Supporting Information - Part B
for
Distance measurements between trityl radicals by pulse dressed electron paramagnetic resonance with phase modulation

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Content

Nomenclature and compound numbering

The nomenclature used in this Supporting Information for the rulers and their building blocks is demonstrated with bis-trityl ruler **2** in Figure S1. The 1,4-phenylene, ethynylene, and butadiynylene units are abbreviated with P, E, and B (B = EE), respectively, and trityl represents the trityl moiety. This code only describes the core structural units of the compounds, but does not contain information on the side chains and other substituents. To name a concrete trityl building block, we use "trityl" for the scaffold shown in red in Figure S1 and give the other substituents in brackets.

bis-trityl ruler **2**
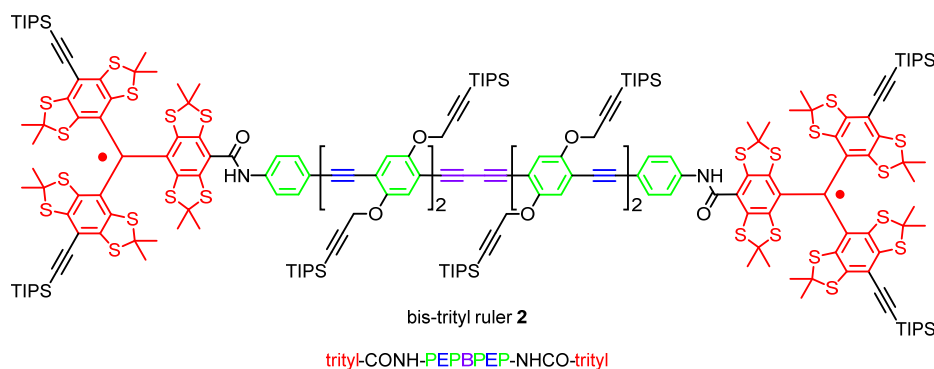
trityl-CONH-PEPBPEP-NHCO-trityl

Figure S1. Illustration of the nomenclature using the example of bis-trityl ruler **2**.

Scheme 1 in the main text provides most of the compound numbers used. The additional compound number **9** belongs to the alkyne dimer shown in Figure S2.
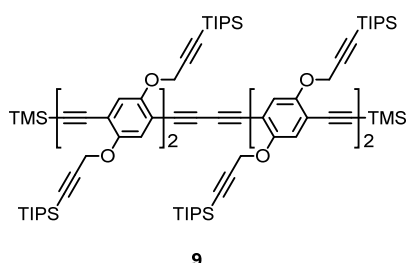

9

Figure S2. Alkyne dimer **9** isolated after Sonogashira-Hagihara coupling using TMS-(EP)$_2$E-H **3b**.

General

Unless otherwise stated, reactions were performed in dried glassware under argon. Argon was passed through anhydrous $CaCl_2$ prior to its use. Degassed solutions were prepared through applying three freeze-pump-thaw cycles. Solvents were removed at a bath temperature of $\sim$ 40 °C and reduced pressure. The products were dried at room temperature at $\sim$ 0.1 mbar.

Unless otherwise stated, commercially available solvents and reagents were used. Since all of these compounds which were used for syntheses had a purity of >98% their molar amounts used in the syntheses were calculated with the compound mass and were not corrected by the manufacturer specified purities. Source, purity, and batch number of the reagents can be found in Table S1. THF (HPLC grade) was dried with sodium/benzophenone prior to its use. For the preparation of aqueous solutions, deionized water was used. Solvents used for extraction and chromatography were of technical grade and were distilled prior to their use. $PdCl_2(PPh_3)_2$ was synthesized according to literature (Heck, 1985), however using 2.1 times the given amount of methanol. The syntheses of trityl[CO_2H/CCTIPS/CCTIPS] **7** (Hintz et al., 2019), TMS-(EP)$_2$E-H **3b** (Qi et al., 2016), and TMS-(EP)$_2$-NH$_2$ **4a** (Ritsch et al., 2019) have been reported elsewhere. Column chromatography was carried out on silica gel 60 (0.035−0.070 mm) without applying pressure. In the procedures reported below, the size of the column is given as diameter x length. The material was loaded onto the column dissolved in a small quantity of the eluent. Thin layer chromatography (TLC) was performed on silica gel 60 containing fluorescent indicator F254. The solid support for the silica gel layer was aluminum foil. The spots were detected with UV light of λ = 254 nm and 366 nm. The compositions of solvent mixtures are given in volume ratios.

NMR spectra were calibrated using the solvent signal as an internal standard [$CDCl_3$: δ (^{1}H) = 7.25, δ (^{13}C) = 77.0; CD_2Cl_2: δ (^{1}H) = 5.32, δ (^{13}C) = 53.8. Signal assignment is supported by DEPT-135, COSY, HMBC, and HMQC experiments.

ESI-MS spectra were recorded from samples dissolved in acetonitrile using an Esquire 3000 ion trap mass spectrometer (Bruker Daltonik) equipped with a standard ESI source. Accurate mass spectrometric measurement of **6b** was performed using a Q-IMS-TOF mass spectrometer Synapt G2Si (Waters, Manchester, UK) in resolution mode, interfaced

to a nano-ESI ion source. Nitrogen served as the nebulizer gas and the dry gas for nano-ESI. Nitrogen was generated by a nitrogen generator NGM 11. Helium 5.0 was used as buffer gas in the IMS entry cell, nitrogen 5.0 was used for IMS. ESI samples were introduced by static nano-ESI using in-house pulled glass emitters. Accurate MS measurements of bis-trityl rulers **1** and **2** were performed using a Bruker solariX MALDI-FTICR-MS mass spectrometer. Samples were mixed with a 10:1 mixture of *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) and dichloromethane. The monoisotopic mass of the compounds is reported.

Table S1. Source, purity, and batch number of commercially available compounds used for reactions.

compound	manufacturer	purity [%]	batch number
Chloroform, dry, over molecular sieve	Acros	99.9	1851540
Dichloromethane	VWR	99.9	15D300512
Diisopropylethylamine, dry, over molecular sieve	Merck	≥ 98	S7323294644
4-Iodoaniline	Acros	99	A0340759
2-Methylbut-3-yn-2-ol	Aldrich	98	1349654 53307311
Methanol	VWR	100.0	17G054004
Piperidine	Alfa Aesar	99	17181722
Potassium carbonate	VWR	100.6	07E020030
Thionyl chloride	Merck	≥ 99.0	S7454854804
Triphenylphosphane	Merck	≥ 99	S5329270917

Synthesis of trityl-CONH-PEPBPEP-NHCO-trityl 1 (bis-trityl ruler 1)

H-(EP)₂-NH₂ 5a. The reaction was performed under argon but without drying the glassware. To a solution of a 85:15 mixture (100 mg) of TMS-(EP)₂-NH₂ **4a** (138 µmol) and Et₂O (24 µmol) in MeOH (6 mL) and CH₂Cl₂ (6 mL) was added K₂CO₃ (29 mg, 0.21 mmol). The suspension consisting of a yellow solution and a colorless solid was stirred at room temperature for 14.5 h. Et₂O (40 mL) and H₂O (10 mL) were added. The organic phase was separated, and the aqueous phase was extracted with Et₂O (2 x 10 mL). The combined organic phases were dried over MgSO₄ · x H₂O and filtered. The solvents were removed. The components of the residual brown oil were separated by column chromatography (3 cm x 15 cm). Elution with pentane/Et₂O 1:1 gave H-(EP)₂-NH₂ **5a** (85 mg, 96%; R_f = 0.31) as a yellow oil. For ^{1}H NMR data see Table S2. For ^{13}C NMR data see Tables S3 and S4. MS (ESI): m/z = 638.5 [M + H]⁺, 660.5 [M + Na]⁺.

H₂N-PEPBPEP-NH₂ 6a. The reaction was performed in air. To a solution of H-(EP)₂-NH₂ **5a** (91 mg, 0.14 mmol) in dry THF (6 mL) and piperidine (706 µL, 7.13 mmol) were added PdCl₂(PPh₃)₂ (4.24 mg, 6.03 µmol) and CuI (4.13 mg, 21.7 µmol). The green solution was stirred at room temperature for 16 h. All volatiles were evaporated. The residual green oil was dissolved in Et₂O (30 mL). The organic phase was washed with a 0.1 M aqueous solution of Na₂H₂EDTA (3 x 10 mL). The combined aqueous phases were extracted with Et₂O (10 mL). The combined organic phases were washed with H₂O (10 mL), dried over MgSO₄ · x H₂O, and filtered. The solvents were removed. The components of the residual brown solid were separated by column chromatography (2 cm x 41 cm). Eluting with Et₂O/pentane 4:1 gave a mixture of unidentified compounds (10 mg; R_f = 0.57, 0.49) as a yellow solid and H₂N-PEPBPEP-NH₂ **6a** (33 mg, 36%; R_f = 0.37) as an orange solid. For ^{1}H NMR data see Table S2. For ^{13}C NMR data see Tables S3 and S4. MS (ESI): m/z = 1273.9 [M + H]⁺, 1295.9 [M + Na]⁺.

Trityl-CONH-PEPBPEP-NHCO-trityl 1 (bis-trityl ruler 1). For the preparation of trityl[COCl/CCTIPS/CCTIPS] **8** the procedure of Shevelev et al. (2014) was followed with making modifications. To a solution of trityl[CO₂H/CCTIPS/CCTIPS] **7** (50 mg, 39 µmol) in dry CHCl₃ (5 mL) was added thionyl chloride (85.4 µL, 1.18 mmol). The red solution was stirred at 50 °C for 90 min. After cooling down to room temperature all volatiles were

evaporated from the dark red solution. The residual dark red solid was dissolved in $CHCl_3$ (4 mL). To this dark red solution cooled with an ice-water bath was added a solution of H_2N-PEPBPEP-NH_2 **6a** (20 mg, 16 µmol) in $CHCl_3$ (6 mL) and $^iPr_2NEt$ (10.7 µL, 62.7 µmol). After 5 min the ice-water bath was removed and the red/brown solution was stirred for 17 h at room temperature. The brown solution was filtered through silica gel (1 cm x 2 cm, rinsing with Et_2O). The resulting solution (20 mL) was diluted with Et_2O (30 mL), washed with 2 M aqueous solution of NaOH (10 mL), 2 M aqueous solution of HCl (10 mL) and H_2O (10 mL), dried over $MgSO_4 \cdot x\ H_2O$, and filtered. The solvents were removed. The components of the residual brown solid were separated by column chromatography (3 cm x 45 cm). Elution with pentane/Et_2O 3:2 gave a mixture (12 mg; R_f = 0.73, 0.00) of unidentified compounds as a brown solid, a mixture (6 mg; R_f = 0.73, 0.58) of trityl-CONH-PEPBPEP-NHCO-trityl **1** and unidentified compounds as a green/brown solid, and trityl-CONH-PEPBPEP-NHCO-trityl **1** (bis-trityl ruler **1**; 24 mg after freeze-drying with benzene, 40%; R_f = 0.58) as a green solid. For ^1H NMR data see Table S2. Accurate MS (MALDI): m/z calcd for $[M + H]^+$, $C_{200}H_{263}N_2O_6S_{24}Si_8{}^+$, 3780.1787; found, 3780.1884.

Synthesis of trityl-CONH-P(EP)₂B(PE)₂P-NHCO-trityl 2 (bis-trityl ruler 2)

TMS-(EP)₃-NH₂ 4b. To a degassed solution of TMS-(EP)$_2$E-H **3b** (200 mg, 175 µmol) and 4-iodoaniline (42 mg, 0.19 mmol) in dry THF (7 mL) and piperidine (0.87 mL, 8.8 mmol) were added $PdCl_2(PPh_3)_2$ (2.51 mg, 3.58 µmol) and CuI (1.29 mg, 6.77 µmol). The orange solution was stirred at room temperature for 46 h. Then, 2-methylbut-3-yn-2-ol (9 µL, 90 µmol) was added and the suspension was stirred for 24 h. All volatiles were evaporated. The residual viscous brown liquid was filtered through silica gel (2 cm x 3 cm, rinsing with Et_2O). The solvents were removed. The components of the residual brown oil were separated by column chromatography (3 cm x 31 cm). Eluting with pentane/Et_2O 3:1 gave as a first fraction a mixture (19 mg; R_f (pentane/Et_2O 3:1) = 0.77; R_f (pentane/Et_2O 1:1) = 0.80) of alkyne dimer **9**, grease, and a small amount of unidentified compounds as yellow solid. As the second fraction a mixture (8 mg; R_f (pentane/Et_2O 3:1) = 0.43; R_f (pentane/Et_2O 1:1) = 0.74) of unidentified compounds, Et_2O, and grease was obtained as

a yellow oil. As the third fraction a mixture (16 mg; R_f (pentane/Et$_2$O 3:1) = 0.09; R_f (pentane/Et$_2$O 1:1) = 0.34) of unidentified compounds, Et$_2$O, and pentane was obtained as a yellow oil. The eluent was changed to pentane/Et$_2$O 1:1 and TMS-(EP)$_3$-NH$_2$ **4b** (186 mg, 86%; R_f (pentane/Et$_2$O 3:1) = 0.09; R_f (pentane/Et$_2$O 1:1) = 0.34) was obtained as a yellow solid. For ^{1}H NMR data of TMS-(EP)$_3$-NH$_2$ **5b** and alkyne dimer **9** see Table S2. For ^{13}C NMR data of TMS-(EP)$_3$-NH$_2$ **5b** see Tables S3 and S4. MS (ESI) of TMS-(EP)$_3$-NH$_2$ **5b**: m/z = 1230.6 [M + H]$^+$, 1252.6 [M + Na]$^+$.

H-(EP)$_3$-NH$_2$ 5b. The reaction was performed under argon but without drying the glassware. To a solution of TMS-(EP)$_3$-NH$_2$ **4b** (150 mg, 122 µmol) in MeOH (6 mL) and CH$_2$Cl$_2$ (6 mL) was added K$_2$CO$_3$ (25 mg, 0.18 mmol). The suspension consisting of a yellow solution and a colorless solid was stirred at room temperature for 14.5 h. Et$_2$O (40 mL) and H$_2$O (10 mL) were added**.** The organic phase was separated, and the aqueous phase was extracted with Et$_2$O (2 x 10 mL). The combined organic phases were dried over MgSO$_4$ · x H$_2$O and filtered. The solvents were removed. The components of the residual orange solid were separated by column chromatography (3 cm x 14 cm). Elution with pentane/Et$_2$O 1:1 gave H-(EP)$_3$-NH$_2$ **5b** (135 mg, 96%; R_f = 0.51) as a yellow solid. For ^{1}H NMR data see Table S2. For ^{13}C NMR data see Tables S3 and S4. MS (ESI): m/z = 1158.8 [M + H]$^+$, 1180.8 [M + Na]$^+$.

H$_2$N-P(EP)$_2$B(PE)$_2$P-NH$_2$ 6b. The reaction was performed in air. To a solution of H-(EP)$_3$-NH$_2$ **5b** (133 mg, 115 µmol) in dry THF (6 mL) and piperidine (568 µL, 5.74 mmol) were added PdCl$_2$(PPh$_3$)$_2$ (3.53 mg, 5.04 µmol) and CuI (1.64 mg, 8.59 µmol). The green solution was stirred at room temperature for 15.5 h. All volatiles were evaporated. The residual green oil was dissolved in Et$_2$O (30 mL). The organic phase was washed with a 0.1 M aqueous solution of Na$_2$H$_2$EDTA (3 x 10 mL). The combined aqueous phases were extracted with Et$_2$O (10 mL). The combined organic phases were washed with H$_2$O (10 mL), dried over MgSO$_4$ · x H$_2$O, and filtered. The solvents were removed. The components of the residual orange solid were separated by column chromatography (2 cm x 46 cm). Eluting with Et$_2$O/pentane 4:1 gave a mixture (10 mg; R_f = 0.71, 0.43) of unidentified compounds and a small amount of H$_2$N-P(EP)$_2$B(PE)$_2$P-NH$_2$ **6b** as a yellow solid. Then, H$_2$N-P(EP)$_2$B(PE)$_2$P-NH$_2$ **6b** (87 mg, 65%; R_f = 0.43) was obtained as yellow solid. For ^{1}H NMR data see Table S2. For ^{13}C NMR data see Tables S3 and S4. Accurate

MS (ESI): m/z calcd for $[M + H + Na]^{2+}$, $C_{144}H_{205}N_2NaO_8Si_8^{2+}$, 1168.6868; found, 1168.6870.

