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Supporting Information

Intra- and Intermolecular Interaction of Anthracene Moieties in 7,8-Disilabicyclo[3.3.0]octadienyl-Bridged Bisanthracenes

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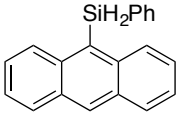
Experimental Procedures

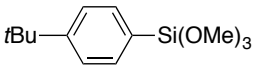
1. General Information

The ^{1}H, ^{13}C and ^{29}Si NMR spectra were recorded with a Bruker BioSpin DRX300 or DRX500 NMR (300 or 500 MHz) spectrometer. The chemical shifts are reported in δ units downfield from the internal reference (Me_4Si). Column chromatography was performed with silica gel (Fuji Silysia PSQ100B). High-resolution mass spectra (HRMS) were measured by a Hitachi High-Technologies Nano Frontier LD. UV/vis spectra were recorded on a SHIMADZU UV-1800 spectrophotometer. Photoluminescence spectra were recorded on a SHIMADZU RF-5300PC spectrofluorometer. Luminescence quantum yields were obtained by a JASCO FP-8200 spectrofluorometer. X-ray crystallographic analysis was carried out by a Rigaku XtaLAB PRO HPC diffractometer with Cu Kα radiation. The structures were solved and refined by Olex2. Thermogravimetric analysis (TGA) was carried out on Shimadzu TGA-50 at a heating rate of 10 ºC/min under a nitrogen flow. DFT calculation was performed with Spartan'16. Unless otherwise noted, available reagents were used without further purification. 4-Methoxyphenylsilane[1] were prepared as according to the literature.

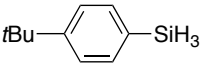
2. Synthesis



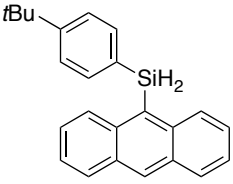
9-(Phenylsilyl)anthracene (1a). In an Ar purged J. Young tube, 9-bromoanthracene (1.54 g, 6.00 mmol) and tetrahydrofuran (24 mL) were placed and cooled to –78 ºC. Then, *n*BuLi (1.6 M in hexane, 4.0 mL, 6.4 mmol) was slowly added, followed by stirring for 30 min. After the addition of trichlorophenylsilane (1.06 mL, 6.60 mmol), the reaction mixture was stirred for 6 h at room temperature. The obtained mixture was added to lithium aluminium hydride (0.228 g, 6.00 mmol) in tetrahydrofuran (3 mL), followed by stirring for 24 h at room temperature. The reaction mixture was quenched with 1 M HCl aq, extracted with hexane, washed with sat. $NaHCO_3$ aq and brine, dried over Na_2SO_4, and concentrated. The residue was purified by recrystallization from ethanol to give a colorless solid (0.854 g, 3.00 mmol, 50 % yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.62 (s, 1H, Ar-*H*), 8.55 (m, 2H, Ar-*H*), 8.08 (m, 2H, Ar-H), 7.61-7.48 (m, 6H, Ar-*H*), 7.40-7.26 (m, 3H, Ar-*H*), 5.70 (s, 2H, -SiH_2-) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 137.8, 135.6, 131.7, 131.4, 131.1, 129.9, 129.5, 128.5, 128.3, 126.6, 126.3, 125.1 ppm. HRMS calcd for $C_{20}H_{16}Si$ $[M]^+$: 284.1016; found: 284.1020.



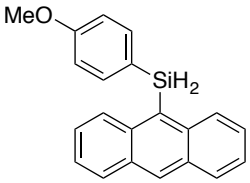
(4-*tert*-Butylphenyl)trimethoxysilane. Mg (2.04 g, 84.0 mmol) and LiCl (3.05 g, 72.0 mmol) were placed in a J. Young tube, which were dried by a heat gun under vacuum. After cooling to room temperature and purging Ar, THF (60 mL) and DIBAL-H (1.5 M in toluene, 0.6 mL, 0.9 mmol) were added. Then, 4-bromo-*tert*-butylbenzene (10.2 mL. 60.0 mmol) was slowly added and the reaction mixture was stirred for 4 h. The Grignard reagent was slowly added to tetramethyl orthosilicate (26.3 mL, 180 mmol) in THF (30 mL) at –45 ºC, followed by stirring for 12 h at room temperature. The mixture was diluted with hexane (180mL), filtered through a plug of Celite® and concentrated. The resulting liquid was purified via distillation (b.p. = 77 ºC, ~0.5 Torr) to give a colorless liquid (9.07 g, 35.7 mmol, 60% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.59 (d, 2H, Ar-*H*, *J* = 8.3 Hz), 7.42 (d, 2H, Ar-*H*, *J* = 8.3 Hz), 3.62 (s, 9H, -Si(OCH_3)$_3$), 1.32 (s, 9H, -C(CH_3)$_3$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.8, 134.8, 126.0, 125.1, 50.9, 34.9, 31.3 ppm. ^{29}Si NMR (99 MHz, $CDCl_3$): δ = –53.2 ppm.



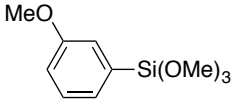
(**4-*tert*-Butylphenyl)silane.** To a 2-neck round bottom flask was added $LiAlH_4$ (2.58 g, 68.0 mmol) and Et_2O (68 mL). The mixture was cooled to –45 ºC and (4-*tert*-butylphenyl)trimethoxysilane was added slowly and allowed to stir for 12 h at room temperature. The excess $LiAlH_4$ was quenched by the addition of EtOAc (53 mL, 544 mmol) at –45 ºC. The mixture was filtered through a plug of Celite® and concentrated to give a colorless liquid (quantitative yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.53 (d, 2H, Ar-*H*, *J* = 8.1 Hz), 7.40 (d, 2H, Ar-*H*, *J* = 8.1 Hz), 4.19 (s, 3H, -SiH_3), 1.32 (s, 9H, -C(CH_3)$_3$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.2, 135.9, 125.3, 124.8, 34.9, 31.3 ppm. ^{29}Si NMR (99 MHz, $CDCl_3$): δ = –59.2 ppm.



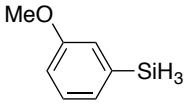
9-(4-*tert*-Butylphenylsilyl)anthracene (1b). To a J. Young tube was added (4-*tert*-butylphenyl)silane (1.36 g, 8.28 mmol) and hexane (12 mL) and cooled to 0 ºC. BCl_3 (1 M in CH_2Cl_2, 3.3 mL, 3.3 mmol) was added and the reaction mixture was stirred for 21 h at room temperature. All the volatiles were removed under reduced pressure and the residue was dissolved in hexane (3 mL), followed by addition to 9-anthryllithium (6.00 mmol, generated by treating 9-bromoanthracene (1.54 g, 6.00 mmol) with *n*-butyllithium (4.0 mL, 6.4 mmol, 1.6 M solution in hexane) in diethyl ether (24 mL) for 30 min at –45 ºC) solution at –45 ºC. After stirring for 1.5 h at room temperature, the reaction mixture was quenched with NH_4Cl aq, extracted with hexane, washed with water and brine, dried over Na_2SO_4, and concentrated. The residue was subjected to column chromatography on silica gel with hexane followed by recrystallization from CH_2Cl_2/MeOH to give a pale yellow solid (1.35 g, 3.96 mmol, 66% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.59 (s, 1H, Ar-*H*), 8.55 (m, 2H, Ar-*H*), 8.05 (m, 2H, Ar-*H*), 7.50 (m, 6H, Ar-*H*), 7.32 (d, 2H, Ar-*H*, *J* = 8.3 Hz), 5.66 (s, 2H, -SiH_2-), 1.26 (s, 9H, -C(CH_3)$_3$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.0, 137.8, 135.5, 131.4, 131.0, 129.5, 128.6, 127.9, 127.1, 126.2, 125.3, 125.1 ppm. ^{29}Si NMR (99 MHz, $CDCl_3$): δ = –49.3 ppm. HRMS calcd for $C_{24}H_{24}Si$ $[M]^+$: 340.1642, found: 340.1648.



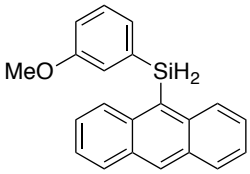
9-(3-Methoxyphenylsilyl)anthracene (1c). According to the procedure for **1b**, the reaction using 4-methoxyphenylsilane (0.820 g, 5.93 mmol), BCl_3 (1 M in CH_2Cl_2, 2.4 mL, 2.4 mmol), 9-bromoanthracene (1.11 g, 4.30 mmol) and *n*-butyllithium (2.9 mL, 4.6 mmol, 1.6 M solution in hexane) afforded 0.414 g (1.32 mmol, 22% yield) of a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.56 (s, 1H, Ar-*H*), 8.52 (dd, 2H, Ar-*H*, *J* = 7.4, 2.3 Hz), 7.49-7.44 (m, 6H, Ar-*H*), 6.81 (d, 2H, Ar-*H*, *J* = 8.7 Hz), 5.65 (s, 2H, -SiH_2-), 3.72 (s, 3H, -OCH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 161.2, 137.8, 137.1, 131.4, 131.0, 129.5, 128.5, 127.2, 126.2, 125.1, 122.1, 114.2, 55.1 ppm. HRMS calcd for $C_{21}H_{18}OSi$ $[M]^+$: 314.1122, found: 314.1116.



(3-Methoxyphenyl)trimethoxysilane. According to the procedure for (4-*tert*-butylphenyl)trimethoxysilane, the reaction using 3-bromoanisole (7.5 mL, 60 mmol), Mg (2.04 g, 84.0 mmol), LiCl (3.05 g, 72.0 mmol) and tetramethyl orthosilicate (26.3 mL, 180 mmol) afforded 5.61 g (24.6 mmol, 41% yield) of a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.33 (ddd, 1H, Ar-*H*, *J* = 8.2, 7.2, 0.5 Hz), 7.23 (dt, 1H, Ar-*H*, *J* = 7.2, 1.0 Hz), 7.18 (d, Ar-*H*, 1H, *J* = 2.8 Hz), 6.99, (ddd, 1H, Ar-*H*, *J* = 8.3, 2.8, 1.1 Hz), 3.83 (s, 3H, Ar-OCH_3), 3.63 (s, 9H, Si-OCH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.3, 131.0, 129.4, 127.1, 119.8, 116.7, 55.3, 51.0 ppm. ^{29}Si NMR (99 MHz, $CDCl_3$): δ = –54.1 ppm. HRMS calcd for $C_{10}H_{17}O_4Si$ $[M+H]^+$: 229.0891, found: 229.0891.

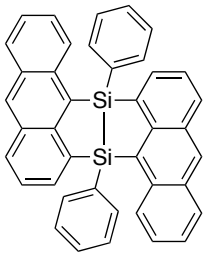


(3-Methoxyphenyl)silane. According to the procedure for (4-*tert*-butylphenyl)silane, the reaction using (3-methoxyphenyl)trimethoxysilane (5.48 g, 24.0 mmol) and $LiAlH_4$ (1.82 g, 48.0 mmol) afforded 3.09 g (22.4 mmol, 93% yield) of a colorless oil. Yield: 93%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.30 (dd, 1H, Ar-*H*, *J* = 8.2, 7.2 Hz), 7.17 (dt, 1H, Ar-*H*, *J* = 7.2, 1.0 Hz), 7.12 (dd, Ar-*H*, 1H, *J* = 2.7, 0.6 Hz), 6.95, (ddd, 1H, Ar-*H*, *J* = 8.3, 2.7, 0.9 Hz), 4.19 (s, 3H, -SiH_3), 3.82 (s, 3H, Ar-OCH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.2, 129.8, 129.5, 128.2, 120.9, 115.8, 55.3 ppm. ^{29}Si NMR (99 MHz, $CDCl_3$): δ = –58.0 ppm.

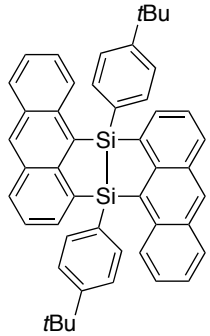


9-(3-Methoxyphenylsilyl)anthracene (1d). According to the procedure for **1b**, the reaction using 3-methoxyphenylsilane (1.14 g, 8.28 mmol), BCl_3 (1 M in CH_2Cl_2, 3.3 mL, 3.3 mmol), 9-bromoanthracene (1.54 g, 6.00 mmol) and *n*-butyllithium (4.0 mL, 6.4 mmol, 1.6 M solution in hexane) afforded 1.10 g (3.50 mmol, 58% yield) of a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.59 (s, 1H, Ar-*H*), 8.52 (d, 2H, Ar-*H*, *J* = 9.4 Hz), 8.05 (m, 2H, Ar-*H*), 7.52-7.46 (m, 4H, Ar-*H*), 7.22 (t, 1H, Ar-*H*, *J* = 7.7 Hz), 7.12 (m, 2H, Ar-*H*), 6.89 (m, 1H, Ar-*H*), 5.66 (s, 2H, -SiH_2-), 3.70 (s, 3H, -OCH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.3, 137.9, 133.2, 131.4, 131.1, 129.54, 129.52, 128.5, 127.8, 126.5, 126.3, 125.1, 120.8, 115.3, 55.2 ppm. ^{29}Si NMR (99 MHz, $CDCl_3$): δ = –48.5 ppm. HRMS calcd for $C_{21}H_{18}OSi$ $[M]^+$: 314.1122, found: 314.1127.

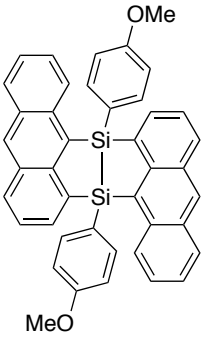
General procedure for ruthenium-catalyzed dimerization of 9-anthrylarylsilanes. In an Ar purged J. Young tube, cyclopentyl methyl ether (1.0 mL), $[RuH_2(CO)(PPh_3)_3]$ (18.4 mg, 0.020 mmol), 9-anthrylarylsilane (0.40 mmol) and cyclooctene (0.80 mmol) were placed. After stirring for 16 h at 115 ºC, the precipitate was collected by filtration at room temperature.



