Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Modular synthesis of pentaarylcyclopentadienyl Ru-based molecular machines via sequential Pd-catalysed cross couplings

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I. Materials and methods

All commercially available chemicals were of reagent grade and were used without further purification. Anhydrous THF, anhydrous toluene, anhydrous acetonitrile, anhydrous triethylamine, *N*,*N*-dimethylformamide, methanol, bis(triphenylphosphine)palladium(II) dichloride, [1,1′-bis(diphenylphosphino)ferrocene]dichloropalladium(II), *n*-butyllithium (2.5 M in hexanes), 1,4-diiodobenzene, magnesium sulfate, glacial acetic acid, hydrobromic acid (33 wt.% in acetic acid), cesium carbonate, pinacol and 2,6-lutidine were purchased from Aldrich. Copper iodide, triruthenium dodecacarbonyl and [1,1′-bis(diphenylphosphino)ferrocene] dichloropalladium(II) (dichloromethane adduct) were purchased from Acros. *N*-(*tert*-butoxycarbonyl)propargylamine, ferroceneboronic acid and trimethylsilyl trifluoromethanesulfonate were purchased from TCI. Monodisperse methoxy-PEG24-propionicacid-*N*-succinimidylester (CAS number 174569-25-6) was purchased from BroadPharm.

Compound **2**,[S1] thallium hydrotris(indazolyl)borate $TlTp^{4Bo,6\text{-}CH2SEt}$,[S2] nickel(II) 5-(4-ethynylphenyl)-10,15,20-tris(3,5-di-*tert*-butylphenyl)porphyrin **A**[S 3] and nickel(II) 5,10,15-tris(3,5-di-*tert*-butylphenyl)-20-[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)]-porphyrin **B**[S3] were synthesized according to the corresponding published procedures.

All reactions were carried out using standard Schlenk techniques under an argon atmosphere. Column chromatography was carried out on 230–400 mesh silica gel (Aldrich) unless otherwise stated. Alumina was purchased from Merck. Microwave reactions were carried out using CEM Discover LabMate. Thin layer chromatography (TLC) was performed on pre-coated aluminum-backed silica gel 60 UV_{254} plates (Macherey–Nagel) with visualization effected using ultraviolet irradiation (λ = 254, 366 nm).

NMR, IR and mass spectra were recorded by the appropriate services of the Toulouse Institute of Chemistry (ICT – FR2599). ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance III HD 500 MHz (cryoprobe Prodigy 5mm BBO, 1H ATMA), Avance 500 MHz (cryoprobe 5mm ^{1}H, ^{13}C) and Avance 300 MHz (probe 5mm BBO BB-1H Z-GRD) spectrometers. Residual solvent signals were used as internal reference for ^{1}H and ^{13}C NMR. Chemical shifts (δ) are reported in ppm. Coupling constants (J) are given in Hz and the following abbreviations have been used to describe the signals: singlet (s); broad singlet (br. s); doublet (d); triplet (t); quadruplet (q); quintuplet (quint); multiplet (m). Full assignments of ^{1}H and ^{13}C NMR spectra were made with the assistance of COSY, HMBC, and HSQC spectra when necessary. IR spectra were recorded with a Nicolet 6700 FTIR–ATR. Only selected characteristic peaks are reported and the following abbreviations have been used: sharp (s); broad (br). High-resolution mass spectra (HRMS) were performed with a Waters GCT Premier spectrometer for desorption chemical ionization (DCI/CH_4), with a Waters Xevo G2 QTof spectrometer for electrospray ionization (ESI), and with a Waters MALDI micro MX spectrometer for matrix-assisted laser desorption ionization (MALDI) (matrix: *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile DTCB; λ = 337 nm). UV/Vis spectra were recorded with a Shimadzu UV-26000 spectrometer (sh = shoulder, ε [$mol^{-1}\,dm^3cm^{-1}$] is reported in parentheses).

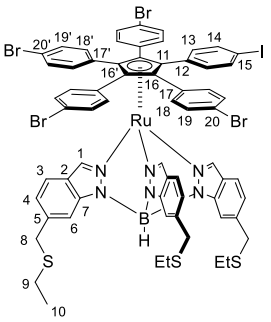
[S1] G. Vives, G. Rapenne, *Tetrahedron* **2008**, *64*, 11462-11468.

[S2] G. Erbland, Y. Gisbert, G. Rapenne, C. Kammerer, *Eur. J. Org. Chem*. **2018**, 4731–4739.

[S3] G. Erbland, S Abid, Y. Gisbert, N. Saffon-Merceron, Y. Hashimoto, L. Andreoni, T. Guérin, C. Kammerer, G. Rapenne, *Chem. Eur. J.* **2019**, *25*, in press.

II. Experimental procedures and characterization

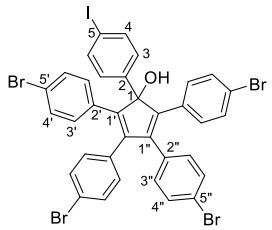
η⁵-1,2,3,4-Tetra(*p*-bromophenyl)-5-(*p*-iodophenyl)cyclopentadienyl hydrotris {6-[(ethylsulfanyl)methyl]indazol-1-yl}borate ruthenium(II) (1):



In a tube for microwave synthesis were placed a magnetic stir bar, ruthenium complex **5** (230 mg, 0.21 mmol, 1 eq.), thallium hydrotris(indazolyl)borate $TlTp^{4Bo,6\text{-}CH2SEt}$ (180 mg, 0.23 mmol, 1.1 eq.) and anhydrous acetonitrile (4 mL). The mixture was then degassed by bubbling argon for 15 minutes, before heating using microwave irradiation (115 °C, pressure up to 5 bar, 250 W, 3x10 minutes, releasing the pressure and manually shaking between each cycle). The resulting suspension was filtered over silica (eluted with CH_2Cl_2) and the solvents were removed in vacuo. The residue was purified by column chromatography (SiO_2, pentane/CH_2Cl_2 7:3) to give complex **1** as an orange solid in 59% yield (190 mg, 0.12 mmol).

*R*f=0.6 (SiO_2, cyclohexane/CH_2Cl_2 4:6);
^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): δ = 7.88 (s, 3H, H_6), 7.80 (d, ^4J = 0.9 Hz, 3H, H_1), 7.40 (AA'BB' pattern, ^3J = 8.5 Hz, 2H, H_{14}), 7.35 (d, ^3J = 8.3 Hz, 3H, H_3), 7.28-7.21 (m, 8H, H_{18} and $H_{18'}$), 7.21-7.15 (m, 8H, H_{19} and $H_{19'}$), 7.09 (AA'BB' pattern, ^3J = 8.5 Hz, 2H, H_{13}), 7.06-7.01 (m, 3H, H_4), 3.90 (s, 6H, H_8), 2.47 (q, ^3J = 7.3 Hz, 6H, H_9), 1.27 (t, ^3J = 7.3 Hz, 9H, H_{10}) ppm;
^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 25 °C): δ = 144.1 (C^2), 140.6 (C^1), 138.2 (C^5), 137.1 (C^{14}), 135.7 (C^{13}), 135.5 (C^{18} and $C^{18'}$), 133.2 (C^{12}), 132.6 (C^{17} and $C^{17'}$), 131.1 (C^{19} and $C^{19'}$), 122.7 (C^4), 122.4 (C^7), 122.3 (C^{20} and $C^{20'}$), 120.4 (C^3), 111.3 (C^6), 94.1 (C^{15}), 87.6 (C^{11}), 87.5 (C^{16}), 87.4 ($C^{16'}$), 36.9 (C^8), 25.7 (C^9), 14.7 (C^{10}) ppm;
HRMS (ESI$^+$): calcd. for $C_{65}H_{54}BBr_4IN_6RuS_3$ $[M]^+$:1573.8473, found 1573.8429.
Crystal data: Crystals suitable for X-Ray diffraction were obtained from the slow evaporation of a solution of complex **1** in a 1:1 mixture of dichloromethane and methanol. CCDC-1958243 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Selected data for **1**: $C_{65}H_{54}BBr_4IN_6RuS_3$, 3/2 CH_2Cl_2 M = 1701.13, monoclinic, space group $P2_1/c$, a = 13.1648(6) Å, b = 24.9566(10) Å, c = 21.5935(9) Å, b = 107.569(2)°, V = 6763.6(5) Å^3, Z = 4, crystal size 0.20 x 0.12 x 0.04 mm^3, 118682 reflections collected (12080 independent, R*int* = 0.1196), 864 parameters, 202 restraints, $R1$ [I>2s(I)] = 0.0737, *wR*2 [all data] = 0.1953, largest diff. peak and hole: 2.655 and –2.104 eÅ^{-3}.

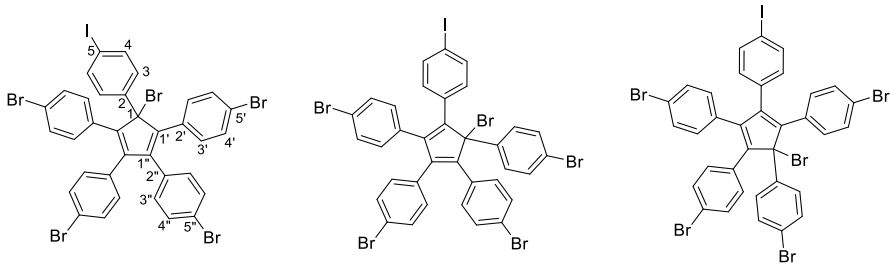
2,3,4,5-Tetra(*p*-bromophenyl)-1-(*p*-iodophenyl)cyclopenta-2,4-dien-1-ol (3):



In a three-neck round-bottom flask under argon were added a magnetic stir bar and 1,4-diiodobenzene (2.12 g, 6.43 mmol, 1.5 eq.). Anhydrous degassed THF (45 mL) was then added, and the resulting solution was cooled down to -78 °C. A solution of *n*-butyllithium (2.5 M in hexanes, 2.6 mL, 6.5 mmol, 1.5 eq.) was added dropwise and the solution was stirred for 30 minutes at -78 °C. A solution of 2,3,4,5-tetra(*p*-bromophenyl)cyclopenta-2,4-dien-1-one **2** (3.0 g, 4.29 mmol, 1 eq.) in degassed anhydrous THF (15 mL) was then cannulated dropwise. The flask was rinsed with 10 mL of degassed anhydrous THF and the resulting dark purple solution was stirred at -78 °C for 3 hours. A saturated aqueous solution of ammonium chloride (10 mL) was added, inducing a sudden color change of the organic phase from dark purple to clear yellow. The crude product was extracted with ethyl acetate (3x15 mL). The organic layers were combined and washed with water (2x30 mL) followed by brine (30 mL). The organic phase was dried using anhydrous magnesium sulfate and the solvents were evaporated in vacuo. The brown/yellow residue was purified by column chromatography (SiO_2, pentane/CH_2Cl_2 7:3) to give product **3** as a pale yellow solid in 94% yield (3.65 g, 4.04 mmol).

R_f = 0.6 (SiO_2, cyclohexane/CH_2Cl_2 6:4);
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.59 (d, ^3J = 8.7 Hz, 2H, H_4), 7.31 (AA'BB' pattern, ^3J = 8.5 Hz, 4H, $H_{4''}$), 7.22 (d, ^3J = 8.7 Hz, 2H, H_3), 7.20 (AA'BB' pattern, ^3J = 8.9 Hz, 4H, $H_{4'}$), 6.83 (AA'BB' pattern, ^3J = 8.9 Hz, 4H, $H_{3'}$), 6.79 (AA'BB' pattern, ^3J = 8.5 Hz, 4H, $H_{3''}$), 2.39 (br. s, 1H, OH) ppm;
^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 25 °C): δ = 147.6 ($C^{1'}$), 141.6 ($C1^{''}$), 139.1 (C^2), 138.0 (C^4), 133.0 ($C^{2''}$), 131.9 ($C^{2'}$), 131.8 ($C^{4''}$), 131.5 ($C^{4'}$ and $C^{3''}$), 131.0 ($C^{3'}$), 127.0 (C^3), 122.2 ($C^{5''}$), 122.1 ($C^{5'}$), 93.1 (C^5), 89.8 (C^1) ppm;
HRMS (DCI/CH_4): calcd. for $C_{35}H_{21}Br_4IO$ $[M]^+$: 903.7334, found 903.7336;
Elemental analysis (%) calcd. for $C_{35}H_{21}Br_4IO$: C 46.50, H 2.34; found: C 46.37, H 2.12;
FT-IR ν (cm^{-1}): 3544 (br, OH).

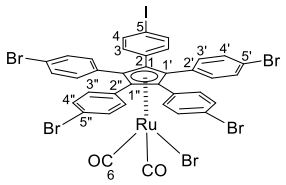
5-Bromo-1,2,3,4-tetra(*p*-bromophenyl)-5-(*p*-iodophenyl)cyclopenta-1,3-diene (4):
(Obtained as a mixture of 3 regioisomers in a 1:2:2 ratio)



2,3,4,5-Tetra(*p*-bromophenyl)-1-(*p*-iodophenyl)cyclopenta-2,4-dien-1-ol **3** (2 g, 2.2 mmol, 1 eq.) was suspended in glacial acetic acid (40 mL). The resulting mixture was heated under argon to 60 °C and a solution of hydrobromic acid (33 wt. % in acetic acid, 10 mL, 57.9 mmol, 26.2 eq.) was added dropwise. The resulting solution was heated at 95 °C under stirring for 2 hours. After cooling down the reaction medium to room temperature, it was poured in water (100 mL). The precipitate was filtered out and rinsed with water (200 mL). The crude product was purified by column chromatography (SiO_2, cyclohexane/CH_2Cl_2 9:1) to give compound **4** as a yellow solid composed of a 1:2:2 mixture of regioisomers (2.05 g, 2.12 mmol, 96% yield).

R_f = 0.6 (SiO_2, cyclohexane/CH_2Cl_2 9:1);
^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): δ = 7.60 (AA'BB' pattern, ^3J = 8.5 Hz, 0.4H, $H_{4\ regio1}$), 7.51 (AA'BB' pattern, ^3J = 8.6 Hz, 0.8H, $H_{4\ regio2}$), 7.43 (AA'BB' pattern, ^3J = 8.6 Hz, 0.8H, $H_{4\ regio3}$), 7.42-7.14 (m,10H, $H_{4'}$ and $H_{4''}$ and H_3), 6.88-6.66 (m, 8H, $H_{3'}$ and $H_{3''}$) ppm;
$^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 25 °C): δ = 148.2, 148.1, 141.5, 138.2 (C^4_{regio1}), 137.7 (C^4_{regio2}), 137.4 (C^4_{regio3}), 135.1, 134.4, 133.6, 133.3, 133.1, 133.0, 132.7, 132.4, 132.3, 132.2, 132.0, 131.9, 131.8, 131.4, 129.7, 129.6, 122.8, 122.5, 122.4, 94.5 (C^5_{regio1}), 94.3 (C^5_{regio2}), 94.2 (C^5_{regio3}), 75.2, 75.1, 75.0 ppm;
HRMS (DCI/CH_4): calcd. For $C_{35}H_{20}Br_5I$ $[M]^+$: 963.6506, found 963.6509.

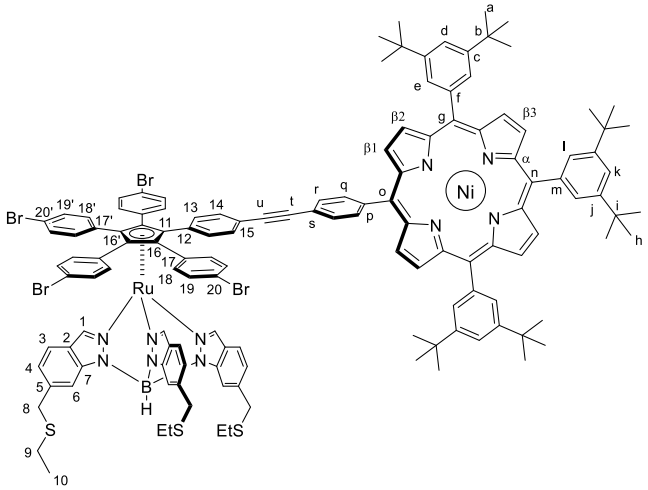
Bromido η^5-1,2,3,4-tetra(*p*-bromophenyl)-5-(*p*-iodophenyl)cyclopentadienyl dicarbonyl ruthenium(II) (5):



In a dry Schlenk tube containing a magnetic stir bar were placed ruthenium cluster Ru_3CO_{12} (85 mg, 0.13 mmol, 1.0 eq.), compound **4** (400 mg, 0.41 mmol, 3.1 eq.) and anhydrous degassed toluene (15 mL) under argon atmosphere. The mixture was heated at 100 °C for 2 hours. The solvents were then removed in vacuo and the crude product was adsorbed on silica and purified by column chromatography (SiO_2, cyclohexane/CH_2Cl_2 9:1) to give pure complex **5** as an orange solid in 72% yield (335 mg, 0.30 mmol).

R_f = 0.3 (SiO_2, cyclohexane/CH_2Cl_2 3:1);
^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): δ = 7.51 (AA'BB' pattern, ^3J = 8.5 Hz, 2H, H_4), 7.31 (AA'BB' pattern, ^3J = 8.6 Hz, 8H, $H_{4'}$ and $H_{4''}$), 6.90 (AA'BB' pattern, ^3J = 8.6 Hz, 8H, $H_{3'}$ and $H_{3''}$), 6.76 (AA'BB' pattern, ^3J = 8.5 Hz, 2H, H_3) ppm;
$^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 25 °C): δ = 196.0 (C^6), 137.9 (C^4), 134.2 (C^3), 134.1 ($C^{3'}$ and $C^{3''}$), 131.9 ($C^{4'}$ and $C^{4''}$), 128.9 (C^2), 128.3 ($C^{2'}$ and $C^{2''}$), 123.7 ($C^{5'}$ and $C^{5''}$), 105.9 (C^1), 105.8 ($C^{1'}$), 105.6 ($C^{1''}$), 95.6 (C^5) ppm;
HRMS (ESI$^-$): calcd. for $C_{38}H_{21}Br_5IO_4Ru$ [M+HCOO]$^-$: 1168.5415, found 1168.5463;
FT-IR ν (cm^{-1}): 2044 (s, CO), 1998 (s, CO).

