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Palladium-Catalyzed Heck-Type Reactions of Allylic Esters with Arylboronic Acids or Potassium Aryltrifluoroborates

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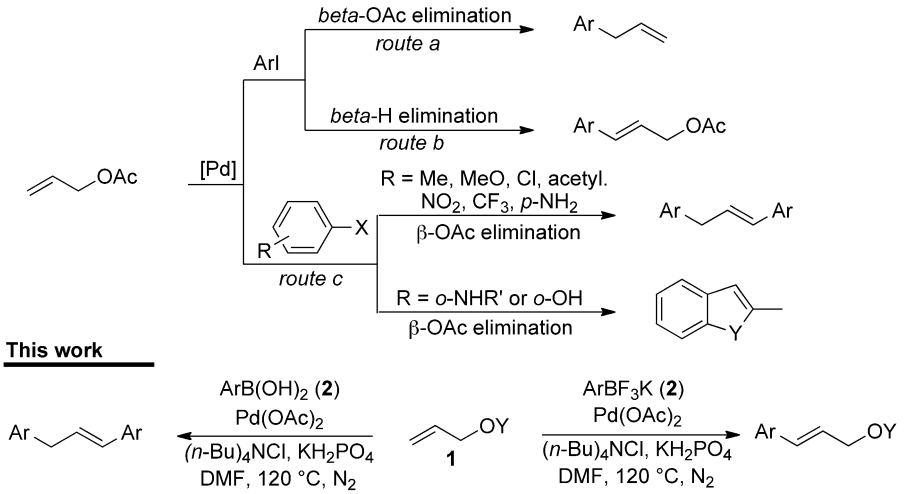
Abstract: A selective and general route to (*E*)-1,3-diaryl-prop-1-enes and (*E*)-3-arylallyl acetates has been developed by palladium-catalyzed Heck-type reactions of allylic esters with arylboronic acids or potassium aryltrifluoroborates. The present method selectively proceeds including β-OAc elimination or β-H elimination on the basis of the boronic acids. Whereas a variety of allylic esters were reacted with arylboronic acids, palladium(II) acetate [$Pd(OAc)_2$], tetra(*n*-butyl)ammonium chloride [$(n\text{-}Bu)_4NCl$] and postassium dihydrogen phosphate (KH_2PO_4) to afford the corresponding diarylation products in moderate to good yields, treatment of allylic esters with potassium aryltrifluoroborates furnished the corresponding monoarylation products.

Keywords: allylic esters; arylboronic acids; Heck reaction; palladium; potassium aryltrifluoroborates

Introduction

The palladium-catalyzed Heck reaction has become a powerful tool for constructing carbon-carbon bonds in organic synthesis[1] and is of growing importance for the pharmaceutical and material industries.[2] In the past several decades, the scope of the Heck reaction has been significantly expanded. However, examples of selective Heck reactions of allylic esters are much less abundant.[3] Lautens and co-workers have



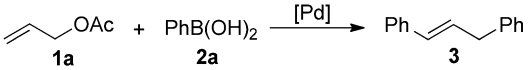
Scheme 1. The Heck reactions of allylic esters.

reported an intermolecular Heck reaction of allylic acetates with aryl iodides to afford the corresponding monoarylation products in good yields, in which a β-OAc elimination process takes place (Scheme 1, route a). Notably, some diarylation side-products were observed in the Lautens procedures, but poor yields and low selectivity hindered the further exploitation.[4c–e,g] Recently, Jiao and co-workers found that allylic esters could selectively undergo the Heck reaction with aryl halides or arylboronic acids including a β-H elimination process, offering the monoarylation ester products alone in moderate to good yields (Scheme 1, route b).[5–6] We also described a selective route for the synthesis of diarylation products by a palladium-catalyzed Heck-type diarylation reaction of allylic esters with aryl halides through β-OAc elimination (Scheme 1, route c).[7] In the presence of $Pd(OAc)_2$, $(n\text{-}Bu)_4NCl$ and Et_3N, allylic esters reacted with various aryl halides smoothly to furnish the respective products in moderate to good yields. Moreover, this methodology was applied in the synthesis of indoles and benzofurans. As part of our continuing interest in applications of allylic esters, we report here the first diarylation reaction between allylic esters and arylboronic acids to prepare unsymmetrical 1,3-diarylpropenes using the $Pd(OAc)_2/(n\text{-}Bu)_4NCl/KH_2PO_4$ catalytic system (Scheme 1). Interestingly, the monoarylation reaction of allylic esters with potassium aryltrifluoroborates also took place, furnishing the corresponding arylallyl acetates in moderate yields. It is noteworthy that the products, unsymmetrical 1,3-diarylpropene compounds, represent the skeleton of colchicine and its derivatives.[8]

