#### Tetrahedron 84 (2021) 131996

Contents lists available at ScienceDirect

### Tetrahedron

journal homepage: www.elsevier.com/locate/tet

# Counteranion-controlled regioselectivity in palladium-catalyzed allylic amination of dienyl allylic carbonates

Meng-Lan Shen<sup>a</sup>, Pu-Sheng Wang<sup>a,\*</sup>, Liu-Zhu Gong<sup>a, b,\*\*</sup>

<sup>a</sup> Hefei National Laboratory for Physical Sciences at the Microscale and Department of Chemistry, University of Science and Technology of China, Hefei, 230026, PR China

<sup>b</sup> Center for Excellence in Molecular Synthesis of CAS, Hefei, 230026, China

#### A R T I C L E I N F O

Article history: Received 19 December 2020 Received in revised form 28 January 2021 Accepted 31 January 2021 Available online 13 February 2021

Keywords: Palladium catalysis Allylic amination Regioselectivity Phosphoramidite Allylic amine

#### ABSTRACT

A regioselective Pd-catalyzed allylic amination reaction of dienyl allylic carbonates and aromatic amines has been developed by means of phosphoramidite-palladium catalysis. The regioselectivity could be altered by the counterion of the  $\pi$ -allylpalladium intermediate. As a result, either branched Z-dienyl allylic amines or linear conjugated allylic amines were generated in high levels of regioselectivity from the same substrates by tuning the reaction conditions.

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#### 1. Introduction

The palladium-catalyzed allylic substitution reaction is one of the most powerful tools for efficient assembly of carbon-carbon and carbon-heteroatom bonds. [1]. These reactions generally proceed via a ( $\pi$ -allyl)palladium intermediate, on which the nucleophile can attack at either of terminus to principally provide two regioisomeric allylation products. [2]. In the past few decades, significant efforts have been made to regulate the regioselectivity in the Pd-catalyzed allylic substitution reaction. [3]. However, much less attention has been paid to the regioselectivity issue in the allylic substitution of dienyl allylic substrates [4], wherein the nucleophilic attack at C-1, C-3 and C-5 of the vinyl ( $\pi$ -allyl)palladium intermediate is principally possible to afford three regioisomers (Scheme 1A). At the early stage, Bäckvall and coworkers disclosed that the C-1/C-3 regioselectivity in the reaction of dienyl acetates with dialkyl malonates mainly depended on reaction temperature and reaction time. [5]. Then, Trost and coworkers found that the nucleophile counterion held profound effect on the regioselectivity. [6]. Interestingly, Hou and coworkers demonstrated that the use of 1,1'-P,N-ferrocene derived ligands was able to alter the C-3/C-5 regioselectivity. [7]. To the best of our knowledge, a controllable C-1/C-5 regioselectivity in Pd-catalyzed allylic substitution of dienyl allylic substrates has not been described, yet.

Allylic amines are not only widely amenable building blocks in organic synthesis [8], but also motifs frequently appearing within many biologically active natural products and pharmaceuticals. [9]. Based on our recent work on the palladium-catalyzed allylic C-H functionalization of 1,4-dienes [10], in which the geometry and coordination pattern of nucleophiles were identified to vary the bond-forming transition states and thereby to determine the E/Zand regioselectivities [10h,10j], we hypothesized that these mechanistic features might be viable to the Pd(0)-catalyzed allylic amination reactions, providing the insight into the access of versatile allylic amine regioisomers. Herein, we will report a palladiumcatalyzed regiocontrollable allylic amination reaction of dienyl allylic carbonates and amines, giving rise to either C-5-selective thermodynamic unfavored Z-dienyl allylic amines with palladium-phosphoramidite catalyst [11] or C-1-selective allylic amines by virtue of phosphoric acid as a co-catalyst (Scheme 1B).







<sup>\*</sup> Corresponding author.

<sup>\*\*</sup> Corresponding author. Hefei National Laboratory for Physical Sciences at the Microscale and Department of Chemistry, University of Science and Technology of China, Hefei, 230026, PR China.

*E-mail addresses*: pusher@ustc.edu.cn (P.-S. Wang), gonglz@ustc.edu.cn (L.-Z. Gong).



Scheme 1. Regioselectivity in the Pd-catalyzed allylic substitution reaction of dienyl allylic substrates.

#### 2. Results and discussion

Our initial investigation focused on evaluating phosphorusbased ligands for the reaction of (*E*)-methyl undeca-1,4-dien-3-yl carbonate 1a and aniline 2a by using Pd(dba)<sub>2</sub> (5 mol%) as precatalyst in THF at 25 °C (Table 1). In the presence of P,N-ligand L1 [12], none of the corresponding allylation products was observed (entry 1). Performing the reaction with either the Trost modular ligand L2 [13] or phosphoramidite ligand L3 mainly furnished C-1selective product 4a in accompany with linear bis-allylation product 5a (entries 2–3). To our delight, the use of bulkier phosphoramidite ligands L4 and L5 [11b] (entries 4–5) with sterically demanding 3,3',5,5'-substituents at the biphenyl backbone smoothly afforded a C-5 and Z-selective product 3a in excellent yields and with high levels of Z/E and regioselectivities. To our surprise, the addition of a Brønsted acid as cocatalyst (entries 6-9) obviously altered the regioselectivity mainly to generate the linear product 4a, and Ph<sub>2</sub>PO<sub>2</sub>H was superior to afford 4a in 65% yield. Furthermore, fine-tuning of the amine moiety of the phosphoramidite ligand with a bulkier substituent offered an enhanced yield of 4a, albeit accompanying with the formation of a small amount of bis-allylation product 5a (entry 10).

Under the optimized reaction conditions, the generality with respect to amines was explored (Scheme 2). A wide range of primary and secondary aromatic amines 2 were nicely tolerated to afford either branched Z-dienyl products 3 under Conditions A or linear product 4 under reaction Conditions B. Either electron-donating or electron-withdrawing substituent at the *ortho-*, *meta*, or *para*-position on the phenyl ring of aromatic amine smoothly furnished the corresponding regiomers (3b-j and 4b-j) in good to excellent yields and with high levels of regioselectivity. Moreover, 1-naphthyl and quinolinyl groups were amenable to afford the branch- and linear selective allylation products (3k-l and 4k-l) in moderate yields, respectively. Notably, indolines and N-alkylani-lines were also well tolerated to give the corresponding products (3m-q and 4m-q) in good to excellent yields and with excellent regioselectivities.

Then, the substrate scope with respect to the dienyl allylic carbonates was examined (Scheme 3). An array of dienyl carbonates bearing different alkyl substituents were able to furnish either C-5 or C-1 amination products (3r-u and 4r-u) in moderate to high yields and with excellent regioselectivities. In addition, functional groups such as ether and alkyne were allowed to undergo the

#### Table 1

Optimization of reaction conditions.<sup>a</sup>



entry	L	H-B	3a (%) <sup>b,c</sup>	4a (%) <sup>b</sup>	5a (%) <sup>b</sup>
1	L1	_	<1	<1	<1
2	L2	_	<1	47 <sup>d</sup>	20
3	L3	_	11	33 <sup>e</sup>	15
4	L4	-	95	<1	<1
5	L5	-	99 (91 <sup>f</sup> )	<1	<1
6	L5	HOAc	<1	17	<1
7	L5	2-FC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> H	<1	16	<1
8	L5	(PhO) <sub>2</sub> PO <sub>2</sub> H	<1	26 <sup>g</sup>	6
9	L5	Ph <sub>2</sub> PO <sub>2</sub> H	11	65 <sup>h</sup>	<1
10	L6	Ph <sub>2</sub> PO <sub>2</sub> H	<1	80 (72 <sup>i</sup> )	13

 $^a$  Reaction conditions: 1a (0.12 mmol), 2a (0.1 mmol), Pd(dba)\_2 (5 mol%), L (6 mol%), H–B (10 mol%), THF (1 mL), 25  $^\circ$ C, 36 h.

<sup>b</sup> The yields were determined by <sup>1</sup>H NMR analysis of the crude reaction mixture based on 1,3,5-triacetylbenzene as the internal standard.

<sup>e</sup> E/Z = 4:1.

<sup>f</sup> Isolated yield, Z/E > 20:1.

- <sup>g</sup> E/Z = 5:1.
- <sup>h</sup> E/Z = 4:1.
- <sup>i</sup> Isolated yield, E/Z = 7:1.

desired reaction with decent results (3v-w and 4v-w). Cyclohexyl and phenyl substituted substrates were also viable to provide the corresponding regiomers (3x-y and 4x-y) in good to excellent yields and with high levels of regioselectivity.

Based on our previous studies [10j], a plausible mechanism for the counteranion-controlled regioselectivity in allylic amination reaction was depicted in Scheme 4. The Pd(0)-phosphoramidite catalyst initially undergoes oxidative addition to a dienyl allylic carbonates **1**, leading to a vinyl  $\pi$ -allyl-Pd intermediate **I**. The hydrogen-bonding interaction between intermediate I and amine **2** forms a  $\pi$ -allyl-Pd complex **II** with *s*-trans geometry, which can reversely convert to another  $\pi$ -allyl-Pd complex III with *s*-*cis* geometry. Due to s-cis diene fragment is shorter than the corresponding s-trans fragment [10j], complex III is favored to provide experimentally observed branch- and Z-selectivity via a SN2'-type nucleophilic attack [6]. In the presence of Ph<sub>2</sub>PO<sub>2</sub>H, however, the  $(\pi$ -ally)palladium species I prefers to undergo an anion exchange to generate a  $\pi$ -ally-Pd complex **IV**, and **IV** is attacked by amine 2 via a counteranion-directed transition state to afford the linear product 4.

