

**Synthesis of π -extended and bowl-shaped sumanene-ferrocene
conjugates and their application in highly selective and sensitive
cesium cations electrochemical sensors**

**ELECTRONIC SUPPLEMENTARY INFORMATION
(ESI)**

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1. Experimental section

1.1. Materials and methods

Chemical reagents and solvents for the synthesis were commercially purchased and purified according to the standard methods, if necessary. Thin layer chromatography (TLC) and preparative thin layer chromatography (PTLC) were performed using Merck Silica gel 60 F254 plates.

The NMR experiments were carried out using a Varian VNMRs 500 MHz spectrometer (^1H NMR at 500 MHz, $^{13}\text{C}\{^1\text{H}\}$ NMR at 125 MHz) equipped with a multinuclear z-gradient inverse probe head. The spectra were recorded at 25 °C and standard 5 mm NMR tubes were used. ^1H chemical shifts (δ) were reported in parts per million (ppm) relative to the solvent signal, *i.e.*, CDCl_3 : δ_{H} (residual CHCl_3) 7.26 ppm, δ_{C} (residual CHCl_3) 77.2 ppm, $\text{THF-}d_6$: δ_{H} (residual THF) 3.58 ppm, C_6D_6 : δ_{H} (residual benzene) 7.16 ppm, $\text{DMSO-}d_6$: δ_{H} (residual DMSO) 2.50 ppm, δ_{C} (residual DMSO) 39.5 ppm. NMR spectra were analyzed with the MestReNova v12.0 software (Mestrelab Research S.L).

ESI-HRMS (TOF) measurements were performed with a Q-Exactive ThermoScientific spectrometer.

UV-vis measurements were performed with the PerkinElmer VWR 1600-PC spectrometer, at room temperature in quartz cuvette of 1 cm length of optical window. For the UV-Vis measurements, the wavelengths for the absorption maxima λ_{max} were reported in nm. Spectrofluorimetric analyzes were performed with a Hitachi F-7100 fluorescence spectrophotometer with the spectral resolution of 1 nm, the wavelengths for the emission maxima were reported in nm.

1.2. Synthesis of sumanene (1)

Sumanene (1) was synthesized following a literature procedure.¹

^1H NMR (CDCl_3 , 500 MHz, ppm), δ_{H} 7.10 (s, 6H), 4.72 (d, $^2J_{\text{H-H}} = 18.1$ Hz, 3H), 3.42 (d, $^2J_{\text{H-H}} = 18.1$ Hz, 3H).

1.3. Synthesis of ferrocenemethylazide (9)

Ferrocenemethylazide (9) was synthesized from ferrocenemethylalcohol following a literature procedure.²

^1H NMR (CDCl_3 , 500 MHz, ppm), δ_{H} 4.24-4.23 (t-like m, $^3J_{\text{H-H}} = 1.8$ Hz, 2H), 4.21-4.20 (t-like m, $^3J_{\text{H-H}} = 1.8$ Hz, 2H), 4.18 (s, 5H), 4.11 (s, 2H).

1.4. Synthesis of 1,3,5-tris(4-iodophenyl)benzene (13)

1,3,5-Tris(4-iodophenyl)benzene (13) was synthesized by means of the thionyl chloride catalyzed trimerization of 4-iodoacetophenone following a literature procedure.³

^1H NMR (CDCl_3 , 500 MHz, ppm), δ_{H} 7.82-7.80 (m, 6H), 7.68 (s, 3H), 7.41-7.39 (m, 6H).

1.5. Synthesis of 1,3,5-tris(4-ethynylphenyl)benzene (15)

1,3,5-Tris(4-ethynylphenyl)benzene (14) was synthesized in the two-step process following a literature procedure.^{4,5} 1,3,5-Tris[4'-[(trimethylsilyl)ethynyl]phenyl]benzene was firstly synthesized from 1,3,5-tris(4-iodophenyl)benzene (13) by Sonogashira

cross-coupling with the use of trimethylsilylacetylene, and the subsequent basic hydrolysis of this intermediate product provided target 1,3,5-tris(4-ethynylphenyl)benzene (**14**).

1,3,5-tris[4'-[(trimethylsilyl)ethynyl]phenyl]benzene:

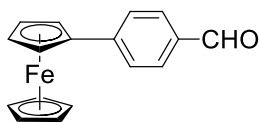
¹H NMR (CDCl₃, 500 MHz, ppm), δ_H 7.75 (s, 3H), 7.64-7.62 (m, 6 H), 7.58-7.56 (m, 6H), 0.28 (s, 27H).

1,3,5-tris(4-ethynylphenyl)benzene (15):

¹H NMR (CDCl₃, 500 MHz, ppm), δ_H 7.76 (s, 13H), 7.67-7.64 (m, 6 H), 7.62-7.60 (m, 6H), 3.16 (s, 3H).

1.6. Synthesis of sumanene-ferrocene conjugate sumFc-1

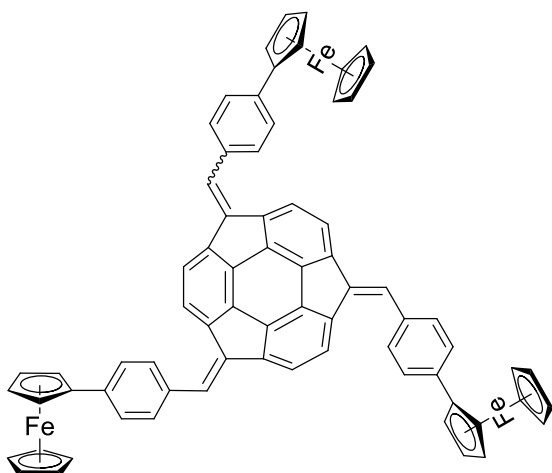
Synthesis of 4-(formylphenyl)ferrocene⁶ (**4**)



To a solution of ferroceneboronic acid (**2**; 200.0 mg, 0.87 mmol, 1 eq), 4-bromobenzaldehyde (**3**; 643.9 mg, 3.5 mmol, 4 eq), and tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄; 100.5 mg, 0.09 mmol, 0.1 eq) in toluene (12 mL) and THF (5 mL), 2M K₂CO₃ aq (2 mL) was added. The reaction mixture was refluxed for 48 hours. Distilled water (6 mL) was added, and the crude product was extracted with CH₂Cl₂ (3x20 mL). Organic layers were combined, washed with water, and brine. After drying with MgSO₄ followed by filtration, volatiles were distilled off on a rotary evaporator. Finally, the product was purified using a column chromatography (SiO₂, 10% AcOEt/hex) to provide 4-(formylphenyl)ferrocene (**4**) as a red solid (192.5 mg, 63%).

¹H NMR (CDCl₃, 500 MHz, ppm), δ_H 9.97 (s, 1H), 7.81-7.78 (m, 2H), 7.61-7.59 (m, 2H), 4.75-4.74 (t-like m, ³J_{H-H} = 1.9 Hz, 2H), 4.44-4.43 (t-like m, ³J_{H-H} = 1.9 Hz, 2H), 4.05 (s, 5H); R_f (10% AcOEt/hex) = 0.62. The NMR data are consistent with the literature.⁶

Synthesis of sumanene-ferrocene conjugate sumFc-1

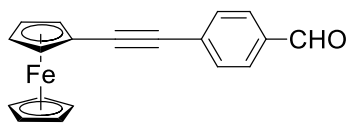


Sumanene (**1**; 10.0 mg, 0.038 mmol, 1 eq) was placed in a test tube. Tetrabutylammonium bromide (TBAB; 6.1 mg, 0.019 mmol, 0.5 eq) was added, followed by the addition of THF (0.2 mL) and NaOH_{aq} (30%; 2 mL). The reaction mixture was stirred for 5 min at 27°C. Solid 4-(formylphenyl)ferrocene (**4**; 69.0 mg, 0.23 mmol, 6 eq) was added in one portion, and the reaction mixture was stirred for 48 hours at 27°C. Distilled water (6 mL) was added, and the crude product was extracted with CH₂Cl₂ (3x20 mL). Organic layers were combined, washed with saturated NH₄Cl, water, and brine. After drying with MgSO₄ followed by filtration, volatiles were distilled off on a rotary evaporator. Finally, the product was purified using a column chromatography (SiO₂, 50% CH₂Cl₂/cyclohexane) to provide the target sumanene-ferrocene conjugate **sumFc-1** as a deep-red solid (27.2 mg, 60%).

¹H NMR (CDCl₃, 500 MHz, ppm), δ_H 7.88-7.78 (m, 6H), 7.62-7.50 (m, 8H), 7.40-7.34 (m, 5.5H), 7.23-7.18 (m, 1.5H), 4.76-4.74 (m, 3H), 4.70-4.68 (m, 3H), 4.41-4.40 (m, 3H), 4.36-4.35 (m, 3H), 4.12-4.06 (4xs, 15H); ¹³C{¹H} NMR (CDCl₃, 125 MHz, ppm), δ_C 147.9, 147.7, 147.5, 147.5, 147.3x2, 146.1, 145.9, 145.6, 145.5, 145.3, 145.2, 143.4, 143.2, 141.6, 141.3, 140.7, 140.6, 140.5, 139.9, 139.8x2, 139.7, 134.0, 133.9, 133.9, 133.8, 132.0x2, 131.3x2, 130.0x4, 128.7, 128.5, 128.4, 128.2, 126.3x3, 123.8, 123.6, 123.5, 123.4x2, 121.9, 120.8, 120.7, 120.6, 84.7x3, 84.6, 70.0., 69.6, 69.5, 66.8, 66.7x2; ESI-HRMS (TOF): calcd. for C₇₂H₄₈Fe₃ [M]⁺ = 1080.1799, found: m/z 1080.1791; UV-Vis, λ_{max} (CHCl₃:CH₃OH = 1:1 v/v) 275, 365, 510 nm; R_f (50% CH₂Cl₂/cyclohexane) = 0.47.

1.7. Synthesis of sumanene-ferrocene conjugate sumFc-2

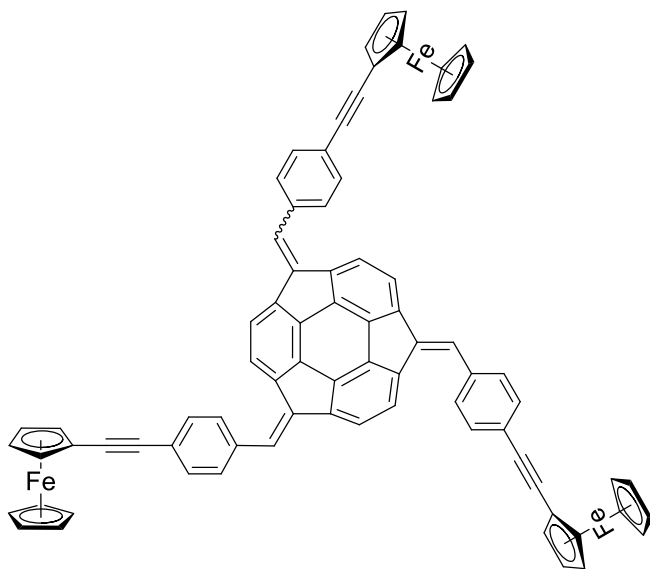
Synthesis of 4-(ferrocenylethynyl)benzaldehyde (**7**)



4-Iodobenzaldehyde (**6**; 152.3 mg, 0.66 mmol, 1 eq), bis(triphenylphosphine)palladium(II) dichloride ($\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$; 23.2 mg; 0.033 mmol, 0.05 eq), and copper(I) iodide (CuI ; 13.0 mg; 0.066 mmol, 0.10 eq) were added to a reaction flask. The content of the tube was evacuated and filled with argon. Triethylamine (TEA; 30 mL) was added, and the mixture was stirred for 15 min at 60°C under argon atmosphere. A solution of ethynylferrocene (**5**; 205.0 mg; 0.98 mmol, 1.5 eq) in TEA (15 mL) was added via syringe. The reaction mixture was stirred for 24 hours at 60°C under argon atmosphere. Distilled water (40 mL) was added, and the crude product was extracted with CH_2Cl_2 (3x20 mL). Organic layers were combined, washed with 1M HCl (5x10 mL), and water. After drying with MgSO_4 followed by filtration, volatiles were distilled off on a rotary evaporator. Finally, the product was purified using a column chromatography (SiO_2 , 30% hex/ CHCl_3) to provide 4-(ferrocenylethynyl)benzaldehyde (**7**) as a red solid (173.8 mg, 84%).

^1H NMR (CDCl_3 , 500 MHz, ppm) δ_{H} 10.01 (s, 1H), 7.85-7.82 (m, 2H), 7.63-7.61 (m, 2H), 4.54-4.54 (t-like m, $^3J_{\text{H-H}} = 1.8$ Hz, 2H), 4.30-4.30 (t-like m, $^3J_{\text{H-H}} = 1.8$ Hz, 2H), 4.26 (s, 5H); R_f (30% hex/ CHCl_3) = 0.46. The NMR data are consistent with the literature.⁷

Synthesis of sumanene-ferrocene conjugate sumFc-2 by the reaction between sumanene (**1**) and 4-(ferrocenylethynyl)benzaldehyde (**7**)



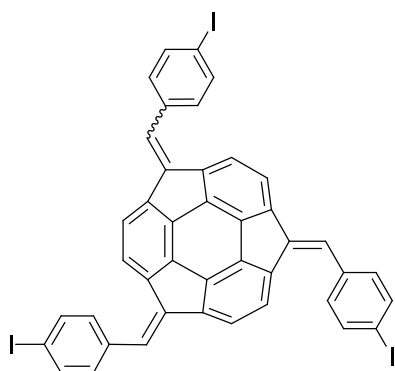
Sumanene (**1**; 10.0 mg, 0.038 mmol, 1 eq) was placed in a test tube. TBAB (6.1 mg, 0.019 mmol, 0.5 eq) was added, followed by the addition of THF (0.2 mL) and NaOH_{aq} (30%; 2 mL). The reaction mixture was stirred for 5 min at 27°C. Solid 4-(ferrocenylethynyl)benzaldehyde (**7**; 71.5 mg, 0.23 mmol, 6 eq) was added in one portion, and the reaction mixture was stirred for 48 hours at 27°C. Distilled water (6 mL) was added, and the crude product was extracted with CH_2Cl_2 (3x20 mL). Organic layers were combined,

washed with saturated NH_4Cl , water, and brine. After drying with MgSO_4 followed by filtration, volatiles were distilled off on a rotary evaporator. Finally, the product was purified using a column chromatography (SiO_2 , 50% CH_2Cl_2 /hexane) to provide the target sumanene-ferrocene conjugate **sumFc-2** as a deep-red solid (39.4 mg, 86%).

^1H NMR ($\text{THF}-d_6$, 500 MHz, ppm) δ_{H} 7.95-7.88 (m, 6H), 7.58-7.51 (m, 10H), 7.47-7.47 (m, 2H), 7.30-7.29 (m, 3H), 4.54-4.53 (m, 3H), 4.50-4.50 (m, 3H), 4.30-4.28 (m, 3H), 4.27-4.25 (m, 11H), 4.23-4.22 (2xs, 7H); ^1H NMR (CDCl_3 , 500 MHz, ppm) δ_{H} 7.90-7.80 (m, 6H), 7.61-7.52 (m, 6H), 7.50-7.47 (m, 1.5H), 7.38-7.34 (m, 5H), 7.26 (s, 1H), 7.18-7.15 (m, 1.5H), 4.56-4.55

(m, 3H), 4.53-4.52 (m, 3H), 4.30-4.28 (m, 11H), 4.27-4.25 (m, 10H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 125MHz, ppm) δ_{C} 147.7, 147.6, 147.4, 147.3, 146.0, 145.7, 145.4, 143.4, 143.1, 141.5, 141.3, 140.9, 140.8x2, 140.7, 135.7, 135.6x2, 135.5, 131.7x4, 129.8x4, 128.2, 128.0, 127.9, 127.6, 124.5x2, 124.4x2, 123.9, 123.7, 123.6, 123.5, 123.4, 121.1x2, 121.0, 121.8, 90.7, 90.6x3, 86.1x2, 86.0x2, 71.7x2, 70.2x2, 69.2, 69.1, 65.2x3, 61.1; ESI-HRMS (TOF): calcd. for $\text{C}_{78}\text{H}_{48}\text{Fe}_3[\text{M}]^+$ = 1152.1799, found: m/z 1152.1787; UV-Vis, λ_{max} ($\text{CHCl}_3:\text{CH}_3\text{OH} = 1:1$ v/v) 260, 370, 500 nm; R_f (50% $\text{CH}_2\text{Cl}_2/\text{hex}$) = 0.55.

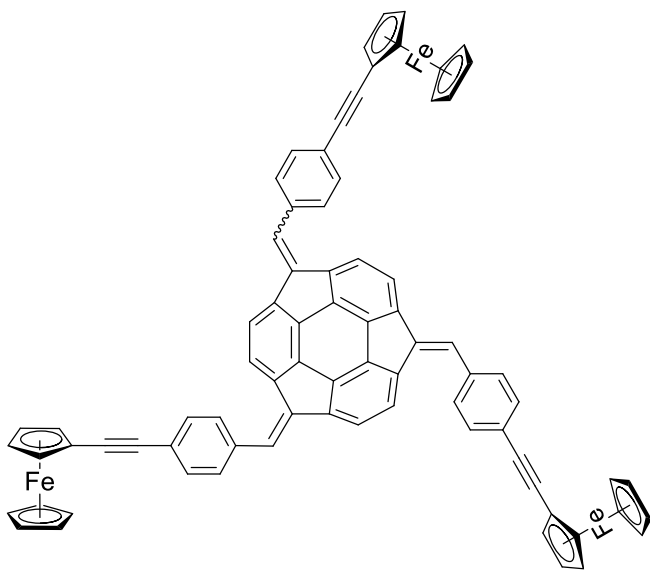
Synthesis of tris[(4-iodophenyl)methidene]sumanene (**8a**)



Sumanene (**1**; 10.0 mg, 0.038 mmol, 1 eq) was placed in a test tube. TBAB (6.1 mg, 0.019 mmol, 0.5 eq) was added, followed by the addition of THF (0.2 mL) and NaOH_{aq} (30%; 2 mL). The reaction mixture was stirred for 5 min at 27°C. Solid 4-iodobenzaldehyde (**6a**; 54.3 mg, 0.23 mmol, 6 eq) was added in one portion, and the reaction mixture was stirred for 48 hours at 27°C. Distilled water (6 mL) was added, and the crude product was extracted with CH_2Cl_2 (3x20 mL). Organic layers were combined, washed with saturated NH_4Cl , water, and brine. After drying with MgSO_4 followed by filtration, volatiles were distilled off on a rotary evaporator. Finally, the product was purified using a column chromatography (SiO_2 , 50% $\text{CH}_2\text{Cl}_2/\text{hexane}$) to provide tris[(4-iodophenyl)methidene]sumanene (**8a**) as an orange solid (21.4 mg, 62%).

^1H NMR (CDCl_3 , 500 MHz, ppm) δ_{H} 7.81-7.74 (m, 6H), 7.63-7.53 (m, 6H), 7.38-7.35 (m, 2H), 7.31-7.26 (m, 3H), 7.24 (s, 1H), 7.13-7.10 (m, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 125MHz, ppm) δ_{C} 149.3, 149.2; 149.1, 148.9, 147.7x2, 147.6, 147.4x2, 147.3x2, 145.9, 145.7, 145.5, 145.4x2, 143.2, 143.0, 141.5, 141.2, 141.1, 141.0, 138.0x2, 135.9, 135.8, 135.7, 135.6, 131.4x2, 127.6, 127.3x2, 127.0, 123.8, 123.6x2, 123.4, 121.2, 121.1, 121.0, 120.9, 94.9, 94.8, 94.7x2; ESI-HRMS (TOF): calcd. for $\text{C}_{42}\text{H}_{21}\text{I}_3[\text{M}]^+$ = 905.8772, found: m/z 905.8760; R_f (50% $\text{CH}_2\text{Cl}_2/\text{hex}$) = 0.51.

Synthesis of sumanene-ferrocene conjugate *sumFc-2* by the Sonogashira cross-coupling between tris[(4-iodophenyl)methidene]sumanene (8a**) and ethynylferrocene (**5**)**

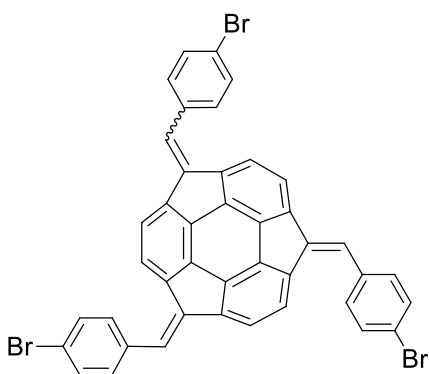


Tris[(4-iodophenyl)methidene]-sumanene (**8**; 15.0 mg, 0.02 mmol, 1 eq), Pd(PPh₃)₂Cl₂ (2.2 mg; 0.003 mmol, 0.15 eq), and CuI (1.2 mg; 0.006 mmol, 0.3 eq) were added to a reaction flask. The content of the tube was evacuated and filled with argon. TEA (5 mL) was added, and the mixture was stirred for 15 min at 60°C under argon atmosphere. A solution of ethynylferrocene (**5**; 17.0 mg; 0.08 mmol, 4 eq) in TEA (2.5 mL) was added via syringe. The reaction mixture was stirred for 24 hours at 60°C under argon atmosphere.

Distilled water (10 mL) was added, and the crude product was extracted with CH₂Cl₂ (3x20 mL). Organic layers were combined, washed with 1M HCl (3x10 mL), and water. After drying with MgSO₄ followed by filtration, volatiles were distilled off on a rotary evaporator. Finally, the product was purified using a column chromatography (SiO₂, 50% hex/CHCl₃) to provide the target sumanene-ferrocene conjugate **sumFc-2** as a deep-red solid (21.5 mg, 95%).

The spectral data for **sumFc-2** obtained with this method conformed to that presented above.

Synthesis of tris[(4-bromophenyl)methidene]sumanene (8b**)**



Sumanene (**1**; 10.0 mg, 0.038 mmol, 1 eq) was placed in a test tube. TBAB (6.1 mg, 0.019 mmol, 0.5 eq) was added, followed by the addition of THF (0.2 mL) and NaOH_{aq} (30%; 2 mL). The reaction mixture was stirred for 5 min at 27°C. Solid 4-bromobenzaldehyde (**6b**; 42.6 mg, 0.23 mmol, 6 eq) was added in one portion, and the reaction mixture was stirred for 48 hours at 27°C. Distilled water (6 mL) was added, and the crude product was extracted with CH₂Cl₂ (3x20 mL). Organic layers were combined, washed with saturated NH₄Cl,

water, and brine. After drying with MgSO₄ followed by filtration, volatiles were distilled off on a rotary evaporator. Finally, the product was purified using a column chromatography (SiO₂, 50% CH₂Cl₂/hexane) to provide tris[(4-bromophenyl)methidene]sumanene (**8b**) as an orange solid 17.4 mg, 60%).

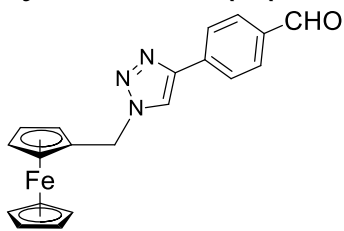
¹H NMR (CDCl₃, 500 MHz, ppm) δ_H 7.78-7.68 (m, 6H), 7.62-7.54 (m, 6H), 7.39-7.32 (m, 6H), 7.16-7.13 (m, 3H); ¹³C{¹H} NMR (CDCl₃, 125MHz, ppm) δ_C 147.7x2, 147.5, 147.4x2, 146.0, 145.8, 145.6, 145.5x2, 143.3, 143.0, 141.5, 141.3, 141.1, 141.0, 135.3, 135.2x2, 135.1, 132.1, 132.0, 131.3x2, 127.5, 127.3, 127.2, 127.0, 123.8, 123.7, 123.6, 123.4, 123.1, 123.0x2, 121.2,

121.2, 121.1, 121.0; ESI-HRMS (TOF): calcd. for $C_{42}H_{21}Br_3 [M]^+$ = 763.9167, found: m/z 763.9155; R_f (50% CH_2Cl_2 /hex) = 0.68.

The **sumFc-2** synthesis yield starting from tris[(4-bromophenyl)methidene]sumanene (**8b**) and ethynylferrocene (**5**) was 52%.

1.8. Synthesis of sumanene-ferrocene conjugate sumFc-3

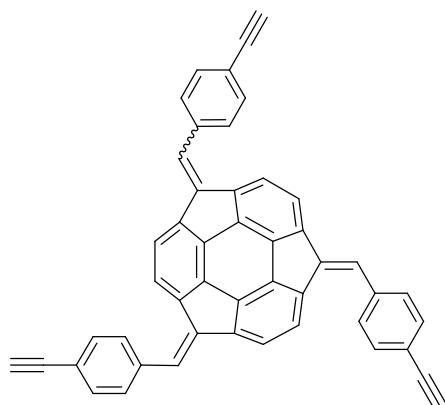
Synthesis of 4-(1-(ferrocenylmethyl)-1*H*-1,2,3-triazol-4-yl)benzaldehyde (**11**)



Ferrocenemethylazide (**9**; 241.0 mg, 1.0 mmol, 1 eq), 4-ethynylbenzaldehyde (**10**; 130.1 mg, 1.0 mmol, 1 eq), copper(II) sulphate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$; 62.4 mg, 0.25 mmol, 0.25 eq) and sodium ascorbate (148.6 mg, 0.75 mmol, 0.75 eq) were placed in a reaction flask. DMF (40 mL) was added. The reaction mixture was stirred for 24 hours at 50°C. Distilled water (100 mL) was added, and the formed precipitate was filtrated on a nylon membrane (0.45 μm). The resultant solid was dissolved in CHCl_3 (50 mL). After drying with MgSO_4 followed by filtration, volatiles were distilled off on a rotary evaporator. Finally, the product was purified using a column chromatography (SiO_2 , CHCl_3) to provide 4-(1-(ferrocenylmethyl)-1*H*-1,2,3-triazol-4-yl)benzaldehyde (**11**) as a yellow solid (280.0 mg, 75%).

^1H NMR (CDCl_3 , 500 MHz, ppm), δ_{H} 10.01 (s, 1H), 7.97-7.95 (m, 2H), 7.92-7.90 (m, 2H), 7.74 (s, 1H), 5.37 (s, 1H), 4.33-4.32 (t-like m, $^3J_{\text{H-H}} = 1.9$ H, 2H), 4.26-4.25 (t-like m, $^3J_{\text{H-H}} = 1.9$ H, 2H), 4.22 (s, 5H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 125 MHz, ppm), δ_{C} 191.8, 146.5, 136.6, 135.9, 130.5, 126.1, 120.2, 80.5, 69.5, 69.2x2, 50.5; ESI-HRMS (TOF): calcd. for $\text{C}_{20}\text{H}_{17}\text{FeN}_3\text{O}$ $[\text{M}]^+$ = 371.0716, found: m/z 371.0711; R_f (CHCl_3) = 0.40.

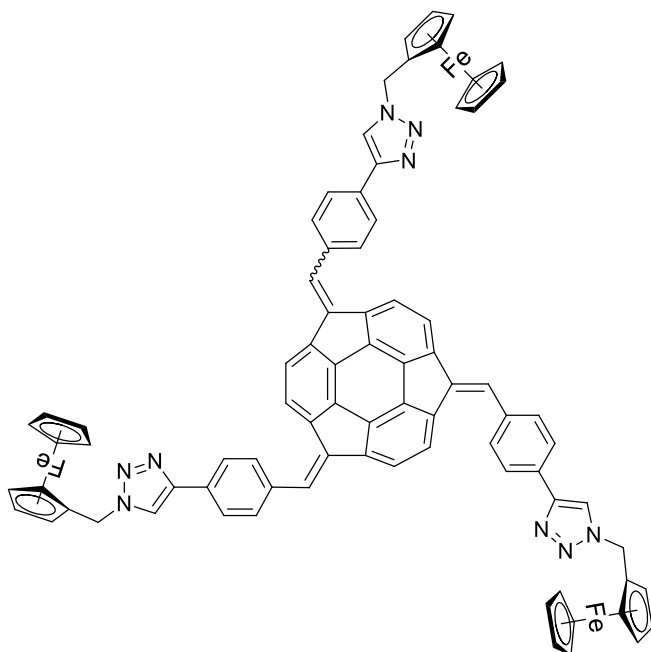
Synthesis of tris[(4-ethynylphenyl)methidene]sumanene (**12**)



Sumanene (**1**; 20.0 mg, 0.076 mmol, 1 eq) was placed in a test tube. TBAB (12.2 mg, 0.038 mmol, 0.5 eq) was added, followed by the addition of THF (0.4 mL) and NaOH_{aq} (30%; 4 mL). The reaction mixture was stirred for 5 min at 27°C. Solid 4-ethynylbenzaldehyde (**10**; 59.1 mg, 0.456 mmol, 6 eq) was added in one portion, and the reaction mixture was stirred for 48 hours at 27°C. Distilled water (6 mL) was added, and the crude product was extracted with CH_2Cl_2 (3x20 mL). Organic layers were combined, washed with saturated NH_4Cl , water, and brine. After drying with MgSO_4 followed by filtration, volatiles were distilled off on a rotary evaporator. Finally, the product was purified using a column chromatography (SiO_2 , 50% CH_2Cl_2 /hexane) to provide tris[(4-ethynylphenyl)methidene]sumanene (**12**) as a red solid (22.9 mg, 50%).

^1H NMR (CDCl_3 , 500 MHz, ppm) δ_{H} 7.88-7.78 (m, 6H), 7.61-7.53 (m, 6H), 7.41-7.33 (m, 6H), 7.16-7.15 (m, 3H), 3.21-3.17 (4xs, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 125MHz, ppm) δ_{C} 147.8, 147.7, 147.6, 147.4x2, 147.3, 146.0, 145.7x2, 145.6, 145.4x2, 143.3, 143.0, 141.5, 141.3x2, 141.2x2, 136.9, 136.8x2, 136.7, 132.6, 132.5x3, 129.7x4, 127.8, 127.6, 127.5, 127.3, 123.9, 123.7, 123.6, 123.5, 122.5x2, 122.4x2, 121.2, 121.1, 121.0, 120.9, 83.7x3, 83.6, 78.9, 78.8x3; ESI-HRMS (TOF): calcd. for $\text{C}_{48}\text{H}_{24}$ $[\text{M}]^+$ = 600.1873, found: m/z 600.1872; R_f (3% $\text{CH}_3\text{OH}/\text{CHCl}_3$) = 0.50.

Synthesis of sumanene-ferrocene conjugate *sumFc-3* by the click chemistry between tris[(4-ethynylphenyl)methidene]sumanene (12) and ferrocenemethylazide (9)

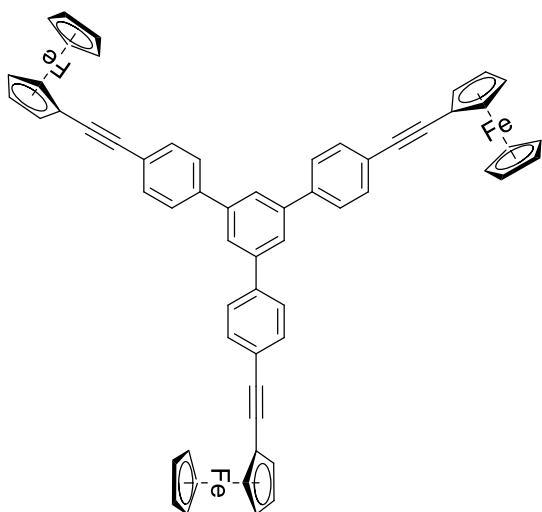


Ferrocenemethylazide (**9**; 12.5 mg, 0.052 mmol, 3 eq), tris[(4-ethynylphenyl)methidene]sumanene (**12**; 10.0 mg, 0.017 mmol, 1 eq), $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (6.2 mg, 0.025 mmol, 1.5 eq) and sodium ascorbate (14.9 mg, 0.075 mmol, 4 eq) were placed in a reaction flask. DMF (4 mL) was added. The reaction mixture was stirred for 48 hours at 50°C. Distilled water (15 mL) was added, and the formed precipitate was filtrated on a nylon membrane (0.45 μm). The resultant solid was dissolved in CHCl_3 (30 mL). After drying with MgSO_4 followed by filtration, volatiles were distilled off on a rotary evaporator.

Finally, the product was purified using a column chromatography (SiO_2 , 5% $\text{CH}_3\text{OH}/\text{CHCl}_3$) to provide the target sumanene-ferrocene conjugate **sumFc-3** as a deep-red solid (16.6 mg, 74%).

^1H NMR (CDCl_3 , 500 MHz, ppm), δ_{H} 7.91-7.80 (m, 12H), 7.79 (s, 1H), 7.75 (s, 1H), 7.70-7.69 (2xs, 1H), 7.44-7.38 (m, 1.5H), 7.32-7.27 (m, 4H), 7.23 (s, 1H), 7.17-7.17 (m, 1H), 7.08-7.04 (m, 1.5H), 5.37-5.34 (4xs, 6H), 4.36-4.35 (m, 3H), 4.33-4.32 (m, 3H), 4.26-4.24 (m, 6H), 4.23-4.21 (4xs, 15H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 125 MHz, ppm), δ_{C} 147.6, 147.4x3, 147.3, 147.1, 147.0x2, 145.8, 145.4x2, 145.3, 145.1, 144.0, 143.2, 142.9, 141.3, 140.7, 140.6x3, 140.4, 136.1x2, 136.0x2, 131.0x2, 130.9x2, 130.3x2, 128.1, 127.9, 127.7, 127.6, 125.9x3, 123.7, 123.6, 123.5, 123.2, 120.9, 120.8x2, 120.7, 119.8, 119.6x2, 119.5, 81.1, 81.0x2, 80.9, 69.3, 69.1, 50.4x2, 50.3; ESI-HRMS (TOF): calcd. for $\text{C}_{81}\text{H}_{57}\text{Fe}_3\text{N}_9$ $[\text{M}]^+$ = 1323.2780, found: m/z 1323.2780; UV-Vis, λ_{max} (CHCl_3 : CH_3OH = 1:1 v/v) 278, 380, 480 nm; R_f (50% CH_2Cl_2 /hex) = 0.60.

1.9. Synthesis of 1,3,5-triphenylbenzene-ferrocene conjugate **14**

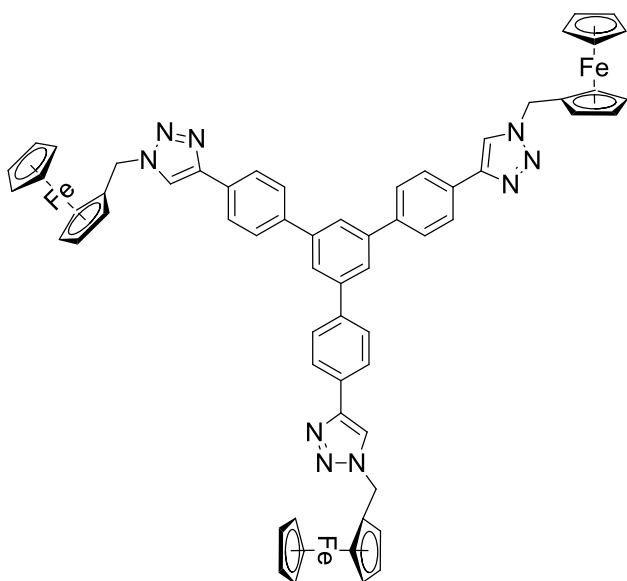


1,3,5-Tris(4-iodophenyl)benzene (**13**; 50.0 mg; 0.079 mmol, 1 eq), Pd(PPh₃)₂Cl₂ (7.7 mg; 0.011 mmol, 0.15 eq), and CuI (4.2 mg; 0.024 mmol, 0.30 eq) were added to a reaction flask. The content of the tube was evacuated and filled with argon. Triethylamine (TEA; 10 mL) was added, and the mixture was stirred for 15 min at 60°C under argon atmosphere. A solution of ethynylferrocene (**5**; 61.3 mg; 0.316 mmol, 4.0 eq) in TEA (5 mL) was added via syringe. The reaction mixture was stirred for 24 hours at 60°C under argon atmosphere. Distilled water (6 mL) was added, and the crude product was extracted with CH₂Cl₂

(3x20 mL). Organic layers were combined, washed with 1M HCl (4x15 mL), and water. After drying with MgSO₄ followed by filtration, volatiles were distilled off on a rotary evaporator. Finally, the product was purified using a column chromatography (SiO₂, 50% hex/CH₂Cl₂), and further with preparative thin layer chromatography (PTLC; SiO₂, 50% hex/CH₂Cl₂) to provide 1,3,5-triphenylbenzene-ferrocene conjugate (**14**) as a red solid (58.1 mg, 80%).

¹H NMR (CDCl₃, 500 MHz, ppm), δ_H 7.80 (s, 3H), 7.69-7.67 (m, 6H), 7.62-7.60 (m, 6H), 4.54-4.54 (t-like m, ³J_{H-H} = 1.8 H, 6H), 4.27-4.25 (m, 21H); ¹H NMR (C₆D₆, 500 MHz, ppm), δ_H 7.70-7.69 (m, 6H), 7.60 (s, 3H), 7.37-7.36 (m, 6H), 4.56-4.45 (t-like m, ³J_{H-H} = 1.8 H, 6H), 4.12 (s, 15H), 3.98-3.97 (t-like m, ³J_{H-H} = 1.8 H, 6H); 142.0, 140.2, 132.0, 127.3, 125.1, 123.5, 89.6, 85.7, 71.6, 70.2, 69.1, 65.4; ESI-HRMS (TOF): calcd. for C₆₀H₄₂Fe₃ [M]⁺ = 930.1329, found: m/z 930.1332; UV-Vis, λ_{max} (CHCl₃:CH₃OH = 1:1 v/v) 245, 312, 368 nm; R_f (50% hex/CH₂Cl₂) = 0.45.

1.10. Synthesis of 1,3,5-triphenylbenzene-ferrocene conjugate **16**



Ferrocenemethylazide (**9**; 71.0 mg, 0.246 mmol, 3.1 eq), 1,3,5-tris(4-ethynylphenyl)benzene (**15**; 30.0 mg, 0.079 mmol, 1 eq), CuSO₄·5H₂O (29.6 mg, 0.119 mmol, 1.5 eq) and sodium ascorbate (62.8 mg, 0.317 mmol, 4 eq) were placed in a reaction flask. DMF (8 mL) was added. The reaction mixture was stirred for 24 hours at 50°C. Distilled water (60 mL) was added, and the formed precipitate was filtrated on a nylon membrane (0.45 μm). The resultant solid was dissolved in CH₂Cl₂ (60 mL). After drying with MgSO₄ followed by filtration, volatiles were distilled off on a rotary evaporator. Finally, the product was purified using a column chromatography

(SiO₂, 3% CH₃OH/CHCl₃) to provide 1,3,5-triphenylbenzene-ferrocene conjugate **16** as a yellow solid (56.5 mg, 65%).

¹H NMR (CDCl₃, 500 MHz, ppm), δ_H 7.91-7.90 (m, 6H), 7.81 (s, 3H), 7.75-7.73 (m, 6H), 7.69 (s, 3H), 5.37 (s, 6H), 4.35-4.44 (t-like bm, ³J_{H-H} = 1.8 H, 6H), 4.26-4.25 (t-like bm, ³J_{H-H} = 1.8 H, 6H), 4.22 (s, 15H); ¹H NMR (DMSO-*d*₆, 500 MHz, ppm), δ_H 8.67 (s, 3H), 7.99-7.98 (m, 15H), 5.38 (s, 6H), 4.43-4.42 (t-like m, ³J_{H-H} = 1.9 H, 6H), 4.22-4.21 (m, 21H); ¹³C{¹H} NMR (DMSO-*d*₆, 125 MHz, ppm), δ_C 146.0, 141.1, 139.3, 130.2, 127.7, 125.6, 124.1, 121.2, 82.4, 68.8, 68.7, 68.4, 49.2; ESI-HRMS (TOF): calcd. for C₆₃H₅₁Fe₃N₉[M]⁺ = 1101.2310, found: *m/z* 1101.2316; UV-Vis, λ_{max} (CHCl₃:CH₃OH = 1:1 *v/v*) 238, 292 nm; R_f (3% CH₃OH/CHCl₃) = 0.56.

1.11. Electrochemical studies

Materials. Dichlorometane (DCM, Sigma-Aldrich), dimethyl sulfoxide (DMSO, Merck) tetrabutylammonium hexafluorophosphate (TBAPF₆, Sigma-Aldrich), tetrabutylammonium tetrafluoroborate (TBABF₄, Sigma-Aldrich), cesium nitrate (CsNO₃, Sigma-Aldrich), potassium nitrate (KNO₃, Sigma-Aldrich), sodium nitrate (NaNO₃, Sigma-Aldrich), barium nitrate (Ba(NO₃)₂, Sigma-Aldrich) and perfluorinated resin solution containing Nafion™ (nafion™, Sigma-Aldrich) were used without additional purification.

Voltammetry. The voltammetric measurements (cyclic voltammetry and differential pulse voltammetry) were performed with using an Autolab, model PGSTAT 12 potentiostat in the three-electrode system consisting of: (i) working electrode (glassy carbon disc electrode, GC; 3.0 mm in diameter, BAS, UK), (ii) reference electrode (Ag/AgCl/3 M KCl) and (iii) counter electrode (Pt plate with surface area at least 1 cm²). Each time, before the measurements or electrode modification, the surface of the working electrode was mechanically cleaned by polishing on a wet pad with addition a 1 μm Al₂O₃ powder. Then, the electrode was rinsed with a direct stream of ultrapure water (Hydrolab, conductivity of ~ 0.056 μS·cm⁻¹) to remove residue of alumina. In all experiments, the electrochemical cell was kept in a Faraday cage to minimize the electrical noise.

Preparation of recognition layers (GC/sumFc-TBAPF₆-nafion™). Before each modification the GC electrode was oxidized in 0.1 M H₂SO₄ by cycling in the potential range -0.35 - 1.3 - -0.35 V with scan rate 100 mV·s⁻¹. The oxidation process was aimed at generating carboxyl groups involved in the immobilization of the receptor layer. Next, the surface was dried and the 10-μL droplet of 20 μM **sumFc-1 – sumFc-3** solution (CH₂Cl₂ : DMSO (1:1 v/v)) with addition of 100 mM TBAPF₆ and 5% nafion™ was placed onto the electrode surface. Then, the electrode was left to dry in the desiccator. Before the cesium cations (Cs⁺) titration the recognition layers (GC/sumFc-TBAPF₆-nafion™) were first cycled in the 50 mM TBABF₄ aqueous solution in the potential range 0.0 – 1.1 – 0. V with scan rate 100 mV·s⁻¹ until a stable voltammogram was obtained.

