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Tripodal Ru(II) complexes with conjugated and non-conjugated rigid-rod bridges for semiconductor nanoparticles sensitization

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Abstract—Three tripodal Ru(II)-polypyridyl complexes have been synthesized as models to study long-range electron transfer in TiO_2 semiconductor nanoparticles thin films, in particular to study the effect of the conjugation of the bridge containing the Ru complex and for distance dependence studies. The tripodal sensitizers, which are 1,3,5,7-tetraphenyladamantane derivatives having three COOMe anchoring groups and one rigid-rod bridge substituted with a Ru(II) complex, are the longest prepared to date (Ru-to-footprint distance ~24 Å). Two have a rigid-rod bridge made of two *p*-ethynylphenylene units $(Ph\text{-}E)_2$ capped with a 4-2,2′-bipyridyl (bpy) ligand or a 5-1,10-phenanthrolinyl (phen) ligand for the Ru complex. The third tripod, which contains a bpy ligand for the Ru complex, has one bicyclo[2.2.2]octylene (Bco) unit in place of a *p*-phenylene (Ph) unit and is the first example of a tripodal sensitizer with a non-conjugated bridge.

1. Introduction

The photoexcitation of dyes covalently bound to TiO_2 nanoparticles thin films is an important step in dye-sensitized (Grätzel) solar cells and other optoelectronic systems based on wide band gap semiconductors.[1] Polypyridine complexes of Ru(II), the classical photosensitizing dyes for solar cells, are generally bound to the TiO_2 nanoparticles through anchoring groups directly attached on one or more ligands. Carboxylate (COOR) or phosphonate ($PO(OR)_2$) groups are frequently used for this purpose because they form strong bonds with TiO_2 surfaces.[1a] To bind the sensitizers, we[2] and others[3,4] have developed rigid linkers that have the shape of tripods and rigid-rods.[5] The design of linkers of varying complexity for the functionalization of semiconductor nanoparticle is a recent and promising development in this field.[6]

For clarity, in this paper we call bridge (b) the moiety that is placed between the anchoring groups (A) and the chromophore or sensitizer (S), and tripodal linker the molecule that contains both the bridge and the anchoring groups, as shown in Figure 1. Tripodal sensitizer, or tripod, is the tripodal linker capped with the Ru complex. We reported the study of tripodal sensitizers based on tetraphenylmethane and 1,3,5,7-tetraphenyladamantane, and having one *p*-ethynylphenylene (Ph-E) unit as the bridge carrying Ru-polypyridyl complexes.[2b–d] These molecules are rigid and stand perpendicularly to the surface when all three COOR anchoring groups are bound. Because of this binding geometry, the distance of the Ru complex from the semiconductor is fixed, and tripodal sensitizers are useful models to study interfacial electron transfer processes.

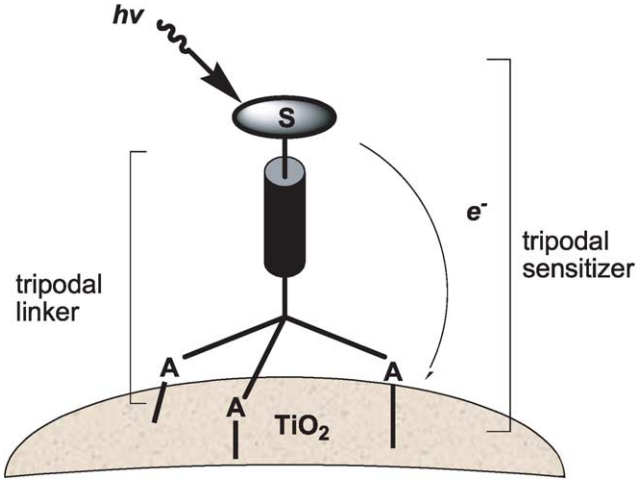

Figure 1. Schematic representation of the components of a tripodal sensitizer bound to a TiO_2 nanoparticle. These are: the sensitizing chromophore (S) and the tripodal linker, containing a rigid-rod bridge (b) and three anchoring groups (A).

Keywords: Titanium dioxide; Sensitization; ruthenium complexes; Tripods.
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The Ru-to-footprint distance (d) in our previous series of tripods was 15–18 Å.[2] In this paper we report the synthesis and characterization of the longest (d = 24 Å) tripods prepared to date and the first example of a tripodal sensitizer with a non-conjugated bridge (**1**, **2** and **3** in Figure 2). Both **1** and **2** contain a bridge made of two *p*-ethynylphenylene units, $(Ph\text{-}E)_2$, but differ in the ligands for the Ru complex (a phen ligand in **1** and a bpy ligand in **2**). Tripod **3** is analogous to the bpy-based **2**, but contains a bicyclo[2.2.2]-octylene unit (Bco) in the bridge in place of a *p*-phenylene (Ph) unit.[7]

The study of tripodal Ru-polypyridyl sensitizers bound to TiO_2 thin films has shown that the metal-to-ligand charge transfer (MLCT) excited state is localized on the bpy ligand attached to the bridge and that the bridge conjugation can influence the electron injection process.[2] This is not surprising, as the influence of $(Ph\text{-}E)_n$[8a–c] groups and other conjugated substituents[8d,9e] on the photophysical properties of Ru-polypyridyl complexes has been demonstrated. We observed this effect in the interfacial charge injection in **1** and **2** bound to TiO_2 thin films (**1**/TiO_2 and **2**/TiO_2).[2a] The electron injection in Ru complexes that are directly bound to the surface, for instance $Ru(dcb)(bpy)_2^{2+}$,[7] occurs in $\tau <$ 80 fs.[1a,9] As expected, slower rates were observed in **1**/TiO_2 and **2**/TiO_2.[2a] The kinetics were fit using bi-exponential decays,[1,9,10] with **1** injecting faster than **2**. In both cases, there was a slow ($\tau \sim 3$ ps) component ascribed to the long-range injection, together with a sub-picosecond component ($\tau \sim 240$ fs for **1**/TiO_2 and ~ 450 fs for **2**/TiO_2).[2a] The ultrafast component was rationalized considering the extensive π-conjugation of the bridge. The faster injection exhibited by the phen-based **1**/TiO_2 with respect to the bpy-based **2**/TiO_2 was attributed to the stronger electronic coupling between the phen ligand and the bridge.[2a,11] In summary, the study of **1** and **2** reinforced the concept that the conjugated bridge plays an important role in the interfacial electron injection. To probe this effect, we have now prepared **3**, which contains a non-conjugated bridge.

Hydrocarbon cage compounds that have been used to prepare non-conjugated bridges connecting an electron donor–acceptor[12] pair include cubane,[13] stellane,[14] adamantane,[15] [*n*]staffanes[16] and bicyclo[2.2.2]octane.[17,18] The use of rigid-rod molecules for this purpose has been reviewed.[19] We selected to incorporate one bicyclo[2.2.2]-octylene unit in the bridge because it is an excellent insulator of electronic effects,[17c] as shown by a comparison of the LUMO delocalization in the bridges of **2** and **3** (Figure 3).

At the same time, the replacement of a Ph with a Bco does not significantly change the length of the molecule (Figure 2, inset). These properties make **3** an ideal model to study the bridge conjugation effect on the rate of electron injection. Also, models **1**–**3** will be useful, together with other tripods, in distance dependence studies to investigate the mechanism(s) for the electron injection. In this paper we report the syntheses of **1** and **2** (for which we had reported preliminary data but not the synthesis) and the new model **3** through two different routes.

2. Synthesis

Scheme 1 shows the two synthetic routes employed. The key step in both routes, step 1, involves the monosubstitution of a tetrahedral precursor (**I**) to prepare a derivative having one group different from the other three. Since this is a statistical step, it requires a separation. The alkyne of the tripodal linker (**II**) is capped with the chromophore in the last step, so that a variety of tripodal sensitizers (**III**) can be prepared from this intermediate.

