Supporting Information

C–H Activation Route to Dibenzo[*a,e*]pentalenes: Annulation of Arylacetylenes Promoted by $PdCl_2$/AgOTf/*o*-chloranil

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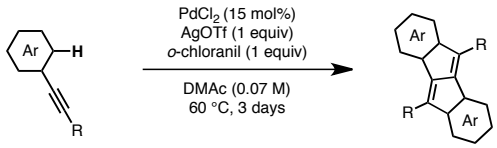
Table of Contents

1. General

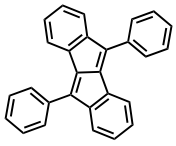
Unless otherwise noted, all reagents including anhydrous solvents were obtained from commercial suppliers and used without further purification. Substituted diphenylacetylenes **1b**, **1c**, **1d**, **1e** were prepared according to literature procedure.[1] 2,6,2',6'-Tetradeuteriodiphenyletyne **1a-*d*** was prepared from deuteriobromobenzene, which was prepared according to literature procedure.[2,3] AgOTf was stored in a glove box filled by argon prior to use. *o*-chloranil was recrystallized from benzene prior to use. Column chromatography was performed with silica gel 60 (230–400 mesh). Preparative thin-layer chromatography (PTLC) was performed using silica-coated plates prepared in our laboratory (325 mesh, 5% binder, 0.75 mm thickness). Synthetic manipulations that required an inert atmosphere (where noted) were carried out under nitrogen using standard Schlenk techniques or in an inert-atmosphere glove box. Analythical thin-layer chromatograghy (TLC) was performed using E. Merck silica gel 60 F_{254} precoated plates (0.25 mm). The developed chromatogram was analyzed by UV lamp (254 nm and 365 nm), ethanolic phosphomolybdic acid. Gas chromatography (GC) was conducted on a Shimadzu GC-2010 instrument equipped with a HP-5 column (30 m × 0.25 mm, Hewlett-Packard). GC yields are expressed vs. *n*-undecane as an internal standard. High-resolution mass spectra (HRMS) were obtained from a JMS-T100TD instrument (DART). Elemental analysis were recorded on Yanaco MT-6. Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL ECA-600 (^{1}H NMR 600 MHz, ^{13}C NMR 150 MHz) spectrometers. Chemical shifts for ^{1}H NMR are expressed in parts per million (ppm) relative to solvent signal ^{1}H ($CHCl_3$: 7.26 ppm; $CHDCl_2$: 5.30 ppm) and ^{13}C ($CDCl_3$: 77.0 ppm; CD_2Cl_2: 53.8 ppm).

2. General procedure



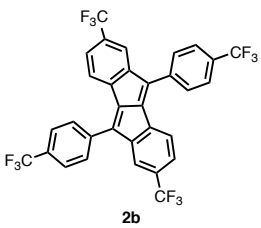
1 **2**

To a heat-dried screw-capped test tube were added a magnetic stirring bar, **1** (400 μmol), $PdCl_2$ (10.6 mg, 60 μmol) and *o*-chloranil (97.2 mg, 400 μmol). The screw-capped test tube was introduced inside an argon atmosphere glovebox. To the tube was added AgOTf (102 mg, 400 μmol). The screw-capped tube was taken out of the glovebox, and to it was added anhydrous DMAc (6 mL). The test tube was sealed and the resulting mixture was stirred at 60 °C for 3 days. After cooling to room temperature, contents were diluted with $CHCl_3$. The organic layer was passed on a short silica plug, eluted with $CHCl_3$ and the solvents were evaporated under reduced pressure to afford the crude reaction mixture. The crude reaction mixture was extracted by 20 ml $CHCl_3$ in two times to remove residual DMAc and purified by silica gel column chromatography to afford product. For most products, the reaction could be performed by low catalyst loading with slight loss of product yield. In those cases, $PdCl_2$ (3.54 mg, 20 μmol, 5 mol%) was used and the reaction mixture was stirred at 80 °C for 18 h.



2a

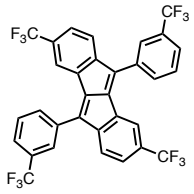
Following general procedure with **1a** (71 mg, 400 μmol). The crude product was purified by silica gel column chromatography using 10:1 (v/v) hexane/$CHCl_3$ as the mobile phase to afford **2a** as a red solid (36 mg, 52%). The product was recrystallized with $CHCl_3$/pentane at room temperature to obtain red needle crystal for X-ray crystallography. ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 6.85 (1H, td, *J* = 8, 1 Hz), 6.90 (1H, td, *J* = 8, 1 Hz), 7.03 (1H, d, *J* = 7 Hz), 7.21 (1H, d, *J* = 7 Hz), 7.45 (1H, tt, *J* = 7, 1 Hz), 7.52 (2H, t, *J* = 8 Hz), 7.67 (2H, dd, *J* = 8, 1 Hz); ^{1}H-NMR (600 MHz, CD_2Cl_2): δ = 6.86 (1H, t, *J* = 7 Hz), 6.92 (1H, t, *J* = 7 Hz), 7.03 (1H, d, *J* = 7 Hz), 7.21 (1H, d, *J* = 7 Hz), 7.47 (1H, t, *J* = 7 Hz), 7.54 (2H, t, *J* = 7 Hz), 7.68 (2H, d, *J* = 7 Hz); ^{13}C-NMR (150 MHz, $CDCl_3$): 121.9, 122.5, 127.4, 127.8, 128.5, 128.7, 128.8, 133.9, 135.2, 140.7, 143.1, 149.7; HR-MS (DART MS) *m/z* calcd. for $C_{28}H_{11}$ $[MH]^+$: 355.14868, found: 355.14849; mp: 259 °C. Local maxima of UV-Vis absorption: 428, 448 nm.



2b

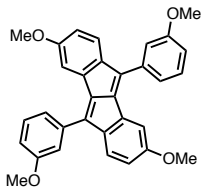
Following general procedure with **1b** (124 mg, 400 μmol). The crude product was purified by silica gel column chromatography using 10:1 (v/v) hexane/$CHCl_3$ as the mobile phase to afford **2b** as a red solid (99.2 mg, 79%). The product was recrystallized with $CHCl_3$/pentane at room temperature to obtain red needle crystal for X-ray crystallography. ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.19 (1H, s), 7.21 (1H,

d, *J* = 8 Hz), 7.24 (1H, d, *J* = 8 Hz), 7.77 (2H, d, *J* = 8 Hz), 7.86 (2H, d, *J* = 8 Hz); C^{13} NMR (150 MHz, $CDCl_3$, 60 °C) 119.4 (q, *J* = 3 Hz), 122.2, 123.8 (q, *J* = 272 Hz), 125.8 (q, *J* = 5 Hz), 126.3 (q, *J* = 5 Hz), 128.7, 131.0, 131.2, 132.0 (q, *J* = 33 Hz), 136.2, 137.6, 141.1, 143.9, 149.6; HR-MS (DART MS) *m/z* calcd. for $C_{32}H_{15}F_{12}$ $[MH]^+$: 627.09821, found: 627.09869; mp: not melt or decomposed. Local maxima of UV-Vis absorption: 424, 450 nm.



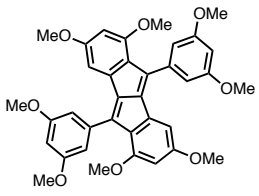
2c

Following general procedure with **1c** (126 mg, 400 μmol). The crude product was purified by silica gel column chromatography using 10:1 (v/v) hexane/$CHCl_3$ as the mobile phase to afford **2c** as a red solid (65.9 mg, 53%). ^{1}H-NMR (600 MHz, CD_2Cl_2): δ = 7.17 (1H, d, *J* = 8 Hz), 7.31 (1H, d, *J* = 8 Hz), 7.38 (1H, s), 7.77 (1H, t, *J* = 8 Hz), 7.83 (1H, d, *J* = 8 Hz), 7.89 (1H, d, *J* = 8 Hz), 7.97 (1H, d, *J* = 1 Hz); HR-MS (DART MS) *m/z* calcd. for $[MH]^+$: 627.09821, found: 627.09830; mp: 259 °C; elemental analysis calcd. for $C_{32}H_{14}F_{12}$: C 61.35, H 2.25, F 36.39 :found C 61.18, H 2.13. Local maxima of UV-Vis absorption: 423, 446 nm.



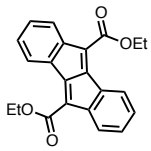
2e

Following general procedure with **1e** (95.6 mg, 400 μmol). The crude product was purified by silica gel column chromatography using 10:1 (v/v) hexane/$CHCl_3$ as the mobile phase to afford **2e** as a brown solid (63.3 mg, 66%). The product was recrystallized with $CHCl_3$/pentane at room temperature to obtain brown needle crystal for X-ray crystallography. ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 3.71 (3H, s), 3.87 (3H, s), 6.38 (1H, dd, *J* = 8, 2 Hz), 6.88 (1H, d, *J* = 2 Hz), 6.95 (1H, d, *J* = 8 Hz), 6.97 (1H, ddd, *J* = 8, 3, 1 Hz), 7.19 (1H, dd, *J* = 3, 2 Hz), 7.24 (1H, ddd, *J* = 8, 3, 2 Hz), 7.42 (1H, t, *J* = 8 Hz); ^{13}C NMR (150mHz, $CDCl_3$): 55.4 (2C), 110.0, 110.2, 113.4, 114.7, 120.8, 123.1, 129.8, 135.3 (4°), 137.1 (4°), 141.0 (4°), 141.3 (4°), 142.0 (4°), 159.8 (4°), 160.1 (4°); HR-MS (DART MS) *m/z* calcd. for $C_{32}H_{27}O_4$ $[MH]^+$: 475.19093, found: 475.19091; mp: decomposed at 180 °C. Local maxima of UV-Vis absorption: 453, 474 nm.



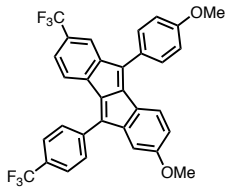
2f

Following general procedure with **1f** (120 mg, 400 μmol). The crude product was purified by silica gel column chromatography using 2:1 (v/v) hexane/EtOAc as the mobile phase and then recrystallized with $CHCl_3$/pentane at room temperature to afford **2f** as a violet block crystal (18.0 mg, 15%). ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 3.56 (3H, s), 3.65 (3H, s), 3.81 (6H, s), 5.98 (1H, s), 6.43 (1H, s), 6.48 (1H, s), 6.76 (2H, d, *J* = 1 Hz); ^{13}C NMR (150MHz, $CDCl_3$): 55.3 (2C), 55.4, 97.5, 101.1, 101.9, 106.7, 127.7 (4°), 137.4 (4°), 138.7 (4°), 140.5 (4°), 142.6 (4°), 156.0 (4°), 159.9 (4°), 161.7 (4°); HR-MS (DART MS) *m/z* calcd. for $C_{36}H_{35}O_8$ $[MH]^+$: 595.23319, found: 595.23329; mp: 251-254°C. Local maxima of UV-Vis absorption: 494, 507 nm.



2g

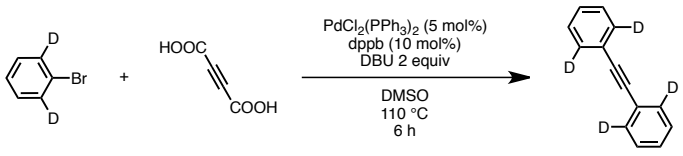
Following low catalyst loading procedure with **1g** (66 μL, 400 μmol). The crude product was purified by silica gel column chromatography using 10:1 (v/v) hexane/EtOAc as the mobile phase to afford **2g** as a brown solid (28.7 mg, 83 μmol). **2g** was recrystallized with $CHCl_3$/pentane for X-ray crystallography. ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 1.45 (3H, t, *J* = 7 Hz), 4.42 (2H, q, J = 7 Hz), 6.92 (1H, td, *J* = 8, 1 Hz), 6.98 (1H, td, *J* = 8, 1 Hz), 7.48 (1H, d, *J* = 7 Hz), 7.49 (1H, d, *J* = 7 Hz); ^{13}C-NMR (150 MHz, $CDCl_3$): 14.3, 61.1, 125.0, 127.4, 128.4, 130.3, 130.6, 132.5, 147.7, 153.6, 163.5; HR-MS (DART MS) *m/z* calcd. for $C_{22}H_{19}O_4$ $[MH]^+$: 347.12833, found: 347.12833; mp: 140-142 °C.



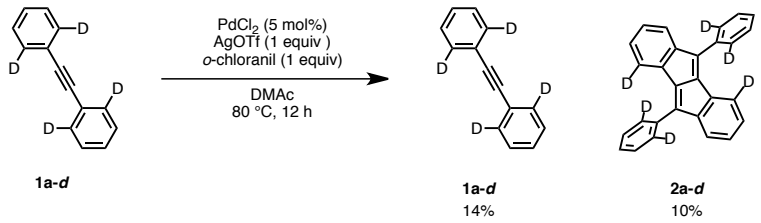
2bd

Following general procedure with **1d** (62.8 mg, 200 μmol) and **1b** (47.6 mg, 200 μmol). The crude product was purified by silica gel column chromatography using 10:1 (v/v) hexane/$CHCl_3$ as the mobile phase to afford **2d** as a red solid (25.8 mg, 41 μmol) and **2bd** as a black solid (29.1 mg, 53 μmol). **2bd** was recrystallized with $CHCl_3$/pentane for X-ray crystallography. ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 3.75 (3H, s), 3.91 (3H, s), 6.42 (1H, d, *J* = 8 Hz), 6.58 (1H, s), 7.10 (4H, m), 7.19 (1H, s), 7.21 (1H, d, *J* = 8 Hz), 7.61 (2H, d, *J* = 8 Hz), 7.73 (2H, d, *J* = 8 Hz), 7.79 (2H, d, *J* = 8 Hz) ^{13}C-NMR (150 MHz, CD_2Cl_2): 30.1, 55.9, 111.1, 111.9, 114.9 111.8, 121.6, 123.6, 124.8, 125.7, 126.3, 127.7, 129.4, 130.2, 131.3, 137.7, 138.7, 140.1, 143.5, 144.5, 151.0, 151.4, 161.0; HR-MS (DART MS) *m/z* calcd. for $C_{32}H_{21}F_6O_2$ $[MH]^+$: 551.14457, found: 551. 14449; mp: 255-257 °C. Local maxima of UV-Vis absorption: 433, 452 nm.

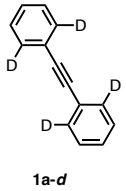
3. Procedure for deuterium-labeling experiment



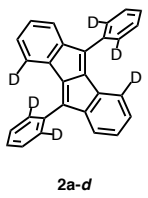
To a Schlenk tube containing a magnetic stirring bar were added 2-butynedioic acid and $PdCl_2(PPh_3)_2$ (40 mg, 57 μmol), 1,4-bis(diphenylphosphino)butane (49 mg, 114 μmol). Then, the Schlenk tube was sealed by septum and the contents were evacuated, then back-filled with argon gas. After dry DMSO (5 mL), 1,8-diazabicycloundec-7-ene (346 mg, 2.3 mmol) and 1-bromo-2,6-deuteriobenzene[2,3] (364 mg, 2.3 mmol) were added via syringe through septum. The resultant mixture was stirred at 110 °C for 6 h. After the reaction mixture was cooled to room temperature, diluted with Et_2O (ca. 15 ml) and saturated aqueous solution of NH_4Cl (50 ml). Then, the mixture solution was extracted with Et_2O (20 ml × 2). The combined organic phase was subjected to silica gel column chromatography using 100% hexane as the mobile phase to afford **1h** as white solid (103 mg, 50%).



Following general procedure with **1a-*d*** (69 mg, 400 mmol). The reaction mixture was stirred at 80 °C for 12 h. And crude product was purified by silica gel column chromatography using 10:1 (v/v) hexane/$CHCl_3$ as the mobile phase and to afford **2a-*d*** (10 %, 6.8 mg).

