Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Humidity Sensors based on Molecular Rectifiers

Ryan P. Sullivan,[a] Eduardo Castellanos-Trejo,[a] Renate Ma,[b] Mark E. Welker,[b] and Oana D. Jurchescu*[a]

[a] *Department of Physics, Center for Functional Materials, Wake Forest University, Winston-Salem, NC, 27109, USA*

[b] *Department of Chemistry, Center for Functional Materials, Wake Forest University, Winston-Salem, NC, 27109, USA*

Experimental Details

(E)-1-([2,2'-bithiophen]-5-yl)-N-(3-(triethoxysilyl)propyl)methanimine

To a solution of anhydrous Na_2SO_4 (3.0 g) and [2,2'-bithiophene]-5-carbaldehyde (prepared as described previously) (0.266 g, 1.37 mmol) in anhydrous dichloromethane (DCM) (5 mL), Aminopropyltriethoxysilane (APTES) (395 µL, 1.69 mmol, 1.23 eq) was added dropwise and the reaction was magnetically stirred under nitrogen overnight at room temperature. The reaction solvent was filtered, and the reaction flask was rinsed with fresh anhydrous DCM (5 mL). The reaction solvent was evaporated *in vacuo* and the obtained product was dried under a high vacuum. The product was isolated as an orange liquid. (0.532 g, 1.32 mmol, 96%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.28 (m, 1H), 7.24 (m, 2H), 7.19 – 7.08 (m, 2H), 7.06 – 6.98 (m, 1H), 3.88 – 3.77 (q, *J* = 7.0 Hz, 6H), 3.57 (td, *J* = 6.9, 1.3 Hz, 2H), 1.88 – 1.75 (m, 2H), 1.23 (t, *J* = 7.0 Hz, 9H), 0.72 – 0.59 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.08, 141.15, 140.26, 137.18, 130.78, 128.02, 125.25, 124.57, 123.55, 63.94, 58.39, 24.24, 18.33, 8.01. HRMS calcd. for $C_{18}H_{27}NO_3S_2Si$: 398.12799 $[M + H]^+$, found: 398.12725. [1]

(E)-1-(thiophen-2-yl)-N-(3-triethoxysilyl)propyl)methanimine

To a solution of anhydrous Na_2SO_4 (3.0 g) and thiophene-2-carbaldehyde (93 µL, 0.112 g, 1.00 mmol) in anhydrous DCM (5mL), APTES (239 µL, 1.02 mmol, 1.02 eq) was added dropwise and the reaction was magnetically stirred under nitrogen for 2 h at room temperature. The reaction solvent was filtered and evaporated *in vacuo* and the obtained product was then dried under a high vacuum. (E)-1-(thiophen-2-yl)-N-(3-triethoxysilyl)propyl)methanimine was isolated as a white liquid (0.199 g, 0.632 mmol, 63%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.35 (m, *J* = 1.2 Hz, 1H), 7.38 (d, *J* = 5.0 Hz, 1H), 7.29 (dd, *J* = 3.7, 1.2 Hz, 1H), 7.06 (dd, *J* = 4.9, 3.5 Hz, 1H), 3.82 (q, *J* = 7.0 Hz, 6H), 3.57 (td, *J* = 6.9, 1.4 Hz, 2H), 1.87 – 1.75 (m, 2H), 1.22 (t, *J* = 7.0 Hz, 9H), 0.76 – 0.60 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.24, 142.69, 130.08, 128.55, 127.28, 63.97, 58.38, 24.19, 18.32, 7.98. HRMS (FTMS + p ESI) for $C_{14}H_{25}NO_3SSi$ 316.14027 $[M + H]^+$, found 316.13917.

Triethoxy(octyl)silane

Purchased from Fisher Scientific.