Results and Discussion

The reaction between allyl acetate (**1a**) and phenylboronic acid (**2a**) was investigated to optimize the reaction conditions, and the results are summarized in Table 1. Initially, the reaction between allyl acetate (**1a**) and phenylboronic acid (**2a**) was tested under the reported reaction conditions:[7] a trace of diarylation product **3** was observed in the presence of $Pd(OAc)_2$, $(n\text{-}Bu)_4NCl$ and Et_3N for 12 h (entry 1). To our delight, the yield of the desired product **3** was enhanced to 41% when K_2CO_3 combined with DMF was used to replace the Et_3N/MeCN system (entry 2). It is noteworthy that the configuration of the carbon-carbon double bond in product **3** was determined according to the diagnostic ^{1}HNMR spectra. Encouraged by this result, a series of bases, such as Cs_2CO_3, NaOMe, $NaHCO_3$, K_3PO_4, K_2HPO_4 and KH_2PO_4, was examined (entries 3–8). The results demonstrated that the reaction gave the best yield when using KH_2PO_4 base (entry 8). Subsequently, a number of other solvents, including DMSO, toluene, CH_3CN and dioxane,

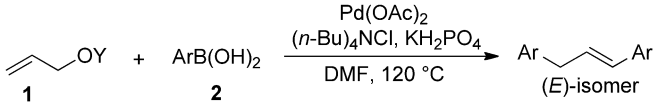
Table 1. Screening for optimal conditions.[a]



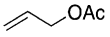
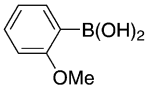
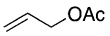
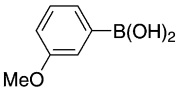
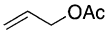
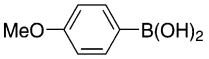
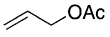
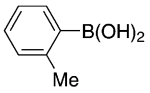
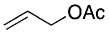
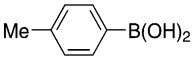
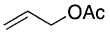
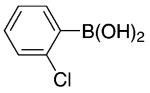
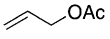
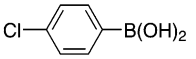
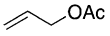
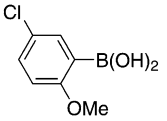
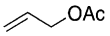
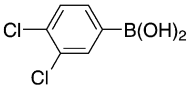
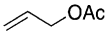
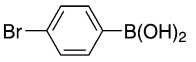
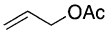
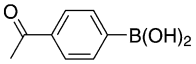
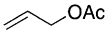
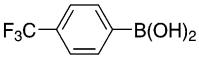
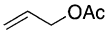
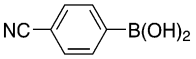
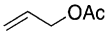
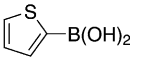
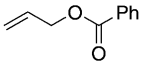
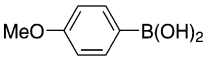
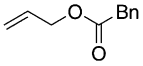
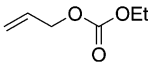
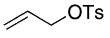
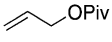
#	[Pd]	Additive	Base	Solvent	Yield [%][b]
1	$Pd(OAc)_2$	(n-$Bu)_4NCl$	Et_3N	MeCN	trace
2	$Pd(OAc)_2$	(n-$Bu)_4NCl$	K_2CO_3	DMF	41
3	$Pd(OAc)_2$	(n-$Bu)_4NCl$	Cs_2CO_3	DMF	52
4	$Pd(OAc)_2$	(n-$Bu)_4NCl$	NaOMe	DMF	trace
5	$Pd(OAc)_2$	(n-$Bu)_4NCl$	$NaHCO_3$	DMF	56
6	$Pd(OAc)_2$	(n-$Bu)_4NCl$	K_3PO_4	DMF	51
7	$Pd(OAc)_2$	(n-$Bu)_4NCl$	K_2HPO_4	DMF	40
8	$Pd(OAc)_2$	(n-$Bu)_4NCl$	KH_2PO_4	DMF	68
9	$Pd(OAc)_2$	(n-$Bu)_4NCl$	KH_2PO_4	DMSO	20
10	$Pd(OAc)_2$	(n-$Bu)_4NCl$	KH_2PO_4	toluene	36
11	$Pd(OAc)_2$	(n-$Bu)_4NCl$	KH_2PO_4	MeCN	28
12	$Pd(OAc)_2$	(n-$Bu)_4NCl$	KH_2PO_4	dioxane	48
13	$Pd(PPh_3)_2Cl_2$	(n-$Bu)_4NCl$	KH_2PO_4	DMF	25
14	$PdCl_2$	(n-$Bu)_4NCl$	KH_2PO_4	DMF	45
15	$Pd_2(dba)_3$	(n-$Bu)_4NCl$	KH_2PO_4	DMF	32
16	$Pd(OAc)_2$	(n-$Bu)_4NF$	KH_2PO_4	DMF	trace
17	$Pd(OAc)_2$	(n-$Bu)_4NBr$	KH_2PO_4	DMF	41
18	$Pd(OAc)_2$	(n-$Bu)_4NOAc$	KH_2PO_4	DMF	37
19[b]	$Pd(OAc)_2$	(n-$Bu)_4NCl$	KH_2PO_4	DMF	88
20[b,c]	$Pd(OAc)_2$	(n-$Bu)_4NCl$	KH_2PO_4	DMF	65
21[b,d]	$Pd(OAc)_2$	(n-$Bu)_4NCl$	KH_2PO_4	DMF	90
22[b,e]	$Pd(OAc)_2$	(n-$Bu)_4NCl$	KH_2PO_4	DMF	51
23[b,f]	$Pd(OAc)_2$	(n-$Bu)_4NCl$	KH_2PO_4	DMF	83

