Supporting Information

Highly Efficient Synthesis of Polyfluorinated Dendrons Suitable for Click Chemistry

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1. General Information

All reactions were carried out under stirring. Reactions under inert gas were carried out in flasks equipped with septa under argon (supplied by using a standard manifold with vacuum and argon lines). Analytical TLC was performed on MERCK ready-to-use plates with silica gel 60 (F254). Column chromatography: MERCK silica gel 60, 0.04–0.063 mm. IR spectra were recorded by using FT-IR Bruker ALPHA-T spectrometer. The samples were measured by using the attenuated total reflexion (ATR) technique. The transmission intensities of the bands were characterized as follows: s = strong (11–40%), m = medium (41–70%), w = weak (71–90%), vw = very weak (91–100%) transmission. NMR spectra were recorded at 25 °C by using Bruker AM 400 (400 (^{1}H), 376.5 (^{19}F) and 100 MHz (^{13}C)) and Bruker DRX 500 (500 (^{1}H) and 125 MHz (^{13}C)) spectrometer. All spectra are referenced to tetramethylsilane as standard ($\delta = 0$ ppm) by using the signals of the solvent:

$CDCl_3$: 7.26 ppm ($CHCl_3$) or 77.16 ppm ($^{13}CDCl_3$)

The spectra were analyzed according to first order. Multiplicities of the signals are described as follows: s = singlet, d= doublet, m = multiplet, m_c = centered multiplet. Coupling constants (*J*) are given in Hz. Multiplicities in the ^{13}C NMR spectra were determined by DEPT (distortionless enhancement by polarization transfer) measurements and are described as follows: + = primary or tertiary C-atom, – = secondary C-atom, and C_q = quaternary C-atom. Mass spectra (EI) were obtained by using a Finnigan MAT 90 spectrometer. MALDI-TOF mass spectra were obtained by using a Bruker Biflex IV spectrometer with a pulsed ultraviolet nitrogen laser, 200 µJ at 337 nm and a time-of-flight mass analyzer with a 125 cm linear flight path. A 1:1 mixture of 2,5-dihydroxybenzoic acid and α-cyano-4-hydroxycinnamic acid (dissolved in H_2O/acetonitrile (1:1) with 0.1% TFA) was used as matrix. Reversed phase preparative HPLC was performed using Jasko LC-NetII/ADC Series, equipped with a C18 Vydac 218TP Series (Grace Davison Discovery Sciences, 5 µm, 22 × 250 mm). Flow rate: 15 mL/min; solvent A: 0.1% TFA in water; solvent B: 0.1% TFA in acetonitrile.

2. Experimental Procedures and Characterization

General procedure 1: Sonogashira coupling with trimethylsilylacetylene

Trimethylsilylacetylene (2.00 equiv.) was added to a solution of the respective iodide (**1**-$OC(CF_3)_3$, **3** or **5**, 1.00 equiv.), $Pd(PPh_3)_2Cl_2$ (0.05 equiv.), and CuI (0.10 equiv.) in dry NEt_3/THF (2:1) under argon atmosphere. The mixture was stirred at 45 °C (4 h to overnight). Afterwards a saturated solution of aqueous NH_4Cl was added and the product was extracted with dichloromethane. The combined organic layers were dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude product was purified by using column chromatography.

General Procedure 2: Deprotection of trimethylsilylalkynes

K_2CO_3 (1.30 equiv.) was added to a solution of the respective trimethylsilylalkyne (**2**-$SiMe_3$, **4**-$SiMe_3$, or **6**-$SiMe_3$, 1 equiv.) in dry methanol. The suspension was stirred for 1.5 d at room temperature. Afterwards H_2O was added and the product was collected by filtration, washed with methanol and dried under vacuum.

General Procedure 3: Copper(I)-catalyzed azide-alkyne cycloaddition

1,3-Bis(azidomethyl)-5-iodobenzene (**1**-N_3, 1.00 equiv., 30% in DMF) was added to a solution of the respective alkyne (**2**-H or **4**-H, 2.20 equiv.), $Cu(CH_3CN)_4PF_6$ (0.20 equiv.) and 2,6-lutidine (0.20 equiv.) in dry THF under argon atmosphere. The mixture was stirred for 2 d at 40 °C. Afterwards a half-saturated solution of aqueous NH_4Cl was added and the product was extracted with dichloromethane. The combined organic layers were dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude product was purified by using column chromatography.

1,3-Bis(bromomethyl)-5-iodobenzene (1-Br):

The preparation and properties of compound **1**-Br have been reported in reference 1.

1,3-Bis(azidomethyl)-5-iodobenzene (1-N_3):

The preparation and properties of compound 1-N3 have been reported in reference 1.

1-Iodo-3,5-bis((perfluoro-*tert*-butoxy)methyl)benzene (1-$OC(CF_3)_3$):

Sodium perfluoro-*tert*-butanolate (2.76 g, 10.7 mmol) was added to a solution of 1,3-bis(bromomethyl)-5-iodobenzene (**1**-Br) (1.90 g, 4.87 mmol) in dry DMF (7.4 mL). The mixture was stirred for 18 h at room temperature. Subsequently, the product was precipitated by adding H_2O (25 mL). The precipitate was collected by filtration and washed with H_2O (25 mL). The crude product was purified via column chromatography (cyclohexane/EtOAc 12:1) to yield iodide **1**-$OC(CF_3)_3$ (2.99 g, 88%) as a white solid.

m.p. 108 °C; $R_f = 0.72$ (cyclohexane/EtOAc 12:1); IR (ATR): $\tilde{\nu} = 1574$ (w), 1451 (vw), 1396 (vw), 1243 (s), 1181 (m), 1131 (s), 1011 (m), 968 (s), 867 (m), 827 (vw), 770 (w), 736 (m), 725 (s), 659 (w), 598 (w), 570 (w), 538 (m), 512 (w), 490 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 5.00$ (s, 4 H, CH_2), 7.32 (s, 1 H, CH_{ar}), 7.66 (s, 2 H, CH_{ar}) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 69.9$ (–, CH_2), 80.1 (C_q, decet, $^2J_{C,F} = 30$ Hz, $C(CF_3)_3$), 94.4 (C_q, C_{ar}), 120.5 (C_q, q, $^1J_{C,F} = 293$ Hz, CF_3), 125.8 (+, CH_{ar}), 136.7 (+, CH_{ar}), 137.6 (C_q, C_{ar}) ppm; ^{19}F NMR (376.5 MHz, $CDCl_3$): $\delta = -70.1$ (s, CF_3) ppm; EI MS: m/z (%): 700 (94) $[M]^+$, 681 (13) $[M–F]^+$, 573 (80) $[M–I]^+$, 465 (100) $[M–C_4F_9O]^+$; HRMS: m/z calcd. for $C_{16}H_7F_{18}IO_2$: 699.9203; found: 669.9201.

((3,5-Bis((perfluoro-*tert*-butoxy)methyl)phenyl)ethynyl)trimethylsilane (2-$SiMe_3$):

After purification (chromatography with cyclohexane as eluent) trimethylsilylalkyne **2**-$SiMe_3$ (2.47 g, 89%) was obtained as white solid from iodide **1**-$OC(CF_3)_3$ (2.90 g, 4.14 mmol) after stirring for 4 h according to general procedure 1 by using 29 mL dry NEt_3, 14.5 mL dry THF, 30 mL NH_4Cl solution and 3 × 60 mL CH_2Cl_2 for the extraction.

m.p. 151 °C; $R_f = 0.39$ (cyclohexane); IR (ATR): $\tilde{\nu} = 2971$ (vw), 2155 (vw), 1603 (vw), 1459 (vw), 1396 (vw), 1248 (m), 1180 (w), 1136 (m), 1006 (w), 970 (m), 929 (w), 907 (vw), 875 (w), 842 (m), 779 (vw), 760 (w), 736 (w), 725 (w), 670 (w), 627 (vw), 538 (w), 496 (w), 416 (vw) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.26$ (s, 9 H, $Si(CH_3)_3$), 5.01 (s, 4 H, CH_2), 7.31 (s, 1 H, CH_{ar}), 7.41 (d, $^4J_{H,H} = 1.2$ Hz, 2 H, CH_{ar}) ppm; ^{13}C NMR

(100 MHz, $CDCl_3$): $\delta = 0.0$ (+, $Si(CH_3)_3$), 70.5 (–, CH_2), 79.9 (C_q, decet, $^2J_{C,F} = 30$ Hz, $C(CF_3)_3$), 96.0 (C_q, C≡C), 103.7 (C_q, C≡C), 120.5 (C_q, q, $^1J_{C,F} = 295$ Hz, CF_3), 124.3 (C_q, C_{ar}), 126.7 (+, CH_{ar}), 131.4 (+, CH_{ar}), 135.8 (C_q, C_{ar}) ppm; ^{19}F NMR (376.5 MHz, $CDCl_3$): $\delta = -70.1$ (s, CF_3) ppm; EI MS: *m*/*z* (%): 670 (97) $[M]^+$, 655 (100) $[M-CH_3]^+$, 439 (100) $[M-C_5H_3F_8O]^+$, 435 (54) $[M-C_4F_9O]$+; HRMS: *m*/*z* calcd. for $C_{21}H_{16}F_{18}O_2Si$: 670.0632; found: 670.0630.

1-Ethynyl-3,5-bis((perfluoro-*tert*-butoxy)methyl)benzene (2-H):

Alkyne **2**-H (2.17 g, >99%) was obtained as white solid from trimethylsilylalkyne **2**-$SiMe_3$ (2.46 g, 3.66 mmol) according to general procedure 2 by using 90 mL dry methanol as solvent.

m.p. 119 °C; IR (ATR): $\tilde{\nu}$ = 3316 (w), 1386 (vw), 1244 (m), 1182 (w), 1137 (m), 1001 (m), 969 (m), 907 (vw), 876 (w), 805 (vw), 771 (vw), 736 (w), 725 (m), 650 (w), 627 (w), 538 (w), 495 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 3.13$ (s, 1 H, C≡CH), 5.03 (s, 4 H, CH_2), 7.33 (s, 1 H, CH_{ar}), 7.44 (s, 2 H, CH_{ar}) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 70.4$ (–, CH_2), 78.6 (C_q, C≡C), 80.1 (C_q, decet, $^2J_{C,F} = 30$ Hz, $C(CF_3)_3$), 82.5 (C_q, C≡C), 120.5 (C_q, q, $^1J_{C,F} = 293$ Hz, CF_3), 123.4 (C_q, C_{ar}), 126.8 (+, CH_{ar}), 131.4 (+, CH_{ar}), 136.0 (C_q, C_{ar}) ppm; ^{19}F NMR (376.5 MHz, $CDCl_3$): $\delta = -70.1$ (s, CF_3) ppm; EI MS: *m*/*z* (%): 598 (100) $[M]^+$, 363 (65) $[M-C_4F_9O]^+$, 115 (62) $[M-C_9HF_{18}O_2]^+$; HRMS: *m*/*z* calcd. for $C_{18}H_8F_{18}O_2$: 598.0237; found: 598.0238.

1,1'-((5-Iodo-1,3-phenylene)bis(methylene))bis(4-(3,5-bis((perfluoro-*tert*-butoxy)-methyl)phenyl-1*H*-1,2,3-triazole) (3):

After purification (chromatography with eluent cyclohexane/EtOAc 2:1) iodide **3** (1.73 g, 92%) was obtained as white solid from alkyne **2**-H (1.65 g, 2.76 mmol) according to general procedure 3 by using 15 mL dry THF, 60 mL half-saturated NH_4Cl solution and 2 × 100 mL CH_2Cl_2 for the extraction.

m.p. 190 °C; $R_f = 0.30$ (cyclohexane/EtOAc 2:1); IR (ATR): $\tilde{\nu}$ = 1573 (vw), 1468 (vw), 1390 (vw), 1243 (s), 1140 (m), 1049 (w), 1012 (m), 968 (m), 870 (w), 799 (w), 772 (w), 753 (w), 736 (m), 726 (m), 658 (vw), 603 (vw), 538 (w), 493 (w) cm^{-1}; ^1H NMR

(400 MHz, $CDCl_3$): $\delta = 5.09$ (s, 8 H, CH_2), 5.53 (s, 4 H, CH_2), 7.24 (s, 1 H, CH_{ar}), 7.36 (s, 2 H, CH_{ar}), 7.66 (s, 2 H, CH_{ar}), 7.76 (s, 6 H, CH_{ar}) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 53.2$ (–, CH_2), 70.8 (–, CH_2), 80.1 (C_q, decet, $^2J_{C,F} = 30$ Hz, $C(CF_3)_3$), 95.6 (C_q, C_{ar}), 120.2 (+, CH_{ar}), 120.5 (C_q, q, $^1J_{C,F} = 293$ Hz, CF_3), 125.3 (+, CH_{ar}), 126.6 (+, CH_{ar}), 126.8 (+, CH_{ar}), 131.3 (C_q, C_{ar}), 136.5 (+, CH_{ar}), 137.4 (C_q, C_{ar}), 137.8 (C_q, C_{ar}), 147.6 (C_q, C_{ar}) ppm; ^{19}F NMR (376.5 MHz, $CDCl_3$): $\delta = -70.1$ (s, CF_3) ppm; MALDI-TOF MS: *m/z*: 1533 $[M+Na]^+$, 1511 $[M+H]^+$.

