Electronic Supplementary Information

Highly enantioselective synthesis of silahelicenes using Ir-catalyzed [2+2+2] cycloaddition

Takanori Shibata,*[a] Toshifumi Uchiyama,[a] Yusuke Yoshinami,[a]
Satoru Takayasu,[a] Kyoji Tsuchikama,[a] and Kohei Endo[b]

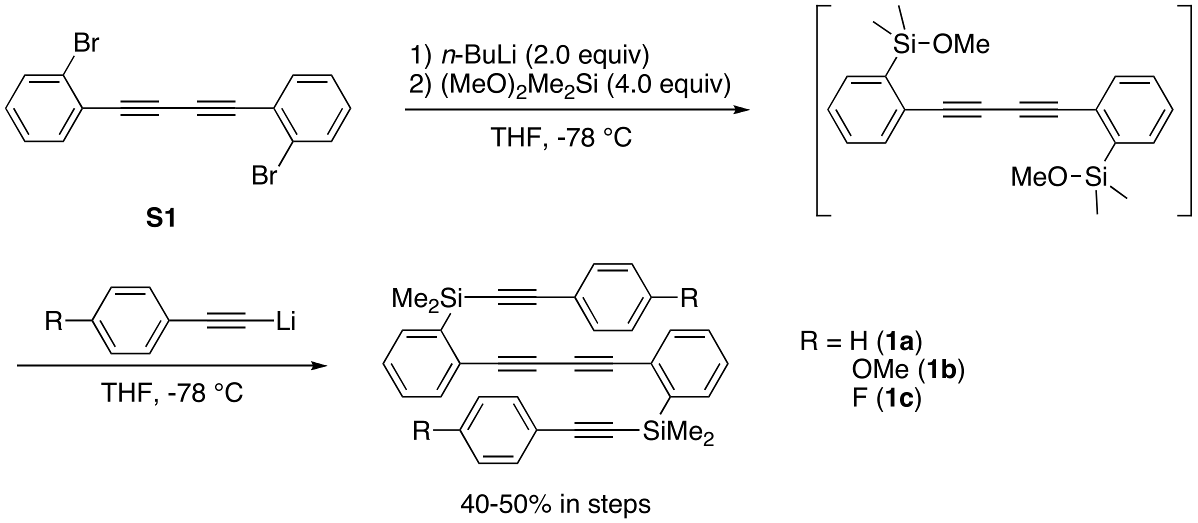
[a] Department of Chemistry and Biochemistry, School of Advanced Science and Engineering,
Waseda University, Tokyo, 169-8050, Japan and
[b] Waseda Institute for Advanced Study, Shinjuku, Tokyo, 169-8050, Japan
Email: tshibata@waseda.jp

1) Experimental details and characterization data for all new compounds

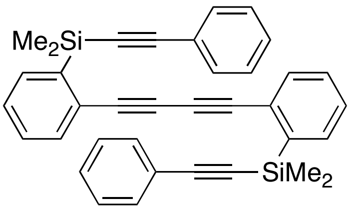
General information: ^{1}H NMR spectra were recorded on JEOL AL-400 (400 MHz) spectrometers. The chemical shifts were reported in parts per million (δ) relative to internal standard TMS (0 ppm) for $CDCl_3$. The peak patterns are indicated as follows: s, singlet; d, doublet; dd, doublet of doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, *J*, are reported in Hertz (Hz). ^{13}C NMR spectra were obtained by JEOL AL-400 (100 MHz) spectrometers and referenced to the internal solvent signals (central peak is 77.0 ppm in $CDCl_3$). $CDCl_3$ was used as an NMR solvent. High-resolution mass spectra (HRMS) were measured on a JEOL JMS-SX102A with FAB (Fast Atomic Bombardment) method, and IR spectra were recorded by a IR Horiba FT730 spectrometer. Preparative thin-layer chromatography (PTLC) was performed with silica gel-precoated glass plates (Merck 60 GF_{254}) prepared in our laboratory, Flash column chromatography was performed over silica gel 200-300. All reagents were weighed and handled in air and backfilled under argon at room temperature. Unless otherwise noted, all reactions were performed under an argon atmosphere. All reagents were purchased from Wako, Kanto, Aldrich and TCI and used without further purification. Anhydrous xylene and THF were degassed prior to use.

Preparation of tetraynes 3a, b, c

1,4-Bis(2-bromophenyl)buta-1,3-diyne (**S1**) was prepared by the literature procedure.[1] The dibromide was di-lithiated at -78 °C, then di-silylated by dimethoxydimethylsilane. In the solution of the *in-situ* generated methoxy silane, a THF solution of alkynyllithiums, which were prepared from the corresponding terminal alkynes in another pot, was transferred by cannula. The yields of this protocol fluctuated around 40-50%.

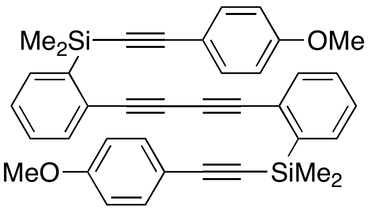


Scheme S1



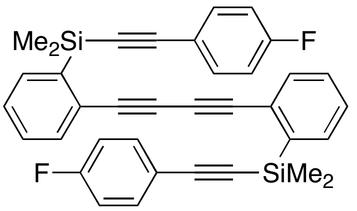
1a

1,4-Bis(2-(dimethyl(2-phenylethynyl)silyl)phenyl)buta-1,3-diyne (1a); Pale yellow solid (mp 110°C); IR (CH_2Cl_2) 2160, 849, 833, 758 cm^{-1}, ^{1}H-NMR δ 0.63 (s, 12H), 7.28-7.41 (m, 10H), 7.55-7.56 (m, 6H), 7.91-7.93 (m, 2H); ^{13}C NMR δ -0.8, 77.5, 83.4, 91.8, 107.4, 123.0, 126.7, 128.2, 128.5, 129.4, 132.1, 133.3, 135.3, 140.7 (a pair of aromatic peaks is overlapped); HRMS (FAB, positive) m/z Calcd. for $C_{36}H_{30}Si_2$, 518.1910 (M); found, 518.1886 (M).



1b

1,4-Bis(2-(dimethyl-(2-(4-methoxyphenyl)ethynyl)silyl)phenyl)buta-1,3-diyne (1b); Pale yellow solid (mp 107 °C); IR (CH_2Cl_2) 2156, 1604, 1508, 1250, 854, 831 cm^{-1}; ^{1}H-NMR δ = 0.62 (s, 12H), 3.81 (s, 6H), 6.82 (dd, J = 2.4, 8.5 Hz, 4H), 7.33-7.41 (m, 4H), 7.49 (dd, J = 2.4, 8.5 Hz, 4H), 7.53-7.57 (m, 2H), 7.90-7.94 (m, 2H); ^{13}C NMR δ -0.7, 55.2, 77.5, 83.4, 90.2, 107.6, 113.8, 115.1, 126.7, 128.4, 129.3, 133.3, 133.6, 135.3, 141.0, 159.9; HRMS (FAB, positive) m/z Calcd. for $C_{38}H_{35}O_2Si_2$, 579.2176 ([M+1]$^+$); found, 579.2156 ([M+1]$^+$).

