Design and Characterization of Novel Pyridylbenzimidazole based Ruthenium (II) Complexes, and their Evaluation in Singlet Oxygen Generation

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Materials and equipment

***Reactants and solvents**:*
Unless otherwise noted, all reactions were carried out in oven-dried glassware
Commercially available chemicals were purchased from from ABCR, Acros Organics, Sigma-Aldrich, Alfa Aesar, Combi-Blocks, Carbolution, Fluorochem, and TCI Europe and used as received unless otherwise stated. The following solvents were dried by distillation over the drying agents indicated in parentheses: THF (Sodium), Dichloromethane (CaH_2). Additional anhydrous solvents were purchased from Acros Organics, SigmaAldrich, Alfa Aesar and stored over molecular sieves under an argon atmosphere.

***Purifications**:*
Chromatography was performed on silica gel (Merck Kiesel gel 60, grading 40-63 µm) or alumina neutral gel.

Reactant Analysis:
Reactions were monitored by TLC carried out on silica 0,25 mm (60 F254, Merck) using UV light as visualizing agent. For staining, the TLC plates were dipped into a solution basic aqueous permanganate (1 g $KMnO_4$, 6 g K_2CO_3 and 0.1 g KOH in 100 mL H_2O) and developed with a heat gun.

NMR analysis
Nuclear Magnetic Resonance (NMR) Spectroscopy: ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) were measured at 293K on a Brucker Avance 400 MHz spectrometer. Chemical shifts are reported in parts per million (ppm) downfield from residual solvents peaks and coupling constants are reported as Hertz (Hz). Splitting patterns are designated as singlet (s), broad singlet (br. s), doublet (d), triplet (t), quartet (q), quintet (quint), multiplet (m). Splitting patterns that could not be interpreted or easily visualized are designated as multiplet (m).

LCMS analysis
LC-MS spectra were recorded on a Waters Acquity UPLC® equipped PDA eλ Detector and SQ Detector 2, mobile phase A: H_2O + 0.1% formic acid, mobile phase B: acetonitrile + 0.1% formic acid.

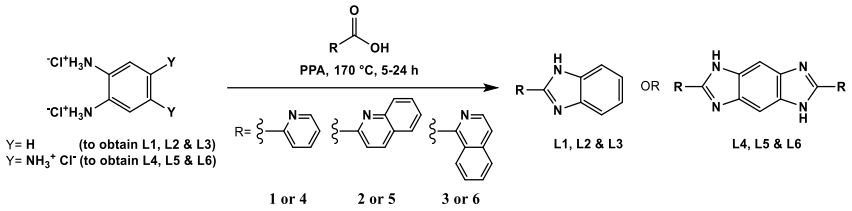
HRMS analysis
High-resolution mass spectra (HRMS) were performed on a Waters Xevo® G2-XS QTof mass spectrometer.

Photophysical analysis
UV-Visible absorption spectra were measured on a Cary 50 spectrophotometer from VARIAN in quartz cuvette 1 cm or on a Molecular Device SpectraMax M5e in a 96-well plate.
Fluorescence analysis was performed on a Fluoromax-4 from Horiba Jobin Yvon in quartz cuvette 1 cm.

Electrochemical analysis
The oxidation–reduction behaviour was determined by cyclic voltammetry using a potentiostat (Origaflex OGF500). A glass carbon working electrode, a platinum wire counter electrode, and an $Ag/AgNO_3$ reference electrode were used for CV studies. All solutions were deoxygenated with N_2 and measurements were made in $TBABF_4$ dissolved in acetonitrile and calibrated using ferrocene as a reference (vs couple Fc/Fc^{+}).

Synthesis of Ligands

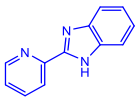
General procedure of synthesis of L1-6 ligands



Scheme S1. Synthetic scheme of ligands (**L1-L6**).

Carboxylic acid (1.2 equiv.) and o-phenylenediamine chloride (1 equiv., 0.6 mM) in syrupy phosphoric acid was stirred at 170 °C for 5-24 h. The mixture was poured into a beaker of cold water (125 mL/mmol diamine) under vigorous stirring. After cooling, the bulky precipitate was collected by filtration, rinsed 3 times with water, then with a minimal amount of methanol, before being dried under reduced pressure. The resulting product was suspended in a minimum of 10% aqueous sodium carbonate solution until a neutral pH was achieved. Then, it was filtered via a fritted glass funnel, washed 3 times with water, 3 times with a minimal amount of methanol, and 3 times with dichloromethane, before being dried under reduced pressure to give **L** ligands as a (white or brown) powder.

Synthesis of L1 ligand



2-(pyridin-2-yl)-1*H*-benzo[*d*]imidazole

L1

L1 was prepared from 103.7 mg of quinoline-2-carboxylic acid (0.84 mmol, 1.1 equiv.) and 143.1 mg of o-phenylenediamine chloride (0.79 mmol, 1 equiv.) in 1.2 mL syrupy phosphoric acid according to general procedure to yield **L1** as a white powder (25 mg, 16% yield) after for 5 h.

R_f: 0.37 (3/7 Hexane/EtOAc).

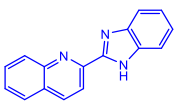
^{1}H NMR (400 MHz, DMSO): 13.10 (br s, 1H), 8.74 (br d, 1H, ^3J= 3.7 Hz), 8.34 (br d, 1H, ^3J= 7.8 Hz), 8.00 (br t, 1H, ^3J = 7.8 Hz, ^3J = 7.4 Hz), 7.71 (br d, 1H, ^3J = 7.4 Hz), 7.59-7.46 (m, 2H), 7.29-7.16 (m, 2H).

^{13}C NMR (101 MHz, DMSO): 150.7 (C_Q), 149.4 (C), 148.5 (C_Q), 143.9 (C_Q), 137.6 (C), 134.9 (C_Q), 124.7 (C), 123.1 (C), 121.9 (C), 121.4 (C), 119.3 (C), 112.1 (C).

LCMS (ESI+) m/z: $[M+H]^+$ calcd for $C_{12}H_{10}N_3^+$: 196, found: 196.

tr = 1.81 min.

Synthesis of L2 ligand



2-(1*H*-benzo[*d*]imidazol-2-yl)quinoline

L2

L2 was prepared from 117.2 mg of quinoline-2-carboxylic acid (0.679 mmol, 1.2 equiv.) and 104.5mg of o-phenylenediamine chloride (0.577 mmol, 1 equiv.) in 1mL syrupy phosphoric acid (PPA) according to general procedure to yield **L2** as a white powder (118 mg, 83% yield) after for 24 h.

R_f: 0.41 (3/7 Hexane/EtOAc).

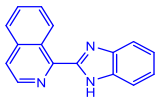
^{1}H NMR (400 MHz, DMSO): 13.24 (br s, 1H), 8.55 (d, 1H, ^3J = 8.6 Hz), 8.49 (d, 1H, ^3J = 8.6 Hz), 8.17 (br d, 1H), 8.07 (br d, 1H), 7.87 (br t, 1H), 7.76-7.62 (m, 3H), 7.33-7.21 (2br d, 2H).

^{13}C NMR (101 MHz, DMSO): 150.8 (C_Q), 148.8 (C_Q), 147.2 ($3C_Q$), 137.4 (C), 130.5 (C), 128.8 (C), 128.3 (C), 128.1 (C_Q), 127.3 (3C), 122.8 (2C), 119.3 (C).

LCMS (ESI+) m/z: $[M+H]^+$ calcd for $C_{16}H_{12}N_3^+$: 246, found: 246.

tr = 2.83 min.

Synthesis of L3 ligand



1-(1*H*-benzo[*d*]imidazol-2-yl)isoquinoline

L3

L3 was prepared from 98.2 mg of isoquinoline-2-carboxylic acid (0.550 mmol, 1 equiv.) and 99.5 mg of o-phenylenediamine chloride (0.567 mmol, 1 equiv.) in 0.6 mL syrupy phosphoric acid (PPA) according to general procedure to yield **L3** as a yellow powder (98.4 mg, 73% yield) after for 24 h.

R_f: 0.62 (3/7 Hexane/EtOAc).

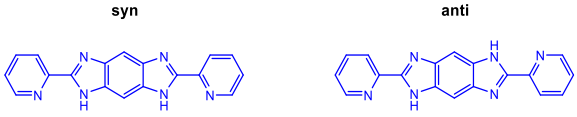
^{1}H NMR (400 MHz, DMSO): 13.23 (br s, 1H), 10.14-10.08 (br ddd, 1H), 8.71 (d, 1H, ^3J = 8.6 Hz), 8.11-8.07 (br ddd, 1H), 8.01 (d, 1H, ^3J = 8.6 Hz), 7.90-7.81 (m, 3H), 7.61 (br dt, 1H, ^3J = 8.0 Hz), 7.32 (td, 1H, ^3J = 8.0 Hz), 7.26 (td, 1H, ^3J = 8.0 Hz).

^{13}C NMR (101 MHz, DMSO): 151.2 (C_Q), 146.7 (C_Q), 144.1 (C_Q), 141.7 (C), 136.8 (C_Q), 134.0 (C_Q), 130.7 (C), 128.7 (C), 127.8 (C), 127.3 (C), 126.0 (C_Q), 123.7 (C), 122.4 (C), 122.0 (C), 119.7 (C), 112.1 (C).

LCMS (ESI+) m/z: $[M+H]^+$ calcd for $C_{16}H_{12}N_3^+$: 246, found: 246.

tr = 3.10 min.

Synthesis of L4 ligand



2,6-di(pyridin-2-yl)-1,7-dihydrobenzo[1,2-*d*:4,5-*d'*]diimidazole

L4 (ratio: 0.5/0.5 syn/anti)

L4 was prepared from 88.4 mg of quinaldic acid (0.72 mmol, 2.2 equiv.) and 101.0 mg of o-phenylenediamine chloride (0.356 mmol, 1 equiv.) in 2mL syrupy phosphoric acid (PPA) according to general procedure to yield **L4** as a dark pink/orange powder (114 mg, quantitative yield) after for 24 h.

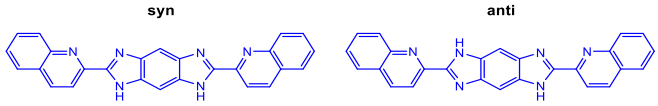
^{1}H NMR (400 MHz, DMSO): 12.92 (br s, 2H), 8.74 (br d, 2H, ^{3}J = 4.4 Hz), 8.35 (br d, 2H, ^{3}J = 7.7 Hz), 8.01 (br dd, 2H, ^{3}J = 7.7 Hz, ^{3}J = 7.4 Hz), 7.93 (s, 0.5xH), 7.74 (s, 1H), 7.59 (s, 0.5xH), 7.56-7.49 (m, 2H).

^{13}C NMR (101 MHz, DMSO): 151.6 ($2C_Q$), 151.2 ($2C_Q$), 149.4 (C), 148.6 ($2C_Q$), 142.7 (C_Q), 141.5 (C_Q), 137.6 (C), 137.5 (C), 133.5 (C), 124.6 (C), 121.4 (C), 121.3 (C), 107.6 (C), 99.4 (C), 92.4 (C).

LCMS (ESI+) m/z: $[M+H]^+$ calcd for $C_{18}H_{13}N_6^+$: 313, found: 313.

tr = 2.09 min.

Synthesis of L5 ligand



2,6-di(quinolin-2-yl)-1,7-dihydrobenzo[1,2-*d*:4,5-*d'*]diimidazole

L5 (ratio: 0.5/0.5 syn/anti)

L5 was prepared from 128 mg of quinaldic acid (0.81 mmol, 2.3 equiv.) and 104.9 mg of o-phenylenediamine chloride (0.37 mmol, 1 equiv.) in 2.2 mL syrupy phosphoric acid (PPA) according to general procedure to yield **L5** as a dark pink/orange powder (122 mg, quantitative yield) after for 5 h.

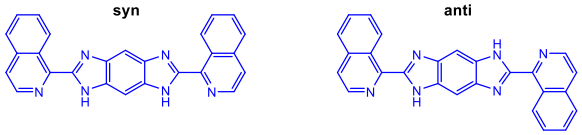
^{1}H NMR (400 MHz, DMSO): 13.07 (s, 2H), 8.58 (d, 1H, $^{3}J_{H11\text{-}H12}$ = 8.6 Hz), 8.53(dd, 2H, ^{3}J = 8.6 Hz, ^{3}J = 3.0 Hz), 8.18 (br d, 2H), 8.08 (m, 3H), 7.88 (m, 3H), 7.75 (s, 0.5xH), 7.69 (br td, 2H).

^{13}C NMR (101 MHz, DMSO): 151.4 (C_Q), 148.8 (C_Q), 148.7 (C_Q), 147.3 (C_Q), 142.7 (C_Q), 141.7 (C_Q), 137.4 (2C), 134.2 (C_Q), 133.2 (C_Q), 130.5 (2C), 128.8 ($2C_Q$), 128.3(C), 128.1 (C), 127.3 (2C), 119.3 (2C), 108.1 (C), 100.1 (2C), 92.7 (C).

LCMS (ESI+) m/z: $[M+H]^+$ calcd for $C_{26}H_{17}N_6^+$: 413, found: 413.

tr = 3.09 min.

Synthesis of L6 ligand



2,6-di(isoquinolin-1-yl)-1,7-dihydrobenzo[1,2-*d*:4,5-*d'*]diimidazole

L6 (ratio: 0.5/0.5 syn/anti)

L6 was prepared from 138.6 mg of isoquinoline-1-carboxylic acid (0.80 mmol, 4.0 equiv.) and 57.0 mg of o-phenylenediamine chloride (0.20 mmol, 1 equiv.) in 2mL syrupy phosphoric acid (PPA) according to general procedure to yield **L6** as a dark brown powder with a purple glint (33.2 mg, 40 % yield) for 5 h.

^{1}H NMR (400 MHz, DMSO): 13.10 (s, 2H), 10.28-10.17 (m, 2H), 8.73 (d, 2H, ^{3}J = 5.5 Hz), 8.24 (s, 0.5xH), 8.13-8.08 (m, 2H), 8.01 (br d, 2H, ^{3}J = 5.5 Hz), 7.94 (s, 1H), 7.92-7.86 (m, 4H), 7.69 (s, 0.5xH).

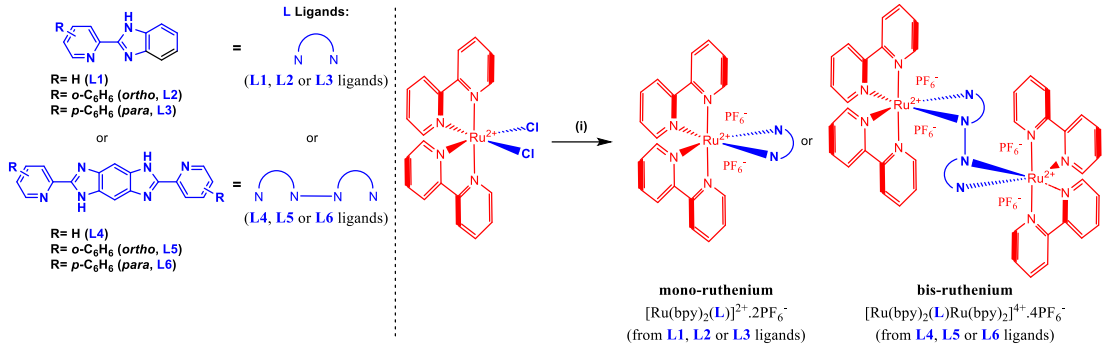
^{13}C NMR (101 MHz, DMSO): 152.3 (C_Q), 151.9 (C_Q), 146.6 (C_Q), 143.0 (C_Q), 142.0 (C_Q), 141.8 (C), 141.7 (C), 136.8 (C_Q), 133.1 (C_Q), 130.7 (C), 128.7 & 128.6 (2C), 128.0 (C), 127.3 (2C), 126.1 (C_Q), 126.0 (C_Q), 122.3 (2C), 108.5 (C), 100.0 (C), 92.1 (C).

LCMS (ESI+) m/z: $[M+H]^+$ calcd for $C_{26}H_{17}N_6^+$: 413, found: 413.

tr = 3.15 min.

Synthesis of Ruthenium Complexes

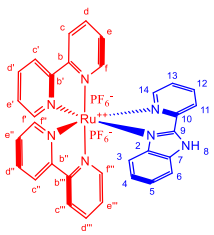
General procedure of synthesis for Ru1-6 complexes :



Scheme S2. Synthetic scheme of ruthenium complexes (**Ru1-Ru6**). (i) Ligands (**L1-L6**), 2-ethoxyethanol, microwave, 190 W, 197 °C, 20 minutes.

1 equiv. of ligand **L** (0.060 mM) and 1 equiv. (to afford mono-ruthenium) or 2 equiv. (to afford bis-ruthenium) of $Ru(bpy)_2Cl_2$ were suspended in 2-ethoxyethanol before being heated in a micro-wave at 197 °C during 20 min. After 20 minutes of middle stirring, the red/orange solution was evaporated before being suspended in water and precipitated by adding a cold saturated aqueous solution of KPF_6. The red precipitate was filtered via a fritted glass funnel, washed 3 times with water and rinsed 3 times with diethyl ether. The dark red precipitate was dissolved in DCM and the DCM filtrate was evaporated under reduced pressure. The resulting product was purified by chromatography on neutral alumina column (elution with ACN/DCM, 30/70) to give **Ru** ruthenium complexes (26 to 70 % yields) as a red/orange ochre powder after lyophilization.

Ru1, $[Ru(bpy)_2L1].2PF_6$



Ru1

Ru1 was prepared from 30.2 mg of **L1** (0.155 mmol, 1 equiv.) and 89 mg of $Ru(bpy)_2Cl_2$ (0.184 mmol, 1.2 equiv.) suspended in 2.6 mL of 2-ethoxyethanol according to general procedure to yield **Ru1** as a red/orange ochre powder (97.6 mg, 70% yield) after for 20 minutes of reaction.

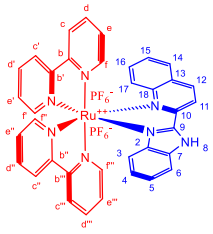
R_f: 0.25 (3/7 CH_3CN/CH_2Cl_2).

^{1}H NMR (400 MHz, DMSO): 8.84-8.77 (m, 3H), 8.72 (d, 1H, ^3J = 8.0 Hz), 8.33 (br d, 1H, ^3J = 8.0 Hz), 8.18 (td, 1H, ^3J = 8.0 Hz, ^4J = 1.5 Hz), 8.12 (td, 1H, ^3J = 8.0 Hz, ^4J = 1.5 Hz), 8.06 (td, 1H, ^3J = 8.0 Hz, ^4J = 1.5 Hz), 8.00-7.96 (m, 1H), 7.97-7.92 (m, 1H), 7.89 (br d, 1H, ^3J = 8.0 Hz), 7.83 (br d, 1H, ^3J = 8.0 Hz), 7.57-7.45 (m, 5H), 7.56-7.50 (m, 1H), 7.50-7.45 (m, 1H), 7.28 (td, 1H, ^3J = 7.3 Hz, ^4J = 1.5 Hz), 6.90 (td, 1H, ^3J = 8.1 Hz, ^4J = 1.0 Hz), 6.61 (td, 1H, ^3J = 8.1 Hz, ^4J = 1.0 Hz), 5.45 (dt, 1H, ^3J = 8.1 Hz, ^4J = 1.0 Hz).

