Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Probing Local Structure of Glass with Orientation-Dependent Luminescence

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1. General Information

Commercially available reagents and solvents were used as received, without further purification. Single crystals were grown by the slow diffusion of ethanol ((*S*)-**3a**-E) or hexane ((*S*)-**3a**-H, *rac*-**3a**, **3b**) into dichloromethane solutions. Crystalline powder samples for PXRD, photoluminescence spectroscopy, and thermal analysis were obtained by adding dichloromethane solution to ethanol, followed by filtration. Glass samples for the PXRD analysis were prepared by cooling the melt on glass plates or in vials with ice, followed by crushing. Film samples for photoluminescence spectra were prepared by addition of the macrocycles to 20 wt% toluene solution of ZEONEX 480 solution, followed by spin-coating onto glass plates. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker BioSpin DRX500 NMR or JEOL JNM-ECZ500R spectrometer. (500 MHz) spectrometer, with sample solutions prepared using CD_2Cl_2. Chemical shifts are reported in δ units downfield of the internal reference (Me_4Si). High-resolution mass spectra (HRMS) were recorded using a Bruker Compact (APCI) or a Hitachi High-Technologies Nano Frontier LD (ESI) spectrometer. The PXRD experiments were performed on a Bruker D8 ADVANCE diffractometer with Cu Kα (λ = 1.5406 Å) at room temperature. Simulated PXRD patterns were obtained using Mercury 2020.

2. Synthesis

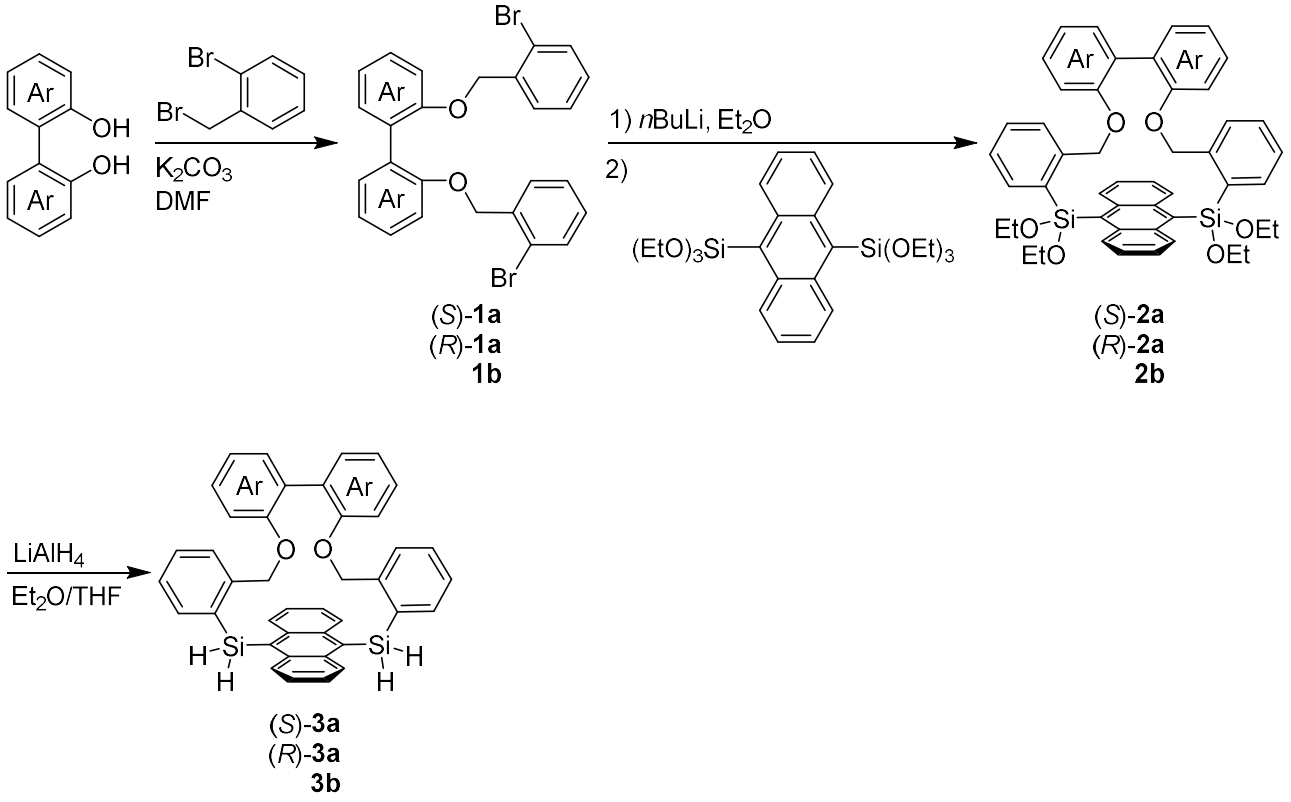
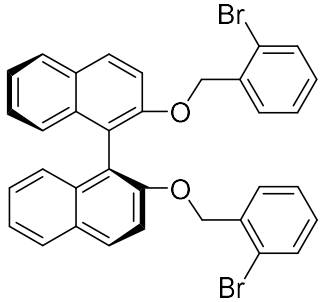


Fig. S1 Synthesis of macrocycles.

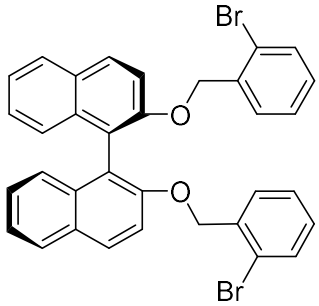
(*S*)-2,2'-Bis(2-bromobenzyloxy)-1,1'-binaphthyl ((*S*)-1a)



A solution of (*S*)-(–)-1,1'-bi-2-naphthol (4.58 g, 16.0 mmol), 2-bromobenzyl bromide (12.0 g, 48.0 mmol), potassium carbonate (8.85 g, 64.0 mmol) in *N,N*-dimethylformamide (48 mL) was stirred at 70 ºC for 11 h, followed by addition of water (ca. 100 mL). The precipitate was collected by filtration and washed by water and methanol. The crude product was purified by recrystallization from dichloromethane/methanol to give a white solid (9.12 g, 14.6 mmol, 91% yield). Mp: 137-139 ºC ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 8.01 (d, 2H, Ar-*H*, *J* = 9.0 Hz), 7.92 (d, 2H, Ar-*H*, *J* = 8.2 Hz), 7.46 (m, 4H, Ar-*H*), 7.37 (ddd, 2H, Ar-*H*, *J* = 8.1, 6.7, 1.4 Hz), 7.26 (ddd, 2H, Ar-*H*, *J* = 8.4, 6.8, 1.5 Hz), 7.21 (d, 2H, Ar-*H*, *J* = 8.5 Hz), 7.03 (ddd, 2H, Ar-*H*, *J* = 7.9, 7.4, 1.8 Hz), 6.94 (td, 2H, Ar-*H*, *J* = 7.5, 1.2 Hz), 6.87 (m, 2H, Ar-*H*), 5.13 (m, 4H, -OCH_2-) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 154.4, 137.2, 134.7, 132.7,

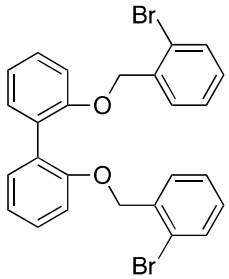
130.15, 130.10, 129.3, 128.7, 128.6, 127.8, 127.1, 125.8, 124.5, 122.0, 120.8, 115.9, 71.0 ppm. HRMS (ESI-TOF) calcd for $C_{34}H_{24}Br_2O_2$ [M]$^+$: 622.0138; found: 622.0156. $[\alpha]_D^{20}$ = -42 (*c* = 1.00, THF).

(*R*)-2,2'-Bis(2-bromobenzyloxy)-1,1'-binaphthyl ((*R*)-1a)



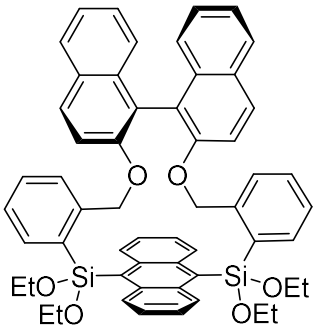
A solution of (*R*)-(–)-1,1'-bi-2-naphthol (2.86 g, 10.0 mmol), 2-bromobenzyl bromide (6.00 g, 24.0 mmol), potassium carbonate (4.15 g, 30.0 mmol) in *N,N*-dimethylformamide (30 mL) was stirred at 70 ºC for 46 h, followed by addition of water (ca. 50 mL). The mixture was extracted with diethyl ether, washed with water and brine, dried over $MgSO_4$, and concentrated. The crude product was purified by recrystallization from dichloromethane/ethanol to give a white solid (4.49 g, 7.19 mmol, 72% yield). Mp: 137-139 ºC ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 8.00 (d, 2H, Ar-*H*, *J* = 9.2 Hz), 7.91 (m, 2H, Ar-*H*), 7.47-7.42 (m, 4H, Ar-*H*), 7.36 (ddd, 2H, Ar-*H*, *J* = 8.2, 6.7, 1.2 Hz), 7.25 (t, 2H, Ar-*H*, *J* = 7.4 Hz), 7.19 (d, 2H, Ar-*H*, *J* = 8.1 Hz), 7.03 (t, 2H, Ar-*H*, *J* = 7.5 Hz), 6.92 (t, 2H, Ar-*H*, *J* = 7.5 Hz), 6.85 (d, 2H, Ar-*H*, *J* = 7.5 Hz), 5.16-5.07 (m, 4H, -OCH_2-) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 154.3, 137.2, 134.7, 132.7, 130.1, 129.3, 128.7, 128.5, 127.8, 127.0, 125.8, 124.4, 121.9, 120.7, 115.8, 70.8 ppm. HRMS (APCI-TOF) calcd for $C_{34}H_{25}Br_2O_2$ [M+H]$^+$: 623.0216; found: 623.0202. $[\alpha]_D^{20}$ = +47 (*c* = 1.00, THF).

2,2'-Bis(2-bromobenzyloxy)biphenyl (1b)



A solution of 2,2'-dihydoroxybiphenyl (1.49 g, 8.00 mmol), 2-bromobenzyl bromide (6.00 g, 24.0 mmol), potassium carbonate (4.42 g, 32.0 mmol) in *N,N*-dimethylformamide (24 mL) was stirred at 70 ºC for 11 h, followed by addition of water (ca. 50 mL). The mixture was extracted with diethyl ether, washed with water and brine, dried over Na_2SO_4, and concentrated. The residue was subjected to column chromatography on silica gel with hexane/ethyl acetate (100/1 to 100/2) to give a white solid (3.55 g, 6.77 mmol, 85% yield). Mp: 65-66 ºC. ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 7.50 (m, 2H, Ar-*H*), 7.35 (m, 4H, Ar-*H*), 7.19 (d, 2H, Ar-*H*, *J* = 6.8 Hz), 7.09 (m, 6H, Ar-*H*), 7.01 (m, 2H, Ar-*H*), 5.06 (s, 4H, -OCH_2-) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 156.4, 137.1, 132.8, 132.1, 129.4, 129.3, 128.9, 128.7, 127.9, 122.0, 121.5, 113.0, 70.1 ppm. HRMS (ESI-TOF) calcd for $C_{26}H_{21}Br_2O_2$ [M+H]$^+$: 522.9903; found: 522.9908.

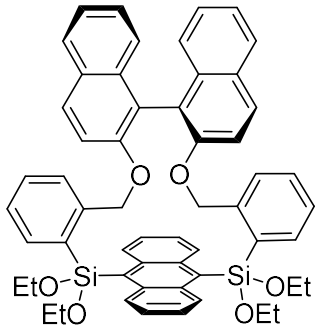
Macrocycle (*S*)-2a



*n*BuLi in hexane (1.6 M, 4.5 mL, 7.2 mmol) was added dropwise to a suspension of (*S*)-2,2'-bis(2-bromobenzyloxy)-1,1'-binaphthyl (2.25 g, 3.60 mmol) in diethyl ether (36 mL) at –17 ºC under Ar. After stirring at –17 ºC for 1 h, 9,10-bis(triethoxysilyl)anthracene[1] (1.81 g, 3.60 mmol) in diethyl ether (36 mL) was added over 2 h at –17 ºC, followed by stirring at room temperature for 19 h. The reaction mixture was quenched with aq. 1 M HCl. The organic layer was collected, washed with water and brine, dried over Na_2SO_4, and concentrated. The residue was subjected to column chromatography on silica gel with hexane/ethyl acetate (100:1 to 100:3) to give a pale yellow solid (1.75 g, 2.04 mmol, 57% yield). Mp: 123-127 ºC ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 9.02 (d, 2H,

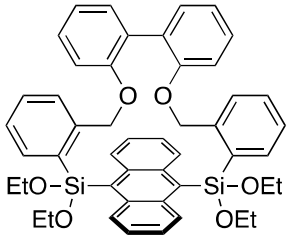
Ar-*H*, *J* = 8.8 Hz), 8.35 (d, 2H, Ar-*H*, *J* = 8.8 Hz), 8.26 (d, 2H, Ar-*H*, *J* = 7.5 Hz), 7.78 (d, 2H, Ar-*H*, *J* = 8.5 Hz), 7.66 (d, 2H, Ar-*H*, *J* = 9.1 Hz), 7.38 (m, 2H, Ar-*H*), 7.27 (m, 6H, Ar-*H*), 7.16 (m, 4H, Ar-*H*), 7.05 (d, 2H, Ar-*H*, *J* = 8.5 Hz), 6.92 (d, 2H, Ar-*H*, *J* = 7.9 Hz), 6.76 (d, 2H, Ar-*H*, *J* = 9.1 Hz), 4.13 (d, 2H, -OCH_2-, *J* = 14.5 Hz), 4.00 (m, 2H, -CH_2-CH_3), 3.89 (m, 6H, -CH_2-CH_3), 3.63 (d, 2H, -OCH_2-, *J* = 14.5 Hz), 1.37 (t, 6H, -CH_2-CH_3, *J* = 6.9 Hz), 1.23 (t, 6H, -CH_2-CH_3, *J* = 7.0 Hz) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 155.4, 143.9, 137.3, 137.1, 135.4, 134.1, 134.0, 132.6, 130.7, 130.4, 130.0, 129.8, 128.7, 128.5, 127.1, 126.8, 125.9, 125.8, 125.4, 125.2, 124.2, 120.6, 117.5, 73.0, 59.8, 18.73, 18.66 ppm. ^{29}Si NMR (99 MHz, CD_2Cl_2): δ = –31.1 ppm. HRMS (ESI-TOF) calcd for $C_{56}H_{52}O_6Si_2$ [M]$^+$: 876.3297; found: 876.3306. $[\alpha]_D^{20}$ = +14 (*c* = 1.00, THF).

Macrocycle (*R*)-2a



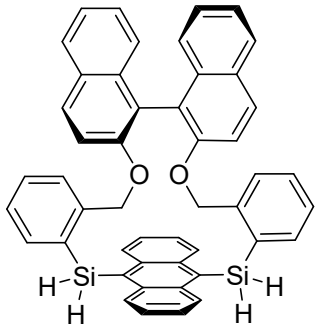
*n*BuLi in hexane (1.6 M, 4.0 mL, 6.4 mmol) was added dropwise to a suspension of (*R*)-2,2'-bis(2-bromobenzyloxy)-1,1'-binaphthyl (2.00 g, 3.20 mmol) in diethyl ether (32 mL) at 0 ºC under Ar. After stirring at 0 ºC for 15 min, 9,10-bis(triethoxysilyl)anthracene (1.61 g, 3.20 mmol) in diethyl ether (32 mL) was added over 40 min at 0 ºC, followed by stirring at room temperature for 20 h. The reaction mixture was quenched with aq. 1 M HCl. The organic layer was collected, washed with water and brine, dried over $MgSO_4$, and concentrated. The residue was subjected to column chromatography on silica gel with hexane/toluene (2:1 to 2:3) to give a pale yellow solid (0.647 g, 0.738 mmol, 23% yield). Mp: 127-130 ºC. ^{1}H NMR (500 MHz, CD_2Cl_2): δ =9.03 (d, 2H, Ar-*H*, *J* = 9.2 Hz), 8.34 (d, 2H, Ar-*H*, *J* = 8.6 Hz), 8.26 (d, 2H, Ar-*H*, *J* = 7.2 Hz), 7.78 (d, 2H, Ar-*H*, *J* = 8.6 Hz), 7.67 (d, 2H, Ar-*H*, *J* = 8.6 Hz), 7.39 (t, 2H, Ar-*H*, *J* = 7.2 Hz), 7.33-7.23 (m, 6H, Ar-*H*), 7.17 (t, 2H, Ar-*H*, *J* = 7.6 Hz), 7.13 (t, 2H, Ar-*H*, *J* = 7.6 Hz), 7.04 (d, 2H, Ar-*H*, *J* = 8.6 Hz), 6.93 (d, 2H, Ar-*H*, *J* = 8.0 Hz), 6.76 (d, 2H, Ar-*H*, *J* = 9.2 Hz), 4.13 (d, 2H, -OCH_2-, *J* = 14.9 Hz), 4.04-3.97 (m, 2H, -CH_2-CH_3), 3.94-3.83 (m, 6H, -CH_2-CH_3), 3.62 (d, 2H, -OCH_2-, *J* = 14.9 Hz), 1.37 (t, 6H, -CH_2-CH_3, *J* = 6.9 Hz), 1.23 (t, 6H, -CH_2-CH_3, *J* = 6.9 Hz) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 155.3, 143.9, 137.2, 137.1, 135.3, 134.1, 133.9, 132.6, 130.7, 130.4, 130.0, 128.7, 128.4, 127.1, 126.7, 125.9, 125.8, 125.4, 125.2, 124.2, 120.6, 117.4, 72.9, 59.8, 18.72, 18.65 ppm. HRMS (APCI-TOF) calcd for $C_{56}H_{53}O_6Si_2$ [M+H]$^+$: 877.3375; found: 877.3359. $[\alpha]_D^{20}$ = -14 (*c* = 1.00, THF)

Macrocycle 2b



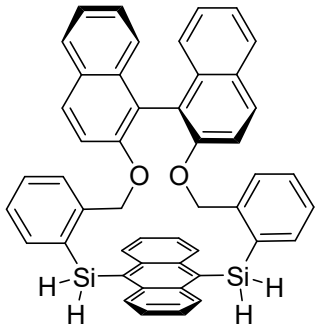
*n*BuLi in hexane (1.6 M, 2.5 mL, 4.0 mmol) was added dropwise to a suspension of 2,2'-bis(2-bromobenzyloxy)biphenyl (1.05 g, 2.00 mmol) in diethyl ether (40mL) at –17 ºC under Ar. After stirring at –17 ºC for 1 h, 9,10-bis(triethoxysilyl)anthracene (1.01 g, 2.00 mmol) in diethyl ether (40 mL) was added over 2 h at –17 ºC, followed by stirring at room temperature for 19 h. The reaction mixture was quenched with aq. 1 M HCl. The organic layer was collected, washed with water and brine, dried over Na_2SO_4, and concentrated. The residue was subjected to column chromatography on silica gel with hexane/toluene (3/1 to 1/1) to give a pale yellow solid (0.296 g, 0.381 mmol, 19% yield). Mp: 208-210 ºC ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 9.17 (d, 2H, Ar-*H*, *J* = 9.1 Hz), 8.33 (dd, 2H, Ar-*H*, *J* = 7.4, 1.1 Hz), 8.21 (d, 2H, Ar-*H*, *J* = 8.8 Hz), 7.43 (t, 2H, Ar-*H*, *J* = 7.3 Hz), 7.34 (m, 4H, Ar-*H*), 7.13 (dd, 2H, Ar-*H*, *J* = 7.4, 1.7 Hz), 7.06 (m, 6H, Ar-*H*), 6.91 (td, 2H, Ar-*H*, *J* = 7.4, 1.0 Hz), 6.38 (dd, 2H, Ar-*H*, *J* = 8.2, 1.0 Hz), 4.29 (d, 2H, -OCH_2-, *J* = 15.8 Hz), 4.22 (m, 2H, -CH_2-CH_3), 4.12 (dq, 2H, -CH_2-CH_3 *J* = 10.3, 7.0 Hz), 4.01 (dq, 2H, -CH_2-CH_3 *J* = 10.2, 7.0 Hz), 3.82 (dq, 2H, -CH_2-CH_3 *J* = 10.2, 7.0 Hz), 3.45 (d, 2H, -OCH_2-, *J* = 16.1 Hz), 1.38 (br, t, 6H, -CH_2-CH_3, *J* = 7.1 Hz), 1.36 (br, t, 6H, -CH_2-CH_3, *J* = 7.1 Hz) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 157.5, 144.0, 137.2, 135.5, 134.0, 131.9, 131.2, 130.79, 130.77, 129.1, 128.9, 128.2, 126.9, 125.6, 125.3, 124.4, 121.7, 114.2, 72.7, 60.1, 59.8, 18.8, 18.7 ppm. ^{29}Si NMR (99 MHz, CD_2Cl_2): δ = –32.0 ppm. HRMS (ESI-TOF) calcd for $C_{48}H_{48}O_6Si_2$ [M]$^+$: 776.2984; found: 776.2984.

