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Nickel-catalyzed decarboxylative coupling reaction of alkynyl carboxylic acids and allyl acetates

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ABSTRACT

The coupling reaction of aryl alkynyl carboxylic acids and allyl acetates was carried out in the presence of nickel catalyst to produce the allyl alkynes in good yields. The optimized condition is that alkynyl carboxylic acid (1.0 equiv), allyl acetate (2.0 equiv), Ni(OAc)₂·4H₂O (10 mol %), AgOAc (10 mol %), and zinc (1.0 equiv) were reacted at 100 °C for 0.5 h. In addition, when allyl alcohol was employed instead of allyl acetate, the desired product was obtained in good yield. In addition, when the reaction was carried out in the presence of base such as DBU and Cs₂CO₃, the allene compounds were formed in good yield.

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Transition-metal-catalyzed cross coupling reactions are one of the most important methods to construct the carbon-carbon and carbon-hetero atom bonds.¹ Among them, named reactions such as Kumada, Mizoroki-Heck, Negishi, Migita-Kosugi-Stille, Suzuki, Hiyama, Sonogashira, and Buchwald-Hartwig couplings have been well studied and widely used.² Generally, they consist of coupling of aryl halides (or pseudohalides) and nucleophiles in the presence of palladium or nickel catalyst. For the bond formation of sp² carbon and sp carbon, Sonogashira coupling reaction, which involves the coupling reaction of aryl halides and terminal alkyne in the presence of palladium as a catalyst and copper as a co-catalyst has been most frequently used.³

As shown in Scheme 1, in 2008, we first reported the decarboxylative coupling reaction of alkynyl carboxylic acids with aryl iodides and bromides to construct the bond of Csp and Csp².⁴ Since then, a number of decarboxylative coupling reactions of alkynyl carboxylic acids have been reported by several groups including our group.⁵ The group of Lee, P. H. reported the coupling reaction with vinyl and aryl triflates by using Ag₂O.⁶ Li group extended the Pd-catalyzed decarboxylative coupling to aryl chlorides and benzyl halides by optimizing the ligand such as X-Phos.⁷ Furthermore, copper-catalyzed decarboxylative coupling reactions were first accomplished by You and Xue group,⁸ and modified by Mao group.⁹ Instead of aryl halides as coupling partner, aryl boronic acid has been employed by Loh group.¹⁰ In addition, the decarboxylative carbon–heteroatom such as C–N and C–P cross-couplings have also been reported.¹¹ Moreover, the decarboxylative homocouplings,¹² the decarboxylative carbonylations,¹³ the decarboxylations¹⁴, and the multicomponent coupling reactions¹⁵ with alkynyl carboxylic acids have also been developed by our group and others.

The reason for the increase in attention toward the alkynyl carboxylic acid as an alkyne source is that alkynyl carboxylic acid has several advantages with respect to storage and handling. Especially, it is a good reagent to serve as an alkyne source with low molecular weight.¹⁶ In addition, alkynyl carboxylic acid was easily prepared from the one-step coupling reaction of propiolic acid and aryl iodide. ^{5f} However, although a number of decarboxylative coupling reactions have been developed, there is no available report on nickel-catalyzed decarboxylative coupling system. In addition, a few examples of allylation have been reported in the intermolecular decarboxylative coupling even though allyl alkynes are important building blocks.¹⁷

For the preparation of allyl alkynes, copper¹⁸ and nickel¹⁹-catalyzed allylation of alkyne has been reported. However, the reported methods are associated with certain drawbacks. The condition of strong base imparts narrow scope of substrates and the employment of carbon-metal bond reagents leads to generation of metal waste problem. In addition, some cases still need long reaction times and presence of an inert atmosphere. In the case of nickelcatalyzed coupling reaction of allyl acetate and terminal alkynes, only one example on coupling reaction of phenyl acetylene and allyl acetate is available, and moreover it requires air sensitive nickel (0). Therefore, the simple and more general method still needs to





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Scheme 1. The decarboxylative coupling reactions of alkynyl carboxylic acids.