^{13}C NMR (101 MHz, DMSO): 159.0 (C_Q), 158.0 (C_Q), 157.7 (C_Q), 157.0 ($2C_Q$), 155.1 (C_Q), 151.8 (C), 151.4 (C), 150.9 (C), 150.8 (C), 150.3 (C), 147.4 (C_Q), 144.9 (C_Q), 137.4 (C), 136.8 (2C), 136.7 (2C), 127.7 (C), 127.4 (2C), 126.9 (C), 124.7 (C), 124.3 (C), 124.0 (C), 123.8 (C), 123.7 (C), 121.6 (C), 120.8 (C), 120.0 (C), 119.3 (C), 112.4 (C).

HRMS (ESI-TOF) m/z : $[M-2PF_6]^{2+}$ calcd for $C_{32}H_{24}N_7Ru$: 304.5612 ; found 304.5613. **HRMS (ESI-TOF) m/z :** $[M-H-2PF_6]^+$ calcd for $C_{32}H_{23}N_7Ru$: 608.1145; found 608.1144.

Ru2, $[Ru(bpy)_2L2].2PF_6$



Ru2

Ru2 was prepared from 26.0 mg of **L2** (0.106 mmol, 1 equiv.) and 85.0 mg of $Ru(bpy)_2Cl_2$ (0.175 mmol, 1.65 equiv.) was suspended in 2 mL of 2-ethoxyethanol according to general procedure to yield **Ru2** as an orange powder (46.8 mg, 46% yield) after for 20 minutes of reaction.

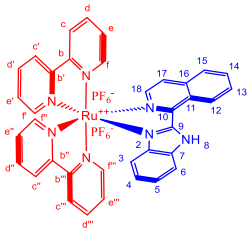
R_f: 0.68 (3/7 CH_3CN/CH_2Cl_2).

^{1}H NMR (400 MHz, DMSO): 15.14 (br s, 1H), 8.92 (d, 1H, ^3J = 8.0 Hz), 8.85 (d, 1H, ^3J = 8.0 Hz), 8.76 (2d, 2H, ^3J = 8.1 Hz, ^3J = 8.0 Hz,), 8.66 (2d, 2H, ^3J = 8.1 Hz, ^3J = 8.0 Hz), 8.27 (t, 1H, ^3J = 8.0 Hz), 8.21-8.15 (t, 1H, ^3J = 8.0 Hz), 8.19-8.12 (m, 1H), 8.15-8.08 (m, 2H), 8.06 (d, 1H, ^3J = 8.0 Hz), 7.99 (t, 1H, ^3J = 8.0 Hz), 7.85 (d, 1H, ^3J = 8.0 Hz), 7.81 (d, 1H, ^3J = 8.1 Hz), 7.66-7.58 (m, 2H), 7.53 (t, 1H, ^3J = 8.0 Hz), 7.48-7.43 (m, 2H), 7.48-7.43 (m, 1H), 7.32 (m, 2H), 7.23 (d, 1H, ^3J = 8.8 Hz), 6.94 (t, 1H, ^3J = 8.4 Hz, ^3J = 7.3 Hz), 5.42 (d, 1H, ^3J = 8.4 Hz).

^{13}C NMR (101 MHz, DMSO): 158.3 (C_Q), 157.5 ($2C_Q$), 156.8 ($2C_Q$), 153.3 (C), 152.4 (C), 151.1 (C), 150.8 (C), 149.5 (C_Q), 142.7 (C_Q), 139.6 (C), 139.5 (C), 138.2 (C), 137.6 (C), 137.3 (C), 137.2 (C), 136.0 (C_Q), 131.5 (C), 129.8 (C), 128.8 (C_Q), 128.4 (C_Q), 128.3 (C_Q), 128.1 (C), 127.8 (C), 127.6 (C), 127.6 (C), 124.6 (C), 124.4 (C), 124.2 (C), 124.0 (C), 123.9 (C), 123.8 (C), 119.5 (C), 115.8 (C), 114.3 (C).

HRMS (ESI-TOF) m/z : $[M\text{-}2PF_6]^{2+}$ calcd for $C_{36}H_{27}N_7Ru$: 329.5691 ; found 329.5688. **HRMS (ESI-TOF) m/z** : $[M\text{-}H\text{-}2PF_6]^{+}$ calcd for $C_{36}H_{26}N_7Ru$: 658.1302; found 658.1306.

Ru3, $[Ru(bpy)_2L3].2PF_6$



Ru3

Ru3 was prepared from 26.0 mg of **L3** (0.106 mmol, 1 equiv.) and 54.0 mg of **$Ru(bpy)_2Cl_2$** (0.111 mmol, 1.05 equiv.) were suspended in 2 mL of 2-ethoxyethanol according to general procedure to yield **Ru3** as an orange ochre powder (40.9 mg, 43% yield) after for 20 minutes of reaction.

R_f: 0.34 (3/7 CH_3CN/CH_2Cl_2).

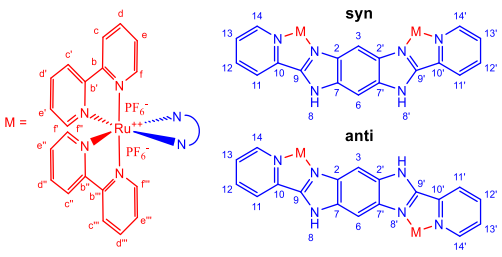
^{1}H NMR (400 MHz, DMSO): 10.70 (d, 1H, ^3J = 8.5 Hz), 8.87-8.81 (2d, 2H, ^3J = 8.2 Hz), 8.79 (d, 1H, ^3J = 8.2 Hz), 8.73 (d, 1H, ^3J = 8.2 Hz), 8.20 (br td, 1H, ^3J = 8.2 Hz), 8.15 (br td, 1H, ^3J = 8.2 Hz), 8.04-7.97 (m, 3H), 7.96-7.92 (m, 2H), 7.88-7.83 (m, 3H), 7.71-7.66 (2d, 2H, ^3J = 8.0 Hz), 7.56 (2br td, 2H, ^3J = 8.2 Hz), 7.46-7.38 (m, 4H) , 6.99 (br dd, 1H, ^3J = 7.4 Hz), 6.67 (br t, 1H, ^3J = 8.2 Hz, ^3J = 7.4 Hz), 5.53 (d, 1H, ^3J = 8.2 Hz).

^{13}C NMR (101 MHz, DMSO): 160.3 (C_Q), 157.8 (C_Q), 157.5 (C_Q), 157.0 (C_Q), 156.9 (C_Q), 153.8 (C_Q), 152.8 (C_Q), 151.6 (C), 151.3 (C), 151.1 (C), 150.8 (C), 147.5 (C_Q), 144.1 (C_Q), 141.8 (C), 136.9 (2C), 136.7 (C), 136.2 (C), 135.5 (C_Q), 131.5 (C), 129.2 (C), 127.9 (C), 127.5 (C), 127.3 (C), 127.1 (C), 127.0 (C), 126.6 (C_Q), 124.3 (C_Q), 124.0 (C), 123.8 (C), 123.7 (C), 122.2 (C), 121.5 (C), 120.5 (C), 119.8 (C), 112.7 (C).

HRMS (ESI-TOF) m/z : $[M\text{-}2PF_6]^{2+}$ calcd for $C_{36}H_{27}N_7Ru$: 329.5691 ; found 329.5689. **HRMS (ESI-TOF) m/z :** $[M\text{-}H\text{-}2PF_6]^{+}$ calcd for $C_{36}H_{26}N_7Ru$ 658.1302; found 658.1301.

Synthesis of Bis-Ruthenium complexes

Ru4, $[Ru(bpy)_2](L4)[Ru(bpy)_2].4PF_6$



Ru4 (syn/anti)

Ru4 was prepared from 14.2 mg of **L4** (0.045 mmol, 1 equiv.) and 45.2 mg of $Ru(bpy)_2Cl_2$ (0.093 mmol, 2 equiv.) were suspended in 1.6 mL of 2-ethoxyethanol according to general procedure to yield **Ru4** as a dark orange solid (53 mg, 69% yield) after for 20 minutes of reaction.

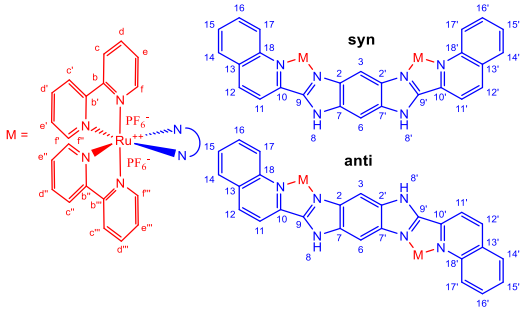
R_f: 0.25 (3/7 CH_3CN/CH_2Cl_2).

^{1}H NMR (400 MHz, DMSO): 14.55 (br s, 2H), 8.91 (d, 1H, ^3J = 8.2 Hz), 8.89-8.77 (m, 7H), 8.71 (br d, 2H, ^3J = 8.2 Hz), 8.57-8.47 (m, 2H), 8.28-8.06 & 8.04-7.99 (2m, 13H), 7.97 (d, 1H, ^3J = 8.2 Hz), 7.85-7.78 & 7.77-7.65 (2m, 13H), 7.57-7.48 & 7.45-7.40 (2m, 9H), 7.34 (m, 1H), 5.89 (m, 2H).

^{13}C NMR (101 MHz, DMSO): 157.8 (C_Q), 157.7 (C_Q), 157.4 (C_Q), 156.7 (C_Q), 156.6 (C_Q), 154.0 (C_Q), 153.9 (C_Q), 152.4 (C), 152.0 (C), 151.7 (C), 151.6 (C), 151.6 (C), 148.3 (C), 147.1 (C), 140.4 (C_Q), 140.2 (C_Q), 138.5 (C), 138.5 (C), 138.5 (C), 138.2 (C), 137.8 (C), 137.7 (C), 137.6 (C), 137.4 ($2C_Q$), 132.7 (C), 128.1 (2C), 128.0 (C), 127.9 (C), 127.8 (C), 127.7 (C), 127.6 (C), 124.7 (C), 124.5 (C), 124.4 (C), 124.2 (C), 124.1 (C), 98.1 (2C).

HRMS (ESI-TOF) m/z: $[M\text{-}H\text{-}4PF_6]^{3+}$ calcd for $C_{58}H_{43}N_{14}Ru_2$: 379.7303; found 379.7298. **HRMS (ESI-TOF) m/z :** $[M\text{-}2H\text{-}4PF_6]^{2+}$ calcd for $C_{58}H_{42}N_{14}Ru_2$: 569.0916; found 569.0912.

Ru5, $[Ru(bpy)_2](L5)[Ru(bpy)_2].4PF_6$



Ru5 (syn/anti)

Ru5 was prepared from 32.5 mg of **L5** (0.073 mmol, 1 equiv.) and 70 mg of $Ru(bpy)_2Cl_2$ (0.145 nmmol, 2 equiv.) was suspended in 2.5 mL of 2-ethoxyethanol according to general procedure to yield **Ru5** as a dark orange solid (19.5 mg, 18% yield) after for 20 minutes of reaction.

R_f: 0.34 (3/7 CH_3CN/CH_2Cl_2).

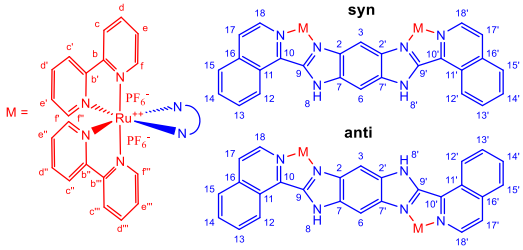
^{1}H NMR (400 MHz, DMSO): 9.02 (br d, 1H, ^3J = 8.0 Hz), 8.92 (br d, 2H, ^3J = 8.0 Hz), 8.77 (br d, 1H, ^3J = 8.5 Hz), 8.72 (br d, 1H, ^3J = 8.5 Hz), 8.67 (br d, 1H, ^3J = 8.5 Hz), 8.63 (br d, 1H, ^3J = 8.5 Hz), 8.55 (br d, 1H, ^3J = 8.5 Hz), 8.47-8.37 (m, 4H), 8.36-8.29 (m, 2H), 8.20 (br d, ^3J = 5.5 Hz, 1H), 8.16-8.03 (m, 7H), 8.00-7.90 (m, 5H), 7.89-7.82 (m, 2H), 7.77 (br d, 1H, ^3J = 5.7 Hz), 7.62-7.56 (m, 3H), 7.53 (br t, 1H, ^3J = 8.0 Hz), 7.49-7.42 (m, 3H), 7.42-7.37 (m, 2H), 7.36-7.31 (m, 1H), 7.31-7.28 (m, 1H), 7.28-7.25 (m, 1H), 7.21-7.12 (m, 4H), 7.02 (br d, 1H, ^3J = 5.7 Hz), 5.47 & 5.43 (2s, 2H).

^{13}C NMR (101 MHz, DMSO): 158.6 (C_Q), 158.5 ($2C_Q$), 158.4 (C_Q), 158.3 (C_Q), 157.6 (C_Q), 157.2 (C_Q), 157.1 (C_Q), 157.0 (C_Q), 156.6 (3C), 154.5 (2C), 152.8 (C), 152.5 (C), 152.0 (C_Q), 151.9 (C_Q), 149.3 (C_Q), 138.0 (C), 137.9 (C), 137.4 (2C), 136.8 (C), 136.7 (C), 136.5 (2C), 136.0 (C_Q), 131.6 (C), 131.5 (C), 130.5 (C), 128.6

(C_Q), 128.3 (C_Q), 127.9 (2C), 127.3 (C), 127.0 (3C), 126.8 (C), 124.3 (C), 124.2 (C), 124.1 (C), 124.0 (C), 123.9 (C), 123.8 (C), 123.7 (C), 123.6 (C), 123.5 (C), 119.5 (C), 99.3 (C).

HRMS (ESI-TOF) m/z : $[M\text{-}2H\text{-}4PF_6]^{2+}$ calcd for $C_{66}H_{46}N_{14}Ru_2$: 619.1074 ; found 619.1071. **HRMS (ESI-TOF) m/z :** $[M\text{-}H\text{-}3PF_6]^{+}$ calcd for $C_{66}H_{47}F_6N_{14}PRu_2$: 692.0933; found 692.0931.

Ru6, $[Ru(bpy)_2](L6)[Ru(bpy)_2].4PF_6$



Ru6 (syn/anti)

Ru6 was prepared from 27 mg of **L6** (0.065 mmol, 1 equiv.) and 70 mg of $Ru(bpy)_2Cl_2$ (0.145 mmol, 2 equiv.) were suspended in 2.6 mL of 2-ethoxyethanol according to general procedure to yield **Ru6** as a dark orange solid (65 mg, 56%yield) after for 20 minutes of reaction.

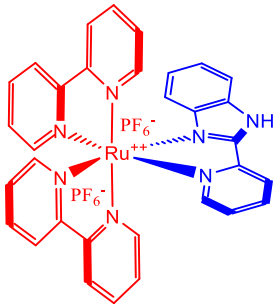
R_f: 0.46 (3/7 CH_3CN/CH_2Cl_2).

^{1}H NMR (400 MHz, DMSO): 10.5 (m, 2H), 8.96 (br d, 2H), 8.92-8.72 (m, 10H), 8.69 (br d, 1H), 8.36-8.27 (m, 1H), 8.18-8.11 (m, 2H), 8.07-7.99 (m, 3H), 7.99-7.93 (m, 3H), 7.93-7.77 (m, 6H), 7.77-7.72 (m, 2H), 7.72-7.63 (m, 2H), 7.63-7.52 (m, 4H), 7.48-7.38 (m, 2H), 7.38-7.25 (m, 2H), 5.86 (s, 1H), 5.79 (s, 1H).

^{13}C NMR (101 MHz, DMSO): not obtained as a result of poor solubility.

HRMS (ESI-TOF) m/z : $[M\text{-}H\text{-}4PF_6]^{3+}$ calcd for $C_{66}H_{47}N_{14}Ru_2$: 413.0742; found 413.07545. **HRMS (ESI-TOF) m/z :** $[M\text{-}2H\text{-}4PF_6]^{2+}$ calcd for $C_{66}H_{46}N_{14}Ru_2$: 619.1074; found 619.1074.

Cyclic voltammetry



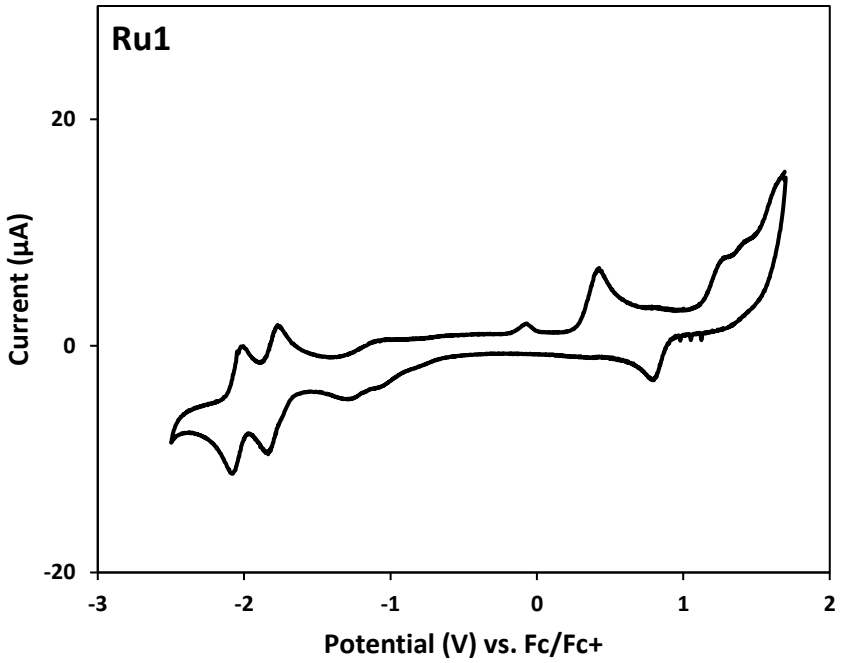
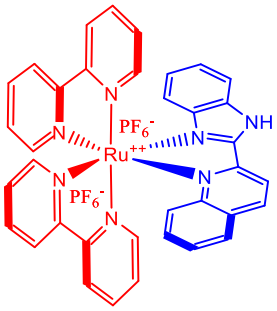


Figure S1. Cyclic voltammogram of **Ru1** (2 mM) in 0.1 M Bu_4NPF_6 acetonitrile electrolyte, scan rate 0.3 V/s.