Macrocycle (*S*)-3a



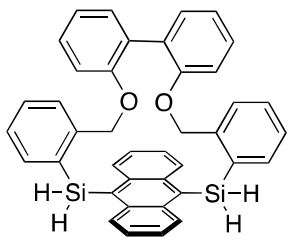
Macrocycle **(*S*)-2a** (1.36 g, 1.60 mmol) in diethyl ether (3.2 mL) was added dropwise to a suspension of lithium aluminium hydride (0.121 g, 3.20 mmol) in diethyl ether (3.2 mL) at 0 ºC under Ar. After stirring at room temperature for 11.5 h, the reaction mixture was quenched with aq. 1 M HCl. The mixture was extracted with diethyl ether, washed with water and brine, dried over Na_2SO_4, and concentrated. The residue was subjected to column chromatography on silica gel with hexane/toluene (3:1 to 1:1) to give a pale yellow solid (0.715 g, 1.02 mmol, 64% yield). Mp: 210-212 ºC. ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 8.65 (d, 2H, Ar-*H*, *J* = 9.1 Hz), 8.15 (d, 2H, Ar-*H*, *J* = 8.8 Hz), 7.97 (d, 2H, Ar-*H*, *J* = 7.2 Hz), 7.76 (d, 2H, Ar-*H*, *J* = 8.2 Hz), 7.62 (d, 2H, Ar-*H*, *J* = 8.8 Hz), 7.46 (t, 2H, Ar-*H*, *J* = 7.7 Hz), 7.30 (m, 6H, Ar-*H*), 7.23 (ddd, 2H, Ar-*H*, *J* = 8.4, 6.8, 1.3 Hz), 7.10 (m, 4H, Ar-*H*), 6.74-6.63 (m, 4H, Ar-*H*), 5.87 (d, 2H, -SiH_2-, *J* = 4.1 Hz), 5.40 (d, 2H, -SiH_2-, *J* = 4.4 Hz), 4.15 (d, 2H, -OCH_2-, *J* = 12.3 Hz), 3.95 (d, 2H, -OCH_2-, *J* = 12.6 Hz) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 154.7, 144.3, 137.3, 137.0, 136.8, 134.1, 132.1, 131.3, 130.8, 130.2, 129.6, 129.3, 128.4, 128.0, 127.8, 126.7, 126.3, 126.0, 125.8, 124.4, 121.2, 117.8, 72.9 ppm. ^{29}Si NMR (99 MHz, CD_2Cl_2): δ = –45.7 ppm. HRMS (ESI-TOF) calcd for $C_{48}H_{36}O_2Si_2Na$ [M+Na]$^+$: 723.2146; found: 723.2144. $[\alpha]_D^{20}$ = -32 (*c* = 1.00, THF).

Macrocycle (*R*)-3a



Macrocycle **(*R*)-2a** (0.526 g, 0.600 mmol) in diethyl ether (3.0 mL) was added dropwise to a suspension of lithium aluminium hydride (45.5 mg, 1.20 mmol) in diethyl ether (3.0 mL) at 0 ºC under Ar. After stirring at room temperature for 9 h, the reaction mixture was quenched with aq. 1 M HCl. The mixture was extracted with diethyl ether, washed with water and brine, dried over $MgSO_4$, and concentrated. The residue was subjected to column chromatography on silica gel with hexane/toluene (3:1 to 1:1) to give a pale yellow solid (0.279 g, 0.398 mmol, 66% yield). Mp: 210-212 ºC. ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 8.64 (d, 2H, Ar-*H*, *J* = 9.2 Hz), 8.13 (d, 2H, Ar-*H*, *J* = 8.6 Hz), 7.96 (dd, 2H, Ar-*H*, *J* = 7.5, 1.2 Hz), 7.75 (d, 2H, Ar-*H*, *J* = 8.6 Hz), 7.62 (d, 2H, Ar-*H*, *J* = 8.6 Hz), 7.48-7.43 (m, 2H, Ar-*H*), 7.32-7.26 (m, 6H, Ar-*H*), 7.22 (t, 2H, Ar-*H*, *J* = 7.5 Hz), 7.12-7.05 (m, 4H, Ar-*H*), 6.69 (d, 2H, Ar-*H*, *J* = 8.6 Hz), 6.65 (d, 2H, Ar-*H*, *J* = 7.5 Hz), 5.86 (d, 2H, -SiH_2-, *J* = 4.6 Hz), 5.39 (d, 2H, -SiH_2-, *J* = 4.6 Hz), 4.14 (d, 2H, -OCH_2-, *J* = 12.6 Hz), 3.93 (d, 2H, -OCH_2-, *J* = 12.6 Hz) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 154.6, 144.2, 137.3, 136.9, 136.7, 134.0, 132.1, 131.2, 130.8, 130.1, 129.6, 129.3, 128.3, 127.9, 127.7, 126.7, 126.3, 125.9, 125.8, 124.4, 121.1, 117.7, 72.9 ppm. HRMS (APCI-TOF) calcd for $C_{48}H_{37}O_2Si_2$ [M+H]$^+$: 701.2327; found: 701.2357. $[\alpha]_D^{20}$ = +35 (*c* = 1.00, THF).

Macrocycle 3b



Macrocycle **2b** (0.233 g, 0.300 mmol) in diethyl ether (24 mL) and THF (3.0 mL) was added dropwise to a suspension of lithium aluminium hydride (22.8 mg, 0.600 mmol) in diethyl ether (3.0 mL) at 0 ºC under Ar. After stirring at room temperature for 21 h, the reaction mixture was quenched with aq. 1 M HCl. The mixture was extracted with THF, washed with brine, dried over Na_2SO_4, and concentrated. The residue was recrystallized from dichloromethane/ethanol to give a pale yellow solid (0.129 g, 0.215 mmol,

72% yield). The single crystal for X-ray analysis was obtained by recrystallization from dichloromethane/hexane. Mp: 265-267 ºC ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 8.69 (d, 2H, Ar-*H*, *J* = 8.7 Hz), 8.08 (m, 4H, Ar-*H*), 7.42 (m, 6H, Ar-*H*), 7.22 (m, 4H, Ar-*H*), 7.03 (dd, 2H, Ar-*H*, *J* = 7.4, 1.7 Hz), 6.94 (m, 2H, Ar-*H*), 6.74 (td, 2H, Ar-*H*, *J* = 7.5, 1.1 Hz), 6.43 (dd, 2H, Ar-*H*, *J* = 8.4, 1.0 Hz), 5.93 (d, 2H, -SiH_2-, *J* = 4.4 Hz), 5.51 (d, 2H, -SiH_2-, *J* = 4.4 Hz), 4.27 (d, 2H, -OCH_2-, *J* = 13.6 Hz), 3.96 (d, 2H, -OCH_2-, *J* = 13.6 Hz) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 156.5, 144.5, 137.4, 137.2, 136.5, 131.9, 131.5, 131.0, 130.8, 129.4, 129.1, 128.8, 128.0, 127.8, 126.8, 126.4, 125.8, 121.3, 114.4, 72.4 ppm. ^{29}Si NMR (99 MHz, CD_2Cl_2): δ = –46.1 ppm. HRMS (ESI-TOF) calcd for $C_{40}H_{32}O_2Si_2Na$ $[M+Na]^+$: 623.1833; found: 623.1845. T_{d1} = 252 ºC. T_{d5} = 333 ºC.

3. NMR Spectra

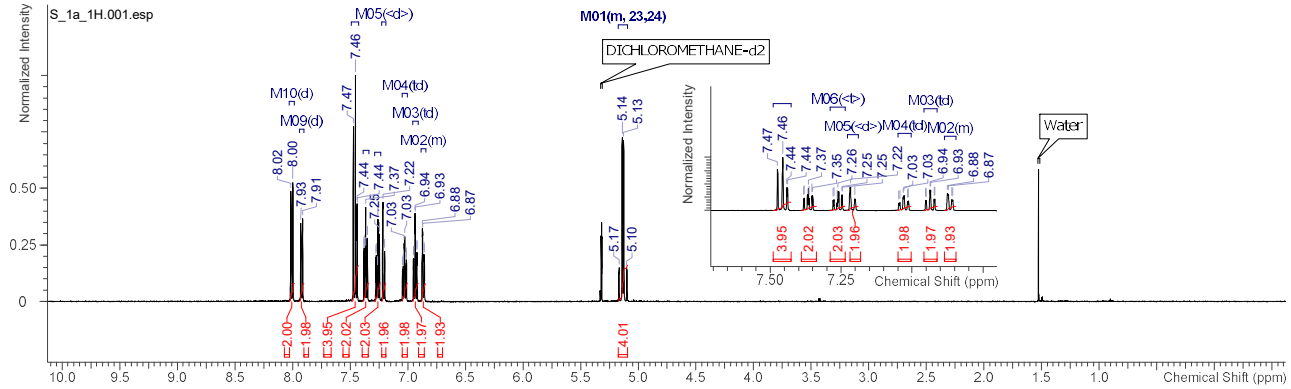


Fig. S2 ^{1}H NMR spectrum of (*S*)-**1a** (20 ^{o}C, CD_2Cl_2).

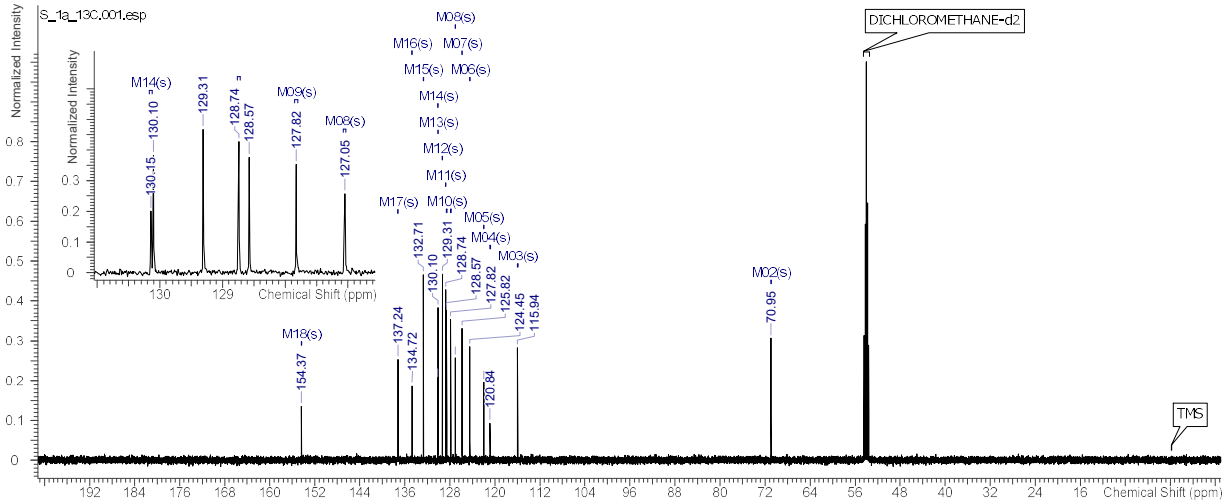


Fig. S3 ^{13}C NMR spectrum of (*S*)-**1a** (20 ^{o}C, CD_2Cl_2).

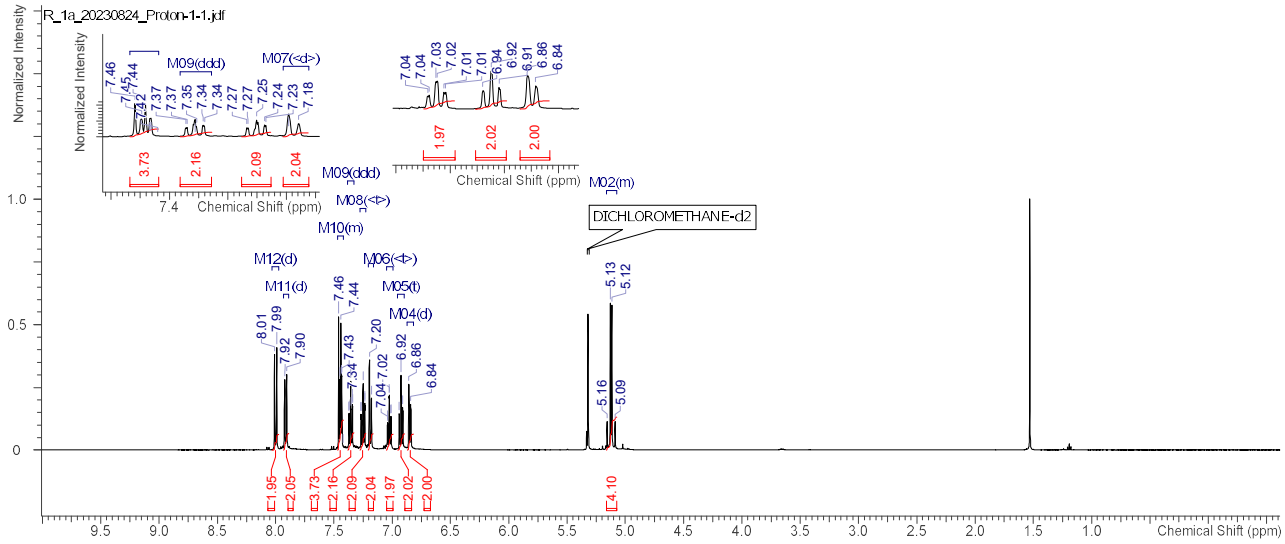


Fig. S4 ^{1}H NMR spectrum of (*R*)-**1a** (20 ^{o}C, CD_2Cl_2).

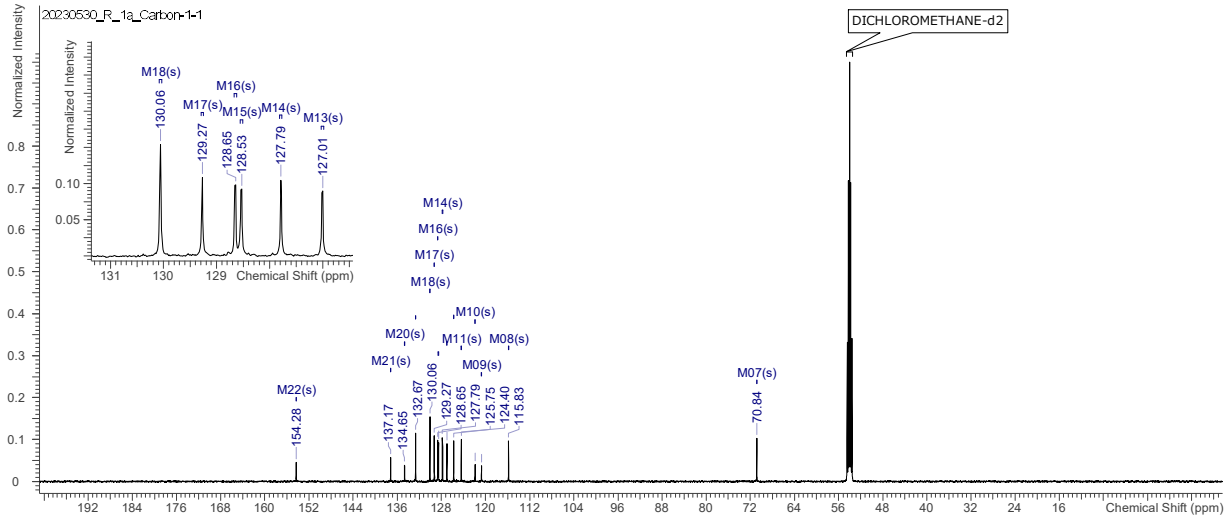


Fig. S5 ^{13}C NMR spectrum of (*R*)-**1a** (20 ^{o}C, CD_2Cl_2).

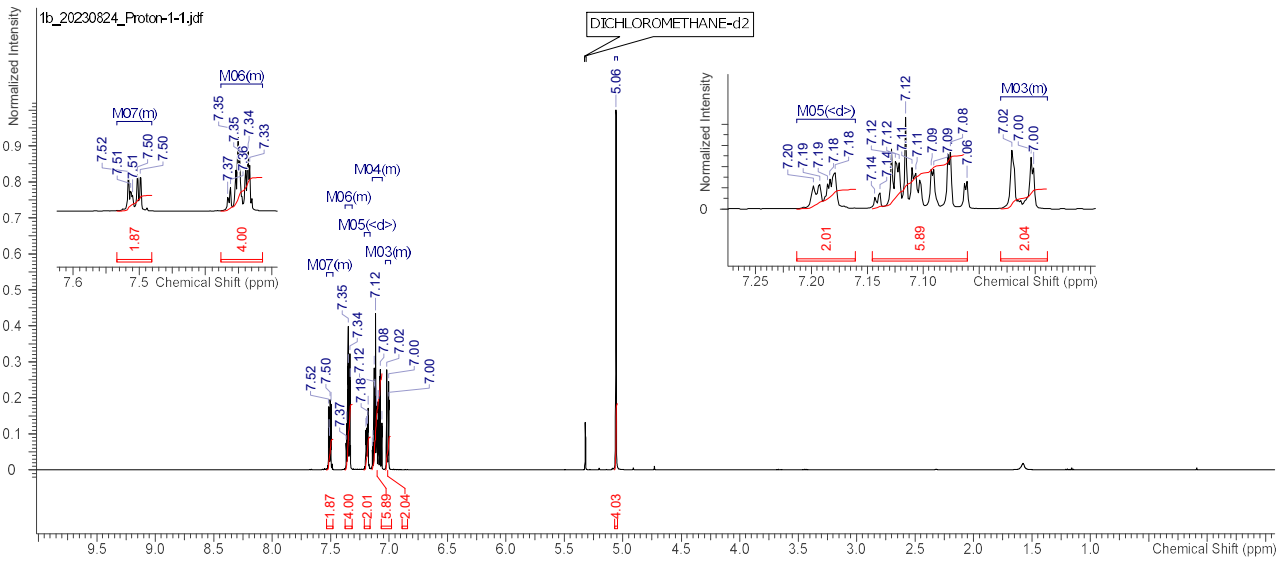


Fig. S6 ^{1}H NMR spectrum of **1b** (20 ^{o}C, CD_2Cl_2).

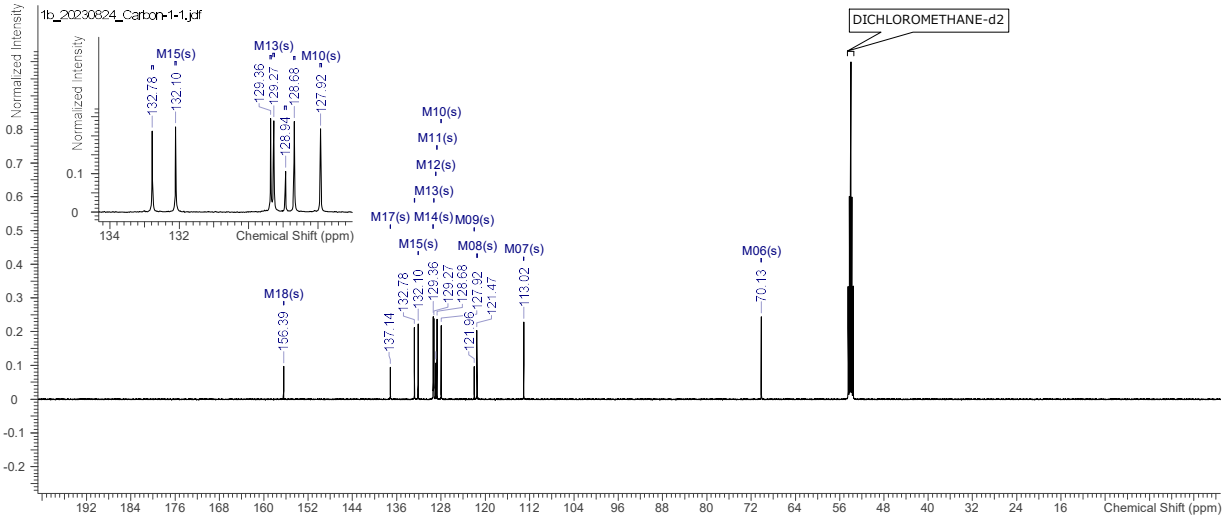


Fig. S7 ^{13}C NMR spectrum of **1b** (20 ^{o}C, CD_2Cl_2).

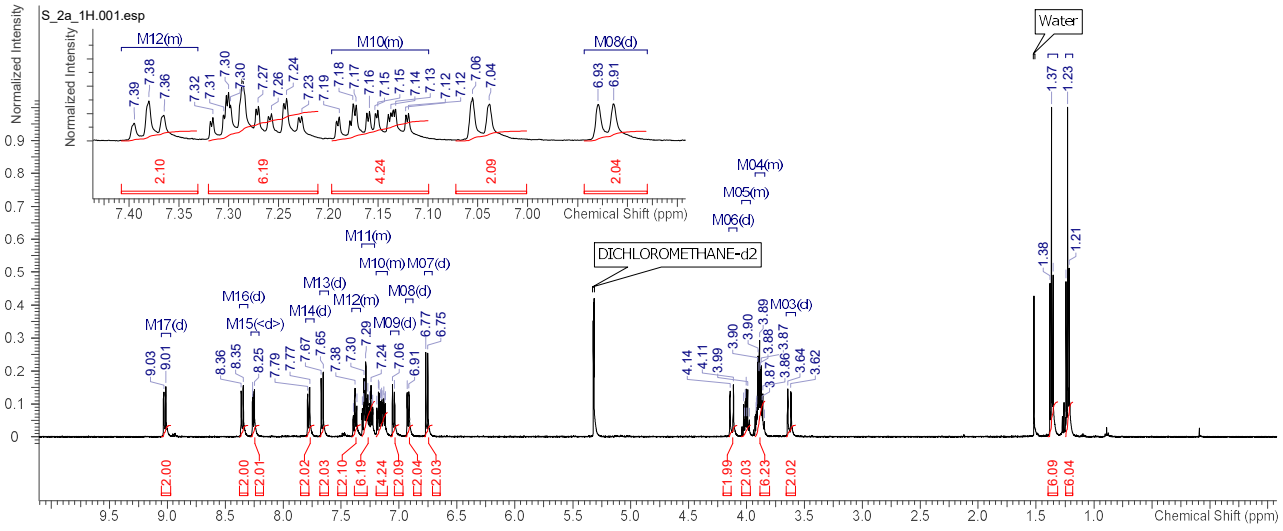


Fig. S8 ^{1}H NMR spectrum of (*S*)-**2a** (20 ^{o}C, CD_2Cl_2).

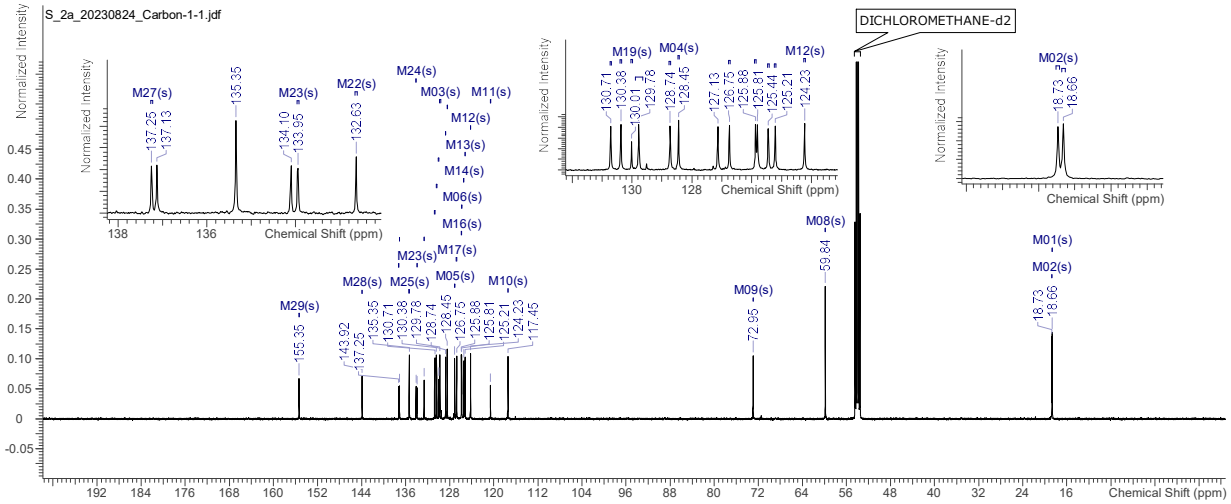


Fig. S9 ^{13}C NMR spectrum of (*S*)-**2a** (20 ^{o}C, CD_2Cl_2).

