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I. Synthesis of target complexes M1-M5

I.1. Synthetic routes employed for the synthesis of molecules M1-M5

a. Synthesis of molecules M1-M4

The four molecules **M1**-**M4** were prepared according to a common modular synthetic approach relying on the post-functionalisation of a 1,2,3,4,5-penta(*p*-halogenophenyl)cyclopentadienyl hydrotris(indazolyl)borate ruthenium(II) key precursor (**1a** or **1b**, Scheme S1), based on our previous work on the synthesis of ruthenium-based molecular machines.[S1-S3]

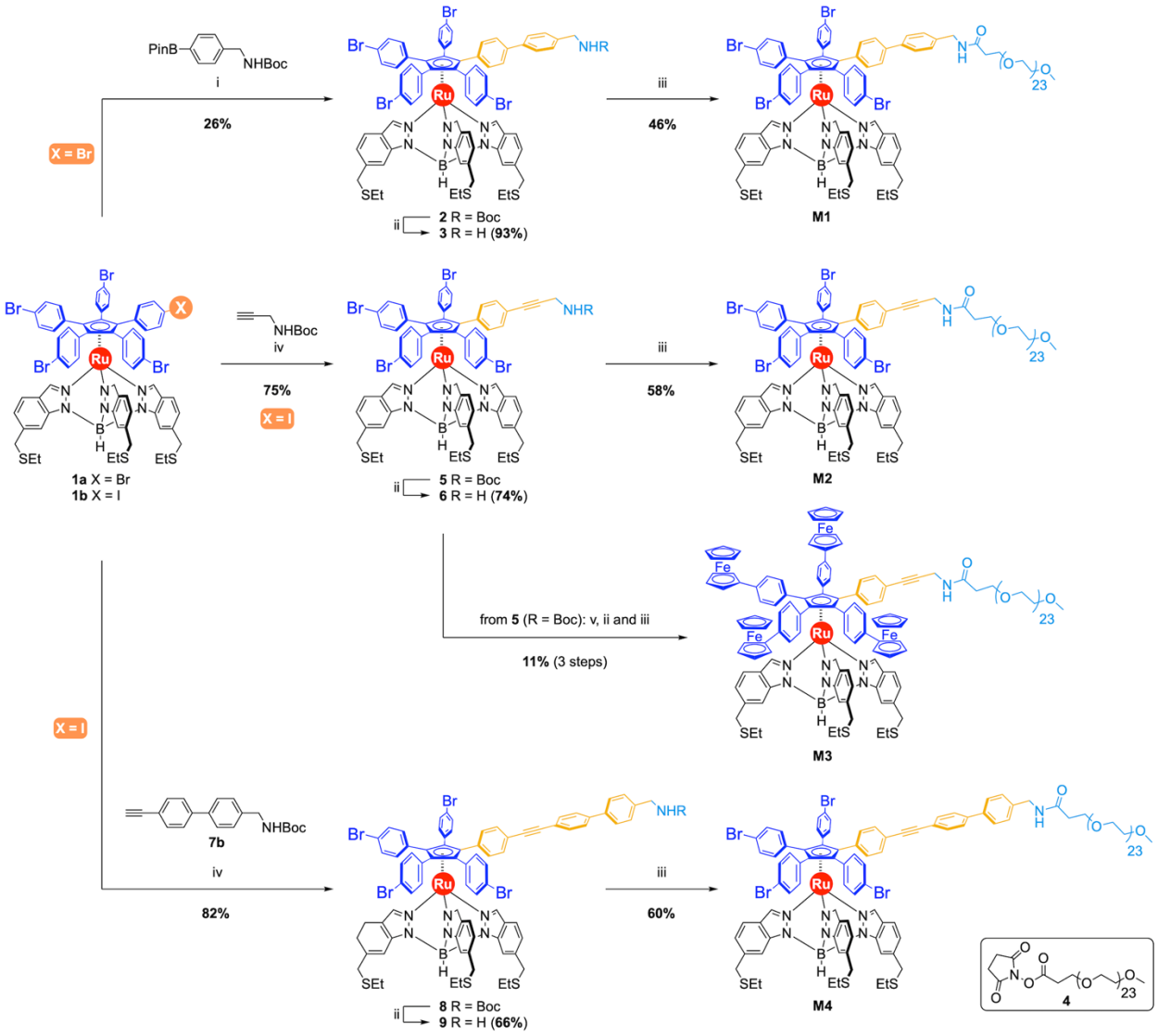
For molecules **M1**, **M2** and **M4**, incorporating four 4-bromophenyl substituents on the cyclopentadienyl core, our strategy involved a single cross-coupling reaction in a first step to introduce the appropriate hydrocarbon spacer, followed by the cleavage of the Boc-protecting group. Condensation of the resulting primary amine with the monodisperse $mPEG_{24}$-NHS ester reagent (**4**), terminated by a carboxylic acid preactivated as its *N*-hydroxysuccinimidyl ester, finally yielded the target compounds.

This synthetic route was first implemented for **M1** starting from key precursor **1a**, which incorporates five identical 4-bromophenyl substituents on the cyclopentadienyl ligand. A Suzuki-Miyaura coupling was achieved under statistical conditions using 4-(aminomethyl)phenylboronic acid pinacol ester as coupling partner, the latter being protected as *tert*-butylcarbamate. Using one equivalent of coupling partner with $PdCl_2$(dppf) as catalyst and Cs_2CO_3 as base in a DMF / H_2O (1%) mixture at 100 °C, the desired product **2** resulting from a single coupling was obtained in 26% yield.[S3] In the next step, cleavage of the Boc protecting group was performed under mild conditions, involving trimethylsilyl triflate and 2,6-lutidine in dichloromethane followed by a treatment with methanol, to give the corresponding free benzylamine **3** in 93% yield. The latter was finally reacted with monodisperse PEG_{24} precursor **4** in the presence of triethylamine in DMF at room temperature to give the target molecule **M1** in 46% yield (11% over 3 steps, from precursor **1a**).

As opposed to this statistical monofunctionalisation of precursor **1a**, we have recently demonstrated that desymmetrised ruthenium complex **1b**, incorporating a preactivated 4-iodophenyl fragment, chemoselectively undergoes single cross-coupling reactions.[S1,S2] This approach proved particularly efficient for the construction of a single phenylethynyl moiety via Sonogashira coupling, allowing for high levels of iodophenyl vs bromophenyl discrimination in complex **1b**. **M2** and **M4** were thus synthesised via a single coupling of precursor **1b** with Boc-protected propargyl amine or reagent **7b**, respectively, in the presence of catalytic amounts of $PdCl_2(PPh_3)_2$ and CuI to afford monofunctionalised complexes **5** and **8** in 75-82% yield. Subsequent deprotection of the primary amine followed by condensation with monodisperse PEG_{24} reagent **4** successfully gave the target molecules **M2** and **M4**, in 43% and 40% yield over 2 steps, respectively.

In the case of **M3**, an extra four-fold Suzuki-Miyaura reaction was required as an intermediate step to introduce the four ferrocenyl moieties.[S1] Complex **5**, resulting from the Sonogashira coupling between precursor **1b** and Boc-protected propargyl amine, was thus submitted to a Suzuki-Miyaura reaction in the presence of a large excess of ferroceneboronic acid pinacol ester. Subsequent deprotection of the amine

and condensation with PEG precursor **4** gave the desired molecule **M3** in 11% yield over 3 steps (from intermediate **5**).



Scheme S1. *Synthesis of the series of PEG-derivatised molecules **M1**-**M4**.*
*Reagents and conditions: i) $PdCl_2(dppf)$ cat., Cs_2CO_3, DMF / H_2O (1%), 100 °C, 48h; ii) a) TMSOTf, 2,6-lutidine, CH_2Cl_2, 0 °C to rt, 2h, b) MeOH; iii) $mPEG_{24}$-NHS ester (**4**), NEt_3, DMF, rt, 24h; iv) $PdCl_2(PPh_3)_2$ cat., CuI cat., THF / NEt_3 4:1, 40 °C, 24h; v) ferroceneboronic acid pinacol ester, $PdCl_2(dppf)$ cat., Cs_2CO_3, DMF / H_2O (1%), 100 °C, 72h.*

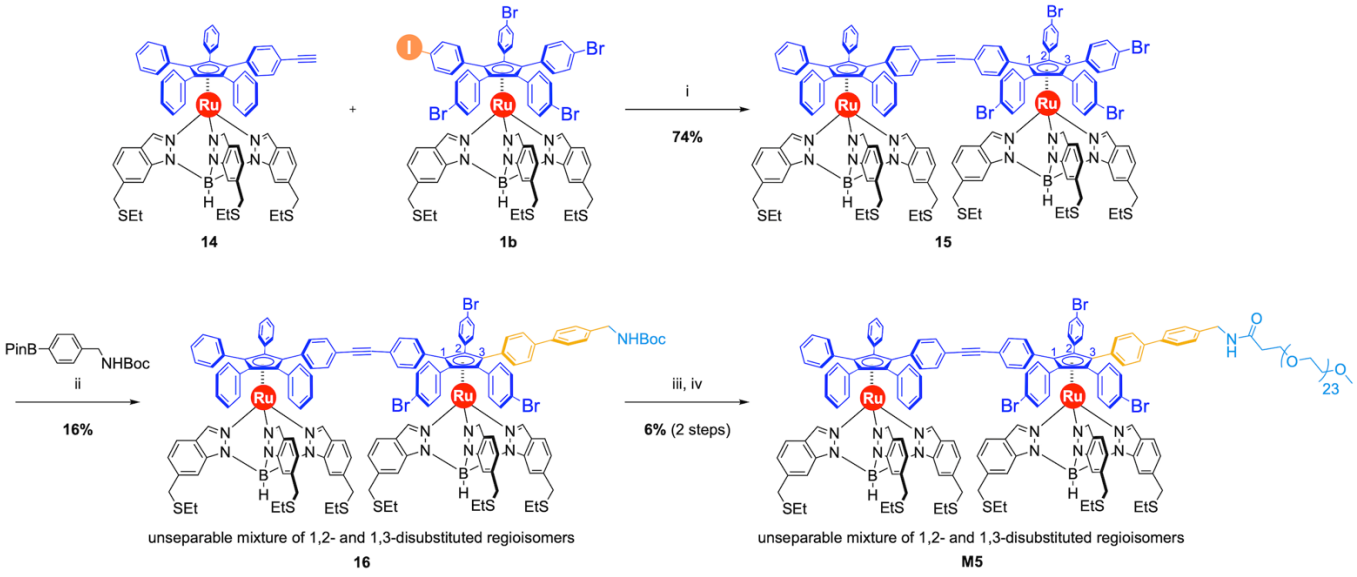
b. Synthesis of dinuclear ruthenium complex M5

In dinuclear ruthenium complex **M5**, the upper rotating subunit of complex **M1** has been covalently linked via an ethynyl bridge to the pentaarylcyclopentadienyl ligand of a second ruthenium complex. Dinuclear complex **M5** was thus prepared according to a convergent synthetic route involving the desymmetrised key precursor **1b** and ruthenium complex **14**, in which the cyclopentadienyl ligand bears a single ethynylphenyl substituent surrounded by four phenyl groups (Scheme S2).

A chemoselective Sonogashira coupling between the iodinated position of precursor **1b** and terminal alkyne **14** in the presence of $PdCl_2(PPh_3)_2$ and CuI as co-catalysts gave the dinuclear complex **15** in 74% yield. Introduction of the 4,4'-biphenyl spacer and of the PEG_{24} chain were next achieved according to the synthetic route detailed above for the preparation of **M1** (see section I.1.a). A Suzuki-Miyaura reaction under statistical conditions first allowed the coupling with a single Boc-protected benzylamine fragment and the resulting dinuclear complex **16** was obtained in 16% yield as an unseparable mixture of 1,2- and 1,3-disubstituted regioisomers (only the 1,3-disubstituted isomer is depicted on Scheme S2 for clarity). This mixture of regioisomers is due to the possible functionalisation of the bromophenyl groups located in positions 2 or 3 of the cyclopentadienyl ring, with respect to the position of the bridging ethynylphenyl moiety.

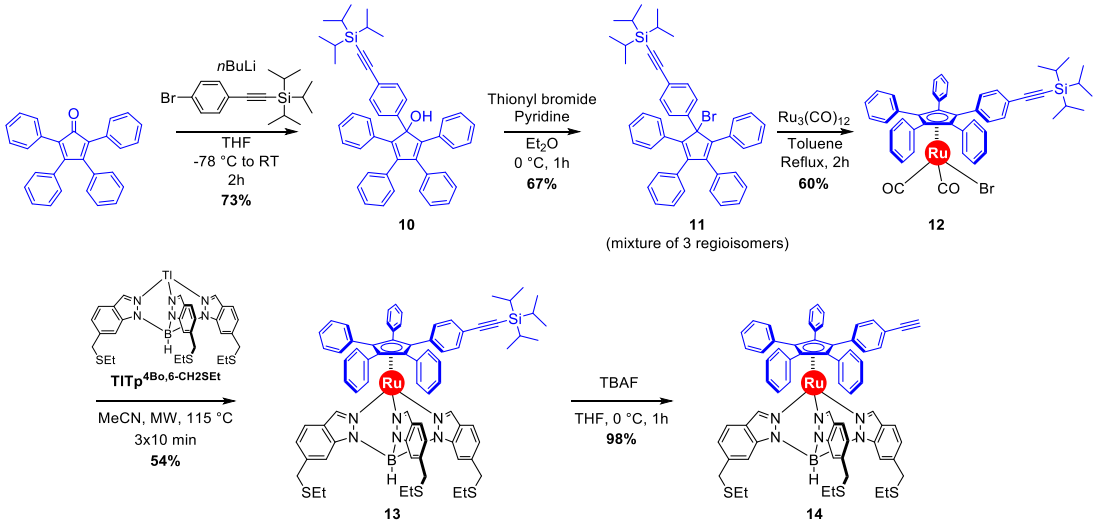
It is important to note that the AFM-based Force Spectroscopy experiments are carried out at the single molecule scale, with the blocked rotation of the cyclopentadienyl ligands expected to take place upon adsorption of each dinuclear complex **M5** regardless of its 1,2- or 1,3-substitution pattern. As a consequence, the target dinuclear complex **M5** has been used in single-molecule AFM experiments as a mixture of 1,2- and 1,3-disubstituted isomers.

The next steps of the synthesis of complex **M5** were thus performed on the mixture of regioisomers, first with the cleavage of the Boc protecting group under mild conditions followed by condensation of the resulting benzylamine with monodisperse PEG_{24} precursor **4** in deuterated DMF at 40 °C. The target dinuclear complex **M5** was obtained in 6% yield over two steps as an unseparable mixture of 1,2- and 1,3-disubstituted regioisomers (the low yield is mostly related to purification issues).



Scheme S2. *Synthesis of dinuclear ruthenium complex **M5**.*
*Reagents and conditions: i) $PdCl_2(PPh_3)_2$ cat., CuI cat., THF / NEt_3 4:1, 40 °C, 24h; ii) $PdCl_2(dppf)$ cat., Cs_2CO_3, DMF / H_2O (1%), 100 °C, 48h; iii) a) TMSOTf, 2,6-lutidine, CH_2Cl_2, 0 °C to rt, 2h, b) MeOH; iv) mPEG$_{24}$-NHS ester (**4**), NEt_3, DMF-d_7, 40 °C, 48h*

Precursor **14** was in turn synthesised in five steps from commercially-available 2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-one (Scheme S3). Treatment of [(4-bromophenyl)ethynyl]-triisopropylsilane[S4] with *n*-butyllithium delivered the corresponding aryl lithium species, which was added onto tetraphenylcyclopentadienone to give cyclopentadienol **10**. The latter was next brominated by treatment with thionyl bromide and pyridine to afford in 67% yield bromocyclopentadiene **11** as a mixture of three regioisomers. Subsequent reaction with ruthenium(0) cluster $Ru_3(CO)_{12}$ led to an insertion into the C-Br bond to yield piano-stool ruthenium(II) complex **12**, carrying a desymmetrised pentaarylcyclopentadienyl ligand. Ligand exchange in the presence of the thallium salt of thioether-functionalised hydrotris(indazolyl)borate **TlTp$^{4Bo,6\text{-}CH2SEt}$** [S5] followed by a deprotection using tetrabutylammonium fluoride finally gave the desired ruthenium(II) complex **14** bearing a terminal alkyne in 53% yield over two steps.



Scheme S3. *Synthesis of key intermediate* ***14*** *from 2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-one.*

I.2. Synthesis and characterisation of new compounds

a. Materials and methods

Commercial reagents and solvents: All chemicals and solvents were purchased from commercial suppliers unless otherwise stated and were purified, if needed, using standard laboratory techniques such as distillation, drying with 4 Å molecular sieves or filtration over a relevant stationary phase.
1,1'-Bis(diphenylphosphino)ferrocene dichloropalladium(II), TBAF (1.0 M in THF), 2,6-lutidine, anhydrous triethylamine, bis(triphenylphosphine)palladium(II) dichloride, cesium carbonate, copper(I) iodide, *n*-butyllithium (2.5 M in hexanes), *N*-(*tert*-butoxycarbonyl) 4-(aminomethyl)phenylboronic acid pinacol ester and thionyl bromide were purchased from Aldrich. 2,3,4,5-Tetraphenylcyclopenta-2,4-dien-1-one, *N*-(*tert*-butoxycarbonyl)propargylamine and trimethylsilyl trifluoromethanesulfonate were purchased from TCI chemicals. Pyridine was purchased from Alfa Aesar. Monodisperse PEG chain $mPEG_{24}$-NHS ester (**4**) was purchased from BroadPharm. Triruthenium dodecacarbonyl was purchased from Fluorochem or Aldrich. Anhydrous solvents were all purchased from Aldrich. Deuterated solvents were purchased from Eurisotop.

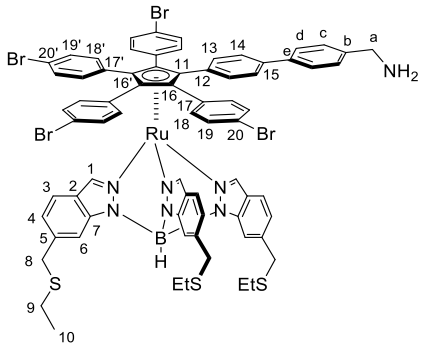
Reported compounds: The following compounds were synthesised according to literature procedures reported by us or others, and were fully characterised using routine characterisation techniques: key precursors **1a**[S5] and **1b**,[S1] complex **2**,[S3] complex **5**,[S1] **M3**,[S1] [(4-bromophenyl) ethynyl] triisopropylsilane[S4] and thallium hydrotris{6-[(ethylsulfanyl)methyl]indazol-1-yl}borate **TlTp$^{4Bo,6\text{-}CH2SEt}$**.[S5]

Synthesis and purification: Reactions were carried out using standard Schlenk techniques under an argon atmosphere or using a glovebox under argon ([H_2O] and [O_2] < 2 ppm.). Column chromatography was carried out on 230–400 mesh silica gel (Aldrich) or alumina (Merck). Celite 545 was purchased from Merck. Thin layer chromatography (TLC) was performed on pre-coated aluminum-backed silica gel 60 UV254 plates (Macherey–Nagel or Merck) with visualisation effected using ultraviolet irradiation (λ = 254, 366 nm).

Analysis: NMR spectroscopy and mass spectrometry analysis were performed by the appropriate services of the Toulouse Institute of Chemistry (ICT – UAR 2599).
^{1}H and ^{13}C NMR were recorded on Avance 300 MHz (probe 5mm BBO BB-1H Z-GRD), Bruker Avance III HD 500 MHz (cryoprobe Prodigy 5mm BBO, 1H ATMA) and Avance 500 MHz (cryoprobe 5mm 1H, 13C) spectrometers. Residual solvent signals were used as internal reference. 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, HSQC and NOESY spectra.
High-resolution mass spectra (HR-MS) were performed with a Waters GCT Premier spectrometer for desorption chemical ionisation (DCI-CH_4), with a Waters Xevo G2 QTof spectrometer for electrospray ionisation (ESI), and with a Waters MALDI micro MX spectrometer for matrix-assisted laser desorption ionisation (MALDI) (matrix: *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile DTCB; λ = 337 nm).

b. Experimental procedures and characterisations

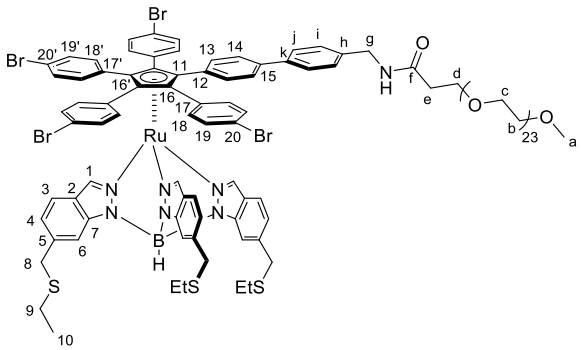
Complex 3:



Complex **2**[S3] (18 mg, 11 µmol, 1.0 eq.) was placed in a Schlenk tube containing a magnetic stir bar and dissolved in anhydrous dichloromethane (1 mL). The solution was degassed by bubbling argon for 15 minutes before being cooled down to 0 °C. 2,6-Lutidine (25.5 µL, 0.218 mmol, 20 eq.) was added under an argon flow, followed by trimethylsilyl trifluoromethanesulfonate (19.7 µL, 0.109 mmol, 10 eq.). The solution was stirred at 0 °C for one hour, followed by one hour at room temperature. Methanol (3 mL) was added and the solvents were removed *in vacuo*. The crude product was partially purified by column chromatography (SiO_2, MeOH/EtOAc 0:10 to 10:90). The partially purified product was then dissolved in a minimal amount of CH_2Cl_2, and precipitated with a mixture of diethyl ether and hexane (1:1). The precipitate was filtered, rinsed with 10 mL of a Et_2O/hexane 1:1 solution and redissolved in CH_2Cl_2. The CH_2Cl_2 was evaporated giving complex **3** as an orange solid in 93% yield (15.7 mg, 10.1 µmol).

R_f = 0.4 (SiO_2, MeOH/CH_2Cl_2 5:100). **^{1}H NMR** (500 MHz, CD_2Cl_2, 25 °C): δ = 7.88 (br. s, 3H, H_6), 7.84 (d, ^3J = 0.9 Hz, 3H, H_1), 7.53 (AA'BB' pattern, ^3J = 8.4 Hz, 2H, H_d), 7.40 (AA'BB' pattern, ^3J = 8.5 Hz, 2H, H_{13}), 7.37 (AA'BB' pattern, ^3J = 8.2 Hz, 2H, H_c), 7.32 (AA'BB' pattern, ^3J = 8.5 Hz, 3H, H_3), 7.30-7.26 (m, 6H, H_{14} and H_{18} or $H_{18'}$), 7.24 (AA'BB' pattern, ^3J = 8.7 Hz, 4H, H_{18} or $H_{18'}$), 7.20 (AA'BB' pattern, ^3J = 8.8 Hz, 4H, H_{19} or $H_{19'}$), 7.16 (AA'BB' pattern, ^3J = 8.7 Hz, 4H, H_{19} or $H_{19'}$), 7.01 (dd, ^3J = 8.5 Hz, ^4J = 1.4 Hz, 3H, H_4), 4.09 (br. s, 2H, H_a), 3.88 (s, 6H, H_8), 2.45 (q, ^3J = 7.3 Hz, 6H, H_9), 1.26 (t, ^3J = 7.4 Hz, 9H, H_{10}) ppm. **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2, 25 °C): δ = 146.1 (C^2), 141.6 (C^e), 140.7 (C^1), 140.2 (C^b), 139.3 (C^{15}), 138.1 (C^5), 135.6 (C^{18} and $C^{18'}$), 134.4 (C^{13}), 132.9 (C^{17} and $C^{17'}$ and C^{12}), 131.0 (C^{19} and $C^{19'}$), 129.8 (C^c), 127.9 (C^d), 126.3 (C^{14}), 122.7 (C^4), 122.5 (C^7), 122.2 (C^{20} and $C^{20'}$), 120.4 (C^3), 111.3 (C^6), 88.3 (C^{11}), 87.6 (C^{16} or $C^{16'}$), 87.2 (C^{16} or $C^{16'}$), 44.4 (C^a), 36.9 (C^8), 25.7 (C^9), 14.7 (C^{10}) ppm. C^b could not be distinguished using ^{13}C{^{1}H} NMR but was assigned using the appropriate correlation spot on HMBC NMR. **HR-MS** (MALDI): calcd. for $C_{72}H_{62}BBr_4N_7RuS_3$ $[M]^+$: 1553.0088, found 1553.0175.

Complex M1:

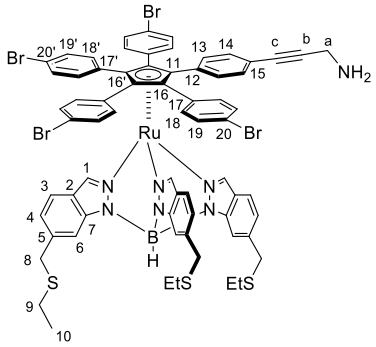


In a Schlenk tube were placed a stir bar, complex **3** (10 mg, 6.4 µmol, 1.0 eq.), monodisperse $mPEG_{24}$-NHS ester (**4**) (39 mg, 3.2 µmol, 5.0 eq.), anhydrous DMF (1 mL) and anhydrous triethylamine (3.6 µL, 26 µmol, 4.0 eq.). The mixture was degassed by bubbling argon for 15 minutes and stirred at room temperature for 24 hours. The solvent was then evaporated and the residue was dissolved in ethyl acetate (10 mL) and washed with water (10 mL). The aqueous layer was then extracted with 3x10 mL of ethyl acetate. The combined organic layers were evaporated to dryness, and the residue was purified by column

chromatography (SiO_2, CH_2Cl_2/MeOH 5%). 1 mL of distilled water was subsequently added to the residue, followed by acetone until complete solubilisation. The acetone was then partially removed by rotary evaporation, inducing the precipitation of the product, which was recovered by filtration over celite and rinsed with 20 mL of distilled water. The precipitate was redissolved in acetone which was then evaporated to give complex **M1** as a glassy orange solid in 46% yield (7.9 mg, 3.0 µmol).

***R*f** = 0.72 (SiO_2, MeOH/CH_2Cl_2 10:90). **^{1}H NMR** (500 MHz, CD_2Cl_2, 25 °C): δ = 7.89 (br. s, 3H, H_6), 7.85 (d, ^3J = 0.9 Hz, 3H, H_1), 7.49 (AA'BB' pattern, ^3J = 8.4 Hz, 2H, H_j), 7.40 (AA'BB' pattern, ^3J = 8.4 Hz, 2H, H_{13}), 7.37-7.25 (m, 11H, H_3, H_i, H_{14}, H_{18} or $H_{18'}$), 7.25 (AA'BB' pattern, ^3J = 8.6 Hz, 4H, H_{18} or $H_{18'}$), 7.20 (AA'BB' pattern, ^3J = 8.7 Hz, 8H, H_{19} and $H_{19'}$), 7.03 (dd, ^3J = 8.4 Hz, ^4J = 1.5 Hz, 3H, H_4), 6.85 (t, ^3J = 6.0 Hz, 1H, NH), 4.42 (d, ^3J = 6.1 Hz, 2H, H_g), 3.90 (s, 6H, H_8), 3.73 (t, ^3J = 5.8 Hz, 2H, H_d), 3.62-3.48 (m, 92H, H_b and H_c), 3.34 (s, 3H, H_a), 2.48 (t, ^3J = 5.7 Hz, 2H, H_e), 2.47 (q, ^3J = 7.4 Hz, 6H, H_9), 1.28 (t, ^3J = 7.3 Hz, 9H, H_{10}) ppm. **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2, 25 °C): δ = 171.6 (C^f), 144.1 (C^2), 140.7 (C^1), 140.1 (C^{15}), 139.1 (C^h and C^k), 138.1 (C^5), 135.7 (C^{18} and $C^{18'}$), 134.3 (C^{13}), 133.0 (C^{17} and $C^{17'}$), 132.3 (C^{12}), 131.0 (C^{19} and $C^{19'}$), 128.2 (C^i), 127.2 (C^j), 126.2 (C^{14}), 122.7 (C^4), 122.4 (C^7), 122.2 (C^{20} and $C^{20'}$), 120.4 (C^3), 111.3 (C^6), 88.7 (C^{11}), 87.7 (C^{16} or $C^{16'}$), 87.1 (C^{16} or $C^{16'}$), 72.3 (C^b and C^c), 70.8 (C^b and C^c), 70.6 (C^b and C^c), 67.6 (C^d), 59.0 (C^a), 43.1 (C^g), 37.4 (C^e), 36.9 (C^8), 25.7 (C^9), 14.8 (C^{10}) ppm. **HR-MS** (MALDI): calcd. for $C_{122}H_{160}BBr_4N_7O_{25}RuS_3$ $[M]^+$: 2651.6509, found 2651.6592.

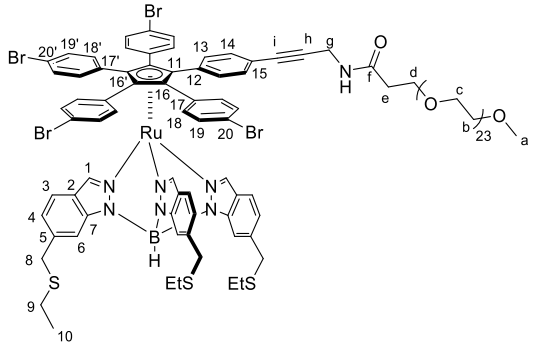
Complex 6:



Complex **5**[S1] (29 mg, 18 µmol, 1.0 eq.) was placed in a Schlenk tube containing a magnetic stir bar and dissolved in anhydrous dichloromethane (1 mL). The solution was degassed by bubbling argon for 15 minutes before being cooled down to 0 °C. 2,6-Lutidine (42 µL, 360 µmol, 20 eq.) was added under an argon flow, followed by trimethylsilyl trifluoromethanesulfonate (33 µL, 180 µmol, 10 eq.). The solution was stirred at 0 °C for one hour, followed by one hour at room temperature. Methanol (2 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 90:10), dried *in vacuo*, redissolved in dichloromethane (5 mL) and methanol (10 mL) was added. The dichloromethane was removed by rotary evaporation inducing precipitation of complex **6**. The suspension was cooled down to 0 °C, filtered on a celite plug and the solid was rinsed with methanol (5 mL). Complex **6** was finally redissolved in dichloromethane and dried *in vacuo* to afford an orange solid in 74% yield (20 mg, 13 µmol).