1.12. Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS)

Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS). The LSX-213 laser ablation system (Nd:YAG, λ= 213nm) by CETAC (USA) was coupled to ICP-MS NexION 300D spectrometer by Perkin Elmer (USA). The energy (E=3mJ) of the laser beam was focused on the surface of the analysed samples on the area with a diameter of 100 μm. Transient signals were registered for selected isotopes (²³Na, ³⁹K, ⁵⁷Fe, ¹³³Cs, ¹³⁷Ba) during a multi-line (n=3) ablation with the scan rate SR=100 μm/s; 20Hz repetition rate and time delay (10 s) between ablation of the subsequent lines. The operating conditions of the used ICP-MS system are: plasma power: 1400 W; carrier gas flow (Ar): 0.88 L·min⁻¹; sweeps: 1; readings: 24321; repeats: 1; dwell time: 1 ms.

2. NMR spectra

2.1. Spectra

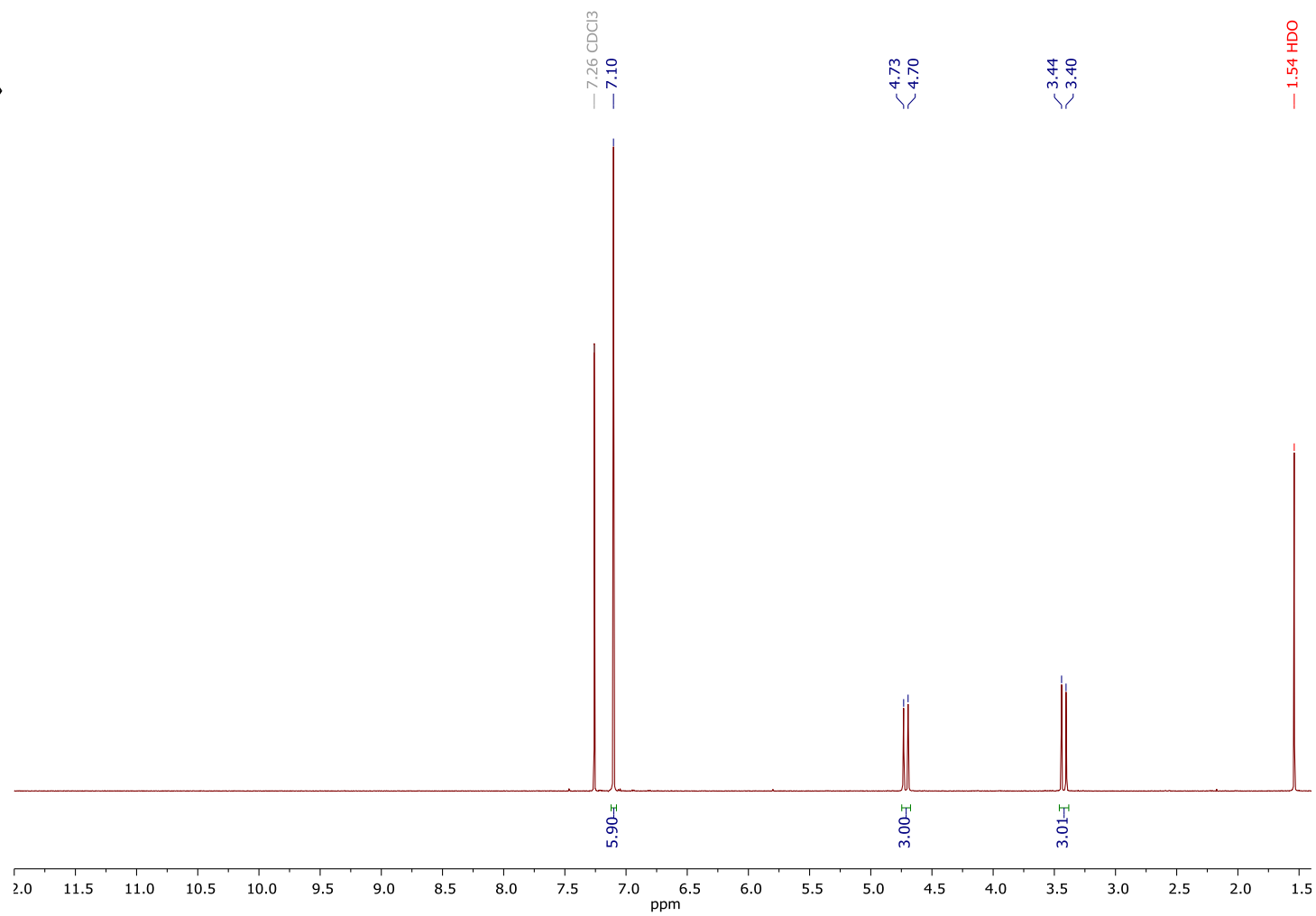
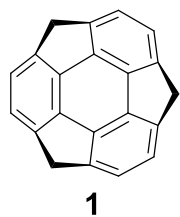


Figure S1. ¹H NMR (500 MHz, CDCl₃) spectrum of sumanene (**1**).

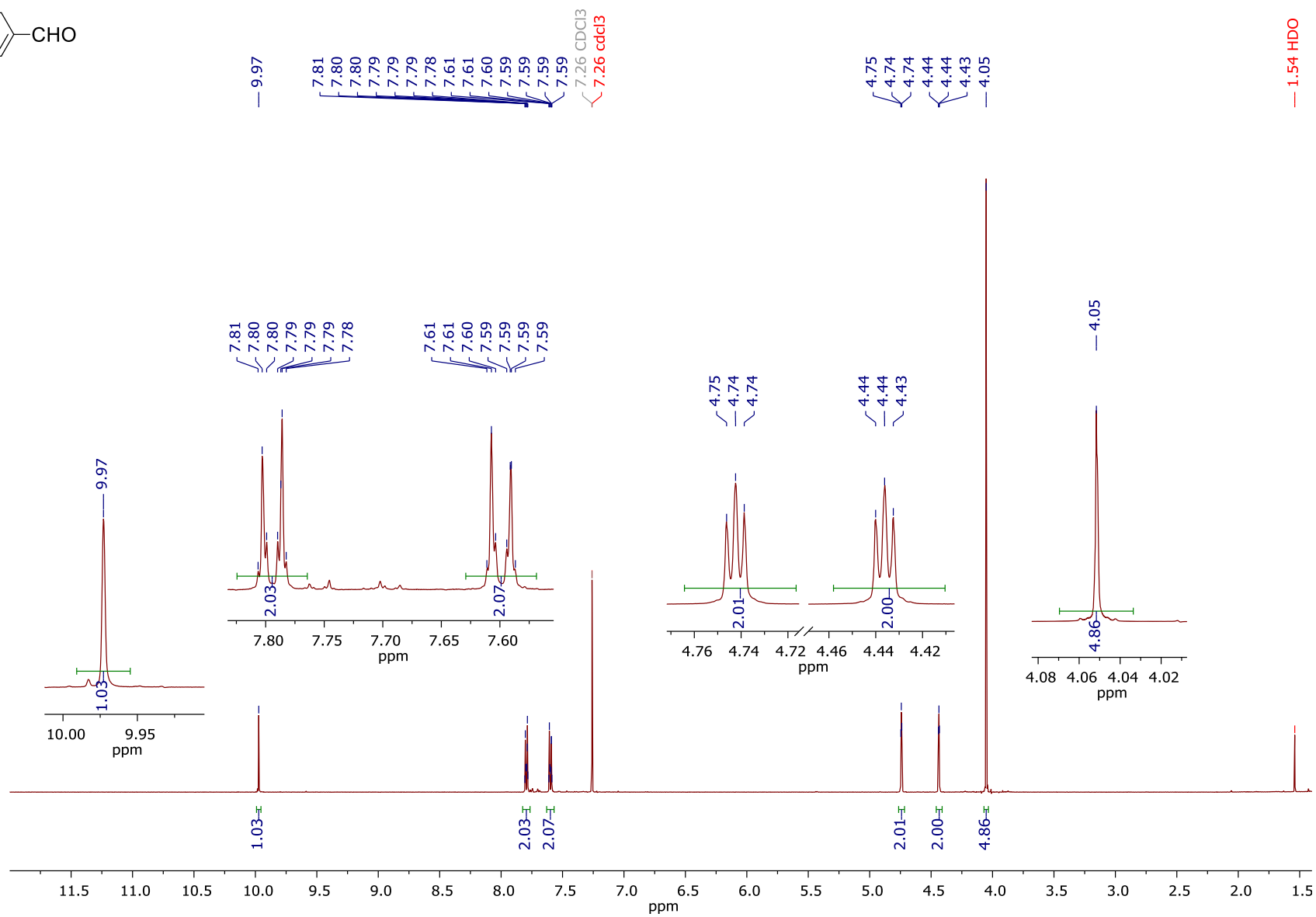
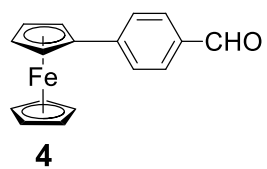
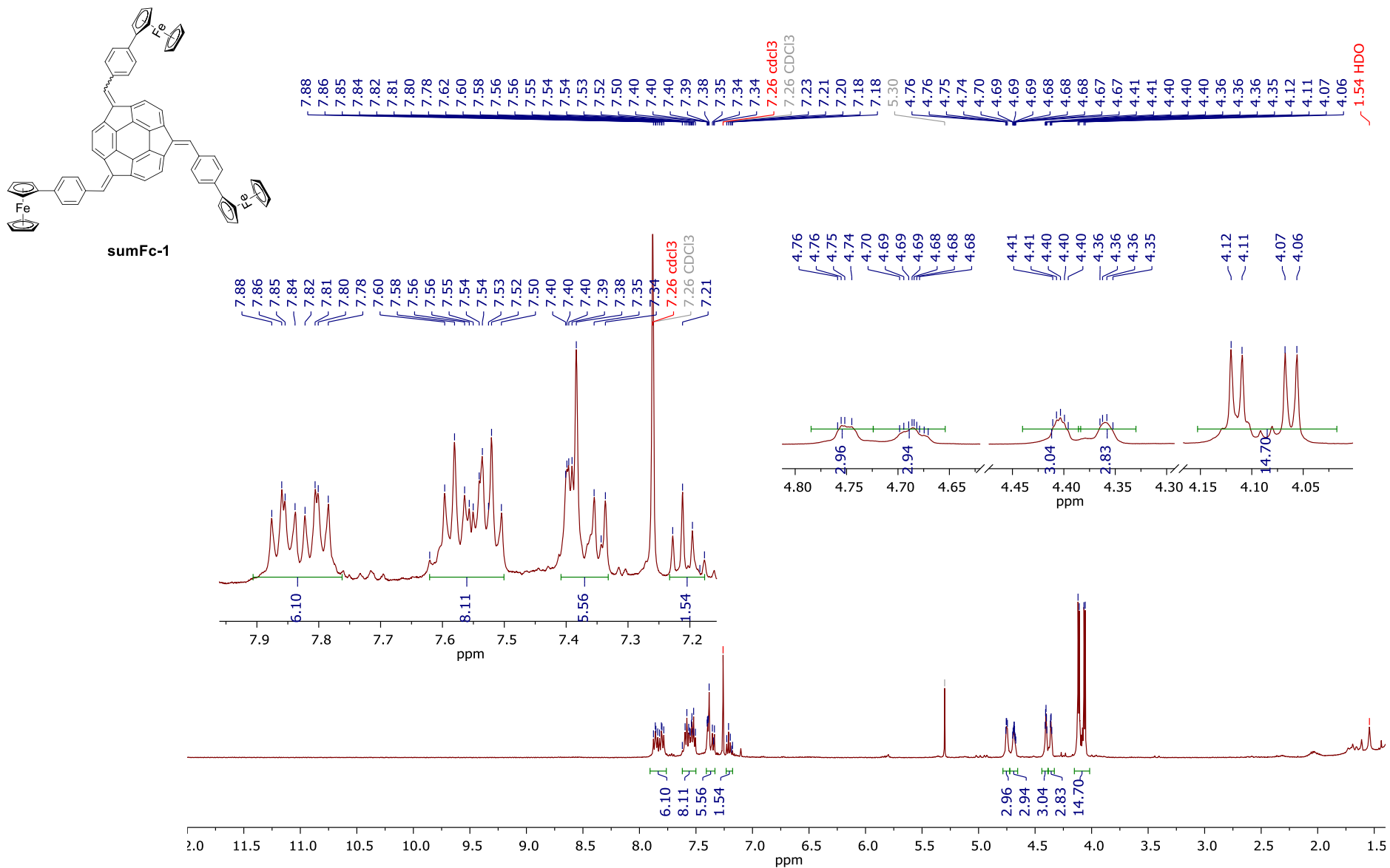


Figure S2. ¹H NMR (500 MHz, CDCl₃) spectrum of 4-(formylphenyl)ferrocene (**4**).



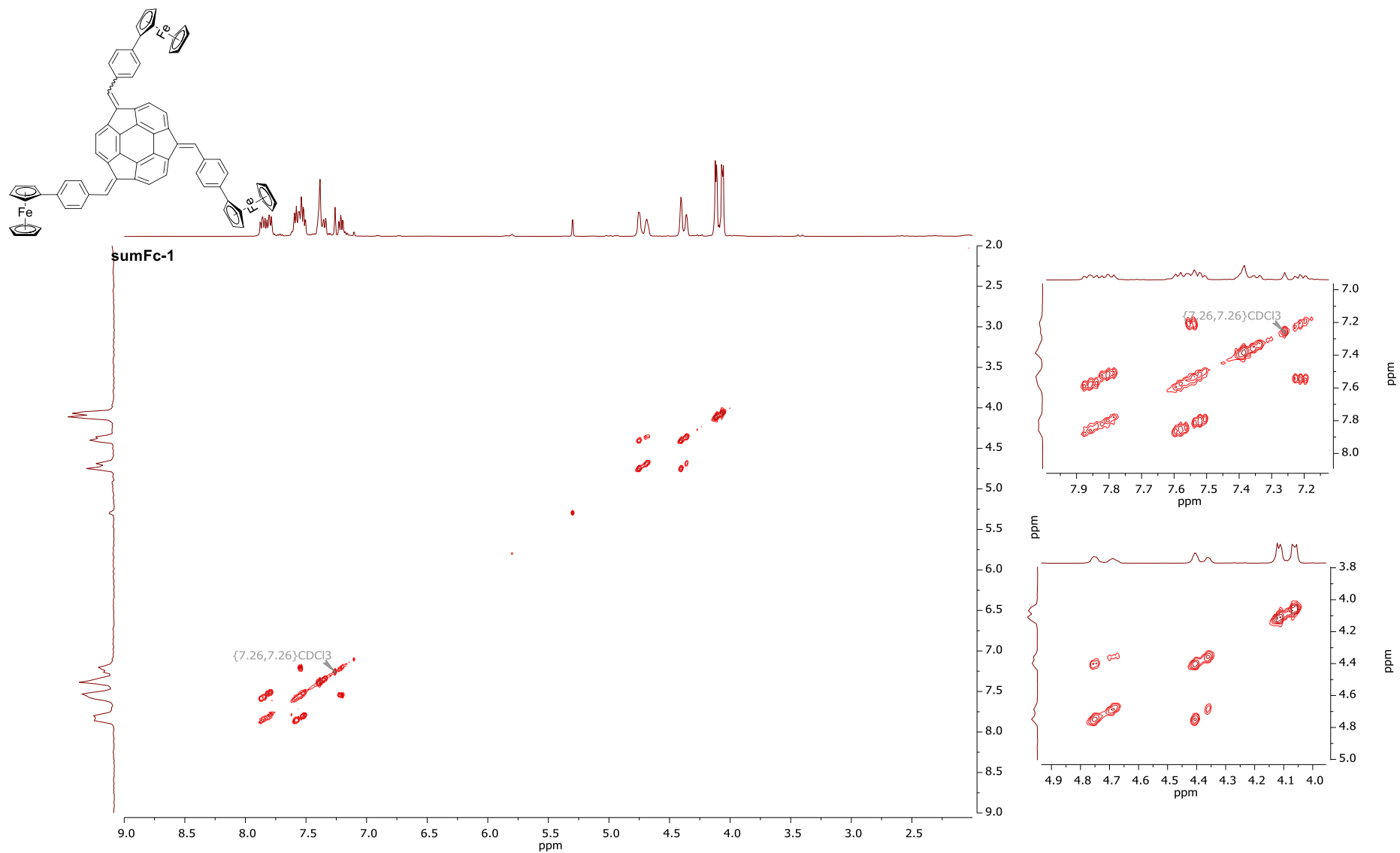


Figure S4. ^1H - ^1H COSY NMR (500 MHz, CDCl_3) spectrum of sumanene-ferrocene conjugate **sumFc-1**.

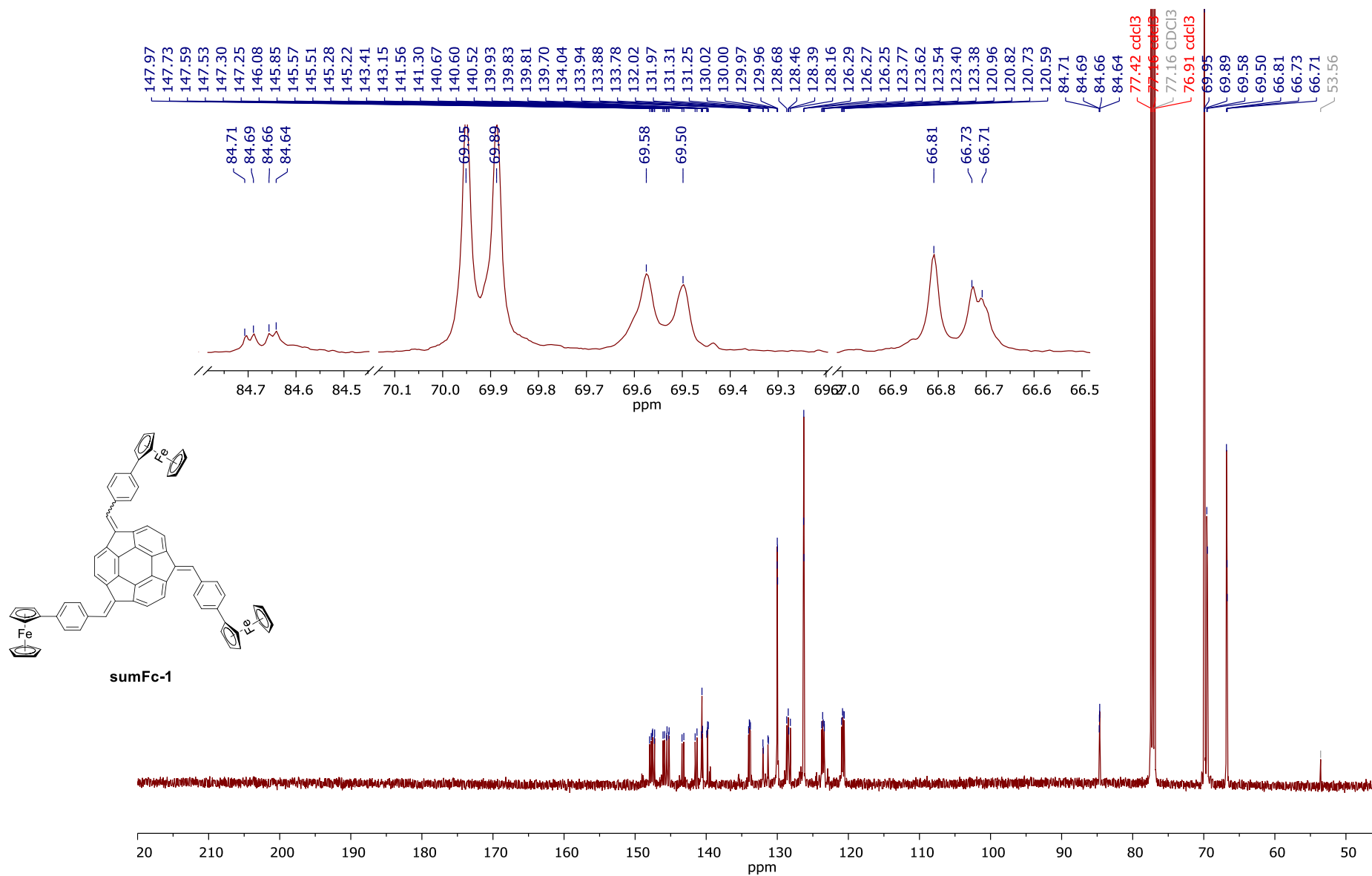


Figure S5. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) spectrum of sumanene-ferrocene conjugate **sumFc-1**.

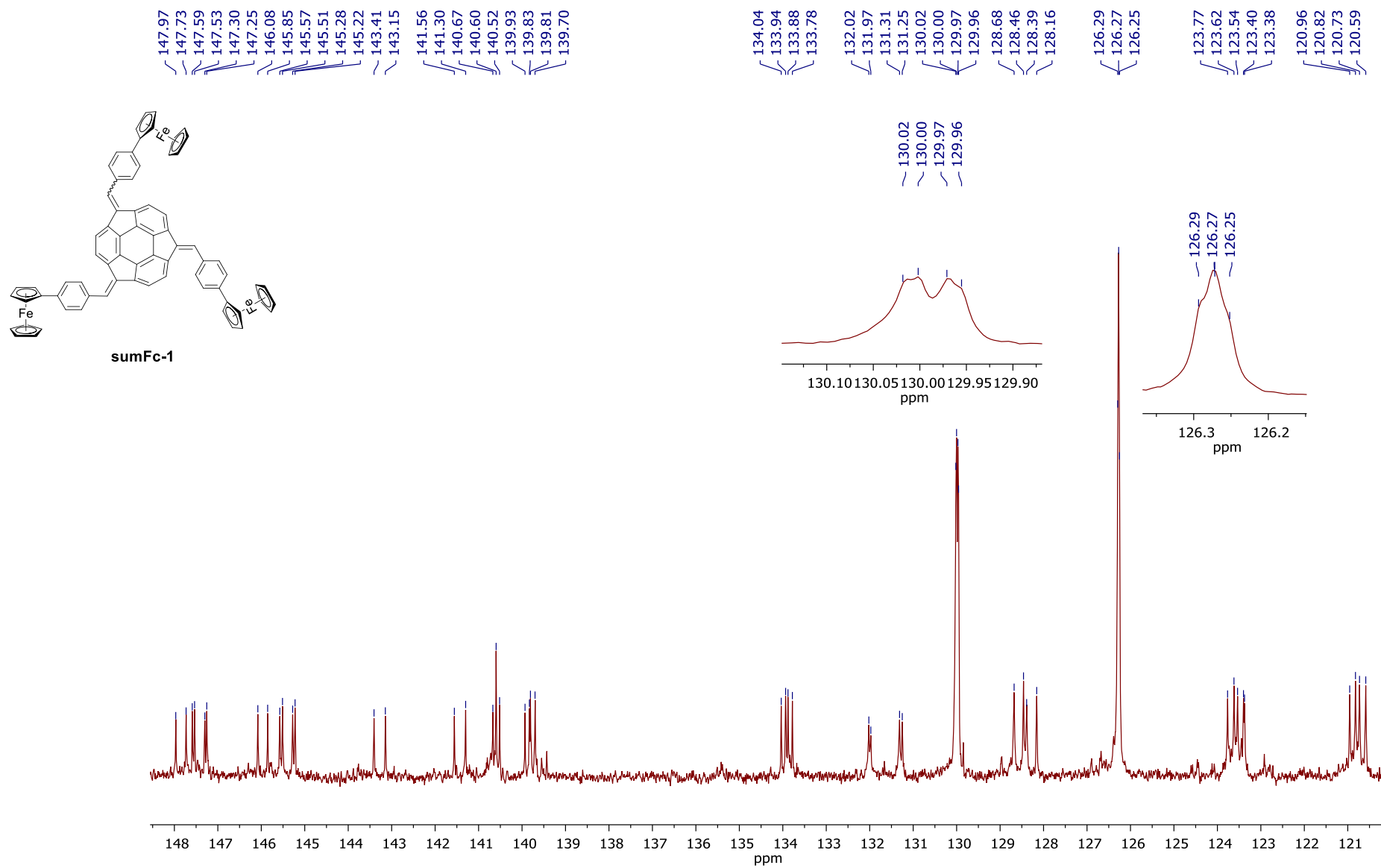


Figure S6. 149-120 ppm inset of the $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) spectrum of sumanene-ferrocene conjugate **sumFc-1**.

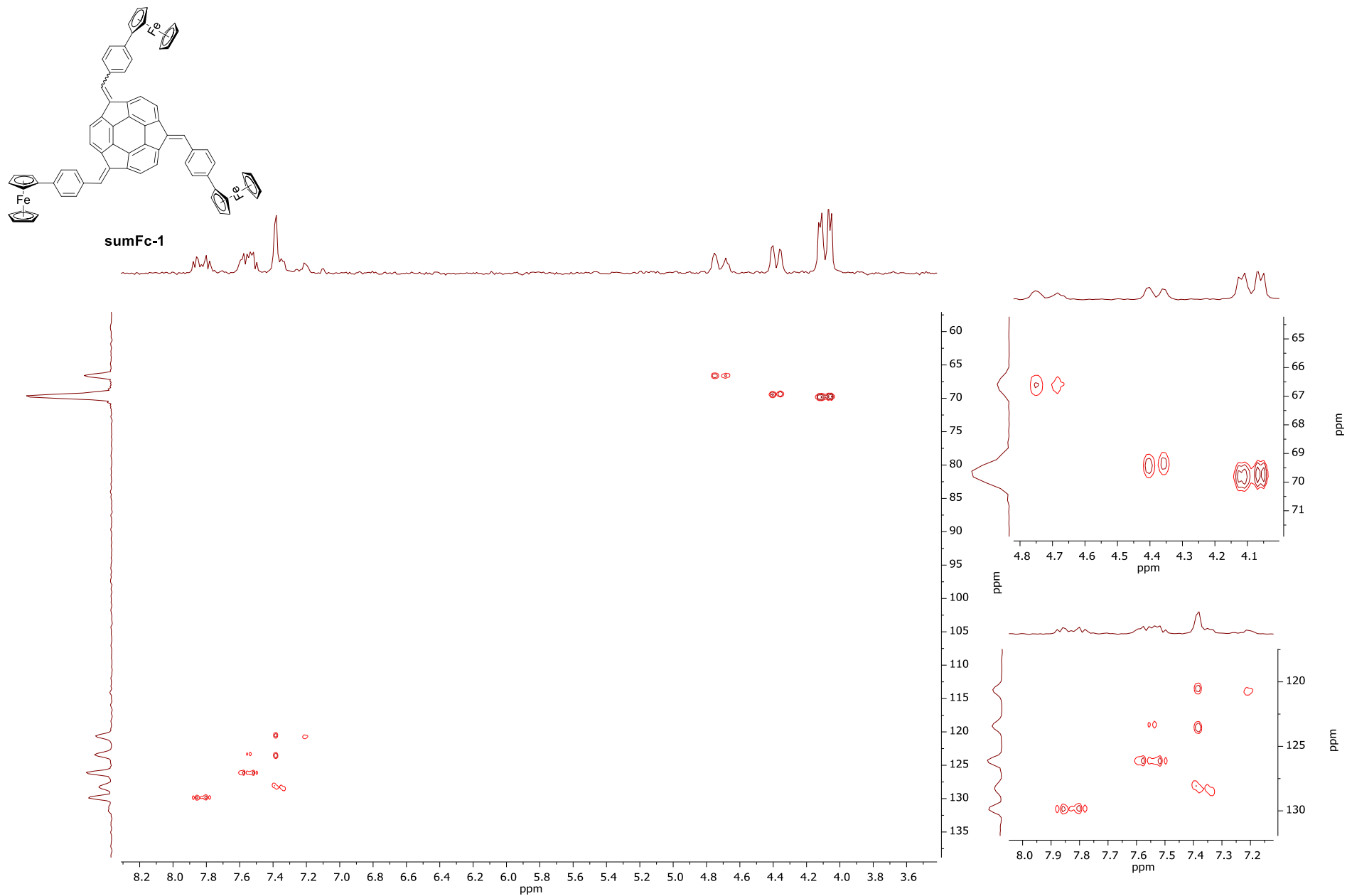


Figure S7. ^1H - ^{13}C HSQC NMR (CDCl_3) spectrum of sumanene-ferrocene conjugate **sumFc-1**.

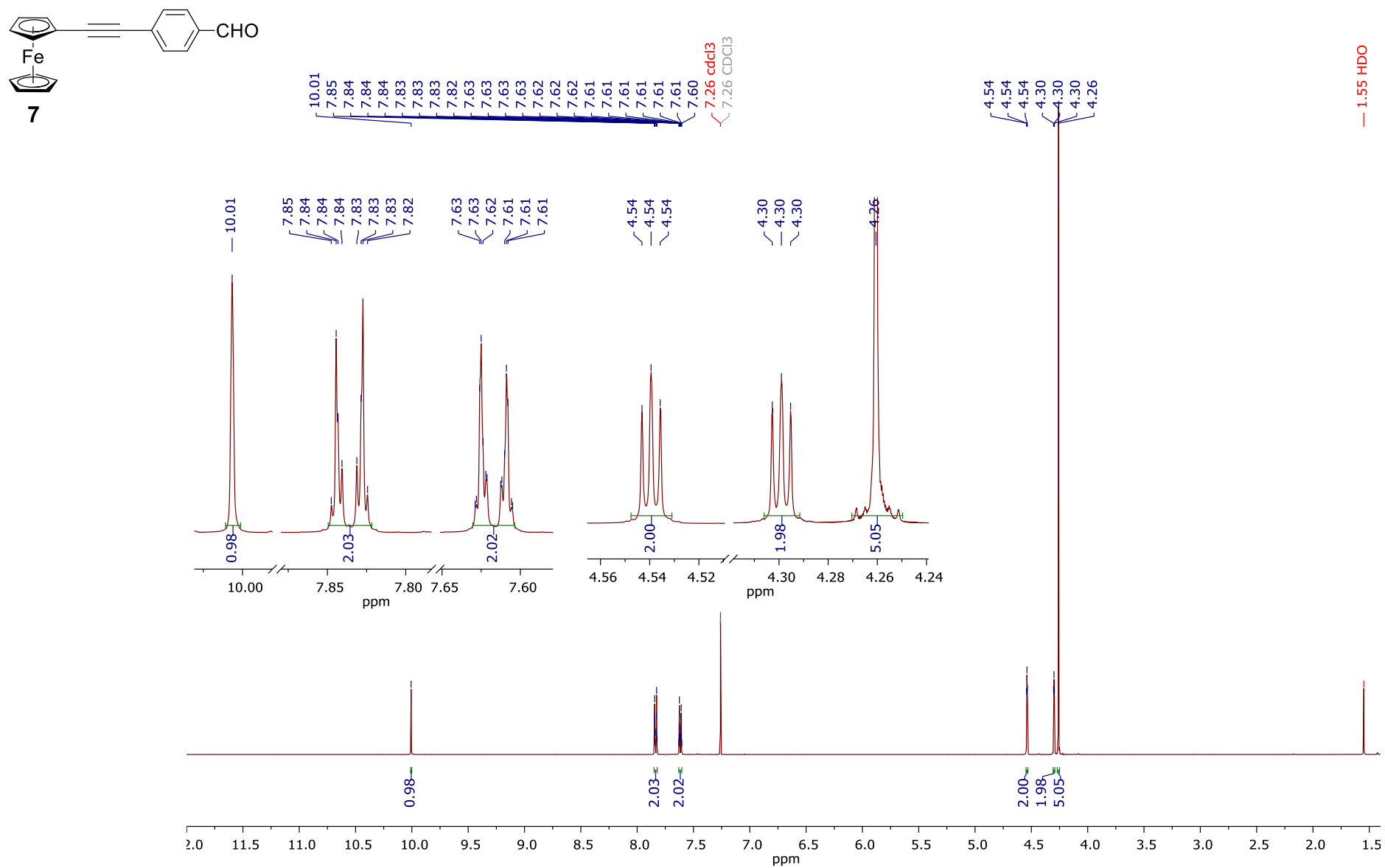


Figure S8. $^1\text{H NMR}$ (500 MHz, CDCl_3) spectrum of 4-(ferrocenylethynyl)benzaldehyde (**7**).

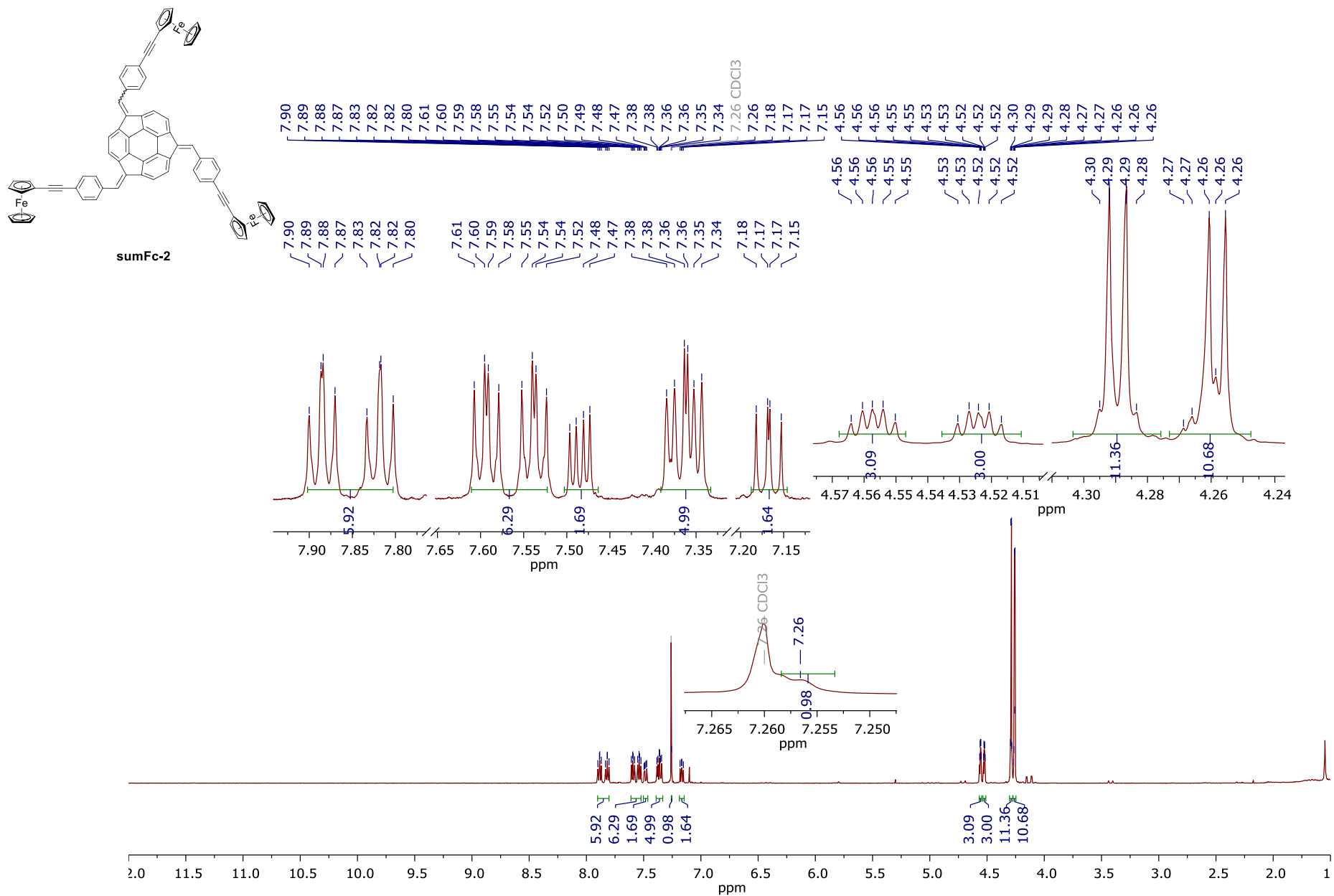


Figure S9. ¹H NMR (500 MHz, CDCl₃) spectrum of sumanene-ferrocene conjugate **sumFc-2**.

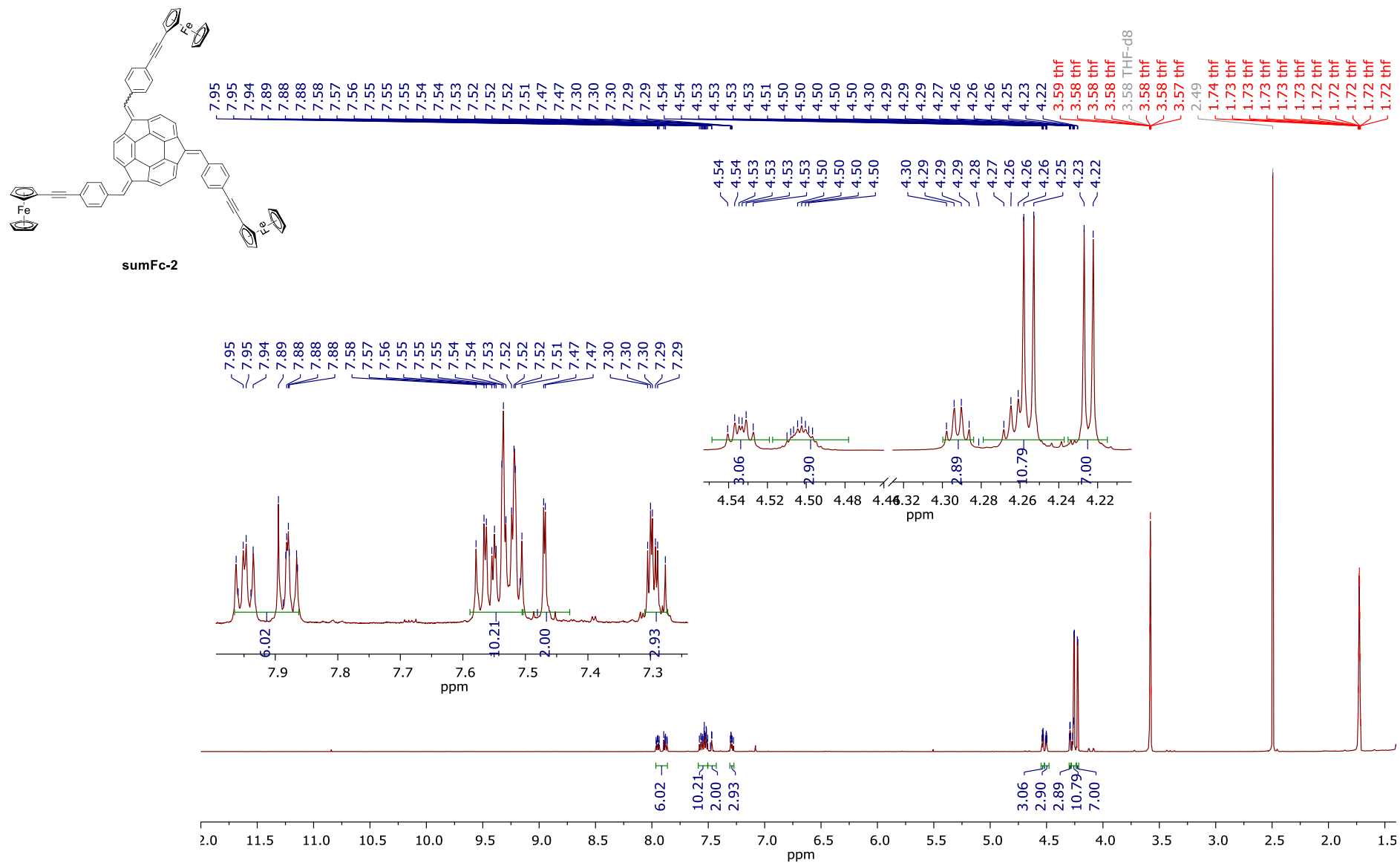


Figure S10. ^1H NMR (500 MHz, THF-d_8) spectrum of sumanene-ferrocene conjugate **sumFc-2**.

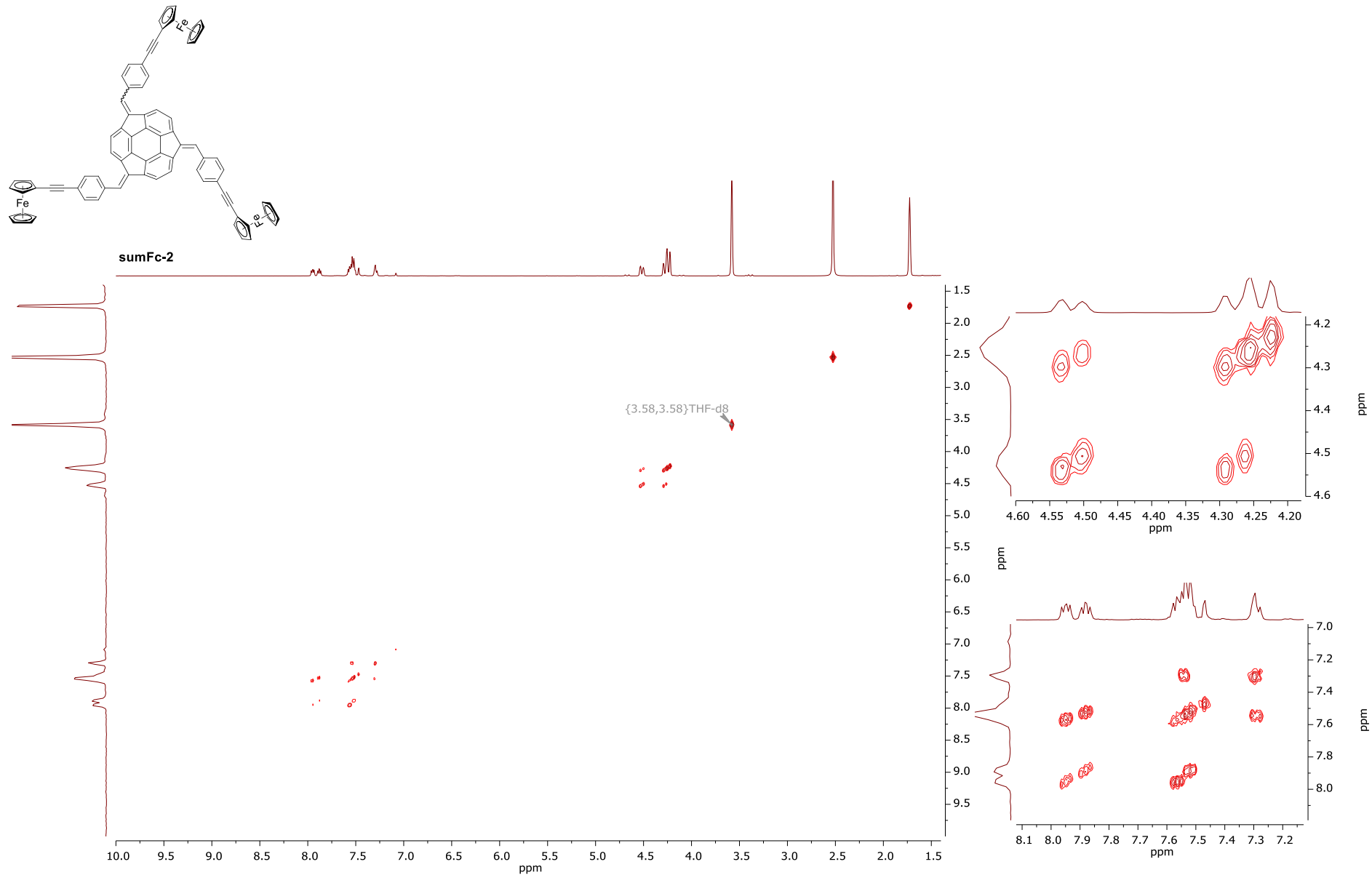


Figure S11. ^1H - ^1H COSY NMR (500 MHz, THF-d_8) spectrum of sumanene-ferrocene conjugate **sumFc-2**.