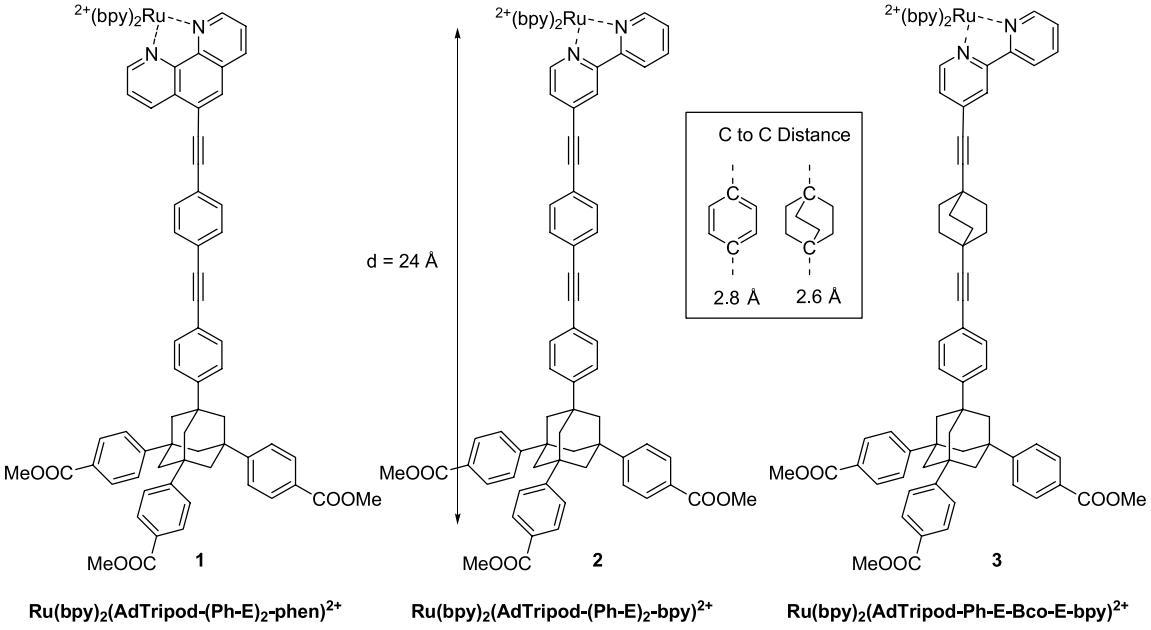


Figure 2. Tripodal sensitizers **1**, **2** and **3**. The counterion is PF_2^- in all cases. Note the phen ligand in **1** and bpy ligand in **2**. Tripod **3** contains a Bco unit that retains the axial symmetry and has the same length as a Ph unit (inset). The distance (d) of the Ru center to the footprint (the plane defined by the three surface-bound oxygen atoms) in **1**–**3** is 24 Å.[7]

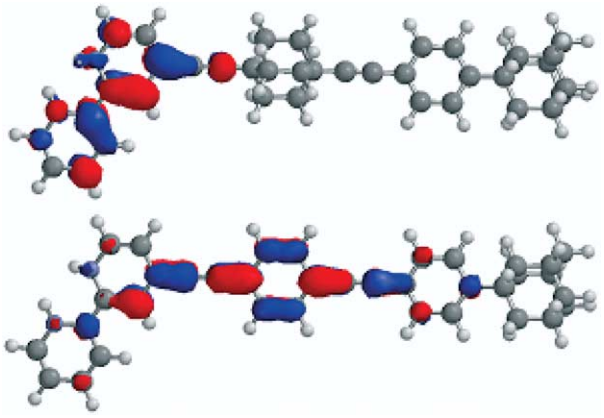


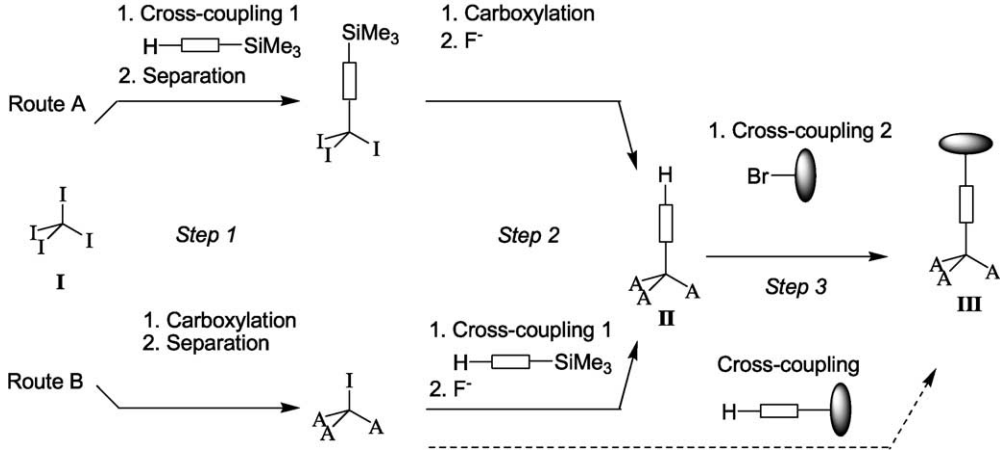
Figure 3. LUMO of a bpy-E-Bco-E-Ph bridge (top) and of a bpy-E-Ph-E-Ph bridge (bottom) connected to the adamantane core of the tripod (Spartan '02, Wavefunction, Inc.).

In Route A the rigid-rod bridge is introduced via cross-coupling in step 1 and the three remaining iodine groups are converted into anchoring groups via metal–halogen exchange and carboxylation in step 2. This order is reversed in route B. A potentially useful aspect of this reversal is that steps 2 and 3 can be combined by performing the cross-coupling with an ethynyl bridge carrying the chromophore (Scheme 1, dashed arrow).[20] Also, since the tricarboxylation is performed first, the bridge (with or without the chromophore) can be attached in a non-statistical cross-coupling to form **II**, thereby minimizing the loss of the valuable rigid-rod bridge. Results obtained with the two approaches are discussed below.

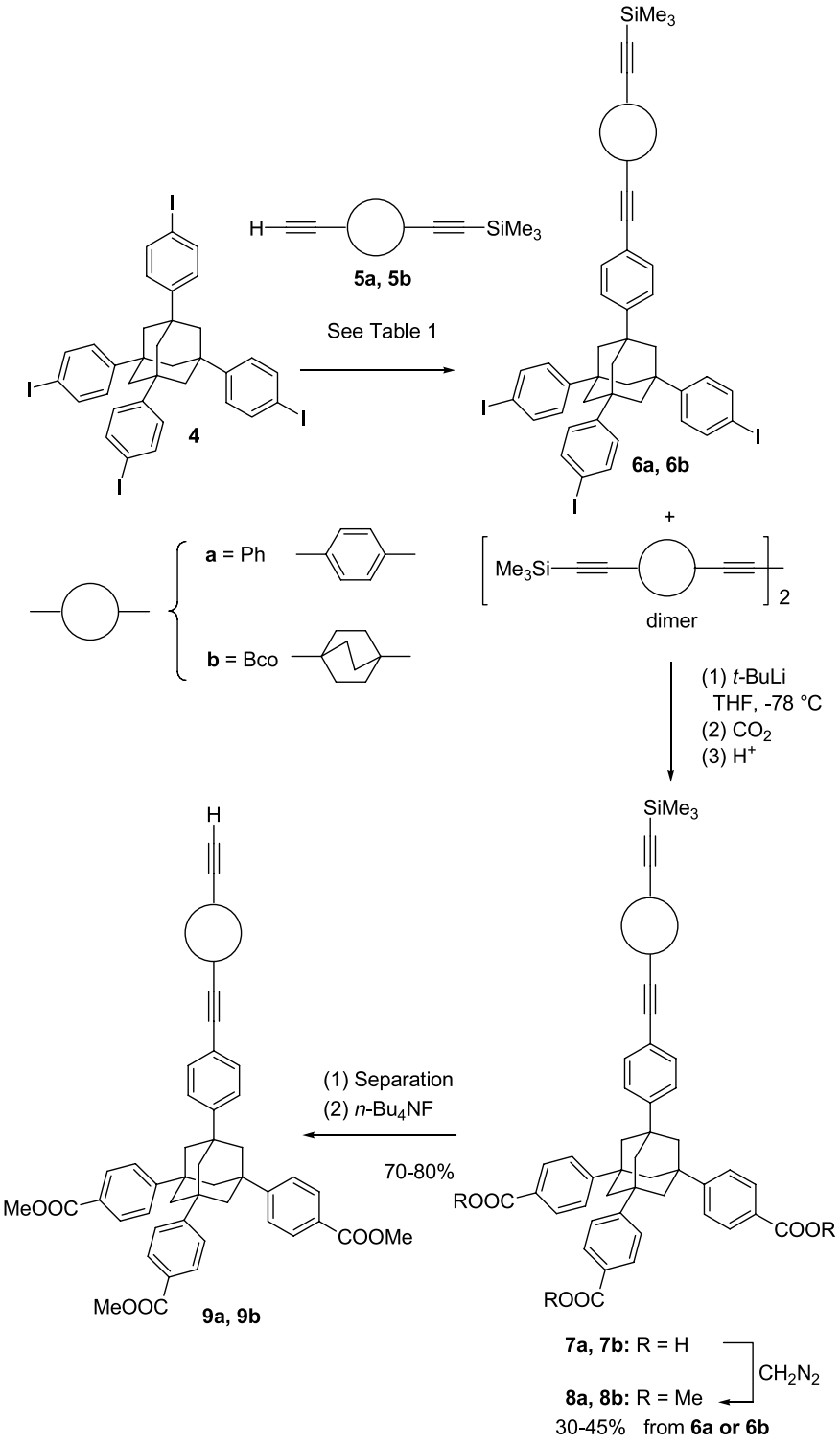
Route A (Schemes 2 and 3) follows the same sequence reported to prepare shorter tripods,[2c] but the use of longer bridges required different conditions in the first and last steps of the synthesis. In general, we observed that cross-coupling reactions proceeded in lower yields or were more sluggish as the size of the tripodal linker or of the bridge increased.

