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Influence of the Linker Length on the Cytotoxicity of Homobinuclear Ruthenium(II) and Gold(I) Complexes

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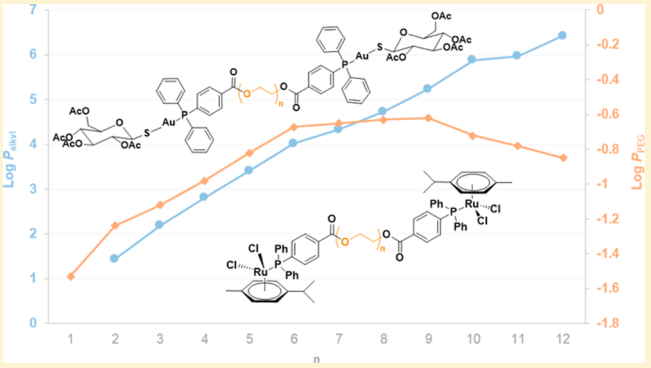
Supporting Information

ABSTRACT: Dinuclear metal complexes have emerged as a promising class of anticancer compounds with the ability to cross-link biomolecular targets. Here, we describe two novel series of phosphine-linked dinuclear ruthenium(II) *p*-cymene and gold(I) complexes, in which the length of the connecting poly(ethylene glycol) chain has been systematically modified. The impact of the multinuclearity, lipophilicity, and linker length on the antiproliferative activity of the compounds on tumorigenic (A2780 and A2780cisR) and nontumorigenic (HEK-293) cell lines was assessed. The dinuclear ruthenium(II) complexes were considerably more cytotoxic than their mononuclear counterparts, and a correlation between the lipophilicity of the linker and the cytotoxicity was observed, whereas the cytotoxicity of the gold(I) series is independent of these factors.



INTRODUCTION

The clinical success of cisplatin resulted in considerable efforts being directed toward the development of other platinum-based therapeutics.[1] However, the need to overcome the adverse side effects and intrinsic or acquired resistance to these compounds led to the investigation of alternative metals for their therapeutic potential.[2] Ruthenium(III) complexes imidazolium [*trans*-tetrachloro(1*H*-imidazole)(*S*-dimethyl sulfoxide)-ruthenate(III)][3] and indazolium *trans*-[tetrachlorobis(1*H*-indazole)ruthanate(III)] (KP1019)[4−6] and its sodium analogue (NKP1339)[7] have completed phase I and I/II clinical trials. Ruthenium(II) organometallic compounds have also attracted attention because they exhibit a number of promising pharmacological properties.[8−10] For example, the so-called RAPTA complexes (Figure 1),[11] of the general formula [Ru(η^6-arene)(PTA)X_2] (PTA = 1,3,5-triaza-7-phosphaadamantane), and the RAED complexes, [Ru(η^6-arene)(en)Cl]$^+$ (en = ethylenediamine),[12] have been particularly well studied for their anticancer properties. RAPTA-C[13] and RAED-C,[14] (where C = *p*-cymene) along with their derivatives exhibit an array of promising in vitro and in vivo properties.[9,12,13,15−19] Interestingly, crystallographic studies on the nucleosome core particle have shown that the choice of ligand strongly influences the biomolecular target of ruthenium(II) arene complexes with RAED-C preferentially binding to DNA and RAPTA-C binding to the histone proteins.[20,21] Mononuclear gold(I) phosphine complexes have been evaluated for anticancer properties and exhibit promising activity.[22−25] Auranofin (1-thio-β-D-glucopyranose-2,3,4,6-tetraacetato-*S*)(triethylphosphine)gold(I) (Figure 1), which is used clinically for the treatment of rheumatoid arthritis,[25,26] is currently being repositioned as an anticancer drug.[27−32] Similar to RAPTA complexes,[33,34] auranofin preferentially binds to cysteine-rich proteins such as thioredoxin reductase (TrX).[35−37]

Multinuclearity, i.e., covalently connecting two or more metal centers via an appropriate linker, emerged as an approach to introducing new modes of action to overcome resistance in chemoresistant cancers.[38] The trinuclear platinum compound [{*trans*-PtCl$(NH_3)_2$}$_2$-μ-(*trans*-Pt$(NH_3)_2${$H_2N(CH_2)_6$-NH_2}$_2$]$^{4+}$] (BBR3464; Figure 1) can overcome cisplatin resistance, and it exhibits a profile of antitumor efficacy distinct from that of cisplatin in a number of preclinical models.[39] However, despite successfully passing phase I clinical trials, BBR3464 failed a phase II evaluation, with only a minor response observed in small lung cancer and gastric/gastroesophageal adenocarcinoma.[40,41]

A growing number of multinuclear ruthenium(II) and gold(I) complexes have also been reported.[38] Interest in homobimetallic ruthenium(II) complexes has focused on the structure−reactivity investigations and the use of bioactive bridging ligands such as thiosemicarbazones.[42,43] The influence of the spacer length on in vitro anticancer activity has previously been explored using bis(pyridinone)alkane linkers (η^6-*p*-cymene)Ru(*O*,*O*-$C_6H_5O_2N(CH_2)_nNC_6H_5O_2$-*O*,*O*)Ru-($\eta^6$-*p*-cymene) (RU1, with n = 3, 6, 12; Figure 1), where the cytotoxicity correlates to the lipophilicity, which increases with increasing linker length.[44] Both proteins and DNA were identified as possible targets for the dinuclear ruthenium(II) complexes, which hydrolyze rapidly to form active diaqua

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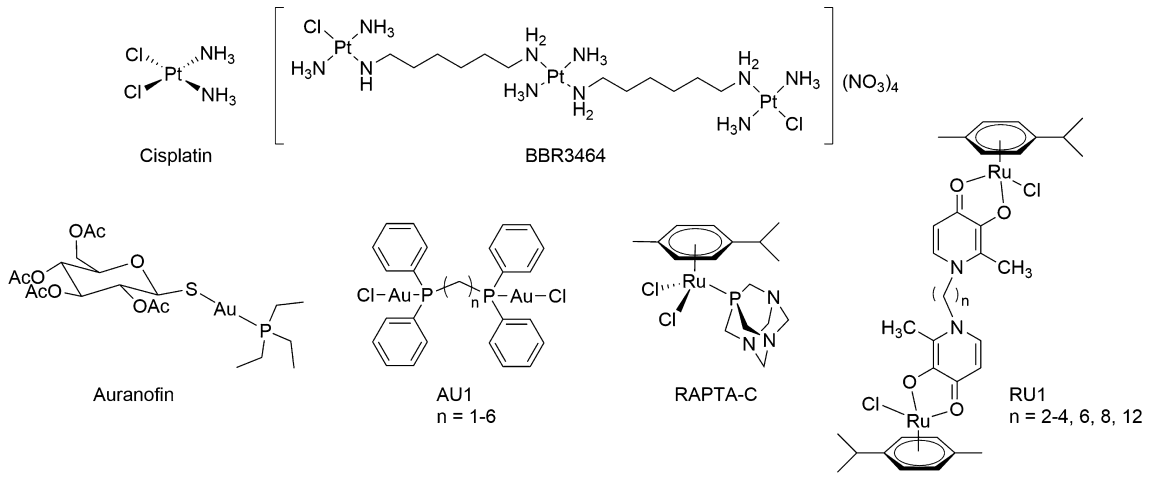
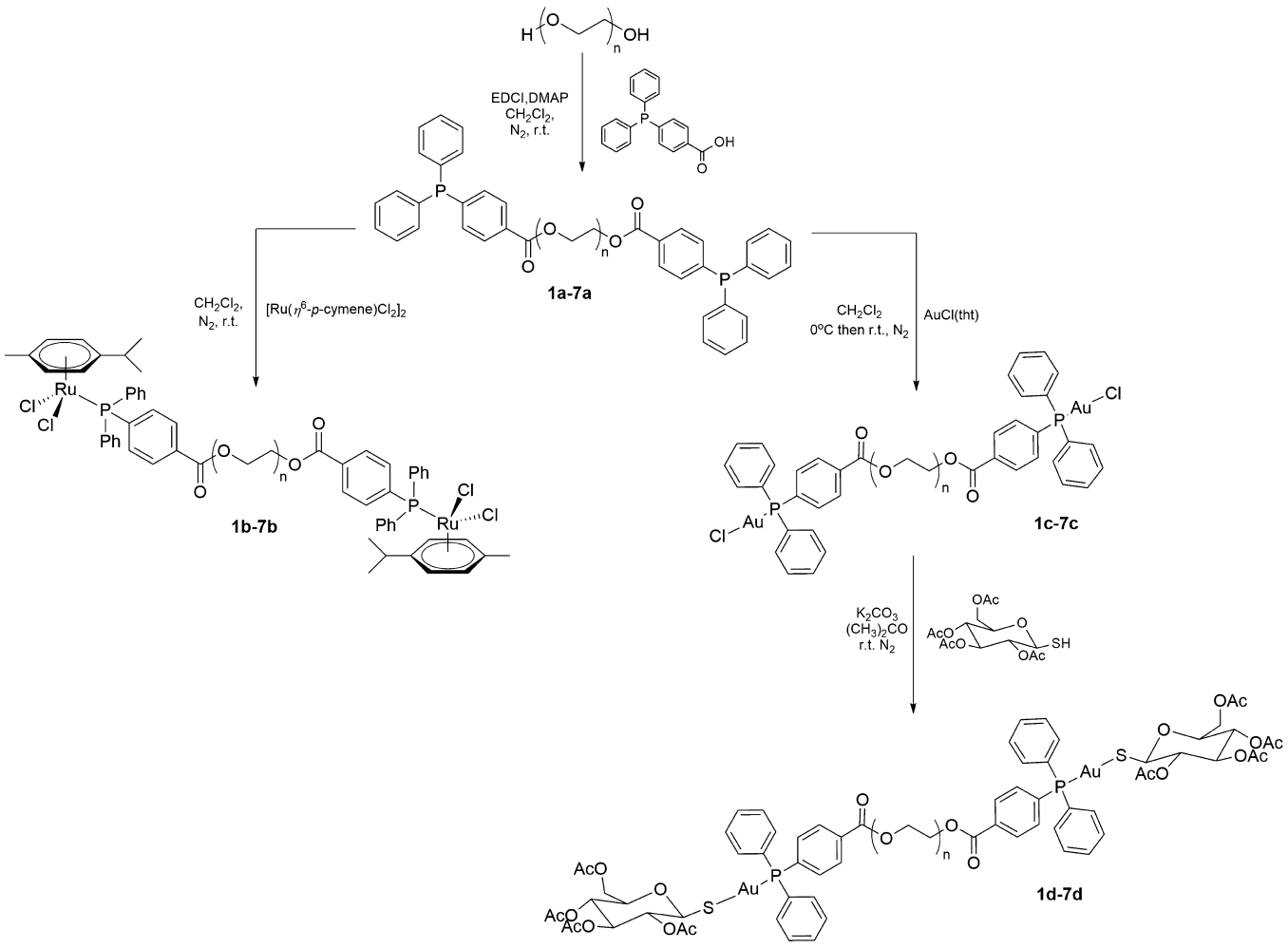


Figure 1. Selected examples of dinuclear complexes inspired by well-known monometallic drugs.

Scheme 1. Synthesis of the Diphosphine Ligands (1a−7a), Diruthenium(II) *p*-Cymene Complexes (1b−7b), Digold(I) Chloride Intermediates (1c−7c), and Digold(I) β-D-Thioglucosetetraacetate Complexes (1d−7d), Where *n* = 1−6 and 8



species.[45] Interestingly, the cytotoxicity of the complex with the longest bridging ligand was attributed to the ability of the complex to form both DNA−DNA and DNA−protein cross-links.[46] A RAED-type binuclear complex, $[(Ru(\eta^6\text{-biphenyl})Cl(en))_2(CH_2)_6]^{2+}$, similarly bearing an alkyl linker, has been shown to form interstrand DNA cross-links.[47] Flexible alkyl spacers used in acylpyrazolonato-bridged ruthenium(II) complexes led to complexes with a higher cytotoxicity than those of related compounds with rigid phenyl spacers.[48] Attempts were made to investigate poly(ethylene glycol) (PEG) linkers; however, the bis(nicotinate)/bis(isonicotinate) ligands were unstable in solution.[49] Homobinuclear ruthenium(II) complexes linked by different stereochemically configured 1,2-diphenylethylenediamine spacers exhibit open and closed

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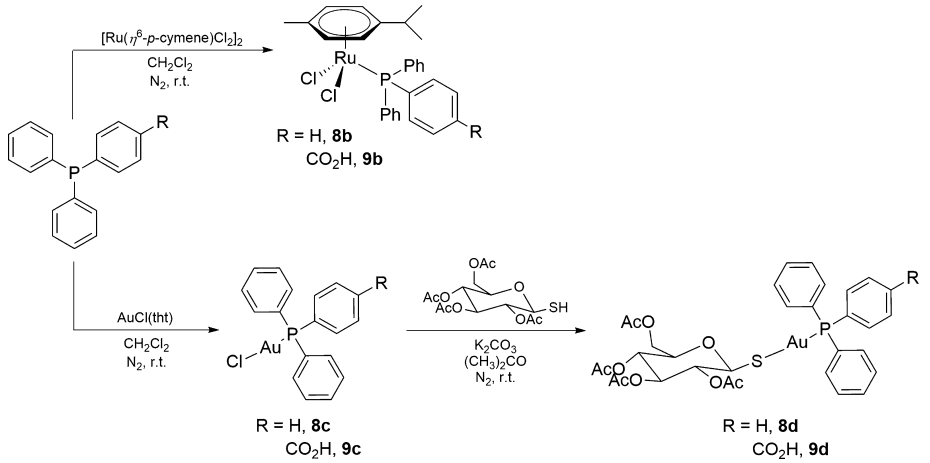
Scheme 2. Synthesis of Mononuclear Ruthenium(II) *p*-Cymene (8b and 9b) and Gold(I) (8d and 9d) Complexes



conformations. The dinuclear complexes are considerably more cytotoxic than the monomers but did not display cancer cell selectivity.[50] Consequently, a strategy was subsequently developed to generate dinuclear ruthenium(II) complexes directly in cancer cells.[51]

Significant efforts have also been devoted to the development of diphosphinegold(I) complexes.[52−58] However, little attention has been paid to the nature of the linker in homobinuclear gold(I) complexes. A series of $[(AuCl)_2(Ph_2P\text{-}(CH_2)_nPPh_2)]$ (where n = 1−6) complexes were prepared and evaluated in vitro against murine B16 melanoma cells (AU1; Figure 1). The cytotoxicity initially decreases with the linker length, n = 1 (6 μM) and 2 (8 μM), up to n = 3, where a plateau is reached (n = 3−6, IC_{50} = 2−3 μM).[59] Alkyl linkers were also assessed in phosphine-bridged dinuclear gold(I) alkynyl complexes linked via $(CH_2)_n$ (where n = 1 and 4) groups.[60] More recently, investigations into the lipophilicity have included the exchange of hydrophobic PPh_3 ligands with more lipophilic PEt_3 ligands in dinuclear phosphinegold(I) sulfanylcarboxylate complexes resulting in lower IC_{50} values against selected cell lines.[61] Other investigations include the optimization of TrX inhibition bridging bis(N-heterocyclic carbene) ligands,[62−64] alkylnyl ligands,[60,65−67] and thiocarbonates.[68,69]

Because the use of alkyl chains produced a general dependence between the linker length and cytotoxicity, correlating with increasing lipophilicity, we decided to evaluate the effect of PEG chains. Herein, we report the synthesis, structural characterization, and antiproliferative activity of two series of dinuclear complexes based on ruthenium(II) and gold(I) systems. The diruthenium(II) and digold(I) centers are linked via PEG chains of varying length, while the basic structures of the parent drugs RAPTA-C and auranofin are maintained. This strategy allows the influence of the linker length on the cytotoxicity to be studied and compared to their monometallic precursors.

RESULTS AND DISCUSSION

Two series of homobinuclear ruthenium(II) *p*-cymene, **1b−7b**, and gold(I), **1d−7d**, derivatives were prepared using the routes shown in Scheme 1. Universal diphosphine ligands **1a−7a** were synthesized via an esterification reaction between 4-(diphenylphosphanyl)benzoic acid and the appropriate ethylene glycol in the presence of *N*-ethyl-*N*′-[3-(dimethylamino)-propyl]carbodiimide hydrochloride (EDCI), a coupling agent, and 4-(dimethylamino)pyridine (DMAP), a basic catalyst. Ligands **1a−7a** were isolated by chromatographic purification in moderate yields (36−64%).

The diruthenium(II) *p*-cymene complexes **1b−7b** were obtained in high yield (96−98%) in a single step from the reaction of the appropriate ligands **1a−7a** with the $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2]_2$ dimer, under inert conditions in dry dichloromethane (CH_2Cl_2; Scheme 1). The binuclear gold(I) β-D-thioglucosetetraacetate complexes **1d−7d** were prepared by following a two-step strategy (Scheme 1). The intermediate binuclear gold(I) chloride complexes, **1c−7c**, were obtained in good yield (95−98%) from direct reaction of the appropriate diphosphine ligands **1a−7a** with $Au^ICl(tht)$ (tht = tetrahydrothiophene), freshly prepared following an adapted literature procedure.[70,71] The subsequent reaction of **1c−7c** with the β-D-thioglucosetetraacetate ligand under basic conditions (K_2CO_3) in acetone or ethanol (EtOH)/water (H_2O) affords the desired gold(I) complexes **1d−7d** in good yield (84−96%).[71,72]

Mononuclear complexes were also prepared to provide a structure−activity comparison between the binuclear complexes and the parent drugs, RAPTA-C and auranofin. The mononuclear ruthenium(II) *p*-cymene (**8b** and **9b**) and gold(I) (**8d** and **9d**) complexes, containing 4-(diphenylphosphanyl)-benzoic acid and triphenylphosphine ligands, were prepared from the direct reaction of phosphines with the $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2]_2$ dimer and $Au^ICl(tht)$ precursors, respectively (Scheme 2).

All compounds were characterized by ^1H, ^{31}P, and ^{13}C NMR spectroscopy, mass spectrometry (MS), and elemental analysis. In the ^{31}P NMR spectra, the phosphine ligands **1a−7a** produce a singlet between −4.99 and −5.08 ppm. In the binuclear complexes, the peaks shift to higher frequencies, with singlet resonances observed at 24.94−25.00 ppm for **1b−7b**, 33.01−33.14 ppm for **1c−7c**, and 38.71−38.79 ppm for **1d−7d**, confirming coordination of the phosphorus centers to the metal ions. The mononuclear complexes also give rise to singlets observed in the same range as the binuclear species, i.e., at 24.18 ppm for **8b**, 25.28 ppm for **9b**, 33.19 ppm for **8c**, 33.21 ppm for **9c**, 38.83 ppm for **8d**, and 38.82 ppm for **9d**.

The ^1H NMR spectra of the ligands **1a−7a** and complexes also show distinct differences. The multiplet corresponding to eight protons ortho to the C−P bond on the phenyl rings shifts from 7.29−7.39 to 7.76−7.83 ppm ($\Delta\delta_H \approx 0.4$ ppm), with a larger shift to 7.85−7.98 ppm ($\Delta\delta_H \approx 0.6$ ppm) observed for

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the four ortho protons on the functionalized ring. Similarly, a shift of $\Delta\delta_H \approx 0.2$ ppm to higher frequencies is observed, from 7.29−7.39 ppm (**1a**−**7a**) to 7.45−7.60 ppm (**1c**−**7c** and **1d**−**7d**), corresponding to the 12 protons ortho to the C−P bond in the gold(I) complexes. Complex **8b** possesses two multiplets in the aromatic region: 7.77−7.85 ppm, corresponding to the six phenyl protons ortho to the C−P bond, and 7.46−7.32 ppm, corresponding to the nine meta and para protons. In contrast, the ^{1}H NMR spectra of complexes **8c** and **8d** contain only one aromatic multiplet that corresponds to all 15 protons of the triphenylphosphine ligand (**8c**, 7.42−7.58 ppm; **8d**, 7.42−7.59 ppm). Complex **9b** possesses a multiplet at 7.97−8.00 ppm corresponding to the four protons of the functionalized ring, whereas in **9c** and **9d**, the multiplets corresponding to the two protons ortho to the C−P bond are observed at 8.05−8.19 ppm in **9c** and 7.81−7.90 ppm in **9d**.

Coordination of the ligands to the metal ions is denoted by the peaks corresponding to the carbon atoms directly connected to the phosphorus center shifting to lower frequencies (with increased $^1J_{C,P}$ coupling constants) in the ^{13}C NMR spectra. In the diruthenium(II) *p*-cymene complexes **1b**−**7b**, a shift of $\Delta\delta_C \approx 4.9$ ppm and coupling of $\Delta^1J_{C,P} \approx 28$ Hz were observed for the two C−P carbon atoms on the functionalized ring and $\Delta\delta_C \approx 3$ ppm and $\Delta^1J_{C,P} \approx 34$ Hz for the peaks corresponding to the four C−P carbon atoms on the phenyl rings. An analogous effect was observed for the digold(I) complexes, for **1c**−**7c**, there is a shift of $\Delta\delta_C \approx 9.6$ ppm and a coupling of $\Delta^1J_{C,P} \approx 45$ Hz, corresponding to the two C−P carbon atoms on the functionalized ring and a shift of $\Delta\delta_C \approx 8.5$ ppm and $\Delta^1J_{C,P} \approx 52$ Hz representing the four C−P carbon atoms on the phenyl rings. A comparable, but slightly less pronounced, effect is observed in the ^{13}C NMR spectra of **1d**−**7d**, and in the mononuclear complexes, similar changes are also observed.

The impact of increasing PEG chain length on the electronic environment of the metal centers is negligible, with all coupling constants and ^{31}P peaks remaining consistently similar throughout the series.

The most abundant peaks observed in the electrospray ionization MS (ESI-MS) spectra may be assigned to $[M + H]^+$ and $[M + Na]^+$ ions for ligands **1a**−**9a**, $[M - Cl]^+$ ions for **1b**−**9b**, $[M + Na]^+$ ions for **1c**−**8c**, $[M - H]^-$ ions for **9c**, $[M - Cl]^+$ ions for **1d**−**7d**, and $[M + H]^+$ ions for **8d**−**9d**.

The solid-state structures of **9b** and **9c** were established by single-crystal X-ray diffraction analysis, confirming the expected molecular structures. Single crystals of **9b** were grown via the slow evaporation of chloroform from a concentrated solution (Figure 2). **9b** contains four independent molecules in each asymmetric unit (Figure S1) compared to the two found for RAPTA-C.[73] Key bond parameters are compared with those of RAPTA-C (Table 1) and, overall, the arrangement around the ruthenium(II) center is remarkably similar to that of **9b**, adopting the familiar half-sandwich three-legged piano-stool geometry. The mean Ru−η^6 distance is longer in **9b** (1.706−1.723 Å) than in RAPTA-C (1.692−1.701 Å), and the same trend is observed for the Ru−P bond lengths [**9b**, 2.363(2)−2.3691(19) Å; RAPTA-C, 2.296(2)−2.298(3) Å]. The average Ru−Cl bond lengths and Cl−Ru−Cl angles are similar for both complexes; however, a difference is observed in the average P−Ru−Cl angles, with those in **9b** (88.78−89.91°) being consistently larger than those in RAPTA-C (84.04−87.25°). In the crystal of **9b**, intermolecular hydrogen bonds between the carboxylic acid groups are observed, leading to the formation of homodimeric assemblies (Figure S2).