#### 3. Conclusion

In conclusion, we have developed a counteranion-controlled regioselective allylic amination reaction between dienyl allylic carbonates and aromatic amines enabled by phosphoramidite-

 $<sup>^{</sup>c}$  Z/E > 20:1.

<sup>&</sup>lt;sup>d</sup> E/Z > 20:1.



Scheme 3. Scope of dienyl allylic carbonates. <sup>a</sup>A 2:1 mixture of branched and linear dienyl allylic carbonates was used. <sup>b</sup>A 2.5:1 mixture of branched and linear dienyl allylic carbonates was used. <sup>c</sup>Linear dienyl allylic carbonate was used.

I/b > 20:1: E/Z = 13:1

 $l/b > 20.1 \cdot F/7 = 11.1$ 

I/b > 20:1: E/Z = 8:1.

palladium catalysis. Regioselection to respectively access branched Z-dienvl and linear E-dienvl amines can be controlled by tuning the counterions. This protocol tolerates a wide scope of substrates, giving rise to both regiomers from the same substrates.

#### 4. Experimental section

I/b > 20:1: E/Z = 7:1

#### 4.1. General

NMR spectra were recorded on a Brucker-400 MHz spectrometer. Mass spectra were recorded on a Thermo LTQ Orbitrap XL (ESI+) or a P-SIMS-Gly of Brucker Daltonics Inc (EI+). Infrared Tetrahedron 84 (2021) 131996



Scheme 4. Plausible mechanism.

spectra were recorded on a Nicolet MX-1E FT-IR spectrometer. Starting materials and solvents were purchased from commercial suppliers (Aldrich, Alfa, TCI, Adamas-beta) and used as supplied unless otherwise stated.

#### 4.2. General procedure for the synthesid of 3a-3y and 4a-4y

**Condition A.** To a flame-dried and Ar-purged Schlenk tube were added Pd(dba)<sub>2</sub> (0.01 mmol), L5 (0.012 mmol) and a stirring bar. The Schlenk tube was then evacuated and filled with nitrogen. This cycle was repeated for three times and followed by the sequential addition of THF (2 mL), aniline (0.2 mmol) and dienyl carbonate (0.24 mmol) via syringes. The mixture was stirred at 25 °C for 36 h. The product 3 was purified by column chromatography on silica gel.

Condition B. To a flame-dried and Ar-purged Schlenk tube were added Pd(dba)<sub>2</sub> (0.01 mmol), L6 (0.012 mmol), diphenylphosphinic acid (0.02 mmol) and a stirring bar. The Schlenk tube was then evacuated and filled with nitrogen. This cycle was repeated for three times and followed by the sequential addition of THF (2 mL), aniline (0.2 mmol) and dienyl carbonate (0.24 mmol) via syringes. The mixture was stirred at 25 °C for 36 h. The product 4 was purified by column chromatography on silica gel.

#### 4.2.1. (*Z*)-*N*-(*undeca*-1,3-*dien*-5-*yl*)*aniline* (3*a*)

Yield: 91%; red oil; b/l > 20:1; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.15 (dd, *I* = 8.3, 7.5 Hz, 2H), 6.81–6.70 (m, 1H), 6.68 (t, *J* = 7.4 Hz, 1H), 6.57 (d, *J* = 7.7 Hz, 2H), 6.11 (t, *J* = 10.9 Hz, 1H), 5.36–5.13 (m, 3H), 4.30-4.17 (m, 1H), 3.63 (s, 1H), 1.76-1.65 (m, 1H), 1.57-1.45 (m, 1H), 1.42-1.22 (m, 8H), 0.89 (t, I = 6.7 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 147.57, 135.47, 131.82, 130.38, 129.18, 118.83, 117.34, 113.31, 51.15, 36.25, 31.80, 29.28, 25.79, 22.64, 14.12; IR (KBr): γ 3408, 2927, 1601, 1502, 1260, 992, 747, 690 cm<sup>-1</sup>; HRMS (ESI) calculated for C<sub>17</sub>H<sub>25</sub>N [M+H]<sup>+</sup>: 244.2060, found 244.2061.

#### 4.2.2. (Z)-2-methoxy-N-(undeca-1,3-dien-5-yl)aniline (3b)

Yield: 88%; yellow oil; b/l > 20:1; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.87–6.73 (m, 3H), 6.66 (td, J = 7.8, 1.3 Hz, 1H), 6.57 (d, J = 7.8 Hz, 1H), 6.12 (t, J = 11.1 Hz, 1H), 5.33–5.20 (m, 3H), 4.28–4.19 (m, 2H), 3.86 (s, 3H), 1.82-1.71 (m, 1H), 1.62-1.52 (m, 1H), 1.45-1.27 (m, 8H), 0.90 (t, J = 6.6 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  146.75, 137.51, 135.82, 131.91, 130.14, 121.20, 118.58, 116.35, 110.71, 109.41, 55.39, 50.93, 36.23, 31.79, 29.29, 25.82, 22.63, 14.09; IR (KBr): y 3425, 2928, 1602, 1455, 1221, 1030, 905, 733 cm<sup>-1</sup>; HRMS (ESI) calculated for C<sub>18</sub>H<sub>27</sub>NO [M+H]<sup>+</sup>: 274.2165, found 274.2165.

#### *4.2.3.* (*Z*)-2-chloro-*N*-(undeca-1,3-dien-5-yl)aniline (3c)

Yield: 90%; red oil; b/l > 20:1; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.24 (dd, J = 7.7, 1.3 Hz, 1H), 7.09 (td, J = 7.9, 1.4 Hz, 1H), 6.75 (dt, J = 16.7, 10.2 Hz, 1H), 6.61 (dd, J = 12.2, 4.6 Hz, 2H), 6.13 (t, J = 11.2 Hz, 1H), 5.34–5.21 (m, 3H), 4.31 (s, 1H), 4.29–4.21 (m, 1H), 1.83–1.70 (m, 1H), 1.65–1.52 (m, 1H), 1.47–1.25 (m, 8H), 0.90 (t, J = 6.8 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  143.39, 134.92, 131.56, 130.55, 129.07, 127.68, 119.20, 119.12, 117.12, 112.07, 51.09, 36.10, 31.77, 29.23, 25.76, 22.64, 14.13; IR (KBr):  $\gamma$  3415, 2928, 1597, 1509, 1322, 1033, 907, 739 cm<sup>-1</sup>; HRMS (ESI) calculated for C<sub>17</sub>H<sub>24</sub>NCl [M+H]<sup>+</sup>: 278.1670, found 278.1673.

#### 4.2.4. (Z)-3-ethyl-N-(undeca-1,3-dien-5-yl)aniline (3d)

Yield: 93%; red oil; b/l > 20:1; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.07 (t, *J* = 7.7 Hz, 1H), 6.86–6.68 (m, 1H), 6.55 (d, *J* = 7.4 Hz, 1H), 6.44 (s, 1H), 6.41 (d, *J* = 8.0 Hz, 1H), 6.12 (t, *J* = 11.0 Hz, 1H), 5.39–5.14 (m, 3H), 4.37–4.14 (m, 1H), 3.57 (s, 1H), 2.56 (q, *J* = 7.6 Hz, 2H), 1.71 (dt, *J* = 20.4, 6.8 Hz, 1H), 1.55 (d, *J* = 7.0 Hz, 1H), 1.46–1.27 (m, 8H), 1.21 (t, *J* = 7.6 Hz, 3H), 0.91 (t, *J* = 6.6 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 147.63, 145.26, 135.55, 131.89, 130.25, 129.05, 118.64, 117.12, 113.05, 110.69, 51.16, 36.25, 31.79, 29.27, 29.00, 25.78, 22.62, 15.39, 14.09; IR (KBr):  $\gamma$  3404, 2928, 1605, 1466, 1264, 1098, 906, 789 cm<sup>-1</sup>; HRMS (ESI) calculated for C<sub>19</sub>H<sub>29</sub>N [M+H]<sup>+</sup>: 272.2373, found 272.2371.

#### 4.2.5. (Z)-3-isopropyl-N-(undeca-1,3-dien-5-yl)aniline (3e)

Yield: 89%; yellow oil; b/l > 20:1; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.09 (t, *J* = 7.8 Hz, 1H), 6.80 (dt, *J* = 16.7, 10.7 Hz, 1H), 6.59 (d, *J* = 7.5 Hz, 1H), 6.48 (s, 1H), 6.42 (dd, *J* = 7.9, 1.9 Hz, 1H), 6.13 (t, *J* = 11.0 Hz, 1H), 5.34–5.21 (m, 3H), 4.36–4.17 (m, 1H), 3.60 (s, 1H), 2.91–2.73 (m, 1H), 1.80–1.65 (m, 1H), 1.59–1.47 (m, 1H), 1.46–1.28 (m, 8H), 1.23 (dd, *J* = 6.9, 2.0 Hz, 6H), 0.92 (t, *J* = 6.6 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 149.95, 147.61, 135.63, 131.91, 130.23, 129.03, 118.66, 115.79, 111.64, 110.87, 51.19, 36.27, 34.25, 31.80, 29.29, 25.80, 23.97, 23.92, 22.63, 14.10; IR (KBr):  $\gamma$  3404, 2958, 1605, 1484, 1271, 1073, 905, 775 cm<sup>-1</sup>; HRMS (ESI) calculated for C<sub>20</sub>H<sub>31</sub>N [M+H]<sup>+</sup>: 286.2529, found 286.2528.

