Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

for

Planar Tris-*N*-Heterocyclic Carbenes

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General information:

Air and moisture sensitive reactions were carried out under an atmosphere of N_2 using standard Schlenk techniques or inside the glovebox. Toluene and hexane were dried via passing through the molecular sieves packed drying column under nitrogen. THF and C_6D_6 were dried using Na/K alloy, and distilled under inert atmosphere. ^{1}H and ^{13}C NMR spectra were recorded using Bruker Avance III 400 MHz NMR and Bruker AVIII 500MHz FT-NMR. The ^{1}H and ^{13}C NMR spectra reported in ppm (δ) are relative to the chemical shift of solvent residual signals for $CDCl_3$ at 7.26 and 77.00 ppm, DMSO-d_6 at 2.50 and 39.52 ppm, C_6D_6 at 7.16 ppm and 128.4 ppm, THF-d_8 at 3.58, 1.73 ppm, 25.4, 67.6 ppm, and CD_2Cl_2 at 5.32 ppm and 54.0 ppm. The elemental analysis was recorded on Thermo Flash 2000. The ESI MASS was recorded on Bruker micrOTOF-QII. The solid-state NMR was recorded on BRUKER AVIII 600 WB SSNMR.

X-ray Crystallography: Diffraction data were collected at T = 150(2) K with a Bruker AXS APEX CCD diffractometer equipped with a rotation anode using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Diffraction data were collected over the full sphere and were corrected for absorption. Cell parameters were retrieved and refined using DENZO-SMN software[1] on all reflections. Data reduction was performed with DENZO-SMN software. Structural analysis was conducted using the SHELXTL program on a personal computer. All the structures were solved and refined using the SHELXL-97 program by full-matrix least-squares on F^2 values. Hydrogen atoms were added to the structure models in calculated positions. Crystallographic data have been deposited at the Cambridge Crystallographic Data Center with deposition number CCDC-936892, CCDC-936893, and CCDC-936894, for **1b**, **2a**, and **3a**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

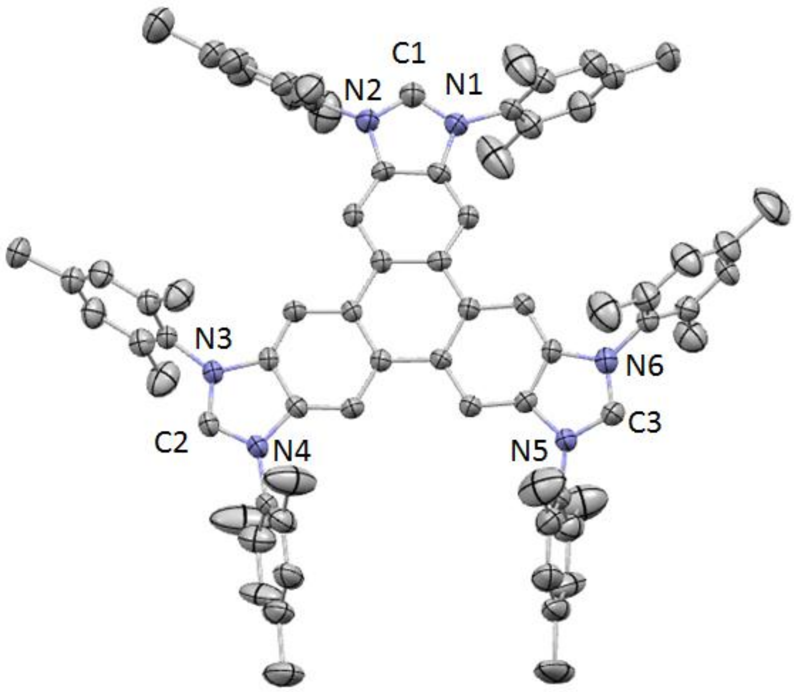


Figure S-1. Molecular structure of [**1b**]$^{3+}$. Thermal ellipsoids were drawn at 50 % probability. Counter anions, hydrogen atoms, and solvent molecules were omitted for clarity. Selected bond lengths (Å) and angles (deg): N(1)-C(1) 1.326(8), N(2)-C(1) 1.334(8), N(3)-C(2) 1.323(7), N(4)-C(2) 1.329(7), N(5)-C(3) 1.331(8), N(6)-C(3) 1.326(8), N(1)-C(1)-N(2) 111.4(6), N(3)-C(2)-N(4) 111.0(5), N(5)-C(3)-N(6) 111.1(5).

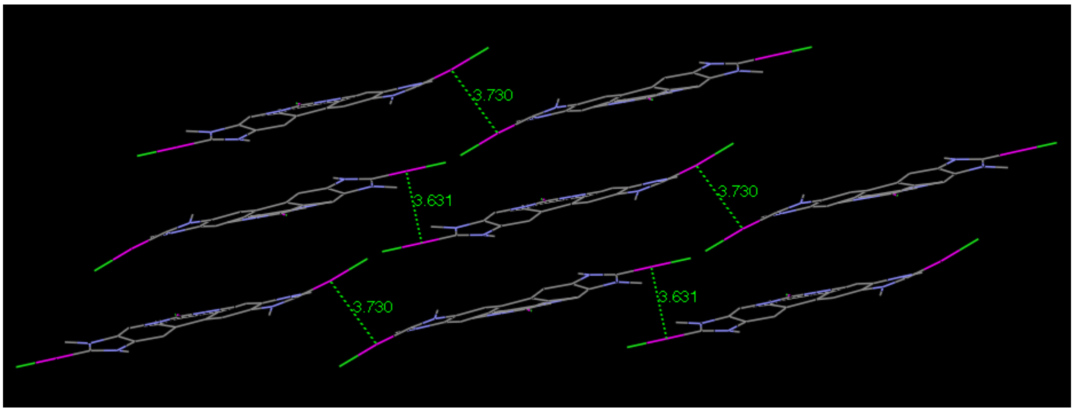


Figure S-2. Intermolecular Au-Au interaction found in the crystal structure of **3a**.

Table S-1. Crystal data and structure refinement for [**1b**]$[BF_4]_3$

Identification code	ic15836 ([**1b**]$[BF_4]_3$)
Empirical formula	C76.50 H78 B3 Cl3 F12 N6 O
Formula weight	1464.23
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	a = 18.1690(3) Å
	b = 35.2816(6) Å
	c = 23.4175(4) Å
	$\alpha = 90°$
	$\beta = 98.6191(6)°$
	$\gamma = 90°$
Volume	14841.8(4) $Å^3$
Z	8
Density (calculated)	1.311 g/cm^3
Absorption coefficient	0.202 mm^{-1}
F(000)	6088
Crystal size	0.40 x 0.25 x 0.25 mm^3
Theta range for data collection	1.05 to 25.00°.
Index ranges	-21<=h<=21, -41<= k <= 41, -25<=l<=27
Reflections collected	71682
Independent reflections	26028 [R(int) = 0.0503]
Completeness to theta = 25.00°	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.961 and 0.936
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	26028 / 263 / 1859
Goodness-of-fit on F^2	1.009
Final R indices [I > 2sigma(I)]	R1 = 0.1369, wR2 = 0.3159
R indices (all data)	R1 = 0.2059, wR2 = 0.3466
Largest diff. peak and hole	2.135 and -1.190 e $Å^{-3}$

Table S-2. Crystal data and structure refinement for **2a**

Identification code	ic15984 (**2a**)
Empirical formula	C75 H90 N6
Formula weight	1075.53
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/m
Unit cell dimensions	a = 8.4291(3) Å
	b = 33.6359(11) Å
	c = 11.6153(3) Å
	α□= 90°□
	β□= 93.9449(10)°
	γ = 90°
Volume	3285.37(18) Å^3
Z	2
Density (calculated)	1.087 g/cm^3
Absorption coefficient	0.063 mm^{-1}
F(000)	1164
Crystal size	0.50 x 0.35 x 0.11 mm^3
Theta range for data collection	1.21 to 25.00°.
Index ranges	-9<=h<=9, -36<=k<=39, -13<=l<=13
Reflections collected	17070
Independent reflections	5808 [R(int) = 0.0459]
Completeness to theta = 25.00°	98.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.996 and 0.956
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5808 / 0 / 404
Goodness-of-fit on F^2	1.062
Final R indices [I > 2sigma(I)]	R1 = 0.0449, wR2 = 0.1145
R indices (all data)	R1 = 0.0843, wR2 = 0.1411
Largest diff. peak and hole	0.147 and -0.288 e Å^{-3}

