

Palladium/Phosphite or Phosphate Catalyzed Oxidative Coupling of Arylboronic Acids with Alkynes to Produce 1,4-Diaryl-1,3-butadienes

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Abstract: The intermolecular oxidative coupling of arylboronic acids with internal alkynes efficiently proceeds in a 2:2 manner in the presence of palladium acetate, a triaryl phosphite or phosphate, and silver carbonate as catalyst, ligand, and oxidant, re-

spectively, to produce the corresponding 1,4-diaryl-1,3-butadiene derivatives.

Keywords: arylation; C–C coupling; dienes; multi-component reactions; palladium; phosphite ligands

Introduction

The transition-metal-catalyzed arylation of internal alkynes by halogenated or metalated aromatic reagents through carbometalation is a powerful tool for constructing π -conjugated molecules.^[1] Some of these reactions are carried out with addition of various terminators including organometallic reagents,^[2] alkenes,^[3] and terminal alkynes^[4] to give rise to three-component coupling products. In other cases, the reactions involve cyclometalation in the terminal step to yield cyclic compounds.

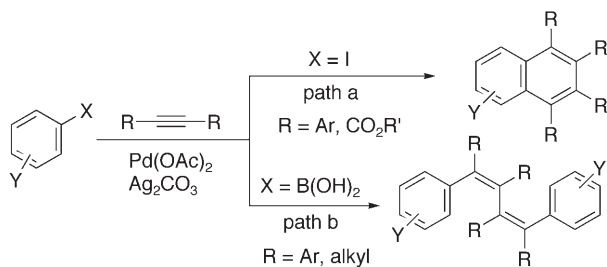
As an example for the latter case, we have reported an effective protocol for the palladium-catalyzed 1:2 coupling of aryl iodides with diphenylacetylene as well as acetylenedicarboxylates in the presence of a silver salt as a base to afford the corresponding naphthalenes (path a in Scheme 1).^[5] The Pd/Ag catalytic system has also been applied to the reaction of aryl-

boronic acids with diarylacetylenes to form 2:2 coupling products, 1,4-diaryl-1,3-butadienes (path b).^[6] In this coupling, the silver salt acts as an oxidant.^[7,8] The reaction appears to be synthetically useful as a simple and straightforward route to multiarylated butadienes. Although the reaction with dialkylacetylenes takes place to give 1,2,3,4-tetraalkyl-1,4-diarylbutadienes having good solubilities, the product yields are moderate to low due to the facile deactivation of the palladium catalyst under the oxidative conditions.^[6,7b]

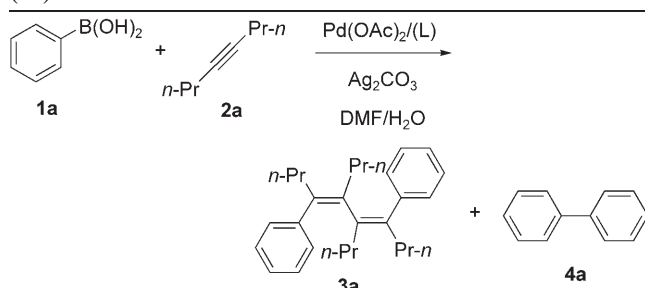
In the course of our study of the catalytic processes involving carbometalation of alkynes,^[3a–b,5,6,9] we observed a notable ligand effect in the 2:2 coupling of arylboronic acids with dialkylacetylenes in that it can proceed selectively and efficiently under palladium catalysis by employing a triaryl phosphite to give the corresponding highly substituted 1,3-butadienes. In addition, it has also been found that the 2:2 coupling of arylboronic acids with diarylacetylenes is considerably enhanced by addition of a triaryl phosphate rather than the phosphite.

Results and Discussion

When phenylboronic acid (**1a**) (2 mmol) was reacted with 4-octyne (**2a**) (4 mmol) in the presence of Pd(OAc)₂ (0.05 mmol) and Ag₂CO₃ (2 mmol) as a catalyst and an oxidant, respectively, in DMF/H₂O (9:1) at 120 °C for 3 h, 4,7-diphenyl-5,6-dipropyl-4,6-decadiene (**3a**) was formed in 45% yield along with a trace amount of direct homo-coupling product, bi-



Scheme 1. Coupling of aryl iodides and boronic acids with alkynes.

