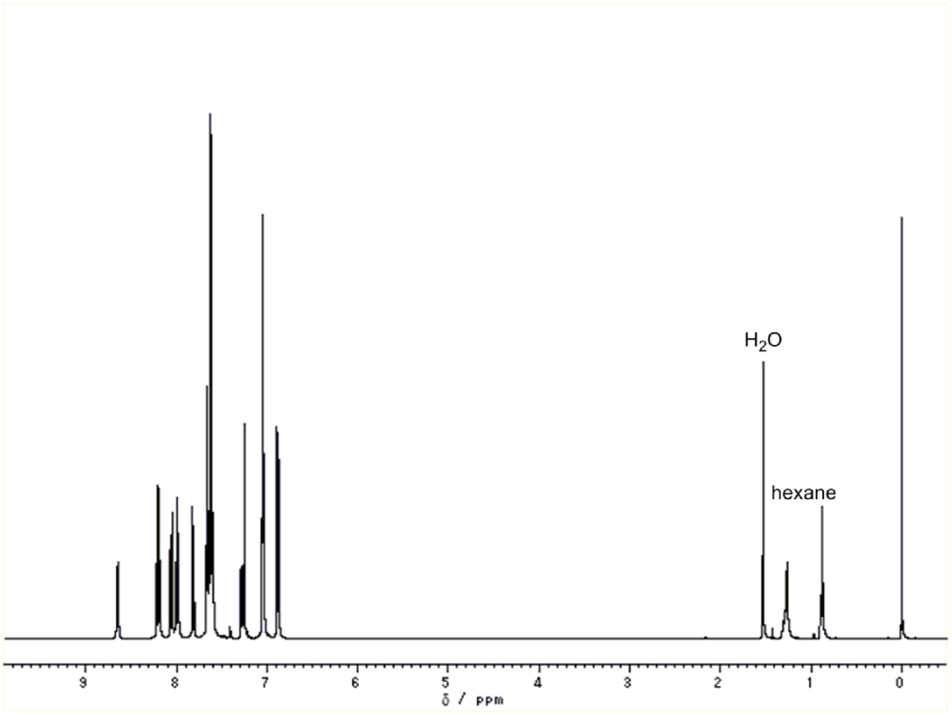


Figure S25. ^{1}H NMR spectrum of **3pFF**.

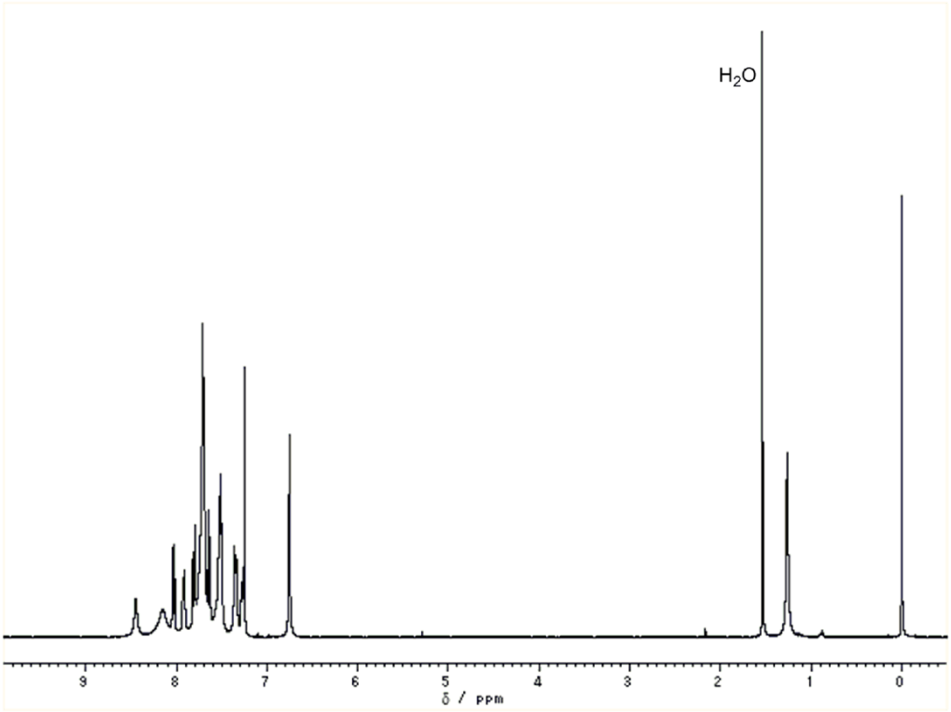


Figure S26. ^{1}H NMR spectrum of **3mCF**.

