Electronic Supplementary Information

Unsymmetrical Starburst Triarylamines: Synthesis, Properties, and Characteristics of OFETs

Dheepika Ramachandran, [a] Srinita Sonalin, [a] Predhanekar Mohamed Imran,[b] Samuthira Nagarajan*[a]

[a.]*Department of Chemistry, Central University of Tamil Nadu, Thiruvarur- 610 005, India.*
Email: snagarajan@cutn.ac.in
[b.]*Department of Chemistry, Islamiah College, Vaniyambadi - 635 752, India.*

Table of Contents

Materials and instruments

Triphenylamine, $POCl_3$, tetrakis (triphenylphosphine) palladium, and all the boronic acids (naphthyl boronic acid, biphenyl boronic acid, thiophene-3-boronic acid, benzeneboronic acid, 4- methoxy phenyl boronic acid, 3-nitrophenyl boronic acid, 4-trifluoromethyl boronic acid) were used as purchased from the commercial sources. N, N-Dimethylformamide (DMF) and triethylamine used were anhydrous. All the other solvents (AR grade) were used as received.

^{1}H NMR and ^{13}C NMR were recorded in Bruker 400 MHz spectrometer in $CDCl_3$. Chemical shifts reported against TMS. Absorption spectra of compounds were measured by JASCO UV-NIR spectrophotometer. Fluorescence measurements were obtained from Perkin Elmer Spectrofluorimeter LS55. Electrochemical studies were done with CH Instruments: Electrochemical Workstation (CHI 6035D). Perkin Elmer FT-IR was employed to read about the characteristic functional groups. High-resolution mass spectra were recorded in ThermoExactivePlus UHPLC-MS. Thermal studies carried out in TA thermal analyser.

General considerations

All the photophysical properties were investigated at room temperature in anhydrous dichloromethane solvent, concentration was fixed 10^{-5}M for absorption spectra and 10^{-7}M for emission spectra. Electrochemical behaviour of the synthesised compounds were investigated using CHI-Electrochemical Workstation at room temperature. Electrochemical cell was comprised of glassy carbon working electrode, Pt wire as counter electrode and a SCE (saturated calomel electrode) reference electrode. The system was calibrated externally using Fc/Fc^+ as a standard. Working electrode was polished thoroughly with Alumina (1, 0.5 and 0.3 micron respectively) and used. 0.1M solution of tetrabutylammonium hexaflourophosphate in CH_3CN was the supporting electrolyte. Thermal behaviour was investigated in N_2 atmosphere at a scan rate of 10°C per minute.

Experimental procedure

Compound **1** was synthesized from a two-step synthetic sequence of Vilsmayer-Hack formylation followed by iodination of commercially available triphenylamine (TPA) **Scheme 1.** Then the precursor was subjected Pd-catalysed Suzuki coupling reactions to reach the desired products. All the molecules were confirmed spectroscopically and characterized.

**4-(Bis(4-iodophenyl)amino)benzaldehyde 1:**
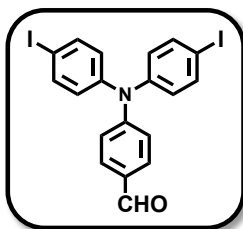
(a) Vilsmayer-Hack formylation: ^{i}Phosphorus oxychloride (1.85 mL, 20 mmol) was added dropwise to DMF (5.6 mL, 73 mmol) which was stirred at 0°C and this formylating mixture was allowed to stir for an hour in same condition. To this triphenylamine (5 g, 20 mmol) was added, temperature raised to 80 °C and continued for 4 hours. As monitored by TLC, reaction mixture was cooled to room temperature and quenched with water. Neutralised by 20 % aqueous NaOH. Brownish yellow product was washed with water and extracted with DCM finally washed with brine solution and dried over anhydrous Na_2SO_4. Purified by column chromatography using 2% ethyl acetate in hexane. Pale yellow solid (4.8 g, 88 %) (b) Iodination: Under stirring 4-(diphenylamino)benzaldehyde (2.5 g, 9.2 mmol) was dissolved in 10 mL of glacial acetic acid and 2 mL water with KI (2 g, 11.9 mmol) and allowed to stir at 80 °C for one hour. Then KIO_3 (1.91 g, 9.2 mmol) was added and reaction continued for 3 hours at 100°C. Monitored by TLC. After completion of reaction

quenched with water and cooled to room temperature. Formed brown yellow precipitate (4.45 g, 92 %) was filtered under pressure washed with plenty of water to remove excess of acetic acid.

General procedure for Suzuki coupling: 4-(Bis(4-iodophenyl)amino)benzaldehyde **1** (500 mg, 0.95 mmol) is dissolved in anhydrous THF and 2 M aqueous Na_2CO_3. 10 mol% of $Pd(PPh_3)_4$ added under N_2 atmosphere at room temperature and stirred for 20 minutes then corresponding boronic acid added and temperature raised to reflux. Reaction continued for 7 hours and monitored by TLC. After that cooled to room temperature and solvent removed under vacuum. Remaining residue extracted with DCM washed thrice with distilled water finally with brine solution dried over anhydrous Na_2SO_4. Purified by column chromatography (SiO_2) in hexane ethyl acetate system.

**4-(Bis(4-(naphthalen-2-yl)phenyl)amino)benzaldehyde 2:**
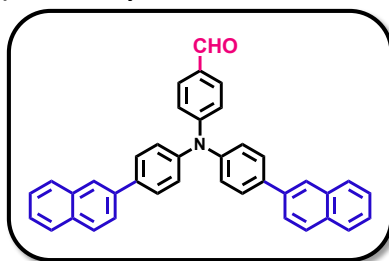
Yellow solid. Yield: 80%. ^{1}H NMR (400MHz, $CDCl_3$): δ (ppm) 9.86 (s, 1H), 8.05 (s, 2H), 7.94-7.86 (m, 6H), 7.76-7.71 (m, 8H), 7.53-7.47 (m, 4H), 7.33 (d, J = 8.4Hz, 4H), 7.19 (d, J = 8.4Hz, 2H) ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 190.57, 153.12, 145.49, 137.73, 137.55, 133.72, 132.65, 131.46, 129.60, 128.67, 128.51, 128.23, 127.73, 126.48, 126.45, 126.34, 126.09, 125.55, 125.27, 120.21. HRMS (ESI) m/z calcd for $C_{39}H_{27}NO$ [M+H] 526.2171, found 526.2178.

4-(Di([1,1':4',1''-terphenyl]-4-yl)amino)benzaldehyde 3:
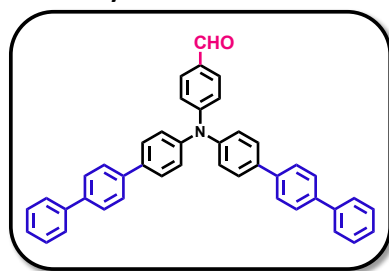
Yellow solid. Yield: 69%. ^{1}H NMR (400MHz, $CDCl_3$): δ (ppm) 9.85 (s, 1H), 7.74 (d, J = 8.4Hz, 2H), 7.69 (s, 8H), 7.66-7.63 (t, 8H), 7.48-7.45 (t, J = 7.2Hz, 2H), 7.38-7.35 (t, J = 7.2Hz, 2H), 7.29(d, J = 8.4Hz, 2H), 7.17(d, J = 8Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 190.49, 153.08, 145.44, 140.59, 140.17, 139.11, 137.31, 131.40, 129.61, 128.87, 128.25, 127.59, 127.43, 127.22, 127.03, 126.37, 120.19, HRMS (ESI) m/z calcd for $C_{43}H_{31}NO$ [M+H] 577.2406, found 577.2486.

4-(Bis(4-(thiophen-3-yl)phenyl)amino)benzaldehyde 4:
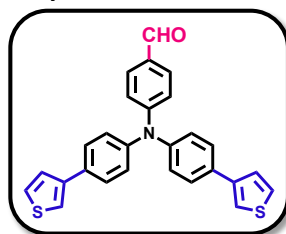
Yellow solid. Yield: 92%. ^{1}H NMR (400MHz, $CDCl_3$): δ (ppm) 9.87 (s, 1H), 7.70 (d, J=8.8Hz, 2H), 7.57 (d, J=8.4Hz, 2H), 7.42 (s, 1H), 7.42-7.33 (m, 4H), 7.20-7.17(m, 5H), 7.07 (d, J=8.8Hz, 2H) ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 153.20, 146.06,

145.12, 141.47, 132.60, 131.36, 129.81, 129.75, 129.29, 127.65, 126.44, 126.35, 126.34, 126.13, 125.23, 125.14, 120.14, 119.65, 119.36. HRMS (ESI) m/z calcd for $C_{27}H_{19}NOS2$ [M+H] 437.090, found 437.0863.

**4-(Di([1,1'-biphenyl]-4-yl)amino)benzaldehyde 5:**
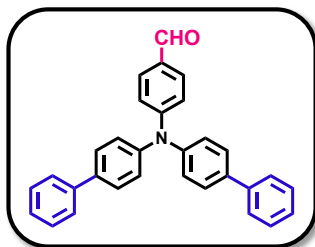
Half white solid. Yield: 86.4%.^{1}H NMR (400MHz, CDCl$_3$) δ (ppm): 9.84 (s, 1H), 7.74 (d, 2H) 7.60 (dd, 8H), 7.47 (t, 4H), 7.37 (t, 2H), 7.26 (d, 4H), 7.15 (d, J=8.8Hz, 2H) ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) 190.52, 153.12, 145.35, 140.24, 137.87, 131.40, 129.49, 128.88, 128.37, 127.35, 126.89, 126.35, 120.04. HRMS (ESI) m/z calcd for $C_{31}H_{23}NO$ [M+H] 426.1858, found 426.1852.

4-(Bis(4'-methoxy-[1,1'-biphenyl]-4-yl)amino)benzaldehyde 6:
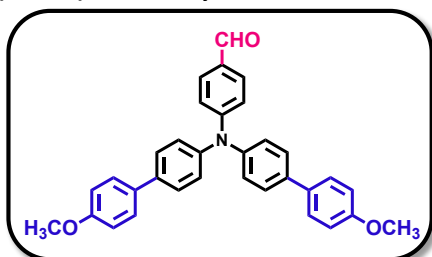
White solid. Yield: 91%.^{1}H NMR (400MHz, CDCl$_3$): δ (ppm) 9.82 (s,1H), 7.72 (d, J=8.8Hz, 2H), 7.54 (dd, 8H), 7.25 (d, J=8.4Hz,4H), 7.13 (d, J=8.8Hz, 2H), 6.99 (d, J=8.8Hz, 4H), 3.86 (s, 3H) ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) 190.48, 159.19 153.23, 144.74, 137.57, 132.78, 131.38, 129.22, 127.91, 127.87, 126.44, 119.63, 114.30, 55.37. HRMS (ESI) m/z calcd for $C_{33}H_{27}NO_3$ [M+H] 486.2069, found 486.2072.

