Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Modular Synthetic Strategies for Dipyrrolopyrazines

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General Information

Chemicals were purchased from commercial suppliers and used without further purification or synthesised by members of the *Hashmi* group using known literature procedures. Solvents were bought from commercial suppliers (abcr, Acros, Alfa Aesar, BLDPharm, Carbolution, Chempur, Fluka, Merck, Sigma Aldrich and TCI) and used without further purification. Dry solvents were dispensed from a Braun MB SPS-800 solvent purification system and used directly. Deuterated solvent for NMR spectroscopy were bought from Eurisiotop and Sigma Aldrich. Reactions excluding oxygen and moisture were performed using standard air-free techniques under an atmosphere of dry nitrogen with a rotary oil pump.

Melting points (m.p.) were measured in open glass capillaries on a Stuart SMP10 melting point apparatus and are uncorrected.

Rf-values were determined by analytical thin layer chromatography (TLC) on aluminium sheets coated with silica gel produced by Macherey-Nagel (ALUGRAM® Xtra SIL G/25 UV254). Detection is accomplished using UV-light (254 and 365 nm).

Nuclear magnetic resonance spectroscopy (NMR) was performed at the department of organic chemistry under supervision of Dr. J. Graf. If not stated otherwise, all spectra were recorded at room temperature. As measuring devices, the BRUKER AVANCE DRX-300, BRUKER AVANCE III 400, BRUKER AVANCE III 500, BRUKER AVANCE III 600 and Bruker Avance Neo 700 were used. Spectra were internally referenced to residual deuterated solvent. Chemical shifts are given in ppm and coupling constants are given in Hz.

In **^{1}H-NMR** spectra the following abbreviations are used to describe the observed multiplicities: “s” (singlet), “d” (doublet), “t” (triplet), “q” (quartet), “qi” (quintet), “m” (multiplet), “dd” (doublet of a doublet). **^{13}C-NMR** spectra are proton decoupled and were interpreted with the help of DEPT- and/or 2D-spectra. The following abbreviations are used to describe the observed carbon multiplicities: “s” quaternary carbon, “d” CH carbon “t” CH_2 carbon and “q” CH_3 carbon. All spectra were analysed using MestReNova 14.2.

Mass spectrometry (MS) and **high-resolution mass spectrometry (HR/MS)** were recorded at the mass spectrometry facility of the department of organic chemistry under supervision of Dr. J. Gross on the following spectrometers JEOL AccuTOF GCx (EI), Bruker ApexQe hybrid 9.4 T FT-ICR (ESI, MALDI, DART), Finnigan LCQ (ESI), Bruker AutoFlex Speed (MALDI) and Bruker timsTOFfleX (ESI, MALDI).

For **flash column chromatography** silica gel (Sigma-Aldrich, pore size 60 Å, 70-230 mesh, 63-200 μm) was used as stationary phase. As eluents different mixtures of petroleum ether (PE), ethyl acetate (EA) or dichloromethane (DCM) were used.

Infrared spectroscopy (IR) was performed using a FT-IR Bruker LUMOS with a Germanium ATR-crystal. The most significant bands are reported in wavenumbers (cm^{-1}) and solvent or matrix are mentioned in brackets.

Ultraviolet/Vis (UV/VIS) absorption spectra were measured on a JASCO V-670 spectrometer.

UV-Vis spectra (UV/VIS) were recorded on a Jasco UV-Vis V-660.

Fluorescence spectra were recorded on a Jasco FP6500. Quantum yields (QY) were recorded on a PTI QuantaMaster 40 with Ulbricht Sphere.

X-ray crystallography was carried out at the chemistry department of Heidelberg University under the supervision of Dr. F. Rominger on the following instruments: Bruker Smart APEX II Quazar (with Momicrosource) and Stoe Stradivari (with Co-microsource and Pilatus detector). The structures were processed with Mercury 4.3.0.3.

TGA/DSC were conducted with the Mettler Toledo TGA/DSC1 STARe System in 40-µl Al crucibles for the temperature range 30 – 400 °C.

General Procedures

GP1 Sonogashira

A baked-out Schlenk flask was evacuated and backfilled with nitrogen three times. In this flask, a mixture of equal parts of anhydrous THF and Et_3N was degassed and aryl halide (1.00 eq.) and $PdCl_2(PPh_3)_2$ (10 mol%) were dissolved and the mixture was degassed again. Afterwards CuI (4 mol%) and the corresponding alkyne (2.20 eq.) were added and mixture was stirred at 60 °C overnight. The solvent was removed, the crude product was adsorbed onto silica gel, purified using flash column chromatography, followed by centrifugation with 3x 4 mL pentane and 1x 4 mL MeOH and then dried under vacuum.

GP2 Sonogashira

A baked-out Schlenk flask was evacuated and backfilled with nitrogen three times. In this flask a mixture of equal parts anhydrous THF and Et_3N was degassed and aryl halide (1.00 eq.) and $PdCl_2(PPh_3)_2$ (10 mol%) were dissolved and the mixture was degassed again. Afterwards CuI (4.00 mol%) and the corresponding alkyne (2.20 eq.) were added and mixture was stirred at 70 °C for 48 h. The solvent was removed, the crude product was adsorbed onto silica gel, purified using flash column chromatography and dried under vacuum.

GP3 Cu(I)-cyclisation

1 eq. of **BA** is cyclised with 0.20 eq. CuI in a mixture of 1:1 THF/Et_3N at 70 °C overnight. The solvent is removed under vacuum and the crude product purified *via* flash column chromatography on silica gel.

GP4 Au(I)-cyclisation

1 eq. of **BA** is cyclised with 0.10 eq. $IPrAuNTf_2$ in DCE at 60 °C overnight. After removing the solvent under vacuo, the crude product was centrifuged with 3x pentane and 1x MeOH to afford the product.

Optimisation Screenings

Prior the described Route for **DBC** in the manuscript (Scheme 2). The first approach towards **DBC** started by using 2,5-dibromo-3,6-dichloropyrazine**.** The conditions for the Buchwald-Hartwig reaction were optimised using this precursor and then applied to *tert*-butyl (5-bromo-3,6-dichloropyrazin-2-yl)carbamate.

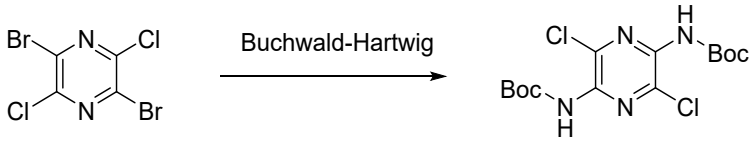


Table 1: Buchwald-Hartwig Screening prior to Scheme 2, we optimised with the precursor 2,5-dibromo-3,6-dichloropyrazine. *Mono coupled product **3**. Screening reactions were carried out on a 326 µmol scale with 1.00 eq. (100.0 mg) of 2,5-dibromo-3,6-dichloropyrazine. The given yields constitute isolated yields after flash column chromatography.

Entry	**Ligand**	**base**	***Eq.*** **$Pd(OAc)_2$**	***Eq.*** ***Ligand***	***Eq.*** ***base***	***time*** **(h)**	***T*** **(°C)**	***Yield*** ***(%)***
1	-	Cs_2CO_3	-	-	3.00	24	80	-
2	-	Cs_2CO_3	-	-	3.00	96	80	-
3	-	Cs_2CO_3	-	-	3.00	96	100	-
4	DPEPhos	KO^{t}Bu	0.03	0.03	2.10	24	rt	
5	DPEPhos	KO^{t}Bu	0.10	0.10	2.10	24	60	21*
6	XPhos	KO^{t}Bu	0.05	0.05	2.10	24	rt	-
7	XantPhos	KO^{t}Bu	0.05	0.05	2.10	24	rt	-
8	XantPhos	KO^{t}Bu	0.05	0.1	2.10	24	100	8
9	XantPhos	Cs_2CO_3	0.05	0.10	2.10	48	100	11
10	XantPhos	Cs_2CO_3	0.06	0.10	3.00	96	60	10
11	XantPhos	KO^{t}Bu	0.06	0.8	3.00	24	80	17
12	**XantPhos**	**KO^{t}Bu**	**0.06**	**0.8**	**3.00**	**48**	**60**	**24**
13	XantPhos	NaOMe	0.06	0.8	3.00	48	60	-

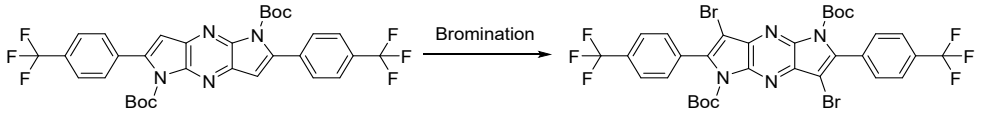


Table 2: Bromination Screening. Entry 4.: 19% of mono-brominated product (NMR yield). Screening reactions were carried out on a 15.5 µmol scale with 1.00 eq. (10.0 mg) of **DPPB2**. 2.20 eq. of NBS (1.76 mg, 30.9 µmol) were used as a bromination agent. NMR yields are given.[2]

entry	t (°C)	Time (h)	solvent	Yield A (%)
1	rt	0.5	$CHCl_3$	-
2	rt	3	$CHCl_3$	-
3	50	6	$CHCl_3$	-
4	50	24	$CHCl_3$	19*
5	**75**	**5**	**MeCN**	**quant.**

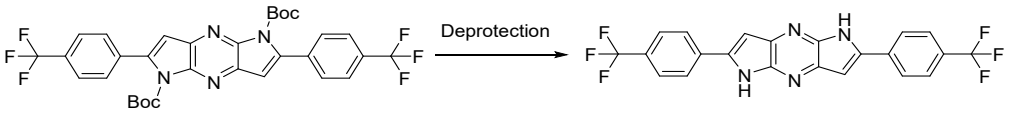


Table 3: Screening Deprotection. Screening reactions were carried out on a 15.5 µmol scale with 1.00 eq. (10.0 mg) of **DPPB2**. NMR yields are given. The given yields for entry 3 & 6 constitute isolated yields after flash column chromatography.

entries	Reagent	t (°C)	Time (h)	solvent	Yield (%)
1	TBAF[3]	80	0.5	THF	10
2	TBAF[3]	70	5	THF	50
2	-	180^{vacuo}	3	-	Decomp.
3	**$(COCl)_2$[4]**	**rt.**	**24**	**MeOH**	**80**
4	HCl[5]	rt.	3	Dioxane	20
5	HCl[5]	rt.	3	EtOH	10
6	**TMSOTf / 2,6-lutidine[6]**	**0 °C – rt.**	**5**	**DCM**	**71**
7	TFA[7]	0 °C – rt.	5	DCM	42

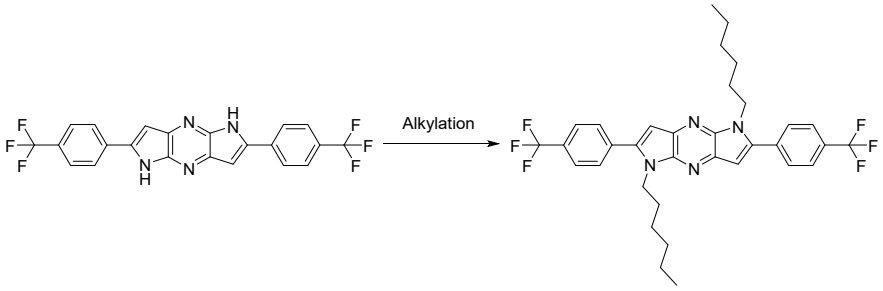
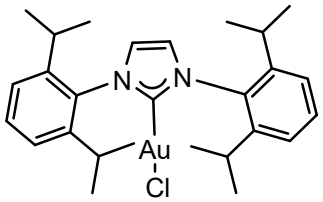


Table 4: Screening reactions were carried out on a 67.2 µmol scale with 1.00 eq. (30.0 mg) of **DPP2**. The given yields constitute isolated yields after flash column chromatography.[8]

entry	base	alkylhalide	T (°C)	Time (h)	solvent	Yield (%)
1	4 eq.KO*t*Bu	20 eq. 1-iodohexane	rt	2	DMSO	mixture
2	6 eq.KO*t*Bu	20 eq. 1-iodohexane	rt	24	DMSO	mixture
3	3 eq.KO*t*Bu	8 eq. 1-bromohexane	Rt	24	THF	mixture
4	3 eq.KO*t*Bu	40 eq. 1-bromohexane	45	96	THF	8
5	3 eq.KO*t*Bu	20 eq. 1-bromohexane	100	24	toluene	11
6	3.2 eq.K_2CO_3	2.8 eq. 1-bromohexane	80	48	DMF	35
7	**6 eq. Cs_2CO_3**	**2.2 eq. 1-bromohexane**	**rt.**	**24**	**DMF**	**79**

Synthesis of Compounds

IPrAuCl

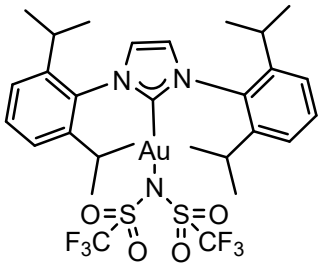


According to the Grela et al., [AuCl(DMS)] (1.00 g, 2.36 mmol, 1.00 eq.), IPrHCl (746 mg, 2.59 mmol, 1.10 eq.) and K_2CO_3 (488 mg, 3.54 mmol, 1.50 eq.) were suspended in 75 mL acetone and stirred at rt overnight. The solvent was evaporated *in vacuo* and then absorbed onto Celite®. After purification via flash column chromatography (DCM) 80% of a colorless solid were obstained (1.17 g, 1.89 mmol).

^{1}H NMR (301 MHz, CD_2Cl_2) δ 7.56 (t, *J* = 7.8 Hz, 2H), 7.34 (d, *J* = 7.8 Hz, 4H), 7.23 (s, 2H), 2.56 (d, *J* = 6.5 Hz, 4H), 1.33 (d, *J* = 6.9 Hz, 12H), 1.22 (d, *J* = 6.9 Hz, 12H).

The spectroscopic data correspond to those previously reported in the literature.[9]

IPrAuNTf$_2$



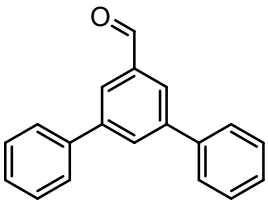
According to Grela et al., [IPrAuCl] (1.00 g, 1.61 mmol, 1.00 eq.) was dissolved in 20 mL DCM at rt in the absence of light. Then 1.05 eq. of $AgNTf_2$ (656 µmol, 1.05 eq.) were added and the mixture was stirred under ultra-sonification for 15 min. The excess AgCl was removed via a short filtration over Celite ® to yield 1.21 g of the catalyst (1.40 mmol, 87%).

^{1}H NMR (301 MHz, $CDCl_3$) δ 7.54 (t, *J* = 7.8 Hz, 2H), 7.36 – 7.25 (m, 6H), 2.47 (hept., *J* = 6.8 Hz, 4H), 1.31 (d, *J* = 6.9 Hz, 12H), 1.23 (d, *J* = 6.9 Hz, 12H)

^{19}F NMR (283 MHz, $CDCl_3$) δ -75.99 (s, 6F).

The spectroscopic data correspond to those previously reported in the literature.[9]

[1,1':3',1''-Terphenyl]-5'-carbaldehyde



A degassed solution of $Pd(OAc)_2$ (85.1 mg, 378 µmol, 0.10 eq.) and PPh_3 (398 mg, 1.52 mmol, 0.40 eq.) in toluene/H_2O (50 mL, 1:1) was stirred for 10 minutes at room temperature. 3,5-Dibromobenzaldehyde (1.00 g, 3.79 mmol, 1 eq.), phenylboronic acid (1.39 g, 11.4 mmol, 3.00 eq.), and Na_2CO_3 (1.20 g, 11.4 mmol, 3.0 eq.) were sequentially added to the reaction mixture in a Schlenk flask. The reaction mixture was then heated to 100°C overnight and then let to cool to rt. The crude reaction mixture was washed with water, extracted with EtOAc, dried with $MgSO_4$ and then subjected to flash-column (PE/EA 50:1) yielding 91% (890 mg, 3.45 mmol) of a colorless solid.

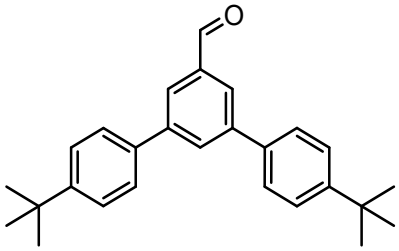
R_f (DCM) = 0.57

^{1}H NMR (300 MHz, $CDCl_3$) δ 10.16 (s, 1H), 8.08 (s, 3H), 7.69 (d, *J* = 8.0 Hz, 4H), 7.64 – 7.37 (m, 6H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 192.47 (d, 1C), 142.91 (s, 2C), 139.87 (s, 2C), 137.58 (d, 1C), 131.99 (d, 1C), 129.19 (d, 4C), 128.28 (d, 2C), 127.39 (d, 4C), 127.32 (d, 2C).

The spectroscopic data correspond to those previously reported in the literature.[10]

4,4''-Di-*tert*-butyl-[1,1':3',1''-terphenyl]-5'-carbaldehyde



A degassed solution of $Pd(OAc)_2$ (85.1 mg, 378 µmol, 0.1 eq.) and PPh_3 (397 mg, 1.52 mmol, 0.40 eq.) in toluene/H_2O (50 mL, 1:1) was stirred for 10 minutes at room temperature. 3,5-Dibromobenzaldehyde (1.00 g, 3.79 mmol, 1.00 eq.), (4-(*tert*-butyl)phenyl)boronic acid (2.02 g, 11.37 mmol, 3.00 eq.), and Na_2CO_3 (1.20 g, 11.37 mmol, 3.00 eq.) were sequentially added to the reaction mixture in a Schlenk flask. The reaction mixture was then heated to 100 °C overnight and then let to cool to rt. The crude reaction mixture was washed with water, extracted with EtOAc, dried with $MgSO_4$ and then subjected to flash-column chromatography (PE/EA 100:1) yielding 88% (622 mg, 1.60 mmol) of a colorless oil.

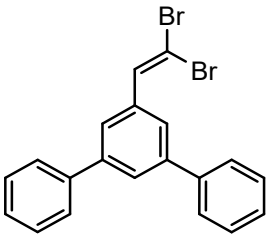
R_f (DCM) = 0.50

^{1}H NMR (300 MHz, $CDCl_3$) δ 10.14 (s, 1H), 8.04 (s, 3H), 7.63 (d, *J* = 8.1 Hz, 4H), 7.52 (d, *J* = 8.6 Hz, 4H), 1.39 (s, 18H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 192.24 (d, 1C), 151.10 (s, 2C), 142.37 (s, 1C), 137.27 (s, 2C), 136.74 (s, 2C), 131.35 (d, 1C), 126.72 (d, 4C), 126.61 (d, 2C), 125.83 (d, 4C), 34.48 (s, 2C), 31.18 (q, 6C).

The spectroscopic data correspond to those previously reported in the literature.[11]

5'-(2,2-Dibromovinyl)-1,1':3',1''-terphenyl



In a baked-out Schlenk flask, 2.00 equivalents of carbon tetrabromide (770 mg, 2.32 mmol) was added to a solution of 4.00 equivalents of triphenylphosphine (1.22 g, 4.65 mmol) in 20 mL of anhydrous DCM at 0 °C. The resulting mixture was stirred at 0 °C for 30 min until completely dissolved. In another flame dried Schlenk flask, 1.00 equivalent of [1,1':3',1''-terphenyl]-5'-carbaldehyde (300 mg, 1.16 mmol) was dissolved in 10 mL of anhydrous DCM. This solution was then transferred to the first Schlenk flask via a Teflon cannula. The combined reaction mixture was stirred at 0 °C for 30 minutes and then at room temperature for an additional 3 h. The reaction quenched with a saturated solution of $NaHCO_3$. The resulting phases were separated, and the aqueous layer was extracted with DCM. The combined organic layers were dried with $MgSO_4$, and the solvent was then removed under reduced pressure. The crude product was then purified *via* flash-column chromatography (PE:EA 200:1) to afford 327 mg (789 µmol, 68%) of a colorless solid.

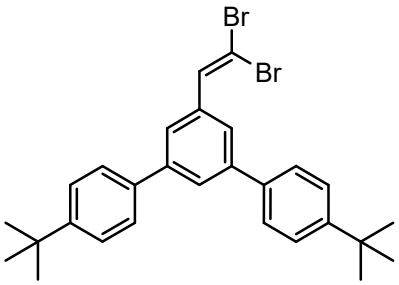
R_f (DCM) = 0.84

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.74 (s, 2H), 7.65 – 7.59 (m, 4H), 7.48 (t, *J* = 7.5 Hz, 4H), 7.39 (t, *J* = 7.3 Hz, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 142.20 (s, 2C), 140.74 (s, 2C), 136.91 (d, 1C), 136.43 (d, 2C), 129.05 (d, 4C), 127.87 (d, 2C), 127.42 (d, 4C), 126.41 (d, 2C), 126.23 (d, 2C), 90.59 (s, 1C).

The spectroscopic data correspond to those previously reported in the literature.[10]

4,4''-Di-*tert*-butyl-5'-(2,2-dibromovinyl)-1,1':3',1''-terphenyl



In a baked-out Schlenk flask, 2.00 equivalents of carbon tetrabromide (895 mg, 2.70 mmol) was added to a solution of 4.00 equivalents of triphenylphosphine (1.42 g, 5.40 mmol) in 20 mL of anhydrous DCM at 0 °C. The resulting mixture was stirred at 0 °C for 30 min until completely dissolved. In another flame dried Schlenk flask, 1.00 equivalent of 4,4''-di-*tert*-butyl-[1,1':3',1''-terphenyl]-5'-carbaldehyde (500 mg, 1.35 mmol) was dissolved in 10 mL of anhydrous DCM. This solution was then transferred to the first Schlenk flask via a Teflon cannula. The combined reaction mixture was stirred at 0 °C for 30 minutes and then at room temperature for an additional 3 h. The reaction was quenched with a saturated solution of $NaHCO_3$. The resulting phases were separated, and the aqueous layer was extracted with DCM. The combined organic layers were dried with $MgSO_4$, and the solvent was then removed under reduced pressure. The crude product was then purified *via* flash-column chromatography (PE:EA 200:1) to afford 615 mg (1.17 mmol, 87%) of a colorless oil.

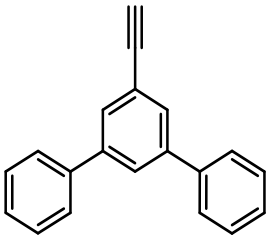
R_f (DCM) = 0.90

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.73 (s, 2H), 7.63 – 7.54 (m, 5H), 7.51 (d, *J* = 8.6 Hz, 4H), 1.40 (s, 18H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 150.90 (s, 2C), 141.93 (s, 2C), 137.88 (s, 2C), 137.06 (d, 1C), 136.23, 127.03 (d, 4C), 126.16 (d, 1C), 125.98 (d, 4C), 125.84 (d, 2C), 90.22 (s, 1C), 34.74 (s, 2C), 31.52 (q, 6C)).

The spectroscopic data correspond to those previously reported in the literature.[11]

5'-Ethynyl-1,1':3',1''-terphenyl



In a flame dried Schlenk flask, 1.00 equivalent of 5'-(2,2-dibromovinyl)-1,1':3',1''-terphenyl (500 mg, 1.21 mmol) was dissolved in 20 mL of tetrahydrofuran (THF) and cooled to -78 °C. Then, 2.50 equivalents of *n*-BuLi solution (2.5 M in hexane, 1.21 mL, 3.02 mmol) were added dropwise, and the resulting solution was stirred overnight. The reaction was quenched by addition of an ice-cold saturated solution of NH_4Cl. The resulting phases were separated, and the aqueous layer was extracted with DCM. The combined organic layers were then dried with $MgSO_4$. The solvent was removed under reduced pressure, and the crude product was filtered through a short silica gel plug using a DCM as eluent. The solvent was evaporated again under reduced pressure to give the desired compound as a colorless oil (292 mg, 1.15 mmol, 95% yield).

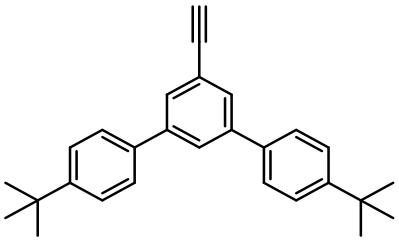
$\mathbf{R_f}$ (DCM) = 0.91

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.71 (s, 2H), 7.63 (d, *J* = 7.0 Hz, 4H), 7.52 – 7.43 (m, 4H), 7.39 (t, *J* = 7.3 Hz, 2H), 3.13 (s, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 142.18 (s, 2C), 140.38 (s, 2C), 129.83 (d, 2C), 129.05 (d, 4C), 127.95 (d, 2C), 127.36 (d, 4C), 126.85 (d, 1C), 123.17 (q, 1C), 83.75 (s, 1H), 77.36 (d, 1H).

The spectroscopic data correspond to those previously reported in the literature.[10]

4,4''-Di-*tert*-butyl-5'-ethynyl-1,1':3',1''-terphenyl



In a flame dried flask, 1.00 equivalent of 4,4''-di-*tert*-butyl-5'-(2,2-dibromovinyl)-1,1':3',1''-terphenyl (500 mg, 949 µmol) was dissolved in 20 mL of tetrahydrofuran (THF) and cooled to -78 °C. Then, 2.50 equivalents of *n*-BuLi solution (2.5 M in hexane, 949 mmL, 2.37 mmol) were added dropwise, and the resulting solution was stirred overnight. The reaction was quenched by addition of an ice-cold saturated solution of NH_4Cl. The resulting phases were separated, and the aqueous layer was extracted with DCM. The combined organic layers were then dried with $MgSO_4$. The solvent was removed under reduced pressure, and the crude product was filtered through a short silica gel plug using a DCM as eluent. The solvent was evaporated again under reduced pressure to give the desired compound as a colorless oil (313 mg, 854 µmol, 90% yield).

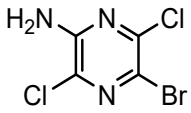
R_f (DCM) = 0.89

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.68 (s, 2H), 7.57 (d, *J* = 8.7 Hz, 4H), 7.49 (d, *J* = 8.2 Hz, 4H), 3.12 (s, 1H), 1.38 (s, 18H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 151.01 (s, 2C), 141.91 (s ,2C), 137.51 (s, 2C), 129.44 (d, 2C), 126.98 (d, 4C), 126.58 (d, 1C), 125.99 (d, 4C), 122.98 (s, 1C), 83.96 (s, 1C), 77.36 (d, 1C), 34.75 (s, 2C), 31.51 (q, 6C).

The spectroscopic data correspond to those previously reported in the literature.[11]

5-Bromo-3,6-dichloropyrazine 2-amine (2)

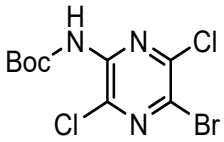


5-Bromo-3-chloropyrazine 2-amine (10.1 g, 48.7 mmol, 1.00 eq.) was dissolved in dry methanol (300 mL). NCS (7.21 g, 54.0 mmol, 1.10 eq.) was added to the mixture and the reaction was stirred at 50 °C for 24 h. The mixture was cooled to room temperature and distilled water (200 mL) was added, the precipitate was filtered off and washed with distilled water (300 mL) and petrol ether (150 mL). The product was dried under vacuum. The product was obtained as an off-white solid (10.2 g, 41.8 mmol, 86 %).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 5.12 (s, 2H).

The spectroscopic data correspond to those previously reported in the literature.[5]

***Tert*-butyl (5-bromo-3,6-dichloropyrazin-2-yl)carbamate (3)**



In a round-bottom flask, 1.00 equivalent of 5-bromo-3,6-dichloropyrazin-2-amine (8.00 g, 32.9 mmol) was dissolved in a mixture of THF/Et_3N (200 mL/40 mL). To this solution were added 3.5 equivalents of Boc_2O (25.2 g, 115 mmol) and 0.10 equivalents of 4-DMAP (402 mg, 3.29 mmol). The resulting reaction mixture was stirred at rt overnight. After completion of the reaction, the solvent was removed in vacuo. The crude product was washed with water and the aqueous layer was extracted with ethyl acetate and then purified *via* flash-column chromatography (PE:DCM 50:1) to yield 96% of *tert*-butyl (5-bromo-3,6-dichloropyrazin-2-yl)carbamate (10.85 g, 31.6 mmol)

R_f (DCM) = 0.78

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.43 (s, 9H).

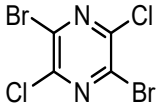
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 148.89 (s, 2C), 146.33 (s, 1C), 144.32 (s, 1C), 143.99 (s, 1C), 136.50 (s, 1C), 85.15 (s, 1C), 27.93 (q, 3C).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2987, 2937, 1777, 1720, 1505, 1458, 1384, 1370, 1307, 1270, 1240, 1149, 1111, 1044, 1032, 851, 812, 773, 640, 614.

HR/MS (EI^+): *m/z* calcd. for $C_9H_{10}N_3O_2Cl_2Br^+$: [M-Boc$^+$] 340.9328, found: 340.9353.

m.p.[°C]**:** 109 – 114.

2,5-Dibromo-3,6-dichloropyrazine



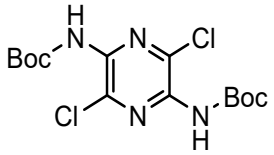
5-Bromo-3,6-dichloropyrazine 2-amine (10.2 g, 41.8 mmol, 1.00 eq.) was dissolved in THF (100 mL). The mixture was cooled to 0 °C and HBr (48 % in water, 200 mL) was slowly added. Afterwards $NaNO_2$ (7.21 g, 104.5 mmol, 2.50 eq.) was added over 75 min and the mixture was stirred at 0 °C for another 1.5 h. Ice cold water (200 mL) and KOH (100 g) were added to quench the reaction and the mixture was extracted with ethyl acetate. The organic phases were collected, washed with distilled water, dried over $MgSO_4$ and the solvent was removed under reduced pressure. The product was purified by flash column chromatography (SiO_2, PE/EA 20:1). The solvent was removed under reduced pressure and the product was dried under vacuum. The product was obtained as a colorless solid (10.13 g, 33.0 mmol, 79 %).

R_f (PE/EA 20:1) = 0.70

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 146.84 (s, 2C), 136.49 (s, 2C).

The spectroscopic data correspond to those previously reported in the literature.[5]

Di-*tert*-butyl (3,6-dichloropyrazine-2,5-diyl) dicarbamate (DBC)



Tert-butyl (5-bromo-3,6-dichloropyrazin-2-yl)carbamate (3.00 g, 8.75 mmol, 1.00 eq) was dissolved in dry, degassed toluene (36 mL) under nitrogen atmosphere. Then *tert*-butyl carbamate (1.74 g, 14.8 mmol, 1.70 eq.), KO^tBu (2.06 g, 18.4 mmol, 2.10 eq.), $Pd(OAc)_2$ (117 mg, 524 µmol, 6 mol-%) and Xantphos (404 mg, 699 µmol, 8 mol-%) were added and the mixture was stirred for 48 h at 60 °C under a N_2-atmosphere. The mixture was filtered over silica gel and the filter washed with EA and DCM. The solvent of the filtrate was removed under vacuum, the crude product was adsorbed onto silica gel and purified using flash column chromatography (SIO_2, PE/EA 10:1). The solvent was removed under reduced pressure and the *tert*-butyl carbamate remaining in the product was sublimated off (50 °C, 10^{-2} mbar). The product was obtained as an off-white solid (1.86 g, 4.90 mmol, 56 %).

R_f (PE/EA 5:1) = 0.40

^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.11 (s, 2H), 1.53 (s, 18H).

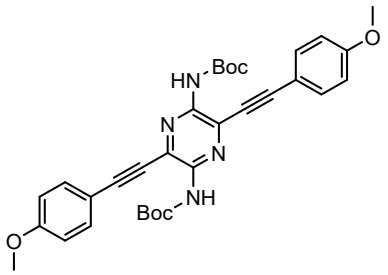
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ [ppm] = 150.2 (s, 2C), 139.1 (s, 2C), 133.3 (s, 2C), 82.7 (s, 2C), 28.3 (q, 6C).

HR/MS (EI$^+$): *m/z* calcd. For $C_{14}H_{20}Cl_2N_4O_4^+$: [M^+] 378.0856, found: 378.0856, correct isotope distribution.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3319, 2976, 2936, 1719, 1507, 1391, 1365, 1320, 1243, 1135, 1049, 1022, 942, 836, 763.

m.p. [°C]: 189 – 194.

di-tert-butyl (3,6-bis((4-methoxyphenyl)ethynyl)pyrazine-2,5-diyl)dicarbamate (BA1)



According to **GP1**: A mixture of 6 mL THF/Et_3N (1:1) was degassed in a baked out Schlenk flask for 20 min. **DBC** (100 mg, 264 µmol, 1.00 eq.), $Pd(PPh_3)_2Cl_2$ (18.5 mg, 26.4 µmol, 0.10 eq.) and 1-ethynyl-4-methoxybenzene (139 mg, 1.05 mmol, 4.00 eq.) were subsequently added. After stirring for 5 min CuI (2.51 mg, 13.8 µmol, 0.04 eq.) was added last. After stirring for 24 h at 60 °C the reaction was treated according to **GP1**. After purification via flash-column chromatography (PE/EA 10:1 -> EA), the obtained orange solid was additionally centrifuged with 3 mL pentane (3x) and 3 mL MeOH (1x) to yield 114 mg (200 µmol, **76%**) of an orange solid.

R_f (PE/EA 3:1) = 0.45

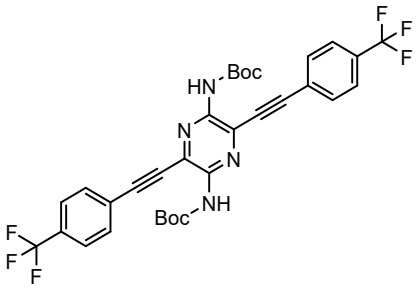
^{1}H NMR (301 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.9 Hz, 2H), 7.38 (s, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 3.85 (s, 6H), 1.55 (s, 18H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 160.98 (s, 2C), 150.80 (s, 2C), 143.96(s, 2C), 133.94 (d, 4C), 125.90 (s, 2C), 114.44 (d, 4C), 113.38 (s, 2C), 99.72 (s, 2C), 83.37 (s, 2C), 81.86 (s, 2C), 55.53 (q, 2C), 28.39 (q, 6C).
HR/MS (MALDI$^+$, DCTB): *m/z* calcd. for $C_{32}H_{34}N_4O_6^+$: [M$^+$] 570.2473, found: 570.2477.
IR(ATR)[cm^{-1}]: 3324, 2975, 2938, 2839, 2549, 2207, 1890, 1709, 1605, 1568, 1501, 1432, 1391, 1294, 1250, 1143, 1055, 1025, 908, 860, 830, 772, 729.
UV-Vis [nm]: 245, 290, 317, 408.

Fluorescence (DCM): λ_{Ex} = 315 nm, λ_{Max} = 454 nm; Φ = 90 %

m.p. [°C]: 220 – 225.

Di-*tert*-butyl (3,6-bis((4-(trifluoromethyl)phenyl)ethynyl)pyrazine-2,5-diyl)dicarbamate (BA2)



According to **GP1**: A mixture of 12 mL THF/Et_3N (1:1) was degassed in a baked out Schlenk flask for 20 min. **DBC** (250 mg, 659 µmol, 1.00 eq.), $Pd(PPh_3)_2Cl_2$ (46.3 mg, 65.9 µmol, 0.10 eq.) and 1-ethynyl-4-(trifluoromethyl)benzene (449 mg, 2.64 mmol, 4.00 eq.) were subsequently added. After stirring for 5 min CuI (5.02 mg, 26.4 µmol, 0.04 eq.) was added last. After stirring for 24 h at 60 °C the reaction was treated according to **GP1**. After purification via flash-column chromatography (PE/EA 10:1 -> EA), the obtained orange solid was additionally centrifuged with 3 mL pentane (3x) and 3 mL MeOH (1x) to yield 370 mg (573 µmol, **87%**) of a bright yellow powder.

R_f (PE/EA 1:1) = 0.61

$^1H\{^{19}F\}$ NMR (600 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.32 (s, 2H), 1.55 (s, 18H).

^{19}F NMR (283 MHz, $CDCl_3$) δ -63.10.

$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 150.52 (s, 2C), 144.30 (s, 2C), 132.35 (d, 4C), 131.46 (s, q, *J* = 32.9 Hz, 2C), 126.09 (s, 2C), 125.53 (d, q, *J* = 3.8 Hz, 4C)), 124.83 (s, 2C), 123.57 (s, d, *J* = 272.4 Hz, 2C), 97.06 (s, 2C), 85.72 (s, 2C), 82.14 (s, 2C), 28.16 (q, 6C).

HR/MS (MALDI$^+$, DCTB): *m/z* calcd. for $C_{32}H_{28}N_4F_6O_4Na^+$: [$M^+$] 669.1907, found: 669.1916.

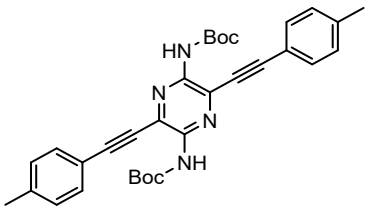
IR(ATR)[cm^{-1}]: 3322, 3013, 2977, 2212, 1712, 1614, 1508, 1439, 1393, 1368, 1320, 1253.

UV-Vis [nm]: 251, 265, 300, 392.

Fluorescence (DCM): λ_{Ex} = 395 nm, λ_{Max} = 452 nm; Φ = 49%

m.p. [°C]: 222 – 227.

Di-*tert*-butyl (3,6-bis(p-tolylethynyl)pyrazine-2,5-diyl)dicarbamate (BA3)



According to **GP1**: A mixture of 10 mL THF/Et_3N (1:1) was degassed in a baked out Schlenk flask for 20 min. **DBC** (170 mg, 448 µmol, 1.00 eq.), $Pd(PPh_3)_2Cl_2$ (31.5 mg, 44.8 µmol, 0.10 eq.) and 1-ethynyl-4-methylbenzene (208 mg, 1.79 mmol, 4.00 eq.) were subsequently added. After stirring for 5 min CuI (4.27 mg, 22.41 µmol, 0.04 eq.) was added last. After stirring for 24 h at 60 °C the reaction was treated according to **GP1**. After purification via flash-column chromatography (PE/EA 10:1 -> EA), the obtained orange solid was additionally centrifuged with 3 mL pentane (3x) and 3 mL MeOH (1x) to yield 159 mg (295 µmol, **66%**) of a yellow powder.

R_f (PE/EA 4:1) = 0.23

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.1 Hz, 4H), 7.40 (s, 2H), 7.21 (d, *J* = 8.4 Hz, 4H), 2.40 (s, 6H), 1.55 (s, 18H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 150.78 (s, 2C), 144.13 (s, 2C), 140.54 (s, 2C), 132.22 (d, 4C), 129.54 (d, 4C), 125.93 (s, 2C), 118.33 (s, 2C), 99.72 (s, 2C), 83.71 (s, 2C), 81.94 (s, 2C), 28.40 (q, 6C), 21.84 (q, 2C).

HR/MS (MALDI$^+$, DCTB): *m/z* calcd. for $C_{32}H_{34}N_4O_4^+$: [M^+] 538.2575, found: 538.2576.

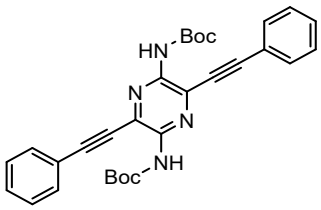
IR(ATR)[cm^{-1}]: 3331, 2981, 2935, 2228, 1721, 1476, 1404, 1371, 1260, 1229, 1150, 1061, 1027, 908, 870, 823, 785, 762, 739, 691, 641.

UV-Vis [nm]: 235, 265, 302, 394.

Fluorescence (DCM): λ_{Ex} = 300/395 nm, λ_{Max} = 447 nm; Φ = 84%

m.p. [°C]: 226 – 231.

Di-*tert*-butyl (3,6-bis(phenylethynyl)pyrazine-2,5-diyl)dicarbamate (BA4)



According to **GP1**: A mixture of 3 mL THF/Et_3N (1:1) was degassed in a baked out Schlenk flask for 20 min. **DBC** (50.0 mg, 131 µmol, 1.00 eq.), $Pd(PPh_3)_2Cl_2$ (9.25 mg, 13.1 µmol, 0.10 eq.) and ethynylbenzene (53.9 mg, 527 µmol, 4 eq.) were subsequently added. After stirring for 5 min CuI (1.00 mg, 5.27 µmol, 0.04 eq.) was added last. After stirring for 24 h at 60 °C the reaction was treated according to **GP1**. After purification via flash-column chromatography (PE/EA 10:1 -> EA), the obtained orange solid was additionally centrifuged with 3 mL pentane (3x) and 3 mL MeOH (1x) to yield 61.0 mg (119 µmol, **90%**) of a bright yellow powder.

R_f (PE/EA 1:1) = 0.40

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 – 7.60 (m, 4H), 7.47 – 7.38 (m, 8H), 1.55 (s, 18H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 150.78 (s, 2C), 144.24 (s, 2C), 132.30 (d, 4C), 130.05 (d, 2C), 128.76 (d, 4C), 126.02 (s, 2C), 121.37 (s, 2C), 99.30 (s, 2C), 84.10 (s, 2C), 82.05 (s, 2C), 28.40 (q, 6C).

HR/MS (MALDI$^+$, DCTB): *m/z* calcd. for $C_{30}H_{30}N_4O_4Na^+$: [M^+] 533.2159, found: 533.2170.

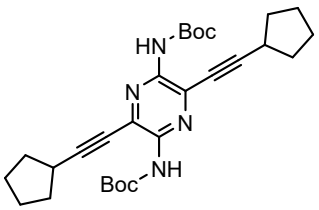
IR(ATR)[cm^{-1}]: 3331, 2981, 2935, 2228, 1721, 1476, 1404, 1371, 1260, 1229, 1150, 1061, 1027, 908, 870, 823, 785, 762, 739, 691, 641.

UV-Vis [nm]: 235, 265, 302, 394.

Fluorescence (DCM): λ_{Ex} = 300/395 nm, λ_{Max} = 447 nm; Φ = 84%

m.p. [°C]: 213 – 218.

Di-*tert*-butyl (3,6-bis(cyclopentylethynyl)pyrazine-2,5-diyl)dicarbamate (BA5)



According to **GP1**: A mixture of 6 mL THF/Et_3N (1:1) was degassed in a baked out Schlenk flask for 20 min. **DBC** (90.0 mg, 237 µmol, 1.00 eq.), $Pd(PPh_3)_2Cl_2$ (16.7 mg, 23.7 µmol, 0.10 eq.) and ethynylcyclopentane (89.4 mg, 949 µmol, 4 eq.) were subsequently added. After stirring for 5 min CuI (1.81 mg, 9.49 µmol, 0.04 eq.) was added last. After stirring for 24 h at 60 °C the reaction was treated according to **GP1**. After purification via flash-column chromatography (PE/EA 10:1 -> EA), the obtained orange solid was additionally centrifuged with 3 mL pentane (3x) and 3 mL MeOH (1x) to yield 93.9 mg (189 µmol, **80%**) of an orange solid.

R_f (PE/EA 3:1) = 0.45

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (s, 2H), 3.02 – 2.84 (m, 2H), 2.09 – 1.94 (m, 5H), 1.87 – 1.69 (m, 11H), 1.51 (s, 18H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 150.76 (s, 2C), 143.95 (s, 2C), 125.79 (s, 2C), 105.72 (s, 2C), 81.54 (s, 2C), 75.52 (s, 2C), 33.65 (t, 4C), 31.10 (d, 2C), 28.38 (q, 6C), 25.23 (t, 4C).

HR/MS (MALDI$^+$, DCTB): *m/z* calcd. for $C_{28}H_{38}N_4O_4Na^+$: [M^+] 517.2785, found: 517.2795.

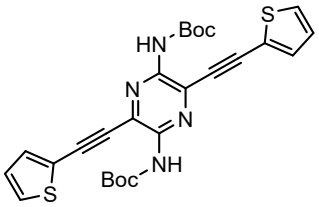
IR(ATR)[cm^{-1}]: 3410, 2962, 2933, 2869, 2224, 1722, 1505, 1481, 1452, 1392, 1367, 1325, 1238, 1140, 1074, 1053, 1019, 887, 847, 761, 695.

UV-Vis [nm]: 253, 282, 369.

Fluorescence (DCM): λ_{Ex} = 370 nm, λ_{Max} = 417 nm; Φ = 49%

m.p. [°C]: 142 – 147.

Di-*tert*-butyl (3,6-bis(thiophen-2-ylethynyl)pyrazine-2,5-diyl)dicarbamate (BA6)



According to **GP1**: A mixture of 3 mL THF/Et_3N (1:1) was degassed in a baked out Schlenk flask for 20 min. **DBC** (50.0 mg, 131 µmol, 1.00 eq.), $Pd(PPh_3)_2Cl_2$ (9.25 mg, 13.1 µmol, 0.10 eq.) and 2-ethynylthiophene (57.0 mg, 527 µmol, 4.00 eq.) were subsequently added. After stirring for 5 min CuI (1.00 mg, 5.27 µmol, 0.04 eq.) was added last. After stirring for 24 h at 60 °C the reaction was treated according to **GP1**. After purification via flash-column chromatography (PE/EA 10:1 -> EA), the obtained brown solid was additionally centrifuged with 3 mL pentane (3x) and 3 mL MeOH (1x) to yield 48.2 mg (92.3 µmol, **70%**) of a yellow solid.

R_f (PE/EA 3:1) = 0.30

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 – 7.42 (m, 4H), 7.29 (s, 2H), 7.07 (dd, *J* = 5.1, 3.7 Hz, 18H), 1.55 (s, 18H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 150.53 (s, 2C), 143.80 (2, 2C), 134.34 (d, 2C), 129.78 (s, 2C), 127.48 (s, 2C), 125.71 (s, 2C), 121.03 (s, 2C), 92.59 (s, 2C), 87.80 (s, 2C), 81.89 (s, 2C), 28.18 (q, 6C).

HR/MS (EI^+): *m/z* calcd. for $C_{16}H_{10}N_4S_2^+$: [M-2Boc$^+$] 322.0341, found: 322.0327.

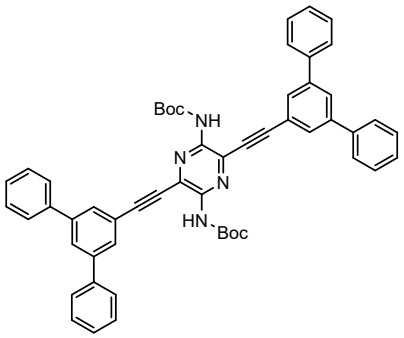
IR(ATR)[cm^{-1}]: 3331, 2978, 2932, 2209, 1717, 1479, 1436, 1390, 1370, 1340, 1252, 1233, 1152, 1062, 908, 856, 772, 722, 697.

UV-Vis [nm]: 233, 271, 316, 405.

Fluorescence (DCM): λ_{Ex} = 350/410 nm, λ_{Max} = 458 nm; Φ = 16%

m.p. [°C]: 199 – 204.

Di-*tert*-butyl (3,6-bis([1,1':3',1''-terphenyl]-5'-ylethynyl)pyrazine-2,5-diyl)dicarbamate (BA7)



According to **GP1**: A mixture of 6 mL THF/Et_3N (1:1) was degassed in a baked out Schlenk flask for 20 min. **DBC** (100 mg, 264 µmol, 1.00 eq.), $Pd(PPh_3)_2Cl_2$ (18.5 mg, 26.4 µmol, 0.10 eq.) and 5'-ethynyl-1,1':3',1''-terphenyl (158 mg, 580 µmol mmol, 2.20 eq.) were subsequently added. After stirring for 5 min CuI (2.51 mg, 13.8 µmol, 0.04 eq.) was added last. After stirring for 24 h at 60 °C the reaction was treated according to **GP1**. After purification via flash-column chromatography (PE/EA 10:1 -> EA), the obtained brown solid was additionally centrifuged with 3 mL pentane (3x) and 3 mL MeOH (1x) to yield 101 mg (121 µmol, **47%**) of a brown solid.

R_f (PE/EA 1:1) = 0.68

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (t, *J* = 1.7 Hz, 2H), 7.83 (d, *J* = 1.7 Hz, 3H), 7.68 – 7.64 (m, 8H), 7.52 – 7.45 (m, 10H), 7.44 – 7.39 (m, 5H), 1.56 (s, 18H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 150.75 (s, 2C), 144.41 (s, 2C), 142.47 (d, 4C), 140.02 (d, 4C), 129.73 (d, 4C), 129.14 (d, 8C), 128.16 (d, 4C), 127.87 (d, 2C), 127.33 (d, 8C), 126.06 (s, 2C), 122.30 (s, 2C), 99.42 (s, 2C), 84.34 (s, 2C), 82.12 (s, 2C), 28.41 (q, 6C).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3057, 3035, 2976, 2931, 2213, 1718, 1591, 1514, 1497, 1436, 1414, 1392, 1366, 1331, 1241, 1148, 1096, 1074, 1051, 1028, 878, 845, 758, 696, 614.

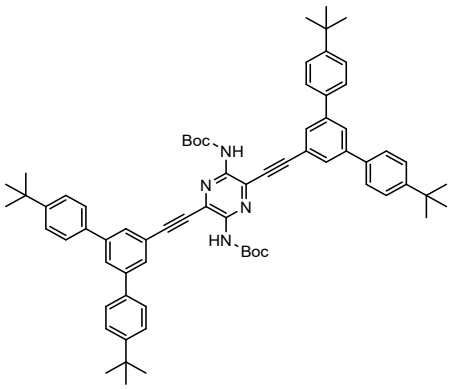
HR/MS (MALDI$^+$, DCTB): *m/z* calcd. for $C_{54}H_{46}N_4O_4Na^+$: [M^+] 837.3411, found: 837.3418.

UV-Vis [nm]: 249, 304, 398.

Fluorescence (DCM): λ_{Ex} = 400 nm, λ_{Max} = 451 nm; Φ = 65 %

m.p. [°C]: 215 – 220.

Di-*tert*-butyl (3,6-bis((4,4''-di-*tert*-butyl-[1,1':3',1''-terphenyl]-5'-yl)ethynyl)pyrazine-2,5-diyl)dicarbamate (BA8)



According to **GP1**: A mixture of 6 mL THF/Et_3N (1:1) was degassed in a baked out Schlenk flask for 20 min. **DBC** (100 mg, 264 µmol, 1.00 eq.), $Pd(PPh_3)_2Cl_2$ (18.5 mg, 26.4 µmol, 0.10 eq.) and 4,4''-di-*tert*-butyl-5'-ethynyl-1,1':3',1''-terphenyl (213 mg, 580 µmol mmol, 2.20 eq.) were subsequently added. After stirring for 5 min CuI (2.51 mg, 13.8 µmol, 0.04 eq.) was added last. After stirring for 24 h at 60 °C the reaction was treated according to **GP1**. After purification via flash-column chromatography (PE/EA 10:1 -> EA), the obtained yellow solid was additionally centrifuged with 3 mL pentane (3x) and 3 mL MeOH (1x) to yield 159 mg (153 µmol, **58%**) of a bright yellow powder.

R_f (PE/EA 1:1) = 0.74

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (t, *J* = 1.7 Hz, 2H), 7.80 (d, *J* = 1.8 Hz, 4H), 7.60 (d, *J* = 8.4 Hz, 8H), 7.51 (d, *J* = 8.5 Hz, 8H), 7.49 (s, 2H), 1.57 (s, 18H), 1.39 (s, 36H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 151.22 (s, 4C), 150.76 (s, 2C), 144.40 (s, 2C), 142.18 (s, 4C), 137.15 (s, 4C), 129.32 (d, 4C), 127.57 (d, 2C), 126.95 (d, 4C), 126.09 (d, 4C), 125.99 (s, 2C), 122.13 (s, 2C), 99.71 (s, 2C), 84.14 (s, 2C), 82.09 (s, 2C), 34.77 (s, 4C), 31.49 (q, 12C), 28.42 (q, 6C).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3420, 2963, 2902, 2867, 2208, 1752, 1591, 1510, 1456, 1393, 1364, 1232, 1138, 1052, 880, 828, 773, 691, 655.

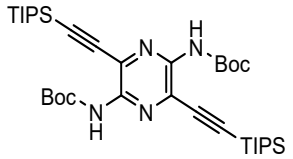
HR/MS (MALDI$^+$, DCTB): *m/z* calcd. for $C_{70}H_{78}N_4O_4^+$: [M^+] 1038.6018, found: 1038.6054.

UV-Vis [nm]: 259, 313, 402.

Fluorescence (DCM): λ_{Ex} = 400 nm, λ_{Max} = 451 nm; Φ = 93 %

m.p. [°C]: 287 – 292.

Di-*tert*-butyl (3,6-bis((triisopropylsilyl)ethynyl)pyrazine-2,5-diyl)dicarbamate (BA9)



According to **GP1**: A mixture of 3 mL THF/Et_3N (1:1) was degassed in a baked out Schlenk flask for 20 min. **DBC** (50.0 mg, 131 µmol, 1.00 eq.), $Pd(PPh_3)_2Cl_2$ (9.25 mg, 13.1 µmol, 0.10 eq.) and ethynyltriisopropylsilane (53.9 mg, 527 µmol, 4.00 eq.) were subsequently added. After stirring for 5 min CuI (1.00 mg, 5.27 µmol, 0.04 eq.) was added last. After stirring for 24 h at 60 °C the reaction was treated according to **GP1**. Purification via flash-column chromatography (PE/EA 10:1 -> EA) obtained 24.7 mg (36.9 µmol, **28%**) of a green oil.

$\mathbf{R_f}$ (PE/EA 1:1) = 0.75

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 (s, 2H), 1.51 (s, 18H), 1.15 (s, 36H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 150.64 (s, 2C), 144.73 (s, 2C), 125.12 (s, 2C), 104.47 (s, 2C), 100.57 (s, 2C), 81.77 (s, 2C), 28.34 (q, 6C), 18.83 (q, 6C), 11.26 (d, 2C).

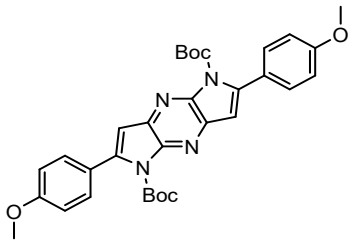
HR/MS (MALDI$^+$, DCTB): *m/z* calcd. for $C_{36}H_{62}N_4O_4Si_2^+$: [M^+] 670.4304, found: 670.4304.

IR(ATR)[cm^{-1}]: 2944, 2866, 2152, 1742, 1510, 1462, 1419, 1370, 1236, 1145, 1072, 1017, 996, 920, 883, 819, 789, 762, 732, 679.

UV-Vis [nm]: 262, 281, 384.

Fluorescence (DCM): λ_{Ex} = 385 nm, λ_{Max} = 428 nm; Φ = 76%

Di-*tert*-butyl 2,6-bis(4-methoxyphenyl)dipyrrolo[2,3-b:2',3'-e]pyrazine-1,5-dicarboxylate (DPPB1)



According to **GP2**: A mixture of 3 mL THF/Et_3N (1:1) was degassed in a baked out Schlenk flask for 20 min. **DBC** (40.0 mg, 105 µmol, 1.0 eq.), $Pd(PPh_3)_2Cl_2$ (7.40 mg, 10.5 µmol, 0.1 eq.) and 1-ethynyl-4-methoxybenzene (55.7 mg, 422 µmol, 4.00 eq.) were subsequently added. After stirring for 5 min CuI (2.01 mg, 10.6 µmol, 0.04 eq.) was added last. After stirring for 48 h at 70 °C the reaction was treated according to **GP2**. After purification via flash-column chromatography (PE/EA 10:1 -> EA), 42.0 mg (73.8 µmol, **70%**) of an orange solid was obtained.

R_f (PE/EA 3:1) = 0.55

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.8 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 6.82 (s, 2H), 3.88 (s, 6H), 1.35 (s, 18H).

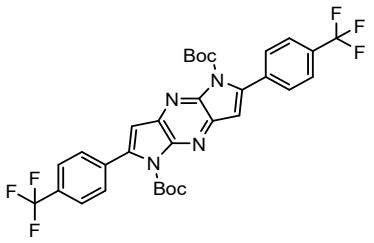
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 160.04 (s, 2C), 148.44 (s, 2C), 143.95 (s, 2C), 142.47 (s, 2C), 136.51 (s, 2C), 129.93 (d, 4C), 126.60 (s, 2C), 113.73 (d, 4C), 107.51 (d, 2C), 84.61 (s, 2C), 55.60 (q, 2C), 27.68 (q, 6C).

HR/MS (MALDI$^+$, DCTB): *m/z* calcd. for $C_{32}H_{34}N_4O_6^+$: [M^+] 570.2473, found: 570.2466.
IR(ATR)[cm^{-1}]: 2975, 2929, 2849, 1747, 1609, 1579, 1516, 1496, 1462, 1367, 1340, 1320, 1280, 1249, 1175, 1148, 1121, 1055, 1025, 930, 843, 807, 791, 768, 744, 724, 695, 608.
UV-Vis [nm]: 230, 280, 379.

Fluorescence (DCM): λ_{Ex} = 380 nm, λ_{Max} = 442 nm; Φ = 74 %

m.p.: > 300 °C

Di-*tert*-butyl 2,6-bis(4-(trifluoromethyl)phenyl)dipyrrolo[2,3-b:2',3'-e]pyrazine-1,5-dicarboxylate (DPPB2)



According to **GP2**: A mixture of 6 mL THF/Et_3N (1:1) was degassed in a baked out Schlenk flask for 20 min. **DBC** (75.0 mg, 197 µmol, 1.00 eq.), $Pd(PPh_3)_2Cl_2$ (13.9 mg, 19.8 µmol, 0.10 eq.) and 1-ethynyl-4-(trifluoromethyl)benzene (135 mg, 791 µmol, 4.00 eq.) were subsequently added. After stirring for 5 min CuI (1.51 mg, 7.91 µmol, 0.04 eq.) was added last. After stirring for 48 h at 70 °C the reaction was treated according to **GP2**. After purification via flash-column chromatography (PE/EA 10:1 -> EA), 116 mg (180 µmol, **91%**) of an orange solid was obtained.

R_f (PE/EA 1:1) = 0.68

$^1H\{^{19}F\}$ NMR (600 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.63 (d, *J* = 8.1 Hz, 2H), 6.95 (s, 2H), 1.32 (s, 18H).

