

Electronic Supplementary Material for

Bi-stability mediated by spirocyan ruthenium alkynyl complexes

Mark C. Walkey, Lindsay T. Byrne, Matthew J. Piggott, Paul J. Low and George A. Koutsantonis

S1.0 Synthesis

S1.1 Synthetic Route

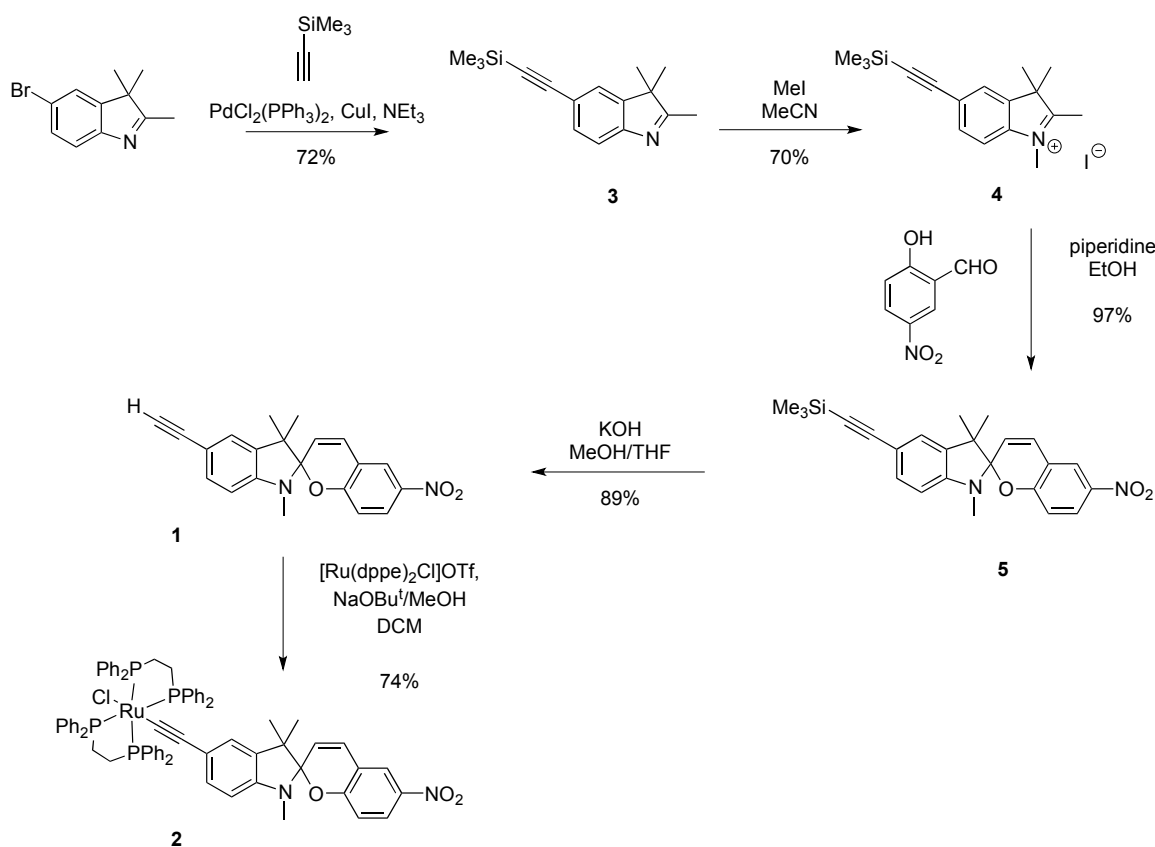
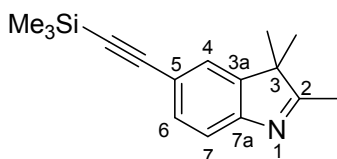


Figure 1 The synthetic route used to make the ligand **1** and the ruthenium complex **2**

S1.2 General Information

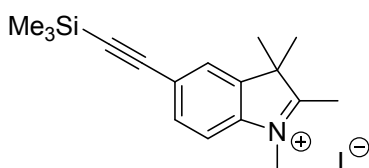
Solvents for general procedures were distilled prior to use, while anaerobic solvents used in the synthesis of **2** prepared by appropriate means¹ and stored under argon. Organic extracts were dried over MgSO_4 . Thin-layer chromatography was performed on Chem-Supply 60 F₂₅₄ silica gel plates and visualised with UV light (254 nm). Nuclear magnetic resonance spectra were acquired on a Bruker AV-600 spectrometer and referenced with respect to residual solvent signals or an external capillary of 85% H_3PO_4 for ^{31}P NMR spectra. Assignments were made with the aid of DEPT, HSQC and HMBC experiments. Infrared spectra were recorded on a PerkinElmer Spectrum One FT-IR spectrometer with an ATR attachment. Mass spectra were recorded on a Waters LCT Premier mass spectrometer using electrospray (ES) ionisation. UV-vis experiments were performed on a Cary 5000 UV-vis-NIR spectrometer and a handheld UV lamp (254 nm) was used for ring-opening of **1** and **2**. 5-Bromo-2,3,3-trimethyl-3H-indole² and $[\text{Ru}(\text{dppe})_2\text{Cl}]\text{OTf}$ ³ were

prepared according to literature procedures. Other reagents were obtained from commercial suppliers and used as received.



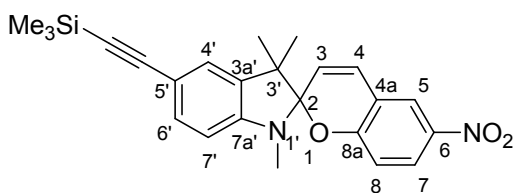
2,3,3-Trimethyl-5-((trimethylsilyl)ethynyl)-3H-indole (**3**)

A stirred mixture of 5-bromo-2,3,3-trimethyl-3H-indole (6.23 g, 27.6 mmol), Pd(PPh₃)₂Cl₂ (582 mg, 0.829 mmol, 3 mol%), CuI (158 mg, 0.831 mmol, 3 mol%) and trimethylsilylacetylene (7.90 mL, 55.5 mmol) in NEt₃ (90 mL) was heated under reflux for 2.25 h. After cooling to room temperature the reaction mixture was diluted with ether (100 mL) and washed with H₂O (2 × 100 mL) and brine (100 mL). The organic phase was dried and evaporated, leaving a red-brown, oily residue. The residue was subjected to rapid silica filtration to give **3** as a yellow oil (4.86 g, 72%). R_f (1:1 hexanes:EtOAc): 0.35; IR (ATR) ν_{max} cm⁻¹: 2154 (C≡C), 1575 (C=N), 1249 (Si-C); ¹H NMR (600 MHz, CDCl₃): δ 7.43 (d, *J* = 7.8 Hz, 1H, H7), 7.41 (dd, *J* = 7.8, 1.2 Hz, 1H, H6) 7.38 (d, *J* = 1.2 Hz, 1H, H4), 2.27 (s, 3H, C2-Me), 1.28 (s, 6H, *gem*-Me), 0.25 (s, 9H, SiMe₃); ¹³C NMR (150 MHz, CDCl₃) δ 189.6 (C2), 154.0 (C7a), 145.8 (C3a), 132.1 (C6), 125.2 (C4), 119.9 (C7), 119.8 (C5), 105.7 (SiC≡C), 93.9 (SiC≡C), 53.8 (C3), 23.1 (*gem*-Me), 15.6 (C2-CH₃), 0.14 (SiMe₃).