4-(Bis(3'-nitro-[1,1'-biphenyl]-4-yl)amino)benzaldehyde 7:
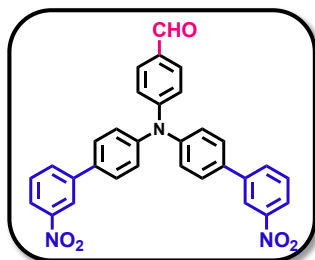
Brown solid. Yield: 85.2%. ^{1}H NMR (400MHz, CDCl$_3$): δ (ppm) 9.88 (s, 1H), 8.46(t, 2H), 8.22 (dd, 2H), 7.93 (d, J=7.6Hz, 2H), 7.79 (d, J=8.8Hz, 2H), 7.65-7.61 (m, 7H), 7.32 (d, J=8.4Hz, 4H), 7.21 (d, J=8.8Hz, 2H)^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) 190.53, 152.54, 148.80, 146.51, 141.87, 135.11, 132.69, 131.45, 130.40, 129.88, 128.56, 126.26, 123.27, 122.08, 121.67, 121.18. HRMS (ESI) m/z calcd for $C_{31}H_{21}N_3O_5$ [M+H] 516.1554, found 516.1504.

4-(Bis(4'-(trifluoromethyl)-[1,1'-biphenyl]-4-yl)amino)benzaldehyde 8:
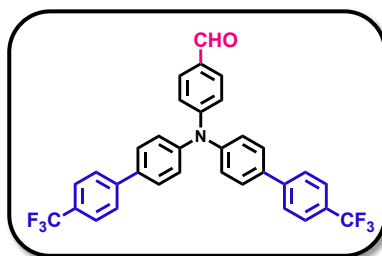
Brown solid. Yield: 92.7%. ^{1}H NMR (400MHz, CDCl$_3$): δ (ppm) 9.87 (s, 1H), 7.83 (t, 2H), 7.78-7.74 (m, 4H), 7.69-7.68 (m, 1H), 7.62-7.55 (m, 8H), 7.38 (d, 1H), 7.30 (d. J=8.8Hz, 4H), 7.18(d, J=8.4Hz, 2H) ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm)190.50, 152.77, 146.06, 141.02, 136.30,135.23, 131.77, 131.45, 131.41, 131.13, 130.81, 130.25, 130.11, 130.05, 129.37, 128.52, 128.22, 127.72, 127.67, 127.61, 126.31, 125.51, 124.02, 123.98, 123.73, 123.69, 123.65, 123.61, 122.80, 120.69, 120.10. HRMS (ESI) m/z calcd for C$_{33}$H$_{21}$NOF$_6$ [M+H] 562.160, found 562.157.

Thermal behaviour of molecules

Thermal stability and morphology of the molecules play an important role in electronics, especially to improve lifetime and efficiency of the device. **Figure 4** shows the DSC behavior of compounds at a heating rate of 10 °C min^{-1} under nitrogen atmosphere. Melting points were observed as sharp peaks and decomposition was observed as broad curves around 400 °C. Compound **3** has the high melting point 243 °C and heat capacity calculated was 89.6 J/g. Comparing all molecules with **1**, it is evident that their melting temperature increased greatly, concluding that thermal stability of all the new π extended molecules is upgraded and durability of the devices assured. Values extracted from differential calorimetric analysis are given in **Table 3**. Interestingly, compounds **4** and **5** are showing two sharp melting peaks and the reason may be the existence of polymorphs. Compounds are showing comparatively high decomposition temperature (~400 °C) than other triarylamine compounds[ii].

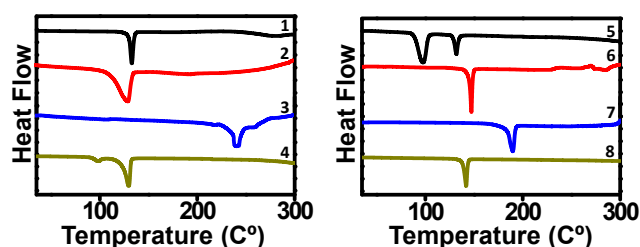**Figure S1.** DSC thermogram of compounds **1-8**

Table 1. Thermal behavior of compounds **1-8**

	T$_m$ °C	T$_d$ °C	Heat capacity J/g
1	130	247	92.9
2	124	469	85.2
3	243	412	89.6
4	92, 130	425	2.4, 20.7
5	93, 128	398	11.8, 2
6	191	389	167.9
7	182	418	70.4
8	137	427	52.3

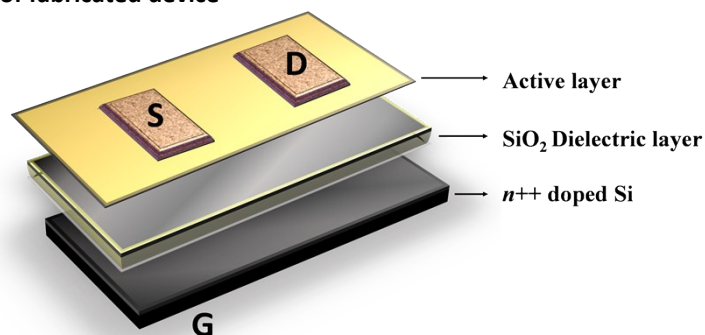**Schematic representation of fabricated device**

Figure S2. Schematic representation of OFET device

FET architecture opted for device fabrication was bottom gate top contact as represented in the **Figure S1**. Active semiconducting material coated over SiO_2 and annealed at 60 °C to remove the residual solvents.

Film morphology

To have a clear vision about the device performance, morphology of the active layer was investigated. Films over SiO_2 dielectric layer was analysed by non-contact mode atomic force microscopy (AFM) and scanning electron microscope (SEM). 2 and 3 dimensional images of films obtained by AFM are given in the **Figure S2**. The surface roughness was 0.987 nm for compound **2,** 1nm for compound **3** and **4.**
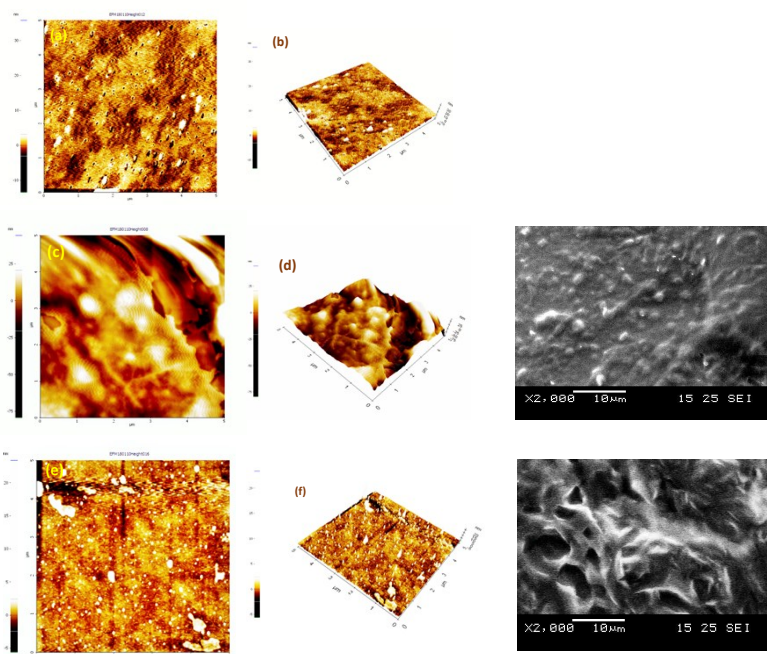
Figure S3. Non-contact mode AFM images of thin films over SiO_2 dielectric layer (a, b) compound **2** (**c, d**) compound **3** (**e, f**) compound **4** and SEM images of **3** and **5** (Right).

Computational studies:

Triarylamine molecules with different π extensions were explored theoretically to observe their electronic and charge

transport properties. DFT: B3LYP *ab initio* approach is used to elucidate the structural properties of all molecules. The optimisation of all molecules were done starting from MOPAC and ending with Gaussian at the DFT-B3LYP (6-31g*) level of theory for ground state (S_0). The PBE functional was used to compute the Density of States (DOS), which gave insight into the Fermi levels of the molecules. This depends on density of non-locality states as well by LSDA (low spin density approximation) theory. For comparison ab-intio calculations were also done using Gaussian -09 software using B3LYP parameters. The optimized geometry was fed to VASP for further calculations. Precise single crystal parameters of each molecule were predicted successfully using MedeA and used to construct poly crystals. Increment of the molecule to a polycrystalline level was attained by Discovery Studio Viewer and improbable point groups were ruled out. The polymorph prediction calculation were done with 10 most popular space groups such as P21/c, P2, Pbca, Pna2, Cc, Pbcn and C2 (Cambridge Structural database reference). All the space groups were tried sequentially to monitor interactions and packing measurements and optimized. Dihedral angle between –CHO substituted arm and the other two phenyl conjugated arms is calculated and tabulated. **(Table S2)** Molecules are having dipole moments ranging from 2.0 to 3.8 D. Bond lengths and charges of central nitrogen atom and carbon atoms connected to N atom is also calculated. Generalized representation of molecule is given in **Figure S4.** All stabilised geometrical properties at ground state is given in **Table S2.**
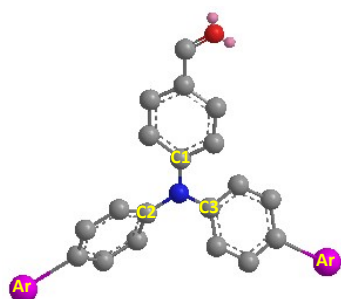
Figure S4. Generalised representation of molecule

Table S2. Geometrical parameters of predicted single crystals **1-8** at ground state S_0

	Bond length (Å)				Charges			Dihedral	Dipole
	N-C1	**N-C2**	**N-C3**	**N**	**C1**	**C2**	**C3**	angle (°)	moment (D)
1	1.372	1.371	1.372	-1.016	0.310	0.300	0.301	149.72	2.066
2	1.372	1.372	1.373	-0.605	0.241	0.240	0.239	145.72	2.456
3	1.372	1.372	1.371	-0.603	0.246	0.240	0.227	151.83	2.409
4	1.372	1.372	1.372	-0.606	0.241	0.237	0.243	145.22	2.008
5	1.523	1.542	1.544	-0.725	0.322	0.329	0.329	139.32	2.406
6	1.464	1.499	1.198	-0.724	0.306	0.303	0.300	145.38	3.336
7	1.461	1.497	1.492	-0.722	0.306	0.309	0.302	153.67	3.852
8	1.370	1.376	1.372	-0.606	0.227	0.255	0.235	144.62	2.079

All geometrical parameters for molecules 1-8 at ground state S_0 are given in **Table S2**. Packing of all molecules with respect to predicted crystal structures (**Figure S7**) and single crystal parameters given in **Table S3**. Hopping direction and interatomic distance also calculated and projected in **Figure S6** and **Table S4**. The optimised geometry was fed to the MedeA which further predicted the crystal pattern of each molecule using the VASP software at the DFT-PBE-GGA level of theory, suitable for large molecules with predictable material properties. This calculation enabled the estimation of Density of States (DOS) of the molecule in the graphical form **(Figure S5)**. In semiconductors the DOS refers to 2D quantum states. Using the Schrodinger's' equation, k-space volume of single state cube (the smallest unit in space to accommodate one electron) was calculated. Compound **3** has maximum volume. The higher value shows more dense packing per unit and smaller 2D state. Quantum dots are a semiconductor crystal that contains electron, hole or electron pair to zero dimensions. Packing distances predicted by these values are visualized. From medeA data we arrived at the carrier mobilities of all compound in the range of 10^{-6} $m^2 V^{-1} s^{-1}$. The values are given in the table (**Table**

S4) indicates very good value for hopping factor. Molecule **7** has a value of 0.425x10⁻⁶, the highest among the series. Obviously, the Fermi levels are also very high for the molecule and outrageous HOMO-LUMO distribution is also discussed. This molecule possesses largest value in the nearest possible pathway predicted by MedeA for the Space group P21.