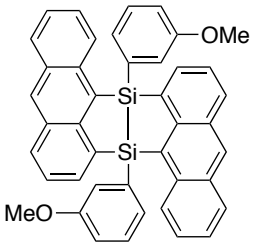
2a. According to the general procedure, the reaction of **1a** (114 mg, 0.400 mmol) afforded 43.8 mg (77.8 μmol, 39% yield) of a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.50 (s, 2H, Ar-*H*), 8.37 (m, 4H, Ar-*H*), 8.03 (m, 4H, Ar-*H*), 7.69 (m, 4H, Ar-*H*), 7.56 (dd, 2H, Ar-*H*, *J* = 8.4, 6.5 Hz), 7.46-7.28 (m, 10H, Ar-*H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 138.9, 137.2, 136.5, 136.4, 134.9, 132.0, 131.7, 131.3, 130.71, 130.66, 130.5, 129.7, 129.3, 128.4, 125.9, 125.3 ppm. HRMS (ESI-TOF) calcd for $C_{40}H_{26}Si_2$: 562.1573, found: 562.1545. T_{d5} = 401 ºC.



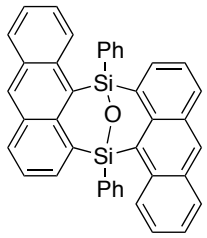
2b. According to the general procedure, the reaction of **1b** (136 mg, 0.400 mmol) afforded 37.0 mg (54.8 μmol, 27% yield) of a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.48 (s, 2H, Ar-*H*), 8.38 (m, 2H, Ar-*H*), 8.36 (dd, 2H, Ar-*H*, *J* = 6.5, 1.3 Hz), 8.02 (ddd, 2H, Ar-*H*, *J* = 8.5, 1.3, 0.6 Hz), 7.99 (m, 2H, Ar-*H*), 7.63 (d, 4H, Ar-*H*, *J* = 8.5 Hz), 7.54 (dd, 2H, Ar-*H*, *J* = 8.4, 6.4 Hz), 7.41 (m, 4H, Ar-*H*), 7.34 (d, 4H, Ar-*H*, *J* = 8.5 Hz), 1.30 (s, 18H, -C(CH_3)$_3$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 152.7, 146.7, 139.4, 137.1, 136.8, 136.6, 134.7, 131.9, 131.7, 130.8, 130.5, 130.4, 129.3, 127.6, 125.6, 125.4, 125.22, 125.17, 34.9, 31.3 ppm. ^{29}Si NMR (99 MHz, $CDCl_3$): δ = -27.2 ppm.



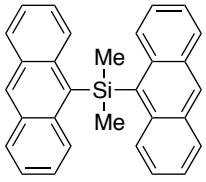
2c. According to the general procedure, the reaction of **1c** (126 mg, 0.400 mmol) afforded 36.9 mg (59.2 μmol, 30% yield) of a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.46 (s, 2H, Ar-*H*), 8.41 (m, 2H, Ar-*H*), 8.33 (dd, 2H, Ar-*H*, *J* = 6.4, 1.2 Hz), 7.99 (m, 4H, Ar-*H*), 7.60 (d, 4H, Ar-*H*, *J* = 8.8 Hz), 7.53 (dd, 2H, Ar-*H*, *J* = 8.4, 6.4 Hz), 7.41 (m, 4H, Ar-*H*), 6.86 (d, 4H, Ar-*H*, *J* = 8.8 Hz), 3.77 (s, 6H, -OCH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 161.1, 146.8, 139.4, 138.0, 137.2, 136.8, 134.7, 131.9, 131.7, 130.7, 130.5, 130.4, 129.3, 125.7, 125.3, 125.2, 121.5, 114.4, 55.2 ppm. HRMS (ESI-TOF) calcd for $C_{42}H_{31}O_2Si_2$ $[M+H]^+$: 623.1857, found: 623.1875.



2d. According to the general procedure, the reaction of **1d** (126 mg, 0.400 mmol) afforded 55.5 mg (89.1 μmol, 45% yield) of a yellow solid. ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 8.54 (s, 2H, Ar-*H*), 8.39 (m, 4H, Ar-*H*), 8.04 (m, 4H, Ar-*H*), 7.58 (dd, 2H, Ar-*H*, *J* = 8.4, 6.5 Hz), 7.46 (m, 4H, Ar-*H*), 7.26 (m, 6H, Ar-*H*), 6.94 (m, 2H, Ar-*H*), 3.64 (s, 6H, -OCH_3) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 159.9, 147.0, 138.8, 137.3, 136.4, 135.3, 132.9, 132.2, 132.0, 131.0, 130.8, 130.7, 129.9, 129.6, 128.8, 126.2, 125.7, 125.6, 121.8, 115.6, 55.4 ppm. HRMS (ESI-TOF) calcd for $C_{42}H_{30}O_2Si_2$ $[M]^+$: 622.1779, found: 622.1783.



3a. In an Ar purged J. Young tube, toluene (0.8 mL), **2a** (22,5 mg, 0.040 mmol) and NMO (9.4 mg, 0.080 mmol) were placed. After stirring for 9 h at 80 ºC, ethanol was added to precipitate the products. The precipitate was collected by filtration, affording 21.8 mg (37.7 μmol, 94% yield) as a yellow solid. ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 8.58 (s, 2H, Ar-*H*), 8.30 (dd, 2H, Ar-*H*, *J* = 6.4, 1.4 Hz), 8.27 (dd, 2H, Ar-*H*, *J* = 8.8, 0.8 Hz), 8.13 (ddd, 2H, Ar-H, *J* = 8.5, 1.4, 0.6 Hz), 7.98 (dt, 2H, Ar-*H*, *J* = 8.4, 0.6 Hz), 7.78 (dd, 4H, Ar-*H*, *J* = 8.1, 1.4 Hz), 7.59 (dd, 2H, Ar-*H*, *J* = 8.5, 6.4 Hz), 7.51 (ddt, 2H, Ar-*H*, *J* = 8.1, 6.9, 1.3 Hz), 7.42-7.38 (m, 6H, Ar-*H*), 7.29 (ddd, 2H, Ar-*H*, *J* = 8.8, 6.6, 1.4 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.9, 136.9, 136.3, 134.2, 133.9, 133.3, 132.7, 132.4, 132.2, 131.3, 131.2, 129.8, 129.7, 129.5, 128.6, 125.6, 125.4, 124.6 ppm. HRMS (ESI-TOF) calcd for $C_{40}H_{27}OSi_2$ $[M+H]^+$: 579.1595, found: 579.1595.



Bis(9-anthryl)dimethylsilane (BADMS). In an Ar purged J. Young tube, 9-bromoanthracene (1.54 g, 6.00 mmol) and diethyl ether (30 mL) were placed and cooled to –45 ºC. Then, *n*BuLi (1.6 M in hexane, 4.0 mL, 6.4 mmol) was slowly added, followed by stirring for 30 min. After the addition of dichlorodimethylsilane (0.36 mL, 3.00 mmol), the reaction mixture was stirred for 49 h at room temperature. The mixture was quenched with NH_4Cl aq, extracted with toluene, washed with water and brine, dried over Na_2SO_4, and concentrated. The residue was purified by recrystallization from dichloromethane/ethanol to give 0.724 g (1.75 mmol, 50 % yield) of a colorless solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.52 (dd, 4H, Ar-*H*, *J* = 9.0, 0.8 Hz), 8.46 (s, 2H, Ar-*H*), 7.97 (dt, 4H, Ar-H, *J* = 8.4, 0.7 Hz), 7.34 (ddd, 4H, Ar-*H*, *J* = 8.4, 6.5, 1.0 Hz), 7.19 (ddd, 4H, Ar-*H*, *J* = 9.0, 6.5, 1.4 Hz), 1.25 (s, 6H, -CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 137.27, 136.32, 131.58, 130.27, 129.72, 128.21, 125.4, 124.7, 8.2 ppm. ^{29}Si NMR (99 MHz, $CDCl_3$): δ = -9.1 ppm.

3. Thermogravimetric Analysis

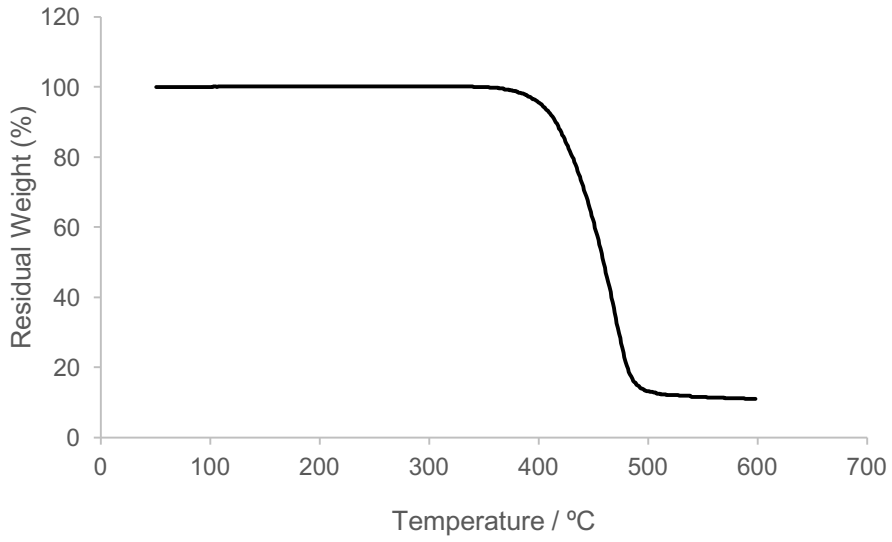


Figure S1. TGA thermogram of **2a** (heating rate: 10 ºC/min, under N_2 (50 mL/min)).

4. UV-vis and Photoluminescence Properties

Table S1. Photophysical properties of ADMS, BADMS, **2** and **3a**.

Compound	λ_{abs}/nm[a],[b] (ε/10^{-5} $M^{-1}cm^{-1}$)[c]	$\lambda_{em,chloroform}$/nm[a],[d]	$\Phi_{f,chloroform}$[a],[e]	$\lambda_{em,powder}$/nm[d]	$\Phi_{f,powder}$[e]
ADMS	351 (0.055), 369 (0.083), 390 (0.077)	396, 419	0.50	427, 447	0.46
BADMS	355 (0.143), 374 (0.234), 395 (0.259)	406, 424	0.40	435	0.02
2a	368 (0.159), 388 (0.226), 412 (0.295)	422, 445	0.10	560	0.10
2b	368 (0.111), 389 (0.154), 413 (0.200)	424, 444	0.06	536	0.12
2c	367 (0.108), 388 (0.142), 413 (0.178)	427, 441	0.02	541	0.13
2d	368 (0.096), 389 (0.136), 412 (0.178)	423, 444	0.17	532	0.25
3a	367 (0.117), 386 (0.160), 409 (0.177)	420, 443	0.60	470	0.15

[a] 10 μM in chloroform. [b] Observed absorption maximum at the longest wavelength. [c] Molar extinction coefficient. [d] Observed fluorescent maxima. [e] Fluorescent quantum yield determined by a calibrated integrating sphere system.

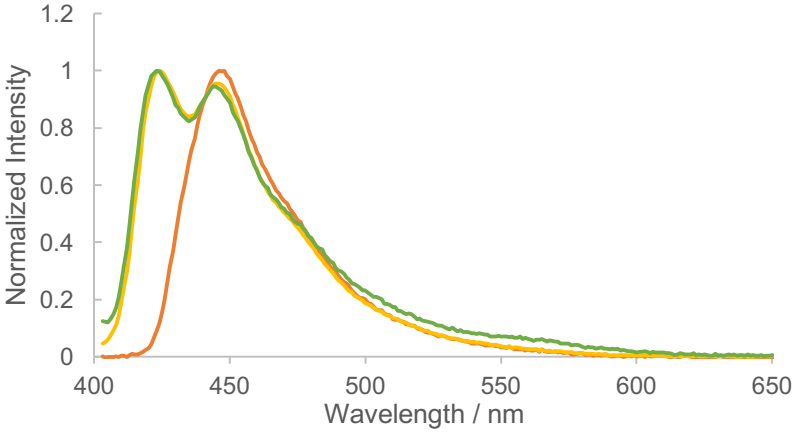


Figure S2. Normalized photoluminescence spectra of **2a** solutions (1.0 mM (red), 0.10 μM (yellow) and 0.10 μM (green) in chloroform).

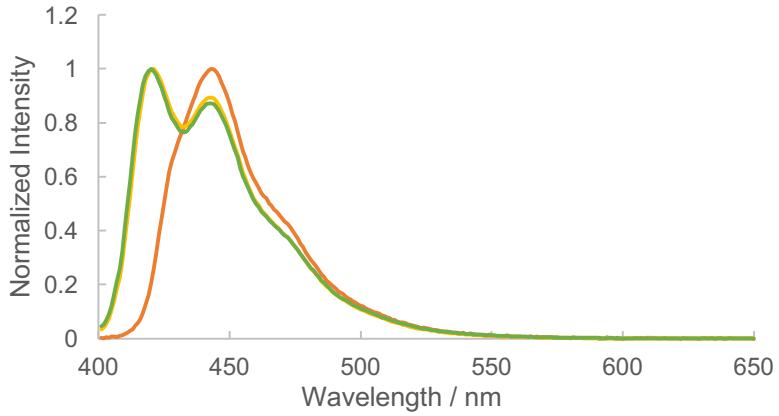


Figure S3. Normalized photoluminescence spectra of **3a** solutions (1.0 mM (red), 0.10 μM (yellow) and 0.10 μM (green) in chloroform).

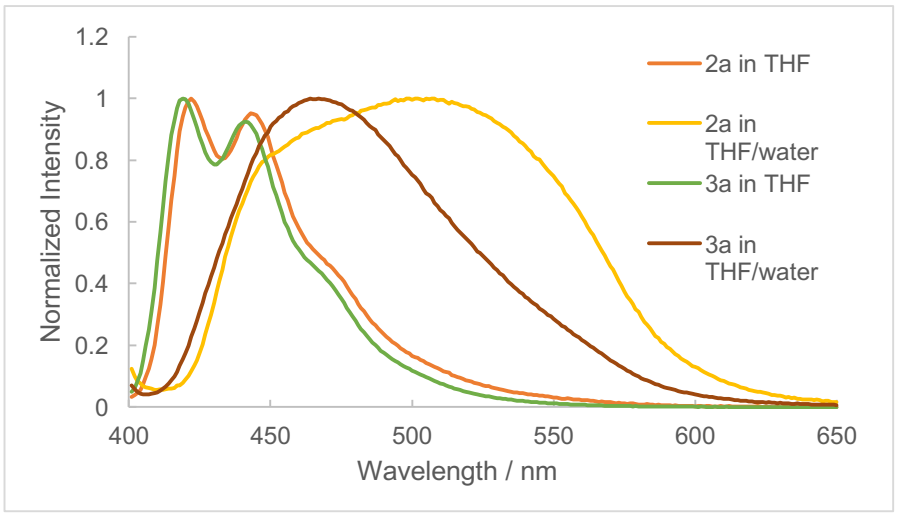


Figure S4. Normalized photoluminescence spectra of **2a** in THF (10 μM), **2a** in THF/water (1:99 (v/v), 10 μM), **3a** in THF (10 μM) and **3a** in THF/water (1:99 (v/v), 10 μM).