^{19}F NMR (283 MHz, $CDCl_3$) δ -62.65 (s, 6F).

$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 147.85 (s, 2C), 142.82 (s, 2C), 142.63 (s, 2C), 136.72 (s, 2C), 130.72 (s, q: $J_{C\text{-}F}$ = 32.8 Hz), 129.02 (d, 4C), 125.25 (d, q: $J_{C\text{-}F}$ = 3.7 Hz, 4C), 124.09 (s, q: $J_{C\text{-}F}$ = 816.3 Hz, 2C), 123.19 (s, 2C), 109.05 (d, 2C), 85.41 (s, 2), 27.55 (q, 6C).

HR/MS (MALDI$^+$, DCTB): *m/z* calcd. for $C_{32}H_{28}N_4F_6O_4Na^+$: [M+$Na^+$] 669.1907, found: 669.1912.

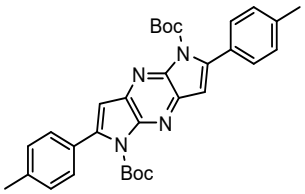
IR(ATR)[cm^{-1}]: 2981, 2936, 1757, 1619, 1411, 1369, 1320, 1274, 1149, 1107, 1067, 1050, 1017, 933, 841, 817, 767, 687, 635, 617.

UV-Vis [nm]: 241, 275, 367.

Fluorescence (DCM): λ_{Ex} = 370 nm, λ_{Max} = 427 nm; Φ = 46%

m.p.: > 300 °C.

Di-*tert*-butyl 2,6-di-p-tolyldipyrrolo[2,3-b:2',3'-e]pyrazine-1,5-dicarboxylate (DPPB3)



According to **GP2**: A mixture of 3 mL THF/Et_3N (1:1) was degassed in a baked out Schlenk flask for 20 min. **DBC** (40.0 mg, 105 µmol, 1.00 eq.), $Pd(PPh_3)_2Cl_2$ (7.4 mg, 10.55 µmol, 0.10 eq.) and 1-ethynyl-4-methybenzene (49.0 mg, 422 µmol, 4.00 eq.) were subsequently added. After stirring for 5 min CuI (2.01 mg, 10.6 µmol, 0.04 eq.) was added last. After stirring for 48 h at 70 °C the reaction was treated according to **GP2**. After purification via flash-column chromatography (PE/EA 10:1 -> EA), 34.1 mg (63.3 µmol, **60%**) of an orange powder was obtained.

$\mathbf{R_f}$ (DCM) = 0.38

^{1}H NMR (301 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.7 Hz, 2H), 7.63 (d, *J* = 8.5 Hz, 2H), 6.95 (s, 2H), 2.43 (s, 6H), 1.33 (s, 18H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 148.40 (s, 2C), 144.30 (s, 2C), 142.51 (s, 2C), 138.56 (s, 2C), 136.59 (s, 2C), 131.27 (s, 2C), 128.93 (d, 4C), 128.58 (d, 4C), 107.74 (d, 2C), 84.64 (s, 2C), 29.85 (q, 2C), 27.63 (q, 6C).

HR/MS (EI^+): *m/z* calcd. for $C_{32}H_{34}N_4O_4^+$: $[M^+]$ 538.2575, found: 538.2645.

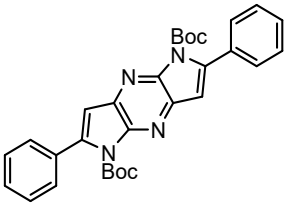
IR(ATR)[cm^{-1}]: 3006, 2977, 2922, 2852, 1749, 1575, 1496, 1458, 1368, 1342, 1319, 1278.

UV-Vis [nm]: 239, 277, 373.

Fluorescence (DCM): λ_{Ex} = 375 nm, λ_{Max} = 430 nm; Φ = 72 %

m.p.: > 300 °C

Di-*tert*-butyl 2,6-diphenyldipyrrolo[2,3-b:2',3'-e]pyrazine-1,5-dicarboxylate (DPPB4)



According to **GP3** 10.0 mg (19.6 µmol, 1.00 eq.) of **BA4** was cyclised with 0.20 eq. CuI (0.75 mg, 3.92 µmol) in 1 mL of a 1:1 THF/Et_3N mixture at 70 °C overnight. After removing the solvent in vacuo, the crude product was purified with flash-column chromatography on silica gel eluting with DCM affording 9.20 mg (18.0 µmol, 92%) as a yellow solid.

R_f (PE/EA 5:1) = 0.43

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (m, 10H), 6.89 (s, 2H), 1.31 (s, 18H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 148.23 (s, 2C), 144.21 (s, 2C), 142.52 (s, 2C), 136.63 (s, 2C), 134.17 (d, 2C), 128.70 (d, 4C), 128.28 (d, 4C), 108.07 (d, 2C), 84.74 (s, 2C), 27.55 (q, 6C).

HR/MS (MALDI$^+$, DCTB): *m/z* calcd. for $C_{30}H_{30}N_4O_4Na^+$: [M+Na$^+$] 533.2159, found: 533.2271.

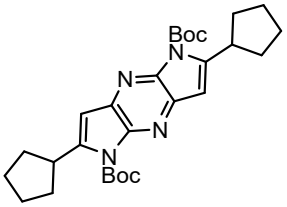
IR(ATR)[cm^{-1}]: 2978, 2926, 2854, 1756, 1561, 1486, 1446, 1369, 1345, 1278, 1230, 1154, 1121, 1057, 932, 844, 809, 770, 722, 702.

UV-Vis [nm]: 239, 272, 366.

Fluorescence (DCM): λ_{Ex} = 370 nm, λ_{Max} = 426 nm; Φ = 78%

m.p.: > 300 °C

Di-*tert*-butyl 2,6-dicyclopentyldipyrrolo[2,3-b:2',3'-e]pyrazine-1,5-dicarboxylate (DPPB5)



According to **GP3** 10.0 mg (20.2 µmol, 1.00 eq.) of **BA5** was cyclised with 0.20 eq. CuI (0.77 mg, 4.04 µmol) in 1 mL of a 1:1 THF/Et_3N mixture at 70 °C overnight. After removing the solvent under vacuo, the crude product was purified with flash-column chromatography on silica gel eluting with DCM affording 9.60 mg (19.4 µmol, 96%) as a yellow solid.

R_f (PE/EA 2:1) = 0.35

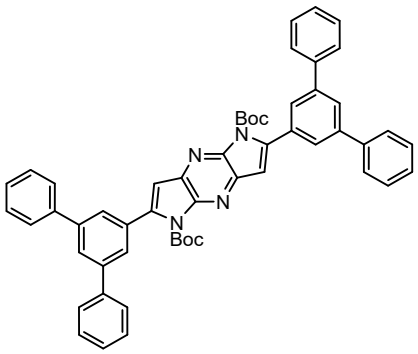
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.63 (s, 2H), 3.75 (p, *J* = 7.5 Hz, 2H), 2.15 (m, 4), 1.80 (m, 4H), 1.74 (m, 4H), 1.70 (s, 18H), 1.57 (m, 4H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 149.68 (s, 2C), 149.08 (s, 2C), 141.93 (s, 2C), 136.01 (s, 2C), 103.56 (d, 2C), 84.59 (s, 2C), 39.82 (q, 6C), 33.03 (t, 4C), 28.27 (d, 2C), 24.80 (t, 4C).

HR/MS (MALDI$^+$, DCTB): *m/z* calcd. for $C_{28}H_{38}N_4O_4K^+$: [M+K$^+$]: 533.2525, found: 533.2535.
IR(ATR)[cm^{-1}]: 2956, 2870, 1737, 1567, 1453, 1368, 1345, 1277, 1255, 1216, 1155, 1095, 861, 769.
UV-Vis [*nm*]: 239, 265, 346.

Fluorescence (DCM): λ_{Ex} = 350 nm, λ_{Max} = 460 nm; Φ = 34%

m.p. [°C]: 194 – 199.

Di-*tert*-butyl 2,6-di([1,1':3',1''-terphenyl]-5'-yl)dipyrrolo[2,3-b:2',3'-e]pyrazine-1,5-dicarboxylate (DPPB7)



According to **GP3** 10.0 mg (12.3 µmol, 1.00 eq.) of **BA7** was cyclised with 0.20 eq. CuI (0.47 mg, 2.45 µmol) in 1 mL of a 1:1 THF/Et_3N mixture at 70 °C overnight. After removing the solvent in vacuo, the crude product was purified with flash-column chromatography on silica gel eluting with DCM affording 9.80 mg (12.0 µmol, 97%) as a yellow solid.

R_f (PE/EA 1:1) = 0.72

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (s, 2H), 7.70 (d, *J* = 6.3 Hz, 12H), 7.49 (t, *J* = 6.0 Hz, 8H), 7.43 (t, *J* = 4.9 Hz, 4H), 7.02 (s, 2H), 1.28 (s, 18H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 148.01 (s, 2C), 143.83 (s, 2C), 142.32 (s, 2C), 141.76 (s, 4C), 140.36 (s, 4C), 136.53 (s, 2C), 135.08 (s, 2C), 128.95 (d, 8C), 127.77 (d, 4C), 127.13 (d, 8C), 126.19 (d, 4C), 125.99 (d, 2C), 108.06 (d, 2C), 84.61, 27.39.

HR/MS (MALDI$^+$, DCTB): *m/z* calcd. for $C_{54}H_{46}N_4O_4^+$: [M^+] 814.3514, found: 814.3519.

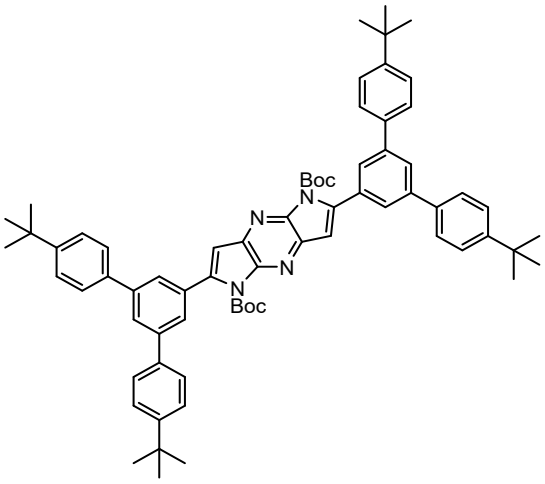
IR(ATR)[cm^{-1}]: 3060, 3036, 2977, 2931, 1746, 1596, 1558, 1498, 1457, 1426, 1369, 1337, 1293, 1271, 1258, 1217, 1148, 1124, 1073, 1051, 1032, 961, 882, 845, 760, 699, 643, 614.

UV-Vis [nm]: 247, 371.

Fluorescence (DCM): λ_{Ex} = 370 nm, λ_{Max} = 430 nm*;* Φ = = 67%

m.p. [°C]: > 300 °C

Di-*tert*-butyl 2,6-bis(4,4''-di-*tert*-butyl-[1,1':3',1''-terphenyl]-5'-yl)dipyrrolo[2,3-b:2',3'-e]pyrazine-1,5-dicarboxylate (DPPB8)



According to **GP3** 10.0 mg (12.3 µmol, 1.00 eq.) of **BA8** was cyclised with 0.20 eq. CuI (0.37 mg, 1.92 µmol) in 1 mL of a 1:1 THF/Et_3N mixture at 70 °C overnight. After removing the solvent in vacuo, the crude product was purified with flash-column chromatography on silica gel eluting with DCM affording 9.60 mg (12.0 µmol, 96%) as a yellow solid.

R_f (PE/EA 1:1) = 0.72

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (s, 2H), 7.70 – 7.59 (m, 11H), 7.52 (d, *J* = 8.4 Hz, 7H), 6.99 (s, 2H), 1.39 (s, 36H), 1.26 (s, 18H).

^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 150.89 (s, 4C), 148.11 (s, 2C), 144.13 (s, 2C), 142.40 (s, 2C), 141.56 (s, 4C), 137.59 (s, 4C), 136.63 (s, 2C), 135.12 (s, 2C), 126.83 (d, 8C), 125.97 (d, 8C), 125.87 (d, 4C), 125.78 (d, 2C), 108.06 (d, 2C), 84.61 (s, 2C), 34.63 (s, 4C), 31.37 (q, 6C), 27.50 (q, 12C).

HR/MS (MALDI$^+$, DCTB): *m/z* calcd. for $C_{70}H_{78}N_4O_4^+$ [M^+] 1038.6018, found: 1038.6027.

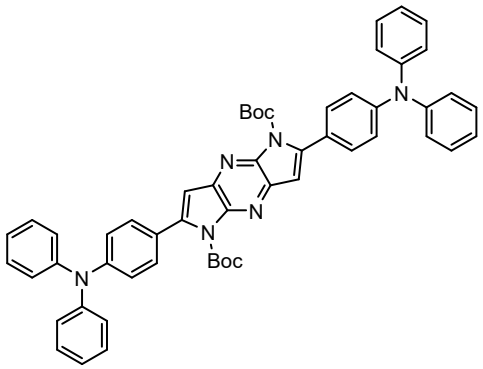
IR(ATR)[cm^{-1}]: 2963, 2868, 1750, 1596, 1556, 1513, 1460, 1393, 1367, 1338, 1293, 1271, 1227, 1151, 1122, 1072, 1018, 963, 886, 831, 765, 707, 613.

UV-Vis [nm]: 252, 365.

Fluorescence (DCM): λ_{Ex} = 365 nm, λ_{Max} = 432 nm; Φ = 74%

m.p. [°C]: > 300 °C

Di-*tert*-butyl 2,6-bis(4-(diphenylamino)phenyl)dipyrrolo[2,3-b:2',3'-e]pyrazine-1,5-dicarboxylate (DPPB10)



According to **GP1**: A mixture of 3 mL THF/Et_3N (1:1) was degassed in a baked out Schlenk flask for 20 min. **DBC** (51.0 mg, 135 µmol, 1.00 eq.), $Pd(PPh_3)_2Cl_2$ (9.44 mg, 13.5 µmol, 0.10 eq.) and 4-ethynyl-N,N-diphenylaniline (145 mg, 537 mmol, 4.00 eq.) were subsequently added. After stirring for 5 min CuI (1.02 mg, 5.38 µmol, 0.04 eq.) was added last. After stirring for 24 h at 60 °C the reaction was treated according to **GP1**. After purification via flash-column chromatography (PE/EA 10:1 -> EA), 57.9 mg (68.6 µmol, **51%**) of a green solid was obtained.

R_f (PE/EA 5:1) = 0.43

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.8 Hz, 4H), 7.31 – 7.26 (m, 8H), 7.20 – 7.10 (m, 12H), 7.07 (t, *J* = 6.7 Hz, 4H), 6.85 (s, 2H), 1.42 (s, 18H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 148.41 (s, 2C), 148.32 (s, 2C), 147.53 (s, 4C), 143.99 (s, 2C), 142.67 (s, 2C), 136.57 (s, 2C), 129.55 (d, 8C), 129.50 (d, 4C), 127.45 (s, 2C), 124.97 (d, 8C), 123.60 (d, 4C), 122.51 (d, 4C), 107.52 (d, 2C), 84.70 (s, 2C), 27.74 (q, 6C).

HR/MS (MALDI$^+$, DCTB): *m/z* calcd. for $C_{54}H_{48}N_6O_4^+$: [M^+] 844.3732, found: 844.3741.

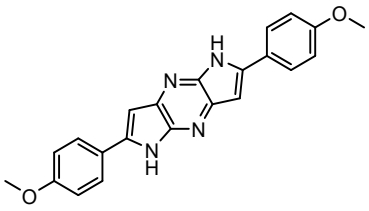
IR(ATR)[cm^{-1}]: 3044, 2980, 2928, 2850, 1749, 1589, 1490, 1366, 1348, 1321, 1280, 1222, 1150, 1120, 1078, 1053, 1031, 932, 847, 792, 751, 696, 677, 649, 623.

UV-Vis [nm]: 240, 302, 414.

Fluorescence (DCM): λ_{Ex} = 415 nm, λ_{Max} = 514 nm; Φ = 85%

m.p. [°C]: 253 – 258.

2,6-bis(4-methoxyphenyl)-1,5-dihydrodipyrrolo[2,3-b:2',3'-e]pyrazine (DPP1)



According to **GP4** 50.0 mg (74.5 µmol, 1.00 eq.) of **BA1** was cyclised with 0.10 eq. $IPrAuNTf_2$ (6.56 mg, 7.45 µmol) in 5 mL DCE at 60 °C overnight. After removing the solvent in vacuo, the crude product was centrifuged with 3 mL pentane 4x and 3 mL MeOH 2x affording 31.0 mg (65.9 µmol, 88%) of a bright yellow solid.

$\mathbf{R_f}$ (PE/EA 3:2) = 0.44

^{1}H NMR (600 MHz, DMSO) δ 11.87 (s, 2H), 7.95 (d, *J* = 5.2 Hz, 4H), 7.05 (d, *J* = 8.9 Hz, 4H), 6.91 (s, 2H), 3.83 (s, 6H).

^{13}C NMR (151 MHz, DMSO) δ 159.42 (s, 2C), 141.55 (s, 2C), 140.38 (s, 2C), 135.31 (s, 2C), 126.79 (d, 4C), 124.35 (s, 2C), 114.42 (d, 4C), 95.33 (d, 2C), 55.29 (q, 2C).

HR/MS (MALDI$^+$, DCTB): *m/z* calcd. for $C_{22}H_{18}N_4O_2^+$: [M^+] 370.1424, found: 370.1422.

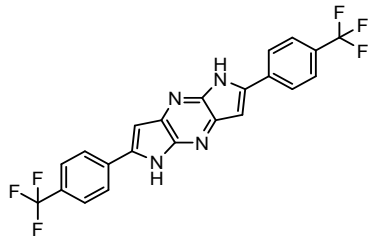
IR(ATR)[cm^{-1}]: 3113, 2918, 2849, 1733, 1542, 1496, 1439, 1320, 1299, 1222, 1109, 1021, 906, 838, 805, 779, 719, 687, 664, 648.

UV-Vis [nm]: 366, 417, 436.

Fluorescence (DMSO): λ_{Ex} = 380 nm, λ_{Max} = 462 nm; Φ = 85%

m.p. [°C]: > 300.

2,6-Bis(4-(trifluoromethyl)phenyl)-1,5-dihydrodipyrrolo[2,3-b:2',3'-e]pyrazine (DPP2)



According to **GP4** 50.0 mg (77.3 µmol, 1.00 eq.) of **BA2** was cyclised with 0.10 eq. $IPrAuNTf_2$ (5.97 mg, 7.73 µmol) in 5 mL DCE at 60 °C overnight. After removing the solvent in vacuo, the crude product was centrifuged with 3 mL pentane 4x and 3 mL MeOH 2x affording 34.5 mg (77.3 µmol, 100%) of a bright yellow solid.

R_f (PE/EA 1:1) = 0.54

^{1}H{^{19}F} NMR (700 MHz, DMSO) δ 12.29 (d, *J* = 2.2 Hz, 2H), 8.24 (d, *J* = 8.2 Hz, 4H), 7.86 (d, *J* = 8.2 Hz, 4H), 7.28 (d, *J* = 2.1 Hz, 2H).

^{19}F {^{1}H} NMR (283 MHz, DMSO) δ -60.97.

^{13}C NMR {^{1}H,^{19}F} (126 MHz, DMSO) δ 142.21 (s, 2C), 139.44 (s, 2C), 135.86 (s, 2C), 135.41 (s, 2C), 128.18 (s, 2C), 126.01 (d, 4C), 125.92 (d, 4C), 124.25 (s, 2C), 98.74 (d, 2C).

HR/MS (MALDI$^+$, DCTB): *m/z* calcd. for $C_{22}H_{12}N_4F_6^+$: [M^+] 446.0961, found: 446.0957.

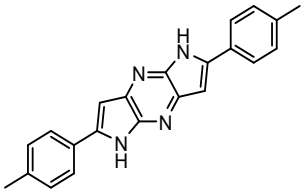
IR(ATR)[cm^{-1}]: 3216, 2926, 1932, 1617, 1549, 1446, 1318, 1277, 1252, 1171, 1111, 1068, 1016, 907, 840, 789, 746, 719, 685.

UV-Vis [nm]: 291, 417, 440.

Fluorescence (DMSO): λ_{Ex} = 440 nm, λ_{Max} = 478 nm; Φ = 67%

m.p. [°C]: > 300 °C / 400 °C (TGA measurement)

2,6-Di-p-tolyl-1,5-dihydrodipyrrolo[2,3-b:2',3'-e]pyrazine (DPP3)



According to **GP4** 50.0 mg (92.8 µmol, 1 eq.) of **BA3** was cyclised with 0.1 eq. $IPrAuNTf_2$ (8.03 mg, 9.82 µmol) in 5 mL DCE at 60 °C overnight. After removing the solvent in vacuo, the crude product was centrifuged with 3 mL pentane 4x and 3 mL MeOH 2x affording 30.2 mg (89.1 µmol, 96%) of a bright yellow solid.

R_f (PE/EA 5:1) = 0.22

^{1}H NMR (600 MHz, DMSO) δ 11.93 (s, 2H), 7.90 (d, *J* = 8.3 Hz, 4H), 7.30 (d, *J* = 7.8 Hz, 4H), 6.98 (s, 2H), 2.36 (s, 6H).

^{13}C{^{1}H} NMR (151 MHz, DMSO) δ 141.25 (s, 2C), 140.63 (s, 2C), 137.84 (s, 2C), 135.41, 129.54 (d, 4C), 129.12 (s, 1C), 125.31 (d, 4C), 96.07 (d, 2C), 20.91 (q, 2C).

HR/MS (MALDI$^+$, DCTB): *m/z* calcd. for $C_{22}H_{18}N_4^+$: [M$^+$] 338.1526, found: 338.1453.

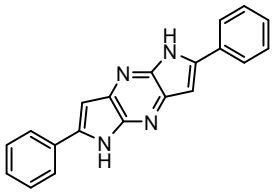
IR(ATR)[cm^{-1}]: 3167, 3137, 3021, 2913, 2857, 2721, 1913, 1743, 1612, 1552, 1499, 1451, 1367, 1323, 1297, 1276, 1248, 1217, 1199, 1118, 1021, 908, 825, 806, 786, 725, 694, 649, 632.

UV-Vis [nm]: 247, 253, 286, 414, 432.

Fluorescence (DMSO): λ_{Ex} = 415 nm, λ_{Max} = 453 nm; Φ = 81%

m.p. [°C]: > 300.

2,6-Diphenyl-1,5-dihydrodipyrrolo[2,3-b:2',3'-e]pyrazine (DPP4)



According to **GP4** 15.0 mg (29.4 µmol, 1.00 eq.) of **BA4** was cyclised with 0.10 eq. $IPrAuNTf_2$ (2.54 mg, 2.94 µmol) in 1.5 mL DCE at 60 °C overnight. After removing the solvent in vacuo, the crude product was centrifuged with 3 mL pentane 4x and 3 mL MeOH 2x affording 9.12 mg (29.4 µmol, 100%) of a bright yellow solid.

R_f (PE/EA 1:1) = 0.56

^{1}H NMR (600 MHz, DMSO) δ 12.04 (s, 1H), 8.02 (d, *J* = 8.1 Hz, 3H), 7.49 (t, *J* = 7.8 Hz, 3H), 7.38 (t, *J* = 6.7 Hz, 2H), 7.07 (s, 1H).

^{13}C{^{1}H} NMR (151 MHz, DMSO) δ 141.76 (s, 2C), 140.65 (s, 2C), 135.52 (s, 2C), 131.63 (s, 2C), 128.98 (d, 4C), 128.34 (d, 2C), 125.40 (d, 4C), 96.70 (d, 2C).

HR/MS (MALDI$^+$, DCTB): *m/z* calcd. for $C_{20}H_{14}N_4^+$: [M^+] 310.1213, found: 310.1213.

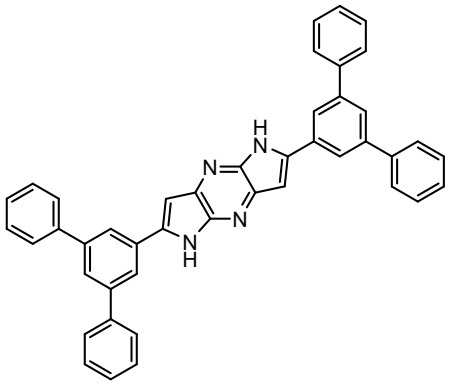
IR(ATR)[cm^{-1}]: 3172, 3139, 3050, 2869, 1955, 1898, 1829, 1602, 1556, 1482, 1458, 1423, 1365, 1323, 1298, 1277, 1246, 1201, 1158, 1075, 1030, 970, 907, 850, 811, 792, 758, 722, 695, 669, 643.

UV-Vis [nm]: 247, 284, 411, 430.

Fluorescence (DMSO): λ_{Ex} = 415 nm, λ_{Max} = 449 nm; Φ = 74%

m.p. [°C]: > 300.

2,6-Di([1,1':3',1''-terphenyl]-5'-yl)-1,5-dihydrodipyrrolo[2,3-b:2',3'-e]pyrazine (DPP7)



According to **GP4** 10.0 mg (12.3 µmol, 1.00 eq.) of **BA7** was cyclised with 0.10 eq. $IPrAuNTf_2$ (1.05 mg, 1.21 µmol) in 1 mL DCE at 60 °C overnight. After removing the solvent in vacuo, the crude product was centrifuged with 3 mL pentane 4x and 3 mL MeOH 2x affording 7.47 mg (12.2 µmol, 99%) of a bright orange solid.

R_f (PE/EA 1:1) = 0.62

^{1}H NMR (600 MHz, DMSO) δ 12.28 (s, 2H), 8.35 (d, *J* = 1.7 Hz, 3H), 7.98 – 7.90 (m, 8H), 7.56 (d, *J* = 7.8 Hz, 6H), 7.45 (d, *J* = 7.3 Hz, 4H), 7.38 (d, *J* = 2.1 Hz, 2H).

^{13}C{^{1}H} NMR (101 MHz, DMSO) δ 141.91 (s, 2C), 141.55 (s, 4C), 140.55 (s, 2C), 139.73 (s, 4C), 135.69 (s, 2C), 132.87 (s, 2C), 128.90 (d, 8C), 127.84 (d, 4C), 127.12 (d, 8C), 124.79 (d, 2C), 122.77 (d, 4C), 97.53 (d, 2C).

HR/MS (MALDI$^+$, DCTB): *m/z* calcd. for $C_{46}H_{30}N_4^+$: [M$^+$] 614.2465, found: 614.2467.

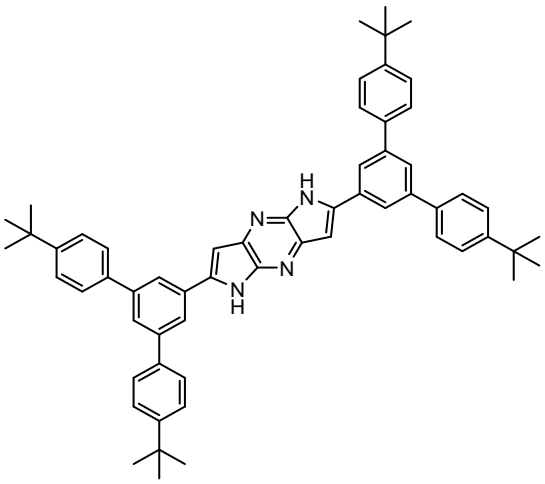
IR(ATR)[cm^{-1}]: 3057, 3035, 1765, 1737, 1593, 1575, 1546, 1497, 1460, 1407, 1293, 1246, 1193, 1078, 1030, 940, 921, 876, 809, 793, 757, 726, 696, 655, 613.

UV-Vis [nm]: 255, 333, 417, 435.

Fluorescence (DCM): λ_{Ex} = 415 nm, λ_{Max} = 457 nm; Φ = 69%

m.p. [°C]: > 300 °C

2,6-Bis(4,4''-di-*tert*-butyl-[1,1':3',1''-terphenyl]-5'-yl)-1,5-dihydrodipyrrolo[2,3-b:2',3'-e]pyrazine (DPP8)



According to **GP4** 10.0 mg (9.62 µmol, 1.00 eq.) of **BA8** was cyclised with 0.20 eq. $IPrAuNTf_2$ (3.33 mg, 3.85 µmol) in 1 mL DCE at 60 °C overnight. After removing the solvent in vacuo, the crude product was centrifuged with 3 mL pentane 4x and 3 mL MeOH 2x affording 1.94 mg (2.31 µmol, 24%) of a bright yellow solid.

R_f (PE/EA 2:1) = 0.66

^{1}H NMR (600 MHz, DMSO) δ 12.24 (s, 2H), 8.29 (s, 4H), 7.85 (d, *J* = 7.5 Hz, 8H), 7.56 (d, *J* = 8.4 Hz, 8H), 7.33 (s, 2H), 1.36 (s, 36H).

^{13}C{^{1}H} NMR (151 MHz, DMSO) δ 150.35 (s, 4C), 141.91 (s, 2C), 141.48 (s, 4C), 137.05 (s, 2C), 135.68 (s, 4C), 132.80 (s, 2C), 128.72 (s, 2C), 126.85 (d, 8C), 125.90 (d, 2C), 125.74 (d, 8C), 122.46 (d, 4C), 97.44 (d, 2C), 34.37 (s, 4C), 31.18 (q, 12C).

HR/MS (MALDI$^+$, DCTB): *m/z* calcd. for $C_{60}H_{62}N_4^+$: [M$^+$] 838.4969, found: 838.4958.

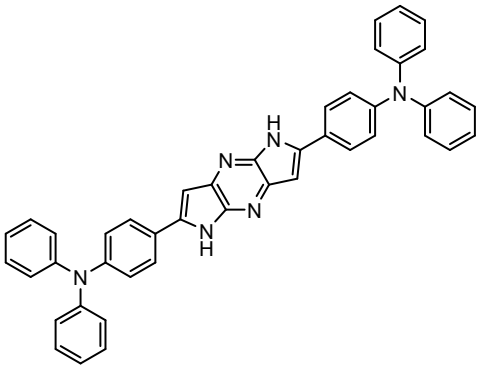
IR(ATR)[cm^{-1}]: 2960, 2903, 2866, 1907, 1730, 1597, 1543, 1513, 1460, 1391, 1362, 1297, 1270.

UV-Vis [nm]: 253, 412, 441.

Fluorescence (DCM): λ_{Ex} = 415 nm, λ_{Max} = 457 nm; Φ = 50%

m.p. [°C]: > 300 °C

4,4'-(1,5-Dihydrodipyrrolo[2,3-b:2',3'-e]pyrazine-2,6-diyl)bis(N,N-diphenylaniline) (DPP10)



According to Burgess et al.[6] 1.00 eq. of **DPPB10** (60.0 mg, 71.0 µmol) were dissolved in 20 mL DCM at 0 °C. After the addition of 4 mL 2,6-lutidine the mixture was stirred for 15 min. Then 20 eq. (315 mg, 1.42 mmol) of TMSOTf were added dropwise and the reaction was stirred for an additional 5 h and allowed to warm up to rt. The solution was cooled to 0 °C and quenched with concentrated $CuSO_{4(aq)}$. The product was extracted with EA and purified through precipitation with pentane and washed with pentane/MeOH (3x) to yield 71% of product (32.5 mg, 50.4 µmol).

R_f (PE/EA 1:1) = 0.21

^{1}H NMR (600 MHz, DMSO) δ 11.89 (s, 2H), 7.90 (d, *J* = 9.5 Hz, 2H), 7.37 (d, *J* = 9.1 Hz, 8H), 7.12 (m, 12H), 7.00 (m, 4H), 6.90 (d, *J* = 2.2 Hz, 2H).

^{13}C{^{1}H} NMR (101 MHz, DMSO) δ 146.75 (s, 4C), 146.65 (s, 2C), 140.27 (s, 2C), 129.68 (d, 8C), 129.64 (d, 8C), 126.47 (s, 2c), 124.60 (d, 4C), 124.46 (d, 4C), 123.57 (d, 4C), 122.47 (s, 2C), 122.20 (s, 2C), 95.66 (d, 2C).

HR/MS (MALDI$^+$, DCTB): *m/z* calcd. for $C_{44}H_{32}N_6^+$: [M$^+$] 644.2683, found: 644.2696.

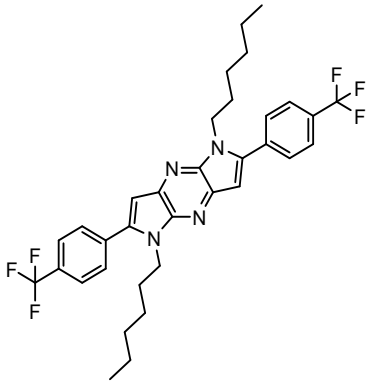
IR(ATR)[cm^{-1}]: 3430, 2956, 2932, 2870, 1650, 1595, 1580, 1530, 1489, 1451, 1407, 1372, 1324, 1270, 1233, 1169, 1129, 1110, 1067, 1016, 981, 917, 895, 857, 809, 765, 749, 670.

UV-Vis [nm]: 254, 281, 456.

Fluorescence (DCM): λ_{Ex} = 254 nm, λ_{Max} = 281 nm; Φ = 7%

m.p. [°C]: 274 – 279.

1,5-Dihexyl-2,6-bis(4-(trifluoromethyl)phenyl)-1,5-dihydrodipyrrolo[2,3-b:2',3'-e]pyrazine (ADPP1)



6.00 eq. Cs_2CO_3 (87.6 mg, 268 µmol) were added to a solution of 1.00 eq of **DPP2** (20.0 mg, 44.8 µmol) in 2.4 mL DMF. After stirring for 30 min at rt, 2.2 eq he (16.3 mg, 13.8 µL, 98.6 µmol) were added and the mixture was stirred overnight. The mixture was washed with brine and purified via flash-column chromatography and centrifugation with pentane (3 x 4 mL) to obtain an orange solid in a 79% yield (21.8 mg, 35.4 µmol).

R_f (PE/EA 4:1) = 0.54

$^1H\{^{19}F\}$ (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.1 Hz, 4H), 7.72 (d, *J* = 8.2 Hz, 4H), 6.78 (s, 2H), 4.44 (t, *J* = 7.5 Hz, 4H), 1.68 (m, 4H), 1.20 – 1.12 (m, 12H), 0.81 – 0.75 (m, 6H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 143.18 (s ,2C), 142.06 (s, 2C), 136.46 (s, 2C), 135.17 (s, 2C), 130.65 (s, q, *J* = 32.8 Hz, 2C), 129.40 (d, 4C), 125.88 (d, q, *J* = 4.0 Hz, 4C), 124.20 (s, q, *J* = 272.2Hz, 2C), 101.18 (2C, d), 43.09 (2C, t), 31.35 (2C, t), 26.39 (2C, t), 22.56 (2C, t), 14.04 (2C, q).

^{19}F NMR (471 MHz, $CDCl_3$) δ -62.59 (s, 6F).

HR/MS (MALDI$^+$, DCTB): *m/z* calcd. for $C_{34}H_{36}F_6N_4^+$: [M^+] 614.2839, found: 614.2845.

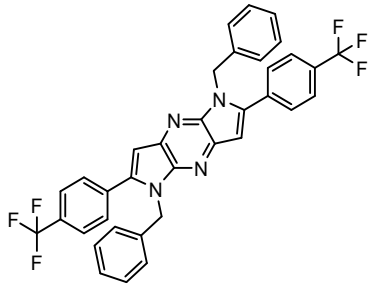
IR(ATR)[cm^{-1}]: 2959, 2927, 2855, 1734, 1618, 1457, 1414, 1322, 1260, 1167, 1129, 1109, 1068, 1017, 850, 797, 685.

UV-Vis [nm]: 237, 276, 369, 412.

Fluorescence (DMSO): λ_{Ex} = 410 nm, λ_{Max} = 456 nm; Φ = 43%

m.p. [°C]: 210 – 215 °C

1,5-Dibenzyl-2,6-bis(4-(trifluoromethyl)phenyl)-1,5-dihydrodipyrrolo[2,3-b:2',3'-e]pyrazine (ADPP2)



6.00 eq. Cs_2CO_3 (87.6 mg, 268 µmol) were added to a solution of 1.00 eq of **DPP2** (20.0 mg, 44.8 µmol) in 2.4 mL DMF. After stirring for 30 min at rt, 2.2 eq benzylbromide (16.9 mg, 11.7 µL, 98.6 µmol) were added and the mixture was stirred overnight. The mixture was washed with brine and purified via flash-column chromatography and centrifugation with pentane (3 x 4 mL) to obtain an orange solid in a 90% yield (25.3 mg, 40.3 µmol).

R_f (PE/EA 4:1) = 0.30

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.1 Hz, 4H), 7.57 (d, *J* = 8.1 Hz, 4H), 7.28 – 7.18 (m, 6H), 7.04 – 6.99 (m, 4H), 6.86 (s, 2H), 5.65 (s, 4H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 143.60 (s, 2C), 142.43 (s, 2C), 138.13 (s, 2C), 135.84 (s, 2C), 135.34 (s, 2C), 130.70 (s, q, *J* = 32.7 Hz, 2C), 129.49 (d, 4C), 128.83 (d, 4C), 127.51 (d, 2C), 126.62, (d, 4C) 125.79 (d, q, *J* = 7.3 Hz, 4C) , 124.10 (s, q, *J* = 272.2 Hz, 2C), 101.73 (d, 2C), 46.48 (t, 2C).

^{19}F NMR (283 MHz, $CDCl_3$) δ -62.64 (s, 6F).

HR/MS (MALDI$^+$, DCTB): *m/z* calcd. for $C_{36}H_{24}F_6N_4$: [M^+] 626.1900, found: 626.1891.

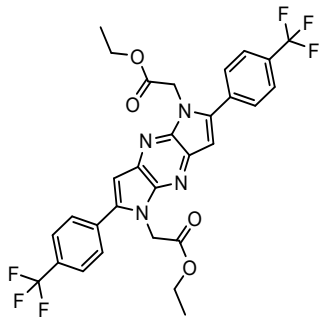
IR(ATR)[cm^{-1}]: 1985, 1737, 1618, 1497, 1432, 1381, 1357, 1321, 1211, 1194, 1165, 1105, 1067, 1029, 1015, 935, 879, 843, 787, 756, 743, 718, 683, 657, 631.

UV-Vis [nm]: 275, 375.

Fluorescence (DMSO): λ_{Ex} = 380 nm, λ_{Max} = 456 nm; Φ = 67%

m.p. [°C]: 249 – 254 °C

Diethyl 2,2'-(2,6-bis(4-(trifluoromethyl)phenyl)dipyrrolo[2,3-b:2',3'-e]pyrazine-1,5-diyl)diacetate (ADPP3)



6.00 eq. Cs_2CO_3 (87.6 mg, 268 µmol) were added to a solution of 1.00 eq of **DPP2** (20.0 mg, 44.8 µmol) in 2.4 mL DMF. After stirring for 30 min at rt, 2.2 eq ethyl 2-bromoacetate (16.5 mg, 10.9 µL, 98,5 µmol) were added and the mixture was stirred overnight. The mixture was washed with brine and purified via flash-column chromatography and centrifugation with pentane (3 x 4 mL) to obtain an orange solid in a 99% yield (27.4 mg, 44.4 µmol).

R_f (PE/EA 1:1) = 0.56

^{1}H NMR (301 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.2 Hz, 4H), 7.68 (d, *J* = 8.1 Hz, 4H), 6.85 (s, 2H), 5.11 (s, 4H), 4.18 (q, *J* = 7.1 Hz, 4H), 1.22 (t, *J* = 7.1 Hz, 6H).

^{19}F NMR (283 MHz, $CDCl_3$) δ -62.70 (s, 6F).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.90 (s, 2), 143.42 (s, 2C), 142.38 (s, 2C), 135.46, 135.31 (s, 2C), 130.97 (s, q, *J* = 32.7 Hz, 2C), 129.47 (d, 4C), 126.03 (d, q, *J* = 3.8 Hz, 4C), 124.08 (s, q, *J* = 272.2 Hz, 2C), 102.09 (d, 2C), 61.93 (t, 2C), 44.50 (t, 2C), 14.22 (q, 2C).

HR/MS (MALDI$^+$, DCTB): *m/z* calcd. for $C_{30}H_{24}F_6N_4O_4$ [M^+] 618.1696, found: 618.1710.

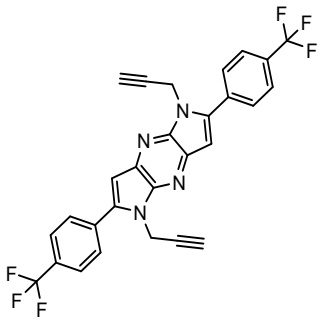
IR(ATR)[cm^{-1}]: 2985, 1737, 1618, 1552, 1498, 1432, 1380, 1321, 1211, 1194, 1164, 1105, 1067, 1015, 976, 935, 908, 878, 842, 787, 756, 743, 718, 683, 657, 632.

UV-Vis [nm]: 275, 377.

Fluorescence (DMSO): λ_{Ex} = 380 nm, λ_{Max} = 448 nm; Φ = 67%

m.p. [°C]: 200 – 205 °C

1,5-Di(prop-2-yn-1-yl)-2,6-bis(4-(trifluoromethyl)phenyl)-1,5-dihydrodipyrrolo[2,3-b:2',3'-e]pyrazine (ADPP4)



6.00 eq. Cs_2CO_3 (87.6 mg, 268 µmol) were added to a solution of 1.00 eq of **DPP2** (20.0 mg, 44.8 µmol) in 2.4 mL DMF. After stirring for 30 min at rt, 2.2 eq propagylbromide (11.7 mg, 9.97 µL, 98.5 µmol) were added and the mixture was stirred overnight. The mixture was washed with brine and purified via flash-column chromatography and centrifugation with pentane (3 x 4 mL) to obtain an orange solid in a 77% yield (18.0 mg, 34.5 µmol).

R_f (PE/EA 4:1) = 0.31

^{1}H NMR (301 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.1 Hz, 4H), 7.84 (d, *J* = 8.2 Hz, 4H), 6.94 (s, 2H), 5.16 (d, *J* = 2.5 Hz, 4H), 2.40 – 2.32 (m, 2H).

^{19}F NMR (283 MHz, $CDCl_3$) δ -62.68 (s, 6F).

^{13}C NMR (151 MHz, $CDCl_3$) δ 143.04 (s, 2C), 141.89 (s, 2C), 135.48 (s, 2C), 135.32 (s, 2C), 130.96 (s, q, *J* = 32.8 Hz, 2C), 129.46 (d, 4C), 126.10 (d, q, *J* = 3.8 Hz, 4C), 124.13 (s, q, *J* = 272.2 Hz, 2C), 102.18 (d, 2C), 79.08 (s, 2C), 73.01 (d, 2C), 32.83 (t, 2C).

HR/MS (MALDI$^+$, DCTB): *m/z* calcd. for $C_{28}H_{16}F_6N_4$ [M^+] 522.1274, found: 522.1274.

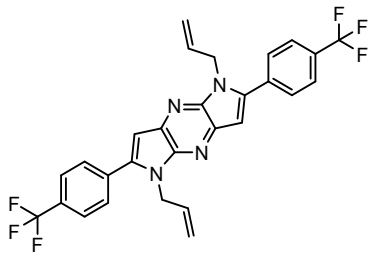
IR(ATR)[cm^{-1}]: 3309, 2129, 1619, 1550, 1498, 1425, 1386, 1348, 1317, 1227, 1196, 1169, 1154, 1121, 1109, 1067, 1017, 964, 950, 934, 844, 790, 733, 713, 683, 641.

UV-Vis [nm]: 274, 381.

Fluorescence (DMSO): λ_{Ex} = 380 nm, λ_{Max} = 452 nm; Φ = 65%

m.p. [°C]: 266 – 271 °C

1,5-Diallyl-2,6-bis(4-(trifluoromethyl)phenyl)-1,5-dihydrodipyrrolo[2,3-b:2',3'-e]pyrazine (ADPP5)



6.00 eq. Cs_2CO_3 (87.6 mg, 268 µmol) were added to a solution of 1.00 eq of **DPP2** (20.0 mg, 44.8 µmol) in 2.4 mL DMF. After stirring for 30 min at rt, 2.2 eq allylbromide (11.9 mg, 10.1 µL, 98.5 µmol) were added and the mixture was stirred overnight. The mixture was washed with brine and purified via flash-column chromatography and centrifugation with pentane (3 x 4 mL) to obtain an orange solid in a 68% yield (16.0 mg, 30.5 µmol).

R_f (PE/EA 4:1) = 0.35

^{1}H NMR (600 MHz, C_6D_6) δ 7.29 (d, *J* = 8.1 Hz, 4H), 7.24 (d, *J* = 8.1 Hz, 4H), 6.93 (s, 2H), 5.78 (ddt, *J* = 17.7, 10.4, 4.5 Hz, 2H), 4.89 (dd, *J* = 10.5, 1.5 Hz, 2H), 4.72 (tdd, *J* = 7.2, 3.2, 1.7 Hz, 6H).

^{19}F NMR (283 MHz, $CDCl_3$) δ -62.65 (s, 6F).

^{13}C NMR (151 MHz, C_6D_6) δ 143.42 (s, 2C), 142.68 (s, 2C), 136.07 (s, 2C), 135.87 (s, 2C), 134.41 (s, 2C), 130.31 (s, q, *J* = 32.4 Hz, 2C), 129.36 (d, 4C), 125.76 (d, q, *J* = 3.8 Hz, 4C), 124.30 (s, q, *J* = 272.2 Hz, 2C), 116.35 (t, 2C), 45.22 (t, 2C).

HR/MS (MALDI$^+$, DCTB): *m/z* calcd. for $C_{28}H_{20}F_6N_4$ [M^+] 526.1587, found: 526.1585.

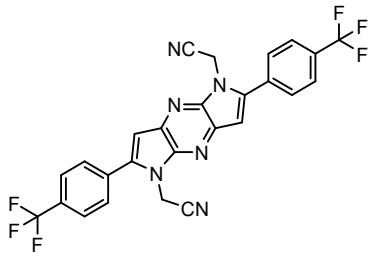
IR(ATR)[cm^{-1}]: 2925, 1617, 1549, 1497, 1416, 1383, 1360, 1316, 1224, 1193, 1162, 1124, 1107, 1069, 1018, 997, 926, 849, 788, 734, 716, 685, 657, 633, 608.

UV-Vis [nm]: 285, 374.

Fluorescence (DMSO): λ_{Ex} = 380 nm, λ_{Max} = 454 nm; Φ = 63%

m.p. [°C]: 225 – 230 °C

2,2'-(2,6-bis(4-(trifluoromethyl)phenyl)dipyrrolo[2,3-b:2',3'-e]pyrazine-1,5-diyl)diacetonitrile (ADPP6)



6.00 eq. Cs_2CO_3 (87.6 mg, 268 µmol) were added to a solution of 1.00 eq of **DPP2** (20.0 mg, 44.8 µmol) in 2.4 mL DMF. After stirring for 30 min at rt, 2.2 eq 2-bromoacetonitrile (11.8 mg, 6.87 µL, 98.5 µmol) were added and the mixture was stirred overnight. The mixture was washed with brine (50 mL) and purified via flash-column chromatography and centrifugation with pentane (3 x 4 mL) to obtain an orange solid in a 90% yield (21.2 mg, 40.3 µmol).

R_f (PE/EA 4:1) = 0.44

^{1}H NMR (301 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.2 Hz, 4H), 7.79 (d, *J* = 8.2 Hz, 4H), 6.96 (s, 2H), 5.26 (s, 4H).

^{19}F NMR (283 MHz, $CDCl_3$) δ -62.82 (s, 6F).

^{13}C NMR (151 MHz, C_6D_6) δ 143.09 (s, 2C), 142.04 (s, 2C), 135.58 (S, 2C), 133.99 (s, 2C), 131.88 (s, q, *J* = 33.0 Hz, 2C), 129.56 (d, 4C), 126.59 (d, q, *J* = 3.7 Hz 4C), 123.88 (s, q, *J* = 272.4 Hz, 2C), 114.91 (s, 2C), 103.73 (d, 2C), 31.23 (t, 2C).

HR/MS (MALDI$^+$, DCTB): *m/z* calcd. for $C_{26}H_{14}F_6N_4$ [M^+] 524.1179, found: 524.1173.

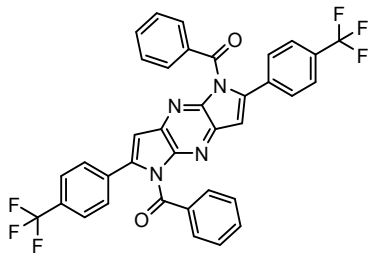
IR(ATR)[cm^{-1}]: 2990, 2942, 1616, 1494, 1426, 1383, 1347, 1316, 1225, 1192, 1159, 1126, 1109, 1067, 1014, 961, 911, 849, 836, 790, 743, 730, 710, 685, 655.

UV-Vis [nm]: 276, 376.

Fluorescence (DMSO): λ_{Ex} = 380 nm, λ_{Max} = 440 nm; Φ = 65%

m.p. [°C]: 272 – 277 °C

(2,6-bis(4-(trifluoromethyl)phenyl)dipyrrolo[2,3-b:2',3'-e]pyrazine-1,5-diyl)bis(phenylmethanone) (ACDPP)



Benzoyl chloride (18.9 mg, 15.6 µL, 134 µmol) was added to a mixture containing **DPP2** (20.0 mg, 44.8 µmol), DMAP (0.9 mg, 6.7 mmol) and Et_3N (5.4 mg, 7.5 µL, 53.8 µmol) and) in 1 mL DCM at rt. overnight.[12] After washing with brine (30 mL) and extracting with ethylacetate,. the resulting organic phase was then dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was centrifuged with $CHCl_3$ (2x 4 mL) and pentane (2x 4 mL) to yield 46% of a colourless solid (13.5 mg, 20.6 µmol).

R_f (PE/EA 1:1) = 0.52

^{1}H NMR (600 MHz, THF) δ 8.05 (dd, *J* = 8.3, 1.3 Hz, 4H), 7.75 – 7.71 (m, 2H), 7.69 (d, *J* = 2.1 Hz, 8H), 7.56 (t, *J* = 7.8 Hz, 4H), 7.09 (s, 2H).

^{13}C NMR (151 MHz, THF) δ 169.38 (s, 2C), 145.22 (s, 2C), 144.57 (s, 2C), 136.98 (s, 2C), 136.70 (s, 2C), 135.45 (s, 2C), 135.11 (d, 2C), 132.41 (d, 4C), 130.87 (s, q, *J* = 32.3 Hz, 2C), 129.54 (d, 4C), 129.40 (d, 4C), 126.47 (d, q, *J* = 3.8 Hz, 4C), 125.42 (s, q, *J* = 271.9 Hz, 2C), 109.41 (d, 2C).

^{19}F NMR (283 MHz, THF) δ -65.31 (s, 6F).

HR/MS (MALDI$^+$, DCTB): *m/z* calcd. for $C_{36}H_{20}F_6N_4O_2$ [M^+] 654.1485, found: 654.1487.

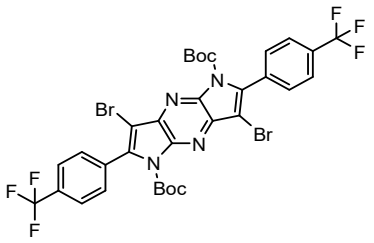
IR(ATR)[cm^{-1}]: 3341, 2909, 1786, 1725, 1599, 1451, 1321, 1274, 1212, 1172, 1035, 1016, 996, 897, 778, 703, 617.

UV-Vis [nm]: 383.

Fluorescence (DMSO): λ_{Ex} = 380 nm, λ_{Max} = 450 nm*;* Φ = 37%

m.p. [°C]: > 300 °C

Di-*tert*-butyl 3,7-dibromo-2,6-bis(4-(trifluoromethyl)phenyl)dipyrrolo[2,3-b:2',3'-e]pyrazine-1,5-dicarboxylate (BrDPPB)



To a solution of **DPPB2** (10.0 mg, 15.5 µmol, 1.00 eq.) in MeCN (0.5 mL) *N*-bromosuccinimide (2.20 mg, 38.7 µmol, 2.5 eq.) was added and the reaction stirred at 75 °C overnight. The crude mixture was washed with water (2x 10 mL) and extracted with DCM. The combined organic layers were washed, dried over Na_2SO_4 and the solvent was removed in vacuo. The off-white solid was further centrifuged with pentane (3x 4 mL) and MeOH (1x 4 mL) to obtain the product in a quantitative yield. (12.4 mg, 15.5 µmol, quant.).

R_f (PE/EA 1:1) = 0.80

$^1H\{^{19}F\}$ NMR (600 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.3 Hz, 4H), 7.67 (d, *J* = 8.1 Hz, 4H), 1.47 (s, 18H).

$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 147.36 (s, 2C), 140.98 (s, 2C), 140.27 (s, 2C), 135.53 (s, 2C), 135.06 (s, 2C), 131.22 (s, q: $J_{C\text{-}F}$ = 32.7 Hz, 2C), 130.18 (d, 4C) 125.38 (d, q: $J_{C\text{-}F}$ = 7.6 Hz, 4C), 124.05 (d, q: $J_{C\text{-}F}$ = 272.4 Hz), 99.29 (s, 2C), 86.10 (s, 2C), 27.83 (q, 6C).

^{19}F NMR (283 MHz, $CDCl_3$) δ -62.12 (s, 6F).

HR/MS (MALDI$^+$, DCTB): *m/z* calcd. for $C_{32}H_{26}Br_2F_6N_4O_4Na^+$: [$M^+$] 825.0117, found: 825.0130, correct isotope distribution.

IR(ATR)[cm^{-1}]: 2986, 2927, 2853, 1757, 1620, 1561, 1458, 1407, 1370, 1348, 1320, 1270, 1218, 1146, 1107, 1092, 1065, 1018, 949, 930, 861, 756, 686.

UV-Vis [nm]: 246, 273, 368.

