

HETEROCYCLES, Vol. 94, No. 11, 2017, pp. 2132 - 2140. © 2017 The Japan Institute of Heterocyclic Chemistry
 Received, 11th September, 2017, Accepted, 27th September, 2017, Published online, 6th October, 2017
 DOI: 10.3987/COM-17-13812

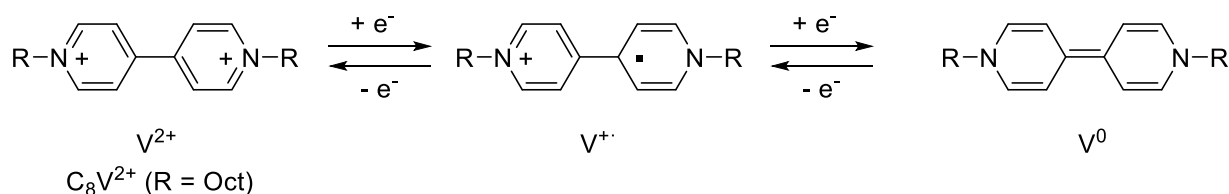
SYNTHESIS OF DENDRIMER-TYPE VILOGEN AND ITS USE IN Pd-MEDIATED HOMOCOUPLING OF ARYL HALIDES

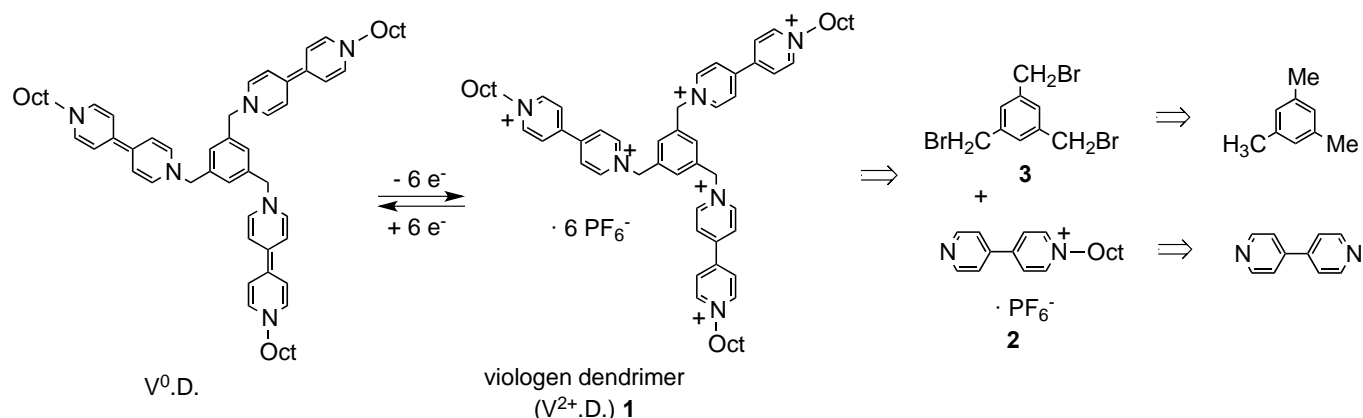
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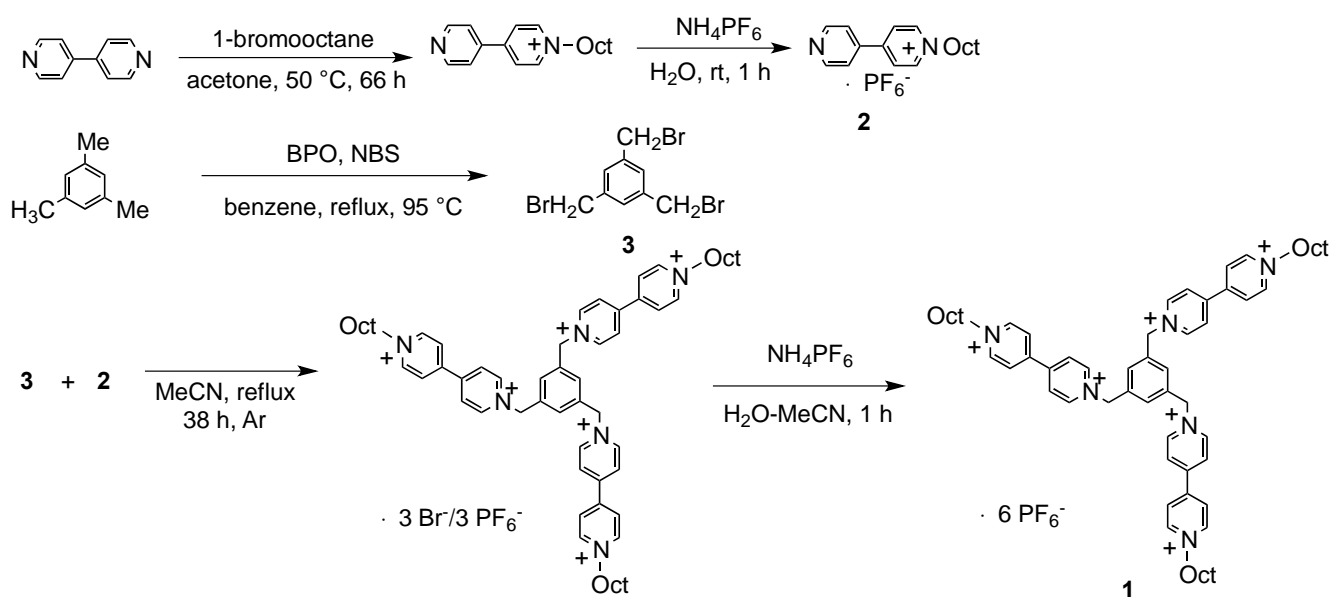
Abstract – Dendrimer-type viologen (V^{2+} .D.) was prepared from mesitylene and 4,4'-bipyridyl. Electroreduction of V^{2+} .D. gave the corresponding quinoid (V^0 .D.), which promoted Pd-catalyzed homocoupling of aryl bromides Ar-Br to give the corresponding biaryls Ar-Ar in moderate to good yields.