Table 1. Reaction of phenylboronic acid (**1a**) with 4-octyne (**2a**).^[a]

Entry	L [mmol]	Time [h]	% Yield of 3a ^[b]	4a [mmol]
1 ^[c]	-	3	45	tr
2	-	1	47	tr
3 ^[d]	-	1	41	0.31
4	(2-furyl) ₃ P (0.1)	1	30	0.45
5	$\text{Ph}_3\text{P}=\text{O}$ (0.1)	1	45	tr
6	$(\text{C}_6\text{F}_5)_3\text{P}$ (0.1)	1	44	tr
7	4-phenylpyridine (0.1)	3	50	0.07
8	$(\text{PhO})_3\text{P}$ (0.1)	1	55	tr
9	$(\text{PhO})_3\text{P}$ (0.05)	3	60	0.04
10 ^[e]	$(\text{PhO})_3\text{P}$ (0.05)	3	67 (65)	0.28
11 ^[e]	$[(4\text{-MeC}_6\text{H}_4)\text{O}]_3\text{P}$ (0.05)	3	85 (75)	0.52
12 ^[e]	$(\text{PhO})_3\text{P}=\text{O}$ (0.05)	1	74	0.33
13 ^[e]	$[(4\text{-MeC}_6\text{H}_4)\text{O}]_3\text{P}=\text{O}$ (0.05)	1	73	0.37
14 ^[e,f]	$[(4\text{-MeC}_6\text{H}_4)\text{O}]_3\text{P}$ (0.05)	3	16	tr

^[a] Reaction conditions: $[\mathbf{1a}]:[\mathbf{2a}]:[\text{Pd}(\text{OAc})_2]:[\text{Ag}_2\text{CO}_3] = 2:4:0.05:2$ (in mmol), in $\text{DMF}/\text{H}_2\text{O}$ (9:1, 5 mL) under N_2 at 140°C .

^[b] GC yield based on the amount of **1a** (entries 1–9) or **2a** (entries 10–13) used. Value in parentheses indicates yield after purification.

^[c] At 120°C .

^[d] In DMF (5 mL).

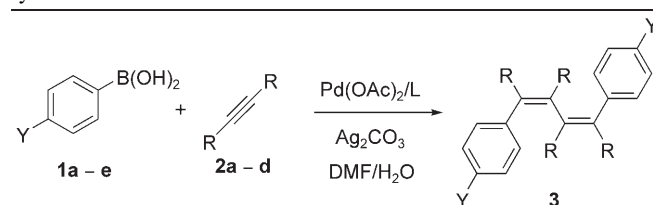
^[e] **1a** (4 mmol) and **2a** (2 mmol) were used.

^[f] $\text{Cu}(\text{OAc})_2\cdot\text{H}_2\text{O}$ (4 mmol) and K_2CO_3 (4 mmol) were used in place of Ag_2CO_3 .

phenyl (**4a**) (Table 1, entry 1). Thus, the reaction stopped at a moderate conversion, which may be attributed to catalyst deactivation. The result is comparable to those observed previously in 1,4-dioxane/ H_2O and 1-propanol.^[6] At a higher temperature of 140°C , the initial reaction rate was enhanced, but the yield of **3a** was not improved (entry 2). In pure DMF , the yield of by-product **4a** increased (entry 3). For elongating catalyst lifetime, a number of monodentate ligands (0.1 mmol) were added in the reaction medium (entries 4–8). Among them, triphenyl phosphite was found to improve the yield of **3a** up to 55% (entry 8). Decreasing the amount of the phosphite to 0.05 mmol somewhat increased the yield (entry 9). Under the conditions using an excess amount of **1a** (4 mmol) with **2a** (2 mmol), the yield of **3a** was enhanced to 67%, while the amount of **4a** also increased as expected (entry 10). Finally, **3a** was obtained in 85% yield, when the reaction was conducted using tris(4-methylphenyl) phosphite as a ligand (entry 11). This yield is almost twice as high as that in our previous report.^[6] It is possible that the phosphite ligands are oxidized to the corresponding phosphates under the oxidative conditions with the silver salt. While the phosphates showed substantial effects (entries 12 and 13), they were less effective than tris(4-methylphenyl) phosphite. Under the conditions using $\text{Cu}(\text{OAc})_2\cdot\text{H}_2\text{O}$ as an oxidant combined with K_2CO_3 in place of the silver salt, the reaction was sluggish (entry 14). The NMR spectra of **3a** isolated in entry 11 indicated that it has the (4*Z*,6*Z*) configuration, as previously reported,^[6] without contamination by any other geometrical isomers.