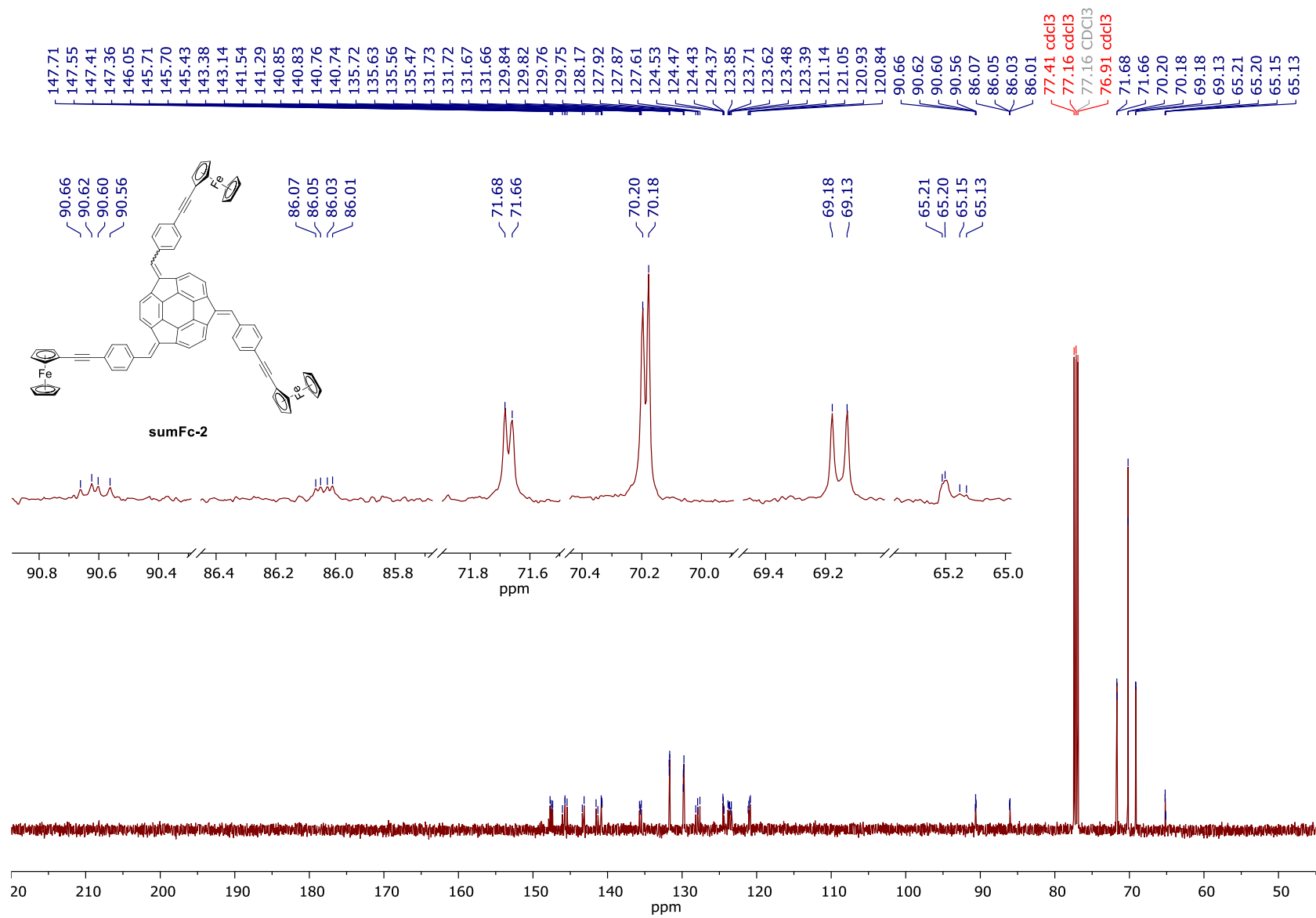


Figure S12. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) spectrum of sumanene-ferrocene conjugate **sumFc-2**.

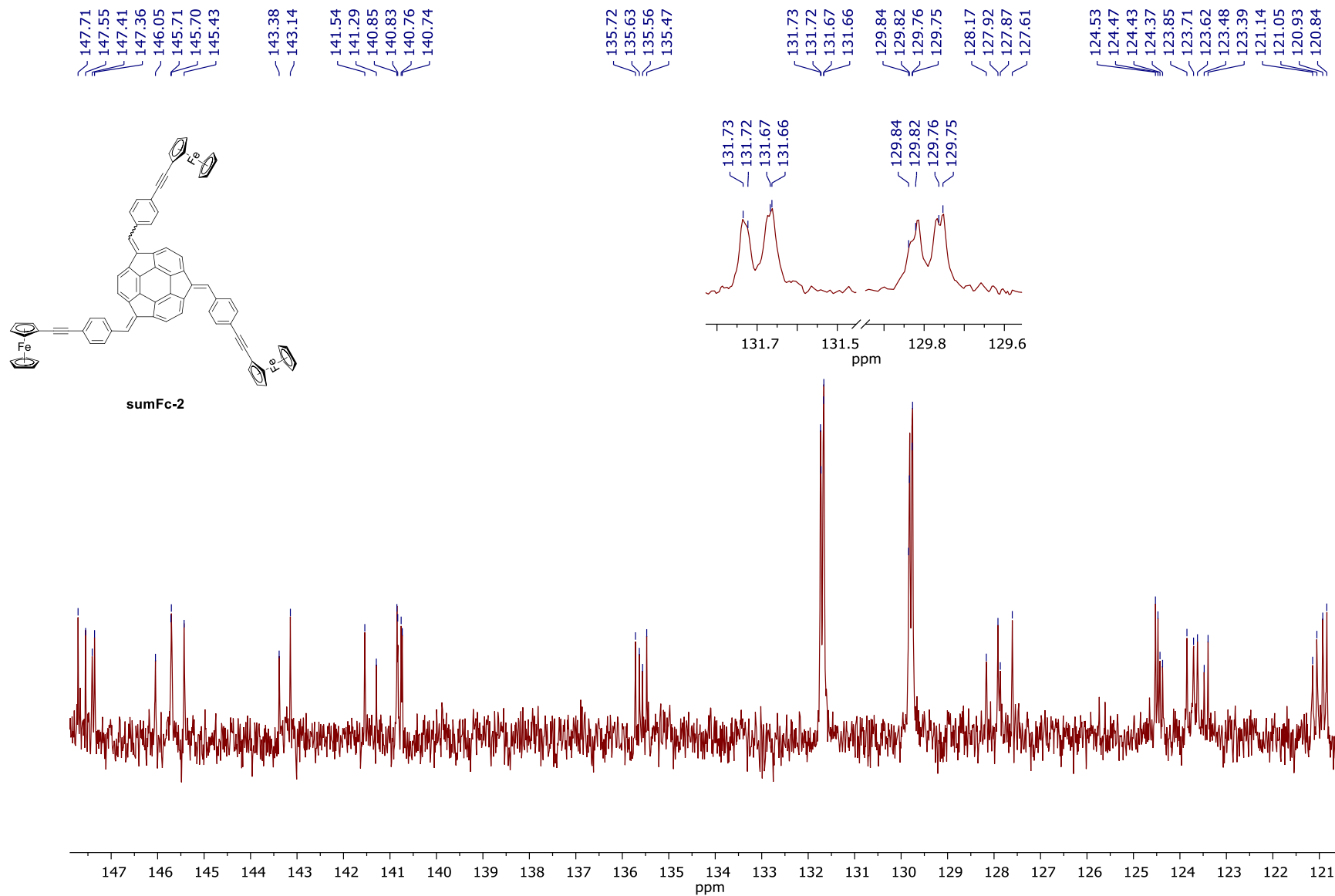


Figure S13. 148-120 ppm inset of the $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) spectrum of sumanene-ferrocene conjugate **sumFc-2**.

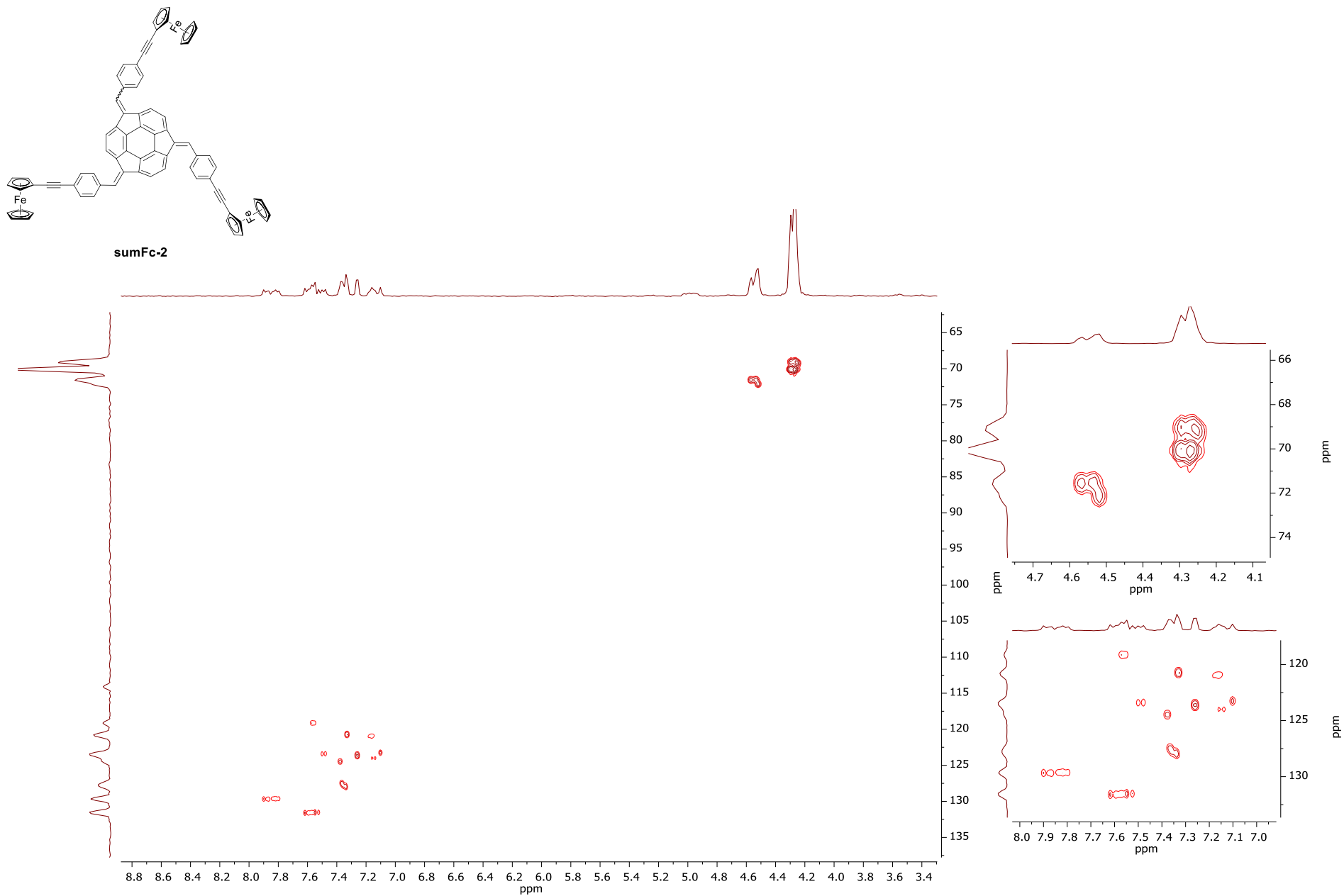


Figure S14. ^1H - ^{13}C HSQC NMR ($\text{THF-}d_6$) spectrum of sumanene-ferrocene conjugate **sumFc-2**.

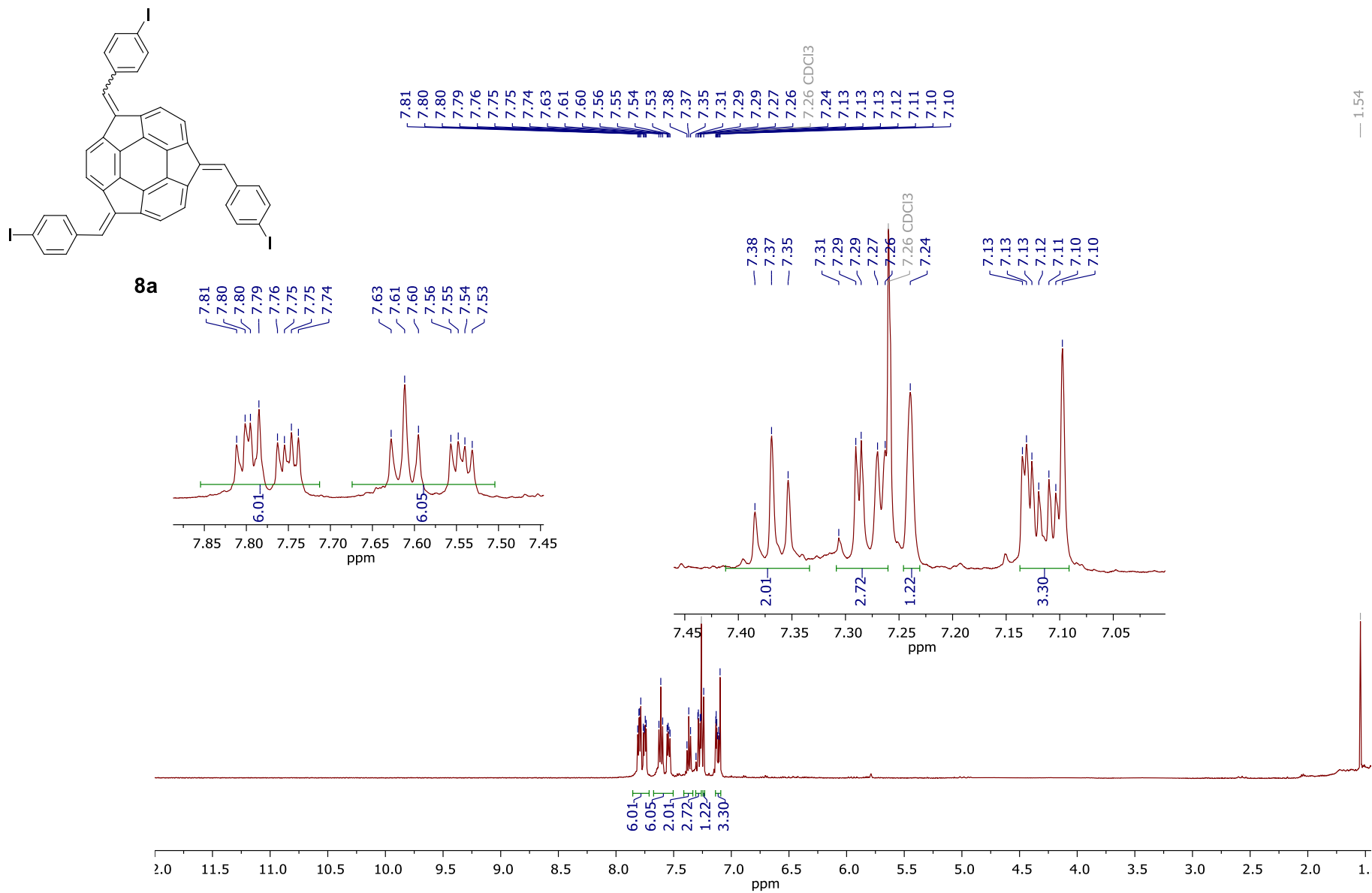


Figure S15. ¹H NMR (500 MHz, CDCl₃) spectrum of tris[(4-iodophenyl)methidene]sumanene (**8a**).

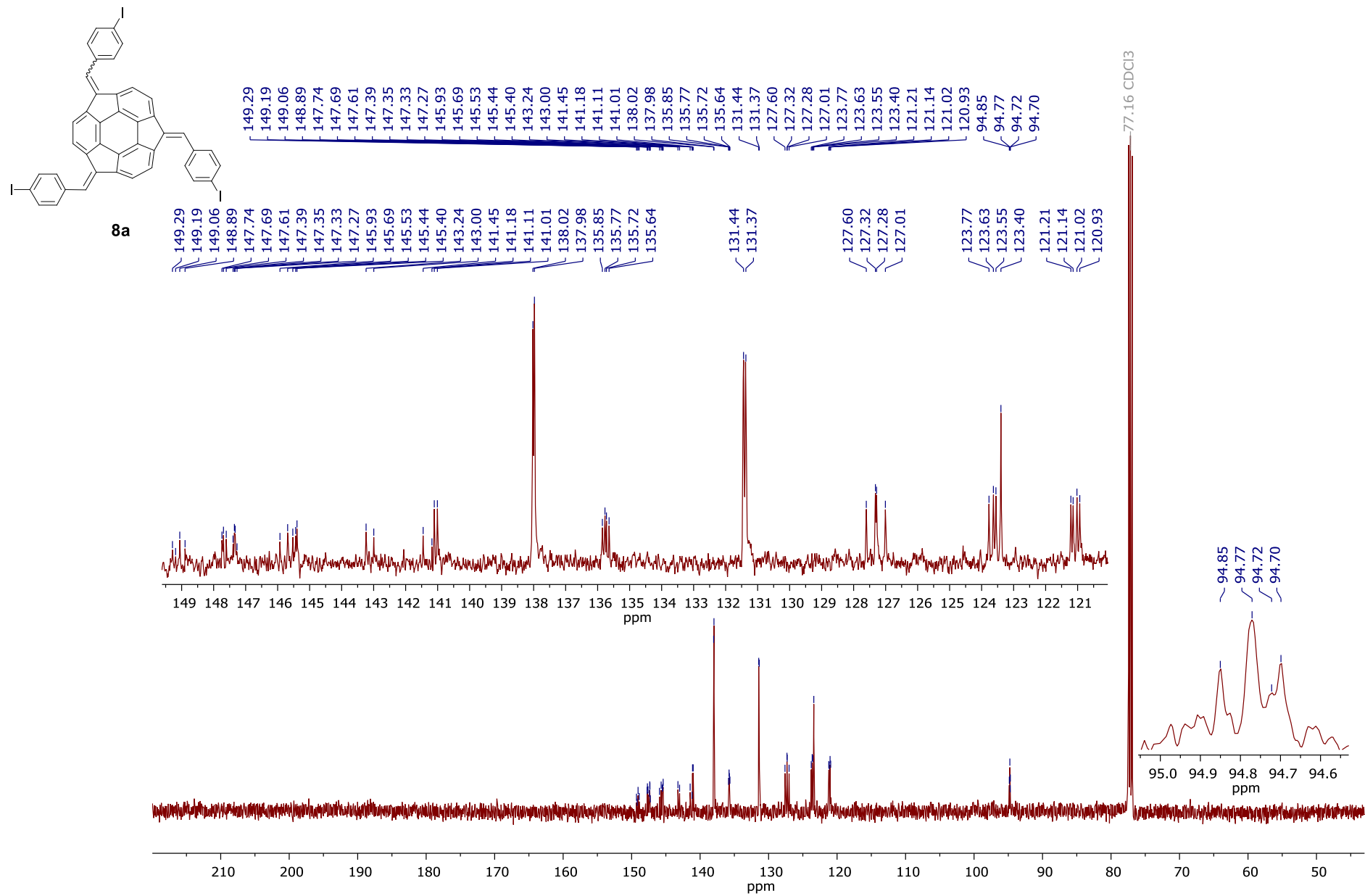


Figure S16. ¹³C{¹H} NMR (125 MHz, CDCl₃) spectrum tris[(4-iodophenyl)methidene]sumanene (**8a**).

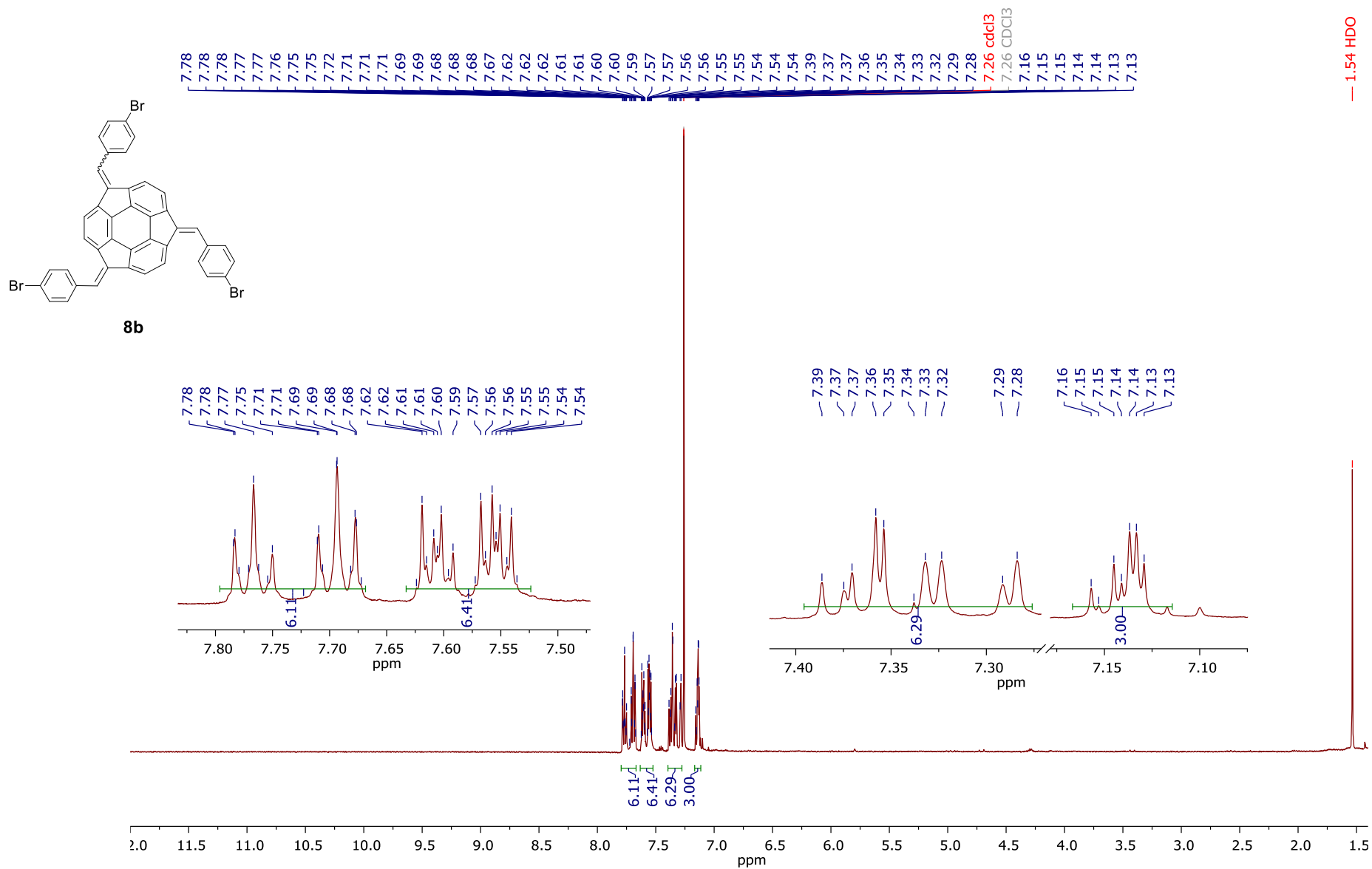


Figure S17. $^1\text{H NMR}$ (500 MHz, CDCl_3) spectrum of tris[(4-bromophenyl)methidene]sumanene (**8b**).

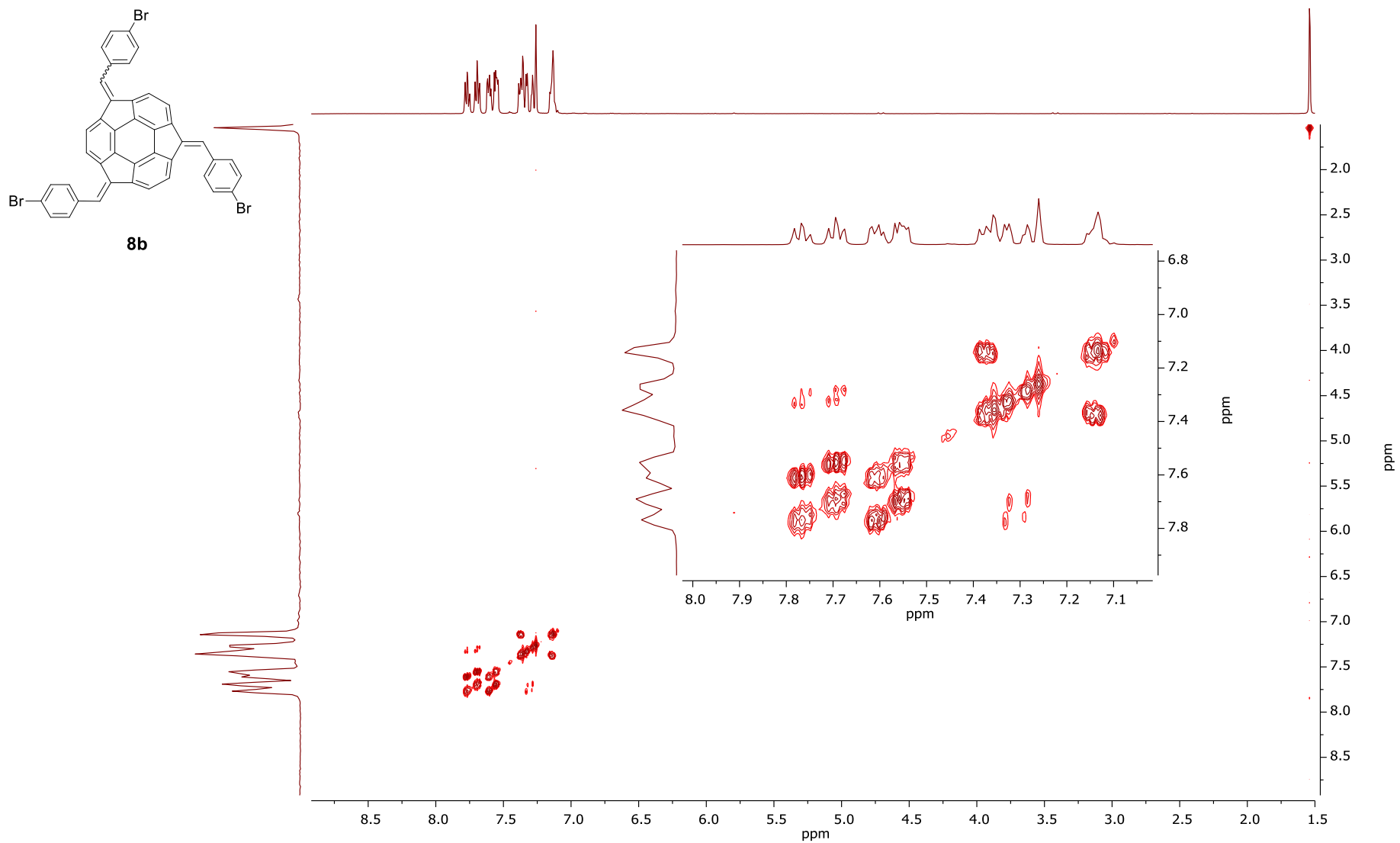


Figure S18. ^1H - ^1H COSY NMR (500 MHz, CDCl_3) spectrum of tris[4-bromophenyl)methidene]sumanene (**8b**).

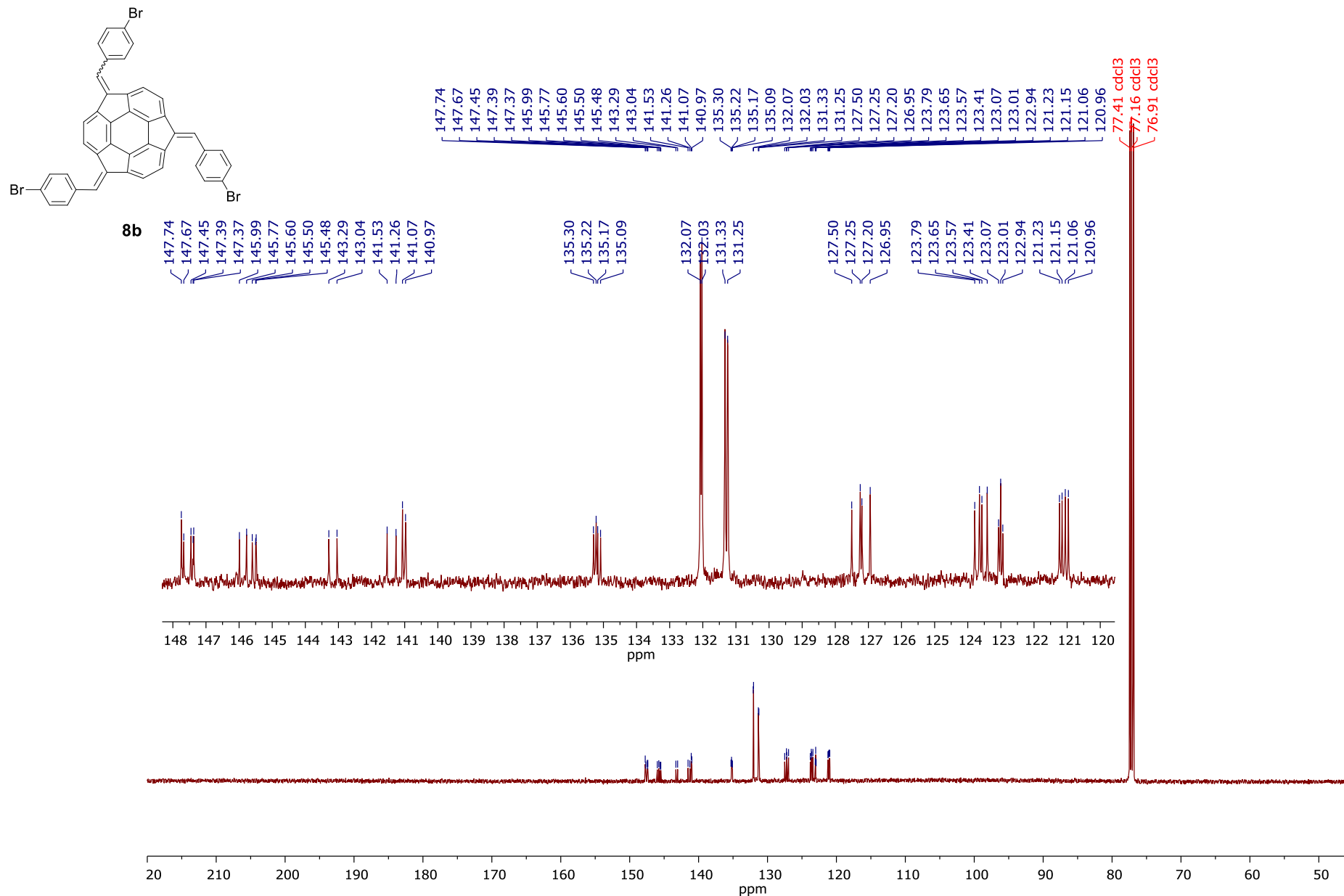


Figure S19. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) spectrum tris[(4-bromophenyl)methidene]sumanene (**8b**).

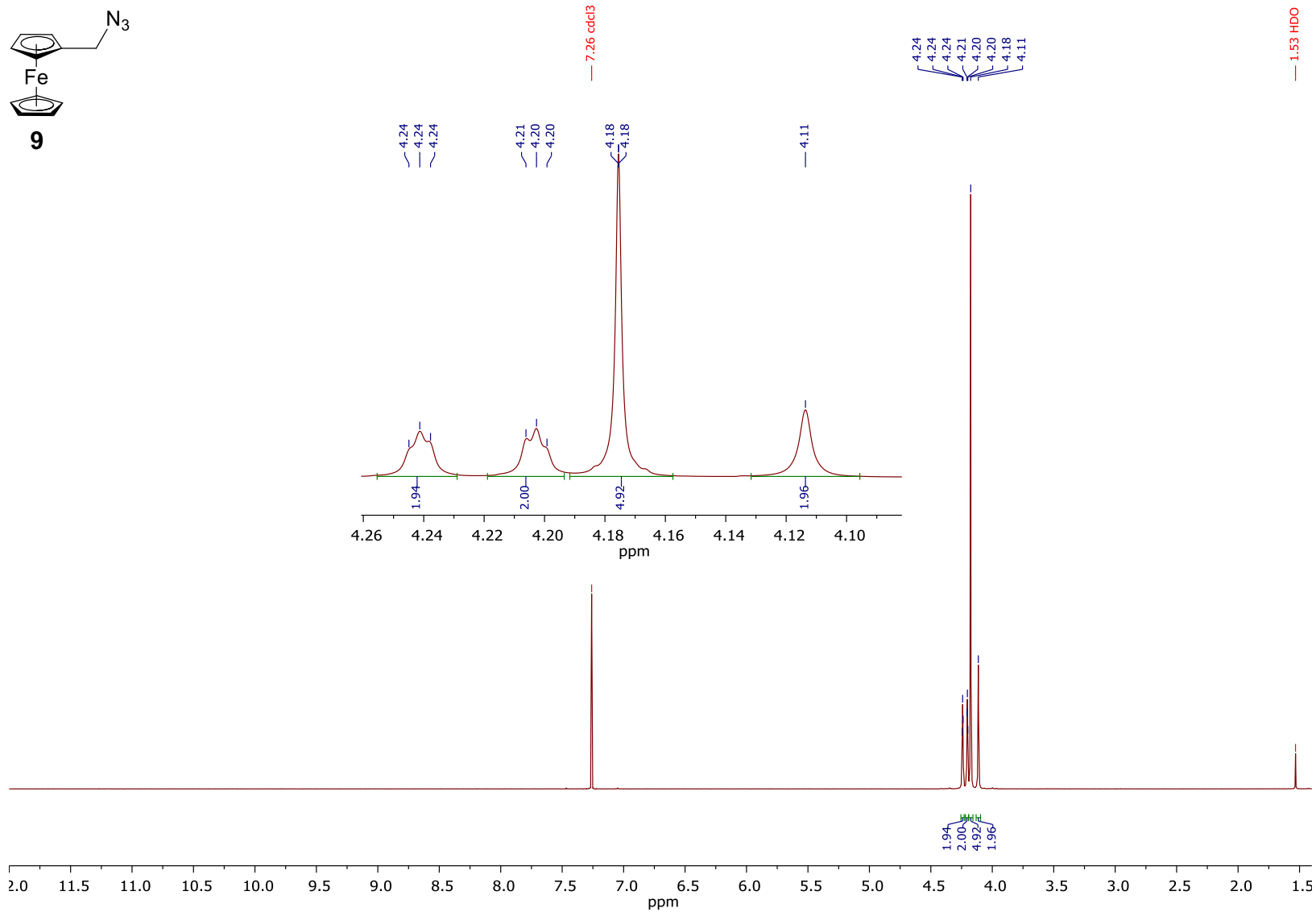


Figure S20. $^1\text{H NMR}$ (500 MHz, CDCl_3) spectrum of ferrocenemethylazide (**9**).

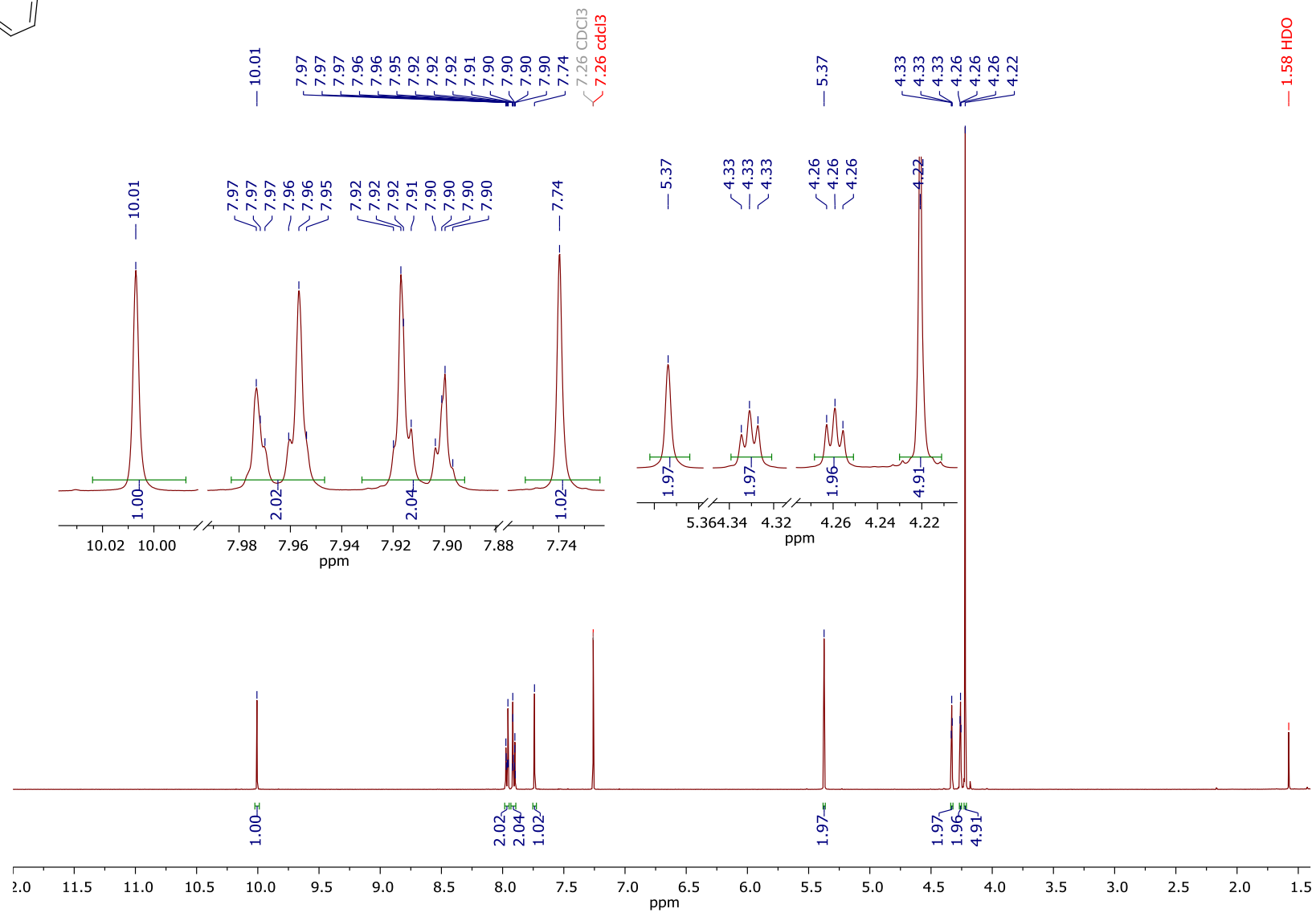
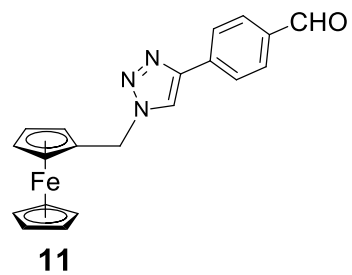


Figure S21. ¹H NMR (500 MHz, CDCl₃) spectrum of 4-(1-(ferrocenylmethyl)-1H-1,2,3-triazol-4-yl)benzaldehyde (**11**).

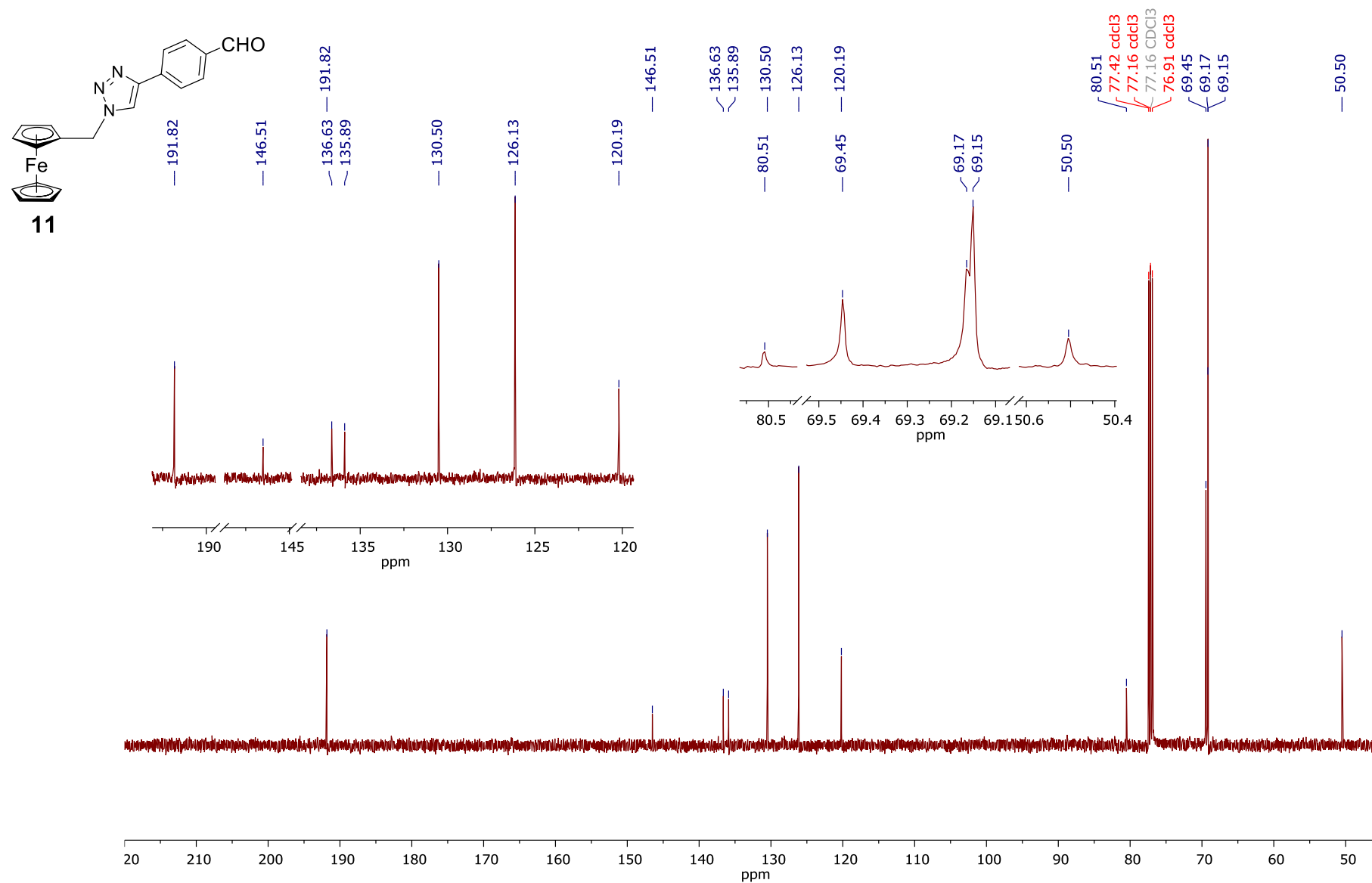


Figure S22. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) spectrum of 4-(1-(ferrocenylmethyl)-1H-1,2,3-triazol-4-yl)benzaldehyde (11).