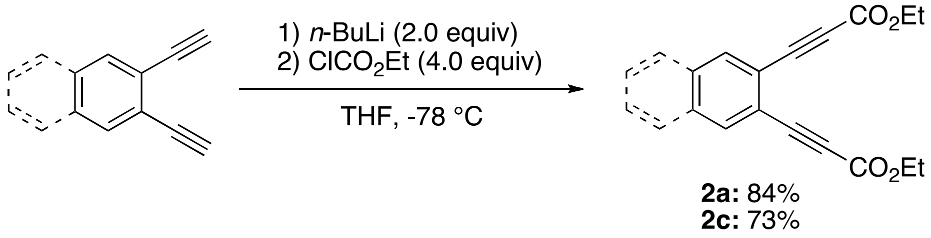


1c

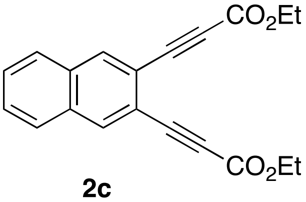
1,4-Bis(2-(dimethyl-(2-(4-fluorophenyl)ethynyl)silyl)phenyl)buta-1,3-diyne (1c); Pale yellow solid (mp 124 °C); IR (CH_2Cl_2) 2160, 1504, 1232, 1205, 1155, 1128 cm^{-1}; ^{1}H-NMR δ 0.62 (S, 12H), 6.94-7.01 (m, 4H), 7.35-7.42 (m, 4H), 7.49-7.57 (m, 6H), 7.85-7.89 (m, 2H); ^{13}C NMR δ -0.7, 77.6, 83.5, 91.7, 106.3, 115.6 (d, $J_{C\text{-}F}$ = 21.5 Hz), 119.2 (d, $J_{C\text{-}F}$ = 4.1 Hz), 126.8, 128.6, 129.5, 133.5, 134.2 (d, $J_{C\text{-}F}$ = 8.3 Hz), 135.2, 140.7, 162.8 (d, $J_{C\text{-}F}$ = 250.3 Hz); HRMS (FAB, positive) m/z Calcd. for $C_{36}H_{28}F_2Si_2$, 554.1698 ([M]); found, 554.1701 ([M]).

Preparation of diynes 2a, c

Diyne **2a** was prepared by the literature procedure.[2] Diyne **2c** was prepared by the di-ethoxycarbonylation of 2,3-diethynylnaphthalene[3] by using the same protocol for the synthesis of **2a**.



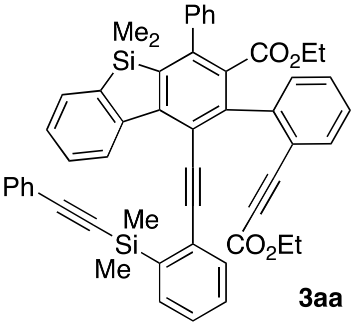
Scheme S2



2c

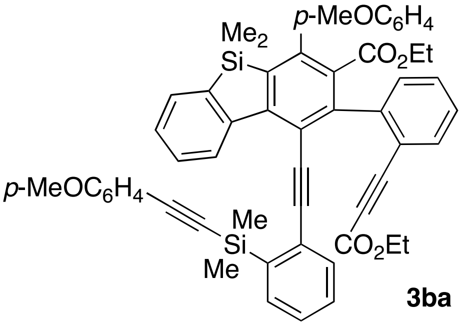
2,3-Bis((ethoxycalbonyl)ethynyl)naphthalene (2c); Pale brown solid (mp 69 ºC); IR (CH_2Cl_2) 2220, 1709, 1466, 1292, 1259, 1209 cm^{-1}; ^{1}H-NMR δ 1.38 (t, J = 7.1 Hz, 6H), 4.34 (q, J = 7.1 Hz, 4H), 7.61 (dd, J = 3.3, 6.3 Hz, 2H), 7.83 (dd, J = 3.3, 6.3 Hz, 2H), 8.18 (s, 2H); ^{13}C NMR δ 14.1, 62.3, 83.3, 84.1, 118.9, 128.1,128.8, 132.8, 134.9, 153.8; HRMS (FAB, positive) m/z Calcd. for $C_{20}H_{17}O_4$, 321.1127 ($[M+1]^+$); found, 321.1133 ($[M+1]^+$).

General procedure for Ir-catalyzed [2+2+2] cycloaddition of tetraynes with diynes
(*S*,*S*)-EtFerroTANE (4.4 mg, 0.01 mmol) and $[IrCl(cod)]_2$ (3.4 mg, 0.005 mmol) were stirred in xylene (0.1 ml) at room temperature. After the addition of a xylene solution (0.4 mL) of tetrayne **1** (0.05 mmol), the mixture was stirred at room temperature for 5 min. To the reaction mixture, a xylene solution of diyne **2** (0.10 mmol) was added dropwisely at 100 °C over 10 min, and it was further stirred at 100 °C for 2-4 h. The solvent was removed under reduced pressure, and the crude products were purified by TLC (Toluene-EtOAc, 20:1) to give analytically pure cycloadduct **3**. Its enantiomeric excess was determined by HPLC analysis using a chiral column.