η^5-1,2,3,4-Tetra(*p*-bromophenyl)-5-{*p*-[nickel(II) 10,15,20-tris(3,5-di-*tert*-butylphenyl) porphyrin-5-yl]phenylethynylphenyl}cyclopentadienyl hydrotris{6-[(ethylsulfanyl) methyl]indazol-1-yl}borate ruthenium(II) (6):

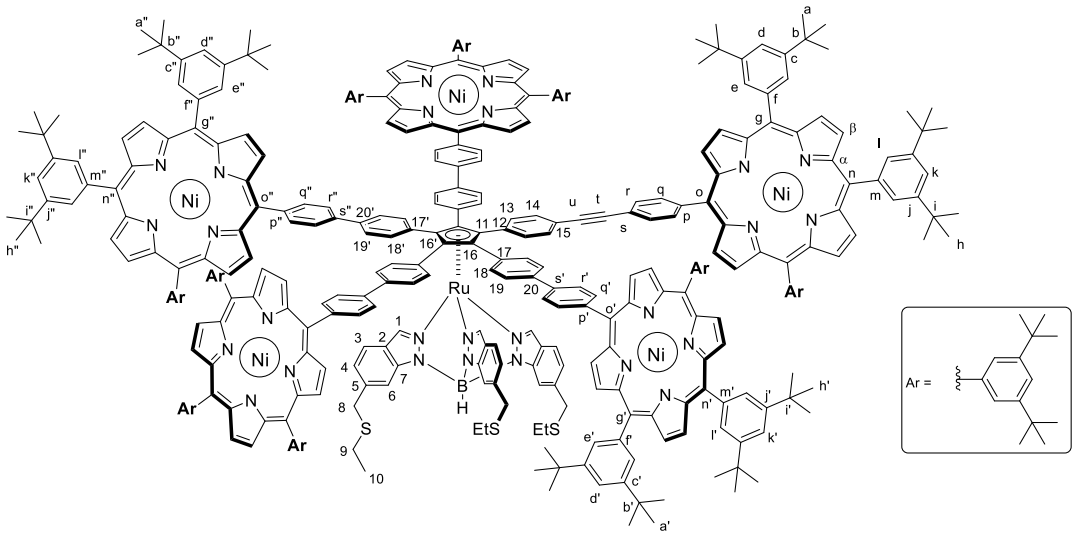


In a Schlenk tube under argon, complex **1** (20 mg, 13 µmol, 1.0 eq.), nickel(II) 5-(4-ethynylphenyl)-10,15,20-tris(3,5-di-*tert*-butylphenyl)porphyrin **A** (19.7 mg, 19 µmol, 1.5 eq.), $Pd(PPh_3)_2Cl_2$ (0.9 mg, 1.3 µmol, 10 mol%) and CuI (0.15 mg, 0.8 µmol, 6 mol%) were successively added, followed by anhydrous THF (4 mL) and anhydrous NEt_3 (1 mL). The system was degassed for 10 min and stirred for 24 h at 45 °C. After evaporation of the solvents, the residue was suspended in dichloromethane and filtered. The organic phase was then washed with water (2x10 mL), dried over magnesium sulfate, and the solvent was removed in vacuo. The crude product was purified first by column chromatography on neutral alumina (cyclohexane/CH_2Cl_2 gradient from 9:1 up to 0:1) then on silica gel (cyclohexane/CH_2Cl_2 2:1) to give complex **6** as a red solid in 51% yield (16 mg, 6.5 µmol).

R_f = 0.5 (SiO_2, cyclohexane/CH_2Cl_2 1:1);
^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): δ = 8.80 (d, ^3J = 4.9 Hz, 2H, $H_{β2}$), 8.79 (s, 4H, $H_{β3}$), 8.74 (d, ^3J = 4.9 Hz, 2H, $H_{β1}$), 8.02 (AA'BB' pattern, ^3J = 8.5 Hz, 2H, H_q), 7.91 (br. s, 3H, H_6), 7.89 (d, ^4J = 1.9 Hz, 4H, H_e), 7.89 (d, ^4J = 1.9 Hz, 2H, H_l), 7.87 (s, 3H, H_1), 7.80 (AA'BB' pattern, ^3J = 8.5 Hz, 2H, H_r), 7.77 (t, ^4J = 1.9 Hz, 2H, H_d), 7.77 (t, ^4J = 1.9 Hz, 1H, H_k), 7.42-7.38 (m, 5H, H_{13} and H_3), 7.35 (AA'BB' pattern, ^3J = 8.3 Hz, 2H, H_{14}), 7.30 (AA'BB' pattern, ^3J = 8.8 Hz, 4H, H_{18}), 7.27 (AA'BB' pattern, ^3J = 8.8 Hz, 4H, $H_{18'}$), 7.25 (AA'BB' pattern, ^3J = 8.8 Hz, 4H, H_{19} or $H_{19'}$), 7.22 (AA'BB' pattern, ^3J = 8.8 Hz, 4H, H_{19} or $H_{19'}$), 7.06 (d, ^3J = 8.4 Hz, 3H, H_4), 3.91 (s,

6H, H_8), 2.48 (q, ^3J = 7.4 Hz, 6H, H_9), 1.48 (s, 54H, H_a and H_h), 1.28 (t, ^3J = 7.4 Hz, 9H, H_{10}) ppm;
$^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 25 °C): δ = 149.5 (C^c and C^j), 144.1 (C^2), 143.4 (C^α), 143.3 (C^α), 142.7 (C^α), 141.8 (C^p), 140.7 (C^1), 140.3 (C^f and C^m), 138.2 (C^5), 135.6 (C^{18} and $C^{18'}$), 134.2 (C^q), 134.0 (C^{13} and C^{12}), 132.8 (C^β), 132.8 (C^{17} and $C^{17'}$), 132.7 (C^{15}), 132.6 (C^β), 131.9 (C^β), 131.1 (C^{14}), 131.1 (C^{19} and $C^{19'}$), 130.4 (C^r), 129.2 (C^e), 129.1 (C^l), 122.9 (C^s), 122.7 (C^4), 122.5 (C^7), 122.3 (C^{20} and $C^{20'}$), 121.8 (C^d and C^k), 120.9 (C^n), 120.8 (C^g), 120.5 (C^3), 118.3 (C^o), 111.4 (C^6), 90.7 (C^t), 90.5 (C^u), 88.3 (C^{11}), 87.6 (C^{16} or $C^{16'}$), 87.6 (C^{16} or $C^{16'}$), 36.9 (C^8), 35.3 (C^b and C^i), 31.8 (C^a and C^h), 25.7 (C^9), 14.8 (C^{10}) ppm;
UV/Vis (CH_2Cl_2): λ_{max} (ε) = 418 (254 000), 529 nm (18 000 $mol^{-1}dm^3cm^{-1}$);
HRMS (MALDI): calcd. for $C_{135}H_{129}BBr_4N_{10}NiRuS_3$ $[M]^+$: 2478.4785, found 2478.4609.

η⁵-1,2,3,4-Tetra{*p*-[nickel(II) 10,15,20-tris(3,5-di-*tert*-butylphenyl)porphyrin-5-yl]-4,4'-biphenyl}-5-{*p*-[nickel(II) 10,15,20-tris(3,5-di-*tert*-butylphenyl)porphyrin-5-yl] phenylethynylphenyl}cyclopentadienyl hydrotris{6-[(ethylsulfanyl)methyl]indazol-1-yl} borate ruthenium(II) (7):

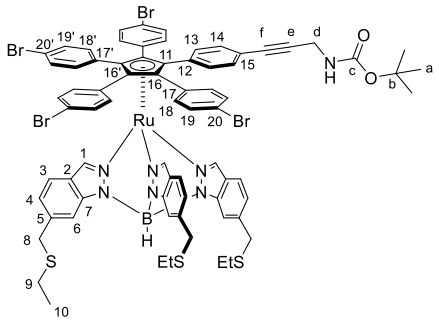


In a Schlenk tube, complex **6** (20 mg, 8.1 µmol, 1.0 eq.), nickel(II) 5,10,15-tris(3,5-di-*tert*-butylphenyl)-20-[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)]porphyrin **B** (73 mg, 64.6 µmol, 8.0 eq.), $Pd(dppf)Cl_2$ (2.6 mg, 3.2 µmol, 40 mol%) and Cs_2CO_3 (32 mg, 97 µmol, 12.0 eq.) were successively introduced under argon atmosphere in 2.5 mL of a degassed solution of DMF and water (99:1). The system was then degassed by three freeze-pump-thaw cycles and stirred at 100 °C for 48 h. After cooling to room temperature, the solvents were evaporated in vacuo and the residue was adsorbed onto silica and further purified by column chromatography (SiO_2, heptane/CH_2Cl_2 2:1) affording complex **7** as a red solid in 36% yield (18 mg, 2.9 µmol).

R_f = 0.7 (SiO_2, cyclohexane/CH_2Cl_2 1:1);
^1H NMR (500 MHz, CD_2Cl_2, 25 °C): δ = 8.84-8.73 (m, 40H, H_β), 8.32 (s, 3H, H_1), 8.14-8.09 (m, 8H, $H_{q',q''}$), 8.06 (br. s, 3H, H_6), 8.04-8.00 (m, 10H, $H_{r',r''}$ and H_q), 7.94 (AA'BB' pattern , ^3J = 8.3 Hz, 4H, $H_{18'}$), 7.92-7.85 (m, 36H, H_{18} and H_r and $H_{e,e',e''}$ and $H_{l,l',l''}$), 7.84-7.80 (m, 10H, H_{19} and

$H_{19'}$ and H_{13}), 7.79-7.77 (m, 5H, $H_{k,k',k''}$), 7.75 (t, ^4J = 1.8 Hz, 2H, H_d), 7.71 (t, ^4J = 1.8 Hz, 4H, $H_{d'}$ or $H_{d''}$), 7.71 (t, ^4J = 1.8 Hz, 4H, $H_{d'}$ or $H_{d''}$), 7.57 (d, ^3J = 8.5 Hz, 3H, H_3), 7.56 (d, ^3J = 8.4 Hz, 2H, H_{14}), 7.14 (d, ^3J = 8.7 Hz, 3H, H_4), 3.99 (s, 6H, H_8), 2.54 (q, ^3J = 7.4 Hz, 6H, H_9), 1.48 (s, 90H, $H_{h, h',h''}$), 1.45 (s, 36H, H_a), 1.42 (s, 144H, $H_{a',a''}$), 1.33 (t, ^3J = 7.4 Hz, 9H, H_{10}) ppm;
$^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 25 °C): δ = 149.5 ($C^{c,c',c''}$ and $C^{j,j',j''}$), 144.3 (C^2), 143.4 (C^{α}), 143.3 (C^{α}), 143.0 (C^{α}), 142.7 (C^{α}), 141.7 (C^p), 141.1 (C^1), 140.7 ($C^{p',p''}$), 140.4 ($C^{m,m',m''}$), 140.3 ($C^{f,f',f''}$), 140.1($C^{s',s''}$), 140.0 ($C^{20,20'}$), 138.0 (C^5), 135.4 (C^{12}), 135.0 ($C^{18,18'}$), 134.7 ($C^{q',q''}$), 134.5 (C^{13}), 134.2 (C^q), 134.0 (C^{17} or $C^{17'}$), 133.9 (C^{17} or $C^{17'}$), 132.8 (C^{β}), 132.7 (C^{β}), 132.6 (C^{β}), 132.5 (C^{β}), 132.1 (C^{β}), 131.9 (C^{β}), 131.2 (C^{14}), 130.5 (C^r), 129.1 ($C^{e,e',e''}$ and $C^{l,l',l''}$), 126.6 ($C^{19,19'}$), 125.8 ($C^{r',r''}$), 123.0 (C^s), 122.8 (C^7 and C^{15}), 122.6 (C^4), 121.7 ($C^{d,d',d''}$ and $C^{k,k',k''}$), 120.7 ($C^{g,g',g''}$ and $C^{n,n',n''}$), 120.6 (C^3), 118.8 ($C^{o',o''}$), 118.3 (C^o), 111.5 (C^6), 90.6 (C^u), 90.5 (C^t), 88.7 (C^{11}), 88.5 ($C^{16,16'}$), 37.0 (C^8), 35.3 ($C^{b,b',b''}$ and $C^{i,i',i''}$), 31.8 ($C^{a,a',a''}$ and $C^{h,h',h''}$), 25.8 (C^9), 14.8 (C^{10}) ppm;
UV/Vis (CH_2Cl_2): λ_{max} (ε) = 418 (1 396 000), 529 nm (107 000 $mol^{-1}dm^3cm^{-1}$);
HRMS (MALDI): calcd. for $C_{407}H_{429}BN_{26}Ni_5RuS_3$ $[M]^+$: 6185.9474, found 6185.9556.

η⁵-1,2,3,4-Tetra(*p*-bromophenyl)-5-{*p*-[3'-(*tert*-butoxycarbonylamino)propyn-1'-yl] phenyl}cyclopentadienyl hydrotris{6-[(ethylsulfanyl)methyl]indazol-1-yl}borate ruthenium(II) (8):

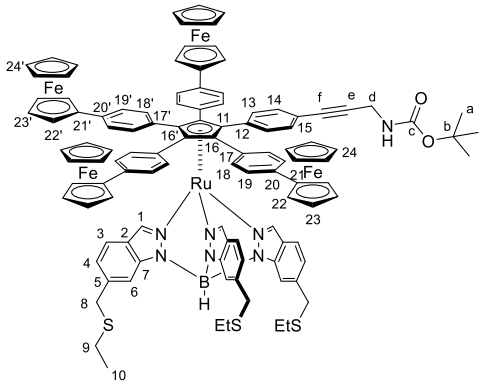


Compound **1** (100 mg, 63.5 µmol, 1.0 eq.), *N*-(*tert*-butoxycarbonyl)propargylamine (19.7 mg, 127 µmol, 2.0 eq.) and a magnetic stir bar were placed in a Schlenk tube. Anhydrous THF (2 mL) and anhydrous triethylamine (0.5 mL) were added and the mixture was degassed by bubbling argon for 20 minutes. $Pd(PPh_3)_2Cl_2$ (4.6 mg, 6.4 µmol, 10 mol%) and CuI (0.6 mg, 3.2 µmol, 5 mol%) were added under an argon flow. The resulting mixture was then stirred under argon in the dark at 40 °C for 24 hours. The solvents were removed in vacuo and the crude product was purified by column chromatography (SiO_2, CH_2Cl_2) to give complex **8** as an orange solid in 75% yield (76 mg, 47 µmol).

R_f = 0.6 (SiO_2, CH_2Cl_2);
^1H NMR (500 MHz, CD_2Cl_2, 25 °C): δ = 7.91 (br. s, 3H, H_6), 7.81 (d, ^3J = 0.8 Hz, 3H, H_1), 7.35 (dd, ^3J = 8.4 Hz, ^4J = 0.8 Hz, 3H, H_3), 7.29 (AA'BB' pattern, ^3J = 8.7 Hz, 2H, H_{13}), 7.25-7.15 (m, 16H, $H_{18,18'}$ and $H_{19,}H_{19'}$), 7.11 (AA'BB' pattern, ^3J = 8.7 Hz, 2H, H_{14}), 7.04 (dd, ^3J = 8.4 Hz, ^4J = 1.4 Hz, 3H, H_4), 4.80 (br. s, 1H, NH), 4.05 (d, ^3J = 6.0 Hz, 2H, H_d), 3.91 (s, 6H, H_8), 2.47 (q, ^3J = 7.4 Hz, 6H, H_9), 1.42 (s, 9H, H_a), 1.28 (t, ^3J = 7.4 Hz, 9H, H_{10}) ppm;
$^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 25 °C): δ = 155.5 (C^c), 144.1 (C^2), 140.6 (C^1), 138.1 (C^5), 135.5 (C^{18} and $C^{18'}$), 133.8 (C^{13}), 133.8 (C^{15}), 132.7 (C^{17} or $C^{17'}$), 132.6 (C^{17} or $C^{17'}$), 131.1 (C^{19}

and $C^{19'}$ and C^{14}), 122.7 (C^4), 122.4 (C^{20} and $C^{20'}$), 122.2 (C^7 and C^{12}), 120.4 (C^3), 111.4 (C^6), 88.1 (C^{11}), 87.5 (C^{16} or $C^{16'}$), 87.3 (C^{16} or $C^{16'}$), 87.2 (C^e), 82.5 (C^f), 80.1 (C^b), 37.0 (C^8), 31.4 (C^d), 28.5 (C^a), 25.8 (C^9), 14.7 (C^{10}) ppm;
HRMS (ESI$^+$): calcd. for $C_{73}H_{67}BBr_4N_7O_2RuS_3$ $[MH]^+$:1602.0378, found 1602.0365.

Η^5-1,2,3,4-Tetra(*p*-ferrocenylphenyl)-5-{*p*-[3'-(*tert*-butoxycarbonylamino)propyn-1'-yl] phenyl}cyclopentadienyl hydrotris{6-[(ethylsulfanyl)methyl]indazol-1-yl}borate ruthenium(II) (9):

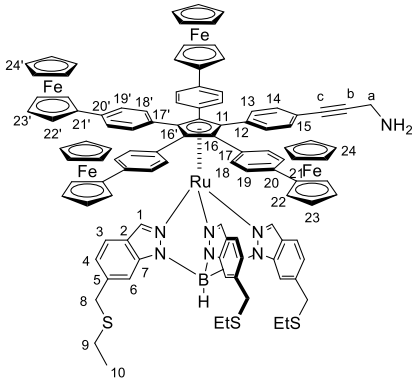


Compound **8** (80 mg, 50 µmol, 1.0 eq.), ferroceneboronic acid pinacol ester (250 mg, 0.8 mmol, 16 eq.) and cesium carbonate (160 mg, 0.5 mmol, 10 eq.) were placed in a Schlenk tube with a magnetic stir bar. A mixture of DMF (2 mL) and water (0.02 mL) was added and the resulting suspension was degassed by three freeze-pump-thaw cycles. $Pd(dppf)Cl_2{\cdot}CH_2Cl_2$ (16.3 mg, 20 µmol, 40 mol%) was added under an argon flow and the reaction medium was heated at 100 °C for 72 h under stirring. The solvents were evaporated and the residue was dissolved in dichloromethane (1 mL). Heptane (10 mL) was then added and the dichloromethane was removed by rotary evaporation, thereby inducing precipitation of the crude product whilst excess boronic acid was solubilized. After cooling down to 0° C with an ice bath, the crude product was filtered, rinsed with ice-cold pentane (40 mL) before purification by column chromatography (SiO_2, CH_2Cl_2/heptane 8:2) to afford pure compound **9** as an orange solid in 16% yield (16 mg, 7.9 µmol).