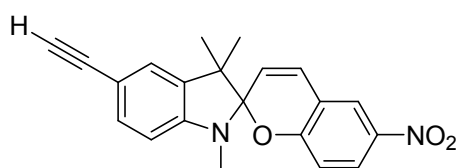
1,2,3,3-Tetramethyl-5-((trimethylsilyl)ethynyl)-3H-indolium iodide (**4**)

A black solution of **3** (4.84 g, 19.9 mmol) and MeI (2.5 mL, 40 mmol) in MeCN (30 mL) was heated under reflux for 4.5 h. The reaction mixture was cooled to room temperature and the solvent was evaporated. The residue was suspended in EtOAc (30 mL) and the solid was collected by vacuum filtration, washed with EtOAc and Et₂O and air dried to give **4** as a dark grey solid (5.35 g, 70%). IR (ATR) ν_{max} (cm⁻¹): 2159 (C≡C), 1592 (C=N), 1245 (C-Si); ¹H NMR (600 MHz, CDCl₃): δ 7.65 (dd, *J* = 8.4, 1.2 Hz, 1H, H6), 7.61 (d, *J* = 8.4 Hz, 1H, H7), 7.59 (m, 1H, H4), 4.26 (s, 3H, NCH₃), 3.12 (s, 3H, C2-Me), 1.66 (s, 6H, *gem*-Me), 0.27 (s, 9H, SiMe₃); ¹³C NMR (150 MHz, CDCl₃): δ 196.8 (C2), 141.5, 141.4, 133.4 (C6), 126.8 (C4), 125.8 (C5), 115.3 (C7), 102.9 (SiC≡C), 98.9 (SiC≡C), 54.8 (C3), 37.6 (N-Me), 23.3 (*gem*-Me), 17.6 (C2-CH₃), -0.1 (SiMe₃); HRMS (ES+) calcd for C₁₇H₂₄NSi⁺: 270.1678, found 270.1679.



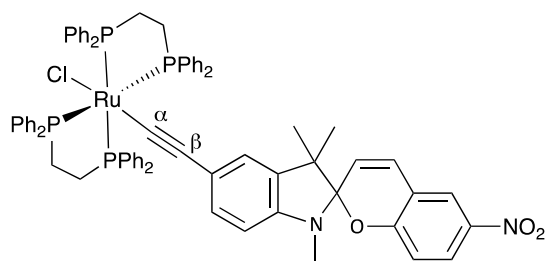
1',3',3'-Trimethyl-6-nitro-5'-((trimethylsilyl)ethynyl)spiro[chromene-2,2'-indoline] (**5**)

A stirred solution of 5-nitrosalicylaldehyde (407 mg, 2.43 mmol), **4** (888 mg, 2.31 mmol) and piperidine (456 mg, 5.36 mmol) in EtOH (50 mL) was heated under reflux under Ar for 1.75 h. The solvent was evaporated and the residue was redissolved in DCM (50 mL). The solution was washed with Na₂CO₃ (50 mL), water (50 mL) and brine (50 mL), dried and evaporated. An attempt to recrystallize the product from DCM/hexanes led to the precipitation of a brown solid, which was filtered off. The mother liquors were evaporated to give **5** as a yellow-brown solid (931 mg, 2.23 mmol, 97%). R_f (20% EtOAc/hexanes): 0.7; IR (ATR) ν_{\max} (cm⁻¹): 2147 (C≡C); ¹H NMR (600 MHz, CDCl₃): δ 8.02 (dd, *J* = 8.7, 2.7 Hz, 1H, H7), 8.00 (d, *J* = 2.4 Hz, 1H, H5), 7.35 (dd, *J* = 8.1, 1.5 Hz, 1H, H6'), 7.18 (d, *J* = 1.6 Hz, 1H, H4'), 6.93 (d, *J* = 10.2 Hz, 1H, H4), 6.74 (d, *J* = 9.0 Hz, 1H, H8), 6.46 (d, *J* = 7.8 Hz, 1H, H7'), 5.83 (d, *J* = 10.2 Hz, 1H, H3), 2.74 (s, 3H, N-Me), 1.27 (s, 3H, *gem*-Me_a), 1.16 (s, 3H, *gem*-Me_b), 0.24 (s, 9H, SiMe₃); ¹³C NMR (150 MHz, CDCl₃): δ 159.6 (C8a), 148.1 (C7a'), 141.3 (C6), 136.3 (C3a'), 132.7 (C6'), 128.6 (C4), 126.1 (C7), 125.6 (C4'), 122.9 (C5), 121.3 (C3), 118.7 (C4a), 115.6 (C8), 114.0 (C5'), 106.9 (C7'), 106.4 (SiC≡C), 106.3 (C2), 91.7 (SiC≡C), 52.2 (C3'), 28.9 (N-Me), 25.8 (*gem*-Me_a), 20.0 (*gem*-Me_b), 0.30 (SiMe₃); HRMS (ES+) calcd for C₂₄H₂₇N₂O₃Si⁺ [M + H]⁺ 419.1791, found 419.1778.



5'-Ethynyl-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] (**1**)

A solution of KOH (121 mg, 2.16 mmol) in MeOH (10 mL) was added to a stirred solution of **5** (628 mg, 1.50 mmol) in THF (20 mL). The combined solution was stirred for 1 h under Ar in the dark. The solvent was evaporated and the residue was dissolved in DCM (20 mL). The solution was washed with water (2 × 20 mL). The yellow aqueous washes were then back-extracted with CHCl₃ (2 × 20 mL). The combined organic phase was washed with brine (50 mL), dried and evaporated giving **1** as a yellow-brown powder (464 mg, 89%). δ 8.03 (dd, *J* = 8.7, 2.7 Hz, 1H, H7), 8.01 (d, *J* = 3.0 Hz, 1H, H5), 7.37 (dd, *J* = 8.4, 1.8 Hz, 1H, H6'), 7.20 (d, *J* = 1.8 Hz, 1H, H4'), 6.94 (d, *J* = 10.2 Hz, 1H, H4), 6.77 (d, *J* = 8.4 Hz, 1H, H8), 6.48 (d, *J* = 7.8 Hz, 1H, H7'), 5.83 (d, *J* = 10.2 Hz, 1H, H3), 3.00 (s, 1H, HC≡C), 2.75 (s, 3H, N-Me), 1.28 (s, 3H, *gem*-Me_a), 1.18 (s, 3H, *gem*-Me_b); IR (ATR) ν_{\max} (cm⁻¹): 3257 (HC≡) 2096 (C≡C); ¹³C NMR (150 MHz, CDCl₃): δ 159.6 (C8a), 148.3 (C7a'), 141.3 (C6), 136.5 (C3a'), 132.8 (C6'), 128.7 (C4), 126.1 (C7), 125.7 (C4'), 122.9 (C5), 121.2 (C3), 118.6 (C4a), 115.6 (C8), 112.8 (C5'), 106.9 (C7'), 106.2 (C2), 84.8 (HC≡C), 75.2 (HC≡C), 52.2 (C3'), 28.9 (N-Me), 25.9 (*gem*-Me_a), 20.0 (*gem*-Me_b). The ¹H NMR data agree with those previously reported.⁴



trans-((1',3',3'-Trimethyl-6-nitrospiro[chromene-2,2'-indolin]-5'-yl)ethynyl) ruthenium(II)(dppe)₂chloride (**2**)