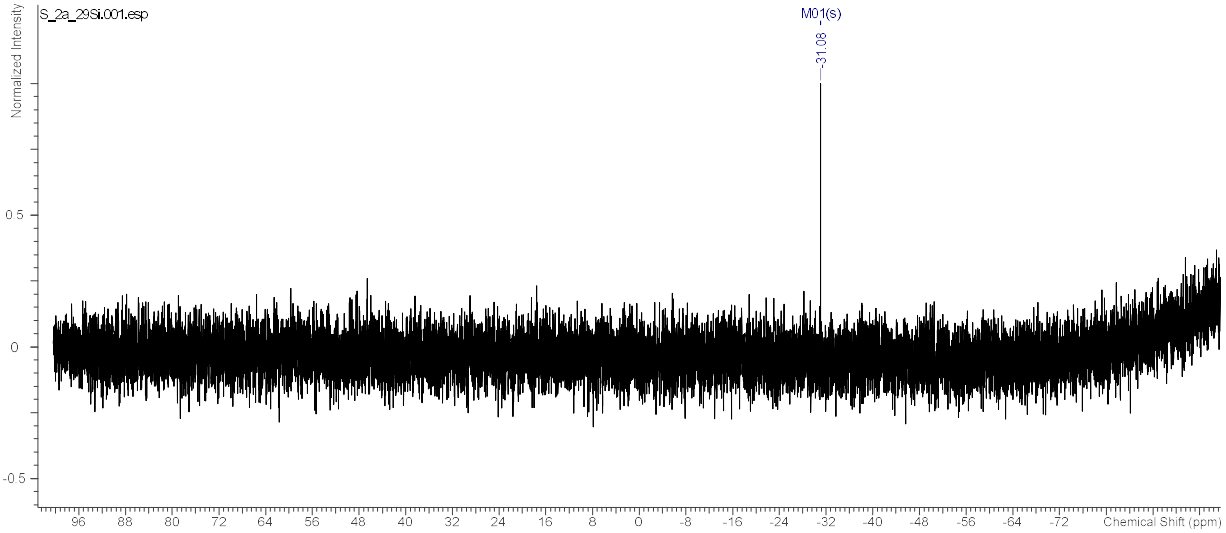


Fig. S10 ^{29}Si NMR spectrum of (*S*)-**2a** (20 ^{o}C, CD_2Cl_2).

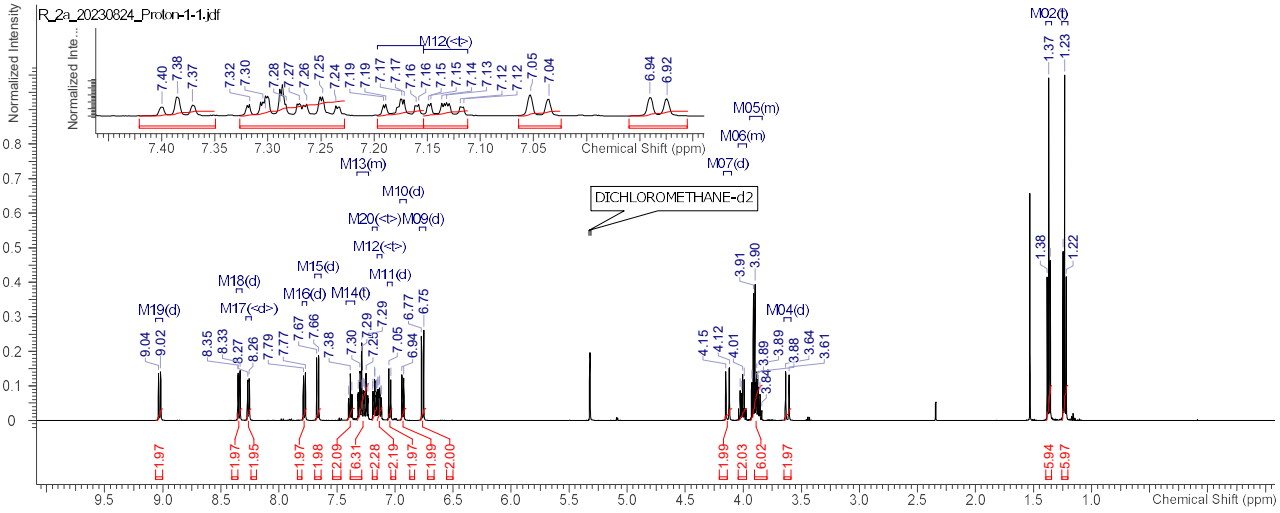


Fig. S11 ^{1}H NMR spectrum of (*R*)-**2a** (20 ^{o}C, CD_2Cl_2).

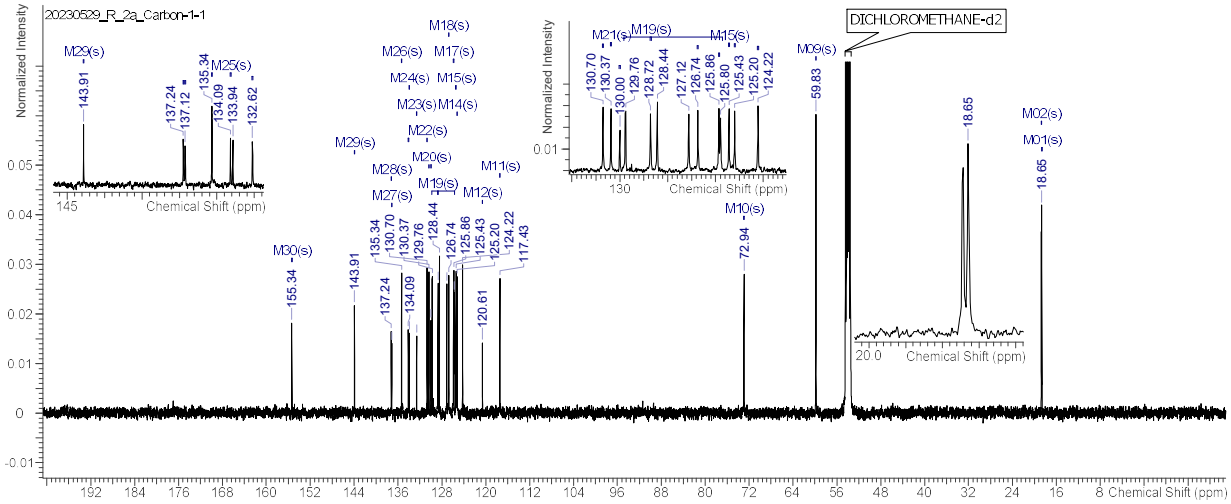


Fig. S12 ^{13}C NMR spectrum of (*R*)-**2a** (20 ^{o}C, CD_2Cl_2).

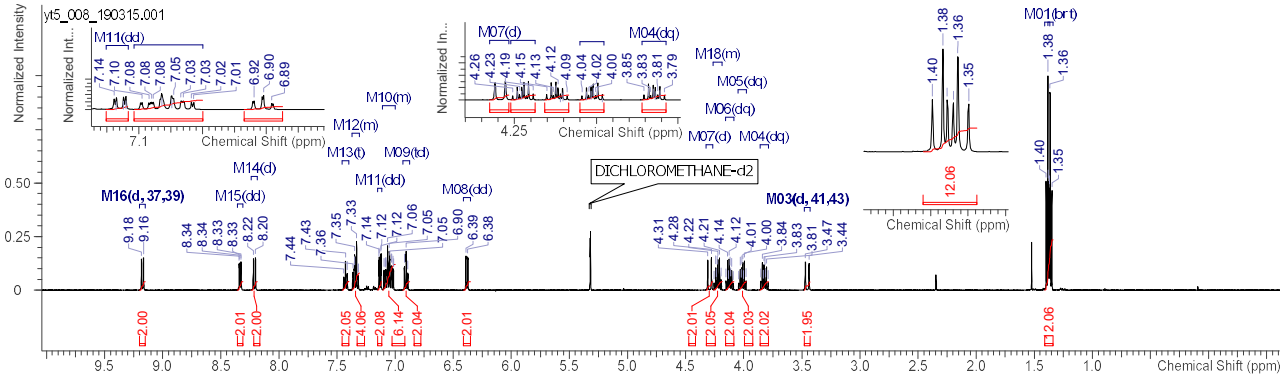


Fig. S13 ^{1}H NMR spectrum of **2b** (20 ^{o}C, CD_2Cl_2).

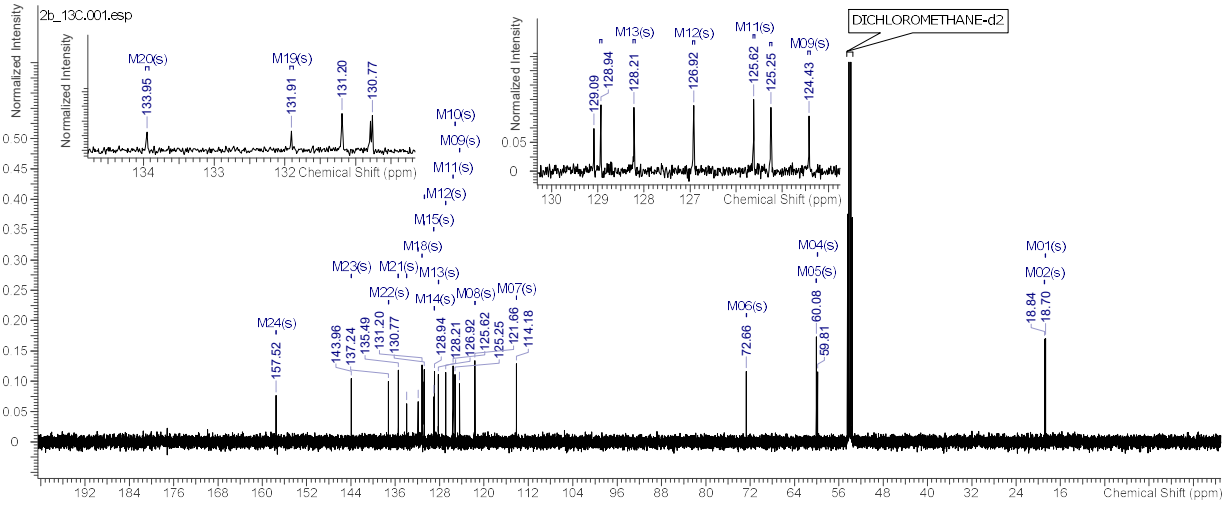


Fig. S14 ^{13}C NMR spectrum of **2b** (20 ^{o}C, CD_2Cl_2).

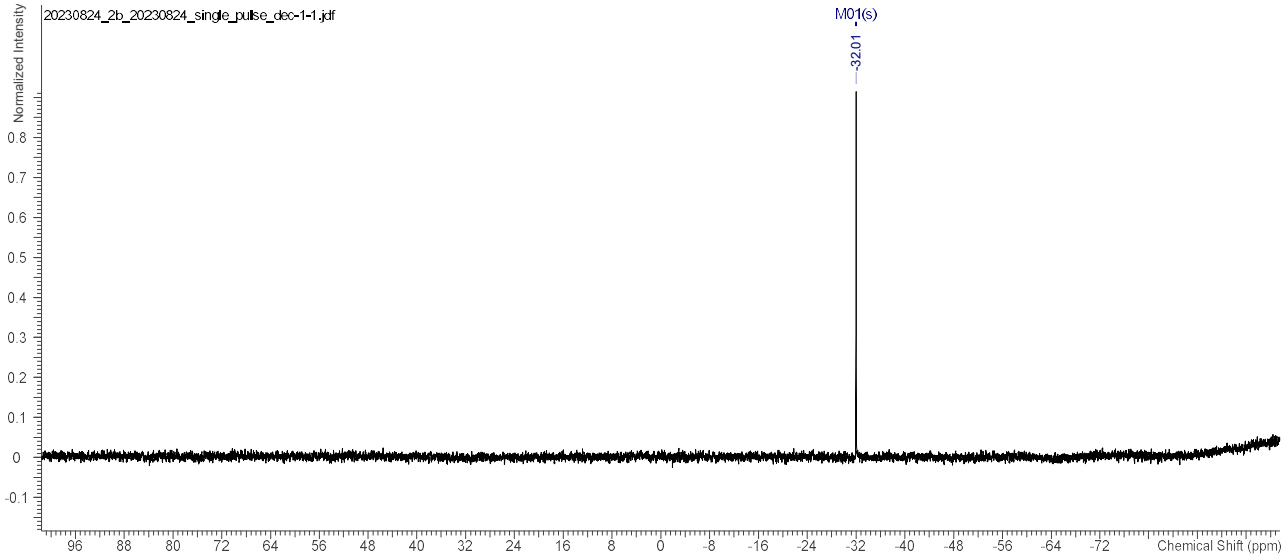


Fig. S15 ^{29}Si NMR spectrum of **2b** (20 ^{o}C, CD_2Cl_2).

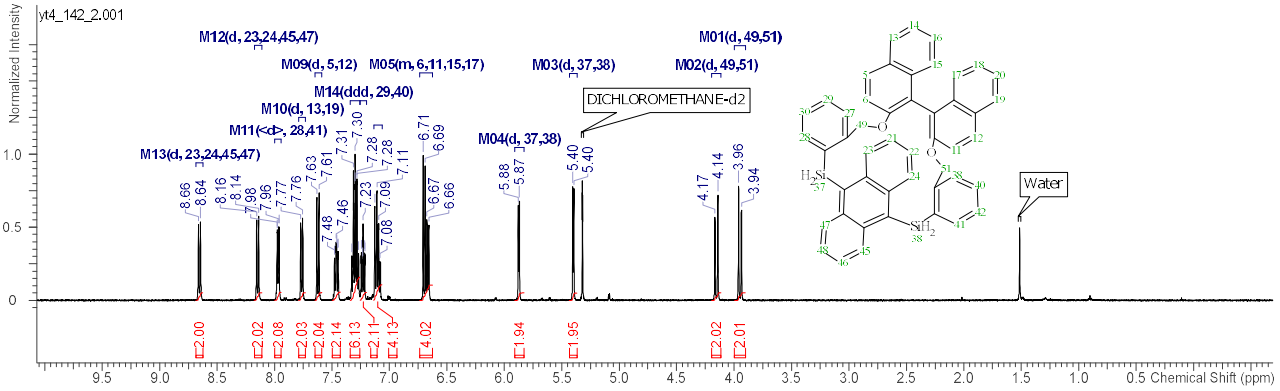


Fig. S16 ^{1}H NMR spectrum of (*S*)-**3a** (20 ^{o}C, CD_2Cl_2).

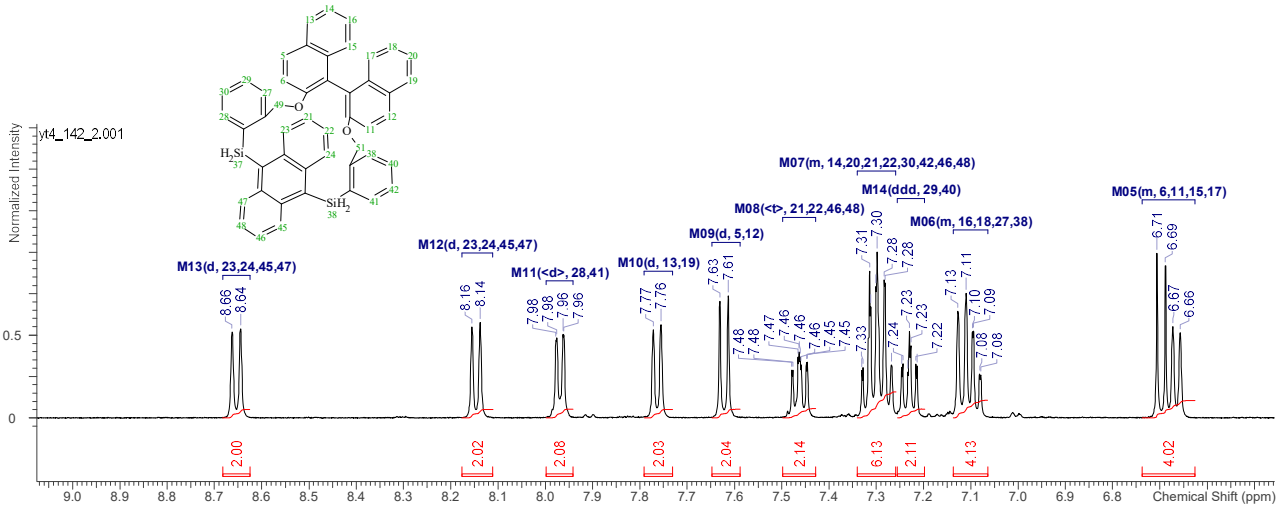


Fig. S17 Extended ^{1}H NMR spectrum of (*S*)-**3a** (20 ^{o}C, CD_2Cl_2).

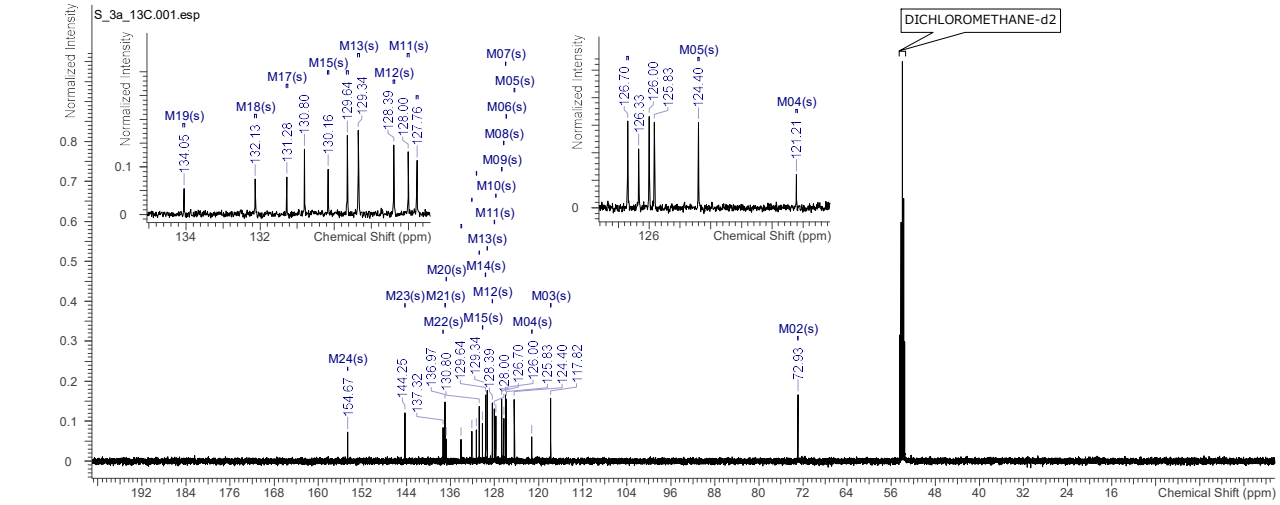


Fig. S18 ^{13}C NMR spectrum of (*S*)-**3a** (20 ^{o}C, CD_2Cl_2).

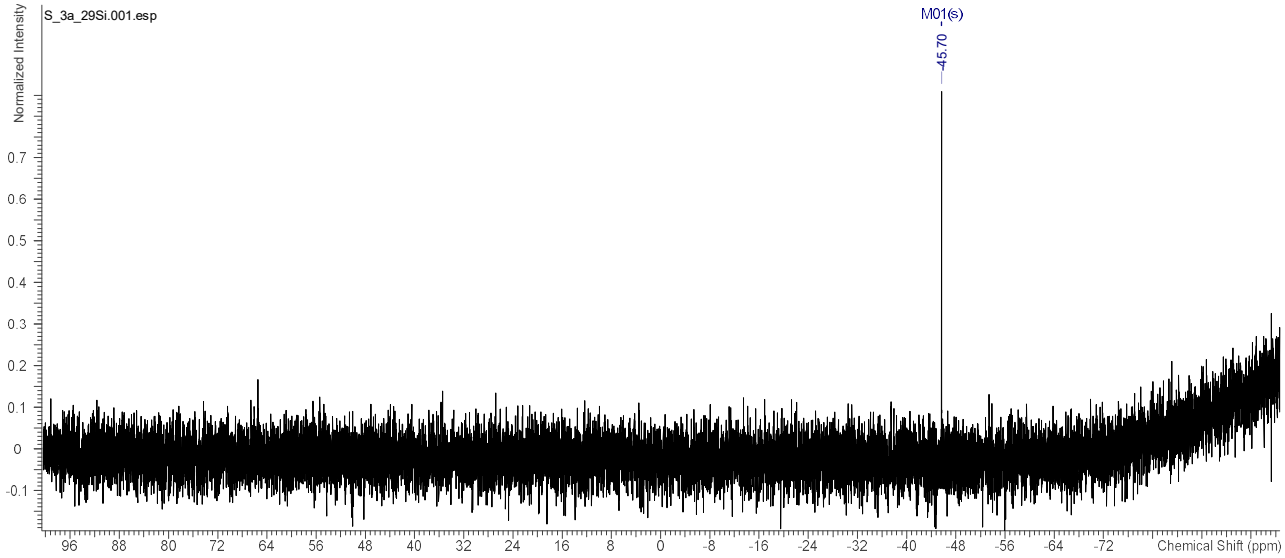


Fig. S19 ^{29}Si NMR spectrum of (*S*)-**3a** (20 ^{o}C, CD_2Cl_2).