Viologens (V^{2+}), 1,1'-dialkyl-4,4'-bipyridinium salts, are stable precursors of organic reductant.¹ V^{2+} is easily obtained by alkylation of 4,4'-bipyridine. Reduction of V^{2+} gives the corresponding radical cation (V^+) and quinoid (V^0): Chemical reductants such as zinc and $\text{Na}_2\text{S}_2\text{O}_4$ give V^+ , which reduces some redox enzymes such as nitrogenase² and alcohol dehydrogenase.³ On the other hand, electro-reduction of V^{2+} can generate V^0 . One-electron reduction of octyl viologen (C_8V^{2+}) occurs at -0.74 V ($\text{C}_8\text{V}^+/\text{C}_8\text{V}^{2+}$) and -1.15 V ($\text{C}_8\text{V}^0/\text{C}_8\text{V}^+$), respectively, in DMF vs Ag/Ag^+ . Redox potential of the $\text{C}_8\text{V}^0/\text{C}_8\text{V}^+$ couple indicates that C_8V^0 works as an alternative reductant of zinc (Zn/Zn^{2+} : -0.97 V vs. Ag/Ag^+). Indeed, C_8V^0 reduces Pd(II) reagents to Pd(0) species, which promote reductive homocoupling of aryl bromides Ar-Br to give the corresponding biaryls Ar-Ar.⁴ Though redox $\text{C}_8\text{V}^+/\text{C}_8\text{V}^{2+}$ and $\text{C}_8\text{V}^0/\text{C}_8\text{V}^+$ are reversible under cyclic voltammetry conditions, irreversible dimerization of C_8V^+ often occurs in bulk⁵ and recycle use of C_8V^{2+} is difficult. To avoid the coupling of V^+ , we synthesized dendrimer-type viologen (V^{2+} .D.)⁶ and found that 1) electro-reduction of V^{2+} .D. gave the corresponding quinoid V^0 .D., and 2) the V^0 .D. promoted the Pd-catalyzed homocoupling of aryl halides to afford biaryl Ar-Ar.