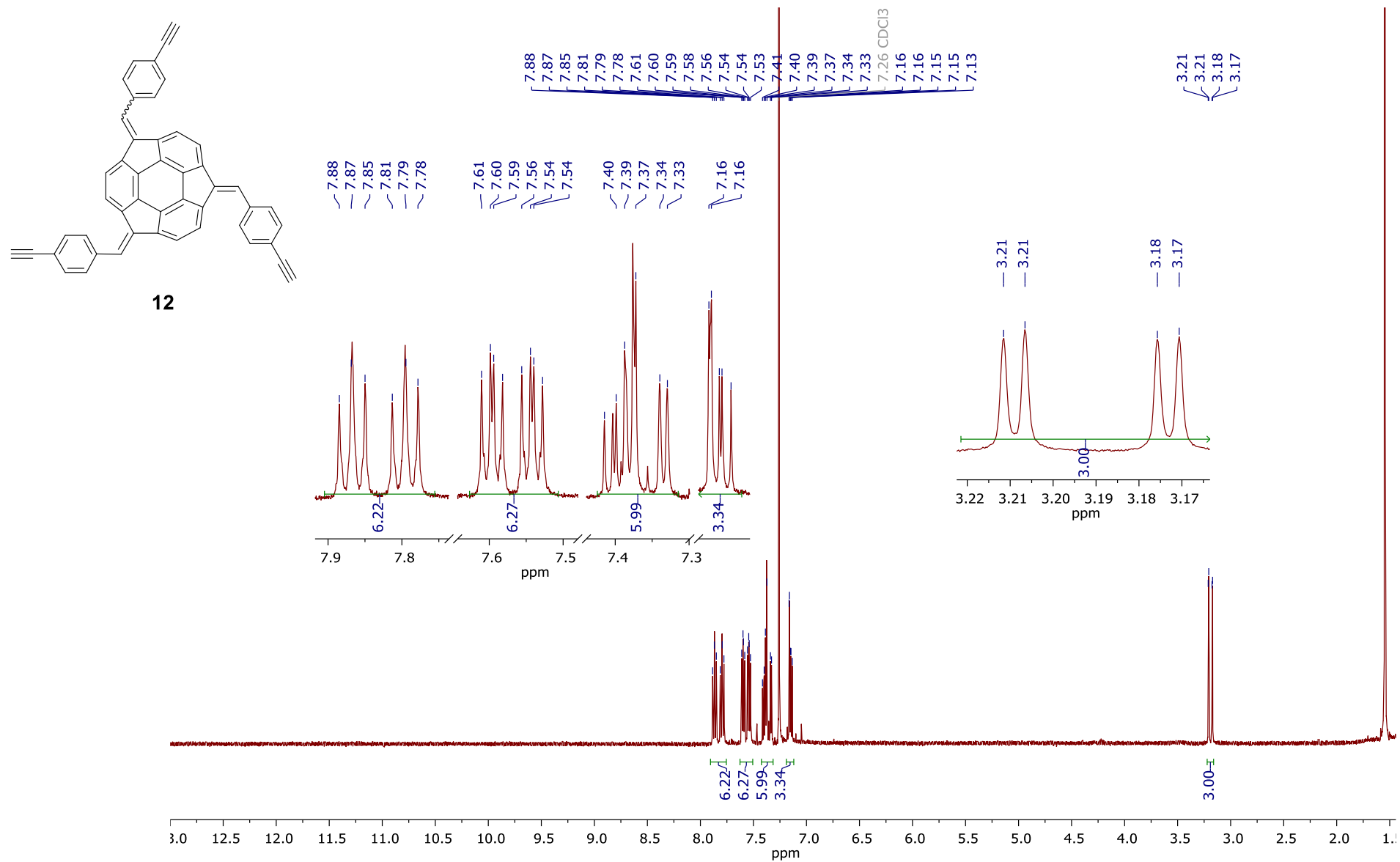


Figure S23. ¹H NMR (500 MHz, CDCl₃) spectrum of tris[(4-ethynylphenyl)methidene]sumanene (**12**).

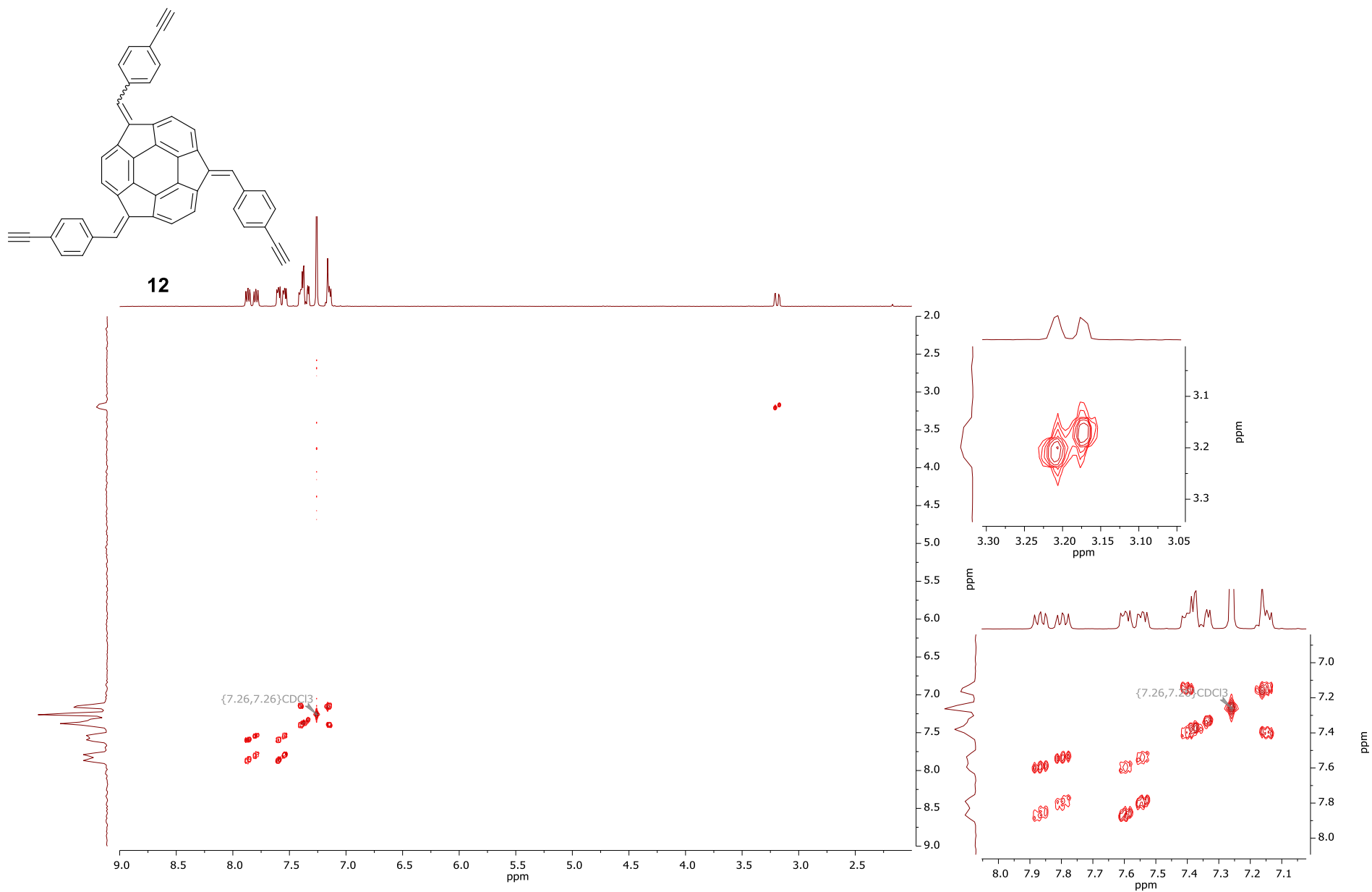


Figure S24. ^1H - ^1H COSY NMR (500 MHz, CDCl_3) spectrum of tris[(4-ethynylphenyl)methidene]sumanene (**12**).

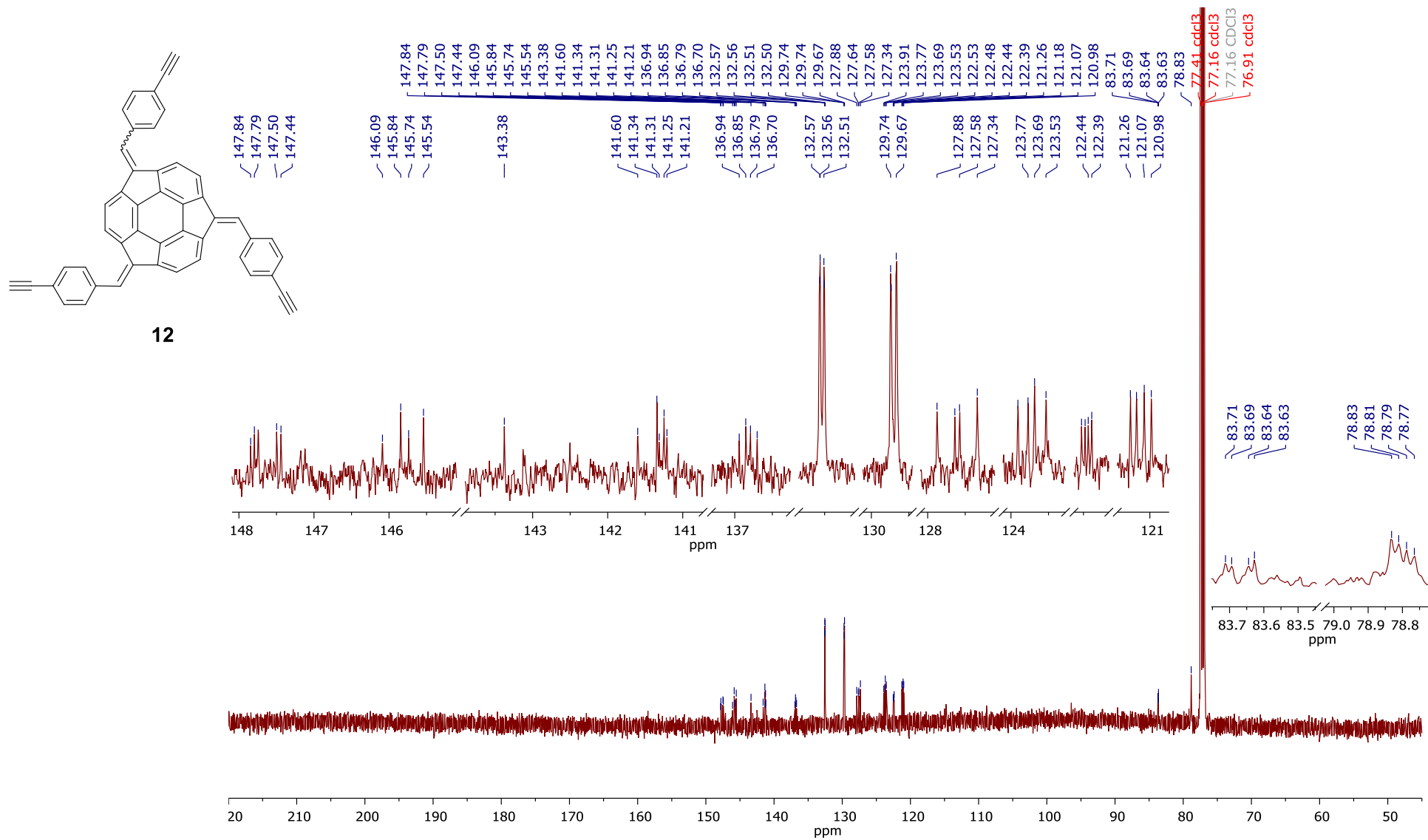


Figure S25. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) spectrum of tris[(4-ethynylphenyl)methidene]sumanene (**12**).



Figure S26. ¹H NMR (500 MHz, CDCl₃) spectrum of sumanene-ferrocene conjugate **sumFc-3**.

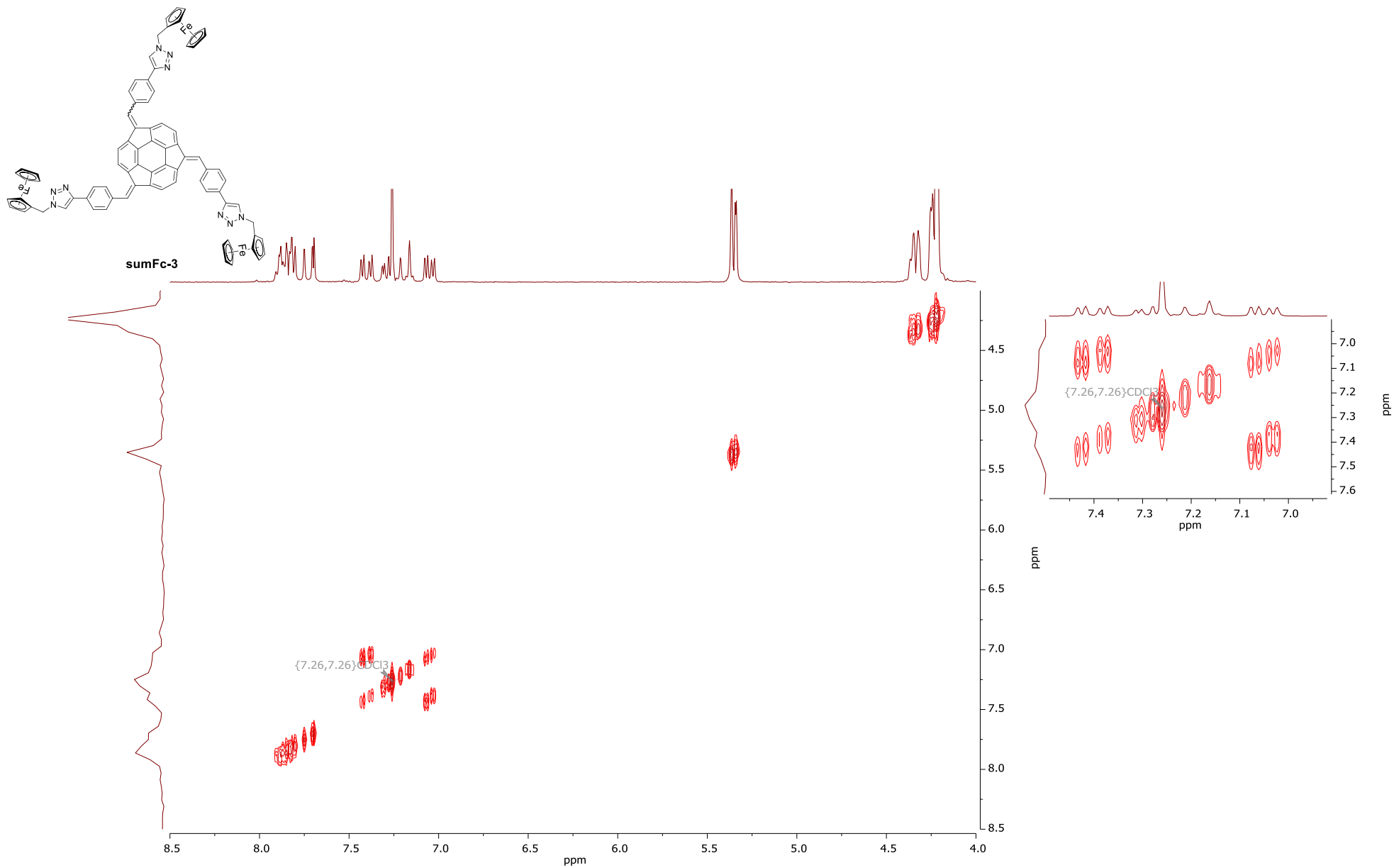


Figure S27. ^1H - ^1H COSY NMR (500 MHz, CDCl_3) spectrum of sumanene-ferrocene conjugate **sumFc-3**.

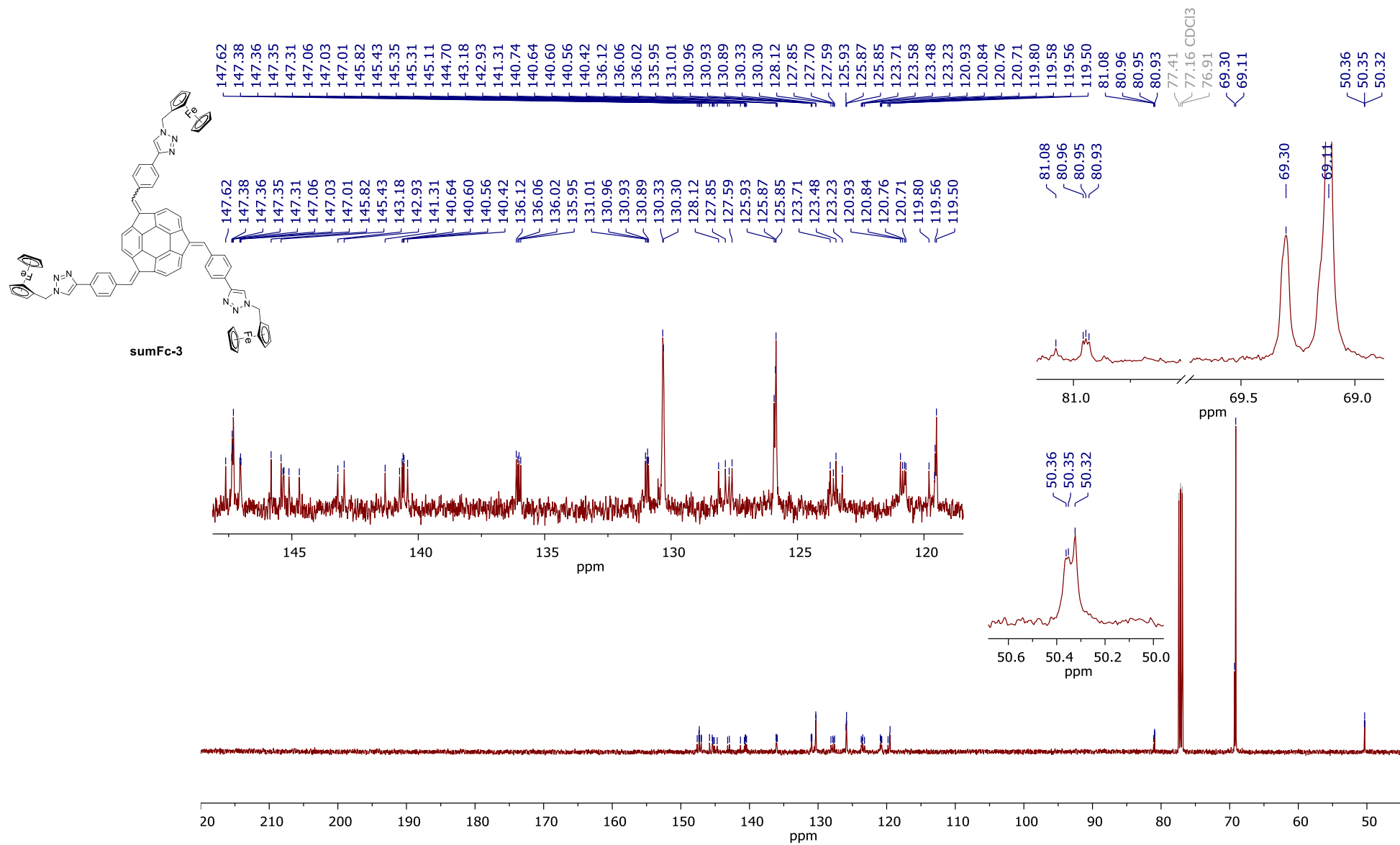


Figure S28. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) spectrum of sumanene-ferrocene conjugate **sumFc-3**.

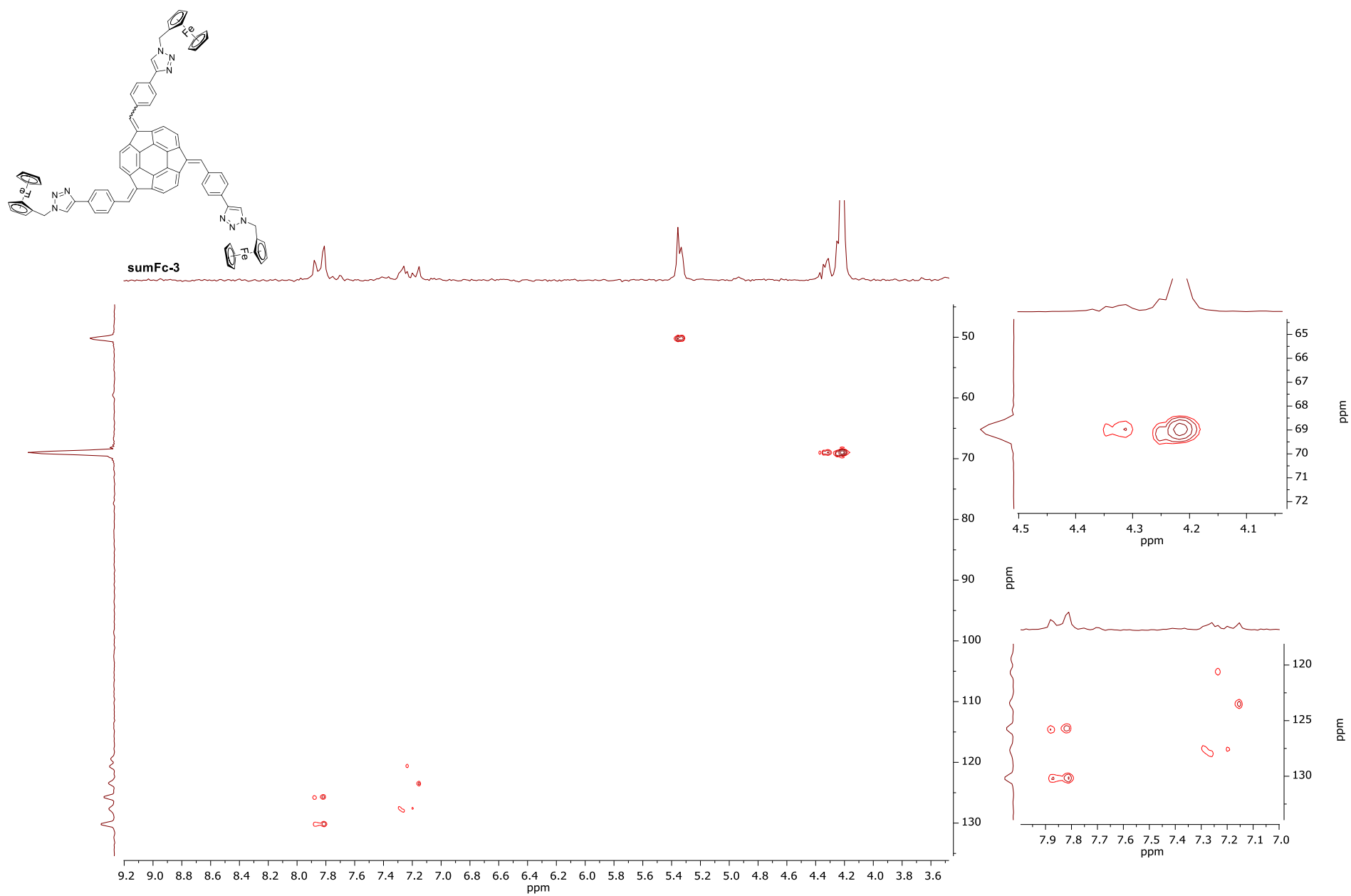


Figure S29. ^1H - ^{13}C HSQC NMR (CDCl_3) spectrum of sumanene-ferrocene conjugate **sumFc-3**.

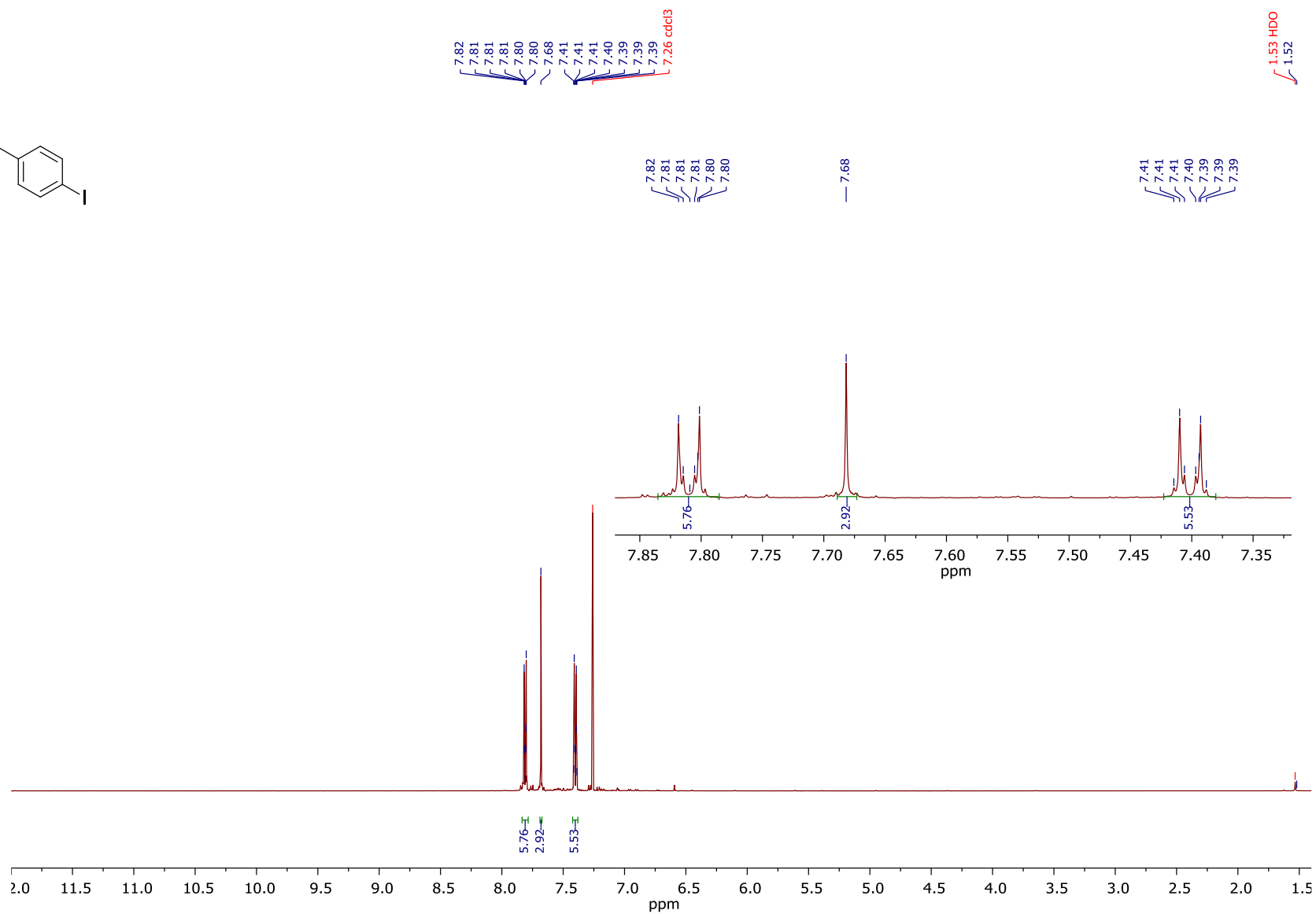
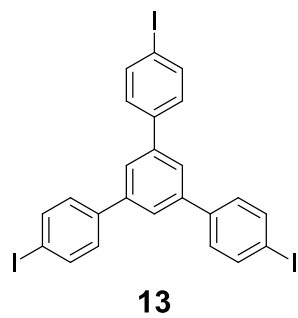


Figure S30. ¹H NMR (500 MHz, CDCl₃) spectrum of 1,3,5-tris(4-iodophenyl)benzene (**13**).

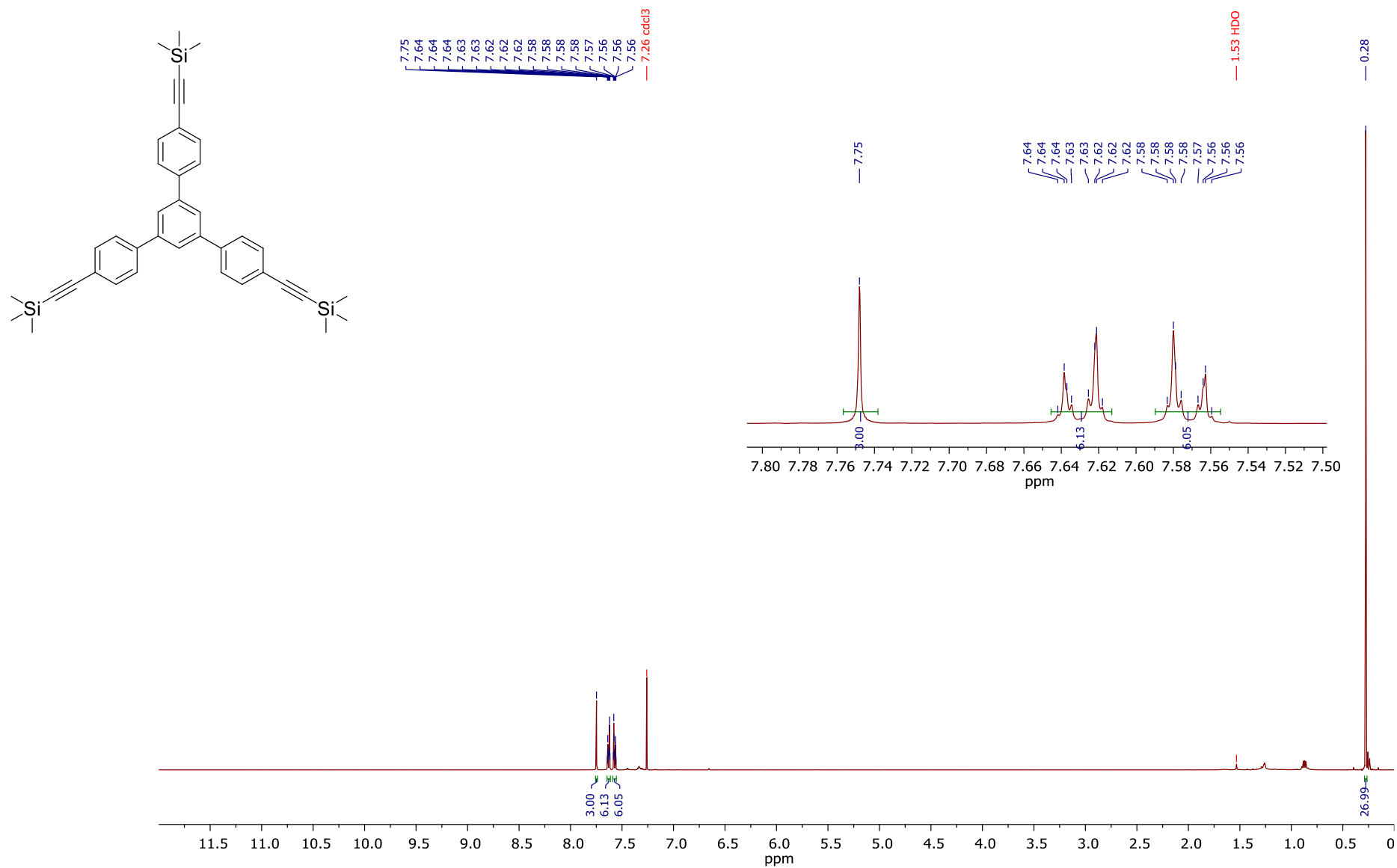


Figure S31. ¹H NMR (500 MHz, CDCl₃) spectrum of 1,3,5-tris[4'-[(trimethylsilyl)ethynyl]phenyl]benzene.

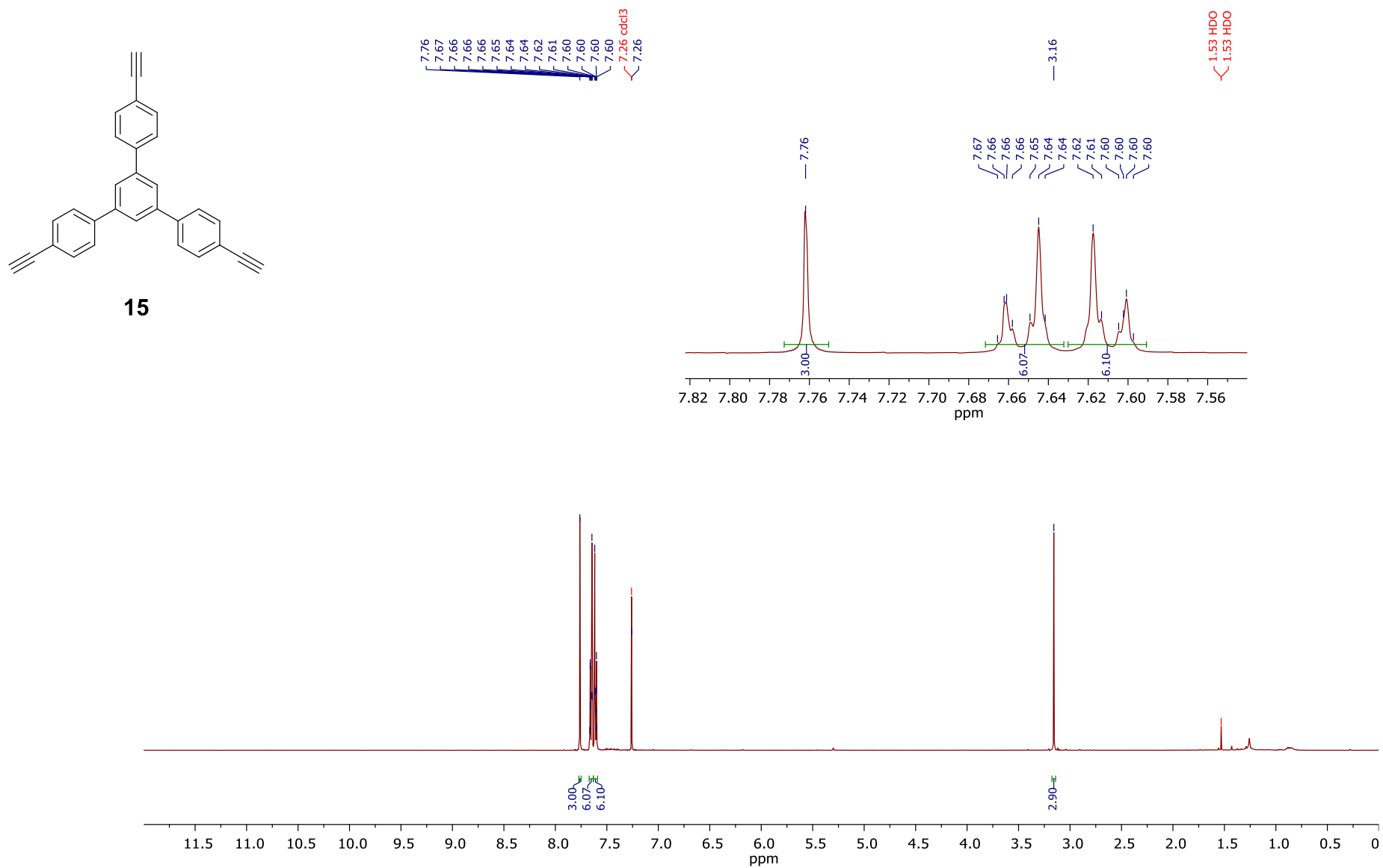
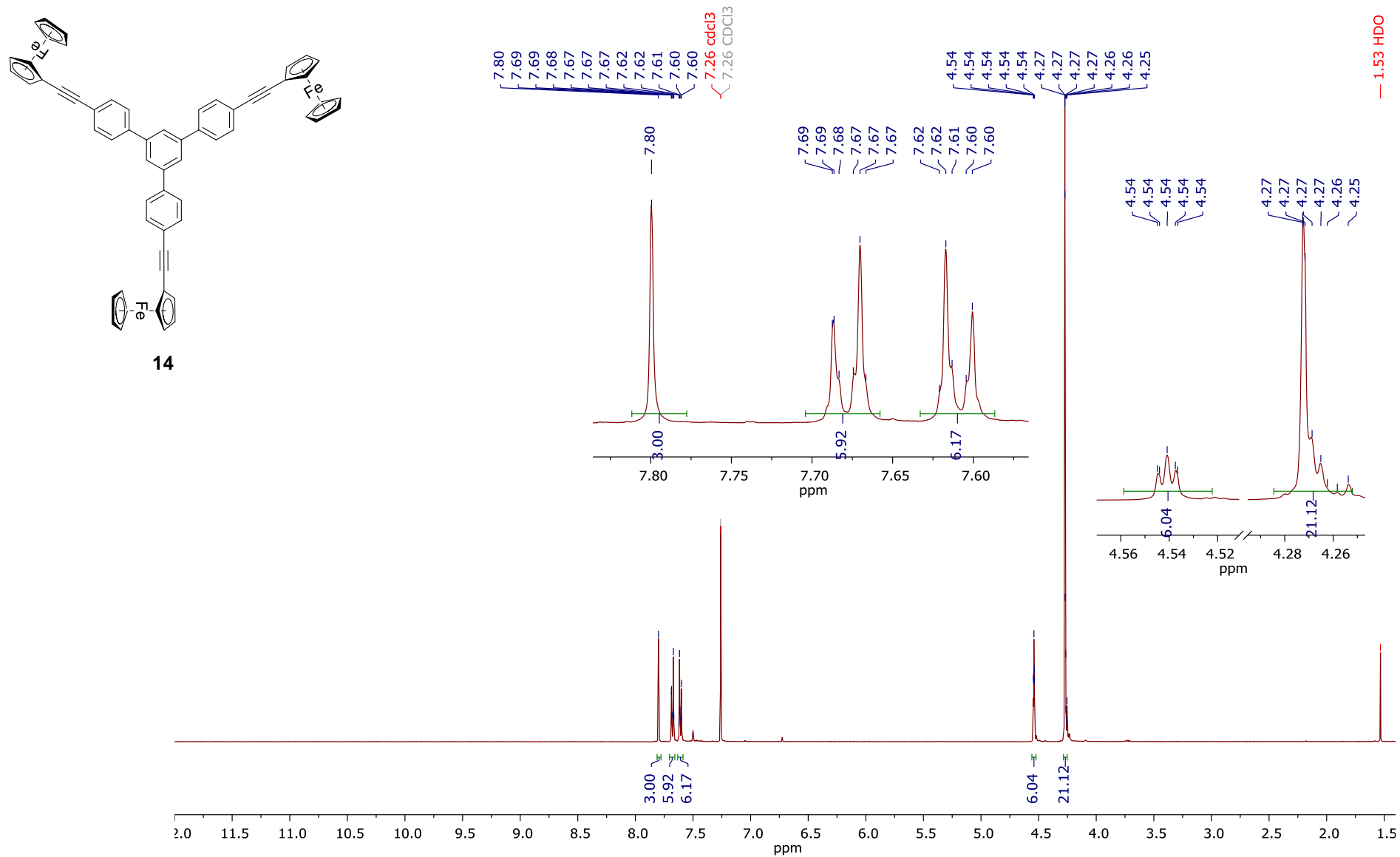


Figure S32. ^1H NMR (500 MHz, CDCl_3) spectrum of 1,3,5-tris(4-ethynylphenyl)benzene (**15**).



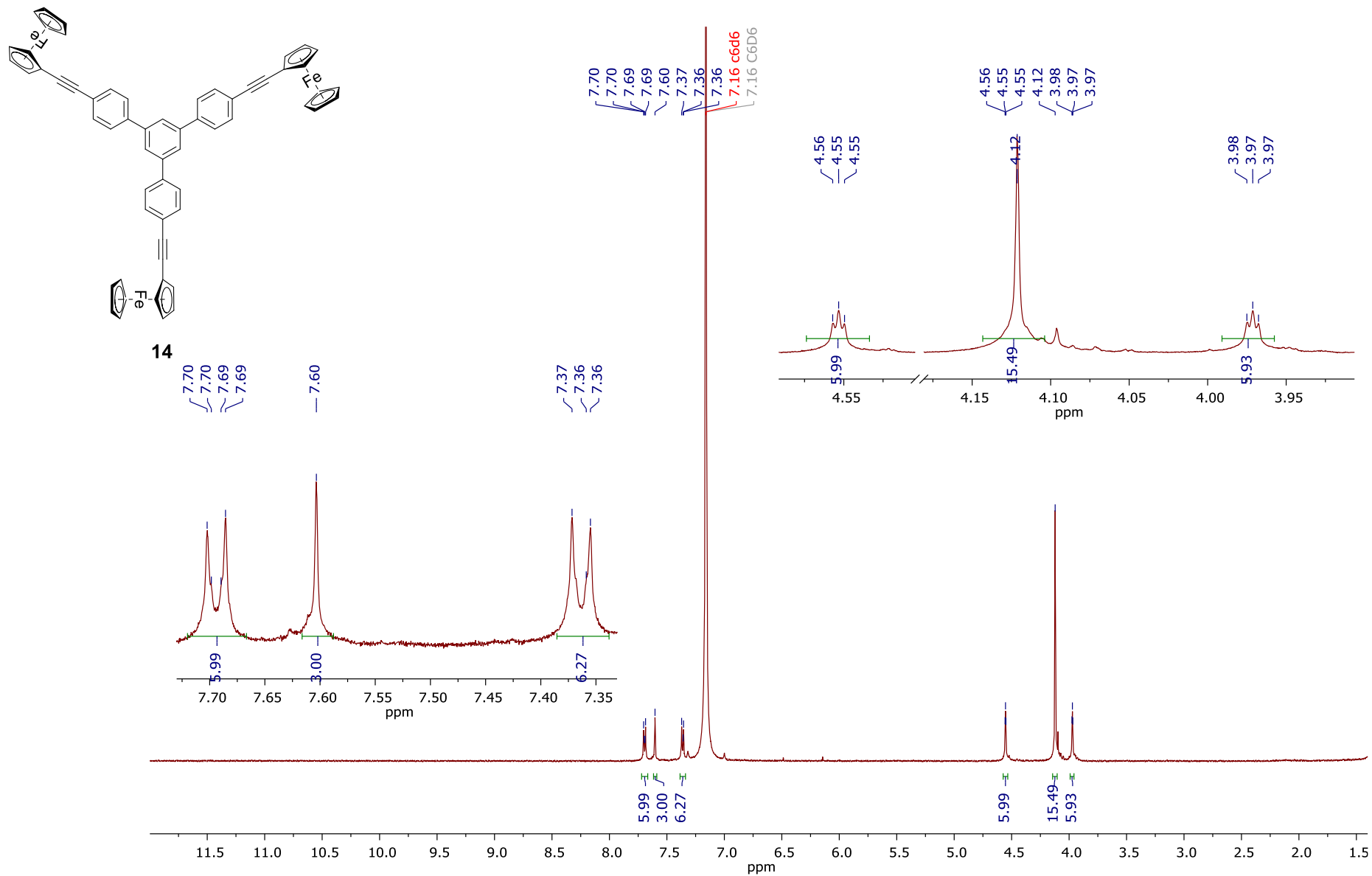


Figure S34. $^1\text{H NMR}$ (500 MHz, C_6D_6) spectrum of 1,3,5-triphenylbenzene-ferrocene conjugate **14**.