#### 4.2.6. (Z)-3-chloro-N-(undeca-1,3-dien-5-yl)aniline (3f)

Yield: 82%; red oil; b/l > 20:1; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.03 (t, *J* = 8.0 Hz, 1H), 6.73 (dt, *J* = 16.8, 10.4 Hz, 1H), 6.63 (dd, *J* = 7.9, 1.1 Hz, 1H), 6.53 (t, *J* = 2.0 Hz, 1H), 6.41 (dd, *J* = 8.2, 1.7 Hz, 1H), 6.13 (t, *J* = 11.0 Hz, 1H), 5.35–5.16 (m, 3H), 4.22–4.13 (m, 1H), 3.71 (s, 1H), 1.72–1.62 (m, 1H), 1.55–1.45 (m, 1H), 1.42–1.26 (m, 8H), 0.89 (t, *J* = 6.8 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 148.65, 134.87, 134.49, 131.52, 130.75, 130.11, 119.32, 117.12, 113.02, 111.42, 51.06, 36.07, 31.77, 29.21, 25.72, 22.62, 14.11; IR (KBr):  $\gamma$  3415, 2927, 1595, 1497, 1322, 1075, 988, 760 cm<sup>-1</sup>; HRMS (ESI) calculated for C<sub>17</sub>H<sub>24</sub>NCl [M+H]<sup>+</sup>: 278.1670, found 278.1673.

#### 4.2.7. (Z)-3-bromo-N-(undeca-1,3-dien-5-yl)aniline (3g)

Yield: 65%; red oil; b/l > 20:1; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.97 (t, *J* = 8.0 Hz, 1H), 6.78 (d, *J* = 7.2 Hz, 1H), 6.75–6.66 (m, 2H), 6.45 (dd, *J* = 8.2, 1.7 Hz, 1H), 6.12 (t, *J* = 11.0 Hz, 1H), 5.38–5.11 (m, 3H), 4.18 (dd, *J* = 15.3, 6.7 Hz, 1H), 3.69 (s, 1H), 1.72–1.62 (m, 1H), 1.54–1.45 (m, 1H), 1.40–1.24 (m, 8H), 0.89 (t, *J* = 6.8 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  148.80, 134.40, 131.51, 130.75, 130.37, 123.13, 120.03, 119.28, 115.99, 111.81, 51.06, 36.06, 31.73, 29.17, 25.67, 22.57, 14.04; IR (KBr):  $\gamma$  3411, 2925, 1592, 1493, 1319, 1067, 985, 799 cm<sup>-1</sup>; HRMS (ESI) calculated for C<sub>17</sub>H<sub>24</sub>NBr [M+H]<sup>+</sup>: 322.1165, found 322.1169.

## 4.2.8. (Z)-4-(trifluoromethoxy)-N-(undeca-1,3-dien-5-yl)aniline (3h)

Yield: 97%; yellow oil; b/l > 20:1; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.00 (d, J = 8.5 Hz, 2H), 6.73 (dt, J = 16.3, 10.8 Hz, 1H), 6.50 (d, *J* = 9.0 Hz, 2H), 6.13 (t, *J* = 11.0 Hz, 1H), 5.37–5.14 (m, 3H), 4.22–4.12 (m, 1H), 3.70 (s, 1H), 1.74–1.63 (m, 1H), 1.57–1.45 (m, 1H), 1.41–1.22 (m, 8H), 0.89 (t, *J* = 6.7 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 146.34, 140.32, 134.85, 131.51, 130.70, 122.33, 119.29, 113.41, 51.35, 36.16, 31.77, 29.23, 25.74, 22.61, 14.09; IR (KBr): γ 3421, 2930, 1612, 1513, 1256, 1160, 914, 826 cm<sup>-1</sup>; HRMS (ESI) calculated for  $C_{18}H_{24}F_{3}NO$  [M+H]<sup>+</sup>: 328.1883, found 328.1881.

#### 4.2.9. (*Z*)-3,4-dimethyl-N-(undeca-1,3-dien-5-yl)aniline (3i)

Yield: 81%; yellow oil; b/l > 20:1; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.92 (d, *J* = 8.1 Hz, 1H), 6.83–6.71 (m, 1H), 6.42 (d, *J* = 2.2 Hz, 1H), 6.35 (dd, *J* = 8.1, 2.4 Hz, 1H), 6.11 (t, *J* = 10.8 Hz, 1H), 5.32–5.17 (m, 3H), 4.26–4.13 (m, 1H), 2.18 (s, 3H), 2.14 (s, 3H), 1.74–1.65 (m, 1H), 1.54–1.44 (m, 1H), 1.42–1.26 (m, 8H), 0.90 (t, *J* = 6.8 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  145.69, 137.19, 135.76, 131.96, 130.27, 130.20, 125.38, 118.60, 115.34, 110.80, 51.32, 36.24, 31.82, 29.29, 25.81, 22.65, 20.08, 18.70, 14.14; IR (KBr):  $\gamma$  3403, 2927, 1617, 1583, 1317, 1216, 1173, 801 cm<sup>-1</sup>; HRMS (ESI) calculated for C<sub>19</sub>H<sub>29</sub>N [M+H]<sup>+</sup>: 272.2373, found 272.2371.

#### 4.2.10. (Z)-3,4-dimethoxy-N-(undeca-1,3-dien-5-yl)aniline (3j)

Yield: 85%; yellow oil; b/l > 20:1; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.82–6.72 (m, 1H), 6.71 (d, J = 8.6 Hz, 1H), 6.23 (d, J = 2.6 Hz, 1H), 6.16–6.08 (m, 2H), 5.31–5.15 (m, 3H), 4.22–4.11 (m, 1H), 3.79 (s, 3H), 3.78 (s, 3H), 1.74–1.62 (m, 1H), 1.56–1.44 (m, 1H), 1.42–1.24 (m, 8H), 0.88 (t, J = 6.8 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  149.82, 142.48, 141.37, 135.90, 131.78, 130.32, 118.88, 113.10, 104.50, 99.17, 56.66, 55.66, 51.90, 36.25, 31.78, 29.29, 25.80, 22.62, 14.12; IR (KBr):  $\gamma$  3383, 2928, 1615, 1515, 1230, 1137, 1025, 904 cm<sup>-1</sup>; HRMS (ESI) calculated for C<sub>19</sub>H<sub>29</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 304.2271, found 304.2270.

#### 4.2.11. (Z)-N-(undeca-1,3-dien-5-yl)naphthalen-1-amine (3k)

Yield: 45%; yellow solid; b/l > 20:1; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.85–7.75 (m, 2H), 7.49–7.40 (m, 2H), 7.31 (t, *J* = 7.9 Hz, 1H), 7.22 (d, *J* = 8.2 Hz, 1H), 6.89–6.76 (m, 1H), 6.56 (d, *J* = 7.2 Hz, 1H), 6.17 (t, *J* = 11.1 Hz, 1H), 5.39–5.28 (m, 2H), 5.25 (d, *J* = 10.1 Hz, 1H), 4.47–4.37 (m, 2H), 1.92–1.80 (m, 1H), 1.72–1.59 (m, 1H), 1.52–1.43 (m, 2H), 1.41–1.24 (m, 6H), 0.90 (t, *J* = 6.9 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  142.65, 135.51, 134.47, 131.94, 130.82, 128.85, 126.71, 125.73, 124.74, 123.53, 119.87, 119.12, 117.37, 105.41, 51.46, 36.39, 31.93, 29.44, 26.00, 22.77, 14.25; IR (KBr):  $\gamma$  3426, 2955, 1581, 1523, 1466, 1103, 783, 767 cm<sup>-1</sup>; HRMS (ESI) calculated for C<sub>21</sub>H<sub>27</sub>N [M+H]<sup>+</sup>: 294.2216, found 294.2217.

#### 4.2.12. (Z)-N-(undeca-1,3-dien-5-yl)quinolin-5-amine (3l)

Yield: 40%; yellow solid; b/l > 20:1; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.87 (d, *J* = 2.9 Hz, 1H), 8.16 (d, *J* = 8.5 Hz, 1H), 7.55–7.49 (m, 1H), 7.46 (d, *J* = 8.3 Hz, 1H), 7.32 (dd, *J* = 8.6, 4.2 Hz, 1H), 6.84–6.71 (m, 1H), 6.58 (d, *J* = 7.5 Hz, 1H), 6.18 (t, *J* = 11.1 Hz, 1H), 5.36–5.22 (m, 3H), 4.43–4.33 (m, 2H), 1.90–1.78 (m, 1H), 1.70–1.60 (m, 1H), 1.50–1.41 (m, 2H), 1.40–1.23 (m, 6H), 0.89 (t, *J* = 6.8 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  150.00, 142.82, 134.72, 131.70, 131.21, 130.51, 128.74, 119.56, 119.36, 118.56, 105.86, 51.57, 36.30, 31.91, 29.40, 25.96, 22.75, 14.23; IR (KBr):  $\gamma$  3447, 2925, 1574, 1465, 1413, 1326, 1097, 788 cm<sup>-1</sup>; HRMS (ESI) calculated for C<sub>20</sub>H<sub>26</sub>N<sub>2</sub> [M+H]<sup>+</sup>: 295.2169, found 295.2170.