1,1'-((5-((Trimethylsilyl)ethynyl)-1,3-phenylene)bis(methylene))bis(4-(3,5-bis((perfluoro-*tert*-butoxy)methyl)phenyl-1*H*-1,2,3-triazole) (4-SiMe$_3$):

After purification (chromatography with eluent cyclohexane/EtOAc 2:1) trimethylsilylalkyne **4**-SiMe$_3$ (1.53 g, 94%) was obtained as white solid from iodide **3** (1.65 g, 1.09 mmol) after stirring overnight according to general procedure 1 by using 8 mL dry NEt_3, 4 mL dry THF, 15 mL NH_4Cl solution and 3 × 30 mL CH_2Cl_2 for the extraction.

m.p. 129 °C; $R_f = 0.30$ (cyclohexane/EtOAc 2:1); IR (ATR): $\tilde{\nu} = 1462$ (vw), 1249 (m), 1138 (m), 1050 (vw), 1010 (w), 970 (w), 845 (w), 736 (w), 538 (vw), 490 (vw) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.22$ (s, 9 H, $Si(CH_3)_3$), 5.08 (s, 8 H, CH_2), 5.54 (s, 4 H, CH_2), 7.23 (s, 1 H, CH_{ar}), 7.35 (s, 2 H, CH_{ar}), 7.42 (s, 2 H, CH_{ar}), 7.74 (s, 2 H, CH_{ar}), 7.76 (s, 4 H, CH_{ar}) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = -0.1$ (+, $Si(CH_3)_3$), 53.7 (–, CH_2), 70.8 (–, CH_2), 80.1 (C_q, decet, $^2J_{C,F} = 30$ Hz, $C(CF_3)_3$), 97.3 (C_q, C≡C), 102.9 (C_q, C≡C), 120.1 (+, CH_{ar}), 120.5 (C_q, q, $^1J_{C,F} = 293$ Hz, CF_3), 125.3 (+, CH_{ar}), 125.6 (C_q, C_{ar}), 126.6 (+, CH_{ar}), 127.4 (+, CH_{ar}), 131.4 (C_q, C_{ar}), 131.8 (+, CH_{ar}), 136.1 (C_q, C_{ar}), 136.5 (C_q, C_{ar}), 147.5 (C_q, C_{ar}) ppm; ^{19}F NMR (376.5 MHz, $CDCl_3$): $\delta = -70.1$ (s, CF_3) ppm; MALDI-TOF MS: *m/z*: 1503 $[M+Na]^+$, 1481 $[M+H]^+$.

1,1'-((5-Ethynyl-1,3-phenylene)bis(methylene))bis(4-(3,5-bis((perfluoro-*tert*-butoxy)-methyl)phenyl-1*H*-1,2,3-triazole) (4-H):

Alkyne **4**-H (1.28 g, 93%) was obtained as white solid from trimethylsilylalkyne **4**-SiMe$_3$ (1.44 g, 972 µmol) according to general procedure 2 by using 30 mL dry methanol as solvent.

m.p. 177 °C; IR (ATR): $\tilde{\upsilon}$ = 1603 (vw), 1468 (vw), 1390 (vw), 1244 (s), 1140 (m), 1049 (w), 1012 (m), 968 (m), 870 (w), 799 (w), 772 (w), 756 (w), 736 (m), 726 (m), 657 (w), 538 (w), 492 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 3.13 (s, 1 H, C≡CH), 5.08 (s, 8 H, CH_2), 5.56 (s, 4 H, CH_2), 7.26 (s, 1 H, CH_{ar}), 7.35 (s, 2 H, CH_{ar}), 7.41 (m_c, 2 H, CH_{ar}), 7.76 (s, 6 H, CH_{ar}) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 53.6 (–, CH_2), 70.8 (–, CH_2), 79.7 (C_q, C≡C), 80.1 (C_q, decet, $^2J_{C,F}$ = 30 Hz, $C(CF_3)_3$), 81.9 (C_q, C≡C), 120.2 (+, CH_{ar}), 120.5 (C_q, q, $^1J_{C,F}$ = 293 Hz, CF_3), 124.5 (C_q, C_{ar}), 125.3 (+, CH_{ar}), 126.6 (+, CH_{ar}), 127.7 (+, CH_{ar}), 131.4 (C_q, C_{ar}), 131.9 (+, CH_{ar}), 136.3 (C_q, C_{ar}), 136.5 (C_q, C_{ar}), 147.5 (C_q, C_{ar}) ppm; ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –70.1 (s, CF_3) ppm; MALDI-TOF MS: *m*/*z*: 1471 $[M+Cu]^+$, 1447 $[M+K]^+$, 1431 $[M+Na]^+$, 1409 $[M+H]^+$.

1,1',1'',1'''-(((1,1'-((5-Iodo-1,3-phenylene)bis(methylene))bis(1*H*-1,2,3-triazole-4,1-diyl))bis(benzene-5,3,1-triyl))tetrakis-(methylene))tetrakis(4-(3,5-bis((perfluoro-*tert*-butoxy)methyl)phenyl)-1*H*-1,2,3-triazole) (5):

After purification (chromatography with eluent cyclohexane/EtOAc 2:3) iodide **5** (722 mg, 77%) was obtained as white solid from alkyne **4**-H (1.00 g, 710 µmol) according to general procedure 3 by using 5 mL dry THF, 30 mL half-saturated NH_4Cl solution and 2 × 50 mL CH_2Cl_2 for the extraction.

m.p. 138–142 °C; R_f = 0.19 (cyclohexane/EtOAc 2:3); IR (ATR): $\tilde{\upsilon}$ = 1771 (vw), 1468 (vw), 1245 (s), 1144 (m), 1048 (w), 1012 (m), 969 (m), 870 (w), 772 (w), 736 (m), 726 (m), 538 (w), 491 (vw) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 5.04 (s, 16 H, CH_2), 5.44 (s, 4 H, CH_2), 5.53 (s, 8 H, CH_2), 7.12 (s, 1 H, CH_{ar}), 7.22 (s, 2 H, CH_{ar}), 7.33 (s, 4 H, CH_{ar}), 7.59 (s, 2 H, CH_{ar}), 7.72 (s, 12 H, CH_{ar}), 7.74 (s, 2 H, CH_{ar}), 7.82 (s, 4 H, CH_{ar}) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 53.1 (–, CH_2), 53.8 (–, CH_2), 70.8 (–, CH_2), 80.0 (C_q, decet, $^2J_{C,F}$ = 30 Hz, $C(CF_3)_3$), 95.5 (C_q, C_{ar}), 120.4 (+, CH_{ar}), 120.5 (C_q, q, $^1J_{C,F}$ = 293 Hz, CF_3), 120.7 (+, CH_{ar}), 125.2 (+, CH_{ar}), 125.7 (+, CH_{ar}), 126.6 (+, CH_{ar}), 126.8 (+, CH_{ar}), 127.3 (+, CH_{ar}), 131.4 (C_q, C_{ar}), 132.4 (C_q, C_{ar}), 136.5 (C_q, C_{ar}), 136.6 (C_q, C_{ar}), 137.4 (+, CH_{ar}), 137.6 (C_q, C_{ar}), 146.9 (C_q, C_{ar}), 147.4 (C_q, C_{ar}) ppm; ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –70.2 (s, CF_3) ppm; MALDI-TOF MS: *m*/*z*: 3153 $[M+Na]^+$, 3131 $[M+H]^+$.

1,1',1'',1'''-(((1,1'-((5-((Trimethylsilyl)ethynyl)-1,3-phenylene)bis(methylene))bis(1*H*-1,2,3-triazole-4,1-diyl))bis(benzene-5,3,1-triyl))tetrakis(methylene))tetrakis(4-(3,5-bis((perfluoro-*tert*-butoxy)methyl)-phenyl)-1*H*-1,2,3-triazole) (6-$SiMe_3$):

After purification (chromatography with eluent cyclohexane/EtOAc 2:3) trimethylsilylalkyne **6**-$SiMe_3$ (545 mg, 82%) was obtained as white solid from iodide **5** (670 mg, 214 µmol) after stirring overnight according to general procedure 1 by using 2 mL dry NEt_3, 1 mL dry THF, 10 mL NH_4Cl solution and 3 × 20 mL CH_2Cl_2 for the extraction.

m.p. 131–136 °C; R_f = 0.22 (cyclohexane/EtOAc 2:3); IR (ATR): $\tilde{\upsilon}$ = 1771 (vw), 1616 (vw), 1466 (vw), 1245 (m), 1144 (w), 1048 (w), 1012 (w), 969 (w), 845 (w), 758 (vw), 736 (w), 726 (w), 605 (vw), 538 (w), 490 (vw), 423 (vw) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 0.18 (s, 9 H, $Si(CH_3)_3$), 5.05 (s, 16 H, CH_2), 5.48 (s, 4 H, CH_2), 5.55 (s, 8 H, CH_2), 7.13 (s, 1 H, CH_{ar}), 7.23 (s, 2 H, CH_{ar}), 7.33 (s, 4 H, CH_{ar}), 7.37 (s, 2 H, CH_{ar}), 7.73 (s, 10 H, CH_{ar}), 7.75 (s, 4 H, CH_{ar}), 7.81 (s, 4 H, CH_{ar}) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = –0.3 (+, $Si(CH_3)_3$), 53.6 (–, CH_2), 53.9 (–, CH_2), 70.8 (–, CH_2), 80.1 (C_q, decet, $^2J_{C,F}$ = 30 Hz, $C(CF_3)_3$), 97.4 (C_q, C≡C), 102.8 (C_q, C≡C), 120.3 (+, CH_{ar}), 120.5 (C_q, q, $^1J_{C,F}$ = 293 Hz, CF_3), 120.6 (+, CH_{ar}), 125.2 (+, CH_{ar}), 125.6 (C_q, C_{ar}), 125.8 (+, CH_{ar}), 126.6 (+, CH_{ar}), 127.3 (+, CH_{ar}), 127.4 (+, CH_{ar}), 131.4 (C_q, C_{ar}), 131.9 (+, CH_{ar}), 132.5 (Cq, C_{ar}), 135.9 (C_q, C_{ar}), 136.4 (C_q, C_{ar}), 136.7 (C_q, C_{ar}), 146.9 (C_q, C_{ar}), 147.4 (C_q, C_{ar}) ppm; ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –70.2 (s, CF_3) ppm; MALDI-TOF MS: *m*/*z*: 3123 $[M+Na]^+$.

1,1',1'',1'''-(((1,1'-((5-Ethynyl)-1,3-phenylene)bis(methylene))bis(1*H*-1,2,3-triazole-4,1-diyl))bis(benzene-5,3,1-triyl))-tetrakis(methylene))tetrakis(4-(3,5-bis((perfluoro-*tert*-butoxy)methyl)phenyl)-1*H*-1,2,3-triazole) (6-H):

Alkyne **6**-H (456 mg, 92%) was obtained as white solid from trimethylsilylalkyne **6**-$SiMe_3$ (505 mg, 163 µmol) according to general procedure 2 by using 6 mL dry methanol as solvent.

m.p. 153–160 °C; IR (ATR): $\tilde{\upsilon}$ = 1614 (vw), 1468 (vw), 1244 (m), 1142 (m), 1048 (w), 1012 (w), 968 (m), 869 (w), 799 (w), 771 (w), 756 (vw), 736 (w), 726 (m), 660 (vw), 538 (w), 492 (vw) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 3.07 (s, 1 H, C≡CH), 5.05 (s, 16 H,

CH_2), 5.49 (s, 4 H, CH_2), 5.55 (s, 8 H, CH_2), 7.15 (s, 1 H, CH_{ar}), 7.24 (s, 2 H, CH_{ar}), 7.33 (s, 4 H, CH_{ar}), 7.36 (m_c, 2 H, CH_{ar}), 7.73 (m_c, 10 H, CH_{ar}), 7.75 (m_c, 4 H, CH_{ar}), 7.81 (s, 4 H, CH_{ar}) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 53.6 (–, CH_2), 53.9 (–, CH_2), 70.8 (–, CH_2), 79.6 (C_q, C≡C), 80.1 (C_q, decet, $^2J_{C,F}$ = 30 Hz, $C(CF_3)_3$), 81.7 (C_q, C≡C), 120.3 (+, CH_{ar}), 120.5 (C_q, q, $^1J_{C,F}$ = 293 Hz, CF_3), 120.7 (+, CH_{ar}), 124.6 (C_q, C_{ar}), 125.2 (+, CH_{ar}), 125.8 (+, CH_{ar}), 126.6 (+, CH_{ar}), 127.3 (+, CH_{ar}), 127.7 (+, CH_{ar}), 131.4 (C_q, C_{ar}), 131.9 (+, CH_{ar}), 132.5 (C_q, C_{ar}), 136.1 (C_q, C_{ar}), 136.5 (C_q, C_{ar}), 136.7 (C_q, C_{ar}), 146.9 (C_q, C_{ar}), 147.4 (C_q, C_{ar}) ppm; ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –70.2 (s, CF_3) ppm; MALDI-TOF MS: *m*/*z*: 3067 $[M+K]^+$.

