Supporting Information

Notable Differences between Oxidized Diruthenium Complexes Bridged by Four Isomeric Diethynyl Benzodithiophene Ligands

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1. Crystallographic Information

Table S1. Crystal Data and Data Collection and Refinement Parameters for Complexes **1 - 3**.

Complexes	3(**1**), $4CH_2Cl_2$, $2(PhCH_3)$	**2**	4(**3**), CH_2Cl_2
Formula	$C_{276}H_{270}Cl_8P_{12}Ru_6S_6$	$C_{86}H_{82}P_4Ru_2S_2$	$C_{345}H_{328}Cl_2P_{16}Ru_8S_8$
FW	5041.01	1505.68	6105.53
Temperature	296(2) K	293(2) K	296(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Cryst. Syst.	Triclinic	Monoclinic	Monoclinic
Space group	*P*-1	$P2_1/m$	$P2/m$
a(Å)	13.848(3)	16.936(3)	16.6322(16)
b(Å)	16.508(3)	11.920(2)	24.054(2)
c(Å)	28.270(6)	20.375(4)	38.040(4)
α(°)	87.931(4)	90	90
β(°)	77.753(4)	111.59(3)	96.785(2)
γ(°)	76.060(3)	90	90
V (Å^3)	6129(2)	3824.6(13)	15112(3)
Z	1	2	2
D_{calc} (mg m^{-3})	1.366	1.307	1.342
Abs. coeff. (mm^{-1})	0.632	0.576	0.602
F(000)	2602	1556	6304
Crystal size (mm^3)	0.23 × 0.20 × 0.02	0.16 × 0.12 × 0.10	0.16 × 0.12× 0.10
θ Range (°)	1.46 to 25.50	1.34 to 22.66	1.00 to 25.50
Index ranges	$-16\le h\le 16$, $-19\le k\le 19$, $-34\le l\le 34$	$-18\le h\le 12$, $-12\le k\le 12$, $-21\le l\le 22$	$-19\le h\le 20$, $-29\le k\le 29$, $-46\le l\le 46$
Reflections collected	40240	16203	109441
Independent reflect.	22489 [*R*(int) = 0.0541]	5030 [*R*(int) = 0.0466]	28003 [*R*(int) = 0.0519]
Data / restr. / param.	22489 / 59 / 1409	5030 / 29 / 451	28003 / 55 / 1755
Goodness-of-fit on F^2	1.010	1.070	1.054
Final *R* indices [$I>2\sigma(I)$]	*R*1 = 0.0741, w*R*2 = 0.2044	*R*1 = 0.0494, w*R*2 = 0.1417	*R*1 = 0.0502, w*R*2 = 0.1298
R indices (all data)	*R*1 = 0.1144, w*R*2 = 0.2413	*R*1 = 0.0696, w*R*2 = 0.1571	*R*1 = 0.0851, w*R*2 = 0.1457

Diff. peak and hole ($e.Å^{-3}$)	1.408 and -0.863	0.501 and -0.357	1.105 and -0.536

Table S2. Selected Bond Lengths (Å) and Angles (deg) in the Crystal Structure of **2** and the DFT-Optimized Structures [**2-H**]$^{n+}$(n = 0, 1, 2)

	2	[**2-H**]	[**2-H**]$^{+}$	[**2-H**]$^{2+}$
Bond Lengths (Å)				
Ru(1)–C(37)	1.985	2.011	1.967	1.933
Ru(1)–P(1, 2)	2.269, 2.268	2.280, 2.282	2.301, 2.303	2.322, 2.323
C(37)–C(38)	1.217	1.229	1.241	1.252
C(38)–C(39)	1.398	1.402	1.381	1.365
C(39)–C(40)	1.352	1.371	1.384	1.393
C(40)–C(41)	1.412	1.439	1.424	1.413
C(41)–C(43)	1.381	1.400	1.399	1.397
C(41)–C(42)	1.384	1.432	1.450	1.464
C(42)–C(43)	1.408	1.393	1.391	1.393
C(42)–S(1)	1.765	1.754	1.742	1.728
S(1)–C(39)	1.791	1.788	1.797	1.810
Bond Angles (deg)				
P(1)–Ru(1)–P(2)	82.54	93.09	92.23	90.87
Ru(1)–C(37)–C(38)	179.29	179.08	178.62	178.20
C(37)–C(38)–C(39)	177.87	178.23	179.62	178.49

Table S3. Selected Bond Lengths (Å) and Angles (deg) in the Crystal Structure of **3** and the DFT-Optimized Structures [**3-H**]$^{n+}$(n = 0, 1, 2)

	3	[**3-H**]	[**3-H**]$^{+}$	[**3-H**]$^{2+}$
Bond Lengths (Å)				
Ru(1A)–C(10A)	2.002	2.012	1.968	1.936
Ru(1A)–P(1A, 2A)	2.275, 2.269	2.281, 2.279	2.302, 2.302	2.323, 2.321
C(10A)–C(9A)	1.215	1.229	1.240	1.251
C(9A)–C(8A)	1.438	1.403	1.381	1.368
C(8A)–C(7A)	1.384	1.373	1.397	1.415
C(7A)–C(2A)	1.441	1.437	1.417	1.401
C(2A)–C(3A)	1.390	1.416	1.427	1.437
C(3A)–C(4A)	1.390	1.385	1.380	1.371
C(4A)–C(5A)	1.390	1.406	1.409	1.419
C(5A)–S(2A)	1.733	1.750	1.733	1.711
S(2A)–C(12A)	1.729	1.782	1.795	1.810
C(8A)–S(1A)	1.753	1.785	1.775	1.773
S(1A)–C(1A)	1.726	1.746	1.747	1.747
C(1A)–C(2A)	1.390	1.418	1.420	1.423
C(1A)–C(6A)	1.390	1.408	1.402	1.400
C(6A)–C(5A)	1.390	1.421	1.440	1.451

C(6A)–C(11A)	1.445	1.434	1.422	1.417
C(11A)–C(12A)	1.389	1.374	1.383	1.388
C(12A)–C(13A)	1.435	1.402	1.383	1.370
C(13A)–C(14A)	1.216	1.229	1.239	1.250
C(14A)–Ru(2A)	2.007	2.010	1.971	1.939
Ru(2A)–P(3A, 4A)	2.267, 2.264	2.281, 2.280	2.300, 2.301	2.322, 2.320
Bond Angles (deg)				
P(1A)–Ru(1A)–P(2A)	82.93	93.07	92.28	91.02
Ru(1A)–C(10A)–C(9A)	174.23	178.88	177.80	177.73
C(10A)–C(9A)–C(8A)	177.02	178.37	177.55	178.04
P(3A)–Ru(2A)–P(4A)	83.57	93.11	92.46	91.06
Ru(1A)–C(14A)–C(13A)	168.87	178.96	178.46	177.73
C(14A)–C(13A)–C(12A)	171.05	178.93	177.43	175.26

Table S4. Selected Bond Lengths (Å) and Angles (deg) from the DFT-Optimized Structures [**4-H**]$^{n+}$(n = 0, 1, 2)

	[**4-H**]	[**4-H**]$^{+}$	[**4-H**]$^{2+}$
Bond Lengths (Å)			
Ru(1)–C(13)	2.011	1.968	1.930
Ru(1)–P(29, 30)	2.281, 2.280	2.302, 2.299	2.322, 2.321
C(13)–C(12)	1.229	1.240	1.253
C(12)–C(11)	1.402	1.379	1.359
C(11)–S(36)	1.781	1.772	1.766
S(36)–C(4)	1.751	1.751	1.752
C(4)–C(5)	1.404	1.389	1.375
C(4)–C(3)	1.419	1.432	1.447
C(3)–C(34)	1.433	1.408	1.384
C(34)–C(11)	1.375	1.402	1.430
Bond Angles (deg)			
P(29)–Ru(1)–P(30)	93.06	92.35	90.99
Ru(1)–C(13)–C(12)	179.28	178.94	178.77
C(13)–C(12)–C(11)	179.80	179.94	178.88

2. IR, UV-vis-NIR Spectroelectrochemical Information

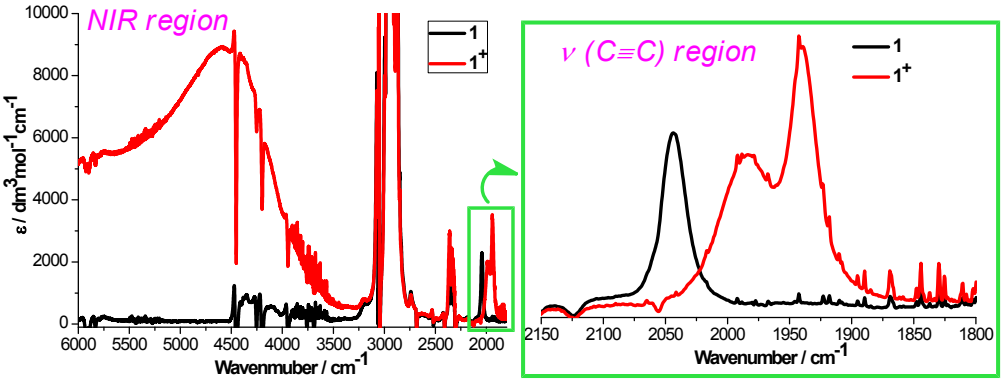

Figure S1. Spectral changes in the IR ν(C≡C) (right) and NIR (left) regions recorded for complexes $[\mathbf{1}]^{n+}$, n = 0 (black) and +1 (red) electrochemically generated in $CH_2Cl_2/10^{-1}$ M n-Bu_4NPF_6 at 223 K within an OTTLE cell.