R_f = 0.6 (SiO_2, CH_2Cl_2/heptane 8:2);
^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): δ = 8.04 (br. s, 3H, H_1), 7.91 (br. s, 3H, H_6), 7.40 (AA'BB' pattern, ^3J = 8.4 Hz, 2H, H_{13}), 7.36-7.27 (m, 11H, $H_{18,18'}$ and H_3), 7.22-7.11 (m, 10H, $H_{19,19'}$ and H_{14}), 7.00 (dd, ^3J = 8.3 Hz, ^4J = 1.4 Hz, 3H, H_4), 4.72 (br. s, 1H, NH), 4.64-4.55 (m, 8H, H_{22} and $H_{22'}$), 4.29 (m, 8H, H_{23} and $H_{23'}$), 4.02 (d, ^3J = 5.8 Hz, 2H, H_d), 3.98-3.95 (m, 20H, H_{24} and $H_{24'}$), 3.90 (s, 6H, H_8), 2.48 (q, ^3J = 7.4 Hz, 6H, H_9), 1.40 (s, 9H, H_a), 1.28 (t, ^3J = 7.4 Hz, 9H, H_{10}) ppm;
$^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 25 °C): δ = 155.1 (C^c), 144.1 (C^2), 140.5 (C^1), 138.8 (C^{20} or $C^{20'}$), 138.7 (C^{20} or $C^{20'}$), 137.7 (C^5), 135.7 (C^{15}), 134.0 (C^{13}), 133.8 (C^{18} or $C^{18'}$), 133.7 (C^{18} or $C^{18'}$), 132.2 (C^{17} or $C^{17'}$), 132.0 (C^{17} or $C^{17'}$), 130.8 (C^{14}), 125.1 (C^{19} and $C^{19'}$), 122.5 (C^7), 122.4 (C^4), 121.8 (C^{12}), 120.4 (C^3), 111.4 (C^6), 88.0 (C^{16} or $C^{16'}$ and C^{11}), 87.8 (C^{16} or $C^{16'}$), 86.7 (C^e), 85.1 (C^{21} and $C^{21'}$), 83.0 (C^f), 79.5 (C^b), 70.5 (C^{24} and $C^{24'}$), 69.9 (C^{23} and $C^{23'}$), 66.9 (C^{22} and $C^{22'}$), 36.9 (C^8), 30.1 (C^d), 28.5 (C^a), 25.7 (C^9), 14.8 (C^{10}) ppm (C^b, C^c and $C^{21/21'}$ are not

distinguished on the ^{13}C-JMod spectrum due to low concentration of the sample, but they do correlate in the 2D HMBC spectrum);
HRMS (MALDI): calcd. for $C_{113}H_{103}BFe_4N_7O_2RuS_3$ $[MH]^+$: 2022.3920, found 2022.3829.

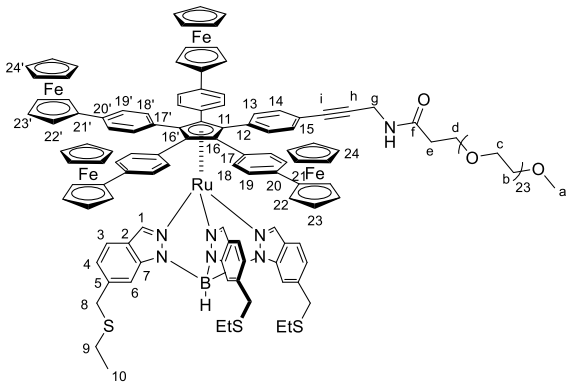
Η^5-1,2,3,4-Tetra(*p*-ferrocenylphenyl)-5-[*p*-(3'-aminopropyn-1'-yl)phenyl] cyclopentadienyl hydrotris{6-[(ethylsulfanyl)methyl]indazol-1-yl}borate ruthenium(II) (10):



Complex **9** (14.5 mg, 7.2 µmol, 1.0 eq.) was placed in a Schlenk tube containing a magnetic stir bar and dissolved in anhydrous dichloromethane (0.5 mL). The solution was degassed by bubbling argon for 15 minutes before being cooled down to 0 °C. 2,6-Lutidine (17 µL, 144 µmol, 20 eq.) was added under an argon flow, followed by trimethylsilyl trifluoromethanesulfonate (13 µL, 72 µmol, 10 eq.). The solution was stirred at 0 °C for one hour, followed by one hour at room temperature. Methanol (0.5 mL) was added and the solvents were removed in vacuo. The crude product was partially purified by column chromatography (SiO_2, CH_2Cl_2/MeOH 9:1), dried in vacuo, redissolved in dichloromethane (1 mL) and heptane (10 mL) was added. The dichloromethane was removed by rotary evaporation inducing precipitation of complex **10**. The mixture was cooled down to 0 °C, filtered on a celite plug and the solid was rinsed with ice cold pentane (50 mL). Complex **10** was finally eluted with dichloromethane and dried in vacuo to afford an orange solid in 81% yield (11.2 mg, 5.8 µmol).

R_f = 0.3 (SiO_2, MeOH/CH_2Cl_2 2:100);
^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): δ = 8.07 (d, ^3J = 1.0 Hz, 3H, H_1), 7.92 (br. s, 3H, H_6), 7.40 (AA'BB' pattern, ^3J = 8.7 Hz, 2H, H_{13}), 7.37-7.30 (m, 11H, H_{18} and $H_{18'}$ and H_3), 7.21-7.17 (m, 8H, H_{19} and $H_{19'}$), 7.12 (AA'BB' pattern, ^3J = 8.7 Hz, 2H, H_{14}), 7.00 (dd, ^3J = 8.3 Hz, ^4J = 1.4 Hz, 3H, H_4), 4.55 (m, 8H, H_{22} and $H_{22'}$), 4.25 (m, 8H, H_{23} and $H_{23'}$), 3.95-3.89 (m, 20H, H_{24} and $H_{24'}$), 3.88 (s, 6H, H_8), 3.51 (br. s, 2H, H_a), 2.48 (q, ^3J = 7.4 Hz, 6H, H_9), 1.28 (t, ^3J = 7.4 Hz, 9H, H_{10}) ppm;
^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 25 °C): δ = 144.1 (C^2), 140.5 (C^1), 138.7 (C^{20} and $C^{20'}$), 137.7 (C^5), 135.1 (C^{15}), 134.0 (C^{13}), 133.9 (C^{18} or $C^{18'}$), 133.8 (C^{18} or $C^{18'}$), 132.1 (C^{17} or $C^{17'}$), 132.0 (C^{17} or $C^{17'}$), 130.7 (C^{14}), 125.1 (C^{19} and $C^{19'}$), 122.6 (C^7 and C^{12}), 122.4 (C^4), 120.4 (C^3), 111.4 (C^6), 91.7 (C^b), 88.0 (C^{16} or $C^{16'}$ and C^{11}), 87.7 (C^{16} or $C^{16'}$), 84.7 (C^{21} or $C^{21'}$), 84.6 (C^{21} or $C^{21'}$), 82.3 (C^c), 70.2 (C^{24} and $C^{24'}$), 69.6 (C^{23} and $C^{23'}$), 66.8 (C^{22} and $C^{22'}$), 36.9 (C^8), 32.4 (C^a), 25.7 (C^9), 14.8 (C^{10}) ppm;
HRMS (MALDI): calcd. for $C_{108}H_{94}BFe_4N_7RuS_3$ $[M]^+$: 1921.3315, found 1921.3230.

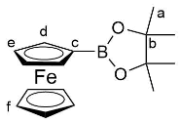
η^5-1,2,3,4-Tetra(*p*-ferrocenylphenyl)-5-{*p*-[3'-(methoxy-PEG24-propionamido)propyn-1'-yl]phenyl}cyclopentadienyl hydrotris{6-[(ethylsulfanyl)methyl]indazol-1-yl}borate ruthenium(II) (11):



In a Schlenk tube were placed a stir bar, compound **10** (9 mg, 4.7 µmol, 1.0 eq.), mPEG$_{24}$-NHS ester (45 mg, 37.1 µmol, 7.9 eq.), anhydrous DMF (0.5 mL) and anhydrous triethylamine (4 µL, 28.8 µmol, 6.1 eq.). The mixture was degassed by bubbling argon for 15 minutes and stirred at room temperature for 24 hours. The solvent was then evaporated and the crude product was purified by a short column chromatography (SiO_2, CH_2Cl_2/MeOH 9:1) followed by an alumina plug (eluted with dichloromethane) to remove hydrolyzed PEG species. Ethanol (10 mL) was then added to the eluate and dichloromethane was removed by rotary evaporation to induce precipitation of complex **11** in ethanol. After cooling down the suspension to 0 °C, the precipitate was filtered and washed with ice-cold ethanol (30 mL) followed by ice-cold pentane (10 mL) to give pure complex **11** as a yellow-orange solid in 85% yield (12 mg, 3.9 µmol).

R_f = 0.5 (SiO_2, MeOH/CH_2Cl_2 4:100);
^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): δ = 8.06 (d, ^3J = 0.9 Hz, 3H, H_1), 7.91 (br. s, 3H, H_6), 7.41 (AA'BB' pattern, ^3J = 8.7 Hz, 2H, H_{13}), 7.37-7.29 (m, 11H, H_{18} and $H_{18'}$ and H_3), 7.20 (AA'BB' pattern, ^3J = 8.7 Hz, 4H, H_{19} or $H_{19'}$), 7.18 (AA'BB' pattern, ^3J = 8.7 Hz, 4H, H_{19} or $H_{19'}$), 7.13 (AA'BB' pattern, ^3J = 8.7 Hz, 2H, H_{14}), 7.00 (dd, ^3J = 8.4 Hz, ^4J = 1.5 Hz, 3H, H_4), 6.65 (t, ^3J = 5.5 Hz, 1H, NH), 4.56-4.53 (m, 8H, H_{22} and $H_{22'}$), 4.26-4.23 (m, 8H, H_{23} and $H_{23'}$), 4.13 (d, ^3J = 5.5 Hz, 2H, H_g), 3.94 (s, 10H, H_{24} or $H_{24'}$), 3.93 (s, 10H, $H_{24'}$ or $H_{24'}$), 3.90 (s, 6H, H_8), 3.67 (t, ^3J = 5.8 Hz, 2H, H_d), 3.57 (m, 92H, OCH_2CH_2O), 3.34 (s, 3H, H_a), 2.48 (q, ^3J = 7.4 Hz, 6H, H_9), 2.40 (t, ^3J = 5.8 Hz, 2H, H_e), 1.28 (t, ^3J = 7.4 Hz, 9H, H_{10}) ppm;
^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 25 °C): δ = 171.2 (C^f), 144.0 (C^2), 140.5 (C^1), 138.8 (C^{20} and $C^{20'}$), 137.7 (C^5), 135.5 (C^{15}), 134.0 (C^{13}), 133.9 (C^{18} or $C^{18'}$), 133.8 (C^{18} or $C^{18'}$), 132.2 (C^{17} or $C^{17'}$), 131.9 (C^{17} or $C^{17'}$), 130.8 (C^{14}), 125.1 (C^{19} and $C^{19'}$), 122.6 (C^7), 122.5 (C^4), 121.9 (C^{12}), 120.4 (C^3), 111.4 (C^6), 88.0 (C^{16} or $C^{16'}$), 87.8 (C^{16} or $C^{16'}$), 87.7 (C^h), 86.8 (C^{11}), 84.6 (C^{21} and $C^{21'}$), 82.6 (C^i), 72.3 (OCH$_2$$CH_2$O), 70.9 (O$CH_2$$CH_2$O), 70.8 (O$CH_2$$CH_2$O), 70.7 (O$CH_2$$CH_2$O), 70.6 (O$CH_2$$CH_2$O), 70.2 ($C^{24}$ and $C^{24'}$), 69.6 (C^{23} and $C^{23'}$), 67.3 (C^d), 66.8 (C^{22} or $C^{22'}$), 66.7 (C^{22} or $C^{22'}$), 59.0 (C^a), 37.10 (C^e), 36.9 (C^8), 29.8 (C^g), 25.7 (C^9), 14.8 (C^{10}) ppm;
HRMS (MALDI): calcd. for $C_{158}H_{192}BFe_4N_7O_{25}RuS_3$ [M]$^+$: 3020.9739, found 3020.9749.

Ferroceneboronic acid pinacol ester

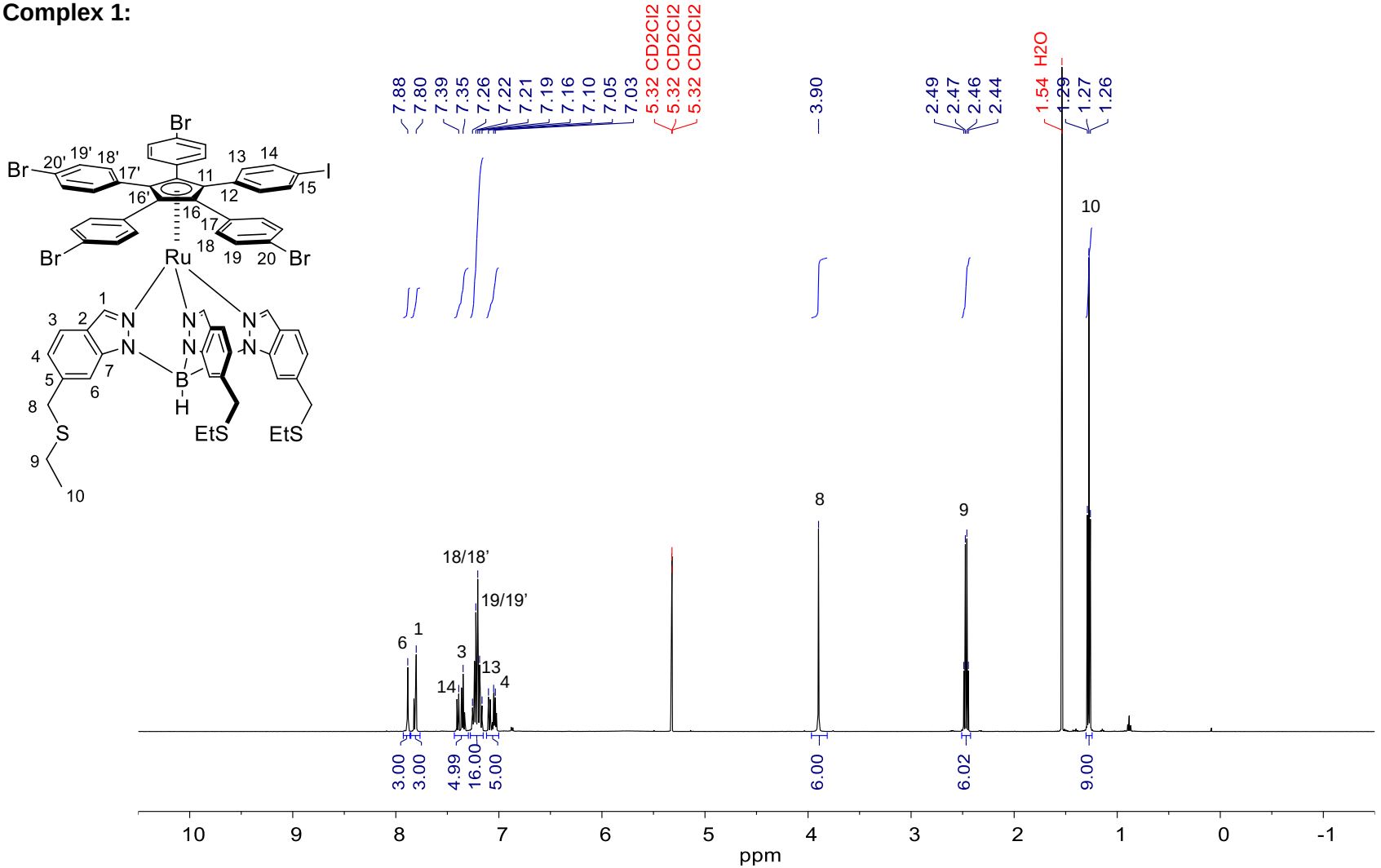


Ferroceneboronic acid (2.43 g, 10.6 mmol, 1 eq.) and pinacol (1.62 g, 13.7 mmol, 1.3 eq.) were placed in a round bottom flask and toluene (250 mL) was added. A Dean Stark head was fitted and the reaction was heated at reflux for three hours. The solvent was then evaporated and the crude product was purified by a short column chromatography (SiO_2, CH_2Cl_2/pentane 7:3) to give pure ferroceneboronic acid pinacol ester as an orange solid in 92% yield (3.05 g, 9.78 mmol).

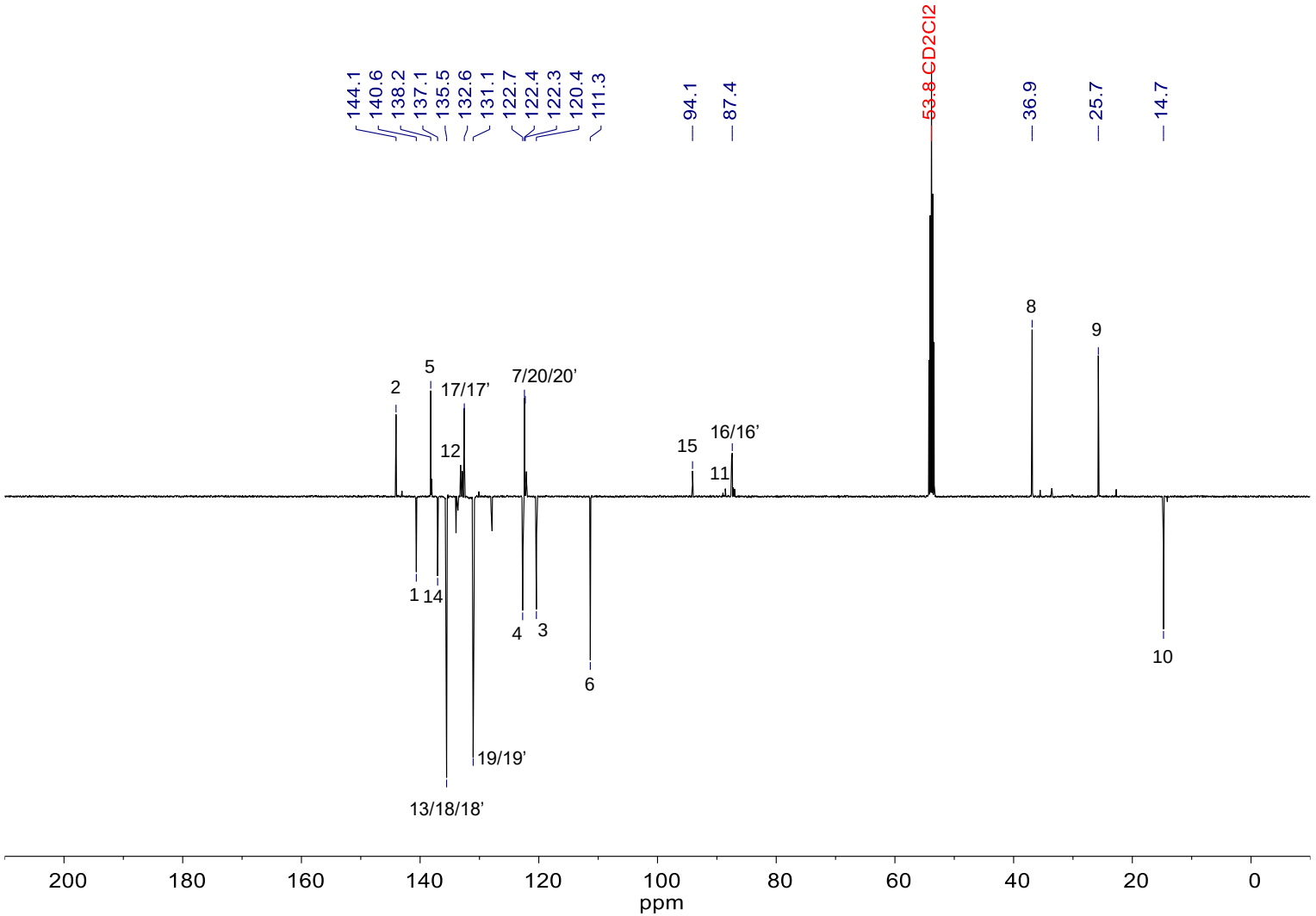
^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C): δ = 4.38 (m, 2H, H_e), 4.35 (m, 2H, H_d), 4.15 (s, 5H, H_f), 1.33 (s, 12H, H_a) ppm;
^{13}C NMR (75 MHz, CD_2Cl_2, 25 °C): δ = 83.5 (C_b), 74.0 (C_e), 72.3 (C_d), 68.8 (C_f), 25.1 (C_a) ppm (C_c, linked to the B atom, is not observed due to line broadening).
The data match those reported in the literature.[S4]

[S4] A. Tlili, A. Voituriez, A. Marinetti, P. Thuéry, T. Cantat, *Chem. Commun*. **2016**, *52*, 7553-7555.

