Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Strategies for optimizing the performance of carbazole thiophene appended unsymmetrical squaraine dyes for DSSC

Suraj Soman,*[,a] M. A. Rahim,[a] S. Lingamoorthy,[a] Cherumuttathu H. Suresh,[c] and Suresh Das*[,a,b]

[a] Photosciences and Photonics Section, Chemical Science and Technology Division, CSIR-National Institute for Interdisciplinary Science and Technology, Trivandrum, 695 019 and Network of Institutes for Solar Energy (NISE), India. Tel: +91-813918534, Fax: +91-471-2491712. E-mail: suraj@niist.res.in

[b] Kerala State Council for Science Technology and Environment, Sasthra Bhavan, Pattom, Thiruvananthapuram 695004, Kerala, India. Tel: +91-9447706202, Fax: +91-471-2540085 E-mail: sureshdas55@gmail.com

[c] Inorganic and Theoretical Chemistry Section, CSIR-National Institute for Interdisciplinary Science and Technology, Trivandrum, 695019, India.

Synthetic procedure followed for CTSQ-2

Synthessis of squarylium chloride

Thionyl chloride (10 mL, 137.6 mmol) in benzene (10 mL) was added dropwise using pressure equalizer to squaric acid (6 g, 56.3 mmol) dissolved in benzene at 80 °C under argon atmosphere. 1 mL DMF was added after half addition of thionyl chloride to dissolve any remaining squaric acid after which thionyl chloride was added completely. The reaction mixture was refluxed for 8 h. Benzene and thionyl chloride was removed and the crude reaction mixture was decanted and precipitated by adding hexane The crystals formed was separated and the mixture was vacuum dried.

Synthesis of alkylated carbazole

Carbazole (3.5 g, 20.93 mmol), anhydrous zinc chloride (7 g, 51.35 mmol) and tertiary butyl chloride (6 mL, 55.1 mmol) was taken in a RB to which nitromethane (75 mL) was added through a pressure equalizer in argon atmosphere at room temperature for 2 h. The reaction mixture was hydrolyzed with distilled water and extracted with DCM using separating funnel and washed three times with distilled water. Magnesium sulphate was added and it was filtered and dried under reduced pressure using rotary evaporator. TLC was checked using silica as solid phase and hexane as mobile phase and characterized using ^{1}H-NMR (500 MHz, $CDCl_3$, TMS): δ 1.49 (t, 18H), δ 7.32 (d, 2H), δ 7.38 (d, 2H), δ 7.83 (s, 2H), δ 8.07 (s, 2H) ppm.

Synthesis of alkylated carbazole thiophene

Alkylated carbazole (3 g, 10.7 mmol), (±)-trans-1,2-diaminocyclohexane (3.3 mL, 27.47mmol), *t*-BuONa (1.3 g, 13.53 mmol), CuI (510 mg, 2.678 mmol) was taken in a RB to which 1,4 dioxan (90 mL) and 2-iodo thiophene (6.75 mL, 32.2 mmol) was added under argon atmosphere at 110 °C. The reaction mixture was kept for 6 h in reflux. The product formed was confirmed from the TLC using silica as stationary phase and hexane as mobile phase. The reaction mixture was filtered and 1,4-dioxane was removed and purified by column chromatography using silica as stationary phase and hexane as mobile phase and was then characterized using ^{1}H-NMR. (500 MHz, $CDCl_3$, TMS): δ 1.46 (m, 9H), δ 7.15 (s, 1H), δ 7.32 (d, J = 4.5 Hz, 1H), δ 7.39 (d, J = 8.5 Hz, 1H), δ 7.49 (d, J = 8.5 Hz, 1H), δ 8.1 (s, 1H) ppm.

Synthesis of Semisquaraine

Alkylated carbazole thiophene (3 g, 8.30 mmol) and squarylium chloride (2.4 g, 16 mmol) was added to 150 mL of dry benzene under argon atmosphere. The reaction was kept refluxing overnight for 80 °C. After the completion of reaction,solvents were removed and dried. It was then subjected to a fast silica column chromatography using 90% $CHCl_3$/hexane solvent mixture. The product obtained was dissolved in 150 mL dry benzene to which 1.5 mL triethyl amine was added under argon atmosphere and kept stirring for 6 h at room temperature. The solvent was removed through rotary evaporator and 2N HCL was added and kept stirring for another 2 h which was finally purified by column chromatography.

Synthesis of CTSQ-2

Semisquarine (250 mg, 0.55 mmol) and alkylated indolium (200 mg, 0.86 mmol) were taken in a RB fixed with Dean Stark apparatus in benzene/butanol (1:1) mixture and refluxed at 100 °C for 8 h. The pure product was separated by silica column chromatography using 3% DCM/CH_3OH solvent mixture. ^{1}H-NMR (500 MHz, $CDCl_3$, TMS): δ 1.47 (t, 18H), δ 1.53 (t, 4H), δ 1.9 (s, 7H), δ 4.35 (d, 2H), δ 6.39 (s, 1H), δ 7.3 (t, J = 9 Hz, 2H), δ 7.41 (d , J = 4Hz, 1H), δ 7.53 (d, J = 8.5 Hz, 2H), δ 7.76 (d, 2H), δ 8.09 (s, 2H), δ 8.16 (d, J = 4 Hz, 1H), δ 8.23 (d, J = 8 Hz, 1H) ppm. Elemental Analysis for $C_{42}H_{42}N_2O_4S$: C, 75.20; H, 6.31; N, 4.18. Found: C, 75.32; H, 6.34; N, 4.10.