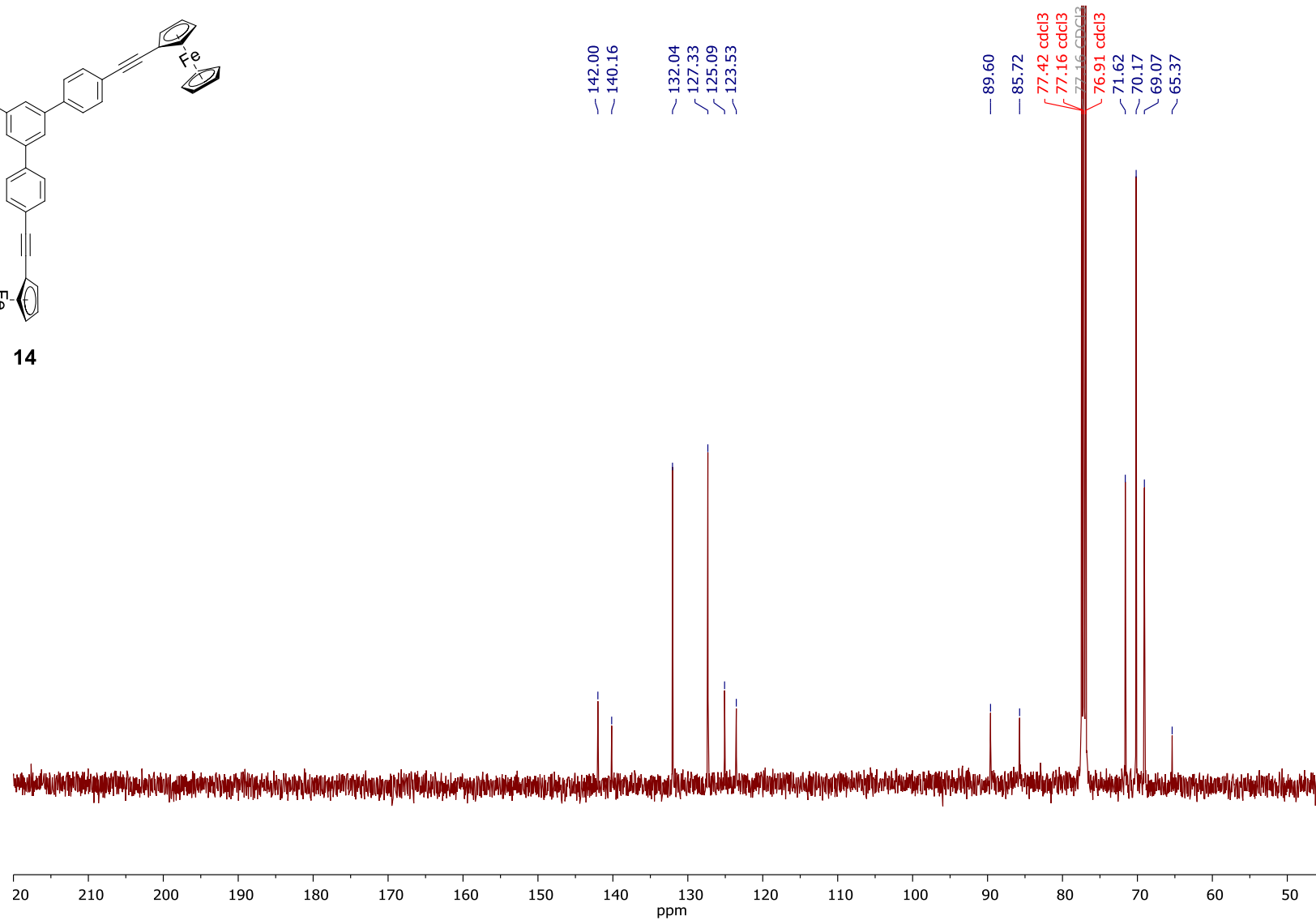
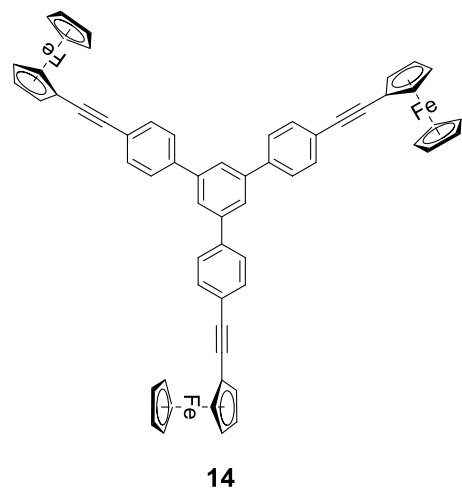


Figure S35. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) spectrum of 1,3,5-triphenylbenzene-ferrocene conjugate **14**.

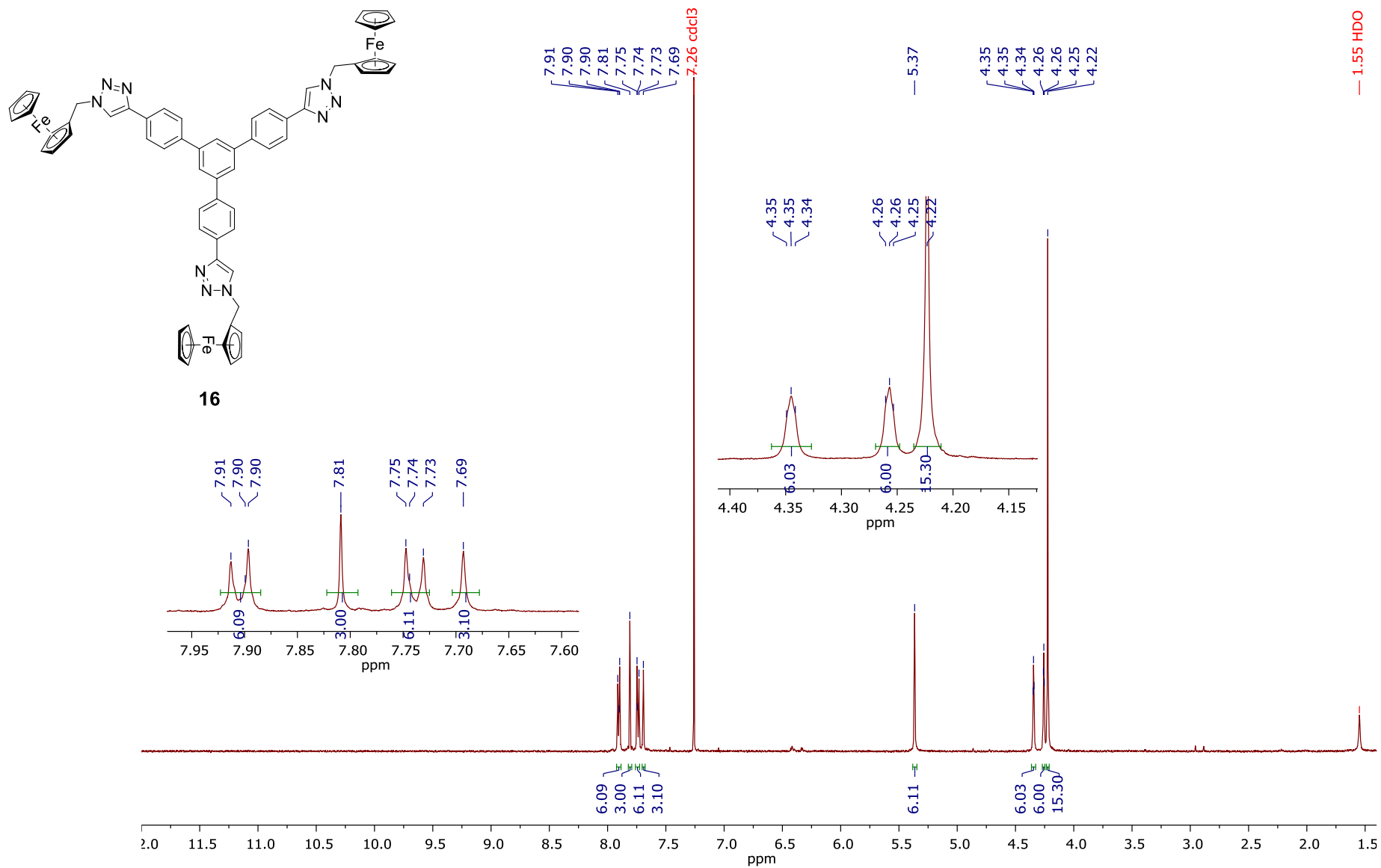


Figure S36. ^1H NMR (500 MHz, CDCl_3) spectrum of 1,3,5-triphenylbenzene-ferrocene conjugate **16**.

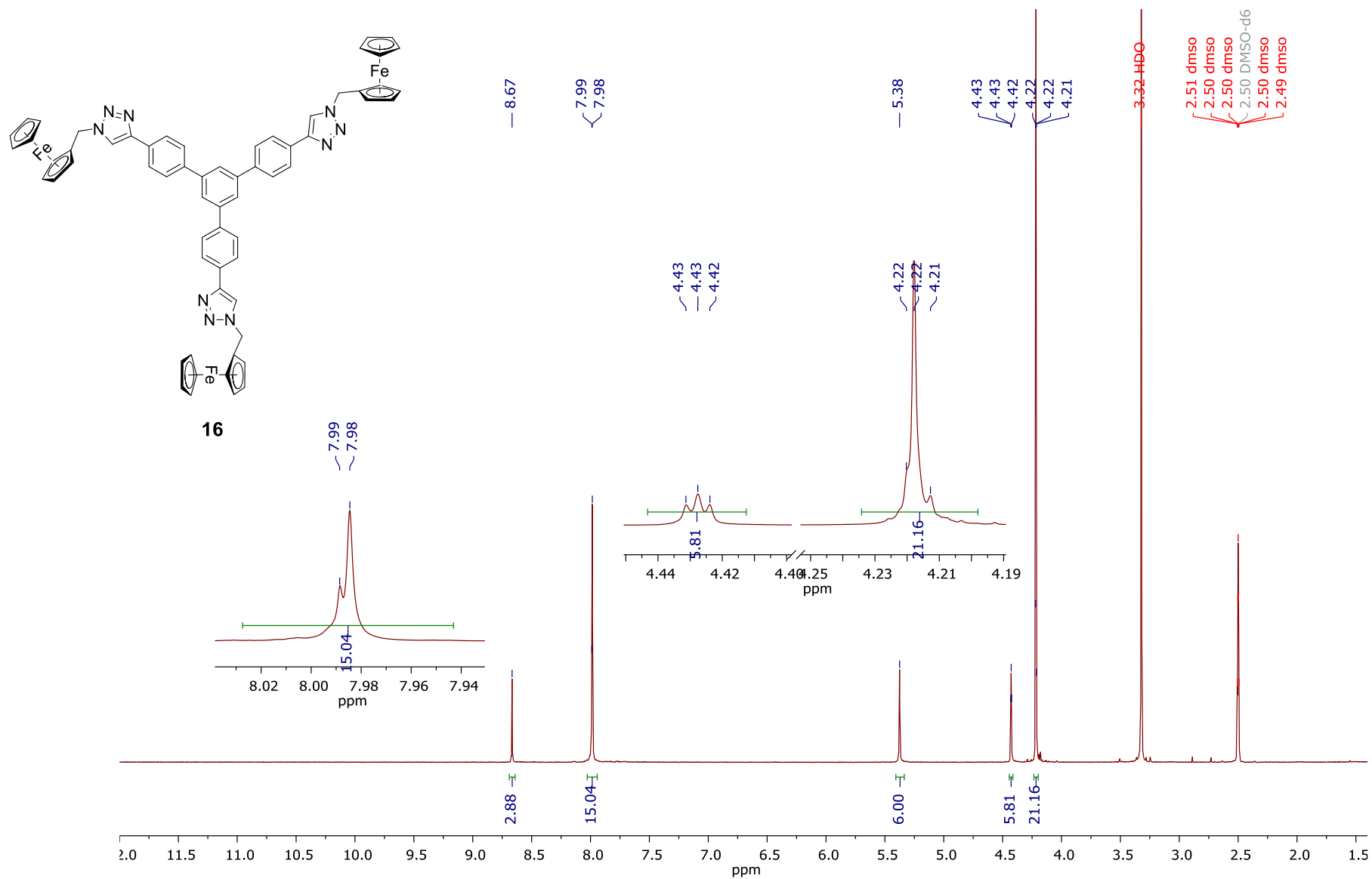


Figure S37. ¹H NMR (500 MHz, DMSO-d₆) spectrum of 1,3,5-triphenylbenzene-ferrocene conjugate **16**.

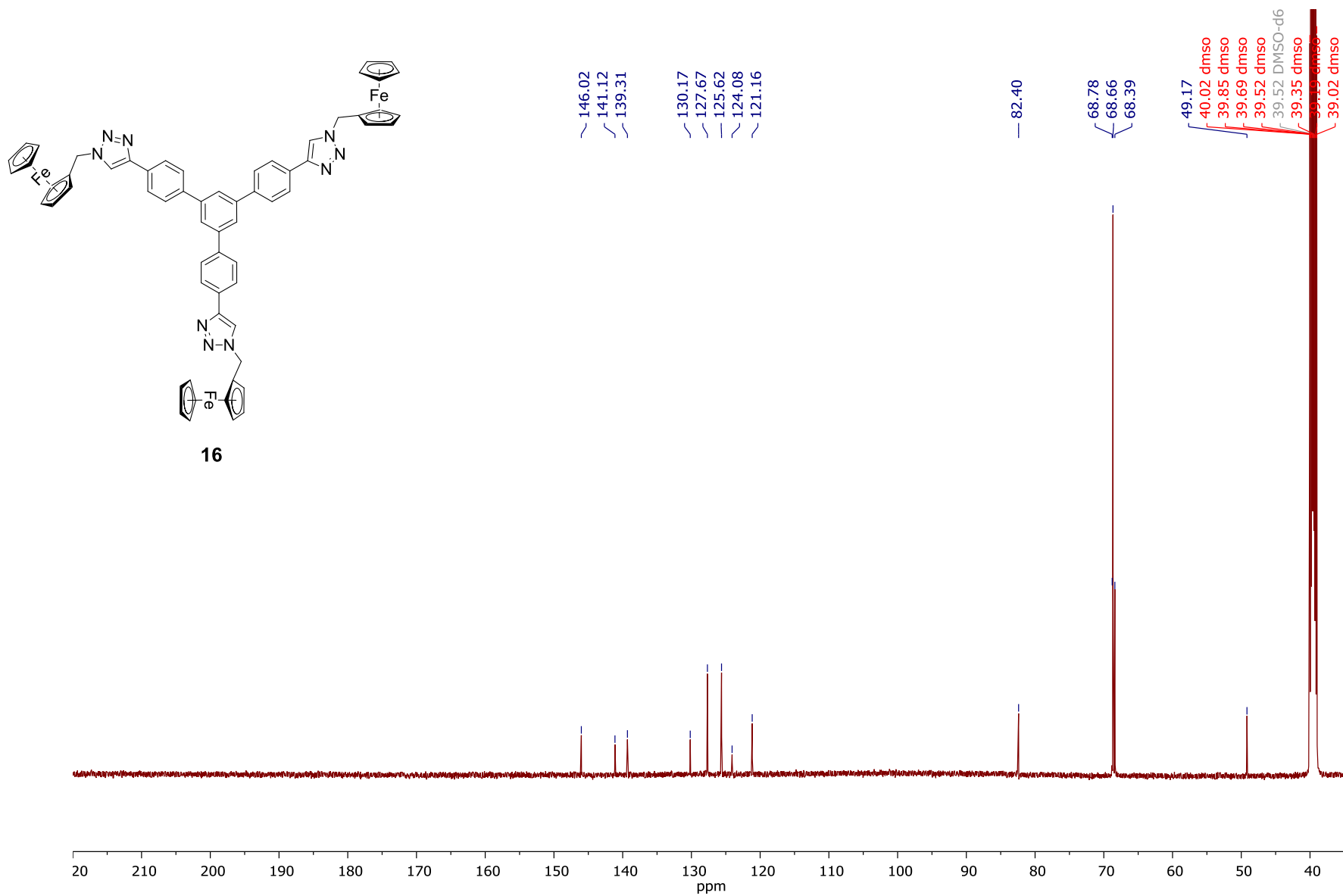


Figure S38. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, DMSO-*d*₆) spectrum of 1,3,5-triphenylbenzene-ferrocene conjugate **16**.

2.2. Additional comments on the NMR spectra of sumanene-ferrocene conjugates

2.2.1. General comment

The NMR spectra of sumanene-ferrocene conjugates **sumFc-1-sumFc-3** consisted of the signals originating from the presence of C_3 symmetrical and unsymmetrical diastereomer (for the respective structures of those isomers, see Figure S39), similarly to NMR spectra of other sumanene derivatives synthesized with this method.⁸⁻¹⁰

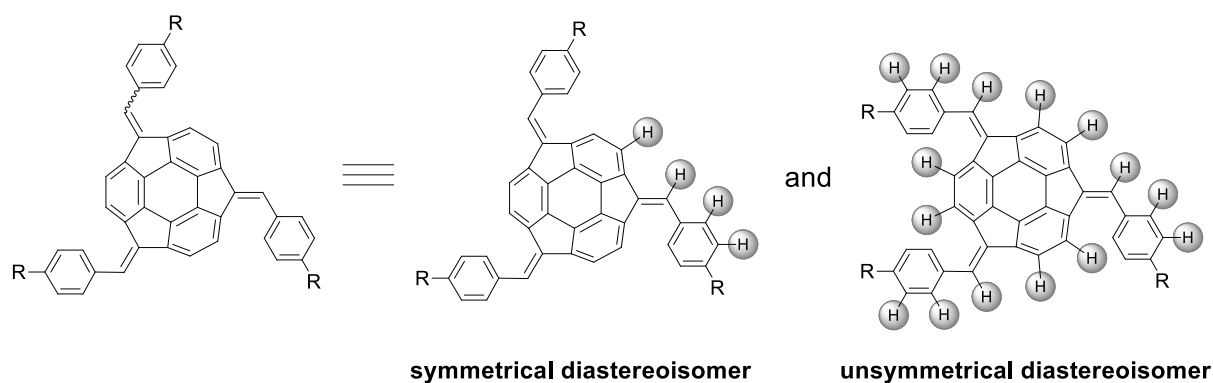


Figure S39. The structures of C_3 symmetrical and unsymmetrical diastereomer of the discussed sumanene derivatives. For clarity, the magnetically inequivalent protons are labeled with grey circles. The same color does not correspond to the same chemical shift in the NMR spectrum.

2.2.2. Comments regarding the NMR spectra of sumanene-ferrocene conjugate **sumFc-1**.

Several groups of multiplets and 4 singlets can be found in the ^1H NMR spectrum of sumanene-ferrocene conjugate **sumFc-1**. Those groups of signals are graphically presented in Figure S40 and are labeled in ^1H NMR spectrum presented in Figure S41.

Seven or twenty-four signals shall be found in the ^1H NMR spectrum of symmetrical and unsymmetrical stereoisomer of **sumFc-1**, respectively. Those signals overlap what results in the presence of several groups of multiplets in the spectrum.

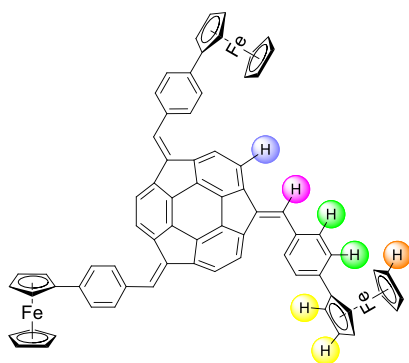
The signals originating from the sumanene skeleton, ferrocene unit and phenylene linkage can be found in the spectrum. The total number of protons (48H), as well as the number of protons within given groups of signals, are consistent with the anticipated values. Noteworthy, the lack of signals coming from the benzylic protons of sumanene also confirms the successful modification of sumanene skeleton (for the reference ^1H NMR spectrum of sumanene, see Figure S1).

Four singlets located at 4.12, 4.11, 4.07 and 4.06 ppm were ascribed to the 15 protons of the unsubstituted cyclopentadienyl (C_p) ring of ferrocene (symmetrical diastereoisomer = 1 signal = 1 x s, unsymmetrical diastereoisomer = 3 signals = 3 x s). ^1H - ^1H COSY NMR analysis confirmed that those signals are indeed four singlets, not two doublets or doublet of doublets (see graphical representation in Figure S42 and the full ^1H - ^1H COSY NMR spectrum in Figure S4).

Four multiplets located at 4.76-4.74, 4.70-4.68, 4.41-4.40 and 4.36-4.35 ppm were ascribed to the 12 protons of the substituted C_p ring of ferrocene (symmetrical diastereoisomer = 2 signals = 2 x t-like m, unsymmetrical diastereoisomer = 6 signals = 6 x t-like m). The presence of multiplets in the spectrum for those signals originates from the fact that characteristic triplet-like multiplets coming from the substituted C_p ring of ferrocene overlap.

Multiplets located at 7.54-7.21 ppm were ascribed to the 9 protons of the sumanene skeleton (6H; symmetrical diastereoisomer = 1 signal = 1 x s, unsymmetrical diastereoisomer = 6 signals = 6 x d) and methidene moieties (3H; symmetrical diastereoisomer = 1 signal = 1 x s, unsymmetrical diastereoisomer = 3 signals = 3 x s). ^1H - ^1H COSY NMR analysis further supported this hypothesis (see graphical representation in Figure S42 and the full ^1H - ^1H COSY NMR spectrum in Figure S4). Multiplet located at ca. 7.54-7.50 ppm overlap with the multiplet located at ca. 7.60-7.54 ppm coming from the sumanene skeleton. This hypothesis has been clearly confirmed with the ^1H - ^1H COSY NMR analysis (see graphical representation in Figure S42 and the full ^1H - ^1H COSY NMR spectrum in Figure S4).

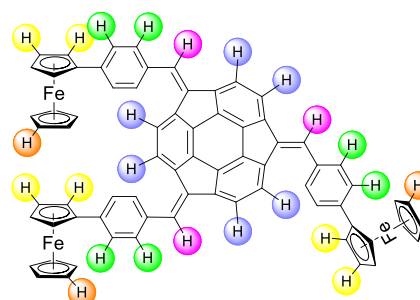
Two multiplets located at 7.88-7.78 and 7.60-7.54 ppm were ascribed to the 12 protons of the phenylene linkage (symmetrical diastereoisomer = 2 signals = 2 x m, unsymmetrical diastereoisomer = 6 signals = 6 x m). This hypothesis has been confirmed with the ^1H - ^1H COSY NMR analysis (see Figure S4).



sumFc-1
symmetrical diastereoisomer

7 signals in ^1H NMR

signal label	intensity	signal types
	6H	s
	3H	s
	2 x 6H = 12H	2 x m
	2 x 6H = 12H	2 x t-like m
	15H	s
total = 48 H		total = 7 signals



sumFc-1
unsymmetrical diastereoisomer

24 signals in ^1H NMR

signal label	intensity	signal types
	6 x 1H	6 x d
	3 x 1H	3 x s
	6 x 2H = 12H	6 x m
	6 x 2H = 12H	6 x t-like m
	3 x 5H = 15H	3 x s
total = 48 H		total = 24 signals

Figure S40. Graphical representation of the number and types of signals observed in the ^1H NMR spectra of sumanene-ferrocene conjugate **sumFc-1**. The same color does not correspond to the same chemical shift in the NMR spectrum.

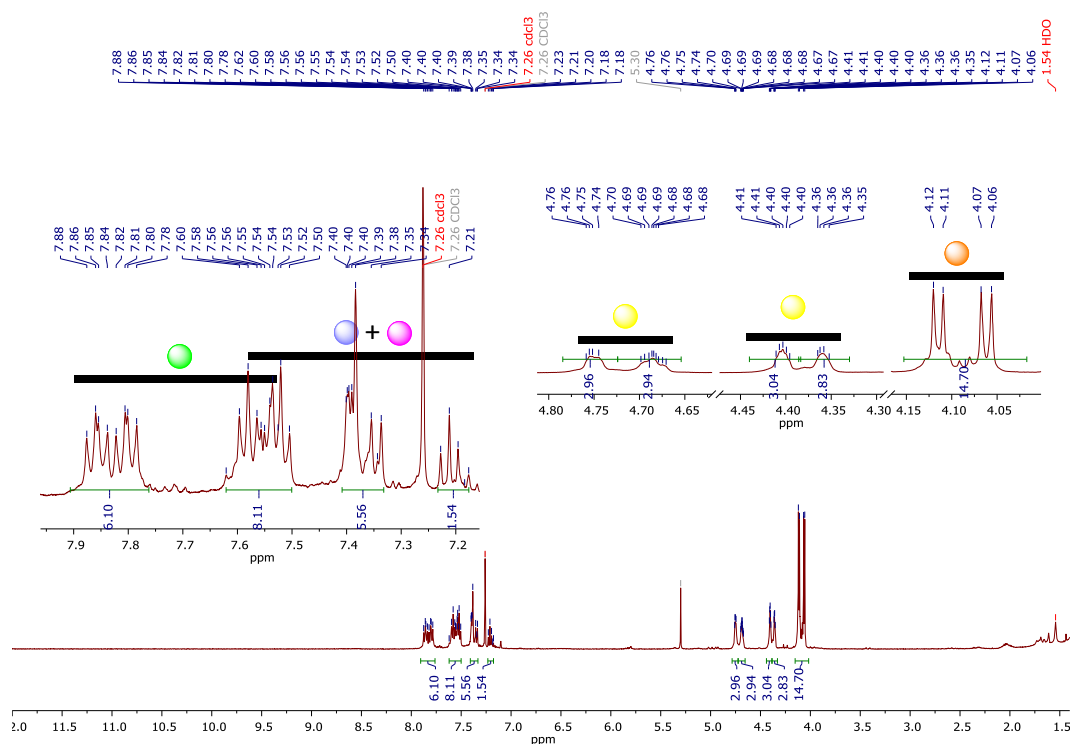


Figure S41. ^1H NMR (500 MHz, CDCl_3) spectrum of sumanene-ferrocene conjugate **sumFc-1** with the signals ascribed to the given groups. For the labels, see Figure S40.

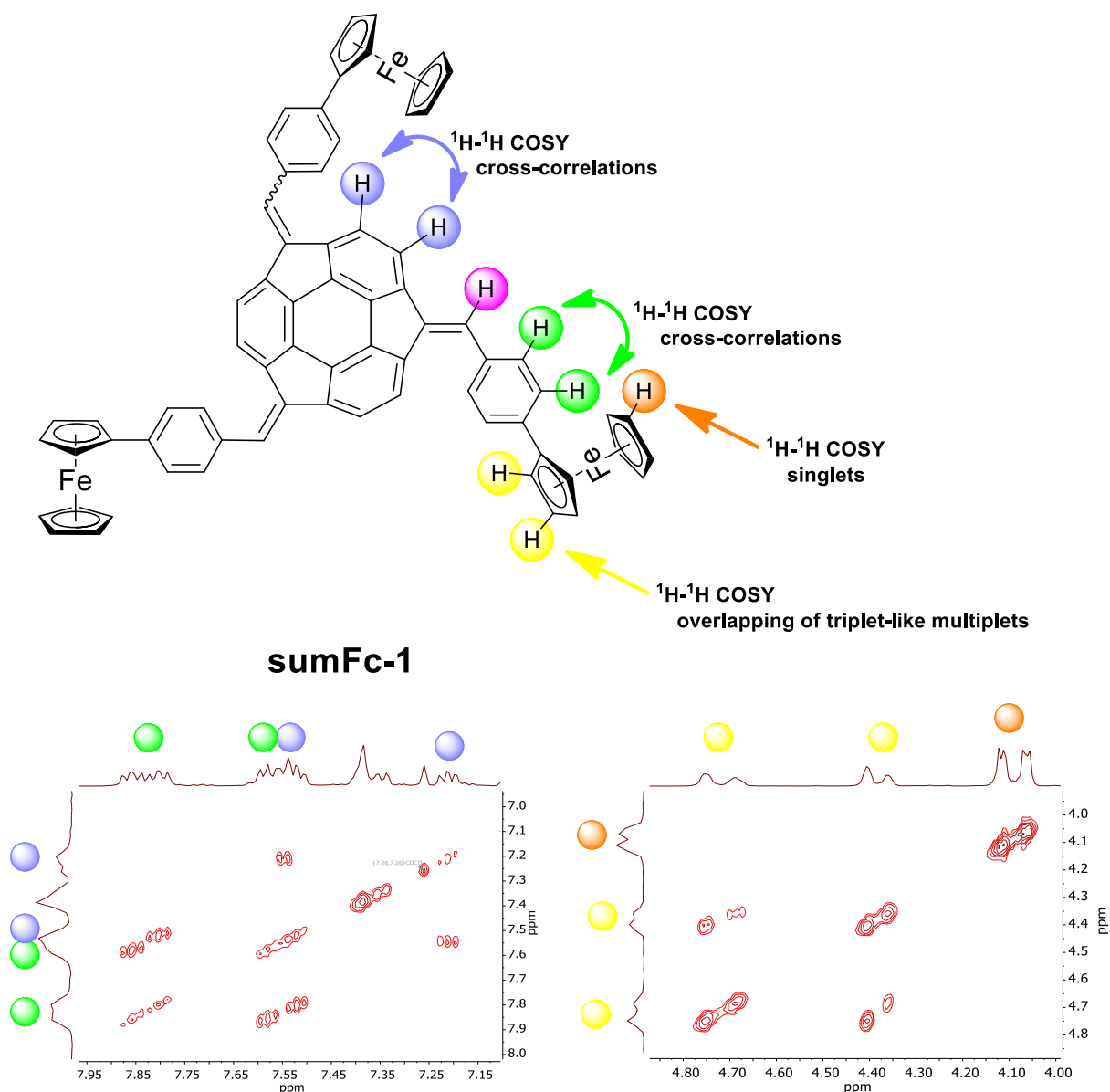


Figure S42. Graphical representation of the types of signals observed in the ^1H NMR spectrum of sumanene-ferrocene conjugate **sumFc-1** and the graphical representation of the cross-correlations in the ^1H - ^1H COSY NMR spectra together with the crucial insets of this spectra. For the full ^1H - ^1H COSY NMR spectrum, see Figure S4.

Sixteen groups of signals can be found in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of sumanene-ferrocene conjugate **sumFc-1**, what is consistent with the anticipated value. Those groups of signals are graphically presented in Figure S43 and are labeled in $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum presented in Figure S44.

Sixteen or forty-eight signals shall be found in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of symmetrical and unsymmetrical stereoisomer of **sumFc-1**, respectively. Noteworthy, within most groups of signals in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **sumFc-1**, four singlets can be observed, what is highly consisted with the anticipated value (symmetrical diastereoisomer = 1 signal = 1 x s, unsymmetrical diastereoisomer = 3 signals = 3 x s), see, e.g., the signal located at 84.7-84.6 ppm (characteristic *ipso* ^{13}C nucleus of substituted Cp ring of ferrocene).

Signals located at 148.0-120.6 ppm were ascribed to the presence of various ^{13}C nucleus coming from the sumanene skeleton, phenylene linkage and methidene moieties.

Signals located at 84.7-66.7 ppm were ascribed to the presence of ferrocene units. Signals located at 70.0-69.9 ppm were ascribed to the ^{13}C nucleus of unsubstituted C_p ring of ferrocene. Signals located at 69.6-69.5 and 66.8-66.7 ppm were ascribed to the ^{13}C nucleus of substituted C_p ring of ferrocene. Signals located at 84.7-84.6 ppm were ascribed to the characteristic *ipso* ^{13}C nucleus of substituted Cp ring of ferrocene.

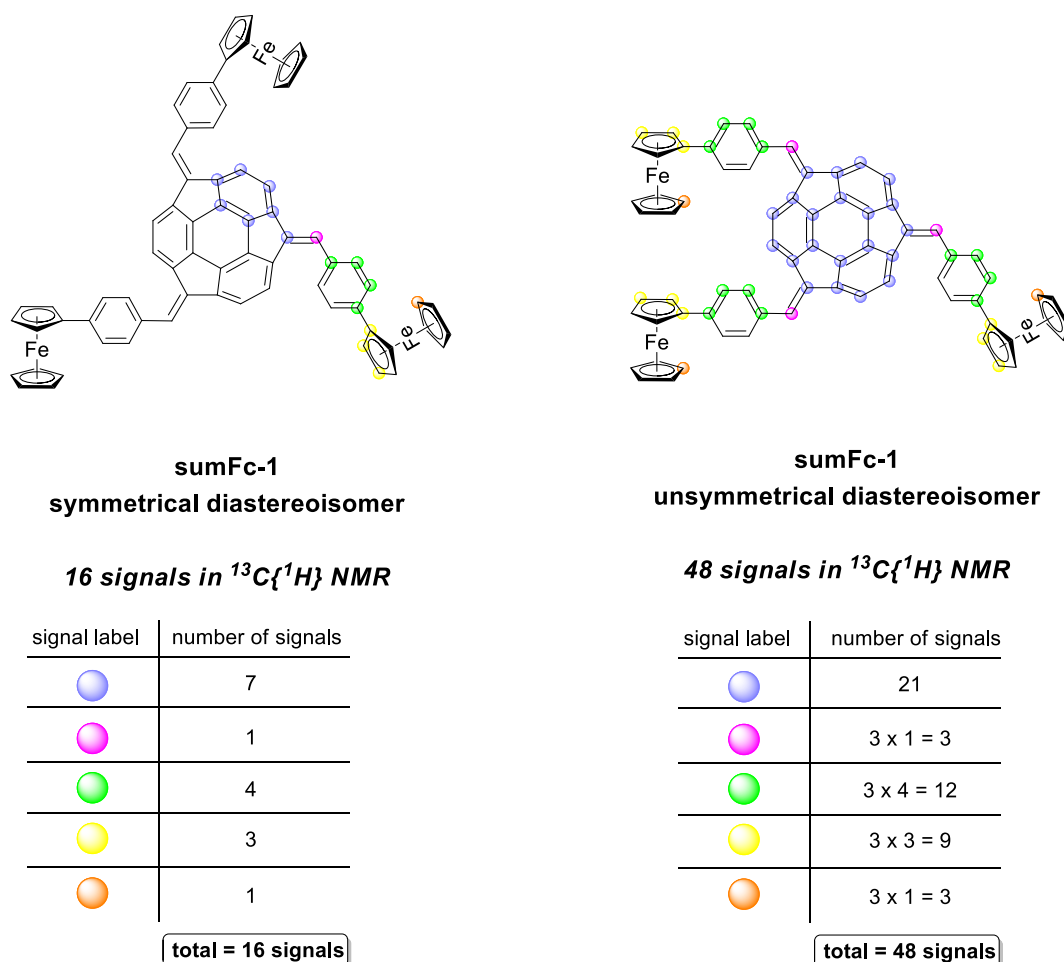


Figure S43. Graphical representation of the number of signals observed in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of sumanene-ferrocene conjugate **sumFc-1**. The same color does not correspond to the same chemical shift in the NMR spectrum.

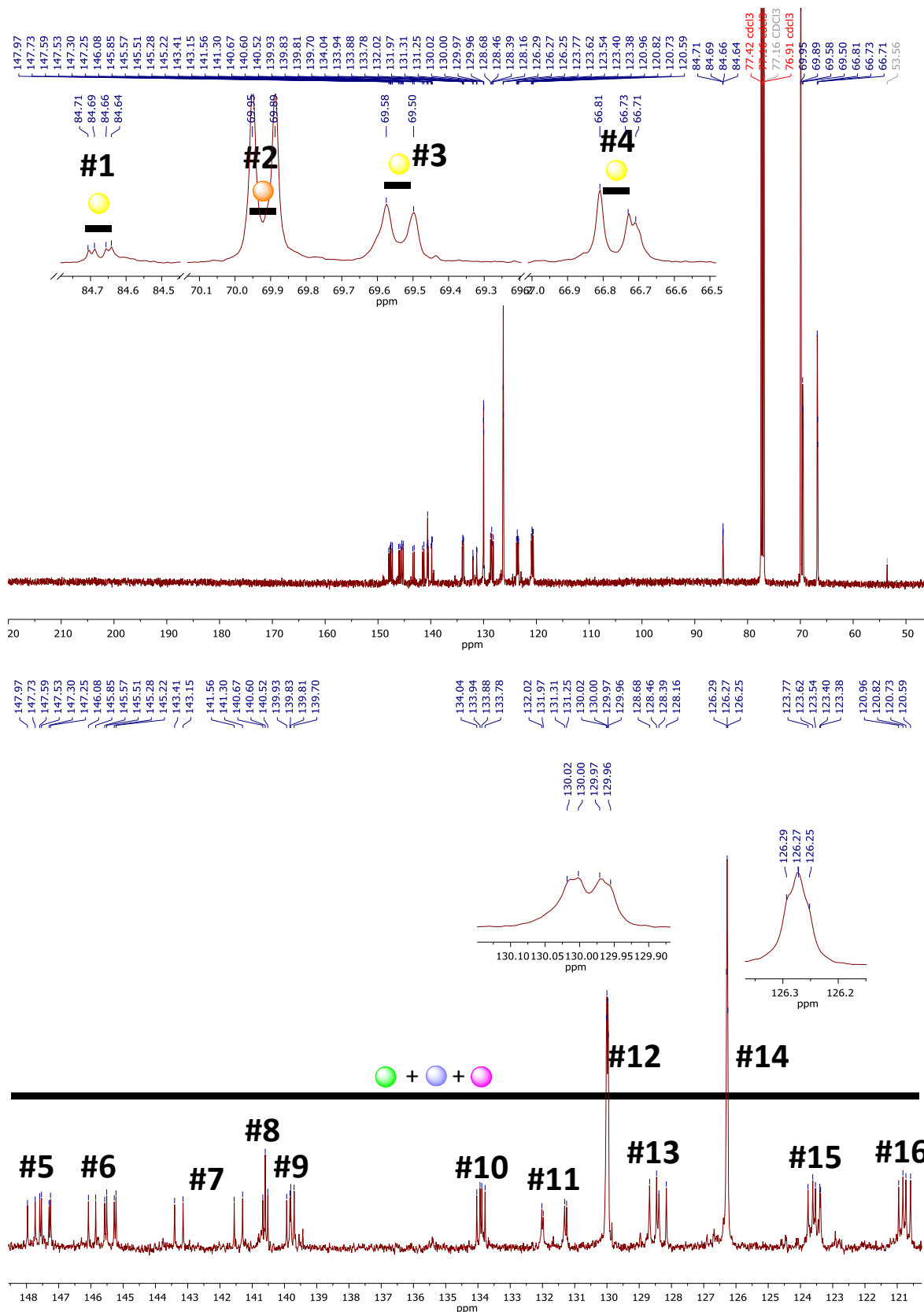


Figure S44. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CHCl_3) spectrum of sumanene-ferrocene conjugate **sumFc-1** with the signals ascribed to the given groups. For the labels, see Figure S43.

The signals originating from the presence of ferrocene in the synthesized compounds overlapped in the ^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, hence, ^1H - ^{13}C HSQC NMR analyses were especially helpful to support the ascription of the signals originating from the presence of ferrocene in the synthesized conjugates **sumFc-1** – **sumFc-3**, see graphical representation for the representative sumanene derivative **sumFc-1** in Figure S45.

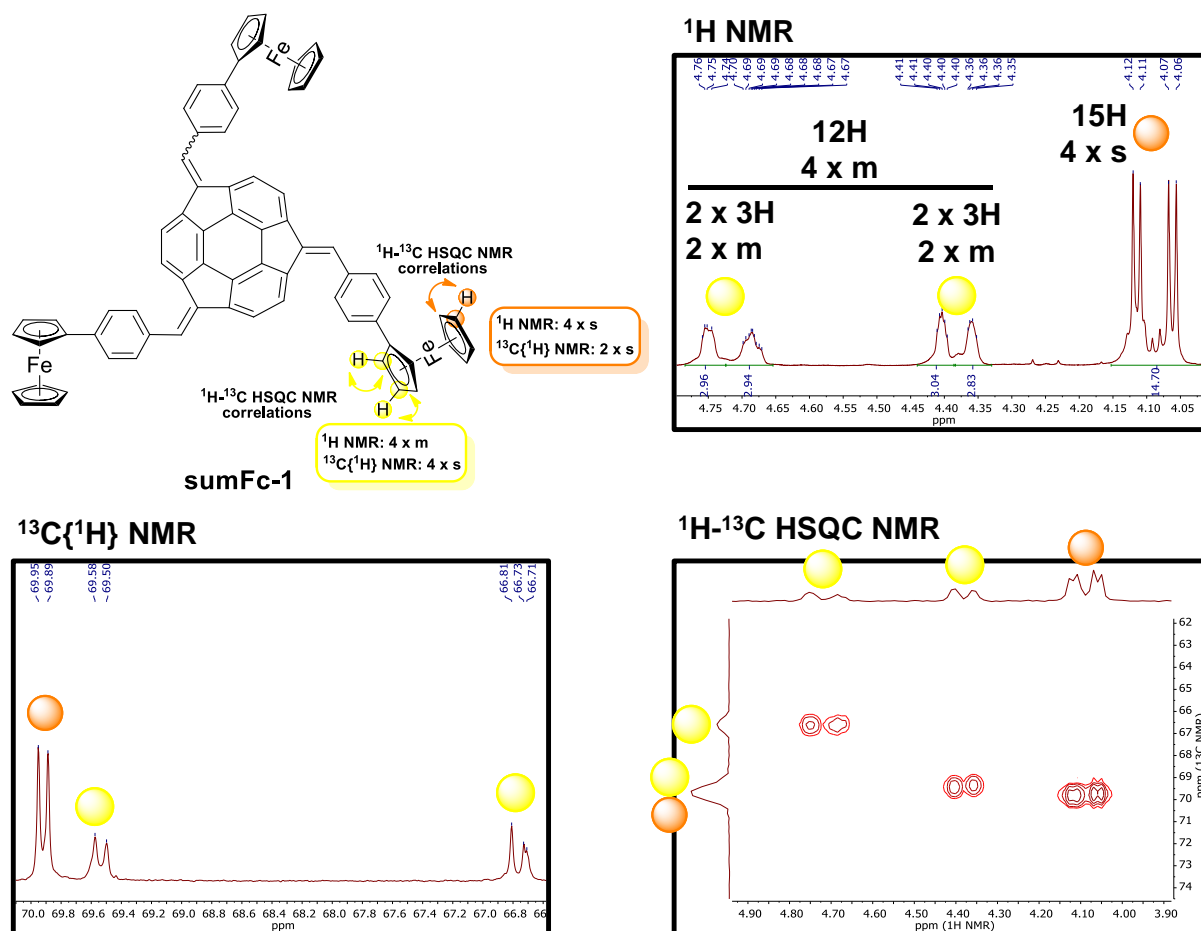


Figure S45. The graphical representation of the correlations in the ^1H - ^{13}C HSQC NMR spectra for the ferrocene unit in sumanene-ferrocene conjugate **sumFc-1** (crucial insets of this spectra are presented). For the detailed discussion on the NMR spectra of **sumFc-1** – **sumFc-3**, see section 2 in Supporting Information

2.2.3. Comments regarding the NMR spectra of sumanene-ferrocene conjugate **sumFc-2**.

Several groups of multiplets and 4 singlets can be found in the ^1H NMR spectrum of sumanene-ferrocene conjugate **sumFc-2**. Those groups of signals are graphically presented in Figure S46 and are labeled in ^1H NMR spectrum presented in Figure S47.