***R*f** = 0.25 (SiO_2, MeOH/CH_2Cl_2 5:100). **^{1}H NMR** (500 MHz, CD_2Cl_2, 25 °C): δ = 7.88 (br. s, 3H, H_6), 7.81 (d, ^4J = 0.9 Hz, 3H, H_1), 7.35 (dd, ^3J = 8.4 Hz, ^4J = 0.8 Hz, 3H, H_3), 7.27 (AA'BB' pattern, ^3J = 8.7 Hz, 2H, H_{13}), 7.25 – 7.17 (m, 16H, $H_{18,\,18'}$, $H_{19,\,19'}$), 7.09 (AA'BB' pattern, ^3J = 8.6 Hz, 2H, H_{14}), 7.04 (dd, ^3J = 8.4 Hz, ^4J = 1.5 Hz, 3H, H_4), 3.90 (s, 6H, H_8), 3.54 (br. s, 2H, H_a), 2.47 (q, ^3J = 7.3 Hz, 6H, H_9), 1.27 (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), 140.7 (C^1), 138.2 (C^5), 135.6 (C^{18} and $C^{18'}$), 133.8 (C^{13}), 133.3 (C^{15}), 132.7 (C^{17} and $C^{17'}$), 130.9 (C^{14}, C^{19} and $C^{19'}$), 123.0 (C^{12}), 122.7 (C^4), 122.4 (C^7), 122.2 (C^{20} and $C^{20'}$), 120.4 (C^3), 111.3 (C^6), 92.2 (C^b), 88.3 (C^{11}), 87.5 (C^{16} or $C^{16'}$), 87.3 (C^{16} or $C^{16'}$), 81.9 (C^c), 36.9 (C^8), 32.5 (C^a), 25.7 (C^9), 14.7 (C^{10}) ppm. **HR-MS** (MALDI): calcd. for $C_{68}H_{59}BBr_4N_7RuS_3$ $[MH]^+$: 1501.9852, found 1501.9845.

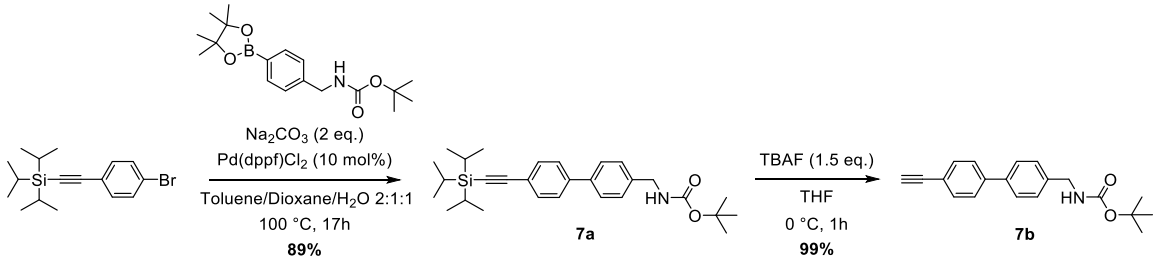
Complex M2:



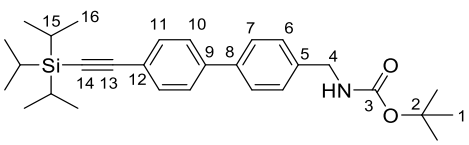
In a Schlenk tube were placed a stir bar, complex **6** (8 mg, 5.3 µmol, 1.0 eq.), monodisperse $mPEG_{24}$-NHS ester (**4**) (32 mg, 27.0 µmol, 5.0 eq.), anhydrous DMF (0.5 mL) and anhydrous triethylamine (3 µL, 21.0 µmol, 4.0 eq.). The mixture was degassed by bubbling argon for 15 minutes and stirred at room temperature for 24 hours. The solvent was then evaporated and the crude product was dissolved in 1 mL of acetone, and 10 mL of brine were added. The residue was extracted with ethyl acetate, the solvents were removed and the residue was purified by a short column chromatography (SiO_2, CH_2Cl_2/MeOH 90:10), followed by a neutral alumina plug eluted with diethyl ether to remove carboxylic acid terminated PEG chains, affording pure complex **M2** as a yellow-orange solid in 58% yield (8 mg, 3.1 µmol).

R_f = 0.53 (SiO_2, MeOH/CH_2Cl_2 5:95). **^{1}H NMR** (500 MHz, CD_2Cl_2, 25 °C): δ = 7.88 (br. s, 3H, H_6), 7.81 (d, ^4J = 0.9 Hz, 3H, H_1), 7.35 (dd, ^3J = 8.2 Hz, ^4J = 0.9 Hz, 3H, H_3), 7.28 (AA'BB' pattern, ^3J = 8.7 Hz, 2H, H_{13}), 7.26 – 7.15 (m, 16H, H_{18}, $H_{18'}$, H_{19} and $H_{19'}$), 7.10 (AA'BB' pattern, ^3J = 8.7 Hz, 2H, H_{14}), 7.04 (dd, ^3J = 8.3 Hz, ^4J = 1.4 Hz, 3H, H_4), 6.77 (br. s, 1H, NH), 4.16 (d, ^3J = 5.5 Hz, 2H, H_g), 3.90 (s, 6H, H_8), 3.71 – 3.67 (m, 2H, H_d), 3.62 – 3.48 (m, 92H, H_b and H_c), 3.34 (s, 3H, H_a), 2.46 (q, ^3J = 7.3 Hz, 6H, H_9), 2.44 (t, ^3J = 5.8 Hz, 2H, H_e), 1.27 (t, ^3J = 7.4 Hz, 9H, H_{10}) ppm. **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2, 25 °C): δ = 171.3 (C^f), 144.1 (C^2), 140.7 (C^1), 138.2 (C^5), 135.5 (C^{18} and $C^{18'}$), 133.8 (C^{13}), 133.7 (C^{15}), 132.6 (C^{17} and $C^{17'}$), 131.0 (C^{14}, C^{19} and $C^{19'}$), 122.7 (C^4), 122.3 (C^7, C^{12}, C^{20} and $C^{20'}$), 120.4 (C^3), 111.3 (C^6), 88.2 (C^h), 87.5 (C^{16} or $C^{16'}$), 87.4 (C^{11}), 87.3 (C^{16} or $C^{16'}$), 82.2 (C^i), 72.3 (C^b or C^c), 70.9 (C^b or C^c), 67.3 (C^d), 59.0 (C^a), 37.1 (C^e), 36.9 (C^8), 29.8 (C^g), 25.7 (C^9), 14.8 (C^{10}) ppm. **HR-MS** (MALDI): calcd. for $C_{118}H_{156}BBr_4N_7O_{25}RuS_3$ $[M]^+$: 2600.6196, found 2600.6191.

***N*-(*tert*-butoxycarbonyl)-4-(aminomethyl)-4'-ethynyl-1,1'-biphenyl (7b):**

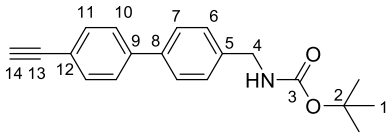


Compound **7b** was obtained in two steps from [(4-bromophenyl)ethynyl]triisopropylsilane[S4] in 88% overall yield. A Suzuki-Miyaura cross-coupling was first achieved using 4-(aminomethyl)phenylboronic acid pinacol ester as coupling partner, the latter being protected as *tert*-butylcarbamate, to give biphenyl intermediate **7a**. Subsequent selective deprotection of the alkyne in the presence of tetrabutylammonium fluoride yielded the desired intermediate **7b**.



In a Schlenk flask were placed a magnetic stir bar, [(4-bromophenyl)ethynyl]triisopropylsilane[S4] (557 mg, 1.65 mmol, 1.1 eq.), *N*-(*tert*-butoxycarbonyl) 4-(aminomethyl)phenylboronic acid pinacol ester (500 mg, 1.5 mmol, 1.0 eq.) and sodium carbonate (318 mg, 3.0 mmol, 2.0 eq.). After quickly evacuating and backfilling the flask with argon, 1,4-dioxane (5 mL), water (5 mL) and toluene (10 mL) were added. The reaction medium was degassed by bubbling argon for 30 minutes before adding $Pd(dppf)Cl_2$ (110 mg, 0.15 mmol, 10 mol%). The mixture was then heated at 100 °C under argon for 17 hours. The crude product was extracted with chloroform (2x50 mL) and washed with water (2x150 mL) twice. The organic layer was dried over magnesium sulfate and the solvents were removed by rotary evaporation. The residue was purified by column chromatography (SiO_2, CH_2Cl_2/heptane 80:20) to give compound **7a** as a white solid in 89% yield (618 mg, 1.3 mmol).

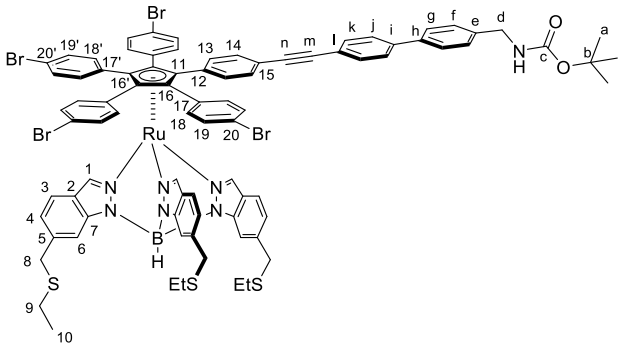
R_f = 0.36 (SiO_2, CH_2Cl_2/hexane 1:1). **^{1}H NMR** (300 MHz, CD_2Cl_2, 25 °C): δ = 7.68 – 7.45 (m, 6H, H_7, H_{10} and H_{11}), 7.36 (AA'BB' pattern, ^3J = 8.2 Hz, 2H, H_6), 5.01 (s, 1H, NH), 4.33 (d, ^3J = 6.1 Hz, 2H, H_4), 1.45 (s, 9H, H_1), 1.15 (m, 21H, H_{15} and H_{16}) ppm. **^{13}C{^{1}H} NMR** (75 MHz, CD_2Cl_2, 25 °C): δ = 156.3 (C^3), 141.1 (C^9), 139.5 (C^5 and C^8), 132.8 (C^{11}), 128.2 (C^6), 127.5 (C^7), 127.2 (C^{10}), 122.8 (C^{12}), 107.4 (C^{13}), 91.8 (C^{14}), 79.6 (C^2), 44.6 (C^4), 28.6 (C^1), 18.9 (C^{16}), 11.8 (C^{15}) ppm. **HR-MS** (DCI-CH_4): calcd. for $C_{29}H_{42}NO_2Si$ $[MH]^+$: 464.2958, found 464.2963.



Compound **7a** (100 mg, 0.216 mmol, 1.0 eq.) was placed in a round bottom flask with a magnetic stir bar and 10 mL of THF. The solution was degassed by bubbling argon for five minutes and cooled down to 0 °C. Then, a solution of TBAF (1.0 M in THF, 0.325 mL, 0.325 mmol, 1.5 eq.) was added dropwise, and the solution was stirred for one hour at 0 °C. After warming up to room temperature, the product was diluted with diethyl ether and washed twice with brine. The organic layer was then dried over magnesium sulfate and the solvents were evaporated using rotary evaporation. The residue was purified by column chromatography (SiO_2, CH_2Cl_2/pentane 1:1 to 1:0) to give pure product **7b** as a white solid in 99% yield (65.5 mg, 0.213 mmol).

R_f = 0.24 (SiO_2, CH_2Cl_2/hexane 1:1). **^{1}H NMR** (300 MHz, CD_2Cl_2, 25 °C): δ = 7.64 – 7.51 (m, 6H, H_7, H_{10} and H_{11}), 7.37 (AA'BB' pattern, ^3J = 8.7 Hz, 2H, H_6), 5.01 (s, 1H, NH), 4.34 (d, ^3J = 6.2 Hz, 2H, H_4), 3.23 (s, 1H, H_{14}), 1.48 (s, 9H, H_1) ppm. **^{13}C{^{1}H} NMR** (75 MHz, CD_2Cl_2, 25 °C): δ = 156.3 (C^3), 141.5 (C^9), 139.6 (C^8), 139.3 (C^5), 133.0 (C^{11}), 128.2 (C^6), 127.5 (C^7), 127.3 (C^{10}), 121.3 (C^{12}), 83.8 (C^{13}), 79.6 (C^2), 78.2 (C^{14}), 44.5 (C^4), 28.6 (C^1) ppm. **HR-MS** (DCI-CH_4): calcd. for $C_{20}H_{22}NO_2$ $[MH]^+$: 308.1651, found 308.1662.

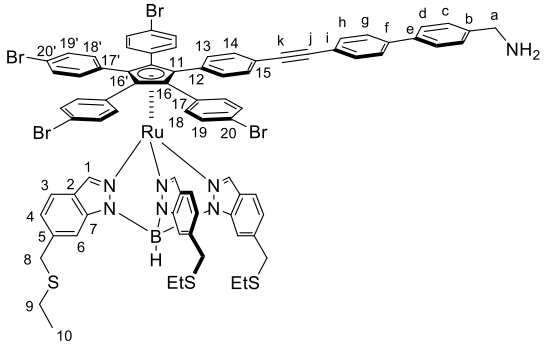
Complex 8:



Complex **1b**[S1] (40 mg, 25.4 µmol, 1.0 eq.), compound **7b** (15.6 mg, 50.8 µmol, 2.0 eq.) and a magnetic stir bar were placed in a Schlenk tube. Anhydrous THF (1 mL) and anhydrous triethylamine (0.25 mL) were added and the mixture was degassed quickly by bubbling argon. $Pd(PPh_3)_2Cl_2$ (2.7 mg, 3.8 µmol, 15 mol%) and CuI (approx. 0.5 mg, 2.5 µmol, 10 mol%) were added under an argon flow. The resulting mixture was then degassed by three successive freeze-pump-thaw cycles, before being 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/pentane gradient from 70:30 to pure CH_2Cl_2) to give complex **8** as an orange solid in 82% yield (36.5 mg, 20.8 µmol).

R_f = 0.58 (SiO_2, CH_2Cl_2). **^{1}H NMR** (500 MHz, CD_2Cl_2, 25 °C): δ = 7.91 (br. s, 3H, H_6), 7.85 (d, ^4J = 0.8 Hz, 3H, H_1), 7.64 – 7.51 (m, 6H, H_g, H_j and H_k), 7.41 – 7.33 (m, 7H, H_3, H_{13} and H_f), 7.30 – 7.18 (m, 18H, H_{14}, $H_{18, 18'}$, $H_{19, 19'}$), 7.05 (dd, ^3J = 8.4 Hz, ^4J = 1.4 Hz, 3H, H_4), 5.00 (br. s, 1H, NH), 4.32 (d, ^3J = 6.6 Hz, 2H, H_d), 3.91 (s, 6H, H_8), 2.47 (q, ^3J = 7.3 Hz, 6H, H_9), 1.45 (s, 9H, H_a), 1.28 (t, ^3J = 7.4 Hz, 9H, H_{10}) ppm. **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2, 25 °C): δ = 156.2 (C^c), 144.1 (C^2), 141.1 (C^h), 140.6 (C^1), 139.6 (C^i and C^e), 138.2 (C^5), 135.6 (C^{18} and $C^{18'}$), 133.9 (C^{13}), 133.8 (C^{15}), 132.7 (C^{17} and $C^{17'}$), 132.3 (C^g), 129.7 (C^{14}, C^{19} and $C^{19'}$), 128.1 (C^f), 127.4 (C^j and C^k), 122.8 (C^4), 122.3 (C^l, C^7, C^{12}, C^{20} and $C^{20'}$), 120.4 (C^3), 111.3 (C^6), 90.6 (C^m), 90.0 (C^n), 88.3 (C^{11}), 87.6 (C^{16} or $C^{16'}$), 87.2 (C^{16} or $C^{16'}$), 79.6 (C^b), 44.53 (C^d), 36.9 (C^8), 28.5 (C^a), 25.7 (C^9), 14.8 (C^{10}) ppm. **HR-MS** (MALDI): calcd. for $C_{85}H_{74}BBr_4N_7O_2RuS_3$ $[M]^+$: 1753.0895, found 1753.0657.

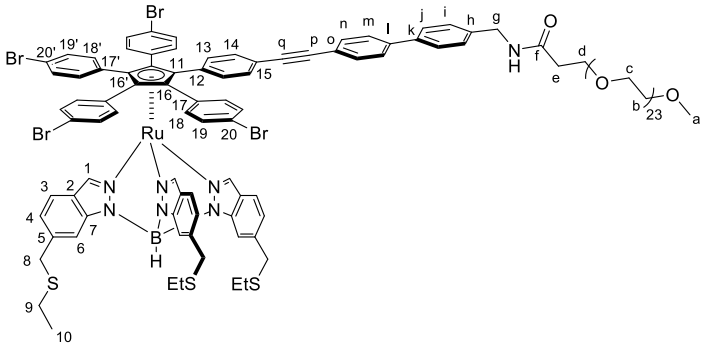
Complex 9:



Complex **8** (29.0 mg, 16.5 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 (40 µL, 343 µmol, 21 eq.) was added under an argon flow, followed by trimethylsilyl trifluoromethanesulfonate (30 µL, 166 µmol, 10 eq.). The solution was stirred at 0 °C for one hour, followed by one hour at room temperature. Methanol (2 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 90:10), 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 **9**. The suspension was cooled down to 0 °C, filtered on a celite plug and the solid was rinsed with ice cold pentane (50 mL). Complex **9** was finally redissolved in dichloromethane and dried *in vacuo* to afford a glassy orange solid in 66% yield (18.0 mg, 10.9 µmol).

***R*f** = 0.28 (SiO_2, MeOH/CH_2Cl_2 10:90). **^{1}H NMR** (500 MHz, CD_2Cl_2, 25 °C): δ = 7.89 (s, 3H, H_6), 7.84 (d, ^4J = 0.9 Hz, 3H, H_1), 7.61 – 7.51 (m, 6H, H_d, H_g and H_h), 7.45 (d, ^3J = 8.1 Hz, 2H, H_c), 7.38 – 7.32 (m, 5H, H_3 and H_{13}), 7.29 – 7.16 (m, 18H, H_{14}, $H_{18,\,18'}$, $H_{19,\,19'}$), 7.04 (dd, ^3J = 8.4 Hz, ^4J = 1.5 Hz, 3H, H_4), 3.94 (s, 2H, H_a), 3.90 (s, 6H, H_8), 2.47 (q, ^3J = 7.4 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), 141.0 (C^e and C^f), 140.7 (C^1), 139.6 (C^b), 138.2 (C^5), 135.6 (C^{18} and $C^{18'}$), 133.9 (C^{13}), 133.8 (C^{15}), 132.7 (C^{17} and $C^{17'}$), 132.4 (C^g or C^h), 131.1 (C^{14}, C^{19} and $C^{19'}$), 128.7 (C^c), 127.5 (C^d and C^g or C^h), 122.8 (C^{12}), 122.7 (C^4), 122.5 (C^7, C^{20} and $C^{20'}$), 122.3 (C^i), 120.4 (C^3), 111.3 (C^6), 90.6 (C^j), 90.0 (C^k), 88.3 (C^{11}), 87.6 (C^{16} or $C^{16'}$), 87.2 (C^{16} or $C^{16'}$), 45.5 (C^a), 36.9 (C^8), 25.7 (C^9), 14.7 (C^{10}) ppm. **HR-MS** (MALDI): calcd. for $C_{80}H_{66}BBr_4N_7RuS_3$ $[M]^+$: 1653.0404, found 1653.0441.

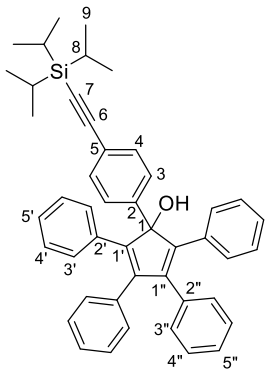
Complex M4:



In a Schlenk tube were placed a stir bar, complex **9** (9 mg, 5.4 µmol, 1.0 eq.), monodisperse $mPEG_{24}$-NHS ester (**4**) (60 mg, 49.4 µmol, 7.9 eq.), anhydrous DMF (0.5 mL) and anhydrous triethylamine (6 µL, 43.2 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 residue was purified by a short column chromatography (SiO_2, CH_2Cl_2/MeOH 90:10) followed by a neutral alumina plug (eluted with dichloromethane) to remove hydrolysed PEG species. Ethanol (10 mL) was then added to the eluate and dichloromethane was removed by rotary evaporation to induce precipitation of complex **M4** 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 **M4** as an orange solid in 60% yield (9 mg, 3.3 µmol).

***R*f** = 0.64 (SiO_2, MeOH/CH_2Cl_2 10:90). **^{1}H NMR** (500 MHz, CD_2Cl_2, 25 °C): δ = 7.89 (br. s, 3H, H_6), 7.84 (br. s, 3H, H_1), 7.63 – 7.51 (m, 6H, H_j, H_m and H_n), 7.41 – 7.32 (m, 7H, H_3, H_{13} and H_i), 7.29 – 7.15 (m, 18H, H_{14}, $H_{18,\,18'}$, $H_{19,\,19'}$), 7.04 (dd, ^3J = 8.5 Hz, ^4J = 1.4 Hz, 3H, H_4), 6.94 (t, ^3J = 5.9 Hz, 1H, NH), 4.45 (d, ^3J = 6.0 Hz, 2H, H_g), 3.90 (s, 6H, H_8), 3.75 (t, ^3J = 5.7 Hz, 2H, H_d), 3.65 – 3.48 (m, 92H, H_b and H_c), 3.33 (s, 3H, H_a), 2.50 (t, ^3J = 5.4 Hz, 2H, H_e), 2.47 (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 = 171.7 (C^f), 144.1 (C^2), 141.1 (C^k), 140.7 (C^1), 139.3 (C^l and C^h), 138.2 (C^5), 135.6 (C^{18} and $C^{18'}$), 133.9 (C^{13}), 133.8 (C^{15}), 132.7 (C^{17} and $C^{17'}$), 132.4 (C^m or C^n), 131.1 (C^{14}, C^{19} and $C^{19'}$), 128.3 (C^i), 127.4 (C^j and C^m or C^n), 122.8 (C^{12}), 122.7 (C^4), 122.5 (C^o and C^7), 122.3 (C^{20} and $C^{20'}$), 120.4 (C^3), 111.3 (C^6), 90.6 (C^p), 90.0 (C^q), 88.4 (C^{11}), 87.6 (C^{16} or $C^{16'}$), 87.2 (C^{16} or $C^{16'}$), 72.3 (C^c or C^b), 70.9 (C^c or C^b), 67.6 (C^d), 59.0 (C^a), 43.1 (C^g), 37.4 (C^e), 36.9 (C^8), 25.7 (C^9), 14.7 (C^{10}) ppm. **HR-MS** (MALDI): calcd. for $C_{130}H_{164}BBr_4N_7NaO_{25}RuS_3$ $[M+Na]^+$: 2275.670 , found 2775.678.

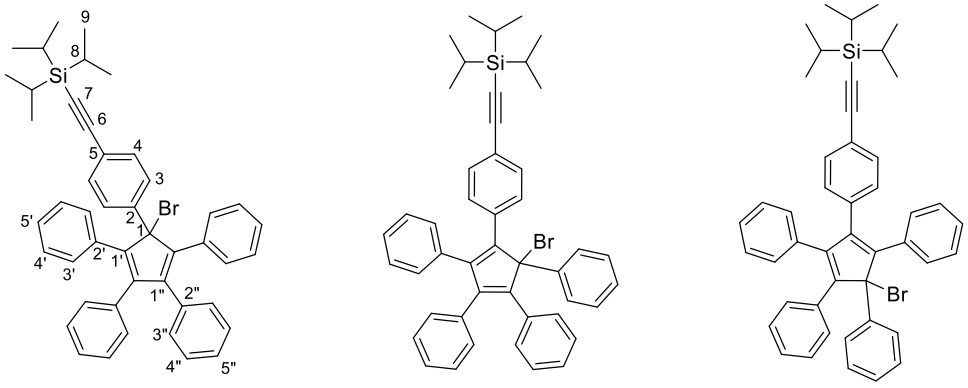
2,3,4,5-Tetraphenyl-1-[4'-(triisopropylsilylethynyl)phenyl]cyclopenta-2,4-dien-1-ol (10):



In a three-neck round-bottom flask under argon were introduced a magnetic stir bar and [(4-bromophenyl)ethynyl]triisopropylsilane[S4] (1.05 g, 3.12 mmol, 1.5 eq.). Degassed anhydrous THF (8 mL) was then added, and the resulting solution was cooled down to -78 °C. A solution of *n*-butyllithium (2.5 M in hexanes, 1.3 mL, 3.12 mmol, 1.5 eq.) was added dropwise and the solution was stirred for 30 minutes at -78 °C. The resulting mixture was canulated onto a solution of 2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-one (0.8 g, 2.08 mmol, 1.0 eq.) in degassed anhydrous THF (15 mL) at -78 °C. The resulting dark purple solution was stirred at this temperature for 1.5 hours and allowed to warm up to room temperature. A saturated aqueous solution of ammonium chloride (10 mL) was added and the crude product was extracted with ethyl acetate (3x20 mL). The organic layers were combined and washed with water (2x40 mL) followed by brine (40 mL). The organic layer was dried using anhydrous magnesium sulfate and the solvents were evaporated *in vacuo*. The residue was purified by column chromatography (SiO_2, CH_2Cl_2/pentane 20:80) to give cyclopentadienol **10** as a pale-yellow solid in 73% yield (0.98 g, 1.52 mmol).

R_f = 0.44 (SiO_2, CH_2Cl_2/pentane 40:60). **^{1}H NMR** (300 MHz, CD_2Cl_2, 25 °C): δ = 7.57 (d, ^3J = 8.6 Hz, 2H, H_4), 7.42 (d, ^3J = 8.6 Hz, 2H, H_3), 7.22 – 7.00 (m, 20H, $H_{3'}$, $H_{3''}$, $H_{4'}$, $H_{4''}$, $H_{5'}$ and $H_{5''}$), 2.62 (br. s, 1H, OH), 1.15 (m, 21H, H_8 and H_9) ppm. **^{13}C{^{1}H} NMR** (75 MHz, CD_2Cl_2, 25 °C): δ = 148.2 ($C^{1'}$ or $C^{1''}$), 143.4 ($C^{1'}$ or $C^{1''}$), 141.2 (C^2), 135.5 ($C^{2'}$ or $C^{2''}$), 134.3 ($C^{2'}$ or $C^{2''}$), 132.6 (C^3), 130.2 ($C^{3'}$ or $C^{3''}$), 129.9 ($C^{3'}$ or $C^{3''}$), 128.3 ($C^{4'}$ or $C^{4''}$), 128.2 ($C^{4'}$ or $C^{4''}$), 127.6 ($C^{5'}$ or $C^{5''}$), 127.5 ($C^{5'}$ or $C^{5''}$), 125.6 (C^4), 122.4 (C^5), 107.4 (C^1), 91.0 (C^7), 90.6 (C^6), 18.9 (C^9), 11.4 (C^8) ppm. **HR-MS** (DCI-CH_4): calcd. for $C_{46}H_{46}OSi$ $[M]^+$: 642.3318, found 642.3331.

5-Bromo-1,2,3,4-tetraphenyl-5-[4'-(triisopropylsilylethynyl)phenyl]cyclopenta-1,3-diene (11):
(Obtained as a mixture of 3 regioisomers)

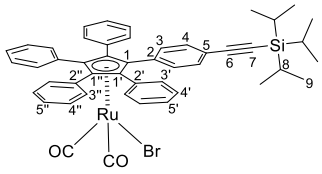


Compound **10** (440 mg, 0.69 mmol, 1.0 eq.) was placed in a Schlenk tube containing a magnetic stir bar under argon. Anhydrous diethyl ether (17 mL) and freshly distilled pyridine (69 µL, 0.86 mmol, 1.25 eq.) were added. The mixture was cooled down to 0 °C and thionyl bromide (66 µL, 0.86 mmol, 1.25 eq.) was added. The medium was then allowed to warm up to room temperature under stirring over the course of one hour. The reaction was neutralised by slow addition of the reaction medium to 10 mL of a 1M HCl aqueous solution. After separation of the phases, the aqueous layer was extracted with CH_2Cl_2 (200 mL),

and washed three times with water (3x200 mL). The organic layer was dried over magnesium sulfate and the solvents were removed by rotary evaporation. The crude product was purified by column chromatography (SiO_2, pentane 100% to CH_2Cl_2/pentane 95:5) to afford the desired brominated product **11** in 67% yield (326 mg, 0.46 mmol) as a yellow solid composed of a mixture of regioisomers (the ratio could not be determined because of overlapping of ^{1}H NMR signals).

***R*$_f$** = 0.62 (SiO_2, CH_2Cl_2/hexane 30:70). **^{1}H NMR** (500 MHz, CD_2Cl_2, 25 °C): δ = 7.51 – 7.47 (m, 1.64H, H_{Ar}), 7.45 (AA'BB' pattern, *J* = 8.7 Hz, 0.31H, H_{Ar}), 7.36 (AA'BB' pattern, *J* = 8.7 Hz, 0.26H, H_{Ar}), 7.27 (m, 3.04H, H_{Ar}), 7.22 – 6.90 (m, 18.50H, H_{Ar}), 1.13 (s, 3.04H, H_8 and H_9), 1.10 (s, 8.79H, H_8 and H_9), 1.08 (s, 9.17H, H_8 and H_9). **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2, 25 °C): δ = 149.4 ($C^{quat\text{-}Ar}$), 149.3 ($C^{quat\text{-}Ar}$), 148.9 ($C^{quat\text{-}Ar}$), 148.5 ($C^{quat\text{-}Ar}$), 148.1 ($C^{quat\text{-}Ar}$), 147.9 ($C^{quat\text{-}Ar}$), 143.2 ($C^{quat\text{-}Ar}$), 142.8 ($C^{quat\text{-}Ar}$), 142.4 ($C^{quat\text{-}Ar}$), 142.2 ($C^{quat\text{-}Ar}$), 141.7 ($C^{quat\text{-}Ar}$), 136.6 ($C^{quat\text{-}Ar}$), 135.9 ($C^{quat\text{-}Ar}$), 135.8 ($C^{quat\text{-}Ar}$), 135.3 ($C^{quat\text{-}Ar}$), 135.0 ($C^{quat\text{-}Ar}$), 135.0 ($C^{quat\text{-}Ar}$), 135.0 ($C^{quat\text{-}Ar}$), 134.8 ($C^{quat\text{-}Ar}$), 134.5 ($C^{quat\text{-}Ar}$), 134.5 ($C^{quat\text{-}Ar}$), 134.5 ($C^{quat\text{-}Ar}$), 134.4 ($C^{quat\text{-}Ar}$), 133.7 ($C^{quat\text{-}Ar}$), 132.4 ($C^{CH\text{-}Ar}$), 131.7 ($C^{CH\text{-}Ar}$), 131.4 ($C^{CH\text{-}Ar}$), 131.3 ($C^{CH\text{-}Ar}$), 130.9 ($C^{CH\text{-}Ar}$), 130.8 ($C^{CH\text{-}Ar}$), 130.6 ($C^{CH\text{-}Ar}$), 130.4 ($C^{CH\text{-}Ar}$), 130.4 ($C^{CH\text{-}Ar}$), 130.3 ($C^{CH\text{-}Ar}$), 130.3 ($C^{CH\text{-}Ar}$), 128.9 ($C^{CH\text{-}Ar}$), 128.9 ($C^{CH\text{-}Ar}$), 128.8 ($C^{CH\text{-}Ar}$), 128.8 ($C^{CH\text{-}Ar}$), 128.4 ($C^{CH\text{-}Ar}$), 128.4 ($C^{CH\text{-}Ar}$), 128.3 ($C^{CH\text{-}Ar}$), 128.2 ($C^{CH\text{-}Ar}$), 128.1 ($C^{CH\text{-}Ar}$), 127.9 ($C^{CH\text{-}Ar}$), 127.9 ($C^{CH\text{-}Ar}$), 127.9 ($C^{CH\text{-}Ar}$), 127.8 ($C^{CH\text{-}Ar}$), 127.8 ($C^{CH\text{-}Ar}$), 127.8 ($C^{CH\text{-}Ar}$), 127.7 ($C^{CH\text{-}Ar}$), 127.7 ($C^{CH\text{-}Ar}$), 127.7 ($C^{CH\text{-}Ar}$), 127.7 ($C^{CH\text{-}Ar}$), 127.6 ($C^{CH\text{-}Ar}$), 126.1 ($C^{CH\text{-}Ar}$), 125.7 (C^{quat}), 123.4 (C^5), 122.6 (C^5), 122.5 (C^5), 107.3 (C^1), 107.2 (C^1), 106.8 (C^1), 92.0 (C^7), 91.7 (C^7), 91.7 (C^7), 77.0 (C^6), 76.7 (C^6), 76.6 (C^6), 18.8 (C^9), 18.8 (C^9), 18.8 (C^9), 11.7 (C^8), 11.7 (C^8), 11.7 (C^8). **HR-MS** (DCI-CH_4): calcd. For $C_{46}H_{45}SiBr$ $[M]^+$: 704.2474, found 704.2451.

