

Supporting Information

for

Disilane-bridged architectures with high optical transparency for optical limiting

Hongjie Feng,¹ Zhikuan Zhou,^{1*} Aviwe May,² Jiaying Chen,¹ John Mack,^{2*} Tebello

Nyokong,² Lizhi Gai¹ & Hua Lu^{1*}

¹ Key Laboratory of Organosilicon Chemistry and Material Technology of Ministry of Education, and Key Laboratory of Organosilicon Material of Zhejiang Province, Hangzhou Normal University, Hangzhou 311121, China

² Institute for Nanotechnology Innovation, Department of Chemistry, Rhodes University, Makhanda 6140, South Africa

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1. Experimental Section

General, Measurement, and Materials.

Reagents and solvents were purchased from commercial suppliers and used without further purification unless otherwise indicated. All air and moisture-sensitive reactions were carried out under an argon atmosphere in glassware that was dried in an oven at 120 °C and cooled under a stream of inert gas before use. Tetrahydrofuran was refluxed with sodium and distilled out immediately before use. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker DRX400 spectrometer and referenced to the residual proton signals of deuterated solvents (CDCl₃: 7.26 ppm; CD₂Cl₂: 5.32 ppm). HR-MS data were recorded on a Bruker Daltonics microTOF-Q II spectrometer. All solvents used for the spectroscopic measurements were of UV spectroscopic grade (Aldrich).

Synthetic Methods.

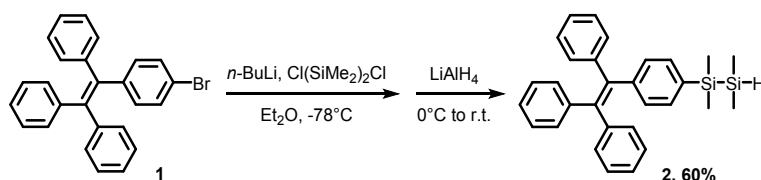
Table S1 Optimization of reaction conditions for the synthesis of **3a**.

Entry	Catalyst loading	Base	Solvent	Temperature	Yield(%) ^a
1	1 mol%	DIPEA (1.0 equiv.)	Toluene	0°C	24
2	1 mol%	DIPEA (1.0 equiv.)	THF	0°C	10
3	1 mol%	DIPEA (1.0 equiv.)	Mesitylene	0°C	32
4	1 mol%	K ₃ PO ₄ (1.0 equiv.)	Mesitylene	0°C	0
5	1 mol%	Et ₃ N (1.0 equiv.)	Mesitylene	0°C	0
6	2 mol%	DIPEA (1.5 equiv.)	Mesitylene	0°C	36
7	3 mol%	DIPEA (1.5 equiv.)	Mesitylene	0°C	40
8	3 mol%	DIPEA (1.5 equiv.)	Mesitylene	R.T. (25°C)	47
9	4 mol%	DIPEA (1.5 equiv.)	Mesitylene	R.T. (25°C)	30
10	5 mol%	DIPEA (1.5 equiv.)	Mesitylene	R.T. (25°C)	24

Reaction condition: **2** (1 mmol, 1.0 equiv.), base (x mmol, x equiv.), Pd(P(*t*-Bu)₃)₂ (x mmol, x mol%) were dissolved in dry solvent (3.0 mL) under an argon atmosphere, the reaction mixture was stirred until the starting material was not observable on TLC.

(a) ¹H NMR yield.

Synthesis of **2**.



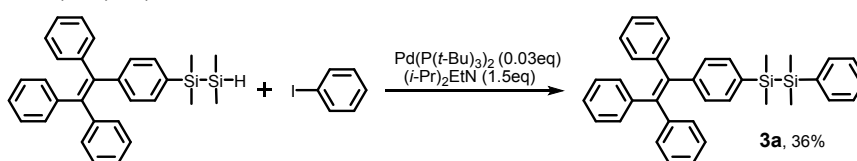
(2-(4-Bromophenyl)ethene-1,1,2-triyl)tribenzene **1** (2 g, 5 mmol) was dissolved in dry ether under argon and cooled to -78 °C, *n*-BuLi (3.2 mL, 5 mmol, 1.6 M in hexane) was added dropwise. The mixture was stirred at -78°C for 1.5 h and then quickly warmed to 0 °C. In another flask, 1,2-dichlorotetramethyldisilane (1 mL, 5 mmol) was dissolved in dry ether (50 mL) under an argon

atmosphere and cooled to $-78\text{ }^{\circ}\text{C}$. The previous TPE-Li mixture was transferred into the flask and stirred for 2 h. The reaction mixture was gradually warmed up to room temperature, LiAlH_4 (189.5 mg, 5.0 mmol) was added, and the mixture was stirred overnight. The reaction was carefully quenched with water, and the aqueous layer was extracted three times with dichloromethane. The combined organic layer was washed with water and dried over sodium sulfate. The solvent was purified by chromatography over silica gel (9:1 petroleum ether/dichloromethane) to give compound **2** as a white powder (1.34 g, 60%).

^1H NMR (400 MHz, CDCl_3): δ 7.20 (d, $J = 8$ Hz, 2H), 7.11 - 7.07 (m, 9H), 7.05 - 6.98 (m, 8H), 3.70 - 3.64 (m, 1H), 0.33 (s, 6H), 0.06 (d, $J = 4$ Hz, 6H).

^{13}C NMR (100 MHz, CDCl_3): δ 143.79, 141.17, 137.01, 133.13, 131.49, 130.76, 127.76, 126.52, -3.59, -6.52 ppm.

Synthesis of **3a**, **3b**, **3c**, and **3d**



Under an argon atmosphere, compound **2** (449 mg, 1 mmol) and *bis*(tri-*tert*-butylphosphine) palladium(0) (15.3 mg, 0.03 mmol) were added to a solution of iodobenzene (111 μL , 1 mmol) in dry mesitylene (4 mL). *N,N*-Diisopropylethylamine (248 μL , 1.5 mmol) was added dropwise. The reaction mixture was stirred for 3 d at room temperature. The complete consumption of **2** was confirmed by TLC. The crude product was purified by chromatography over silica gel (1:10 DCM/petroleum ether) and recrystallized from pentane to afford **3a** at a yield of 36% (189 mg).

^1H NMR (400 MHz, CDCl_3): δ 7.23 (s, 4H), 7.08 (t, $J = 6.8$ Hz, 12H), 7.02-6.97 (m, 6H), 6.94 (d, $J = 7.5$ Hz, 2H), 0.24 (s, 6H), 0.22 (s, 6H).

^{13}C NMR (100 MHz, CD_2Cl_2): δ 144.16, 141.42, 139.40, 137.35, 134.24, 133.49, 131.58, 130.75, 128.69, 128.19-127.86, 126.75, 30.10, -3.94, -4.15.

HRMS-ESI: m/z : calcd. $[\text{C}_{36}\text{H}_{36}\text{Si}_2+\text{Na}]^+$ $m/z = 547.2248$, found $m/z = 547.2245$

Compounds **3b**, **3c** and **3d** were obtained as white solid by using similar procedures to that for **3a** in yields of 32%, 36% and 30%, respectively.

3b: ^1H NMR (400 MHz, CDCl_3): δ 7.30 (d, $J = 7.9$ Hz, 2H), 7.23 (s, 1H), 7.10 (d, $J = 1.8$ Hz, 11H), 7.04 (d, $J = 7.2$ Hz, 7H), 6.97 (s, 2H), 1.32 (s, 9H), 0.27 (s, 6H), 0.23 (s, 6H).

^{13}C NMR (100 MHz, CDCl_3): δ 151.38, 143.88, 141.16, 137.15, 135.40, 133.90, 133.26, 131.49, 130.64, 127.74, 126.51, 124.74, 29.70, -3.51, -4.05.

HRMS-ESI: m/z : calcd. $[\text{C}_{40}\text{H}_{44}\text{Si}_2+\text{Na}]^+$ $m/z = 603.2874$, found $m/z = 639.2864$.

3c: ^1H NMR (400 MHz, CDCl_3): δ 7.21 (d, $J = 8.5$ Hz, 2H), 7.10 (t, $J = 6.6$ Hz, 11H), 7.03 (dd, $J = 6.1, 3.5$ Hz, 6H), 6.97 (d, $J = 7.9$ Hz, 2H), 6.85 (d, $J = 8.4$ Hz, 2H), 3.81 (s, 3H), 0.26 (s, 6H), 0.22 (s, 6H).

^{13}C NMR (100 MHz, CD_2Cl_2): δ 160.47, 144.16, 141.46, 137.54, 135.58, 133.50, 131.59, 130.71, 129.77, 127.99 - 127.97, 126.74, 113.74, 55.31, -3.72, -4.14.