Seven or twenty-four signals shall be found in the ^1H NMR spectrum of symmetrical and unsymmetrical stereoisomer of **sumFc-2**, respectively. Those signals overlap what results in the presence of several groups of multiplets in the spectrum.

The signals originating from the sumanene skeleton, ferrocene unit and phenylene linkage can be found in the spectrum. The total number of protons (48H), as well as the number of protons within given groups of signals, are consistent with the anticipated values. Noteworthy, the lack of signals coming from the benzylic protons of sumanene also confirms the successful modification of sumanene skeleton (for the reference ^1H NMR spectrum of sumanene, see Figure S1).

Four singlets located at 4.26, 4.25, 4.23 and 4.22 ppm were ascribed to the 15 protons of the unsubstituted C_p ring of ferrocene (symmetrical diastereoisomer = 1 signal = 1 x s, unsymmetrical diastereoisomer = 3 signals = 3 x s). ^1H - ^1H COSY NMR analysis confirmed that those signals are indeed four singlets, not two dublets or dublet of dublets (see graphical representation in Figure S48 and the full ^1H - ^1H COSY NMR spectrum in Figure S11).

Four multiplets located at 4.27-4.26, 4.30-4.28, 4.51-4.50 and 4.54-4.53 ppm were ascribed to the 12 protons of the substituted C_p ring of ferrocene (symmetrical diastereoisomer = 2 signals = 2 x t-like m, unsymmetrical diastereoisomer = 6 signals = 6 x t-like m). The presence of multiplets in the spectrum for those signals originates from the fact that the characteristic triplet-like multiplets coming from the substituted C_p ring of ferrocene overlap. Noteworthy, in the 4.27-4.25 ppm area of the spectrum, two singlets (unsubstituted C_p ring of ferrocene) and one multiplet (substituted C_p ring of ferrocene) overlap. This observation has been also confirmed with the ^1H - ^1H COSY NMR analysis (see graphical representation in Figure S48 and the full ^1H - ^1H COSY NMR spectrum in Figure S11).

Multiplets located at 7.30-7.29, 7.48-7.47 and 7.54-7.51 ppm were ascribed to the 9 protons of the sumanene skeleton (6H; symmetrical diastereoisomer = 1 signal = 1 x s, unsymmetrical diastereoisomer = 6 signals = 6 x d) and methidene moieties (3H; symmetrical diastereoisomer = 1 signal = 1 x s, unsymmetrical diastereoisomer = 3 signals = 3 x s). ^1H - ^1H COSY NMR analysis further supported this hypothesis (see graphical representation in Figure S48 and the full ^1H - ^1H COSY NMR spectrum in Figure S11).

Multiplets located at 7.58-7.53, 7.89-7.88 and 7.95-7.94 ppm were ascribed to the 12 protons of the phenylene linkage (symmetrical diastereoisomer = 2 signals = 2 x m, unsymmetrical diastereoisomer = 6 signals = 6 x m). This hypothesis has been clearly confirmed with the ^1H - ^1H COSY NMR analysis (see graphical representation in Figure S48 and the full ^1H - ^1H COSY NMR spectrum in Figure S11). Multiplet located at 7.58-7.53 ppm overlap with the multiplet located at 7.54-7.51 ppm coming from the sumanene skeleton.

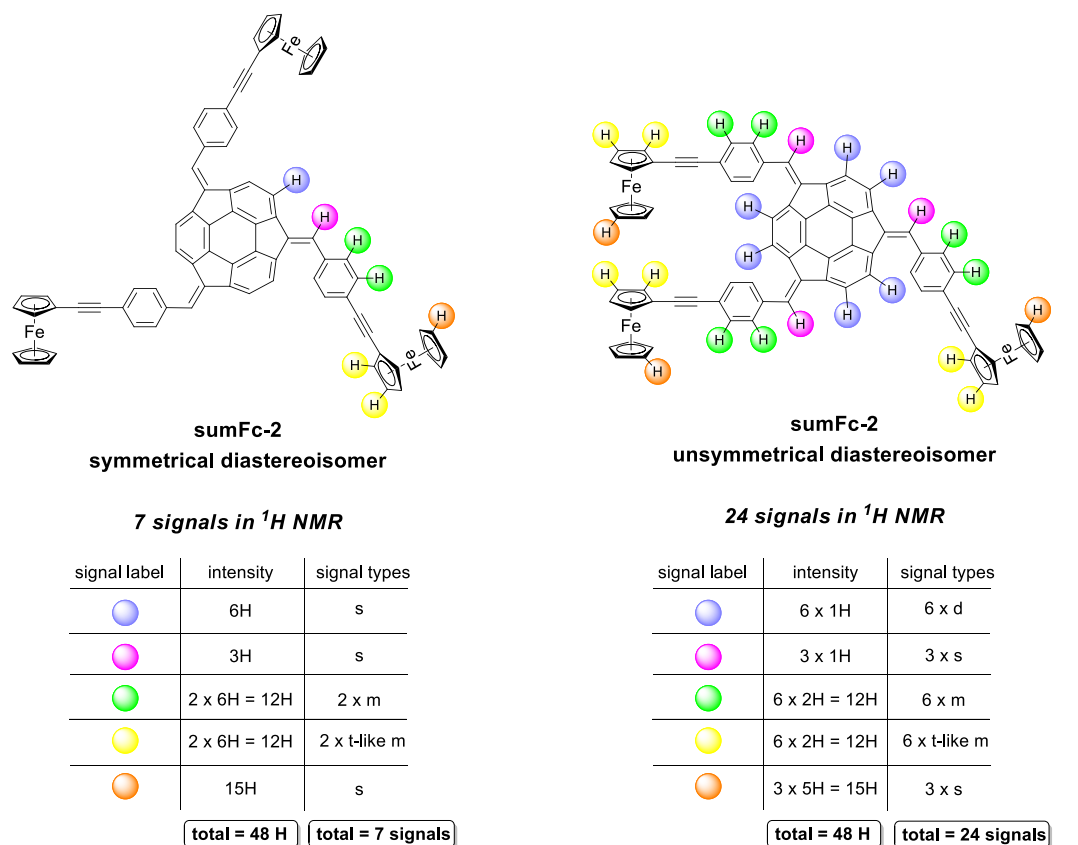
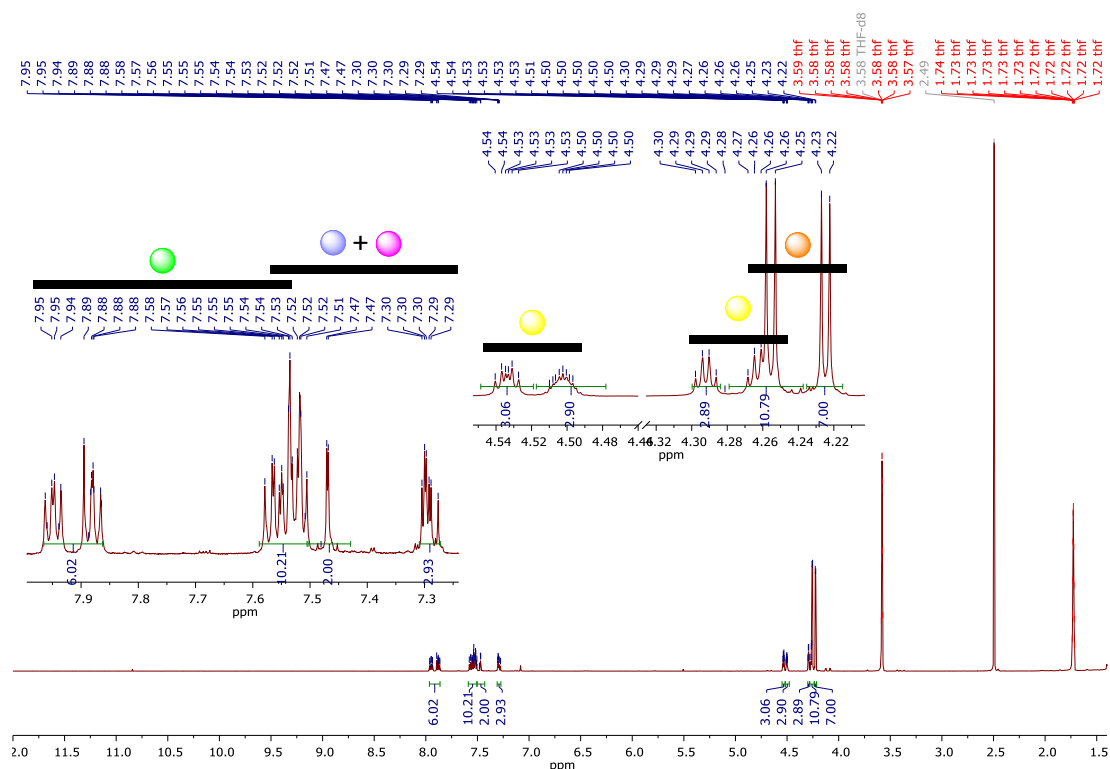


Figure S46. Graphical representation of the number of signals observed in the ^1H NMR spectra of sumanene-ferrocene conjugate **sumFc-2**. The same color does not correspond to the same chemical shift in the NMR spectrum.



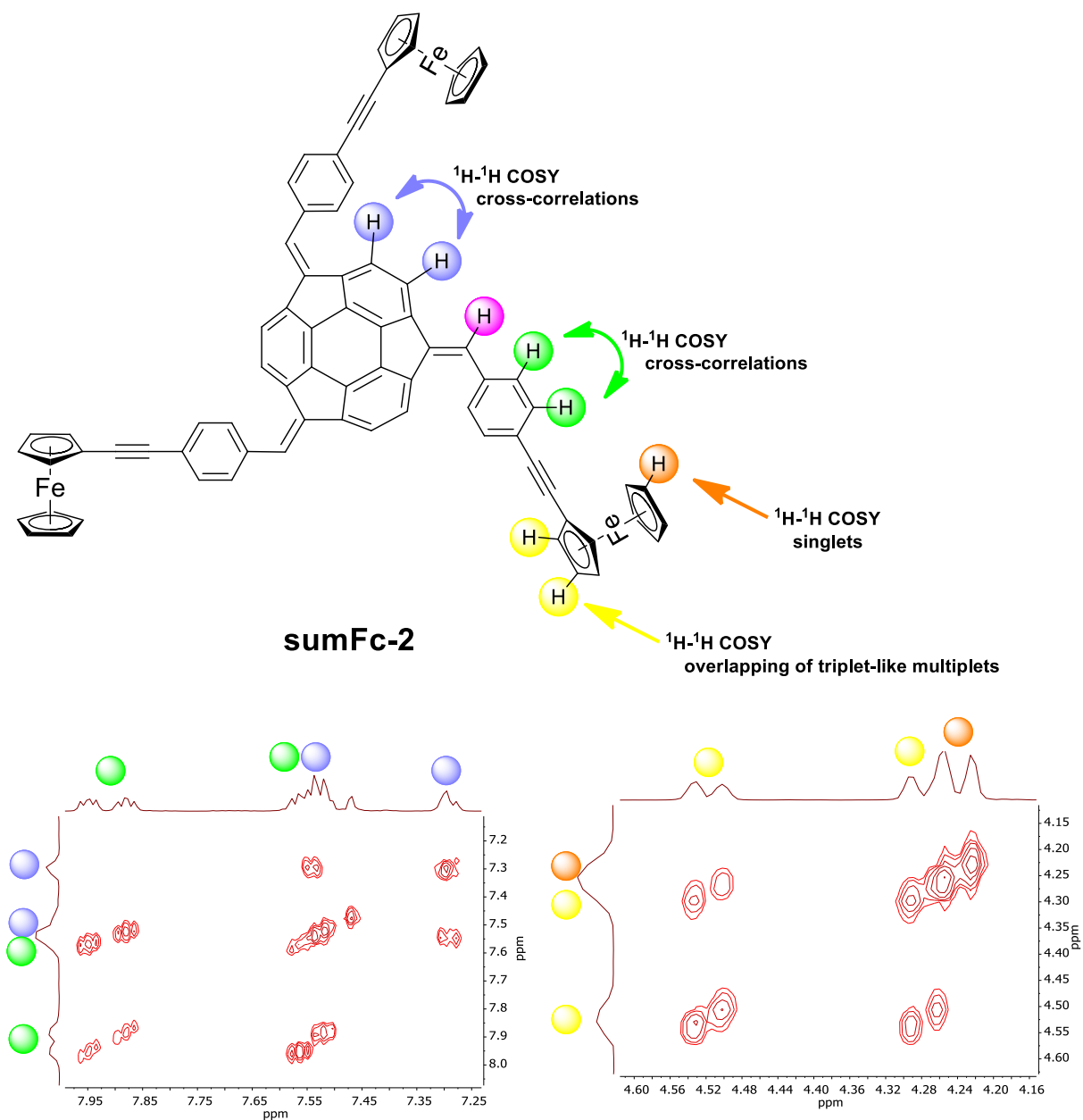


Figure S48. Graphical representation of the types of signals observed in the ^1H NMR spectrum of sumanene-ferrocene conjugate **sumFc-2** and the graphical representation of the cross-correlations in the ^1H - ^1H COSY NMR spectra together with the crucial insets of this spectra. For the full ^1H - ^1H COSY NMR spectrum, see Figure S11.

Eighteen groups of signals can be found in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of sumanene-ferrocene conjugate **sumFc-2**, what is consistent with the anticipated value. Those groups of signals are graphically presented in Figure S49 and are labeled in $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum presented in Figure S50.

Eighteen or fifty-four signals shall be found in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of symmetrical and unsymmetrical stereoisomer of **sumFc-2**, respectively. Noteworthy, within most groups of signals in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **sumFc-2**, four singlets can be observed, what is highly consisted with the anticipated value (symmetrical diastereoisomer = 1 signal = 1 x s, unsymmetrical diastereoisomer = 3 signals = 3 x s), see, e.g., the signal located at 65.2-65.1 ppm (^{13}C nucleus of the acetylene linkage).

Signals located at 147.7-120.8 ppm were ascribed to the presence of various ^{13}C nucleus coming from the sumanene skeleton, phenylene linkage and methidene moieties.

Signals located at 90.6-65.1 ppm were ascribed to the presence of ferrocene units and acetylene linkages. Signals located at 70.2 ppm were ascribed to the ^{13}C nucleus of unsubstituted C_p ring of ferrocene. Signals located at 71.7 and 69.2-69.1 ppm were ascribed to the ^{13}C nucleus of substituted C_p ring of ferrocene. Signals located at 86.1-86.0 ppm were ascribed to the characteristic *ipso* ^{13}C nucleus of substituted C_p ring of ferrocene. Signals located at 90.6 ppm and 65.2-65.1 ppm were ascribed to the ^{13}C nucleus of acetylene linkage.

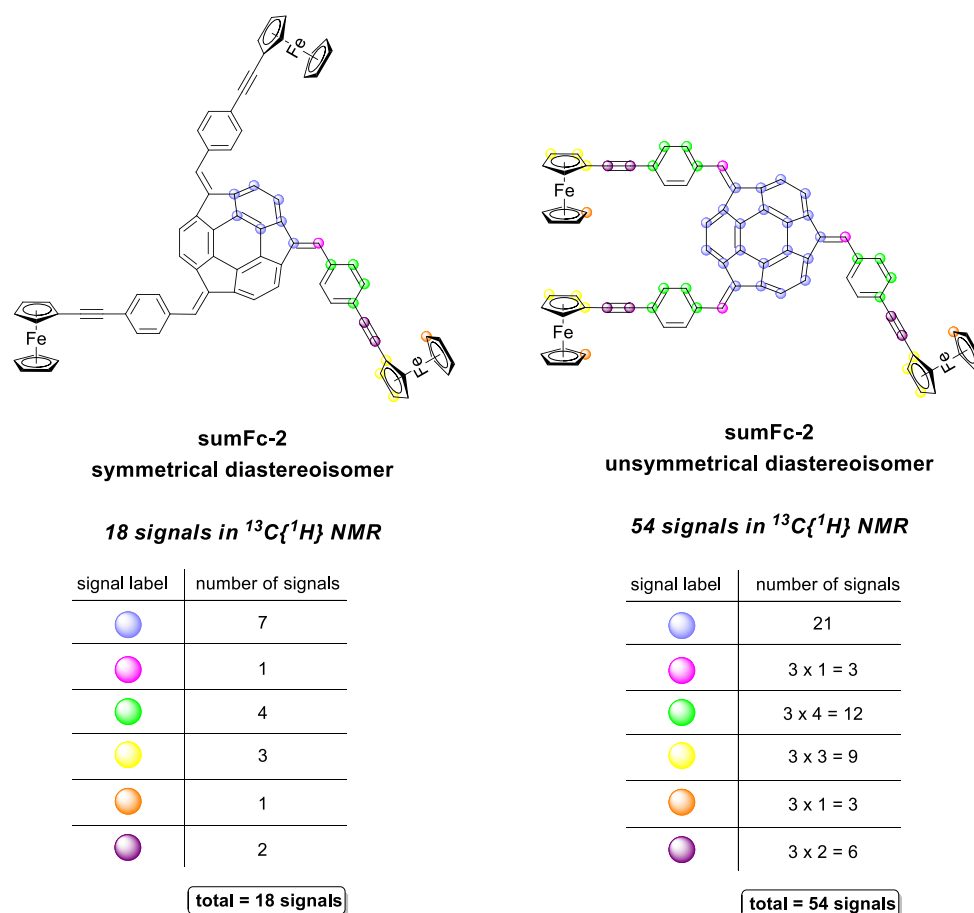


Figure S49. Graphical representation of the number and types of signals observed in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of sumanene-ferrocene conjugate **sumFc-2**. The same color does not correspond to the same chemical shift in the NMR spectrum.

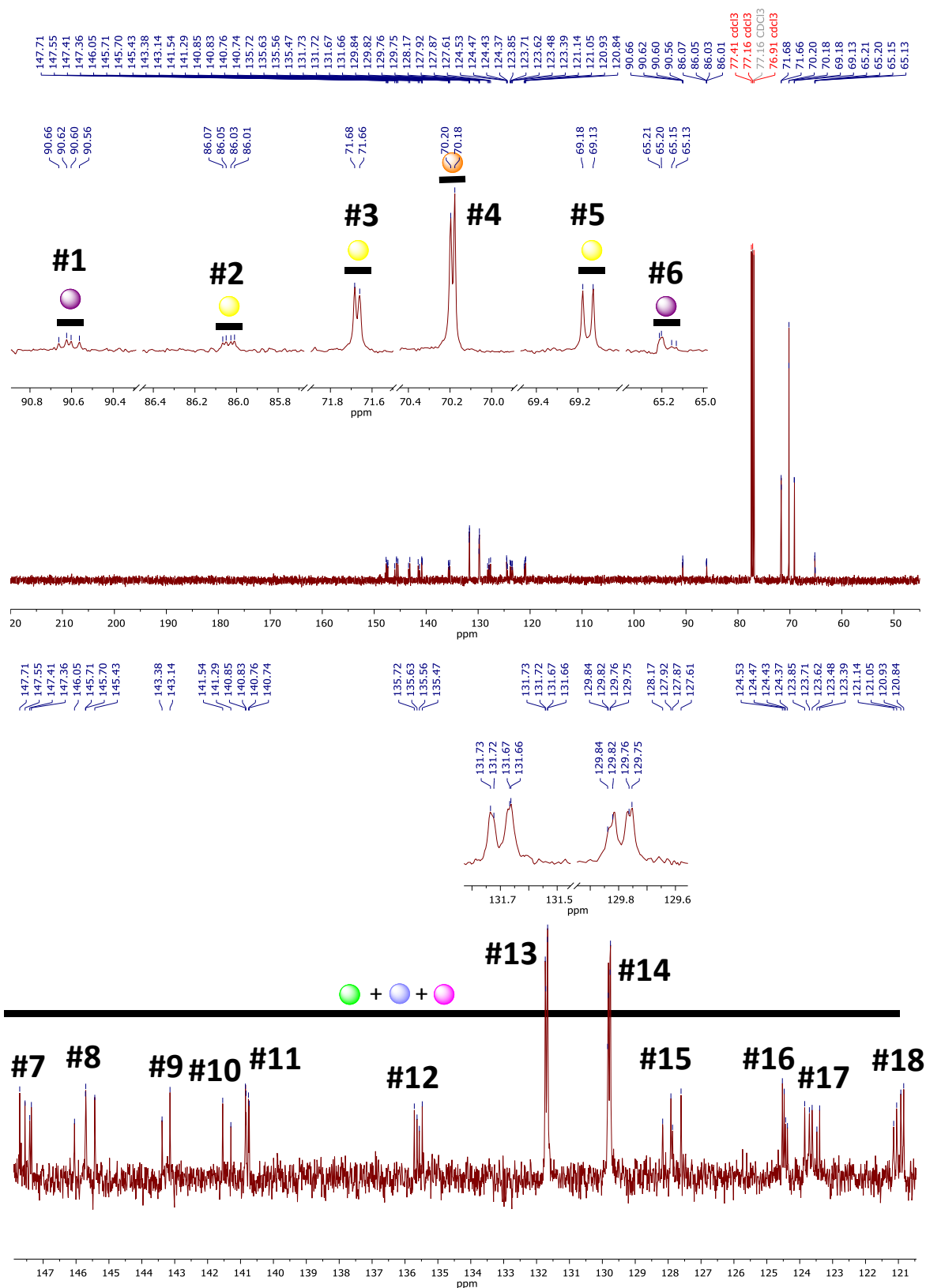


Figure S50. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CHCl_3) spectrum of sumanene-ferrocene conjugate **sumFc-2** with the signals ascribed to the given groups. For the labels, see Figure S49.

2.2.4. Comments regarding the NMR spectra of sumanene-ferrocene conjugate **sumFc-3**.

Several groups of multiplets and three groups of singlets can be found in the ^1H NMR spectrum of sumanene-ferrocene conjugate **sumFc-3**. Those groups of signals are graphically presented in Figure S51 and are labeled in ^1H NMR spectrum presented in Figure S52.

Nine or thirty signals shall be found in the ^1H NMR spectrum of symmetrical and unsymmetrical stereoisomer of **sumFc-3**, respectively. Those signals overlap what results in the presence of several groups of multiplets in the spectrum.

The signals originating from the sumanene skeleton, ferrocene unit, methylene group, phenylene and 1,2,3-triazole linkage can be found in the spectrum. The total number of protons (57H), as well as the number of protons within given groups of signals, are consistent with the anticipated values. Noteworthy, the lack of signals coming from the benzylic protons of sumanene also confirms the successful modification of sumanene skeleton (for the reference ^1H NMR spectrum of sumanene, see Figure S1).

Singlets located at 4.23-4.21 ppm were ascribed to the 15 protons of the unsubstituted C_p ring of ferrocene (symmetrical diastereoisomer = 1 signal = 1 x s, unsymmetrical diastereoisomer = 3 signals = 3 x s). ^1H - ^1H COSY NMR analysis confirmed that those signals are indeed singlets, not two doublets or doublet of doublets (see graphical representation in Figure S53 and the full ^1H - ^1H COSY NMR spectrum in Figure S27).

Multiplets located at 4.38-4.23 ppm were ascribed to the 12 protons of the substituted C_p ring of ferrocene (symmetrical diastereoisomer = 2 signals = 2 x t-like m, unsymmetrical diastereoisomer = 6 signals = 6 x t-like m). The presence of multiplets in the spectrum for those signals originates from the fact that the characteristic triplet-like multiplets coming from the substituted C_p ring of ferrocene overlap.

Four singlets located at 5.38-5.33 ppm were ascribed to the 6 protons of the methylene linkage (symmetrical diastereoisomer = 1 signal = 1 x s, unsymmetrical diastereoisomer = 3 signals = 3 x s). ^1H - ^1H COSY NMR analysis confirmed that those signals are indeed four singlets, not two doublets or doublet of doublets (see graphical representation in Figure S53 and the full ^1H - ^1H COSY NMR spectrum in Figure S27).

Multiplets located at 7.45-7.00 were ascribed to the 9 protons of the sumanene skeleton (6H; symmetrical diastereoisomer = 1 signal = 1 x s, unsymmetrical diastereoisomer = 6 signals = 6 x d) and methidene moieties (3H; symmetrical diastereoisomer = 1 signal = 1 x s, unsymmetrical diastereoisomer = 3 signals = 3 x s). ^1H - ^1H COSY NMR analysis further supported this hypothesis (see graphical representation in Figure S53 and the full ^1H - ^1H COSY NMR spectrum in Figure S27).

Four singlets located at 7.80-7.68 ppm were ascribed to the 3 protons of the 1,2,3-triazole linkage (symmetrical diastereoisomer = 1 signal = 1 x s, unsymmetrical diastereoisomer = 3 signals = 3 x s). ^1H - ^1H COSY NMR analysis confirmed that those signals are indeed four singlets, not two doublets or doublet of doublets (see graphical representation in Figure S53 and the full ^1H - ^1H COSY NMR spectrum in Figure S27).

Multiplets located at 7.93-7.82 ppm were ascribed to the 12 protons of the phenylene linkage (symmetrical diastereoisomer = 2 signals = 2 x m, unsymmetrical diastereoisomer = 6 signals = 6 x m). This hypothesis has been confirmed with the ^1H - ^1H COSY NMR analysis (see graphical representation in Figure S53 and the full ^1H - ^1H COSY NMR spectrum in Figure S27).

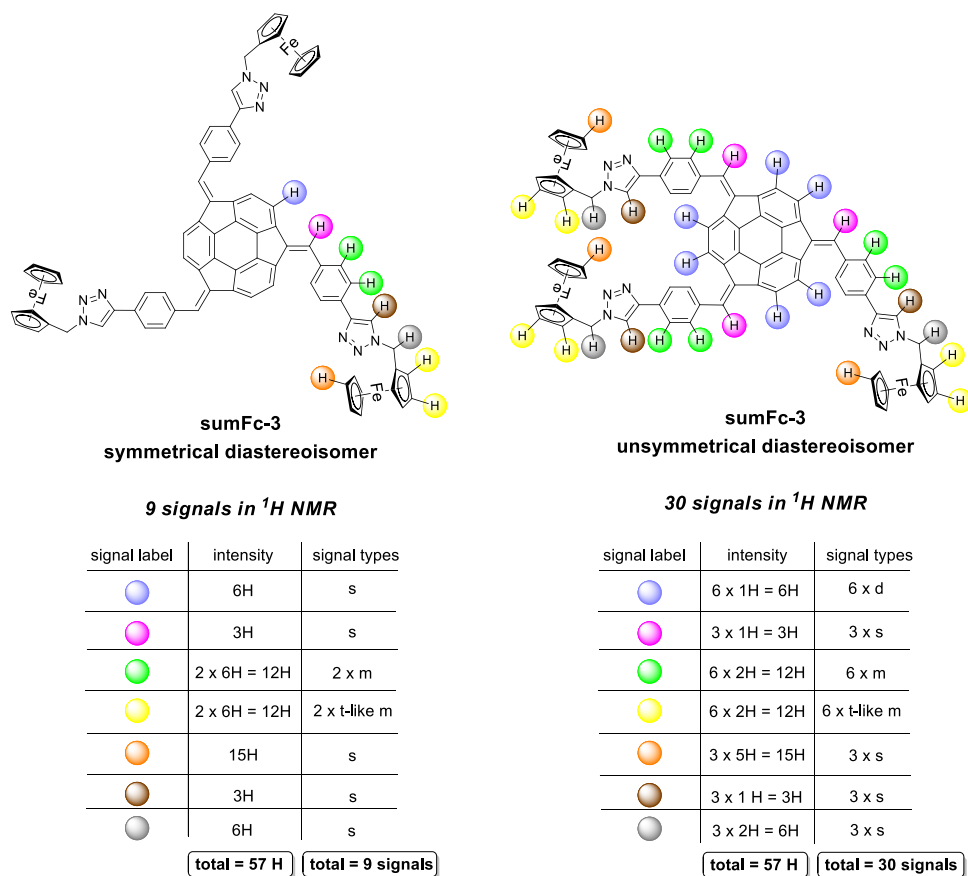


Figure S51. Graphical representation of the number and types of signals observed in the ^1H NMR spectra of sumanene-ferrocene conjugate **sumFc-3**. The same color does not correspond to the same chemical shift in the NMR spectrum.

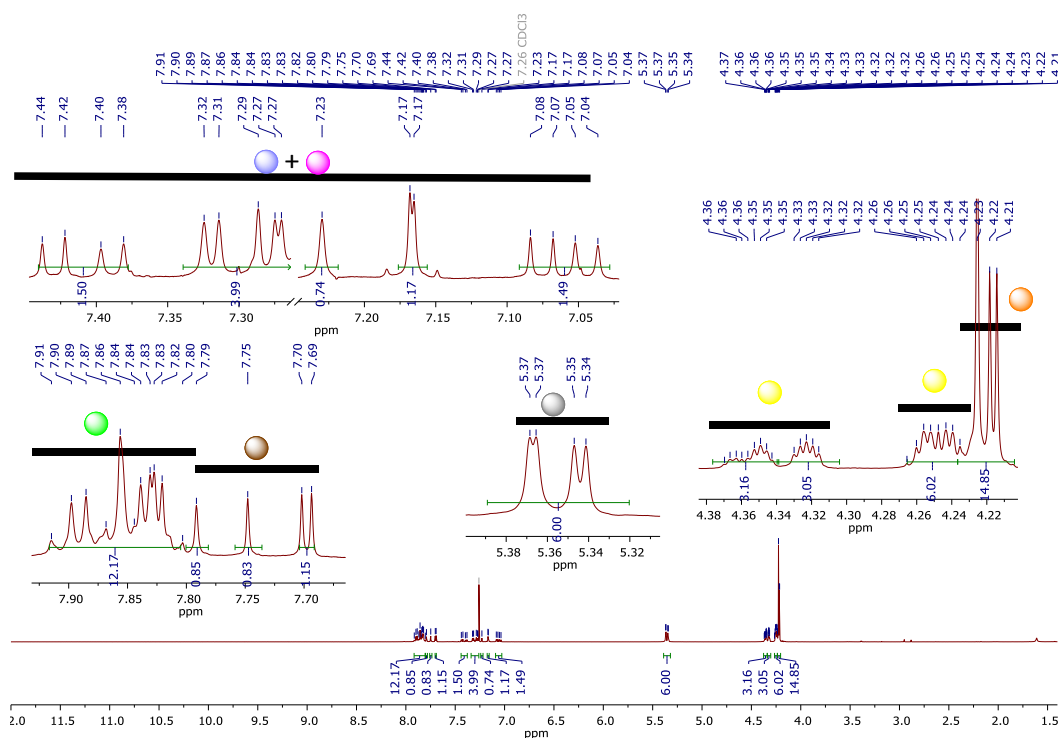


Figure S52. ^1H NMR (500 MHz, CDCl_3) spectrum of sumanene-ferrocene conjugate **sumFc-3** with the signals ascribed to the given groups. For the labels, see Figure S51.

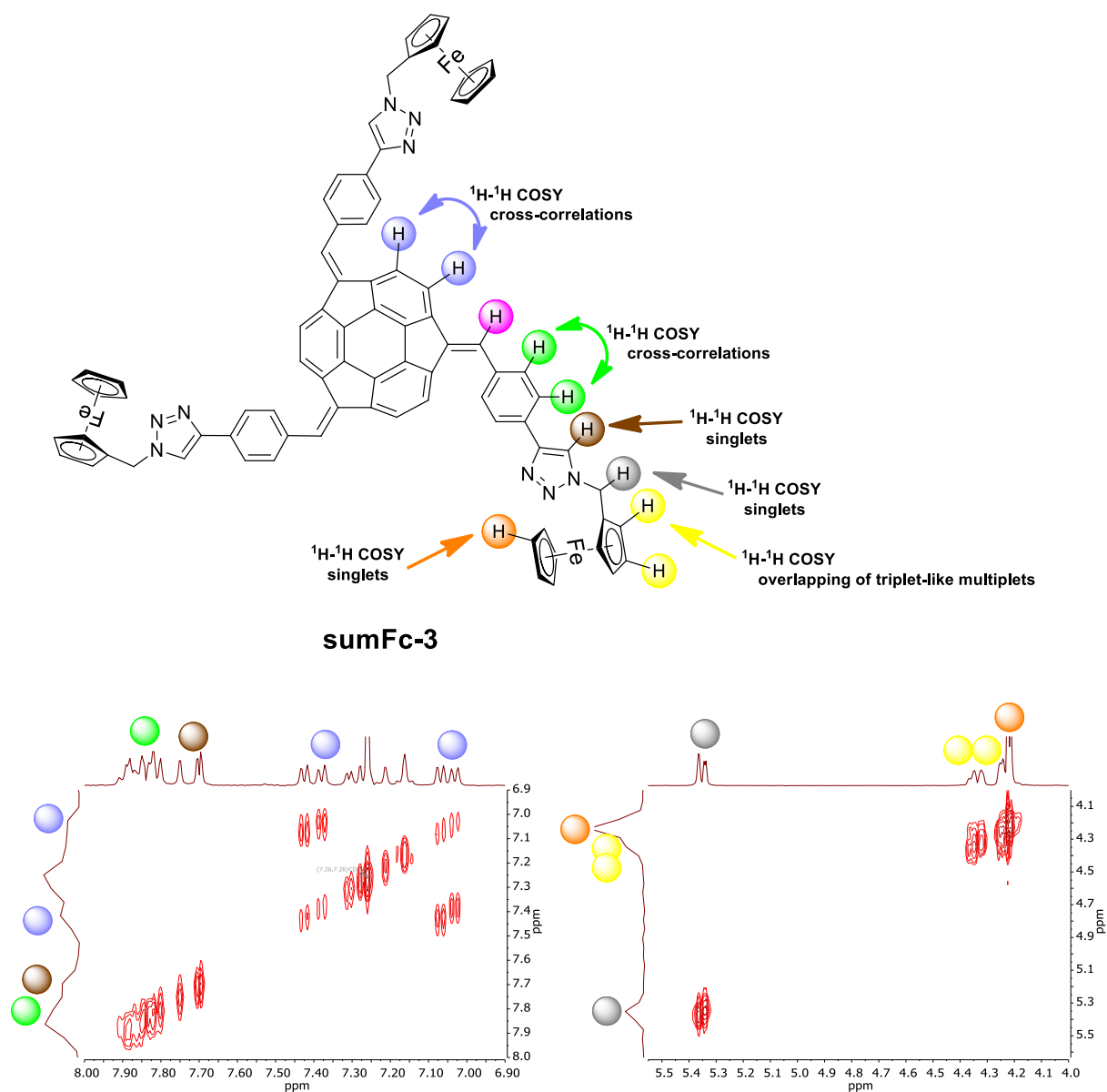


Figure S53. Graphical representation of the types of signals observed in the ^1H NMR spectrum of sumanene-ferrocene conjugate **sumFc-3** and the graphical representation of the cross-correlations in the ^1H - ^1H COSY NMR spectra together with the crucial insets of this spectra. For the full ^1H - ^1H COSY NMR spectrum, see Figure S27.

The successful synthesis of **sumFc-3** was also supported by the comparison between ^1H NMR (500 MHz, CDCl_3) spectra of ferrocenemethylazide (**9**), tris[(4-ethynylphenyl)methidene]sumanene (**12**), and sumanene-ferrocene conjugate **sumFc-3**, see Figure S54. The following essential conclusions shall be noted:

- The signals (four singlets) located at 7.80–7.68 ppm in the spectrum of **sumFc-3** originate from the presence of the 1,2,3-triazole skeletons that were formed in the *click chemistry* process.
- The signals (four singlets) located at ca. 5.35 ppm in the spectrum of **sumFc-3** that originate from the presence of the methylene groups, are shifted in comparison to the respective singlet in the spectrum of ferrocenemethylazide (**9**; 4.10 ppm).
- No signals originating from the presence of acetylene groups (compound **12**, 3.22–3.16 ppm, four singlets) were found in the spectrum of **sumFc-3**.

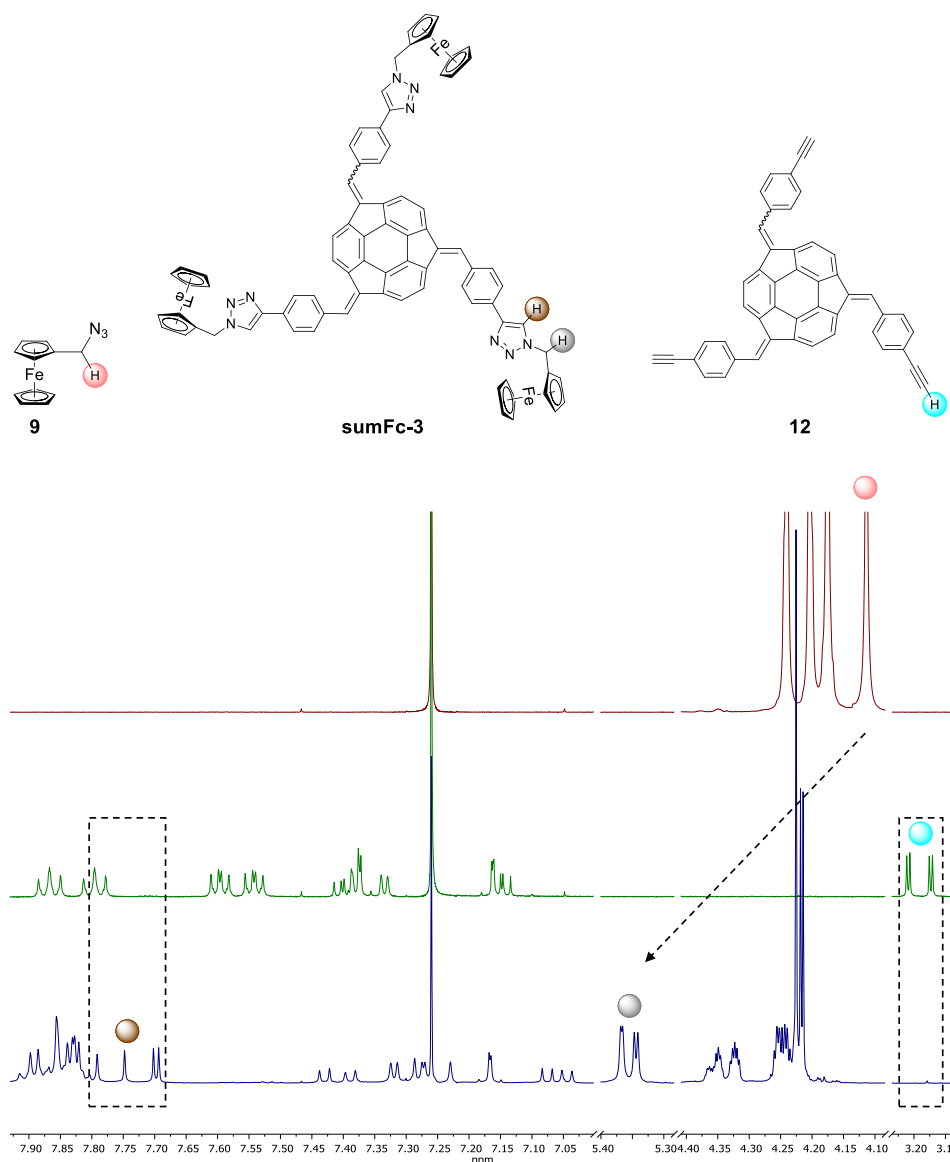


Figure S54. Comparison between ^1H NMR (500 MHz, CDCl_3) spectra of ferrocenemethylazide (**9**; red), tris[(4-ethynylphenyl)methidene]sumanene (**12**; green), and sumanene-ferrocene conjugate (**sumFc-3**; blue). The crucial signals were ascribed to the given groups with the labels.

Nineteen groups of signals can be found in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of sumanene-ferrocene conjugate **sumFc-3**, what is consistent with the anticipated value. Those groups of signals are graphically presented in Figure S55 and are labeled in $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum presented in Figure S56.

Nineteen or fifty-seven signals shall be found in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of symmetrical and unsymmetrical stereoisomer of **sumFc-3**, respectively. Noteworthy, within most groups of signals in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **sumFc-3**, four singlets can be observed, what is highly consisted with the anticipated value (symmetrical diastereoisomer = 1 signal = 1 x s, unsymmetrical diastereoisomer = 3 signals = 3 x s), see, e.g., the signal located at 81.1-81.0 ppm (characteristic *ipso* ^{13}C nucleus of substituted Cp ring of ferrocene).

Signals located at 147.6-119.5 ppm were ascribed to the presence of various ^{13}C nucleus coming from the sumanene skeleton, methidene moieties, phenylene and 1,2,3-triazole skeletons.

Signals located at 81.1-81.0 ppm were ascribed to the presence of ferrocene units. Signals located at 81.1-81.0 ppm were ascribed to the characteristic *ipso* ^{13}C nucleus of unsubstituted Cp ring of ferrocene. Signals located at 69.3-69.1 ppm were ascribed to the ^{13}C nucleus of substituted and unsubstituted Cp ring of ferrocene.

Direct comparison of $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) spectra of 4-(1-(ferrocenylmethyl)-1*H*-1,2,3-triazol-4-yl)benzaldehyde (**11**; blue), and sumanene-ferrocene conjugate (**sumFc-3**; red) is presented in Figure S57. It can be concluded that the $^{13}\text{C}\{^1\text{H}\}$ spectrum of the target sumanene-ferrocene conjugate **sumFc-3** comprises the similar groups of signals as the reference spectrum of **11** (excluding the CHO signal located at 191.8 ppm).

