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Regioselective control by a catalyst switch in palladium-catalyzed benzylallylation of arylethylidene malononitriles

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ABSTRACT

Regioselective control by a catalyst switch in palladium-catalyzed benzylallylation of arylethylidene malononitriles (α-benzyl-β-allylation versus α-allyl-β-benzylation) is described. The three-component reaction of 2-(bromomethyl)naphthalenes, arylethylidene malononitriles, and allyltributylstannane proceeds smoothly with palladium nanoparticles as a catalyst to provide α-benzyl-β-allylation products in good yields. The regioselectivity of the benzylallylation reaction is completely overturned with $Pd(PPh_3)_4$ as the catalyst instead of palladium nanoparticles to obtain α-allyl-β-benzylation products in moderate to good yields.

1. Introduction

The palladium-catalyzed bisfunctionalization of activated olefins as a promising and powerful tool for the construction of two chemical bonds in one-pot procedures has achieved remarkable progress [1,2]. Many palladium-catalyzed methods, including alkynylallylation [3], bisallylation [4–9], propargylallylation [10], acetoallylation [11], alkoxyallylation [12], cyanoallylation [13], aminoallylation [14], and hydroallylation [15] have been developed over the past two decades for the bisfunctionalization of activated olefins. We have recently reported a new type of palladium-catalyzed bisfunctionalization reaction of activated olefins, namely, benzylallylation of activated olefins, which proceeds with chemo- and regioselectivity via π-benzyl–π-allylpalladium intermediates in the presence of palladium nanoparticles [16].

In the course of our continuous research on palladium-catalyzed benzylallylation of activated olefins with 2-(bromomethyl)naphthalenes as benzylating regents, we found that the regioselectivity of the benzylallylation reaction can be easily controlled with a catalyst switch. Scheme 1 shows that the three-component reaction of 2-(bromomethyl)naphthalenes **1**, arylethylidene malononitriles **2**, and allyltributylstannane proceeded smoothly in the presence of palladium nanoparticles generated in situ as a catalyst to provide α-benzyl-β-allylation products **3** in good yields. The regioselectivity of the three-component reaction was completely overturned with $Pd(PPh_3)_4$ as the catalyst instead of palladium nanoparticles to obtain α-allyl-β-benzylation products **4** in moderate to good yields. The observations are reported in this paper.

2. Results and discussion

Initially, the α-benzyl-β-allylation reactions of arylethylidene malononitriles **2** with 2-(bromomethyl)naphthalenes **1** and allyltributylstannane occurred at the conditions similar to those employed in our previous work [16]. The results are summarized in Table 1. The three-component reaction of 2-(bromomethyl)naphthalene (**1a**), 2-benzylidenemalononitrile (**2a**), and allyltributylstannane proceeded smoothly in the presence of palladium nanoparticles, which were generated in situ from $Pd_2(dba)_3$ and TBAB, in THF at 60 °C to provide α-benzyl-β-allylation product **3a** in 80% yield (entry 1). Good yields similar to that of **3a** were observed when 2-(4-fluorobenzylidene)malononitrile (**2b**), 2-(4-chlorobenzylidene) malononitrile (**2c**), and 2-(4-bromobenzylidene)malononitrile (**2d**) were employed at optimized reaction conditions (entries 2–4 versus

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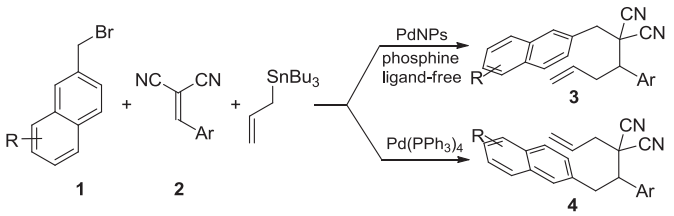
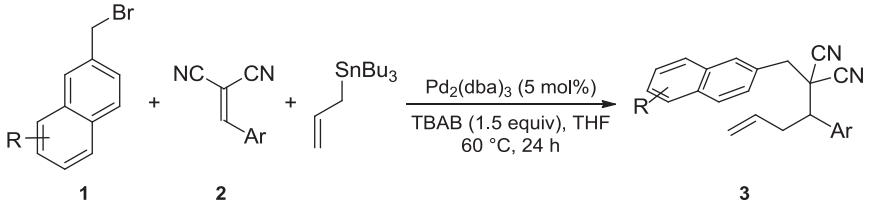


Scheme 1. Regioselective control in the three-component reaction of **1**, **2**, and allyltributylstannane with a catalyst switch.

entry 1; 80%–86%). The Cl and Br atoms linked to the benzene ring were maintained in the structures of products **3c** and **3d** at the reaction conditions. These atoms provide opportunities for further functionalization of these compounds. Compared with activated olefin substrates **2a**–**d**, activated olefin substrates **2e** and **2f**, which bear an electron-donating group (Me or OMe) at the *para* position of the benzene ring, exhibited relatively low reactivity to provide target products **3e** and **3f** in 78% and 76% yields, respectively (entries 5 and 6). The use of naphthyl- and thienyl-containing activated olefin substrates **2g** and **2h** led to the formation of α-benzyl-β-allylation products also in good yields (entries 7 and 8). Other bromide substrates **1b**–**f** that contain a halogen atom (Cl or Br) and methoxy

