



HAL
open science

Synthesis of symmetric and dissymmetric star-shaped pentaarylcyclopentadienyl Ru(II) complexes containing styryl-BODIPY fragments

Melissa Dumartin, Seifallah Abid, Yohan Gisbert, Nathalie Saffon-Merceron, Sheng Gao, Nicola Armaroli, Barbara Ventura, Claire Kammerer, Gwénaél Rapenne

► To cite this version:

Melissa Dumartin, Seifallah Abid, Yohan Gisbert, Nathalie Saffon-Merceron, Sheng Gao, et al.. Synthesis of symmetric and dissymmetric star-shaped pentaarylcyclopentadienyl Ru(II) complexes containing styryl-BODIPY fragments. *Chemistry Letters*, 2024, 53 (1), 10.1093/chemle/upad003 . hal-04637341

HAL Id: hal-04637341

<https://hal.science/hal-04637341v1>

Submitted on 5 Jul 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Synthesis of Symmetric and Dissymmetric Star-shaped Pentaarylcyclopentadienyl Ru(II) Complexes Containing Styryl-BODIPY Fragments

Melissa Dumartin,¹ Seifallah Abid,¹ Yohan Gisbert,¹ Nathalie Saffon-Merceron,² Sheng Gao,³ Nicola Armaroli,³ Barbara Ventura,³ Claire Kammerer,^{*1} Gwénaél Rapenne^{*1,4}

¹CEMES, Université de Toulouse, CNRS, 29 rue Marvig, F-31055 Toulouse Cedex 4, France

²Université de Toulouse, UPS, ICT UAR2599, 118 route de Narbonne, F-31062 Toulouse, France

³Istituto per la Sintesi Organica e la Fotoreattività, CNR-ISOF, Via Gobetti 101, 40129 Bologna, Italy

⁴Division of Materials Science, Nara Institute of Science and Technology, NAIST, 8916-5 Takayama-cho, Ikoma, Nara 630-0192, Japan

E-mail: rapenne@cemes.fr

1 We synthesised star-shaped ruthenium(II) complexes
2 containing one or five styryl-BODIPY units arranged
3 around a central trisindazolylrutheniumcyclopentadienyl
4 fragment. A symmetric complex was obtained following a
5 five-fold Suzuki-Miyaura reaction of the pentabrominated
6 key precursor while desymmetrisation was next achieved
7 via a modular synthetic approach based on sequential
8 chemoselective Suzuki-Miyaura reactions on a key building
9 block bearing one iodophenyl and four bromophenyl groups.

10 Keywords: Ruthenium, BODIPY, Desymmetrization

11 With the ultimate goal to create complex
12 nanomachineries,¹ various types of molecular motors² or
13 gears³ have been designed but only a few are based on
14 coordination complexes. With a large number of metals and
15 a wide variety of ligands available, coordination chemistry
16 is a very versatile and efficient tool to assemble mechanical
17 subunits to prepare synthetic molecular machines.⁴ In the
18 last decade, we designed and synthesised a series of star-
19 shaped molecular motors⁵ and gears subunits⁶ based on
20 heteroleptic ruthenium(II) complexes containing a
21 hydrotris(indazolyl)-borate ligand as anchoring platform and
22 a functionalised pentaarylcyclopentadienyl ligand as
23 rotating subunit. These compounds interestingly exhibited
24 controlled clockwise or anticlockwise unidirectional rotation
25 once anchored on metallic surfaces.⁷

26 As nanosized movable entities, molecular machines
27 can be fuelled by various sources of energy such as light,
28 chemicals or electrons. Chemical fuels generate waste while
29 addressing electrons at the single-molecule level remains
30 highly challenging, so light appears to be a particularly
31 clean and easy to operate as well as highly efficient and
32 non-invasive source of energy.⁸ In our efforts to expand the
33 set of mechanical tasks performed by our rotary molecular
34 machines, it was envisioned to exploit light as a stimulus
35 and integrate a photoactivable function in their design,
36 allowing for instance the light-induced engagement or
37 disengagement of cogwheels within a train of molecular
38 gears. It is thus of prime importance to explore the
39 possibility to incorporate various kinds and numbers of
40 photoactive subunits in the backbone of our ruthenium(II)-
41 based molecular motors and gears. This goal requires the
42 development of synthetic strategies allowing to obtain not
43 only symmetric structures but also desymmetrised
44 complexes, which are more challenging to be prepared but
45 also more promising in terms of properties as shown for
46 obtaining high unidirectionality in previously reported
47 molecular motors.⁷

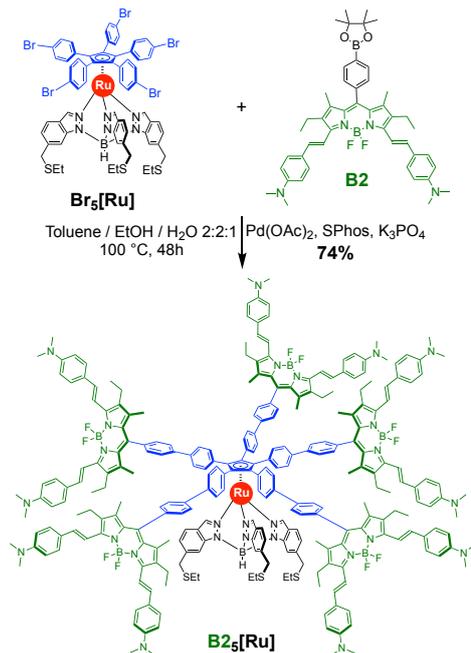
48 In our effort to build up such photoactive systems, we
49 report in this paper the synthesis of extended star-shaped
50 molecules based on pentaarylcyclopentadienyl
51 ruthenium(II) complexes functionalised with five peripheral
52 photoactive BODIPY units. In a preliminary work, the
53 photophysical properties of such complexes were
54 investigated, demonstrating that they are viable platforms
55 for the creation of systems that can be photoactivated.⁹ To
56 this end, two strongly fluorescent BODIPYs were selected:
57 **B1** as a standard fluorescent BODIPY fragment and **B2** as a
58 derivative incorporating two photochemically isomerisable
59 styryl groups on the pyrrole α -positions for photo-
60 mechanical applications. The symmetric ruthenium(II)
61 complex **B2₅[Ru]** was then synthesised as well as a
62 desymmetrised ruthenium(II) complex with four BODIPYs
63 and one styryl-BODIPY **B1₄B2₁[Ru]** (Scheme 1 and 2). The
64 parent compound **B1₅[Ru]** has been previously
65 synthesised¹⁰ but the absence of photochemically
66 isomerisable styryl groups drastically limits its potentialities
67 in light-induced motions.

68 Our general strategy for the synthesis of the symmetric
69 target compound **B2₅[Ru]** relies on the post-
70 functionalisation of a ruthenium(II) complex as key
71 intermediate, incorporating a thioether-functionalised
72 hydrotris(indazolyl)borate tripod in combination with a
73 penta(*p*-halogenophenyl)cyclopentadienyl ligand.¹¹ A
74 variety of transition metal-catalysed cross-coupling
75 reactions are tolerated, which leads in a divergent manner to
76 a family of piano-stool ruthenium complexes with a five-
77 fold substituted cyclopentadienyl ligand, exhibiting
78 potential mechanical functions stimulated by light. However,
79 when desymmetrised cyclopentadienyl units are desired, the
80 synthetic strategy appeared to be much more challenging
81 than anticipated. In the course of our previous work towards
82 desymmetrised complexes, we explored the chemoselective
83 functionalization of penta(4-halogenophenyl)cyclopenta-
84 dienyl ruthenium complex **Br₄I₁[Ru]** incorporating a single
85 aryl iodide moiety. The discrimination of aryl iodides over
86 bromides, although largely exploited in cross-couplings
87 such as Sonogashira or Stille couplings, remains difficult in
88 the case of Suzuki-Miyaura coupling, due to a change of
89 rate-determining step in the catalytic cycle. In a previous
90 paper,^{6c} we reported the successful single Suzuki-Miyaura
91 cross-coupling of complex **Br₄I₁[Ru]** using copper(I)
92 thiophene-2-carboxylate (CuTC) as a stoichiometric
93 additive in the presence of the mild Pd(PPh₃)₄ catalyst in
94 THF. Unfortunately, these conditions are restricted to the
95 use of boronic acids as coupling partners, since an

1 interaction between the latter and CuTC is expected to occur
 2 prior to the actual coupling. Indeed, when these conditions
 3 were tested for the coupling of precursor **Br₄I₁[Ru]** with
 4 boronic ester **B2**, no conversion was observed. Since
 5 boronic acid function should be avoided in **B2** due to the
 6 presence of amino groups, we explored alternative reaction
 7 conditions that could favour a chemoselective
 8 functionalization of **Br₄I₁[Ru]** in the presence of a boronic
 9 ester.

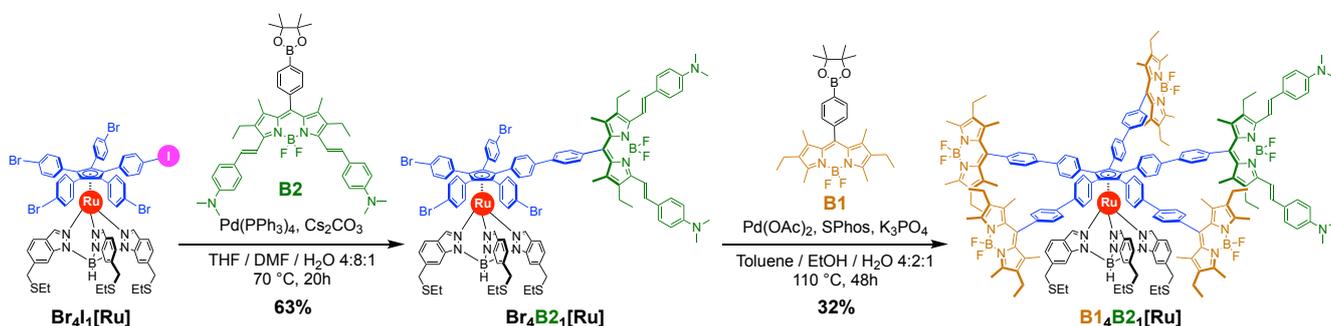
10 The styryl-BODIPY **B2** was prepared from BODIPY
 11 **B1** via a double Knoevenagel condensation with *p*-
 12 dimethylaminobenzaldehyde in the presence of piperidine
 13 and acetic acid. The reaction was run in refluxing toluene
 14 and a Dean-Stark apparatus was used to trap water. The
 15 selective formation of *trans*-styryl moieties on both pyrrole
 16 α -positions was achieved with a 20% yield. This moderate
 17 yield is mostly related to purification issues. **B2** was
 18 characterised by mass spectrometry as well as ¹H, ¹³C, ¹¹B
 19 and ¹⁹F NMR spectroscopy. The ¹⁹F NMR spectrum of **B2**
 20 exhibits a quadruplet shifted to -139.1 ppm with a coupling
 21 constant *J* (¹¹B-¹⁹F) of 35.0 Hz. The *trans*-configuration of
 22 the *p*-dimethylaminostyryl fragments was unambiguously
 23 confirmed by ¹H NMR spectroscopy, which revealed a 16.6
 24 Hz coupling constant between vinylic protons. Next, styryl-
 25 BODIPY derivative **B2** was used as coupling partner in a
 26 Suzuki-Miyaura reaction with key intermediate **Br₅[Ru]** in
 27 the presence of Pd(OAc)₂/SPhos as catalytic system and
 28 K₃PO₄ as base, to afford the five-fold substituted target
 29 compound **B₂₅[Ru]** in 74% yield (Scheme 1), corresponding
 30 to 94% yield per newly-formed C-C bond. The use of a
 31 biphasic solvent system combining toluene/ethanol/water
 32 (2:2:1) is the key to increase the reaction efficiency.
 33 Without this biphasic solvent system, only trace amounts of
 34 **B₂₅[Ru]** were observed. **B₂₅[Ru]** was characterised by mass
 35 spectrometry as well as ¹H, ¹³C, ¹¹B and ¹⁹F NMR
 36 spectroscopy. In the ¹H NMR spectrum (Fig. S5),
 37 integration of the two AA'BB' systems corresponding to the
 38 4,4'-biphenyl linkers and of the methyl and ethyl groups
 39 located on the pyrrole rings, as compared to protons
 40 belonging to the equivalent indazole rings shows that five
 41 styryl-BODIPY moieties have been grafted. In addition, the
 42 coupling constant of 16.4 Hz between the two sets of 10
 43 vinyl protons confirms the *trans*-geometry of the styryl units.