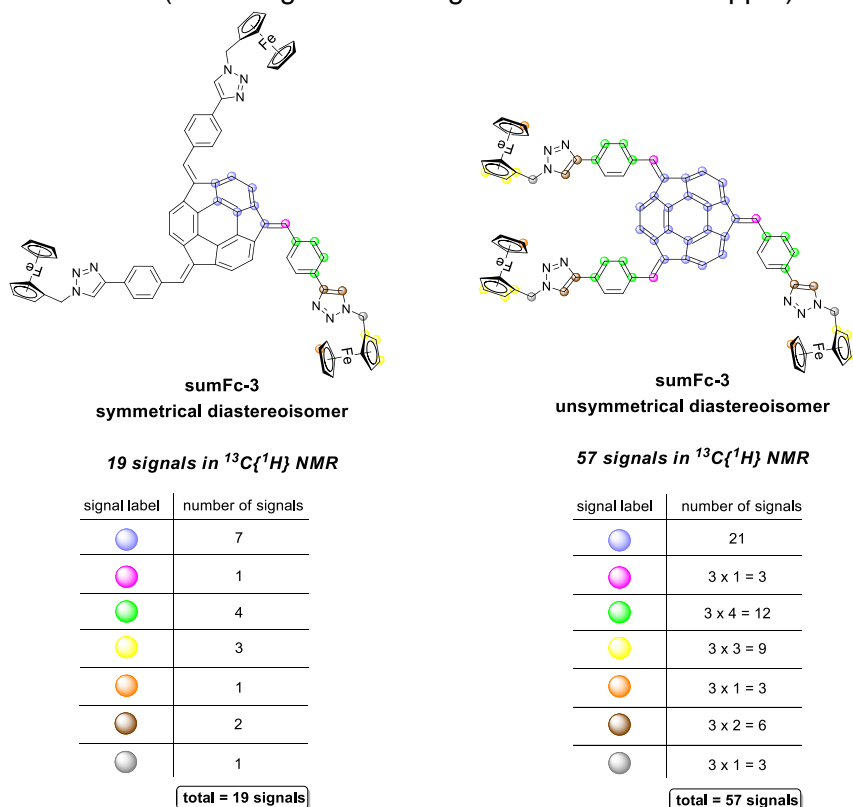


Figure S55. Graphical representation of the number and types of signals observed in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of sumanene-ferrocene conjugate **sumFc-3**. The same color does not correspond to the same chemical shift in the NMR spectrum. The same color does not correspond to the same chemical shift in the NMR spectrum.

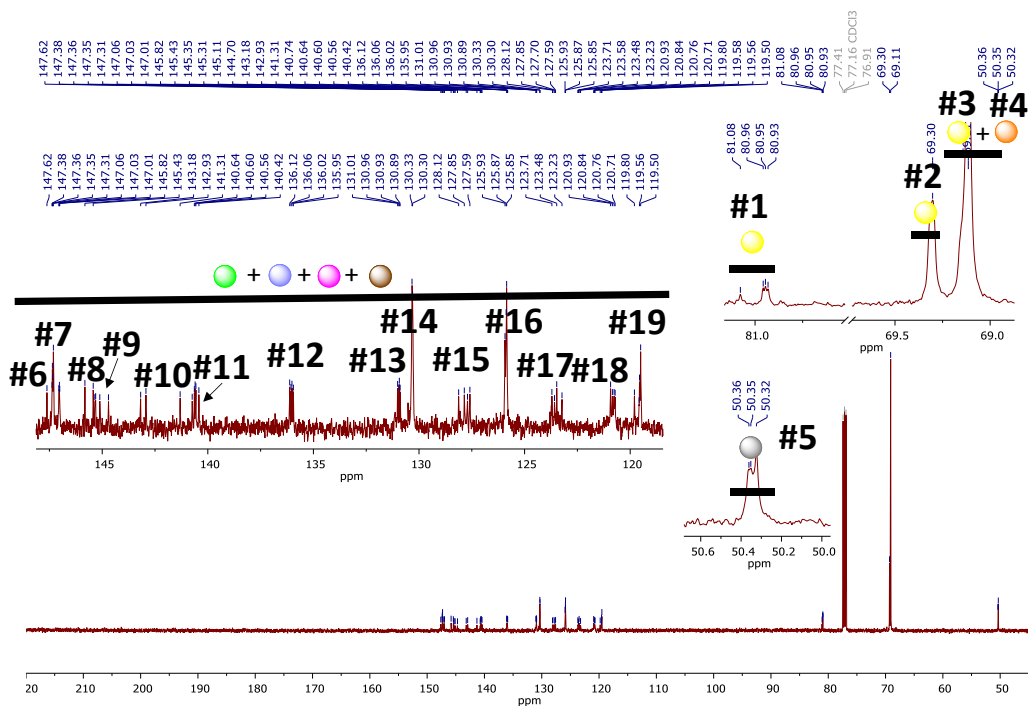


Figure S56. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CHCl_3) spectrum of sumanene-ferrocene conjugate **sumFc-3** with the signals ascribed to the given groups. For the labels, see Figure S55.

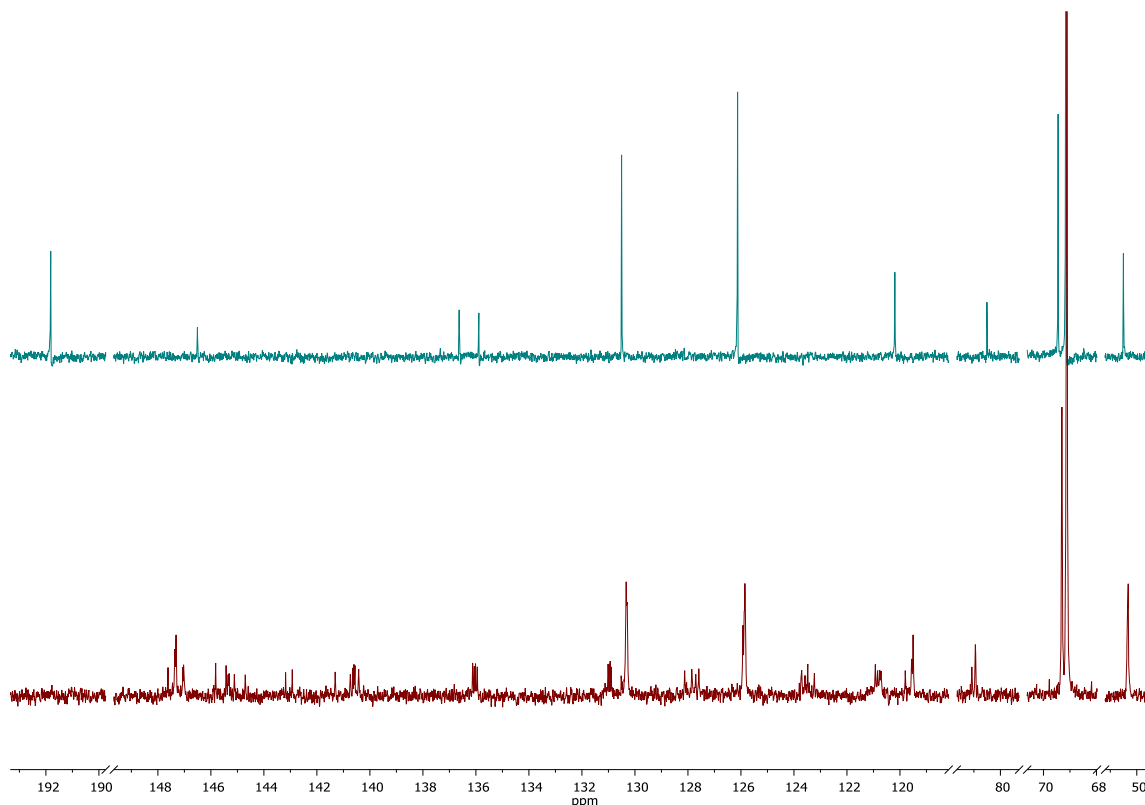


Figure S57. Comparison between $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) spectra of 4-(1-(ferrocenylmethyl)-1*H*-1,2,3-triazol-4-yl)benzaldehyde (**11**; blue), and sumanene-ferrocene conjugate (**sumFc-3**; red).

3. HRMS spectra

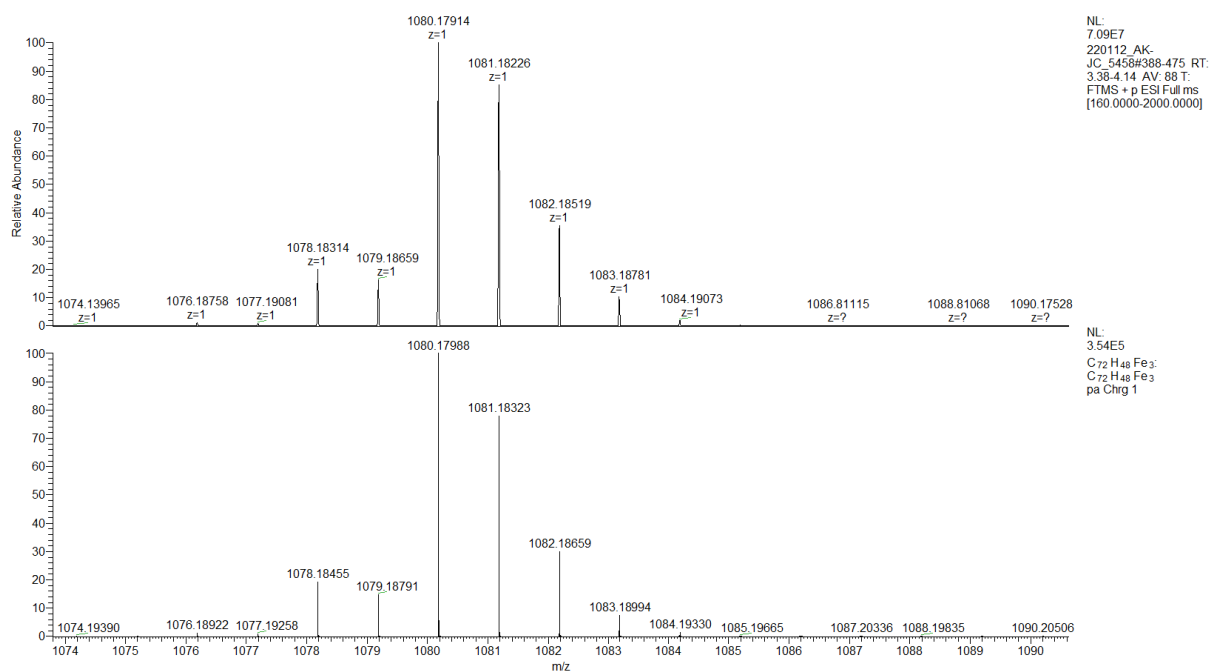


Figure S58. ESI-HRMS(TOF) spectrum of sumanene-ferrocene conjugate **sumFc-1**.

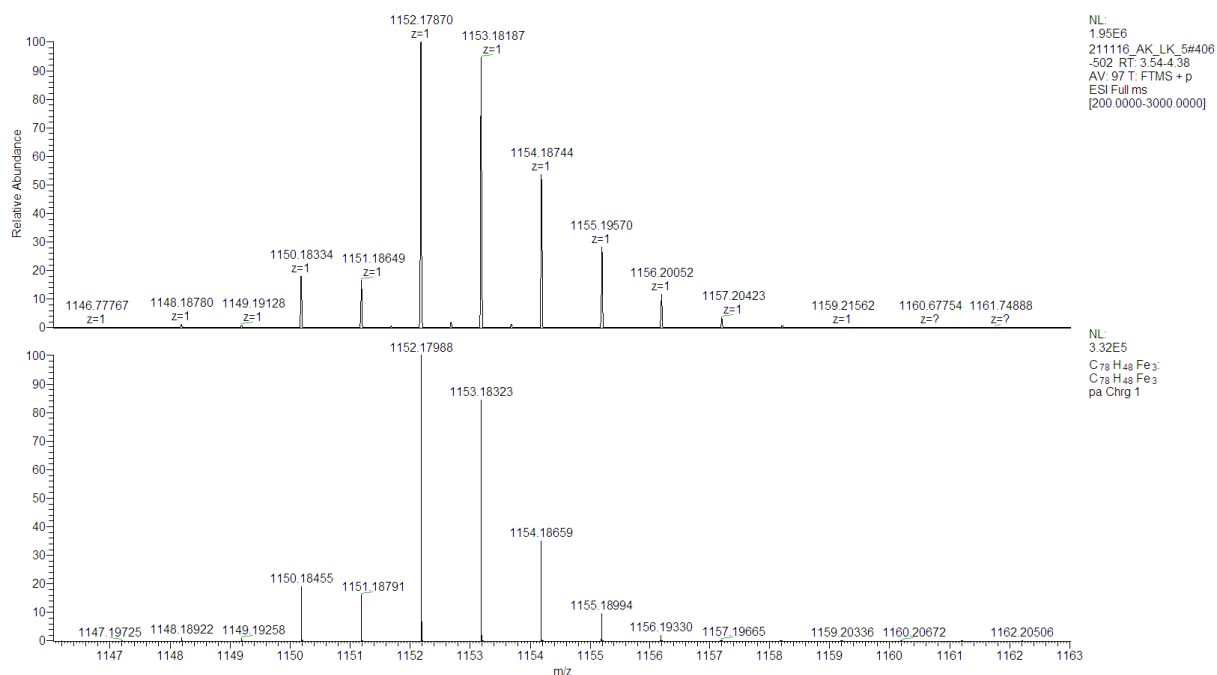


Figure S59. ESI-HRMS(TOF) spectrum of sumanene-ferrocene conjugate **sumFc-2**.

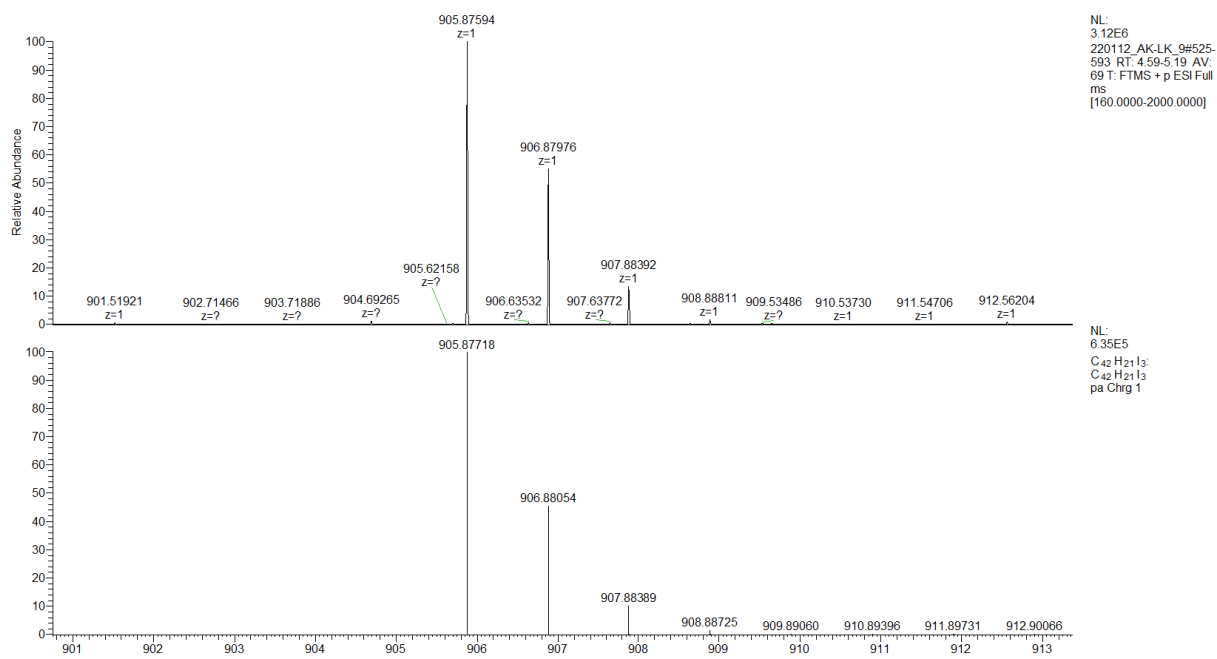


Figure S60. ESI-HRMS(TOF) spectrum of tris[(4-iodophenyl)methidene]sumanene (**8a**).

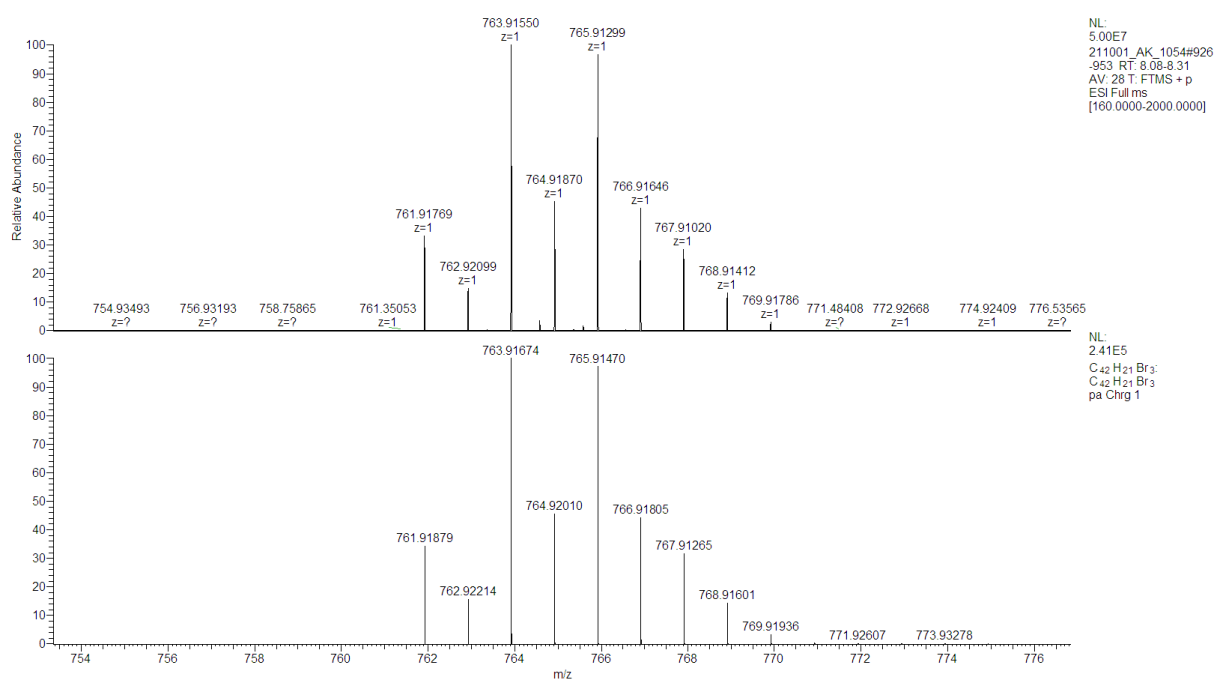


Figure S61. ESI-HRMS(TOF) spectrum of tris[(4-bromophenyl)methidene]sumanene (**8b**).

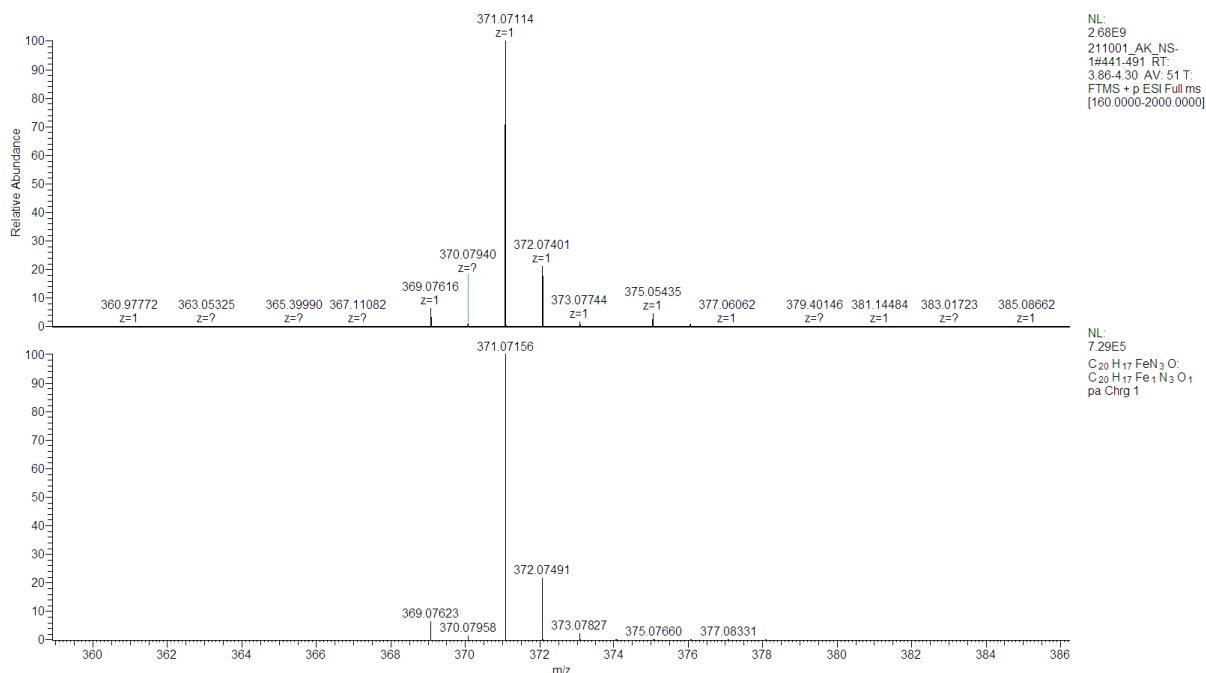


Figure S62. ESI-HRMS(ToF) spectrum of 4-(1-(ferrocenylmethyl)-1H-1,2,3-triazol-4-yl)benzaldehyde (**11**).

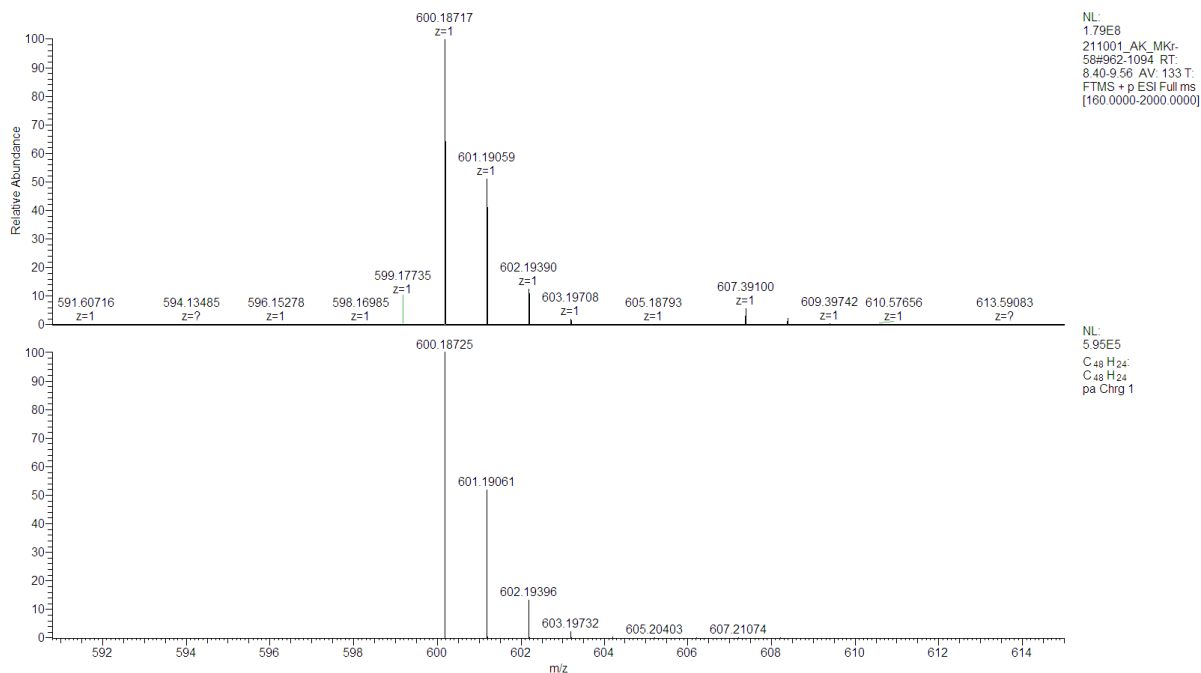


Figure S63. ESI-HRMS(ToF) spectrum of tris[(4-ethynylphenyl)methidene]sumanene (**12**).

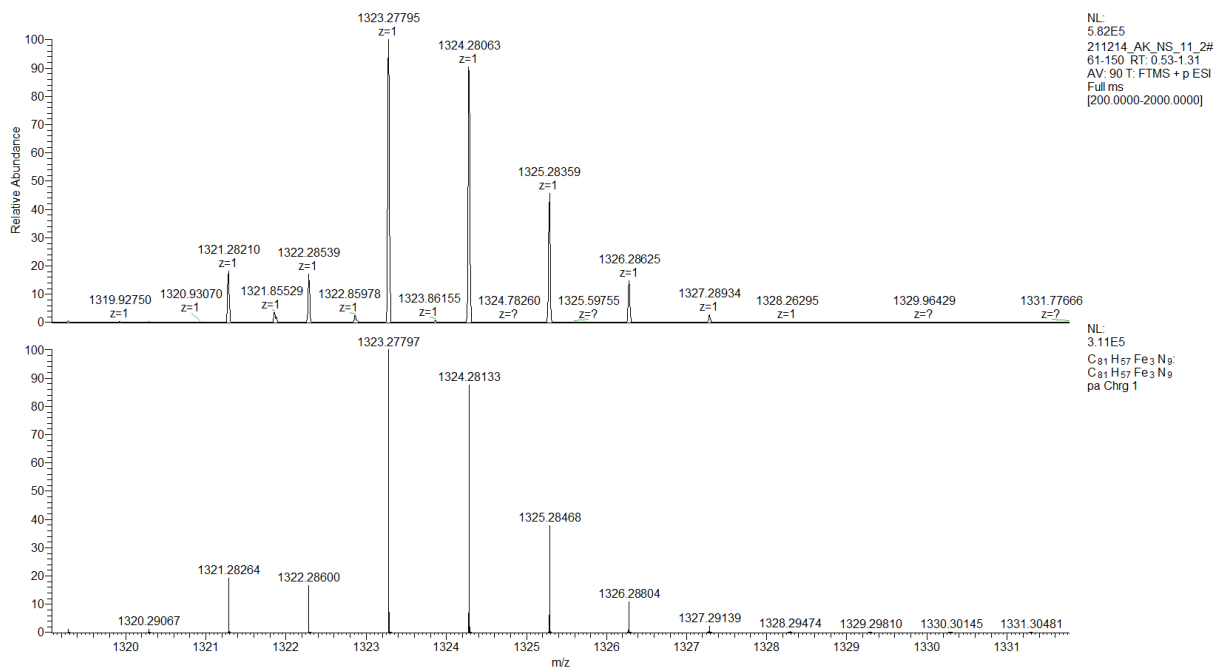


Figure S64. ESI-HRMS(ToF) spectrum of sumanene-ferrocene conjugate **sumFc-3**.

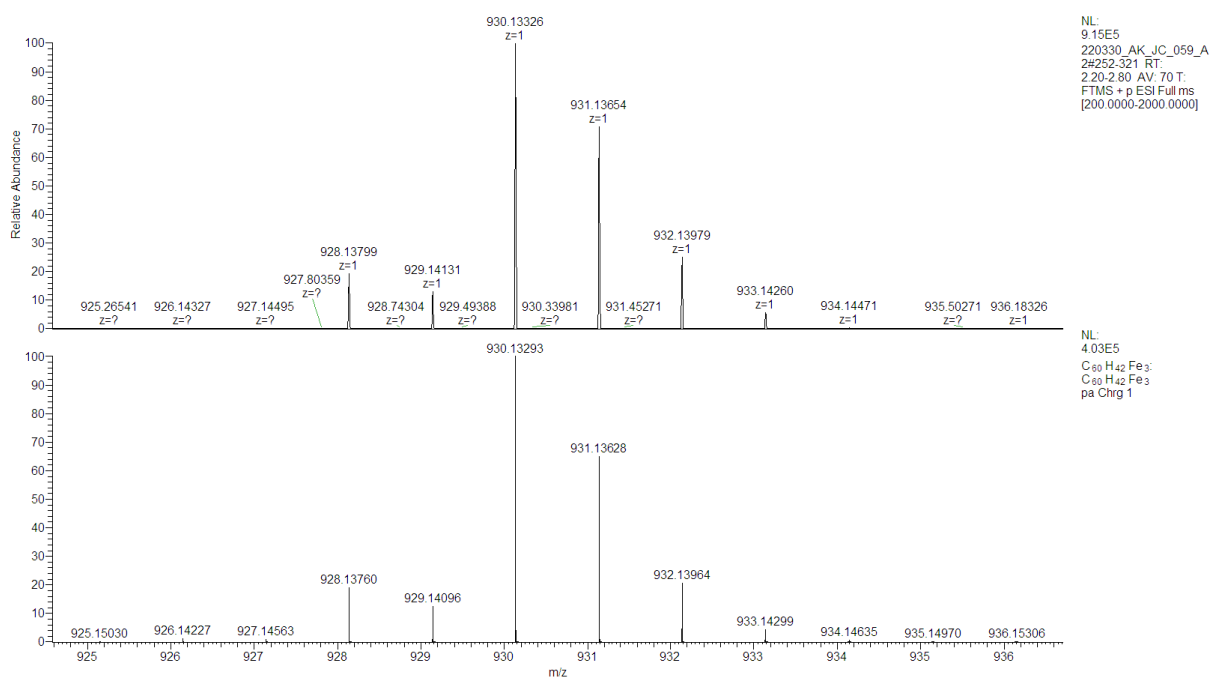


Figure S65. ESI-HRMS(ToF) spectrum of compound **14**.

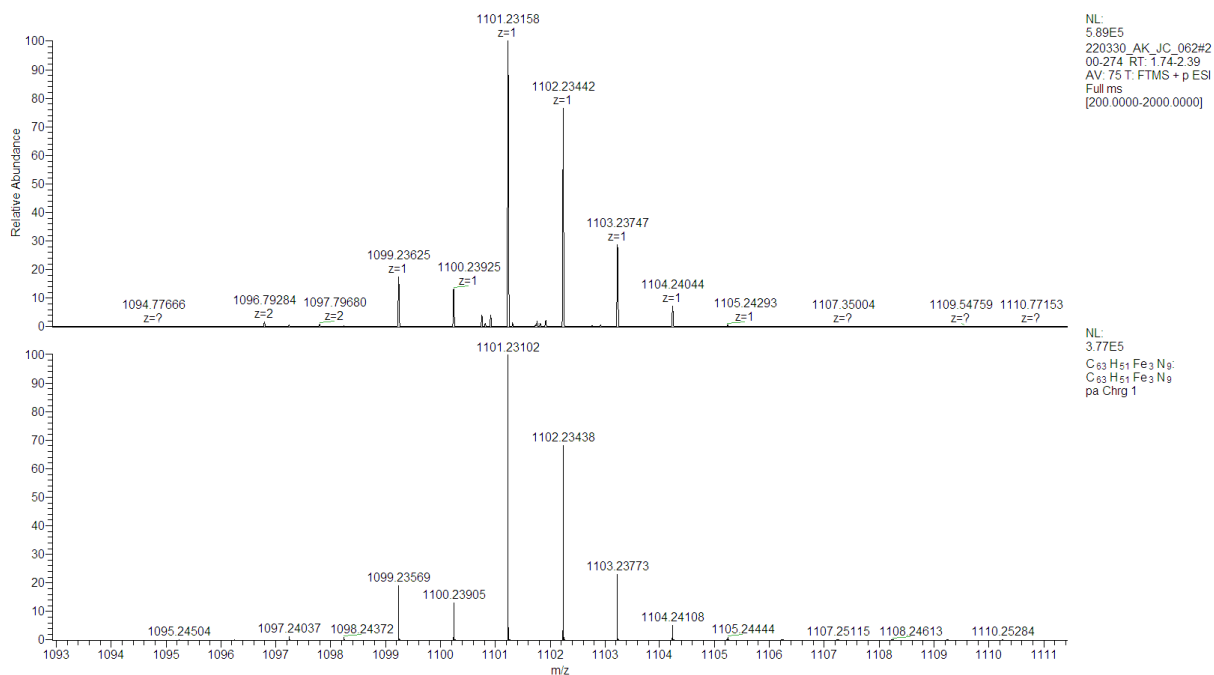


Figure S66. ESI-HRMS(ToF) spectrum of compound **16**.

4. UV-vis and emission spectra

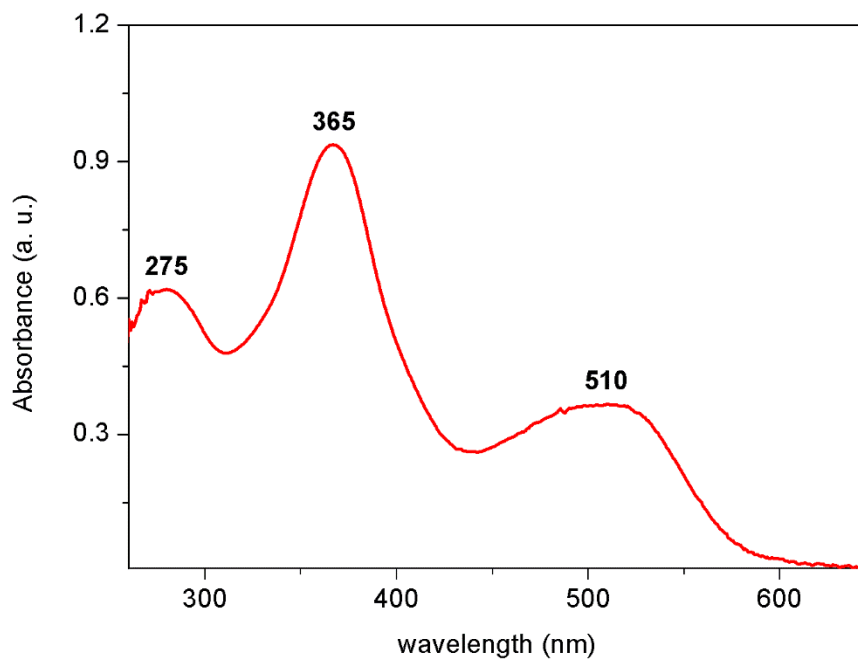


Figure S67. UV-vis spectrum of sumanene-ferrocene conjugate **sumFc-1** (concentration: 0.02 mM, solvent: CHCl₃:CH₃OH = 1:1 v/v).

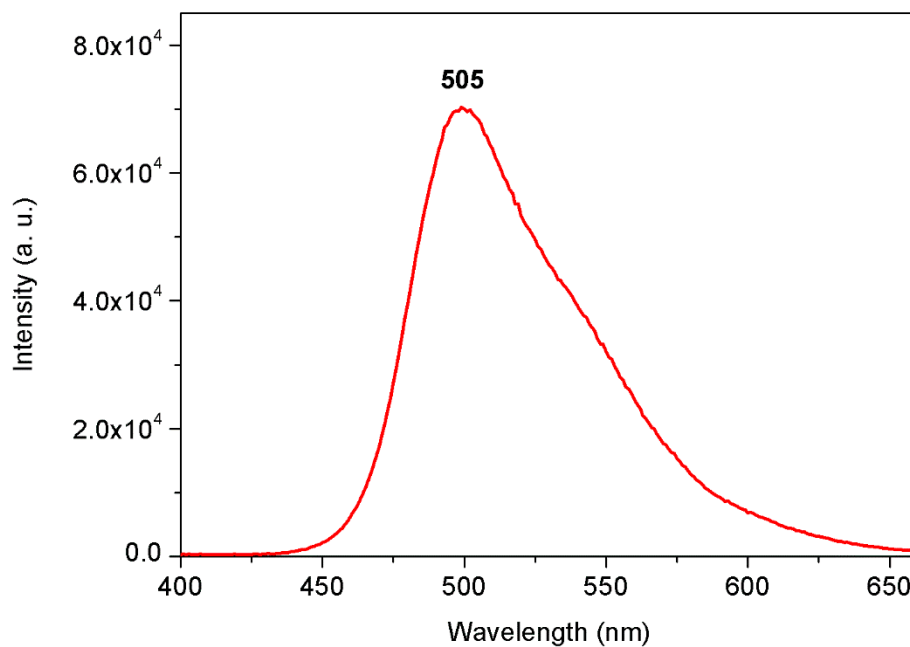


Figure S68. Emission spectrum of sumanene-ferrocene conjugate **sumFc-1** (concentration: 0.02 mM, solvent: CHCl₃:CH₃OH = 1:1 v/v, λ_{ex} = 380 nm).

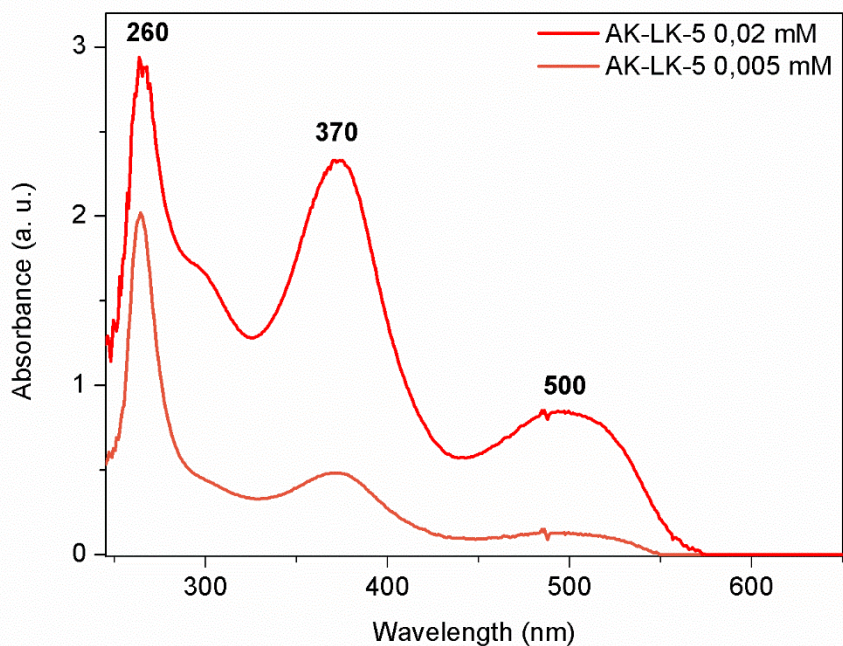


Figure S69. UV-vis spectrum of sumanene-ferrocene conjugate **sumFc-2** (solvent: $\text{CHCl}_3:\text{CH}_3\text{OH} = 1:1$ v/v).

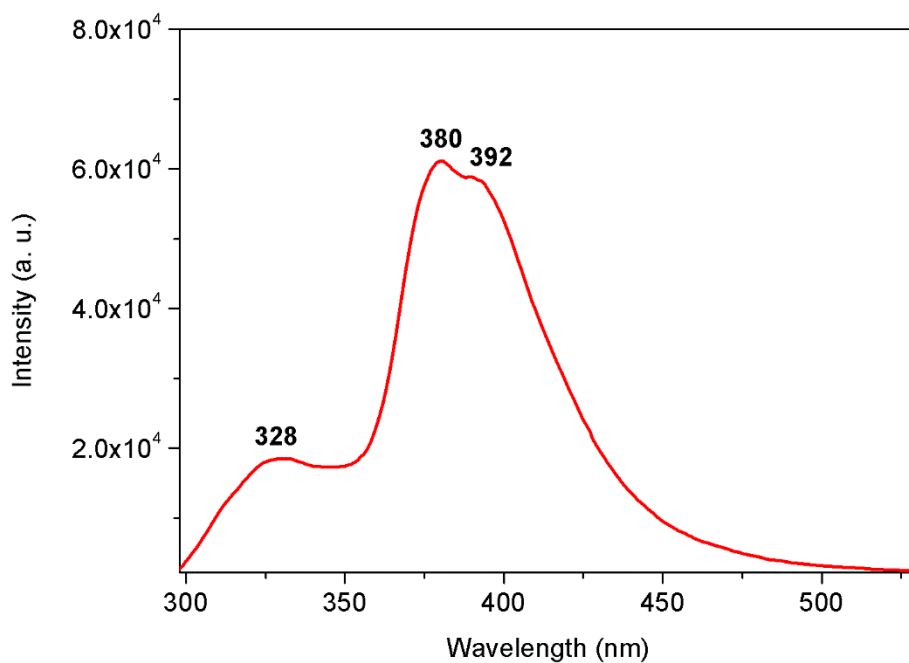


Figure S70. Emission spectrum of sumanene-ferrocene conjugate **sumFc-2** (concentration: 0.02 mM, solvent: $\text{CHCl}_3:\text{CH}_3\text{OH} = 1:1$ v/v; $\lambda_{\text{ex}} = 280$ nm).

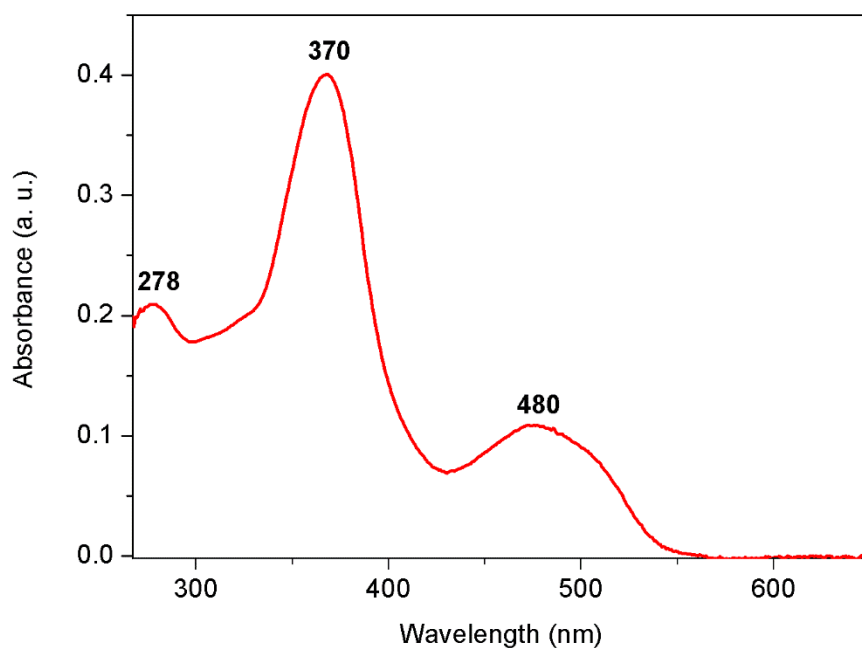


Figure S71. UV-vis spectrum of sumanene-ferrocene conjugate **sumFc-3** (concentration: 0.02 mM, solvent: CHCl_3 : CH_3OH = 1:1 v/v).

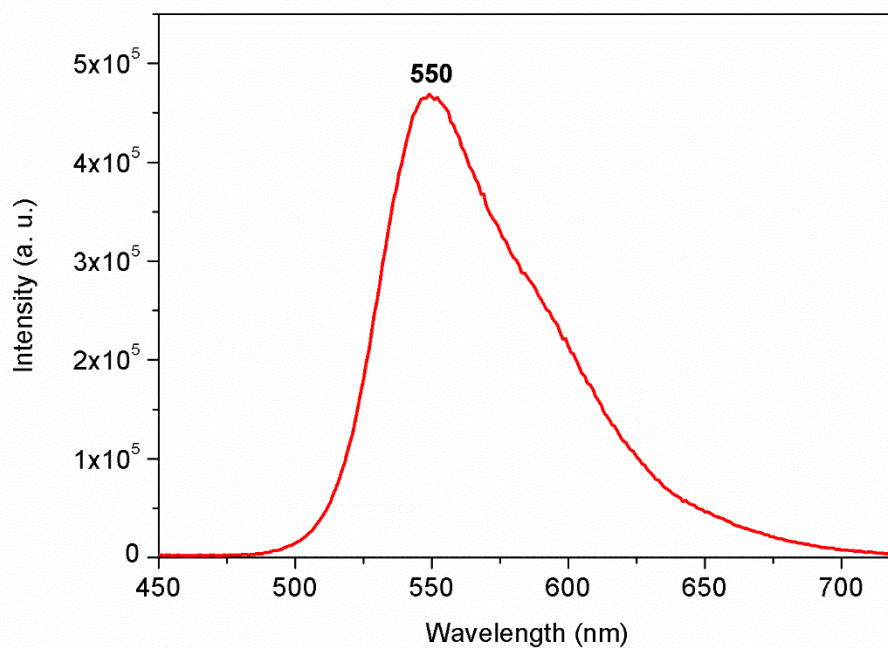


Figure S72. Emission spectrum of sumanene-ferrocene conjugate **sumFc-3** (concentration: 0.02 mM, solvent: CHCl_3 : CH_3OH = 1:1 v/v; λ_{ex} = 370 nm).