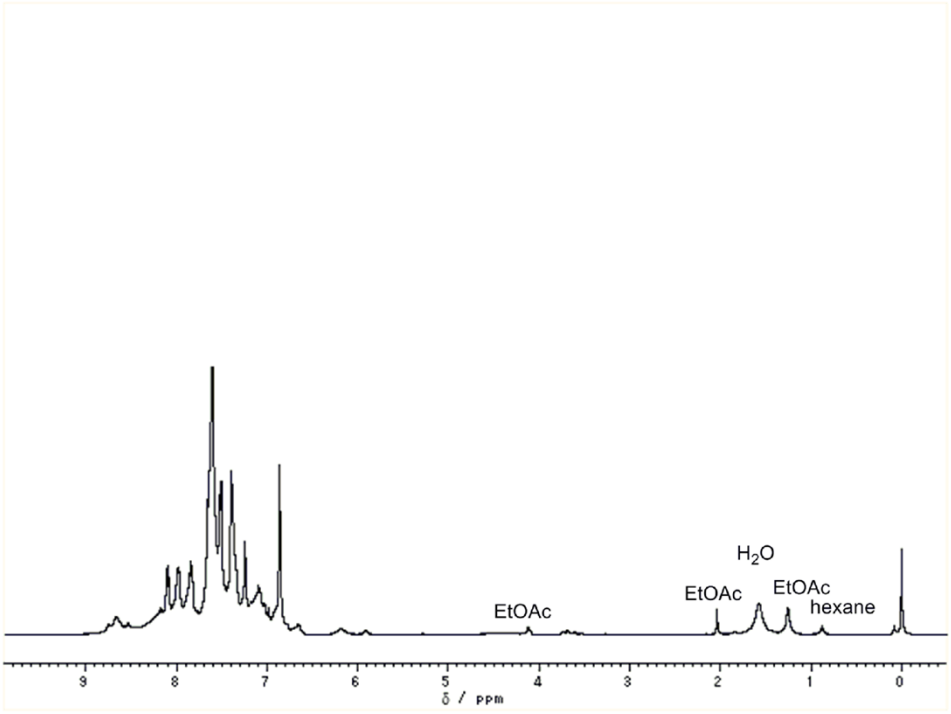


Figure S27. ^{1}H NMR spectrum of **3mFF**.

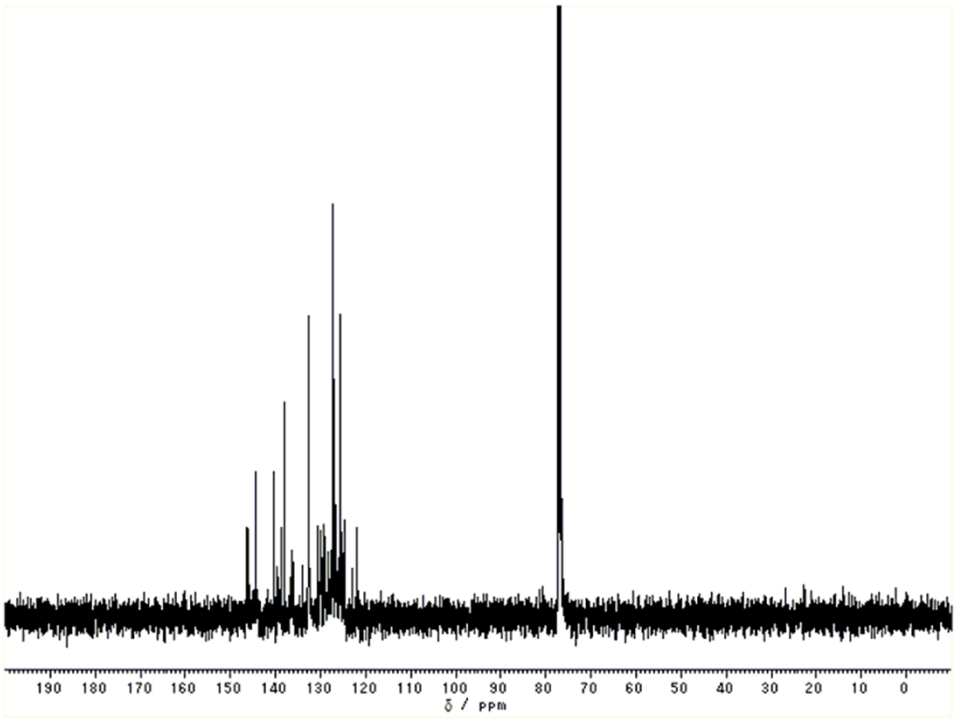


Figure S28. ^{13}C NMR spectrum of **3mFF**.