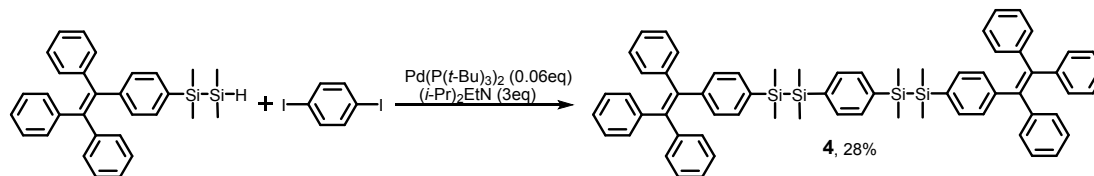
HRMS-ESI: m/z : calcd. $[\text{C}_{42}\text{H}_{40}\text{OSi}_2+\text{Na}]^+$ $m/z = 639.2510$, found $m/z = 639.2516$.

3d: ^1H NMR (400 MHz, CD_2Cl_2): δ 7.37 (t, $J = 7.8$ Hz, 2H), 7.24 (d, $J = 8.2$ Hz, 2H), 7.10-7.00 (m, 20H), 6.96 (d, $J = 7.8$ Hz, 2H), 6.91 (d, $J = 8.2$ Hz, 2H), 0.28 (s, 6H), 0.25 (s, 6H).

^{13}C NMR (100 MHz, CD_2Cl_2): δ 158.06, 157.31, 144.24, 141.42, 135.79, 133.50, 131.57, 130.73, 130.15, 126.75, 123.77, 119.47, 118.25, -3.81, -4.20.

HRMS-ESI: m/z : calcd. $[\text{C}_{42}\text{H}_{40}\text{OSi}_2+\text{Na}]^+$ $m/z = 639.2510$, found $m/z = 639.2516$.

Synthesis of 4.



Compound **2** (898 mg, 2 mmol), 1,4-diodobenzene (330 mg, 1 mmol) and *bis*(tri-*tert*-butylphosphine) palladium (0) (31 mg, 0.06 mmol) were dissolved in 4 mL dry mesitylene under argon. *N,N*-Diisopropylethylamine (496 μL , 3 mmol) was added dropwise to the solution at room temperature. The reaction mixture was stirred for 3 d at room temperature. The complete consumption of compound **2** was confirmed by TLC. The solution was removed under reduced pressure. The crude product was loaded onto a silica gel flash column (4:6 petroleum ether/dichloromethane) and recrystallized from pentane to afford product **4** as a white powder (272 mg, 28%).

^1H NMR (400 MHz, CD_2Cl_2): δ 7.38 (t, $J = 7.9$ Hz, 2H), 7.22 (d, $J = 8.4$ Hz, 2H), 7.15 – 7.00 (m, 20H), 6.95 (d, $J = 7.9$ Hz, 2H), 6.90 (d, $J = 8.3$ Hz, 2H), 0.28 (s, 6H), 0.26 (s, 6H).

^{13}C NMR (100 MHz, CDCl_3): δ 144.00-143.65, 141.15, 136.96, 133.18, 131.49, 130.64, 127.74, 126.53, 38.29, 31.39, 29.86, -4.09.

HRMS-ESI: m/z : calcd. $[\text{C}_{66}\text{H}_{66}\text{Si}_4+\text{K}]^+$ $m/z = 1009.3873$, found $m/z = 1009.3864$.

2. Properties Analysis

Thermo Properties

Thermogravimetric analysis (TGA) was undertaken with a Netzsch TG 209 F1 instrument. The thermal stability of the samples under a nitrogen atmosphere was determined by measuring their weight loss while heating at a rate of 10 °C /min from 25 °C to 700 °C. The differential scanning calorimetry (DSC) analysis was performed under a nitrogen atmosphere on a TA Instruments DSC 2920 heating at a rate of 10 °C /min from 25 °C to 260 °C.

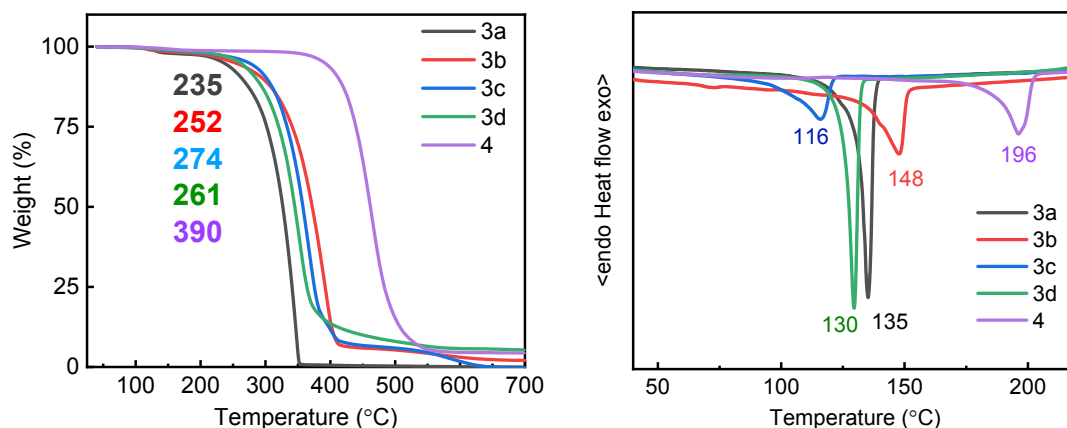


Figure S1 (a) TGA and (b) DSC thermograms of **3a-d** and **4** recorded under N₂ at a heating rate of 10 °C min⁻¹.

Spectroscopic Measurements

UV-visible absorption spectra were recorded on a Shimadzu 1800 spectrophotometer. Fluorescence spectra and the fluorescence lifetimes of the samples were determined with a Horiba Jobin Yvon Fluorolog-3 spectrofluorimeter. The goodness of the fits of the single exponential decays were assessed by using chi-squared (χ_R^2) and autocorrelation function $C(j)$ values. Low residuals ($\chi_R^2 < 1.2$) were consistently observed. For samples in solution, absorption and emission measurements were carried out in 1 × 1 cm quartz cuvettes. The absolute quantum yields (Φ_F) and emission spectra in the solid state were measured on Horiba Jobin Yvon Fluorolog-3 spectrofluorimeter with an integrating sphere. For all measurements, the temperature was kept constant at (298 ± 2) K.

When the fluorescence decays were monoexponential, the rate constants of radiative (k_r) and nonradiative (k_{nr}) deactivation were calculated from the measured fluorescence quantum yield and fluorescence lifetime (τ) according to Equations (1) and (2):