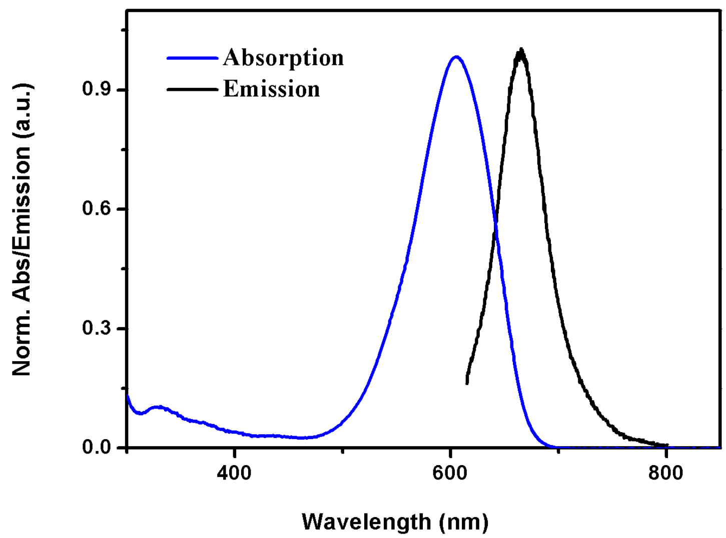


Figure S1: Normalized absorption and emission spectra of CTSQ-1 in CH_2Cl_2

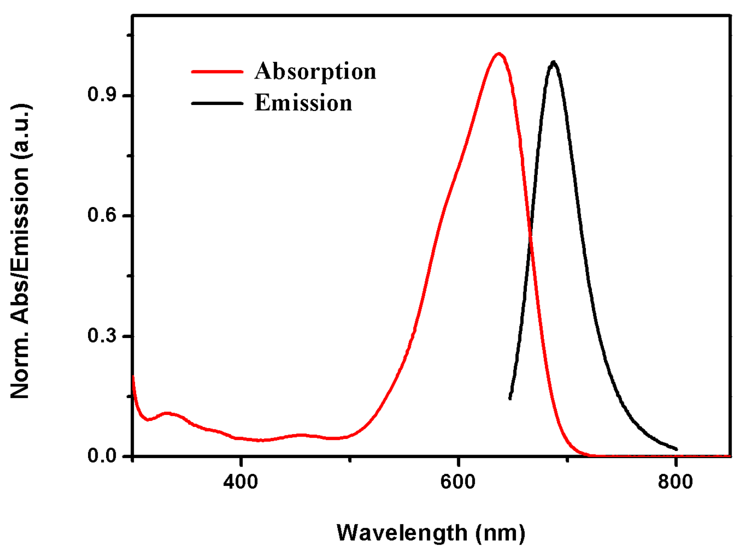


Figure S2: Normalized absorption and emission spectra of CTSQ-2 in CH_2Cl_2

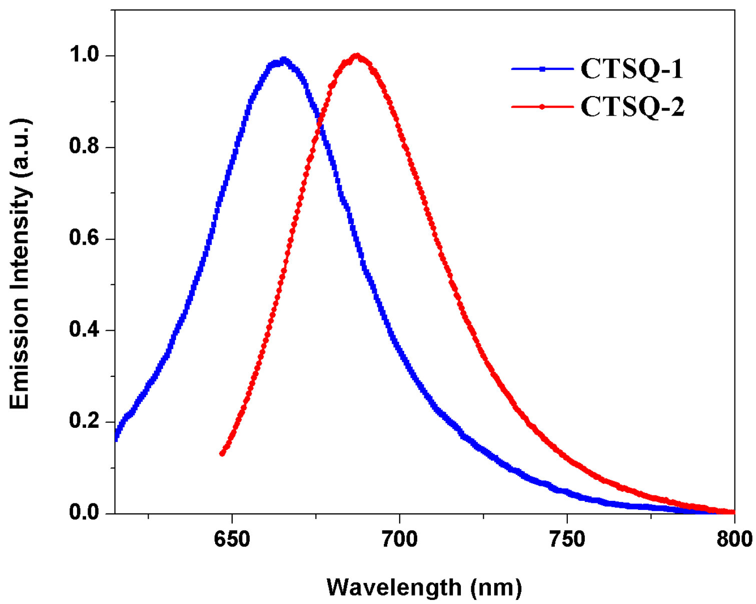


Figure S3: Normalized emission spectra of CTSQ-1 and CTSQ-2 in CH_2Cl_2

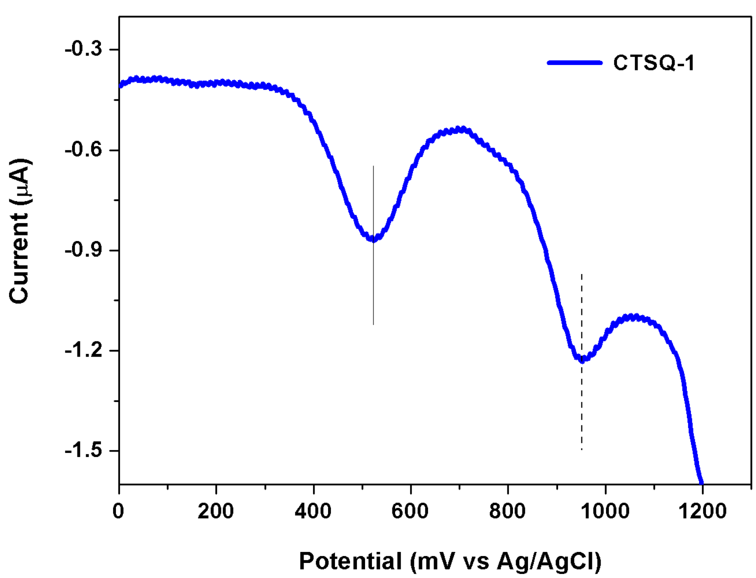


Figure S4: Square wave voltammetry of CTSQ-1 in CH_2Cl_2

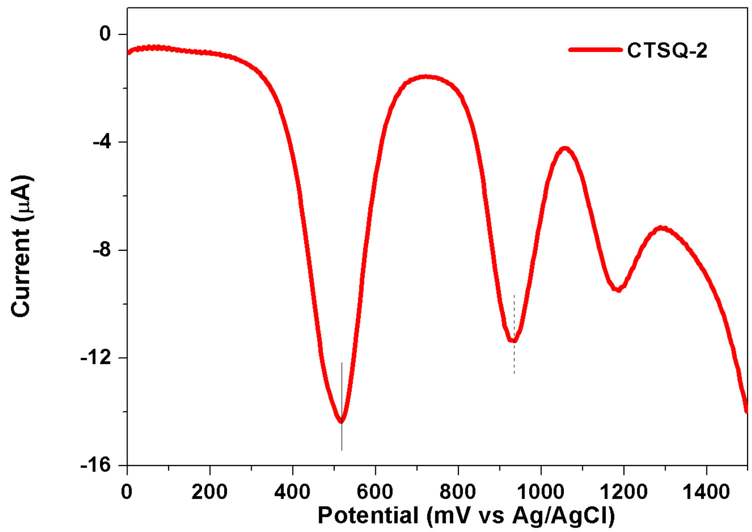


Figure S5: Square wave voltammetry of CTSQ-2 in CH_2Cl_2

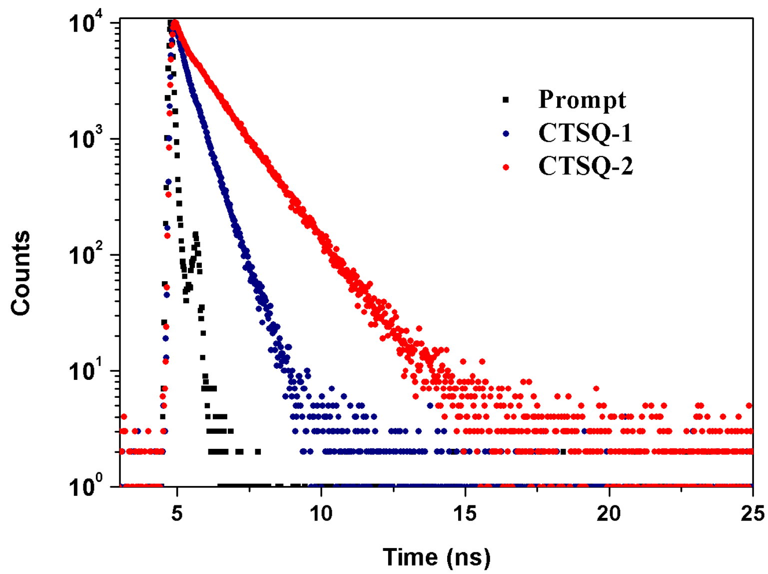


Figure S6: Lifetime decay plots of CTSQ-1 and CTSQ-2 in CH_2Cl_2

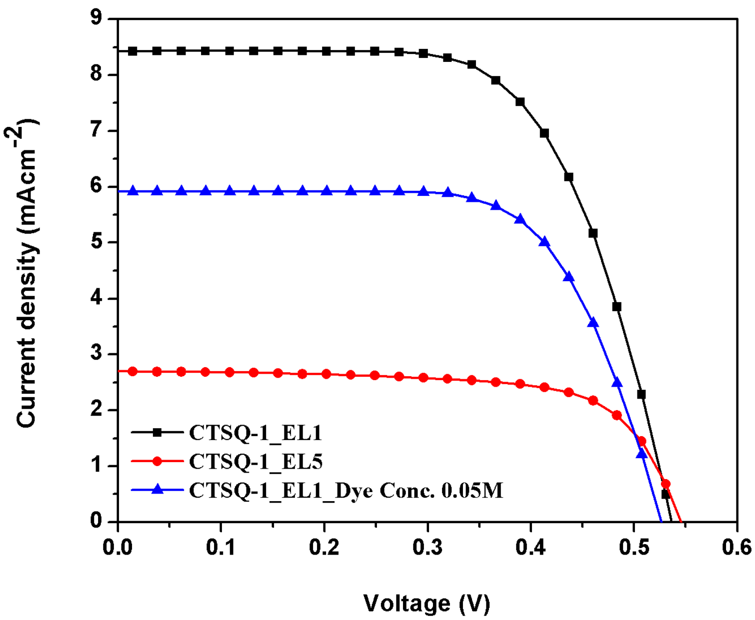
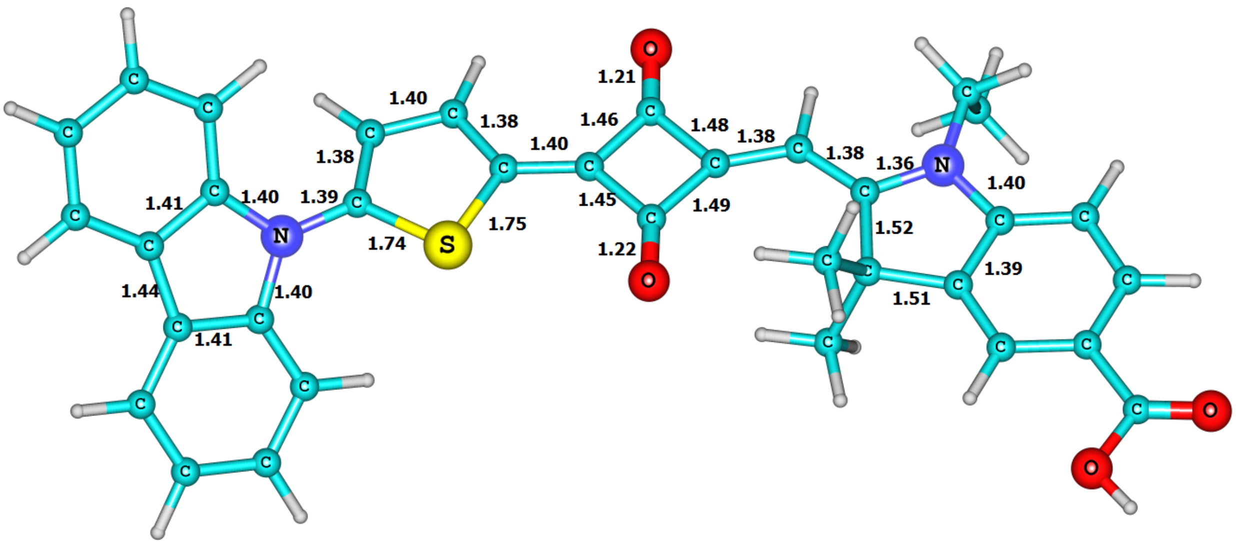


Figure S7: J-V characteristics of CTSQ-1 corresponding to entries 1, 5 and 6 in Table 2

Theoretical Calculations done using Gaussian 09[1]

CTSQ-1



CTSQ-2

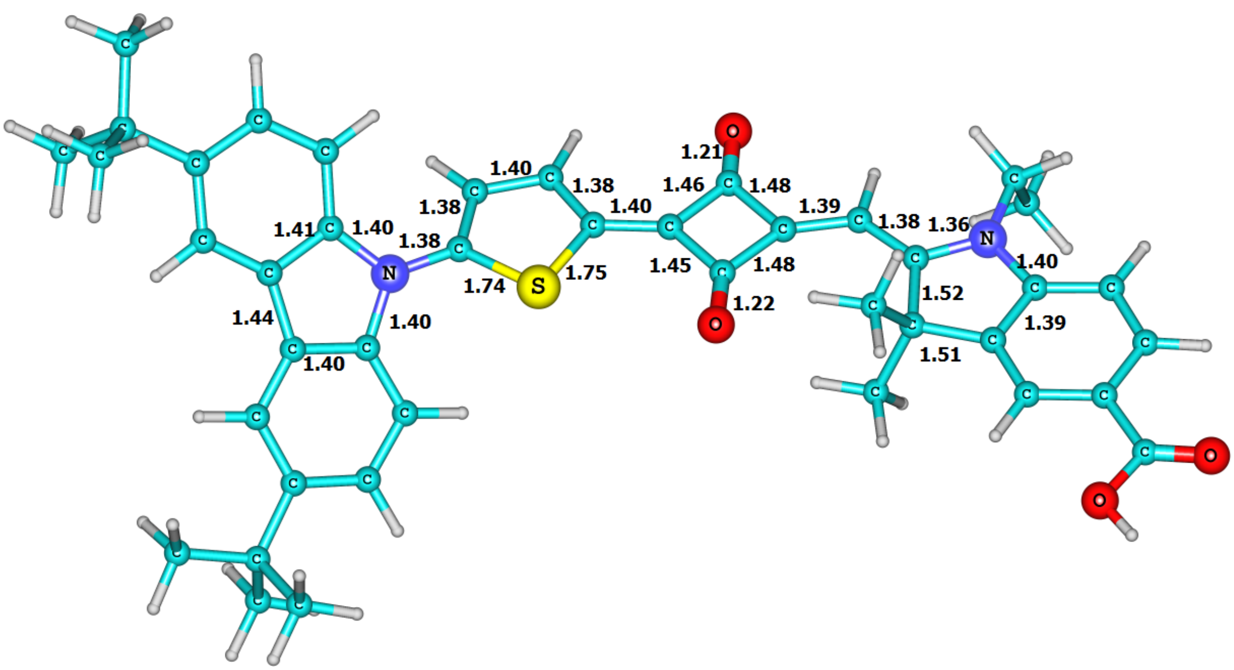


Figure S8: Optimized geometry of CTSQ-1 and CTSQ-2 with bond lengths

CTSQ-1

Cartesian coordinates in Å (Optimized geometry using M06/6-311G(d,p)[2] level DFT)

Total Energy = -2119.07174618 au.

C	5.106767000	2.136338000	-1.480884000
C	5.674043000	3.322975000	-1.917561000
C	6.972582000	3.687242000	-1.556642000
C	7.737874000	2.861298000	-0.752384000
C	7.190300000	1.665683000	-0.299944000
C	5.876587000	1.320032000	-0.663554000