44 Finally, both the ¹¹B and ¹⁹F NMR spectra (Fig. S7 and Fig.
 45 S8) exhibit a single signal located at 1.32 ppm and -139.1
 46 ppm, respectively, in agreement with the chemical shifts
 47 observed for the BODIPY unit of precursor **B2**. This
 48 indicates that all styryl-BODIPYs are equivalent in this five-
 49 fold substituted ruthenium complex.
 50



51 **Scheme 1.** Synthesis of the symmetric **B₂₅[Ru]** starting from **Br₅[Ru]**.

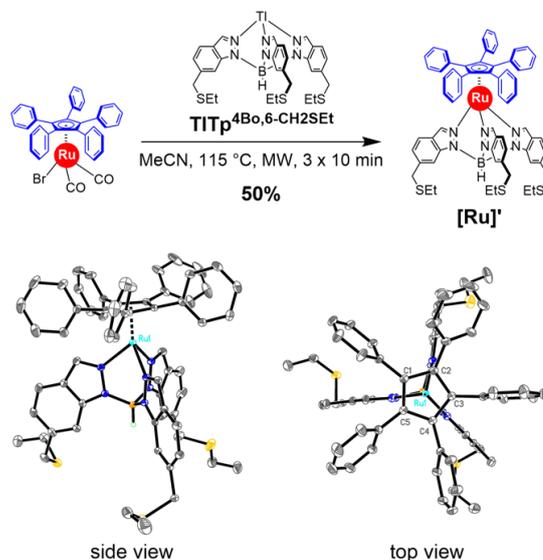
52 To synthesise the desymmetrised complex
 53 **B₁₄B₂₁[Ru]** bearing different BODIPYs, the penta(*p*-
 54 halogenophenyl)cyclopentadienyl ruthenium(II) key
 55 building block, incorporating a single *p*-iodophenyl group
 56 (**Br₄I₁[Ru]**, Scheme 2) was prepared.⁶ Thanks to the
 57 difference in reactivities of aryl iodides vs bromides in
 58 palladium-catalysed cross-couplings, this platform was
 59 expected to allow the sequential introduction of substituents
 60 on the cyclopentadienyl ligand to yield desymmetrised
 61 ruthenium complexes in a controlled manner.



Scheme 2. Synthesis of the desymmetrised star-shaped Ru-based system **B₁₄B₂₁[Ru]** starting from key intermediate **Br₄I₁[Ru]**.

1 As already explained, boronic acid function should be
 2 avoided in **B2** due to the presence of amino groups. Then,
 3 we explored alternative reaction conditions that could
 4 favour a chemoselective functionalization of **Br₄I₁[Ru]** in
 5 the presence of a boronic ester. We already knew that the
 6 conditions used for the coupling of **Br₅[Ru]** with **B1** or **B2**
 7 (*i.e.* Pd(OAc)₂, SPhos, K₃PO₄ in toluene/EtOH/H₂O at
 8 100 °C) lead to very efficient coupling of aryl bromides and
 9 would thus be detrimental to a chemoselective coupling. We
 10 thus turned to conditions used previously in our group for
 11 the statistical monocoupling of **Br₅[Ru]** (*i.e.* PdCl₂(dppf),
 12 Cs₂CO₃ in DMF/H₂O at 100 °C),¹² employing a less
 13 activated catalyst such as Pd(PPh₃)₄ and lowering the
 14 temperature to 70 °C to favour the oxidative addition of the
 15 weaker C-I bond (Scheme 2).⁶ This strategy proved to be
 16 successful, and the coupling of **Br₄I₁[Ru]** with **B2** took
 17 place with high chemoselectivity to give rise to **Br₄B₂₁[Ru]**
 18 in 63% yield via a single Suzuki-Miyaura coupling. The
 19 four remaining *p*-bromophenylene groups were
 20 subsequently submitted to distinct Suzuki-Miyaura coupling
 21 conditions in the presence of an excess of BODIPY-
 22 derivative **B1**. Compared with the conditions for
 23 iodophenylene functionalisation, the Pd(OAc)₂/SPhos
 24 catalytic system was employed here in combination with
 25 K₃PO₄ as base at a higher temperature (110 °C). Again,
 26 the use of a biphasic solvent system combining
 27 toluene/ethanol/water (4:2:1) appeared crucial. The
 28 desymmetrised target complex **B₁₄B₂₁[Ru]** was obtained in
 29 32% yield, thus corresponding to 75% yield per single C-C
 30 coupling.

31 Both complexes were characterised by mass
 32 spectrometry as well as ¹H, ¹³C, ¹¹B and ¹⁹F NMR
 33 spectroscopy. Looking in detail at the ¹H-NMR in the 7.9-
 34 8.2 ppm region, two signals corresponding to the indazol
 35 ring (Fig S13, protons a and b) are surrounded by small
 36 signals integrating for a few %. Since the MALDI-TOF MS
 37 spectrum showed one single peak, we believe this signals
 38 correspond to isomers with the alkene bond of the **B2**
 39 fragment in the *Z* configuration. Due to the loss of C₅
 40 symmetry on the cyclopentadienyl ligand, the ¹H and ¹³C
 41 NMR spectra are more complex (Fig. S13 and Fig. S14,
 42 respectively, for **B₁₄B₂₁[Ru]**) compared to the BODIPY-
 43 substituted symmetric counterpart **B₂₅[Ru]**. In the ¹H NMR
 44 spectrum of intermediate **Br₄B₂₁[Ru]** (Fig. S9), integration
 45 of the methyl and ethyl groups located on the pyrrole rings,
 46 as compared to protons belonging to the equivalent indazole
 47 rings, clearly shows that a single styryl-BODIPY moiety has
 48 been coupled. The *trans*-configuration of the styryl groups
 49 is again confirmed by the 17.0 Hz coupling constant
 50 between the vinyl protons. In the case of the target complex
 51 **B₁₄B₂₁[Ru]**, the ¹⁹F NMR spectrum (Figure 2) exhibits two
 52 distinct signals located at -139.3 ppm and -145.7 ppm,
 53 respectively, with an integral ratio of 1 to 4. These chemical
 54 shifts are in full agreement with those observed for
 55 precursors **B2** (-139.1 ppm) and **B1** (-145.7 ppm), which
 56 shows that the ruthenium(II) complex incorporates a single
 57 styryl-BODIPY unit combined with four BODIPY moieties.
 58 This is also confirmed by the integral ratios in the ¹H NMR
 59 spectrum and by mass spectrometry.



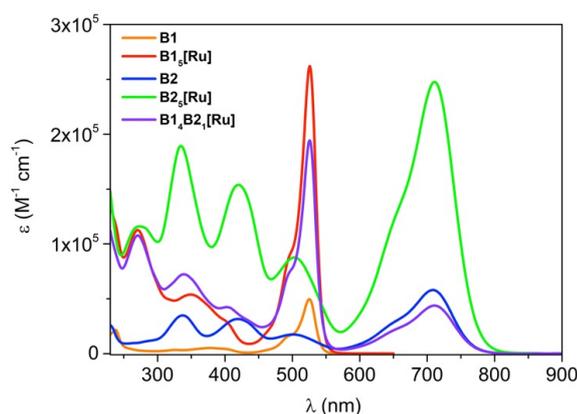
60 The model system **[Ru]'** incorporating a bare
 61 pentaphenylcyclopentadienyl ligand in combination with the
 62 thioether-functionalised hydrotris(indazolyl)borate tripod
 63 (Scheme 3), has been also synthesized to help in the
 64 assignment of the signals of ¹H and ¹³C NMR spectra and to
 65 have an X-ray structure of the central part of our molecules.

66 **Scheme 3.** Synthesis of model compound **[Ru]'** (top), and side view
 67 (bottom left) and top view (bottom right) of the molecular structure of
 68 ruthenium complex **[Ru]'**. Thermal ellipsoids are drawn at 30%
 69 probability. Hydrogen atoms (except for B-H), solvent molecule and
 70 disordered atoms are omitted for clarity. The centroid of the
 71 cyclopentadienyl ligand is distant from the ruthenium atom by 1.80 Å
 72 and the average distance between the three coordinated nitrogens and
 73 the ruthenium centre is 2.14 Å.

74 This compound was synthesised starting from the
 75 known bromido dicarbonyl η⁵-1,2,3,4,5-
 76 pentaphenylcyclopentadienyl ruthenium(II)¹² *via* a ligand
 77 exchange process in the presence of thallium
 78 hydrotris(indazolyl)borate **TITp**^{4Bo,6-CH2SEt} ¹¹ in acetonitrile
 79 under microwave irradiation (Scheme 3, top). Complex
 80 **[Ru]'** was obtained in 50% yield and fully characterised by
 81 mass spectrometry, elemental analysis and NMR
 82 spectroscopy. Single crystals were also obtained by slow
 83 evaporation of a 1:2 methanol/CH₂Cl₂ solution of complex
 84 **[Ru]'**, thus allowing the resolution of its structure by X-ray
 85 diffraction (Scheme 3, bottom). The X-ray structure is
 86 similar to previous structures obtained for this family of
 87 Ru(II) complexes^{5,6} bearing a pentaphenylcyclopentadienyl
 88 and a trisindazolylborate ligand with the later binding in a
 89 facial tripodal mode (*i.e.* κ³-*N,N',N''*). The complex has a
 90 piano stool structure with the cp ligand fitting in the vacant
 91 spaces of the tripodal ligand.

92 The absorption spectra of **B1**, **B2**, **B₂₅[Ru]** and
 93 **B₁₄B₂₁[Ru]** were recorded in CH₂Cl₂ at 298 K (Figure 4).
 94 The main absorption parameters are collected for each
 95 compound in the experimental section. Complexes **B₂₅[Ru]**
 96 and **B₁₄B₂₁[Ru]** show an intense band in the UV region
 97 peaked around 270 nm like analogous ruthenium

1 complexes⁹ with similar molar absorption coefficients. In
 2 the visible region, the absorption spectra of **B2** and **B2₅[Ru]**
 3 are similar, with an absorption peak around 710 nm.
 4 Compared with **B1** which exhibit an absorption peak around
 5 525 nm, and due to the effect of styryl fragments, the
 6 absorption spectra of **B2** and **B2₅[Ru]** are red-shifted. As
 7 expected, the extinction coefficient of **B2₅[Ru]** is almost
 8 five times higher than that of **B2**, in line with the presence
 9 of five styryl-BODIPY moieties in the complex. Finally,
 10 **B1₄B2₁[Ru]**, with four BODIPY and one styryl-BODIPY
 11 arms, exhibits both the absorption features at 526 nm (from
 12 **B1**) and 711 nm (from **B2**) with an intensity about four
 13 times larger than that of **B1** and almost equal to **B2** at their
 14 respective absorption wavelengths. This illustrates the
 15 additivity of the absorption features of the different
 16 chromophores in this compound.
 17



18 **Figure 1.** Absorption spectra of compounds **B1**, **B1₅[Ru]**, **B2**, **B2₅[Ru]**
 19 and **B1₄B2₁[Ru]** in CH₂Cl₂ at 298 K.