[a] *Reaction conditions:* **1a** (0.2 mmol), **2a** (0.5 mmol), [Pd] (10 mol%), additive (1.5 equiv.) and base (2 equiv.) in solvent (2 mL) at 120 °C for 12 h under N_2 atmosphere.
[b] DMF (anhydrous) as solvent for 6 h.
[c] $Pd(OAc)_2$ (5 mol%).
[d] **1a** (1.0 mmol) and **2a** (2.5 mmol) for 6 h.
[e] At 100 °C for 12 h.
[f] Under air atmosphere.

Table 2. Palladium-catalyzed diarylation reactions of allylic esters (**1**) with arylboronic acids (**2**).[a]

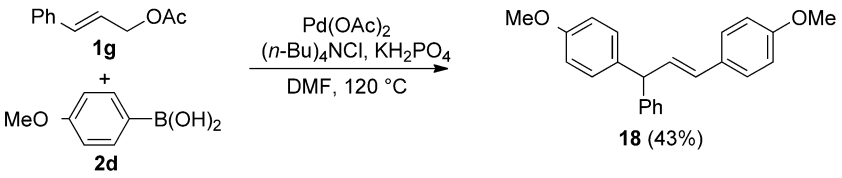


1 2

Entry	Allylic ester **1**		Arylboronic acid *2*		Time [h]	Yield[b] (Product)
1		**1a**		**2b**	8	72% (**4**)
2		**1a**		**2c**	6	76% (**5**)
3		**1a**		**2d**	6	84% (**6**)
4		**1a**		**2e**	6	66% (**7**)
5		**1a**		**2f**	7	82% (**8**)
6		**1a**		**2g**	7	56% (**9**)
7		**1a**		**2h**	8	72% (**10**)
8		**1a**		**2i**	8	62% (**11**)
9		**1a**		**2j**	7	72% (**12**)
10		**1a**		**2k**	8	70% (**13**)
11		**1a**		**2l**	11	64% (**14**)
12		**1a**		**2m**	12	72% (**15**)
13		**1a**		**2n**	11	77% (**16**)
14[c]		**1a**		**2o**	16	67% (**17**)
15		**1b**		**2d**	8	71% (**6**)
16		**1c**		**2d**	9	70% (**6**)
17		**1d**		**2d**	6	75% (**6**)
18		**1e**		**2d**	7	81% (**6**)
19		**1f**		**2d**	6	80% (**6**)

[a] *Reaction conditions:* **1** (0.2 mmol), **2** (0.5 mmol), $Pd(OAc)_2$ (10 mol%), $(n\text{-}Bu)_4NCl$ (1.5 equiv.) and KH_2PO_4 (2 equiv.) in DMF (2 mL, anhydrous) at 120 °C under N_2 atmosphere.
[b] Isolated yield.
[c] At 100 °C.

were investigated, but they were inferior to DMF in terms of yields (entries 9–12). Screening revealed that three other palladium catalysts, $PdCl_2$, $PdCl_2(PPh_3)_2$ and $Pd_2(dba)_3$, have reactivity to catalyze this reac-



Scheme 2. Diarylation of cinnamyl acetate (**1g**) with 4-methoxyphenylboronic acid (**2d**).

tion, but they were less efficient than $Pd(OAc)_2$ (entries 13–15). Notably, the phase-transfer catalysts, quaternary ammonium salts, were found to affect the reaction: The yield was lowered to some extent when using $(n\text{-Bu})_4NF$, $(n\text{-Bu})_4NBr$ or $(n\text{-Bu})_4NOAc$ as the phase-transfer catalysts (entries 16–18).[9] It was interesting to find that the yield of the desired product **3** was increased sharply to 88% when using anhydrous DMF media (entry 19). However, the yield was reduced to 65% when the reaction was carried out at a loading of 5 mol% $Pd(OAc)_2$ (entry 20). Gratifyingly, a good yield was still achieved from the reaction of allyl acetate (**1a**) on a 1-mmol scale: a 90% yield of the desired product **3** was obtained in the presence of $Pd(OAc)_2$, $(n\text{-Bu})_4NCl$, KH_2PO_4 and anhydrous DMF (entry 21). Among the reaction temperatures examined, it turned out that the reaction at 120 °C offered the best yield (entries 19 and 22). It is noteworthy that the yield of **3** was decreased slightly under an air atmosphere (entries 19 and 23).

