Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Amphipathic Metal-Containing Macromolecules with Photothermal Properties

Xumin He,*[a] Xiehua He,[a] Shenyan Li,[a] Kaiyue Zhuo,[a] Weixiang Qin,[a] Shuyu Dong,[b] Jiangxi Chen,[b] Lei Ren,[b] Gang Liu,[c] and Haiping Xia*[a]

[a]State Key Laboratory of Physical Chemistry of Solid Surfaces and Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China.

[b]Department of Biomaterials and Department of Materials Science and Engineering, College of Materials, Xiamen University, Xiamen, 361005, China.

[c]State Key Laboratory of Molecular Vaccinology and Molecular Diagnostics, Center for Molecular Imaging and Translational Medicine, School of Public Health, Xiamen University, Xiamen 361005, China.

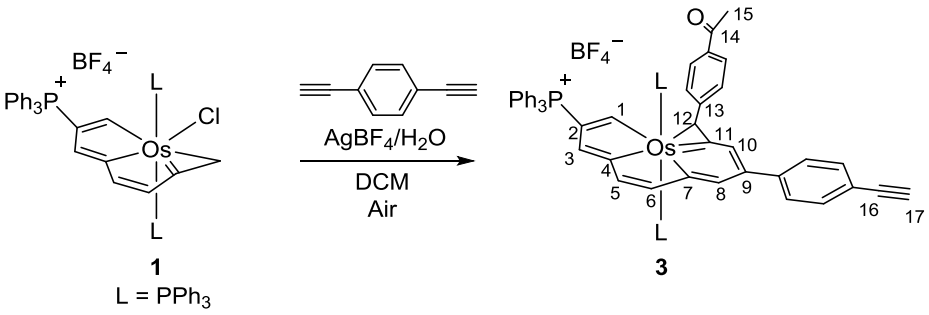
Contents

Experimental Procedures

1. General Procedures

All of the reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques unless otherwise stated. Complex **1**,[1] 1-azido-2-(2-methoxyethoxy)ethane,[2] and methoxypolyethylene glycol azides (mPEG-N_3)[3] were prepared according to the procedures reported in the literature. CuBr was suspended in EtOH for 2 h to remove $CuBr_2$ before use. Other commercial reagents were used without further purification. Nuclear magnetic resonance (NMR) spectroscopic experiments were performed using a Bruker AVIII-400 (^{1}H 400.1 MHz, ^{13}C 100.6 MHz, ^{31}P 162.0 MHz) at room temperature. ^{1}H and ^{13}C NMR chemical shifts (δ) are relative to tetramethylsilane, and ^{31}P NMR chemical shifts are relative to 85% H_3PO_4. The absolute values of the coupling constants are given in Hertz. Multiplicities are abbreviated as singlet (s), doublet (d), triplet (t), multiplet (m), and broad (br). High-resolution mass spectrometry (HRMS) experiments were performed using a Bruker En Apex Ultra 7.0T FT-MS. Elemental analysis data were collected using a Vario EL III elemental analyzer. Matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) spectra were collected using a Bruker MALDI-TOF mass spectrometer (2, 5-dihydroxybenzoic acid (DHB) was used as a matrix). The number-average molecular weight (Mn) was estimated by gel permeation chromatography (GPC, Agilent 1100 Series). The GPC system was equipped with a refractive-index detector and gel columns (Waters Styragel HR 3 and HR 1) maintained at 35 °C. Tetrahydrofuran was used as the eluent at a flow rate of 1.0 mL/min. The gel columns were calibrated with narrow-molecular-weight polystyrene standards (PDI ≤ 1.05, Shoko, Japan). Infrared (IR) spectra were recorded using a Nicolet 380. The UV-Vis spectra of complex **3** and Macromolecules **6-8** (5.0×10^{-2} mmol/mL) measured in dichloromethane at room temperature were obtained using a UV spectrophotometer (Shimadzu UV2550).

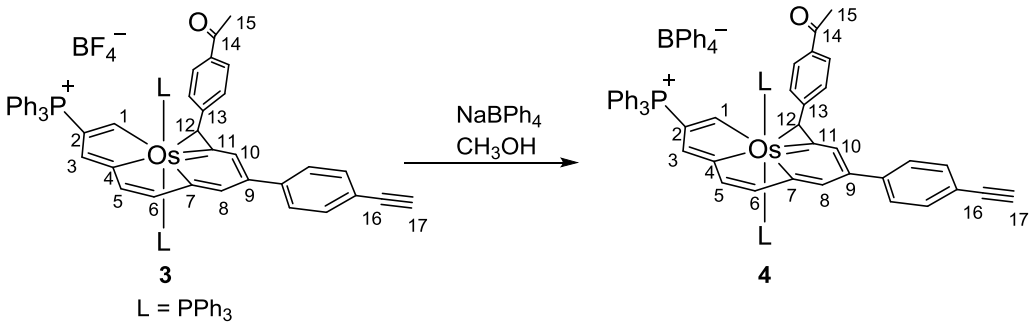
2. Synthesis Procedure and Analytical Data for Complex 3



To a mixture of 1, 4-diethynylbenzene (66 mg, 0.52 mmol), silver tetrafluoroborate (80 mg, 0.44 mmol) and complex **1** (200 mg, 0.17 mmol) was added 10 mL of wet dichloromethane. The reaction mixture was stirred at room temperature for 4 h to give a brown solution with a black precipitate. The black precipitate was removed by filtration, and the filtrate was reduced under vacuum to approximately 2 mL. The residue was loaded onto a neutral alumina (200-300 mesh) column and eluted with dichloromethane/methanol (v/v = 20/1). The yellow-brown band was collected, and the solvent was removed under vacuum. The resultant residue was washed with diethyl ether (5 mL × 3) to give a brown solid of complex **3**, which was dried under vacuum. Yield: 132 mg, 56%.

^{1}H NMR plus ^{1}H-^{13}C HSQC (400.1 MHz, $CDCl_3$): δ = 13.24 (d, J_{PH} = 21.6 Hz, 1H, H1), 8.71 (s, 1H, H3), 8.06 (s, 1H, H8), 7.83 (s, 1H, H10), 7.64 (s, 1H, H5), 7.57 (s, 1H, H6), 6.68 (dd, J_{PH} = 13.9, 1H, H12), 3.32 (s, 1H, H17), 2.49 (s, 3H, H15), 8.04-5.74 ppm (53H, other aromatic protons). ^{31}P{^{1}H} NMR (162.0 MHz, $CDCl_3$): δ = 9.71 (t, J_{PP} = 6.5 Hz, C*P*Ph_3), -9.50 (dd, J_{PP} = 253.5 Hz, J_{PP} = 6.5 Hz, Os*P*Ph_3), -18.55 (dd, J_{PP} = 253.5 Hz, J_{PP} = 6.5 Hz, Os*P*Ph_3). ^{13}C{^{1}H} NMR plus DEPT-135, ^{1}H-^{13}C HMBC and ^{1}H-^{13}C HSQC (100.6 MHz, $CDCl_3$): δ = 231.0 (t, J_{PC} = 7.5 Hz, C7), 217.4 (br, C11), 207.9 (br, C1), 201.0 (dt, J_{PC} = 25.8 Hz, J_{PC} = 6.2 Hz, C4), 197.7 (s, C14), 164.2 (s, C6), 160.2 (s, C5), 155.9 (s, C13), 142.8 (s, C9), 137.2 (d, J_{PC} = 24.8 Hz, C3), 128.8 (s, C8), 120.7 (d, J_{PC} = 87.0 Hz, C2), 114.3 (s, C10), 83.7 (s, C17), 79.8 (s, C16), 26.9 (s, C15), 15.5 (s, C12), 134.5-124.7 ppm (other aromatic carbons). Elemental analysis calcd (%) for $C_{82}H_{64}BF_4OP_3Os$: C 68.62, H 4.49; found: C 68.40, H 4.68. HRMS (ESI): m/z calcd for $[C_{82}H_{64}OOsP_3]^+$, 1349.3779; found 1349.3782. FT-IR (cm^{-1}): 3295 (≡C-H).

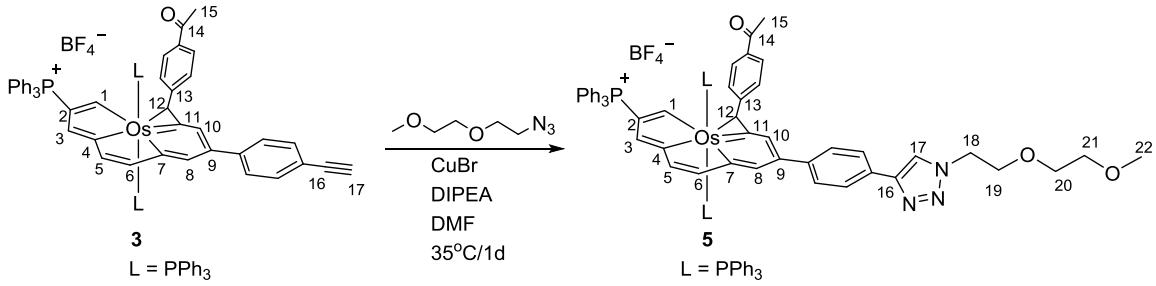
3. Synthesis Procedure and Analytical Data for Complex 4



$NaBPh_4$ (29 mg, 0.084 mmol) was dissolved in 0.5 mL of CH_3OH, and the resultant solution was slowly injected into a solution of complex **3** (100 mg, 0.07 mmol) in CH_3OH (3 mL). The reaction mixture was stirred at room temperature for 2 min to give a brown suspension. The brown solid of complex **4** was collected by filtration, washed with CH_3OH (3 mL × 3), and then dried under vacuum. Yield: 93 mg, 85%.

^{1}H NMR plus ^{1}H-^{13}C HSQC (400.1 MHz, $CDCl_3$): δ = 13.21 (d, J_{PH} = 22.5 Hz, 1H, H1), 8.67 (s, 1H, H3), 8.05 (s, 1H, H8), 6.68 (s, 1H, H12), 3.30 (s, 1H, H17), 2.46 (s, 3H, H15), 8.04-5.73 ppm (73H, other aromatic protons). ^{31}P{^{1}H} NMR (162.0 MHz, $CDCl_3$): δ = 9.57 (t, J_{PP} = 6.5 Hz, C*P*Ph_3), -9.82 (dd, J_{PP} = 253.5 Hz, J_{PP} = 6.5 Hz, Os*P*Ph_3), -18.72 (dd, J_{PP} = 253.5 Hz, J_{PP} = 6.5 Hz, Os*P*Ph_3). ^{13}C{^{1}H} NMR plus DEPT-135, ^{1}H-^{13}C HMBC and ^{1}H-^{13}C HSQC (100.6 MHz, $CDCl_3$): δ = 231.7 (t, J_{PC} = 7.5 Hz, C7), 217.4 (t, J_{PC} = 5.1 Hz, C11), 207.9 (br, C1), 201.0 (dt, J_{PC} = 25.8 Hz, J_{PC} = 6.2 Hz, C4), 197.7 (s, C14), 164.2 (s, C6), 160.2 (s, C5), 155.9 (s, C13), 142.8 (s, C9), 137.2 (d, $J_{P\text{-}C}$ = 24.8 Hz, C3), 128.6 (s, C8), 120.7 (d, J_{PC} = 87.0 Hz, C2), 114.3 (s, C10), 83.7 (s, C17), 79.8 (s, C16), 26.8 (s, C15), 15.6 (s, C12), 134.5-124.7 ppm (other aromatic carbons). Elemental analysis calcd (%) for $C_{106}H_{84}BOOsP_3$: C 76.34, H 5.08; found: C 76.00, H 5.16.

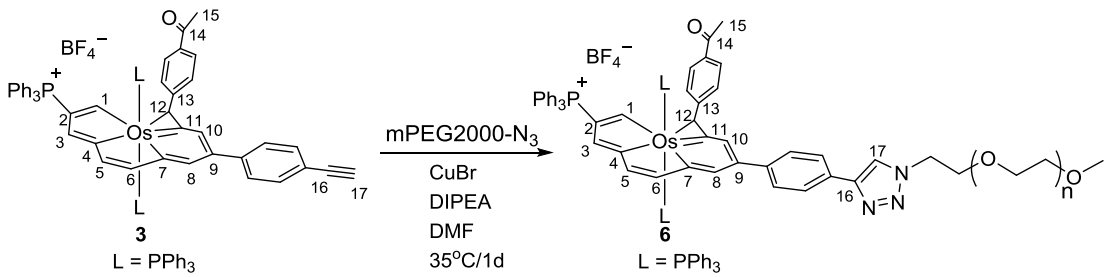
4. Synthesis Procedure and Analytical Data for Complex 5



N,*N*-Diisopropylethylamine (DIPEA) (14 μL, 0.085 mmol) was added to a mixture of complex **3** (200 mg, 0.14 mmol), CuBr (4 mg, 0.028 mmol) and 1-azido-2-(2-methoxyethoxy)ethane (61 mg, 0.42 mol) in *N*,*N*-dimethylformamide (DMF) (3 mL). The reaction mixture was stirred at 35 °C for 1 d to give a brown suspension. CuBr was removed by filtration, and diethyl ether (15 mL) was added to the filtrate to give a yellow-brown precipitate, which was collected by filtration. The yellow-brown precipitate was loaded onto a polystyrene-gel column (Bio-Beads TM S-X3, 200-400 mesh) and eluted by chloroform. The yellow-brown band was collected, and the solvent was removed under vacuum to give a yellow-brown solid of complex **5**, which was washed with diethyl ether (5 mL × 3) and dried under vacuum. Yield: 153 mg, 69%.