Viologen dendrimer (V²⁺.D., **1**) was prepared by alkylation of 1-octylbipyridinium hexafluorophosphate (**2**) with 1,3,5-tris(bromomethyl)benzene (**3**). 1-Octylbipyridinium hexafluorophosphate (**2**) was synthesized as follows: Alkylation of 4,4'-bipyridyl with 1-bromooctane gave a mixture of 1,1'-dioctyl-4,4'-bipyridinium dibromide and 1-octylbipyridinium bromide, which were easily separated by filtration. Ion exchange of the latter with [NH₄⁺][PF₆⁻] afforded **2**. 1,3,5-Tris(bromomethyl)benzene (**3**) was obtained by radical bromination of mesitylene using NBS/cat. benzoyl peroxide. Coupling of **2** and **3**, followed by ion exchange with [NH₄⁺][PF₆⁻] gave 1,1',1''-[benzene-1,3,5-triyltris(methylene)]tris[(octyl)-4-pyridin-4-ylpyridinium] hexafluorophosphate [V²⁺.D.] (**1**, 84% yield) as colorless solids.



Electrochemical behavior of **1** was investigated by means of cyclic voltammetry (CV) in DMF (Figure 1). In CV of **1**, two reversible redox waves were observed at $E_{1/2} = -0.76$ V ($V^{2+}.D./V^{+}.D.$) and -1.19 V ($V^{+}.D./V^0.D.$) (vs. Ag/AgCl), which were almost the same as those of C_8V^{2+}/C_8V^{+} and C_8V^{+}/C_8V^0 . As only one relatively sharp redox wave was observed at each potential, it was considered that three viologen units were reduced at the same time.

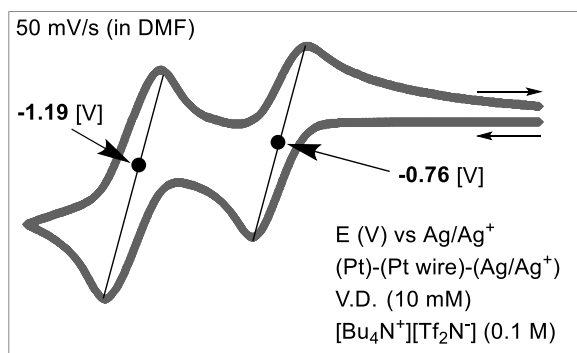
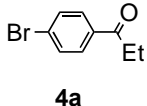
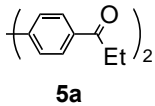


Figure 1. Cyclic Voltammetry of **1**

Pd/**1**-Promoted homocoupling reaction of aryl bromides Ar-Br **4** proceeded smoothly to give the corresponding biaryl Ar-Ar **5**. Typical procedure is as follows (Table 1, Entry 1): In an undivided cell equipped with a Zn sacrificial anode (1.5×1.0 cm²) and a Pt cathode (1.5×1.0 cm²) was placed a DMF (3 mL) solution of 4-bromopropiophenone (**4a**, 0.25 mmol), **1** (0.078 mmol), $[Bu_4N^+][Tf_2N^-]$ (0.30 mmol), and a catalytic amount of $PdCl_2(PPh_3)_2$ (0.012 mmol). The solution was electrolyzed under constant current conditions (10 mA) at 60 °C until 2 F/mol-**4a** of electricity was passed. Usual work-up and purification by silica-gel column chromatography gave 4,4'-dipropanoylbiphenyl (**5a**, 89% yield).

Table 1. Optimization of Pd cat. and Electrodes

		$V^{2+}.D.$ (0.075 mmol) $[Bu_4N^+][Tf_2N^-]$ (0.3 mmol) $PdCl_2(PPh_3)_2$ (0.012 mmol) (Zn)-(Pt), Undiv. Cell DMF (3 mL), 10 mA, 2 F/mol- 4a , 60 °C									
		 4a				 5a					
Entry	Pd cat	Anode	Cathode	5a ^a	4a ^a	Entry	Pd cat	Anode	Cathode	5a ^a	4a ^a
1	$PdCl_2(PPh_3)_2$	Zn	Pt	89	n.d. ^b	5	$PdCl_2(PPh_3)_2$	Mg	Pt	n.d. ^b	n.d. ^b
2	none	Zn	Pt	n.d. ^b	81	6	$PdCl_2(PPh_3)_2$	Ni	Pt	92	n.d. ^b
3	$PdCl_2$	Zn	Pt	17	33	7	$PdCl_2(PPh_3)_2$	Zn	Zn	94	n.d. ^b
4	$PdCl_2(PhCN)_2$	Zn	Pt	n.d. ^b	78	8	$PdCl_2(PPh_3)_2$	Zn	CP	72	n.d. ^b

^aIsolated yields. ^bNot detected.