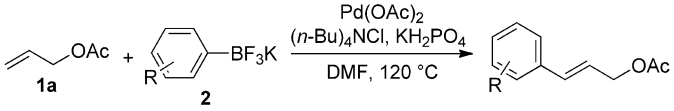
As shown in Table 2, the scope of both allylic esters **1** and arylboronic acids **2** reaction partners for the reaction was explored under the optimal reaction conditions. In the presence of $Pd(OAc)_2$, $(n\text{-Bu})_4NCl$, and KH_2PO_4, a variety of arylboronic acids **2b–2n** was employed to react with allyl acetate (**1a**) (entries 1–13). The results disclosed that several functional groups, including MeO, Me, Cl, acetyl, CF_3 and CN, on the aromatic ring of boronic acids **2** were tolerated well. MeO-substituted arylboronic acids **2b–2d**, for instance, underwent the diarylation with substrate **1a** in good yields, and the order of their reactivity is: *para*-MeO > *meta*-MeO > *ortho*-MeO (entries 1–3). We were pleased to observe that substrates **2e** and **2f** bearing a *ortho*-Me or a *para*-Me group were consistent with the optimal conditions (entries 4 and 5). Importantly, the chloro substitution in arylboronic acids **2g–2k** can be tolerated in this diarylation reaction, thereby facilitating additional modifications at the halogenated positions (entries 6–10). Screening also disclosed that the optimal conditions were compatible with electron-deficient arylboronic acids **2l–2n** (entries 11–13). Notably, heteroarylboronic acid **2o** was also a suitable substrate for the reaction with substrate **1a** in moderate yield (entry 14).

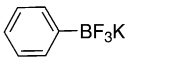
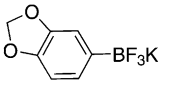
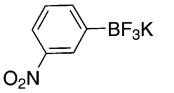
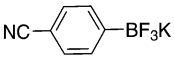
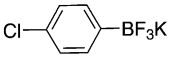
A series of allylic esters **1b–1f** was subsequently investigated in the presence of 4-methoxyphenylboronic acid (**2d**), $Pd(OAc)_2$, $(n\text{-Bu})_4NCl$, and KH_2PO_4 (entries 15–19). The results indicated that various allylic esters, including allyl benzoate (**1b**), allyl 2-phenylacetate (**1c**), allyl ethyl carbonate (**1d**), allyl 4-methylbenzenesulfonate (**1e**) and allyl pivalate (**1f**), were successfully diarylated with boronic acid **2d** in good yields (entries 15–19). For example, the reaction of allyl 4-methylbenzenesulfonate (**1e**) with 4-methoxyphenylboronic acid (**2d**), $Pd(OAc)_2$, $(n\text{-Bu})_4NCl$ and KH_2PO_4 proceeded smoothly to afford the desired product **6** in 81% yield (entry 18).

Notably, cinnamyl acetate (**1g**) could also react with 4-methoxyphenylboronic acid (**2d**) smoothly to provide (*E*)-4,4′-(3-phenylprop-1-ene-1,3-diyl)bis(methoxybenzene) (**18**) in 43% yield (Scheme 2). These findings suggest that the reaction proceeds in a manner involving an olefin isomerization process.

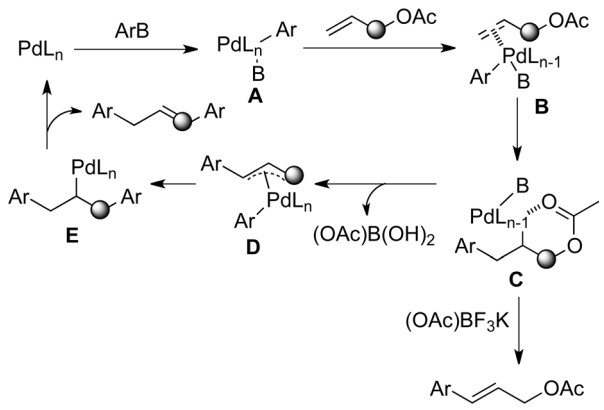
To our surprise, the selectivity was shifted towards the monoarylation products when commercially available potassium aryltrifluoroborates **2** was used to

Table 3. Palladium-catalyzed monoarylation reaction of allyl acetate (**1a**) with potassium aryltrifluoroborates (**2**).[a]



Entry	$ArBF_3K$ **2**		Time [h]	Isolated yield [%] (Product)
1		**2o**	12	55 (**19**)
2		**2p**	10	61 (**20**)
3		**2q**	16	35 (**21**)
4		**2r**	13	44 (**22**)
5		**2s**	11	48 (**23**)

[a] *Reaction conditions:* **1a** (0.2 mmol), **2** (0.5 mmol), $Pd(OAc)_2$ (10 mol%), $(n\text{-Bu})_4NCl$ (1.5 equiv.) and KH_2PO_4 (2 equiv.) in DMF (2 mL, anhydrous) at 120 °C under N_2 atmosphere.