In the first step, 1,3,5,7-tetrakis(4-iodophenyl)-adamantane[21] (**4**) was reacted with 1-ethynyl-4-trimethylsilyl-ethynyl-benzene (**5a**)[5b] or 1-ethynyl-4-trimethyl-silylethynyl-bicyclo[2.2.2]octane (**5b**),[22] to afford monosubstituted **6a** or **6b**, respectively, in a Sonogashira cross-coupling reaction (Scheme 2).[23,24] Both mono-deprotected alkynes **5a** and **5b** were prepared from the corresponding 1,4-bis(trimethylsilyl)ethynes, using 1 equiv. of MeLi·LiBr complex as the nucleophile.[5b,25] The reaction was performed at −78 °C for **5a** and at rt for **5b**. In both cases the crude material was a 1:1 mixture (GC/MS) of the monodeprotected compound and the starting material, with only traces of dialkyne. After this mixture was employed in the cross-coupling step, the unreacted 1,4-bis(trimethyl-silyl)ethyne was easily isolated in pure form and used again. The Sonogashira conditions that we had used previously[2d] ($Pd(PPh_3)_2Cl_2$/CuI/*i*-Pr_2NH) resulted in almost complete dimerization of **5a** or **5b**. Dimerization of the alkyne, a common side reaction in Sonogashira reactions, is not a problem when the alkyne is added in large excess. In this case, **5a** and **5b** are added in equimolar amount to **4**, and **5b** is not expendable because it is prepared via a multistep synthesis.[20,21] Our experience with the synthesis of rigid-rod sensitizers prepared from **5a** and methyl 5-bromo-1,3-benzenedicarboxylate[5b] indicated that the use of $Pd(dba)_2$/CuI/PPh_3 under argon minimizes the dimerization of **5a**. By employing these conditions we were able to prepare **6a** and **6b** in 28–36% yields and to inhibit the dimerization (Table 1, entries 2 and 5).

For the synthesis of **6b**, we also used the cross-coupling procedure reported by Albinsson and coworkers (Table 1, entry 4),[18] but in our case the purification of the product was not practical. Although **4** and alkyne **5a** or **5b** were reacted in equimolar ratio, the step is statistical and di- and tri-substituted products and unreacted **4** were recovered together with monosubstituted **6a** or **6b**. The mono-substituted products **6a** and **6b** were both isolated in this step for characterization purposes. For preparative purposes, however, it is easier to remove unreacted **4** from the crude material and use this purified mixture in the following step. The di- and tri- substituted products are useful inter-mediates, and we are pursuing their conversion into di- and tri-chromophoric antennas. Metal–halogen exchange with *t*-BuLi followed by quenching with CO_2 and acidification afforded the acids **7a** (or **7b**), which are insoluble materials. Treatment with diazomethane and purification of the more soluble esters by column chromatography (or separation if the carboxylation is performed on the statistical mixture



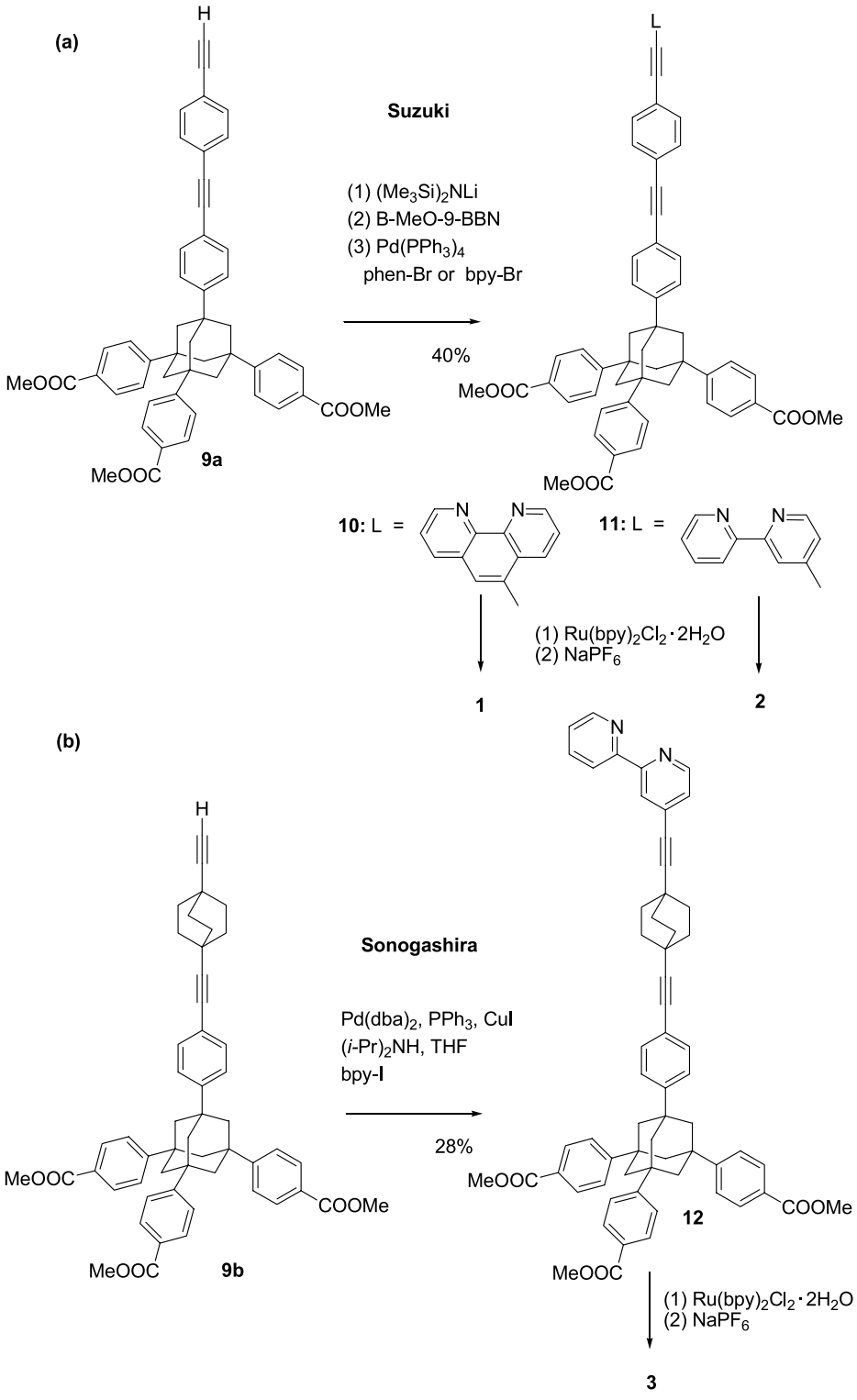
Scheme 1.



Scheme 2.

from the first step) afforded tricarboxylic esters **8a** or **8b**. The TMS-alkyne was deprotected using *n*-Bu_4NF to form alkyne **9a** or **9b**. The yield from **6a** or **6b** is 30–45%. ^1H NMR spectra showed a significant upfield shift of the alkyne proton in **9b** (δ_H (C≡C*H*)=2.10 ppm) compared to **9a** (δ_H (C≡C*H*)=3.17 ppm) suggesting that the terminal alkyne on the Bco unit is less acidic. This observation may account for the significantly lower reactivity of **9b**, and the need for two different cross-coupling procedures in the last step (Scheme 3a).

A Suzuki-type reaction[26] was employed to react **9a** with 4-bromo-2,2′-bipyridine[27] or 5-bromo-1,10-phenanthroline[28] to afford **11** and **10**, respectively. This procedure involves deprotonation of the alkyne, treatment with B-methoxy-9-BBN and then cross-coupling of the resulting



Scheme 3.

ethynylboronate with the aryl halide in the presence of Pd(0) catalyst. The Sonogashira reaction was avoided, because the presence of Cu(I) leads to the dimerization of **9a**. The non-conjugated ethyne **9b**, however, did not react in Suzuki conditions. The cross-coupling of **9b** required Sonogashira conditions and the more reactive 4-iodo-2,2′-bipyridine[29] (Scheme 3b). Tripodal linker **12** could be obtained only in this way, albeit only in 28% yields and with substantial dimerization of **9b**. Finally, the tripodal Ru(II) complexes **1**, **2** and **3** were prepared from the phen- or bpy-substituted tripodal linkers **10**, **11** and **12**, respectively.

Given our interest in tripodal sensitizers, we tested a potentially shorter route in which the anchoring groups are introduced first (Scheme 1, Route B). Carboxylation of **4** afforded a mixture of mono-, di- and tri-substituted esters.