$$k_r = \Phi_F / \tau \quad (1)$$

$$k_{nr} = (1 - \Phi_F) / \tau \quad (2)$$

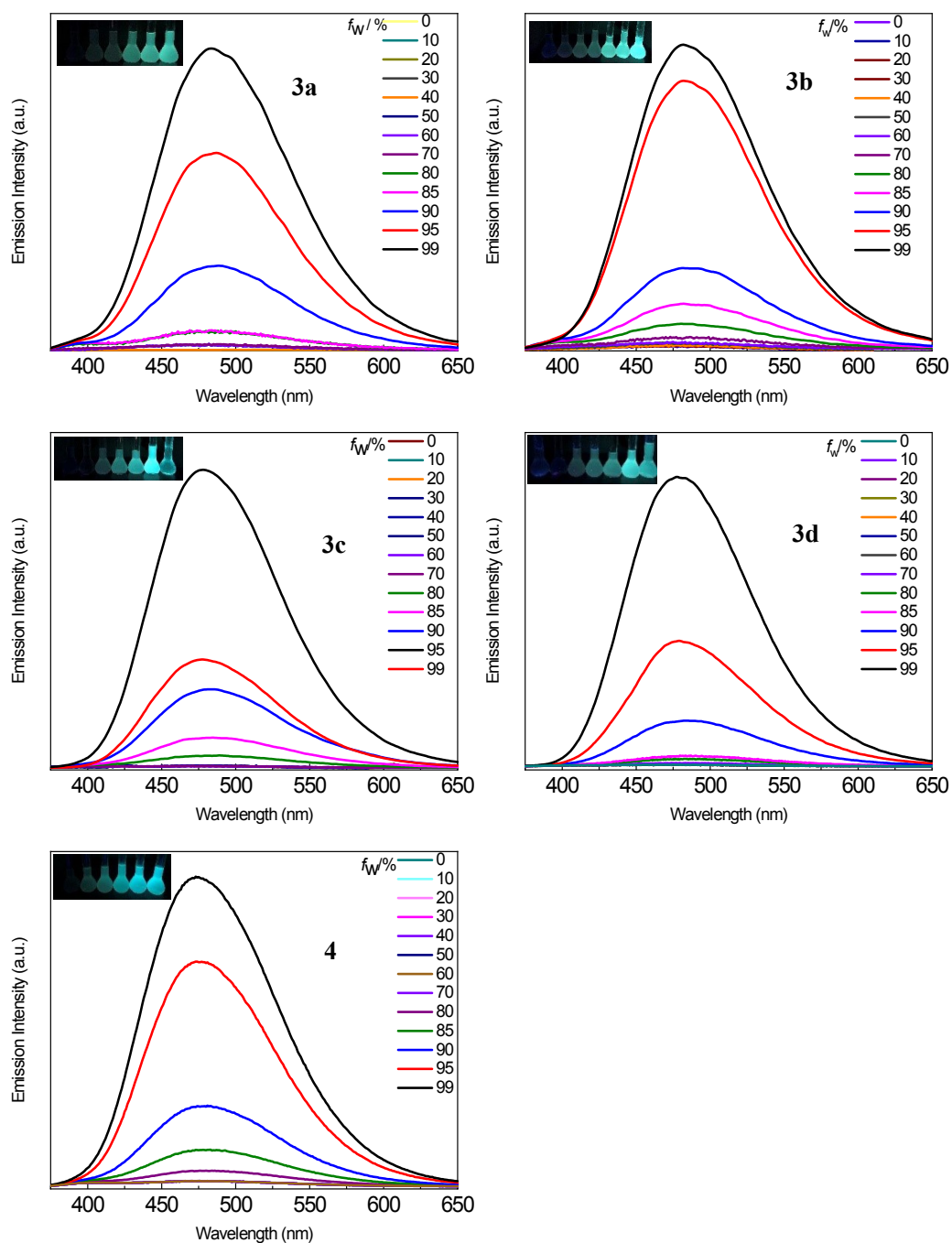


Figure S2 Aggregation effect of **3a**, **3b**, **3c**, **3d** and **4**. Definition of f_w is as follows: $f_w = V_{\text{water}} / (V_{\text{THF}} + V_{\text{water}})$. Fluorescence photographs of **3a**, **3b**, **3c**, **3d** and **4** in water/THF with different f_w under UV illumination ($\lambda_{ex} = 360$ nm). Emission spectra of **3a**, **3b**, **3c**, **3d** and **4** in THF/water mixtures with different water fractions (f_w).

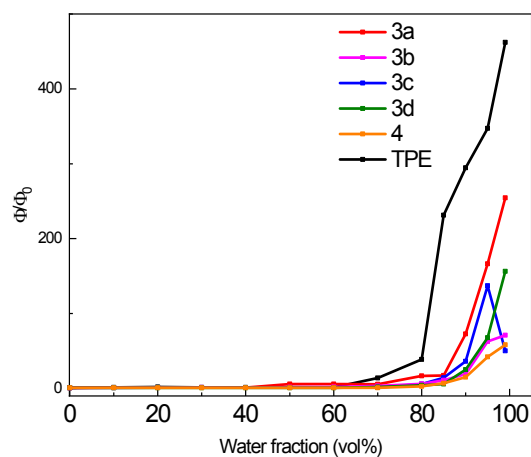


Figure S3 Plots of PL intensity ratio (Φ/Φ_0) of **3a**, **3b**, **3c**, **3d** and **4** versus water fraction in H₂O/THF mixtures. Φ_0 = emission intensity in THF. (10^{-4} M, $\lambda_{\text{ex}} = 310$ nm).

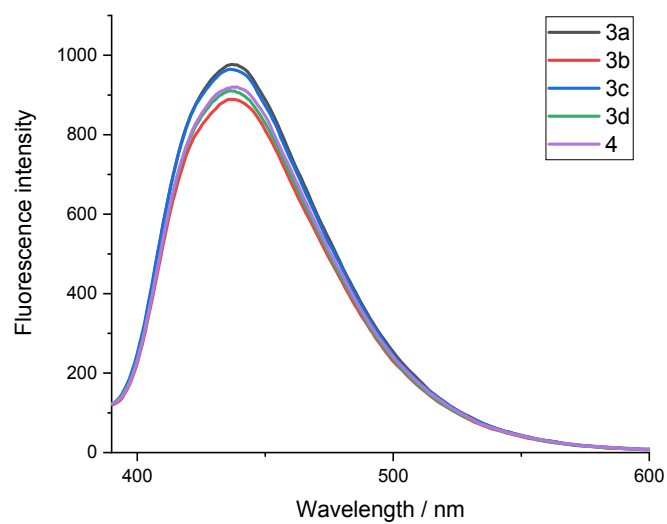


Figure S4 Plots of PL spectra of **3a**, **3b**, **3c**, **3d** and **4** in 2-MeTHF at 77K. (10^{-4} M, $\lambda_{\text{ex}} = 310$ nm).

Table S2 Quantum yields of **TPE**, **3a**, **3b**, **3c**, **3d** and **4** under various conditions.

Conditions	TPE	3a	3b	3c	3d	4
Powder	25%	17%	52%	47%	65%	92%
Drop-cast film	20%	46%	37%	30%	41%	44%
95% H ₂ O/THF c = 10^{-4} M	36%	12%	8%	11%	6%	12%
95% H ₂ O/THF c = 5×10^{-5} M	34%	6%	4%	6%	6%	14%
77 K in 2-Methylfuran	91%	85%	85%	95%	97%	94%

Crystallographic Data

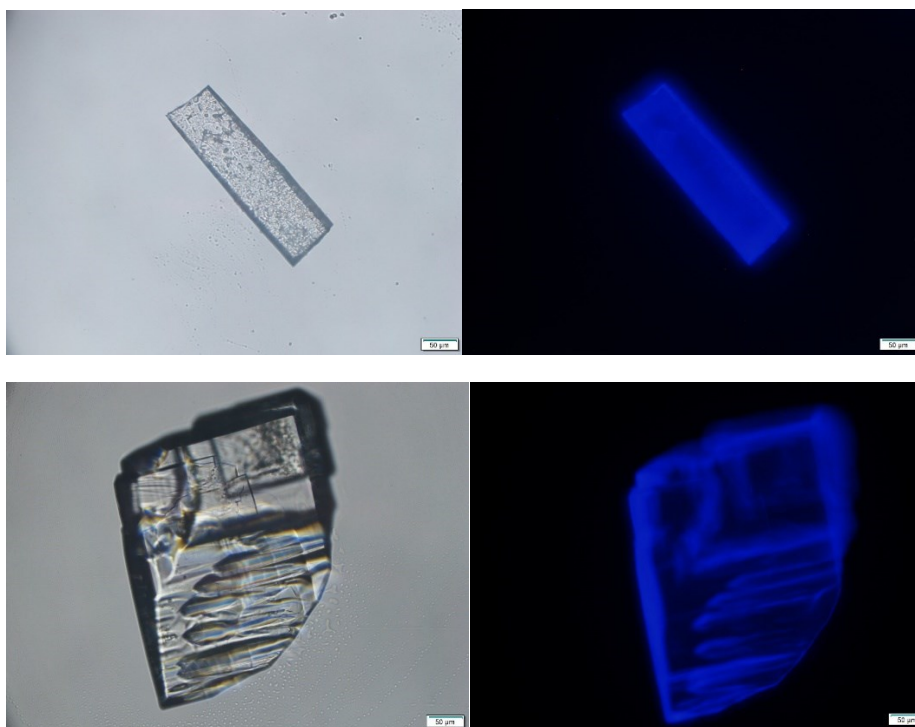
Diffraction data were collected on a Bruker Smart Apex II CCD diffractometer or Bruker AXS Apex II diffractometer with graphite-monochromated Mo-K α ($\lambda = 0.71073$ Å). An empirical (multi-scan) or numerical absorption correction was applied with the program SADABS.^[S4] The structures were solved by the direct method and subsequently refined on F^2 by using full-matrix least-squares techniques (SHELXTL).^[S5] The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located at calculated positions or found in the F_{map} . A summary of the crystallographic data and selected experimental information are given in Table S3 and Table S4. CCDC 2061563-2061564 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre. The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [E-mail: deposit@ccdc.cam.ac.uk].

Table S3 Crystallographic data for **3c**.

Empirical formula	C ₃₇ H ₃₈ OSi ₂
Formula weight	554.85
Temperature / K	296.15
Crystal system	monoclinic
Space group	P2 ₁
a / Å	9.2671(15)
b / Å	10.1603(16)
c / Å	17.650(3)
α / °	90
β / °	99.289(4)
γ / °	90
Volume / Å ³	1640.07
Z	2
ρ_{calc} / cm ³	1.124
μ / mm ⁻¹	0.134
Crystal size / mm ³	0.25 × 0.12 × 0.12
Goodness-of-fit on F ²	0.973
Final R indexes [$I \geq 2\sigma(I)$]	R ₁ = 0.0587, wR ₂ = 0.1193
Final R indexes [all data]	R ₁ = 0.1390, wR ₂ = 0.1511

Table S4 Crystallographic data for **3d**.