Scheme 3. Possible mechanism.

react with allyl acetate (**1a**) under the optimal conditions (Table 3).[10] For example, treatment of allyl acetate (**1a**) with potassium phenyltrifluoroborate (**2o**), $Pd(OAc)_2$, $(n\text{-}Bu)_4NCl$, and KH_2PO_4 furnished a monoarylation product **18** in 55% yield (entry 1). Substrate **2p** with a five-membered oxygen-containing ring was also suitable for the reaction under the same conditions (entry 2). Gratifyingly, several functional groups, NO_2, CN and Cl, on the aryl rings of the potassium aryltrifluoroborates **2** were perfectly tolerated (entries 3–5).

The results disclosed that the presence of air lowered the activity of the Pd catalytic system to some extent (Table 1), implying that the present reaction may not proceed *via* an oxidative Heck-type process. Moreover, the monoarylation products were obtained from the reaction between potassium aryltrifluoroborates **2** and allyl acetate (**1a**) under the present optimal conditions. Therefore, a possible mechanism was proposed as outlined in Scheme 3. Oxidative addition of PdL_n with $ArB(OH)_2$ takes place to afford intermediate **A**.[3a–c] Subsequently, complexation of intermediate **A** with allyl acetate furnishes intermediate **B**, followed by addition to give intermediate **C**. Intermediate **C** can participate in two pathways: (i) the generation of allyl-Pd intermediate **D** involving decomposition of OAc group using arylboronic acids, and (ii) the ocurrence of reductive elimination to yield 3-arylallyl acetates in the presence of potassium aryltrifluoroborates. The reason is that the potassium aryltrifluoroborate salts are more stable than the boronic acids resulting in the ocurrence of reductive elimination prior to the generation of allylPd intermediate **D**. AllylPd intermediate **D** subsequently undergoes the second addition leading to intermediate **E**. Finally, reductive elimination of intermediate **E** takes place to furnish diarylallyl acetates and regenerate the active PdL_n species.

Conclusions

In summary, we have described a new protocol for the selective synthesis of polysubstituted olefins by palladium-catalyzed Heck-type reactions of allylic esters with boronic acids and their salts. The present method selectively proceeds involving β-OAc elimination or β-H elimination in dependence on the boronic acids and their salts, which provides a simple and selective approach to polysubstituted olefins synthesis.

Experimental Section

Typical Experimental Procedure for the Palladium-Catalyzed Diarylation Reactions of Allylic Esters (1) with Arylboronic Acids (2)

To a Schlenk tube were added allylic ester **1** (0.2 mmol), arylboronic acid **2** (0.5 mmol), $Pd(OAc)_2$ (10 mol%), $(n\text{-}Bu)_4NCl$ (1.5 equiv.), KH_2PO_4 (2.0 equiv.) and anhydrous DMF (2 mL). Then the content of the tube was stirred at 120 °C (oil bath temperature) under an N_2 atmosphere for the indicated time until complete consumption of starting material as monitored by TLC and GC-MS analysis. After the reaction was finished, the reaction mixture was cooled to room temperature, diluted in diethyl ether, and washed with brine, extracted with EtOAc, dried over anhydrous Na_2SO_4, and evaporated under vacuum. The residue was purified by flash column chromatography on silica gel (EtOAc/petroleum ether) to afford the desired products.

(*E*)-Prop-1-ene-1,3-diyldibenzene (3):[7] Colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38–7.17 (m, 10H), 6.46 (d, *J* = 15.9 Hz, 1H), 6.40–6.31 (m, 1H), 3.55 (d, *J* = 6.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 140.2, 137.5, 131.1, 129.3, 128.7, 128.5, 128.3, 127.1, 126.2, 126.1, 39.4; MS (EI 70 eV): *m/z* (%) = 194 (M^+, 100), 179 (44), 116 (57), 115 (93), 93 (54).

(*E*)-2,2′-(Prop-1-ene-1,3-diyl)bis(methoxybenzene) (4):[7] Colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 7.5 Hz, 1H), 7.32–7.14 (m, 3H), 6.92–6.82 (m, 4H), 6.77–6.65 (m, 1H), 6.42–6.32 (m, 1H), 3.83 (s, 3H), 3.82 (s, 3H), 3.56 (d, *J* = 6.9 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.3, 156.4, 129.8, 129.5, 129.1, 127.9, 127.2, 126.8, 126.5, 125.4, 120.6, 120.5, 110.8, 110.3, 55.4 (2C), 33.8; MS (EI, 70 eV): *m/z* (%) = 254 (M^+, 100), 223 (59), 145 (34), 115 (34), 91 (50).