Table 2 summarizes the results for the reactions of various arylboronic acids **1a–e** with dialkylacetylenes **2a–d**.^[a]

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Table 2. Reaction of arylboronic acids **1a–e** with dialkylacetylenes **2a–d**.^[a]

Entry	Substrates				Time [h]	L ^[b]	Product, % Yield ^[c]
	1	Y	2	R			
1	1a	H	2b	<i>n</i> -Bu	1	A	3b , 64 (62)
2						B	3b , 55
3	1a	H	2c	<i>n</i> -heptyl	1	A	3c , 84 (81)
4						B	3c , 82
5	1a	H	2d	<i>i</i> -pentyl	3	A	3d , 77 (75)
6						B	3d , 72
7 ^[d]	1b	Cl	2a	<i>n</i> -Pr	3	A	3e , 72 (59)
8 ^[d]	1c	CO_2Me	2a	<i>n</i> -Pr	1	B	3f , 71 (62)
9	1d	Me	2a	<i>n</i> -Pr	3	B	3g , 71 (62) ^[e]
10	1e	OMe	2a	<i>n</i> -Pr	3	A	3h , 63 (57) ^[f]

^[a] Reaction conditions: $[\mathbf{1}]:[\mathbf{2}]:[\text{Pd}(\text{OAc})_2]:[\text{L}]:[\text{Ag}_2\text{CO}_3] = 4:2:0.05:0.05:2$ (in mmol), in $\text{DMF}/\text{H}_2\text{O}$ (9:1, 5 mL) at 140°C under N_2 .

^[b] A = $(\text{PhO})_3\text{P}$, B = $[(4\text{-MeC}_6\text{H}_4)\text{O}]_3\text{P}$.

^[c] GC yield based on the amount of **1** (entries 7 and 8) or **2** (entries 1–6, 9 and 10) used. Value in parentheses indicates yield after purification.

^[d] **1** (2 mmol) and **2** (4 mmol) were used.

^[e] (4*Z*,6*Z*):(4*E*,6*E*) = 1:0.14.

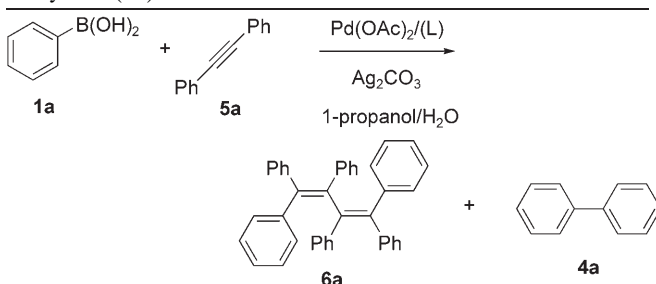
^[f] (4*Z*,6*Z*):(4*E*,6*Z*):(4*E*,6*E*) = 1:0.11:0.25.

2a–d in the presence of $\text{Pd}(\text{OAc})_2/\text{phosphite}$. In the reaction of **1a** with dialkylacetylenes **2b–d**, the catalyst system with $(\text{PhO})_3\text{P}$ ligand (ligand A) unexpectedly gave similar or slightly better results compared with those using $[(4\text{-MeC}_6\text{H}_4)\text{O}]_3\text{P}$ (ligand B)

(Table 2, entries 1–6). In these reactions, the corresponding dienes **3b–d** were obtained in 55–84% yields as single major cross-coupling products. In the reactions of electron-poor boronic acids **1b** and **1c**, better results were obtained under conditions using excess alkyne **2a**. Thus, the reactions of **1b** and **1c** (2 mmol) with **2a** (4 mmol) gave dienes **3e** and **3f** in 72 and 71% yields, respectively (entries 7 and 8). Electron-rich boronic acids **1d** and **1e** also underwent the coupling with **2a** to afford dienes **3g** and **3h** in 71 and 63% yields (entries 9 and 10). The NMR spectra of the products indicated that they contained minor amounts of their geometrical isomer(s) [**3g**: (4*Z*,6*Z*):-(4*E*,6*E*) = 1:0.14, **3h**: (4*Z*,6*Z*):(4*E*,6*Z*):(4*E*,6*E*) = 1:0.11:0.25].