Trityl-CONH-P(EP)₂B(PE)₂P-NHCO-trityl 2 (bis-trityl ruler 2). For the preparation of trityl[CO₂Cl/CCTIPS/CCTIPS] **8** the procedure of Shevelev et al. (2014) was followed with making modifications. To a solution of trityl[CO₂H/CCTIPS/CCTIPS] **7** (28 mg, 22 μmol) in dry CHCl₃ (5 mL) was added thionyl chloride (47.0 μL, 684 μmol). The red solution was stirred at 50 °C for 90 min. After cooling down to room temperature all volatiles were evaporated. The residual red/brown solid was dissolved in CHCl₃ (5 mL). To this dark red solution cooled with an ice-water bath was added a solution of H₂N-P(EP)₂B(PE)₂P-NH₂ **6b** (20 mg, 8.6 μmol) in CHCl₃ (5 mL) and ^{i}Pr₂NEt (5.9 μL, 34.7 μmol). After 10 min the ice-water bath was removed, and the red solution was stirred for 19 h at room temperature. The brown solution containing a small amount of colorless solid was diluted with Et₂O (30 mL), washed with a 2 M aqueous solution of HCl (10 mL) and H₂O (10 mL), dried over MgSO₄ · x H₂O, and filtered. The filtrate was filtered through silica gel (2 cm x 3 cm, rinsing with Et₂O). The solvents were removed. The components of the residual green solid were separated by column chromatography (3 cm x 45 cm). Elution with pentane/Et₂O 7:3 gave a mixture (5 mg; R_f = 0.88) of unidentified compounds as a brown solid, trityl-CONH-P(EP)₂B(PE)₂P-NHCO-trityl **2** (bis-trityl ruler **2**; 24 mg after freeze-drying with benzene, 58%; R_f = 0.66) as a green solid, and a 63:29:8 mixture (4 mg, R_f = 0.66) of pentane, Et₂O, and trityl-CONH-P(EP)₂B(PE)₂P-NHCO-trityl **2** (8% yield) as a green/brown solid. For ^{1}H NMR data see Table S2. Accurate MS (MALDI): m/z calcd for $[M + ^iPrOH + H]^+$, $C_{267}H_{367}N_2O_{11}S_{24}Si_{12}^+$, 4880.8748; found, 4880.8712.

Influence of the trityl radical moiety on the NMR spectra

Because it is paramagnetic, the trityl radical moiety takes a distance dependent influence on the NMR signals of the compounds. In Figure S3 a cutout of the bis-trityl rulers **1** and **2** is shown. The signals of the hydrogen atoms in the area marked with red are not found in the ¹H NMR spectra. The signals of hydrogen atoms in the green highlighted area are observed and are sometimes broadened.
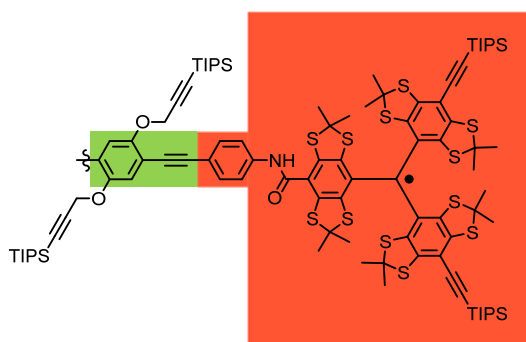

Figure S3. Cutout of the bis-trityl rulers **1** and **2**. Hydrogen atoms, whose NMR signals are affected by the unpaired electron spin, are marked with colors.

NMR data

Table S2. ^{1}H NMR (500 MHz) data.

compound, solvent	H_{benz} ortho to NH_2	H_{benz} ortho to OCH_2	H_{benz} meta to NH_2	$C_{benz}OCH_2$	NH_2	C≡CH	SiCHMe$_2$	SiMe$_3$
1 CD$_2$Cl$_2$	---	7.31 (s, 2H), 7.21 (br s, 2H)	---	4.85, 4.84, both s with large overlap, together 8H	---	---	1.08 (s, 42H), 1.06 (s, 42H)	---
2 CD$_2$Cl$_2$	---	7.32 (s, 2H), 7.29 (br s, 2H), 7.25 (s) overlapping with 7.23 (br s) together 4H	---	4.87, 4.86, 4.84, all s with large overlap, together 16H	---	---	1.07, 1.06, both s with large overlap, together 168H	---
4b CD$_2$Cl$_2$	7.31 (AA'XX' spin system, 2H)	7.29 (s, 1H), 7.26 (s, 1H), 7.19 (s, 1H), 7.17 (s, 1H)	6.65 (AA'XX' spin system, 2H)	4.85 (s, 2H), 4.84 (s, 2H), 4.81 (s, 2H), 4.78 (s, 2H)	3.95 (s, 2H)	---	1.063, 1.062, 1.058, all s with large overlap, together 84H	0.26 (s, 9H)
5a CD$_2$Cl$_2$	7.31 (AA'XX' spin system, 2H)	7.25 (s, 1H), 7.21 (s, 1H)	6.64 (AA'XX' spin system, 2H)	4.80 (s, 2H), 4.79 (s, 2H)	3.95, 3.93, both s with large overlap, together 1.7H$^\#$	3.38 (s, 1H)	1.066 (s, 21H), 1.065 (s, 21H)	---
5b CD$_2$Cl$_2$	7.32 (AA'XX' spin system, 2H)	7.30 (s, 1H), 7.29 (s, 1H), 7.23 (s, 1H), 7.20 (s, 1H)	---	4.854 (s, 2H), 4.848 (s, 2H), 4.82 (s, 2H), 4.80 (s, 2H)	3.95, 3.93, both s with overlap, together 1.7H$^\#$	3.40 (s, 1H)	1.07, 1.061, 1.059, 1.056, all s with large overlap, together 84H	---
6a CD$_2$Cl$_2$	7.31 (AA'XX' spin system, 4H)	7.27 (s, 2H), 7.22 (s, 2H)	6.64 (AA'XX' spin system, 4H)	4.82 (s, 4H), 4.80 (s, 4H)	3.95, 3.93, both s with large overlap, together 1.9H$^{\#\#}$	---	1.07 (s, 42H), 1.05 (s, 42H)	---
6b CD$_2$Cl$_2$	7.32 (AA'XX' spin system, 4H)	7.31 (s, 2H), 7.30 (s, 2H), 7.26 (s, 2H), 7.20 (s, 2H)	---	4.861, 4.858, both s with large overlap, together 8H, 4.84 (s, 4H), 4.82 (s, 4H)	3.95 (s, 4H)	---	1.073 (s, 42H), 1.069 (s, 42H), 1.061 (s, 42H), 1.055 (s, 42H)	---
9 CDCl$_3$	---	7.27 (s, 2H), 7.25 (s, 2H), 7.22 (s, 2H), 7.15 (s, 2H)	---	4.82 (s, 4H), 4.80 (s, 4H), 4.79 (s, 4H), 4.75 (s, 4H)	---	---	1.040, 1.036, both s with large overlap, together 126H; 1.02 (s, 42H)	0.25 (s, 18H)

benz = benzene; $^\#$A singlet with an integral corresponding to 2H is expected. Partial exchange with deuterium led to two singlets assigned to NH$_2$ and NDH. $^{\#\#}$A singlet with an integral corresponding to 4H is expected. Partial exchange with deuterium led to two singlets assigned to NH$_2$ and NDH.

Table S3. ^{13}C NMR (125 MHz) data: signals with a chemical shift above 70 ppm.

compound, solvent	C_benzO	C_benzNH₂	C_benzH meta to C_benzNH₂	C_benzH meta to C_benzNH*	C_benzH ortho to C_benzNH*	C_benz para to C_benzNH*	C_benzH ortho to C_benzO	C_benzC≡C (benz = substituted alkoxybenzene)	C_benzH ortho to C_benzNH₂	C_benz para to C_benzNH₂	CH₂C≡C	C_benzC≡C para to C_benzNH*	CH₂C≡C	C_benzC≡CC_benz (benz = substituted alkoxybenzene)	C_benzC≡C para to C_benzNH₂	C≡C-C≡C	TMSC≡C	C≡CH
4b CD₂Cl₂	153.1, 152.9, 152.6, 152.5	147.7	133.3	---	---	---	120.3, 119.4, 119.1, 119.0	115.8, 115.0, 114.5, 113.6,	114.8	112.4	102.2, [102.15, 102.14], 101.9	---	90.6, 90.5, 90.2, 90.1	96.8, 91.8, 91.1, 83.7	---		[100.87, 100.86]	---
5a CD₂Cl₂	153.5, 152.3	147.8	133.3	---	---	---	120.0, 118.7	116.2, 112.3	114.8	112.3	102.1, 102.0	96.7, 83.4	90.5, 90.2	---	---	---	---	82.7, 79.9
5b CD₂Cl₂	153.5, 153.0, 152.6, 152.5	147.7	133.3	---	---	---	120.6, 119.4, 119.1, 118.8	115.9, 115.5, 113.6, 113.3	114.9	112.4	102.3, 102.2, 102.1, 101.9	---	90.6, 90.5*², 90.1	96.8, 91.8, 90.9, 83.7	---	---		83.1, 79.8
6a CD₂Cl₂	154.4, 152.2	147.8	133.4	---	---	---	119.8, 118.6	116.8, 111.9	114.8	112.3	102.0, 101.9	---	90.7, 90.4	---	97.5, 83.7, 79.6, 79.3	---	---	---
6b CD₂Cl₂	154.4, 153.0, 152.53, 152.47	147.7	133.3	---	---	---	120.5, 119.4, 119.1, 118.7	116.1, 115.9, 113.6, 112.9	114.9	112.4	102.2, 102.1, 102.0, 101.8	---	90.8, 90.7, 90.5, 90.1	96.9, 92.5, 91.1, 83.7, 79.7, 79.6	---	---	---	---

benz = benzene. Signals reported in square brackets overlap. *^{n} means the signal has n-fold intensity compared to the other signals in the series.

Table S4. ^{13}C NMR (125 MHz) data: signals with a chemical shift below 70 ppm.

compound, solvent	CH₂C≡C	CHMe₂	CHMe₂	SiMe₃
4b CD₂Cl₂	58.6, 58.5	18.7	[11.51, 11.49]	0.0
5a CD₂Cl₂	58.6, 58.3	[18.68, 18.67]	11.5	---
5b CD₂Cl₂	58.7, 58.6*², 58.4	[18.72, 18.70, 18.69]	[11.52, 11.50, 11.49]	---
6a CD₂Cl₂	58.6, 58.3	18.7	[11.52, 11.49]	---
6b CD₂Cl₂	58.7, [58.59, 58.58], 58.4	18.70 with shoulder at 18.71	[11.52*³, 11.49]	---

Signals reported in square brackets overlap. *^{n} means the signal has n-fold intensity compared to the other signals in the series.

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Figures of NMR spectra
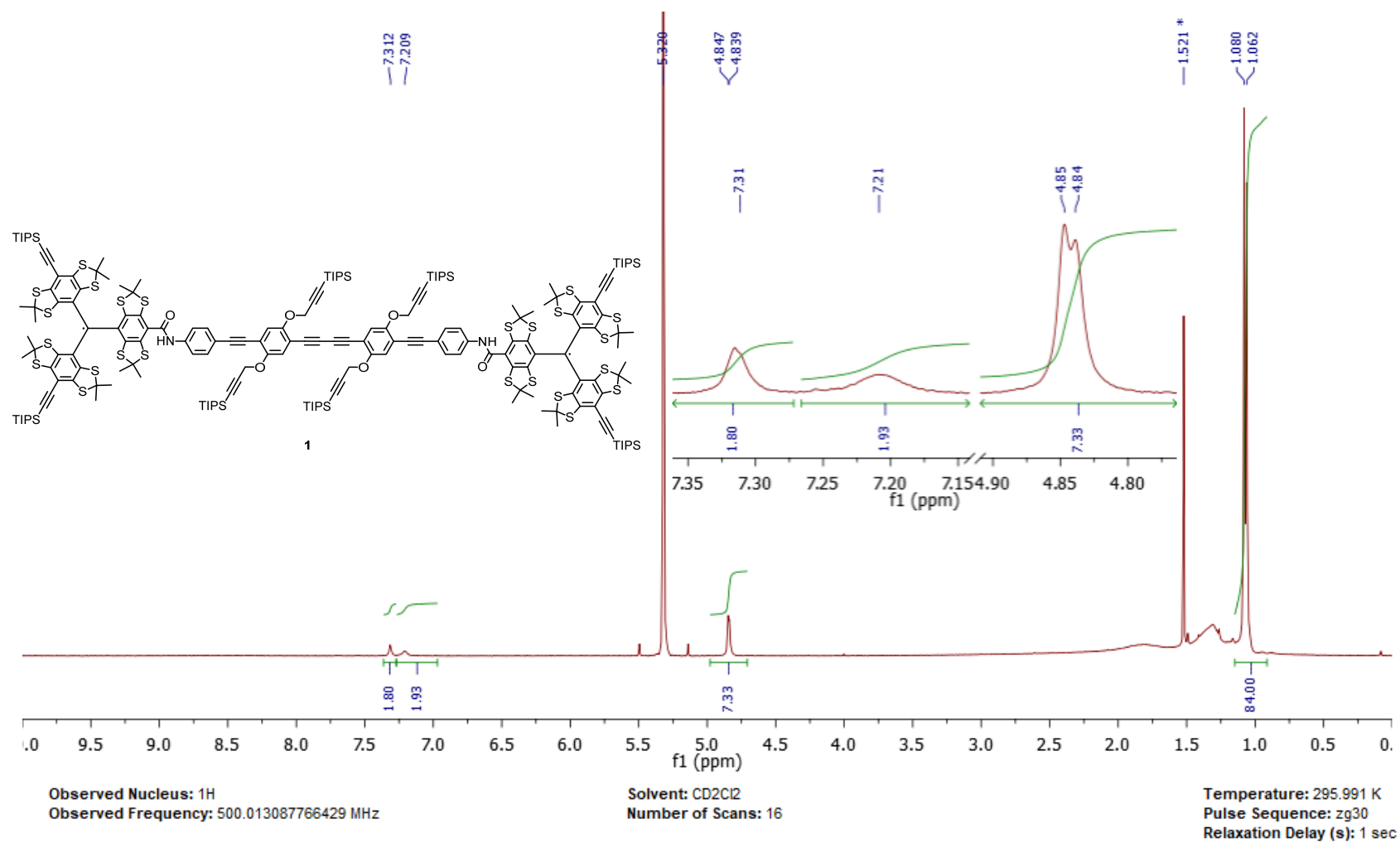
Figure S4. ^{1}H NMR spectrum of trityl-PEPBPEP-trityl **1**. *H_2O.
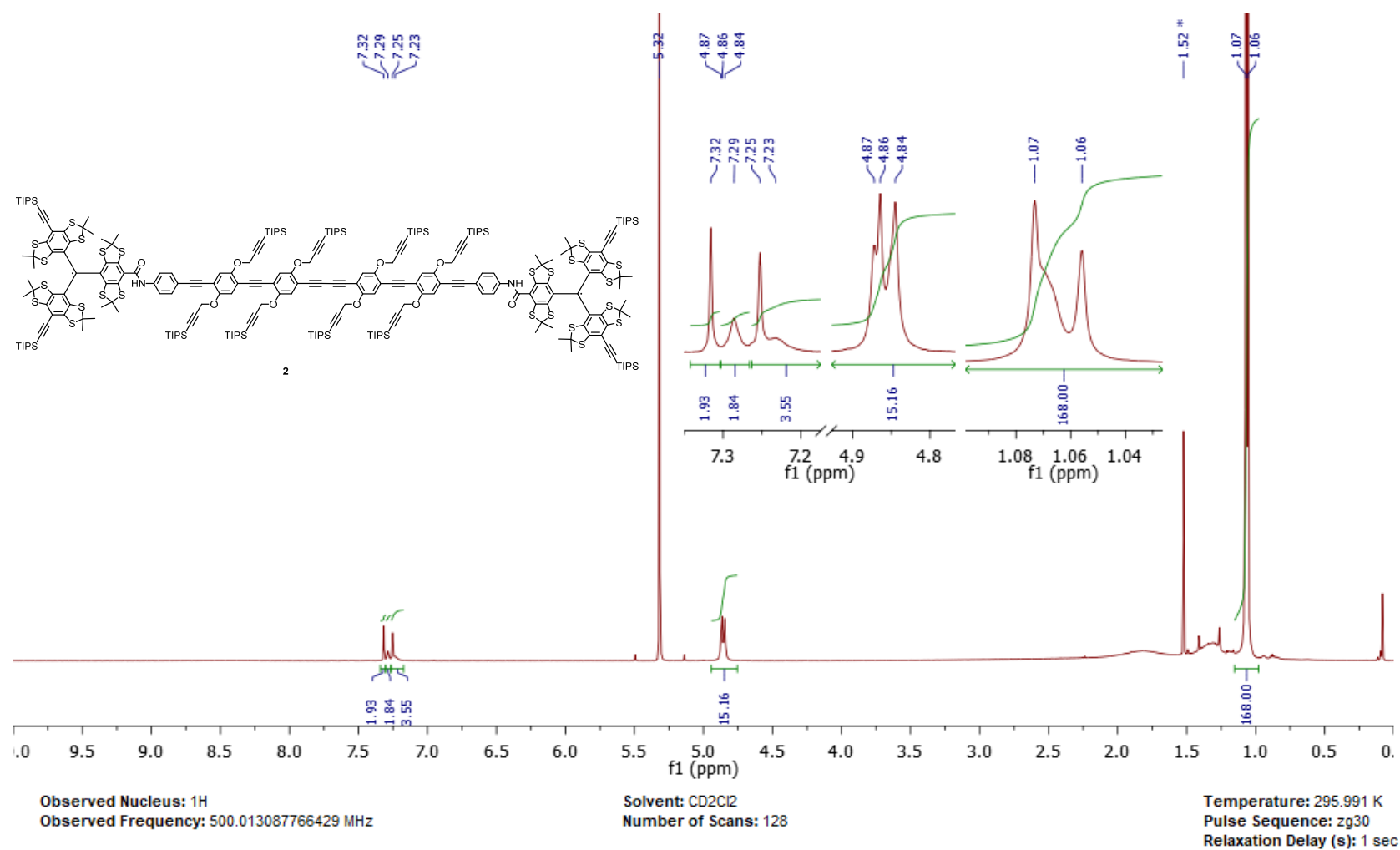
Figure S5. ^{1}H NMR spectrum of trityl-P(EP)$_2$BP(EP)$_2$-trityl **2**. *H$_2$O.