20 In conclusion, star-shaped ruthenium(II) complexes
 21 incorporating one (**B1₄B2₁[Ru]**), or five (**B2₅[Ru]**)
 22 photoisomerisable styryl-BODIPY units (**B2**) have been
 23 synthesised and characterised by ¹H, ¹³C, ¹¹B and ¹⁹F
 24 NMR spectroscopy, absorption and HR-mass
 25 spectrometry. The symmetric complex **B2₅[Ru]** was
 26 obtained following a five-fold Suzuki-Miyaura
 27 coupling with the corresponding BODIPY-substituted
 28 phenylboronic acid pinacol ester precursor **B2**. The
 29 dissymmetric **B1₄B2₁[Ru]** was obtained *via* two
 30 consecutive Suzuki-Miyaura chemoselective couplings
 31 under different conditions, starting from the
 32 preactivated key building block **Br₄I₁[Ru]**. The
 33 absorption spectra showed the additivity of the features
 34 of the different chromophores in the ruthenium(II)
 35 complexes containing five BODIPYs (**B1**), five styryl-
 36 BODIPYs (**B2**) and in the desymmetrised complex
 37 bearing four **B1** and one **B2** fragment. Work is now
 38 underway to investigate the photochemical and
 39 photophysical properties of these extended ruthenium
 40 complexes in more details, such as photoinduced
 41 electron and/or energy transfer processes. The *trans-cis*

42 photoisomerisation of the styryl subunits will also be
 43 studied, with the goal to explore the potential of such
 44 ruthenium(II) complexes as mechanically-active
 45 components of photodeformable materials.
 46

47 This work has received funding from the JSPS
 48 KAKENHI Grant-in-Aid for Challenging Research
 49 (20K21131), the JSPS KAKENHI Grant-in-Aid for Basic
 50 Research A (22H00325), the CNR (Project PHEEL) and the
 51 European Union's Horizon 2020 research and innovation
 52 program under the project MEMO (grant agreement No
 53 766864). YG thanks the University Toulouse III Paul
 54 Sabatier for a PhD Fellowship. Special thanks are given to
 55 Ms. Yoshiko Nishikawa (NAIST) for her admirable
 56 contribution to the measurements of high mass compounds
 57 (MALDI).
 58

59 References and Notes

- 60 1 V. Balzani, A. Credi and M. Venturi, *Molecular Devices and*
 61 *Machines. Concepts and Perspectives for the Nanoworld*, 2nd ed.
 62 Wiley-VCH, Weinheim, 2008.
 63 2 T. R. Kelly, H. De Silva and R. A. Silva, *Nature* **1999**, **401**, 150;
 64 N. Koumura, R. W. J. Zijlstra, R. A. van Delden, N. Harada, B. L.
 65 Feringa, *Nature* **1999**, **401**, 152; D. A. Leigh, J. K. Y. Wong, F.
 66 Dehez, F. Zerbetto, *Nature* **2003**, **424**, 174; M. von Delius, E. M.
 67 Geertsema, D. A. Leigh, *Nat. Chem.* **2010**, **2**, 96; H.-P. Jacquot
 68 de Rouville, R. Garbage, F. Ample, A. Nickel, J. Meyer, F.
 69 Moresco, C. Joachim and G. Rapenne, *Chem. Eur. J.*, **2012**, **18**,
 70 8925–8928; L. Greb, A. Eichhöfer, J.-M. Lehn, *Angew. Chem.*
 71 *Int. Ed.* **2015**, **54**, 14345; M. Guentner, M. Schildhauer, S.
 72 Thumser, P. Mayer, D. Stephenson, P. J. Mayer, H. Dube, *Nat.*
 73 *Commun.* **2015**, **6**, 8406; J. T. Foy, Q. Li, A. Goujon, J.-R.
 74 Colard-Itté, G. Fuks, E. Moulin, O. Schiffmann, D. Dattler, D. P.
 75 Funeriu, N. Giuseppone, *Nat. Nanotechnol.* **2017**, **12**, 540; S.
 76 Kassem, T. van Leeuwen, A. S. Lubbe, M. R. Wilson, B. L.
 77 Feringa, D. A. Leigh, *Chem. Soc. Rev.* **2017**, **46**, 2592; M.
 78 Baroncini, S. Silvi, A. Credi, *Chem. Rev.* **2020**, **120**, 200; D.
 79 Dattler, G. Fuks, J. Heiser, E. Moulin, A. Perrot, X. Yao, N.
 80 Giuseppone, *Chem. Rev.* **2020**, **120**, 310; V. García-López, D.
 81 Liu, J. M. Tour, *Chem. Rev.* **2020**, **120**, 79.
 82 3 H. Ube, Y. Yasuda, H. Sato, M. Shionoya, *Nat. Commun.* **2017**, **8**,
 83 14296; D. K. Frantz, A. Linden, K. K. Baldrige, J. S. Siegel, *J.*
 84 *Am. Chem. Soc.* **2012**, **134**, 1528; K. H. Au Yeung, T. Kühne, F.
 85 Eisenhut, M. Kleinwächter, Y. Gisbert, R. Robles, N. Lorente, G.
 86 Cuniberti, C. Joachim, G. Rapenne, C. Kammerer, F. Moresco, *J.*
 87 *Phys. Chem. Lett.* **2020**, **11**, 6892; Y. Gisbert, S. Abid, C.
 88 Kammerer, G. Rapenne, *Chem. Eur. J.* **2021**, **27**, 12019; A.
 89 Gerwien, F. Gnannt, P. Mayer, H. Dube, *Nat. Chem.* **2022**, **14**,
 90 670.
 91 4 A. Goswami, S. Saha, P. K. Biswas, M. Schmittel, *Chem. Rev.*
 92 **2020**, **120**, 125.
 93 5 G. Vives, H.-P. Jacquot de Rouville, A. Carella, J.-P. Launay,
 94 G. Rapenne, *Chem. Soc. Rev.* **2009**, **38**, 1551; C. Kammerer,
 95 G. Rapenne, *Eur. J. Inorg. Chem.* **2016**, 2214.
 96 6 Y. Gisbert, S. Abid, G. Bertrand, N. Saffon-Merceron, C.
 97 Kammerer, G. Rapenne, *Chem. Commun.* **2019**, **55**, 14689; Y.
 98 Gisbert, C. Kammerer, G. Rapenne, *Chem. Eur. J.*, **2021**, **27**,
 99 16242; S. Abid, Y. Gisbert, M. Kojima, N. Saffon-Merceron, J.
 100 Cuny, C. Kammerer, G. Rapenne, *Chem. Sci.* **2021**, **12**, 4709; K.
 101 Omoto, M. Shi, K. Yasuhara, C. Kammerer and G. Rapenne,
 102 *Chem. Eur. J.*, **2023**, **29**, e202203483.
 103 7 U. G. E. Perera, F. Ample, H. Kersell, Y. Zhang, G. Vives, J.
 104 Echeverría, M. Grisolia, G. Rapenne, C. Joachim, S.-W. Hla, *Nat.*
 105 *Nanotechnol.* **2013**, **8**, 46; Y. Zhang, J. P. Calupitan, T. Rojas, R.
 106 Tumbleson, G. Erbland, C. Kammerer, T. M. Ajayi, S. Wang, L.

1 A. Curtiss, A. T. Ngo, S. E. Ulloa, G. Rapenne, S.-W. Hla, *Nat.*
2 *Commun.* **2019**, *10*, 3742.
3 8 V. Balzani, A. Credi, M. Venturi, *Chem. Soc. Rev.*, **2009**, *38*,
4 1542; S. Silvi, M. Venturi, A. Credi, *Chem. Commun.* **2011**, *47*,
5 2483.
6 9 S. Gao, Y. Gisbert, G. Erbland, S. Abid, C. Kammerer, A.
7 Venturini, G. Rapenne, B. Ventura, N. Armaroli, *Phys. Chem.*
8 *Chem. Phys.*, **2021**, *23*, 17049.
9 10 G. Erbland, S. Abid, Y. Gisbert, N. Saffon-Merceron, Y.
10 Hashimoto, L. Andreoni, T. Guérin, C. Kammerer, G.
11 Rapenne, *Chem. Eur. J.* **2019**, *25*, 16328.
12 11 A. Carella, G. Vives, T. Cox, J. Jaud, G. Rapenne, J.-P.
13 Launay, *Eur. J. Inorg. Chem.*, **2006**, 980–987; G. Erbland, Y.
14 Gisbert, G. Rapenne, C. Kammerer, *Eur. J. Org. Chem.* **2018**,
15 4731.
16 12 X. Li, Y. Gisbert, D. Sluysmans, G. Rapenne, C. Kammerer, A.-
17 S. Duwez, *ChemRxiv* **2023**, 10.26434/chemrxiv-2023-mgq5f-
18 v2
19 13 B. Martín-Matute, M. Edin, K. Bogár, F. B. Kaynak, J.-E.
20 Bäckvall, *J. Am. Chem. Soc.*, **2005**, *127*, 8817.
21
22

Supplementary Information

I. Experimental section

1. Synthesis and characterisation

General methods. All chemicals and solvents were purchased from commercial suppliers and were used without further purification. 4-Dimethylaminobenzaldehyde, piperidine, potassium phosphate, tetrakis(triphenylphosphine) palladium(0), palladium(II) acetate, 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (SPhos), cesium carbonate were purchased from Aldrich. Acetic acid was purchased from Acros.

The precursors employed in the synthesis of new target compounds **B2₅[Ru]**, **B1₄B2₁[Ru]** and **[Ru]'** were prepared according to previously reported procedures: **B1¹**, penta(*p*-bromophenyl)cyclopentadienyl hydrotris (indazolyl)borate ruthenium(II) **Br₅[Ru]**,² 1-(*p*-iodophenyl)-2,3,4,5-tetra(*p*-bromophenyl)cyclopentadienylhydrotris (indazolyl)borate ruthenium(II) **Br₄I₁[Ru]**,³ thallium hydrotris{6-[(ethylsulfanyl)methyl]indazol-1-yl}borate **TITp**^{4Bo,6-CH₂SET}⁴ and bromido dicarbonyl η⁵-1,2,3,4,5-pentaphenyl cyclopentadienyl ruthenium(II).⁴

All reactions were carried out using standard Schlenk techniques under an argon atmosphere. Microwave reactions were carried out by using a CEM Discover LabMate microwave reactor. Column chromatography was carried out on 230–400 mesh silica gel (Aldrich) unless otherwise stated. Thin layer chromatography (TLC) was performed on pre-coated aluminum-backed silica gel 60 UV254 plates (Macherey–Nagel) with visualization effected using ultraviolet irradiation (λ = 254, 366 nm).

¹H, ¹³C, ¹¹B and ¹⁹F NMR spectra 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). Residual solvent signals were used as internal references for ¹H and ¹³C NMR, and ¹¹B and ¹⁹F NMR spectra were referenced according to the solvent. 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); doublet (d); triplet (t); quadruplet (q); quintuplet (quint); multiplet (m); broad (br.). Full assignments of ¹H and ¹³C NMR spectra were made with the assistance of COSY, HSQC and HMBC spectra. The full width of ¹H NMR and ¹³C NMR spectra is shown on purpose in the Supporting Information section; in case some minor impurities such as grease or solvent traces are present, the corresponding peaks have been assigned. It must be noted that due to the quadrupolar relaxation (proton coupled with the nuclear spin of the boron atom), the ¹H-NMR signal of the BH proton and the ¹¹B-NMR signal of the Boron is very broad and difficult to locate (For instance see C. Lopez et al, *J. Inorg. Chim. Acta* **1990**, *176*, 195).

High-resolution mass spectra (HRMS) were performed with a Waters Xevo G2 QTOF spectrometer for electrospray ionization (ESI). The MALDI-TOF mass spectrometry was performed using Bruker Daltonics Autoflex II spectrometer and JEOL JMS-S300 spectrometer (matrix: *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene] malononitrile DTCB). Elemental analysis was performed using a PerkinElmer 2400 Series II CHNS Organic Elemental Analyzer.

Absorption spectra were collected with a Perkin-Elmer Lambda 950 spectrophotometer by using 1 cm optical path quartz cuvettes. Spectrofluorimetric grade CH₂Cl₂ (Merck Uvasol[®]) was used as solvent.

Crystallographic data for compound **[Ru]'** were collected on a Bruker-AXS D8-Venture diffractometer equipped with a Photon III-C14 detector using Mo Kα radiation (λ=0.71073 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.^{19 5} The structure was solved using an intrinsic phasing method (SHELXT),^{20 6} and refined using the least-squares method on *F2*.^{21 7} 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 sp³ carbon and 1.2 times for all other carbon atoms. The solvent molecule (CH₂Cl₂) and a thioether group were found to be disordered over two positions, for which occupancies were refined. Several restraints (SAME, SIMU, DELU) were applied to refine these disordered parts and to avoid the collapse of the structure during the least-squares refinement by the large anisotropic displacement parameters. Hydrogen on boron atom was located by difference Fourier map and was freely refined.

2. Model compound B2. 4-Dimethylaminobenzaldehyde (292 mg, 1.96 mmol, 3 equiv.), piperidine (0.97 mL, 9.78 mmol, 15 equiv.) and acetic acid (19 μ L, 0.33 mmol, 0.5 equiv.) were added to a solution of precursor **B1** (330 mg, 0.65 mmol, 1 equiv.) in toluene (30 mL) under argon. The resulting mixture was refluxed for 24h using a Dean–Stark apparatus. After cooling down to room temperature, the solution was extracted with dichloromethane (3 x 30 mL) and the organic layers combined. The organic phase was washed with a saturated NaCl solution (1 x 50 mL) and water (2 x 50 mL), then dried over Na₂SO₄ and the solvent was evaporated under vacuum. The crude mixture was dissolved in dichloromethane and filtered through a silica pad. The pad was rinsed with dichloromethane and methanol, and the filtrate was evaporated. The crude mixture was then purified by silica gel chromatography (SiO₂, CH₂Cl₂/MeOH gradient from 98:2 to 80:20). The pure compound **B2** was obtained in 20% yield (100 mg, 0.13 mmol) as a black powder with iridescent reflections.