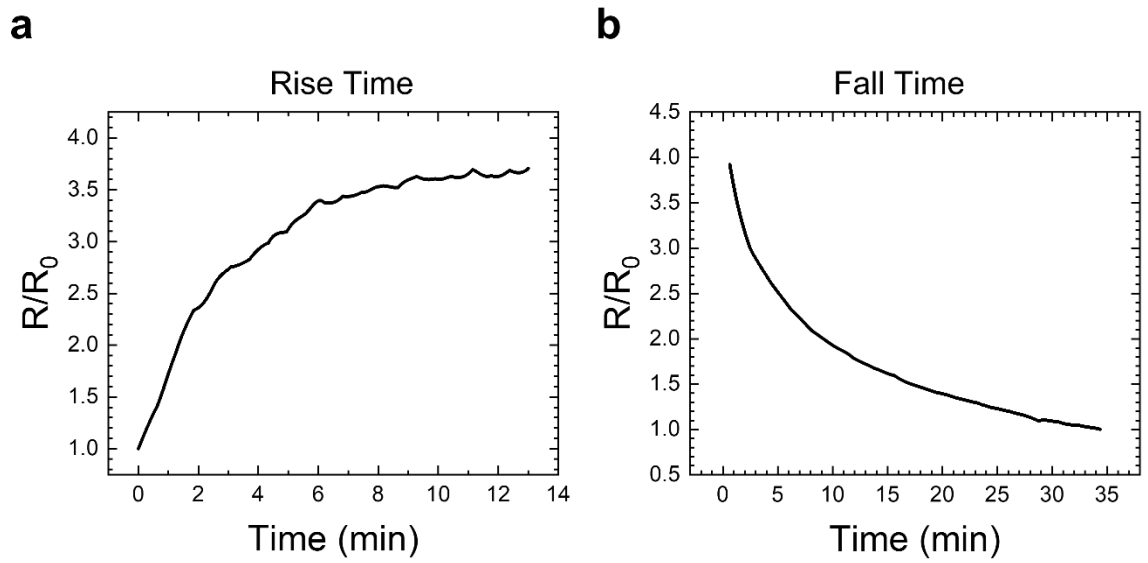

Fig. S1 The rectification response times of BT-TESP-MA when in a EGaIn/SAM/SiO_2/Si device architecture normalized to the rectification when in dry air to go from 0 to 70% RH (a) and 70 to 0% RH (b).

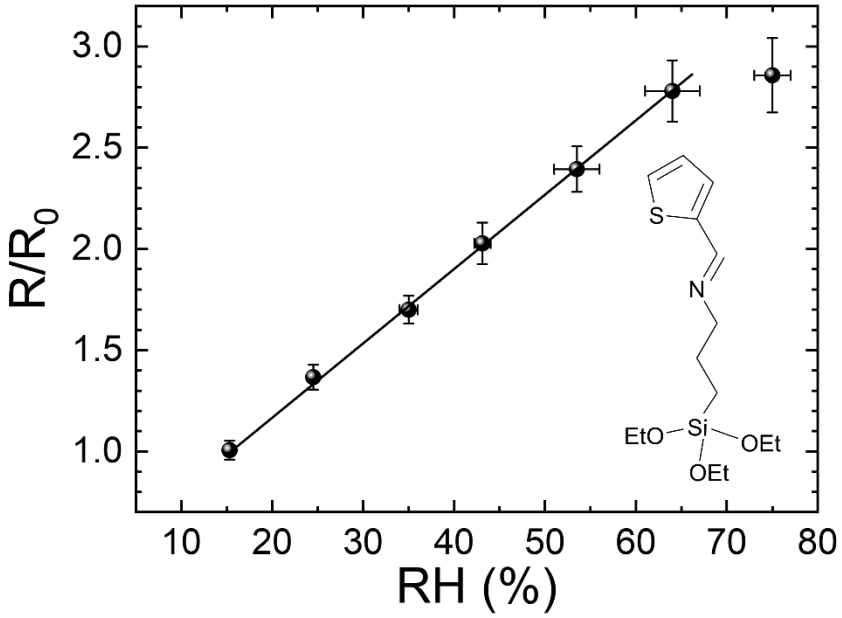

Fig. S2 The structure of *(E)-1-(thiophen-2-yl)-N-(3-triethoxysilyl)propyl)methanimine* along with the corresponding rectification response to relative humidity (RH) when in a EGaIn/SAM/SiO_2/Si device architecture normalized to the rectification when in dry air. Device was exposed to specific RH for 10 min before measuring.

