Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supplementary information

Enamine-based hole transporting materials for vacuum-deposited perovskite solar cells

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Experimental details

General

Chemicals were purchased from Sigma-Aldrich and TCI Europe and used as received without further purification. The course of the reactions was monitored by TLC (thin layer chromatography) on ALUGRAM SIL G/UV254 plates and developed with UV light. Silica gel (grade 9385, 230–400 mesh, 60 Å, Aldrich) was used for column chromatography. The 1H and 13C NMR spectra were taken on Bruker Avance III 400 (400 MHz) spectrometer at room temperature. The chemical shifts, expressed in δ (ppm) are relative to a (CH3)4Si (TMS, 0 ppm) internal standard. Elemental analysis was performed with an Exeter Analytical CE-440 elemental analyzer, Model 440 C/H/N/. Thermogravimetric analysis (TGA) was performed on a Q50 thermogravimetric analyzer (TA Instruments) at a scan rate of 10 K min-1 in the nitrogen atmosphere. Differential scanning calorimetry (DSC) was performed on a Q10 calorimeter (TA Instruments) at a heating rate of 10 K/min in the nitrogen atmosphere. The glass transition temperatures for the investigated compounds were determined during the second heating scan. Melting point for crystalline materials were observed using Mel-Temp DigiMelt MPA 161 melting point apparatus at a heating rate 1 C°/min.

Optical measurements

Absorption spectra of the dilute solutions in toluene (concentration 10^{-4} M) and on glass substrate were recorded on a UV/Vis–NIR spectrophotometer, Lambda 35 (Perkin–Elmer). Fluorescence of the investigated compounds in toluene (concentration 10^{-5} M) and on glass substrate were recorded on Edinburgh Instruments fluorescence spectrophotometer FLS920.

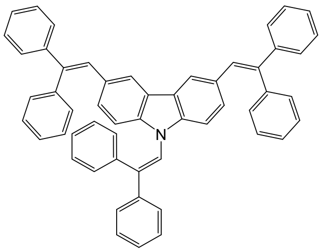
Ionization energy measurements (*IE*)

The ionization energy of the layers of the synthesized compounds was measured by electron photoemission in air (the error of this method is evaluated as ±0.03eV). The samples were prepared by dissolution in THF and the solutions were coated on Al plates pre-coated with approximately 0.5 μm thickness of a methyl methacrylate and methacrylic acid copolymer adhesive layer. The thickness of the transporting material layer was 0.5 – 1 μm. The organic materials investigated are stable enough to oxygen that the measurements may be carried out in the presence of air. The samples were illuminated with monochromatic light from a quartz monochromator fitted with a deuterium lamp. The power of the incident light beam was (2–5)·10^{-8} W. A negative voltage (-330 V) was supplied to the sample substrate. The counter electrode with a 4.5 · 15 mm^2 slit for illumination was placed 8 mm 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 photocurrent (I) flowed in the circuit under illumination. The value of I is strongly dependent on the incident-light photon energy (hν). The dependence $I^{0.5}$ on incident-light quanta energy hν was plotted from the experiment results. Usually the dependence of I on the incident light quantum energy is described well by the linear relationship $I^{0.5} = f(h\nu)$ near the threshold. The linear part of this dependence was extrapolated to the hν axis and the *IE* value was determined as the photon energy at the interception point.

Charge carrier mobility measurements

The samples for the charge carrier mobility measurements were prepared by spin coating solutions of the synthesized compounds in tetrahydrofuran onto PS films with a conductive Al layer. The layer thickness was in the range 5 – 10 μm. The charge drift mobility was measured by XTOF. An electric field was created by positive corona charging. The charge carriers were generated at the layer surface by illumination with pulses of a nitrogen laser (pulse duration = 2 ns, λ = 337 nm). The layer surface potential decrease as a result of pulse illumination was up to 1–5% of the 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 on a linear or double logarithmic scale. The drift mobility was calculated by the formula $\mu = d^2/U_0t_t$ (d is the layer thickness, U_0 is the surface potential at the moment of illumination).

Synthesis of the materials

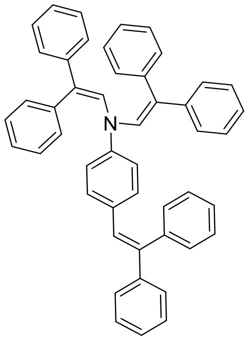


3,6,9-tris(2,2-diphenylvinyl)-9H-carbazole (H1): a mixture of carbazole (1g, 6mmol), diphenylacetaldehyde (3.52g, 18.0mmol) and camphor-10-sulfonic acid (β) (1.39g, 6mmol) were dissolved in toluene (12ml + volume of the Dean-Stark trap). The mixture was heated for 5 hours at reflux. At the end of the reaction (TLC control 1/24 acetone/n-hexane) the mixture was cooled to room temperature and extracted with ethyl acetate. The organic layer was dried over anhydrous Na_2SO_4, filtered and solvent was removed. The crude product was purified by column chromatography (1/24 acetone/n-hexane) to give **H1** as white crystals (m. p. 213-215°C) Yield: 1.8g (42%).

Elemental analysis calcd (%) for $C_{54}H_{39}N$ (701.91g/mol): C 92.40; H 5.60; N 2.00. Found: 92.17; H 5.71; N 2.12.

^{1}H NMR ($CDCl_3$, 400MHz, ppm): δ 7.44 (s, 2H); 7.38-7.16 (m, 25H); 7.11-7.01 (m, 6H), 7.00-6.93 (m, 2H), 6.92-6.82 (m, 4H).

^{13}C NMR ($CDCl_3$, 101MHz, ppm): δ 143.76; 140.74; 140.66; 140.60; 139.63; 138.66; 138.15; 130.52; 129.84; 129.43; 128.80; 128.73; 128.34; 128.25; 128.21; 127.82; 127.72; 127.49; 127.25; 127.19; 123.48; 121.04; 120.29; 110.04.

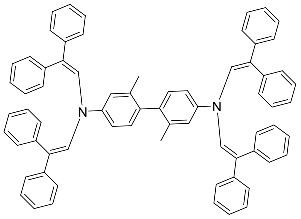


N**,*****N*****,4-tris(2,2-diphenylethenyl)aniline (H2):** a mixture of aniline (0.5g, 5.4mmol), diphenylacetaldehyde (3.45g, 20.1mmol) and camphor-10-sulfonic acid (β) (1.24g, 5.4mmol) were dissolved in THF (10ml + volume of the Dean-Stark trap). The mixture was heated for 6 hours at reflux. At the end of the reaction (TLC control 2/23 toluene/n-hexane) the mixture was cooled to room temperature and extracted with ethyl acetate. The organic layer was dried over anhydrous Na_2SO_4, filtered, the solvent was removed. The crude product was dissolved in 17ml THF and poured into 250ml ethanol to remove the excess amount of aldehyde. The acquired powder was purified by column chromatography (2/23 toluene/n-hexane) to give **H2** as yellow crystals (m. p. 230-232°C). Yield: 1.4g (42%).

Elemental analysis calcd (%) for $C_{48}H_{37}N$ (627.83g/mol): C 91.83; H 5.94; N 2.23. Found: 91.97; H 5.67; N 2.36.