R_f = 0.6 (SiO₂, pure CH₂Cl₂). **¹H NMR** (500 MHz, CD₂Cl₂, 25 °C): δ = 7.88 (AA'BB' pattern, 2H, H_a), 7.57 (d, ³J=16.6 Hz, 2H, H_k), 7.53 (d, ³J=8.5 Hz, 4H, H_h), 7.36 (AA'BB' pattern, 2H, H_b), 7.22 (d, ³J=16.9 Hz, 2H, H_j), 6.75 (d, ³J=8.9 Hz, 4H, H_i), 3.03 (br. s, 12H, H_d), 2.65-2.61 (m, 4H, H_e), 1.38 (s, 12H, H_c), 1.33 (s, 6H, H_g), 1.16 (t, ³J=7.5 Hz, 6H, H_f) ppm. **¹³C{¹H} NMR** (126 MHz, CD₂Cl₂, 25 °C): δ = 151.4 (C₁₀), 150.6 (C₈), 139.6 (C₃ and C₄), 138.8 (C₆), 136.5 (C_j), 135.5 (C_a), 133.9 (C₅ and C₇), 129.2 (C₂), 129.0 (C_h), 128.8 (C_b), 125.9 (C₉), 115.7 (C_k), 112.5 (C_i), 84.5 (C₁), 40.5 (C_d), 25.2 (C_c), 18.8 (C_e), 14.2 (C_f), 11.8 (C_g) ppm. **¹¹B NMR** (160 MHz, CD₂Cl₂, 25 °C): δ = 1.29 (t, *J*(¹¹B-¹⁹F)=35.0 Hz) ppm. The signal corresponding to the boronic acid pinacol ester function could not be precisely assigned. **¹⁹F NMR** (471 MHz, CD₂Cl₂, 25 °C): δ = -139.1 (q, *J*(¹¹B-¹⁹F)=35.0 Hz) ppm. **UV-Vis** (CH₂Cl₂): λ_{\max} , nm (ϵ_{\max} , M⁻¹ cm⁻¹) = 337 (35000), 419 (32000), 501 (17000), 709 (58000). **HRMS** (ESI⁺): calcd. for C₄₇H₅₇B₂F₂N₄O₂ [M+H]⁺: 769.4636, found 769.4639.

3. Model complex [Ru]'. In a 10 mL microwave reactor were placed a magnetic stir bar, bromido dicarbonyl η^5 -1,2,3,4,5-pentaphenylcyclopentadienyl ruthenium(II)¹⁸ (110 mg, 0.16 mmol, 1.0 eq.), thallium hydrotris(indazolyl)borate **TITp**^{4Bo,6-CH₂Set} (170 mg, 0.22 mmol, 1.35 eq.) and anhydrous acetonitrile (5 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, 3 x 10 minutes, releasing the pressure and manually shaking between each cycle). The resulting suspension was filtered over silica (eluted with CH₂Cl₂) and the solvents were removed *in vacuo*. The residue was purified by column chromatography (SiO₂, CH₂Cl₂/pentane 40:60 to 60:40) to give complex **[Ru]'** as an orange solid in 50% yield (91 mg, 0.08 mmol).

R_f = 0.22 (SiO₂, Hexane/CH₂Cl₂ 60:40). **¹H NMR** (500 MHz, CD₂Cl₂, 25 °C): δ = 7.89 (br. s, 6H, H_a and H_b), 7.41 (dd, ³J = 8.4 Hz, ⁴J = 1.3 Hz, 10H, H_h), 7.28 (d, ³J = 7.8 Hz, 3H, H_c), 7.13 (m, 5H, H_j), 7.05 - 6.99 (m, 13H, H_d and H_i), 3.90 (s, 6H, H_e), 2.47 (q, ³J = 7.4 Hz, 6H, H_f), 1.28 (t, ³J = 7.4 Hz, 9H, H_g) ppm. **¹³C{¹H} NMR** (126 MHz, CD₂Cl₂, 25 °C): δ = 144.0 (C₃), 141.0 (C_b), 137.7 (C₂), 134.3 (C₅), 134.2 (C_h), 127.5 (C_i and C_j), 122.5 (C₄), 122.4 (C_d), 120.3 (C_c), 111.4 (C_a), 88.5 (C₁), 36.9 (C_e), 25.7 (C_f), 14.8 (C_g) ppm. **UV-Vis** (CH₂Cl₂): λ_{\max} ,

nm (ϵ_{\max} , $M^{-1} \text{ cm}^{-1}$) = 268 (131000), 343 (38000). **HRMS** (ESI⁺): calcd. for $C_{65}H_{60}BN_6RuS_3$ [M+H]⁺: 1133.3201, found 1133.3201. **Elemental analysis** (%) calcd. for $C_{65}H_{59}BN_6RuS_3$: C 68.95, H 5.25, N 7.42, found: C 68.91, H 4.78, N 7.42. **Crystal data**: Crystals suitable for X-Ray diffraction analysis were obtained by slow evaporation of a 1:2 methanol/ CH_2Cl_2 solution of complex **[Ru]'**. The title compound co-crystallised with dichloromethane. Selected data for **[Ru]'**: $C_{65}H_{59}BN_6RuS_3 \cdot CH_2Cl_2$, $M = 1217.16$, triclinic, space group $P\bar{1}$, $a = 12.1788(6) \text{ \AA}$, $b = 14.1325(6) \text{ \AA}$, $c = 18.1834(9) \text{ \AA}$, $\alpha = 100.0807(18)^\circ$, $\beta = 98.3306(18)^\circ$, $\gamma = 103.7255(18)^\circ$, $V = 2936.0(2) \text{ \AA}^3$, $Z = 2$, crystal size $0.300 \times 0.240 \times 0.140 \text{ mm}^3$, 146385 reflections collected (14545 independent, $R_{int} = 0.0416$), 783 parameters, 169 restraints, $R_1 [I > 2\sigma(I)] = 0.0327$, $wR_2 [\text{all data}] = 0.0893$, largest diff. peak and hole: 1.336 and $-0.864 \text{ e. \AA}^{-3}$. For more details, see the Supporting Information section. CCDC-2246796 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

4. Complex $B_2[Ru]$. In a dry Schlenk tube under argon, precursor **Br₅[Ru]** (12 mg, 7.8 μmol , 1 equiv.), palladium(II) acetate (0.6 mg, 2.7 μmol , 0.35 equiv.), K_3PO_4 (17 mg, 78 μmol , 10 equiv.), boronic acid pinacol ester **B2** (60 mg, 78 μmol , 10 equiv.), and 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (SPhos, 2 mg, 4.6 μmol , 0.6 equiv.) were successively introduced into degassed toluene/ethanol/water (2:2:1, 2.5 mL). The resulting suspension was stirred at 100 °C for 48 hours, and completion of the reaction was monitored by TLC (SiO_2 , CH_2Cl_2 /cyclohexane 1:1). The reaction mixture was cooled to room temperature, and the solvents evaporated. The crude residue was then triturated in ethyl acetate and the solid was recovered by filtration and washed several times with ethyl acetate. The brownish, iridescent powder was isolated as pure ruthenium complex **B₂[Ru]** in 74% yield (25 mg, 5.8 μmol).

$R_f = 0.9$ (SiO_2 , CH_2Cl_2 /MeOH 99.5:0.5). **¹H NMR** (500 MHz, CD_2Cl_2 , 25 °C): $\delta = 8.13$ (s, 3H, H_a), 7.99 (s, 3H, H_b), 7.74 (m, 20H, H_q and H_s), 7.59–7.51 (m, 40H, H_k and H_m and H_r), 7.44 (d, $^3J = 8.6 \text{ Hz}$, 3H, H_c), 7.37 (d, $^3J = 7.9 \text{ Hz}$, 10H, H_p), 7.22 (d, $^3J = 16.4 \text{ Hz}$, 10H, H_i), 7.09 (d, $^3J = 8.6 \text{ Hz}$, 3H, H_d), 6.73 (d, $^3J = 8.4 \text{ Hz}$, 20H, H_n), 3.95 (s, 6H, H_e), 3.01 (s, 60H, H_o), 2.62 (br q, $^3J = 8.1 \text{ Hz}$, 20H, H_j), 2.51 (q, $^3J = 7.4 \text{ Hz}$, 6H, H_f), 1.37 (s, 30H, H_h), 1.30 (t, $^3J = 7.4 \text{ Hz}$, 9H, H_g), 1.15 (t, $^3J = 7.5 \text{ Hz}$, 30H, H_j) ppm. **¹³C{¹H} NMR** (126 MHz, CD_2Cl_2 , 25 °C): $\delta = 151.4$ (C₁₂), 150.6 (C₁₀), 144.2 (C₁₃), 141.2 (C_a), 140.8 (C₄), 139.2 (C₃ and C₆), 138.7 (C₈), 138.1 (C₁₅), 136.5 (C_i), 135.9 (C₅), 135.0 (C_s), 133.9 (C₂ and C₇ and C₉), 130.0 (C_p), 129.0 (C_m), 127.6 (C_q), 126.1 (C_r), 125.9 (C₁₁), 122.7 (C_d), 122.6 (C₁₄), 120.5 (C_c), 115.7 (C_k), 112.5 (C_n), 111.5 (C_b), 88.6 (C₁), 40.5 (C_o), 37.0 (C_e), 25.8 (C_f), 18.8 (C_i), 14.8 (C_g), 14.3 (C_j), 11.9 (C_h) ppm. **¹¹B NMR** (160 MHz, CD_2Cl_2 , 25 °C): $\delta = 1.32$ (t, $J(^{11}B-^{19}F) = 35.0 \text{ Hz}$) ppm. **¹⁹F NMR** (471 MHz, CD_2Cl_2 , 25 °C): $\delta = -139.1$ (m) ppm. **UV-Vis** (CH_2Cl_2): λ_{\max} , nm (ϵ_{\max} , $M^{-1} \text{ cm}^{-1}$) = 273 (116000), 335 (189000), 420 (154000), 503 (88000), 711 (248000). **HRMS** (MALDI): calcd. for $C_{270}H_{274}B_6F_{10}N_{26}RuS_3$ [M]⁺: 4335.0970, found 4335.1084.

5. Complex $Br_4B_2[Ru]$. In a dry Schlenk tube under argon, precursor **Br₄[Ru]** (60 mg, 38 μmol , 1 equiv.), $Pd(PPh_3)_4$ (4.4 mg, 3.8 μmol , 0.1 equiv.), cesium carbonate (25 mg, 76 μmol , 2 equiv.) and boronic acid pinacol ester **B2** (30 mg, 38 μmol , 1 equiv.) were successively introduced into a mixture of degassed THF/DMF/water (2:4:0.5, 6.5 mL). The resulting mixture was stirred at 70 °C for 20 hours, and completion of the reaction was monitored by TLC (SiO_2 , CH_2Cl_2 /cyclohexane 75:25). Upon completion of the reaction, the crude mixture was allowed to cool to room temperature and evaporated to dryness. The crude solid was dissolved in 50 mL of dichloromethane and washed with 2 x 10 mL of water. The organic phase was then dried over $MgSO_4$ and evaporated. The crude compound was purified by flash chromatography on basic alumina, using mixtures of dichloromethane and cyclohexane as eluent, to afford the pure compound **Br₄B₂[Ru]** as a black solid with red-brown reflections in 63% yield (50 mg, 24 μmol).