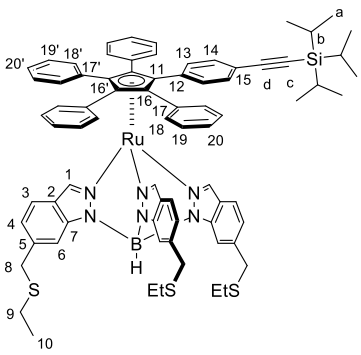
Bromido dicarbonyl η^5-1,2,3,4-tetraphenyl-5-[4'-(triisopropylsilylethynyl)phenyl]cyclopentadienyl ruthenium(II) (12):



In a dry Schlenk tube containing a magnetic stir bar were placed ruthenium cluster Ru_3CO_{12} (62 mg, 0.10 mmol, 0.4 eq.), compound **11** (as a mixture of regioisomers) (172 mg, 0.24 mmol, 1.0 eq.) and anhydrous degassed toluene (10 mL) under argon atmosphere. The mixture was heated at reflux 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, CH_2Cl_2/pentane 30:70) to give pure complex **12** as an orange solid in 60% yield (147 mg, 0.17 mmol).

***R*$_f$** = 0.60 (SiO_2, CH_2Cl_2/pentane 1:1). **^{1}H NMR** (500 MHz, CD_2Cl_2, 25 °C): δ = 7.27 – 7.03 (m, 22H, H_{Ar}), 6.99 (AA'BB' pattern, ^3J = 8.6 Hz, 2H, H_3), 1.11 (m, 21H, H_8 and H_9) ppm. **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2, 25 °C): δ = 197.1 (C^{CO}), 132.8 ($C^{3'}$ or $C^{3''}$), 132.8 ($C^{3'}$ or $C^{3''}$), 132.7 (C^3), 131.6 (C^4), 130.3 (C^2), 130.0 ($C^{2'}$ or $C^{2''}$), 130.0 ($C^{2'}$ or $C^{2''}$), 128.9 ($C^{5'}$ or $C^{5''}$), 128.9 ($C^{5'}$ or $C^{5''}$), 128.4 ($C^{4'}$ or $C^{4''}$), 128.2 ($C^{4'}$ or $C^{4''}$), 123.9 (C^5), 107.3 ($C^{1'}$ or $C^{1''}$), 107.1 (C^6), 106.8 (C^1), 106.6 ($C^{1'}$ or $C^{1''}$), 92.7 (C^7), 18.8 (C^9), 11.7 (C^8) ppm. **HR-MS** (ESI+): calcd. for $C_{48}H_{46}BrO_2RuSi$ $[MH]^+$: 863.1502, found 863.1500.

η^5-1,2,3,4-Tetraphenyl-5-[4'-(triisopropylsilylethynyl)phenyl]cyclopentadienyl hydrotris{6-[(ethylsulfanyl)methyl]indazol-1-yl}borate ruthenium(II) (13):

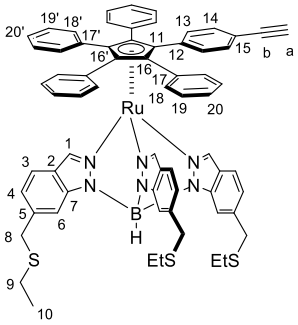


In a tube for microwave synthesis were placed a magnetic stir bar, ruthenium complex **12** (110 mg, 0.13 mmol, 1.0 eq.), thallium hydrotris(indazolyl)borate **TlTp$^{4Bo,6\text{-}CH2SEt}$** [S1] (201 mg, 0.25 mmol, 2.0 eq.) and anhydrous acetonitrile (4 mL). The mixture was then degassed by bubbling 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, CH_2Cl_2/pentane 1:1) to give complex **13** as an orange solid in 54% yield (90.3 mg, 0.07 mmol).

Caution! *This step involves the use and production of very toxic thallium salts. Appropriate safety measures should be discussed and implemented before reproducing this experiment.*

R_f = 0.45 (SiO_2, CH_2Cl_2/pentane 1:1). **^{1}H NMR** (500 MHz, CD_2Cl_2, 25 °C): δ = 7.89 (br. s, 6H, H_1 and H_6), 7.43 – 7.37 (m, 8H, $H_{18,\ 18'}$), 7.35 (AA'BB' pattern, ^3J = 8.7 Hz, 2H, H_{13}), 7.30 (d, ^3J = 8.3 Hz, 3H, H_3), 7.18 – 7.09 (m, 6H, H_{14} and $H_{20,\ 20'}$), 7.07 – 6.98 (m, 11H, H_4 and $H_{19,\ 19'}$), 3.90 (s, 6H, H_8), 2.47 (q, ^3J = 7.4 Hz, 6H, H_9), 1.28 (t, ^3J = 7.4 Hz, 9H, H_{10}), 1.08 (m, 21H, H_a and H_b) ppm. **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2, 25 °C): δ = 144.0 (C^2), 141.0 (C^1), 137.8 (C^5, C^{17} and $C^{17'}$), 135.1 (C^{12}), 134.2 (C^{18} and $C^{18'}$), 134.0 (C^{13}), 131.0 (C^{14}), 127.7 (C^{20} and $C^{20'}$), 127.5 (C^{19} and $C^{19'}$), 122.5 (C^7 and C^{15}), 122.4 (C^4), 120.3 (C^3), 111.4 (C^6), 107.2 (C^d), 91.7 (C^c), 88.8 (C^{16} or $C^{16'}$), 88.3 (C^{11}), 88.0 (C^{16} or $C^{16'}$), 36.9 (C^8), 25.7 (C^9), 18.8 (C^a), 14.7 (C^{10}), 11.7 (C^b) ppm. **HR-MS** (ESI$^+$): calcd. for $C_{78}H_{80}BN_6RuS_3Si$ [MH]$^+$:1313.4539, found 1313.4570.

η^5-1,2,3,4-Tetraphenyl-5-(4'-ethynyl)cyclopentadienyl hydrotris{6-[(ethylsulfanyl)methyl] indazol-1-yl}borate ruthenium(II) (14):

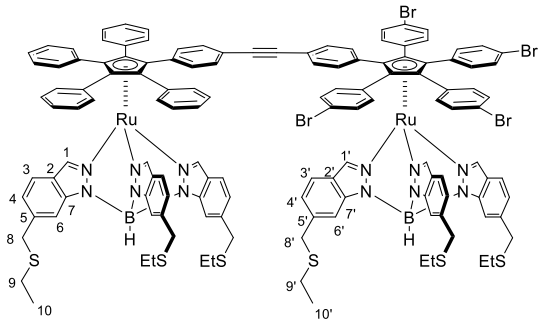


Complex **13** (58.7 mg, 0.04 mmol, 1 eq.) was placed in a round bottom flask with a magnetic stir bar, and dissolved in anhydrous THF (2 mL). The solution was cooled down to 0 °C and TBAF (1.0 M in THF, 0.07 mL, 0.07 mmol, 1.5 eq.) was added slowly. The solution was stirred at this temperature for one hour and filtered through a SiO_2 plug, eluted with CH_2Cl_2. The solvents were removed, and the crude product was purified by a short column chromatography (SiO_2, CH_2Cl_2/pentane 10:90) to give pure complex **14** as an orange solid in 98% yield (50.6 mg, 0.04 mmol).

R_f = 0.41 (SiO_2, CH_2Cl_2/pentane 1:1). **^{1}H NMR** (500 MHz, CD_2Cl_2, 25 °C): δ = 7.89 (br. s, 3H, H_6), 7.88 (s, 3H, H_1), 7.42 – 7.35 (m, 10H, H_{13} and $H_{18,\ 18'}$), 7.29 (d, ^3J = 8.4 Hz, 3H, H_3), 7.17 – 7.11 (m, 6H, H_{14} and $H_{20,\ 20'}$), 7.06 – 6.97 (m, 11H, H_4 and $H_{19,\ 19'}$), 3.90 (s, 6H, H_8), 3.08 (s, 1H, H_a), 2.47 (q, ^3J = 7.4 Hz, 6H, H_9), 1.27 (t, ^3J = 7.4 Hz, 9H, H_{10}) ppm. **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2, 25 °C): δ = 144.0 (C^2), 140.9 (C^1), 137.8 (C^5, C^{17} and $C^{17'}$), 135.7 (C^{12}), 134.1 (C^{13}, C^{18} and $C^{18'}$), 131.2 (C^{14}), 127.7 (C^{20} and $C^{20'}$), 127.6 (C^{19} and $C^{19'}$), 122.5 (C^7), 122.4 (C^4), 121.1 (C^{15}), 120.3 (C^3), 111.4 (C^6), 88.7 (C^{16} or $C^{16'}$), 88.3 (C^{16} or $C^{16'}$), 87.7 (C^{11}), 83.7 (C^b), 78.0

(C^a), 36.9 (C^8), 25.7 (C^9), 14.7 (C^{10}) ppm. **HR-MS** (ESI^+): calcd. for $C_{67}H_{60}BN_6RuS_3$ $[MH]^+$:1157.3202, found 1157.3184.

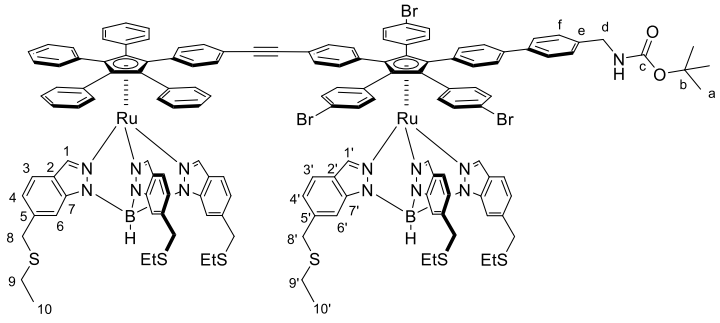
Complex 15:



Complex **1b**[S1] (48 mg, 30.3 µmol, 1.0 eq.), complex **14** bearing a free alkyne (52.5 mg, 45.4 µmol, 1.5 eq.) and a magnetic stir bar were placed in a Schlenk tube under argon. Anhydrous THF (2 mL) and anhydrous triethylamine (0.5 mL) were added and the mixture was degassed by a freeze-pump-thaw cycle. $Pd(PPh_3)_2Cl_2$ (2.17 mg, 3.0 µmol, 10 mol%) and CuI (0.3 mg, 1.5 µmol, 5 mol%) were added under an argon flow. The suspension was degassed again by two successive freeze-pump-thaw cycles and 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/pentane 50:50 to 70:30) to give complex **15** as an orange solid in 74% yield (58 mg, 22 µmol).

R_f = 0.38 (SiO_2, CH_2Cl_2/hexane 40:60). **^{1}H NMR** (500 MHz, CD_2Cl_2, 25 °C): δ = 7.90 (s, 6H, $H_{6, 6'}$), 7.89 (m, 3H, H_1 or $H_{1'}$), 7.83 (s, 3H, H_1 or $H_{1'}$), 7.44 – 7.11 (m, 40H, H_{Ar}), 7.07 – 7.00 (m, 16H, H_{Ar}), 3.91 (s, 12H, $H_{8, 8'}$), 2.47 (q, ^3J = 7.4 Hz, 12H, $H_{9, 9'}$), 1.29 (t, ^3J = 7.4 Hz, 18H, $H_{10, 10'}$) ppm. **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2, 25 °C): δ = 144.1 (C^2 or $C^{2'}$), 144.0 (C^2 or $C^{2'}$), 140.9 (C^1 or $C^{1'}$), 140.7 (C^1 or $C^{1'}$), 138.2 (C^5 or $C^{5'}$), 137.8 (C^5 or $C^{5'}$), 136.5 ($C^{quat\text{-}Ar}$), 135.5 ($C^{CH\text{-}Ar}$), 135.2 ($C^{quat\text{-}Ar}$), 134.1 (C^{CHAr}), 134.0 ($C^{quat\text{-}Ar}$), 133.9 ($C^{CH\text{-}Ar}$), 133.8 ($C^{quat\text{-}Ar}$), 132.7 ($C^{quat\text{-}Ar}$), 132.6 ($C^{quat\text{-}Ar}$), 131.6 ($C^{CH\text{-}Ar}$), 131.1 ($C^{CH\text{-}Ar}$), 130.9 ($C^{CH\text{-}Ar}$), 130.6 ($C^{CH\text{-}Ar}$), 127.7 ($C^{CH\text{-}Ar}$), 127.6 ($C^{CH\text{-}Ar}$), 127.5 ($C^{CH\text{-}Ar}$), 122.7 (C^4 or $C^{4'}$), 122.5 (C^7 or $C^{7'}$), 122.5 (C^4 or $C^{4'}$), 122.3 (C^7 or $C^{7'}$), 122.0 ($C^{quat\text{-}Ar}$), 120.4 (C^3 or $C^{3'}$), 120.3 (C^3 or $C^{3'}$), 111.4 (C^6 and $C^{6'}$), 90.6 ($C^{quat\text{-}alkyne}$), 89.9 ($C^{quat\text{-}alkyne}$), 88.8 ($C^{quat\text{-}Cp}$), 88.8 ($C^{quat\text{-}Cp}$), 88.3 ($C^{quat\text{-}Cp}$), 88.2 ($C^{quat\text{-}Cp}$), 88.1 ($C^{quat\text{-}Cp}$), 88.0 ($C^{quat\text{-}Cp}$), 87.6 ($C^{quat\text{-}Cp}$), 87.5 ($C^{quat\text{-}Cp}$), 87.2 ($C^{quat\text{-}Cp}$), 36.9 (C^8 and $C^{8'}$), 25.7 (C^9 and $C^{9'}$), 14.8 (C^{10} and $C^{10'}$) ppm. **HR-MS** (ESI^+): calcd. for $C_{132}H_{112}B_2Br_4N_{12}Ru_2S_6$ $[M]^+$:2602.2485, found 2602.2542.

Complex 16 (obtained as an unseparable mixture of 1,2- and 1,3-disubstituted regioisomers):

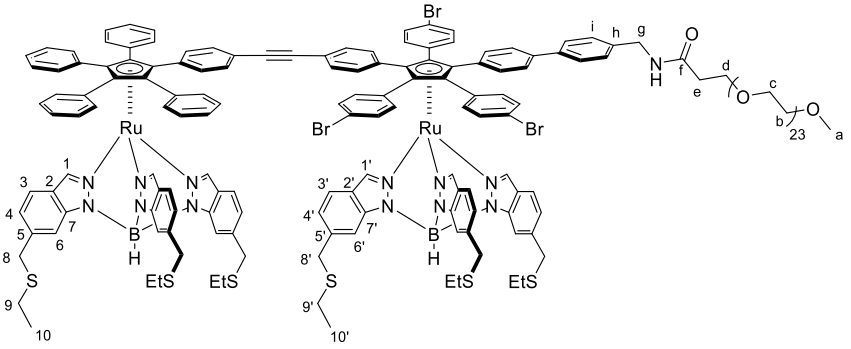


In a Schlenk tube were placed a stir bar, complex **15** (52.5 mg, 20.2 µmol, 1.0 eq.), *N*-(*tert*-butoxycarbonyl) 4-(aminomethyl) phenylboronic acid pinacol ester (6.1 mg, 18.2 µmol, 0.9 eq.), cesium carbonate Cs_2CO_3 (13.2 mg, 40.4 µmol, 2.0 eq.), DMF (0.4 mL) and water (4 µL). The resulting suspension was degassed by a freeze-pump-thaw cycle and $Pd(dppf)Cl_2$ (1.5 mg, 2 µmol, 10 mol%) was added under an argon flow. The reaction was then heated to 100 °C for 48 hours. After cooling down to room temperature, the crude suspension was filtered over a plug of silica (eluted

with CH_2Cl_2), the solvents were removed using rotary evaporation and the crude residue was purified by column chromatography (SiO_2, CH_2Cl_2/pentane 80:20 to 100:0). Complex **16** was obtained in 16% yield (8.8 mg, 3.2 µmol) as an orange solid and as an unseparable mixture of 1,2- and 1,3-disubstituted regioisomers.

R_f = 0.56 (SiO_2, CH_2Cl_2/hexane 20:80). **^{1}H NMR** (500 MHz, CD_2Cl_2, 25 °C): δ = 7.88 (s, 6H, H_6), 7.87 (s, 3H, H_1 or $H_{1'}$), 7.85 (s, 3H, H_1 or $H_{1'}$), 7.49 – 7.47 (m, 3H, H_{Ar}), 7.42 – 7.07 (m, 43H, H_{Ar}), 7.04 – 6.98 (m, 14H, H_{Ar}), 4.94 (br. s, 1H, NH), 4.28 (d, ^3J = 5.4 Hz, 2H, H_d), 3.89 (br. s, 12H, $H_{8,8'}$), 2.46 (q, ^3J = 7.4 Hz, 12H, $H_{9,9'}$), 1.42 (s, 9H, H_a), 1.27 (t, ^3J = 7.4 Hz, 18H, $H_{10,10'}$) ppm. For $H_{8,8'}$, $H_{9,9'}$ and $H_{10,10'}$ two similar signals with identical coupling constants are overlapping due to the presence of regioisomers. **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2, 25 °C): δ = 156.2 (C^c), 144.1 (C^2 or $C^{2'}$), 144.0 (C^2 or $C^{2'}$), 140.9 (C^1 or $C^{1'}$), 140.7 (C^1 or $C^{1'}$), 140.0 ($C^{quat\text{-}Ar}$), 139.3 (C^e), 138.1 (C^5 or $C^{5'}$), 137.8 (C^5 or $C^{5'}$), 135.7 ($C^{CH\text{-}Ar}$), 135.6 ($C^{CH\text{-}Ar}$), 135.2 ($C^{quat\text{-}Ar}$), 134.3 ($C^{CH\text{-}Ar}$), 134.1 ($C^{CH\text{-}Ar}$), 134.1 ($C^{CH\text{-}Ar}$), 134.0 ($C^{CH\text{-}Ar}$), 133.1 ($C^{quat\text{-}Ar}$), 133.0 ($C^{quat\text{-}Ar}$), 132.9 ($C^{quat\text{-}Ar}$), 132.8 ($C^{quat\text{-}Ar}$), 132.5 ($C^{quat\text{-}Ar}$), 132.4 ($C^{quat\text{-}Ar}$), 132.4 ($C^{quat\text{-}Ar}$), 131.0 ($C^{CH\text{-}Ar}$), 130.9 ($C^{CH\text{-}Ar}$), 130.6 ($C^{CH\text{-}Ar}$), 128.1 (C^f), 127.6 ($C^{CH\text{-}Ar}$), 127.5 ($C^{CH\text{-}Ar}$), 127.3 ($C^{CH\text{-}Ar}$), 126.2 ($C^{CH\text{-}Ar}$), 122.6 (C^4 or $C^{4'}$), 122.5 (C^7 and $C^{7'}$), 122.4 (C^4 or $C^{4'}$), 122.2 ($C^{quat\text{-}Ar}$), 122.0 ($C^{quat\text{-}Ar}$), 120.4 (C^3 or $C^{3'}$), 120.3 (C^3 or $C^{3'}$), 111.3 (C^6 and $C^{6'}$), 90.4 ($C^{quat\text{-}alkyne}$), 90.0 ($C^{quat\text{-}alkyne}$), 88.8 ($C^{quat\text{-}Cp}$), 88.4 ($C^{quat\text{-}Cp}$), 88.1 ($C^{quat\text{-}Cp}$), 88.1 ($C^{quat\text{-}Cp}$), 88.0 ($C^{quat\text{-}Cp}$), 87.8 ($C^{quat\text{-}Cp}$), 87.7 ($C^{quat\text{-}Cp}$), 87.5 ($C^{quat\text{-}Cp}$), 87.2 ($C^{quat\text{-}Cp}$), 86.9 ($C^{quat\text{-}Cp}$), 79.5 (C^b), 44.5 (C^d), 36.9 (C^8 and $C^{8'}$), 28.5 (C^a), 25.7 (C^9 and $C^{9'}$), 14.7 (C^{10} and $C^{10'}$) ppm. C^b, C^c and C^d did not appear on the ^{13}C{^{1}H} NMR but their chemical shifts were attributed thanks to correlations on HMBC and HSQC 2D-NMR spectra. **HR-MS** (MALDI): calcd. for $C_{144}H_{128}B_2Br_3N_{13}O_2Ru_2S_6$ $[M]^+$: 2728.4500, found 2728.4729.

Complex M5 (obtained as an unseparable mixture of 1,2- and 1,3-disubstituted regioisomers):



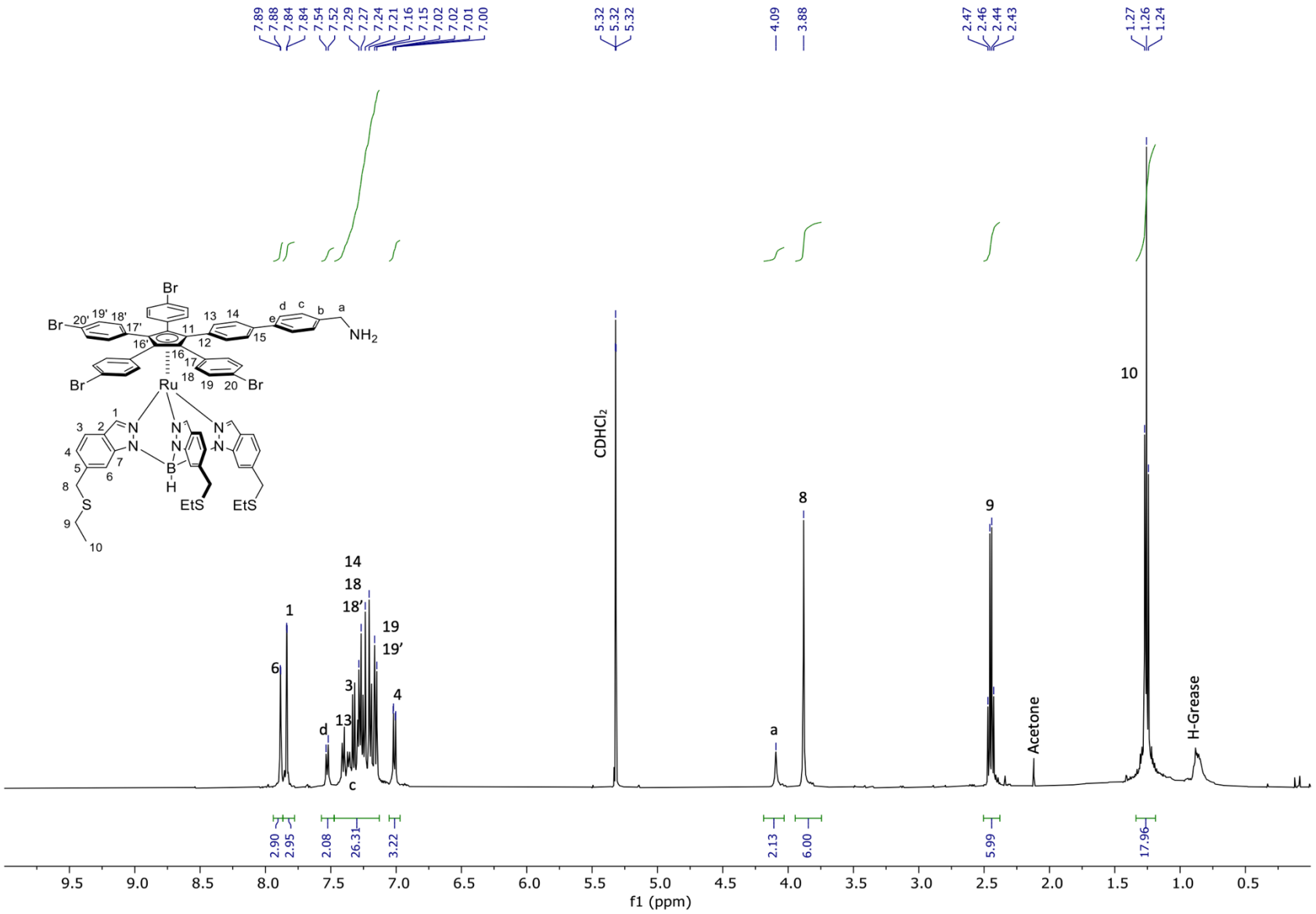
Complex **16** (as a mixture of 1,2- and 1,3-disubstituted regioisomers) (8 mg, 2.9 µmol, 1.0 eq.) was dissolved in anhydrous CH_2Cl_2 (0.5 mL). The solution was cooled down to 0 °C. Then, 2,6-lutidine (25 µL, 59 µmol, 20 eq.) and trimethylsilyl trifluoromethanesulfonate (5 µL, 30 µmol, 10 eq.) were successively added. The solution was stirred for one hour at 0 °C, followed by one more hour at room temperature. Methanol (1 mL) was then added to quench the reaction. The solvents were removed *in vacuo* and the residue was purified thanks to a short column chromatography (SiO_2, MeOH/CH_2Cl_2 2.5/97.5). The partially purified product was then dissolved in a minimal amount of CH_2Cl_2, and heptane (5 mL) was added. CH_2Cl_2 was removed by rotary evaporation and the precipitate was filtered over celite, rinsed with pentane and finally recovered in CH_2Cl_2. CH_2Cl_2 was evaporated again to give the Boc-deprotected complex bearing a free benzylamine as an orange solid in 58% yield (4.5 mg, 1.7 µmol).

R_f = 0.24 (SiO_2, MeOH/CH_2Cl_2 5:95).

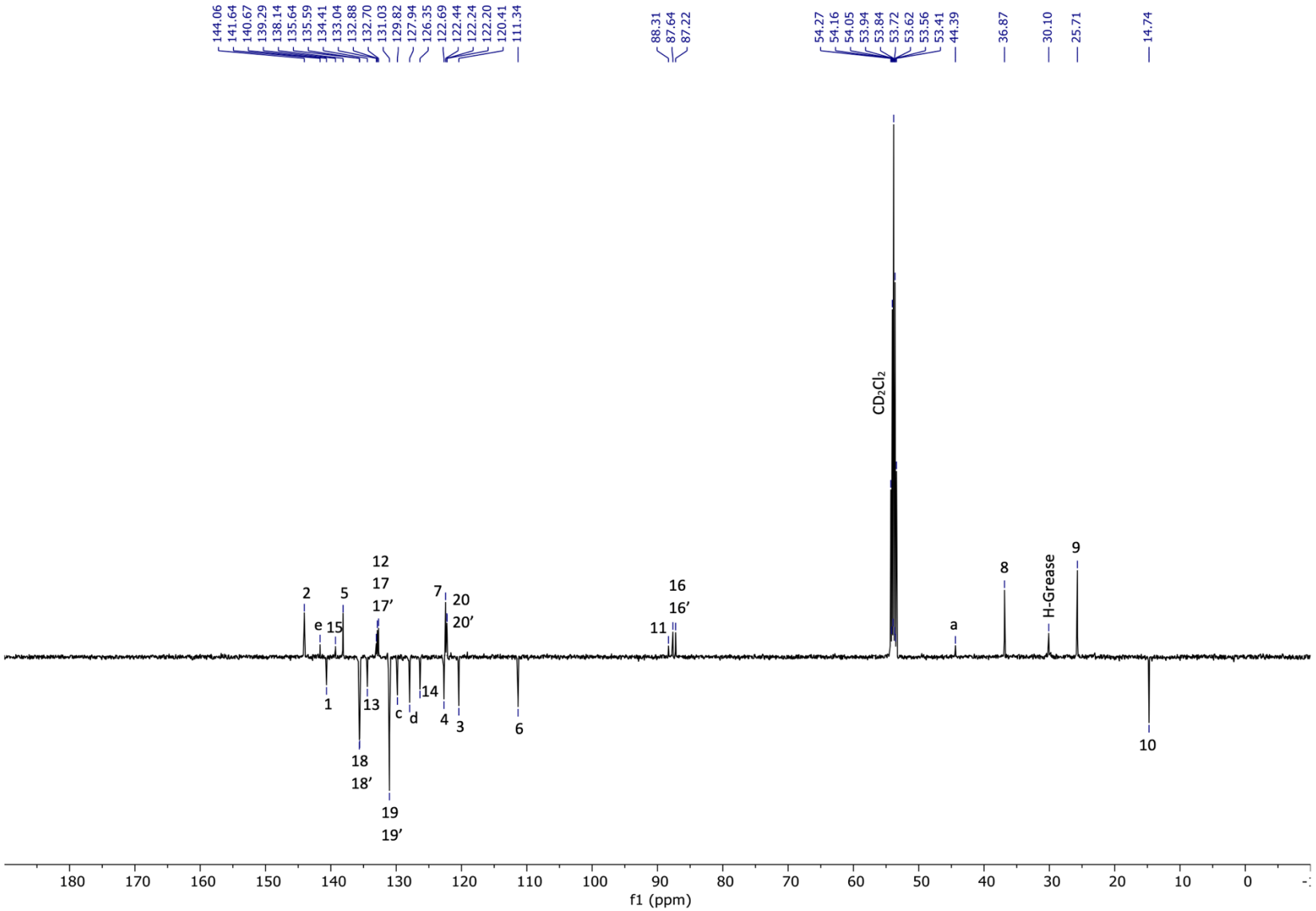
The previous complex bearing a free benzylamine (2.0 mg, 0.8 µmol, 1.0 eq.) was next introduced in a J-Young NMR tube along with $mPEG_{24}$-NHS ester (**4**) (4.6 mg, 3.8 µmol, 5 eq.), deuterated *N,N*-dimethylformamide (DMF-d_7) (0.5 mL) and anhydrous triethylamine (1 µL, 7.6 µmol, 10 eq.). The mixture was degassed by three successive freeze-pump-thaw cycles and heated at 40 °C for 48 hours. The solvent was then evaporated and the crude product was adsorbed on silica and washed with ethyl acetate (10 mL) and CH_2Cl_2 (10 mL) which induced elution of eventual leftover starting material and excess PEG chain but not of the desired compound. The product was then eluted with DMF and the solvent was removed *in vacuo*. The residue was then dissolved in a minimal amount of CH_2Cl_2 and heptane was added. CH_2Cl_2 was removed by rotary evaporation to induce precipitation, and the precipitate was filtered over celite and washed with cold pentane. Finally, the pure compound was recovered in CH_2Cl_2, evaporated to dryness to give complex **M5** in 11% yield (0.3 mg, 0.08 µmol, 6% yield over two steps) as an orange amorphous solid and as an unseparable mixture of 1,2- and 1,3-disubstituted regioisomers.