^1H NMR ($CDCl_3$, 400MHz, ppm): δ 7.40 – 7.21 (m, 16H); 7.14 – 7.01 (m, 10H); 6.97 (d, J = 8.6 Hz, 3H), 6.87 (d, J = 8.6 Hz, 2H), 6.42 (d, J = 7.5 Hz, 4H), 5.81 (s, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz, ppm) δ 144.33; 143.46; 141.26; 140.74; 140.57; 140.00; 132.37; 131.12; 130.59; 130.25; 129.54; 128.91; 128.61; 128.55; 128.21; 127.73; 127.63; 127.47; 127.44; 127.29; 127.21; 126.77; 116.45.

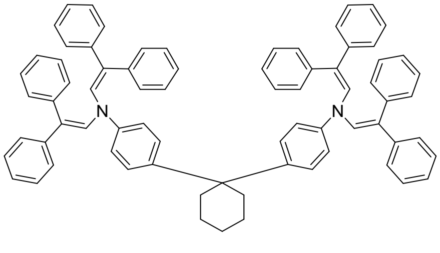


***N^4,N^4,$N^{4'}$,$N^{4'}$*-tetrakis(2,2-diphenylethenyl)-2,2'-dimethyl[1,1'-biphenyl]-4,4'-diamine (H3):** a mixture of m-tolidine (0.6g, 2.8mmol), diphenylacetaldehyde (2.66g, 13.6mmol) and camphor-10-sulfonic acid (β) (0.66g, 2.8mmol) were dissolved in toluene (7ml + volume of the Dean-Stark trap). The mixture was heated for 3 hours at reflux. Afterwards (TLC control 1/24 v/v diethyl ether/n-hexane) the reaction mixture was cooled and poured to 130ml of ethyl acetate giving yellow crystals (m. p. 337-339°C) that were filtered and then washed with ethyl acetate and ethanol (1/4 v/v). Yield: 0.94 g (36%).

Elemental analysis calcd (%) for $C_{70}H_{56}N_2$ (925.23g/mol): C 90.87; H 6.10; N 3.03. Found: 90.76; H 5.98; N 3.26.

^{1}H NMR ($CDCl_3$, 400MHz, ppm): δ 7.40 – 7.27 (m, 14H); 7.16 – 7.04 (m, 22H); 7.02-6.96 (m, 4H), 6.52-6.47 (m, 6H), 5.95 (s, 4H), 2.13-2.05 (m, 6H).

^{13}C NMR ($CDCl_3$, 101 MHz, ppm) δ 144.66, 141.57, 140.17, 137.45, 135.25, 131.64, 130.67, 129.67, 129.20, 129.06, 128.55, 127.76, 127.66, 127.15, 126.67, 118.41, 114.62, 20.34.



***N1^4*,*N1^4*,*N3^4*,*N3^4*-tetrakis(2,2-diphenylethenyl)-2^3,2^4,2^5,2^6-tetrahydro-2^{2}H-[1^1,2^1:2^1,3^1-terphenyl]-1^4,3^4-diamine (H4):** a mixture of 1,1-bis(4-aminophenyl)cyclohexane (1.2g, 4.5mmol), diphenylacetaldehyde (4.4g, 22.5mmol) and camphor-10-sulfonic acid (β) (1.04g, 4.5mmol) were dissolved in THF (9ml + volume of the Dean-Stark trap). The mixture was heated for 4 hours at reflux. Afterwards (TLC control 2/23 v/v diethyl ether/n-hexane) the reaction mixture was cooled and poured to 180ml of methanol giving yellow amorphous mass that was filtered and then washed with methanol. The crude product was purified by column chromatography (2/23 v/v diethyl ether/n-hexane) to give **H4** as yellow crystals (m. p. 308-310°C). Yield: 1.8g (41%).

Elemental analysis calcd (%) for $C_{74}H_{62}N_2$ (979.32g/mol): C 90.76; H 6.38; N 2.86. Found: 90.63; H 6.24; N 3.13.

^{1}H NMR ($CDCl_3$, 400MHz, ppm): δ 7.32 – 7.26 (m, 12H); 7.24 – 7.20 (m, 4H); 7.14-7.00 (m, 24H), 6.48-6.44 (m, 8H), 5.88 (s, 4H), 2.27 (s, 4H) 1.62-1.48 (m, 6H).

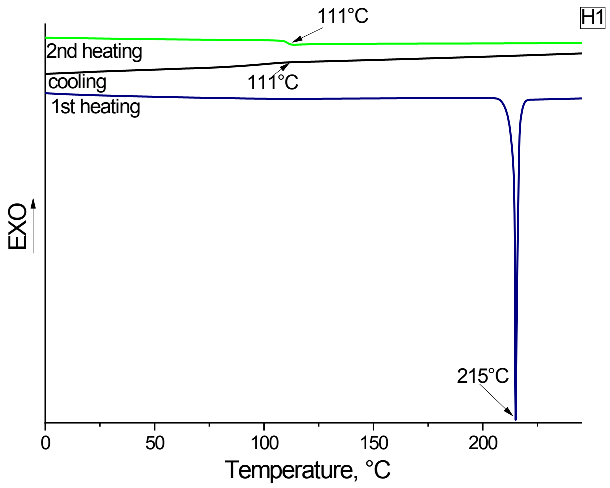
^{13}C NMR ($CDCl_3$, 101 MHz, ppm) δ 143.15, 142.25, 141.57, 140.11, 131.39, 129.64, 129.00, 128.48, 127.86, 127.70, 127.60, 127.06, 126.56, 117.20, 45.32, 37.30, 26.46, 22.93.

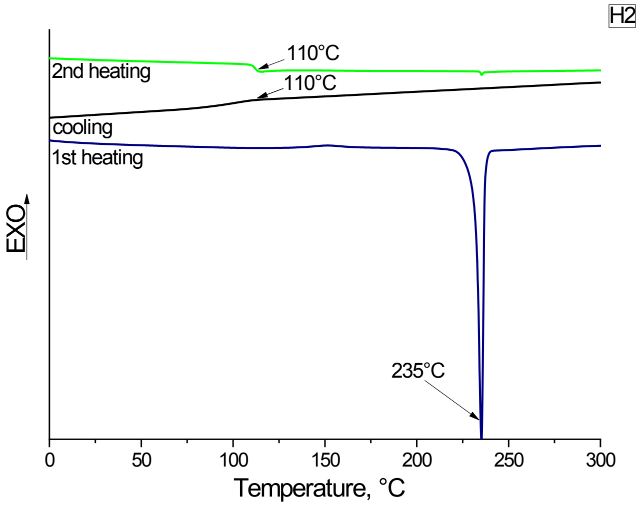
Device fabrication and characterization

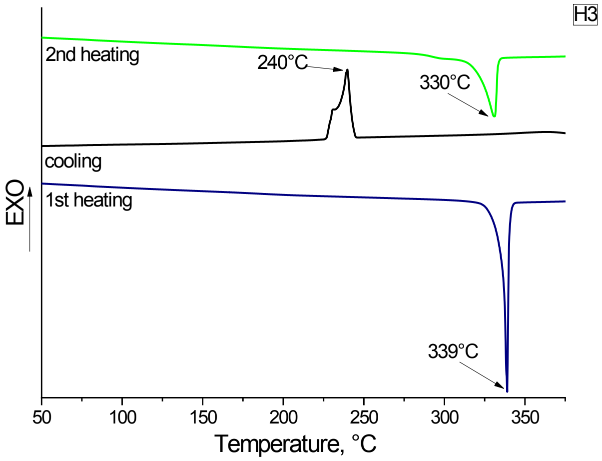
Photolithographically patterned ITO-coated glass substrates were used as substrates. MoO_3 and 2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) were purchased from Lumtec, fullerene (C60) was purchased from Sigma Aldrich. CH_3NH_3I (MAI) and PbI2 were purchased from Lumtec. All materials were used as received.