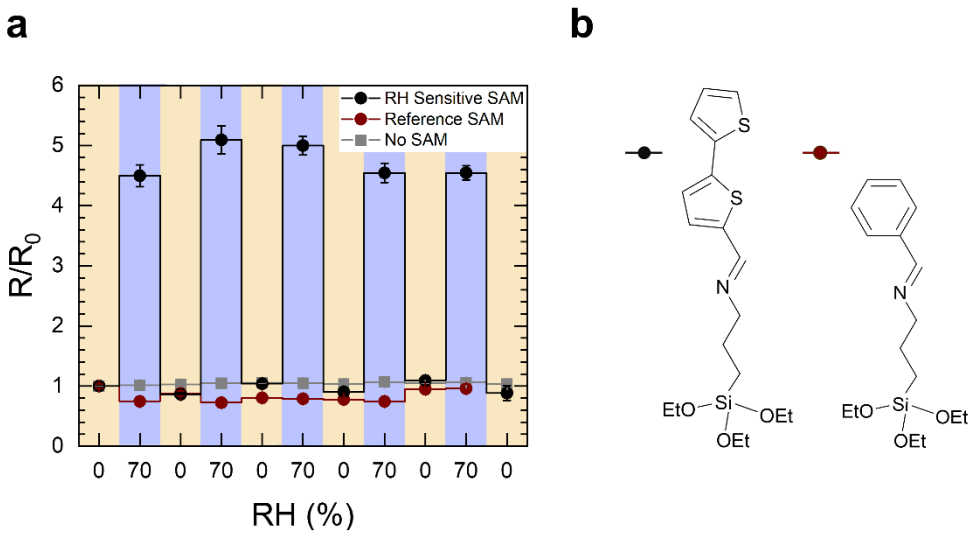

Fig. S3 (a) The rectification responses to relative humidity of BT-TESP-MA (RH Sensitive SAM), (E)-1-phenyl-N-(3(triethoxysilyl)propyl)-methanimine (Reference SAM) when measured in a EGaIn/SAM/SiO_2/Si device architecture normalized to the rectification when in dry air. The response of the sample with no SAM is also included. During measurements, an exposure time of 10 min was used when introducing 70% RH and 30 min when introducing dry air. (b) The chemical structures of BT-TESP-MA (left) and the Reference SAM (right).