Complex 1:

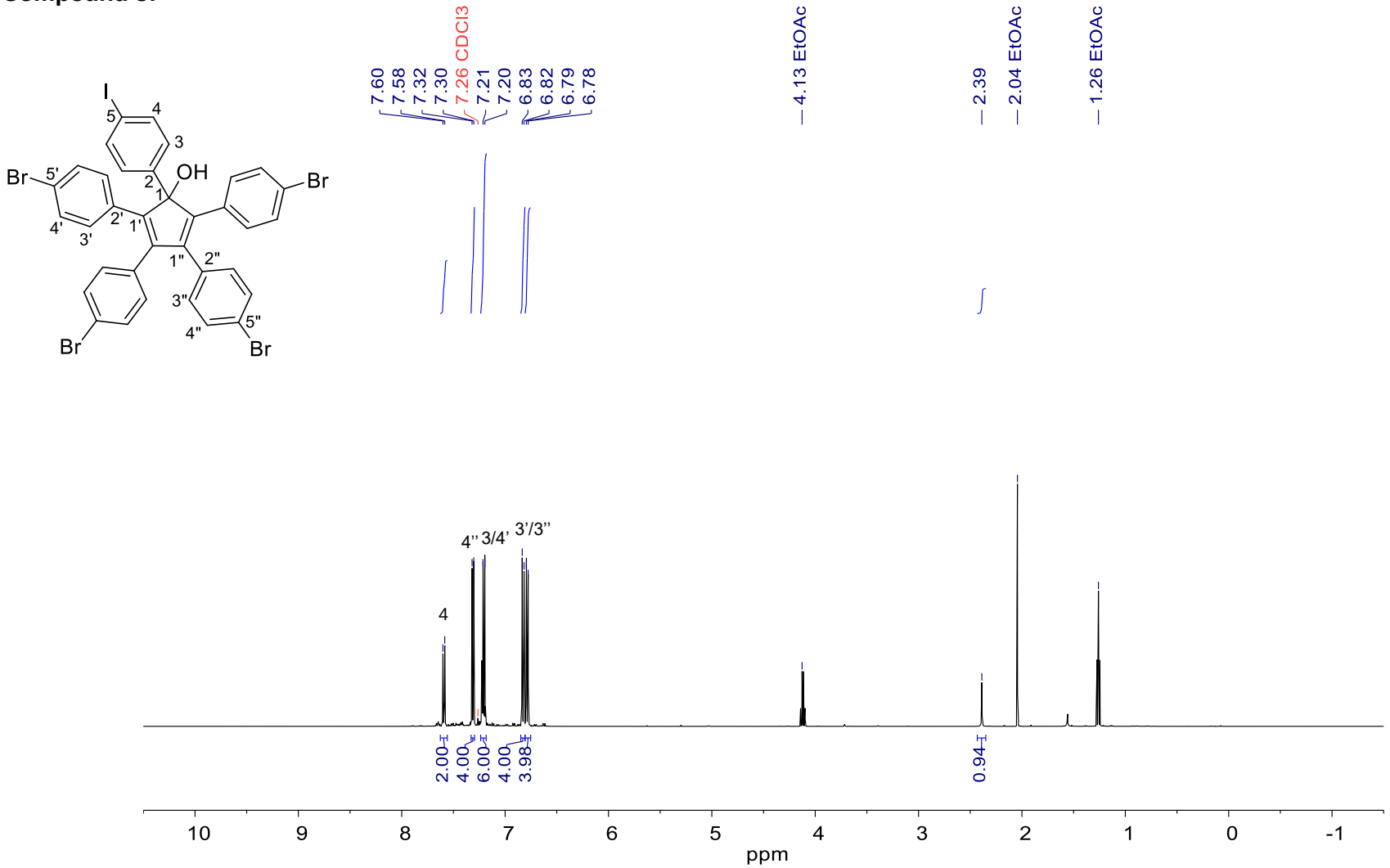


^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C) of complex **1**

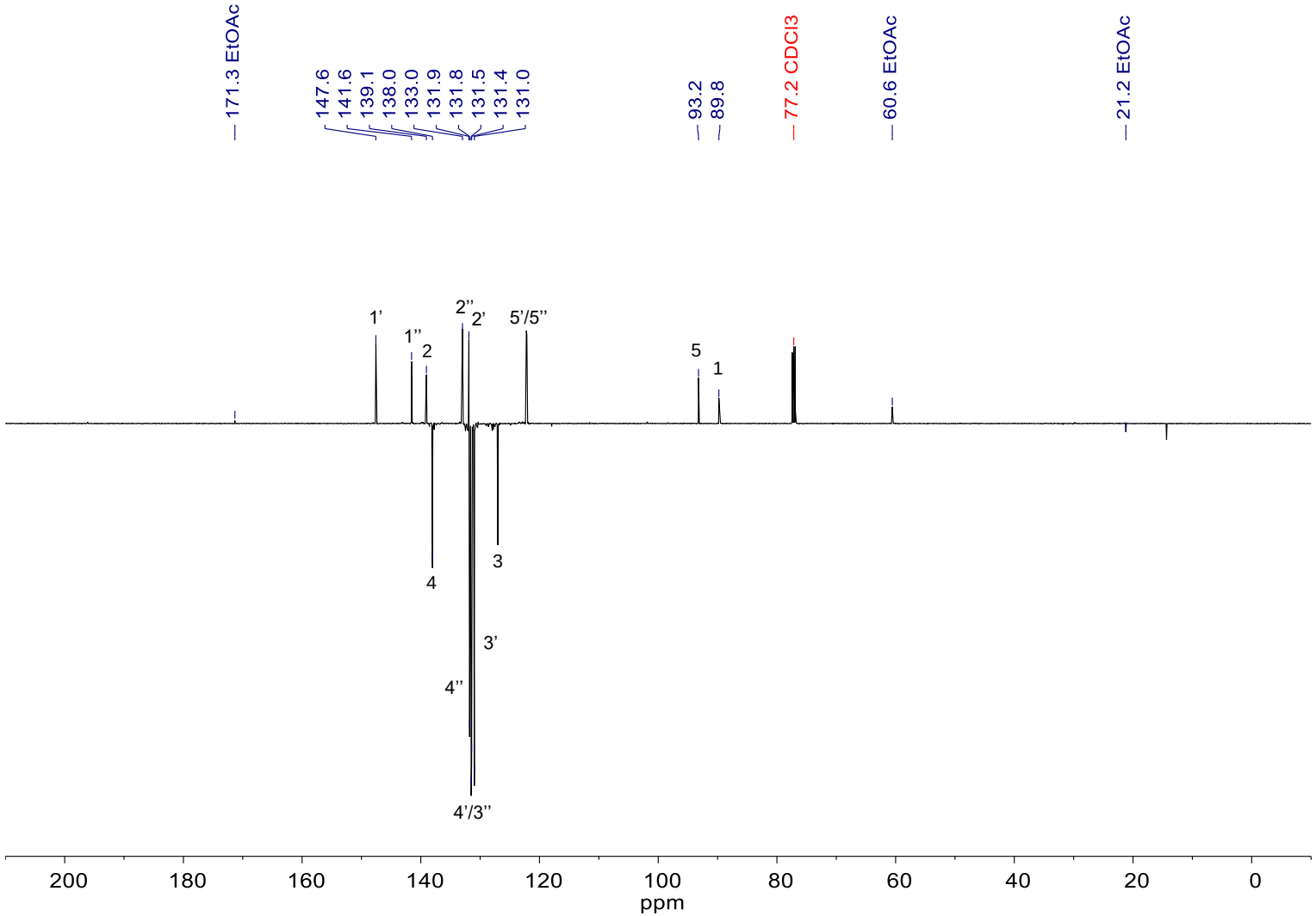


^{13}C-Jmod NMR (126 MHz, CD_2Cl_2, 25 °C) of complex **1**

Compound 3:

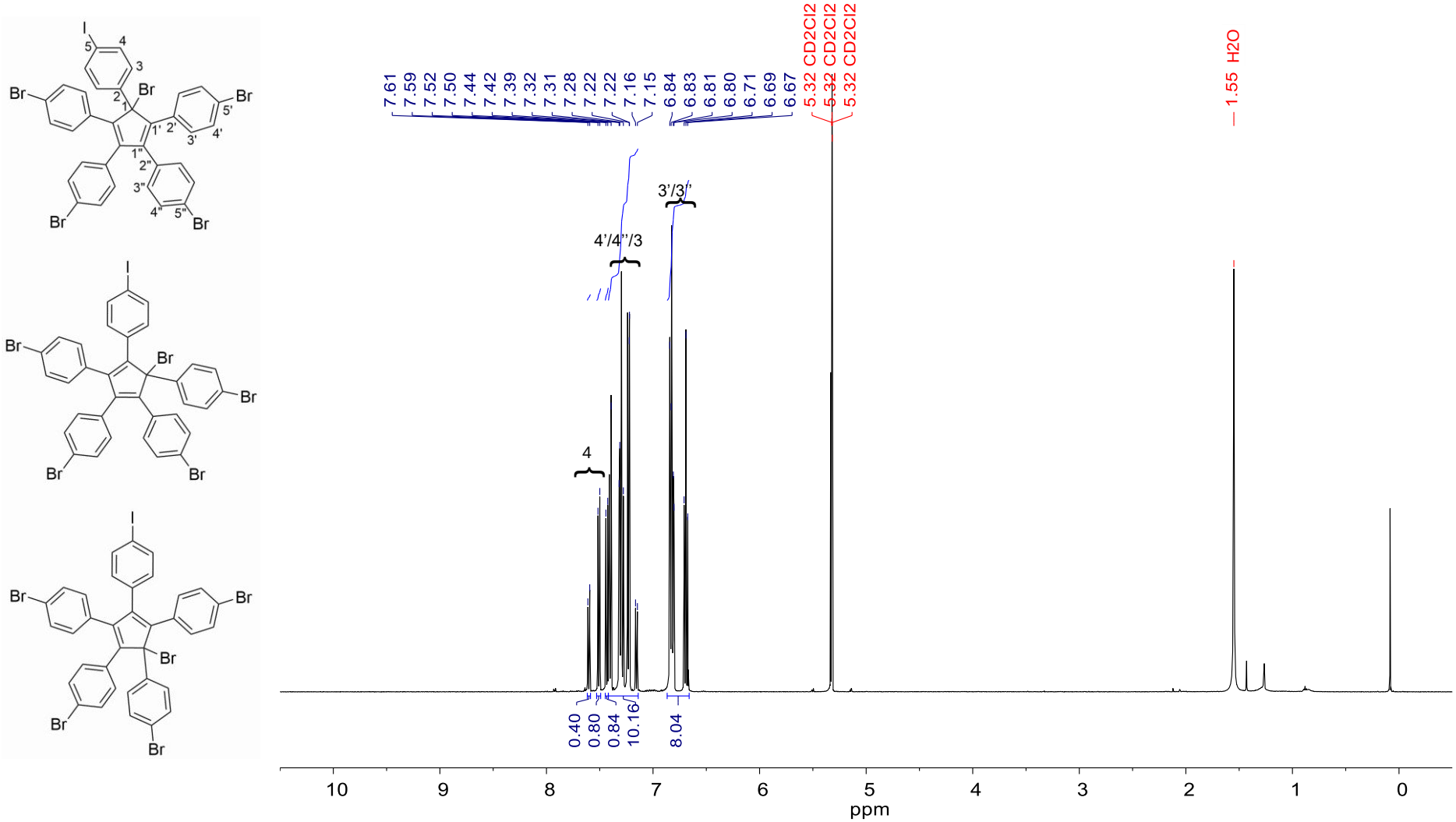


^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of compound **3**

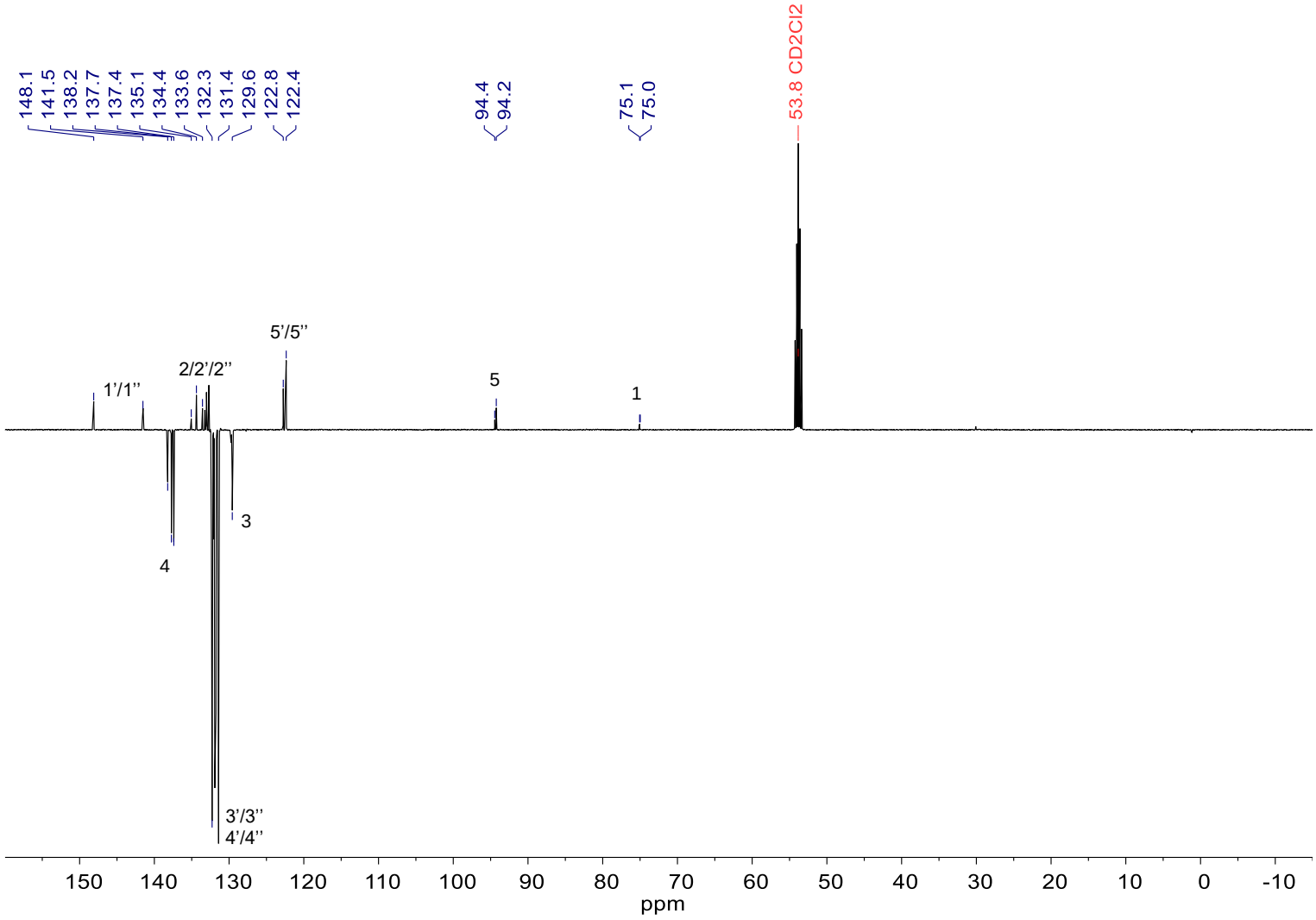


^{13}C-Jmod NMR (126 MHz, $CDCl_3$, 25 °C) of compound **3**

Compound 4 (obtained as a 1:2:2 mixture of regioisomers):