Table S-3. Crystal data and structure refinement for **3a**

Identification code	ic15945 (**3a**)
Empirical formula	C47 H65 Au3 Cl3 N6 O0.50
Formula weight	1419.30
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 12.7469(4) Å
	b = 13.1572(4) Å
	c = 16.3788(6) Å
	α = 97.980(2)°
	β = 96.687(2)°
	γ = 100.337(2)°
Volume	2647.87(15) $Å^3$
Z	2
Density (calculated)	1.780 g/cm^3
Absorption coefficient	8.478 mm^{-1}
F(000)	1362
Crystal size	0.17 x 0.08 x 0.08 mm^3
Theta range for data collection	1.27 to 25.00°.
Index ranges	-15<=h<=15, -15<=k<=15, -19<=l<=19
Reflections collected	23539
Independent reflections	9282 [R(int) = 0.0589]
Completeness to theta = 25.00°	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.512 and 0.371
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9282 / 118 / 576
Goodness-of-fit on F^2	1.050
Final R indices [I > 2sigma(I)]	R1 = 0.0703, wR2 = 0.1980
R indices (all data)	R1 = 0.1089, wR2 = 0.2299
Largest diff. peak and hole	5.458 and -2.768 e $Å^{-3}$

Synthesis of 2,3,6,7,10,11-hexakis(tert-butylamine)triphenylene

Catalyst for Buchwald–Hartwig coupling was prepared by heating a 10 mL toluene solution containing 1,3-bis (2,6-diisopropylphenyl)imidazolium chloride (0.17 g, 0.4 mmol), NaO^{t}Bu (0.06 g, 0.62 mmol), and Pd(OAc)$_2$ (0.05 g, 0.23 mmol) at 100 ^{o}C for 30 minutes. Afterward, the catalyst solution was added into another flask containing 2,3,6,7,10,11-hexabromotriphenylene (2.84 g, 4 mmol), and NaO^{t}Bu (2.88 g, 30 mmol) in toluene (50 mL). The *tert*-butyl amine (2.5 mL, 23.8 mmol) was added, and the reaction mixture was stirred at 100 ^{o}C for 2 days. After reaction, the insoluble gray precipitates were filtered off under inert atmosphere over celite, and solvent was removed under reduced pressure to afford the hexamine as brown solids (2.6 g, yield 98%). ^{1}H NMR (CDCl$_3$, 400 MHz, ppm): δ 7.85 (s, 6H), 3.83 (s, 6H), 1.40 (s, 54H). ^{13}C NMR (CDCl$_3$, 100 MHz, ppm): δ 137.8, 123.5, 113.5, 52.3, 30.0.

Synthesis of 2,3,6,7,10,11-hexakis(mesitylamine)triphenlene

The reaction follows the same procedure applied for hexakis(*tert*-butylamine)-triphenylene by using 2,4,6-trimethylaniline (3.65 mL, 26 mmol) as amine source. Upon completion, the solution mixture was filtered over celite under nitrogen, and all volatiles were removed under reduced pressure. The solid residue was then washed with hexane to afford the desire product as dark green solids (2.1 g, yield 50 %). ^{1}H NMR (CDCl$_3$, 400 MHz, ppm): δ 6.91 (s, 6H), 6.85 (s, 12H), 5.26 (s, 6H), 2.44 (s, 18H), 2.10 (s, 36H). ^{13}C NMR (CDCl$_3$, 100 MHz, ppm): δ 136.9, 134.3, 133.4, 132.8, 129.3, 123.0, 107.3, 21.1, 18.1.

Synthesis of [1a][BF$_4$]$_3$

To a solution of 2,3,6,7,10,11-hexakis(*tert*-butylamine)triphenylene (1 g) in degassed triethylorthoformate (15 mL) was added HBF$_4$ ether solution (2 mL, excess). The solution was stirred for overnight at room temperature. After reaction, diethyl ether was added to precipitate the azolium salt. The solids were collected by filtration and washed with ether for several times. The [**1a**][BF$_4$]$_3$ was further purified by recrystallization from CH$_3$CN/diethyl ether to give [**1a**][BF$_4$]$_3$ as pale yellow solids (1.23 g, yield 85%). ^{1}H NMR (DMSO-d$_6$, 400 MHz, ppm): δ 9.19 (s, 6H), 9.17 (s, 3H), 2.04 (s, 54H). ^{13}C NMR (DMSO-d$_6$, 100 MHz, ppm): δ 142.6, 131.3, 126.8, 112.0, 61.9, 28.5. Anal. calcd for ([**1a**][BF$_4$]$_3$•3H$_2$O): C, 53.91; H, 6.94; N, 8.38; Found: C, 53.44; H, 6.61; N, 8.33; ESI MASS: m/z calcd for $C_{45}H_{63}BF_4N_6$ [[**1a**][BF$_4$]]$^{2+}$: 387.2570, Found: 387.2571.

Synthesis of [1b][BF$_4$]$_3$

The reaction follows the same procedure for [**1a**][BF$_4$]$_3$ with 2,3,6,7,10,11-hexakis(mesitylamine)triphenylene (0.8 g, 0.79 mmol) as starting material. However, 3 days of reaction time was required for complete conversion. After reaction, diethyl ether was added to precipitate the product. The solids were collected by filtration. The residue was suspended in THF, and added diethyl ether to induce the precipitate as compound [**1b**][BF$_4$]$_3$ as black solids (0.94 g, yield 91%). ^{1}H NMR (DMSO-d$_6$, 400 MHz, ppm): δ 10.39 (s, 3H), 8.81 (s, 6H), 7.32 (s, 12H), 2.45 (s, 18H), 2.11 (s, 36H). ^{13}C NMR (DMSO-d$_6$, 100 MHz, ppm): δ 148.1, 141.2, 135.5, 131.1, 129.9, 129.6, 128.3, 110.6, 20.7, 17.2. Anal. calcd for ([**1b**][BF$_4$]$_3$•3H$_2$O): C, 65.52; H, 5,94; N, 6.11; Found: C, 66.00; H, 6.00; N, 5.90; ESI MASS: m/z calcd for $C_{75}H_{75}BF_4N_6$ [[**1b**][BF$_4$]]$^{2+}$: 573.3042, Found: 573.3027.

Synthesis of 2a

To a solution of [**1a**][BF$_4$]$_3$ (200 mg) in THF (15 mL) was added potassium hydride (42 mg, 5 eq.), and potassium *tert*-butoxide (1 mg). The solution was allowed to stir at room temperature for 2 hours. Then, the solvent was removed under reduced pressure, and free carbene was extracted with benzene. The collected benzene solution was brought to dryness under reduced pressure to give compound **2a** as pale yellow solids (91 mg, yield 62.7%). Crystals of **2a** were obtained via slow evaporation of a benzene solution of **2a** at room temperature inside glove-box. ^{1}H NMR (C$_6$D$_6$, 400 MHz, ppm): δ 9.02 (s, 6H), 1.96 (s, 54H). ^{13}C NMR (C$_6$D$_6$, 125 MHz, ppm): δ 230.4, 135.4, 124.6, 106.78, 57.4, 30.4.

Synthesis of 2b

To a solution of [**1b**][BF$_4$]$_3$ (100 mg) in THF (15 mL) was added potassium hydride (15 mg, 5 eq.), and potassium *tert*-butoxide (1 mg). The solution was stirred at room temperature for 2 hours. Then, the solvent was removed under reduced pressure, and the crude product was re-dissolved in benzene. After filtration, the filtrate was evaporated to give compound **2b** as light brown solids (46.4 mg, yield 58%). ^{1}H NMR (C$_6$D$_6$, 400 MHz, ppm): δ 8.25 (s, 6H), 6.74 (s, 12H), 2.25 (s, 18H), 2.01 (s, 36H). ^{13}C NMR (THF-d$_8$, 125 MHz, ppm): δ 231.4, 135.9, 125.0, 107.2, 58.2, 31.0.