3aa

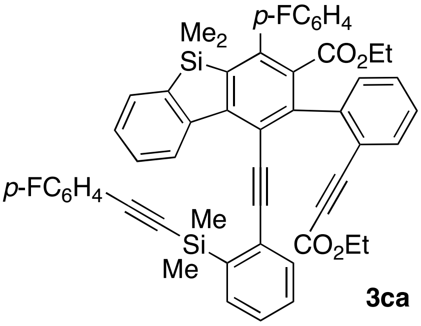
Ethyl 9,9-dimethyl-3-(2-(2-(ethoxycarbonyl)ethynyl)phenyl)-4-(2-(2-(dimethyl-(2-phenylethynyl)-silyl)phenyl)ethynyl)-1-phenyl-silafluorene-2-carboxylate (3aa); Pale brown solid (mp 74 ºC); IR (CH_2Cl_2) 2979, 2216, 2158, 1728, 1706, 1444, 1294, 1250, 1223, 1192 cm^{-1}; ^{1}H-NMR δ 0.06 (s, 3H), 0.18 (s, 3H), 0.40 (s, 3H), 0.44 (s, 3H), 0.67 (t, *J* = 7.19 Hz, 3H), 1.09 (t, *J* = 7.19 Hz, 3H), 3.64 (q, *J* = 7.19 Hz, 2H), 4.04-4.12 (m, 2H), 7.14-7.16 (m, 1H), 7.23-7.24 (m, 17H), 7.58-7.62(m, 2H), 7.89-7.91 (m, 1H) 9.27 (d, *J* = 7.99 Hz, 1H); ^{13}C NMR δ -2.9, -2.1, -0.1, 13.3, 13.9, 60.6, 61.8, 77.2, 83.3, 85.4, 91.7, 92.3, 101.0, 107.3, 117.1, 120.5, 122.9, 125.6, 127.6, 127.6, 127.8, 127.8, 127.9, 128.0, 128.1, 128.6, 129.1, 130.0, 130.1, 130.2, 132.0, 132.1, 132.8, 133.3, 133.5, 135.1, 138.2, 140.8, 140.8, 141.0, 143.7, 144.0, 145.1, 147.0, 148.2, 154.1, 167.8 (a pair of Si-Me peaks is overlapped); HRMS (FAB, positive) m/z Calcd. for $C_{52}H_{44}O_4Si_2$, 788.2778 (M); found, 788.2791 (M); $[\alpha]^{20}_D$= 120.5 (c 1.065, $CHCl_3$, 93% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak OD-H: 4 × 250 nm, UV detector: λ = 254 nm, r.t., eluent: 1% *i*-PrOH in hexane, flow rate: 1.0 mL/min, retention time: 7.5 min for major isomer and 8.5 min for minor isomer).



3ba

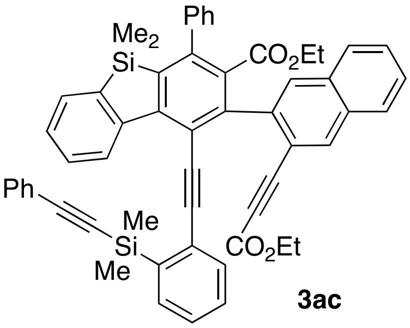
Ethyl 9,9-dimethyl-3-(2-(2-(ethoxycarbonyl)ethynyl)phenyl)-4-(2-(2-(dimethyl-(2-(4-methoxyphenyl)ethynyl)silyl)phenyl)ethynyl)-1-(4-methoxy)phenyl-silafluorene-2-carboxylate (3ba); Brown solid (mp 75 ºC); IR (CH_2Cl_2) 1726, 1709, 1506, 1294, 1259, 1192, 1093 cm^{-1}; ^{1}H-NMR δ 0.08 (s, 3H), 0.20 (s, 3H), 0.38 (s, 3H), 0.42(s, 3H), 0.71 (t, *J* = 7.1 Hz, 3H), 1.08 (t, *J* =

7.1 Hz, 3H), 3.66 (q, J = 7.1 Hz, 2H), 3.80 (s, 3H), 3.87 (s, 3H), 4.03-4.12 (m, 2H), 6.78 (dd, J = 2.2, 8.8, 2H), 6.93 (d, J = 7.8 Hz, 2H), 7.11-7.15 (m, 1H), 7.27-7.45 (m, 11H), 7.57-7.63 (m, 2H), 7.87-7.91 (m, 1H), 9.26 (d, J = 8.0 Hz, 1H); ^{13}C NMR δ -2.7, -1.9, 0.1, 13.5, 14.0, 55.4, 60.7, 61.9, 83.4, 85.6, 90.8, 91.8, 101.1, 107.5, 113.1, 113.9, 115.2, 117.1, 120.7, 125.8, 127.6, 127.9, 128.0, 128.1, 129.2, 130.1, 130.2, 130.4, 130.5, 130.6, 130.6, 130.7, 132.2, 133.3, 133.3, 133.4, 133.6, 135.3, 138.5, 141.1, 141.3, 143.8, 144.0, 144.8, 147.2, 148.2, 154.2, 159.3, 159.9, 168.1 (a pair of Si-Me peaks is overlapped); (FAB, positive) m/z Calcd. for $C_{54}H_{49}O_6Si_2$, 849.3068 ([M+1]$^+$); found, 849.3088 ([M+1]$^+$); $[\alpha]^{22}_D$= 106.3 (c 0.835, $CHCl_3$, 94% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak IB-H (double): 4 × 250 nm, UV detector: λ = 254 nm, r.t., eluent: 2% *i*-PrOH in hexane, flow rate: 1.0 mL/min, retention time: 28.5 min for major isomer and 27 min for minor isomer).



3ca

Ethyl 9,9-dimethyl-3-(2-(2-(ethoxycarbonyl)ethynyl)phenyl)-4-(2-(2-(dimethyl-(2-(4-fluorophenyl)ethynyl)silyl)phenyl)ethynyl)-1-(4-fluoro)phenyl-silafluorene-2-carboxylate (3ca); Brown solid (mp 67 ºC); IR (CH_2Cl_2) 1726, 1709, 1506, 1294, 1259, 1192, 1093 cm^{-1}; ^{1}H-NMR δ 0.08 (s, 3H), 0.18 (s, 3H), 0.40 (s, 3H), 0.42 (s, 3H), 0.71 (t, J = 7.1 Hz, 3H), 1.10 (t, J = 7.1, 3H), 3.66 (q, J = 7.1 Hz, 2H), 4.02-4.16 (m, 2H), 6.92 (dd, J = 7.1, 10.0, 2H), 7.07-7.20 (m, 3H), 7.26-7.49 (m, 11H), 7.60 (dd, J = 7.8, 10.8 Hz, 2H), 7.81-7.89 (m, 1H), 9.27 (d, J = 7.8 Hz, 1H); ^{13}C NMR δ -2.4, -1.7, 0.3, 13.8, 14.3, 61.1, 62.2, 83.9, 85.7, 92.1, 92.4, 101.6, 106.5, 115.1 (d, $J_{C\text{-}F}$ = 20.1 Hz), 115.1 (d, $J_{C\text{-}F}$ = 20.1 Hz), 115.8 (d, $J_{C\text{-}F}$ = 22.3 Hz), 117.8, 119.5 (d, $J_{C\text{-}F}$ = 4.2 Hz), 121.0, 126.1, 128.1, 128.3, 128.4, 128.5, 129.6, 130.5, 130.5, 130.8, 131.4 (d, $J_{C\text{-}F}$ = 6.4 Hz), 131.8 (d, $J_{C\text{-}F}$ = 5.3 Hz), 132.6, 133.5, 133.7, 134.0, 134.4 (d, $J_{C\text{-}F}$ = 8.5 Hz), 135.4, 137.1 (d, $J_{C\text{-}F}$ = 3.2 Hz), 138.5, 141.2, 141.5, 144.0, 144.3, 144.4, 147.3, 148.7, 154.5, 162.9 (d, $J_{C\text{-}F}$ = 248.0 Hz), 163.0 (d, $J_{C\text{-}F}$ = 250.1 Hz), 168.2 (a pair of Si-Me peaks is overlapped); (FAB, positive) m/z Calcd. for $C_{52}H_{42}O_4F_2Si_2$, 824.2590 ([M]); found, 824.2587 ([M]); $[\alpha]^{15}_D$= 131.2 (c 1.180, $CHCl_3$, 90% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak AD-H : 4 × 250 nm, UV detector: λ = 254 nm, r.t., eluent: 2% *i*-PrOH in hexane, flow rate: 1.0 mL/min, retention time: 8 min for major isomer and 6.5 min for minor isomer).