^{1}H NMR plus ^{1}H-^{13}C HSQC (400.1 MHz, $CDCl_3$): δ = 13.20 (d, J_{PH} = 20.6 Hz, 1H, H1), 8.69 (s, 1H, H3), 8.42 (s, 1H, H17), 7.91 (s, 1H, H10), 7.64 (s, 1H, H5), 7.57 (s, 1H, H6), 6.58 (s, 1H, H12), 4.70 (t, 2H, H18), 4.02 (t, 2H, H20), 4.48 (t, 2H, H19), 3.70 (t, 2H, H21), 3.41 (s, 3H, H22), 2.49 (s, 3H, H15), 8.26-5.77 ppm (53H, other aromatic protons). ^{31}P{^{1}H} NMR (162.0 MHz, $CDCl_3$): δ = 9.61 (t, J_{PP} = 6.5 Hz, C*P*Ph_3), -9.24 (dd, J_{PP} = 253.5 Hz, J_{PP} = 6.5 Hz, Os*P*Ph3), -18.54 (dd, J_{PP} = 253.5 Hz, J_{PP} = 6.5 Hz, Os*P*Ph_3). ^{13}C{^{1}H} NMR plus DEPT-135, ^{1}H-^{13}C HMBC and ^{1}H-^{13}C HSQC (100.6 MHz, $CDCl_3$): δ = 231.4 (t, J_{PC} = 7.3 Hz, C7), 217.3 (t, J_{PC} = 5.1 Hz, C11), 207.9 (br, C1), 200.9 (br, C4), 197.7 (s, C14), 163.9 (s, C6), 160.1 (s, C5), 159.9 (s, C16), 155.9 (s, C13), 147.5 (s, C17), 141.9 (s, C9), 137.4 (d, J_{PC} = 23.5 Hz, C3), 128.8 (s, C8), 122.3 (s, C18), 120.8 (d, J_{PC} = 88.2 Hz, C2), 114.6 (s, C10), 72.18 (s, C21), 70.89 (s, C19), 69.83 (s, C20), 59.48 (s, C22), 50.89 (s, C18), 26.9 (s, C15), 15.5 (s, C12), 134.5-126.0 ppm (other aromatic carbons). Elemental analysis calcd (%) for $C_{87}H_{75}BF_4N_3O_3P_3Os$: C 66.11, H 4.78, N 2.66. Found: C 65.80, H 4.48, N 2.52. HRMS (ESI): m/z calcd for $[C_{87}H_{75}N_3O_3P_3Os]^+$, 1494.4630; found 1494.4643.

5. Synthesis Procedure and Analytical Data for Macromolecule 6



DIPEA (8 μL, 0.046 mmol) was added to a mixture of complex **3** (129 mg, 0.090 mmol), CuBr (2 mg, 0.014 mmol) and mPEG2000-N_3 (150 mg, 0.075 mol) in DMF (4 mL). The reaction mixture was stirred at 35 °C for 1 d to give a yellow-brown suspension. CuBr was removed by filtration, and diethyl ether (15 mL) was added to the filtrate to give a yellow-brown precipitate, which was collected by filtration. The yellow-brown precipitate was loaded onto a polystyrene-gel column (Bio-Beads TM S-X3, 200-400 mesh) and eluted

with chloroform. The yellow-brown band was collected, and the solvent was removed under vacuum to give a yellow-brown solid of macromolecule **6**, which was washed with diethyl ether (5 mL × 3) and dried under vacuum. Yield: 167 mg, 65%.

^{1}H-NMR (400.1 MHz, $CDCl_3$): δ = 13.10 (d, J_{PH} = 21.5 Hz, H1), 8.60 (s, H3), 8.27 (s, H17), 2.41 (s, H15), 3.57 (s, -OCH_2CH_2O-). ^{31}P{^{1}H} NMR (162.0 MHz, $CDCl_3$): δ = 9.61 (t, J_{PP} = 6.5 Hz, C*P*Ph_3), -9.50 (dd, apparent d, J_{PP} = 254.5 Hz, Os*P*Ph_3), -18.54 (dd, apparent d, J_{PP} = 254.5 Hz, Os*P*Ph_3). MALDI-TOF-MS: molecular weight distribution ranged from *ca.* 2700 Da to 3708 Da.

6 Synthetic Procedure and Analytical Data for Macromolecule 7

The synthetic procedure for macromolecule **7** was similar to that for macromolecule **6**. Yield: 185 mg, 67%. ^{1}H-NMR (400.1 MHz, $CDCl_3$): δ = 13.13 (d, J_{PH} = 20.4 Hz, H1), 8.61 (s, H3), 8.28 (s, H17), 2.41 (s, H15), 3.58 (s, -OCH_2CH_2O-). ^{31}P{^{1}H} NMR (162.0 MHz, $CDCl_3$): δ = 9.91 (t, J_{PP} = 6.5 Hz, C*P*Ph_3), -9.40 (dd, J_{PP} = 254.5 Hz, $J_{P\text{-}P}$ = 6.5 Hz, Os*P*Ph_3), -18.34 (dd, J_{PP} = 254.5 Hz, J_{PP} = 6.5 Hz, Os*P*Ph_3). $M_{n,GPC}$: 7816.6 g/mol; M_w/M_n: 1.0271. MALDI-TOF-MS: molecular weight distribution ranged from *ca.* 5200 Da to 7050 Da.

7. Synthetic Procedure and Analytical Data for Macromolecule 8

The synthetic procedure of macromolecule **8** was similar to that for macromolecule **6**. Yield: 187 mg, 63%. ^{1}H-NMR (400.1 MHz, $CDCl_3$): δ = 13.26 (br, H1), 8.64 (s, H3), 8.08 (s, H17), 3.56 (br, -OCH_2CH_2O-). ^{31}P{^{1}H} NMR (162.0 MHz, $CDCl_3$): δ = 9.42 (s, C*P*Ph_3), -9.67 (d, J_{PP} = 254.5 Hz, Os*P*Ph_3), -18.68 (d, J_{PP} = 254.5 Hz, Os*P*Ph_3). $M_{n,GPC}$: 16154 g/mol; M_w/M_n: 1.0108. MALDI-TOF-MS: molecular weight distribution ranged from *ca.* 8860 Da to 11970 Da.

8. Water Solubility of Macromolecules 6-8

Table S1. Water solubility of Macromolecules **6**-**8**.

Macromolecule	Solubility	Color
6	1 mg/mL	Light-yellow
7	6 mg/mL	Yellow
8	15 mg/mL	Brown

9. X-ray Crystallographic Analysis

A crystal suitable for X-ray diffraction of complex 4 was grown from a solution of dichloroethane layered with diethyl ether. Single-crystal X-ray diffraction data were collected on a Rigaku R-AXIS SPIDER IP CCD area detector using graphite-monochromated CuKα radiation (λ = 1.54184 Å). The data were corrected for absorption effects using the multi-scan technique. The structures were solved by the Patterson function, completed by subsequent difference Fourier map calculations, and refined by full-matrix least-squares on F^2 using the Olex2 program package. All of the non-hydrogen atoms were refined anisotropically unless otherwise stated. The hydrogen atoms were placed at their idealized positions and refined using a riding model unless otherwise stated. The solvent molecules CH_2Cl_2, phenyl groups on PPh_3 complex **4** are disordered and were refined using suitable restraints. The X-ray crystal structures have been deposited in the Cambridge Crystallographic Data Centre (CCDC) under deposition number CCDC-1535925.

Table S2 Crystal data for complex **4**

	4·3CH_2Cl_2
Empirical formula	$C_{109}H_{90}BCl_6OOsP_3$
Formula weight	1922.43
Temperature/K	173
Crystal system	triclinic
Space group	P-1
a/Å	13.8163(5)
b/Å	18.0472(5)
c/Å	18.3229(6)
α/°	79.946(3)
β/°	89.601(3)
γ/°	82.370(3)
Volume/$Å^3$	4458.2(2)
Z	2
$\rho_{calc}g/cm^3$	1.432
μ/mm^{-1}	5.262
F(000)	1960.0
Crystal size/mm^3	0.1 × 0.1 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.38 to 124.28
Index ranges	-15 ≤ h ≤ 15, -18 ≤ k ≤ 20, -19 ≤ l ≤ 20
Reflections collected	41288
Independent reflections	13981 [R_{int} = 0.0446, R_{sigma} = 0.0498]
Data/restraints/parameters	13981/0/1137
Goodness-of-fit on F^2	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0358, wR_2 = 0.0887
Final R indexes [all data]	R_1 = 0.0397, wR_2 = 0.0917
Largest diff. peak/hole / e $Å^{-3}$	1.02/-1.35

10. Supplementary Figures

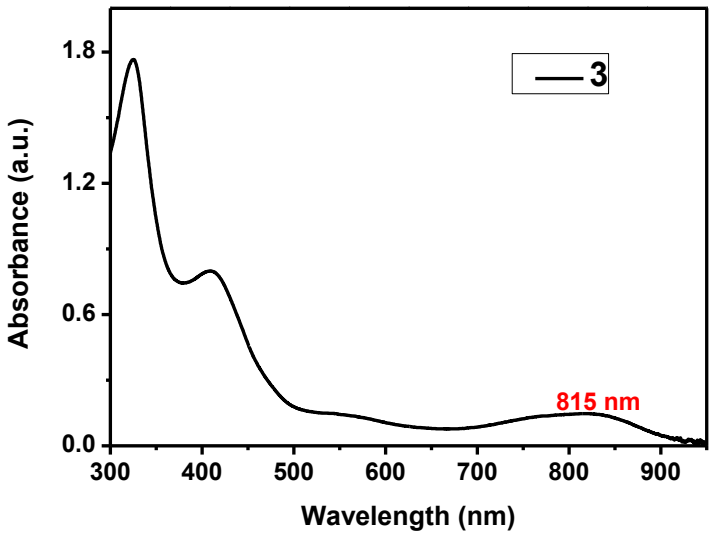


Figure S1 UV/Vis absorption spectrum of complex **3**.

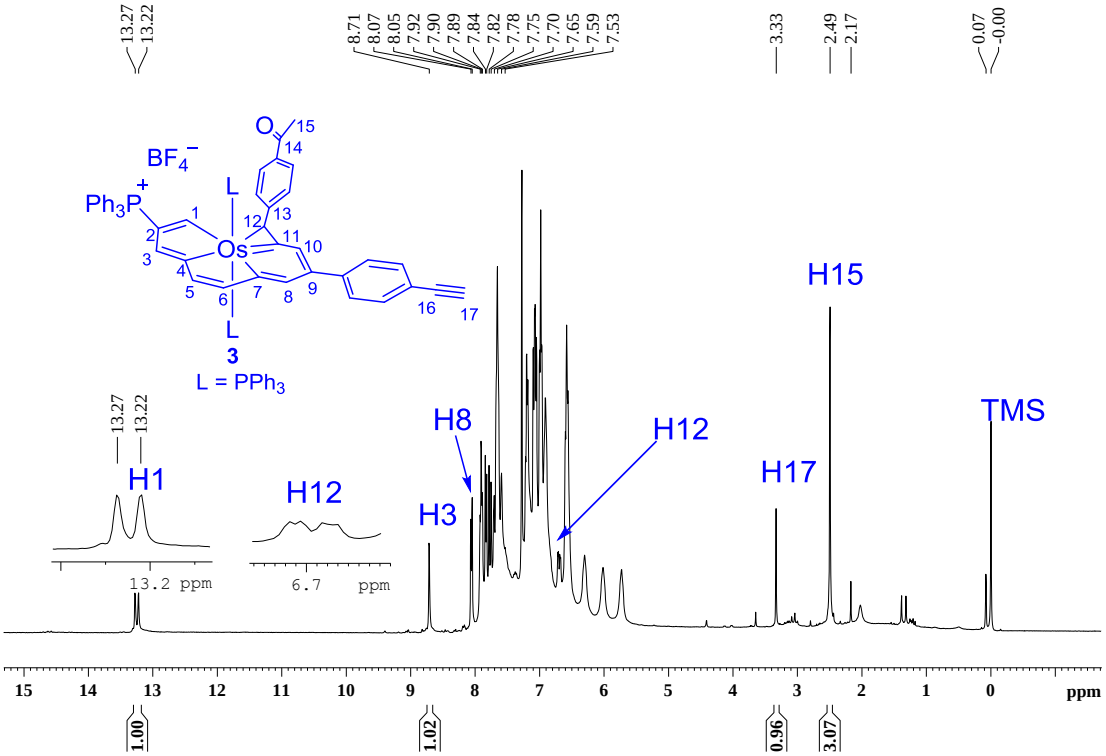


Figure S2 The ^{1}H NMR (400.1 MHz, $CDCl_3$) spectrum of complex **3**.