R_f: A reliable R_f value could not be determined for this compound due to important tailing on TLCs.
^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): δ = 7.93 – 7.87 (m, 12H, $H_{1,\,1'}$ and $H_{6,\,6'}$), 7.60 – 6.95 (m, 60H, H_{Ar}), 4.45 (d, ^3J = 6.1 Hz, 2H, H_g), 3.93 (br. s, 12H, $H_{8,\,8'}$), 3.77 (t, ^3J = 5.8 Hz, 2H, H_d), 3.66 – 3.45 (m, 92H, H_b and H_c), 3.37 (s, 3H, H_a), 2.52 – 2.47 (m, 14H, $H_{9,\,9'}$ and H_e), 1.31 (t, ^3J = 7.4 Hz, 18H, $H_{10,\,10'}$) ppm. **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2, 25 °C): δ = 171.2 (C^f), 143.6 (C^2 and $C^{2'}$), 140.5 (C^1 or $C^{1'}$), 140.3 (C^1 or $C^{1'}$), 139.7 ($C^{quat\text{-}Ar}$), 138.5 (C^h), 137.7 (C^5 or $C^{5'}$), 137.4 (C^5 or $C^{5'}$), 135.3 ($C^{CH\text{-}Ar}$), 135.2 ($C^{CH\text{-}Ar}$), 134.8 ($C^{quat\text{-}Ar}$), 133.7 ($C^{CH\text{-}Ar}$), 133.6 ($C^{CH\text{-}Ar}$), 132.6 ($C^{quat\text{-}Ar}$), 132.4 ($C^{quat\text{-}Ar}$), 132.0 ($C^{quat\text{-}Ar}$), 130.6 ($C^{CH\text{-}Ar}$), 130.5 ($C^{CH\text{-}Ar}$), 130.2 ($C^{CH\text{-}Ar}$), 127.8 (C^i), 127.2 ($C^{CH\text{-}Ar}$), 127.1 ($C^{CH\text{-}Ar}$), 126.8 ($C^{CH\text{-}Ar}$), 125.8 ($C^{CH\text{-}Ar}$), 122.2 (C^4 or $C^{4'}$), 122.0 (C^7 or $C^{7'}$), 122.0 (C^4 or $C^{4'}$), 121.7 (C^7 or $C^{7'}$), 120.0 (C^3 or $C^{3'}$), 119.9 (C^3 or $C^{3'}$), 110.9 (C^6 or $C^{6'}$), 90.0 ($C^{quat\text{-}alkyne}$), 89.6 ($C^{quat\text{-}alkyne}$), 88.4 ($C^{quat\text{-}Cp}$), 87.7 ($C^{quat\text{-}Cp}$), 87.3 ($C^{quat\text{-}Cp}$), 87.2 ($C^{quat\text{-}Cp}$), 71.9 (C^b and C^c), 70.5 (C^b and C^c), 67.2 (C^d), 58.6 (C^a), 42.7 (C^g), 37.0 (C^e), 36.5 (C^8 and $C^{8'}$), 25.3 (C^9 and $C^{9'}$), 14.3 (C^{10} and $C^{10'}$) ppm. **HR-MS** (MALDI): calcd. for $C_{189}H_{218}B_2Br_3N_{13}O_{25}Ru_2S_6Na$ $[M+Na]^+$: 3751.0281, found 3751.0292.

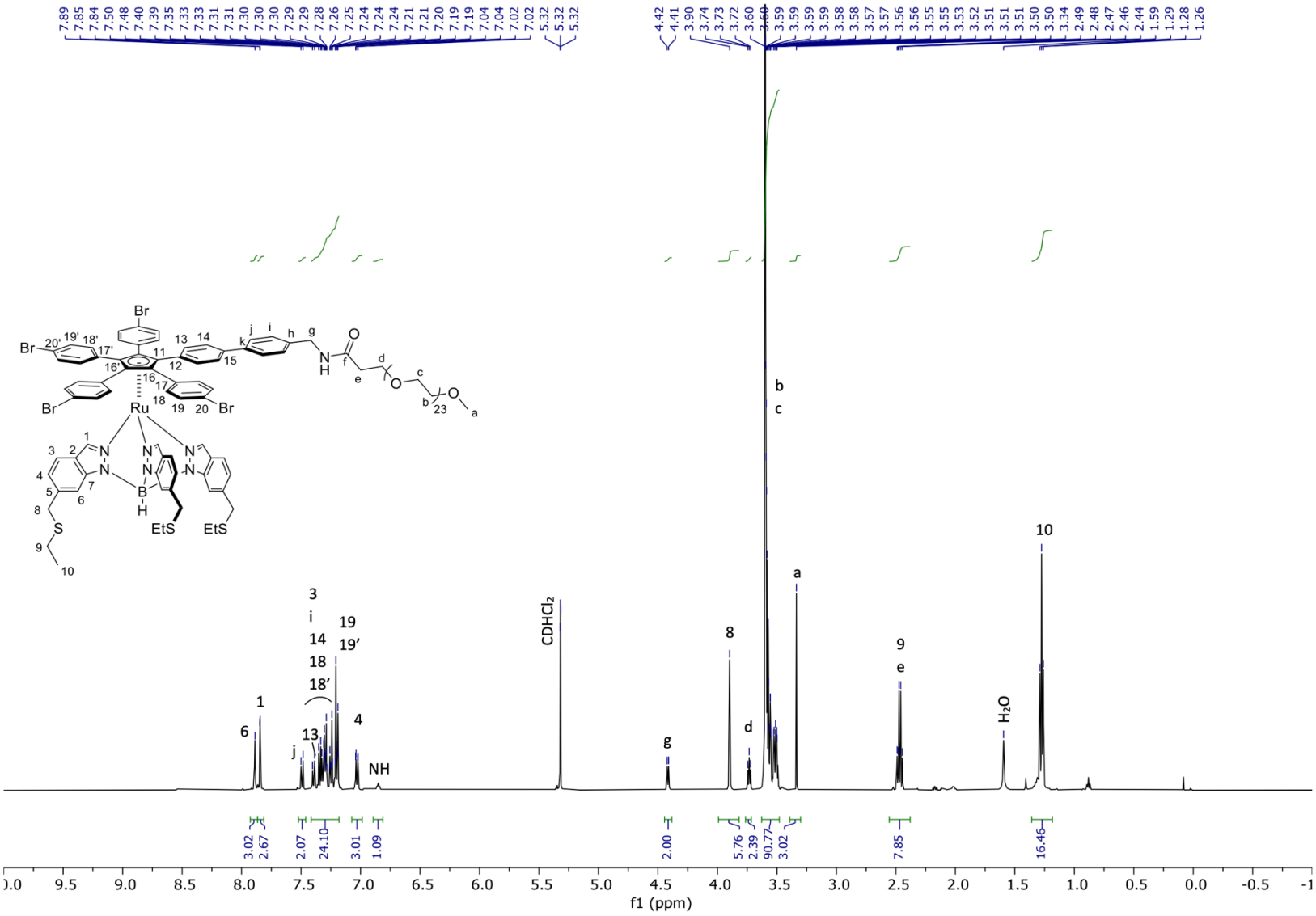
c. NMR spectra of the compounds



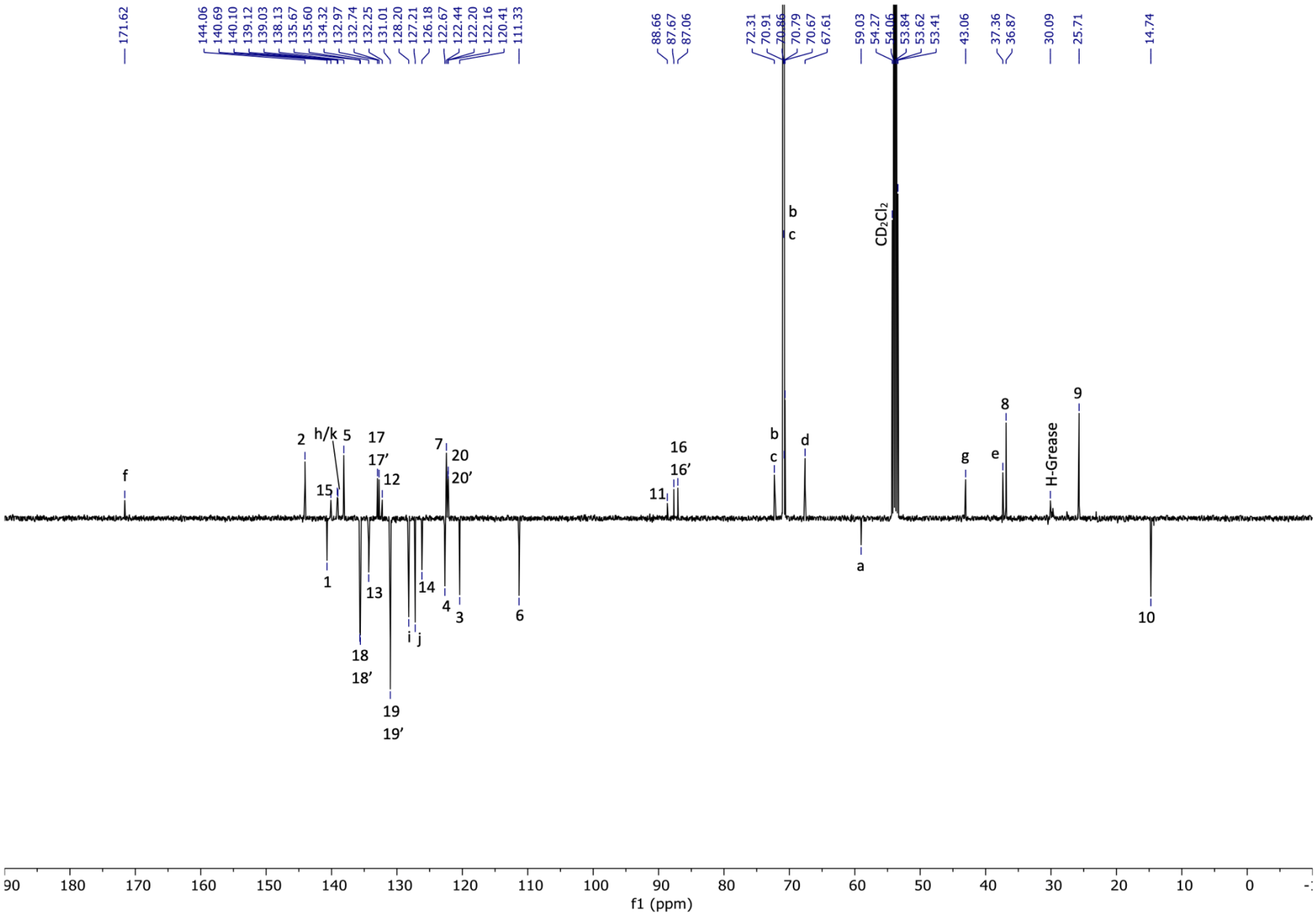
^{1}H-NMR of complex **3** (500 MHz, CD_2Cl_2, 25°C).



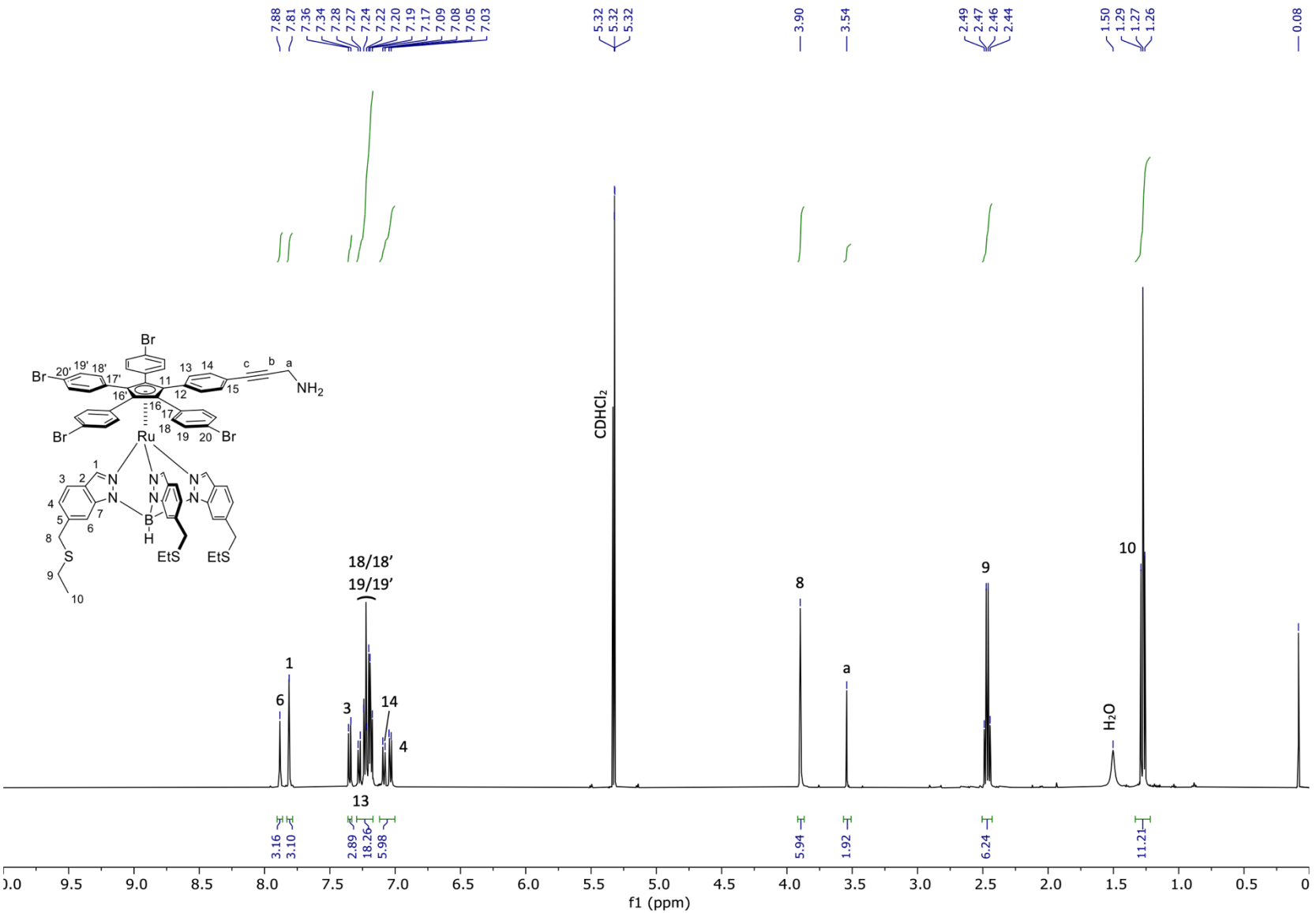
^{13}C-Jmod-NMR of complex **3** (126 MHz, CD_2Cl_2, 25°C).



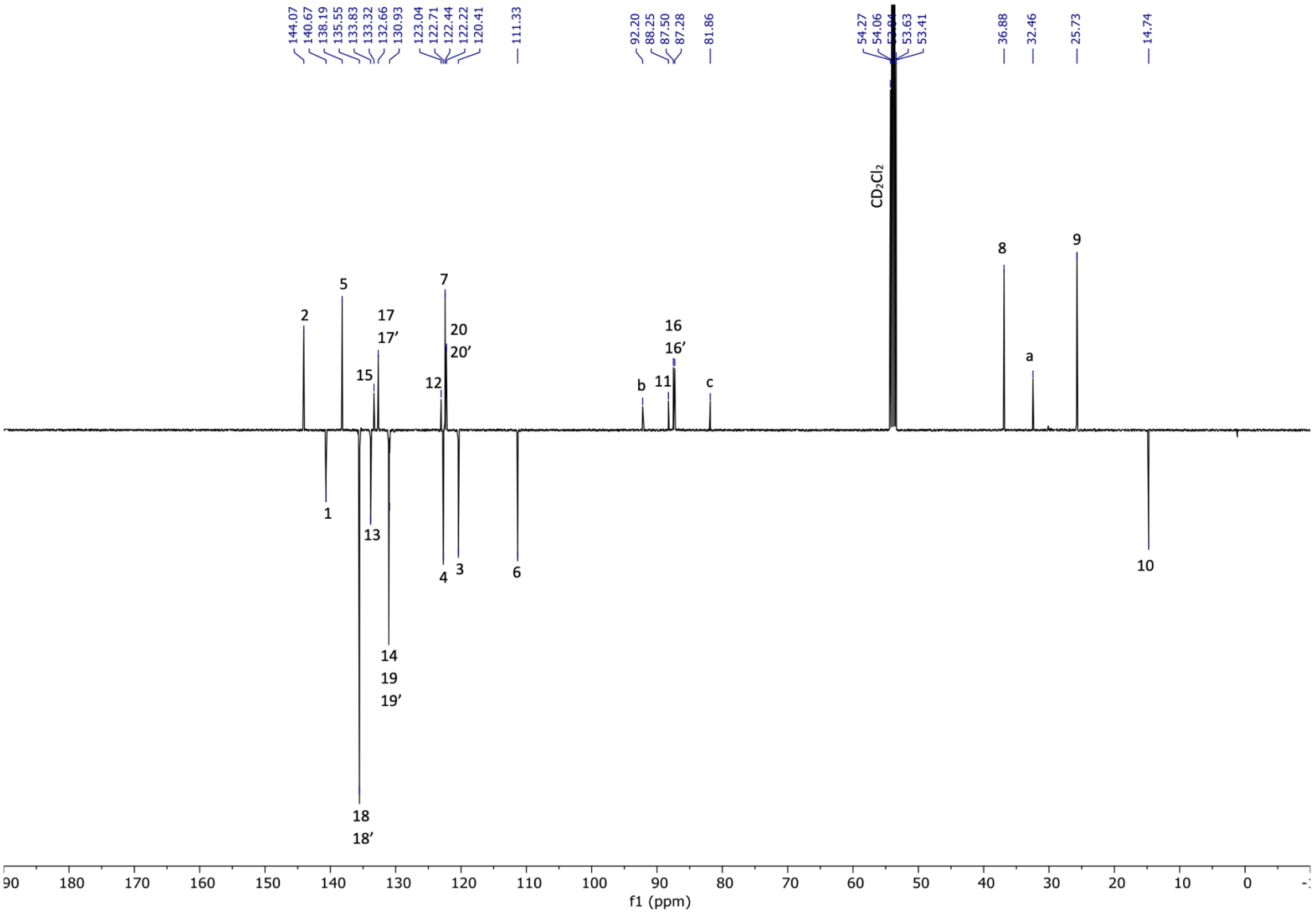
^{1}H-NMR of complex **M1** (500 MHz, CD_2Cl_2, 25°C).



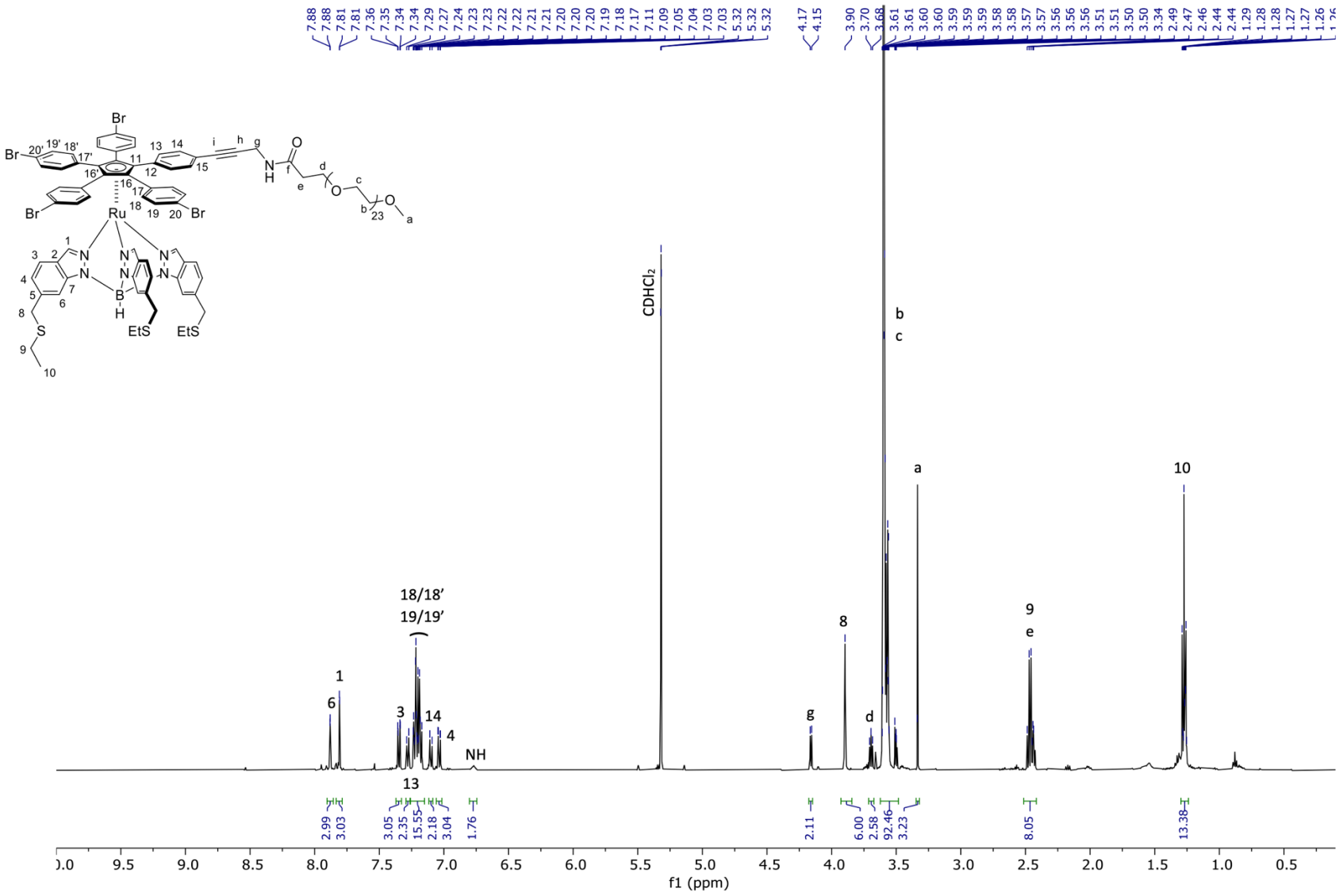
^{13}C-Jmod-NMR of complex **M1** (126 MHz, CD_2Cl_2, 25°C).



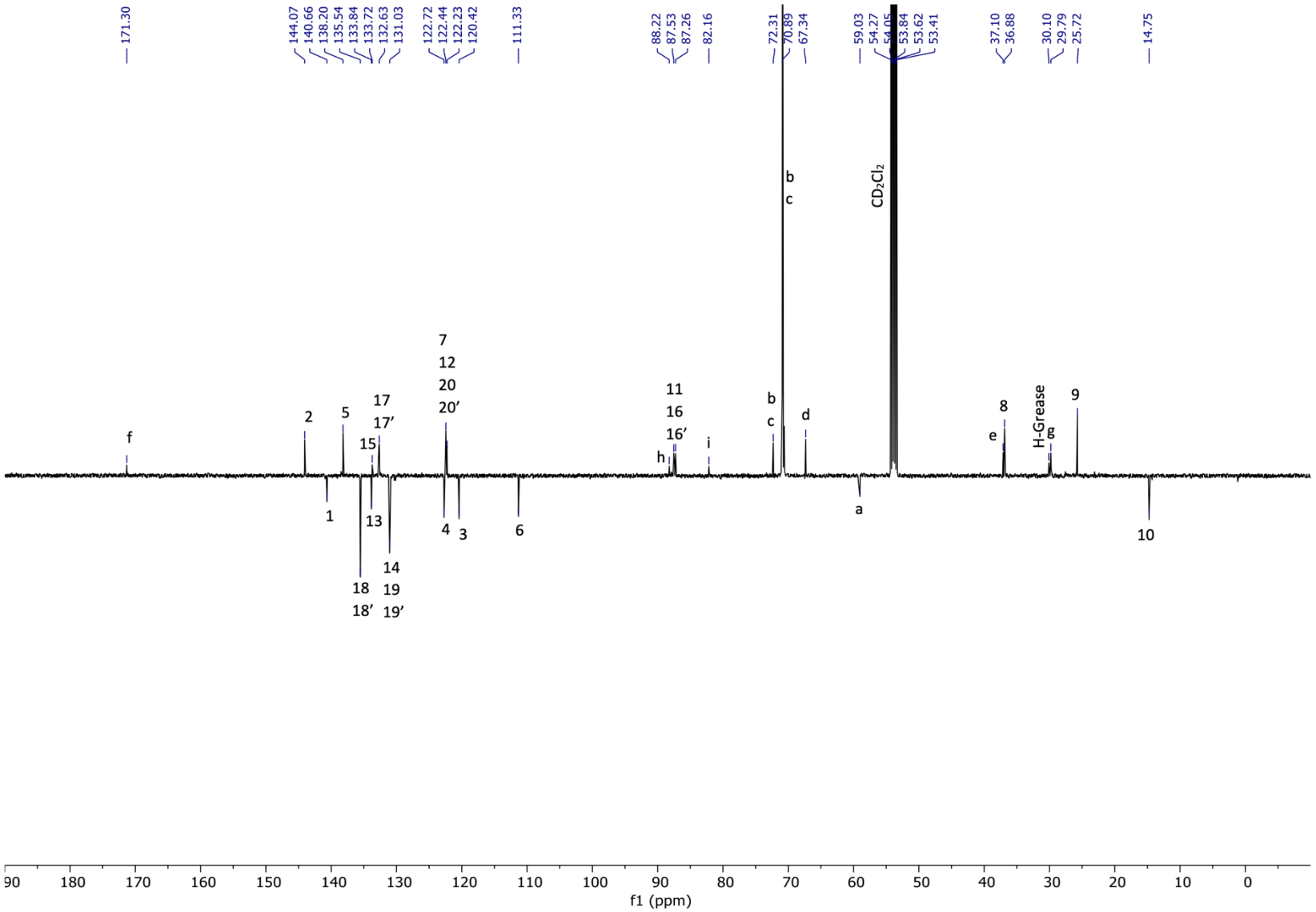
^{1}H-NMR of complex **6** (500 MHz, CD_2Cl_2, 25°C).



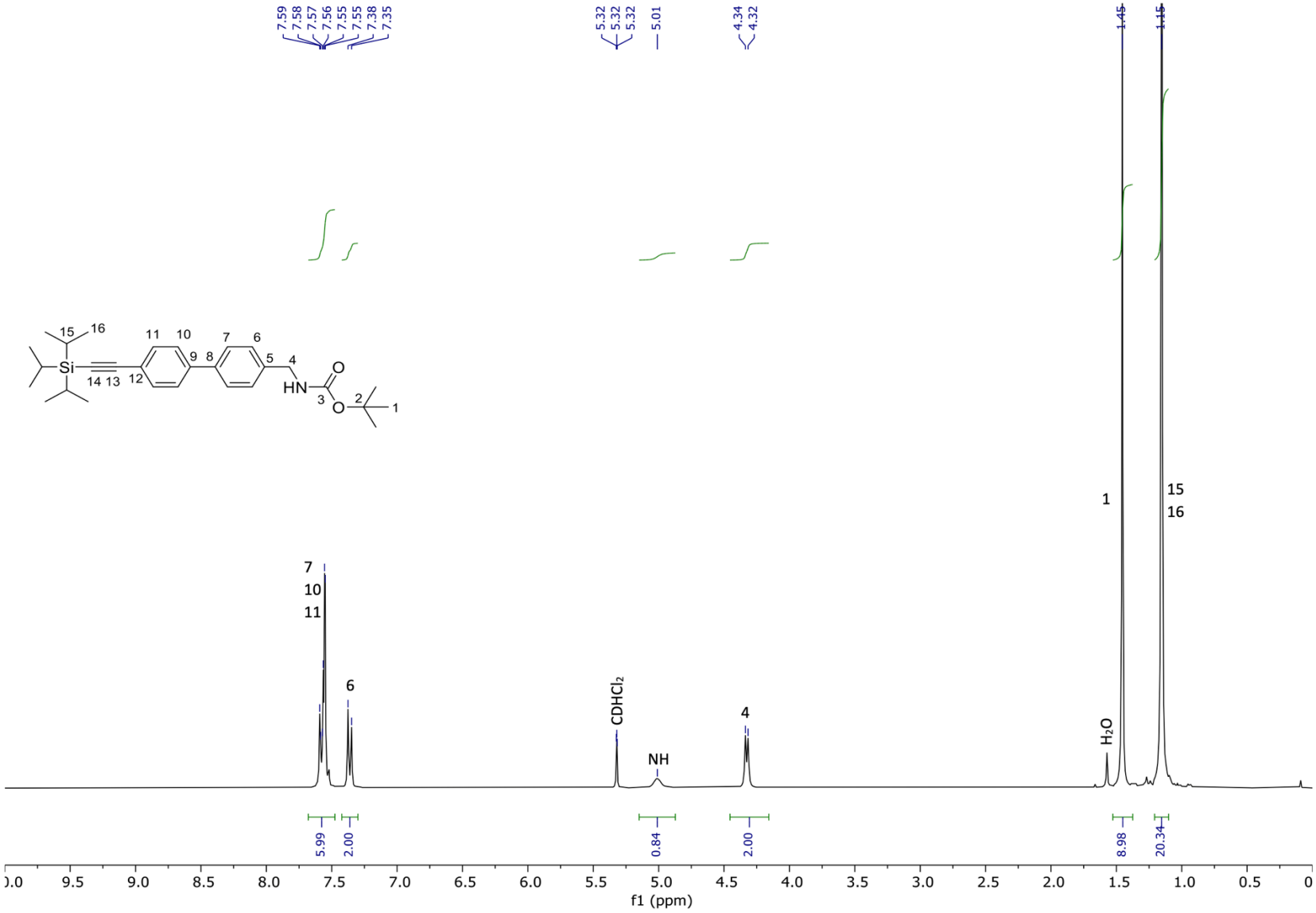
^{13}C-Jmod-NMR of complex **6** (126 MHz, CD_2Cl_2, 25°C).