1,1',1'',1'''-(((1,1'-((5-(1-(2,5,8,11,14,17,20,23,26,29,32,35-Dodecaoxyheptatriacontan-37-yl)-1*H*-1,2,3-triazole-4-yl)-1,3-phenylene)bis(methylene))bis(1*H*-1,2,3-triazole-4,1-diyl))bis(benzene-5,3,1-triyl))tetrakis(methylene))tetrakis(4-(3,5-bis-((perfluoro-*tert*-butoxy)methyl)phenyl)-1*H*-1,2,3-triazole) (7):

O-(2-Azidoethyl)-*O*'-methylundecaethylene glycol (42.2 mg, 72.0 µmol) was added to a solution of alkyne **6**-H (109 mg, 36.0 µmol), $Cu(CH_3CN)_4PF_6$ (2.7 mg, 7.20 µmol) and 2,6-lutidine (1.0 µL, 7.20 µmol) in dry THF (1 mL) under argon atmosphere. The mixture was stirred for 2.5 d at room temperature. Afterwards H_2O (2 mL) was added and the product was extracted with EtOAc (3 × 5 mL). The solvent was evaporated under reduced pressure. The crude product was purified via RP-HPLC to yield triazole **7** (40.6 mg, 31%) as a viscous, colorless oil.

IR (ATR): $\tilde{\upsilon}$ = 3128 (vw), 2876 (vw), 1768 (vw), 1614 (vw), 1468 (vw), 1246 (m), 1144 (m), 1049 (w), 1012 (w), 969 (m), 841 (w), 772 (vw), 757 (vw), 736 (w), 726 (m), 538 (w), 492 (vw) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$+TFA): δ = 3.37 (s, 3 H, CH_3), 3.53–3.65 (m, 44 H, CH_2), 3.86–3.94 (m, 2 H, CH_2), 4.56–4.65 (m, 2 H, CH_2), 5.04 (s, 16 H, CH_2), 5.59 (s, 8 H, CH_2), 5.62 (s, 4 H, CH_2), 7.38 (s, 4 H, CH_{ar}), 7.41 (s, 1 H, CH_{ar}), 7.44 (s, 2 H, CH_{ar}), 7.66 (s, 8 H, CH_{ar}), 7.87 (s, 6 H, CH_{ar}), 8.03–8.14 (m, 4 H, CH_{ar}), 8.21–8.37 (m, 3 H, CH_{ar}) ppm; ^{13}C NMR (125 MHz, $CDCl_3$+TFA): δ = 51.5 (–, CH_2), 54.4 (–, CH_2), 58.8 (+, CH_3), 68.8 (–, CH_2), 69.1–70.1 (m, –, CH_2), 70.3 (–, CH_2), 70.5 (–, CH_2), 71.4 (–, CH_2), 80.0 (C_q, decet, $^2J_{C,F}$ = 30 Hz, $C(CF_3)_3$), 120.5 (C_q, q, $^1J_{C,F}$ = 293 Hz, CF_3), 121.9 (+, CH_{ar}), 122.7 (+, CH_{ar}), 123.7 (C_q, C_{ar}), 125.5 (+, CH_{ar}), 126.9 (+, CH_{ar}), 127.0 (+, CH_{ar}), 127.3 (+, CH_{ar}), 128.8 (+, CH_{ar}), 129.0 (C_q, C_{ar}), 129.4 (+, CH_{ar}), 130.3 (C_q, C_{ar}), 130.7 (+, CH_{ar}), 136.2 (C_q, C_{ar}), 136.3 (C_q, C_{ar}), 136.8 (C_q, C_{ar}), 144.9 (C_q, C_{ar}), 146.1 (C_q, C_{ar}), 146.7 (C_q, C_{ar}) ppm; ^{19}F NMR (376.5 MHz, $CDCl_3$+TFA): $\delta = -70.8$ (s, CF_3) ppm; MALDI-TOF MS: m/z: 3635 $[M-H+Na]^+$.

3. ^{1}H and ^{13}C NMR Data

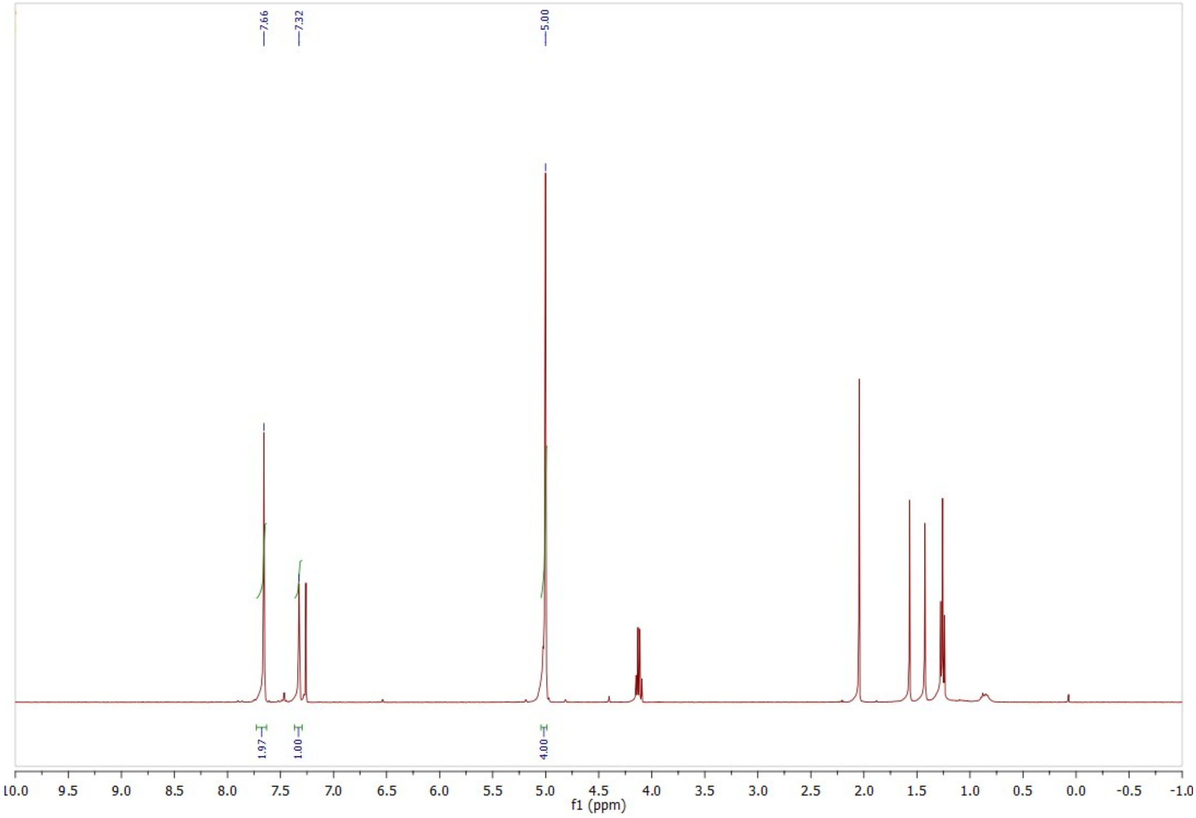

Figure S1. ^{1}H NMR ($CDCl_3$, 400 MHz) of molecule **1**-$OC(CF_3)_3$.

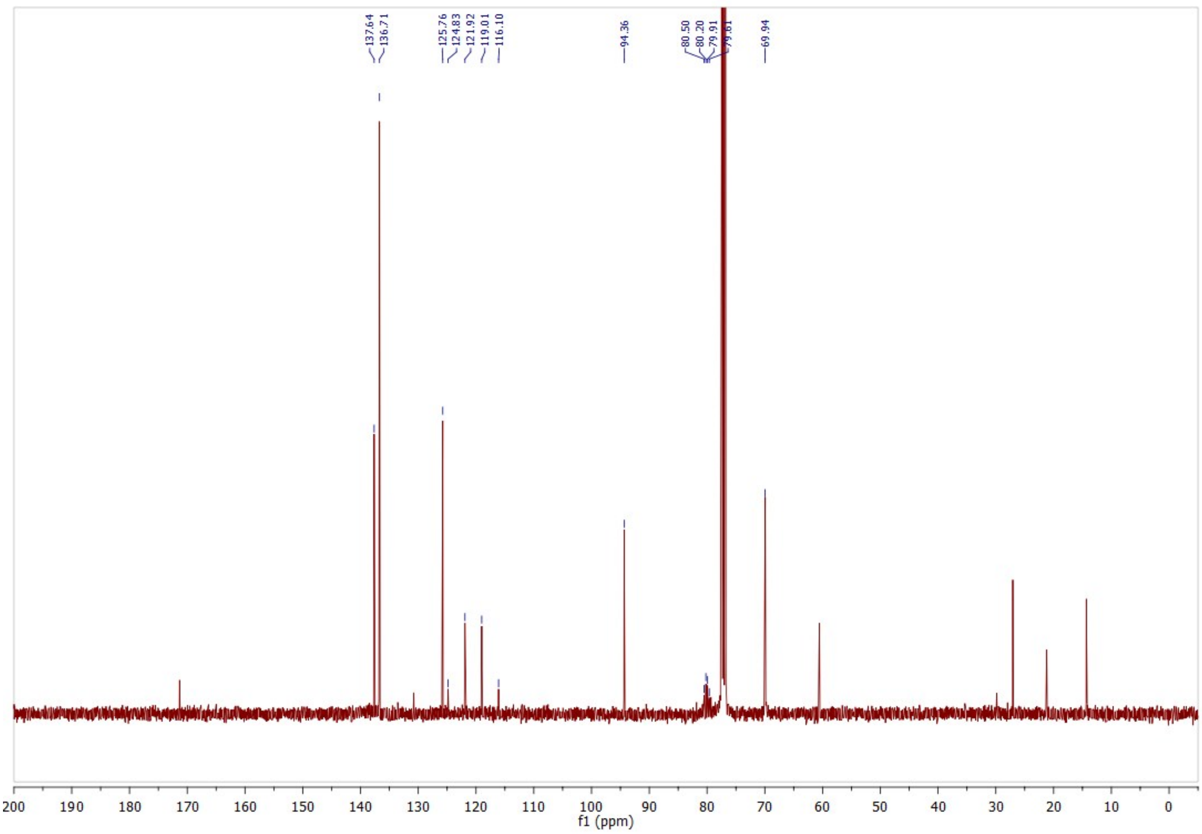

Figure S2. ^{13}C NMR ($CDCl_3$, 100 MHz) of molecule **1**-$OC(CF_3)_3$.