Table S3. Crystal structure and lattice parameters at ground level S_0

	Type	Sides			Angles			
		A	B	C	α	B	γ	μ
1	Triclinic (**CC**)	15.05	13.35	6.46	93.13	89.24	89.00	2.066
2	Triclinic (**PNA-21**)	25.45	16.15	5.89	89.62	88.09	89.90	2.456
3	Triclinic (**P-21**)	28.07	17.79	5.80	87.81	91.33	90.06	2.409
4	Triclinic (**P-1**)	19.84	14.96	5.97	89.20	89.54	90.15	2.008
5	Triclinic (**P-21-C**)	20.28	15.74	6.11	89.55	89.4	90.32	2.406
6	Triclinic (**P-1**)	24.00	16.64	6.41	90.72	89.80	90.70	3.336
7	Triclinic (**P-21**)	20.53	16.82	9.25	90.09	89.78	90.07	3.858
8	Triclinic (**P-1**)	23.06	16.14	6.48	90.20	88.44	89.71	2.079

Orbital overlap leading to efficient charge transfer is also a key concept while orienting the structure. HOMO's and LUMO's were keenly observed and their interacting distances maximum was chosen for the hopping values. It was possible to choose good number of hopping values but in given crystal structure only a few were considered. Orbital overlaps have been excluded from figure to present a simplified outlook.

Table S4. Interatomic distance, band gap and mobility of compounds **1-8**

	Volume	Density	Interatomic distance(Å)	DOS band gap(eV) DFT GGA-PBE	Charge carrier mobility (m²V⁻¹s⁻¹)
1	1297.08	0.672	H-I 2.112 / N-H 3.115	2.1088	0.146 ×10⁻⁶
2	2421.71	0.360	O-H 9.557 / N-H 6.525	2.0072	0.089 ×10⁻⁶
3	2896.79	0.331	O-H 3.785 / N-O 2.861	2.0148	0.081 ×10⁻⁶
4	1775.72	0.409	S-N 1.529 / O-H 6.985	1.9932	0.097 ×10⁻⁶
5	1951.78	0.362	N-O 2.904 / H-O 4.191	2.0185	0.110 ×10⁻⁶
6	2561.22	0.315	H-O 4.742 / N-H 6.570	1.9872	0.141 ×10⁻⁶
7	3199.29	0.268	N-O 9.135 / O-H 6.284	1.4841	0.425 ×10⁻⁶
8	2411.98	0.387	H-F 11.273 / N-F 11.773	2.0811	0.140 ×10⁻⁶

Qualitative representation of HOMO and LUMO were visualized using Gaussview and Chemcraft

33333
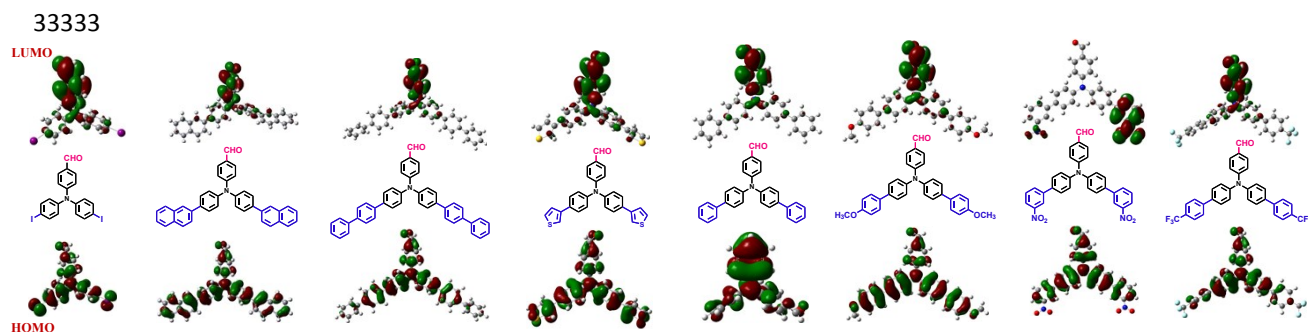
Figure S5. Spatial distributions of FMOs of compounds **1-8**

Electron density in HOMO is distributed all over triarylamine donor moiety and LUMO towards the acceptor moiety Figure **4** shows FMOs of all the compounds. Molecule **7** with NO_2 group has outrageous distribution than other molecules. Nitro group increases electron affinity and as the stabilization effect LUMO is located over NO_2 than on HOMO.[iii] From an analysis of all the HOMOs and LUMOs of the molecules, it is inferred that all the molecules have very high percentage of the HOMO's on the central triarylamine moiety and less percentage of the LUMO's on the derivative sides (**Figure S5**). This substantiate the π extensions are introduced without affecting the peculiarity of orbitals. **Table 2** shows that predicted band gap values (DFT-B3LYP) are in agreement with experimental value. But values predicted by VASP at the PBA levels varies because of fermi level added in crystalline structure.