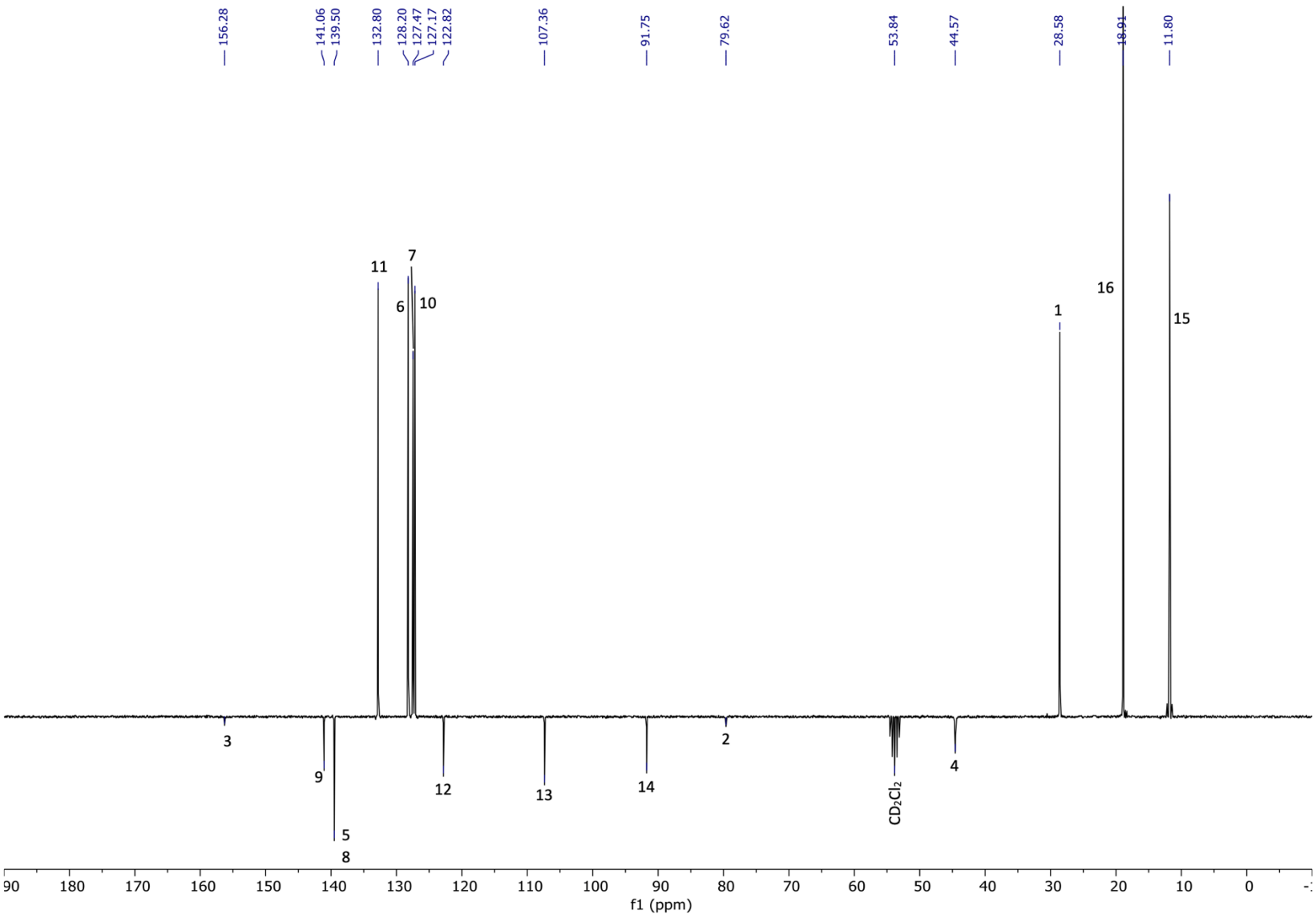
^{1}H-NMR of complex **M2** (500 MHz, CD_2Cl_2, 25°C).



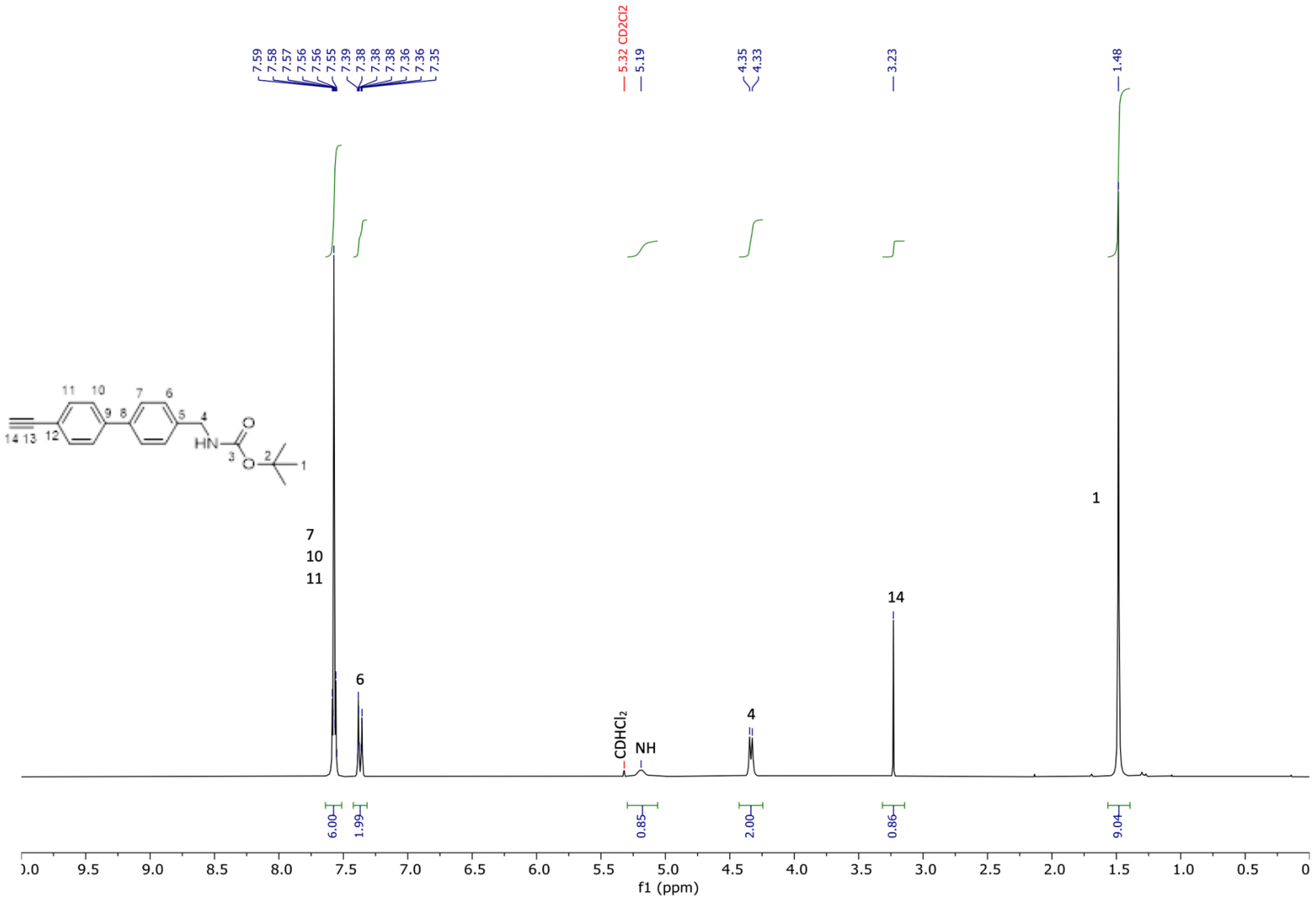
^{13}C-Jmod-NMR of complex **M2** (126 MHz, CD_2Cl_2, 25°C).



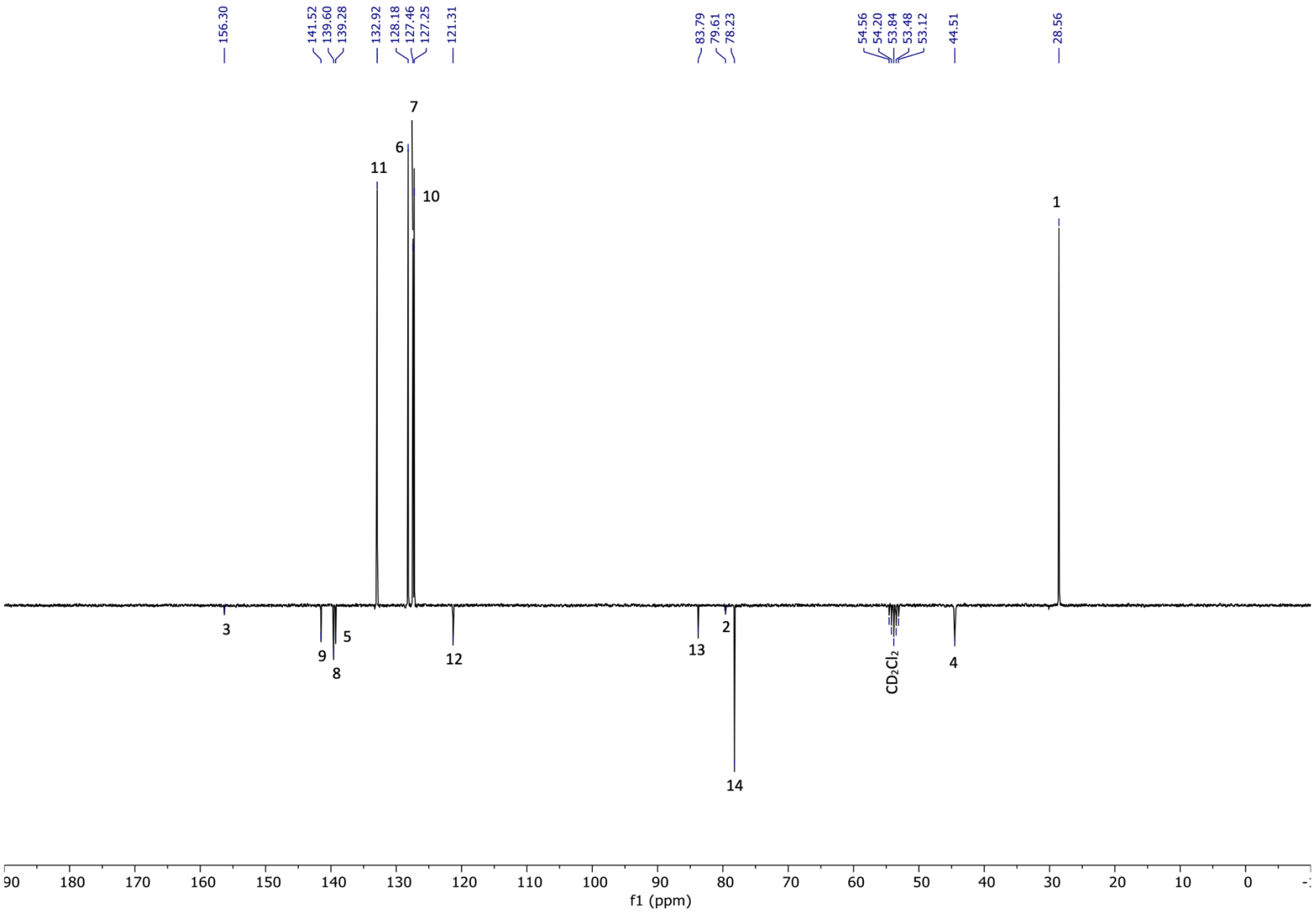
^{1}H-NMR of compound **7a** (300 MHz, CD_2Cl_2, 25°C).



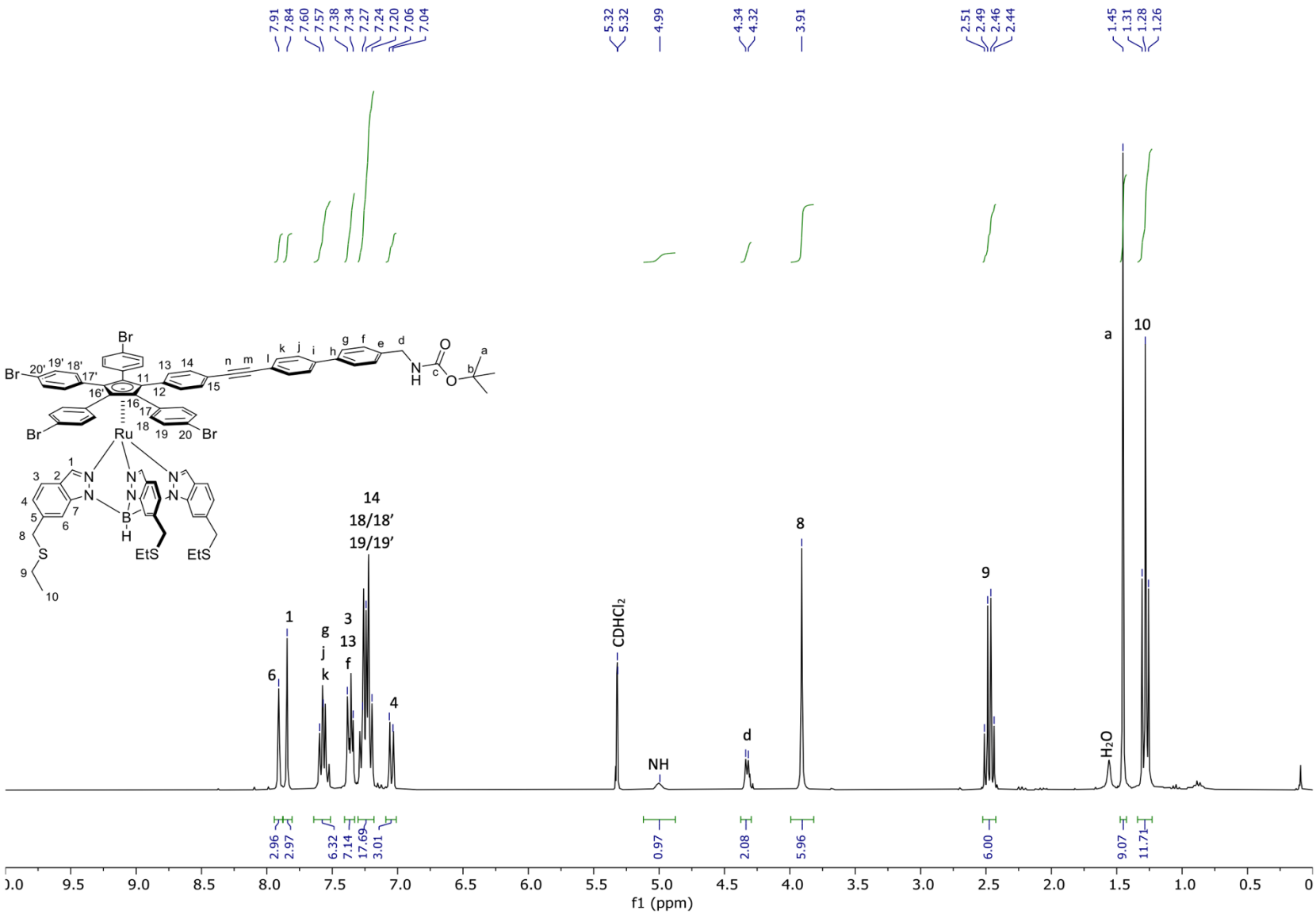
^{13}C-Jmod-NMR of compound **7a** (75 MHz, CD_2Cl_2, 25°C).



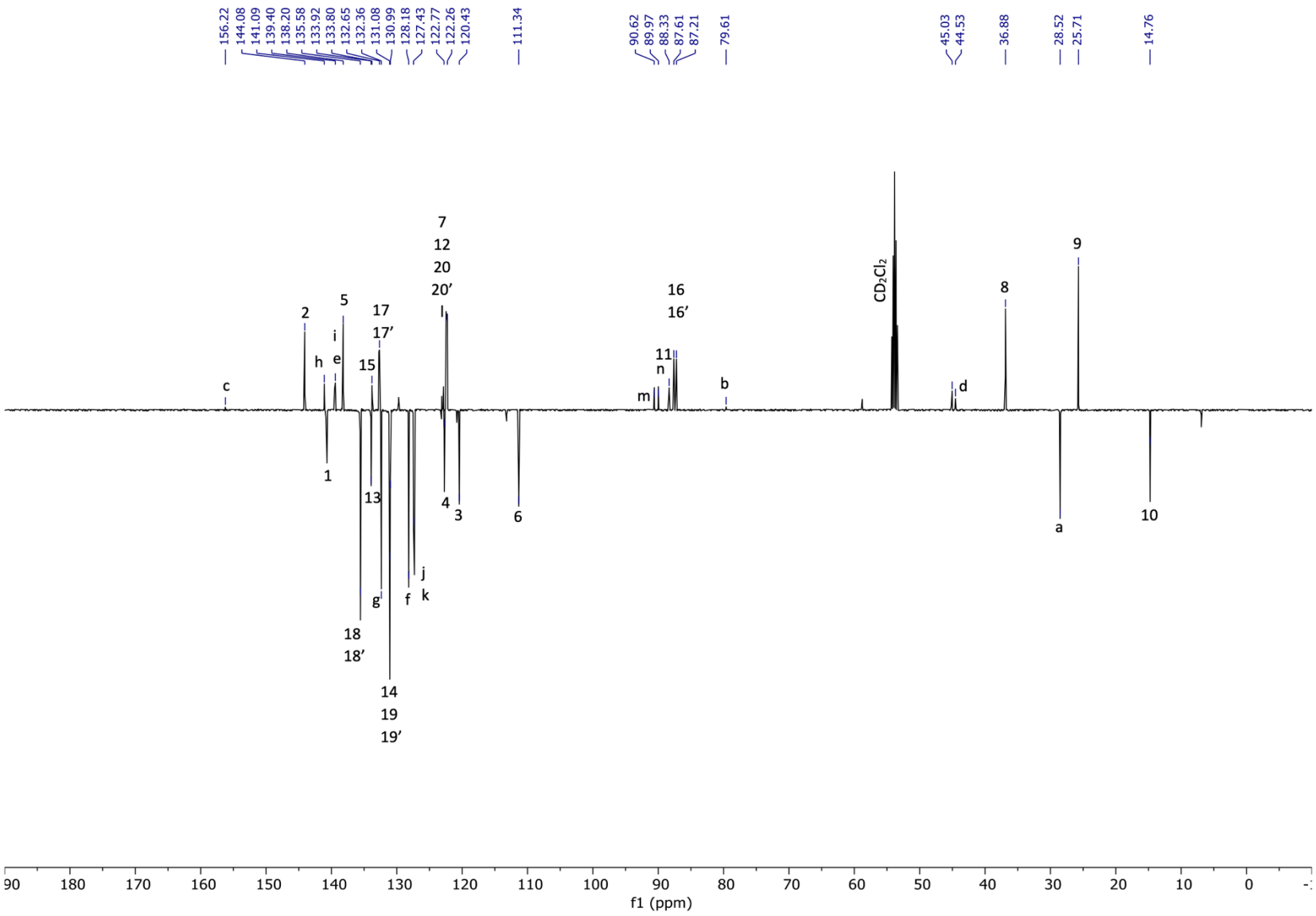
^{1}H-NMR of compound **7b** (300 MHz, CD_2Cl_2, 25°C).



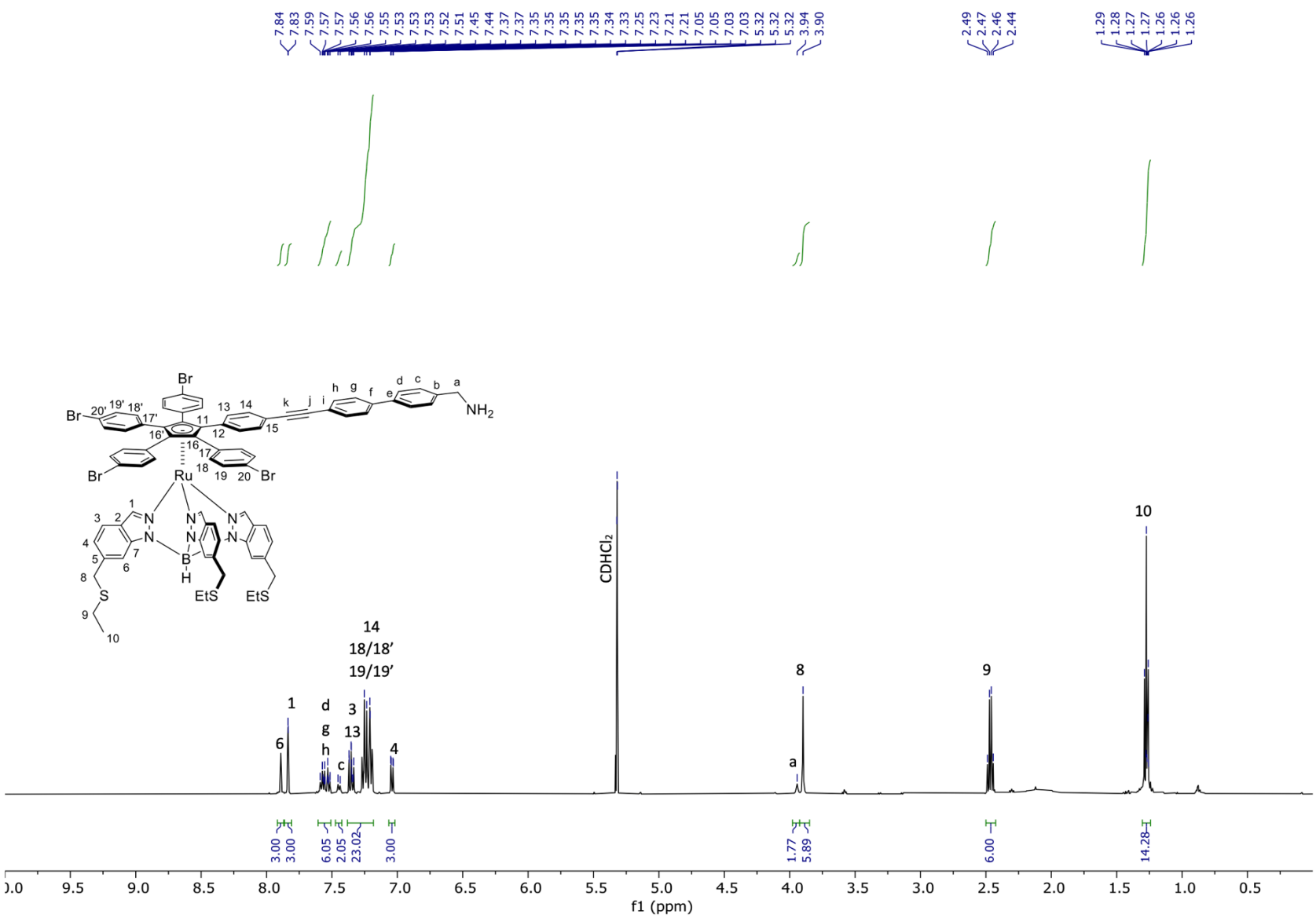
^{13}C-Jmod-NMR of compound **7b** (75 MHz, CD_2Cl_2, 25°C).



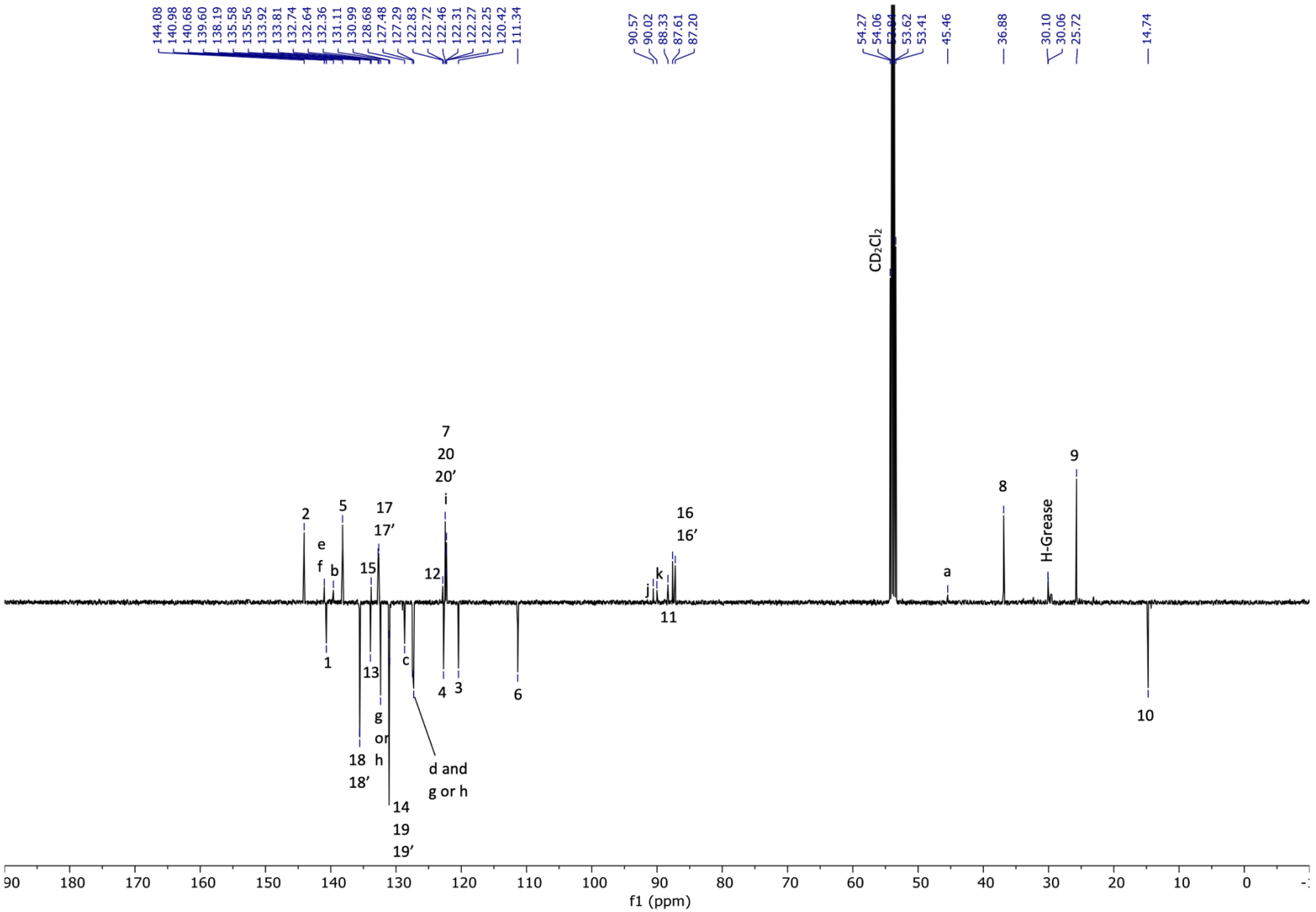
^{1}H-NMR of complex **8** (300 MHz, CD_2Cl_2, 25°C).



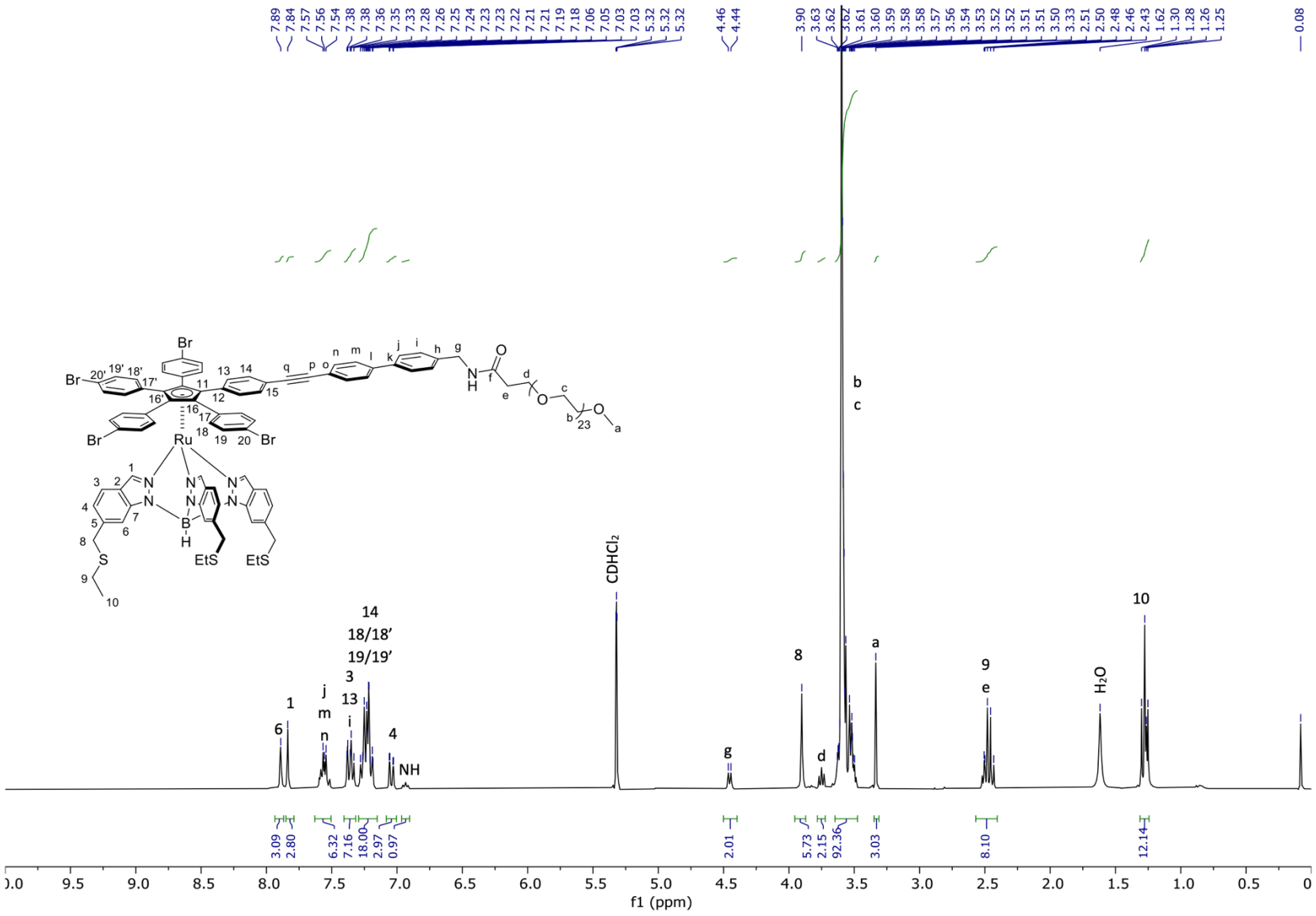
^{13}C-Jmod-NMR of complex **8** (126 MHz, CD_2Cl_2, 25°C).