ITO-coated glass substrates were subsequently cleaned with soap, water and isopropanol in an ultrasonic bath, followed by UV-ozone treatment. They were transferred to a vacuum chamber integrated into a nitrogen-filled glovebox (H_2O and $O_2 < 0.1$ ppm) and evacuated to a pressure of 10^{-6} mbar. The vacuum chamber used to sublime the HTMs, ETL and MAPI is equipped with six temperature-controlled evaporation sources (Creaphys) fitted with ceramic crucibles. The sources were directed upward with an angle of approximately 90° with respect to the bottom of the evaporator. The substrate holder to evaporation source distance is approximately 20 cm. Three quartz crystal microbalance (QCM) sensors were used: two monitoring the deposition rate of each evaporation source and a third one close to the substrate holder monitoring the total deposition rate. The materials were sublimed and the evaporation rate was controlled by separate QCM sensors obtaining precisely the deposited thickness. For the perovskite deposition, MAI and PbI_2 were coevaporated by measuring the deposition rate of each material in a different sensor and obtaining the total perovskite thickness in the third one, leading to a 500 nm-thick film. MoO_3 and Ag were evaporated in a third vacuum chamber using tantalum boats by applying currents ranging from 2.0 to 4.8 A.

The J–V curves of the solar cells were recorded using a Keithley 2612A Source-Meter with 0.01 V steps and integrating the signal for 20 ms after a 10 ms delay, corresponding to a speed of about 0.3 V s^{-1}. The devices were illuminated under a Wavelabs Sinus 70 LED solar simulator. The light intensity was calibrated before every measurement using a calibrated Si reference diode. Solar cell stability measurements were recorded using a maximum power point tracking system, with a white LED light source at 1 sun equivalent, developed by Candlelight. During the stability measurements, the encapsulated devices were exposed to a flow of N_2 gas; temperature was stabilized at 300 K during the entire measurement using a water-circulating cooling system controlled by a Peltier element; J–V curves were recorded every 10 min.


H1
111°C
2nd heating
cooling
111°C
1st heating
EXO
215°C
0
50
100
150
200
Temperature, °C


H2
110°C
2nd heating
110°C
cooling
1st heating
EXO
235°C
0
50
100
150
200
250
300
Temperature, °C



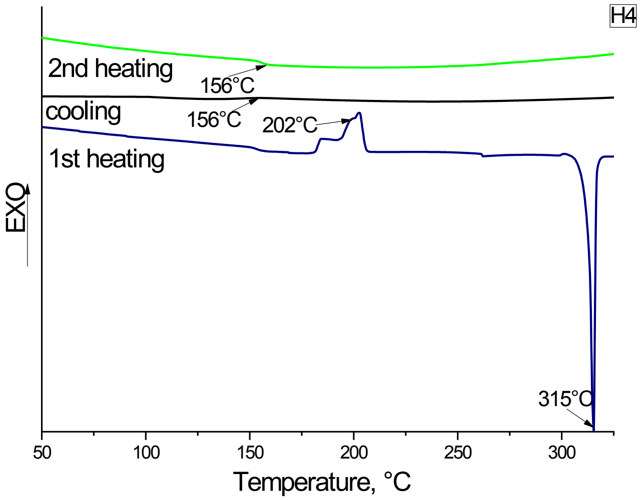


Figure **S1**. DSC graphs of HTMs **H1**, **H2**, **H3** and **H4**.

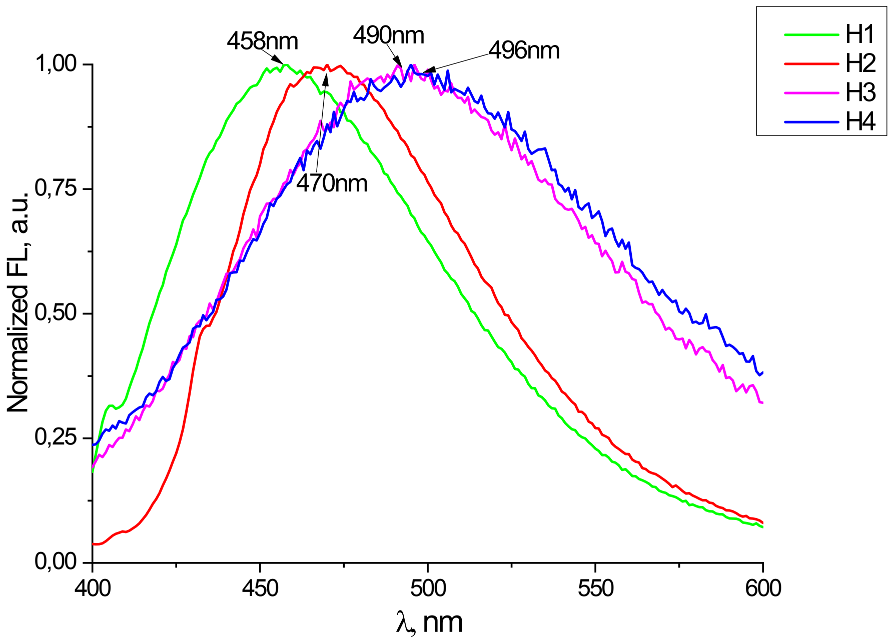


Figure S2. H1, **H2**, **H3**, **H4** fluorescence spectra in toluene. For **H1** λ_{ex}=360nm, **H2** λ_{ex}=382nm. **H3** and **H4** λ_{ex}=345nm.

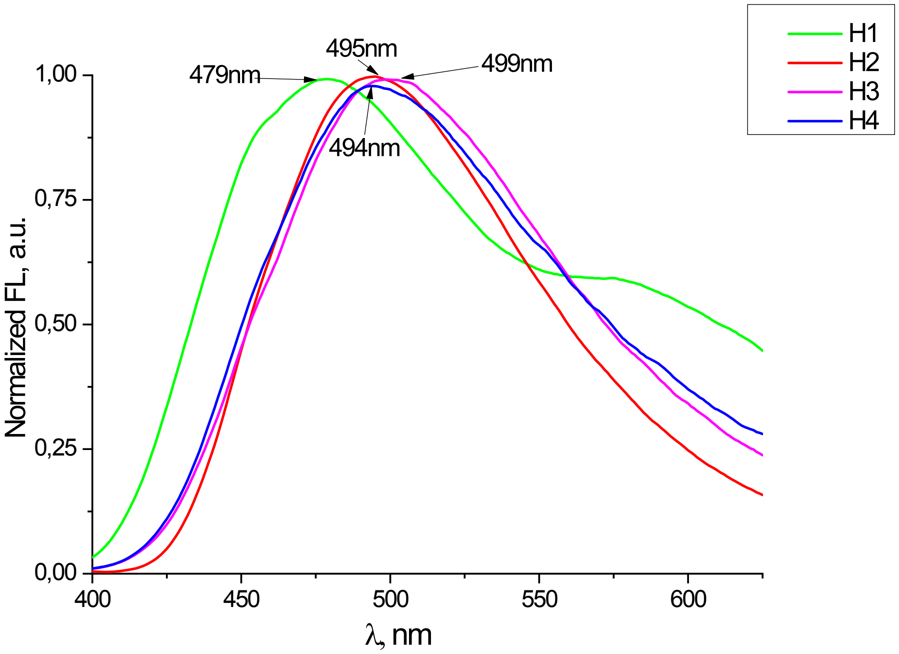


Figure S3. HTM fluorescence spectra on glass substrate. For **H1** (λ_{ex}=360nm), **H2** (λ_{ex}=382nm), **H3** and **H4** (λ_{ex}=345nm).