#### 4.2.13. (*Z*)-6-chloro-1-(undeca-1,3-dien-5-yl)indoline (3 m)

Yield: 52%; red oil; b/l > 20:1; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.89 (d, J = 7.7 Hz, 1H), 6.75–6.63 (m, 1H), 6.53 (dd, J = 7.7, 1.8 Hz, 1H), 6.31 (d, J = 1.7 Hz, 1H), 6.16 (t, J = 11.0 Hz, 1H), 5.41 (t, J = 10.1 Hz, 1H), 5.26 (dd, J = 17.6, 13.4 Hz, 2H), 4.34–4.23 (m, 1H), 3.52–3.39 (m, 2H), 2.90 (t, J = 8.3 Hz, 2H), 1.78–1.68 (m, 1H), 1.56–1.48 (m, 1H), 1.39–1.24 (m, 8H), 0.89 (t, J = 6.9 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  152.64, 133.06, 131.84, 129.44, 128.46, 124.86, 119.49,

116.47, 107.10, 52.81, 47.51, 32.83, 31.92, 29.32, 27.79, 26.47, 22.77, 14.23; IR (KBr):  $\gamma$  3418, 2928, 1606, 1489, 1472, 1262, 905, 802 cm  $^{-1}$ ; HRMS (ESI) calculated for  $C_{19}H_{26}NCI\ [M+H]^+$ : 304.1827, found 304.1829.

#### 4.2.14. (*Z*)-6-nitro-1-(undeca-1,3-dien-5-yl)indoline (3n)

Yield: 56%; yellow oil; b/l > 20:1; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.46 (dd, *J* = 7.9, 1.9 Hz, 1H), 7.07 (dd, *J* = 13.8, 4.9 Hz, 2H), 6.71 (dt, *J* = 16.7, 10.7 Hz, 1H), 6.18 (t, *J* = 11.0 Hz, 1H), 5.38 (t, *J* = 10.1 Hz, 1H), 5.33–5.24 (m, 2H), 4.44–4.31 (m, 1H), 3.62–3.48 (m, 2H), 3.02 (t, *J* = 8.6 Hz, 2H), 1.80–1.68 (m, 1H), 1.63–1.49 (m, 1H), 1.40–1.22 (m, 8H), 0.88 (t, *J* = 6.8 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 152.32, 148.68, 137.79, 132.33, 131.54, 128.63, 123.91, 120.12, 113.07, 100.52, 52.79, 47.38, 32.79, 31.90, 29.30, 28.23, 26.44, 22.75, 14.22; IR (KBr): γ 3400, 2925, 1589, 1492, 1440, 1263, 1075, 907 cm<sup>-1</sup>; HRMS (ESI) calculated for C<sub>19</sub>H<sub>26</sub>N<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup>: 315.2067, found 315.2069.

#### 4.2.15. (Z)-N-ethyl-N-(undeca-1,3-dien-5-yl)aniline $(3^{\circ})$

Yield: 74%; red oil; b/l > 20:1; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.22 (t, *J* = 7.8 Hz, 2H), 6.76 (d, *J* = 8.4 Hz, 2H), 6.69 (t, *J* = 7.2 Hz, 1H), 6.55 (dt, *J* = 16.8, 10.6 Hz, 1H), 6.12 (t, *J* = 11.0 Hz, 1H), 5.45 (t, 1H), 5.22 (d, *J* = 16.8 Hz, 1H), 5.12 (d, *J* = 10.1 Hz, 1H), 4.56–4.45 (m, 1H), 3.35–3.21 (m, 2H), 1.77–1.67 (m, 1H), 1.55–1.45 (m, 1H), 1.34–1.23 (m, 8H), 1.12 (t, *J* = 7.0 Hz, 3H), 0.87 (t, *J* = 6.7 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  148.48, 132.45, 132.05, 131.61, 129.27, 118.97, 116.52, 113.84, 55.67, 39.76, 33.92, 31.94, 29.45, 26.58, 22.76, 14.33, 14.23; IR (KBr):  $\gamma$  3433, 2927, 1596, 1502, 1266, 1180, 1037, 905 cm<sup>-1</sup>; HRMS (ESI) calculated for C<sub>19</sub>H<sub>29</sub>N [M+H]<sup>+</sup>: 272.2373, found 272.2373.

### 4.2.16. (Z)-4-methoxy-N-methyl-N-(undeca-1,3-dien-5-yl)aniline (3p)

Yield: 71%; red oil; b/l > 20:1; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.88–6.77 (m, 4H), 6.60–6.46 (m, 1H), 6.11 (t, J = 11.1 Hz, 1H), 5.42 (t, J = 9.8 Hz, 1H), 5.20 (d, 1H), 5.11 (d, J = 10.1 Hz, 1H), 4.44–4.33 (m, 1H), 3.77 (s, 3H), 2.72 (s, 3H), 1.76–1.65 (m, 1H), 1.55–1.44 (m, 1H), 1.34–1.24 (m, 8H), 0.88 (t, J = 6.8 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  152.42, 145.22, 132.36, 131.45, 131.24, 118.69, 116.90, 114.65, 57.87, 55.81, 33.51, 32.98, 31.94, 29.40, 26.57, 22.74, 14.20; IR (KBr):  $\gamma$  3451, 2928, 1618, 1510, 1243, 1180, 1040, 907 cm<sup>-1</sup>; HRMS (ESI) calculated for C<sub>19</sub>H<sub>29</sub>NO [M+H]<sup>+</sup>: 288.2322, found 288.2319.

## 4.2.17. (Z)-4-(methyl(undeca-1,3-dien-5-yl)amino)benzonitrile (3q)

Yield: 66%; red oil; b/l > 20:1; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.45 (d, J = 9.0 Hz, 2H), 6.70 (d, J = 9.0 Hz, 2H), 6.45 (dt, J = 16.8, 10.7 Hz, 1H), 6.14 (t, J = 11.0 Hz, 1H), 5.40 (t, 1H), 5.27 (d, J = 16.7 Hz, 1H), 5.18 (d, J = 10.1 Hz, 1H), 4.69–4.59 (m, 1H), 2.81 (s, 3H), 1.77–1.67 (m, 1H), 1.64–1.54 (m, 1H), 1.34–1.19 (m, 8H), 0.86 (t, J = 6.7 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  152.48, 133.68, 132.21, 131.63, 129.73, 120.75, 120.25, 111.80, 97.60, 55.09, 33.55, 31.81, 31.57, 29.22, 26.30, 22.65, 14.13; IR (KBr):  $\gamma$  3390, 2927, 1604, 1517, 1385, 1179, 1094, 814 cm<sup>-1</sup>; HRMS (ESI) calculated for C<sub>19</sub>H<sub>26</sub>N<sub>2</sub> [M+Na]<sup>+</sup>: 305.1988, found 305.1988.

#### 4.2.18. (Z)-N-(hexa-3,5-dien-2-yl)aniline (3r)

Yield: 78%; yellow oil; b/l > 20:1; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.16 (t, *J* = 7.5 Hz, 2H), 6.82–6.71 (m, 1H), 6.71–6.67 (m, 1H), 6.58 (d, 2H), 6.06 (t, *J* = 11.1 Hz, 1H), 5.34 (t, 1H), 5.30–5.20 (m, 2H), 4.46–4.35 (m, 1H), 1.33 (d, *J* = 6.6 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  147.54, 136.74, 131.67, 129.58, 129.30, 118.97, 117.61, 113.51, 46.86, 22.30; IR (KBr):  $\gamma$  3404, 2925, 1602, 1285, 1179, 994, 792, 748 cm<sup>-1</sup>; HRMS (ESI) calculated for C<sub>12</sub>H<sub>15</sub>N [M+H]<sup>+</sup>: 174.1277, found 174.1273.

#### 4.2.19. (Z)-N-(hepta-4,6-dien-3-yl)aniline (3s)

Yield: 84%; yellow oil; b/l > 20:1; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.15 (dd, *J* = 8.5, 7.4 Hz, 2H), 6.81–6.71 (m, 1H), 6.69 (t, *J* = 7.3 Hz, 1H), 6.60–6.56 (m, 2H), 6.14 (t, *J* = 11.0 Hz, 1H), 5.33–5.18 (m, 3H), 4.22–4.11 (m, 1H), 1.81–1.69 (m, 1H), 1.61–1.50 (m, 1H), 0.99 (t, *J* = 7.4 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  147.71, 135.16, 132.01, 130.81, 129.30, 118.94, 117.50, 113.47, 52.75, 29.20, 10.43; IR (KBr):  $\gamma$  3403, 2928, 1602, 1503, 1315, 1264, 748, 691 cm<sup>-1</sup>; HRMS (ESI) calculated for C<sub>13</sub>H<sub>17</sub>N [M+H]<sup>+</sup>: 188.1434, found 188.1431.

#### 4.2.20. (Z)-N-(deca-1,3-dien-5-yl)aniline (3t)

Yield: 93%; yellow oil; b/l > 20:1; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.20–7.10 (m, 2H), 6.83–6.72 (m, 1H), 6.70 (dd, *J* = 11.6, 4.2 Hz, 1H), 6.58 (d, 2H), 6.13 (t, *J* = 10.9 Hz, 1H), 5.33–5.20 (m, 3H), 4.28–4.20 (m, 1H), 3.58 (s, 1H), 1.76–1.65 (m, 1H), 1.59–1.46 (m, 1H), 1.44–1.28 (m, 6H), 0.91 (t, *J* = 9.1, 4.6 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  147.68, 135.57, 131.92, 130.48, 129.28, 118.92, 117.45, 113.42, 51.25, 36.31, 31.89, 25.60, 22.72, 14.18; IR (KBr):  $\gamma$  3407, 2928, 1601, 1502, 1262, 881, 747, 691 cm<sup>-1</sup>; HRMS (ESI) calculated for C<sub>16</sub>H<sub>23</sub>N [M+H]<sup>+</sup>: 230.1903, found 230.1900.