Fluorescence (DCM): λ_{Ex} = 368 nm, λ_{Max} = 430 nm; Φ = 2%

m.p. [°C]: > 300 °C

NMR Spectra

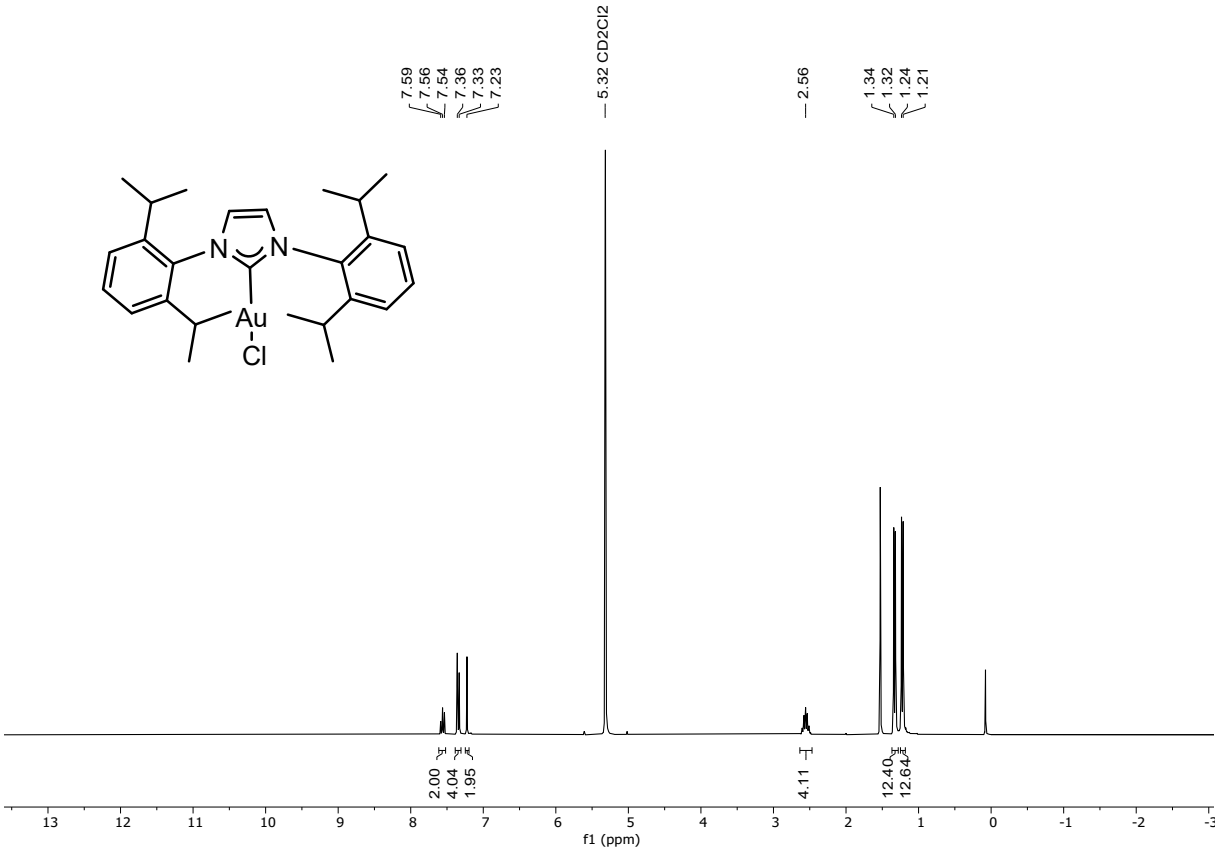


*Figure 1: **^{1}H NMR** (301 MHz, CD_2Cl_2) of IPrAuCl (301 MHz, CD_2Cl_2).*

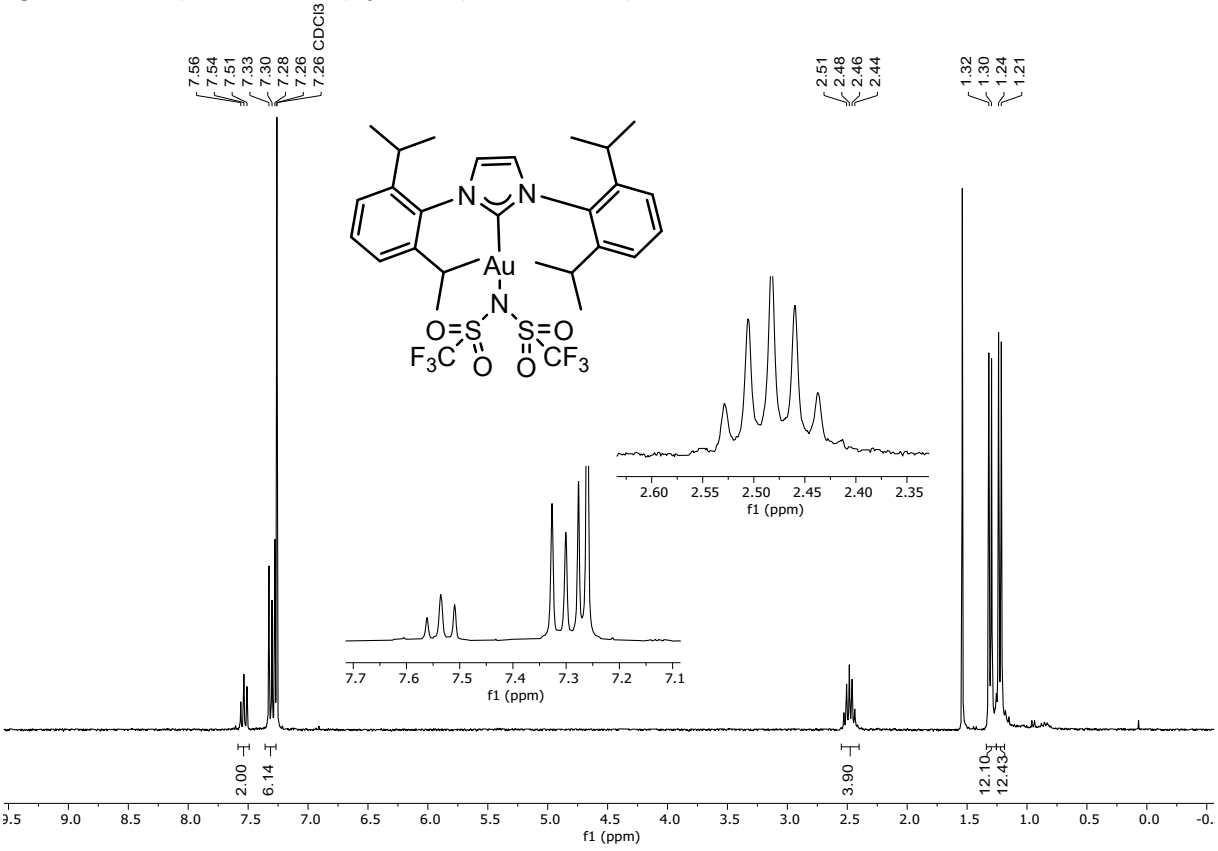


*Figure 2: **^{1}H NMR** (301 MHz, $CDCl_3$) of IPrAuNTf_2.*

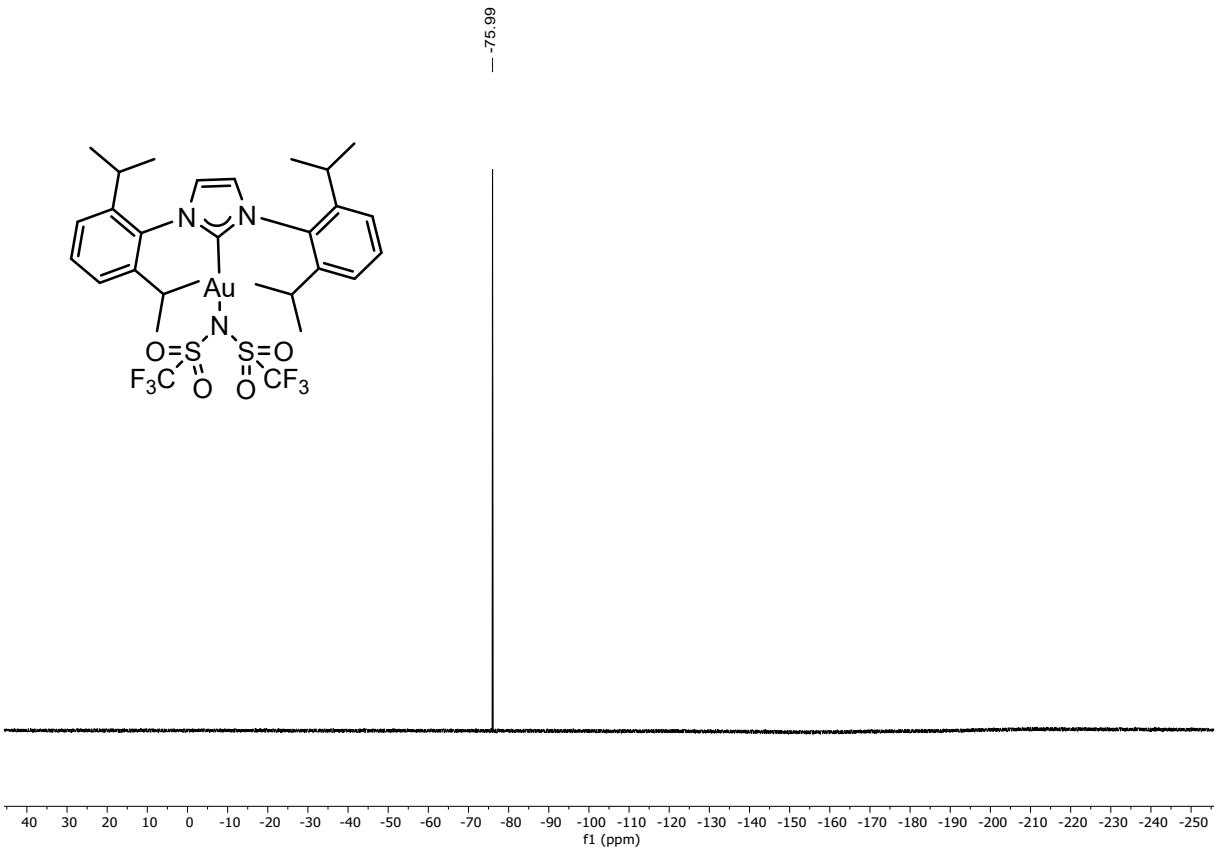


*Figure 3: **^{19}F NMR** (283 MHz, $CDCl_3$) of IPrAuNTf_2.*

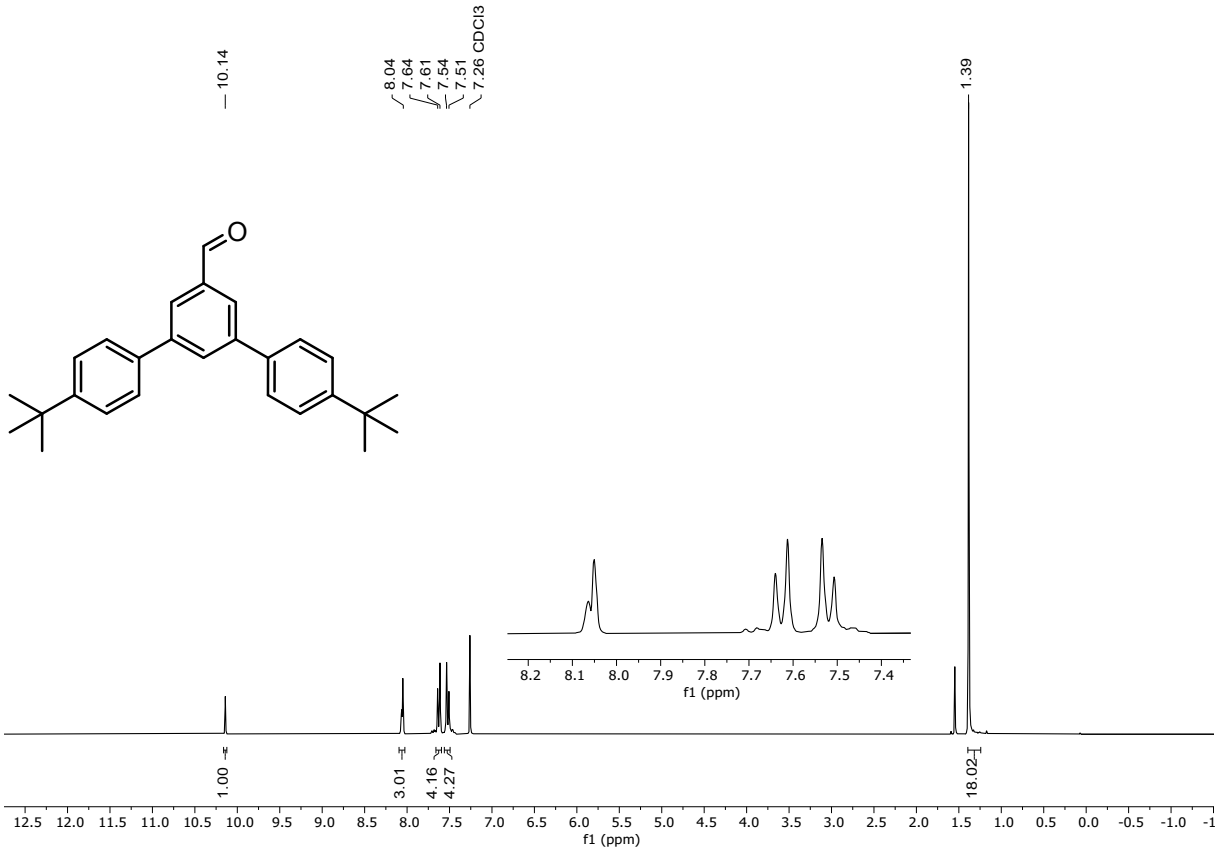


*Figure 4: **^{1}H NMR** (300 MHz, $CDCl_3$) of 4,4''-di-tert-butyl-[1,1':3',1''-terphenyl]-5'-carbaldehyde.*

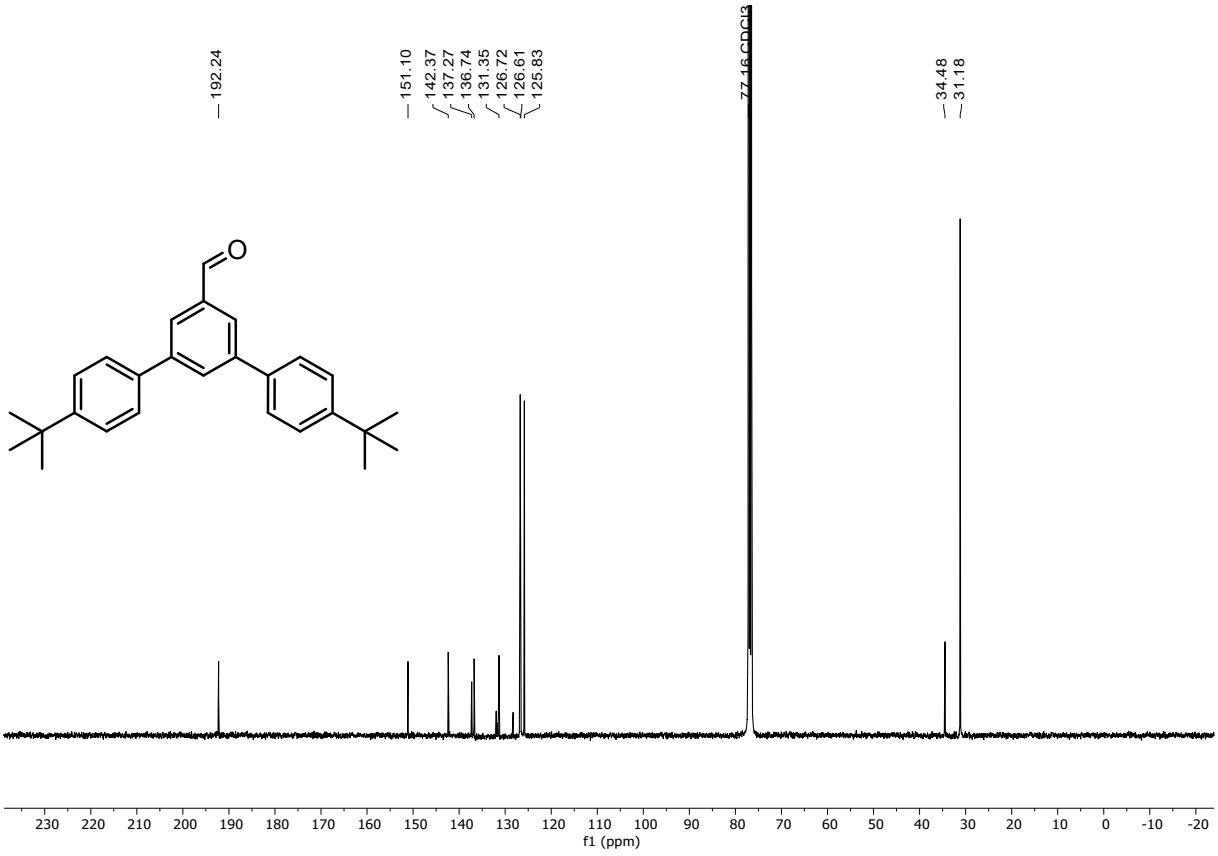


*Figure 5: **$^{13}C\{^{1}H\}$ NMR** (126 MHz, $CDCl_3$) of 4,4''-di-tert-butyl-[1,1':3',1''-terphenyl]-5'-carbaldehyde.*

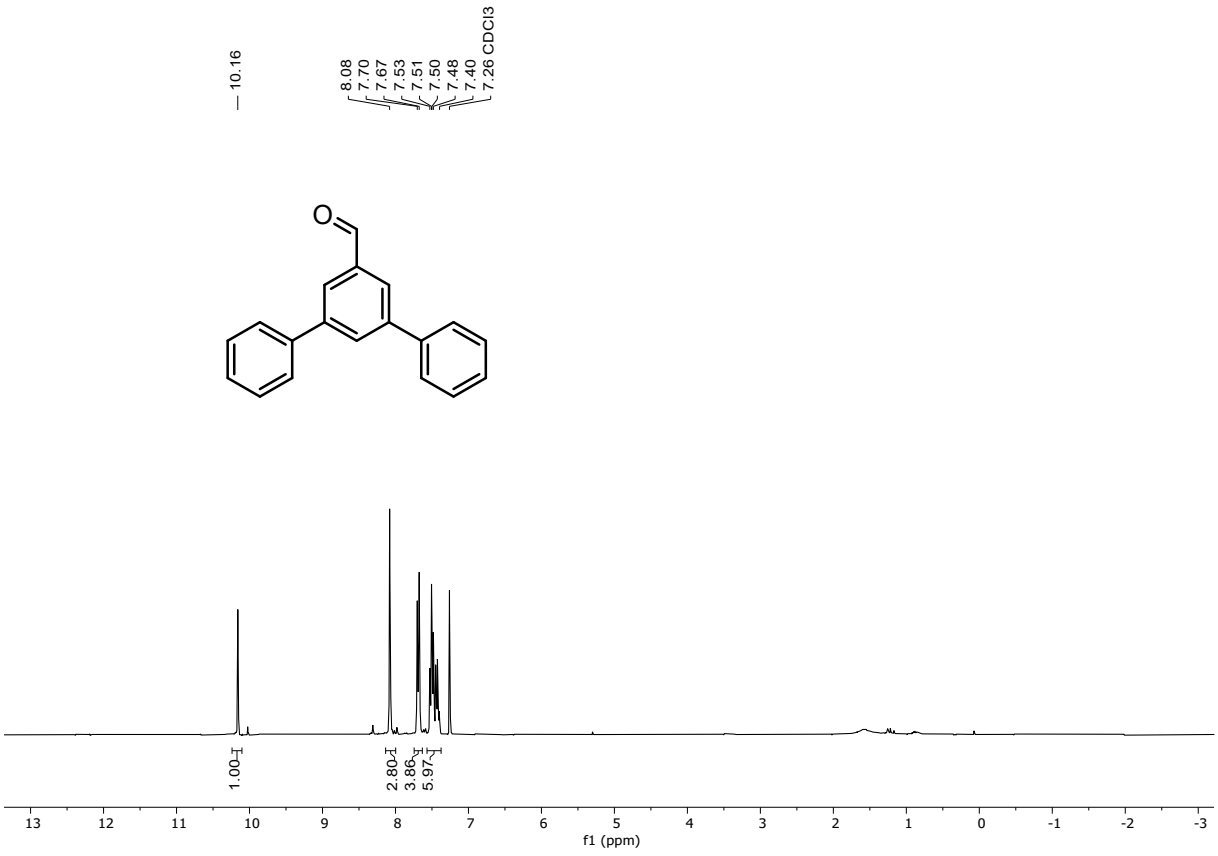


*Figure 6: **^{1}H NMR** (300 MHz, $CDCl_3$)of [1,1':3',1''-terphenyl]-5'-carbaldehyde.*

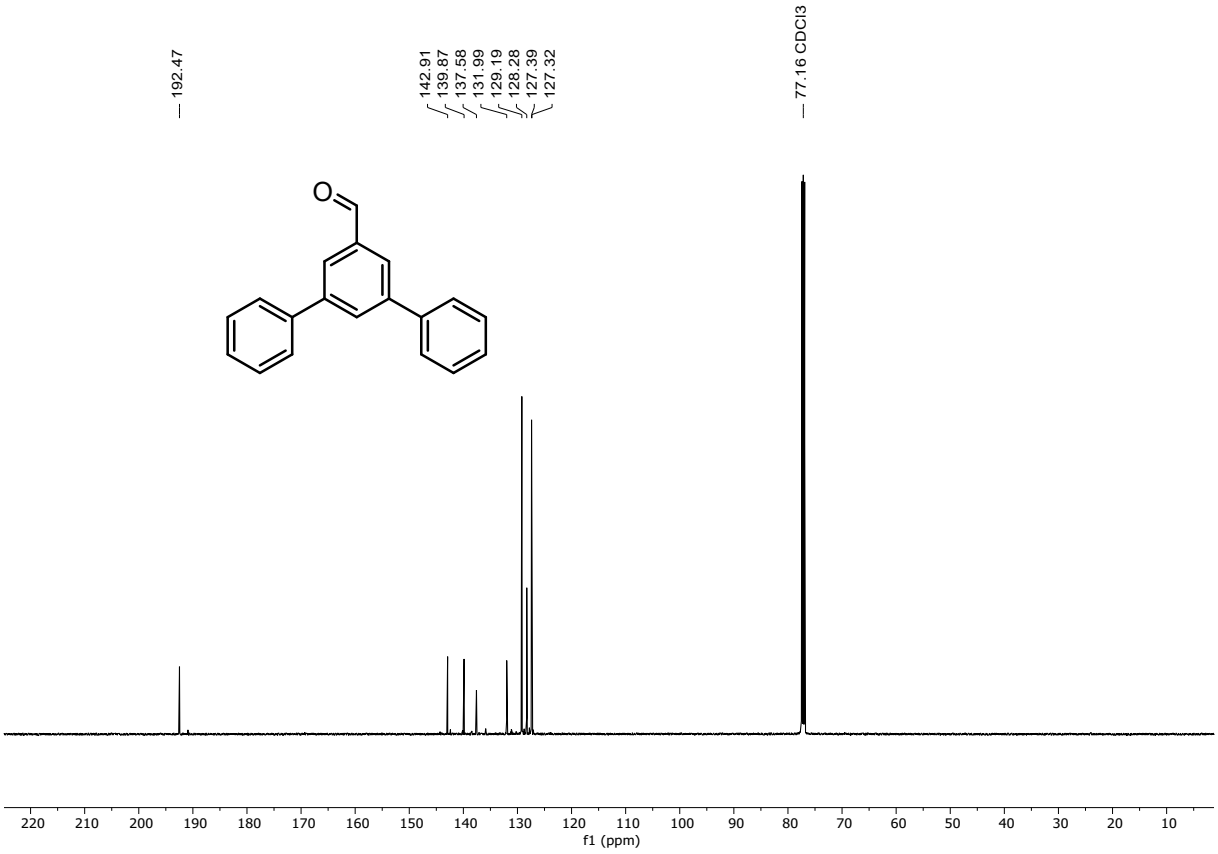


*Figure 7: **$^{13}C\{^{1}H\}$ NMR** (126 MHz, $CDCl_3$) of [1,1':3',1''-terphenyl]-5'-carbaldehyde.*

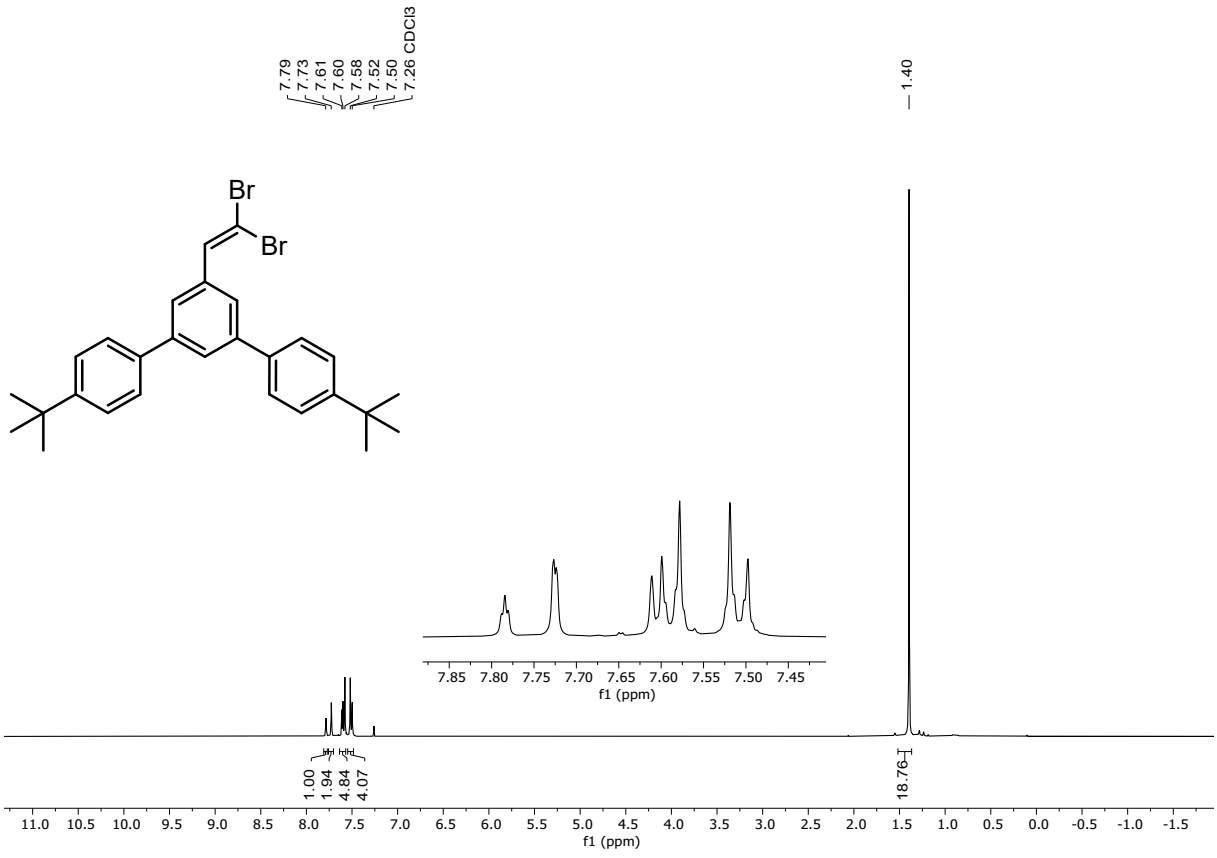


*Figure 8: **^{1}H NMR** (400 MHz, $CDCl_3$) of 4,4''-di-tert-butyl-5'-(2,2-dibromovinyl)-1,1':3',1''-terphenyl.*

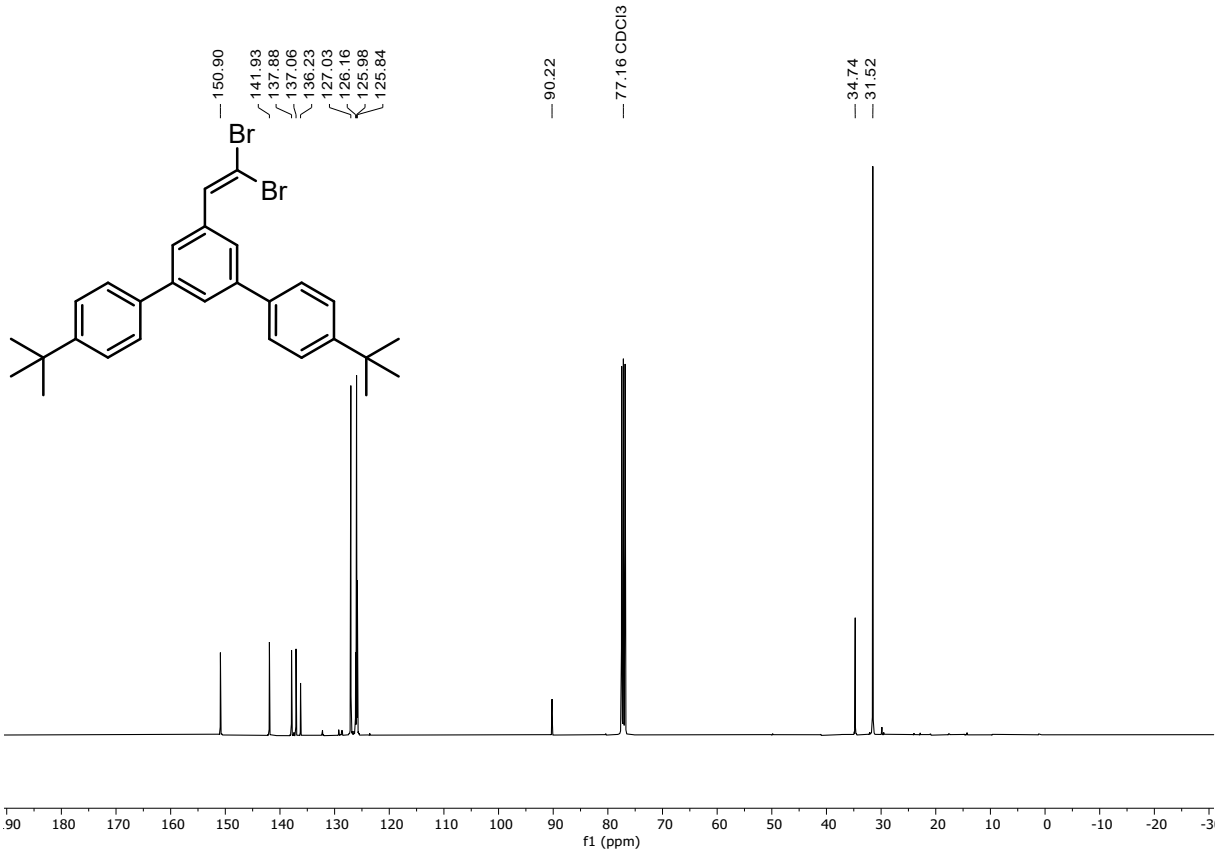


*Figure 9: **$^{13}C\{^{1}H\}$ NMR** (101 MHz, $CDCl_3$) of 4,4''-di-tert-butyl-5'-(2,2-dibromovinyl)-1,1':3',1''-terphenyl.*

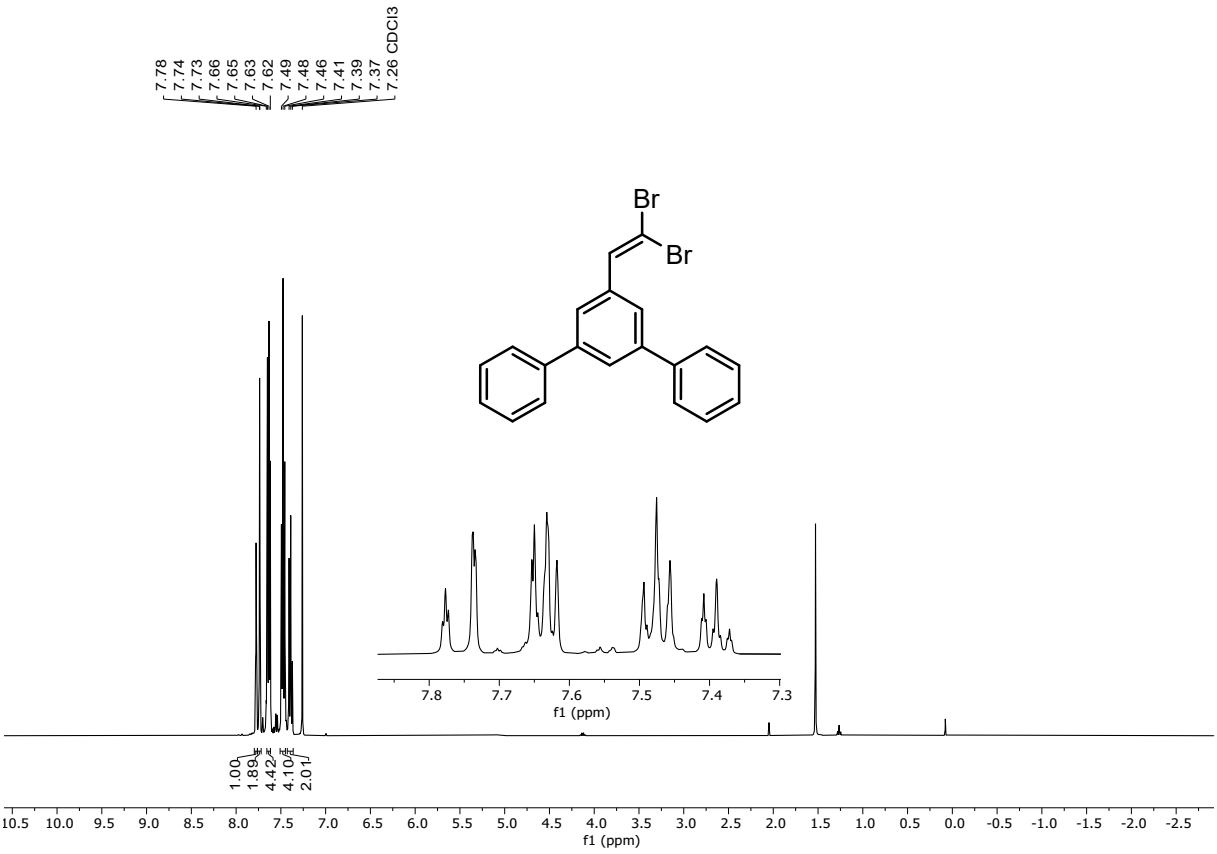


*Figure 10: **^{1}H NMR** (400 MHz, $CDCl_3$) of 5'-(2,2-dibromovinyl)-1,1':3',1''-terphenyl.*

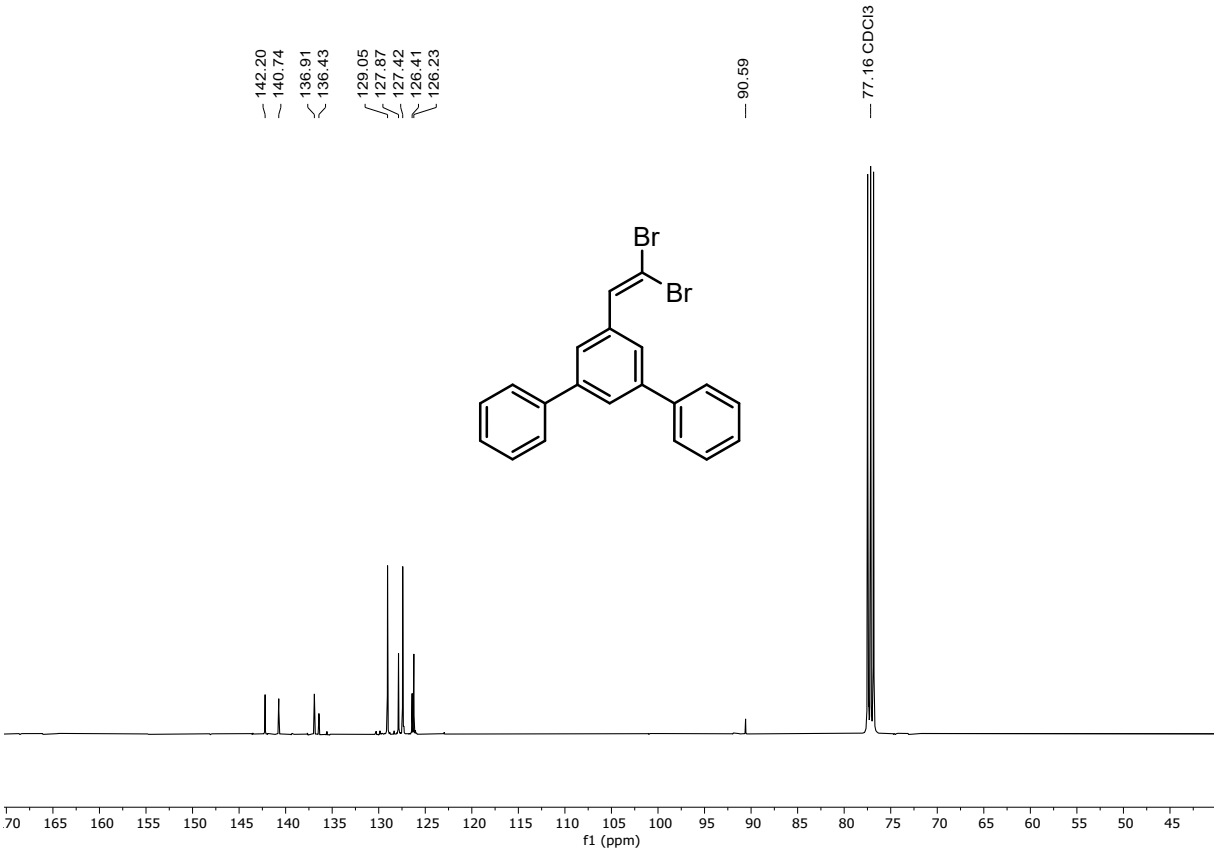


*Figure 11: **$^{13}C\{^{1}H\}$ NMR** (101 MHz, $CDCl_3$) of 5'-(2,2-dibromovinyl)-1,1':3',1''-terphenyl.*

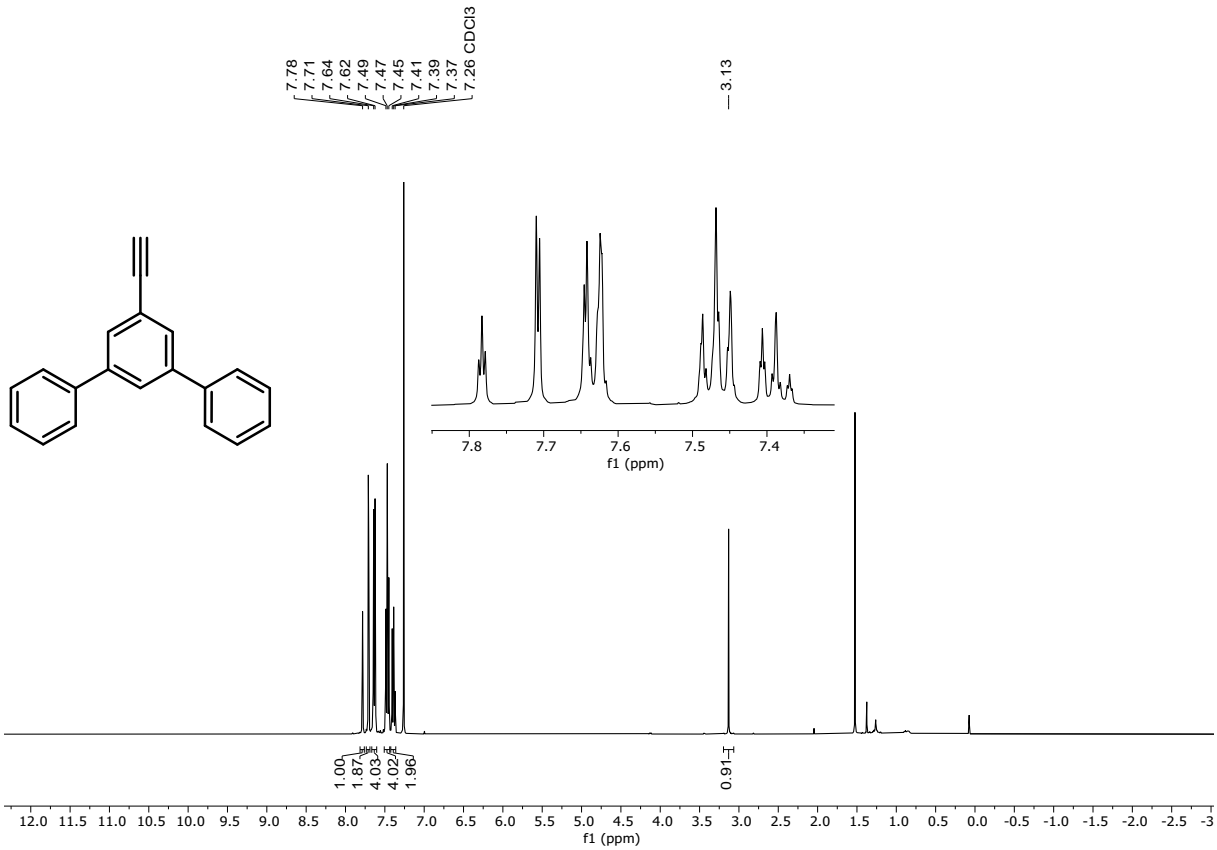


*Figure 12: **^{1}H NMR** (400 MHz, $CDCl_3$) of 5'-ethynyl-1,1':3',1''-terphenyl.*

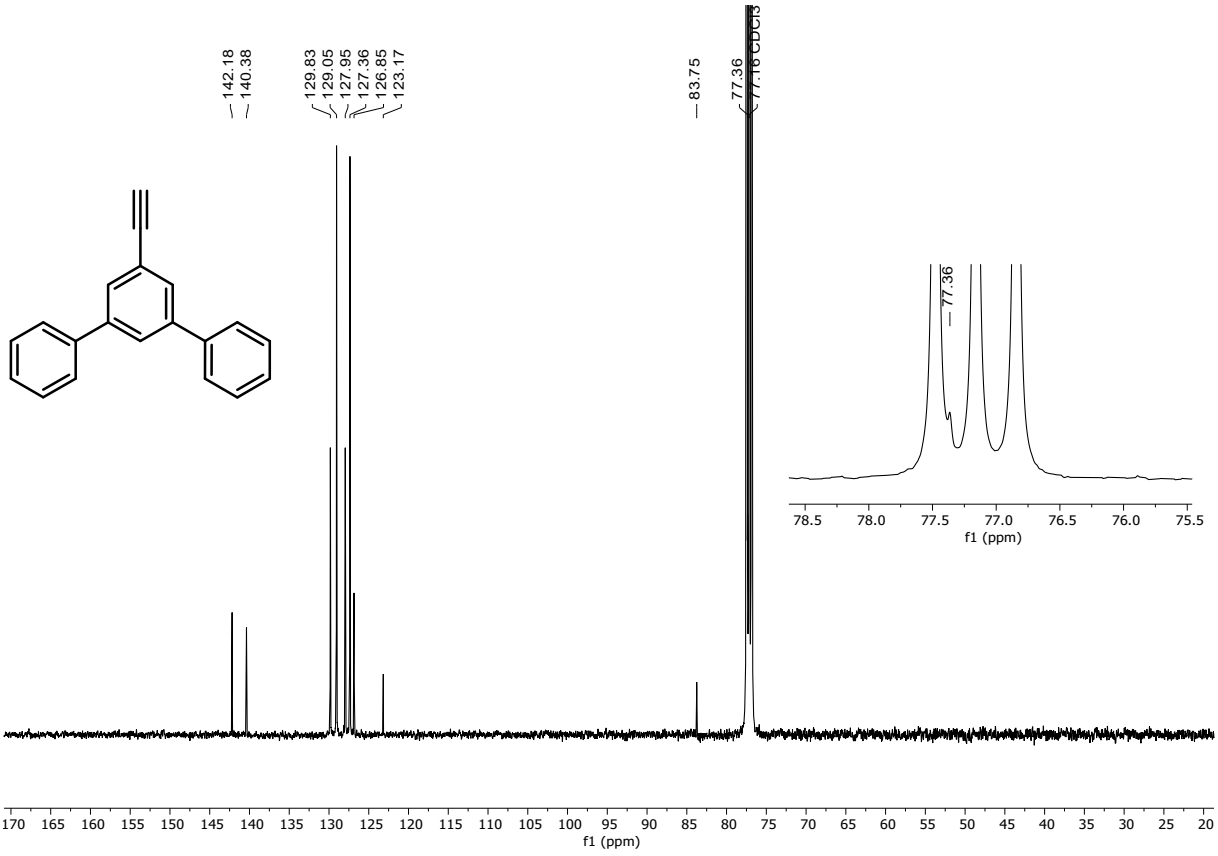


*Figure 123: **$^{13}C\{^{1}H\}$ NMR** (101 MHz, $CDCl_3$) of 5'-ethynyl-1,1':3',1''-terphenyl.*

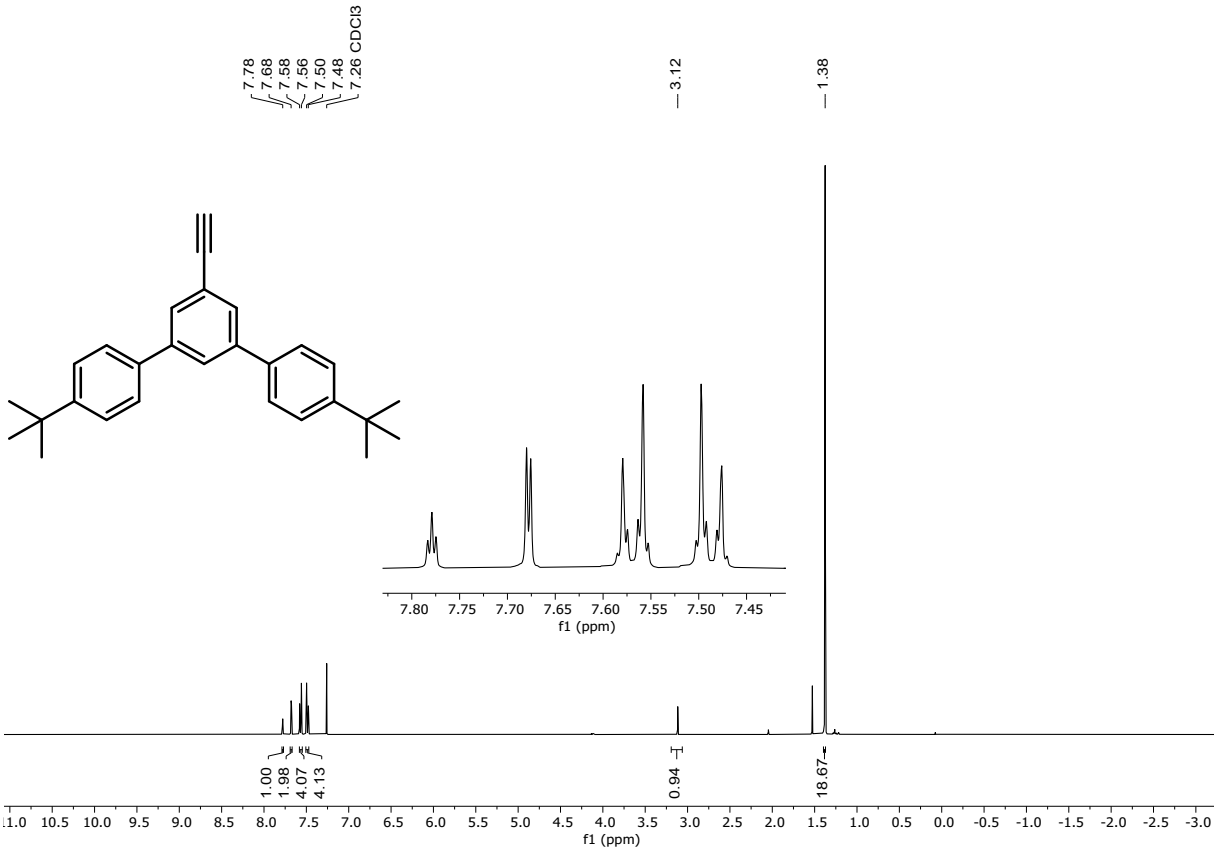


*Figure 134: **^{1}H NMR** (400 MHz, $CDCl_3$) of 4,4''-di-tert-butyl-5'-ethynyl-1,1':3',1''-terphenyl.*

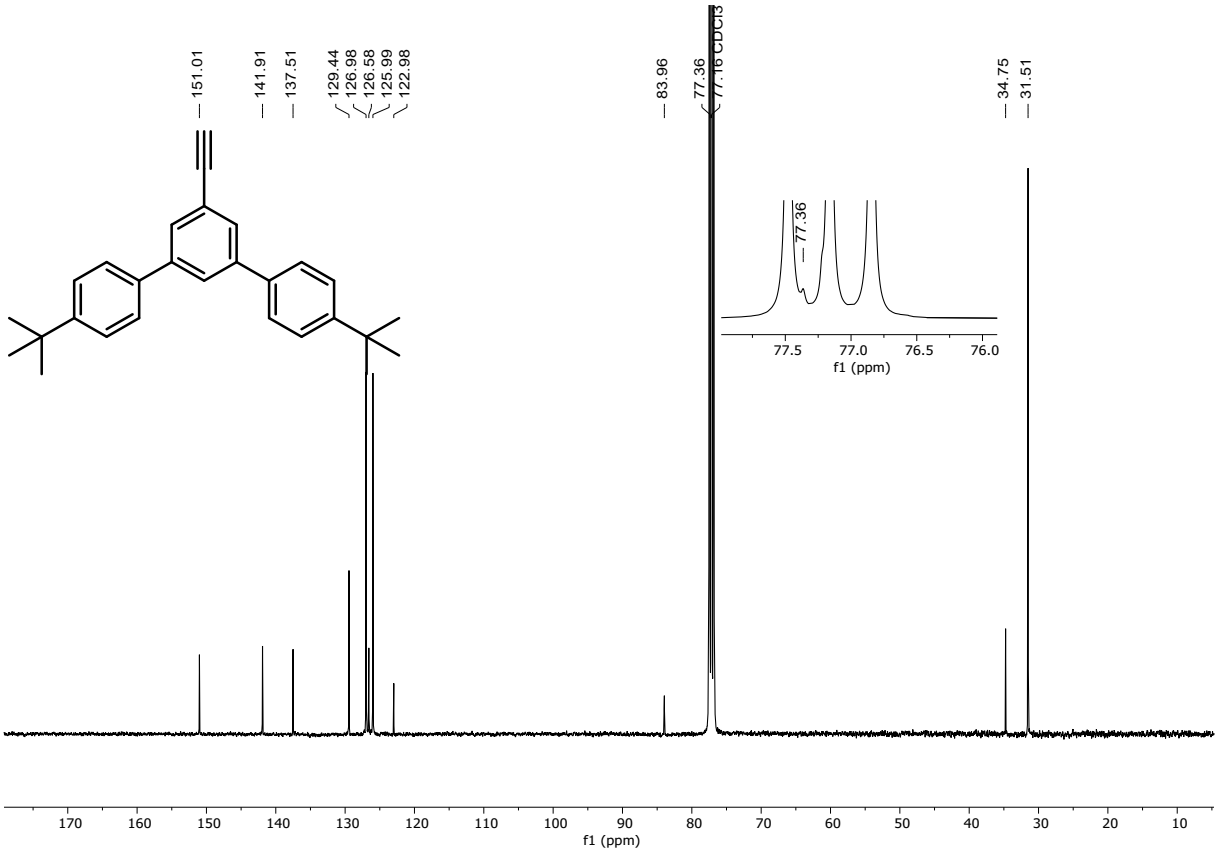


*Figure 145: **$^{13}C\{^{1}H\}$ NMR** (101 MHz, $CDCl_3$) of 4,4''-di-tert-butyl-5'-ethynyl-1,1':3',1''-terphenyl.*

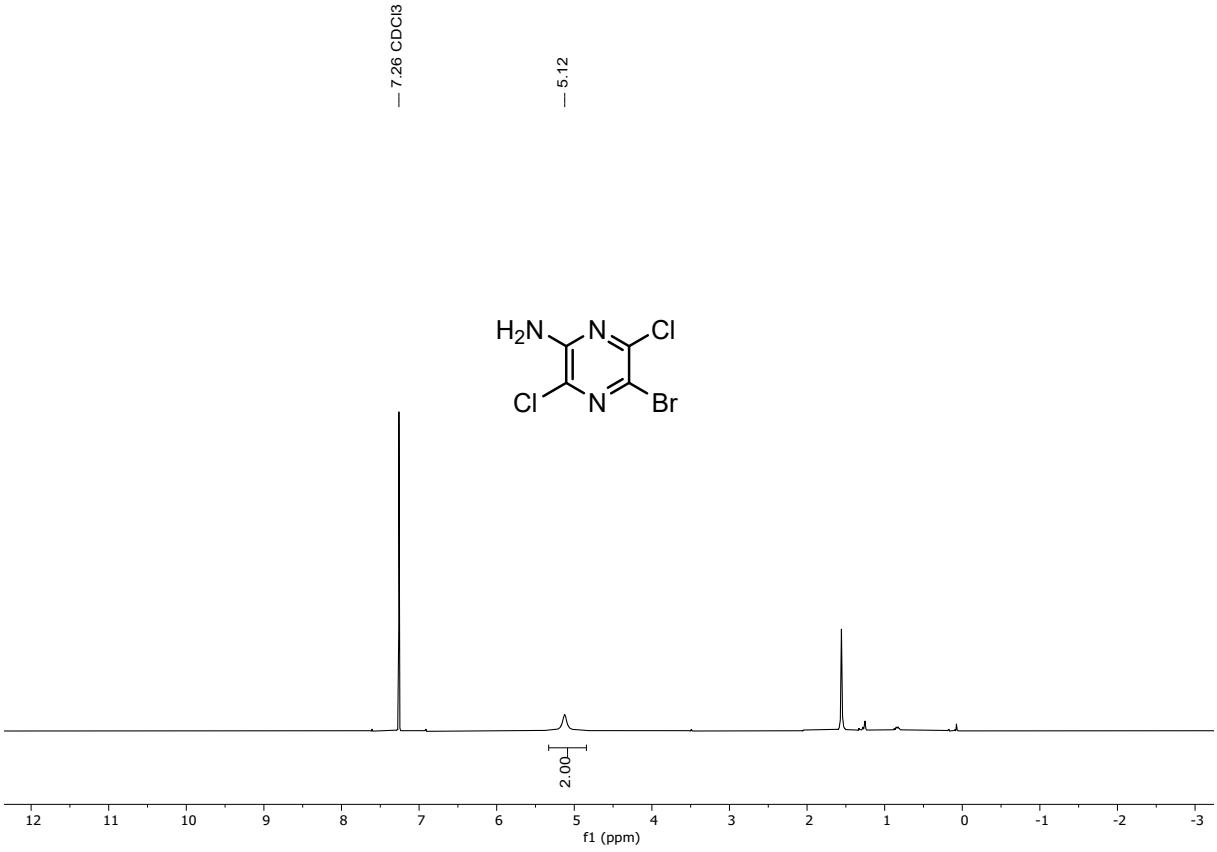


*Figure 15: **^{1}H-NMR** (300 MHz, $CDCl_3$): of 5-bromo-3,6-dichloropyrazin-2-amine (**2**).*

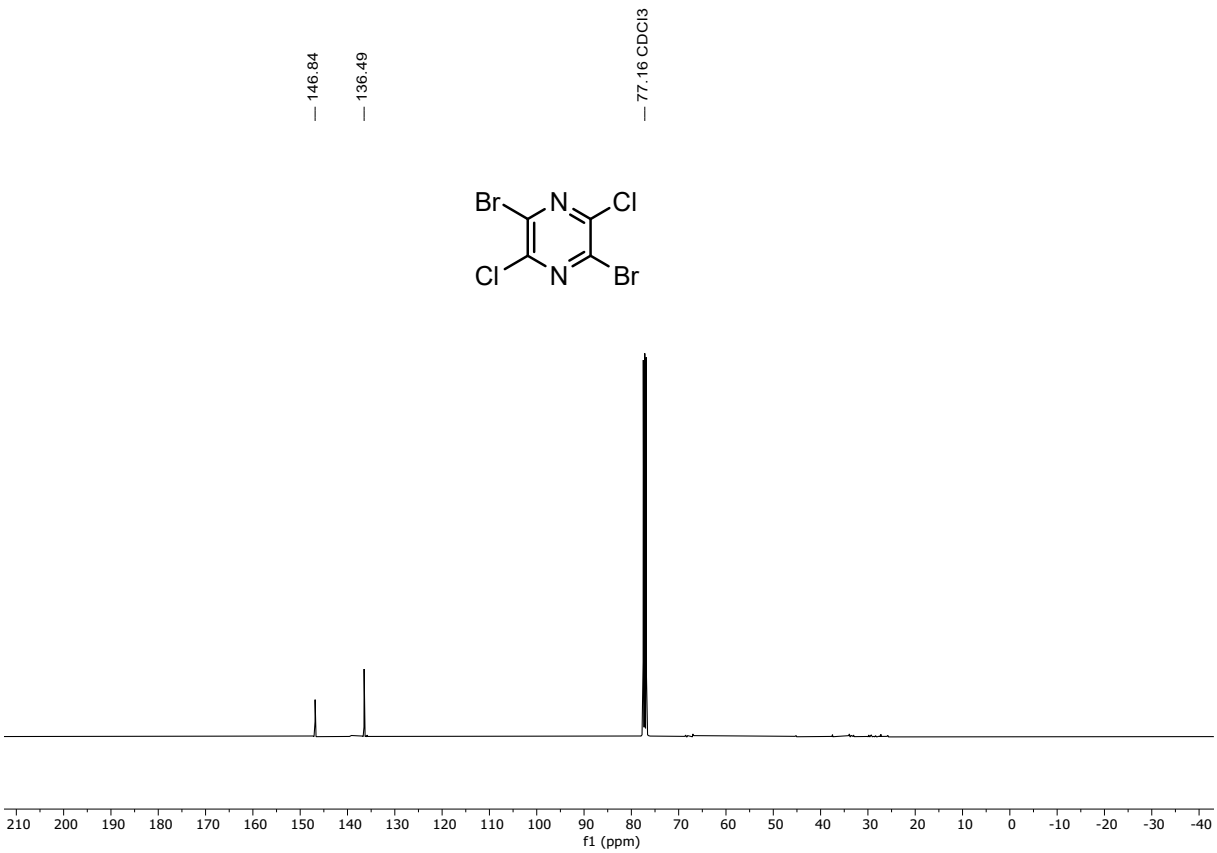


*Figure 16: **$^{13}C\{^{1}H\}$ NMR** (101 MHz, $CDCl_3$): of 2,5-dibromo-3,6-dichloropyrazine.*

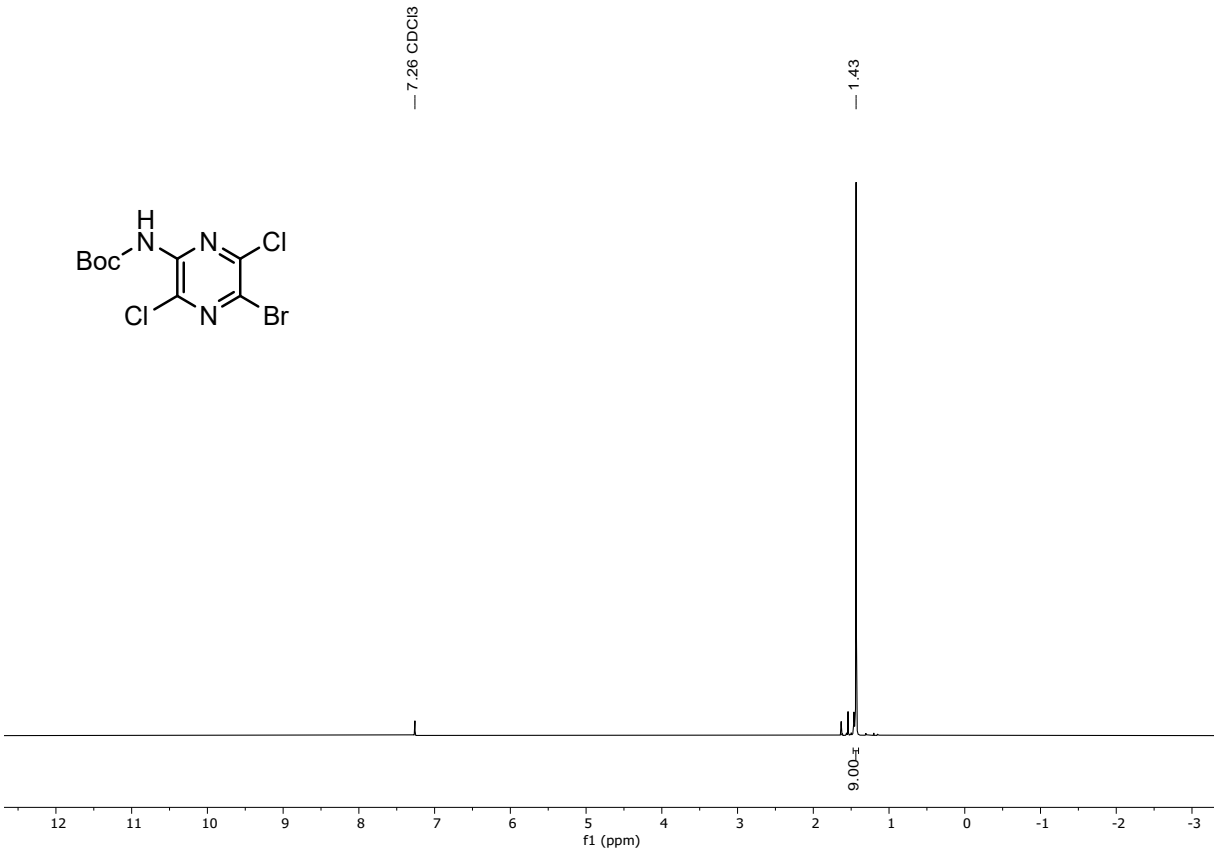


*Figure 17: **^{1}H NMR** (500 MHz, $CDCl_3$) of tert-butyl (5-bromo-3,6-dichloropyrazin-2-yl)carbamate (**3**).*

