Supporting Information

Quadruply Hydrogen Bonding Modules as Highly Selective Nanoscale Adhesive Agents

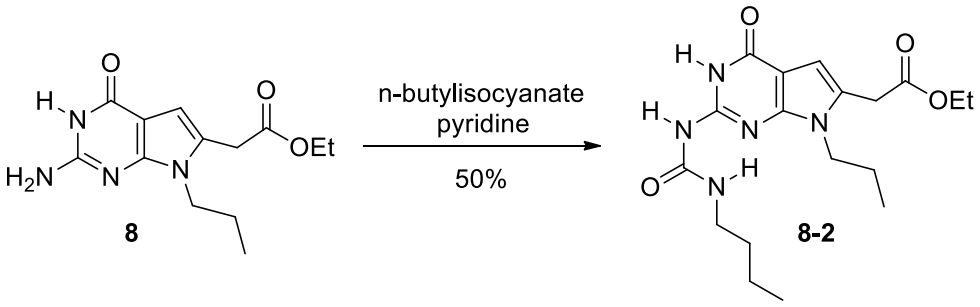
Yagang Zhang, Cyrus A. Anderson & Steven C. Zimmerman*

Department of Chemistry, 600 South Mathews Avenue,

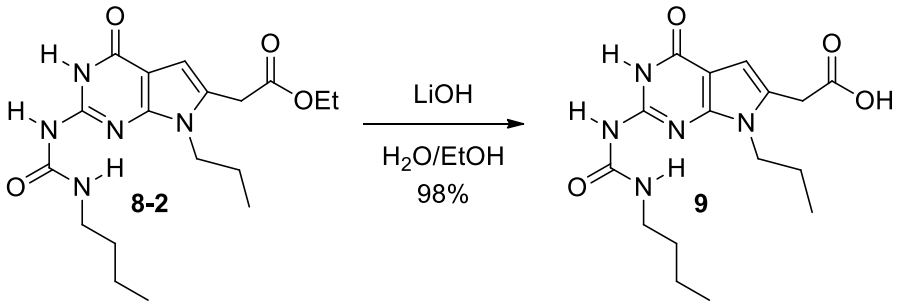
University of Illinois at Urbana-Champaign, Urbana, IL 61801

Table of Contents

Synthetic procedures

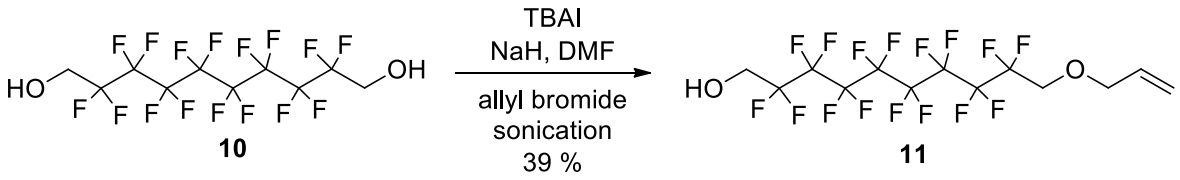


Ethyl 2-(2-(3-butylureido)-4-oxo-7-propyl-4,7-dihydro-3H-pyrrolo[2,3-d]pyrimidin-6-yl) acetate (8-2). To a stirred solution of **8** 3.37g (12.1 mmol) (**8** was synthesized according to a published procedure[Error! Bookmark not defined.]) in 60 mL pyridine was added n-butyl isocyanate 4.09 mL (36.3 mmol) via an additional funnel under N_2. The reaction was refluxed for 16h and cooled to rt. Crude product was concentrated in *vacuo* and purified by silica gel column chromatography (AcOEt:CH_2Cl_2, 1:1 v/v) to afford **7** (2.29 g, 50%) as pale white solid. mp 183-184 °C; TLC (AcOEt:CH_2Cl_2, 1:1 v/v): R_f =0.21; ^{1}H NMR (500 MHz, $CDCl_3$): δ 11.28 (s, 1H), 9.42 (s, 1H), 8.92 (bs, 1H), 6.82 (s, 1H), 4.16 (q, J = 7.0, 2H), 3.95 (t, J = 7.5, 2H), 3.71 (s, 2H), 3.45 (q, J = 6.0, 2H), 1.71-1.78 (m, 2H), 1.58-1.64 (m, 2H), 1.42-1.29 (m, 2H), 1.26 (t, J = 7.0, 3H), 0.95 (t, J = 7.0, 3H), 0.91 (t, J = 7.0, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.0, 159.2, 154.2, 148.4, 146.5, 145.5, 127.2, 103.3, 102.6, 61.5, 44.6, 40.1, 33.2, 31.9, 23.6, 20.3, 14.2, 13.9, 11.4; ESI-HR-MS calcd. for $(C_{18}H_{27}N_5O_4+H)^+$, 378.2141; found, 378.2140.

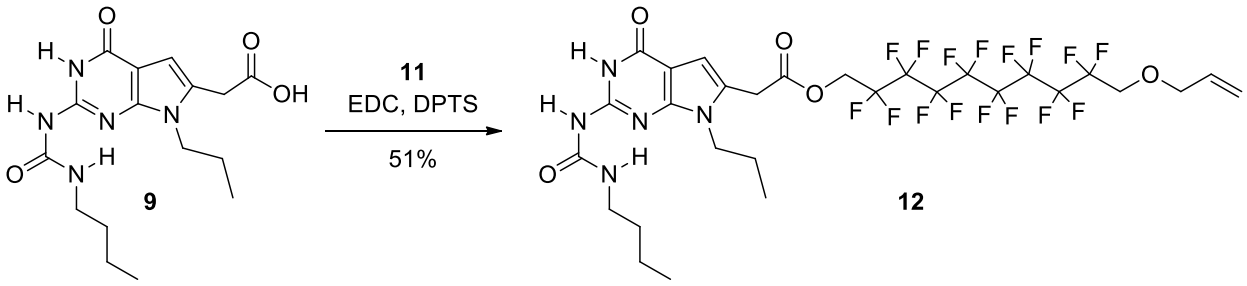


2-(2-(3-Butylureido)-4-oxo-7-propyl-4,7-dihydro-3H-pyrrolo[2,3-d]pyrimidin-6-yl)acetic acid (9). To **8-2** 0.660 g (1.75 mmol) was added 24 mL of a (1:1 v/v) mixture of 10% aqueous LiOH/ethanol and was stirred at room temperature for 2 h. The reaction mixture was neutralized via drop wise addition of ice cold 2 N aqueous HCl, the resulting solid was filtered and washed

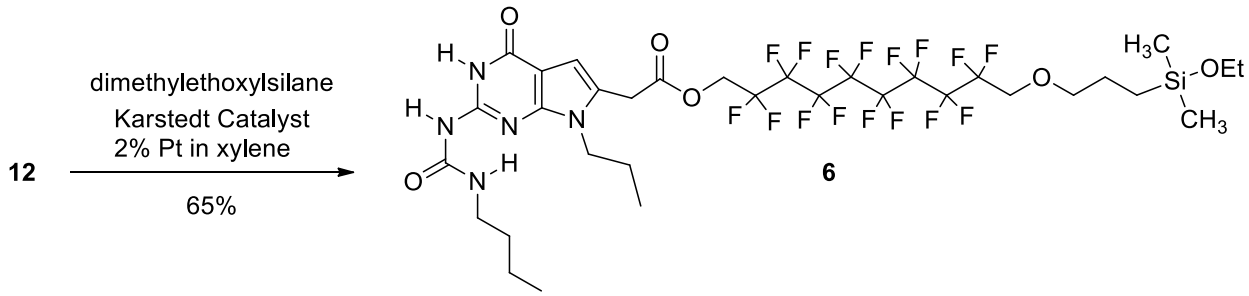
with 70 mL ice cold water 20 mL ice cold ethanol, dried under high vacuum pump. to afford **9** (0.600 g, 98%) as yellow liquid. mp 198-199 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ 12.58 (bs, 1H), 11.41 (s, 1H), 8.32 (s, 1H), 7.16 (s, 1H), 6.24 (s, 1H), 3.89 (q, J = 7.5, 2H), 3.70 (s, 2H), 3.15 (q, J = 6.0, 2H), 1.62-1.68 (m, 2H), 1.42-1.47 (m, 2H), 1.29-1.35 (m, 2H), 0.90 (t, J = 7.0, 3H), 0.84 (t, J = 7.5, 3H), 0.91 (t, J = 7.5, 3H); ^{13}C NMR (126 MHz, DMSO-d_6): δ 171.5, 147.9, 147.7, 127.4, 101.8, 101.5, 43.6, 38.7, 32.3, 31.3, 23.0, 19.4, 13.6, 11.1; ESI-HR-MS calcd. for $(C_{16}H_{23}N_5O_4+H)^+$, 350.1828; found, 350.1834.



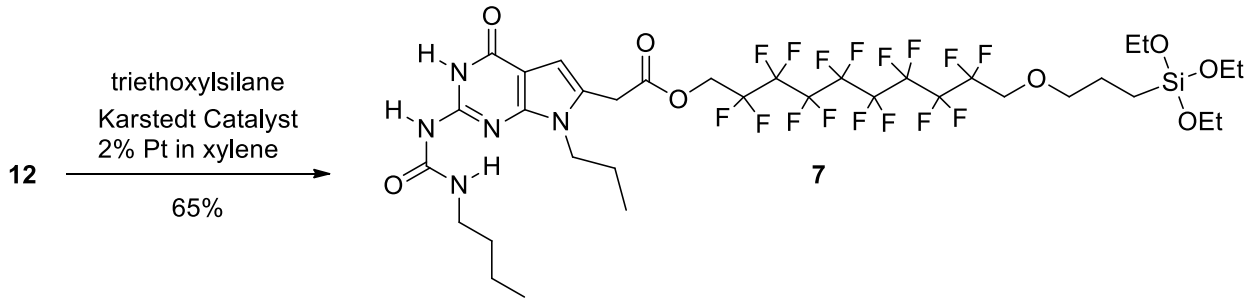
10-(Allyloxy)-2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9-hexadecafluorodecan-1-ol (11) To a stirred solution of 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9-hexadecafluoro-1,10-decanediol **10** (3.00g, 6.49 mmol) in 30 mL anhydrous DMF in a Schlenk flask under argon was added sodium hydride (60% in mineral oil, 0.336 g, 8.40 mmol). After the reaction mixture was sonicated for 10 min, ally bromide (0.728 mL, 8.40 mmol) and tetrabutylammonium iodide (1.20 g, 3.25 mmol) was added. The reaction was sonicated under argon at ambient temperature for 3 h. The solvent was removed in *vacuo* and the residue was taken up in 40 mL 5% HCl. The solution was extracted with ethyl acetate (3 × 50 mL). Combined organic layer was washed with 0.2 M $Na_2S_2O_3$ (2 × 20 mL) and brine (30 mL). The organic layer was dried over sodium sulfate, concentrated in *vacuo* and purified by silica gel column chromatography (AcOEt:petroleum ether, 1:4 v/v) to afford **11** (1.27 g, 39%) as a white solid. mp 32-33 °C; TLC (AcOEt:petroleum ether, 1:4 v/v): R_f =0.60 ($KMnO_4$ stains); ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.84-5.92 (m, 1H), 5.26-5.34 (m, 2H), 4.13 (d, J = 6.0, 2H), 4.07 (t, J = 14.0, 2H), 3.92 (t, J = 14.0, 2H), 2.61 (bs, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 133.1, 118.9, 118.9, 116.1, 115.9, 115.7, 113.8, 113.6, 111.2, 111.1, 73.6, 66.9, 66.7, 66.5, 60.9, 60.7, 60.5; ESI-HR-MS calcd. for $(C_{13}H_{10}F_{16}O_2+Na)^+$, 525.0323; found, 525.0329.



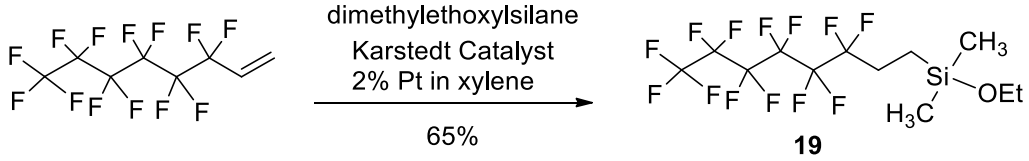
10-(Allyloxy)-2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9-hexadecafluorodecyl 2-(2-(3-butylureido)-4-oxo-7-propyl-4,7-dihydro-3H-pyrrolo[2,3-d]pyrimidin-6-yl)acetate (12). To a solution **9** 0.150 g (0.429 mmol) in 15 mL of dichloromethane was added **11** 0.216g (0.429 mmol) and 4-(dimethylamino)pyridinium 4-toluenesulfonate (DPTS, was synthesized according to a published procedure[1]) 0.060g (0.206 mmol). The reaction mixture was stirred for 15 min and 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) 0.107 g (0.558 mmol) was added. The reaction mixture was heated to reflux for 14 h. The flask was cooled to rt and the solution was diluted with 60 mL CH_2Cl_2 and was washed with water (3 × 20 mL), saturated aqueous sodium bicarbonate (20 mL), and brine (20 mL). The organic layer was dried over sodium sulfate, concentrated in *vacuo* and purified by silica gel column chromatography (MeOH:CH_2Cl_2, 1:9 v/v) to afford **12** (0.183 g, 51%) as slightly yellow solid. mp 98-100 °C; TLC (MeOH:CH_2Cl_2, 1:9 v/v): R_f =0.37; ^{1}H NMR (500 MHz, $CDCl_3$): δ 11.29 (s, 1H), 9.43 (s, 1H), 8.91 (bs, 1H), 6.89 (s, 1H), 5.83-5.91 (m, 1H), 5.25-5.34 (m, 2H), 4.71 (t, J = 14.0, 2H), 4.13 (d, J = 5.5, 2H), 3.92 (t, J = 14.0, 4H), 3.84 (s, 2H), 3.44 (q, J = 6.0, 2H), 1.73-1.77 (m, 2H), 1.59-1.65 (m, 2H), 1.44-1.48 (m, 2H), 0.96 (t, J = 7.5, 3H), 0.92 (t, J = 7.5, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 168.6, 159.3, 154.1, 148.6, 146.8, 133.2, 125.8, 118.8, 110.9, 103.9, 102.6, 73.5, 66.9, 66.7, 66.5, 60.3, 60.1, 59.9, 44.7, 40.1, 32.3, 31.9, 23.6, 20.4, 13.9, 11.4; ESI-HR-MS calcd. for $(C_{29}H_{31}N_5O_5F_{16}+H)^+$, 834.2148; found, 834.2144.



10-(3-(Ethoxydimethylsilyl)propoxy)-2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9-hexadecafluorodecyl 2-(2-(3-butylureido)-4-oxo-7-propyl-4,7-dihydro-3H-pyrrolo[2,3-d]pyrimidin-6-yl)acetate (6). To a 10 mL pear shaped flask with **12** 0.150 g (0. 180 mmol) was added dimethylethoxysilane 3.60 mL (24.8 mmol) and 24.0 µL Karstedt catalyst (Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution in xylene, Pt ~2 %). The reaction mixture was refluxed with stirring for 8 h. The open end of condensing column was equipped with a drying tube to prevent any moisture get into the flask. After the reaction, the excessive amount of dimethylethoxysilane was removed under high vacuum (~0.3 mm Hg) at 50°C and the crude product was further dried in *vacuo* and purified by silica gel column chromatography ($MeOH:CH_2Cl_2$, 5:95 v/v) to afford **6** (0.127 g, 75%) as pale white solid. TLC ($MeOH:CH_2Cl_2$, 5:95 v/v): R_f =0.27; ^1H NMR (500 MHz, $CDCl_3$): δ 11.29 (s, 1H), 9.43 (s, 1H), 8.91 (bs, 1H), 6.89 (s, 1H), 4.68 (t, J = 14.0, 2H), 3.92 (t, J = 14.0, 2H), 3.92 (t, J = 10.0, 2H), 3.85 (s, 2H), 3.65 (q, J = 7.0, 2H), 3.56 (t, J = 7.0, 2H), 3.45 (q, J = 7.0, 2H), 1.73-1.78 (m, 2H), 1.58-1.68 (m, 4H), 1.44-1.49 (m, 2H), 1.18 (t, J = 7.0, 3H), 0.95 (t, J = 7.5, 3H), 0.92 (t, J = 7.5, 3H), 0.60 (t, J = 8.5, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 168.6, 159.3, 154.1, 148.6, 146.8, 125.8, 113.7, 111.1, 103.9, 102.6, 75.9, 68.1, 67.9, 60.1, 58.4, 44.7, 40.1, 32.4, 31.9, 23.6, 23.4, 20.4, 18.6, 13.9, 12.2, 11.4, -2.1; ESI-HR-MS calcd. for $(C_{33}H_{43}N_5O_6F_{16}Si+H)^+$, 938.2805; found, 938.2781.



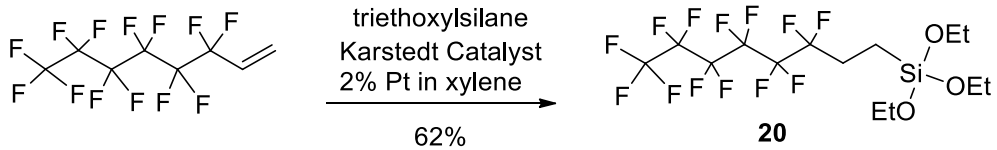
2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9-Hexadecafluoro-10-(3-(triethoxysilyl)propoxy)decyl 2-(2-(3-butylureido)-4-oxo-7-propyl-4,7-dihydro-3H-pyrrolo[2,3-d]pyrimidin-6-yl)acetate (**7**). To a 10 mL pear shaped flask with **12** 0.150 g (0.180 mmol) was added triethoxysilane 3.2 mL (16.5 mmol) and 24.0 µL Karstedt catalyst (Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution in xylene, Pt ~2 %). The reaction mixture was heated with stirring at 76°C for 24 h. The open end of condensing column was equipped with a drying tube to prevent any moisture get into the flask. After the reaction, the excessive amount of triethoxysilane was removed under high vacuum (~0.3 mm Hg) at 50°C and the crude product was further dried in *vacuo* and purified by silica gel column chromatography (MeOH:CH_2Cl_2, 5:95 v/v) to afford **7** (0.117 g, 65%) as grey white solid. TLC (MeOH:CH_2Cl_2, 5:95 v/v): R_f =0.31; ^{1}H NMR (500 MHz, $CDCl_3$): δ 11.28 (s, 1H), 9.43 (s, 1H), 8.90 (bs, 1H), 6.89 (s, 1H), 4.68 (t, J = 14.0, 2H), 3.93 (t, J = 14.0, 2H), 3.92 (t, J = 10.5, 2H), 3.85 (s, 2H), 3.85 (q, J = 7.0, 6H), 3.57 (t, J = 6.5, 2H), 3.45 (q, J = 7.0, 2H), 1.69-1.78 (m, 4H), 1.59-1.64 (m, 2H), 1.44-1.49 (m, 2H), 1.22 (t, J = 7.0, 9H), 0.95 (t, J = 7.5, 3H), 0.93 (t, J = 7.5, 3H), 0.65 (t, J = 8.5, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 168.6, 159.3, 154.1, 148.6, 146.8, 125.7, 111.1, 104.0, 102.6, 75.3, 68.1, 67.9, 60.4, 60.2, 58.5, 44.7, 40.1, 32.4, 31.9, 23.6, 23.1, 22.9, 20.4, 18.4, 13.9, 11.4, 6.3; ESI-HR-MS calcd. for $(C_{35}H_{47}N_5O_8F_{16}Si+H)^+$, 998.3017; found, 998.3012.