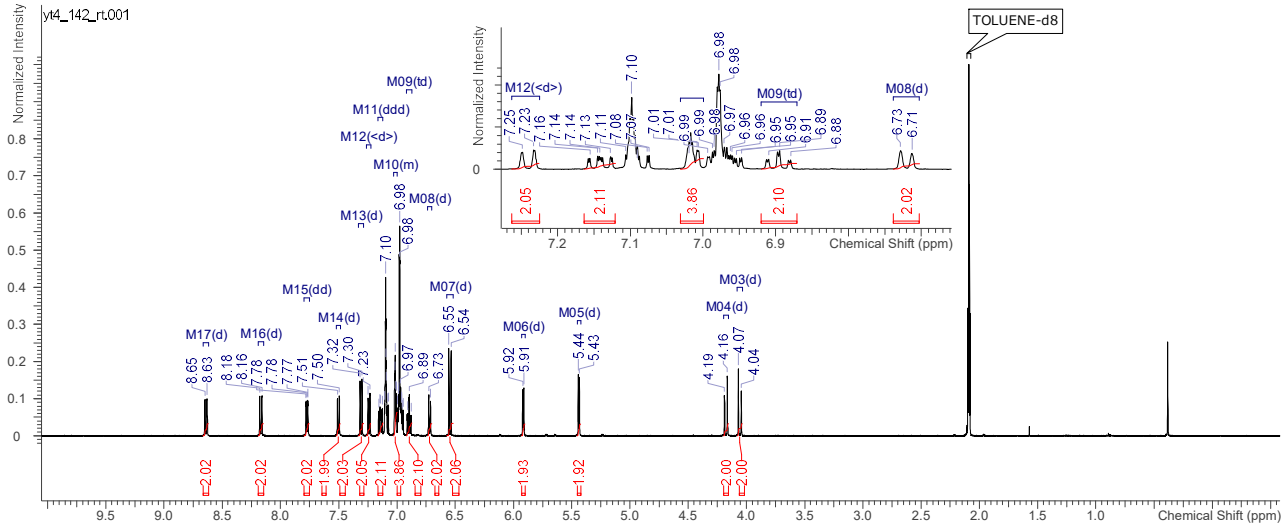


Fig. S20 ^{1}H NMR spectrum of (*S*)-**3a** (20 ^{o}C, toluene-d_8).

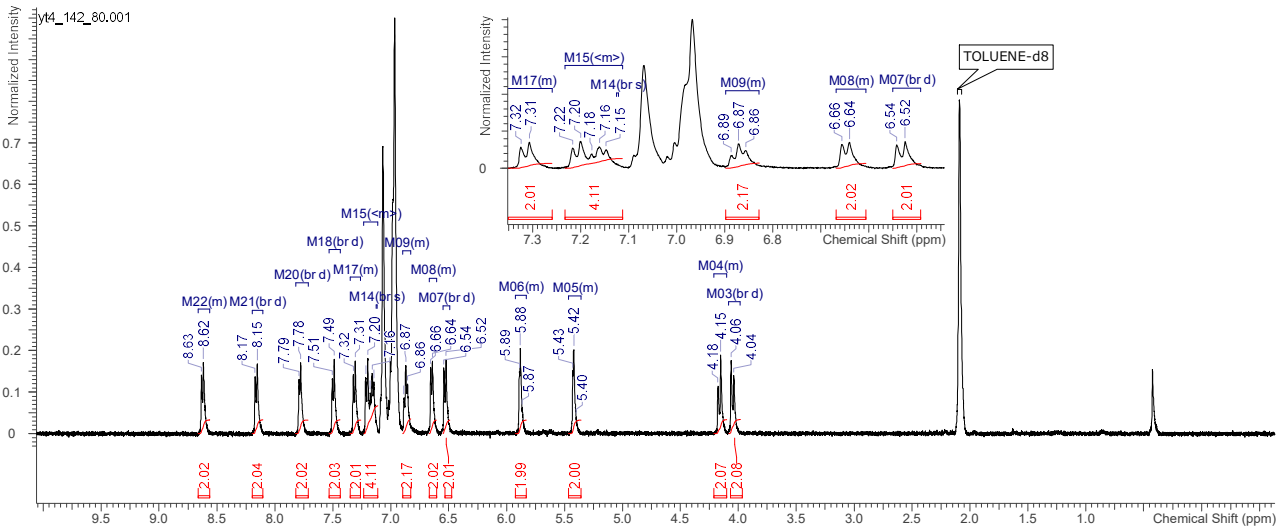


Fig. S21 ^{1}H NMR spectrum of (*S*)-**3a** (80 ^{o}C, toluene-d_8).

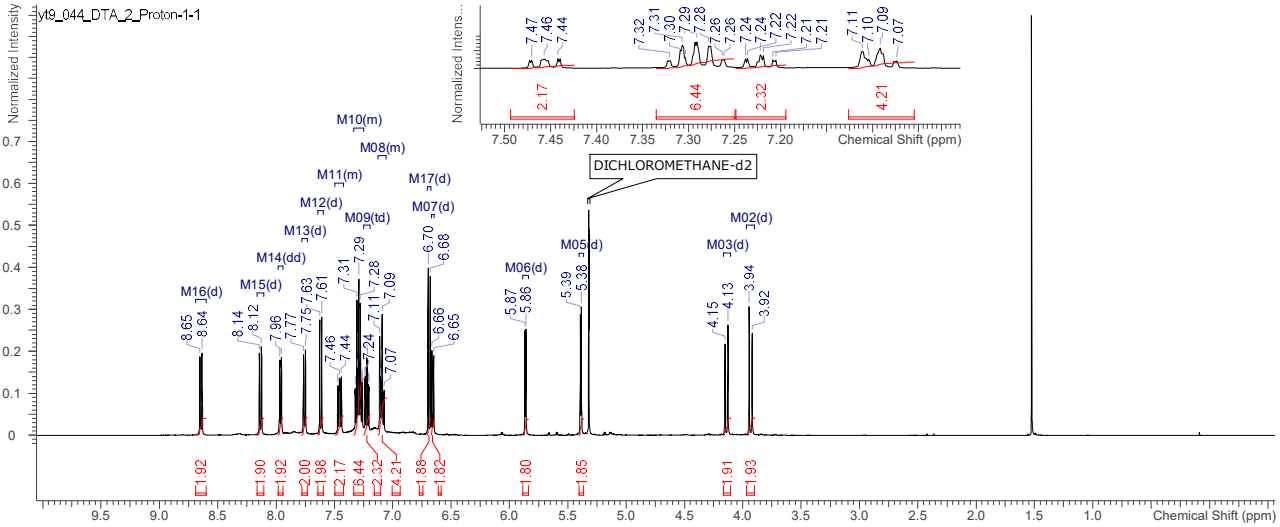


Fig. S22 ^{1}H NMR spectrum of (*S*)-**3a** after heating to 220 ^{o}C (20 ^{o}C, CD_2Cl_2).

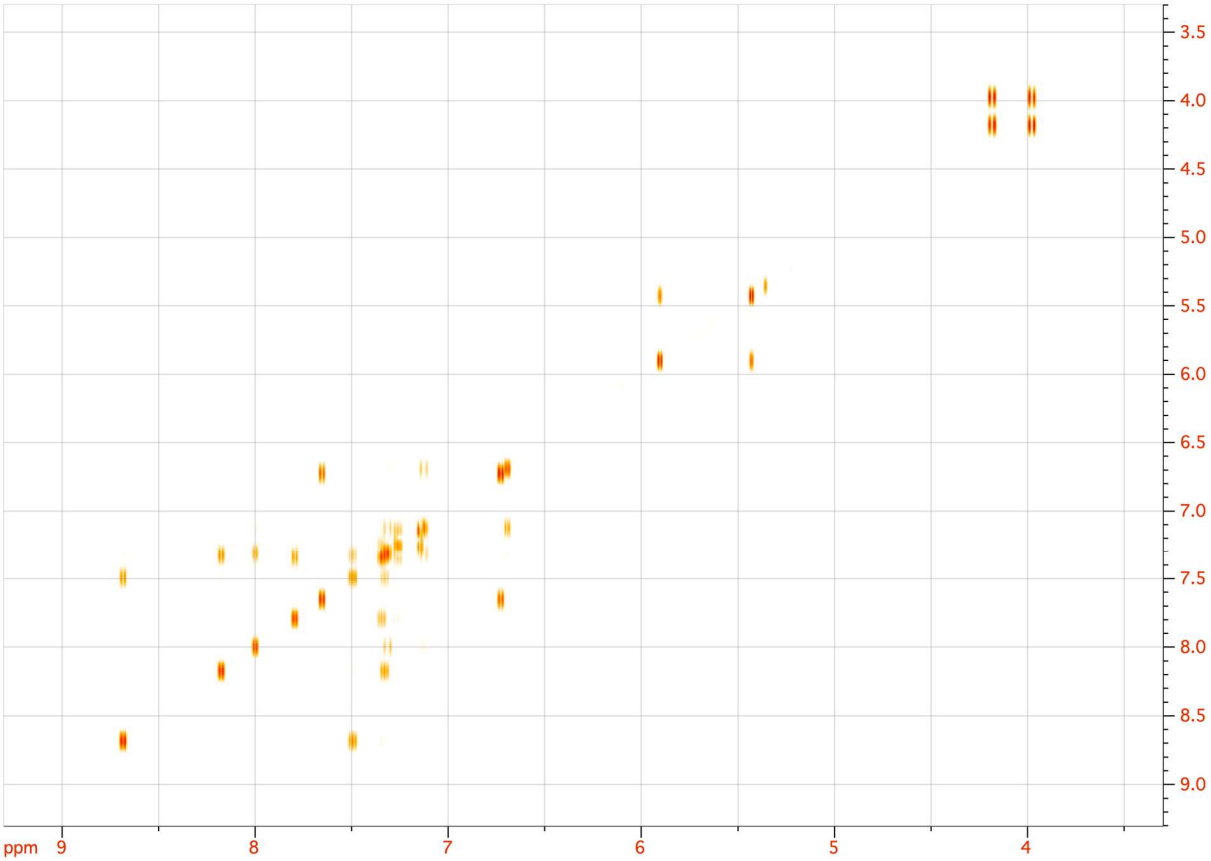


Fig. S23 H-H COSY spectrum of (*S*)-**3a** (20 ^{o}C, CD_2Cl_2).

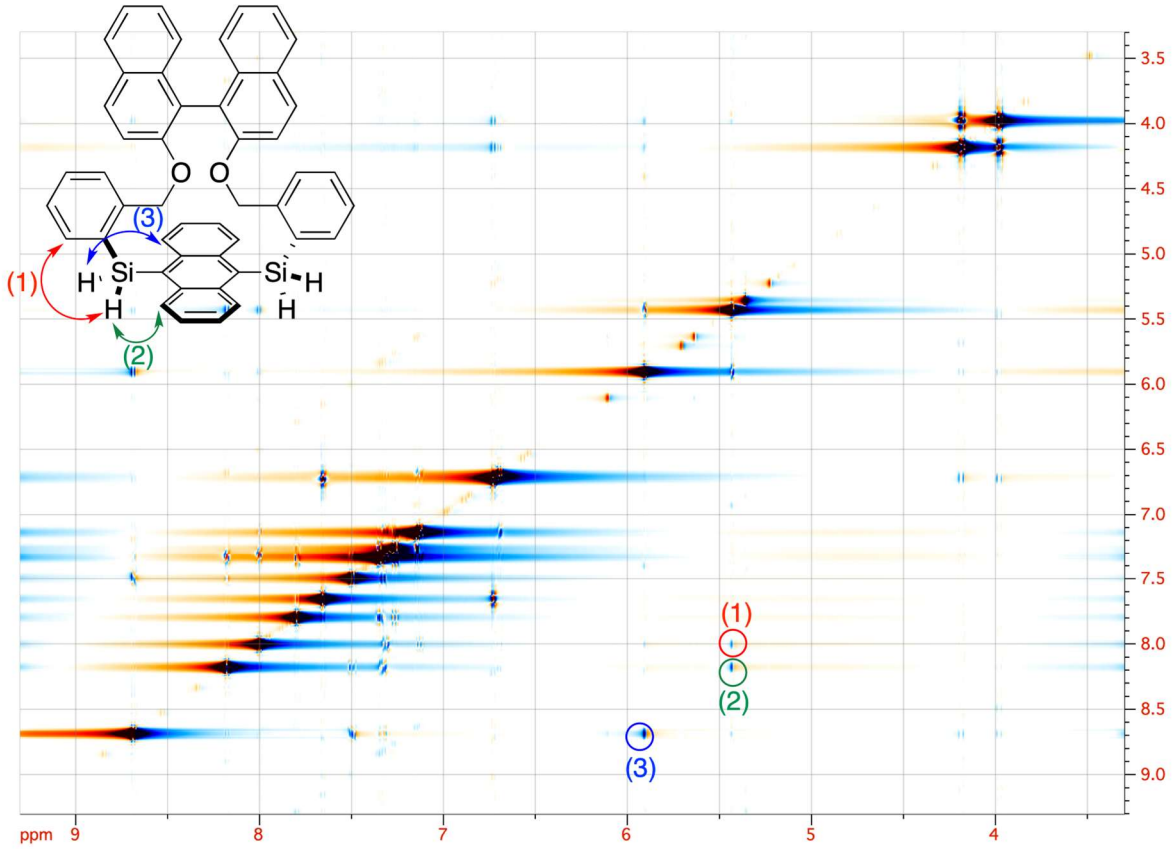


Fig. S24 NOESY spectrum of (*S*)-**3a** (20 °C, CD_2Cl_2).

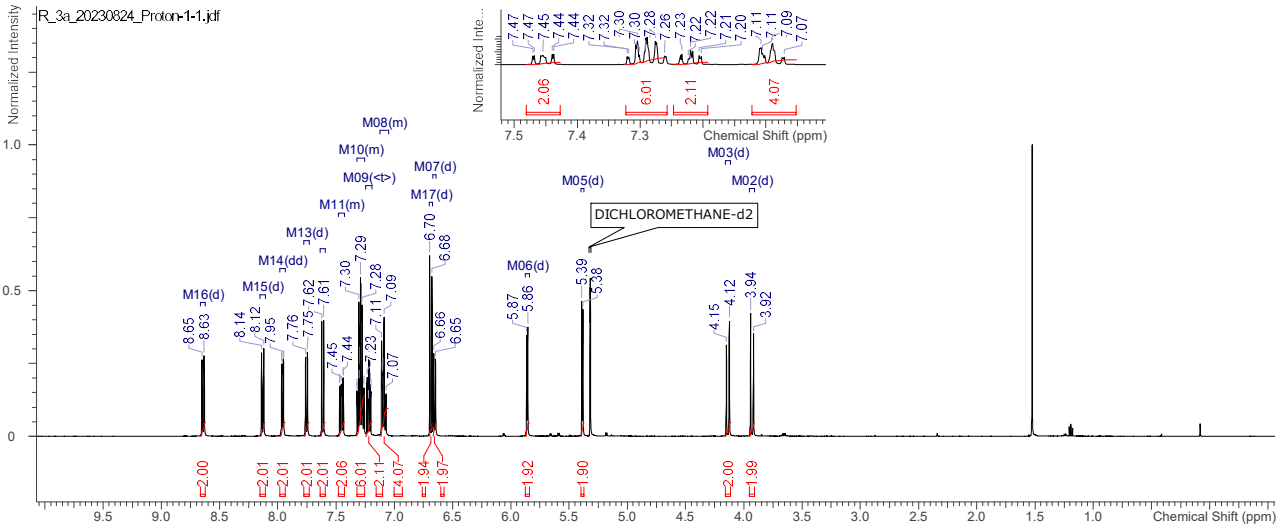


Fig. S25 ^{1}H NMR spectrum of (*R*)-**3a** (20 °C, CD_2Cl_2).

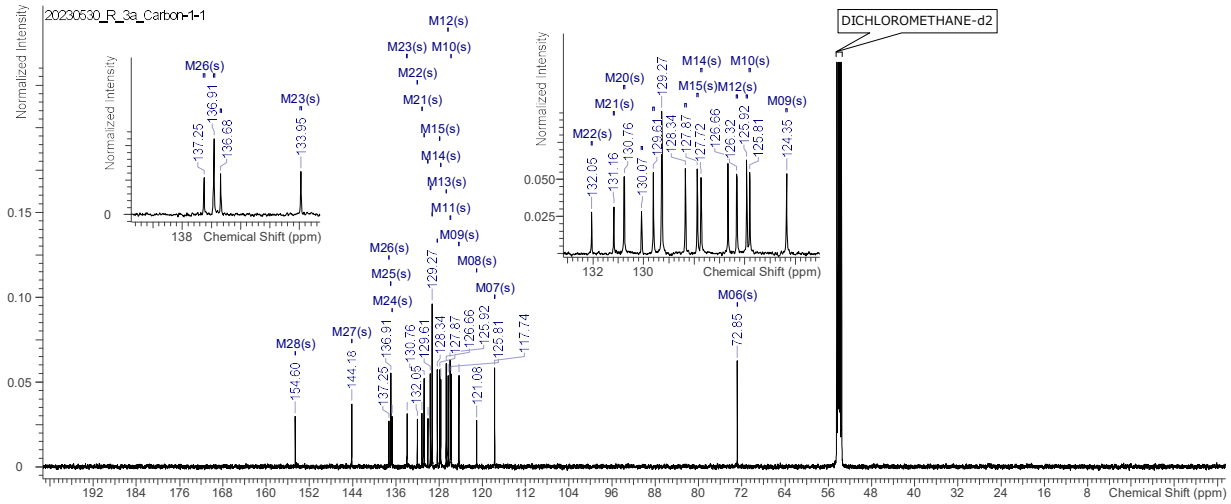


Fig. S26 ^{13}C NMR spectrum of (*R*)-**3a** (20 ^{o}C, CD_2Cl_2).

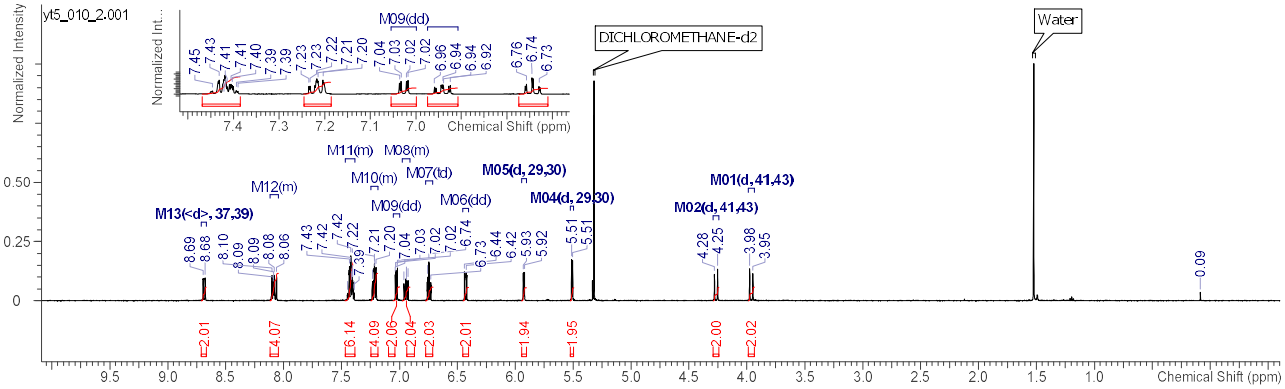


Fig. S27 ^{1}H NMR spectrum of **3b** (20 ^{o}C, CD_2Cl_2).

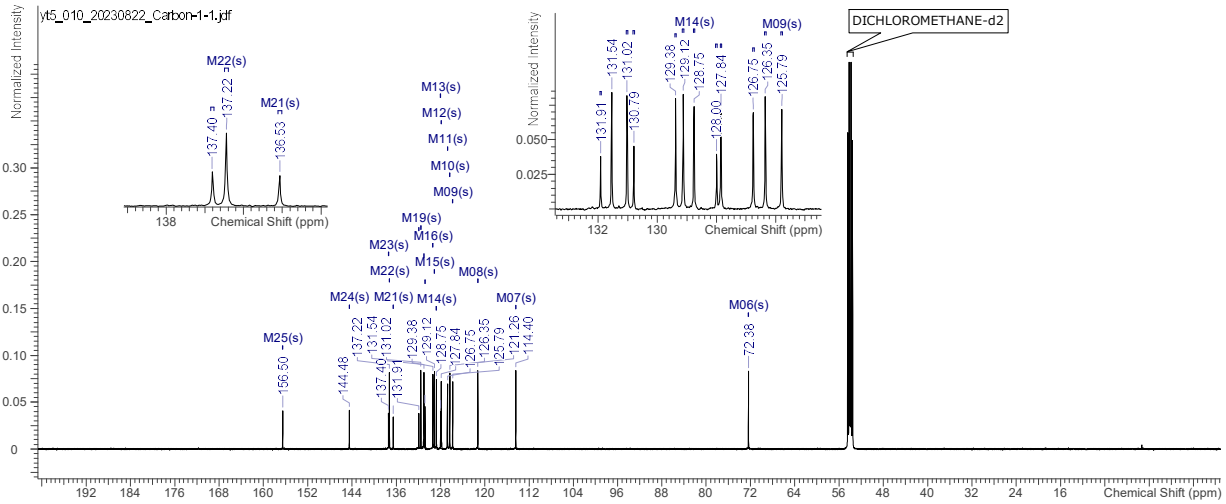


Fig. S28 ^{13}C NMR spectrum of **3b** (20 ^{o}C, CD_2Cl_2).