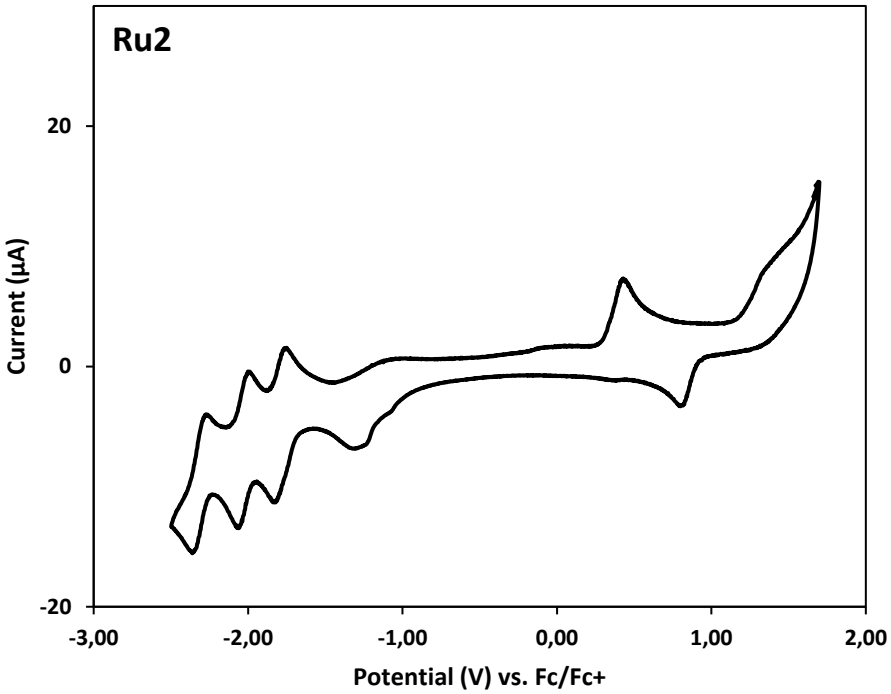
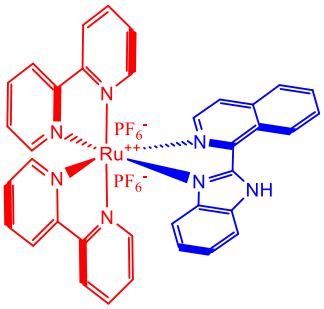


Figure S2. Cyclic voltammogram of **Ru2** (2 mM) in 0.1 M Bu_4NPF_6 acetonitrile electrolyte, scan rate 0.3 V/s.



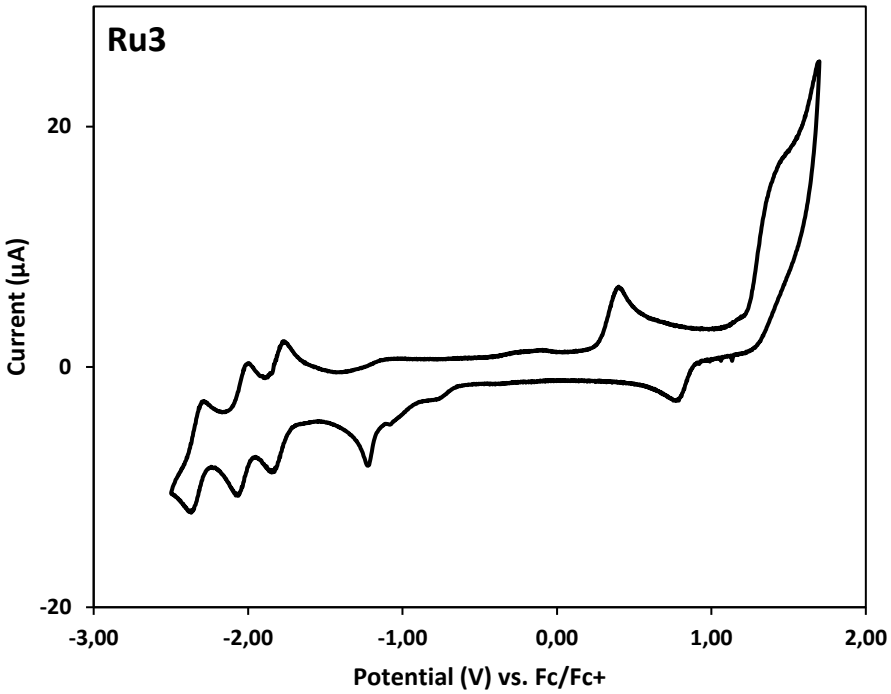
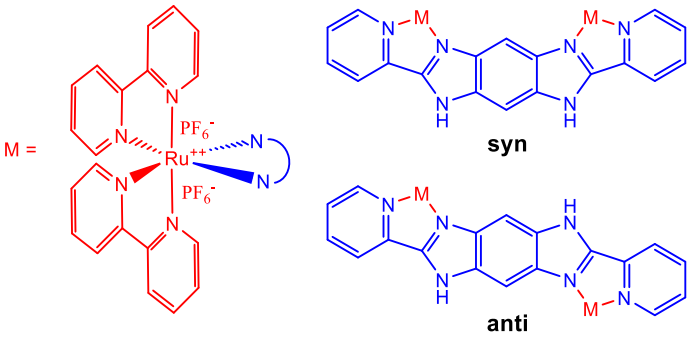


Figure S3. Cyclic voltammogram of **Ru3** (2 mM) in 0.1 M Bu_4NPF_6 acetonitrile electrolyte, scan rate 0.3 V/s.



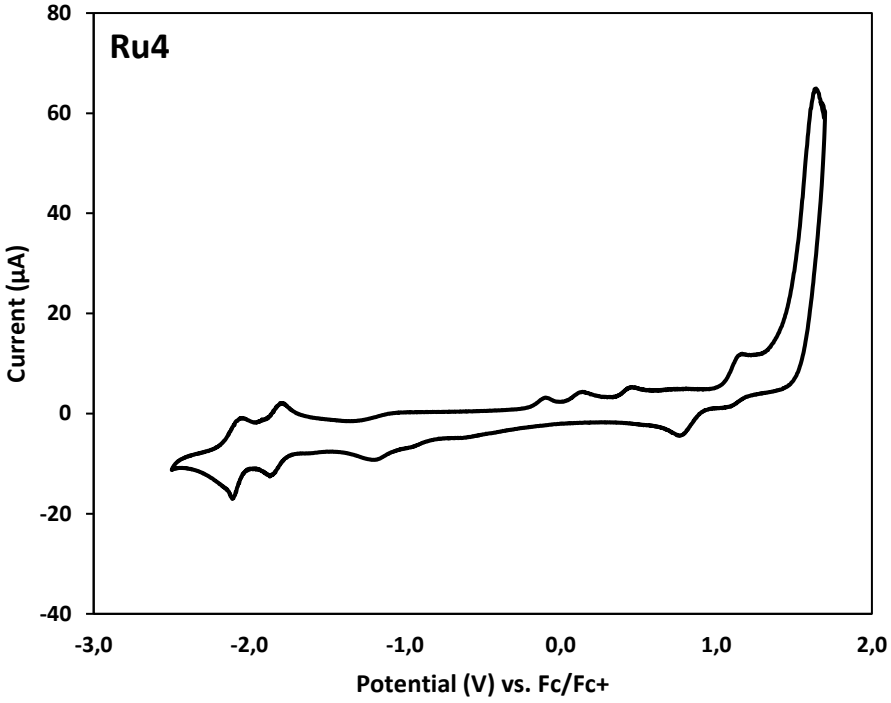
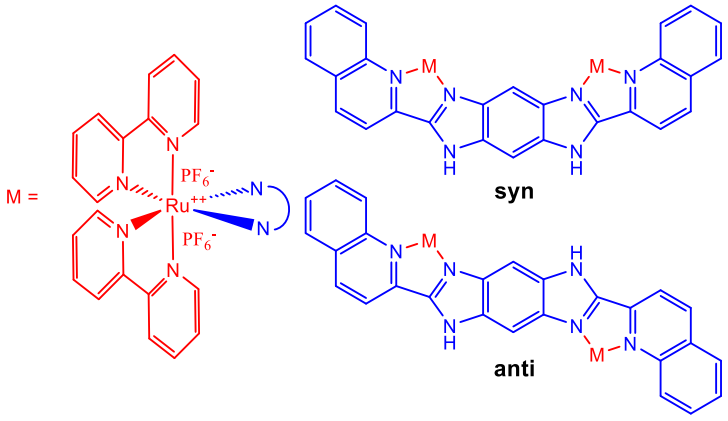


Figure S4. Cyclic voltammogram of **Ru4** (2 mM) in 0.1 M Bu_4NPF_6 acetonitrile electrolyte, scan rate 0.3 V/s.



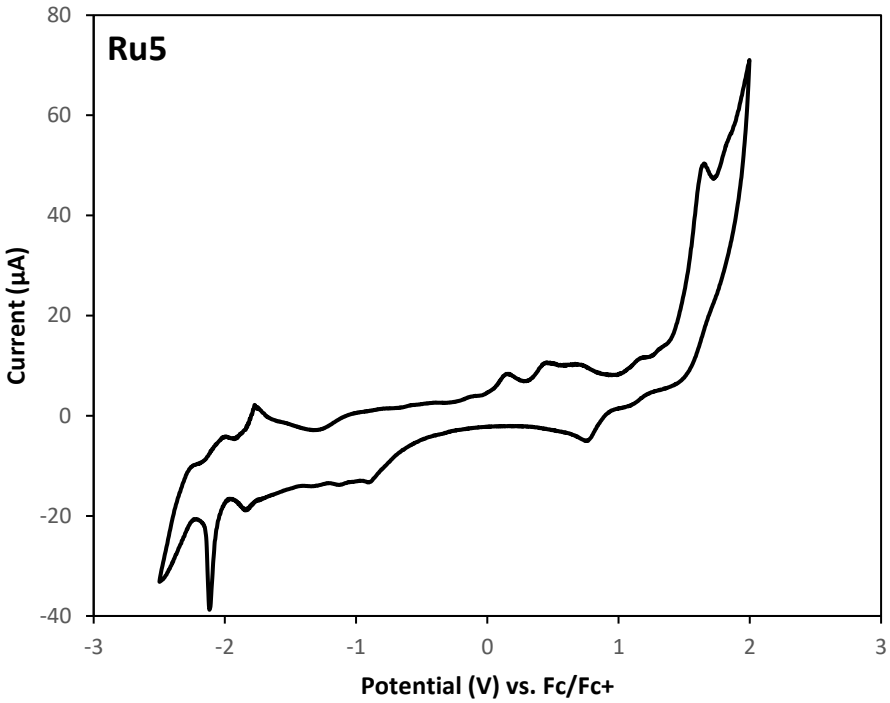
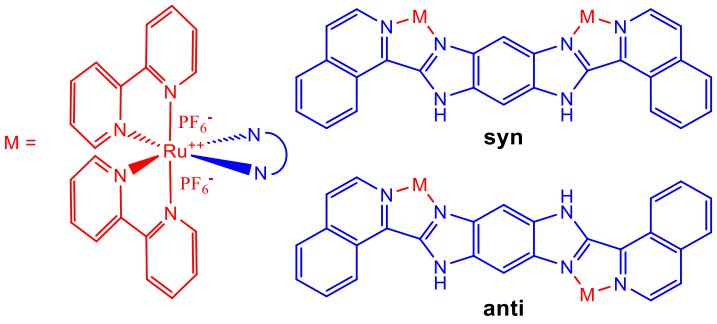


Figure S5. Cyclic voltammogram of **Ru5** (2 mM) in 0.1 M Bu_4NPF_6 acetonitrile electrolyte, scan rate 0.3 V/s.



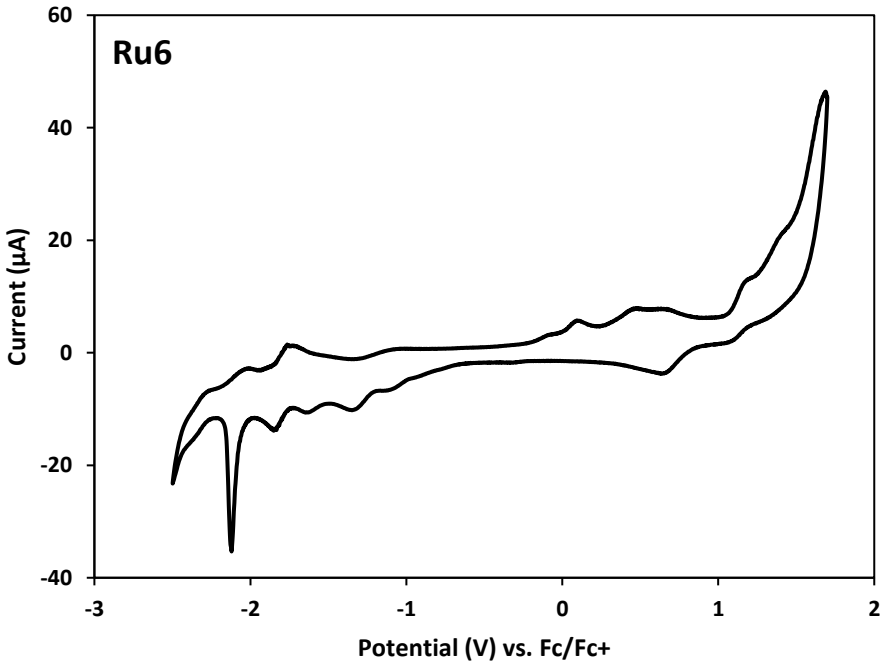


Figure S6. Cyclic voltammogram of **Ru6** (2 mM) in 0.1 M Bu_4NPF_6 acetonitrile electrolyte, scan rate 0.3 V/s.

Absorbance and fluorescence spectra

Ligands

Each spectrum was recorded with a concentration of ligands at [30 µM] for absorbance and at [7.5 µM] for fluorescence. The fluorescence spectra were measured at the long-wave excitation wavelength of the corresponding ligands.

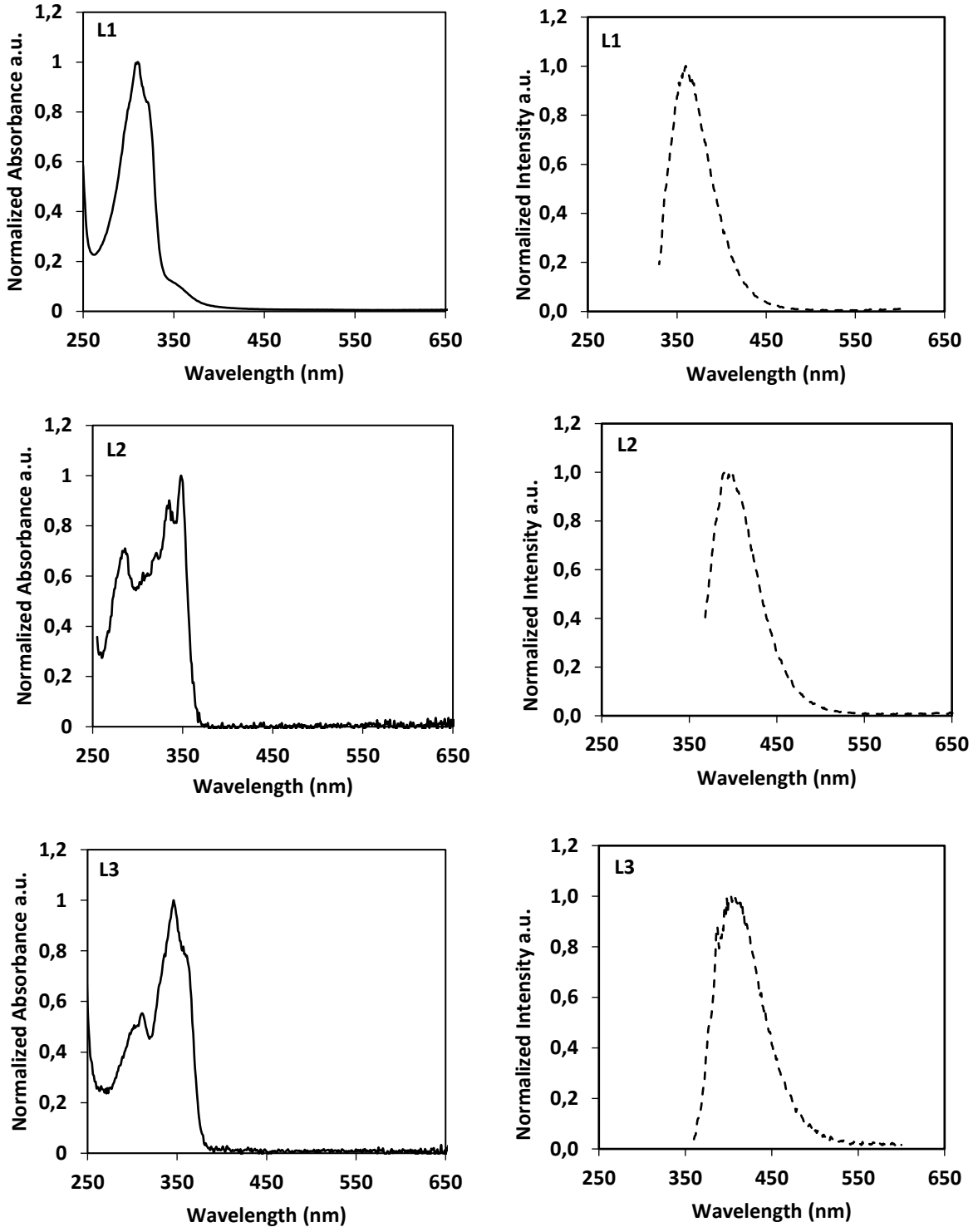


Figure S7. UV–Vis spectra (Absorbance, full line) at 30 µM in CH_3CN and emission spectra excited at 450 nm (Intensity, dotted line) at 7.5 µM in CH_3CN of **L1-L3**.

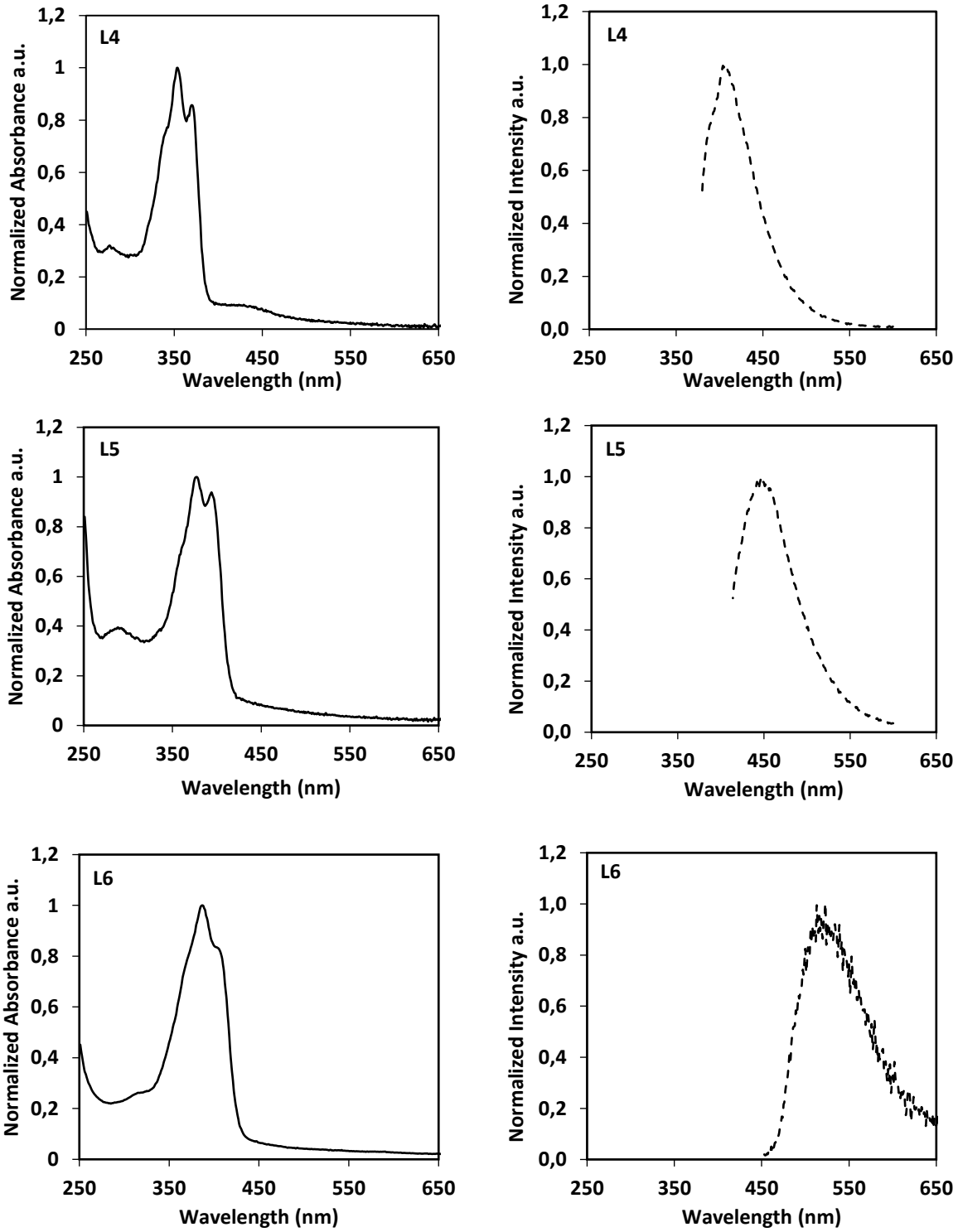


Figure S8. UV–Vis spectra (Absorbance, full line) at 30 µM in CH_3CN and emission spectra excited at 450 nm (Intensity, dotted line) at 7.5 µM in CH_3CN of **L3-L6**.