Cost estimation

In order to estimate the cost, data have been collected from chemical suppliers (Sigma-Aldrich, TCI, Acros Organics, Fischer Chemicals, Oakwood Chemical and Eurochemicals) for all used chemicals. The cost of HTM **H2** was calculated in February 2020, while the cost of the synthesis of Spiro-TTB, in November 2019.

Table S1. Materials, quantities and cost for the synthesis of **H2**.

Chemicals	Weight reagent (g/g)	Weight solvent (g/g)	Weight Workup (g/g)	Price of chemicals (€/kg)	Cost of chemical (€/g product)	Total cost (€/g)
Aniline	0.36			36.42	0.00	
Diphenylacetaldehyde	2.8			3578.52	10.02	
10-Camphorsulfonic acid	0.9			260.0	0.23	
THF		20	17	8.88	0.33	
Ethyl acetate			125	2.85	0.35	
Ethanol			250	6.08	1.52	
Toluene			80	2.46	0.20	
Hexane			920	3.16	2.90	

Silica gel			100	18.60	1.86	
Na_2SO_4			20	6.08	0.12	
H2	4.06	20	1617			17.53

17.53€=19.23$

Table S2. Materials quantities and cost for the synthesis of Spiro-TTB.

Chemicals	Weight reagent (g/g)	Weight solvent (g/g)	Weight Workup (g/g)	Price of chemicals ($/kg)	Cost of chemical ($/g product)	Cost per step ($/step)
2-Bromoanline	0.99			706.70	0.70	
Hydrochloric acid	3.49			62.60	0.22	
$NaNO_2$	0.48			31.66	0.02	
Potassium iodide	1.43			108.35	0.15	
Acetonitrile		12.38		6.08	0.08	
Dichloromethane			295	11.16	3.29	
$MgSO_4$			2	54.24	0.08	
2-Bromoiodobenzene	**6.39**	**12.38**	**297**			**4.54**
Phenylboronic acid	0.67			1419.73	0.96	
K_2CO_3	1.83			6.74	0.01	
$PdCl_2(PPh_3)_2$	0.06			16701.40	0.93	
Dimethoxyethane		13.49		94.77	1.28	
Diethyl ether			159	22.89	3.63	

$MgSO_4$			2	54.24	0.08	
Heptane			284	4.59	1.30	
Ethyl acetate			160	3.63	0.58	
Silica gel			390	44.41	17.34	
2-Bromobiphenyl	**2.56**	**13.49**	**995**			**26.11**
9-Fluorenone	0.87			162.72	0.14	
Magnesium	0.13			36.32	0.00	
Tetrahydrofuran		3.17		6.94	0.03	
Methanol			136	2.21	0.30	
Hydrochloric acid (5%)			19	3.13	0.06	
Acetic acid			90	40.12	3.63	
9,9'-Spirobi[9*H*-fluorene]	**1**	**3.17**	**245**			**4.16**
Iodic acid	1.2			371.09	0.44	
Sulfuric acid		0.31		74.74	0.02	
Acetic acid		14		40.12	0.56	
Potassium hydroxide			0.14	21.21	0.00	
Toluene			142	4.08	0.58	

2,2',7,7'-Tetraiodo-9,9'-spirobifluorene	**1.2**	**14.31**	**142.14**			**1.6**
Potassium *t*-butoxide	1.05			1.05	0.16	
$\mathrm{Pd(OAc)_2}$	0.012			44499.40	0.53	
$\mathrm{P}(t\mathrm{Bu})_3$	0.022			53053.50	1.17	
Toluene		12		4.08	0.05	
Dichloromethane			728	11.16	8.12	
$\mathrm{Na_2SO_4}$			1	12.79	0.01	
Ethyl acetate			2	3.63	0.01	
Silica gel			263	66.41	17.47	
4,4′-Dimethyldiphenylamine	1.057			2800	2.96	
Total	**13.291**	**55.35**	**2673.14**			**66.89**

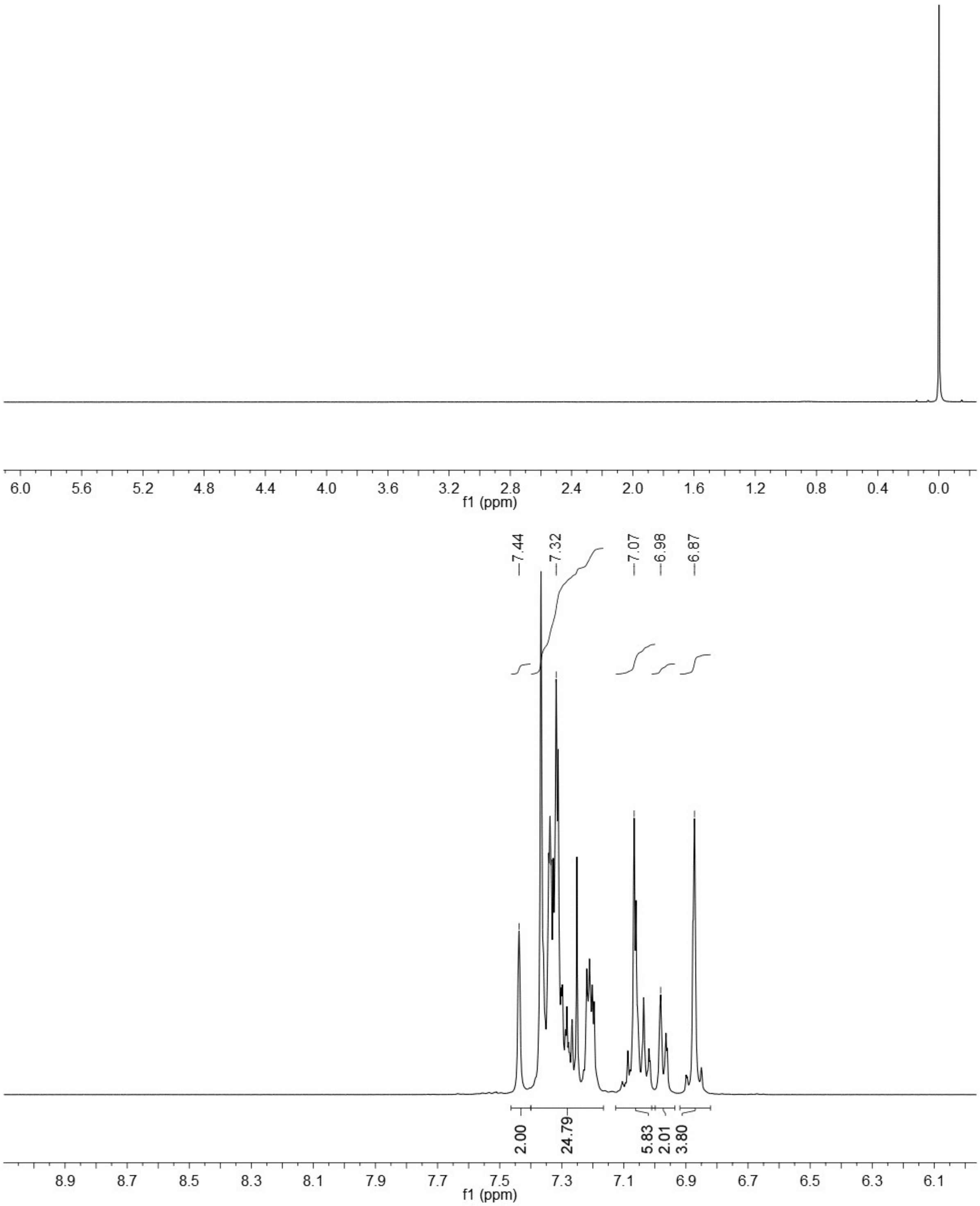


Figure S4. *3,6,9-tris(2,2-diphenylvinyl)-9H-carbazole (H1)* ^{1}*H NMR (400 MHz,* $CDCl_3$*, δ, ppm).*