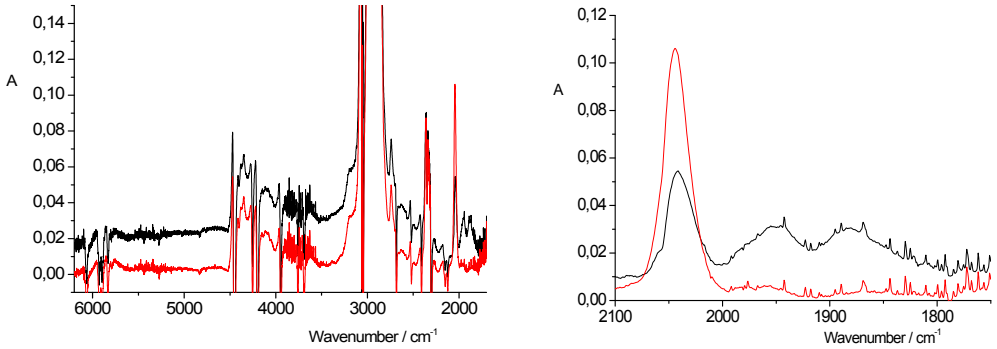

Figure S2. IR spectral changes obtained in the IR ν(C≡C) (right) and NIR (left) regions recorded during the irreversible oxidation of neutral **2** (red) in CH_2Cl_2 at 223 K.

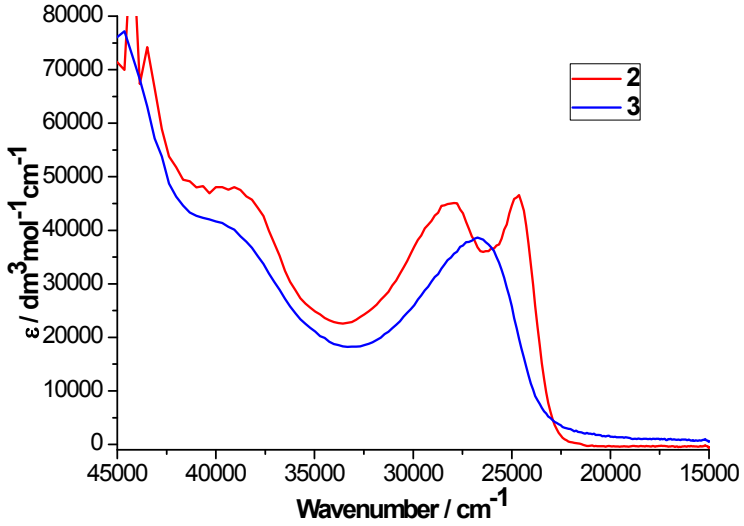

Figure S3. UV-vis absorption spectra of complexes **2** and **3** in CH_2Cl_2 at 293 K.

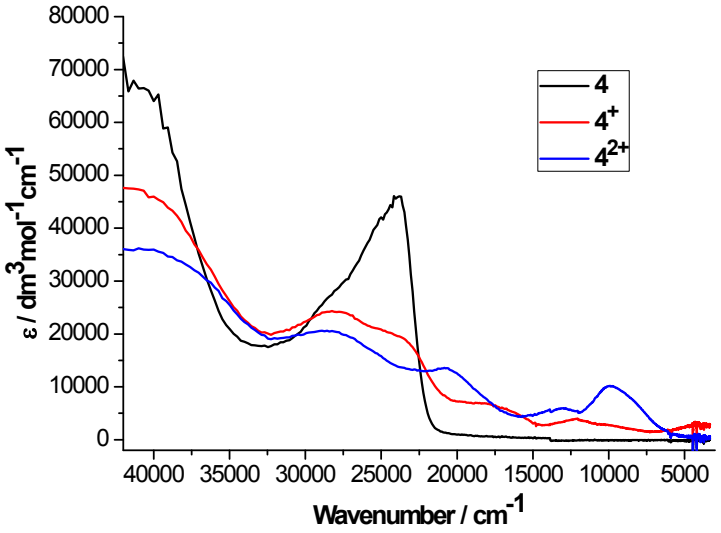

Figure S4. The UV-vis-NIR spectra of $[\mathbf{4}]^{n+}$ (n = 0, 1, 2) collected in the course of the stepwise oxidation of **4** in dichloromethane at 293 K within an OTTLE cell.

3. DFT Calculations

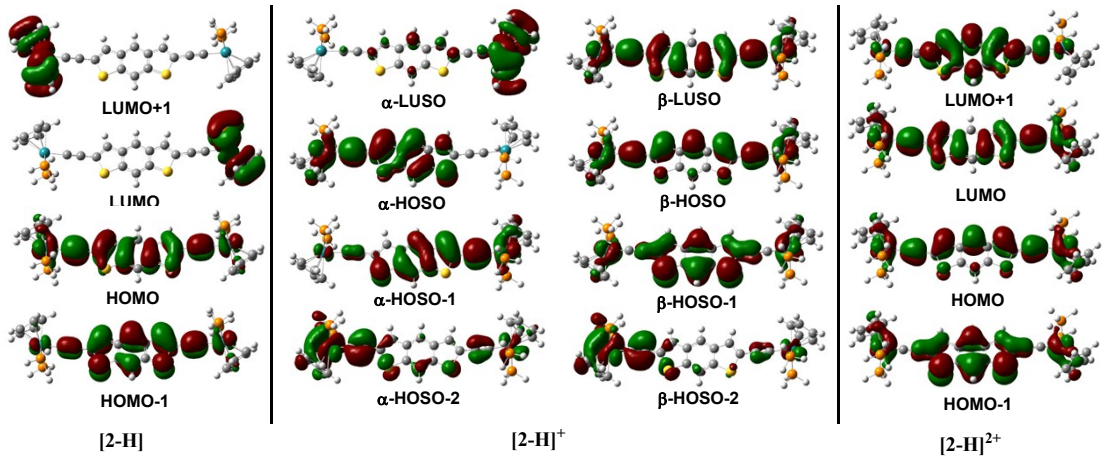

Figure S5. Selected molecular orbitals in the redox series [**2-H**]$^{n+}$ (*n* = 0, 1, 2) plotted with contour values ±0.04 (e/bohr^3)$^{1/2}$

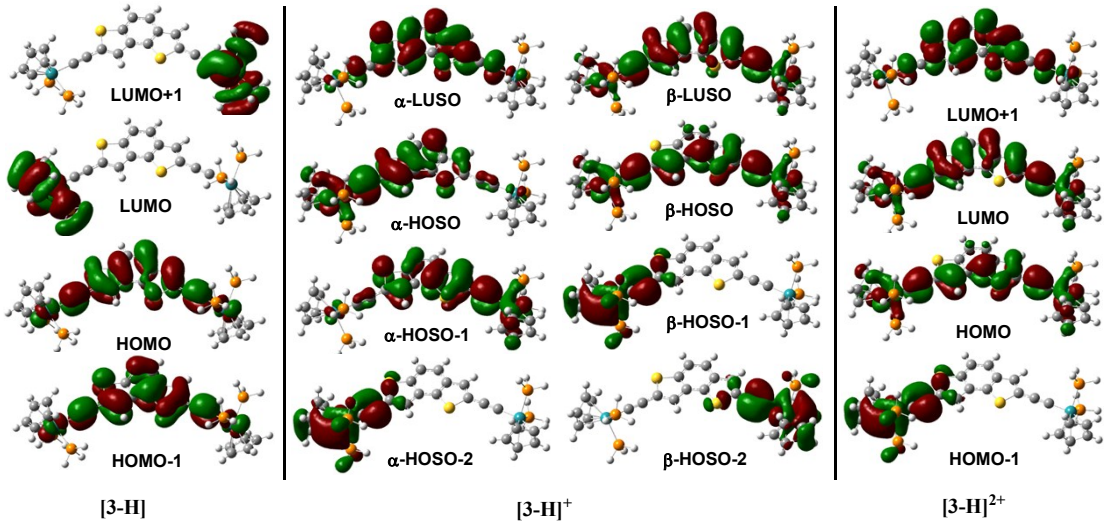

Figure S6. Selected molecular orbitals in the redox series [**3-H**]$^{n+}$ (*n* = 0, 1, 2) plotted with contour values ±0.04 (e/bohr^3)$^{1/2}$