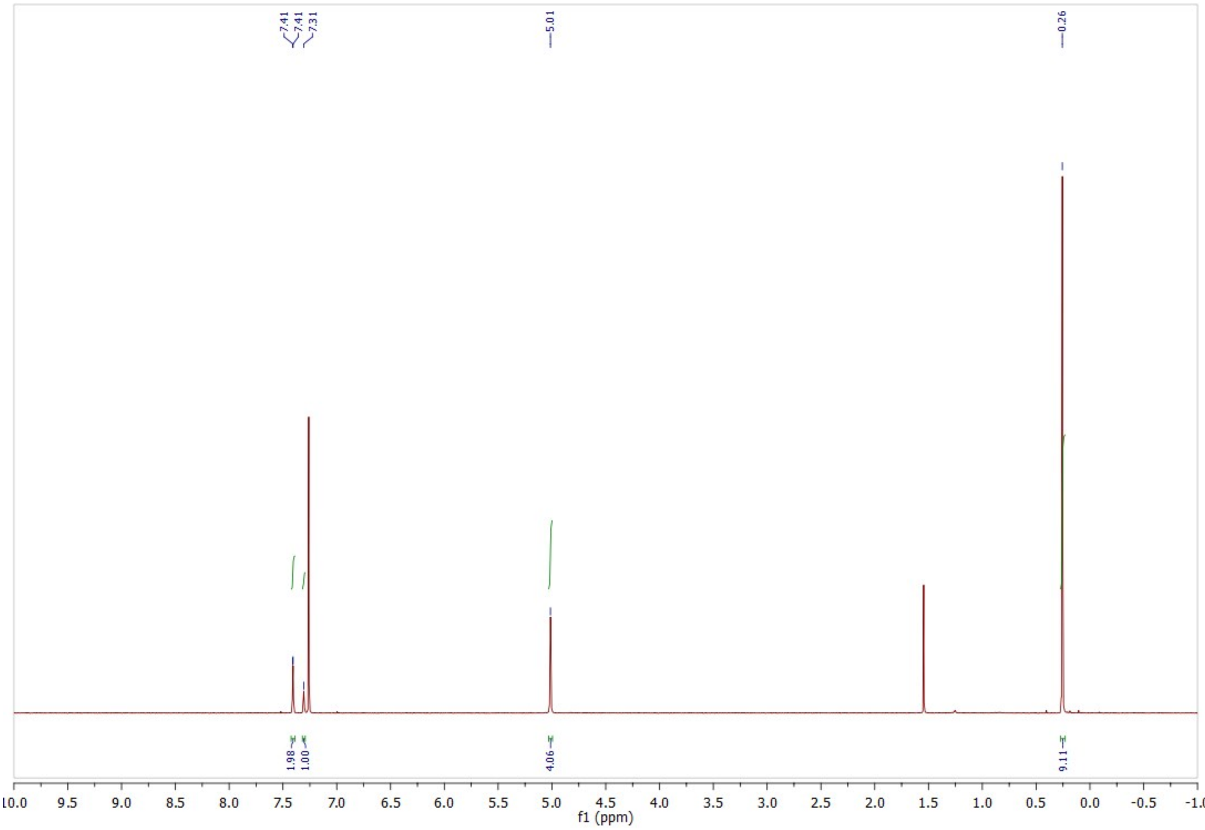

Figure S3. ^{1}H NMR ($CDCl_3$, 400 MHz) of molecule **2**-$SiMe_3$.

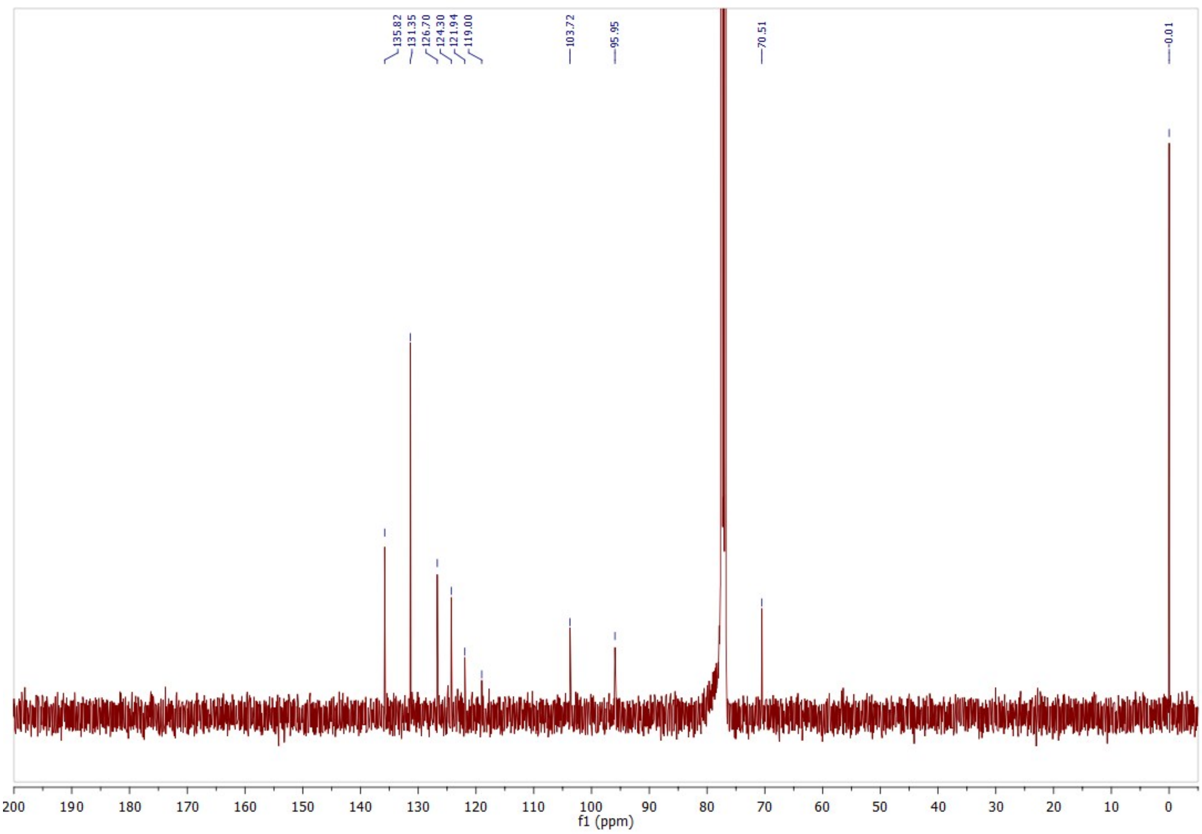

Figure S4. ^{13}C NMR ($CDCl_3$, 100 MHz) of molecule **2**-$SiMe_3$.

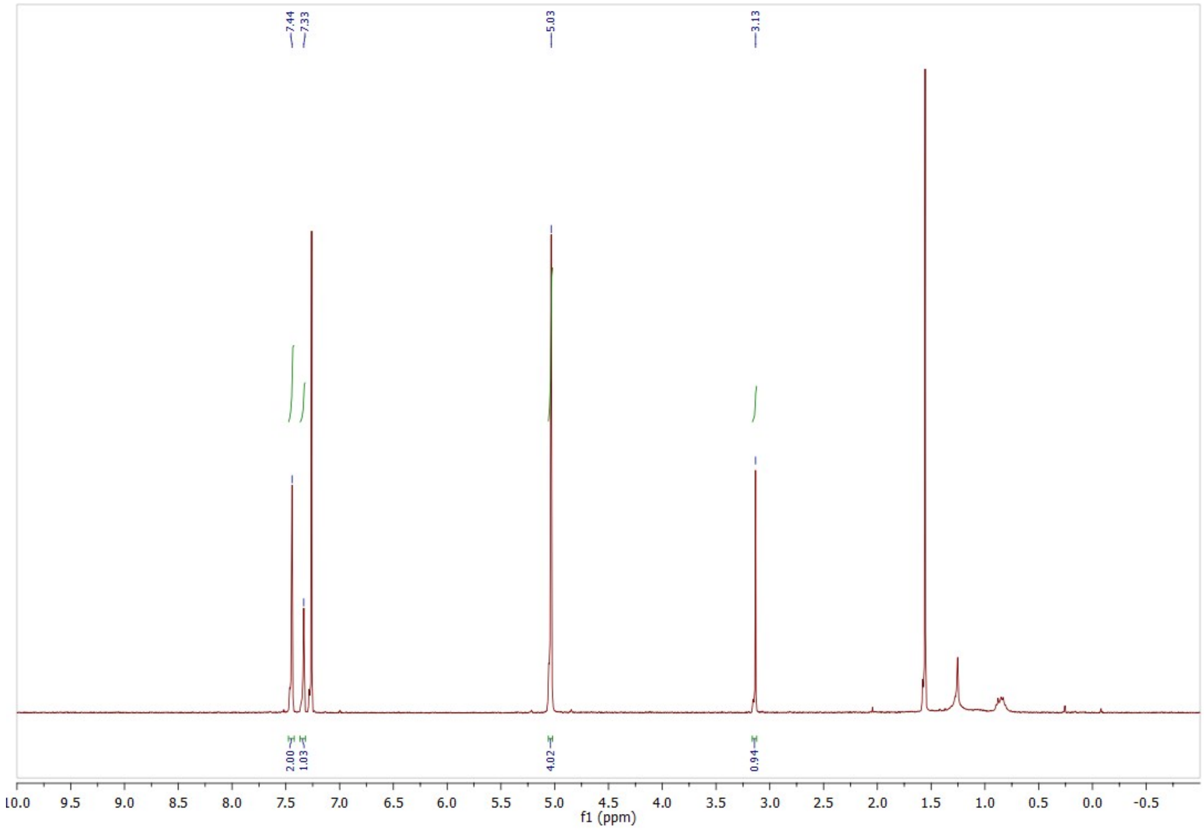

Figure S5. ^{1}H NMR ($CDCl_3$, 400 MHz) of molecule **2**-H.

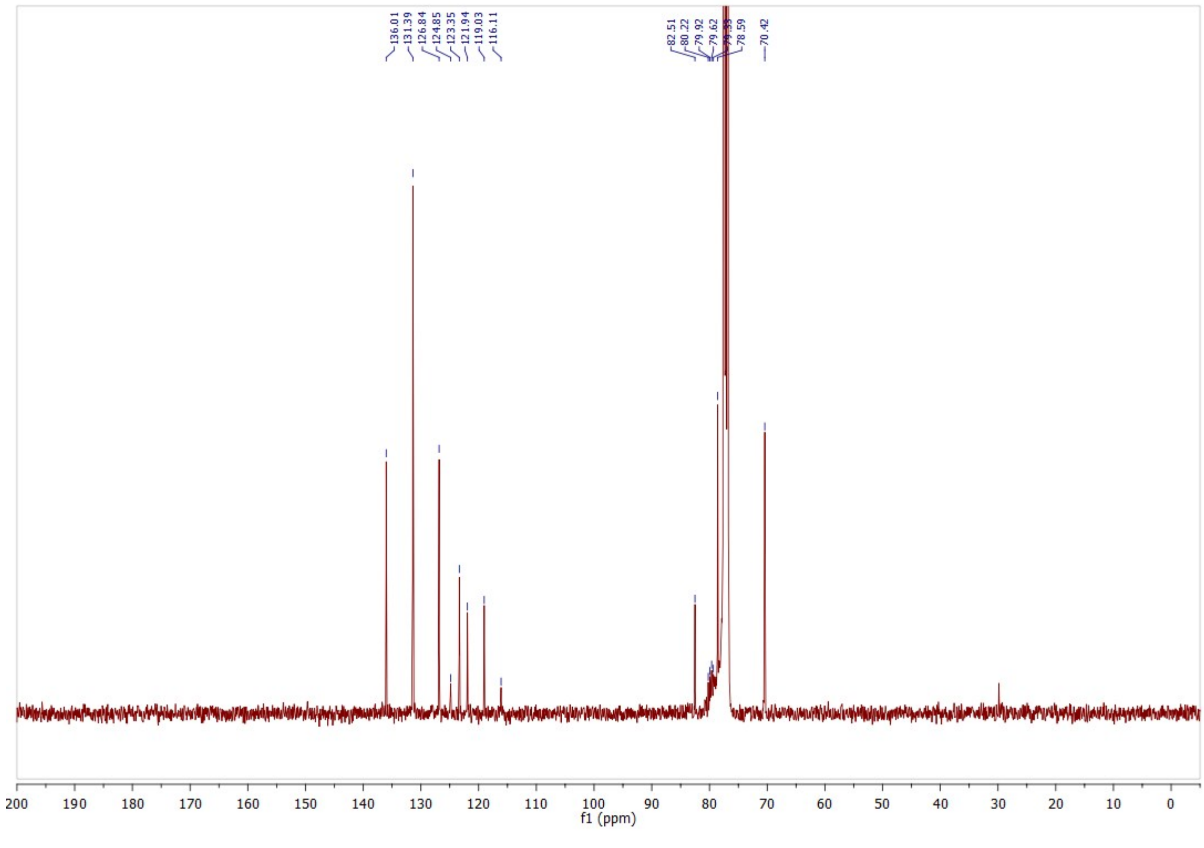

Figure S6. ^{13}C NMR ($CDCl_3$, 100 MHz) of molecule **2**-H.