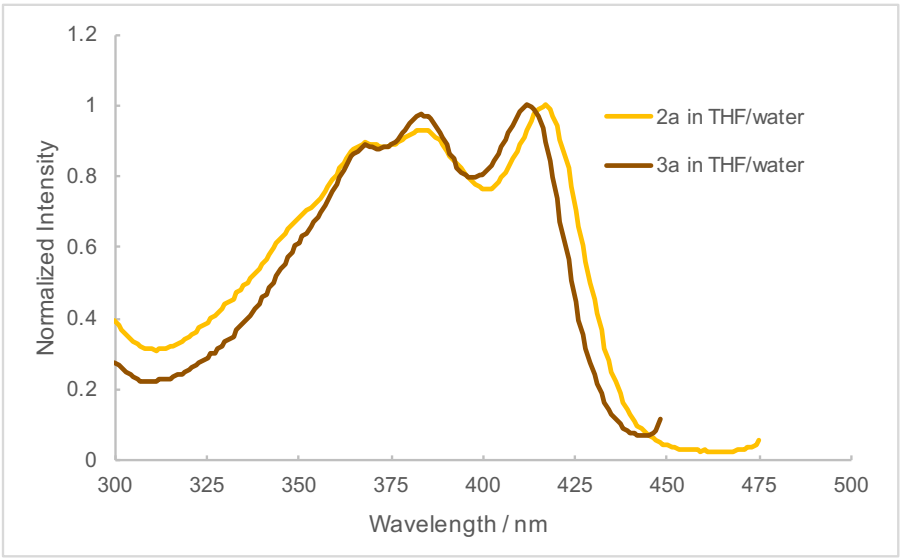


Figure S5. Normalized excitation spectra of **2a** in THF/water (1:99 (v/v), 10 μM, Em: 490 nm) and **3a** in THF/water (1:99 (v/v), 10 μM, Em: 463 nm).

5. DFT calculation

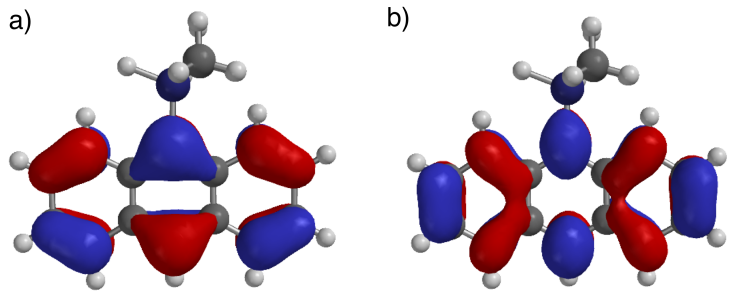


Figure S6. a) HOMO (–7.3 eV) and b) LUMO (–0.4 eV) lobes of ADMS calculated at ωB97X-D/def2-SVPD//ωB97X-D/def2-SV(P) level.

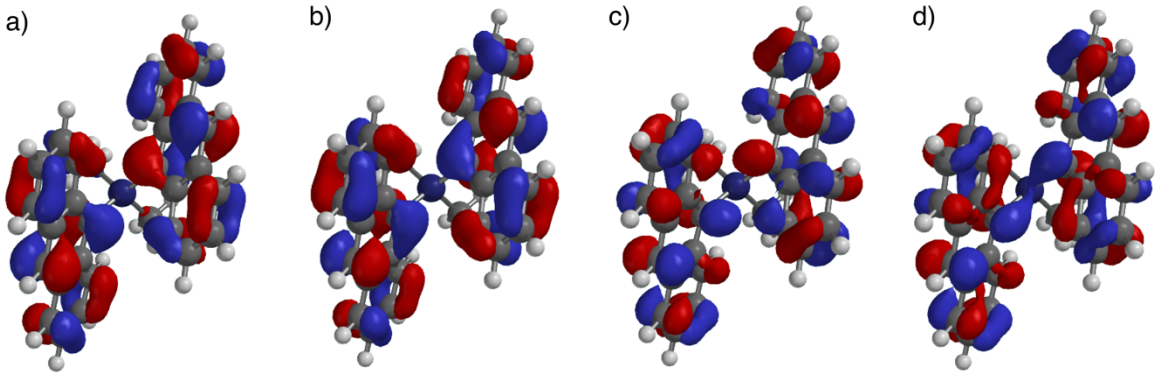


Figure S7. a) HOMO–1 (–7.3 eV), b) HOMO (–7.2 eV), c) LUMO (–0.4 eV) and d) LUMO+1 (–0.3 eV) lobes of BADMS calculated at ωB97X-D/def2-SVPD//ωB97X-D/def2-SV(P) level.

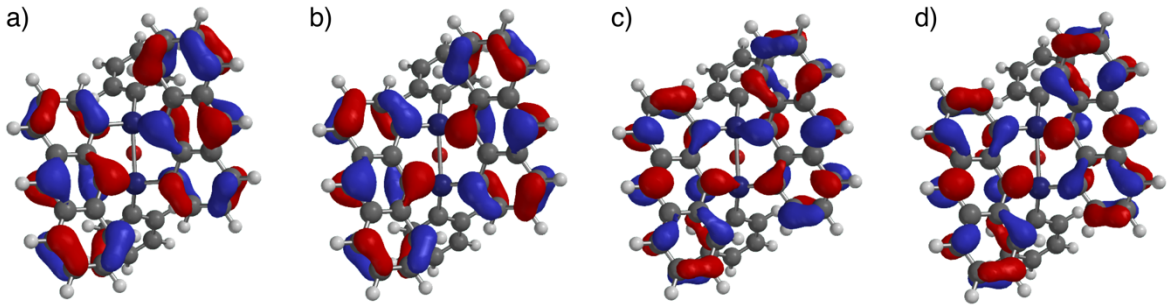


Figure S8. a) HOMO–1 (–7.4 eV), b) HOMO (–7.3 eV), c) LUMO (–0.6 eV) and d) LUMO+1 (–0.4 eV) lobes of **3a** calculated at ωB97X-D/def2-SVPD//ωB97X-D/def2-SV(P) level.

Table S2. Results of TD-DFT Calculation at ωB97X-D/def2-SVPD//ωB97X-D/def2-SV(P) level.

Compound	Energy gap / nm	Oscillator strength	MO component
ADMS	329	0.167	HOMO-LUMO (92%)
BADMS	327	0.115	HOMO–1-LUMO (46%) HOMO-LUMO+1 (45%)
	344	0.222	HOMO-LUMO (69%) HOMO–1-LUMO+1 (25%)
2a	330	0.146	HOMO–1-LUMO (53%) HOMO-LUMO+1 (37%)
	345	0.328	HOMO-LUMO (74%) HOMO–1-LUMO+1 (19%)
3a	331	0.118	HOMO–1-LUMO (54%) HOMO-LUMO+1 (37%)
	343	0.285	HOMO-LUMO (68%) HOMO–1-LUMO+1 (25%)

Table S3. Cartesian coordinates of ADMS optimized by DFT calculation at ωB97X-D/def2-SV(P) level.

Atom	X	Y	Z
H	-0.495031	5.366225	0.232877
C	-0.394413	4.2775	0.25685
H	-0.367187	4.063238	-1.872124
C	-0.323913	3.560623	-0.900961
C	-0.210628	2.235832	1.560483
C	-0.191843	2.133291	-0.883268
C	-0.335702	3.595692	1.506261
C	-0.132188	1.42662	0.372617
C	-0.119455	1.420645	-2.079309
H	-0.391365	4.169341	2.435975
H	-0.169476	1.755692	2.536735
C	0.00845	0.032236	-2.094344
H	-0.163957	1.96425	-3.028788
C	0.082444	-0.679854	-3.335814
C	0.066127	-0.683213	-0.846984
H	0.240945	-2.711612	-0.029636
C	-0.002453	0.011244	0.390955
C	0.206518	-2.038047	-3.364723
H	0.037284	-0.104151	-4.265455
H	0.262658	-2.572279	-4.317152
C	0.262263	-2.762857	-2.139587
H	0.360067	-3.85205	-2.160716
C	0.194898	-2.112863	-0.939266
Si	0.085623	-0.995352	2.010411

H	0.013381	-0.08588	3.192788
C	-1.394356	-2.153926	2.18301
H	-2.329133	-1.565285	2.175274
H	-1.340737	-2.687363	3.149187
H	-1.470748	-2.907377	1.381675
C	1.73775	-1.892714	2.179082
H	1.787438	-2.397465	3.160779
H	2.564496	-1.161462	2.13501
H	1.922246	-2.648679	1.39816

Table S4. Cartesian coordinates of BADMS optimized by DFT calculation at ωB97X-D/def2-SV(P) level.

Atom	X	Y	Z
Si	0	0	-1.683349
C	-0.249529	-1.492037	-2.820559
H	-0.706582	-2.363038	-2.321551
H	0.76043	-1.797648	-3.150783
H	-0.833762	-1.258916	-3.727569
C	0.249529	1.492037	-2.820559
H	0.706582	2.363038	-2.321551
H	-0.76043	1.797648	-3.150783
H	0.833762	1.258916	-3.727569
H	1.381986	3.201527	1.978503
C	0.404248	2.720398	1.886533
H	0.889264	1.893987	0.008181
C	0.122659	1.972913	0.778438
C	-1.794058	2.312743	2.785457
C	-1.146354	1.320565	0.597937
C	-0.56358	2.88606	2.918895
C	-2.126609	1.532034	1.630366
C	-1.448024	0.50587	-0.525979
H	-0.319763	3.480625	3.803816
H	-4.132479	1.112187	2.293317
H	-2.557338	2.443317	3.558901
C	-2.774675	0.027939	-0.6769
C	-3.22647	-0.681439	-1.841935
C	-3.752622	0.246965	0.35783
H	-5.79494	-0.103326	1.020794
C	-3.395086	0.968105	1.496739
C	-4.503789	-1.154743	-1.956795

H	-2.543474	-0.821337	-2.676924
H	-4.807287	-1.678209	-2.868017
C	-5.448534	-0.963568	-0.907878
H	-6.464609	-1.354609	-1.010765
C	-5.078643	-0.276654	0.211622
H	4.807287	1.678209	-2.868017
C	4.503789	1.154743	-1.956795
H	2.543474	0.821337	-2.676924
C	3.22647	0.681439	-1.841935
C	5.078643	0.276654	0.211622
C	2.774675	-0.027939	-0.6769
C	5.448534	0.963568	-0.907878
C	3.752622	-0.246965	0.35783
C	1.448024	-0.50587	-0.525979
H	6.464609	1.354609	-1.010765
H	4.132479	-1.112187	2.293317
H	5.79494	0.103326	1.020794
C	1.146354	-1.320565	0.597937
C	-0.122659	-1.972913	0.778438
C	2.126609	-1.532034	1.630366
H	2.557338	-2.443317	3.558901
C	3.395086	-0.968105	1.496738
C	-0.404248	-2.720398	1.886533
H	-0.889264	-1.893987	0.008182
H	-1.381986	-3.201527	1.978503
C	0.56358	-2.88606	2.918895
H	0.319763	-3.480625	3.803816
C	1.794058	-2.312743	2.785457

Table S5 Cartesian coordinates of **2a** optimized by DFT calculation at ωB97X-D/def2-SV(P) level.

Atom	X	Y	Z
H	-1.697513	-6.572949	-2.634768
C	-1.309429	-5.631451	-2.235779
H	0.617596	-5.857318	-3.140998
C	-0.031918	-5.237783	-2.514716
C	-1.680002	-3.631919	-0.913238
C	0.489082	-4.006321	-2.000017
C	-2.14585	-4.811318	-1.42283

C	-0.34413	-3.176636	-1.17249
C	1.793269	-3.592783	-2.286213
H	-3.169097	-5.131329	-1.20698
H	-2.337917	-3.022255	-0.289115
C	2.303822	-2.387009	-1.800535
H	2.429813	-4.229121	-2.910317
C	3.64226	-1.972896	-2.101141
C	1.47447	-1.548276	-0.977723
C	0.155981	-1.961645	-0.653499
C	4.136815	-0.794972	-1.621201
H	4.262015	-2.624833	-2.72486
H	5.160777	-0.488845	-1.853452
C	3.31323	0.050763	-0.820517
H	3.736051	0.994146	-0.45736
C	2.021381	-0.288096	-0.504284
Si	0.826646	0.794285	0.475992
Si	-0.827948	-0.792803	0.475022
H	-3.735606	-0.993567	-0.463741
C	-3.312435	-0.049923	-0.825794
C	-2.021104	0.289082	-0.507648
C	-3.639784	1.973838	-2.106777
C	-1.473479	1.549129	-0.980603
C	-4.134925	0.79586	-1.627545
C	-2.301653	2.38784	-1.804611
C	-0.155258	1.962256	-0.655005
H	-5.158582	0.489754	-1.861181
H	-2.425944	4.229822	-2.914805
H	-4.25888	2.625981	-2.730934
C	0.346228	3.176325	-1.174748
C	1.682559	3.630306	-0.915532
C	-0.485757	4.00596	-2.003528
H	-0.611999	5.856302	-3.145824
C	-1.790089	3.593212	-2.290276
C	2.149998	4.808503	-1.426419
H	2.340031	3.019863	-0.291648
H	3.173831	5.127123	-1.211307
C	1.314642	5.628891	-2.240204
H	1.703852	6.569644	-2.639847
C	0.036767	5.236396	-2.519136

C	1.627528	1.639651	1.944037
C	2.79035	2.862012	4.195118
C	2.725228	1.053956	2.594138
C	1.123443	2.850157	2.445977
C	1.698815	3.457265	3.561226
C	3.303239	1.658886	3.710148
H	3.139265	0.110584	2.222007
H	0.273235	3.333184	1.951938
H	1.294844	4.402169	3.936558
H	4.158716	1.188264	4.203762
H	3.243714	3.338844	5.069281
C	-1.631324	-1.63815	1.94173
C	-2.797188	-2.861647	4.190623
C	-1.126996	-2.848181	2.444613
C	-2.730809	-1.053538	2.589697
C	-3.310425	-1.659122	3.704562
C	-1.703791	-3.455766	3.558881
H	-0.275667	-3.330525	1.951833
H	-3.145109	-0.110618	2.216715
H	-4.167503	-1.189492	4.196346
H	-1.299564	-4.400212	3.935081
H	-3.251818	-3.338951	5.063867

Table S6. Cartesian coordinates of **3a** optimized by DFT calculation at ωB97X-D/def2-SV(P) level.