(*E*)-3,3′-(Prop-1-ene-1,3-diyl)bis(methoxybenzene) (5): Colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.20 (t, *J* = 7.5 Hz, 2H), 6.97–6.89 (m, 2H), 6.83–6.75 (m, 4H), 6.44 (d, *J* = 15.6 Hz, 1H), 6.39–6.29 (m, 1H), 3.80 (s, 6H), 3.52 (d, *J* = 6.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.8 (2C), 141.7, 138.9, 131.1, 129.4, 129.3, 121.1, 119.7, 118.8, 114.4, 112.9, 111.5, 111.4, 55.2 (2C), 39.3; MS (EI, 70 eV): *m/z* (%) = 254 (M^+, 100), 223 (59), 145 (34), 115 (34), 91 (50); HR-MS (EI): *m/z* = 254.1305, for $C_{17}H_{18}O_2$ (M^+): calcd. 254.1307.

(*E*)-4,4′-(Prop-1-ene-1,3-diyl)bis(methoxybenzene) (6):[7] Colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.30–7.25 (m, 2H), 7.16 (d, *J* = 8.7 Hz, 2H), 6.37 (d, *J* = 15.9 Hz, 1H), 6.24–6.14 (m, 1H), 3.79 (s, 6H), 3.46 (d, *J* = 6.9 Hz, 2H);

^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.8, 158.0, 132.5, 130.4, 130.1, 129.6, 127.5, 127.1, 113.9 (2C), 55.3 (2C), 38.4; MS (EI, 70 eV): *m/z* (%) = 254 (M^+,100), 223 (49), 145 (38), 115 (32), 121 (23).

(*E*)-2,2′-(Prop-1-ene-1,3-diyl)bis(methylbenzene) (7):[7] Colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43–7.39 (m, 1H), 7.21–7.12 (m, 7H), 6.58 (d, *J* = 15.6 Hz, 1H), 6.24–6.14 (m, 1H), 3.54 (m, 2H), 2.35 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 138.4, 136.7, 136.4, 135.0, 130.2, 130.1, 129.9, 129.1, 128.9, 127.0, 126.4, 126.0, 125.6, 126.1, 37.2, 19.8, 19.4; MS (EI, 70 eV): *m/z* (%) = 222 (M^+, 100), 207 (98), 115 (78), 91 (21).

(*E*)-4,4′-(Prop-1-ene-1,3-diyl)bis(methylbenzene) (8):[7] Colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.25–7.23 (m, 3H), 7.12–7.08 (m, 5H), 6.41 (d, *J* = 15.6 Hz , 1H), 6.33–6.23 (m, 1H), 3.49 (d, *J* = 6.6 Hz, 2H), 2.33 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 137.2, 136.7, 135.6, 134.7, 130.7, 129.2, 129.1, 128.5, 128.4, 125.9, 38.9, 21.0 (2C); MS (EI, 70 eV): *m/z* (%) = 222 (M^+, 100), 207 (98), 115 (78), 91 (21).

(*E*)-2,2′-(Prop-1-ene-1,3-diyl)bis(chlorobenzene) (9): Colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.53–7.47 (m, 1H), 7.40–7.12 (m, 8H), 6.87 (d, *J* = 15.6 Hz, 1H), 6.37–6.27 (m, 1H), 3.71 (d, *J* = 6.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 138.4, 136.8, 136.4, 135.0, 130.2 (2C), 129.9, 129.1, 129.0, 127.0, 126.4, 126.1, 126.0, 125.6, 37.2; MS (EI, 70 eV): *m/z* (%) = 264 (M^++2, 27), 262 (M^+, 41), 227 (100), 192 (58), 115 (78); HR-MS (EI): *m/z* = 262.0313, calcd. for $C_{15}H_{12}{}^{35}Cl_2$ (M^+): 262.0316.

(*E*)-4,4′-(Prop-1-ene-1,3-diyl)bis(chlorobenzene) (10):[11] Colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.29–7.25 (m, 6H), 7.16 (d, *J* = 4.8 Hz, 2H), 6.40–6.36 (m, 1H), 6.31–6.26 (m, 1H), 3.50 (d, *J* = 3.9 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 138.2, 135.7, 132.8, 132.1, 130.2, 130.0, 129.3, 128.7, 128.6, 127.3, 38.6 (2C); MS (EI, 70 eV): *m/z* (%) = 264 (M^++2, 29), 262 (M^+, 45), 227 (100), 192 (35), 115 (56).