#### *4.2.21.* (*Z*)-*N*-(*tetradeca*-1,3-*dien*-5-*yl*)*aniline* (3*u*)

Yield: 84%; yellow oil; b/l > 20:1; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.15 (dd, J = 8.3, 7.4 Hz, 2H), 6.82–6.71 (m, 1H), 6.67 (t, J = 7.3 Hz, 1H), 6.59–6.55 (m, 2H), 6.12 (t, J = 10.8 Hz, 1H), 5.34–5.15 (m, 3H), 4.28–4.17 (m, 1H), 3.61 (s, 1H), 1.76–1.65 (m, 1H), 1.57–1.46 (m, 1H), 1.44–1.23 (m, 14H), 0.89 (t, J = 6.8 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  147.72, 135.60, 131.97, 130.48, 129.29, 118.89, 117.48, 113.47, 51.31, 36.38, 32.02, 29.72, 29.69, 29.44, 25.94, 22.81, 14.24; IR (KBr):  $\gamma$  3407, 2925, 1602, 1503, 1261, 993, 747, 691 cm<sup>-1</sup>; HRMS (ESI) calculated for C<sub>20</sub>H<sub>31</sub>N [M+H]<sup>+</sup>: 286.2529, found 286.2526.

#### 4.2.22. (Z)-N-(10-(benzyloxy)deca-1,3-dien-5-yl)aniline (3v)

Yield: 84%; red oil; b/l > 20:1; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.37–7.33 (m, 4H), 7.32–7.27 (m, 1H), 7.15 (dd, *J* = 8.4, 7.4 Hz, 2H), 6.80–6.71 (m, 1H), 6.69 (t, *J* = 7.3 Hz, 1H), 6.57 (d, 2H), 6.11 (t, *J* = 10.9 Hz, 1H), 5.32–5.18 (m, 3H), 4.51 (s, 2H), 4.29–4.17 (m, 1H), 3.53–3.42 (m, 2H), 1.74–1.61 (m, 3H), 1.57–1.48 (m, 1H), 1.46–1.37 (m, 4H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  147.61, 138.74, 135.42, 131.87, 130.55, 129.28, 128.48, 127.75, 127.63, 119.02, 117.48, 113.42, 72.98, 70.36, 51.18, 36.26, 29.77, 26.31, 25.76; IR (KBr):  $\gamma$  3402, 2933, 1601, 1503, 1260, 1100, 748, 695 cm<sup>-1</sup>; HRMS (ESI) calculated for C<sub>23</sub>H<sub>29</sub>NO [M+H]<sup>+</sup>: 336.2322, found 336.2318.

#### 4.2.23. (Z)-N-(10-phenyldeca-1,3-dien-9-yn-5-yl)aniline (3w)

Yield: 90%; yellow solid; b/l > 20:1; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.43–7.38 (m, 2H), 7.31–7.27 (m, 3H), 7.18–7.12 (m, 2H), 6.83-6.72 (m, 1H), 6.70 (dd, J = 10.5, 4.1 Hz, 1H), 6.59 (dd, J = 8.6, 0.9 Hz, 2H), 6.14 (t, J = 11.1 Hz, 1H), 5.32–5.25 (m, 2H), 5.21 (d, J = 10.1 Hz, 1H), 4.37–4.28 (m, 1H), 3.65 (s, 1H), 2.48 (t, J = 6.6 Hz, 2H), 1.96–1.87 (m, 1H), 1.79–1.67 (m, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  147.50, 135.06, 131.79, 131.70, 130.82, 129.32, 128.34, 127.77, 123.91, 119.29, 117.59, 113.47, 89.70, 81.36, 50.83, 35.23, 25.03, 19.36; IR (KBr):  $\gamma$  3401, 2925, 1601, 1503, 1315, 1250, 754, 691 cm<sup>-1</sup>; HRMS (ESI) calculated for C<sub>22</sub>H<sub>23</sub>N [M+H]<sup>+</sup>: 302.1903, found 302.1905.

#### 4.2.24. (Z)-N-(1-cyclohexylpenta-2,4-dien-1-yl)aniline (3x)

Yield: 72%; yellow oil; b/l > 20:1; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.13 (dd, *J* = 8.4, 7.4 Hz, 2H), 6.79–6.69 (m, 1H), 6.65 (t, *J* = 7.3 Hz, 1H), 6.55 (d, *J* = 7.7 Hz, 2H), 6.15 (t, *J* = 11.0 Hz, 1H), 5.31–5.16 (m, 3H), 4.05 (dd, *J* = 9.6, 6.3 Hz, 1H), 1.90 (d, *J* = 12.4 Hz, 1H), 1.82–1.62 (m, 6H), 1.21–1.02 (m, 4H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 147.89, 133.63, 132.20, 131.08, 129.29, 118.86, 117.27, 113.34, 56.01, 43.31, 30.02, 29.12, 26.65, 26.44; IR (KBr):  $\gamma$  3415, 2923, 1601, 1502, 1258, 1003, 746, 690 cm<sup>-1</sup>; HRMS (ESI) calculated for C<sub>17</sub>H<sub>23</sub>N [M+H]<sup>+</sup>: 242.1903, found 242.1899.

#### 4.2.25. (Z)-N-(1-phenylpenta-2,4-dien-1-yl)aniline (3y)

Yield: 90%; yellow solid; b/l > 20:1; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.44 (d, J = 7.3 Hz, 2H), 7.37 (t, J = 7.5 Hz, 2H), 7.29 (t, J = 7.2 Hz, 1H), 7.16 (dd, J = 8.4, 7.5 Hz, 2H), 6.86 (dt, J = 16.7, 10.7 Hz, 1H), 6.74 (t, J = 7.3 Hz, 1H), 6.61 (d, J = 7.7 Hz, 2H), 6.18 (t, J = 10.9 Hz, 1H), 5.61 (t, J = 9.8 Hz, 1H), 5.40–5.33 (m, 2H), 5.28 (d, J = 10.1 Hz, 1H), 4.05 (s, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  147.35, 142.75, 133.38, 131.71, 130.51, 129.27, 128.96, 127.43, 126.70, 120.15, 117.90, 113.72, 55.92; IR (KBr):  $\gamma$  3407, 2924, 1601, 1501, 1313, 1265, 749, 699 cm<sup>-1</sup>; HRMS (ESI) calculated for C<sub>17</sub>H<sub>17</sub>N [M+H]<sup>+</sup>: 236.1434, found 236.1430.

#### 4.2.26. N-((2E,4E)-undeca-2,4-dien-1-yl)aniline (4a)

Yield: 72%; yellow oil; E/Z = 7:1; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.18 (t, J = 7.8 Hz, 2H), 6.72 (t, J = 7.3 Hz, 1H), 6.63 (d, J = 7.8 Hz, 2H), 6.24 (dd, J = 15.1, 10.5 Hz, 1H), 6.04 (dd, J = 15.1, 10.5 Hz, 1H), 5.74–5.62 (m, 2H), 3.78 (d, J = 5.9 Hz, 2H), 2.13–2.04 (m, 2H), 1.40–1.34 (m, 2H), 1.33–1.24 (m, 8H), 0.89 (t, J = 6.7 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 148.23, 135.26, 132.43, 129.52, 129.35, 127.89, 117.60, 113.11, 46.01, 32.77, 31.86, 29.36, 29.02, 22.75, 14.25; IR (KBr): γ 3410, 2955, 1602, 1504, 1094, 987, 747, 690 cm<sup>-1</sup>; HRMS (ESI) calculated for C<sub>17</sub>H<sub>25</sub>N [M+H]<sup>+</sup>: 244.2060, found 244.2060.

#### 4.2.27. 2-methoxy-N-((2E,4E)-undeca-2,4-dien-1-yl)aniline (4b)

Yield: 98%; red oil; E/Z = 11:1; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.91–6.86 (m, 1H), 6.79 (dd, J = 7.9, 1.3 Hz, 1H), 6.69 (td, J = 7.7, 1.5 Hz, 1H), 6.63 (dd, J = 7.8, 1.4 Hz, 1H), 6.26 (dd, J = 15.2, 10.4 Hz, 1H), 6.06 (dd, J = 15.1, 10.4 Hz, 1H), 5.77–5.64 (m, 2H), 4.33 (s, 1H), 3.85 (s, 3H), 3.81 (d, J = 5.9 Hz, 2H), 2.12–2.04 (m, 2H), 1.42–1.26 (m, 8H), 0.90 (t, J = 6.8 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  146.96, 138.16, 135.02, 132.23, 129.62, 128.11, 121.37, 116.63, 110.24, 109.45, 55.48, 45.70, 32.76, 31.85, 29.36, 29.01, 22.75, 14.24; IR (KBr):  $\gamma$  3425, 2955, 1602, 1511, 1244, 1125, 987, 733 cm<sup>-1</sup>; HRMS (ESI) calculated for C<sub>18</sub>H<sub>27</sub>NO [M+H]<sup>+</sup>: 274.2165, found 274.2167.

#### 4.2.28. 2-chloro-N-((2E,4E)-undeca-2,4-dien-1-yl)aniline (4c)

Yield: 96%; yellow oil; E/Z = 8:1; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.27–7.22 (m, 1H), 7.14–7.09 (m, 1H), 6.68–6.59 (m, 2H), 6.23 (dd, J = 15.2, 10.5 Hz, 1H), 6.04 (dd, J = 15.1, 10.5 Hz, 1H), 5.72–5.62 (m, 2H), 4.41 (s, 1H), 3.82 (d, J = 5.3 Hz, 2H), 2.11–2.02 (m, 2H), 1.40–1.25 (m, 8H), 0.88 (t, J = 6.8 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 144.01, 135.51, 132.64, 129.44, 129.21, 127.89, 127.14, 119.27, 117.35, 111.59, 45.60, 32.77, 31.86, 29.34, 29.03, 22.75, 14.23; IR (KBr):  $\gamma$  3418, 2925, 1598, 1510, 1321, 1033, 986, 739 cm<sup>-1</sup>; HRMS (ESI) calculated for C<sub>17</sub>H<sub>24</sub>NCl [M+H]<sup>+</sup>: 278.1670, found 278.1673.