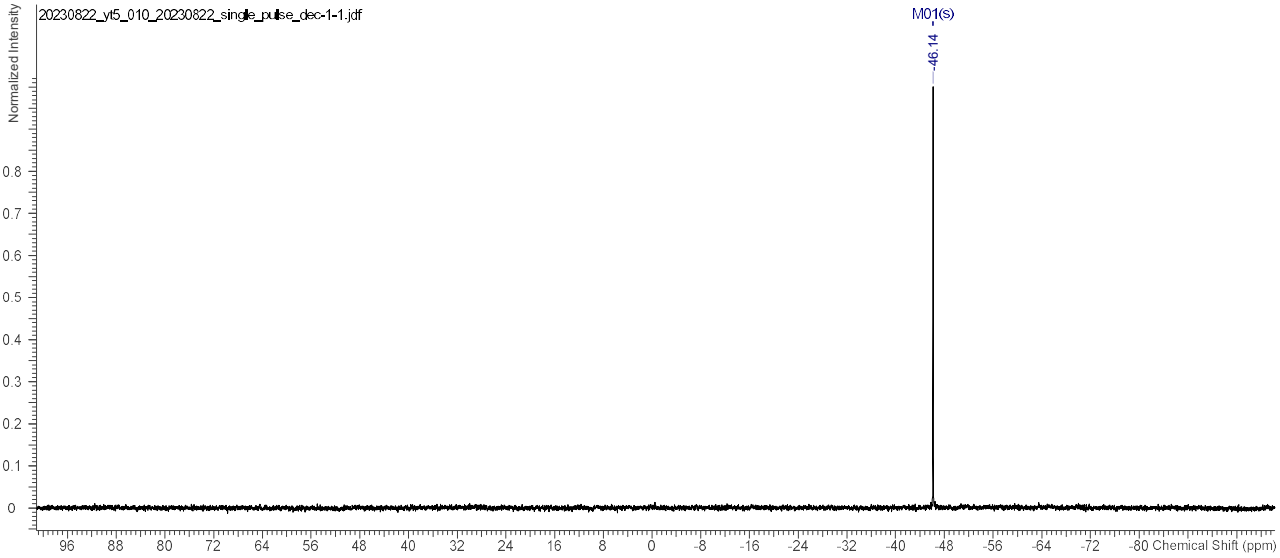


Fig. S29 ^{29}Si NMR spectrum of **3b** (20 ^{o}C, CD_2Cl_2).

4. Cryatallography

A suitable crystal was mounted with mineral oil on a glass fiber and transferred to the goniometer of a Bruker D8 VENTURE or Rigaku XtaLAB PRO HPC CCD diffractometer with Cu Kα (α = 1.5418 α, (*S*)-**3a**-E, (*S*)-**3a**-H, **3b**) or Mo Kα radiation (α = 0.71073 α, *rac*-**3a**). The structures were solved by direct methods using SHELXT or Olex2, and refined using Olex2. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed on the carbon atoms according to the AFIX instructions.

Table S1 Crystallographic data

Crystal	(*S*)-**3a**-E	(*S*)-**3a**-H	*rac*-**3a**	**3b**
Chemical formula	$C_{48}H_{36}O_2Si_2$	$C_{48}H_{35.787}O_2Si_2$	$C_{48}H_{36}O_2Si_2$	$C_{40}H_{32}O_2Si_2$
Formula weight	700.90	700.78	700.99	600.87
Color	colorless	yellow	yellow	green
Shape	block	block	block	block
Crystal system	triclinic	monoclinic	monoclinic	triclinic
Space group	*P*1	*P* 1 2_1 1	*P* 1 $2_1/n$ 1	$P\bar{1}$
a (Å)	11.5209(5)	11.19827(2)	11.2799(5)	10.45340(10)
b (Å)	11.6461(5)	27.60749(6)	17.2391(8)	12.10100(10)
c (Å)	28.3488(12)	18.08478(4)	18.9684(7)	13.64410(10)
β (°)	91.906(2)	90.5504(2)	102.339(1)	104.5240(10)
Volume	3723.5(3)	5590.76(2)	3603.3(3)	1530.15(3)
Z	4	6	4	2
D_{calc} (g/cm^3)	1.250	1.249	1.292	1.304
R_1 ($I > 2\sigma(I)$)	0.0609	0.0358	0.0336	0.0386
wR_2 (All reflections)	0.1751	0.1014	0.0855	0.1042
Reflections ($I > 2\sigma(I)$)	25617	21511	6607	5873
Temperature (K)	223	223	93	223
CCDC number	2264847	1916744	2264848	1916745

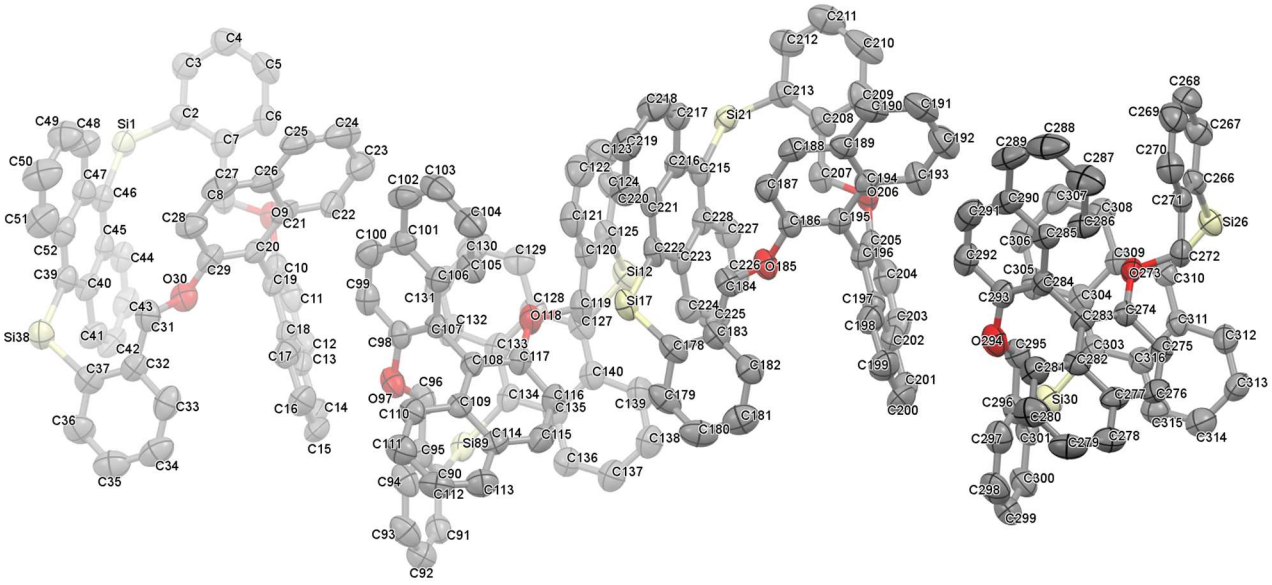


Fig. S30 X-ray crystal structure of (*S*)-**3a**-E. Thermal ellipsoids were drawn at a 50% probability level. Hydrogen atoms were omitted for clarity.

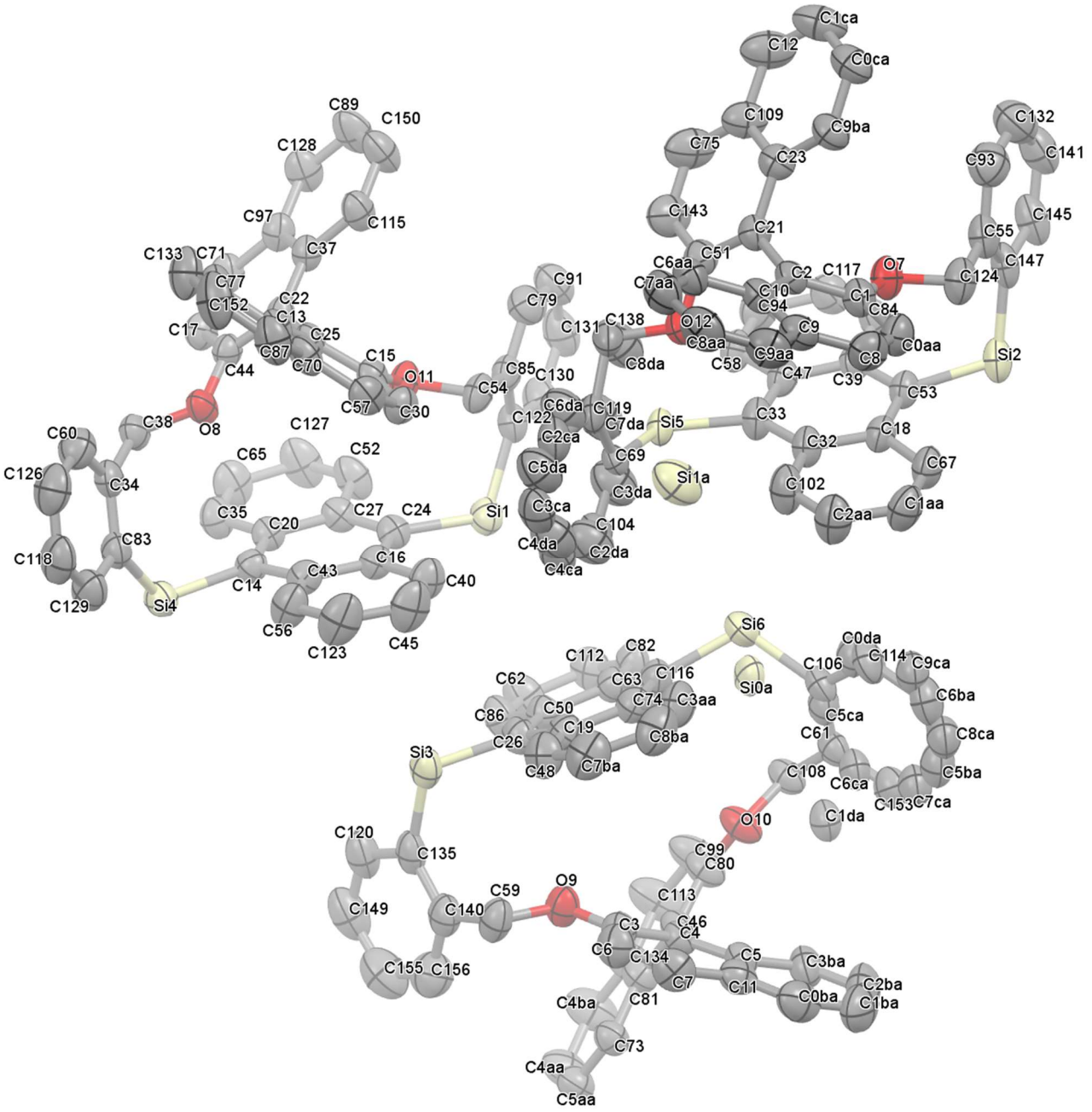


Fig. S31 X-ray crystal structure of (*S*)-**3a**-H. Thermal ellipsoids were drawn at a 50% probability level. Hydrogen atoms were omitted for clarity.

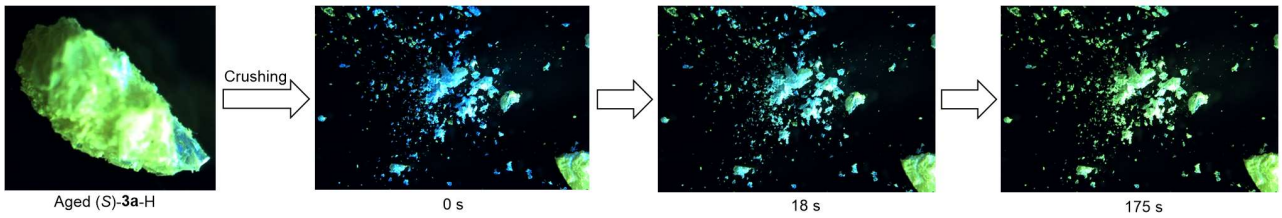


Fig. S32 Photographs of (*S*)-**3a**-H. Aged (*S*)-**3a**-H exhibited green luminescence. Immediately after crushing, the inner portion exhibited blue luminescence. The color gradually changed to green within 3 min.

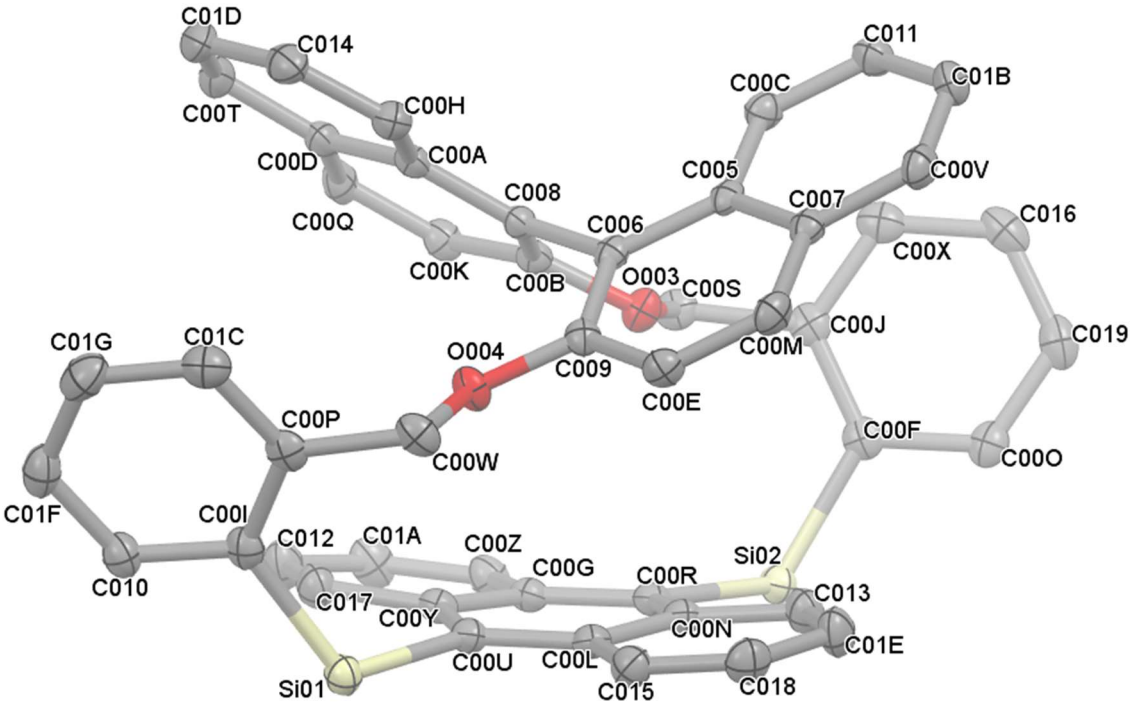


Fig. S33 X-ray crystal structure of *rac*-**3a**. Thermal ellipsoids were drawn at a 50% probability level. Hydrogen atoms were omitted for clarity.

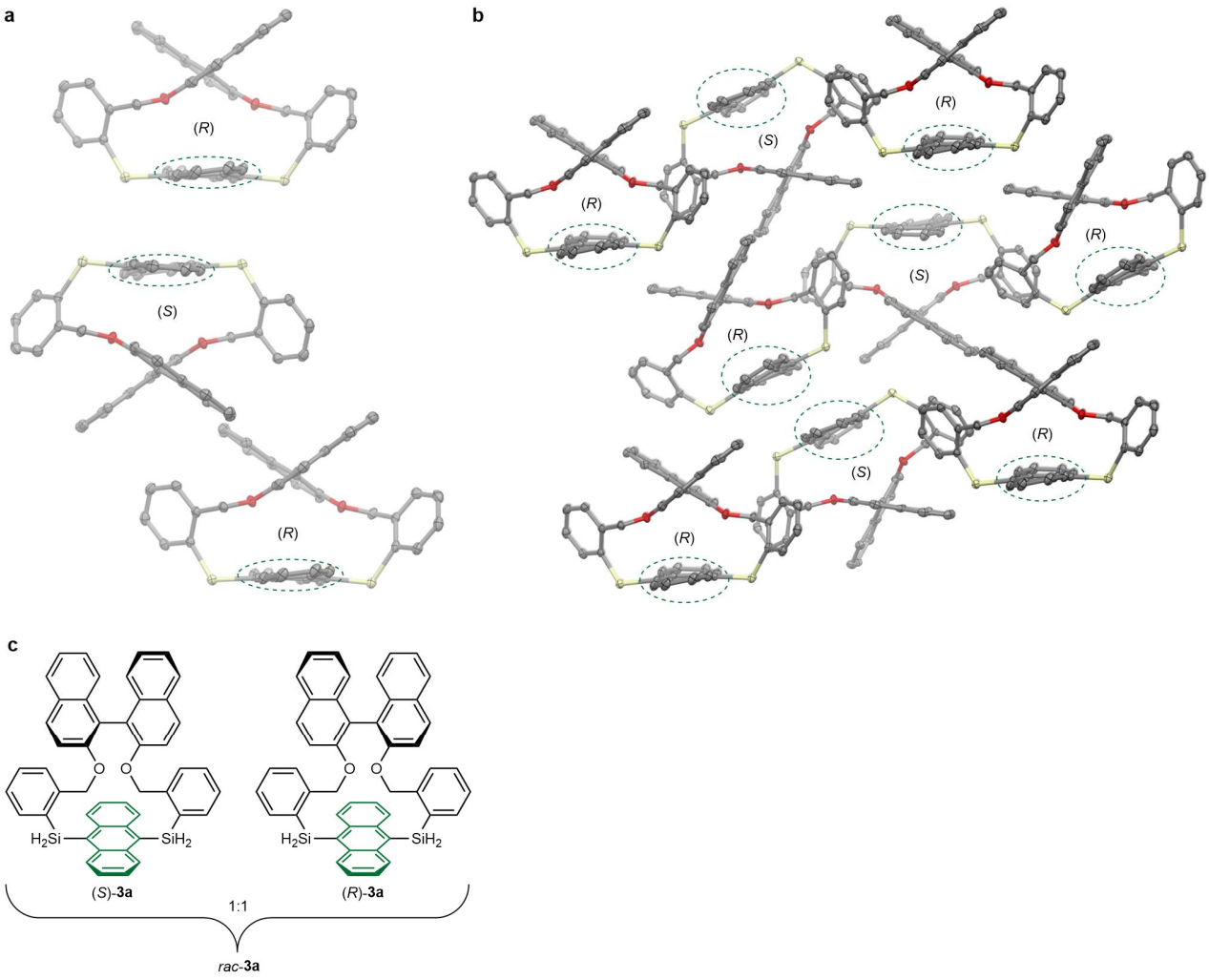


Fig. S34 Crystal Packing of *rac*-**3a**. **a** Head-to-head and tail-to-tail structures of *rac*-**3a**. **b** Packing structure of *rac*-**3a**. **c** Chemical structure. Thermal ellipsoids were drawn at a 50% probability level. Hydrogen atoms were omitted for clarity. The anthracene rings are indicated by broken green lines.

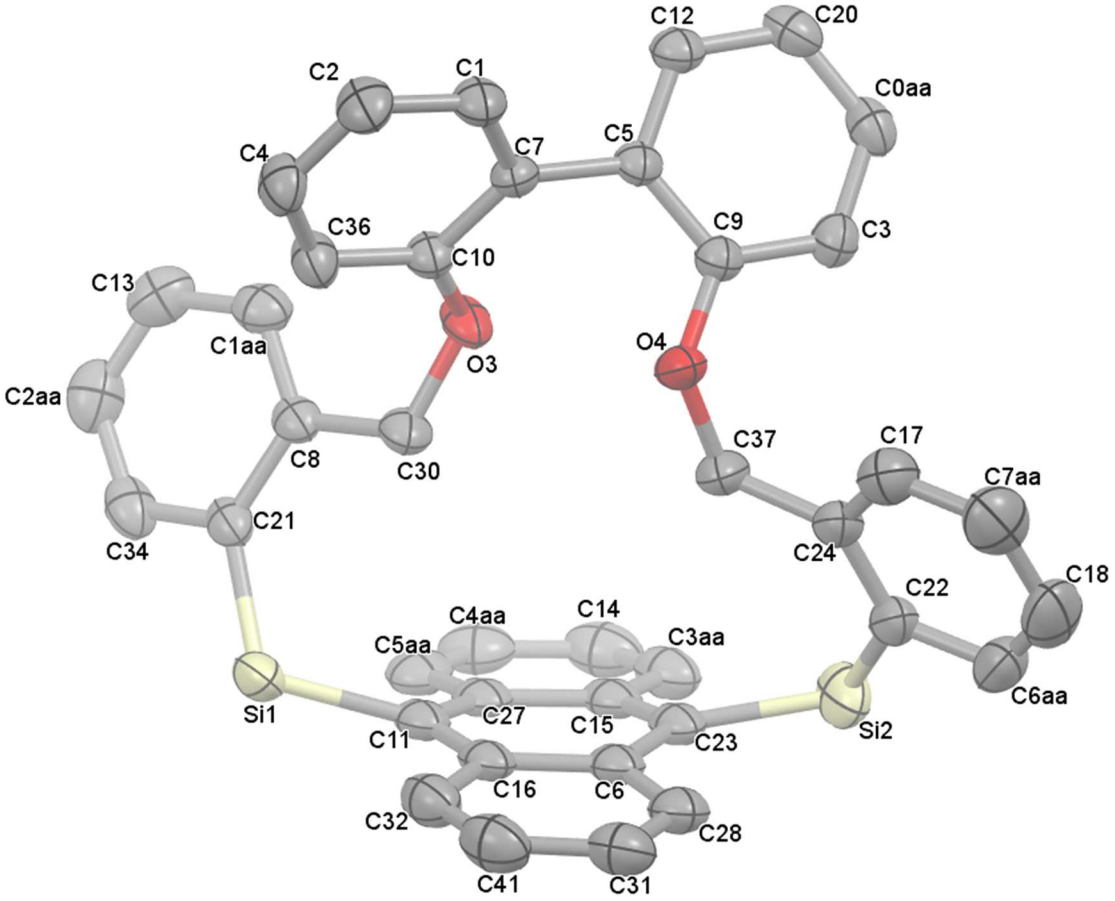


Fig. S35 X-ray crystal structure of *rac*-**3a**. Thermal ellipsoids were drawn at a 50% probability level. Hydrogen atoms were omitted for clarity.

5. Density functional theory (DFT) calculation

5.1. Dimerization energy

DFT calculations were performed using ORCA 5.0[31]. The initial dimeric structures were extracted from the crystal structures, followed by optimization of hydrogens using the r^{2}SCAN-3c[30] which includes D4 dispersion correction and also gCP correction to remove BSSE. The dimerization energies (ΔE_{total}) were evaluated using the sum of the interaction energy (ΔE_{int}) and strain energy (ΔE_{strain}). The term ΔE_{int} denotes the energy difference between the dimers and monomers with a dimeric conformation. ΔE_{strain} is the energy difference between the dimeric and monomeric conformers.