The DOS band gap values predicted by MedeA ranges from 1.484 eV to 2.108 eV (**Table S4**). A good spread of the Fermi levels shows the possible states the electron can move. Here, compound 3 found to have the highest fermi level and lowest band gap among all. And it is expected to have good physical properties when constituted to poly crystalline level. Compounds 2 and 5 shows moderate fermi level. In all the molecules deviation is negligible and can be concluded to possess very good electronic property. .
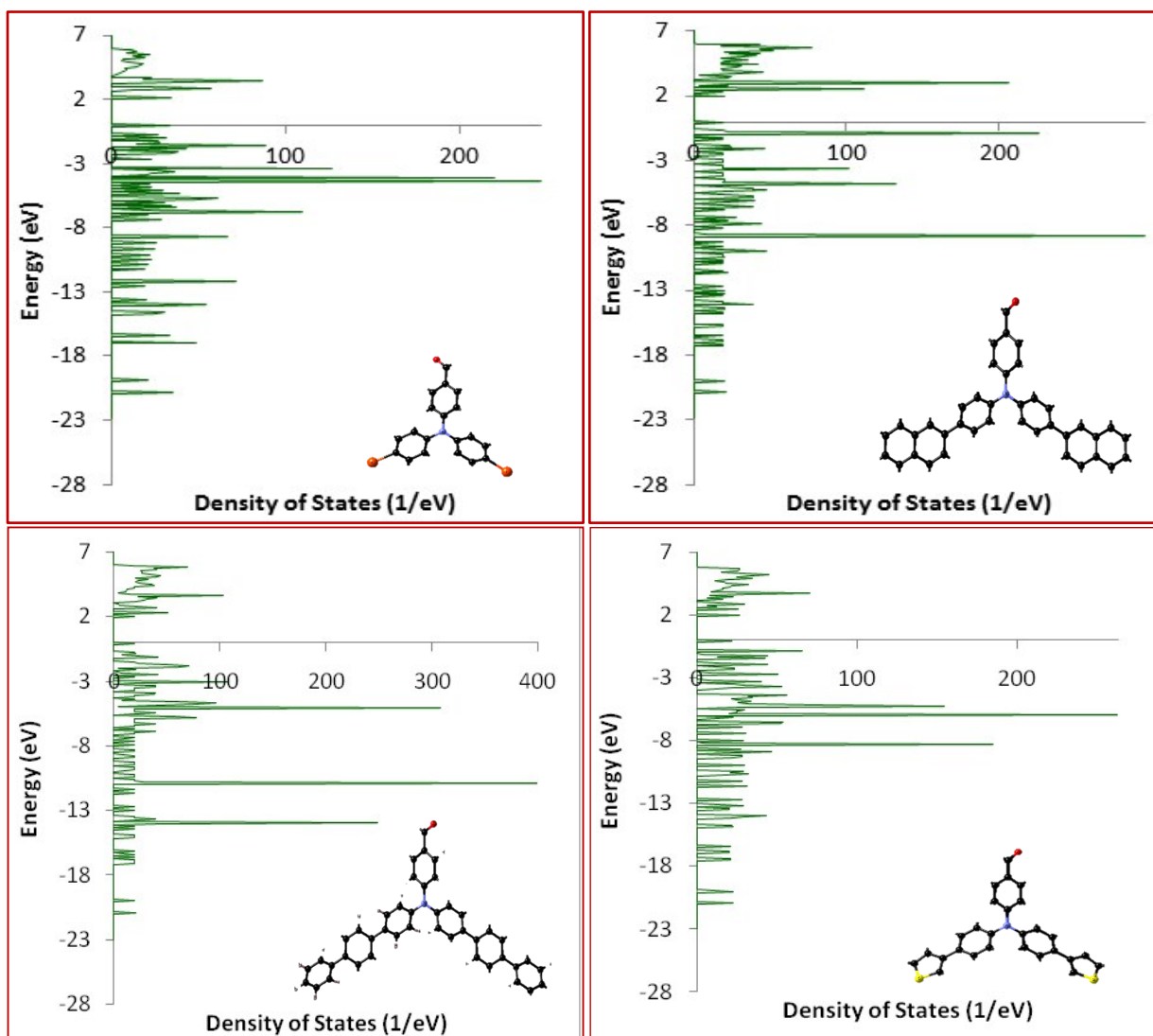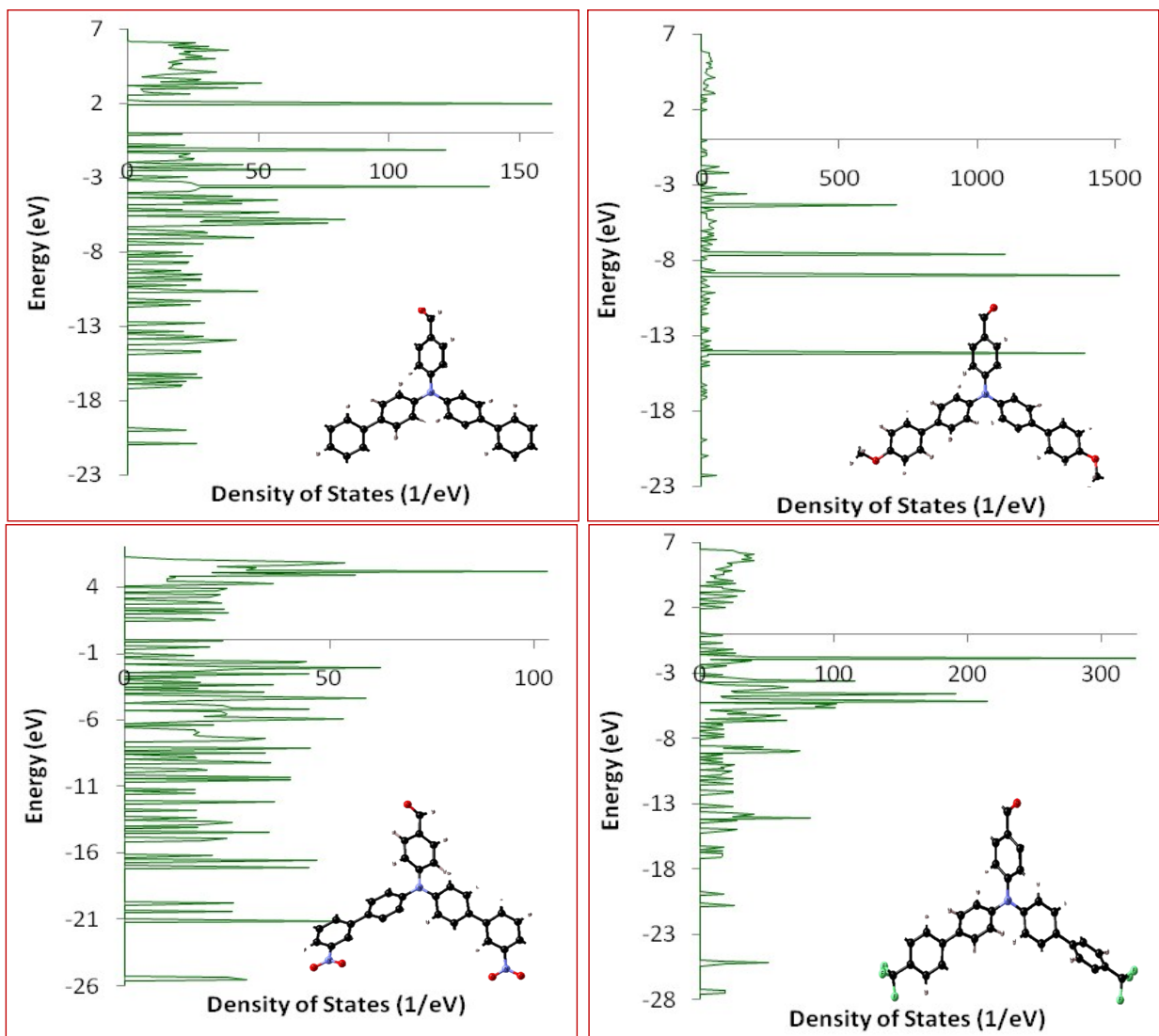
Figure S6. Density of States graphs of compounds **1-8** (Inset is stabilized ground state structures)
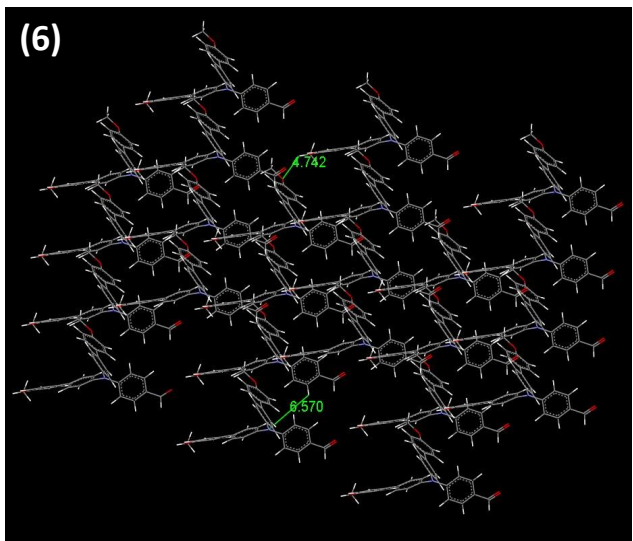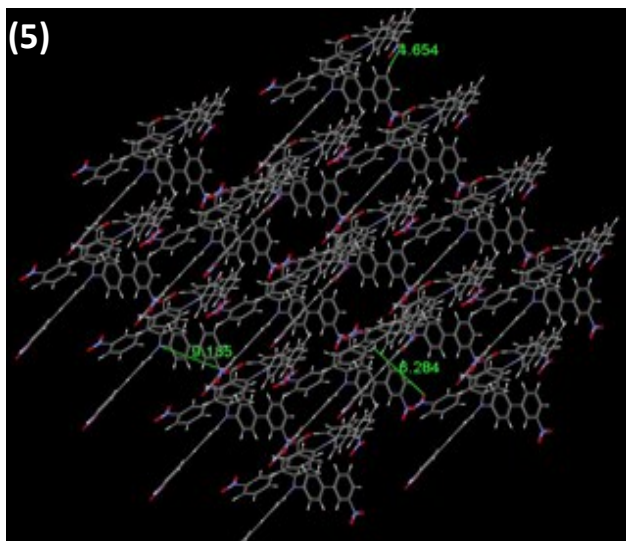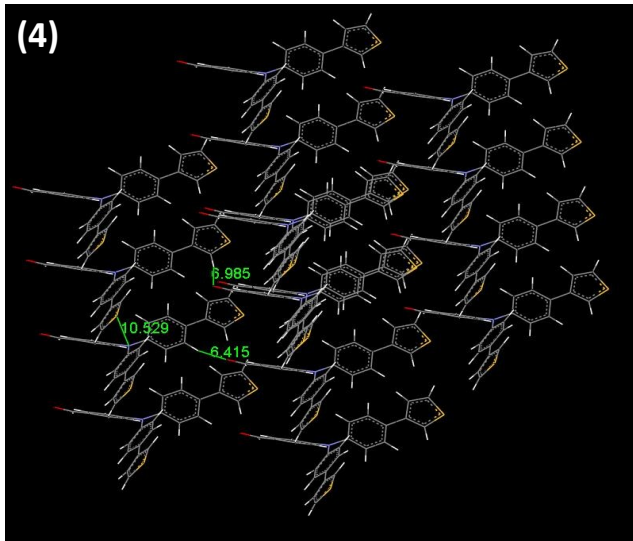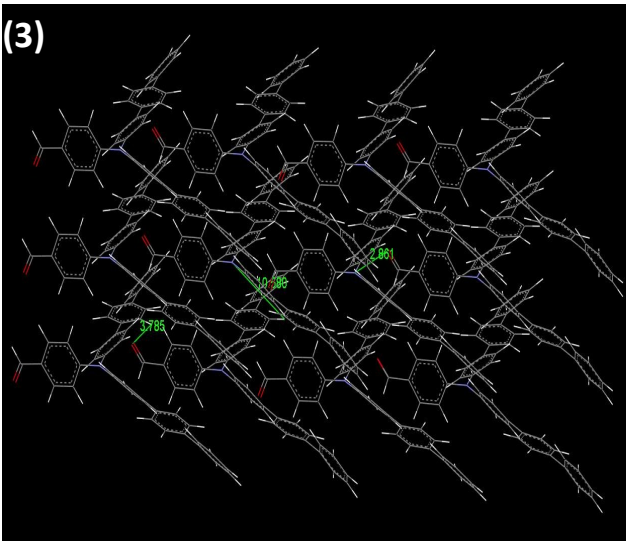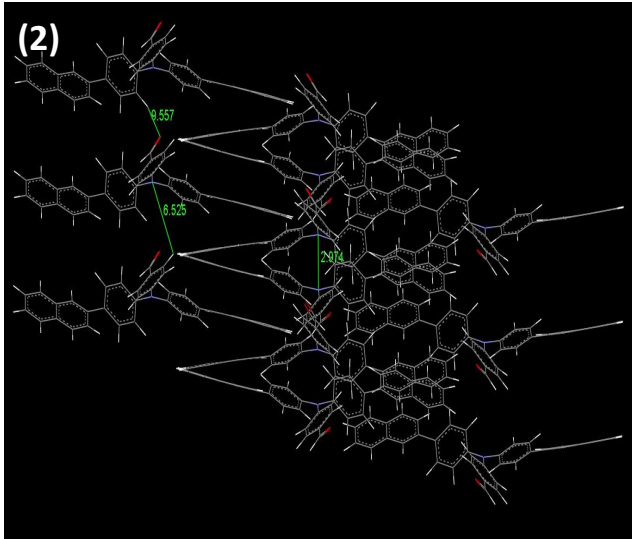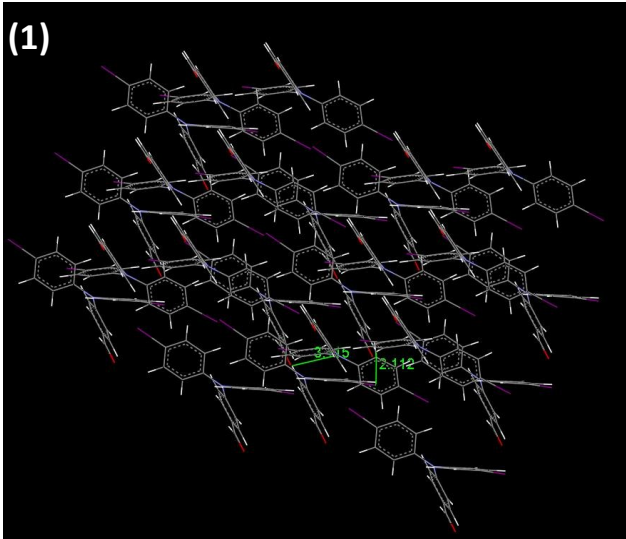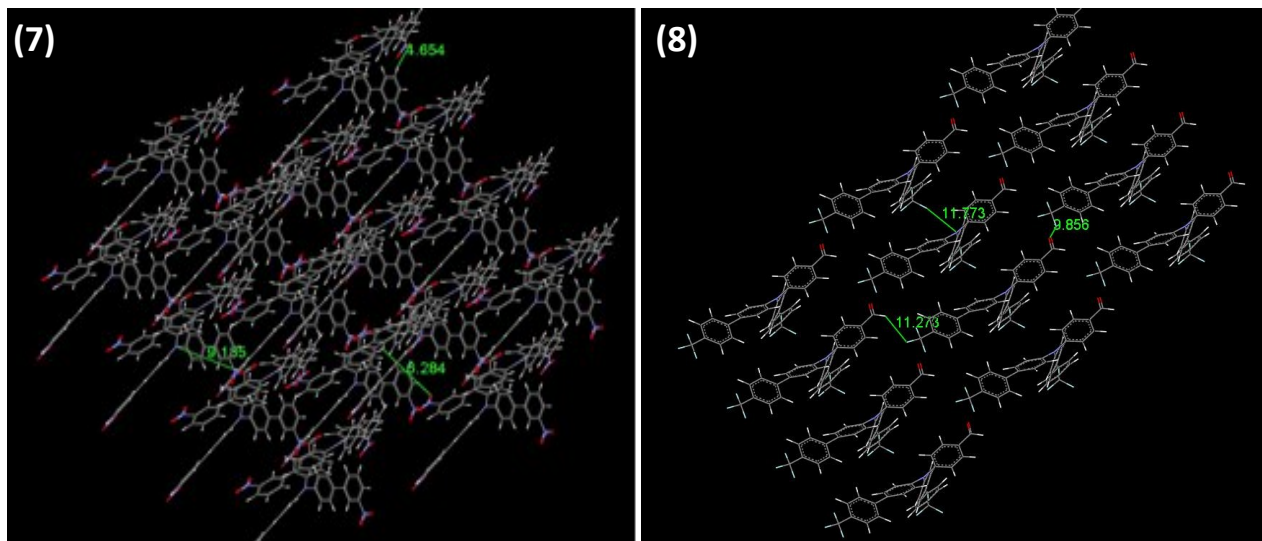
Figure S7. Polymorph predictions at polycrystalline level
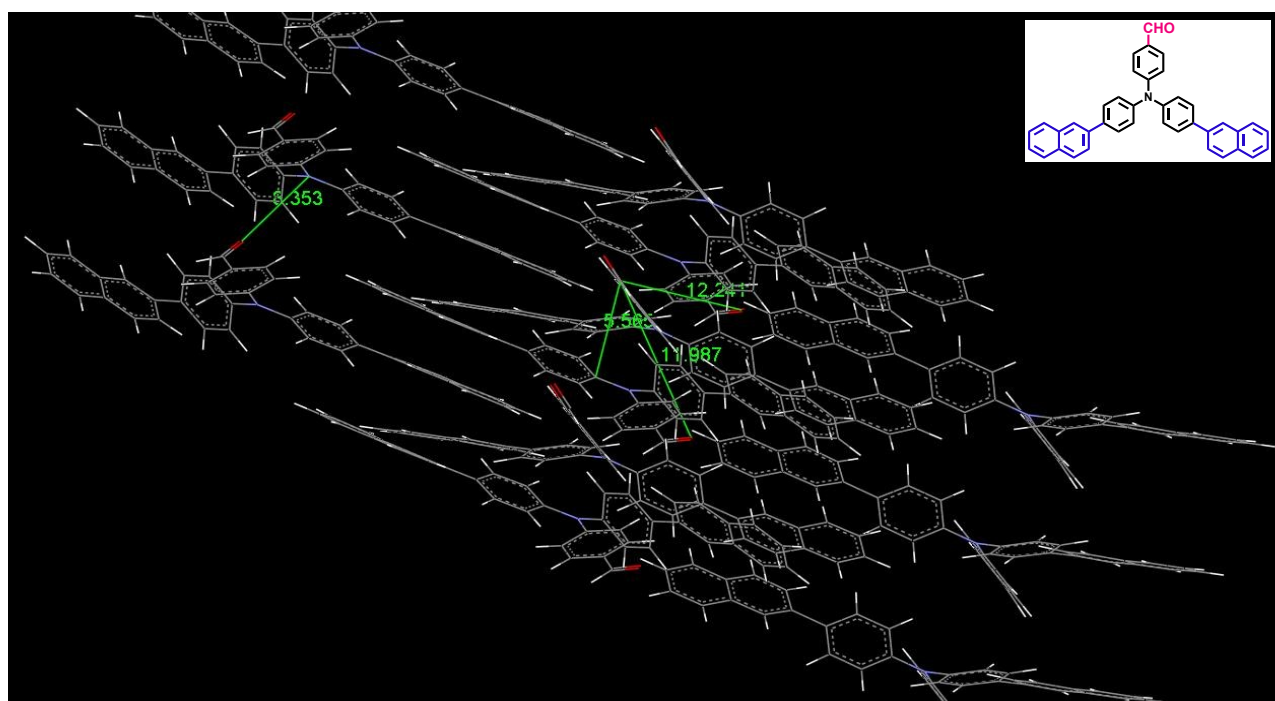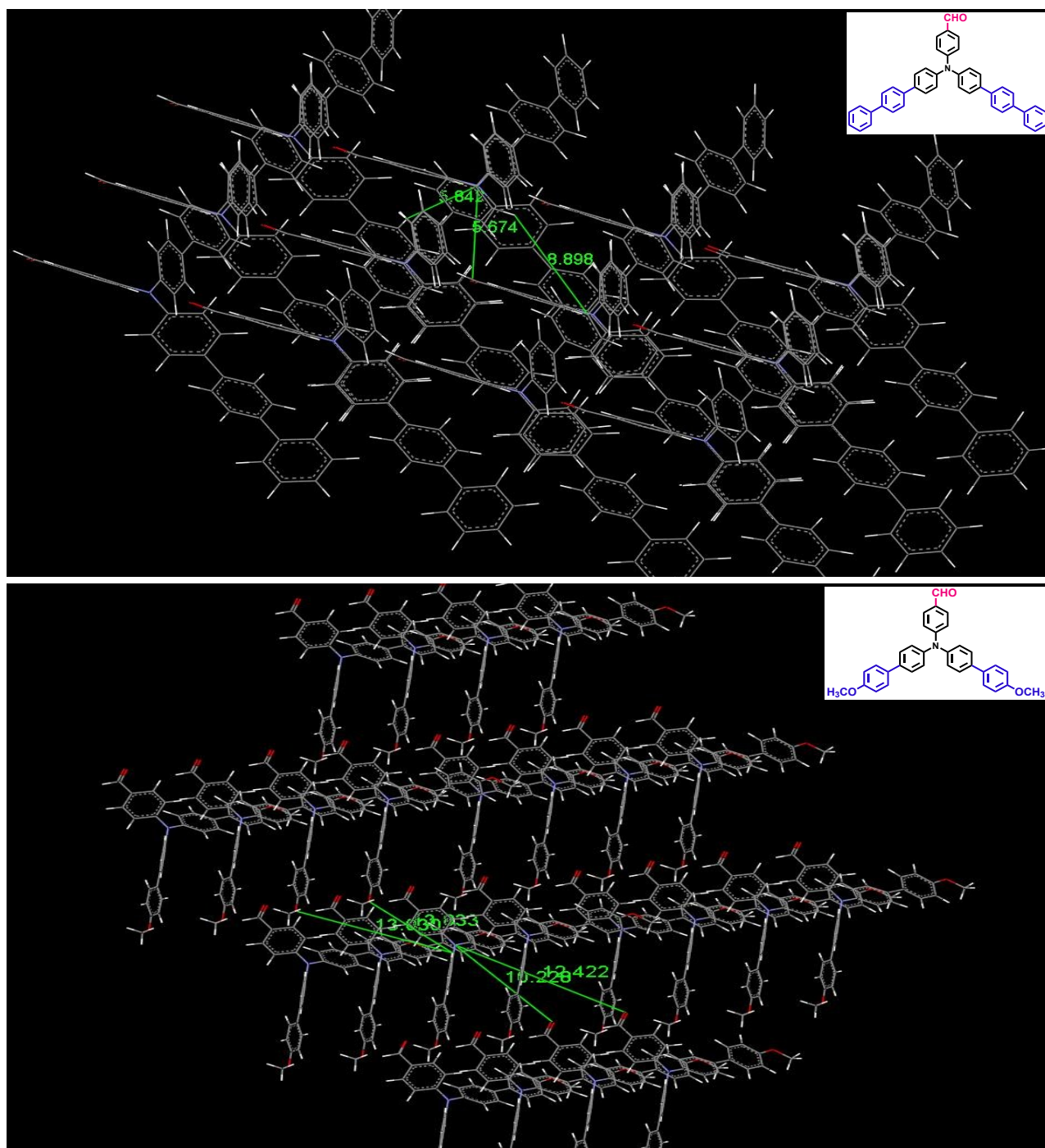
Figure S8. Hopping distance prediction at polycrystalline packing.