Table 1. Reaction conditions for the cross-coupling reaction of **4** with alkyne **5a** or **5b**[a]

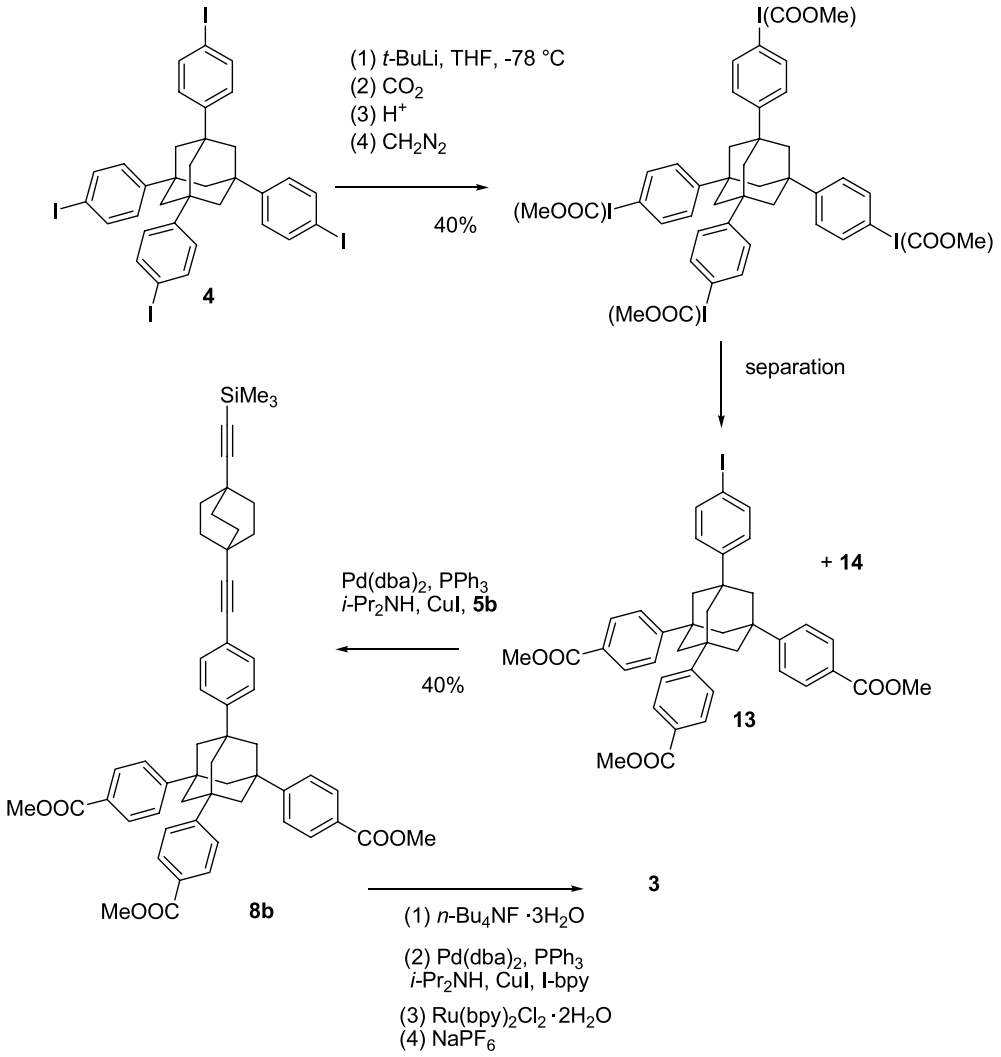
Entry	Alkyne[b]	Amine	Catalysts	Solvent	Product yield (%)	Dimer of **5a** or **5b** yield (%)
1	**5a**	Et_3N[c]	$Pd(dba)_2$, PPh_3, CuI	Benzene/THF	**6a** 30	15
2	**5a**	*i*-Pr_2NH[c]	$Pd(dba)_2$, PPh_3, CuI	Benzene/THF	**6a** 36	10
3	**5a**	*i*-Pr_2NEt[c]	$Pd(dba)_2$, PPh_3, CuI	Benzene/THF	**6a** Traces	34
4	**5b**	Piperidine[d]	$Pd(PPh_3)_4$	Piperidine[d]	**6b** 23[e]	25
5	**5b**	*i*-Pr_2NH[c]	$Pd(dba)_2$, PPh_3, CuI	THF	**6b** 28	20

[a] All reactions were performed at room temperature.
[b] The alkyne was added in 1–1.2 equiv. Any increase leads to more dimer.
[c] The amine was added in 20% excess with respect to **4**.
[d] The amine was used as the solvent.
[e] Piperidine was distilled in vacuo from the crude material.

Separation of this statistical mixture afforded **13**, which has one iodine available for the cross-coupling and three COOMe anchoring groups, in 15–20% yield from **4** (Scheme 4).

Although we could not separate compound **13** from an impurity, **14**, (See Supplementary data),[30] this crude material was used in the cross-coupling step with **5b** and unreacted **14** was separated from the product afterwards. Monosubstituted **9b** was thus obtained in ~40% yield from **13**. The tripodal sensitizer **3** was prepared from **9b** using the same procedures shown in Scheme 2.

In conclusion, Route B yielded **3** in the same overall yield as Route A (~6% for route A and ~6–8% for route B). The main advantage is that the cross-coupling step proceeds in higher yields (40%) and without wasting the precious bridge in a statistical reaction. We are currently improving this route and the use of a chromophore-substituted alkyne, as suggested in Scheme 1 (dashed line), is being explored.



Scheme 4.

Table 2. Absorption and fluorescence data for CH_3CN solutions of **1–3** and reference complexes

Entry	Sensitizer	λ_{abs} (nm) (ε, $M^{-1}\,cm^{-1}$)	[a]λ_F (nm)	τ (μs)	$\phi_F \times 10^{-2}$
1	**1**	449 (2.3×10^4)	606	1.4	10
2	**2**	463 (2.8×10^4)	638	2.2	12
3	**3**	456 (1.6×10^4)	624	1.6	14
4	[b]$Ru(bpy)_2(phen)^{2+}$	450	620		
5	[b]$Ru(bpy)_3^{2+}$	452	626	0.8[b]	

[a] The solutions were de-oxygenated by freeze-pump-thaw. $\lambda_{ex}=450$ nm.
[b] From Ref. 2b, in acetonitrile.

3. Solution photophysical properties of 1–3

The solution absorption and fluorescence data of tripodal sensitizers **1–3** are reported in Table 2, together with two reference complexes. A comparison of the absorption spectra between the bpy-based tripodal complexes **2** and **3**, shown in Figure 4, clearly shows an effect due to differences in the bridge structure.

The visible absorption spectra of **2** and **3** both displayed the broad band typical of the MLCT excited state at ~450 nm, while the $\pi \rightarrow \pi^*$ ligand-centered band at ~350 nm is present only in the spectrum of the bpy-tripod with the conjugated bridge (**2**) (Figure 4). The MLCT band for **2** was centered at 463 nm and red-shifted with respect to the same band in the spectrum of the bpy-tripod with the non-conjugated bridge (**3**) and of the reference $Ru(bpy)_3$. This shift was observed in the rt fluorescence spectra (Table 2). Specifically, the fluorescence spectrum of the bpy-based tripod with the conjugated bridge **2** was about 14 nm red-shifted with respect to the spectrum of the corresponding tripod with the Bco unit in the bridge, **3**, and of the reference $Ru(bpy)_3^{2+}$ (Table 2, entries 2, 3 and 5).

4. Summary

We have described the synthesis of three long (d=24 Å) tripodal Ru-polypyridyl sensitizers (**1–3**) via two synthetic routes. Although the overall yields from both routes are low, the compounds are of interest to study the effect of the bridging unit in electron transfer studies at nanoparticle interfaces, and the 'reversal' route B tested here may prove more useful that the method reported before. The bridge carrying the chromophore is conjugated in phen-based **1** and bpy-based **2**, and carries a bicyclo[2.2.2]octylene unit in bpy-based **3**. The photophysical study of **1**/TiO_2[2a] and **2**/TiO_2[2a], and the shorter tripods[2b–d] had suggested that the conjugated bridges influence the interfacial kinetic processes, and the models described here will allow to fully test this hypothesis.

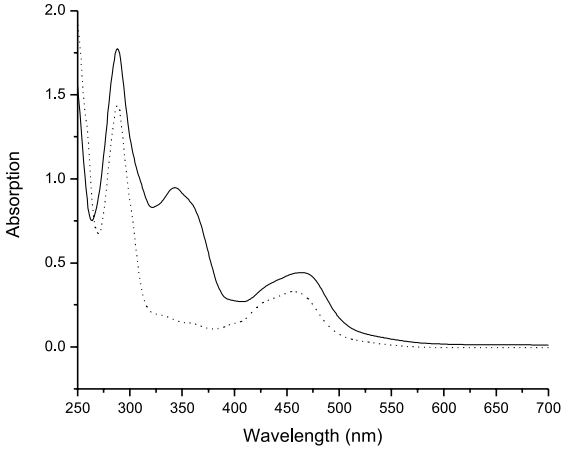


Figure 4. Absorption spectra of acetonitrile solutions of $Ru(bpy)_2(AdTripod\text{-}(Ph\text{-}E)_2\text{-}bpy)^{2+}$ **2** (—) and $Ru(bpy)_2(AdTripod\text{-}Ph\text{-}E\text{-}Bco\text{-}E\text{-}bpy)^{2+}$ **3** (- - -).

5. Experimental

5.1. General experimental methods

Instrumentation. ^1H (499.90 MHz) and ^{13}C (124.98 MHz) NMR spectra were obtained on a Varian INOVA 500 spectrometer and recorded in $CDCl_3$ unless otherwise noted. The ^1H spectra were referenced to Me_4Si, or to residual $CHCl_3$ (7.27 ppm) for the compounds containing the TMS group. The ^{13}C spectra were referenced to the central line of the solvent. Chemical shifts (δ) are given in parts per million (ppm) and reported to a precision of ± 0.01 ppm. Proton coupling constants (J) are given in Hz and reported to a precision of ± 0.1 Hz. High-resolution mass spectra (FAB-MS) and elemental analyses were obtained from commercial facilities. UV–vis absorbance data were collected on a VARIAN Cary-500 spectrophotometer, and photoluminescence (PL) measurements were performed on a VARIAN Cary-Eclipse Fluorescence Spectrophotometer. Measurements were run in CH_3CN in 1 cm quartz cuvettes. The solvent for the fluorescence spectra was de-oxygenated by three cycles of freeze-pump-thaw or by bubbling solvent-saturated nitrogen. The solutions were 0.005 mM (**2**) and 0.015 mM (**3**) in acetonitrile for the fluorescence spectra and 0.02 mM (**2** and **3**) for the absorption spectra. IR spectra were performed on a Mattson Research Series 1 FT-IR (KBr).