Table 1

Optimization of decarboxylative allylation^a

	√→→→ √OH	+ OAc	cat. Ni / Ligand Additive solvent, 100 °C, 0.5 h		<u> </u>	
	1a	2a				
Entry	Ni	Ligand	Additive ^b	Zn ^c	Solvent	Yield ^d (%)
1	Ni(PPh ₃) ₂ Cl ₂	-	AgOAc	-	Toluene	Trace
2	$Ni(PPh_3)_2Cl_2$	_	AgOAc	-	Diglyme	Trace
3	$Ni(PPh_3)_2Cl_2$	_	AgOAc	-	DMF	14
4	$Ni(PPh_3)_2Cl_2$	_	AgOAc	-	DMSO	25
5	NiCl ₂	_	AgOAc	-	DMSO	29
6	NiF ₂	_	AgOAc	-	DMSO	27
7	Ni(OAc) ₂ ·4H ₂ O	_	AgOAc	-	DMSO	32
8	Ni(OAc) ₂ ·4H ₂ O	dppb	AgOAc	-	DMSO	65
9	Ni(OAc) ₂ ·4H ₂ O	dppe	AgOAc	-	DMSO	54
10	Ni(OAc) ₂ ·4H ₂ O	dppf	AgOAc	-	DMSO	38
11	Ni(OAc) ₂ ·4H ₂ O	BINAP	AgOAc	-	DMSO	18
12	Ni(OAc) ₂ ·4H ₂ O	Xantphos	AgOAc	-	DMSO	12
13	Ni(OAc) ₂ ·4H ₂ O	dppb	AgOAc	Zn	DMSO	96
14	Ni(OAc) ₂ ·4H ₂ O	dppb	_	Zn	DMSO	82
15	Ni(OAc) ₂ ·4H ₂ O	dppb	_	-	DMSO	Trace
16	Ni(OAc) ₂ ·4H ₂ O	dppb	KOAc	Zn	DMSO	88
17	Ni(OAc) ₂ ·4H ₂ O	dppb	K ₂ CO ₃	Zn	DMSO	86
18 ^e	$Ni(OAc)_2 \cdot 4H_2O$	dppb	AgOAc	Zn	DMSO	55
19 ^f	$Ni(OAc)_2 \cdot 4H_2O$	dppb	AgOAc	Zn	DMSO	28
20 ^g	$Ni(OAc)_2 \cdot 4H_2O$	dppb	AgOAc	Zn	DMSO	48

^a Reaction condition: **1a** (0.3 mmol), **2a** (0.6 mmol), nickel catalyst (0.03 mmol), ligand (0.036 mmol), and additives were reacted in solvent (1.0 mL) at 100 °C for 0.5 h. ^b 0.03 mmol was used.

^c 0.3 mmol was used.

^d Determined by gas chromatography with internal standard.

^e The reaction time was 3 h.

^f The reaction temperature was 80 °C.

^g 5 mol % Ni(OAc)₂· $4H_2O$ was used.

be developed. Herein, for the first time in the literature we report a nickel-catalyzed decarboxylative coupling reaction of the aryl alkynyl carboxylic acids and allyl acetate (or alcohol).

To find the optimized condition for the nickel-catalyzed decarboxylative allylation, the coupling of phenyl propiolic acid and allyl acetate was chosen as a model reaction. The results are summarized in Table 1. First, a variety of solvents was tested. Toluene and diglyme did not result in the formation of the coupling product (entries 1 and 2). DMF and DMSO afforded the desired product in 14% and 25% yields, respectively (entries 3 and 4). The nickel source seemed to have a minor effect on the yields of the reaction: Ni(PPh₃)₂Cl₂, NiCl₂, NiF₂, and Ni(OAc)₂·4H₂O all performed similarly (entries 4–7). Among them, Ni(OAc)₂·4H₂O as the nickel source, we employed a variety of ligands. Among the ligands tested, 1,4-bis(diphenylphosphino)butane (dppb) showed the best result (entry 8). Whereas, 1,2-bis(diphenylphosphino)ethane (dppe) and 1,1'-bis(diphenylphosphino)ferrocene (dppf) gave the coupled product in 54% and 38% yields, respectively (entries 9 and 10). However, BINAP and Xantphos showed poor yields (entries 11 and 12). When zinc dust was added as a reducing agent, the yield was increased to 96% (entry 13). When the reaction was carried out in the presence of zinc dust without AgOAc, the yield was 82% (entry 14). However, no coupled product was formed without AgOAc or Zn (entry 15). In addition, other additives such as KOAc and K_2CO_3 afforded lower yields than AgOAc (entries 16 and 17). When the reaction time was increased to 3 h, the yield of product was decreased. The product was converted