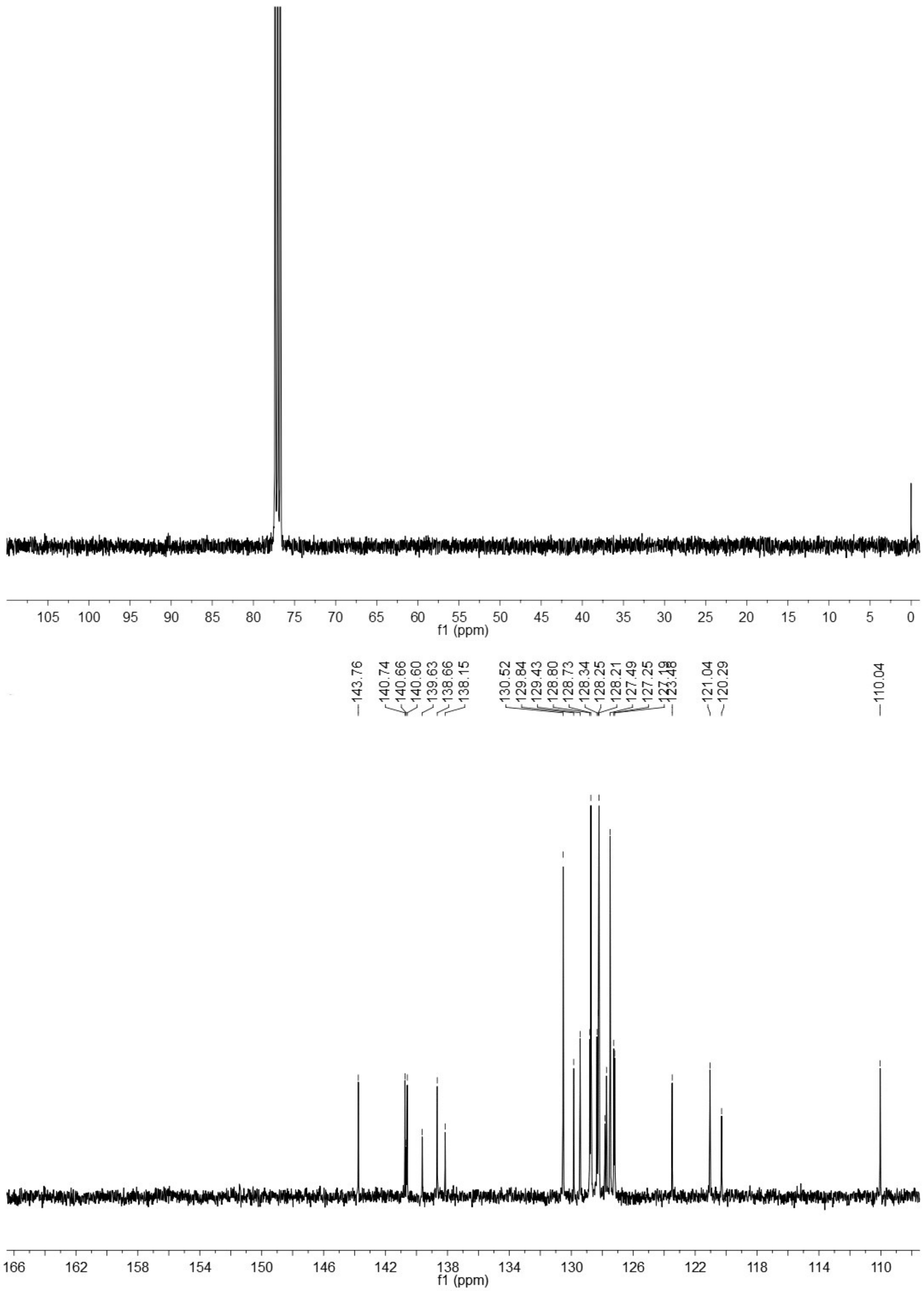


Figure S5. *3,6,9-tris(2,2-diphenylvinyl)-9H-carbazole (H1)* ^{13}*C NMR (101 MHz,* $CDCl_3$*, δ, ppm).*