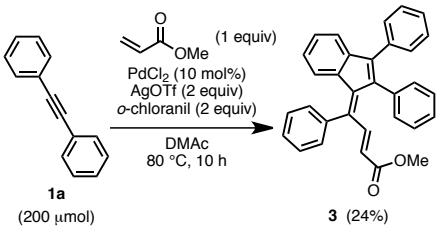


^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.35 (3H, broad); ^{2}H-NMR (600 MHz, $CHCl_3$): 7.58 (2H, s)



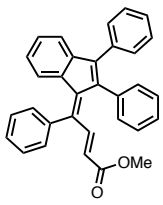
^{1}H-NMR (600 MHz, CD_2Cl_2): δ = 6.86 (1H, d, *J* = 7 Hz), 6.92 (1H, t, *J* = 7 Hz), 7.04 (1H, d, *J* = 7 Hz), 7.47 (1H, t, *J* = 7 Hz), 7.54 (2H, d, *J* = 7 Hz); ^{2}H-NMR (600 MHz, CD_2Cl_2): 7.25 (s, 1H), 7.72 (s, 2H); HR-MS (DART MS) *m/z* calcd. for $C_{28}H_{13}D_6$ $[MH]^+$: 361.18634, found: 361.18631.

4. Procedure for trapping experiment with methyl acrylate



To a heat-dried screw-capped test tube were added a magnetic stirring bar, **1a** (35.6 mg, 200 μmol), $PdCl_2$ (3.5 mg, 20 μmol) and *o*-chloranil (97.2 mg, 400 μmol). The screw-capped test tube was introduced inside an argon atmosphere glovebox. To the tube was added AgOTf (102 mg, 400 μmol). The screw-capped tube was taken out of the glovebox, and to it was added anhydrous DMAc (1 mL) and methylacrylate (22 μL, 200 μmol). The test tube was sealed and the resulting mixture was stirred at 80 °C for 10 h. After cooling to room temperature, contents were diluted with $CHCl_3$. The organic layer was passed on a short silica plug, eluted with EtOAc and the solvents were evaporated under reduced pressure to afford the crude reaction mixture. The crude reaction mixture was extracted by 20 ml EtOAc in two times to remove residual DMAc and purified by silica gel column chromatography using 10:1 (v/v) Hexane/EtOAc as the

mobile phase to afford the product as a red solid (10.6 mg, 24%). The product was recrystallized with $CHCl_3$/pentane at room temperature to obtained red crystal for X-ray crystallography.



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^{1}H-NMR (600 MHz, $CDCl_3$): δ = 3.49 (3H, s), 5.31 (1H, d, *J* = 15 Hz), 5.89 (1H, d, *J* = 7.2 Hz), 6.80 (1H, td, *J* = 5.4, 1.2 Hz), 7.11 (1H, td, *J* = 7.8, 1.8), 7.18 (1H, d, *J* = 7.8 Hz), 7.22-7.25 (3H, m), 7.26-7.36 (9H, m), 7.50 (2H, d, *J* = 2.4 Hz), 7.51 (1H, d, *J* = 1.2 Hz), 7.62 (1H, d, *J* = 15 Hz); ^{13}C-NMR (150 MHz, $CDCl_3$): 51.2, 120.4, 124.1, 125.2, 125.6, 127.1, 127.4, 127.9, 128.0, 128.4, 129.1, 129.4, 130.5, 134.2, 136.5, 137.7, 137.9, 138.7, 141.4, 143.3, 144.0, 144.3, 145.4, 166.8; HR-MS (DART MS) *m/z* calcd. for $C_{32}H_{25}O_2$ $[MH]^+$: 441.18545, found: 441.18548; mp:190-192 °C.

5. X-ray crystallography

Details of the crystal data and a summary of the intensity data collection parameters for obtained products are listed in below table. Suitable crystals were mounted with mineral oil on a glass fiber and transferred to the goniometer of a Rigaku Saturn CCD diffractometer. Graphite-monochromated Mo Kα radiation (λ = 0.71070 Å) was used. The structures were solved by direct methods with (SIR-97)[4] and refined by full-matrix least-squares techniques against F^2 (SHELXL-97)[5]. The intensities were corrected for Lorentz and polarization effects. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using AFIX instructions. (Table S1)

Table S1. Crystallographic data and structure refinement details for products.

	2a	**2b**	**2e**	**2f**	**2g**	**2bd**	**3**
formula	$C_{28}H_{18}$	$C_{32}H_{14}F_{12}$	$C_{32}H_{25}O_4$	$C_{36}H_{34}O_8$	$C_{22}H_{18}O_4$	$C_{32}H_{20}F_6O_2$	$C_{32}H_{24}O_2$
fw	354.42	626.43	473.52	594.63	346.36	550.48	440.51
T (K)	103(2)	103(2)	103(2)	103(2)	103(2)	103(2)	103(2)
λ (Å)	0.71070	0.71070	0.71070	0.71070	0.7107	0.71070	0.71070
cryst syst	Monoclinic	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
space group	*C*2/*c*	*P*-1	*P*-1	$P2_1/c$	$P2_1/n$	$P2_1/n$	*P*-1
a (Å)	23.095(10)	8.283(9)	14.463(8)	11.380(3)	11.675(3)	17.550(5)	10.094(6)
b (Å)	48.656(17)	12.769(18)	15.645(9)	8.787(2)	5.0054(8)	7.3020(18)	12.055(7)
c (Å)	18.761(13)	13.17(2)	17.602(10)	15.360(5)	14.303(3)	18.848(5)	19.805(11)
α (deg)	90	80.39(9)	107.771(10)	90	90	90	81.395(20)
β (deg)	122.671(5)	77.65(11)	98.2863(12)	111.613(3)	98.451(12)	94.759(5)	80.70(2)
γ (deg)	90	71.77(10)	105.005(10)	90	90	90	89.36(2)
V (Å^3)	1774.7(13)	1285(3)	3554(3)	1428.0(7)	826.7(3)	2407.1(11)	2351.0(2)
Z	4	2	6	2	2	4	4
D_{calc}, (g / cm^3)	1.327	1.619	1.327	1.383	1.391	1.519	1.244
μ (mm^{-1})	0.075	0.155	0.087	0.097	0.095	0.125	0.076
F(000)	744	628	1494	628	364	1128	928
cryst size (mm)	0.20 × 0.05 × 0.05	0.10 × 0.05 × 0.02	0.50 × 0.05 × 0.03	0.10 × 0.10 × 0.05	0.15 × 0.10 × 0.05	0.15 × 0.05 × 0.05	0.20 × 0.01 × 0.01
2θ range, (deg)	3.54–25.00	3.19–25.00	3.01–25.00	3.01–25.00	4.22–25.00	3.02–25.00	3.03–25.00
reflns collected	5444	8312	23908	9082	4986	15510	124676
indep reflns/R_{int}	1550/0.0356	4401/0.0779	12266/0.0704	2502/0.1014	1433/0.0376	4231/0.1178	8052/0.0968
params	164	397	984	203	119	363	615
GOF on F^2	1.124	0.984	1.057	1.159	1.093	1.000	1.021
R_1, wR_2 [I>2σ(I)]	0.0645, 0.1576	0.1086, 0.2672	0.1158, 0.2795	0.1478, 0.4388	0.0628, 0.1517	0.0671, 0.1506	0.1334, 0.3020
R_1, wR_2 (all data)	0.0790, 0.1690	0.1760, 0.3426	0.1944, 0.3452	0.1671, 0.4444	0.0751, 0.1671	0.1171, 0.1803	0.2815, 0.4027

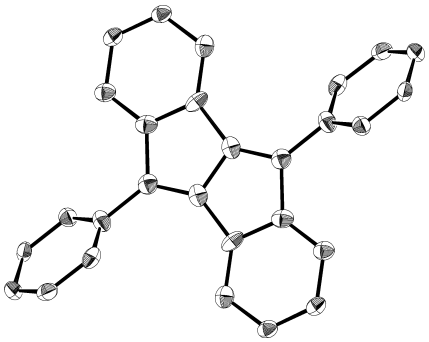

Figure S1. ORTEP drawing of **2a** with 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity. Half of the entire structure constitutes an asymmetric unit.

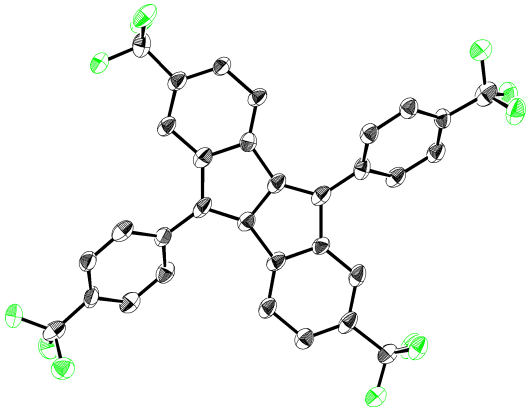

Figure S2. ORTEP drawing of **2b** with 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity.

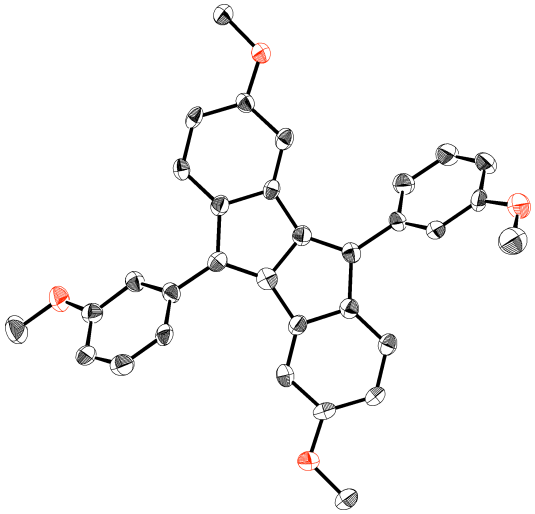

Figure S3. ORTEP drawing of **2e** with 50% thermal ellipsoids. Three of four independent molecules and all

hydrogen atoms are omitted for clarity.

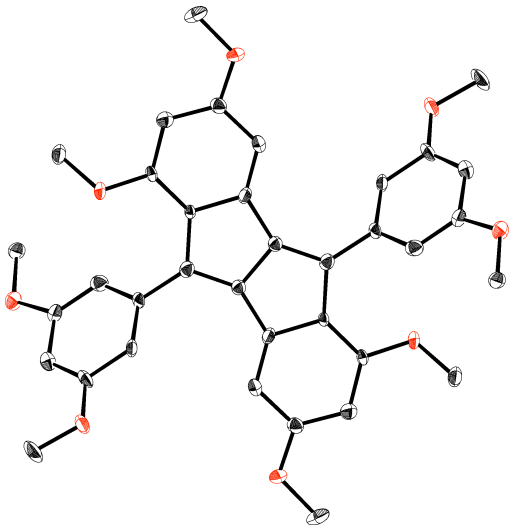

Figure S4. ORTEP drawing of **2f** with 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity. Half of the entire structure constitutes an asymmetric unit.

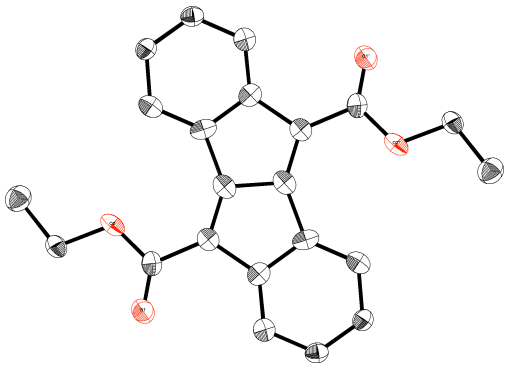

Figure S5. ORTEP drawing of **2g** with 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity. Half of the entire structure constitutes an asymmetric unit.

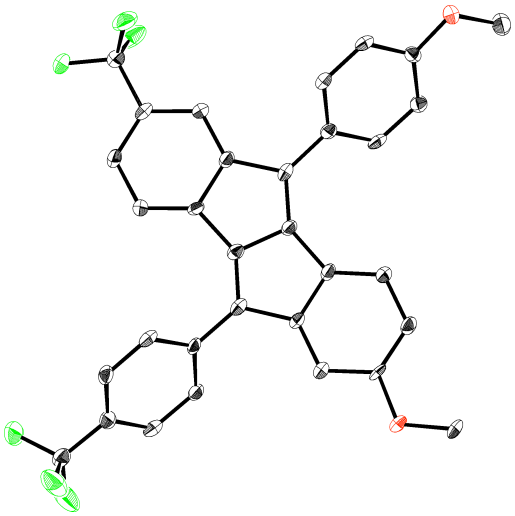

Figure S6. ORTEP drawing of **2bd** with 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity.

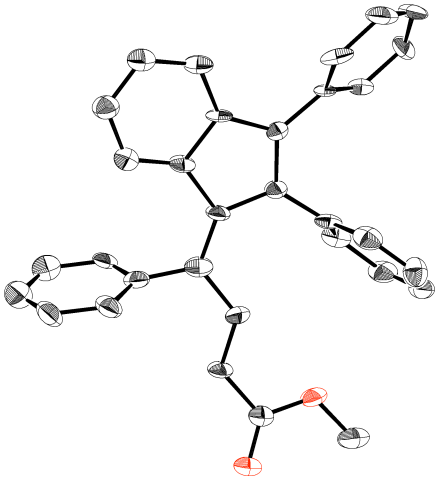

Figure S7. ORTEP drawing of **3** with 50% thermal ellipsoids. One of two independent molecules and all hydrogen atoms are omitted for clarity.

6. Photophysical study

UV/Vis absorption spectra were recorded on a Shimadzu UV- 3510 spectrometer with a resolution of 0.5 nm.

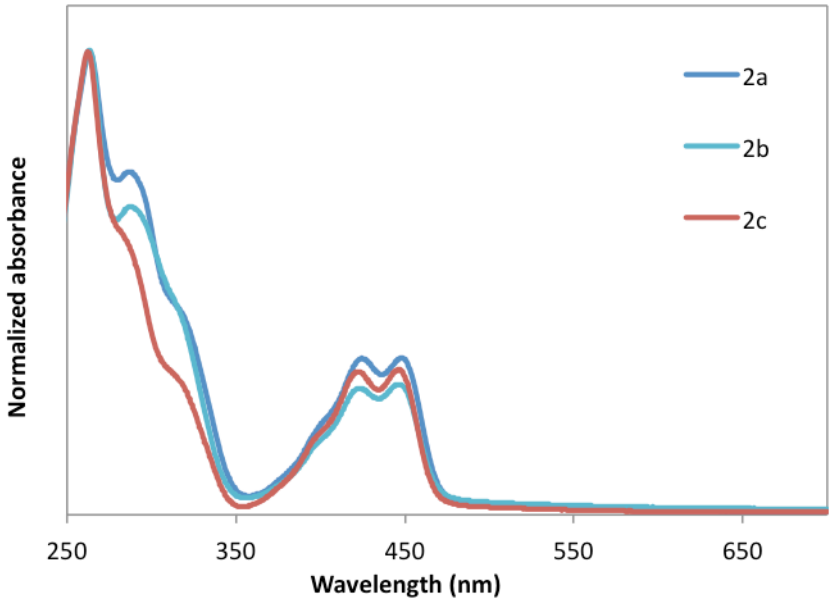

Figure S8. Normalized absorption spectra of **2a**, **2b** and **2c** in $CHCl_3$

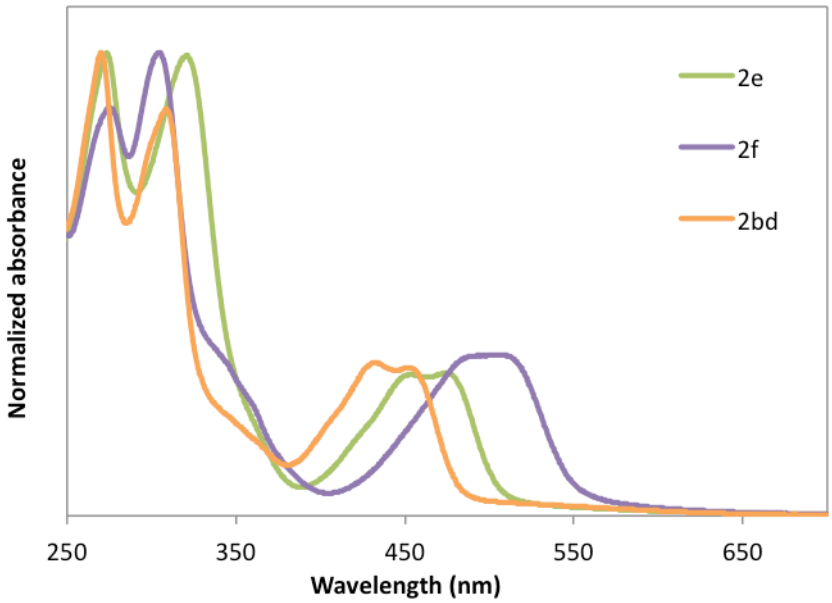

Figure S9. Normalized absorption spectra of **2e**, **2f** and **2bd** in $CHCl_3$

7. Computational study

The Gaussian 09 program[9] running on a SGI Altix4700 system was used for optimization (B3LYP/6-31G(d)).[10] All structures were optimized without any symmetry assumptions. Zero-point energy, enthalpy, and Gibbs free energy at 298.15 K and 1 atm were estimated from the gas-phase studies unless otherwise noted. Harmonic vibration frequency calculations at the same level were performed to verify all stationary points as local minima (with no imaginary frequency).