N	5.566529000	0.075966000	-0.100047000
C	6.679313000	-0.366155000	0.627102000
C	6.834591000	-1.514374000	1.391556000
C	8.047999000	-1.695589000	2.035887000
C	9.078471000	-0.759608000	1.927156000
C	8.909364000	0.390179000	1.175799000
C	7.700041000	0.594914000	0.520020000
C	4.372697000	-0.614736000	-0.230188000
C	4.231728000	-1.953904000	-0.519303000
C	2.896622000	-2.366391000	-0.523346000
C	2.009368000	-1.341806000	-0.246203000
S	2.845085000	0.164765000	0.064464000
C	0.615316000	-1.431196000	-0.226509000
C	-0.452657000	-0.479991000	0.007421000
C	-1.439012000	-1.571781000	-0.194618000
C	-0.330292000	-2.522305000	-0.424143000
O	-0.274960000	-3.707318000	-0.672125000
O	-0.476341000	0.712645000	0.261404000
C	-2.783449000	-1.902932000	-0.224225000
C	-3.912603000	-1.130750000	-0.037753000
N	-5.162282000	-1.668729000	-0.077850000
C	-6.145897000	-0.687133000	0.070622000
C	-5.526953000	0.542907000	0.261937000
C	-4.031437000	0.362462000	0.220612000
C	-7.525235000	-0.829369000	0.043778000
C	-8.282828000	0.315828000	0.230716000
C	-7.681311000	1.556316000	0.435429000
C	-6.286718000	1.672923000	0.451091000
C	-5.483124000	-3.066309000	-0.329209000
C	-3.420363000	1.178324000	-0.923013000
C	-3.405460000	0.741413000	1.567914000
C	-5.611027000	-3.360339000	-1.810936000
H	4.100368000	1.859896000	-1.774983000
H	5.092708000	3.980952000	-2.555705000
H	8.752414000	3.137159000	-0.478744000