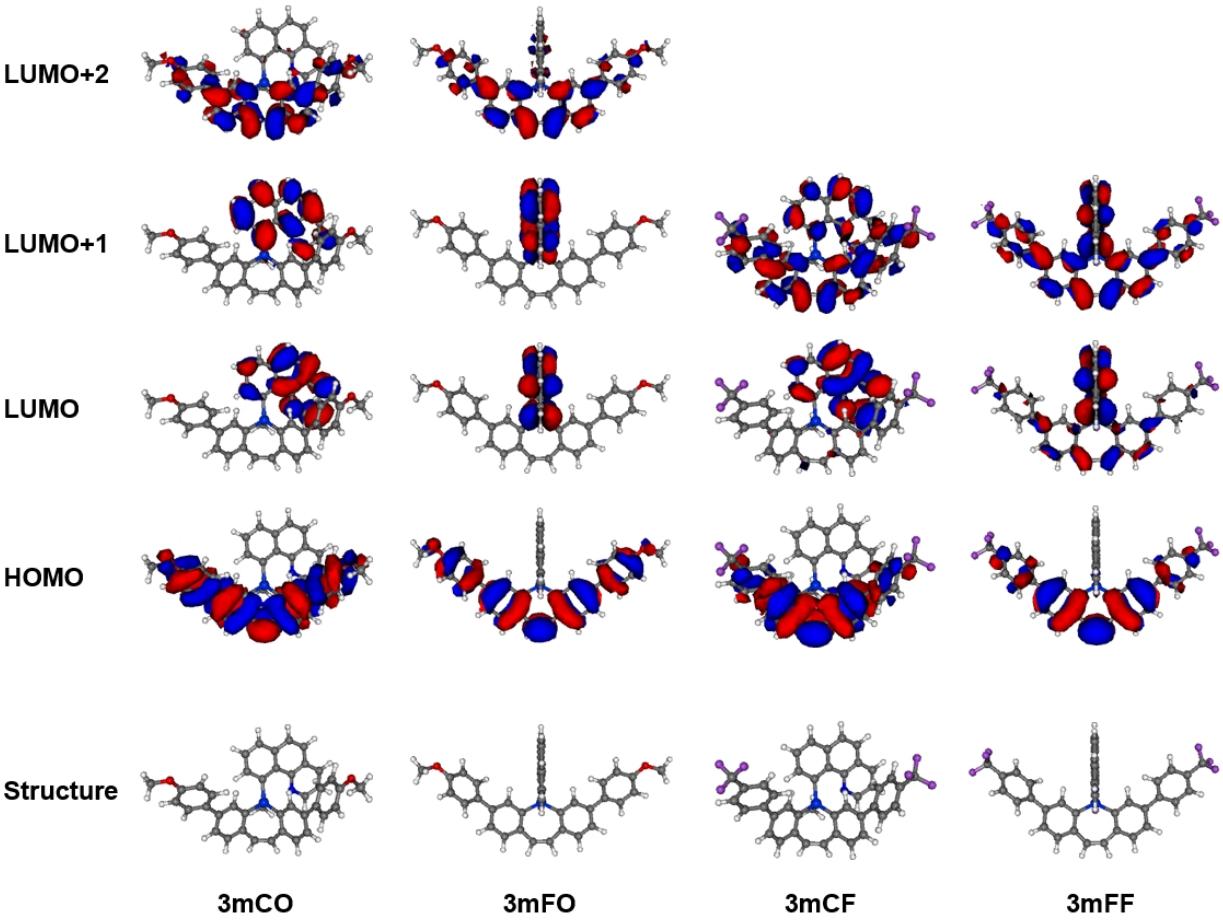
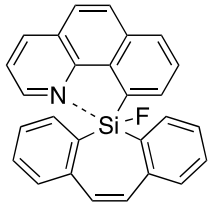


Figure S29. Optimized structures and Kohn-Sham orbital diagrams of the compounds (PBE0-D3(bj)/def2-TZVPP//TPSS-D3(bj)/def2-SVP).

Table S1. Structural parameters of **4** calculated with various functionals



4

Functional	Si–N bond (Å)	TBP_e (%)
M06L	2.86	45
B97-D3(bj)	2.54	60
B3LYP-D3(bj)	2.54	69
revPBE-D3(bj)	2.50	62
TPSSh-D3(bj)	2.44	77
TPSS-D3(bj)	2.43	68
M06-2X	2.37	80
expt.[a]	2.34	79

[a] Crystal structure (Tokoro, Y.; Tanaka, K.; Chujo, Y. *Org. Lett.* **2013,** 15, 2366.)