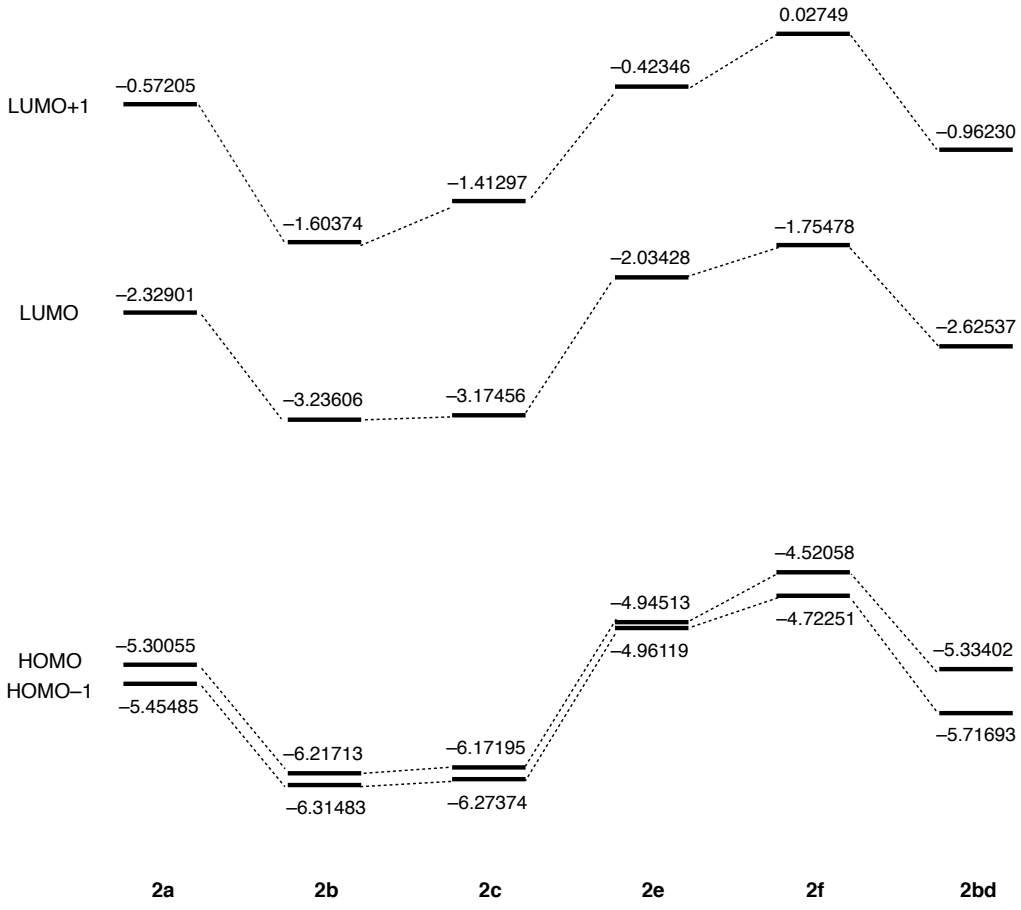

Figure S10. Molecular orbital energies of **2a**, **2b**, **2c**, **2e**, **2f**, and **2bd** (eV).

Table S2. Uncorrected and thermal-corrected (298K) energies of stationary points (Hartree).[a]

compound	E	E+ZPE	H	G
2a	-1077.82546879	-1077.457127	-1077.436021	-1077.505942
2b	-2425.97440875	-2425.587410	-2425.551417	-2425.661385
2c	-2425.97440266	-2425.587341	-2425.551370	-2425.660812
2e	-1535.91597071	-1535.416890	-1535.385183	-1535.478989
2f	-1993.99276266	-1993.363882	-1993.321130	-1993.440069
2bd	-1980.94735624	-1980.504108	-1980.470304	-1980.572482

[a] E: electronic energy; H (=E+ZPE+E_{vib}+E_{rot}+E_{trans}+RT): sum of electronic and themal enthalpies; G (=H–TS): sum of electronic and thermal free energies.

Table S3. Cartesian coordinates of optimized species.

2a

C	0.384854	0.621489	-0.056160	H	2.960231	2.080285	0.013672	H	-0.863423	6.044609	1.604026
C	-0.384854	-0.621489	-0.056160	C	3.069635	-1.830621	0.007862	H	1.924283	5.366486	-1.601426
C	-1.803278	-0.259655	-0.013833	C	4.254629	-1.077662	0.032460	H	0.833996	6.918755	0.009351
C	-2.981996	-0.995129	0.014516	H	5.135374	0.885167	0.070918	C	0.110909	-3.130757	-0.011097
C	-1.848045	1.167462	0.002976	H	3.113769	-2.915419	-0.011977	C	-0.849629	-3.639409	-0.904183
C	-4.210481	-0.315222	0.044995	H	5.213511	-1.588883	0.040493	C	0.728333	-4.022875	0.884910
H	-2.960231	-2.080285	0.013672	C	-0.458581	1.701175	-0.020614	C	-1.185841	-4.991941	-0.897384
C	-3.069635	1.830621	0.007862	C	0.458581	-1.701175	-0.020614	H	-1.313549	-2.966357	-1.619160
C	-4.254629	1.077662	0.032460	C	-0.110909	3.130757	-0.011097	C	0.384854	-5.373933	0.895245
H	-5.135374	-0.885167	0.070918	C	-0.728333	4.022875	0.884910	H	1.458695	-3.645391	1.594139
H	-3.113769	2.915419	-0.011977	C	0.849629	3.639409	-0.904183	C	-0.571261	-5.864381	0.003635
H	-5.213511	1.588883	0.040493	C	-0.384854	5.373933	0.895245	H	-1.924283	-5.366486	-1.601426
C	1.803278	0.259655	-0.013833	H	-1.458695	3.645391	1.594139	H	0.863423	-6.044609	1.604026
C	2.981996	0.995129	0.014516	C	1.185841	4.991941	-0.897384	H	-0.833996	-6.918755	0.009351
C	1.848045	-1.167462	0.002976	H	1.313549	2.966357	-1.619160				
C	4.210481	0.315222	0.044995	C	0.571261	5.864381	0.003635				

2b

C	-0.582418	0.441044	-0.095351	C	-1.737149	-0.296641	-0.057176	H	5.166042	-2.425015	-1.620209
C	0.582382	-0.441118	-0.095162	C	1.737102	0.296571	-0.056805	H	6.087890	0.272006	1.595620
C	0.089655	-1.817846	-0.048457	C	-3.126696	0.183943	-0.043798	C	-7.207676	1.590113	-0.036602
C	0.710607	-3.060106	-0.019966	C	-4.067714	-0.342517	0.859735	C	7.207728	-1.589904	-0.035339
C	-1.335774	-1.728520	-0.028176	C	-3.544745	1.186795	-0.937047	C	2.303932	5.378100	0.096512
C	-0.078899	-4.218070	0.016815	C	-5.377643	0.127538	0.878547	C	-2.303938	-5.378233	0.096261
H	1.792019	-3.145282	-0.026297	H	-3.761101	-1.100461	1.573523	F	-2.633588	-5.669187	1.377731
C	-2.111977	-2.878097	-0.018665	C	-4.855731	1.652718	-0.924971	F	-3.466139	-5.254542	-0.584300
C	-1.470490	-4.128724	0.008988	H	-2.837228	1.584614	-1.657967	F	-1.656228	-6.456413	-0.396557
H	0.394867	-5.193457	0.038256	C	-5.775803	1.125241	-0.014775	F	1.656021	6.456568	-0.395377
H	-3.195154	-2.827792	-0.041947	H	-6.088344	-0.272252	1.594170	F	3.465732	5.254660	-0.584805

C	-0.089715	1.817772	-0.048659	H	-5.165560	2.425493	-1.620780	F	2.634399	5.668354	1.377930
C	-0.710681	3.060022	-0.020469	C	3.126660	-0.183990	-0.043155	F	-7.784387	1.492872	1.181016
C	1.335720	1.728451	-0.027932	C	3.544989	-1.186584	-0.936557	F	-7.310072	2.876988	-0.436081
C	0.078808	4.218004	0.016468	C	4.067433	0.342321	0.860720	F	-7.957268	0.852604	-0.887913
H	-1.792091	3.145187	-0.027130	C	4.855998	-1.652435	-0.924278	F	7.310292	-2.876702	-0.435019
C	2.111902	2.878030	-0.018251	H	2.837675	-1.584250	-1.657762	F	7.784181	-1.492835	1.182415
C	1.470387	4.128666	0.009104	C	5.377386	-0.127664	0.879735	F	7.957445	-0.852200	-0.886372
H	-0.394968	5.193386	0.037702	H	3.760609	1.100088	1.574604				
H	3.195089	2.827735	-0.041206	C	5.775820	-1.125130	-0.013729				

2c

C	-0.607036	0.406921	-0.514955	C	-1.717427	-0.395126	-0.482080	H	5.288060	-2.143308	-2.039728
C	0.606969	-0.406766	-0.515156	C	1.717364	0.395267	-0.482148	H	6.876725	-1.103432	-0.432449
C	0.192637	-1.810123	-0.472026	C	-3.132850	0.005322	-0.474353	C	-6.350841	-0.862984	1.363280
C	0.885730	-3.010259	-0.444952	C	-4.043632	-0.583730	0.418205	C	6.350999	0.862604	1.362818
C	-1.235306	-1.802418	-0.459123	C	-3.604111	0.990925	-1.360093	C	0.906739	-5.515614	-0.321617
C	0.158721	-4.213909	-0.419505	C	-5.380529	-0.186347	0.430162	C	-0.906764	5.515719	-0.319916
H	1.969393	-3.035790	-0.448694	H	-3.700253	-1.327153	1.128928	F	2.073157	-5.475307	-1.007741
C	-1.941948	-2.998581	-0.460292	C	-4.941372	1.381977	-1.346816	F	1.221488	-5.816436	0.960199
C	-1.235236	-4.209533	-0.436487	H	-2.915930	1.434424	-2.073330	F	0.188678	-6.553059	-0.804285
H	-3.026883	-3.008923	-0.486389	C	-5.836286	0.797247	-0.451453	F	-0.188791	6.553286	-0.802454
H	-1.774687	-5.150317	-0.438486	H	-5.288327	2.143786	-2.038653	F	-1.221273	5.816216	0.962036
C	-0.192696	1.810265	-0.471453	H	-6.876801	1.103500	-0.431450	F	-2.073309	5.475587	-1.005832
C	-0.885780	3.010397	-0.443942	C	3.132784	-0.005192	-0.474679	F	6.930907	1.937838	0.779016
C	1.235250	1.802555	-0.458770	C	3.603934	-0.990589	-1.360704	F	5.745202	1.304955	2.485998
C	-0.158765	4.214038	-0.418272	C	4.043671	0.583627	0.417929	F	7.348622	0.032472	1.735992
H	-1.969444	3.035933	-0.447525	C	4.941193	-1.381661	-1.347671	F	-5.744937	-1.305411	2.486374
C	1.941893	2.998717	-0.459718	H	2.915667	-1.433914	-2.073967	F	-7.348561	-0.033040	1.736612
C	1.235188	4.209664	-0.435470	C	5.380563	0.186225	0.429642	F	-6.930624	-1.938218	0.779353
H	3.026825	3.009064	-0.485965	H	3.700378	1.326876	1.128874				
H	1.774641	5.150448	-0.437288	C	5.836212	-0.797159	-0.452265				

2e

C	0.413430	0.601886	-0.305075	C	0.378844	-1.722725	-0.268301	O	5.354796	0.880171	-0.170445
C	-0.413430	-0.601886	-0.305075	C	0.041933	3.133361	-0.261303	O	-5.354796	-0.880171	-0.170445
C	-1.811707	-0.171955	-0.260910	C	-0.545762	4.051713	0.616956	O	0.780498	-6.187676	1.540257
C	-3.016080	-0.852946	-0.233880	C	1.042374	3.584641	-1.145902	O	-0.780498	6.187676	1.540257
C	-1.786598	1.259832	-0.243371	C	-0.142205	5.393403	0.629820	C	-6.607404	-0.217956	-0.136933
C	-4.220166	-0.118384	-0.202350	H	-1.303168	3.736946	1.326722	H	-6.706489	0.414159	0.755664
H	-3.070456	-1.935834	-0.236444	C	1.433285	4.918220	-1.132773	H	-6.762900	0.399103	-1.032131
C	-2.980157	1.967284	-0.238089	H	1.485149	2.888290	-1.850405	H	-7.362682	-1.005740	-0.106758
C	-4.205038	1.279407	-0.214084	C	0.852473	5.834810	-0.250058	C	6.607404	0.217956	-0.136933
H	-2.982354	3.052954	-0.255748	H	2.199873	5.261690	-1.822466	H	6.762900	-0.399103	-1.032131
H	-5.128699	1.846165	-0.206280	H	1.176190	6.869173	-0.258657	H	7.362682	1.005740	-0.106758
C	1.811707	0.171955	-0.260910	C	-0.041933	-3.133361	-0.261303	H	6.706489	-0.414159	0.755664
C	3.016080	0.852946	-0.233880	C	-1.042374	-3.584641	-1.145902	C	0.413430	-7.555505	1.611269
C	1.786598	-1.259832	-0.243371	C	0.545762	-4.051713	0.616956	H	1.036466	-7.992271	2.394025
C	4.220166	0.118384	-0.202350	C	-1.433285	-4.918220	-1.132773	H	-0.644279	-7.677544	1.880480

H	3.070456	1.935834	-0.236444	H	-1.485149	-2.888290	-1.850405	H	0.605374	-8.076050	0.663402
C	2.980157	-1.967284	-0.238089	C	0.142205	-5.393403	0.629820	C	-0.413430	7.555505	1.611269
C	4.205038	-1.279407	-0.214084	H	1.303168	-3.736946	1.326722	H	-1.036466	7.992271	2.394025
H	2.982354	-3.052954	-0.255748	C	-0.852473	-5.834810	-0.250058	H	0.644279	7.677544	1.880480
H	5.128699	-1.846165	-0.206280	H	-2.199873	-5.261690	-1.822466	H	-0.605374	8.076050	0.663402
C	-0.378844	1.722725	-0.268301	H	-1.176190	-6.869173	-0.258657				