#### 4.2.29. 3-ethyl-N-((2E,4E)-undeca-2,4-dien-1-yl)aniline (4d)

Yield: 82%; yellow oil; *E*/*Z* = 9:1; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.11 (t, *J* = 7.7 Hz, 1H), 6.58 (d, *J* = 7.7 Hz, 1H), 6.50–6.45 (m, 2H), 6.25 (dd, *J* = 15.1, 10.6 Hz, 1H), 6.05 (dd, *J* = 15.0, 10.5 Hz, 1H), 5.75–5.64 (m, 2H), 3.78 (d, *J* = 6.0 Hz, 2H), 2.58 (q, *J* = 7.6 Hz, 2H), 2.11–2.04 (m, 2H), 1.39–1.28 (m, 8H), 1.23 (t, *J* = 7.6 Hz, 3H), 0.90 (t, *J* = 6.8 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 148.36, 145.54, 135.16, 132.42, 129.60, 129.29, 128.04, 117.39, 112.86, 110.48, 46.13, 32.76, 31.86, 29.37, 29.16, 29.01, 22.75, 15.66, 14.23; IR (KBr): γ 3412, 2960, 1605, 1507, 1332, 1104, 987, 694 cm<sup>-1</sup>; HRMS (ESI) calculated for C<sub>19</sub>H<sub>29</sub>N [M+H]<sup>+</sup>: 272.2373, found 272.2373.

#### 4.2.30. 3-isopropyl-N-((2E,4E)-undeca-2,4-dien-1-yl)aniline (4e)

Yield: 93%; yellow oil; E/Z = 8:1; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.12 (t, J = 7.8 Hz, 1H), 6.62 (d, J = 7.6 Hz, 1H), 6.54–6.44 (m, 2H), 6.25 (dd, J = 15.1, 10.5 Hz, 1H), 6.05 (dd, J = 15.0, 10.4 Hz, 1H),

5.74–5.64 (m, 2H), 3.79 (d, J = 6.0 Hz, 2H), 2.87–2.79 (m, 1H), 2.12–2.04 (m, 2H), 1.41–1.28 (m, 8H), 1.24 (d, J = 6.9 Hz, 6H), 0.90 (t, J = 6.8 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  150.19, 148.32, 135.15, 132.48, 129.61, 129.28, 128.05, 115.96, 111.61, 110.53, 46.18, 34.37, 32.76, 31.86, 29.37, 29.01, 24.10, 22.75, 14.23; IR (KBr):  $\gamma$  3415, 2925, 1605, 1466, 1336, 988, 776, 698 cm<sup>-1</sup>; HRMS (ESI) calculated for C<sub>20</sub>H<sub>31</sub>N [M+H]<sup>+</sup>: 286.2529, found 286.2530.

#### 4.2.31. 3-chloro-N-((2E,4E)-undeca-2,4-dien-1-yl)aniline (4f)

Yield: 95%; yellow oil; E/Z = 9:1; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.07 (t, J = 8.0 Hz, 1H), 6.69–6.65 (m, 1H), 6.58 (t, J = 2.1 Hz, 1H), 6.49–6.45 (m, 1H), 6.22 (dd, J = 15.1, 10.4 Hz, 1H), 6.04 (dd, J = 15.1, 10.4 Hz, 1H), 5.74–5.60 (m, 2H), 3.75 (d, J = 5.9 Hz, 2H), 2.11–2.03 (m, 2H), 1.42–1.24 (m, 8H), 0.89 (t, J = 6.8 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  149.31, 135.62, 135.09, 132.75, 130.28, 129.36, 127.04, 117.37, 112.63, 111.36, 45.74, 32.77, 31.85, 29.32, 29.02, 22.75, 14.25; IR (KBr):  $\gamma$  3418, 2925, 1500, 1323, 1265, 988, 909, 740 cm<sup>-1</sup>; HRMS (ESI) calculated for C<sub>17</sub>H<sub>24</sub>NCl [M+H]<sup>+</sup>: 278.1670, found 278.1673.

#### 4.2.32. 3-bromo-N-((2E,4E)-undeca-2,4-dien-1-yl)aniline (4g)

Yield: 91%; red oil; E/Z = 10:1; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.01 (t, J = 8.0 Hz, 1H), 6.83–6.79 (m, 1H), 6.74 (t, J = 2.1 Hz, 1H), 6.53–6.50 (m, 1H), 6.22 (dd, J = 15.2, 10.4 Hz, 1H), 6.04 (dd, J = 15.1, 10.4 Hz, 1H), 5.73–5.60 (m, 2H), 3.75 (d, J = 5.9 Hz, 2H), 2.12–2.03 (m, 2H), 1.45–1.23 (m, 8H), 0.89 (t, J = 6.8 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  149.46, 135.64, 132.78, 130.58, 129.36, 126.99, 123.36, 120.27, 115.54, 111.76, 45.72, 32.77, 31.85, 29.32, 29.01, 22.75, 14.25; IR (KBr):  $\gamma$  3415, 2924, 1594, 1495, 1320, 985, 919, 887 cm<sup>-1</sup>; HRMS (ESI) calculated for C<sub>17</sub>H<sub>24</sub>NBr [M+H]<sup>+</sup>: 322.1165, found 322.1168.

## 4.2.33. 4-(trifluoromethoxy)-N-((2E,4E)-undeca-2,4-dien-1-yl) aniline (4h)

Yield: 99%; red oil; E/Z = 7:1; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.04 (d, 2H), 6.56 (d, 2H), 6.24 (dd, J = 15.1, 10.4 Hz, 1H), 6.05 (dd, J = 15.0, 10.4 Hz, 1H), 5.74–5.62 (m, 2H), 3.76 (d, J = 6.0 Hz, 2H), 2.12–2.04 (m, 2H), 1.42–1.23 (m, 8H), 0.90 (t, J = 8.0, 5.7 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  147.00, 135.60, 132.74, 129.39, 127.27, 122.52, 113.30, 113.24, 46.12, 32.78, 31.86, 29.33, 29.03, 22.76, 14.23; IR (KBr):  $\gamma$  3418, 2957, 1612, 1514, 1222, 1159, 1116, 987 cm<sup>-1</sup>; HRMS (ESI) calculated for C<sub>18</sub>H<sub>24</sub>F<sub>3</sub>NO [M+H]<sup>+</sup>: 328.1883, found 328.1885.

#### 4.2.34. 3,4-dimethyl-N-((2E,4E)-undeca-2,4-dien-1-yl)aniline (4i)

Yield: 71%; yellow oil; E/Z = 10:1; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.94 (d, J = 8.0 Hz, 1H), 6.46 (d, 1H), 6.41 (dd, J = 8.0, 2.5 Hz, 1H), 6.23 (dd, J = 15.2, 10.4 Hz, 1H), 6.04 (dd, J = 15.1, 10.4 Hz, 1H), 5.73–5.63 (m, 2H), 3.75 (d, J = 5.9 Hz, 2H), 2.20 (s, 3H), 2.16 (s, 3H), 2.10–2.04 (m, 2H), 1.41–1.26 (m, 8H), 0.89 (t, J = 6.8 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  146.43, 137.40, 135.07, 132.23, 130.38, 129.61, 128.28, 125.67, 115.07, 110.61, 46.41, 32.77, 31.86, 29.37, 29.02, 22.76, 20.19, 18.84, 14.25; IR (KBr):  $\gamma$  3404, 2925, 1617, 1509, 1318, 1261, 1122, 987 cm<sup>-1</sup>; HRMS (ESI) calculated for C<sub>19</sub>H<sub>29</sub>N [M+H]<sup>+</sup>: 272.2373, found 272.2370.

### 4.2.35. 3,4-dimethoxy-N-((2E,4E)-undeca-2,4-dien-1-yl)aniline (4j)

Yield: 68%; red oil; *E*/*Z* = 10:1; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.74 (d, *J* = 8.5 Hz, 1H), 6.26–6.19 (m, 2H), 6.16 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.03 (dd, *J* = 15.1, 10.5 Hz, 1H), 5.72–5.63 (m, 2H), 3.83 (s, 3H), 3.80 (s, 3H), 3.73 (d, *J* = 6.0 Hz, 2H), 2.09–2.03 (m, 2H), 1.40–1.25 (m, 8H), 0.88 (t, *J* = 6.7 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 150.02, 143.11, 141.71, 135.22, 132.46, 129.53, 128.05, 113.21, 103.91, 99.21, 56.76, 55.80, 46.91, 32.74, 31.83, 29.33, 28.99, 22.73, 14.22; IR (KBr): γ 3387, 2926, 1615, 1515, 1209, 1027,897, 790 cm<sup>-1</sup>; HRMS (ESI)

#### calculated for C<sub>19</sub>H<sub>29</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 304.2271, found 304.2270.