Synthesis of 3a

To a solution of **2a** (100 mg) in THF (10 mL) was added AuCl(SMe$_2$) (151 mg, 3.5 eq.). The solution was stirred at room temperature for 2 hours. After reaction, the solution was filtered through celite, and the filtrate was brought to dryness under reduced pressure. The residue was re-dissolved in CH$_2$Cl$_2$ and all insoluble solids were filtered off. Afterward, the clear CH_2Cl_2 solution was poured into diethyl ether to afford compound **3a** as yellow precipitates (150 mg, yield 74%). Crystals were obtained via slow diffusion of diethyl ether into a CH_3CN/CH_2Cl_2 (1:1) solution of **3a** at ambient temperature. ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 9.02 (s, 6H), 2.39 (s, 54H). ^1H NMR (CD_2Cl_2, 400 MHz, ppm): δ 9.10 (s, 6H), 2.42 (s, 54H). ^{13}C NMR (CD_2Cl_2, 100 MHz, ppm): δ 182.3, 134.3, 125.3, 109.6, 62.62, 32.9. Anal. calcd for **3a**: C, 39.10; H, 4.38; N, 6.08; Found: C, 38.09; H, 4.23; N, 5.90; ESI MASS: m/z calcd for $C_{45}H_{60}Au_3Cl_4N_6$ [**3a**+Cl]$^-$: 1415.2636, Found: 1415.2598.

Synthesis of 3b

To a solution of **2b** (100 mg) in THF (10 mL) was added AuCl(SMe_2) (97.6 mg, 3.5 eq.). The solution was stirred at room temperature for 2 hours. After reaction, the solution was filtered through celite, and the filtrate was brought to dryness under reduced pressure. The residue was re-dissolved in CH_2Cl_2 and all insoluble solids were filtered off. Afterward, the clear CH_2Cl_2 solution was poured into diethyl ether to afford compound **3b** as dark brown precipitates (112.9 mg, yield 68%). ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.89 (s, 6H), 7.12 (s, 12H), 2.45 (s, 18H) 2.05 (s, 36H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 185.2, 140.8, 135.5, 133.6, 131.5, 130.1, 128.2, 106.4, 21.3, 17.9. ESI MASS: m/z calcd for $C_{75}H_{72}Au_3Cl_4N_6$ [**3b**+Cl]$^-$: 1787.3575, Found: 1787.3544.

Synthesis of silver coordination polymer (2a-Ag)

To a solution of **2a** (100 mg) in THF (15 mL) was added silver trifluoromethanesulfonate (57 mg, 1.5 eq.) to result in light brown opaque solution. The solution was allowed to stir at room temperature for 1 day with the exclusion of light. After reaction, the coordination polymer was collected as dark-brown solid by filtration (56 mg, Yield 35%). The observed ^{13}C resonances at 179 ppm, 172 ppm, and 161 ppm in solid-state NMR are assigned to the internal **2a**-Ag$_3$ units, peripheral **2a**-Ag$_{(3-x)}$ units, and terminal urea moieties, respectively.

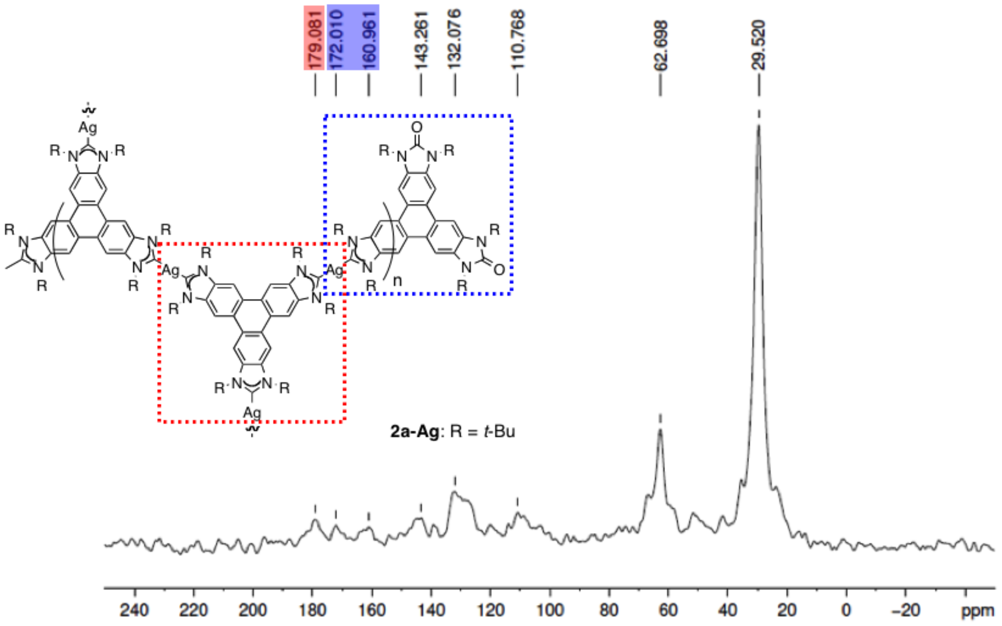
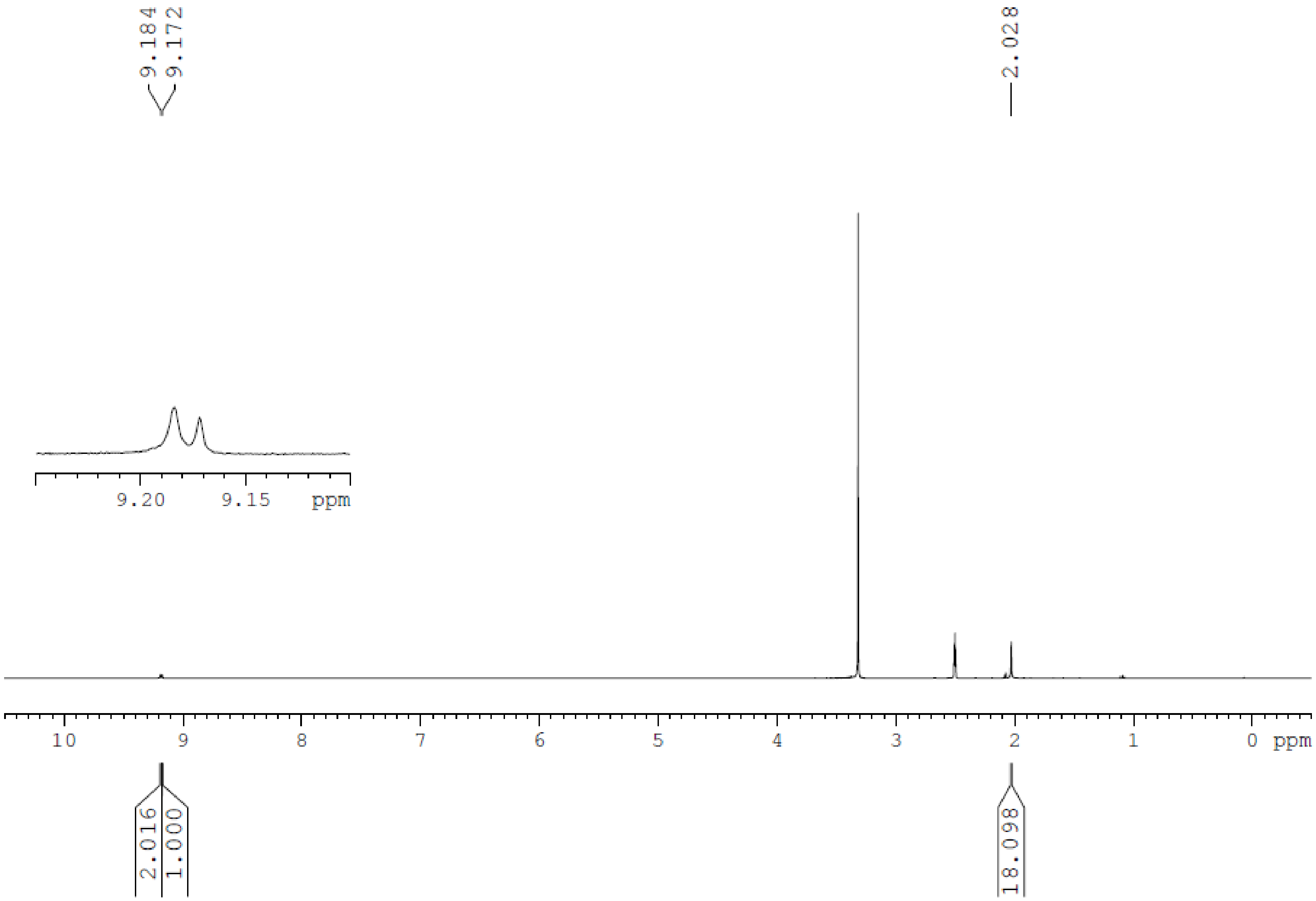
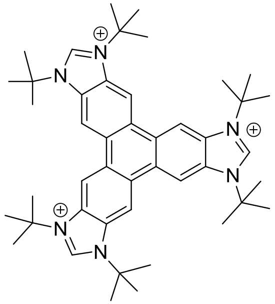