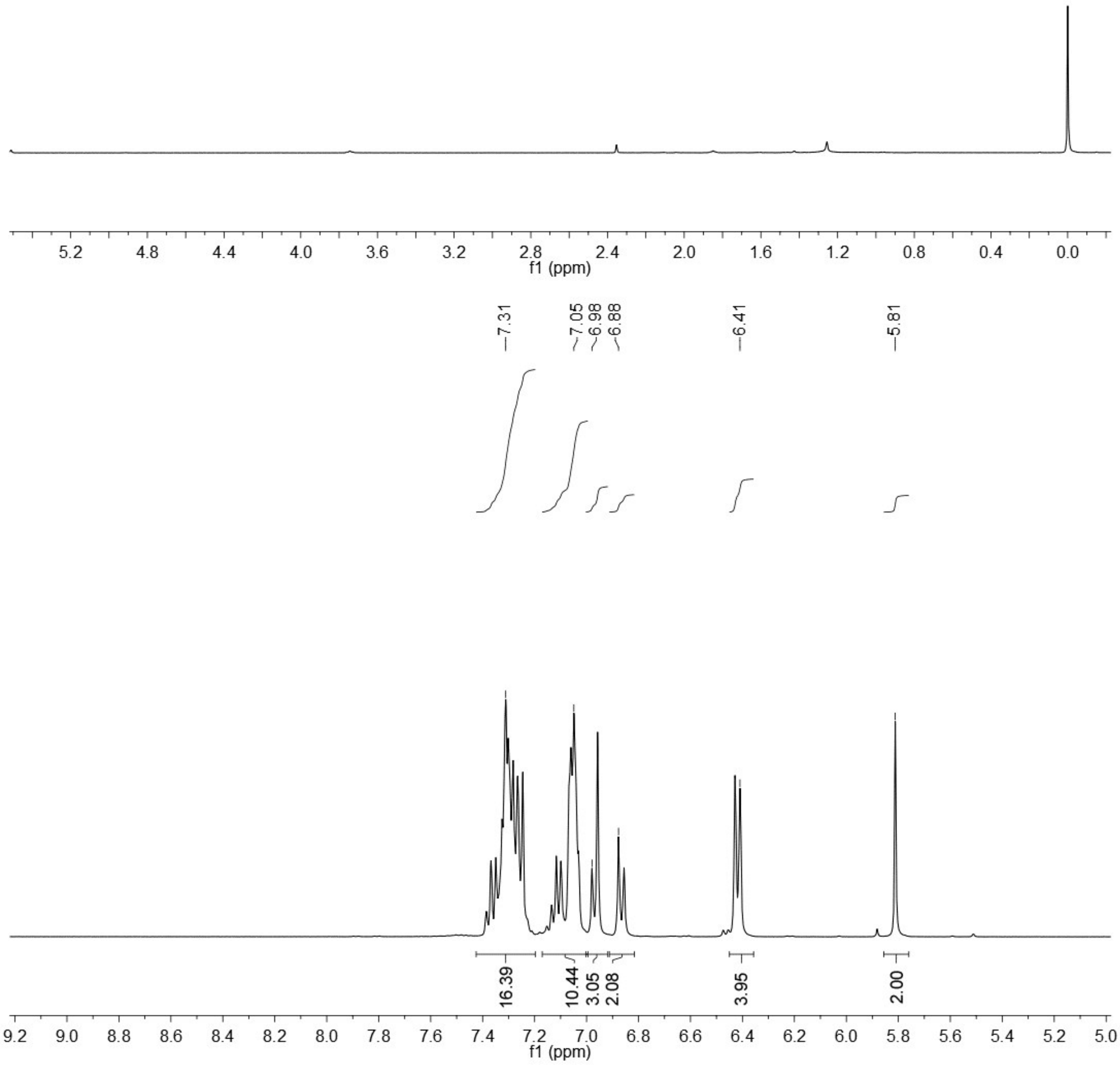


Figure S6. *N,N,4-tris(2,2-diphenylethenyl)aniline (H2)* ^{1}H *NMR (400 MHz,* $CDCl_3$*, δ, ppm).*

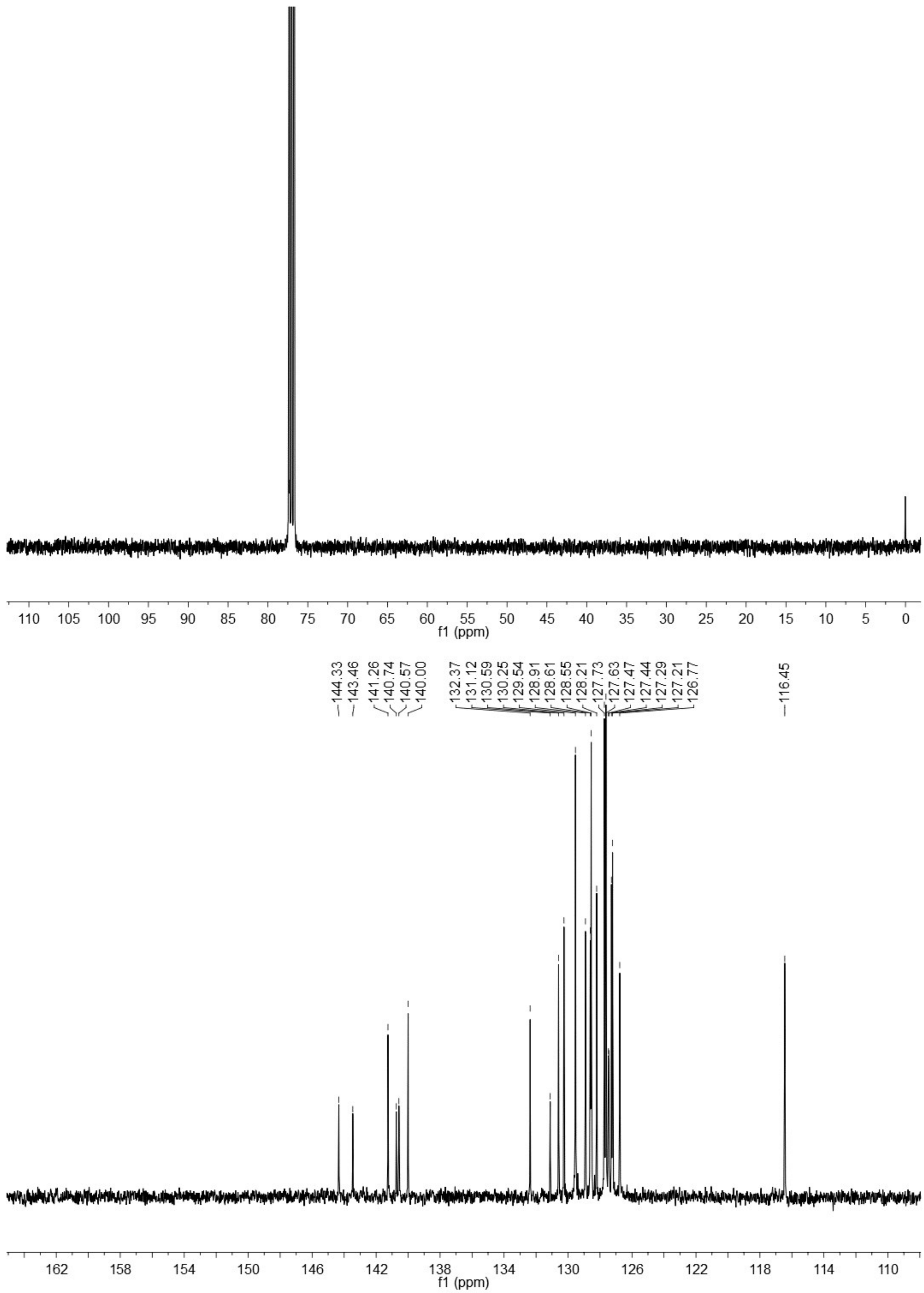


Figure S7. *N,N,4-tris(2,2-diphenylethenyl)aniline (H2)* ^{13}C *NMR (101 MHz,* $CDCl_3$*, δ, ppm).*