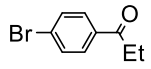
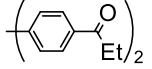
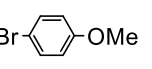
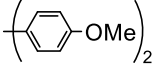
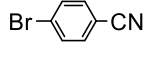
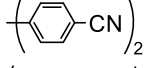
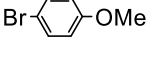
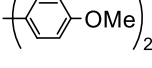
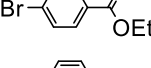
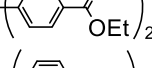
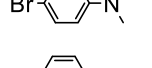
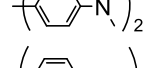
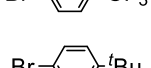
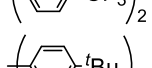
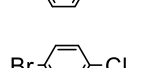
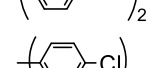
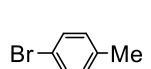
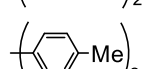
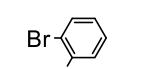
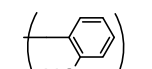
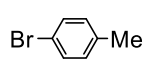
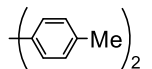
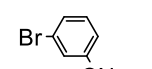
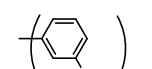
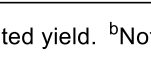
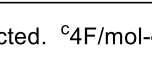
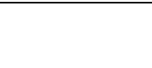
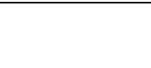
Without catalyst, the reaction did not proceed at all (Entry 2), and the reaction hardly proceeded with other Pd catalysts such as PdCl₂ and PdCl₂(PhCN)₂ (Entries 3, 4), indicating that stabilization of low valent Pd with phosphine ligand is indispensable.

The homocoupling of **4a** was carried out with several electrode materials (Entries 5-8). The coupling reaction proceeded with Zn and Ni (Entry 6) anodes, while Mg rod ($\phi = 6$ mm, Entry 5) anode did not proceed the reaction and **4a** disappeared. On the other hand, the reaction proceeded smoothly with Zn or CP (carbon paper) cathode to give **5a** in 94% and 72% yields (Entries 7, 8). It is noteworthy that **5a** was obtained in low yield (28%) when Zn powder was used as a reductant without electrolysis.

The yield of **5a** was 89% at 10 mA, and was gradually decreased to 81% with increase of current value up to 60 mA. Since the current value could only be increased up to 10 mA when C₈V²⁺ was used, the reaction time can be shortened considerably.

The amount of **1** was examined. The yield was kept more than 81% even when **1** decreased to 10 mol%. The reaction hardly proceeded without **1**, though **4a** disappeared, suggesting that **4a** was reduced directly at the cathode.⁷

Table 2. Pd/**1**-Promoted Homocoupling of Aryl Halides **4** to Biaryls **5**

Entry	4	5	Yield/% ^a		Entry	4	5	Yield/% ^a			
			5	4				5	4		
1			5a	89	n.d. ^b	8			5g	21	n.d. ^b
2			5b	96	n.d. ^b	9 ^c			5g	13	33
3			5c	83	n.d. ^b	10			5h	43	n.d. ^b
4			5d	78	n.d. ^b	11			5i	n.d. ^b	5
5			5e	83	n.d. ^b	12			5j	93	n.d. ^b
6			5f	55	n.d. ^b	13			5k	61	n.d. ^b
7 ^c			5f	83	n.d. ^b	14			5l	89	n.d. ^b

^aIsolated yield. ^bNot detected. ^c4F/mol-**4**.

In a similar manner, the reductive coupling of several aryl halides **4** was carried out (Table 2). The homocoupling reaction with substrates having electron-withdrawing group proceeded smoothly to give the corresponding biaryls in good yields. (Entries 1-4). On the other hand, substrates having electron-donating group gave the corresponding biaryls in moderate yields (Entries 5-10). The reaction

did not occur with aryl chloride, the starting material disappeared (Entry 11). It seems that the $\text{Ar-Pd}^{\text{II}}\text{-Cl}$ did not form and the substrate was reduced directly at the platinum cathode. When *p*-bromochlorobenzene was used as the substrate, the coupling proceeded only on the bromo side (Entry 12). The coupling reaction influenced by steric hindrance: Biaryls were obtained from 4-bromobenzonitrile and 3-bromobenzonitrile in 96% and 89% yields (Entries 2, 14), respectively, whereas 2-bromobenzonitrile gave **5k** in 61% yields (Entry 13).