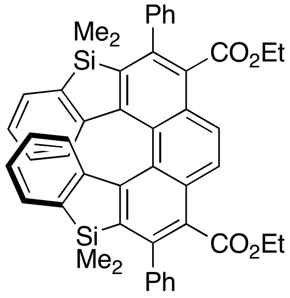
3ac

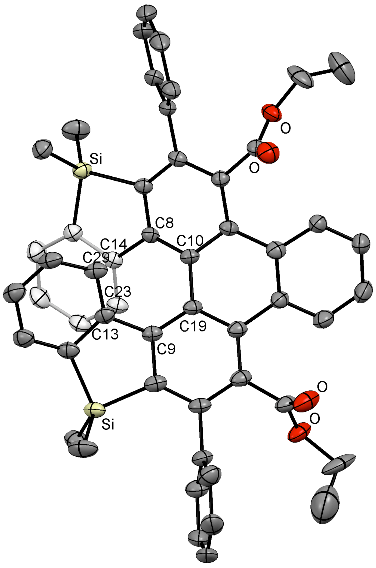
Ethyl 9,9-dimethyl-3-(3-(2-(ethoxycarbonyl)ethynyl)napht-2-yl)-4-(2-(2-(dimethyl-(2-phenylethynyl)silyl)phenyl)ethynyl)-1-phenyl-silafluorene-2-carboxylate (3ah); Pale green solid (mp 82 ºC); IR (CH_2Cl_2) 1726, 1707, 1639, 1444, 1263, 1205, 845, 783 cm^{-1}; ^{1}H-NMR δ 0.03

(s, 3H), 0.14 (s, 3H), 0.24 (s, 3H), 0.34 (s, 3H), 0.55 (t, *J* = 7.1 Hz, 3H), 1.06 (t, *J* = 7.1 Hz, 3H), 3.47-3.62 (m, 2H), 4.01-4.13 (m, 2H) 6.99-7.16 (m, 2H), 7.18-7.31 (m, 5H), 7.34-7.53 (m, 10H), 7.59 (d, *J* = 6.8 Hz, 1H), 7.76 (dd, *J* = 2.2, 6.8 Hz, 2H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.86 (s, 1H), 8.17 (s, 1H), 9.28 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR δ -3.2, -1.7, -0.6, -0.4, 13.2, 13.8, 60.5, 61.8, 83.1, 85.9, 92.0, 92.2, 100.9, 107.2, 117.6, 118.7, 122.9, 125.7, 126.9, 127.5, 127.7, 127.8, 127.9, 127.9, 128.0, 128.1, 128.5, 129.0, 129.0, 129.3, 130.2, 131.9, 132.0, 132.1, 133.3, 133.4, 133.6, 134.4, 135.0, 138.1, 138.9, 140.8, 140.8, 141.0, 143.7, 145.0, 147.1, 148.2, 154.1, 167.9; (FAB, positive) m/z Calcd. for $C_{56}H_{47}O_4Si_2$, 839.3013 ([M+1]$^+$); found, 839.3048 ([M+1]$^+$); $[\alpha]^{21}_D$= 28.6 (c 1.025, $CHCl_3$, 93% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak IA-H : 4 × 250 nm, UV detector: λ = 254 nm, r.t., eluent: 2% *i*-PrOH in hexane, flow rate: 1.0mL/min, retention time: 12.5 min for major isomer and 8.5 min for minor isomer).

General procedure for Ni-mediated intramolecular [2+2+2] cycloaddition of triynes

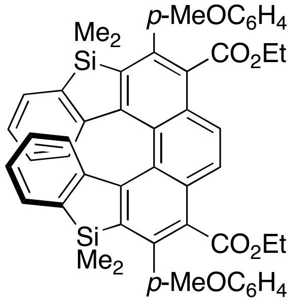
[Ni(cod)$_2$] (5.5 mg, 0.020 mmol) and triphenylphosphine (10.5 mg, 0.040 mmol) were stirred in THF (1.5 ml) at room temperature. After the addition of a THF solution (1.0 ml) of triyne **3** (0.02 mmol), the reaction mixture was stirred at room temperature for 4 h. The solvent was removed under reduced pressure, and the crude product were purified by TLC (Toluene-Acetone, 50:1) to give analytically pure cycloadduct **5**. Its enantiomeric excess was determined by HPLC analysis using a chiral column.





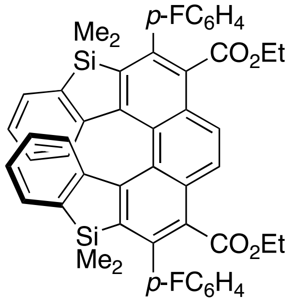
5aa

2,7-Di-(ethoxycarbonyl)-1,8-diphenyl-9,9,18,18-tetramethyl-9,18-disilaindeno[2,3-*c*]indeno-[3,2-*g*]triphenylene (5aa); Pale yellow solid; IR (CH_2Cl_2) 1722, 1227, 1207, 1144, 1093, 1065, 1022 cm^{-1}, ^{1}H-NMR δ -0.11 (s, 6H), 0.10 (s, 6H), 1.06 (t, *J* = 7.19, 6H), 4.10-4.18 (m, 4H), 6.85-6.93 (m, 4H), 7.18 (d, *J* = 7.59, 4H), 7.45-7.48 (m, 12H), 8.18-8.20 (m, 2H); ^{13}C NMR δ -3.9, 2.3, 13.6, 61.4, 124.6, 124.7, 126.4, 126.9, 127.2, 127.5, 127.6, 127.9, 128.7, 128.8, 129.6, 130.8, 131.7, 132.0, 139.7, 140.0, 141.2, 144.9, 148.9, 149.2, 171.1; HRMS (FAB, positive) m/z Calcd. for $C_{52}H_{44}O_4Si_2$, 788.2778 (M); found, 788.2781 (M); $[\alpha]^{19}_D$= 1063 (c 0.450, $CHCl_3$, >99% ee).
Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak IA: 4 × 250 nm, UV detector: λ = 254 nm, r.t., eluent: 20% CH_2Cl_2 in hexane, flow rate: 1.0 mL/min, retention time: 9 min for major isomer and 12 min for minor isomer). Crystallographic data of this compound have been deposited at the Cambridge Crystallographic Data Centre (CCDC 844257).



