Electronic Supplementary Information (ESI) for:

One small step in synthesis, a big leap in charge mobility:

diphenylethenyl substituted triphenylamines

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$t=25\,^{\circ}\mathrm{C}$ $\mu_h = 0.017\ \mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$

μ (cm^2/Vs)

$E^{1/2}$ (V/cm)$^{1/2}$
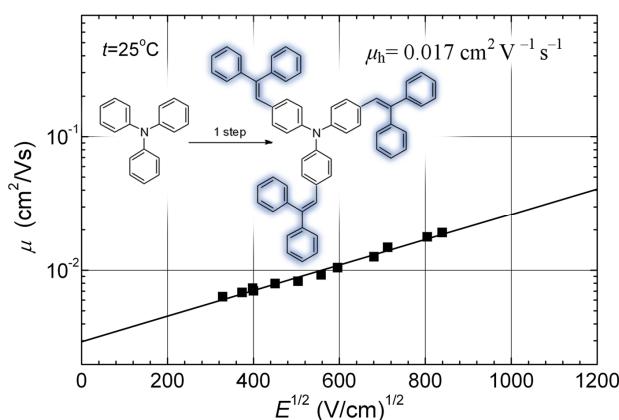
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General

All chemicals were purchased from Aldrich and used as received without further purification. The ^{1}H NMR spectra were recorded on a Varian Unity Inova (300 MHz) spectrometer at room temperature. All the data are given as chemical shifts in δ (ppm), $(CH_3)_4Si$ (TMS, 0 ppm) was used as an internal standard. The course of the reactions products were monitored by TLC on ALUGRAM SIL G/UV254 plates and developed with I_2 or UV light. Silica gel (grade 62, 60–200 mesh, 150 Å, Aldrich) was used for column chromatography. Elemental analysis was performed with an Exeter Analytical CE-440 Elemental. Melting points were determined using Electrothermal Mel-Temp melting point apparatus. MS were recorded on an Aligent 110 (series MS with VL) apparatus. The UV-vis spectra were recorded as dilute solutions of the synthesized compounds in THF on Perkin Elmer Lambda 35 spectrophotometer. Microcells with an internal width of 1 mm were used. The DSC and TGA measurements were carried out on a Mettler DSC 30 calorimeter at a scan rate of 10 K/min. AFM analysis was carried out on a Nanonics Atomic Force Microscope, in air and at room temperature, using the intermittent-contact mode.

The ionization energy E_I of the layers of the synthesized compounds was measured by the electron photoemission in air method. The samples for the ionization energy measurement were prepared by dissolving materials in THF and were coated on Al plates pre-coated with ~0.5 μm thick methylmethacrylate and methacrylic acid copolymer adhesive layer. The thickness of the transporting material layer was 0.5-1 μm.

Usually the photoemission experiments are carried out in vacuum and high vacuum is one of the main requirements for these measurements. If vacuum is not high enough the sample surface oxidation and gas adsorption are influencing the measurement results. In our case, however, the organic materials investigated are stable enough to oxygen and the measurements may be carried out in the air.

The samples were illuminated with monochromatic light from the quartz monochromator with deuterium lamp. The power of the incident light beam was $(2-5) \cdot 10^{-8}$ W. The negative voltage of −300 V was supplied to the sample substrate. The counter-electrode with the 4.5x15 mm^2 slit for illumination was placed at 8 mm distance from the sample surface. The counter-electrode was connected to the input of the BK2-16 type electrometer, working in the open input regime, for the photocurrent measurement. The $10^{-15} - 10^{-12}$ A strong photocurrent was flowing in the circuit under illumination. The photocurrent I is strongly dependent on the incident light photon energy hν. The $I^{0.5} = f(h\nu)$ dependence was plotted. Usually the dependence of the photocurrent on incident light quanta energy is well described by linear relationship between $I^{0.5}$ and $h\nu$ near the threshold.[1,2] The linear part of this dependence was

[1] E. Miyamoto, Y. Yamaguchi, M. Yokoyama, *Electrophotography*, 1989, **28**, 364.

[2] M. Cordona, L. Ley, *Top. Appl. Phys.*, 1978, **26**, 1.

[3] E. Montrimas, V. Gaidelis, A. Pazera, *Lith. J. Phys.*, 1966, **6**, 569.

[4] S. M. Vaezi-Nejad, *Int. J. Electron.*, 1987, **62**, 361.

[5] Y. Archie, C. Chan, C. Juhasz, *Int. J. Electron.*, 1987, **62**, 625.

[6] M. Thelakkat, H. W. Schmidt, *Adv. Mater.*, 1998, **10**, 219.

extrapolated to the hν axis and I_p value was determined as the photon energy at the interception point.

The samples for the hole mobility measurements were prepared by spin-coating the solutions of the synthesized compounds on the polyester films with conductive Al layer. The layer thickness was in the range 5-10 μm.

The hole drift mobility was measured by xerographic time of flight technique (XTOF).[3-5] Electric field was created by positive corona charging. The charge carriers were generated at the layer surface by illumination with pulses of nitrogen laser (pulse duration was 2 ns, wavelength 337 nm). The layer surface potential decrease as a result of pulse illumination was up to 1-5 % of initial potential before illumination. The capacitance probe that was connected to the wide frequency band electrometer measured the speed of the surface potential decrease dU/dt. The transit time t_t was determined by the kink on the curve of the dU/dt transient in double logarithmic scale. The drift mobility was calculated by the formula $\mu=d^2/U_0t_t$, where d is the layer thickness, U_0 – the surface potential at the moment of illumination.

CV measurements were carried out by a three-electrode assembly cell from Bio-Logic SAS and a micro-AUTOLAB Type III potentiostat-galvanostat. The measurements were carried out at a glassy carbon electrode in dichlormethane solutions containing 0.1 M tetrabutylammonium perchlorate as electrolyte and Ag/AgNO$_3$ as the reference electrode. Each measurement was calibrated with ferrocene (Fc). Oxidation potentials were obtained as an average value between each anodic and corresponding cathodic potential: $E_{1/2}^{red/ox}= 1/2(E_{pc} + E_{pa})$. HOMO energy levels were estimated on the basis of the reference energy level of ferrocene (4.8 eV below the vacuum level[6]) according to HOMO = 4.8 + ($E_{1/2}$ - $E_{1/2}^{FC}$) eV below the vacuum level. The optical band gaps (E_g^{opt}, eV) estimated from the edges of electronic absorption spectra, LUMO values estimated using equation LUMO = HOMO - E_g.