(*E*)-2,2′-(Prop-1-ene-1,3-diyl)bis(4-chloro-1-methoxybenzene) (11): Colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38–7.36 (m, 1H), 7.14–7.10 (m, 3H), 6.79–6.74 (m, 2H), 6.68–6.54 (m, 1H), 6.36–6.26 (m, 1H), 3.83 (s, 3H), 3.82 (s, 3H), 3.50 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.8, 154.9, 130.5, 129.7, 129.6, 128.1, 127.5, 126.9, 126.2, 125.6, 125.3, 124.9, 111.9, 111.4, 55.7 (2C), 33.62; MS (EI, 70 eV): *m/z* (%) = 324 (M^++2, 30), 322 (M^+, 58), 286 (74), 178 (49), 165 (23), 145 (100); HR-MS (EI): *m/z* = 322.0525, calcd. for $C_{17}H_{16}{}^{35}Cl_2O_2$ (M^+): 322.0527.

(*E*)-4,4′-(Prop-1-ene-1,3-diyl)bis(1,2-dichlorobenzene) (12):[11] Colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43–7.39 (m, 1H), 7.37–7.35 (m, 2H), 7.31–7.30 (m, 1H), 7.16 (d, *J* = 8.4 Hz, 1H), 7.05 (d, *J* = 8.4 Hz, 1H), 6.34 (d, *J* = 15.9 Hz, 1H), 6.30–6.23 (m, 1H), 3.49 (d, *J* = 5.1 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 139.7, 137.1, 132.7, 132.5, 131.1, 130.6, 130.5(2C), 129.9(2C), 129.7, 128.1, 127.9, 125.4, 38.2; MS (EI, 70 eV): *m/z* (%) = 332 (M^+, 63), 294 (89), 189 (37),149 (100), 94 (46).

(*E*)-4,4′-(prop-1-ene-1,3-diyl)bis(bromobenzene) (13): White solid; mp 65.9–67.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.48–7.44 (m, 4H), 7.25 (d, *J* = 8.5 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.42–6.32 (m, 2H), 3.52 (d, *J* = 6.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 138.8, 136.2, 131.7, 131.6, 130.45, 130.4, 129.4, 127.7, 121.0, 120.2, 38.7; LR-MS (EI, 70 eV): *m/z* (%) = 354 (M^++2, 10), 352 (M^+, 20), 350 (M^+−2, 10), 192 (100), 115 (43), 271 (25), 273 (25); HR-MS (EI): *m/z* = 349.9306, calcd. for $C_{15}H_{12}{}^{79}Br_2$ (M^+): 349.9310.

(*E*)-4,4′-(Prop-1-ene-1,3-diyl)bis(acetophenone) (14):[7] Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.86–7.82 (m, 2H), 7.35 (d, *J* = 8.7 Hz, 2H), 7.25 (d, *J* = 8.7 Hz, 2H), 6.45–6.37 (m, 2H), 3.50 (d, *J* = 2.7 Hz, 2H), 2.53 (s, 3H), 2.51 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 197.8, 197.6, 145.2, 141.8, 135.6, 131.1, 130.9, 128.9, 128.8, 128.7, 128.5, 126.2, 39.3, 26.6 (2C); MS (EI, 70 eV): *m/z* (%) = 278 (M^+, 100), 263 (97), 235 (41), 207 (26), 124 (32).

(*E*)-4,4′-(Prop-1-ene-1,3-diyl)bis((trifluoromethyl)benzene) (15): Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.51–7.46 (m, 4H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 6.41 (d, *J* = 16.0 Hz, 1H), 6.38–6.32 (m, 1H), 3.50 (d, *J* = 6.0 Hz , 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.6, 140.6, 130.8, 130.6, 129.0, 128.7, 126.4 (d, *J* = 9.4 Hz, 1C), 125.6 (2C), 125.5 (2C), 124.3 (q, *J* = 270.3 Hz, 1C), 39.1; MS (EI, 70 eV): *m/z* (%) = 330 (M^+, 72), 261 (100), 246 (17), 183 (36), 115 (45); HR-MS (ESI): *m/z* = 330.0841, calcd. for $C_{17}H_{12}F_6$ (M^+): 330.0843.

(*E*)-4,4′-(Prop-1-ene-1,3-diyl)dibenzonitrile (16): Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.71 (d, *J* = 8.5 Hz, 2H), 7.63 (d, *J* = 8.5 Hz, 2H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 6.58 (d, *J* = 16.0 Hz, 1H), 6.36–6.32 (m, 1H), 4.69 (dd, *J* = 5.0 Hz, 1.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.5, 140.7, 132.9, 132.4, 131.8, 127.9, 127.4, 127.1, 118.8, 118.4, 112.4, 111.3, 30.9; MS (EI, 70 eV): *m/z* (%) = 244 (M^+, 85), 243 (100), 140 (27), 89 (18), 228 (16); HR-MS (EI): *m/z* = 244.0998, calcd. for $C_{17}H_{12}N_2$ $(M)^+$: 244.1001.