H	6.033721000	-2.238165000	1.496155000
H	8.196231000	-2.583943000	2.641773000
H	9.704321000	1.126940000	1.101523000
H	5.080342000	-2.589393000	-0.742398000
H	2.540210000	-3.366732000	-0.743129000
H	-2.933174000	-2.962182000	-0.437222000
H	-8.003654000	-1.789031000	-0.121382000
H	-9.366867000	0.271364000	0.219997000
H	-5.826249000	2.643689000	0.608327000
H	-6.416479000	-3.282694000	0.200183000
H	-4.713113000	-3.685106000	0.139195000
H	-2.331138000	1.095070000	-0.919287000
H	-3.673473000	2.235063000	-0.784324000
H	-3.819799000	0.857614000	-1.891041000
H	-2.317265000	0.651841000	1.526880000
H	-3.805738000	0.118809000	2.375144000
H	-3.646563000	1.786180000	1.792864000
H	-4.667316000	-3.167387000	-2.329178000
H	-6.384057000	-2.732988000	-2.265715000
H	-5.880239000	-4.407237000	-1.972394000
C	-8.567081000	2.722529000	0.628157000
O	-9.768841000	2.686712000	0.615396000
O	-7.881507000	3.863502000	0.826514000
H	-8.542674000	4.558647000	0.940932000
H	10.016581000	-0.934980000	2.443802000
H	7.383706000	4.625205000	-1.915623000

CTSQ-2

Cartesian coordinates in Å (Optimized geometry using M06/6-311G(d,p) level DFT)

Total Energy = -2433.40955202 au.

C	3.462726000	1.943832000	-1.077043000
C	4.080969000	3.178475000	-1.147308000
C	5.410291000	3.394429000	-0.742908000
C	6.131108000	2.308530000	-0.264527000
C	5.536429000	1.052485000	-0.184149000
C	4.202839000	0.880061000	-0.580379000
N	3.848693000	-0.466220000	-0.419031000
C	4.963763000	-1.149337000	0.086350000
C	5.107283000	-2.475866000	0.452430000
C	6.337801000	-2.882366000	0.950044000
C	7.423487000	-2.008221000	1.096710000
C	7.241583000	-0.674285000	0.737962000
C	6.023056000	-0.238395000	0.238940000

C	2.621143000	-1.039342000	-0.696863000
C	2.405208000	-2.243643000	-1.332226000
C	1.051202000	-2.577319000	-1.407764000
C	0.221605000	-1.626804000	-0.839183000
S	1.140414000	-0.299212000	-0.159465000
C	-1.173339000	-1.650058000	-0.796540000
C	-2.173957000	-0.743539000	-0.268796000
C	-3.231190000	-1.686799000	-0.708997000
C	-2.192629000	-2.594625000	-1.240113000
O	-2.218894000	-3.668504000	-1.801183000
O	-2.113808000	0.335703000	0.296989000
C	-4.595447000	-1.928299000	-0.751540000
C	-5.662449000	-1.180175000	-0.297632000
N	-6.947237000	-1.620905000	-0.404594000
C	-7.854709000	-0.667795000	0.065169000
C	-7.146814000	0.430134000	0.540779000
C	-5.670400000	0.189372000	0.363236000
C	-9.240392000	-0.725848000	0.090307000
C	-9.909902000	0.362780000	0.625981000
C	-9.217602000	1.469661000	1.114356000
C	-7.819296000	1.505341000	1.071277000
C	-7.372593000	-2.879779000	-0.998521000
C	-5.055401000	1.255869000	-0.547811000
C	-4.968280000	0.147692000	1.725572000
C	-7.594041000	-2.755696000	-2.493452000
H	2.437340000	1.821743000	-1.408023000
H	3.502624000	4.012277000	-1.535027000
H	7.164514000	2.420552000	0.049304000
H	4.285631000	-3.179775000	0.368246000
H	6.445217000	-3.923072000	1.234834000
H	8.050644000	0.044252000	0.847693000
H	3.214120000	-2.832281000	-1.747476000
H	0.641072000	-3.463852000	-1.878694000
H	-4.821854000	-2.880764000	-1.232448000
H	-9.789600000	-1.578054000	-0.295646000
H	-10.993793000	0.379197000	0.674153000
H	-7.288053000	2.373048000	1.450858000
H	-8.290588000	-3.184148000	-0.485660000
H	-6.623428000	-3.640972000	-0.765322000
H	-3.975616000	1.116092000	-0.635092000
H	-5.227769000	2.244740000	-0.109050000
H	-5.519580000	1.238828000	-1.539655000
H	-3.890476000	0.018657000	1.602900000
H	-5.376390000	-0.653285000	2.351224000
H	-5.133361000	1.099750000	2.241975000
H	-6.668606000	-2.469911000	-3.001683000

H	-8.351216000	-1.996268000	-2.712449000
C	8.778291000	-2.466908000	1.633254000
C	9.124668000	-1.678023000	2.898970000
H	10.091932000	-2.006367000	3.298406000
H	9.192730000	-0.602400000	2.707659000
H	8.365317000	-1.832569000	3.673780000
C	9.854319000	-2.224185000	0.570861000
H	9.940913000	-1.164486000	0.309540000
H	10.833069000	-2.558716000	0.935809000
H	9.625506000	-2.776810000	-0.347488000
C	8.792779000	-3.951089000	1.986997000
H	9.783400000	-4.227143000	2.364782000
H	8.063262000	-4.191785000	2.768647000
H	8.585051000	-4.581471000	1.114914000
C	6.003014000	4.796020000	-0.851272000
C	7.447634000	4.849774000	-0.364284000
H	7.828673000	5.872677000	-0.456328000
H	7.533461000	4.559347000	0.689176000
H	8.102108000	4.199687000	-0.956261000
C	5.979983000	5.251311000	-2.313320000
H	4.963354000	5.287653000	-2.717778000
H	6.410524000	6.255788000	-2.406326000
H	6.565206000	4.570092000	-2.941414000
C	5.181150000	5.768131000	0.000219000
H	5.186211000	5.462979000	1.052724000
H	5.602202000	6.778863000	-0.064169000
H	4.137824000	5.821425000	-0.326542000
H	-7.932355000	-3.707129000	-2.911691000
C	-10.012859000	2.586122000	1.663804000
O	-11.213071000	2.611831000	1.732240000
O	-9.244326000	3.604117000	2.093503000
H	-9.851414000	4.275941000	2.430456000