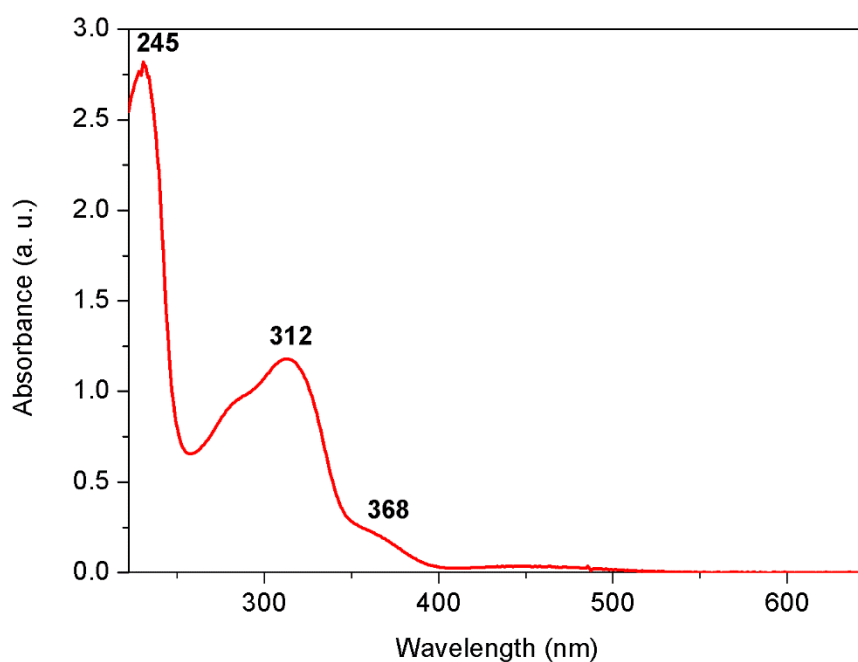


Figure S73. UV-vis spectrum of compound **14** (concentration: 0.02 mM, solvent: $\text{CHCl}_3:\text{CH}_3\text{OH} = 1:1$ v/v).

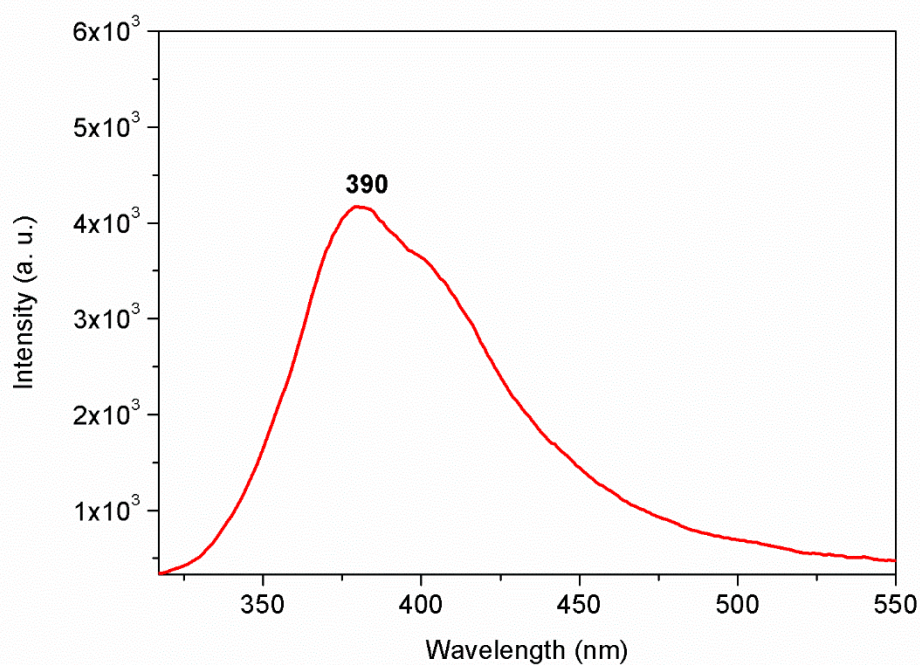


Figure S74. Emission spectrum of compound **14** (concentration: 0.02 mM, solvent: $\text{CHCl}_3:\text{CH}_3\text{OH} = 1:1$ v/v, $\lambda_{\text{ex}} = 290$ nm).

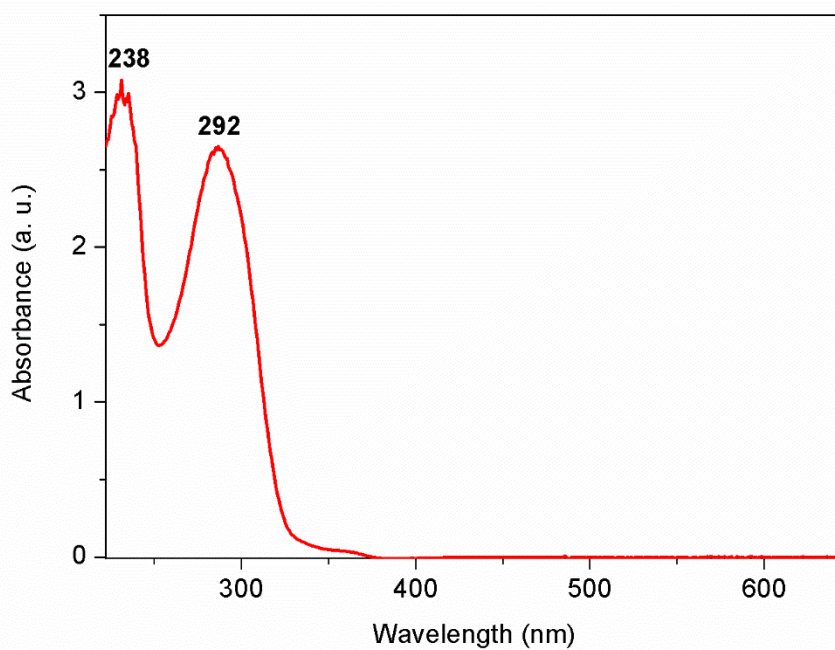


Figure S75. UV-vis spectrum of compound **16** (concentration: 0.02 mM, solvent: $\text{CHCl}_3:\text{CH}_3\text{OH} = 1:1$ v/v).

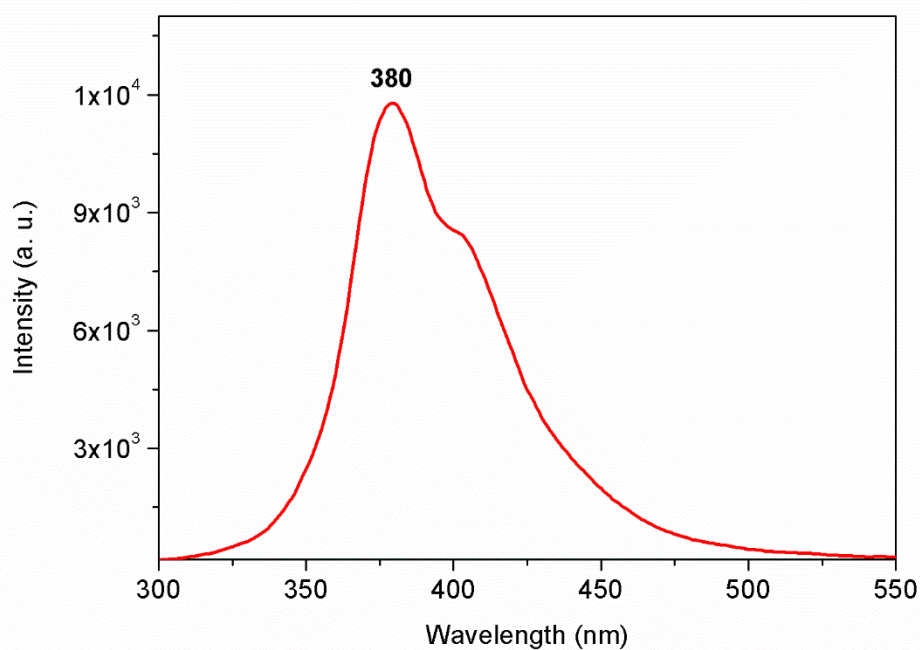


Figure S76. Emission spectrum of compound **16** (concentration: 0.02 mM, solvent: $\text{CHCl}_3:\text{CH}_3\text{OH} = 1:1$ v/v, $\lambda_{\text{ex}} = 290$ nm).

5. Spectrofluorimetric analyzes on the interactions between sumanene-ferrocene conjugates sumFc-1 – sumFc-3 and cesium cations

In order to provide the solubility of both **sumFc-1 – sumFc-3** and cesium salt, the measurements were carried out in methanol-chloroform mixture (1:1 v/v). Appropriate volumes of 1 mM CsCl solution were mixed with 1 mM solution of sumanene-ferrocene conjugates (**sumFc-1 – sumFc-3**) to reach given sumanene-to-metal cation molar ratio. The excitation wavelength was 380 nm, 280 nm, 370 nm for **sumFc-1**, **sumFc-2**, and **sumFc-3**, respectively. The concentration of sumanene-ferrocene conjugate in each sample was 0.02 mM.

Complex stoichiometries were estimated with the Job's plot (method of continuous variation).^{9–12}

The apparent binding constants (K_{app}) were estimated with the Benesi-Hildebrand method^{13,14}, using the following equation:

$$\frac{1}{I - I_0} = \frac{1}{a} + \frac{1}{a \cdot K_{app} \cdot C(\text{Cs}^+)}$$

where I_0 and I are the fluorescence intensities of sumanene-ferrocene conjugate in the absence and presence of cesium cations, respectively, a is a constant, and $C(\text{Cs}^+)$ is the concentration of cesium cations in solution. The association constant was determined as a ratio of intercept-to-slope of $1/(I - I_0)$ vs. $1/C(\text{Cs}^+)$ linear plot.

The above-discussed spectra and data are presented below.

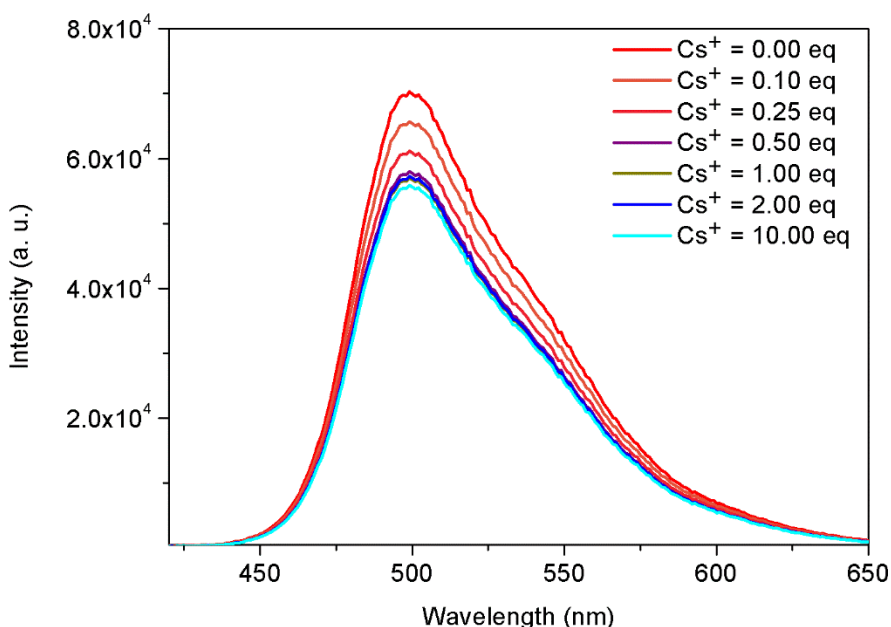


Figure S77. Emission spectra ($\lambda_{ex} = 380$ nm) of sumanene-ferrocene conjugate **sumFc-1** in the presence of various amounts (equivalents = eq) of cesium cations.

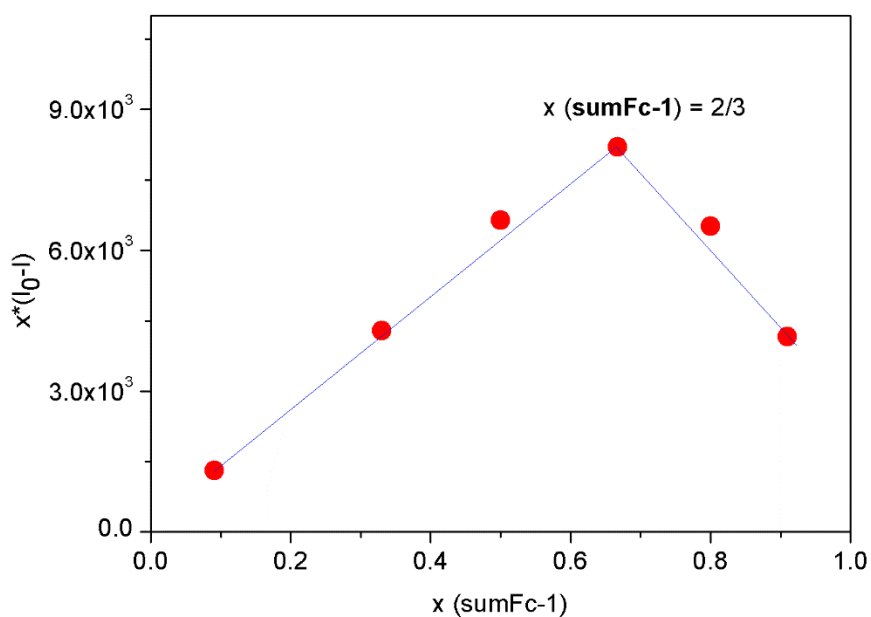


Figure S78. Job's plot regarding the interactions between sumanene-ferrocene conjugate **sumFc-1** and cesium cations (x stands for the molar fraction of sumanene-ferrocene conjugate **sumFc-1**; I_0 and I are the fluorescence intensities of sumanene-ferrocene conjugate **sumFc-1** in the absence and in the presence of cesium cations).

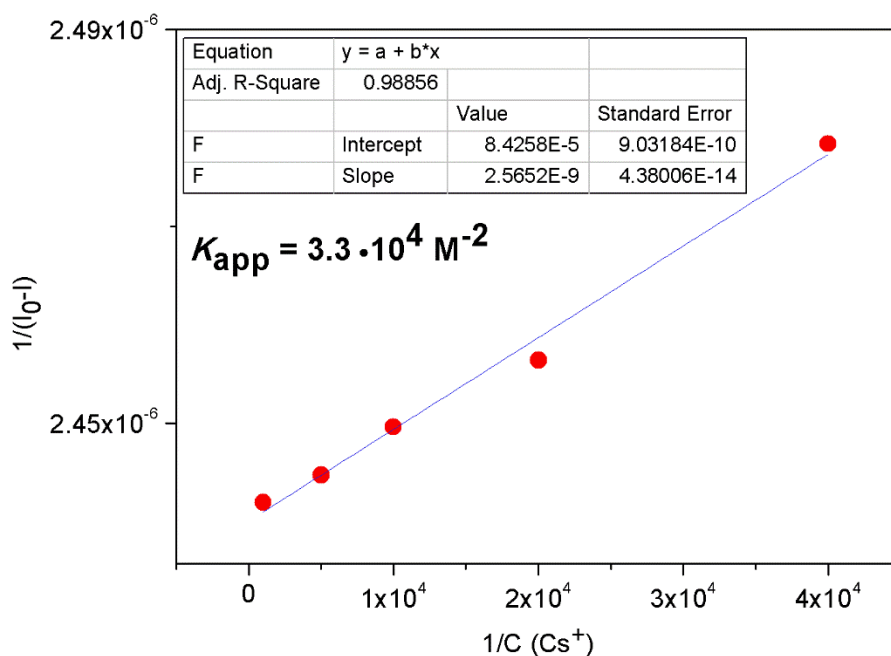


Figure S79. Benesi-Hildebrand plot regarding the interactions between sumanene-ferrocene conjugate **sumFc-1** and cesium cations (C stands for the molar concentration of cesium cations in the sample; I_0 and I are the fluorescence intensities of sumanene-ferrocene conjugate **sumFc-1** in the absence and in the presence of cesium cations). The linear fit data and the calculated K_{app} are also presented.

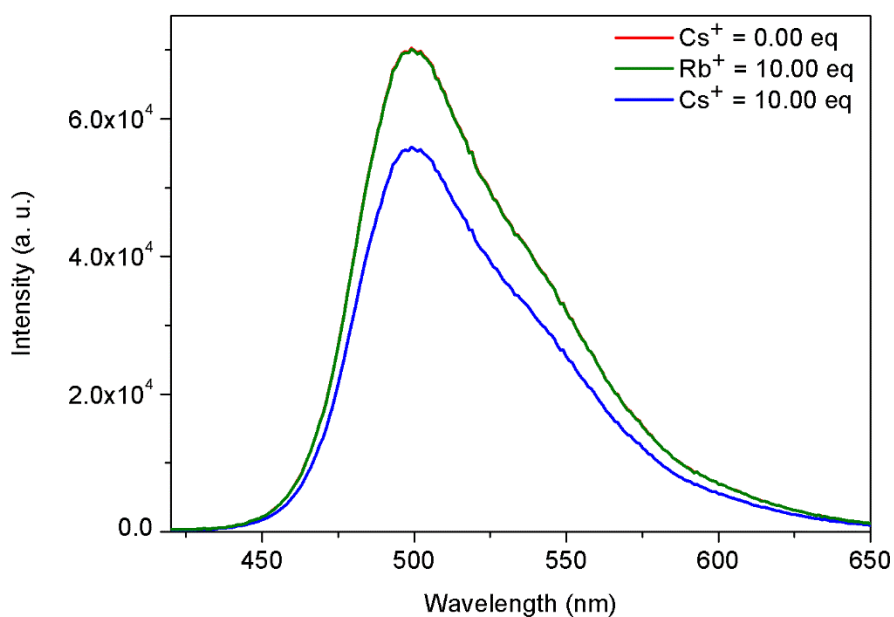


Figure S80. Emission spectra ($\lambda_{\text{ex}} = 380 \text{ nm}$) of sumanene-ferrocene conjugate **sumFc-1** in the absence and in the presence of rubidium cations (10 eq); spectrum of sumanene-ferrocene conjugate **sumFc-1** in the presence of cesium cations (10 eq) is also presented for comparison.

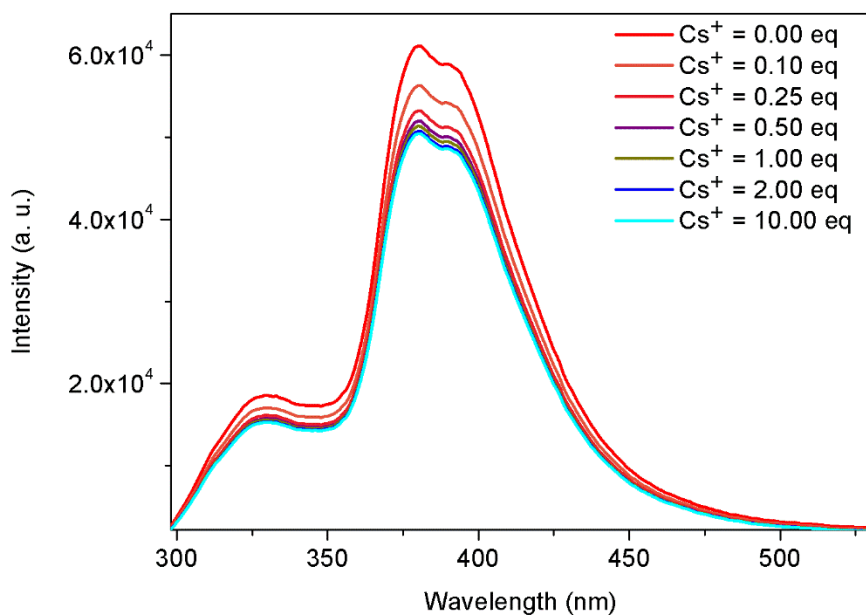


Figure S81. Emission spectra ($\lambda_{\text{ex}} = 280 \text{ nm}$) of sumanene-ferrocene conjugate **sumFc-2** in the presence of various amounts (equivalents = eq) of cesium cations.

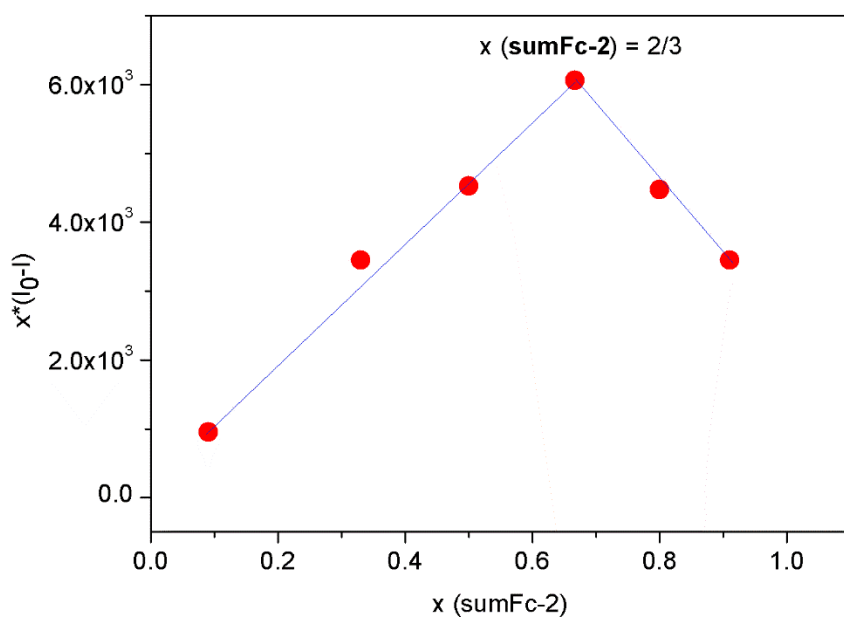


Figure S82. Job's plot regarding the interactions between sumanene-ferrocene conjugate **sumFc-2** and cesium cations (x stands for the molar fraction of sumanene-ferrocene conjugate **sumFc-2**; I_0 and I are the fluorescence intensities of sumanene-ferrocene conjugate **sumFc-2** in the absence and in the presence of cesium cations).

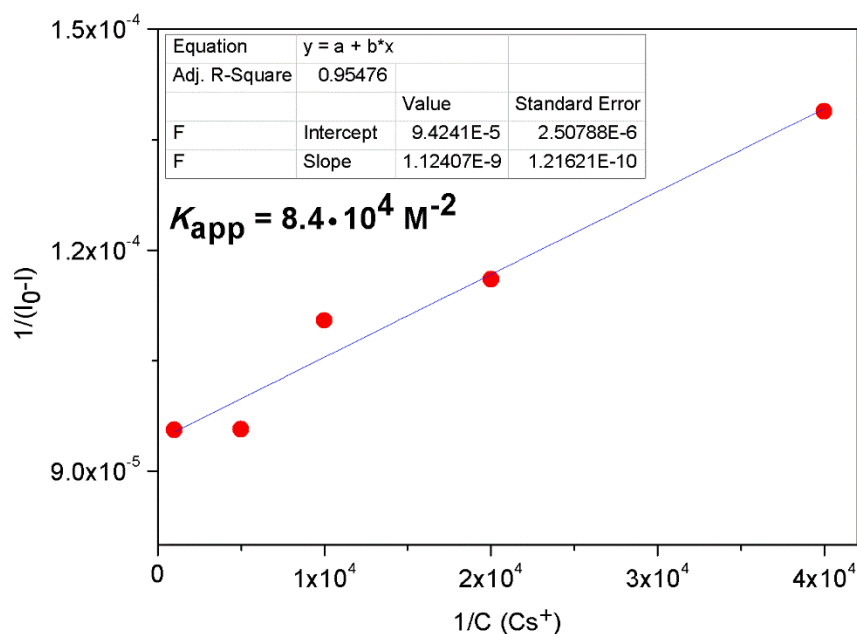


Figure S83. Benesi-Hildebrand plot regarding the interactions between sumanene-ferrocene conjugate **sumFc-2** and cesium cations (C stands for the molar concentration of cesium cations in the sample; I_0 and I are the fluorescence intensities of sumanene-ferrocene conjugate **sumFc-2** in the absence and in the presence of cesium cations). The linear fit data and the calculated K_{app} are also presented.

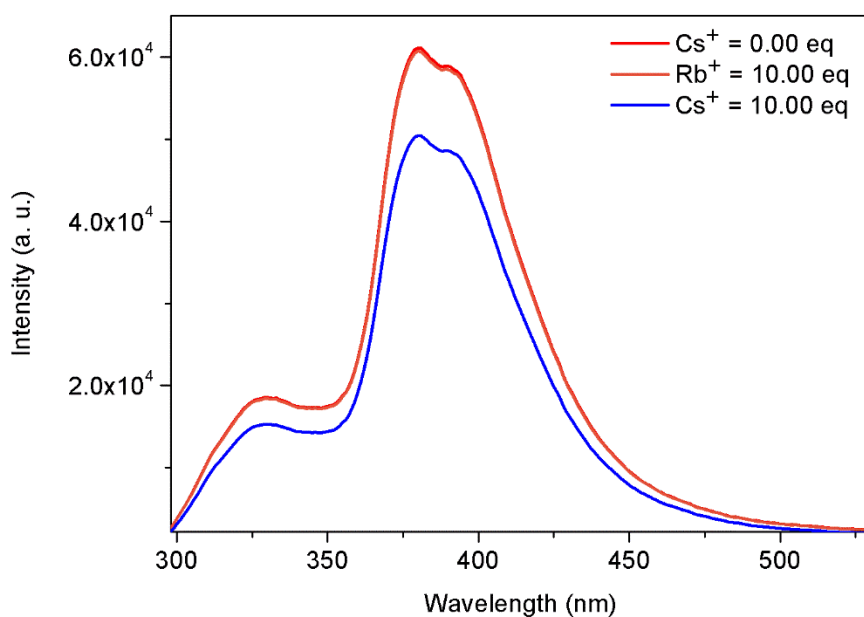


Figure S84. Emission spectra ($\lambda_{\text{ex}} = 280 \text{ nm}$) of sumanene-ferrocene conjugate **sumFc-2** in the absence and in the presence of rubidium cations (10 eq); spectrum of sumanene-ferrocene conjugate **sumFc-2** in the presence of cesium cations (10 eq) is also presented for comparison.

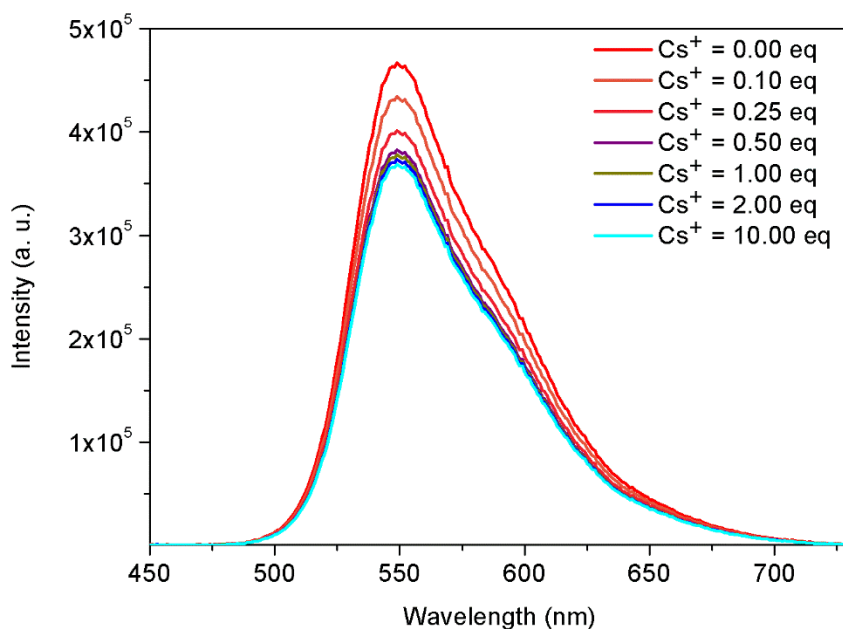


Figure S85. Emission spectra ($\lambda_{\text{ex}} = 370 \text{ nm}$) of sumanene-ferrocene conjugate **sumFc-3** in the presence of various amounts (equivalents = eq) of cesium cations.

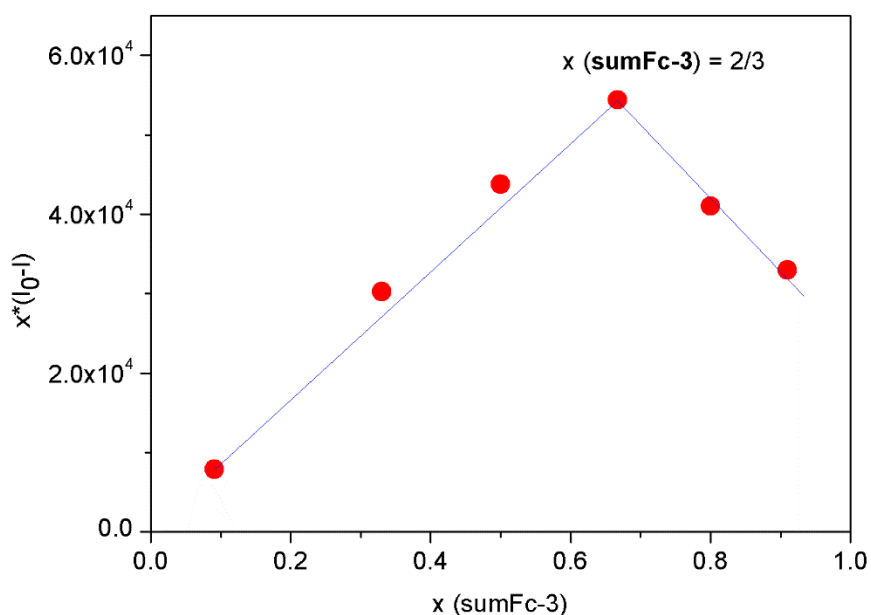


Figure S86. Job's plot regarding the interactions between sumanene-ferrocene conjugate **sumFc-3** and cesium cations (x stands for the molar fraction of sumanene-ferrocene conjugate **sumFc-3**; I_0 and I are the fluorescence intensities of sumanene-ferrocene conjugate **sumFc-3** in the absence and in the presence of cesium cations).

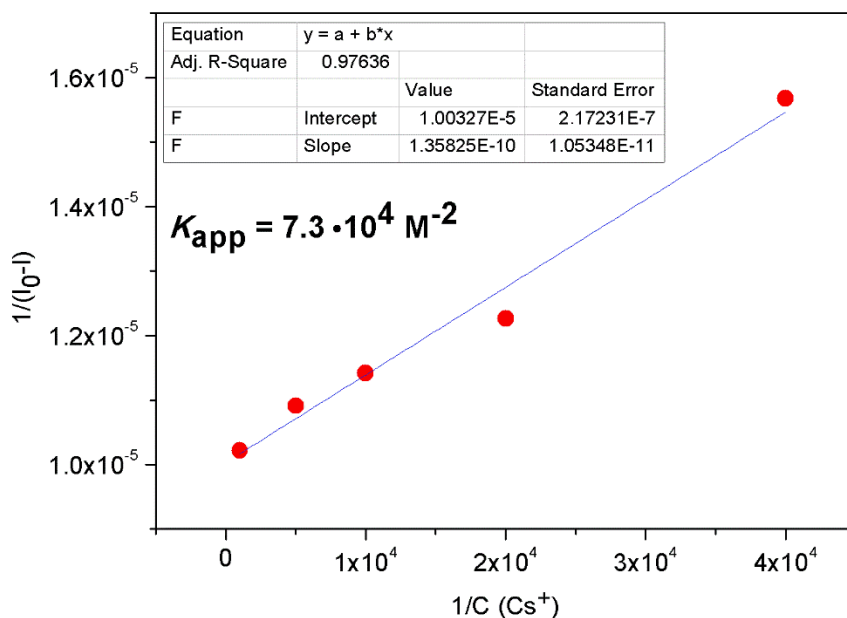


Figure S87. Benesi-Hildebrand plot regarding the interactions between sumanene-ferrocene conjugate **sumFc-3** and cesium cations (C stands for the molar concentration of cesium cations in the sample; I_0 and I are the fluorescence intensities of sumanene-ferrocene conjugate **sumFc-3** in the absence and in the presence of cesium cations). The linear fit data and the calculated K_{app} are also presented.

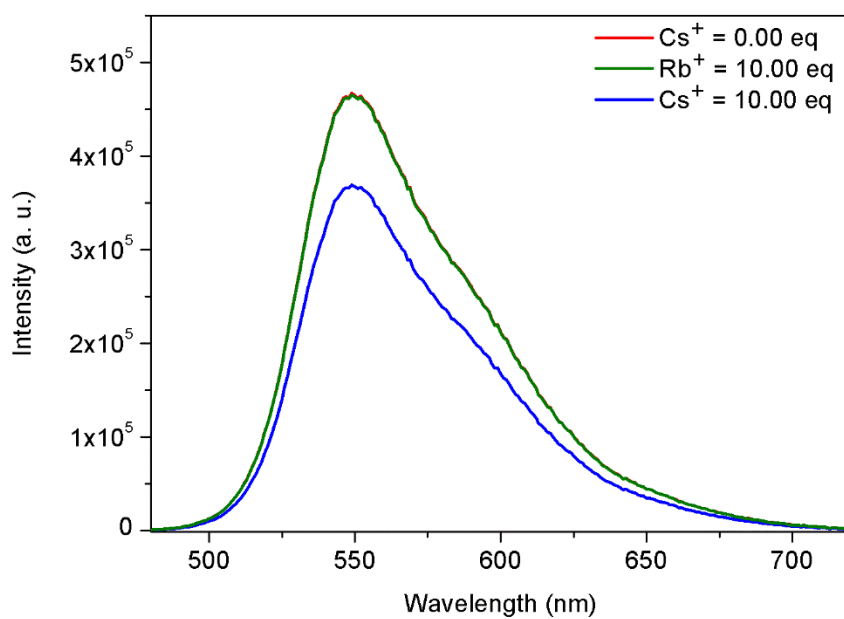


Figure S88. Emission spectra ($\lambda_{\text{ex}} = 370$ nm) of sumanene-ferrocene conjugate **sumFc-3** in the absence and in the presence of rubidium cations (10 eq); spectrum of sumanene-ferrocene conjugate **sumFc-3** in the presence of cesium cations (10 eq) is also presented for comparison.

6. Calculation

The calculations were performed for the representative symmetrical diastereoisomer of sumanene-ferrocene conjugate **sumFc-3** and its complex with Cs⁺. Theoretical calculations were performed using *Gaussian16* program.¹⁵

The structure of symmetrical diastereoisomer of sumanene-ferrocene conjugate **sumFc-3** was optimized using B3LYP functional¹⁶ – Density Functional Theory (DFT) with 6-311++G(d,p) basis set¹⁷. The initial structure was generated manually in the *GaussView* program¹⁸. For the DFT-optimized structure of symmetrical diastereoisomer of sumanene-ferrocene conjugate **sumFc-3**, see Figure S89.

To illustratively visualize the potential structure of the formed sandwich complexes between two sumanene bowls within **sumFc-3** (representative symmetrical diastereoisomer) and Cs⁺, the optimization using *Gaussian16* program was also performed. Notably, sandwich complex consists of 301 atoms in total, including a heavy, electron-rich cesium cation. Thus, the semi-empirical PM6 method^{19–21} was used in order to illustratively visualize the approximate geometry of the molecule. For the optimized structure of two symmetrical diastereoisomers of sumanene-ferrocene conjugate **sumFc-3** and Cs⁺, see Figure S90.

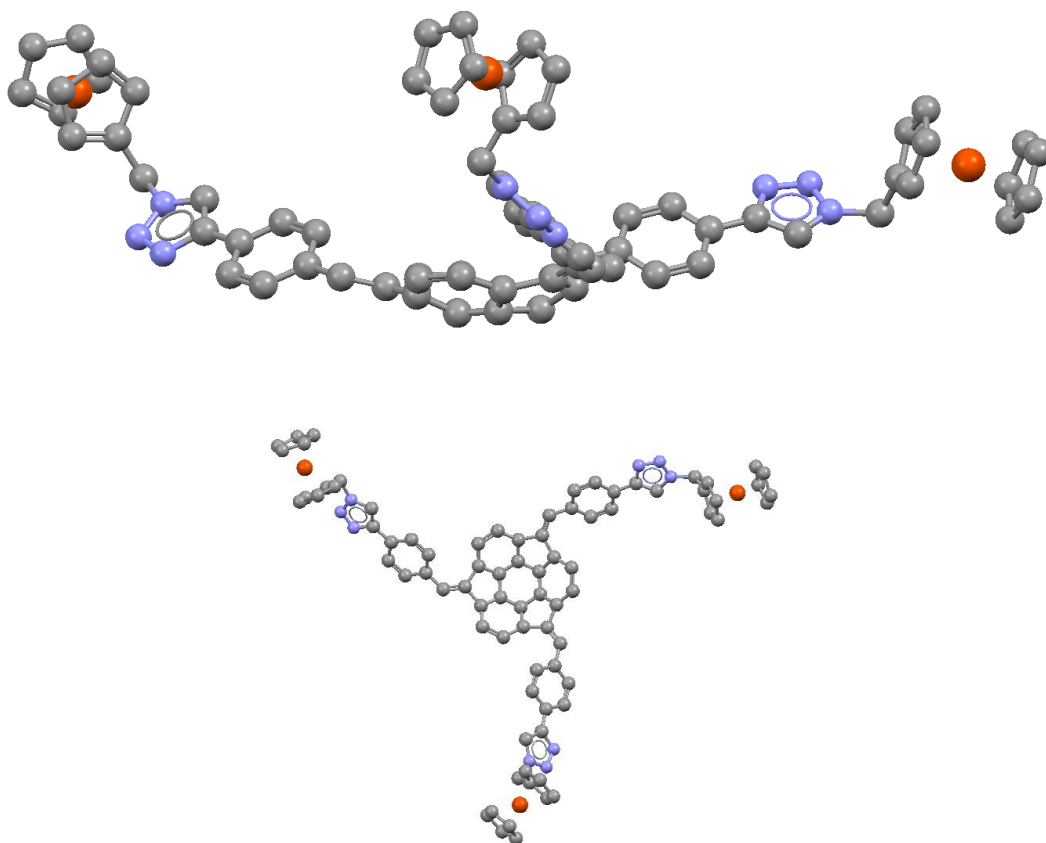


Figure S89. DFT-optimized structure of the sumanene-ferrocene conjugate **sumFc-3** (symmetrical diastereoisomer) viewed from two different perspectives. Hydrogens were omitted for clarity.

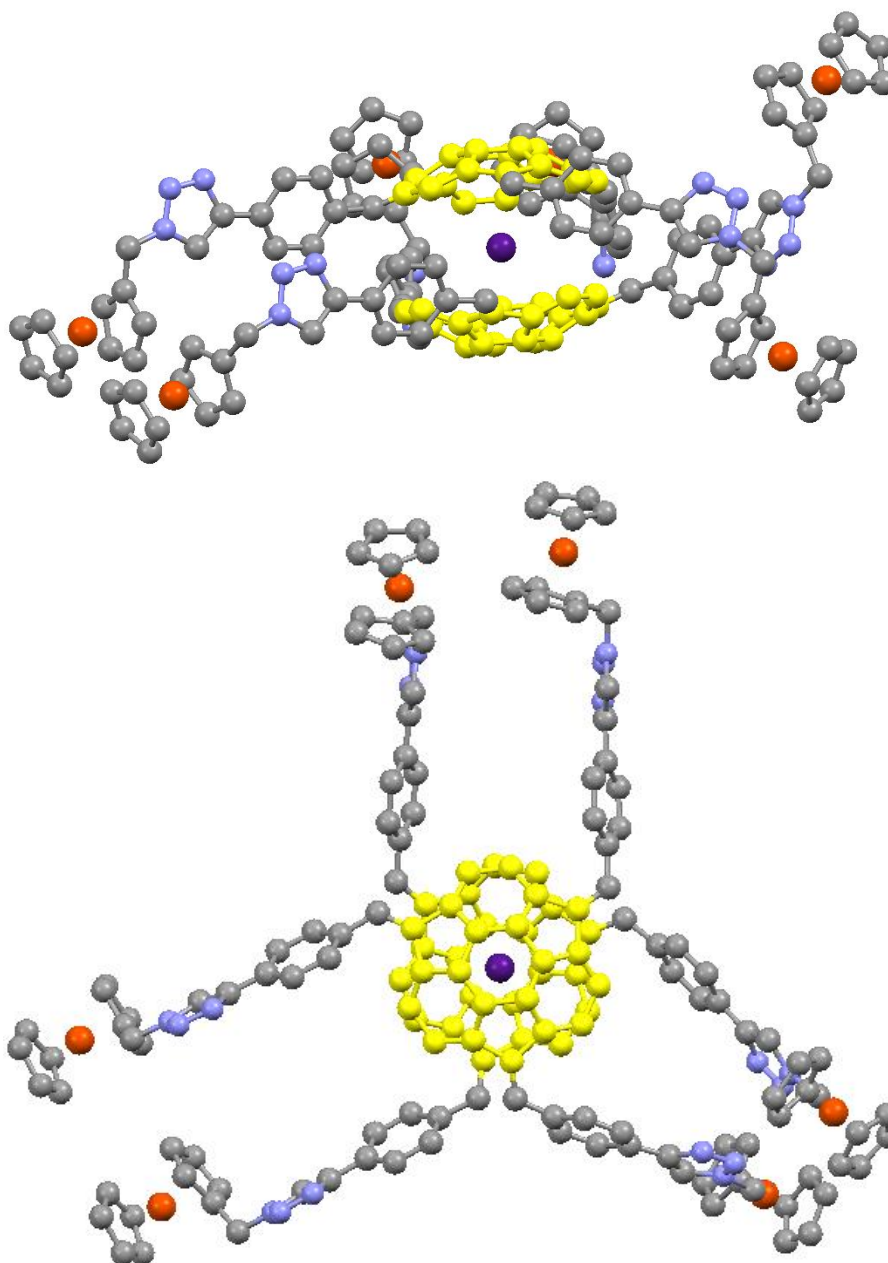


Figure S90. PM6-optimized structures of the formed sandwich complex between the representative two symmetrical diastereoisomers of sumanene-ferrocene conjugate **sumFc-3** and Cs⁺. For clarity, hydrogens are omitted and the sumanene bowls are marked yellow. The views from two different perspectives are presented.

7. References

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