Next, the reaction of boronic acid **1a** with diphenylacetylene (**5a**) was also examined using the present catalytic systems. When **1a** (3 mmol) was treated with **5a** (2 mmol) in the presence of Pd(OAc)₂ (0.05 mmol) and Ag₂CO₃ (2 mmol) in 1-propanol/H₂O (9:1) at 120 °C for 1 h, 1,1,2,3,4,4-hexaphenyl-1,3-butadiene (**6a**) was produced in 74% yield (Table 3, entry 1).

Table 3. Reaction of phenylboronic acid (**1a**) with diphenylacetylene (**5a**).^[a]



Entry	L [mmol]	Time [h]	% Yield of 6a ^[b]	4a [mmol]
1	-	1	74	0.27
2	(PhO) ₃ P (0.1)	1	73	0.24
3	(PhO) ₃ P=O (0.1)	1	84	0.23
4	(PhO) ₃ P=O (0.05)	1	84	0.20
5	[(4-MeC ₆ H ₄)O] ₃ P=O (0.05)	0.5	91 (82)	0.20
6	(EtO) ₃ P=O (0.05)	1	73	0.25
7	(PhO) ₂ (HO)P=O (0.05)	0.5	80	0.41
8 ^[c]	[(4-MeC ₆ H ₄)O] ₃ P=O (0.05)	1	76	0.18

^[a] Reaction conditions: [**1a**]:[**5a**]:[Pd(OAc)₂]:[Ag₂CO₃] = 3:2:0.05:2 (in mmol), in 1-propanol/H₂O (9:1, 5 mL) under N₂ at 120 °C.

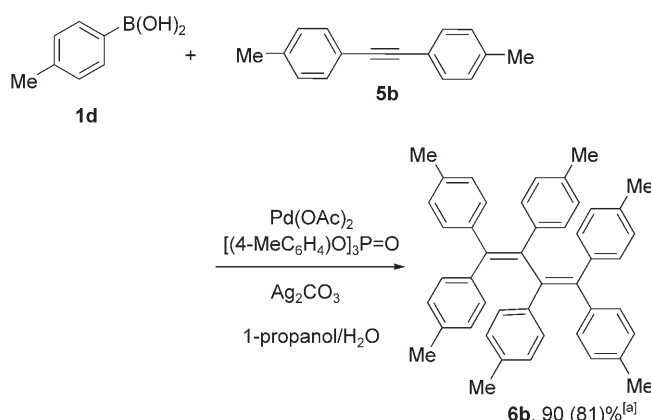
^[b] GC yield based on the amount of **5a** used. Value in parentheses indicates yield after purification.

^[c] At 80 °C.

Addition of triphenyl phosphite (0.1 mmol) showed no apparent effect (entry 2). However, the yield of **6a** was improved to 84% by addition of triphenyl phos-

phate (0.1 or 0.05 mmol) (entries 3 and 4). Among some phosphates examined (entries 3–6), tris(4-methylphenyl) phosphate gave the best yield of 91% (entry 5). The use of diphenyl phosphate increased the yield of biphenyl **4a**, but it was less effective for the cross-coupling (entry 7).

In the presence of the catalyst system of Pd(OAc)₂/[(4-MeC₆H₄)O]₃P=O, the reaction of (4-methylphenyl)boronic acid (**1d**) with bis(4-methylphenyl)acetylene (**5b**) also proceeded smoothly to form 1,1,2,3,4,4-hexakis(4-methylphenyl)-1,3-butadiene (**6b**) in 81% isolated yield (Scheme 2). This is significantly higher than that obtained previously in the absence of the phosphate (58%).^[6]

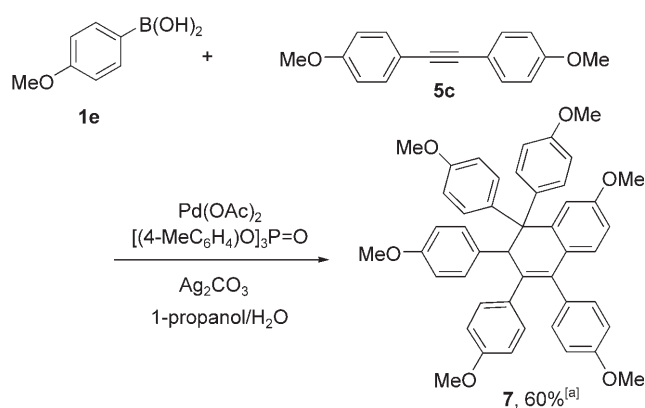


Scheme 2. Reaction of (4-methylphenyl)boronic acid (**1d**) with di(4-methylphenyl)acetylene (**5b**). Reaction conditions: [**1d**]:[**5b**]:[Pd(OAc)₂]:[(4-MeC₆H₄)O]₃P=O]:[Ag₂CO₃] = 1.5:1:0.025:0.025:1 (in mmol), in 1-propanol/H₂O (9:1, 2.5 mL) under N₂ at 120 °C for 0.5 h.^[a] GC yield. Value in parentheses indicates yield after purification.