Observed Nucleus: 1H
Observed Frequency: 500.013087766429 MHz

Solvent: CD2Cl2
Number of Scans: 128

Temperature: 295.991 K
Pulse Sequence: zg30
Relaxation Delay (s): 1 sec
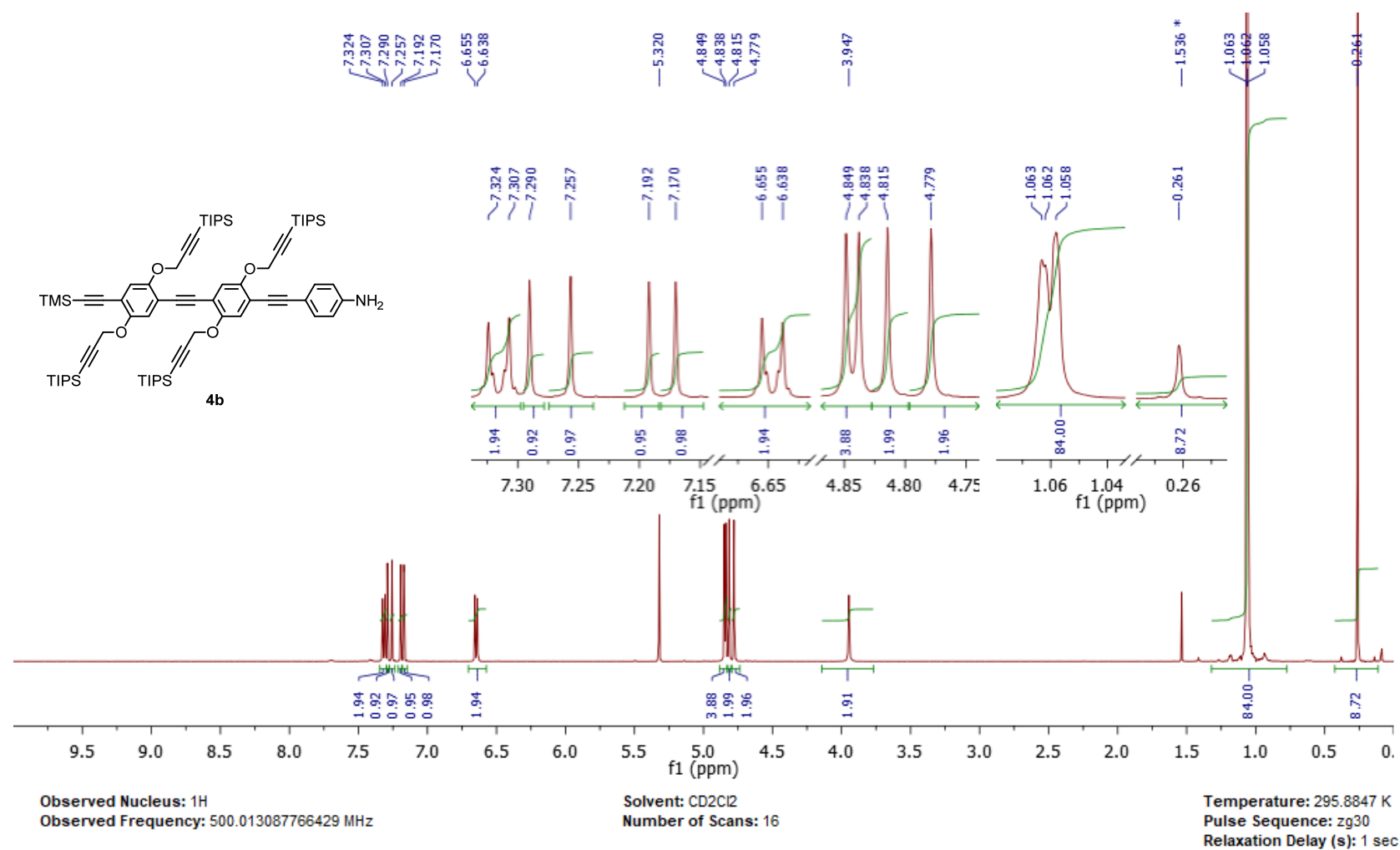
Figure S6. ^{1}H NMR spectrum of TMS-(EP)$_3$-NH$_2$ **4b**. *H$_2$O.

Observed Nucleus: 1H
Observed Frequency: 500.013087766429 MHz

Solvent: CD2Cl2
Number of Scans: 16

Temperature: 295.8847 K
Pulse Sequence: zg30
Relaxation Delay (s): 1 sec
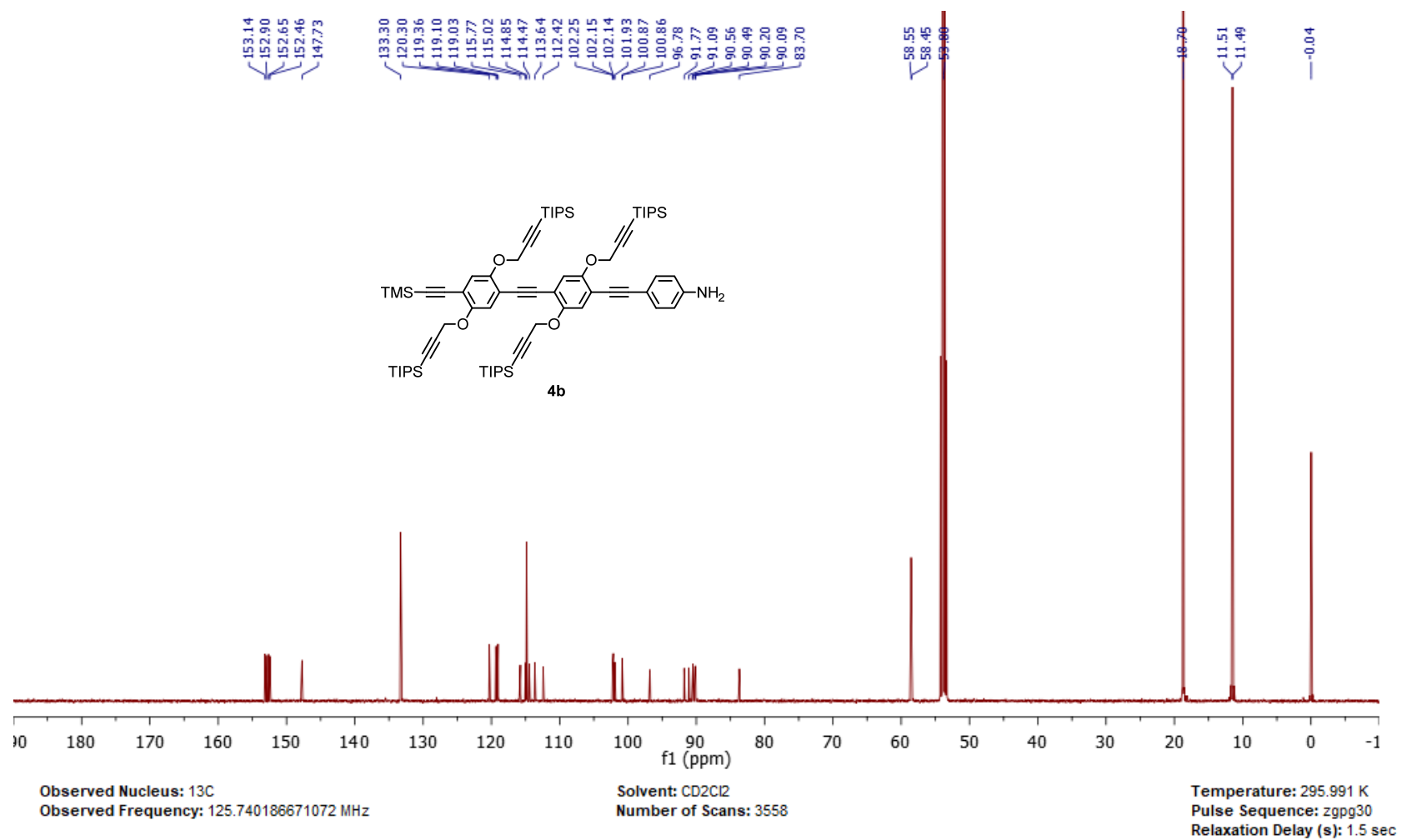
Figure S7. ^{13}C NMR spectrum of TMS-(EP)$_3$-NH$_2$ **4b**.