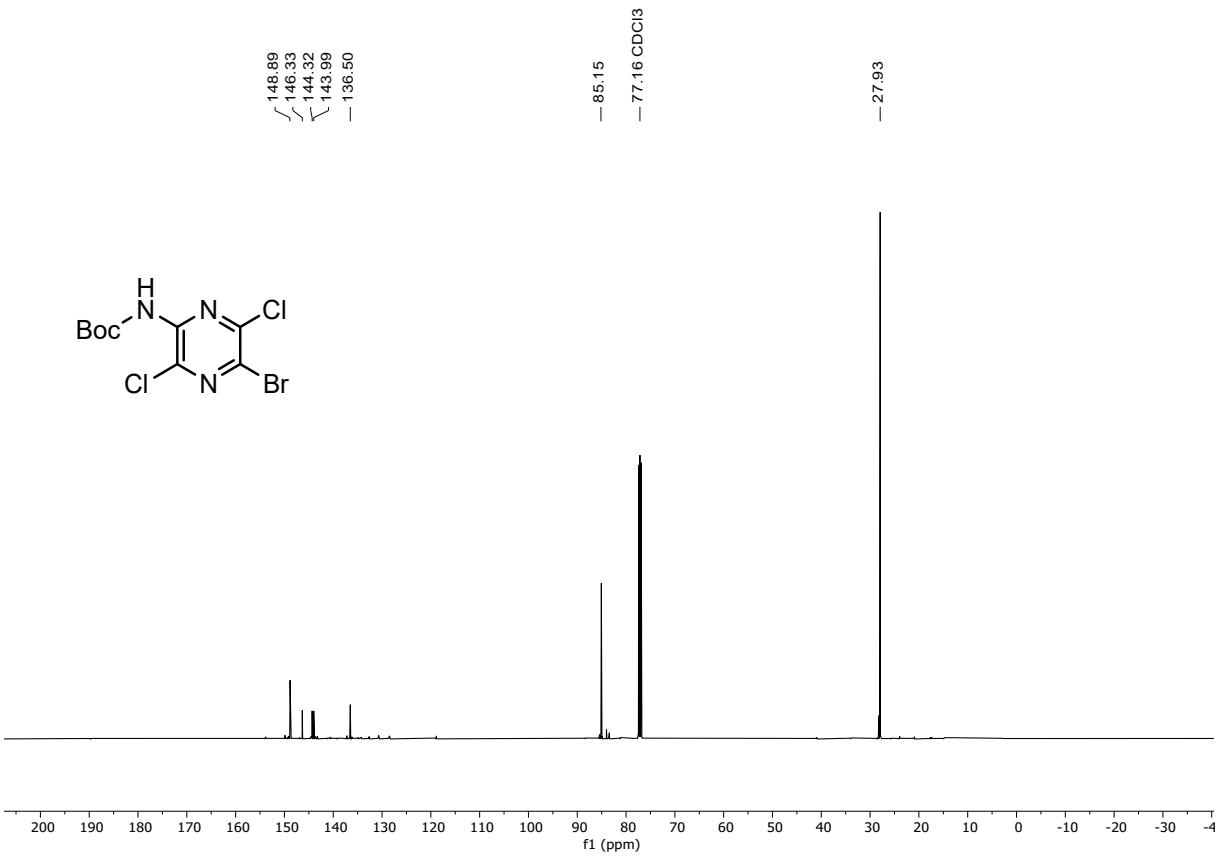


*Figure 18: **$^{13}C\{^{1}H\}$ NMR** (126 MHz, $CDCl_3$) of tert-butyl (5-bromo-3,6-dichloropyrazin-2-yl)carbamate (**3**).*

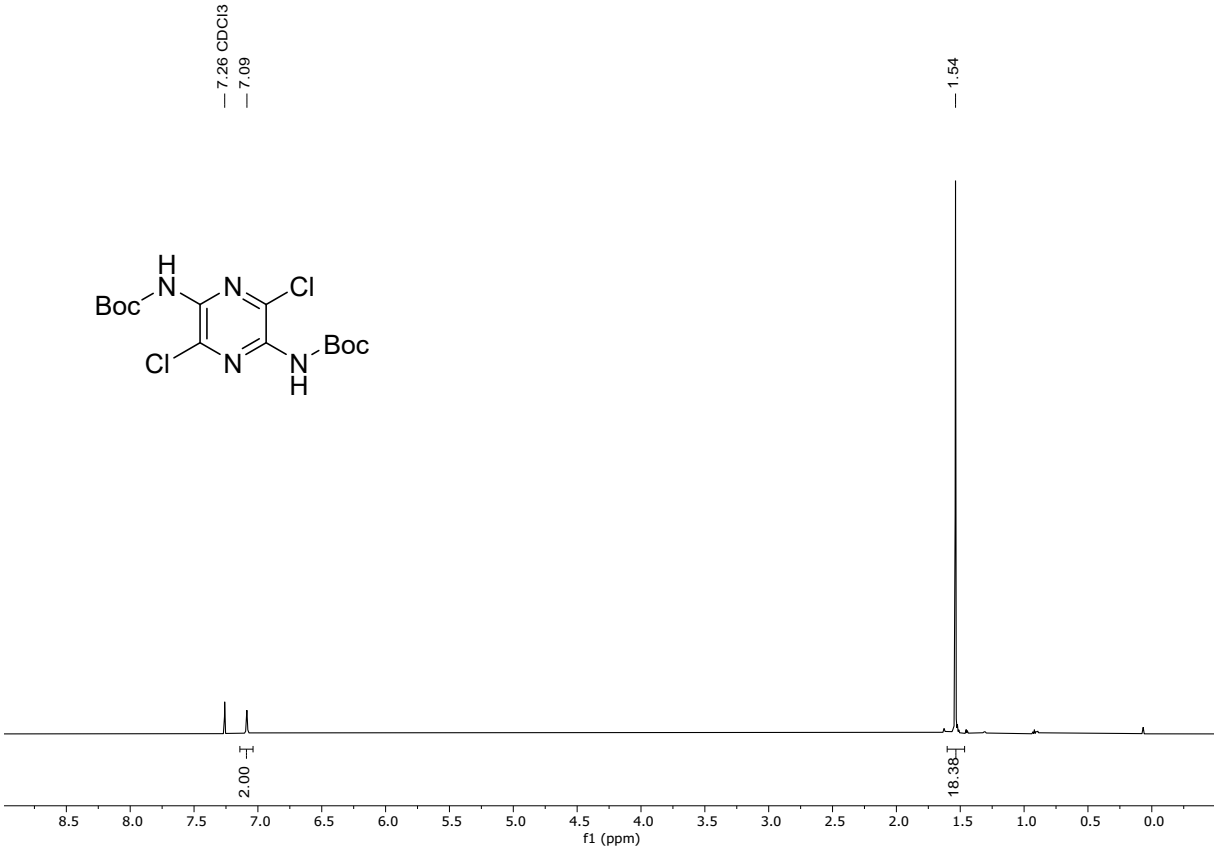


*Figure 19: **^{1}H-NMR** (600 MHz, $CDCl_3$): of Di-tert-butyl (3,6-dichloropyrazine-2,5-diyl) dicarbamate (**DBC**).*

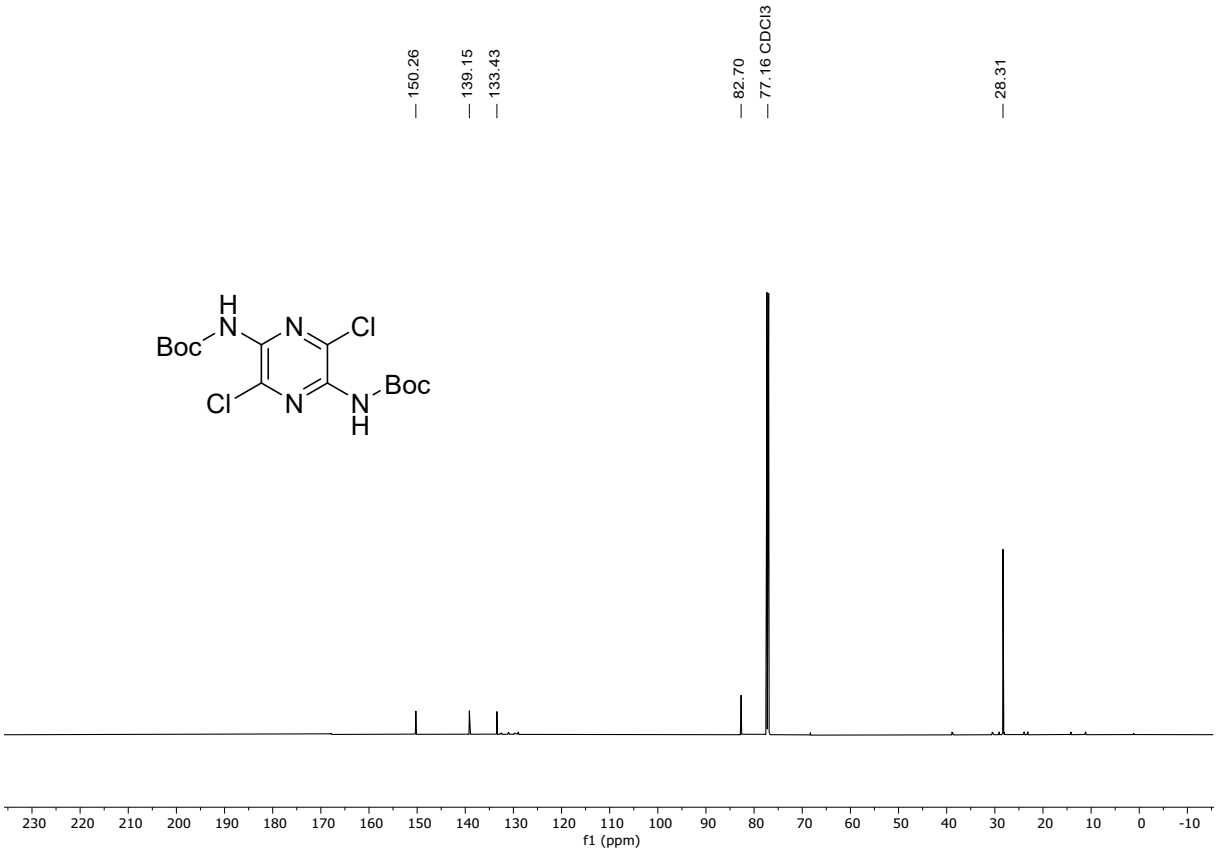


*Figure 20: **$^{13}C\{^{1}H\}$ NMR** (151 MHz, $CDCl_3$): of Di-tert-butyl (3,6-dichloropyrazine-2,5-diyl) dicarbamate.*

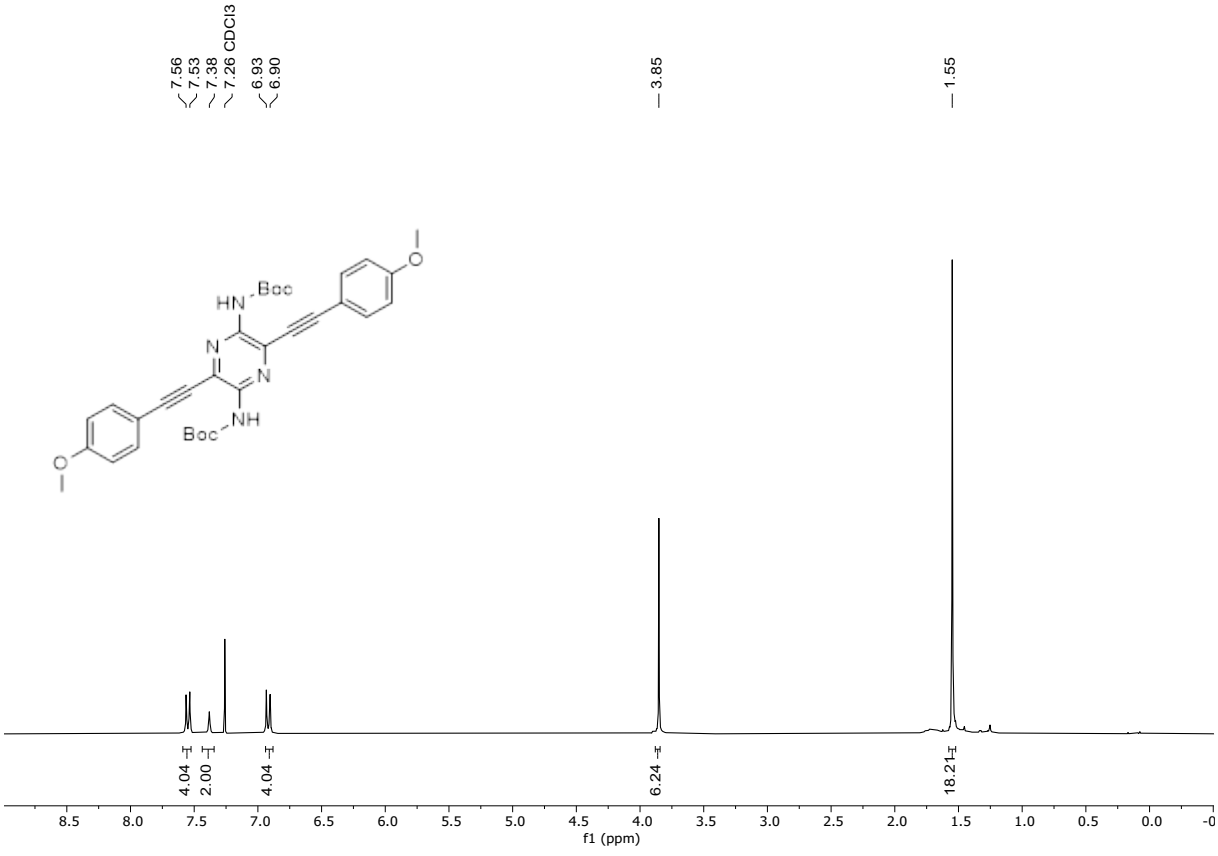


*Figure 21: **^{1}H NMR** (301 MHz, $CDCl_3$) of **BA1**.*

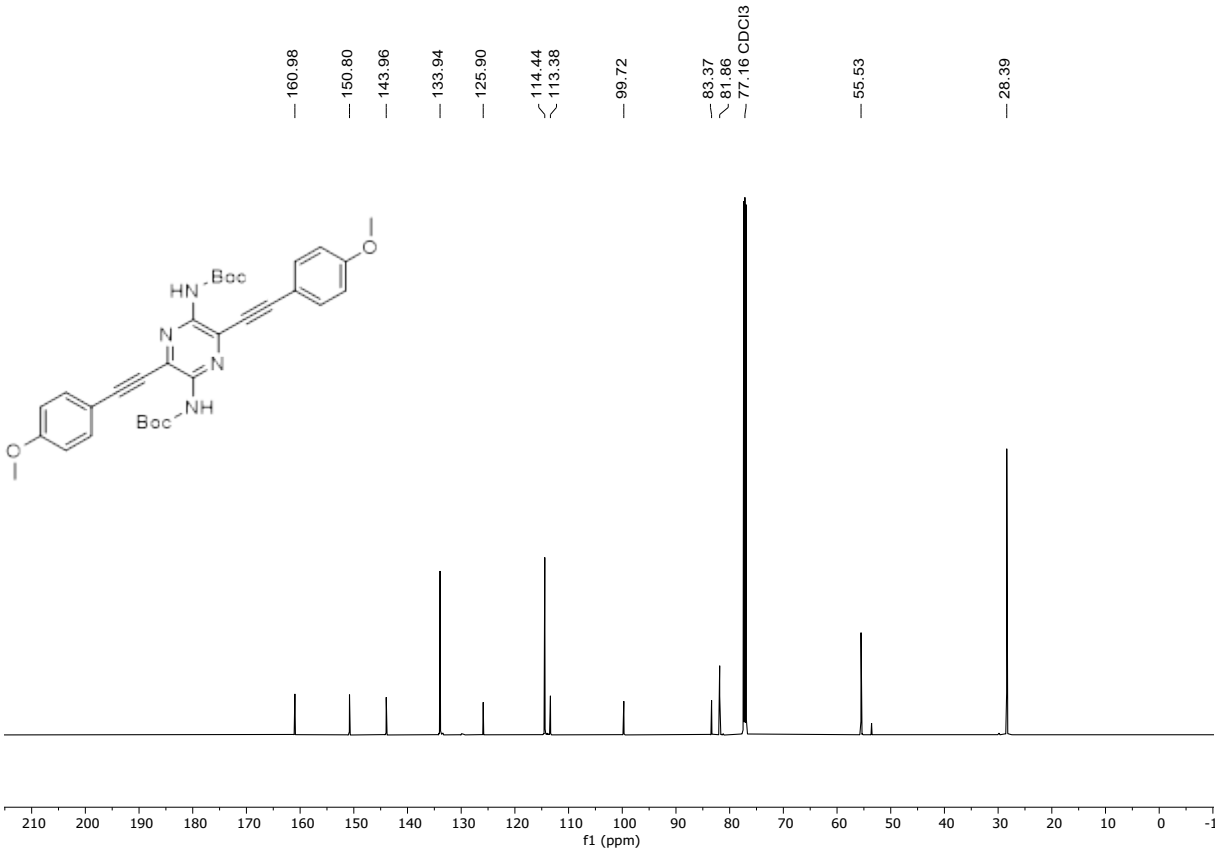


*Figure 22: **$^{13}C\{^{1}H\}$ NMR** (151 MHz, $CDCl_3$) of **BA1**.*

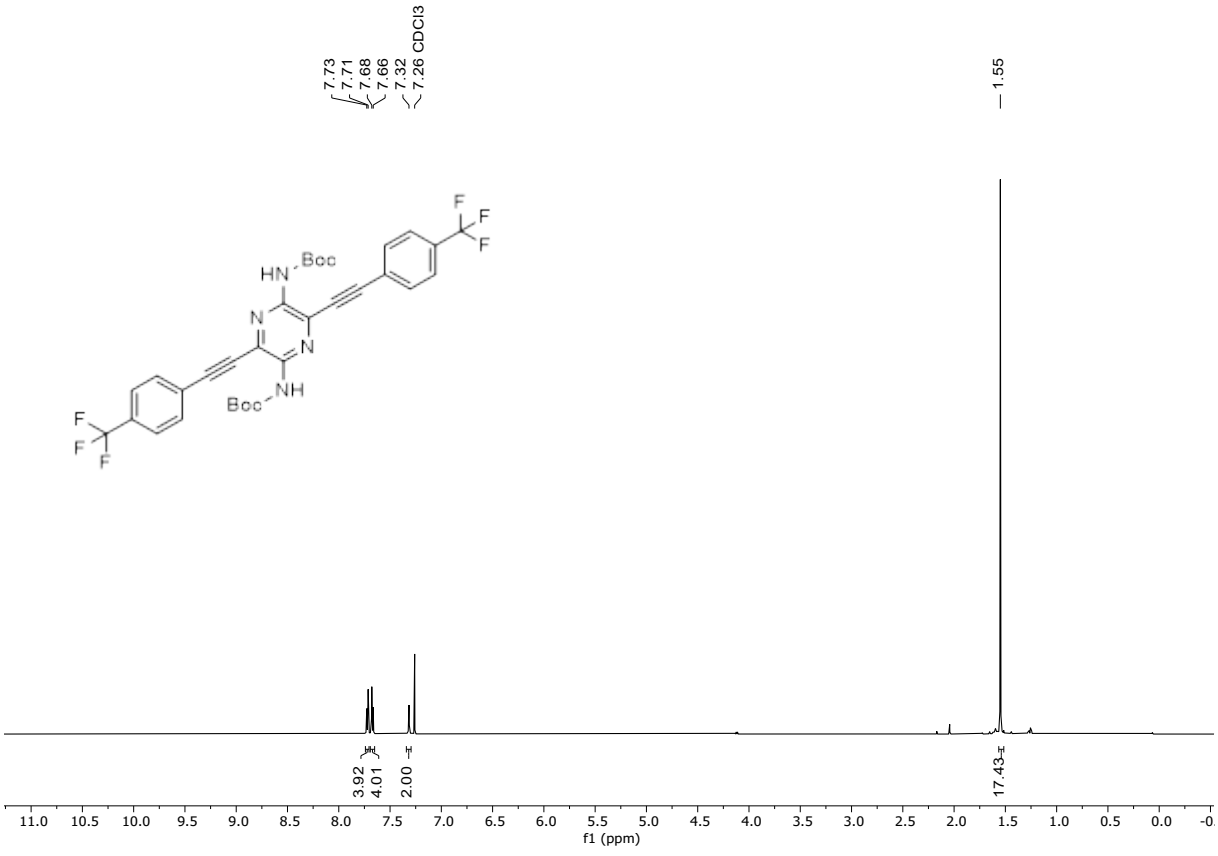


*Figure 23: **$^{1}H\{^{19}F\}$ NMR** (600 MHz, $CDCl_3$) of **BA2**.*

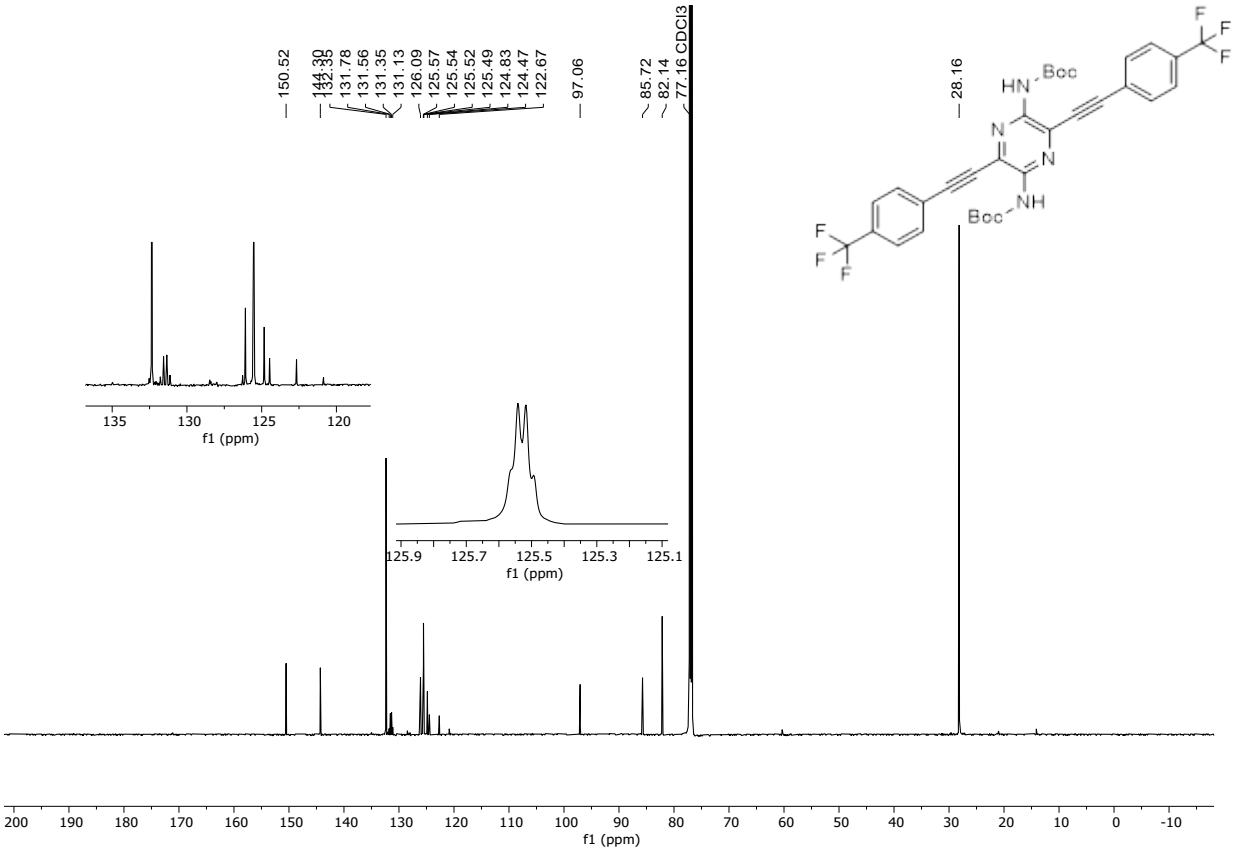


*Figure 24: **$^{13}C\{^{1}H\}$ NMR** (151 MHz, $CDCl_3$) of **BA2.**.*

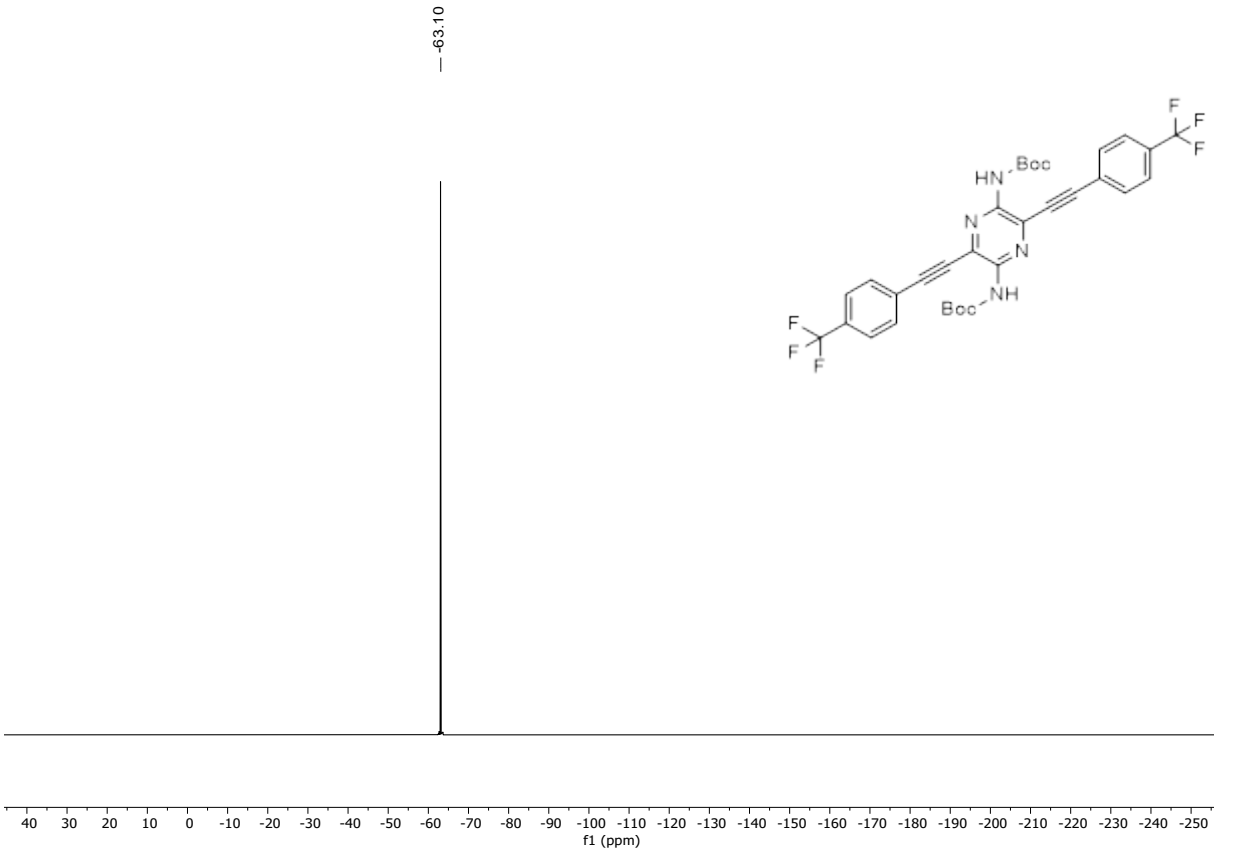


*Figure 25: **^{19}F NMR $\{^{1}H\}$** (283 MHz, $CDCl_3$) of **BA2**.*

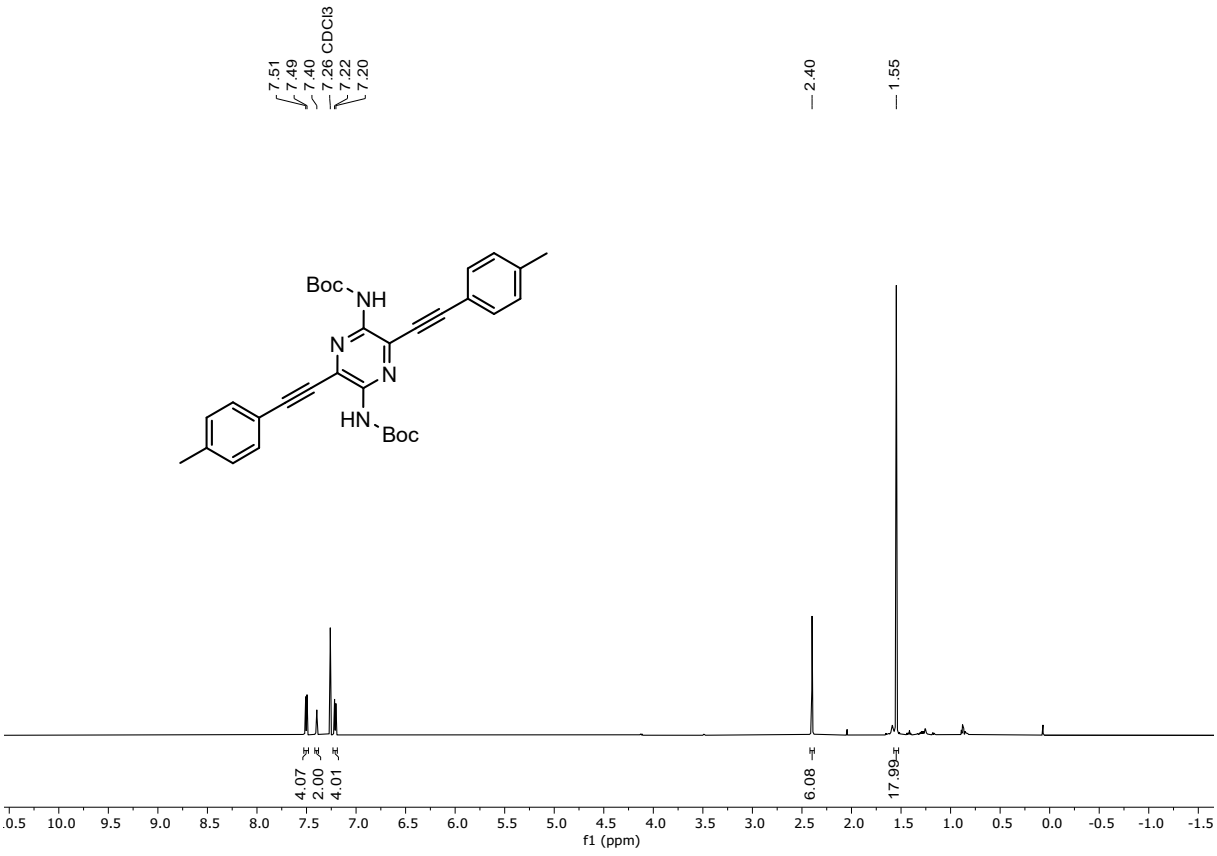


*Figure 26: **^{1}H NMR** (600 MHz, $CDCl_3$) of **BA3.***

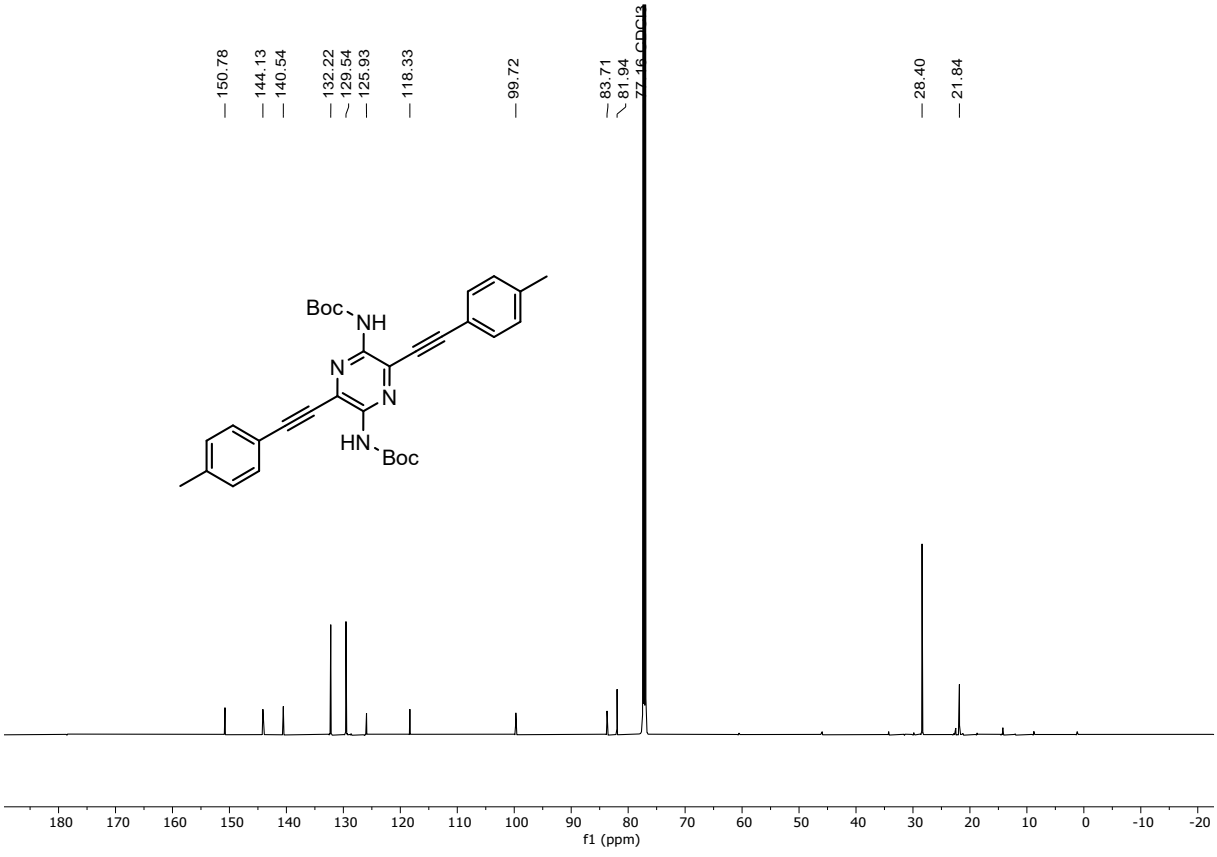


*Figure 27: **$^{13}C\{^{1}H\}$ NMR** (151 MHz, $CDCl_3$) of **BA3**.*

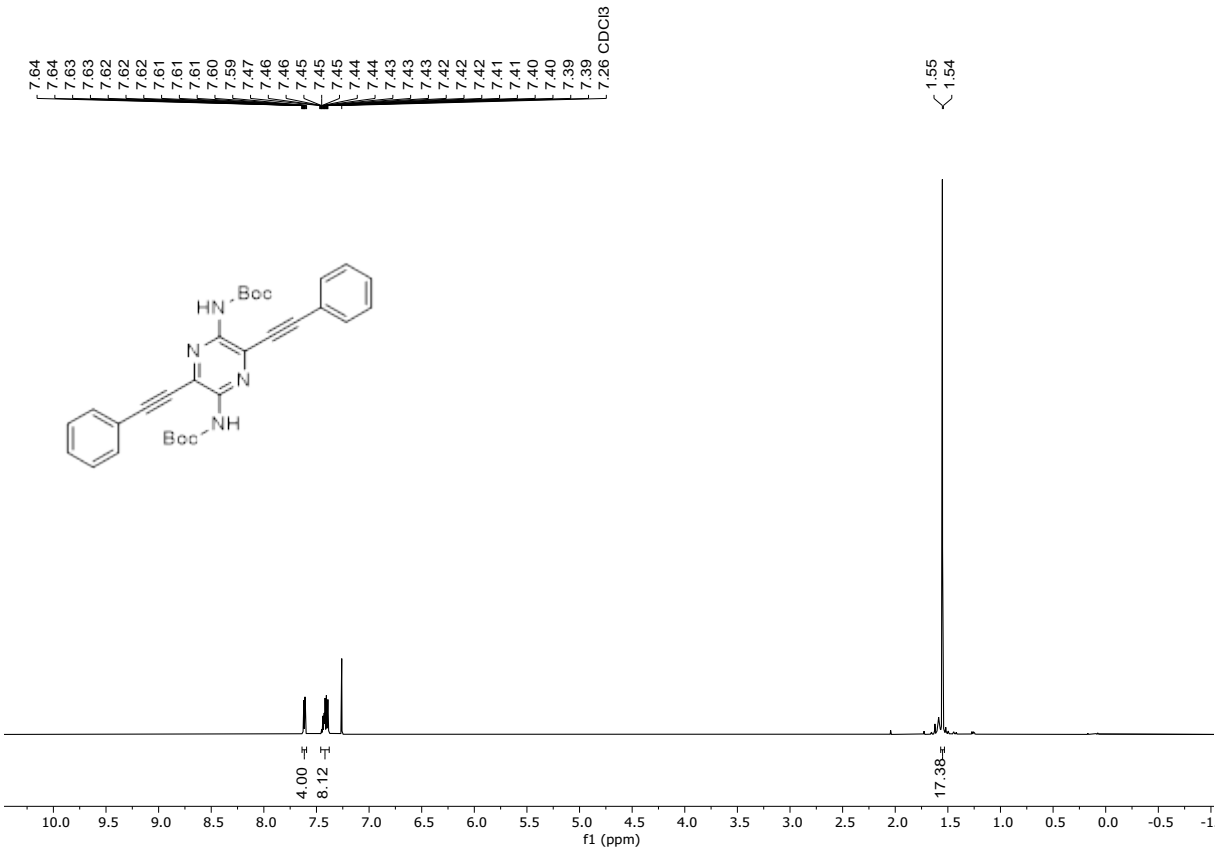


*Figure 28: **^{1}H NMR** (600 MHz, $CDCl_3$) of **BA4.***

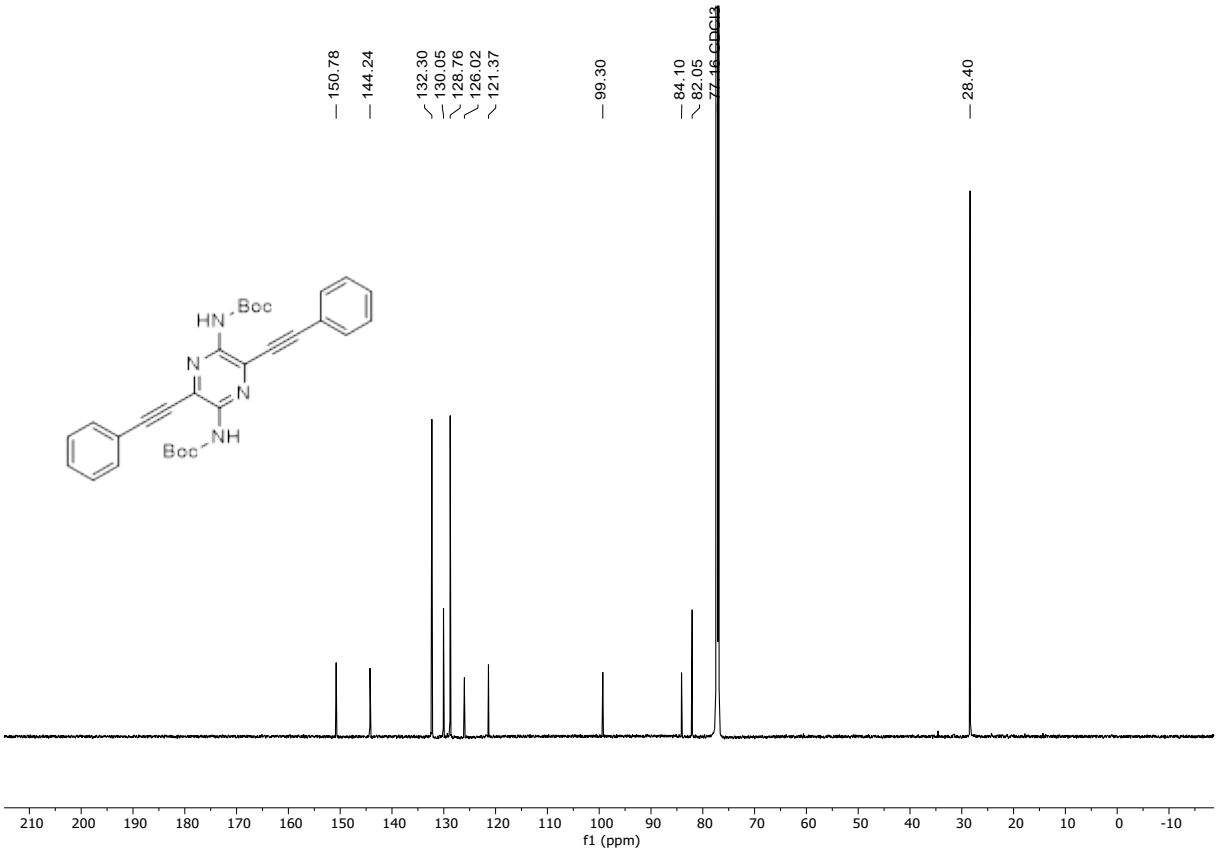


*Figure 29: **$^{13}C\{^{1}H\}$ NMR** (151 MHz, $CDCl_3$) of **BA4**.*

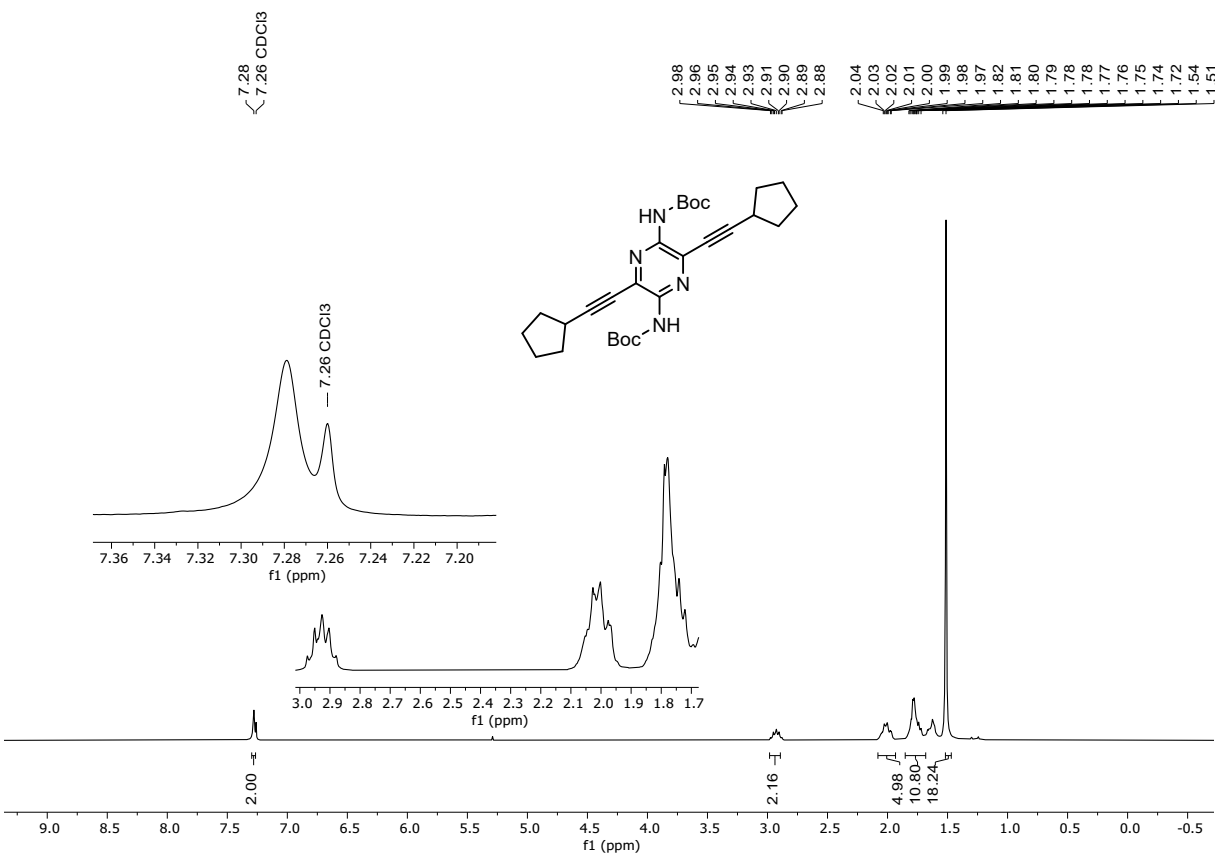


Figure 30 ***^{1}H NMR*** *(300 MHz, $CDCl_3$) of* ***BA5****.*

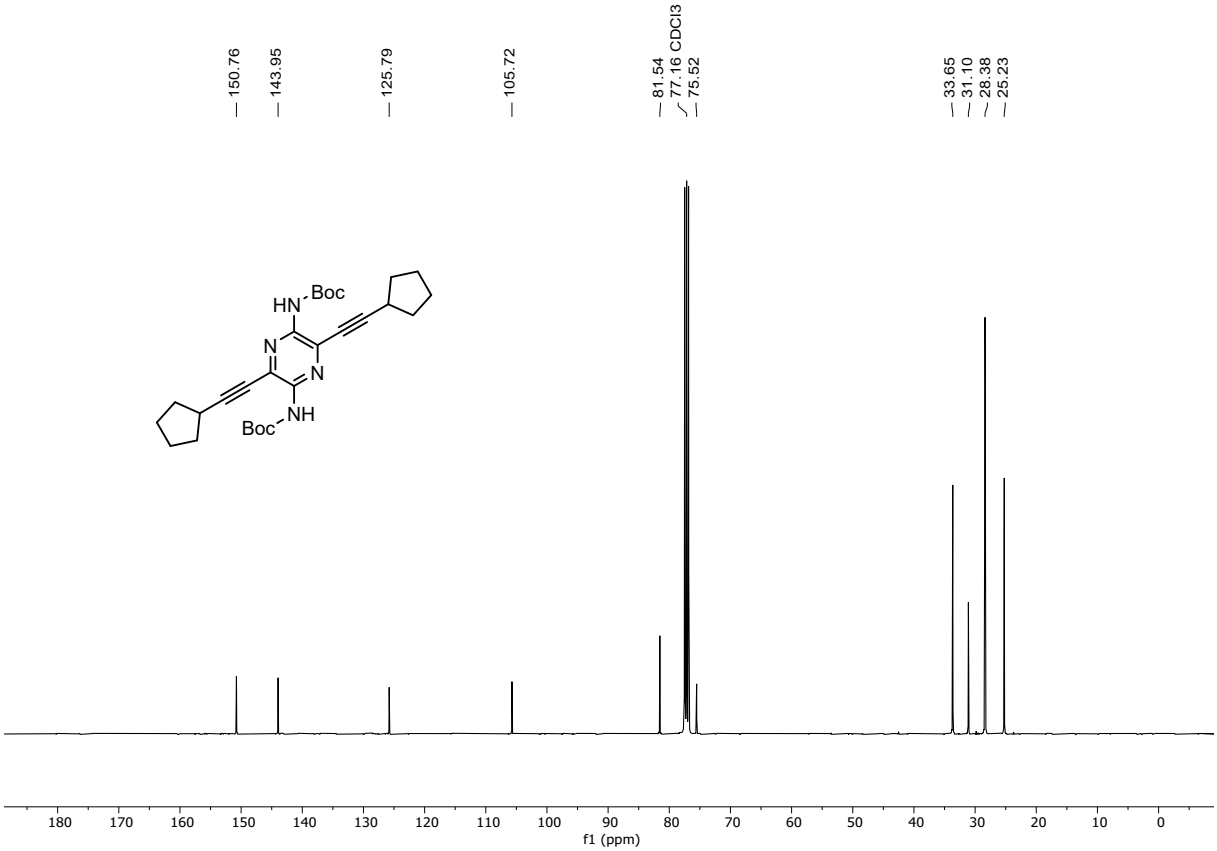


Figure 31: ***$^{13}C\{^{1}H\}$ NMR*** *(101 MHz, $CDCl_3$) of* ***BA5****.*

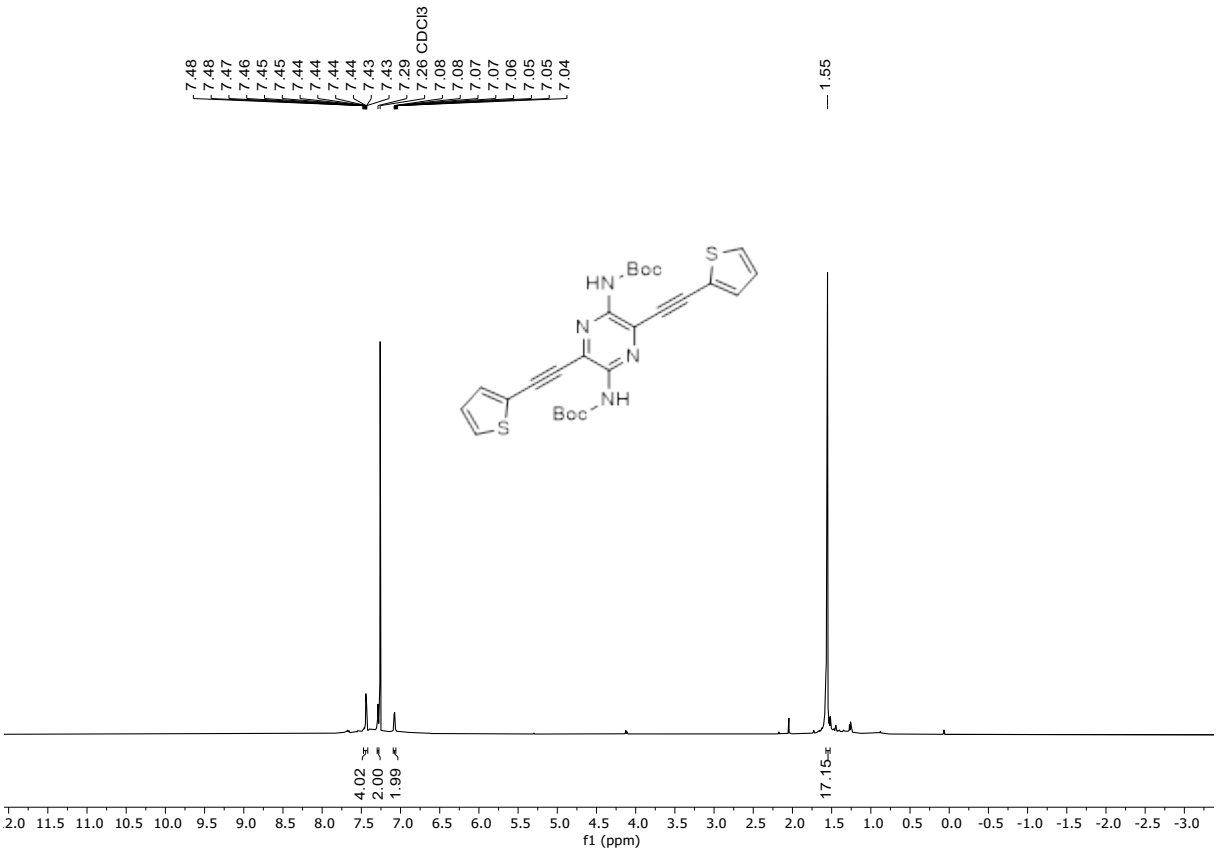


Figure 32 ***^{1}H NMR*** *(600 MHz, $CDCl_3$) of* ***BA6****.*

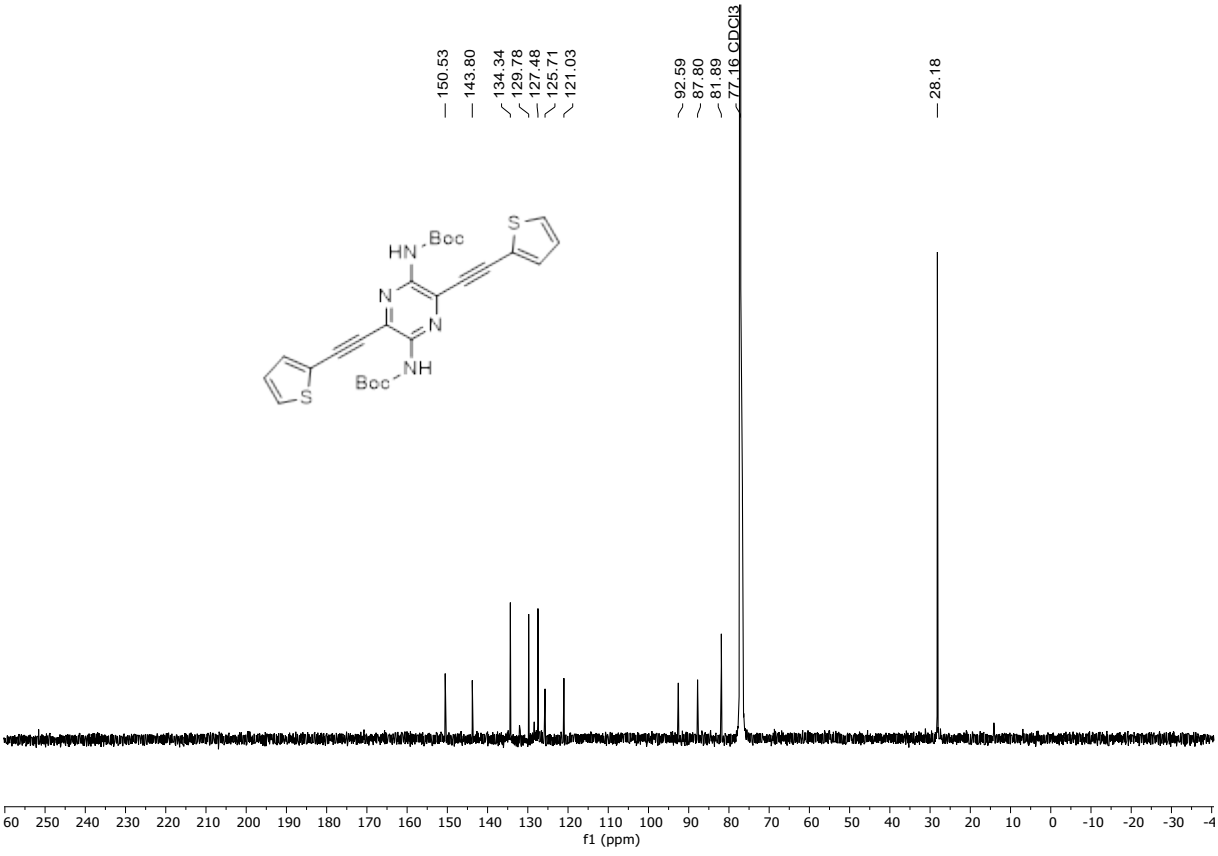


Figure 33: ***$^{13}C\{^{1}H\}$ NMR*** *(151 MHz, $CDCl_3$)of* ***BA6.***

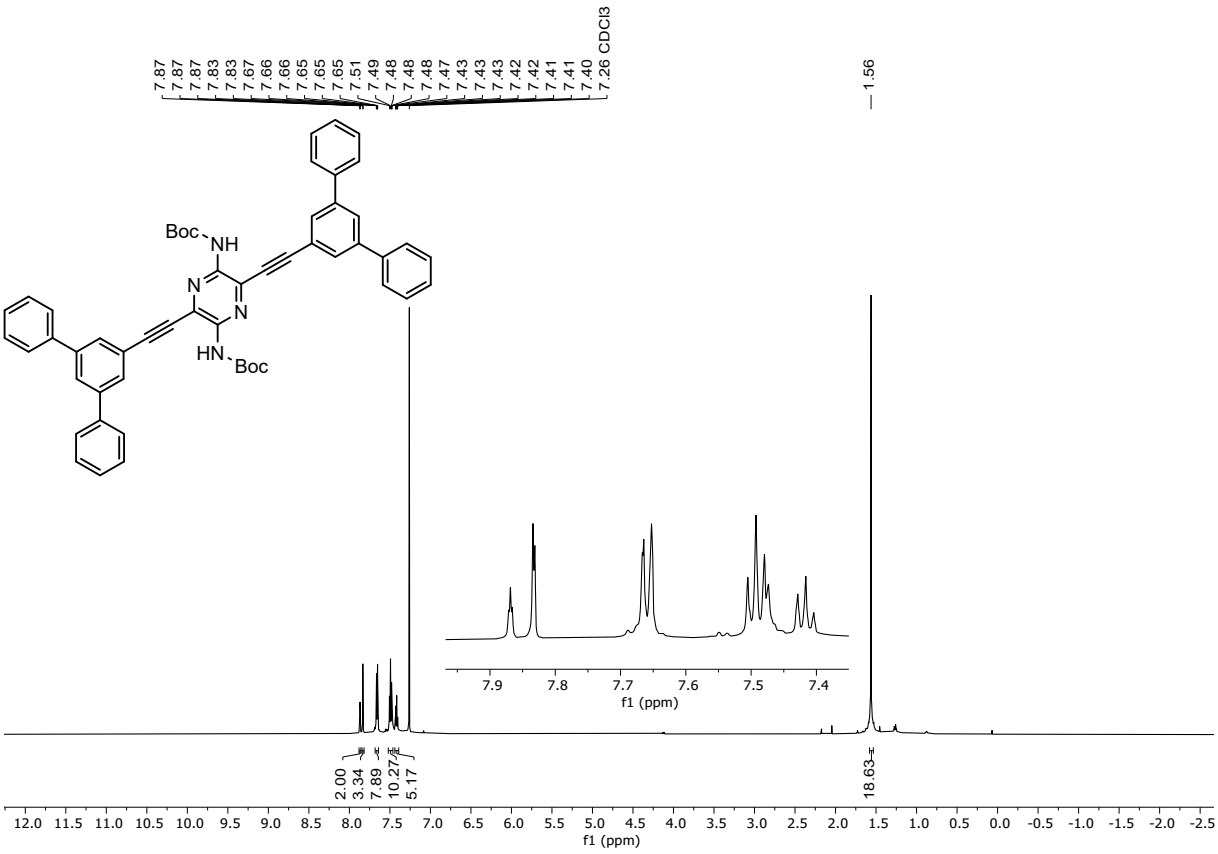


*Figure 34: **^{1}H NMR** (600 MHz, $CDCl_3$) of **BA7**.*

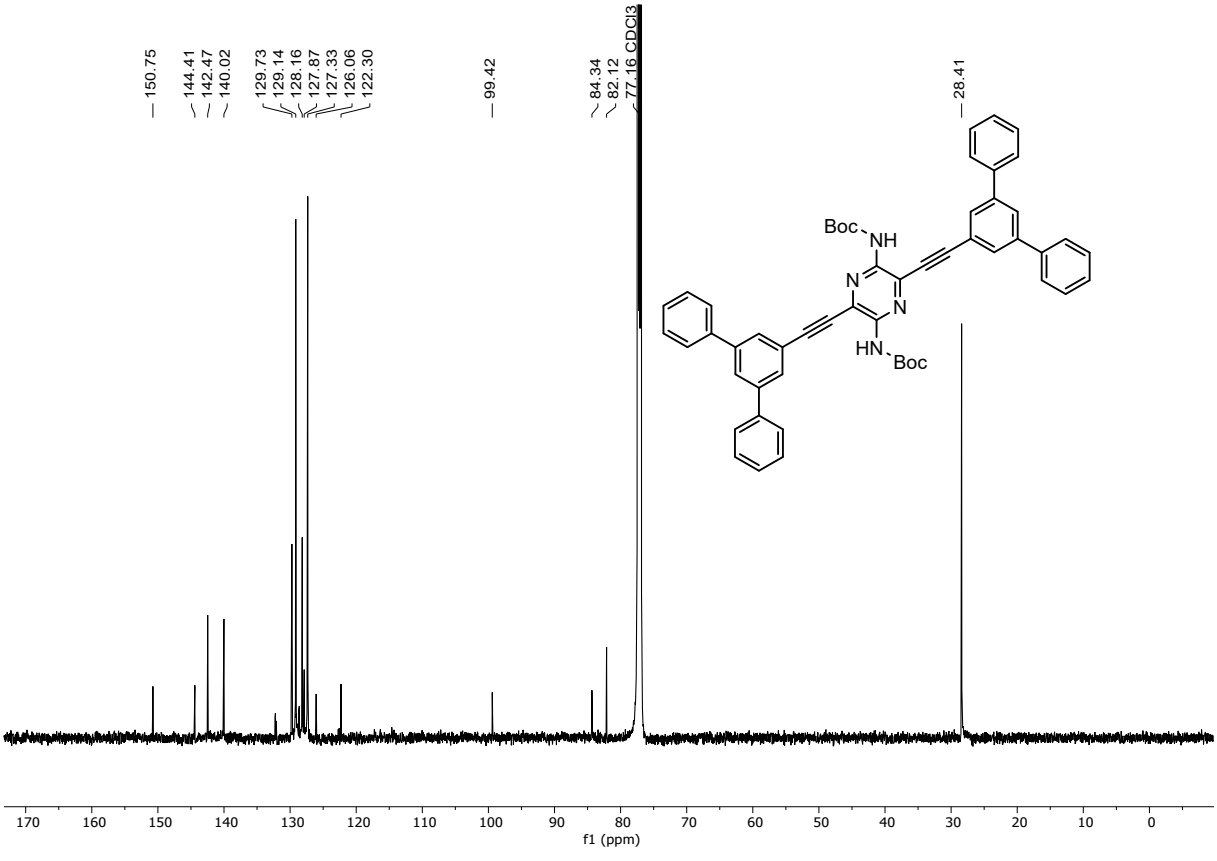


*Figure 35: **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) of **BA7**.*