2f

C	-0.319368	0.651587	0.154525	H	-0.887393	3.113540	1.807658	H	0.288151	-7.444880	-2.452063
C	0.319368	-0.651587	0.154525	C	-0.281870	5.840894	-0.139782	H	-1.141528	-7.882215	-1.469123
C	1.764829	-0.432637	0.109926	H	-0.521235	6.893057	-0.203532	C	0.790062	7.280995	-2.319213
C	2.838510	-1.307157	0.104595	C	-0.347609	-3.100314	0.025384	H	1.314269	7.599717	-3.222574
C	1.949422	0.987694	0.083239	C	0.484141	-3.692868	0.984741	H	-0.288151	7.444880	-2.452063
C	4.137482	-0.771081	0.081677	C	-0.865032	-3.880101	-1.016362	H	1.141528	7.882215	-1.469123
H	2.711844	-2.382750	0.125205	C	0.790062	-5.054060	0.902002	O	-1.600481	5.537137	1.893180
C	3.254227	1.494763	0.100050	H	0.887393	-3.113540	1.807658	O	1.600481	-5.537137	1.893180
C	4.351768	0.610749	0.088125	C	-0.546916	-5.236178	-1.096268	O	-3.404191	-2.849931	0.132673
H	5.357909	1.004443	0.090186	H	-1.510706	-3.448853	-1.771501	O	3.404191	2.849931	0.132673
C	-1.764829	0.432637	0.109926	C	0.281870	-5.840894	-0.139782	C	4.706918	3.404478	0.154395
C	-2.838510	1.307157	0.104595	H	0.521235	-6.893057	-0.203532	H	5.266242	3.092542	1.046669
C	-1.949422	-0.987694	0.083239	O	-5.145798	1.694202	0.065282	H	5.279880	3.134803	-0.743077
C	-4.137482	0.771081	0.081677	O	5.145798	-1.694202	0.065282	H	4.565756	4.486701	0.177653
H	-2.711844	2.382750	0.125205	O	-1.096354	-5.908726	-2.155464	C	-4.706918	-3.404478	0.154395
C	-3.254227	-1.494763	0.100050	O	1.096354	5.908726	-2.155464	H	-5.266242	-3.092542	1.046669
C	-4.351768	-0.610749	0.088125	C	6.485473	-1.235983	0.053951	H	-5.279880	-3.134803	-0.743077
H	-5.357909	-1.004443	0.090186	H	6.700086	-0.632047	-0.838281	H	-4.565756	-4.486701	0.177653
C	0.625092	1.649288	0.097947	H	6.720311	-0.646795	0.950973	C	1.971049	-6.903081	1.859188
C	-0.625092	-1.649288	0.097947	H	7.109170	-2.132072	0.039669	H	2.527619	-7.150830	0.944918
C	0.347609	3.100314	0.025384	C	-6.485473	1.235983	0.053951	H	2.617141	-7.059914	2.725287
C	0.865032	3.880101	-1.016362	H	-6.720311	0.646795	0.950973	H	1.097221	-7.564613	1.937840
C	-0.484141	3.692868	0.984741	H	-7.109170	2.132072	0.039669	C	-1.971049	6.903081	1.859188
C	0.546916	5.236178	-1.096268	H	-6.700086	0.632047	-0.838281	H	-2.527619	7.150830	0.944918
H	1.510706	3.448853	-1.771501	C	-0.790062	-7.280995	-2.319213	H	-2.617141	7.059914	2.725287
C	-0.790062	5.054060	0.902002	H	-1.314269	-7.599717	-3.222574	H	-1.097221	7.564613	1.937840

2bd

C	-0.886909	0.800195	-0.023180	C	-2.015485	0.021204	0.014307	H	4.940293	-1.850406	-1.659978
C	0.309113	-0.041384	-0.049540	C	1.439561	0.733165	-0.017484	H	5.811642	0.837331	1.577476
C	-0.132274	-1.436312	-0.016294	C	-3.419250	0.447556	0.031686	C	6.973623	-0.961086	-0.094619
C	0.535234	-2.653909	-0.013232	C	-4.365777	-0.155783	0.886755	C	-2.389653	-5.082233	0.084350
C	-1.559889	-1.397994	0.017929	C	-3.868431	1.476389	-0.811020	F	-2.737626	-5.387901	1.358660
C	-0.208660	-3.842929	0.010720	C	-5.687911	0.261179	0.904805	F	-3.542678	-5.002932	-0.620202
H	1.619108	-2.697216	-0.030381	H	-4.049504	-0.939354	1.568377	F	-1.695258	-6.138741	-0.394250
C	-2.289916	-2.576659	0.011735	C	-5.197313	1.899610	-0.810099	F	7.119200	-2.240229	-0.507190
C	-1.601554	-3.804217	0.013602	H	-3.167967	1.937119	-1.501352	F	7.569082	-0.852637	1.113883
H	0.301876	-4.799790	0.013091	C	-6.117435	1.292052	0.054118	F	7.683956	-0.190131	-0.951876
H	-3.374159	-2.567321	-0.006108	H	-6.411626	-0.193746	1.573742	O	-7.434987	1.622954	0.143247
C	-0.437850	2.189685	0.033583	H	-5.503555	2.687794	-1.488378	O	1.876220	5.651633	0.135093

C	-1.083586	3.415977	0.093118	C	2.844486	0.297902	-0.026779	C	-7.930809	2.655563	-0.696097
C	0.991622	2.150010	0.033548	C	3.287058	-0.677472	-0.938670	H	-7.819197	2.399816	-1.757802
C	-0.335306	4.604302	0.139419	C	3.779658	0.843887	0.871396	H	-8.991374	2.750374	-0.457262
H	-2.167289	3.472788	0.108304	C	4.613443	-1.097786	-0.949830	H	-7.427389	3.611110	-0.499248
C	1.734141	3.318228	0.054805	H	2.583959	-1.090878	-1.655109	C	1.277462	6.936672	0.188312
C	1.061686	4.556947	0.111347	C	5.105727	0.421328	0.866186	H	0.642470	7.121978	-0.688120
H	-0.856991	5.552716	0.190859	H	3.455415	1.582591	1.597270	H	0.679563	7.065763	1.100215
H	2.818566	3.320298	0.025747	C	5.527452	-0.550011	-0.045383	H	2.102657	7.651015	0.193771

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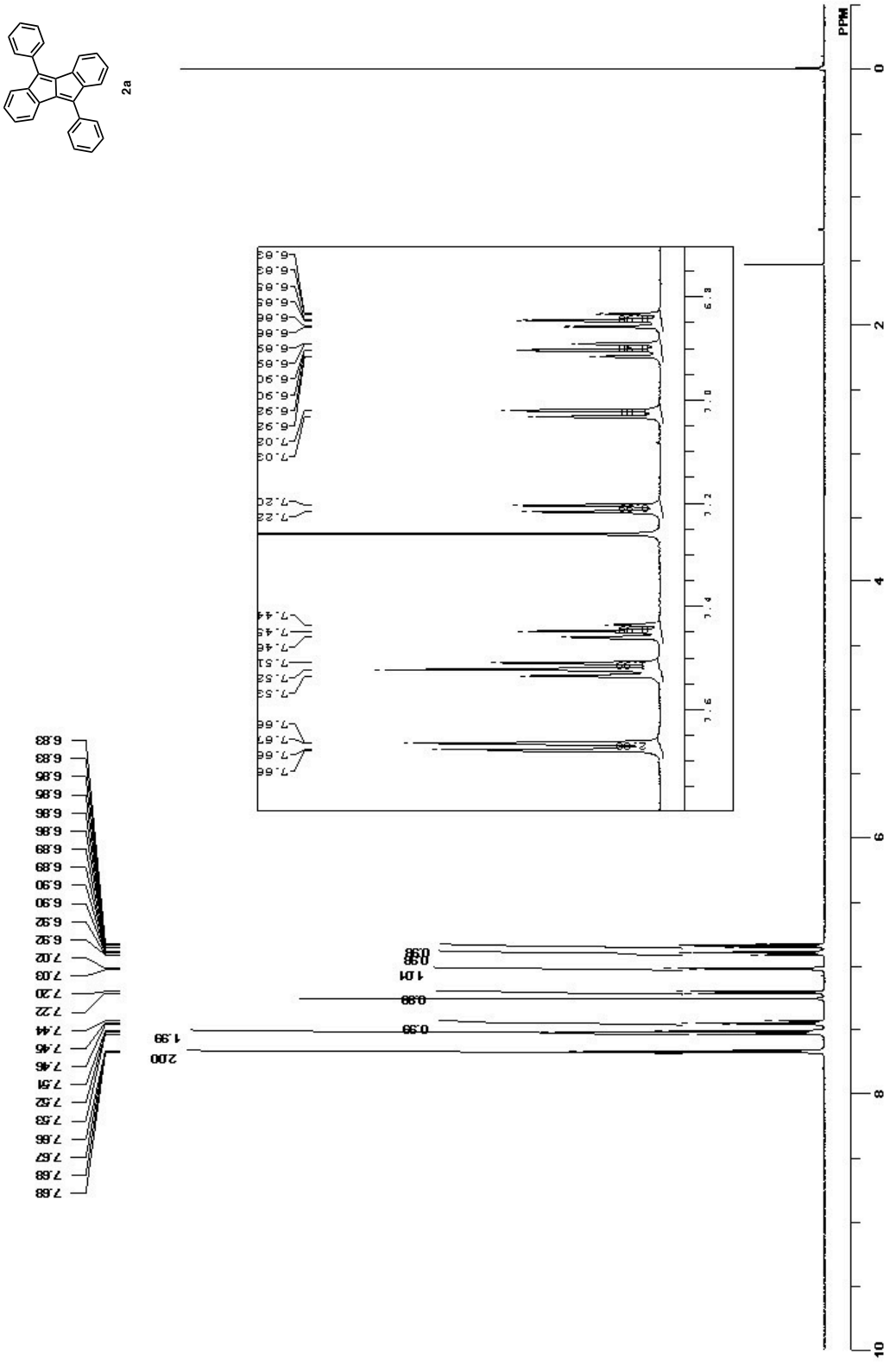
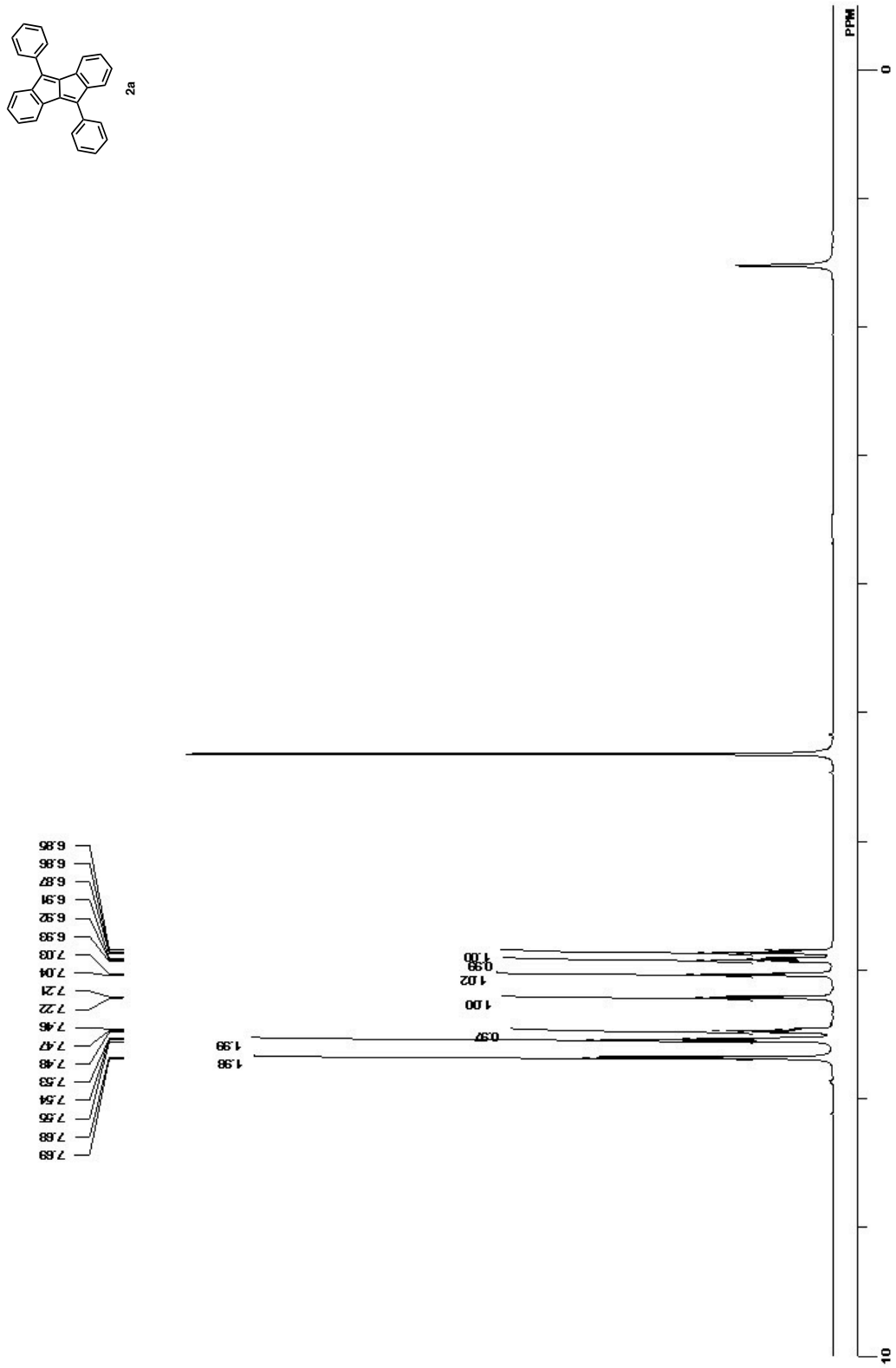
9. ^{1}H and ^{13}C NMR Spectra

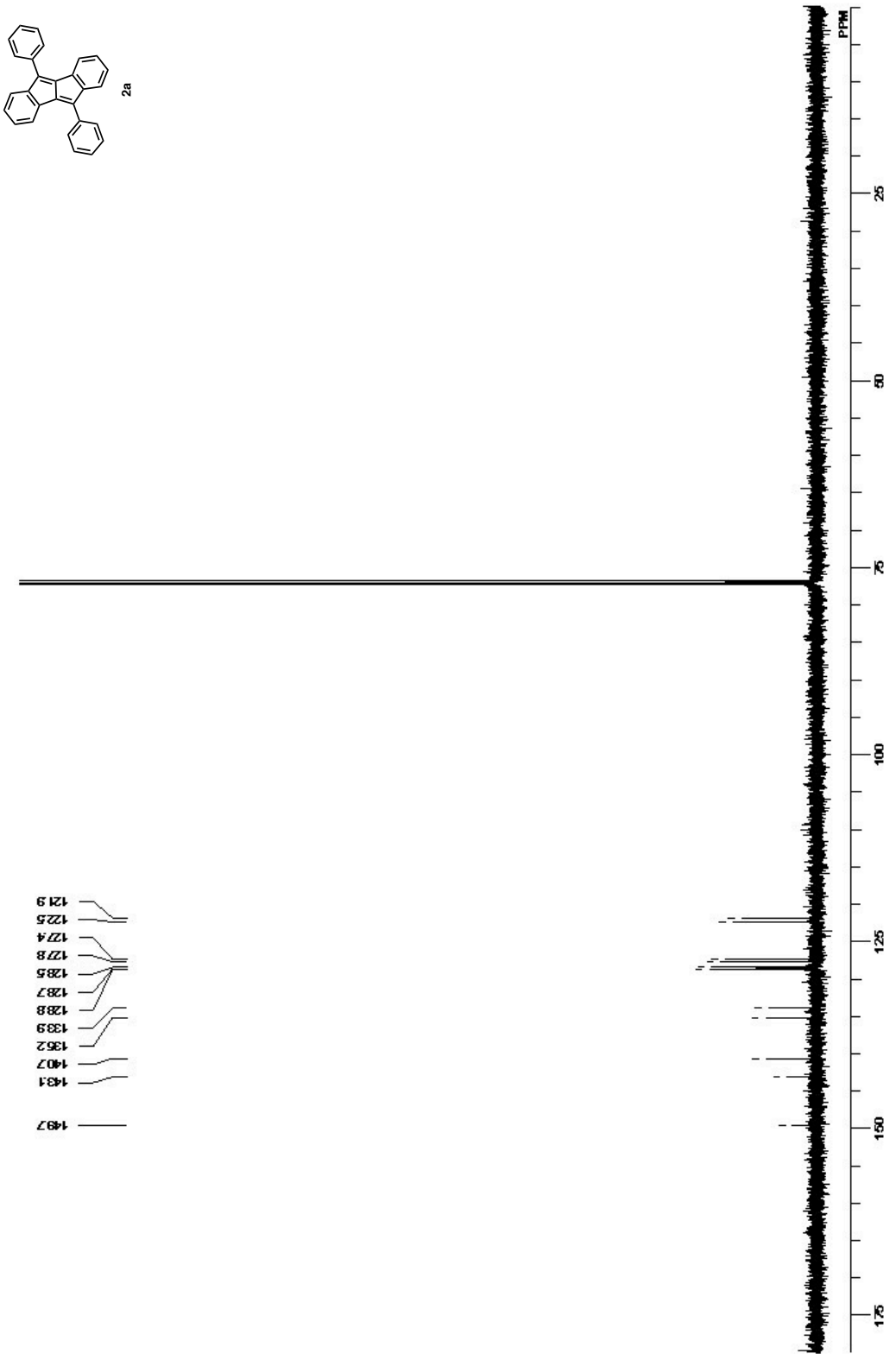
^{1}H NMR spectrum of **2a** ($CDCl_3$, 600 MHz)