Ruthenium complexes

Each spectrum was carried out with a concentration of ligands at [20 µM] in acetonitrile for the absorbance and the fluorescence. The fluorescence spectra were measured at an excitation wavelength of 450 nm.

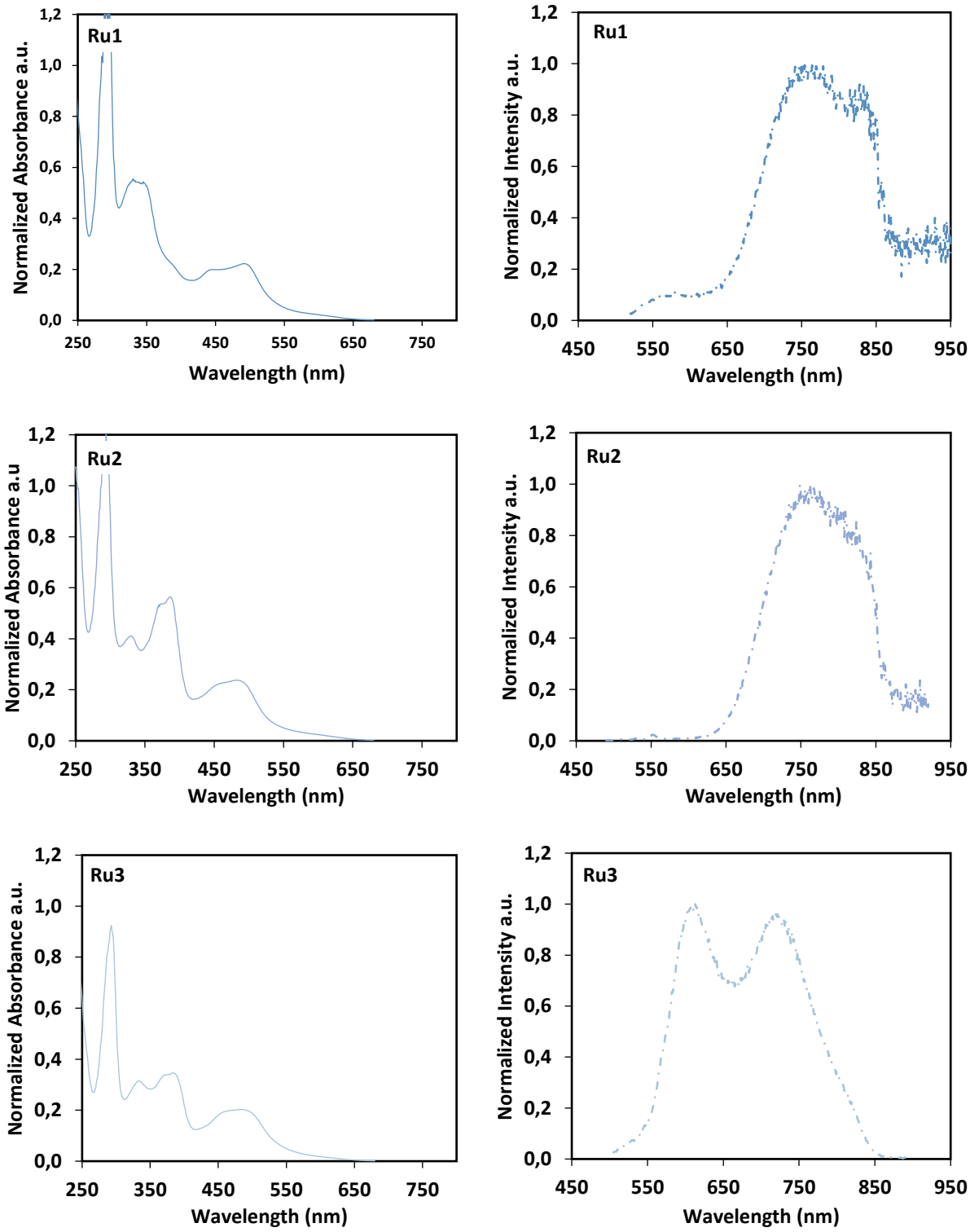


Figure S9. UV–Vis spectra (Absorbance, full line) and emission spectra excited at 450nm (Intensity, dotted line) of **Ru1-Ru3** at 20 µM in CH_3CN.

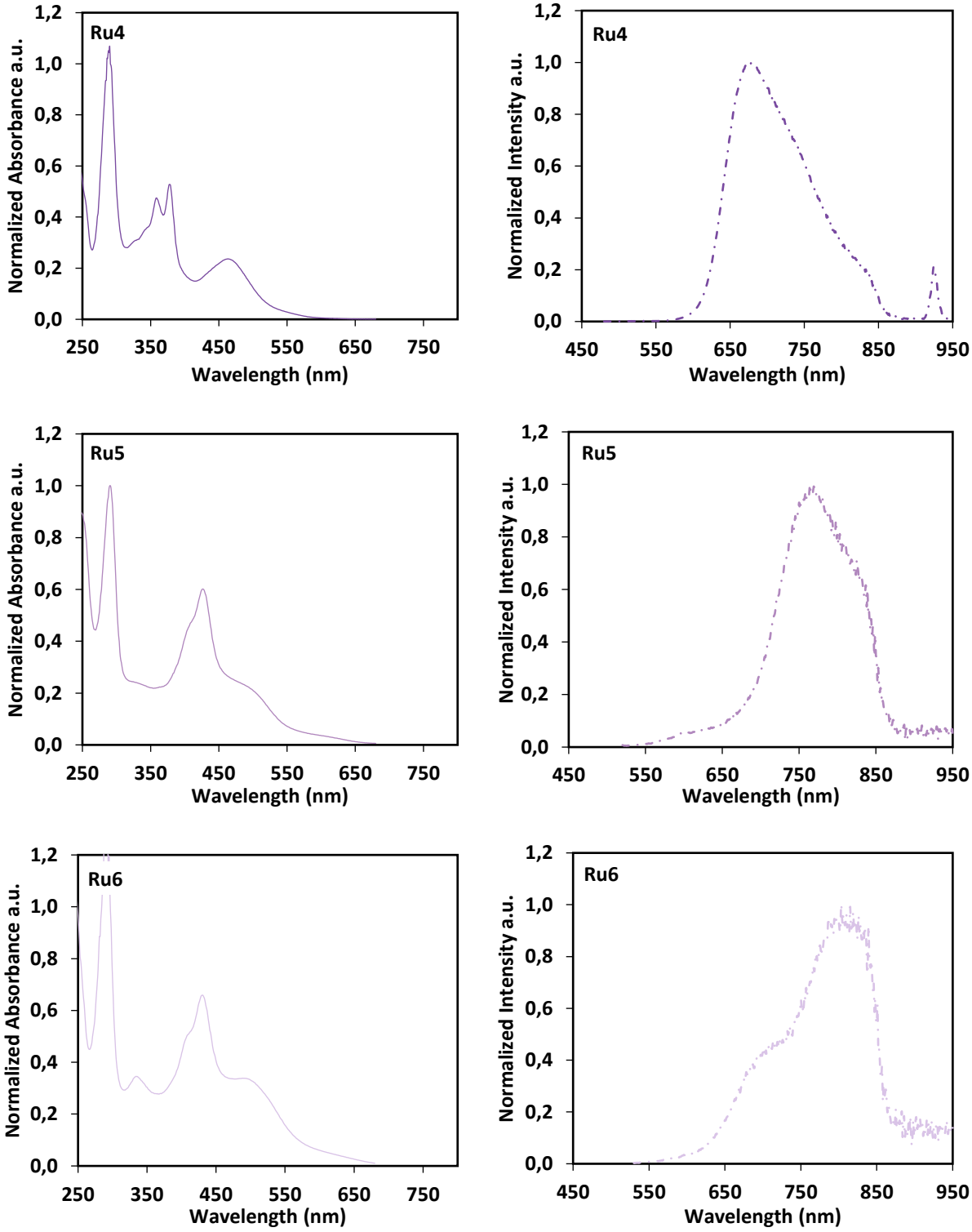


Figure S10. UV–Vis spectra (Absorbance, full line) and emission spectra excited at 450nm (Intensity, dotted line) of **Ru4**-**Ru6** at 20 µM in CH_3CN.

	Absorption		Emission				
Compounds	**λ max nm (ε in $10^{-3}.M^{-1}.cm^{-1}$)**	**λmax [c] nm**	**λmax[c] nm**	**λmax[d] nm**	**Δ Stokes**	**Φ [e] %**	**E_{0-0} eV**
L1	310 (60.0) [a]		360		50		
L2	285 (0.90) ; 335 (1.10) ; 348 (1.29) [a]		391		43		
L3	312 (1.08) ; 346 (1.85) [a]		403		57		
L4	279 (1.57) ; 354 (4.97) [a] ; 367 (4.27)		406		52		
L5	292 (2.00) ; 377 (5.03) [a] ; 393 (4.73)		462		85		
L6	390 (26.53) [a] ; 406 (21.90)		517		142		
Ru1	293 (67.34) ; 340 (31.20) ; 389 (9.34)	446 (11.48) ; 491 (12.60) [b]	567 ; 751	580 ; 749 ; 815	121 ; 260 [b]	0.95	2.36
Ru2	295 (63.14) ; 332 (23.36) ; 368 (30.04) ; 388 (32.26)	457 (12.84) ; 483 (13.64) [b]	762	762	279 [b]	0.55	2.00
Ru3	291 (51.74) ; 334 (18.10) ; 370 (19.34) ; 390 (19.00)	462 (11.30) ; 484 (11.68) [b]	607 ; 729	613 ; 719	145 ; 245	0.22	2.32
Ru4	287 (58.38) ; 306 (19.16) ; 379 (30.22)	462 (13.80) [b]	676	676	214 [b]	0.57	2.14
Ru5	292 (40.88) ; 406 (18.82) ; 429 (24.80)	504 (8.30) [b]	618 ; 762	764	260[b]	0.38	2.11
Ru6	289 (69.54) ; 408 (28.94) ; 432 (37.52)	508 (18.10) [b]	705 ; 802	705 ; 803	273 [b] ; 295	0.17	2.02

Table 1. All measurements were performed at 30 µM for Ligands and 50 µM for Ru1-6 in CH_3CN at 293K. [a] values corresponding at λ max of CT. [b] values corresponding at λ max of MLCT. [c] values with λ excitation = 450 nm. [d] values with λ excitation = λ max MCLT. [e] Φ Quantum yield was calculated according to the equation, using $[Ru(bpy)_3]^{2+}$ (Φ = 1.8 %) as the standard [i].

Study of the photostability

To study the photostability of ligands in acetonitrile, UV-Visible absorption spectra were measured on a Molecular Device SpectraMax M5e in a 96-well plate at 50 µM. First, a UV analysis was performed with the plate reader at t0. Then, the plate was irradiated with Lumidox II LED Arrays (white light) for 48 h with UV analyses at different irradiation times (30 min, 1 h, 2 h and 20 h).

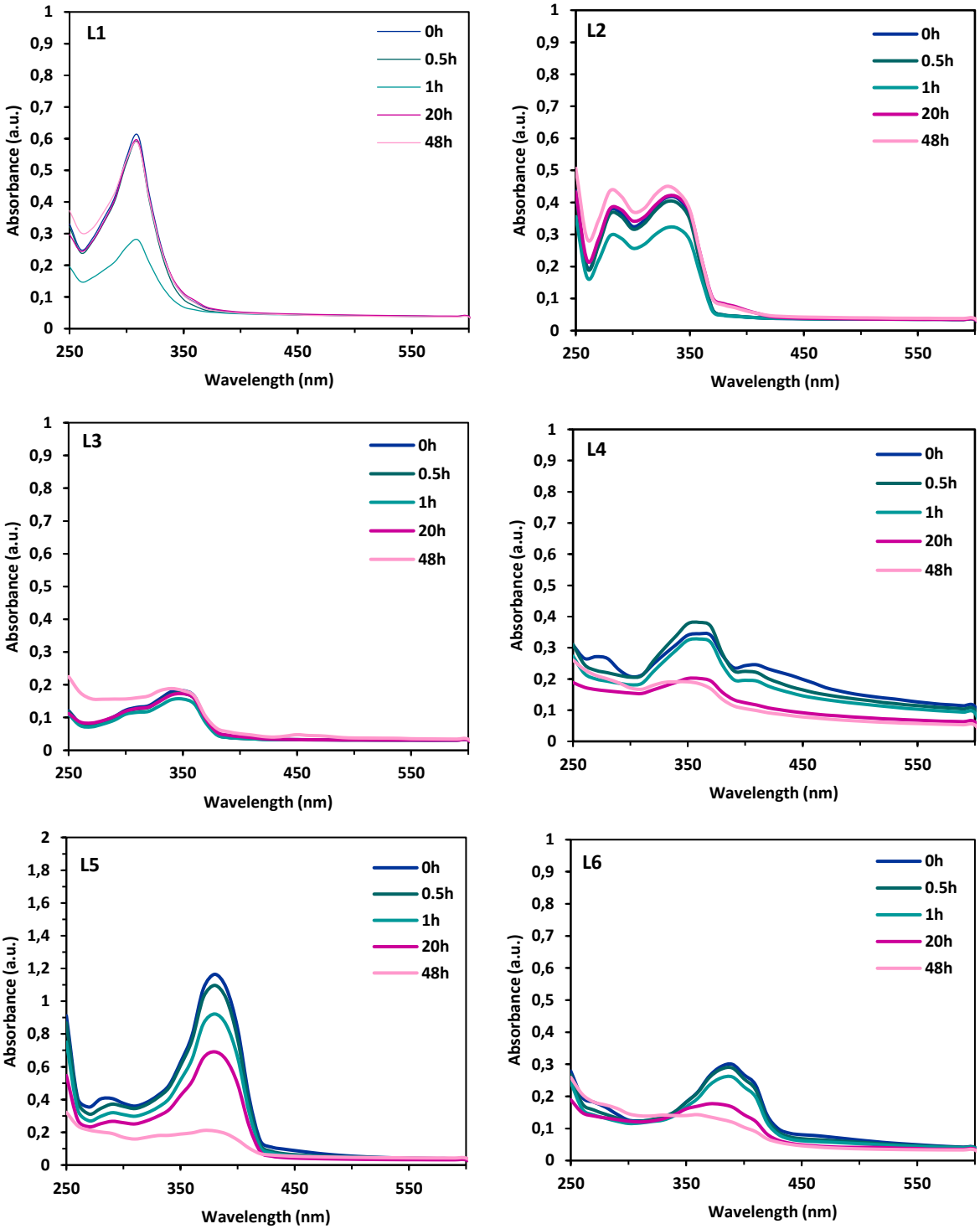


Figure S11. UV–Vis spectra of **L1-L6** at 50 µM in CH_3CN after white light LED irradiation at different times.

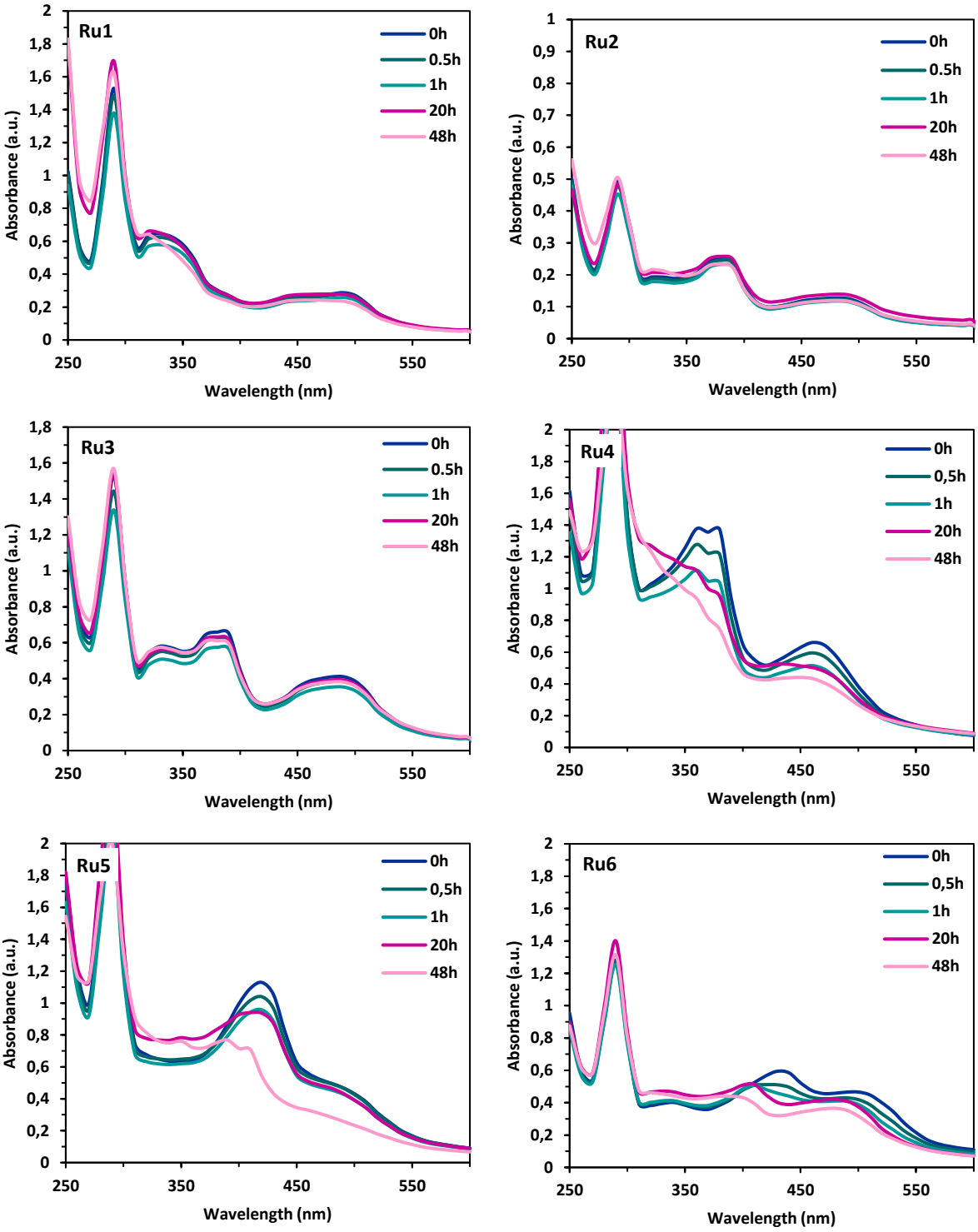
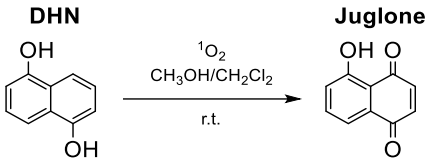


Figure S12. UV–Vis spectra of **Ru1-Ru6** at 50 µM in CH_3CN after white light irradiation at different times.