19

Ethoxydimethyl(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silane (19). To a 10 mL pear shaped flask with 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-octene 0.800 mL (3.00 mmol) was added dimethylethoxysilane 1.76 mL (12.0 mmol) and 36.0 µL Karstedt catalyst (Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution in xylene, Pt ~2 %). The reaction mixture was refluxed with stirring for 18 h. The open end of condensing column was equipped with a drying tube to prevent any moisture get into the flask. After the reaction, the crude was dissolved in 20 mL CH_2Cl_2 and filtered. The solvent was removed in *vacuo* and the product was kept under high vacuum (~0.3 mm Hg) for 4 h to afford **19** (0.876 g, 65%) as clear colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.75 (q, J = 7.0, 2H), 2.07 (m, 2H), 1.21 (t, J = 7.0, 2H),

0.80 (m, 2H), 0.10 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 58.6, 57.9, 25.4, 18.5, 7.6, 6.0, 1.1, 0.0, -0.9, -2.2.



20

Triethoxy(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silane (20). To a 10 mL pear shaped flask with 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-octene 0.800 mL (3.00 mmol) was added triethoxysilane 0.698 mL (3.60 mmol) and 36.0 µL Karstedt catalyst (Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution in xylene, Pt ~2 %). The reaction mixture was heated with stirring at 82°C for 9 h. The open end of condensing column was equipped with a drying tube to prevent any moisture get into the flask. After the reaction, the crude was dissolved in 25 mL CH_2Cl_2 and filtered. The solvent was removed in *vacuo* and the product was kept under high vacuum (~0.3 mm Hg) for 4 h to afford **20** (0.948 g, 62%) as clear colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.85 (q, J = 7.0, 6H), 2.12-2.15 (m, 2H), 1.22 (t, J = 7.0, 9H), 0.81-0.85 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 59.3, 58.9, 25.3, 25.1, 18.3, 18.1, 9.2, 0.64.

^{1}H and ^{13}C NMR Spectra

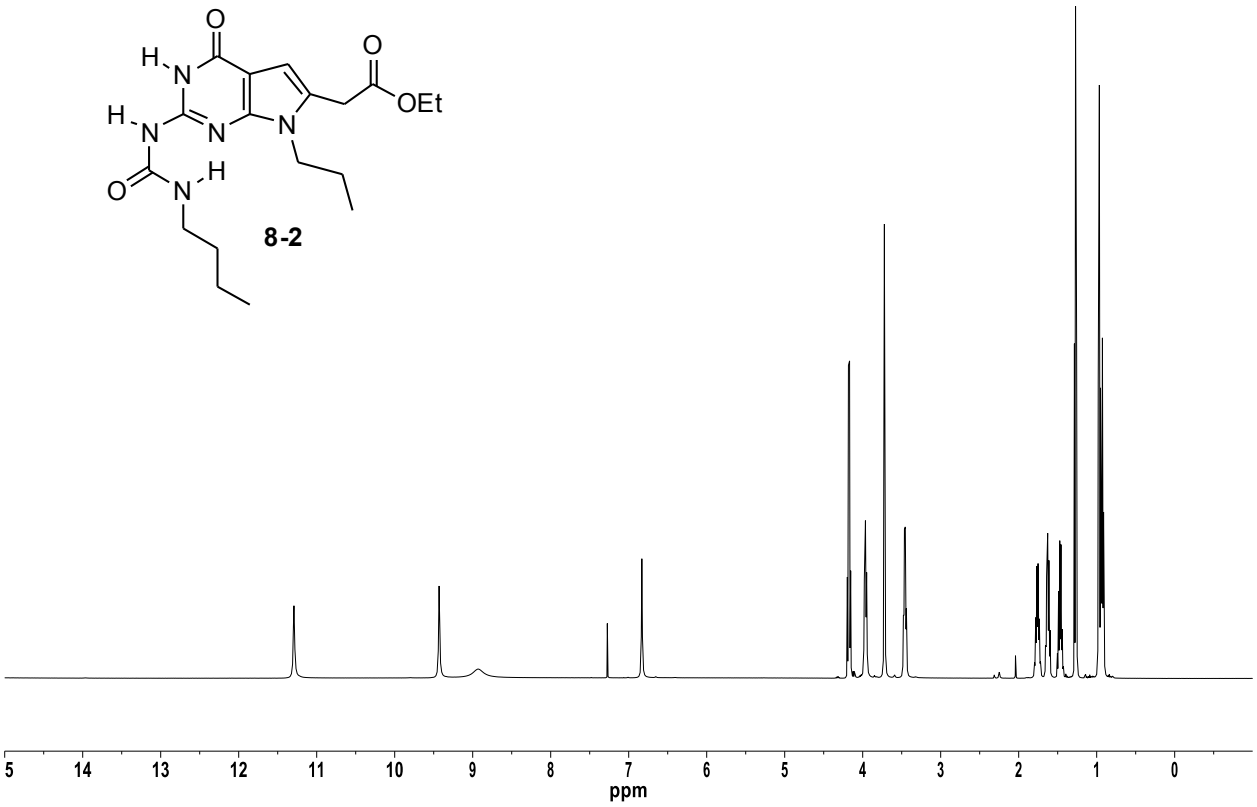


Figure S1 | Compound **8-2**, ^{1}H NMR (500 MHz, $CDCl_3$)

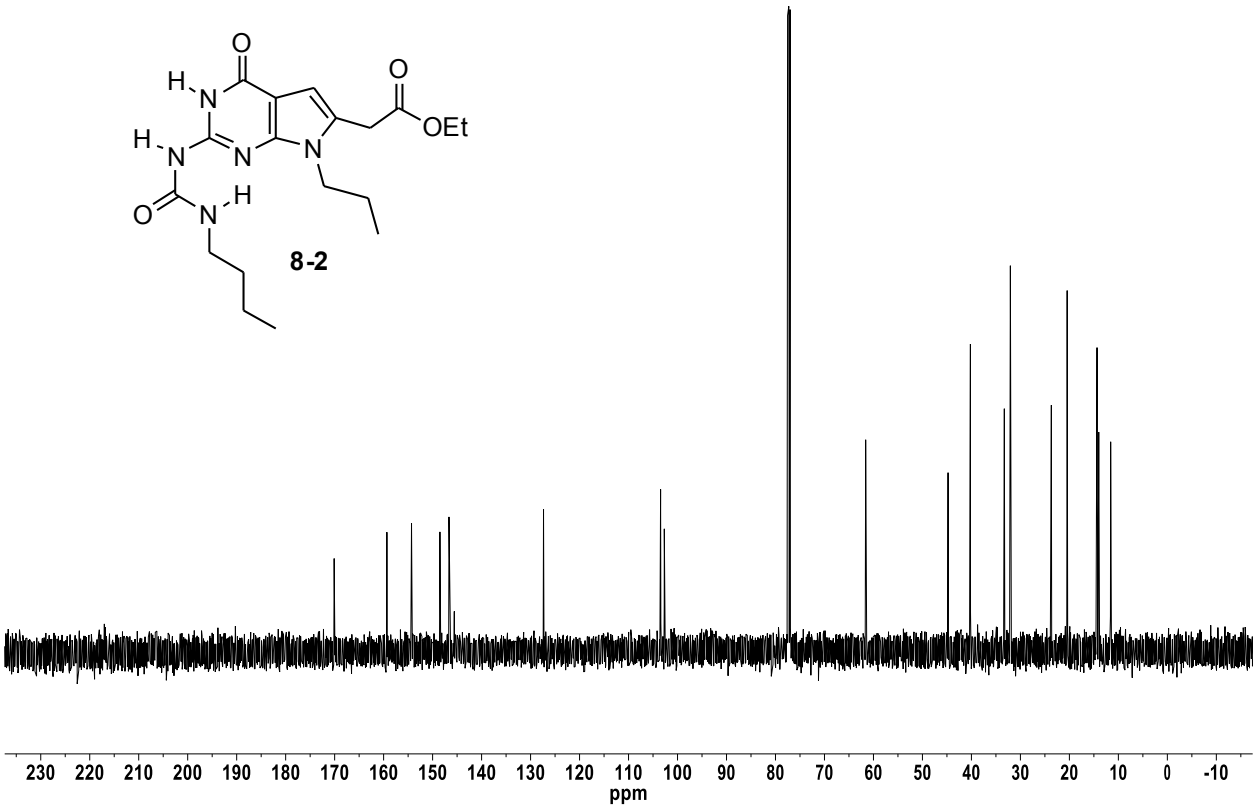


Figure S2 | Compound **8-2**, ^{13}C NMR (126 MHz, $CDCl_3$)

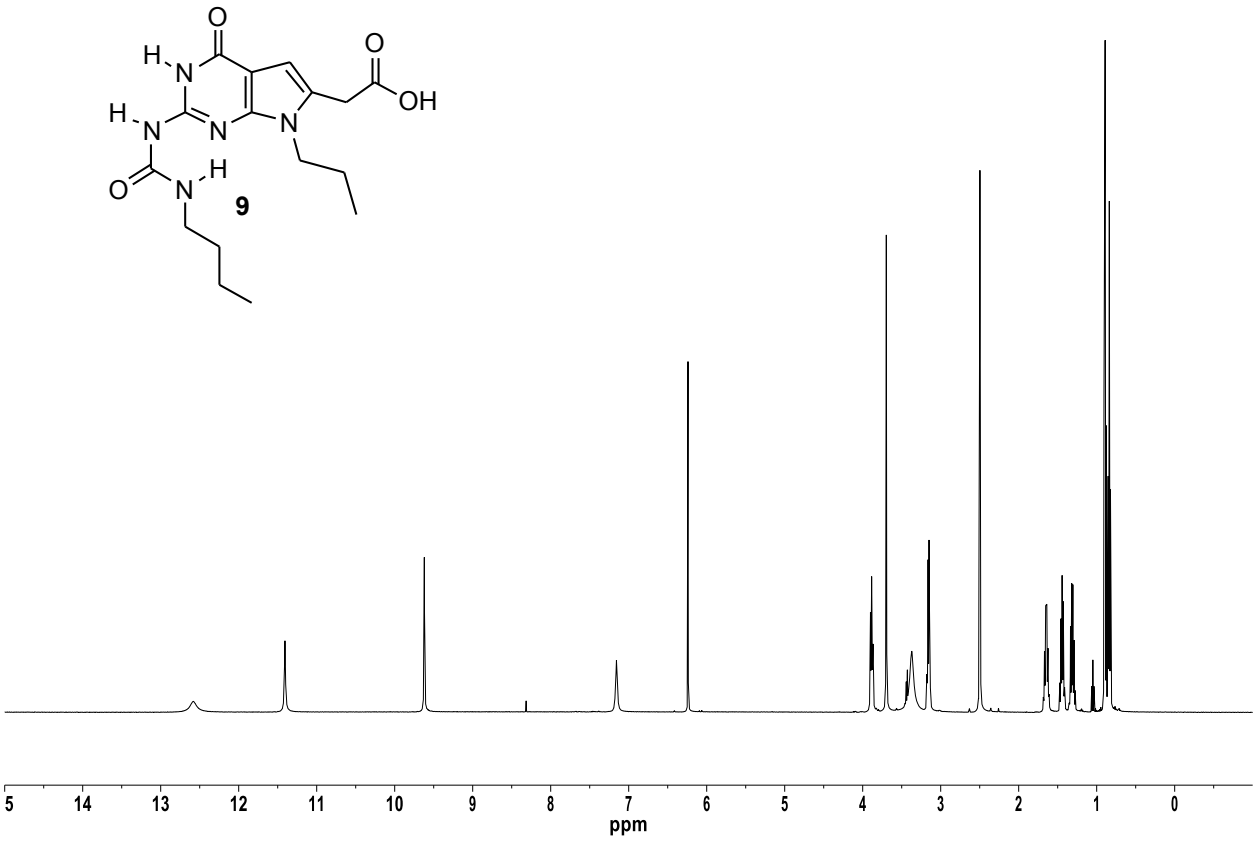


Figure S3 | Compound **9**, ^{1}H NMR (500 MHz, DMSO-d_6)

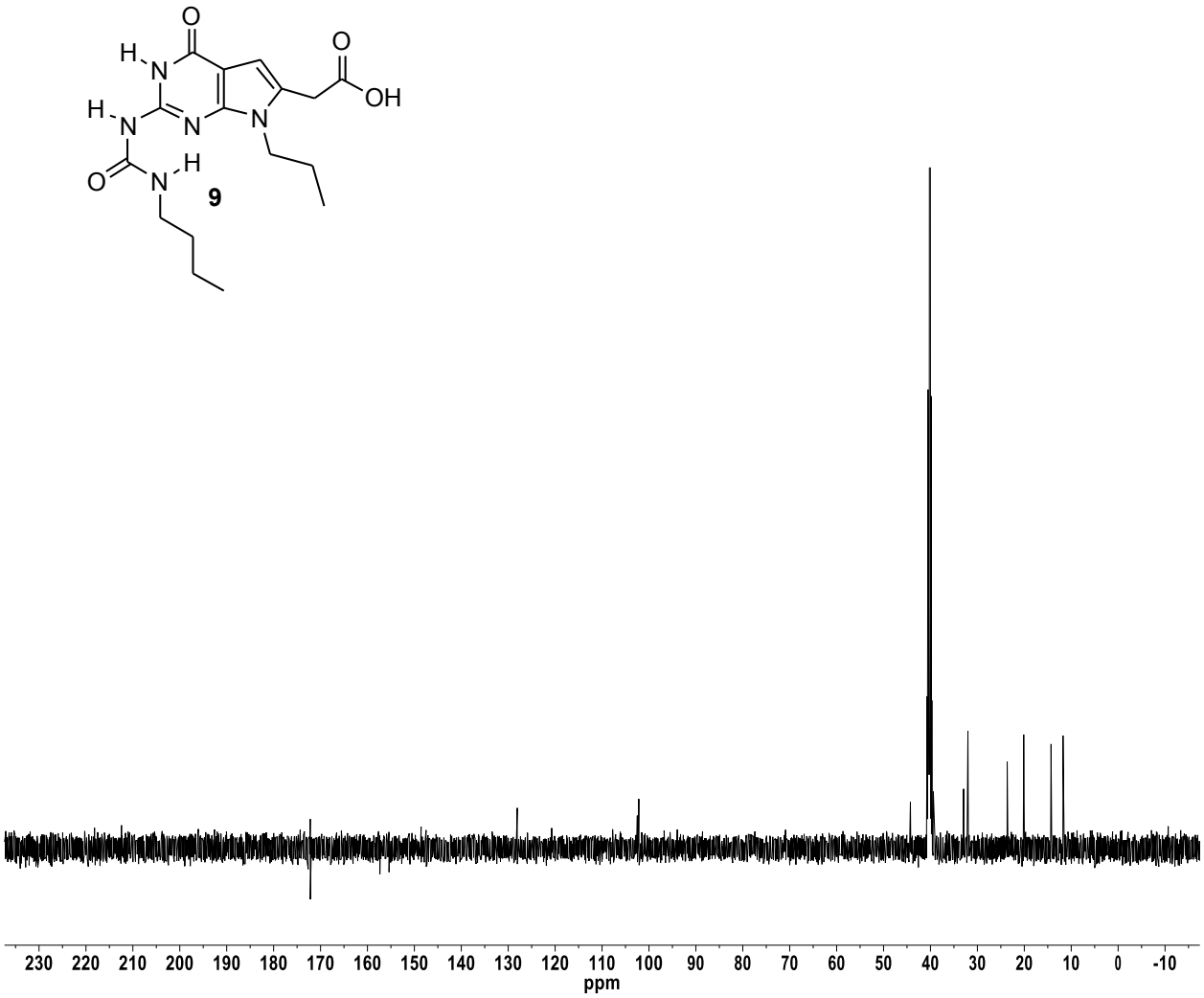


Figure S4 | Compound **9**, ^{13}C NMR (126 MHz, DMSO-d_6)

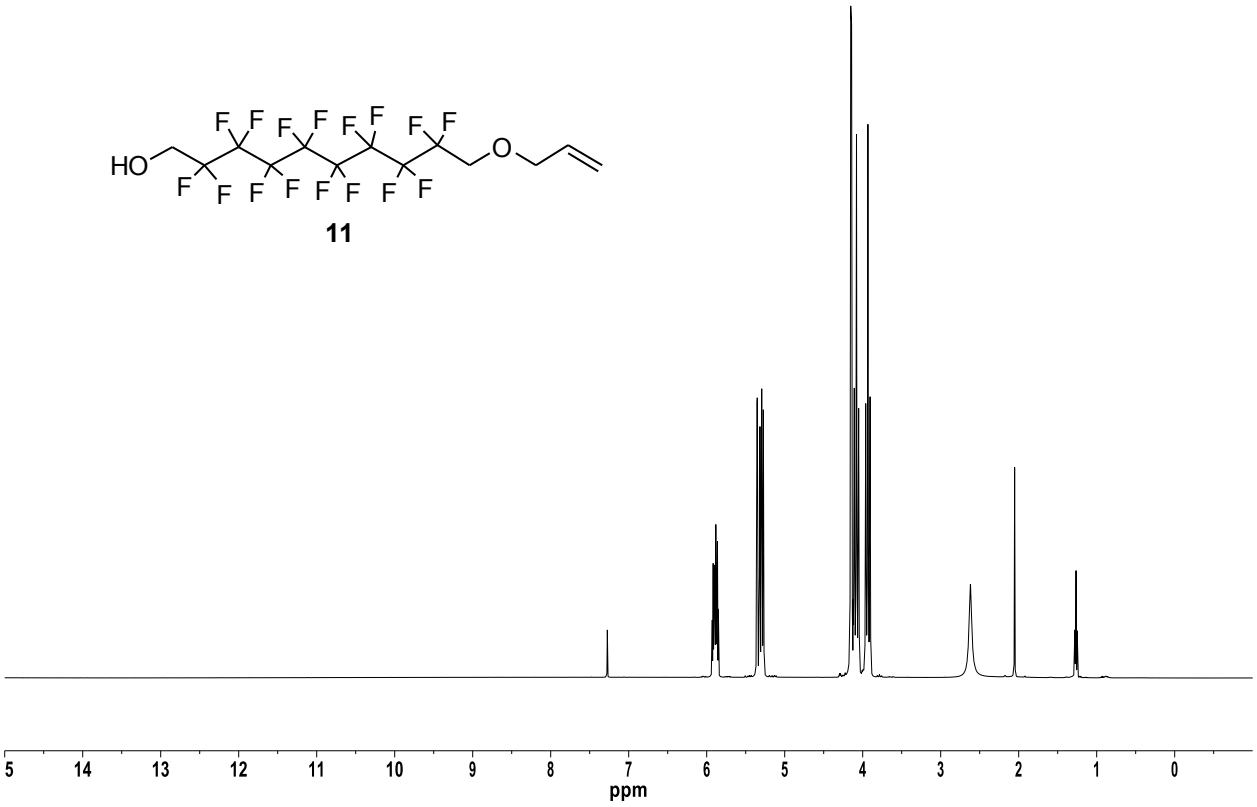


Figure S5 | Compound **11**, ^{1}H NMR (500 MHz, $CDCl_3$)