Materials and general procedures. All reactions were performed under nitrogen or argon atmosphere with glassware oven-dried and then flamed in vacuo unless otherwise specified. Column chromatography was performed using silica gel (40 μm average particle size). Thin layer chromatography (TLC) was performed using silica gel plates with fluorescent indicator and UV light as detection method. Phosphomolybdic 10% ethanolic solution and heat or iodine vapors were used as developing agents for compounds that do not absorb in the UV–vis (for instance **5b**). 'Standard workup' in the synthetic procedures refers to the following sequence: (a) the aqueous layer is extracted with the indicated solvent three times; (b) the organic layers are collected and dried over Na_2SO_4 anhyd; (c) the solvent is evaporated in vacuo on a rotary evaporator. Monoglyme

(1,2-dimethoxyethane) was distilled over sodium/benzophenone ketyl. THF (purchased anhydrous grade) was distilled over sodium/benzophenone ketyl. Benzene was distilled over sodium/benzophenone ketyl, CH_2Cl_2 was distilled over CaH_2, CBr_4 was recrystallized from ethanol and PPh_3 from hexane. We observed improved yields when we used CO_2(g) from a lecture bottle rather than generated from dry ice. Pd(0) catalysts were stored and handled in a glove box. The following solution reagents were purchased from Acros or Aldrich and were not titrated prior to use: *t*-BuLi (1.5 M solution in pentane), MeLi·LiBr complex (2.2 M solution in diethyl ether), Lithium bis(trimethylsilyl)amide (1.0 M solution in hexane), 9-methoxy-9-borobicyclo[3.3.3]nonane (B-methoxy-9-BBN, 1.0 M solution in hexane), *n*-BuLi (1.6 M solution in hexane). 4-Bromo-2,2′-bipyridine,[27] 5-bromo-1,10-phenanthroline,[28] 4-iodo-2,2′-bipyridine,[29] 1,3,5,7-tetrakis(4-iodophenyl)adamantane **4**,[21] **5a**[5b] and **5b**[22] were synthesized following literature procedures. *CAUTION*. To avoid explosion, diazomethane was prepared using exclusively glassware with smooth joints (Aldrich) from Diazald (Aldrich), MeOH, and KOH aq. following described procedures.[31]

5.2. Synthesis of tripodal sensitizers 1–3

5.2.1. 1,3,5-(4-Iodophenyl)-7-[4-(1-trimethylsilylethynyl-4-ethynyl-phenyl)phenyl]-adamantane (6a). A 1:1 mixture (GC/MS) of **5a**[5b] and 1,4-bis(trimethylsilylethynyl)-benzene (300 mg of mixture, 0.64 mmol of **5a**) was added to a solution of **4**[21] (515 mg, 0.54 mmol) in *i*-Pr_2NH (0.12 mL), benzene (25 mL) and THF (25 mL) at rt, followed by $Pd(dba)_2$ (18 mg, 0.027 mmol), PPh_3 (28 mg, 0.108 mmol), and CuI (10 mg, 0.054 mmol). The mixture was stirred at rt under nitrogen for 24 h and filtered. TLC ($CHCl_3$/hexane, 10/90) showed 5 spots corresponding to: 1,4-bis(trimethylsilylethynyl)-benzene (R_f=0.95), the dimer from **5a** (R_f=0.6), **4** (R_f=0.4), **6a** (R_f=0.26), di-substituted product (R_f=0.17). The mixture was separated by column chromatography ($CHCl_3$/hexane, 1/9) to afford **6a** (207 mg, 36%). Mp 194–196 °C. ^{1}H NMR δ_H: 7.68 (d, 6H, *J*=9.0 Hz, PhI), 7.51 (d, 2H, *J*=8.5 Hz), 7.44 (two s, 4H), 7.43 (d, 2H, *J*=8.5 Hz), 7.21 (d, 6H, *J*=9.0 Hz, PhI), 2.09 and 2.07 (two s, 12H, C*H*$_2$(Ad)), 0.25 (s, 9H, $SiMe_3$). ^{13}C NMR δ_C: 149.1, 148.4, 137.5, 131.9, 131.7, 131.3, 127.1, 125.0, 123.3, 122.8, 121.0, 104.6 (C≡C), 96.3 (C≡C), 91.7 (I-*C*), 91.1 (–C≡C–), 89.0 (–C≡C–), 46.7 (*C*H_2(Ad)), 39.2 and 39.0 (*C*(Ad)), −0.1 ($SiMe_3$). Anal. calcd for $C_{47}H_{41}I_3Si$: C, 55.64; H, 4.07. Found: C, 55.33; H, 4.29.

5.2.2. 1,3,5-(4-Iodophenyl)-7-[4-(1-trimethylsilylethynyl-4-ethynyl-[2.2.2]bicyclooctyl)phenyl]-adamantane (6b). A 1:1 mixture (GC/MS) of 1,4-bis(trimethylsilylethynyl)-bicyclo[2.2.2]octane and 1-ethynyl-4-trimethylsilylethynyl-bicyclo[2.2.2]octane (**5b**) (342 mg, ~0.58 mmol of **5b**) was added to a solution of **4** (535 mg, 0.57 mmol) in *i*-Pr_2NH (0.12 mL) and THF (80 mL) at rt, followed by $Pd(dba)_2$ (18 mg, 0.028 mmol), PPh_3 (28 mg, 0.108 mmol), CuI (10 mg, 0.054 mmol). The mixture was stirred at rt for 24 h and filtered. GC/MS shows the formation of dimer from **5b**. TLC ($CHCl_3$/hexane, 1/9) showed three spots: two were assigned to **4** (R_f=0.35) and **6b** (R_f=0.18). The mixture was separated by column chromatography ($CHCl_3$/hexane, 1/9) to afford **6b** (170 mg, 28%). ^{1}H NMR δ_H: 7.68 (d, 6H, *J*=8.5 Hz, PhI), 7.33 (s, 4H), 7.2 (d, 6H, *J*=8.5 Hz, PhI), 2.06 (s, 12H, C*H*$_2$ (Ad)), 1.83 (d, 12H, *J*=7.5 Hz, C*H*$_2$ (Bco)), 0.13 (s, 9H, $SiMe_3$). ^{13}C NMR δ_C: 148.7, 148.2, 137.7, 131.8, 127.4, 124.9, 122.1, 114.1 (C≡C), 96.7 (C≡C), 91.9 (I-*C*), 83.9 (C≡C), 80.5 (C≡C), 46.9 (*C*H_2(Ad)), 39.3 (*C*(Ad)), 32.0 (*C*H_2(Bco)), 27.1 and 26.9 (*C*(Bco)), 0.5 ($SiMe_3$). IR (cm^{-1}): 3032 (*ν*C–H(Ar)), 2942 and 2863 (*ν*C–H(aliph.)), 2155 (*ν*C≡C), 1509, 1485, 1454, 1393, 1356, 1247, 1002, 790.

5.2.3. 1,3,5-(4-Carboxyphenyl)-7-[4-(1-trimethylsilylethynyl-4-ethynyl-phenyl)phenyl]-adamantane (7a). To a solution of **6a** (580 mg, 0.57 mmol) in THF (20 mL) cooled to −78 °C was added dropwise over 20 min *t*-BuLi (5.5 mmol, 4.5 mL of a 1.5 M pentane solution). The mixture was stirred for an additional 15 min and CO_2 was bubbled into the reaction mixture. An abundant yellow precipitate formed. The cooling bath was removed, the mixture was allowed to warm to rt, and water (50 mL) and hexane (50 mL) were added. The clear aqueous layer was separated, cooled with a water/ice bath and acidified with ~10% HCl aq. A pale yellow precipitate formed. Standard workup with $CHCl_3$ afforded 0.42 g of a pale yellow powder. The crude material was used in the next step.

5.2.4. 1,3,5-(4-Carboxyphenyl)-7-[4-(1-trimethylsilylethynyl-4-ethynyl-[2.2.2]bicyclooctyl)phenyl]-adamantane (7b). This was prepared using the same procedure using **6b** (416 mg, 0.4 mmol) in THF (20 mL), *t*-BuLi (3.8 mmol, 2.5 mL of a 1.5 M pentane solution). The pale yellow precipitate was collected by filtration to afford 260 mg of crude material that was used in the next step.