Study of the ROS generation

The singlet oxygen generation

To detect singlet oxygen production by ruthenium complexes, 1,5-dihydroxynaphtalene (DHN) was used. 2700 µL of DHN (340 µM and 93 µL of ruthenium complexes (1 mM, 10 mol% vs. DHN), dissolved in a mixture of MeOH/DCM (1/9) solution that has been pre-saturated with oxygen for 10 min, were added to a quartz cuvette 1 cm containing 207 µL of a mixture MeOH/DCM (1/9) solution. The final concentrations of DHN and ruthenium complexes were 310 µM and 31 µM, respectively. The concentration of DHN is deliberately higher than that of ruthenium because the latter absorb in the same region as DHN. Then, the mixture was illuminated with a Kessil® A160WE LED at 456 nm at room temperature for 60 seconds with UV analyses every 5 seconds. The $^1O_2$ generation rate was determined from the increase in absorbance of juglone at 420 nm over time. To characterize the difference in the rate of $^1O_2$ produced by different samples, the ratios $(A-A_0)/A_0$ of absorbance of juglone in presence of ruthenium A and the initial absorbance of juglone A_0 at 420 nm at different irradiation times, were calculated and plotted as the ordinate for the irradiation time. 310 µM of DHN; 31 µM of [Ru] in a 3mL vial of a mixture MeOH/DCM (1/9, v/v) saturated in oxygen under irradiation at 456 nm.



Scheme S3. Synthetic scheme of oxidation of DHN in juglone.

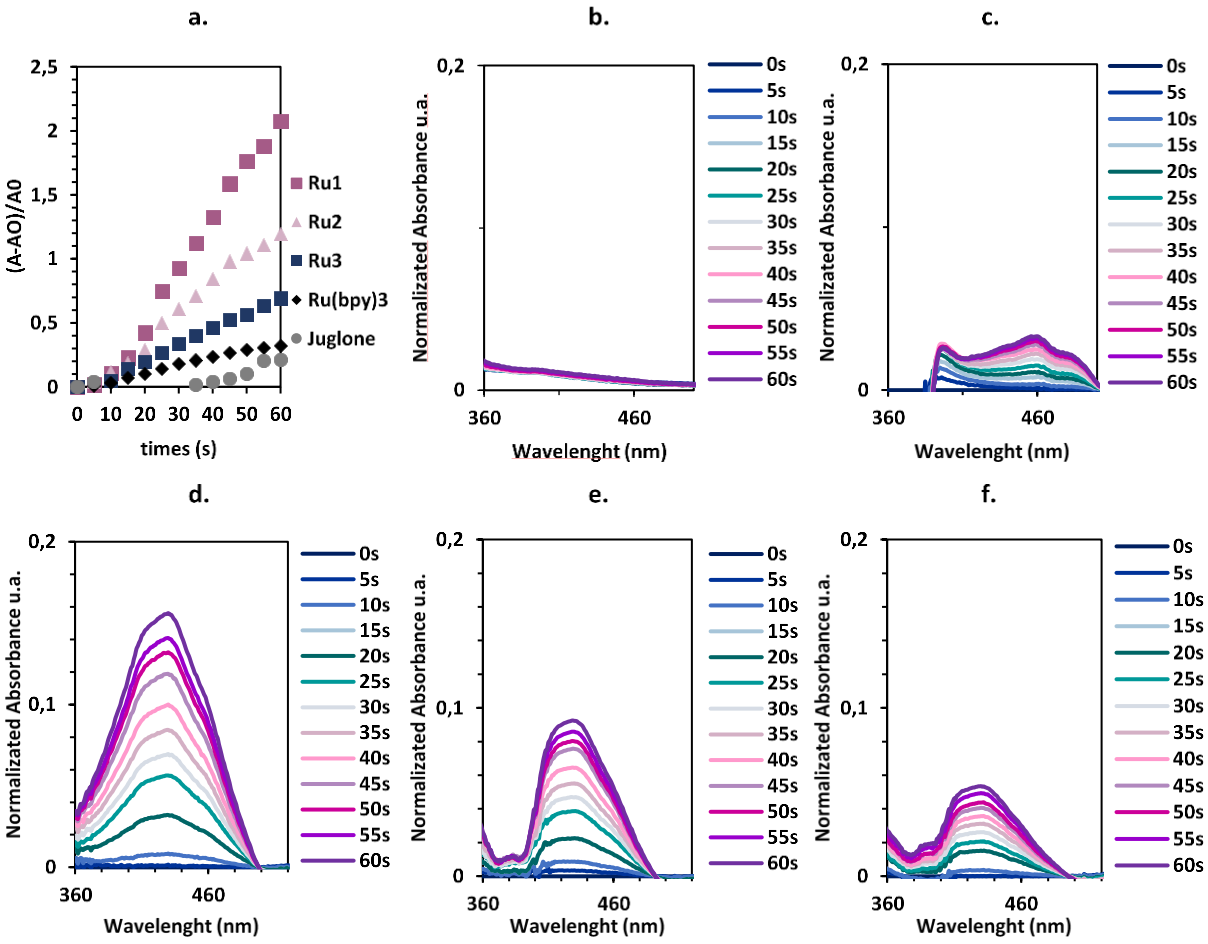
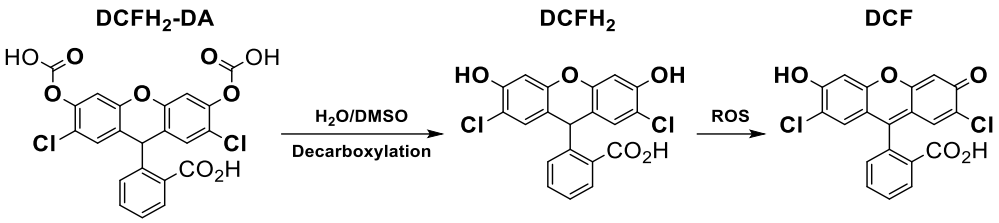


Figure S13. (a) Graphical representation of singlet oxygen production of **Ru1-Ru3** correlated with the increase of the intensity of juglone absorption band (at 420 nm) at different times (0 to 60 seconds). UV–Vis spectra of **(b) DHN**, **(c) Ru(bpy)$_3$.2PF$_6$**, **(d) Ru1, (e) Ru2,** and **(f) Ru3**. Ru at 31 µM and **DHN** at 310 µM in a mixture of MeOH/DCM (1/9, v/v) after irradiation at 456 nm at different times (0 to 60 seconds).

The ROS generation by a SET mechanism

To detect ROS production via a SET mechanism by ruthenium, 2',7'-Dichlorodihydrofluorescein diacetate (DCFH) was used. 15 µL of DCFH (1 mM in DMSO) and 15 µL of ruthenium complexes (1 mM in DMSO) were added to a quartz cuvette 1 cm containing 2970 µL of H_2O. The final concentrations of DCFH and ruthenium were 10 µM in a mixture DMSO/H_2O (1/99) for each compound. DCFH was used as the total ROS indicator. Then, the mixture was illuminated with a Kessil® A160WE LED at 456 nm (under 40 mW.cm^{-2}) and at room temperature for 60 seconds with fluorescence analyses every 5 seconds. The fluorescence spectra of conversion of DCFH to DCF (excited at 488 nm) were continuously monitored during the predefined irradiation time. The ROS generation rate was determined from the increase in fluorescence of DCFH at 520 nm over time. To characterize the difference in the rate of ROS produced by different samples, the ratios $\mathbf{I/I_0}$ of fluorescence of DCF in presence of ruthenium **I** and the initial fluorescence of DCF $\mathbf{I_0}$ at 520 nm at different irradiation times, were calculated and plotted as the ordinate for the irradiation time. 10 µM of DCFH; 10 µM of [Ru] in a vial 3mL of a mixture DMSO/H_2O (1/99, v/v) under irradiation at 456 nm.



Scheme S4. Synthetic scheme of oxidation of DCFH-DA in DCF.

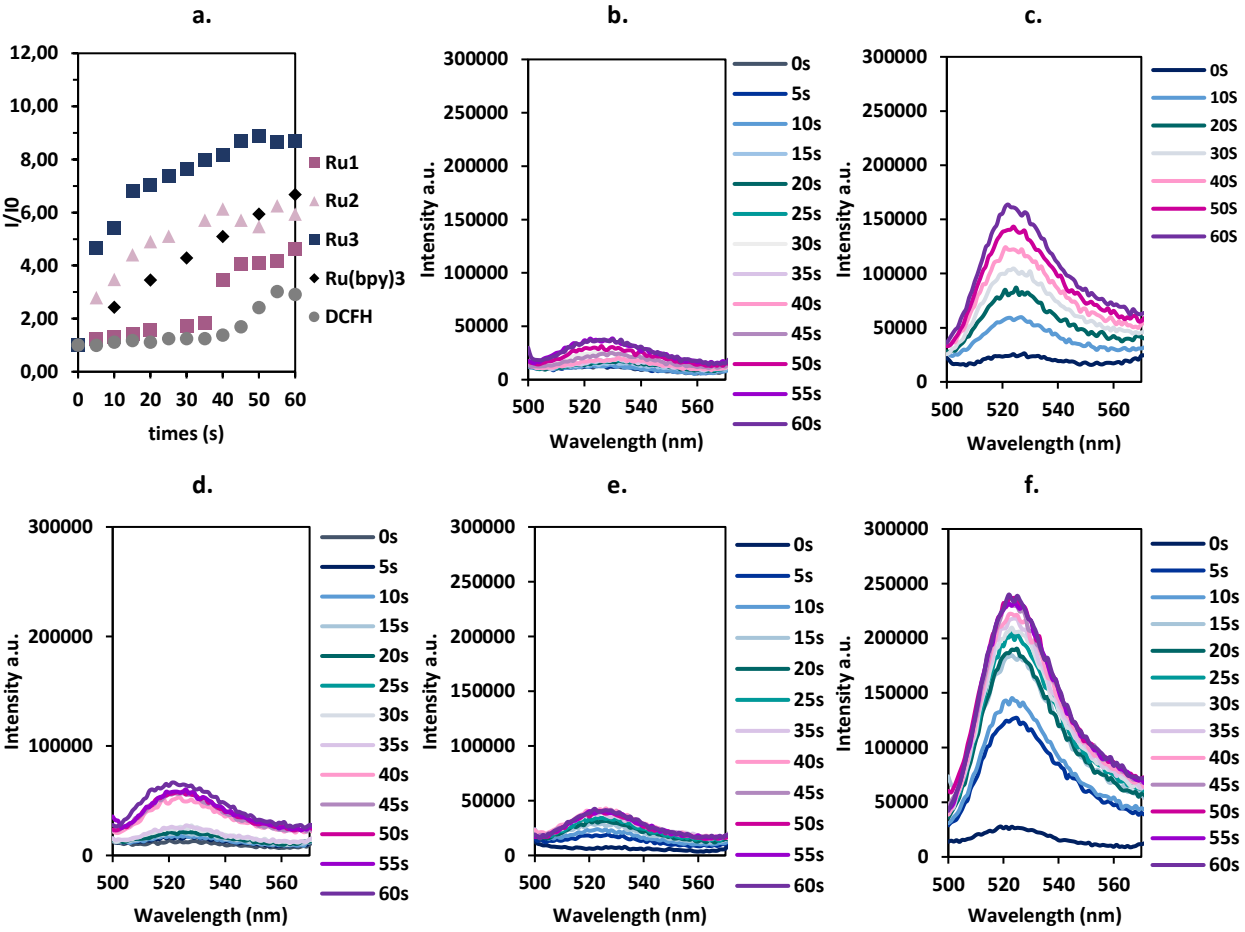
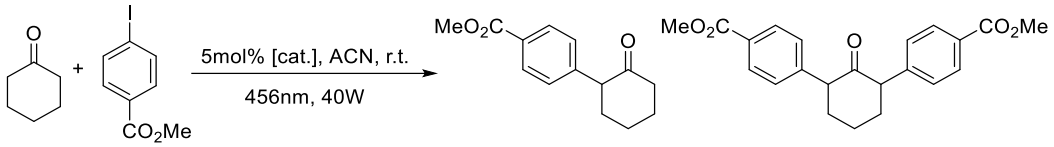


Figure S14. (a) Graphical representation of ROS production of **Ru1-Ru3** correlated with the increase of the intensity of DCF emission band (at 520 nm) at different times (0 to 60 seconds). Emission spectra excited at 488 nm of **(b) DCFH**, and **DCFH** in presence of **(c) Ru(bpy)$_3$.2PF$_6$**, **(d) Ru1**, **(e) Ru2**, and **(f) Ru3**. **Ru1-Ru3** and **DCFH** at 10 µM in a mixture DMSO/H_2O (1/99, v/v) after irradiation at 456 nm.

Model photo-reaction by SET mechanism



Scheme S5. Synthetic scheme of a-arylation of cyclohexanone.

Cyclohexanone (1 equiv., [0.1 M]), methyl 4-iodobenzoate ester (1 equiv.) and pyrrolidine (2 equiv.) in acetonitrile was stirred in presence of catalysts (5 mol%, 0.005 mmol) under 456 nm irradiation for 17h30 at room temperature in a sealed vial. For each experiment, 3 vials were using (without photocatalyst, with photocatalyst **Ru**, without light). The following experiments were monitored by LC-MS analysis using an intern standard (IS = biphenyl at 1 mM).

Entry	Conditions	% Iodide SM[a]	Monosubstituted %Conversion (1)	Disubstituted %Conversion (2)
1	w/o catalyst	100	0	0
2	$Ru(bpy)_3.2PF_6$	11	28	61
3	$Ru(bpy)_3.2PF_6$, w/o light	100	0	0
4	Ru1	71	4	25
5	Ru1, w/o light	100	0	0
6	Ru2	76	0	24
7	Ru2, w/o light	100	0	0
8	Ru3	14	22	64
9	Ru3, w/o light	100	0	0

Table 2. Results of the alpha-arylation experiment realized at 0.1 M of starting material in 1mL of acetonitrile.

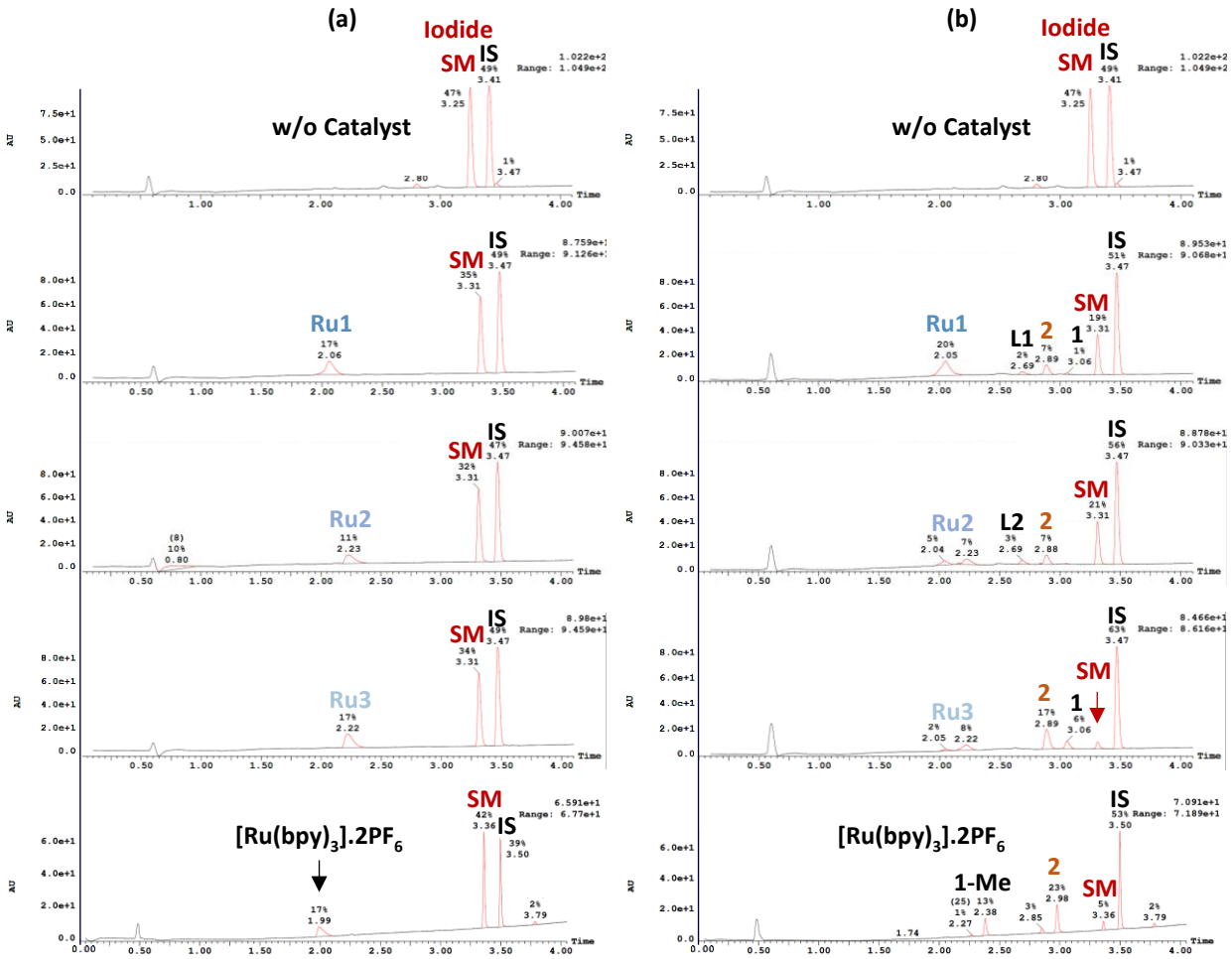
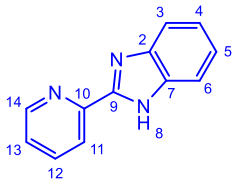


Figure S15. LC-MS spectra **(a)** after 17h30 of reaction at room temperature without light (w/o light) and **(b)** after 17h30 reaction at room temperature under irradiation at 456 nm. **IS** = biphenyl (3.5 min); **1** = monosubstituted (3.1 min); **1-Me** = carboxylate monosubstituted (2.4 min); **2** = disubstituted (2.9 min) ; and **SM** = Iodide start material (3.3 min).