$R_f = 0.65$ (SiO_2 , CH_2Cl_2 /cyclohexane 75:25). **¹H NMR** (500 MHz, CD_2Cl_2 , 25 °C): $\delta = 7.90$ (s, 3H, H_a), 7.87 (s, 3H, H_b), 7.71 (d, $^3J = 8.1 \text{ Hz}$, 2H, H_r), 7.58–7.51 (m, 6H, H_i and H_m), 7.46 (s, 4H, H_p and H_q), 7.37–7.35 (m, 5H, H_c and H_s), 7.34–7.31 (m, 4H, H₁₉ or H_{19'}), 7.28–7.25 (m,

4H, H₁₉ or H_{19'}), 7.23-7.19 (m, 10H, H_k and H₂₀ and H_{20'}), 7.05 (dd, ³J=8.4 Hz, ⁴J=1.4 Hz, 3H, H_d), 6.75 (d, ³J=8.5 Hz, 4H, H_n), 3.91 (s, 6H, H_e), 3.03 (s, 12H, H_o), 2.65-2.60 (m, 4H, H_i), 2.47 (q, ³J=7.4 Hz, 6H, H_f), 1.37 (s, 6H, H_h), 1.28 (t, ³J=7.4 Hz, 9H, H_g), 1.16 (t, ³J=7.5 Hz, 6H, H_j) ppm. **¹³C{¹H} NMR** (126 MHz, CD₂Cl₂, 25 °C): δ = 151.4 (C₁₄), 150.6 (C₁₂), 144.1 (C₁₅), 140.7 (C_b), 140.6 (C₆), 139.5 (C₅), 138.7 (C₈), 138.2 (C₁₇), 136.5 (C_k), 136.4 (C₁₀), 136.0 (C₇), 135.7 (C₁₉ or C_{19'}), 135.6 (C₁₉ or C_{19'}), 134.5 (C_p), 133.9 (C₁₁), 133.1 (C₄), 133.0 (C_{18'}), 132.8 (C₉), 132.7 (C₁₈), 131.1 (C₂₀ and C_{20'}), 130.0 (C_s), 129.0 (C_m), 127.6 (C_r), 126.2 (C_q), 125.9 (C₁₃), 122.7 (C_d), 122.5 (C₁₆), 122.3 (C₂₁ or C_{21'}), 122.2 (C₂₁ or C_{21'}), 120.4 (C_c), 115.7 (C_i), 112.5 (C_n), 111.4 (C_a), 88.8 (C₁), 87.7 (C₂ or C₃), 87.1 (C₂ or C₃), 40.5 (C_o), 36.9 (C_e), 25.7 (C_f), 18.8 (C_i), 14.8 (C_g), 14.2 (C_j), 11.9 (C_h) ppm. **¹¹B NMR** (160 MHz, CD₂Cl₂, 25 °C): δ = 1.30 (t, J(¹¹B-¹⁹F)=34.7 Hz) ppm. **¹⁹F NMR** (471 MHz, CD₂Cl₂, 25 °C): δ = -139.2 (q, J(¹¹B-¹⁹F)=35.0 Hz) ppm. **HRMS** (MALDI): calcd. for C₁₀₆H₉₈B₂Br₄F₂N₁₀RuS₃ [M]⁺: 2088.3079, found 2088.3196.

6. Complex B₁B₂[Ru]. In a dry Schlenk tube under argon, ruthenium complex **Br₄B₂[Ru]** (40 mg, 19 μmol, 1 equiv.), palladium(II) acetate (1.5 mg, 6.7 μmol, 0.35 equiv.), K₃PO₄ (41 mg, 190 μmol, 10 equiv.), boronic acid pinacol ester **B1** (78 mg, 150 μmmol, 8 equiv.) and 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (SPhos, 4.7 mg, 11 μmol, 0.6 equiv.) were successively introduced into a mixture of degassed toluene/ethanol/water (4:2:1, 7 mL). The resulting suspension was stirred at 110 °C for 48 hours, and completion of the reaction was monitored by TLC (SiO₂, pure CH₂Cl₂). Upon completion of the reaction, the crude mixture was allowed to cool to room temperature, evaporated to dryness and dichloromethane was added. The organic phase was washed with water (2 x 30 mL), dried over MgSO₄ and evaporated. Column chromatography was carried out on basic alumina (activity I) eluting with a gradient of CH₂Cl₂/cyclohexane from 30:70 to 100:0 and the pure compound **B₁B₂[Ru]** was isolated in 32% yield (20 mg, 6.1 μmol) as a dark pink solid with green reflections.

R_f = 0.5 (SiO₂, CH₂Cl₂/MeOH 99.5:0.5). **¹H NMR** (500 MHz, CD₂Cl₂, 25 °C): δ = 8.09 (s, 3H, H_a), 7.97 (s, 3H, H_b), 7.74-7.71 (m, 20H, H_q and H_{q'} and H_s and H_{s'}), 7.57-7.51 (m, 16H, H_{k'} and H_m and H_r and H_{r'}), 7.40 (d, ³J=8.4 Hz, 3H, H_c), 7.36 (d, ³J=8.0 Hz, 2H, H_{p'}), 7.32 (dd, ³J=8.4 Hz, ⁴J=2.2 Hz, 8H, H_p), 7.22 (br. d, ³J=15.1 Hz, 2H, H_i), 7.06 (dd, ³J=8.4 Hz, ⁴J=1.4 Hz, 3H, H_d), 6.74 (d, ³J=8.4 Hz, 4H, H_n), 3.94 (s, 6H, H_e), 3.03 (br. s, 12H, H_o), 2.61 (m, 4H, H_{i'}), 2.50 (q, ³J=7.4 Hz, 6H, H_f), 2.47 (s, 24H, H_k), 2.30 (q, ³J=7.4 Hz, 16H, H_i), 1.35 (s, 6H, H_{n'}), 1.32 (s, 24H, H_h), 1.30 (t, ³J=7.4 Hz, 9H, H_g), 1.14 (t, ³J=7.5 Hz, 6H, H_{j'}), 0.96 (t, ³J=7.4 Hz, 24H, H_j) ppm. **¹³C{¹H} NMR** (126 MHz, CD₂Cl₂, 25 °C): δ = 154.1 (C₁₀), 151.4 (C₁₂), 144.2 (C₁₃), 141.1 (C_a), 140.8 (C₄ and C_{4'}), 140.7 (C_{10'}), 140.4 (C₆), 139.2 (C_{8'}), 139.2 (C₃ and C_{3'}), 139.2 (C_{6'}), 138.9 (C₈), 138.0 (C₁₅), 136.4 (C_i), 135.3 (C₅ and C_{5'}), 135.0 (C_s and C_{s'}), 133.9 (C₂ and C_{2'}), 133.8 (C_{7'} and C_{9'}), 133.3 (C₉), 131.3 (C_{p'}), 131.0 (C₇), 129.3 (C_p), 129.0 (C_m), 127.6 (C_q), 127.5 (C_{q'}), 126.1 (C_r and C_{r'}), 125.9 (C₁₁), 122.6 (C_d), 122.6 (C₁₄), 120.4 (C_c), 115.6 (C_{k'}), 112.5 (C_n), 111.5 (C_b), 88.6 (C₁), 88.5 (C₁ and C_{1''}), 40.5 (C_o), 37.0 (C_e), 25.8 (C_f), 19.1 (C_{i'}), 17.4 (C_i), 14.8 (C_g and C_j), 14.3 (C_{j'}), 12.7 (C_k), 12.2 (C_h), 11.9 (C_{h'}) ppm. C₁ did not appear on the ¹³C{¹H} spectrum but its chemical shift was assigned thanks to correlations on HSQC and HMBC NMR spectra. **¹¹B NMR** (160 MHz, CD₂Cl₂, 25 °C): δ = 1.29 (t, J(¹¹B-¹⁹F)=32.7 Hz), 0.74 (t, J(¹¹B-¹⁹F)=33.6 Hz) ppm. **¹⁹F NMR** (471 MHz, CD₂Cl₂, 25 °C): δ = -139.3 (m, 2F), -145.7 (m, 8F) ppm. **UV-Vis** (CH₂Cl₂): λ_{max}, nm (ε_{max}, M⁻¹ cm⁻¹) = 271 (108000), 339 (72000), 403 (42000), 526 (194000), 711 (44000). **HRMS** (MALDI): calcd. for C₁₉₈H₂₀₃B₆F₁₀N₁₈RuS₃ [M+H]⁺: 3286.5076, found 3286.5120.

7. References

1. G. Erbland, S. Abid, Y. Gisbert, N. Saffon-Merceron, Y. Hashimoto, L. Andreoni, T. Guérin, C. Kammerer and G. Rapenne, *Chem. Eur. J.*, **2019**, *25*, 16328.
2. G. Erbland, Y. Gisbert, G. Rapenne and C. Kammerer, *Eur. J. Org. Chem.*, **2018**, 4731.
3. Y. Gisbert, S. Abid, G. Bertrand, N. Saffon-Merceron, C. Kammerer and G. Rapenne, *Chem. Commun.*, **2019**, *55*, 14689.

4. B. Martín-Matute, M. Edin, K. Bogár, F. B. Kaynak and J.-E. Bäckvall, *J. Am. Chem. Soc.*, **2005**, *127*, 8817.
5. Bruker, SADABS, Bruker AXS Inc., Madison, Wisconsin, USA, **2008**.
6. ShelXT, G. M. Sheldrick, University of Göttingen, *Acta Crystallogr. Sect. A*, **2015**, *71*, 3-8.
7. ShelXL, G. M. Sheldrick, University of Göttingen, *Acta Crystallogr. Sect. C*, **2015**, *71*, 3-8.

II. NMR spectra of new compounds

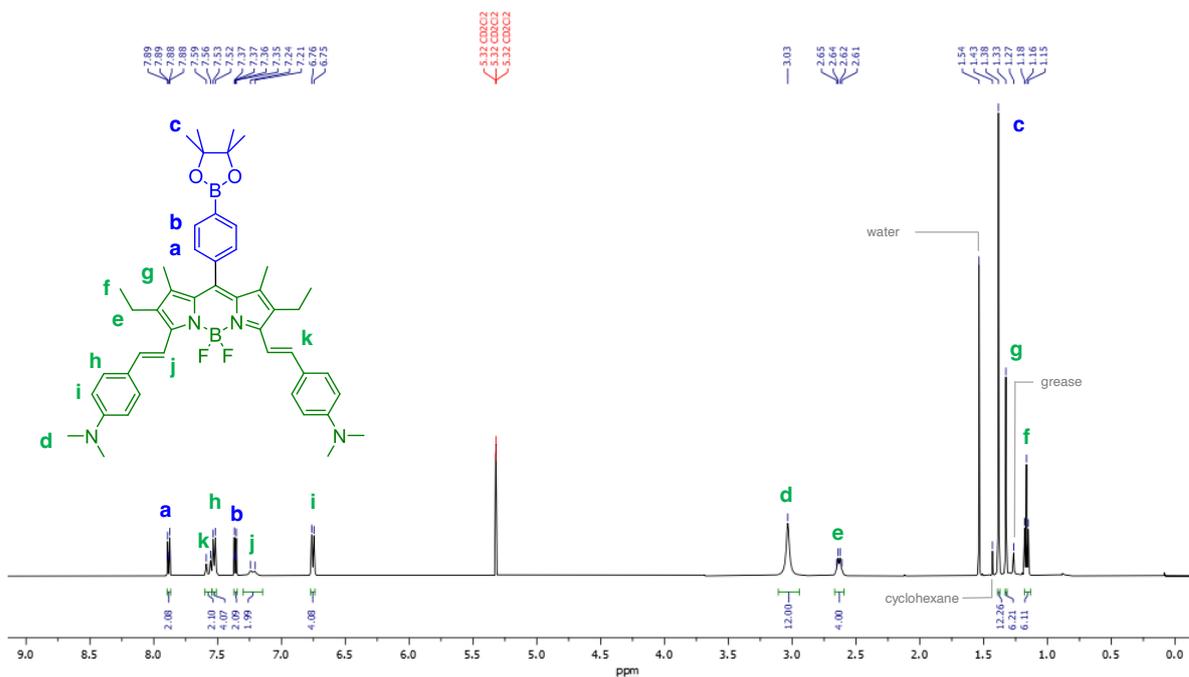


Fig. S1. ^1H NMR spectrum (500 MHz) of compound **B2** in CD_2Cl_2 recorded at 25 °C.

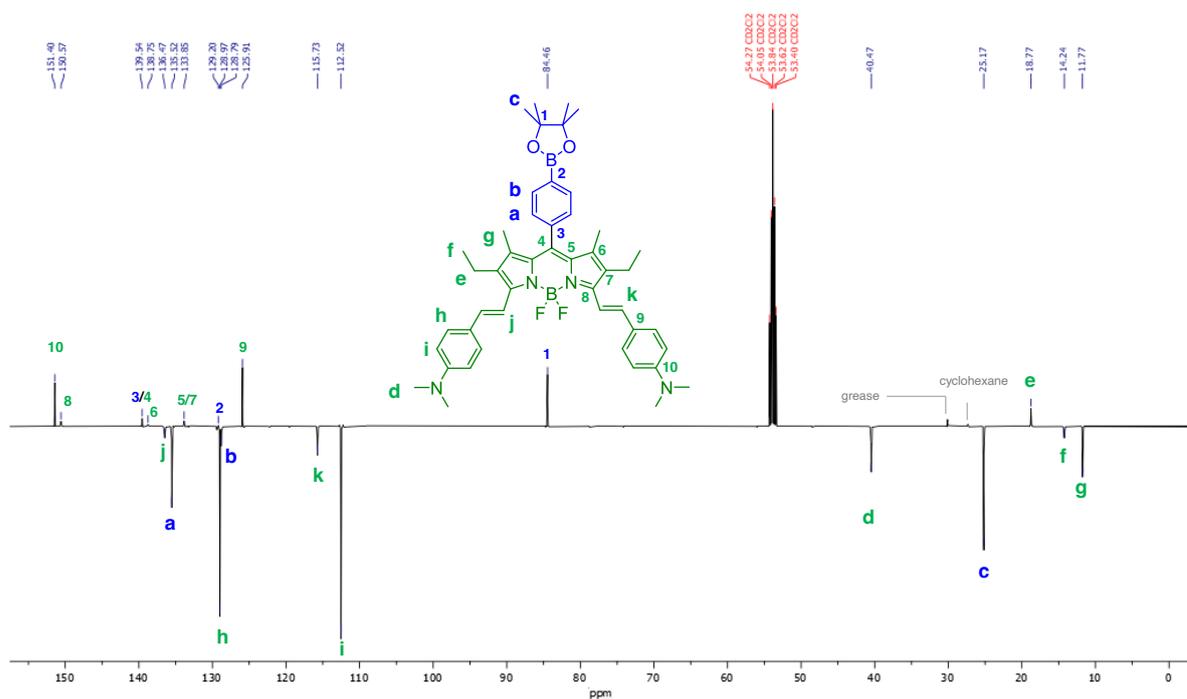


Fig. S2. ^{13}C NMR spectrum (126 MHz - JMOD) of compound **B2** in CD_2Cl_2 recorded at 25 °C.