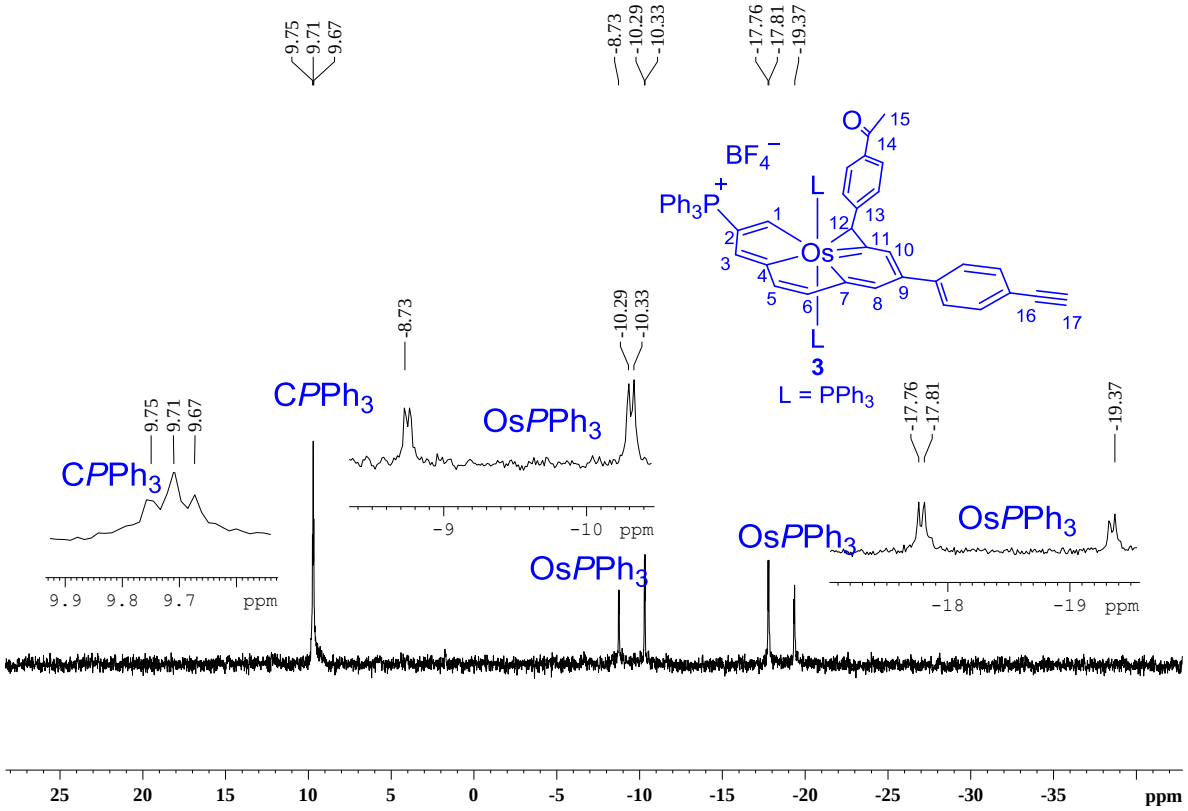


Figure S3 The $^{31}P\{^{1}H\}$ NMR (162.0 MHz, $CDCl_3$) spectrum of complex **3**.

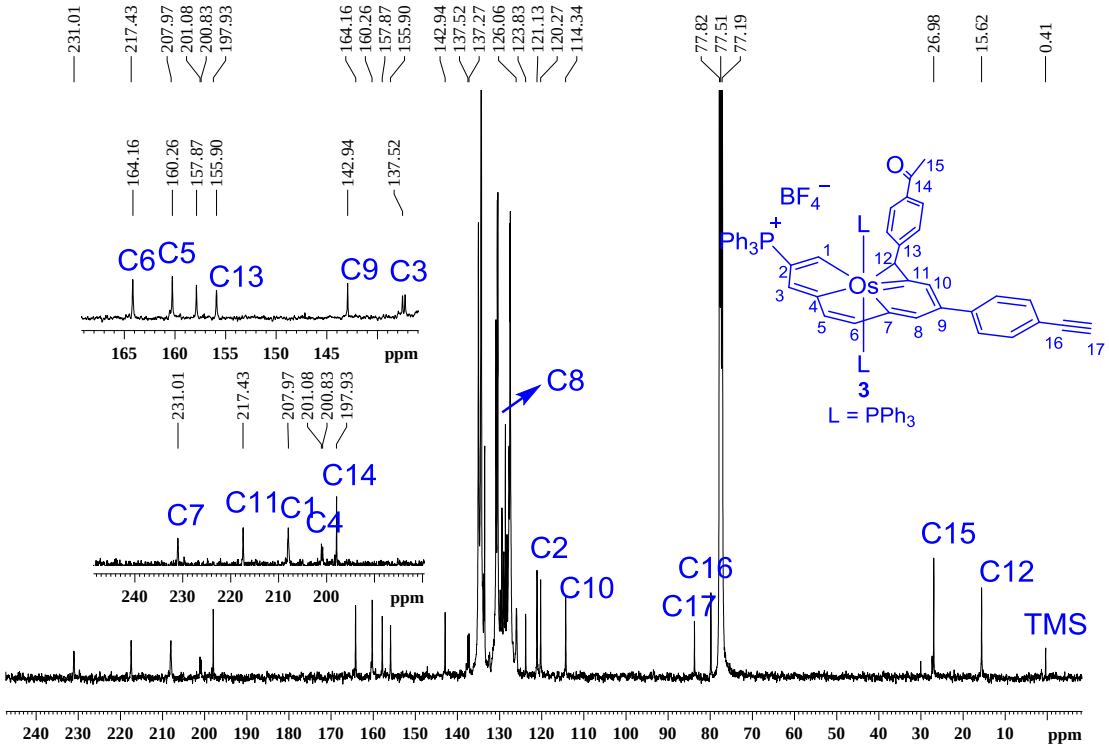


Figure S4 The $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$) spectrum of complex **3**.

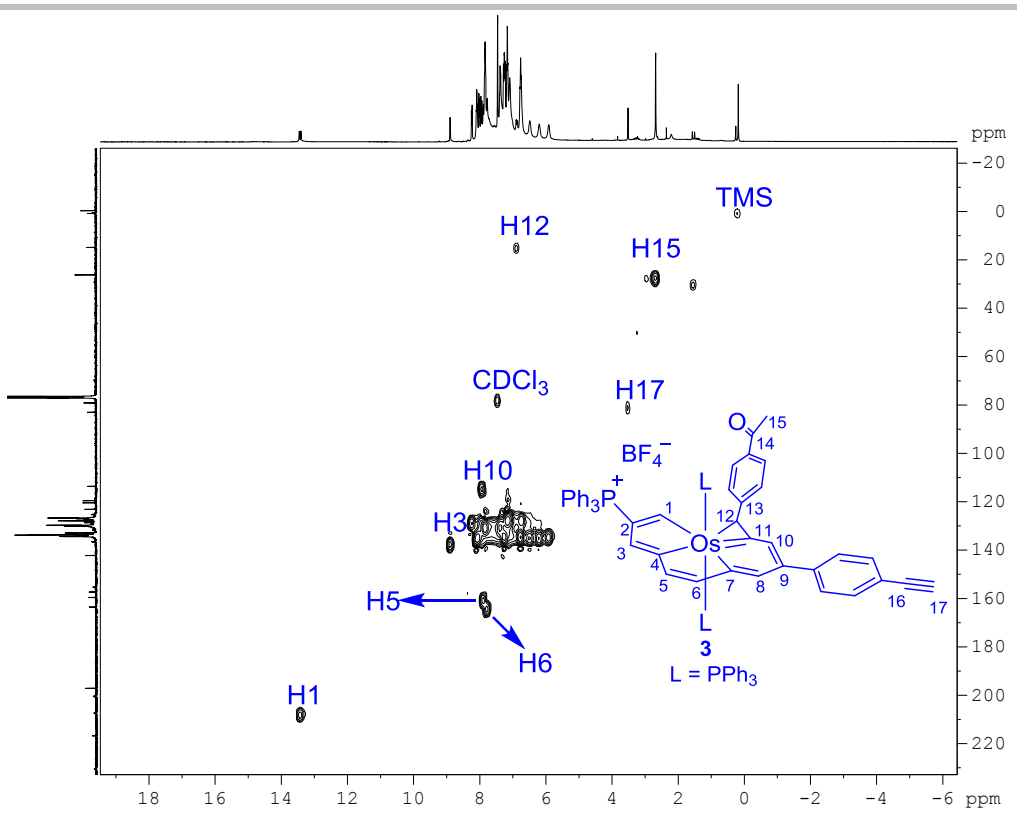


Figure S5 ^{1}H-^{13}C HSQC (100.6 MHz, $CDCl_3$) spectrum of complex **3**.

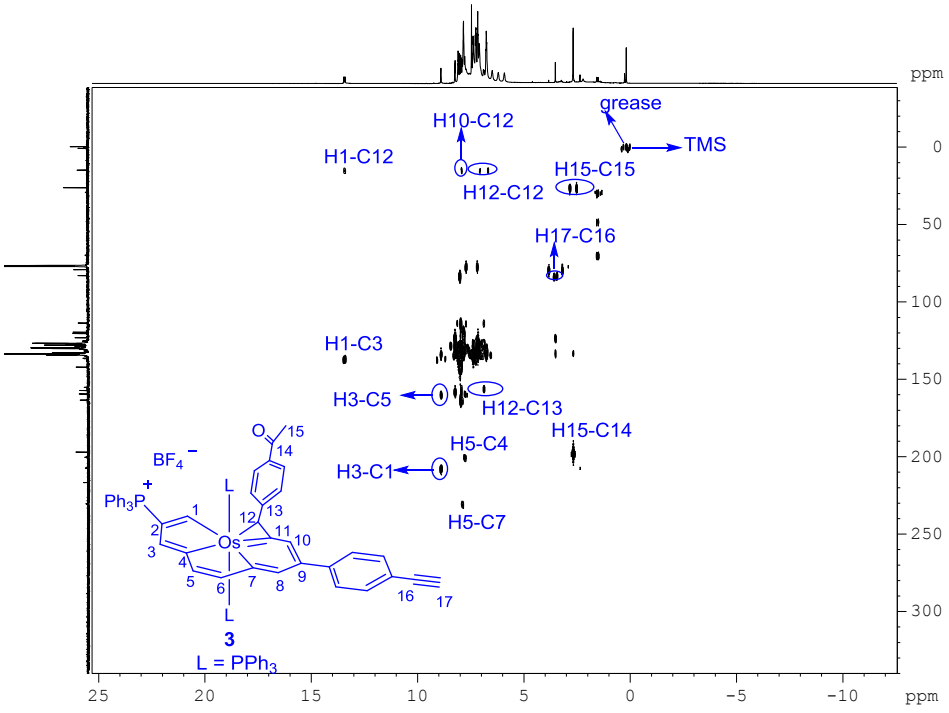


Figure S6 ^{1}H-^{13}C HMBC (100.6 MHz, $CDCl_3$) spectrum of complex **3**.