(*E*)-2,2′-(Prop-1-ene-1,3-diyl)dithiophene (17):[7] Colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.17–7.11 (m, 2H), 6.96–6.91 (m, 3H), 6.86–6.85 (m, 1H), 6.51 (d, *J* = 15.6 Hz, 1H), 6.25–6.16 (m, 1H), 3.70 (d, *J* = 6.9 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.7, 142.3, 128.0, 127.3, 127.0, 125.1, 124.9, 124.6, 123.9, 123.8, 33.1; MS (EI, 70 eV): *m/z* (%) = 206 (M^+, 100), 205 (32), 173 (26), 97 (34).

(*E*)-4,4′-(3-Phenylprop-1-ene-1,3-diyl)bis(methoxybenzene) (18):[7] Colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.33–7.26 (m, 4H), 7.24–7.19 (m, 3H), 7.16–7.13 (m, 2H), 6.86–6.82 (m, 4H), 6.55–6.47 (m, 1H), 6.26 (d, *J* = 14.4 Hz, 1H), 4.82 (d, *J* = 7.2 Hz, 1H), 3.80 (s, 3H), 3.79 (s, 3H); ^{13}C (NMR 125 MHz): δ = 159.0, 158.1, 144.1, 135.9, 130.8, 130.6, 130.2, 129.6, 128.6, 128.4, 127.4, 126.6, 126.3, 113.9, 113.8, 55.3 (2C), 53.4; MS (EI, 70 eV): *m/z* (%) = 330 (M^+, 100), 299 (56), 222 (90), 221 (33), 121 (41).

(*E*)-Cinnamyl acetate (19):[5b] Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.32–7.30 (m, 2H), 7.26–7.23 (m, 2H), 7.19–7.16 (m, 1H), 6.58 (d, *J* = 16.0 Hz, 1H), 6.24–6.18 (m, 1H), 4.66–4.64 (m, 2H), 2.02 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.8, 136.2, 134.2, 128.6, 128.1, 126.6, 123.2, 65.1, 21.0; IR (KBr): ν = 1741 cm^{-1}; MS (EI, 70 eV): *m/z* (%) = 176 (M^+, 1), 133 (48), 115 (100), 92 (40), 77 (22).

(*E*)-3-(Benzo[*d*][1,3]dioxol-5-yl)allyl acetate (20):[12] Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.87–6.86 (m, 1H), 6.75–6.74 (m, 1H), 6.70–6.68 (m, 1H), 6.49 (d, *J* = 15.1 Hz, 1H), 6.08–6.03 (m, 1H), 6.02–5.89 (m, 2H), 4.62 (d, *J* = 4.5 Hz, 2H), 2.03 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.9, 148.1, 147.7, 134.1, 130.7, 121.5, 121.3, 108.3, 105.8, 101.2, 65.2, 21.0; IR (KBr): ν = 1732 cm^{-1}; MS (EI, 70 eV):

m/*z* (%) = 220 (M^+, 98), 103 (100), 131 (96), 177 (45), 91 (46).

(*E*)-3-(3-Nitrophenyl)allyl acetate (21): Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.18 (s, 1H), 8.05–8.03 (m, 1H), 7.64–7.61 (m, 1H), 7.45–7.42 (m, 1H), 6.63 (d, *J* = 16.0 Hz, 1H), 6.39–6.33 (m, 1H), 4.71–4.69 (m, 2H), 2.06 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.8, 148.6, 138.0, 132.4, 131.2, 129.6, 126.7, 122.6, 121.2, 64.3, 20.9; IR (KBr): ν = 1726 cm^{-1}; MS (EI, 70 eV): *m*/*z* (%) = 221 (M^+, 17), 162 (13), 161 (29), 115 (100), 77 (13); HR-MS (EI): *m*/*z* = 221.0686, calcd. for $C_{11}H_{11}NO_4$ $(M)^+$: 221.0688.

(*E*)-3-(4-Cyanophenyl)allyl acetate (22):[5b] Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.54 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 6.58 (d, *J* = 17.0 Hz, 1H), 6.39–6.30 (m, 1H), 4.69–4.68 (m, 2H), 2.05 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.7, 140.7, 132.9, 132.5, 131.8, 127.9, 127.4, 127.1, 118.8, 111.3, 64.4, 20.9; IR (KBr): ν = 1738 cm^{-1}; MS (EI, 70 eV): *m*/*z* (%) = 201 (M^+, 34), 159 (100), 140 (86), 130 (94), 89 (16).

(*E*)-3-(4-Chlorophenyl)allyl acetate (23):[5b] Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.25–7.19 (m, 4H), 6.52 (*J* = 16.0 Hz, 1H), 6.21–6.16 (m, 1H), 4.65–4.64 (m, 2H), 2.03 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.8, 134.7, 133.8, 132.8, 128.8, 127.8, 123.9, 64.8, 20.9; IR (KBr): ν = 1749 cm^{-1}; MS (EI, 70 eV): *m*/*z* (%) = 212 (M^++2, 7.5), 210 (M^+, 22.5), 168 (30), 116 (33), 115 (100).

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