Synthesis

General procedure

Corresponding triarylamine was dissolved in toluene (20 mL per gram + volume of the Dean-Stark trap), (+/-)-camphor-10-sulfonic acid (1.0 equiv.) was added and the mixture was heated at reflux for 20 min. Afterwards diphenylacetaldehyde (1.5 equiv. per reactive functional group) was added, and reflux continued using a Dean-Stark trap. After termination of the reaction the solution was extracted with toluene. The organic layer was dried over anhydrous $MgSO_4$, filtered, solvent was removed and the residue purified by column chromatography.
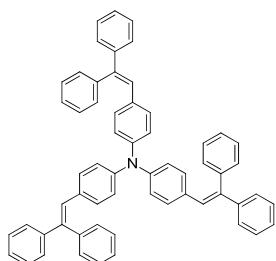
Tris[4-(2,2-diphenylethenyl)phenyl]amine (1)

Triphenylamine (1 g, 4.08 mmol), (+/-)-camphor-10-sulfonic acid (0.95 g, 4.08 mmol), and diphenylacetaldehyde (3.2 g, 16.32 mmol) were used (reaction time 8 hours). After extraction (toluene), the crude product was purified by column chromatography (acetone/*n*-hexane 3/47, *v/v*) to give bright yellow powder.

Yield: 68 % (2.16 g); M.p.: 197–198°C.

^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 7.37–7.17 (m, 30H), 6.87 (s, 3H), 6.78 (dd, J_1= 24.9 Hz, J_2= 8.7 Hz, 12H).

^{13}C NMR (75 MHz, CDCl$_3$, δ, ppm): 145.7, 143.6, 141.1, 140.7, 132.0, 130.5, 130.3, 128.9, 128.3, 127.6, 127.5, 127.4, 123.5.

MS(APCI$^+$, 20 V), m/z: 779 ([M+H]$^+$).

Elemental analysis. Calcd. for $C_{60}H_{45}N$ (%):C 92.39, H 5.81, N 1.80. Found (%): C 92.47, H 5.75, N 1.78.
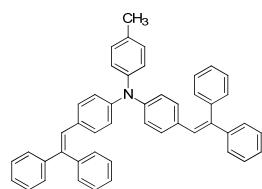
N, N-Bis[4-(2,2- diphenylethenyl)phenyl]-4-methylaniline (2)

4,4'-Dimethyltriphenylamine (1 g, 3.86 mmol), (+/-)-camphor-10-sulfonic acid (0.89 g, 3.86 mmol), and diphenylacetaldehyde (2.27 g, 11.58 mmol) of were used (reaction time 5 hours). After extraction (toluene), the crude product was purified by column chromatography (ethyl acetate/*n*-hexane 1/24, *v/v*) to give bright yellow powder.

Yield: 71 % (1.69 g).

^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 7.36-7.17 (m, 20H), 6.96 (dd, J_1= 29.3 Hz, J_2= 8.3 Hz, 4H), 6.87 (s, 2H), 6.78 (dd, J_1= 24.1 Hz, J_2= 8.8 Hz, 8H), 2.27 (s, 3H).

^{13}C NMR (75 MHz, CDCl$_3$, δ, ppm): 146.3, 144.6, 143.7, 140.8, 133.5, 131.4, 130.5, 130.1, 128.9, 128.3, 127.7, 127.5, 127.3, 125.7, 122.6, 21.0.

MS(APCI$^+$, 20 V), m/z: 615 ([M+H]$^+$).

Elemental analysis. Calcd. for C$_{47}$H$_{37}$N (%):C 91.67, H 6.06, N 2.27. Found (%): C 91.55, H 6.10, N 2.35.
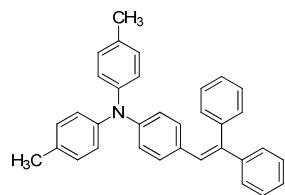
4-(2,2-Diphenylethenyl)-N,N-bis[(4-methyl)phenyl]aniline (3)

4-Methyltriphenylamine (1 g, 3.66 mmol), (+/-)-camphor-10-sulfonic acid (0.85 g, 3.66 mmol), and diphenylacetaldehyde (1.08 g, 5.49 mmol) were used (reaction time 5 hours). After extraction (toluene), the crude product was purified by column chromatography (acetone/*n*-hexane 1/24, *v/v*) to give pale yellow powder (1.24 g, 75 %).

Yield: 75 % (1.24 g); m.p.: 137–139°C.

^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 7.38-7.14 (m, 10H), 6.98 (dd, J_1= 22.9 Hz, J_2= 8.5 Hz, 8H), 6.88 (s, 1H), 6.78 (dd, J_1= 26.1 Hz, J_2= 8.8 Hz, 4H), 2.28 (s, 6H).

^{13}C NMR (75 MHz, CDCl$_3$, δ, ppm): 147.0, 145.1, 143.7, 141.0, 140.3, 132.9, 130.4, 130.0, 128.9, 128.1, 127.9, 127.4, 127.2, 125.1, 121.3, 21.0.

MS(APCI$^+$, 20 V), m/z: 451 ([M+H]$^+$).

Elemental analysis. Calcd. for C$_{34}$H$_{29}$N (%): C 90.43, H 6.47, N 3.10. Found C 90.35, H, 6.58, N 3.07.