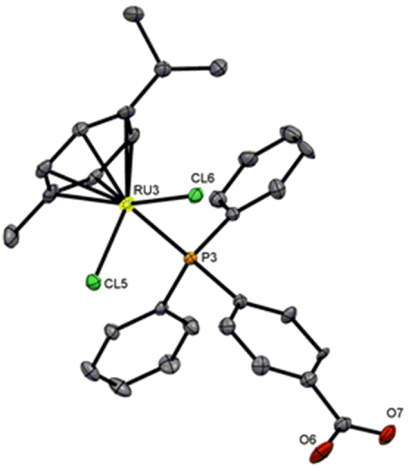

Figure 2. Solid-state structure of one of the four independent molecules in **9b**. Thermal ellipsoids are 50% equiprobability envelopes. Hydrogen atoms and solvent molecules ($CHCl_3$) are omitted for clarity.

Table 1. Comparison of Selected Bond Lengths (Å) and Angles (deg) in RAPTA-C[73] and 9b

	RAPTA-C[a]	9b[b]
Ru−η^6	1.692, 1.701	1.709, 1.723, 1.706, 1.714
Ru−P	2.296(2), 2.298(3)	2.363(2), 2.3691(19), 2.364(2), 2.3651(19)
Ru−Cl_{ave}	2.421, 2.426	2.420, 2.420, 2.425, 2.420
Cl−Ru−Cl	87.25(8), 88.97(9)	89.85(7), 88.52(7), 89.50(7), 87.51(6)
P−Ru−Cl_{ave}	85.26, 84.04	89.16, 88.78, 89.91, 89.35

[a]In the crystal of RAPTA-C, there are two independent molecules in the asymmetric unit. [b]In **9b**, there are four independent complexes in the asymmetric unit.

The slow diffusion of tetrahydrofuran (THF) into a saturated solution of **9c** in $CDCl_3$ afforded crystals suitable for X-ray diffraction analysis (Figure 3). The bond parameters around the gold(I) center in **9c** are presented in Table 2 and compared with those of auranofin.[74] The Au−P bond distance in **9c** [2.233(9) Å] is comparable to the value observed in auranofin

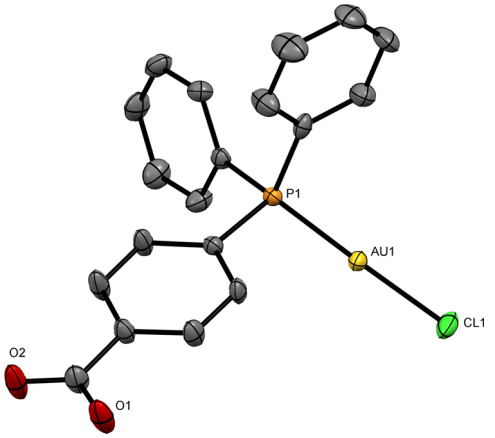

Figure 3. Solid-state structure of **9c**. Thermal ellipsoids are 50% equiprobability envelopes. Hydrogen atoms are omitted for clarity.

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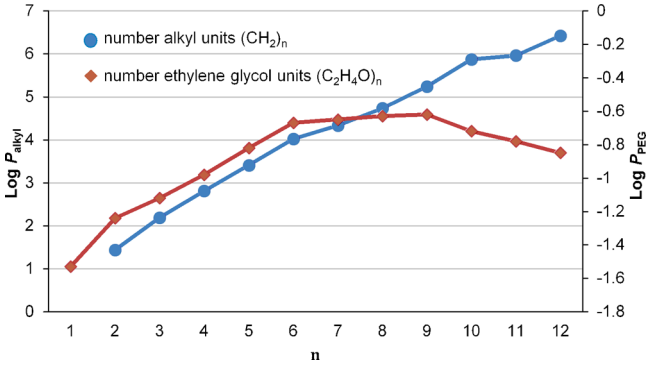
Table 2. Comparison of Selected Bond Lengths (Å) and Angles (deg) in Auranofin[74] and 9c

auranofin		9c	
Au−P	2.259	Au−P	2.233(9)
Au−S	2.293	Au−Cl	2.286(10)
P−Au−S	173.6	P−Au−Cl	178.07(3)

(2.259 Å). Despite the different labile ligands, i.e., thiol versus chloride, the Au−Cl bond in **9c** [2.286(10) Å] is similar in length to the Au−S bond in auranofin (2.293 Å). However, the nature of the labile ligand influences the angle around the gold(I) center; the P−Au−Cl [178.07(3)°] angle in **9c** is larger than the auranofin P−Au−S angle (173.6°). The crystal network in **9c** reveals dimeric arrangements due to intermolecular hydrogen-bonding interactions of the carboxylic acid group (Figure S3).

The lipophilicity has previously been correlated to increasing cytotoxicity in dinuclear ruthenium(II) complexes (RU1; Figure 1).[45] Consequently, the partition coefficients (log *P*) of PEG chains and alkyl chains were calculated.[75,76] As expected, the lipophilicity of the alkanes increases with increasing chain length (Chart 1), a trend that is transferred

Chart 1. Calculated Partition Coefficients for Alkyl Chains and PEG Chains as a Function of the Length[a]



[a]The calculated log P_{alkyl} value of methane (n = 1) was omitted for clarity.

to diruthenium complexes bearing alkyl linkers of the structure (η^6-*p*-cymene)Ru(*O*,*O*-$C_6H_5O_2N(CH_2)_nNC_6H_5O_2$-*O*,*O*)Ru-($\eta^6$-*p*-cymene) ($n$ = 3, 6, and 12).[45] In contrast, PEG chains have limited lipophilicity, with the hydrophobicity increasing with the chain length up to hexakis(ethylene glycol), where a plateau is reached. According to calculations, octakis(ethylene glycol) is the most lipophilic with a log *P* value of −0.63, and longer PEG chains become increasingly hydrophilic. The plateau, consisting of PEG chains 6−9, have similar log *P* values in the range −0.62 to −0.67. Log $P_{octanol/H_2O}$ values were determined experimentally for **1b**−**7b** and **1d**−**7d** using the shake-flask method (Table 1).[77] The log *P* values reside in the lipophilic range for both series. Digold(I) β-D-thioglucosetetraacetate complexes **1d**−**7d** are more hydrophilic than their ruthenium counterparts **1b**−**7b** because of the presence of two β-D-thioglucosetetraacetate ligands. For the shorter chain lengths, **1b**−**4b** and **1d**−**3d**, the lipophilicity was shown to increase with increasing chain length for both series. However, for complexes bearing longer chain lengths, **5b**−**7b** and **5d**−**7b**, the log *P* values remain essentially constant despite increasing chain length, values of which are 1.4−1.5 and 0.3−0.4, respectively.

The cytotoxicity of the **1a**−**7a** ligands and ruthenium(II) *p*-cymene **1b**−**9b** and gold(I) β-D-thioglucosetetraacetate **1d**−**9d** complexes was assessed against human ovarian carcinoma cell lines, A2780 and A2780cisR, with the latter having acquired resistance to cisplatin and nontumoral human embryonic kidney (HEK-293) cells using the 3-(4,5-dimethyl-2-thiazolyl)-2,5-diphenyl-2*H*-tetrazolium bromide (MTT) assay (Table 3). The cytotoxicities of 4-(diphenylphosphanyl)benzoic acid, triphenylphosphine, auranofin, cisplatin, and RAPTA-C were evaluated for comparison purposes. Elemental analysis indicates that CH_2Cl_2 and $CDCl_3$ are present in some compounds; therefore, their cytotoxicities were evaluated at IC_{50} concentration, and they were found to be inactive.

All compounds were predissolved in dimethyl sulfoxide (DMSO), and their stability in this solvent was confirmed via ^1H and ^{31}P NMR spectroscopy (Figures S4−S7), before being immediately diluted into the appropriate cell culture medium. Further stability studies under pseudocell culture conditions of 100 mM NaCl in H_2O and 5% DMSO were conducted on **2d**, **4d**, and **6d** complexes over 72 h. The stability was monitored via ESI-MS(+) (Figures S8−S10), and all complexes showed good stability under these conditions.

The original RAPTA series possess low cytotoxicities with IC_{50} values of >200 μM against a range of cell lines.[11] As discussed above, the structures of **9b** and RAPTA-C are comparable, and the similarities are reflected in their cytotoxicities, with IC_{50} values >200 μM determined against all tested cell lines. However, the mononuclear ruthenium(II) complex **8b**, bearing a hydrophobic triphenylphosphine ligand, is considerably more cytotoxic than **9b**, with an IC_{50} of 42 ± 1 μM. A similar trend is present with **8d** and **9d**, with **9d** being ca. 14-fold more cytotoxic than **8d**. The free ligands triphenylphosphine and 4-(diphenylphosphanyl)benzoic acid also present respective IC_{50} values of 85 ± 7 and >200 μM against the A2780 cell line; the differences may be attributed to the differences in the lipophilicity. However, the impact of global charge may be of influence.

The diphosphine ligands **1a**−**7a** are inactive at concentrations of up to 500 μM on the three cell lines. The dinuclear complexes **1b**−**7b** and **1d**−**7d** are considerably more cytotoxic than the mononuclear complexes **9b** and **9d** against all cell lines. The complexes containing the mono(ethylene glycol) linker (**1b** and **1d**) are considerably less cytotoxic than the complexes with longer linkers (**2b**−**7b** and **2d**−**7d**). In contrast, in a series of diruthenium(II) *p*-cymene complexes with bridging bis(nicotinate)/bis(isonicotinate) ligands, only the complex with the shortest mono(ethylene glycol) linker possessed moderate activity against a range of cell lines including the human melanoma (518A2) cell line (IC_{50} = 53 ± 1 μM).[49]

The diruthenium(II) *p*-cymene complexes **2b**−**7b** exhibit IC_{50} values in the low micromolar range against the A2780 cell line. The cytotoxicity toward the cisplatin-resistant cell line (A2780cisR) remains in the low micromolar range, with up to 2-fold loss in cytotoxicity compared to the A2780 cisplatin-sensitive cell line for **3b** and **5b**. No selectivity was observed toward the cancer cell lines, with the values obtained for the nontumorigenic HEK-293 cell line being similar in magnitude. The cytotoxicities of these dinuclear complexes are comparable to those of previously investigated series including the series of rigid RAPTA-type dinuclear complexes, linked via the

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Table 3. Calculated Log *P* Values and in Vitro Antiproliferative Activities of Compounds 1b−9b and 1d−9d against Human Ovarian Carcinoma (A2780), Human Ovarian Carcinoma Cisplatin Resistant (A2780cisR), and Human Embryonic Kidney 293 (HEK-293) Cell Lines after 72 h of Exposure[a]

compound	log $P_{octanol/H_2O}$	A2780	A2780cisR	HEK-293
1b	1.3 ± 0.1	60 ± 2	110 ± 3	66 ± 1
2b	1.3 ± 0.1	10 ± 0.1	11.0 ± 0.7	12.2 ± 0.5
3b	1.6 ± 0.1	19.4 ± 0.3	37.6 ± 1.6	19.6 ± 1.1
4b	1.8 ± 0.3	11.3 ± 0.1	14.6 ± 0.3	14.7 ± 0.9
5b	1.4 ± 0.05	6.4 ± 0.7	12.9 ± 3.7	6.8 ± 0.2
6b	1.4 ± 0.02	7.3 ± 0.3	10.5 ± 0.1	9.1 ± 0.1
7b	1.5 ± 0.02	11.6 ± 0.9	14.1 ± 7.7	14.2 ± 0.3
8b		42 ± 1	35 ± 7	47 ± 1
9b		>200	>200	>200
1d	0.4 ± 0.3	1.5 ± 0.1	4.7 ± 0.1	3.3 ± 0.3
2d	0.9 ± 0.1	0.22 ± 0.03	0.67 ± 0.02	1.2 ± 0.1
3d	0.7 ± 0.2	0.19 ± 0.02	0.91 ± 0.01	1.2 ± 0.1
4d	0.6 ± 0.1	0.19 ± 0.02	1.1 ± 0.1	1.2 ± 0.1
5d	0.3 ± 0.2	0.22 ± 0.02	1.4 ± 0.1	1.4 ± 0.1
6d	0.4 ± 0.3	0.17 ± 0.01	1.4 ± 0.04	1.4 ± 0.1
7d	0.3 ± 0.2	0.25 ± 0.02	1.4 ± 0.4	1.4 ± 0.1
8d		0.54 ± 0.07	1 ± 0.1	1.8 ± 0.2
9d		6.9 ± 0.8	12.0 ± 2	11.7 ± 0.4
$(C_6H_5)_2PC_6H_4CO_2H$		>200	>200	>200
$P(C_6H_5)_3$		85 ± 7		
cisplatin		1.3 ± 0.2	11 ± 1	9 ± 1
RAPTA-C		>200	>200	>200
auranofin		1.3 ± 0.5	1.5 ± 0.5	1.9 ± 0.6

[a]Values are given as the mean ± standard deviation (μM).

functionalization of the η^6-arene, where the most active complex has an IC_{50} of 3.7 ± 0.6 μM against the A2780 cell line.[50]

The relationship between the linker length and cytotoxicity on the A2780 cell line shows increasing cytotoxicity with increasing linker length between **3b** and **5b**, which correlates with the increasing lipophilicity of the linkers. However, **2b** with the bis(ethylene glycol) linker is ca. 2-fold more cytotoxic than **3b**. The lipophilicity is essentially constant for compounds **6b** and **7b**, with the IC_{50} values being 7.3 ± 0.3 and 11.6 ± 0.9 μM, respectively.

The digold(I) β-D-thioglucosetetraacetate complexes **1d−7d** are highly cytotoxic on all three tested cell lines, with IC_{50} values in the low micromolar range. Compounds **2d−7d** are highly cytotoxic against A2780 cells (with IC_{50} values between 0.17 and 0.25 μM), while being significantly less active, up to 8-fold, on the cisplatin-resistant A2780cisR cell line. The IC_{50} values of **1d−7d** on nontumorigenic HEK-293 cells are very similar to those on A2780cisR cells. Interestingly, no major differences are observed between the activities of the digold(I) complexes **2d−7d** and the mononuclear complex **8d**, containing the hydrophobic PPh_3 ligand, whereas **9d**, with the more hydrophilic phosphine ligand, i.e., $(C_6H_5)_2PC_6H_4CO_2H$, is ca. 35-fold less cytotoxic in A2780 cells and ca. 10-fold less cytotoxic in A2780cisR and HEK-293 cells. With the exception of complexes **1d** and **9d**, the activities are in the same order as those of auranofin.

Complexes **2d−7d** display a narrow range of IC_{50} values between 0.17 ± 0.01 and 0.25 ± 0.02 μM and, thus, there is no discernible correlation with the linker length and associated lipophilicity. However, the series is significantly more cytotoxic than $[(AuCl)_2(Ph_2P\text{-}(CH_2)_nPPh_2)]$ (where n = 1−6), in which the most active complexes (n = 3, 5, and 6) have IC_{50} values of ca. 2 μM, again murine B16 melanoma cells.[59] A trend was observed in this alkyl-linked series with 3-fold (n = 1) and 4-fold (n = 2) higher cytotoxicities for the more lipophilic complexes.[59] The series is also significantly more cytotoxic than the phosphine-bridged dinuclear gold(I) alkynyl complexes bearing alkyl linkers, where no correlation was observed between the cytotoxicity and linker length.[60]

CONCLUDING REMARKS

The synthesis of two series of homobinuclear RAPTA-like ruthenium(II) *p*-cymene complexes **1b−7b** and auranofin-like gold(I) complexes **1d−7d**, linked via diphosphine-modified PEG chains of varying length, was successfully achieved. The antiproliferative activity of these compounds was determined against tumorigenic and nontumorigenic cell lines, and a distinct increase the cytotoxicity was observed for both series compared to the mononuclear precursors **9b** and **9d**. There is a correlation between the lipophilicity and cytotoxicity of the diruthenium(II) complexes, which reaches a plateau where the lipophilicity no longer increases with the length of the PEG chain, i.e., when n = 6. In contrast, the cytotoxicities of all of the digold(I) complexes lie within a narrow range and are not readily correlated to the linker length and associated lipophilicity.

EXPERIMENTAL SECTION

Materials. $RuCl_3 \cdot 3H_2O$ was purchased from Precious Metals Online. All other chemical reagents were purchased from Aldrich, Alfa Aesar, Acros, and TCI Chemicals and used without further purification. $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2]_2$[78] and AuCl(tht)[70,71] were prepared following literature procedures. CH_2Cl_2 was dried and degassed using a PureSolv solvent purification system (Innovative Technology Inc.). Thin-layer chromatography was conducted on Merck 60 F254

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TLC silica-gel-coated aluminum sheets and verified by a UV lamp at 254 nm and $KMnO_4$ staining. Purification of the ligands was achieved via a manual chromatograph using silica gel (Silicycle R12030B) or a Varian 971-FP flash chromatography system using prepackaged silica gel columns (Luknova).

Instrumentation and Methods. ^1H (400 MHz), ^{13}C (101 MHz), and ^{31}P (162 MHz) NMR spectra were recorded on a Bruker Avance II 400 spectrometer at 298 K. Chemical shifts are reported in parts per million and referenced to deuterated solvent residual peaks ($CDCl_3$: ^1H, δ 7.26 ppm; $^{13}C\{^1H\}$, δ 77.16 ppm). Coupling constants (J) are reported in hertz. High-resolution ESI-MS spectra were obtained on a Thermo-Finnigan LCQ Deca XP Plus quadropole ion-trap instrument operated in positive-ion or negative-ion mode. Elemental analyses were carried out by the microanalytical laboratory at EPFL using a Thermo Scientific Flash 2000 organic elemental analyzer. UV−vis spectra were recorded using a SpectroMax M5e multimode microplate reader (using *SoftMax Pro* software, version 6.2.2). The diffraction data of compounds **9b** and **9c** were measured at low temperature [100(2) K] using Mo Kα radiation on a Bruker APEX II CCD diffractometer equipped with a Kappa geometry goniometer. The data sets were reduced by *EvalCCD*[79] and then corrected for absorption.[80] The solutions and refinements were performed by *SHELX*.[81,82] The crystal structures were refined using full-matrix least squares based on F^2, with all non-hydrogen atoms anisotropically defined. Hydrogen atoms were placed in calculated positions by means of the "riding" model. The log P values of PEG and alkyl linker compounds were predicted using the Virtual Computational Chemistry Lab (VCCLAB).[75,76] The experimental log $P_{octanol/H_2O}$ values were determined using the shake-flask method,[77] and the absorbance of each fraction was recorded using a SpectroMax M5e multimode microplate reader (using *SoftMax Pro* software, version 6.2.2). The absorbance of the MTT assay 96-well plates was recorded using a SpectroMax M5e multimode microplate reader (using *SoftMax Pro* software, version 6.2.2).

Synthesis. *General Procedure for the Synthesis of the Diphosphine Ligands* ***1a−7a.*** 4-(Diphenylphosphanyl)benzoic acid (2.2 equiv) and EDCI (2.4 equiv) were dissolved in CH_2Cl_2 (50 mL) and stirred under N_2 at room temperature (RT) for 15 min. The appropriate ethylene glycol (1.0 equiv) and DMAP (0.4 equiv) were added, and the mixture was further stirred for 24 h at RT. The reaction mixture was washed with H_2O (150 mL), and the aqueous phase was reextracted with CH_2Cl_2 (2 × 100 mL). The organic phase was washed with brine (150 mL), dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The treated product was purified by flash column chromatography using an adapted elution system of hexanes/ethyl acetate or CH_2Cl_2/methanol. The product was recovered as a colorless viscous solid.

Compound ***1a.*** According to the general procedure, 4-(diphenylphosphanyl)benzoic acid (0.900 g, 2.938 mmol, 2.2 equiv), mono(ethylene glycol) (0.075 mL, 1.345 mmol, 1 equiv), EDCI (0.614 g, 3.203 mmol, 2.4 equiv), and DMAP (0.065 g, 0.532 mmol, 0.4 equiv) were stirred for 24 h in CH_2Cl_2 (50 mL). Yield: 0.216 g, 0.338 mmol, 25%. Elem anal. Calcd for $C_{40}H_{32}O_4P_2$: C, 75.23; H, 5.05. Found: C, 75.55; H, 5.23. ^1H NMR ($CDCl_3$): δ_H 7.97 (4H, m, 4O(C═O)(*Ar*)CC*H*CHCP, $^3J_{H,H}$ = 8.6 Hz, $^4J_{H,H}$ = 1.4 Hz), 7.29−7.40 (24H, m, 4O(C═O)(*Ar*)CCHC*H*CP, 8P(*Ar*)CC*H*CHCH, 8P(*Ar*)CCHC*H*CH, 4P(*Ar*)CCHCHC*H*), 4.64 (4H, s, *Ar*(C═O)O(CH_2)$_2$O). ^{31}P NMR ($CDCl_3$): δ_P −4.99 (2P). ^{13}C NMR ($CDCl_3$): δ_C 166.3 (2C, 2O(C═O)(*Ar*)CCHCHCP), 144.6 (2C, d, 2O(C═O)(*Ar*)CCHCHCP, $^1J_{C,P}$ = 15 Hz), 136.3 (4C, d, 4P(*Ar*)*C*CHCHCH, $^1J_{C,P}$ = 11 Hz), 134.2 (8C, d, 8P(*Ar*)*C*CHCHCH, $^2J_{C,P}$ = 20 Hz), 133.3 (4C, d, 4O(C═O)(*Ar*)CCHCHCP, $^2J_{C,P}$ = 19 Hz), 129.8 (2C, 2O(C═O)(*Ar*)CCHCHCP), 129.5 (4C, d, 4O(C═O)(Ar)CCHCHCP, $^3J_{C,P}$ = 6 Hz), 129.3 (4C, 4P(*Ar*)CCHCHCH), 128.8 (8C, d, 8P(*Ar*)CCHCHCH, $^3J_{C,P}$ = 7 Hz), 63.0 (2C, 2(*Ar*)(C═O)O(CH_2)$_2$O). ESI-MS(+). Calcd: m/z 639.1854 ([M + H]$^+$ $C_{40}H_{33}O_4P_2^+$). Found: m/z 639.1853.

Compound ***2a.*** According to the general procedure, 4-(diphenylphosphanyl)benzoic acid (0.900 g, 2.938 mmol, 2.2 equiv), bis(ethylene glycol) (0.128 mL, 1.349 mmol, 1 equiv), EDCI (0.614 g, 3.203 mmol, 2.4 equiv), and DMAP (0.065 g, 0.532 mmol, 0.4 equiv) were stirred for 24 h in CH_2Cl_2 (50 mL). Yield: 0.328 g, 0.480 mmol, 36%. Elem anal. Calcd for $C_{42}H_{36}O_5P_2$: C, 73.89; H, 5.32. Found: C, 73.56; H, 5.51. ^1H NMR ($CDCl_3$): δ_H 7.94−7.97 (4H, m, 4O(C═O)(*Ar*)CC*H*CHCP, $^3J_{H,H}$ = 8.5 Hz, $^4J_{H,H}$ = 1.5 Hz), 7.29−7.39 (24H, m, 4O(C═O)(*Ar*)CCHC*H*CP, 8P(*Ar*)CC*H*CHCH, 8P(*Ar*)CCHC*H*CH, 4P(*Ar*)CCHCHC*H*), 4.46−4.49 (4H, m, 2*Ar*(C═O)OCH_2CH_2O), 3.82−3.87 (4H, m, 2*Ar*(C═O)OCH_2CH_2O). ^{31}P NMR ($CDCl_3$): δ_P −5.08 (2P). ^{13}C NMR ($CDCl_3$): δ_C 166.4 (2C, 2O(*C*═O)(*Ar*)CCHCHCP), 144.3 (2C, d, 2O(C═O)(*Ar*)CCHCHCP, $^1J_{C,P}$ = 14 Hz), 136.3 (4C, d, 4P(*Ar*)*C*CHCHCH, $^1J_{C,P}$ = 11 Hz), 134.1 (8C, d, 8P(*Ar*)*C*CHCHCH, $^2J_{C,P}$ = 20 Hz), 133.2 (4C, d, 4O(C═O)(*Ar*)CCHCHCP, $^2J_{C,P}$ = 19 Hz), 130.0 (2C, 2O(C═O)(*Ar*)CCHCHCP), 129.5 (4C, d, 4O(C═O)(Ar)CCHCHCP, $^3J_{C,P}$ = 6 Hz), 129.3 (4C, 4P(*Ar*)CCHCHCH), 128.8 (8C, d, 8P(*Ar*)CCHCHCH, $^3J_{C,P}$ = 7 Hz), 69.3 (2C, 2(*Ar*)(C═O)OCH_2CH_2O), 64.2 (2C, 2(*Ar*)(C═O)OCH_2CH_2O). ESI-MS(+). Calcd for $C_{42}H_{37}O_5P_2^+$: m/z 682.6925 ([M + H]$^+$). Found: m/z 683.2112. Calcd for $C_{42}H_{36}NaO_5P_2^+$: 705.1931 ([M + Na]$^+$). Found: m/z 705.1936.