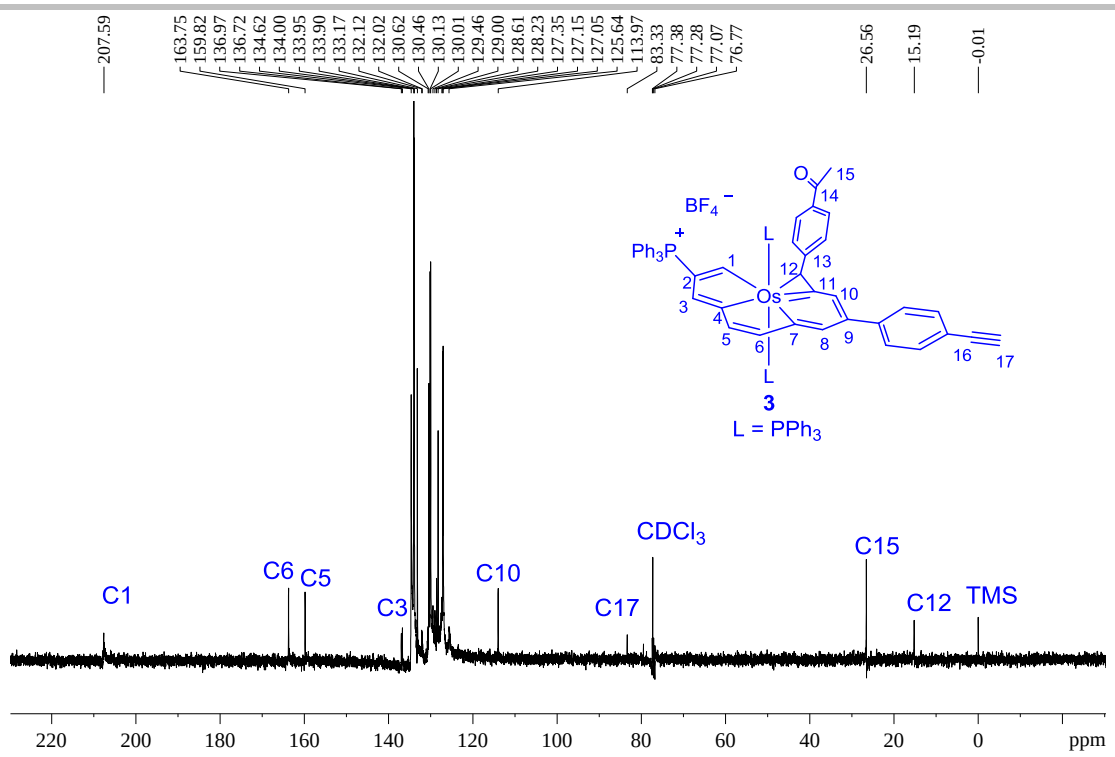


Figure S7 DEPT-135 spectrum (100.6 MHz, $CDCl_3$) of complex **3**.

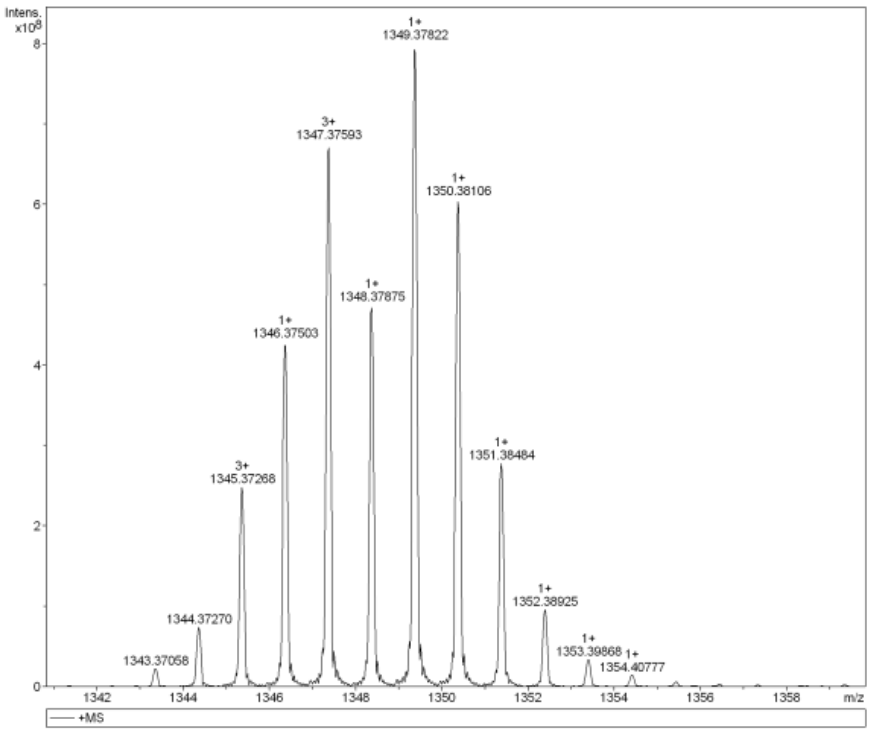


Figure S8. ESI-MS spectrum of $[\mathbf{3}]^+$ measured in methanol.

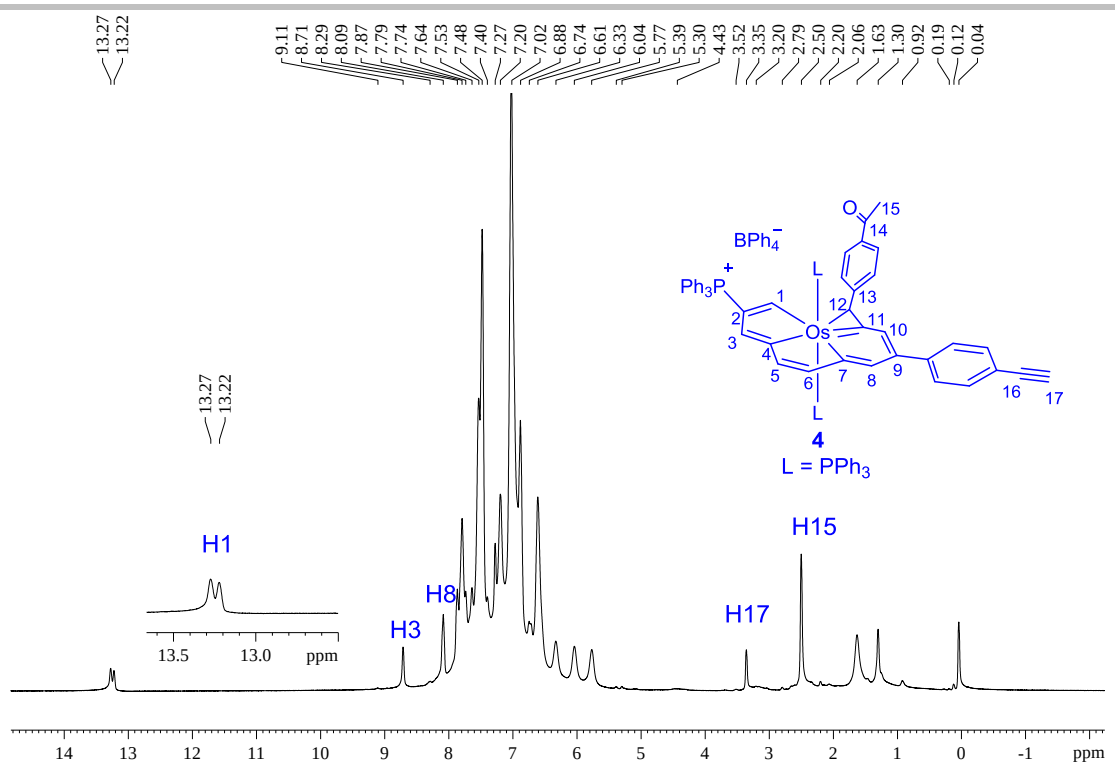


Figure S9 The ^{1}H NMR (400.1 MHz, $CDCl_3$) spectrum of complex **4**.

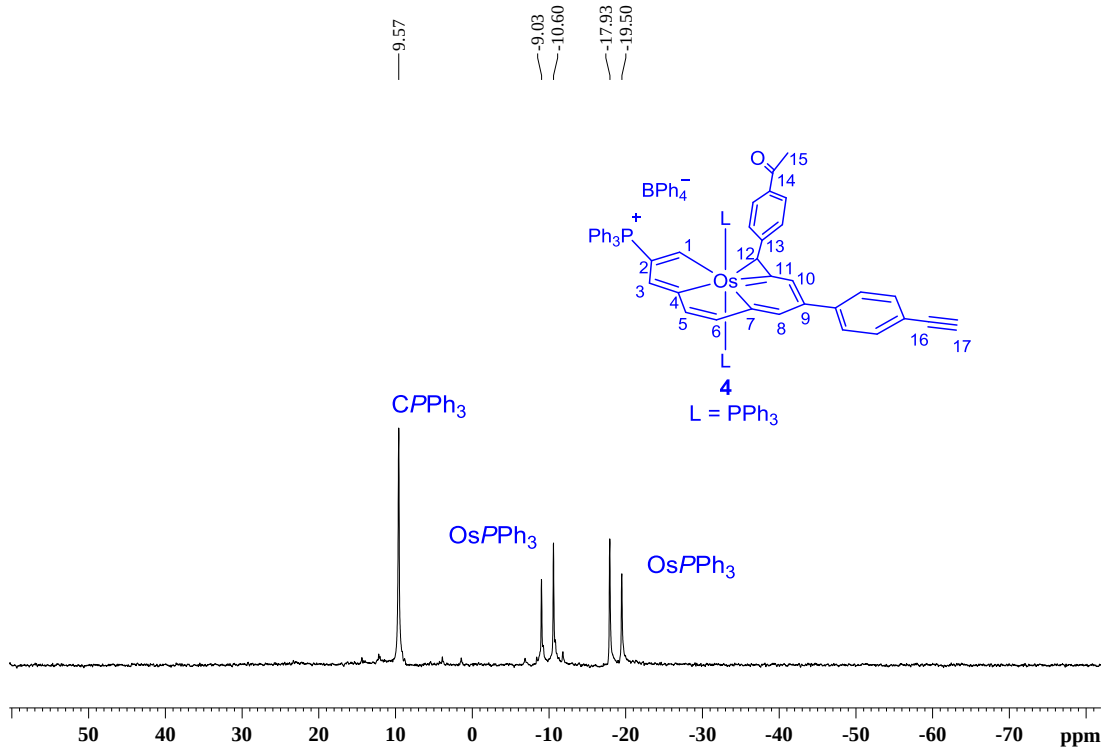


Figure S10 The $^{31}P\{^{1}H\}$ NMR (162.0 MHz, $CDCl_3$) spectrum of complex **4**.

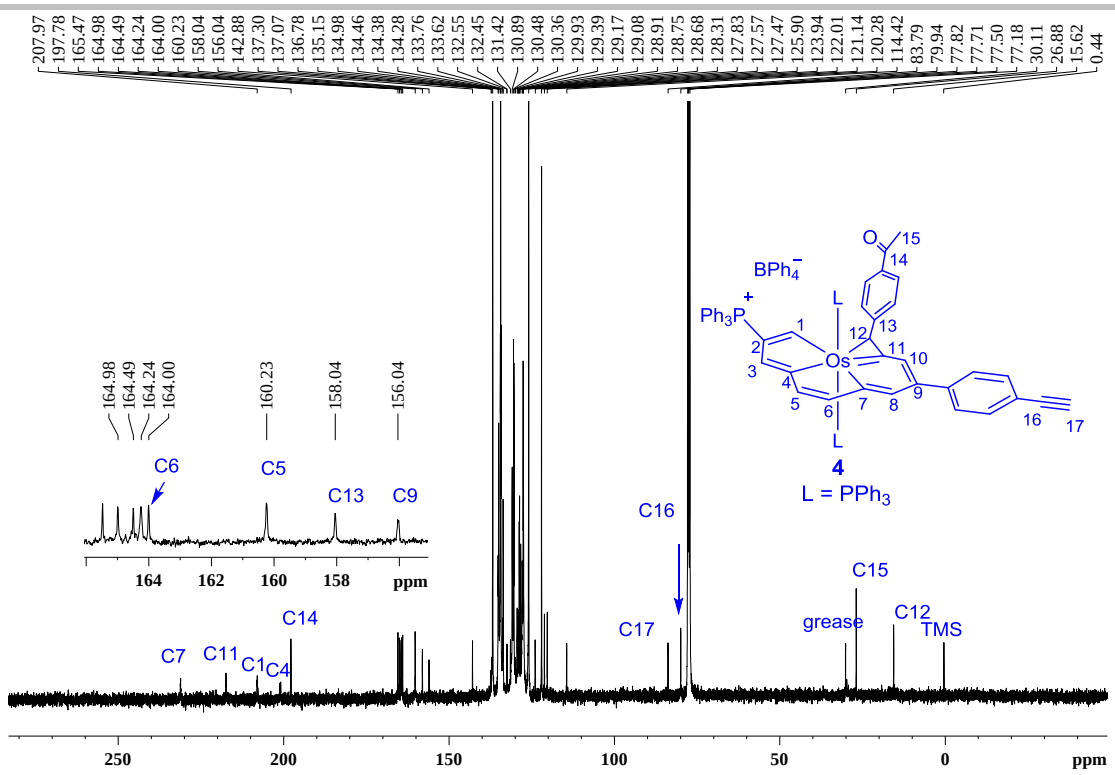


Figure S11 The $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$) spectrum of complex **4**.