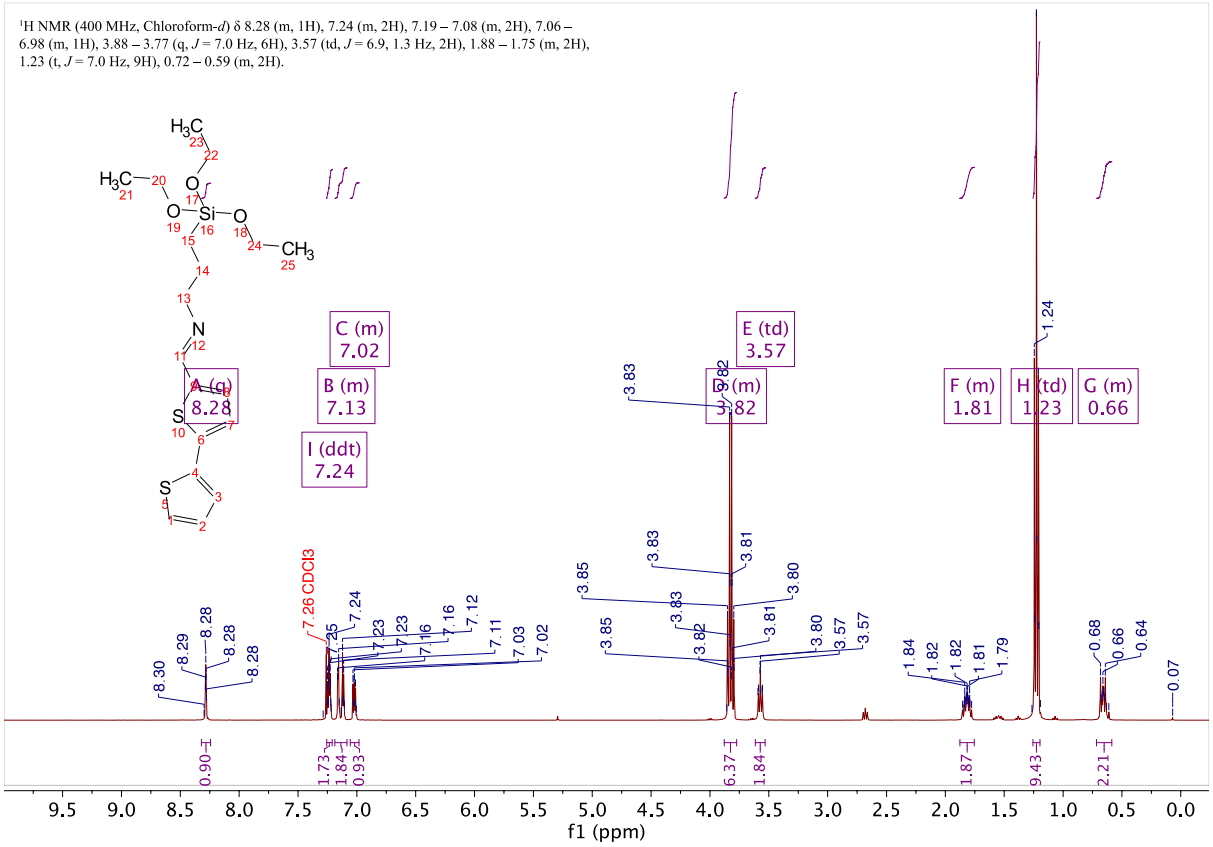

Fig. S4 (E)-1-([2,2'-bithiophen]-5-yl)-N-(3-(triethoxysilyl)propyl)methanimine ^{1}H NMR.