Spectra



L1

400MHz, $_{d6}$DMSO

13.10

8.74

8.34

8.00

7.71

7.59

7.46

7.29

7.16

2.50

1.00

0.96

0.96

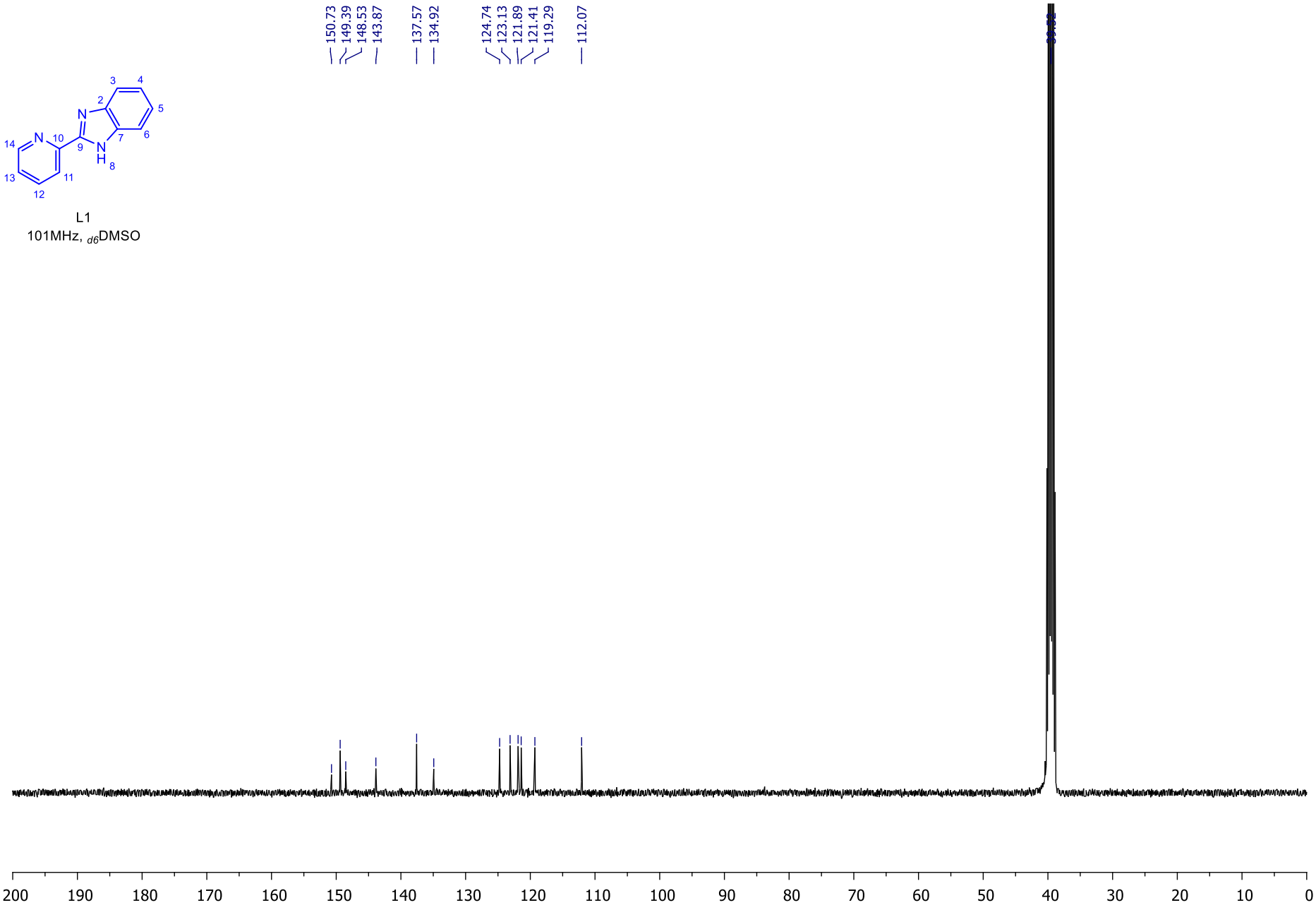
0.98

0.99

2.01

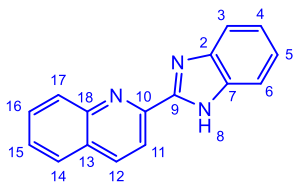
1.98

16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1



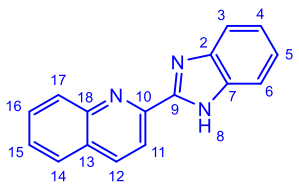
L1

101MHz, $_{d6}$DMSO



L2

400MHz, $_{d6}$DMSO

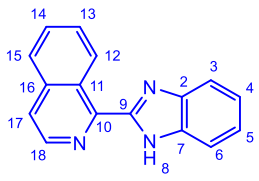


L2

101MHz, $_{d6}$DMSO

150.79
148.79
147.21
137.42
130.48
128.76
128.26
128.09
127.31
122.81
119.25
39.52

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0



L3

400MHz, $_{d6}$DMSO

13.23

10.14

10.07

8.71

8.13

8.06

8.02

7.91

7.81

7.63

7.31

7.26

2.50

1.00

1.07

1.06

1.05

1.01

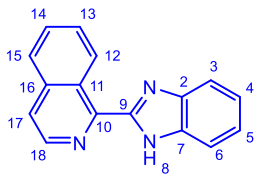
3.19

1.07

1.10

1.10

16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0

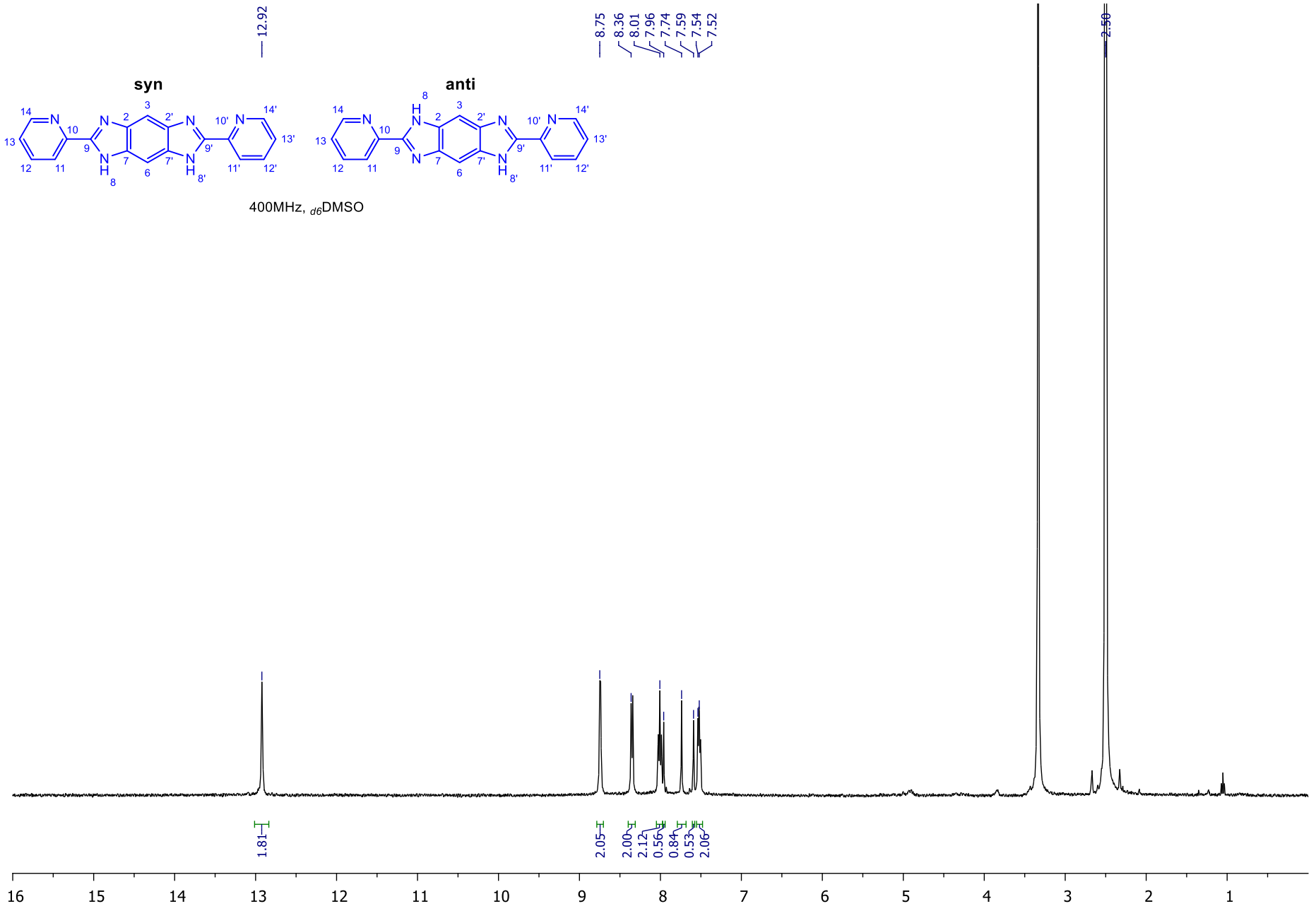


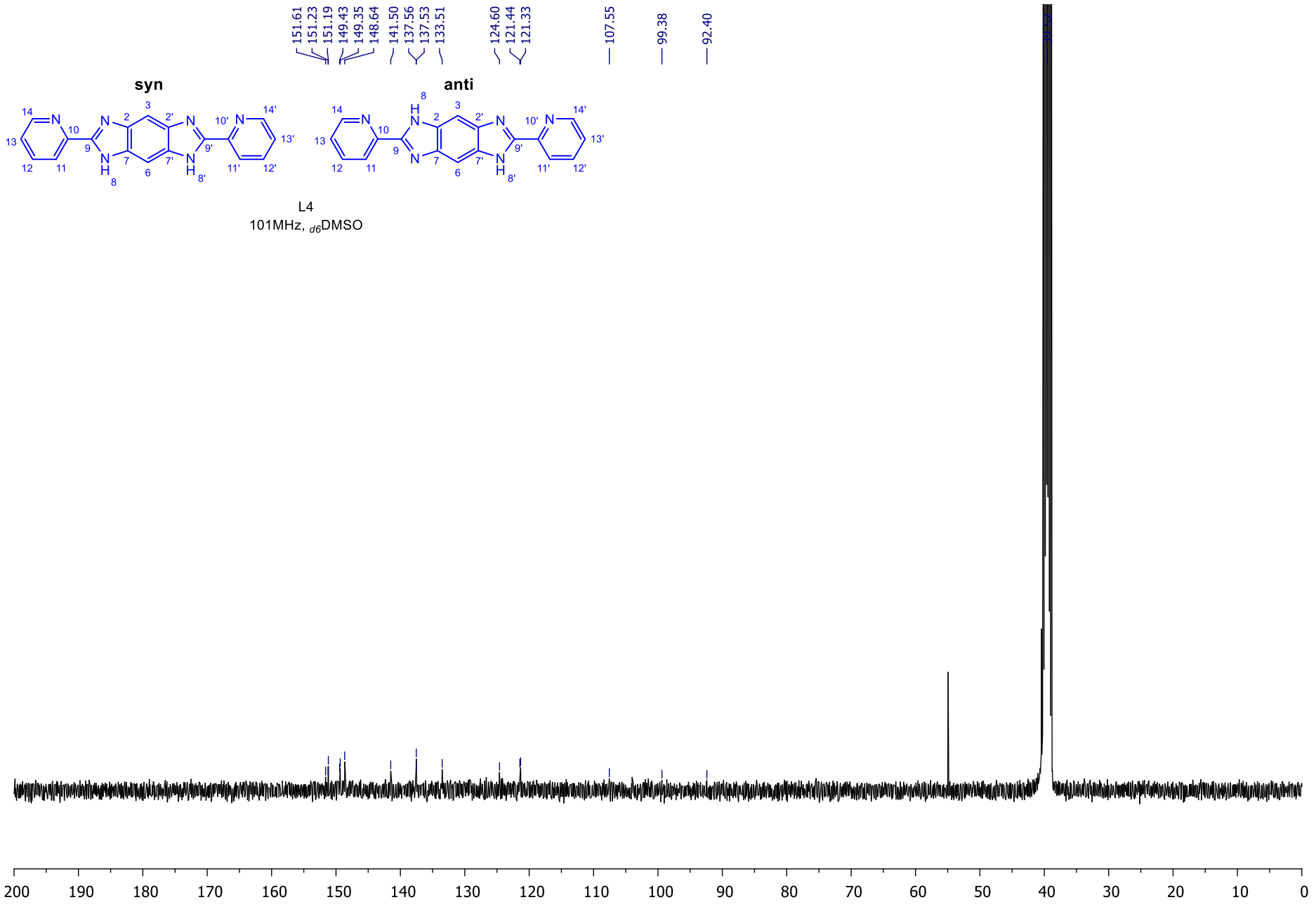
L3

101MHz, $_{d6}$DMSO

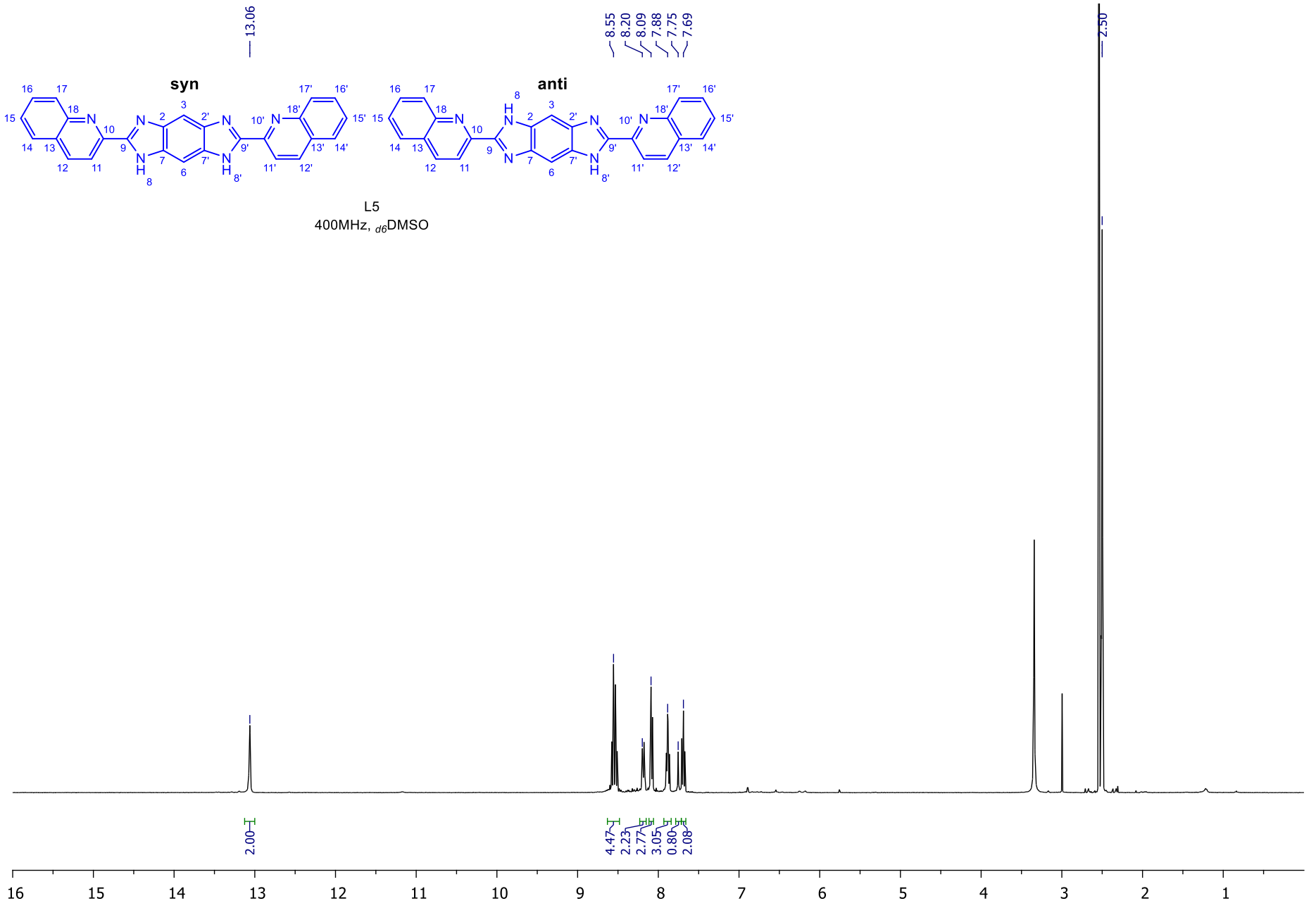
151.19
146.65
144.08
141.68
136.80
134.03
130.67
128.66
127.83
127.26
125.97
123.67
122.39
121.97
119.74
112.08
39.52

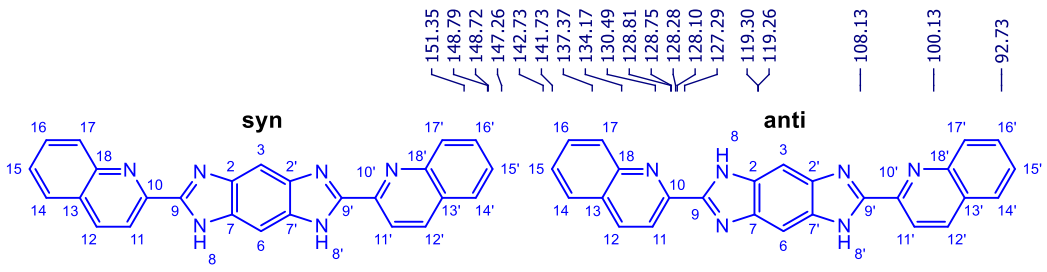
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


12.92
8.75
8.36
8.01
7.96
7.74
7.59
7.54
7.52
2.50
syn
anti
400MHz, d6DMSO
1.81
2.05
2.00
2.12
0.56
0.84
0.53
2.06
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1