5.2.5. 1,3,5-(4-Carbomethoxyphenyl)-7-[4-(1-trimethylsilylethynyl-4-ethynyl-phenyl)phenyl]-adamantane (8a). A solution of the mixture of acids (200 mg) in ethyl ether (10 mL) was treated with CH_2N_2 (see General). The solvent was removed in vacuo and the crude material was purified by column chromatography (AcOEt/hexane, 1/4) to afford 110 mg of **8a** (R_f=0.4) (yield from **6a** ~45%). Mp 196–198 °C. ^{1}H NMR δ_H: 8.04 (d, 6H, *J*=8.5 Hz, *Ph*COOMe), 7.56 (d, 6H, *J*=8.5 Hz, *Ph*COOMe), 7.53 (d, 2H, *J*=8.5 Hz), 7.47 (d, 2H, *J*=8.5 Hz), 7.45 and 7.44 (two s, 4H), 3.91 (s, 9H, COO*Me*), 2.20 (s, 12H, C*H*$_2$), 0.25 (s, 9H, $SiMe_3$). ^{13}C NMR δ_C: 166.9 (*C*OOMe), 153.8, 149.0, 131.9, 131.8, 131.4, 129.8, 128.3, 125.1 (two carbons), 123.3, 122.8, 121.1, 104.6 (C≡C), 96.3 (C≡C), 91.1 (C≡C), 89.0 (C≡C), 52.1 (COO*Me*), 46.6 (*C*H_2(Ad)), 39.6 and 39.3 (*C*(Ad)), −0.1 ($SiMe_3$). IR (cm^{-1}): 3037 (*ν*C–H(Ar)), 2951 and 2898 (*ν*C–H(aliph.)), 2156 (*ν*C≡C), 1931.5, 1724.3 (*ν*C=O), 1608 (*ν*C– C(Ar)), 1512, 1436, 1406, 1358, 1281 (*ν*C–O), 1192, 1110 (*ν*C–O), 1018, 866, 844 (*δ*Ar), 762. Anal. calcd for $C_{53}H_{50}O_6Si$: C, 78.49; H, 6.21. Found: C, 78.32, H, 6.11.

5.2.6. 1,3,5-(4-Carbomethoxyphenyl)-7-[4-(1-trimethylsilylethynyl-4-ethynyl-[2.2.2]bicyclooctyl)phenyl]-adamantane (8b). A solution of the mixture of acids (0.26 g) in ethyl ether (10 mL) was treated with CH_2N_2 (see General). TLC (AcOEt/hexane, 20/80) showed three spots, with **8b**

R_f=0.31. The mixture was purified by silica gel column chromatography (AcOEt/hexane, 1/4) to afford **8b** as a white powder (100 mg, yield from **6b** ~30%). ^{1}H NMR δ_H: 8.05 (d, 6H, J=8.5 Hz, *Ph*COOMe), 7.56 (d, 6H, J=8.5 Hz, *Ph*COOMe), 7.37 (s, 4H), 3.92 (s, 9H, COO*Me*), 2.19 (two s, 12H, CH_2(Ad)), 1.84 (two s, 12H, CH_2(Bco)), 0.14 (s, 9H, $SiMe_3$). ^{13}C NMR δ_C: 167.0 (*C*OOMe), 154.1, 148.1, 131.8, 130.0, 128.4, 125.3, 124.9, 122.2, 114.0 (C≡C), 96.6 (C≡C), 83.9 (C≡C), 80.4 (C≡C), 52.3 (COO*Me*), 46.9 and 46.8 (*C*H_2(Ad)), 39.8 and 39.3 (*C*(Ad)), 31.9 (*C*H_2(Bco)), 27.0 and 26.9 (*C*(Bco)), 0.5 ($SiMe_3$). IR (cm^{-1}): 2945 and 2864 (νC–H(aliph.)), 2162 (νC≡C), 1724 (ν C=O), 1932, 1611 (νC–C(Ar)), 1572, 1509, 1436, 1408, 1357, 1282 (νC–O), 1192, 1110 (νC–O), 1017, 961, 847 (δAr). HMRS (FAB) for $C_{55}H_{59}O_6Si$, MH^+= 843.4076.

5.2.7. 1,3,5-(4-Carbomethoxyphenyl)-7-[4-(1,4-bis-(ethynyl)phenyl)phenyl]-adamantane (9a). nBu$_4$NF·3H$_2$O (540 mg, 1.72 mmol) was added to a solution of **8a** (700 mg, 0.86 mmol) in CH_3CN (20 mL) and benzene (20 mL) at rt with stirring. After 1.5 h, water (20 mL) was added. Standard workup with CH_2Cl_2 and purification by column chromatography (AcOEt/hexane, 1/4) afforded **9a** as a white powder (R_f=0.3) (450 mg, Avg. yield for this step ~75%). Mp 214–216 °C. ^{1}H NMR δ_H: 8.04 (d, 6H, J=9.0 Hz, *Ph*COOMe), 7.56 (d, 6H, J=9.0 Hz, *Ph*COOMe), 7.54 (2H, d, J=8.5 Hz), 7.47 (m, 6H), 3.92 (s, 9H, COO*Me*), 3.17 (s, 1H, C≡C*H*), 2.21 and 2.20 (two s, 12H, CH_2(Ad)). ^{13}C NMR δ_C: 166.9 (*C*OOMe), 153.8, 149.1, 132.1, 131.8, 131.4, 129.8, 128.3, 125.1 (two carbons), 123.7, 121.8, 121.0, 91.2 (C≡C), 88.8 (C≡C), 83.3 (C≡C), 78.9 (C≡C), 52.1 (COO*Me*), 46.6 (*C*H_2(Ad)), 39.6 and 39.3 (*C*(Ad)). IR (cm^{-1}): 3302 (ν ≡C–H), 3037 (νC–H(Ar)), 2950 and 2919 (νC–H(aliph.)), 2849, 2565 (νC≡C), 2216.4 (νC≡C), 1931, 1724 (νC=O), 1611 (νC–C(Ar)), 1514, 1435, 1405, 1282 (νC–O), 1191, 1111 (νC–O), 1018, 837 (δAr), 765.0. Anal. calcd for $C_{50}H_{42}O_6$: C, 81.28; H, 5.73. Found: C, 80.99, H, 5.57.

5.2.8. 1,3,5-(4-Carbomethoxyphenyl)-7-[4-(1,4-bis-(ethynyl)[2.2.2]bicyclooctyl)phenyl]-adamantane (9b). This was prepared following the same procedure using **8b** (81 mg, 0.09 mmol) in CH_3CN (10 mL) and nBu$_4$NF·3H$_2$O (45 mg, 0.3 mmol). Column chromatography (AcOEt/hexane, 1/4) afforded **9b** as a white powder (R_f= 0.25) (53 mg, Avg. yield for this step ~75%). ^{1}H NMR δ_H: 8.04 (d, 6H, J=9.0 Hz, *Ph*COOMe), 7.56 (d, 6H, J=9.0 Hz, *Ph*COOMe), 7.37 (d, 4H, J=2.5 Hz), 3.92 (s, 9H, COO*Me*), 2.19 (two s, 12H, CH_2(Ad)), 2.10 (s, 1H, C≡C*H*), 1.85 (two s, 12H, CH_2(Bco)). ^{13}C NMR δ_C: 167.2 (*C*OOMe), 154.1, 148.2, 131.9, 130.0, 128.5, 125.3, 125.0, 122.2, 96.5 (C≡C), 91.4 (C≡C), 80.6 (C≡C), 68.3 (C≡C), 52.3 (COO*Me*), 46.9 and 46.8 (*C*H_2(Ad)), 39.8 and 39.3 (*C*(Ad)), 31.9 (*C*H_2(Bco)), 26.9 and 26.3 (*C*(Bco)). IR (cm^{-1}): 3302 (ν≡C–H), 3056 (νC–H(Ar)), 2943 and 2865 (νC–H(aliph.)), 2224 (νC≡C), 2107 (νC≡C), 1932, 1724 (νC=O), 1610 (νC–C(Ar)), 1571, 1508, 1438, 1406, 1356, 1282 (νC–O), 1193, 1110 (νC–O), 1018, 967, 898, 853 (δAr), 834 (δAr). HMRS (FAB) for $C_{52}H_{51}O_6$, MH^+=771.3690.