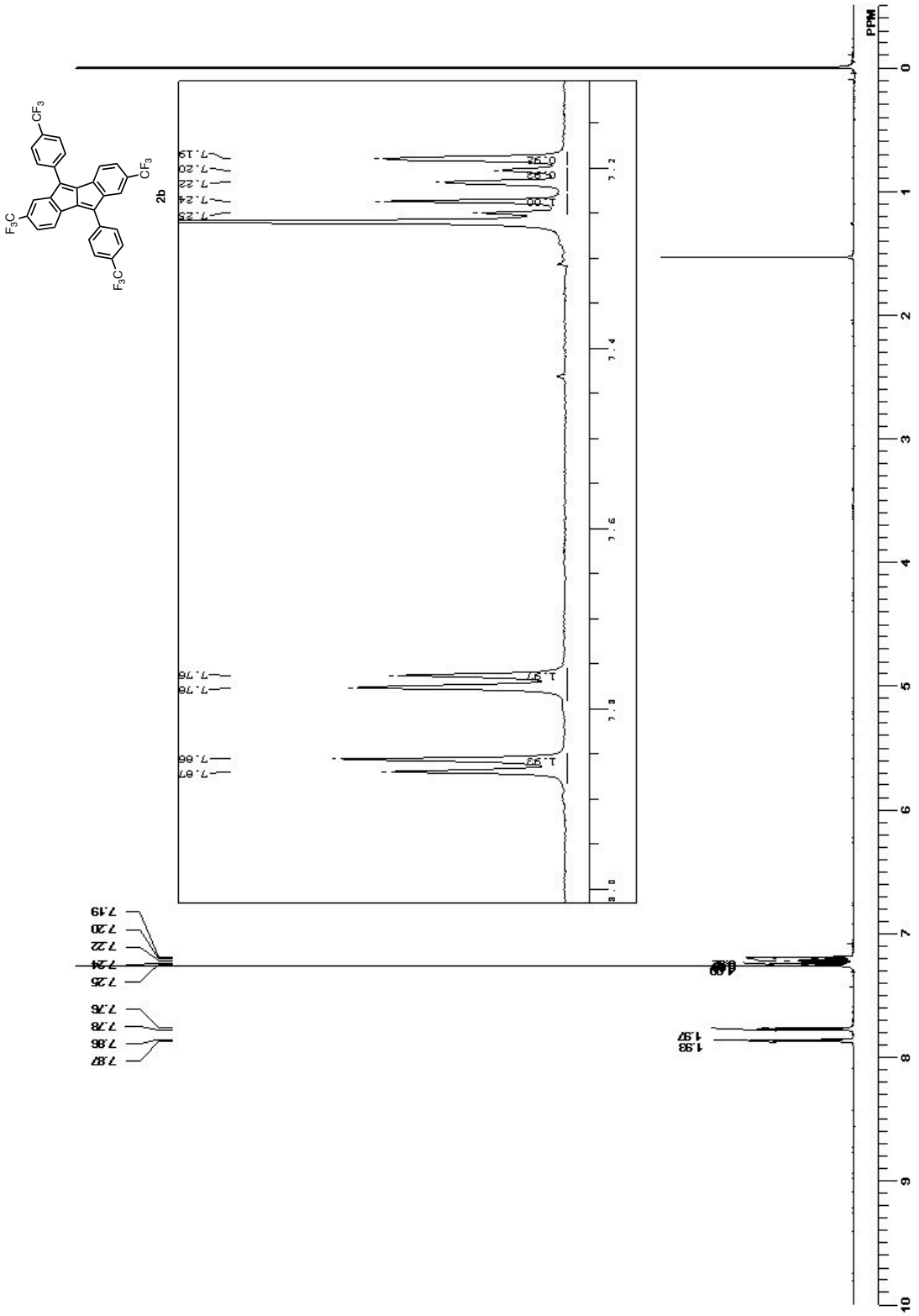
^{1}H NMR spectrum of **2a** (CD_2Cl_2, 600 MHz)



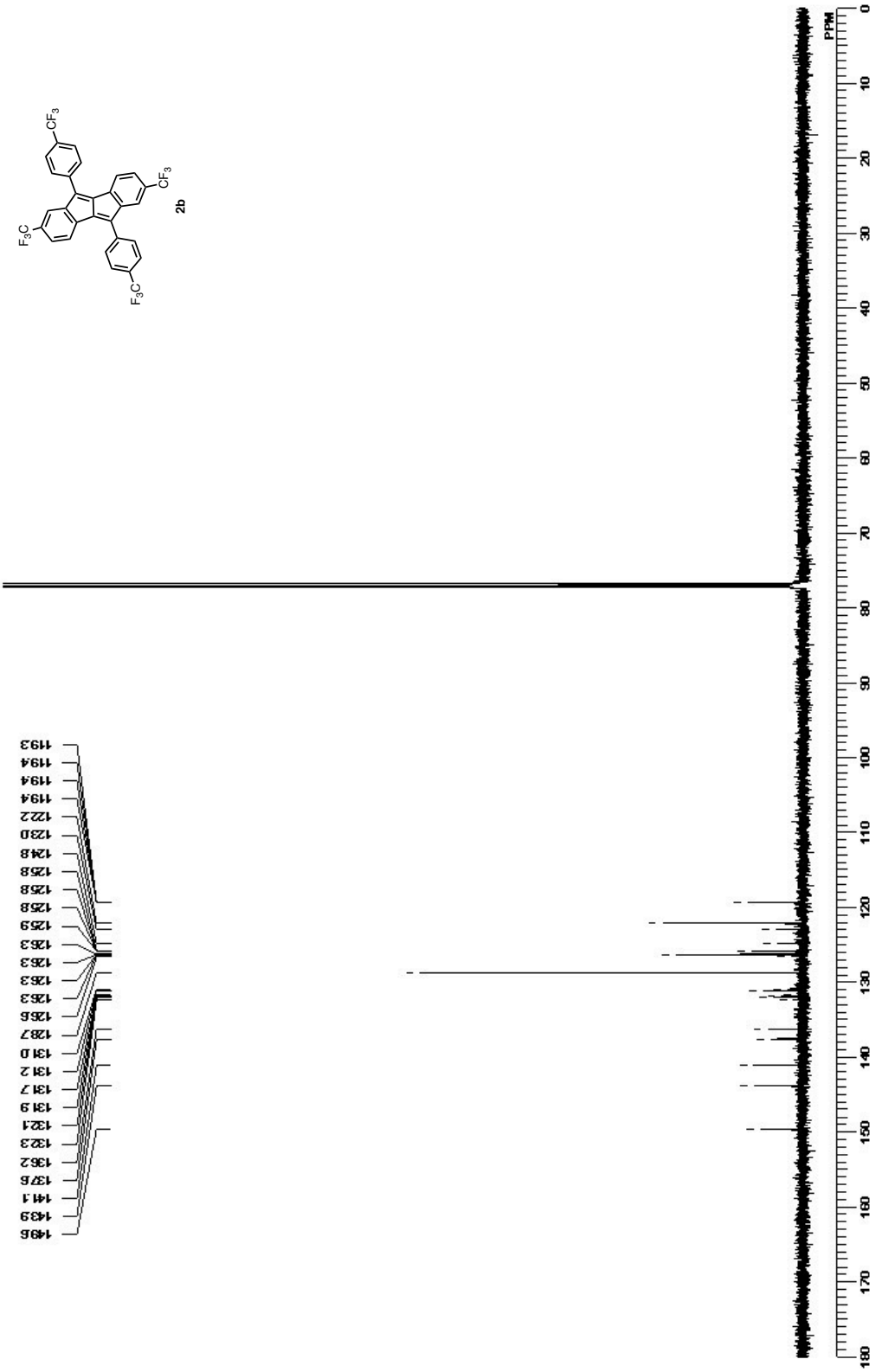
^{13}C NMR spectrum of **2a** ($CDCl_3$, 150 MHz)



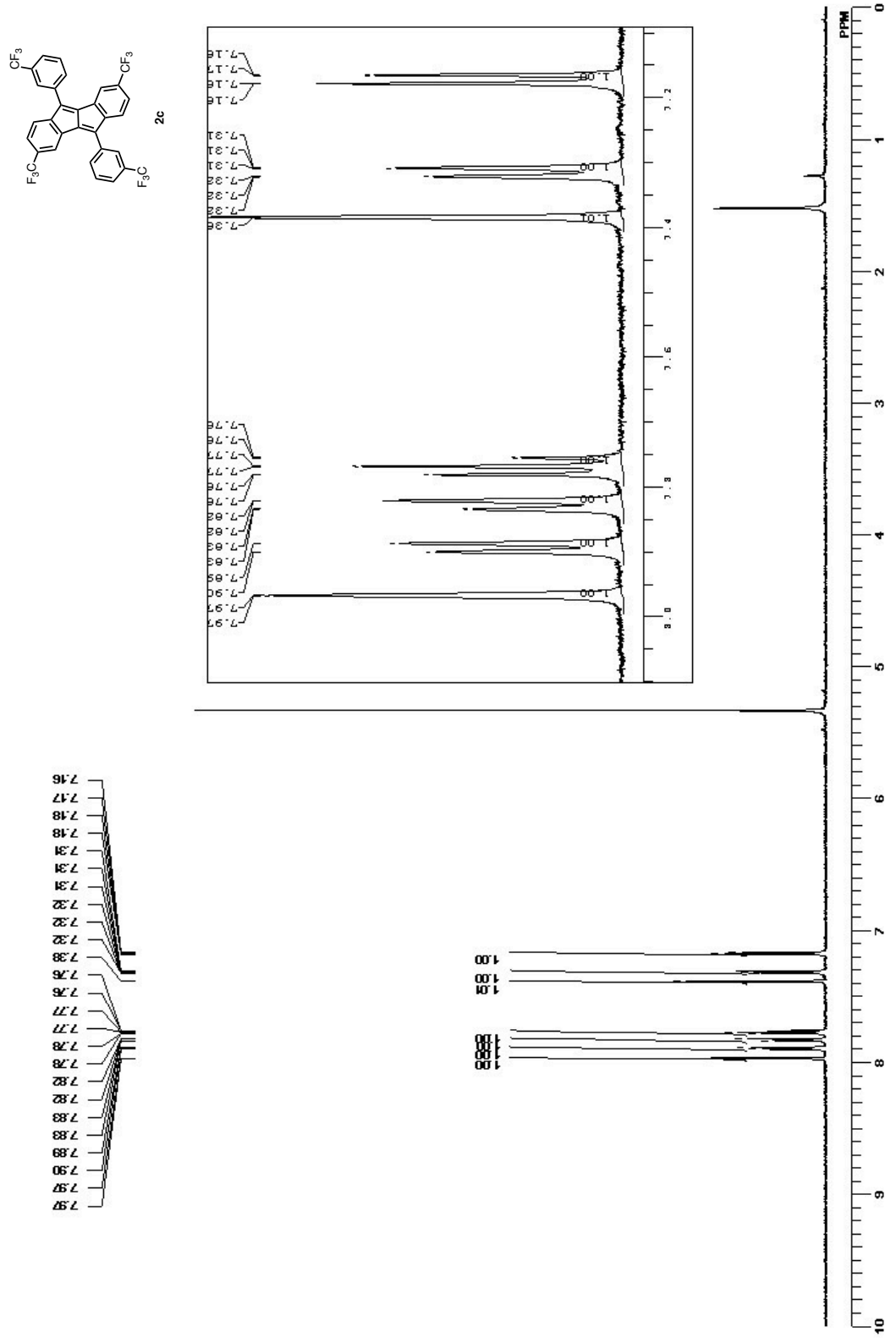
^{1}H NMR spectrum of **2b** ($CDCl_3$, 600 MHz)



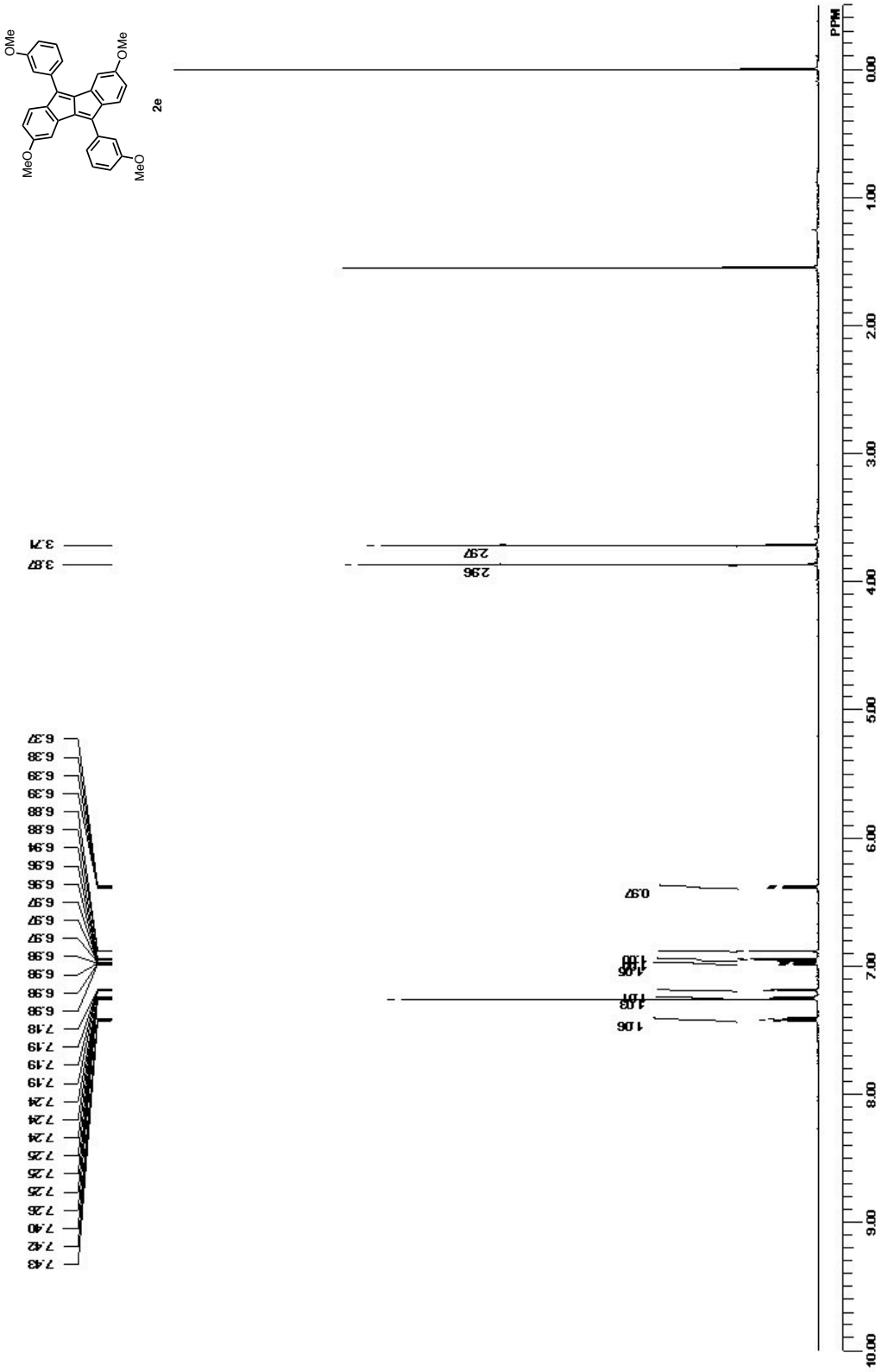
^{13}C NMR spectrum of **2b** ($CDCl_3$, 150 MHz)