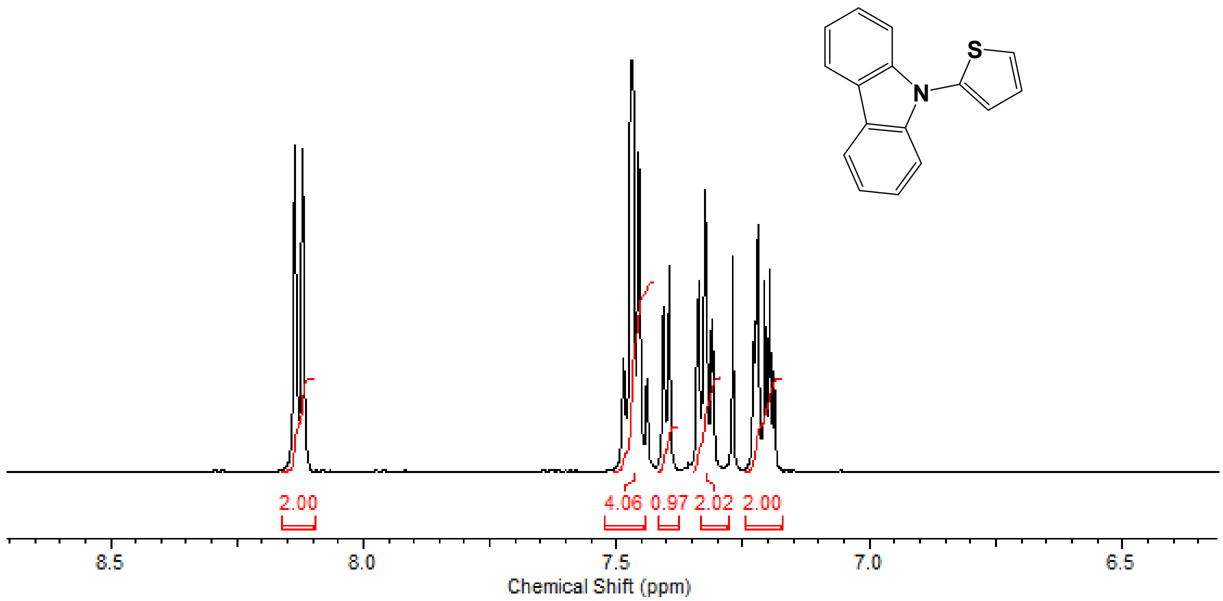


Figure S9: ^{1}H NMR spectra of carbazole thiophene

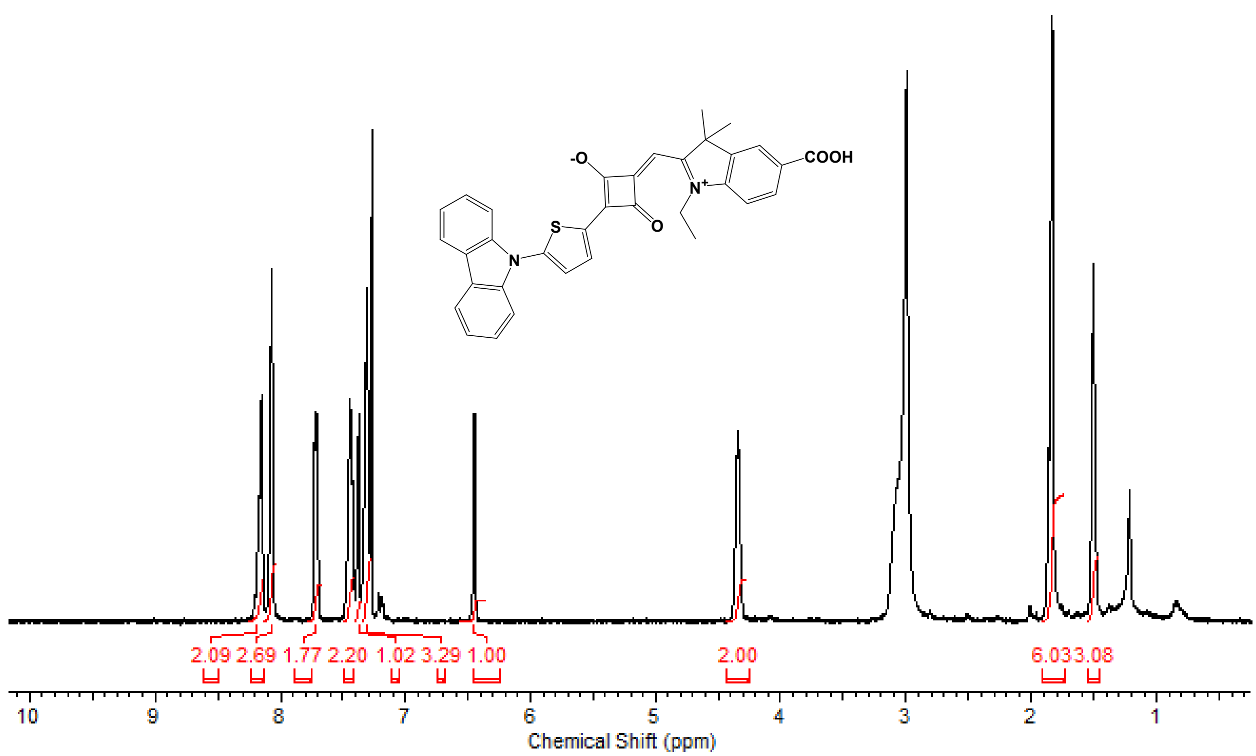


Figure S10: ^{1}H NMR spectra of CTSQ-1

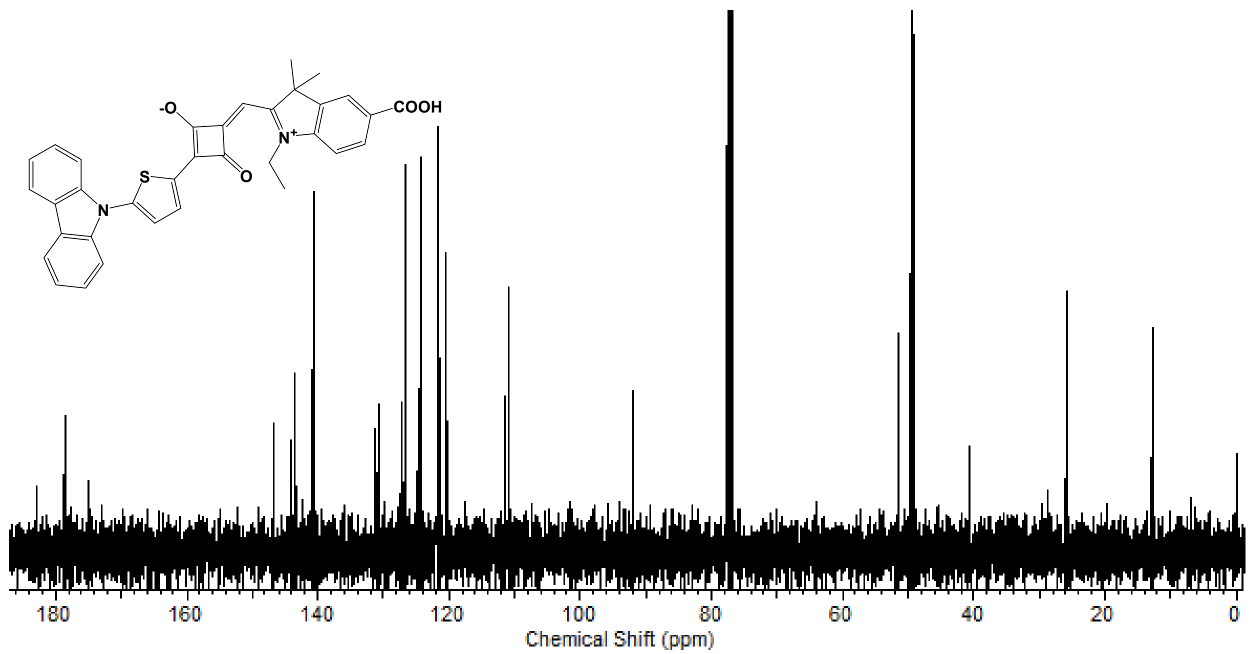


Figure S11: ^{13}C NMR spectra of CTSQ-1

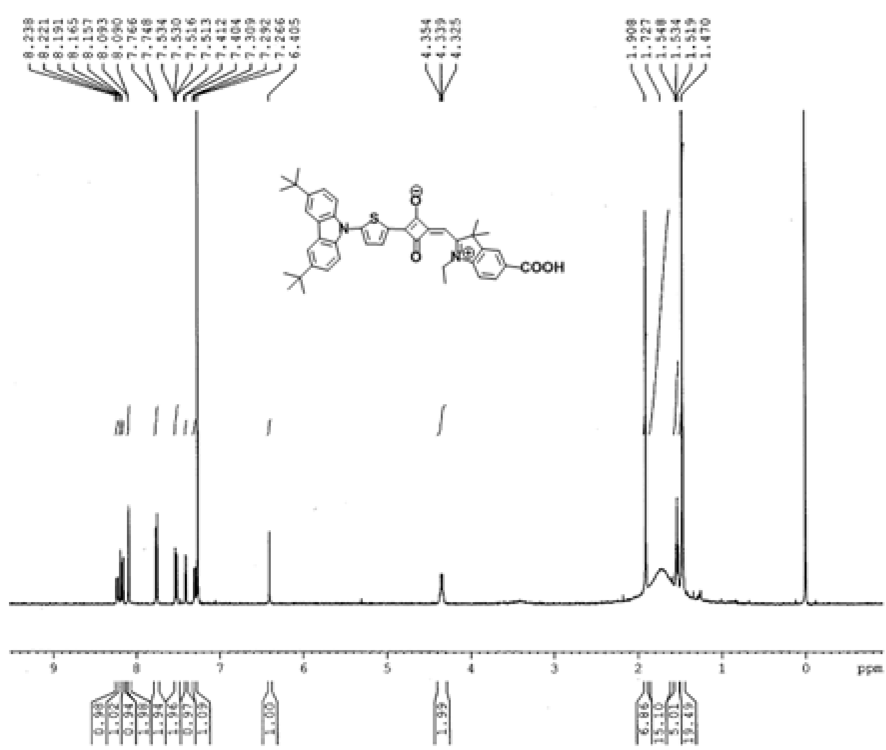