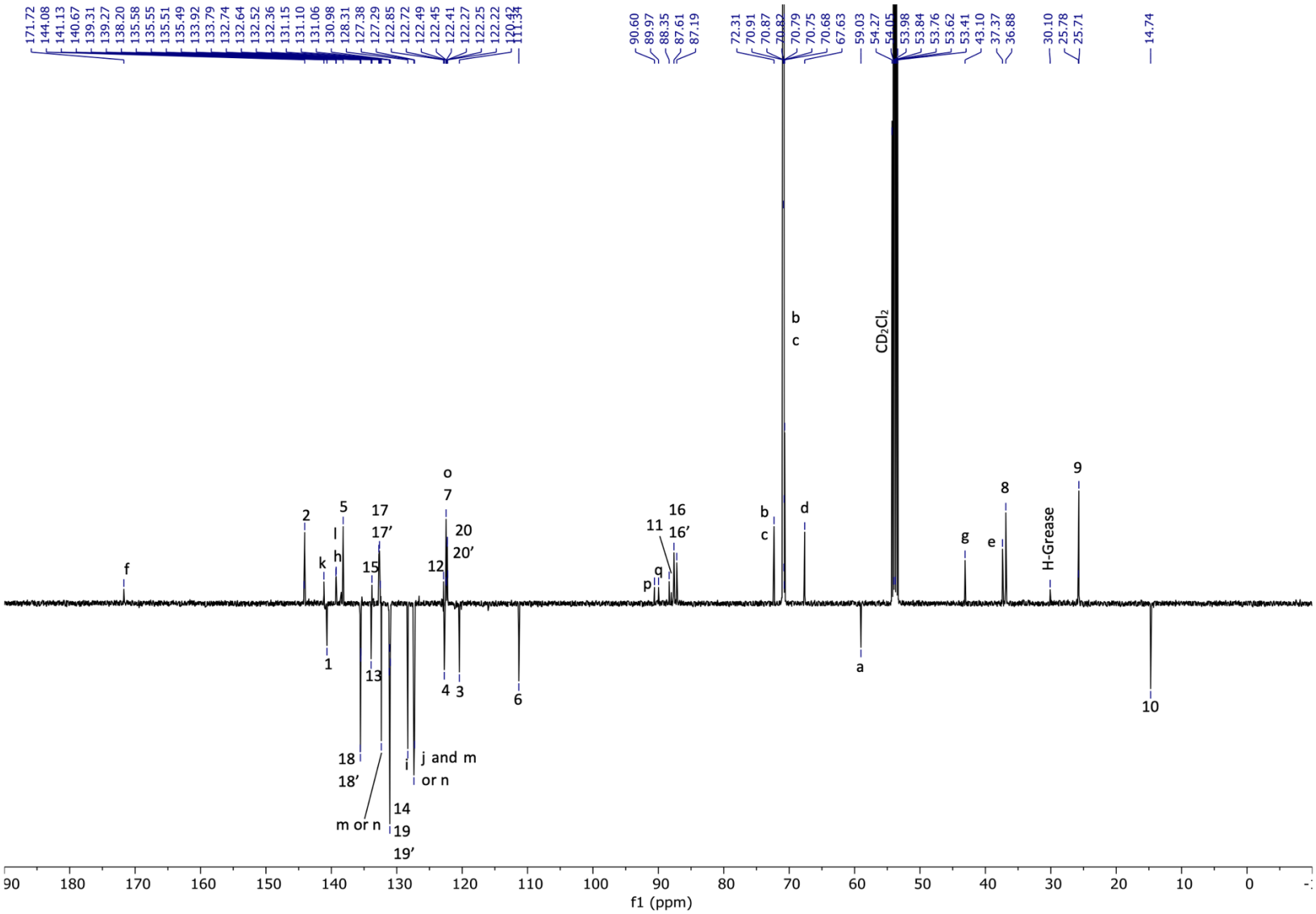
^{1}H-NMR of complex **9** (500 MHz, CD_2Cl_2, 25°C).



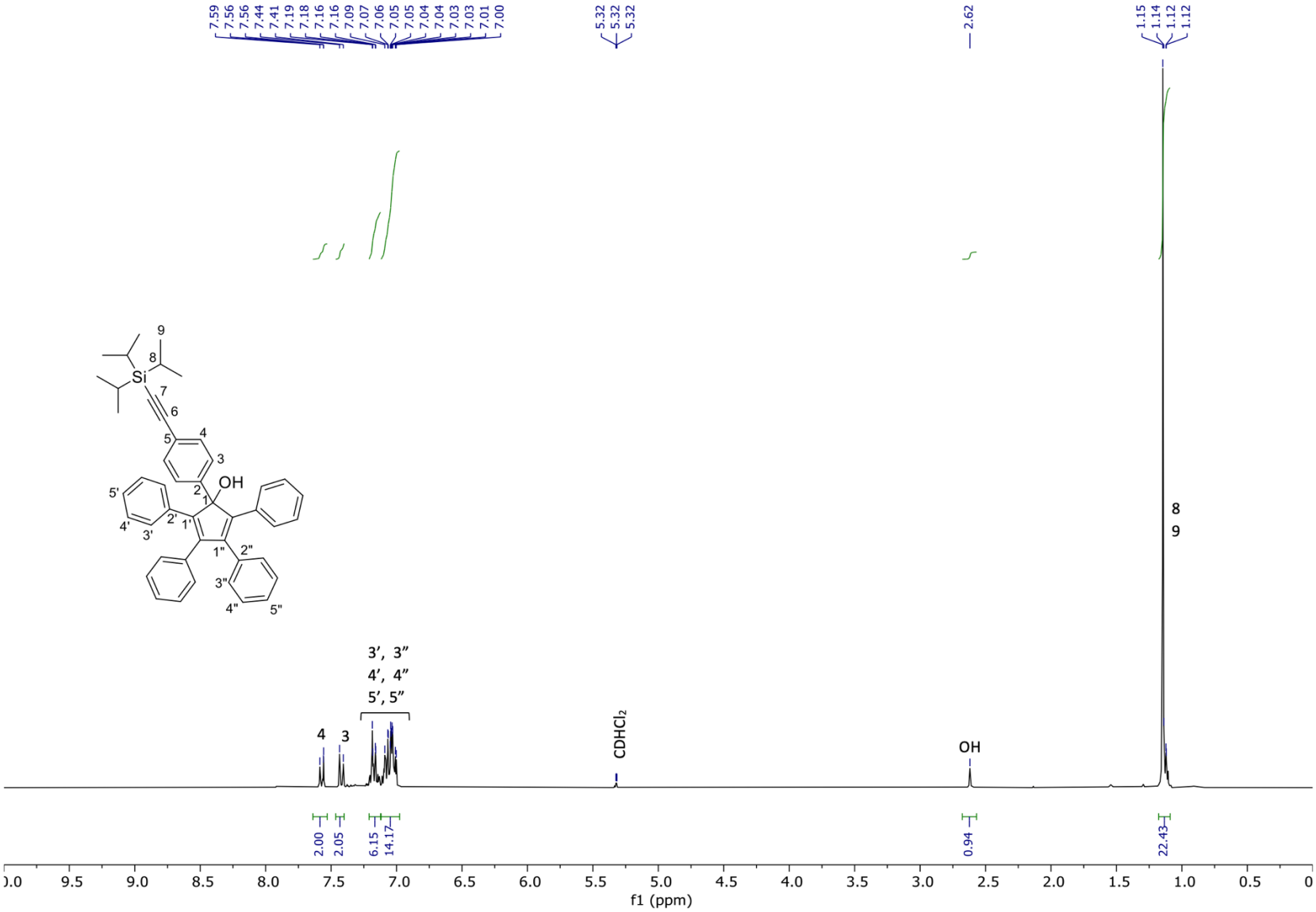
^{13}C-Jmod-NMR of complex **9** (126 MHz, CD_2Cl_2, 25°C).



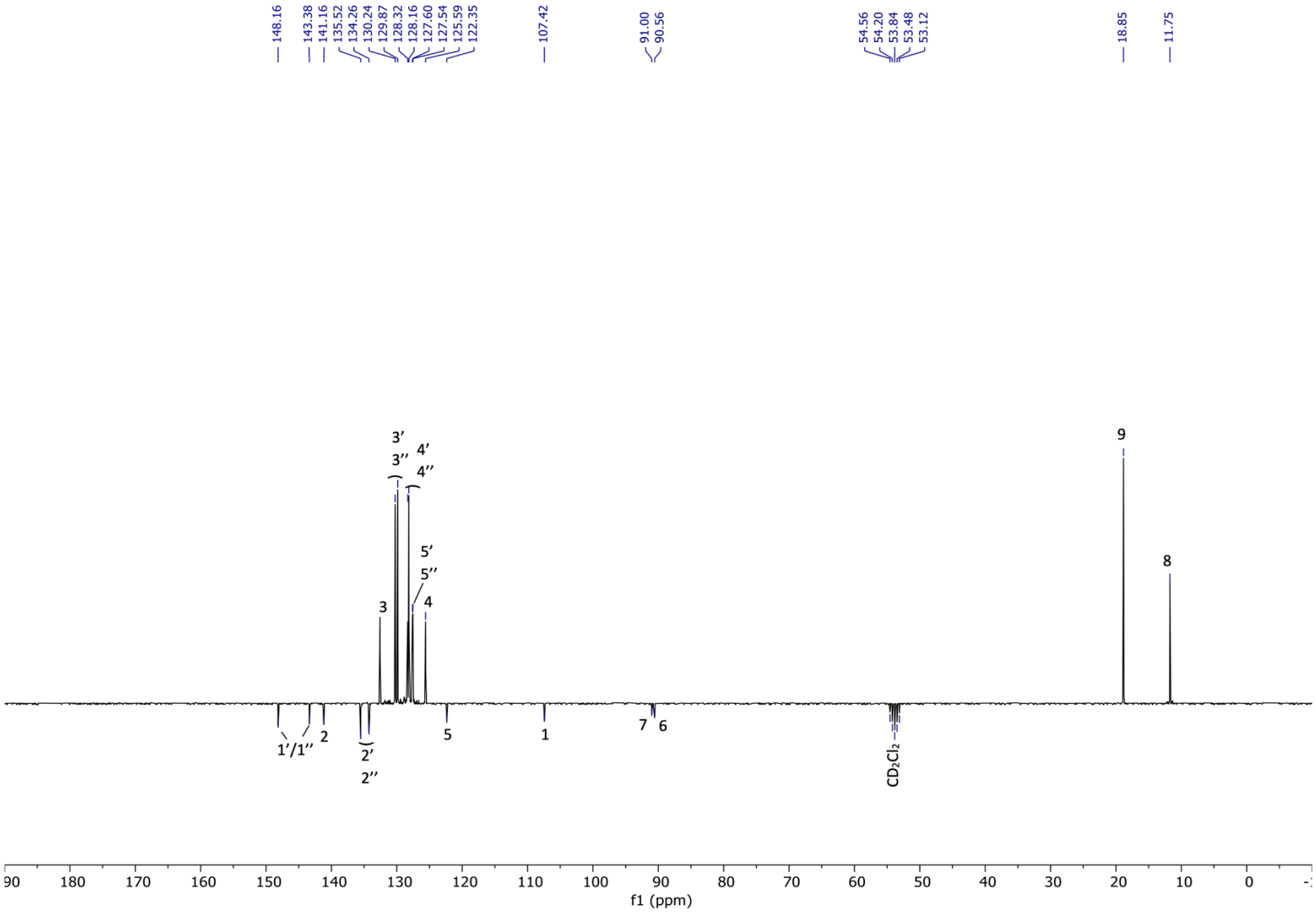
^{1}H-NMR of complex **M4** (300 MHz, CD_2Cl_2, 25°C).



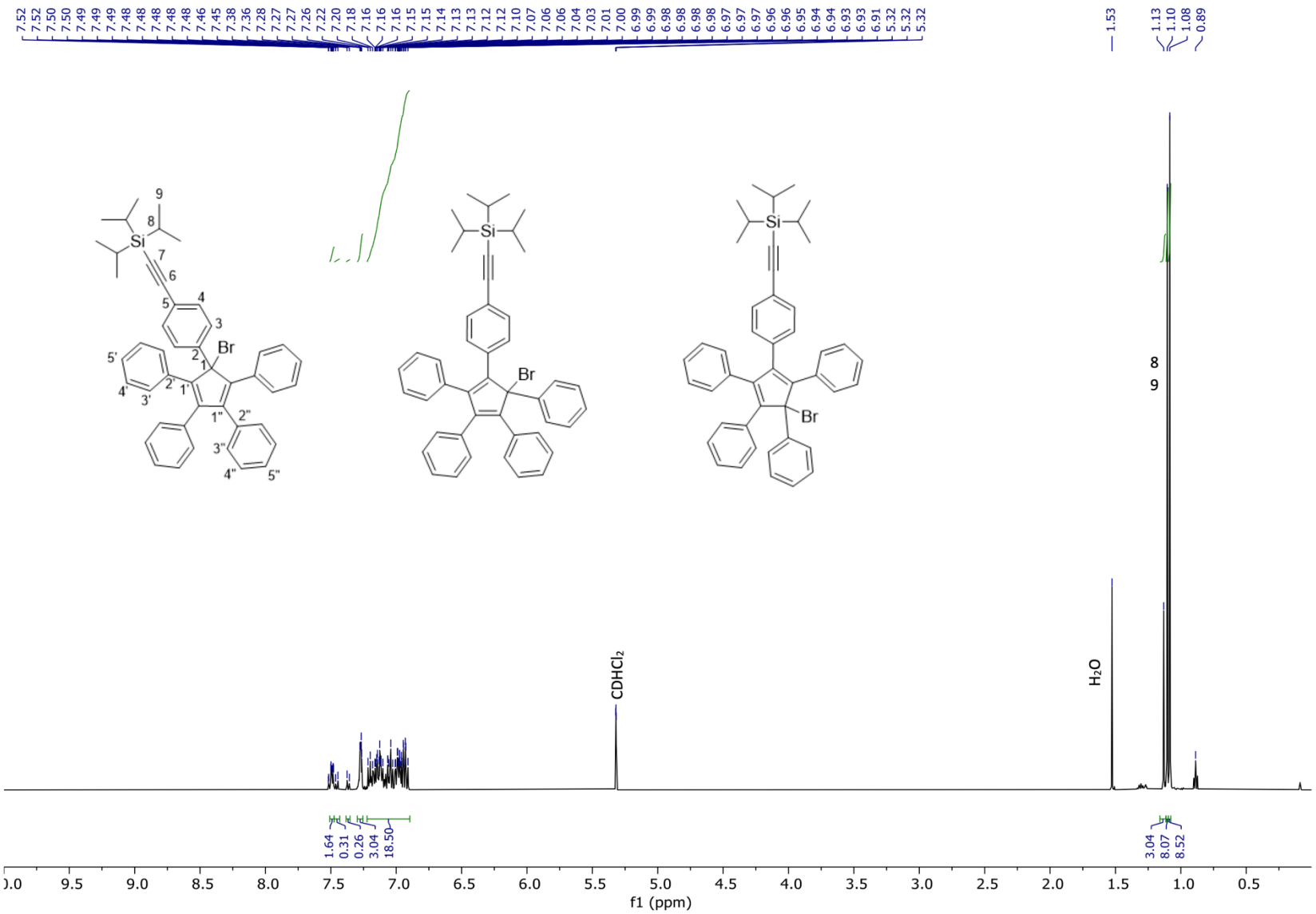
^{13}C-Jmod-NMR of complex **M4** (126 MHz, CD_2Cl_2, 25°C).



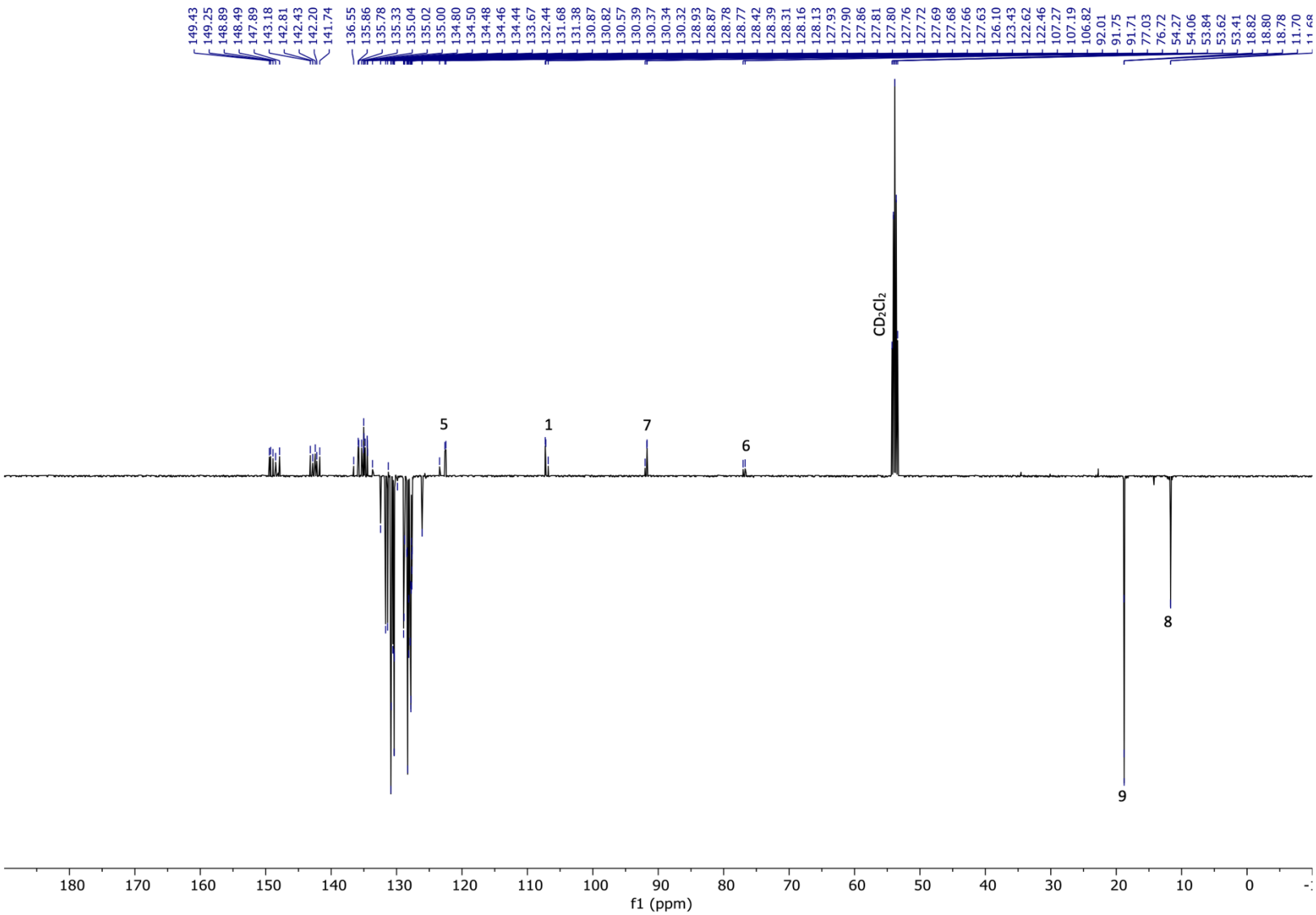
^{1}H-NMR of compound **10** (300 MHz, CD_2Cl_2, 25°C).



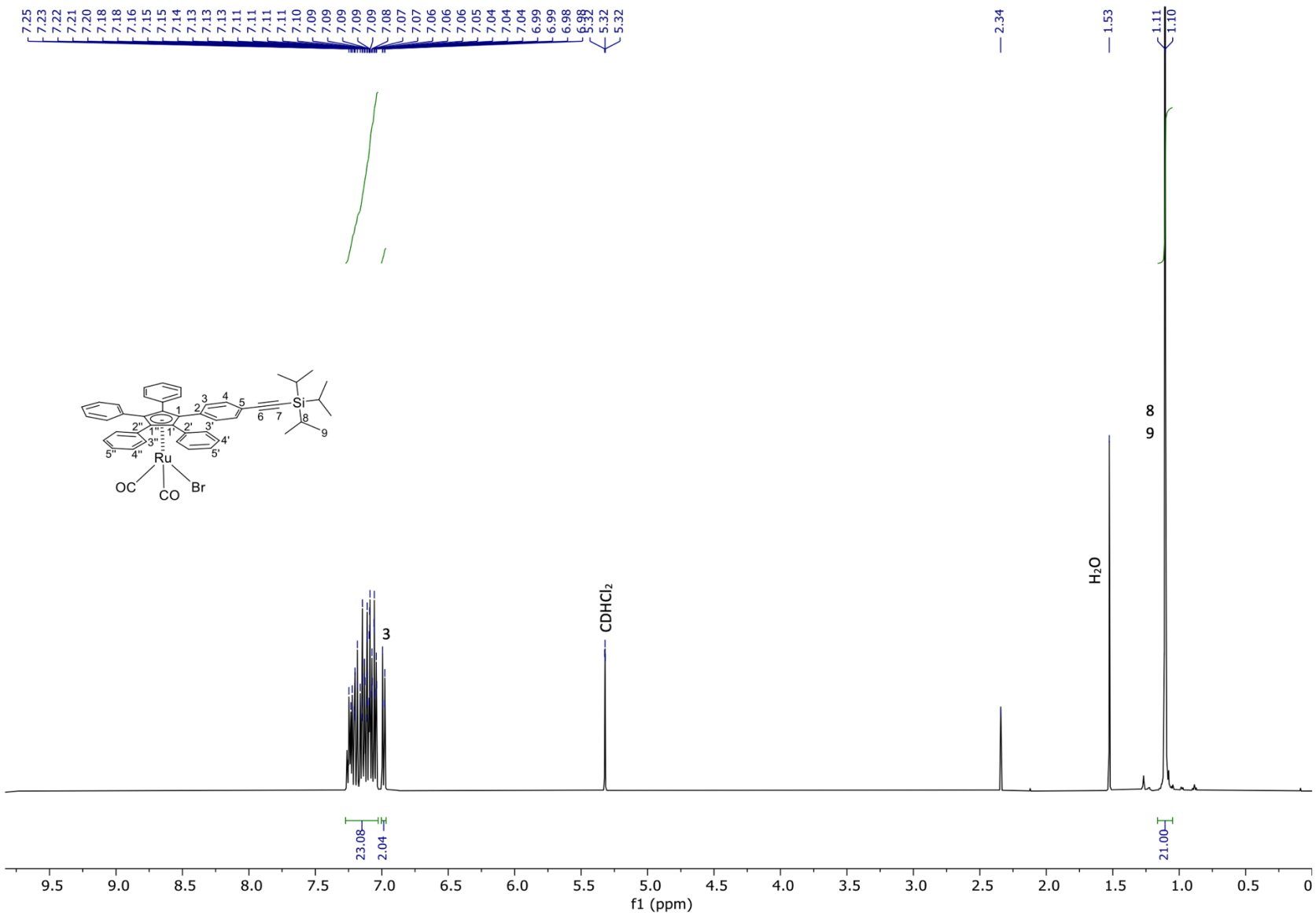
^{13}C-Jmod-NMR of compound **10** (75 MHz, CD_2Cl_2, 25°C).



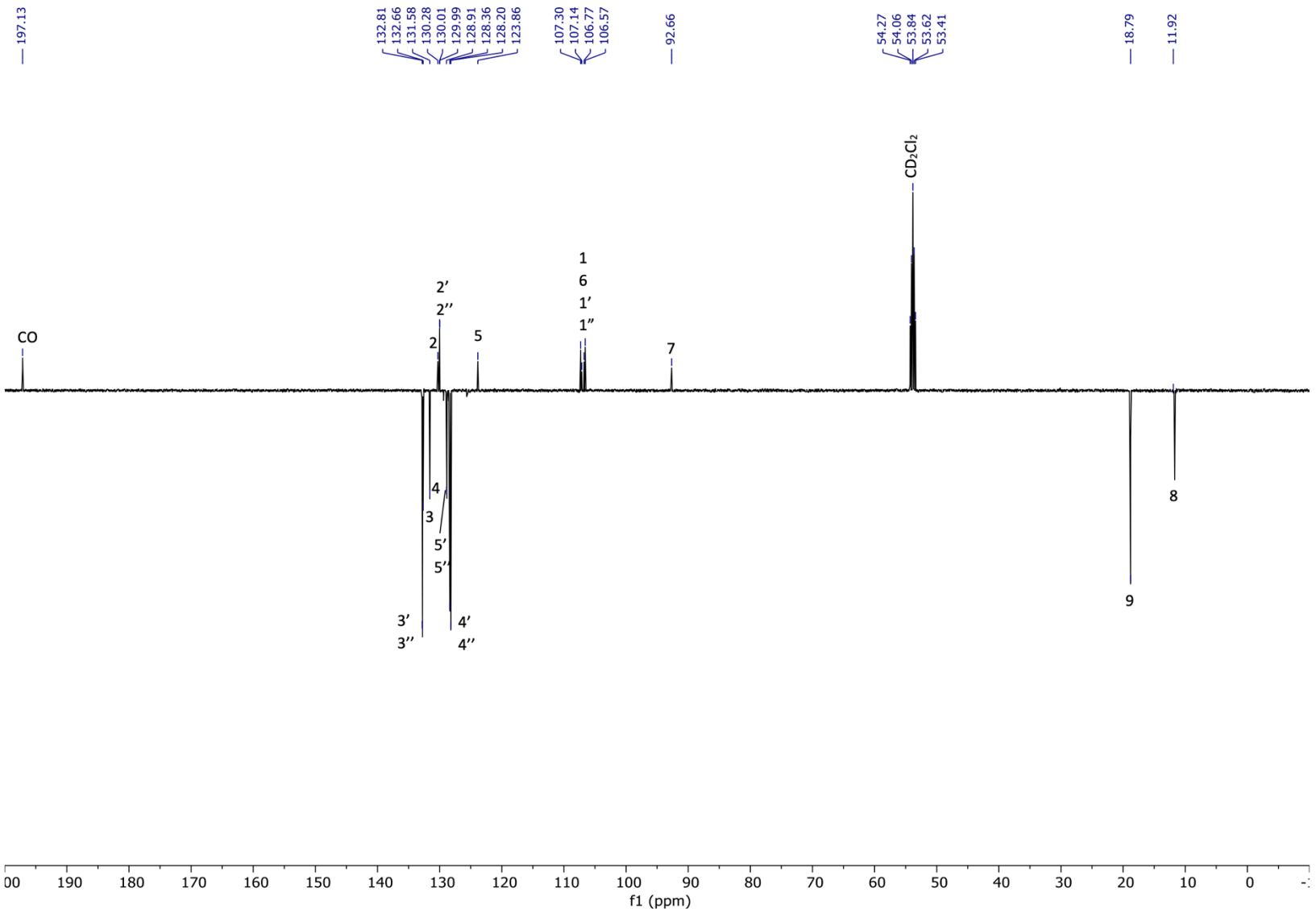
^{1}H-NMR of compound **11**, obtained as a mixture of 3 regioisomers (500 MHz, CD_2Cl_2, 25°C).



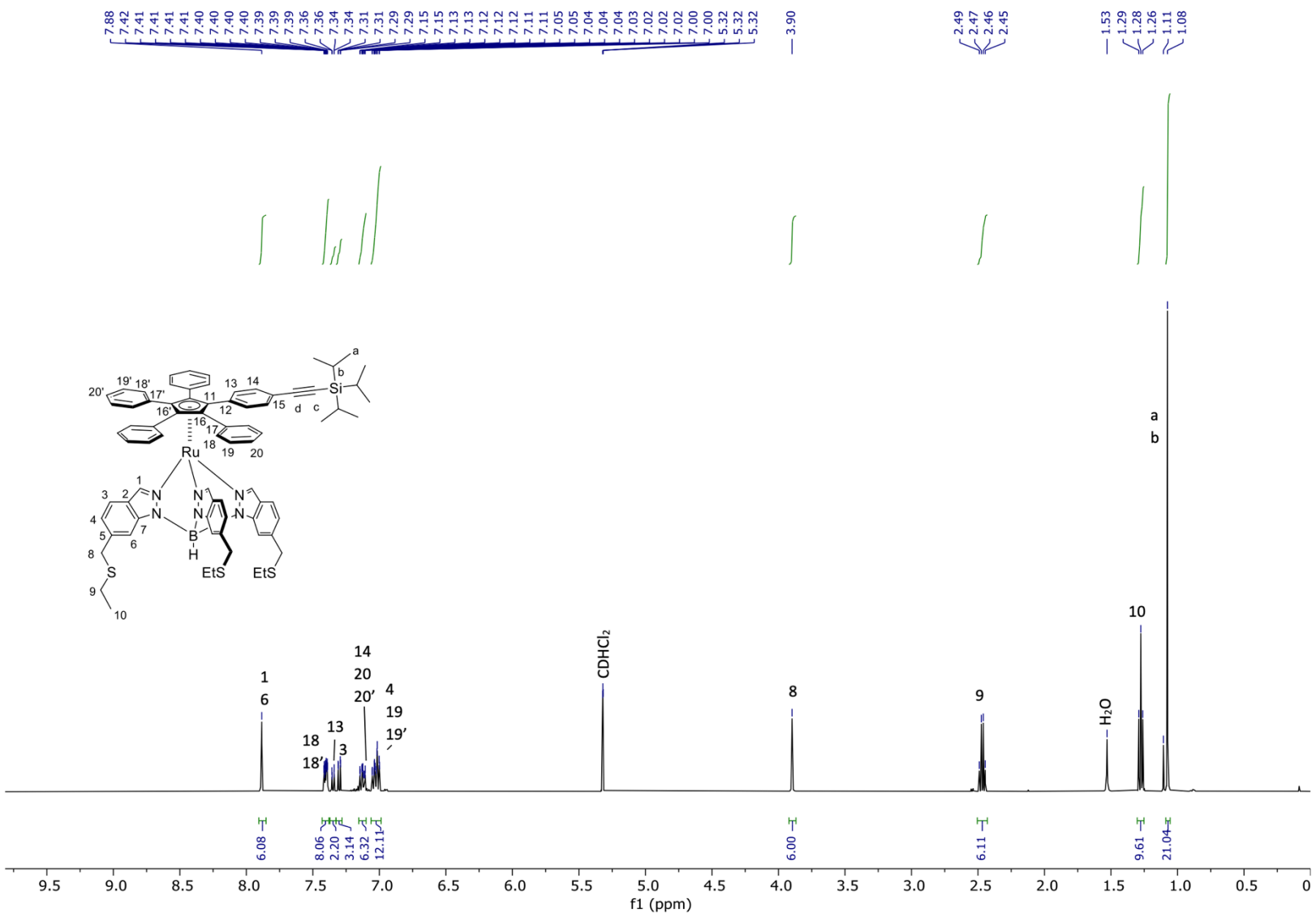
^{13}C-Jmod-NMR of compound **11**, obtained as a mixture of 3 regioisomers (126 MHz, CD_2Cl_2, 25°C).