Atom	X	Y	Z
H	0.800644	-6.142389	-3.344309
C	0.826321	-5.214383	-2.766377
H	2.794757	-4.671564	-3.41086
C	1.925037	-4.40542	-2.802221
C	-0.286513	-3.687244	-1.243737
C	1.965404	-3.183218	-2.056202
C	-0.300641	-4.838922	-1.979152
C	0.848732	-2.806346	-1.234754
C	3.077883	-2.343379	-2.109701
H	-1.188659	-5.477173	-1.968472
H	-1.175983	-3.42903	-0.666215
C	3.102803	-1.119294	-1.441645
H	3.943399	-2.639916	-2.711551

C	4.242672	-0.259874	-1.571261
C	1.980306	-0.716805	-0.631327
C	0.883046	-1.610376	-0.47134
C	4.270631	0.963914	-0.974469
H	5.087287	-0.607744	-2.174133
H	5.140787	1.617827	-1.077821
C	3.136549	1.404076	-0.233087
H	3.164258	2.411733	0.197045
C	2.02271	0.620616	-0.055758
Si	-0.493576	-1.288632	0.80468
Si	0.494974	1.288304	0.805204
H	-3.163598	-2.410856	0.197191
C	-3.135541	-1.403215	-0.232982
C	-2.021226	-0.6203	-0.056137
C	-4.241406	0.261378	-1.570667
C	-1.978622	0.71718	-0.631429
C	-4.269707	-0.962449	-0.973957
C	-3.101175	1.120361	-1.441311
C	-0.88106	1.610232	-0.47142
H	-5.140079	-1.616062	-1.077307
H	-3.941364	2.641538	-2.710855
H	-5.085953	0.609483	-2.17348
C	-0.846273	2.806185	-1.23484
C	0.289705	3.686	-1.244195
C	-1.962883	3.183785	-2.056068
H	-2.791305	4.672729	-3.410706
C	-3.075887	2.344563	-2.109161
C	0.304696	4.837618	-1.979613
H	1.179444	3.426514	-0.667648
H	1.193265	5.475111	-1.969372
C	-0.822233	5.213927	-2.766455
H	-0.795943	6.14184	-3.344519
C	-1.921756	4.40598	-2.802062
O	0.000692	-0.000363	1.740703
C	0.834945	2.740494	1.932332
C	1.331542	4.817897	3.764015
C	1.967397	2.714431	2.762928
C	-0.048057	3.824849	2.04743
C	0.196264	4.85542	2.95423

C	2.216893	3.743985	3.669773
H	2.666294	1.873012	2.706721
H	-0.942741	3.869912	1.418331
H	-0.503793	5.692607	3.028981
H	3.104851	3.706698	4.307767
H	1.52523	5.627132	4.474529
C	-0.836653	-2.740773	1.930936
C	-1.338814	-4.818598	3.760422
C	0.040982	-3.830049	2.041517
C	-1.966542	-2.709994	2.764851
C	-2.218647	-3.739664	3.670814
C	-0.206245	-4.860995	2.94708
H	0.933339	-3.878663	1.409229
H	-2.660978	-1.864663	2.712086
H	-3.104294	-3.698614	4.311774
H	0.48919	-5.702354	3.017888
H	-1.534784	-5.628007	4.470116

6. NMR spectra

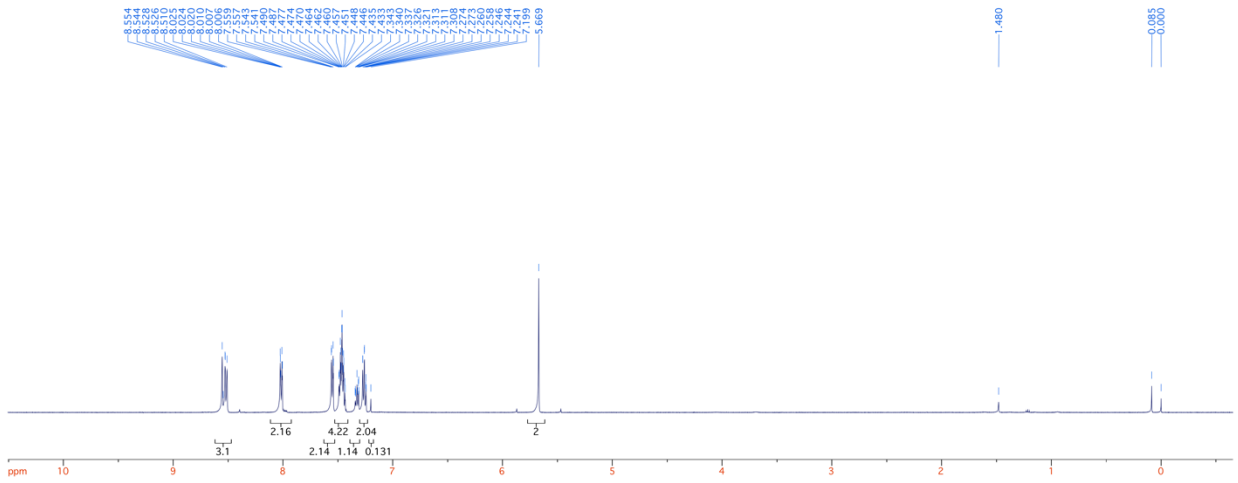


Figure S9. ^{1}H NMR spectrum of **1a**.

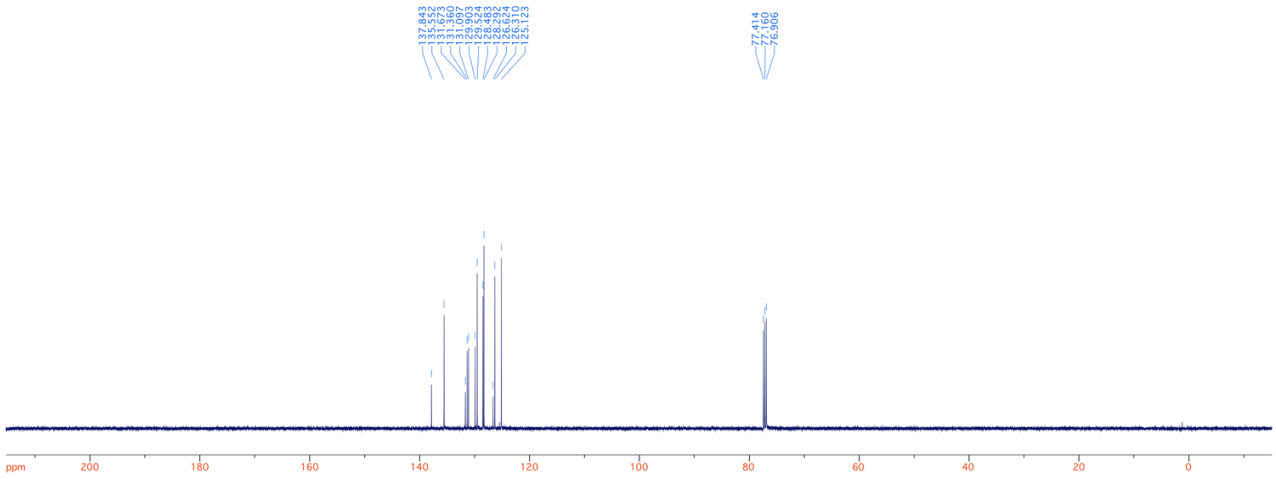


Figure S10. ^{13}C NMR spectrum of **1a**.

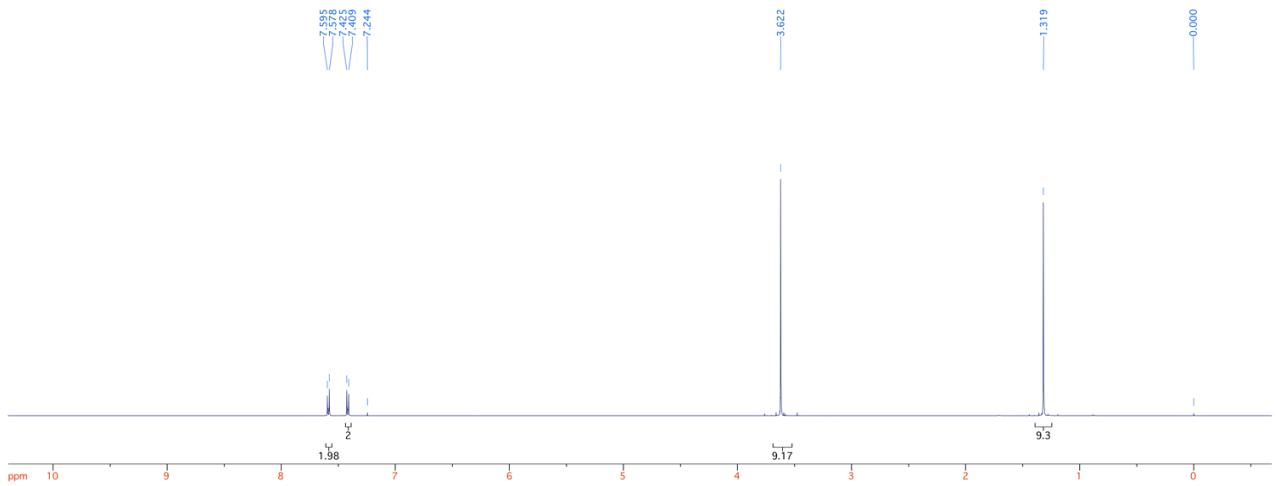


Figure S11. ^{1}H NMR spectrum of (4-*tert*-butylphenyl)trimethoxysilane.

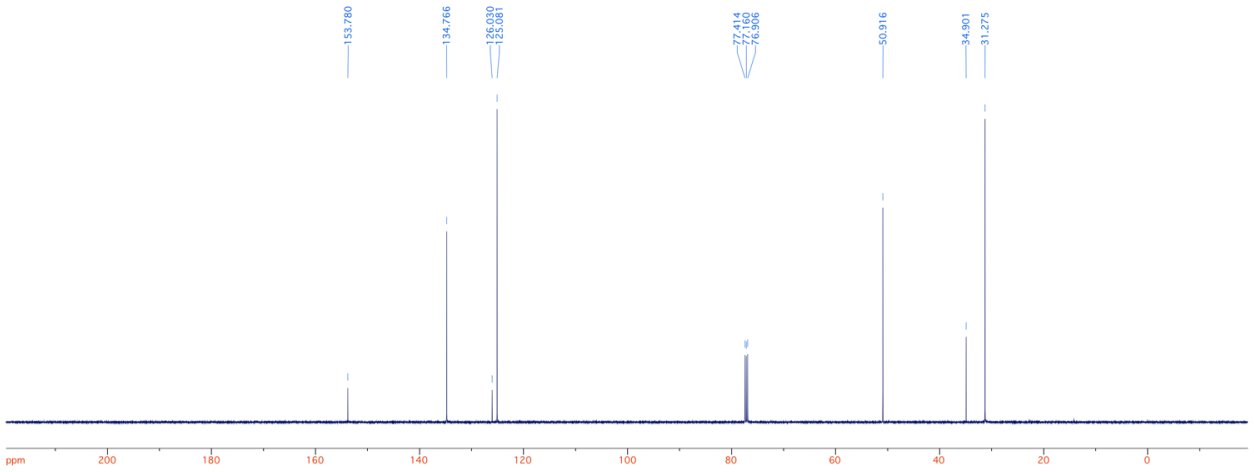


Figure S12. ^{13}C NMR spectrum of (4-*tert*-butylphenyl)trimethoxysilane.

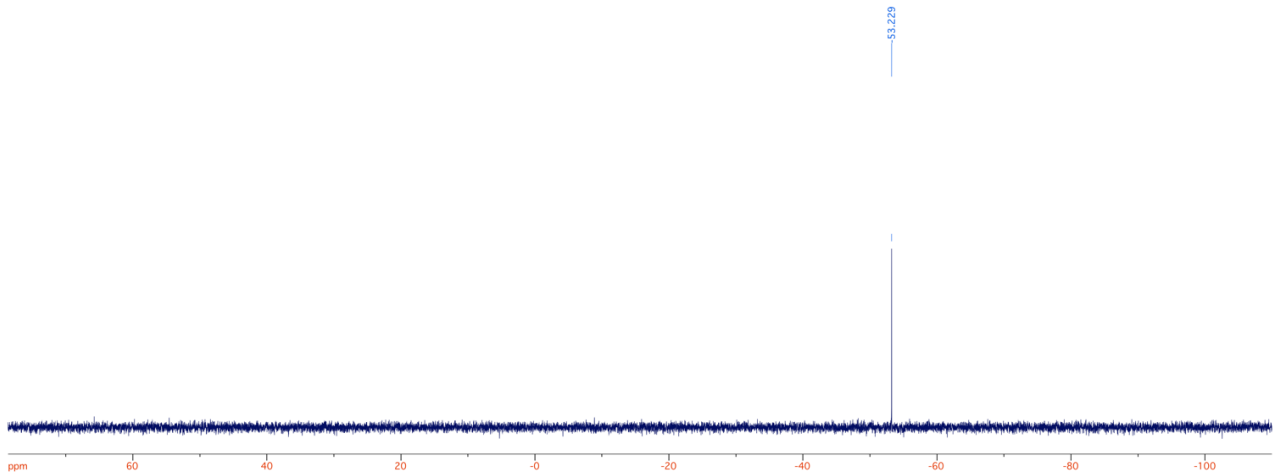


Figure S13. ^{29}SiNMR spectrum of (4-*tert*-butylphenyl)trimethoxysilane.