Figure S12: ^{1}H NMR spectra of CTSQ-2

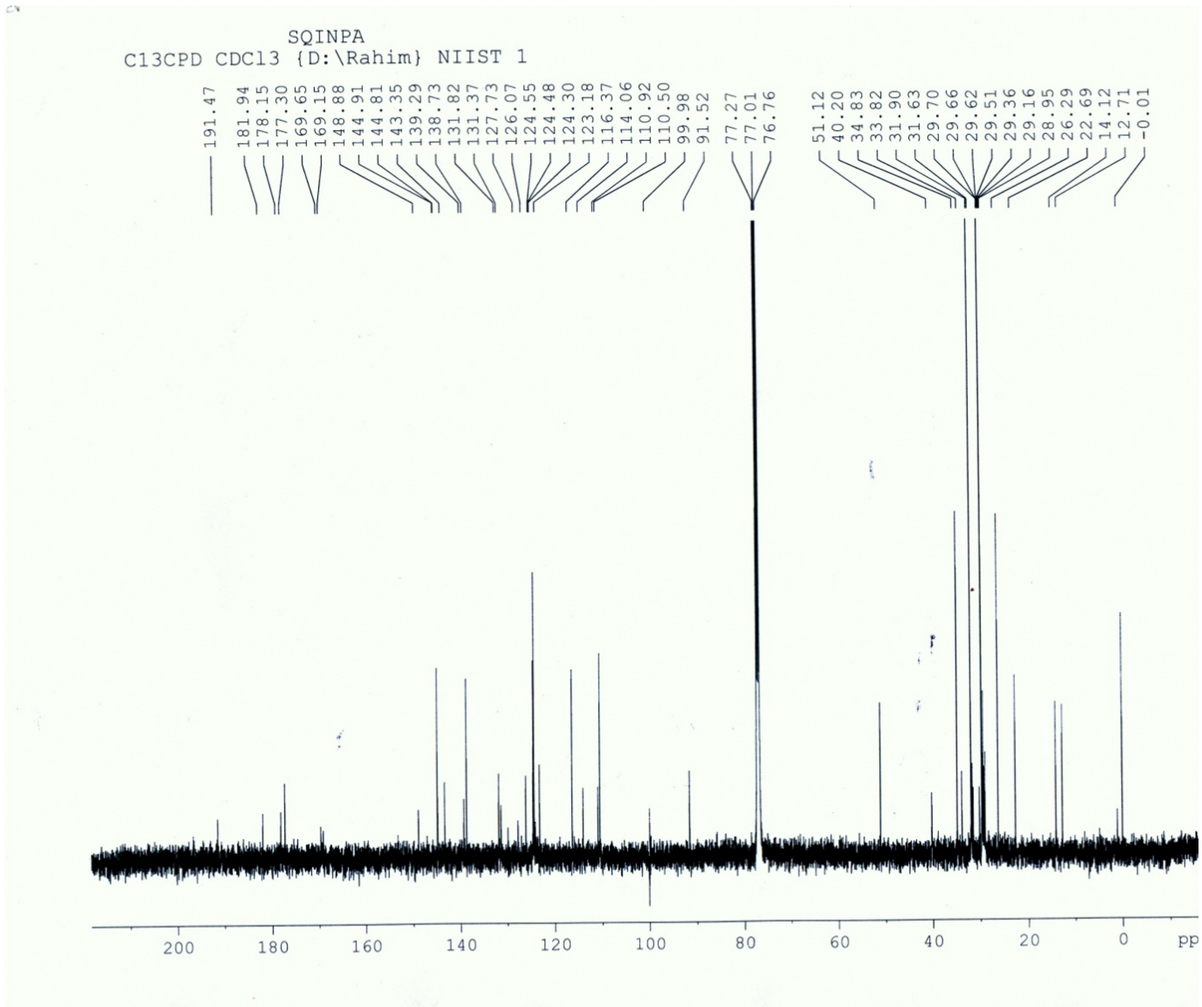


Figure S13: ^{13}C NMR spectra of CTSQ-2

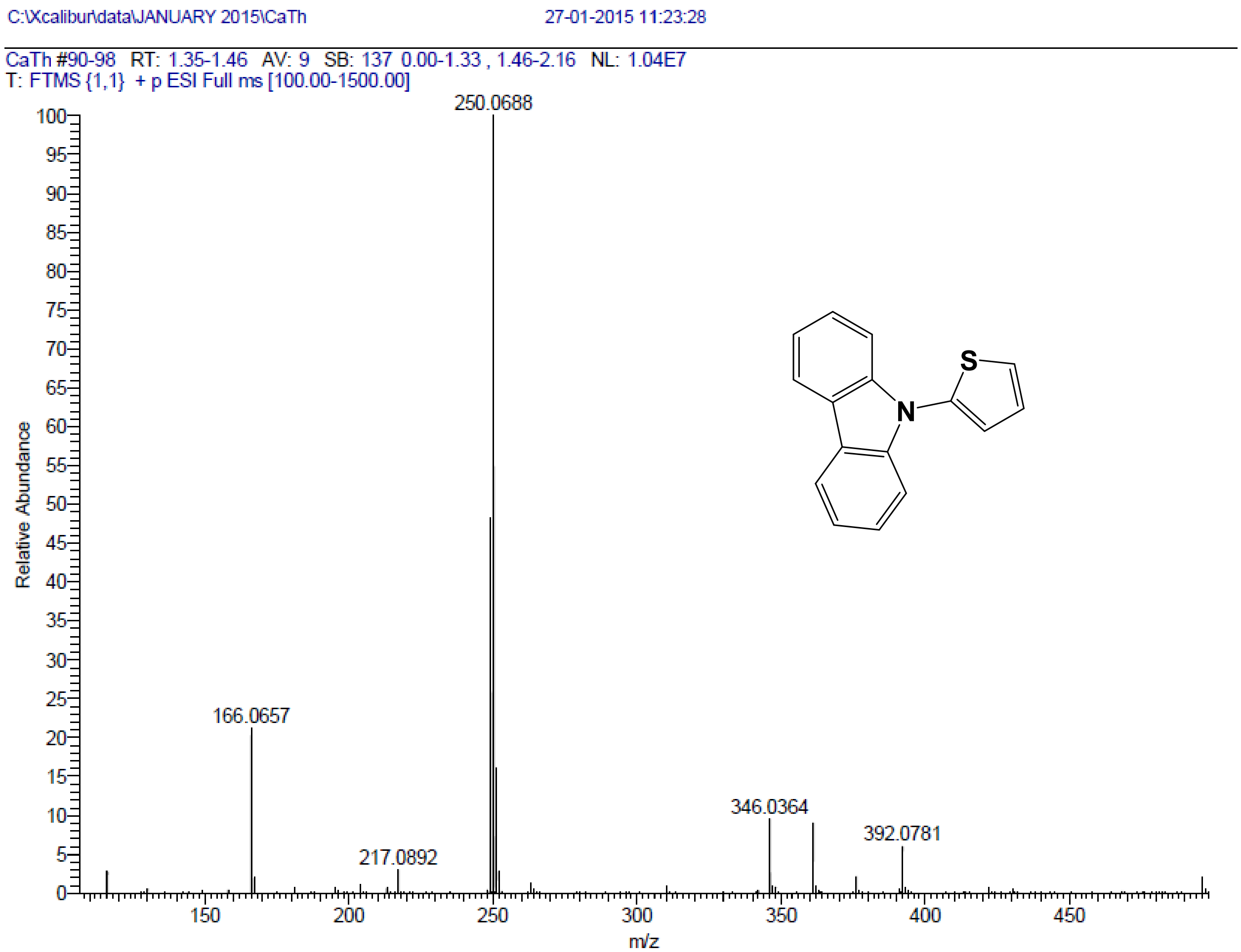


Figure S14: Mass spectra of carbazole thiophene

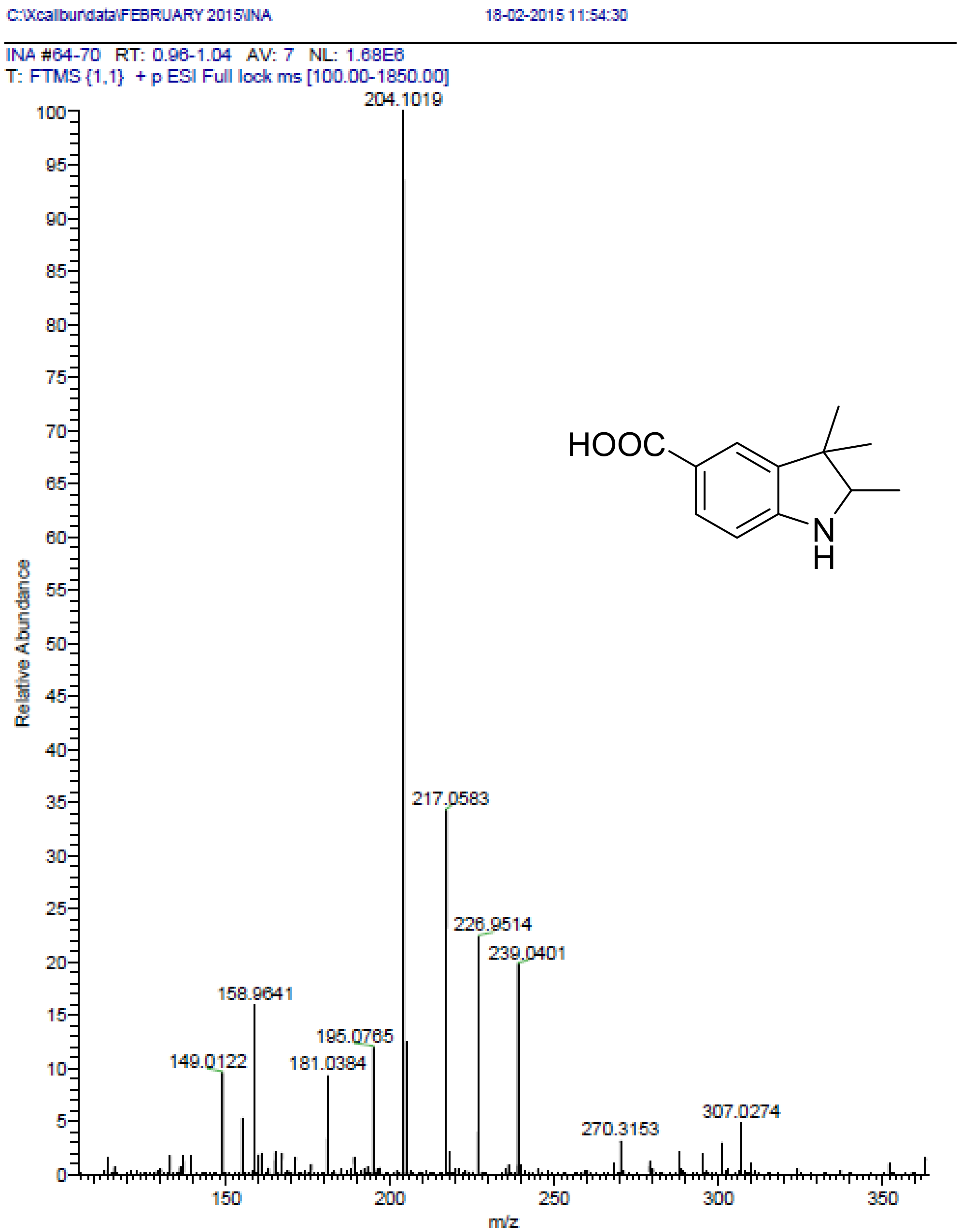


Figure S15: Mass spectra of indole acid