A plausible mechanism, similar to that using C_8V^{2+} , is shown in Figure 1. At the cathode, $\text{V}^{2+}\cdot\text{D}$ would be reduced to $\text{V}^0\cdot\text{D}$. Pd^{II} was reduced with quinoid $\text{V}^0\cdot\text{D}$ to afford Pd^0 , and oxidative addition of Ar-Br to Pd^0 species would generate $\text{Ar-Pd}^{\text{II}}\text{-Br}$. Further reduction of $\text{Ar-Pd}^{\text{II}}\text{-Br}$ with $\text{V}^0\cdot\text{D}$ would afford Ar-Pd^0 . The second oxidative addition of Ar-Br on Ar-Pd^0 would afford $\text{Ar-Pd}^{\text{II}}\text{-Ar}$, then reductive elimination would give Ar-Ar and Pd^0 .

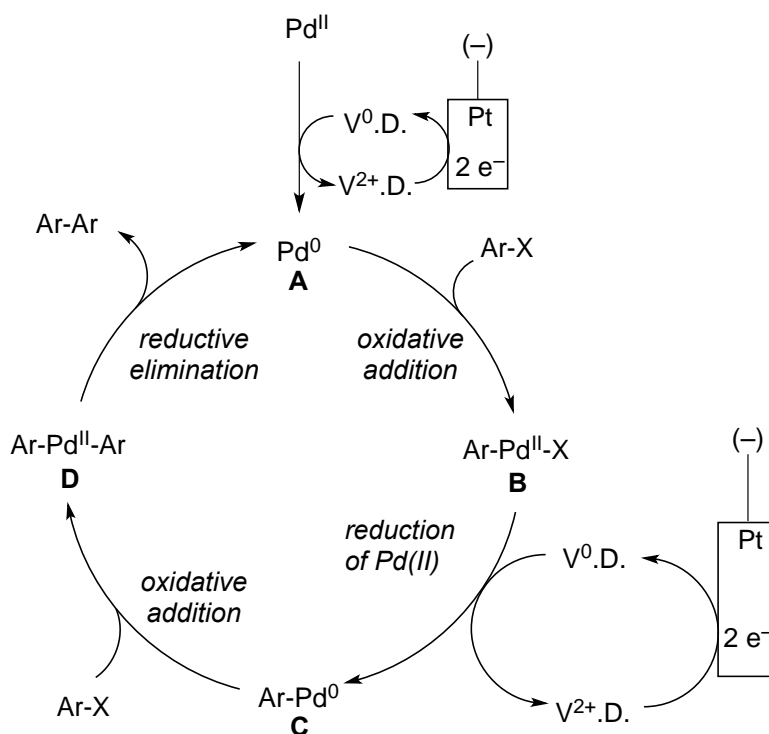


Figure 2. A Plausible Mechanism of Homocoupling Reaction of Aryl Halides

In conclusion, dendrimer-type viologen **1** was synthesized by alkylation of 1-octylbipyridinium hexafluorophosphate with 1,3,5-tris(bromomethyl)benzene. $\text{Pd}/\mathbf{1}$ -promoted homocoupling of aryl bromides Ar-Br proceeded smoothly to give the corresponding biaryls Ar-Ar in moderate to good yields. A catalytic amount of **1** promoted the homocoupling efficiently.

EXPERIMENTAL

IR spectra were obtained on a JASCO FT/IR-4100 spectrometer. ^1H NMR and ^{13}C NMR spectra were measured using a JEOL ECS-400 (^1H NMR 400 MHz, ^{13}C NMR 100 MHz). Cyclic Voltammetry (CV) was determined on BAS ALS/DY2323. Elemental analysis was obtained on Perkin Elmer PE 2400 Series II CHNS/O Analyzer.