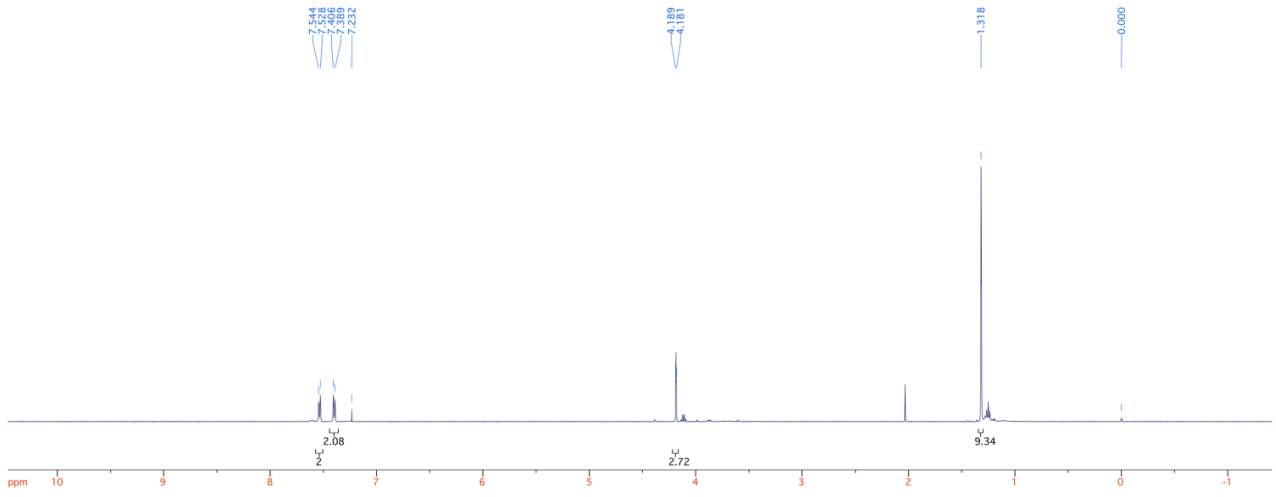


Figure S14. ^{1}H NMR spectrum of (4-*tert*-butylphenyl)silane.

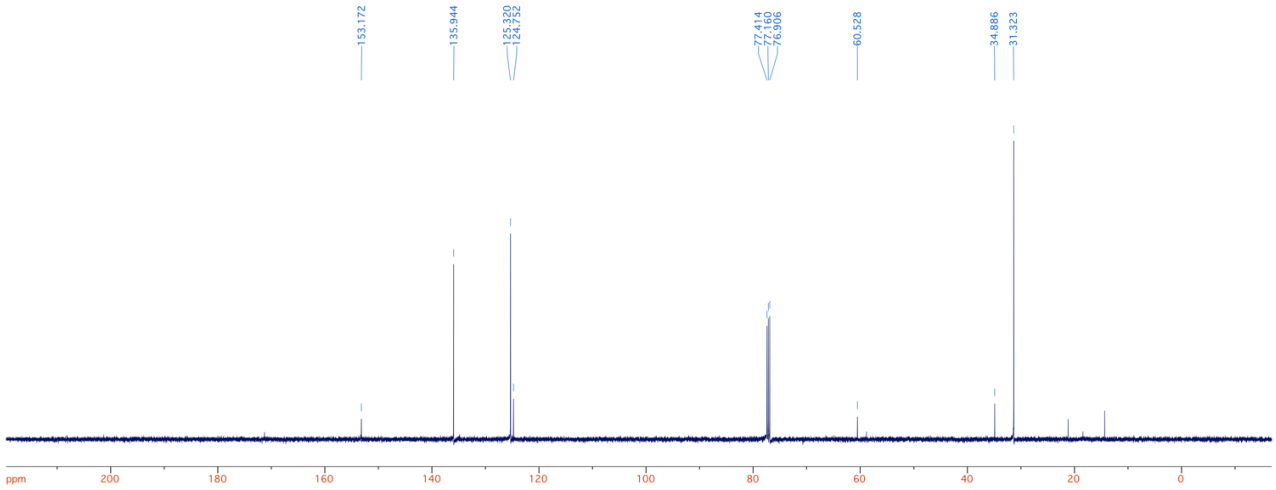


Figure S15. ^{13}C NMR spectrum of (4-*tert*-butylphenyl)silane.

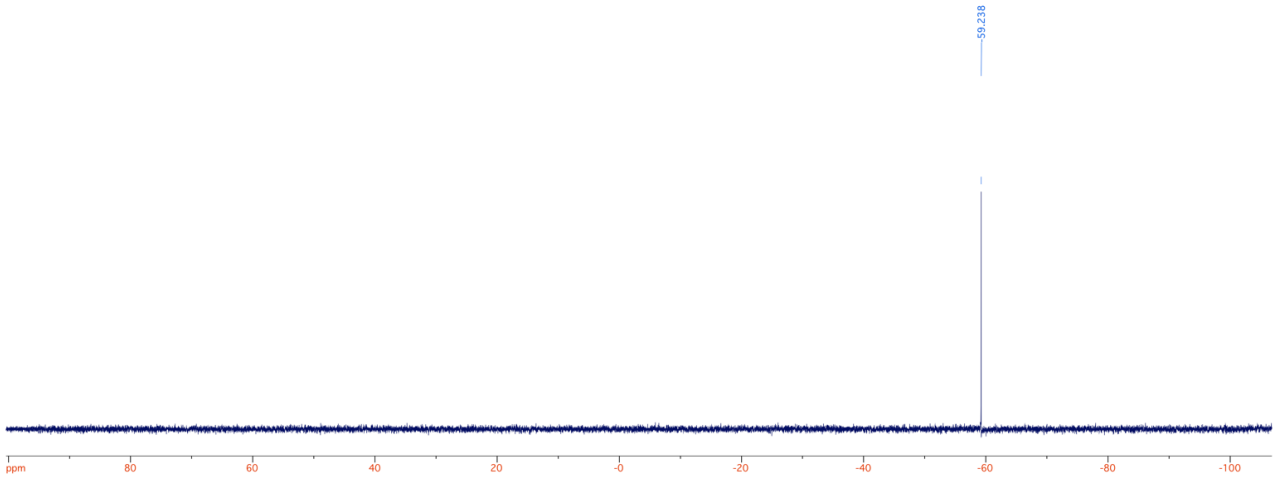


Figure S16. ^{29}Si NMR spectrum of (4-*tert*-butylphenyl)silane.

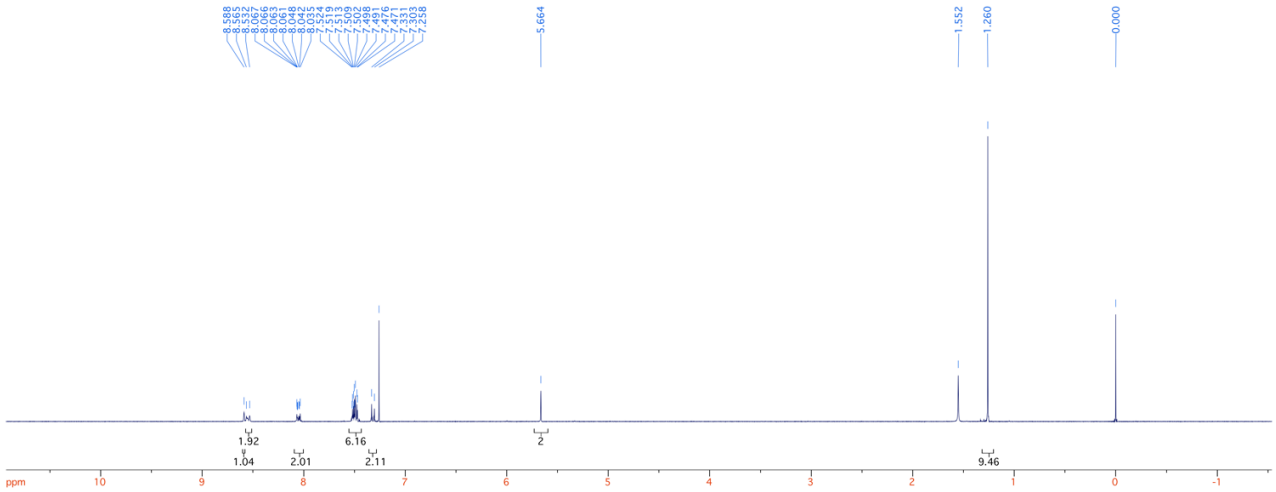


Figure S17. ^{1}H NMR spectrum of **1b**.

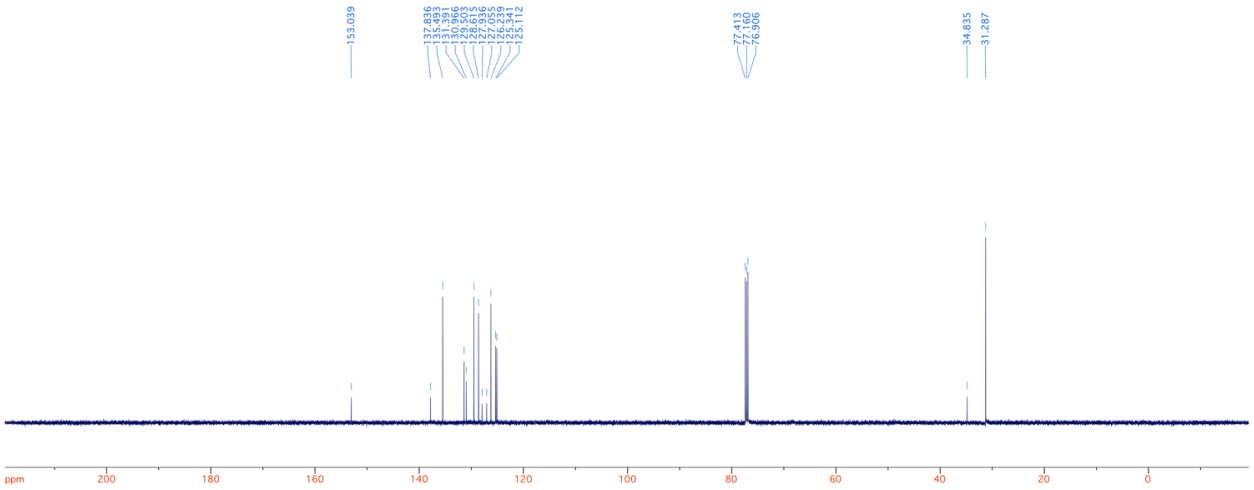


Figure S18. ^{13}C NMR spectrum of **1b**.

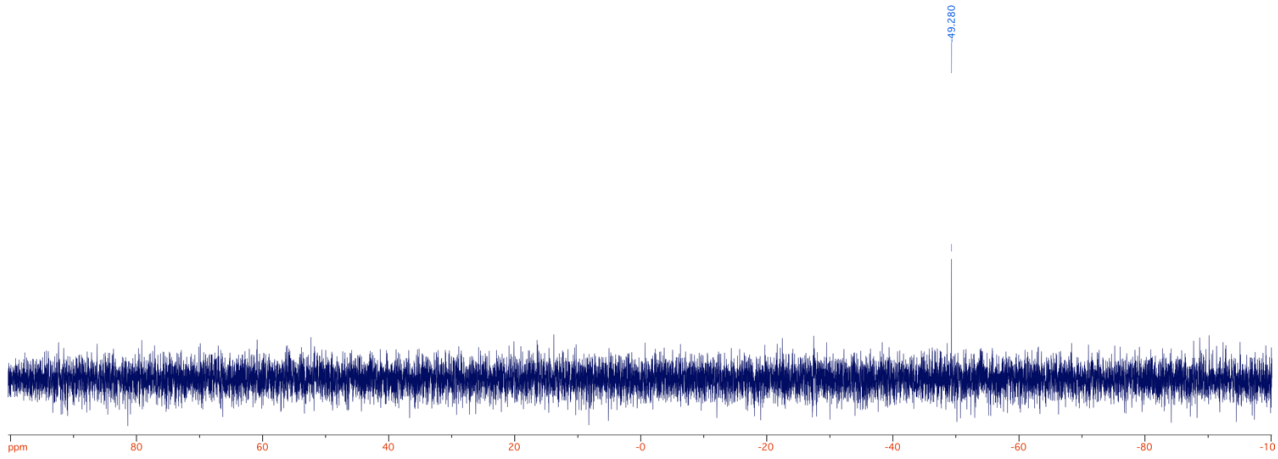


Figure S19. ^{29}Si NMR spectrum of **1b**.

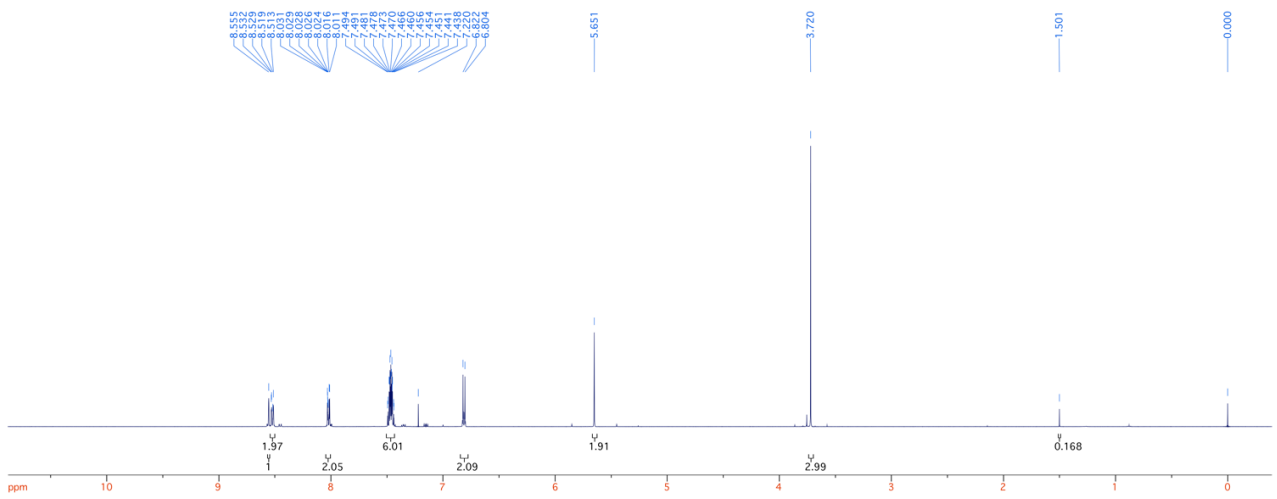


Figure S20. ^{1}H NMR spectrum of **1c**.