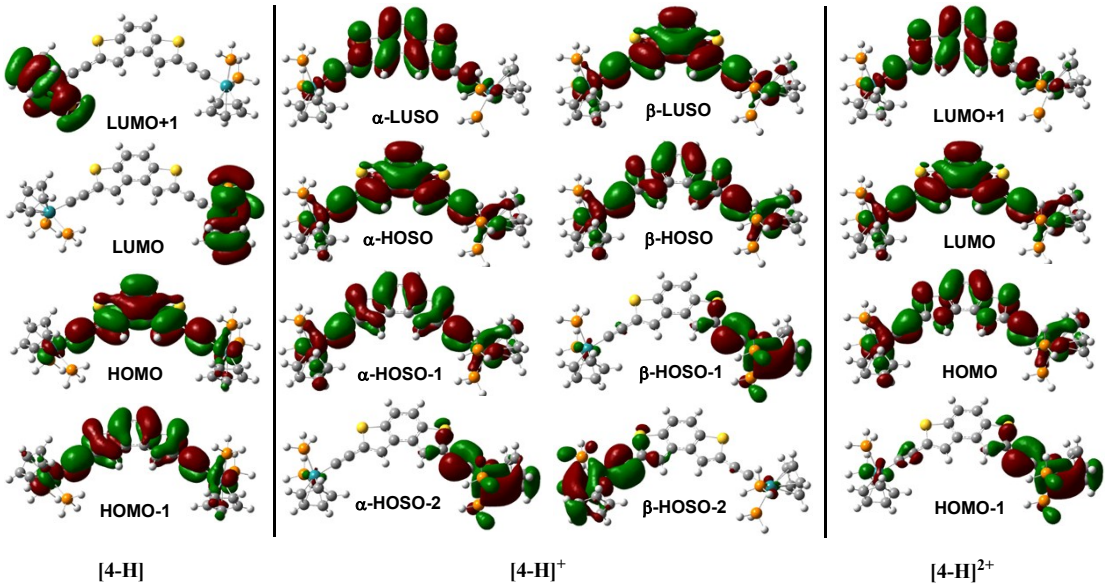

Figure S7. Selected molecular orbitals in the redox series [**4-H**]$^{n+}$ (*n* = 0, 1, 2) plotted with contour values ±0.04 (e/bohr^3)$^{1/2}$

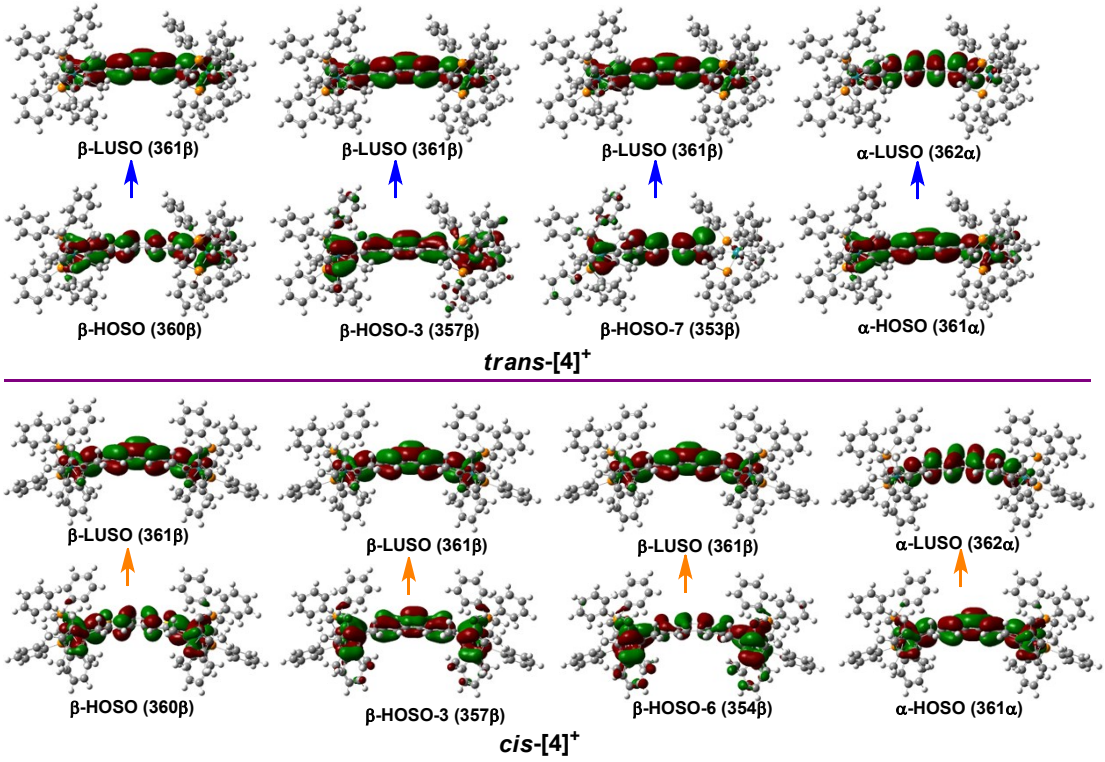

Figure S8. Isosurface plots of molecular orbitals involved in the major electronic excitations calculated for *trans*-[**4**]$^+$ and *cis*-[**4**]$^+$

Table S5. Energies and composition of selected molecular orbitals of model complex [**1-H**].

MO	Orbitals	eV	Cp1	$(PH_3)_2$1	Ru1	(C≡C)1	$C_{10}H_4S_2$	(C≡C)2	Ru2	$(PH_3)_2$2	Cp2
181	L+5	-0.03	2	4	34	1	0	1	41	4	2
180	L+4	-0.22	8	4	34	5	0	4	28	4	8

179	L+3	-0.22	8	4	28	4	0	5	34	4	8
178	L+2	-0.71	1	1	3	9	72	9	3	1	1
177	L+1	-0.85	25	22	50	0	0	0	0	0	0
176	LUMO	-0.85	0	0	0	0	0	0	50	22	25
175	HOMO	-4.22	1	1	8	14	52	14	8	1	1
174	H-1	-5.00	4	2	17	17	20	17	17	2	4
173	H-2	-5.03	1	0	3	3	86	3	3	0	1
172	H-3	-5.03	3	1	28	16	4	16	28	1	3
171	H-4	-5.42	3	1	28	16	4	16	28	1	3
170	H-5	-5.94	12	3	22	10	8	9	19	3	12

Table S6. Energies and composition of selected molecular orbitals of model complex [**1-H**]$^{+}$.

MO	Orbitals	eV	Cp1	$(PH_3)_2$1	Ru1	(C≡C)1	$C_{10}H_4S_2$	(C≡C)2	Ru2	$(PH_3)_2$2	Cp2
181α	α-LUSO+5	-2.56	1	1	3	10	70	10	3	1	1
180β	β-LUSO+5	-2.67	10	6	28	5	0	5	28	6	10
180α	α-LUSO+4	-2.72	10	6	28	5	0	5	28	6	10
179β	β-LUSO+4	-2.68	10	6	28	5	0	5	28	6	10
179α	α-LUSO+3	-2.72	10	6	28	5	0	5	28	6	10
178β	β-LUSO+3	-3.30	12	10	23	0	0	0	27	12	14
178α	α-LUSO+2	-3.34	0	0	0	0	0	0	49	22	26
177β	β-LUSO+2	-3.30	14	12	27	0	0	0	23	10	12
177α	α-LUSO+1	-3.34	26	22	49	0	0	0	0	0	0
176β	β-LUSO+1	-3.61	1	1	4	10	68	10	4	1	1
176α	α-LUSO	-3.88	1	1	3	9	72	9	3	1	1
175β	β-LUSO	-6.01	2	1	9	13	50	13	9	1	2
175α	α-HOSO	-7.04	2	1	10	13	48	13	10	1	2
174β	β-HOSO	-7.30	4	2	18	14	24	14	18	2	4
174α	α-HOSO-1	-7.78	5	2	22	13	16	13	22	2	5
173β	β-HOSO-1	-7.86	2	1	6	3	76	3	6	1	2
173α	α-HOSO-2	-7.98	1	0	4	2	86	2	4	0	1
172β	β-HOSO-2	-8.03	4	1	29	14	4	14	29	1	4
172α	α-HOSO-3	-8.08	4	1	29	13	6	13	29	1	4
171β	β-HOSO-3	-8.05	4	1	29	13	6	13	29	1	4
171α	α-HOSO-4	-8.09	4	1	29	13	6	13	29	1	13
170β	β-HOSO-4	-8.44	13	3	22	9	4	9	22	3	13
170α	α-HOSO-5	-8.47	13	3	22	9	4	9	22	3	13
169β	β-HOSO-5	-8.44	13	3	22	9	4	9	22	3	13

Table S7. Energies and composition of frontier molecular orbitals of model complex [**1-H**]$^{2+}$.

MO	Orbitals	eV	Cp1	$(PH_3)_2$1	Ru1	(C≡C)1	$C_{10}H_4S_2$	(C≡C)2	Ru2	$(PH_3)_2$2	Cp2
180	L+5	-5.27	10	6	27	5	0	5	27	6	10

179	L+4	-5.28	2	1	5	10	64	10	5	1	2
178	L+3	-5.89	13	12	24	0	0	0	24	12	13
177	L+2	-5.89	13	12	24	0	0	0	24	12	13
176	L+1	-6.63	1	1	4	10	68	10	4	1	1
175	LUMO	-8.74	2	1	10	12	50	12	10	1	2
174	HOMO	-10.07	5	2	18	11	28	11	18	2	5
173	H-1	-10.63	3	1	7	2	74	2	7	1	3
172	H-2	-10.77	3	1	29	14	6	14	29	1	3
171	H-3	-10.79	3	1	29	14	6	14	29	1	3
170	H-4	-10.99	14	2	22	9	6	9	22	2	14
169	H-5	-11.00	14	2	22	9	6	9	22	2	14

Table S8. Energies and composition of selected molecular orbitals of model complex [**2-H**].