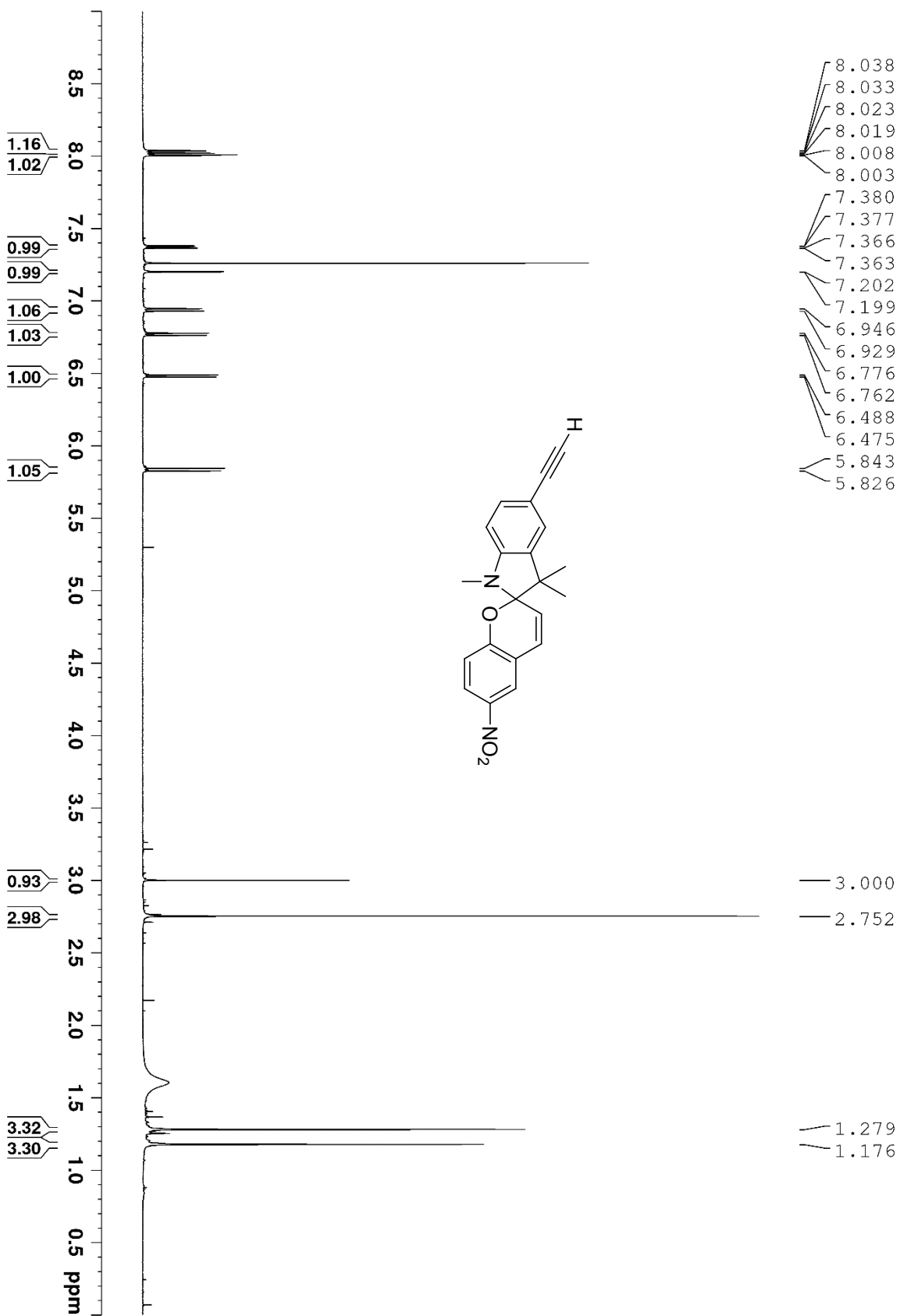
A dark red solution of [Ru(dppe)₂Cl]OTf (217 mg, 0.200 mmol) and **1** (69 mg, 0.20 mmol) in DCM (5 mL) was stirred for 2 h under Schlenk conditions. A saturated solution of NaOBu^t in dry MeOH (5 mL added via cannula, resulting in a dark green/yellow solution. Most of the solvent was evaporated to give a

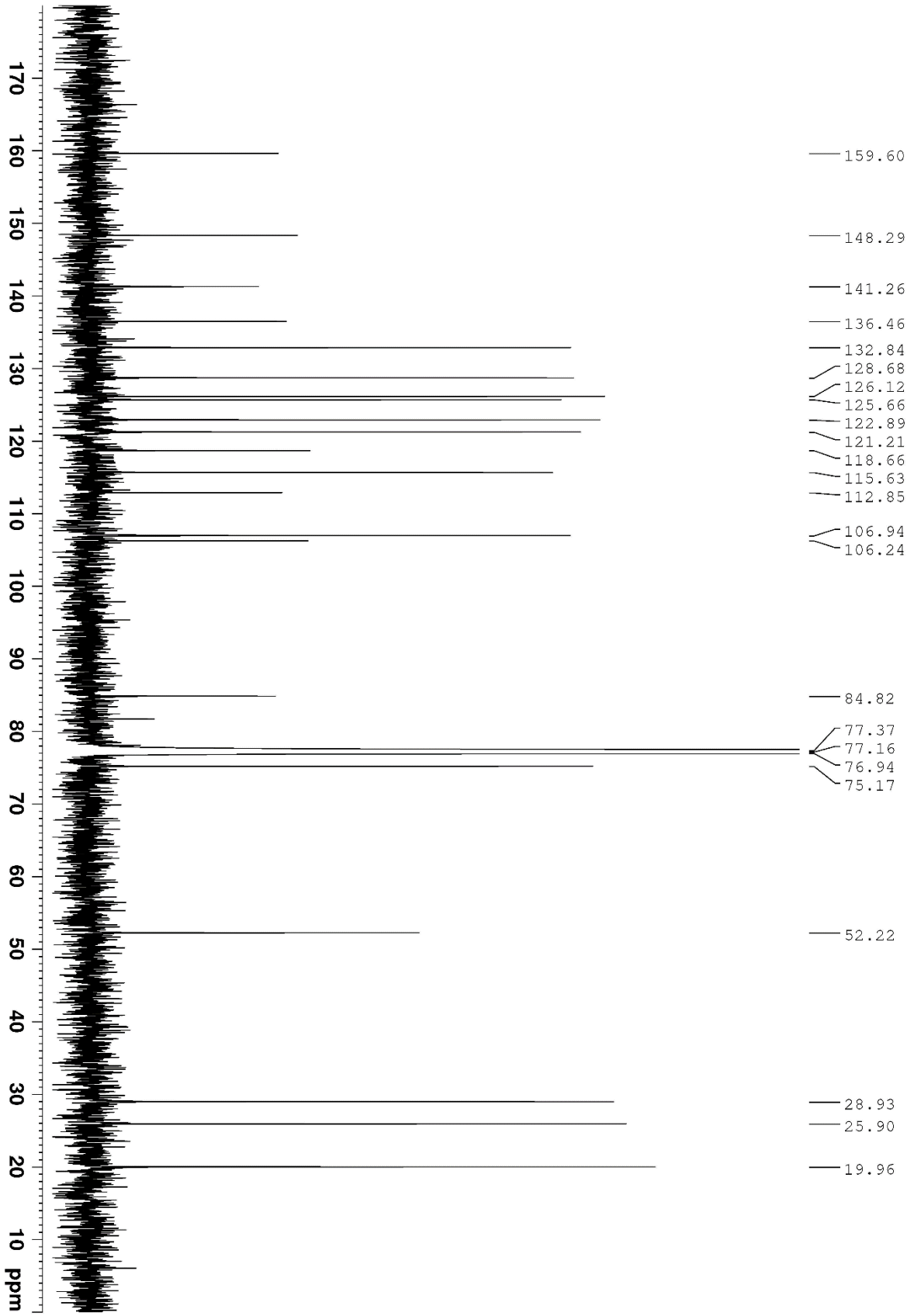
suspension. The precipitate was collected by vacuum filtration and air-dried to give **2** as a dark green powder (190 mg, 74%*). IR (ATR) ν_{\max} (cm^{-1}): 2041 ($\text{C}\equiv\text{C}$); ^1H NMR (600 MHz, C_6D_6) δ 7.74 (br m, 8H, *o*-Ph), 7.72 (d, $J = 3$ Hz, 1H, H5), 7.66 (br m, 8H, *o*-Ph'), 7.64 (dd, $J = 9, 3$ Hz, 1H, H7), 7.53 (dd, $J = 7.8, 1.2$ Hz, 1H, H6'), 7.33 (d, $J = 1.2$ Hz, 1H, H4'), 7.09 (m, 4H, *p*-Ph), 7.04 (m, 8H, *m*-Ph), 6.95 (m, 12H, *m*-Ph' + *p*-Ph'), 6.63 (d, $J = 7.8$ Hz, 1H, H7'), 6.27 (d, $J = 9$ Hz, 1H, H8), 6.18 (d, $J = 10.2$ Hz, 1H, H4), 5.48 (d, $J = 10.2$ Hz, 1H, H3), 2.60 (s, 3H, N-CH₃), 2.49 (br m, 4H, PCH₂), 1.96 (br m, 4H, P'CH₂), 1.55 (s, 3H, *gem*-CH_{3a}), 1.31 (s, 3H, *gem*-CH_{3b}); ^{13}C NMR (150 MHz, C_6D_6) δ 159.9 (C8a), 144.1 (C7a'), 141.5 (C6), 139.9 (*ipso*-Ph'), 138.9 (*ipso*-Ph), 135.9 (C3a'), 134.7 (*o*-Ph), 134.2 (*o*-Ph'), 129.7 (C6'), 128.8 (*p*-Ph'), 128.5 (*p*-Ph), 128.4 (C4), 127.4 (*m*-Ph'), 127.3 (*m*-Ph), 127.0 (quint, $J = 12.4$ Hz, Ru-C \equiv C), 126.0 (C7), 125.3 (C5'), 124.5 (C4'), 122.9 (C5), 121.5 (C3), 118.9 (C4a), 116.3 (Ru-C \equiv C), 115.4 (C8), 107.5 (C7'), 106.9 (C2), 52.6 (C3'), 33.2 (m, PCH₂CH₂P), 29.1 (N-CH₃), 26.4 (*gem*-CH_{3a}), 20.8 (*gem*-CH_{3b}); ^{31}P NMR (121.5 MHz, C_6D_6) δ 69.4. HRMS (ES+) calcd for $\text{C}_{73}\text{H}_{65}\text{N}_2\text{O}_3\text{P}_4^{102}\text{Ru}^+ [\text{M} - \text{Cl}]^+$ 1243.2989, found 1243.2994. Anal. * Calcd for $\text{C}_{73}\text{H}_{65}\text{N}_2\text{O}_3\text{P}_4\text{ClRu}$: C, 68.57; H, 5.12; N, 2.19. Found: C, 66.54; H, 5.59; N, 2.17.