#### 4.2.36. N-((2E.4E)-undeca-2.4-dien-1-vl)naphthalen-1-amine (4k)

Yield: 99%; yellow solid; E/Z = 8:1; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.84–7.78 (m, 2H), 7.49–7.42 (m, 2H), 7.36 (t, J = 7.9 Hz, 1H), 7.27–7.25 (m, 1H), 6.64 (d, J = 7.1 Hz, 1H), 6.33 (dd, J = 15.2, 10.4 Hz, 1H), 6.10 (dd, J = 15.1, 10.4 Hz, 1H), 5.87–5.79 (m, 1H), 5.76–5.67 (m, 1H), 4.43 (s, 1H), 3.96 (d, J = 6.0 Hz, 2H), 2.14–2.05 (m, 2H), 1.44–1.21 (m, 8H), 0.91 (t, J = 9.1, 4.5 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 143.33, 135.51, 134.39, 132.89, 129.52, 128.79, 127.48, 126.74, 125.82, 124.82, 123.57, 120.01, 117.61, 104.81, 46.23, 32.79, 31.87, 29.35, 29.03, 22.76, 14.26; IR (KBr): γ 3445, 2926, 1622, 1524, 1278, 1114, 987, 767 cm<sup>-1</sup>; HRMS (ESI) calculated for C<sub>21</sub>H<sub>27</sub>N [M+H]<sup>+</sup>: 294.2216, found 294.2217.

#### 4.2.37. N-((2E,4E)-undeca-2,4-dien-1-yl)quinolin-5-amine (4l)

Yield: 50%; yellow solid; E/Z = 8:1; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.87 (dd, J = 4.2, 1.6 Hz, 1H), 8.20–8.14 (m, 1H), 7.56 (t, 1H), 7.49 (d, J = 8.4 Hz, 1H), 7.32 (dd, J = 8.5, 4.2 Hz, 1H), 6.65 (d, J = 6.9 Hz, 1H), 6.31 (dd, J = 15.2, 10.4 Hz, 1H), 6.08 (dd, J = 15.1, 10.5 Hz, 1H), 5.82–5.66 (m, 2H), 4.43 (s, 1H), 3.94 (d, J = 5.7 Hz, 2H), 2.08 (t, 2H), 1.40–1.24 (m, 8H), 0.88 (t, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 150.12, 149.32, 143.49, 135.89, 133.27, 130.50, 129.35, 128.79, 126.83, 119.45, 118.78, 118.61, 105.18, 46.24, 32.79, 31.85, 29.32, 29.02, 22.75, 14.25; IR (KBr): γ 3441, 2923, 1586, 1530, 1325, 1109, 937, 788 cm<sup>-1</sup>; HRMS (ESI) calculated for C<sub>20</sub>H<sub>26</sub>N<sub>2</sub> [M+H]<sup>+</sup>: 295.2169, found 295.2171.

#### 4.2.38. 6-chloro-1-((2E,4E)-undeca-2,4-dien-1-yl)indoline (4 m)

Yield: 90%; red oil; *E*/*Z* = 9:1; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.94 (dd, *J* = 7.7, 1.0 Hz, 1H), 6.59 (dd, *J* = 7.7, 1.9 Hz, 1H), 6.43 (d, *J* = 1.8 Hz, 1H), 6.21 (dd, *J* = 15.1, 10.4 Hz, 1H), 6.04 (dd, *J* = 15.1, 10.5 Hz, 1H), 5.73–5.55 (m, 2H), 3.69 (d, *J* = 6.4 Hz, 2H), 3.37 (t, *J* = 8.4 Hz, 2H), 2.91 (dd, *J* = 12.3, 4.5 Hz, 2H), 2.11–2.03 (m, 2H), 1.40–1.22 (m, 8H), 0.89 (t, *J* = 6.9 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 153.49, 135.39, 133.53, 133.13, 129.42, 128.86, 125.79, 125.03, 117.13, 107.45, 53.39, 50.67, 32.78, 31.87, 29.34, 29.04, 28.06, 22.76, 14.26; IR (KBr):  $\gamma$  3417, 2925, 1606, 1489, 1327, 1073, 988, 789 cm<sup>-1</sup>; HRMS (ESI) calculated for C<sub>19</sub>H<sub>26</sub>NCl [M+H]<sup>+</sup>: 304.1827, found 304.1830.

#### 4.2.39. 6-nitro-1-((2E,4E)-undeca-2,4-dien-1-yl)indoline (4n)

Yield: 92%; red solid; E/Z = 8:1; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.51 (dd, J = 7.9, 2.1 Hz, 1H), 7.17 (d, J = 2.1 Hz, 1H), 7.09 (d, J = 8.0 Hz, 1H), 6.23 (dd, J = 15.2, 10.4 Hz, 1H), 6.03 (dd, J = 15.1, 10.4 Hz, 1H), 5.74–5.65 (m, 1H), 5.61–5.53 (m, 1H), 3.78 (d, J = 6.4 Hz, 2H), 3.48 (t, J = 8.5 Hz, 2H), 3.02 (t, J = 8.5 Hz, 2H), 2.12–2.01 (m, 2H), 1.42–1.22 (m, 8H), 0.88 (t, J = 6.9 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  153.01, 148.69, 138.10, 135.81, 133.98, 129.21, 124.75, 124.05, 113.48, 100.70, 52.95, 50.13, 32.75, 31.83, 29.27, 29.01, 28.46, 22.73, 14.23; IR (KBr):  $\gamma$  3409, 2925, 1615, 1494, 1338, 1145, 988, 736 cm<sup>-1</sup>; HRMS (ESI) calculated for C<sub>19</sub>H<sub>26</sub>N<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup>: 315.2067, found 315.2070.

#### 4.2.40. N-ethyl-N-((2E,4E)-undeca-2,4-dien-1-yl)aniline (4°)

Yield: 96%; yellow oil; E/Z = 10:1; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.20 (dd, J = 8.8, 7.3 Hz, 2H), 6.69 (d, J = 8.1 Hz, 2H), 6.65 (t, J = 7.3 Hz, 1H), 6.13 (dd, J = 15.0, 10.4 Hz, 1H), 6.02 (dd, J = 14.9, 10.5 Hz, 1H), 5.65–5.54 (m, 2H), 3.90 (d, J = 5.1 Hz, 2H), 3.36 (q, J = 7.0 Hz, 2H), 2.08–2.01 (m, 2H), 1.37–1.23 (m, 8H), 1.15 (t, J = 7.1 Hz, 3H), 0.87 (t, J = 6.8 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 148.37, 134.56, 131.57, 129.62, 129.31, 127.45, 115.86, 112.22, 51.83, 44.66, 32.77, 31.86, 29.38, 29.04, 22.75, 14.24, 12.34; IR (KBr): γ 3444, 2925, 1598, 1505, 1374, 1189, 988, 745 cm<sup>-1</sup>; HRMS (ESI) calculated for C<sub>19</sub>H<sub>29</sub>N [M+H]<sup>+</sup>: 272.2373, found 272.2374.

### 4.2.41. 4-methoxy-N-methyl-N-((2E,4E)-undeca-2,4-dien-1-yl) aniline (4p)

Yield: 90%; red oil; *E*/*Z* = 11:1; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.83 (d, *J* = 9.2 Hz, 2H), 6.73 (d, *J* = 9.2 Hz, 2H), 6.14 (dd, *J* = 15.1, 10.4 Hz, 1H), 6.02 (dd, *J* = 14.9, 10.5 Hz, 1H), 5.69–5.54 (m, 2H), 3.84 (d, *J* = 5.9 Hz, 2H), 3.76 (s, 3H), 2.83 (s, 3H), 2.09–2.01 (m, 2H), 1.38–1.25 (m, 8H), 0.88 (t, *J* = 6.8 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 151.88, 144.74, 134.72, 132.40, 129.63, 127.10, 115.04, 114.79, 55.96, 55.89, 38.83, 32.77, 31.87, 29.38, 29.04, 22.76, 14.25; IR (KBr): γ 3440, 2925, 1614, 1511, 1243, 1103, 1040, 988 cm<sup>-1</sup>; HRMS (ESI) calculated for C<sub>19</sub>H<sub>29</sub>NO [M+H]<sup>+</sup>: 288.2322, found 288.2319.

### 4.2.42. 4-(methyl((2E,4E)-undeca-2,4-dien-1-yl)amino) benzonitrile (4q)

Yield: 72%; yellow oil; *E*/*Z* = 9:1; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.45 (d, *J* = 9.1 Hz, 2H), 6.64 (d, *J* = 9.0 Hz, 2H), 6.11–5.96 (m, 2H), 5.70–5.61 (m, 1H), 5.55–5.47 (m, 1H), 3.98 (d, *J* = 5.4 Hz, 2H), 3.00 (s, 3H), 2.08–2.02 (m, 2H), 1.36–1.23 (m, 8H), 0.87 (t, *J* = 6.8 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  151.86, 135.79, 133.61, 132.48, 129.09, 124.51, 111.68, 97.56, 53.89, 38.13, 32.75, 31.83, 29.27, 29.01, 22.73, 14.23; IR (KBr):  $\gamma$  3389, 2924, 1605, 1382, 1177, 987, 921, 815 cm<sup>-1</sup>; HRMS (ESI) calculated for C<sub>19</sub>H<sub>26</sub>N<sub>2</sub> [M+Na]<sup>+</sup>: 305.1988, found 305.1989.