Empirical formula	$C_{42}H_{40}OSi_2$
Formula weight	616.92
Temperature / K	296.15
Crystal system	monoclinic
Space group	$P2_1/c$
$a / \text{\AA}$	15.375(11)
$b / \text{\AA}$	10.245(7)
$c / \text{\AA}$	24.152(17)
$\alpha / ^\circ$	90
$\beta / ^\circ$	106.812(15)
$\gamma / ^\circ$	90
Volume / \AA^3	3642(4)
Z	4
$\rho_{\text{calc}} / \text{cm}^3$	1.125
μ / mm^{-1}	0.127
Crystal size / mm^3	$0.15 \times 0.15 \times 0.12$
Goodness-of-fit on F^2	1.004
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0605$, $wR_2 = 0.1341$
Final R indexes [all data]	$R_1 = 0.1463$, $wR_2 = 0.1712$

**Figure S5** Photographs of **3c** and **3d** exposed to white light and 365 nm UV light.

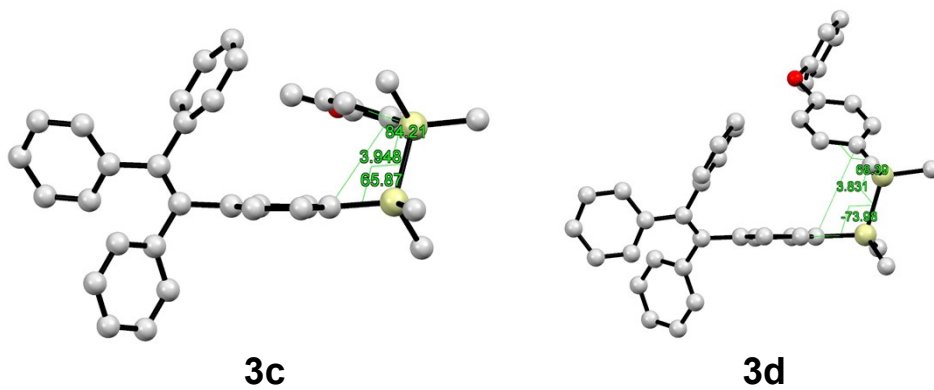


Figure S6 The torsion angles between the Si-Si σ -bonding axis and the phenyl plane, and the distances between the *ipso* carbon atoms on the phenyl rings.

Theoretical Calculations

The G09W software package was used to carry out a DFT geometry optimization using the B3LYP functional with 6-31G(d) basis sets. UV-visible spectra were calculated by using the time-dependent density functional theory (TD-DFT) approach with the B3LYP functional and 6-31G(d) basis sets.

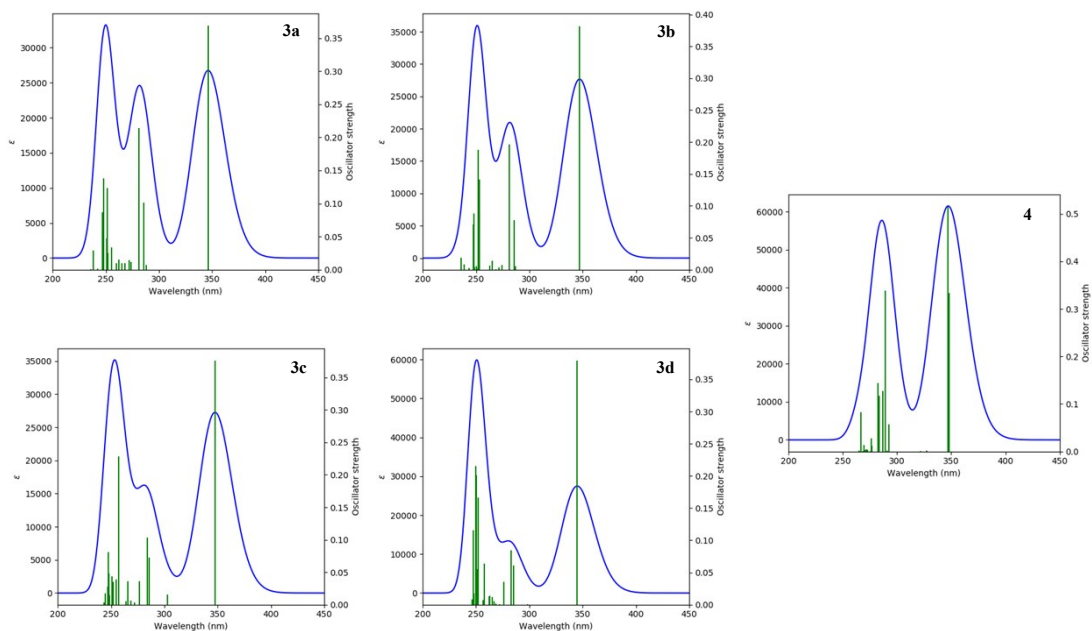
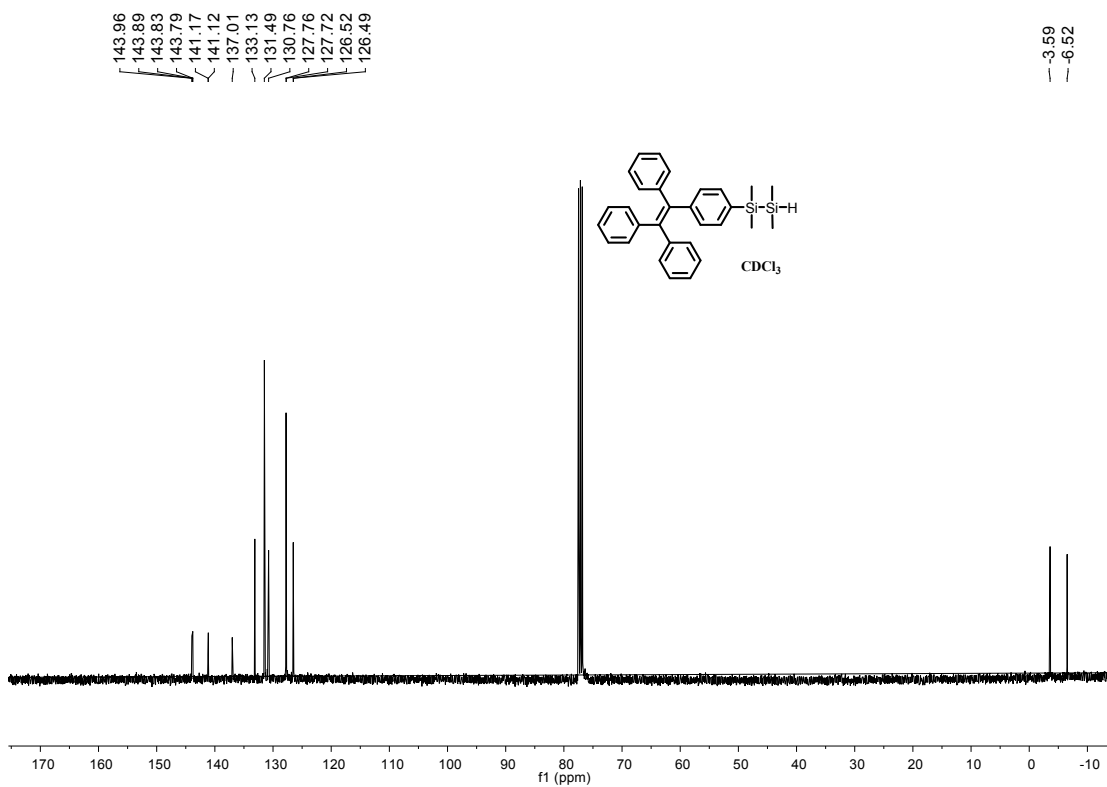
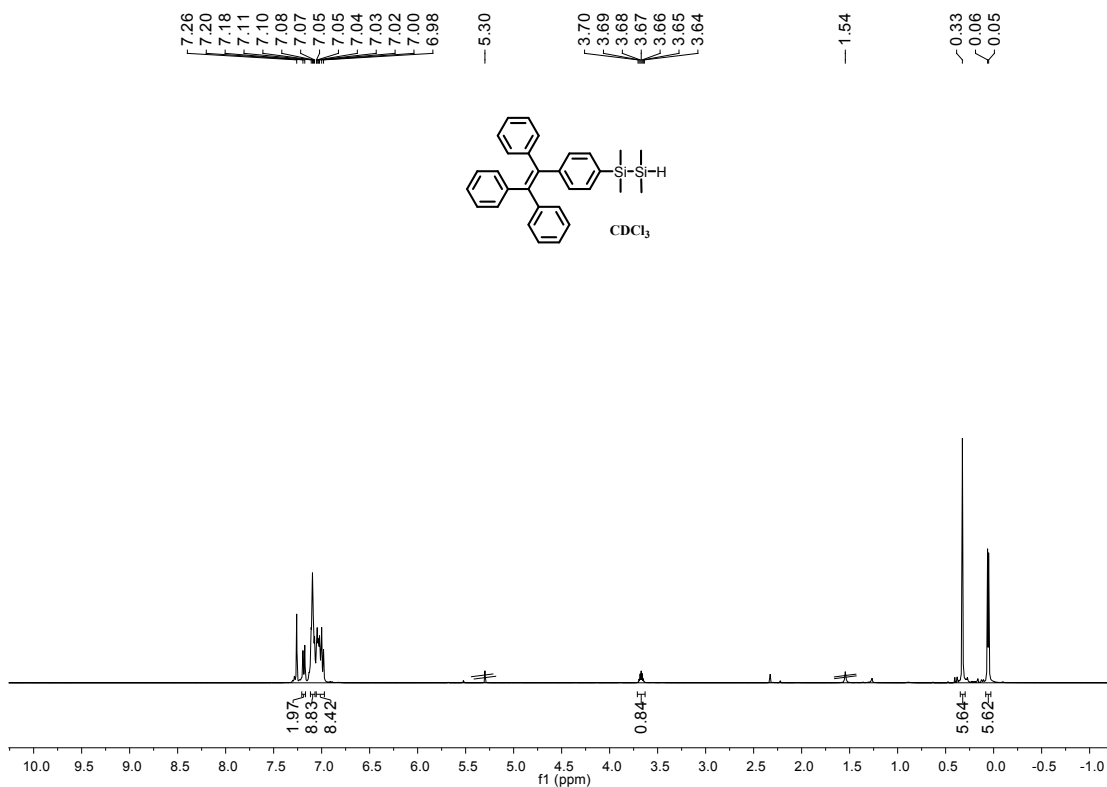
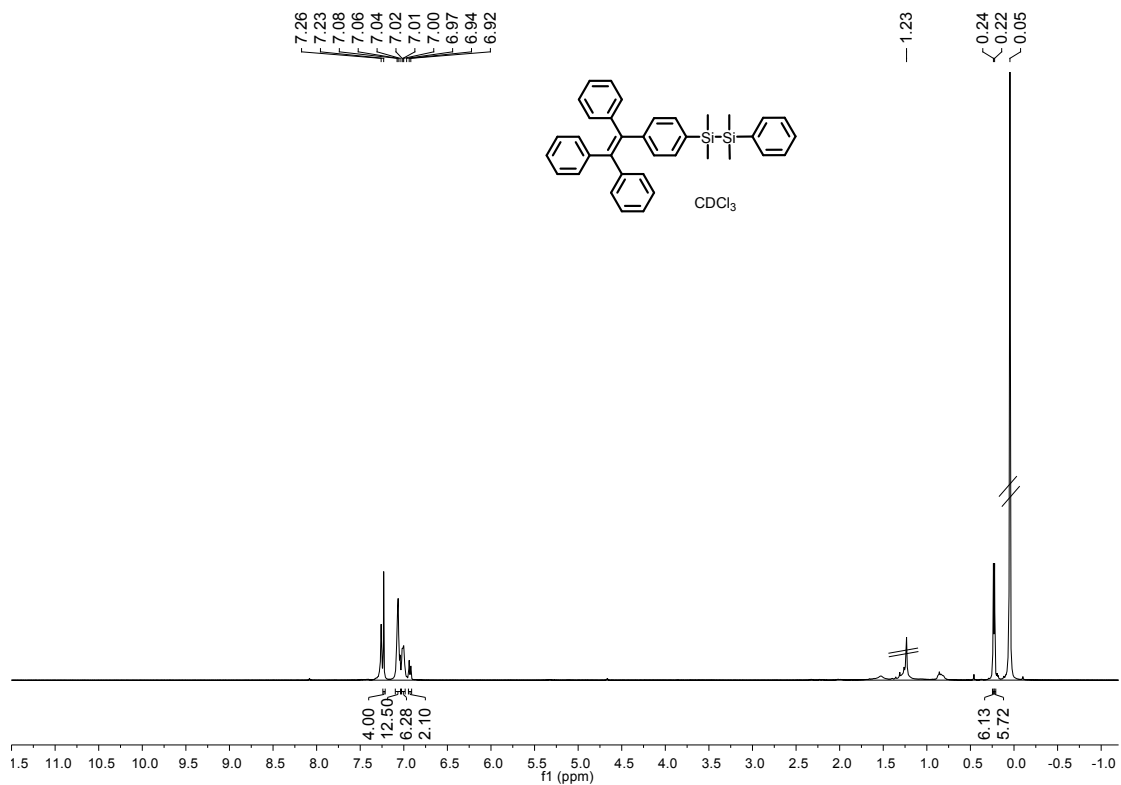