Compound ***3a.*** According to the general procedure, 4-(diphenylphosphanyl)benzoic acid (0.900 g, 2.938 mmol, 2.2 equiv), tris(ethylene glycol) (0.179 mL, 1.340 mmol, 1 equiv), EDCI (0.614 g, 3.203 mmol, 2.4 equiv), and DMAP (0.065 g, 0.532 mmol, 0.4 equiv) were stirred for 24 h in CH_2Cl_2 (50 mL). Yield: 0.446 g, 0.614 mmol, 46%. Elem anal. Calcd for $C_{44}H_{40}O_6P_2$: C, 72.72; H, 5.55. Found: C, 72.54; H, 5.58. ^1H NMR ($CDCl_3$): δ_H 7.95−7.98 (4H, m, 4O(C═O)(*Ar*)CC*H*CHCP, $^3J_{H,H}$ = 8.4 Hz, $^4J_{H,H}$ = 1.4 Hz), 7.29−7.38 (24H, m, 4O(C═O)(*Ar*)CCHC*H*CP, 8P(*Ar*)CC*H*CHCH, 8P(*Ar*)CCHC*H*CH, 4P(*Ar*)CCHCHC*H*), 4.43−4.45 (4H, m, 2*Ar*(C═O)OCH_2CH_2O), 3.79−3.82 (4H, m, 2*Ar*(C═O)OCH_2CH_2O), 3.69 (4H, s, 2*Ar*(C═O)O(CH_2)$_2$OCH_2). ^{31}P NMR ($CDCl_3$): δ_P −5.07 (2P). ^{13}C NMR ($CDCl_3$): δ_C 166.4 (2C, 2O(*C*═O)(*Ar*)CCHCHCP), 144.3 (2C, d, 2O(C═O)(*Ar*)CCHCHCP, $^1J_{C,P}$ = 14 Hz), 136.3 (4C, d, 4P(*Ar*)*C*CHCHCH, $^1J_{C,P}$ = 11 Hz), 134.1 (8C, d, 8P(*Ar*)*C*CHCHCH, $^2J_{C,P}$ = 20 Hz), 133.3 (4C, d, 4O(C═O)(*Ar*)CCHCHCP, $^2J_{C,P}$ = 19 Hz), 130.1 (2C, 2O(C═O)(*Ar*)CCHCHCP), 129.5 (4C, d, 4O(C═O)(Ar)CCHCHCP, $^3J_{C,P}$ = 6 Hz), 129.3 (4C, 4P(*Ar*)CCHCHCH), 128.8 (8C, d, 8P(*Ar*)CCHCHCH, $^3J_{C,P}$ = 7 Hz), 70.9 (2C, 2(*Ar*)(C═O)O(CH_2)$_2$OCH_2), 69.4 (2C, 2(*Ar*)(C═O)OCH_2CH_2O), 64.3 (2C, 2(*Ar*)(C═O)OCH_2CH_2O). ESI-MS(+). Calcd for $C_{44}H_{41}O_6P_2^+$: m/z 727.2378 ([M + Na]$^+$). Found: m/z 727.2383. Calcd for $C_{44}H_{40}NaO_5P_2^+$: m/z 749.2198 ([M + H]$^+$). Found: m/z 749.2202

Compound ***4a.*** According to the general procedure, 4-(diphenylphosphanyl)benzoic acid (0.900 g, 2.938 mmol, 2.2 equiv), tetrakis(ethylene glycol) (0.231 mL, 1.338 mmol, 1 equiv), EDCI (0.615 g, 3.203, 2.4 equiv), and DMAP (0.065 g, 0.532 mmol, 0.4 equiv) were stirred for 24 h in CH_2Cl_2 (50 mL). Yield: 0.487 g, 0.632 mmol, 47%. Elem anal. Calcd for $C_{46}H_{44}O_7P_2$: C, 71.68; H, 5.75. Found: C, 71.59, H, 5.83. ^1H NMR ($CDCl_3$): δ_H 7.95−8.00 (4H, m, 4O(C═O)(*Ar*)CC*H*CHCP, $^3J_{H,H}$ = 8.2 Hz, $^4J_{H,H}$ = 1.6 Hz), 7.29−7.38 (24H, m, 4O(C═O)(*Ar*)CCHC*H*CP, 8P(*Ar*)CC*H*CHCH, 8P(*Ar*)CCHC*H*CH, 4P(*Ar*)CCHCHC*H*), 4.43−4.46 (4H, m, 2*Ar*(C═O)OCH_2CH_2O), 3.77−3.80 (4H, m, 2*Ar*(C═O)OCH_2CH_2O), 3.61−3.70 (8H, m, 2*Ar*(C═O)O(CH_2)$_2$O(CH_2)$_2$). ^{31}P NMR ($CDCl_3$): δ_P −5.06 (2P). ^{13}C NMR ($CDCl_3$): δ_C 166.4 (2C, 2O(*C*═O)(*Ar*)CCHCHCP), 144.3 (2C, d, 2O(C═O)(*Ar*)CCHCHCP, $^1J_{C,P}$ = 14 Hz), 136.3 (4C, d, 4P(*Ar*)*C*CHCHCH, $^1J_{C,P}$ = 11 Hz), 134.1 (8C, d, 8P(*Ar*)*C*CHCHCH, $^2J_{C,P}$ = 20 Hz), 133.3 (4C, d, 4O(C═O)(*Ar*)CCHCHCP, $^2J_{C,P}$ = 19 Hz), 130.2 (2C, 2O(C═O)(*Ar*)CCHCHCP), 129.5 (4C, d, 4O(C═O)(Ar)CCHCHCP, $^3J_{C,P}$ = 7 Hz), 129.3 (4C, 4P(*Ar*)CCHCHCH), 128.8 (8C, d, 8P(*Ar*)CCHCHCH, $^3J_{C,P}$ = 7 Hz), 70.77, 70.79, 70.83 (4C, 2(*Ar*)(C═O)O(CH_2)$_2$OCH_2, 2(*Ar*)(C═O)O(CH_2)$_2$OCH_2CH_2), 69.3 (2C, 2(*Ar*)(C═O)OCH_2CH_2O), 64.3 (2C, 2(*Ar*)(C═O)OCH_2CH_2O). ESI-MS(+). Calcd for $C_{46}H_{45}O_7P_2^+$: m/z 771.2641 ([M + H]$^+$). Found: m/z 771.2630. Calcd for $C_{46}H_{44}NaO_7P_2^+$: m/z 793.2460 ([M + Na]$^+$). Found: m/z 793.2451.

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Compound ***5a***. According to the general procedure, 4-(diphenylphosphanyl)benzoic acid (0.800 g, 2.612 mmol, 2.2 equiv), pentakis(ethylene glycol) (0.251 mL, 1.186 mmol, 1 equiv), EDCI (0.546 g, 2.848 mmol, 2.4 equiv), and DMAP (0.058 g, 0.475 mmol, 0.4 equiv) were stirred for 24 h in CH_2Cl_2 (50 mL). Yield: 0.621 g, 0.762 mmol, 64%. Elem anal. Calcd for $C_{48}H_{48}O_8P_2$: C, 70.75; H, 5.94. Found: C, 70.85, H, 6.04. ^{1}H NMR ($CDCl_3$): δ_H 7.96−7.99 (4H, m, 4O(C═O)(*Ar*)CC*H*CHCP, $^3J_{H,H}$ = 8.4 Hz, $^4J_{H,H}$ = 1.6 Hz), 7.28−7.37 (24H, m, 4O(C═O)(*Ar*)CCHC*H*CP, 8P(*Ar*)CC*H*CHCH, 8P(*Ar*)CCHC*H*CH, 4P(*Ar*)CCHCHC*H*), 4.44−4.46 (4H, m, 2*Ar*(C═O)OCH_2CH_2O), 3.79−3.81 (4H, m, 2*Ar*(C═O)-OCH_2CH_2O), 3.65−3.68 (4H, m, 2*Ar*(C═O)O(CH_2)$_2$OCH_2CH_2), 3.61−3.64 (4H, m, 2*Ar*(C═O)O(CH_2)$_2$OCH_2CH_2), 3.62 (4H, s, 2*Ar*(C═O)O(CH_2)$_2$O(CH_2)$_2$OCH_2), ^{31}P NMR ($CDCl_3$): δ_P −5.08 (2P). ^{13}C NMR ($CDCl_3$): δ_C 166.4 (2C, 2O(*C*═O)(*Ar*)-CCHCHCP), 144.3 (2C, d, 2O(C═O)(*Ar*)CCHCHC*P*, $^1J_{C,P}$ = 14 Hz), 136.3 (4C, d, 4P(*Ar*)CCHCHCH, $^1J_{C,P}$ = 11 Hz), 134.1 (8C, d, 8P(*Ar*)C*C*HCHCH, $^2J_{C,P}$ = 20 Hz), 133.2 (4C, d, 4O(C═O)(*Ar*)-CCHCHCP, $^2J_{C,P}$ = 19 Hz), 130.1 (2C, 2O(C═O)(*Ar*)CCHCHCP), 129.5 (4C, d, 4O(C═O)(Ar)C*C*HCHCP, $^3J_{C,P}$ = 6 Hz), 129.1 (4C, 4P(*Ar*)CCHCH*C*H), 128.8 (8C, d, 8P(*Ar*)CCH*C*HCH, $^3J_{C,P}$ = 7 Hz), 70.80, 70.76, 70.73 (6C, 2(*Ar*)(C═O)O(CH_2)$_2$OCH_2, 2(*Ar*)(C═O)O(CH_2)$_2$OCH_2CH_2, 2(*Ar*)(C═O)O(CH_2)$_2$O(CH_2)$_2$OCH_2), 69.3 (2C, 2(*Ar*)(C═O)OCH_2CH_2O), 64.3 (2C, 2(*Ar*)(C═O)-OCH_2CH_2O). ESI-MS(+). Calcd for $C_{48}H_{49}O_8P_2^+$: *m*/*z* 815.2897 ([M + H]$^+$). Found: *m*/*z* 815.2905. Calcd for $C_{48}H_{48}NaO_8P_2^+$: *m*/*z* 837.2722 ([M + Na]$^+$). Found: *m*/*z* 837.2723.

Compound ***6a***. According to the general procedure, 4-(diphenylphosphanyl)benzoic acid (0.800 g, 2.612 mmol, 2.2 equiv), hexakis(ethylene glycol) (0.298 mL, 1.190 mmol, 1 equiv), EDCI (0.546 g, 2.848 mmol, 2.4 equiv), and DMAP (0.058 g, 0.475 mmol, 0.4 equiv) were stirred for 24 h in CH_2Cl_2 (50 mL). Yield: 0.341 g, 0.397 mmol, 33%. Elem anal. Calcd for $C_{50}H_{52}O_9P_2$: C, 69.92; H, 6.10. Found: C, 70.04; H, 6.13. ^{1}H NMR ($CDCl_3$): δ_H 7.96−7.99 (4H, m, 4O(C═O)(*Ar*)CC*H*CHCP, $^3J_{H,H}$ = 8.4 Hz, $^4J_{H,H}$ = 1.2 Hz), 7.28−7.39 (24H, m, 4O(C═O)(*Ar*)CCHC*H*CP, 8P(*Ar*)CC*H*CHCH, 8P(*Ar*)CCHC*H*-CH, 4P(*Ar*)CCHCHC*H*), 4.44−4.47 (4H, m, 2*Ar*(C═O)OCH_2CH_2O), 3.79−3.82 (4H, m, 2*Ar*(C═O)-OCH_2CH_2O), 3.66−3.69 (4H, m, 2*Ar*(C═O)O(CH_2)$_2$OCH_2CH_2), 3.61−3.65 (4H, m, 2*Ar*(C═O)O(CH_2)$_2$OCH_2CH_2), 3.58−3.62 (8H, m, 2*Ar*(C═O)O(CH_2)$_2$O(CH_2)$_2$O(CH_2)$_2$. ^{31}P NMR ($CDCl_3$): δ_P 5.06 (2P). ^{13}C NMR ($CDCl_3$): δ_C 166.3 (2C, 2O(*C*═O)(*Ar*)-CCHCHCP), 144.1 (2C, d, 2O(C═O)(*Ar*)CCHCHC*P*, $^1J_{C,P}$ = 14 Hz), 136.1 (4C, d, 4P(*Ar*)CCHCHCH, $^1J_{C,P}$ = 11 Hz), 133.9 (8C, d, 8P(*Ar*)C*C*HCHCH, $^2J_{C,P}$ = 20 Hz), 133.1 (4C, d, 4O(C═O)(*Ar*)-CCHCHCP, $^2J_{C,P}$ = 19 Hz), 130.0 (2C, 2O(C═O)(*Ar*)CCHCHCP), 129.4 (4C, d, 4O(C═O)(Ar)C*C*HCHCP, $^3J_{C,P}$ = 6 Hz), 129.1 (4C, 4P(*Ar*)CCHCH*C*H), 128.7 (8C, d, 8P(*Ar*)CCH*C*HCH, $^3J_{C,P}$ = 7 Hz), 70.70, 70.65, 70.63, 70.59 (8C, 2(*Ar*)(C═O)O(CH_2)$_2$OCH_2, 2(*Ar*)-(C═O)O(CH_2)$_2$OCH_2CH_2, 2(*Ar*)(C═O)O(CH_2)$_2$O(CH_2)$_2$OCH_2, 2(*Ar*)(C═O)O(CH_2)$_2$O(CH_2)$_2$OCH_2CH_2), 69.2 (2C, 2(*Ar*)(C═O)OCH_2CH_2O), 64.2 (2C, 2(*Ar*)(C═O)OCH_2CH_2O). ESI-MS(+). Calcd for $C_{50}H_{53}O_9P_2^+$: *m*/*z* 859.3165 ([M + H]$^+$). Found: *m*/*z* 859.3168. Calcd for $C_{50}H_{52}NaO_9P_2^+$: *m*/*z* 881.2984 ([M + Na]$^+$). Found: *m*/*z* 881.2988.

Compound ***7a***. According to the general procedure, 4-(diphenylphosphanyl)benzoic acid (0.800 g, 2.612 mmol, 2.2 equiv), octakis(ethylene glycol) (0.440 g, 1.188 mmol, 1 equiv), EDCI (0.546 g, 2.848 mmol, 2.4 equiv), and DMAP (0.058 g, 0.475 mmol, 0.4 equiv) were stirred for 24 h in CH_2Cl_2 (50 mL). Yield: 0.499 g, 0.527 mmol, 45%. Elem anal. Calcd for $C_{54}H_{60}O_{11}P_2$: C, 68.49; H, 6.39. Found: C, 68.16; H, 6.35. ^{1}H NMR ($CDCl_3$): δ_H 7.96−8.00 (4H, m, 4O(C═O)(*Ar*)CC*H*CHCP, $^3J_{H,H}$ = 8.4 Hz, $^4J_{H,H}$ = 1.6 Hz), 7.29−7.37 (24H, m, 4O(C═O)(*Ar*)CCHC*H*CP, 8P(*Ar*)CC*H*CHCH, 8P(*Ar*)CCHC*H*CH, 4P(*Ar*)CCHCHC*H*), 4.45−4.47 (4H, m, 2*Ar*(C═O)OCH_2CH_2O), 3.80−3.82 (4H, m, 2*Ar*(C═O)-OCH_2CH_2O), 3.67−3.70 (4H, m, 2*Ar*(C═O)O(CH_2)$_2$OCH_2CH_2), 3.63−3.66 (4H, m, 2*Ar*(C═O)O(CH_2)$_2$OCH_2CH_2), 3.60−3.62 (8H, m, 2*Ar*(C═O)O(CH_2)$_2$O(CH_2)$_2$O(CH_2)$_2$), 3.61 (8H, s, 2*Ar*(C═O)O(CH_2)$_2$O(CH_2)$_2$O(CH_2)$_2$O(CH_2)$_2$. ^{31}P NMR ($CDCl_3$): δ_P −5.06 (2P). ^{13}C NMR ($CDCl_3$): δ_C 166.4 (2C, 2O(*C*═O)(*Ar*)-CCHCHCP), 144.4 (2C, d, 2O(C═O)(*Ar*)CCHCHC*P*, $^1J_{C,P}$ = 15 Hz), 136.5 (4C, d, 4P(*Ar*)CCHCHCH, $^1J_{C,P}$ = 11 Hz), 134.1 (8C, d, 8P(*Ar*)CCHCHCH, $^2J_{C,P}$ = 20 Hz), 133.3 (4C, d, 4O(C═O)(*Ar*)-CCHCHCP, $^2J_{C,P}$ = 19 Hz), 130.1 (2C, 2O(C═O)(*Ar*)CCHCHCP), 129.5 (4C, d, 4O(C═O)(Ar)C*C*HCHCP, $^3J_{C,P}$ = 6 Hz), 129.3 (4C, 4P(*Ar*)CCHCHCH), 128.8 (8C, d, 8P(*Ar*)CCH*C*HCH, $^3J_{C,P}$ = 7 Hz), 70.92, 70.88, 70.85, 70.81 (12C, 2(*Ar*)(C═O)O(CH_2)$_2$OCH_2, 2(*Ar*)(C═O)O(CH_2)$_2$OCH_2CH_2, 2(*Ar*)(C═O)O(CH_2)$_2$O-(CH_2)$_2$OCH_2, 2(*Ar*)(C═O)O(CH_2)$_2$O(CH_2)$_2$OCH_2CH_2, 2(*Ar*)-(C═O)O(CH_2)$_2$O(CH_2)$_2$O(CH_2)$_2$OCH_2, 2(*Ar*)(C═O)O-(CH_2)$_2$O(CH_2)$_2$O(CH_2)$_2$OCH_2CH_2), 69.4 (2C, 2(*Ar*)(C═O)-OCH_2CH_2O), 64.7 (2C, 2(*Ar*)(C═O)OCH_2CH_2O). ESI-MS(+). Calcd for $C_{54}H_{61}O_{11}P_2^+$: *m*/*z* 947.3684 ([M + H]$^+$). Found: *m*/*z* 947.3671. Calcd for $C_{54}H_{60}NaO_{11}P_2^+$: *m*/*z* 969.3509 ([M + Na]$^+$). Found: *m*/*z* 969.3488.

General Procedure for the Synthesis of the Diruthenium Complexes ***1b***−***7b***. [Ru(η^6-*p*-cymene)Cl]$_2$Cl$_2$ (1 equiv) and the appropriate ligand **1a**−**7a** (1 equiv) in CH_2Cl_2 (12 mL) were stirred for 42 h at RT under N_2 in the dark. The reaction evolution was monitored by ^{1}H and ^{31}P NMR ($CDCl_3$). The reaction mixture was concentrated under reduced pressure and then further dried under high vacuum to yield the product as a red solid.

Compound ***1b***. According to the general procedure, [Ru(η^6-*p*-cymene)Cl]$_2$Cl$_2$ (0.19 g, 0.307 mmol, 1 equiv), **1a** (0.20 g, 0.307 mmol, 1 equiv), and CH_2Cl_2 (12 mL) were stirred for 42 h at RT. The product was isolated as a dark-red solid. Yield: 0.376 g, 0.301 mmol, 98%. Elem anal. Calcd for $C_{60}H_{60}Cl_4O_4P_2Ru_2{\cdot}CH_2Cl_2$: C, 54.84; H, 4.68. Found: C, 54.77; H, 4.93. CH_2Cl_2 originates from the reaction solvent. ^{1}H NMR ($CDCl_3$): δ_H 7.88−7.97 (8H, m, 4O(C═O)(*Ar*)CC*H*CHCP, 4O(C═O)(*Ar*)CCHC*H*CP), 7.77−7.82 (8H, m, 8P(*Ar*)CC*H*CHCH), 7.34−7.44 (12H, m, 8P(*Ar*)CCHC*H*CH, 4P(*Ar*)CCHCHC*H*), 5.20 (4H, d, 4CH$_3$(*Ar*)CCHC*H*C, $^3J_{H,H}$ = 6.1 Hz), 4.98 (4H, d, 4CH$_3$(*Ar*)CC*H*CHC, $^3J_{H,H}$ = 6.1 Hz), 4.58 (4H, s, 2*Ar*(C═O)OCH_2CH_2O), 2.83 (2H, sept, 2(*Ar*)-CCHCHCC*H*(CH$_3$)$_2$, $^3J_{H,H}$ = 7.2 Hz), 1.84 (6H, s, 2CH$_3$(*Ar*)-CCHCHC), 1.09 (12H, d, 2(*Ar*)CCHCHCCH(C*H*$_3$)$_2$, $^3J_{H,H}$ = 7.2 Hz). ^{31}P NMR ($CDCl_3$): δ_P 25.00 (2P). ^{13}C NMR ($CDCl_3$): δ_C 165.8 (2C, 2O(*C*═O)(*Ar*)CCHCHCP), 139.7 (2C, d, 2O(C═O)(*Ar*)-CCHCHCP, $^1J_{C,P}$ = 43 Hz), 134.4 (4C, d, 4O(C═O)(*Ar*)-CCHCHCP, $^2J_{C,P}$ = 9 Hz), 134.3 (8C, d, 8P(*Ar*)CCHCHCH, $^2J_{C,P}$ = 9 Hz), 133.3 (4C, d, 4P(*Ar*)CCHCHCH, $^1J_{C,P}$ = 45 Hz), 130.9 (2C, d, 2O(C═O)(*Ar*)CCHCHCP, $^4J_{C,P}$ = 3 Hz), 130.6 (4C, d, 4P(*Ar*)CCHCHCH, $^4J_{C,P}$ = 2 Hz), 128.8 (4C, d, 4O(C═O)(Ar)-CCHCHCP, $^3J_{C,P}$ = 10 Hz), 128.3 (8C, d, 8P(*Ar*)CCHCHCH, $^3J_{C,P}$ = 10 Hz), 111.46, 111.43 (2C, 2CH$_3$(*Ar*)CCHCHC), 96.4 (2C, 2CH$_3$(*Ar*)CCHCHC), 89.12, 89.09 (4C, 4CH$_3$(*Ar*)CCHCHC), 87.39, 87.34 (4C, 4CH$_3$(*Ar*)CCHCHC), 63.0 (2C, 2(*Ar*)(C═O)OCH_2CH_2O), 30.4 (2C, 2(*Ar*)CHCHCCH(CH$_3$)$_2$), 21.9 (4C, 2(*Ar*)CHCHCCH(CH_3)$_2$), 17.9 (2C, 2CH$_3$(*Ar*)CCHCH). ESI-MS(+). Calcd for $C_{60}H_{60}Cl_2O_4P_2Ru_2^+$: *m*/*z* 1180.1431 ([M − 2Cl]$^+$). Found: *m*/*z* 1180.1499. Calcd for $C_{60}H_{60}Cl_3O_4P_2Ru_2^+$: *m*/*z* 1215.1119 ([M − Cl]$^+$). Found: *m*/*z* 1215.1104. Calcd for $C_{60}H_{60}Cl_4NaO_4P_2Ru_2^+$: *m*/*z* 1273.0706 ([M + Na]$^+$). Found: *m*/*z* 1273.0695. UV−vis: λ_{max} = 250 and 370 nm.