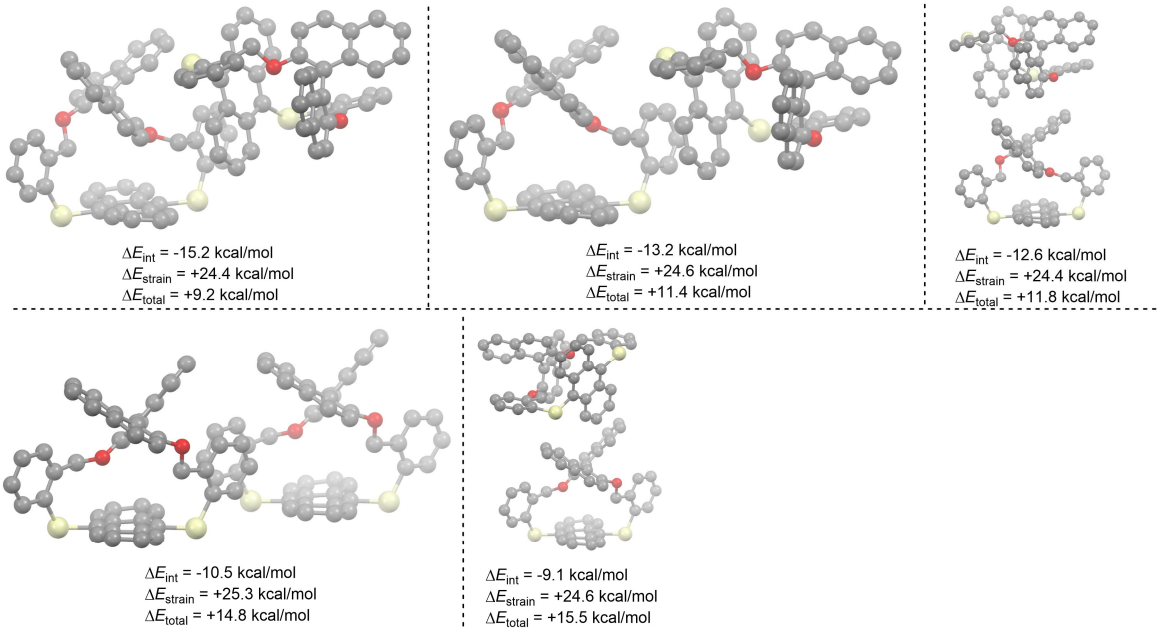


Fig. S36 Dimeric structures of (*S*)-**3a**-E extracted from the crystal structures. The interaction (ΔE_{int}), strain (ΔE_{strain}), and dimerization (ΔE_{total}) energies are represented by the structures. Optimized hydrogen atoms by r^{2}SCAN-3c were omitted for clarity.

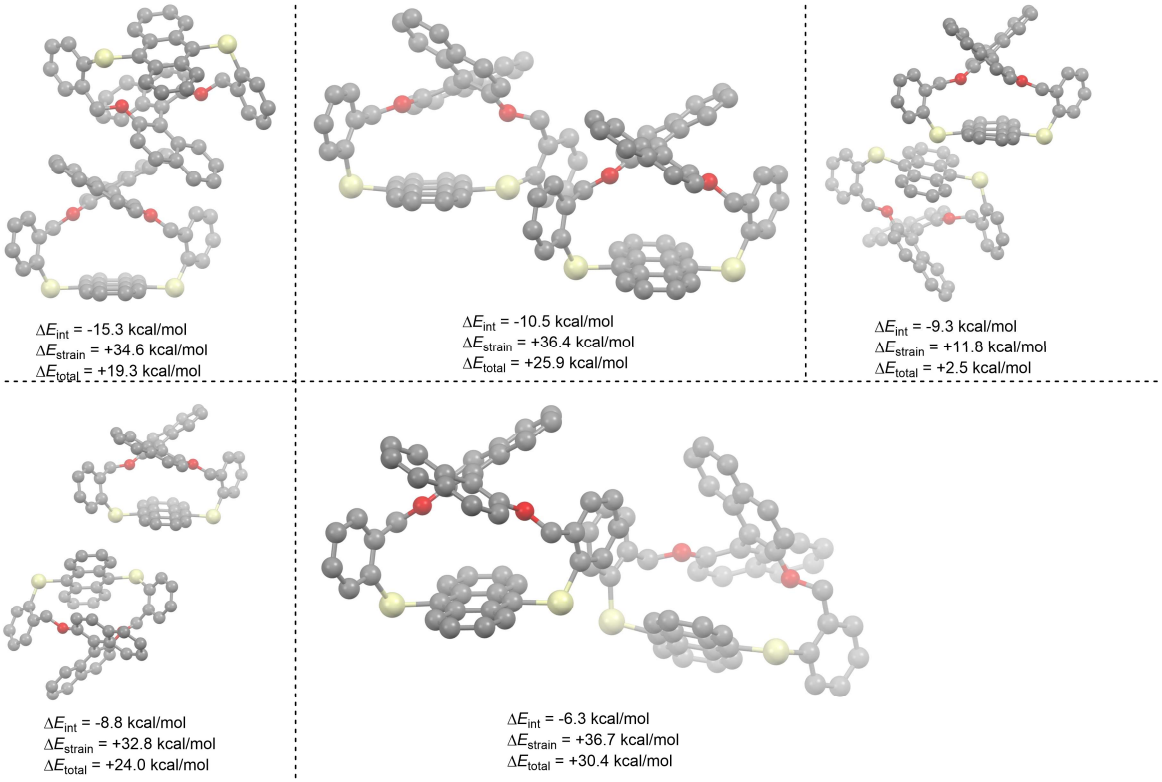


Fig. S37 Dimeric structures of (*S*)-**3a**-H extracted from the crystal structures. The interaction (ΔE_{int}), strain (ΔE_{strain}), and dimerization (ΔE_{total}) energies are represented by the structures. Optimized hydrogen atoms by r^{2}SCAN-3c were omitted for clarity.

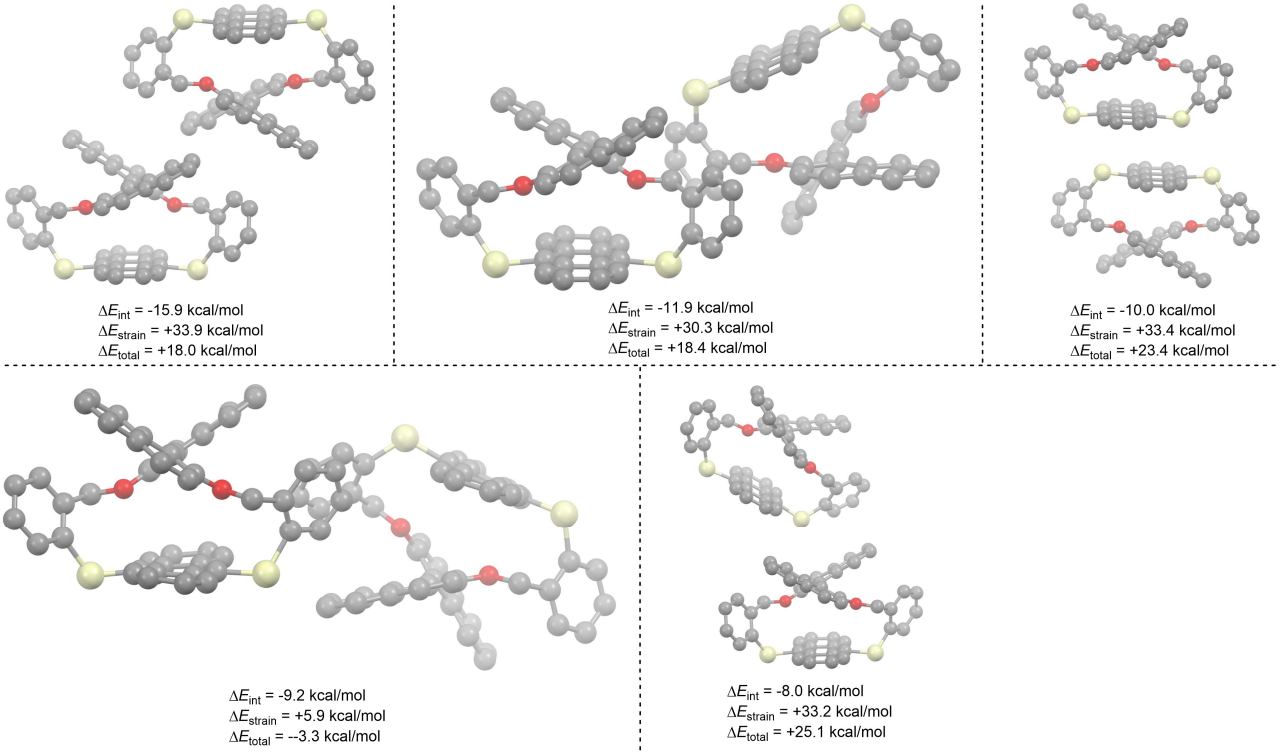


Fig. S38 Dimeric structures of *rac*-**3a** extracted from the crystal structures. The interaction (ΔE_{int}), strain (ΔE_{strain}), and dimerization (ΔE_{total}) energies are represented by the structures. Optimized hydrogen atoms by r^{2}SCAN-3c were omitted for clarity.

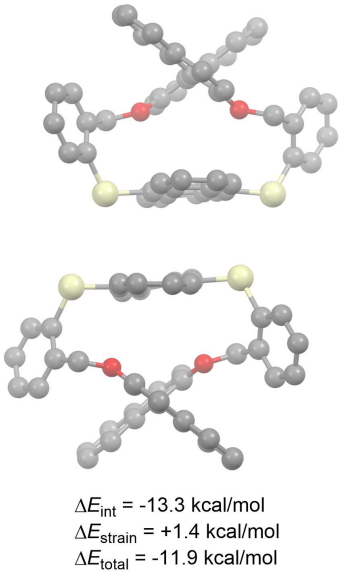


Fig. S39 Virtual dimer of (*S*)-**3a** with π-π interaction optimized by r^{2}SCAN-3c. The interaction (ΔE_{int}), strain (ΔE_{strain}), and dimerization (ΔE_{total}) energies are represented by the structures. Hydrogen atoms were omitted for clarity.

5.2. TD-DFT

Absorption and Emission energies were calculated at PBE0/def2-SVP//PBE0/def2-SVP level with Tamm–Dancoff approximation.

Table S2. Computed electronic absorption transition of 9,10-disilylanthracene using PBE0/def2-SVP//PBE0/def2-SVP.

Excited state	Energy (nm)	f[a]	Composition
1	365.4	0.172189272	HOMO → LUMO (92%)
2	317.5	0.009073822	HOMO–1 → LUMO (55%) HOMO → LUMO+1 (44%)
3	274.6	0.000996964	HOMO–2 → LUMO (86%) HOMO → LUMO+2 (12%)
4	248.9	0.002217679	HOMO–3 → LUMO (98%)
5	245.1	0.000821870	HOMO → LUMO+2 (53%) HOMO → LUMO+3 (25%) HOMO–4 → LUMO (14%)
6	237.4	0.000489571	HOMO → LUMO+3 (43%) HOMO → LUMO+2 (30%) HOMO–4 → LUMO+2 (17%)
7	223.2	1.353841366	HOMO → LUMO+1 (34%) HOMO–1 → LUMO (26%) HOMO–2 → LUMO+1 (13%) HOMO–5 → LUMO (12%)
8	219.3	0.843003770	HOMO–5 → LUMO (26%) HOMO–2 → LUMO+1 (22%) HOMO → LUMO+1 (18%) HOMO–1 → LUMO (14%)
9	216.9	0.126593276	HOMO–4 → LUMO (65%) HOMO → LUMO+3 (29%)
10	206.5	0.026276795	HOMO–5 → LUMO (44%) HOMO–1→ LUMO+2 (35%) HOMO–2 → LUMO+1 (14%)

[a] Oscillator strength.

Table S3. Computed electronic absorption transition of a π-stacked dimer of 9,10-disilylanthracene using PBE0/def2-SVP//PBE0/def2-SVP.

Excited state	Energy (nm)	*f*[a]	Composition
1	433.9	0.000040249	HOMO → LUMO (75%) HOMO–1 → LUMO+1 (19%)
2	429.0	0.026206328	HOMO → LUMO+1 (65%) HOMO–1 → LUMO (29%)
3	378.9	0.000128060	HOMO–1 → LUMO+1 (70%) HOMO → LUMO (18%)
4	362.2	0.240325624	HOMO–1 → LUMO (58%) HOMO → LUMO+1 (26%)
5	321.4	0.000033056	HOMO–2 → LUMO (43%) HOMO → LUMO+2 (31%) HOMO–3 → LUMO+1 (13%)
6	319.4	0.009567309	HOMO–2 → LUMO+1 (39%) HOMO → LUMO+3 (28%) HOMO–1 → LUMO+2 (16%) HOMO–3 → LUMO (13%)
7	298.5	0.000361759	HOMO–3 → LUMO+2 (52%) HOMO–2 → LUMO (36%)
8	296.5	0.028536375	HOMO–3 → LUMO (54%) HOMO–2 → LUMO+1 (33%)
9	284.9	0.014493768	HOMO–4 → LUMO (88%)
10	284.2	0.000033175	HOMO–4 → LUMO+1 (83%)

[a] Oscillator strength.

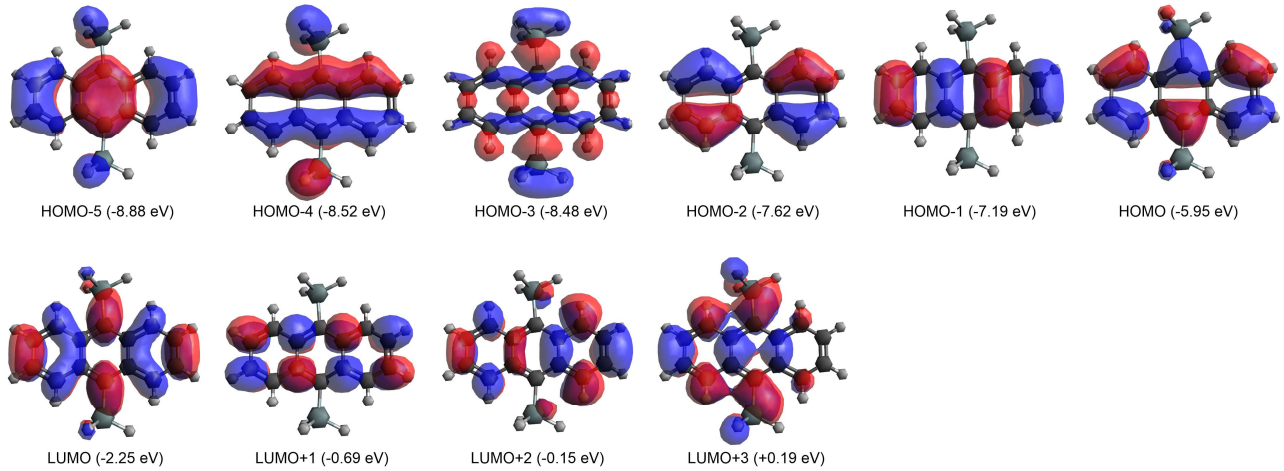


Fig. S40 Frontier orbitals of 9,10-disilylanthracene (PBE0/def2-SVP//PBE0/def2-SVP).

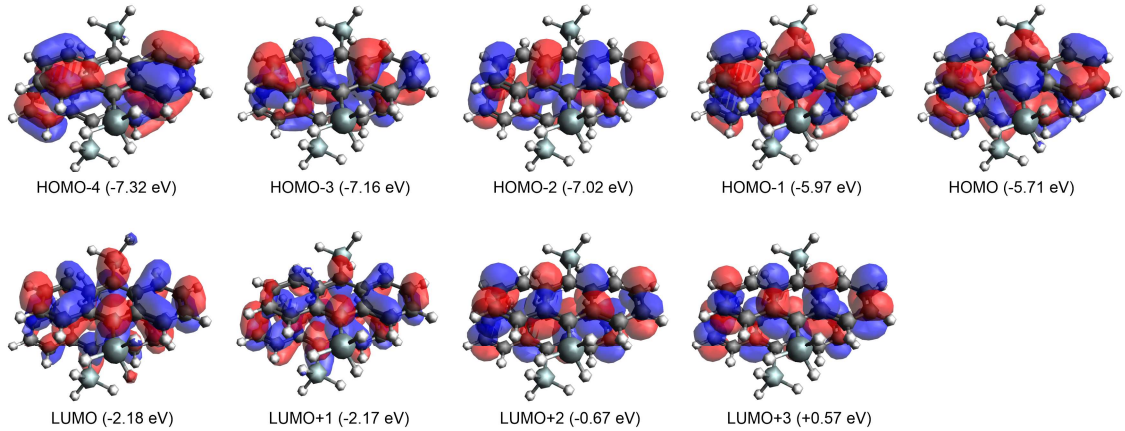


Fig. S41 Frontier orbitals of a π-stacked dimer of 9,10-disilylanthracene (PBE0/def2-SVP//PBE0/def2-SVP).

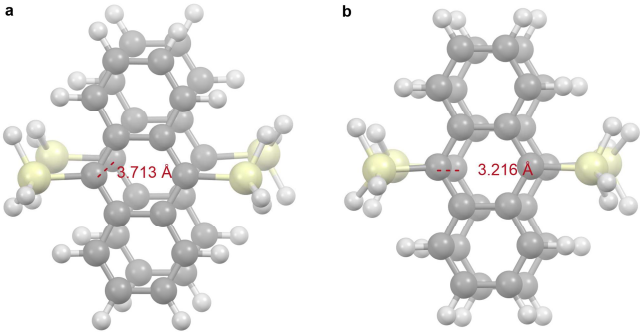


Fig. S42 Optimized structures of a π-stacked dimer of 9,10-disilylanthracene (PBE0/def2-SVP//PBE0/def2-SVP). **a,** S_0. **b,** S_1.

6. Thermal analysis

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed using a Shimadzu DTG-60 analyzer under helium flow. Each sample weighed ~5 mg. The samples were placed in aluminum pans. The heating and cooling rates were 10 K min^{-1} and 2 K min^{-1}, respectively.

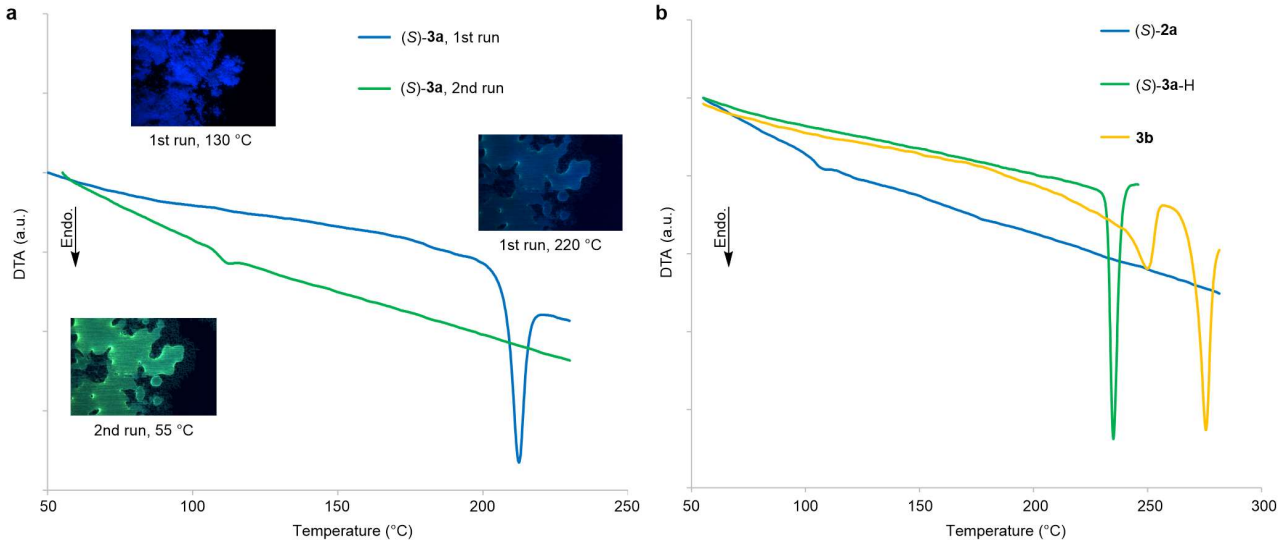


Fig. S43 DTA results at a scanning rate of +10 °C min^{-1}. **a,** The powder of (*S*)-**3a** melted at 212 °C in the first run (blue). In the second run (green), the glass of (*S*)-**3a** showed a baseline shift around 107 °C. **b,** The powder of (*S*)-**2a** (blue) showed a baseline shift around 104 °C, which indicated the powder was glass. The melting point of (*S*)-**3a**-H (green) is 232 °C. The crystals of **3b** (yellow) decomposed and melted above 240 °C so that the crystal structure was maintained in the photoluminescence measurement at 220 °C.

7. UV-vis absorption spectra

UV-vis absorption spectra were obtained using a SHIMADZU UV-1800 spectrometer.

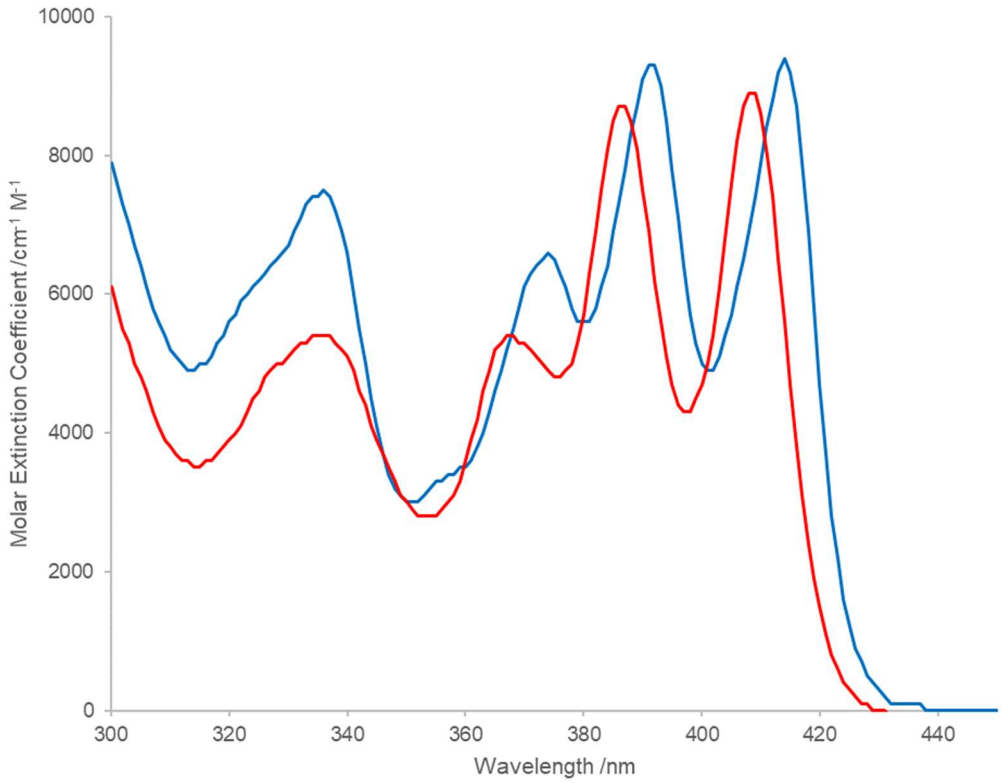


Fig. S44 UV-vis spectra of (*S*)-**2a** (blue) and (*S*)-**3a** (red) in $CHCl_3$ (1.0×10^{-5} M).