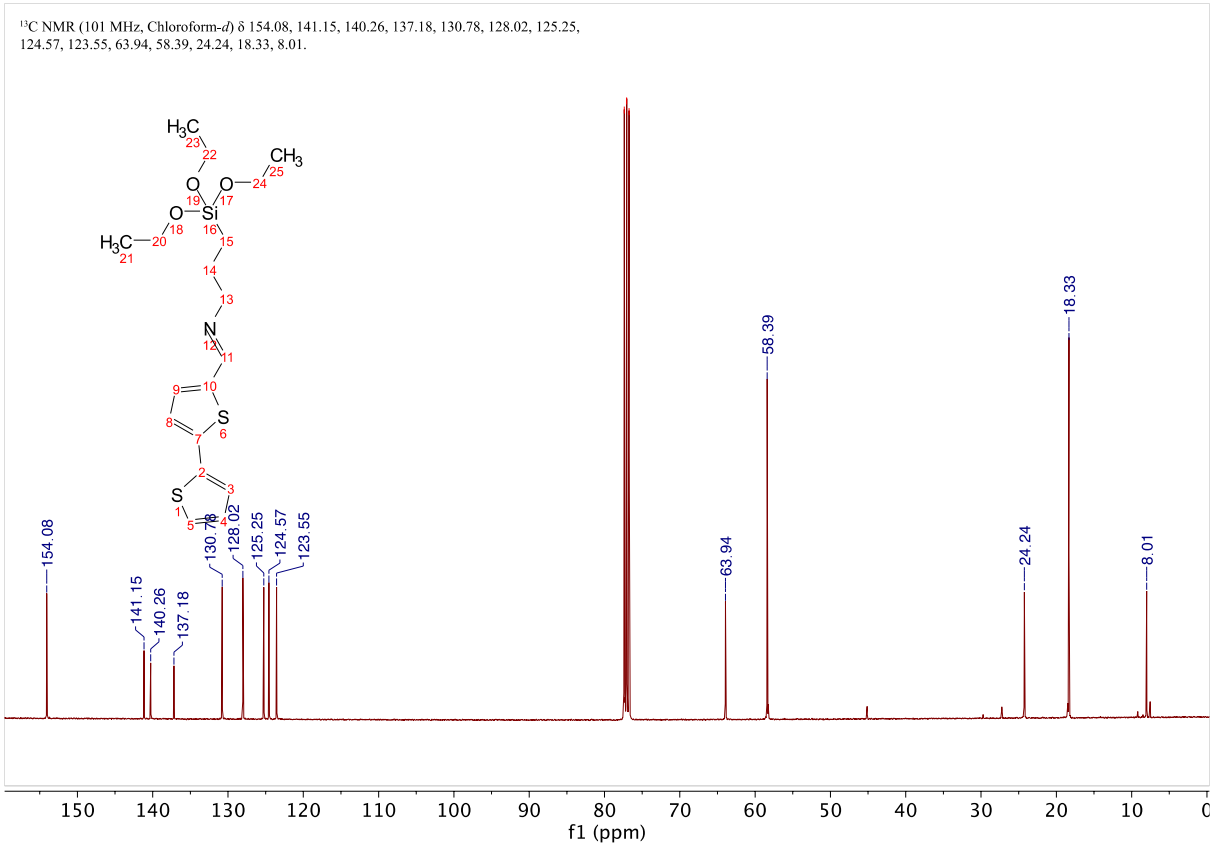

Fig. S5 (E)-1-([2,2'-bithiophen]-5-yl)-N-(3-(triethoxysilyl)propyl)methanimine ^{13}C NMR