Observed Nucleus: 13C
Observed Frequency: 125.740186671072 MHz

Solvent: CD2Cl2
Number of Scans: 3558

Temperature: 295.991 K
Pulse Sequence: zgpg30
Relaxation Delay (s): 1.5 sec
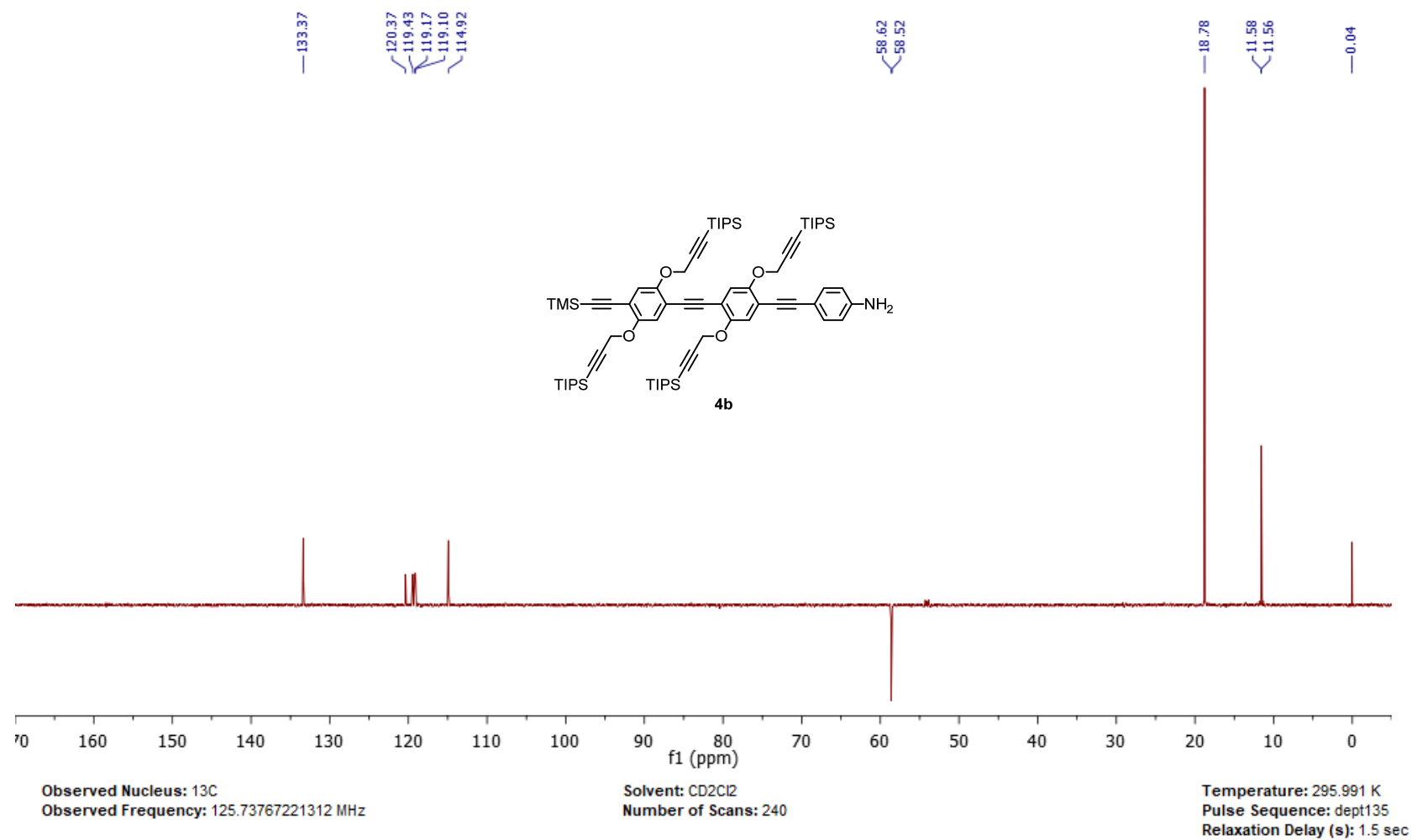
Figure S8. DEPT-135 NMR spectrum of TMS-(EP)₃-NH₂ **4b**.
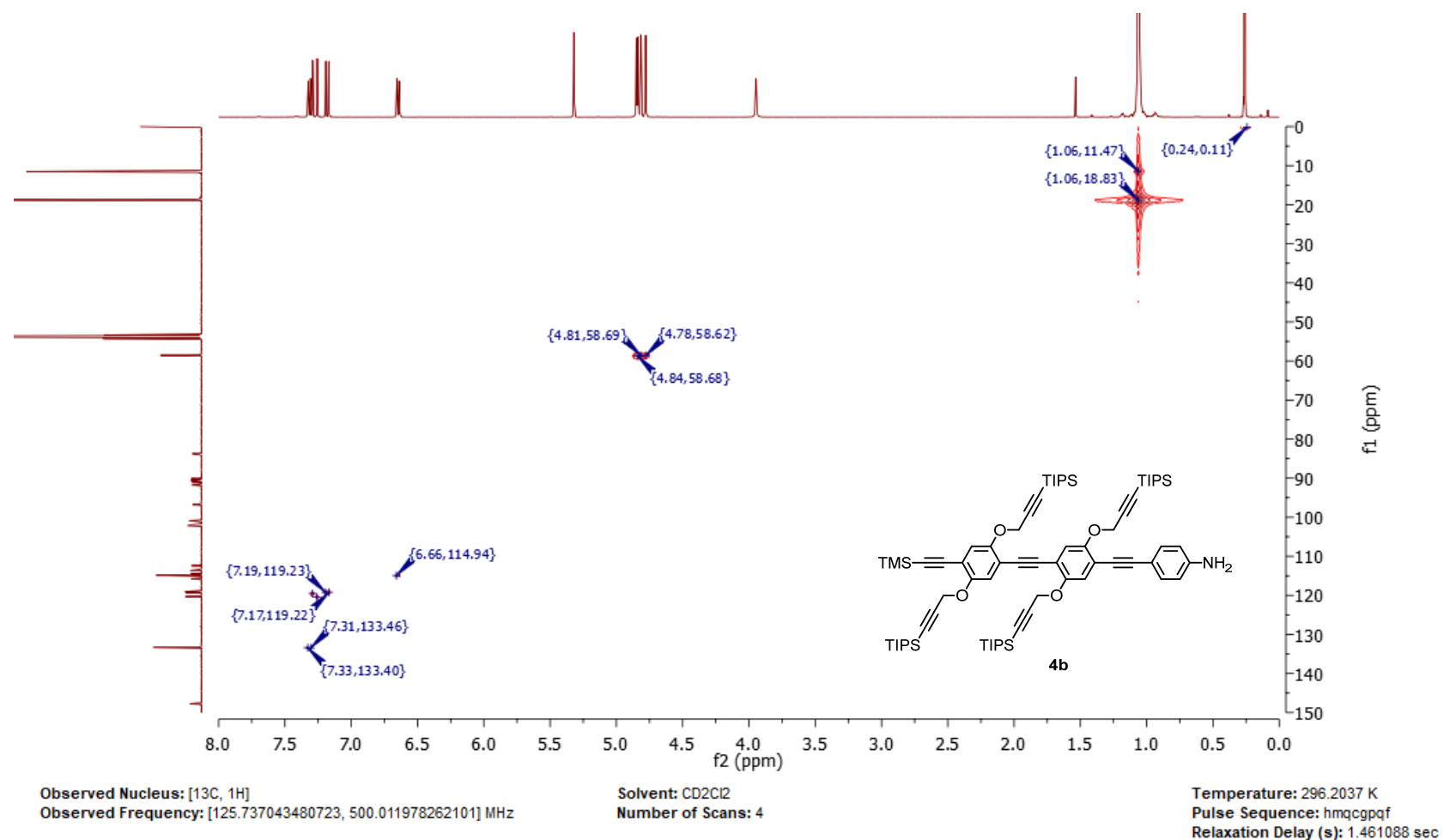
Figure S9. HMQC NMR spectrum of TMS-(EP)$_3$-NH$_2$ **4b**.
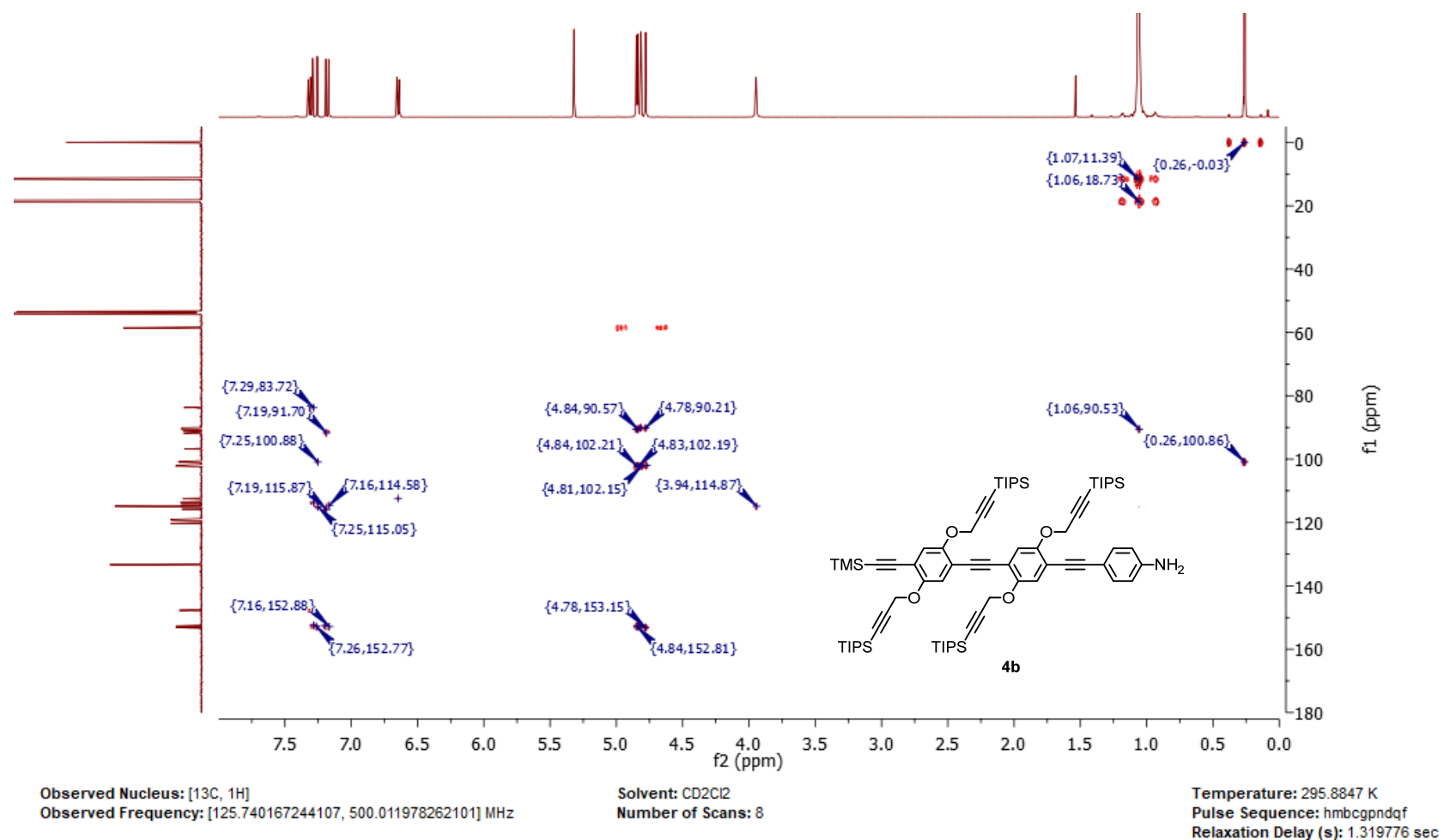
Figure S10. HMBC NMR spectrum of TMS-(EP)₃-NH₂ **4b**.
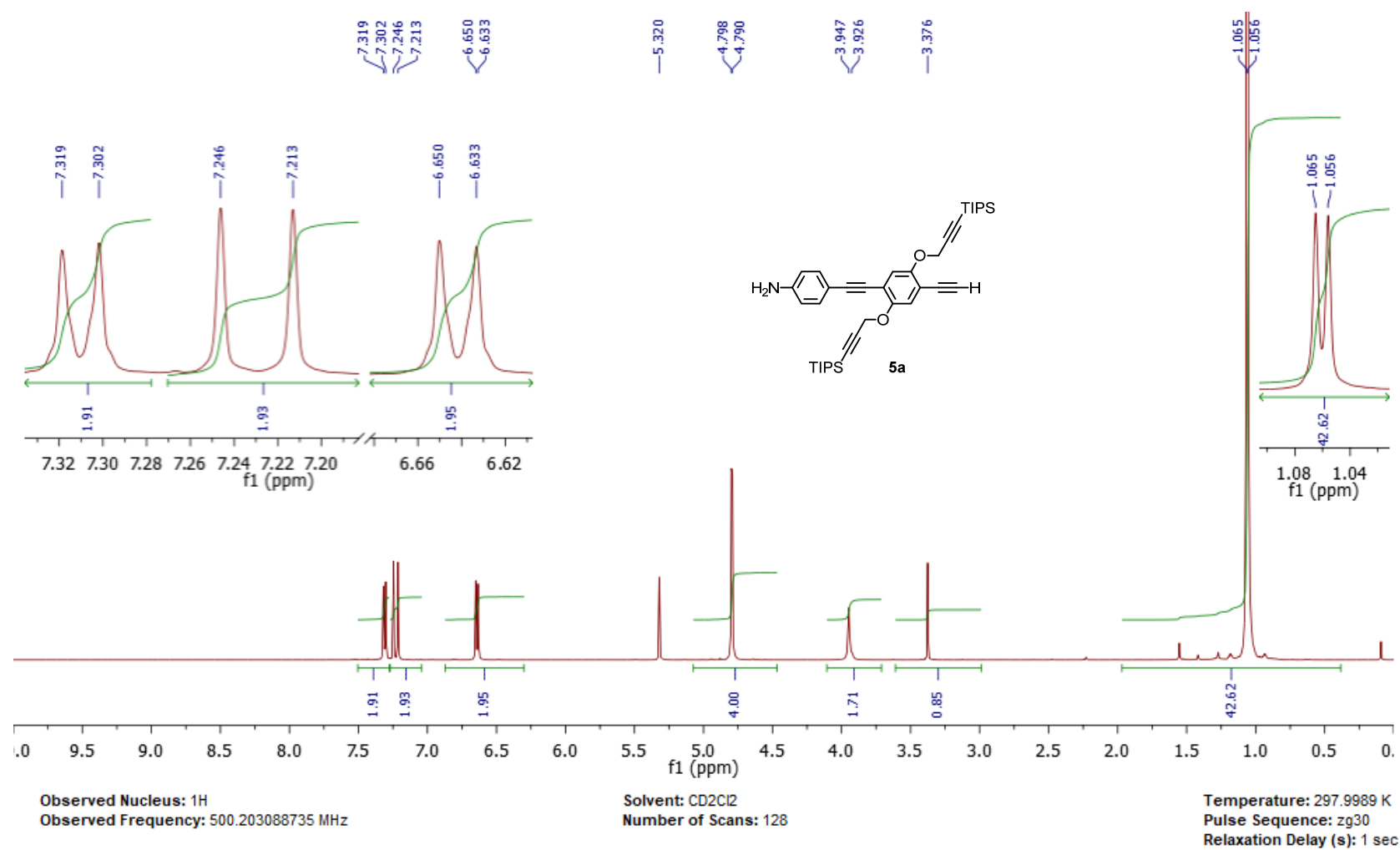
Figure S11. ^{1}H NMR spectrum of H-(EP)$_2$-NH$_2$ **5a**.