Table 2

The decarboxylative allylation using nickel catalyst^a

			0		Ni(OAc) ₂ ·4H ₂ O (10 mol%) dppb (12 mol%)			
	Ar-		+ allyl=OAc		Zn (1.0 equiv)	allyl		
		1	2		DMSO, 100 °C, 0.5 h	3		
Entry	1		2		Product			Yield ^b (%)
1	(О ОН	1a	OAc	2a			Заа	95
2	Me-	1b	OAc	2a	Me-		3ba	79
3	Et-	1c	OAc	2a	Et-		3ca	92
4	^t Bu	1d	OAc	2a	^t Bu		3da	95
5	MeO-	1e	OAc	2a	MeO		3ea	84
6	CI-	1f	OAc	2a	ci-		3fa	54
7	Me → → → O OH	1g	<i>_</i> ∕∕OAc	2a			3ga	92
8	Me OH	1h	OAc	2a	Me		3ha	94
9	С Он	1i	OAc	2a			3ia	88
10	Ne −	1j	OAc	2a			3ja	74
11		1k	OAc	2a			3ka	62
12	⟨¬)→→	1a	OAc n-Pent	2b		}→==→	3ab-L 3ab-B	$\begin{array}{l} 64^c (51/49)^d \\ 61^{c,e} (67/33)^d \end{array}$
13	(О ОН	1a	Ph	2c	Ph		3ac	71

^a Reaction condition: **1** (3.0 mmol), **2** (6.0 mmol), Ni(OAc)₂·4H₂O (0. 3 mmol), dppb (0. 36 mmol), AgOAc (0.3 mmol), and Zn (3.0 mmol) were reacted in DMSO (10.0 mL) at 100 °C for 0.5 h.

^b Isolated yield.²⁰

^c The yield of the mixture of **3ab-L** and **3ab-B**.

^d The ratio of **3ab-L/3ab-B**.²¹

^e Xantphos was used.

into unidentified compounds (entry 18). In addition, when the reaction temperature and the amount of catalyst were decreased to 80 °C and 5 mol %, respectively, both the reactions showed low yield of product (entries 19 and 20). Finally, the optimized condition was obtained as following: alkynyl carboxylic acid (1.0 equiv), allyl acetate (2.0 equiv), Ni(OAc)₂·4H₂O (10 mol %), AgOAc (10 mol %), and zinc (1.0 equiv) were reacted at 100 °C for 0.5 h.

To evaluate further the optimized conditions for the decarboxylative allylation, a variety of aryl alkynyl carboxylic acids were coupled with allyl acetate. The results are summarized in Table 2. The aryl alkynyl carboxylic acids were prepared from the coupling of aryl iodides and propiolic acid in the presence of palladium catalyst. As expected, phenylpropiolic acid afforded the desired product in 95% yield (entry 1). Aryl propiolic acids bearing alkyl substituent at para position such as **1b**, **1c**, and **1d** resulted in the formation of corresponding products in 79%, 92%, and 95% yields, respectively (entries 2–4). Typically, 3-(4-methoxylphenyl)propiolic acid (**1e**) showed 84% yield (entry 5). The 3-(4-chlorophenyl)propiolic acid which has an electron withdrawinggroup afforded the desired product in 54% yield (entry 6). The

Table 3

The decarboxylative coupling reaction of phenyl propiolic acid and allyl alcohol



^a Isolated yield.

Table 4

Synthesis of allenes from the decarboxylative coupling reactions



^a Isolated yield.²⁴

3-(o-tolyl)- and 3-(m-tolyl) propiolic acids also showed good yields (entries 7 and 8). And 3-(naphth-1-yl)propiolic acid showed good yields of product (entry 9). The substrates bearing carbonyl group such as ketone and ester provided the corresponding coupled products in good yields (entries 10 and 11). When oct-1-en-3-yl acetate was employed in the coupling of phenyl propiolic acid, two regioisomers (which are the branched one and the linear one) were formed with the ratio of 51–49. To increase its selectivity, a variety of ligands were rescreened, finally, Xantphos afforded the best result (entry 12). However, when cinnamyl acetate was employed, only linear product was formed (entry 13).