(4-Methoxyphenyl)boronic acid (**1e**) reacted with bis(4-methoxyphenyl)acetylene (**5c**) to afford a cyclized product **7** in 60% yield (Scheme 3). This may be formed *via* the 2:2 coupling, subsequent electrocyclic rearrangement^[10] of the resulting butadiene, and [1,5] hydrogen shift.

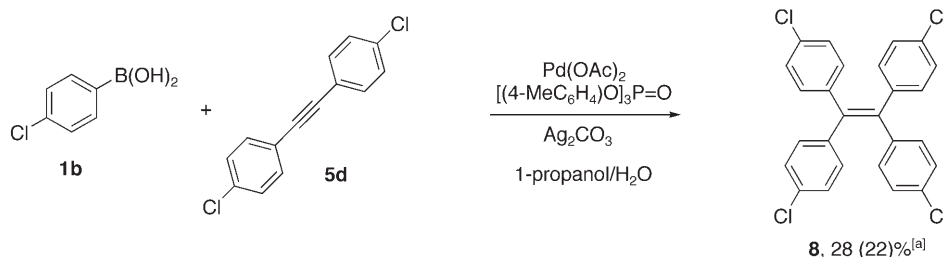
On the other hand, treatment of (4-chlorophenyl)boronic acid (**1b**) with bis(4-chlorophenyl)acetylene (**5d**), even under the conditions using the silver oxidant gave a 2:1 coupling product, 1,1,2,2-tetrakis(4-chlorophenyl)ethane (**8**), albeit with a low yield (Scheme 4). In this case, formation of the expected butadiene could not be detected.

A plausible mechanism for the reaction of arylboronic acids **1** with alkynes **2** or **5** is illustrated in Scheme 5, which is similar to that proposed previously.^[6] The formation of an arylpalladium intermediate **Y** *via* transmetalation between a Pd(II) species (L = ligand or solvent) and **1** followed by insertion of two alkyne molecules forms a dienylypalladium intermedi-

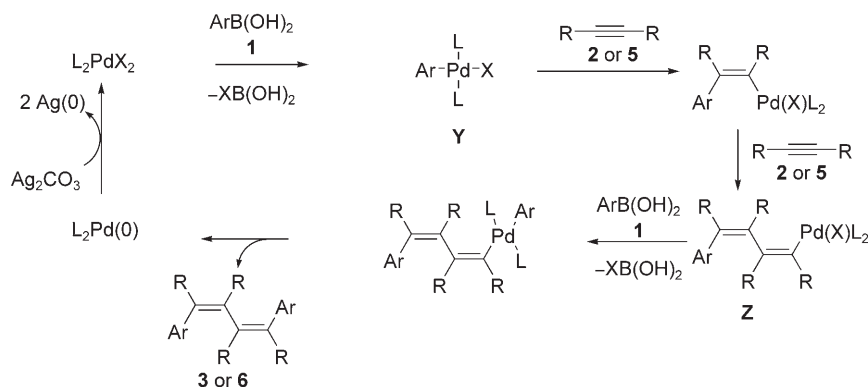


Scheme 3. Reaction of (4-methoxyphenyl)boronic acid (**1e**) with di(4-methoxyphenyl)acetylene (**5c**). *Reaction conditions:* [**1e**]:[**5c**]:[Pd(OAc)₂]:[(4-MeC₆H₄)O]₃P=O]:[Ag₂CO₃] = 1.5:1:0.025:0.025:1 (in mmol), in 1-propanol/H₂O (9:1, 2.5 mL) under N₂ at 120 °C for 0.5 h. ^[a] Isolated yield.

ate **Z**. The successive second transmetalation and reductive elimination give 1,4-diarylated 1,3-diene **3** or **6**.^[11] The L₂Pd(0) species generated in the last step may be reoxidized by the silver salt to close the catalytic cycle. During palladium-catalyzed oxidation reactions, in general, the last reoxidation is considered to be the crucial step to determine catalyst efficiency.