Characterization
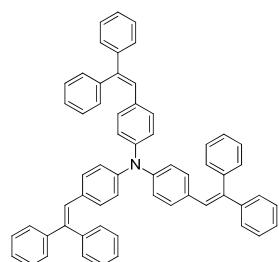
Tris[4-(2,2-diphenylethenyl)phenyl]amine (1). ^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm).
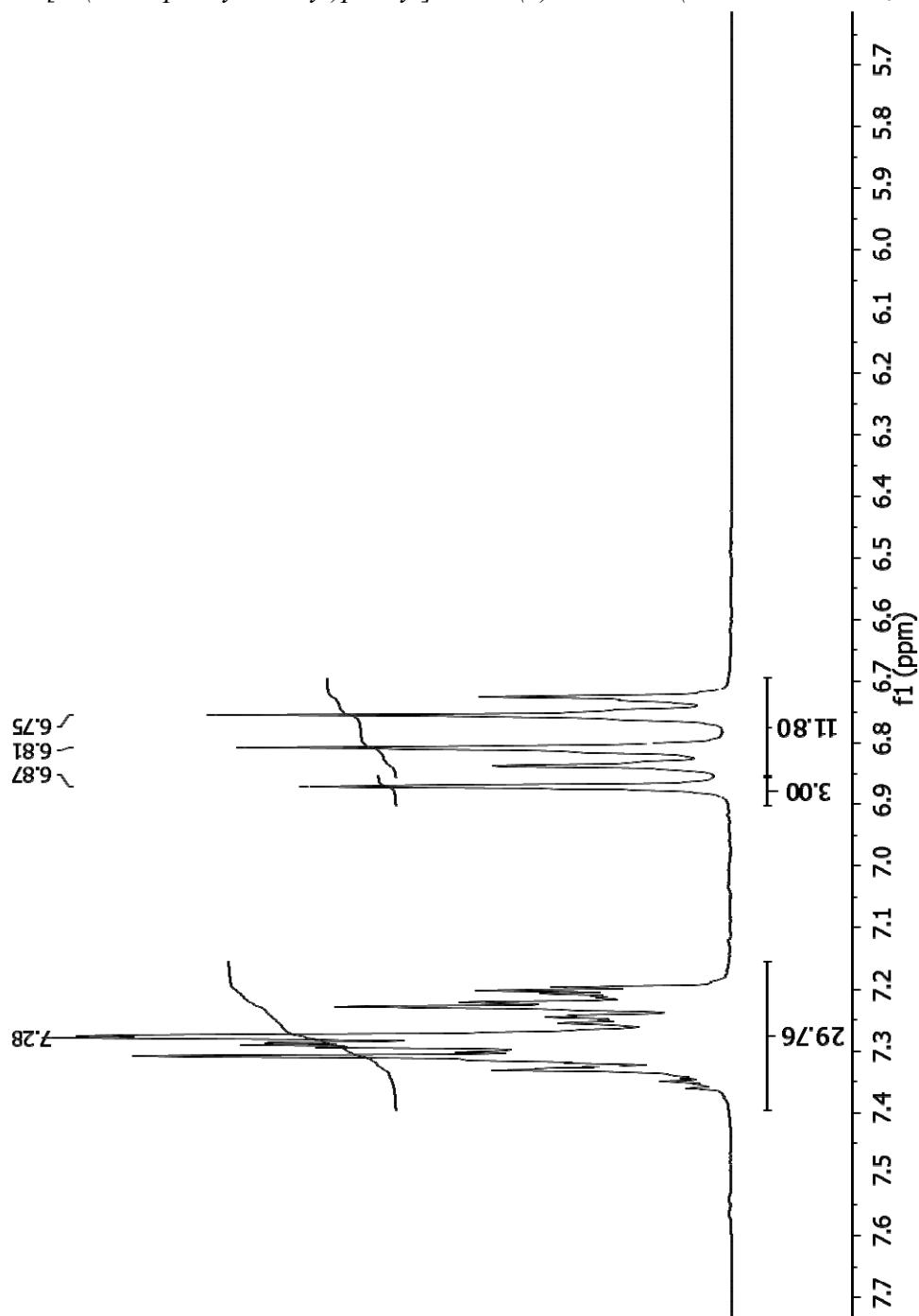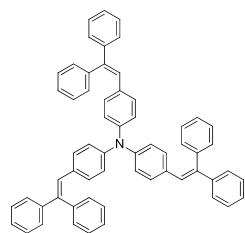
Tris[4-(2,2-diphenylethenyl)phenyl]amine (1). ^{13}C NMR (75 MHz, CDCl$_3$, δ, ppm).
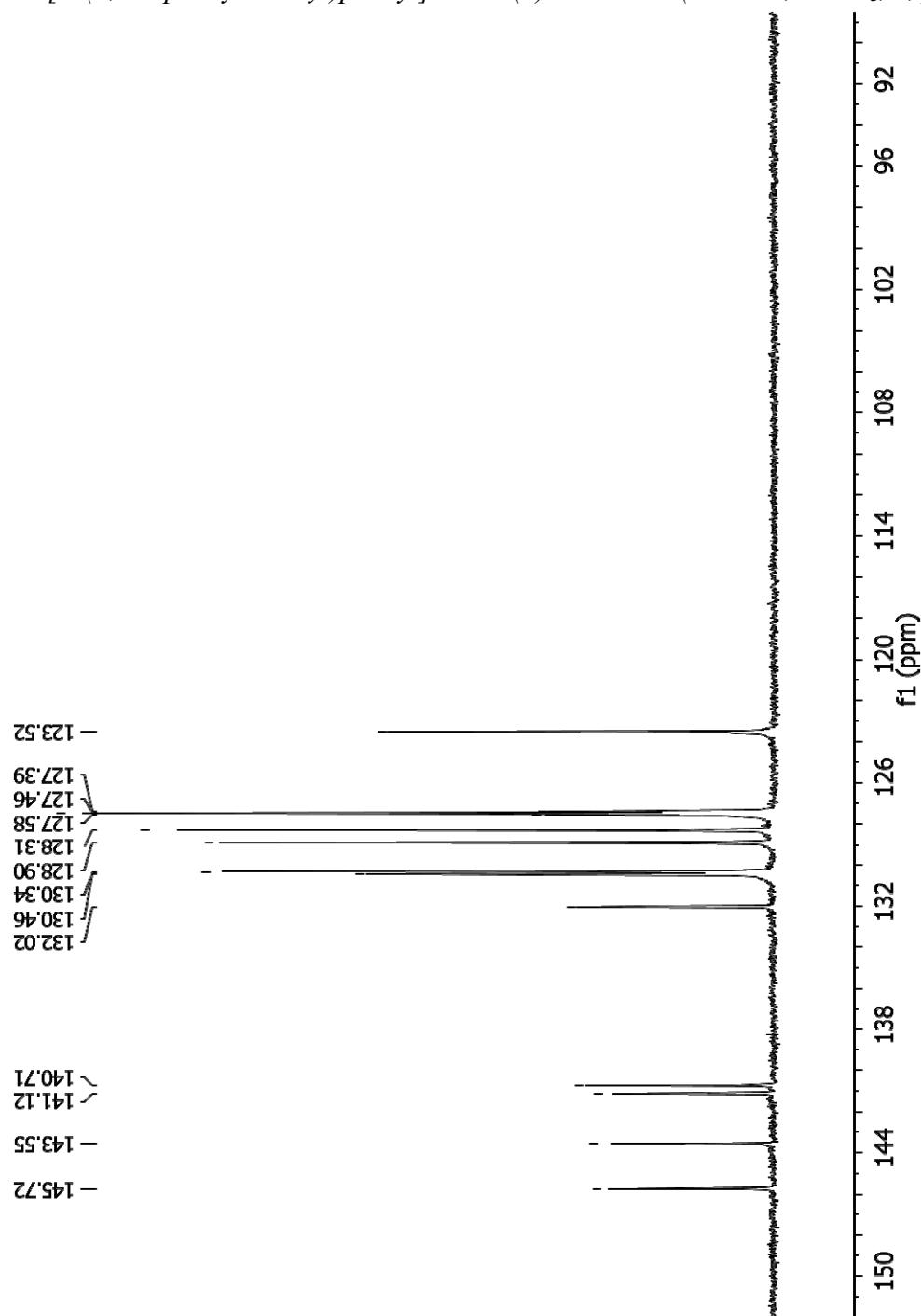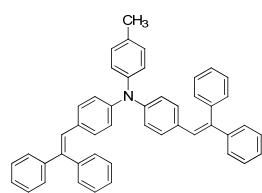
123.52

127.39
127.46
127.58
128.31
128.90
130.34
130.46
132.02

140.71
141.12

143.55

145.72

92
96
102
108
114
120
126
132
138
144
150

f1 (ppm)

N, N-Bis[4-(2,2- diphenylethenyl)phenyl]-4-methylaniline (2). ^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm).