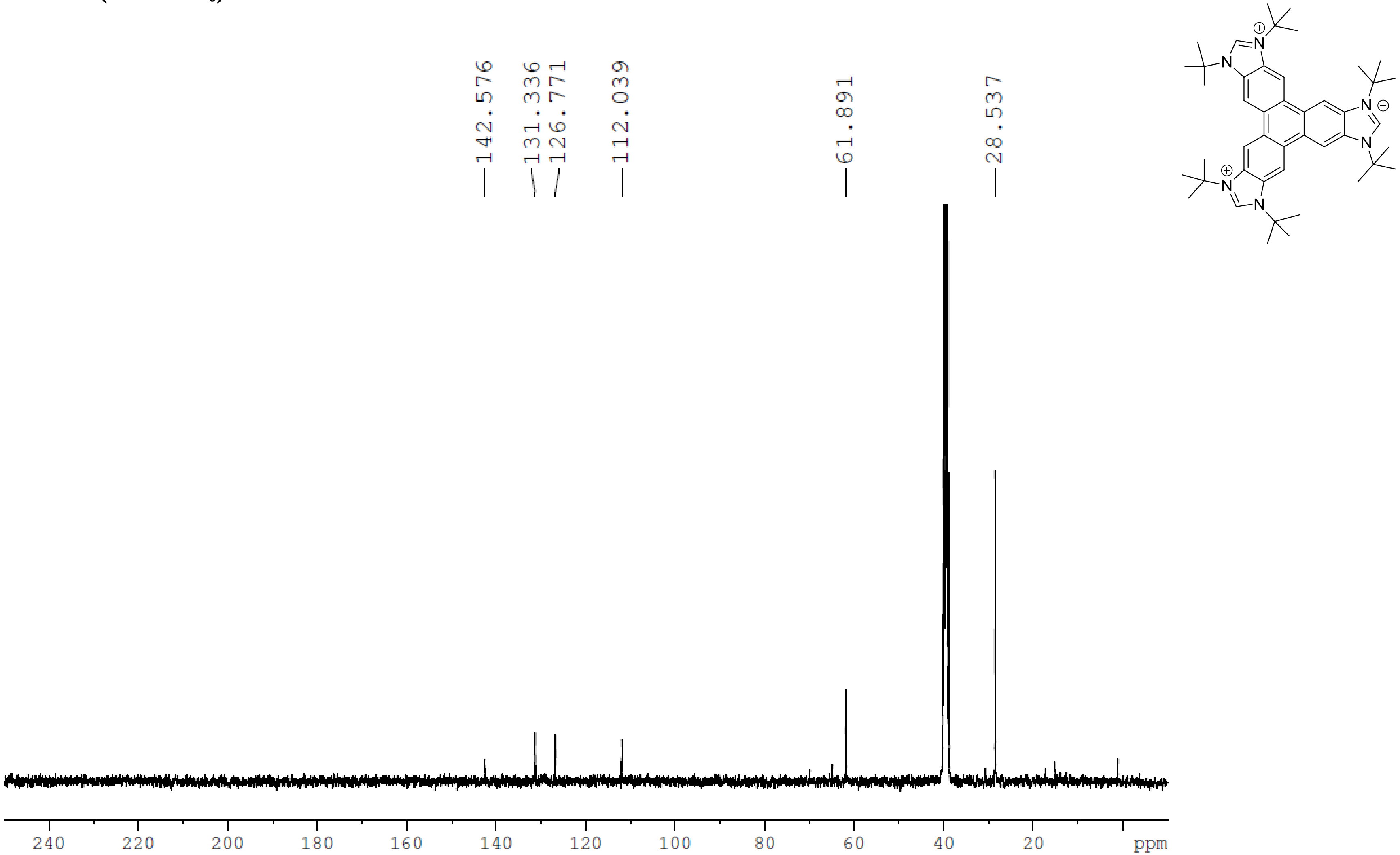
Figure S-3. Solid-state NMR spectrum of **2a-Ag**.

^{1}H NMR of 1a (DMSO-d_6)

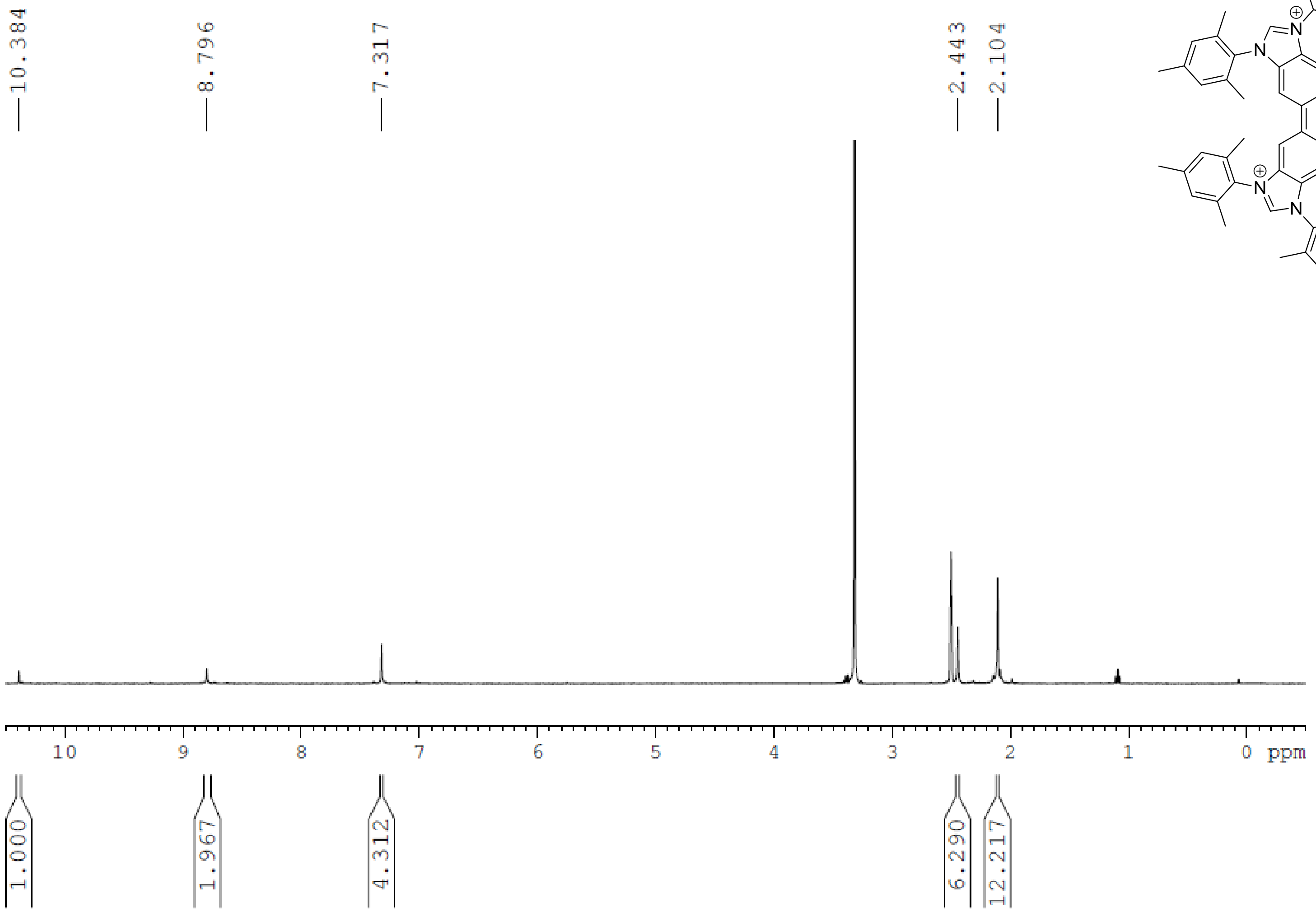


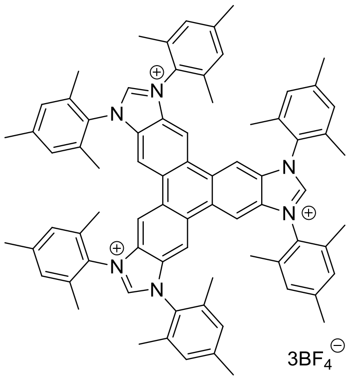


^{13}C NMR of 1a (DMSO-d_6)