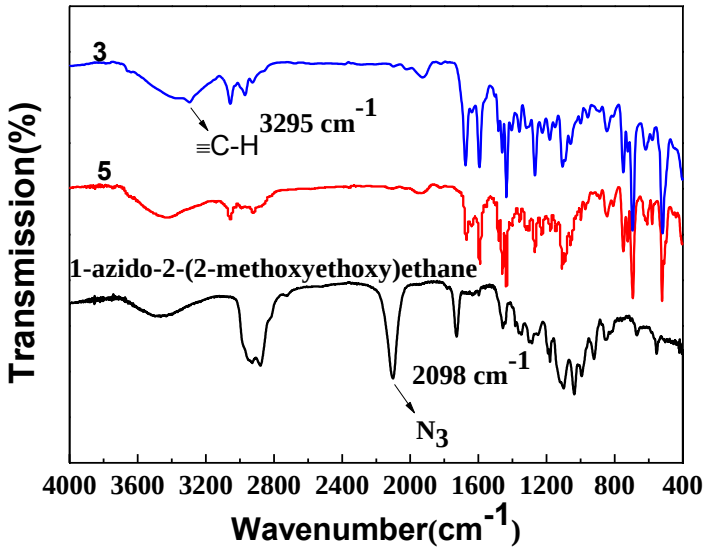


Figure S12 The IR (KBr) spectra of **3**, **5** and **1-azido-2-(2-methoxyethoxy)ethane**.

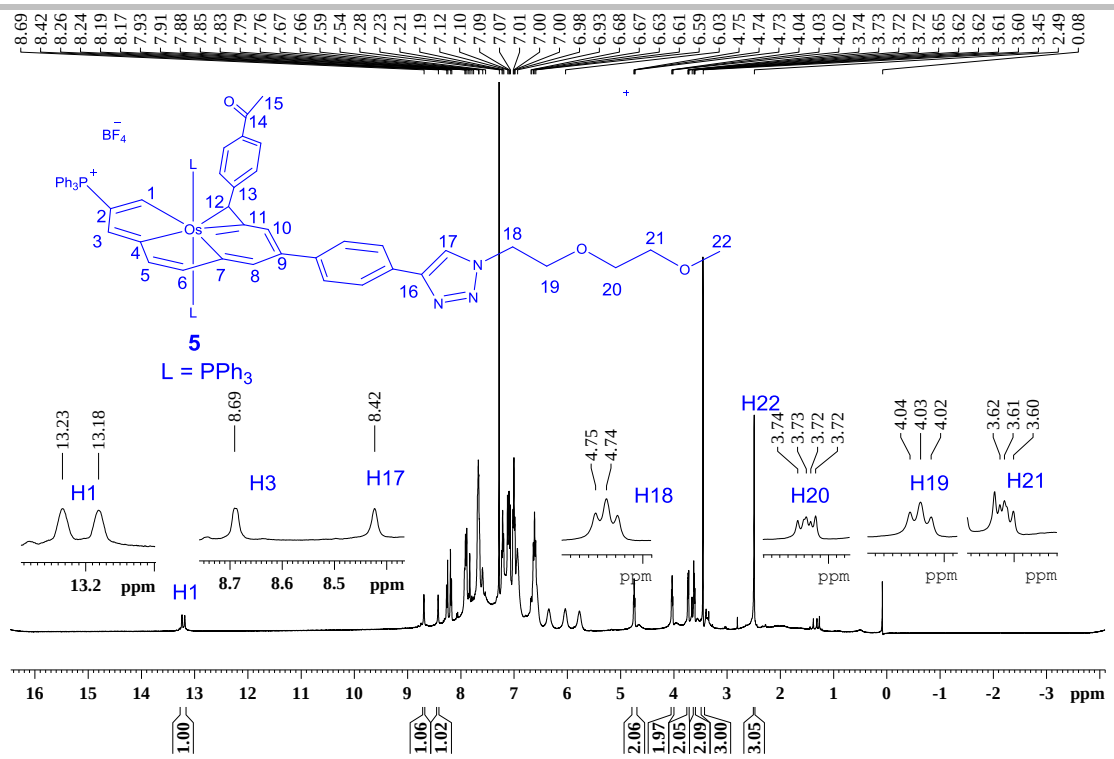


Figure S13 The ^{1}H NMR (400.1 MHz, $CDCl_3$) spectrum of complex **5**.

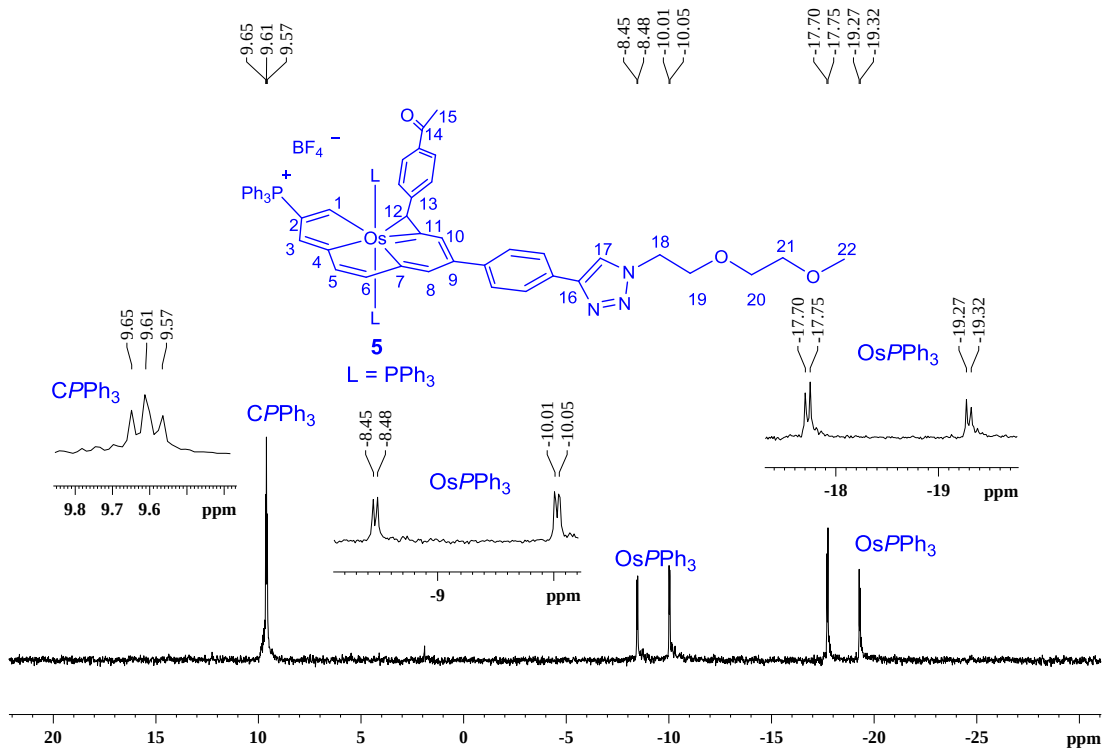


Figure S14 The $^{31}P\{^{1}H\}$ NMR (162.0 MHz, $CDCl_3$) spectrum of complex **5**.

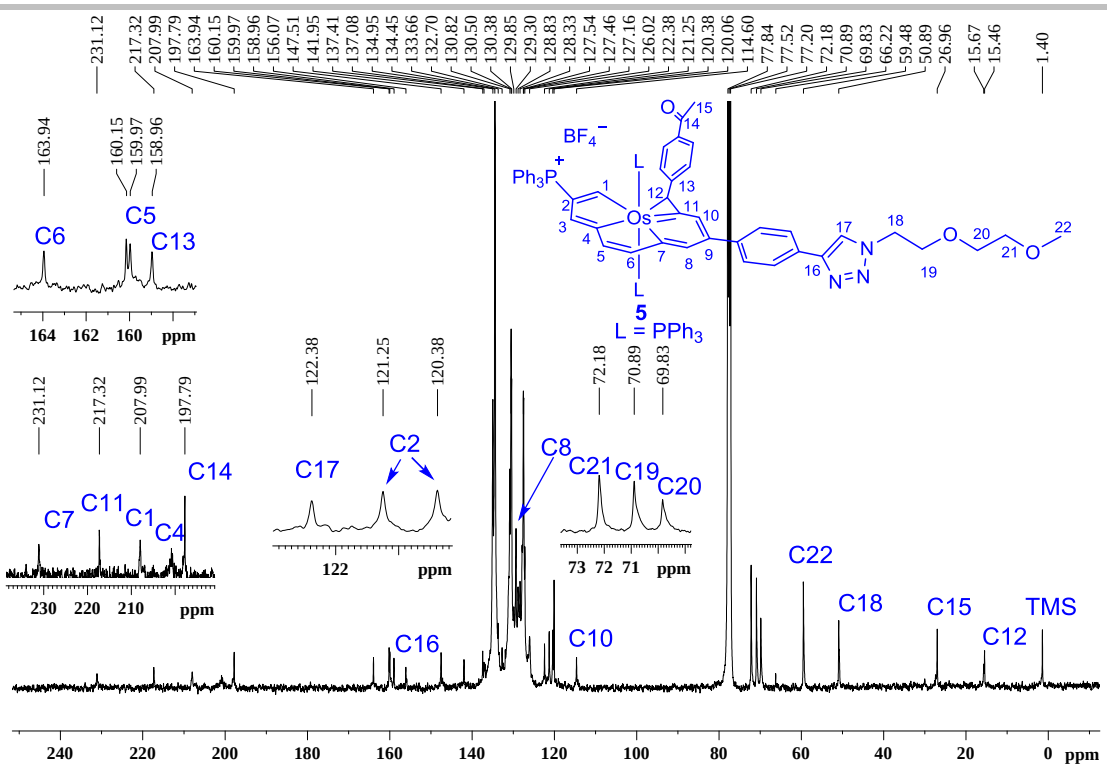


Figure S15 The $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$) spectrum of complex **5**.

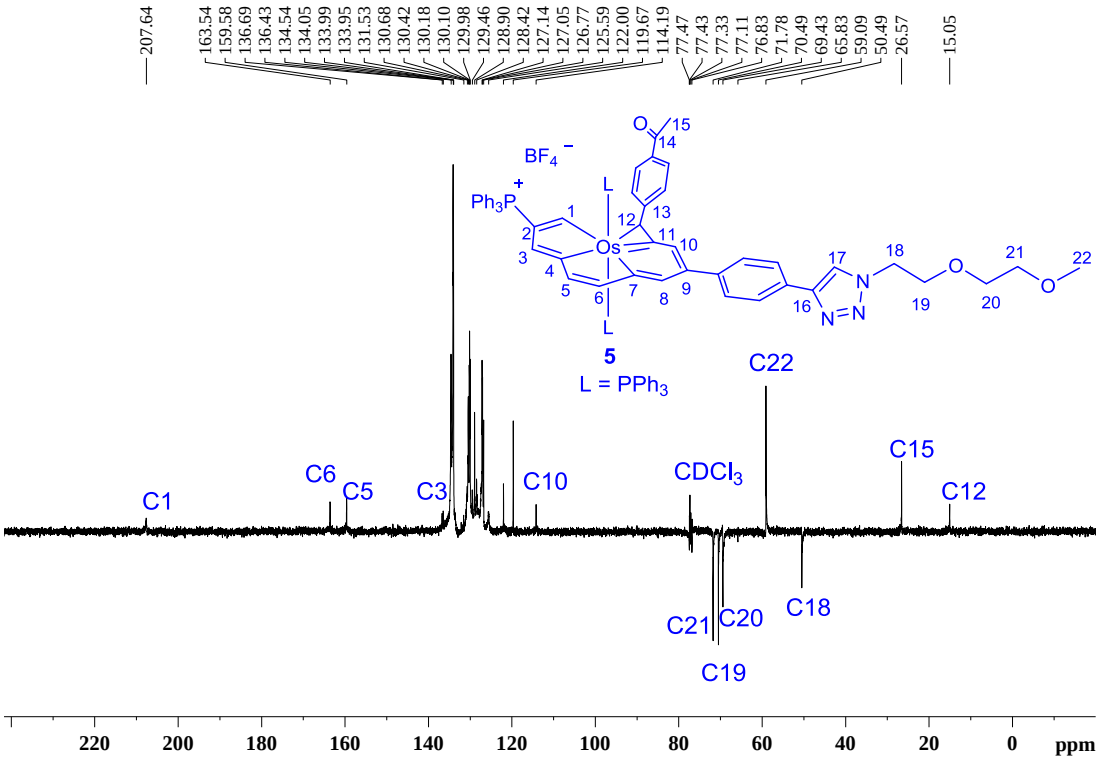


Figure S16 DEPT-135 spectrum (100.6 MHz, $CDCl_3$) of complex **5**.