*N, N-Bis[4-(2,2- diphenylethenyl)phenyl]-4-methylaniline (2). ^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm).*

N, N-Bis[4-(2,2- diphenylethenyl)phenyl]-4-methylaniline (2). ^{13}C NMR (75 MHz, CDCl$_3$, δ, ppm).

N, N-Bis[4-(2,2- diphenylethenyl)phenyl]-4-methylaniline (2). ^{13}C *NMR (75 MHz, CDCl₃, δ, ppm).*

— 20.98
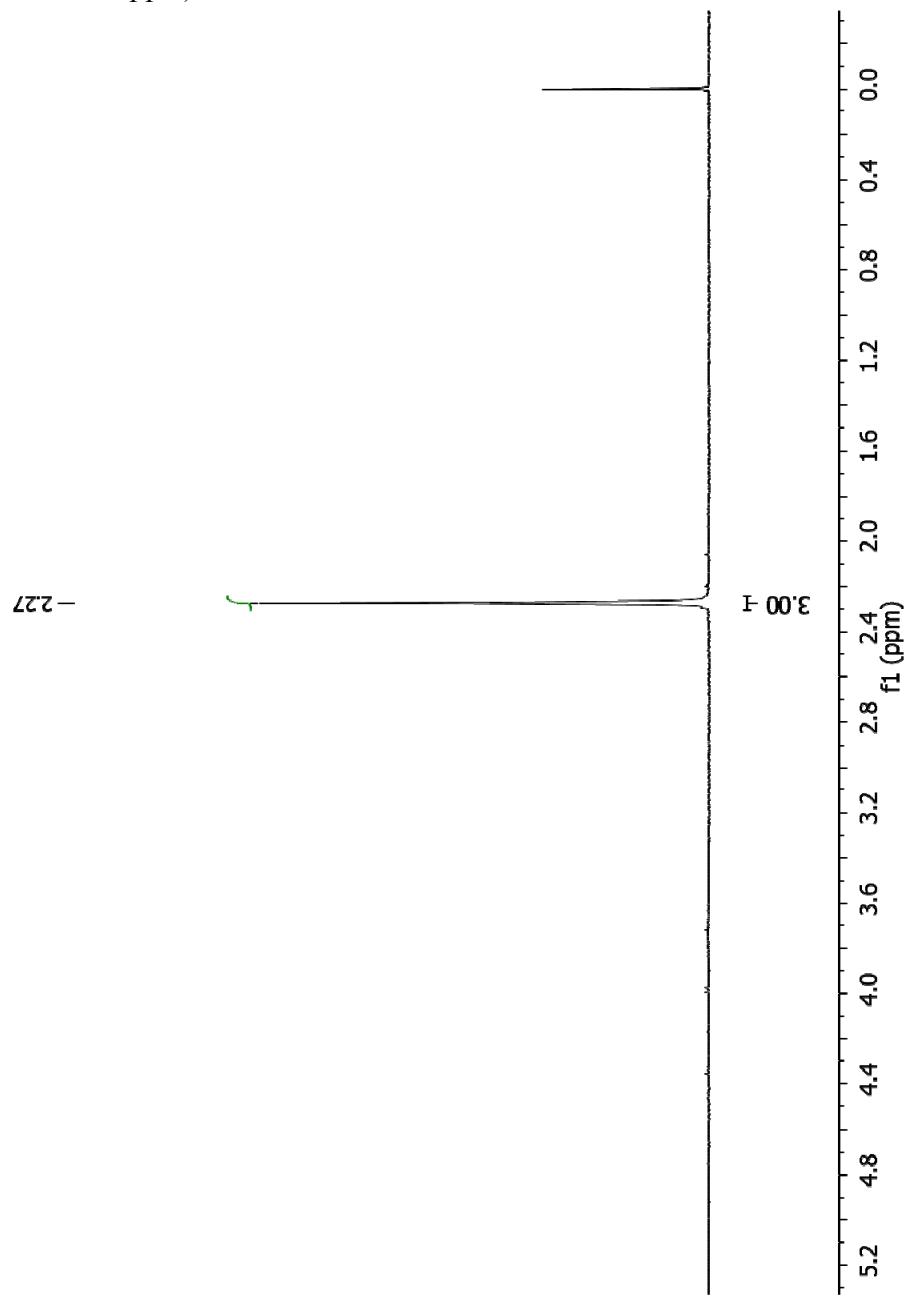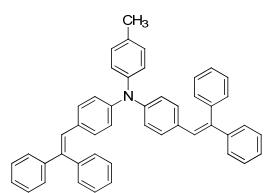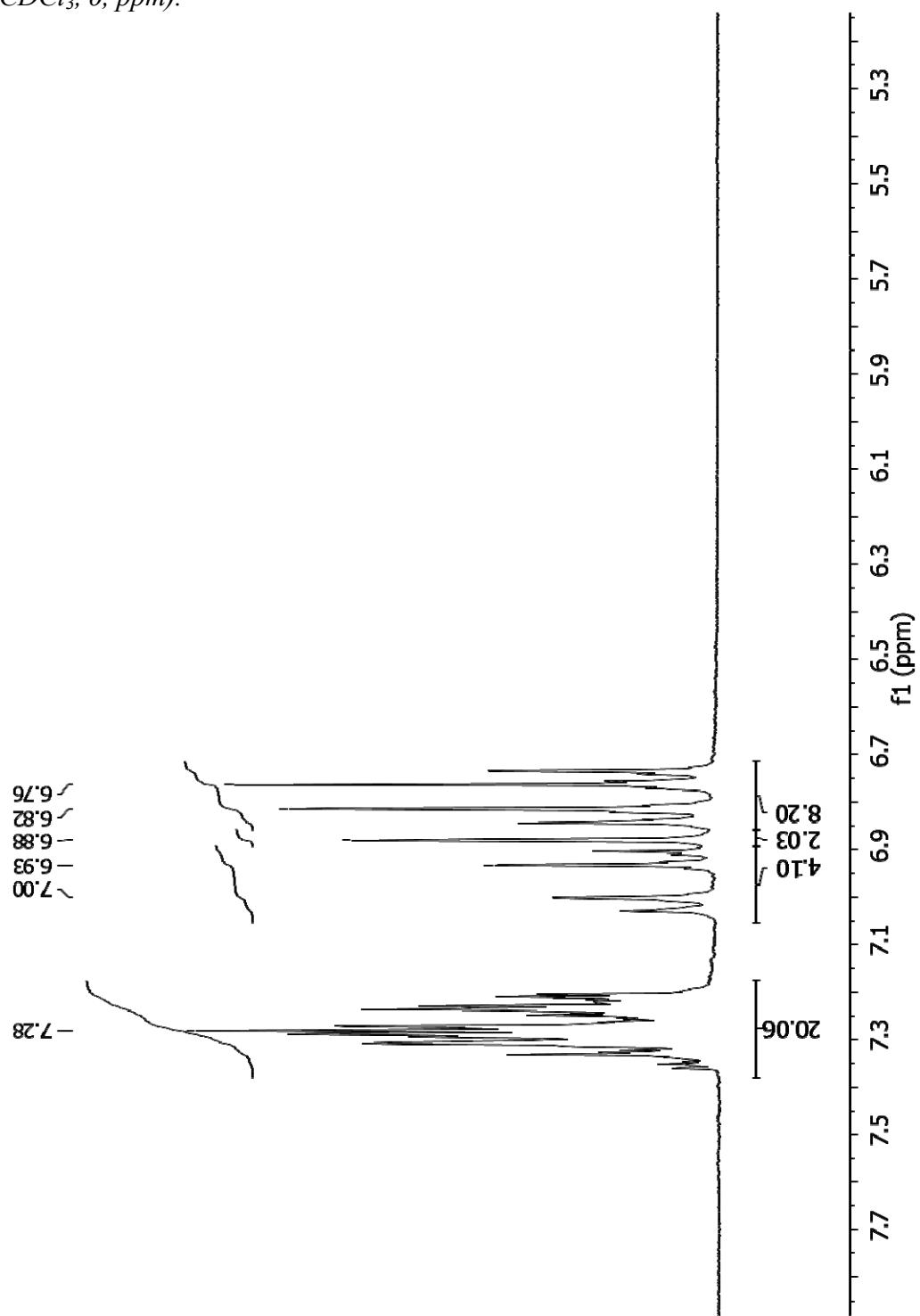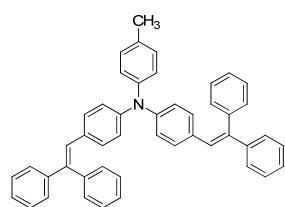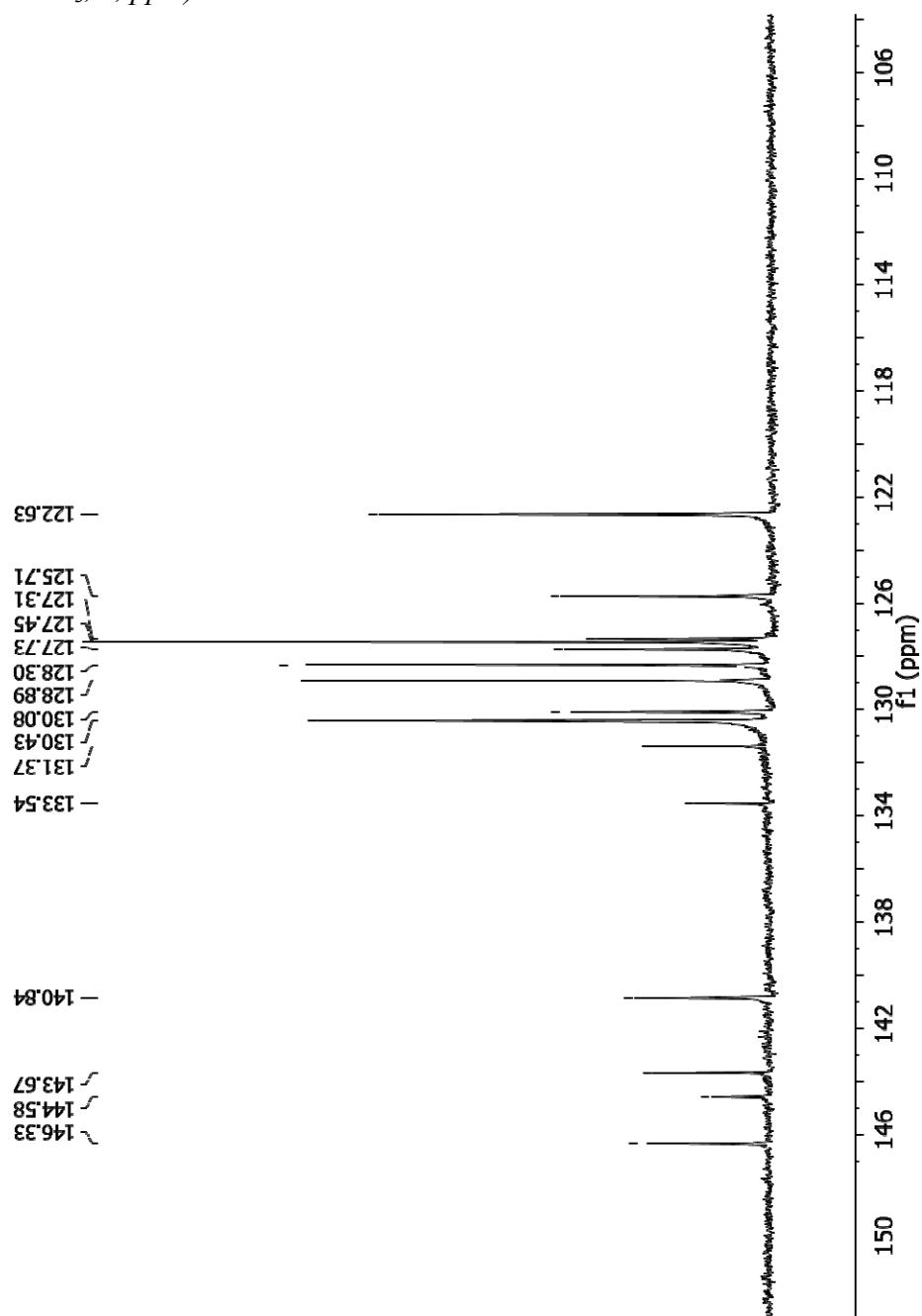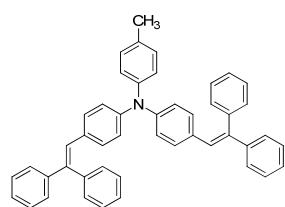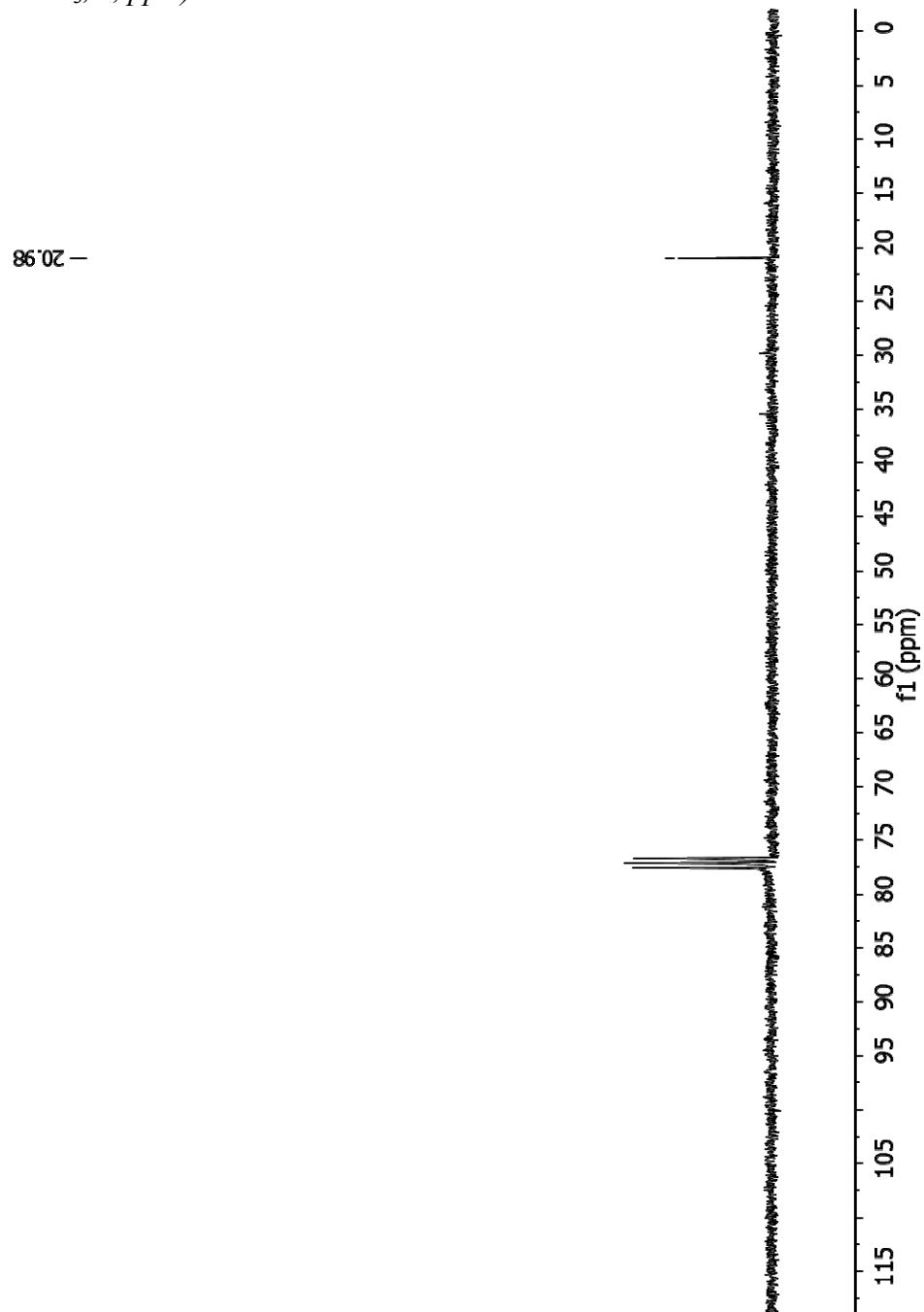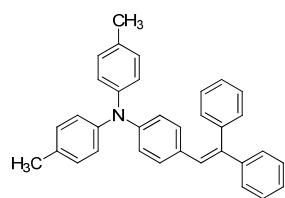