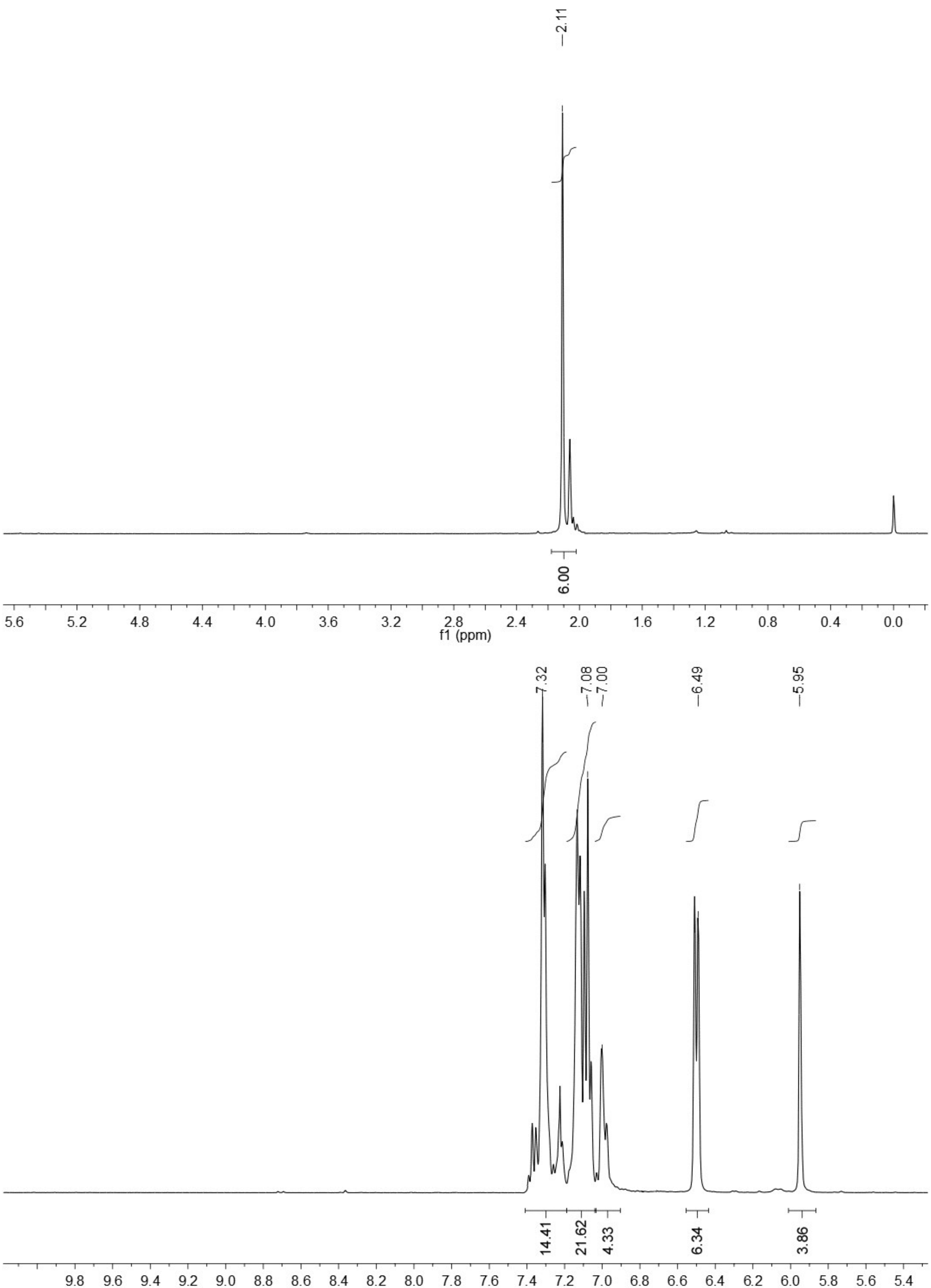


Figure S8. *N^4,N^4,$N^{4'}$,$N^{4'}$-tetrakis(2,2-diphenylethenyl)-2,2'-dimethyl[1,1'-biphenyl]-4,4'-diamine (H3) ^1H NMR (400 MHz, $CDCl_3$, δ, ppm).*

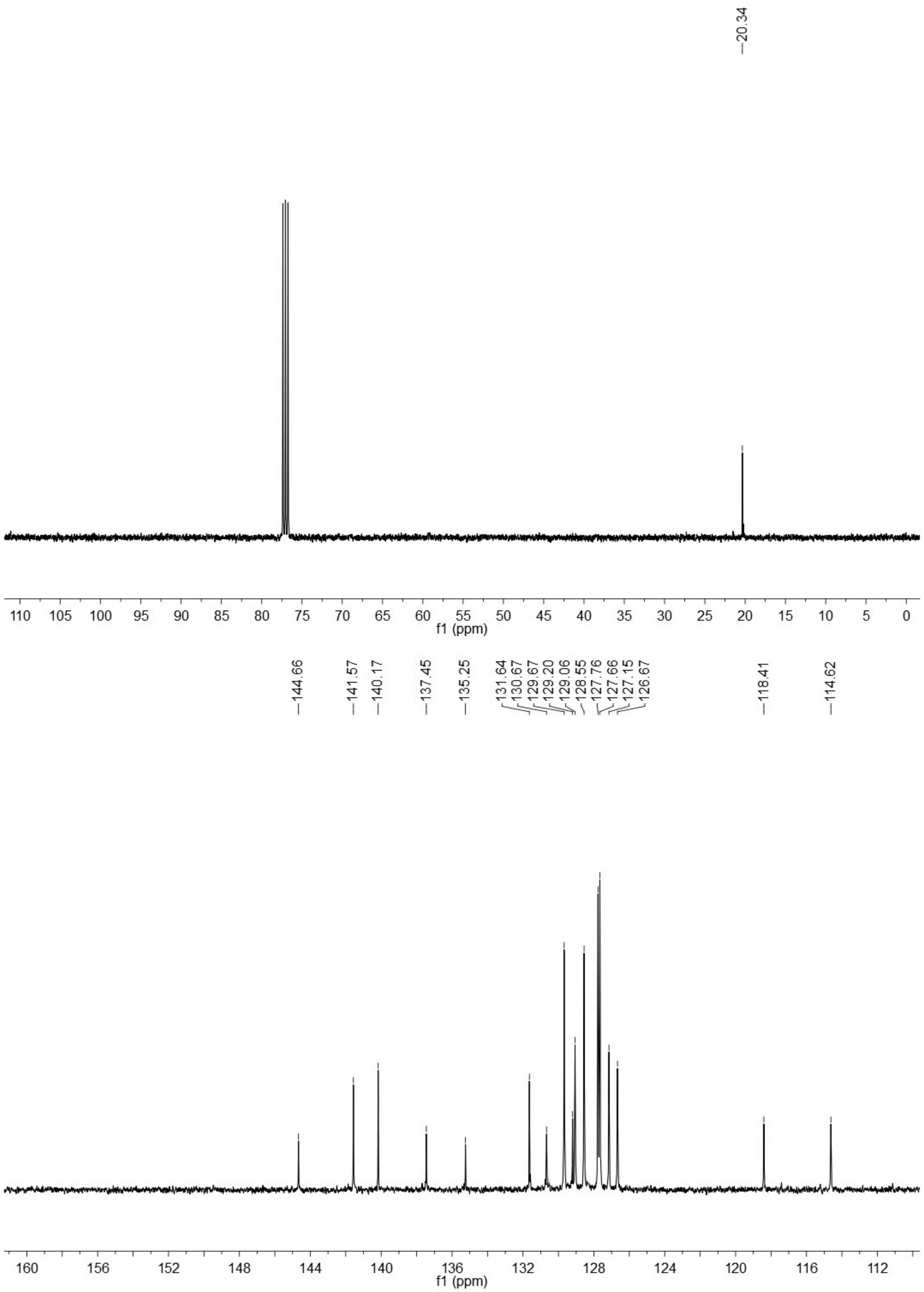


Figure S9. *N^4,N^4,$N^{4'}$,$N^{4'}$-tetrakis(2,2-diphenylethenyl)-2,2'-dimethyl[1,1'-biphenyl]-4,4'-diamine (H3) ^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm).*