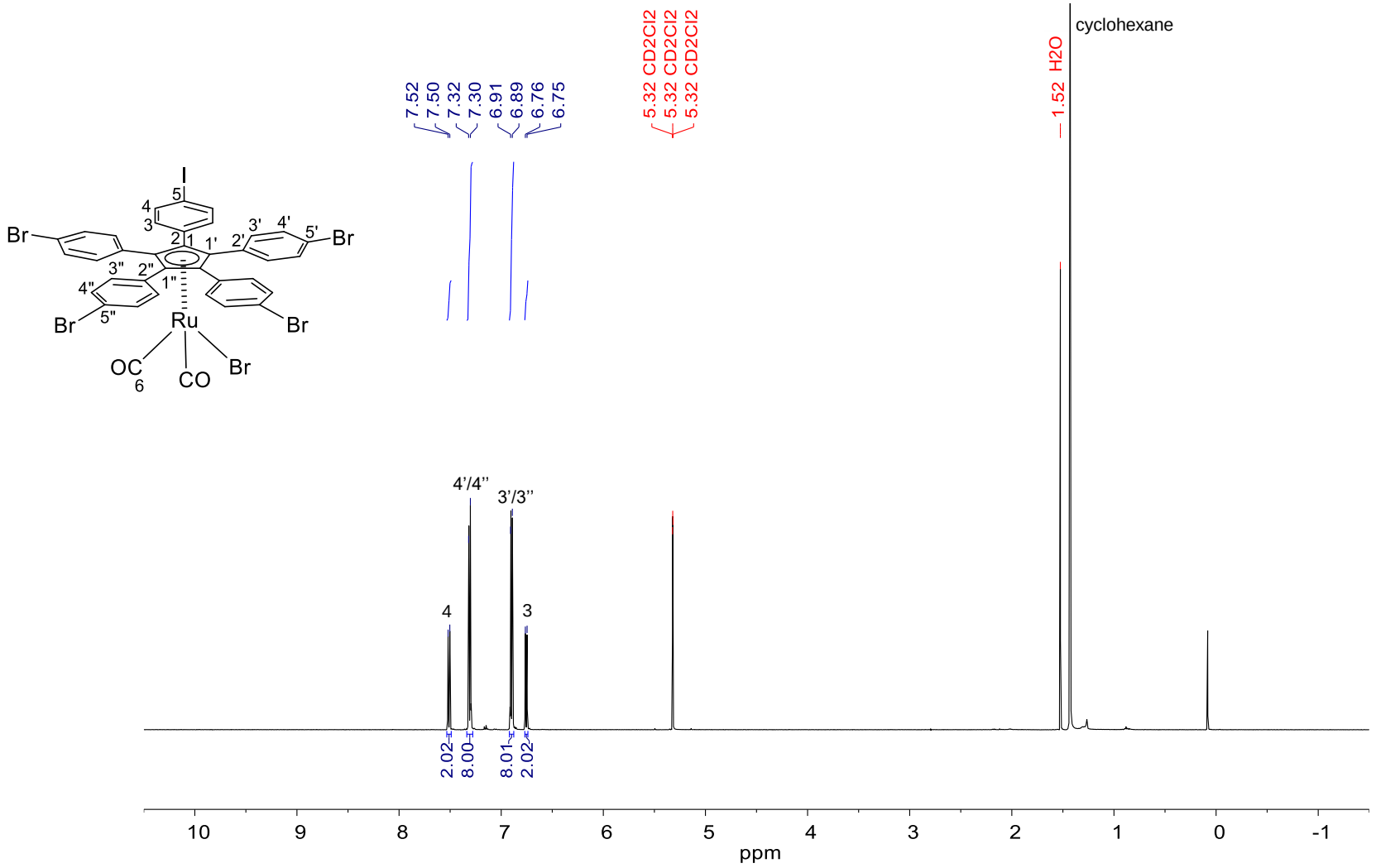


^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C) of compound **4** (as a mixture of regioisomers)

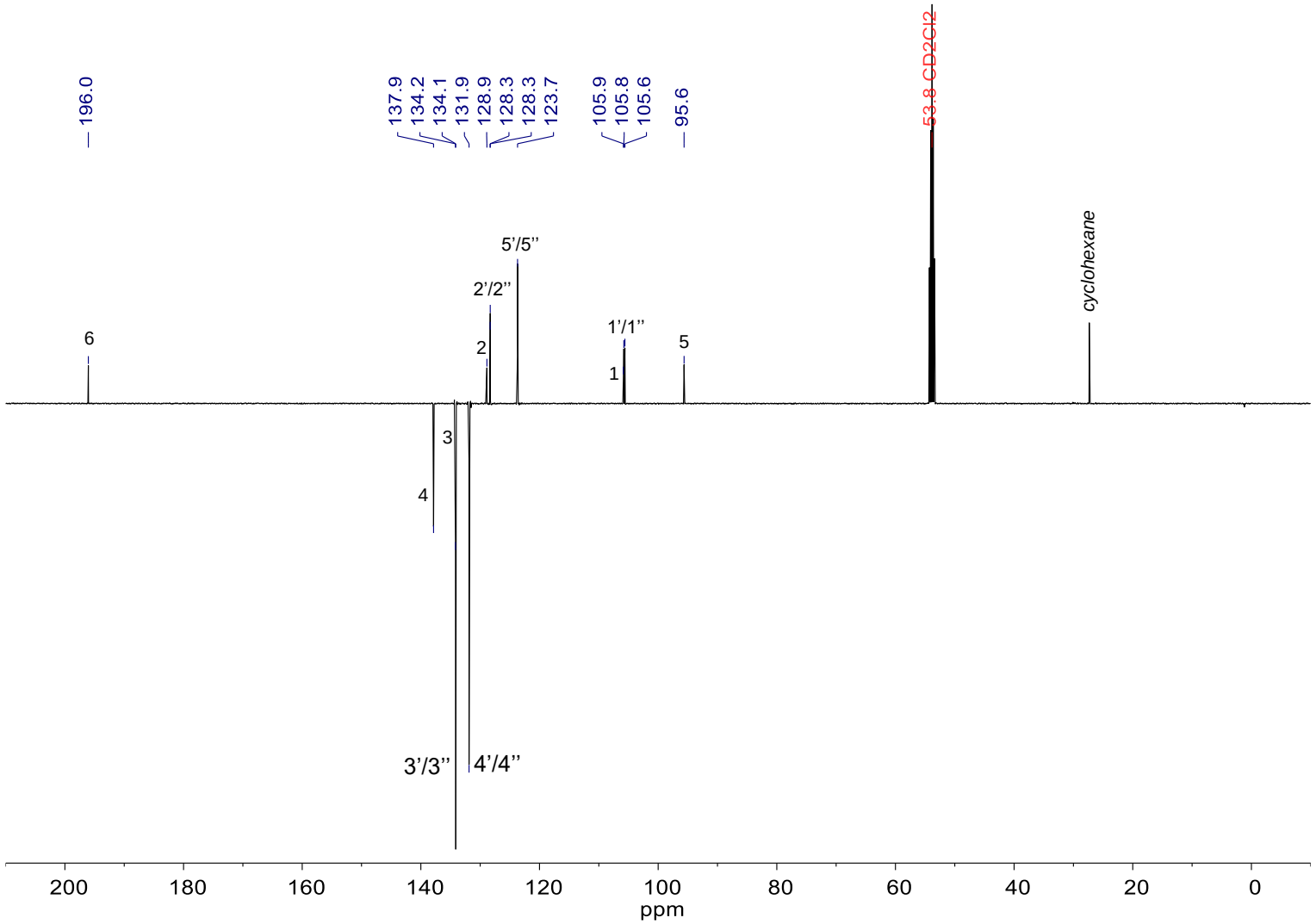


^{13}C-Jmod NMR (126 MHz, CD_2Cl_2, 25 °C) of compound **4** (as a mixture of regioisomers)

Complex 5:

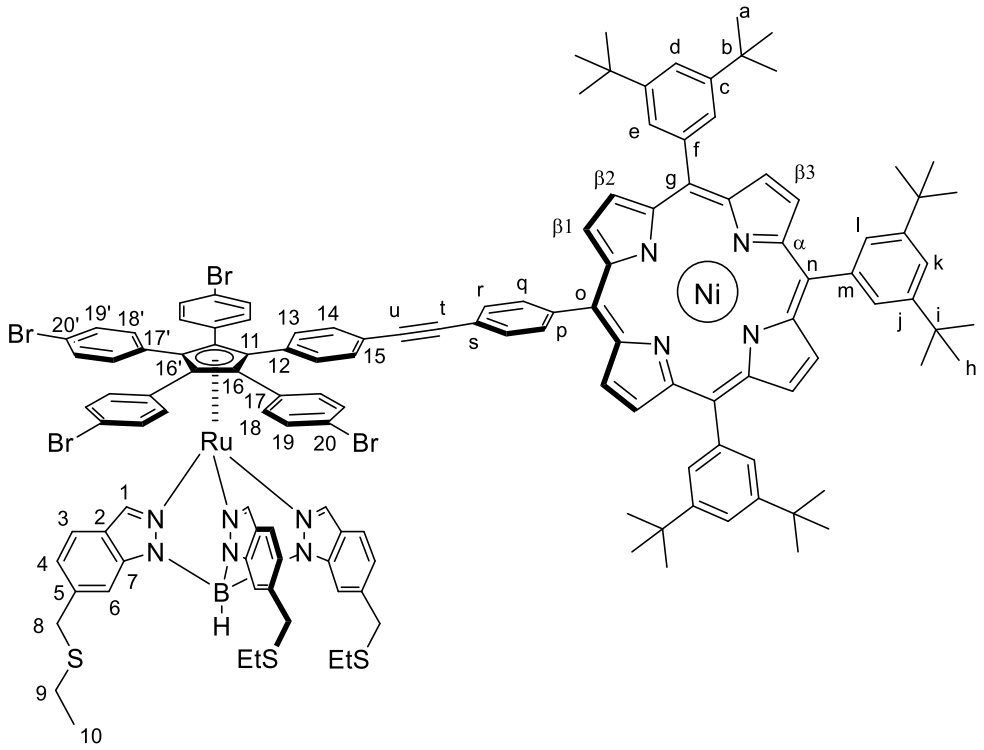


^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C) of complex **5**



^{13}C-Jmod NMR (126 MHz, CD_2Cl_2, 25 °C) of complex **5**

Complex 6: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Ru
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B
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EtS
EtS
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e
f
g
β1
β2
β3
α
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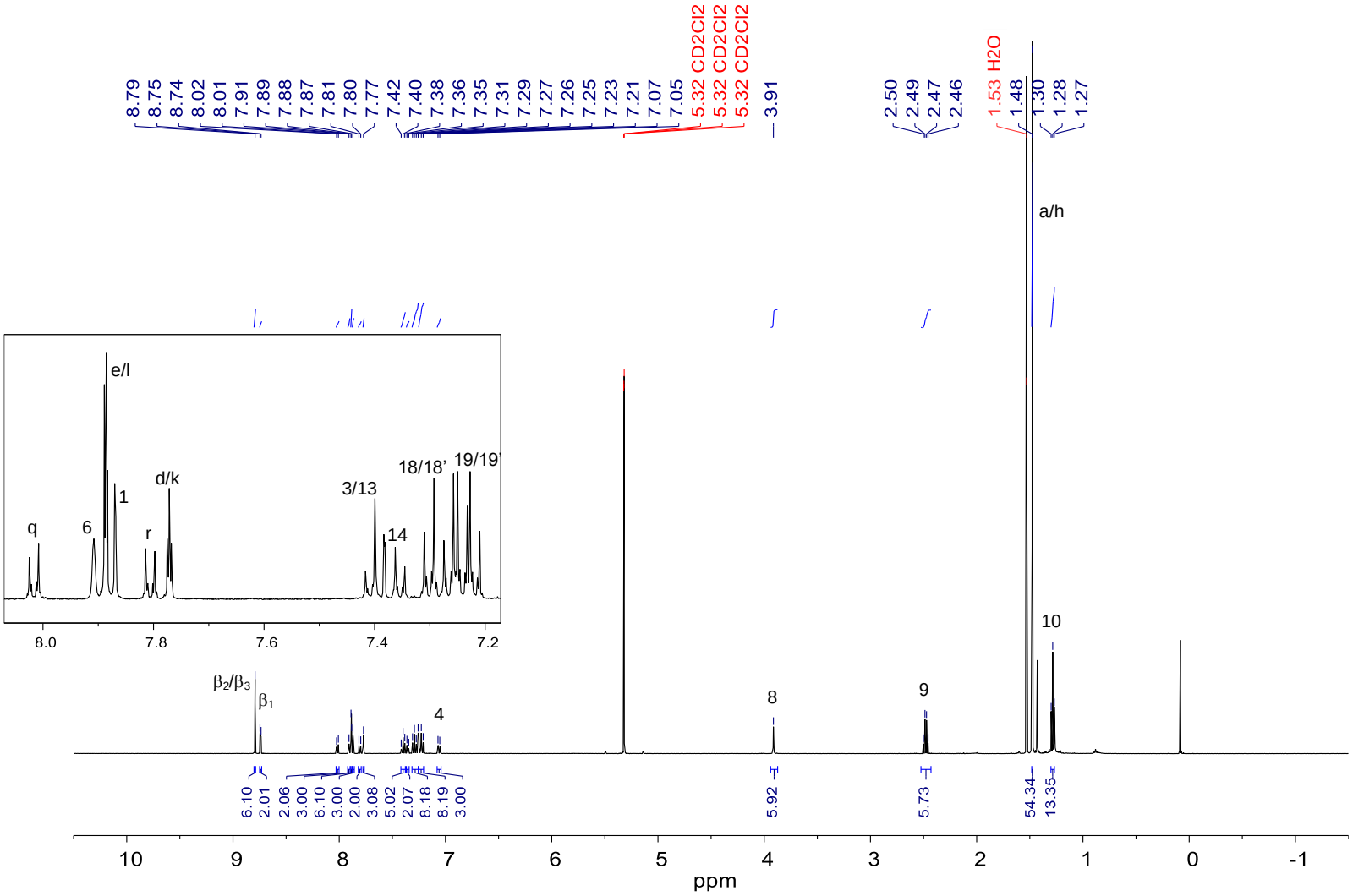
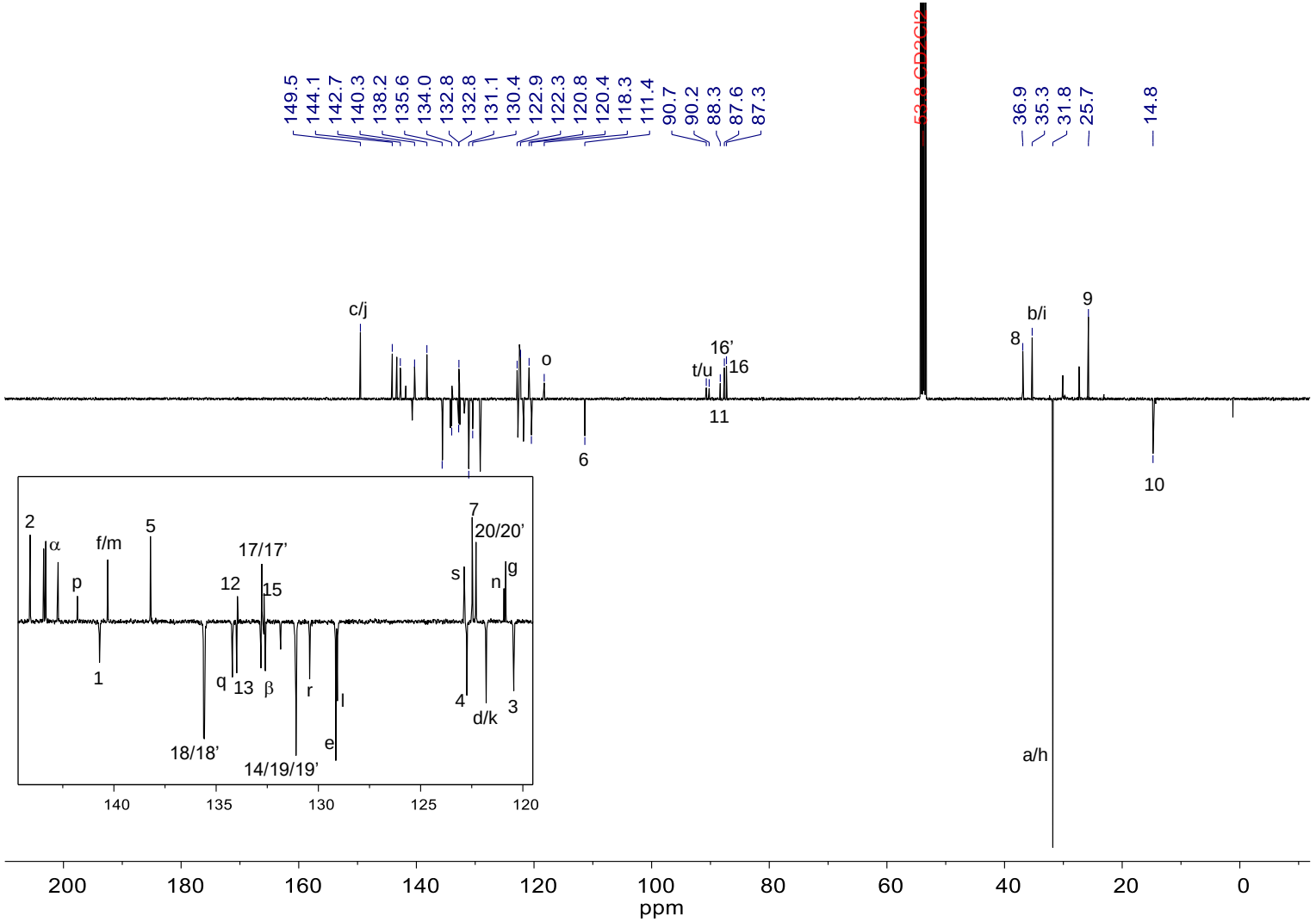
20'