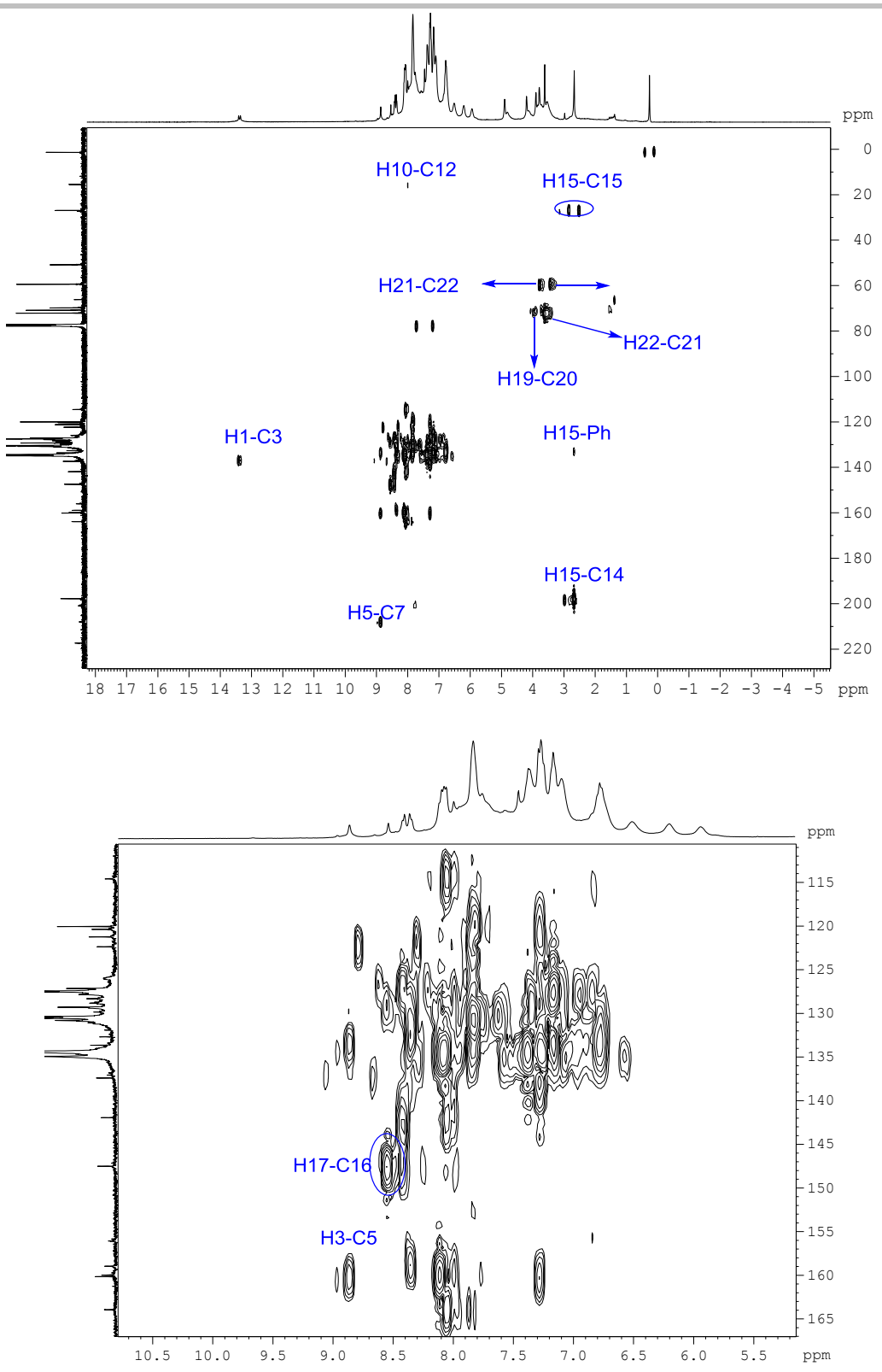


Figure S17 ^{1}H-^{13}C HMBC (100.6 MHz, $CDCl_3$) spectrum of complex **5**.

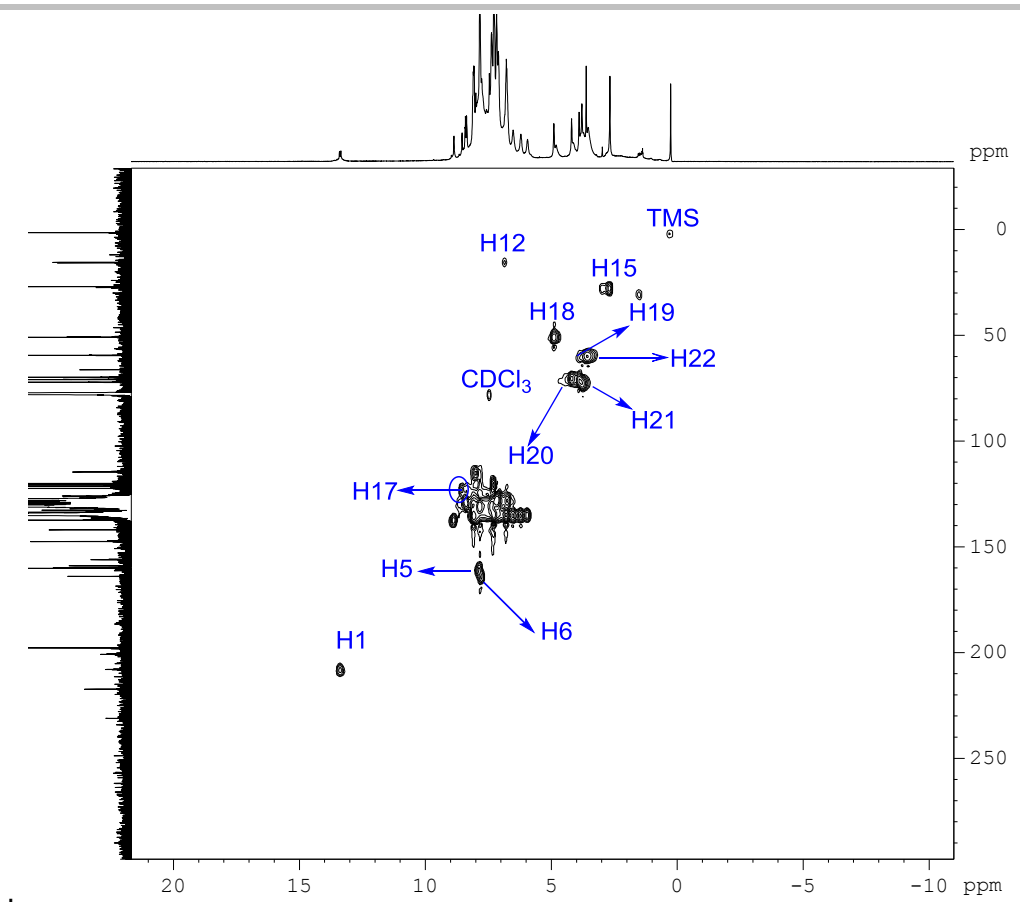


Figure S18 ^{1}H-^{13}C HSQC (100.6 MHz, $CDCl_3$) spectrum of complex **5**.

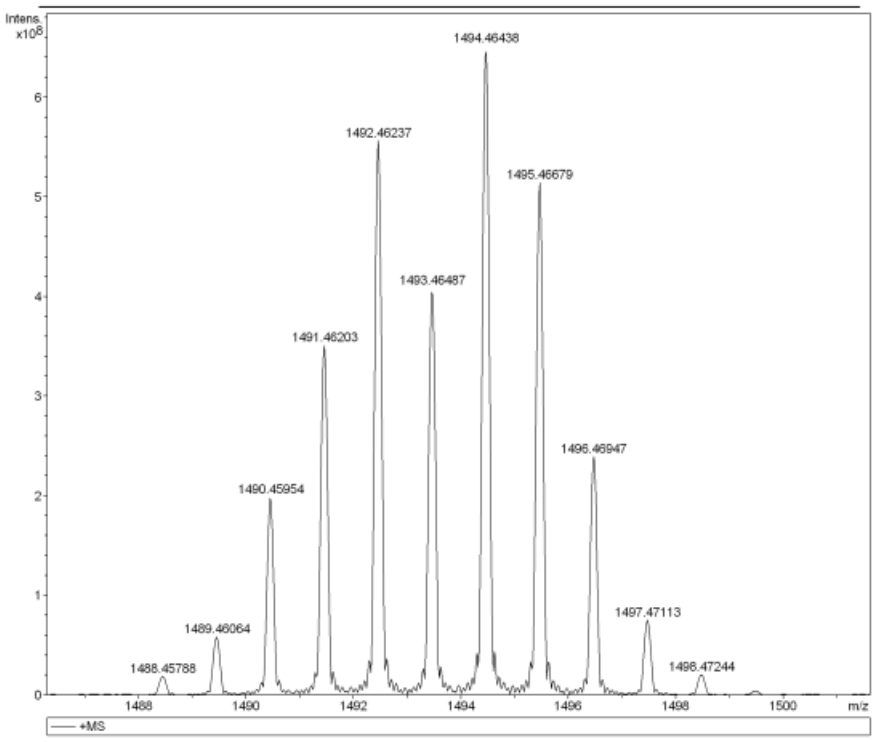


Figure S19 ESI-MS spectrum of [**5**]$^{+}$ measured in methanol.

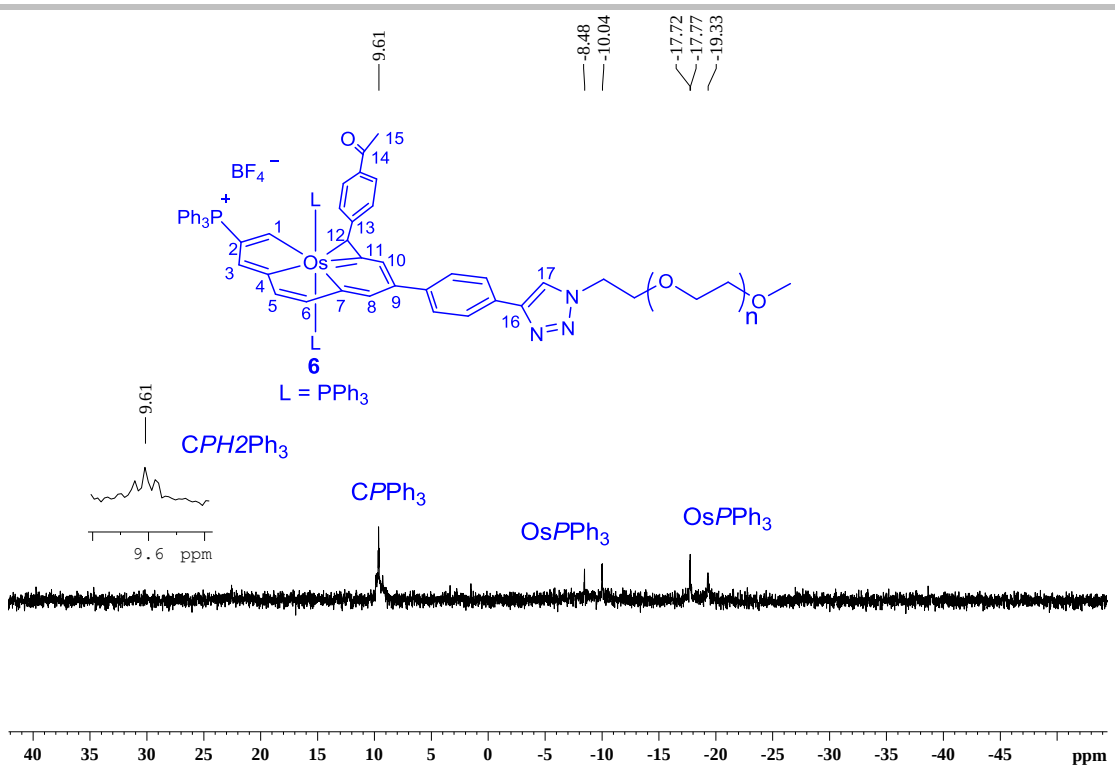


Figure **S20** The $^{31}P\{^{1}H\}$ NMR (162.0 MHz, $CDCl_3$) spectrum of macromolecule **6.**