Figure S9. ^{1}HNMR and ^{13}C NMR spectra of compound **2**
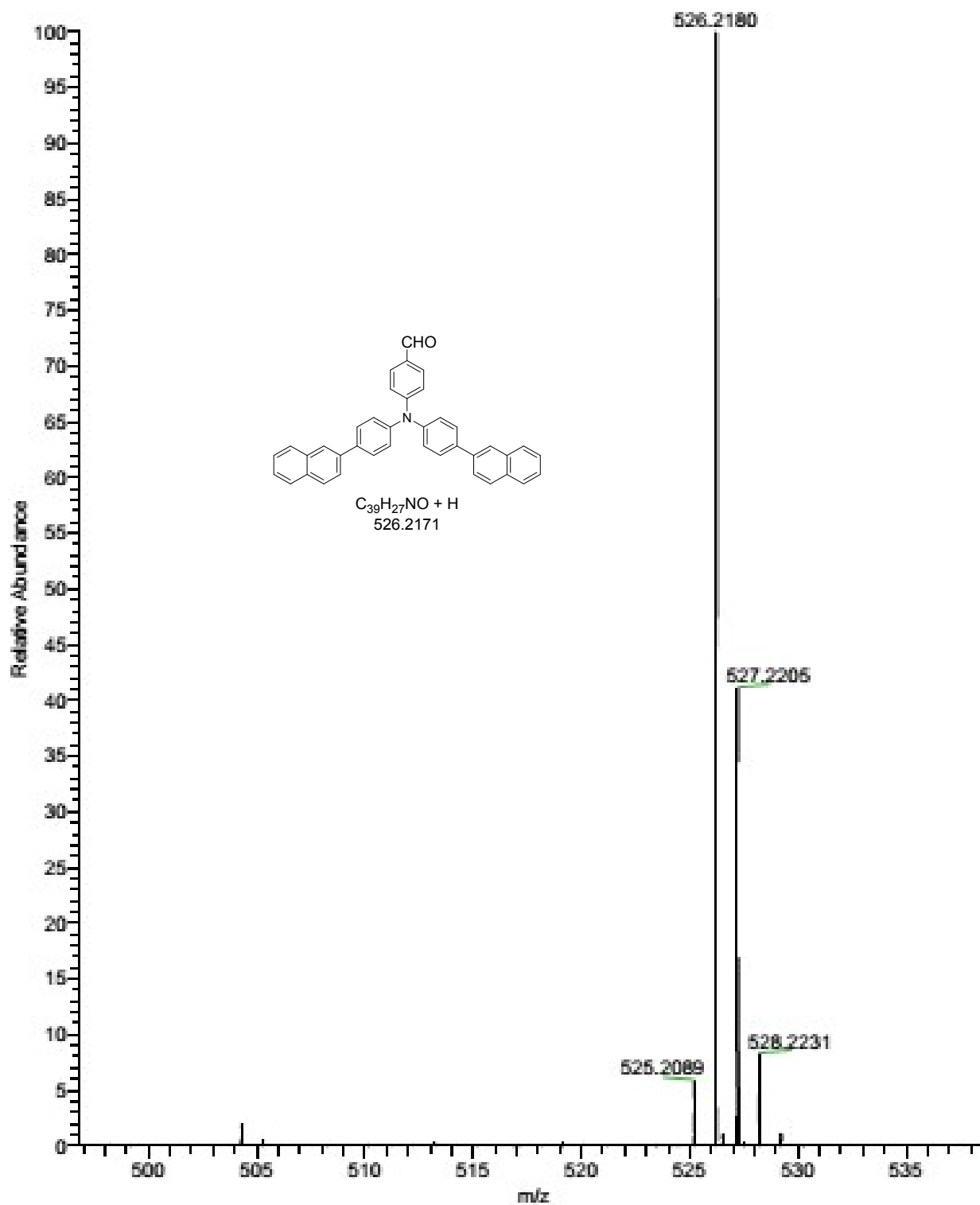
Figure S10. HR-Mass spectra of compound **2**
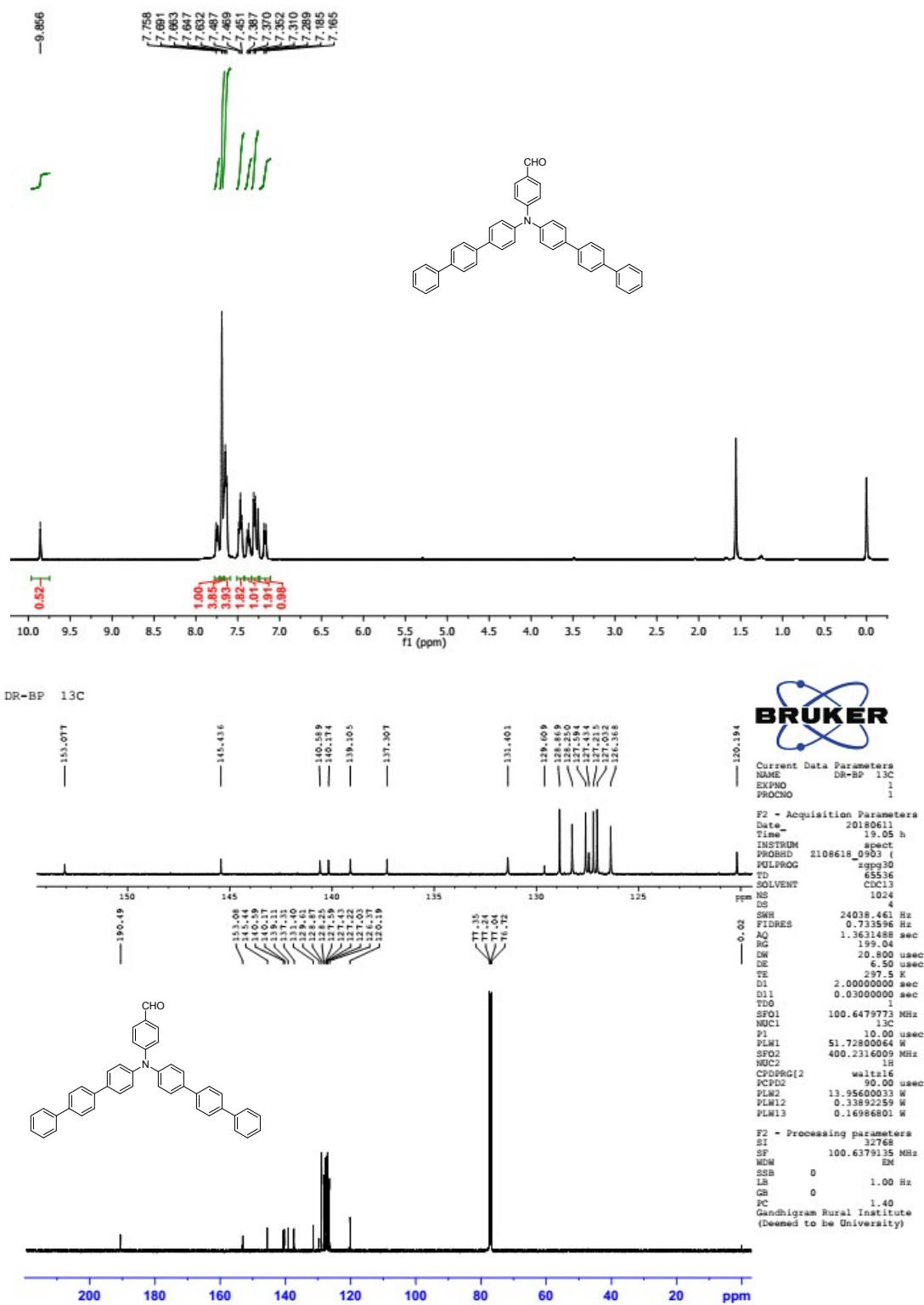
Figure S11. ^{1}HNMR and ^{13}CNMR spectra of compound **3**
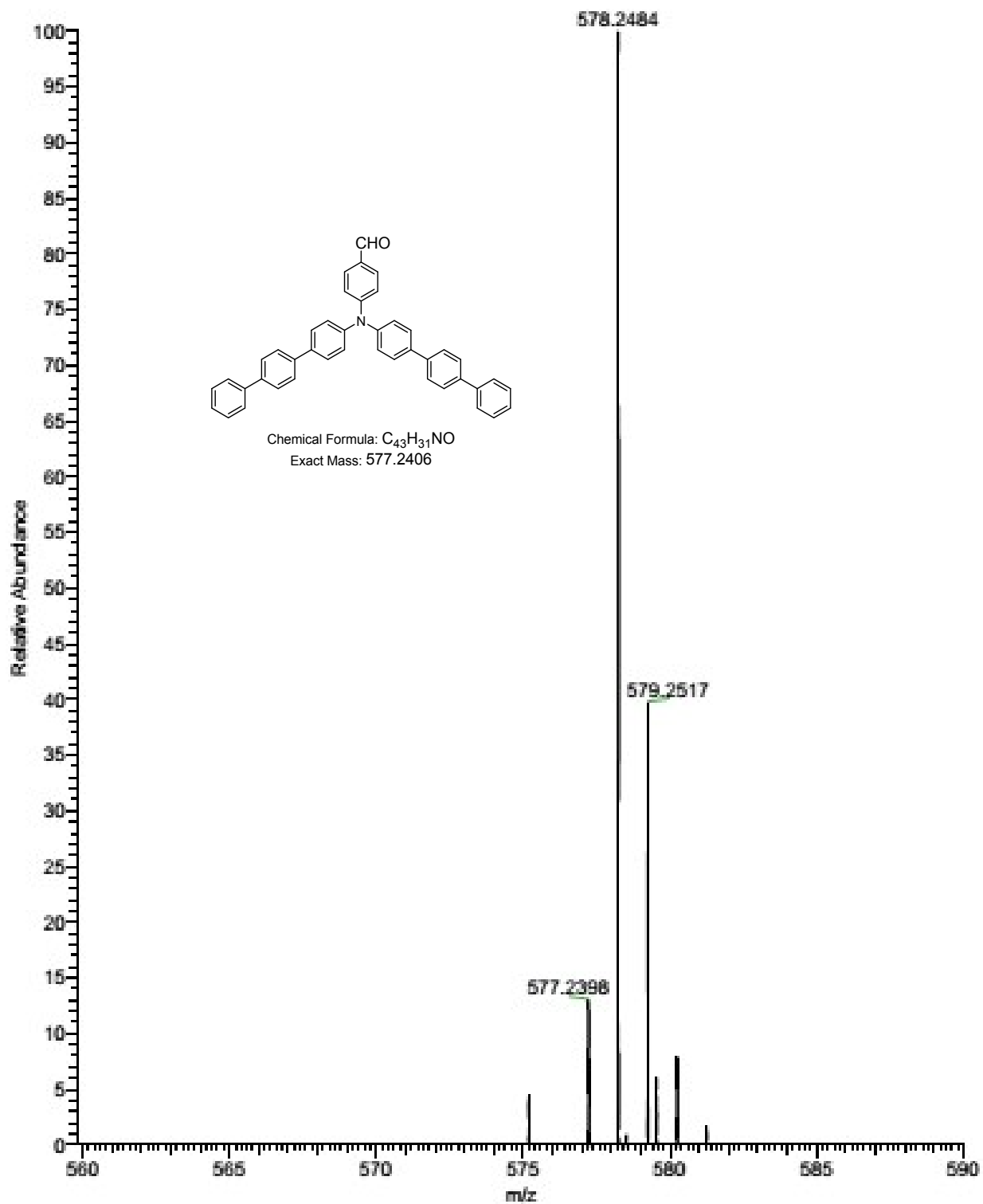
Figure S12. HR-Mass spectra of compound **3**