MO	Orbitals	eV	Cp1	$(PH_3)_2$1	Ru1	(C≡C)1	$C_{10}H_4S_2$	(C≡C)2	Ru2	$(PH_3)_2$2	Cp2
181	L+5	-0.18	1	1	4	7	74	7	4	1	1
180	L+4	-0.21	13	5	48	7	0	2	13	2	4
179	L+3	-0.22	4	2	13	2	0	7	48	5	13
178	L+2	-0.47	1	1	2	8	76	8	2	1	1
177	L+1	-0.84	25	22	50	0	0	0	0	0	0
176	LUMO	-0.84	0	0	0	0	0	0	50	22	25
175	HOMO	-4.46	2	1	12	18	44	12	8	1	2
174	H-1	-4.50	1	1	4	6	65	12	8	1	2
173	H-2	-5.35	2	1	11	6	30	17	27	2	4
172	H-3	-5.39	4	1	36	21	6	11	18	1	2
171	H-4	-5.44	3	1	25	12	18	12	25	1	2
170	H-5	-5.88	7	2	15	5	17	9	27	4	14

Table S9. Energies and composition of selected molecular orbitals of model complexes [**2-H**]$^+$.

MO	Orbitals	eV	Cp1	$(PH_3)_2$1	Ru1	(C≡C)1	$C_{10}H_4S_2$	(C≡C)2	Ru2	$(PH_3)_2$2	Cp2
181α	α-LUSO+5	-2.75	20	11	56	10	0	0	0	0	0
180β	β-LUSO+5	-2.72	0	0	0	0	0	10	56	11	20
180α	α-LUSO+4	-2.77	0	0	0	0	0	10	56	11	20
179β	β-LUSO+4	-2.96	1	1	3	7	76	7	3	1	1
179α	α-LUSO+3	-3.26	1	1	3	8	77	6	2	1	1
178β	β-LUSO+3	-3.27	1	1	3	8	73	9	3	1	1
178α	α-LUSO+2	-3.38	26	23	49	0	0	0	0	0	0
177β	β-LUSO+2	-3.33	26	23	49	0	0	0	0	0	0
177α	α-LUSO+1	-3.39	1	0	2	7	68	9	7	2	4
176β	β-LUSO+1	-3.35	0	0	0	0	0	0	49	22	25
176α	α-LUSO	-3.40	0	0	0	1	6	1	44	22	22
175β	β-LUSO	-6.26	2	1	11	14	44	14	11	1	2

175α	α-HOSO	-7.30	0	2	18	20	59	0	0	0	0
174β	β-HOSO	-6.90	3	1	13	12	42	12	13	1	3
174α	α-HOSO-1	-7.31	1	0	2	2	48	22	19	2	4
173β	β-HOSO-1	-7.93	2	1	10	4	66	4	10	1	2
173α	α-HOSO-2	-8.10	6	1	44	21	10	5	10	1	2
172β	β-HOSO-2	-8.06	6	2	52	25	7	2	5	0	1
172α	α-HOSO-3	-8.14	3	1	15	6	10	18	40	1	6
171β	β-HOSO-3	-8.09	1	0	5	2	7	25	53	1	6
171α	α-HOSO-4	-8.17	4	2	13	5	36	10	23	2	5
170β	β-HOSO-4	-8.44	20	4	34	12	17	2	7	1	3
170α	α-HOSO-5	-8.49	25	5	41	19	6	1	2	0	1
169β	β-HOSO-5	-8.47	5	1	10	4	9	13	34	4	20

Table S10. Energies and composition of selected molecular orbitals of model complex [**2-H**]$^{2+}$.

MO	Orbitals	eV	Cp1	$(PH_3)_2$1	Ru1	(C≡C)1	$C_{10}H_4S_2$	(C≡C)2	Ru2	$(PH_3)_2$2	Cp2
180	L+5	-5.34	21	12	54	11	0	0	0	0	0
179	L+4	-5.94	2	1	5	6	67	6	7	2	4
178	L+3	-5.96	4	3	7	1	2	0	39	19	21
177	L+2	-5.97	21	20	39	1	8	1	5	3	2
176	L+1	-6.10	1	1	3	9	72	9	3	1	1
175	LUMO	-9.08	3	2	13	14	37	13	13	2	3
174	HOMO	-9.63	3	2	12	10	44	10	13	2	3
173	H-1	-10.67	4	2	8	3	66	3	8	2	4
172	H-2	-10.82	2	1	26	15	6	16	30	1	3
171	H-3	-10.85	3	1	30	16	6	15	26	1	2
170	H-4	-11.04	3	1	5	1	5	14	38	5	28
169	H-5	-11.05	28	5	38	14	5	1	5	1	3

Table S11. Energies and composition of selected molecular orbitals of model complex [**3-H**].

MO	Orbitals	eV	Cp1	$(PH_3)_2$1	Ru1	(C≡C)1	$C_{10}H_4S_2$	(C≡C)2	Ru2	$(PH_3)_2$2	Cp2
181	L+5	-0.18	0	0	6	3	64	9	17	0	1
180	L+4	-0.20	0	0	1	0	6	10	56	7	17
179	L+3	-0.21	17	7	56	10	6	0	1	0	0
178	L+2	-0.45	1	0	5	10	78	4	2	0	0
177	L+1	-0.82	0	0	0	0	0	0	50	22	24
176	LUMO	-0.84	24	22	50	0	0	0	0	0	0
175	HOMO	-4.52	1	0	7	13	58	13	7	0	1
174	H-1	-4.66	1	0	8	12	55	14	9	0	1
173	H-2	-5.19	0	0	0	0	4	36	47	4	9
172	H-3	-5.24	9	4	47	36	4	0	0	0	0
171	H-4	-5.57	6	2	29	7	47	1	6	1	1

170	H-5	-5.68	3	1	7	1	21	4	43	4	16

Table S12. Energies and composition of selected molecular orbitals of model complex [**3-H**]$^{+}$.

MO	Orbitals	eV	Cp1	$(PH_3)_2$1	Ru1	(C≡C)1	$C_{10}H_4S_2$	(C≡C)2	Ru2	$(PH_3)_2$2	Cp2
181α	α-LUSO+5	-2.69	19	10	56	10	0	0	0	0	0
180β	β-LUSO+5	-2.76	0	0	0	0	0	10	57	10	19
180α	α-LUSO+4	-2.81	0	0	0	0	0	0	56	10	19
179β	β-LUSO+4	-3.08	1	1	3	7	73	9	4	1	1
179α	α-LUSO+3	-3.19	1	1	2	9	75	8	2	1	1
178β	β-LUSO+3	-3.25	3	1	7	7	72	6	2	1	1
178α	α-LUSO+2	-3.31	26	22	49	0	0	0	0	0	0
177β	β-LUSO+2	-3.27	24	22	45	1	5	0	0	0	0
177α	α-LUSO+1	-3.43	0	0	0	0	0	0	49	22	26
176β	β-LUSO+1	-3.39	0	0	0	0	0	0	49	22	26
176α	α-LUSO	-3.59	0	1	2	6	79	9	2	1	0
175β	β-LUSO	-6.30	2	1	10	12	47	14	11	1	2
175α	α-HOSO	-7.34	6	2	23	23	41	2	2	0	1
174β	β-HOSO	-6.94	3	2	16	15	31	14	14	2	3
174α	α-HOSO-1	-7.41	1	0	2	2	44	23	21	2	5
173β	β-HOSO-1	-8.02	8	2	59	26	0	0	0	0	0
173α	α-HOSO-2	-8.06	8	2	59	26	0	0	0	0	0
172β	β-HOSO-2	-8.13	0	0	0	0	0	27	59	2	7
172α	α-HOSO-3	-8.18	0	0	0	0	0	26	59	2	8
171β	β-HOSO-3	-8.25	7	2	21	5	61	1	2	0	1
171α	α-HOSO-4	-8.43	20	4	34	14	26	0	1	0	1
170β	β-HOSO-4	-8.39	0	0	0	0	62	5	23	2	8
170α	α-HOSO-5	-8.47	13	3	24	10	44	1	3	1	1
169β	β-HOSO-5	-8.41	25	5	43	19	3	0	0	0	0

Table S13. Energies and composition of selected molecular orbitals of model complex [**3-H**]$^{2+}$.

MO	Orbitals	eV	Cp1	$(PH_3)_2$1	Ru1	(C≡C)1	$C_{10}H_4S_2$	(C≡C)2	Ru2	$(PH_3)_2$2	Cp2
180	L+5	-5.36	0	0	0	0	0	10	55	11	22
179	L+4	-5.91	25	18	43	1	12	1	0	0	0
178	L+3	-5.93	3	5	8	9	65	6	3	0	1
177	L+2	-5.99	0	0	0	0	0	0	47	22	27
176	L+1	-6.26	1	1	2	6	76	9	3	1	1
175	LUMO	-9.16	3	2	12	11	43	12	12	2	3
174	HOMO	-9.68	4	2	17	14	31	12	14	2	4
173	H-1	-10.80	7	2	57	28	0	0	0	0	0
172	H-2	-10.87	0	0	0	0	0	28	57	2	7
171	H-3	-11.01	29	5	41	14	5	0	1	0	0

170	H-4	-11.06	9	2	13	5	47	3	12	1	8
169	H-5	-11.09	2	1	3	1	16	13	36	4	24

Table S14. Energies and composition of selected molecular orbitals of model complex [**4-H**].

MO	Orbitals	eV	Cp1	$(PH_3)_2$1	Ru1	(C≡C)1	$C_{10}H_4S_2$	(C≡C)2	Ru2	$(PH_3)_2$2	Cp2
181	L+5	-0.04	0	0	4	0	4	1	71	6	3
180	L+4	-0.21	17	6	61	9	0	0	0	0	0
179	L+3	-0.22	0	0	0	0	0	9	61	6	17
178	L+2	-0.66	0	0	3	8	78	8	3	0	0
177	L+1	-0.83	25	23	50	0	0	0	0	0	0
176	LUMO	-0.85	0	0	0	0	0	0	50	23	25
175	HOMO	-4.33	1	0	6	12	58	14	8	0	1
174	H-1	-4.82	1	1	12	16	44	13	11	1	1
173	H-2	-5.23	8	3	47	35	7	0	0	0	0
172	H-3	-5.39	0	0	0	0	7	31	52	2	6
171	H-4	-5.51	1	1	7	2	76	3	8	1	1
170	H-5	-5.69	13	4	35	4	26	3	11	1	3

Table S15. Energies and composition of selected molecular orbitals of model complex [**4-H**]$^+$.