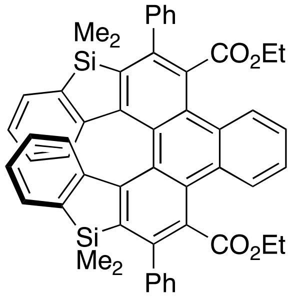
5ba

2,7-Di-(ethoxycarbonyl)-1,8-di-(4-methoxy)phenyl-9,9,18,18-tetramethyl-9,18-disilaindeno[2,3-*c*]indeno[3,2-*g*]triphenylene (5ba); Pale yellow solid (mp 153 ºC); IR (CH_2Cl_2) 1722, 1510, 1288, 1246, 1174, 839 cm^{-1}; ^{1}H-NMR δ -0.07 (s, 6H), 0.13 (s, 6H), 1.11 (t, *J* = 7.1 Hz, 6H), 3.91 (s, 6H), 4.16 (t, *J* = 7.1 Hz, 4H), 6.86 (ddd, *J* = 1.4, 7.4, 7.4 Hz, 2H), 6.88-6.93 (m, 2H), 6.97-7.08 (m, 4H), 7.15 (d, *J* = 7.8 Hz, 2H), 7.17-7.20 (m, 2H), 7.37 (d, *J* = 8.5 Hz, 4H), 7.46 (dd, *J* = 3.5, 9.6 Hz, 2H), 8.21 (dd, *J* = 3.5, 9.6 Hz, 2H); ^{13}C NMR δ -3.9, -2.2, 13.7, 55.3, 61.4, 113.0, 113.1, 124.6, 126.3, 126.8, 127.4, 127.5, 128.6, 130.1, 130.7, 130.9, 131.5, 132.0, 133.5, 140.0, 140.1, 144.6, 148.7, 149.2, 159.1, 171.3; HRMS (FAB, positive) m/z Calcd. for $C_{54}H_{48}O_6Si_2$, 848.2989 (M); found, 848.2972 (M); $[\alpha]^{20}{}_D$= 709 (c 0.705, $CHCl_3$, 92% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak IA (double): 4 × 250 nm, UV detector: λ = 254 nm, r.t., eluent: 10% *i*-PrOH in hexane, flow rate: 1.0 mL/min, retention time: 13 min for major isomer and 11 min for minor isomer).



5ca

2,7-Di-(ethoxycarbonyl)-1,8-di-(4-fluoro)phenyl-9,9,18,18-tetramethyl-9,18-disilaindeno[2,3-*c*]-indeno[3,2-*g*]triphenylene (5ca); Pale yellow solid (mp 154 ºC); IR (CH_2Cl_2) 1722, 1508, 1444, 1257, 1223, 1157, 1093, 843 cm^{-1}, ^{1}H-NMR δ -0.08 (s, 6H), 0.12 (s, 6H), 1.11 (t, *J* = 7.1 Hz, 6H), 4.12-4.20 (m, 4H), 6.87 (ddd, *J* = 1.3, 7.3, 7.3 Hz, 2H), 6.92 (ddd, *J* = 1.3, 7.3, 7.3 Hz, 2H), 7.11-7.24 (m, 8H), 7.38-7.51 (m, 6H), 8.19 (dd, *J* = 3.5, 9.5 Hz, 2H); ^{13}C NMR δ -3.8, -2.1, 13.8, 61.6, 100.0, 114.8 (d, $J_{C\text{-}F}$ = 21.0 Hz), 114.9 (d, $J_{C\text{-}F}$ = 21.9 Hz), 124.6, 124.9, 126.4, 127.1, 127.5, 127.7, 128.8, 130.7 (d, $J_{C\text{-}F}$ = 7.6 Hz), 130.7, 131.6 (d, $J_{C\text{-}F}$ = 7.6 Hz), 131.8, 132.2, 137.2 (d, $J_{C\text{-}F}$ = 2.9 Hz), 139.9, 143.9, 148.9, 149.5, 162.5 (d, $J_{C\text{-}F}$ = 247.0 Hz), 171.1; HRMS (FAB, positive) m/z Calcd. for $C_{52}H_{43}O_4F_2Si_2$, 825.2668 ($[M+1]^+$); found, 825.2634 ($[M+1]^+$); $[\alpha]^{22}{}_D$= 613 (c 1.025, $CHCl_3$, 90% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak IA (double): 4 × 250 nm, UV detector: λ = 254 nm, r.t., eluent: 10% CH_2Cl_2 in hexane, flow rate: 1.0 mL/min, retention time: 23 min for major isomer and 19 min for minor isomer).



5ac

2,9-Di-(ethoxycarbonyl)-1,10-diphenyl-11,11,20,20-tetramethyl-11,20-disilabenzo[n]indeno-[2,3-*c*]indeno[3,2-*g*]triphenylene (5ah); Pale yellow solid (mp >250 ºC); IR (CH_2Cl_2) 1722, 1514, 1442, 1306, 1211, 841 cm^{-1}, ^1H-NMR δ -0.09 (s, 6H), 0.10 (s, 6H), 1.09 (t, *J* = 7.1 Hz, 6H), 4.12-4.27 (m, 4H), 6.85-6.96 (m, 4H), 7.14-7.22 (m, 4H), 7.39-7.56 (m, 12H), 7.79-7.88 (m, 2H), 8.65 (s, 2H); ^{13}C NMR δ -3.8, -2.2, 13.7, 61.4, 124.7, 125.5, 125.7, 126.7, 126.9, 127.6, 127.7, 127.8, 128.2, 128.7, 128.9, 128.9, 129.7, 132.0, 132.2, 132.4, 140.1, 141.1, 145.1, 148.7, 149.3, 171.1; HRMS (FAB, positive) m/z Calcd. for $C_{56}H_{46}O_4Si_2$, 838.2935 ([M]); found, 838.2918 ([M]); $[\alpha]^{25}_D = 561$ (c 0.770, $CHCl_3$, 92% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak IA: 4 × 250 nm, UV detector: λ = 254 nm, r.t., eluent: 10% CH_2Cl_2 in hexane, flow rate: 1.0 mL/min, retention time: 9 min for minor isomer and 21 min for major isomer).

2) References

1. Okamoto, T.; Kudoh, K.; Wakamiya, A.; Yamaguchi, S. *Org. Lett.* **2005**, *7*, 5301.
2. Koenig, B.; Pitsch, W.; Klein, M.; Vasold, R.; Prall, M.; Schreiner, P. R. *J. Org. Chem.* **2001**, *66*, 1742.
3. Taillemite, S.; Aubert, C.; Fichou, D.; Malacria, M. *Tetrahedron Lett.* **2005**, *46*, 832.