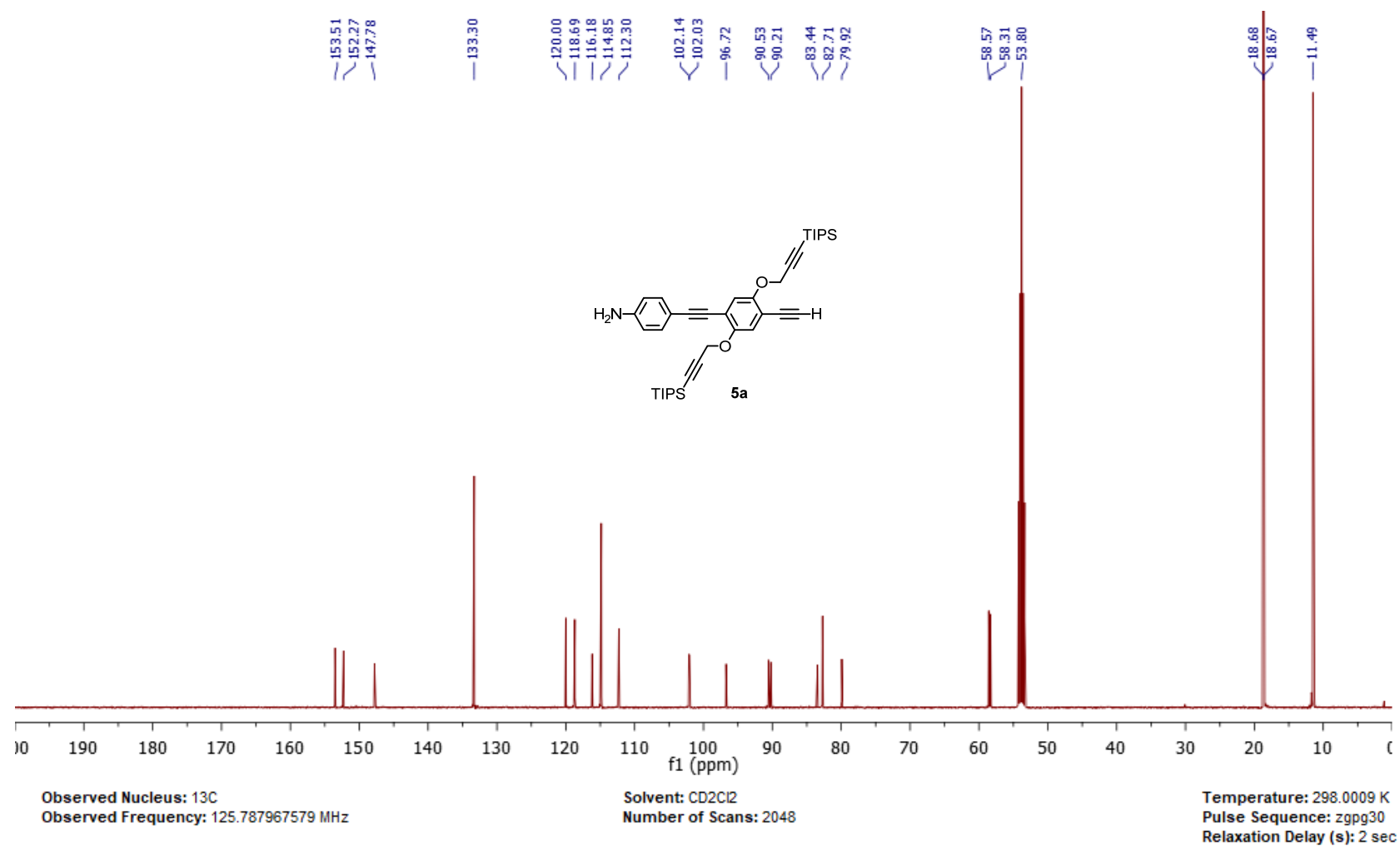
Figure S12. ^{13}C NMR spectrum of H-(EP)$_2$-NH$_2$ **5a**.
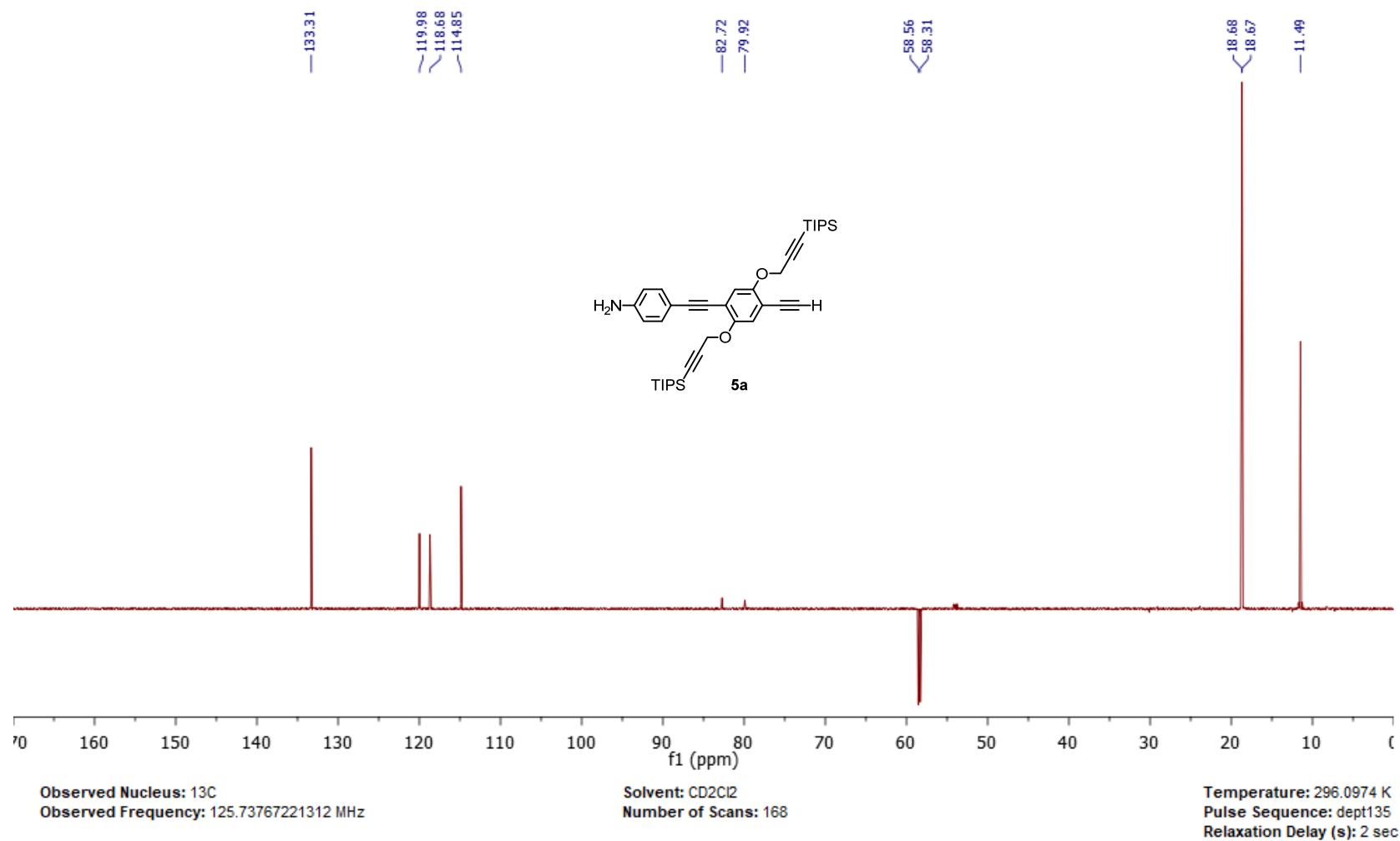
Figure S13. DEPT-135 NMR spectrum of H-(EP)₂-NH₂ **5a**.
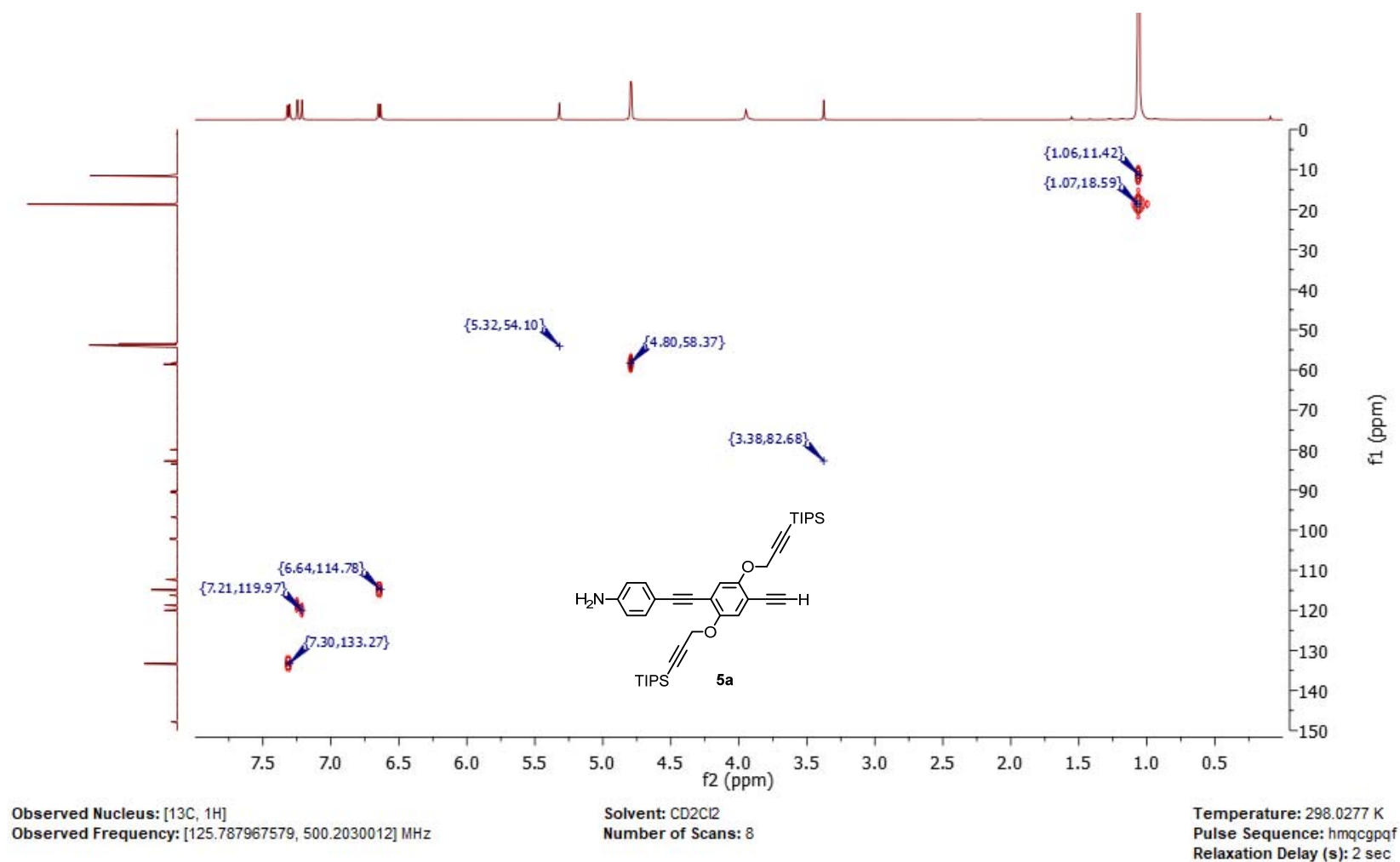
Figure S14. HMQC NMR spectrum of H-(EP)₂-NH₂ **5a**.
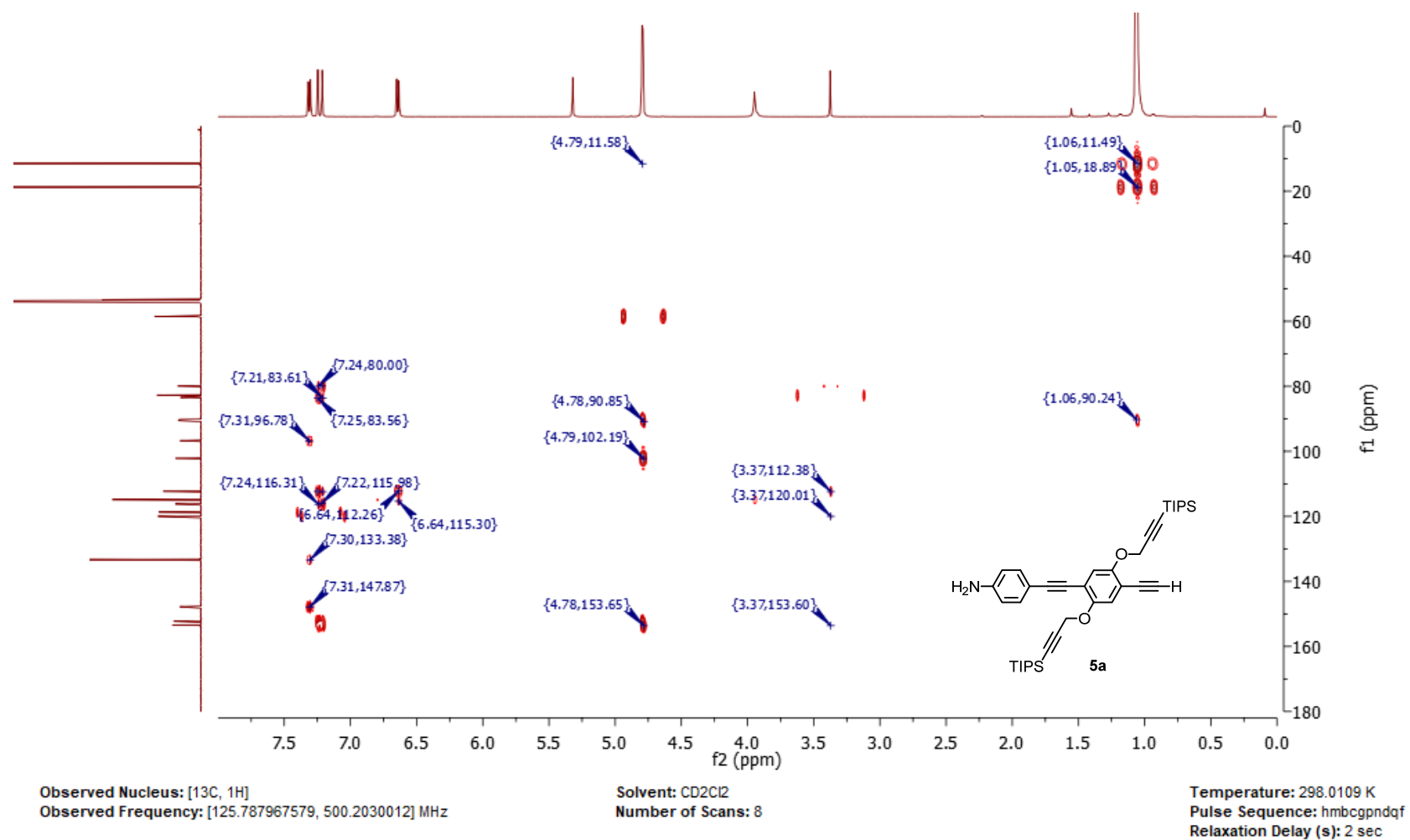
Figure S15. HMBC NMR spectrum of H-(EP)$_2$-NH$_2$ **5a**.
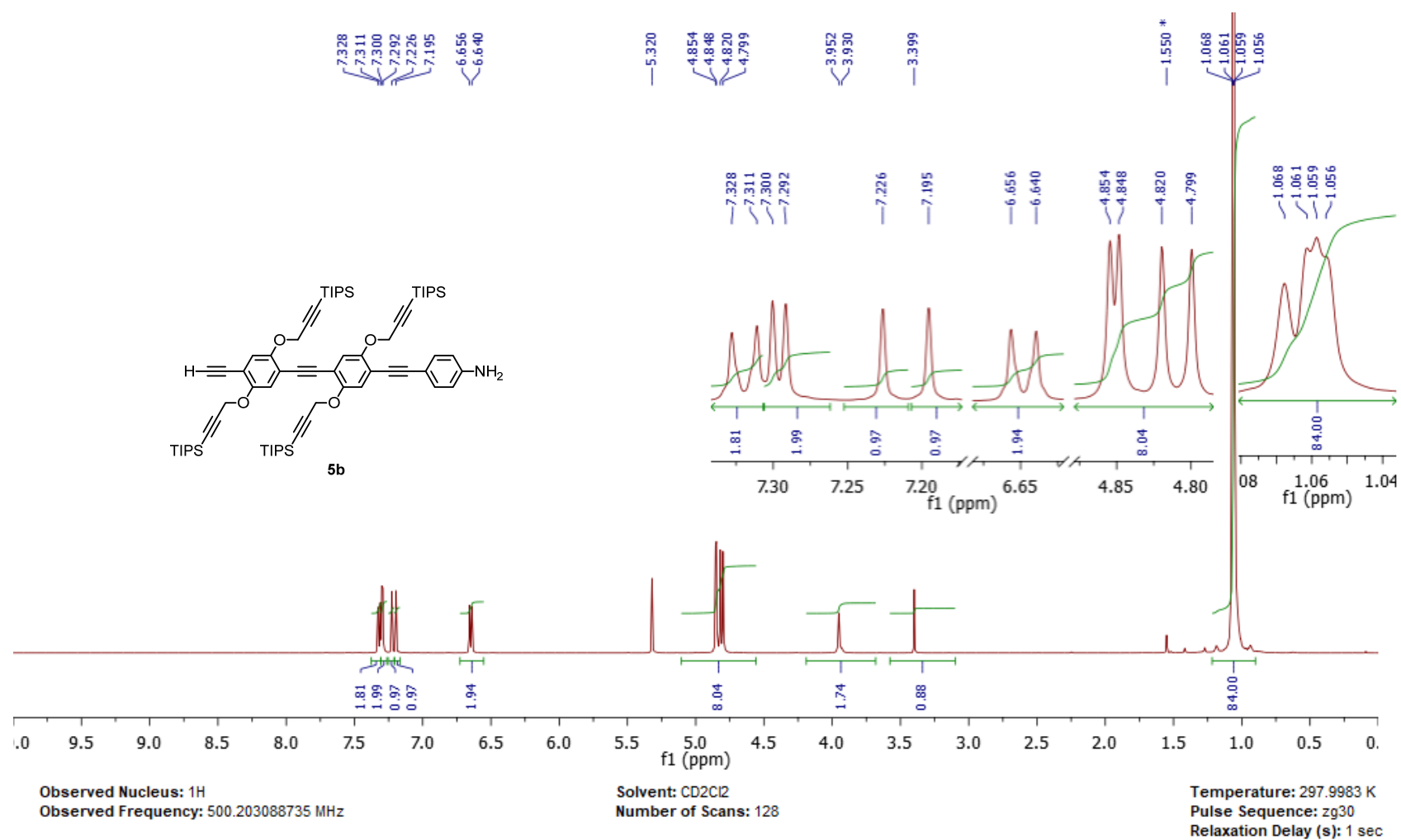
Figure S16. ^{1}H NMR spectrum of H-(EP)$_3$-NH$_2$ **5b**. *H$_2$O.
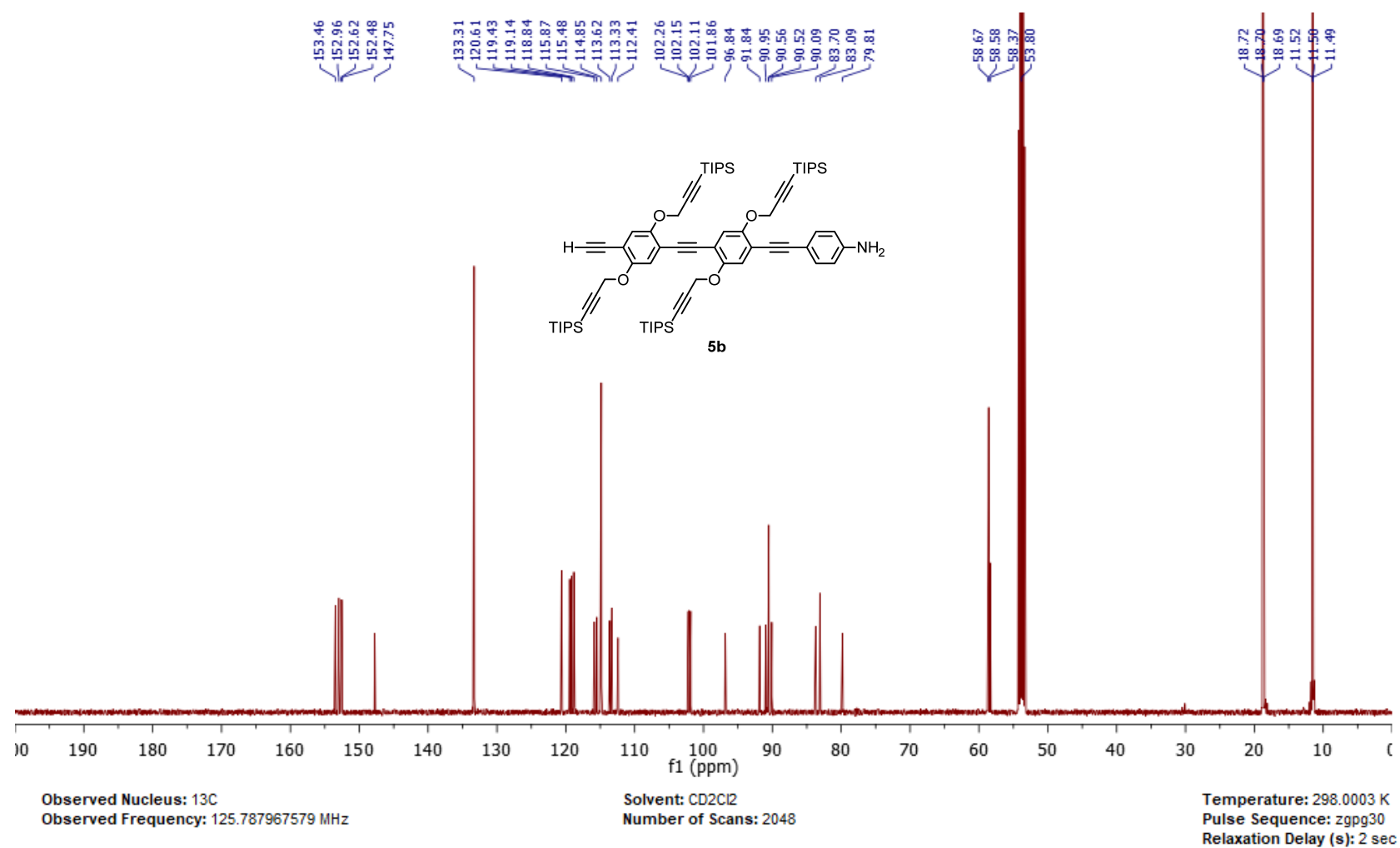
Figure S17. ^{13}C NMR spectrum of H-(EP)$_3$-NH$_2$ **5b**.