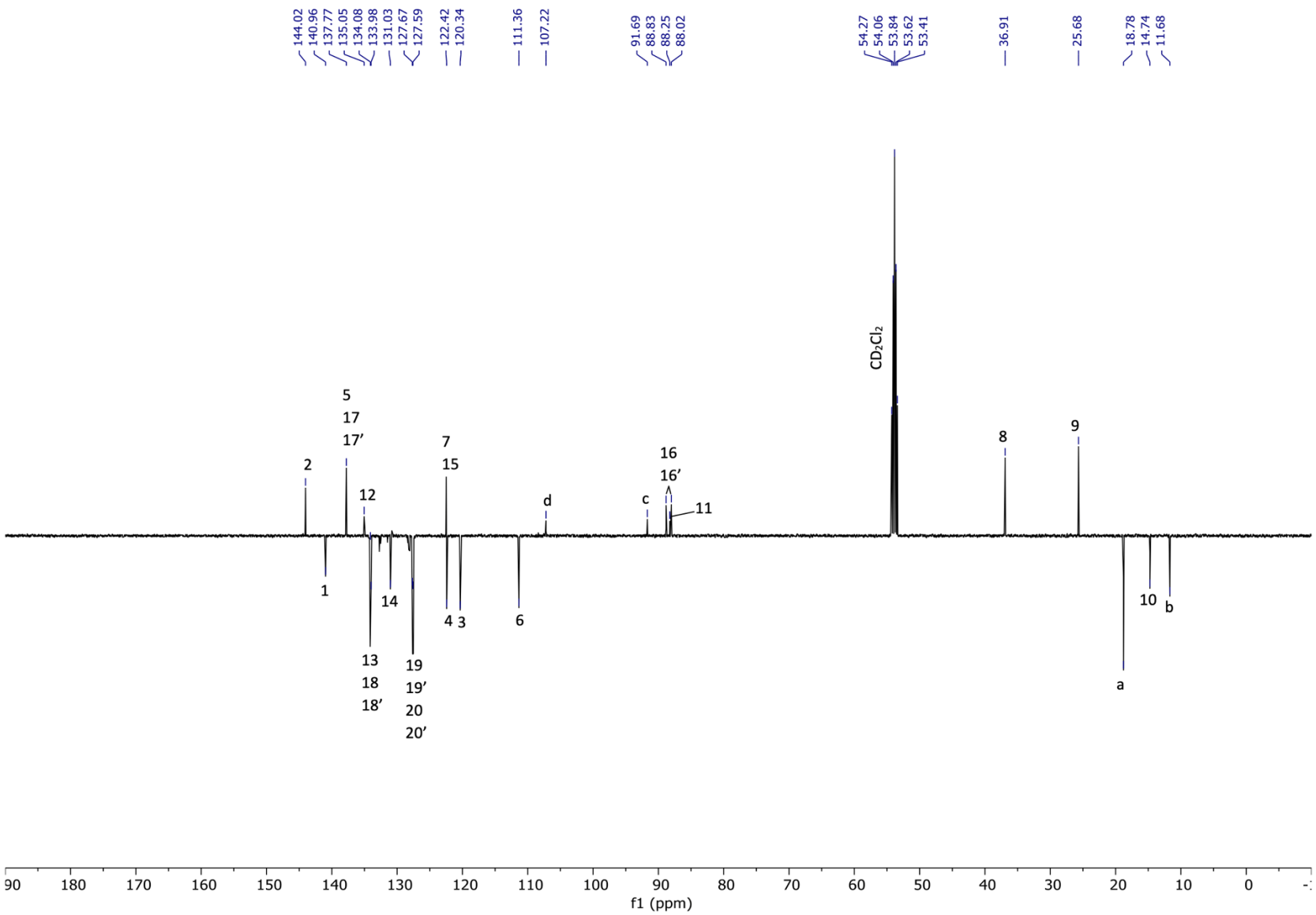
^{1}H-NMR of complex **12** (500 MHz, CD_2Cl_2, 25°C).



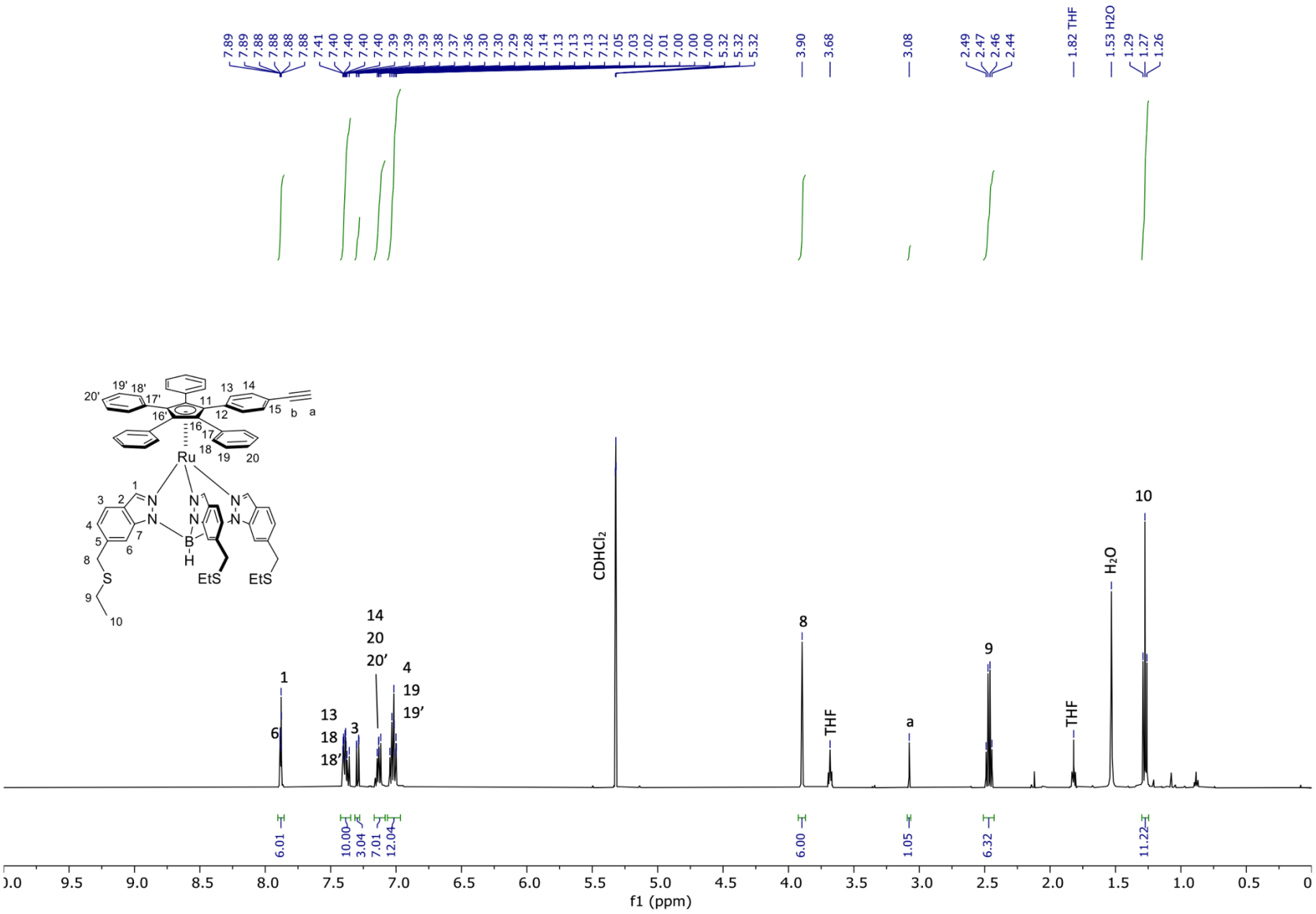
^{13}C-Jmod-NMR of complex **12** (126 MHz, CD_2Cl_2, 25°C).



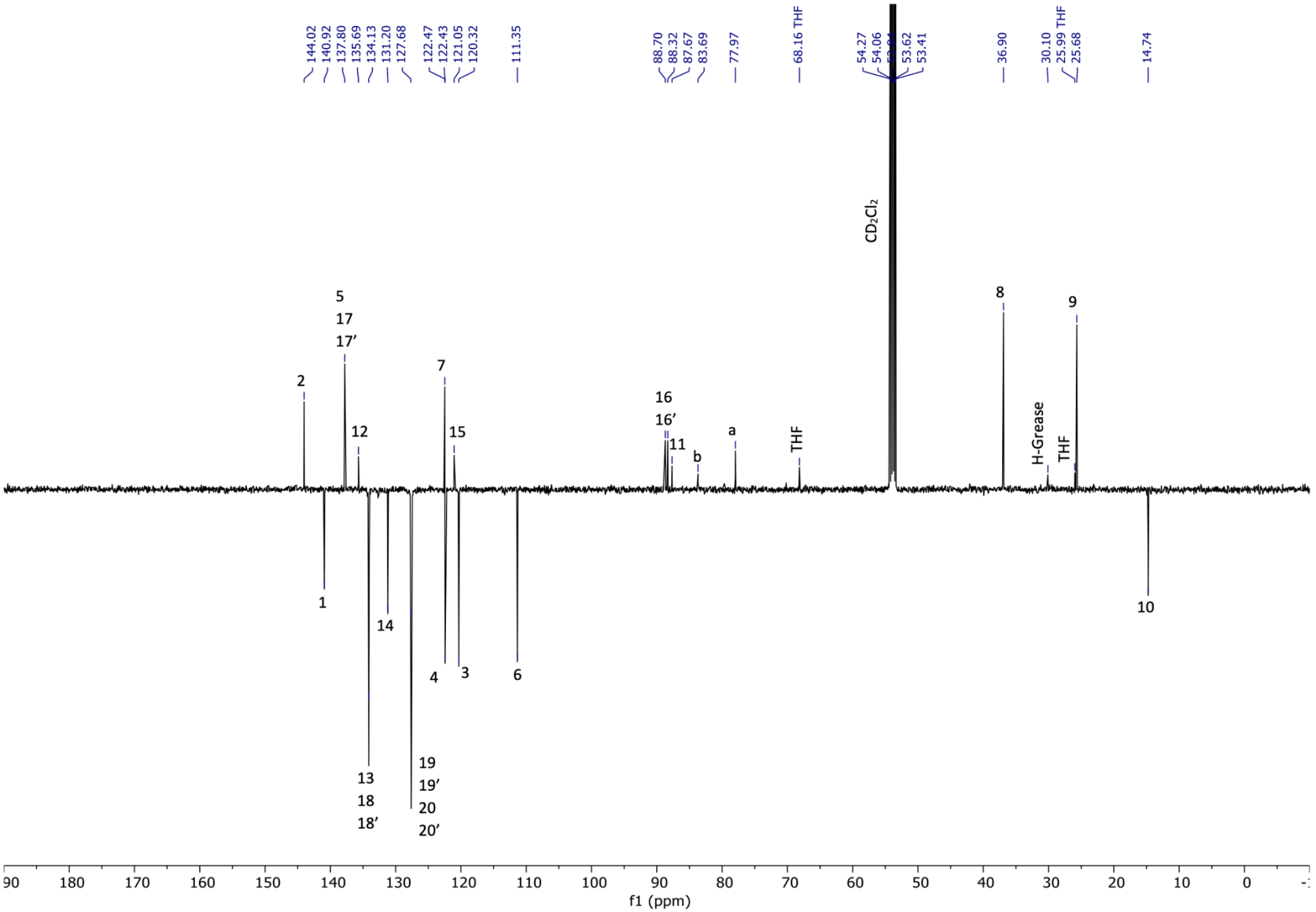
^{1}H-NMR of complex **13** (500 MHz, CD_2Cl_2, 25°C).



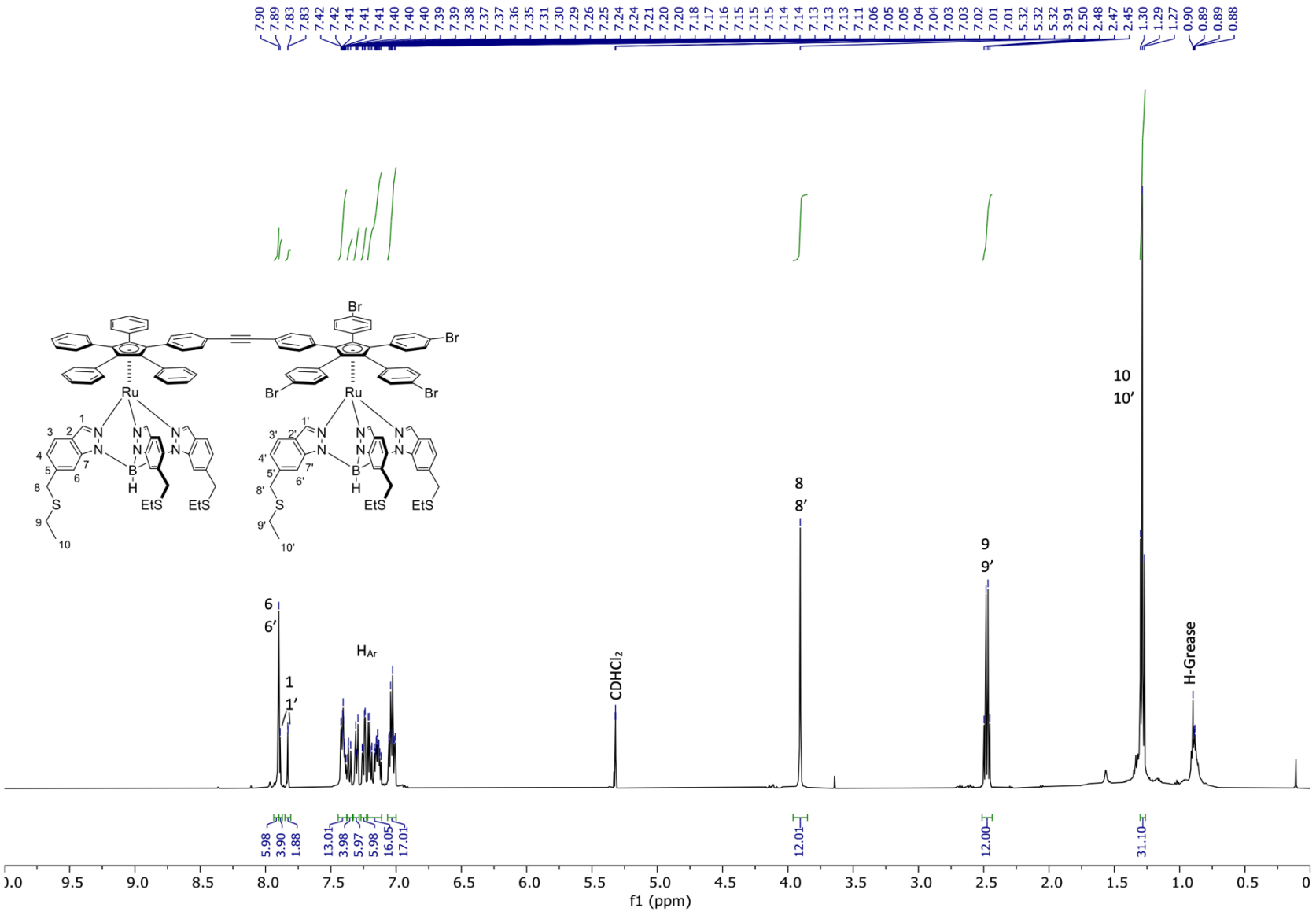
^{13}C-Jmod-NMR of complex **13** (126 MHz, CD_2Cl_2, 25°C).



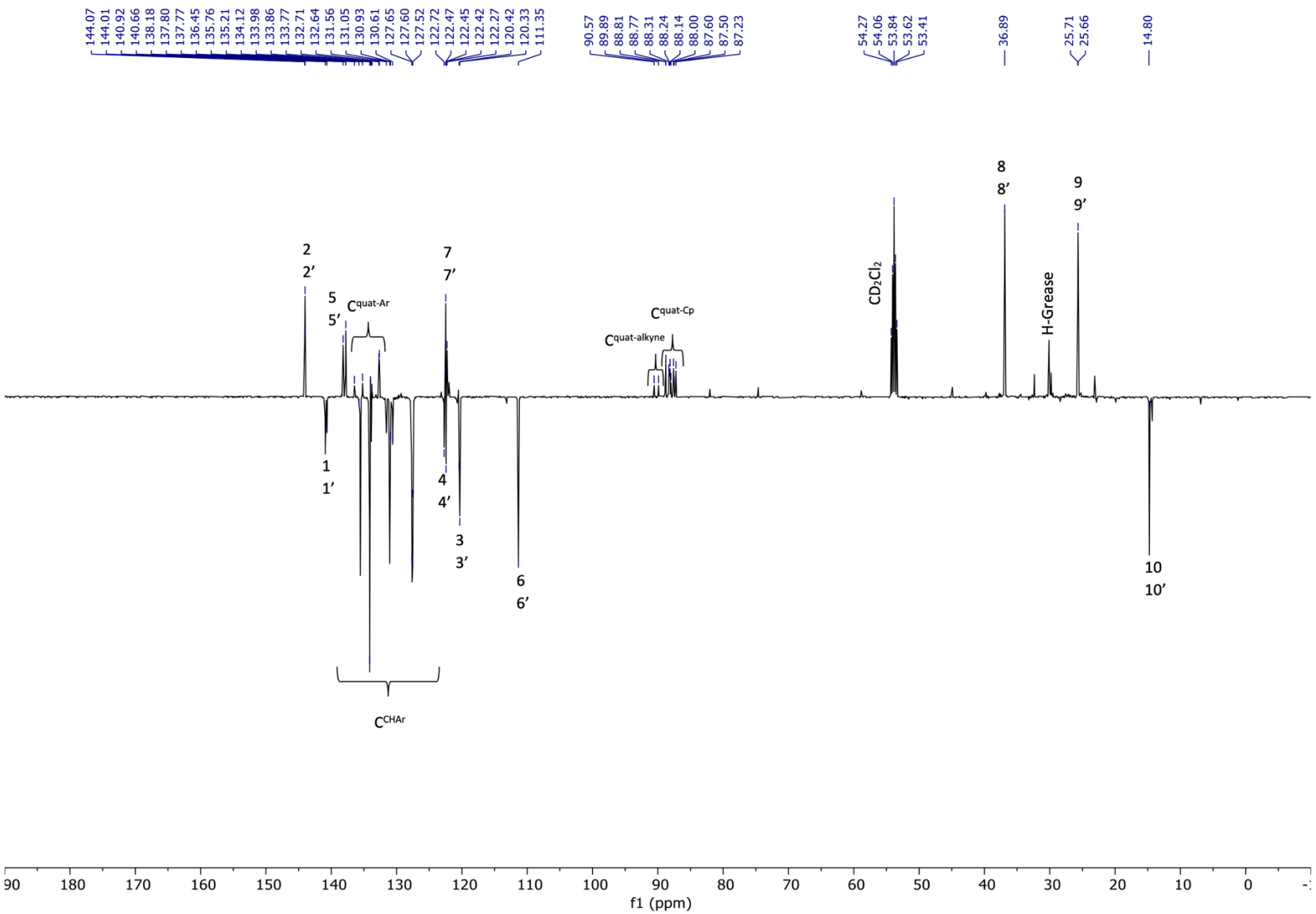
^{1}H-NMR of complex **14** (500 MHz, CD_2Cl_2, 25°C).



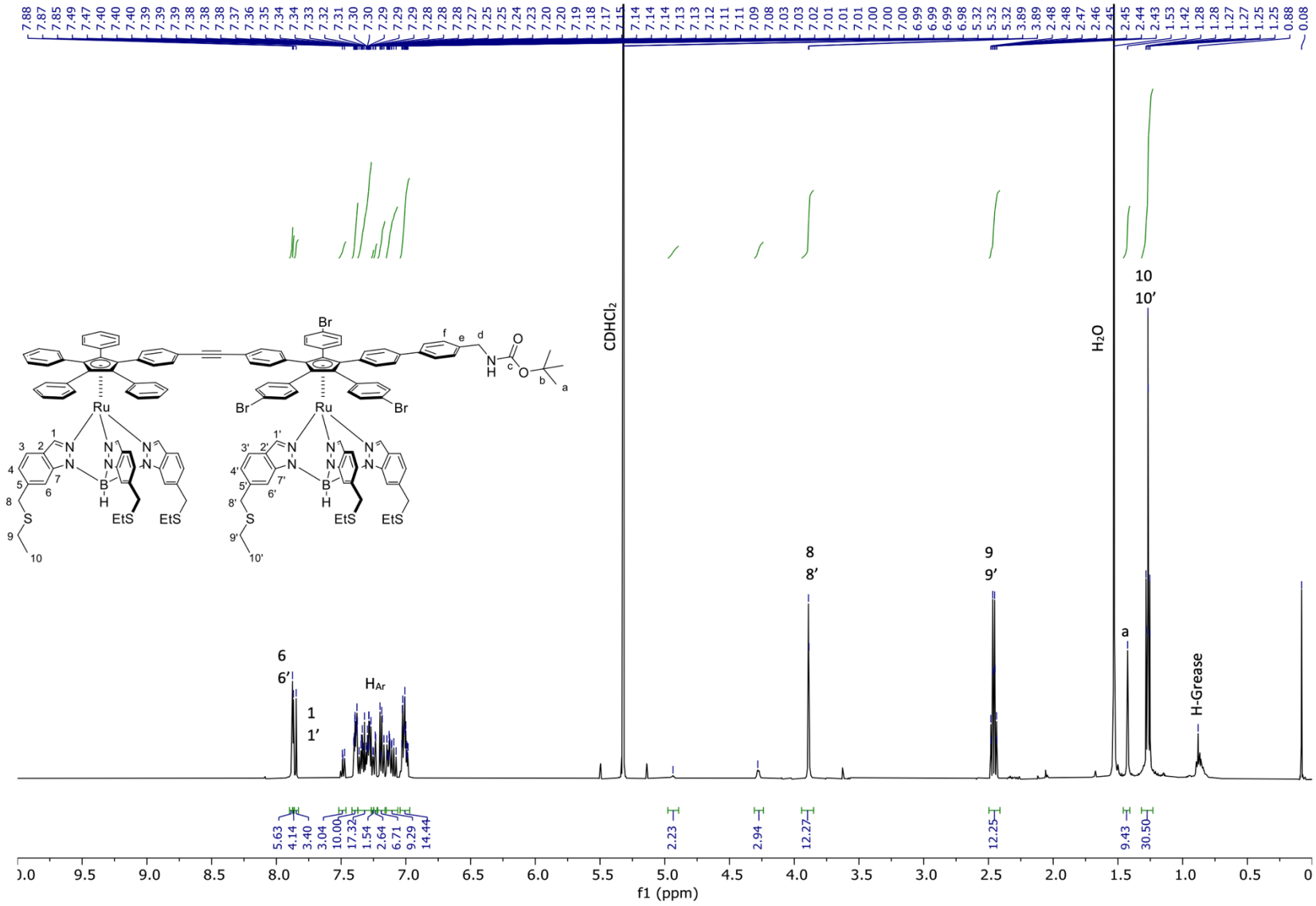
^{13}C-Jmod-NMR of complex **14** (126 MHz, CD_2Cl_2, 25°C).



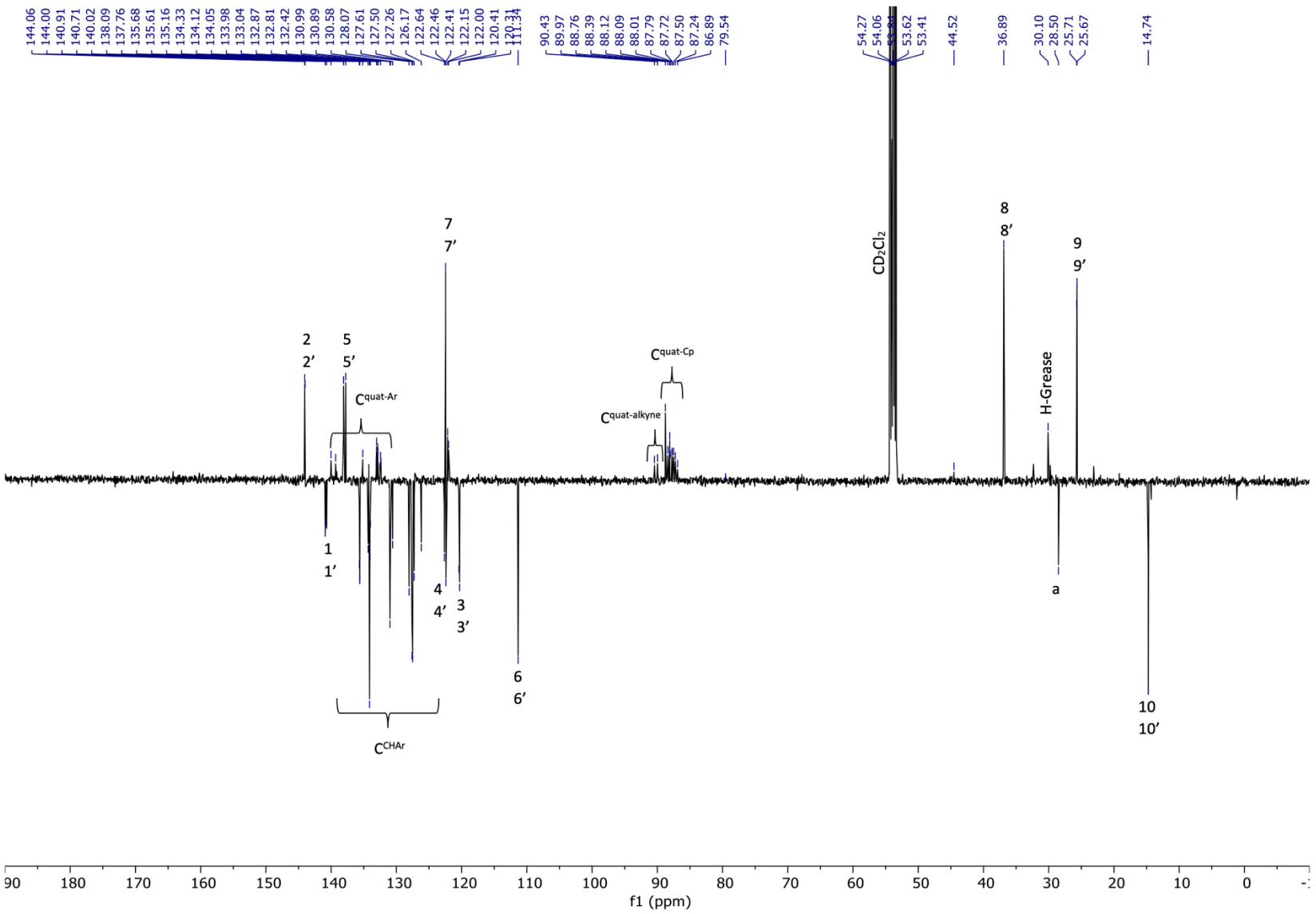
^{1}H-NMR of complex **15** (500 MHz, CD_2Cl_2, 25°C).



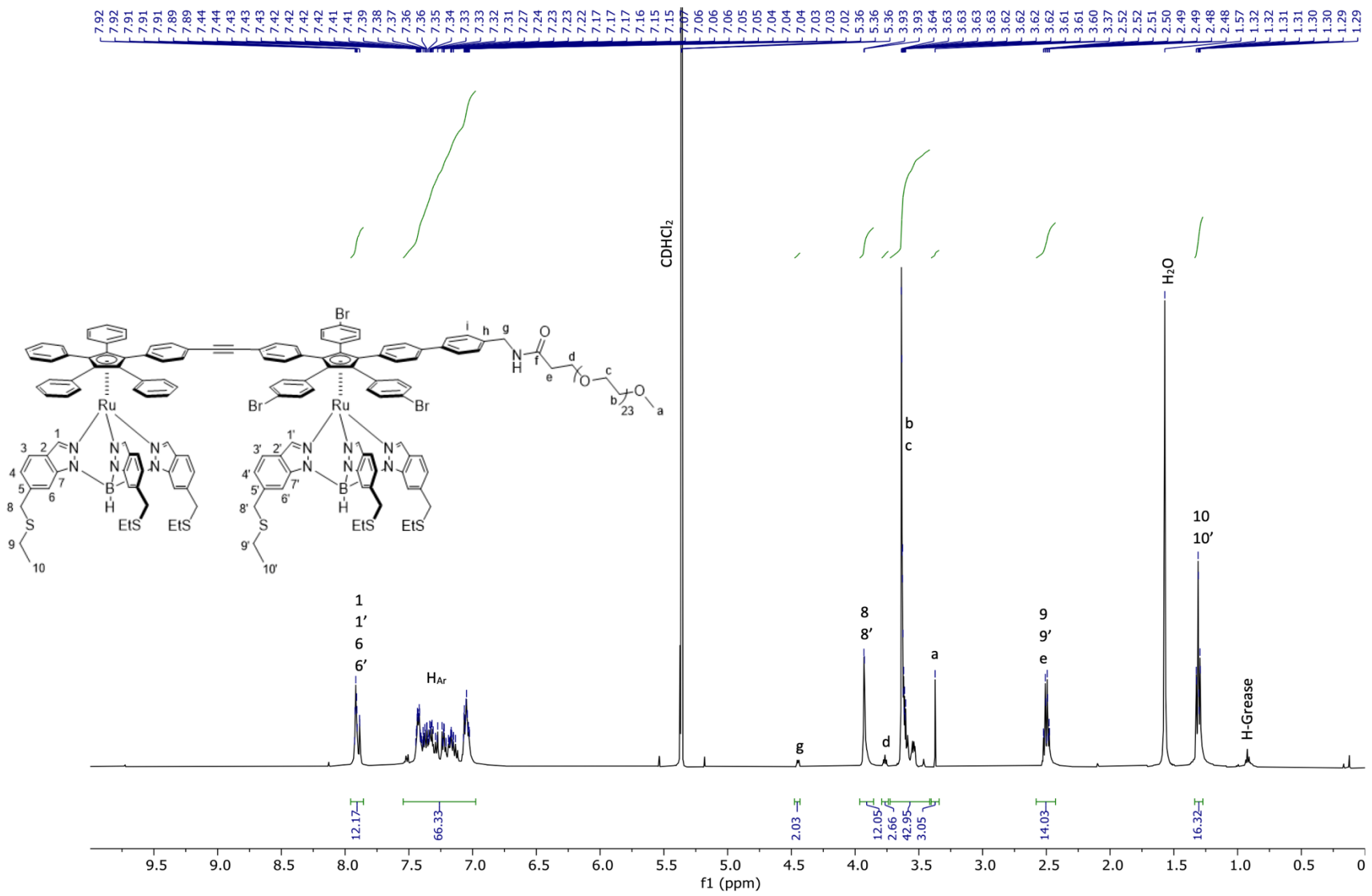
^{13}C-Jmod-NMR of complex **15** (126 MHz, CD_2Cl_2, 25°C).