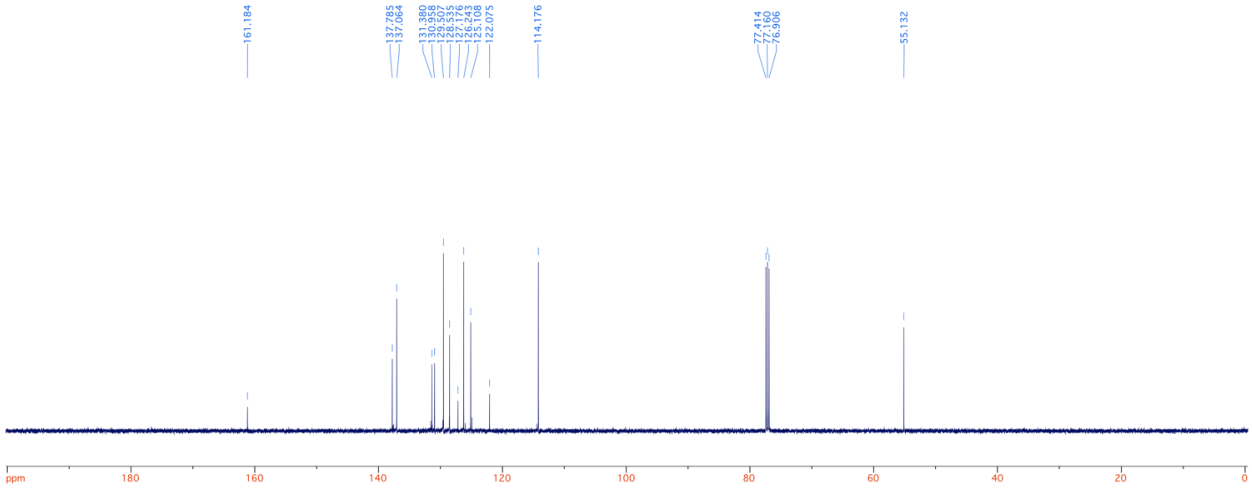


Figure S21. ^{13}C NMR spectrum of **1c**.

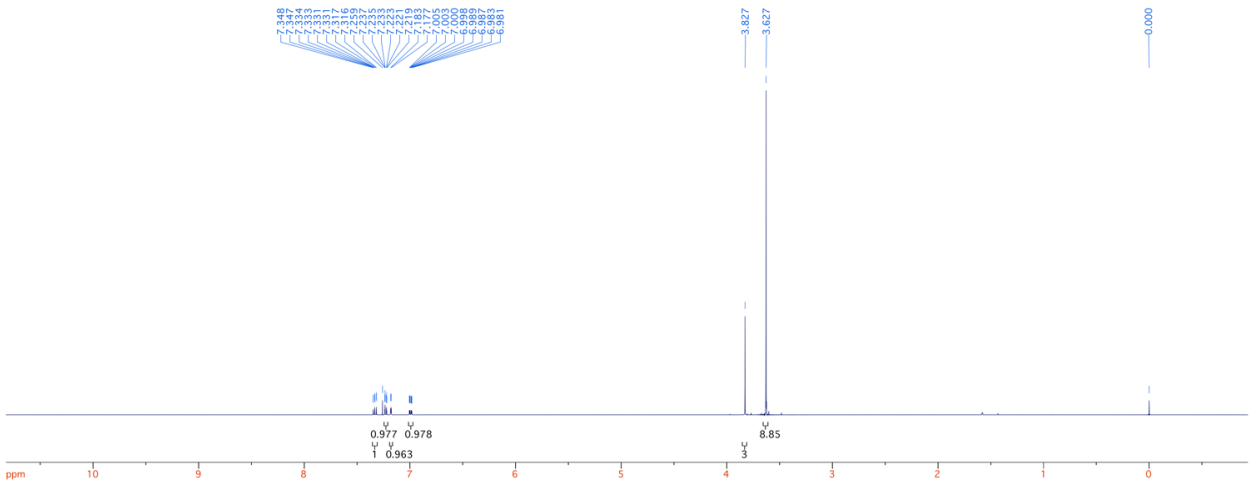


Figure S22. ^{1}H NMR spectrum of (3-methoxyphenyl)trimethoxysilane.

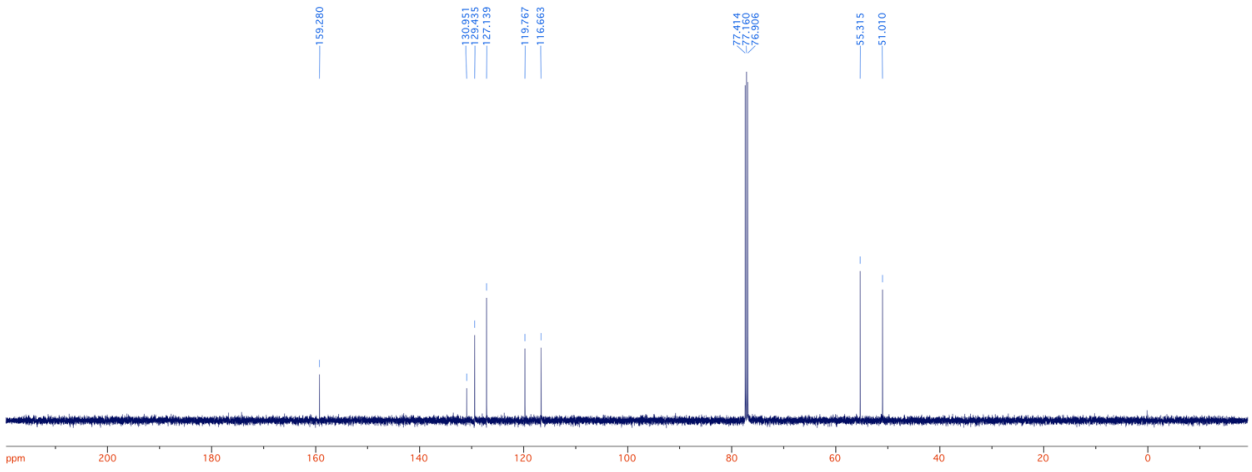


Figure S23. ^{13}C NMR spectrum of (3-methoxyphenyl)trimethoxysilane.

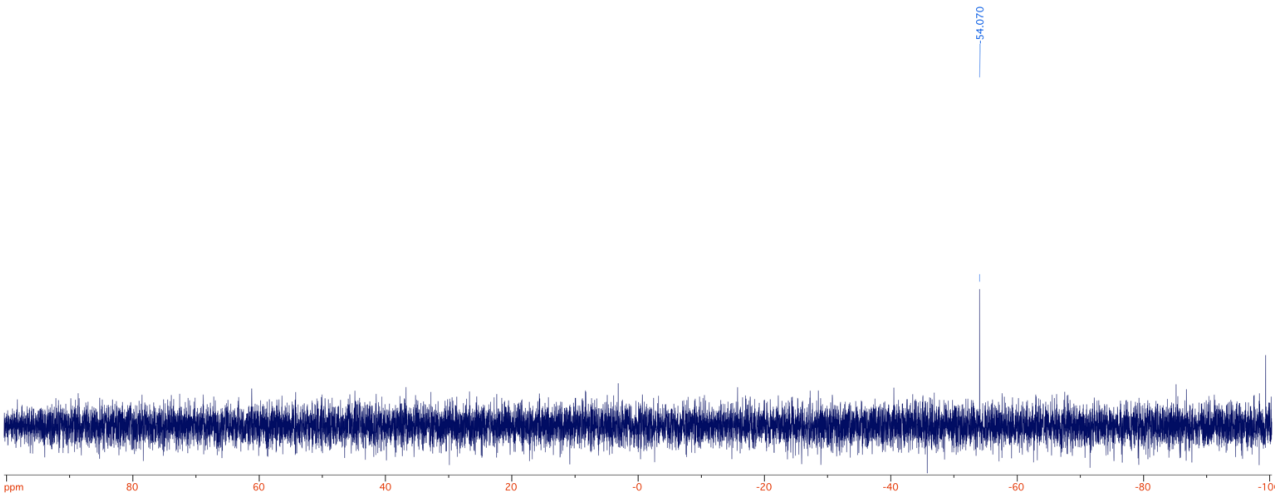


Figure S24. ^{29}SI NMR spectrum of (3-methoxyphenyl)trimethoxysilane.

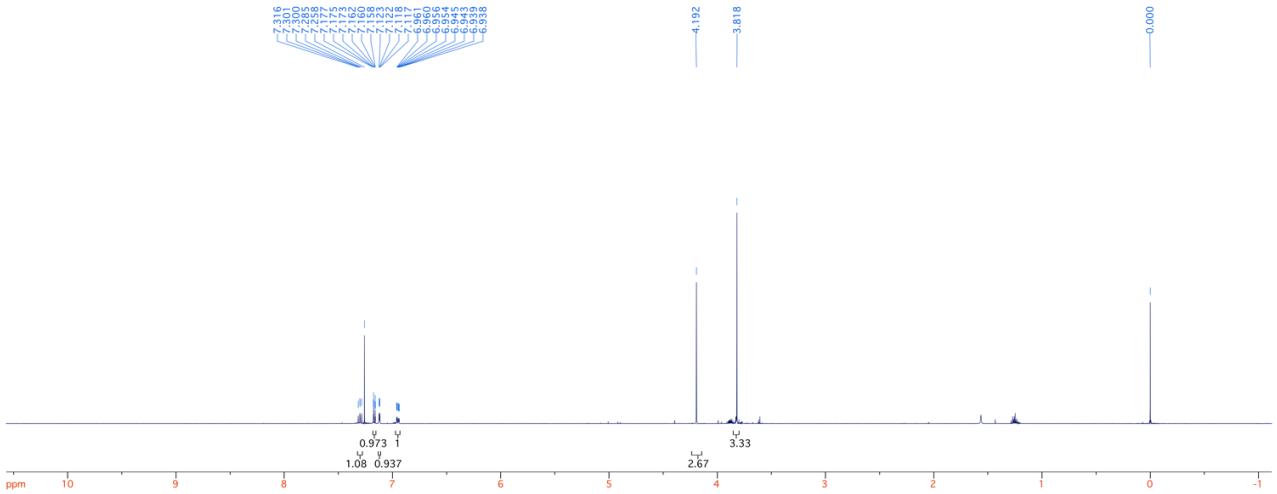


Figure S25. ^{1}H NMR spectrum of (3-methoxyphenyl)silane.

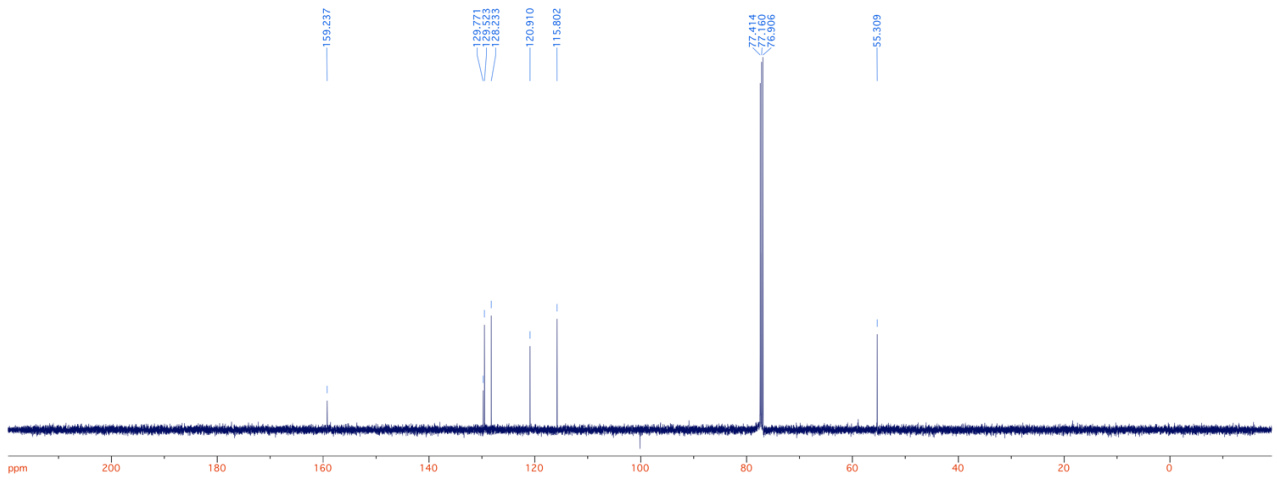


Figure S26. ^{13}C NMR spectrum of (3-methoxyphenyl)silane.

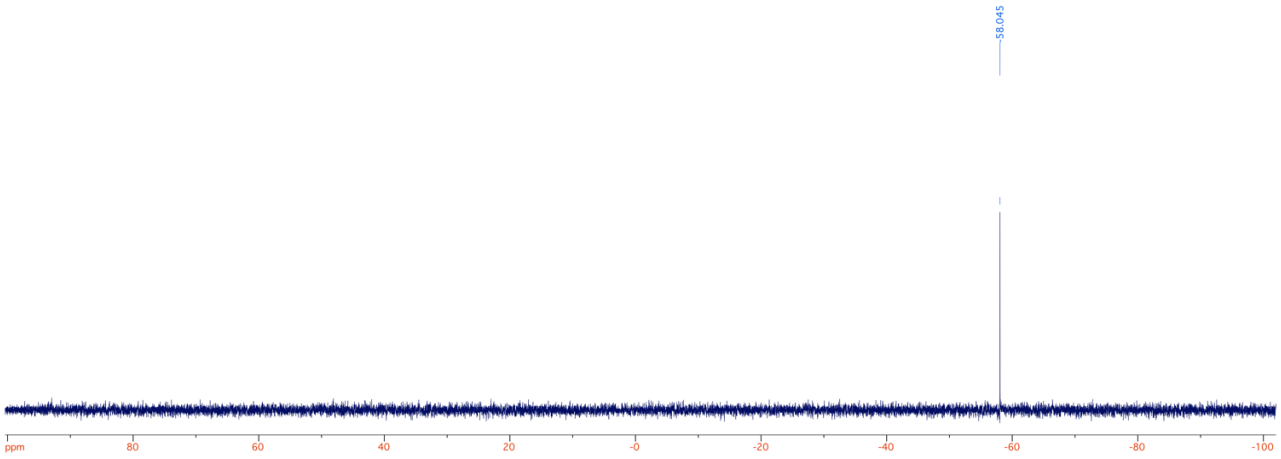


Figure S27. ^{29}Si NMR spectrum of (3-methoxyphenyl)silane.