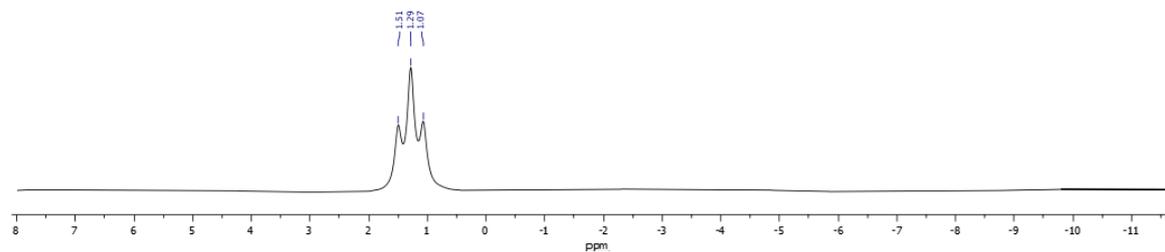


Fig. S3. ^{11}B NMR spectrum (160 MHz) of compound **B2** in CD_2Cl_2 recorded at 25 °C.

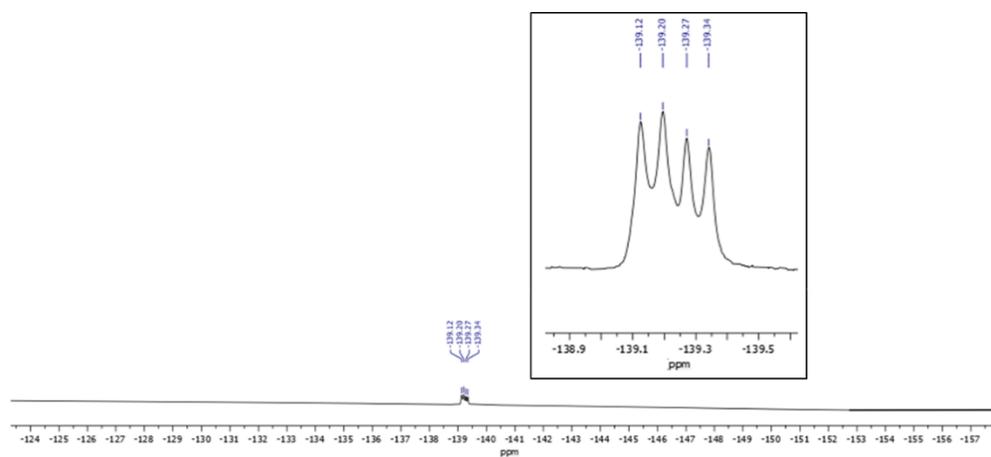


Fig. S4. ^{19}F NMR spectrum (471 MHz) of compound **B2** in CD_2Cl_2 recorded at 25 °C and zoom between -138.9 and -139.5 ppm.

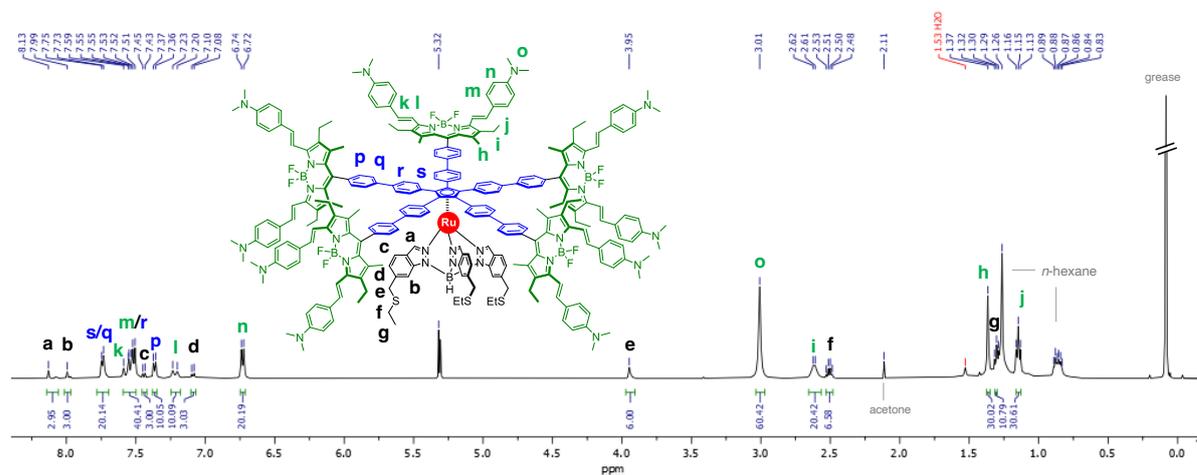


Fig. S5. ^1H NMR spectrum (500 MHz) of complex **B2₅[Ru]** in CD_2Cl_2 recorded at 25 °C.

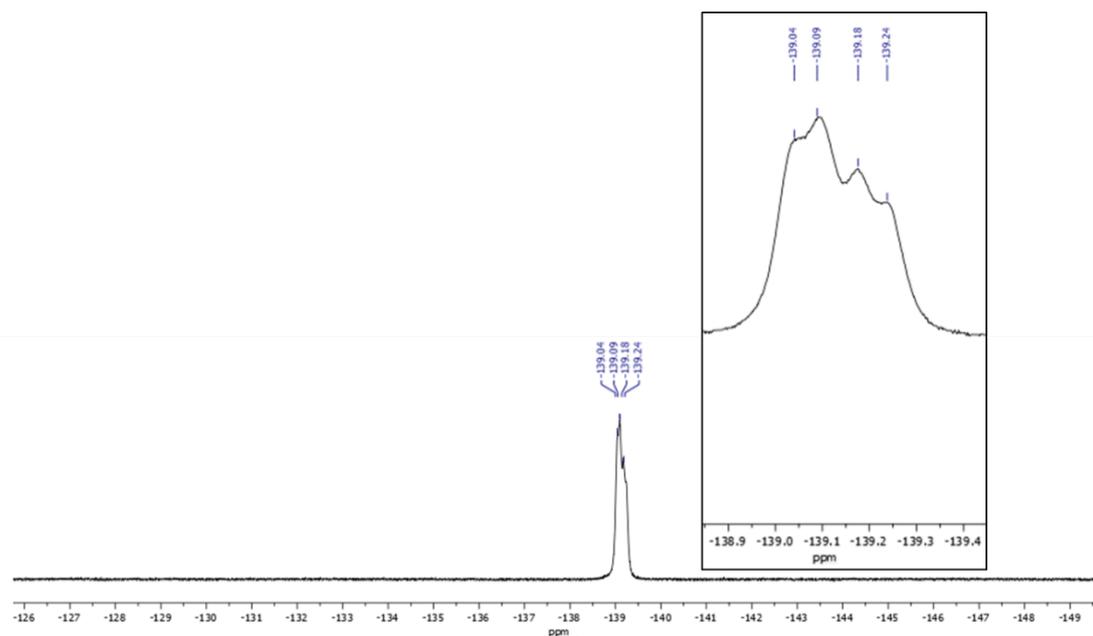


Fig. S7. ^{19}F NMR spectrum (471 MHz) of complex $\text{B}_{25}[\text{Ru}]$ in CD_2Cl_2 recorded at 25 °C and zoom between -138.9 and -139.4 ppm.

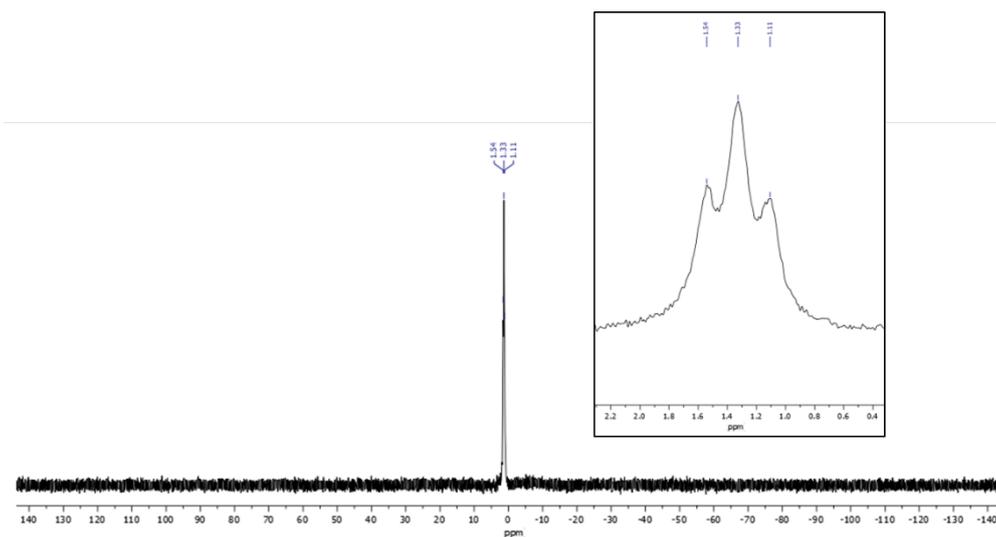


Fig. S8. ^{11}B NMR spectrum (160 MHz) of complex $\text{B}_{25}[\text{Ru}]$ in CD_2Cl_2 recorded at 25 °C, and zoom between 2.2 and 0.4 ppm.

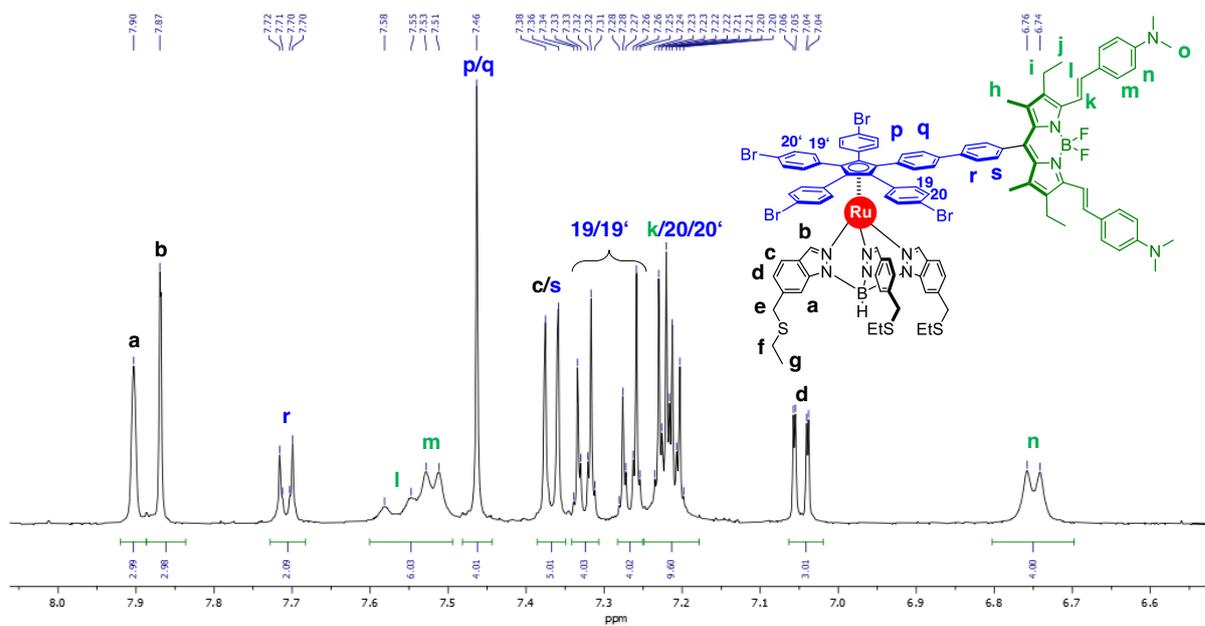
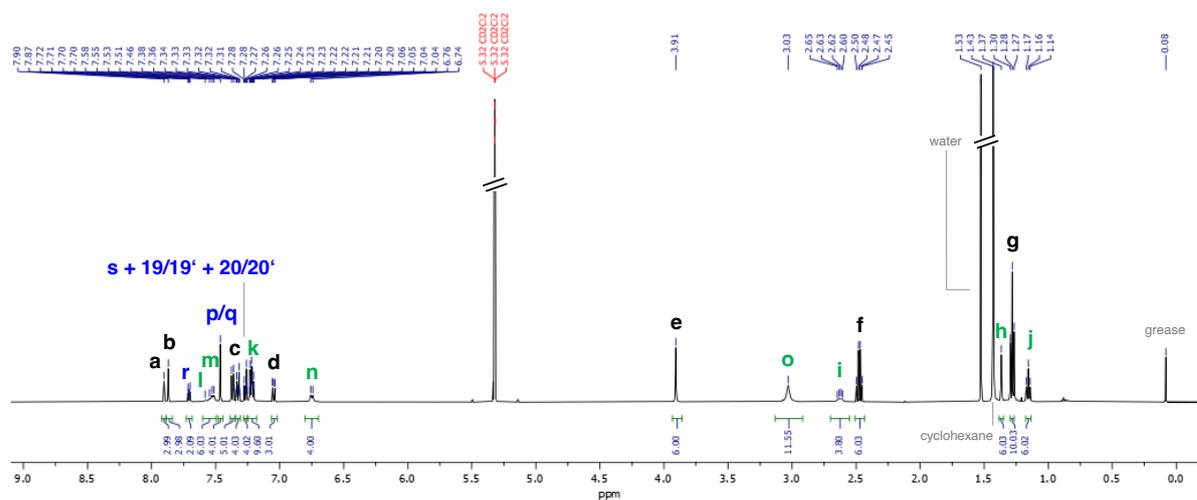