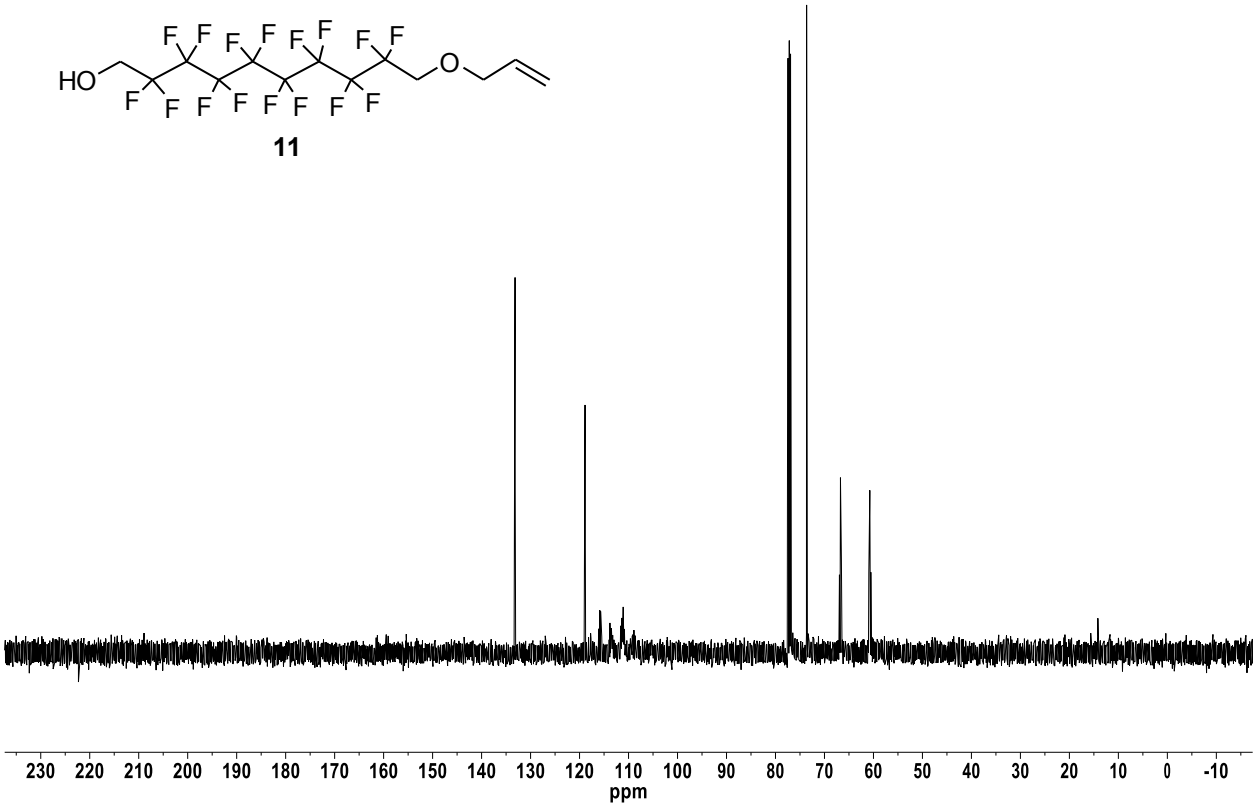


Figure S6 | Compound **11**, ^{13}C NMR (126 MHz, $CDCl_3$)

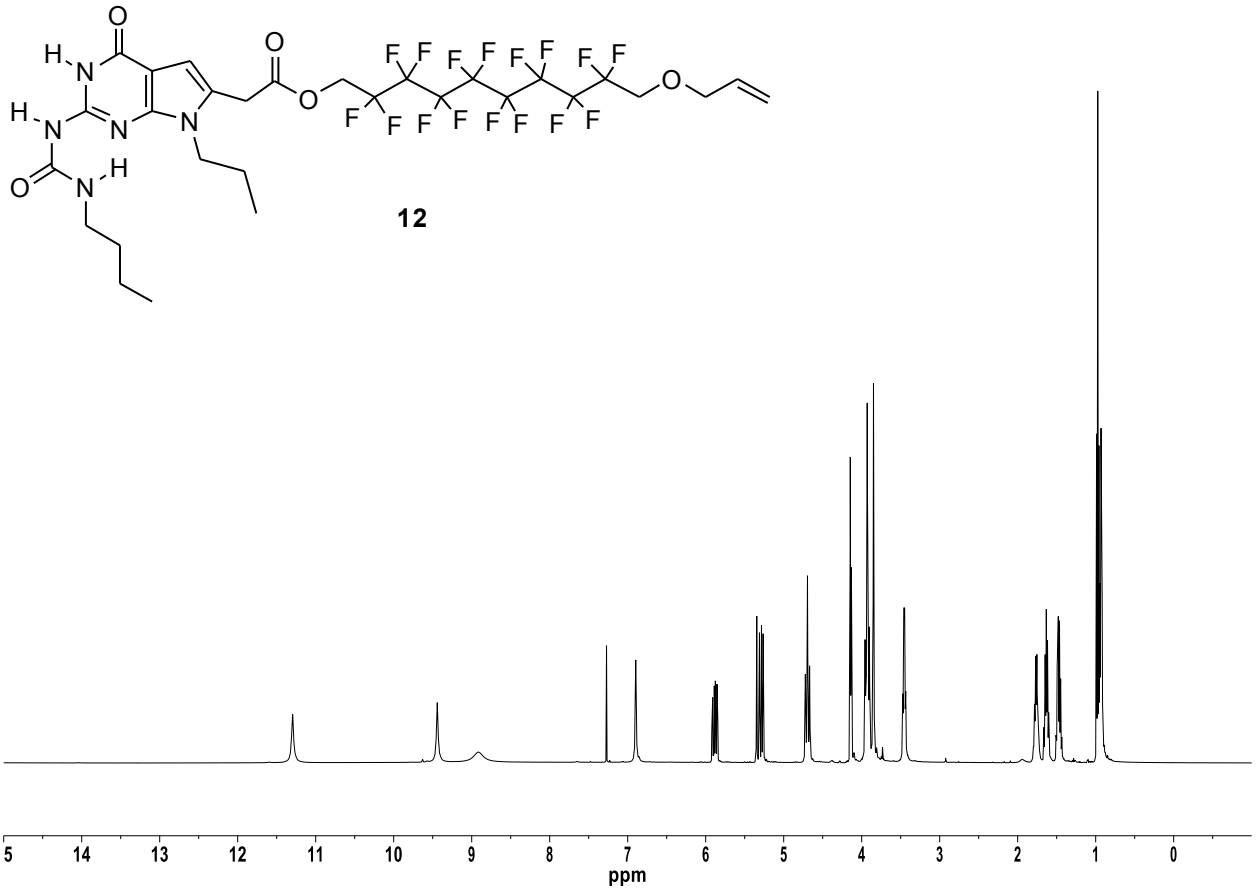


Figure S7 | Compound **12**, ^{1}H NMR (500 MHz, $CDCl_3$)

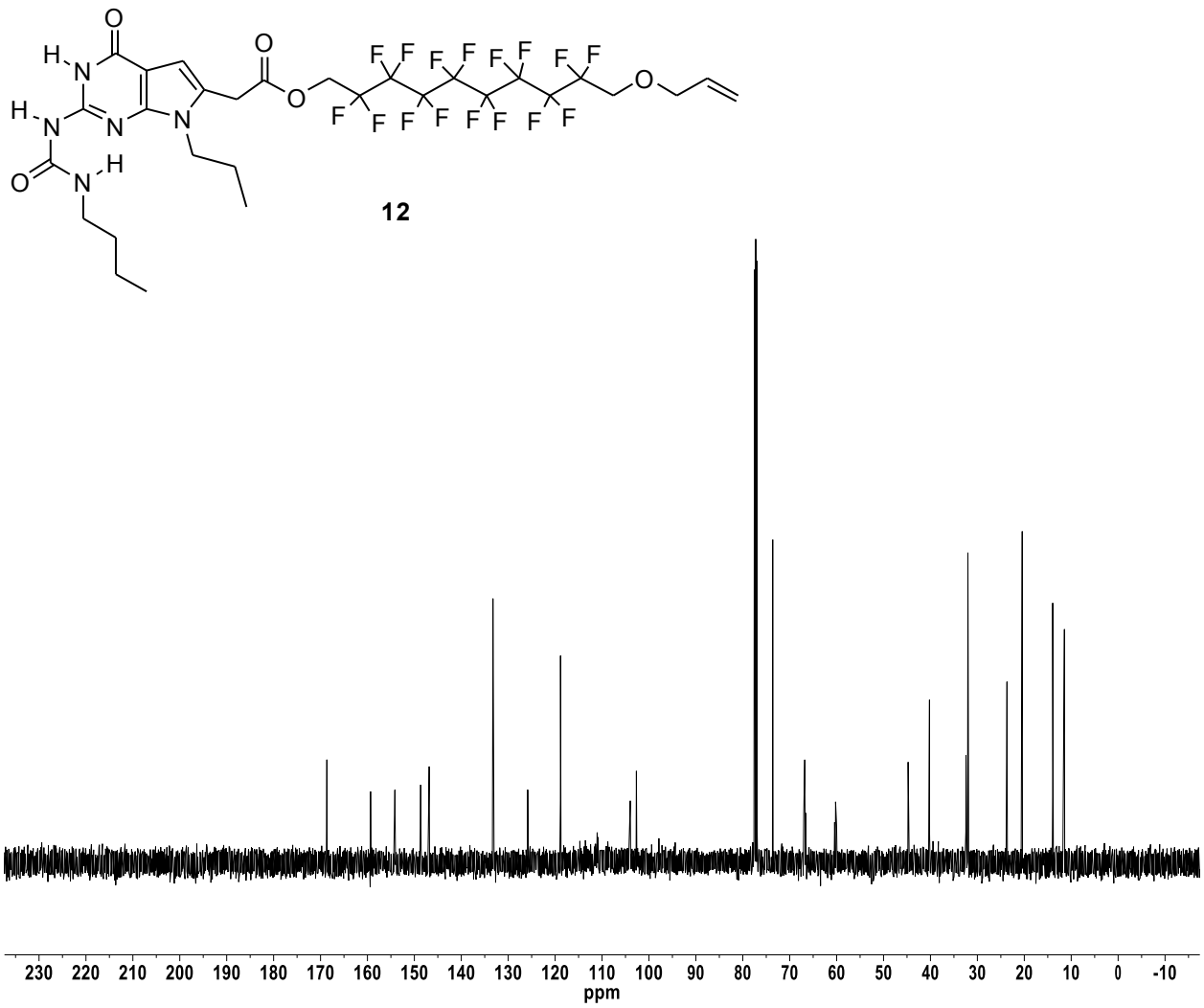


Figure S8 | Compound **12**, ^{13}C NMR (126 MHz, $CDCl_3$)

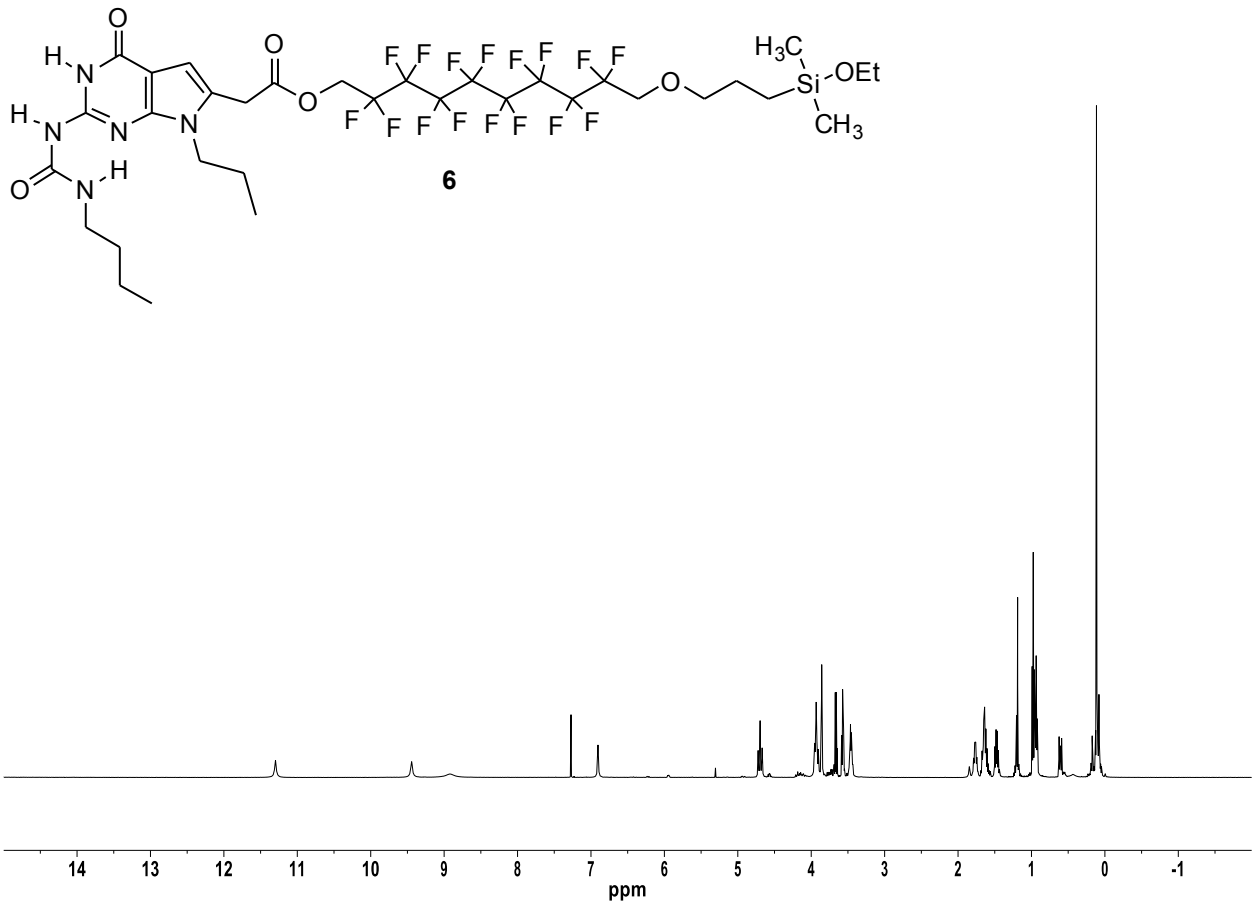


Figure S9 | Compound **6**, ^{1}H NMR (500 MHz, $CDCl_3$)

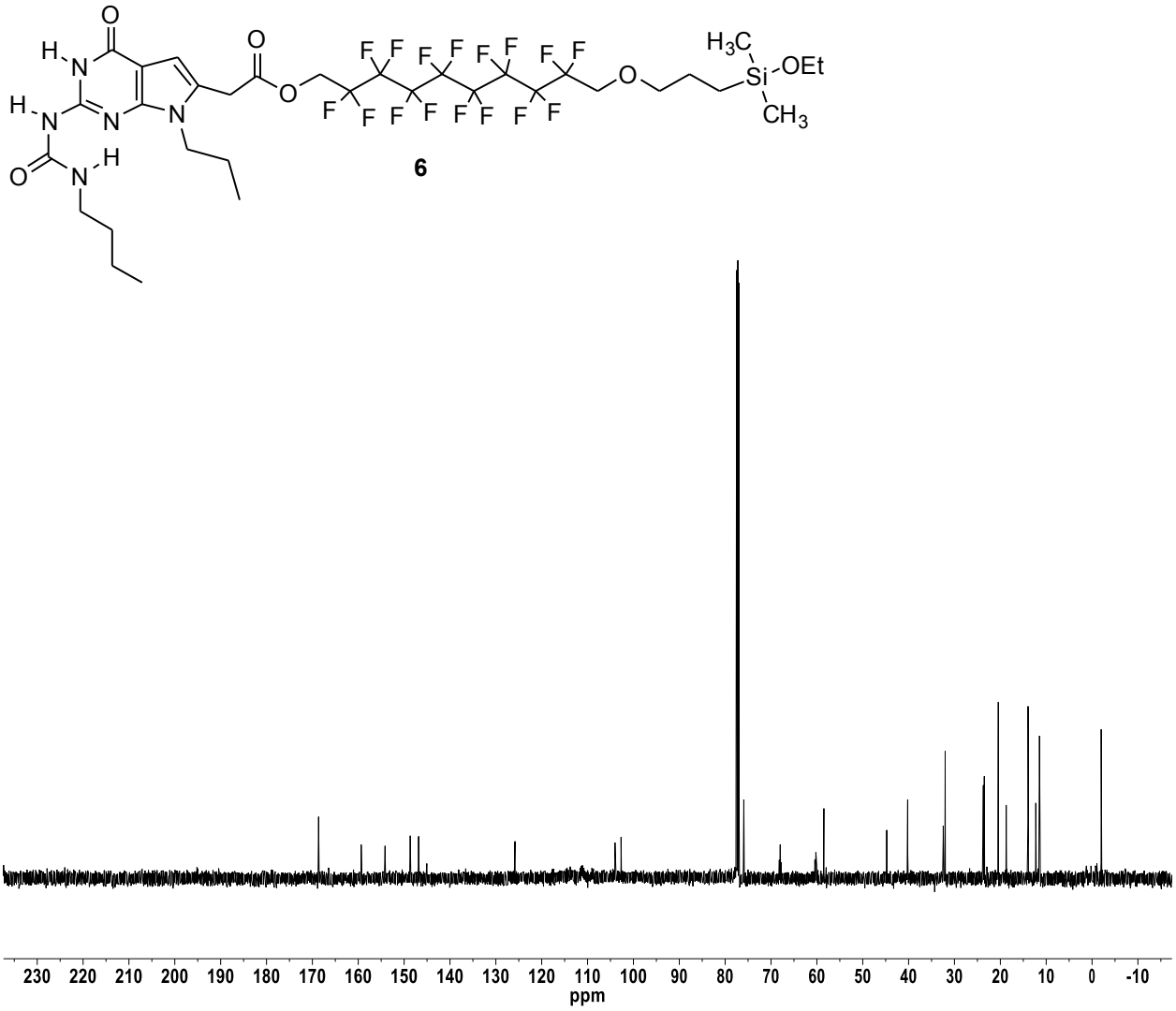


Figure S10 | Compound **6**, ^{13}C NMR (126 MHz, $CDCl_3$)