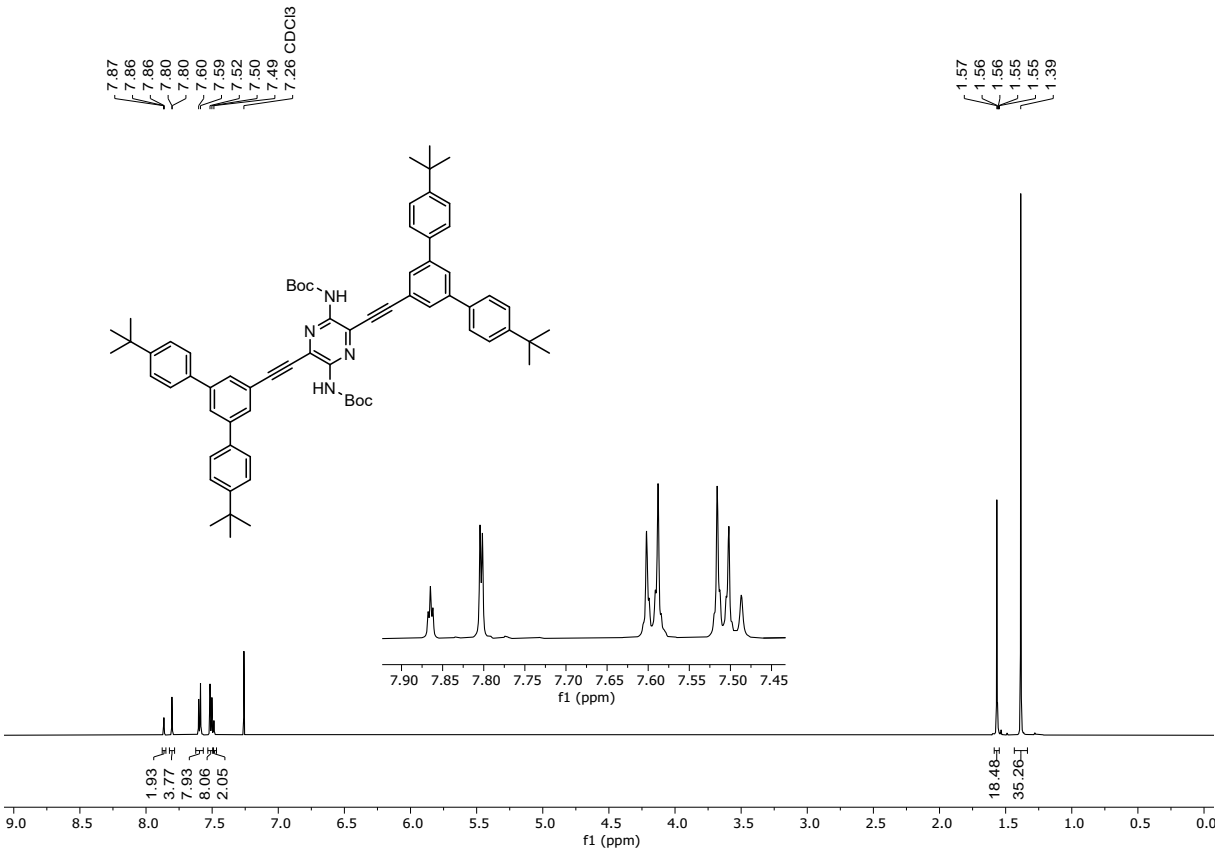


*Figure 36: **^{1}H NMR** (600 MHz, $CDCl_3$)of **BA8**.*

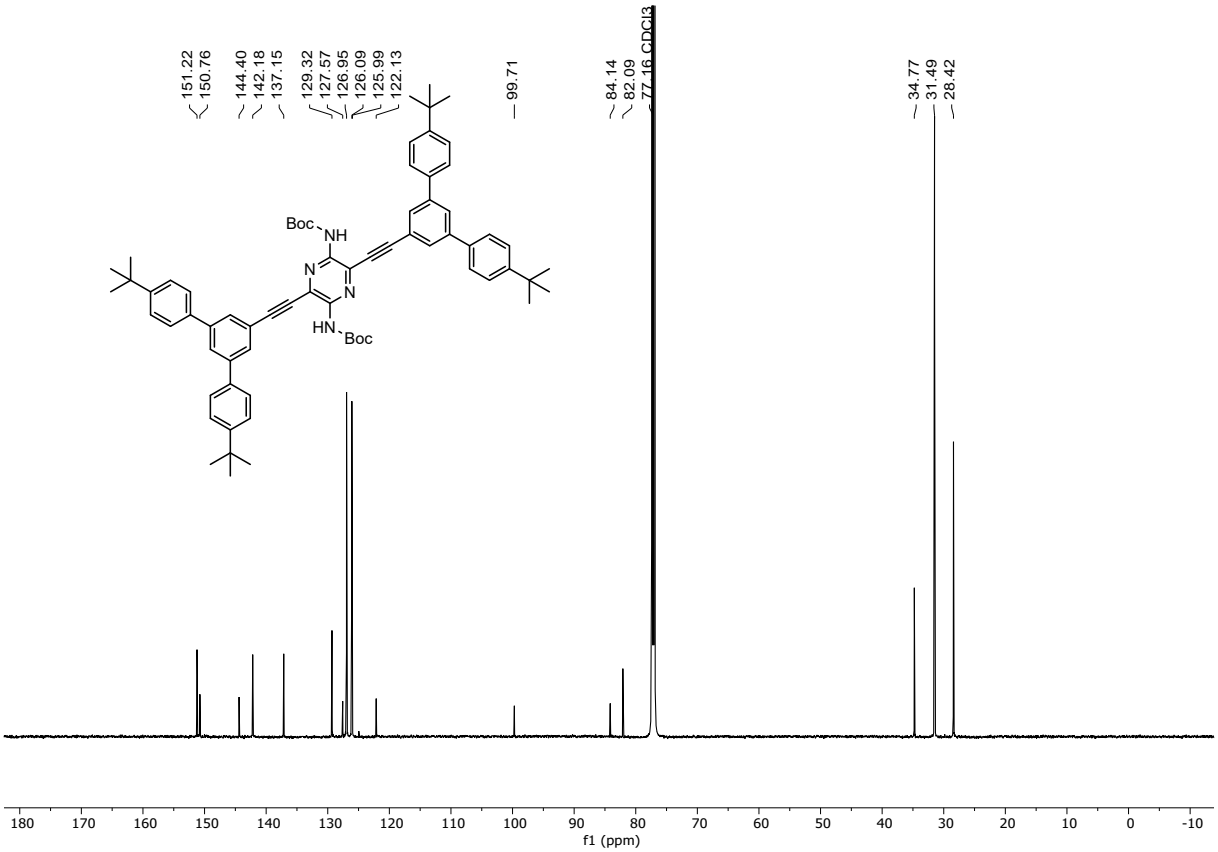


*Figure 37: **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) of **BA8**.*

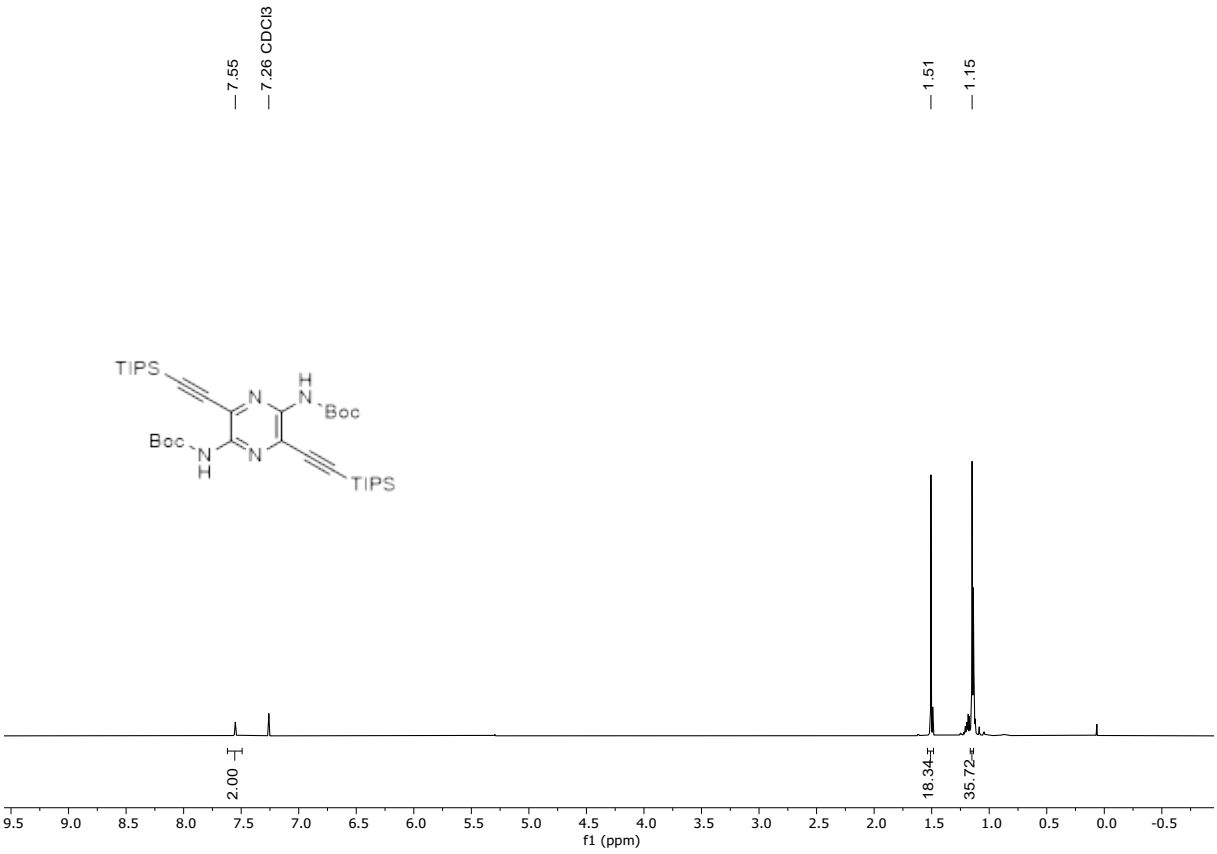


*Figure 38: **^{1}H NMR** (600 MHz, $CDCl_3$) of **BA9**.*

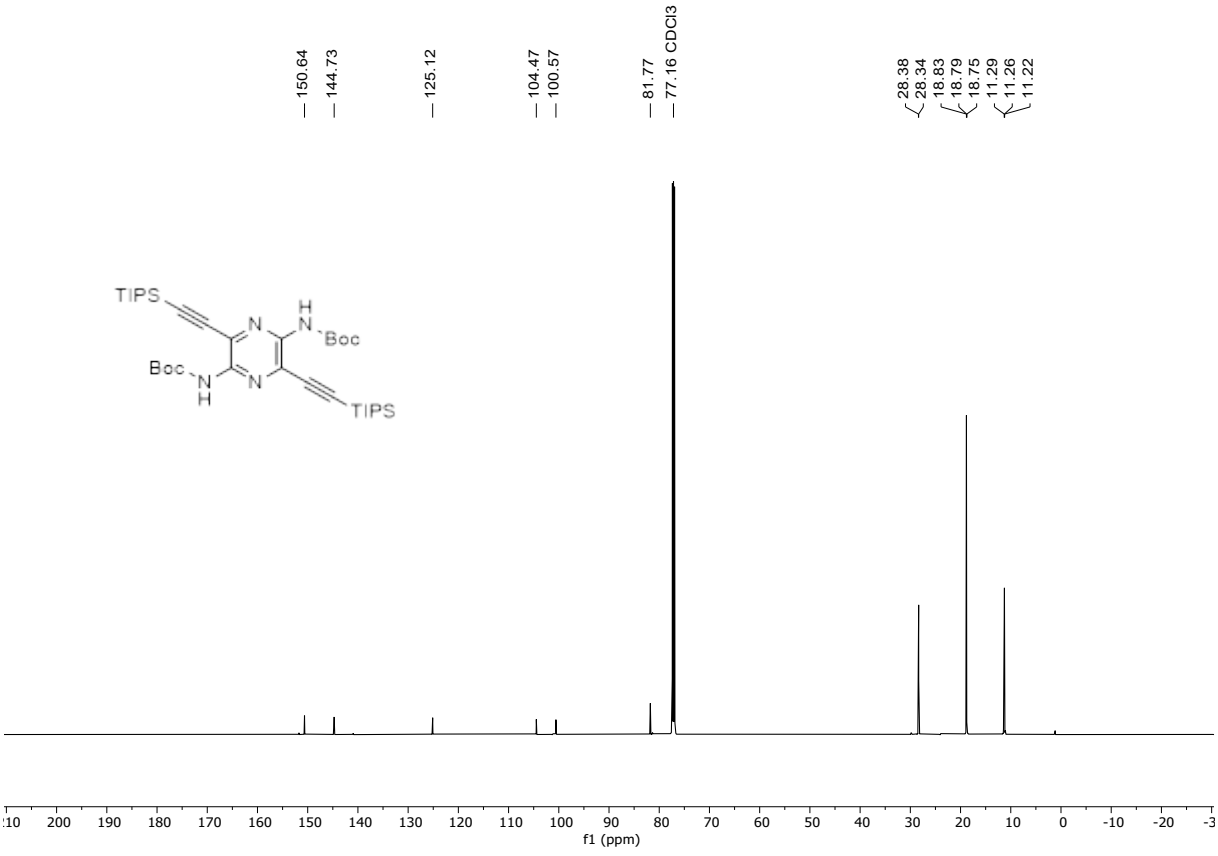


*Figure 39: **$^{13}C\{^{1}H\}$ NMR** (151 MHz, $CDCl_3$) of **BA9**.*

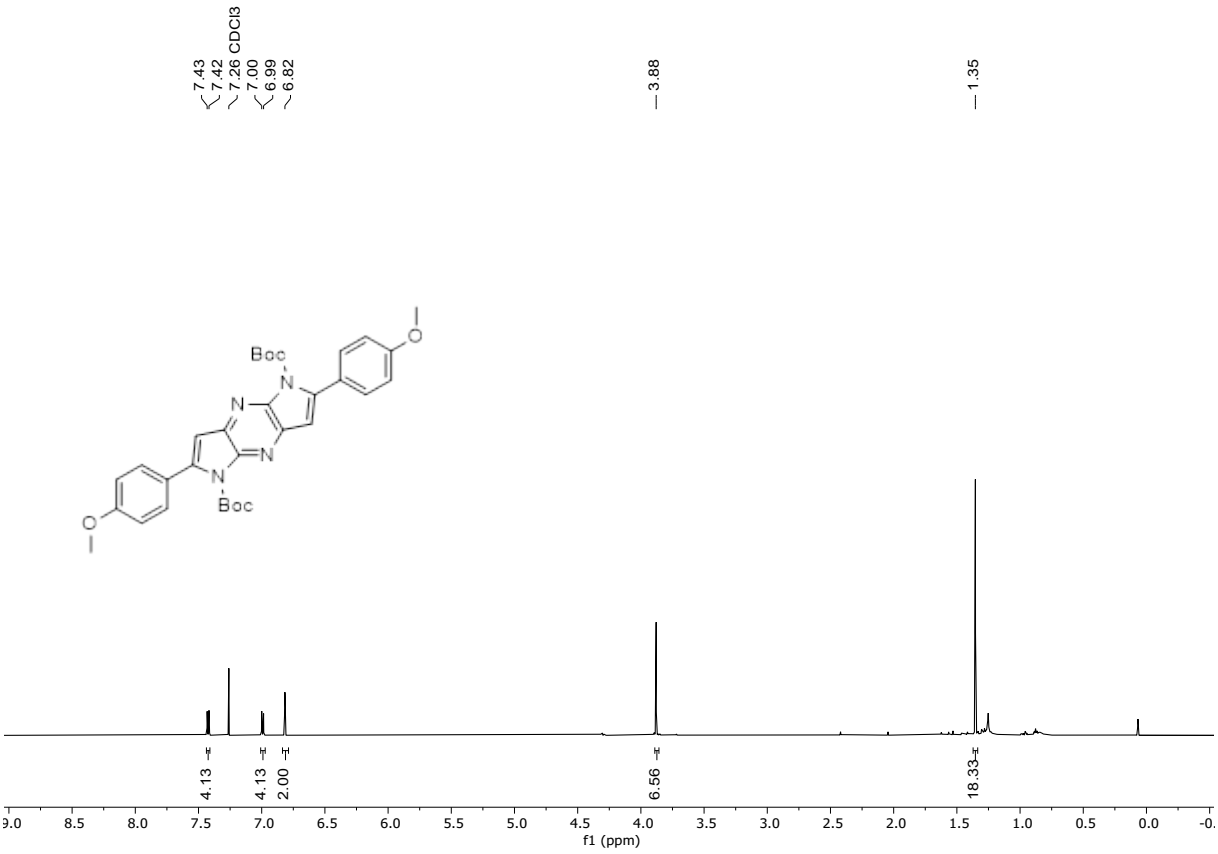


*Figure 40: **^{1}H NMR** (600 MHz, $CDCl_3$) of **DPPB1**.*

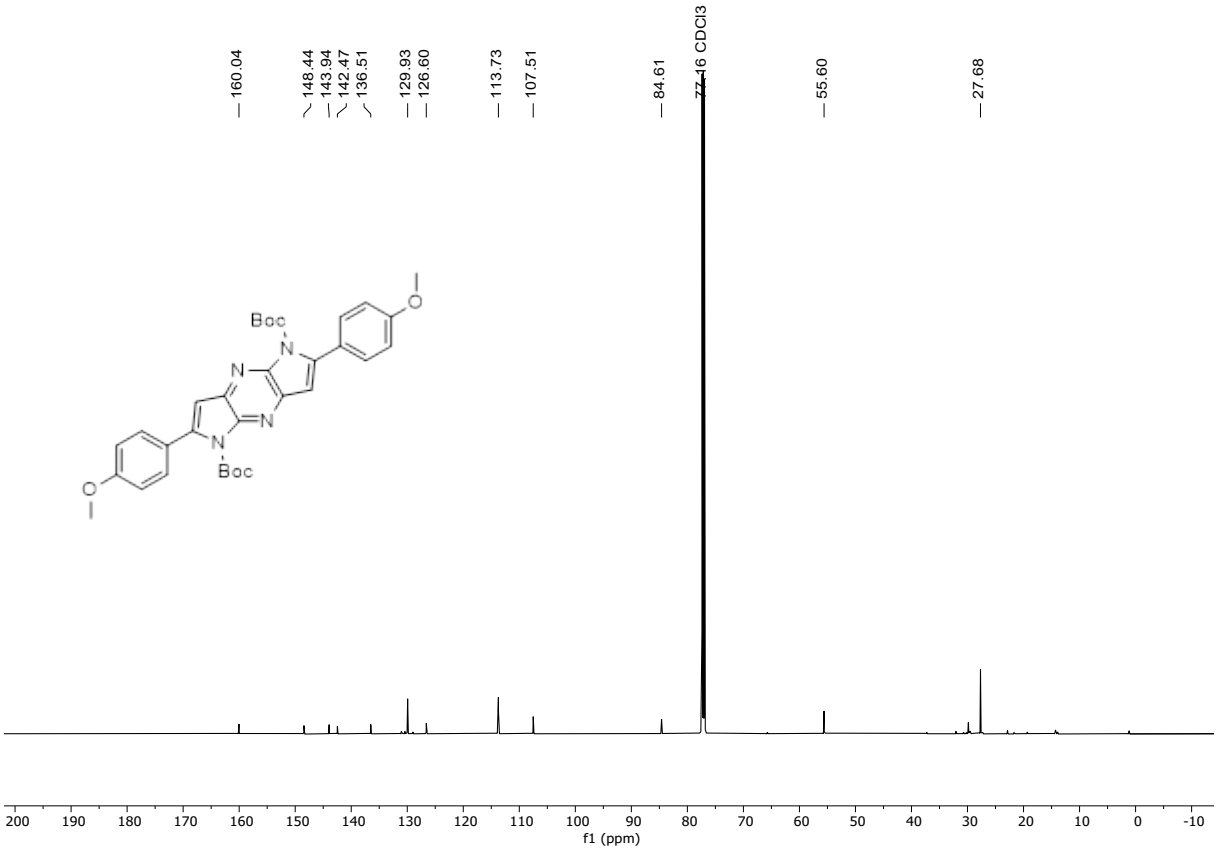


*Figure 41: **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) of **DPPB1**.*