#### 4.2.43. N-((2E,4E)-hexa-2,4-dien-1-yl)aniline (4r)

Yield: 58%; yellow oil; *E*/*Z* = 8:1; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.18 (t, *J* = 7.8 Hz, 2H), 6.72 (t, *J* = 7.3 Hz, 1H), 6.63 (d, *J* = 7.8 Hz, 2H), 6.24 (dd, *J* = 15.0, 10.5 Hz, 1H), 6.07 (dd, 1H), 5.73–5.64 (m, 2H), 3.78 (d, *J* = 5.9 Hz, 2H), 1.76 (d, *J* = 6.6 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  148.23, 132.26, 130.95, 129.53, 129.35, 127.74, 117.61, 113.11, 45.99, 18.24; IR (KBr):  $\gamma$  3409, 2926, 1602, 1504, 1320, 1262, 748, 691 cm<sup>-1</sup>; HRMS (ESI) calculated for C<sub>12</sub>H<sub>15</sub>N [M+H]<sup>+</sup>: 174.1277, found 174.1274.

#### 4.2.44. N-((2E,4E)-hepta-2,4-dien-1-yl)aniline (4s)

Yield: 64%; yellow oil; E/Z = 11:1; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.18 (dd, J = 8.5, 7.4 Hz, 2H), 6.71 (t, J = 7.3 Hz, 1H), 6.63 (dd, J = 8.6, 1.0 Hz, 2H), 6.25 (dd, J = 15.2, 10.2 Hz, 1H), 6.05 (dd, J = 15.1, 10.3 Hz, 1H), 5.76–5.66 (m, 2H), 3.78 (d, J = 5.9 Hz, 2H), 2.14–2.06 (m, 2H), 1.01 (t, J = 7.5 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 148.27, 136.59, 132.43, 129.36, 128.66, 128.01, 117.63, 113.14, 46.03, 25.75, 13.61; IR (KBr):  $\gamma$  3411, 2928, 1602, 1504, 1317, 988, 747, 691 cm<sup>-1</sup>; HRMS (ESI) calculated for C<sub>13</sub>H<sub>17</sub>N [M+H]<sup>+</sup>: 188.1434, found 188.1431.

#### 4.2.45. N-((2E,4E)-deca-2,4-dien-1-yl)aniline (4t)

Yield: 70%; yellow oil; E/Z = 7:1; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.18 (t, J = 7.8 Hz, 2H), 6.72 (t, J = 7.3 Hz, 1H), 6.63 (d, J = 8.1 Hz, 2H), 6.24 (dd, J = 15.1, 10.4 Hz, 1H), 6.05 (dd, J = 15.1, 10.5 Hz, 1H), 5.73–5.62 (m, 2H), 3.78 (d, J = 5.9 Hz, 2H), 2.11–2.04 (m, 2H), 1.43–1.24 (m, 6H), 0.90 (t, J = 6.8 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 148.27, 135.24, 132.45, 129.56, 129.36, 127.92, 117.62, 113.13, 46.03, 32.72, 31.54, 29.07, 22.66, 14.17; IR (KBr):  $\gamma$  3414, 2926, 1602, 1505, 1261, 988, 747, 691 cm<sup>-1</sup>; HRMS (ESI) calculated for C<sub>16</sub>H<sub>23</sub>N [M+H]<sup>+</sup>: 230.1903, found 230.1899.

#### 4.2.46. N-((2E,4E)-tetradeca-2,4-dien-1-yl)aniline (4u)

Yield: 71%; yellow oil; E/Z = 6:1; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.19 (dd, J = 8.6, 7.3 Hz, 2H), 6.75–6.69 (m, 1H), 6.63 (dd, J = 8.6, 1.0 Hz, 2H), 6.25 (dd, J = 15.2, 10.6 Hz, 1H), 6.05 (dd, J = 15.0, 10.6 Hz, 1H), 5.73–5.64 (m, 2H), 3.79 (d, J = 6.1 Hz, 2H), 2.11–2.04 (m, 2H), 1.45–1.24 (m, 14H), 0.90 (t, J = 6.9 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 148.27, 135.23, 132.45, 129.56, 129.35, 127.91, 117.62, 113.13, 46.03, 32.76, 32.04, 29.70, 29.64, 29.46, 29.40, 29.35, 22.82, 14.25; IR (KBr): γ 3416, 2925, 1602, 1504, 1264, 988, 747, 691 cm<sup>-1</sup>; HRMS (ESI) calculated for C<sub>20</sub>H<sub>31</sub>N [M+H]<sup>+</sup>: 286.2529, found 286.2524. 4.2.47. N-((2E,4E)-10-(benzyloxy)deca-2,4-dien-1-yl)aniline (4v)

Yield: 99%; red oil; E/Z = 7:1; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.35 (s, 5H), 7.19 (t, 2H), 6.72 (t, J = 7.3 Hz, 1H), 6.63 (d, J = 7.7 Hz, 2H), 6.24 (dd, J = 15.2, 10.4 Hz, 1H), 6.04 (dd, J = 15.2, 10.5 Hz, 1H), 5.73–5.65 (m, 2H), 4.51 (s, 2H), 3.78 (d, J = 5.9 Hz, 2H), 3.47 (t, J = 6.6 Hz, 2H), 2.10-2.06 (m, 2H), 1.67-1.59 (m, 2H), 1.47-1.33 (m, 4H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 148.22, 138.77, 134.89, 132.34, 129.71, 129.35, 128.48, 128.04, 127.76, 127.62, 117.59, 113.09, 73.00, 70.49, 45.98, 32.66, 29.73, 29.19, 25.87; IR (KBr): y 3410, 2929, 1602, 1504, 1262, 989, 747, 695 cm<sup>-1</sup>; HRMS (ESI) calculated for C<sub>23</sub>H<sub>29</sub>NO [M+H]<sup>+</sup>: 336.2322, found 336.2317.

#### 4.2.48. N-((2E,4E)-10-phenyldeca-2,4-dien-9-yn-1-yl)aniline (4w)

Yield: 67%; red oil; E/Z = 8:1; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.42–7.38 (m, 2H), 7.30–7.26 (m, 3H), 7.19 (dd, I = 8.5, 7.4 Hz, 2H), 6.72 (t, J = 7.3 Hz, 1H), 6.63 (d, J = 7.7 Hz, 2H), 6.25 (dd, J = 15.1, 10.4 Hz, 1H), 6.11 (dd, J = 15.0, 10.5 Hz, 1H), 5.76–5.65 (m, 2H), 3.79 (d, J = 5.9 Hz, 2H), 2.43 (t, J = 7.1 Hz, 2H), 2.30–2.23 (m, 2H), 1.71 (t, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 148.20, 133.65, 132.14, 131.67, 130.49, 129.36, 128.50, 128.33, 127.68, 124.06, 117.62, 113.10, 89.98, 81.09, 45.96, 31.80, 28.34, 18.97; IR (KBr): γ 3411, 2927, 1602, 1504, 1251, 989, 753, 691  $\mbox{cm}^{-1};$  HRMS (ESI) calculated for  $C_{22}H_{23}N$ [M+H]<sup>+</sup>: 302.1903, found 302.1899.

#### 4.2.49. N-((2E,4E)-5-cyclohexylpenta-2,4-dien-1-yl)aniline (4x)

Yield: 73%; yellow oil; E/Z = 13:1; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.18 (dd, J = 8.6, 7.3 Hz, 2H), 6.74–6.69 (m, 1H), 6.63 (dd, J = 8.6, 1.0 Hz, 2H), 6.23 (dd, I = 15.0, 10.5 Hz, 1H), 6.02 (dd, I = 15.5, 10.3 Hz, 1H), 5.75–5.60 (m, 2H), 3.78 (dd, *J* = 6.0, 1.1 Hz, 2H), 2.03–1.95 (m, 1H), 1.77–1.63 (m, 4H), 1.31–1.04 (m, 6H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 148.27, 140.92, 132.71, 129.36, 128.08, 127.04, 117.61, 113.12, 46.04, 40.82, 32.94, 26.28, 26.13; IR (KBr): y 3413, 2923, 1602, 1504, 1257, 988, 747, 691 cm<sup>-1</sup>; HRMS (ESI) calculated for C<sub>17</sub>H<sub>23</sub>N [M+H]<sup>+</sup>: 242.1903, found 242.1898.

#### 4.2.50. N-((2E,4E)-5-phenylpenta-2,4-dien-1-yl)aniline (4y)

Yield: 71%; yellow oil; E/Z = 11:1; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.39–7.36 (m, 2H), 7.30 (dd, J = 8.3, 6.9 Hz, 2H), 7.24–7.15 (m, 3H), 6.77 (dd, *J* = 15.8, 10.6 Hz, 1H), 6.74–6.70 (m, 1H), 6.64 (dd, *J* = 8.6, 1.0 Hz, 2H), 6.51 (d, J = 15.7 Hz, 1H), 6.42 (dd, J = 15.2, 10.5, 0.6 Hz, 1H), 5.97-5.86 (m, 1H), 3.86 (dd, J = 5.8, 1.2 Hz, 2H), 3.81 (s, 1H);  $^{13}$ C NMR (101 MHz, CDCl<sub>3</sub>) & 148.10, 137.31, 132.25, 132.07, 131.33, 129.39, 128.73, 128.42, 127.64, 126.44, 117.72, 113.13, 46.02; IR (KBr): γ 3413, 2924, 1602, 1503, 1260, 989, 747, 691 cm<sup>-1</sup>; HRMS (ESI) calculated for C<sub>17</sub>H<sub>17</sub>N [M+H]<sup>+</sup>: 236.1434, found 236.1430.

#### **Declaration of competing interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Acknowledgments

We are grateful for financial support from the Ministry of Science and Technology of China (2015CB856600), the NSFC (21831007, 21672197), the Chinese Academy of Sciences (Grant No. XDB20020000) and Youth Innovation Promotion Association CAS is gratefully acknowledged.

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2021.131996.

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