A. Crystal Data

Empirical Formula	$C_{52}H_{44}O_4Si_2$
Formula Weight	789.09
Crystal Color, Habit	yellow, prism
Crystal Dimensions	0.600 X 0.200 X 0.200 mm
Crystal System	orthorhombic
Lattice Type	Primitive
Lattice Parameters	a = 10.741(2) Å b = 12.190(2) Å c = 32.074(3) Å V = 4199.9(8) Å^3
Space Group	$P2_12_12_1$ (#19)
Z value	4
D_{calc}	1.248 g/cm^3
F_{000}	1664.00
μ(MoKα)	1.308 cm^{-1}

B. Intensity Measurements

Diffractometer	R-AXIS RAPID
Radiation	MoKα (λ = 0.71075 Å) graphite monochromated
Voltage, Current	50kV, 40mA
Temperature	-150.0^{o}C
Detector Aperture	280 x 256 mm
Data Images	120 exposures
ω oscillation Range (χ=45.0, ϕ=0.0)	0.0 - 180.0^{o}
Exposure Rate	200.0 sec./^{o}
ω oscillation Range (χ=45.0, ϕ=180.0)	0.0 - 180.0^{o}
Exposure Rate	200.0 sec./^{o}
Detector Position	127.40 mm
Pixel Size	0.100 mm
$2\theta_{max}$	55.0^{o}
No. of Reflections Measured	Total: 62484 Unique: 9588 (R_{int} = 0.0551) Friedel pairs: 4245
Corrections	Lorentz-polarization Absorption (trans. factors: 0.954 - 0.974)

C. Structure Solution and Refinement

Structure Solution	Charge Flipping (Superflip)
Refinement	Full-matrix least-squares on F^2
Function Minimized	Σ w $(Fo^2 - Fc^2)^2$
Least Squares Weights	w = 1/ [$\sigma^2(Fo^2)$ + $(0.1000 \cdot P)^2$ + 0.0000 · P] where P = $(Max(Fo^2,0) + 2Fc^2)/3$
$2\theta_{max}$ cutoff	55.0^o
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	9588
No. Variables	523
Reflection/Parameter Ratio	18.33
Residuals: R1 ($I>2.00\sigma(I)$)	0.0576
Residuals: R (All reflections)	0.0654
Residuals: wR2 (All reflections)	0.1727
Goodness of Fit Indicator	1.290
Flack Parameter (Friedel pairs = 4245)	-0.04(12)
Max Shift/Error in Final Cycle	0.001
Maximum peak in Final Diff. Map	2.05 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.61 $e^-/Å^3$

Table 1. Bond lengths (Å)

atom	atom	distance	atom	atom	distance
Si1	C7	1.889(3)	Si1	C16	1.869(3)
Si1	C32	1.865(4)	Si1	C33	1.867(4)
Si2	C12	1.877(3)	Si2	C18	1.865(3)
Si2	C39	1.860(4)	Si2	C45	1.856(4)
O3	C15	1.348(4)	O3	C54	1.441(5)
O4	C15	1.191(4)	O5	C35	1.338(4)
O5	C56	1.459(5)	O6	C35	1.207(4)
C7	C8	1.403(4)	C7	C11	1.411(4)
C8	C10	1.415(4)	C8	C14	1.493(4)
C9	C12	1.415(4)	C9	C13	1.499(4)
C9	C19	1.420(4)	C10	C17	1.410(4)
C10	C19	1.487(4)	C11	C20	1.497(4)
C11	C27	1.392(4)	C12	C25	1.399(4)
C13	C18	1.424(4)	C13	C29	1.399(4)
C14	C16	1.405(4)	C14	C23	1.401(4)
C15	C27	1.507(4)	C16	C44	1.392(5)
C17	C24	1.475(4)	C17	C27	1.421(4)
C18	C37	1.378(4)	C19	C21	1.405(4)
C20	C22	1.404(4)	C20	C41	1.386(5)
C21	C26	1.480(4)	C21	C28	1.411(4)
C22	C49	1.386(4)	C23	C40	1.393(5)
C24	C26	1.419(4)	C24	C34	1.400(4)
C25	C28	1.399(4)	C25	C31	1.503(4)
C26	C42	1.412(4)	C28	C35	1.505(4)
C29	C36	1.395(5)	C30	C34	1.380(4)
C30	C52	1.389(5)	C31	C43	1.375(5)
C31	C48	1.386(5)	C36	C38	1.374(5)
C37	C38	1.395(5)	C40	C47	1.371(5)
C41	C50	1.406(5)	C42	C52	1.371(5)
C43	C55	1.410(5)	C44	C47	1.387(5)
C46	C48	1.395(5)	C46	C53	1.374(7)
C49	C51	1.382(6)	C50	C51	1.355(5)
C53	C55	1.383(7)	C54	C57	1.487(7)
C56	C58	1.292(8)			

Table 2. Bond angles (ᴼ)

atom	atom	atom	angle	atom	atom	atom	angle
C7	Si1	C16	90.33(11)	C7	Si1	C32	119.03(15)
C7	Si1	C33	112.93(13)	C16	Si1	C32	108.88(14)
C16	Si1	C33	116.40(13)	C32	Si1	C33	108.56(15)
C12	Si2	C18	90.80(12)	C12	Si2	C39	116.62(16)
C12	Si2	C45	112.76(14)	C18	Si2	C39	110.05(15)
C18	Si2	C45	115.90(14)	C39	Si2	C45	109.76(15)
C15	O3	C54	117.0(3)	C35	O5	C56	116.7(3)
Si1	C7	C8	109.52(18)	Si1	C7	C11	130.69(18)
C8	C7	C11	119.1(3)	C7	C8	C10	119.7(3)
C7	C8	C14	114.3(3)	C10	C8	C14	126.0(3)
C12	C9	C13	112.9(3)	C12	C9	C19	118.7(3)
C13	C9	C19	128.4(2)	C8	C10	C17	118.8(2)
C8	C10	C19	124.4(3)	C17	C10	C19	116.8(3)
C7	C11	C20	119.4(3)	C7	C11	C27	119.8(3)
C20	C11	C27	120.8(3)	Si2	C12	C9	109.8(2)
Si2	C12	C25	130.0(2)	C9	C12	C25	120.2(3)
C9	C13	C18	114.3(3)	C9	C13	C29	125.7(3)
C18	C13	C29	119.5(3)	C8	C14	C16	114.5(3)
C8	C14	C23	125.8(3)	C16	C14	C23	119.5(3)
O3	C15	O4	124.5(3)	O3	C15	C27	111.1(3)
O4	C15	C27	124.4(3)	Si1	C16	C14	110.22(19)
Si1	C16	C44	129.5(3)	C14	C16	C44	119.6(3)
C10	C17	C24	117.4(3)	C10	C17	C27	117.5(3)
C24	C17	C27	124.4(3)	Si2	C18	C13	109.6(2)
Si2	C18	C37	129.8(2)	C13	C18	C37	119.3(3)
C9	C19	C10	121.9(3)	C9	C19	C21	119.1(3)
C10	C19	C21	118.9(3)	C11	C20	C22	119.4(3)
C11	C20	C41	121.5(3)	C22	C20	C41	119.1(3)
C19	C21	C26	118.2(3)	C19	C21	C28	120.0(3)
C26	C21	C28	121.7(3)	C20	C22	C49	119.9(4)
C14	C23	C40	119.3(3)	C17	C24	C26	119.3(3)
C17	C24	C34	122.6(3)	C26	C24	C34	117.1(3)
C12	C25	C28	119.9(3)	C12	C25	C31	118.6(3)
C28	C25	C31	121.2(3)	C21	C26	C24	119.0(3)
C21	C26	C42	121.9(3)	C24	C26	C42	119.1(3)
C11	C27	C15	117.7(2)	C11	C27	C17	120.8(3)
C15	C27	C17	121.2(3)	C21	C28	C25	119.9(3)