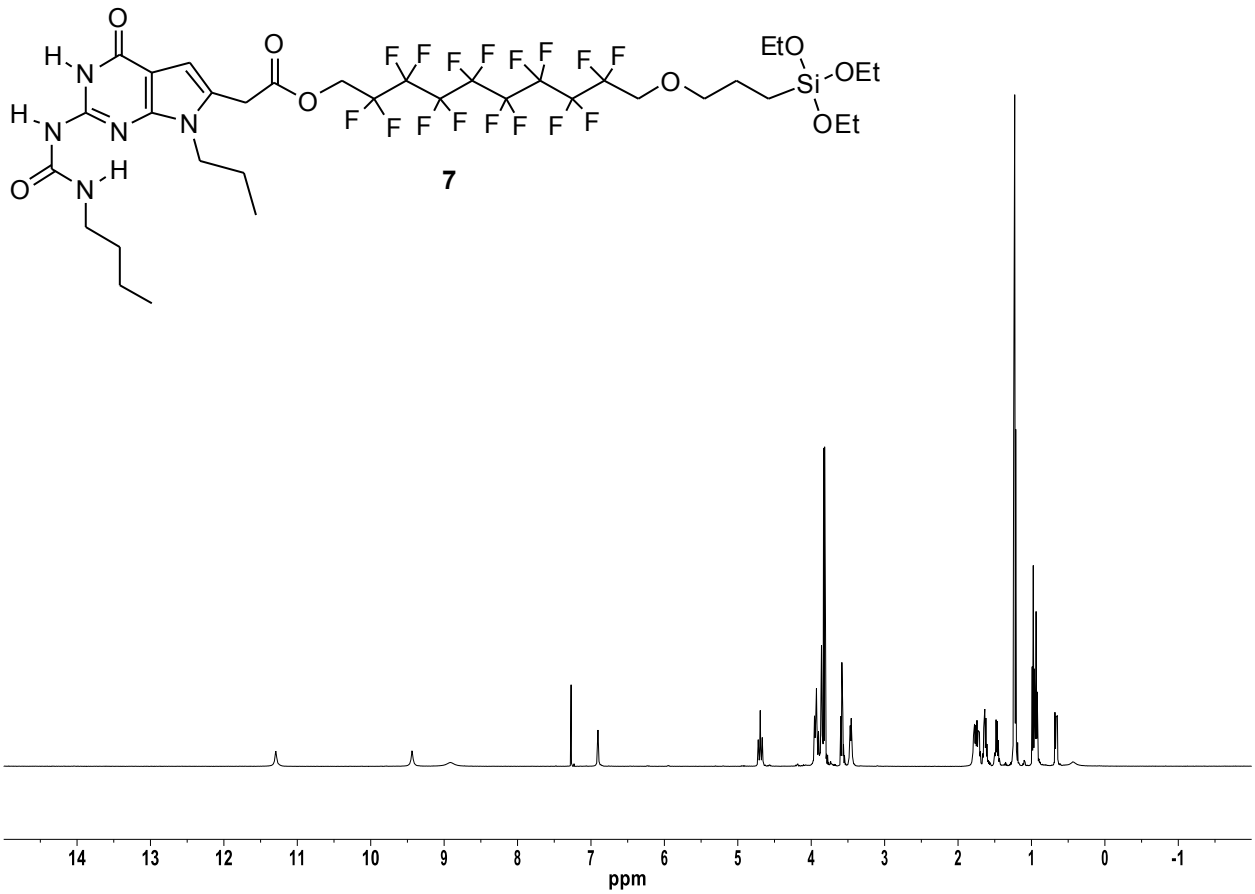


Figure S11 | Compound **7**, ^{1}H NMR (500 MHz, $CDCl_3$)

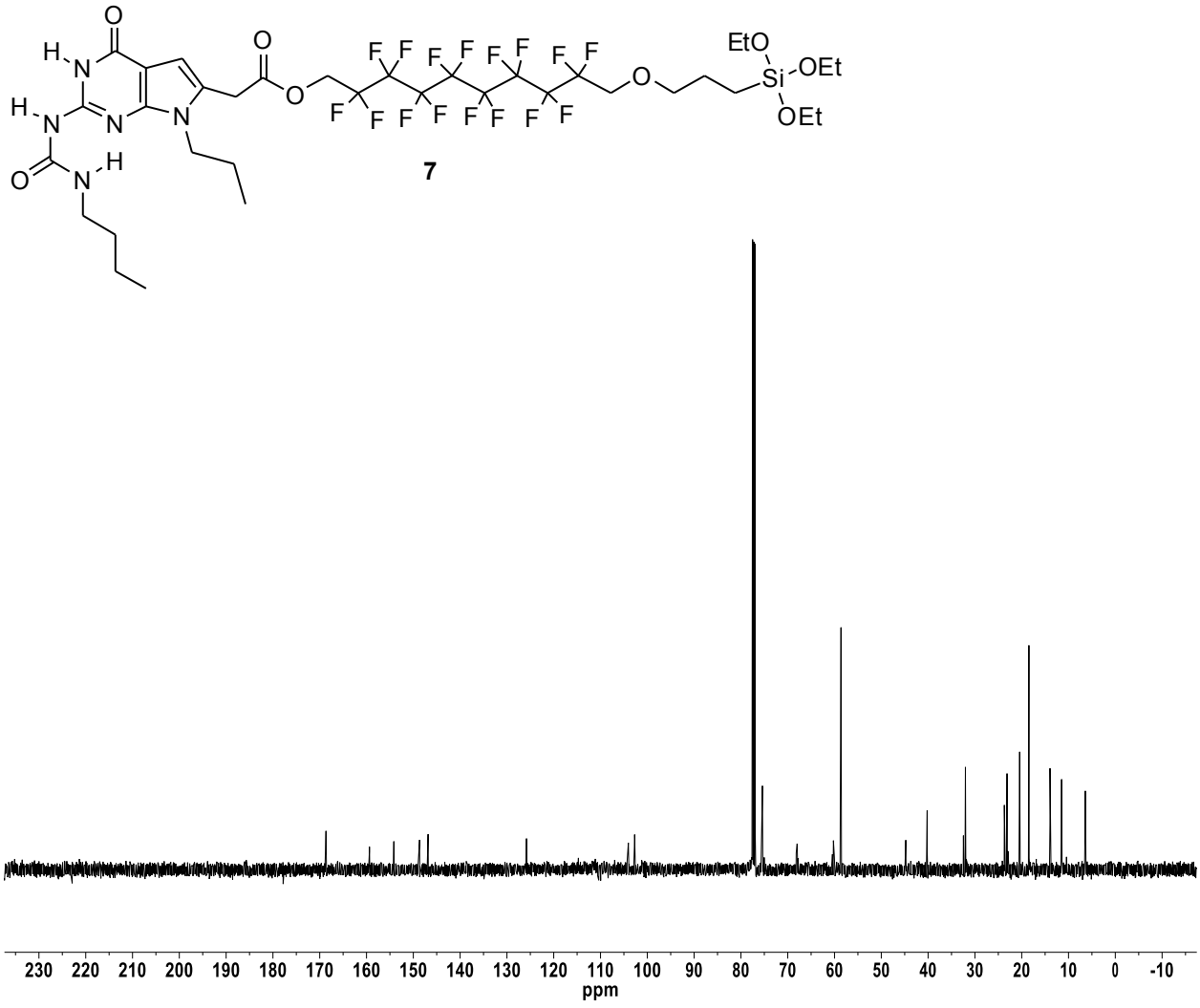


Figure S12 | Compound **7**, ^{13}C NMR (126 MHz, $CDCl_3$)

Elemental composition report of HR-ESI-MS.

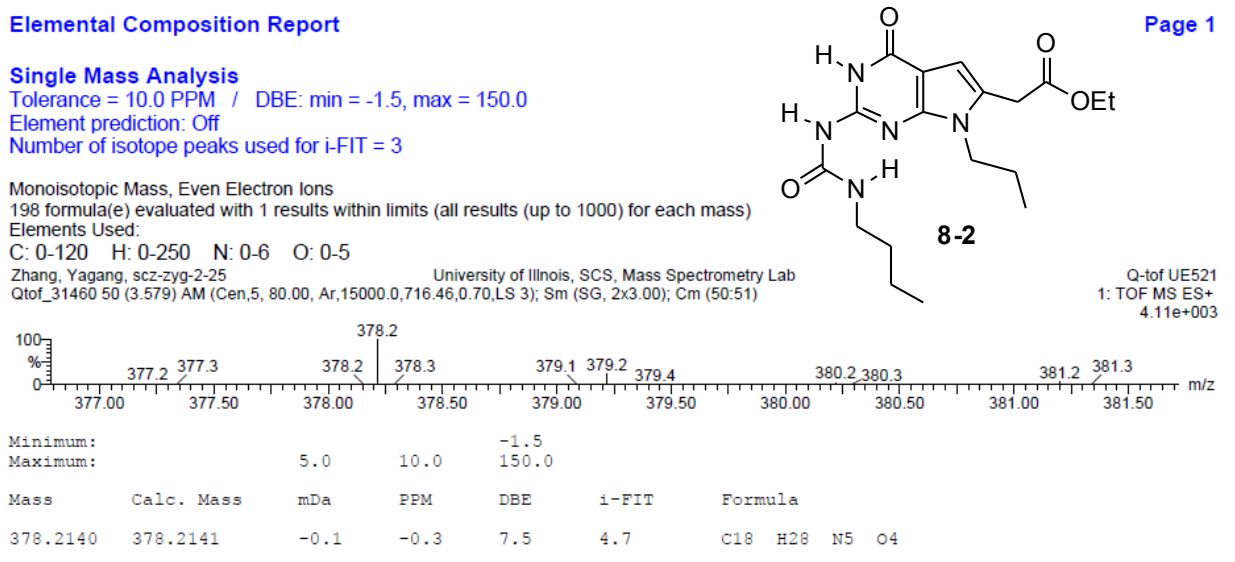


Figure S13 | Elemental composition report of compound 8-2. (HR-ESI-MS)

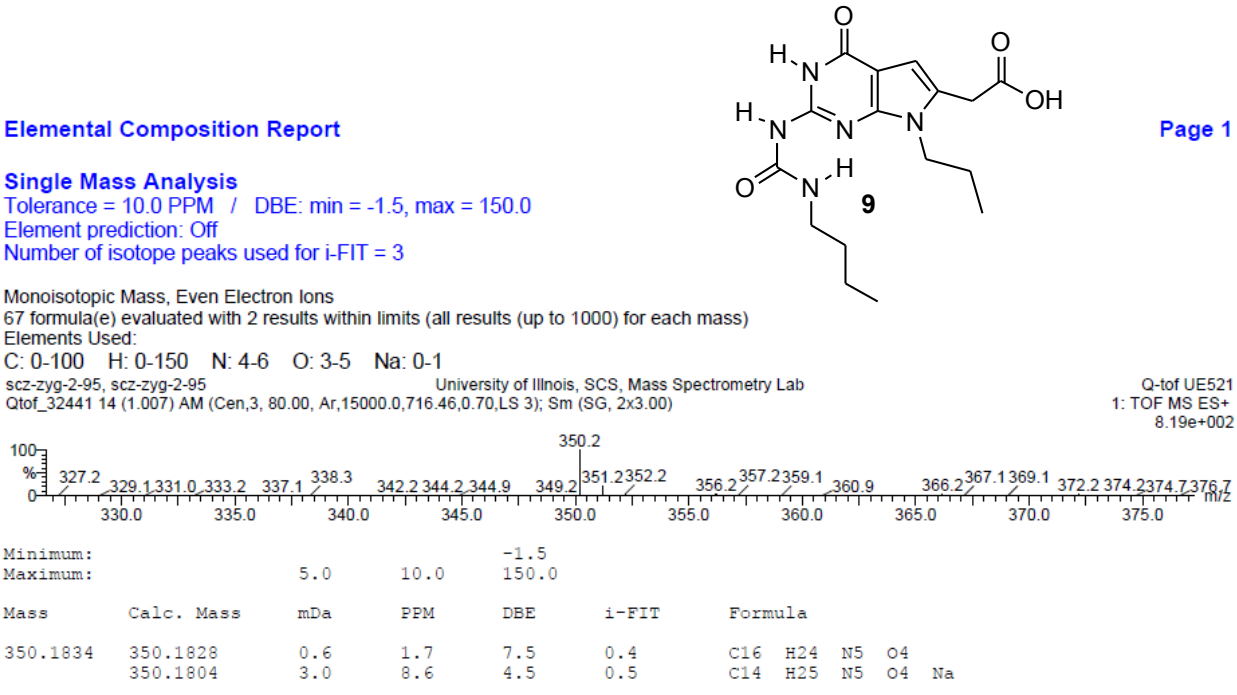
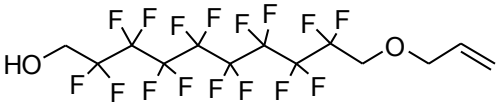


Figure S14 | Elemental composition report of compound 9. (HR-ESI-MS)

Elemental Composition Report Page 1

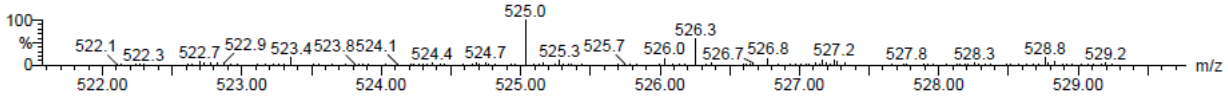
Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 150.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3



11

Monoisotopic Mass, Even Electron Ions
162 formula(e) evaluated with 3 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-100 H: 0-150 N: 0-5 O: 0-5 F: 16-16 Na: 0-1

Zhang, Yagang, scz-zyg-2-47-p1_NaCl University of Illnois, SCS, Mass Spectrometry Lab Q-tof UE521
Qtof_31862B 23 (1.650) AM (Cen,3, 80.00, Ar,15000.0,716.46,0.70,LS 2); Sm (SG, 2x3.00); Cm (23:25) 1: TOF MS ES+
1.48e+002

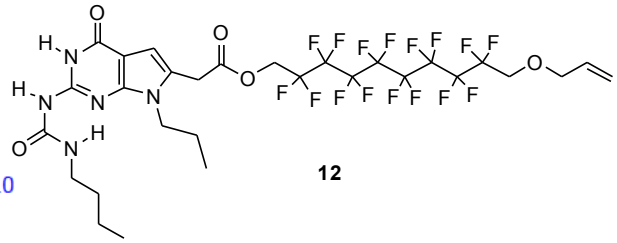


Minimum:				-1.5		
Maximum:		5.0	10.0	150.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
525.0329	525.0323	0.6	1.1	0.5	0.1	C13 H10 O2 F16 Na
	525.0347	-1.8	-3.4	3.5	0.1	C15 H9 O2 F16
	525.0307	2.2	4.2	-0.5	0.4	C10 H9 N2 O4 F16

Figure S15 | Elemental composition report of compound 11. (HR-ESI-MS)

Elemental Composition Report Page 1

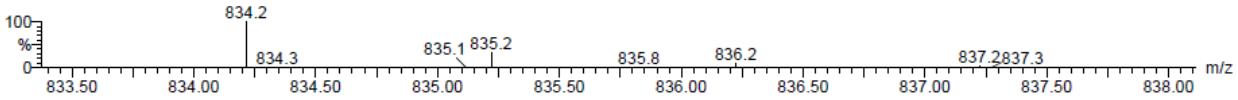
Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 150.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3



12

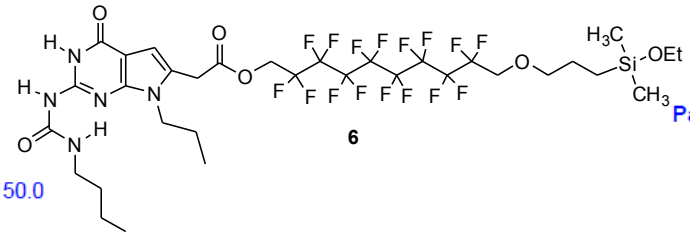
Monoisotopic Mass, Even Electron Ions
248 formula(e) evaluated with 4 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-100 H: 0-150 N: 0-5 O: 0-6 F: 16-16

Zhang, Yagang, scz-zyg-2-105 University of Illnois, SCS, Mass Spectrometry Lab Q-tof UE521
Qtof_32526 42 (1.757) AM (Cen,5, 80.00, Ar,15000.0,716.46,0.70,LS 3); Sm (SG, 2x3.00); Cm (40:42) 1: TOF MS ES+
3.76e+003



Minimum:				-1.5		
Maximum:		5.0	10.0	150.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
834.2144	834.2148	-0.4	-0.5	8.5	2.9	C29 H32 N5 O5 F16
	834.2188	-4.4	-5.3	12.5	16.8	C34 H32 N3 O3 F16
	834.2089	5.5	6.6	17.5	33.2	C36 H28 N5 F16
	834.2076	6.8	8.2	12.5	20.2	C35 H32 N O4 F16

Figure S16 | Elemental composition report of compound 12. (HR-ESI-MS)

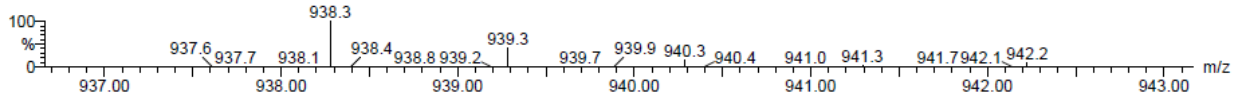


Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 150.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

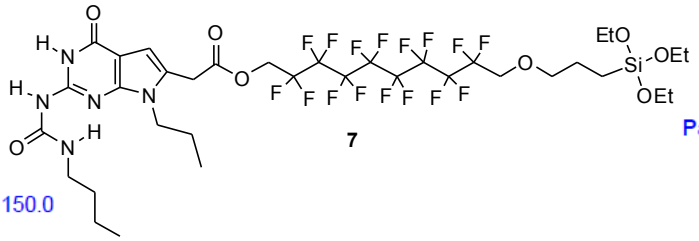
Monoisotopic Mass, Even Electron Ions
48 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-150 H: 0-250 N: 4-5 O: 5-8 F: 16-16 Si: 1-1

Zhang, Yagang, scz-zyg-2-213-2 University of Illnois, SCS, Mass Spectrometry Lab Q-tof UE521
Qtof_34716 32 (1.364) AM (Cen,3, 80.00, Ar,15000.0,716.46,0.70,LS 3); Sm (SG, 2x5.00); Cm (32:33) 1: TOF MS ES+
1.65e+003



Minimum:				-1.5		
Maximum:		5.0	10.0	150.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
938.2781	938.2805	-2.4	-2.6	7.5	0.9	C33 H44 N5 O6 F16 Si

Figure S17 | Elemental composition report of compound 6. (HR-ESI-MS)

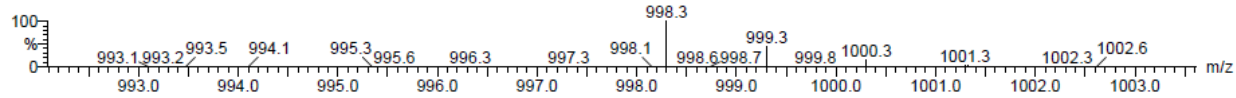


Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 150.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
56 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-150 H: 0-250 N: 4-6 O: 7-9 F: 16-16 Si: 1-1

Zhang, Yagang, scz-zyg-2-215-1 University of Illnois, SCS, Mass Spectrometry Lab Q-tof UE521
Qtof_34823 8 (1.793) AM (Cen,3, 80.00, Ar,15000.0,716.46,0.70); Sm (SG, 2x3.00); Cm (7:8) 2: TOF MS ES+
3.80e+003



Minimum:				-1.5		
Maximum:		5.0	10.0	150.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
998.3012	998.3017	-0.5	-0.5	7.5	2.3	C35 H48 N5 O8 F16 Si

Figure S18 | Elemental composition report of compound 7. (HR-ESI-MS)

Static water contact angle of unmodified/modified glass slides and Si wafers.