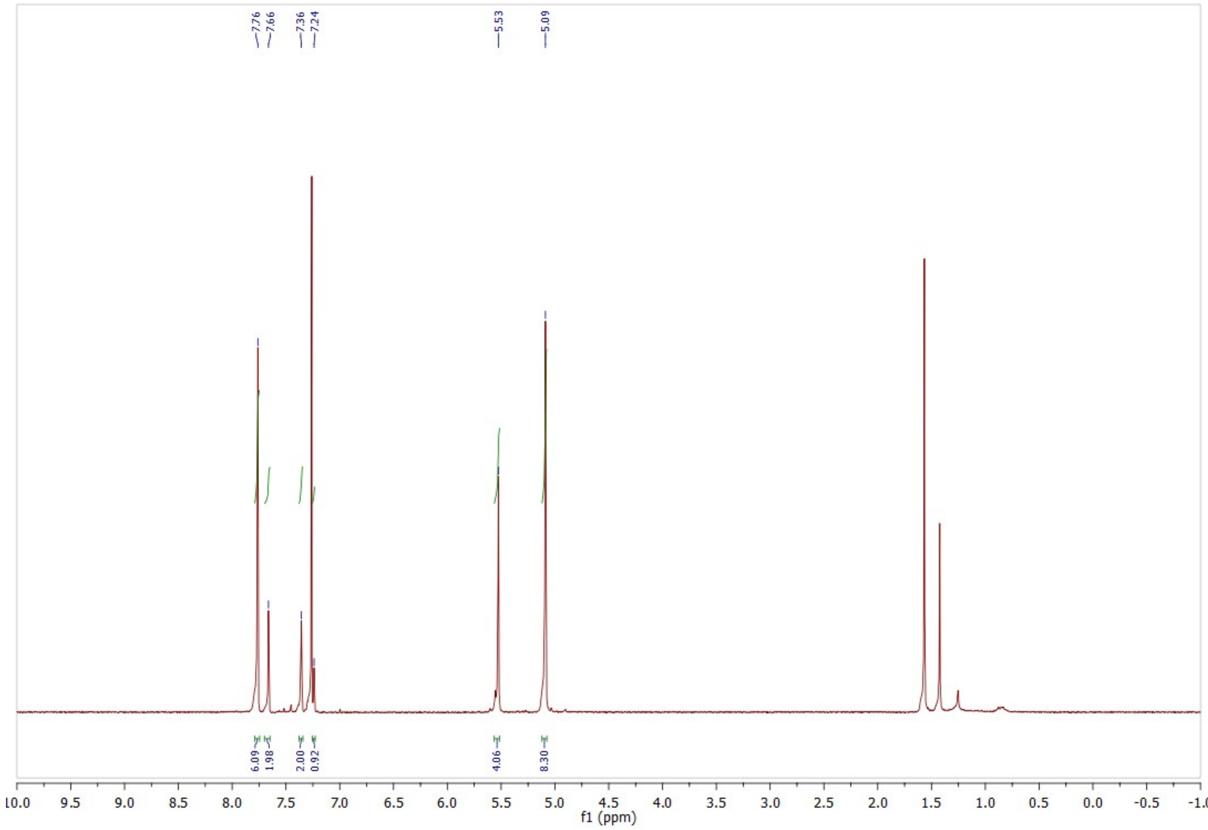

Figure S7. ^{1}H NMR ($CDCl_3$, 400 MHz) of molecule **3**.

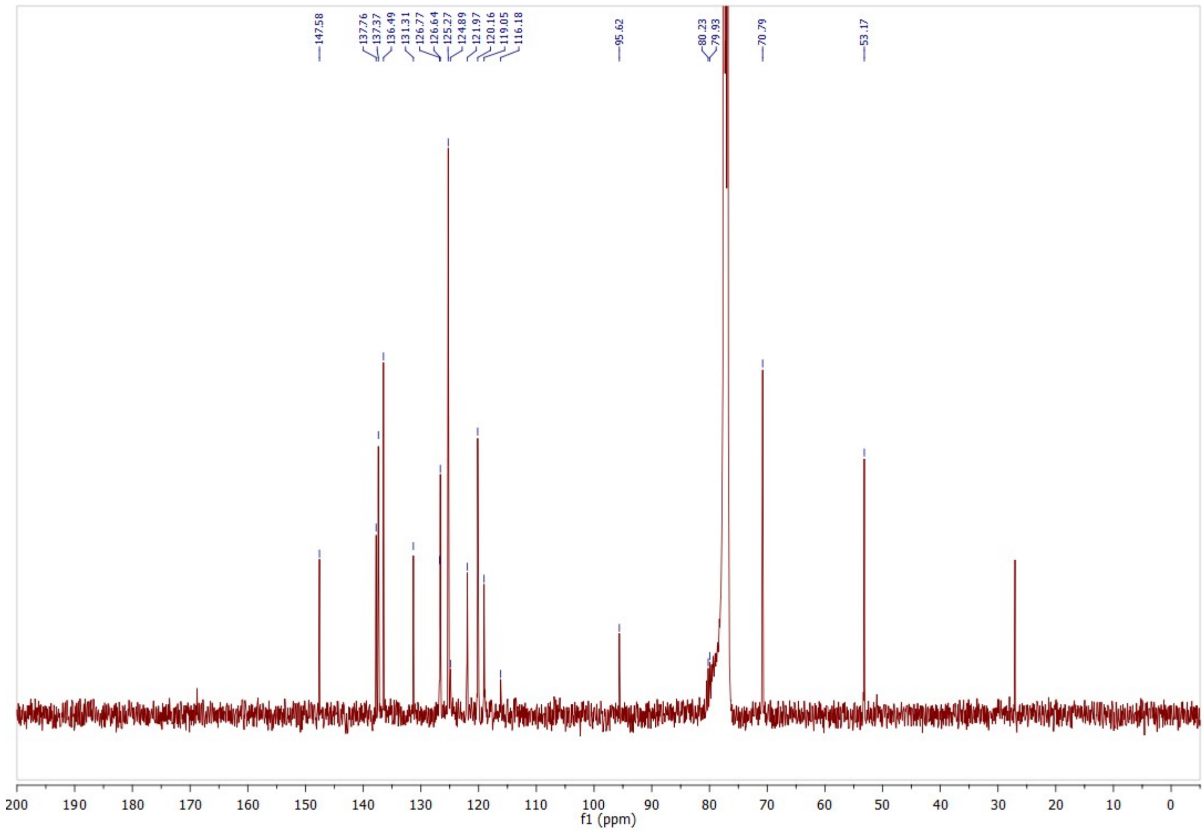

Figure S8. ^{13}C NMR ($CDCl_3$, 100 MHz) of molecule **3**.

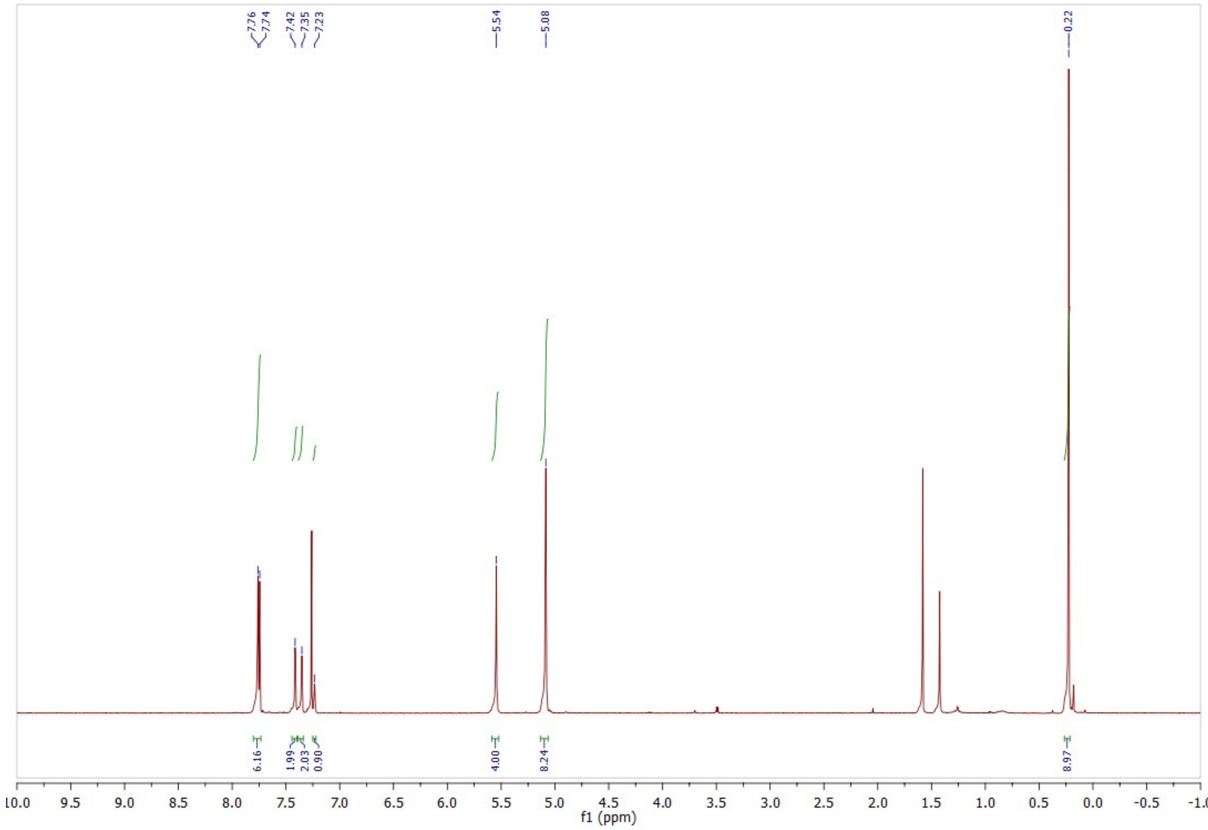

Figure S9. ^{1}H NMR ($CDCl_3$, 400 MHz) of molecule **4**-$SiMe_3$.

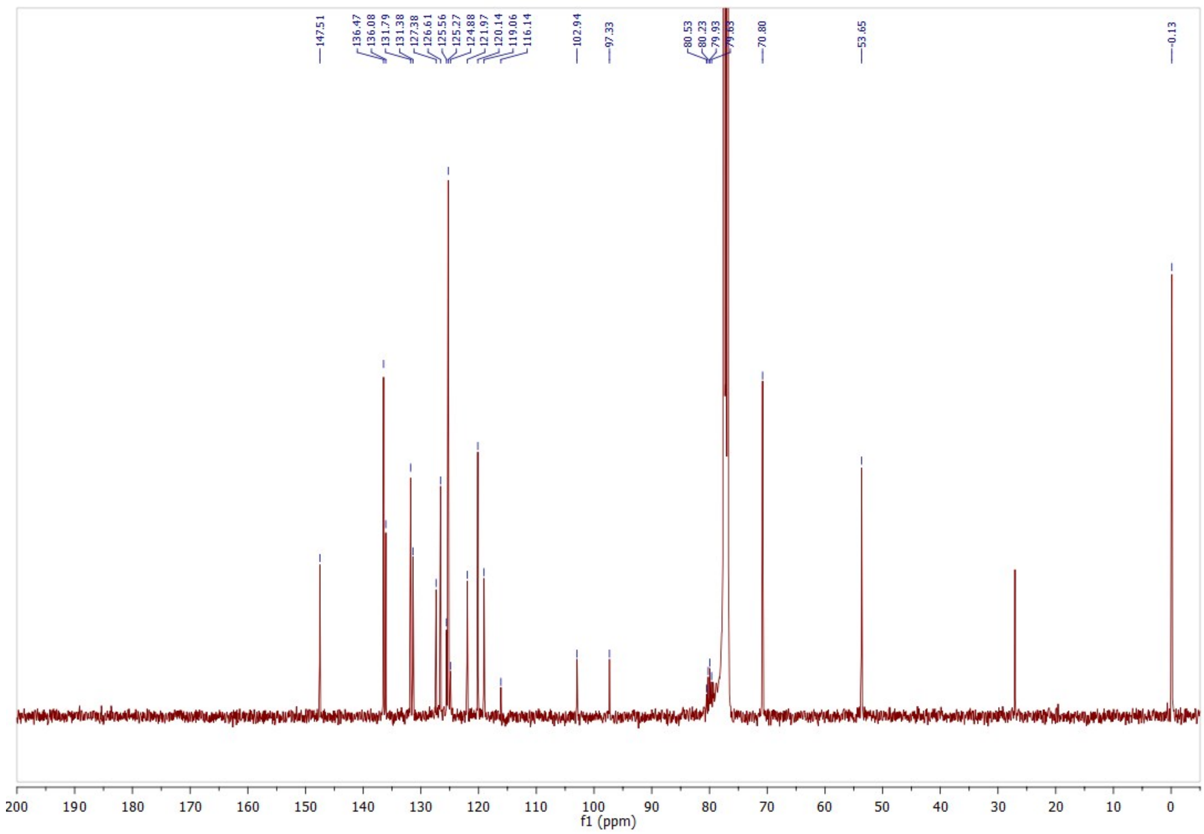

Figure S10. ^{13}C NMR ($CDCl_3$, 100 MHz) of molecule **4**-$SiMe_3$.