Table 2. Bond angles (°) (continued)

atom	atom	atom	angle	atom	atom	atom	angle
C21	C28	C35	125.0(3)	C25	C28	C35	114.7(3)
C13	C29	C36	119.0(3)	C34	C30	C52	119.3(3)
C25	C31	C43	121.0(3)	C25	C31	C48	119.4(3)
C43	C31	C48	119.6(3)	C24	C34	C30	122.8(3)
O5	C35	O6	124.9(3)	O5	C35	C28	111.4(3)
O6	C35	C28	123.5(3)	C29	C36	C38	121.5(3)
C18	C37	C38	120.8(3)	C36	C38	C37	119.5(3)
C23	C40	C47	121.3(3)	C20	C41	C50	119.6(3)
C26	C42	C52	121.4(3)	C31	C43	C55	120.3(4)
C16	C44	C47	120.4(3)	C48	C46	C53	120.4(4)
C40	C47	C44	119.8(3)	C31	C48	C46	120.1(4)
C22	C49	C51	120.4(3)	C41	C50	C51	120.9(4)
C49	C51	C50	120.1(3)	C30	C52	C42	119.9(3)
C46	C53	C55	119.9(3)	O3	C54	C57	108.4(4)
C43	C55	C53	119.6(4)	O5	C56	C58	112.6(5)

Table 3. Torsion Angles(^{o})

(Those having bond angles > 160 or < 20 degrees are excluded.)

atom1	atom2	atom3	atom4	angle	atom1	atom2	atom3	atom4	angle
C7	Si1	C16	C14	0.27(18)	C7	Si1	C16	C44	-170.6(3)
C16	Si1	C7	C8	-6.56(17)	C16	Si1	C7	C11	-176.8(3)
C32	Si1	C7	C8	-118.47(17)	C32	Si1	C7	C11	71.3(3)
C33	Si1	C7	C8	112.47(17)	C33	Si1	C7	C11	-57.8(3)
C32	Si1	C16	C14	121.3(2)	C32	Si1	C16	C44	-49.6(3)
C33	Si1	C16	C14	-115.69(18)	C33	Si1	C16	C44	73.5(3)
C12	Si2	C18	C13	0.24(18)	C12	Si2	C18	C37	-166.7(3)
C18	Si2	C12	C9	-9.77(18)	C18	Si2	C12	C25	171.2(3)
C39	Si2	C12	C9	-122.75(18)	C39	Si2	C12	C25	58.2(3)
C45	Si2	C12	C9	108.89(18)	C45	Si2	C12	C25	-70.1(3)
C39	Si2	C18	C13	119.1(2)	C39	Si2	C18	C37	-47.8(3)
C45	Si2	C18	C13	-115.67(18)	C45	Si2	C18	C37	77.4(3)
C15	O3	C54	C57	134.6(3)	C54	O3	C15	O4	-6.3(4)
C54	O3	C15	C27	171.8(3)	C35	O5	C56	C58	89.8(4)
C56	O5	C35	O6	4.2(4)	C56	O5	C35	C28	-171.4(3)
Si1	C7	C8	C10	-167.47(16)	Si1	C7	C8	C14	11.2(3)
Si1	C7	C11	C20	-2.6(4)	Si1	C7	C11	C27	178.95(16)
C8	C7	C11	C20	-172.1(2)	C8	C7	C11	C27	9.4(4)
C11	C7	C8	C10	4.1(4)	C11	C7	C8	C14	-177.3(2)
C7	C8	C10	C17	-20.6(4)	C7	C8	C10	C19	158.5(3)
C7	C8	C14	C16	-11.6(3)	C7	C8	C14	C23	162.3(3)
C10	C8	C14	C16	166.9(3)	C10	C8	C14	C23	-19.2(4)
C14	C8	C10	C17	161.0(3)	C14	C8	C10	C19	-19.9(4)
C12	C9	C13	C18	-17.3(4)	C12	C9	C13	C29	154.5(3)
C13	C9	C12	Si2	16.6(3)	C13	C9	C12	C25	-164.3(3)
C12	C9	C19	C10	167.3(3)	C12	C9	C19	C21	-16.5(4)
C19	C9	C12	Si2	-165.9(2)	C19	C9	C12	C25	13.2(4)
C13	C9	C19	C10	-15.7(4)	C13	C9	C19	C21	160.5(3)
C19	C9	C13	C18	165.5(3)	C19	C9	C13	C29	-22.6(5)
C8	C10	C17	C24	-148.2(3)	C8	C10	C17	C27	23.1(4)
C8	C10	C19	C9	-34.1(4)	C8	C10	C19	C21	149.6(3)
C17	C10	C19	C9	145.0(3)	C17	C10	C19	C21	-31.2(4)
C19	C10	C17	C24	32.7(4)	C19	C10	C17	C27	-156.1(2)
C7	C11	C20	C22	-53.2(4)	C7	C11	C20	C41	125.8(3)
C7	C11	C27	C15	179.1(2)	C7	C11	C27	C17	-6.6(4)
C20	C11	C27	C15	0.7(4)	C20	C11	C27	C17	174.9(2)
C27	C11	C20	C22	125.2(3)	C27	C11	C20	C41	-55.7(4)