MO	Orbitals	eV	Cp1	$(PH_3)_2$1	Ru1	(C≡C)1	$C_{10}H_4S_2$	(C≡C)2	Ru2	$(PH_3)_2$2	Cp2
181α	α-LUSO+5	-2.77	0	0	0	0	0	10	56	10	20
180β	β-LUSO+5	-2.73	0	0	1	0	0	10	55	10	20
180α	α-LUSO+4	-2.77	20	10	56	10	0	0	0	0	0
179β	β-LUSO+4	-2.73	20	10	55	10	0	0	1	0	0
179α	α-LUSO+3	-2.90	1	1	3	8	74	8	3	1	1
178β	β-LUSO+3	-3.35	0	0	0	0	0	0	49	22	27
178α	α-LUSO+2	-3.39	0	0	0	0	0	0	49	22	27
177β	β-LUSO+2	-3.37	27	22	49	0	0	0	0	0	0
177α	α-LUSO+1	-3.41	27	22	49	0	0	0	0	0	0
176β	β-LUSO+1	-3.62	1	1	3	9	72	9	3	1	1
176α	α-LUSO	-3.85	1	1	3	9	72	9	3	1	1
175β	β-LUSO	-6.12	2	1	9	13	50	13	9	1	2
175α	α-HOSO	-7.17	2	1	10	12	50	12	10	1	2
174β	β-HOSO	-7.20	3	2	16	13	32	13	16	2	3
174α	α-HOSO-1	-7.62	3	2	15	12	36	12	15	2	3
173β	β-HOSO-1	-8.10	0	0	1	1	6	25	57	2	8
173α	α-HOSO-2	-8.14	0	0	1	0	6	24	58	2	9
172β	β-HOSO-2	-8.11	9	2	58	24	6	0	1	0	0
172α	α-HOSO-3	-8.15	9	2	58	24	6	0	1	0	0
171β	β-HOSO-3	-8.25	5	2	17	4	44	4	17	2	5
171α	α-HOSO-4	-8.51	3	1	6	2	22	13	31	4	18

170β	β-HOSO-4	-8.45	1	0	3	1	83	2	6	1	3
170α	α-HOSO-5	-8.53	21	4	35	16	13	2	5	1	3
169β	β-HOSO-5	-8.50	6	1	7	3	8	16	35	4	20

Table S16. Energies and composition of selected molecular orbitals of model complex [**4-H**]$^{2+}$.

MO	Orbitals	eV	Cp1	$(PH_3)_2$1	Ru1	(C≡C)1	$C_{10}H_4S_2$	(C≡C)2	Ru2	$(PH_3)_2$2	Cp2
180	L+5	-5.37	21	11	54	11	0	0	0	0	0
179	L+4	-5.66	1	1	3	8	74	8	3	1	1
178	L+3	-5.99	0	0	0	0	0	0	48	22	28
177	L+2	-6.01	28	22	48	0	0	0	0	0	0
176	L+1	-6.68	1	1	4	10	68	10	4	1	1
175	LUMO	-8.92	2	1	11	12	48	12	11	1	2
174	HOMO	-10.00	4	2	16	11	34	11	16	2	4
173	H-1	-10.88	1	0	4	2	7	23	53	2	8
172	H-2	-10.88	8	2	53	23	7	2	4	0	1
171	H-3	-11.00	7	2	13	4	44	4	15	2	9
170	H-4	-11.09	1	0	2	1	7	16	40	4	27
169	H-5	-11.10	28	5	42	17	5	1	1	0	1

4. NMR Information

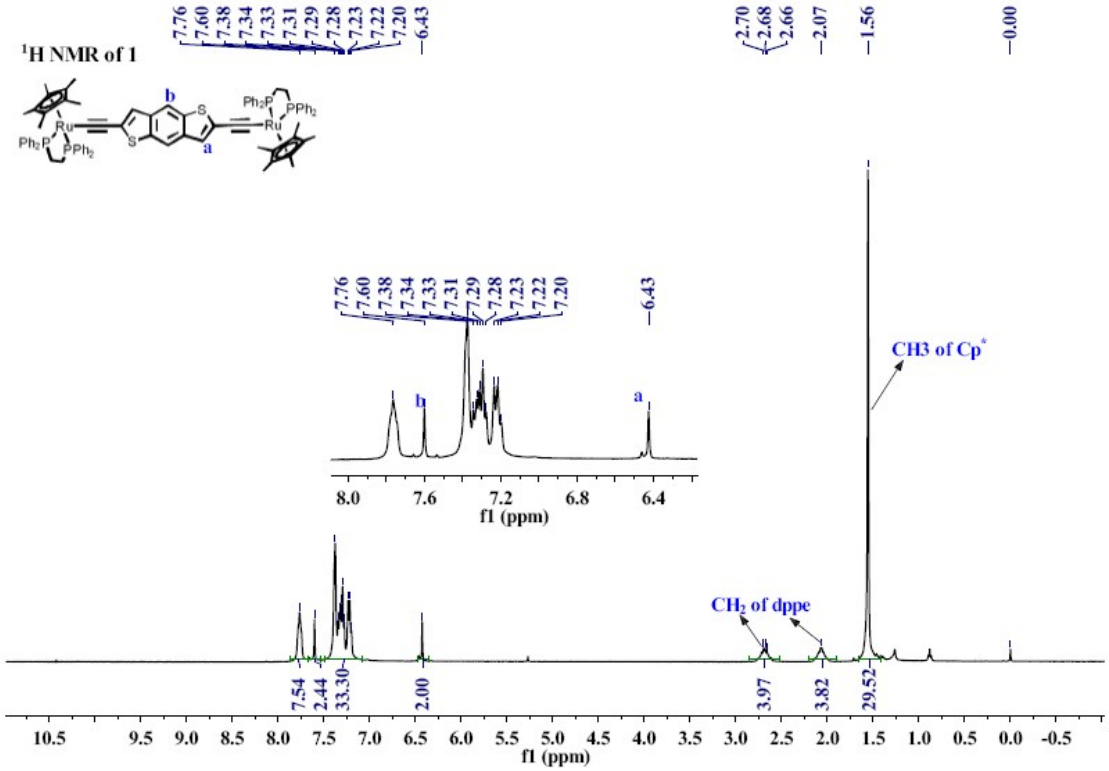

Figure S9. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1**.

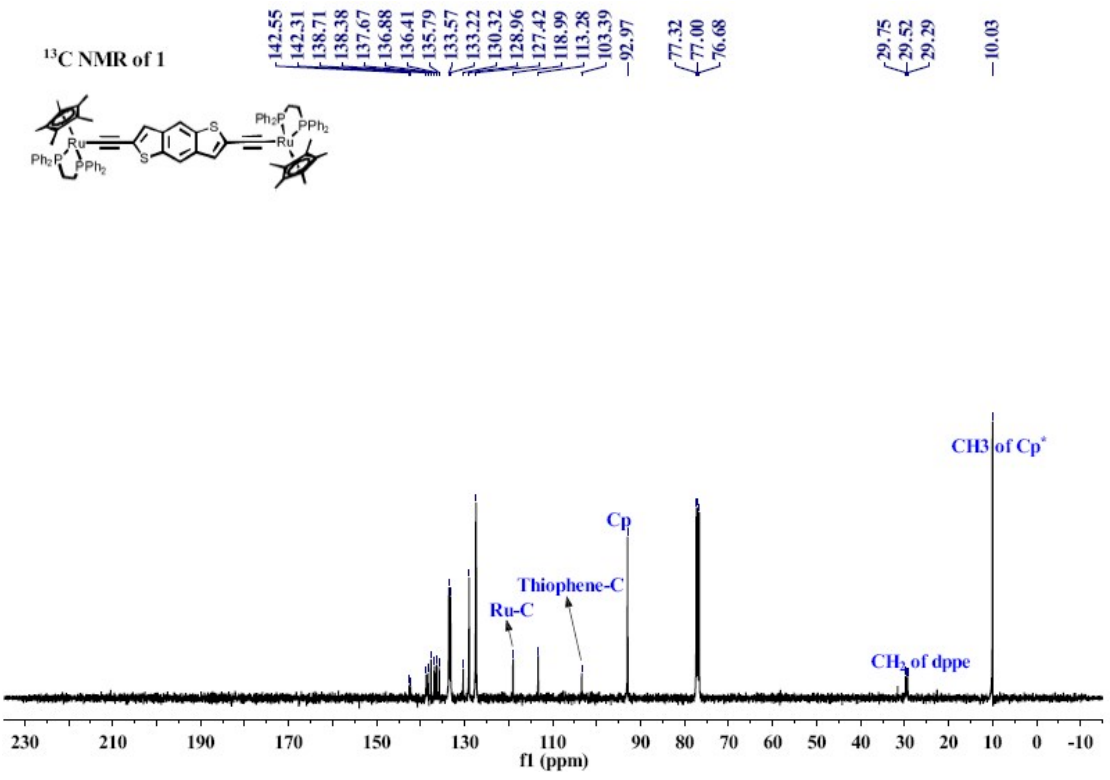

Figure S10. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **1**.