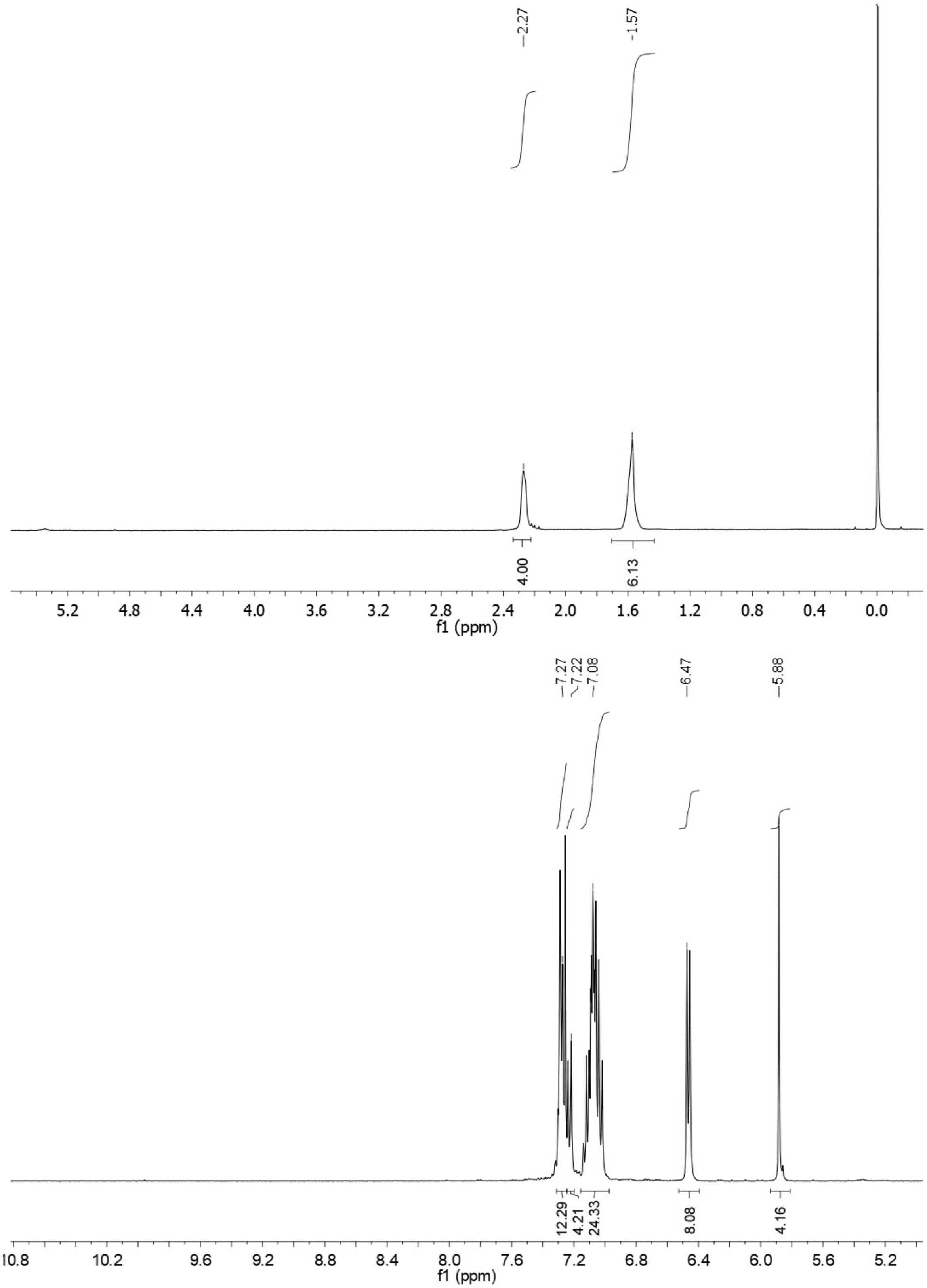


Figure S10. *N1^4,N1^4,N3^4,N3^4-tetrakis(2,2-diphenylethenyl)-2^3,2^4,2^5,2^6-tetrahydro-2^{2}H-[1^1,2^1:2^1,3^1-terphenyl]-1^4,3^4-diamine (H4) ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm).*

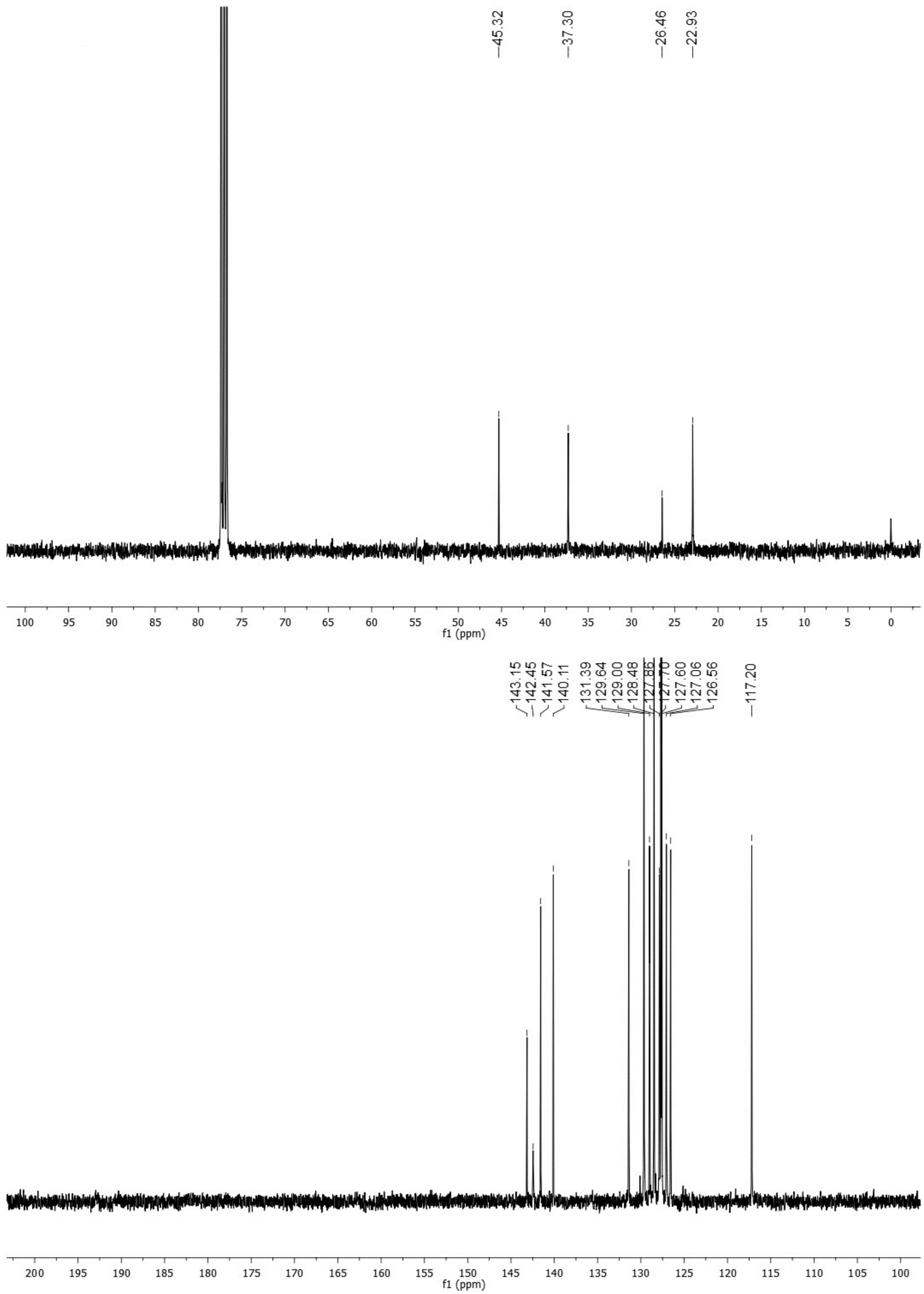


Figure S11. *$N1^4$,$N1^4$,$N3^4$,$N3^4$-tetrakis(2,2-diphenylethenyl)-2^3,2^4,2^5,2^6-tetrahydro-2^2H-[1^1,2^1:2^1,3^1-terphenyl]-1^4,3^4-diamine (H4) ^{13}C NMR (101 MHz, CDCl$_3$, δ, ppm).*