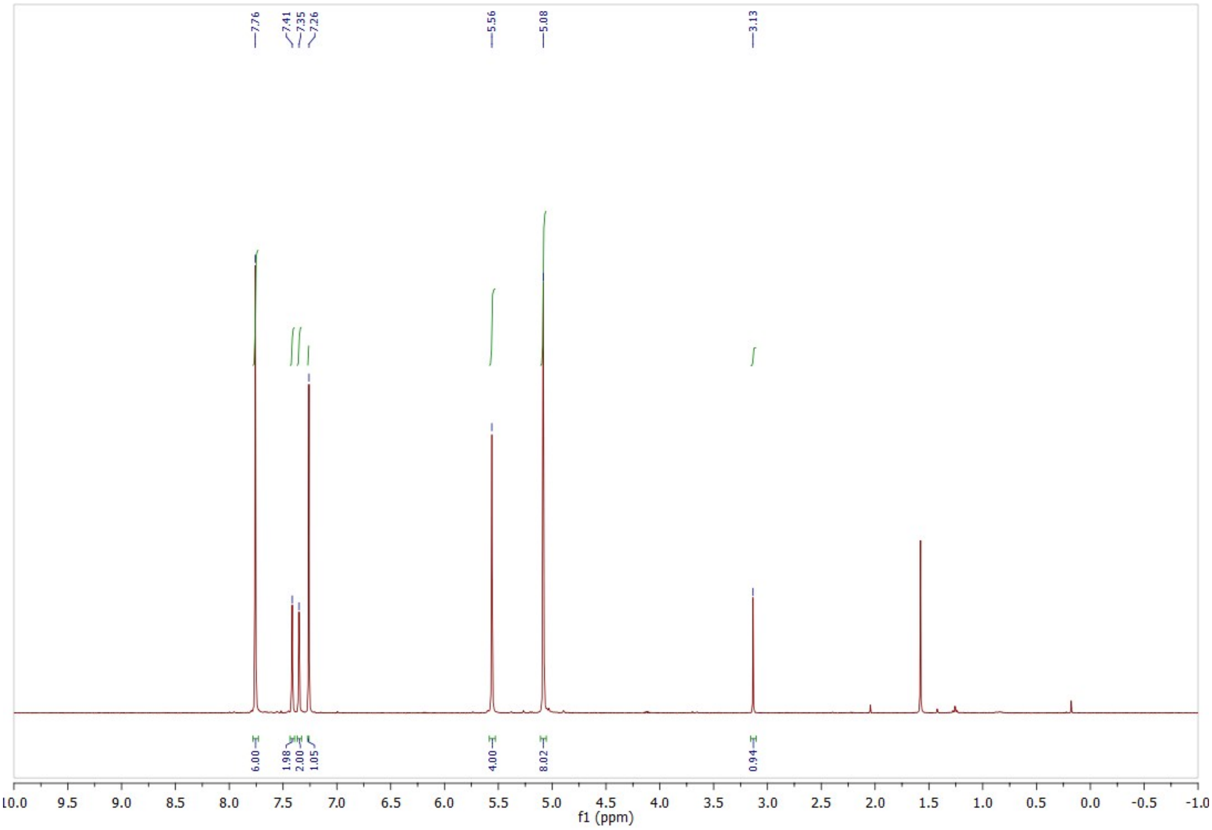

Figure S11. [1]H NMR ($CDCl_3$, 400 MHz) of molecule **4**-H.

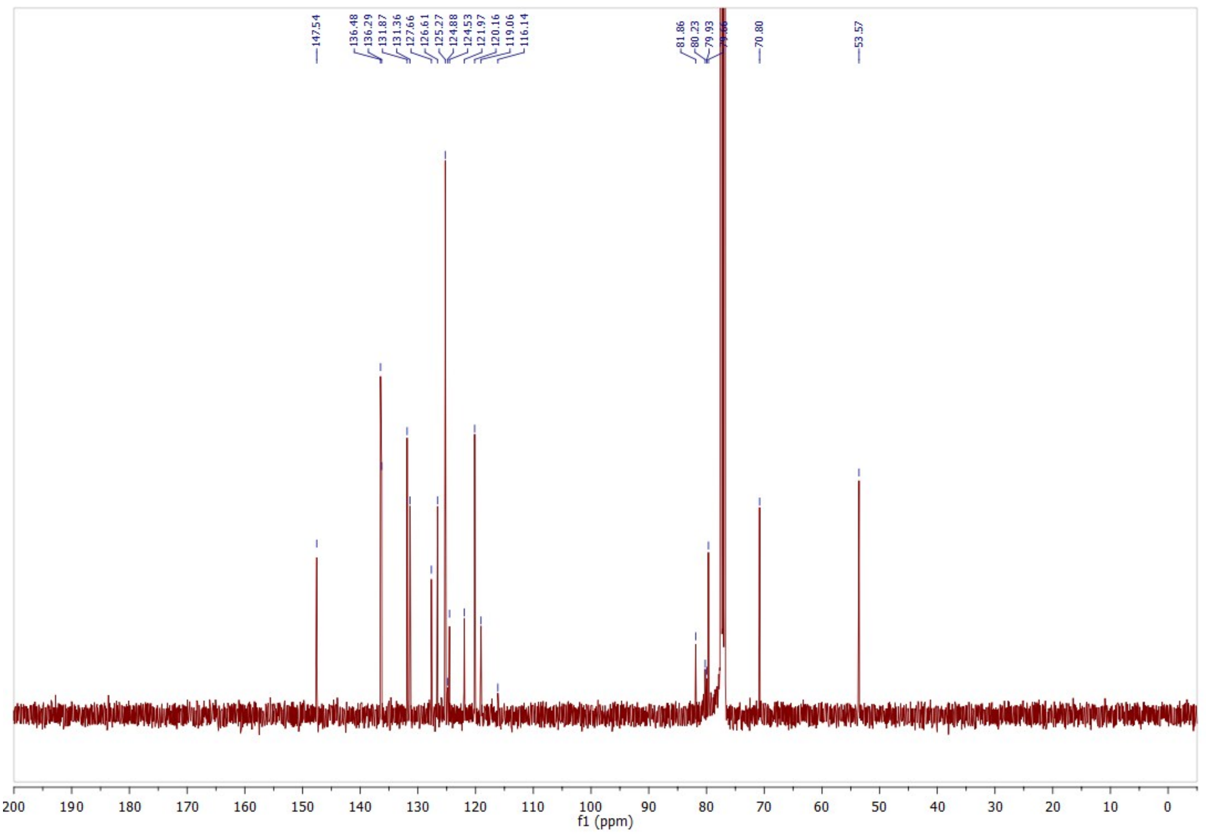

Figure S12. [13]C NMR ($CDCl_3$, 100 MHz) of molecule **4**-H.

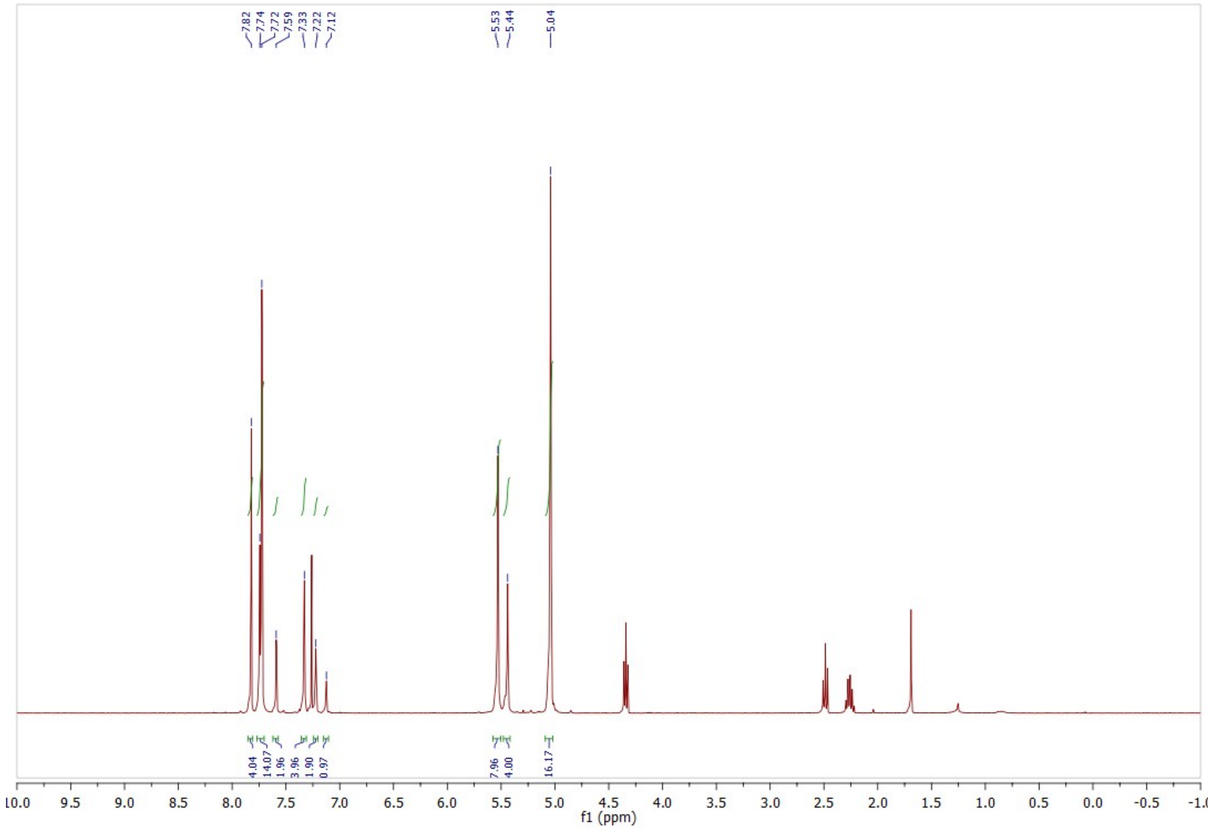

Figure S13. ^{1}H NMR ($CDCl_3$, 400 MHz) of molecule **5**.

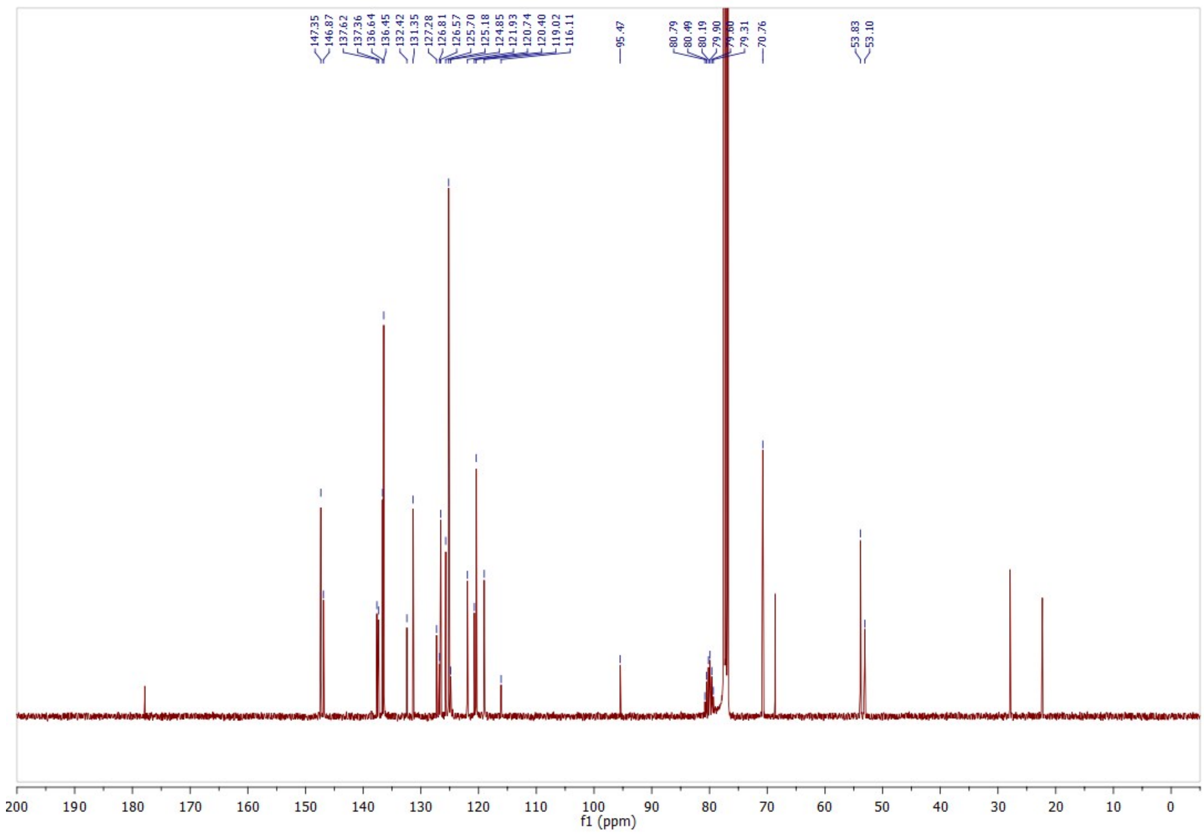

Figure S14. ^{13}C NMR ($CDCl_3$, 100 MHz) of molecule **5**.