8. Photoluminescence Data

Photoluminescence spectra of the solutions were obtained using a SHIMADZU RF-5300PC spectrometer. Photoluminescence spectra of the glasses, crystals and films were obtained using an Ocean Optics USB 4000 fiber spectrometer. The excitation wavelength was 365 nm. The sample temperature was controlled using a MSA FACTORY PH132 hot plate. A portable fan and ice bag was used for rapid cooling to 110-170 °C and 20 °C, respectively. Luminescence spectra and quantum yields of solution were also obtained on the Otsuka Electronics QE-2000 system. Luminescence quantum yields of the glassy and crystalline samples were obtained using a JASCO FP-8500 spectrometer.

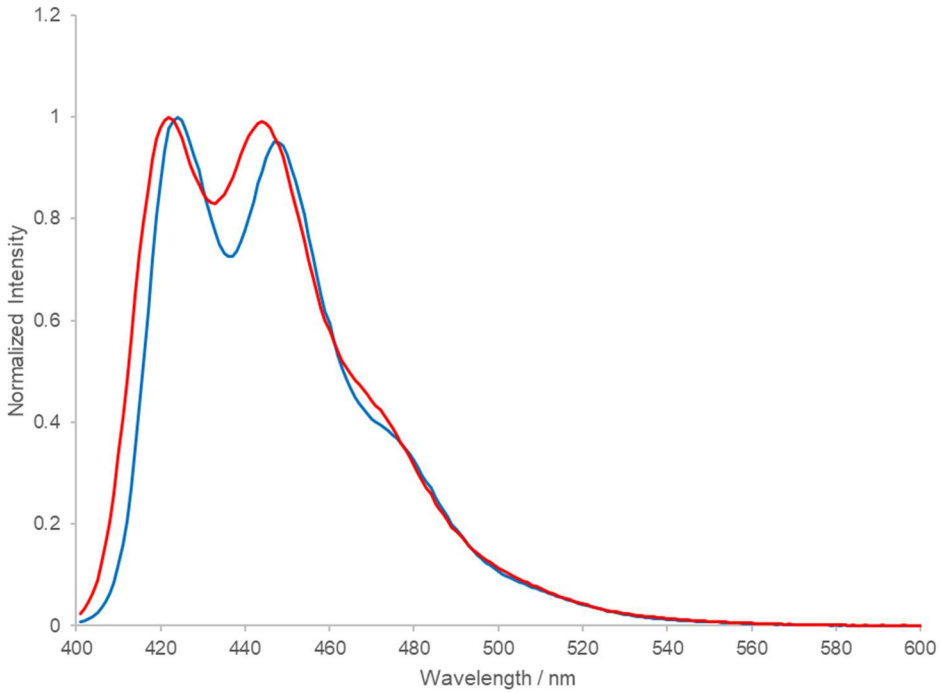


Fig. S45 Photoluminescence spectra of (*S*)-**2a** (blue, λ_{ex} = 391 nm) and (*S*)-**3a** (red, λ_{ex} = 387 nm) in $CHCl_3$ (1.0×10^{-5} M).

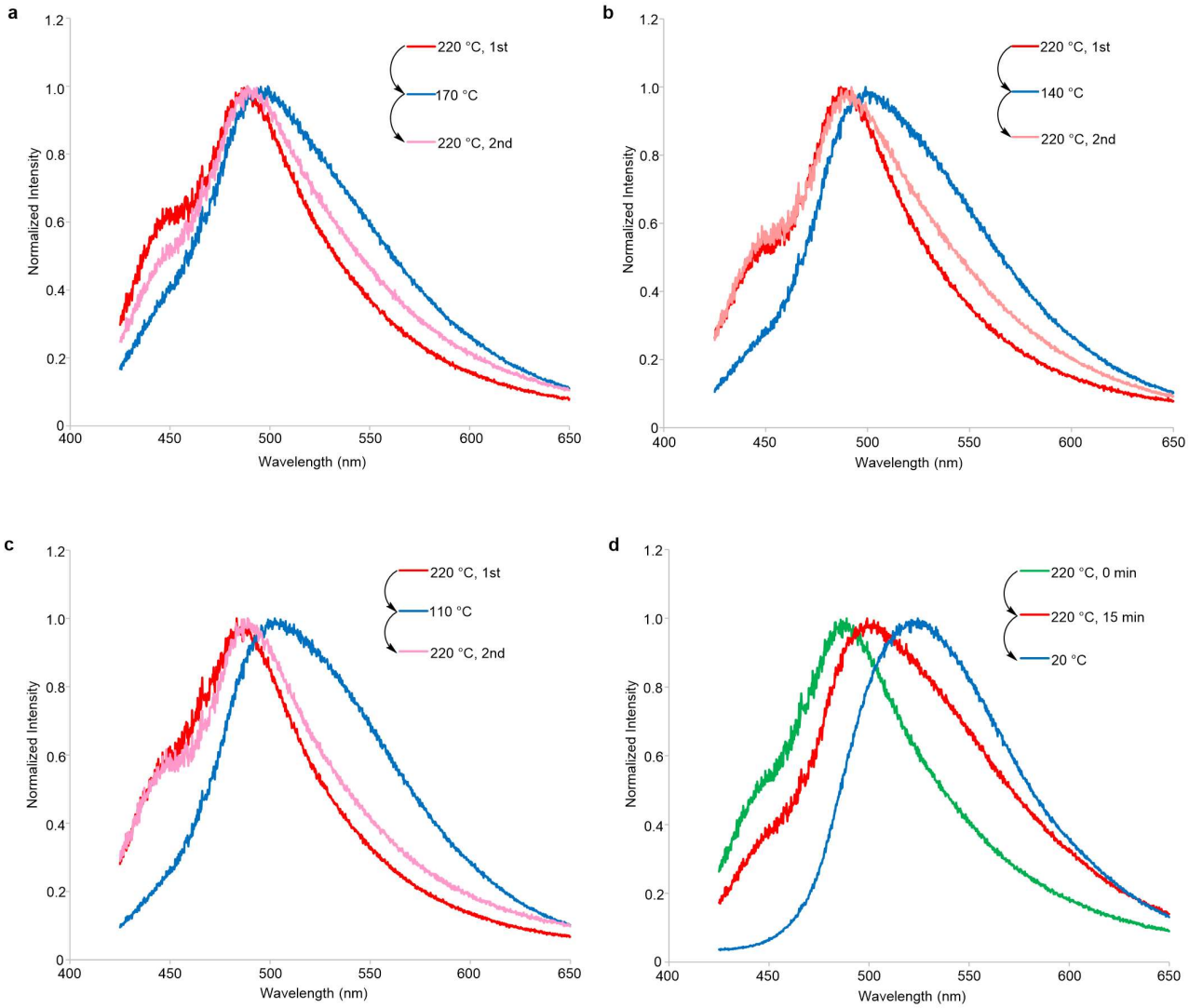


Fig. S46 Photoluminescence spectra of (*S*)-**3a**. **a**, Cooling the melt of (*S*)-**3a** to 170 °C, followed by heating to 220 °C. **b**, Cooling the melt of (*S*)-**3a** to 140 °C, followed by heating to 220 °C. **c**, Cooling the melt of (*S*)-**3a** to 110 °C, followed by heating to 220 °C. **d**, maintaining the melt of (*S*)-**3a** at 220 °C for 15 min, followed by cooling to 20 °C.

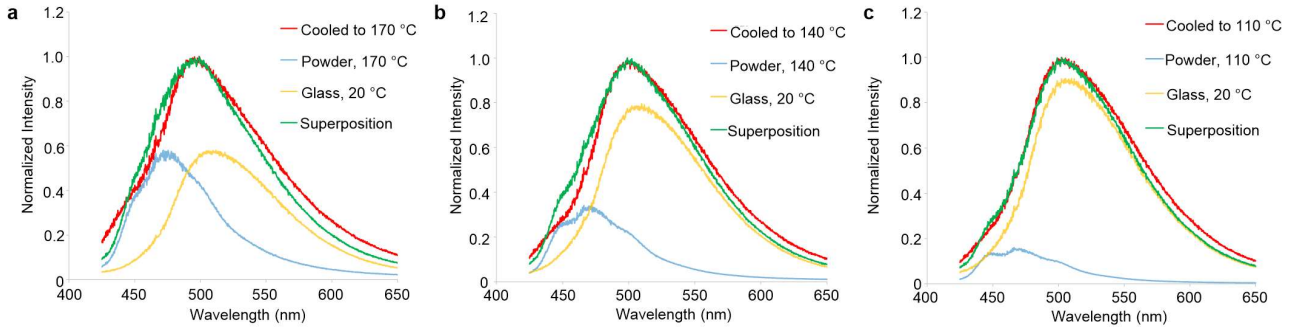


Fig. S47 Fitted photoluminescence spectra of (*S*)-**3a** by superposition of those of the powder and glass samples. **a,** Fitting the sample cooled to 170 °C. **b,** Fitting of the sample cooled to 140 °C. **c,** Fitting of the sample cooled to 110 °C.

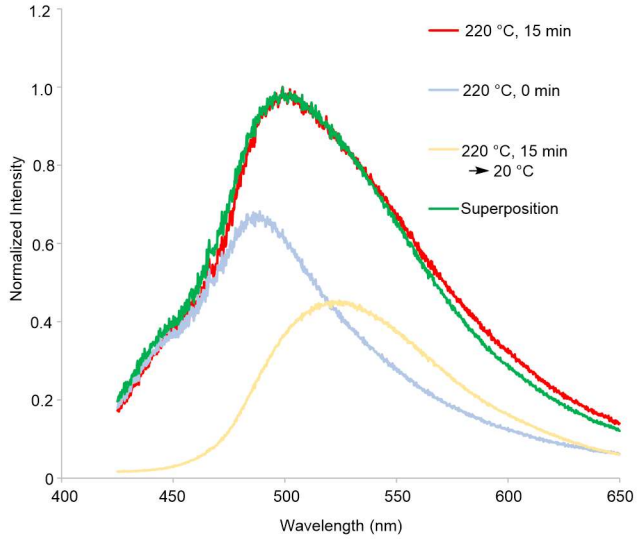


Fig. S48 Fitted photoluminescence spectrum of (*S*)-**3a** by superposition of those immediately after melting and after aging followed by cooling. The superposition fitted well with the spectrum of the sample aged at 220 °C for 15 min, indicating that the dimers with π-π interactions were tightly bound during the aging process.

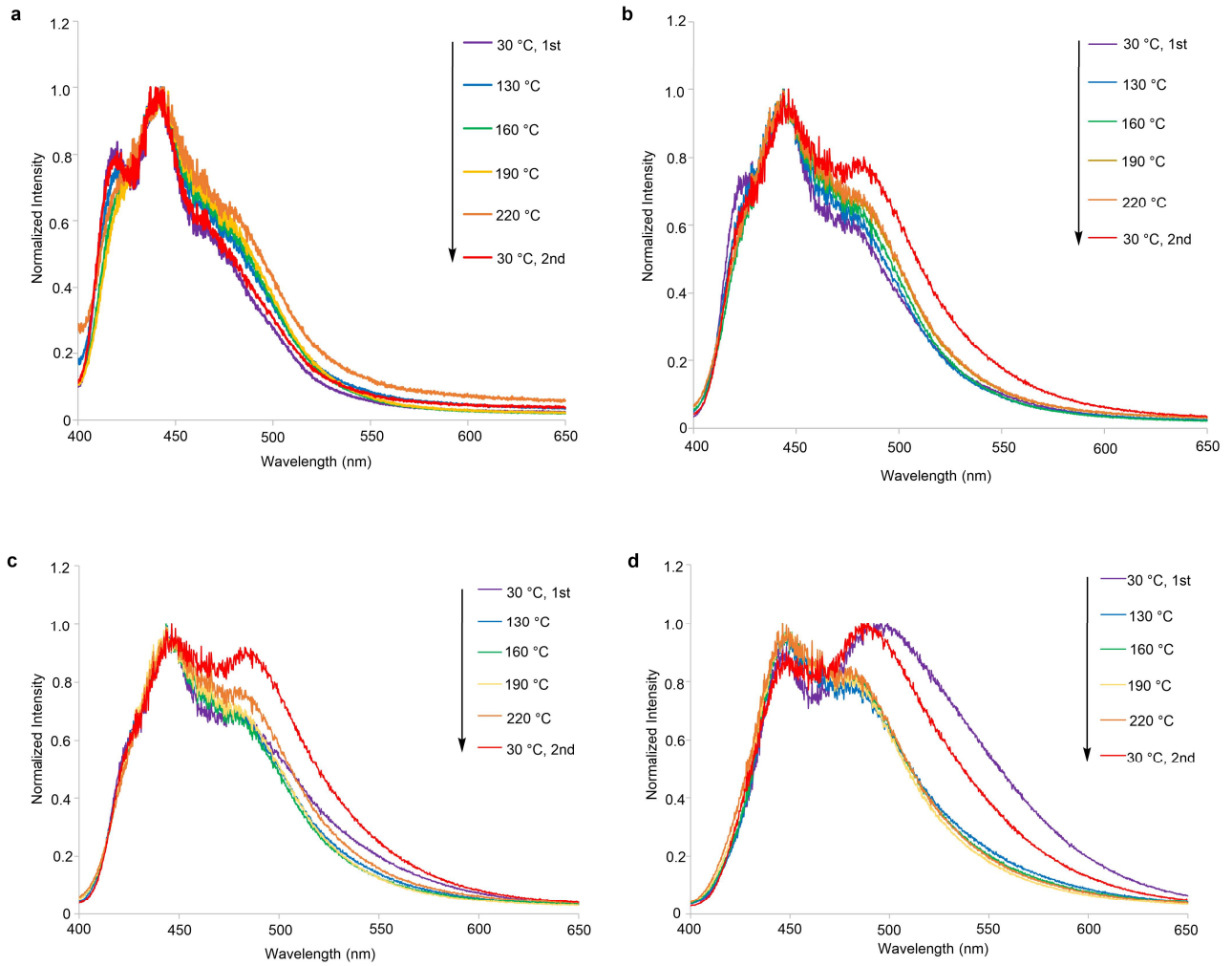


Fig. S49 Photoluminescence spectra of (*S*)-**3a** in ZEONEX at various temperatures. **a,** 2 wt%. **b,** 5 wt%. **c,** 10 wt%. **d,** 20 wt%.

Table S4 Photoluminescence quantum yield

Compound	Condition	Φ_{PL}
(*S*)-**2a**	in $CHCl_3$ (10^{-5} M)	0.99
	powder	0.38
(*S*)-**3a**	in $CHCl_3$ (10^{-5} M)	0.78
	(*S*)-**3a** -E	0.44
	(*S*)-**3a**-H	0.34
	glass	0.57
3b	in $CHCl_3$ (10^{-5} M)	0.85
	crystal	0.76

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) cu_yt4_142_EtOH_2_0m_a

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: cu_yt4_142_EtOH_2_0m_a

```
Bond precision:   C-C = 0.0067 A          Wavelength=1.54178

Cell:           a=11.5209(5)      b=11.6461(5)     c=28.3488(12)
                alpha=90.306(2)   beta=91.906(2)   gamma=101.613(2)
Temperature:    223 K

                 Calculated                Reported
Volume           3723.5(3)                 3723.5(3)
Space group      P 1                       P 1
Hall group       P 1                       P 1
Moiety formula   C48 H36 O2 Si2            C48 H36 O2 Si2
Sum formula      C48 H36 O2 Si2            C48 H36 O2 Si2
Mr               700.95                    700.99
Dx,g cm-3        1.250                     1.250
Z                4                         4
Mu (mm-1)        1.170                     1.169
F000             1472.0                    1478.0
F000'            1477.72
h,k,lmax         13,14,34                  13,14,34
Nref             27244[ 13622]             25617
Tmin,Tmax        0.587,0.748               0.548,0.754
Tmin'            0.514

Correction method= # Reported T Limits: Tmin=0.548 Tmax=0.754
AbsCorr = MULTI-SCAN

Data completeness= 1.88/0.94        Theta(max)= 68.240

R(reflections)= 0.0609( 25265)                wR2(reflections)=
                                              0.1751( 25617)
S = 1.050                  Npar= 1921
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The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

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PLAT089_ALERT_3_C Poor Data / Parameter Ratio (Zmax < 18) ........       6.97 Note
PLAT230_ALERT_2_C Hirshfeld Test Diff for    C14      --C15      .        6.0 s.u.
PLAT230_ALERT_2_C Hirshfeld Test Diff for    C24      --C25      .        6.2 s.u.
PLAT230_ALERT_2_C Hirshfeld Test Diff for    Si21     --C213     .        5.5 s.u.
PLAT230_ALERT_2_C Hirshfeld Test Diff for    C210     --C211     .        5.7 s.u.
PLAT340_ALERT_3_C Low Bond Precision on  C-C Bonds ...............    0.00668 Ang.
PLAT410_ALERT_2_C Short Intra H...H Contact  H344     ..H345     .       1.99 Ang.
                                                     x,y,z  =      1_555 Check
PLAT420_ALERT_2_C D-H Bond Without Acceptor  Si1      --H53      .     Please Check
PLAT420_ALERT_2_C D-H Bond Without Acceptor  Si1      --H54      .     Please Check
PLAT420_ALERT_2_C D-H Bond Without Acceptor  Si38     --H79      .     Please Check
PLAT420_ALERT_2_C D-H Bond Without Acceptor  Si38     --H80      .     Please Check
PLAT420_ALERT_2_C D-H Bond Without Acceptor  Si89     --H141     .     Please Check
PLAT420_ALERT_2_C D-H Bond Without Acceptor  Si89     --H142     .     Please Check
PLAT420_ALERT_2_C D-H Bond Without Acceptor  Si12     --H167     .     Please Check
PLAT420_ALERT_2_C D-H Bond Without Acceptor  Si12     --H168     .     Please Check
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PLAT420_ALERT_2_C D-H Bond Without Acceptor  Si21     --H230     .     Please Check
PLAT420_ALERT_2_C D-H Bond Without Acceptor  Si17     --H255     .     Please Check
PLAT420_ALERT_2_C D-H Bond Without Acceptor  Si17     --H256     .     Please Check
PLAT420_ALERT_2_C D-H Bond Without Acceptor  Si26     --H317     .     Please Check
PLAT420_ALERT_2_C D-H Bond Without Acceptor  Si26     --H318     .     Please Check
PLAT420_ALERT_2_C D-H Bond Without Acceptor  Si30     --H343     .     Please Check
PLAT420_ALERT_2_C D-H Bond Without Acceptor  Si30     --H344     .     Please Check
PLAT767_ALERT_4_C INS Embedded LIST 6 Instruction Should be LIST 4     Please Check
PLAT790_ALERT_4_C Centre of Gravity not Within Unit Cell: Resd.  #          1 Note
             C48 H36 O2 Si2
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.600        225 Report
PLAT913_ALERT_3_C Missing # of Very Strong Reflections in FCF ....         14 Note
PLAT918_ALERT_3_C Reflection(s) with I(obs) much Smaller I(calc) .         64 Check
PLAT939_ALERT_3_C Large Value of Not (SHELXL) Weight Optimized S .      40.61 Check
PLAT987_ALERT_1_C The Flack x is >> 0 -  Do a BASF/TWIN Refinement     Please Check
```