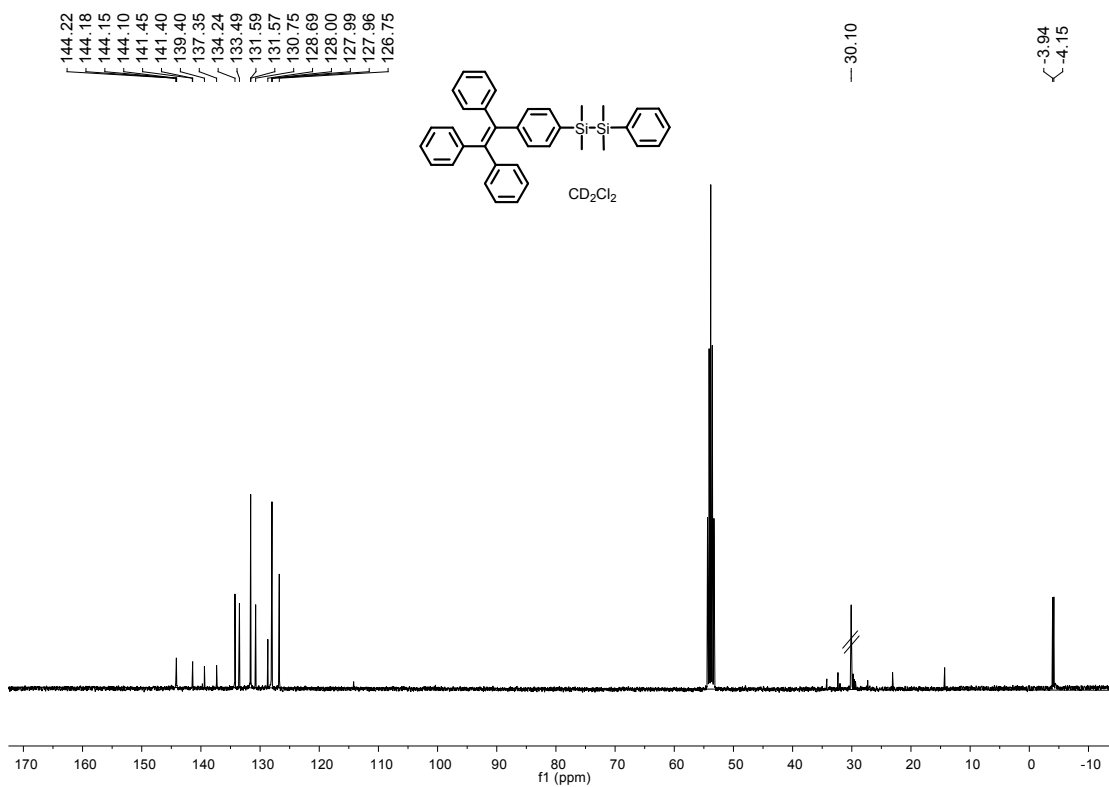
Figure S7 The calculated UV spectra (blue curves) and electronic transition oscillator strength (green bars) of **3a**, **3b**, **3c**, **3d**, and **4** in the gas phase.