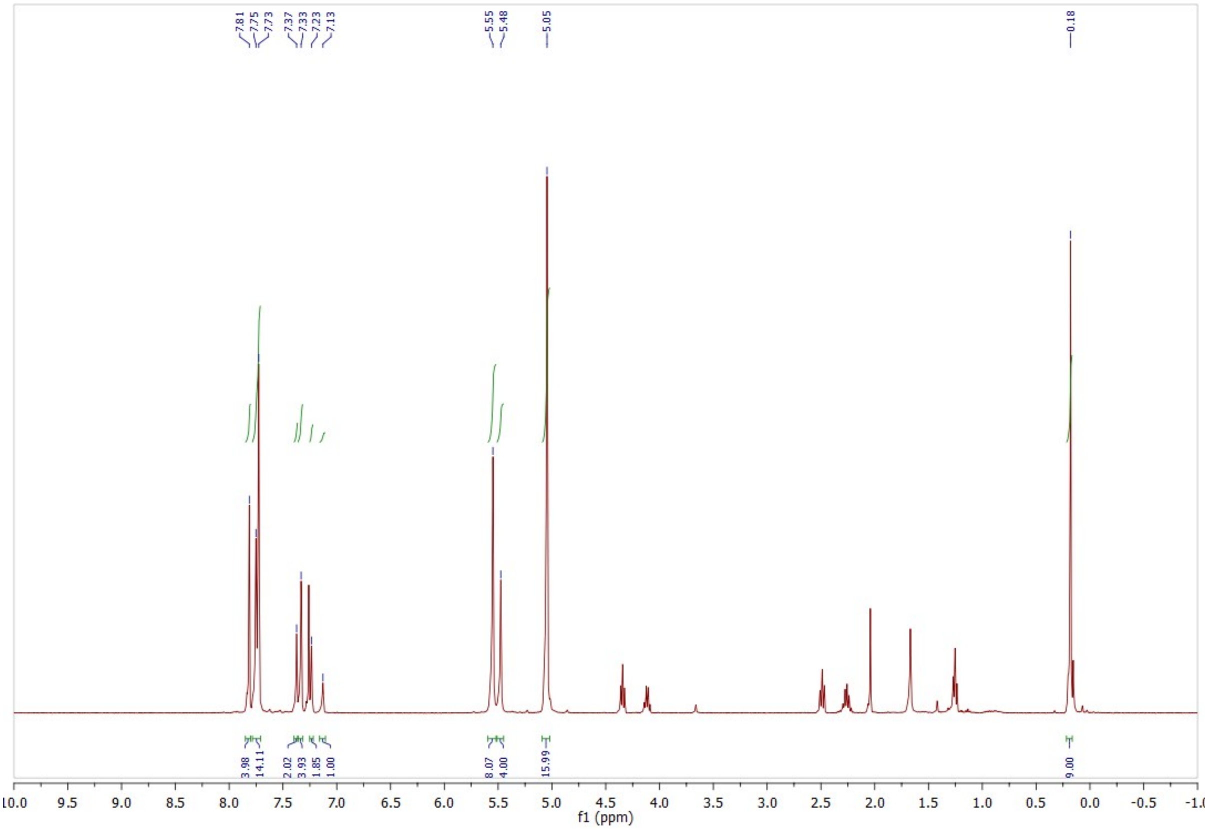

Figure S15. ^{1}H NMR ($CDCl_3$, 400 MHz) of molecule **6**-$SiMe_3$.

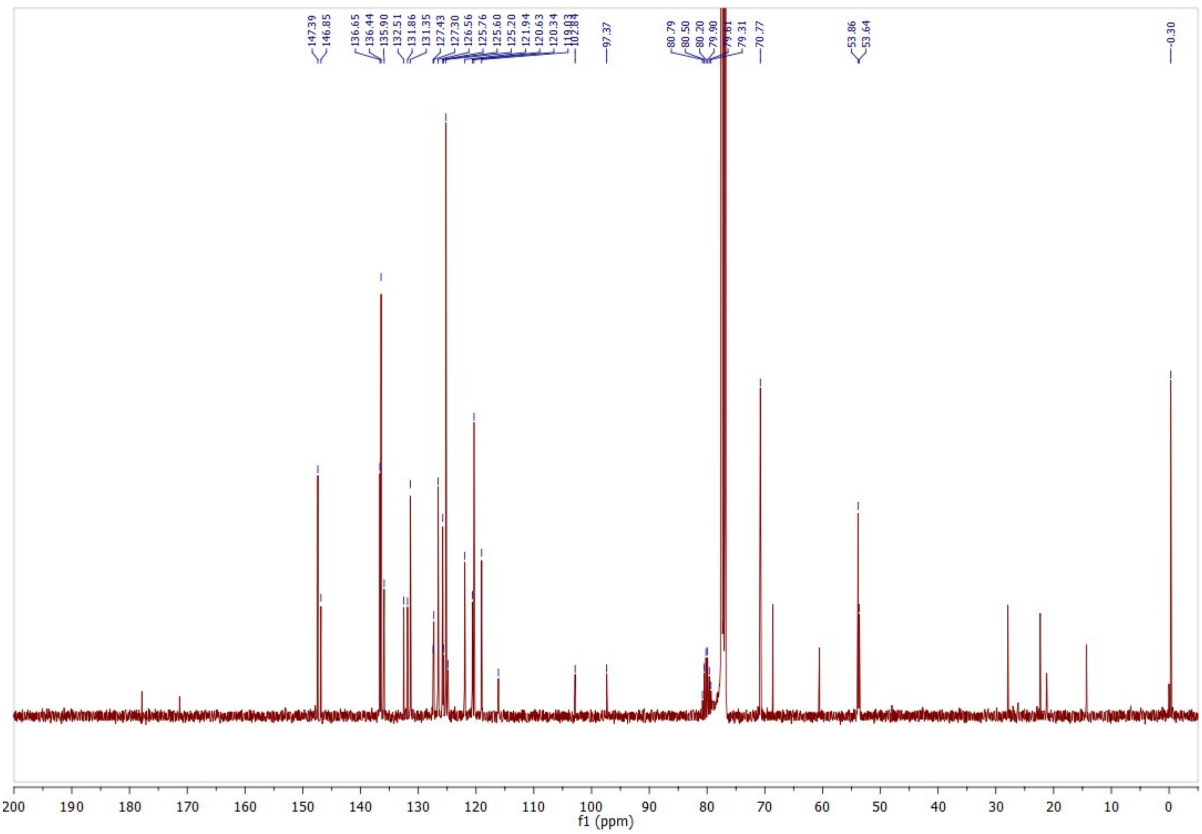

Figure S16. ^{13}C NMR ($CDCl_3$, 100 MHz) of molecule **6**-$SiMe_3$.

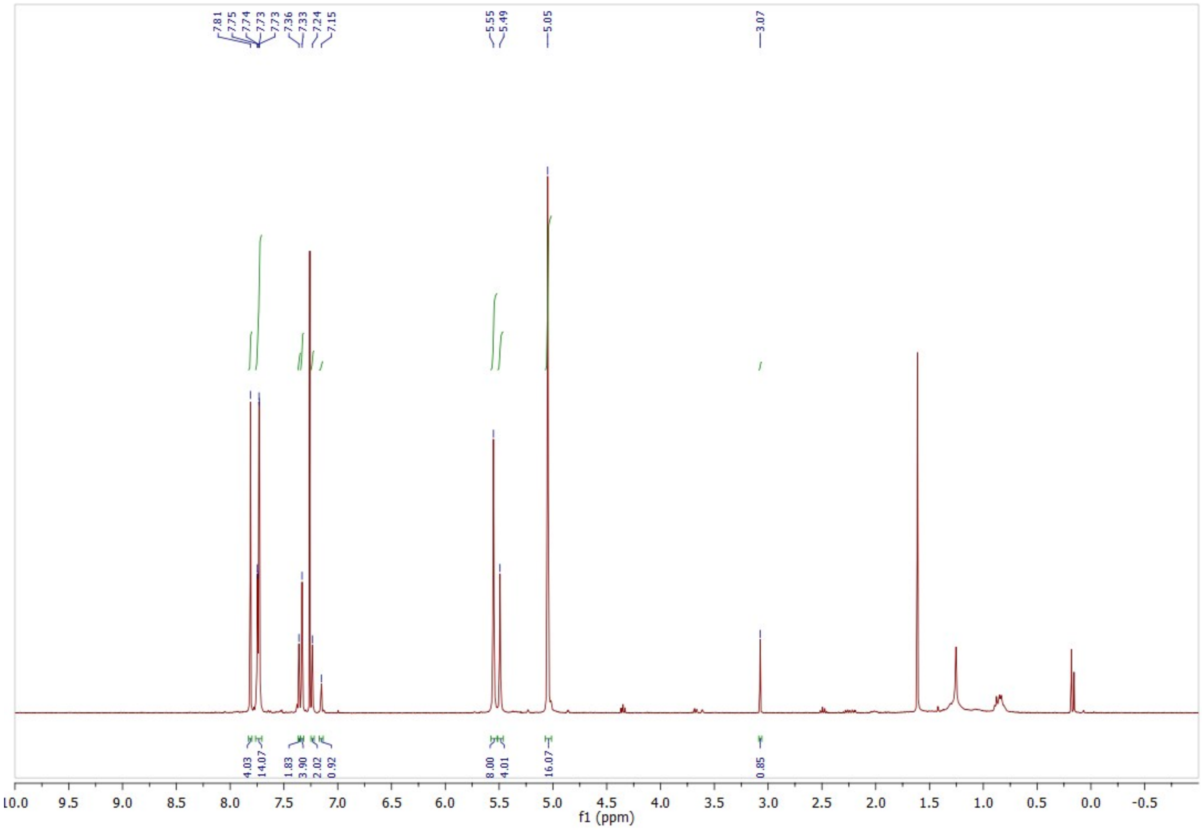

Figure S17. ^{1}H NMR ($CDCl_3$, 400 MHz) of molecule **6**-H.

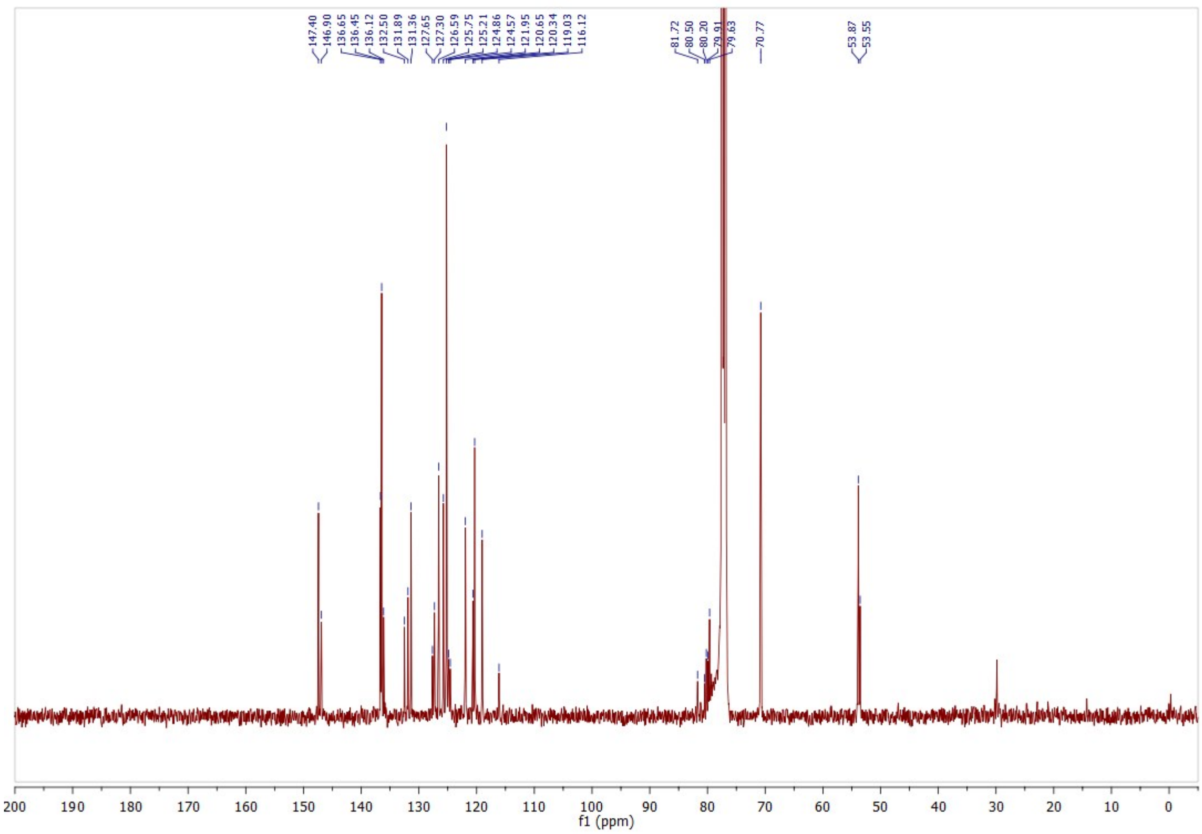

Figure S18. ^{13}C NMR ($CDCl_3$, 100 MHz) of molecule **6**-H.