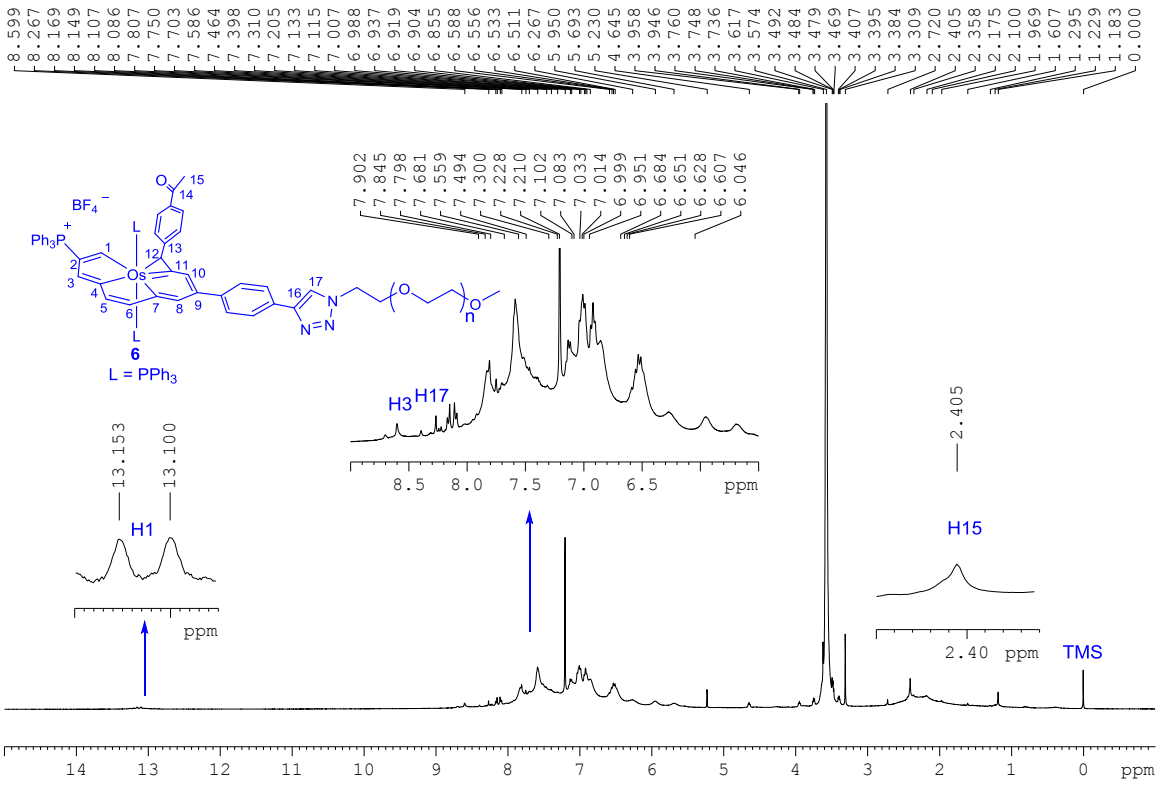


Figure S21 The ^{1}H NMR (400.1 MHz, $CDCl_3$) spectrum of macromolecule **6.**

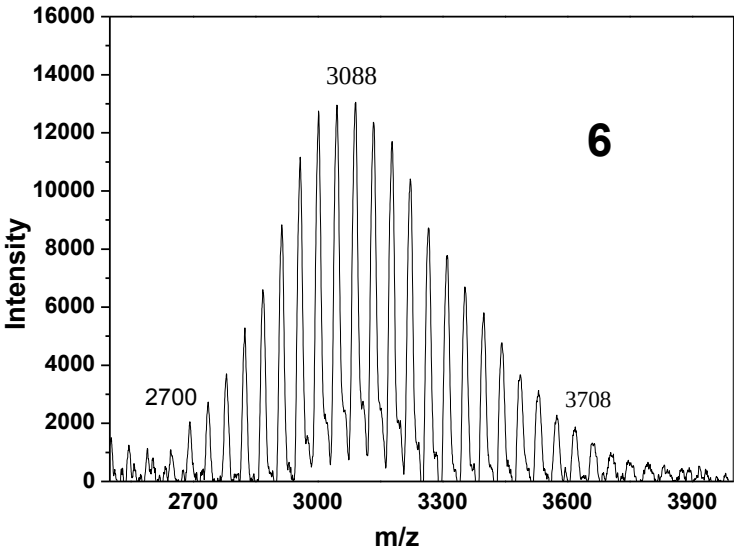


Figure S22 MALDI-TOF (DHB) spectrum of macromolecule **6**.

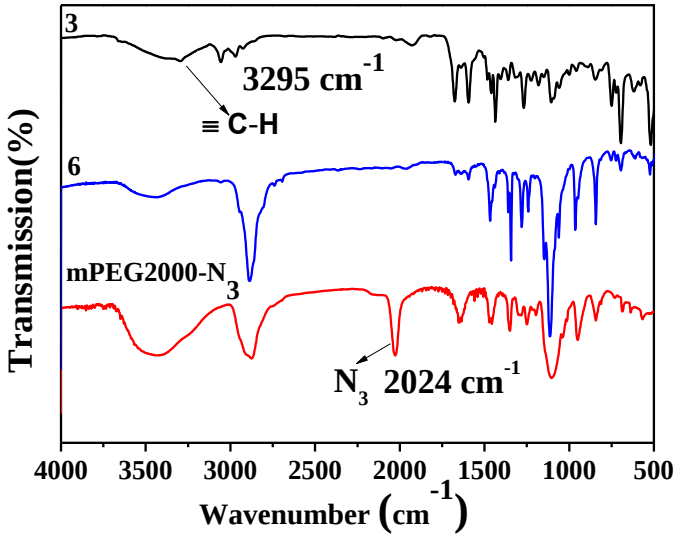


Figure S23 The IR (KBr) spectra of **3**, **mPEG2000-N_3** and macromolecule **6**.

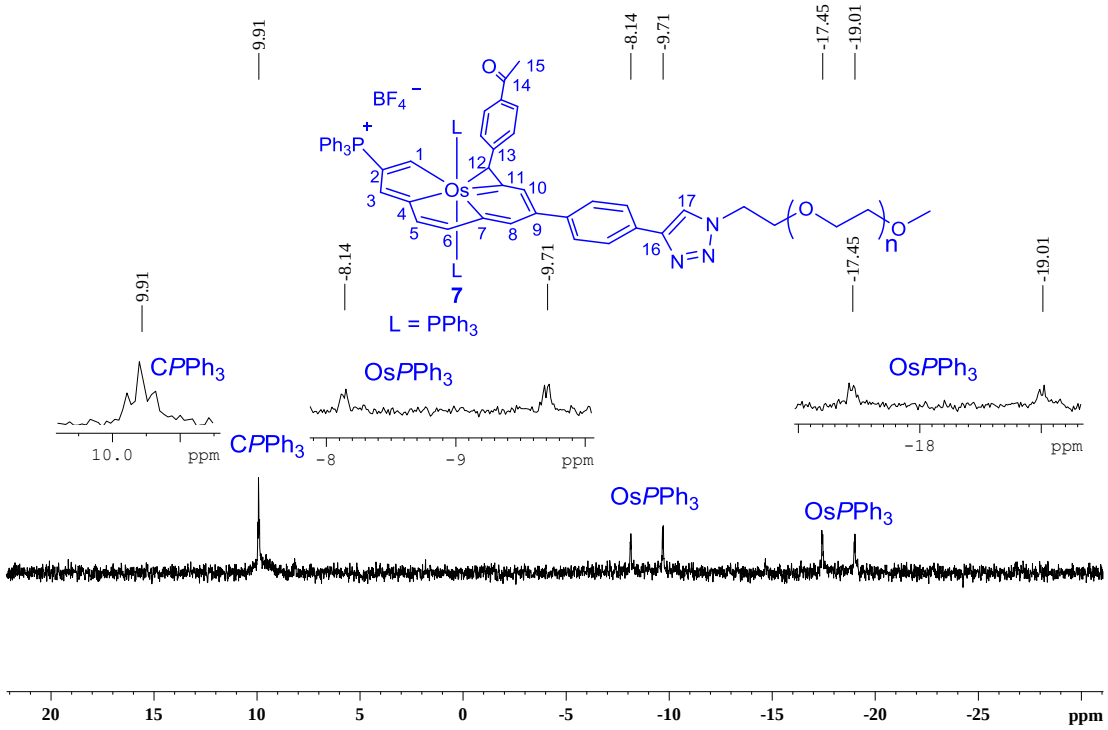


Figure **S24** The $^{31}P\{^{1}H\}$ NMR (162.0 MHz, $CDCl_3$) spectrum of macromolecule **7**.

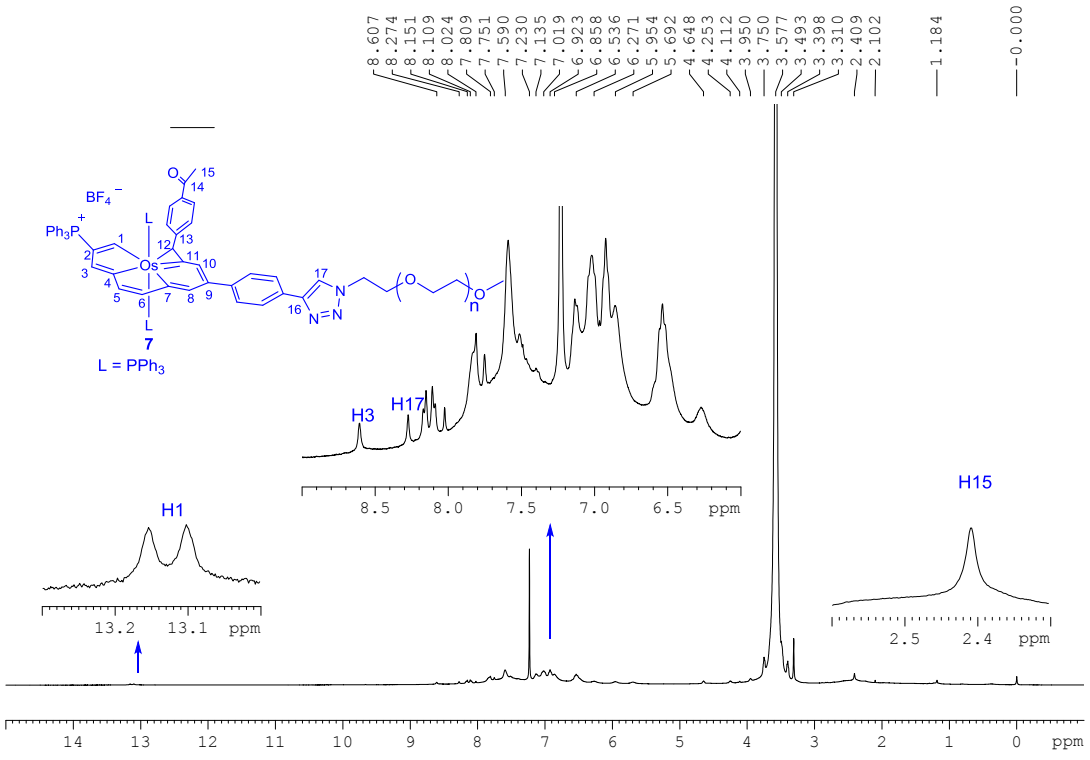


Figure S25 The ^{1}H NMR (400.1 MHz, $CDCl_3$) spectrum of macromolecule **7**.

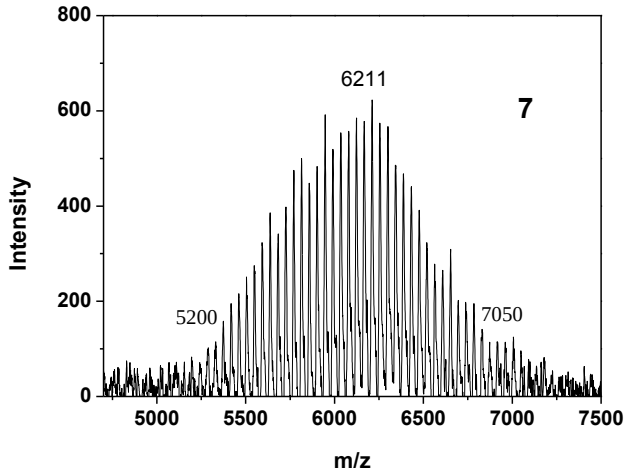


Figure S26 MALDI-TOF (DHB) spectrum of macromolecule **7**.

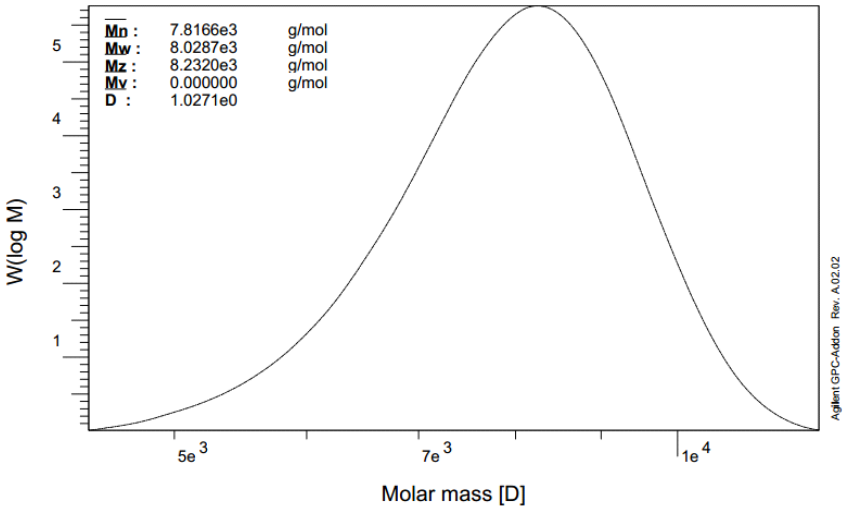


Figure S27 Molecular weight and its distribution of macromolecule **7**

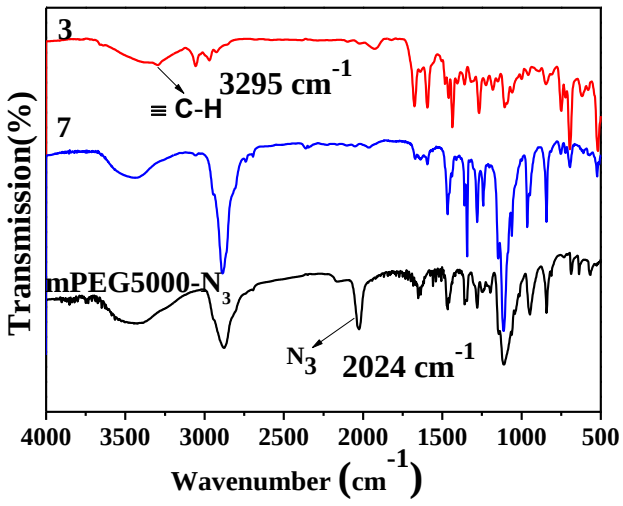


Figure S28 The IR (KBr) spectra of **3**, **mPEG5000-N_3** and macromolecule **7**.