It is well known that allyl acetate is obtained from the reaction of allyl alcohol and acetic anhydride. This information stimulated us to use allyl alcohol instead of allyl acetate for the coupling reaction. As can be seen in Table 3, the coupling reaction of phenylpropiolic acid and allyl alcohol **4** in the presence of acetic anhydride produced the decarboxylative allylation product **3aa** with 74% yield. Even in the absence of acetic anhydride, the allyl alcohol was coupled with phenyl propiolic acid to afford the desired product in 34% yield. When the amount of allyl alcohol was increased to 10 equiv, the yield of product was increased to 68%.

The structure of allene also serves as one of the important building blocks in the organic synthesis.²² We found that the allene compound was obtained when the coupling reaction of phenyl propiolic acid and allyl acetate was carried out in the presence of weak bases such as Cs_2CO_3 and DBU. As shown in Table 4, 1,2,4pentatrienylbenzene (**5a**)²³ was formed in 62% yield in the presence of Cs_2CO_3 , and in 69% yield in the presence of DBU (entries 1 and 2). When the reaction was run with **1b**, the desired product **5b** was formed in 65% yield (entry 3).

In summary, the nickel-catalyzed decarboxylative allylations of aryl alkynyl carboxylic acids were developed. To the best of our knowledge, this is the first nickel-catalyzed decarboxylative coupling reactions in literature so far. The coupling reactions showed the best yield when Ni(OAc)₂·4H₂O (10 mol %), dppb (12 mol %), AgOAc (10 mol %), and Zn (1.0 equiv) were reacted in the presence of DMSO at 100 °C. The presented method has several advantages. The reaction time is short (30 minutes) and the usage of the air stable Ni(OAc)₂·4H₂O with Zn provides the convenient tool without the need of air sensitive nickel (0) source. As an allyl reagent, allyl alcohol was also coupled with aryl alkynyl carboxylic acid to produce the allylated alkynes in good yields. In addition, the allene was obtained through one-pot reaction in the presence of a suitable base.

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- Typical experimental procedure: Ni(OAc)2.4H2O (74.6 mg, 0.3 mmol), 1,4-20. bis(diphenylphosphino)butane (153.5 mg, 0.36 mmol), aryl alkynyl carboxylic acids (3.0 mmol), allyl acetate (6.0 mmol), AgOAc (50.1 mg, 0.3 mmol), and zinc (196.2 mg, 3.0 mmol) were combined with DMSO (10 mL) in a small round-bottomed flask. The resulting mixture was stirred at 100 °C for 0.5 h. The reaction mixture was poured into water and extracted with EtOAc. The solvent was removed under vacuum, and the resulting crude product was purified by flash chromatography on silica gel to give the desired product. Pent-4-en-1-ynylbenzene (3aa):

¹H NMR (300 MHz, CDCl₃) δ 7.46–7.22 (m, 5H), 5.89 (m, 1H), 5.40 (m, 1H), 5.16 (m, 1H), 3.18 (dt, *J* = 5.3 1.8 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 132.4, 131.5, 128.2, 127.7, 123.7, 116.2, 86.5, 82.8, 23.7.

1-Methyl-4-(pent-4-en-1-ynyl)benzene (3ba):

¹H NMR (300 MHz, CDCl₃) δ 7.31 (d, *J* = 8.1 Hz, 2H), 7.09 (d, *J* = 7.8 Hz, 2H), 5.89 (m, 1H), 5.40 (m, 1H), 5.15 (m, 1H), 3.18 (dt, *J* = 5.3, 1.8 Hz, 2H), 2.33 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 137.7, 132.6, 131.4, 128.9, 120.6, 116.1, 85.7, 82.9, 23.7, 21.4

1-Ethyl-4-(pent-4-en-1-vnvl)benzene (3ca):

¹ H NMR (300 MHz, CDCl₃) δ 7.34 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 5.90 (m, 1H), 5.40 (m, 1H), 5.15 (m, 1H), 3.18 (dt, *J* = 5.2, 1.8 Hz, 2H), 2.64 (q, *J* = 7.6 Hz, 2H), 1.22 (t, *J* = 7.6 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 144.0, 132.6, 131.5, 127.7, 120.8, 116.1, 85.7, 82.9, 28.7, 23.7, 16.3.