4-(2,2-Diphenylethenyl)-N,N-bis[(4-methyl)phenyl]aniline (3). ^{1}H NMR (300 MHz, CDCl₃, δ, ppm).
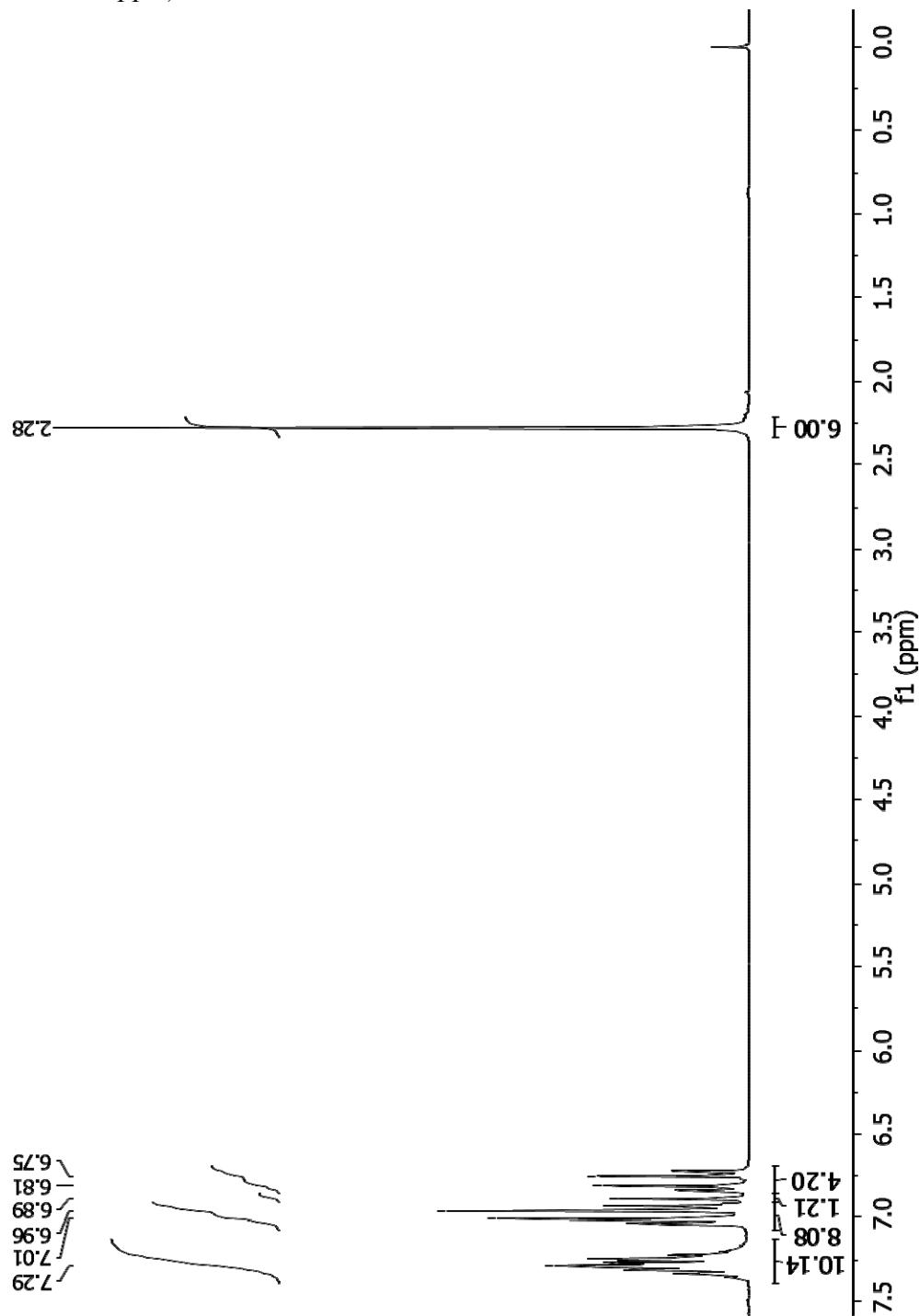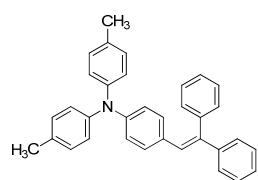
4-(2,2-Diphenylethenyl)-N,N-bis[(4-methyl)phenyl]aniline (3). ^{13}C NMR (75 MHz, CDCl$_3$, δ, ppm).