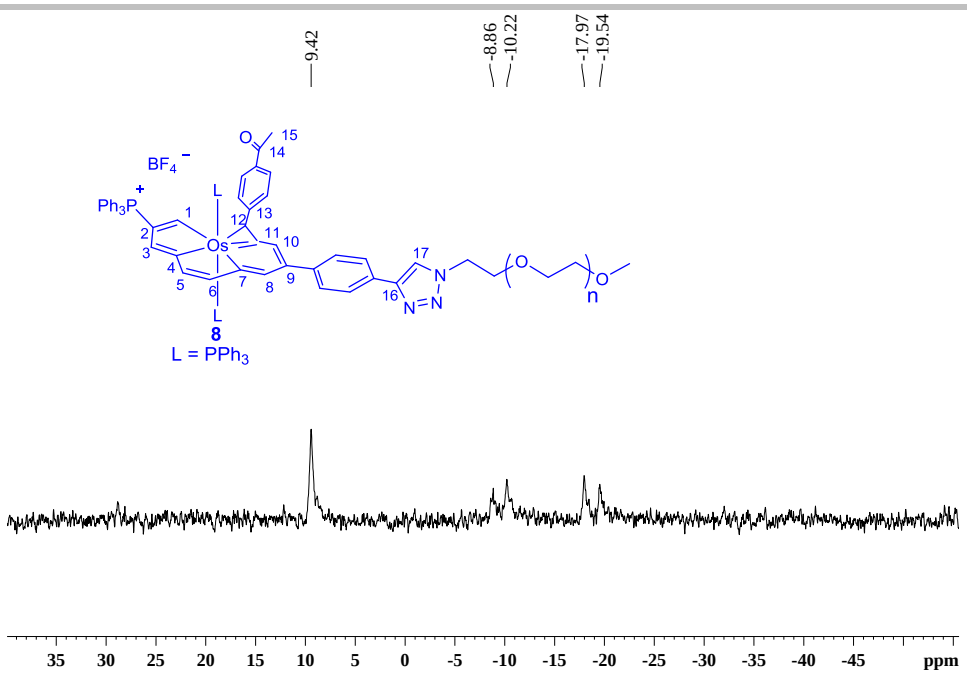


Figure S29 The $^{31}P\{^{1}H\}$ NMR (162.0 MHz, $CDCl_3$) spectrum of macromolecule **8**.

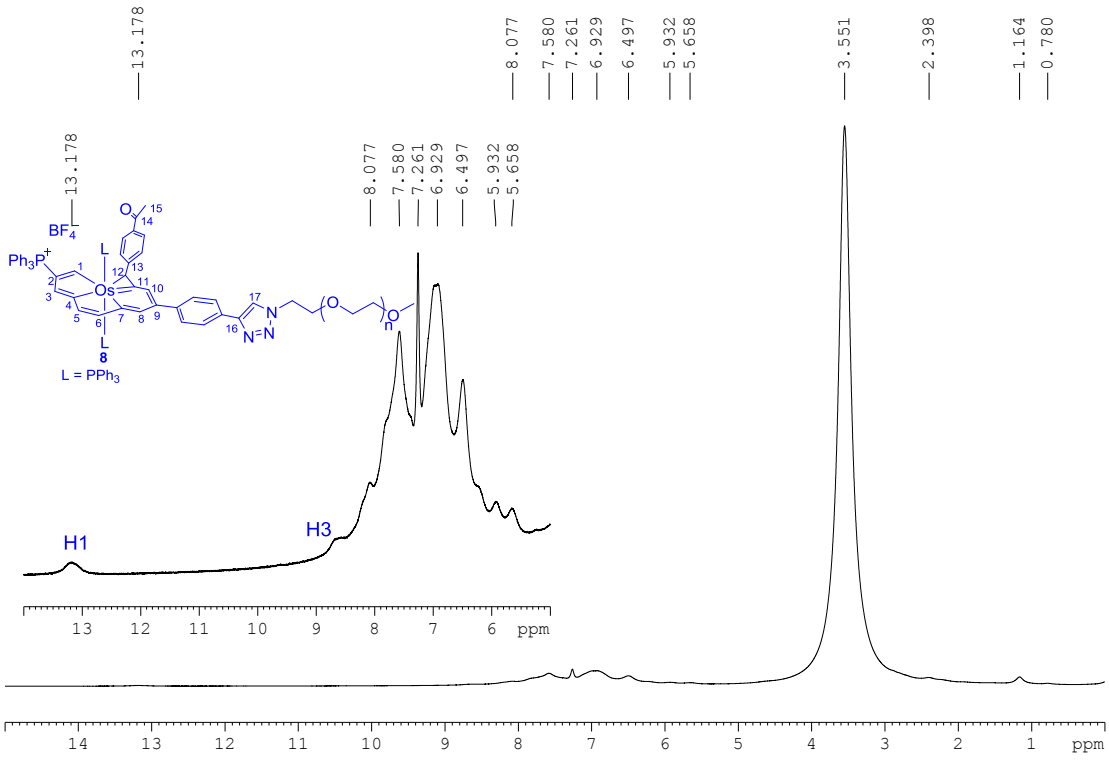


Figure S30 The ^{1}H NMR (400.1 MHz, $CDCl_3$) spectrum of macromolecule **8**.

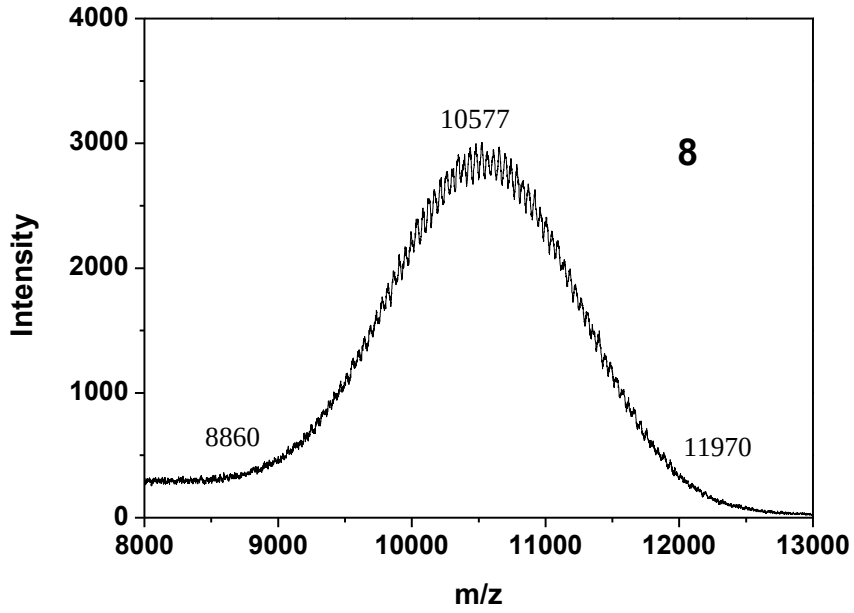


Figure S31 MALDI-TOF (DHB) spectrum of macromolecule **8**.

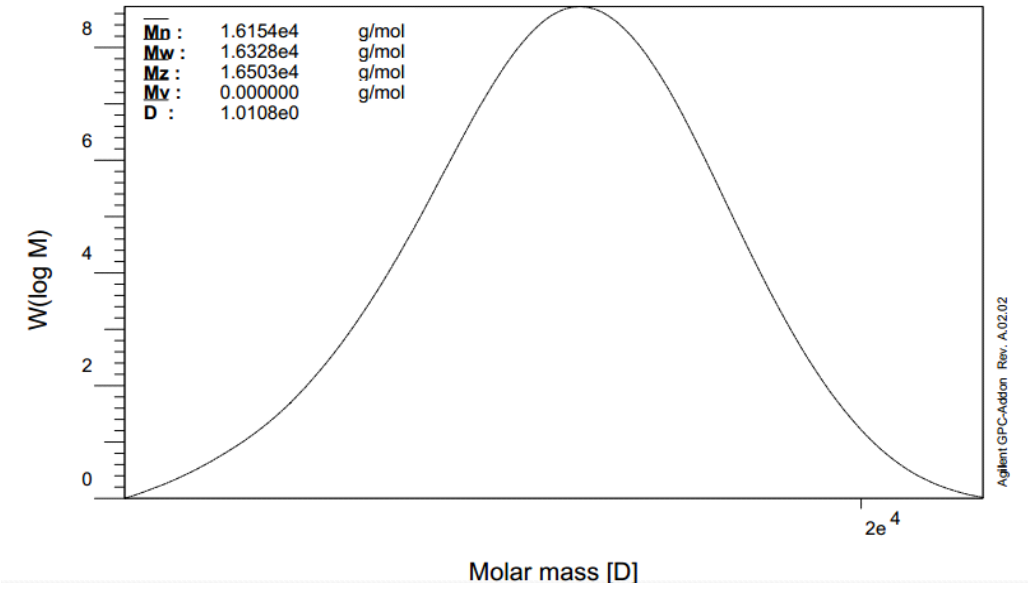


Figure S32 Molecular weight and its distribution of macromolecule **8**

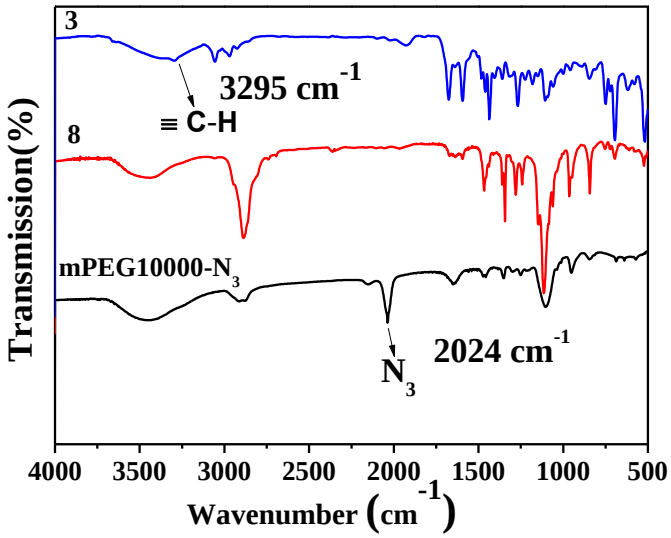


Figure S33 The IR (KBr) spectra of complex **3**, **mPEG10000-N_3** and macromolecule **8**.

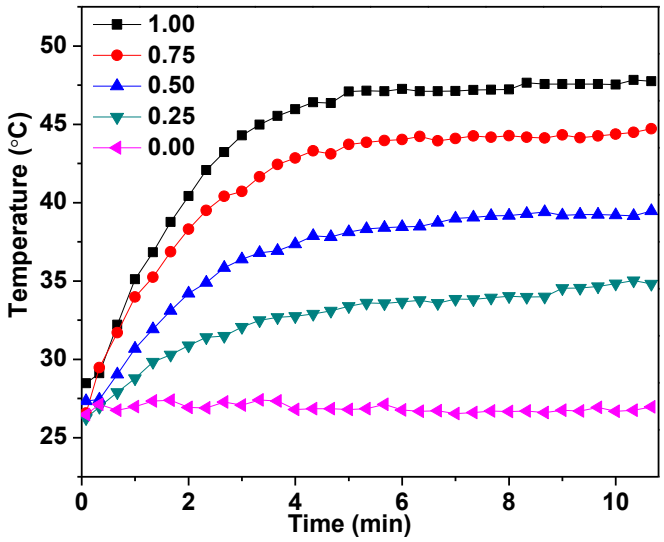


Figure S34 Temperature curves of water and different concentrations of macromolecule **8** (0.25, 0.5, 0.75 and 1.00 mg/mL) irradiated by an 808 nm laser at a power density of 1.0 W/cm^2.

11.References

[1] C. Zhu, X. Zhou, H. Xing, K. An, J. Zhu, H. Xia, *Angew. Chem. Int. Ed.* 2015, **54**, 3102.
[2] A. C. French, A. L. Thompson, B. G. Davis, *Angew. Chem. Int. Ed.* 2009, **48**, 1248.
[3] E. Doganci, M. Gorur, C. Uyanik, F. Yilmaz, *J. Polym. Sci.*, 2014, **52**, 3390.