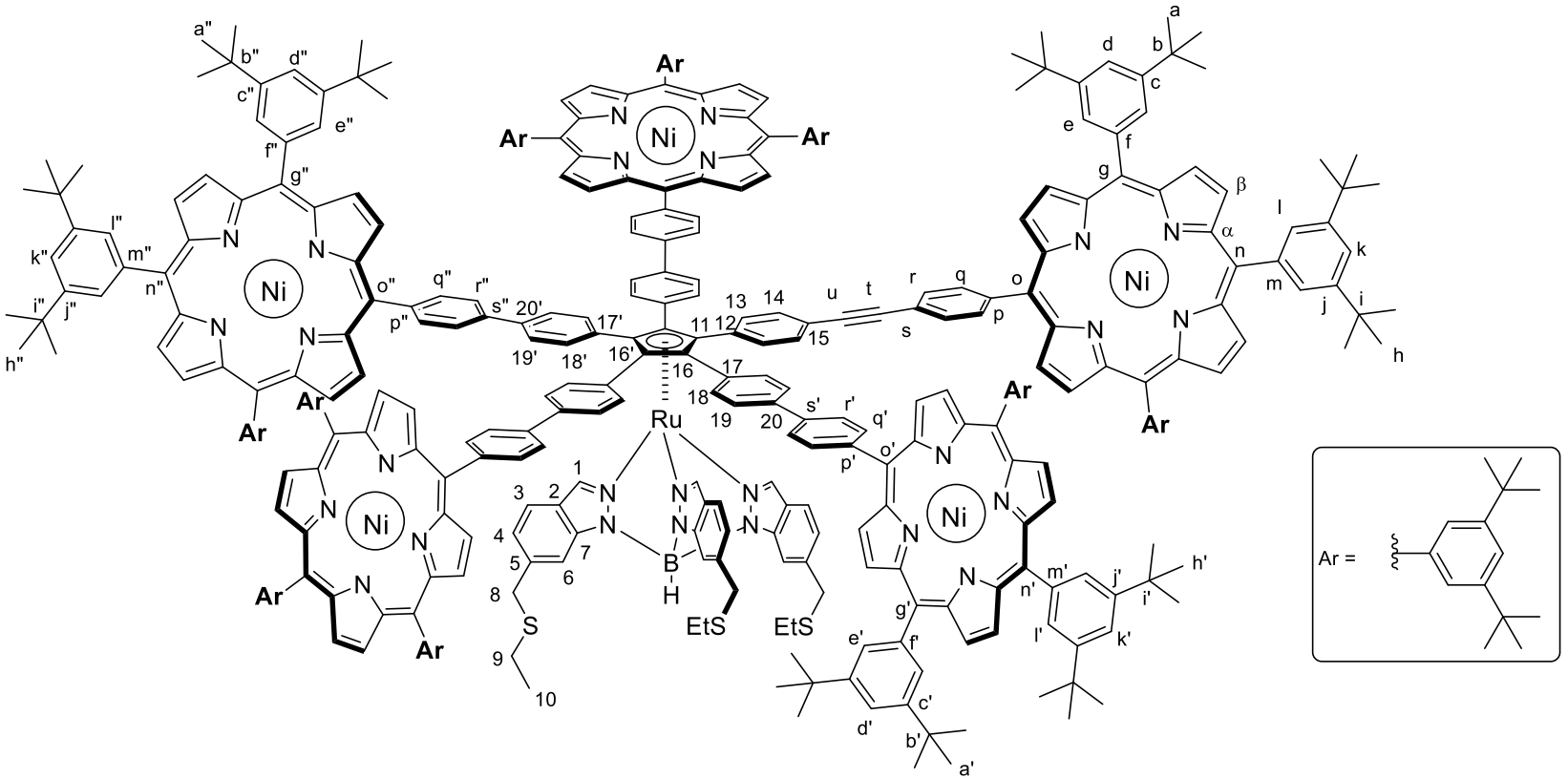


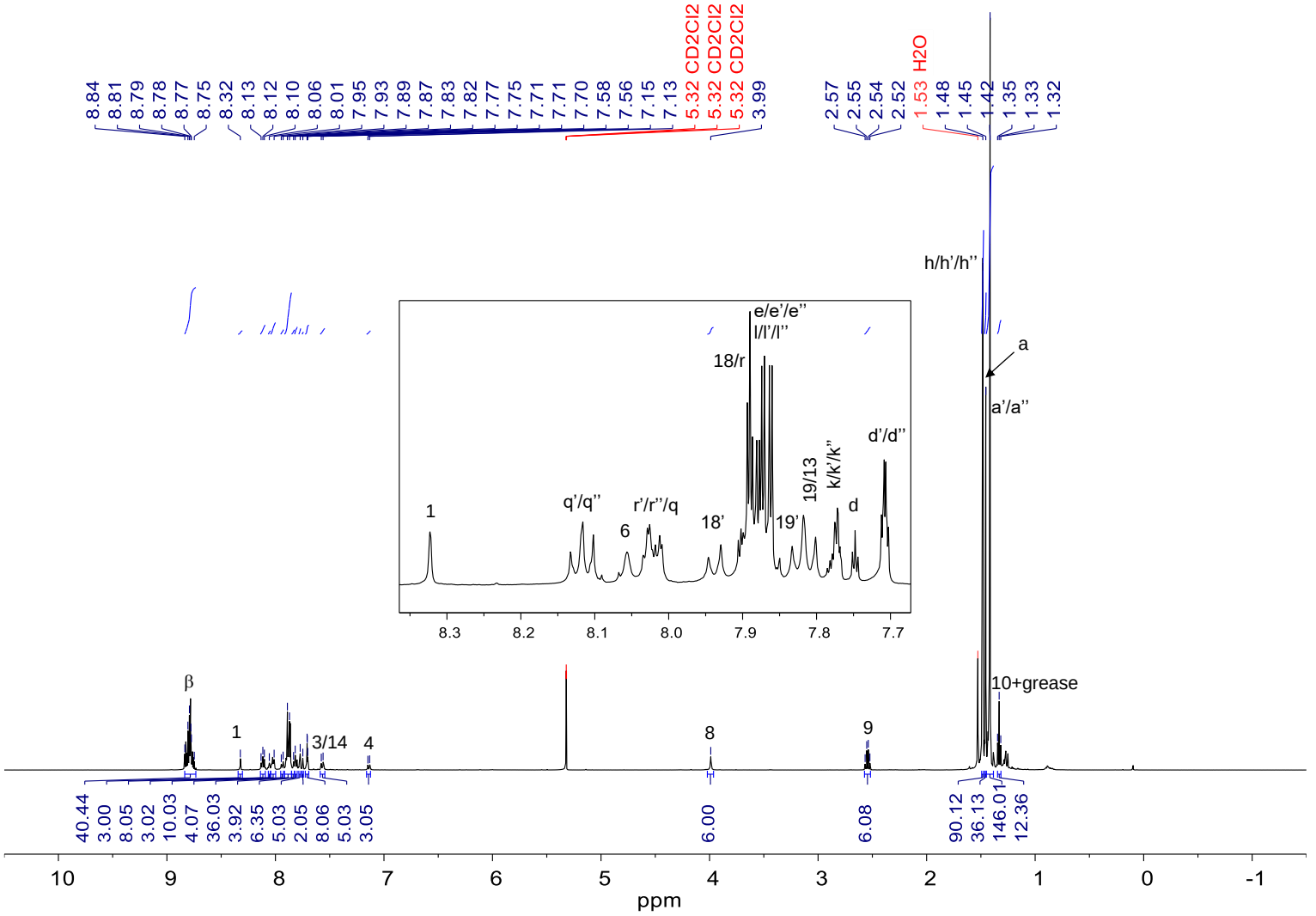
^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C) of complex **6**



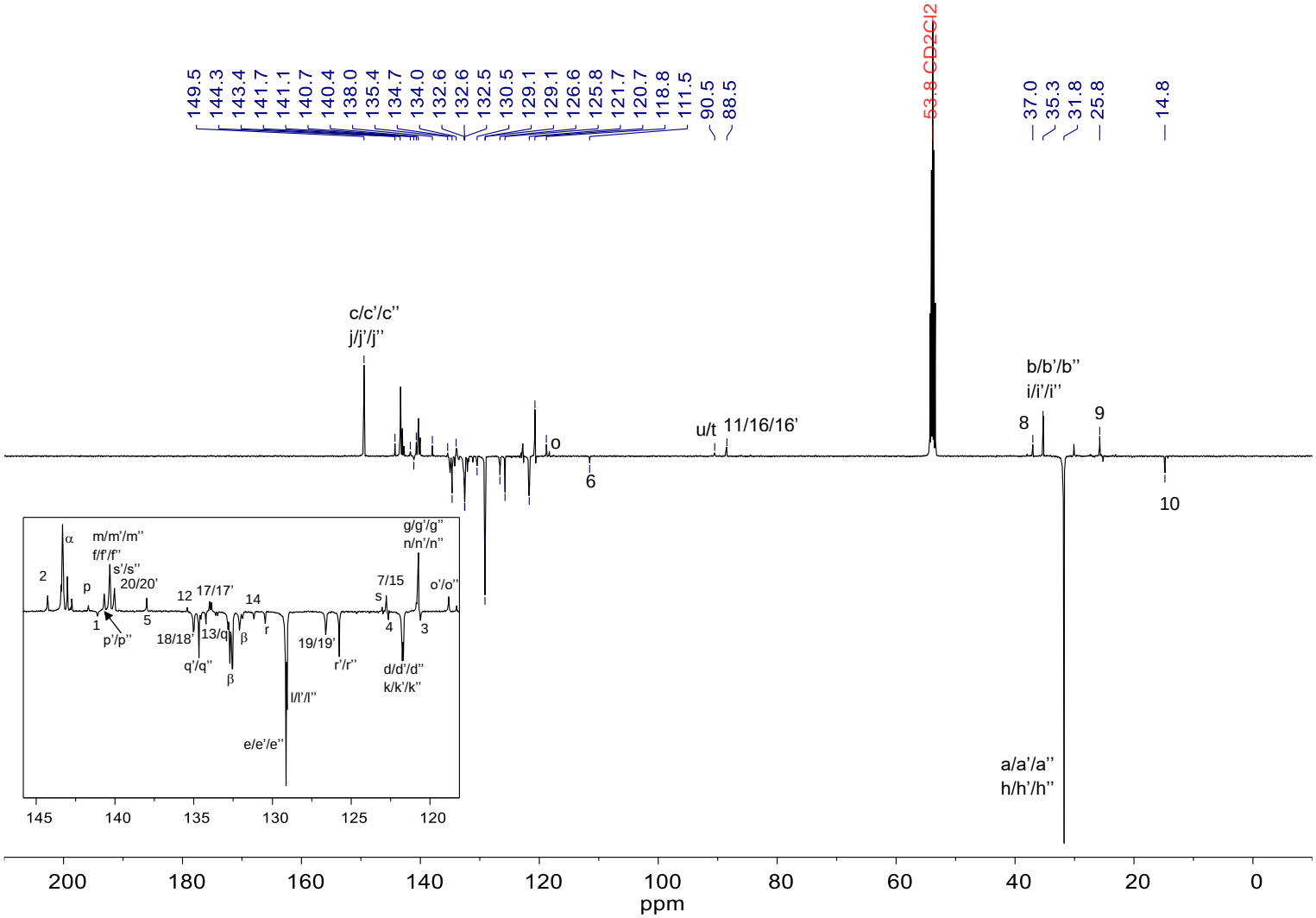
^{13}C-Jmod NMR (126 MHz, CD_2Cl_2, 25 °C) of complex **6**

Complex 7:



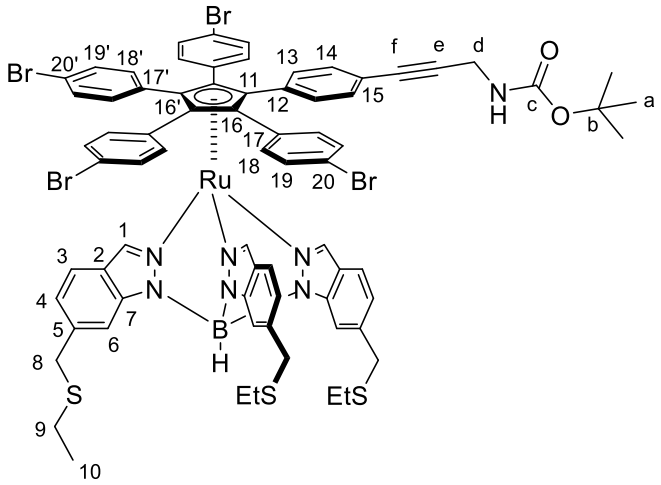


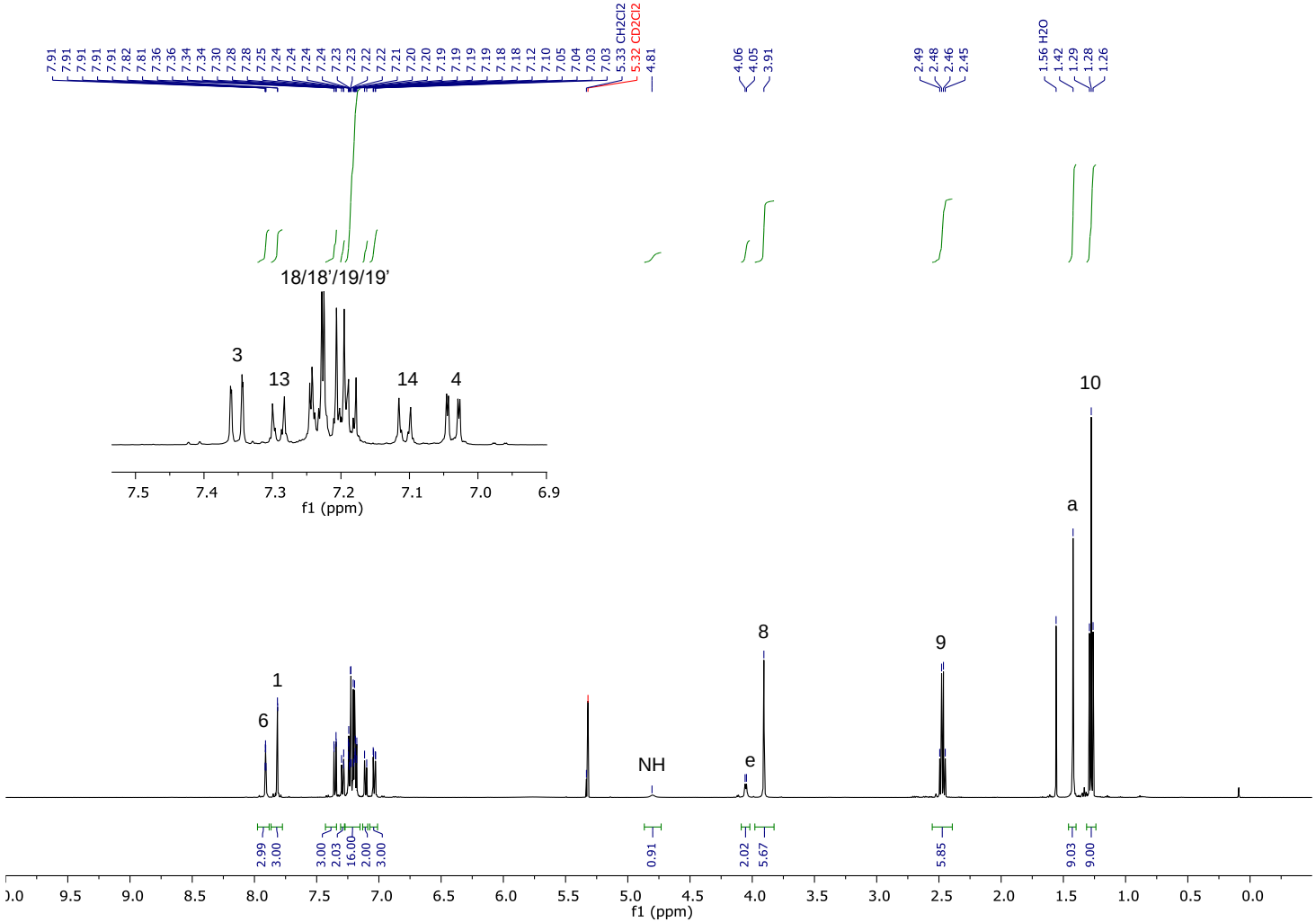
^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C) of complex **7**



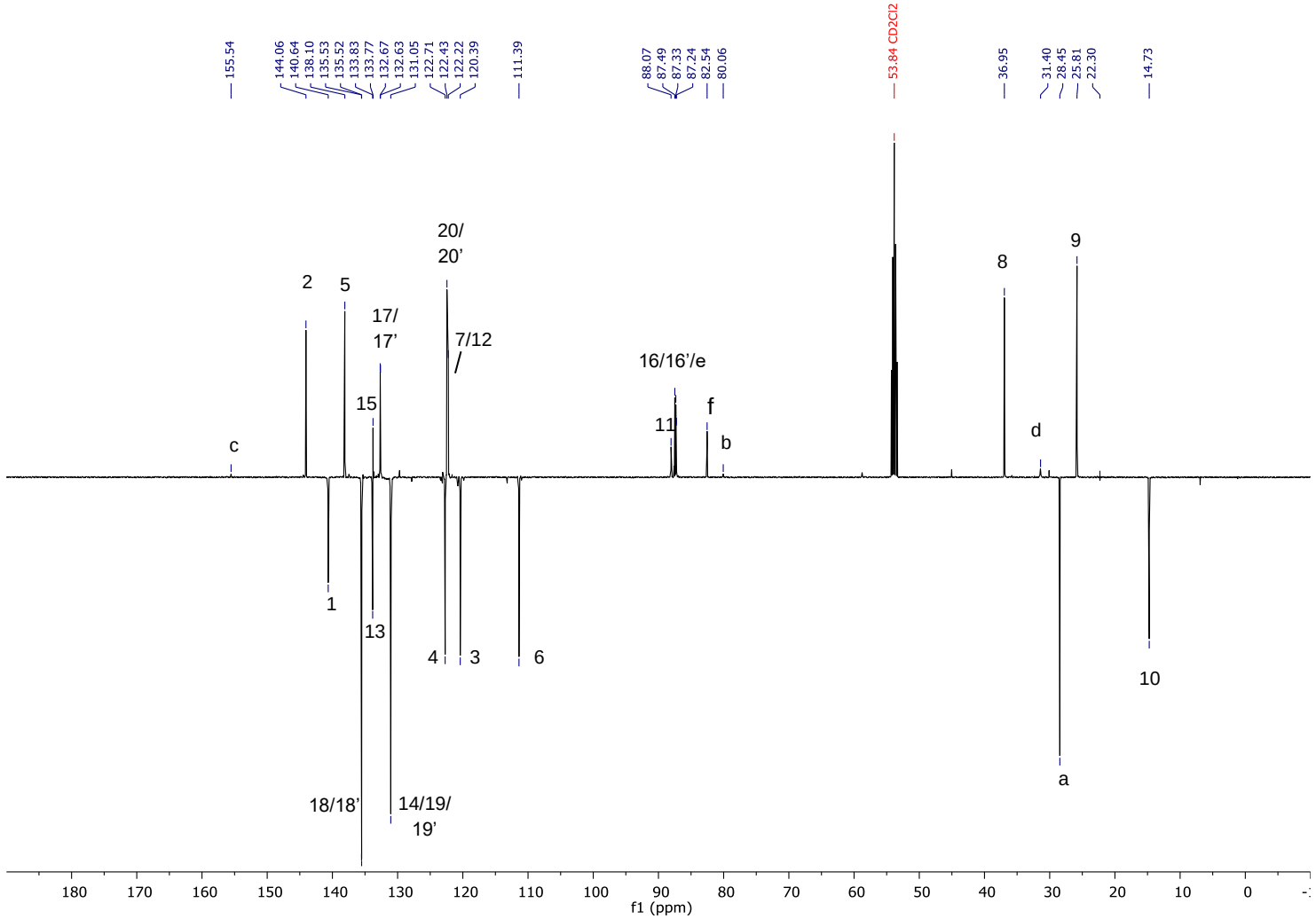
^{13}C-Jmod NMR (126 MHz, CD_2Cl_2, 25 °C) of complex **7**

Complex 8:



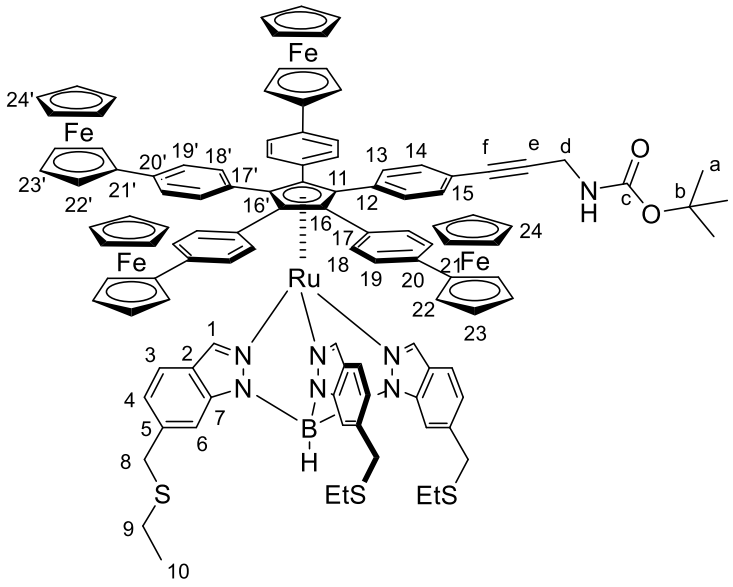


^{1}H NMR (500 MHz, CD_2Cl_2, 25 °) of complex **8**



^{13}C-Jmod NMR (126 MHz, CD_2Cl_2, 25 °C) of complex **8**

Complex 9:


Fe
24'
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21
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24
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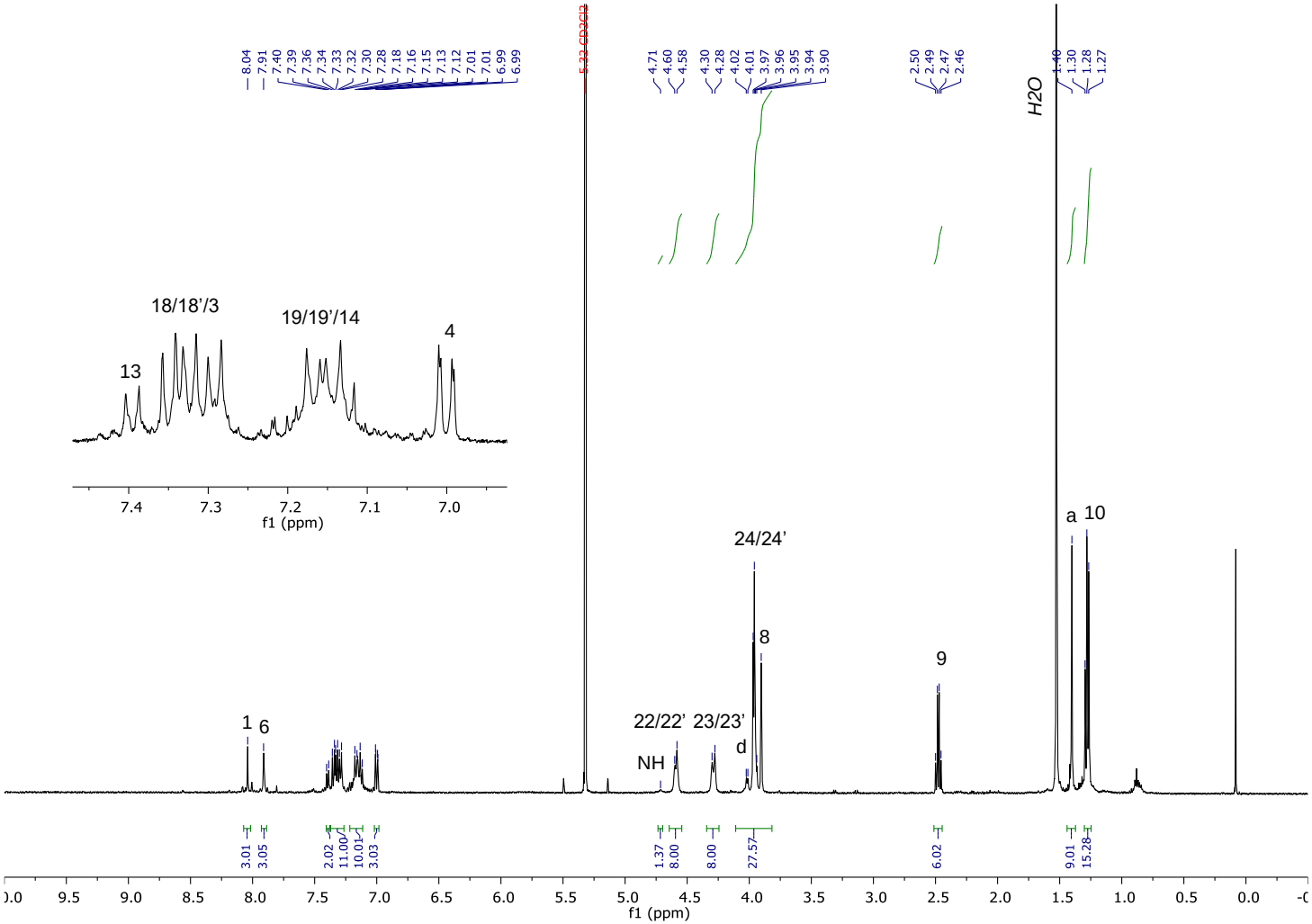
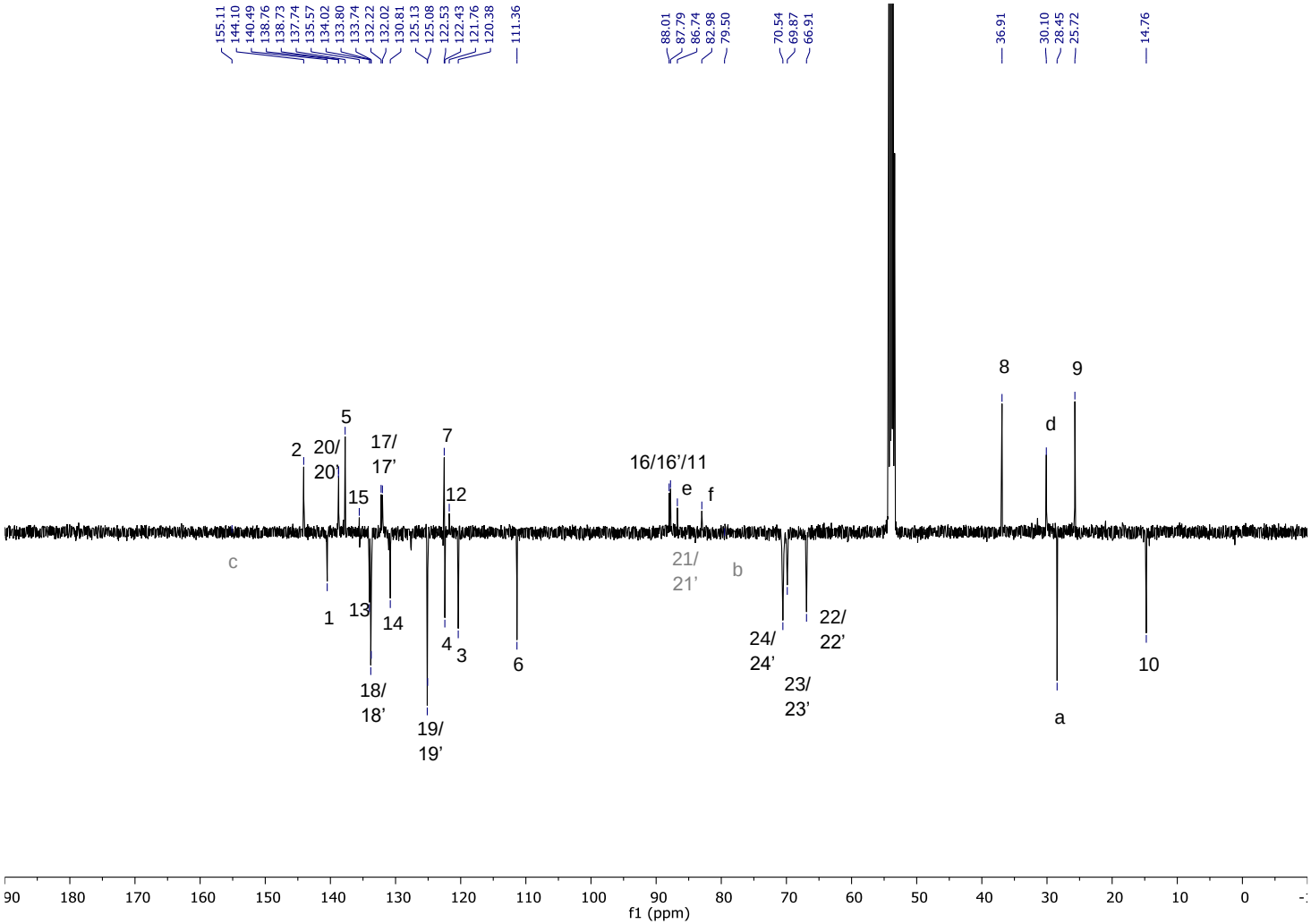
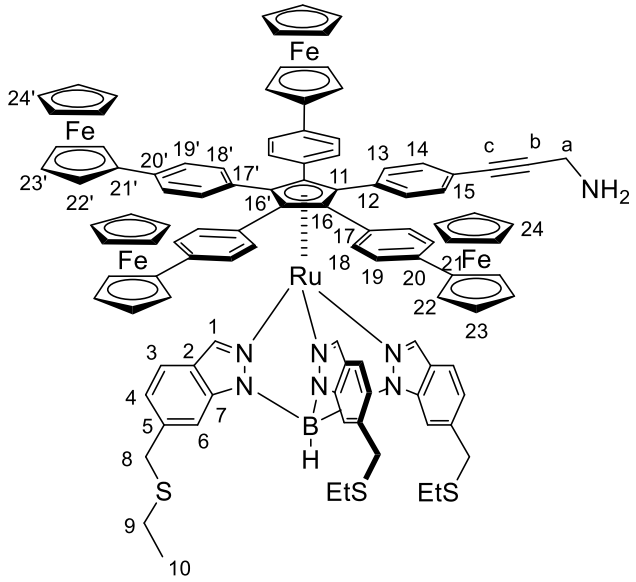


^{1}H NMR (500 MHz, CD_2Cl_2, 25 °) of complex **9**



^{13}C-Jmod NMR (126 MHz, CD_2Cl_2, 25 °C) of complex **9**

Complex 10: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21'
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17'
16'
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13
14
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21
Fe
22
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24
Fe
Ru
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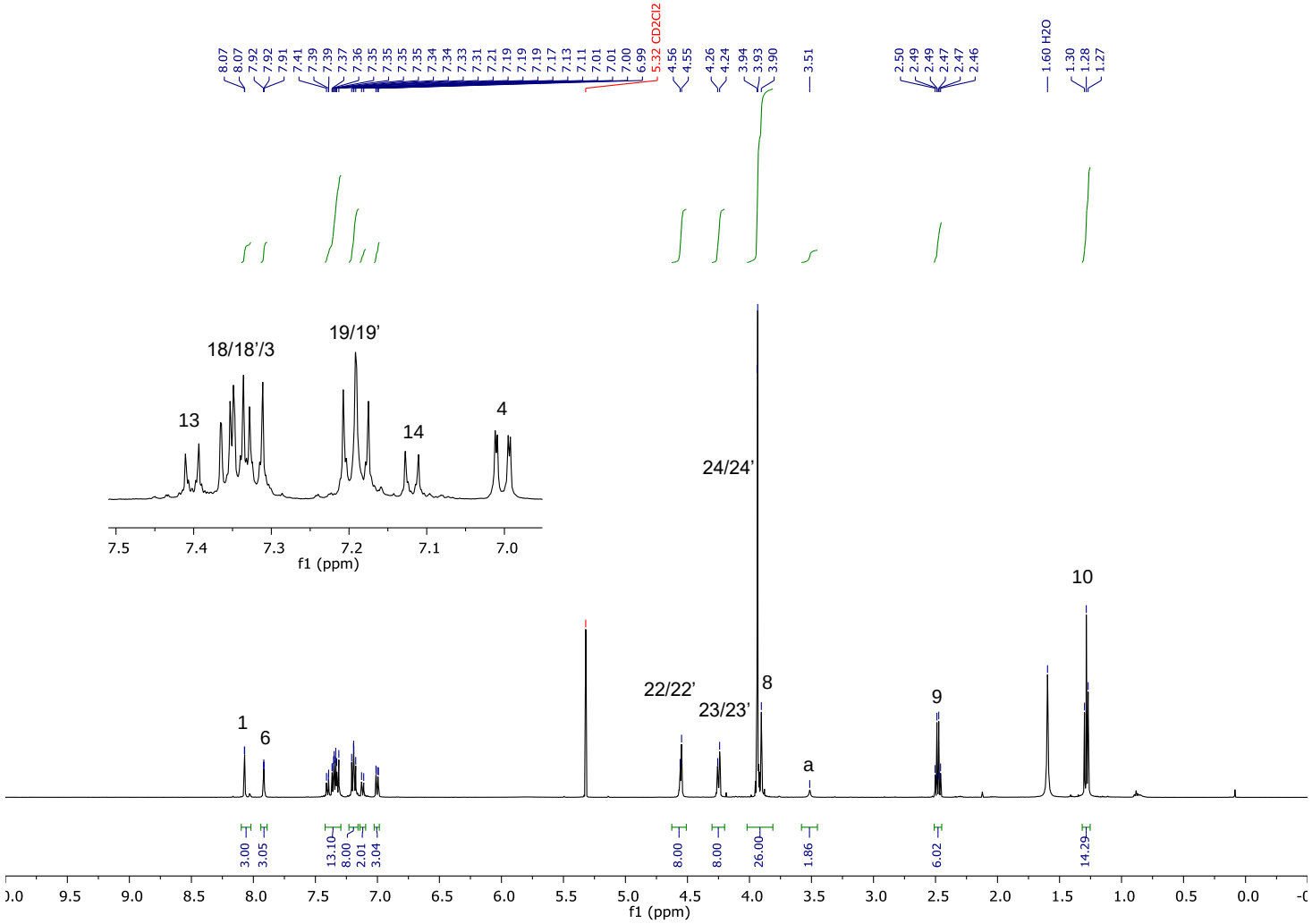
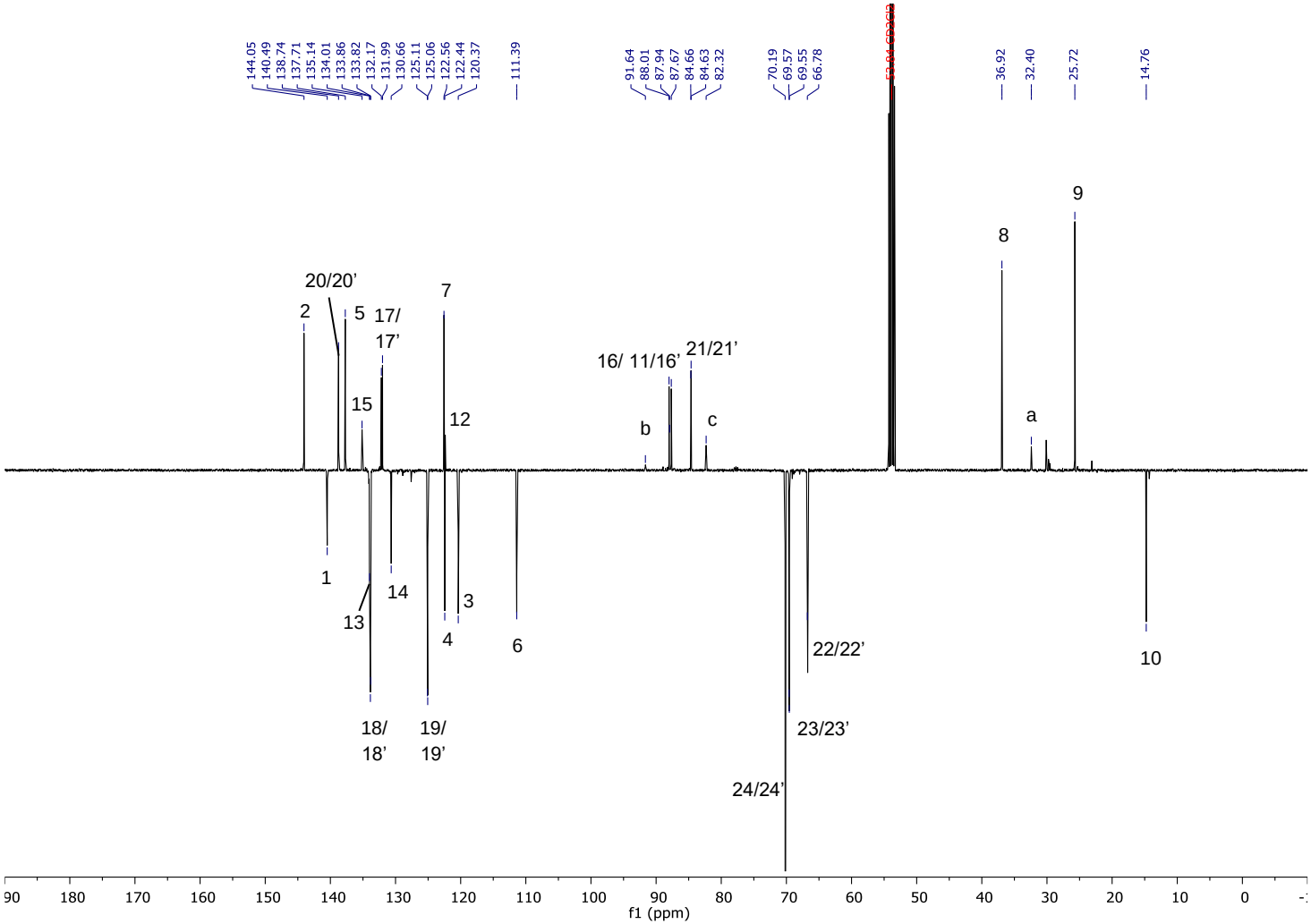
S
EtS
EtS

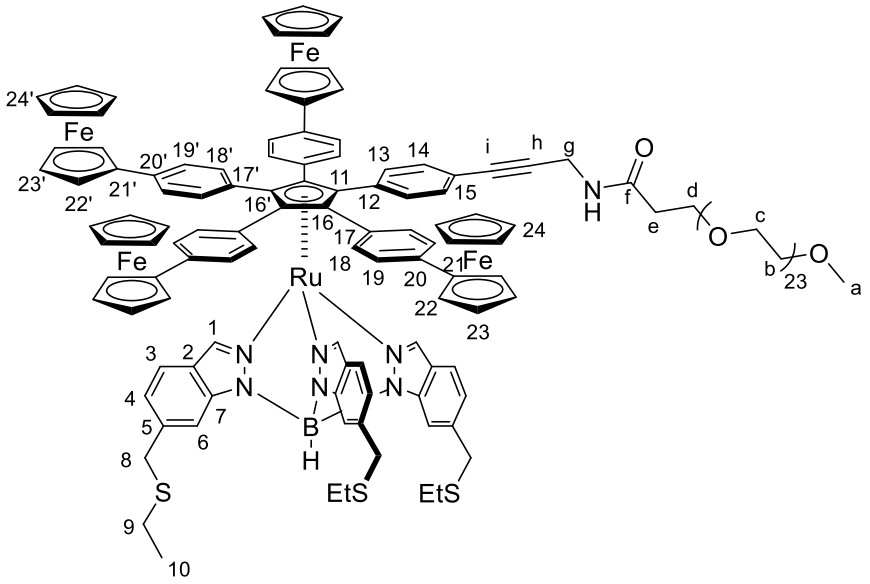


^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C) of complex **10**



^{13}C-Jmod NMR (126 MHz, CD_2Cl_2, 25 °C) of complex **10**

Complex 11:


Fe
24'
Fe
20'
19'
18'
17'
13
14
i
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g
O
23'
22'
21'
16'
11
12
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d
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c
O
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23
O
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16
17
24
Fe
18
19
20
21
Fe
22
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Ru
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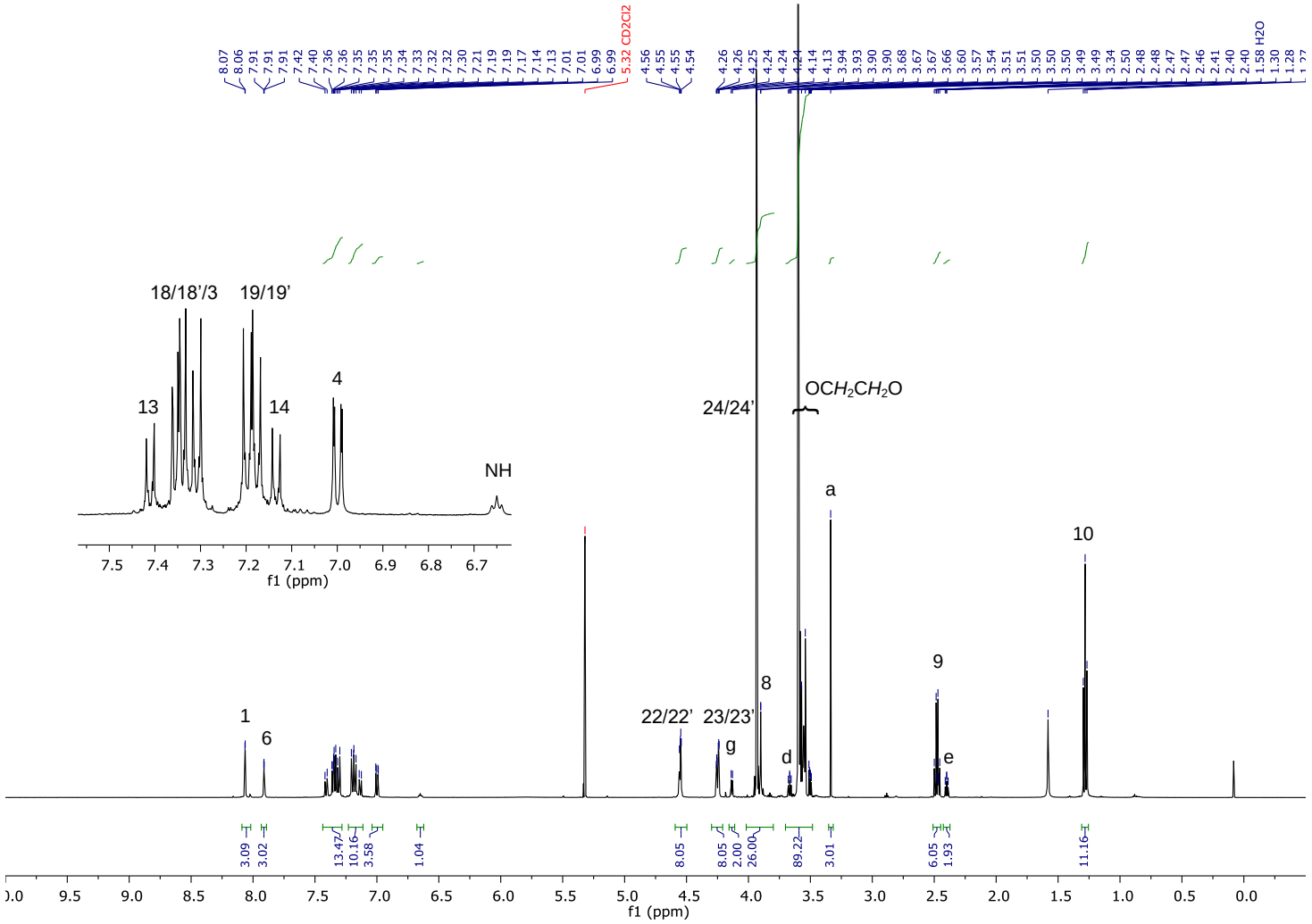
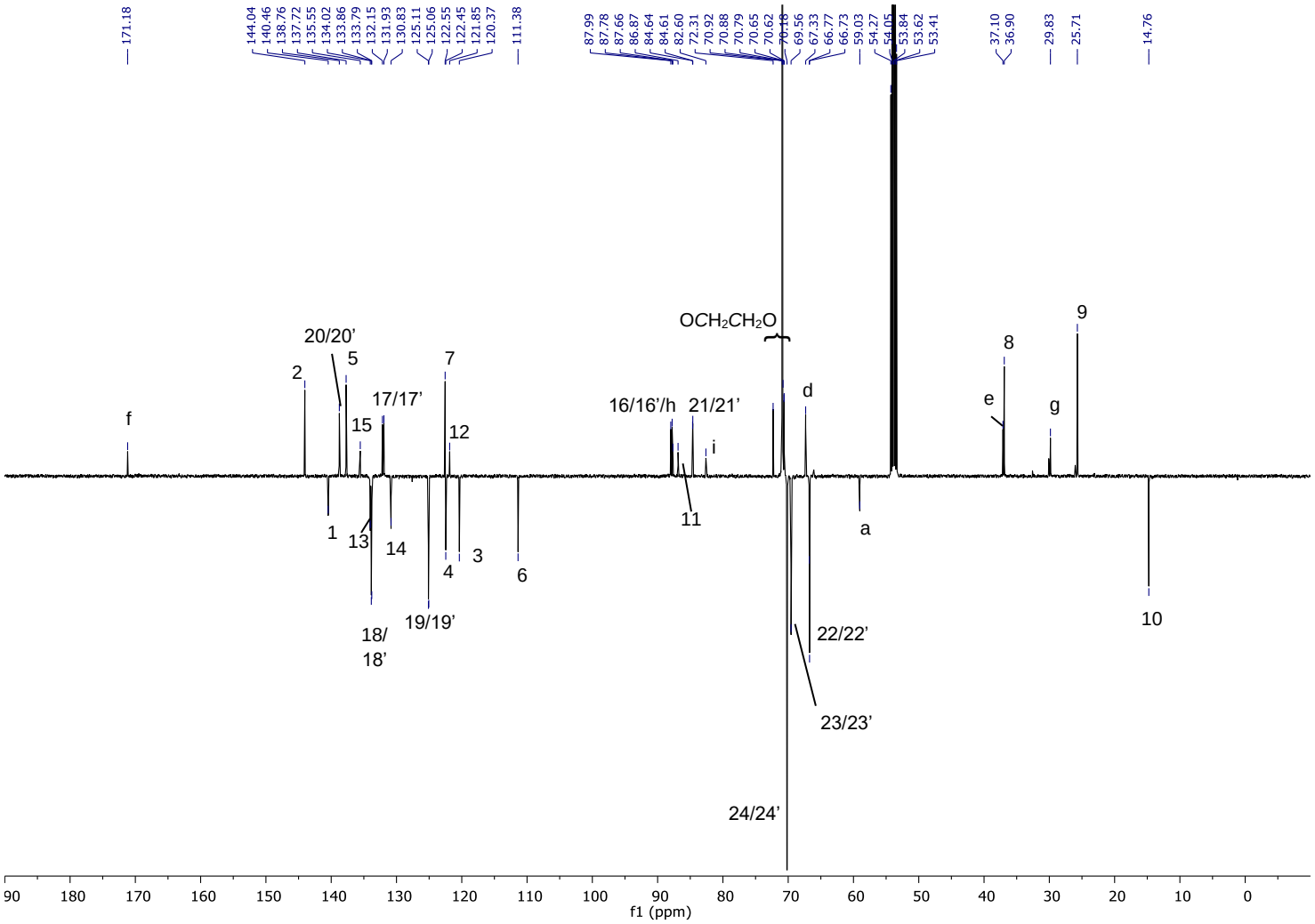
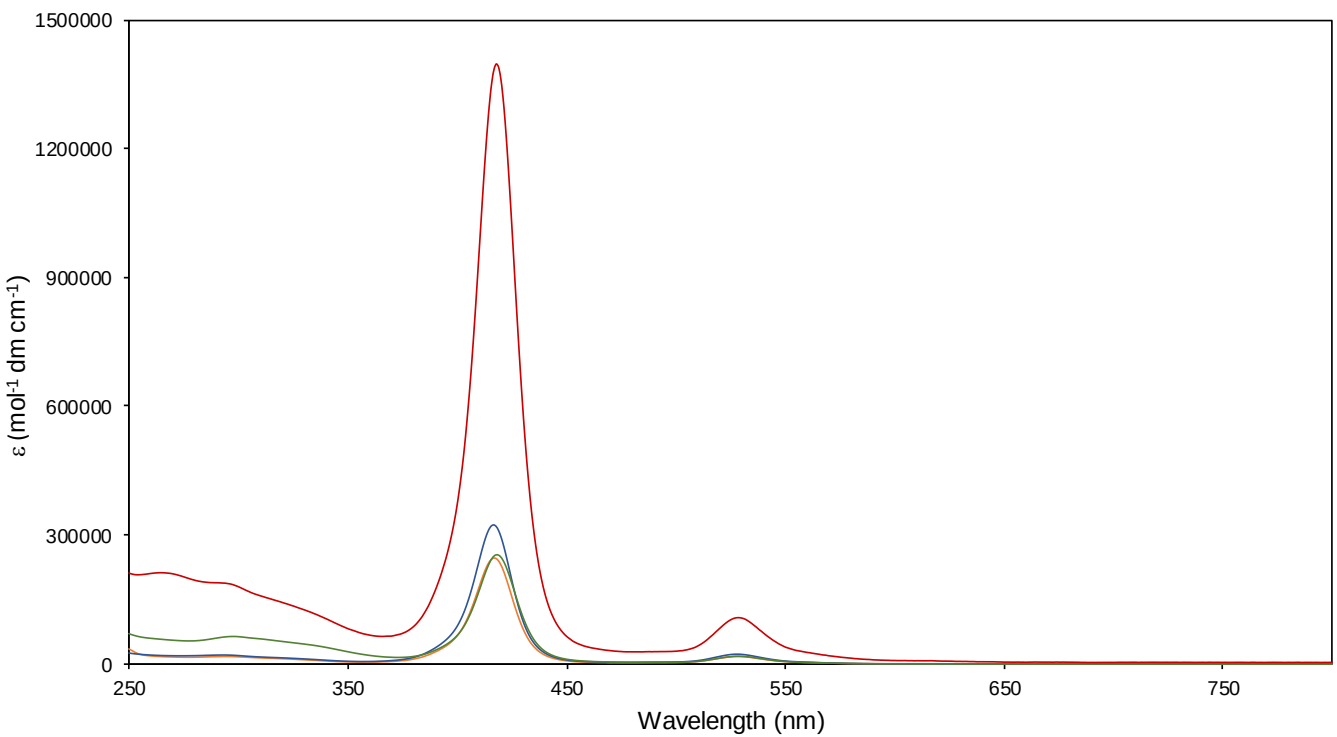


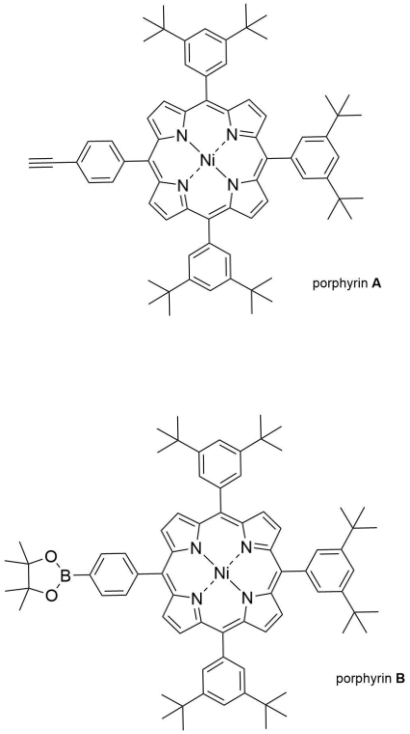
^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C) of complex **11**



^{13}C-Jmod NMR (126 MHz, CD_2Cl_2, 25 °C) of complex **11**

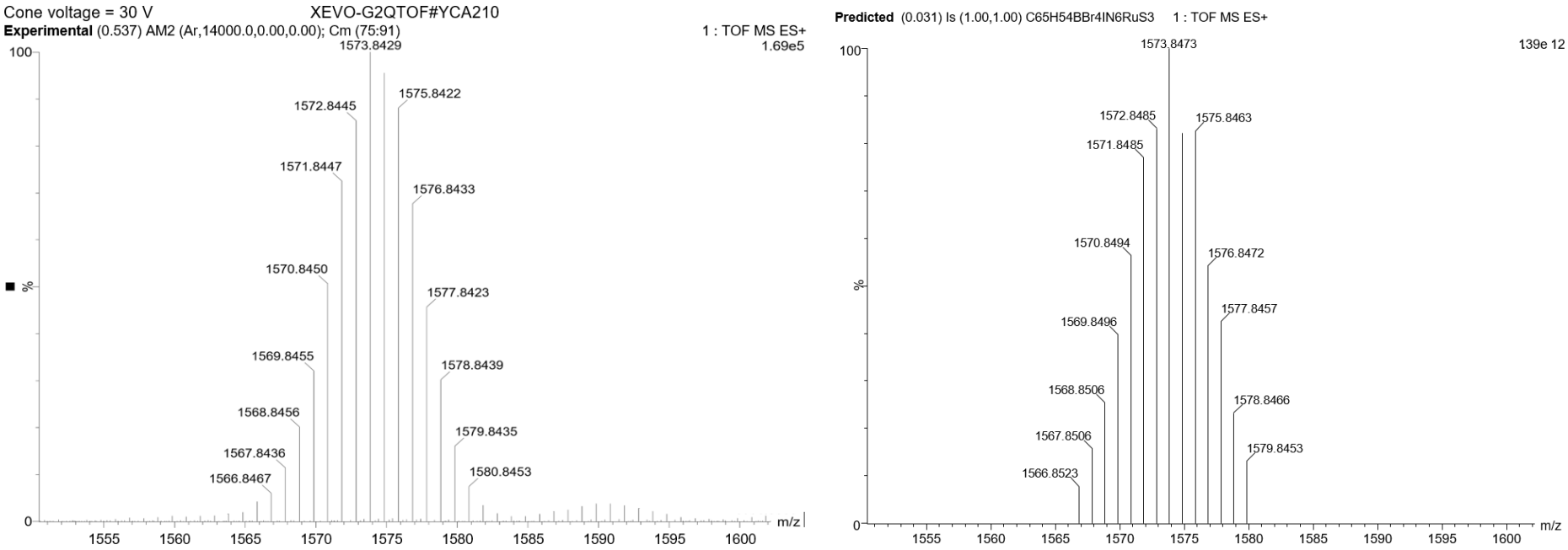
IV. UV-Visible spectroscopy





Absorption spectra in CH_2Cl_2 of porphyrin **A** (orange), porphyrin **B** (green), complex **6** (blue) and complex **7** (red).

V. High-resolution mass spectrometry



High resolution mass spectrum (ESI^+) of complex **1** (left) and simulated isotopic distribution (right).

VI. Crystallographic data

Crystallographic data for compound **1** were collected at 100(2) K on a Bruker-AXS D8-Venture diffractometer equipped with a CMOS detector (Photon 100) and a 30W air-cooled microfocus source using Cu K_α radiation (λ=1.54178 Å). Phi- and omega-scans were used. Space group was determined on the basis of systematic absences and intensity statistics. Semi-empirical absorption correction was employed.[S5] The structure was solved using an intrinsic phasing method (SHELXT),[S6] and refined using the least-squares method on F^2.[S7] All non-H atoms were refined with anisotropic displacement parameters. Hydrogen atoms were refined isotropically at calculated positions using a riding model with their isotropic displacement parameters constrained to be equal to 1.5 times the equivalent isotropic displacement parameters of their pivot atoms for terminal sp^3 carbon and 1.2 times for all other carbon atoms. Hydrogen on boron atom was located by difference Fourier map and was freely refined. Some residual electron density were difficult to modelize and therefore, the SQUEEZE function of PLATON [S8] was used to eliminate the contribution of the electron density in the solvent region from the intensity data, and the solvent-free model was employed for the final refinement.
The halogenated positions of dissymmetric compound **1** (4 Br and 1 I) were disordered: equal xyz and Uij constraints (EXYZ and EADP) were applied to model these disorders. Several restraints (SAME, SADI, SIMU, DELU, ISOR) were used to refine 2 thioether groups disordered over 2 positions.

Crystal data and structure refinement for complex 1:

Identification code	**1**	
Empirical formula	C66.50 H57 B Br4 Cl3 I N6 Ru S3	
Formula weight	1701.13	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 13.1648(6) Å	α= 90°.
	b = 24.9566(10) Å	β= 107.569(2)°.
	c = 21.5935(9) Å	γ = 90°.
Volume	6763.6(5) $Å^3$	
Z	4	
Density (calculated)	1.671 Mg/m^3	
Absorption coefficient	10.534 mm^{-1}	
F(000)	3356	
Crystal size	0.200 x 0.120 x 0.040 mm^3	
Theta range for data collection	4.647 to 67.270°.	
Index ranges	-15<=h<=15, -29<=k<=29, -25<=l<=25	

[S5] Bruker, *SADABS*, Bruker AXS Inc., Madison, Wisconsin, USA, **2008**.
[S6] ShelXT, G. M. Sheldrick, University of Göttingen, *Acta Crystallogr. Sect. A* **2015**, *71*, 3-8.
[S7] ShelXL, G. M. Sheldrick, University of Göttingen, *Acta Crystallogr. Sect. C* **2015**, *71*, 3-8.
[S8] A. L. Spek, *Acta Crystallogr. Sect. C* **2015**, *71*, 9-18.

Reflections collected	118682
Independent reflections	12080 [R(int) = 0.1196]
Completeness to theta = 67.270°	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7528 and 0.4395
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12080 / 202 / 864
Goodness-of-fit on F^2	1.023
Final R indices [I>2sigma(I)]	R1 = 0.0737, wR2 = 0.1759
R indices (all data)	R1 = 0.1073, wR2 = 0.1953
Extinction coefficient	n/a
Largest diff. peak and hole	2.655 and -2.104 e.$Å^{-3}$