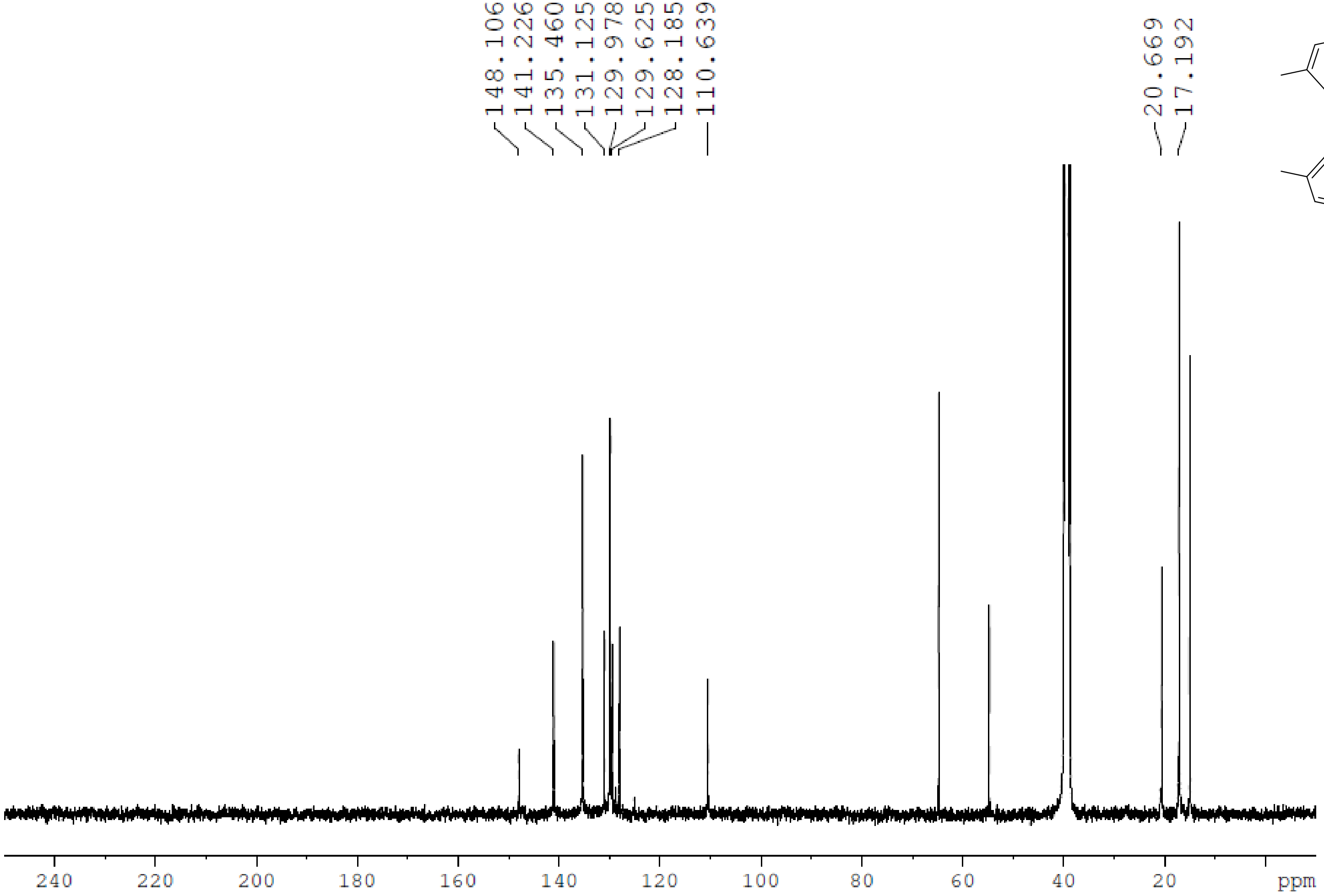


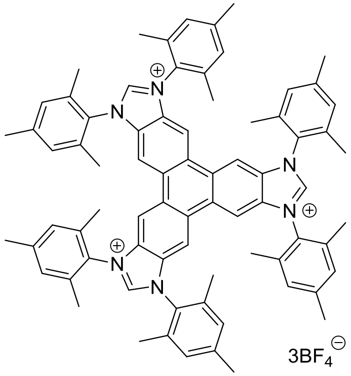
^{1}H NMR of 1b (DMSO-d$_6$)



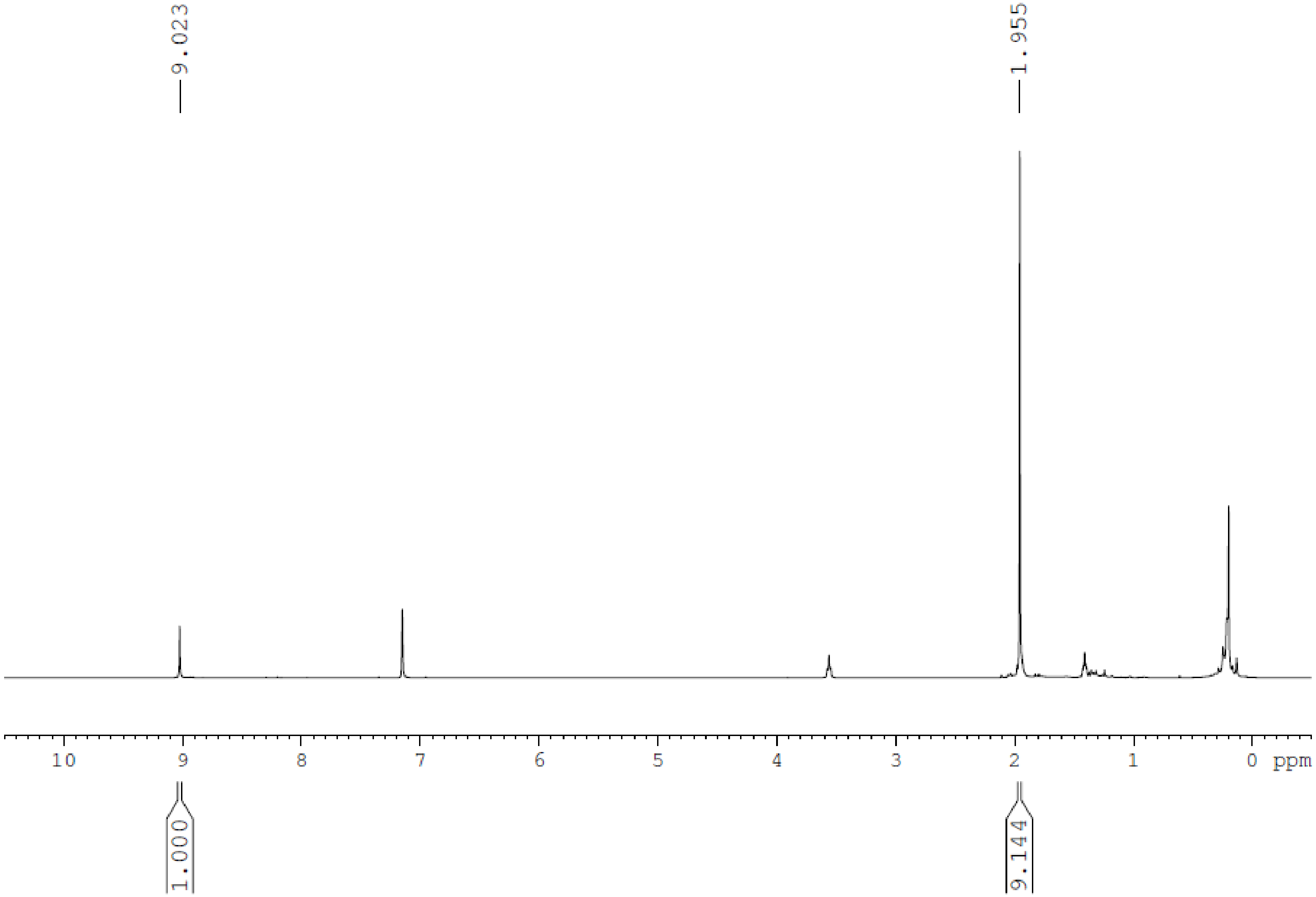


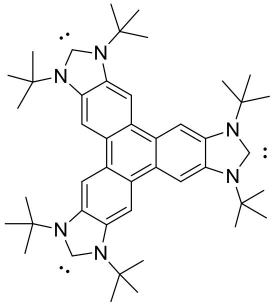
^{13}C NMR of 1b (DMSO-d_6)