Alert level G

```
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite         26 Note
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...          2 Report
PLAT033_ALERT_4_G Flack x Value Deviates > 3.0 * sigma from Zero .      0.252 Note
PLAT068_ALERT_1_G Reported F000 Differs from Calcd (or Missing)...     Please Check
PLAT154_ALERT_1_G The s.u.'s on the Cell Angles are Equal ..(Note)       0.002 Degree
PLAT172_ALERT_4_G The CIF-Embedded .res File Contains DFIX Records          1 Report
PLAT173_ALERT_4_G The CIF-Embedded .res File Contains DANG Records         10 Report
PLAT178_ALERT_4_G The CIF-Embedded .res File Contains SIMU Records          1 Report
PLAT186_ALERT_4_G The CIF-Embedded .res File Contains ISOR Records          1 Report
PLAT188_ALERT_3_G A Non-default SIMU Restraint Value has been used      0.0100 Report
PLAT333_ALERT_2_G Large Aver C6-Ring C-C Dist C127     -C140     .       1.42 Ang.
PLAT333_ALERT_2_G Large Aver C6-Ring C-C Dist C303     -C316     .       1.42 Ang.
PLAT769_ALERT_4_G CIF Embedded explicitly supplied scattering data     Please Note
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd.  #          4 Note
             C48 H36 O2 Si2
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PLAT860_ALERT_3_G Number of Least-Squares Restraints .............         47 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600          8 Note
PLAT933_ALERT_2_G Number of HKL-OMIT Records in Embedded .res File          4 Note
PLAT960_ALERT_3_G Number of Intensities with I  <   - 2*sig(I) ...         43 Check
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          1 Info
PLAT982_ALERT_1_G The  C-f'=    0.0192 Deviates from  IT-value =       0.0181 Check
PLAT982_ALERT_1_G The  O-f'=    0.0524 Deviates from  IT-value =       0.0492 Check
PLAT982_ALERT_1_G The Si-f'=    0.2554 Deviates from  IT-value =       0.2541 Check
PLAT983_ALERT_1_G The  O-f"=    0.0338 Deviates from  IT-Value =       0.0322 Check
PLAT983_ALERT_1_G The Si-f"=    0.3254 Deviates from  IT-Value =       0.3302 Check
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
  30 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  24 ALERT level G = General information/check it is not something unexpected

   8 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
  27 ALERT type 2 Indicator that the structure model may be wrong or deficient
   9 ALERT type 3 Indicator that the structure quality may be low
  10 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

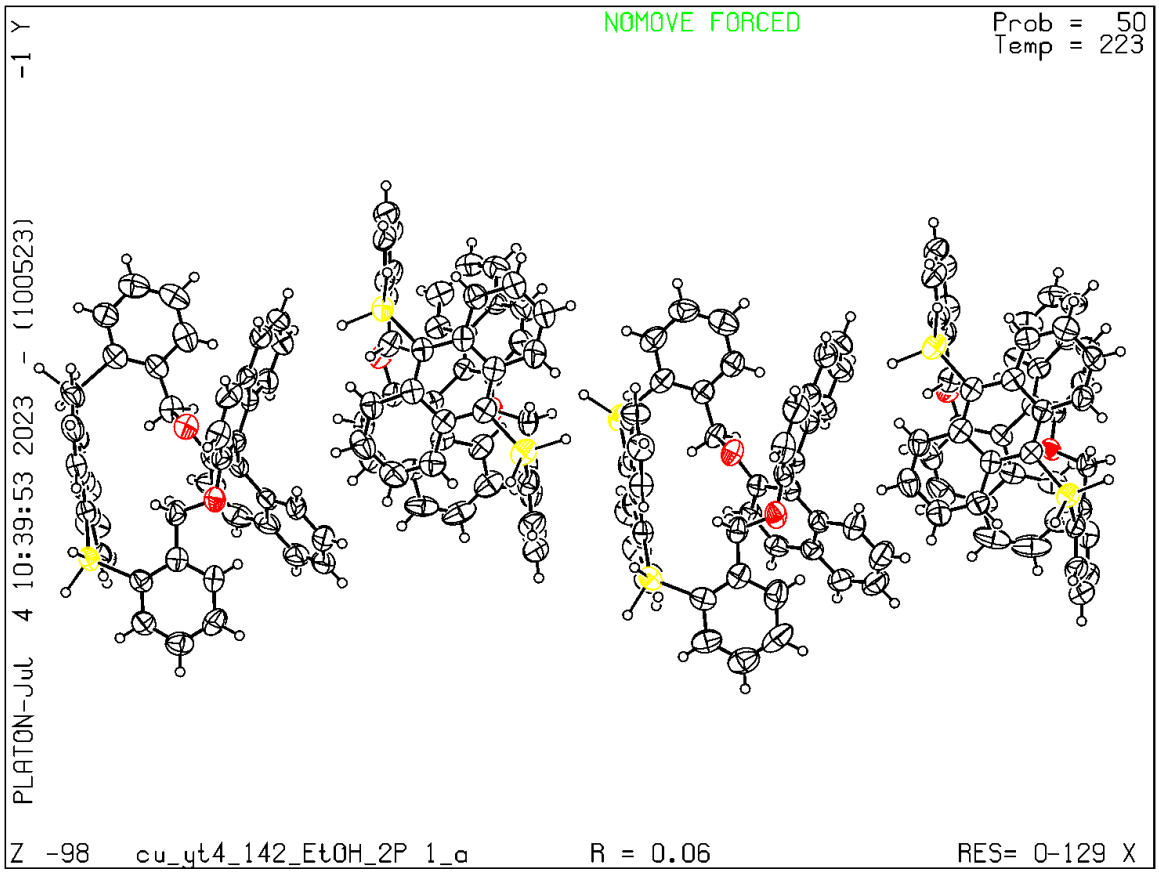
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 10/05/2023; check.def file version of 10/05/2023

Datablock cu_yt4_142_EtOH_2_0m_a - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) yt4_142_190125

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: yt4_142_190125

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Temperature:    223 K

                Calculated                Reported
Volume          5590.76(2)                5590.76(2)
Space group     P 21                      P 1 21 1
Hall group      P 2yb                     P 2yb
                C48 H35.65 O2 Si2, C48
Moiety formula  H35.72 O2 Si2, C48 H36 O2 1(C48 H36 O2 Si2)
                Si2
Sum formula     C144 H107.36 O6 Si6       C48 H35.787 O2 Si2
Mr              2102.20                   700.78
Dx,g cm-3       1.249                     1.249
Z               2                         6
Mu (mm-1)       1.168                     1.168
F000            2206.7                    2215.7
F000'           2215.31
h,k,lmax        13,34,22                  13,33,22
Nref            21962[ 11223]             21511
Tmin,Tmax       0.743,0.832               0.454,1.000
Tmin'           0.719

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AbsCorr = MULTI-SCAN

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R(reflections)= 0.0358( 20973)    wR2(reflections)= 0.1014( 21511)

S = 1.045                 Npar= 1576
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The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

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CRYSC01_ALERT_1_C The word below has not been recognised as a standard
           identifier.
           transparent
PLAT041_ALERT_1_C Calc. and Reported SumFormula    Strings  Differ     Please Check
PLAT089_ALERT_3_C Poor Data / Parameter Ratio (Zmax < 18) ........       7.09 Note
PLAT234_ALERT_4_C Large Hirshfeld Difference O10      --C1DA     .       0.16 Ang.
PLAT410_ALERT_2_C Short Intra H...H Contact  H0CA     ..H5EA     .       1.90 Ang.
                                                     x,y,z  =      1_555 Check
PLAT420_ALERT_2_C D-H Without Acceptor       Si1      --H1A      .     Please Check
PLAT420_ALERT_2_C D-H Without Acceptor       Si1      --H1B      .     Please Check
PLAT420_ALERT_2_C D-H Without Acceptor       Si4      --H4A      .     Please Check
PLAT420_ALERT_2_C D-H Without Acceptor       Si4      --H4B      .     Please Check
PLAT420_ALERT_2_C D-H Without Acceptor       Si3      --H7DA     .     Please Check
PLAT420_ALERT_2_C D-H Without Acceptor       Si2      --H8DA     .     Please Check
PLAT420_ALERT_2_C D-H Without Acceptor       Si2      --H9DA     .     Please Check
PLAT420_ALERT_2_C D-H Without Acceptor       Si3      --H0EA     .     Please Check
PLAT420_ALERT_2_C D-H Without Acceptor       Si5      --H3FA     .     Please Check
PLAT420_ALERT_2_C D-H Without Acceptor       Si5      --H4FA     .     Please Check
PLAT420_ALERT_2_C D-H Without Acceptor       Si6      --H5FA     .     Please Check
PLAT420_ALERT_2_C D-H Without Acceptor       Si6      --H6FA     .     Please Check
PLAT601_ALERT_2_C Structure Contains Solvent Accessible VOIDS of .         38 Ang**3
PLAT790_ALERT_4_C Centre of Gravity not Within Unit Cell: Resd.  #          1 Note
             C48 H35.65 O2 Si2
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.600          7 Report
```

Alert level G

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FORMU01_ALERT_1_G  There is a discrepancy between the atom counts in the
           _chemical_formula_sum and _chemical_formula_moiety. This is
           usually due to the moiety formula being in the wrong format.
           Atom count from _chemical_formula_sum:   C48 H35.787 O2 Si2
           Atom count from _chemical_formula_moiety:C48 H36 O2 Si2
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite         25 Note
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...         16 Report
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings  Differ     Please Check
PLAT045_ALERT_1_G Calculated and Reported Z Differ by a Factor ...       0.33 Check
PLAT068_ALERT_1_G Reported F000 Differs from Calcd (or Missing)...     Please Check
PLAT112_ALERT_2_G ADDSYM Detects New (Pseudo) Symm. Elem         2         85 %Fit
PLAT112_ALERT_2_G ADDSYM Detects New (Pseudo) Symm. Elem         2         85 %Fit
PLAT113_ALERT_2_G ADDSYM Suggests Possible Pseudo/New  Space Group      P2221 Check
PLAT142_ALERT_4_G s.u. on b - Axis Small or Missing ..............    0.00006 Ang.
PLAT143_ALERT_4_G s.u. on c - Axis Small or Missing ..............    0.00004 Ang.
PLAT145_ALERT_4_G s.u. on beta     Small or Missing ..............     0.0002 Degree
PLAT172_ALERT_4_G The CIF-Embedded .res File Contains DFIX Records          5 Report
PLAT173_ALERT_4_G The CIF-Embedded .res File Contains DANG Records          2 Report
PLAT178_ALERT_4_G The CIF-Embedded .res File Contains SIMU Records          2 Report
PLAT186_ALERT_4_G The CIF-Embedded .res File Contains ISOR Records          1 Report
PLAT230_ALERT_2_G Hirshfeld Test Diff for    Si5      --C33      .        7.6 s.u.
PLAT230_ALERT_2_G Hirshfeld Test Diff for    Si1A     --C33      .        6.0 s.u.
PLAT230_ALERT_2_G Hirshfeld Test Diff for    O12      --C138     .        7.2 s.u.
PLAT230_ALERT_2_G Hirshfeld Test Diff for    Si6      --C116     .        5.3 s.u.
PLAT301_ALERT_3_G Main Residue  Disorder ..............(Resd  1  )        15% Note
PLAT301_ALERT_3_G Main Residue  Disorder ..............(Resd  2  )        15% Note
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ...... Resd  1         87.65 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ...... Resd  2         87.72 Check
```

```
PLAT333_ALERT_2_G Large Aver C6-Ring C-C Dist C19      -C74      .       1.42 Ang.
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels .........        123 Note
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd.  #          2 Note
             C48 H35.72 O2 Si2
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd.  #          3 Note
             C48 H36 O2 Si2
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............        209 Note
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).          3 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600         40 Note
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ...          2 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          1 Info
PLAT982_ALERT_1_G The  C-f'=    0.0192 Deviates from  IT-value =       0.0181 Check
PLAT982_ALERT_1_G The  O-f'=    0.0524 Deviates from  IT-value =       0.0492 Check
PLAT982_ALERT_1_G The Si-f'=    0.2554 Deviates from  IT-value =       0.2541 Check
PLAT983_ALERT_1_G The  O-f"=    0.0338 Deviates from  IT-Value =       0.0322 Check
PLAT983_ALERT_1_G The Si-f"=    0.3254 Deviates from  IT-Value =       0.3302 Check
```

```
  0 ALERT level A = Most likely a serious problem - resolve or explain
  0 ALERT level B = A potentially serious problem, consider carefully
 20 ALERT level C = Check. Ensure it is not caused by an omission or oversight
 38 ALERT level G = General information/check it is not something unexpected

 11 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
 26 ALERT type 2 Indicator that the structure model may be wrong or deficient
  6 ALERT type 3 Indicator that the structure quality may be low
 15 ALERT type 4 Improvement, methodology, query or suggestion
  0 ALERT type 5 Informative message, check
```

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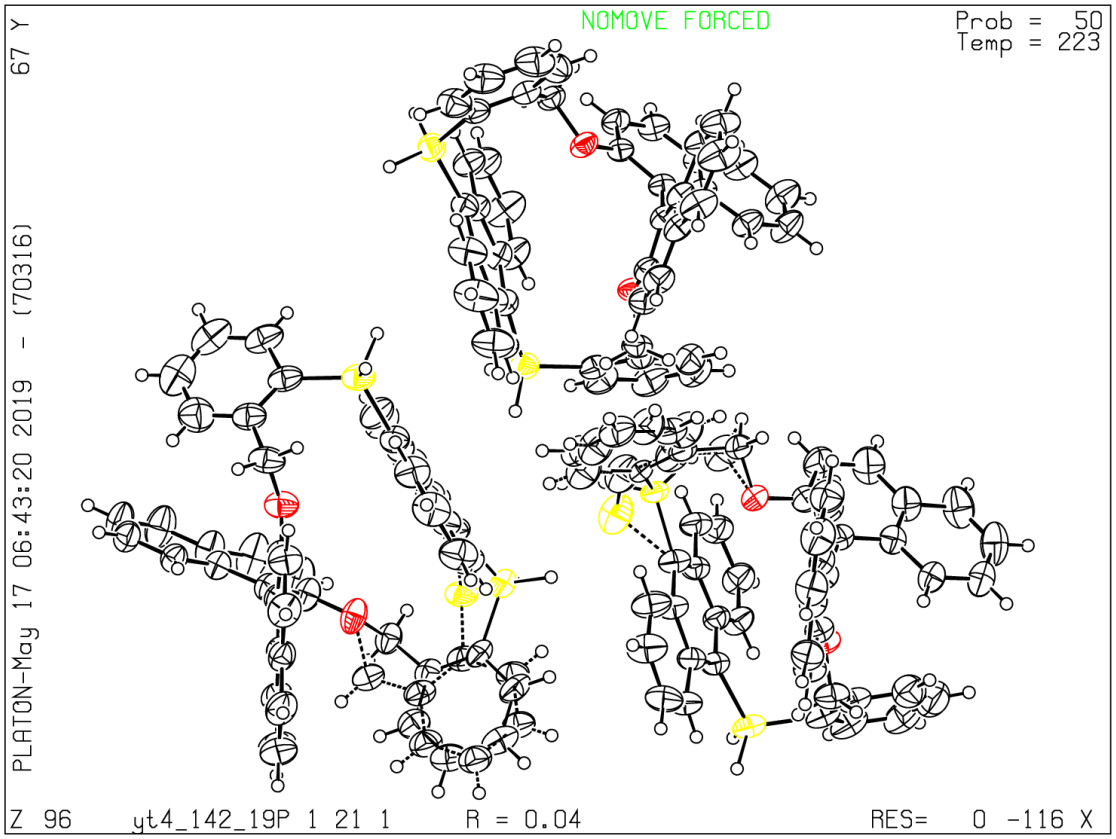
Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 03/05/2019; check.def file version of 29/04/2019

Datablock yt4_142_190125 - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) mo_20221129d3_0m_a

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: mo_20221129d3_0m_a

```
Bond precision:   C-C = 0.0020 A          Wavelength=0.71073

Cell:             a=11.2799(5)     b=17.2391(8)         c=18.9684(7)
                  alpha=90         beta=102.339(1)      gamma=90
Temperature:      93 K

                 Calculated                Reported
Volume           3603.3(3)                 3603.3(3)
Space group      P 21/n                    P 1 21/n 1
Hall group       -P 2yn                    -P 2yn
Moiety formula   C48 H36 O2 Si2            C48 H36 O2 Si2
Sum formula      C48 H36 O2 Si2            C48 H36 O2 Si2
Mr               700.95                    700.99
Dx,g cm-3        1.292                     1.292
Z                4                         4
Mu (mm-1)        0.140                     0.140
F000             1472.0                    1473.2
F000'            1473.19
h,k,lmax         13,20,22                  13,20,22
Nref             6616                      6607
Tmin,Tmax                                  0.705,0.745
Tmin'

Correction method= # Reported T Limits: Tmin=0.705 Tmax=0.745
AbsCorr = NONE

Data completeness= 0.999           Theta(max)= 25.370

R(reflections)= 0.0336( 5630)                wR2(reflections)=
                                             0.0855( 6607)
S = 1.034                  Npar= 485
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
PLAT053_ALERT_1_C Minimum Crystal Dimension Missing (or Error) ...     Please Check
PLAT054_ALERT_1_C Medium  Crystal Dimension Missing (or Error) ...     Please Check
PLAT055_ALERT_1_C Maximum Crystal Dimension Missing (or Error) ...     Please Check
PLAT420_ALERT_2_C D-H Bond Without Acceptor  Si01     --H01A     .     Please Check
PLAT420_ALERT_2_C D-H Bond Without Acceptor  Si01     --H01B     .     Please Check
PLAT420_ALERT_2_C D-H Bond Without Acceptor  Si02     --H02A     .     Please Check
PLAT420_ALERT_2_C D-H Bond Without Acceptor  Si02     --H02B     .     Please Check
PLAT767_ALERT_4_C INS Embedded LIST 6 Instruction Should be LIST 4     Please Check
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ......      2.448 Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.600          7 Report
```

Alert level G

```
PLAT333_ALERT_2_G Large Aver C6-Ring C-C Dist C00G     -C00Y     .       1.43 Ang.
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..........        88 Note
PLAT769_ALERT_4_G CIF Embedded explicitly supplied scattering data     Please Note
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).         1 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600         3 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.        15 Info
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
  10 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   6 ALERT level G = General information/check it is not something unexpected

   3 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   6 ALERT type 2 Indicator that the structure model may be wrong or deficient
   3 ALERT type 3 Indicator that the structure quality may be low
   4 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

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Publication of your CIF in other journals

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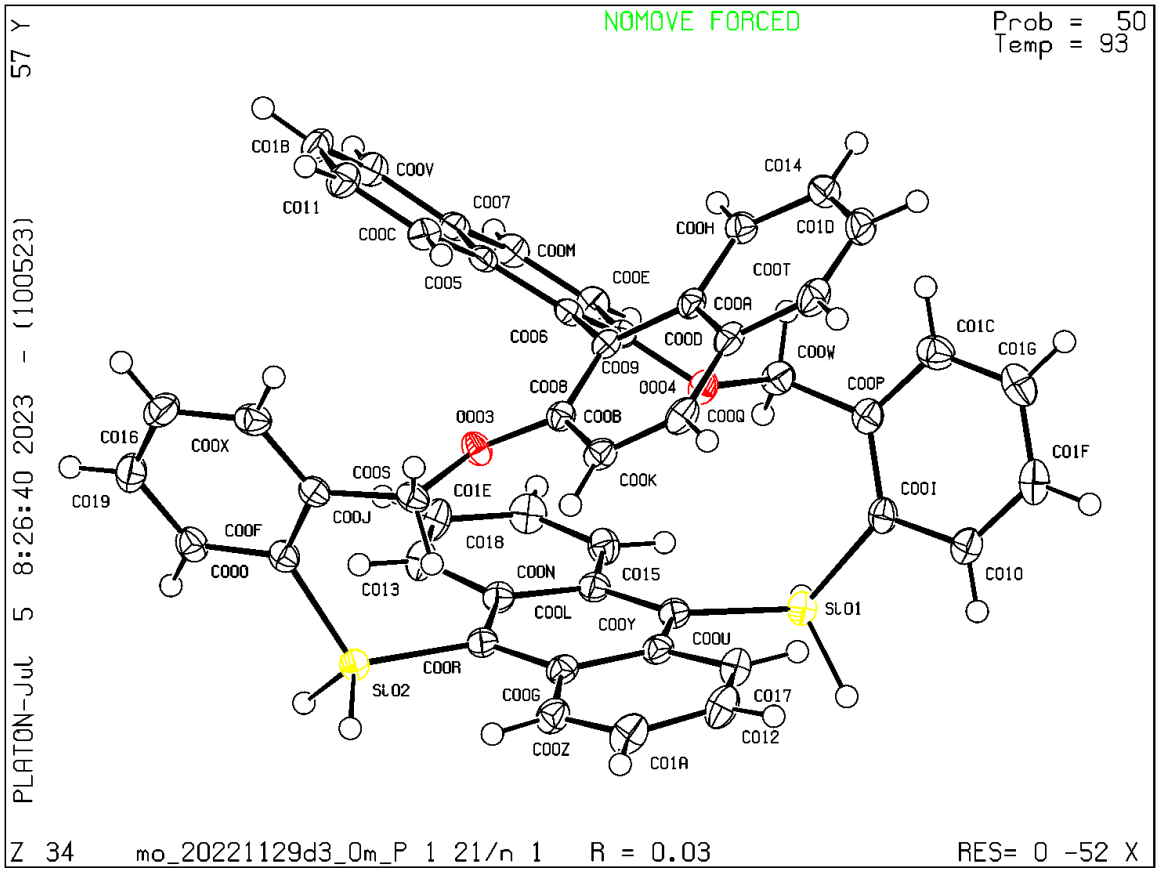
PLATON version of 10/05/2023; check.def file version of 10/05/2023

Datablock mo_20221129d3_0m_a - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) yt5_010_190218

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: yt5_010_190218

```
Bond precision:  C-C = 0.0023 A          Wavelength=1.54184

Cell:          a=10.4534(1)       b=12.1010(1)      c=13.6441(1)
               alpha=110.811(1)   beta=104.524(1)   gamma=95.283(1)
Temperature:   223 K
```

	Calculated	Reported
Volume	1530.15(3)	1530.15(3)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C40 H32 O2 Si2	C40 H32 O2 Si2
Sum formula	C40 H32 O2 Si2	C40 H32 O2 Si2
Mr	600.84	600.87
Dx,g cm-3	1.304	1.304
Z	2	2
Mu (mm-1)	1.329	1.329
F000	632.0	634.7
F000’	634.59	
h,k,lmax	12,14,16	12,14,16
Nref	5994	5873
Tmin,Tmax	0.741,0.819	0.647,1.000
Tmin’	0.688	

```
Correction method= # Reported T Limits: Tmin=0.647 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.980          Theta(max)= 71.750

R(reflections)= 0.0386( 5385)     wR2(reflections)= 0.1042( 5873)

S = 1.041                 Npar= 413
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
CRYSC01_ALERT_1_C The word below has not been recognised as a standard
           identifier.
           transparent
PLAT420_ALERT_2_C D-H Without Acceptor       Si1      --H1A      .     Please Check
PLAT420_ALERT_2_C D-H Without Acceptor       Si1      --H1B      .     Please Check
PLAT420_ALERT_2_C D-H Without Acceptor       Si2      --H2A      .     Please Check
PLAT420_ALERT_2_C D-H Without Acceptor       Si2      --H2B      .     Please Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.600         38 Report
```

Alert level G

```
PLAT068_ALERT_1_G Reported F000 Differs from Calcd (or Missing)...     Please Check
PLAT154_ALERT_1_G The s.u.'s on the Cell Angles are Equal ..(Note)      0.001 Degree
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..........        16 Note
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).         1 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600        81 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.        13 Info
PLAT982_ALERT_1_G The  C-f'=    0.0192 Deviates from  IT-value =       0.0181 Check
PLAT982_ALERT_1_G The  O-f'=    0.0524 Deviates from  IT-value =       0.0492 Check
PLAT982_ALERT_1_G The Si-f'=    0.2554 Deviates from  IT-value =       0.2541 Check
PLAT983_ALERT_1_G The  O-f"=    0.0338 Deviates from  IT-Value =       0.0322 Check
PLAT983_ALERT_1_G The Si-f"=    0.3254 Deviates from  IT-Value =       0.3302 Check
```

---

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PLATON version of 03/05/2019; check.def file version of 29/04/2019

Datablock yt5_010_190218 - ellipsoid plot