Fig. S9. ^1H NMR spectrum (500 MHz) of complex **Br₄B₂[Ru]** in CD_2Cl_2 recorded at 25 °C and zoom of the 8.0-6.6 ppm region (bottom).

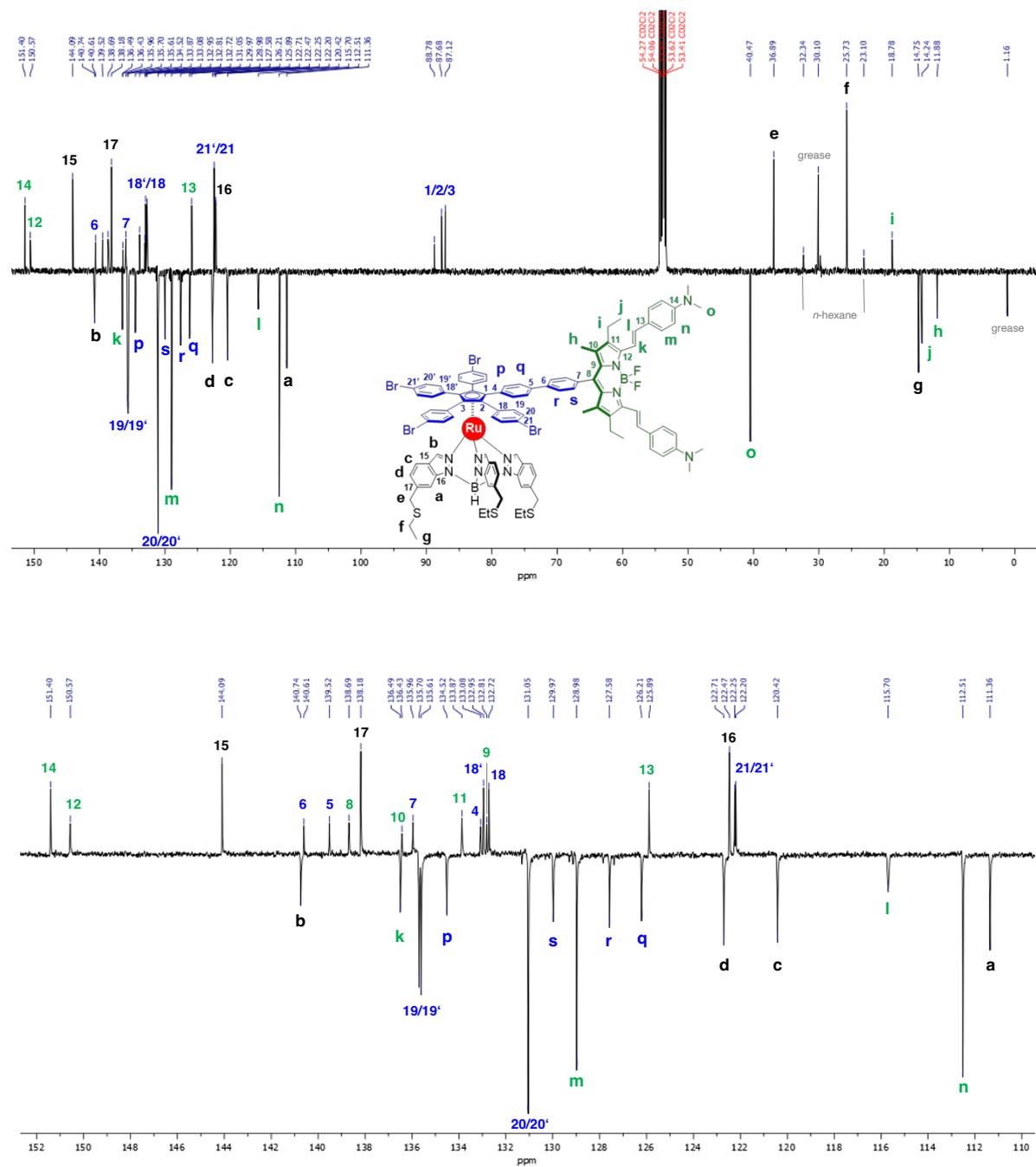


Fig. S10. ^{13}C NMR spectrum (126 MHz - JMOD) of complex $\text{Br}_4\text{B}_2[\text{Ru}]$ in CD_2Cl_2 recorded at 25 °C and zoom of the 152-110 ppm region (bottom).

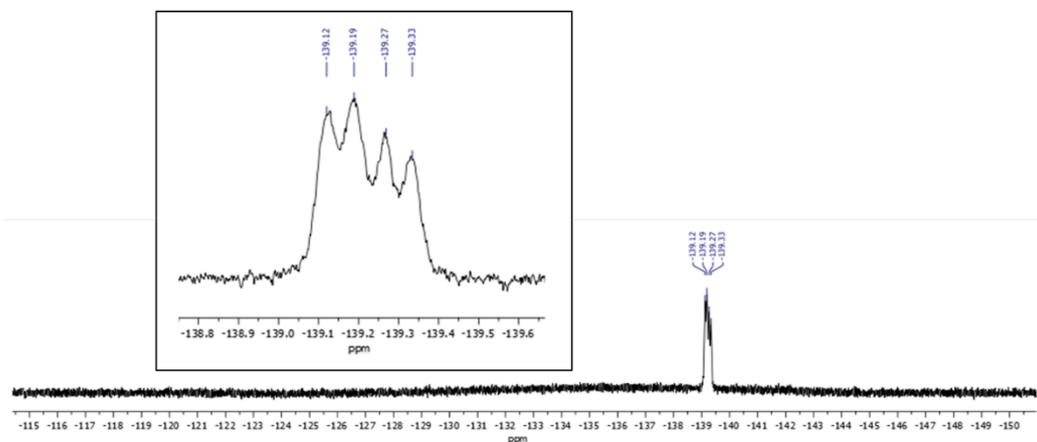


Fig. S11. ^{19}F NMR spectrum (471 MHz) of complex **Br₄B₂[Ru]** in CD_2Cl_2 recorded at 25 °C and zoom between -138.8 and -139.6 ppm.

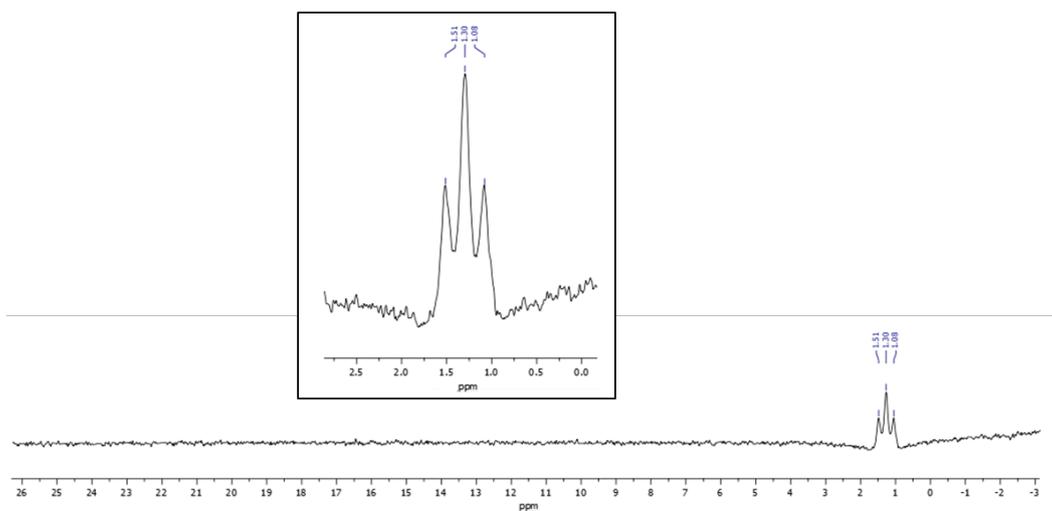


Fig. S12. ^{11}B NMR spectrum (160 MHz) of complex **Br₄B₂[Ru]** in CD_2Cl_2 recorded at 25 °C and zoom between 2.5 and 0.0 ppm.

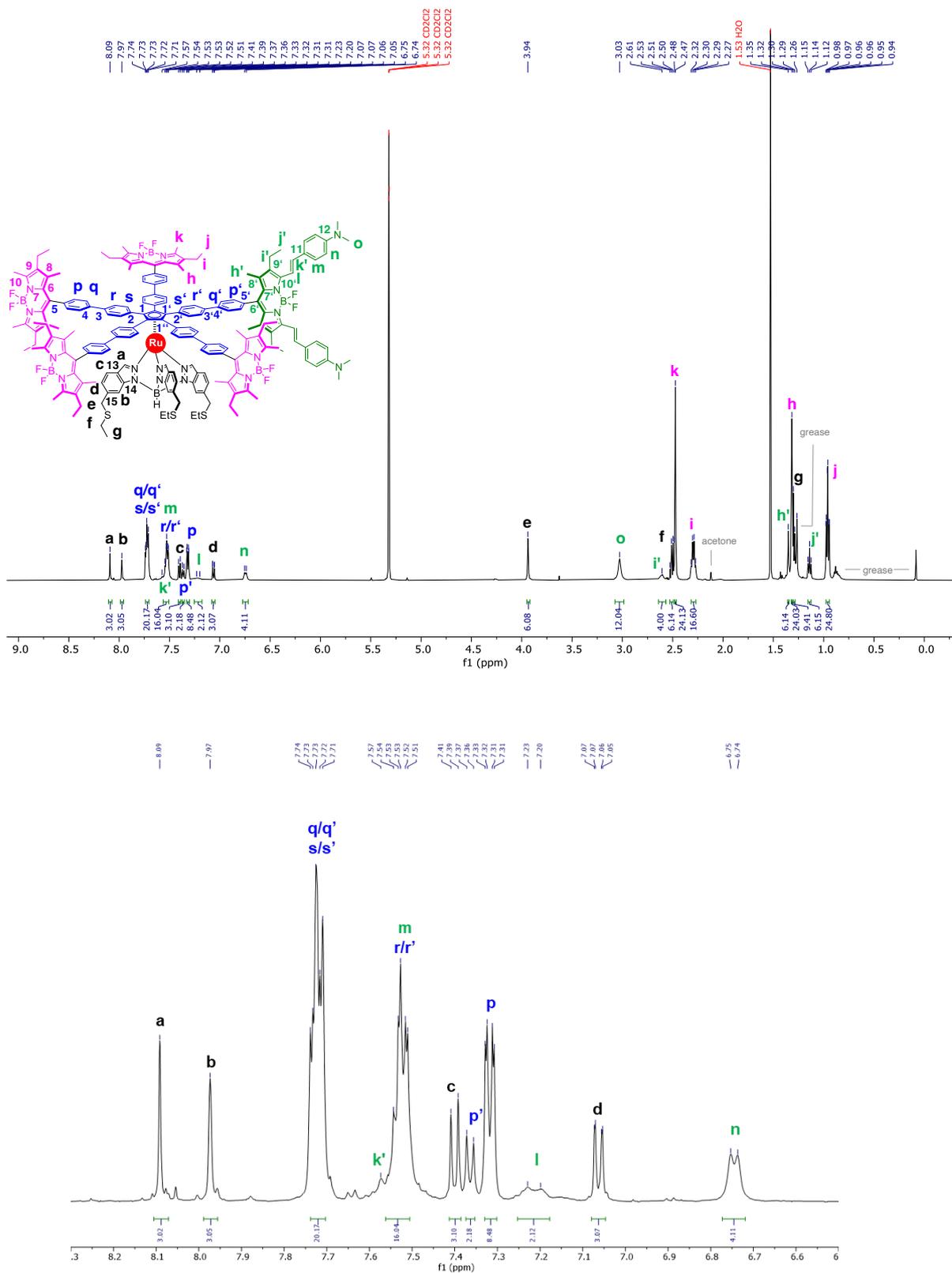


Fig. S13. ¹H NMR spectrum (500 MHz) of complex **B14B21**[Ru] in CD₂Cl₂ recorded at 25 °C and zoom of the 6.5-8.3 ppm region.