*The sample was found to contain an impurity, predominantly dppeO₂ and identified in the spectra below. Chromatographic and other attempts to further purify the material were unsuccessful.

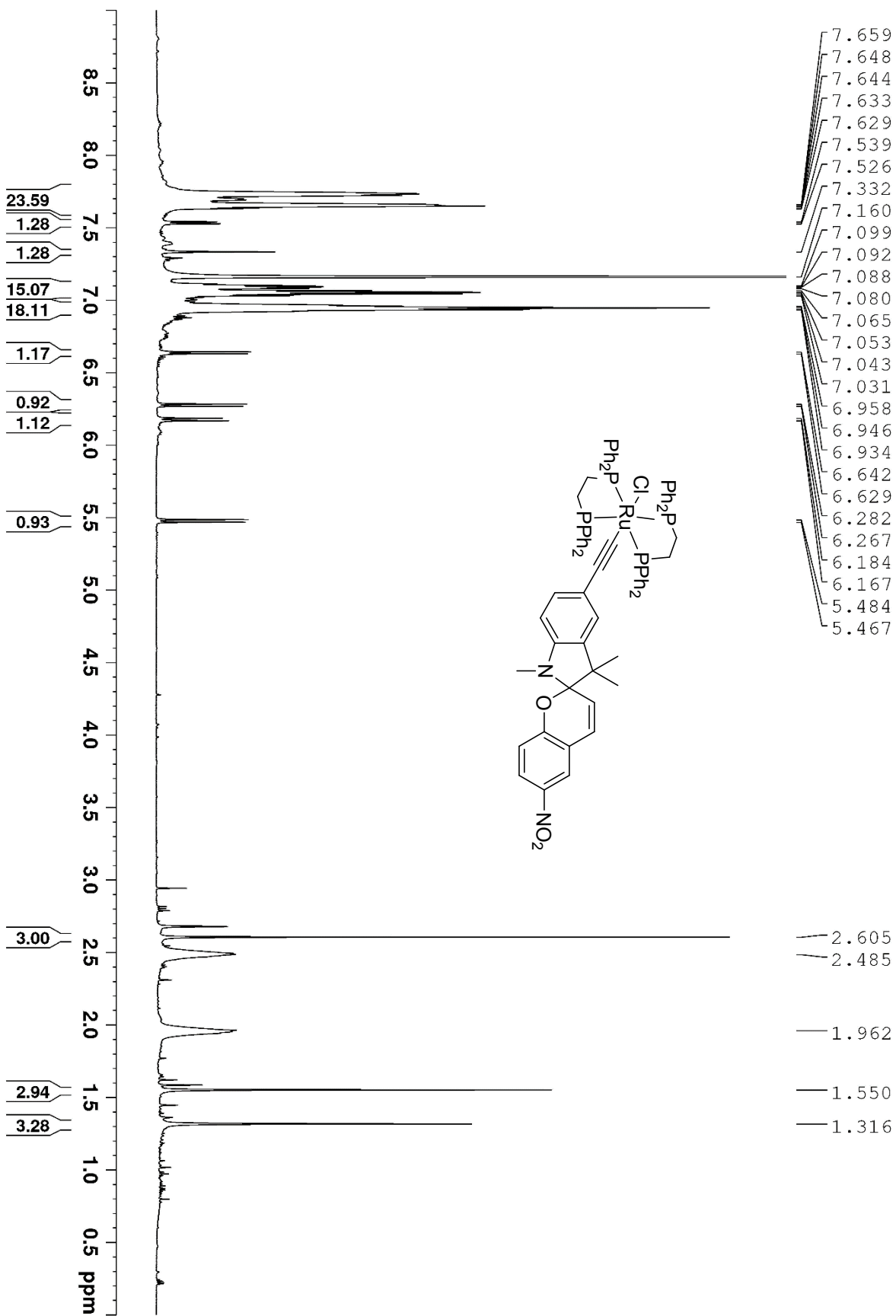
S2.0 Spectra

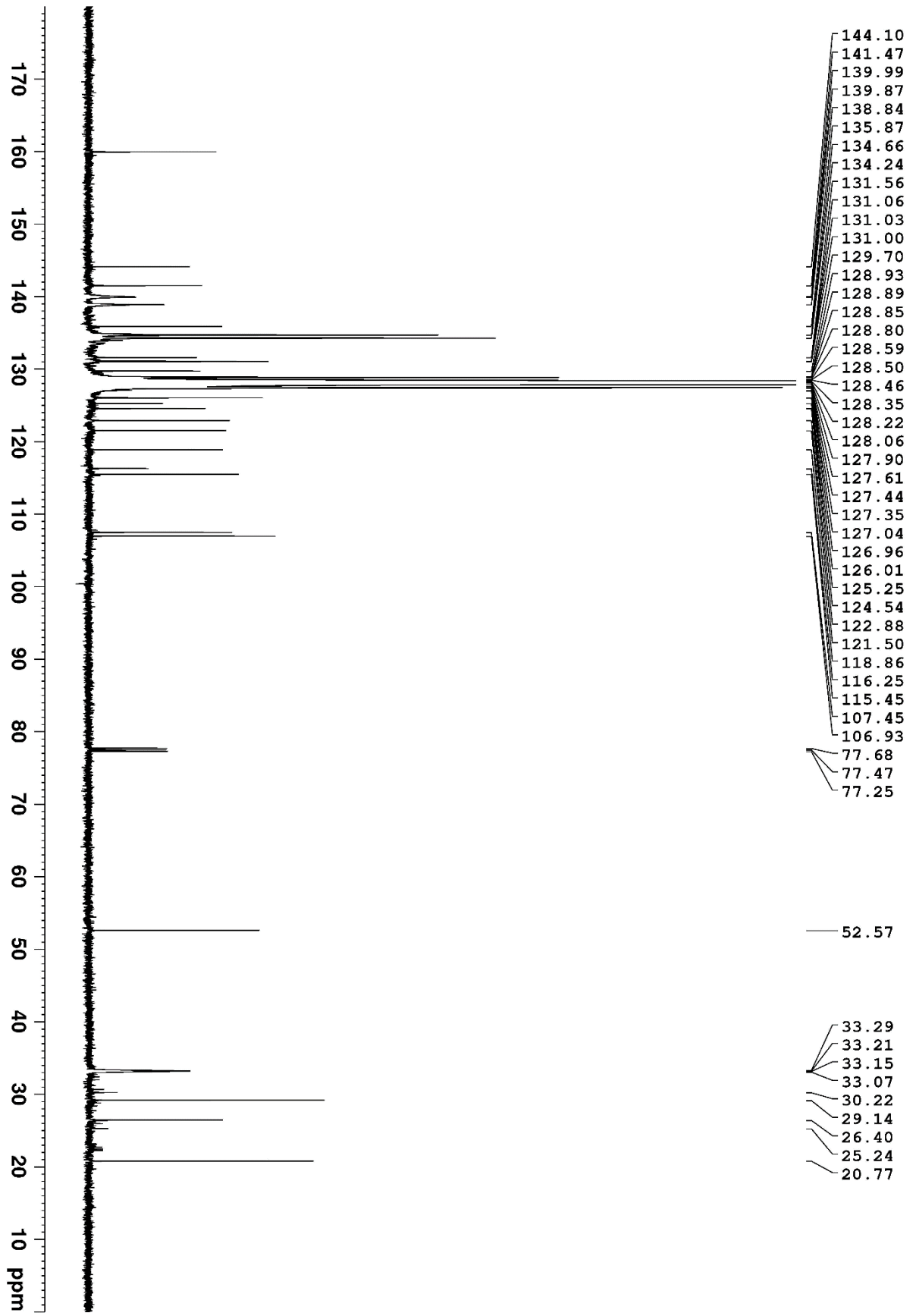