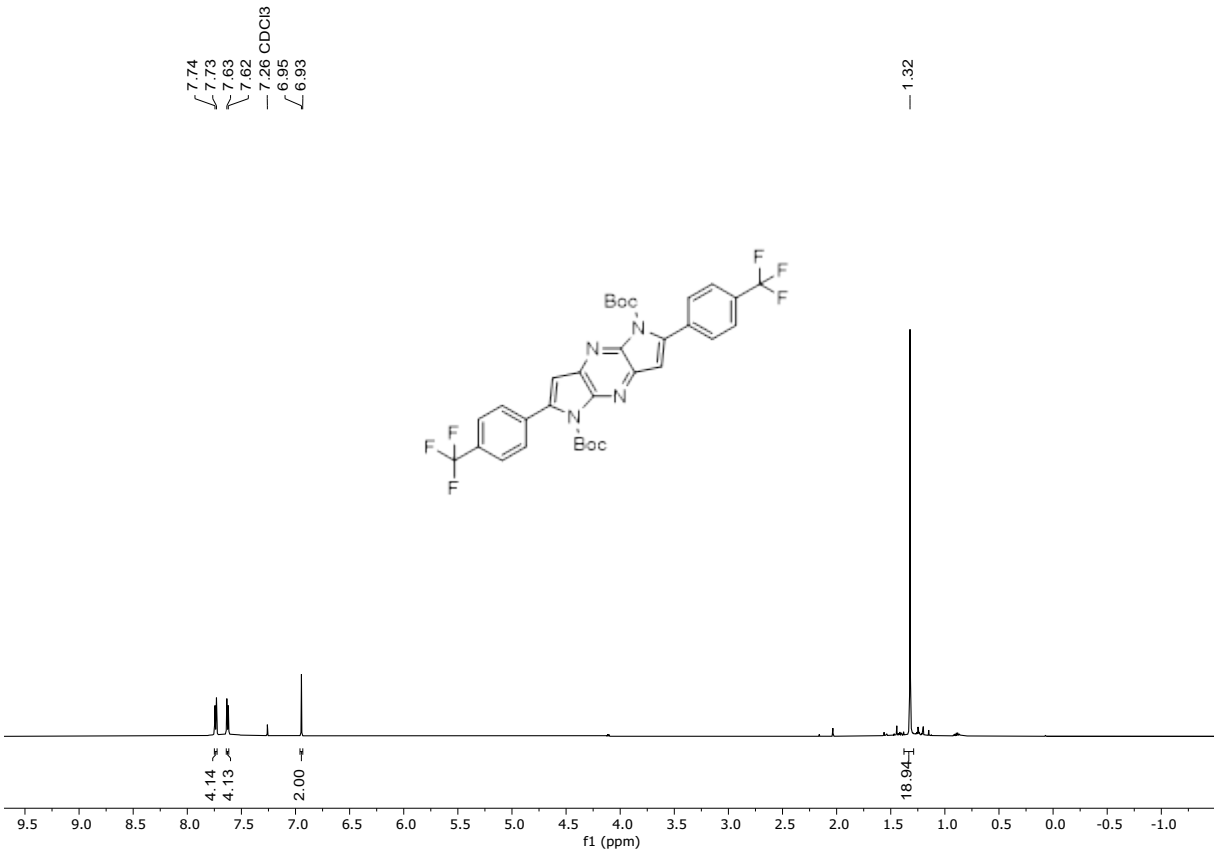


*Figure 42: **$^{1}H\{^{19}F\}$ NMR** (600 MHz, $CDCl_3$) of **DPPB2.***

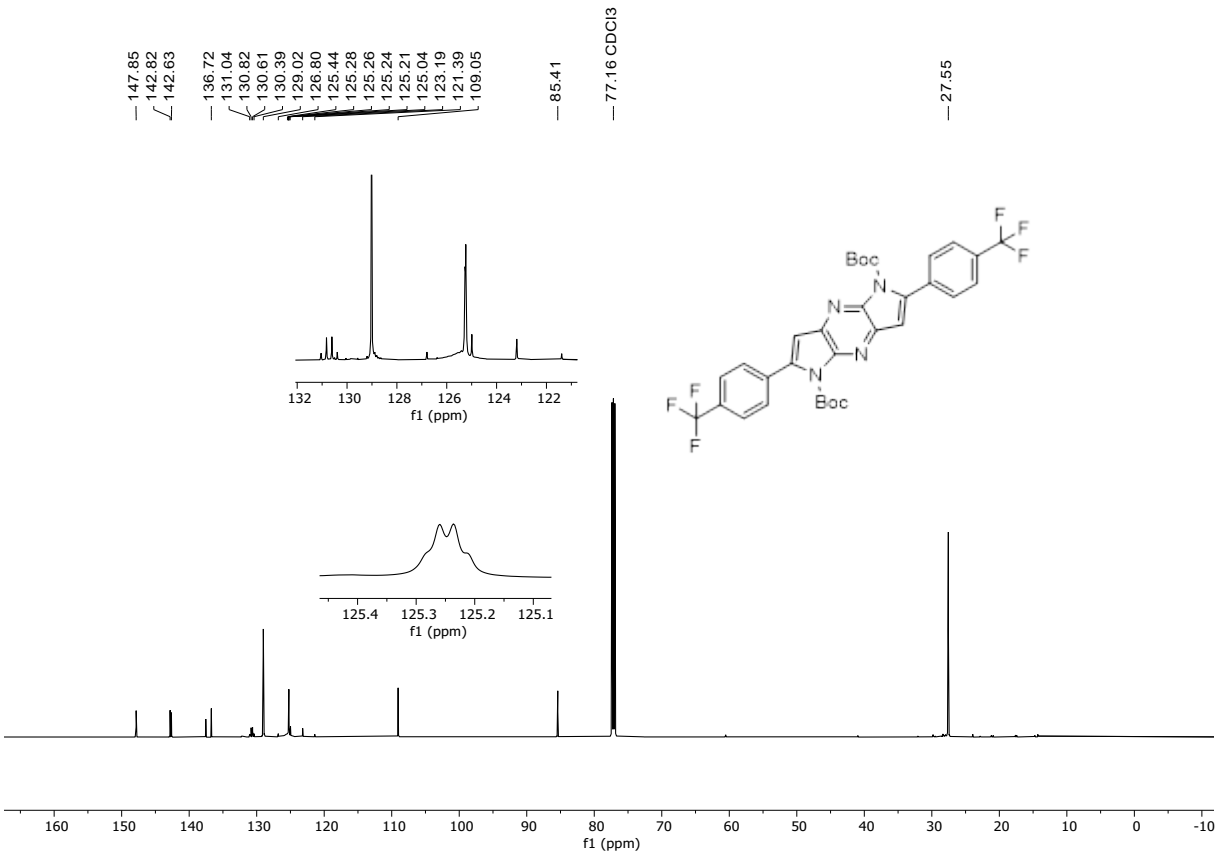


*Figure 43: **$^{13}C\{^{1}H\}$ NMR** (151 MHz, $CDCl_3$) of **DPPB2**.*

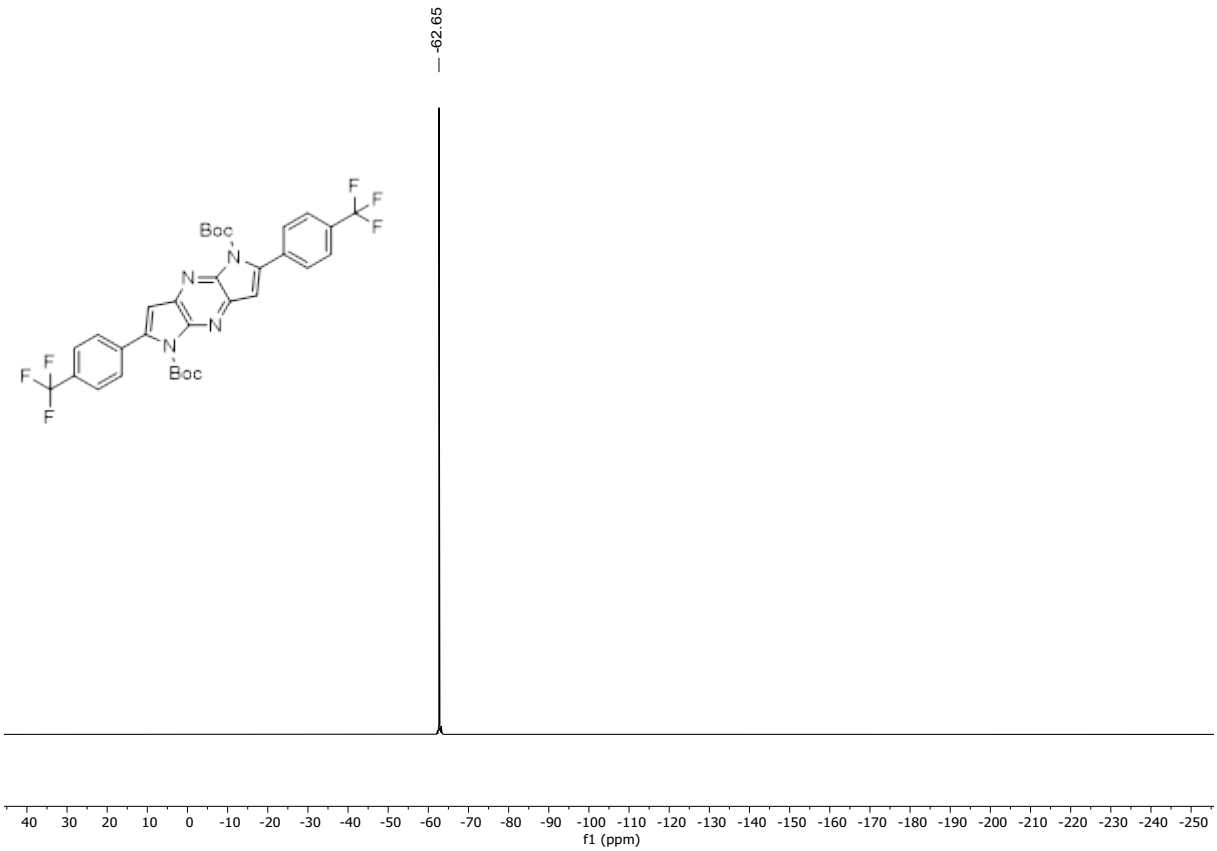


*Figure 44: **$^{1}H\{^{19}F\}$ NMR** (600 MHz, $CDCl_3$)of **DPPB2**.*

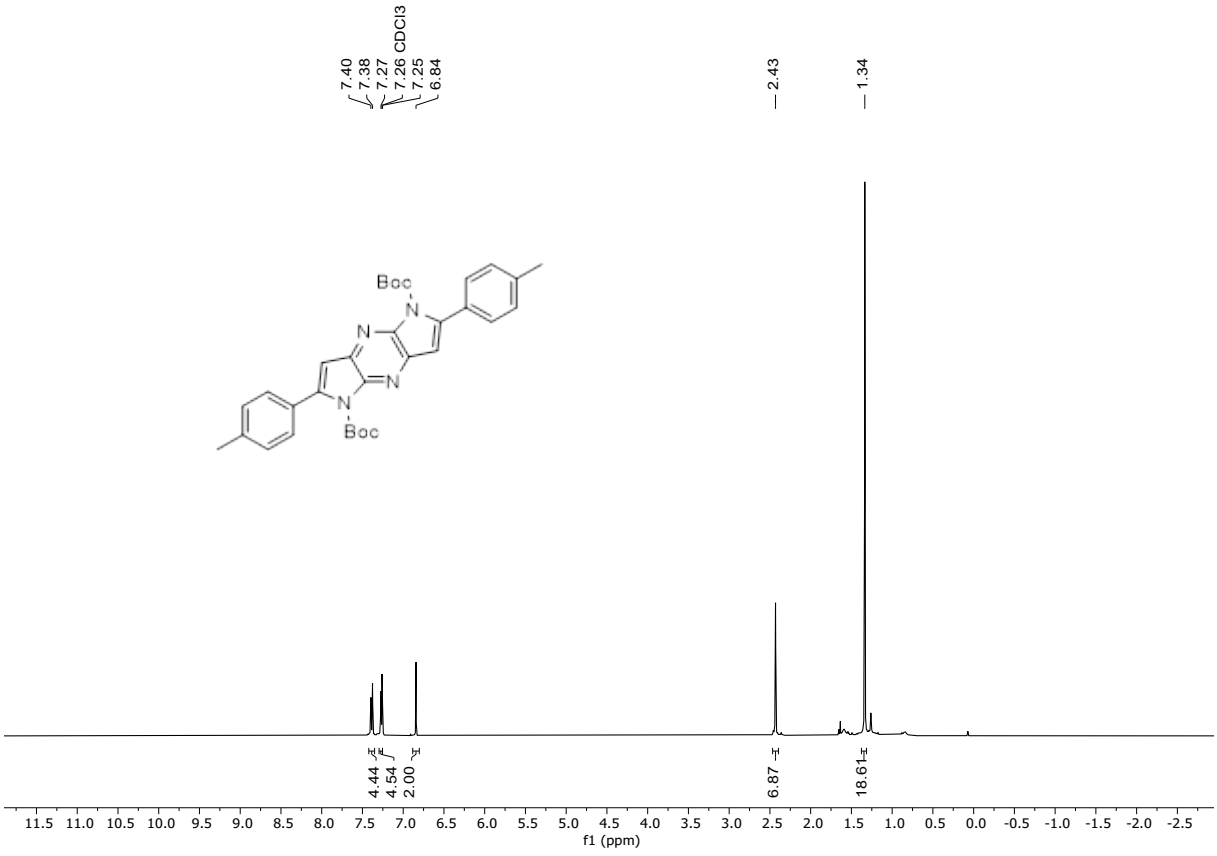


*Figure 45: **^{1}H NMR** (301 MHz, $CDCl_3$) of **DPPB3.***

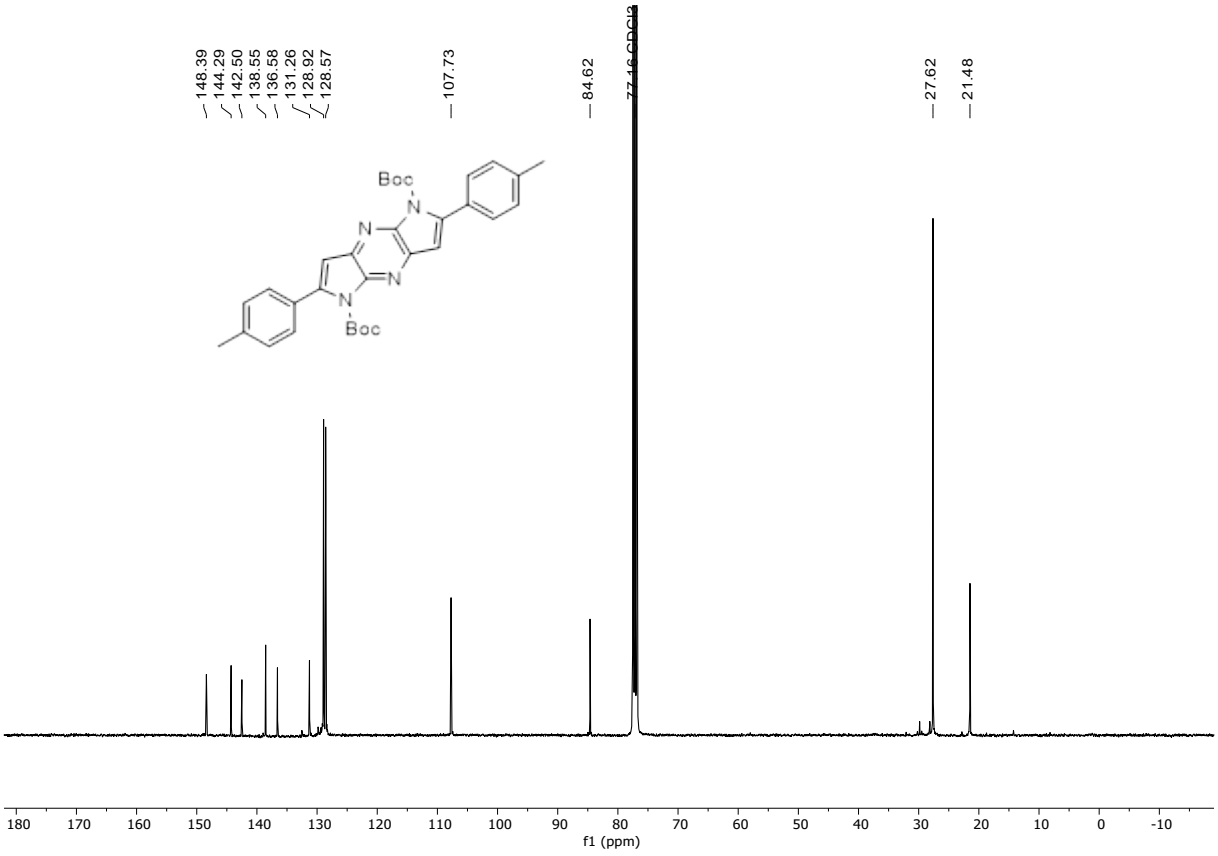


*Figure 46: **$^{13}C\{^{1}H\}$ NMR** (101 MHz, $CDCl_3$) of **DPPB3**.*

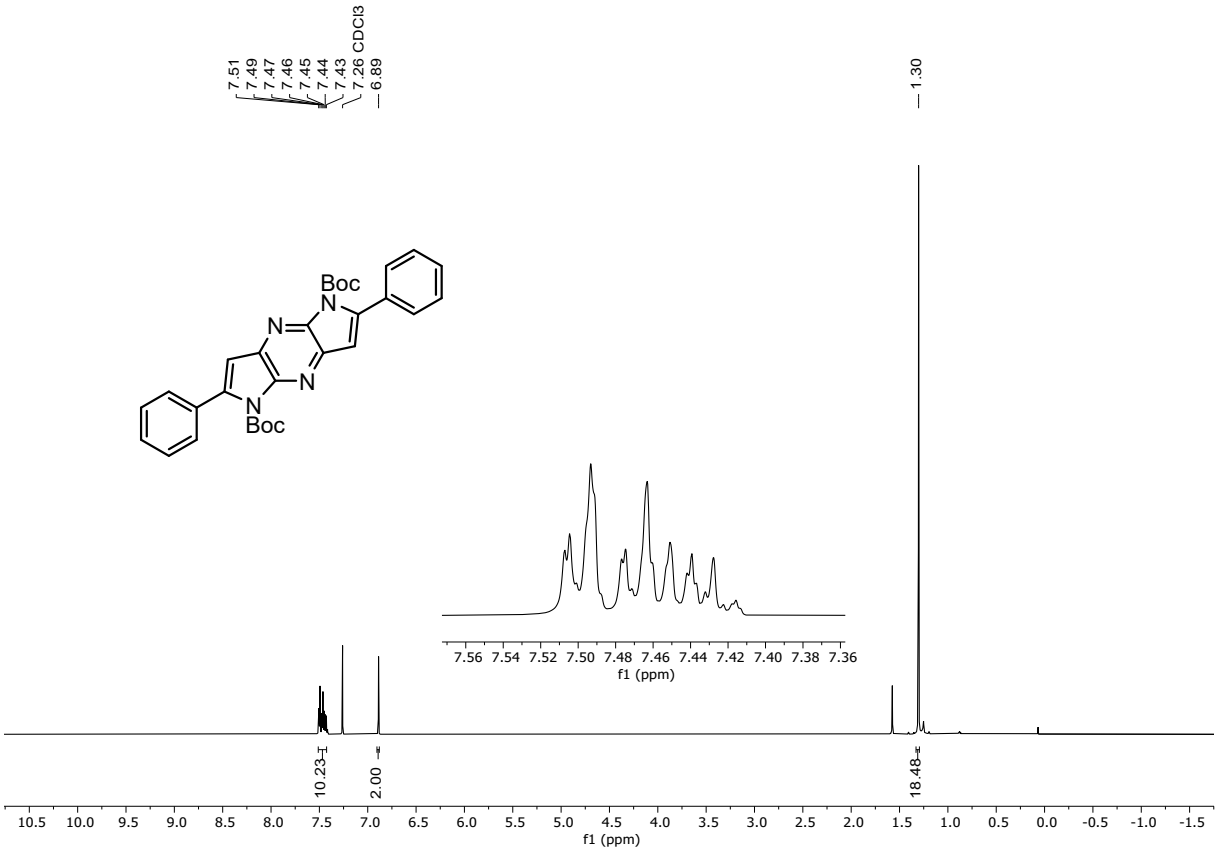


*Figure 47: **^{1}H NMR** (300 MHz, $CDCl_3$) of **DPPB4**.*

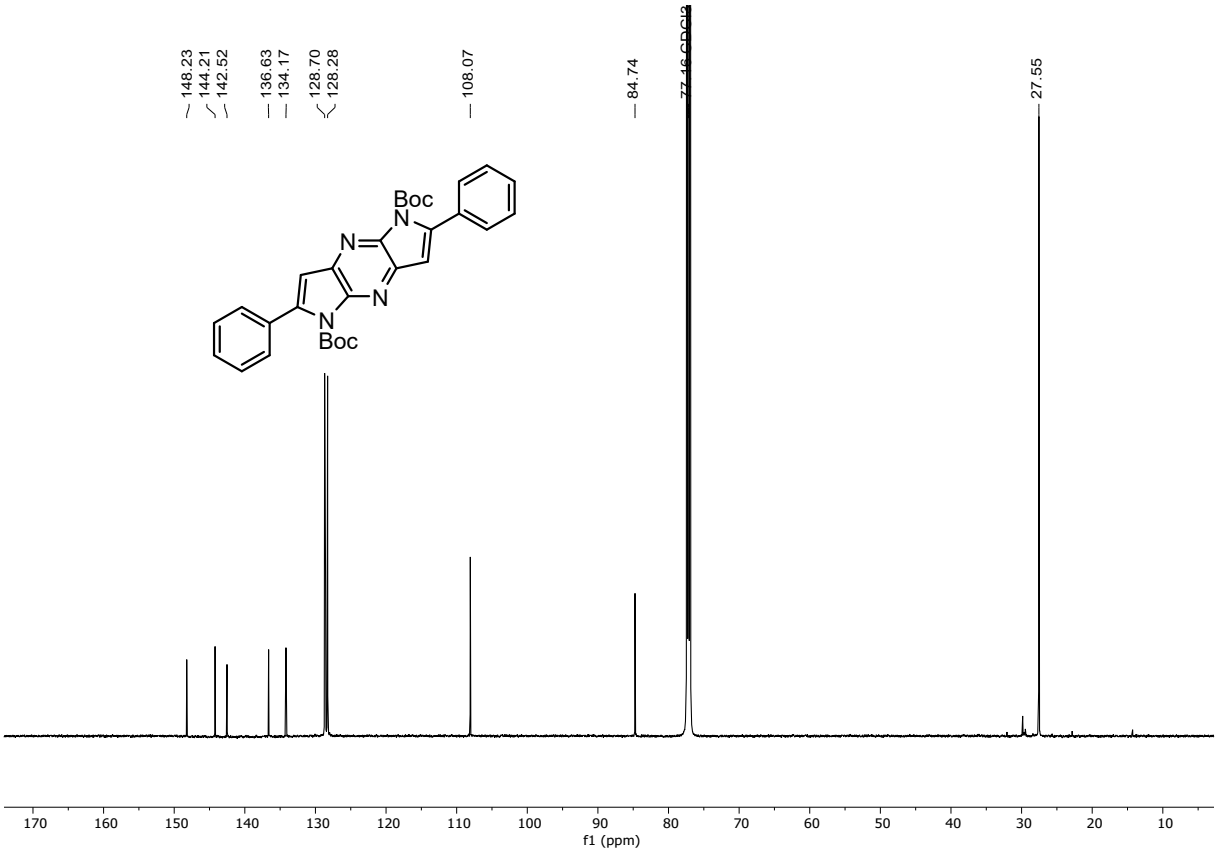


*Figure 48: **$^{13}C\{^{1}H\}$ NMR** (151 MHz, $CDCl_3$) of **DPPB4**.*

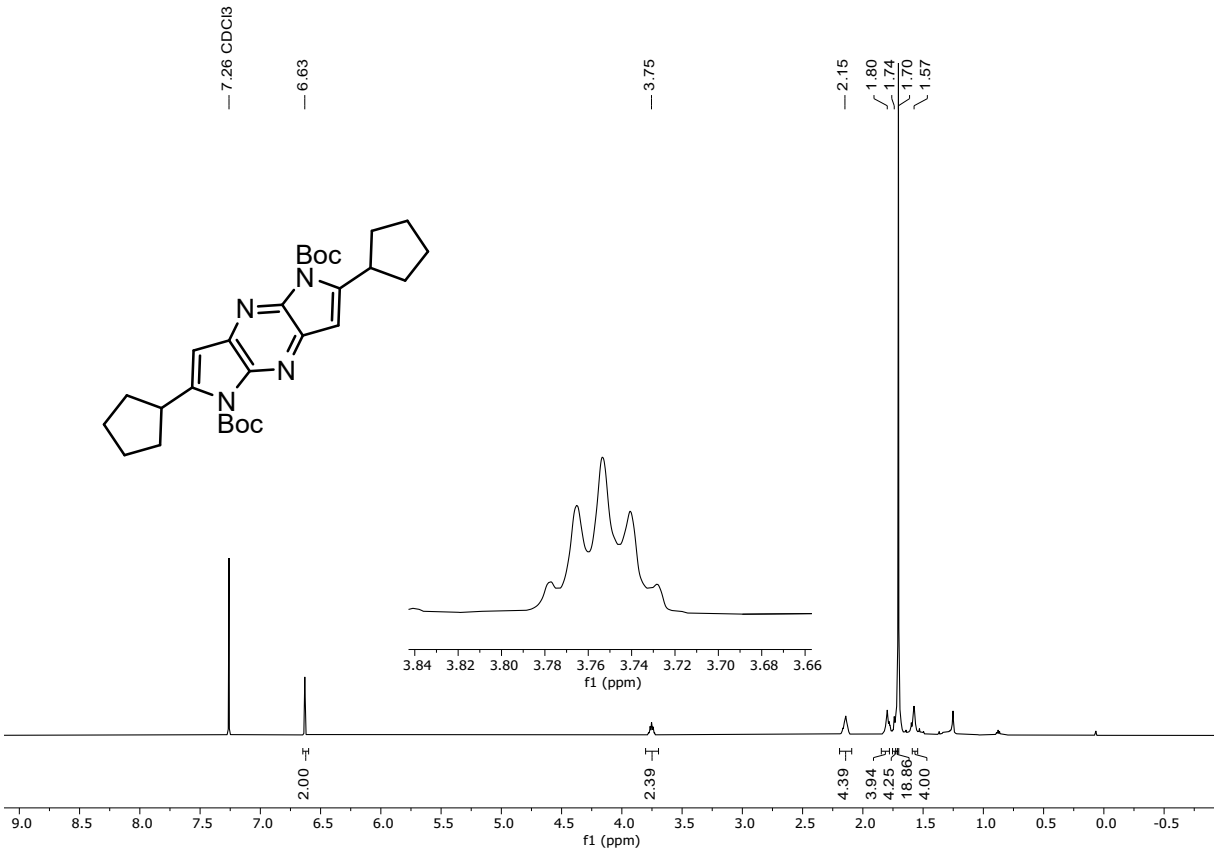


*Figure 49: **^{1}H NMR** (600 MHz, $CDCl_3$)of **DPPB5**.*

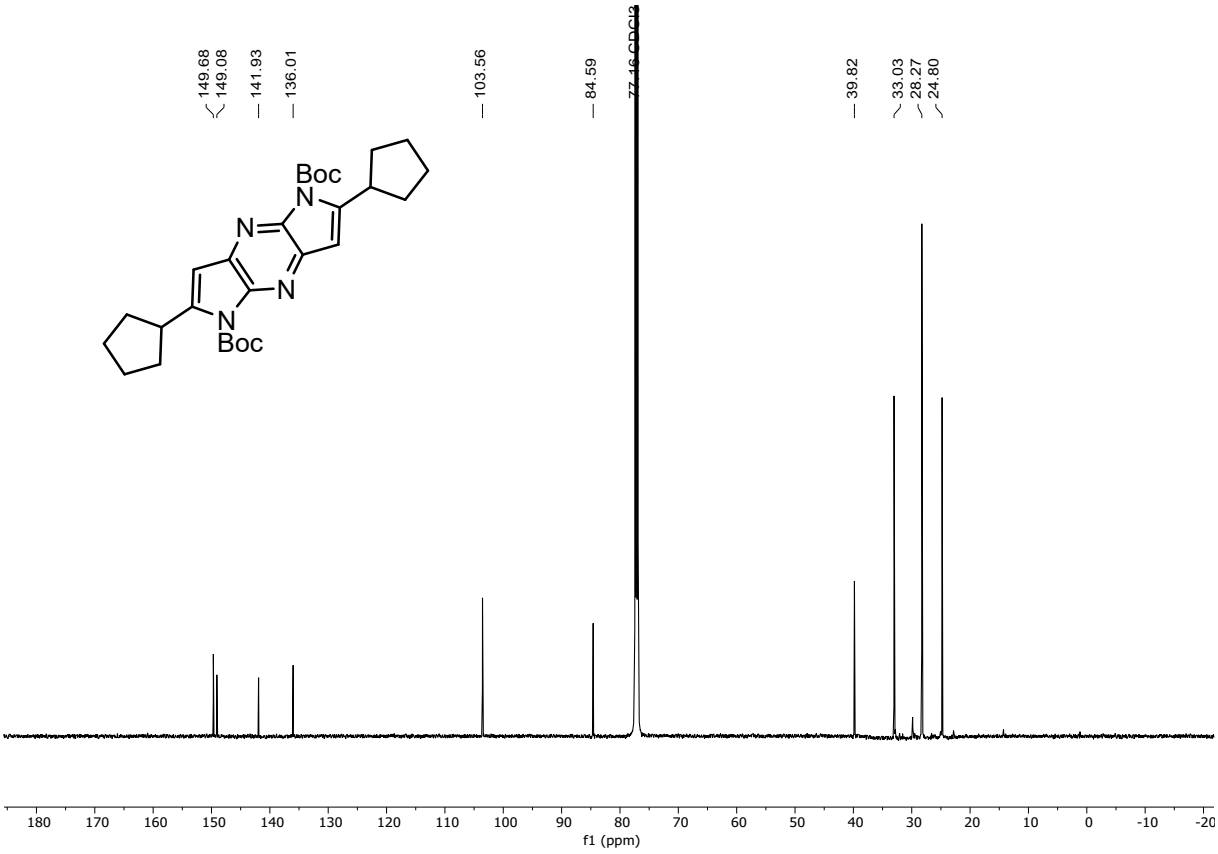


*Figure 50: **$^{13}C\{^{1}H\}$ NMR** (151 MHz, $CDCl_3$) of **DPPB5**.*

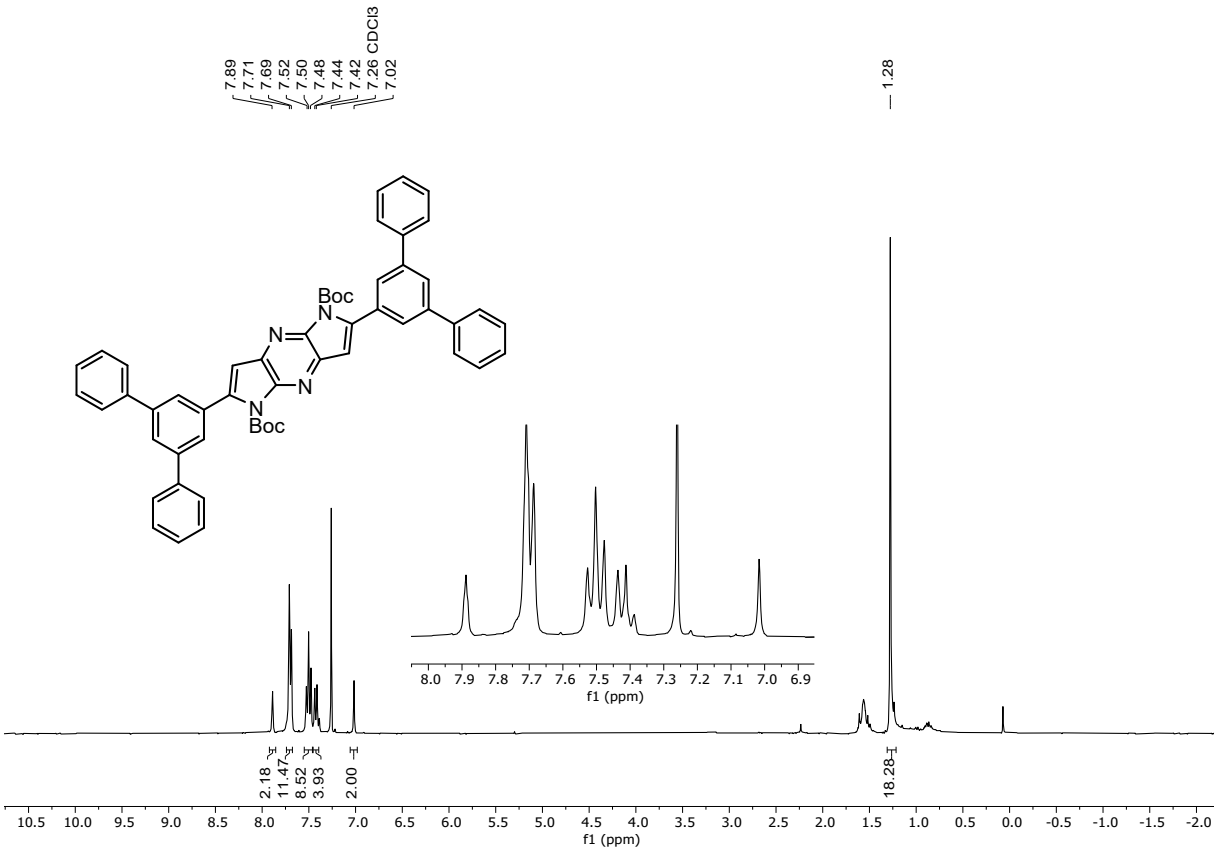


*Figure 51: **^{1}H NMR** (300 MHz, $CDCl_3$) of **DPPB7**.*

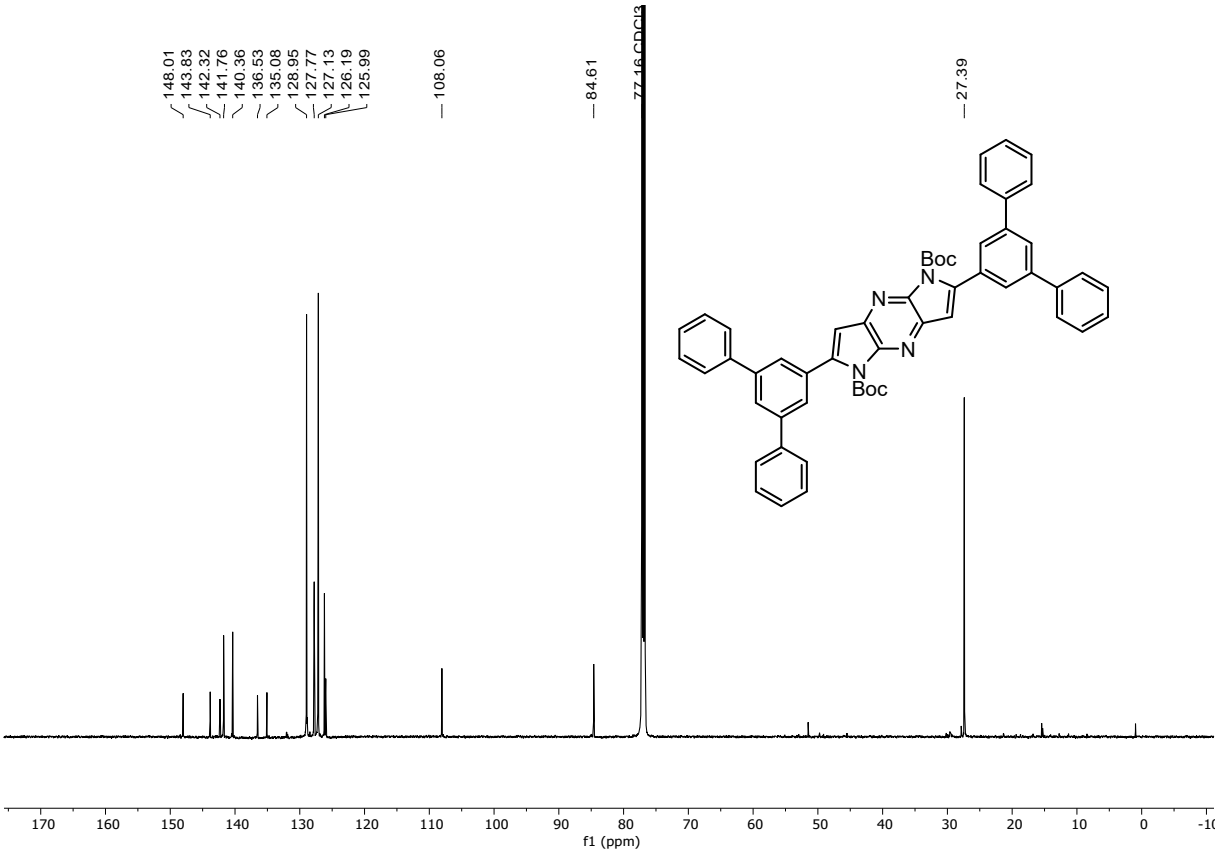


*Figure 52: **$^{13}C\{^{1}H\}$ NMR** (151 MHz, $CDCl_3$) of **DPPB7**.*

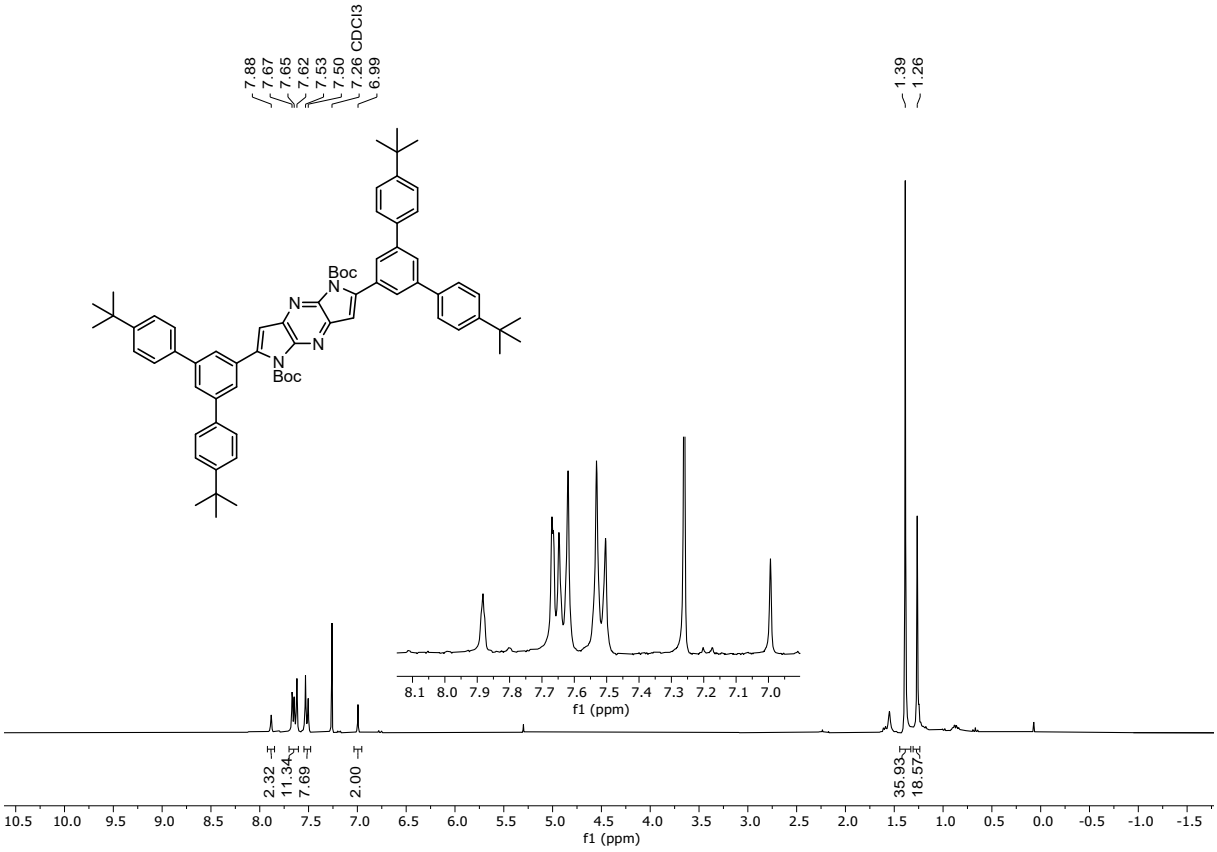


*Figure 53: **^{1}H NMR** (300 MHz, $CDCl_3$) of **DPPB8**.*

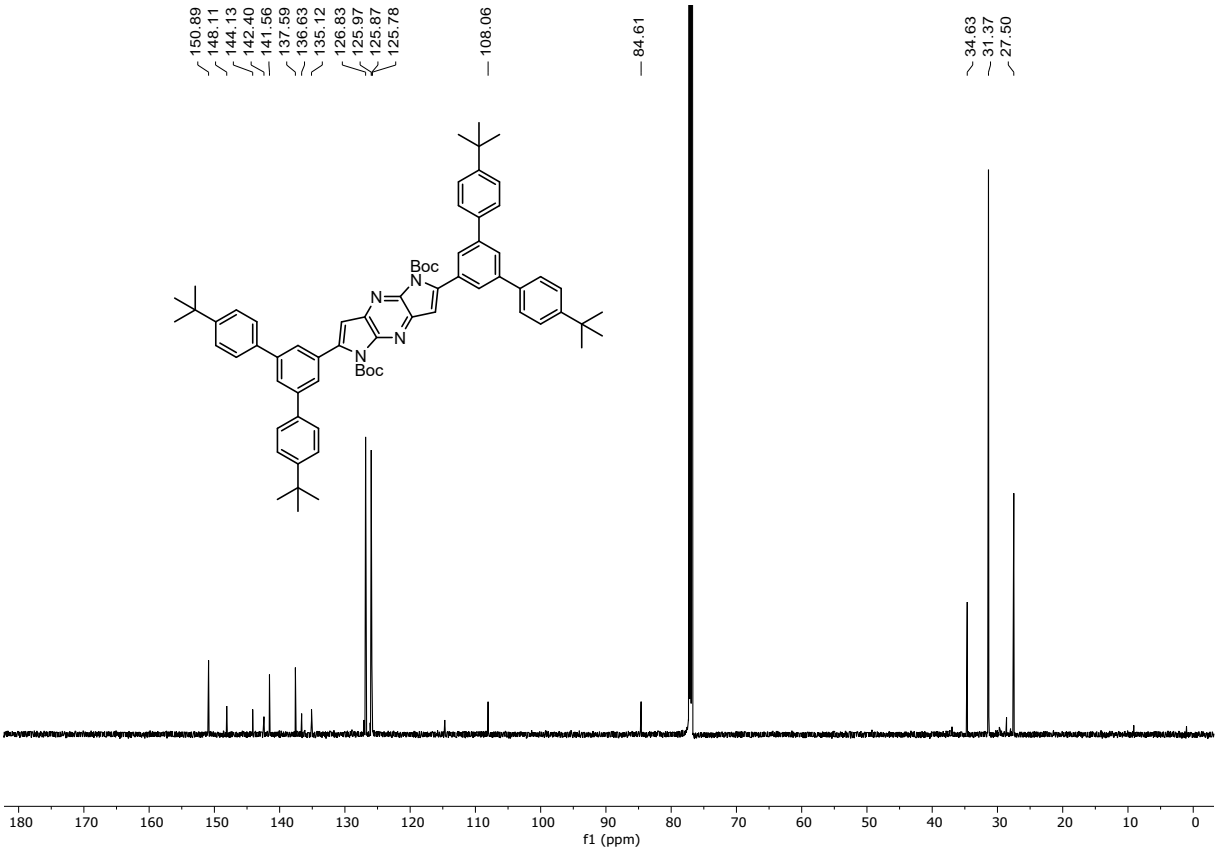


*Figure 54: **$^{13}C\{^{1}H\}$ NMR** (176 MHz, $CDCl_3$) of **DPPB8**.*

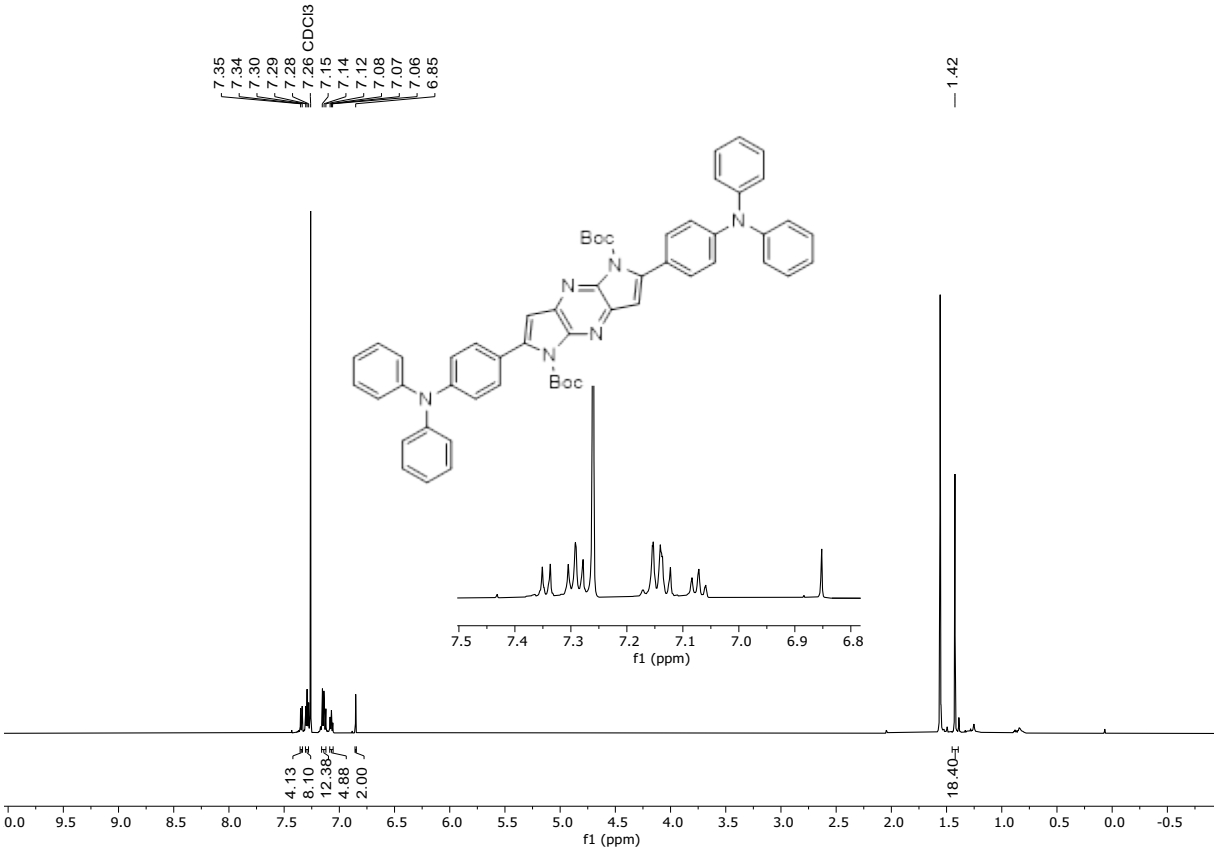


*Figure 55: **^{1}H NMR** (600 MHz, $CDCl_3$) of **DPPB10**.*

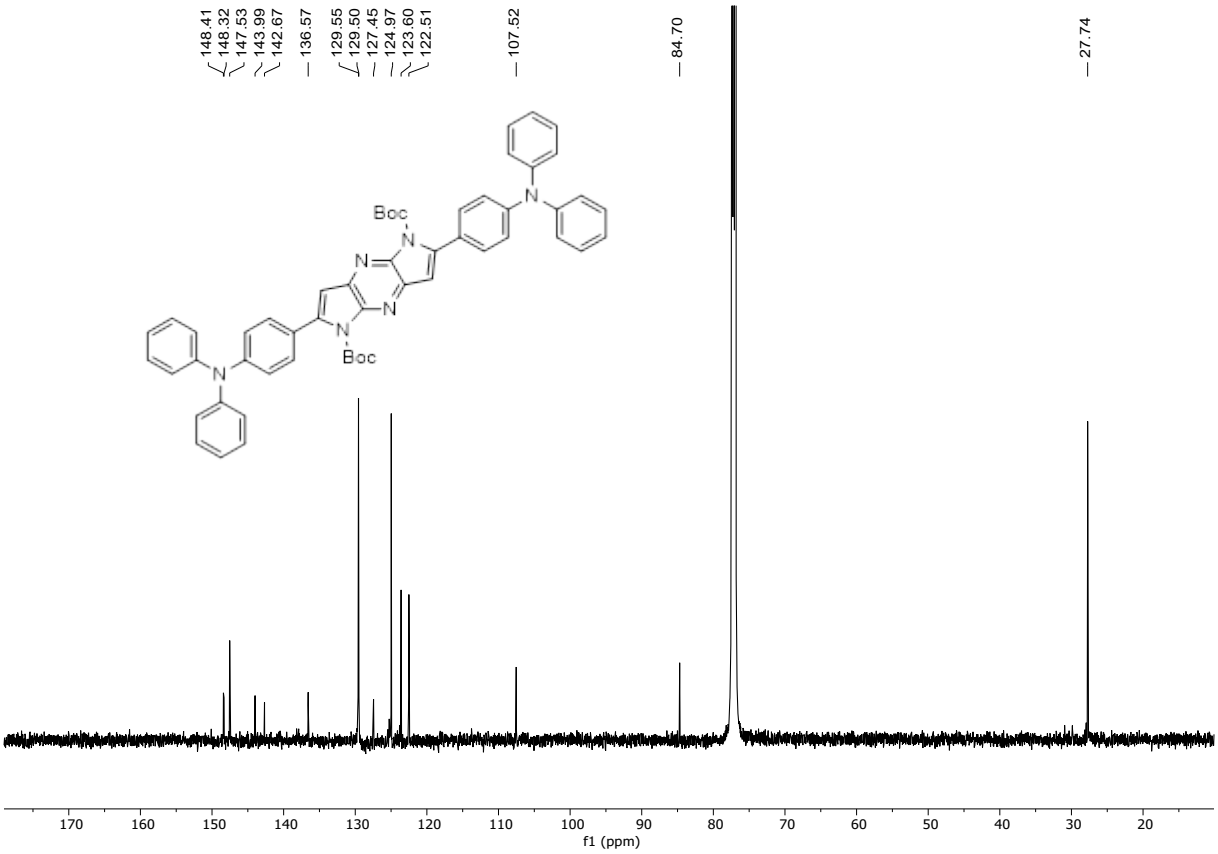


Figure 56: ***$^{13}C\{^{1}H\}$ NMR*** *(151 MHz, $CDCl_3$) of* ***DPPB10****.*

Picture 1: Example of **DPP2** in DMSO depicting low solubility.