Compound ***2b***. According to the general procedure, [Ru(η^6-*p*-cymene)Cl]$_2$Cl$_2$ (0.49 g, 0.808 mmol, 1 equiv), **2a** (0.55 g, 0.808 mmol, 1 equiv), and CH_2Cl_2 (12 mL) were stirred for 42 h at RT. The product was isolated as a dark-red solid. Yield: 1.03 g, 0.791 mmol, 98%. Elem anal. Calcd for $C_{62}H_{64}Cl_4O_5P_2Ru_2$: C, 57.50; H, 4.98. Found: C, 57.76; H, 5.12. ^{1}H NMR ($CDCl_3$): δ_H 7.86−7.96 (8H, m, 4O(C═O)(*Ar*)CC*H*CHCP, 4O(C═O)(*Ar*)CCHC*H*CP), 7.78−7.83 (8H, m, 8P(*Ar*)CC*H*CHCH), 7.36−7.44 (12H, m, 8P(*Ar*)-CCHC*H*CH, 4P(*Ar*)CCHCHC*H*), 5.21 (4H, d, 4CH$_3$(*Ar*)-CCHCHC, $^3J_{H,H}$ = 6.2 Hz), 4.98 (4H, d, 4CH$_3$(*Ar*)CC*H*CHC, $^3J_{H,H}$ = 6.2 Hz), 4.45−4.42 (4H, m, 2*Ar*(C═O)OCH_2CH_2O), 3.83−3.81 (4H, m, 2*Ar*(C═O)OCH$_2$CH_2O), 2.85 (2H, sept, 2(*Ar*)-CCHCHCC*H*(CH$_3$)$_2$, $^3J_{H,H}$ = 6.9 Hz), 1.85 (6H, s, 2CH$_3$(*Ar*)-CCHCHC), 1.09 (12H, d, 2(*Ar*)CCHCHCCH(CH_3)$_2$, $^3J_{H,H}$ = 6.9 Hz). ^{31}P NMR ($CDCl_3$): δ_P 24.95 (2P). ^{13}C NMR ($CDCl_3$): δ_C 166.1

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(2C, 2O(*C*═O)(*Ar*)CCHCHCP), 139.5 (2C, d, 2O(C═O)(*Ar*)-CCHCHCP, $^{1}J_{C,P}$ = 43 Hz), 134.5 (4C, d, 4O(C═O)(*Ar*)-CCHCHCP, $^{2}J_{C,P}$ = 9 Hz), 134.4 (8C, d, 8P(*Ar*)CCHCHCH, $^{2}J_{C,P}$ = 9 Hz), 133.4 (4C, d, 4P(*Ar*)CCHCHCH, $^{1}J_{C,P}$ = 45 Hz), 131.3 (2C, d, 2O(C═O)(*Ar*)CCHCHCP, $^{4}J_{C,P}$ = 2 Hz), 130.7 (4C, d, 4P(*Ar*)CCHCHCH, $^{4}J_{C,P}$ = 2 Hz), 128.8 (4C, d, 4O(C═O)(Ar)-CCHCHCP, $^{3}J_{C,P}$ = 10 Hz), 128.3 (8C, d, 8P(*Ar*)CCHCHCH, $^{3}J_{C,P}$ = 10 Hz), 111.59, 111.56 (2C, 2CH_3(*Ar*)CCHCHC), 96.4 (2C, 2CH_3(*Ar*)CCHCHC), 89.15, 89.12 (4C, 4CH_3(*Ar*)CCHCHC), 87.49, 87.43 (4C, 4CH_3(*Ar*)CCHCHC), 69.4 (2C, 2(*Ar*)(C═O)OCH_2CH_2O), 64.5 (2C, 2(*Ar*)(C═O)OCH_2CH_2O), 30.4 (2C, 2(*Ar*)CHCHCCH$(CH_3)_2$), 22.0 (4C, 2(*Ar*)CHCHCCH$(CH_3)_2$), 17.9 (2C, 2CH_3(*Ar*)CCHCH). ESI-MS(+). Calcd for $C_{62}H_{64}Cl_2O_5P_2Ru_2^+$: *m*/*z* 1224.1693 ([M − 2Cl]$^+$). Found: *m*/*z* 1224.1804. Calcd for $C_{62}H_{64}Cl_3O_5P_2Ru_2^+$: *m*/*z* 1259.1382 ([M − Cl]$^+$). Found: *m*/*z* 1259.1396. Calcd for $C_{62}H_{64}Cl_4NaO_5P_2Ru_2^+$: *m*/*z* 1317.0962 ([M + Na]$^+$). Found: *m*/*z* 1317.0995. UV−vis: λ_{max} = 250 and 370 nm.

Compound ***3b***. According to the general procedure, [Ru(η^6-*p*-cymene)Cl]$_2$Cl$_2$ (0.15 g, 0.251 mmol, 1 equiv), **3a** (0.18 g, 0.251 mmol, 1 equiv), and CH_2Cl_2 (12 mL) were stirred for 42 h at RT. The product was isolated as a dark-red solid. Yield: 0.33 g, 0.246 mmol, 98%. Elem anal. Calcd for $C_{64}H_{66}Cl_4O_6P_2Ru_2{\cdot}CH_2Cl_2$: C, 54.82; H, 4.95. Found: C, 54.75, H, 4.95. CH_2Cl_2 originates from the reaction solvent. ^{1}H NMR ($CDCl_3$): δ_H 7.86−7.94 (8H, m, 4O(C═O)(*Ar*)CC*H*CHCP, 4O(C═O)(*Ar*)CCHC*H*CP), 7.76−7.82 (8H, m, 8P(*Ar*)CC*H*CHCH), 7.34−7.46 (12H, m, 8P(*Ar*)CCHC*H*CH, 4P(*Ar*)CCHCHC*H*), 5.19 (4H, d, 4CH_3(*Ar*)CCHC*H*C, $^{3}J_{H,H}$ = 6.1 Hz), 4.96 (4H, d, 4CH_3(*Ar*)CC*H*CHC, $^{3}J_{H,H}$ = 6.1 Hz), 4.40−4.38 (4H, m, 2*Ar*(C═O)OCH_2CH_2O), 3.77−3.74 (4H, m, 2*Ar*(C═O)OCH_2CH_2O), 3.65 (4H, s, 2*Ar*(C═O)O$(CH_2)_2OCH_2$), 2.83 (2H, sept, 2(*Ar*)CCHCHCC*H*$(CH_3)_2$, $^{3}J_{H,H}$ = 6.9 Hz), 1.83 (6H, s, 2CH_3(*Ar*)CCHCHC), 1.08 (12H, d, 2(*Ar*)CCHCHCCH$(CH_3)_2$, $^{3}J_{H,H}$ = 6.9 Hz). ^{31}P NMR ($CDCl_3$): δ_P 24.94 (2P). ^{13}C NMR ($CDCl_3$): δ_C 166.0 (2C, 2O(*C*═O)-(*Ar*)CCHCHCP), 139.4 (2C, d, 2O(C═O)(*Ar*)CCHCHCP, $^{1}J_{C,P}$ = 44 Hz), 134.4 (4C, d, 4O(C═O)(*Ar*)CCHCHCP, $^{2}J_{C,P}$ = 8 Hz), 134.3 (8C, d, 8P(*Ar*)CCHCHCH, $^{2}J_{C,P}$ = 9 Hz), 133.4 (4C, d, 4P(*Ar*)CCHCHCH, $^{1}J_{C,P}$ = 45 Hz), 131.4 (2C, m, 2O(C═O)(*Ar*)CCHCHCP), 130.7 (4C, m, 4P(*Ar*)-CCHCHCH), 128.8 (4C, d, 4O(C═O)(Ar)CCHCHCP, $^{3}J_{C,P}$ = 10 Hz), 128.3 (8C, d, 8P(*Ar*)CCHCHCH, $^{3}J_{C,P}$ = 10 Hz), 111.50, 111.47 (2C, 2CH_3(*Ar*)CCHCHC), 96.4 (2C, 2CH_3(*Ar*)CCHCHC), 89.09, 89.07 (4C, 4CH_3(*Ar*)CCHCHC), 87.43, 87.38 (4C, 4CH_3(*Ar*)-CCHCHC), 70.8 (2C, 2(*Ar*)(C═O)O$(CH_2)_2OCH_2CH_2$), 69.3 (2C, 2(*Ar*)(C═O)OCH_2CH_2O), 64.4 (2C, 2(*Ar*)(C═O)-OCH_2CH_2O), 30.4 (2C, 2(*Ar*)CHCHCCH$(CH_3)_2$), 22.0 (4C, 2(*Ar*)CHCHCCH$(CH_3)_2$), 17.9 (2C, 2CH_3(*Ar*)CCHCH). ESI-MS(+). Calcd for $C_{64}H_{68}Cl_3O_6P_2Ru_2^+$: *m*/*z* 1303.1644 ([M − Cl]$^+$). Found: *m*/*z* 1303.1660. Calcd for $C_{64}H_{68}Cl_3NaO_6P_2Ru_2^+$: *m*/*z* 1361.1224 ([M + Na]$^+$). Found: *m*/*z* 1361.1219. UV−vis: λ_{max} = 250 and 370 nm.

Compound ***4b***. According to the general procedure, [Ru(η^6-*p*-cymene)Cl]$_2$Cl$_2$ (0.13 g, 0.205 mmol, 1 equiv), **4a** (0.16 g, 0.205 mmol, 1 equiv), and CH_2Cl_2 (12 mL) were stirred for 42 h at RT. The product was isolated as a red solid. Yield: 0.275 g, 0.199 mmol, 97%. Elem anal. Calcd for $C_{66}H_{72}Cl_4O_7P_2Ru_2{\cdot}{}^1/_2CH_2Cl_2$: C, 56.03; H, 5.06. Found: C, 55.67; H, 5.16. CH_2Cl_2 originates from the reaction solvent. ^{1}H NMR ($CDCl_3$): δ_H 7.85−7.95 (8H, m, 4O(C═O)(*Ar*)-CC*H*CHCP, 4O(C═O)(*Ar*)CCHC*H*CP), 7.76−7.81 (8H, m, 8P-(*Ar*)CC*H*CHCH), 7.34−7.42 (12H, m, 8P(*Ar*)CCHC*H*CH, 4P(*Ar*)-CCHCHC*H*), 5.19 (4H, d, 4CH_3(*Ar*)CCHC*H*C, $^{3}J_{H,H}$ = 6.2 Hz), 4.96 (4H, d, 4CH_3(*Ar*)CC*H*CHC, $^{3}J_{H,H}$ = 6.2 Hz), 4.41−4.38 (4H, m, 2*Ar*(C═O)OCH_2CH_2O), 3.75−3.73 (4H, m, 2*Ar*(C═O)-OCH_2CH_2O), 3.64−3.60 (8H, m, 2*Ar*(C═O)O$(CH_2)_2OCH_2CH_2$, 2*Ar*(C═O)O$(CH_2)_2OCH_2CH_2$), 2.83 (2H, sept, 2(*Ar*)-CCHCHCC*H*$(CH_3)_2$, $^{3}J_{H,H}$ = 6.9 Hz), 1.83 (6H, s, 2CH_3(*Ar*)-CCHCHC), 1.08 (12H, d, 2(*Ar*)CCHCHCCH$(CH_3)_2$, $^{3}J_{H,H}$ = 6.9 Hz). ^{31}P NMR ($CDCl_3$): δ_P 24.96 (2P). ^{13}C NMR ($CDCl_3$): δ_C 166.1 (2C, 2O(*C*═O)(*Ar*)CCHCHCP), 139.4 (2C, d, 2O(C═O)(*Ar*)-CCHCHCP, $^{1}J_{C,P}$ = 44 Hz), 134.5 (4C, d, 4O(C═O)(*Ar*)-CCHCHCP, $^{2}J_{C,P}$ = 8 Hz), 134.4 (8C, d, 8P(*Ar*)CCHCHCH, $^{2}J_{C,P}$ = 9 Hz), 133.4 (4C, d, 4P(*Ar*)CCHCHCH, $^{1}J_{C,P}$ = 45 Hz), 131.4 (2C, d, 2O(C═O)(*Ar*)CCHCHCP, $^{4}J_{C,P}$ = 2 Hz), 130.7 (4C, d, 4P(*Ar*)CCHCHCH, $^{4}J_{C,P}$ = 2 Hz), 128.8 (4C, d, 4O(C═O)(Ar)-CCHCHCP, $^{3}J_{C,P}$ = 10 Hz), 128.3 (8C, d, 8P(*Ar*)CCHCHCH, $^{3}J_{C,P}$ = 10 Hz), 111.54, 111.50 (2C, 2CH_3(*Ar*)CCHCHC), 96.4 (2C, 2CH_3(*Ar*)CCHCHC), 89.11, 89.09 (4C, 4CH_3(*Ar*)CCHCHC), 87.46, 87.40 (4C, 4CH_3(*Ar*)CCHCHC), 70.8, 70.4 (4C, 2(*Ar*)(C═O)O$(CH_2)_2OCH_2$, 2(*Ar*)(C═O)O$(CH_2)_2OCH_2CH_2$), 69.2 (2C, 2(*Ar*)(C═O)OCH_2CH_2O), 64.5 (2C, 2(*Ar*)(C═O)OCH_2CH_2O), 30.4 (2C, 2(*Ar*)CHCHCCH$(CH_3)_2$), 22.0 (4C, 2(*Ar*)CHCHCCH-$(CH_3)_2$), 17.9 (2C, 2CH_3(*Ar*)CCHCH). ESI-MS(+). Calcd for $C_{66}H_{72}Cl_2O_7P_2Ru_2^{2+}$: 1312.2206 ([M − 2Cl]$^+$). Found: *m*/*z* 1312.2328. Calcd for $C_{66}H_{72}Cl_3O_7P_2Ru_2^+$: 1347.1900 ([M − Cl]$^+$). Found: *m*/*z* 1347.1923. Calcd for $C_{66}H_{72}Cl_4NaO_7P_2Ru_2^+$: 1405.1487 ([M + Na]$^+$). Found: *m*/*z* 1405.1474. UV−vis: λ_{max} = 250 and 370 nm.

Compound ***5b***. According to the general procedure, [Ru(η^6-*p*-cymene)Cl]$_2$Cl$_2$ (0.16 g, 0.269 mmol, 1 equiv), **5a** (0.22 g, 0.269 mmol, 1 equiv), and CH_2Cl_2 (12 mL) were stirred for 42 h at RT. The product was isolated as a red solid. Yield: 0.38 g, 0.263 mmol, 98%. Elem anal. Calcd for $C_{68}H_{76}Cl_4O_8P_2Ru_2{\cdot}{}^1/_2CH_2Cl_2$: C, 55.98; H, 5.28. Found: C, 55.86; H, 5.34. CH_2Cl_2 originates from the reaction solvent. ^{1}H NMR ($CDCl_3$): δ_H 7.88−7.97 (8H, m, 4O(C═O)(*Ar*)-CC*H*CHCP, 4O(C═O)(*Ar*)CCHC*H*CP), 7.77−7.81 (8H, m, 8P-(*Ar*)CC*H*CHCH), 7.35−7.42 (12H, m, 8P(*Ar*)CCHC*H*CH, 4P(*Ar*)-CCHCHC*H*), 5.20 (4H, d, 4CH_3(*Ar*)CCHC*H*C, $^{3}J_{H,H}$ = 6.1 Hz), 4.96 (4H, d, 4CH_3(*Ar*)CC*H*CHC, $^{3}J_{H,H}$ = 6.1 Hz), 4.42−4.39 (4H, m, 2*Ar*(C═O)OCH_2CH_2O), 3.77−3.74 (4H, m, 2*Ar*(C═O)-OCH_2CH_2O), 3.65−3.56 (12H, m, 2*Ar*(C═O)O$(CH_2)_2OCH_2CH_2$, 2*Ar*(C═O)O$(CH_2)_2OCH_2CH_2$, 2*Ar*(C═O)O$(CH_2)_2$O-$(CH_2)_2OCH_2$), 2.83 (2H, sept, 2(*Ar*)CCHCHCC*H*$(CH_3)_2$, $^{3}J_{H,H}$ = 6.9 Hz), 1.84 (6H, s, 2CH_3(*Ar*)CCHCHC), 1.09 (12H, d, 2(*Ar*)CCHCHCCH$(CH_3)_2$, $^{3}J_{H,H}$ = 6.9 Hz). ^{31}P NMR ($CDCl_3$): δ_P 24.96 (2P). ^{13}C NMR ($CDCl_3$): δ_C 166.1 (2C, 2O(*C*═O)(*Ar*)-CCHCHCP), 139.4 (2C, d, 2O(C═O)(*Ar*)CCHCHCP, $^{1}J_{C,P}$ = 44 Hz), 134.5 (4C, d, 4O(C═O)(*Ar*)CCHCHCP, $^{2}J_{C,P}$ = 7 Hz), 134.4 (8C, d, 8P(*Ar*)CCHCHCH, $^{2}J_{C,P}$ = 9 Hz), 133.4 (4C, d, 4P(*Ar*)CCHCHCH, $^{1}J_{C,P}$ = 45 Hz), 131.4 (2C, d, 2O(C═O)(*Ar*)CCHCHCP, $^{4}J_{C,P}$ = 2 Hz), 130.7 (4C, d, 4P(*Ar*)CCHCHCH, $^{4}J_{C,P}$ = 2 Hz), 128.8 (4C, d, 4O(C═O)(Ar)CCHCHCP, $^{3}J_{C,P}$ = 10 Hz), 128.3 (8C, d, 8P(*Ar*)CCHCHCH, $^{3}J_{C,P}$ = 10 Hz), 111.56, 111.53 (2C, 2CH_3(*Ar*)CCHCHC), 96.4 (2C, 2CH_3(*Ar*)CCHCHC), 89.09, 89.11 (4C, 4CH_3(*Ar*)CCHCHC), 87.41, 87.46 (4C, 4CH_3(*Ar*)CCHCHC), 70.8, 70.7 (6C, 2(*Ar*)(C═O)O$(CH_2)_2OCH_2$, 2(*Ar*)(C═O)O-$(CH_2)_2OCH_2CH_2$, 2(*Ar*)(C═O)O$(CH_2)_2$O$(CH_2)_2OCH_2$), 69.2 (2C, 2(*Ar*)(C═O)OCH_2CH_2O), 64.5 (2C, 2(*Ar*)(C═O)-OCH_2CH_2O), 30.4 (2C, 2(*Ar*)CHCHCCH$(CH_3)_2$), 22.0 (4C, 2(*Ar*)CHCHCCH$(CH_3)_2$), 17.9 (2C, 2CH_3(*Ar*)CCHCH). ESI-MS(+). Calcd for $C_{68}H_{76}Cl_2O_8P_2Ru_2^{2+}$: *m*/*z* 1356.2583 ([M − 2Cl]$^+$). Found: *m*/*z* 1356.2609. Calcd for $C_{68}H_{76}Cl_3O_8P_2Ru_2^+$: *m*/*z* 1391.2168 ([M − Cl]$^+$). Found: *m*/*z* 1391.2207. Calcd for $C_{68}H_{76}Cl_4NaO_8P_2Ru_2^+$: *m*/*z* 1449.1749 ([M + Na]$^+$). Found: *m*/*z* 1449.1803. UV−vis: λ_{max} = 250 and 370 nm.

Compound ***6b***. According to the general procedure, [Ru(η^6-*p*-cymene)Cl]$_2$Cl$_2$ (0.16 g, 0.261 mmol, 1 equiv), **6a** (0.22 g, 0.261 mmol, 1 equiv), and CH_2Cl_2 (12 mL) were stirred for 42 h at RT. The product was isolated as a red solid. Yield: 0.38 g, 0.256 mmol, 98%. Elem anal. Calcd for $C_{70}H_{80}Cl_4O_9P_2Ru_2$: C, 57.14; H, 5.48. Found: C, 57.05, H, 5.64. ^{1}H NMR ($CDCl_3$): δ_H 7.88−7.97 (8H, m, 4O(C═O)(*Ar*)CC*H*CHCP, 4O(C═O)(*Ar*)CCHC*H*CP), 7.78−7.83 (8H, m, 8P(*Ar*)CC*H*CHCH), 7.36−7.45 (12H, m, 8P(*Ar*)CCHC*H*CH, 4P-(*Ar*)CCHCHC*H*), 5.21 (4H, d, 4CH_3(*Ar*)CCHC*H*C, $^{3}J_{H,H}$ = 6.2 Hz), 4.97 (4H, d, 4CH_3(*Ar*)CC*H*CHC, $^{3}J_{H,H}$ = 6.2 Hz), 4.44−4.41 (4H, m, 2*Ar*(C═O)OCH_2CH_2O), 3.79−3.77 (4H, m, 2*Ar*(C═O)-OCH_2CH_2O), 3.67−3.61 (16H, m, 2*Ar*(C═O)O$(CH_2)_2OCH_2CH_2$, 2*Ar*(C═O)O$(CH_2)_2OCH_2CH_2$, 2*Ar*(C═O)O$(CH_2)_2$O-$(CH_2)_2OCH_2$), 2*Ar*(C═O)O$(CH_2)_2$O$(CH_2)_2OCH_2CH_2$), 2.85 (2H, sept, 2(*Ar*)CCHCHCC*H*$(CH_3)_2$, $^{3}J_{H,H}$ = 6.9 Hz), 1.86 (6H, s, 2CH_3(*Ar*)CCHCHC), 1.10 (12H, d, 2(*Ar*)CCHCHCCH$(CH_3)_2$,

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$^{3}J_{H,H}$ = 6.9 Hz). ^{31}P NMR ($CDCl_3$): δ_P 24.96 (2P). ^{13}C NMR ($CDCl_3$): δ_C 166.1 (2C, 2O(C═O)(*Ar*)CCHCHCP), 139.4 (2C, d, 2O(C═O)(*Ar*)CCHCHCP, $^{1}J_{C,P}$ = 44 Hz), 134.5 (4C, d, 4O(C═O)(*Ar*)CCHCHCP, $^{2}J_{C,P}$ = 7 Hz), 134.4 (8C, d, 8P(*Ar*)CCHCHCH, $^{2}J_{C,P}$ = 9 Hz), 133.4 (4C, d, 4P(*Ar*)CCHCHCH, $^{1}J_{C,P}$ = 45 Hz), 131.4 (2C, d, 2O(C═O)(*Ar*)CCHCHCP, $^{4}J_{C,P}$ = 2 Hz), 130.7 (4C, d, 4P(*Ar*)CCHCHCH, $^{4}J_{C,P}$ = 2 Hz), 128.8 (4C, d, 4O(C═O)(Ar)-CCHCHCP, $^{3}J_{C,P}$ = 10 Hz), 128.3 (8C, d, 8P(*Ar*)CCHCHCH, $^{3}J_{C,P}$ = 10 Hz), 111.61, 111.58 (2C, 2CH_3(*Ar*)CCHCHC), 96.4 (2C, 2CH_3(*Ar*)CCHCHC), 89.13, 89.10 (4C, 4CH_3(*Ar*)CCHCHC), 87.49, 87.44 (4C, 4CH_3(*Ar*)CCHCHC), 70.82, 70.73, 70.67 (8C, 2(*Ar*)(C═O)O$(CH_2)_2$OCH_2, 2(*Ar*)(C═O)O$(CH_2)_2$OCH_2CH_2, 2-(*Ar*)(C═O)O$(CH_2)_2$O$(CH_2)_2$OCH_2, 2(*Ar*)(C═O)O$(CH_2)_2$O-$(CH_2)_2$OCH_2CH_2), 69.2 (2C, 2(*Ar*)(C═O)OCH_2CH_2O), 64.5 (2C, 2(*Ar*)(C═O)OCH_2CH_2O), 30.4 (2C, 2(*Ar*)CHCHCCH-$(CH_3)_2$), 22.0 (4C, 2(*Ar*)CHCHCCH$(CH_3)_2$), 17.9 (2C, 2CH_3(*Ar*)-CCHCH). ESI-MS(+). Calcd for $C_{70}H_{80}Cl_2O_9P_2Ru_2^{2+}$: *m*/*z* 1400.2742 ([M − 2Cl]$^+$). Found: *m*/*z* 1400.2695. Calcd for $C_{70}H_{80}Cl_3O_9P_2Ru_2^{+}$: *m*/*z* 1435.2430 ([M − Cl]$^+$). Found: *m*/*z* 1435.2384. Calcd for $C_{70}H_{80}Cl_4NaO_9P_2Ru_2^{+}$: *m*/*z* 1493.2016 ([M + Na]$^+$). Found: *m*/*z* 1493.2328. UV−vis: λ_{max} = 250 and 370 nm.