S18

Figure S13. ^{1}HNMR and ^{13}CNMR spectra of compound **4**

Chemical Formula: $C_{27}H_{19}NOS_2$
Exact Mass: 437.0908
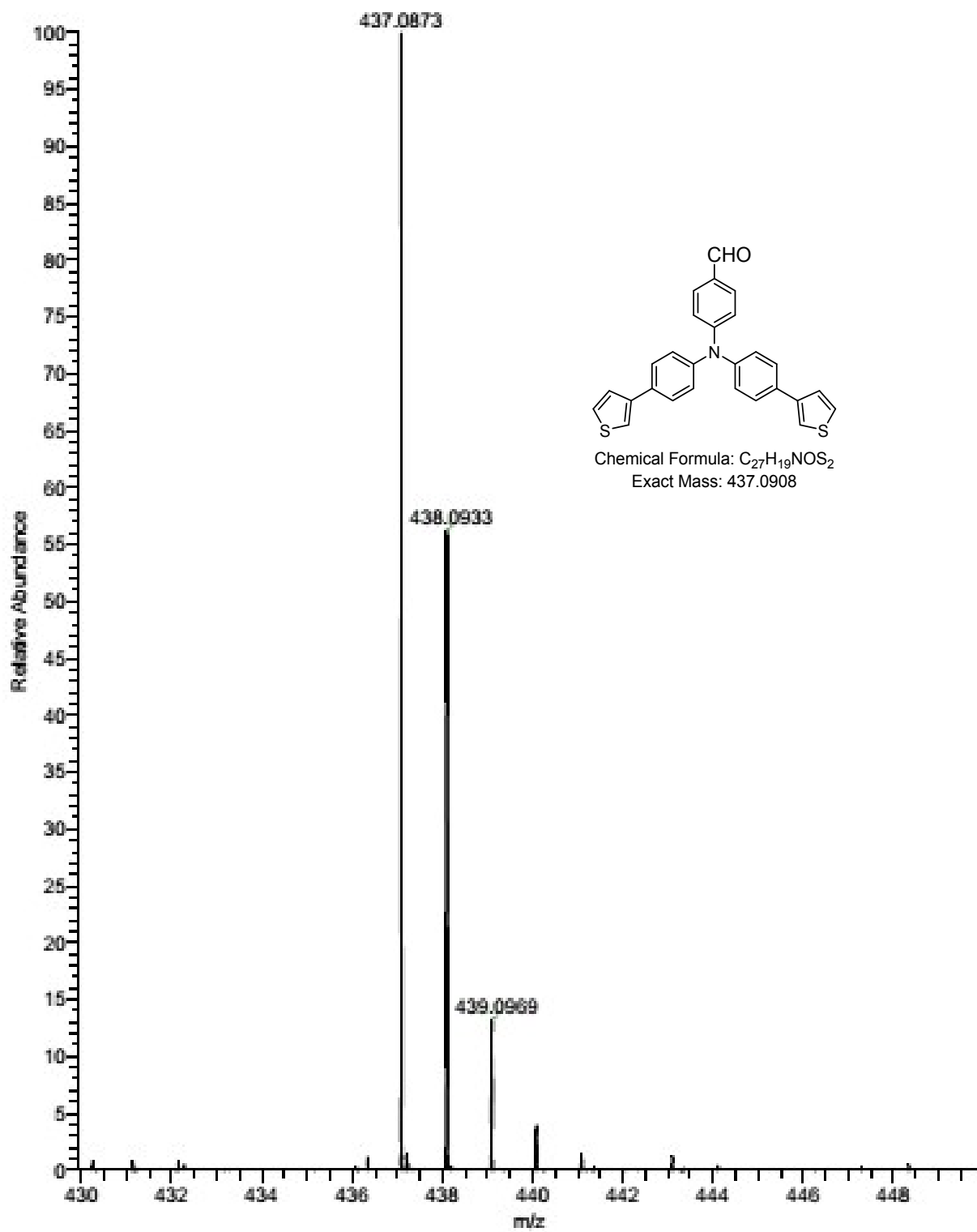
Figure S14. HR-Mass spectra of compound **4**