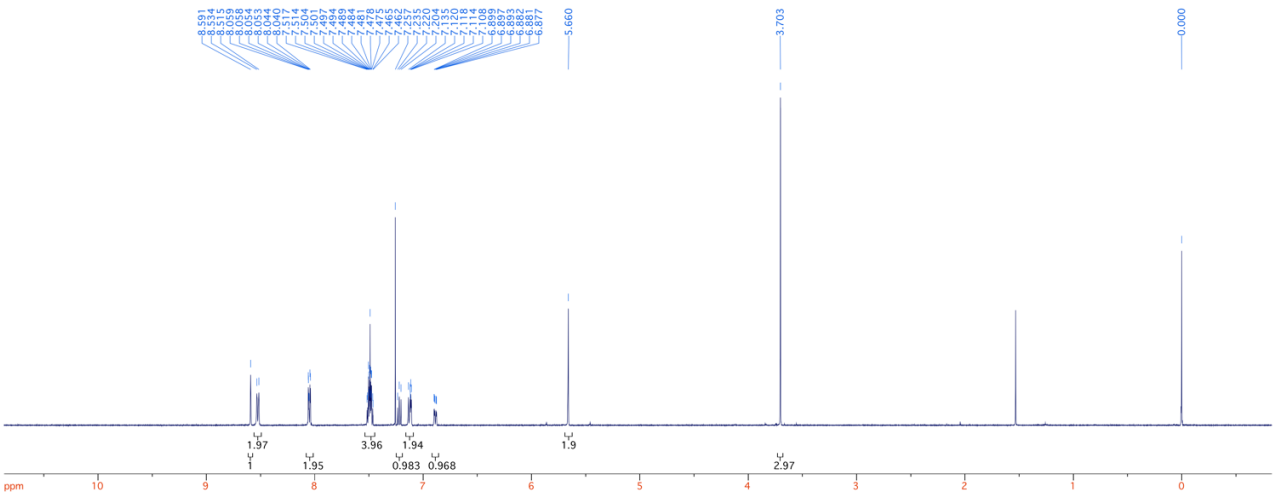


Figure S28. ^{1}H NMR spectrum of **1d**.

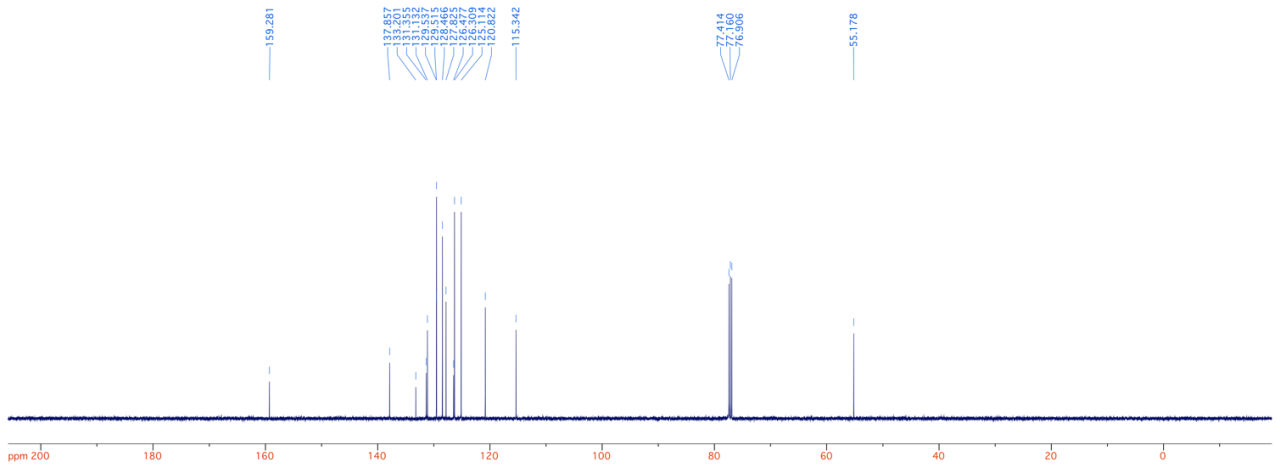


Figure S29. ^{13}C NMR spectrum of **1d**.

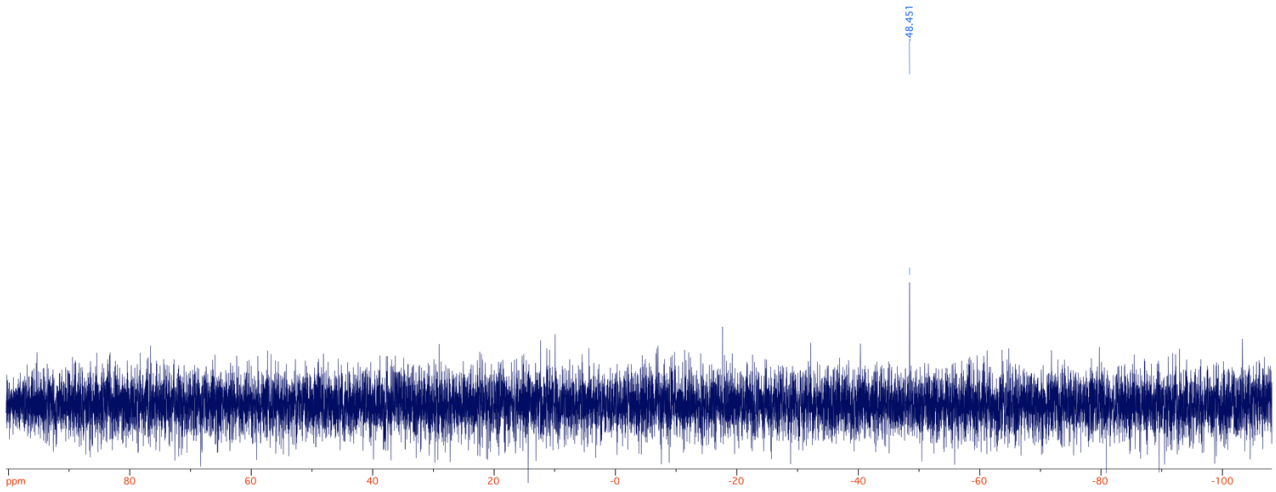


Figure S30. ^{29}Si NMR spectrum of **1d**.

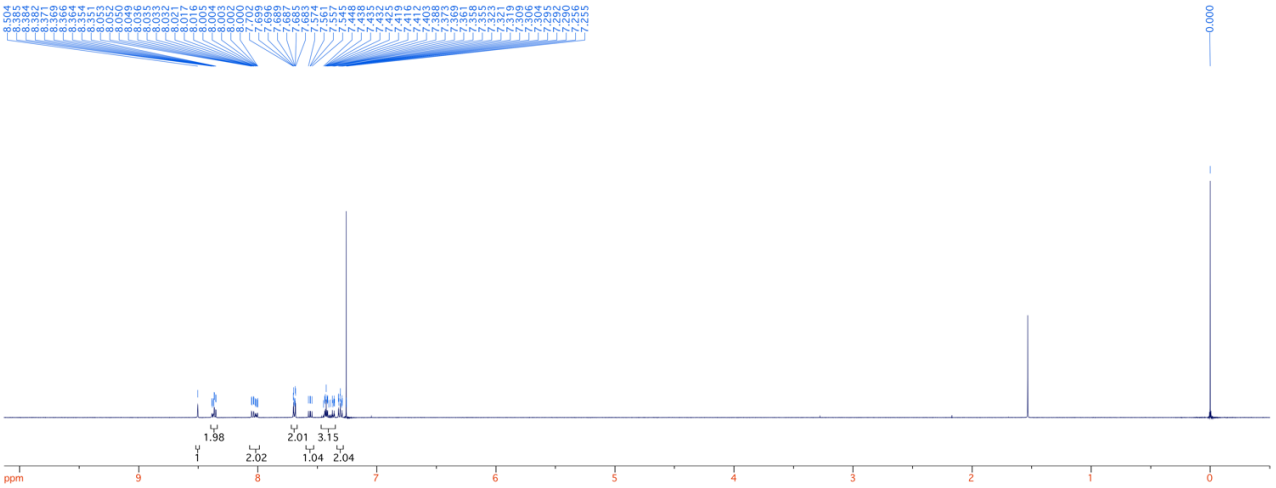


Figure S31. ^{1}H NMR spectrum of **2a**.

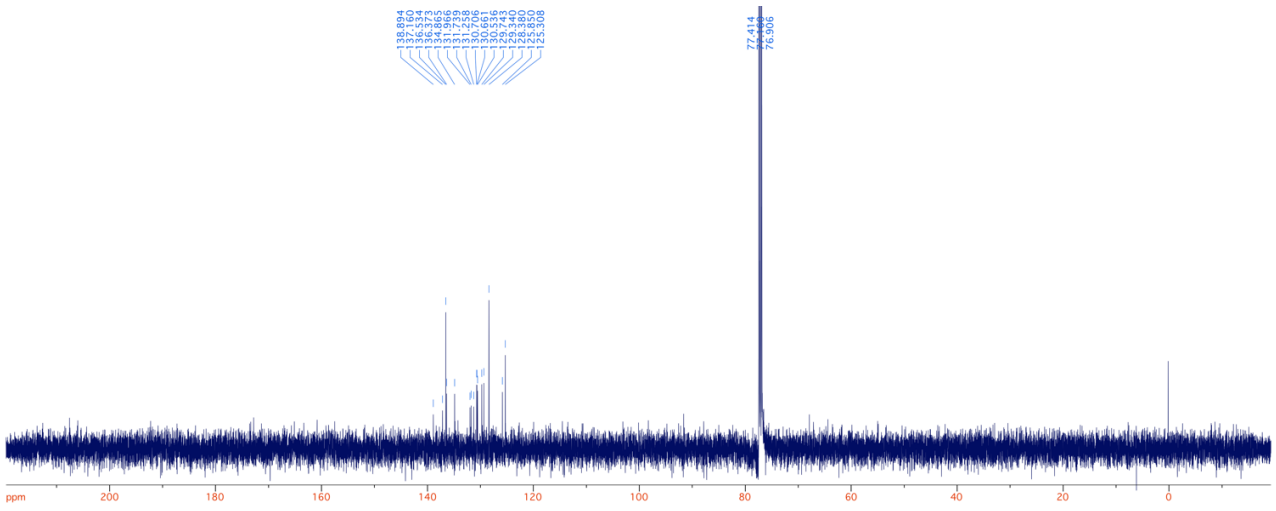


Figure S32. ^{13}C NMR spectrum of **2a**.

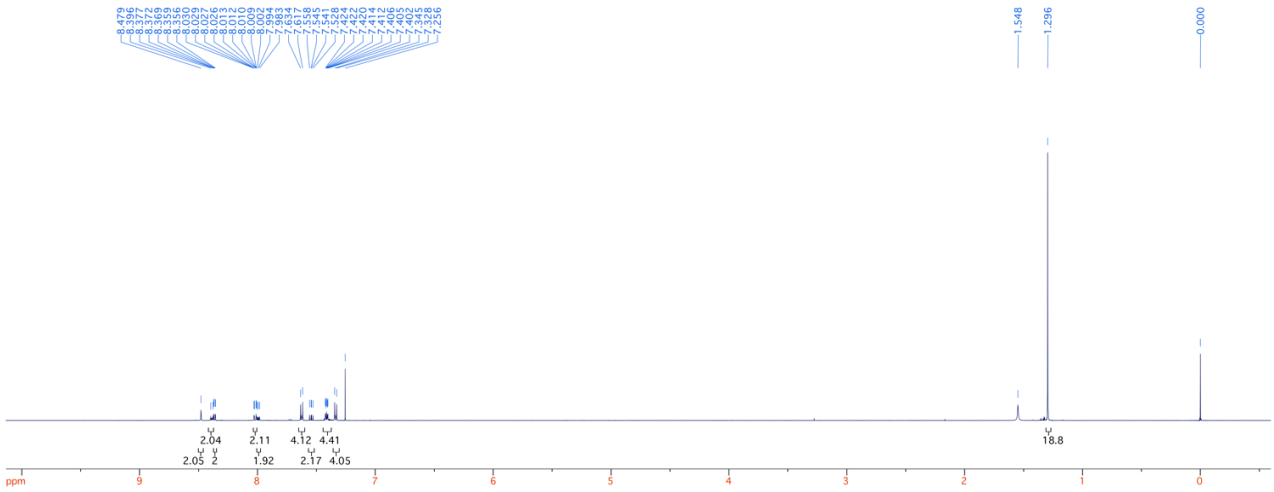


Figure S33. ^{1}H NMR spectrum of **2b**.

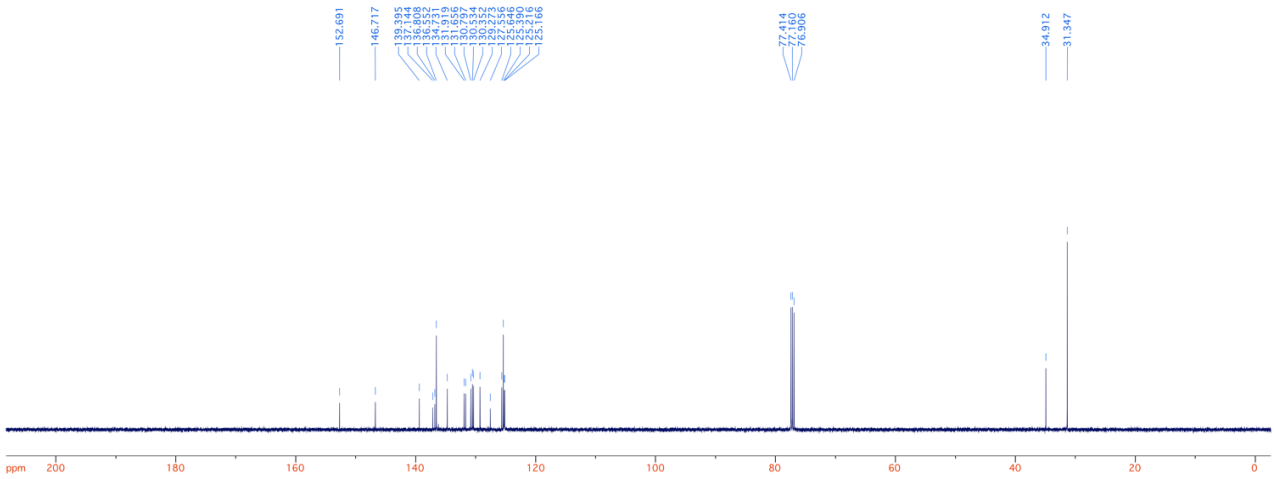


Figure S34. ^{13}C NMR spectrum of **2b**.