Compound ***7b***. According to the general procedure, [Ru(η^6-*p*-cymene)Cl]$_2$Cl$_2$ (0.18 g, 0.299 mmol, 1 equiv), **7a** (0.28 g, 0.299 mmol 1 equiv), and CH_2Cl_2 (12 mL) were stirred for 42 h at RT. The product was isolated as a red solid. Yield: 0.45 g, 0.287 mmol, 96%. Elem anal. Calcd for $C_{74}H_{88}Cl_4O_{11}P_2Ru_2$: C, 57.00; H, 5.69. Found: C, 56.95; H, 5.90. ^{1}H NMR ($CDCl_3$): δ_H 7.88−7.98 (8H, m, 4O(C═O)(*Ar*)CC*H*CHCP, 4O(C═O)(*Ar*)CCHC*H*CP), 7.77−7.83 (8H, m, 8P(*Ar*)CC*H*CHCH), 7.36−7.45 (12H, m, 8P(*Ar*)CCHC*H*CH, 4P-(*Ar*)CCHCHC*H*), 5.21 (4H, d, 4CH_3(*Ar*)CCHC*H*C, $^{3}J_{H,H}$ = 6.2 Hz), 4.98 (4H, d, 4CH_3(*Ar*)CC*H*CHC, $^{3}J_{H,H}$ = 6.2 Hz), 4.44−4.42 (4H, m, 2*Ar*(C═O)OCH_2CH_2O), 3.79−3.77 (4H, m, 2*Ar*(C═O)-OCH_2CH_2O), 3.70−3.61 (16H, m, 2*Ar*(C═O)O$(CH_2)_2$OCH_2CH_2, 2*Ar*(C═O)O$(CH_2)_2$OCH_2CH_2, 2*Ar*(C═O)O$(CH_2)_2$O-$(CH_2)_2$OCH_2), 2*Ar*(C═O)O$(CH_2)_2$O$(CH_2)_2$OCH_2CH_2), 2.85 (2H, sept, 2(*Ar*)CCHCHCC*H*$(CH_3)_2$, $^{3}J_{H,H}$ = 6.9 Hz), 1.85 (6H, s, 2C*H*$_3$(*Ar*)CCHCHC), 1.10 (12H, d, 2(*Ar*)CCHCHCCH(C*H*$_3$)$_2$, $^{3}J_{H,H}$ = 6.9 Hz). ^{31}P NMR ($CDCl_3$): δ_P 24.94 (2P). ^{13}C NMR ($CDCl_3$): δ_C 166.1 (2C, 2O(C═O)(*Ar*)CCHCHCP), 139.4 (2C, d, 2O(C═O)(*Ar*)CCHCHCP, $^{1}J_{C,P}$ = 44 Hz), 134.5 (4C, d, 4O(C═O)(*Ar*)CCHCHCP, $^{2}J_{C,P}$ = 7 Hz), 134.4 (8C, d, 8P(*Ar*)CCHCHCH, $^{2}J_{C,P}$ = 9 Hz), 133.4 (4C, d, 4P(*Ar*)CCHCHCH, $^{1}J_{C,P}$ = 45 Hz), 131.4 (2C, d, 2O(C═O)(*Ar*)CCHCHCP, $^{4}J_{C,P}$ = 2 Hz), 130.7 (4C, d, 4P(*Ar*)CCHCHCH, $^{4}J_{C,P}$ = 2 Hz), 128.8 (4C, d, 4O(C═O)(Ar)-CCHCHCP, $^{3}J_{C,P}$ = 10 Hz), 128.3 (8C, d, 8P(*Ar*)CCHCHCH, $^{3}J_{C,P}$ = 10 Hz), 111.59, 111.56 (2C, 2CH_3(*Ar*)CCHCHC), 96.4 (2C, 2CH_3(*Ar*)CCHCHC), 89.12, 89.09 (4C, 4CH_3(*Ar*)CCHCHC), 87.48, 87.42 (4C, 4CH_3(*Ar*)CCHCHC), 70.81, 70.73, 70.67 (8C, 2(*Ar*)(C═O)O$(CH_2)_2$OCH_2, 2(*Ar*)(C═O)O$(CH_2)_2$OCH_2CH_2, 2-(*Ar*)(C═O)O$(CH_2)_2$O$(CH_2)_2$OCH_2, 2(*Ar*)(C═O)O$(CH_2)_2$O-$(CH_2)_2$OCH_2CH_2), 69.3 (2C, 2(*Ar*)(C═O)OCH_2CH_2O), 64.5 (2C, 2(*Ar*)(C═O)OCH_2CH_2O), 30.4 (2C, 2(*Ar*)CHCHCCH-$(CH_3)_2$), 22.0 (4C, 2(*Ar*)CHCHCCH$(CH_3)_2$), 17.9 (2C, 2CH_3(*Ar*)-CCHCH). ESI-MS(+). Calcd for $C_{74}H_{88}Cl_3O_{11}P_2Ru_2^{+}$: *m*/*z* 1523.2949 ([M − Cl]$^+$). Found: *m*/*z* 1523.2914. Calcd for $C_{74}H_{88}Cl_4NaO_{11}P_2Ru_2^{+}$: *m*/*z* 1581.2535 ([M + Na]$^+$). Found: *m*/*z* 1581.2789. UV−vis: λ_{max} = 250 and 370 nm.

Compound ***8b***. According to the general procedure, [Ru(η^6-*p*-cymene)Cl]$_2$Cl$_2$ (0.30 g, 0.490 mmol, 1 equiv), PPh_3 (0.26 g, 0.979 mmol, 2 equiv), and CH_2Cl_2 (12 mL) were stirred for 42 h at RT. The product was isolated as a dark-red solid. Yield: 0.54 g, 0.950 mmol, 9. Elem anal. Calcd for $C_{28}H_{29}Cl_2PRu$: C, 59.16; H, 5.14. Found: C, 59.26; H, 4.90. ^{1}H NMR ($CDCl_3$): δ_H 7.77−7.85 (6H, m, 6P(*Ar*)CC*H*CHCH), 7.32−7.46 (9H, m, 6P(*Ar*)CCHC*H*CH, 3P-(*Ar*)CCHCHC*H*), 5.19 (2H, d, 2CH_3(*Ar*)CCHC*H*C, $^{3}J_{H,H}$ = 6.2 Hz), 4.98 (2H, d, 2CH_3(*Ar*)CC*H*CHC, $^{3}J_{H,H}$ = 6.2 Hz), 2.84 (1H, sept, (*Ar*)CCHCHCC*H*$(CH_3)_2$, $^{3}J_{H,H}$ = 7.1 Hz), 1.86 (3H, s, C*H*$_3$(*Ar*)-CCHCHC), 1.09 (6H, d, (*Ar*)CCHCHCCH(C*H*$_3$)$_2$, $^{3}J_{H,H}$ = 7.1 Hz). ^{31}P NMR ($CDCl_3$): δ_P 24.18 (1P). ^{13}C NMR ($CDCl_3$): δ_C 134.5 (6C, d, 6P(*Ar*)C*C*HCHCH, $^{2}J_{C,P}$ = 9 Hz), 133.9 (3C, d, 3P(*Ar*)CCHCHCH, $^{1}J_{C,P}$ = 46 Hz), 130.3 (3C, d, 3P(*Ar*)CCHCHC*H*, $^{4}J_{C,P}$ = 2 Hz), 128.1 (8C, d, 8P(*Ar*)CCH*C*HCH, $^{3}J_{C,P}$ = 10 Hz), 111.20, 111.17 (1C, CH_3(*Ar*)CCHCHC), 96.1 (1C, 2CH_3(*Ar*)CCHCHC), 89.18, 89.15 (2C, 2CH_3(*Ar*)CCHCHC), 87.28, 87.23 (2C, 2CH_3(*Ar*)-C*C*HCHC), 30.3 (1C, (*Ar*)CHCHC*C*H$(CH_3)_2$), 22.0 (2C, (*Ar*)-CHCHCC*H*$(CH_3)_2$), 17.8 (1C, *C*H$_3$(*Ar*)CCHCH). ESI-MS(+). Calcd for $C_{28}H_{29}PRu^{2+}$: *m*/*z* 498.1050 ([M − 2Cl]$^+$). Found: *m*/*z* 498.1009. Calcd for $C_{28}H_{29}ClPRu^{+}$: *m*/*z* 533.0739 ([M − Cl]$^+$). Found: *m*/*z* 533.0772.

Compound ***9b***. According to the general procedure, [Ru(η^6-*p*-cymene)Cl]$_2$Cl$_2$ (0.30 g, 0.980 mmol, 1 equiv), 4-(diphenylphosphanyl)benzoic acid (0.30 g, 0.980 mmol, 1 equiv), and CH_2Cl_2 (12 mL), were stirred for 42 h at RT. The product was isolated as a dark-red solid. Yield: 0.59 g, 0.961 mmol, 98%. Elem anal. Calcd for $C_{29}H_{29}Cl_2O_2PRu.{}^1/_2CHCl_3$: C, 52.71; H, 4.42. Found: C, 52.73; H, 4.67. $CHCl_3$ originates from the recrystallization process. ^{1}H NMR ($CDCl_3$): δ_H −7.97−8.00 (4H, m, 2O(C═O)(*Ar*)-C*C*H*C*HCP), 7.78−7.84 (4H, m, 4P(*Ar*)CC*H*CHCH), 7.36−7.45 (6H, m, 4P(*Ar*)CCHC*H*CH, 2P(*Ar*)CCHCHC*H*), 5.22 (2H, d, 2CH_3(*Ar*)CCHC*H*C, $^{3}J_{H,H}$ = 6.1 Hz), 4.99 (2H, d, 2CH_3(*Ar*)-C*C*H*C*HC, $^{3}J_{H,H}$ = 6.1 Hz), 2.84 (1H, sept, (*Ar*)-CCHCHCC*H*$(CH_3)_2$, $^{3}J_{H,H}$ = 6.9 Hz), 1.85 (3H, s, C*H*$_3$(*Ar*)-CCHCHC), 1.10 (6H, d, (*Ar*)CCHCHCCH(C*H*$_3$)$_2$, $^{3}J_{H,H}$ = 6.9 Hz). ^{31}P NMR ($CDCl_3$): δ_P 25.27 (1P). ^{13}C NMR ($CDCl_3$): δ_C 171.1 (1C, O(*C*═O)(*Ar*)CCHCHCP), 140.4 (1C, d, O(C═O)(*Ar*)-CCHCHC*P*, $^{1}J_{C,P}$ = 43 Hz), 134.5 (2C, d, 2O(C═O)(*Ar*)-CCHCHCP, $^{2}J_{C,P}$ = 11 Hz), 134.4 (4C, d, 4P(*Ar*)C*C*HCHCH, $^{2}J_{C,P}$ = 10 Hz), 133.3 (2C, d, 2P(*Ar*)CCHCHCH, $^{1}J_{C,P}$ = 45 Hz), 130.7 (2C, d, 2P(*Ar*)CCHCHC*H*, $^{4}J_{C,P}$ = 1 Hz), 130.5 (1C, d, O(C═O)(*Ar*)CCHCHCP, $^{4}J_{C,P}$ = 2 Hz), 129.3 (2C, d, 2O(C═O)(Ar)-CCHCHCP, $^{3}J_{C,P}$ = 10 Hz), 128.3 (4C, d, 4P(*Ar*)CCHCHCH, $^{3}J_{C,P}$ = 10 Hz), 111.57, 111.61 (1C, CH_3(*Ar*)CCHCHC), 96.5 (1C, CH_3(*Ar*)-*C*CHCHC), 89.06, 89.03 (2C, 2CH_3(*Ar*)CCHCHC), 87.51, 87.46 (2C, 2CH_3(*Ar*)C*C*HCHC), 30.4 (1C, (*Ar*)CHCHC*C*H$(CH_3)_2$), 22.0 (2C, (*Ar*)CHCHCC*H*$(CH_3)_2$), 17.9 (1C, *C*H$_3$(*Ar*)CCHCH). ESI-MS(+). Calcd for $C_{29}H_{29}O_2PRu^{+}$: *m*/*z* 542.0949 ([M − 2Cl]$^+$). Found: *m*/*z* 542.0914. Calcd for $C_{29}H_{29}ClO_2PRu^{+}$: *m*/*z* 577.0637 ([M − Cl]$^+$). Found: *m*/*z* 577.0648. Calcd for $C_{29}H_{29}Cl_2NaO_2PRu^{+}$: *m*/*z* 635.0223 ([M + Na]$^+$. Found: *m*/*z* 635.0228).

General Procedure for the Synthesis of the Digold Intermediates ***1c***−***7c***. The appropriate ligand,**1a**−**7a** (1 equiv), dissolved in dry CH_2Cl_2 (15 mL), was added to a solution of AuCl(tht) (2 equiv) in dry CH_2Cl_2 (10 mL) at 0 °C under N_2. The reaction mixture was stirred at RT for 6 h, and the reaction evolution was monitored by ^{1}H and ^{31}P NMR ($CDCl_3$). The reaction mixture was concentrated under reduced pressure, and the product was washed with hexane (5 × 25 mL) and resolubilized in CH_2Cl_2 (50 mL), before being concentrated and further dried under high vacuum. The product was isolated as a white solid and stored at −20 °C in the dark.

Compound ***1c***. According to the general procedure, AuCl(tht) (0.188 g, 0.588 mmol, 2 equiv), **1a** (0.188 g, 0.294 mmol, 1 equiv), and CH_2Cl_2 (35 mL) were stirred for 6 h at RT. The product was isolated as a white solid. Yield: 0.319 g, 0.289 mmol, 98%. Elem anal. Calcd for $C_{40}H_{32}Au_2Cl_2O_4P_2$: C, 43.54; H, 2.92. Found: C, 43.55; H, 3.02. ^{1}H NMR ($CDCl_3$): δ_H 8.07−8.12 (4H, m, 4O(C═O)(*Ar*)-CC*H*CHCP, $^{3}J_{H,H}$ = 8.4 Hz, $^{4}J_{H,H}$ = 2.1 Hz), 7.45−7.60 (24H, m, 4O(C═O)(*Ar*)CCHC*H*CP, 8P(*Ar*)CC*H*CHCH, 8P(*Ar*)-CCHC*H*CH, 4P(*Ar*)CCHCHC*H*), 4.68 (4H, s, *Ar*(C═O)O-$(CH_2)_2$O). ^{31}P NMR ($CDCl_3$): δ_P 33.14 (2P). ^{13}C NMR ($CDCl_3$): δ_C 165.3 (2C, 2O(C═O)(*Ar*)CCHCHCP), 134.9 (2C, d, 2O(C═O)(*Ar*)CCHCHC*P*, $^{1}J_{C,P}$ = 59 Hz), 134.3 (8C, d, 8P(*Ar*)C*C*HCHCH, $^{2}J_{C,P}$ = 14 Hz), 134.1 (4C, d, 4O(C═O)(*Ar*)CCHCHCP, $^{2}J_{C,P}$ = 14 Hz), 132.9 (2C, d, 2O(C═O)(*Ar*)CCHCHCP, $^{4}J_{C,P}$ = 3 Hz), 132.5 (4C, d, 4P(*Ar*)CCHCHC*H*, $^{4}J_{C,P}$ = 3 Hz), 130.2 (4C, d, 4O(C═O)(*Ar*)CCHCHCP, $^{3}J_{C,P}$ = 12 Hz), 129.6 (8C, d, 8P(*Ar*)CCHCHCH, $^{3}J_{C,P}$ = 12 Hz), 127.9 (4C, d, 4P(*Ar*)CCHCHCH, $^{1}J_{C,P}$ = 63 Hz), 63.3 (2C, 2(*Ar*)(C═O)O$(CH_2)_2$O). ESI-MS(+). Calcd for $C_{40}H_{32}Au_2ClO_4P_2^{+}$: *m*/*z* 1067.0795 ([M − Cl]$^+$). Found: *m*/*z*

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1067.0825. Calcd for $C_{40}H_{32}Au_2Cl_2NaO_4P_2^+$: m/z 1125.0382 ([M + Na]$^+$). Found: m/z 1125.0388.

Compound ***2c***. According to the general procedure, AuCl(tht) (0.235 g, 0.735 mmol, 2 equiv), **2a** (0.250 g, 0.366 mmol,1 equiv), and CH_2Cl_2 (35 mL) were stirred for 6 h at RT. The product was isolated as a white solid. Yield: 0.403 g, 0.351 mmol, 96. Elem anal. Calcd for $C_{42}H_{36}Au_2Cl_2O_5P_2$: C, 43.96; H, 3.16. Found: C, 43.83; H, 3.23. ^{1}H NMR ($CDCl_3$): δ_H 8.06−8.10 (4H, m, 4O(C═O)(*Ar*)CC*H*CHCP, $^3J_{H,H}$ = 8.2 Hz, $^4J_{H,H}$ = 2 Hz), 7.44−7.60 (24H, m, 4O(C═O)(*Ar*)CCHC*H*CP, 8P(*Ar*)CC*H*CHCH, 8P(*Ar*)CCHC*H*CH, 4P(*Ar*)CCHCHC*H*), 4.48−4.50 (4H, m, 2*Ar*(C═O)OC*H*$_2$CH$_2$O), 3.85−3.87 (4H, m, 2*Ar*(C═O)OCH$_2$C*H*$_2$O). ^{31}P NMR ($CDCl_3$): δ_P 33.02 (2P). ^{13}C NMR ($CDCl_3$): δ_C 165.4 (2C, 2O(*C*═O)(*Ar*)CCHCHCP), 134.6 (2C, d, 2O(C═O)(*Ar*)CCHCHC*P*, $^1J_{C,P}$ = 62 Hz), 134.3 (8C, d, 8P(*Ar*)C*C*HCHCH, $^2J_{C,P}$ = 14 Hz), 134.0 (4C, d, 4O(C═O)(*Ar*)CCHCHCP, $^2J_{C,P}$ = 14 Hz), 133.2 (2C, d, 2O(C═O)(*Ar*)CCHCHCP, $^4J_{C,P}$ = 2 Hz), 132.5 (4C, d, 4P(*Ar*)CCHCHC*H*, $^4J_{C,P}$ = 2 Hz), 130.1 (4C, d, 4O(C═O)(*Ar*)-CCHCHCP, $^3J_{C,P}$ = 12 Hz), 129.6 (8C, d, 8P(*Ar*)CCHC*H*CH, $^3J_{C,P}$ = 12 Hz), 128.0 (4C, d, 4P(*Ar*)CCHCHCH, $^1J_{C,P}$ = 63 Hz), 69.2 (2C, 2(*Ar*)(C═O)OCH$_2$CH$_2$O), 64.6 (2C, 2(*Ar*)(C═O)OCH$_2$CH$_2$O). ESI-MS(+). Calcd for $C_{42}H_{36}Au_2ClO_5P_2^+$: m/z 1111.1058 ([M − Cl]$^+$). Found: m/z 1111.1104. Calcd for $C_{42}H_{36}Au_2Cl_2NaO_5P_2^+$: m/z 1169.0644 ([M + Na]$^+$).. Found: m/z 1169.0690

Compound ***3c***. According to the general procedure, AuCl(tht) (0.221 g, 0.692 mmol, 2 equiv), **3a** (0.250 g, 0.344 mmol, 1 equiv), and CH_2Cl_2 (35 mL) were stirred 6 h at RT. The product was isolated as a white solid. Yield: 0.406 g, 0.341 mmol, 98%. Elem anal. Calcd for $C_{44}H_{40}Au_2Cl_2O_6P_2$: C, 44.35; H, 3.38. Found: C, 44.30; H, 3.51. ^{1}H NMR ($CDCl_3$): δ_H 8.07−8.11 (4H, m, 4O(C═O)(*Ar*)CC*H*CHCP, $^3J_{H,H}$ = 8.4 Hz, $^4J_{H,H}$ = 2.2 Hz), 7.45−7.60 (24H, m, 4O(C═O)(*Ar*)CCHC*H*CP, 8P(*Ar*)CC*H*CHCH, 8P(*Ar*)CCHC*H*CH, 4P(*Ar*)CCHCHC*H*), 4.44−4.48 (4H, m, 2*Ar*(C═O)OC*H*$_2$CH$_2$O), 3.79−3.83 (4H, m, 2*Ar*(C═O)OCH$_2$C*H*$_2$O), 3.69 (4H, s, 2*Ar*(C═O)O(CH$_2$)$_2$OC*H*$_2$). ^{31}P NMR ($CDCl_3$): δ_P 33.07 (2P). ^{13}C NMR ($CDCl_3$): δ_C 165.4 (2C, 2O(C═O)(*Ar*)CCHCHCP), 134.5 (2C, d, 2O(C═O)(*Ar*)CCHCHC*P*, $^1J_{C,P}$ = 60 Hz), 134.3 (8C, d, 8P(*Ar*)-C*C*HCHCH, $^2J_{C,P}$ = 14 Hz), 134.2 (4C, d, 4O(C═O)(*Ar*)-CCHCHCP, $^2J_{C,P}$ = 14 Hz), 133.3 (2C, d, 2O(C═O)(*Ar*)*C*CHCHCP, $^4J_{C,P}$ = 3 Hz), 132.5 (4C, d, 4P(*Ar*)CCHCHC*H*, $^4J_{C,P}$ = 2 Hz), 130.2 (4C, d, 4O(C═O)(*Ar*)C*C*HCHCP, $^3J_{C,P}$ = 12 Hz), 129.5 (8C, d, 8P(*Ar*)CCHC*H*CH, $^3J_{C,P}$ = 12 Hz), 128.0 (4C, d, 4P(*Ar*)*C*CHCHCH, $^1J_{C,P}$ = 63 Hz), 70.8 (2C, 2(*Ar*)(C═O)O-(CH$_2$)$_2$OCH$_2$), 69.3 (2C, 2(*Ar*)(C═O)OCH$_2$*C*H$_2$O), 64.7 (2C, 2(*Ar*)(C═O)OCH$_2$CH$_2$O). ESI-MS(+). Calcd for $C_{44}H_{40}Au_2ClO_6P_2^+$: m/z 1155.1320 ([M − Cl]$^+$). Found: m/z 1155.1376. Calcd for $C_{44}H_{40}Au_2Cl_2NaO_6P_2^+$: m/z 1213.0906 ([M + Na]$^+$). Found: m/z 1213.0951.