¹H NMR, ¹³C NMR and HR-MS spectra

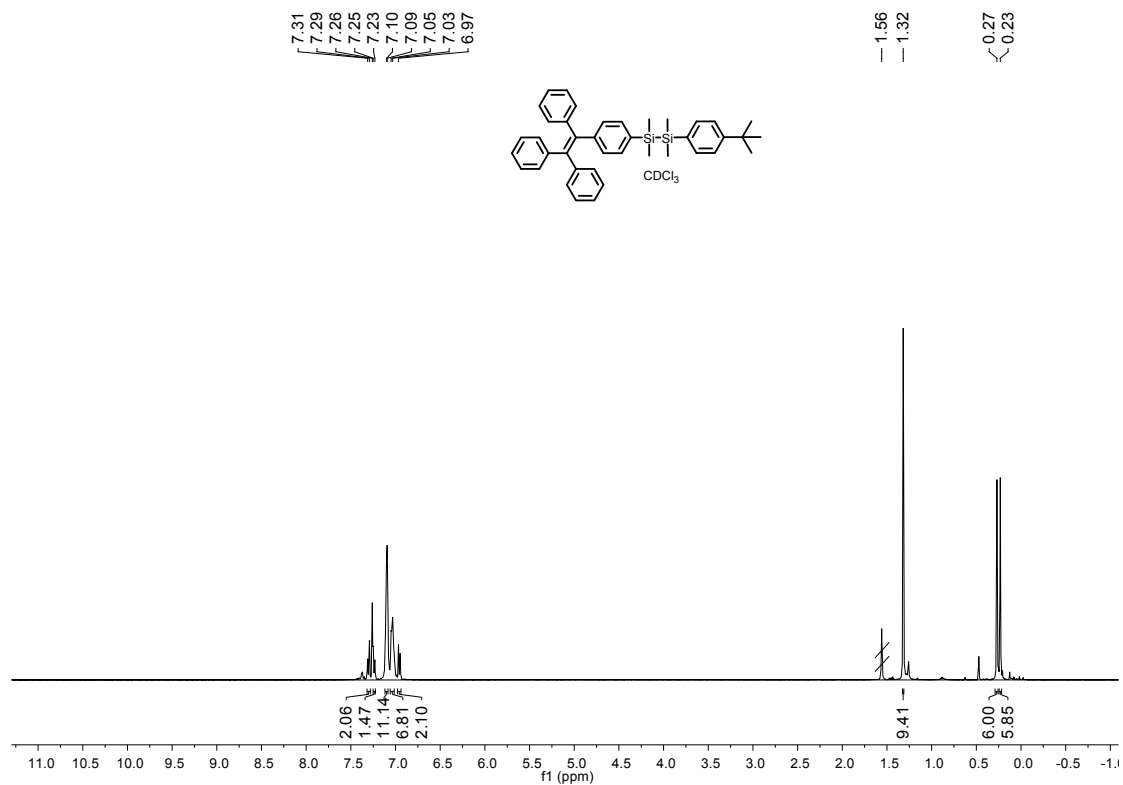




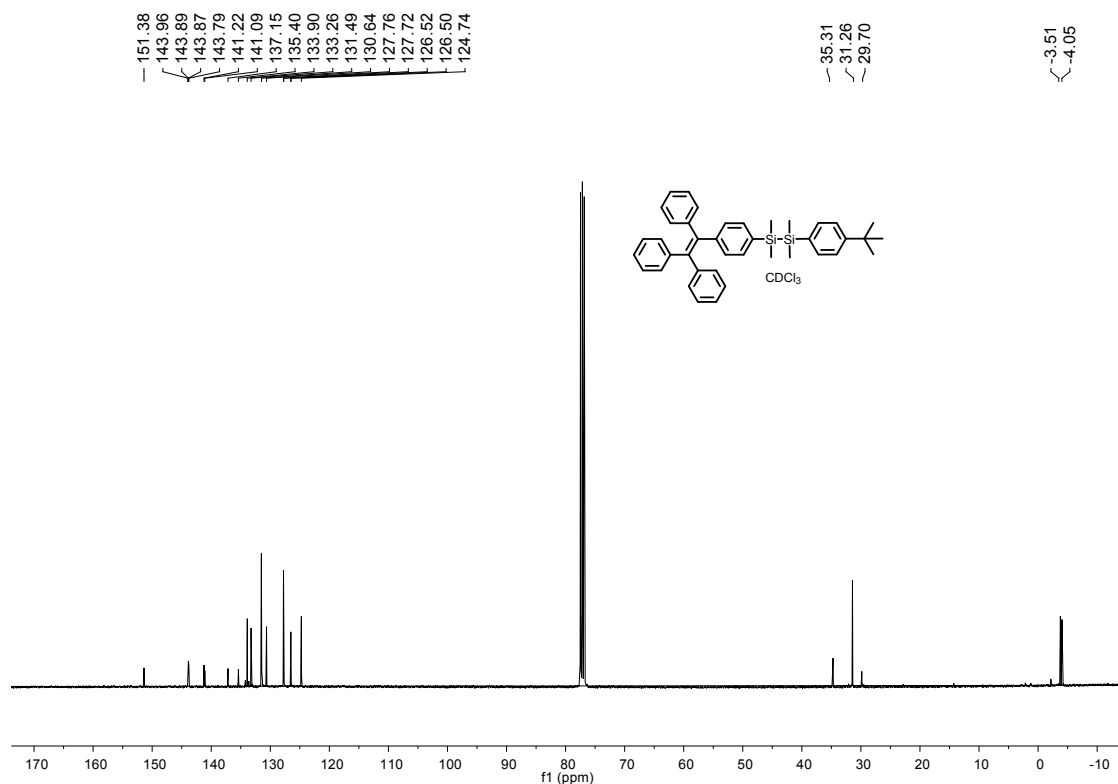
The ^1H NMR spectrum of **3a** (400 MHz, CDCl_3)



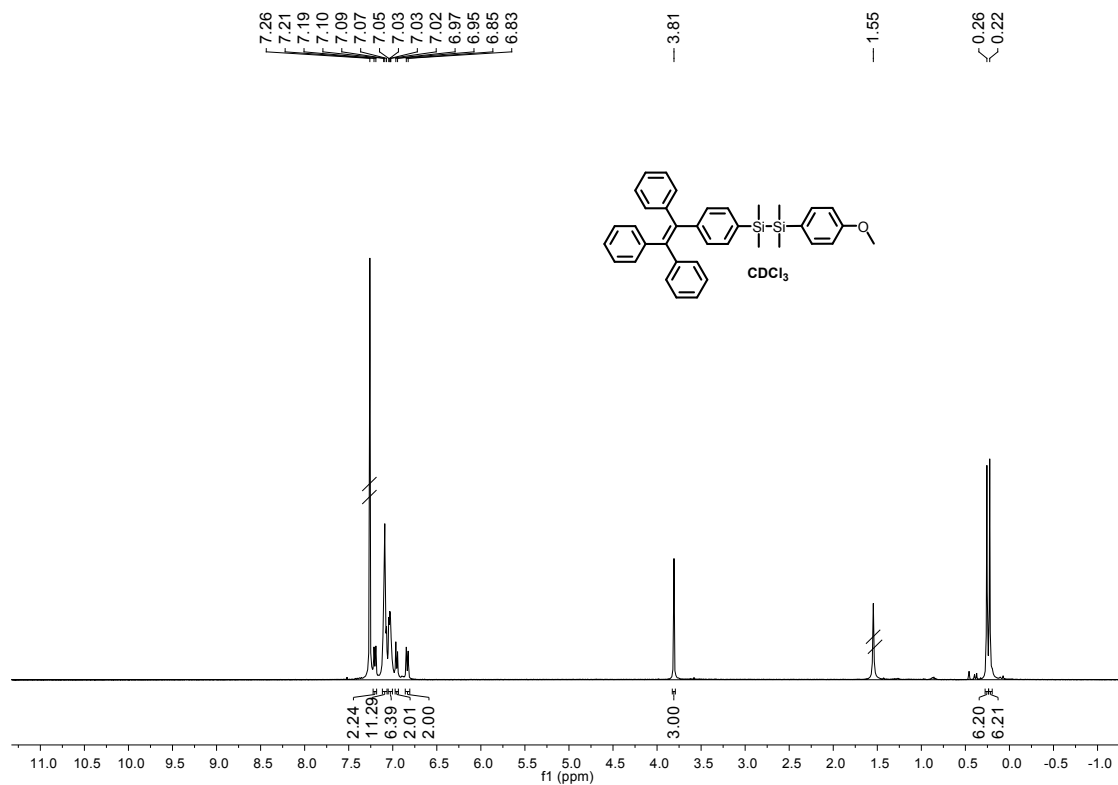
The ^{13}C NMR spectrum of **3a** (100 MHz, CD_2Cl_2).



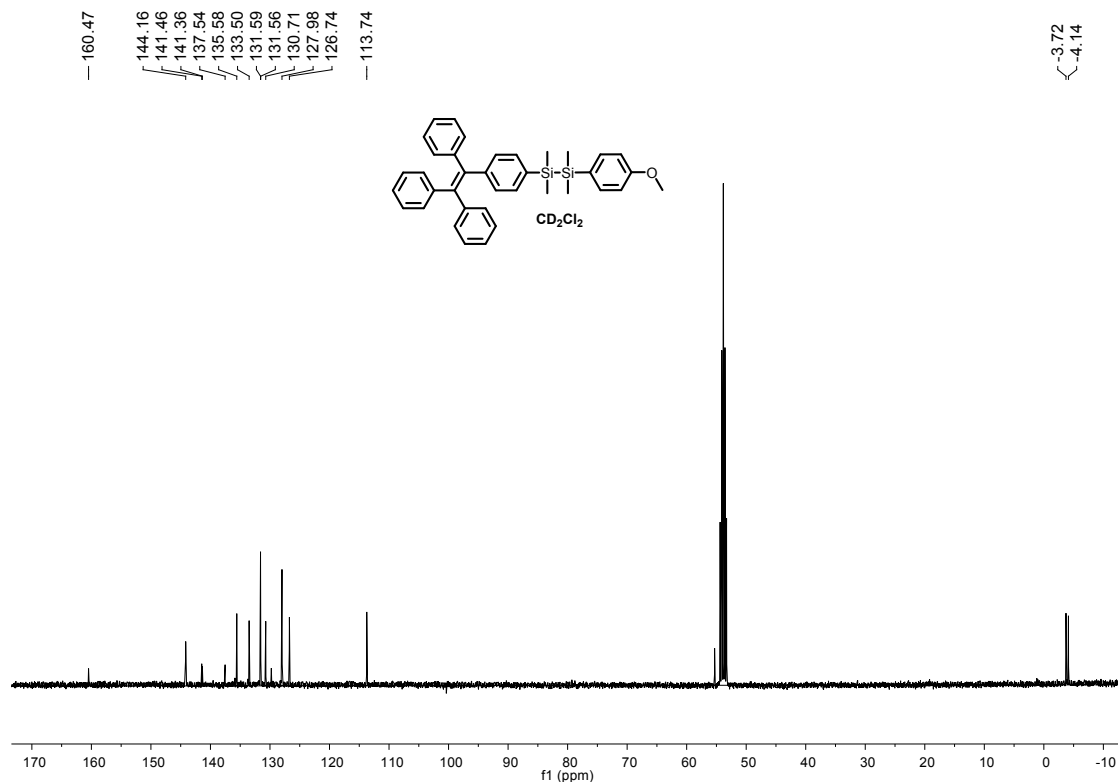
The ¹H NMR spectrum of **3b** (400 MHz, CDCl₃).