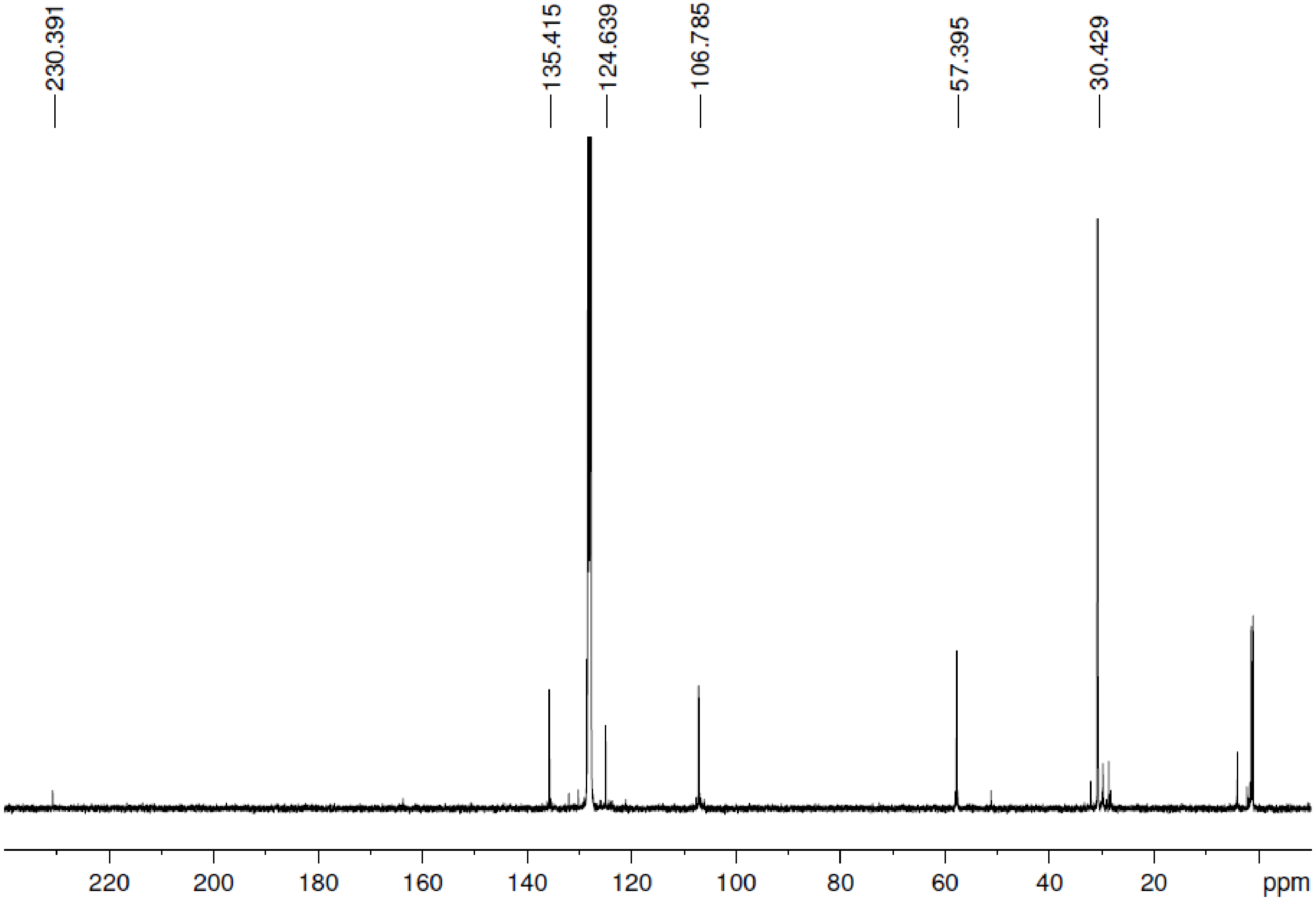


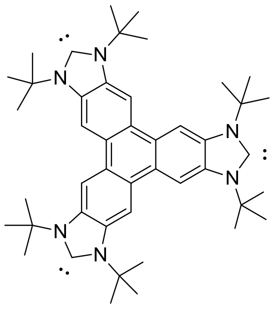
^{1}H NMR of 2a (C_6D_6)



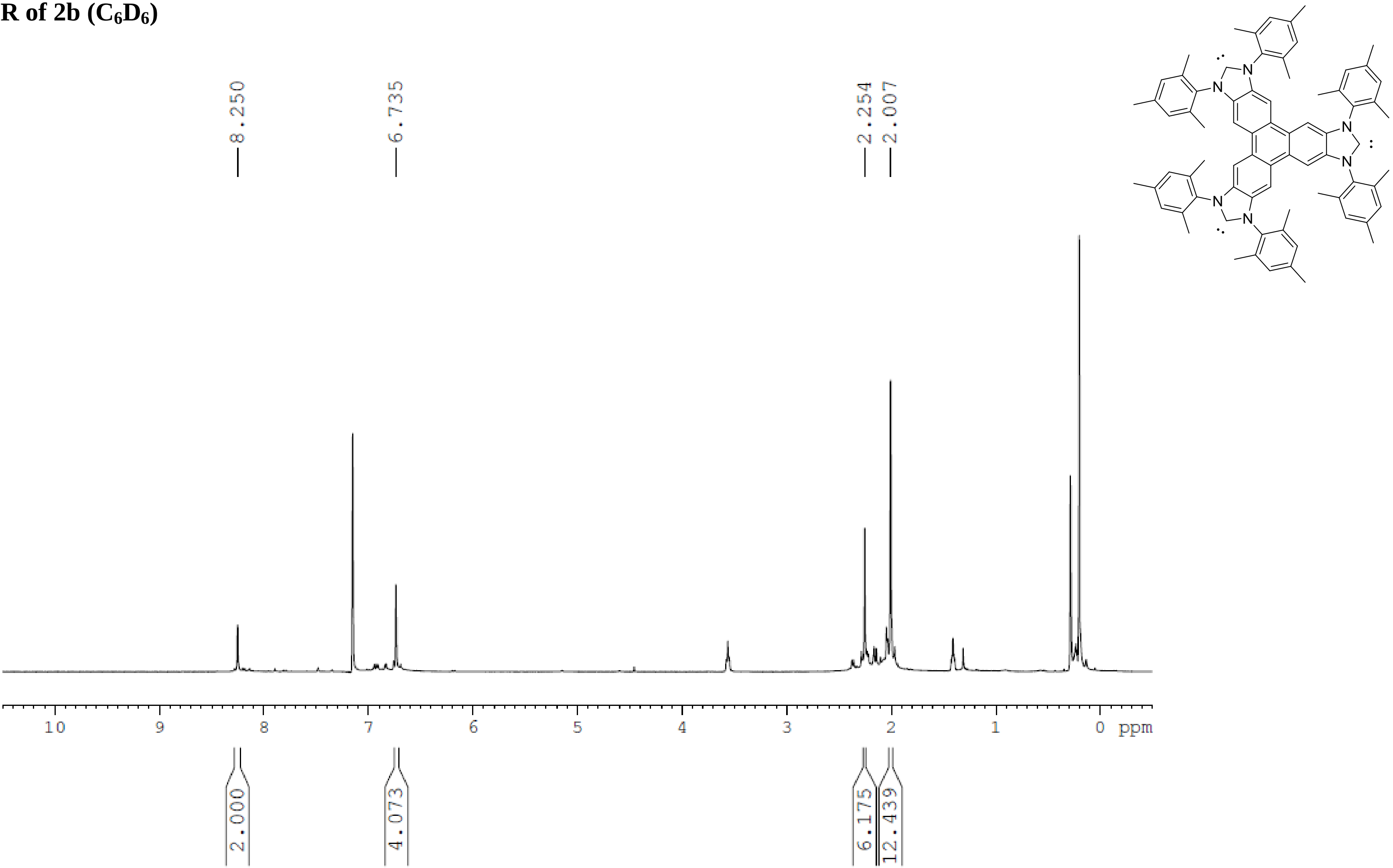


^{13}C NMR of 2a (C_6D_6)