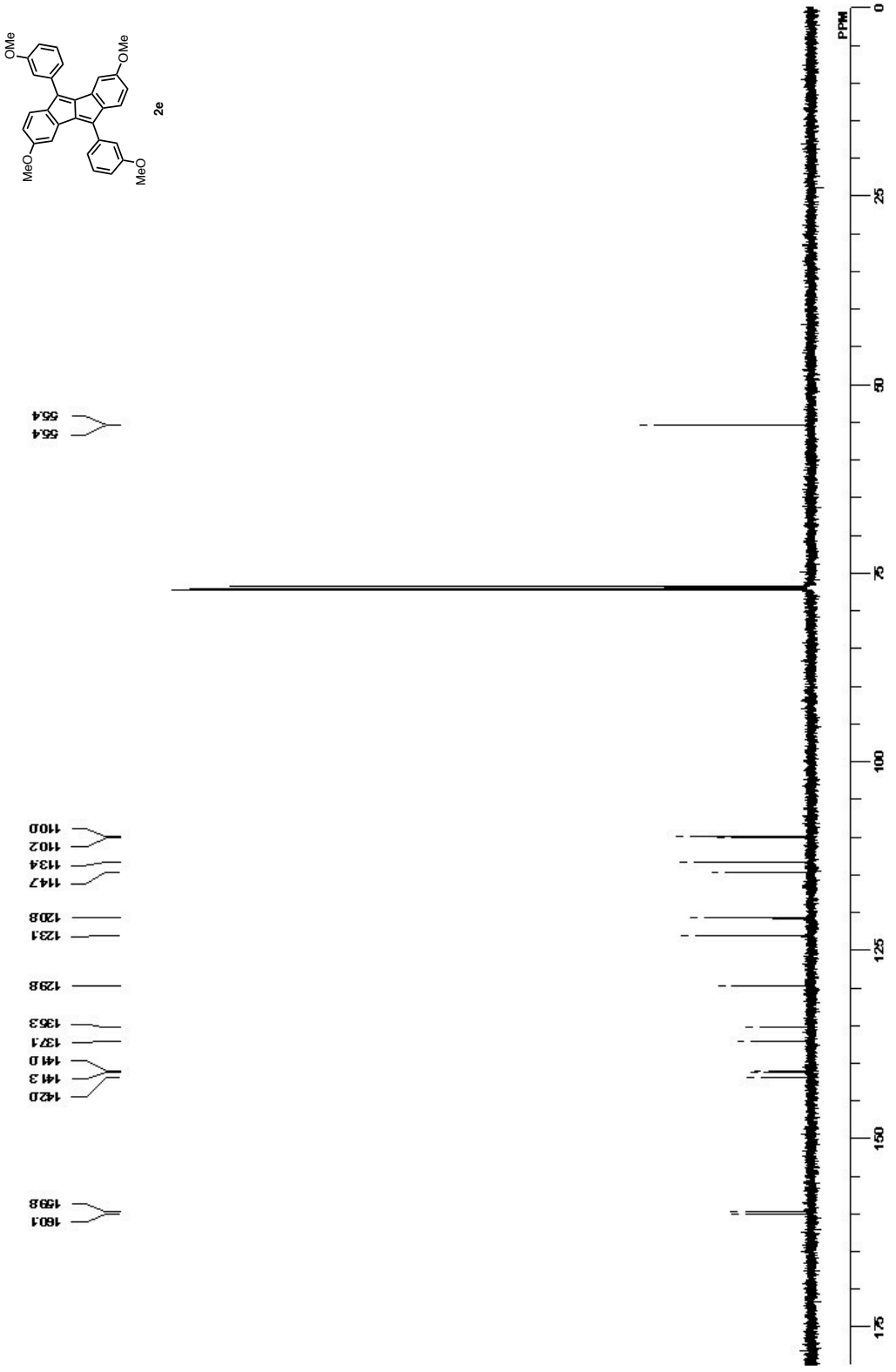
^{1}H NMR spectrum of **2c** (CD_2Cl_2, 600 MHz)



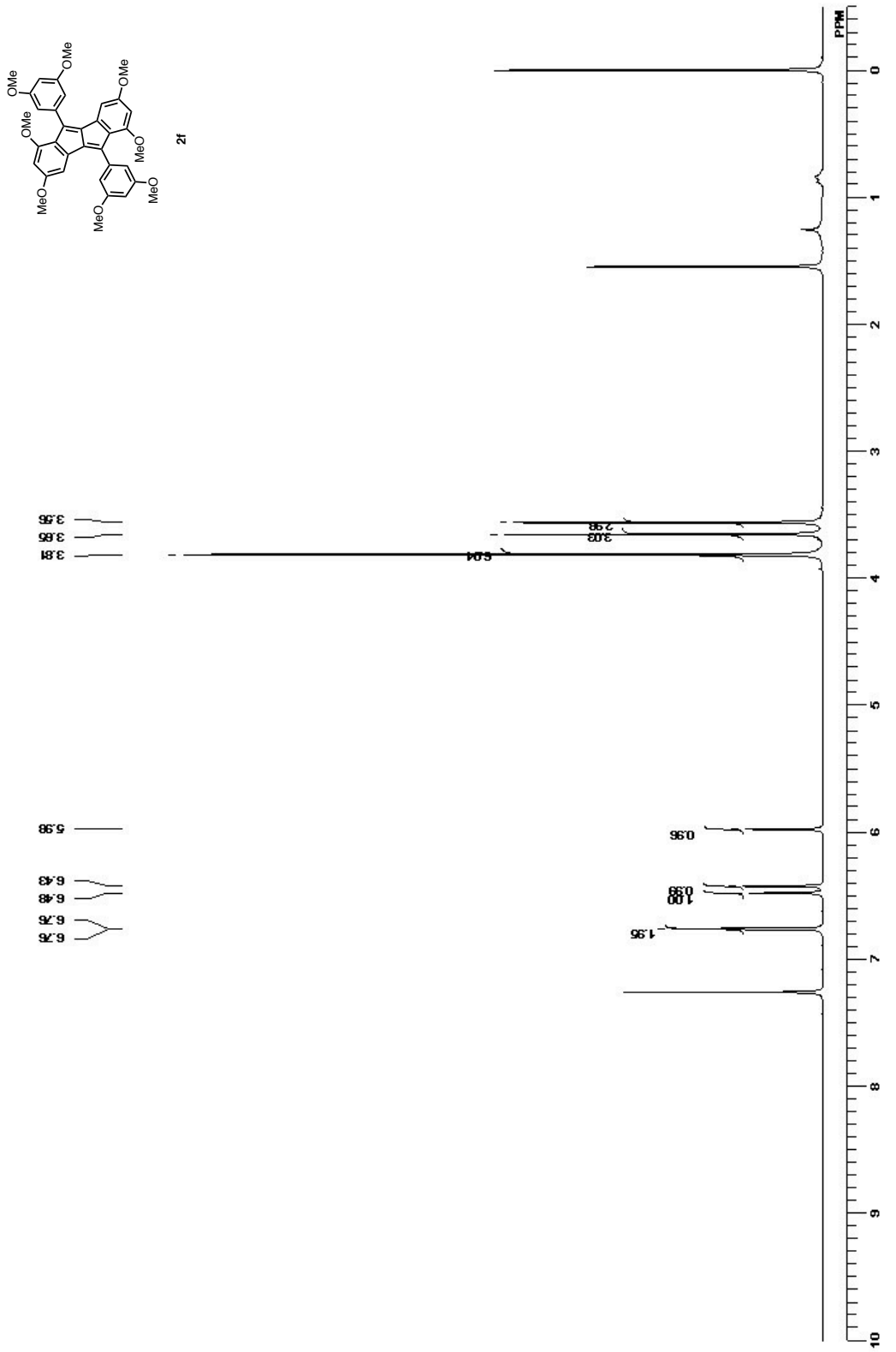
^{1}H NMR spectrum of **2e** ($CDCl_3$, 600 MHz)



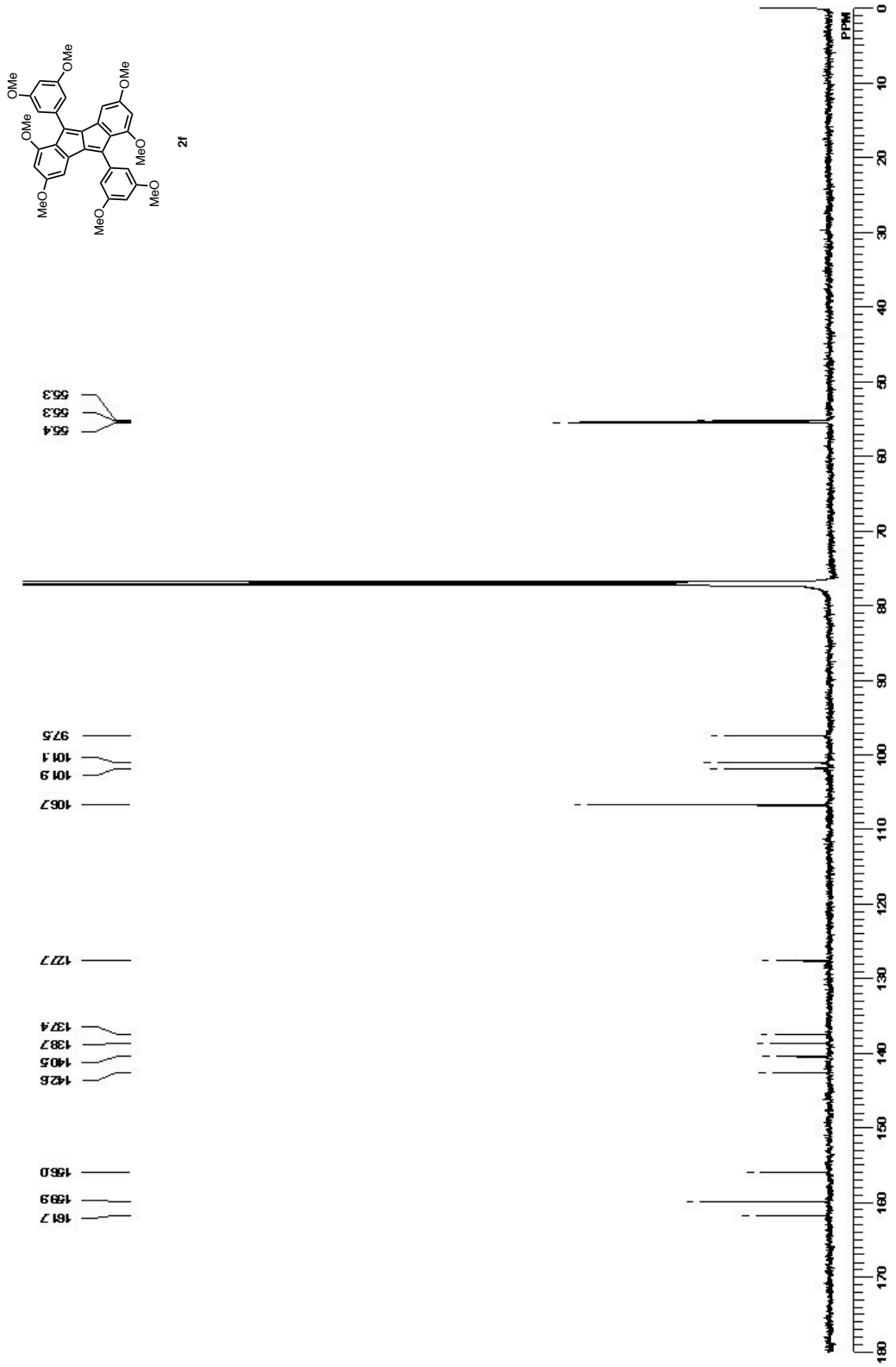
^{13}C NMR spectrum of **2e** ($CDCl_3$, 150 MHz)



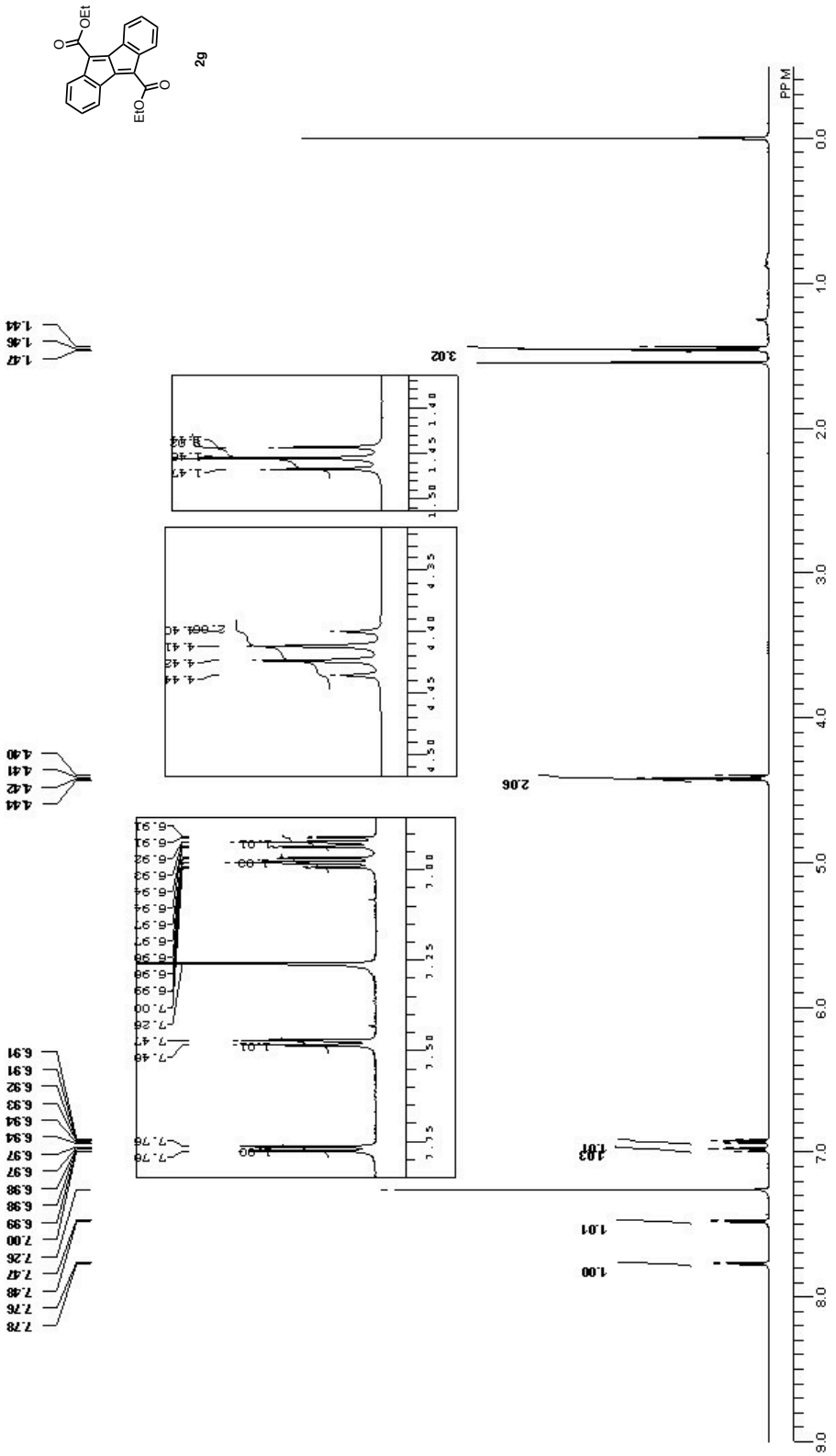
^{1}H NMR spectrum of **2f** ($CDCl_3$, 600 MHz)