Scheme 4. Reaction of (4-chlorophenyl)boronic acid (**1b**) with di(4-chlorophenyl)acetylene (**5d**). *Reaction conditions:* [**1b**]:[**5d**]:[Pd(OAc)₂]:[(4-MeC₆H₄)O]₃P=O]:[Ag₂CO₃] = 1.5:1:0.025:0.025:1 (in mmol), in 1-propanol/H₂O (9:1, 2.5 mL) under N₂ at 120 °C for 0.5 h. ^[a] GC yield. Value in parentheses indicates yield after purification.



Scheme 5. A plausible mechanism for the coupling of arylboronic acids with alkynes.

cy.^[12] While the exact role of the added phosphites and phosphates is not clear at the present stage, they may support unstable Pd(0) or regenerated Pd(II) species to prolong the catalyst's lifetime.^[13–15]

Conclusions

We have shown effective protocols for the palladium-catalyzed oxidative coupling of arylboronic acids with internal alkynes using a triaryl phosphite or phosphate as the ligand to selectively give the corresponding 2:2 coupling products, 1,4-diaryl-1,3-butadienes. These reactions provide a straightforward route to arylated butadienes, which are of interest for their photo- and electrochemical and biological properties.^[16]

Experimental Section

General Remarks

¹H and ¹³C NMR spectra were recorded at 400 and 100 MHz, or 270 MHz and 68 MHz, respectively, for CDCl₃ solutions. MS data were obtained by EI. GC analysis was carried out using a silicon OV-17 column (i. d. 2.6 mm × 1.5 m) or a CBP-1 capillary column (i. d. 0.5 mm × 25 m). GC-MS analysis was carried out using a CBP-1 capillary

column (i. d. 0.25 mm × 25 m). The structures of all products were unambiguously determined by ^1H and ^{13}C NMR with the aid of NOE, COSY, HMQC, and HMBC experiments.

Diarylacetylenes **5b–d** were prepared according to published procedures.^[17] Other starting materials were commercially available. Characterization data of all the products are reported in the Supporting Information.

The following experimental procedure may be regarded as typical in methodology and scale.

Pd-Catalyzed Reaction of Phenylboronic Acid (**1a**) with 4-Octyne (**2a**) (entry 11 in Table 1)

A mixture of phenylboronic acid (**1a**) (4 mmol, 488 mg), 4-octyne (**2a**) (2 mmol, 220 mg), $\text{Pd}(\text{OAc})_2$ (0.05 mmol, 11 mg), $[(4\text{-MeC}_6\text{H}_4\text{O})_3\text{P}]$ (0.05 mmol, 18 mg), Ag_2CO_3 (2 mmol, 551 mg), and 1-methylnaphthalene (ca. 60 mg) as internal standard was stirred in DMF/ H_2O (5 mL, 9:1) under nitrogen at 140 °C. After 3 h, the reaction mixture was cooled to room temperature, Et_2O (100 mL) and water (100 mL) were added, and insoluble materials were removed by filtration through filter paper. Then the organic layer was washed by water (100 mL, three times) and dried over sodium sulfate. GC and GC-MS analyses confirmed the formation of (4*Z*,6*Z*)-4,7-diphenyl-5,6-dipropyl-4,6-decadiene (**3a**) (0.85 mmol, 85%) and biphenyl (**4a**) (0.52 mmol). The product **3a** (279 mg, 75%) was isolated by column chromatography on silica gel using hexane as eluant and subsequent Kugelrohr distillation to remove hydrocarbon impurities such as the internal standard.

Compound **3a**: mp 83–85 °C (lit.^[6] mp 88 °C); ^1H NMR (270 MHz, CDCl_3): δ = 0.77 (t, J = 6.9 Hz, 6H), 0.82 (t, J = 6.9 Hz, 6H), 1.13–1.22 (m, 4H), 1.24–1.44 (m, 4H), 1.56–1.67 (m, 2H), 2.00–2.12 (m, 2H), 2.17–2.29 (m, 4H), 7.06–7.20 (m, 10H); ^{13}C NMR (68 MHz, CDCl_3): δ = 14.2, 14.9, 21.5, 22.8, 36.1, 36.5, 125.5, 127.2, 128.6, 136.6, 139.1, 143.8; MS: m/z = 374 (M^+).

Acknowledgements

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