Compound ***4c***. According to the general procedure, AuCl(tht) (0.208 g, 0.651 mmol, 2 equiv), **4a** (0.250 g, 0.324 mmol, 1 equiv), and CH_2Cl_2 (35 mL) were stirred 6 h at RT. The product was isolated as a white solid. Yield: 0.389 g, 0.315 mmol, 97%. Elem anal. Calcd for $C_{46}H_{44}Au_2Cl_2O_7P_2$: C, 44.71; H, 3.59. Found: C, 44.78; H, 3.57. ^{1}H NMR ($CDCl_3$): δ_H 8.08−8.12 (4H, m, 4O(C═O)(*Ar*)CC*H*CHCP, $^3J_{H,H}$ = 8.4 Hz, $^4J_{H,H}$ = 2 Hz), 7.46−7.60 (24H, m, 4O(C═O)(*Ar*)CCHC*H*CP, 8P(*Ar*)CC*H*CHCH, 8P(*Ar*)CCHC*H*CH, 4P(*Ar*)CCHCHC*H*), 4.46−4.49 (4H, m, 2*Ar*(C═O)OC*H*$_2$CH$_2$O), 3.79−3.82 (4H, m, 2*Ar*(C═O)OCH$_2$C*H*$_2$O), 3.61−3.72 (8H, m, 2*Ar*(C═O)O(CH$_2$)$_2$O(C*H*$_2$)$_2$). ^{31}P NMR ($CDCl_3$): δ_P 33.01 (2P). ^{13}C NMR ($CDCl_3$): δ_C 165.4 (2C, 2O(*C*═O)(*Ar*)CCHCHCP), 134.5 (2C, d, 2O(C═O)(*Ar*)CCHCHCP, $^1J_{C,P}$ = 58 Hz), 134.3 (8C, d, 8P(*Ar*)CCHCHCH, $^2J_{C,P}$ = 14 Hz), 134.0 (4C, d, 4O(C═O)(*Ar*)CCHCHCP, $^2J_{C,P}$ = 14 Hz), 133.3 (2C, d, 2O(C═O)(*Ar*)*C*CHCHCP, $^4J_{C,P}$ = 2 Hz), 132.4 (4C, d, 4P(*Ar*)CCHCHCH, $^4J_{C,P}$ = 2 Hz), 130.1 (4C, d, 4O(C═O)(*Ar*)CCHCHCP, $^3J_{C,P}$ = 12 Hz), 129.5 (8C, d, 8P(*Ar*)CCHCHCH, $^3J_{C,P}$ = 12 Hz), 127.9 (4C, d, 4P(*Ar*)*C*CHCHCH, $^1J_{C,P}$ = 63 Hz), 70.7 (4C, 2(*Ar*)(C═O)O(CH$_2$)$_2$OCH$_2$, 2(*Ar*)(C═O)O(CH$_2$)$_2$OCH$_2$CH$_2$), 69.1 (2C, 2(*Ar*)(C═O)-OCH$_2$CH$_2$O), 64.7 (2C, 2(*Ar*)(C═O)OCH$_2$CH$_2$O). ESI-MS(+). Calcd for $C_{46}H_{44}Au_2ClO_7P_2^+$: m/z 1199.1582 ([M − Cl]$^+$). Found: m/z 1199.1633. Calcd for $C_{46}H_{44}Au_2Cl_2NaO_7P_2^+$: m/z 1257.1168 ([M + Na]$^+$). Found: m/z 1257.1218.

Compound ***5c***. According to the general procedure, AuCl(tht) (0.162 g,0.507 mmol, 2 equiv), **5a** (0.206 g, 0.253 mmol, 1 equiv), and CH_2Cl_2 (35 mL), were stirred for 6 h at RT. The product was isolated as a white solid. Yield: 0.308 g, 0.241 mmol, 95%. Elem anal. Calcd for $C_{48}H_{48}Au_2Cl_2O_8P_2$: C, 45.05; H, 3.78. Found: C, 45.05; H, 3.79. ^{1}H NMR ($CDCl_3$): δ_H 8.09−8.12 (4H, m, 4O(C═O)(*Ar*)CC*H*CHCP, $^3J_{H,H}$ = 8.6 Hz, $^4J_{H,H}$ = 2.4 Hz), 7.46−7.60 (24H, m, 4O(C═O)(*Ar*)CCHC*H*CP, 8P(*Ar*)CC*H*CHCH, 8P(*Ar*)CCHC*H*CH, 4P(*Ar*)CCHCHC*H*), 4.47−4.49 (4H, m, 2*Ar*(C═O)OC*H*$_2$CH$_2$O), 3.80−3.82 (4H, m, 2*Ar*(C═O)OCH$_2$C*H*$_2$O), 3.66−3.68 (4H, m, 2*Ar*(C═O)O(CH$_2$)$_2$OC*H*$_2$CH$_2$), 3.62−3.64 (4H, m, 2*Ar*(C═O)O-(CH$_2$)$_2$OCH$_2$C*H*$_2$), 3.63 (4H, s, 2*Ar*(C═O)O(CH$_2$)$_2$O-(CH$_2$)$_2$OC*H*$_2$). ^{31}P NMR ($CDCl_3$): δ_P 32.99 (2P). ^{13}C NMR ($CDCl_3$): δ_C 165.4 (2C, 2O(*C*═O)(*Ar*)CCHCHCP), 134.3 (2C, d, 2O(C═O)(*Ar*)CCHCHC*P*, $^1J_{C,P}$ = 57 Hz), 134.3 (8C, d, 8P(*Ar*)-C*C*HCHCH, $^2J_{C,P}$ = 14 Hz), 134.0 (4C, d, 4O(C═O)(*Ar*)-CCHCHCP, $^2J_{C,P}$ = 14 Hz), 133.3 (2C, d, 2O(C═O)(*Ar*)*C*CHCHCP, $^4J_{C,P}$ = 2 Hz), 132.4 (4C, d, 4P(*Ar*)CCHCHCH, $^4J_{C,P}$ = 3 Hz), 130.1 (4C, d, 4O(C═O)(*Ar*)C*C*HCHCP, $^3J_{C,P}$ = 12 Hz), 129.5 (8C, d, 8P(*Ar*)CCHC*H*CH, $^3J_{C,P}$ = 12 Hz), 127.9 (4C, d, 4P(*Ar*)CCHCHCH, $^1J_{C,P}$ = 63 Hz), 70.71, 70.66 (6C, 2(*Ar*)(C═O)O(CH$_2$)$_2$OCH$_2$, 2(*Ar*)(C═O)O(CH$_2$)$_2$OCH$_2$CH$_2$, 2(*Ar*)(C═O)O(CH$_2$)$_2$O(CH$_2$)$_2$OCH$_2$), 69.1 (2C, 2(*Ar*)(C═O)OCH$_2$CH$_2$O), 64.7 (2C, 2(*Ar*)(C═O)OCH$_2$CH$_2$O). ESI-MS(+). Calcd for $C_{48}H_{48}Au_2ClO_8P_2^+$: m/z 1243.1844 ([M − Cl]$^+$). Found: m/z 1243.1903. Calcd for $C_{48}H_{48}Au_2Cl_2NaO_8P_2^+$: m/z 1301.1430 ([M + Na]$^+$). Found: m/z 1301.1469.

Compound ***6c***. According to the general procedure, AuCl(tht) (0.192 g,0.601 mmol, 2 equiv), **6a** (0.257 g, 0.299 mmol, 1 equiv), and CH_2Cl_2 (35 mL) were stirred 6 h at RT. The product was isolated as a white solid. Yield: 0.376 g, 0.284 mmol, 95%. Elem anal. Calcd for $C_{50}H_{52}Au_2Cl_2O_9P_2$: C, 45.37; H, 3.96. Found: C, 45.44; H, 3.84. ^{1}H NMR ($CDCl_3$): δ_H 8.08−8.12 (4H, m, 4O(C═O)(*Ar*)CC*H*CHCP, $^3J_{H,H}$ = 8.4 Hz, $^4J_{H,H}$ = 2 Hz), 7.45−7.59 (24H, m, 4O(C═O)(*Ar*)CCHC*H*CP, 8P(*Ar*)CC*H*CHCH, 8P(*Ar*)CCHC*H*CH, 4P(*Ar*)CCHCHC*H*), 4.46−4.49 (4H, m, 2*Ar*(C═O)OC*H*$_2$CH$_2$O), 3.79−3.82 (4H, m, 2*Ar*(C═O)OCH$_2$C*H*$_2$O), 3.65−3.68 (4H, m, 2*Ar*(C═O)O(CH$_2$)$_2$OC*H*$_2$CH$_2$), 3.60−3.64 (4H, m, 2*Ar*(C═O)O-(CH$_2$)$_2$OCH$_2$C*H*$_2$), 3.59−3.62 (8H, m, 2*Ar*(C═O)O(CH$_2$)$_2$O-(CH$_2$)$_2$O(C*H*$_2$)$_2$. ^{31}P NMR ($CDCl_3$): δ_P 33.03 (2P). ^{13}C NMR ($CDCl_3$): δ_C 165.4 (2C, 2O(*C*═O)(*Ar*)CCHCHCP), 134.4 (2C, d, 2O(C═O)(*Ar*)CCHCHC*P*, $^1J_{C,P}$ = 59 Hz), 134.3 (8C, d, 8P(*Ar*)-C*C*HCHCH, $^2J_{C,P}$ = 14 Hz), 134.1 (4C, d, 4O(C═O)(*Ar*)-CCHCHCP, $^2J_{C,P}$ = 14 Hz), 133.4 (2C, 2O(C═O)(*Ar*)CCHCHCP), 132.5 (4C, 4P(*Ar*)CCHCHCH), 130.2 (4C, d, 4O(C═O)(*Ar*)-CCHCHCP, $^3J_{C,P}$ = 12 Hz), 129.5 (8C, d, 8P(*Ar*)CCHCHCH, $^3J_{C,P}$ = 12 Hz), 128.0 (4C, d, 4P(*Ar*)CCHCHCH, $^1J_{C,P}$ = 62 Hz), 70.78, 70.74, 70.68 (8C, 2(*Ar*)(C═O)O(CH$_2$)$_2$OCH$_2$, 2(*Ar*)(C═O)O-(CH$_2$)$_2$OCH$_2$CH$_2$, 2(*Ar*)(C═O)O(CH$_2$)$_2$O(CH$_2$)$_2$OCH$_2$, 2(*Ar*)-(C═O)O(CH$_2$)$_2$O(CH$_2$)$_2$OCH$_2$CH$_2$), 69.2 (2C, 2(*Ar*)(C═O)-OCH$_2$CH$_2$O), 64.8 (2C, 2(*Ar*)(C═O)OCH$_2$CH$_2$O). ESI-MS(+). Calcd for $C_{50}H_{52}Au_2ClO_9P_2^+$: m/z 1287.2106 ([M − Cl]$^+$). Found: m/z 1287.2147.Calcd for $C_{50}H_{52}Au_2Cl_2NaO_9P_2^+$: m/z 1345.1692 ([M + Na]$^+$). Found: m/z 1345.1719.

Compound ***7c***. According to the general procedure, AuCl(tht) (0.230 g, 0.720 mmol, 2 equiv), **7a** (0.340 g, 0.359 mmol, 1 equiv), and CH_2Cl_2 (35 mL) were stirred for 6 h at RT. The product was isolated as a white solid. Yield: 0.485 g, 0.344 mmol, 96%. Elem anal. Calcd for $C_{54}H_{60}Au_2Cl_2O_{11}P_2$: C, 45.94; H, 4.28; Found: C, 45.82; H, 4.04. ^{1}H NMR ($CDCl_3$): δ_H 8.08−8.12 (4H, m, 4O(C═O)(*Ar*)-CC*H*CHCP, $^3J_{H,H}$ = 8.2 Hz, $^4J_{H,H}$ = 2 Hz), 7.45−7.59 (24H, m, 4O(C═O)(*Ar*)CCHC*H*CP, 8P(*Ar*)CC*H*CHCH, 8P(*Ar*)-CCHC*H*CH, 4P(*Ar*)CCHCHC*H*), 4.46−4.49 (4H, m, 2*Ar*(C═O)OC*H*$_2$CH$_2$O), 3.80−3.82 (4H, m, 2*Ar*(C═O)OCH$_2$C*H*$_2$O), 3.66−3.69 (4H, m, 2*Ar*(C═O)O(CH$_2$)$_2$OC*H*$_2$CH$_2$), 3.61−3.64 (4H, m, 2*Ar*(C═O)O(CH$_2$)$_2$OCH$_2$C*H*$_2$), 3.60−3.62 (8H, m, 2*Ar*(C═O)O(CH$_2$)$_2$O(CH$_2$)$_2$O(C*H*$_2$)$_2$, 3.61 (8H, s, 2*Ar*(C═O)O-

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$(CH_2)_2O(CH_2)_2O(CH_2)_2O(CH_2)_2$. ^{31}P NMR ($CDCl_3$): δ_P 33.01 (2P). ^{13}C NMR ($CDCl_3$): δ_C 165.4 (2C, 2O(*C*=O)(*Ar*)CCHCHCP), 134.4 (2C, d, 2O(C=O)(*Ar*)CCHCH*C*P, $^1J_{C,P}$ = 58 Hz), 134.3 (8C, d, 8P(*Ar*)*C*CHCHCH, $^2J_{C,P}$ = 14 Hz), 134.0 (4C, d, 4O(C=O)(*Ar*)CCHCHCP, $^2J_{C,P}$ = 14 Hz), 133.4 (2C, 2O(C=O)(*Ar*)CCHCHCP, $^4J_{C,P}$ = 2 Hz), 132.4 (4C, 4P(*Ar*)CCHCH*C*H, $^4J_{C,P}$ = 2 Hz), 130.2 (4C, d, 4O(C=O)(*Ar*)CCHCHCP, $^3J_{C,P}$ = 12 Hz), 129.5 (8C, d, 8P(*Ar*)CCH*C*HCH, $^3J_{C,P}$ = 12 Hz), 128.0 (4C, d, 4P(*Ar*)CCHCHCH, $^1J_{C,P}$ = 63 Hz), 70.77, 70.72, 70.66 (12C, 2(*Ar*)(C=O)O$(CH_2)_2$OCH_2, 2(*Ar*)(C=O)O$(CH_2)_2$OCH_2CH_2, 2(*Ar*)(C=O)O$(CH_2)_2$O$(CH_2)_2$OCH_2, 2(*Ar*)(C=O)O$(CH_2)_2$O$(CH_2)_2$O$(CH_2)_2$OCH_2CH_2, 2(*Ar*)(C=O)O$(CH_2)_2$O$(CH_2)_2$O$(CH_2)_2$OCH_2, 2(*Ar*)(C=O)O$(CH_2)_2$O$(CH_2)_2$O$(CH_2)_2$OCH_2CH_2), 69.2 (2C, 2(*Ar*)(C=O)O*C*H_2CH_2O), 64.8 (2C, 2(*Ar*)(C=O)O*C*H_2CH_2O). ESI-MS(+). Calcd for $C_{54}H_{60}Au_2ClO_{11}P_2^+$: *m*/*z* 1375.2630 ([M − Cl]$^+$). Found: *m*/*z* 1375.2667. Calcd for $C_{54}H_{60}Au_2Cl_2NaO_{11}P_2^+$: *m*/*z* 1433.2217 ([M + Na]$^+$). Found: *m*/*z* 1433.2239.

Compound ***8c***. According to the general procedure, AuCl(tht) (0.318 g, 0.995 mmol, 1 equiv), PPh_3 (0.260 g, 0.991 mmol, 1 equiv), and CH_2Cl_2 (25 mL) were stirred for 4 h at RT. The product was isolated as a white solid. Yield: 0.471 g, 0.952 mmol, 96%. Elem anal. Calcd for $C_{18}H_{15}AuClP$: C, 43.70; H, 3.06. Found: C, 44.02; H, 2.74. ^1H NMR ($CDCl_3$): δ_H 7.42−7.58 (15H, m, 6P(*Ar*)CC*H*CHCH, 6P(*Ar*)CCHC*H*CH, 3P(*Ar*)CCHCHC*H*). ^{31}P NMR ($CDCl_3$): δ_P 33.19 (1P). ^{13}C NMR ($CDCl_3$): δ_C 134.2 (6C, d, 6P(*Ar*)C*C*HCHCH, $^2J_{C,P}$ = 14 Hz), 132.1 (3C, d, 3P(*Ar*)CCHCH*C*H, $^4J_{C,P}$ = 3 Hz), 129.3 (6C, d, 6P(*Ar*)CCH*C*HCH, $^3J_{C,P}$ = 12 Hz), 128.8 (3C, d, 3P(*Ar*)*C*CHCHCH, $^1J_{C,P}$ = 62 Hz). ESI-MS(+). Calcd for $C_{18}H_{15}AuClNaP^+$: *m*/*z* 517.0163 ([M + Na]$^+$). Found: *m*/*z* 517.0163.

Compound ***9c***. According to the general procedure, AuCl(tht) (0.590 g, 1.846 mmol, 1 equiv), 4-(diphenylphosphanyl)benzoic acid (0.564 g, 1.841 mmol, 1 equiv), and CH_2Cl_2 (25 mL) were stirred for 6 h at RT. The product was isolated as a white solid. Yield: 0.962 g, 1.786 mmol, 97%. Elem anal. Calcd for $C_{19}H_{15}AuClO_2P$: C, 42.36; H, 2.81. Found: C, 42.60; H, 2.59. ^1H NMR ($CDCl_3$): δ_H 8.05−8.19 (2H, m, 2O(C=O)(*Ar*)CC*H*CHCP, $^3J_{H,H}$ = 8.4 Hz, $^4J_{H,H}$ = 2.1 Hz), 7.47−7.64 (12H, m, 2O(C=O)(*Ar*)CCHC*H*CP, 4P(*Ar*)CC*H*CHCH, 4P(*Ar*)CCHC*H*CH, 2P(*Ar*)CCHCHC*H*). ^{31}P NMR ($CDCl_3$): δ_P 33.21 (1P). ^{13}C NMR ($CDCl_3$): δ_C 170.5 (1C, O(*C*=O)(*Ar*)CCHCHCP), 135.8 (1C, d, O(C=O)(*Ar*)CCHCH*C*P, $^1J_{C,P}$ = 58 Hz), 134.4 (4C, d, 2P(*Ar*)*C*CHCHCH, $^2J_{C,P}$ = 14 Hz), 134.1 (2C, d, 2O(C=O)(*Ar*)CCHC*H*CP, $^2J_{C,P}$ = 14 Hz), 132.4 (2C, m, O(C=O)(*Ar*)CCHCHCP, 2P(*Ar*)CCHCHC*H*), 130.6 (2C, d, 2O(C=O)(*Ar*)CCHCHCP, $^3J_{C,P}$ = 12 Hz), 129.6 (4C, d, 4P(*Ar*)CCH*C*HCH, $^3J_{C,P}$ = 12 Hz), 128.1 (2C, d, 2P(*Ar*)CCHCHCH, $^1J_{C,P}$ = 61 Hz). Calcd for $C_{19}H_{15}AuClO_2P$: *m*/*z* 538.0164. ESI-MS(−). Found: *m*/*z* 537.0193 ([M − H]$^-$). Found: *m*/*z* 1074.8335 ([2M − H]$^-$).

General Procedure for the Synthesis of the Digold Complexes ***1d−7d***. The appropriate digold intermediate **1c−7c** (1 equiv) was added to a suspension of *β*-D-thioglucosetetraacetate (2 equiv) and K_2CO_3 (4 equiv) in degassed acetone under N_2. The reaction mixture was stirred under N_2 at RT for 48 h in the dark, and the reaction evolution was verified by ^1H and ^{31}P NMR ($CDCl_3$). The reaction mixture was concentrated under reduced pressure, the crude was resuspended in CH_2Cl_2 and filtered under vacuum. The filtrate was concentrated under reduced pressure and further dried under high vacuum. The product was isolated as a white solid and stored at −20 °C in the dark.

Compound ***1d***. According to the general procedure, *β*-D-thioglucosetetraacetate (0.026 g, 0.071 mmol, 2 equiv), K_2CO_3 (0.050 g, 0.362 mmol, 4 equiv), and **1c** (0.100 g, 0.091 mmol, 1 equiv) in acetone (25 mL) were stirred for 48 h at RT in the dark. The product was isolated as a white solid. Yield: 0.145 g, 0.0824 mmol, 90%. Elem anal. Calcd for $C_{68}H_{70}Au_2O_{22}P_2S_2$: C, 46.42; H, 4.01. Found: C, 46.37; H, 3.92. ^1H NMR ($CDCl_3$): δ_H 8.09−8.12 (4H, m, 4O(C=O)(*Ar*)CC*H*CHCP, $^3J_{H,H}$ = 8.6 Hz, $^4J_{H,H}$ = 2.0 Hz), 7.46−7.63 (24H, m, 4O(C=O)(*Ar*)CCHC*H*CP, 8P(*Ar*)CC*H*CHCH, 8P(*Ar*)CCHC*H*CH, 4P(*Ar*)CCHCHC*H*), 5.12−5.17 (4H, m, SC*H*CHOAc, SCHCHC*H*OAc), 5.05 (2H, t, C*H*CHCH$_2$OAc, $^3J_{H,H}$ = 9.7 Hz), 5.03 (2H, t, SCHC*H*OAc, $^3J_{H,H}$ = 9.2 Hz), 4.67 (4H, s, *Ar*(C=O)O(*CH*$_2$)$_2$O), 4.20 (2H, dd, *CH*$_2$OAc, $^2J_{H,H}$ = 12.2 Hz, $^3J_{H,H}$ = 4.7 Hz), 4.09 (2H, dd, *CH*$_2$OAc, $^2J_{H,H}$ = 12.2 Hz, $^3J_{H,H}$ = 2.3 Hz), 3.75 (2H, ddd, *CH*CH$_2$OAc, $^3J_{H,H}$ = 9.7 Hz, $^3J_{H,H}$ = 4.7 Hz, $^3J_{H,H}$ = 2.3 Hz), 2.04 (6H, s, 2CH$_2$O(C=O)*CH*$_3$), 2.00 (6H, s, 2(C=O)*CH*$_3$), 1.96 (6H, s, 2(C=O)*CH*$_3$), 1.89 (6H, s, 2(C=O)*CH*$_3$). ^{31}P NMR ($CDCl_3$): δ_P 38.71 (2P). ^{13}C NMR ($CDCl_3$): δ_C 170.8 (2C, 2(C=O)CH$_3$), 170.3 (2C, 2(C=O)CH$_3$), 169.7 (2C, 2(C=O)CH$_3$), 169.6 (2C, 2(*C*=O)CH$_3$), 165.4 (2C, 2O(*C*=O)(*Ar*)CCHCHCP), 135.8 (2C, d, 2O(C=O)(*Ar*)CCHCHCP, $^1J_{C,P}$ = 53 Hz), 134.5 (4C, d, 4P(*Ar*)CCHCHCH, $^2J_{C,P}$ = 14 Hz), 134.4 (4C, d, 4P(*Ar*)C*C*HCHCH, $^2J_{C,P}$ = 14 Hz), 134.2 (4C, d, 4O(C=O)(*Ar*)CCHCHCP, $^2J_{C,P}$ = 14 Hz), 132.5 (2C, d, 2O(C=O)(*Ar*)CCHCHCP, $^4J_{C,P}$ = 2 Hz), 132.1 (4C, m, 4P(*Ar*)CCHCHCH), 130.1 (4C, d, 4O(C=O)(*Ar*)CCHCHCP, $^3J_{C,P}$ = 12 Hz), 129.5 (8C, d, 8P(*Ar*)CCH*C*HCH, $^3J_{C,P}$ = 12 Hz), 128.8 (4C, d, 4P(*Ar*)CCHCHCH, $^1J_{C,P}$ = 57 Hz), 83.2 (2C, 2CHCH$_2$OAc), 77.8 (2C, SCHCHCHOAc), 75.9 (2C, SCHCHOAc), 74.2 (2C, SCHCHOAc), 69.0 (2C, 2CHCHCH$_2$OAc), 63.2 (2C, 2(*Ar*)(C=O)O(*CH*$_2$)$_2$O), 62.9 (2C, 2CHCH$_2$(C=O)CH$_3$), 21.2 (2C, 2CH$_2$O(C=O)*CH*$_3$), 20.82 (2C, 2(C=O)*CH*$_3$), 20.77 (2C, 2(C=O)*CH*$_3$), 20.72 (2C, 2(C=O)*CH*$_3$). ESI-MS(+). Calcd for $C_{68}H_{70}Au_2NaO_{22}P_2S_2^+$: *m*/*z* 1781.2499 ([M + Na]$^+$). Found: *m*/*z* 1781.2609. Calcd for $C_{54}H_{51}Au_2O_{13}P_2S^+$: *m*/*z* 1395.1851 ([M − RS$^-$]$^+$). Found: *m*/*z* 1395.2070. UV−vis: λ_{max} = 250 nm.