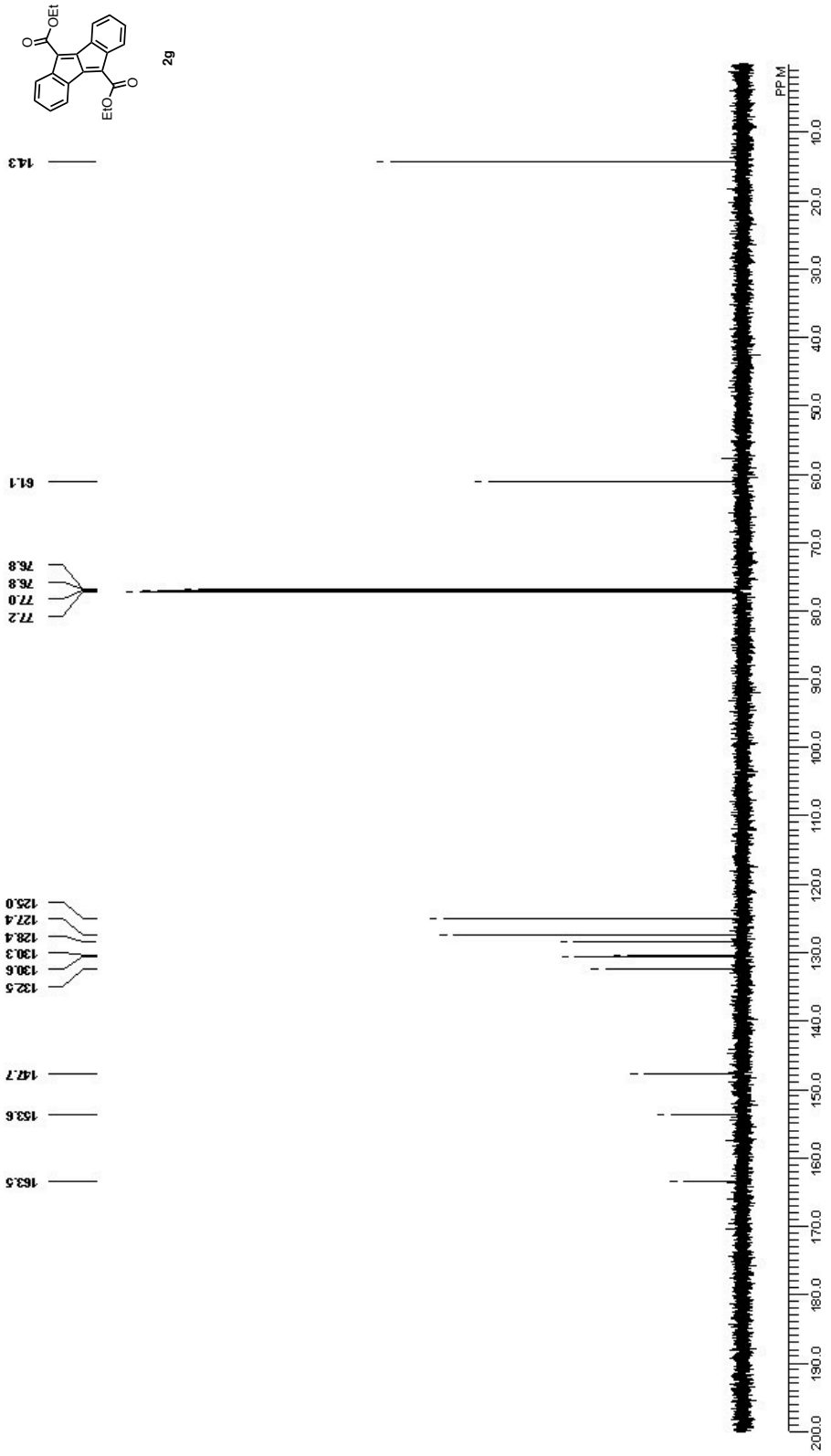
^{13}C NMR spectrum of **2f** ($CDCl_3$, 150 MHz)



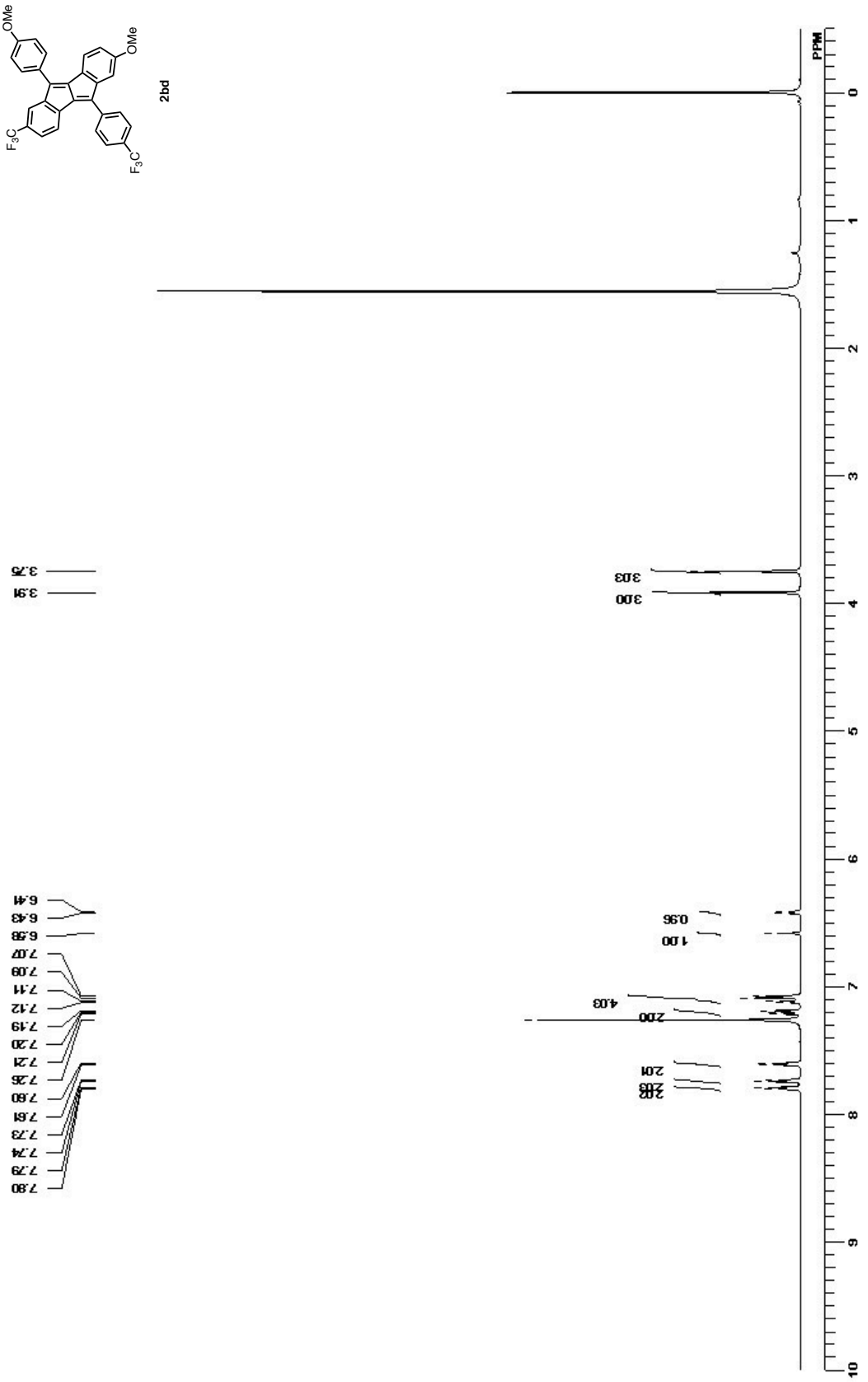
^{1}H NMR spectrum of **2g** ($CDCl_3$, 600 MHz)



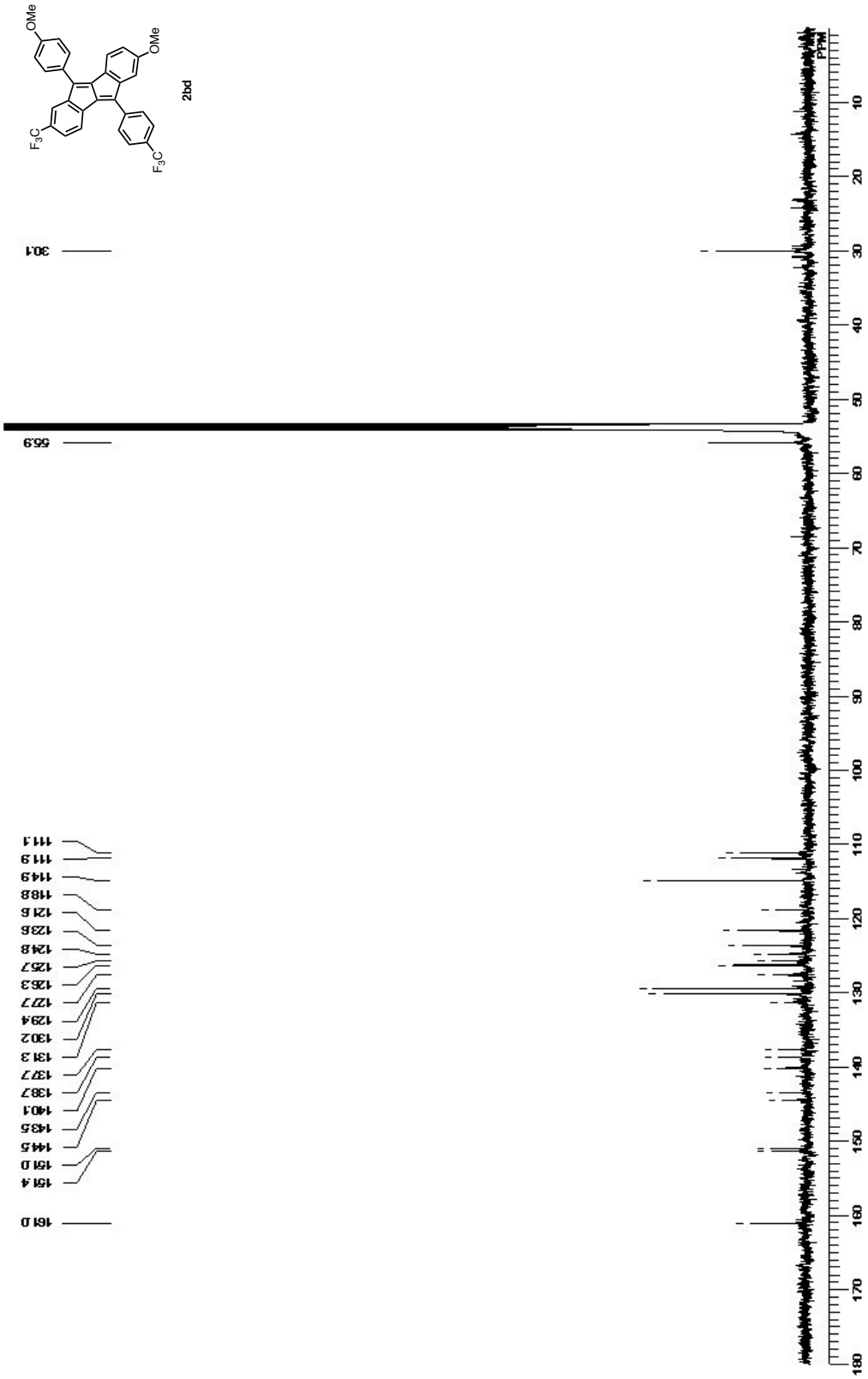
^{13}C NMR spectrum of **2g** ($CDCl_3$, 150 MHz)



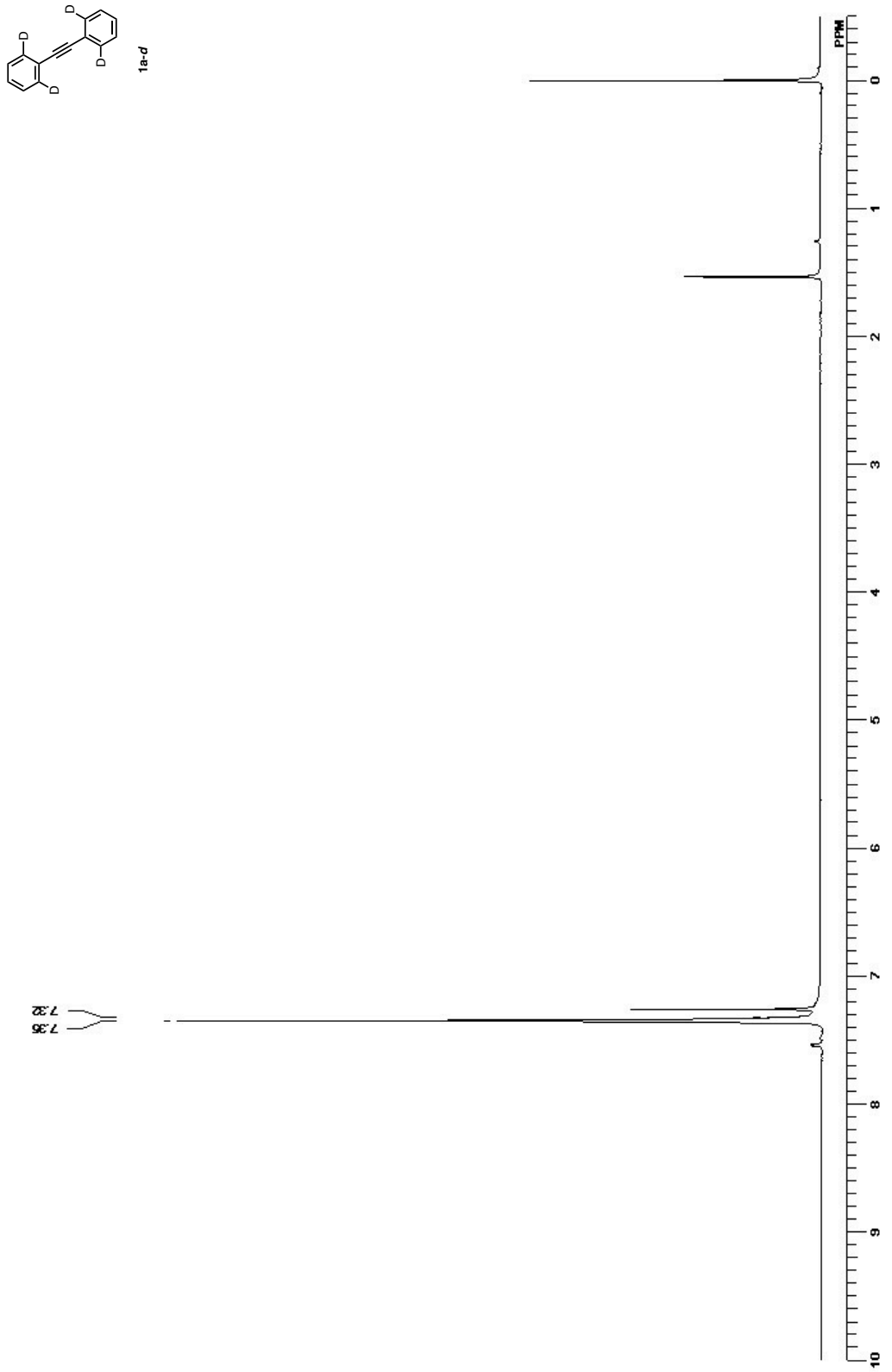
^{1}H NMR spectrum of **2bd** ($CDCl_3$, 600 MHz)