5.2.9. Ad-Tripod-(Ph-E)2-Phen (10). To a solution of **9a** (235 mg, 0.32 mmol) in THF (8 mL) at −78 °C was added lithium bis(trimethylsilyl)amide (0.48 mmol, 0.48 mL of a 1 M hexane solution). After 30 min, B-methoxy-9-BBN (0.48 mmol, 0.48 mL of 1 M hexane) was added. After stirring 2 h at −78 °C, the solution was transferred via cannula to a second flask containing $Pd(PPh_3)_4$ (36 mg, 0.03 mmol) and 5-bromo-1,10-phenanthroline[28] (90 mg, 0.35 mmol) in THF (5 mL). The reaction mixture was refluxed for 24 h, cooled to rt, and standard workup with CH_2Cl_2 afforded a crude material that was purified by column chromatography with the following sequence of eluents: (AcOEt/hexane, 1/4), CH_2Cl_2, (CH_2Cl_2/MeOH, 95/5) to afford **10** as a white powder (140 mg, 47%). Mp 187–189 °C. ^{1}H NMR δ_H: 9.28 (dd, 1H, J=3.0, 1.5 Hz, phen), 9.23 (dd, 1H, J=3.0, 1.5 Hz, phen), 8.86 (dd, 1H, J=8.5, 1.5 Hz, phen), 8.28 (dd, 1H, J=7.5, 1.5 Hz, phen), 8.13 (s, 1H, phen), 8.05 (d, 6H, J=9.0 Hz, *Ph*COOMe), 7.78 (q, 1H, J=4.5 Hz, phen), 7.68 (q, 1H, J=4.5 Hz, phen), 7.66 (d, 2H, J=8.5 Hz), 7.56 (m, 10H), 7.50 (d, 2H, J=8.5 Hz), 3.92 (s, 9H, COO*Me*), 2.21 (s, 12H, CH_2(Ad)). ^{13}C NMR δ_C: 166.88 (*C*OOMe), 153.8, 150.9, 150.6, 149.2, 145.7, 145.5, 136.1, 134.9, 131.8, 131.7 (two carbons), 130.8, 129.8, 128.3 (two carbons), 128.1, 125.1 (two carbons), 123.9, 123.6, 123.5, 122.2, 121.0, 119.8, 95.2 (C≡C), 91.6 (C≡C), 88.9 (C≡C), 87.5 (C≡C), 52.1 (COO*Me*), 46.7 (*C*H_2(Ad)), 39.6 and 39.3 (*C*(Ad)). IR (cm^{-1}): 3035 (νC–H(Ar)), 2946 and 2899 (νC–H(aliph.)), 2842, 2208 (νC≡C), 1930, 1721 (νC=O), 1611 (νC–C(Ar)), 1566, 1511, 1436, 1407, 1282 (νC–O), 1191, 1108 (νC–O), 1019, 835 (δAr), 766. Anal. calcd for $C_{62}H_{48}N_2O_6$: C, 81.20; H, 5.28; N, 3.05. Found: C, 80.62, H, 5.14, N, 2.71.

5.2.10. Ad-Tripod-(Ph-E)$_2$-Bpy (11). Tripodal ligand **11** was prepared using the same procedure using **9a** (150 mg, 0.20 mmol) in THF (5 mL), lithium bis(trimethylsilyl)-amide (0.23 mmol, 0.23 mL of a 1 M hexane solution), B-methoxy-9-BBN (0.23 mmol, 0.23 mL of a 1 M hexane solution), $Pd(PPh_3)_4$ (20 mg, 0.02 mmol), 4-bromo-2,2-bipyridine[27] (89 mg, 0.38 mmol) in THF (5 mL). The crude material was purified by silica gel column chromatography with the following sequence of eluents: (AcOEt/hexane, 1/4), CH_2Cl_2, (CH_2Cl_2/MeOH 95/5) to afford **11** as a white powder (108 mg, 60%). Mp 175–177 °C. ^{1}H NMR δ_H: 8.72 (d, 1H, J=4.5 Hz, bpy), 8.68 (d, 1H, J=5.5 Hz, bpy), 8.55 (s, 1H, bpy), 8.43 (d, 1H, J=8.0 Hz, bpy), 8.05 (d, 6H, J=9.0 Hz, *Ph*COOMe), 7.84 (td, 1H, J=8.0, 2.0 Hz, bpy), 7.57 (m, 12H), 7.49 (d, 2H, J=8.5 Hz), 7.41 (d, 1H, J=5.0 Hz, bpy), 7.35 (t, 1H, J=5.5 Hz, bpy), 3.92 (9H, s, COO*Me*), 2.21 (s, 12H, CH_2(Ad)). ^{13}C NMR δ_C: 166.9 (*C*OOMe), 156.1, 155.4, 153.8, 149.2, 149.2, 149.1, 137.1, 132.3, 131.9, 131.6, 129.8, 128.3, 125.2, 125.1, 125.0, 124.2, 124.1, 123.2, 121.9, 121.2, 121.0, 93.6 (C≡C), 91.6 (C≡C), 88.9 (C≡C), 88.8 (C≡C), 52.1 (COO*Me*), 46.7 (*C*H_2(Ad)), 39.6 and 39.3 (*C*(Ad)). IR (cm^{-1}): 3058 (νC–H(Ar)), 2948, 2897 and 2843 (νC–H(aliph.)), 2207 (νC≡C), 1926, 1722 (νC=O), 1610.0 (νC–C(Ar)), 1582, 1536, 1514, 1459, 1436, 1407, 1282 (νC–O), 1190, 1110 (νC–O), 1018, 836 (δAr), 761.6. Anal. calcd for $C_{60}H_{48}N_2O_6$: C, 80.70; H, 5.42; N, 3.14. Found: C, 79.98, H, 5.43, N, 2.4.

5.2.11. Ad-Tripod-Ph-E-Bco-E-Bpy (12). Terminal alkyne **9b** (260 mg, 0.34 mmol) was added to a solution of 4-iodo-2,2′-bipyridine[29] (115 mg, 0.4 mmol) in i-Pr$_2$NH (0.15 mL)

and THF (40 mL) at rt, followed by $Pd(dba)_2$ (15 mg, 0.02 mmol), PPh_3 (21 mg, 0.08 mmol), CuI (9.5 mg, 0.04 mmol). The mixture was refluxed for 2 days, then cooled to rt and filtered. TLC ($CHCl_3$/MeOH, 98/2) showed three spots: **9b** (R_f=0.45), 4-iodo-2,2′-bipyridine (R_f=0.25) and **12** (R_f=0.15). The crude material was separated by column chromatography with the following sequence of eluents: (AcOEt/hexane, 1/4), $CHCl_3$, ($CHCl_3$/MeOH 98/2) to afford **12** (170 mg, 28%). ^{1}H NMR δ_H: 8.69 (d, 1H, J=4.5 Hz, bpy), 8.58 (d, 1H, J=5.0 Hz, bpy), 8.39 and 8.37 (s, 2H, bpy), 8.04 (d, 6H, J=9.0 Hz, *Ph*COOMe), 7.82 (td, 1H, J=8.0, 2.0 Hz, bpy), 7.56 (d, 6H, J=8.5 Hz, *Ph*COOMe), 7.38 (s, 4H), 7.32 (t, 1H, J=5.5 Hz, bpy), 7.25 (dd, 1H, J=5.0, 1.5 Hz, bpy), 3.92 (s, 9H, COO*Me*), 2.19 (two s, 12H, C*H*$_2$(Ad)), 1.91 (s, 12H, CH_2). ^{13}C NMR δ_C: 167.1 (*C*OOMe), 156.2, 155.9, 154.1, 149.4, 149.2, 148.2, 137.2, 133.3, 131.9, 130.0, 128.5, 125.7, 125.3, 125.0, 124.1, 123.6, 122.2, 121.3, 101.8 (C≡C), 96.4 (C≡C), 80.6 (C≡C), 79.1 (C≡C), 52.3 (COO*Me*), 46.9 and 46.8 (*C*H$_2$(Ad)), 39.8 and 39.3 (*C*(Ad)), 31.9 and 31.8 (*C*H$_2$(Bco)), 27.2 and 27.0 (*C* (Bco)). IR (cm^{-1}): 3060 (νC–H(Ar)), 2946 and 2866 (νC–H(aliph.)), 2226 (νC≡C), 1931, 1724 (νC=O), 1611 (νC–C(Ar)), 1586, 1534, 1509, 1458, 1435, 1409, 1280 (νC–O), 1191, 1112 (νC–O), 1015, 841 (δAr).

5.2.12. Ru(bpy)$_2$(Ad-Tripod-(Ph-E)$_2$-Phen)$^{2+}$ 2PF$_6^-$ (1). A solution of **10** (97 mg, 0.105 mmol) in THF (2 mL) was added to a 1:1 mixture of ethanol/water (10 mL). To the solution, de-oxygenated by bubbling N_2 for ~30 min, was added $Ru(bpy)_2Cl_2\cdot 2H_2O$ (54 mg, 0.105 mmol). The mixture was refluxed for 6 h under nitrogen, cooled to rt and filtered. Addition of $NaPF_6$ to the filtrate formed a red precipitate, which was collected and washed with water several times to afford **1** (130 mg, 80%). ^{1}H NMR δ_H: (CD_3COCD_3): 9.19 (d, 1H, J=8.5 Hz, phen), 8.88 (d, 2H, J=5.0 Hz), 8.84 (t, 3H, J=6.0 Hz), 8.70 (s, 1H, phen), 8.53 (d, 1H, J=4.5 Hz), 8.49 (d, 1H, J=4.5 Hz), 8.27 (m, 2H), 8.18 (m, 4H), 8.03 (d, 6H, J=8.5 Hz, *Ph*COOMe), 7.96 (m, 4H), 7.80 (m, 8H), 7.76 (d, 2H, J=8.5 Hz), 7.66 (m, 4H), 7.61 (d, 2H, J=8.5 Hz), 7.40 (m, 2H), 3.88 (9H, s, COO*Me*), 2.33 and 2.32 (12H, two s, C*H*$_2$(Ad)). ^{13}C NMR δ_C: (CD_3COCD_3): 167.2 (*C*OOMe), 158.4, 158.2, 155.8, 154.2, 153.1, 151.6, 148.8, 148.5, 139.1, 139.0, 137.8, 136.4, 133.1, 132.7, 132.6, 131.6, 130.3, 129.0, 128.8, 128.7, 127.9, 127.8, 126.7, 126.6 (two carbons), 125.4, 125.3, 122.5, 121.3, 98.00 (C≡C), 93.0 (C≡C), 89.2 (C≡C), 86.8 (C≡C), 52.3 (COO*Me*), 47.0 (*C*H$_2$(Ad)), 40.7 and 40.4 (*C*(Ad)). IR (cm^{-1}): 3083 (νC–H(Ar)), 2951 and 2918 (νC–H(aliph.)), 2208 (νC≡C), 1930, 1719 (νC=O), 1609 (νC–C(Ar)), 1515, 1466, 1446, 1434, 1282 (νC–O), 1195, 1111 (νC–O), 1018, 842 (δ(Ar)), 765. Anal. calcd for $C_{82}H_{64}F_{12}N_6O_6P_2Ru$: C, 60.78; H, 3.98; N, 5.19. Found: C, 60.50, H, 3.97, N, 5.03. HRMS (FAB) calcd for $C_{82}H_{64}N_6O_6Ru$ 1330.3931, found 1330.3940.