Compound ***2d***. According to the general procedure, *β*-D-thioglucosetetraacetate (0.107 g, 0.294 mmol, 2 equiv), K_2CO_3 (0.082 g, 0.593 mmol, 4 equiv), and **2c** (0.170 g, 0.148 mmol, 1 equiv) in acetone (25 mL) were stirred for 48 h at RT in the dark. The product was isolated as a white solid. Yield: 0.223 g, 0.123 mmol, 84%. Elem anal. Calcd for $C_{70}H_{74}Au_2O_{23}P_2S_2$: C, 46.62; H, 4.14. Found: C, 46.74; H, 4.10. ^1H NMR ($CDCl_3$): δ_H 8.08−8.12 (4H, m, 4O(C=O)(*Ar*)CC*H*CHCP, $^3J_{H,H}$ = 8.5 Hz, $^4J_{H,H}$ = 2 Hz), 7.47−7.65 (24H, m, 4O(C=O)(*Ar*)CCHC*H*CP, 8P(*Ar*)CC*H*CHCH, 8P(*Ar*)CCHC*H*CH, 4P(*Ar*)CCHCHC*H*), 5.13−5.17 (4H, m, SC*H*CHOAc, SCHCHC*H*OAc), 5.08 (2H, t, C*H*CHCH$_2$OAc, $^3J_{H,H}$ = 9.2 Hz), 5.04 (2H, t, SCHC*H*OAc, $^3J_{H,H}$ = 9.2 Hz), 4.48−4.50 (4H, m, 2*Ar*(C=O)OC*H*$_2$CH$_2$O), 4.21 (2H, dd, C*H*$_2$OAc, $^2J_{H,H}$ = 12.2 Hz, $^3J_{H,H}$ = 4.8 Hz), 4.09 (2H, dd, C*H*$_2$OAc, $^2J_{H,H}$ = 12.2 Hz, $^3J_{H,H}$ = 2.4 Hz), 3.84−3.87 (4H, m, 2*Ar*(C=O)OCH$_2$C*H*$_2$O), 3.75 (2H, ddd, C*H*CH$_2$OAc, $^3J_{H,H}$ = 9.7 Hz, $^3J_{H,H}$ = 4.8 Hz, $^3J_{H,H}$ = 2.4 Hz), 2.04 (6H, s, 2CH$_2$O(C=O)*CH*$_3$), 2.00 (6H, s, 2(C=O)*CH*$_3$), 1.96 (6H, s, 2(C=O)*CH*$_3$), 1.89 (6H, s, 2(C=O)*CH*$_3$). ^{31}P NMR ($CDCl_3$): δ_P 38.77 (2P). ^{13}C NMR ($CDCl_3$): δ_C 170.9 (2C, 2(*C*=O)CH$_3$), 170.4 (2C, 2(*C*=O)CH$_3$), 169.8 (2C, 2(*C*=O)CH$_3$), 169.7 (2C, 2(*C*=O)CH$_3$), 165.6 (2C, 2O(*C*=O)(*Ar*)CCHCHCP), 135.6 (2C, d, 2O(C=O)(*Ar*)CCHCHCP, $^1J_{C,P}$ = 54 Hz), 134.6 (4C, d, 4P(*Ar*)CCHCHCH, $^2J_{C,P}$ = 14 Hz), 134.5 (4C, d, 4P(*Ar*)C*C*HCHCH, $^2J_{C,P}$ = 14 Hz), 134.2 (4C, d, 4O(C=O)(*Ar*)CCHCHCP, $^2J_{C,P}$ = 14 Hz), 132.9 (2C, d, 2O(C=O)(*Ar*)CCHCHCP, $^4J_{C,P}$ = 2 Hz), 132.1 (4C, d, 4P(*Ar*)CCHCHCH, $^4J_{C,P}$ = 2 Hz), 130.1 (4C, d, 4O(C=O)(*Ar*)CCHCHCP, $^3J_{C,P}$ = 12 Hz), 129.5 (8C, d, 8P(*Ar*)CCH*C*HCH, $^3J_{C,P}$ = 12 Hz), 129.0 (4C, d, 4P(*Ar*)CCHCHCH, $^1J_{C,P}$ = 57 Hz), 83.3 (2C, 2CHCH$_2$OAc), 77.8 (2C, SCHCHCHOAc), 75.9 (2C, SCHCHOAc), 74.3 (2C, SCHCHOAc), 69.2 (2C, 2CHCHCH$_2$OAc), 69.1 (2C, 2(*Ar*)(C=O)OCH$_2$CH$_2$O), 64.6 (2C, 2(*Ar*)(C=O)OCH$_2$CH$_2$O), 63.0 (2C, 2CHCH$_2$(C=O)CH$_3$), 21.3 (2C, 2CH$_2$O(C=O)*CH*$_3$), 20.86 (2C, 2(C=O)*CH*$_3$), 20.82 (2C, 2(C=O)*CH*$_3$), 20.77 (2C, 2(C=O)*CH*$_3$). ESI-MS(+). Calcd for $C_{70}H_{74}Au_2NaO_{23}P_2S_2^+$: *m*/*z* 1825.2761 ([M + Na]$^+$). Found: *m*/*z* 1825.2839. Calcd for $C_{56}H_{55}Au_2O_{14}P_2S^+$: *m*/*z* 1439.2113 ([M − RS$^-$]$^+$). Found: *m*/*z* 1439.2242. UV−vis: λ_{max} = 250 nm.

Compound ***3d***. According to the general procedure, *β*-D-thioglucosetetraacetate (0.107 g, 0.294 mmol, 2 equiv), K_2CO_3 (0.081 g, 0.586 mmol, 4 equiv), and **3c** (0.175 g, 0.147 mmol, 1 equiv) in acetone (25 mL) were stirred for 48 h at RT in the dark. The product was isolated as a white solid. Yield: 0.258 g, 0.140 mmol, 95%. Elem anal. Calcd for $C_{72}H_{78}Au_2O_{24}P_2S_2$: C, 46.81; H, 4.26. Found: C, 47.02; H, 3.98. ^1H NMR ($CDCl_3$): δ_H 8.09−8.12 (4H, m, 4O(C=O)(*Ar*)CC*H*CHCP, $^3J_{H,H}$ = 8.5 Hz, $^4J_{H,H}$ = 2.0 Hz), 7.47−7.67 (24H, m, 4O(C=O)(*Ar*)CCHC*H*CP, 8P(*Ar*)CC*H*CHCH, 8P(*Ar*)CCHC*H*CH, 4P(*Ar*)CCHCHC*H*), 5.11−5.18 (4H, m, SC*H*CHOAc,

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SCHCHC*H*OAc), 5.07 (2H, t, C*H*CHCH$_2$OAc, $^3J_{H,H}$ = 9.1 Hz), 5.04 (2H, t, SCHC*H*OAc, $^3J_{H,H}$ = 9.2 Hz), 4.46−4.48 (4H, m, 2*Ar*(C═O)OC*H*$_2$CH$_2$O), 4.22 (2H, dd, C*H*$_2$OAc, $^2J_{H,H}$ = 12.2 Hz, $^3J_{H,H}$ = 4.8 Hz), 4.10 (2H, dd, C*H*$_2$OAc, $^2J_{H,H}$ = 12.2 Hz, $^3J_{H,H}$ = 2.4 Hz), 3.80−3.83 (4H, m, 2*Ar*(C═O)OCH$_2$C*H*$_2$O), 3.76 (2H, ddd, C*H*CH$_2$OAc, $^3J_{H,H}$ = 9.8 Hz, $^3J_{H,H}$ = 4.8 Hz, $^3J_{H,H}$ = 2.4 Hz), 3.69 (4H, s, 2*Ar*(C═O)O(CH$_2$)$_2$OC*H*$_2$), 2.05 (6H, s, 2CH$_2$O(C═O)C*H*$_3$), 2.01 (6H, s, 2(C═O)C*H*$_3$), 1.97 (6H, s, 2(C═O)C*H*$_3$), 1.90 (6H, s, 2(C═O)C*H*$_3$). ^{31}P NMR (CDCl$_3$): δ_P 38.79 (2P). ^{13}C NMR (CDCl$_3$): δ_C 170.9 (2C, 2(C═O)CH$_3$), 170.4 (2C, 2(*C*═O)CH$_3$), 169.8 (2C, 2(C═O)CH$_3$), 169.7 (2C, 2(*C*═O)CH$_3$), 165.6 (2C, 2O(*C*═O)(*Ar*)CCHCHCP), 135.6 (2C, d, 2O(C═O)(*Ar*)CCHCHC*P*, $^1J_{C,P}$ = 53 Hz), 134.6 (4C, d, 4P(*Ar*)C*C*HCHCH, $^2J_{C,P}$ = 14 Hz), 134.5 (4C, d, 4P(*Ar*)CC*H*CHCH, $^2J_{C,P}$ = 14 Hz), 134.2 (4C, d, 4O(C═O)(*Ar*)CCHC*H*CP, $^2J_{C,P}$ = 14 Hz), 133.0 (2C, d, 2O(C═O)(*Ar*)*C*CHCHCP, $^4J_{C,P}$ = 2 Hz), 132.1 (4C, m, 4P(*Ar*)CCHCHCH), 130.1 (4C, d, 4O(C═O)(*Ar*)*C*CHCHCP, $^3J_{C,P}$ = 12 Hz), 129.5 (8C, d, 8P(*Ar*)CCH*C*HCH, $^3J_{C,P}$ = 12 Hz), 129.0 (4C, d, 4P(*Ar*)*C*CHCHCH, $^1J_{C,P}$ = 57 Hz), 83.3 (2C, 2CHCH$_2$OAc), 77.8 (2C, SCHCHCHOAc), 75.9 (2C, SCH*C*HOAc), 74.3 (2C, S*C*HCHOAc), 70.8 (2C, 2(*Ar*)(C═O)O(CH$_2$)$_2$OCH$_2$), 69.3 (2C, 2(*Ar*)(C═O)-OCH$_2$CH$_2$O), 69.1 (2C, 2*C*HCHCH$_2$OAc), 64.6 (2C, 2(*Ar*)(C═O)OCH$_2$CH$_2$O), 63.0 (2C, 2CHC*H*$_2$(C═O)CH$_3$), 21.3 (2C, 2CH$_2$O(C═O)*C*H$_3$), 20.87 (2C, 2(C═O)*C*H$_3$), 20.84 (2C, 2(C═O)CH$_3$), 20.79 (2C, 2(C═O)*C*H$_3$). ESI-MS(+). Calcd for $C_{72}H_{78}Au_2NaO_{24}P_2S_2^+$: *m*/*z* 1869.3023 ([M + Na]$^+$). Found: *m*/*z* 1869.3127. Calcd for $C_{58}H_{59}Au_2O_{15}P_2S^+$: *m*/*z* 1483.2375 ([M − RS$^-$]$^+$). Found: *m*/*z* 1483.2581. UV−vis: λ_{max} = 250 nm.

Compound ***4d***. According to the general procedure, β-D-thioglucosetetraacetate (0.103 g, 0.283 mmol, 2 equiv), K_2CO_3 (0.079 g, 0.572 mmol, 4 equiv), and **4c** (0.175 g, 1 equiv) in acetone (25 mL) were stirred for 48 h at RT in the dark. The product was isolated as a white solid. Yield: 0.233 g, 0.123 mmol, 87%. Elem anal. Calcd for $C_{74}H_{82}Au_2O_{25}P_2S_2$: C, 46.99; H, 4.37. Found: C, 47.02; H, 4.29. ^{1}H NMR (CDCl$_3$): δ_H 8.09−8.13 (4H, m, 4O(C═O)(*Ar*)-CC*H*CHCP, $^3J_{H,H}$ = 8.5 Hz, $^4J_{H,H}$ = 2.0 Hz), 7.46−7.64 (24H, m, 4O(C═O)(*Ar*)CCHC*H*CP, 8P(*Ar*)CC*H*CHCH, 8P(*Ar*)-CCHC*H*CH, 4P(*Ar*)CCHCHC*H*), 5.13−5.18 (4H, m, SC*H*CHOAc, SCHCHC*H*OAc), 5.09 (2H, t, C*H*CHCH$_2$OAc, $^3J_{H,H}$ = 9.6 Hz), 5.04 (2H, t, SCHC*H*OAc, $^3J_{H,H}$ = 9.2 Hz), 4.46−4.48 (4H, m, 2*Ar*(C═O)OC*H*$_2$CH$_2$O), 4.21 (2H, dd, C*H*$_2$OAc, $^2J_{H,H}$ = 12.3 Hz, $^3J_{H,H}$ = 4.8 Hz), 4.10 (2H, dd, C*H*$_2$OAc, $^2J_{H,H}$ = 12.3 Hz, $^3J_{H,H}$ = 2.3 Hz), 3.79−3.81 (4H, m, 2*Ar*(C═O)OCH$_2$C*H*$_2$O), 3.75 (2H, ddd, C*H*CH$_2$OAc, $^3J_{H,H}$ = 9.8 Hz, $^3J_{H,H}$ = 4.8 Hz, $^3J_{H,H}$ = 2.3 Hz), 3.63−3.70 (8H, m, 2*Ar*(C═O)O(CH$_2$)$_2$O(C*H*$_2$)$_2$), 2.04 (6H, s, 2CH$_2$O(C═O)C*H*$_3$), 2.01 (6H, s, 2(C═O)C*H*$_3$), 1.97 (6H, s, 2(C═O)C*H*$_3$), 1.90 (6H, s, 2(C═O)C*H*$_3$). ^{31}P NMR (CDCl$_3$): δ_P 38.71 (2P). ^{13}C NMR (CDCl$_3$): δ_C 170.9 (2C, 2(C═O)CH$_3$), 170.4 (2C, 2(*C*═O)CH$_3$), 169.8 (2C, 2(C═O)CH$_3$), 169.7 (2C, 2(*C*═O)CH$_3$), 165.6 (2C, 2O(*C*═O)(*Ar*)CCHCHCP), 135.5 (2C, d, 2O(C═O)(*Ar*)-CCHCHC*P*, $^1J_{C,P}$ = 54 Hz), 134.5 (4C, d, 4P(*Ar*)C*C*HCHCH, $^2J_{C,P}$ = 14 Hz), 134.4 (4C, d, 4P(*Ar*)CC*H*CHCH, $^2J_{C,P}$ = 14 Hz), 134.1 (4C, d, 4O(C═O)(*Ar*)CCHC*H*CP, $^2J_{C,P}$ = 14 Hz), 133.0 (2C, d, 2O(C═O)(*Ar*)*C*CHCHCP, $^4J_{C,P}$ = 2 Hz), 132.1 (4C, m, 4P(*Ar*)-CCHCHCH), 130.1 (4C, d, 4O(C═O)(*Ar*)*C*CHCHCP, $^3J_{C,P}$ = 12 Hz), 129.5 (8C, d, 8P(*Ar*)CCH*C*HCH, $^3J_{C,P}$ = 12 Hz), 129.0 (4C, d, 4P(*Ar*)*C*CHCHCH, $^1J_{C,P}$ = 57 Hz), 83.3 (2C, 2CHCH$_2$OAc), 77.8 (2C, SCHCHCHOAc), 75.9 (2C, SCHCHOAc), 74.3 (2C, SCHCHOAc), 70.80, 70.78 (4C, 2(*Ar*)(C═O)O(CH$_2$)$_2$OCH$_2$, 2(*Ar*)(C═O)O(CH$_2$)$_2$OCH$_2$CH$_2$), 69.2 (2C, 2(*Ar*)(C═O)-OCH$_2$CH$_2$O), 69.1 (2C, 2*C*HCHCH$_2$OAc), 64.7 (2C, 2(*Ar*)(C═O)OCH$_2$CH$_2$O), 63.0 (2C, 2CHC*H*$_2$(C═O)CH$_3$), 21.3 (2C, 2CH$_2$O(C═O)*C*H$_3$), 20.86 (2C, 2(C═O)*C*H$_3$), 20.82 (2C, 2(C═O)CH$_3$), 20.77 (2C, 2(C═O)*C*H$_3$). ESI-MS(+). Calcd for $C_{74}H_{82}Au_2NaO_{25}P_2S_2^+$: *m*/*z* 1913.3285 ([M + Na]$^+$). Found: *m*/*z* 1913.3390. Calcd for $C_{60}H_{63}Au_2O_{16}P_2S^+$: *m*/*z* 1527.2638 ([M − RS$^-$]$^+$). Found: *m*/*z* 1527.2816. UV−vis: λ_{max} = 250 nm.

Compound ***5d***. According to the general procedure, β-D-thioglucosetetraacetate (0.100 g, 0.274 mmol, 2 equiv), K_2CO_3 (0.076 g, 0.550 mmol, 4 equiv), and **5c** (0.175 g, 0.137 mmol, 1 equiv) in acetone (25 mL) were stirred for 48 h at RT in the dark. The product was isolated as a white solid. Yield: 0.253 g, 0.131 mmol, 96%. Elem anal. Calcd for $C_{76}H_{86}Au_2O_{26}P_2S_2$: C, 47.16; H, 4.48. Found: C, 47.30; H, 4.20. ^{1}H NMR (CDCl$_3$): δ_H 8.09−8.13 (4H, m, 4O(C═O)(*Ar*)CC*H*CHCP, $^3J_{H,H}$ = 8.5 Hz, $^4J_{H,H}$ = 2.0 Hz), 7.46−7.64 (24H, m, 4O(C═O)(*Ar*)CCHC*H*CP, 8P(*Ar*)CC*H*CHCH, 8P(*Ar*)-CCHC*H*CH, 4P(*Ar*)CCHCHC*H*), 5.11−5.17 (4H, m, SC*H*CHOAc, SCHCHC*H*OAc), 5.08 (2H, t, C*H*CHCH$_2$OAc, $^3J_{H,H}$ = 9.6 Hz), 5.04 (2H, t, SCHC*H*OAc, $^3J_{H,H}$ = 9.2 Hz), 4.46−4.48 (4H, m, 2*Ar*(C═O)OC*H*$_2$CH$_2$O), 4.21 (2H, dd, C*H*$_2$OAc, $^2J_{H,H}$ = 12.2 Hz, $^3J_{H,H}$ = 4.7 Hz), 4.10 (2H, dd, C*H*$_2$OAc, $^2J_{H,H}$ = 12.2 Hz, $^3J_{H,H}$ = 2.3 Hz), 3.79−3.82 (4H, m, 2*Ar*(C═O)OCH$_2$C*H*$_2$O), 3.75 (2H, ddd, C*H*CH$_2$OAc, $^3J_{H,H}$ = 10.0 Hz, $^3J_{H,H}$ = 4.7 Hz, $^3J_{H,H}$ = 2.3 Hz), 3.66−3.68 (4H, m, 2*Ar*(C═O)O(CH$_2$)$_2$OC*H*$_2$CH$_2$), 3.60−3.63 (4H, m, 2*Ar*(C═O)O-(CH$_2$)$_2$OCH$_2$C*H*$_2$), 3.62 (4H, s, 2*Ar*(C═O)O(CH$_2$)$_2$O-(CH$_2$)$_2$OC*H*$_2$), 2.04 (6H, s, 2CH$_2$O(C═O)C*H*$_3$), 2.00 (6H, s, 2(C═O)C*H*$_3$), 1.96 (6H, s, 2(C═O)C*H*$_3$), 1.89 (6H, s, 2(C═O)C*H*$_3$). ^{31}P NMR (CDCl$_3$): δ_P 38.73 (2P). ^{13}C NMR (CDCl$_3$): δ_C 170.8 (2C, 2(*C*═O)CH$_3$), 170.4 (2C, 2(*C*═O)CH$_3$), 169.74 (2C, 2(*C*═O)CH$_3$), 169.67 (2C, 2(*C*═O)CH$_3$), 165.6 (2C, 2O(*C*═O)(*Ar*)CCHCHCP), 135.4 (2C, d, 2O(C═O)(*Ar*)CCHCHC*P*, $^1J_{C,P}$ = 54 Hz), 134.5 (4C, d, 4P(*Ar*)C*C*HCHCH, $^2J_{C,P}$ = 14 Hz), 134.4 (4C, d, 4P(*Ar*)CC*H*CHCH, $^2J_{C,P}$ = 14 Hz), 134.1 (4C, d, 4O(C═O)(*Ar*)CCHC*H*CP, $^2J_{C,P}$ = 14 Hz), 133.0 (2C, d, 2O(C═O)(*Ar*)*C*CHCHCP, $^4J_{C,P}$ = 3 Hz), 132.1 (4C, d, 4P(*Ar*)CCHCHCH, $^4J_{C,P}$ = 3 Hz), 130.1 (4C, d, 4O(C═O)(*Ar*)*C*CHCHCP, $^3J_{C,P}$ = 12 Hz), 129.4 (8C, d, 8P(*Ar*)CCH*C*HCH, $^3J_{C,P}$ = 12 Hz), 129.0 (4C, d, 4P(*Ar*)*C*CHCHCH, $^1J_{C,P}$ = 57 Hz), 83.2 (2C, 2CHCH$_2$OAc), 77.8 (2C, SCHCHCHOAc), 75.9 (2C, SCHCHOAc), 74.3 (2C, SCHCHOAc), 70.72, 70.74 (6C, 2(*Ar*)(C═O)O(CH$_2$)$_2$OCH$_2$, 2(*Ar*)(C═O)O-(CH$_2$)$_2$OCH$_2$CH$_2$, 2(*Ar*)(C═O)O(CH$_2$)$_2$O(CH$_2$)$_2$OCH$_2$), 69.2 (2C, 2(*Ar*)(C═O)OCH$_2$CH$_2$O), 69.1 (2C, 2*C*HCHCH$_2$OAc), 64.7 (2C, 2(*Ar*)(C═O)OCH$_2$CH$_2$O), 63.0 (2C, 2CHC*H*$_2$(C═O)CH$_3$), 21.2 (2C, 2CH$_2$O(C═O)*C*H$_3$), 20.84 (2C, 2(C═O)*C*H$_3$), 20.80 (2C, 2(C═O)CH$_3$), 20.75 (2C, 2(C═O)*C*H$_3$). ESI-MS(+). Calcd for $C_{76}H_{86}Au_2NaO_{26}P_2S_2^+$: *m*/*z* 1957.3547 ([M + Na]$^+$). Found: *m*/*z* 1957.3685. Calcd for $C_{62}H_{67}Au_2O_{17}P_2S^+$: *m*/*z* 1571.2900 ([M − RS$^-$]$^+$). Found: *m*/*z* 1571.3116. UV−vis: λ_{max} = 250 nm.