Table S1 | Static water contact angle of glass slides unmodified and modified with QHB coupled silane monomers.

Surface	**Static water contact angle**
Oxidized glass surface	10.0 ± 2.0 °
Octyl-triethoxysilane	92.8 ± 1.6 °
Octyl-monoethoxysilane	83.5 ± 3.1 °
Octyl-F-triethoxysilane	116.5 ± 1.8 °
Octyl-F-monoethoxysilane	91.6 ± 2.6 °
DeUG-F-triethoxysilane	71.0 ± 1.5 °
DeUG-F-monoethoxysilane	67.3 ± 1.9 °

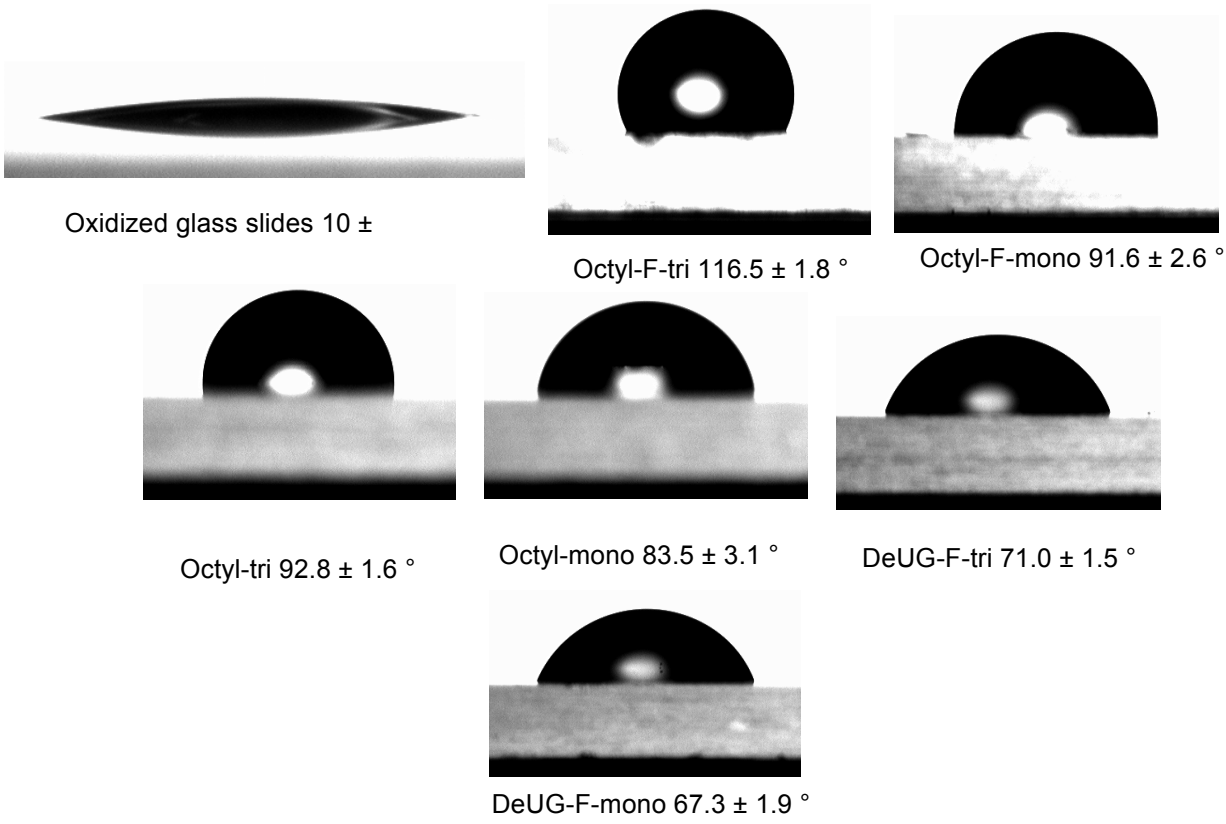


Figure S19 | Static water contact angle of glass slides unmodified and modified with QHB modules coupled silane monomers with fluorinated alkyl linker.

Table S2 | Static water contact angle of Si wafers unmodified and modified with QHB modules coupled silane monomers.

Surface	Static water contact angle
Oxidized Si wafer (Si-OH)	16.0 ± 2.0 °
Octyl-triethoxysilane	94.7 ± 2.3 °
Octyl-monoethoxysilane	90.7 ± 2.6 °
Octyl-F-triethoxysilane	113.7 ± 2.9 °
Octyl-F-monoethoxysilane	102.4 ± 2.2 °
DeUG-F-triethoxysilane	68.5 ± 2.1 °
DeUG-F-monoethoxysilane	63.8 ± 1.9 °

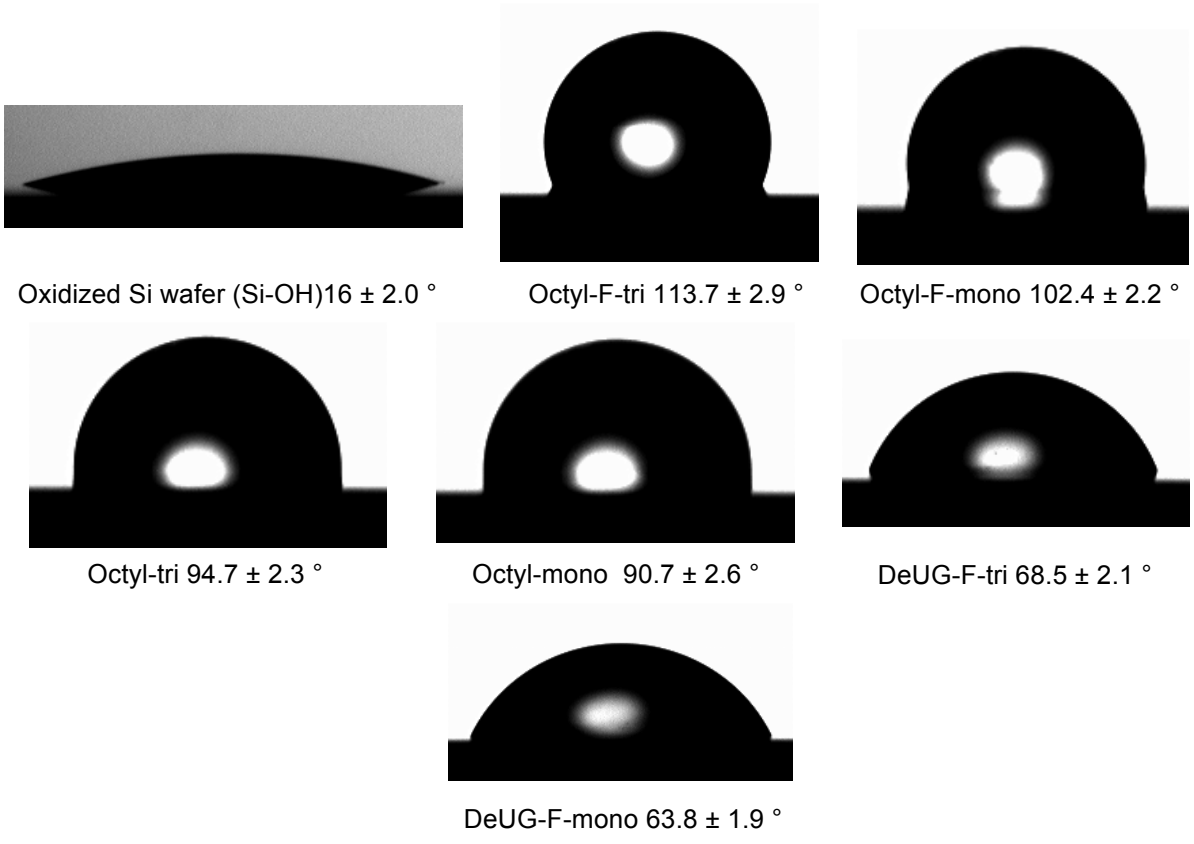


Figure S20 | Static water contact angle of Si wafers unmodified and modified with QHB modules coupled silane monomers with fluorinated alkyl linker.

X-ray photoelectron spectroscopy of modified glass slides.

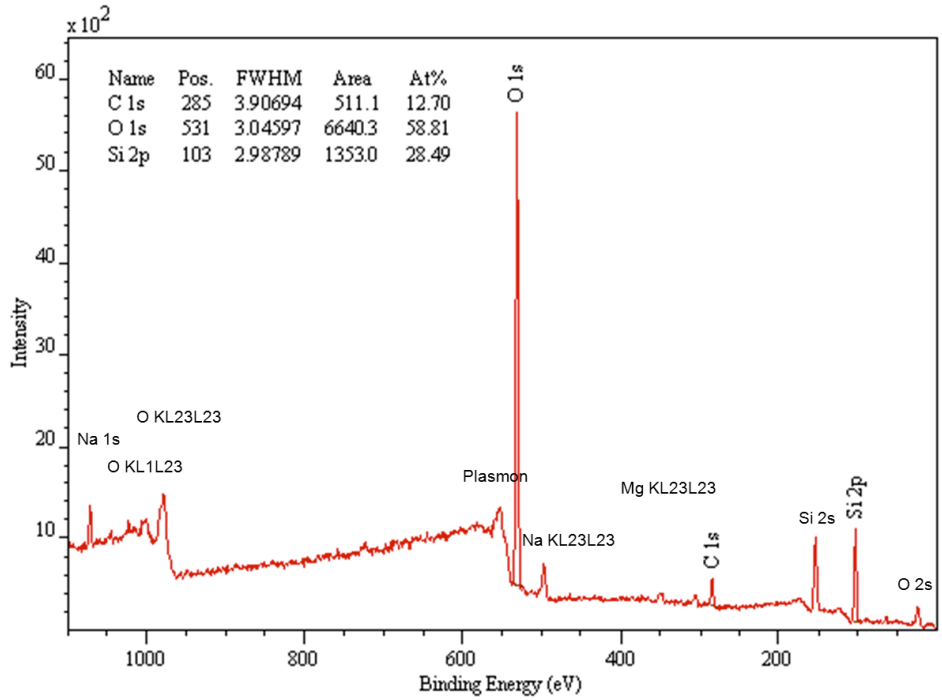


Figure S21 | XPS survey spectra of glass slides modified with Octyl-monoethoxysilane.

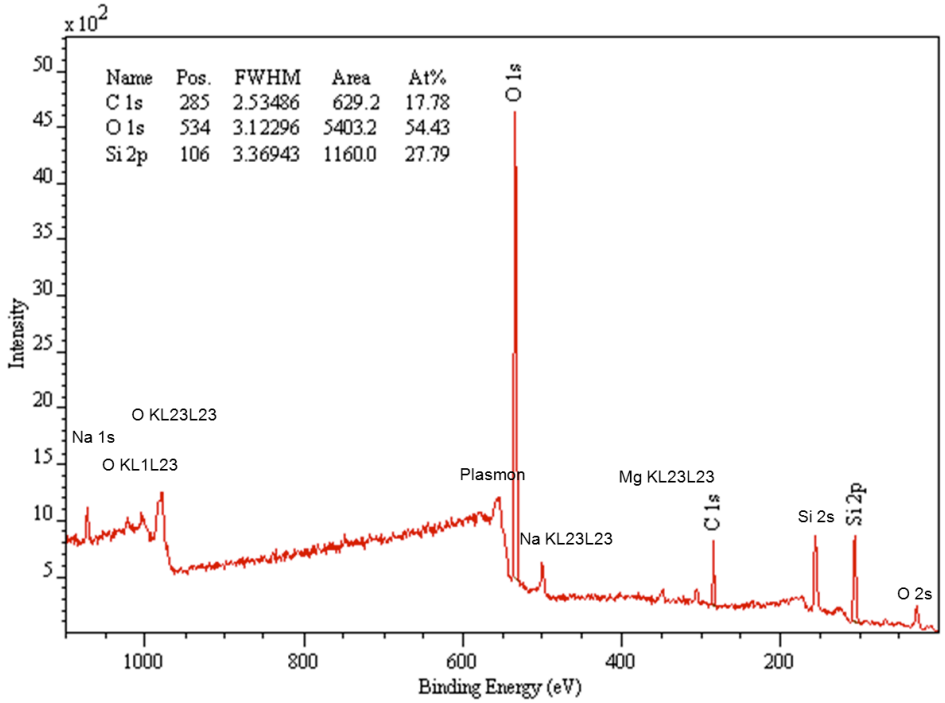


Figure S22 | XPS survey spectra of glass slides modified with Octyl-triethoxysilane.

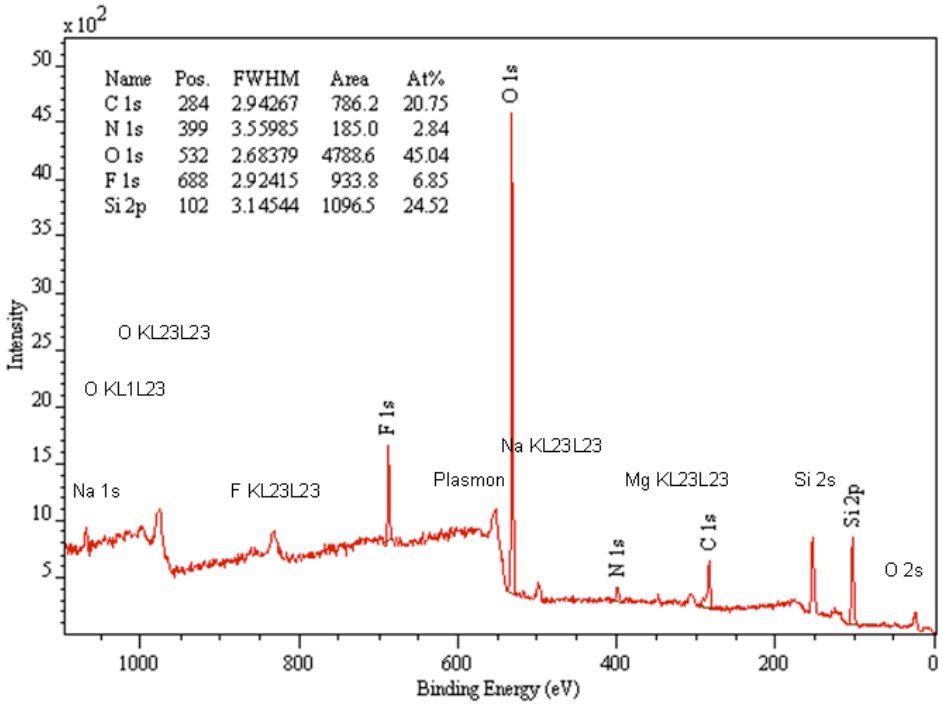


Figure S23 | XPS survey spectra of glass slides modified with DeUG-F-monoethoxysilane.

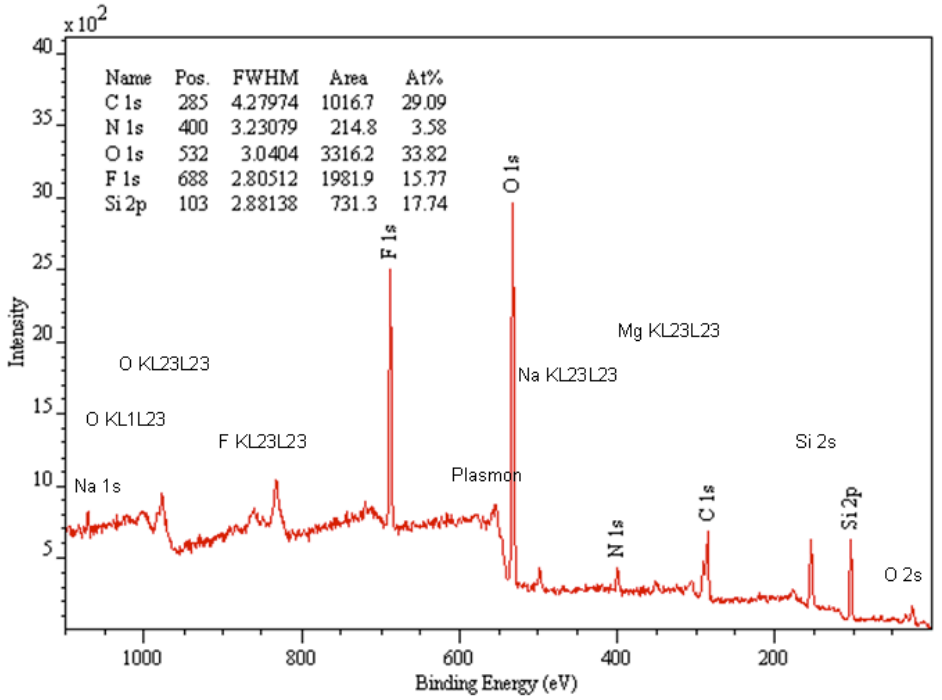


Figure S24 | XPS survey spectra of glass slides modified with DeUG-F-triethoxysilane.

Atomic force microscopy height image and section graph of unmodified/modified glass slides.

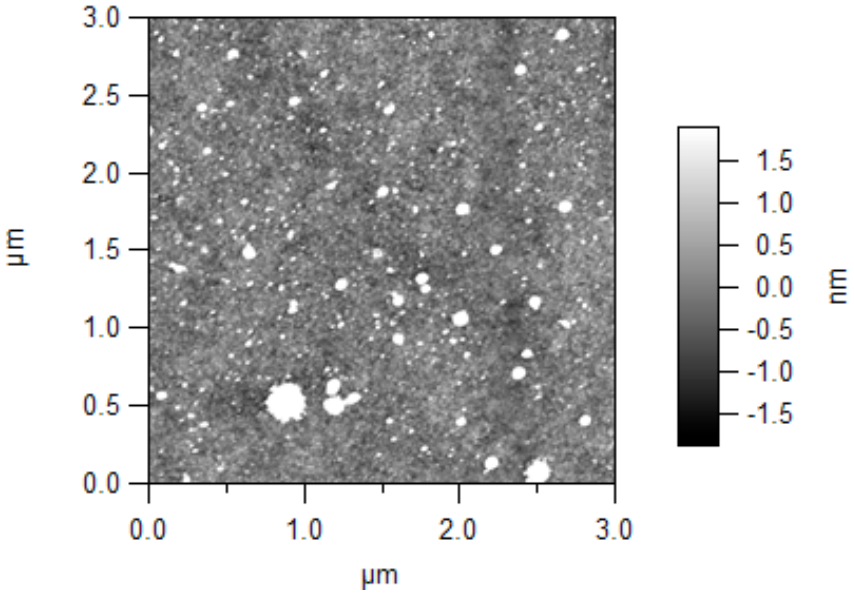


Figure S25 | AFM height image of glass slides out of box.