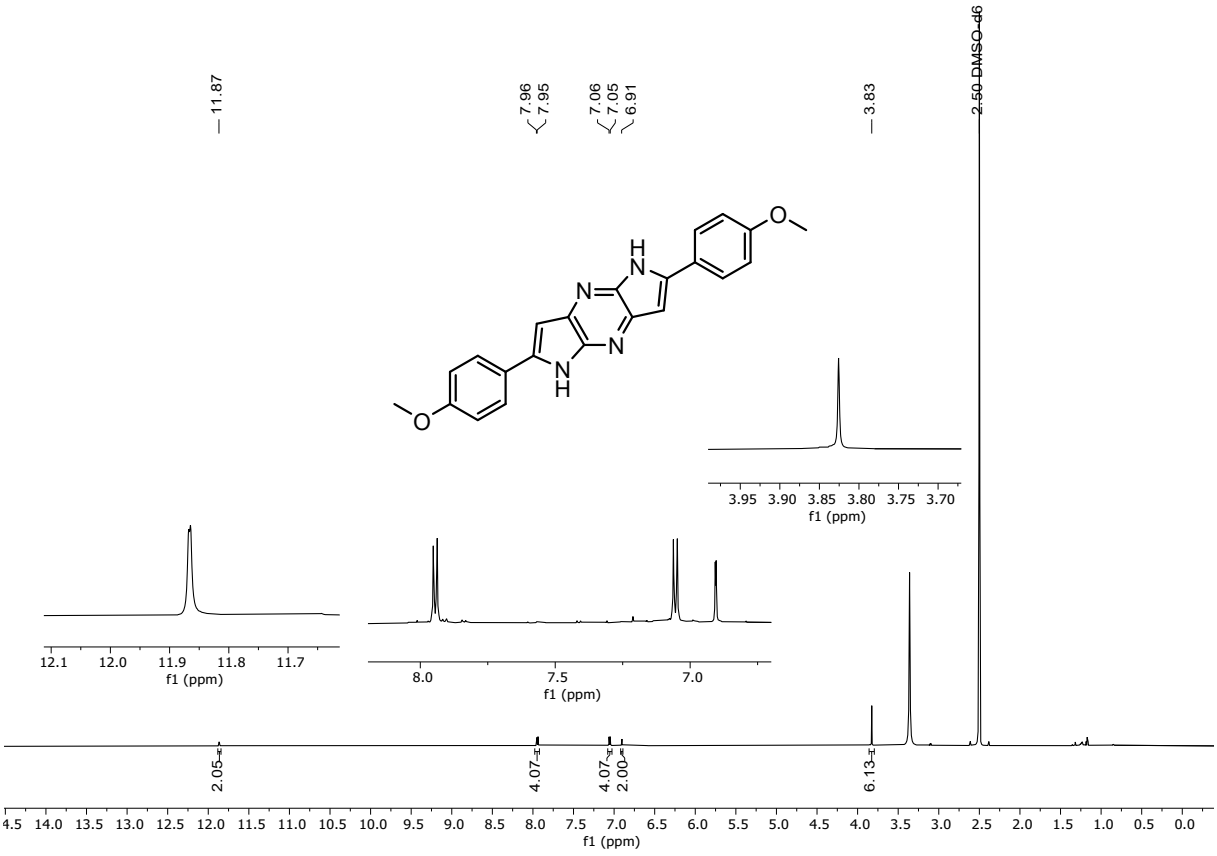


*Figure 57: **^{1}H NMR** (600 MHz, DMSO) of **DPP1.***

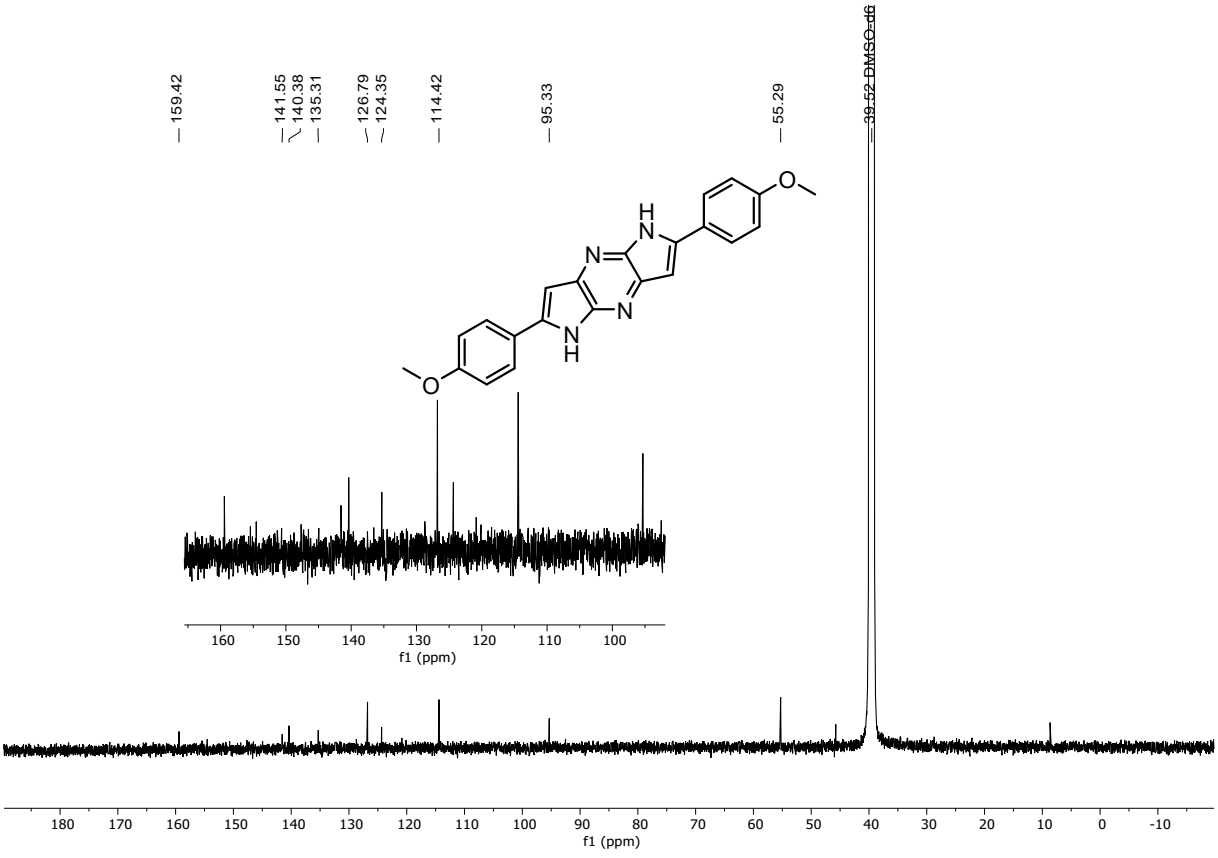


*Figure 58: **^{13}C NMR {^{1}H}** (151 MHz, DMSO) of **DPP1**.*

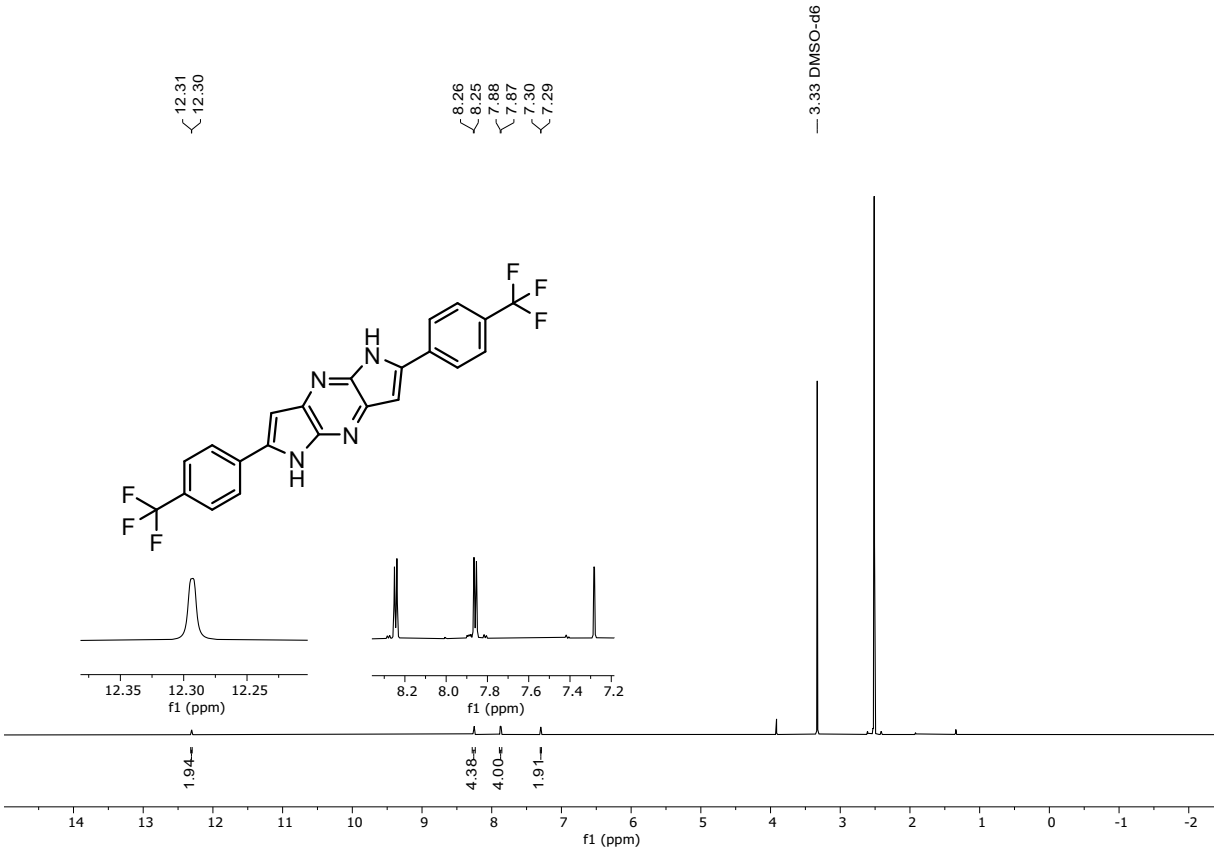


*Figure 59: **$^{1}H\{^{19}F\}$ NMR** (700 MHz, DMSO) of **DPP2**.*

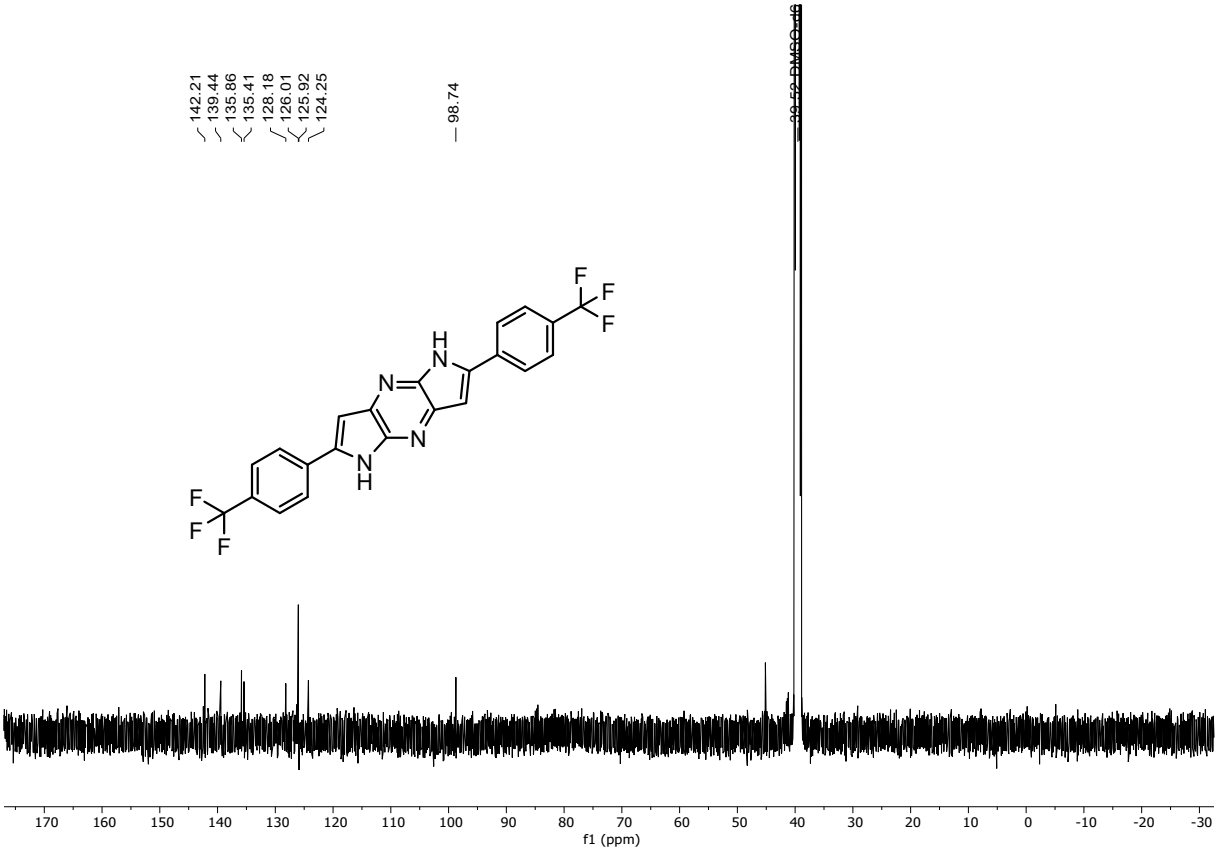


*Figure 60: **^{13}C NMR $\{^{1}H,^{19}F\}$** (126 MHz, DMSO) of **DPP2**.*

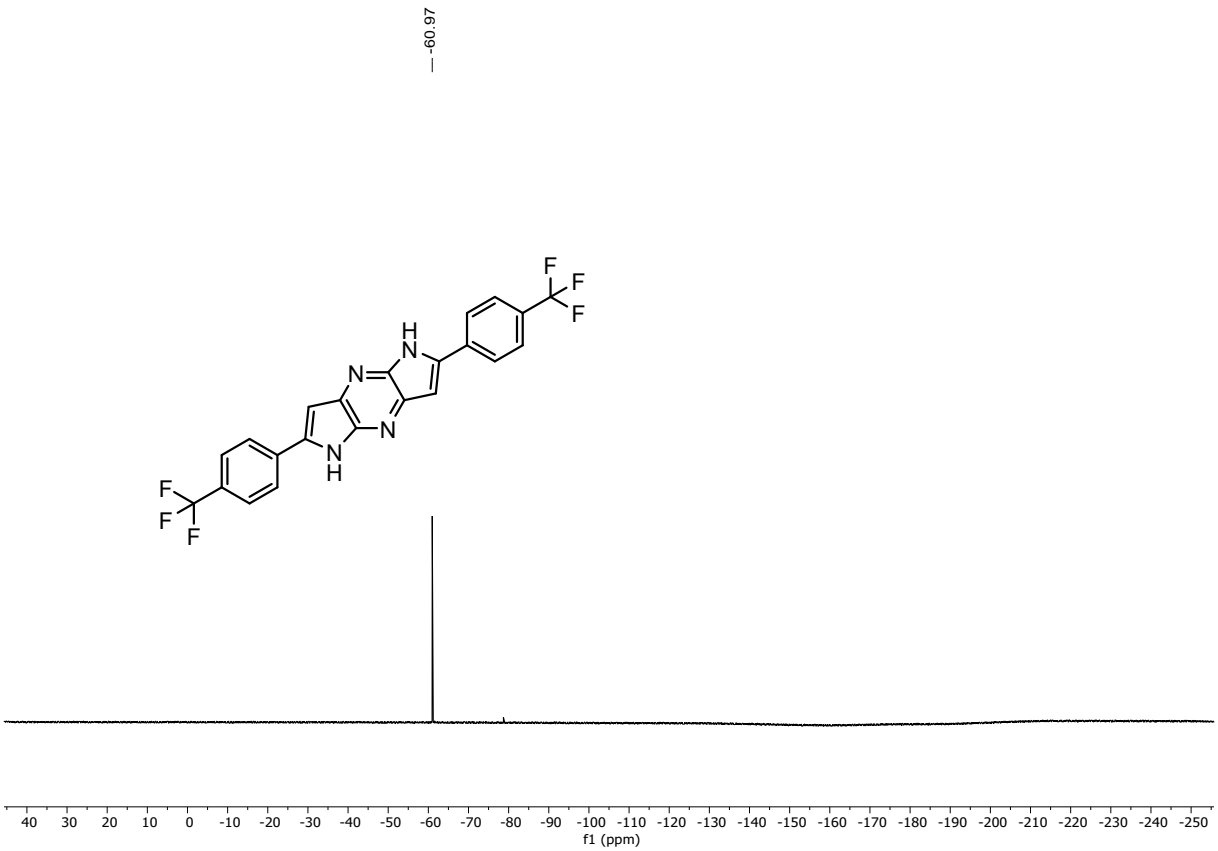


*Figure 61: **^{19}F NMR** (283 MHz, DMSO) of **DPP2**.*

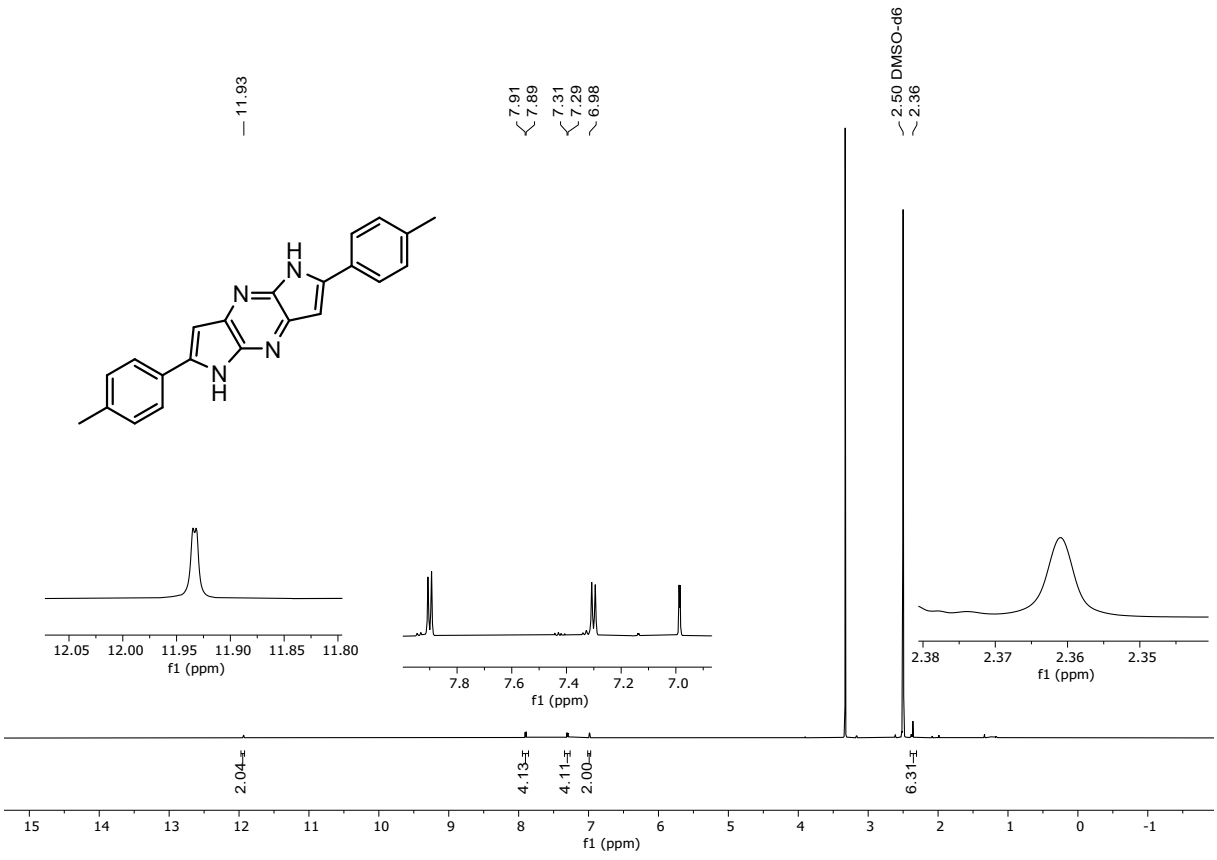


*Figure 62: **^{1}H NMR** (600 MHz, DMSO) of **DPP3**.*

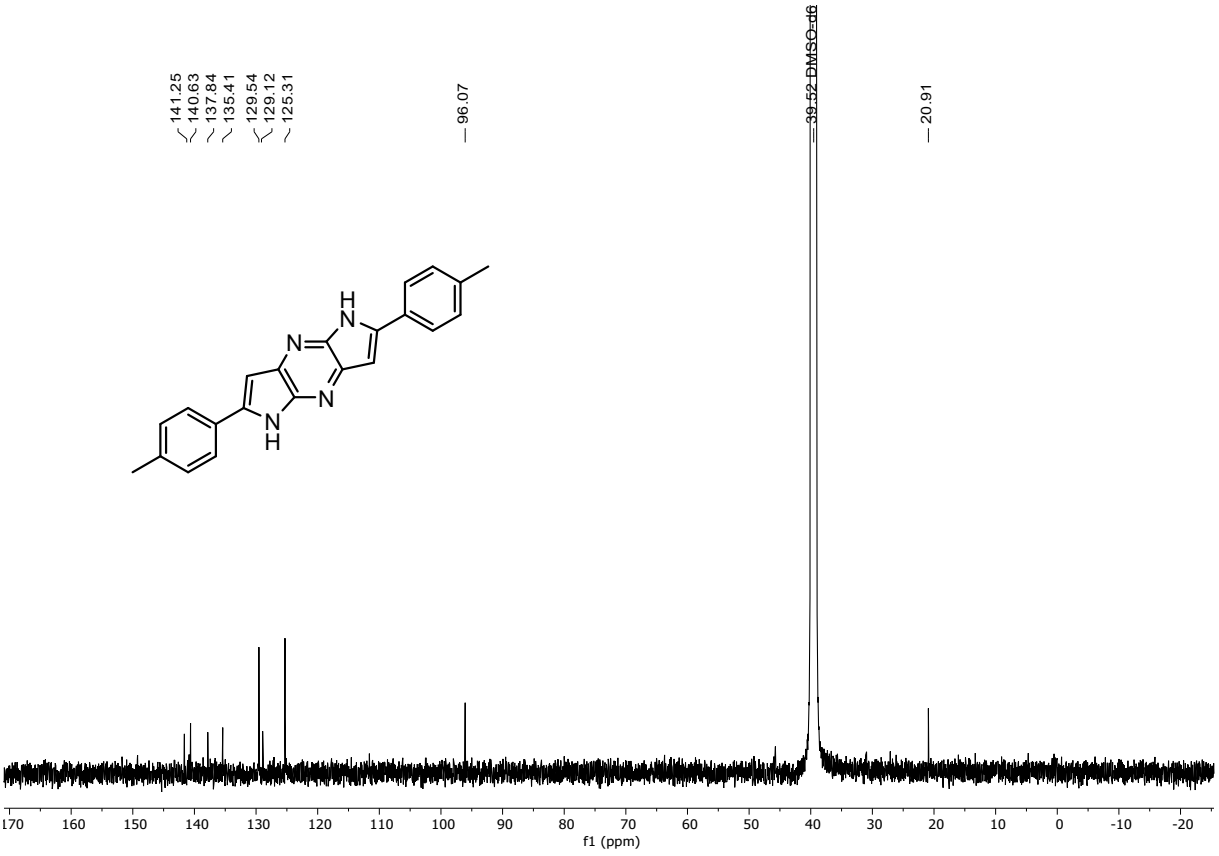


*Figure 63: **$^{13}C\{^{1}H\}$ NMR** (151 MHz, DMSO) of **DPP3**.*

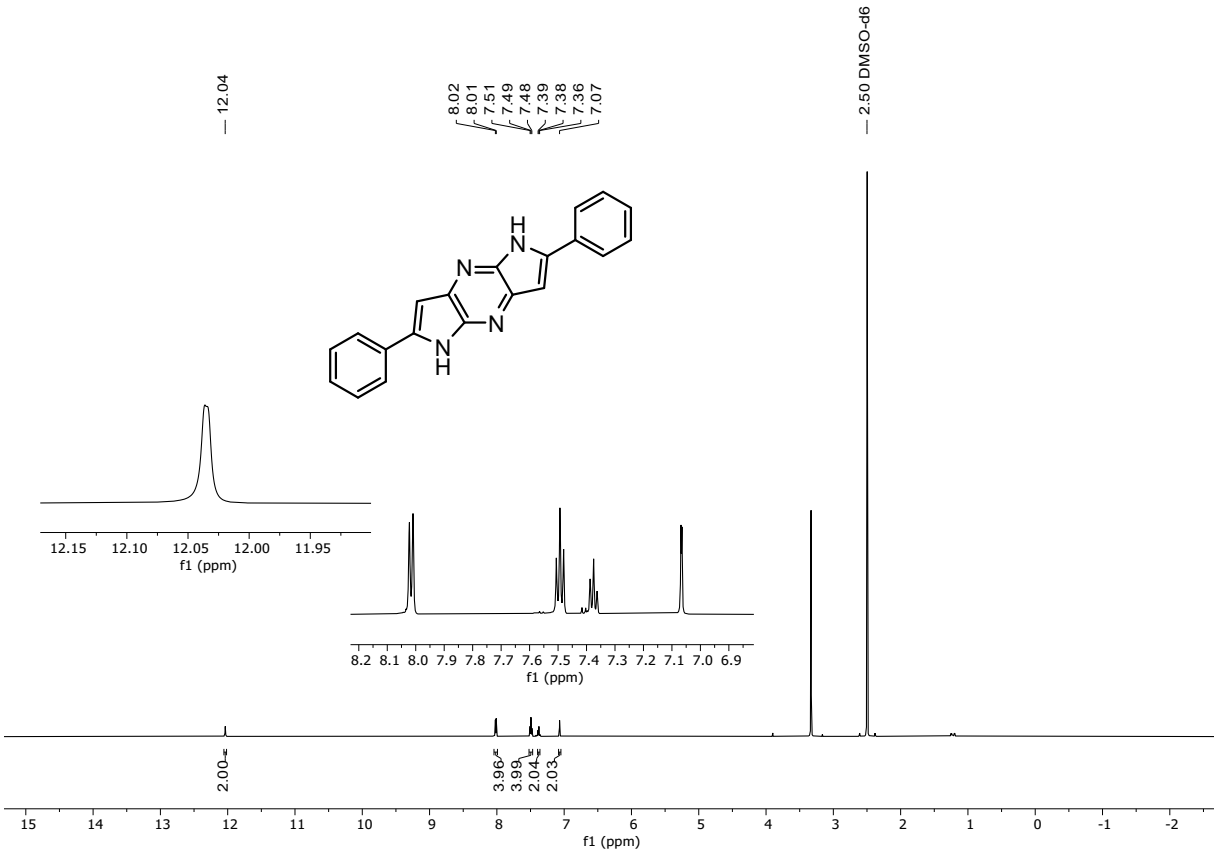


*Figure 64: **^{1}H NMR (**600 MHz, DMSO) of **DPP4**.*

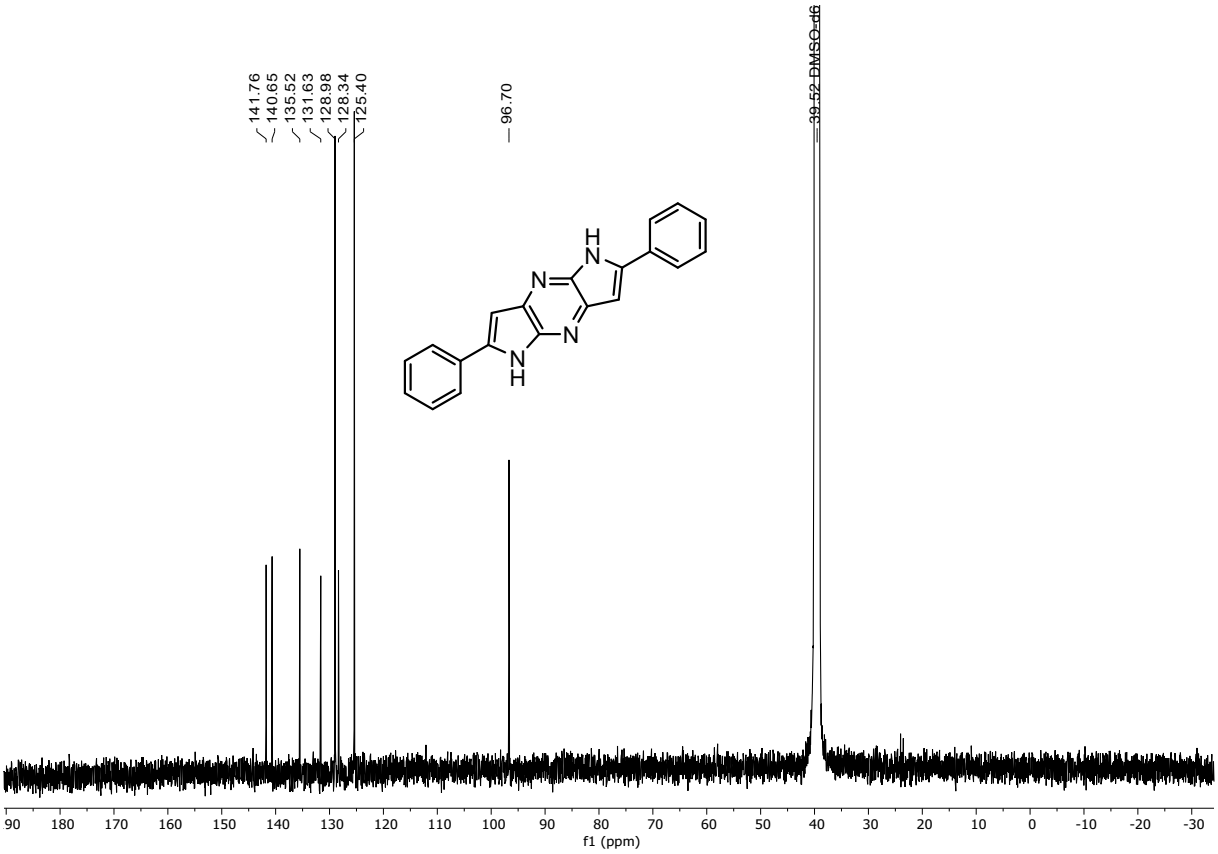


*Figure 65: **$^{13}C\{^{1}H\}$ NMR** (151 MHz, DMSO) of **DPP4**.*

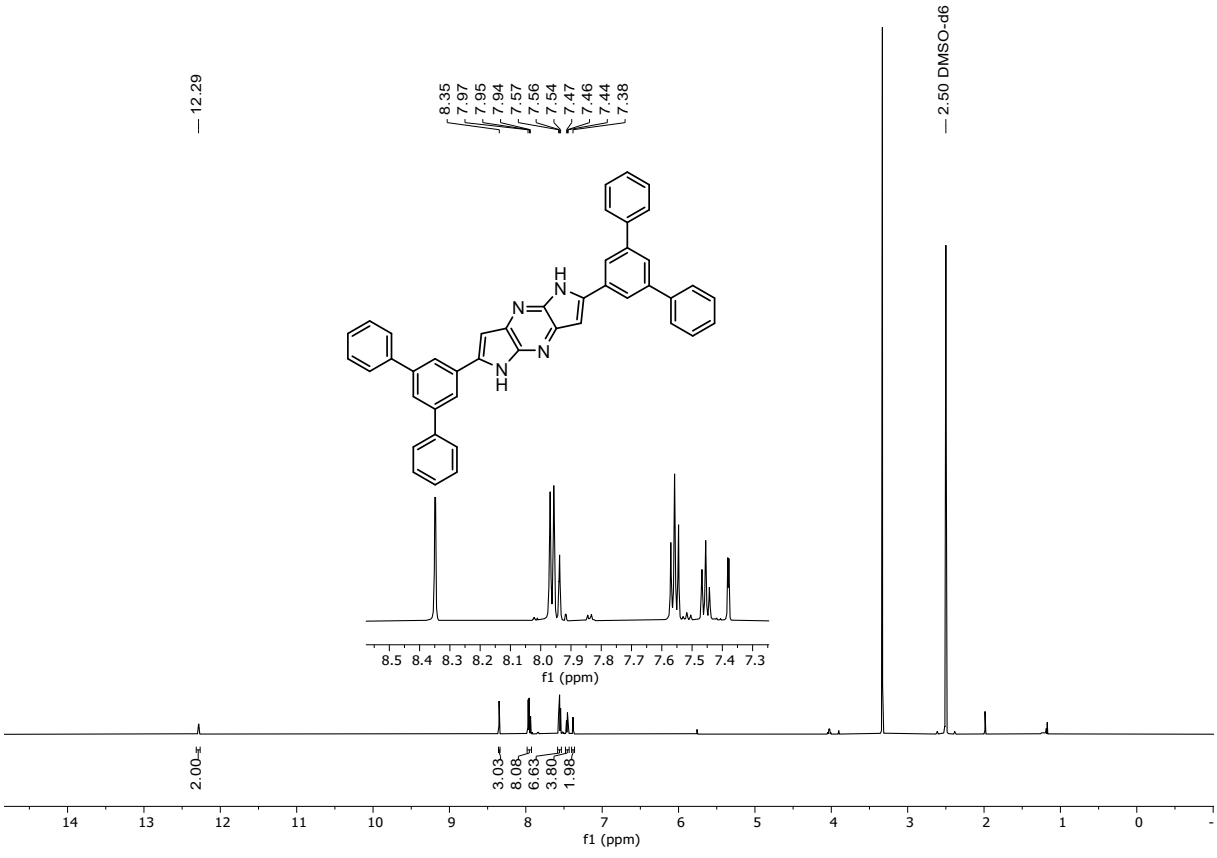


*Figure 66: **^{1}H NMR** (600 MHz, DMSO) of **DPP7**.*

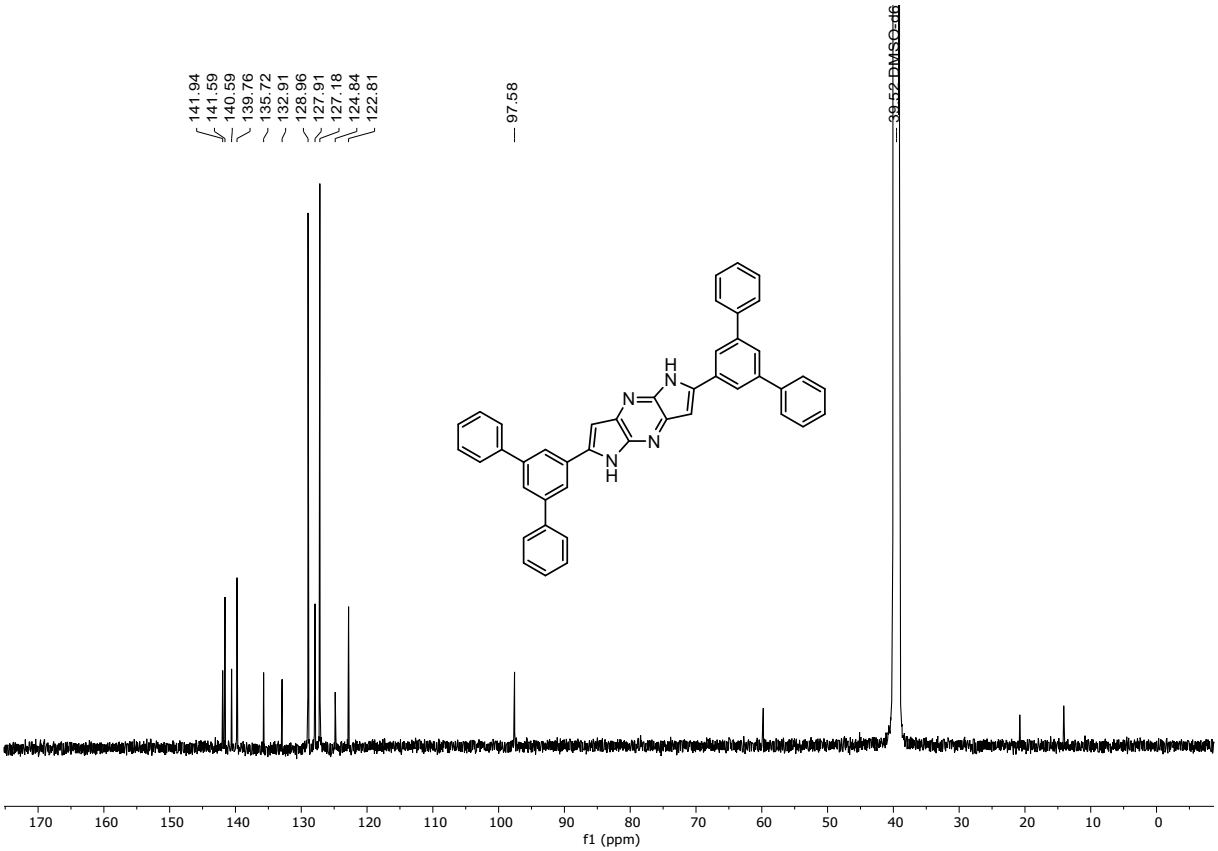


*Figure 67: **$^{13}C\{^{1}H\}$ NMR** (101 MHz, DMSO) of **NHPY_g**.*

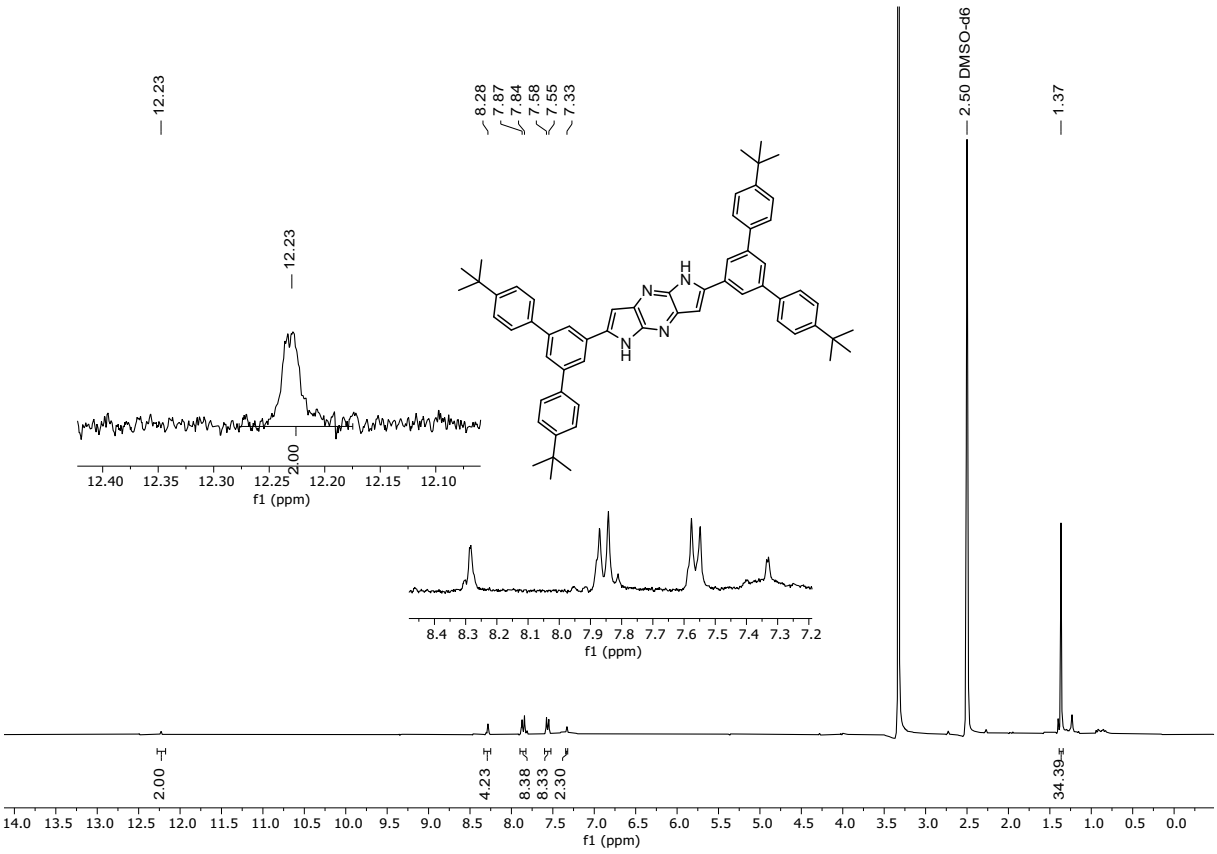


*Figure 68: **^{1}H NMR** (600 MHz, DMSO)of **DPP8**.*

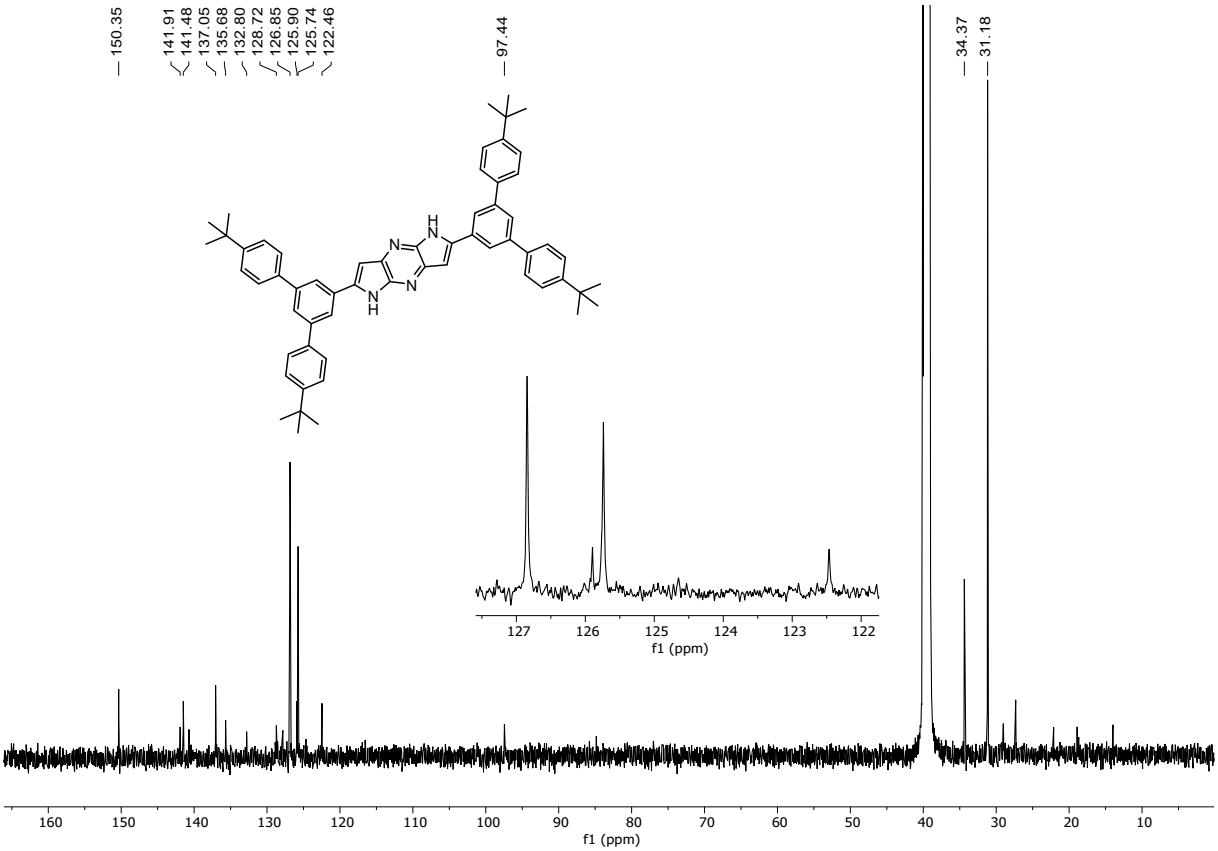


*Figure 69: **$^{13}C\{^{1}H\}$ NMR** (151 MHz, DMSO) of **DPP8**.*

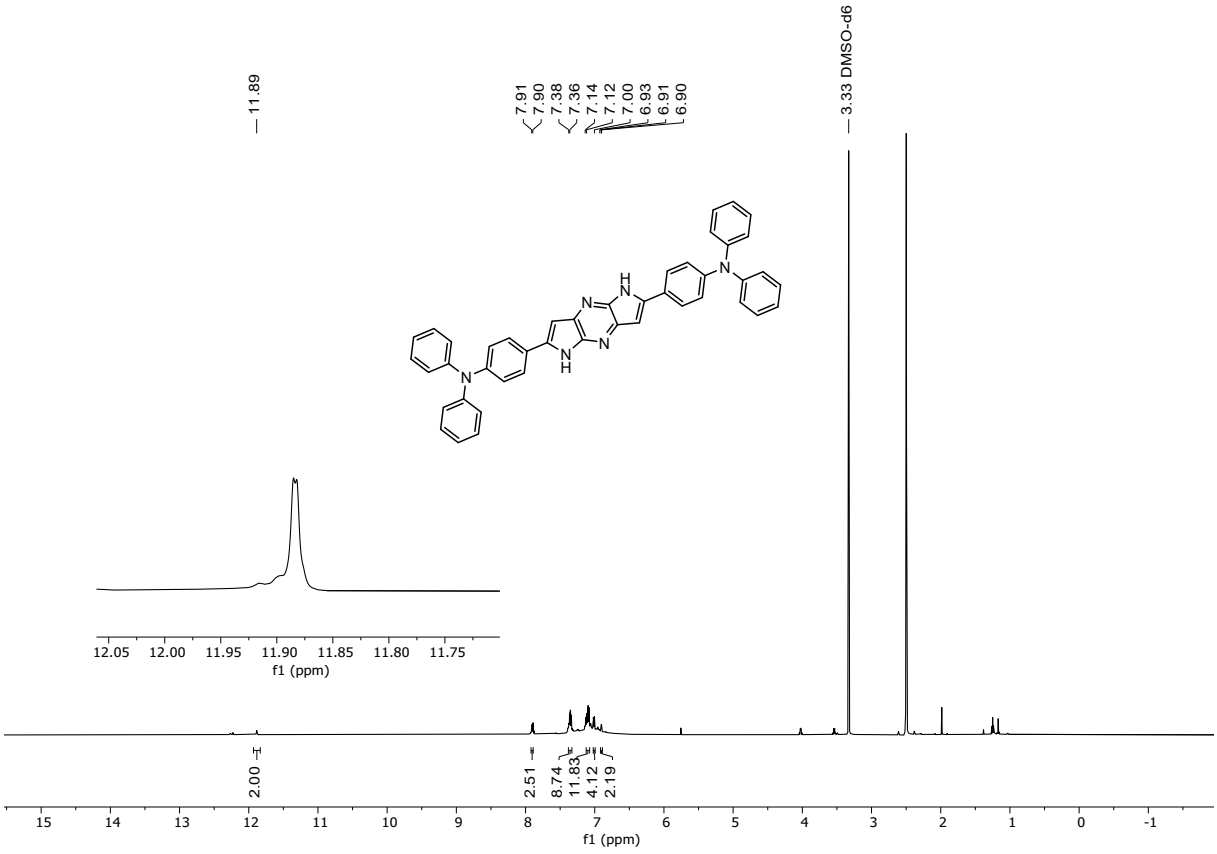


*Figure 70: **^{1}H NMR** (600 MHz, DMSO) of **DPP10.***

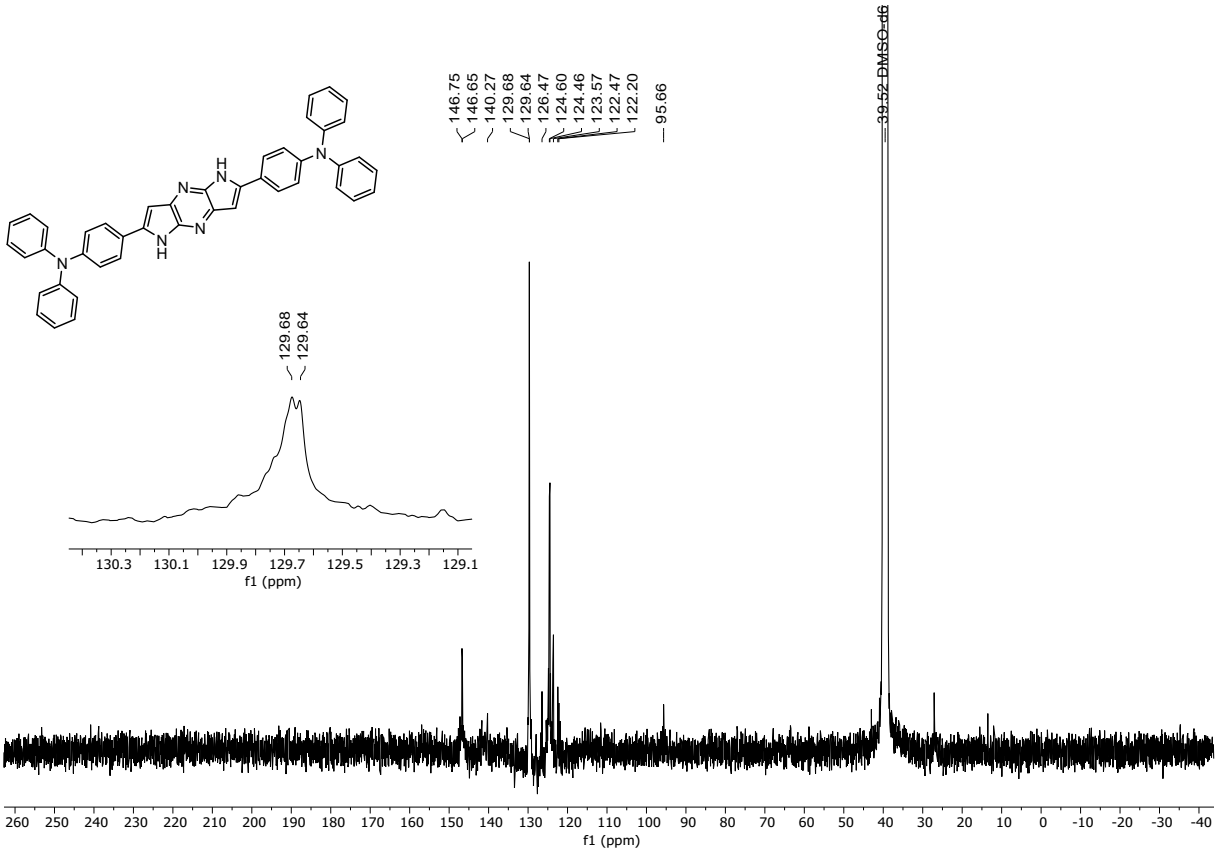


Figure 71: ***$^{13}C\{^{1}H\}$ NMR*** *(101 MHz, DMSO) of* ***DPP10****.*

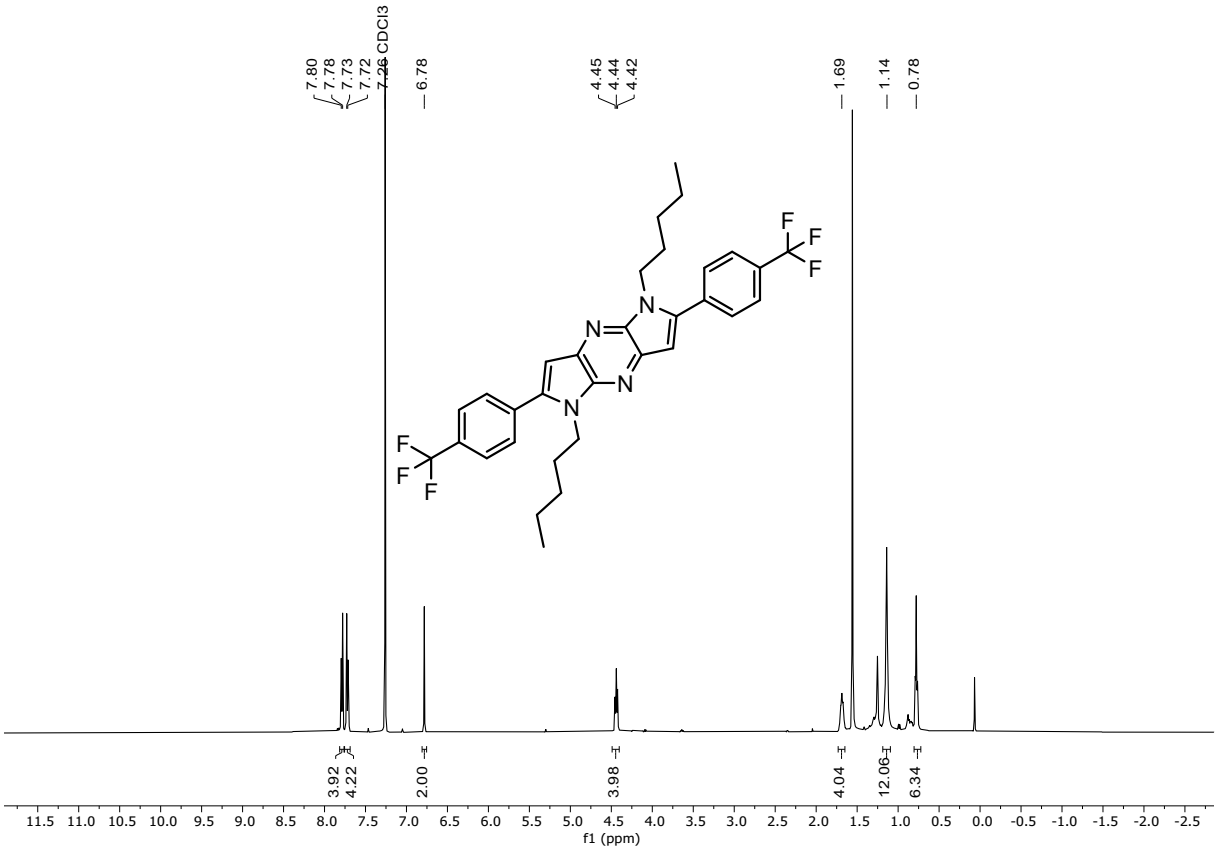


Figure 72: ***$^{1}H\{^{19}F\}$*** *(500 MHz, $CDCl_3$) of* ***ADPP1****.*

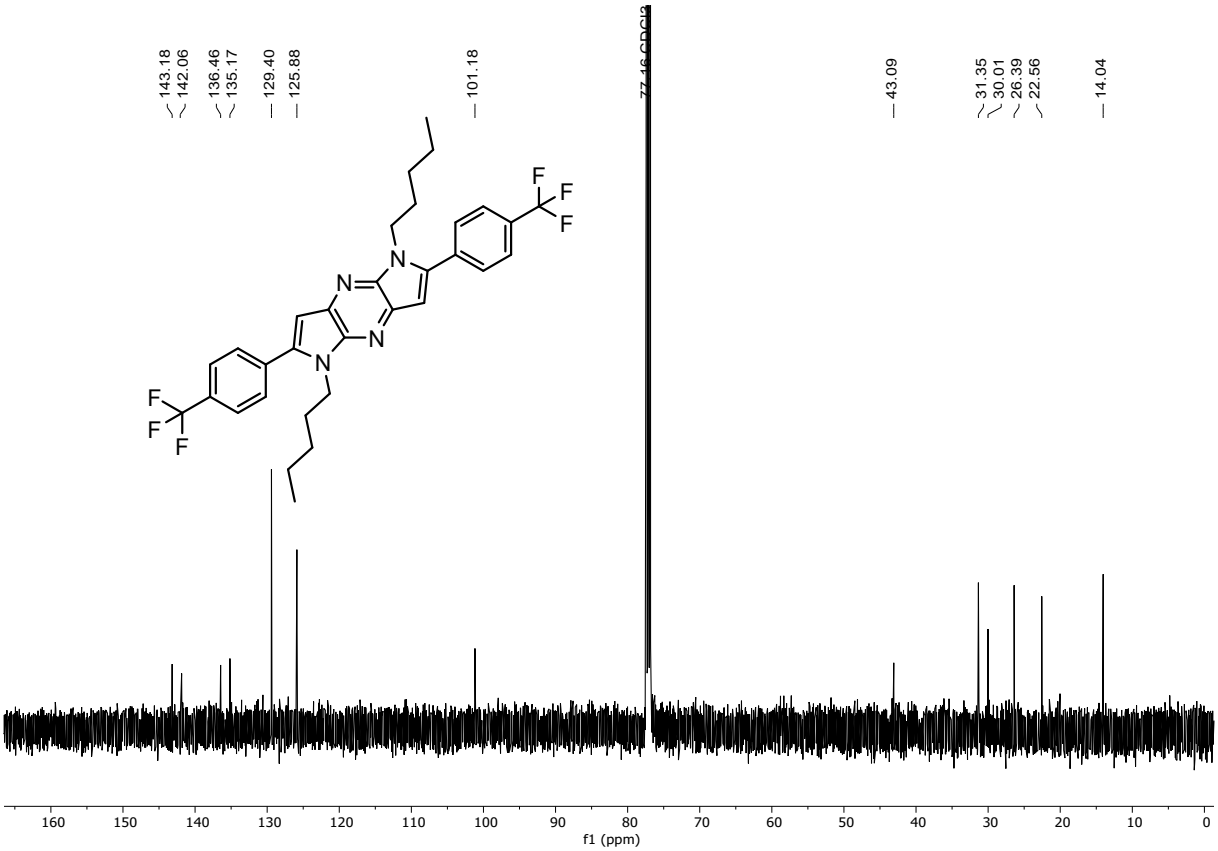


Figure 73: ***^{13}C NMR {^{1}H,^{19}F}*** *(126 MHz, $CDCl_3$) of* ***ADPP1****.*