4-(2,2-Diphenylethenyl)-N,N-bis[(4-methyl)phenyl]aniline (3). ^{13}C *NMR (75 MHz, CDCl₃, δ, ppm).*

— 20.95
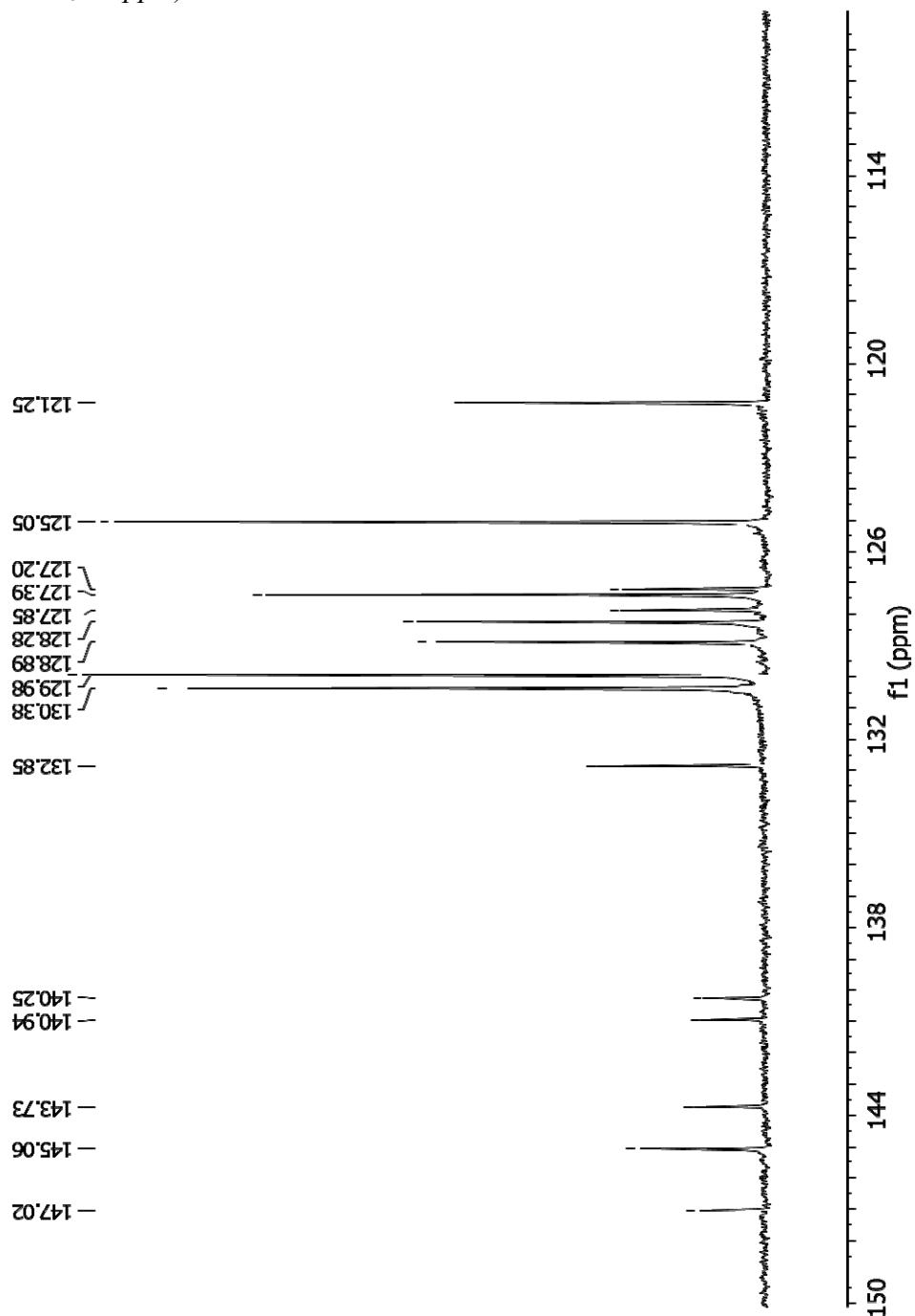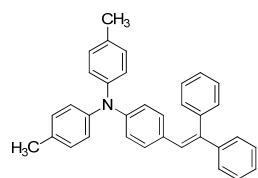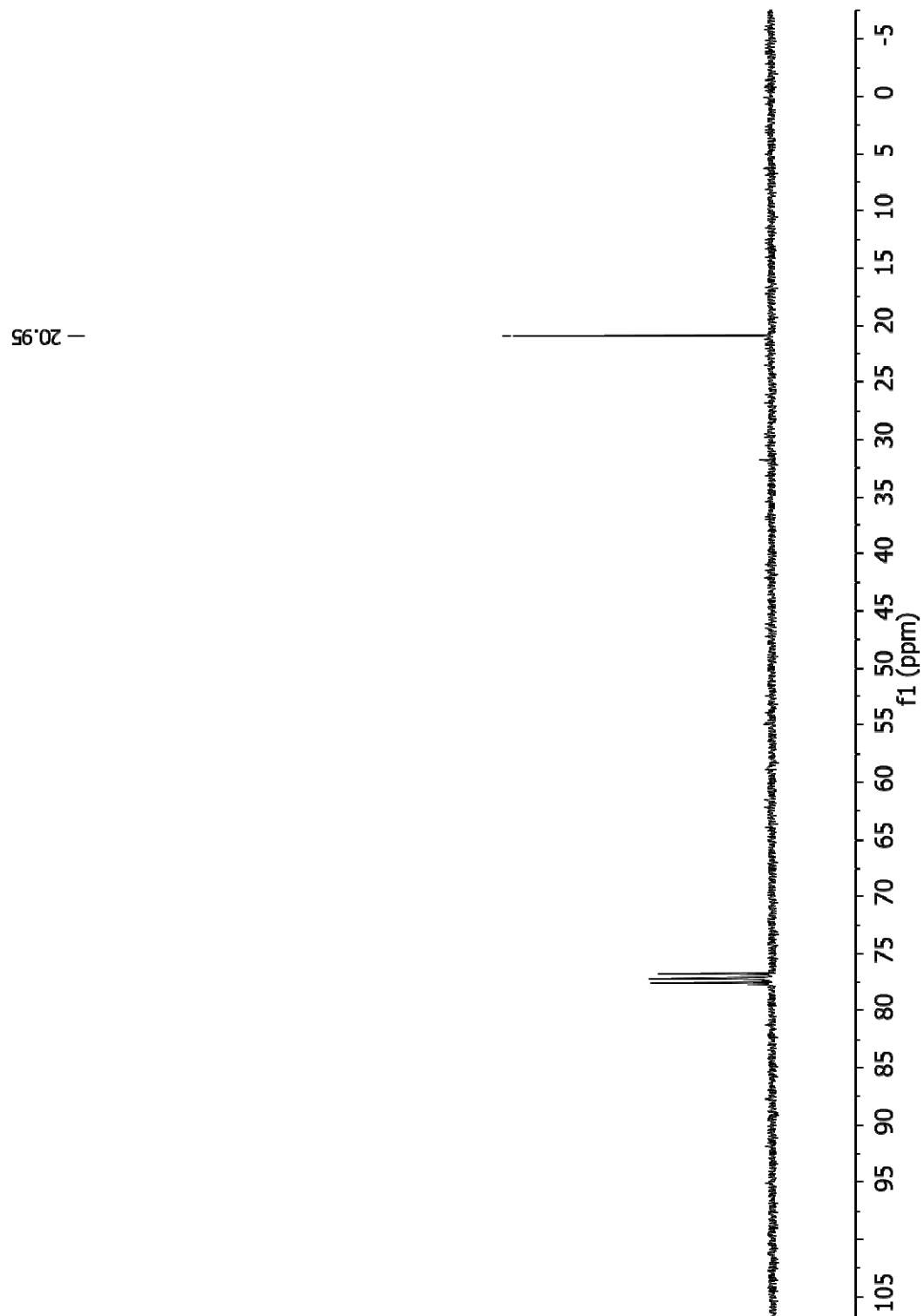
Supporting Figures.
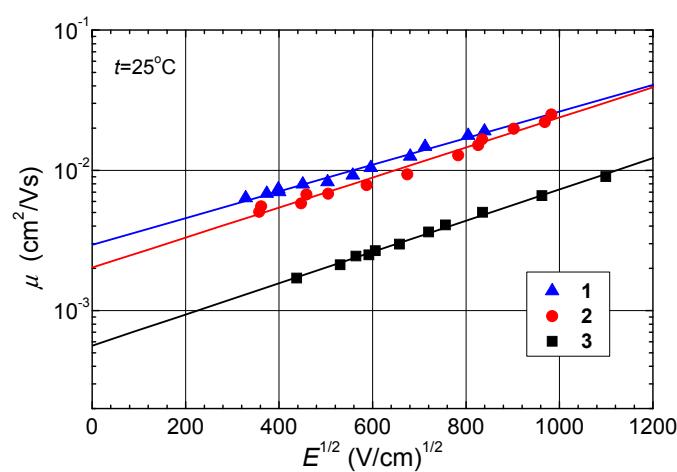
Fig. S1. Electric field dependencies of the hole-drift mobilities (μ) in charge transport layers of compounds **1-3**.
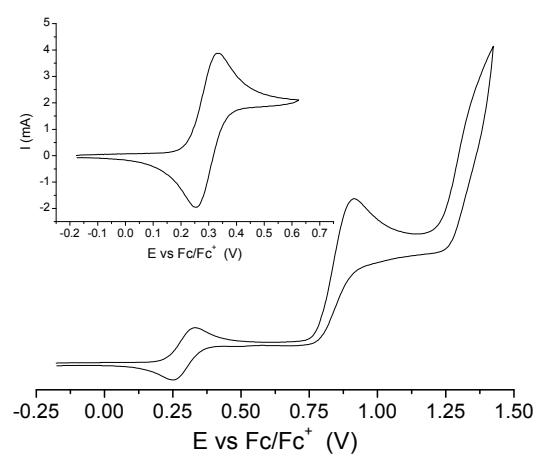