1-tert-Butyl-4-(pent-4-en-1-ynyl)benzene (3da):

¹H NMR (300 MHz, CDCl₃) *o* 7.36 (d, *J* = 8.7 Hz, 2H), 7.30 (d, *J* = 8.7 Hz, 2H), 5.89 (m, 1H), 5.40 (m, 1H), 5.15 (m, 1H), 3.17 (dt, *J* = 5.2, 1.8 Hz, 2H), 1.29 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ 150.8, 132.6, 131.3, 125.2, 120.7, 116.1, 85.7, 82.9, 34.6, 31.2. 23.7.

1-Methoxy-4-(pent-4-en-1-ynyl)benzene (**3ea**):

¹H NMR (300 MHz, CDCl₃) δ 7.36 (d, J = 8.6 Hz, 2H), 6.80 (d, J = 8.9 Hz, 2H), 5.89

(m, 1H), 5.39 (m, 1H), 5.15 (m, 1H), 3.78 (s, 3H), 3.17 (dt, J = 5.3, 1.8 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) & 159.1, 132.9, 132.6, 116.0, 115.8, 113.8, 84.9, 82.6, 55.2, 237

1-Chloro-4-(pent-4-en-1-ynyl)benzene (3fa):

¹H NMR (300 MHz, CDC₃) δ 7.35 (d, *J* = 8.7 Hz, 2H), 7.26 (d, *J* = 9.0 Hz, 2H), 5.89 (m, 1H), 5.38 (m, 1H), 5.17 (m, 1H), 3.18 (dt, *J* = 5.3, 1.8 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 133.7, 132.8, 132.2, 129.6, 122.2, 116.4, 87.6, 81.8, 23.7. 1-Methyl-3-(pent-4-en-1-ynyl)benzene (3ga):

¹H NMR (300 MHz, CDCl₃) δ 7.28-7.04 (m, 4H), 5.89 (m, 1H), 5.40 (m, 1H), 5.15 (m, 1H), 3.18 (dt, *J* = 5.3, 1.8 Hz, 2H), 2.30 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 137.8, 132.5, 132.2, 128.6, 128.1, 123.5, 116.2, 86.1, 83.0, 23.7, 21.2.

1-Methyl-2-(pent-4-en-1-ynyl)benzene (3ha):

1-Methyl-2-(pent-4-en-1-ynyl)benzene (Sna). ¹H NMR (300 MHz, CDCl₃) δ 7.39 (d, J = 7.2 Hz, 1H), 7.18–7.06 (m, 3H), 5.91 1H), 5.43 (m, 1H), 5.16 (m, 1H), 3.23 (dt, J = 5.2, 1.8 Hz, 2H), 2.43 (s, 3H); NMR (75 MHz, CDCl₃) & 139.9, 132.6, 131.9, 129.3, 127.7, 125.4, 123.5, 116.1, 90.4, 81.8, 23.8, 20.7;

1-(Pent-4-en-1-ynyl)naphthalene (3ia):

¹H NMR (300 MHz, CDCl₃) δ 8.36 (m, 1H), 7.85-7.32 (m, 6H), 5.97 (m, 1H), 5.50 (m, 1H), 5.21 (m, 1H), 3.33 (dt, J = 5.2, 1.8 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 133.4, 133.1, 132.5, 130.1, 128.2, 128.1, 126.5, 126.2, 125.2, 121.4, 116.3, 91.5, 80.9, 24.0.

1-(4-(Pent-4-en-1-ynyl)phenyl)ethanone (3ja):

¹H NMR (300 MHz, CDCl₃) δ 7.93–7.84 (m, 2H), 7.54–7.45 (m, 2H), 5.90 (m, 1H), 5.40 (m, 1H), 5.19 (m, 1H), 3.22 (dt, J = 5.3, 1.8 Hz, 2H), 2.59 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) & 197.4, 135.9, 131.9, 131.7, 128.2, 127.0, 116.6, 90.4, 82.2, 26.6. 23.8.