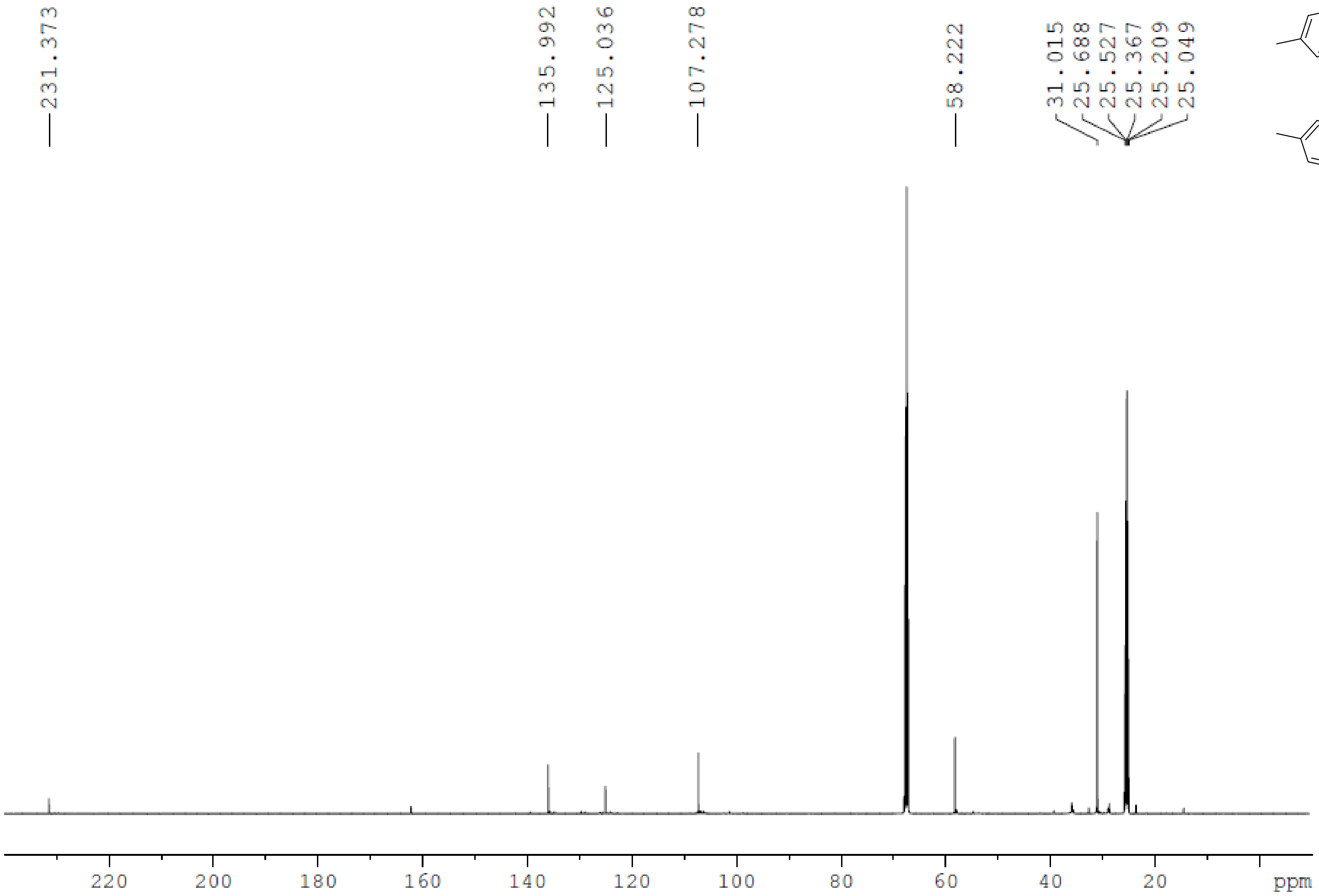


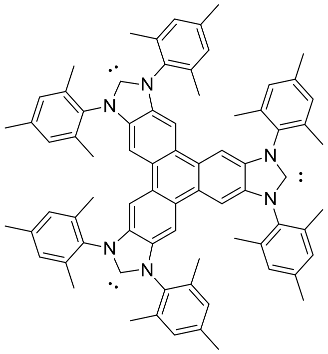


^{1}H NMR of 2b (C_6D_6)

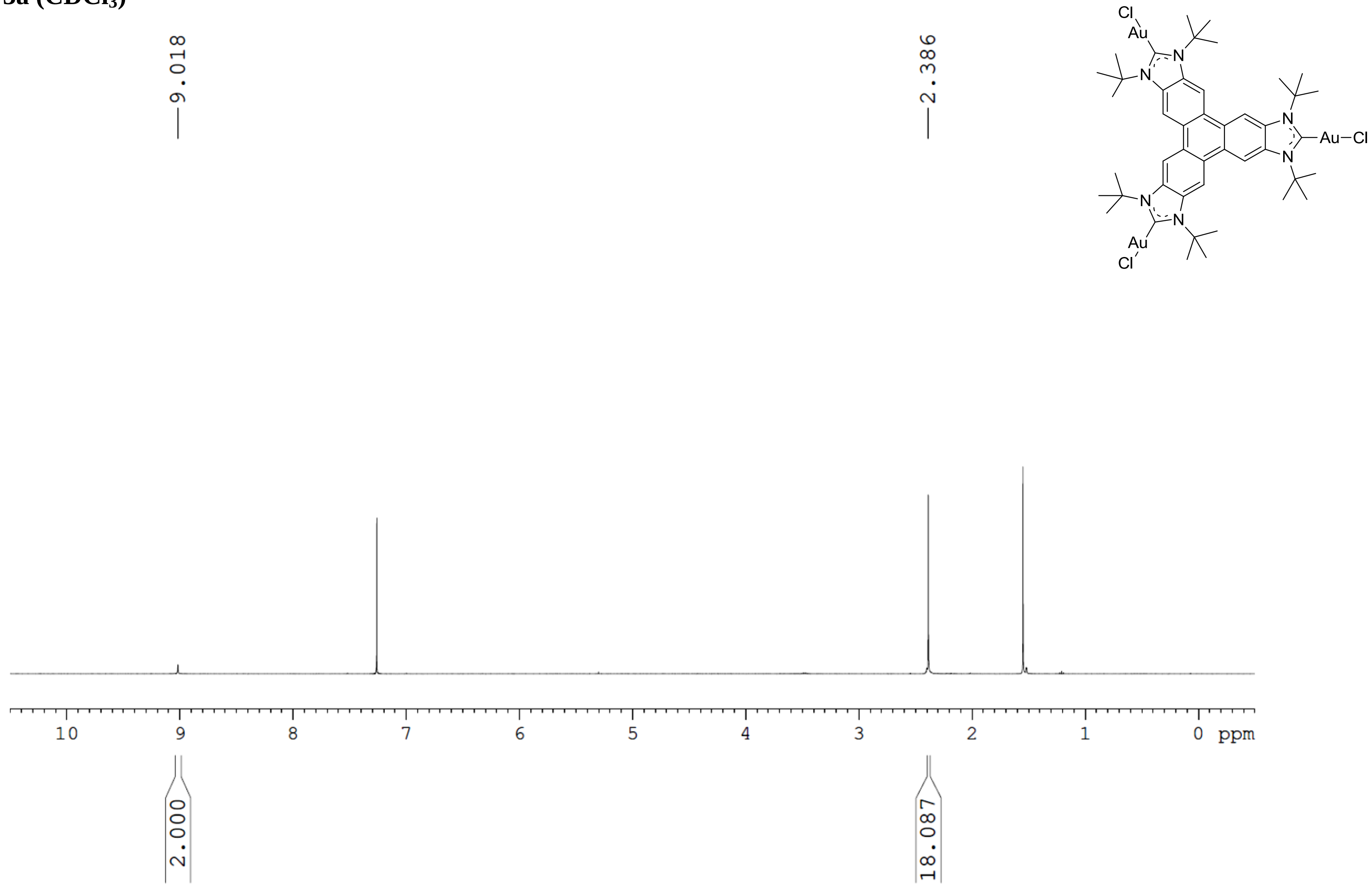


^{13}C NMR of 2b (THF-d_8)