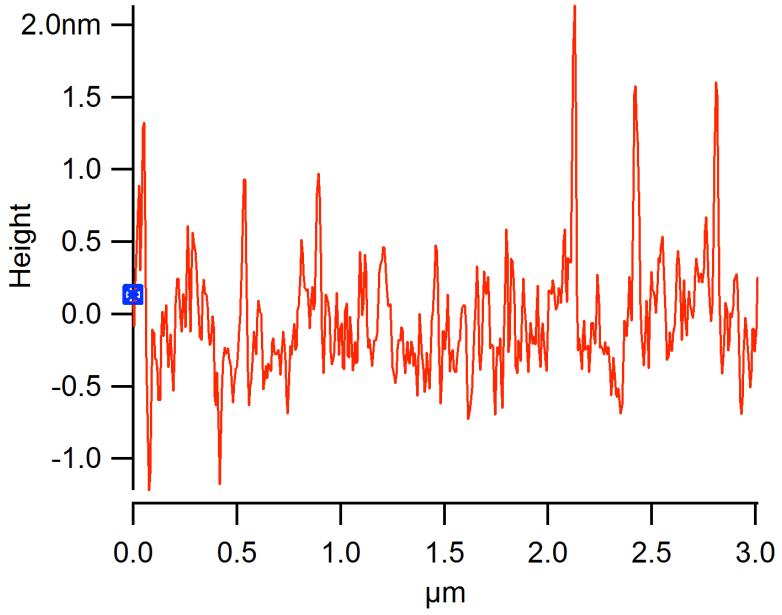


Figure S26 | Section graph of AFM height image of glass slides out of box with Root Mean Square roughness 1.61 nm.

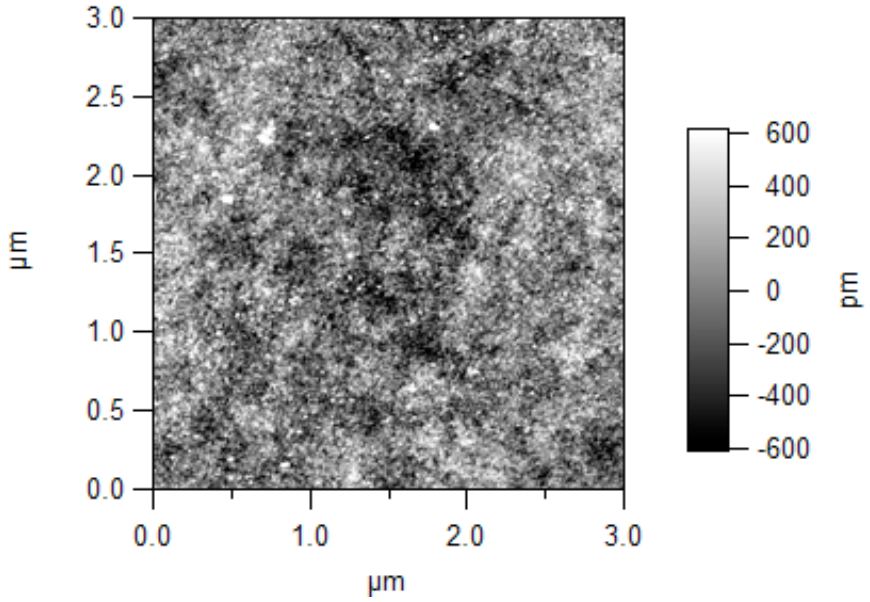


Figure S27 | AFM height image of oxidized (piranha treated) glass slides.

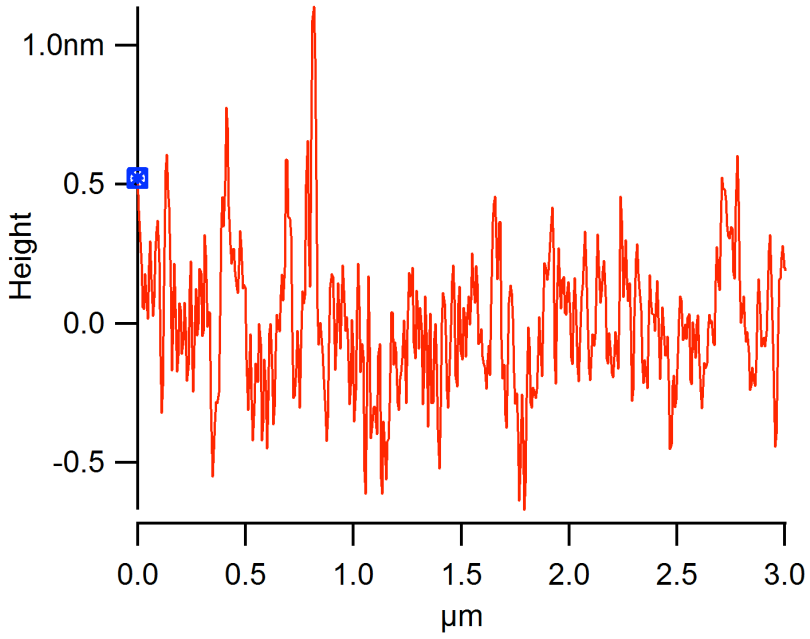


Figure S28 | Section graph of AFM height image of oxidized (Piranha treated) glass slides with Root Mean Square roughness 307 pm.

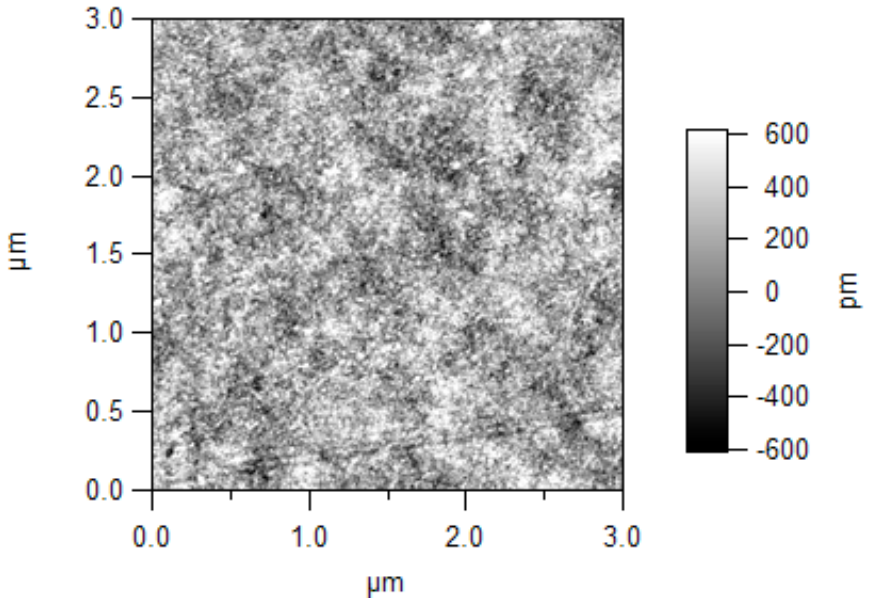


Figure S29 | AFM height image of glass slides modified with DeUG-F-monoethoxysilane.

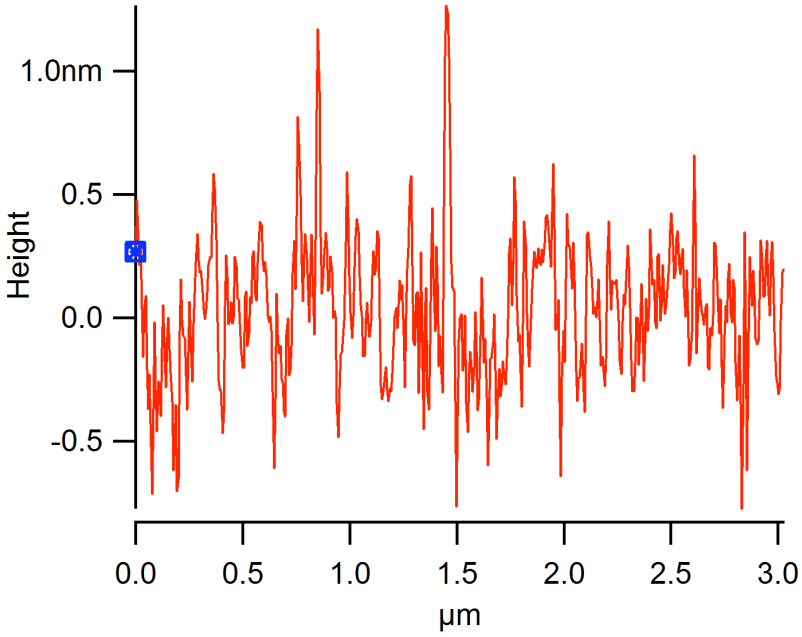


Figure S30 | Section graph of AFM height image of glass slides modified with DeUG-F-monoethoxysilane with Root Mean Square roughness 281 pm.

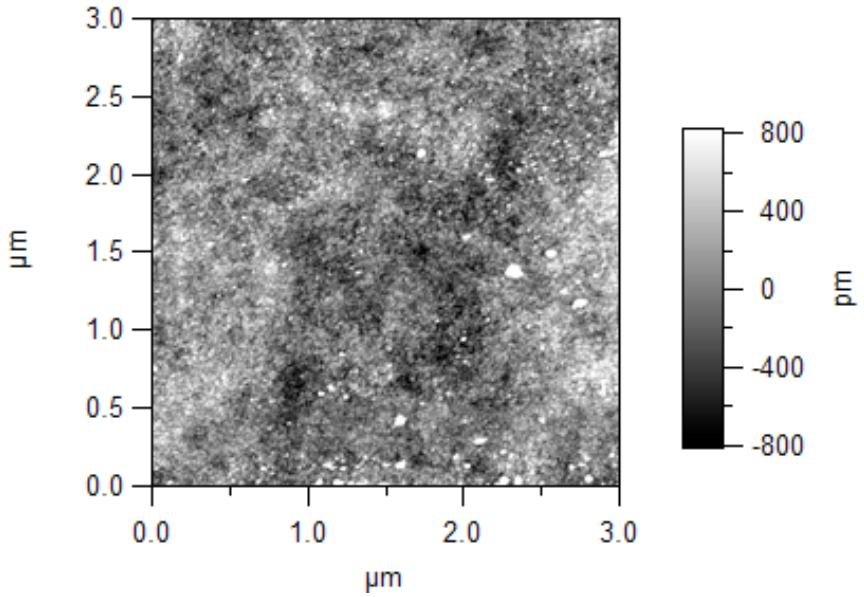


Figure S31 | AFM height image of glass slides modified with DeUG-F-triethoxysilane.

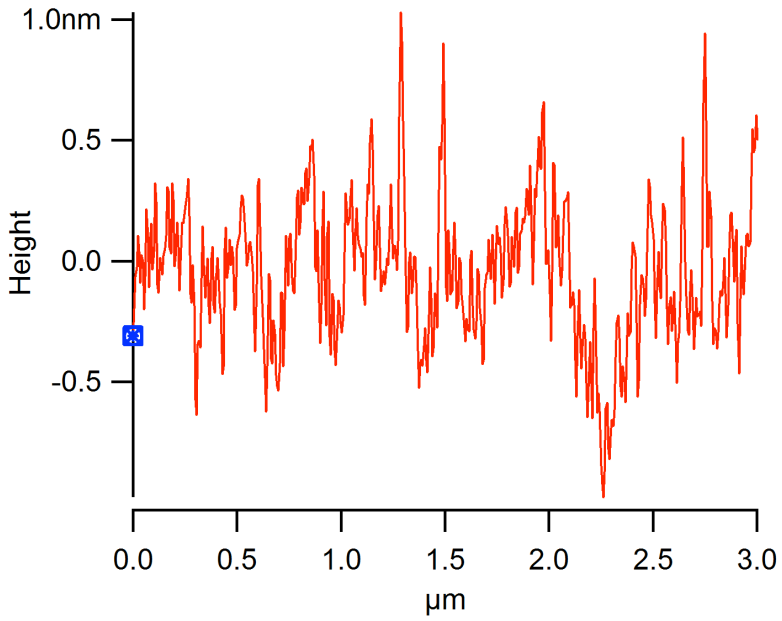


Figure S32 | Section graph of AFM height image of glass slides modified with DeUG-F-triethoxysilane with Root Mean Square roughness 388 pm.

MALDI-TOF-MS of modified Si wafer surface.

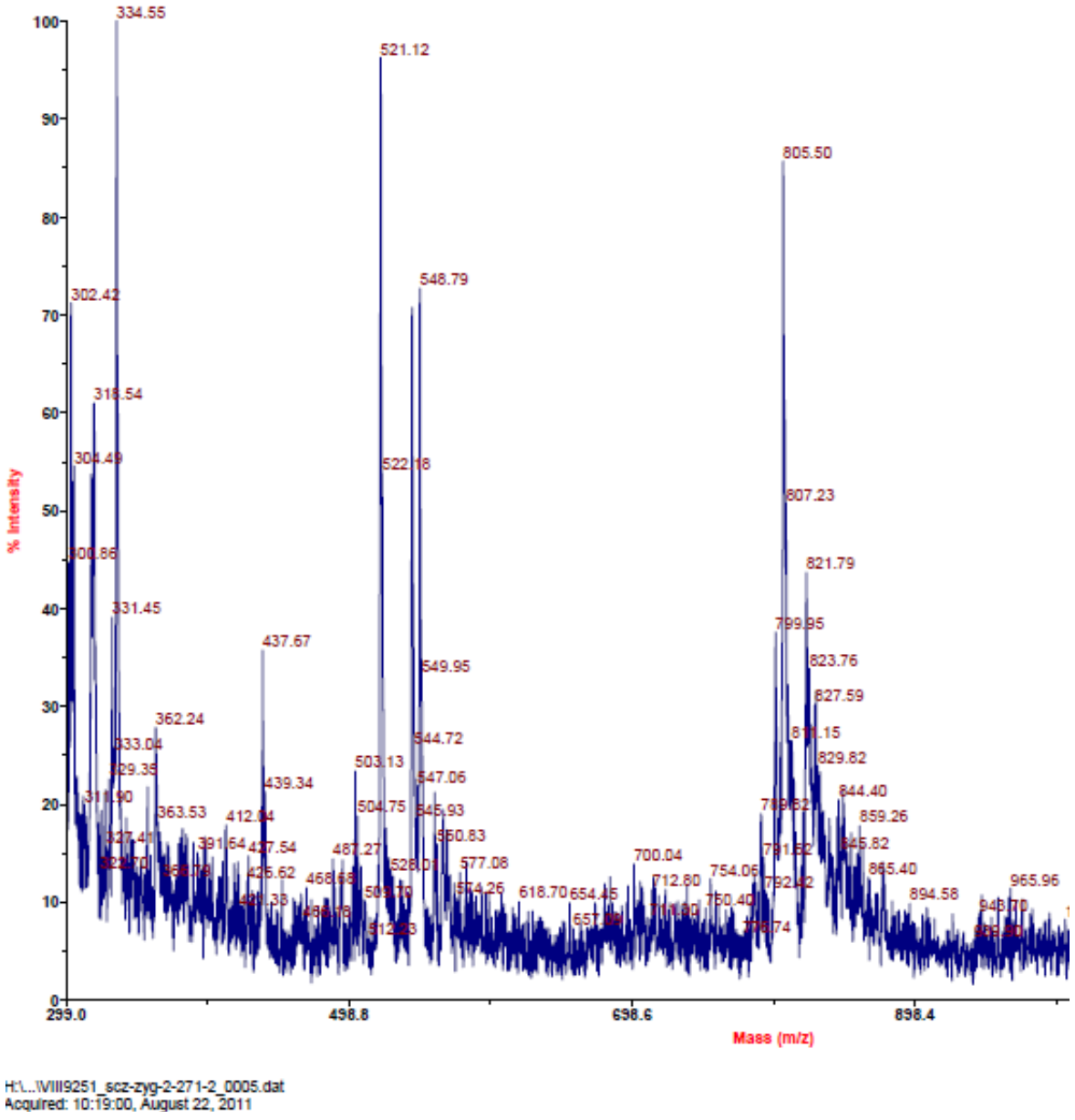


Figure S33 | MALDI fragments chart of DeUG-F-triethoxysilane monomer modified Si wafer surface. Matrix: 2-(4'-hydroxybenzeneazo)benzoic acid (HABA).

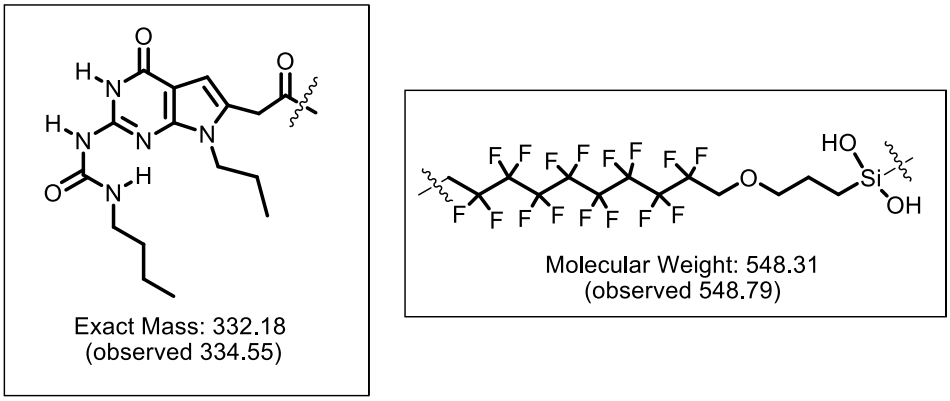


Figure S34 | MALDI characteristic fragments of DeUG-F-triethoxysilane monomer upon ionizing DeUG-F-triethoxysilane monomer modified Si wafer surface. Matrix: 2-(4'-hydroxybenzeneazo)benzoic acid (HABA).