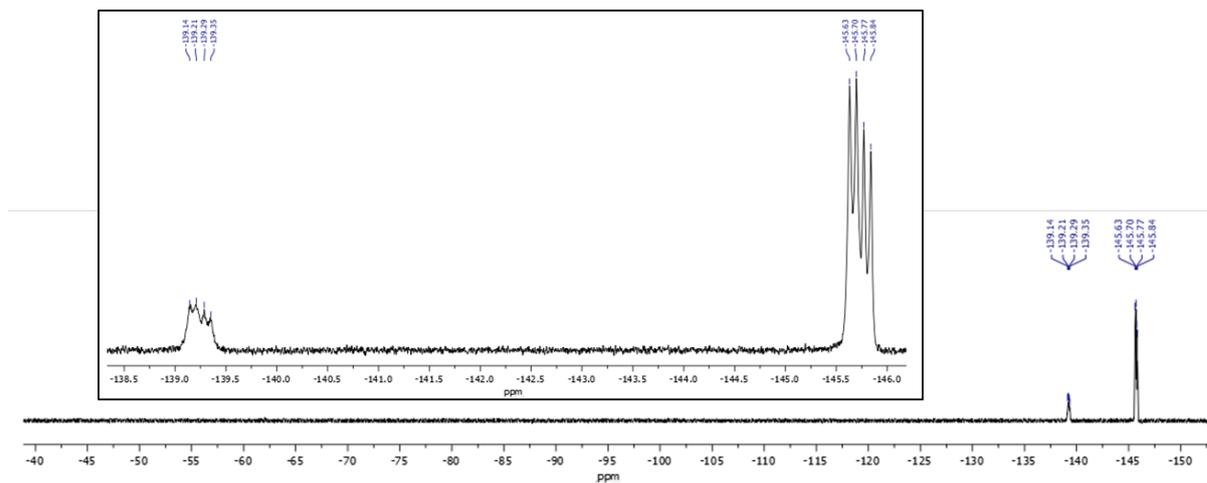


Fig. S15. ^{19}F NMR spectrum (471 MHz) of complex **B1₄B2₁[Ru]** in CD_2Cl_2 recorded at 25 °C and zoom between -138.5 and -146.0ppm

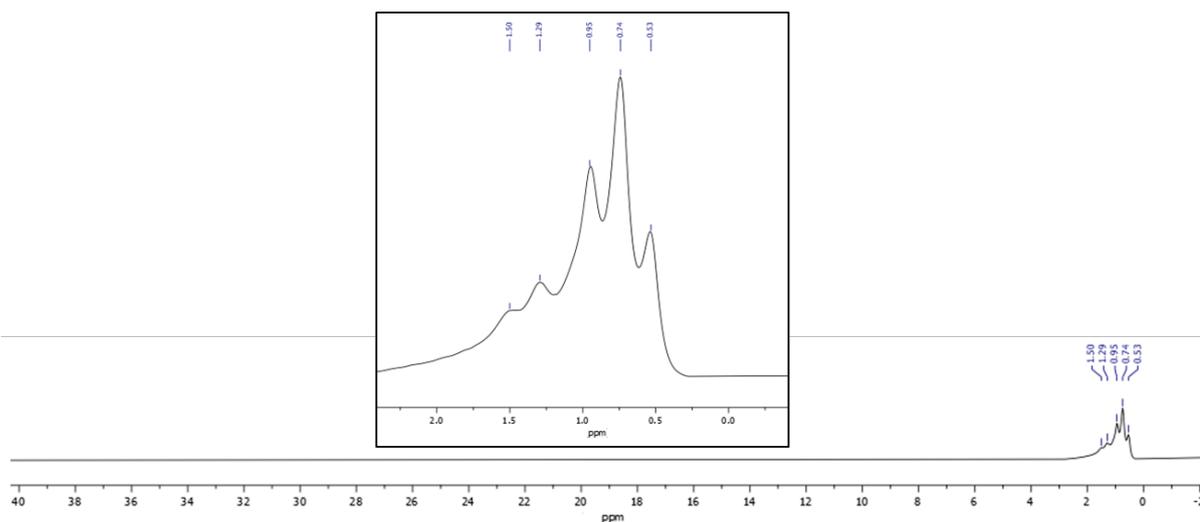


Fig. S16. ^{11}B NMR spectrum (160 MHz) of complex **B1₄B2₁[Ru]** in CD_2Cl_2 recorded at 25 °C and zoom between 2.0 and 0.0 ppm

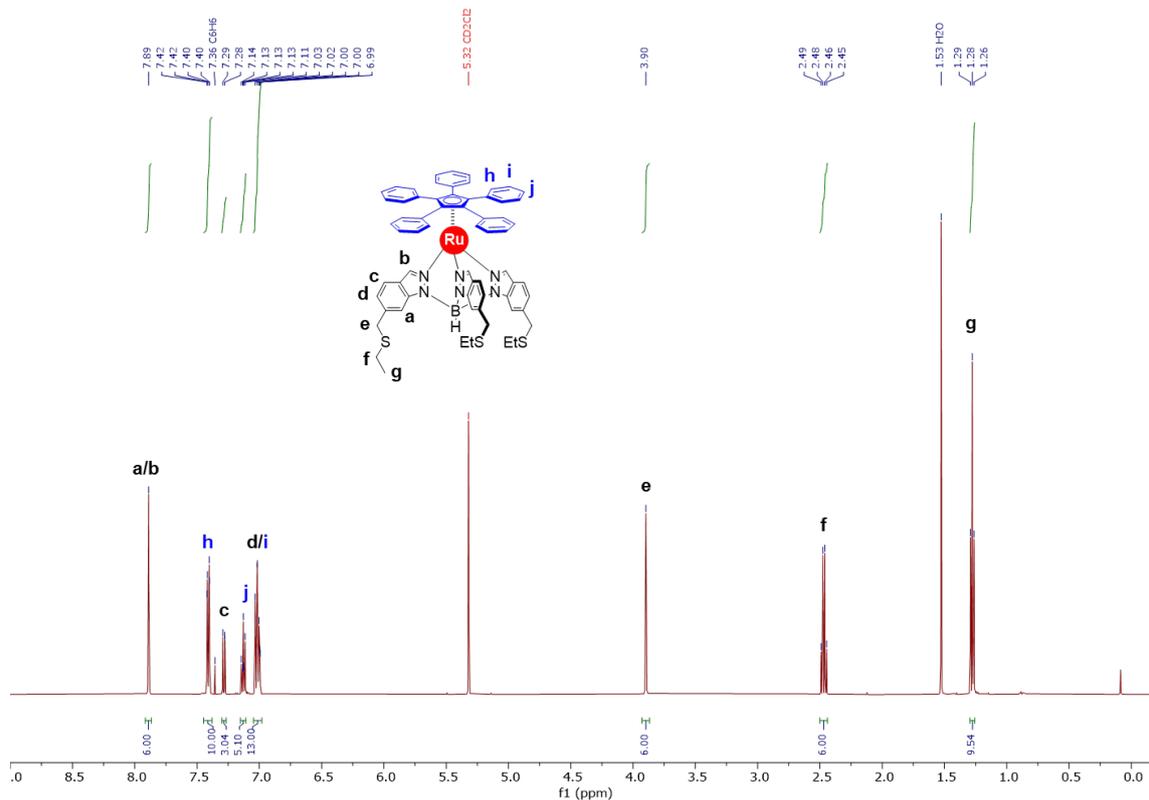


Fig. S17. ^1H NMR spectrum (500 MHz) of complex **[Ru]'** in CD_2Cl_2 recorded at 25 $^\circ\text{C}$.

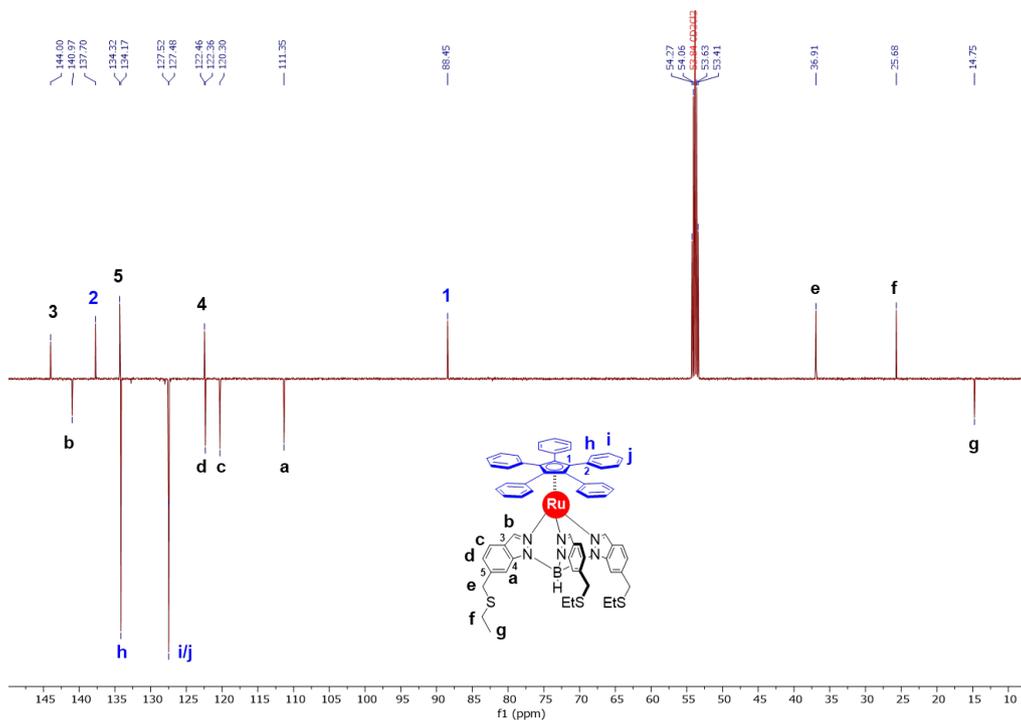


Fig. S18. ^{13}C NMR spectrum (126 MHz - JMOD) of complex **[Ru]'** in CD_2Cl_2 recorded at 25 $^\circ\text{C}$.

Table S1. Crystal data and structure refinement for complex [Ru]’.

Empirical formula	C ₆₅ H ₅₉ BN ₆ RuS ₃ ·CH ₂ Cl ₂	
Formula weight	1217.16	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	<i>P</i> $\bar{1}$	
Unit cell dimensions	a = 12.1788(6) Å	α = 100.0807(18)°.
	b = 14.1325(6) Å	β = 98.3306(18)°.
	c = 18.1834(9) Å	γ = 103.7255(18)°.
Volume	2936.0(2) Å ³	
Z	2	
Density (calculated)	1.377 Mg/m ³	
Absorption coefficient	0.512 mm ⁻¹	
F(000)	1260	
Crystal size	0.300 x 0.240 x 0.140 mm ³	
Theta range for data collection	3.009 to 28.297°.	
Index ranges	-16<=h<=16, -18<=k<=18, -24<=l<=24	
Reflections collected	146385	
Independent reflections	14545 [R(int) = 0.0416]	
Completeness to theta = 25.242°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.7008	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	14545 / 169 / 783	
Goodness-of-fit on F ²	1.047	
Final R indices [I>2sigma(I)]	R1 = 0.0327, wR2 = 0.0850	
R indices (all data)	R1 = 0.0390, wR2 = 0.0893	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.336 and -0.864 e.Å ⁻³	