S2.1 ^1H and ^{13}C NMR spectra of 1

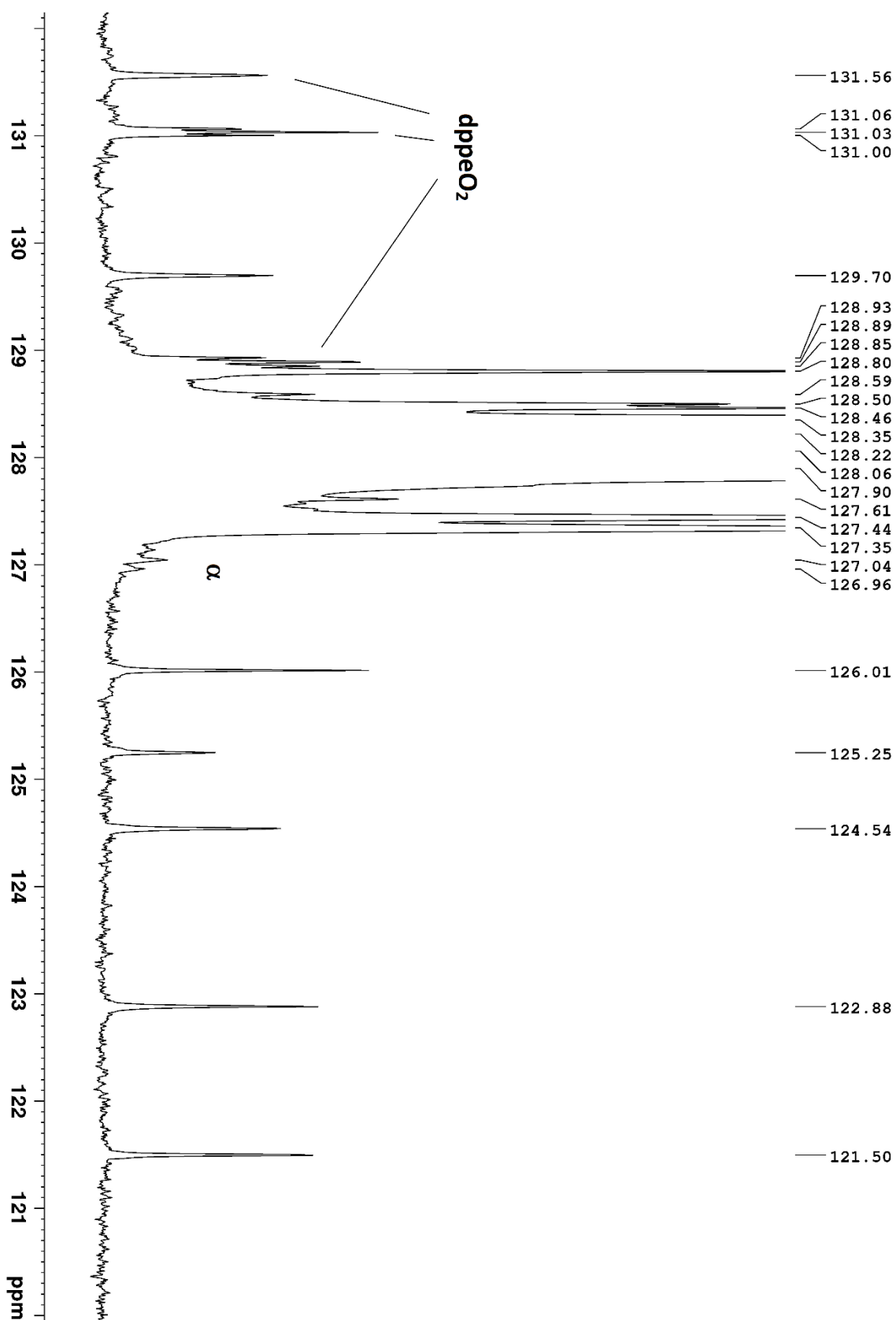


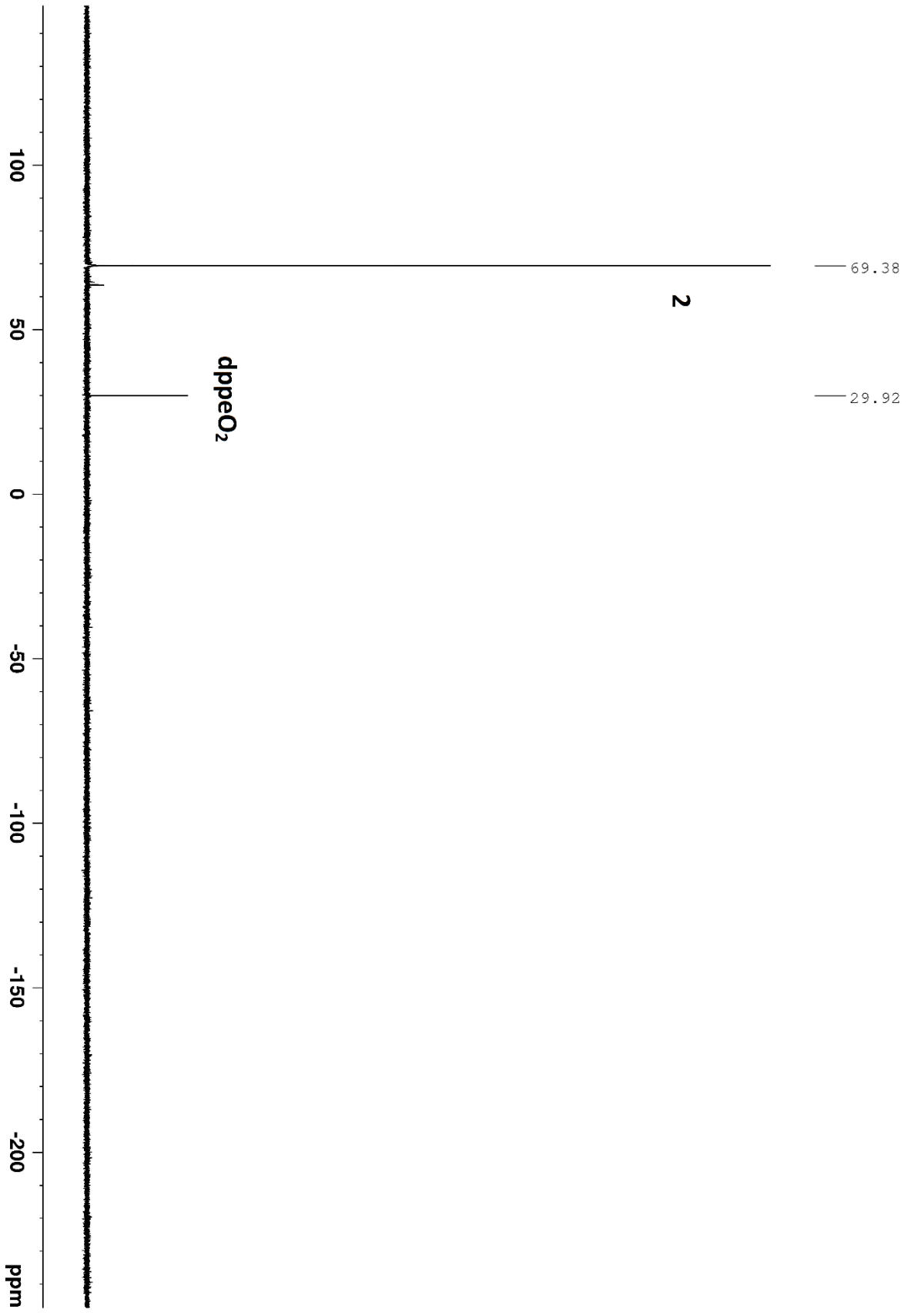


S2.2 ¹H, ¹³C and ³¹P NMR spectra of 2









S3.0 UV-Vis Experiments

S3.1 UV-Vis experiments on ligand 5'-ethynyl-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] (**1**)