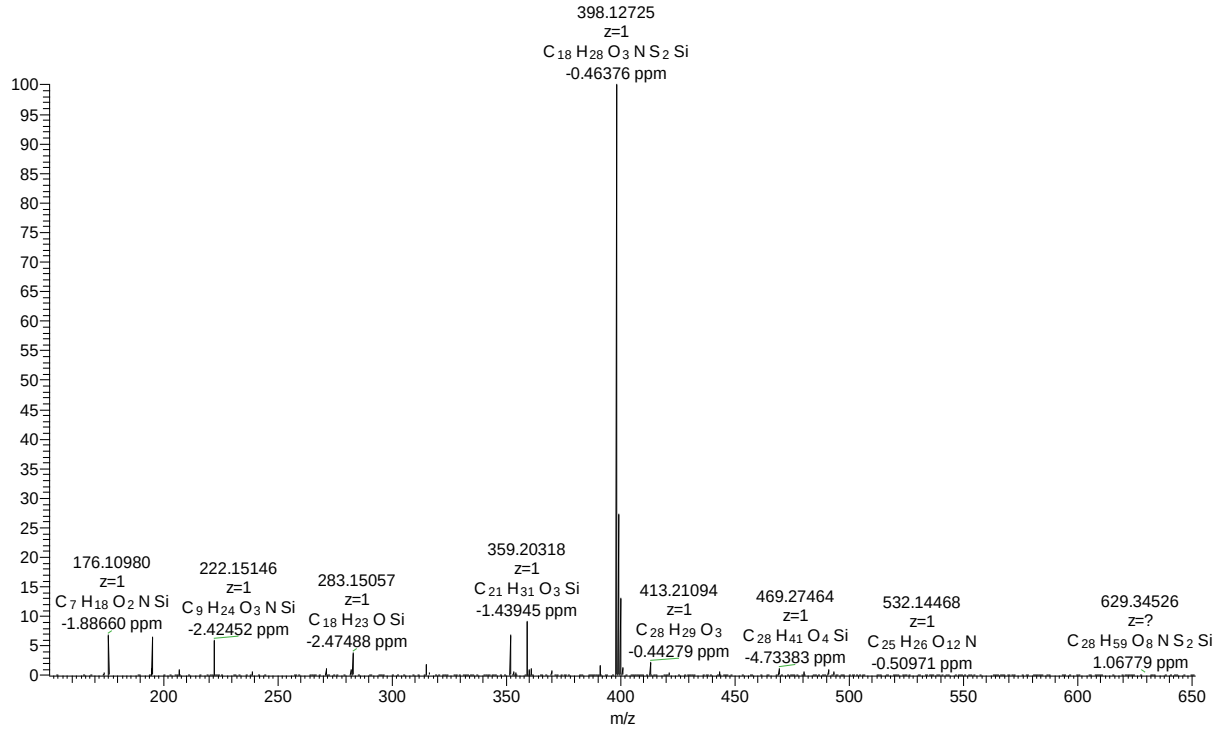

Fig. S6 (E)-1-([2,2'-bithiophen]-5-yl)-N-(3-(triethoxysilyl)propyl)methanimine HRMS.