DR-1 1H

DR-1 13C

Figure S15. ^{1}HNMR and ^{13}CNMR spectra of compound **5**

$C_{31}H_{23}NO + H$
426.1858
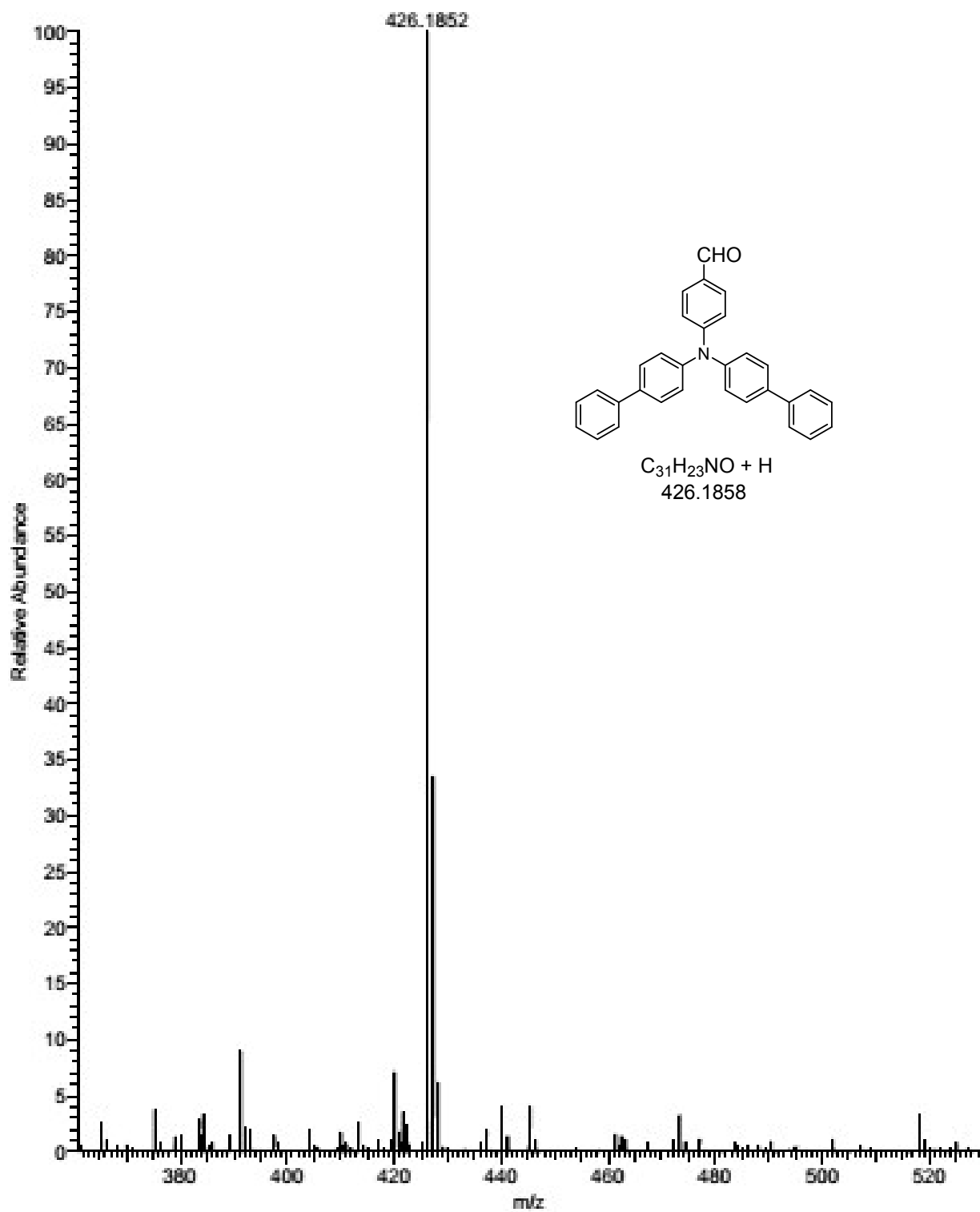
Figure S16. HR-Mass spectra of compound **5**

S22
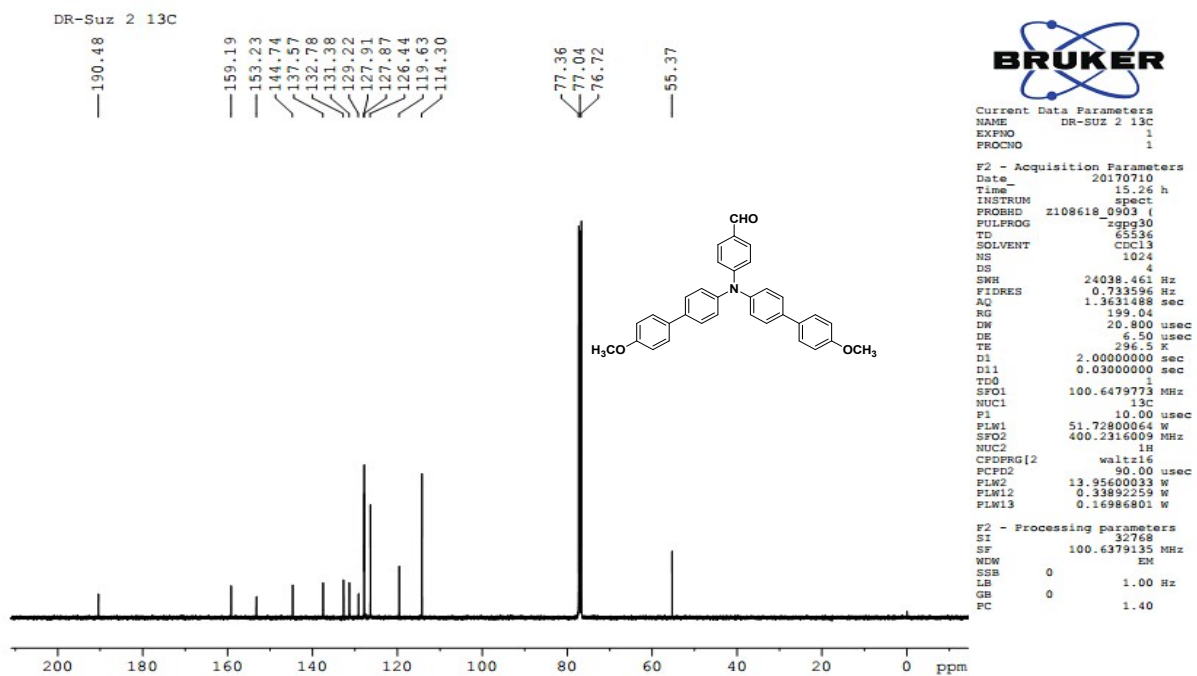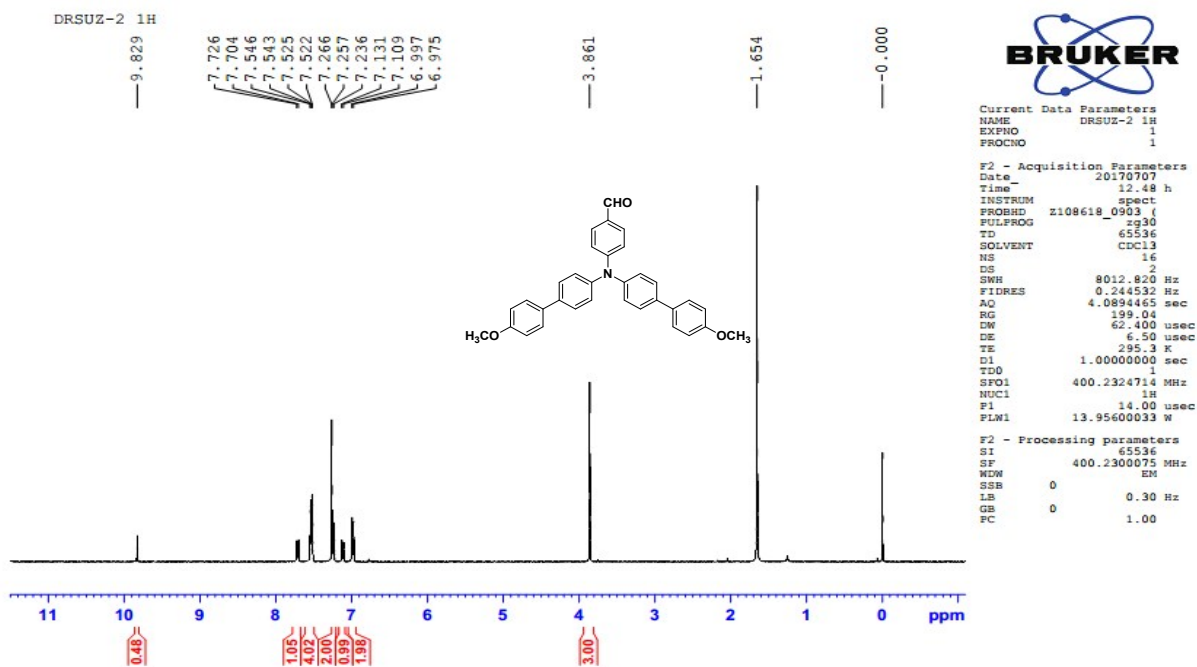
Figure S17. ^{1}HNMR and ^{13}CNMR spectra of compound **6**
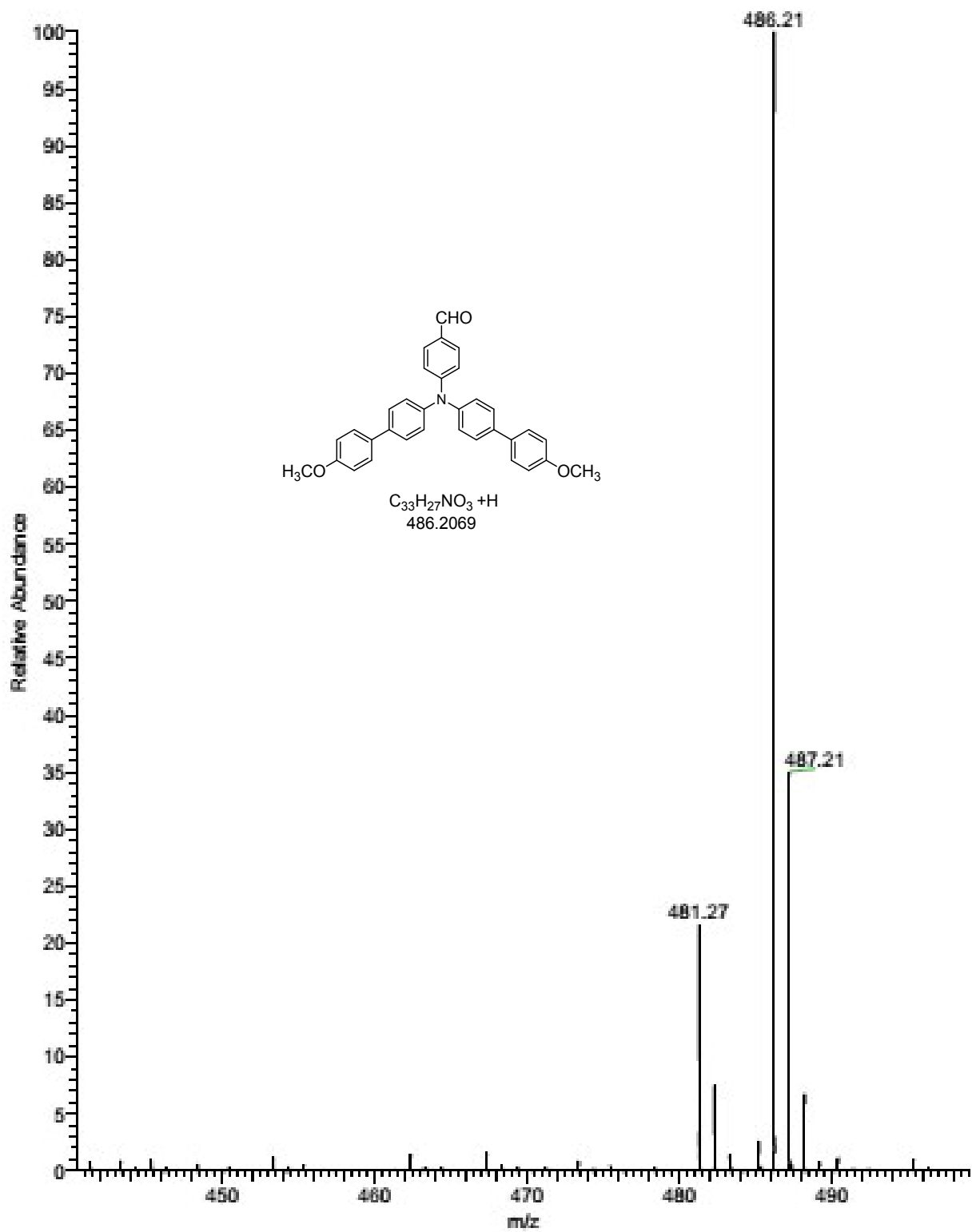
Figure S18. HR-Mass spectra of compound **6**