Table 3. Torsion angles (°) (continued)

atom1	atom2	atom3	atom4	angle	atom1	atom2	atom3	atom4	angle
Si2	C12	C25	C28	178.53(18)	Si2	C12	C25	C31	-7.5(4)
C9	C12	C25	C28	-0.4(4)	C9	C12	C25	C31	173.6(3)
C9	C13	C18	Si2	9.1(3)	C9	C13	C18	C37	177.6(2)
C9	C13	C29	C36	-175.0(3)	C18	C13	C29	C36	-3.5(4)
C29	C13	C18	Si2	-163.3(3)	C29	C13	C18	C37	5.2(4)
C8	C14	C16	Si1	5.9(3)	C8	C14	C16	C44	177.8(2)
C8	C14	C23	C40	-177.6(3)	C16	C14	C23	C40	-4.0(4)
C23	C14	C16	Si1	-168.4(2)	C23	C14	C16	C44	3.5(4)
O3	C15	C27	C11	-65.3(3)	O3	C15	C27	C17	120.5(3)
O4	C15	C27	C11	112.8(3)	O4	C15	C27	C17	-61.4(4)
Si1	C16	C44	C47	170.1(2)	C14	C16	C44	C47	0.0(5)
C10	C17	C24	C26	-9.3(4)	C10	C17	C24	C34	159.2(3)
C10	C17	C27	C11	-9.7(4)	C10	C17	C27	C15	164.4(2)
C24	C17	C27	C11	160.9(3)	C24	C17	C27	C15	-25.1(4)
C27	C17	C24	C26	-179.9(3)	C27	C17	C24	C34	-11.4(4)
Si2	C18	C37	C38	163.18(19)	C13	C18	C37	C38	-2.7(5)
C9	C19	C21	C26	-170.8(3)	C9	C19	C21	C28	7.1(4)
C10	C19	C21	C26	5.5(4)	C10	C19	C21	C28	-176.5(3)
C11	C20	C22	C49	178.3(2)	C11	C20	C41	C50	-178.8(2)
C22	C20	C41	C50	0.3(4)	C41	C20	C22	C49	-0.8(4)
C19	C21	C26	C24	18.1(4)	C19	C21	C26	C42	-160.6(3)
C19	C21	C28	C25	5.8(4)	C19	C21	C28	C35	-166.8(3)
C26	C21	C28	C25	-176.3(3)	C26	C21	C28	C35	11.1(5)
C28	C21	C26	C24	-159.8(3)	C28	C21	C26	C42	21.4(4)
C20	C22	C49	C51	1.1(4)	C14	C23	C40	C47	1.1(4)
C17	C24	C26	C21	-16.5(4)	C17	C24	C26	C42	162.3(3)
C17	C24	C34	C30	-165.1(3)	C26	C24	C34	C30	3.7(4)
C34	C24	C26	C21	174.4(3)	C34	C24	C26	C42	-6.8(4)
C12	C25	C28	C21	-9.2(4)	C12	C25	C28	C35	164.1(3)
C12	C25	C31	C43	87.6(4)	C12	C25	C31	C48	-91.6(4)
C28	C25	C31	C43	-98.6(4)	C28	C25	C31	C48	82.3(4)
C31	C25	C28	C21	177.0(3)	C31	C25	C28	C35	-9.7(4)
C21	C26	C42	C52	-176.4(3)	C24	C26	C42	C52	4.9(5)
C21	C28	C35	O5	-110.2(3)	C21	C28	C35	O6	74.2(4)
C25	C28	C35	O5	76.9(3)	C25	C28	C35	O6	-98.8(3)
C13	C29	C36	C38	-0.7(4)	C34	C30	C52	C42	-4.0(5)
C52	C30	C34	C24	1.8(5)	C25	C31	C43	C55	-179.3(3)

Table 3. Torsion angles (^{o}) (continued)

atom1	atom2	atom3	atom4	angle	atom1	atom2	atom3	atom4	angle
C25	C31	C48	C46	180.0(3)	C43	C31	C48	C46	0.8(5)
C48	C31	C43	C55	-0.2(5)	C29	C36	C38	C37	3.2(5)
C18	C37	C38	C36	-1.5(5)	C23	C40	C47	C44	2.4(5)
C20	C41	C50	C51	0.0(5)	C26	C42	C52	C30	0.7(6)
C31	C43	C55	C53	-0.8(5)	C16	C44	C47	C40	-3.0(5)
C48	C46	C53	C55	-0.5(5)	C53	C46	C48	C31	-0.5(5)
C22	C49	C51	C50	-0.8(5)	C41	C50	C51	C49	0.2(5)
C46	C53	C55	C43	1.1(5)					

Table 4. Intramolecular contacts less than 3.60 Å

atom	atom	distance	atom	atom	distance
Si1	C20	3.381(3)	Si1	C22	3.357(3)
Si2	C31	3.332(3)	O3	C11	2.962(4)
O3	C17	3.471(3)	O3	C20	2.942(3)
O3	C34	3.403(4)	O3	C41	3.208(4)
O4	C11	3.379(4)	O4	C17	3.131(4)
O4	C24	3.436(4)	O4	C34	3.251(4)
O4	C41	3.347(4)	O4	C54	2.698(5)
O5	C21	3.426(4)	O5	C25	3.017(4)
O5	C31	3.004(4)	O5	C42	3.282(4)
O5	C43	3.300(4)	O6	C21	3.255(4)
O6	C25	3.258(4)	O6	C26	3.500(4)
O6	C31	3.505(4)	O6	C42	3.273(4)
O6	C48	3.451(4)	O6	C56	2.702(5)
O6	C58	3.257(8)	C7	C17	2.824(4)
C7	C22	3.083(4)	C7	C29	3.548(4)
C8	C9	3.116(4)	C8	C13	3.192(4)
C8	C27	2.793(4)	C8	C29	2.993(4)
C9	C14	3.205(4)	C9	C23	3.011(4)
C9	C28	2.807(4)	C10	C11	2.793(4)
C10	C13	3.156(4)	C10	C23	3.165(4)
C10	C26	2.826(4)	C10	C29	3.185(4)
C12	C21	2.806(4)	C12	C43	3.327(4)
C12	C48	3.345(5)	C13	C14	3.062(4)
C13	C23	3.209(4)	C13	C38	2.793(5)
C14	C19	3.160(4)	C14	C29	3.201(4)
C14	C47	2.790(5)	C15	C20	2.860(4)
C15	C24	3.085(4)	C15	C34	2.942(4)
C15	C41	2.970(4)	C15	C57	3.490(6)
C16	C40	2.774(4)	C17	C21	2.882(4)
C18	C36	2.779(4)	C19	C23	3.158(4)
C19	C24	2.859(4)	C19	C25	2.814(4)
C19	C29	3.229(4)	C20	C51	2.786(4)
C22	C32	3.314(5)	C22	C50	2.762(6)
C23	C44	2.783(5)	C24	C52	2.819(4)
C26	C30	2.798(4)	C26	C35	3.061(4)
C27	C34	3.042(4)	C27	C41	3.136(4)
C28	C42	3.001(4)	C28	C43	3.444(4)

Table 4. Intramolecular contacts less than 3.60 Å (continued)

atom	atom	distance	atom	atom	distance
C28	C48	3.311(5)	C29	C37	2.791(4)
C31	C35	2.818(4)	C31	C53	2.787(4)
C34	C42	2.749(4)	C35	C42	2.879(4)
C35	C48	3.230(5)	C35	C58	3.063(8)
C41	C49	2.769(5)	C43	C46	2.765(6)
C48	C55	2.770(6)			