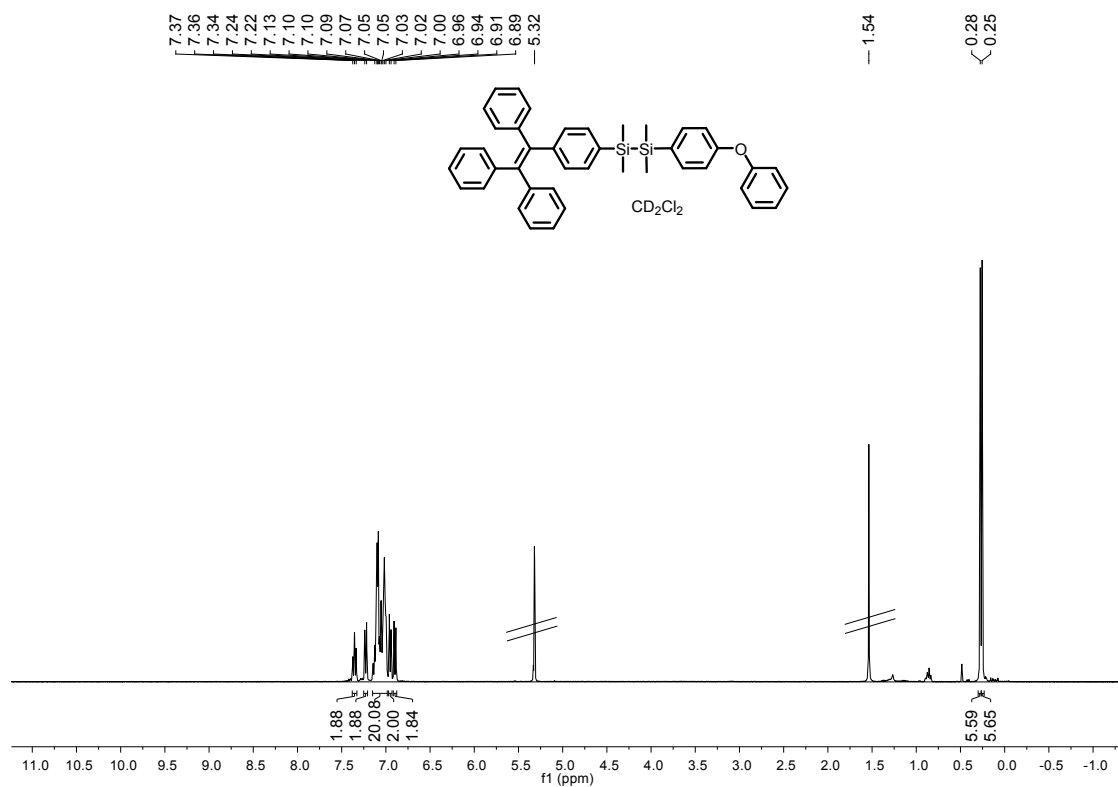
The ¹³C NMR spectrum of **3b** (100 MHz, CDCl₃).



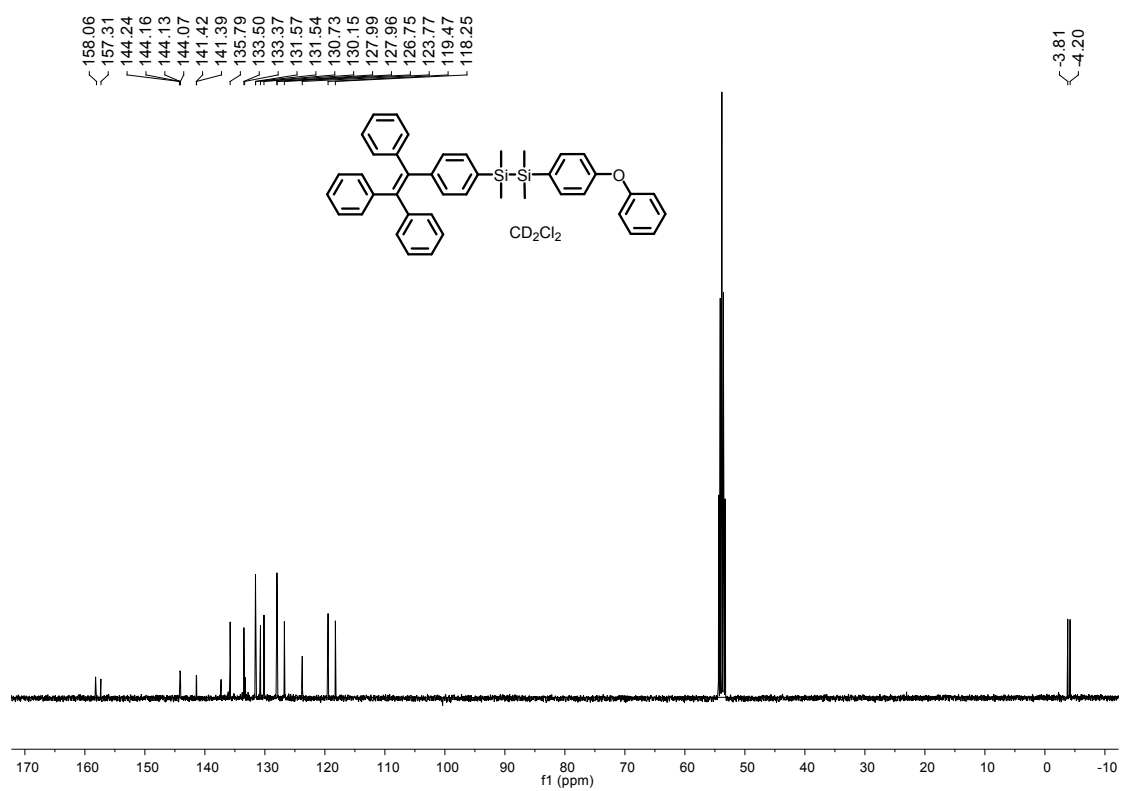
The $^1\text{H NMR}$ spectrum of **3c** (400 MHz, CDCl_3).



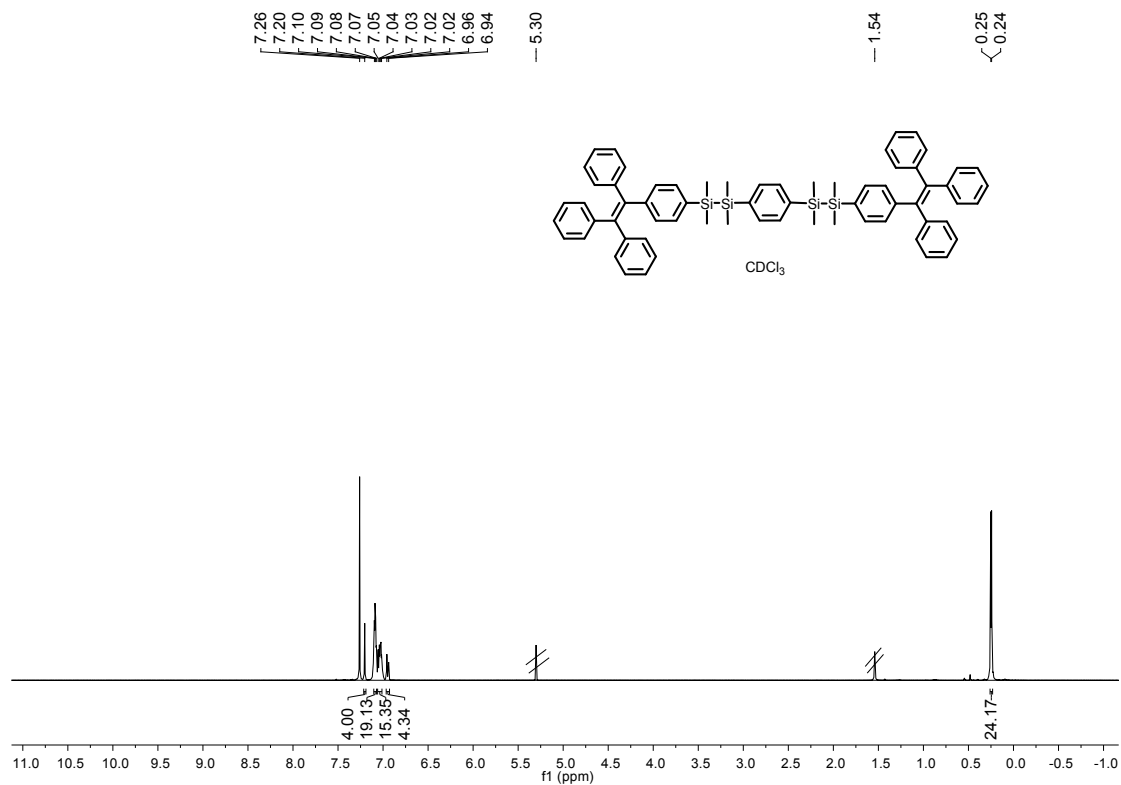
The $^{13}\text{C NMR}$ spectrum of **3c** (100 MHz, CD_2Cl_2).