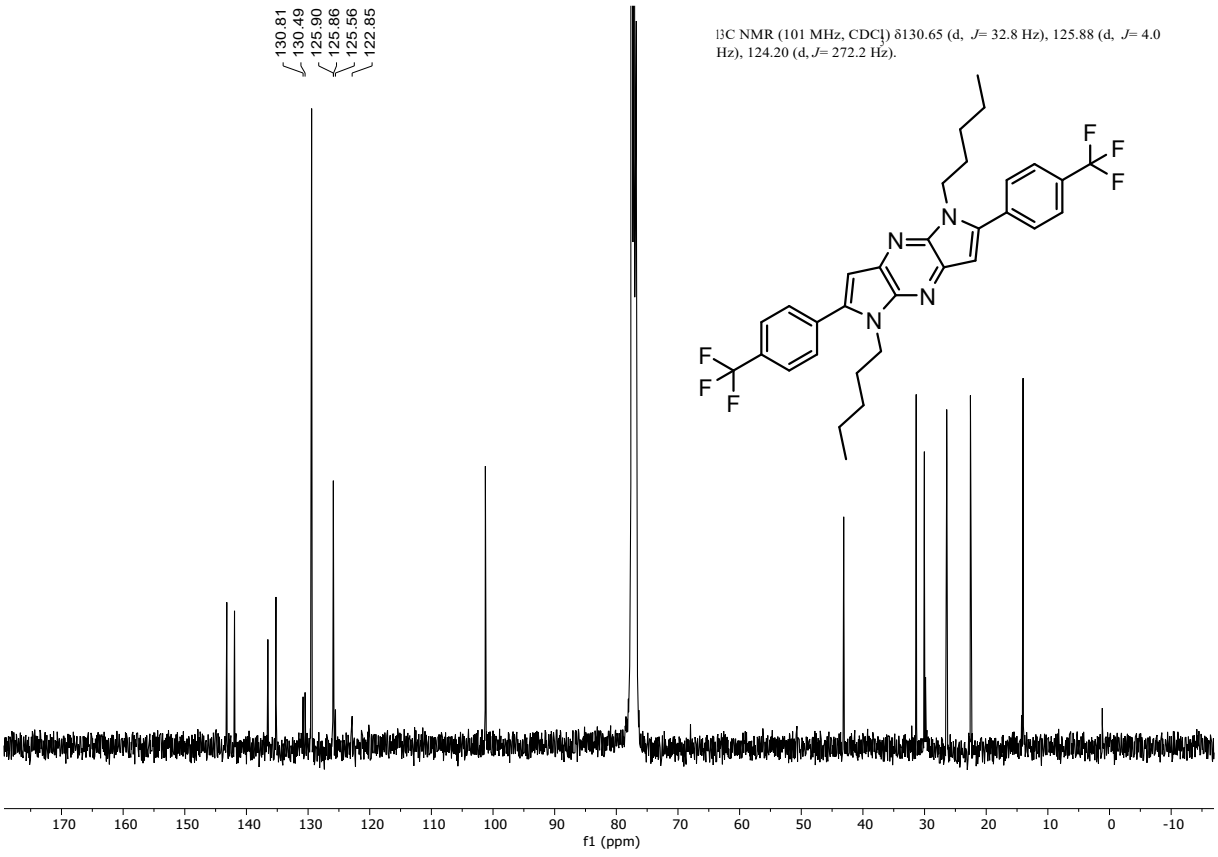


Figure 74: ***^{13}C{^{1}H} NMR*** *(101 MHz, $CDCl_3$) of* ***ADPP1****.*

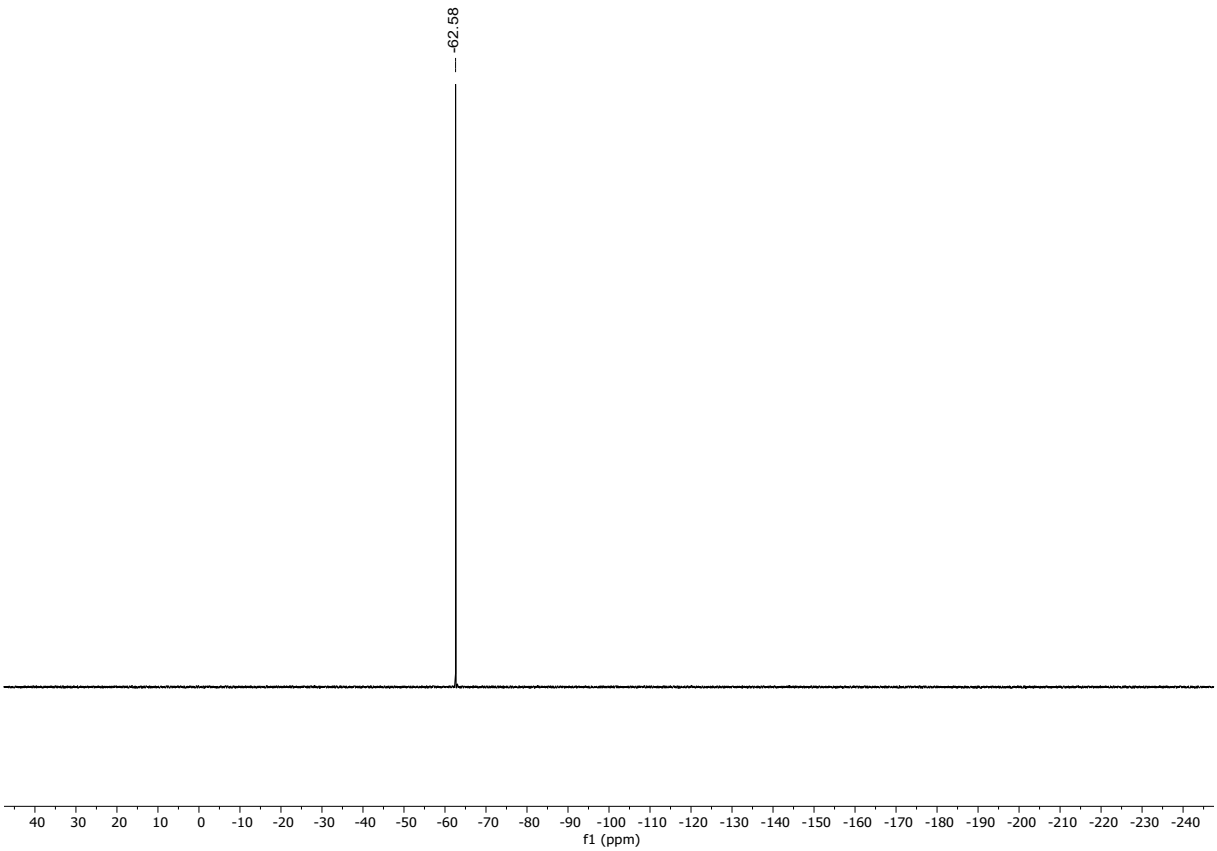


*Figure 75: **$^{19}F\{^{1}H\}$** (283 MHz, $CDCl_3$) of **ADPP1**.*

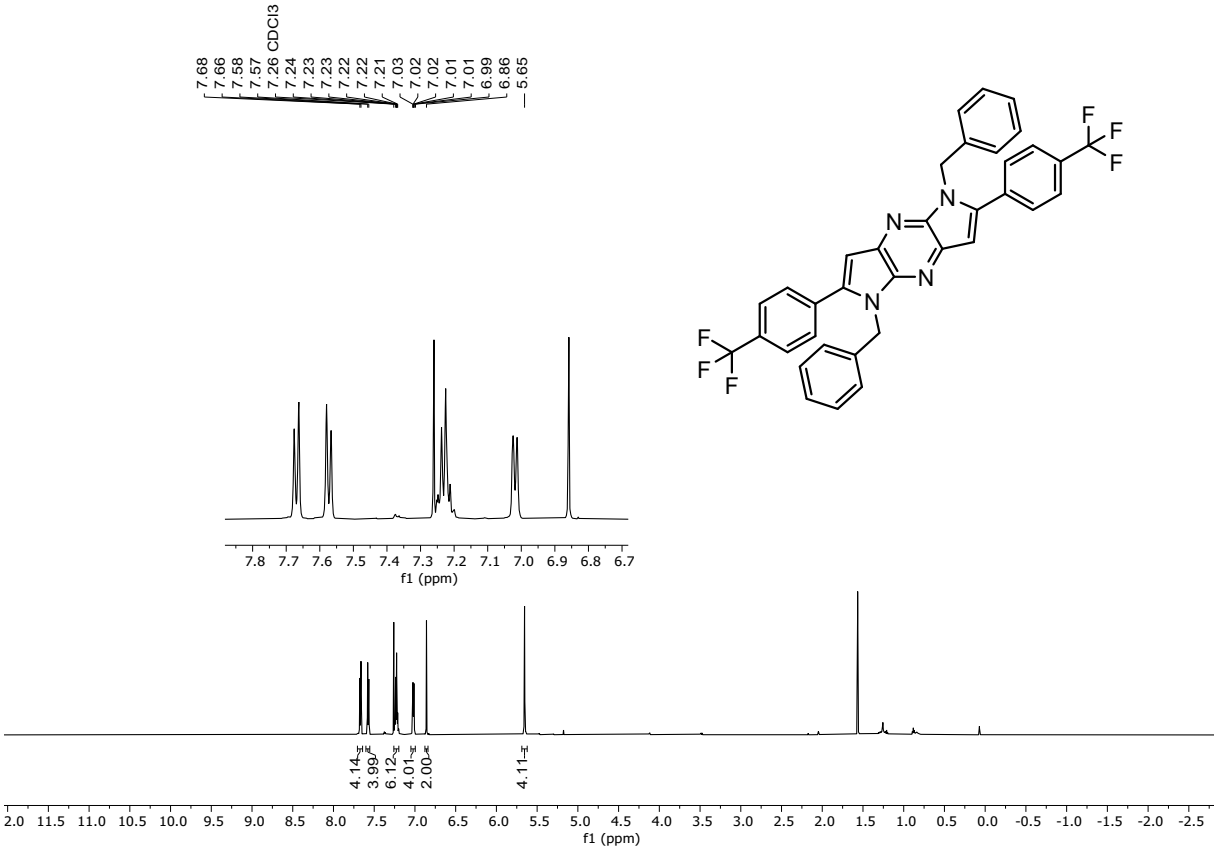


*Figure 76: **^{1}H NMR** (600 MHz, $CDCl_3$) of **ADPP2.***

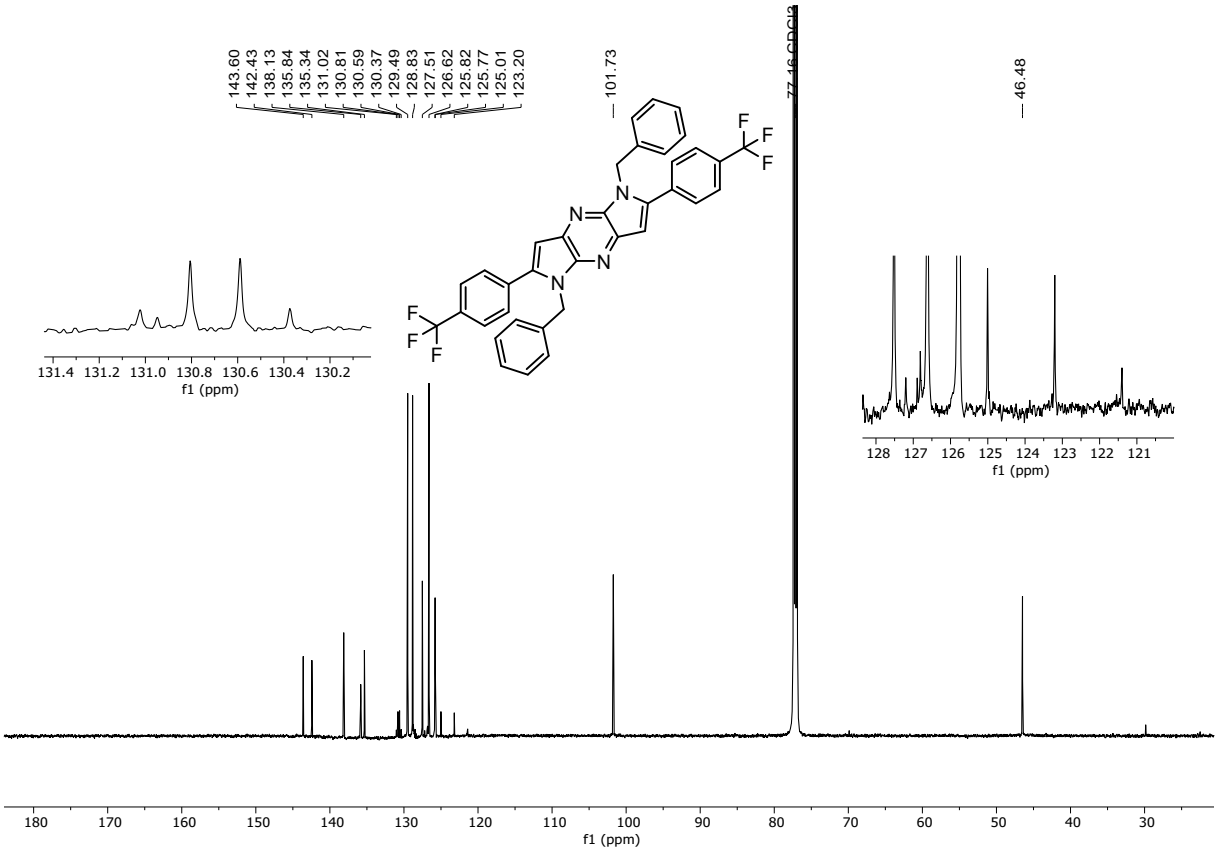


*Figure 77: **$^{13}C\{^{1}H\}$ NMR** (151 MHz, $CDCl_3$) of **ADPP2**.*

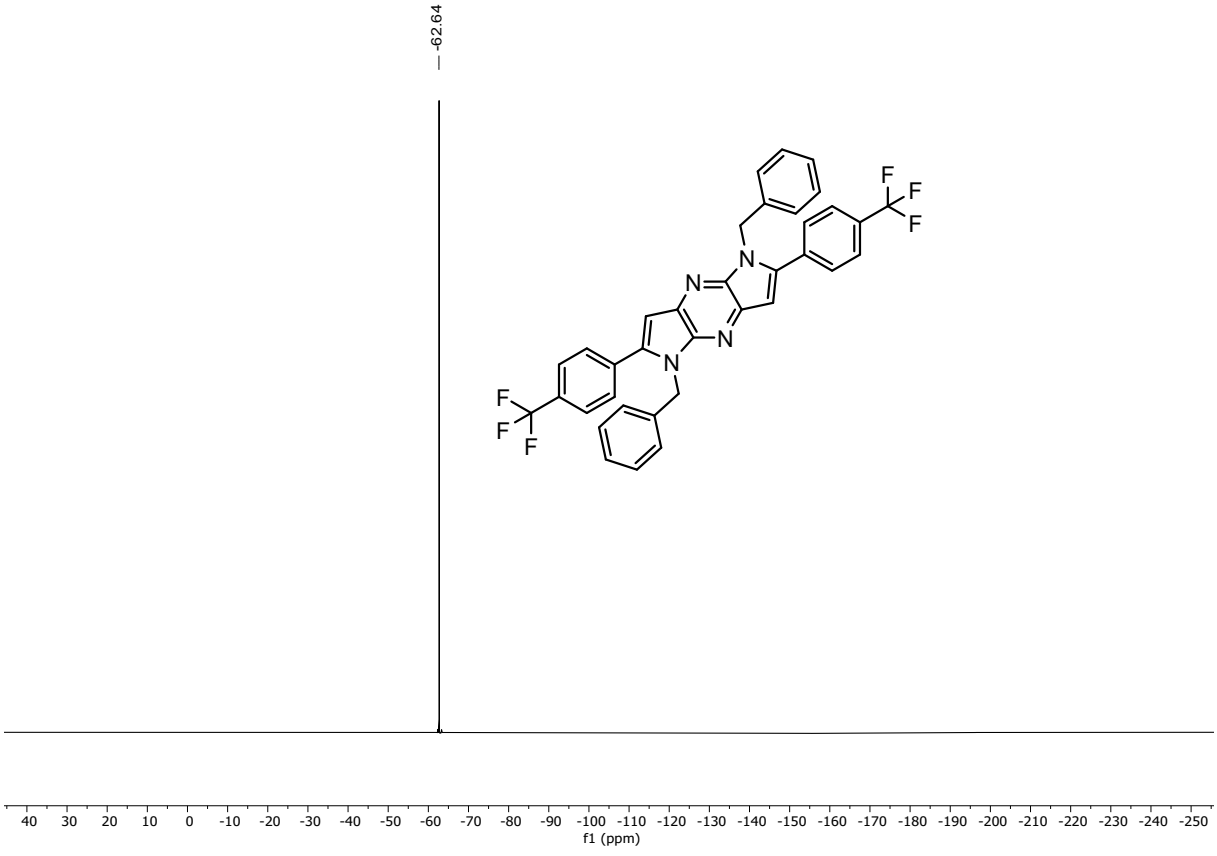


*Figure 78: **^{19}F NMR** (283 MHz, $CDCl_3$) of **ADPP2.***

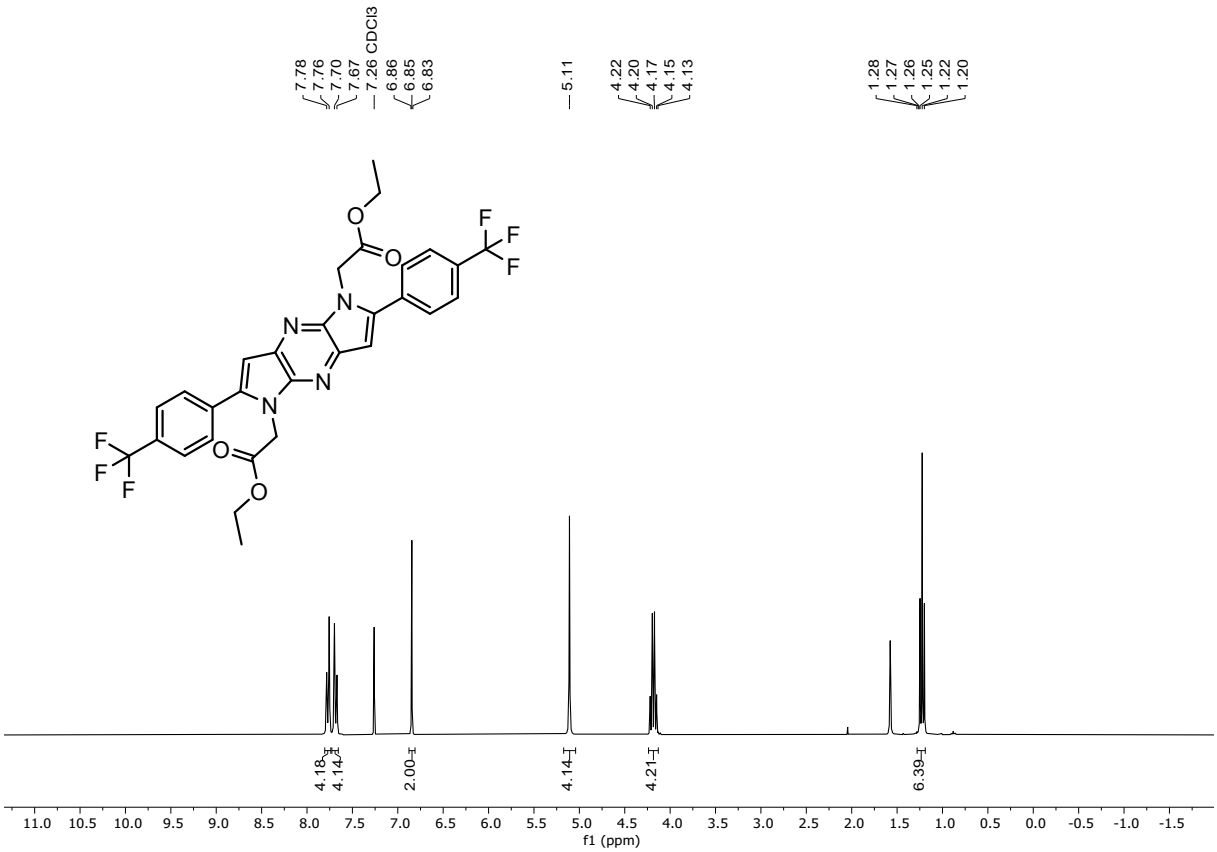


*Figure 79: **^{1}H NMR** (300 MHz, $CDCl_3$) of **ADPP3.***

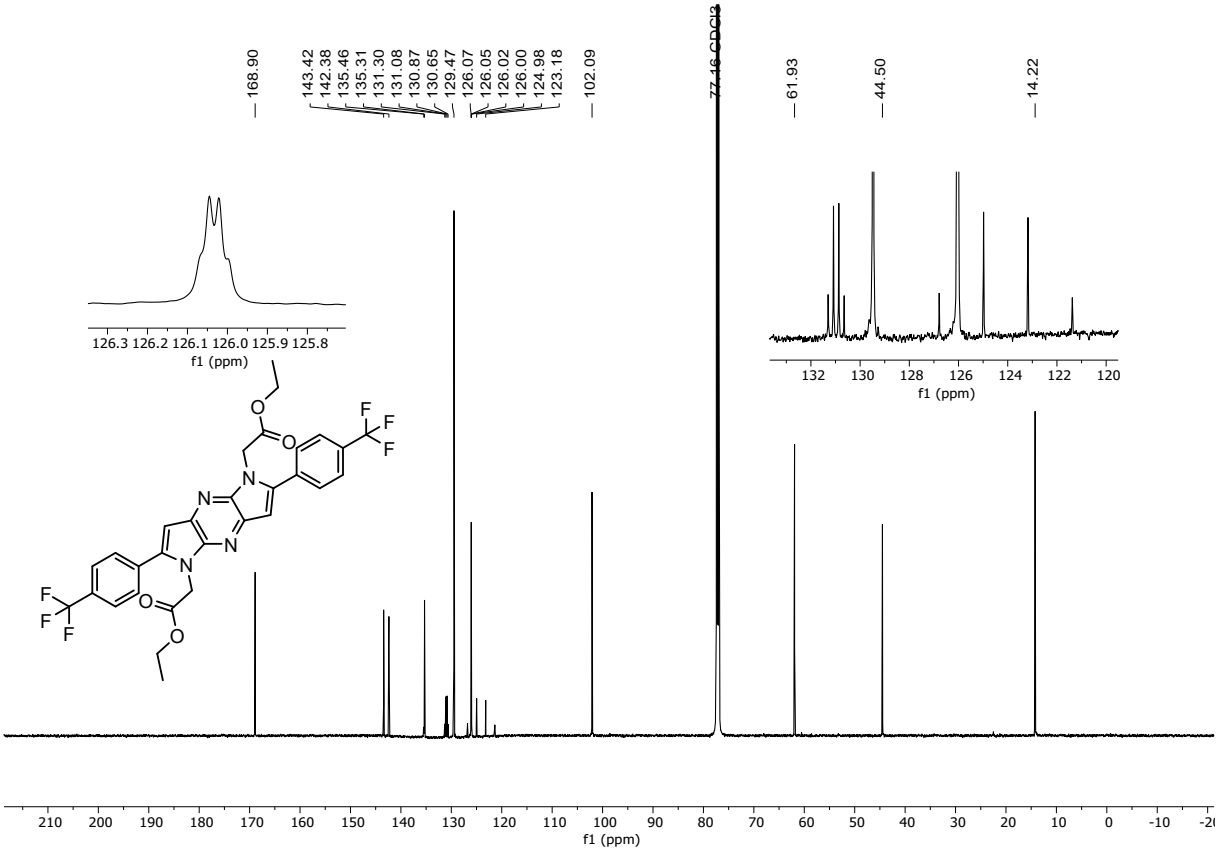


*Figure 80: **$^{13}C\{^{1}H\}$ NMR** (151 MHz, $CDCl_3$) of **ADPP3**.*

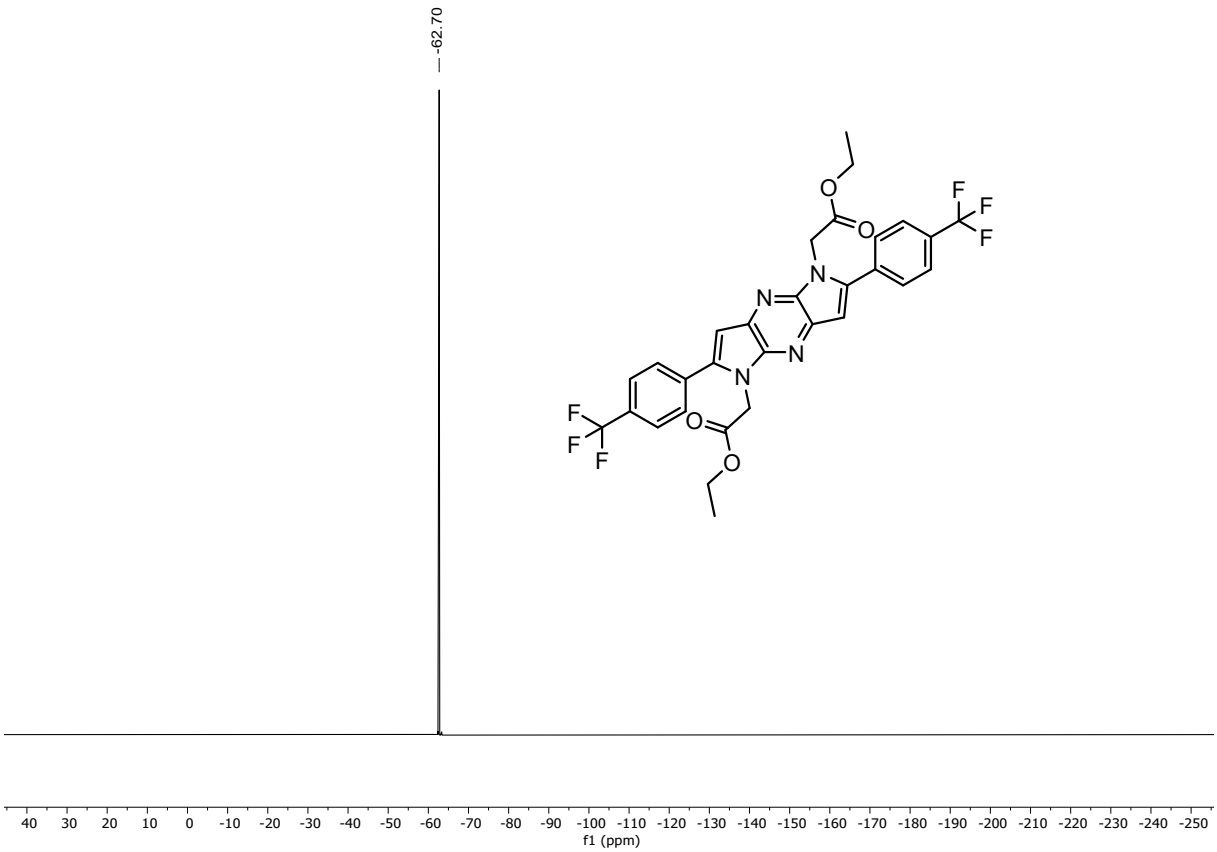


*Figure 81: **^{19}F NMR** (283 MHz, $CDCl_3$) of **ADPP3**.*

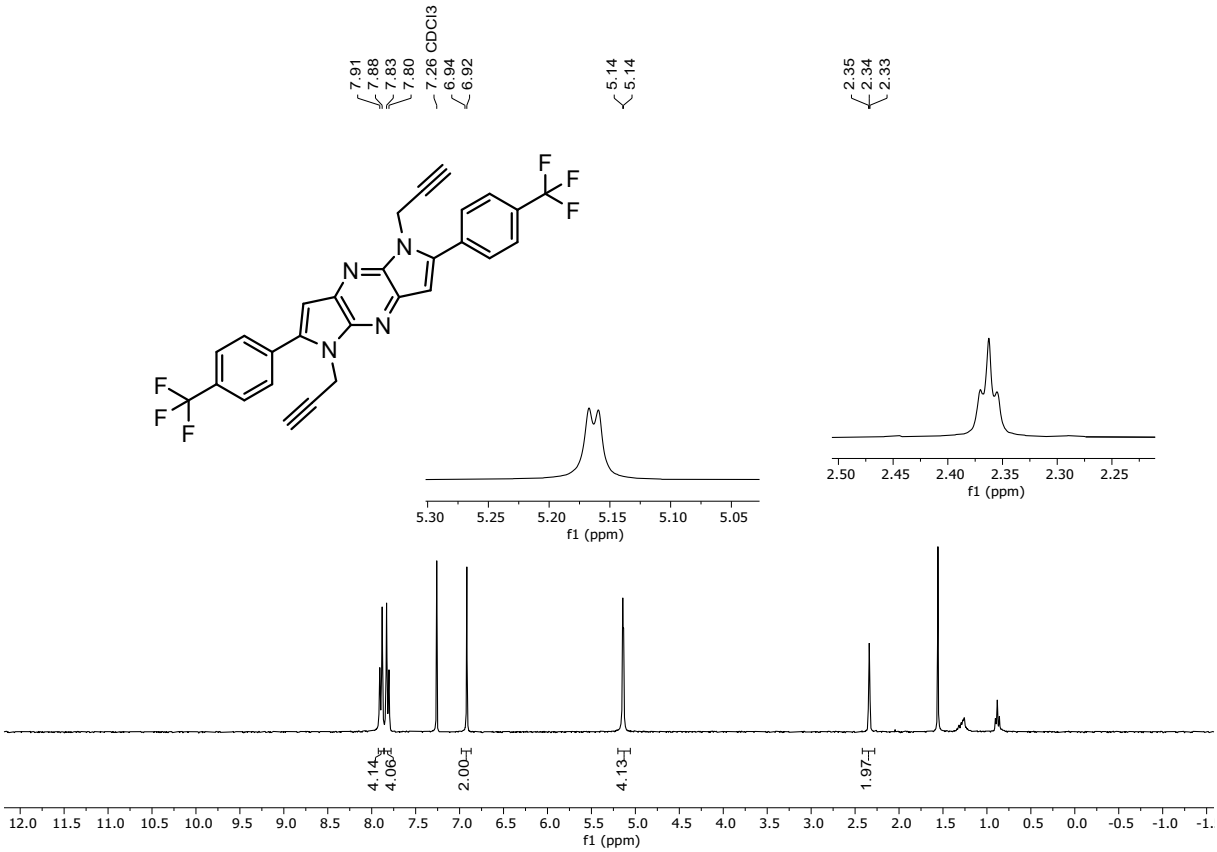


*Figure 82: **^{1}H NMR** (301 MHz, $CDCl_3$) of **ADPP4.***

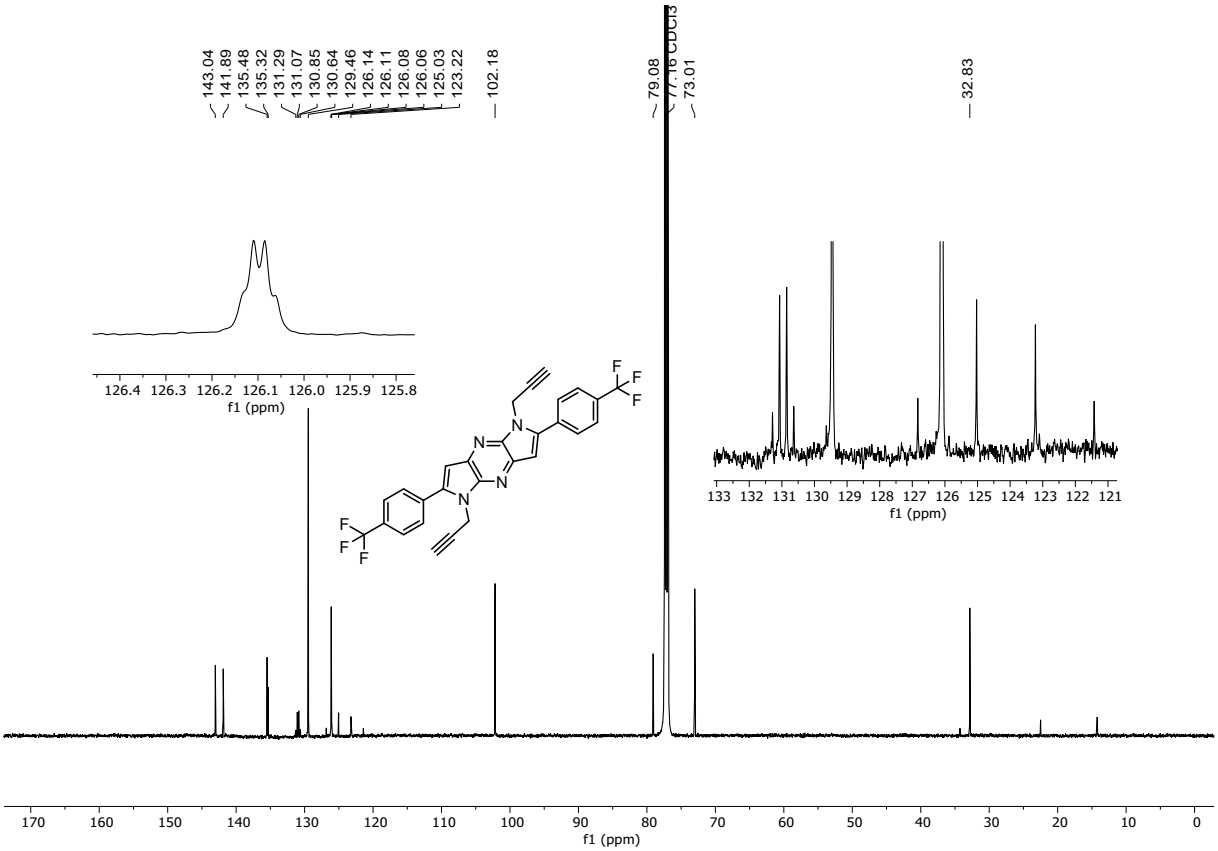


*Figure 83: **$^{13}C\{^{1}H\}$ NMR** (151 MHz, $CDCl_3$) of **ADPP4**.*

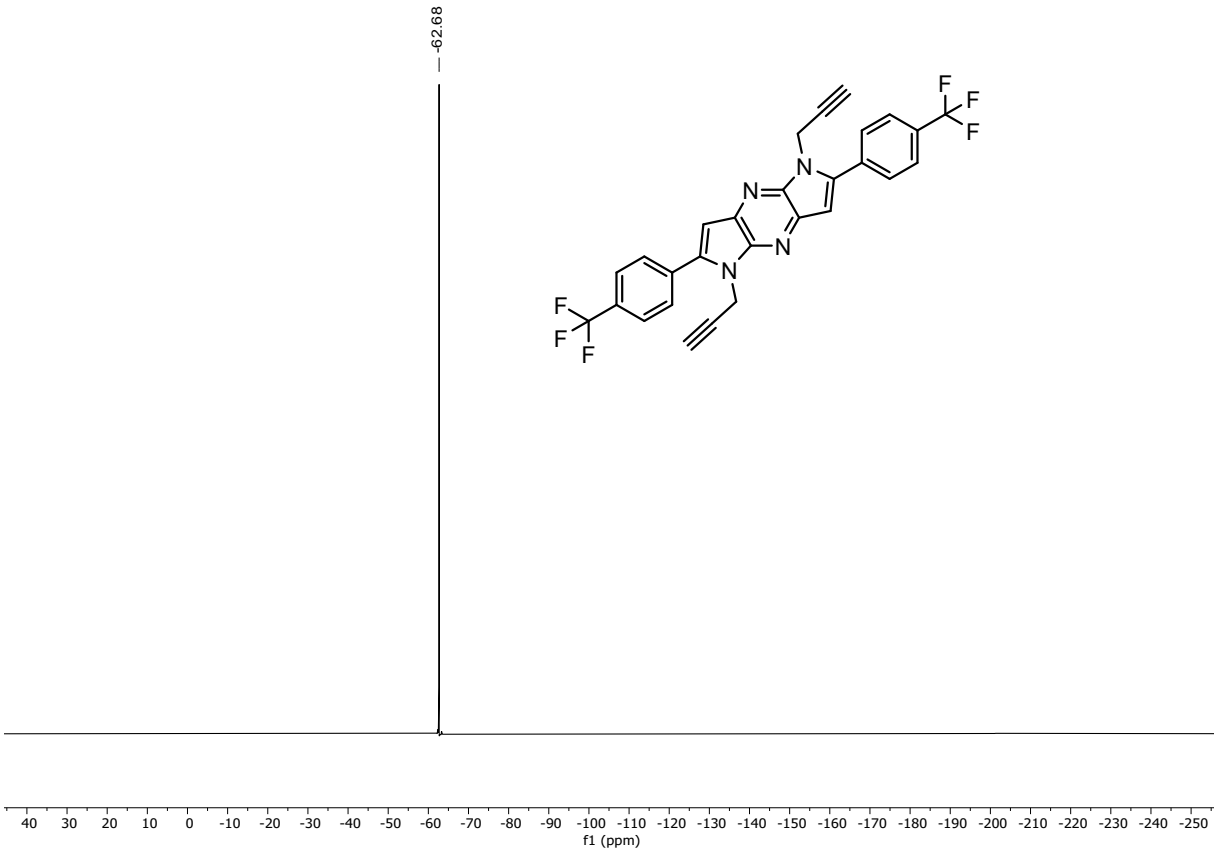


*Figure 84: **^{19}F NMR** (283 MHz, $CDCl_3$) of **ADPP4**.*

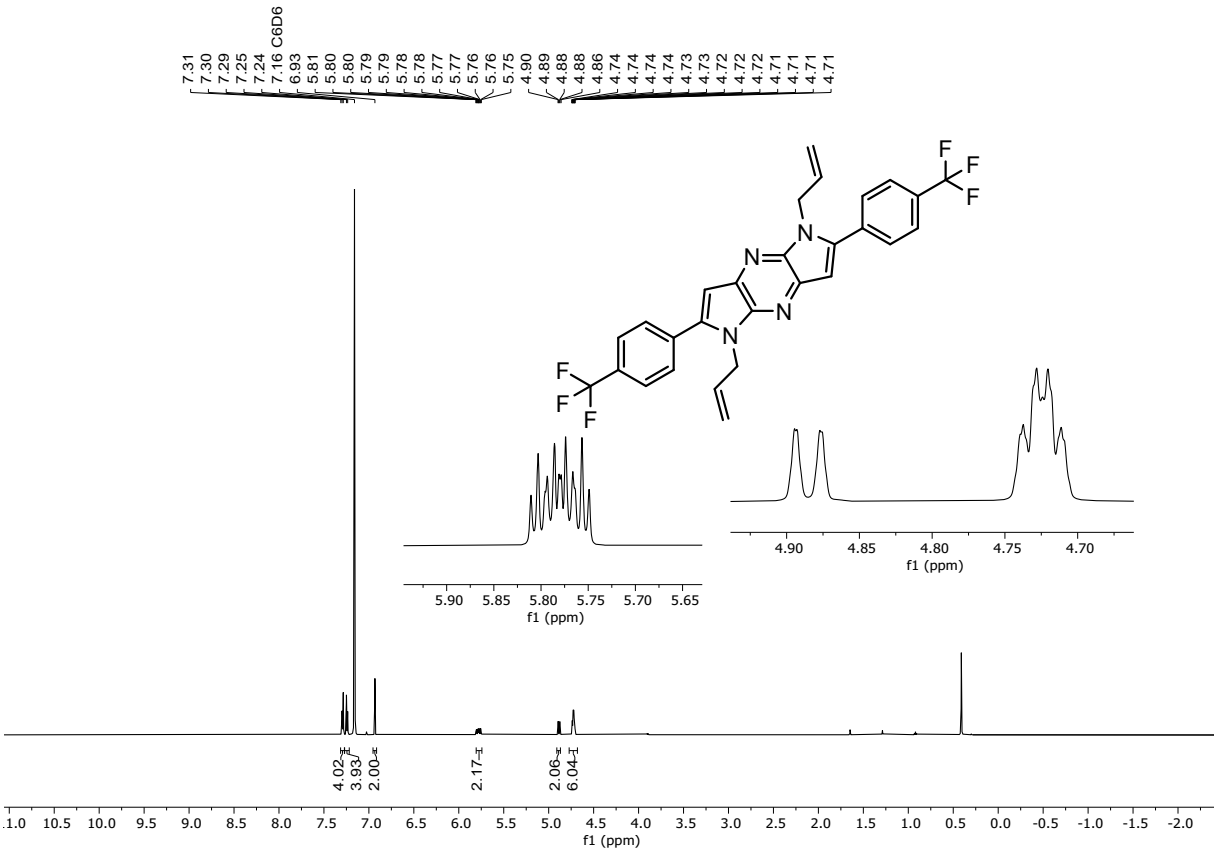


*Figure 85: **^{1}H NMR** (600 MHz, C_6D_6) of **ADPP5.***

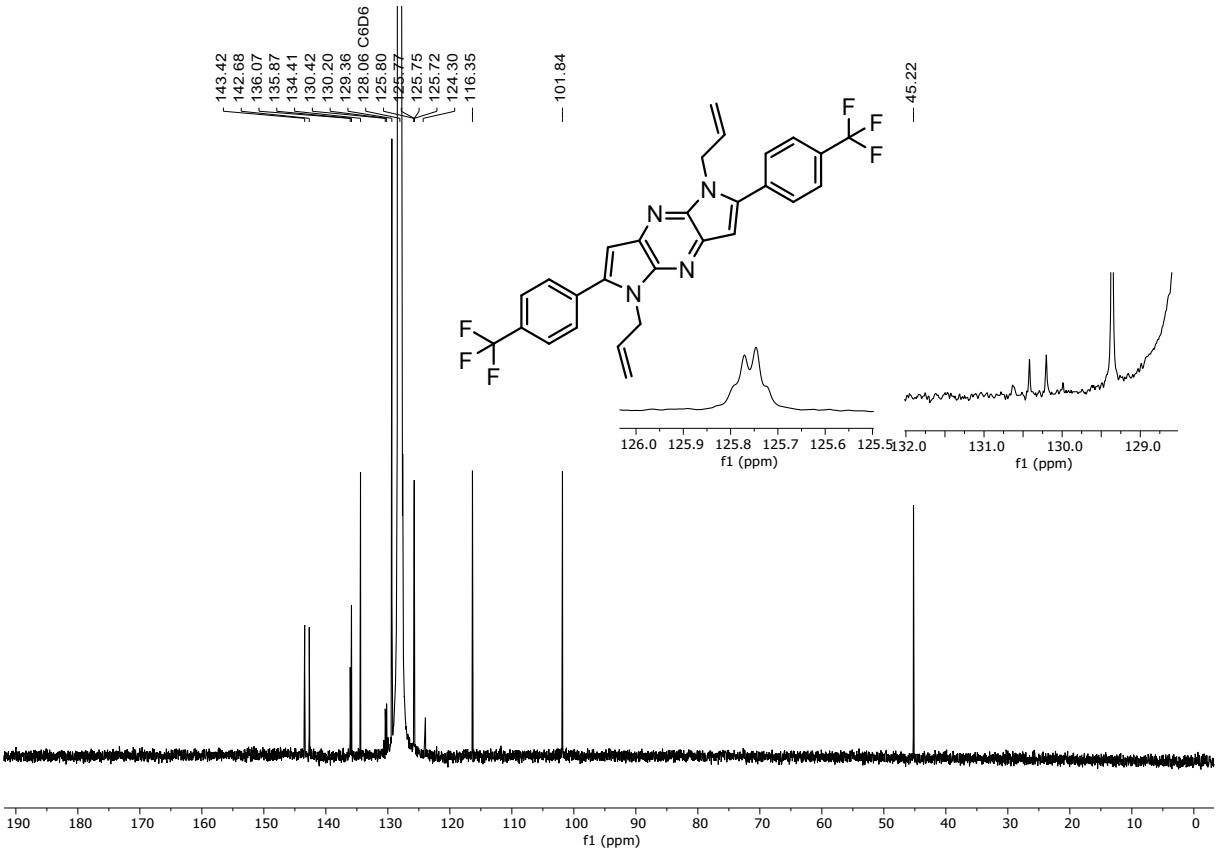


*Figure 86: **^{13}C NMR** (151 MHz, C_6D_6) of **ADPP5.***

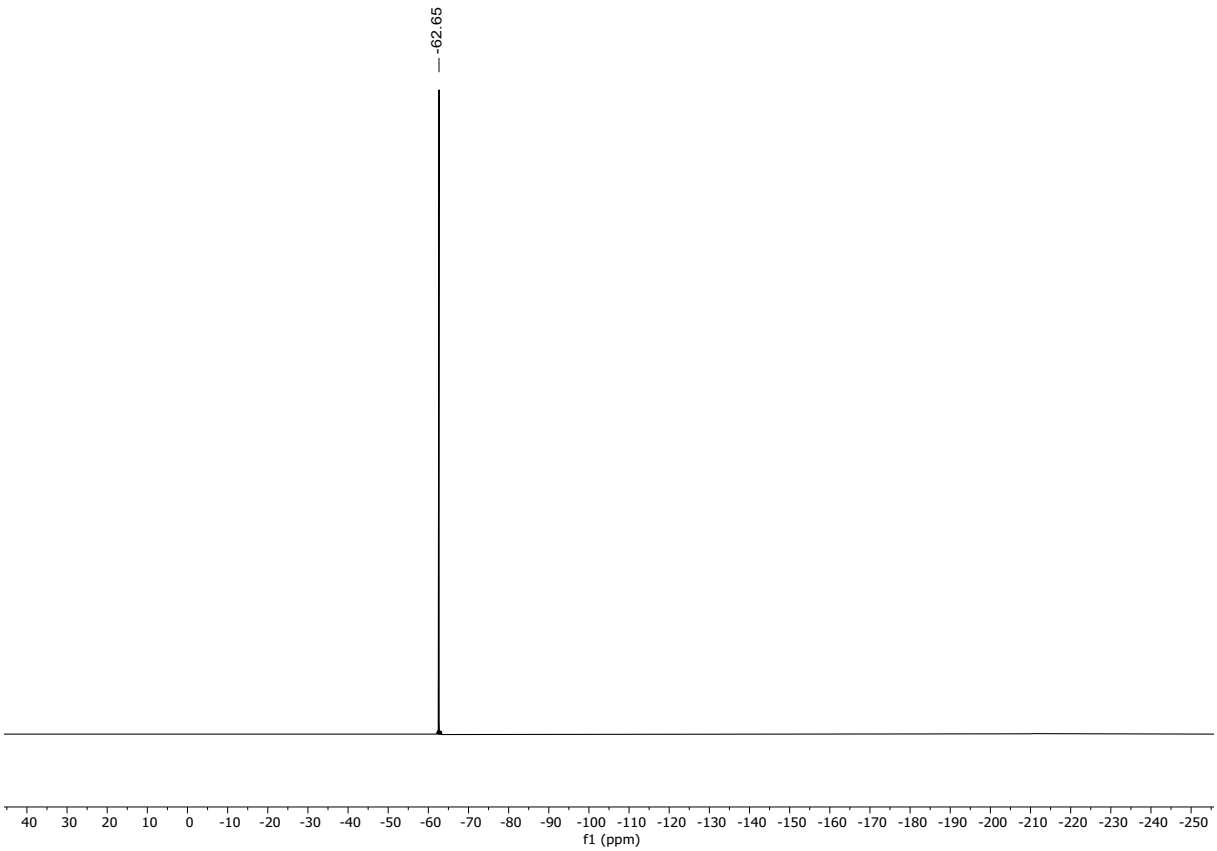


*Figure 87: **^{19}F NMR** (283 MHz, $CDCl_3$) of **ADPP5**.*

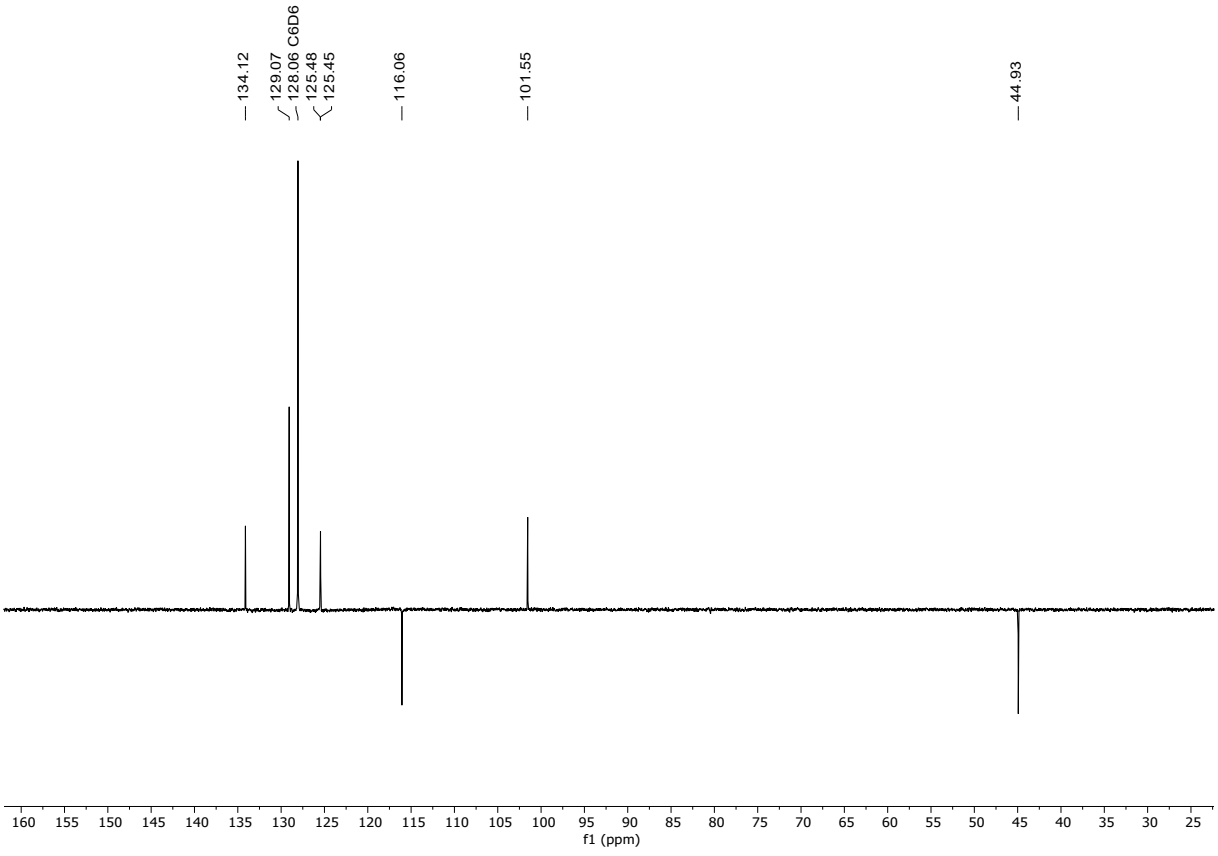


*Figure 88: ^{13}C NMR (151 MHz, C_6D_6) DEPT 135 of **ADPP5.***

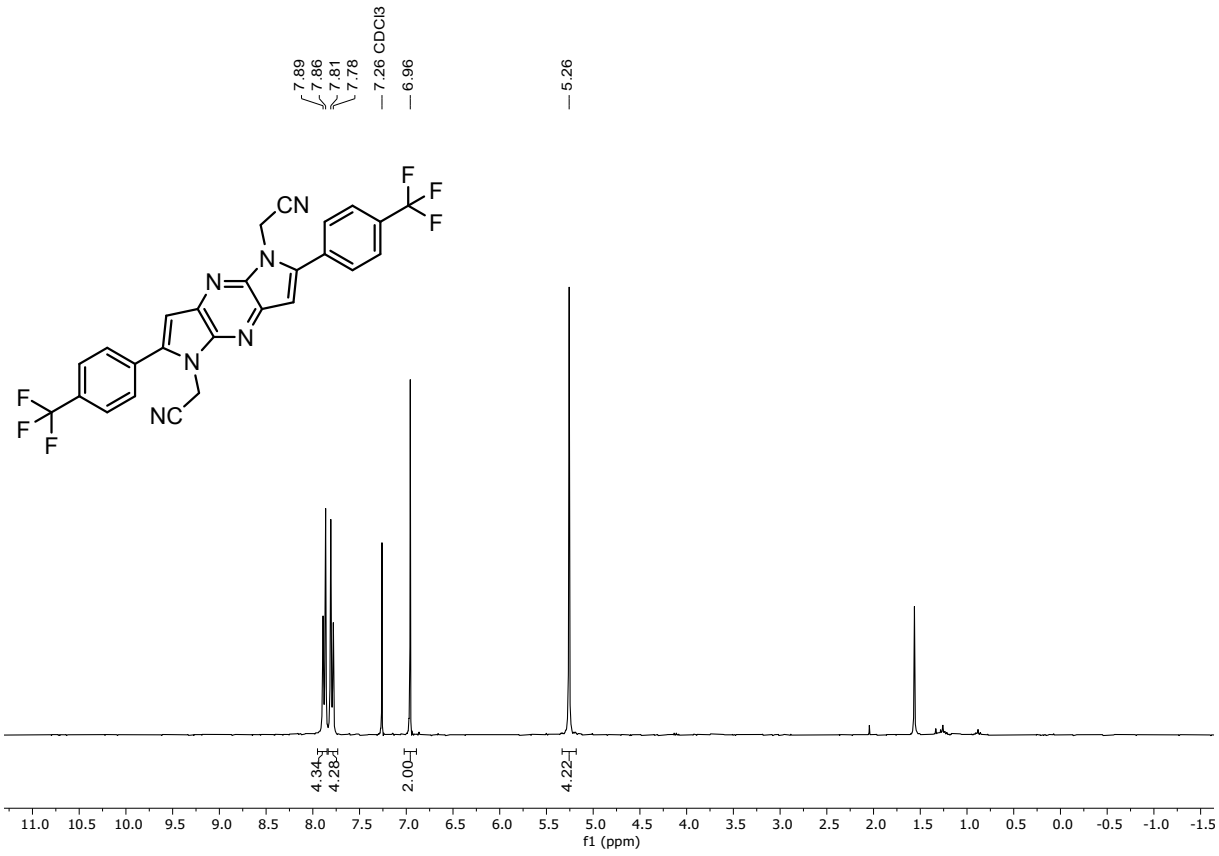


*Figure 89: **^{1}H NMR** (301 MHz, $CDCl_3$) of **ADPP6**.*

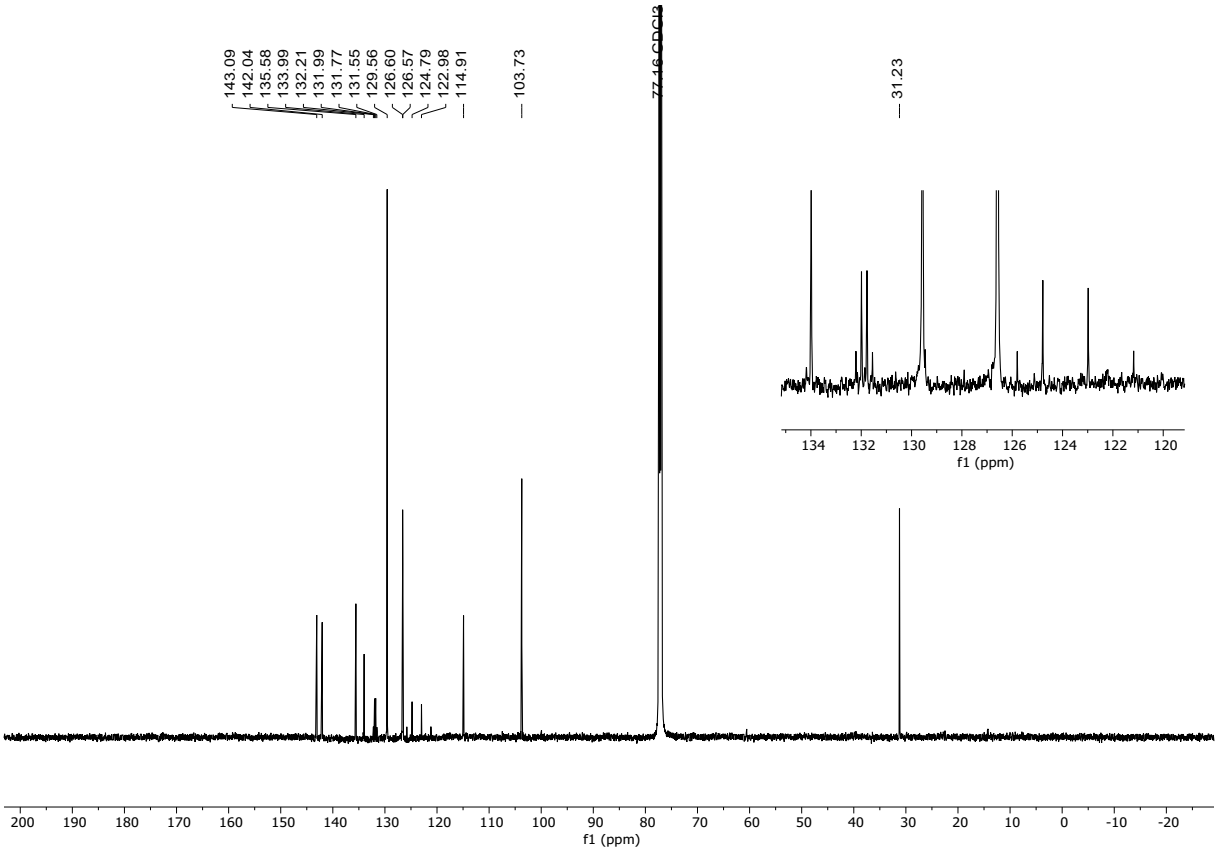


*Figure 90: **^{13}C NMR** (151 MHz, C_6D_6) of **ADPP6.***

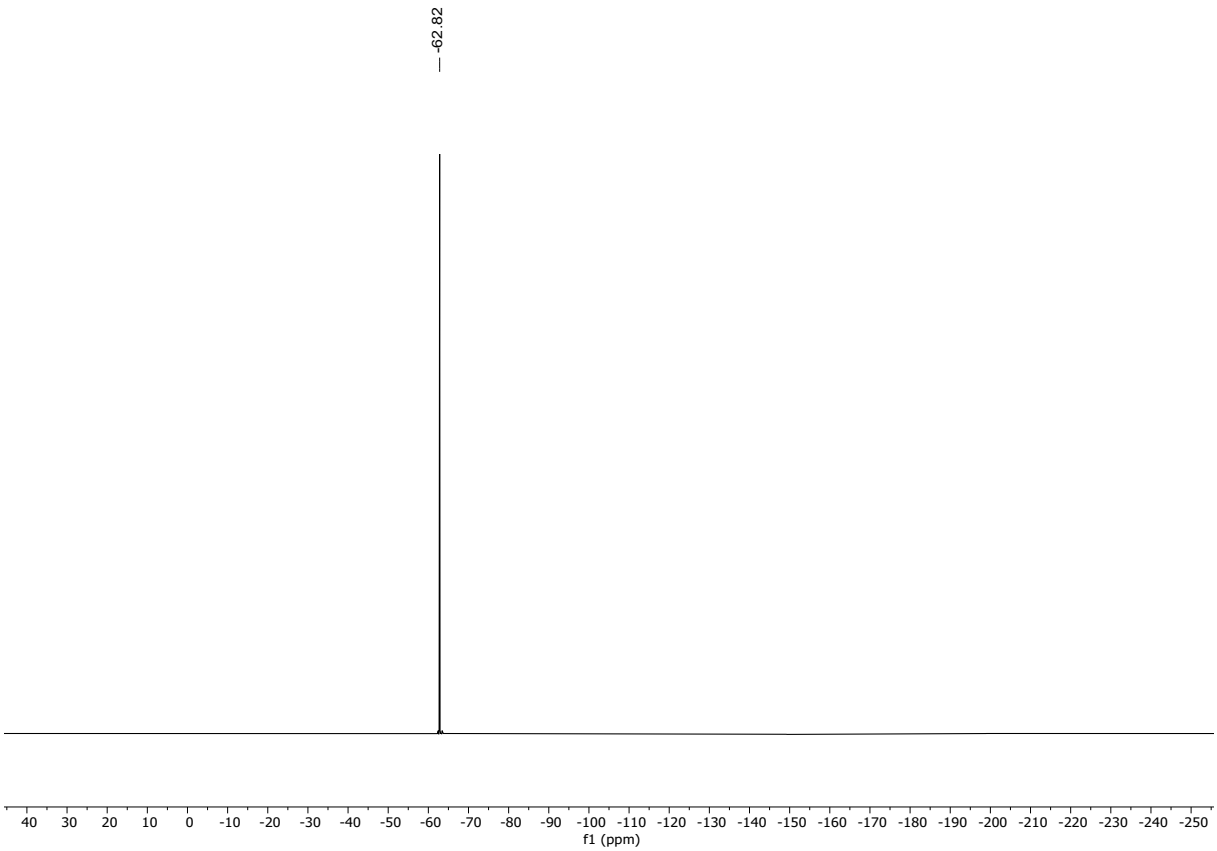


*Figure 91: **^{19}F NMR** (283 MHz, $CDCl_3$) of **ADPP6**.*

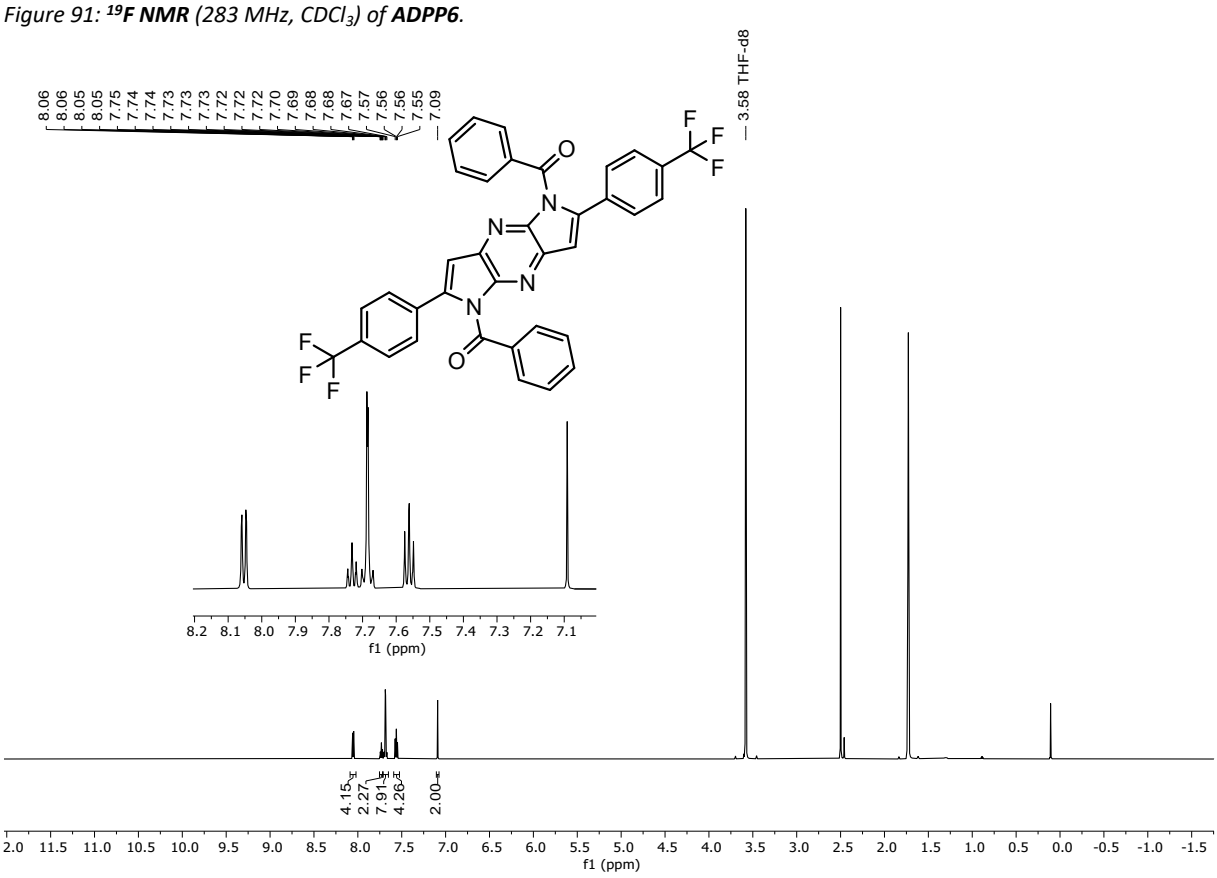


*Figure 92: **^{1}H NMR** (600 MHz, THF) of **ACDPP**.*

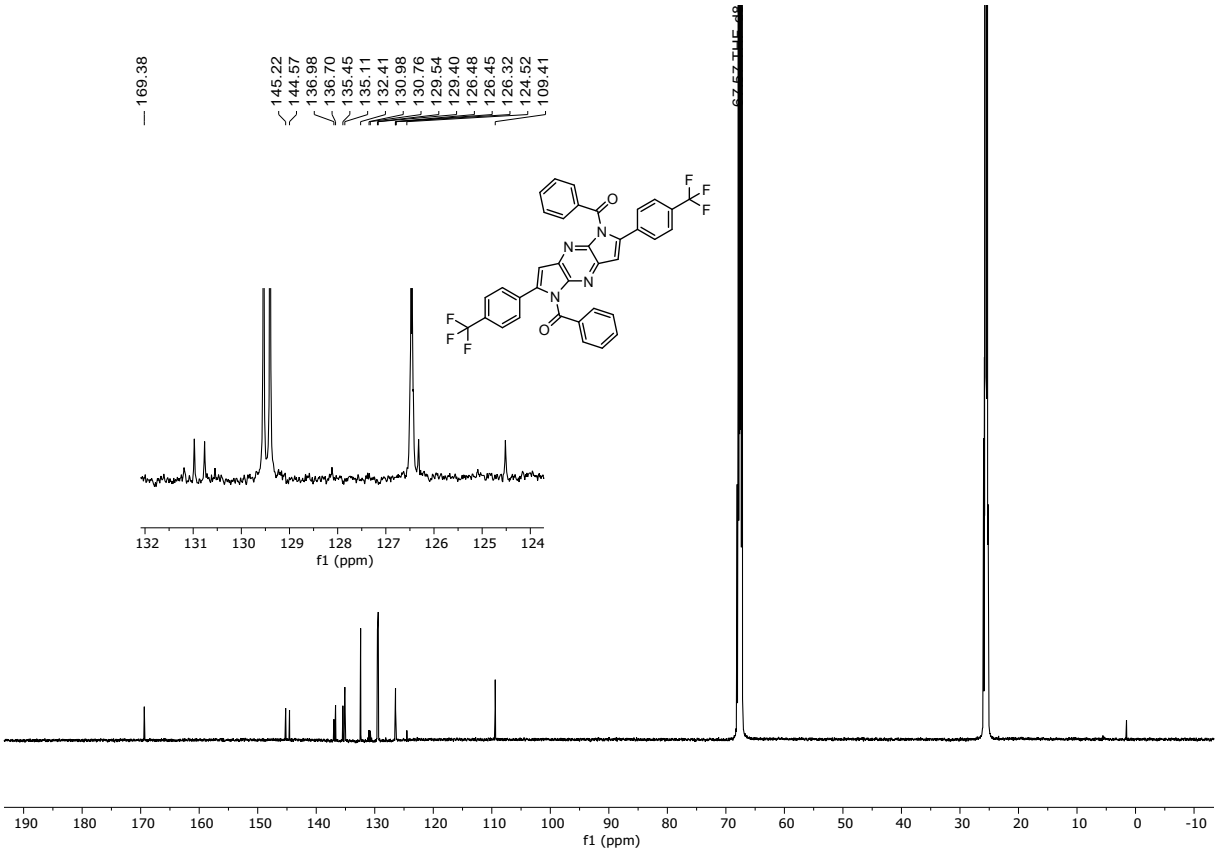


*Figure 93: **^{13}C NMR** (151 MHz, THF) of **ACDPP.***

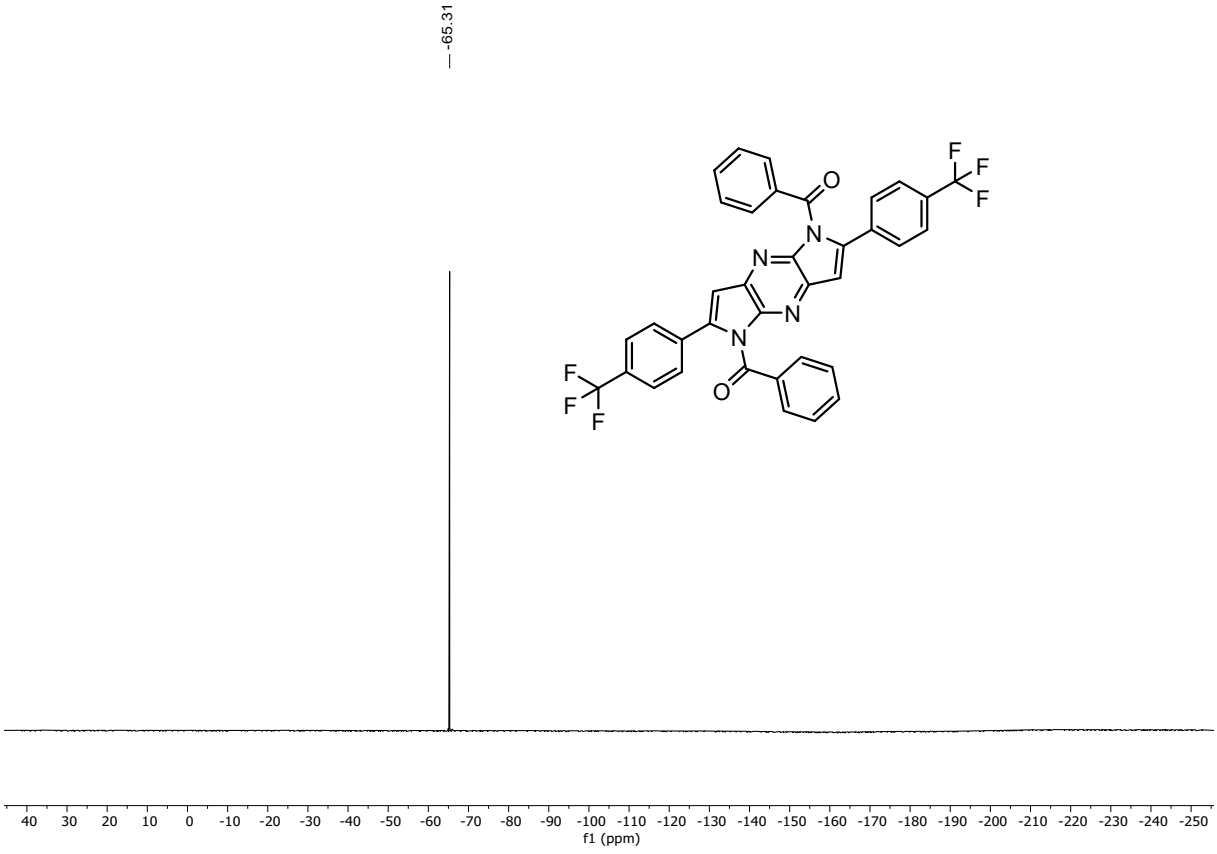


*Figure 94: **^{19}F NMR** (283 MHz, THF) of **ACDPP.***

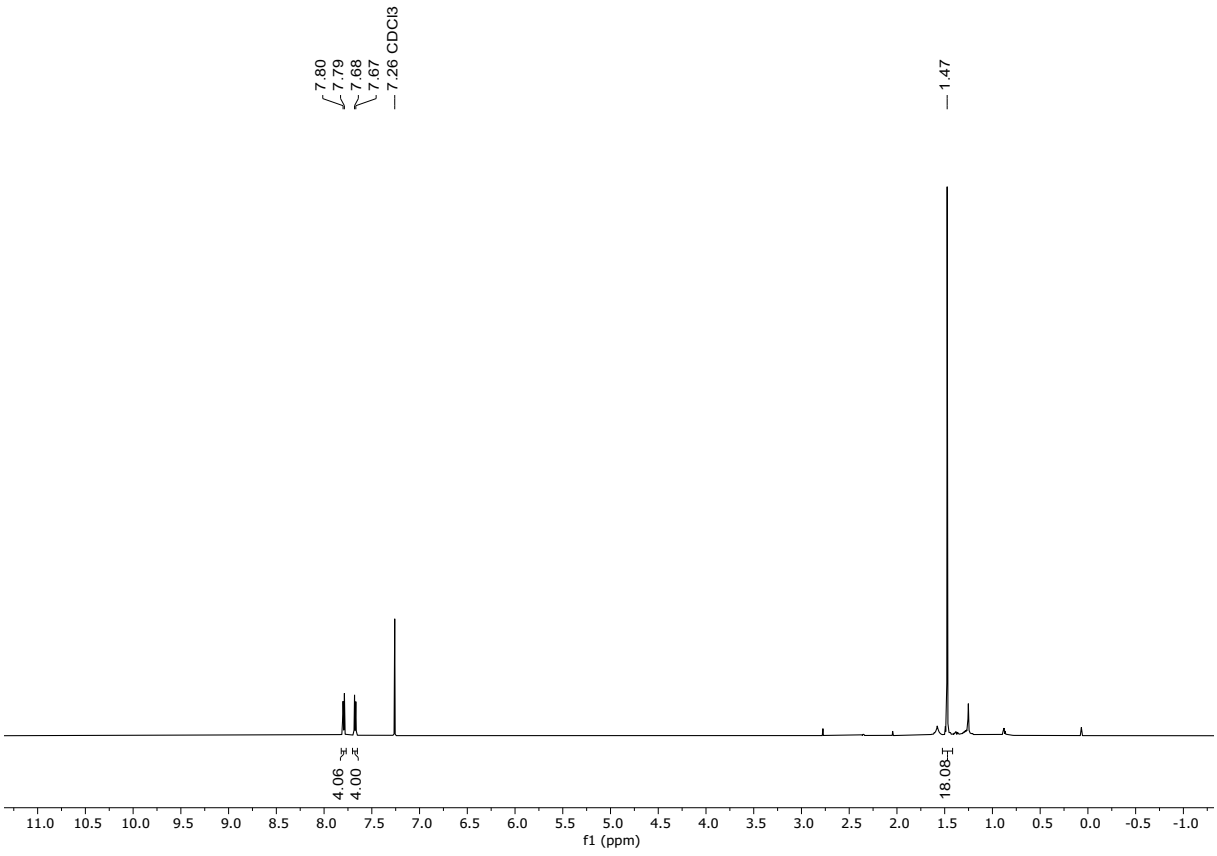


*Figure 95: **$^{1}H\{^{19}F\}$ NMR** (600 MHz, $CDCl_3$)of **BrDPPB.***

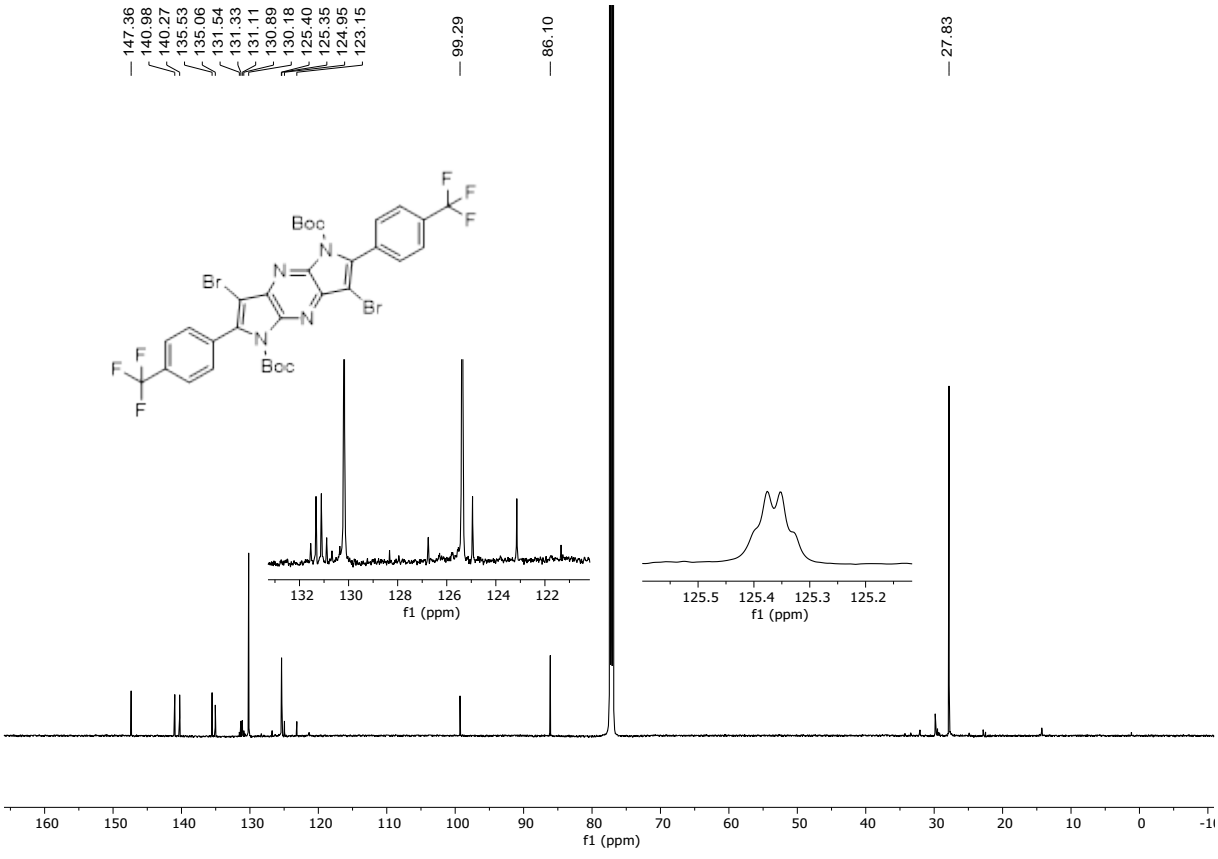


*Figure 96: **$^{13}C\{^{1}H\}$ NMR** (151 MHz, $CDCl_3$) of **BrDPPB**.*

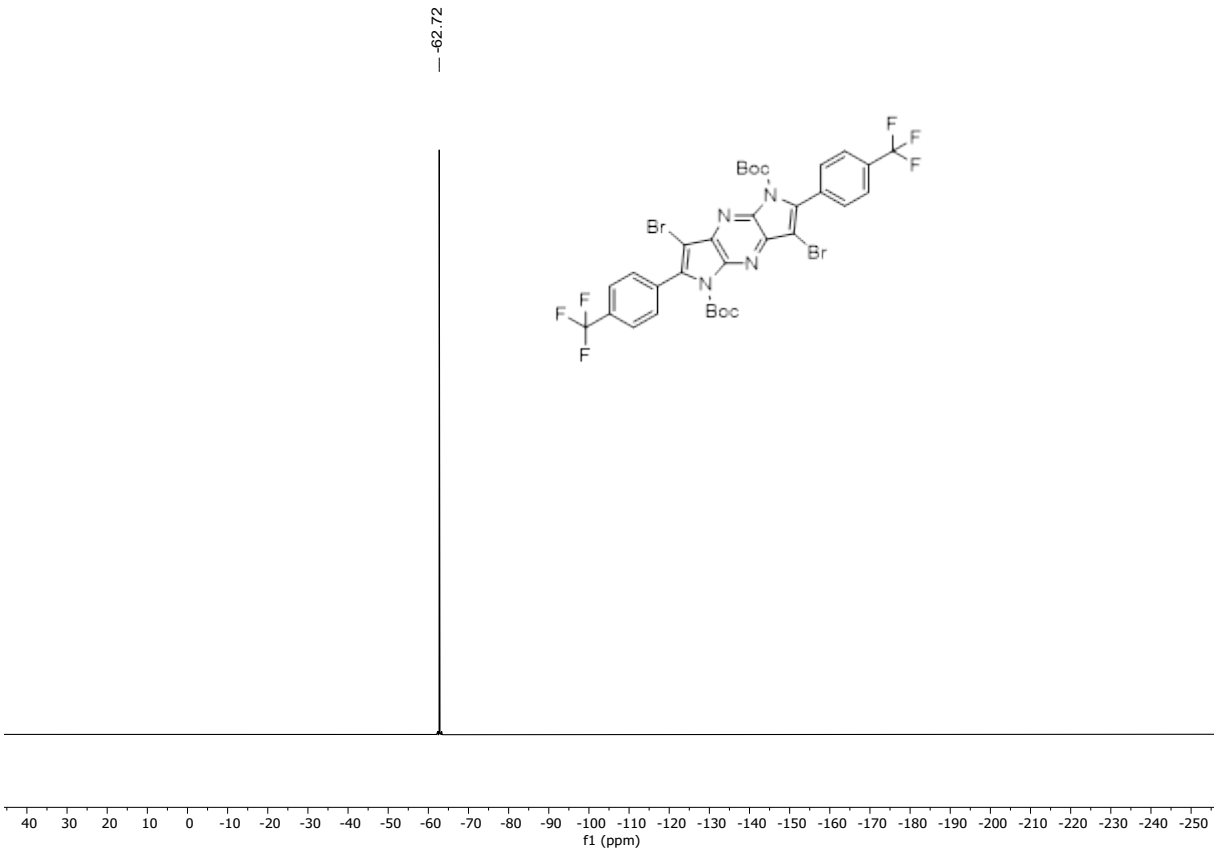
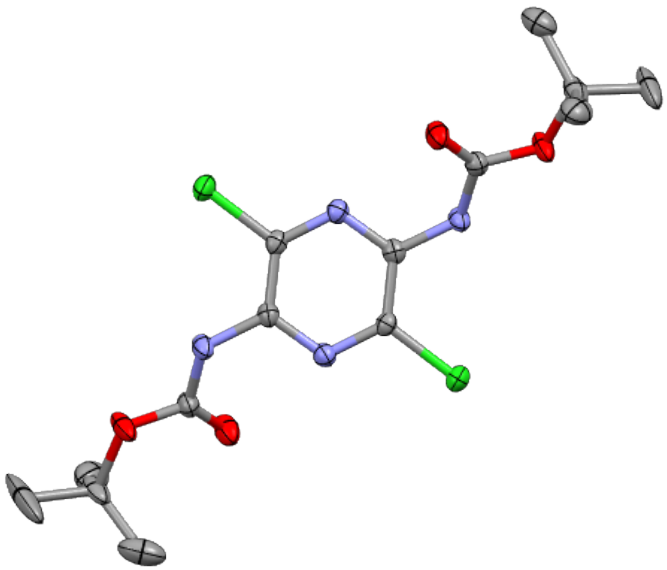


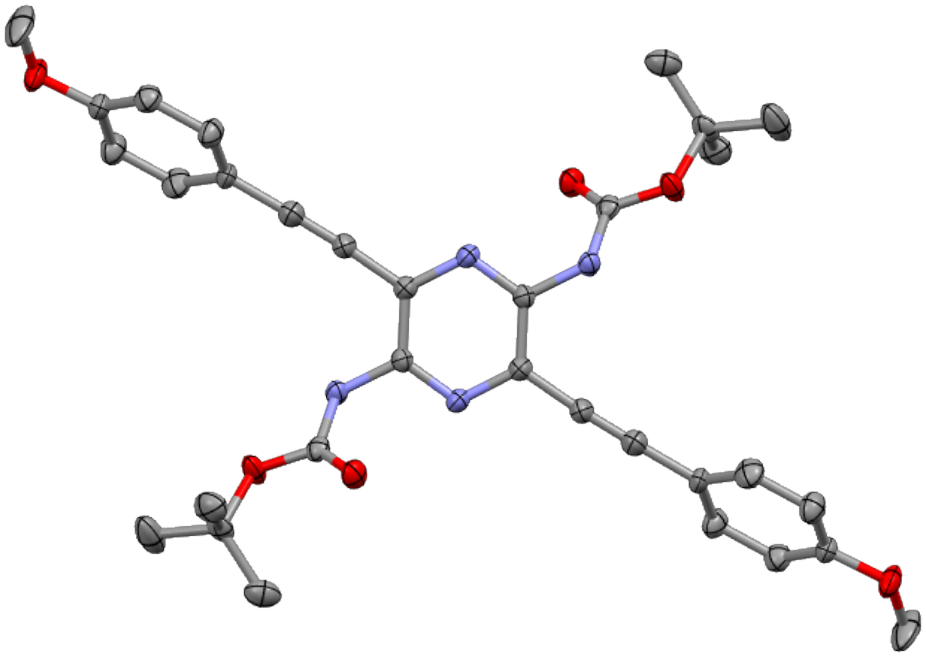
*Figure 97: **$^{1}H\{^{19}F\}$ NMR** (600 MHz, $CDCl_3$) of **BrDPPB**.*

X-Ray Structures

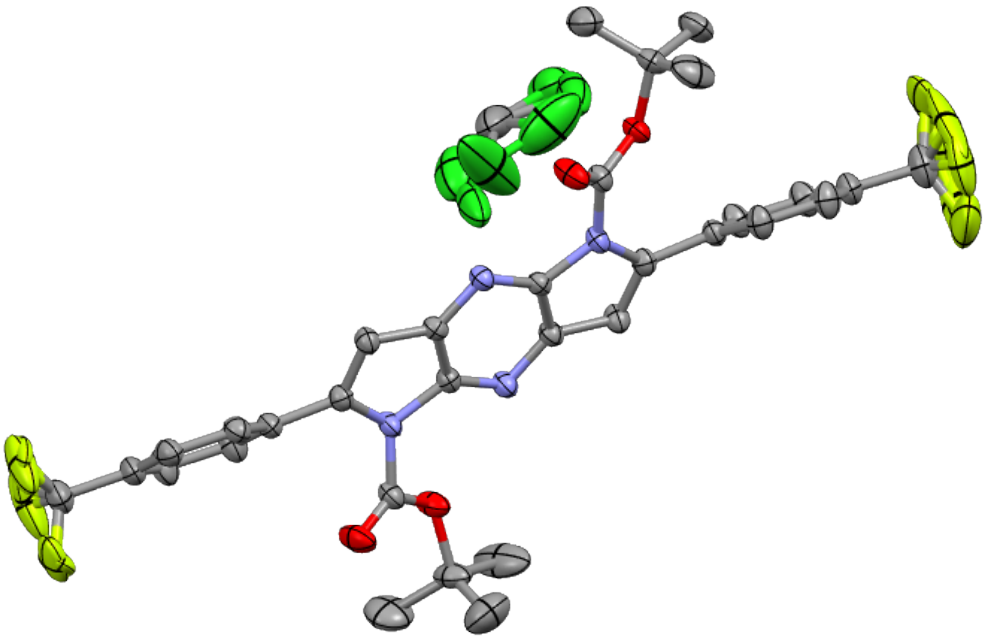
Manuscript number	DBC	
CCDC	2295562	
Empirical formula	$C_{14}H_{20}Cl_2N_4O_4$	
Formula weight	379.24	
Temperature	200(2) K	
Wavelength	1.54178 Å	
Crystal system	monoclinic	
Space group	$P2_1/c$	
Z	4	
Unit cell dimensions	a = 5.1032(2) Å	α =90 deg.
b =	16.1333(4) Å	β = 92.657(3) deg.
c =	21.3655(8) Å	γ = 90 deg.
Volume	1757.16(10) $Å^3$	
Density (calculated)	1.43 g/cm^3	
Absorption coefficient	3.57 mm^{-1}	
Crystal shape	pole	
Crystal size	0.238 x 0.024 x 0.021 mm^3	
Crystal colour	colourless	
Theta range for data collection	5.0 to 64.3 deg.	
Index ranges	-3≤h≤5, -18≤k≤18, -24≤l≤23	
Reflections collected	10481	
Independent reflections	2820 (R(int) = 0.0285)	
Observed reflections	2132 (I > 2σ(I))	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.95 and 0.66	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	2820 / 0 / 231	
Goodness-of-fit on F^2	0.99	
Final R indices (I>2sigma(I))	R1 = 0.033, wR2 = 0.076	
Largest diff. peak and hole	0.25 and -0.24 $eÅ^{-3}$	



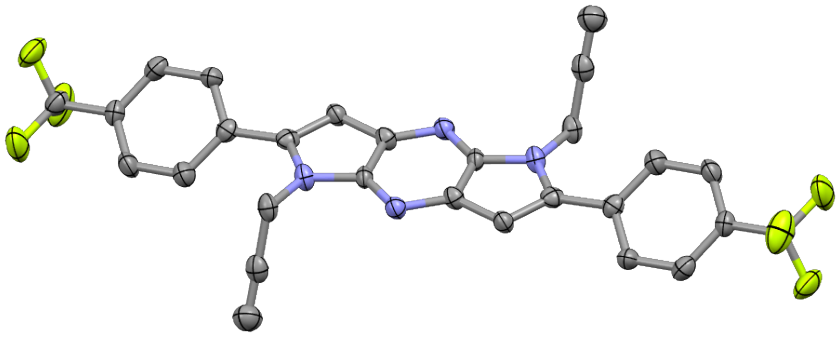
Manuscript number	BA1	
CCDC	2295563	
Empirical formula	$C_{32}H_{34}N_4O_6$	
Formula weight	570.63	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	$P2_1/n$	
Z	2	
Unit cell dimensions	a = 13.620(2) Å	α =90 deg.
	b = 5.1428(8) Å	β =107.679(4) deg.
	c = 22.255(4) Å	γ = 90 deg.
Volume	1485.2(4) $Å^3$	
Density (calculated)	1.28 g/cm^3	
Absorption coefficient	0.09 mm^{-1}	
Crystal shape	plank	
Crystal size	0.200 x 0.037 x 0.012 mm^3	
Crystal colour	yellow	
Theta range for data collection	1.6 to 23.0 deg.	
Index ranges	-14≤h≤14, -5≤k≤5, -24≤l≤24	
Reflections collected	15099	
Independent reflections	2063 (R(int) = 0.1181)	
Observed reflections	1272 (I > 2σ(I))	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.96 and 0.90	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	2063 / 0 / 197	
Goodness-of-fit on F^2	1.05	
Final R indices (I>2sigma(I))	R1 = 0.056, wR2 = 0.100	
Largest diff. peak and hole	0.20 and -0.24 $eÅ^{-3}$	



Manuscript number	DPPB2
CCDC	2295564
Empirical formula	$C_{33}H_{29}Cl_3F_6N_4O_4$
Formula weight	765.95
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Z	2
Unit cell dimensions	a = 10.1680(7) Å α = 89.649(1) deg. b = 10.8563(7) Å β = 77.669(1) deg. c = 18.1982(13) Å γ = 65.299(1) deg.
Volume	1775.1(2) $Å^3$
Density (calculated)	1.43 g/cm^3
Absorption coefficient	0.33 mm^{-1}
Crystal shape	prism
Crystal size	0.126 x 0.077 x 0.055 mm^3
Crystal colour	colourless
Theta range for data collection	2.1 to 25.5 deg.
Index ranges	-12≤h≤12, -13≤k≤13, -21≤l≤22
Reflections collected	28765
Independent reflections	6566 (R(int) = 0.0525)
Observed reflections	4404 (I > 2\s(I))
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.75 and 0.71
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6566 / 0 / 541
Goodness-of-fit on F^2	1.03
Final R indices (I>2σ(I))	R1 = 0.059, wR2 = 0.129
Largest diff. peak and hole	0.82 and -0.69 $eÅ^{-3}$



Manuscript number	ADPP4
Identification code	2312913
Empirical formula	$C_{28}H_{16}F_6N_4$
Formula weight	522.45
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1/c$
Z	2
Unit cell dimensions	a = 13.546(3) Å α =90 deg. b = 11.813(3) Å β =102.679(7) deg. c = 7.2637(17) Å γ = 90 deg.
Volume	1133.9(5) $Å^3$
Density (calculated)	1.53 g/cm^3
Absorption coefficient	0.13 mm^{-1}
Crystal shape	plate
Crystal size	0.090 x 0.038 x 0.012 mm^3
Crystal colour	yellow
Theta range for data collection	1.5 to 27.6 deg.
Index ranges	$-17 \le h \le 17$, $0 \le k \le 15$, $0 \le l \le 9$
Reflections collected	11733
Independent reflections	2497 (R(int) = 0.1071)
Observed reflections	1364 ($I > 2\sigma(I)$)
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.96 and 0.86
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2497 / 0 / 173
Goodness-of-fit on F^2	1.06
Final R indices (I>2sigma(I))	R1 = 0.072, wR2 = 0.118
Largest diff. peak and hole	0.27 and -0.37 $eÅ^{-3}$



TGA-& Stability Measurements

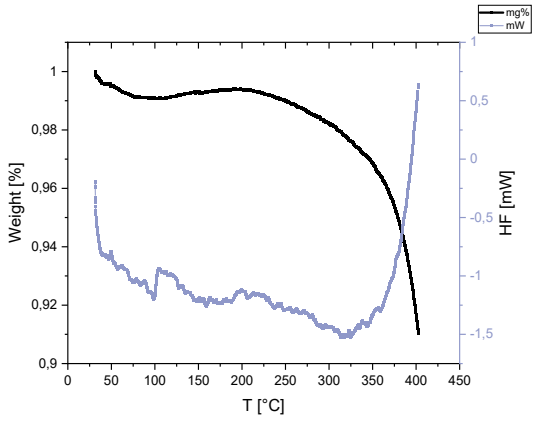


*Figure 98: TGA & DSC Plot of **DPP2.***

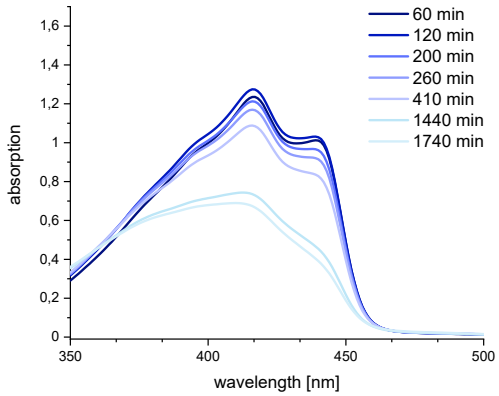


*Figure 99: UV-stability measurement of **DPP2.** Constant irradiation in a distance of 20 cm to the sample with 254 & 365 nm.*

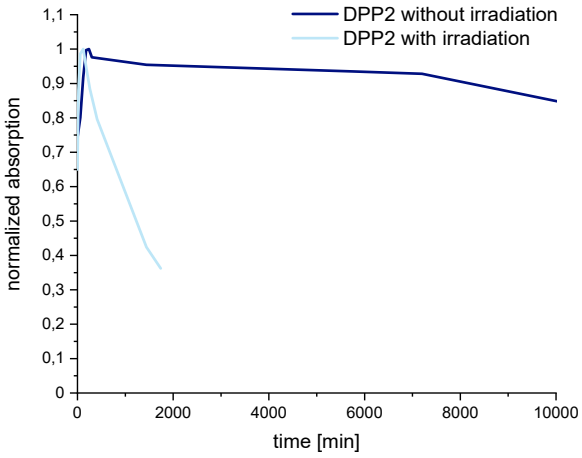


*Figure 100: UV-stability measurement of **DPP2.** Constant irradiation in a distance of 20 cm to the sample with 254 & 365 nm (light blue), ambient measurement without irradiation (dark blue).*

UV/Vis, Fluorescence Characteristics & Spectra

Table 5: Optical properties of synthesised **DPPBs**, **DPPs** & functionalised substrates. **DPPBs**, **ADPPs** and **BrDPPB** were measured in DCM. **ACDPP** & **DPPs** were measured in DMSO. $E_{g(opt)}$ derived from $\Lambda_{onset,abs}$.

Compound	$\lambda_{max,abs}$ [nm]	$\lambda_{max,em}$ [nm]	Stokes Shift [nm] / [cm^{-1}]	$\Lambda_{onset,abs}$ [nm]	$E_{g(opt)}$ [eV]	QY [%]
BA1	409	454	45 /2423	452	2.74	90
BA2	395	452	57 / 3193	447	2.77	49
BA3	399	447	48 / 2691	445	2.78	88
BA4	395	447	53 / 2945	443	2.80	84
BA5	369	417	48 / 3119	419	2.96	49
BA6	410	458	48 / 2556	468	2.65	16
BA7	397	451	54 / 3015	456	2.71	65
BA8	400	451	51 / 2627	460	2.69	93
BA9	385	428	43 /2610	429	2.89	76
DPPB1	380	442	62 / 3691	432	2.87	74
DPPB2	366	423	57 / 3681	412	3.01	46
DPPB3	375	430	55 / 3410	422	2.94	71
DPPB4	370	426	56 / 3552	413	3.00	78
DPPB5	350	402	52 / 3695	387	3.20	34
DPPB7	370	424	54 / 3422	424	2.92	67
DPPB8	368	428	60 / 3809	429	2.89	74
DPPB10	415	514	99 / 4641	477	2.59	85
DPP1	416	462	46 / 2392	460	2.69	85
DPP2	417	455	38 /2002	460	2.69	67
DPP3	415	453	38 / 2021	458	2.71	81
DPP4	415	449	34 / 1825	457	2.71	74
DPP7	415	457	42 / 2214	467	2.65	69
DPP8	415	457	42 / 2214	466	2.66	50
DPP10	458	526	68 / 2822	518	2.39	7
ADPP1	365	456	91 / 5467	452	2.74	43
ADPP2	375	456	71 / 4736	444	2.79	67
ADPP3	377	448	81 / 4203	442	2.80	67
ADPP4	374	454	80 / 4711	447	2.77	63
ADPP5	381	452	71 / 4122	441	2.81	65
ADPP6	376	440	64 / 3868	436	2.84	65
ACDPP	383	450	67 / 3887	431	2.88	37
BrDPPB	368	453	85 / 5099	415	2.99	2

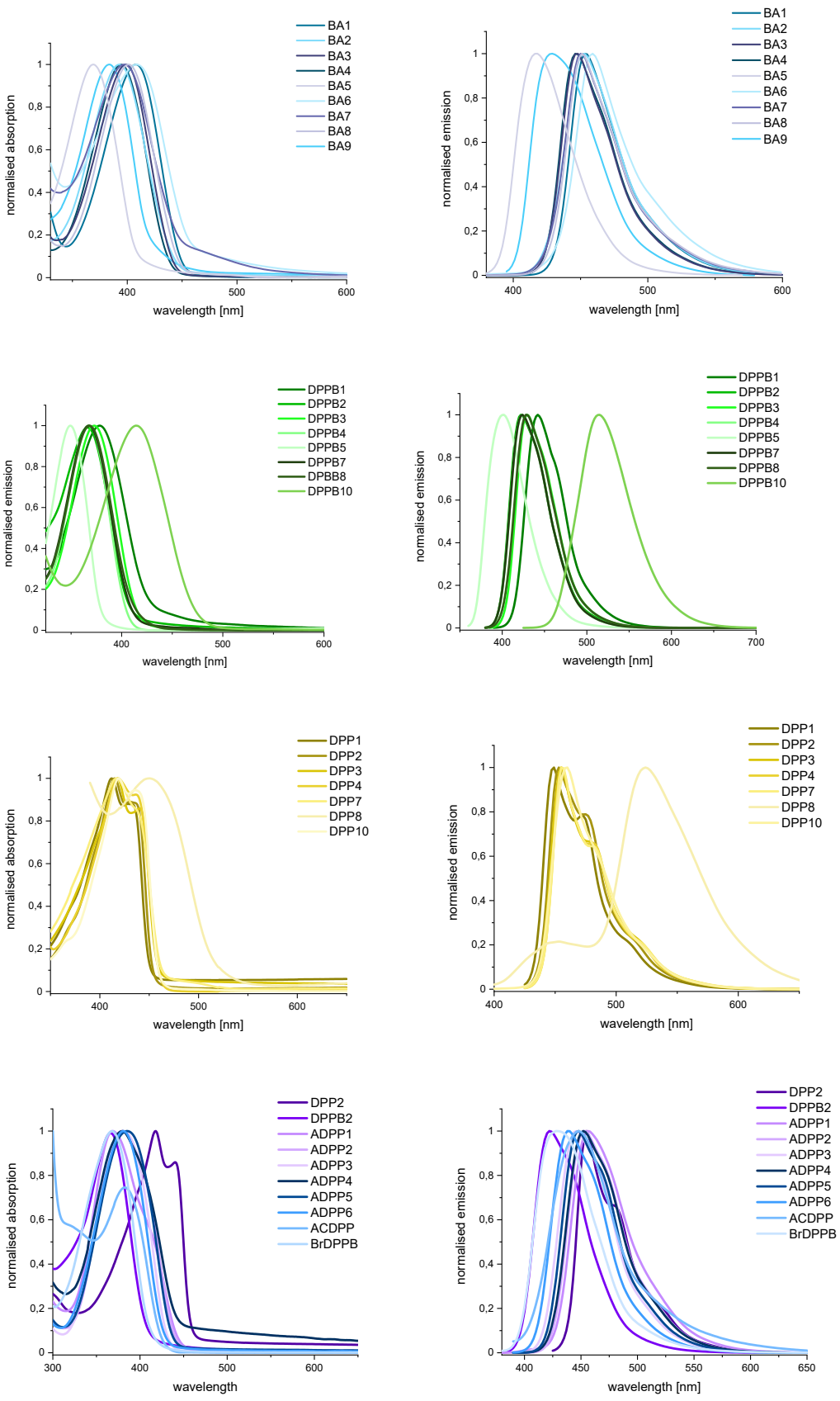


Figure 101: Normalised absorption (left) and normalised emission (right) of all substrates. ***BAs*** *(blue),* ***DPPBs*** *(green),* ***DPPs*** *(yellow) & functionalised derivates (violet).*

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