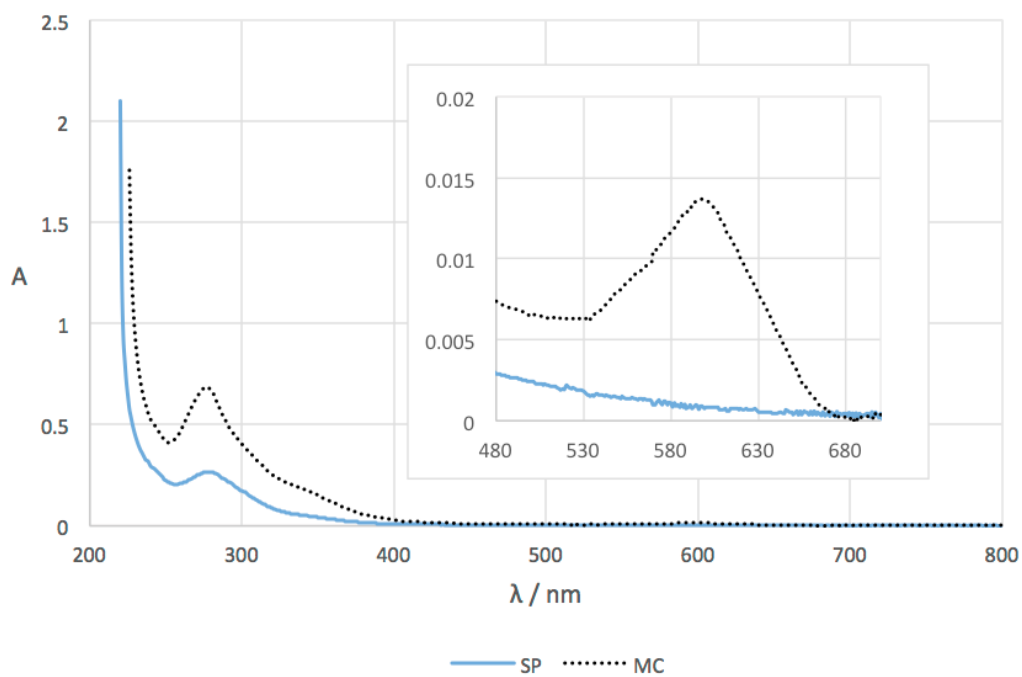


Figure S2 Absorption spectra of **1** in THF at 20°C. SP: solution under ambient conditions. MC: after irradiation with 254 nm light for 5 minutes.

S3.1 UV-Vis experiments on *trans*-((1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indolin]-5'-yl)ethynyl)ruthenium(II)(dppe)₂chloride (**2**)

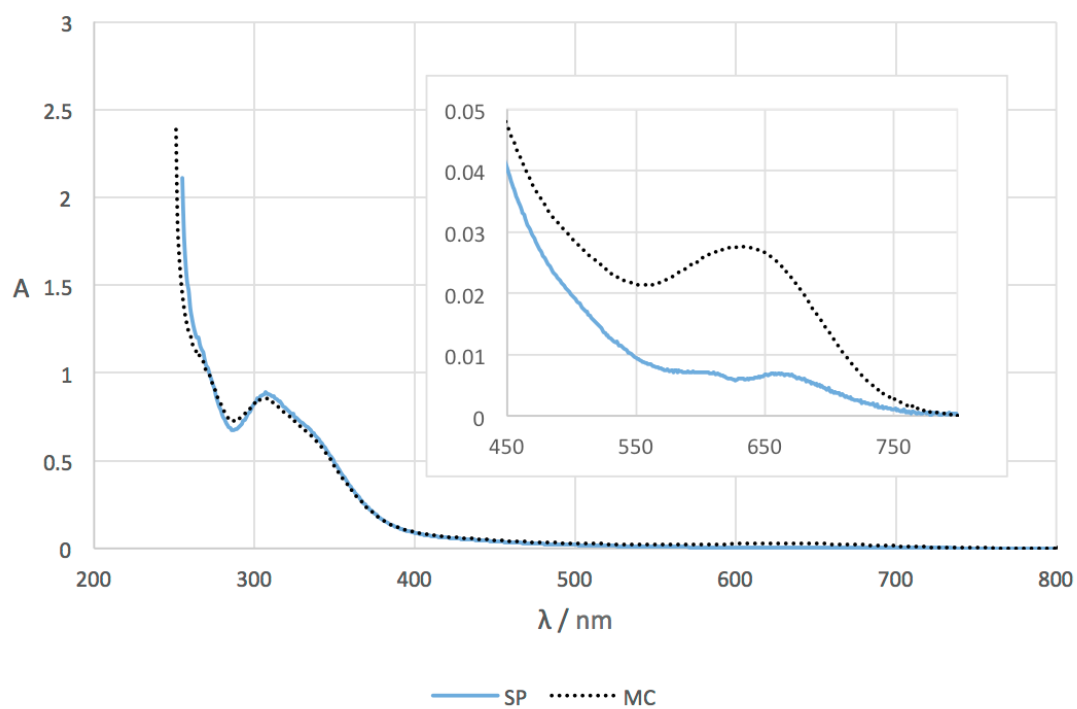


Figure S3 Absorption spectra of **2** in THF at 20°C. SP: solution under ambient conditions. MC: after irradiation with 254 nm light for 5 minutes.

S4.0 Theoretical Calculations

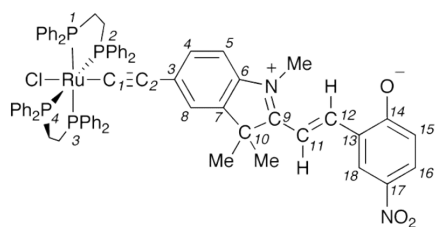
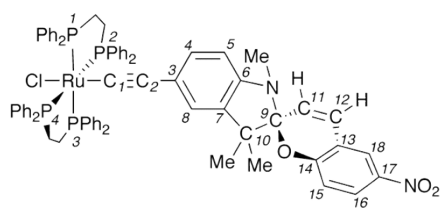


Figure S4. The atom labelling schemes used in the computational work

Table S1. Selected bond lengths (Å) and angles(°) for *trans*-RuCl(C≡CSPNO₂)(dppe)₂ and *trans*-RuCl(C≡CMCNO₂)(dppe)₂