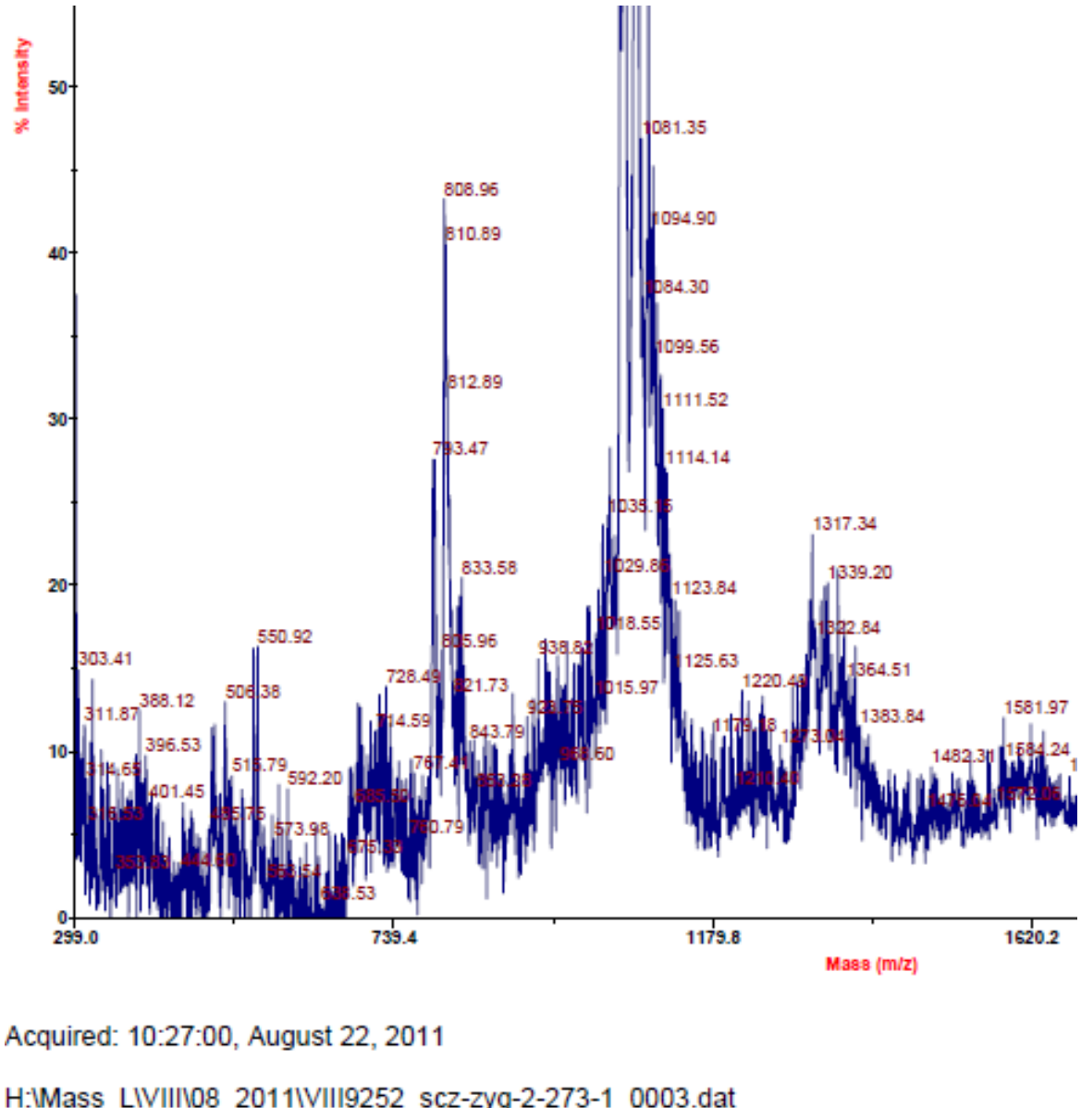


Figure S35 | MALDI fragments chart of DeUG-F-monoethoxysilane monomer modified glass slides surface. Matrix: 2-(4'-hydroxybenzeneazo)benzoic acid (HABA).

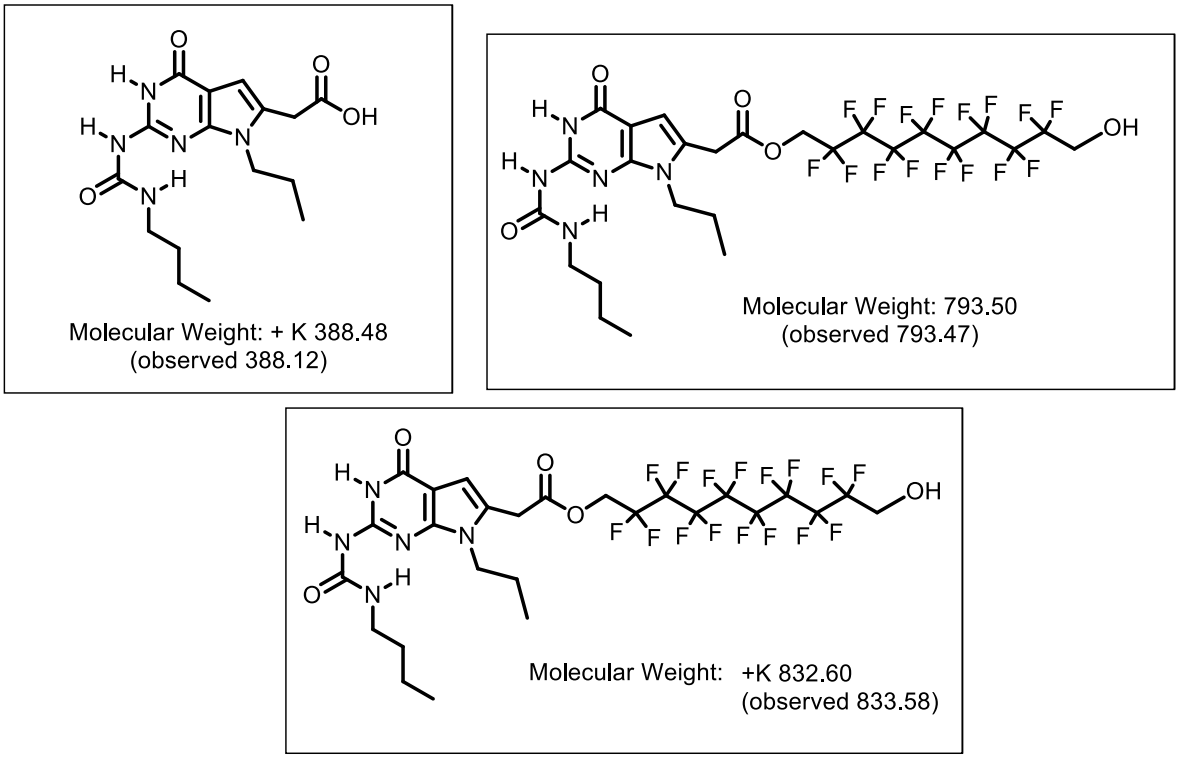


Figure S36 | MALDI characteristic fragments of DeUG-F-monoethoxysilane monomer upon ionizing DeUG-F-monoethoxysilane monomer modified glass slides surface. Matrix: 2-(4'-hydroxybenzeneazo)benzoic acid (HABA).

Thickness of mono-layer on modified Si wafers using ellipsometry measurement.

Film thickness of modified silicon wafers was measured using J. A. Woollam Co. variable-angle spectroscopic ellipsometer. Ellipsometric data were acquired via spectroscopic scan with angle of incidence at 50, 60 and 70˚ and spectral range: 300-1000 nm with revolutions per measurement (Revs/Meas) set at 10. Spot sized analyzed was 1 mm in diameter when incident light is normal to the surface, will be larger when scan with angle of incidence at 50, 60 and 70˚. For Piranha treated Si wafer, sequentially add Si, SiO_2 layer, fix Si layer at 1.00 mm, then do a normal fit to obtain thickness of SiO_2 layer (2.23 nm). For surface modified with various silane monomers, sequentially add Si, SiO_2, Cauchy layer, fix Si layer at 1.00 mm, SiO_2 layer at 2.23 nm, then do a normal fit to obtain thickness of SAM layer.

Table S3 | Thickness of mono-layer on modified Si wafers using various QHB coupled silane monomers.

Surface	Calculated thickness (normal to surface) (nm)	Calculated (30˚ with respect to surface normal) (nm)	Measured Thickness (nm)	Mean squared error (MSE)*
Oxidized Silicon wafer			2.23 ± 0.08	1.17
Octyl-triethoxysilane	1.13	0.97	1.09 ± 0.04	2.22
Octyl-monoethoxysilane	1.13	0.97	0.77 ± 0.02	1.19
Octyl-F-triethoxysilane	1.13	0.97	1.19 ± 0.02	1.29
Octyl-F-monoethoxysilane	1.13	0.97	1.05 ± 0.02	1.18
DeUG-F-triethoxysilane	3.13	2.71	2.85 ± 0.11	1.40
DeUG-F-monoethoxysilane	3.13	2.71	2.71 ± 0.13	1.27

* manual suggests MSE < 10 is a reasonable data fit.

Piranha treated (Oxidized) Silicon wafer surface.

Sequentially add Si, SiO_2 layer, fix Si layer at 1.00 mm, then do a normal fit to obtain thickness of SiO_2 layer. Thickness of the SiO_2 layer 2.232 nm, calculated MSE 1.145.

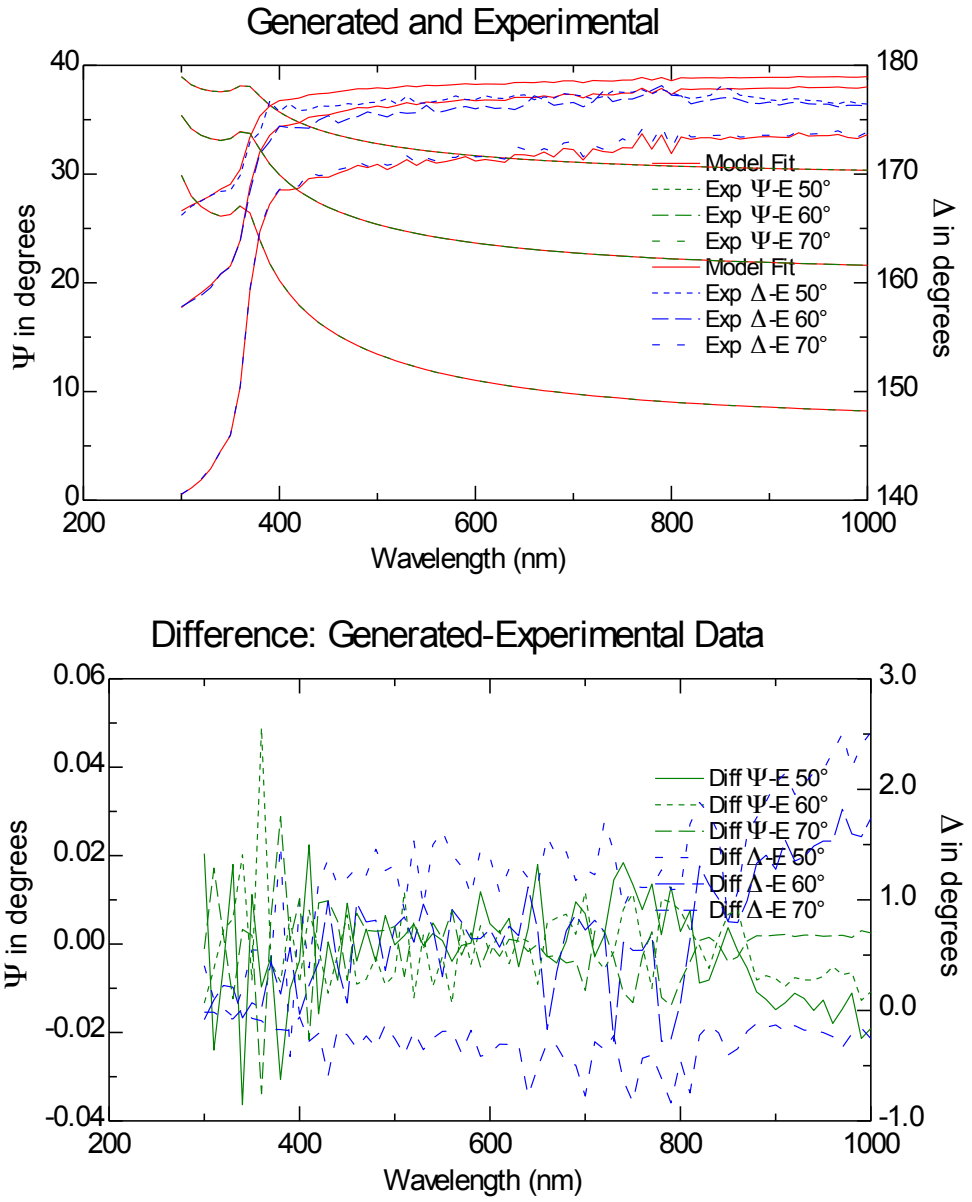


Figure S37 | Piranha treated (Oxidized) Silicon wafer surface. Experimental and model fit of spectroscopic scan data of Ψ and Δ (top), differences of generated and experiment data (bottom).

Octyl-triethoxysilane modified Si wafer surface.

Sequentially add Si, SiO_2, Cauchy layer, fix Si layer at 1.00 mm, SiO_2 layer at 2.23 nm, then do a normal fit to obtain thickness of SAM layer.

Thickness of the SAM layer 1.086 nm, calculated MSE 2.218

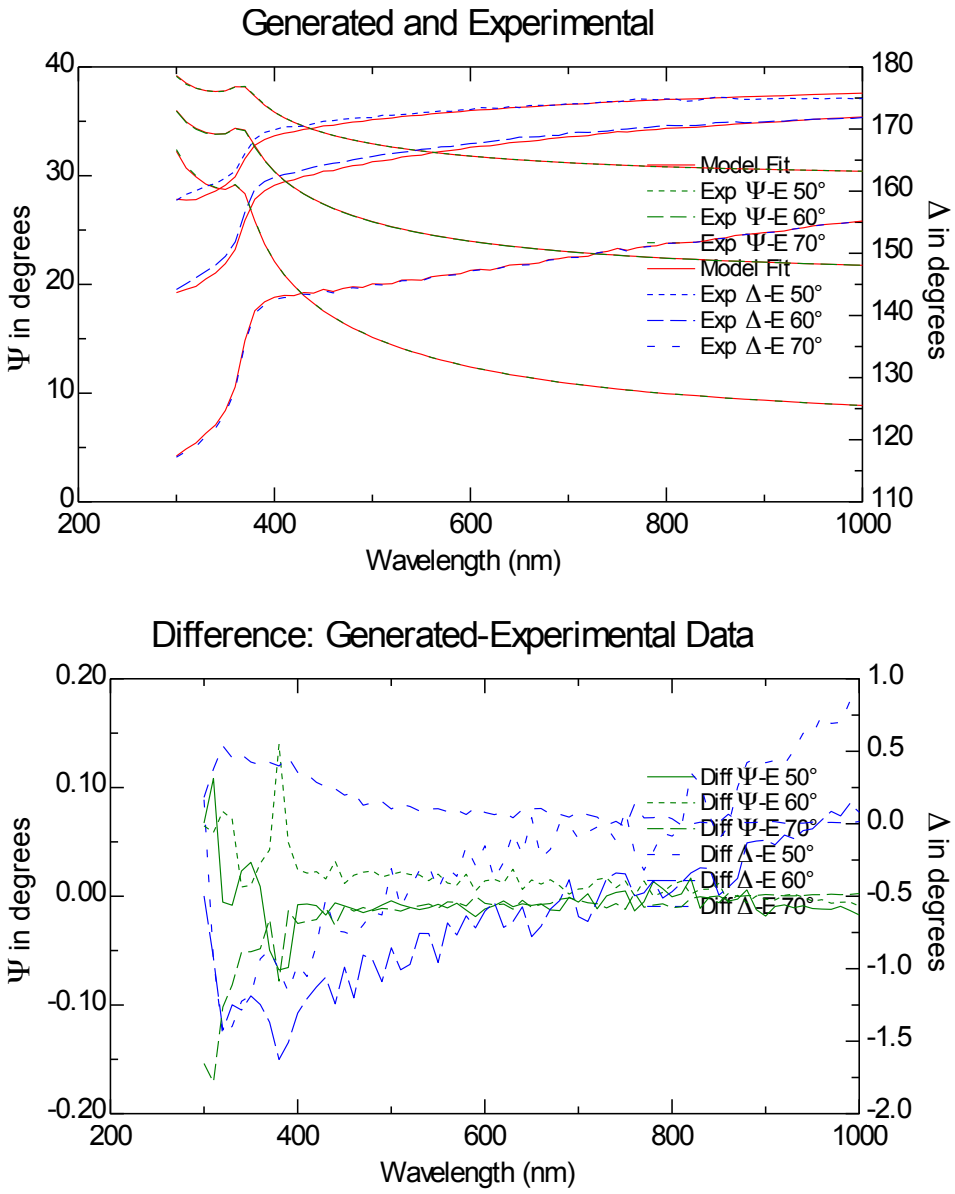


Figure S38 | Octyl-triethoxysilane modified Si wafer surface. Experimental and model fit of spectroscopic scan data of Ψ and Δ (top), differences of generated and experiment data (bottom).

Octyl-monoethoxysilane modified Si wafer surface.

Sequentially add Si, SiO_2, Cauchy layer, fix Si layer at 1.00 mm, SiO_2 layer at 2.23 nm, then do a normal fit to obtain thickness of SAM layer.

Thickness of the SAM layer 0.773 nm, calculated MSE 1.192

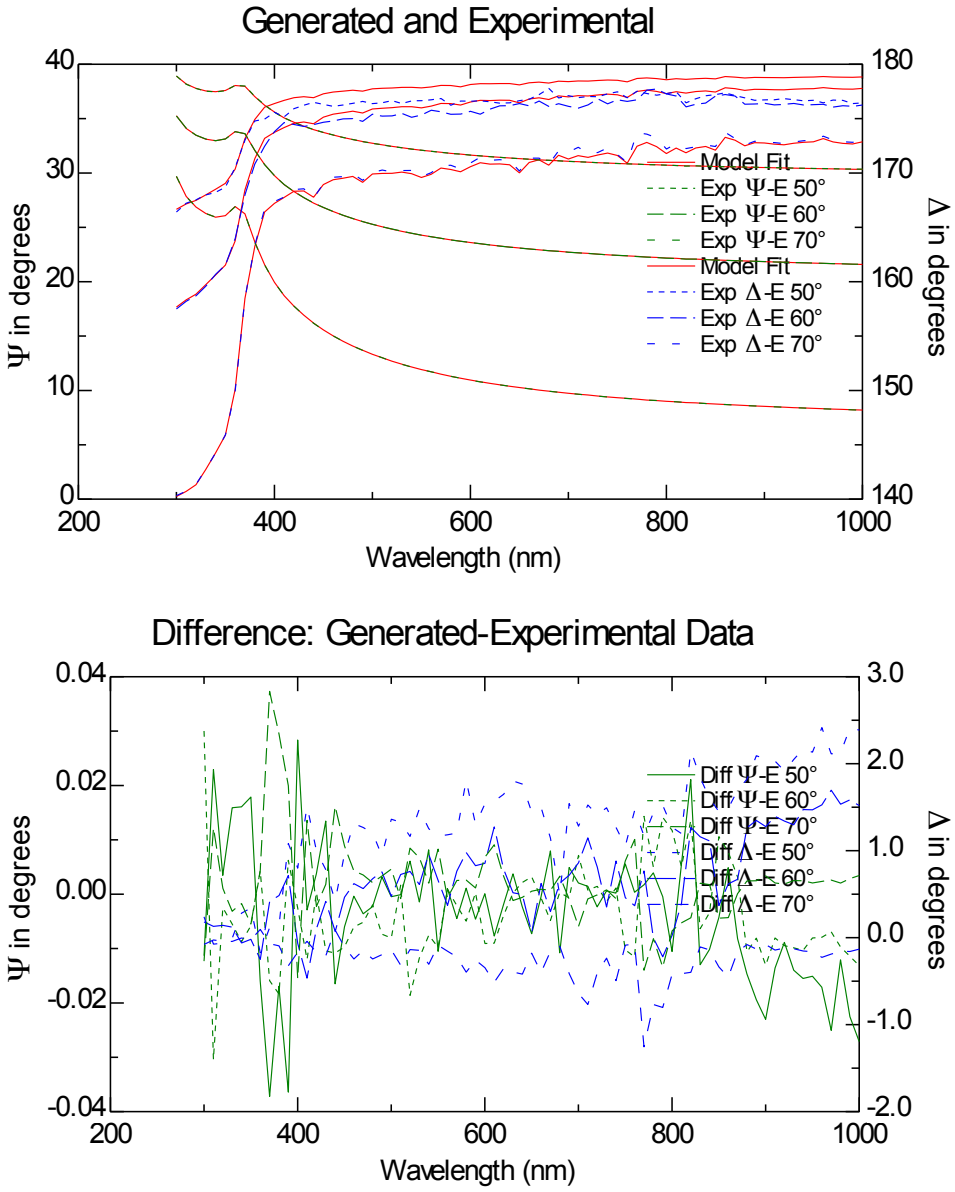


Figure S39 | Octyl-monoethoxysilane modified Si wafer surface. Experimental and model fit of spectroscopic scan data of Ψ and Δ (top), differences of generated and experiment data (bottom).