Observed Nucleus: 13C
Observed Frequency: 125.787967579 MHz

Solvent: CD2Cl2
Number of Scans: 2048

Temperature: 298.0003 K
Pulse Sequence: zgpg30
Relaxation Delay (s): 2 sec
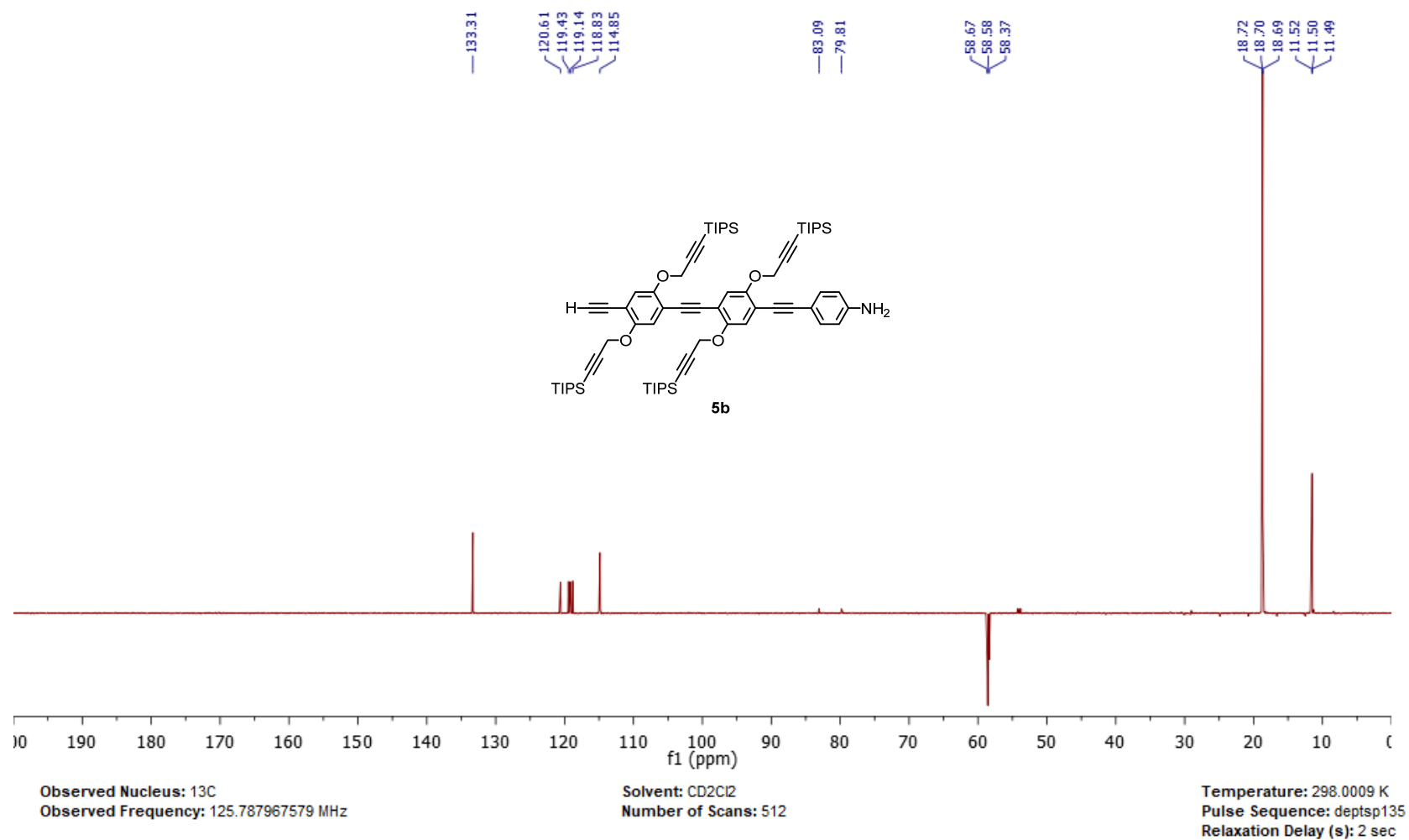
Figure S18. DEPT-135 NMR spectrum of H-(EP)₃-NH₂ **5b**.
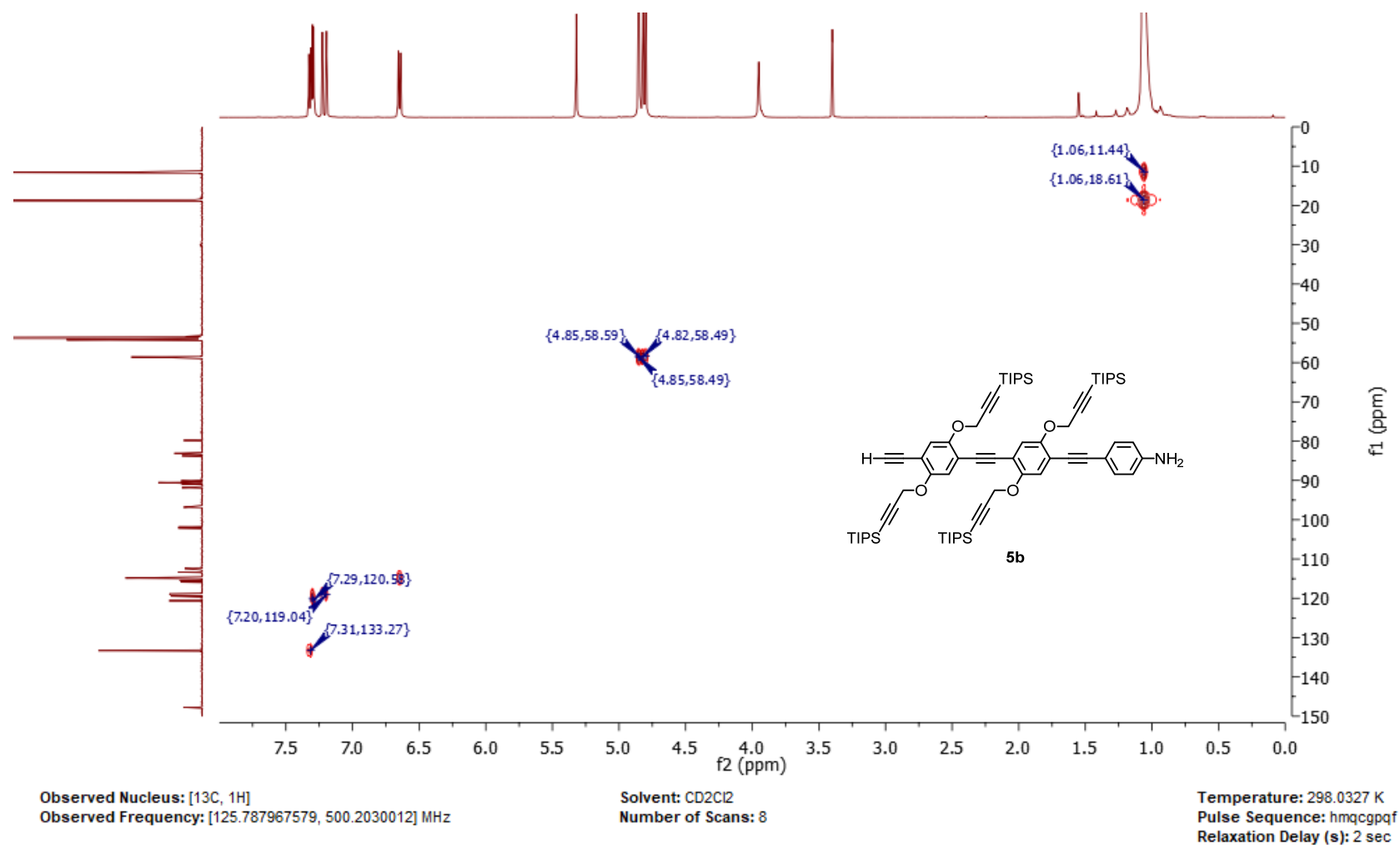
Figure S19. HMQC NMR spectrum of H-(EP)₃-NH₂ **5b**.
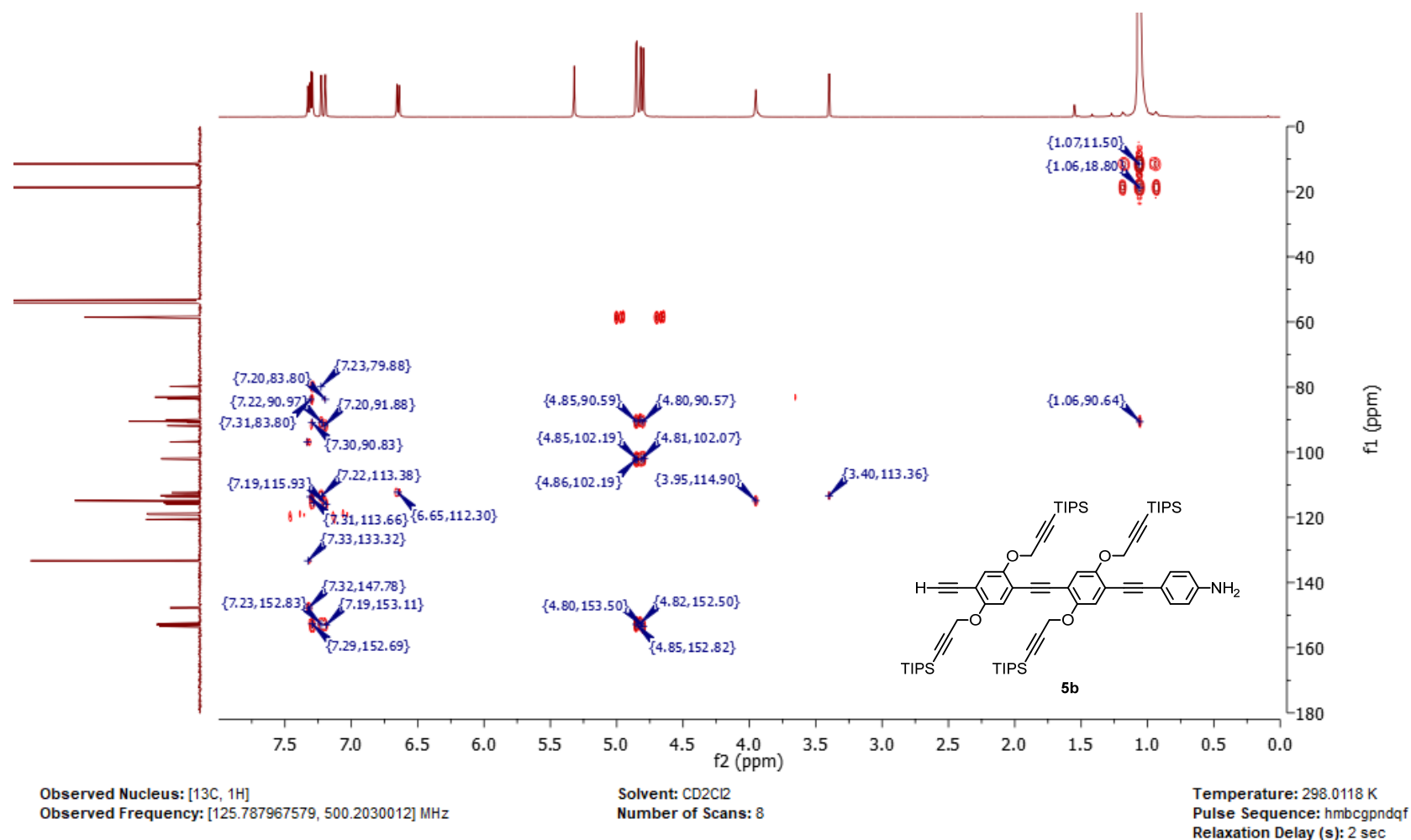
Figure S20. HMBC NMR spectrum of H-(EP)₃-NH₂ **5b**.
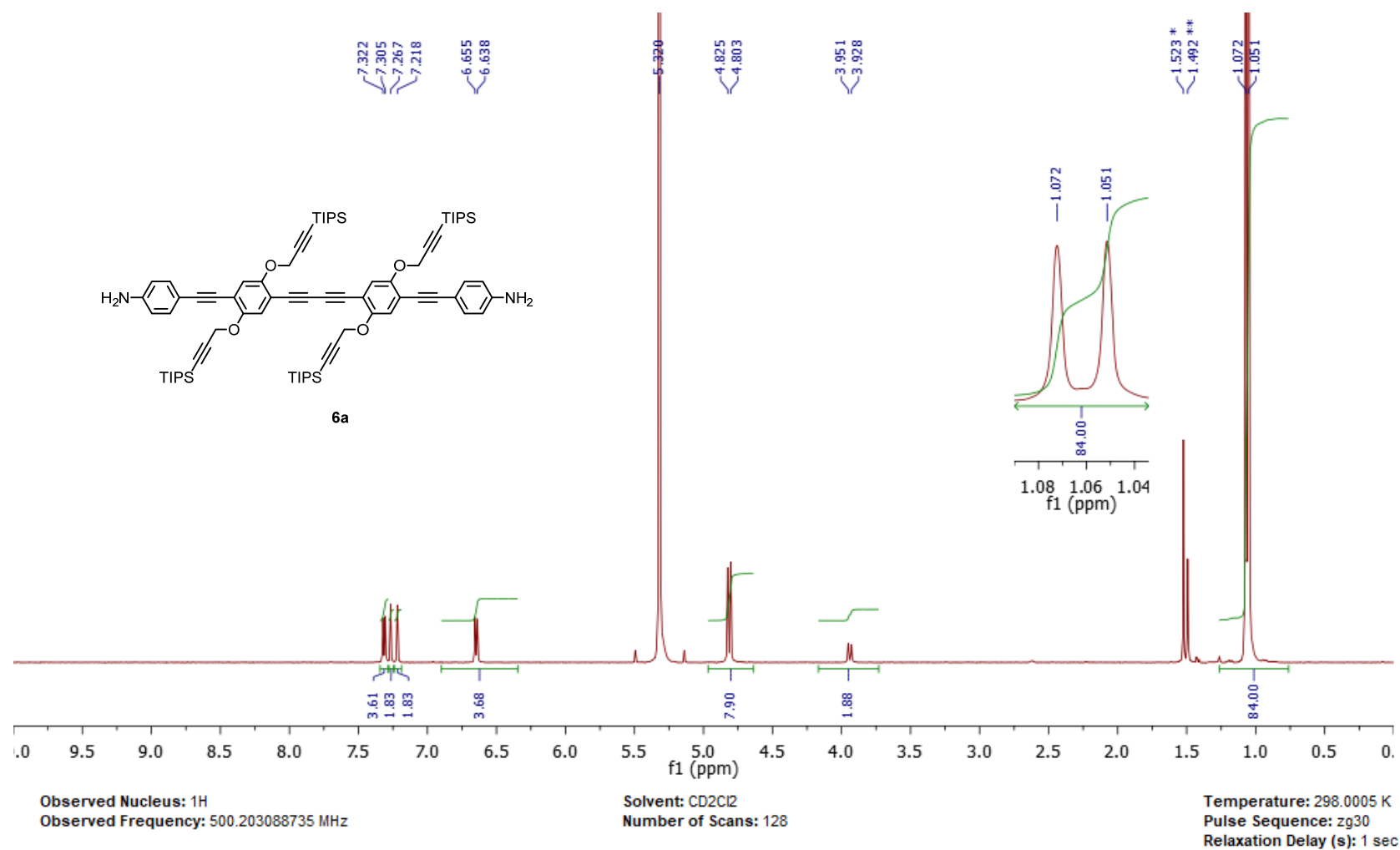
Figure S21. ^{1}H NMR spectrum of H₂N-PEPBPEP-NH₂ **6a**. *H₂O, **HDO.
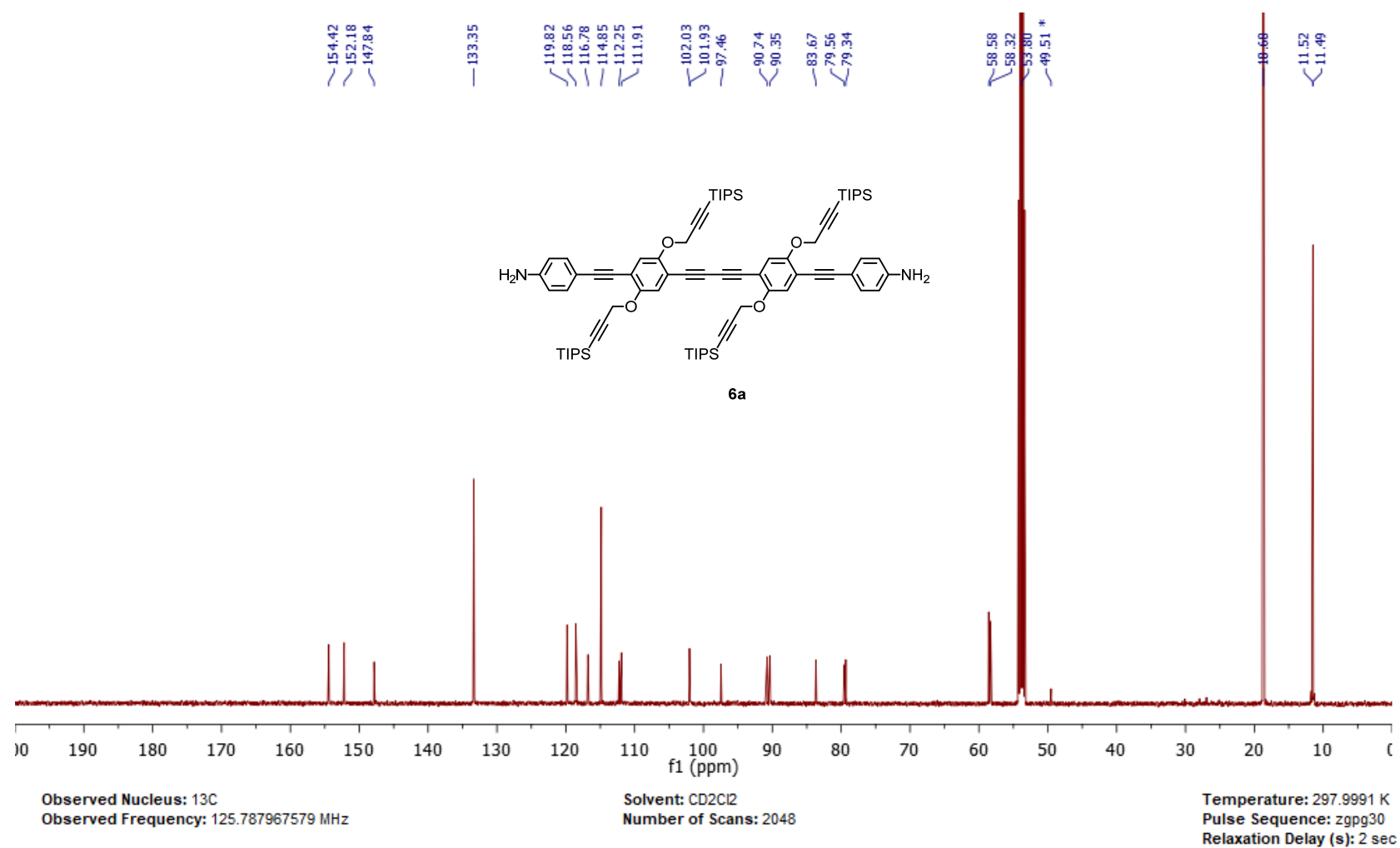
Figure S22. ^{13}C NMR spectrum of H$_2$N-PEPBPEP-NH$_2$ **6a**. *Signal belongs to an unidentified compound.