Fig. S2. Cyclic voltammogram of **1** (scan rate = 50 mV·s^{-1}) in argon-purged dichloromethane solution. Insert shows first oxidation wave.
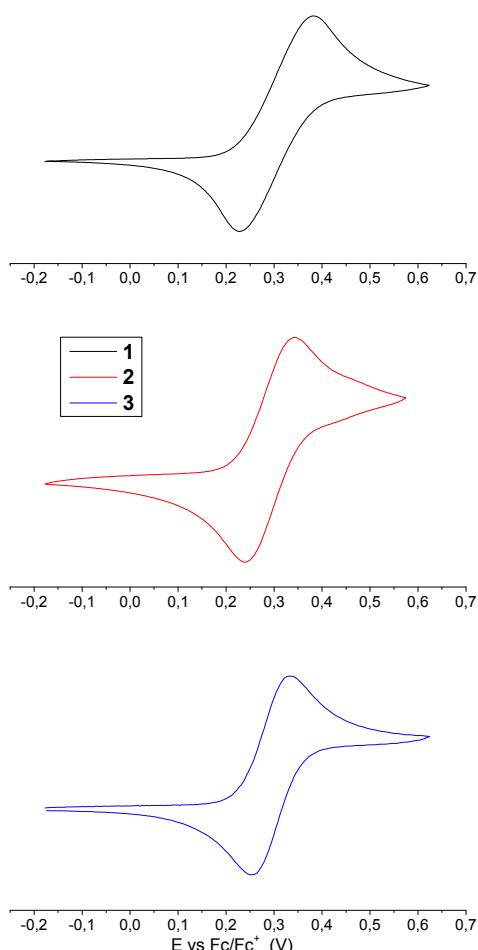
Fig. S3. First oxidation waves of **1-3** (scan rate = 50 mV·s^{-1}) in argon-purged dichloromethane solution.

Table S1. Electrochemical properties of **1–3**

Compound	E_{pc}^{ox} vs Fc [V]	E_{pa}^{ox} vs Fc [V]	$E_{1/2}$ vs Fc [V] [a]	E_{onset} vs Fc [V]
1	0.33	0.25	0.29	0.23
2	0.34	0.24	0.29	0.22
3	0.38	0.23	0.31	0.23

[a] $E_{1/2}= (E_{pa}+E_{pc})/2$; E_{pa} and E_{pc} are peak anodic and peak cathodic potentials, respectively.
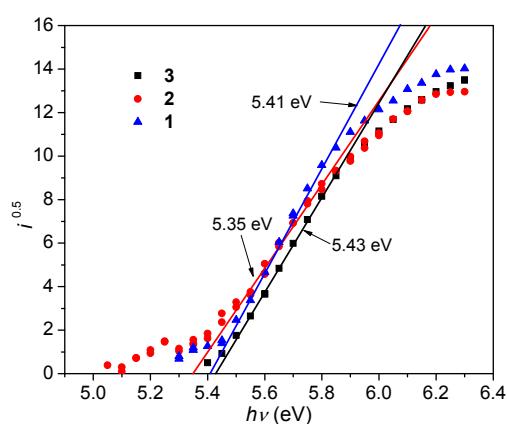
Fig. S4. Photoemission in air spectra of **1-3**.

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