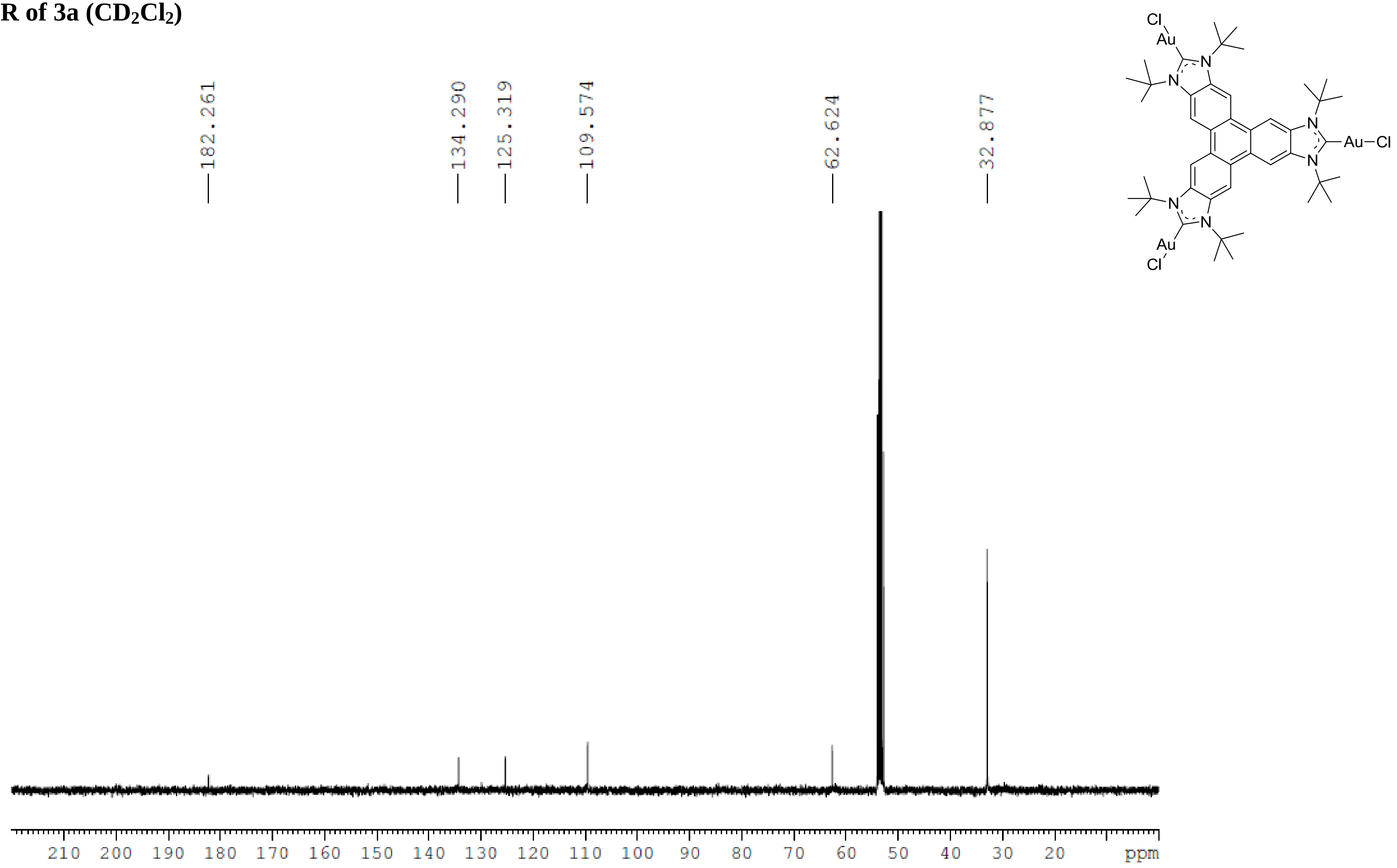




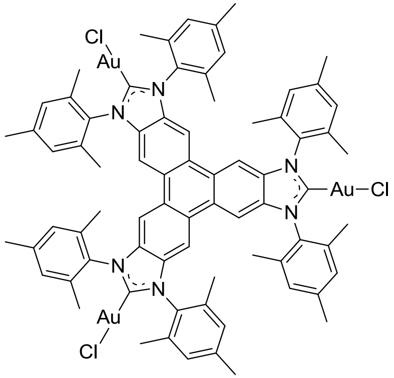
^{1}H NMR of 3a ($CDCl_3$)

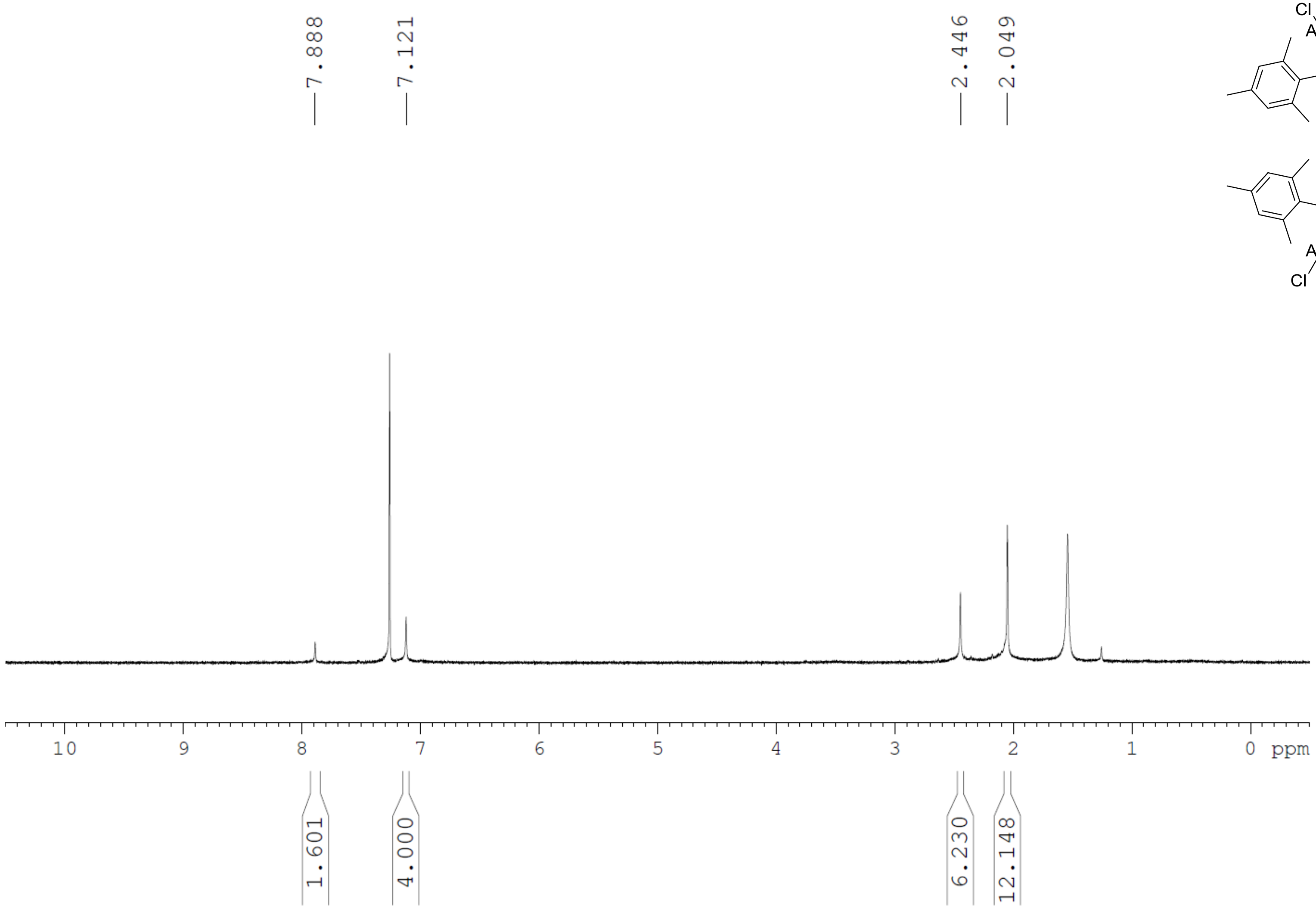


^{13}C NMR of 3a (CD_2Cl_2)



^{1}H NMR of 3b (CDCl$_3$)





^{13}**C NMR of 3b (CDCl$_3$)**