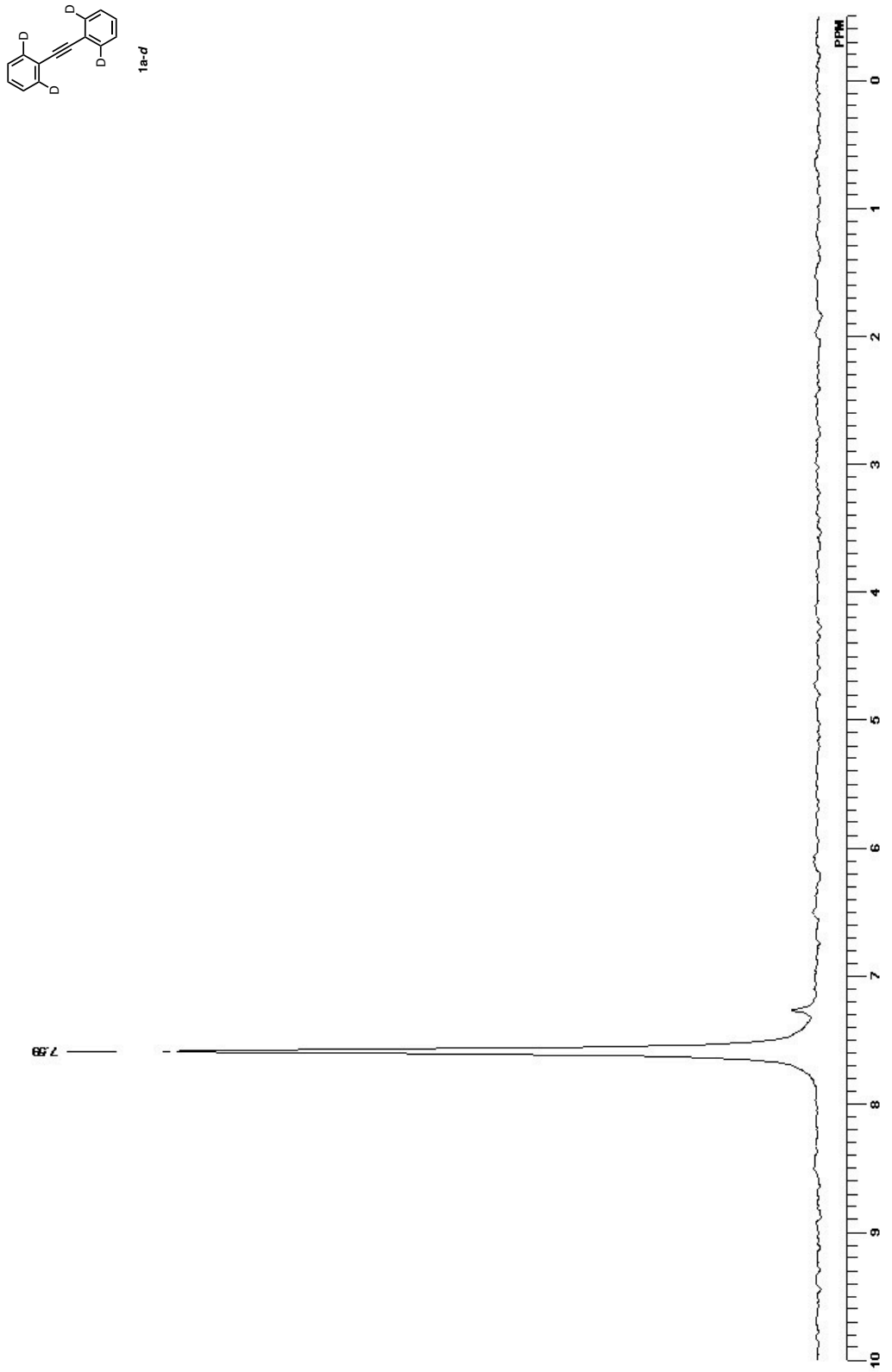
^{13}C NMR spectrum of **2bd** (CD_2Cl_2, 150 MHz)



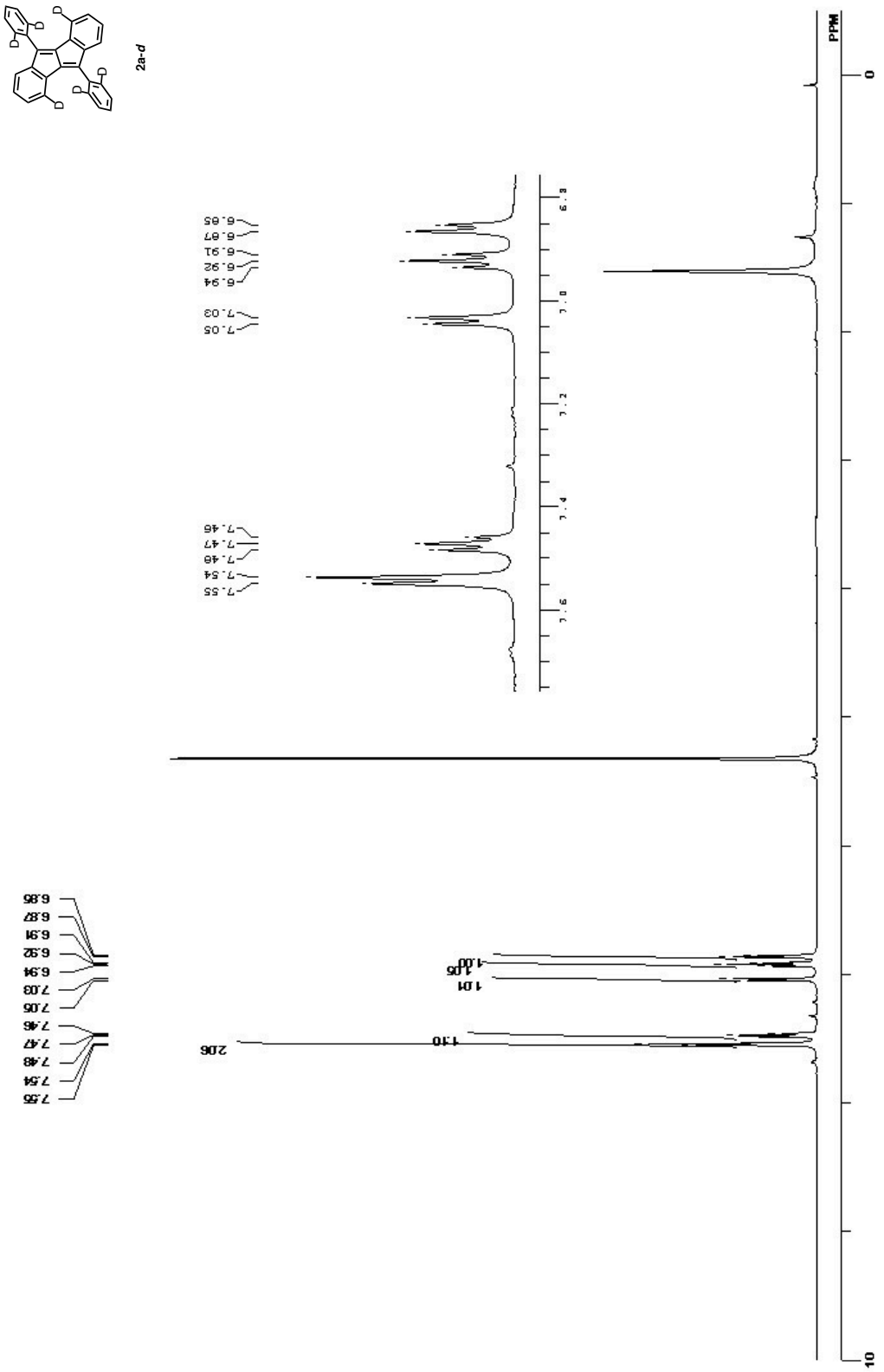
^{1}H NMR spectrum of **1a-*d*** ($CDCl_3$, 600 MHz)



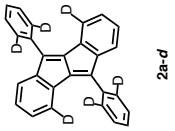
^{2}H NMR spectrum of **1a-*d*** ($CHCl_3$, 600 MHz)

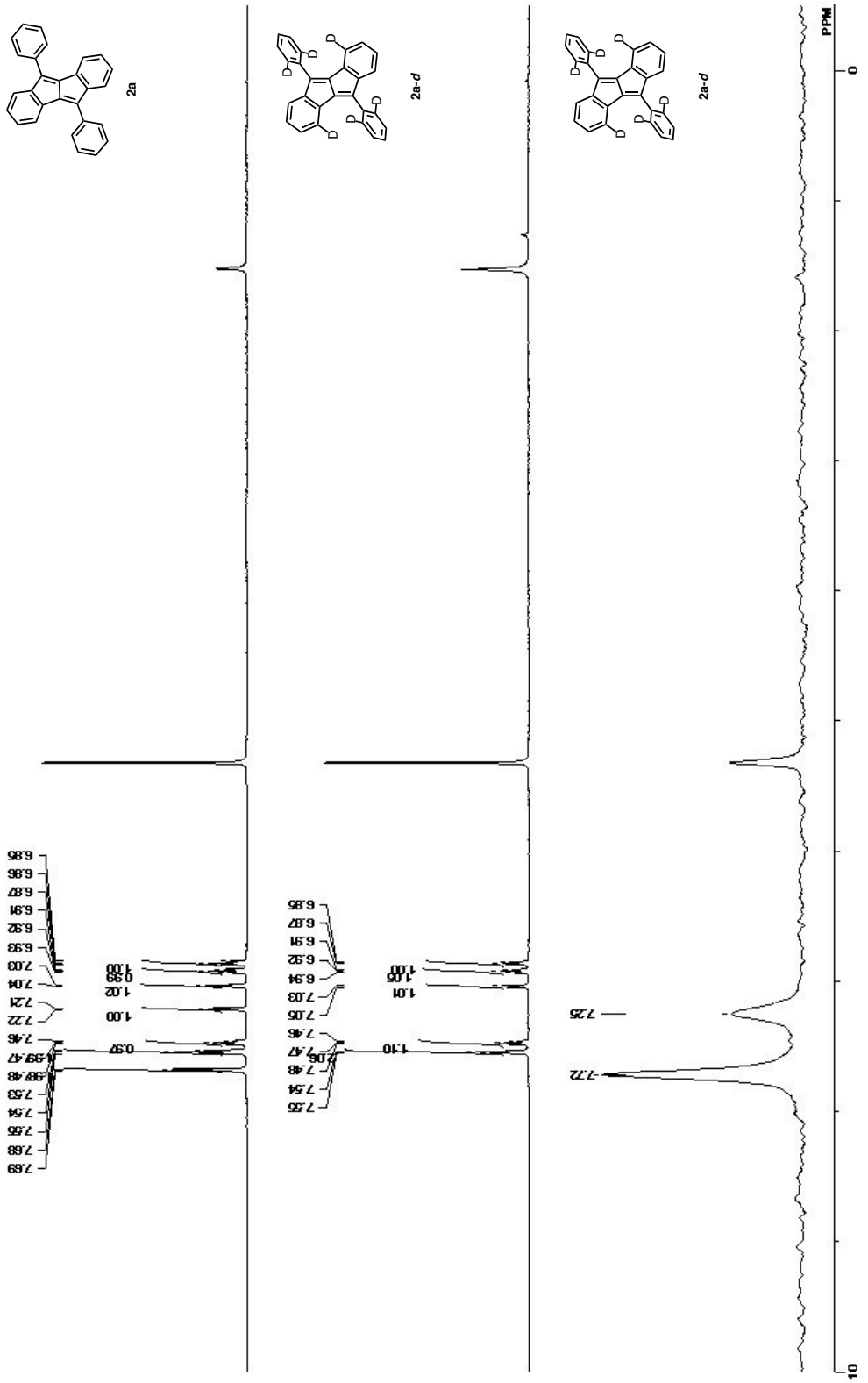


^{1}H NMR spectrum of **2a-*d*** (CD_2Cl_2, 600 MHz)

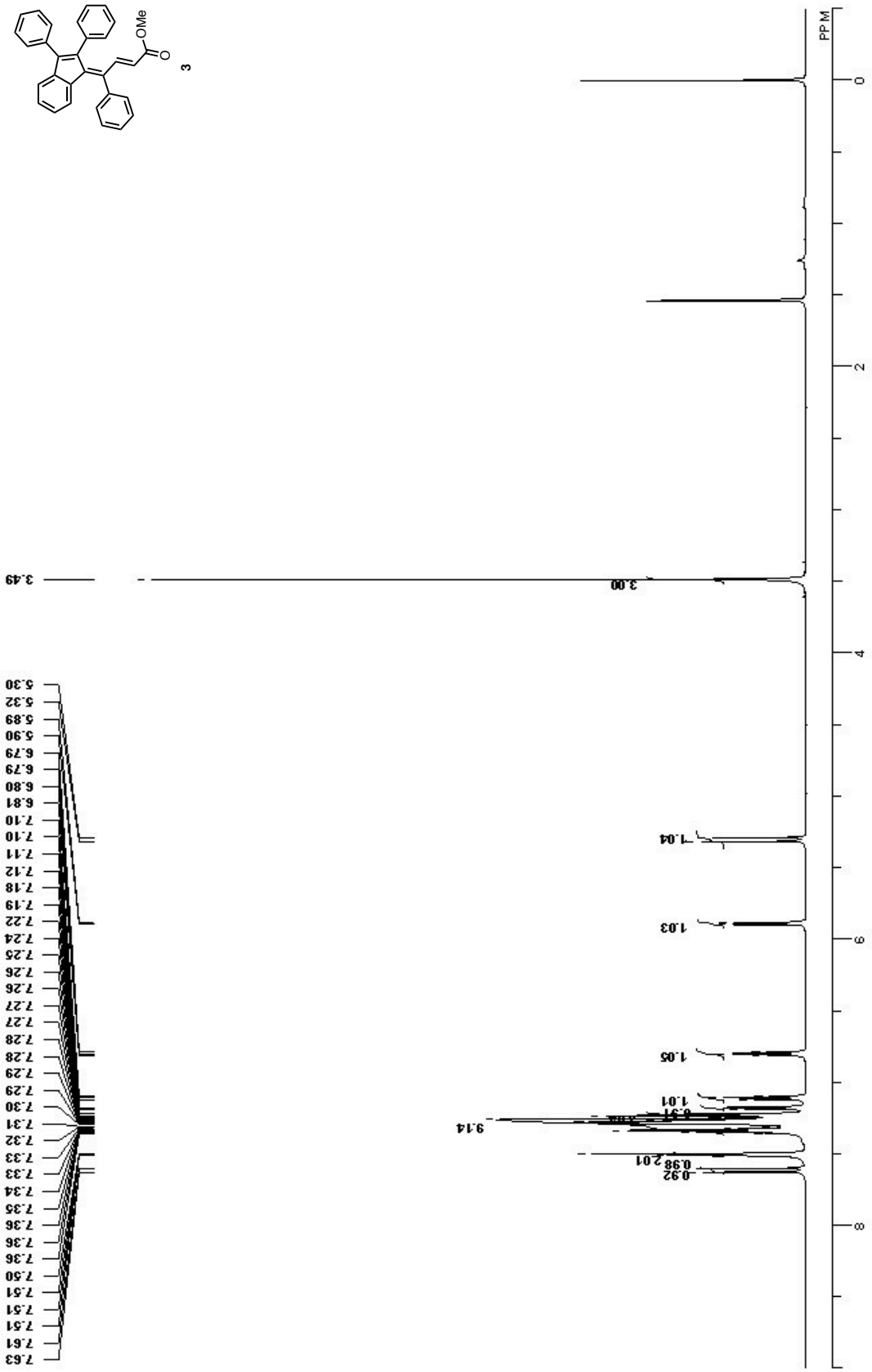


^{2}H NMR spectrum of **2a-*d*** (CH_2Cl_2, 600 MHz)





^{1}H NMR spectrum of **3** ($CDCl_3$, 600 MHz)



^{13}C NMR spectrum of **3** ($CDCl_3$, 150 MHz)