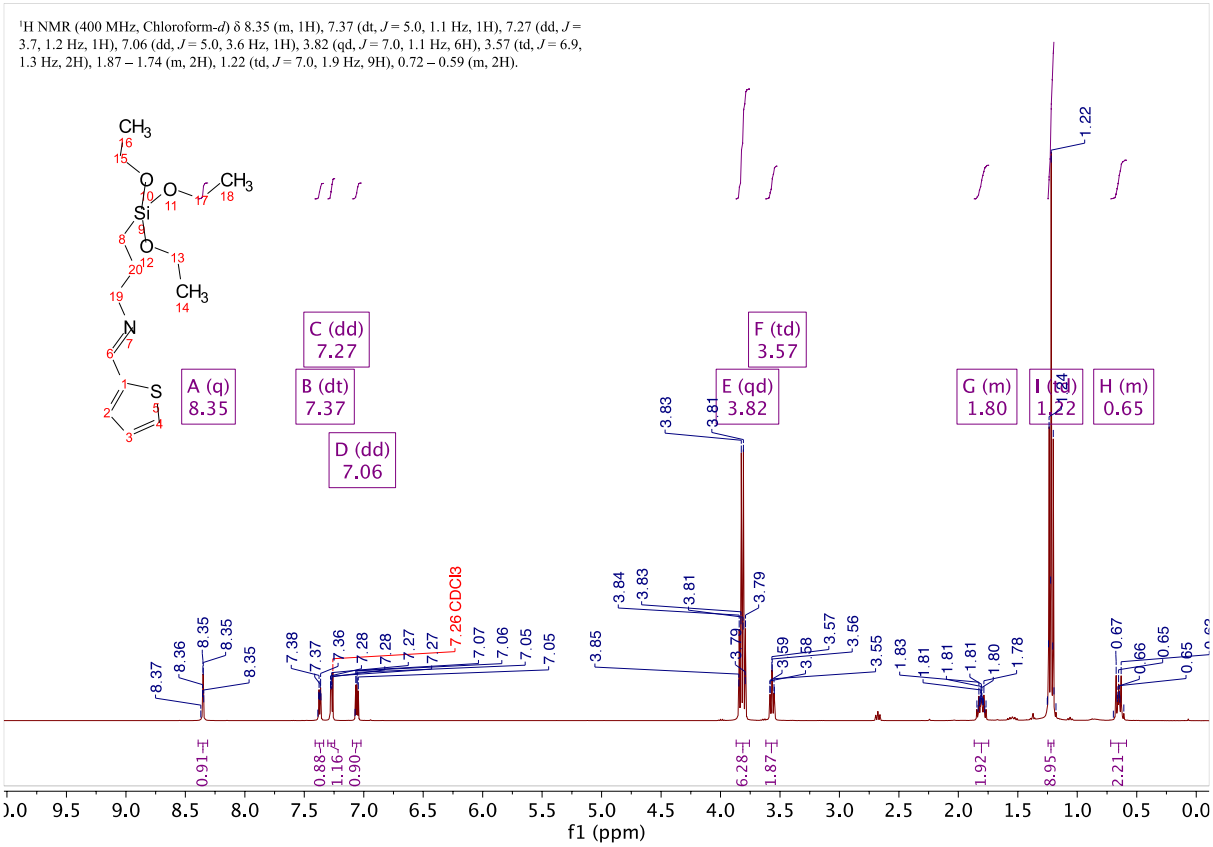

Fig. S7 (E)-1-(thiophen-2-yl)-N-(3-triethoxysilyl)propyl)methanimine ^{1}H NMR.

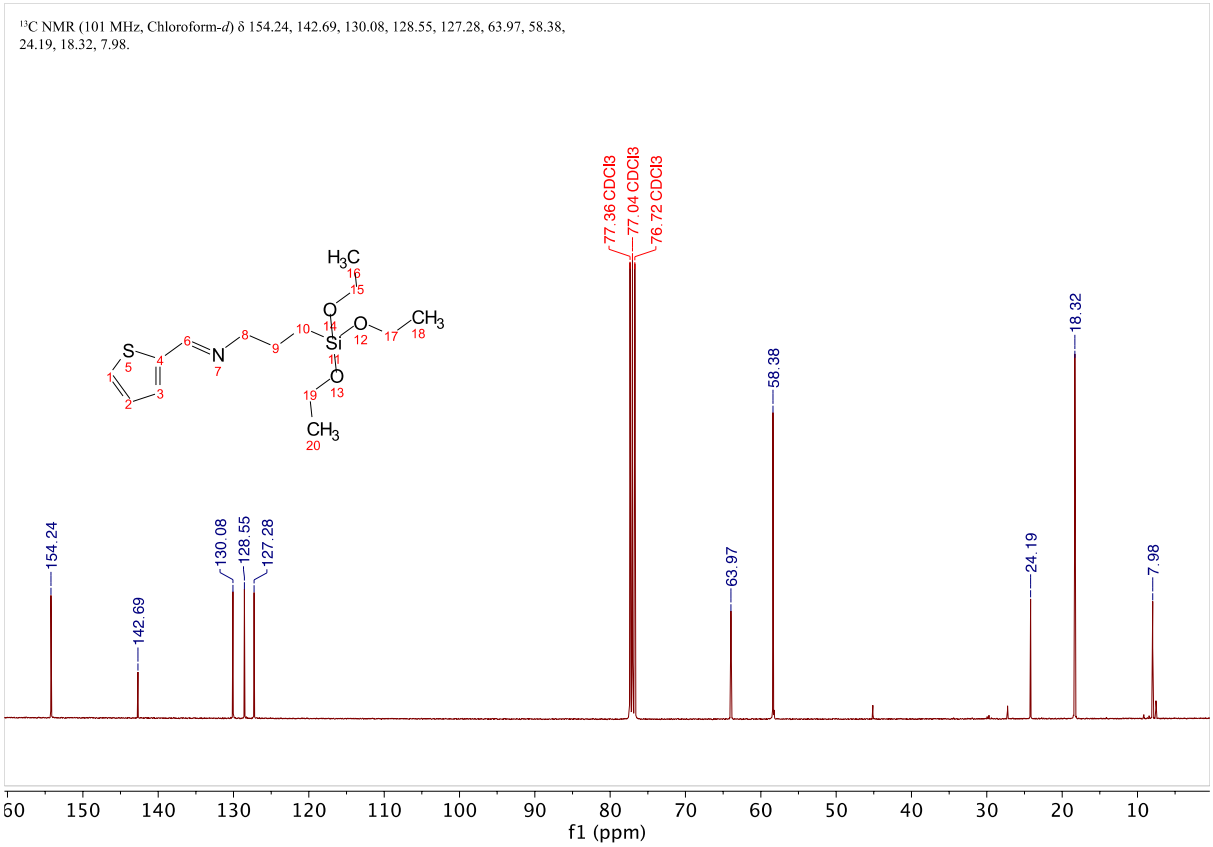

Fig. S8 (E)-1-(thiophen-2-yl)-N-(3-triethoxysilyl)propyl)methanimine ^{13}C NMR.