Synthesis of 1-Octyl-4,4'-bipyridinium Hexafluorophosphate (2).⁸ A mixture of 1-bromooctane (7.8 mL, 45.0 mmol), 4,4'-bipyridyl (4.71 g, 30.2 mmol), and acetone (40 mL) was stirred at 50 °C for 66 h to give yellow precipitates. The resulting mixture was cooled to room temperature and poured into Et₂O (100 mL). The reaction mixture was filtered to remove 1,1'-dioctyl-4,4'-bipyridinium dibromide [C_8V^{2+}][Br⁻]₂ (1.77 g, 3.3 mmol, 11%) as brilliant greenish yellow solids. The filtrate was concentrated under reduced pressure, and the residue was dissolved in deionized water (80 mL). To the solution was added an aqueous solution (20 mL) of NH₄PF₆ (5.50 g, 33.7 mmol). The whole mixture was stirred vigorously at room temperature for 1 h to afford precipitates. The precipitates were filtered and washed with deionized water. The colorless solid was dried overnight *in vacuo* to give 1-octyl-4,4'-bipyridinium hexafluorophosphate (**2**, 6.85 g, 16.5 mmol, 55%) as colorless solids. ^1H NMR (400 MHz, CD₃CN) δ 0.89 (t, J = 6.8 Hz, 3H), 1.29-1.36 (m, 10H), 1.96-2.00 (m, 2H), 4.53 (t, J = 7.6 Hz, 2H), 7.81 (dd, J = 1.8, 4.4 Hz, 2H), 8.31 (d, J = 6.8 Hz, 2H), 8.76 (d, J = 6.8 Hz, 2H), 8.85 (dd, J = 1.8, 4.4 Hz, 2H); ^{13}C NMR (100 MHz, CD₃CN) δ 14.7, 23.7, 26.9, 29.9, 30.1, 32.2, 32.8, 62.9, 123.2, 127.4, 142.6, 146.2, 152.5, 155.4; IR (KBr) 416, 511, 557, 609, 723, 831, 995, 1079, 1181, 1225, 1297, 1413, 1471, 1496, 1527, 1550, 1600, 1644, 2856, 2926, 3062, 3137 cm⁻¹; Anal. Calcd for C₁₈H₂₅F₆N₂P: C, 52.17; H, 6.08; N, 6.76. Found: C, 52.02; H, 6.18; N, 6.76.

Synthesis of 1,3,5-Tris(bromomethyl)benzene (3).⁹ A mixture of mesitylene (5.0 mL, 35.8 mmol), *N*-bromosuccinimide (19.58 g, 110.0 mmol), and benzoyl peroxide (0.29 g, 0.9 mmol) in benzene (150 mL) was heated to reflux for 3.5 h. The reaction mixture was cooled to room temperature and filtered. The filtrate was washed with water and dried over Na₂SO₄. After concentration of the filtrate under reduced pressure, the needle crystals were further recrystallized from ethanol and hexane (1:1) to give 1,3,5-tris(bromomethyl)benzene (**3**, 2.03 g, 5.7 mmol, 16%) as colorless solids. ^1H NMR (400 MHz, CDCl₃) δ 4.46 (s, 6H), 7.36 (s, 3H).

Synthesis of Viologen Dendrimer [V²⁺.D.], 1,1',1''-[Benzene-1,3,5-triyltris(methylene)]tris[(octyl)-4-pyridin-4-ylpyridinium] Hexafluorophosphate (1).¹⁰ A mixture of **3** (0.71 g, 2.0 mmol), **2** (3.73 g, 9.0 mmol), and MeCN (20 mL) was stirred at 100 °C for 38 h to give yellow precipitates. The resulting mixture was cooled to room temperature. To the mixture were added NH₄PF₆ (1.95 g, 12.0 mmol) and deionized water (10 mL). After stirred for 1 h, the whole mixture was concentrated under reduced

pressure to give yellow solids. The solids were dissolved in MeNO₂ and filtered. The MeNO₂ solution was concentrated under reduced pressure to give colorless solids. The mixture was filtered, and the solids were washed with THF until the solids turned to colorless. The colorless solids were dissolved into MeCN and filtered. The filtrate was concentrated under reduced pressure and dried overnight *in vacuo* to give 1,1',1''-[benzene-1,3,5-triyltris(methylene)]tris[(octyl)-4-pyridin-4-ylpyridinium] hexafluorophosphate [V²⁺.D.] (**1**, 2.99 g, 1.7 mmol, 84%) as colorless solids. ¹H NMR (400 MHz, CD₃CN) δ 0.89 (t, *J* = 6.8 Hz, 9H), 1.29-1.37 (m, 30H), 1.98-2.05 (m, 6H), 4.61 (t, *J* = 7.6 Hz, 6H), 5.84 (s, 6H), 7.68 (s, 3H), 8.36-8.41 (m, 12H), 8.88-8.93 (m, 12H); ¹³C NMR (100 MHz, CD₃CN) δ 14.7, 23.6, 26.9, 29.9, 30.0, 32.3, 32.7, 63.5, 64.9, 128.5, 128.8, 133.2, 136.2, 146.9, 147.1, 151.1, 152.0; IR (KBr) 417, 428, 442, 557, 740, 835, 1041, 1174, 1224, 1346, 1453, 1507, 1561, 1640, 2859, 2929, 3076, 3140, 3427, 3667 cm⁻¹; Anal. Calcd for C₆₃H₈₄F₃₆N₆P₆: C, 42.15; H, 4.72; N, 4.68. Found: C, 41.98; H, 4.54; N, 4.68.