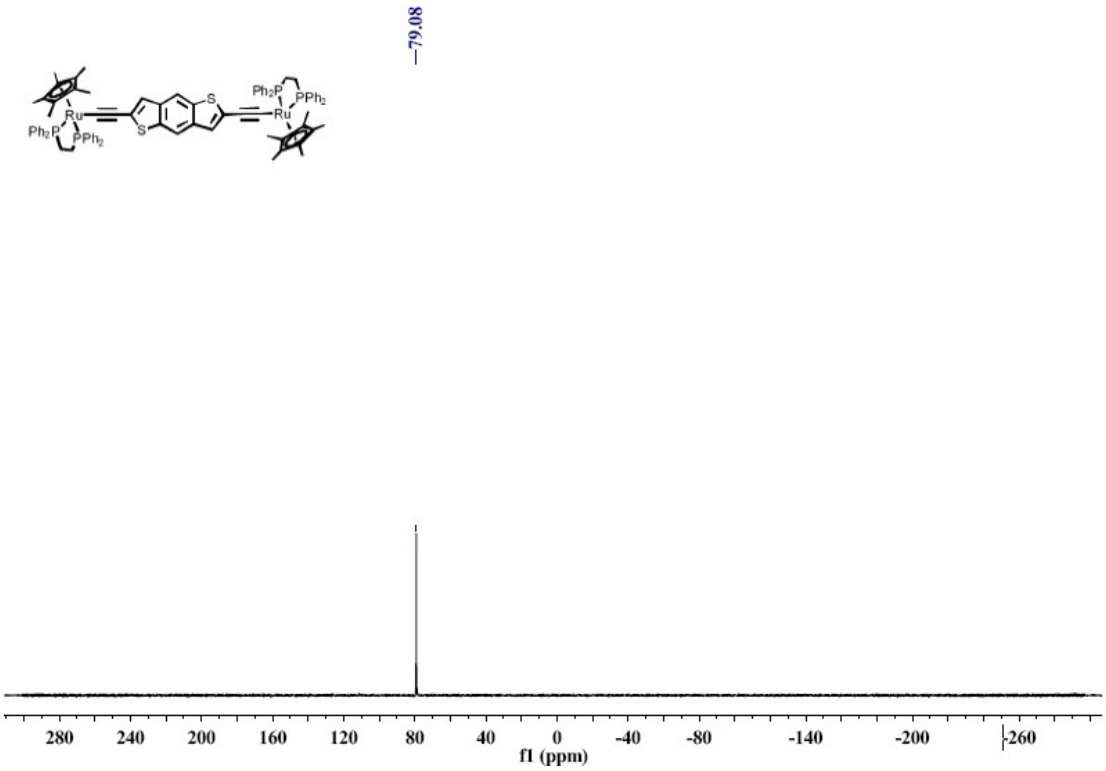

Figure S11. ^{31}P NMR spectrum (160 MHz, $CDCl_3$) of **1**.

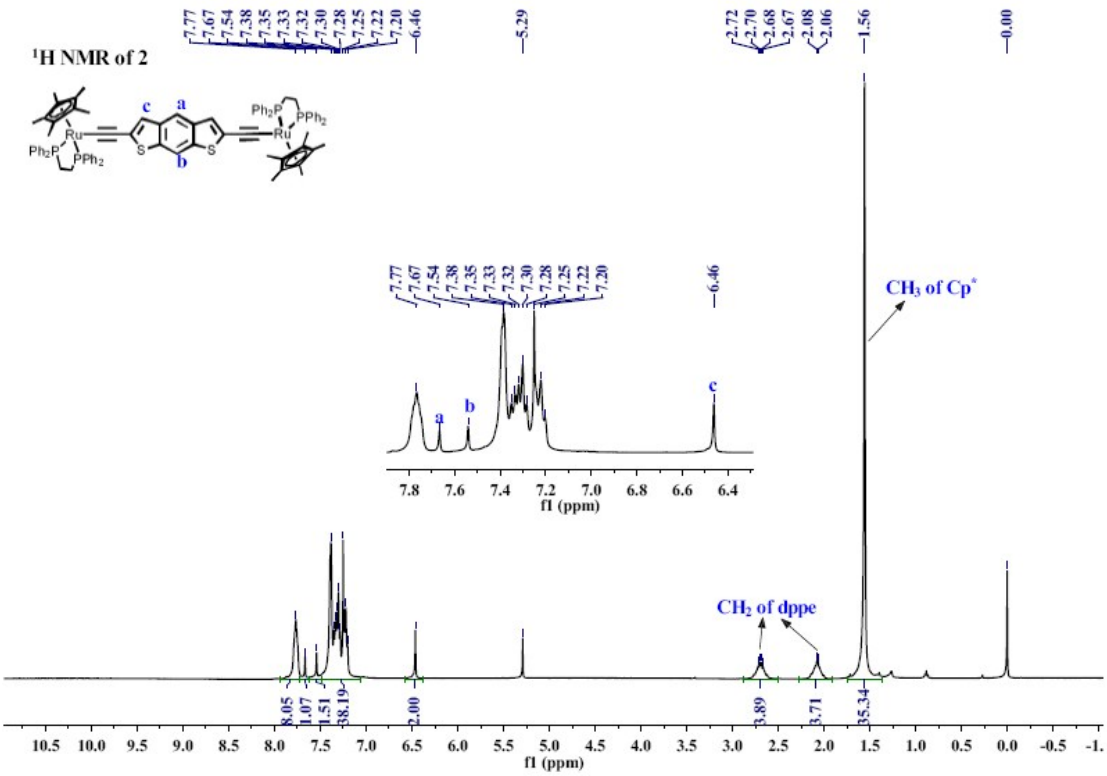

Figure S12. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2**.

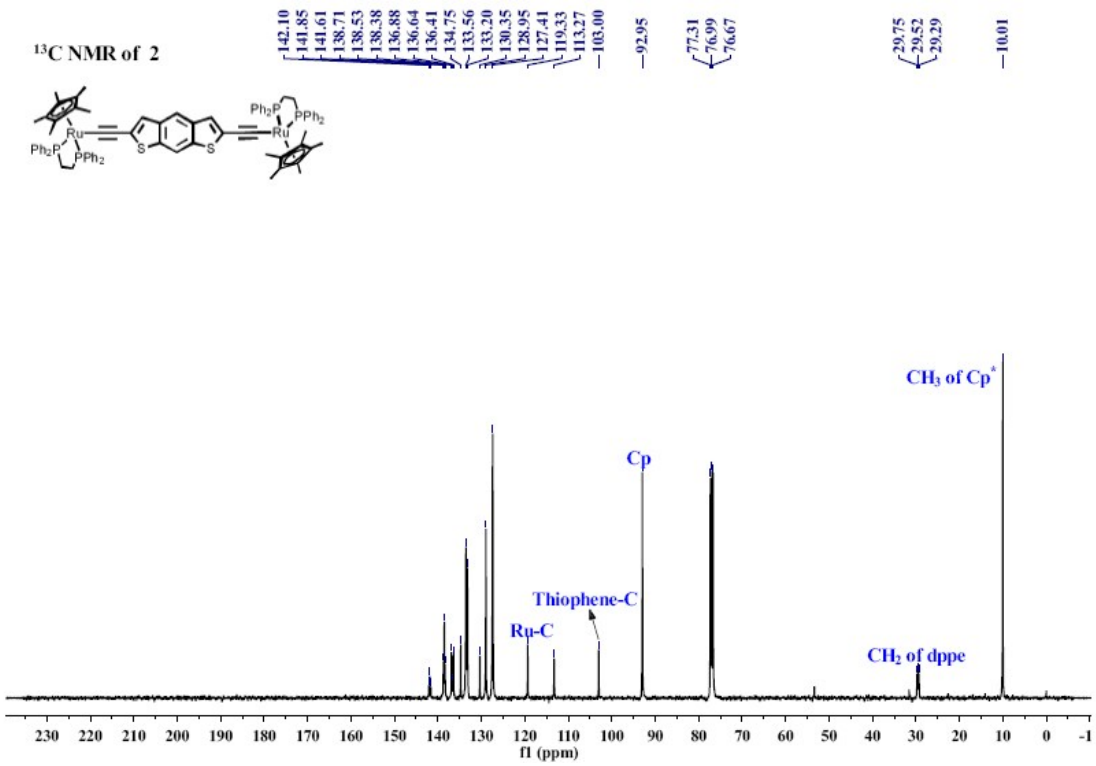

Figure S13. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **2**.