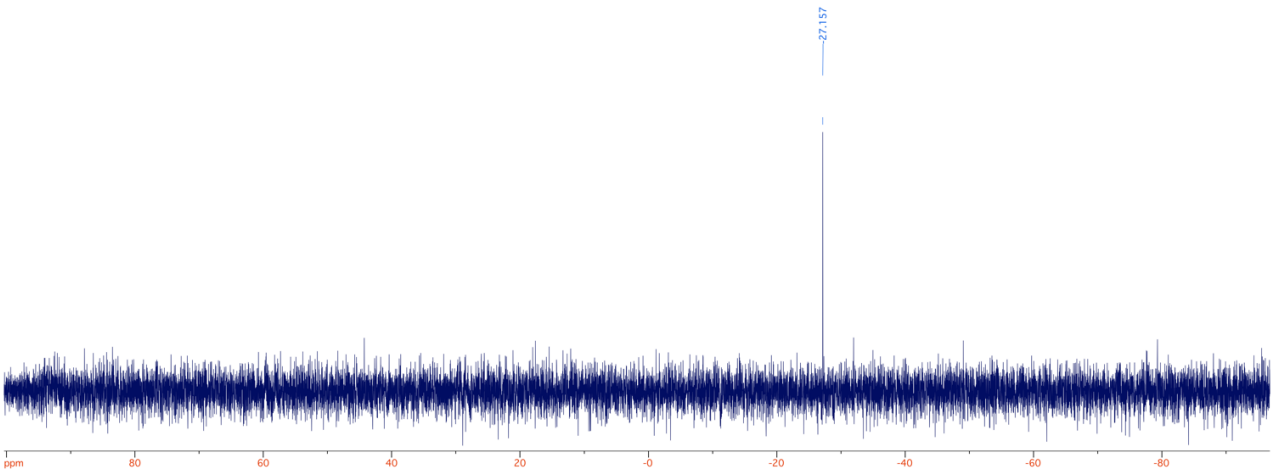


Figure S35. ^{29}Si NMR spectrum of **2b**.

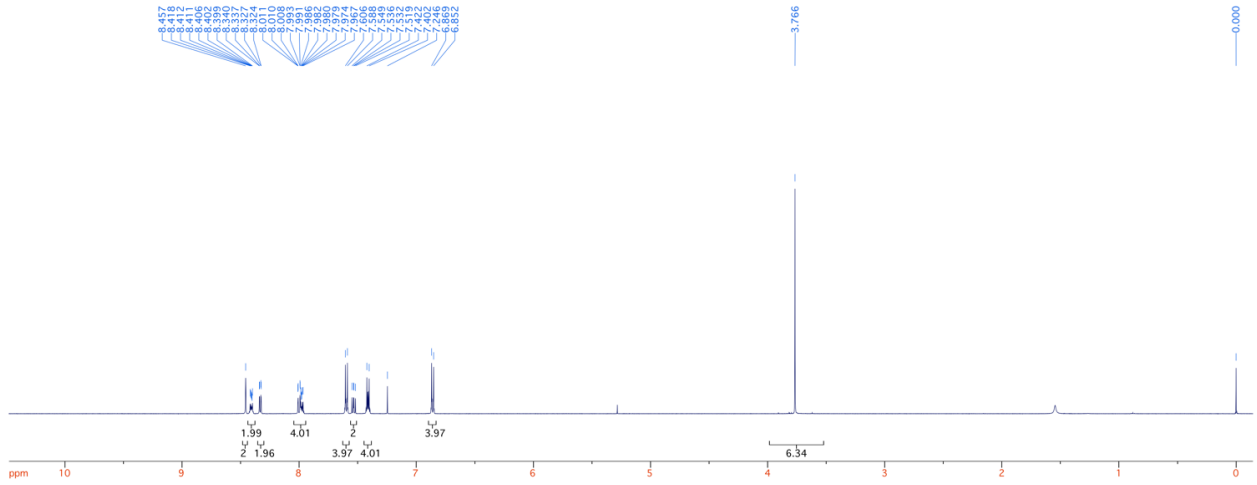


Figure S36. ^{1}H NMR spectrum of **2c**.

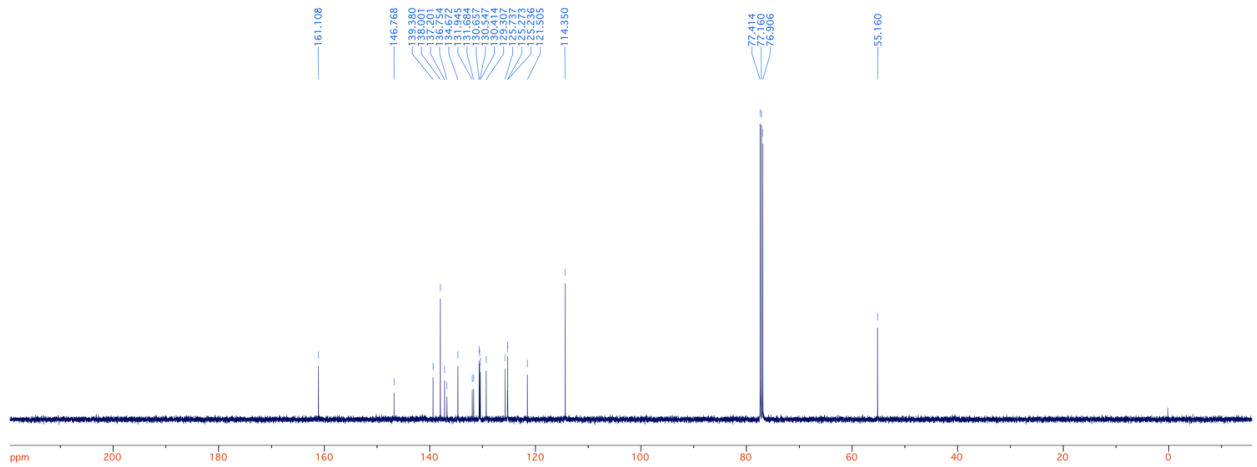


Figure S37. ^{13}C NMR spectrum of **2c**.

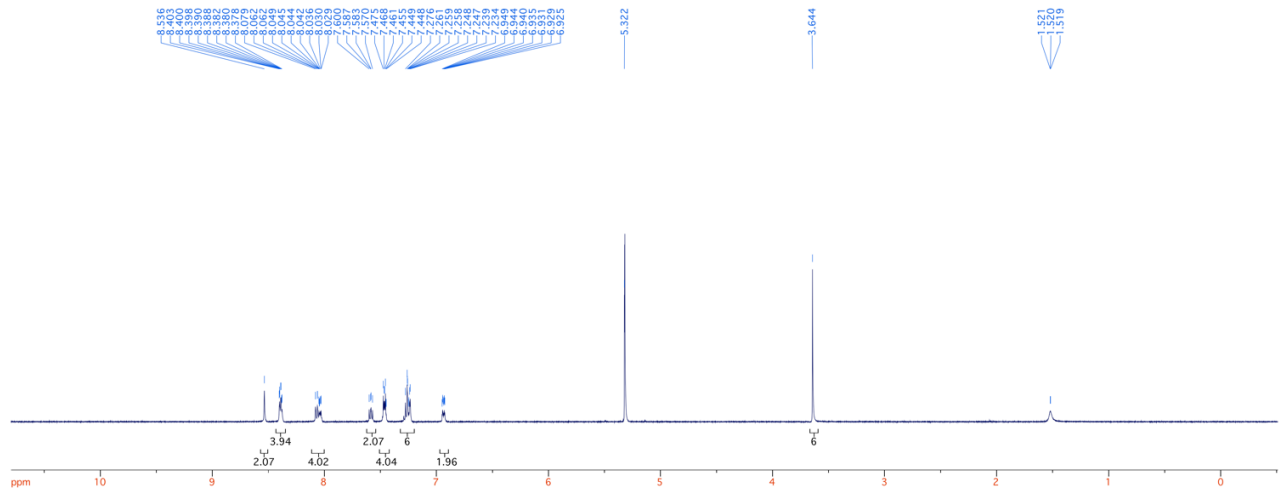


Figure S38. ^{1}H NMR spectrum of **2d**.

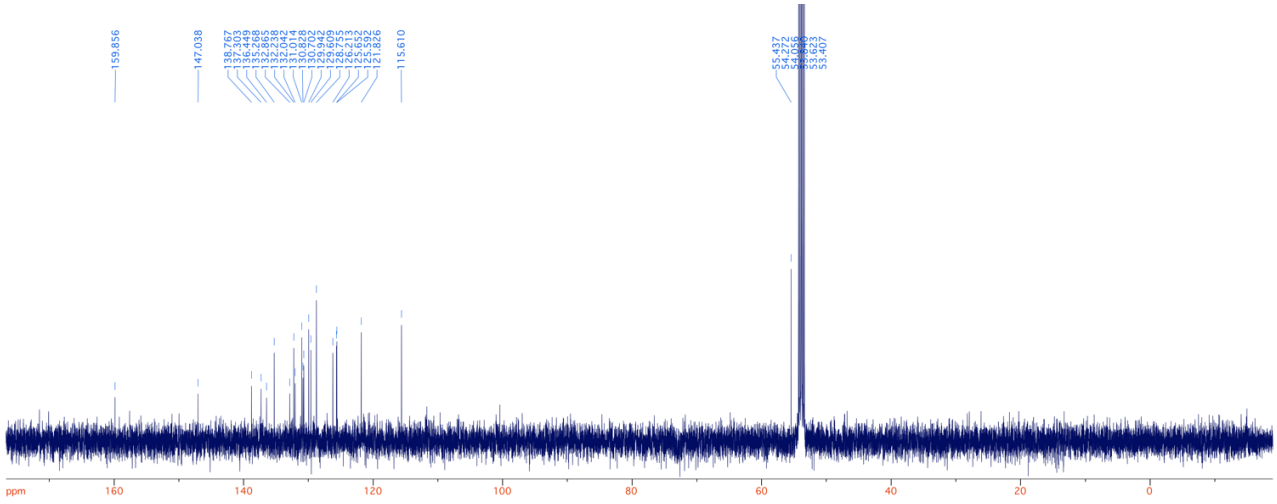


Figure S39. ^{13}C NMR spectrum of **2d**.

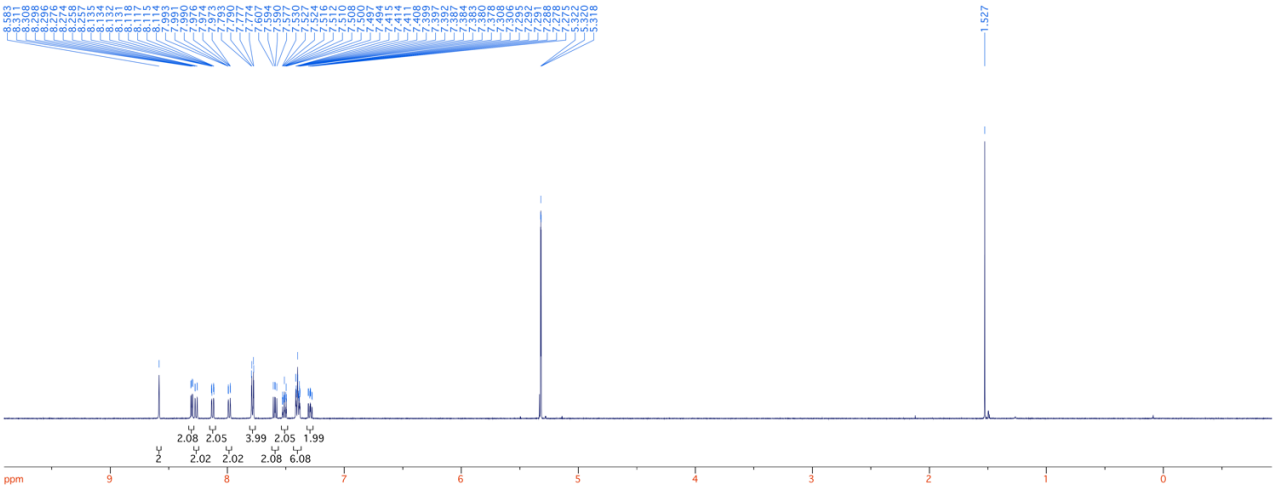


Figure S40. ^{1}H NMR spectrum of **3a**.

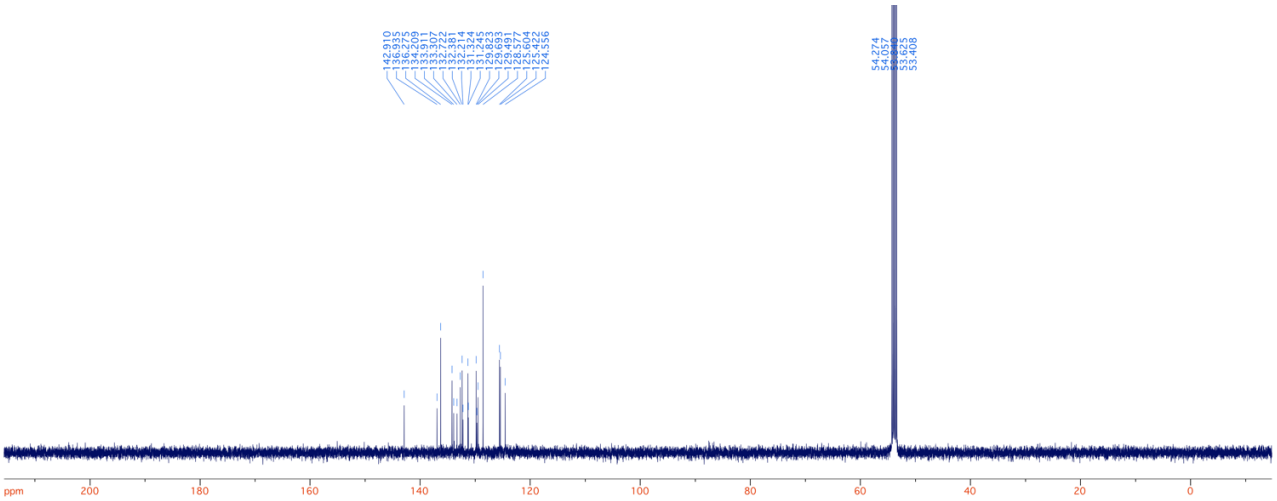


Figure S41. ^{13}C NMR spectrum of **3a**.