	HC≡CSPNO ₂	<i>trans</i> -RuCl(C≡CSPNO ₂)(dppe) ₂ closed	HC≡CMCNO ₂	<i>trans</i> -RuCl(C≡CMCNO ₂)(dppe) ₂ open
Ru-Cl		2.578		2.570
Ru-P1		2.399		2.380
Ru-P2		2.425		2.425
Ru-P3		2.397		2.404
Ru-P4		2.409		2.419
Ru-C1		2.011		2.003
C1-C2	1.211	1.232	1.209	1.233
C2-C3	1.428	1.426	1.428	1.420
C3-C4	1.408	1.411	1.410	1.415
C4-C5	1.398	1.400	1.396	1.396
C5-C6	1.395	1.391	1.391	1.391
C6-C7	1.411	1.405	1.402	1.401
C7-C8	1.377	1.379	1.381	1.379
C3-C8	1.420	1.423	1.415	1.421
C6-N	1.398	1.412	1.424	1.426
N-C9	1.455	1.450	1.360	1.367
C9-C10	1.586	1.586	1.543	1.546
C7-C10	1.527	1.528	1.519	1.521
C9-C11	1.499	1.500	1.394	1.386
C11-C12	1.340	1.340	1.388	1.397
C12-C13	1.456	1.453	1.408	1.397
C13-C14	1.413	1.413	1.488	1.493
C14-C15	1.404	1.404	1.461	1.463
C15-C16	1.384	1.384	1.357	1.356
C16-C17	1.398	1.396	1.428	1.431
C17-C18	1.391	1.389	1.376	1.369
C18-C13	1.392	1.392	1.407	1.412
C14-O	1.365	1.365	1.261	1.258
C17-N	1.446	1.451	1.430	1.441
C9-O	1.522	1.526		
Cl-Ru-C1		175.08		175.62
Ru-C1-C2		176.80		176.62
C1-C2-C3		175.20		175.25
P1-Ru-P2		82.96		82.88
P2-Ru-P3		98.22		98.31
P3-Ru-P4		82.13		82.22
P4-Ru-P1		96.67		96.59

Table S2. Frontier orbital energies (eV) and composition (%).

RuCCSPNO2														
MO		eV	Cl	dppe-1	dppe-2	Ru	C1C2	C6H3	N	Me	C9	CMe2	CH=CH	C6H3ONO2
	332	LUMO	-2.59	0	0	0	0	0	0	0	0	0	0	100
	331	HOMO	-4.65	2	2	25	28	29	9	1	0	0	0	1

HCCSPNO2														
MO		eV				H	C1C2	C6H3	N	Me	C9	CMe2	CH=CH	C6H3ONO2
	92	LUMO	-2.63			0	0	0	0	0	0	0	0	100
	91	HOMO	-5.55			0	14	49	27	4	1	1	1	4

RuCCMCNO2														
MO		eV	Cl	dppe-1	dppe-2	Ru	C1C2	C6H3	N	Me	C9	CMe2	CH=CH	C6H3ONO2
	332	LUMO	-2.77	0	0	0	1	5	7	1	15	2	24	43
	331	HOMO	-4.94	4	2	29	25	20	3	0	0	0	4	11

HCCMCNO2														
MO		eV				H	C1C2	C6H3	N	Me	C9	CMe2	CH=CH	C6H3ONO2
	92	LUMO	-2.92			0	1	7	7	1	17	3	24	40
	91	HOMO	-5.52			0	2	9	8	1	2	1	11	66

Table S3 Mulliken charges of selected atoms

	HC≡CSPNO ₂	<i>trans</i> - RuCl(C≡CSPNO ₂)(dppe) ₂	HC≡CMCNO ₂	<i>trans</i> - RuCl(C≡CMCNO ₂)(dppe) ₂
Ru		0.664288		0.779694
Cl		-0.448428		-0.515449
C1	-0.376443	-0.209644	-0.353014	-0.207211
C2	0.085270	-0.324956	0.093052	-0.296144
C3	-0.126516	-0.081955	-0.116088	-0.101289
C6	0.400181	0.388143	0.389289	0.361784
N-Me	-0.703329	-0.717607	-0.830158	-0.705063
C9	0.364140	0.381015	0.507465	0.369264
C11	-0.192474	-0.178796	-0.234078	-0.271496
C12	-0.134820	-0.135047	-0.136600	-0.138190
C13	-0.053479	-0.043495	-0.092439	-0.043123
C14	0.364615	0.348579	0.366939	0.233393
O	-0.567439	-0.576747	-0.566301	-0.520332

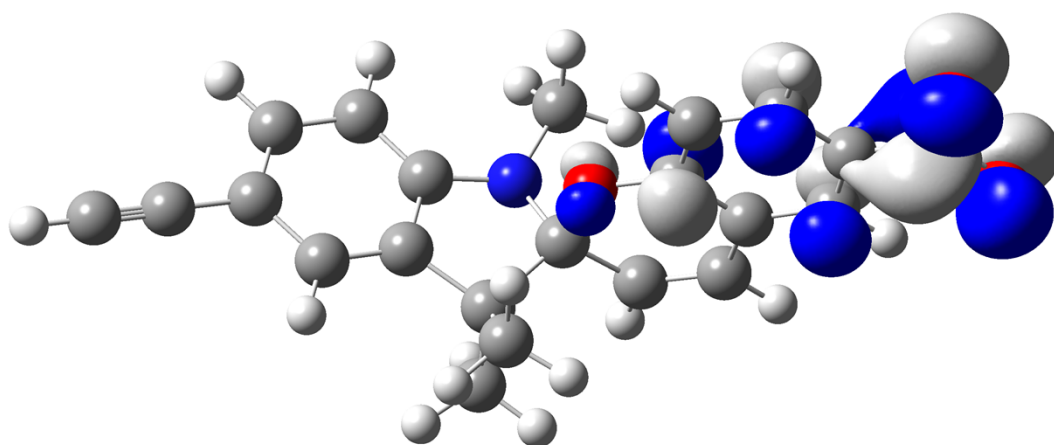


Figure S5 LUMO HCCSPNO₂ (plotted with contour values ± 0.04 (e/bohr³)^{1/2})

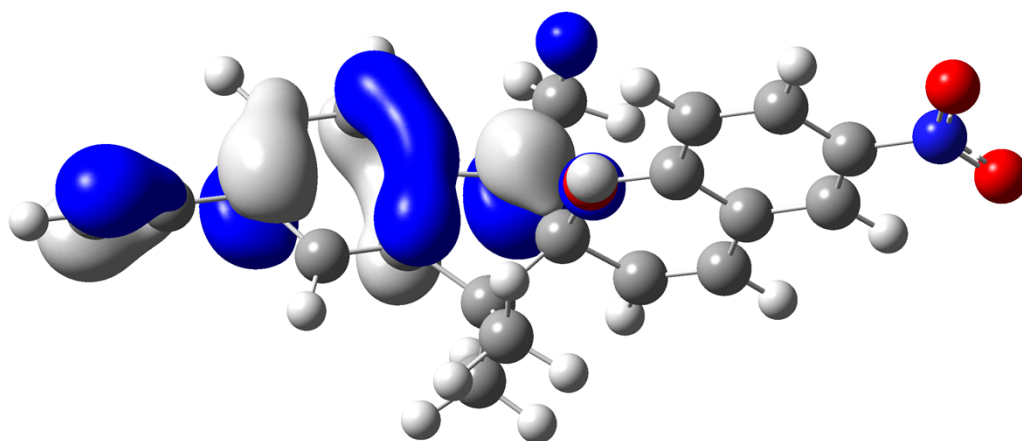


Figure S6 HOMO HCCSPNO₂ (plotted with contour values ± 0.04 (e/bohr³)^{1/2})

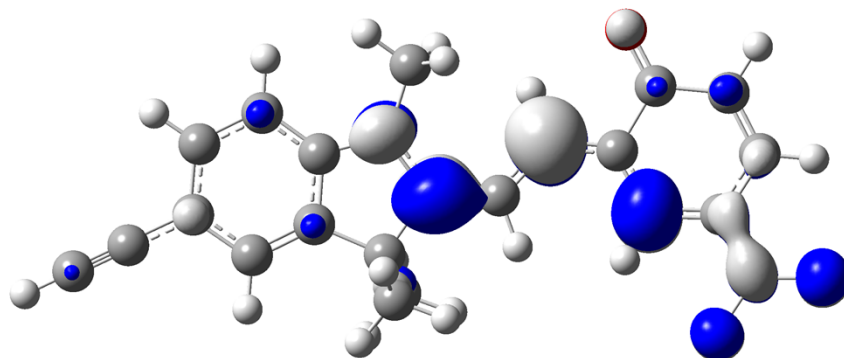


Figure S7 LUMO HCCMCNO₂ (plotted with contour values ± 0.04 (e/bohr³)^{1/2})