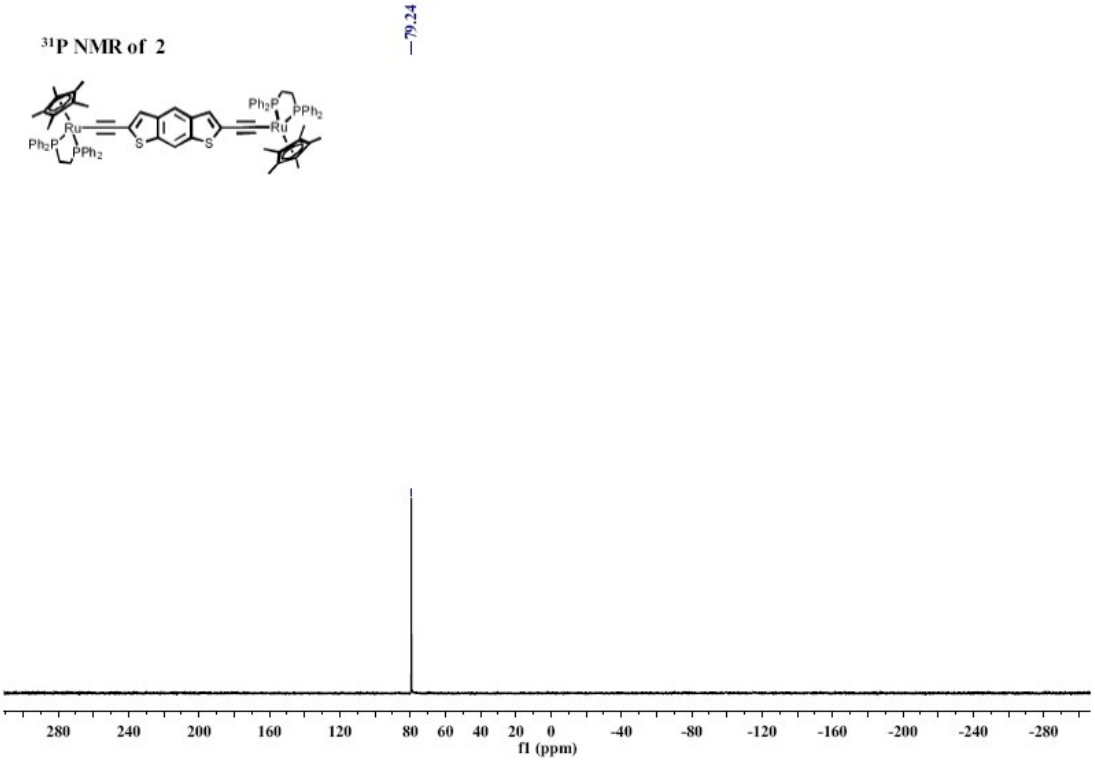

Figure S14. ^{31}P NMR spectrum (160 MHz, $CDCl_3$) of **2**.

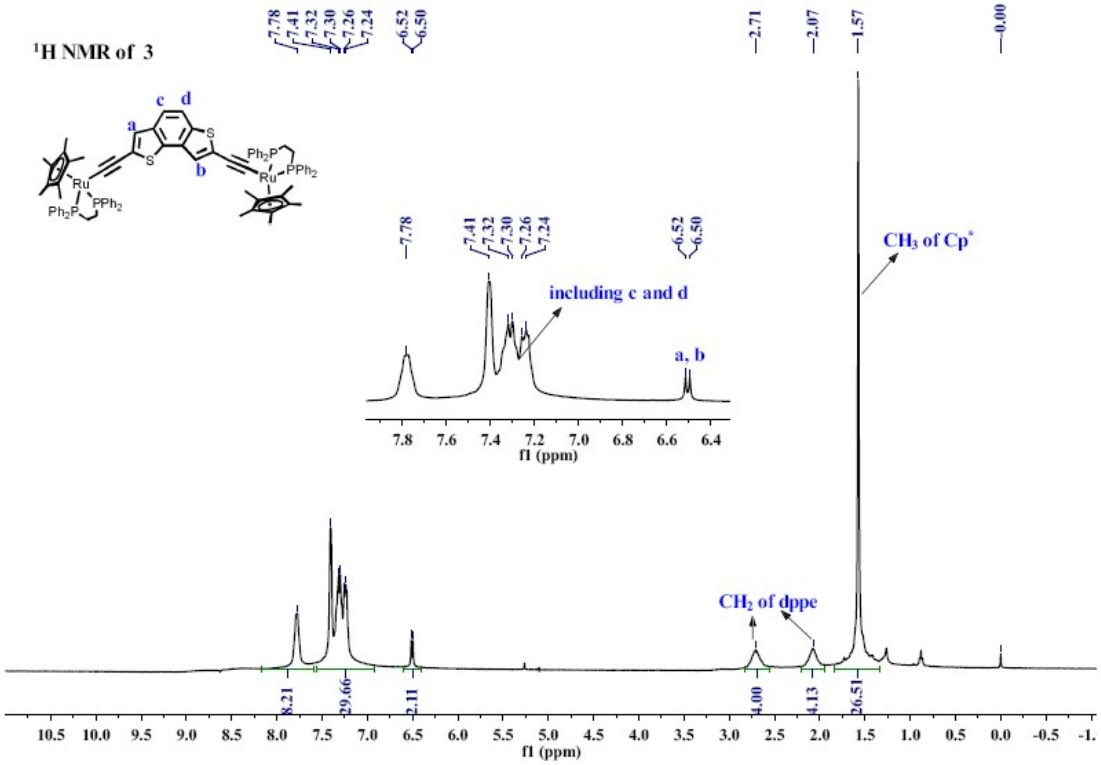

Figure S15. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3**.

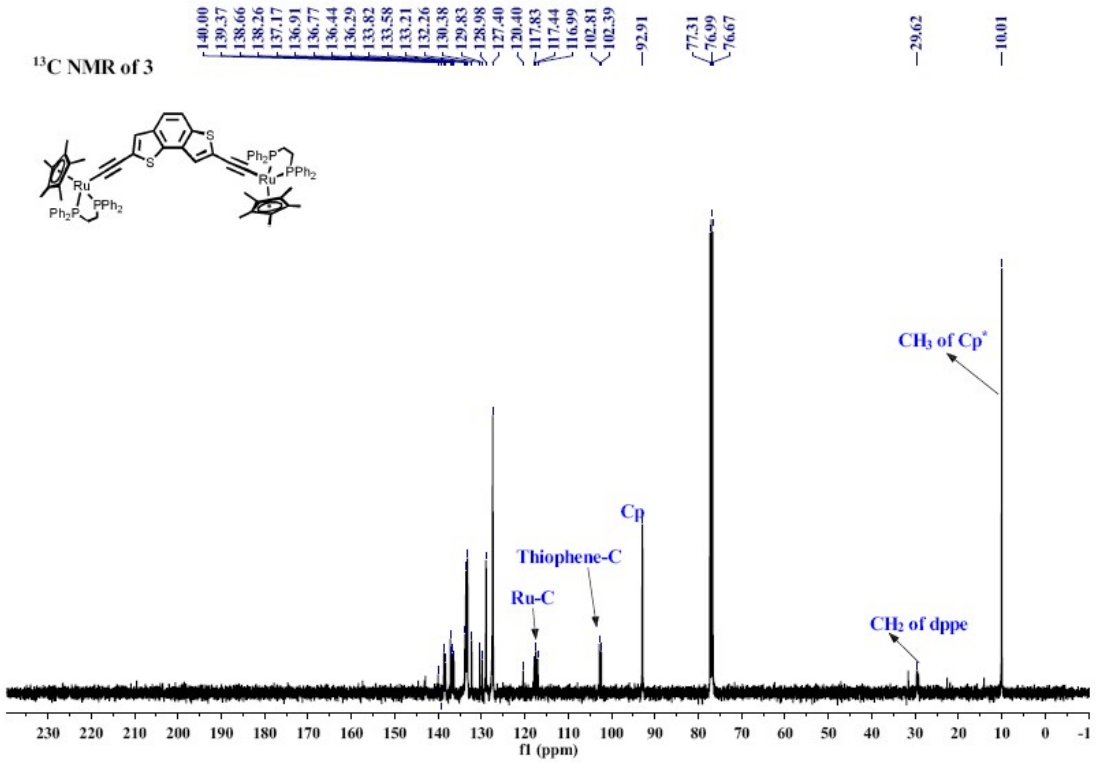

Figure S16. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **3**.

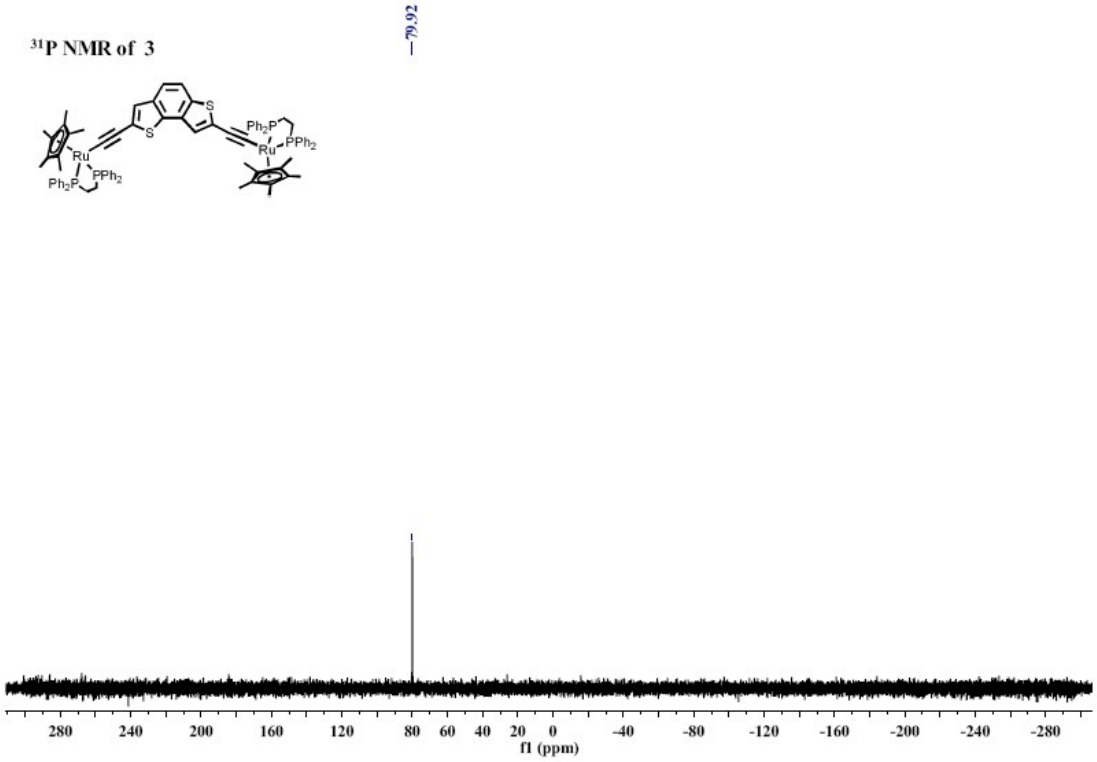

Figure S17. ^{31}P NMR spectrum (160 MHz, $CDCl_3$) of **3**.