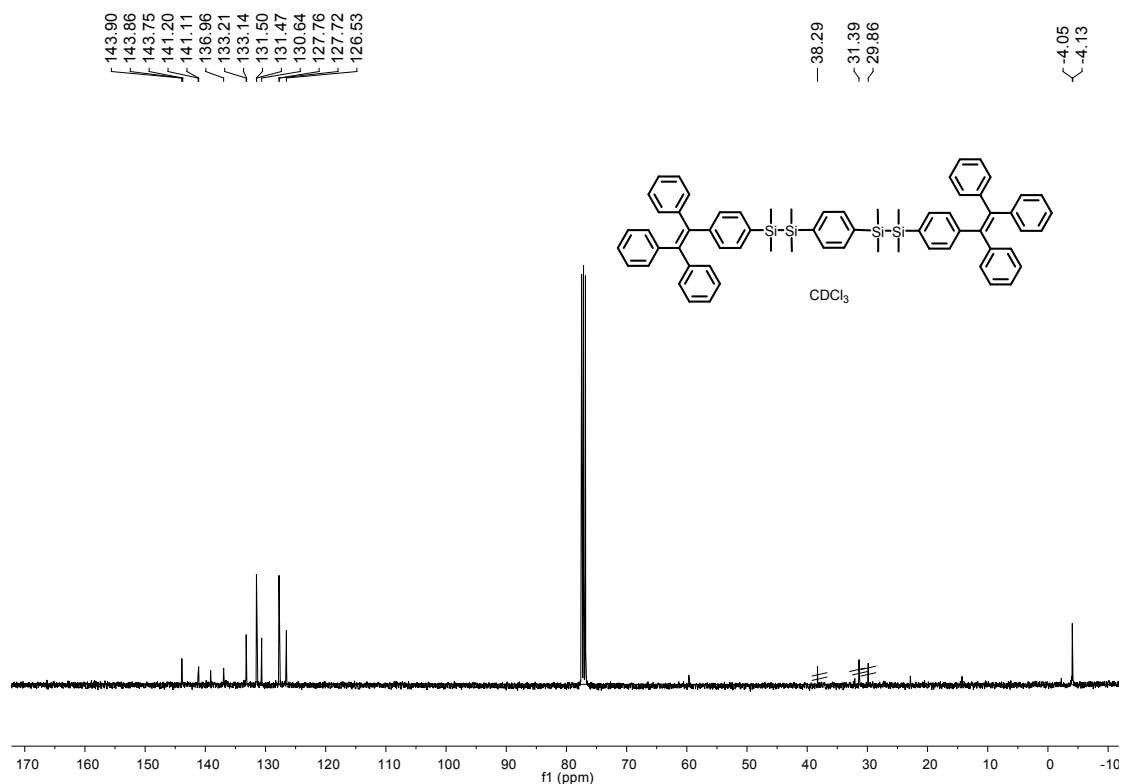
The ^1H NMR spectrum of **3d** (400 MHz, CD_2Cl_2).



The ^{13}C NMR spectrum of **3d** (100 MHz, CD_2Cl_2).



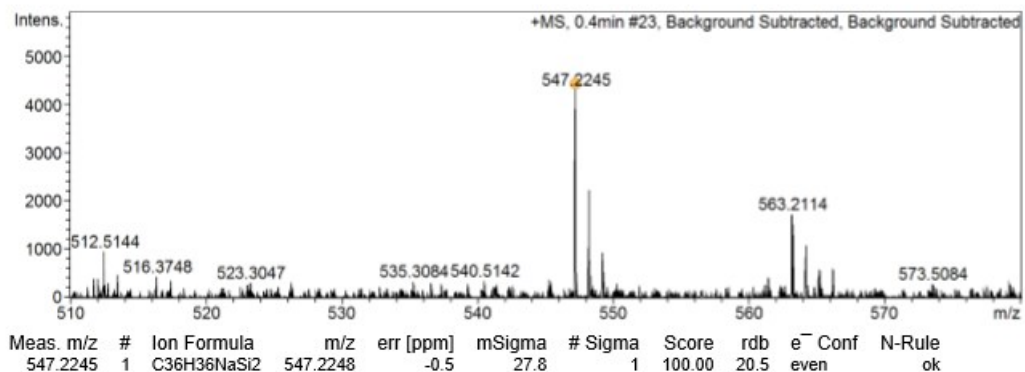
The ^1H NMR spectrum of 4 (400 MHz, CD_2Cl_2).



The ^{13}C NMR spectrum of 4 (100 MHz, CDCl_3).

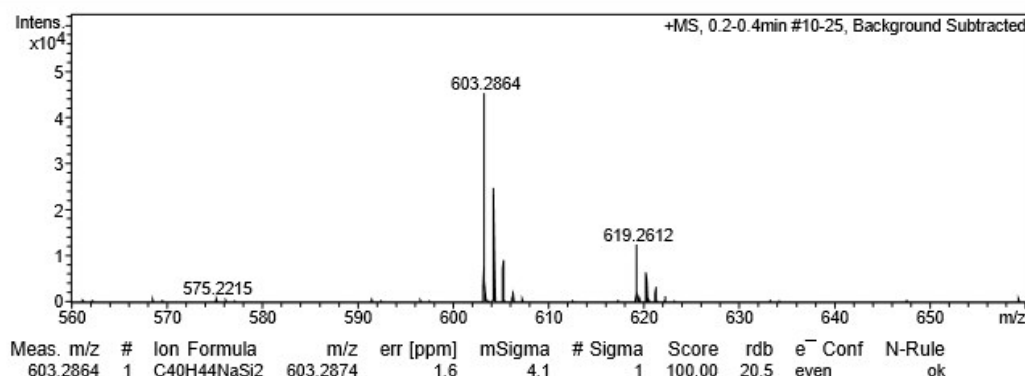
HR-MS data for **3a**

Acquisition Parameter					
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4800 V	Set Dry Heater	220 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	800 m/z	Set Collision Cell RF	120.0 Vpp	Set Divert Valve	Source



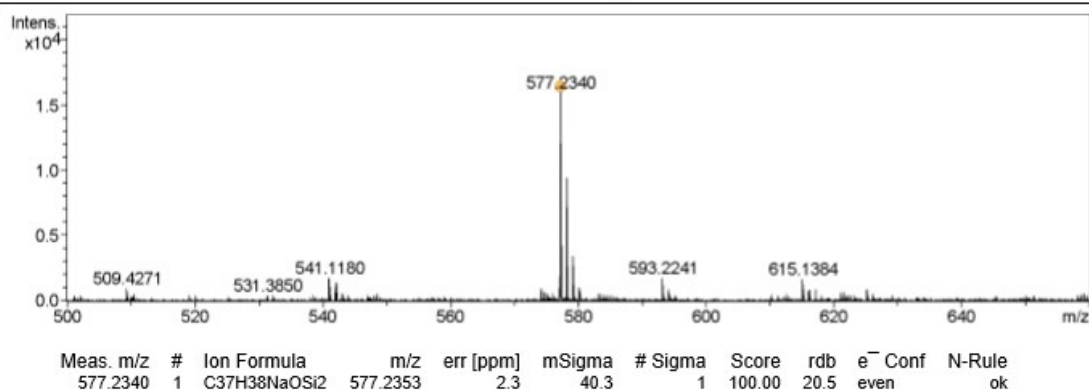
HR-MS data for **3b**

Acquisition Parameter					
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Focus	Active	Set Capillary	4800 V	Set Dry Heater	220 °C
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	750 m/z	Set Collision Cell RF	120.0 Vpp	Set Divert Valve	Waste



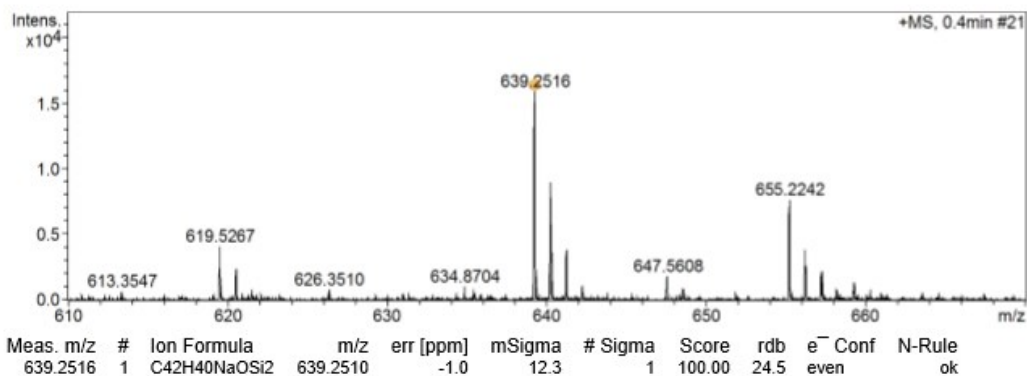
HR-MS data for **3c**

Acquisition Parameter					
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Focus	Active	Set Capillary	4500 V	Set Dry Heater	220 °C
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	700 m/z	Set Collision Cell RF	120.0 Vpp	Set Divert Valve	Waste



HR-MS data for **3d**

Acquisition Parameter					
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4800 V	Set Dry Heater	220 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	800 m/z	Set Collision Cell RF	120.0 Vpp	Set Divert Valve	Source



HR-MS data for **4**

Acquisition Parameter					
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4800 V	Set Dry Heater	220 °C
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1800 m/z	Set Collision Cell RF	120.0 Vpp	Set Divert Valve	Source