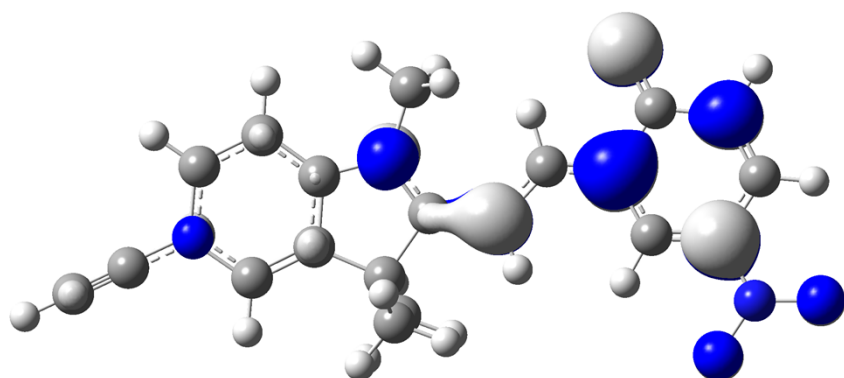


Figure S8 HOMO HCCMCNO₂ (plotted with contour values ± 0.04 (e/bohr³)^{1/2})

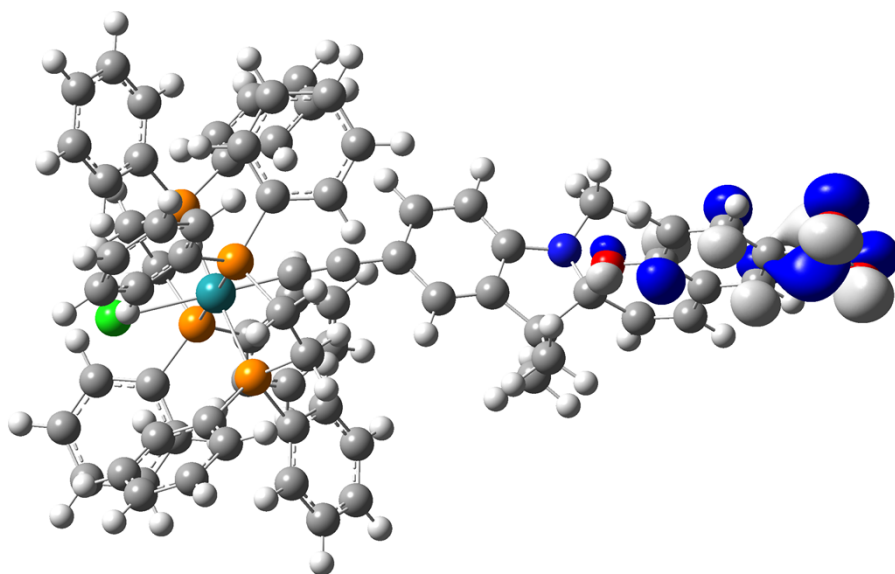


Figure S9 LUMO RuCCSPNO₂ (plotted with contour values ± 0.04 (e/bohr³)^{1/2})

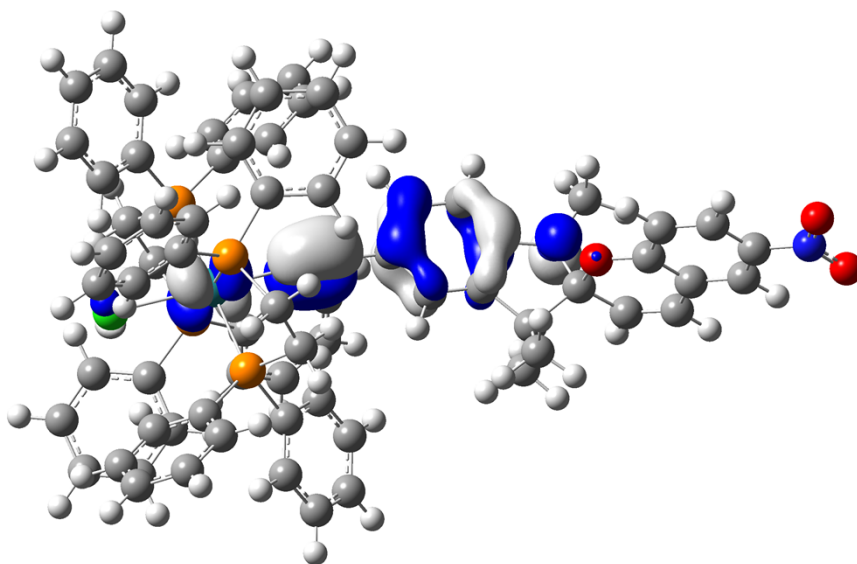


Figure S10 HOMO RuCCSPNO₂ (plotted with contour values ± 0.04 (e/bohr³)^{1/2})

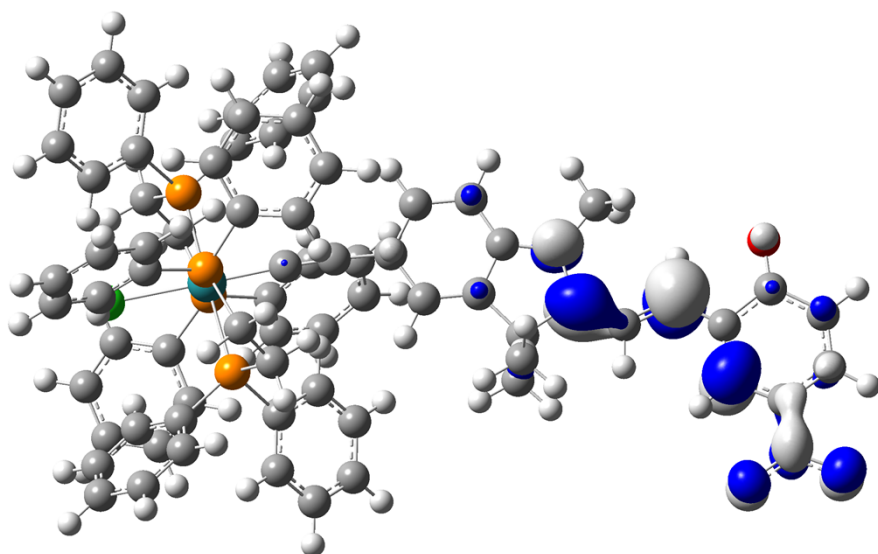


Figure S11 LUMO RuCCMCNO₂ (plotted with contour values ± 0.04 (e/bohr³)^{1/2})

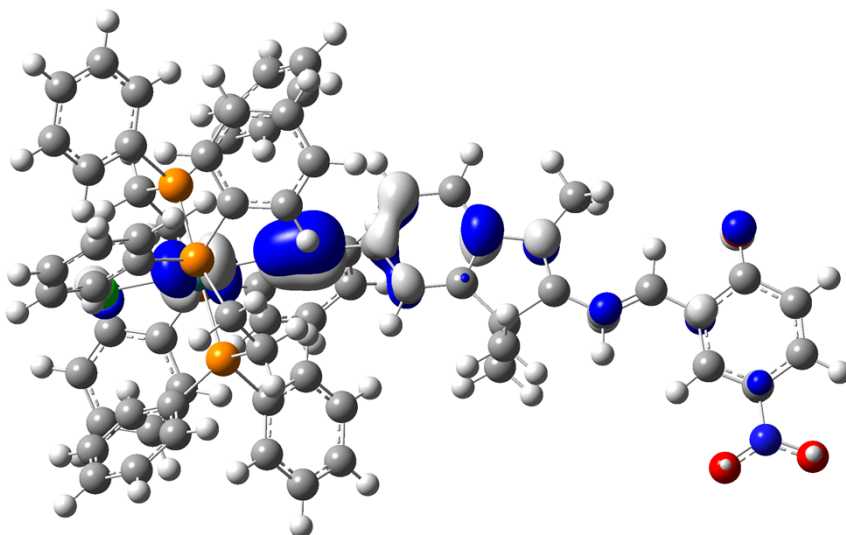


Figure S12 HOMO RuCCMCNO₂ (plotted with contour values ± 0.04 (e/bohr³)^{1/2})

References

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