V²⁺.D./Pd-Mediated Reductive Coupling of 4-Bromopropiophenone (4a). In an undivided cell equipped with a Zn sacrificial anode (1.5 x 1.0 cm²) and a Pt cathode (1.5 x 1.0 cm²) was placed a DMF (3 mL) solution of 4-bromopropiophenone (**4a**, 0.053 g, 0.25 mmol), **1** (0.14 g, 7.6 x 10⁻² mmol), [Bu₄N⁺][Tf₂N⁻] (0.16 g, 0.30 mmol), and a catalytic amount of PdCl₂(PPh₃)₂ (0.0086 g, 1.2 x 10⁻² mmol). The solution was electrolyzed under constant current conditions (10 mA) at 60 °C until 2 F/mol-**4a** of electricity was passed. The reaction mixture was poured into 5% aq. HCl (12 mL). The mixture was extracted with AcOEt (10 mL x 3). The combined organic layer was washed successively with water and brine, dried (Na₂SO₄), and concentrated under reduced pressure. The residue was purified by column chromatography (SiO₂, toluene/AcOEt = 10/1) to afford 4,4'-dipropanoylbiphenyl (**5a**, 0.030 g, 0.11 mmol, 89%).¹¹ *R*_f = 0.58 (toluene/AcOEt = 10/1); ¹H NMR (400 MHz, CDCl₃) δ 1.26 (t, *J* = 6.8 Hz, 6H), 3.06 (q, *J* = 6.8 Hz, 4H), 7.72 (d, *J* = 8.2 Hz, 4H), 8.07 (d, *J* = 8.2 Hz, 4H).

4,4'-Dicyanobiphenyl (7b):¹¹ colorless solids; *R*_f = 0.67 (toluene/AcOEt = 10/1); ¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, *J* = 8.2 Hz, 4H), 7.79 (d, *J* = 8.2 Hz, 4H).

4,4'-Bis(ethoxycarbonyl)biphenyl (7c):¹¹ colorless solids; *R*_f = 0.42 (hexane/AcOEt = 5/1); ¹H NMR (400 MHz, CDCl₃) δ 1.42 (t, *J* = 7.0 Hz, 6H), 4.41 (q, *J* = 7.0 Hz, 4H), 7.69 (d, *J* = 8.2 Hz, 4H), 8.14 (d, *J* = 8.2 Hz, 4H),.

4,4'-Bis(trifluoromethyl)biphenyl (7d):¹² colorless solids; *R*_f = 0.37 (hexane); ¹H NMR (400 MHz, CDCl₃) δ 7.69–7.75 (m, 8H).

4,4'-Di-*tert*-butylbiphenyl (7e):¹³ colorless solids; *R*_f = 0.28 (hexane); ¹H NMR (400 MHz, CDCl₃) δ 1.36 (s, 18H), 7.45 (d, *J* = 8.6 Hz, 4H), 7.53 (d, *J* = 8.6 Hz, 4H).

4,4'-Dimethylbiphenyl (7f):¹² colorless solids; *R*_f = 0.40 (hexane); ¹H NMR (400 MHz, CDCl₃) δ 2.39

(s, 6H), 7.23 (d, $J = 7.6$ Hz, 4H), 7.48 (d, $J = 7.6$ Hz, 4H).

4,4'-Dimethoxybiphenyl (7g):¹¹ colorless solids; $R_f = 0.60$ (toluene); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 3.84 (s, 6H), 6.96 (d, $J = 8.6$ Hz, 4H), 7.48 (d, $J = 8.6$ Hz, 4H).

***N,N,N',N'*-Tetramethylbenzidine (7h):**¹⁴ colorless solids; $R_f = 0.80$ (Et_2O); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 2.93 (s, 12H), 6.66 (d, $J = 8.8$ Hz, 4H), 7.32 (d, $J = 8.8$ Hz, 4H).