Observed Nucleus: 13C
Observed Frequency: 125.787967579 MHz

Solvent: CD2Cl2
Number of Scans: 2048

Temperature: 297.9991 K
Pulse Sequence: zgpg30
Relaxation Delay (s): 2 sec
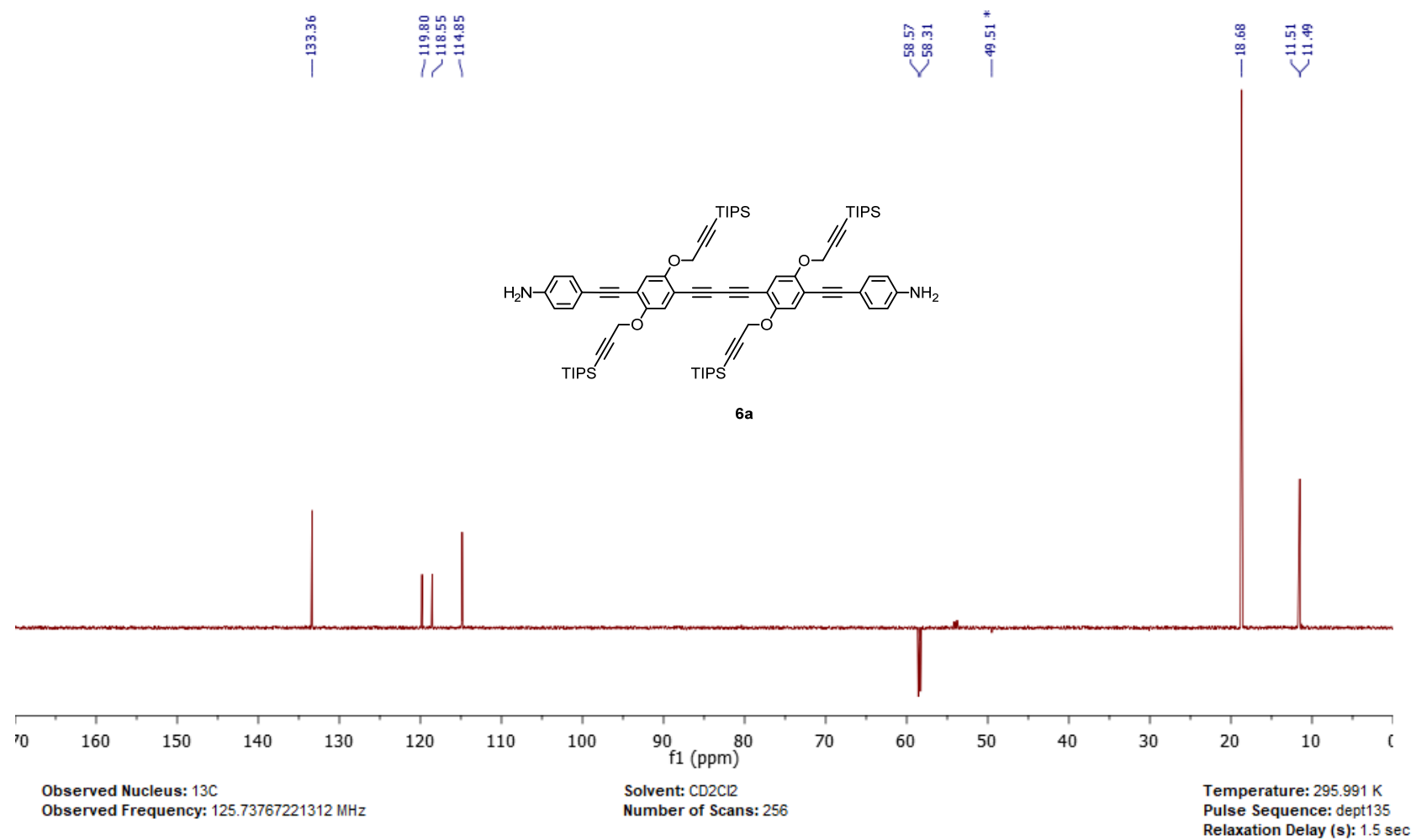
Figure S23. DEPT-135 NMR spectrum of H₂N-PEPBPEP-NH₂ **6a**. *Signal belongs to an unidentified compound.
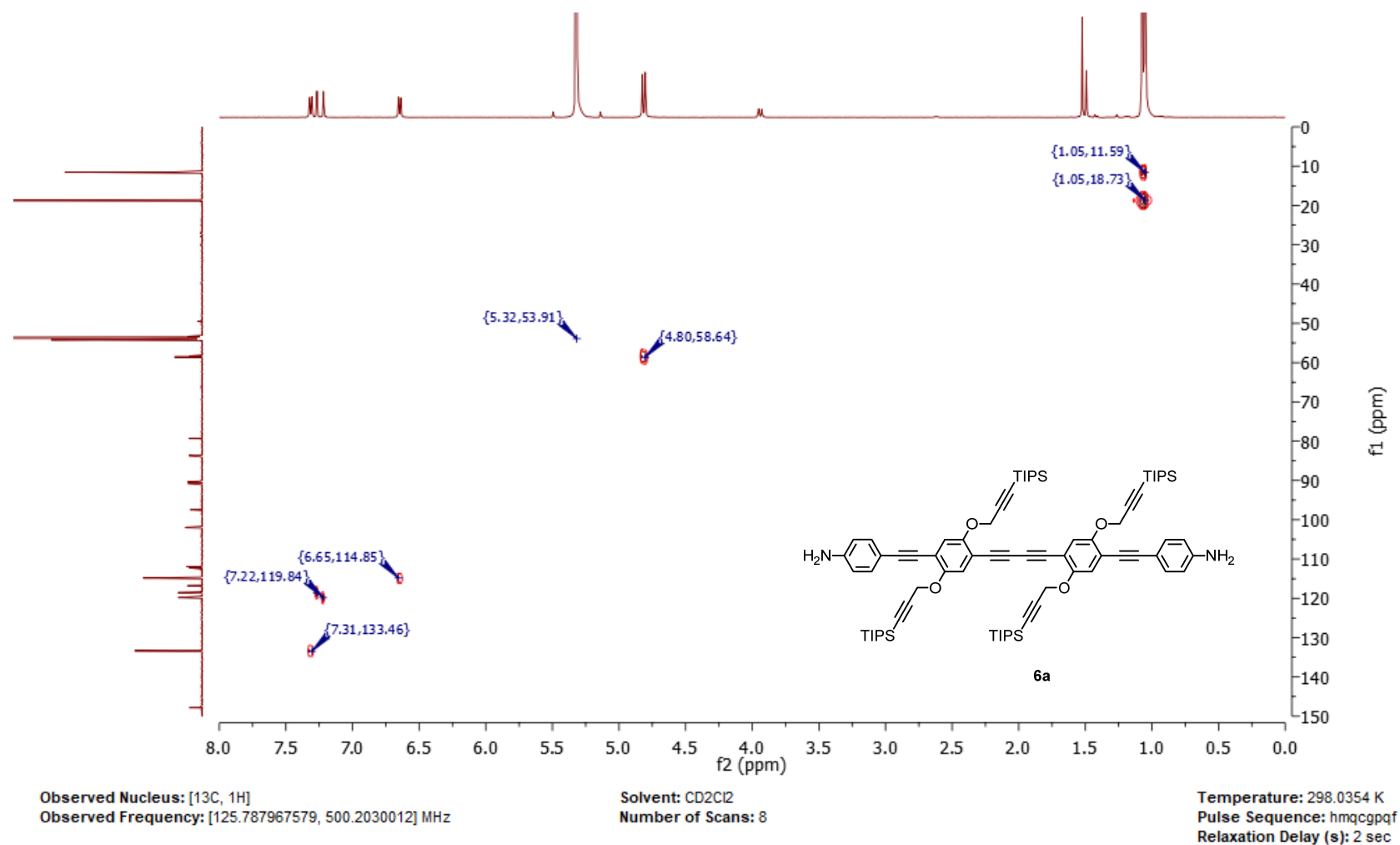
Figure S24. HMQC NMR spectrum of H₂N-PEPBPEP-NH₂ **6a**.
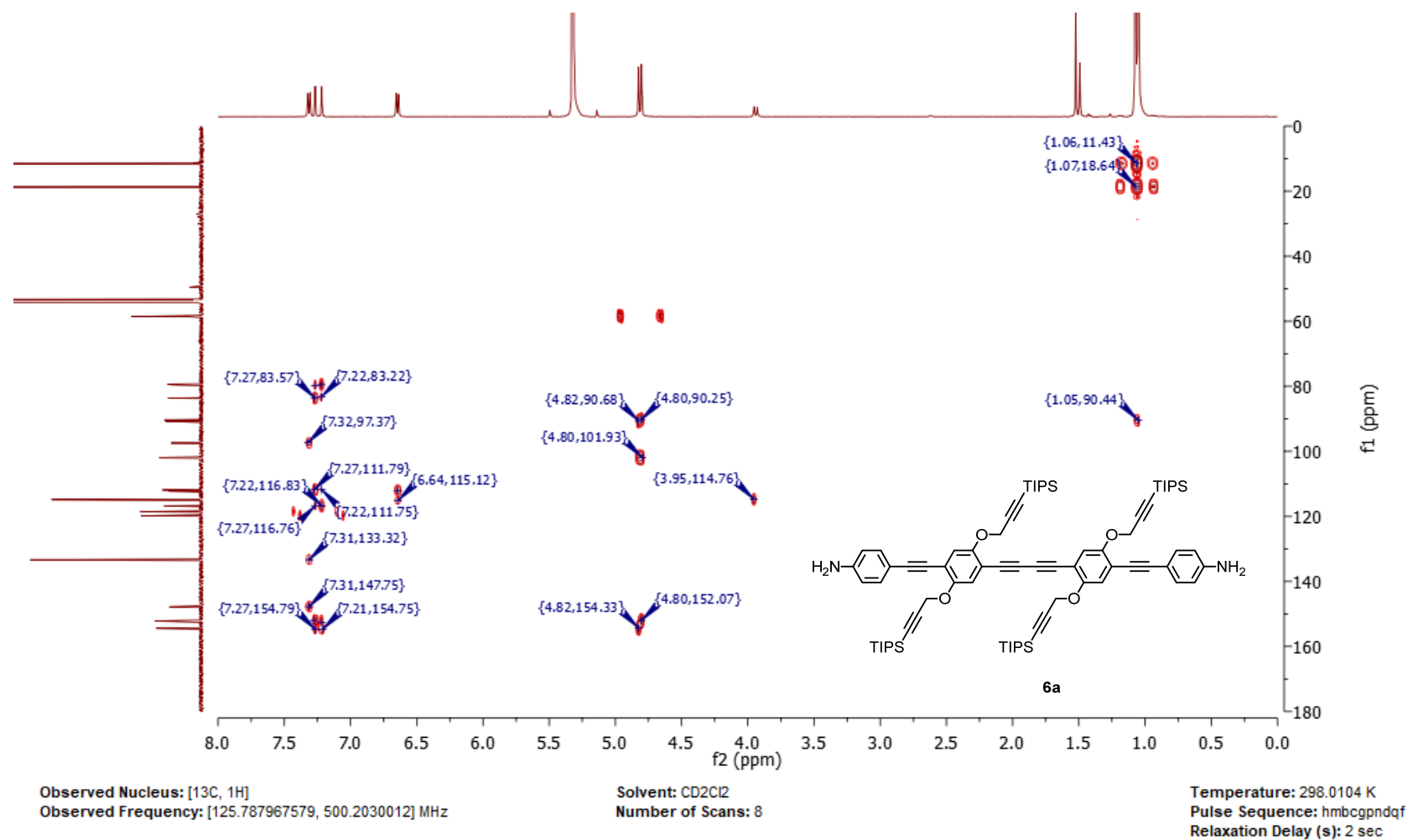
Figure S25. HMBC NMR spectrum of H_2N-PEPBPEP-NH_2 **6a**.
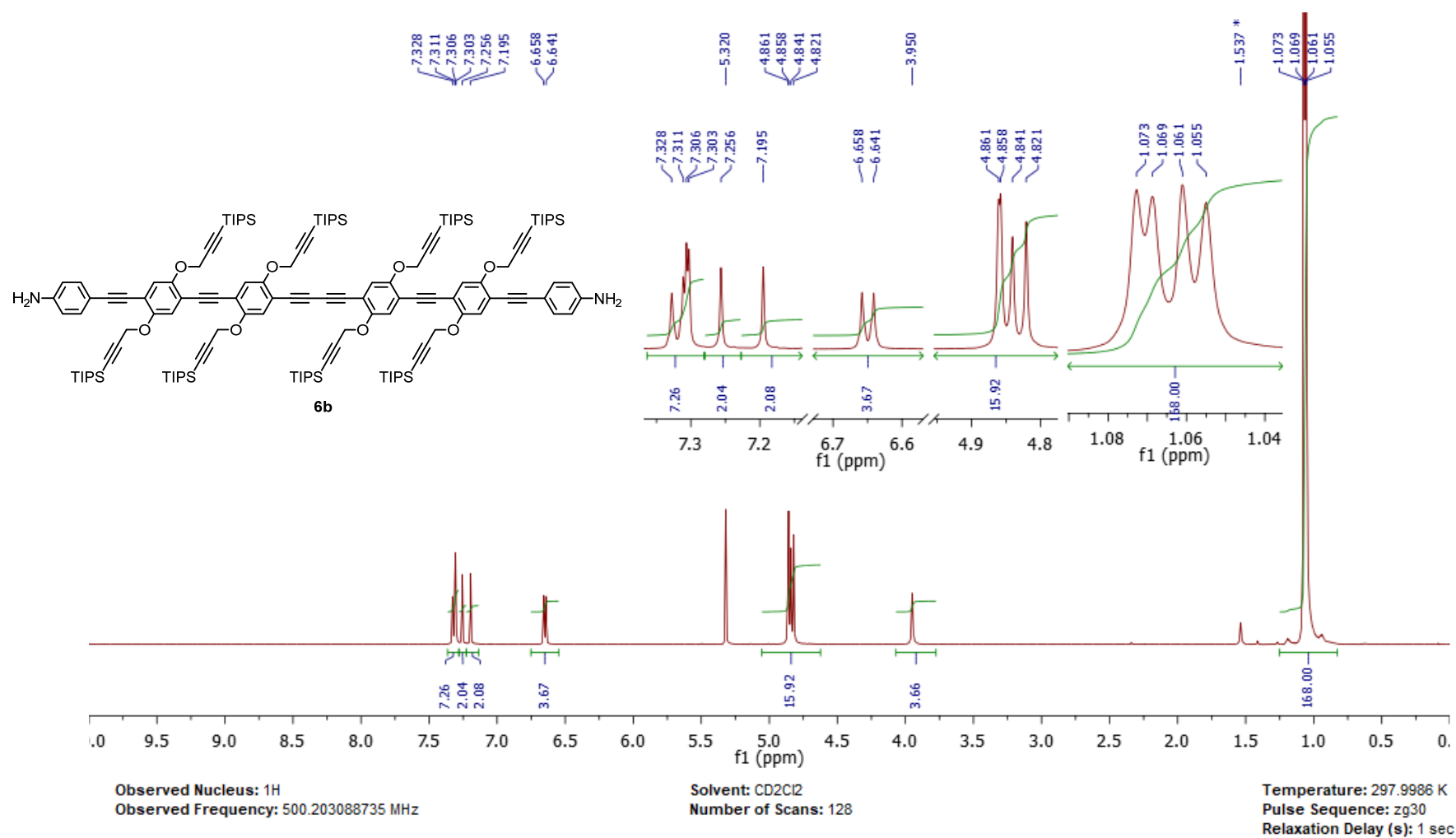
Figure S26. ^{1}H NMR spectrum of $H_2N-P(EP)_2B(PE)_2P-NH_2$ **6b**. *H_2O.
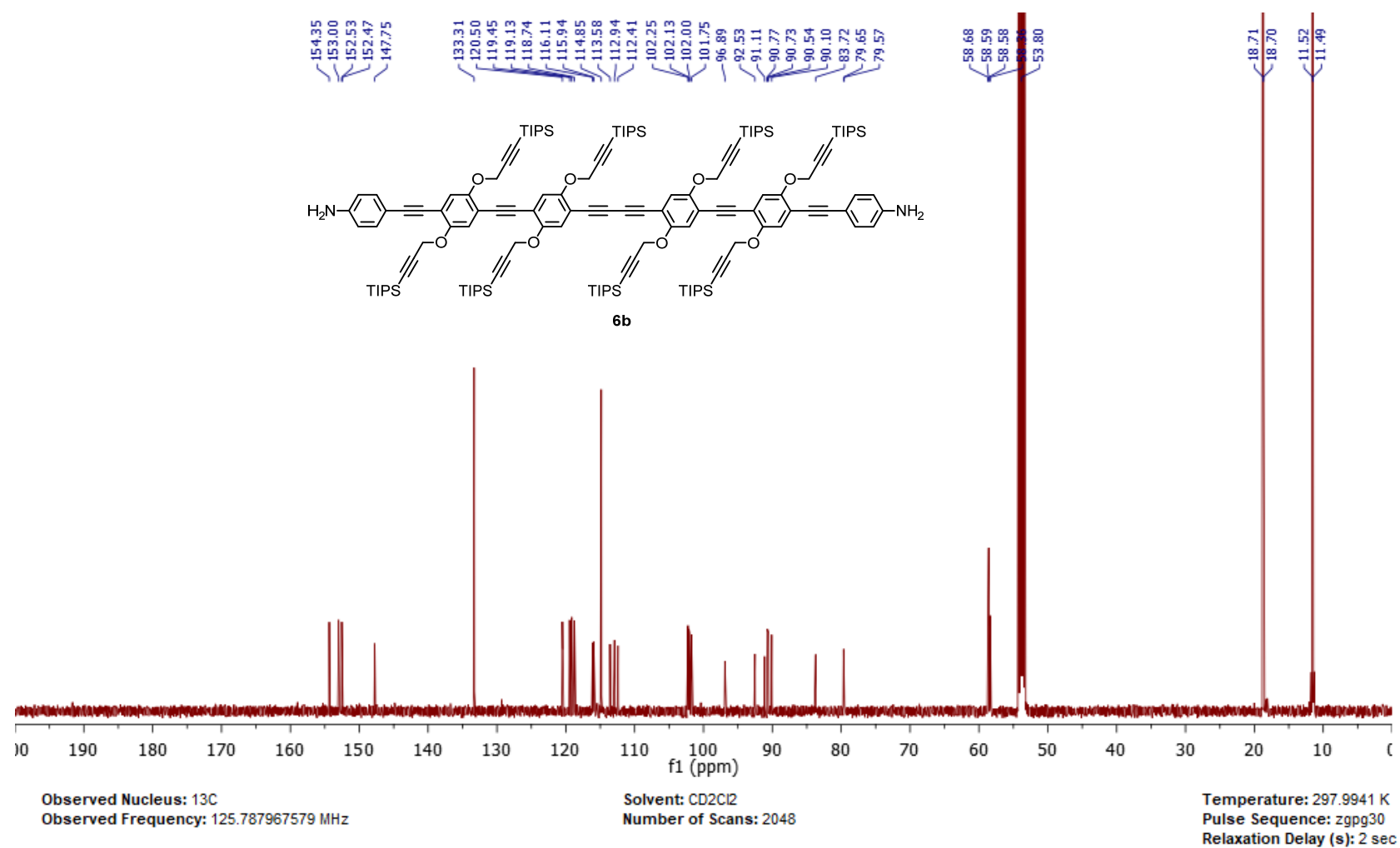