Compound ***6d***. β-D-Thioglucosetetraacetate (0.128 g, 0.351 mmol, 2 equiv), K_2CO_3 (0.053 g, 0.383 mmol, 2.2 equiv), and **6c** (0.232 g, 0.175 mmol, 1 equiv) in a mixture of H$_2$O/EtOH/CH$_2$Cl$_2$ [30 mL, 1:1:1 (v/v/v)] were stirred for 72 h at RT in the dark. The reaction mixture was concentrated to dryness, and the crude was suspended in a mixture of acetone/CH$_2$Cl$_2$ [30 mL, 1:1 (v/v)]. The inorganic salts were removed by filtration, and the filtrate was concentrated under reduced pressure and further dried under vacuum to afford the product as a white solid. Yield: 0.323 g, 0.163 mmol, 94%. Elem anal. Calcd for $C_{78}H_{90}Au_2O_{27}P_2S_2$: C, 47.33; H, 4.58. Found: C, 47.43; H, 4.55. ^{1}H NMR (CDCl$_3$): δ_H 8.10−8.13 (4H, m, 4O(C═O)(*Ar*)CC*H*CHCP, $^3J_{H,H}$ = 8.4 Hz, $^4J_{H,H}$ = 2.0 Hz), 7.45−7.63 (24H, m, 4O(C═O)(*Ar*)CCHC*H*CP, 8P(*Ar*)CC*H*CHCH, 8P(*Ar*)CCHC*H*CH, 4P-(*Ar*)CCHCHC*H*), 5.11−5.17 (4H, m, SC*H*CHOAc, SCHCHC*H*OAc), 5.08 (2H, t, C*H*CHCH$_2$OAc, $^3J_{H,H}$ = 9.6 Hz), 5.04 (2H, t, SCHC*H*OAc, $^3J_{H,H}$ = 9.1 Hz), 4.46−4.49 (4H, m, 2*Ar*(C═O)OC*H*$_2$CH$_2$O), 4.20 (2H, dd, C*H*$_2$OAc, $^2J_{H,H}$ = 12.2 Hz, $^3J_{H,H}$ = 4.8 Hz), 4.10 (2H, dd, C*H*$_2$OAc, $^2J_{H,H}$ = 12.2 Hz, $^3J_{H,H}$ = 2.4 Hz), 3.80−3.82 (4H, m, 2*Ar*(C═O)OCH$_2$C*H*$_2$O), 3.76 (2H, ddd, C*H*CH$_2$OAc, $^3J_{H,H}$ = 9.8 Hz, $^3J_{H,H}$ = 4.8 Hz, $^3J_{H,H}$ = 2.8 Hz), 3.66−3.68 (4H, m, 2*Ar*(C═O)O(CH$_2$)$_2$OC*H*$_2$CH$_2$), 3.62−3.64 (4H, m, 2*Ar*(C═O)O(CH$_2$)$_2$OCH$_2$C*H*$_2$), 3.60−3.63 (8H, m, 2*Ar*(C═O)O-(CH$_2$)$_2$O(CH$_2$)$_2$O(C*H*$_2$)$_2$), 2.04 (6H, s, 2CH$_2$O(C═O)C*H*$_3$), 2.00 (6H, s, 2(C═O)C*H*$_3$), 1.96 (6H, s, 2(C═O)C*H*$_3$), 1.89 (6H, s, 2(C═O)C*H*$_3$). ^{31}P NMR (CDCl$_3$): δ_P 38.78 (2P). ^{13}C NMR (CDCl$_3$): δ_C 170.8 (2C, 2(C═O)CH$_3$), 170.4 (2C, 2(*C*═O)CH$_3$), 169.7 (2C, 2(*C*═O)CH$_3$), 169.6 (2C, 2(*C*═O)CH$_3$), 165.6 (2C, 2O(*C*═O)(*Ar*)CCHCHCP), 135.5 (2C, d, 2O(C═O)(*Ar*)-CCHCHC*P*, $^1J_{C,P}$ = 53 Hz), 134.5 (4C, d, 4P(*Ar*)C*C*HCHCH, $^2J_{C,P}$ = 14 Hz), 134.4 (4C, d, 4P(*Ar*)CC*H*CHCH, $^2J_{C,P}$ = 14 Hz), 134.2 (4C, d, 4O(C═O)(*Ar*)CCHC*H*CP, $^2J_{C,P}$ = 14 Hz), 133.0 (2C, d, 2O(C═O)(*Ar*)*C*CHCHCP, $^4J_{C,P}$ = 2 Hz), 132.1 (4C, m, 4P(*Ar*)-

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CCHCHCH), 130.1 (4C, d, 4O(C=O)(*Ar*)CCHCHCP, $^{3}J_{C,P}$ = 11 Hz), 129.4 (8C, d, 8P(*Ar*)CCHCHCH, $^{3}J_{C,P}$ = 12 Hz), 129.0 (4C, d, 4P(*Ar*)CCHCHCH, $^{1}J_{C,P}$ = 56 Hz), 83.2 (2C, 2CHCH$_2$OAc), 77.8 (2C, SCHCHCHOAc), 75.9 (2C, SCHCHOAc), 74.3 (2C, SCHCHOAc), 70.72, 70.70, 70.63 (8C, 2(*Ar*)(C=O)O(CH$_2$)$_2$OCH$_2$, 2(*Ar*)(C=O)O(CH$_2$)$_2$OCH$_2$CH$_2$, 2(*Ar*)(C=O)O(CH$_2$)$_2$O-(CH$_2$)$_2$OCH$_2$, 2(*Ar*)(C=O)O(CH$_2$)$_2$O(CH$_2$)$_2$OCH$_2$CH$_2$), 69.2 (2C, 2(*Ar*)(C=O)OCH$_2$CH$_2$O), 69.1 (2C, 2CHCHCH$_2$OAc), 64.6 (2C, 2(*Ar*)(C=O)OCH$_2$CH$_2$O), 62.9 (2C, 2CHCH$_2$(C=O)CH$_3$), 21.2 (2C, 2CH$_2$O(C=O)CH$_3$), 20.80 (2C, 2(C=O)CH$_3$), 20.77 (2C, 2(C=O)CH$_3$), 20.72 (2C, 2(C=O)CH$_3$). ESI-MS(+). Calcd for $C_{78}H_{90}Au_2NaO_{27}P_2S_2^+$: *m*/*z* 2001.3809 ([M + Na]$^+$). Found: *m*/*z* 2001.3790. Calcd for $C_{64}H_{71}Au_2O_{18}P_2S^+$: *m*/*z* 1615.3162 ([M − RS$^-$]$^+$). Found: *m*/*z* 1615.3180. UV−vis: λ_{max} = 250 nm.

Compound ***7d.*** *β*-D-Thioglucosetetraacetate (0.130 g, 0.357 mmol, 2 equiv), K_2CO_3 (0.054 g, 0.391 mmol, 2.2 equiv), and **7c** (0.252 g, 0.178 mmol, 1 equiv) in a mixture of H$_2$O/EtOH/CH$_2$Cl$_2$ [30 mL, 1:1:1 (v/v/v)] were stirred for 72 h at RT in the dark. The reaction mixture was concentrated to dryness, and the crude was suspended in a mixture of acetone/CH$_2$Cl$_2$ [30 mL, 1:1 (v/v)]. The inorganic salts were removed by filtration, and the filtrate was concentrated under reduced pressure and further dried under vacuum to afford the product as a white solid. Yield: 0.317 g, 0.153 mmol, 86%. Elem anal. Calcd for $C_{82}H_{98}Au_2O_{29}P_2S_2$: C, 47.63; H, 4.78. Found: C, 47.85; H, 4.60. ^{1}H NMR (CDCl$_3$): δ_H 8.10−8.13 (4H, m, 4O(C=O)(*Ar*)CC*H*CHCP, $^{3}J_{H,H}$ = 8.4 Hz, $^{4}J_{H,H}$ = 2.0 Hz), 7.47−7.64 (24H, m, 4O(C=O)(*Ar*)CCHC*H*CP, 8P(*Ar*)CC*H*CHCH, 8P(*Ar*)CCHC*H*CH, 4P-(*Ar*)CCHCHC*H*), 5.11−5.18 (4H, m, SC*H*CHOAc, SCHCHC*H*OAc), 5.09 (2H, t, C*H*CHCH$_2$OAc, $^{3}J_{H,H}$ = 9.6 Hz), 5.04 (2H, t, SCHC*H*OAc, $^{3}J_{H,H}$ = 9.1 Hz), 4.47−4.49 (4H, m, 2*Ar*(C=O)OC*H*$_2$CH$_2$O), 4.21 (2H, dd, C*H*$_2$OAc, $^{2}J_{H,H}$ = 12.2 Hz, $^{3}J_{H,H}$ = 4.8 Hz), 4.10 (2H, dd, C*H*$_2$OAc, $^{2}J_{H,H}$ = 12.2 Hz, $^{3}J_{H,H}$ = 2.4 Hz), 3.80−3.83 (4H, m, 2*Ar*(C=O)OCH$_2$C*H*$_2$O), 3.76 (2H, ddd, C*H*CH$_2$OAc, $^{3}J_{H,H}$ = 9.8 Hz, $^{3}J_{H,H}$ = 4.8 Hz, $^{3}J_{H,H}$ = 2.4 Hz), 3.66−3.69 (4H, m, 2*Ar*(C=O)O(CH$_2$)$_2$OC*H*$_2$CH$_2$), 3.62−3.65 (4H, m, 2*Ar*(C=O)O(CH$_2$)$_2$OCH$_2$C*H*$_2$), 3.59−3.62 (8H, m, 2*Ar*(C=O)O-(CH$_2$)$_2$O(CH$_2$)$_2$O(C*H*$_2$)$_2$), 2.04 (6H, s, 2CH$_2$O(C=O)C*H*$_3$), 2.00 (6H, s, 2(C=O)C*H*$_3$), 1.97 (6H, s, 2(C=O)C*H*$_3$), 1.90 (6H, s, 2(C=O)C*H*$_3$). ^{31}P NMR (CDCl$_3$): δ_P 38.71 (2P). ^{13}C NMR (CDCl$_3$): δ_C 170.8 (2C, 2(C=O)CH$_3$), 170.4 (2C, 2(*C*=O)CH$_3$), 169.71 (2C, 2(*C*=O)−CH$_3$), 169.65 (2C, 2(C=O)CH$_3$), 165.6 (2C, 2O(*C*=O)(*Ar*)CCHCHCP), 135.4 (2C, d, 2O(C=O)(*Ar*)-CCHCHCP, $^{1}J_{C,P}$ = 53 Hz), 134.5 (4C, d, 4P(*Ar*)CCHCHCH, $^{2}J_{C,P}$ = 14 Hz), 134.4 (4C, d, 4P(*Ar*)CCHCHCH, $^{2}J_{C,P}$ = 14 Hz), 134.1 (4C, d, 4O(C=O)(*Ar*)CCHCHCP, $^{2}J_{C,P}$ = 14 Hz), 133.0 (2C, d, 2O(C=O)(*Ar*)CCHCHCP, $^{4}J_{C,P}$ = 2 Hz), 132.1 (4C, m, 4P(*Ar*)-CCHCHCH), 130.1 (4C, d, 4O(C=O)(*Ar*)CCHCHCP, $^{3}J_{C,P}$ = 12 Hz), 129.4 (8C, d, 8P(*Ar*)CCHCHCH, $^{3}J_{C,P}$ = 12 Hz), 128.9 (4C, d, 4P(*Ar*)CCHCHCH, $^{1}J_{C,P}$ = 57 Hz), 83.2 (2C, 2CHCH$_2$OAc), 77.9 (2C, SCHCHCHOAc), 75.8 (2C, SCHCHOAc), 74.2 (2C, SCHCHOAc), 70.70, 70.68, 70.61 (8C, 2(*Ar*)(C=O)O(CH$_2$)$_2$OCH$_2$, 2(*Ar*)(C=O)O(CH$_2$)$_2$OCH$_2$CH$_2$, 2(*Ar*)(C=O)O(CH$_2$)$_2$O-(CH$_2$)$_2$OCH$_2$, 2(*Ar*)(C=O)O(CH$_2$)$_2$O(CH$_2$)$_2$OCH$_2$CH$_2$), 69.2 (2C, 2(*Ar*)(C=O)OCH$_2$CH$_2$O), 69.0 (2C, 2CHCHCH$_2$OAc), 64.6 (2C, 2(*Ar*)(C=O)OCH$_2$CH$_2$O), 62.9 (2C, 2CHCH$_2$(C=O)CH$_3$), 21.2 (2C, 2CH$_2$O(C=O)CH$_3$), 20.82 (2C, 2(C=O)CH$_3$), 20.78 (2C, 2(C=O)CH$_3$), 20.73 (2C, 2(C=O)CH$_3$). ESI-MS(+). Calcd for $C_{82}H_{98}Au_2NaO_{29}P_2S_2^+$: *m*/*z* 2089.4334 ([M + Na]$^+$). Found: *m*/*z* 2089.4307. Calcd for $C_{68}H_{79}Au_2O_{20}P_2S^+$: *m*/*z* 1703.3686 ([M − RS$^-$]$^+$). Found: *m*/*z* 1703.3684. UV−vis: λ_{max} = 250 nm.

Compound ***8d.*** According to the general procedure, *β*-D-thioglucosetetraacetate (0.258 g, 0.708 mmol, 1 equiv), K_2CO_3 (0.196 g, 1.418 mmol, 2 equiv), and **8c** (0.350 g, 0.707 mmol, 1 equiv) in acetone (25 mL) were stirred for 24 h at RT in the dark. The product was isolated as a white solid. Yield: 0.548 g, 0.666 mmol, 89%. Elem anal. Calcd for $C_{32}H_{34}AuO_9PS$: C, 46.72; H, 4.17. Found: C, 46.97; H, 3.85. ^{1}H NMR (CDCl$_3$): δ_H 7.42−7.59 (15H, m, 6P(*Ar*)CC*H*CHCH, 6P(*Ar*)CCHC*H*CH, 3P(*Ar*)CCHCHC*H*), 5.12−5.17 (2H, m, SC*H*CHOAc, SCHCHC*H*OAc), 5.08 (1H, t, C*H*CHCH$_2$OAc $^{3}J_{H,H}$ = 9.5 Hz), 5.03 (1H, t, SCHC*H*OAc, $^{3}J_{H,H}$ = 9.3 Hz), 4.19 (1H, dd, C*H*$_2$OAc, $^{2}J_{H,H}$ = 12.2 Hz, $^{3}J_{H,H}$ = 4.8 Hz), 4.09 (1H, dd, C*H*$_2$OAc, $^{2}J_{H,H}$ = 12.2 Hz, $^{3}J_{H,H}$ = 2.4 Hz), 3.74 (1H, ddd, C*H*CH$_2$OAc, $^{3}J_{H,H}$ = 9.7 Hz, $^{3}J_{H,H}$ = 4.8 Hz, $^{3}J_{H,H}$ = 2.4 Hz), 2.02 (3H, s, CH$_2$O(C=O)C*H*$_3$), 1.99 (3H, s, (C=O)C*H*$_3$), 1.95 (3H, s, (C=O)C*H*$_3$), 1.87 (3H, s, (C=O)C*H*$_3$). ^{31}P NMR (CDCl$_3$): δ_P 38.83 (1P). ^{13}C NMR (CDCl$_3$): δ_C 170.9 (1C, (C=O)CH$_3$), 170.4 (1C, (*C*=O)CH$_3$), 169.7 (1C, (*C*=O)CH$_3$), 169.7 (1C, (*C*=O)CH$_3$), 134.4 (6C, d, 6P(*Ar*)CCHCHCH, $^{2}J_{C,P}$ = 14 Hz), 131.7 (3C, d, 3P(*Ar*)CCHCHCH, $^{4}J_{C,P}$ = 2 Hz), 129.8 (3C, d, 3P(*Ar*)CCHCHCH, $^{1}J_{C,P}$ = 57 Hz), 129.3 (6C, d, 6P(*Ar*)CCHCHCH, $^{3}J_{C,P}$ = 11 Hz), 83.2 (1C, *C*HCH$_2$OAc), 77.8 (1C, SCHCHCHOAc), 75.8 (1C, SCHCHOAc), 74.3 (1C, SCHCHOAc), 69.1 (1C, CHCHCH$_2$OAc), 63.0 (1C, CHCH$_2$(C=O)CH$_3$), 21.2 (1C, CH$_2$O(C=O)CH$_3$), 20.80 (2C, 2(C=O)CH$_3$), 20.75 (1C, (C=O)CH$_3$). ESI-MS(+). Calcd for $C_{32}H_{34}AuO_9PS$: *m*/*z* 822.1327 ([M + H]$^+$). Found: *m*/*z* 823.1407. Calcd for $C_{32}H_{34}AuNaO_9PS^+$: *m*/*z* 845.1224 ([M + Na]$^+$). Found: *m*/*z* 845.1239.

Compound ***9d.*** According to the general procedure, *β*-D-thioglucosetetraacetate (0.304 g, 0.834 mmol, 1 equiv), K_2CO_3 (0.231 g, 1.671 mmol, 2 equiv), and **9c** (0.450 g, 0.835 mmol, 1 equiv) in acetone (35 mL) were stirred for 48 h at RT in the dark. The product was isolated as a white solid. Yield: 0.687 g, 0.793 mmol, 95%. Elem anal. Calcd for $C_{33}H_{34}AuO_{11}PS{\cdot}CDCl_3$: C, 40.56; H, 3.70. Found: C, 39.96; H, 3.57. CDCl$_3$ originates from the NMR solvent. ^{1}H NMR (CDCl$_3$): δ_H 7.81−7.90 (2H, m, 2O(C=O)(*Ar*)CC*H*CHCP), 7.30−7.48 (12H, m, 2O(C=O)(*Ar*)CCHC*H*CP, 4P(*Ar*)-CC*H*CHCH, 4P(*Ar*)CCHC*H*CH, 2P(*Ar*)CCHCHC*H*), 5.06−5.13 (2H, m, SC*H*CHOAc, SCHCHC*H*OAc), 4.99 (1H, t, C*H*CHCH$_2$OAc, $^{3}J_{H,H}$ = 9.2 Hz), 4.97 (1H, t, SCHC*H*OAc, $^{3}J_{H,H}$ = 9.3 Hz), 4.07 (1H, dd, C*H*$_2$OAc, $^{2}J_{H,H}$ = 12.1 Hz, $^{3}J_{H,H}$ = 5.1 Hz), 4.02 (1H, d, C*H*$_2$OAc, $^{2}J_{H,H}$ = 12.1 Hz), 3.68 (1H, m, C*H*CH$_2$OAc), 2.16 (6H, s, 2CH$_2$O(C=O)C*H*$_3$), 2.00 (3H, s, (C=O)C*H*$_3$), 1.91 (3H, s, (C=O)C*H*$_3$), 1.90 (3H, s, (C=O)C*H*$_3$). ^{31}P NMR (CDCl$_3$): δ_P 38.82 (1P). ^{13}C NMR (CDCl$_3$): δ_C 171.8 (1C, (*C*=O)CH$_3$), 171.4 (1C, (*C*=O)CH$_3$), 170.2 (1C, (*C*=O)CH$_3$), 170.1 (1C, (*C*=O)CH$_3$), 169.8 (1C, O(*C*=O)(*Ar*)CCHCHCP), 141.7 (1C, m, O(C=O)(*Ar*)CCHCHCP), 134.3 (2C, d, 2P(*Ar*)CCHCHCH, $^{2}J_{C,P}$ = 15 Hz), 134.2 (2C, d, 2P(*Ar*)CCHCHCH, $^{2}J_{C,P}$ = 15 Hz), 133.7 (2C, d, 2O(C=O)(*Ar*)CCHCHCP, $^{2}J_{C,P}$ = 14 Hz), 131.9 (3C, m, O(C=O)(*Ar*)CCHCHCP, 2P(*Ar*)CCHCHCH), 129.9 (2C, m, 2P(*Ar*)CCHCHCH), 129.7 (2C, d, 2O(C=O)(*Ar*)CCHCHCP, $^{3}J_{C,P}$ = 11 Hz), 129.4 (2C, d, 2P(*Ar*)CCHCHCH, $^{3}J_{C,P}$ = 11 Hz), 129.3 (2C, d, 2P(*Ar*)CCHCHCH, $^{3}J_{C,P}$ = 12 Hz), 83.2 (1C, CHCH$_2$OAc), 77.5 (1C, SCHCHCHOAc), 75.6 (1C, SCHCHOAc), 74.1 (1C, SCHCHOAc), 69.3 (1C, CHCHCH$_2$OAc), 63.3 (1C, CHCH$_2$(C=O)CH$_3$), 21.2 (1C, CH$_2$O(C=O)CH$_3$), 20.8 (2C, 2(C=O)CH$_3$), 20.7 (1C, (C=O)CH$_3$). ESI-MS(+). Calcd for $C_{33}H_{34}AuO_{11}PS$: *m*/*z* 866.1225 ([M + H]$^+$). Found: *m*/*z* 867.1310. Calcd for $C_{33}H_{34}AuNaO_{11}PS^+$: *m*/*z* 889.1123 ([M + Na]$^+$). Found: *m*/*z* 889.1143. Calcd for $C_{33}H_{34}AuKO_{11}PS^+$: *m*/*z* 905.0862 ([M + K]$^+$). Found: *m*/*z* 905.0881.

Stability Studies. The stability of complexes **1b**−**7b** and **1d**−**7d** in DMSO-*d*^{6} was assessed via ^{1}H (400 MHz) and ^{31}P (162 MHz) NMR at 298 K for 20 min. The stability of complexes **2d**, **4d**, and **6d** in pseudocell culture conditions was assessed in aqueous 100 mM NaCl and 5% DMSO for 72 h at 298 K and monitored via ESI-MS(+).

Cell Culture and in Vitro Antiproliferative Activity. The human ovarian carcinoma (A2780 and A2780cisR) cell lines were obtained from the European Collection of Cell Cultures. The human embryonic kidney (HEK-293) cell line was obtained from ATCC (Sigma, Buchs, Switzerland). Penicillin streptomycin, RPMI 1640 GlutaMAX (where RPMI = Roswell Park Memorial Institute), and DMEM GlutaMAX media (where DMEM = Dulbecco's modified Eagle medium) were obtained from Life Technologies, and fetal bovine serum (FBS) was obtained from Sigma. The cells were cultured in RPMI 1640 GlutaMAX (A2780 and A2780cisR) and DMEM GlutaMAX (HEK-293) media containing 10% heat-inactivated FBS and 1% penicillin streptomycin at 37 °C and CO$_2$ (5%).The A2780cisR cell line was routinely treated with cisplatin (2 *μ*M) in the media. The cytotoxicity was determined using the 3-(4,5-dimethyl-

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2-thiazolyl)-2,5-diphenyl-2*H*-tetrazolium bromide (MTT) assay.[83] Cells were seeded in flat-bottomed 96-well plates as a suspension in a prepared medium (100 μL aliquots and approximately 4300 cells/well) and preincubated for 24 h. Stock solutions of compounds were prepared in DMSO and were rapidly diluted in a medium. The solutions were sequentially diluted to give a final DMSO concentration of 0.5% and a final compound concentration range (0−500 μM). Cisplatin was tested as a positive control (0−100 μM). The compounds were added to the preincubated 96-well plates in 100 μL aliquots, and the plates were incubated for 72 h. MTT (20 μL, 5 mg/mL in Dulbecco's phosphate buffered saline) was added to the cells, and the plates were incubated for a further 4 h. The culture medium was aspirated, and the purple formazan crystals, formed by the mitochondrial dehydrogenase activity of vital cells, were dissolved in DMSO (100 μL/well). The absorbance of the resulting solutions, directly proportional to the number of surviving cells, was quantified at 590 nm using a microplate reader. The percentage of surviving cells was calculated from the absorbance of wells corresponding to the untreated control cells. The reported IC_{50} values (Table 3) are based on the means from three independent experiments, each comprising four tests per concentration level.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.7b01082.

Crystal data and refinement for **9b** and **9c**, partition coefficient data, NMR spectroscopy stability data for **1b**−**7b** and **1d**−**7d**, ESI-MS(+) stability data of **2d**, **4d**, and **6d**, and NMR spectra of all compounds (PDF)

Accession Codes

CCDC 1542726 and 1542742 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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