4,4'-Dichlorobiphenyl (7j):¹¹ $R_f = 0.37$ (hexane); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.41 (d, $J = 8.8$ Hz, 4H), 7.48 (d, $J = 8.8$ Hz, 4H).

2,2'-Dicyanobiphenyl (7k):¹⁵ $R_f = 0.28$ (toluene); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.56-7.60 (m, 4H), 7.73 (t, $J = 8.2$ Hz, 2H), 7.84 (d, $J = 8.2$ Hz, 4H).

3,3'-Dicyanobiphenyl (7l):¹⁶ $R_f = 0.23$ (toluene); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.62 (t, $J = 8.0$, 2H), 7.72 (d, $J = 8.0$ Hz, 2H), 7.80 (d, $J = 8.0$ Hz, 2H), 7.85 (s, 2H).

REFERENCES AND NOTES

- (a) L. Depature and G. Surpateanu, *Heterocycles*, 2002, **57**, 2239; (b) M. Kijima, A. Sakawaki, and T. Sato, *Bull. Chem. Soc. Jpn.*, 1994, **67**, 2323; (c) R. P. Kinghand and J. M. Shreeve, *Inorg. Chem.*, 2003, **42**, 7416; (d) H. Kamogawa and S. Sato, *Bull. Chem. Soc. Jpn.*, 1991, **64**, 321; (e) T. Nagamura, K. Sakai, and T. Ogawa, *J. Chem. Soc., Chem. Commun.*, 1988, 1035.
- V. Fourmond and C. Leger, *Angew. Chem. Int. Ed.*, 2017, **56**, 4388.
- R. Yuan, S. Watanabe, S. Kuwabata, and H. Yoneyama, *J. Org. Chem.*, 1997, **62**, 2494.
- (a) M. Kuroboshi, T. Shiba, and H. Tanaka, *Tetrahedron Lett.*, 2013, **54**, 3666; (b) H. Tanaka, M. Kuroboshi, R. Kataoka, and R. Suzuki, *Electrochemistry* (Tokyo, Japan), 2013, **81**, 356. (c) M. Kuroboshi, T. Yamamoto, and H. Tanaka, *Synlett*, 2013, **24**, 197. (d) M. Kuroboshi, A. Kuwano, and H. Tanaka, *Electrochemistry* (Tokyo, Japan), 2008, **76**, 862.
- (a) B. Claude-Montigny, A. Merlin, and C. Tondre, *J. Phys. Chem.*, 1992, **96**, 4432. (b) M. Ito, H. Sasaki, and M. Takahashi, *J. Phys. Chem.*, 1987, **91**, 3932.
- K. Murugavel, *Polym. Chem.*, 2014, **5**, 5873.
- When C_8V^{2+} was used as catalytic reductant, 30 mol% of C_8V^{2+} gave **5a** from **4a** in 92% yield. See Ref. 4(a).
- Z. Shi, K. G. Neoh, and E. T. Kang, *Biomaterials*, 2005, **26**, 501.
- F. Qiu, C. Tu, Y. Chen, Y. Shi, L. Song, R. Wang, X. Zhu, B. Zhu, D. Yan, and T. Han, *Chem. Eur. J.*, 2010, **16**, 12710.
- S. Asaftei and C. E. De, *J. Med. Chem.*, 2010, **53**, 3480.
- L. Wang, Y. Zhang, L. Liu, and Y. Wang, *J. Org. Chem.*, 2006, **71**, 1284.

12. N. Ma, Z. Zhu, and Y. Wu, [*Tetrahedron*, 2007, **63**, 4625.](#)
13. K. Mitsudo, T. Shiraga, D. Kagen, D. Shi, J. Y. Becker, and H. Tanaka, [*H. Tetrahedron*, 2009, **65**, 8384.](#)
14. Y. Bourne-Branchu, A. Moncomble, M. Corpet, G. Danoun, and C. Gosmini, [*Synthesis*, 2016, **48**, 3352.](#)
15. A. Moncomble, P. L. Folch, and C. Gosmini, [*Chem. Eur. J.*, 2009, **15**, 4770.](#)
16. A. Inoue, K. Kitagawa, H. Shinokubo, and K. Oshima, [*Tetrahedron*, 2000, **56**, 9601.](#)