Figure S27. ^{13}C NMR spectrum of H$_2$N-P(EP)$_2$B(PE)$_2$P-NH$_2$ **6b**.
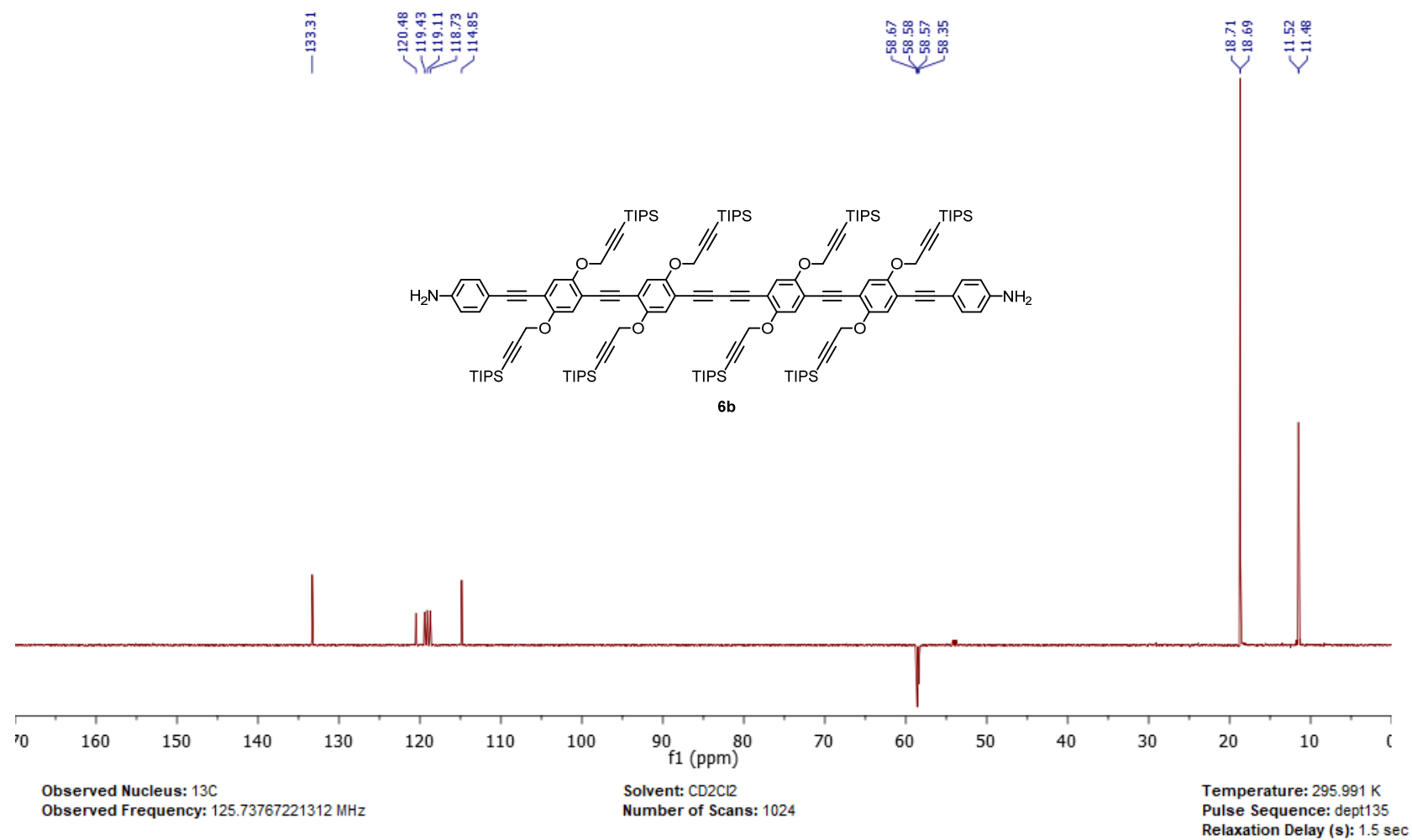
Figure S28. DEPT-135 NMR spectrum of H₂N-P(EP)₂B(PE)₂P-NH₂ **6b**.
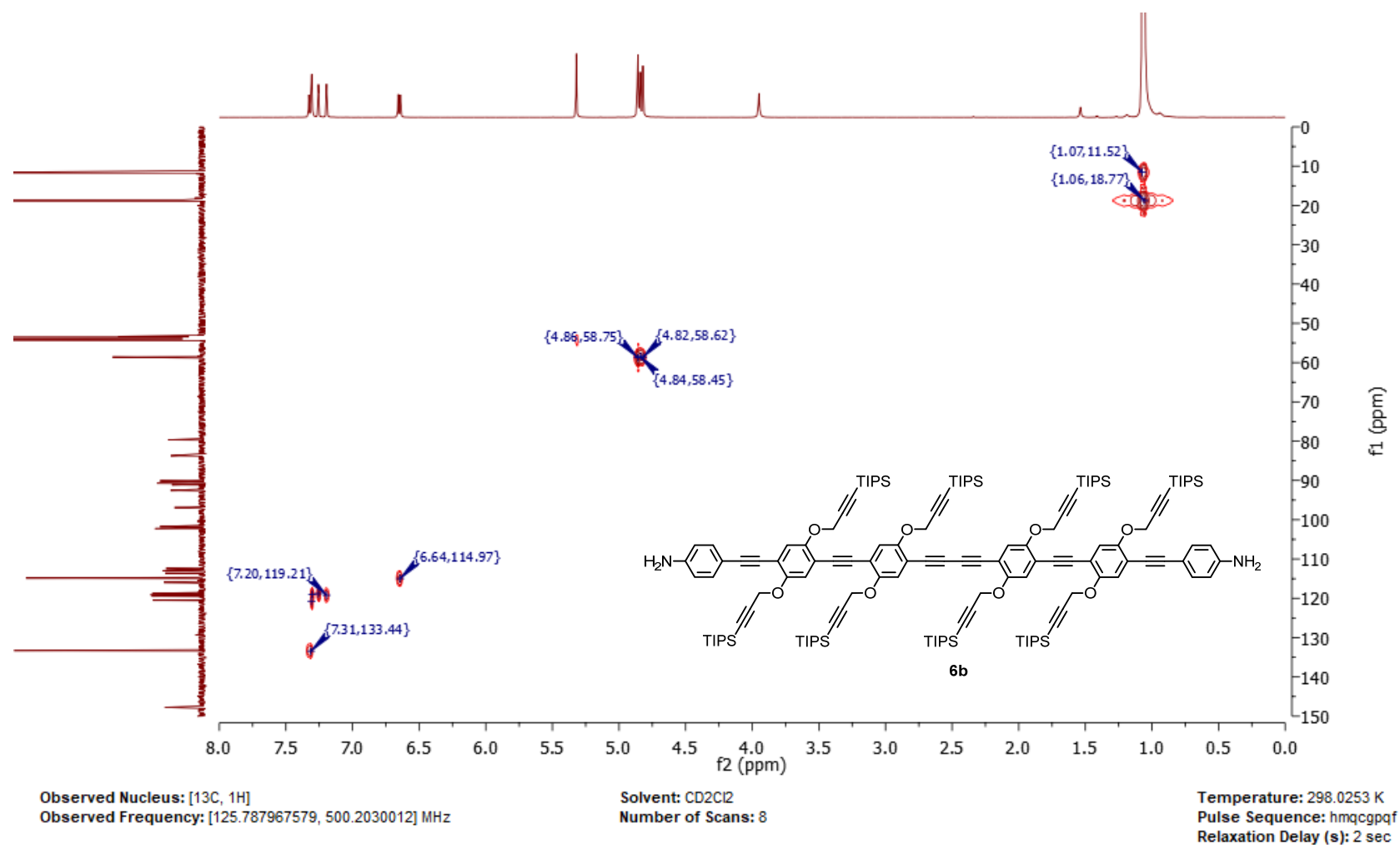
Figure S29. HMQC NMR spectrum of H_2N-$P(EP)_2B(PE)_2P$-NH_2 **6b**.
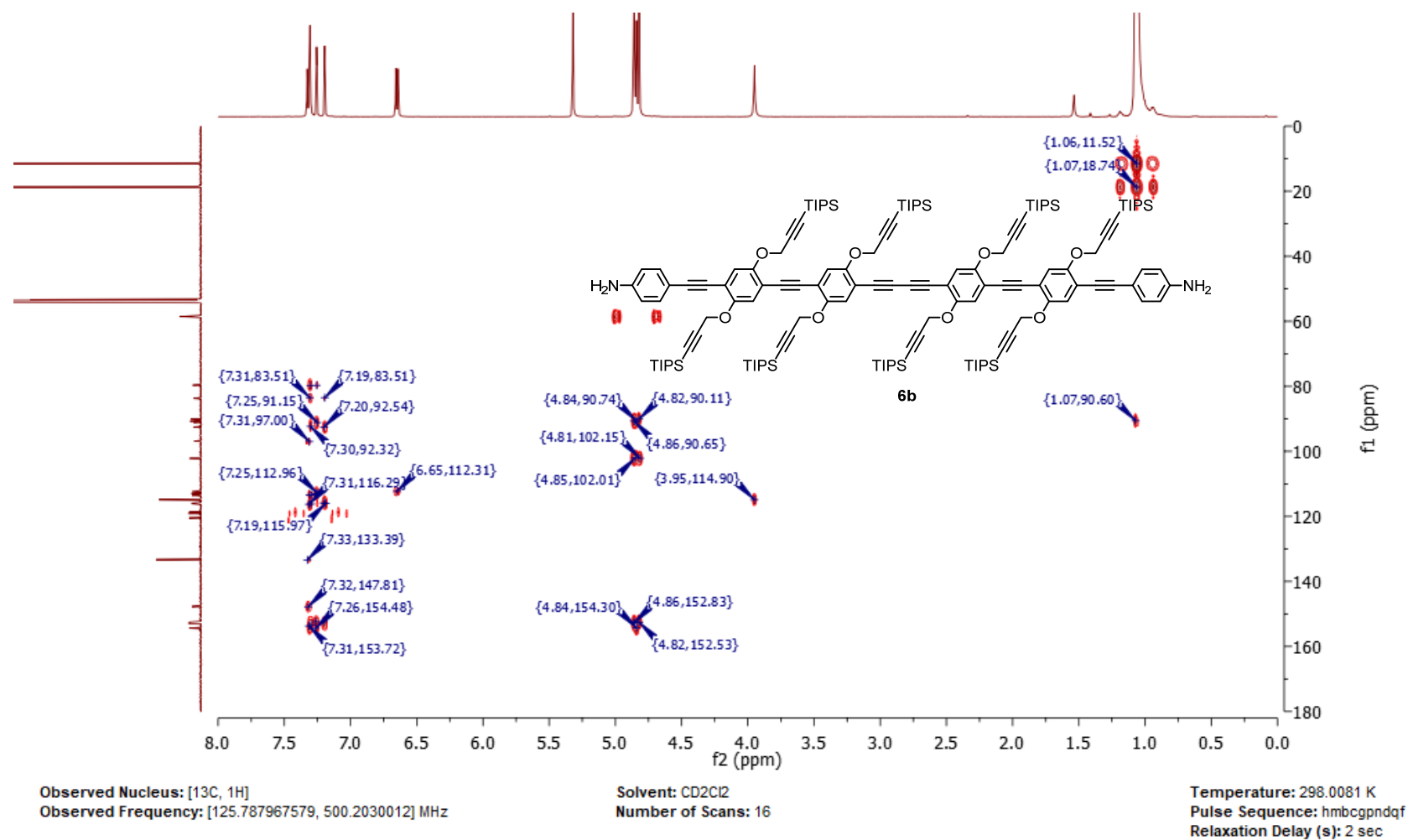
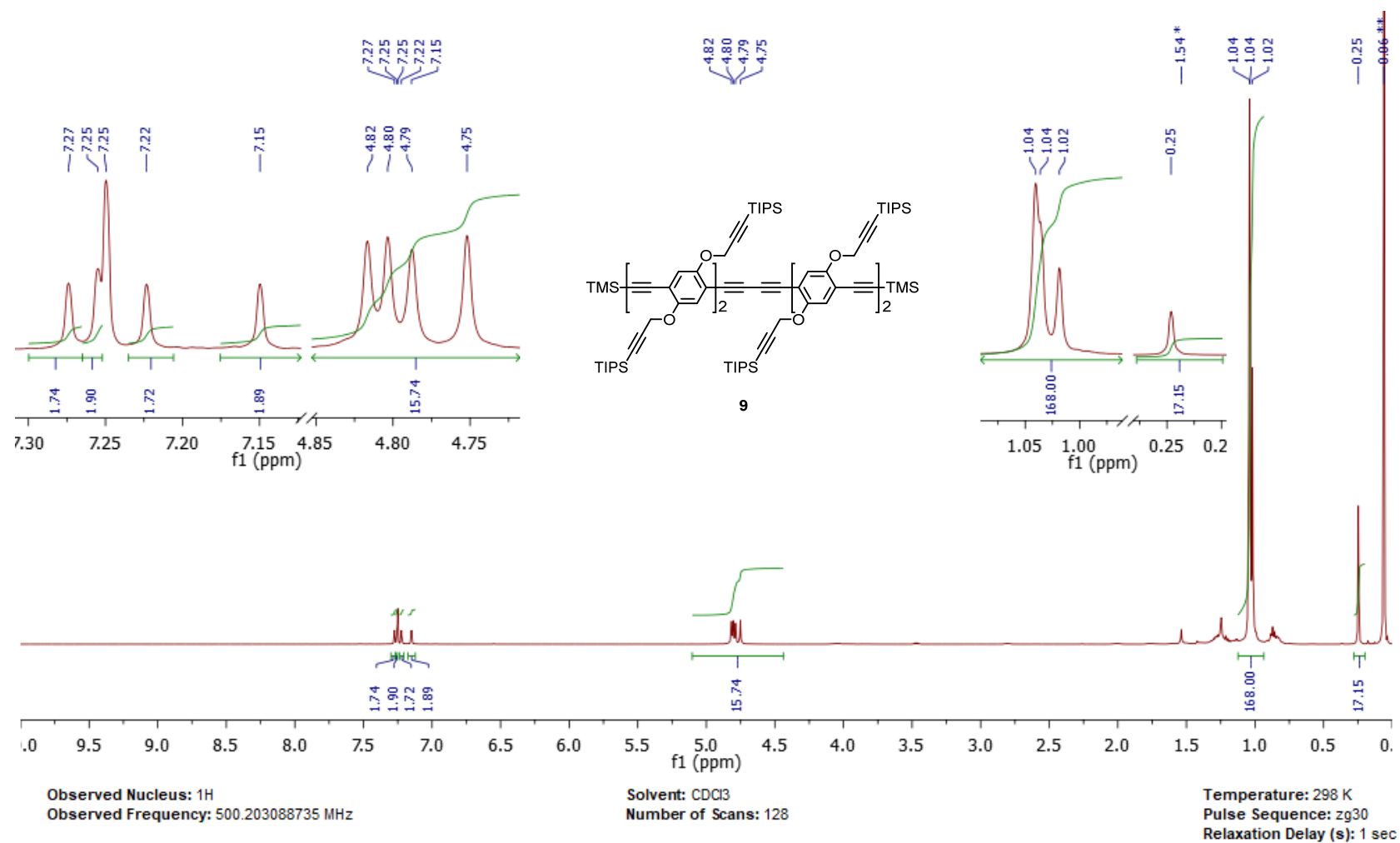**Figure S30.** HMBC NMR spectrum of H₂N-P(EP)₂B(PE)₂P-NH₂ **6b**.

Figure S31. ¹H NMR spectrum of alkyne dimer **9**. *H₂O, **grease.

Observed Nucleus: 1H
Observed Frequency: 500.203088735 MHz

Solvent: CDCl3
Number of Scans: 128

Temperature: 298 K
Pulse Sequence: zg30
Relaxation Delay (s): 1 sec