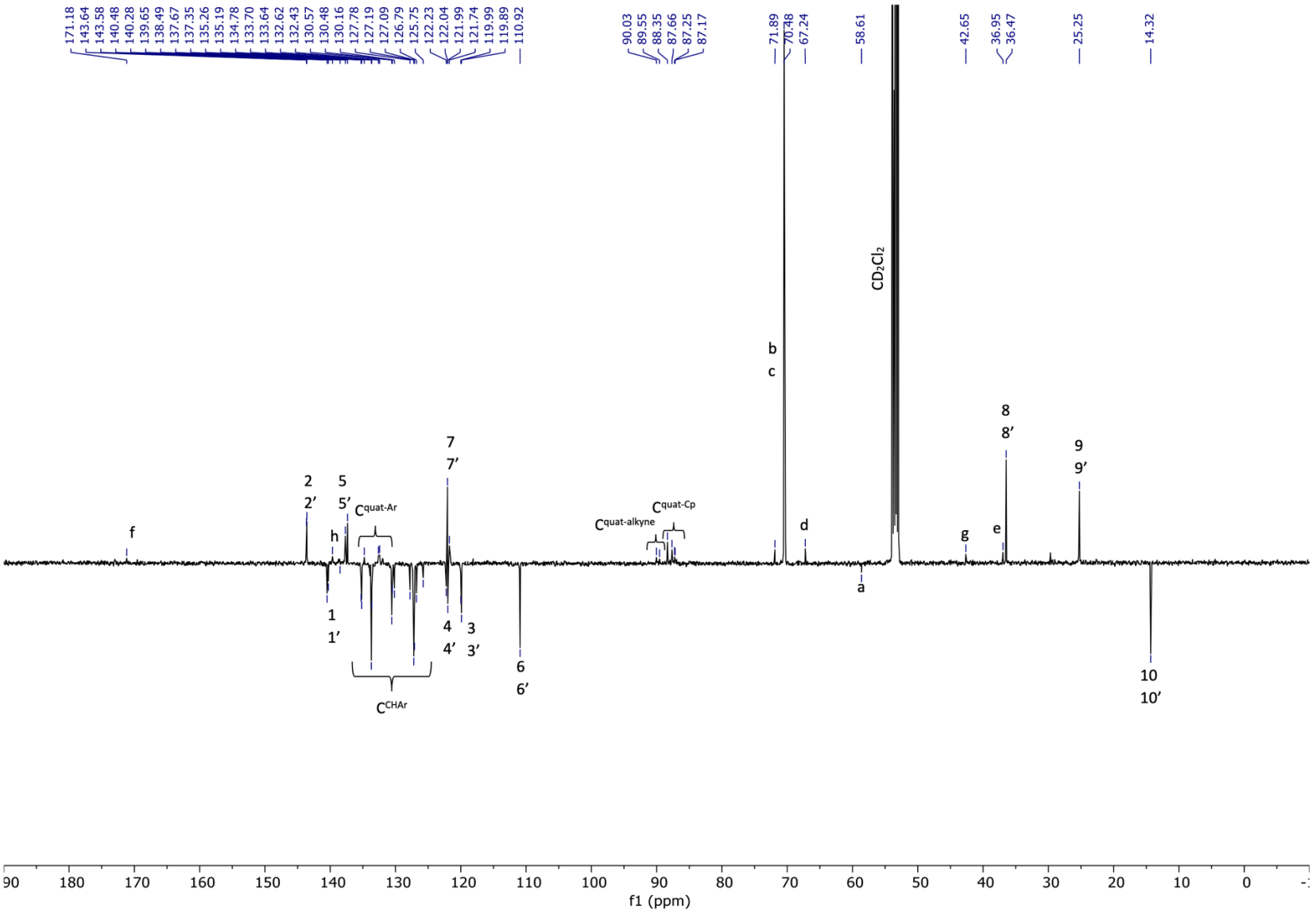
^{1}H-NMR of complex **16**, obtained as an unseparable mixture of 1,2- and 1,3-disubstituted regioisomers (500 MHz, CD_2Cl_2, 25°C).



^{13}C-Jmod-NMR of complex **16**, obtained as an unseparable mixture of 1,2- and 1,3-disubstituted regioisomers (126 MHz, CD_2Cl_2, 25°C).



^{1}H-NMR of complex **M5** as an unseparable mixture of 1,2- and 1,3-disubstituted regioisomers (500 MHz, CD_2Cl_2, 25°C).



^{13}C-Jmod-NMR of complex **M5** as an unseparable mixture of 1,2- and 1,3-disubstituted regioisomers (126 MHz, CD_2Cl_2, 25°C).

II. Grafting of the molecules on Au/Si substrates

The molecules **M1**-**M5** were attached to gold-coated silicon substrates using Au-S interactions, following our previously established protocol[S6-8] to reach low grafting density and favour single-molecule attachment during AFM experiments. Briefly, Au/Si wafers (Sigma-Aldrich) were cut in (2×2 cm^2) substrates, cleaned in a 1:1:5 volume ratio of NH_4OH, H_2O_2, and H_2O solution during 15 min at 65°C, followed by UV-ozone treatment for 15 min (UV-ozone cleaner®, Model 42, Jelight Company Inc.) and finally dipped in EtOH for 20 min. The freshly cleaned gold surfaces were dried with a nitrogen flow and directly incubated for 1 h at room temperature in the grafting solution with a molar ratio of 95:5 (dodecyl sulfide (DDS): organometallic complex) and a organometallic complex concentration of $1 \cdot 10^{-6}$ M in DMF. Subsequent washing with fresh DMF (3 times) provides the final surface that is dried and directly used for AFM experiments (or kept in a desiccator overnight). DDS is used as a passivation agent that disperses the molecules of interest on the surface and decreases unspecific tip-surface adhesion during force experiments.

III. AFM force experiments

AFM experiments were performed using a MFP3D Origin+ (Asylum Research, Oxford Instruments). Experiments were performed in a semi-closed fluid cell. OBL cantilevers (Bruker) with a nominal spring constant of k = 0.03 N·m^{-1} (length: 50-70 µm; width: 28-32 µm; thickness: 0.14-0.22 µm; frequency 19 kHz) were used in all force spectroscopy experiments. The spring constant of each cantilever was determined prior to each experiment, in air, using the thermal and the Sader methods implemented in the AFM software.[S9-10] The grafted surface was installed in the fluid cell filled with the organic solvent and the AFM tip was immersed in the solution away from the surface for 30 min for equilibration of the cantilever. After equilibration time, the speed response of the cantilever was measured on the force-time curves giving a mean value of 4.10^3 nm.s^{-1}. It is important to note that the spring constant of the cantilever is an inner parameter and is not affected by the viscosity of the solvent. However, the solvent viscosity influences the speed response of the cantilever. To avoid any bias originating from the viscous drag of the solvent, the sampling rate was adapted for each pulling velocity accordingly (*i.e.* its higher limit not exceeding the response time of the cantilever).

The molecules were picked up using a pushing force of 500 pN against the substrate to promote the attachment of the linker onto the AFM tip. Force curves were obtained at a fixed velocity of 20, 200, or 1000 nm·s^{-1} (approach and retraction) and with a sample rate of 17 kHz. Force-extension curves were obtained by transforming the deflection-piezo movement curves using the Hooke's law:

$$F = -kx = -k(z - d)$$

with F the force experienced by the molecule, k the spring constant of the cantilever, x the cantilever deflection, z the piezo-movement and d the tip-substrate distance.

The raw deflection-piezo movement curves were sorted out using a home-made routine on IgorPro (WaveMetrics). About 95% of the curves show flat profiles, indicating that no molecule was stretched during the approach-retraction cycle. Such flat curves are discarded. This observation is typical of an experiment performed in highly diluted grafting conditions, favouring single-molecule attachment. About 2% of the curves display only a contact adhesion peak and were discarded. The rest of the curves, about 3%, show single-peak profiles with the repeatable small pseudo-plateau pattern, for the experiments at

200 nm·s^{-1}. End-grafted short molecules like here, and especially in good organic solvent conditions and unfavourable Hamaker-Lifshitz constant, always give rise to very clean single peak profiles.[S6-8]

The profiles were analyzed automatically by a home-made routine. A worm-like chain fit was applied automatically on a force range of 0–100 pN, following the WLC equation:

$$F(D) = \frac{k_B T}{l_p}\left[\frac{D}{L} + \frac{1}{4(1-\frac{D}{L})^2} - \frac{1}{4}\right]$$

with k_B is the Boltzmann constant and T the temperature.

The WLC fit returns the persistence length l_p (related to the flexibility of the molecule) and the contour length L (maximum extended length of the molecule).

The force and length (Δx) of the characteristic small pseudo-plateaus were determined using a home-made routine on IgorPro (WaveMetrics). After adjusting the two WLC fits before and after the plateau profiles, the raw data between the WLC curves (corresponding to the plateau) is linearly fitted. The plateau length is measured as the distance between the two WLC in the plateau region, while the plateau force is the mean force of the linear fit. Histograms were constructed using IgorPro. Raw data were fitted using a Gaussian. Each population is given with its standard deviation. Probability density function (PDF) were also obtained by fitting the data by a Kernel smoothing function (N=1000 points) on MatLab (MathWorks).

For pulling-relaxing experiments, an integrated tool developed by Asylum Research (Oxford Instr.) was used to guide the movement of the tip. Prior to the pulling-relaxing curves, a few standard approach-retraction curves were obtained to determine the InvOLS (inverse optical lever sensitivity) of the cantilever and the distance from the contact point to the maximum contact force (threshold force of 500 pN). Then, between each approach and retraction movement, several pulling and relaxing movements are performed at identical velocity. The distance over which the molecule is pulled is slightly increased at each cycle, in order to maximize the possibility of observing the characteristic pattern associated with the studied molecule. During pulling-relaxing experiments, the tip is kept away from the surface (a few nm away from the contact point) to avoid any perturbation from the surface from one cycle to the next. Usually, 5 pulling-relaxing cycles are performed between each approach and retraction traces. Force curves were obtained at a fixed velocity of 200 nm·s^{-1} (pulling and relaxing) and with a sample rate of 17 kHz. The zero-force and the zero-distance is determined by comparing the approach and retraction traces, the contact point values (force and distance) being used for all the pulling and relaxing traces. All force curves are transformed similarly to the standard force curves. The pulling and relaxing traces are analyzed manually with IgorPro.

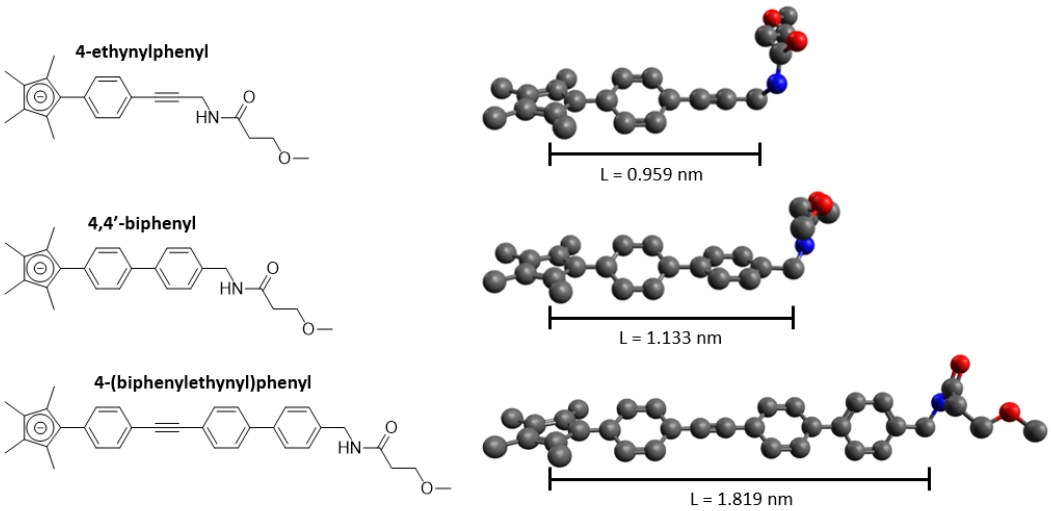
IV. Calculation of the length of the rotors' functionalised arms

IV.1. Computational details and measurement of the lengths

To estimate the lengths L of the functionalised arms incorporating various spacers and compare them to the measured plateau lengths, DFT calculations were performed on simplified analogues of the rotor subunits composed of a tetramethylcyclopentadienyl anion functionalised with the desired spacer, itself linked to a terminal methoxy-substituted propionamide group (Figure below, left).

DFT calculations were performed using the Gaussian 16-B.01 software,[S11] at the ωB97xD/Def2TZVP level of theory. Geometry optimisation was performed in vacuum, followed by a frequency calculation that showed no negative frequency, confirming that the resulting structures correspond to a stationary point of the potential energy surface. Distances calculations were performed on the optimised geometries (Figure below, right) using the centroid and measure functions of the CCDC Mercury software.

The lengths of the functionalised arms (L) were measured from the centre of the cyclopentadienide ring to the benzylic or propargylic carbon terminating the straight section of the spacer (Table below).



Structure of the simplified analogues considered for each spacer type (left) and representation of the corresponding optimised geometries (hydrogen atoms were omitted for clarity) along with indicative scale bars showing the measured lengths L (right).

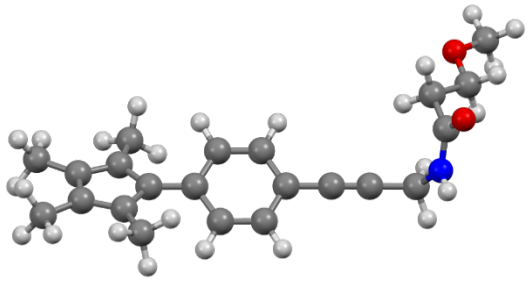
Spacer (rotor derivative)	Length of functionalised arm L (nm)	Maximum rotor diameter = 2 x L (nm)
4-ethynylphenyl (**M2**, **M3**)	0.959	1.918
4,4'-biphenyl (**M1**)	1.133	2.266
4-(biphenylethynyl)phenyl (**M4**)	1.819	3.638

Table S1: Summary of the lengths of functionalised arms (L) according to the spacers and associated maximum rotor diameters.

IV.2 Optimised geometries of the simplified analogues of rotor subunits

a. Model with a 4-ethynylphenyl spacer

Calculation Type: FREQ. Calculation Method: RwB97XD. Basis Set: def2TZVP. Charge: -1. Spin: Singlet. Total Energy: -1059.210093 Hartree. RMS Gradient Norm: 0.000004 Hartree/Bohr. Imaginary Frequency: None.

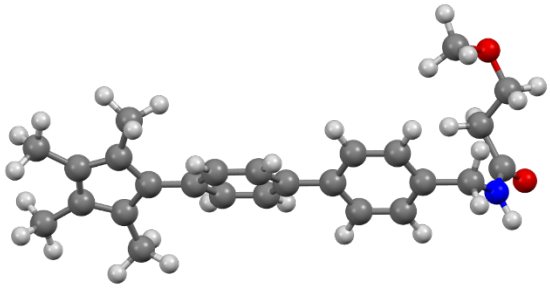


Cartesian coordinates:

C	3.93612	2.65578	0.50546	H	3.15333	2.52217	1.25690
C	4.53467	1.34335	0.08943	H	3.48394	3.21191	-0.32633
C	5.88038	1.12833	-0.17107	H	6.62989	3.13831	0.07369
C	6.98709	2.13771	-0.17926	H	7.46815	2.21126	-1.16309
C	6.07765	-0.25732	-0.42671	H	7.78234	1.88537	0.53387
C	7.40349	-0.85264	-0.78919	H	8.14480	-0.72143	0.00959
C	4.85978	-0.90930	-0.29757	H	7.83317	-0.38959	-1.68669
C	4.62529	-2.36354	-0.58728	H	7.33114	-1.92545	-0.98059
C	3.86757	0.07561	0.02196	H	5.38931	-2.75633	-1.26335
C	2.46961	-0.16282	0.23703	H	3.65697	-2.52832	-1.06716
C	1.97769	-1.38394	0.76291	H	4.64514	-2.99573	0.31038
C	0.63792	-1.61314	0.97129	H	2.68498	-2.14985	1.04696
C	-0.32225	-0.63510	0.67841	H	0.31332	-2.55985	1.38858
C	-1.70488	-0.86414	0.91060	H	-4.77102	-0.32871	1.65333
C	-2.87758	-1.05748	1.11518	H	-4.41267	-1.92223	2.25408
C	-4.29515	-1.27395	1.38276	H	-5.03649	-2.89086	0.23617
N	-5.05541	-1.88599	0.29962	H	-4.49328	0.60606	-0.40776
C	-5.48859	-1.28009	-0.83784	H	-5.33393	0.49798	-1.95776
C	-5.38945	0.23217	-0.90390	H	-6.71899	0.60067	0.76844
C	-6.62629	0.87008	-0.29510	H	-7.52482	0.49763	-0.80688
O	-6.52891	2.26502	-0.42921	H	-7.47489	4.00307	-0.04403
C	-7.63444	2.93568	0.10372	H	-7.74615	2.73854	1.17904
O	-5.98880	-1.92209	-1.74246	H	-8.56616	2.64112	-0.39870
C	0.13764	0.58149	0.15647	H	-0.58323	1.35079	-0.09708
C	1.47721	0.80514	-0.05940	H	1.78013	1.74048	-0.50737
H	4.69381	3.31028	0.94429				

b. Model with a 4,4'-biphenyl spacer

Calculation Type: FREQ. Calculation Method: RwB97XD. Basis Set: def2TZVP. Charge: -1. Spin: Singlet. Total Energy: -1214.119076 Hartree. RMS Gradient Norm: 0.000003 Hartree/Bohr. Imaginary Frequency: None.

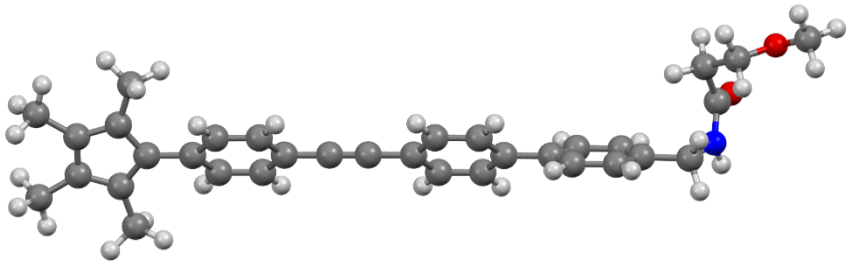


Cartesian coordinates:

C	5.02849	2.55734	-0.38251	H	4.03729	2.75696	0.03371
C	5.48667	1.16115	-0.07527	H	4.96762	2.76987	-1.45835
C	6.78957	0.79832	0.24042	H	7.76576	2.71223	0.02817
C	8.00513	1.67335	0.26599	H	8.76228	1.34781	-0.45924
C	6.80788	-0.58513	0.56720	H	8.49733	1.66890	1.24701
C	8.05312	-1.33783	0.92308	H	8.51863	-0.95410	1.84027
C	5.51213	-1.07748	0.48084	H	8.81712	-1.26795	0.13816
C	5.12070	-2.51596	0.65732	H	7.85509	-2.39910	1.08925
C	4.66115	0.00003	0.07311	H	5.96824	-3.17973	0.46609
C	3.24262	-0.07082	-0.14698	H	4.32421	-2.80489	-0.03379
C	2.40244	-0.95562	0.56952	H	4.76114	-2.74929	1.66844
C	1.04480	-1.03012	0.34837	H	2.83487	-1.56506	1.35040
C	0.40358	-0.21440	-0.58987	H	0.45539	-1.70615	0.95937
C	-1.04513	-0.28795	-0.82034	H	-1.28351	1.79276	-1.29048
C	-1.78506	0.83764	-1.19909	H	-3.69116	1.66205	-1.70228
C	-3.14856	0.76380	-1.42276	H	-5.48860	-0.80705	-2.58746
C	-3.83835	-0.43270	-1.27281	H	-5.72971	0.52686	-1.49118
C	-5.32203	-0.48611	-1.55641	H	-6.46166	-2.22825	-1.13980
N	-6.09603	-1.38857	-0.72495	H	-4.88042	0.25275	0.90342
C	-6.37175	-1.26906	0.60267	H	-5.73857	-0.27670	2.35555
C	-5.85407	-0.03111	1.30169	H	-7.09669	1.28855	0.10123
C	-6.84963	1.12363	1.16054	H	-7.77435	0.86697	1.67865
O	-6.39036	2.32050	1.73395	H	-5.17989	3.91184	1.47828
C	-5.38912	2.96245	0.98753	H	-5.72749	3.16040	-0.03940
O	-7.03794	-2.10603	1.18296	H	-4.46071	2.38278	0.93867
C	-3.11928	-1.55612	-0.88527	H	-3.63293	-2.50121	-0.74884
C	-1.75483	-1.48555	-0.66878	H	-1.21678	-2.38437	-0.39529
C	1.21631	0.67511	-1.30071	H	0.77703	1.29848	-2.07296
C	2.57722	0.73852	-1.09783	H	3.16411	1.39911	-1.72022
H	5.71086	3.29745	0.04416				

c. Model with a 4-(biphenylethynyl)phenyl spacer

Calculation Type: FREQ. Calculation Method: RwB97XD. Basis Set: def2TZVP. Charge: -1. Spin: Singlet. Total Energy: -1214.119076 Hartree. RMS Gradient Norm: 0.000003 Hartree/Bohr. Imaginary Frequency: None.



Cartesian coordinates:

C	-9.02906	-2.36111	-0.03475	C	-6.27550	-0.99746	-0.59969
C	-9.35242	-0.90409	-0.19652	H	-9.87659	-2.90485	0.39035
C	-10.63167	-0.37778	-0.27009	H	-8.17991	-2.51383	0.63647
C	-11.93135	-1.12165	-0.29247	H	-8.77831	-2.85874	-0.98062
C	-10.53837	1.04367	-0.30508	H	-11.78535	-2.20207	-0.23149
C	-11.72631	1.94698	-0.43086	H	-12.49756	-0.92817	-1.21236
C	-9.20281	1.40212	-0.22301	H	-12.58674	-0.83296	0.53902
C	-8.67937	2.80471	-0.33426	H	-12.41517	1.83755	0.41634
C	-8.42760	0.19444	-0.15923	H	-12.31255	1.73448	-1.33383
C	-7.00270	0.10301	-0.07427	H	-11.43767	2.99933	-0.47077
C	-6.20887	1.10599	0.54201	H	-9.39437	3.44918	-0.85203
C	-4.84082	1.02046	0.62220	H	-7.74452	2.84278	-0.89950
C	-4.14535	-0.08099	0.09788	H	-8.48043	3.27324	0.63844
C	-2.73842	-0.17253	0.18511	H	-6.70197	1.94942	1.00284
C	-1.53316	-0.25102	0.26144	H	-4.28103	1.80647	1.11654
C	-0.12293	-0.34347	0.35734	H	0.00763	-2.24234	-0.63127
C	0.56925	-1.44744	-0.15822	H	2.44601	-2.41229	-0.44707
C	1.94367	-1.53396	-0.05891	H	4.25483	0.18885	2.65227
C	2.69108	-0.53140	0.55933	H	6.69179	0.04318	2.83313
C	4.16136	-0.63266	0.67158	H	8.69316	-1.69352	1.80902
C	4.82773	-0.20475	1.82182	H	8.84001	0.00838	1.48638
C	6.20270	-0.29624	1.92558	H	9.36787	-2.23641	-0.32062
C	6.96629	-0.82615	0.89067	H	8.19535	1.18028	-0.57149
C	8.46953	-0.92720	1.06324	H	9.11573	1.43803	-2.05796
N	9.22540	-1.25969	-0.12154	H	10.33343	1.32819	0.75063
C	9.43340	-0.46431	-1.21559	H	9.93926	2.80444	-0.14214
C	9.16255	1.02067	-1.05381	H	13.40704	2.15673	-0.84182
C	10.23317	1.75113	-0.25975	H	12.66549	1.81197	0.73936
O	11.45663	1.66002	-0.93598	H	12.31515	3.34733	-0.09304
C	12.50497	2.27560	-0.24367	H	6.88240	-1.65433	-1.08553
O	9.83423	-0.93677	-2.25764	H	4.45133	-1.46966	-1.27965
C	6.31336	-1.25388	-0.25534	H	2.55599	1.37663	1.53566
C	4.93420	-1.15493	-0.36285	H	0.11576	1.53239	1.36928
C	2.00262	0.56834	1.07195	H	-4.39823	-1.94295	-0.94500
C	0.62899	0.66563	0.97378	H	-6.81331	-1.77426	-1.12328
C	-4.90805	-1.08816	-0.51497				

V. Supplementary Figures

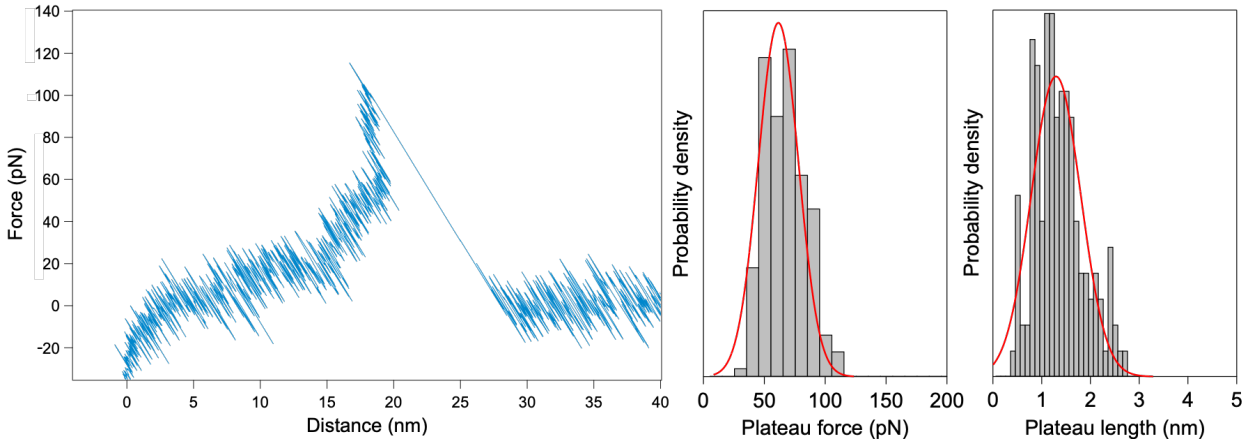


Figure S1. Characteristic force-distance profile obtained for **M2** at a pulling rate of 200 nm.s^{-1} and histograms of the pseudo-plateau force (*N*=174) and pseudo-plateau length (*N*=174).

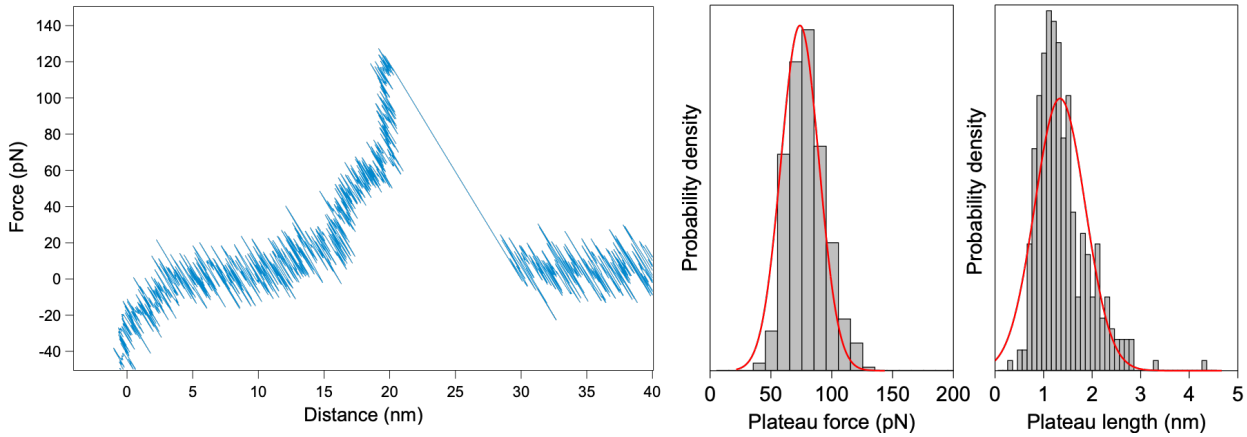


Figure S2. Characteristic force-distance profile obtained for **M3** at a pulling rate of 200 nm.s^{-1} and histograms of the pseudo-plateau force (*N*=337) and pseudo-plateau length (*N*=337).

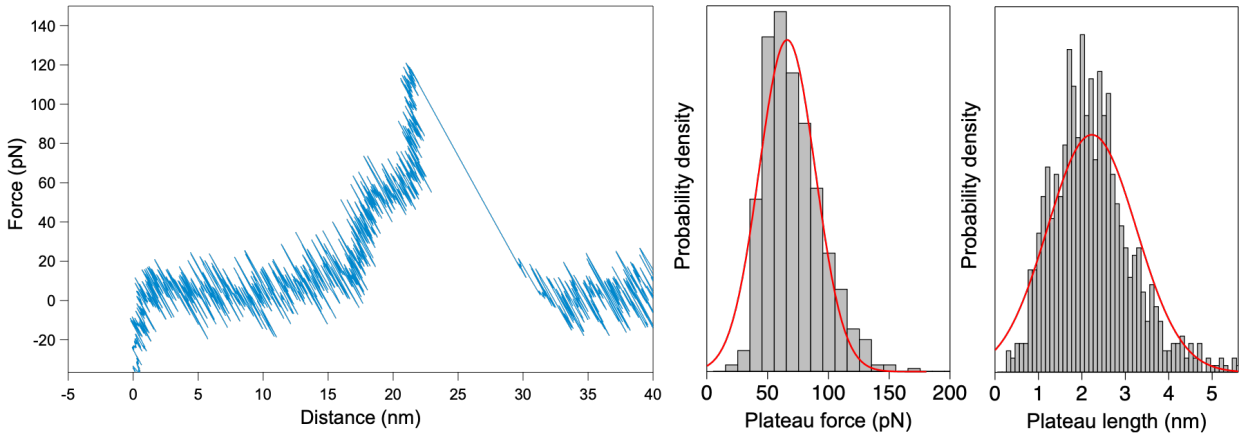


Figure S3. Characteristic force-distance profile obtained for **M4** at a pulling rate of 200 nm.s^{-1} and histograms of the pseudo-plateau force (*N*=354) and pseudo-plateau length (*N*=354).

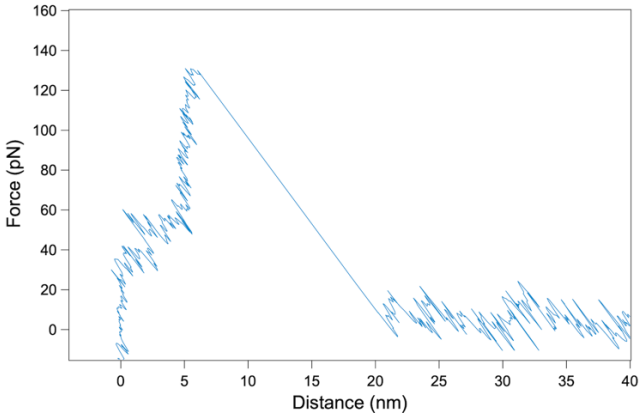


Figure S4. Characteristic force-distance profile obtained for **M1** at a pulling rate of 1000 nm.s^{-1}.

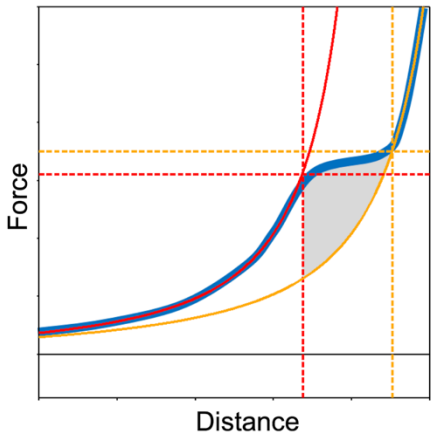


Figure S5. Schematic showing the considered area to measure the cumulative work resulting from the fluctuations (hopping states). This integrated area is below the region of fluctuations (from state A to B, Figure 2a) and between the two WLC fits.

VI. References

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