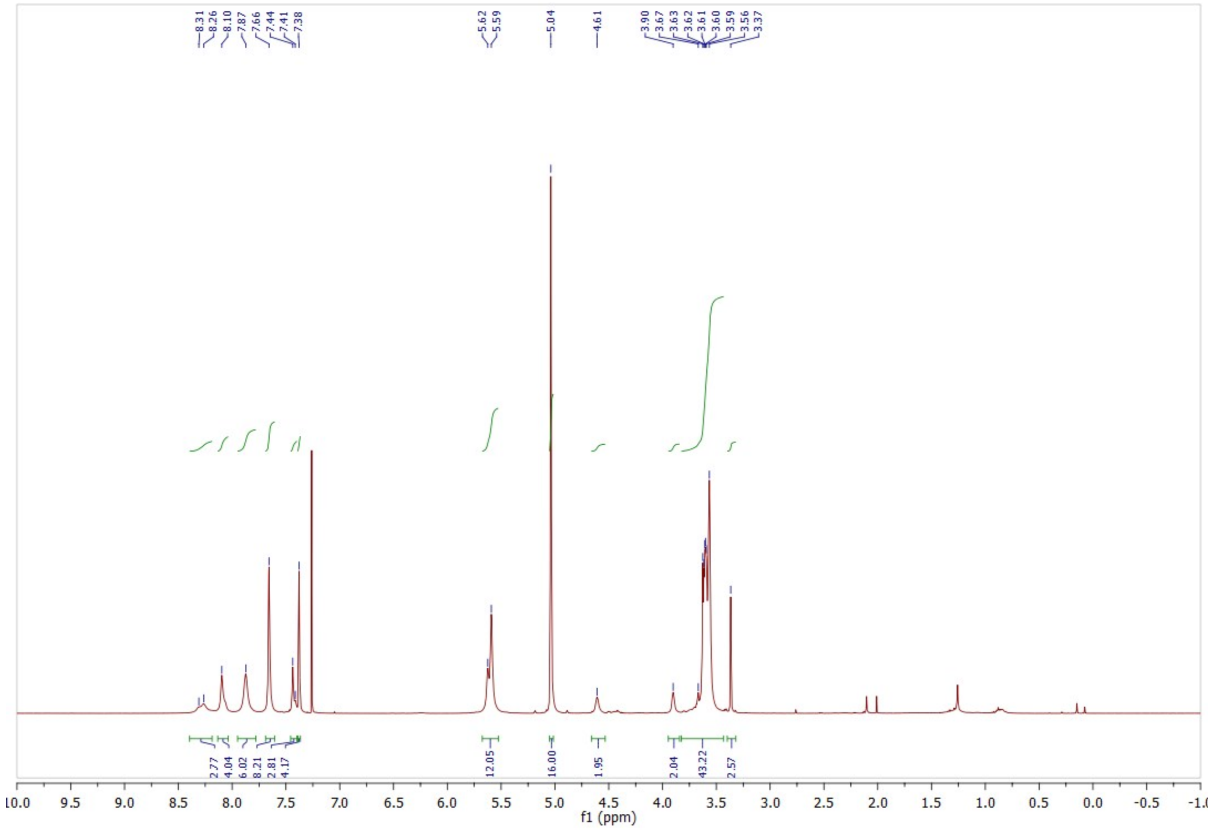

Figure S19. ^{1}H NMR ($CDCl_3$, 500 MHz) of molecule **7**.

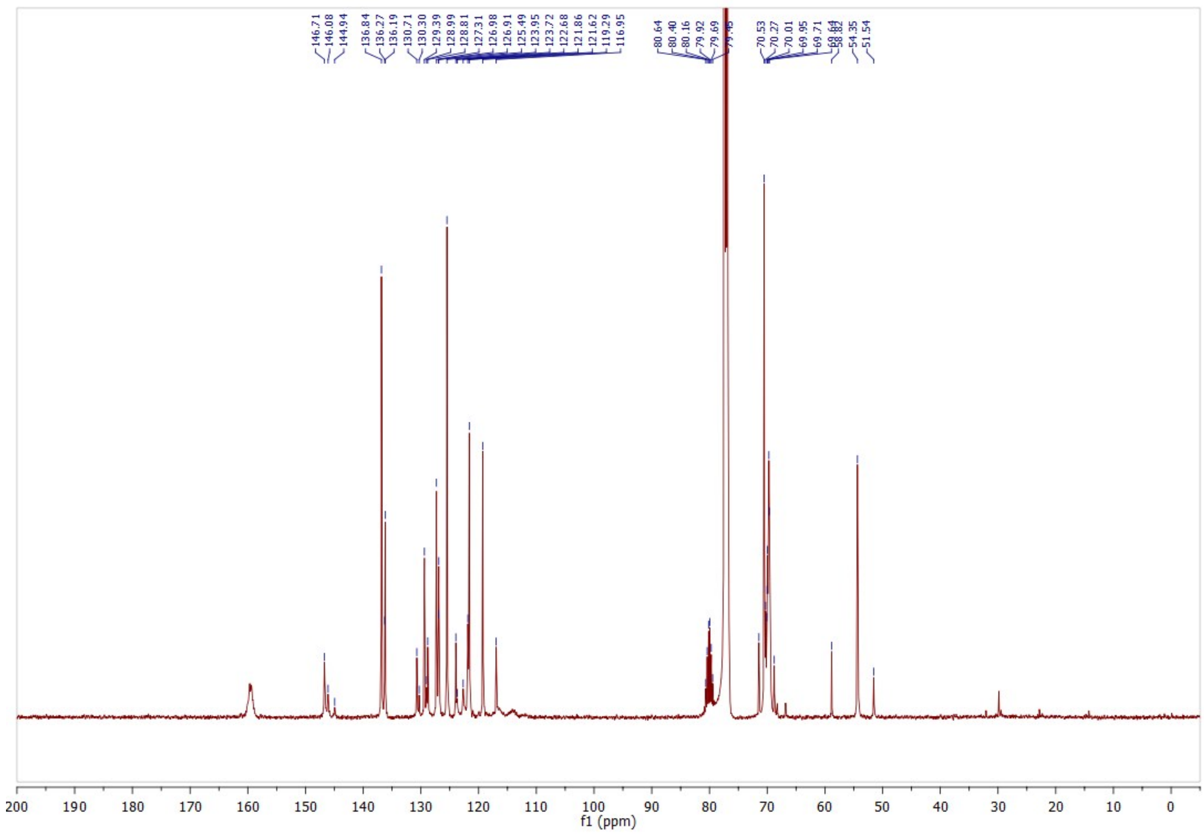

Figure S20. ^{13}C NMR ($CDCl_3$, 125 MHz) of molecule **7**.

4. Crystallographic Data

Crystal Structure Determinations

The single-crystal X-ray diffraction studies were carried out on a Bruker-Nonius Kappa-CCD diffractometer at 123(2) K using MoKα radiation ($\lambda = 0.71073$ Å). Direct methods (SHELXS-97)[2] were used for structure solution and refinement was carried out using SHELXL-97 (full-matric least-squares on F2). Non hydrogen atoms were refined anisotropically. Hydrogen atoms were localized by difference electron density determination and refined using a riding model. A semi-empirical absorption correction was applied.

1-OC(CF_3)$_3$: colourless crystals, $C_{16}H_7F_{18}IO_2$, M = 700.12, crystal size 0.36 × 0.08 × 0.04 mm, triclinic, space group P-1 (No. 2), a = 7.2087(4) Å, b = 11.5510(9) Å, c = 14.1610(8) Å, α = 68.222(5)°, β = 76.825(5)°, γ = 73.919(7)°, V = 1041.75(12) Å^3, Z = 2, ρ(calc) = 2.232 Mg m^{-3}, F(000) = 668, μ = 1.711 mm^{-1}, 13325 reflections ($2\theta_{max}$ = 55°), 4754 unique [R_{int} = 0.031], 334 parameters, $R1$ (for 4448 $I > 2\sigma(I)$) = 0.025, $wR2$ *(all data)* = 0.062, S = 1.06, largest diff. peak and hole 0.624 and –0.650 e Å^{-3}.

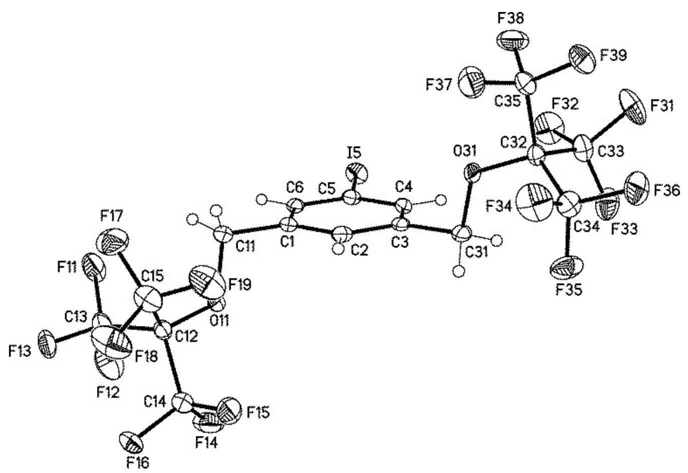

Figure S21. Molecular structure of iodide **1**-OC(CF_3)$_3$ (displacement parameters are drawn at 50% probability level).

2-H: colourless crystals, $C_{18}H_8F_{18}O_2$, M = 598.24, crystal size 0.18 × 0.06 × 0.02 mm, triclinic, space group P-1 (No. 2), a = 7.0303(4) Å, b = 11.8119(10) Å, c = 14.0402(19) Å, α = 68.704(8)°, β = 79.860(6)°, γ = 74.572(5)°, V = 1043.05(18) Å^3, Z = 2, ρ(calc) = 1.905 Mg m^{-3}, F(000) = 588, μ = 0.231 mm^{-1}, 3684 reflections ($2\theta_{max}$ = 50°), 3648 unique [R_{int}

= 0.000], 344 parameters, $R1$ (for 2620 $I > 2\sigma(I)$) = 0.068, $wR2$ *(all data)* = 0.186, S = 1.15, largest diff. peak and hole 0.468 and −0.343 e $Å^{-3}$, non-merohedral twin with 2 domains (BASF = 0.244(4), a HKLF 5 file used in the refinement).

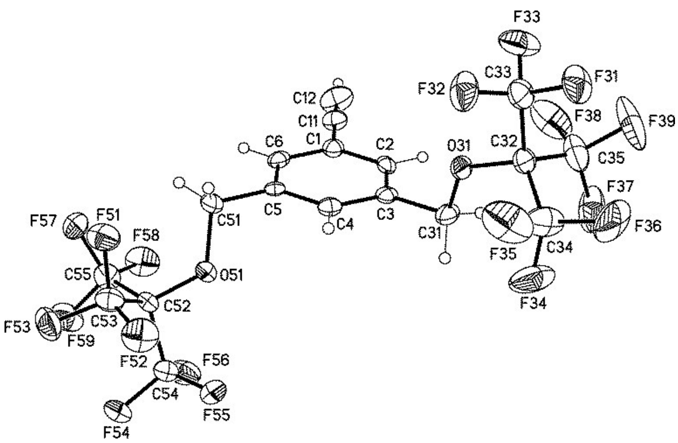

Figure S22. Molecular structure of alkyne **2**-H (displacement parameters are drawn at 50% probability level).

Crystallographic data (excluding structure factors) for the structures reported in this work have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 981372 (**1**-$OC(CF_3)_3$) and CCDC 981373 (**2**-H). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code+(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk).

5. References

1 B. Sookcharoenpinyo, E. Klein, Y. Ferrand, D. B. Walker, P. R. Brotherhood, C. Ke, M. P. Crump, A. P. Davis, *Angew. Chem.*, 2012, **124**, 4664; *Angew. Chem. Int. Ed.*, 2012, **51**, 4586.

2 G. M. Sheldrick, *Acta Cryst.*, 2008, *A64*, 112.