Figure S19. ^{1}HNMR and ^{13}CNMR spectra of compound **7**
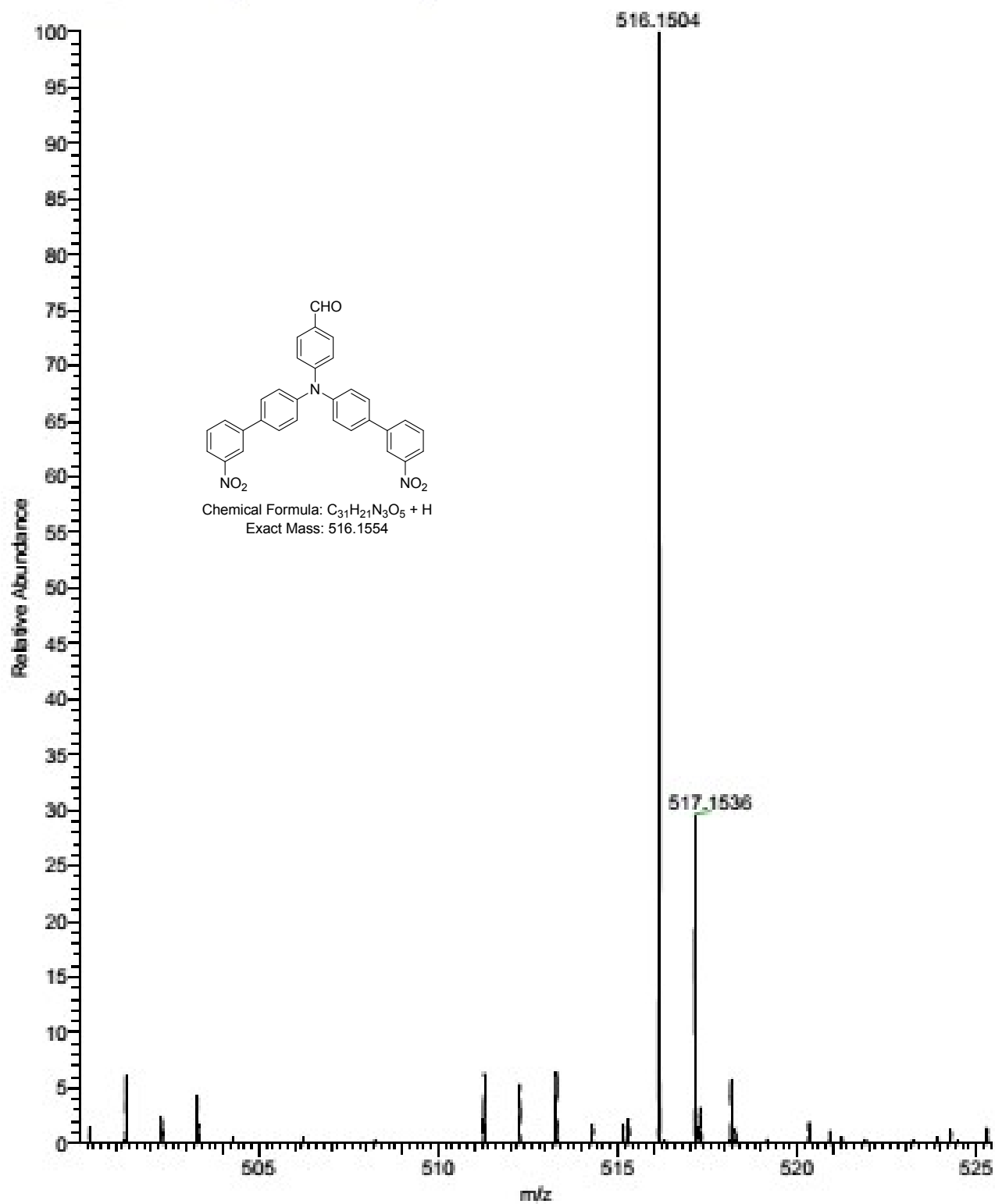
Figure S20. HR-Mass spectra of compound **7**

DR-SUZ-4 1H

9.870
7.837
7.781
7.768
7.764
7.747
7.707
7.702
7.694
7.684
7.623
7.601
7.589
7.579
7.572
7.551
7.381
7.370
7.305
7.283
7.260
7.184
7.163

1.561

-0.000

7.9 7.8 7.7 7.6 7.5 7.4 7.3 ppm

12 11 10 9 8 7 6 5 4 3 2 1 0 ppm

1.00   2.05 4.13 0.77 8.23 1.14 4.03 2.06

Dr-Suz-4 13C

190.50
152.77
146.06
141.02
136.30
135.23
131.77
131.45
131.41
131.13
130.81
130.25
130.11
130.05
129.37
128.52
128.22
127.72
127.67
127.61
126.31
125.51
124.02
123.98
123.73
123.69
123.65
123.61
122.80
120.69
120.10
77.35
77.03
76.72

-0.01

200 180 160 140 120 100 80 60 40 20 0 ppm

Figure S21. ^{1}HNMR and ^{13}CNMR spectra of compound **8**

$C_{33}H_{21}F_6NO + H$
562.1606

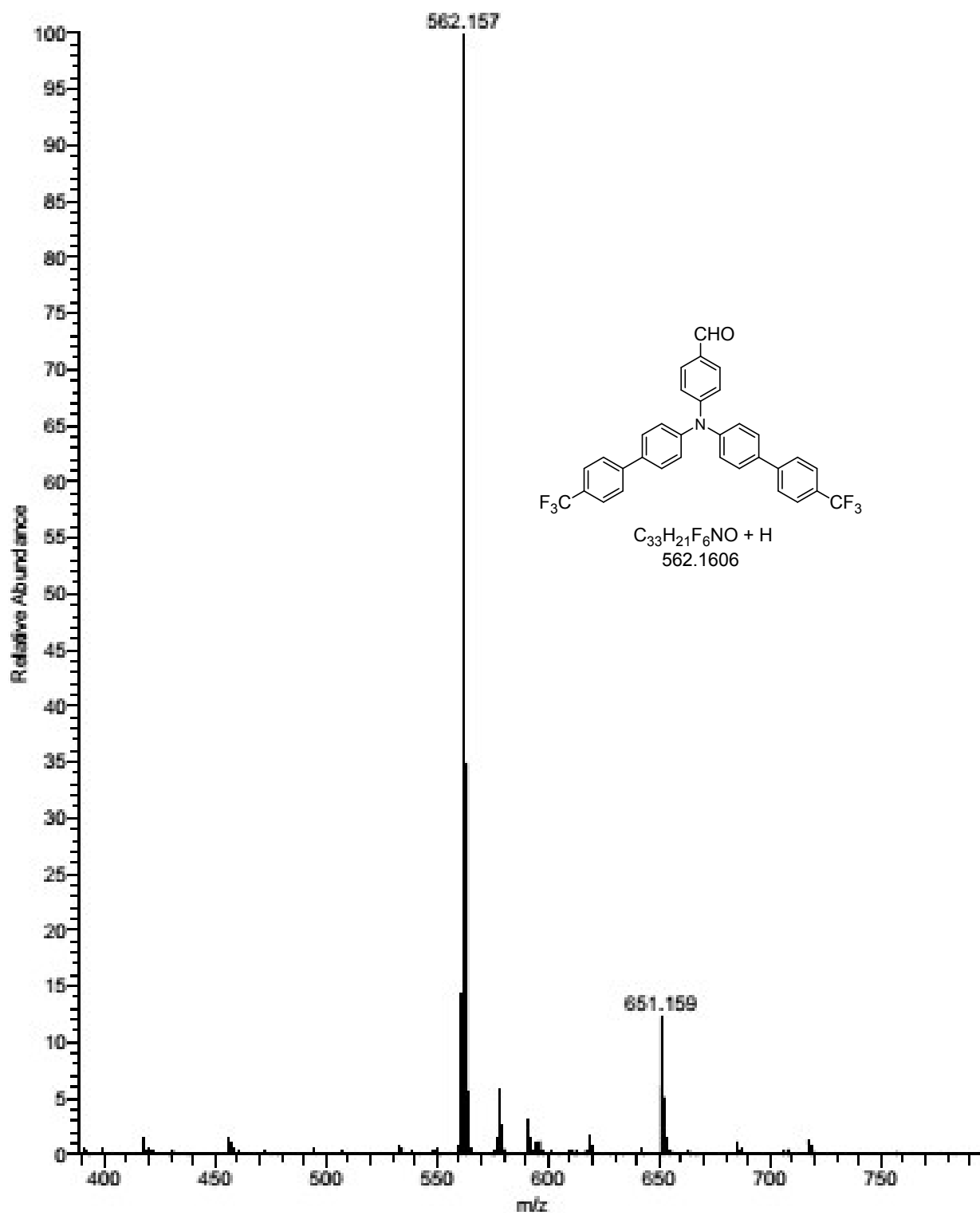**Figure S22.** HR-Mass spectra of compound **8**

S28

(i) C. Quinton, V. A. Rizzo, C. D. Verdes, F. Miomandre and P. Audebert. *Electrochimica Acta* 2013, **110**, 693.

(ii) (a) D. Jana and B. K. Ghorai. *Tetrahedron Letters* 2012, **53***, 1798. (b) H. Wang, L.F. Chen. X. Zhu, C. Wang,

Y. Wan and Hui Wu. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 2014**, 121***, 355.

(iii) P.P Zamora, K. Bieger, D.Vasquez, M. Merino and R. Maurelia. *Int. J. Electrochem. Sci.* 2015, **10**, 10321.