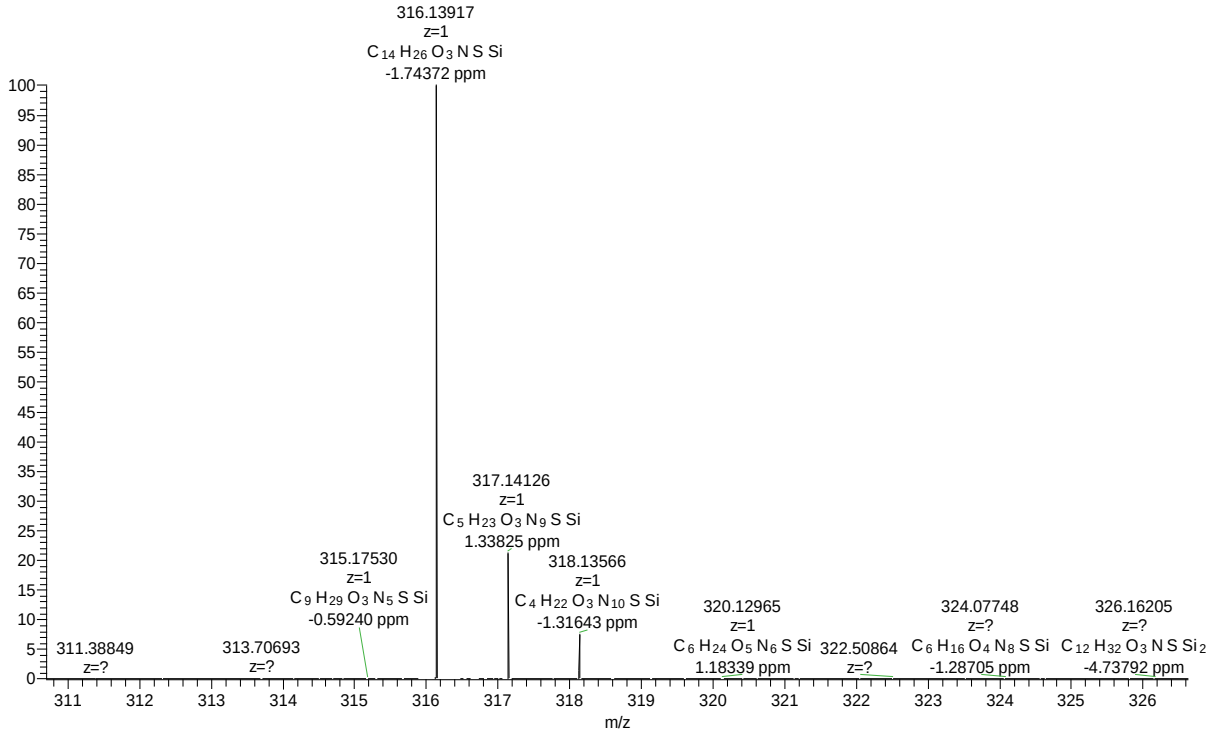

Fig. S9 (E)-1-(thiophen-2-yl)-N-(3-triethoxysilyl)propyl)methanimine HRMS.

References

1 J. Lin, X. Jin, Y. Bu, D. Cao, N. Zhang, S. Li, Q. Sun, C. Tan, C. Gao and Y. Jiang, *Org. Biomol. Chem.*, 2012, **10**, 9734–9746.