5.2.13. Ru(bpy)$_2$(Ad-Tripod-(Ph-E)$_2$-Bpy)$^{2+}$ 2PF$_6^-$ (2). Complex **2** was prepared using the same procedure from **11** (70 mg, 0.075 mmol) in THF (2 mL), ethanol/water (10 mL), $Ru(bpy)_2Cl_2\cdot 2H_2O$ (40 mg, 0.075 mmol), $NaPF_6$ to afford 67 mg of **2** (56% yield). ^{1}H NMR δ_H: (CD_3COCD_3): 8.95 (d, 2H, J=9.0 Hz, bpy), 8.84 (d, 4H, J=8.0 Hz, bpy), 8.25–8.18 (m, 6H), 8.12–8.06 (m, 5H), 8.02 (6H, d, J=8.5 Hz, *Ph*COOMe), 7.81 (6H, d, J=8.5 Hz, *Ph*COOMe), 7.74 (2H, d, J=8.5 Hz), 7.65–7.58 (12H, m), 3.87 (9H, s, COO*Me*), 2.31 and 2.30 (two s, 12H, C*H*$_2$(Ad)). ^{13}C NMR δ_C: (CD_3COCD_3): 167.2 (*C*OOMe), 158.6, 158.1, 158.0, 157.9, 157.7, 155.6, 152.9, 152.8, 152.7, 152.6, 151.6, 139.2, 139.1, 139.0, 133.1, 133.0, 132.7, 132.5, 130.3, 129.7, 129.5, 129.4, 129.1, 129.0, 128.8, 126.9, 126.6, 126.5, 125.9, 125.7, 125.4, 121.8, 121.2, 97.9 (C≡C), 93.2 (C≡C), 89.1 (C≡C), 88.2 (C≡C), 52.2 (COO*Me*), 47.0 and 46.9 (*C*H$_2$(Ad)) 40.6 and 40.4 (*C*(Ad)). IR (cm^{-1}): 3081 (νC–H(Ar)), 2920 and 2849 (νC–H(aliph.)), 2208 (νC≡C), 1718 (νC=O), 1610 (νC–C(Ar)), 1570, 1513, 1469, 1439, 1282 (νC–O), 1192, 1113 (νC–O), 841 (δAr), 763. Calcd for $C_{80}H_{64}F_{12}N_6O_6P_2Ru$: C, 60.19; H, 4.04; N, 5.26. Found: C, 60.13, H, 3.97, N, 5.04. HRMS (FAB) calcd for $C_{80}H_{64}N_6O_6Ru$ 1306.3931, found 1306.3910.

5.2.14. Ru(bpy)$_2$(Ad-Tripod-Ph-E-Bco-E-Bpy)$^{2+}$ 2PF$_6^-$ (3). Complex **3** was prepared using the same procedure, but under argon, from **12** (44 mg, 0.047 mmol) in THF (~1 mL), ethanol/water (10 mL), $Ru(bpy)_2Cl_2\cdot 2H_2O$ (25 mg, 0.048 mmol) and $NaPF_6$ to afford 53 mg of **3** (70% yield). The precipitate was very fine and tended to form a suspension. ^{1}H NMR δ_H: (CD_3COCD_3): 8.90 (d, 1H, J=8.5 Hz, bpy), 8.83 (m, 4H, bpy), 8.74 (d, 1H, J=1.0 Hz, bpy), 8.24 (m, 5H, bpy), 8.17 (d, 1H, J=5.5 Hz, bpy), 8.07 (m, 10H), 7.79 (d, 6H, J=8.5 Hz, *Ph*COOMe), 7.61 (m, 7H), 7.44 (dd, 1H, J=6.0, 1.5 Hz, bpy), 7.36 (d, 2H, J=8.5 Hz), 3.87 (s, 9H, COO*Me*), 2.30 (two s, 12H, C*H*$_2$(Ad)), 1.93 (s, 12H, C*H*$_2$(Bco)). ^{13}C NMR (CD_3COCD_3) δ_C: 184.3, 167.2 (*C*OOMe), 158.4, 158.2, 158.1, 158.0, 157.8, 155.8, 152.9, 153.0, 152.8, 152.7, 139.1, 139.0, 134.2, 132.3, 130.4, 130.1, 129.1, 129.0, 128.8, 127.1, 126.5, 126.3, 125.7, 125.4, 122.5, 107.1 (C≡C), 96.4 (C≡C), 81.6 (C≡C), 78.7 (C≡C), 52.3 (COO*Me*), 47.2 and 47.0 (*C*H$_2$(Ad)), 40.7 and 40.3 (*C*(Ad)), 32.3 and 32.1 (*C*H$_2$(Bco)), 28.2 and 27.6 (*C*(Bco)). IR (cm^{-1}): 3083 (νC–H(Ar)), 2926, 2852 (νC–H(aliph.)), 2225 (νC≡C), 1924, 1718 (νC=O), 1610 (νC–C(Ar)), 1568, 1508, 1464, 1442, 1410, 1362, 1281 (νC–O), 1194, 1112 (νC–O), 1017, 842 (δAr). HRMS (FAB) calcd for $C_{82}H_{72}O_6N_6F_6PRu$ 1483.4199, found 1483.4216.

5.2.15. Synthesis of 8b via Route B (Scheme 4). To a solution of **4**[21] (470 mg, 0.5 mmol) in THF (20 mL) cooled to −78 °C, *n*-BuLi (2 mmol, 1.3 mL of a 1.5 M pentane solution) was added dropwise over 20 min with stirring. The mixture was stirred for additional 20 min and CO_2 was bubbled into the reaction mixture from a flask containing solid CO_2. An abundant yellow precipitate formed. The cooling bath was removed, the mixture was allowed to warm to rt, and water (50 mL) and hexane (50 mL) were added. The aqueous layer was separated, cooled with water/ice bath and acidified by addition of diluted HCl. A pale yellow precipitate formed. This was collected by filtration to afford 360 mg of crude material. This was dissolved in ethyl ether (10 mL), treated with CH_2N_2 (see General) and stirred for 2 h. TLC (AcOEt/hexane, 1/4) showed four spots: R_f=0.77, 0.63, 0.47 and 0.32 corresponding to mono-, di-, tri- and tetra-ester, respectively. The mixture of methyl esters was purified by column chromatography (AcOEt/hexane, 1/4) to afford 70 mg of **13** and **14** in ratio 1.5:1 (^{1}H NMR)

(yield of **13** ~15–20%). The mixture could not be separated by column chromatography or other methods, because both compounds had an identical R_f factor in a variety of eluents, and have identical solubility properties in a variety of solvents. ^{1}H NMR of **13** and **14** δ_H: ($CDCl_3$): 8.04 (d, 6H, J=9.0 Hz, *Ph*COOMe), 7.70 (d, J=9.0 Hz, PhI), 7.57 (s), 7.56 (d, 6H, J=9.0 Hz, *Ph*COOMe), 7.51 (d, J=7.0 Hz), 7.41 (t, J=7.5 Hz), 7.25 (d, J=8.0 Hz, PhI), 3.92 (s, 9H, COO*Me*), 2.19 (two s, 12H, CH_2(Ad)). ^{13}C NMR δ_C: ($CDCl_3$): 167.1 (*C*OOMe), 154.2, 153.9, 148.8, 148.5, 137.8, 130.0, 128.8, 128.5, 128.4, 127.4, 125.3, 125.1, 92.0, 52.3 (COO*Me*), 47.0; 46.9; 46.8 and 46.7 (CH_2(Ad)), 39.8; 39.7 and 39.3 (*C*(Ad)).

A 1:1 mixture (GC/MS) of **5b** (295 mg, ~0.56 mmol of **5b**) was added to a solution of mixture **13** and **14** (410 mg, ~0.56 mmol of **13**) in *i*-Pr_2NH (0.15 mL) and THF (30 mL) at rt, followed by $Pd(dba)_2$ (18.5 mg, 0.028 mmol), PPh_3 (29 mg, 0.11 mmol), and CuI (10 mg, 0.054 mmol). The mixture was stirred at rt for 24 h and filtered. GC/MS of the filtrate shows the formation of dimer from **5b**. TLC ($CHCl_3$/hexane, 1/9) showed two spots: **8b**, R_f=0.48 and **14**, R_f=0.45. The mixture was separated by column chromatography ($CHCl_3$/hexane, 1/9) to afford **8b** (110 mg, 40%). The spectral data were identical to those obtained for **8b** prepared though route A.

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Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.tet.2004.06.124

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