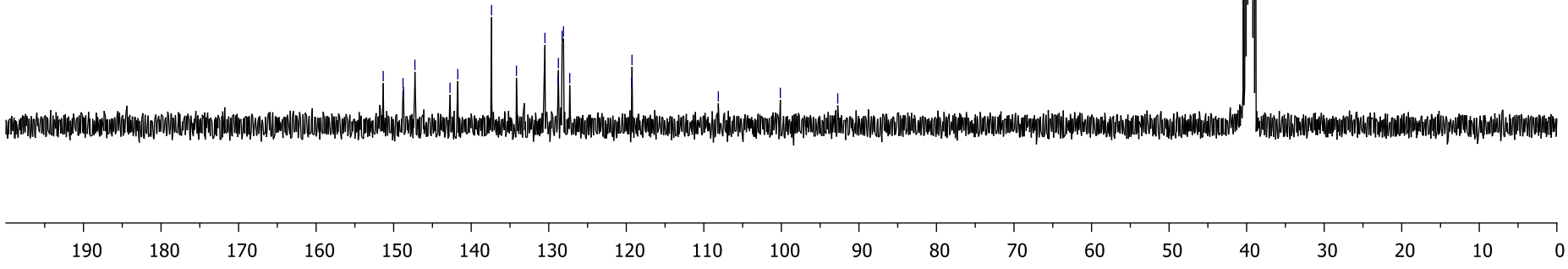


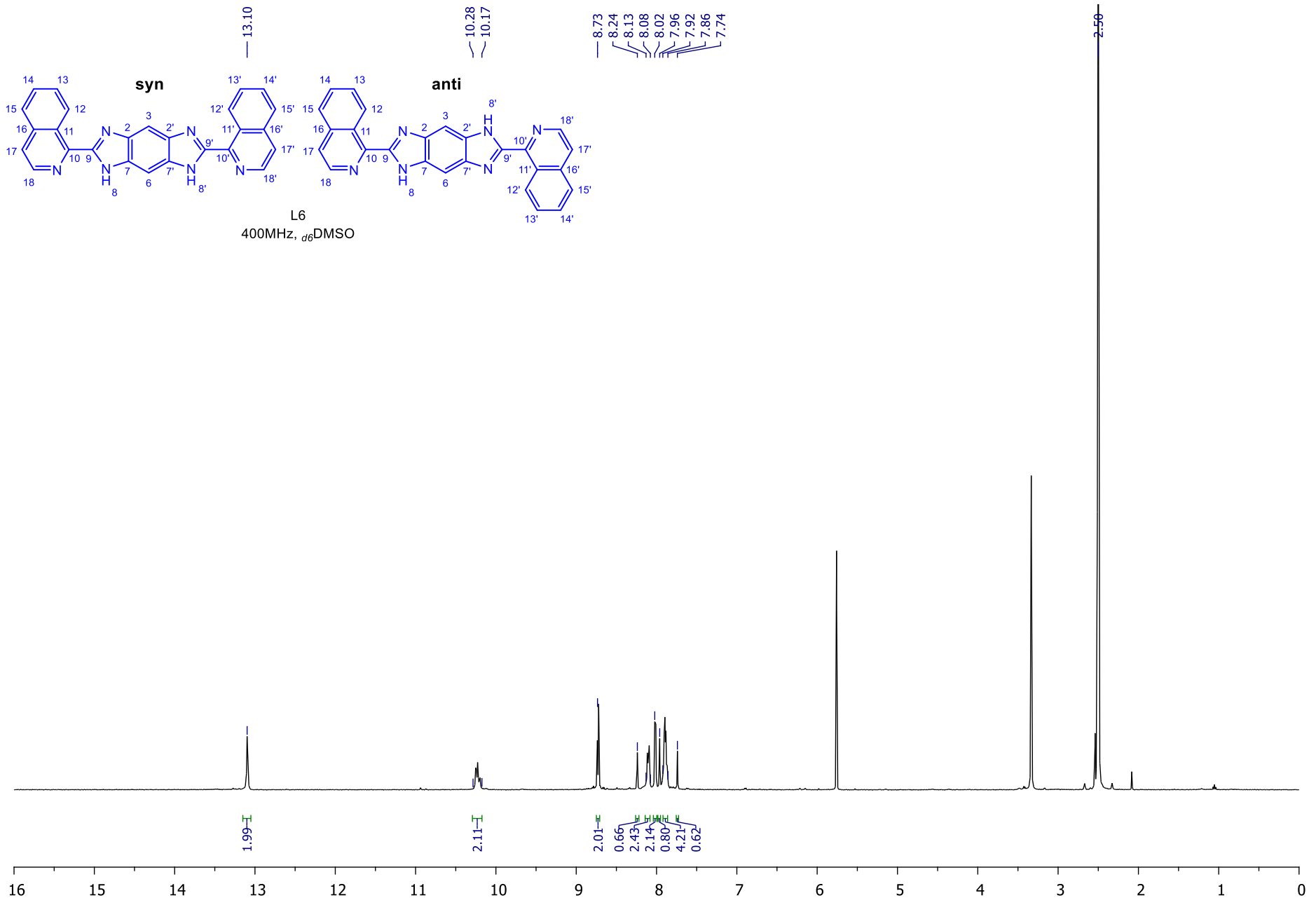
L4
101MHz, $_{d6}$DMSO

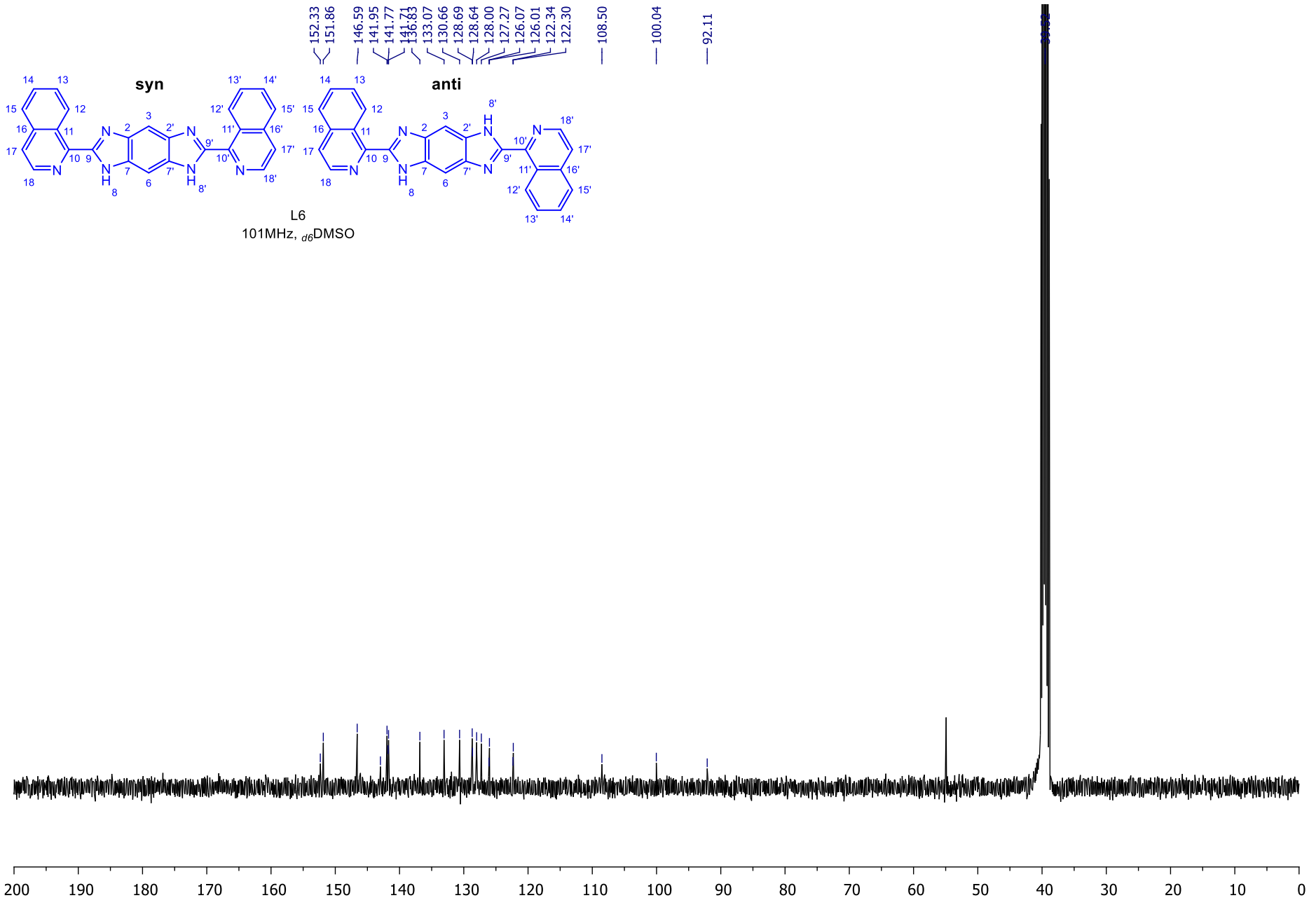

13.06
8.55
8.20
8.09
7.88
7.75
7.69
2.50
syn
anti
L5
400MHz, d6DMSO
2.00
4.47
2.23
2.77
3.05
0.80
2.08
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1

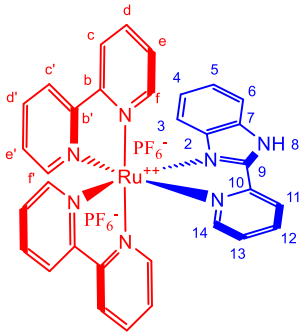


L5
101MHz, $_{d6}$DMSO



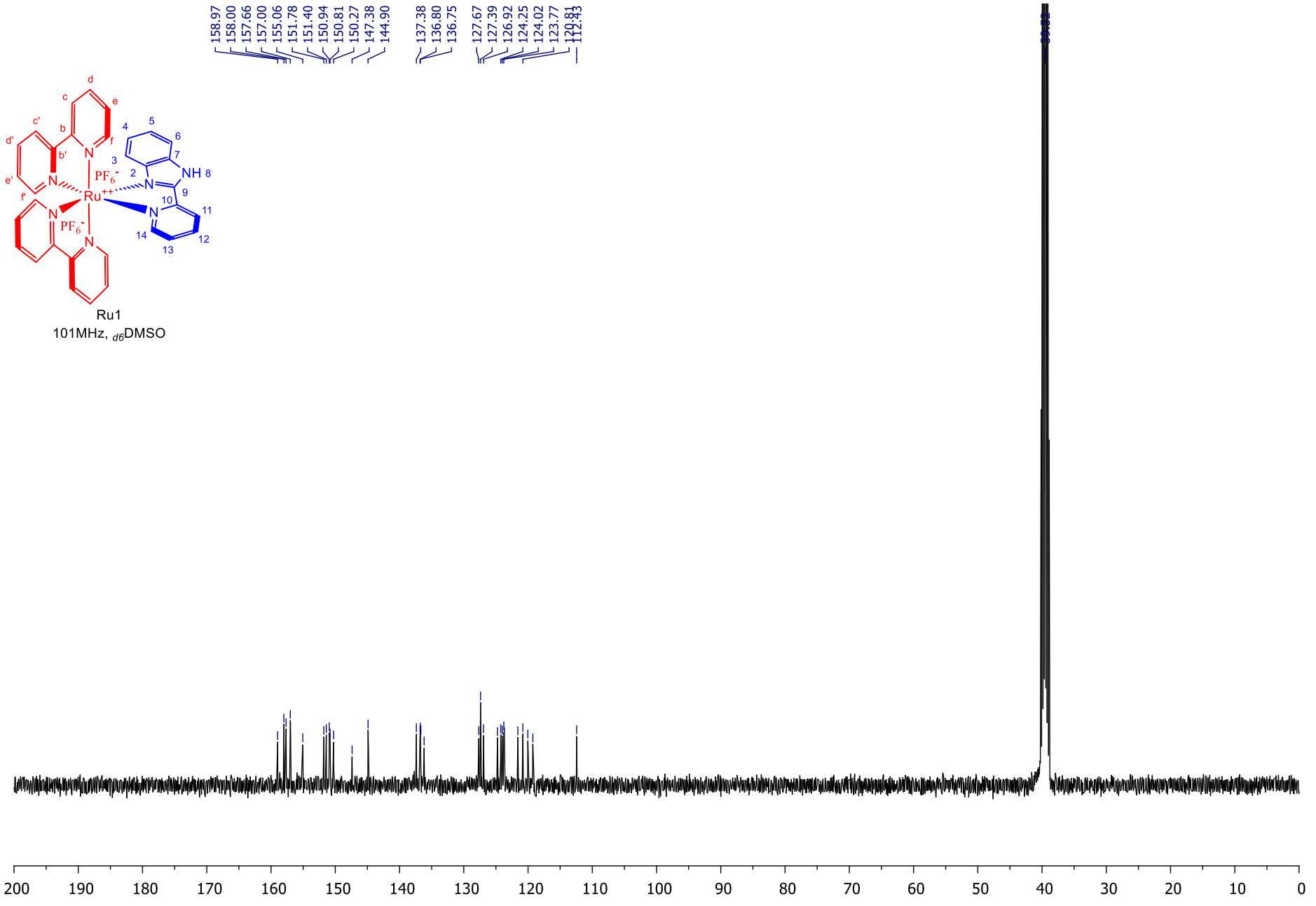

13.10
10.28
10.17
8.73
8.24
8.13
8.08
8.02
7.96
7.92
7.86
7.74
2.50
syn
anti
L6
400MHz, d6DMSO
1.99
2.11
2.01
0.66
2.43
2.14
0.80
4.21
0.62
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0

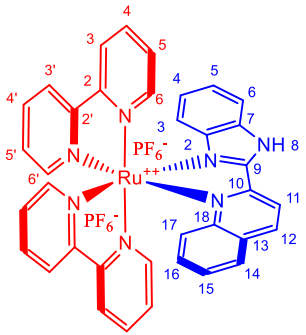

152.33
151.86
146.59
141.95
141.77
141.71
136.83
133.07
130.66
128.69
128.64
128.00
127.27
126.07
126.01
122.34
122.30
108.50
100.04
92.11
syn
anti
L6
101MHz, d6DMSO
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



Ru1

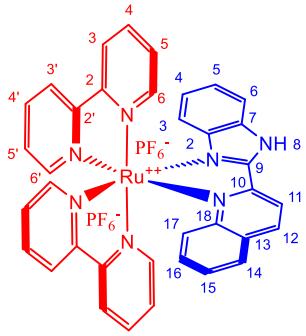
400MHz, $_{d6}$DMSO


158.97
158.00
157.66
157.00
155.06
151.78
151.40
150.94
150.81
150.27
147.38
144.90
137.38
136.80
136.75
127.67
127.39
126.92
124.25
124.02
123.77
120.81
112.43
Ru1
101MHz, d6DMSO
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



Ru2

400MHz, $_{d6}$DMSO

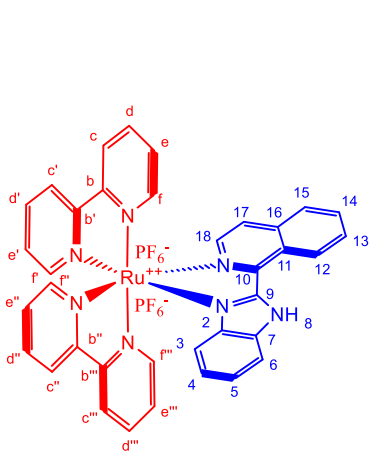


Ru2

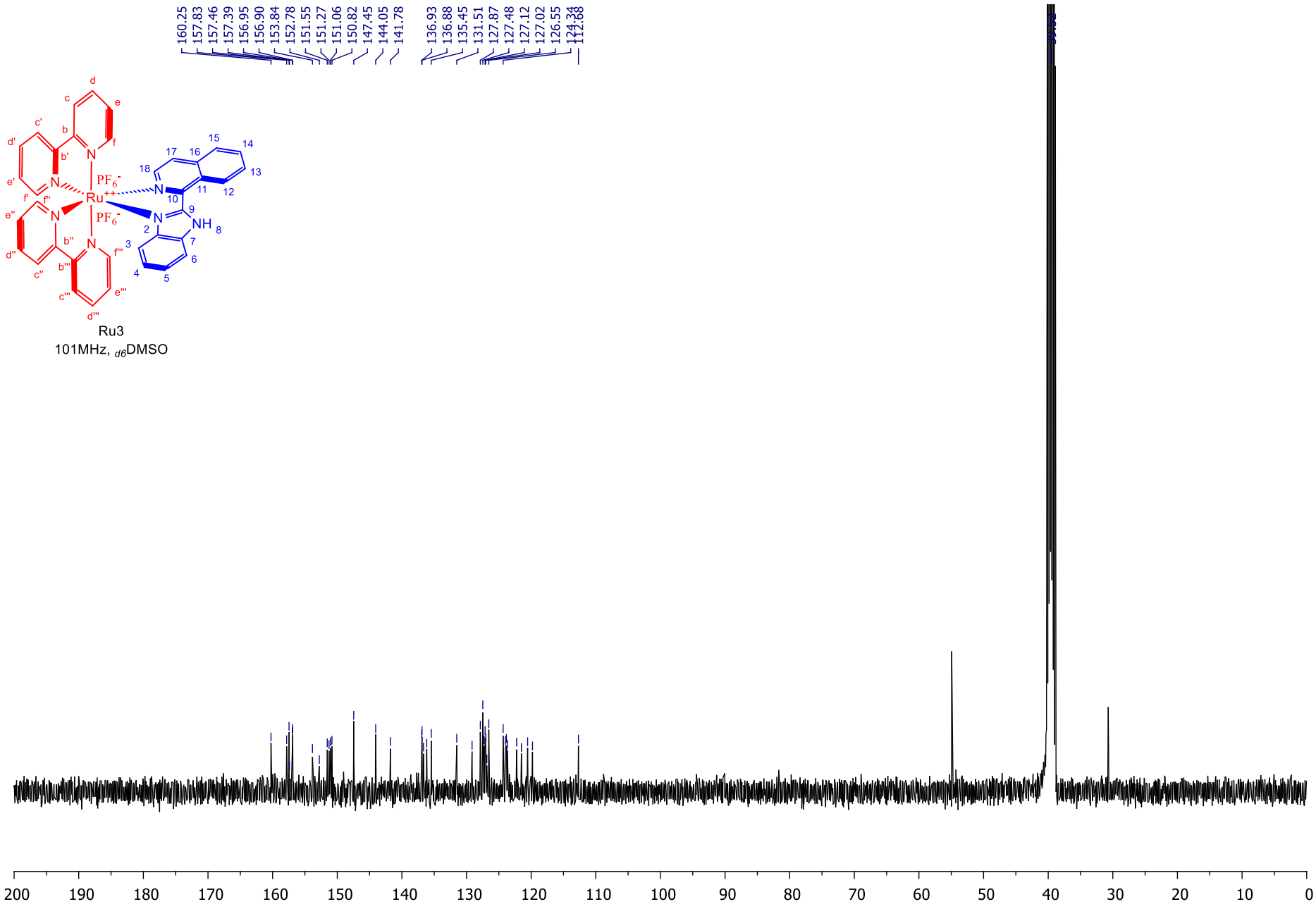
101MHz, $_{d6}$DMSO

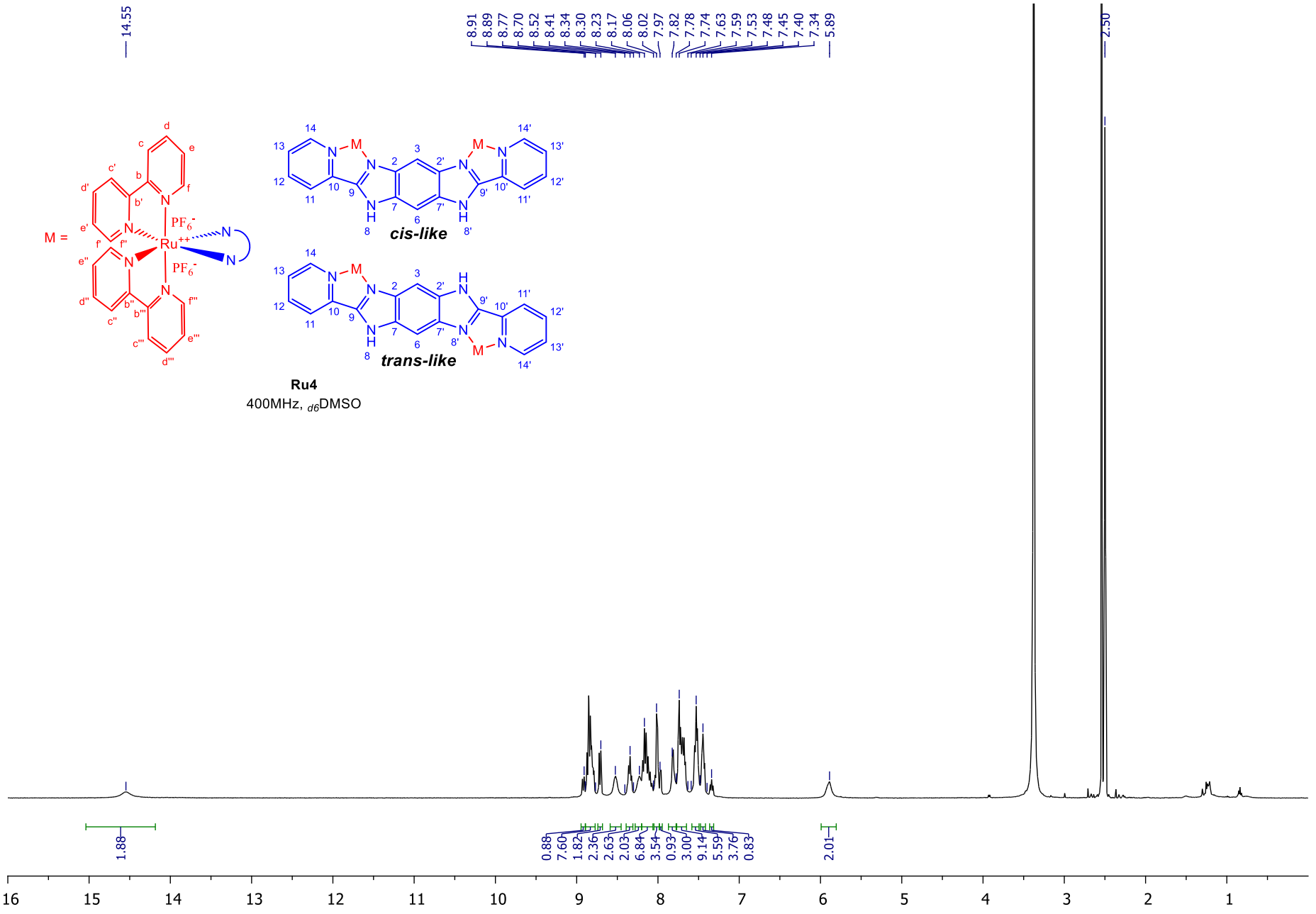
158.30
157.50
156.84
153.33
152.38
151.07
150.84
149.56
142.73
139.47
138.16
137.62
137.30
135.99
131.54
129.84
128.85
128.33
128.08
127.77
127.60
127.55
124.42
124.23
124.00
123.91
119.61
115.86
114.32