Methyl 4-(pent-4-en-1-ynyl)benzoate (3ka):

¹H NMR (300 MHz, CDCl₃) δ 7.97 (m, 2H), 7.47 (m, 2H), 5.90 (m, 1H), 5.40 (m, 1H), 5.18 (m, 1H), 3.91 (s, 3H), 3.22 (dt, J = 5.3, 1.8 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 166.6, 131.9, 131.5, 129.4, 129.1, 128.5, 116.5, 90.0, 82.3, 52.2, 23.8. (E)-Pent-1-en-4-yne-1,5-diyldibenzene (**3ac**):

 $^{(1)}$ H NMR (300 MHz, CDCl₃) δ 7.48–7.19 (m, 10H), 6.70 (dt, *J* = 15.8, 1.8 Hz, 1H), 6.23 (dt, *J* = 15.7, 5.6 Hz, 1H), 3.35 (dd, *J* = 5.6, 1.8 Hz, 2H); ¹³C NMR (75 MHz, 12) (m, 10) (m, CDCl₃) δ 137.1, 131.6, 131.4, 128.8, 128.5, 128.2, 127.8, 127.3, 126.2, 124.2, 123.6, 86.7, 82.8, 23.0.

- The ratio was determined by ¹H NMR: (*E*)-dec-4-en-1-ynylbenzene (**3ab-L**):¹H NMR (300 MHz, CDCl₃) δ 7.42 (m, 2H), 7.30–7.25 (m, 3H), 5.75 (m, 1H), 5.50 (m, 1H), 3.13 (ddd, J = 5.5, 2.8, 1.4 Hz, 2H), 2.05 (dq, J = 6.9, 1.0 Hz, 2H), 1.28-1.31 (m, 6H), 0.90 (t, J = 6.8 Hz, 3H); (3-Vinyloct-1-ynyl)benzene (**3ab-B**): ¹H NMR (300 MHz, CDCl₃) δ 7.42 (m, 2H), 7.29-7.25 (m, 3H), 5.84 (ddd, *J* = 16.9, 10.0, 6.1 Hz, 1H), 5.36 (dt, J = 17.0, 1.6 Hz, 1H), 5.11 (dt, 10.0, 1.5 Hz, 1H), 3.27 (q, / = 6.7 Hz, 1H), 1.46 (m, 2H), 1.32–1.23 (m, 6H), 0.88 (t, / = 6.8 Hz, 3H).
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- Typical experimental procedure: Ni(OAc)₂·4H₂O (74.6 mg, 0.3 mmol), 1,4-24. bis(diphenylphosphino)butane (153.5 mg, 0.36 mmol), aryl alkynyl carboxylic acids (3.0 mmol), allyl acetate (6.0 mmol), AgOAc (50.1 mg, 0.3 mmol), zinc (196.2 mg, 3.0 mmol), and DBU (456.7 mg, 3.0 mmol) were combined with DMSO (10 mL) in a small round-bottomed flask. The resulting mixture was stirred at 100 °C for 2 h. The reaction mixture was poured into water and extracted with EtOAc. The solvent was removed under vacuum, and the resulting crude product was purified by flash chromatography on silica gel to give the desired product.

Penta-1.2.4-trienvlbenzene (5a):

¹H NMR (300 MHz, CDCl₃) δ 7.35–7.16 (m, 5H), 6.42–6.13 (m, 3H), 5.30 (m, 1H). 5.09 (m, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 209.4, 133.8, 132.0, 128.6, 127.1, 126.9, 116.8, 98.3, 95.9.

1-Methyl-4-(penta-1,2,4-trienyl)benzene (5b):

¹ H NMR (300 MHz, CDCl₃) δ 7.21–7.11 (m, 4H), 6.35–6.17 (m, 3H), 5.29 (m, 1H), 5.08 (m, 1H), 2.33 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 209.2, 137.0, 132.3, 130.8, 129.4, 126.9, 116.6, 98.2, 95.7, 29.7.