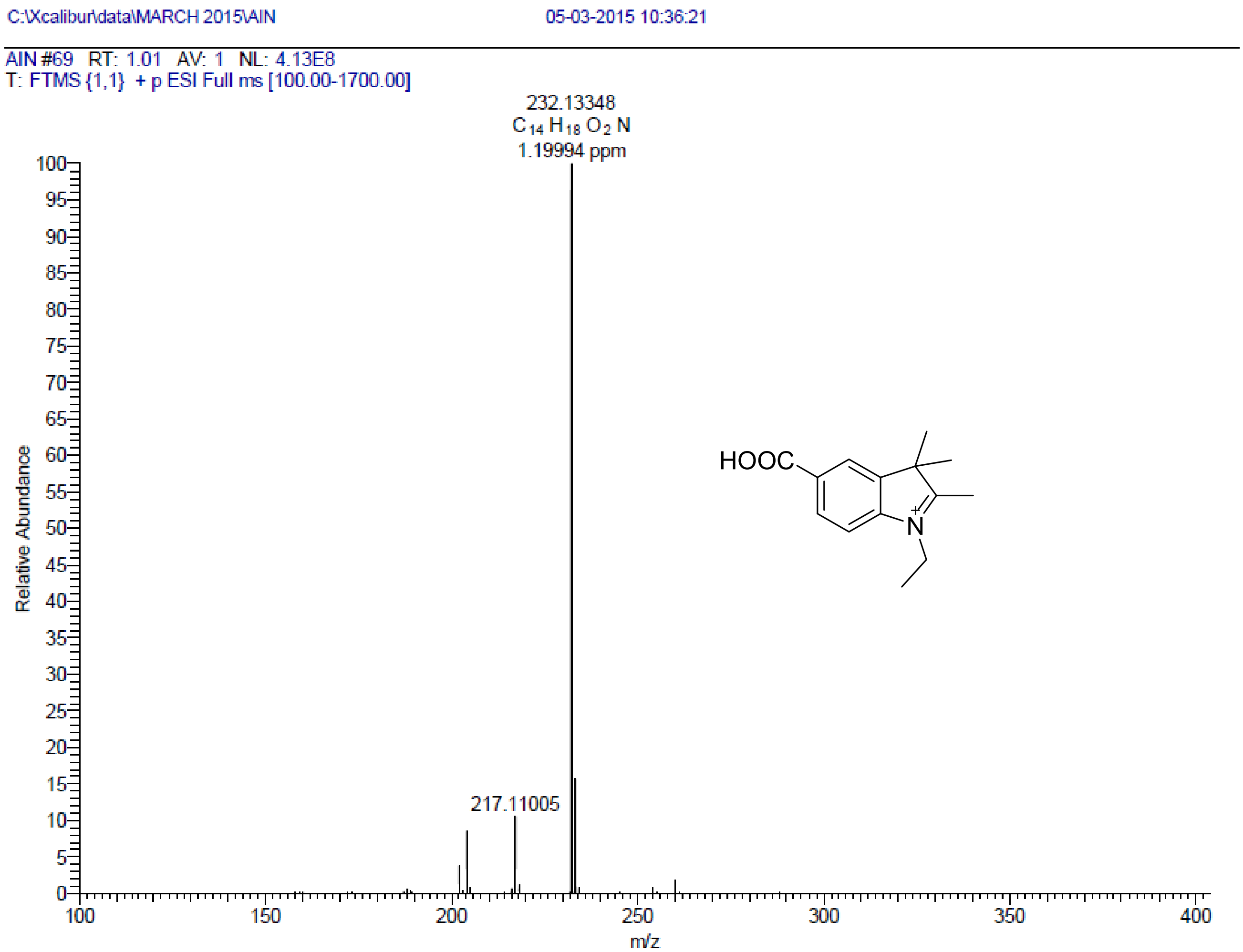


Figure S16: Mass spectra of indolium cation

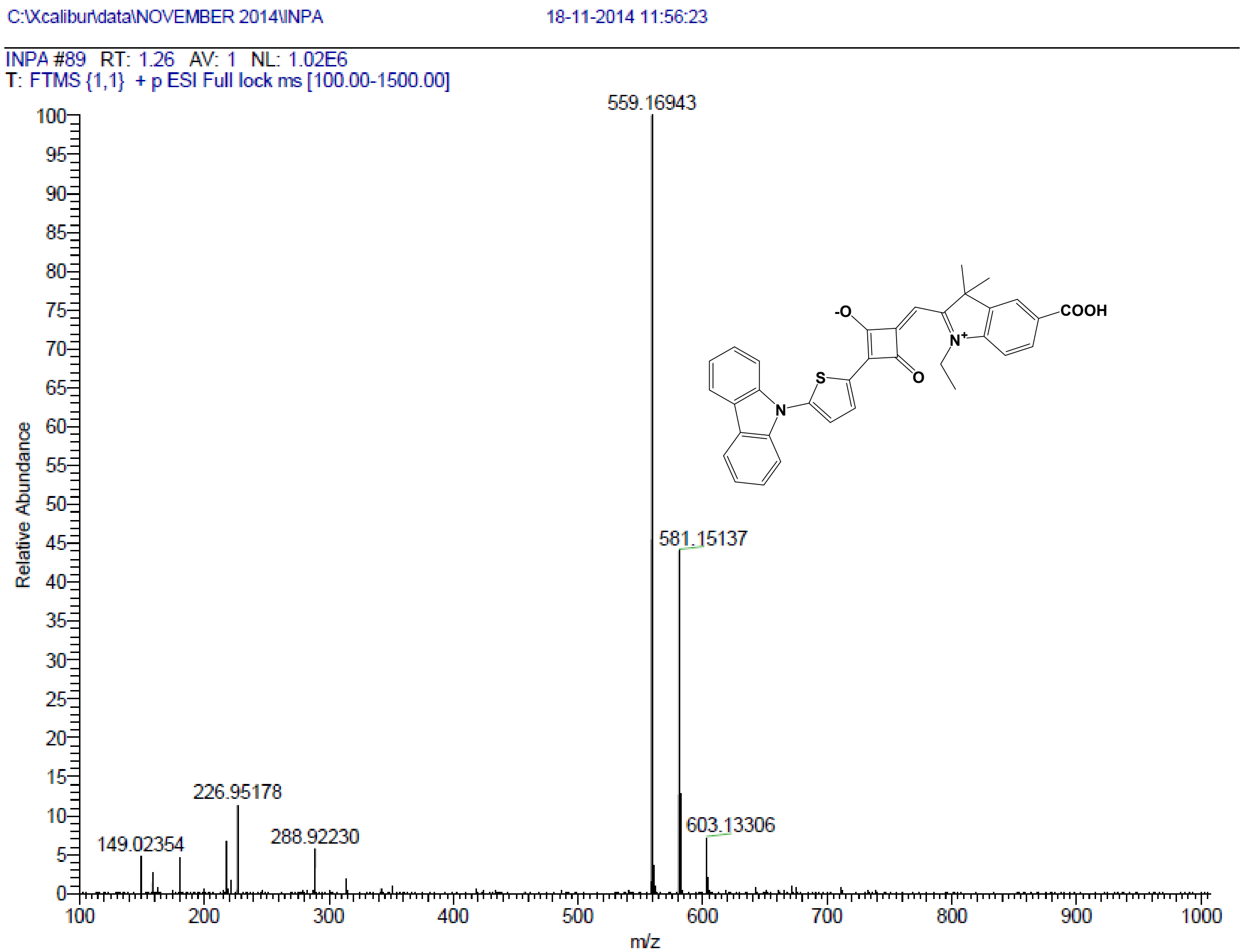


Figure S17: Mass spectra of CTSQ-1

1. (a) M. J. Frisch, Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.;Hratchian,H.P.;Izmaylov,A.F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, .; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven,T.;Montgomery,J.,J.A.;Peralta,J.E.;Ogliaro,F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J.; Revision C.01 ed.; Gaussian, Inc.: Wallingford CT, 2010.

2. Y. Zhao and D. G. Truhlar., *J. Chem. Phys*., 2006, **125**, 194101.