Octyl-F-triethoxysilane modified Si wafer surface.

Sequentially add Si, SiO_2, Cauchy layer, fix Si layer at 1.00 mm, SiO_2 layer at 2.23 nm, then do a normal fit to obtain thickness of SAM layer.

Thickness of the SAM layer 1.190 nm, calculated MSE 1.289

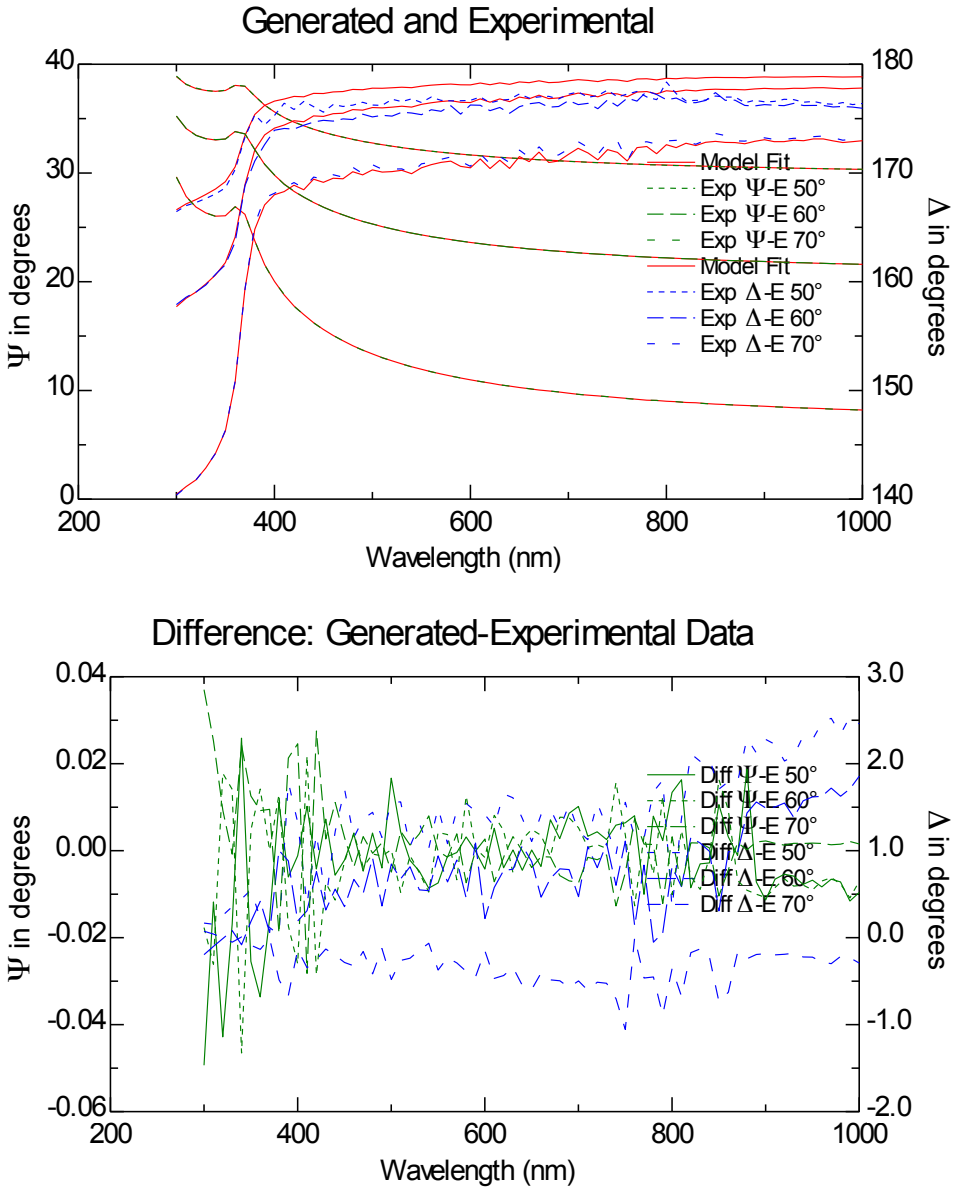


Figure S40 | Octyl-F-triethoxysilane modified Si wafer surface. Experimental and model fit of spectroscopic scan data of Ψ and Δ (top), differences of generated and experiment data (bottom).

Octyl-F-monoethoxysilane modified Si wafer surface.

Sequentially add Si, SiO_2, Cauchy layer, fix Si layer at 1.00 mm, SiO_2 layer at 2.23 nm, then do a normal fit to obtain thickness of SAM layer.

Thickness of the SAM layer 1.052 nm, calculated MSE 1.183

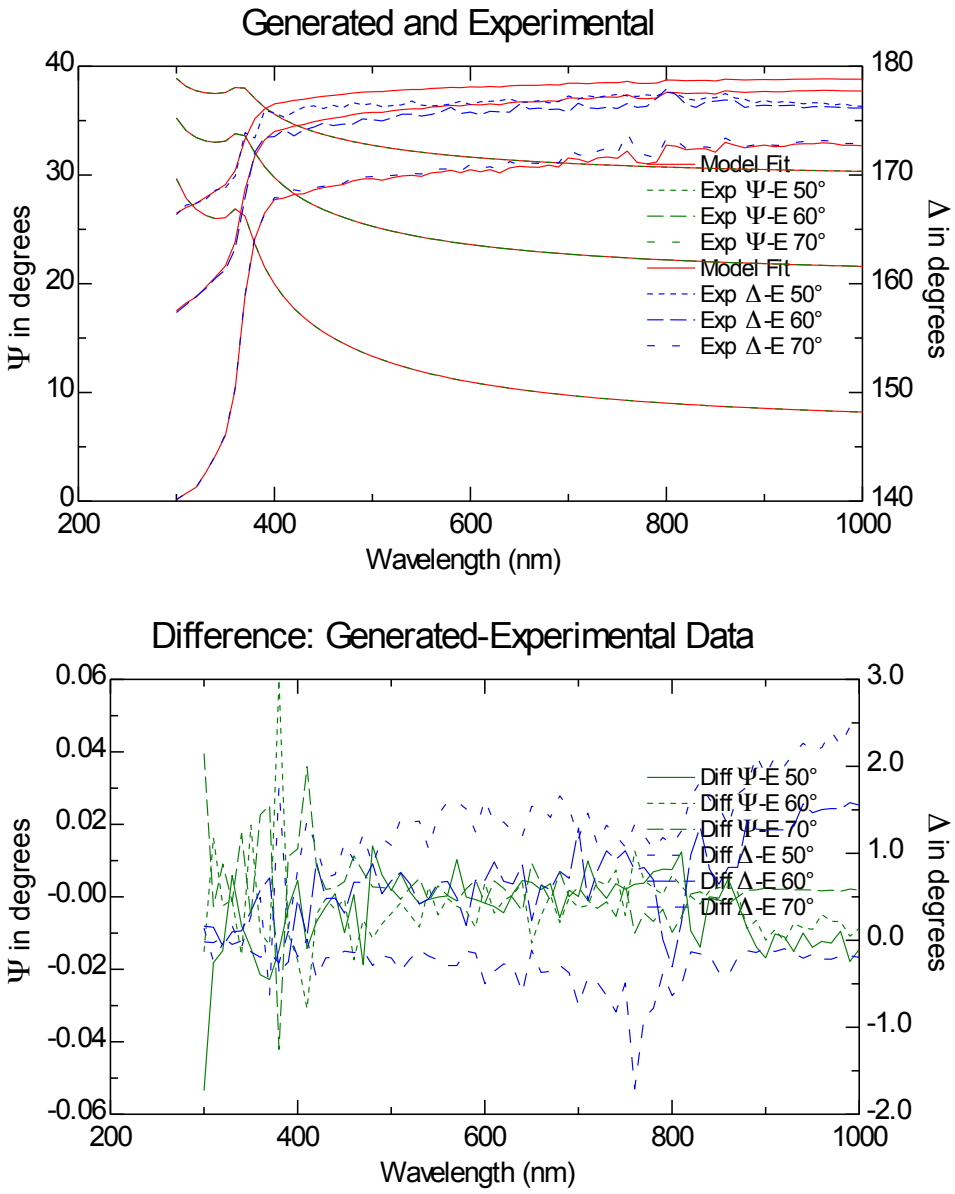


Figure S41 | Octyl-F-monoethoxysilane modified Si wafer surface. Experimental and model fit of spectroscopic scan data of Ψ and Δ (top), differences of generated and experiment data (bottom).

DeUG-F-triethoxysilane modified Si wafer surface.

Sequentially add Si, SiO_2, Cauchy layer, fix Si layer at 1.00 mm, SiO_2 layer at 2.23 nm, then do a normal fit to obtain thickness of SAM layer.

Thickness of the SAM layer 2.850 nm, calculated MSE 1.399

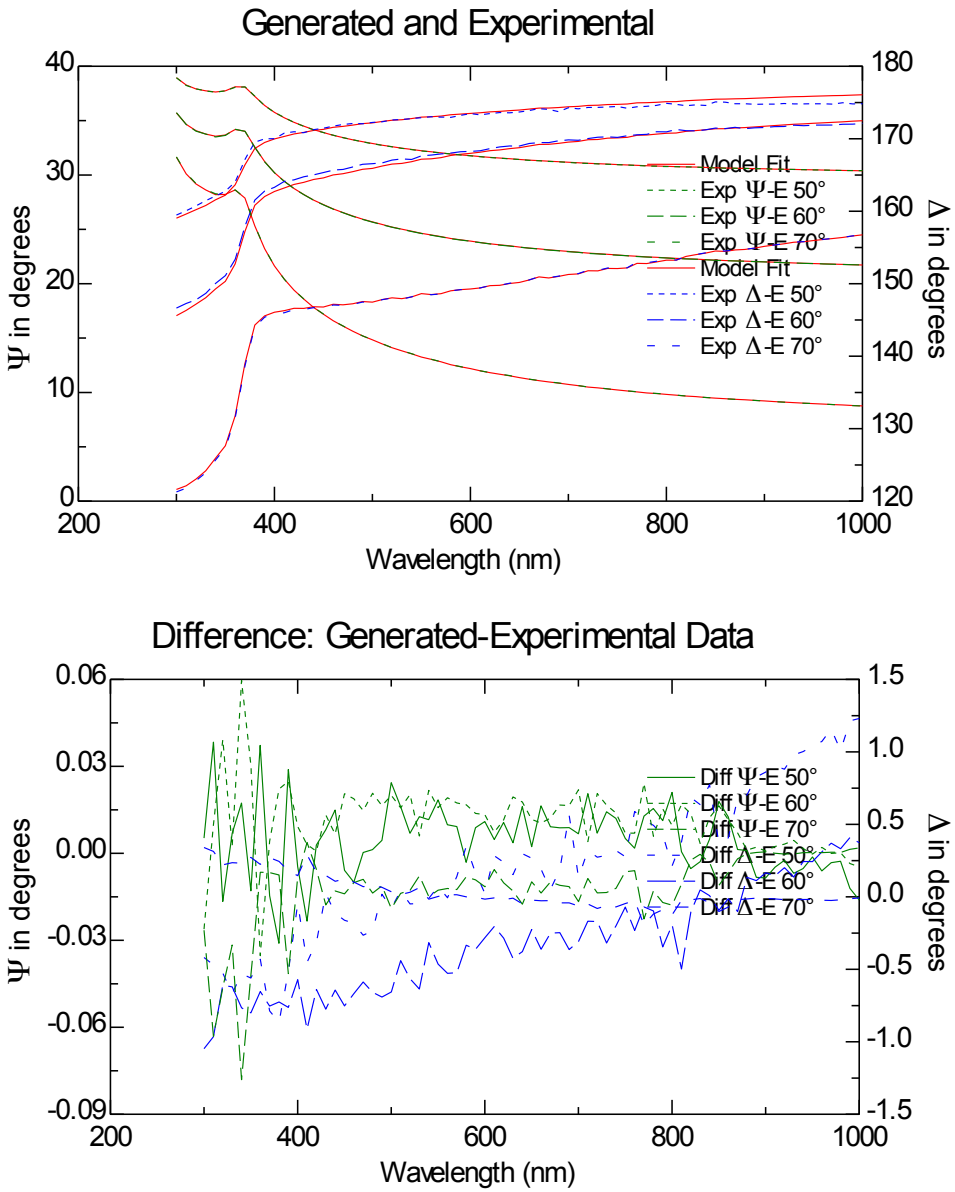


Figure S42 | DeUG-F-triethoxysilane modified Si wafer surface. Experimental and model fit of spectroscopic scan data of Ψ and Δ (top), differences of generated and experiment data (bottom).

DeUG-F-monoethoxysilane modified Si wafer surface.

Sequentially add Si, SiO_2, Cauchy layer, fix Si layer at 1.00 mm, SiO_2 layer at 2.23 nm, then do a normal fit to obtain thickness of SAM layer.

Thickness of the SAM layer 2.708 nm, calculated MSE 1.271

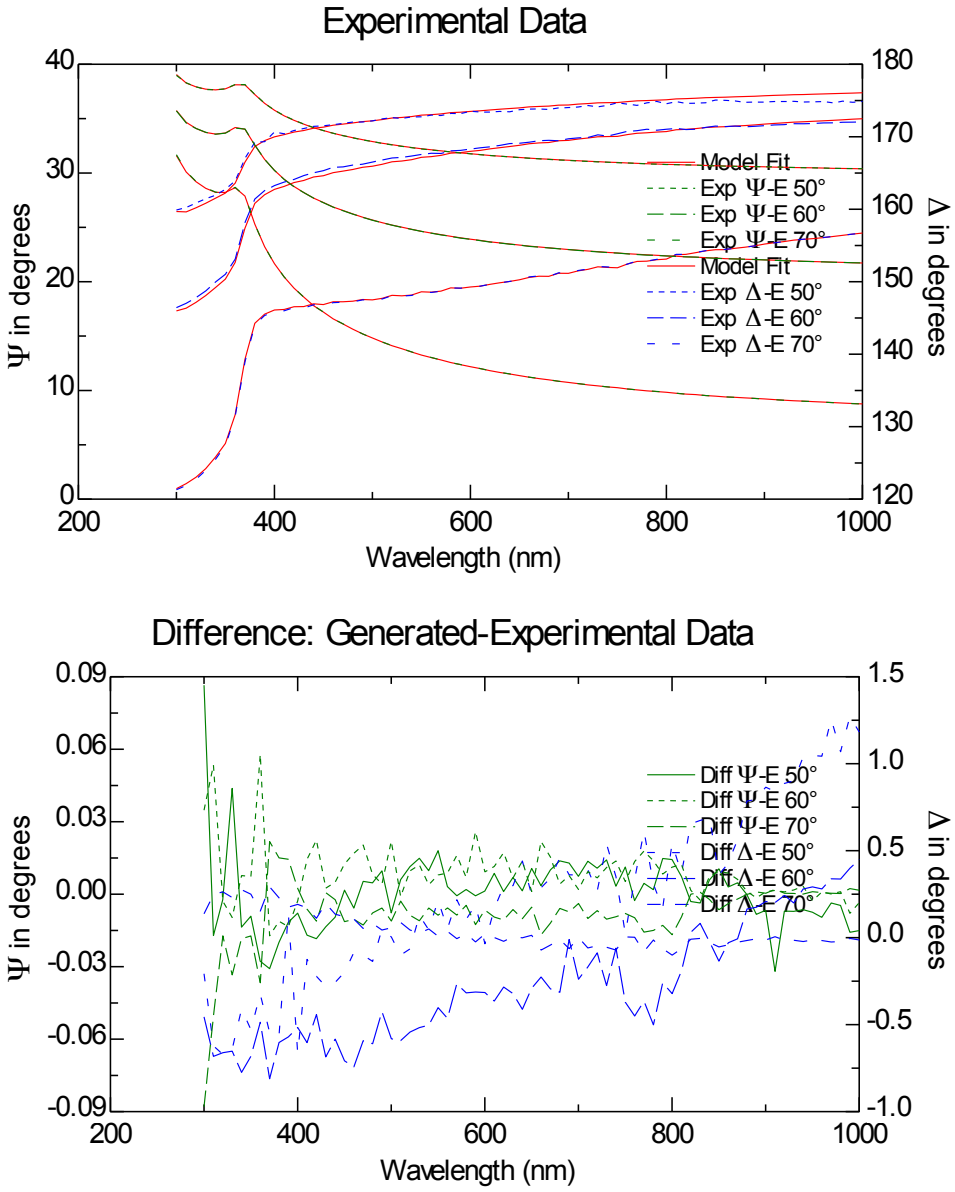


Figure S43 | DeUG-F-triethoxysilane modified Si wafer surface. Experimental and model fit of spectroscopic scan data of Ψ and Δ (top), differences of generated and experiment data (bottom).

Adhesion measurements via Lap-shear experiment.

PS-DAN[2] was synthesized and used as adhesion promoters for glass surface modified with various QHB coupled silane monomers. PS *Mn* (69 KDa), PDI (2.0) was used as control polymer.

Adhesion was measured using Instron Mini 44 load-frame equipped with a 500 N load-cell and Labview 5.1 software (Figure S91). Each lap-shear sample was prepared as following: A pair of glass slides was set using 10 μL of 10 mg/mL of each polymer solution in CH_2Cl_2 with contact area 1.5 cm × 2.5 cm. The sample was clamped with binder clips and cured at room temperature for 24 h before lap shear test. Crosshead speed limit of Instron Mini 44 is 0.05-50 mm/min and maximum load is 50 Kg. For all samples crosshead speed limit was set at 1.0 mm/min. Load (Kg) versus position was plotted and maximum load at fail was recorded. Each data set contains 10 measures. Multiplying the average maximum load at fail by gravitational acceleration constant and divided by contact area give the shear strength in MPa. Error represents plus/minus one standard deviation.

Reference:

[1] Moore, J. S.; Stupp, S. I. *Macromolecules* **1990,** *23,* 65-75.

[2] Anderson, C. A. Synthesis and evaluation of quadruple hydrogen-bonding modules for smart materials applications. PhD dissertation, University of Illinois, **2011.**