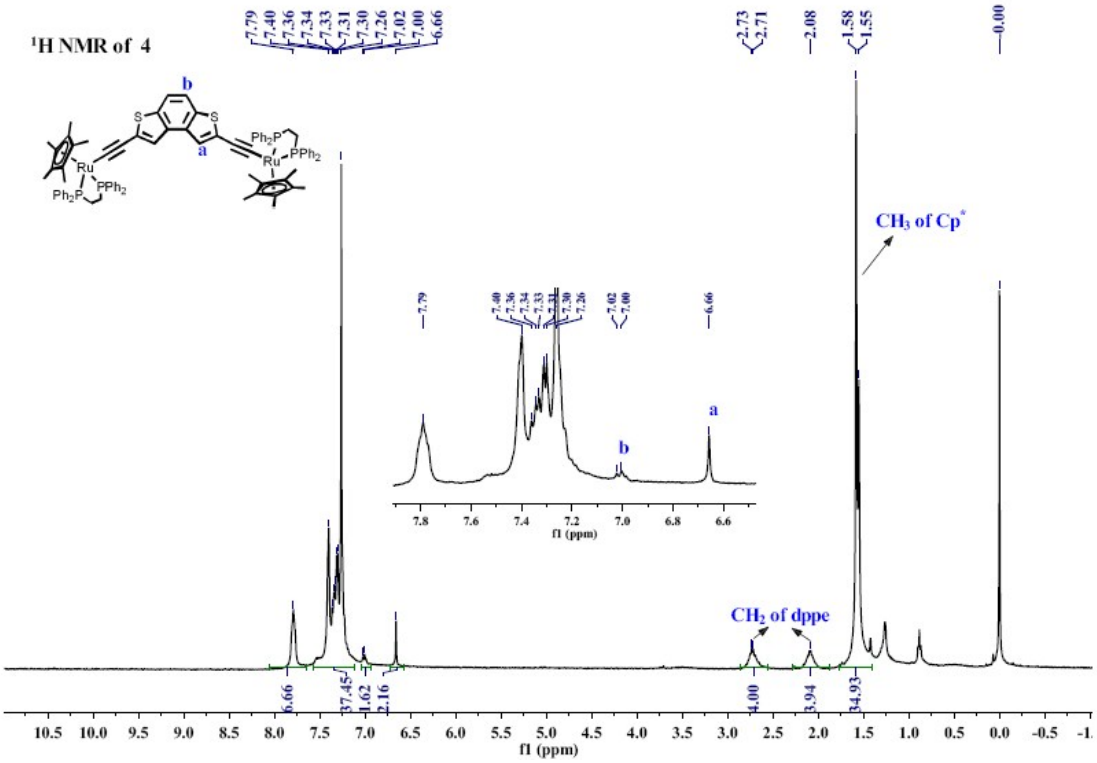

Figure S18. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4**.

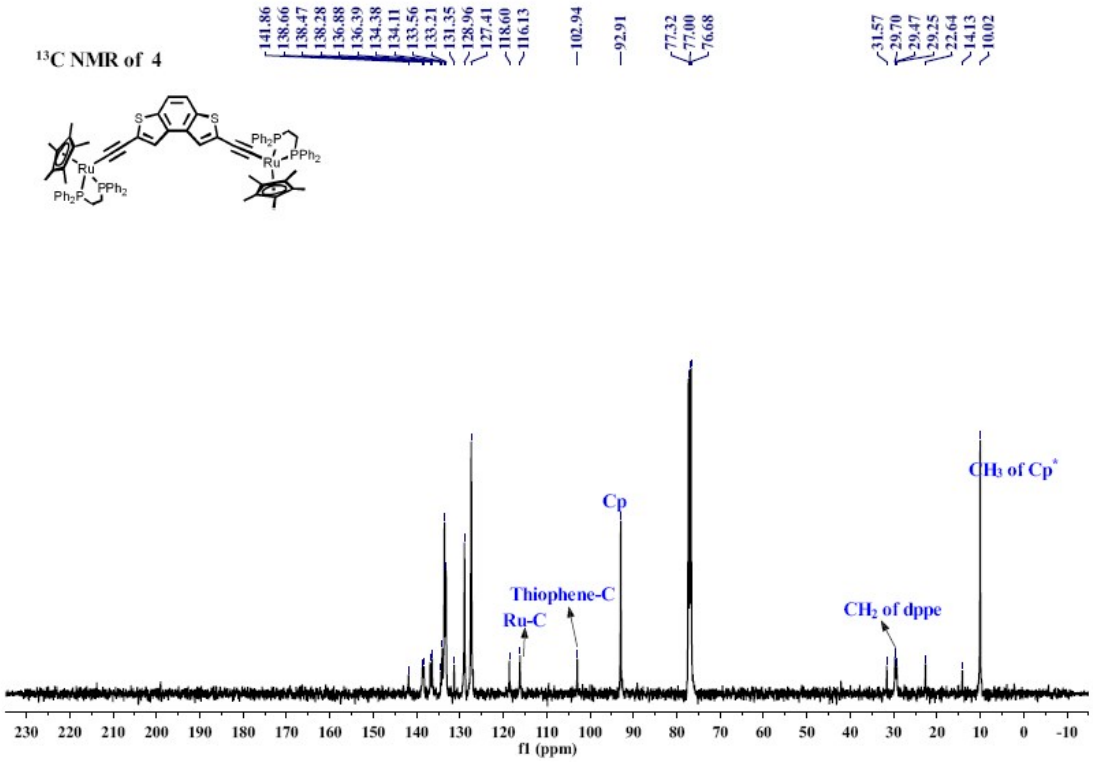

Figure S19. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **4**.

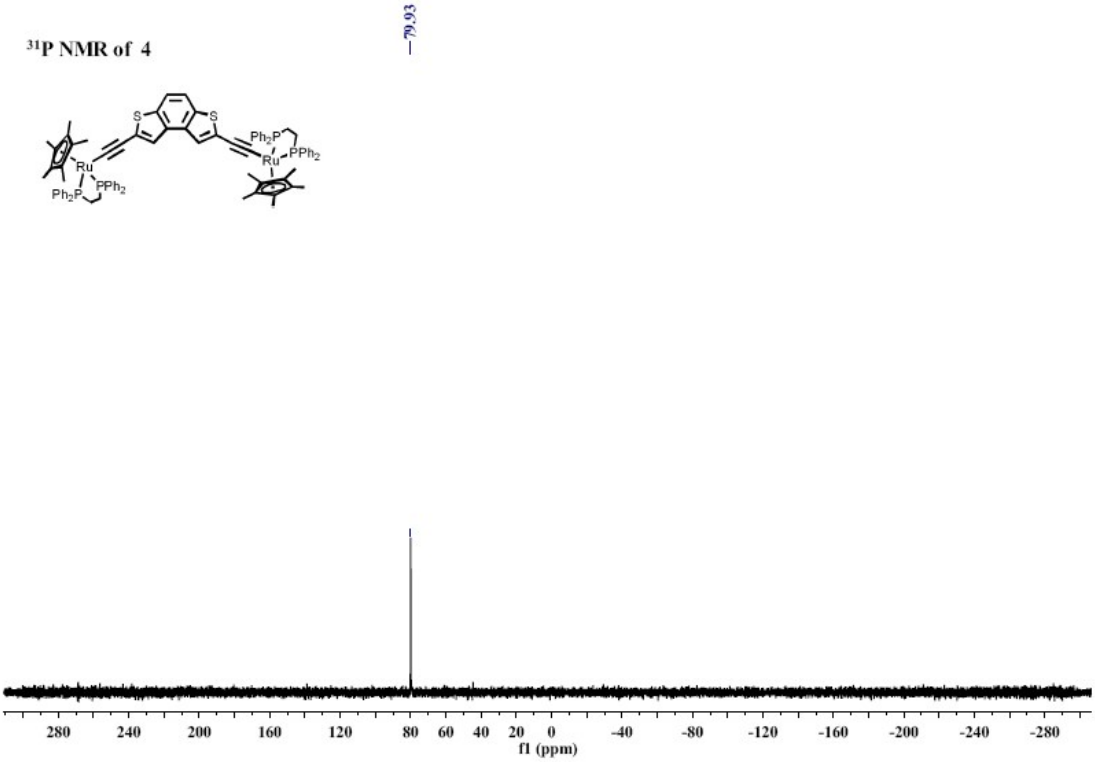

Figure S20. ^{31}P NMR spectrum (160 MHz, $CDCl_3$) of **4**.