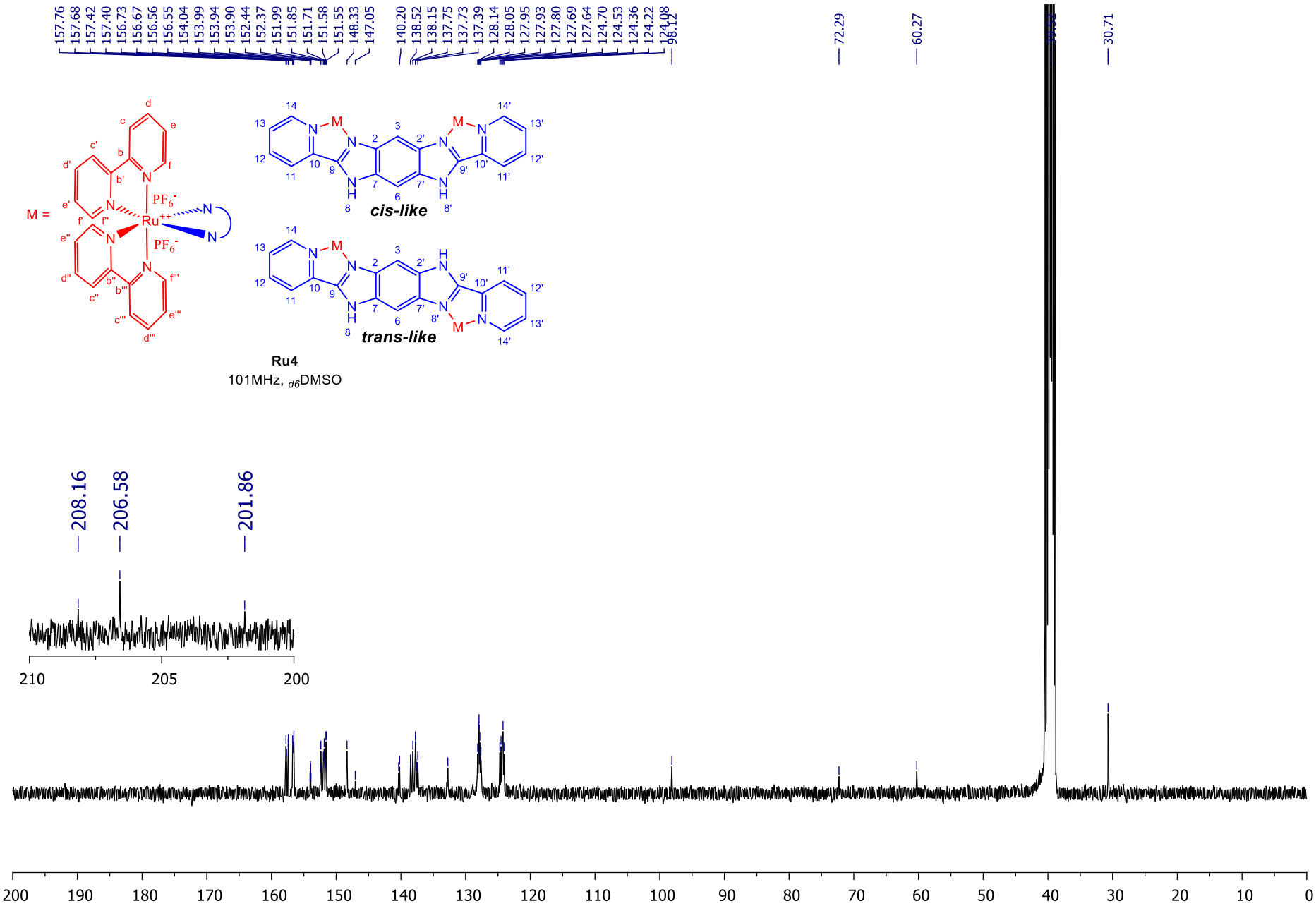
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

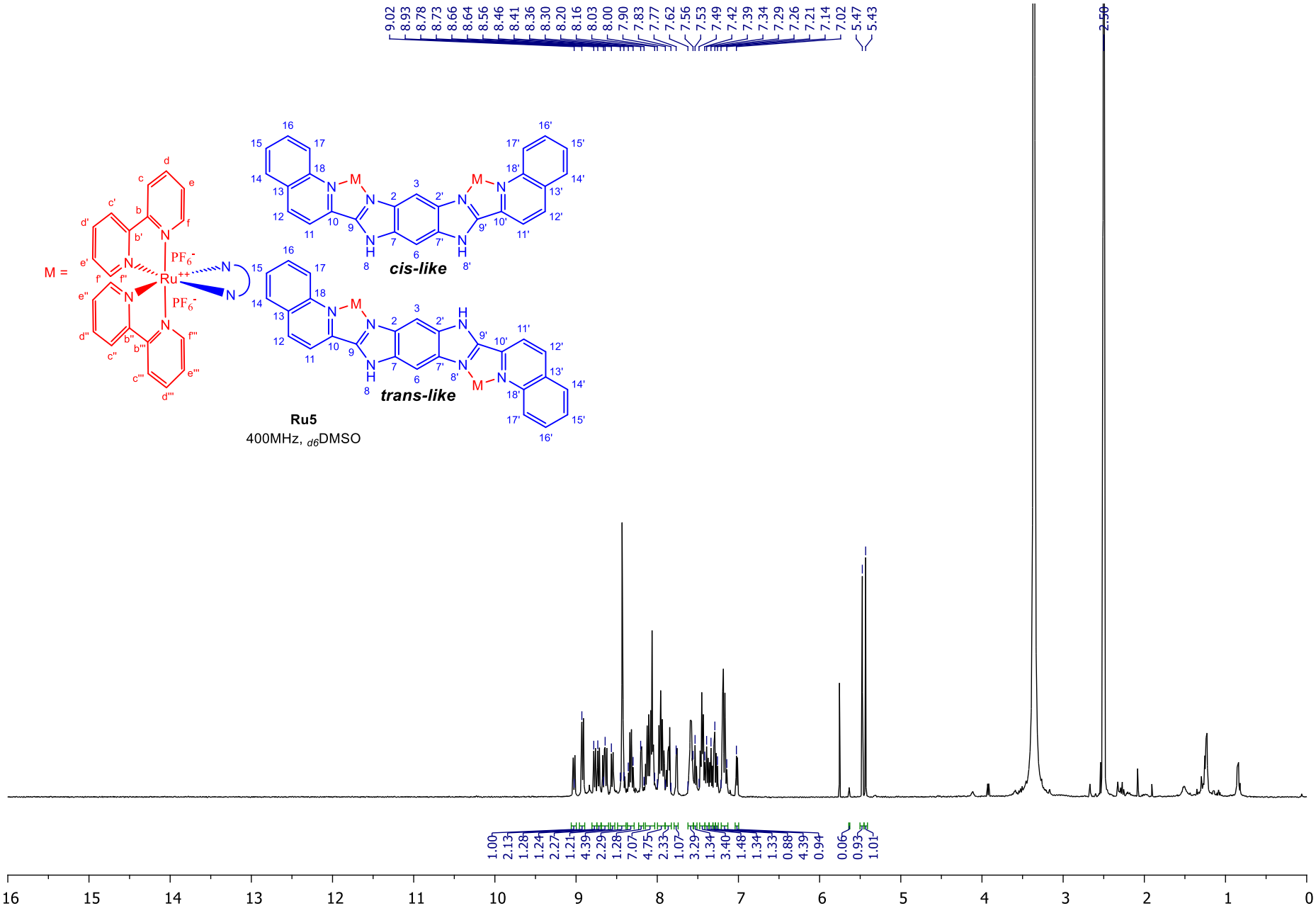


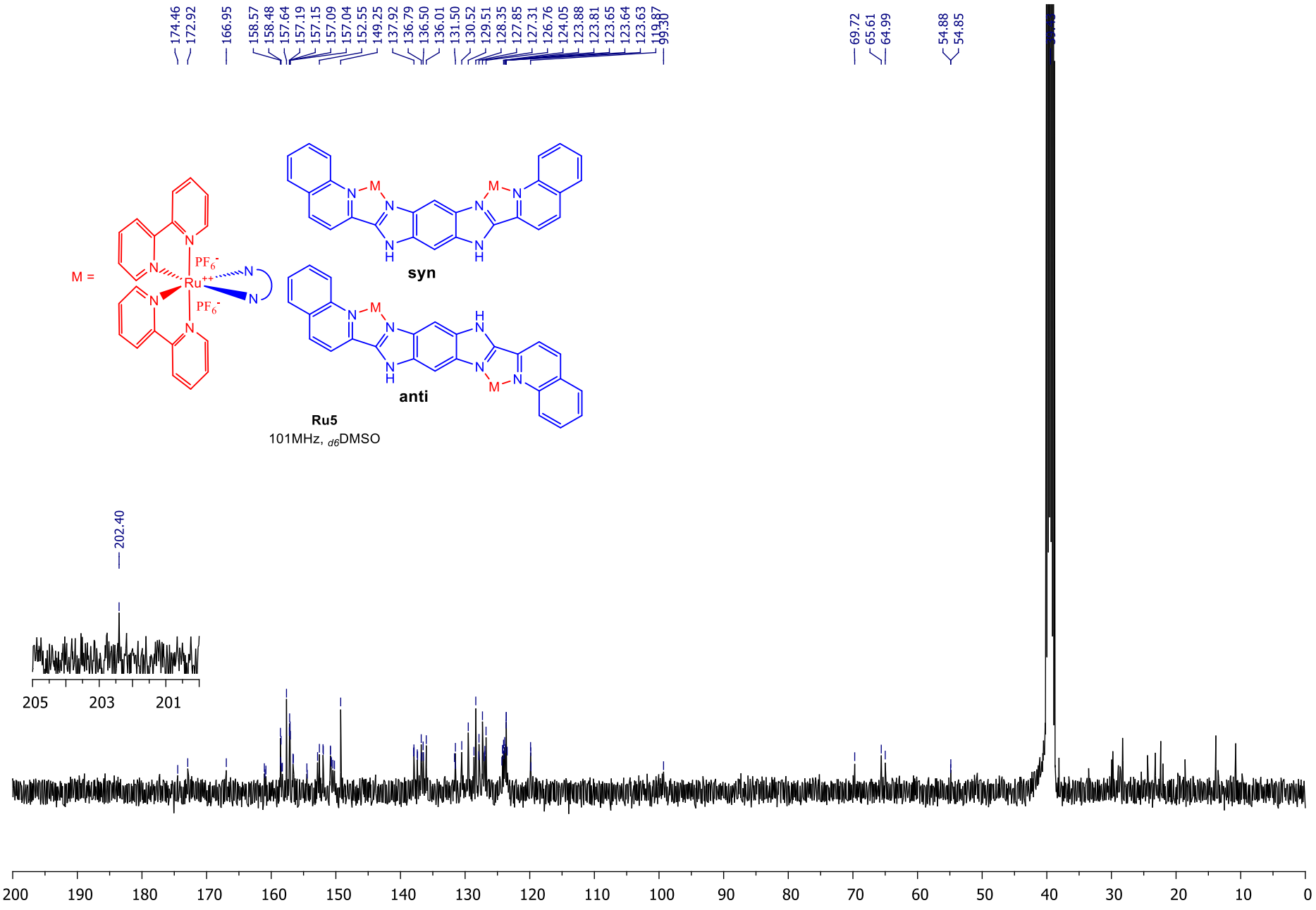
Ru3
400MHz, $_{d6}$DMSO

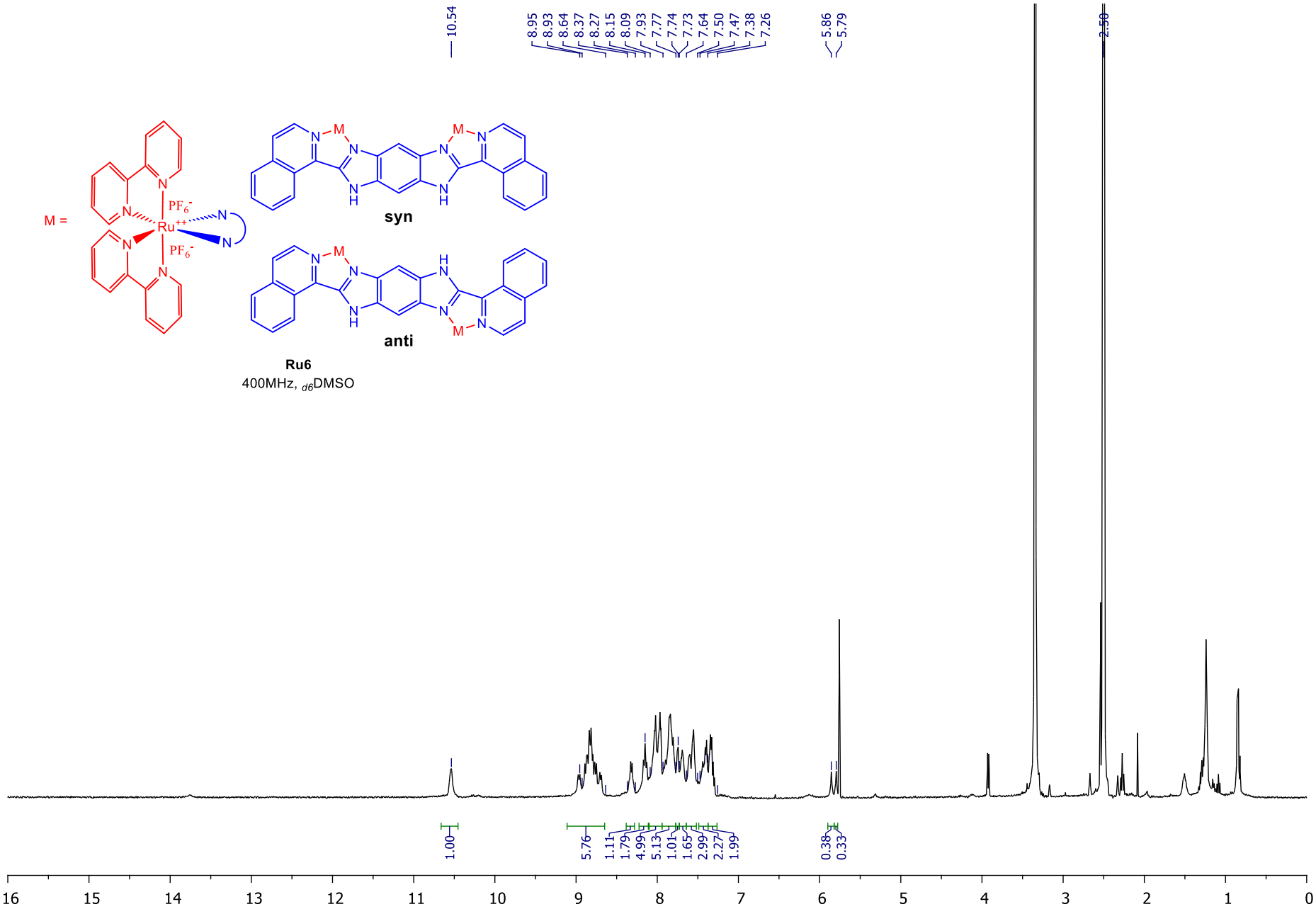

160.25
157.83
157.46
157.39
156.95
156.90
153.84
152.78
151.55
151.27
151.06
150.82
147.45
144.05
141.78
136.93
136.88
135.45
131.51
127.87
127.48
127.12
127.02
126.55
112.68
PF6-
PF6-
Ru++
NH
Ru3
101MHz, d6DMSO
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


14.55
8.91
8.89
8.77
8.70
8.52
8.41
8.34
8.30
8.23
8.17
8.06
8.02
7.97
7.82
7.78
7.74
7.63
7.59
7.53
7.48
7.45
7.40
7.34
5.89
2.50
M =
PF6-
Ru++
PF6-
cis-like
trans-like
Ru4
400MHz, d6DMSO
1.88
0.88
7.60
1.82
2.36
2.63
2.03
6.84
3.54
0.93
3.00
9.14
5.59
3.76
0.83
2.01
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1


157.76
157.68
157.42
157.40
156.73
156.67
156.56
156.55
154.04
153.99
153.94
153.90
152.44
152.37
151.99
151.85
151.71
151.58
151.55
148.33
147.05
140.20
138.52
138.15
137.75
137.73
137.39
128.14
128.05
127.95
127.93
127.80
127.69
127.64
124.70
124.53
124.36
124.22
124.08
98.12
72.29
60.27
30.71
M =
cis-like
trans-like
Ru4
101MHz, d6DMSO
208.16
206.58
201.86
210
205
200
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


9.02
8.93
8.78
8.73
8.66
8.64
8.56
8.46
8.41
8.36
8.30
8.20
8.16
8.03
8.00
7.90
7.83
7.77
7.62
7.56
7.53
7.49
7.42
7.39
7.34
7.29
7.26
7.21
7.14
7.02
5.47
5.43
2.50
M =
PF6-
Ru++
PF6-
cis-like
trans-like
Ru5
400MHz, d6DMSO
1.00
2.13
1.28
1.24
2.27
1.21
4.39
2.29
1.28
7.07
4.75
2.33
1.07
3.29
1.34
3.40
1.48
1.34
1.33
0.88
4.39
0.94
0.06
0.93
1.01
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0


174.46
172.92
166.95
158.57
158.48
157.64
157.19
157.15
157.09
157.04
152.55
149.25
137.92
136.79
136.50
136.01
131.50
130.52
129.51
128.35
127.85
127.31
126.76
124.05
123.88
123.81
123.65
123.64
123.63
119.87
99.30
69.72
65.61
64.99
54.88
54.85
202.40
M =
PF6-
Ru++
PF6-
N
N
N
N
N
N
syn
anti
Ru5
101MHz, d6DMSO
205
203
201
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


M =
PF6-
Ru++
PF6-
N
M
H
syn
anti
Ru6
400MHz, d6DMSO
10.54
8.95
8.93
8.64
8.37
8.27
8.15
8.09
7.93
7.77
7.74
7.73
7.64
7.50
7.47
7.38
7.26
5.86
5.79
2.50
1.00
5.76
1.11
1.79
4.99
5.13
1.01
1.65
2.99
2.27
1.99
0.38
0.33
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0

[i] Inorg. Chem. 1987, 26, 578-585