Table 1
Palladium-catalyzed α-benzyl-β-allylation reaction of arylethylidene malononitriles with 2-(bromomethyl)naphthalenes and allyltributylstannane.[a]



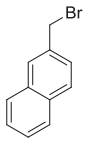
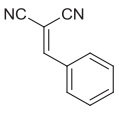
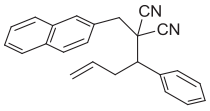
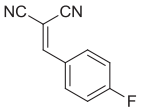
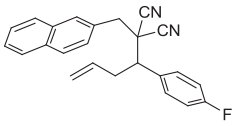
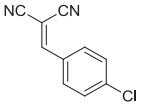
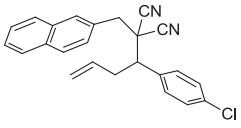
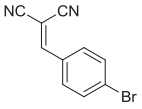
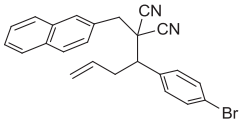
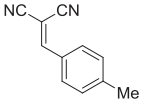
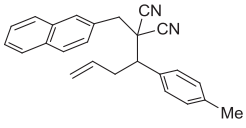
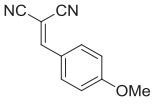
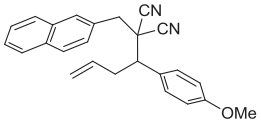
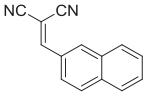
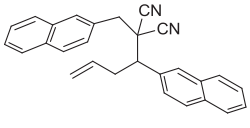
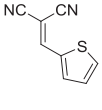
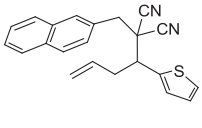
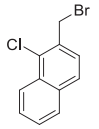
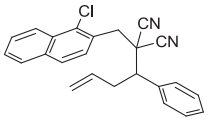
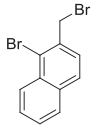
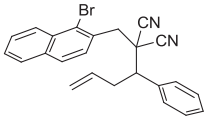
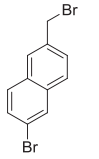
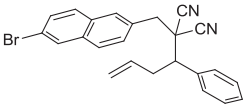
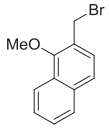
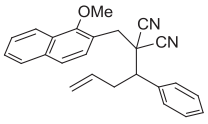
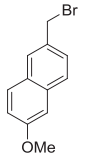
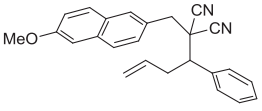
Entry	Bromide **1**	Activated olefin **2**	Product **3**	Yield (%)[b]
1	 **1a**	 **2a**	 **3a**	80
2	**1a**	 **2b**	 **3b**	80
3	**1a**	 **2c**	 **3c**	82
4	**1a**	 **2d**	 **3d**	86
5	**1a**	 **2e**	 **3e**	78
6	**1a**	 **2f**	 **3f**	76
7	**1a**	 **2g**	 **3g**	80
8	**1a**	 **2h**	 **3h**	74

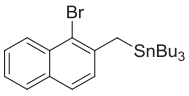
Table 1 (*continued*)

Entry	Bromide **1**	Activated olefin **2**	Product **3**	Yield (%)[b]
9	 **1b**	**2a**	 **3i**	70
10	 **1c**	**2a**	 **3j**	65
11	 **1d**	**2a**	 **3k**	72
12	 **1e**	**2a**	 **3l**	74
13	 **1f**	**2a**	 **3m**	81

[a] Reaction conditions: 2-(bromomethyl)naphthalene (**1**, 0.6 mmol), arylethylidene malononitrile (**2**, 0.5 mmol), allyltributylstanane (0.6 mmol, 198.6 mg), $Pd_2(dba)_3$ (5 mol %, 22.9 mg), and TBAB (1.5 equiv, 241.8 mg) in THF (2 mL) at 60 °C for 24 h.
[b] Isolated yield.

(MeO) group at the naphthalene ring, respectively, were subsequently examined with **2a** as the activated olefin substrate. Corresponding products **3i**–**m** were also obtained in satisfactory to good yields (entries 9–13; 65%–81%). These results suggest that the reactivity of bromide substrates is not influenced by the substituent property (electron withdrawing versus electron donating).

The α-allyl-β-benzylation reactions of arylethylidene malononitriles with 2-(bromomethyl)naphthalenes and allyltributylstannane were observed with $Pd(PPh_3)_4$ as the catalyst. The results are presented in Table 2. α-Allyl-β-benzylation product **4a** was isolated in 70% yield from the palladium-catalyzed three-component reaction of 2-(bromomethyl)naphthalene (**1a**), 2-benzylidenemalononitrile (**2a**), and allyltributylstannane (entry 1). Slightly reduced yields were observed when activated olefin substrates **2b**–**d** were employed in this type of bisfunctionalization reaction (entries 2–4; 65%–67%). The Cl and Br atoms linked to the benzene ring were also maintained in the structures of products **4c** and **4d** at the reaction conditions. As observed in the aforementioned α-benzyl-β-allylation reaction, activated olefin substrates **2e** and **2f** also exhibited relatively low reactivity in the α-allyl-β-benzylation reaction. Products **4e** and **4f** were obtained in 56% and 49% yields, respectively (entries 5 and 6). Naphthyl- and thienyl-containing activated olefin substrates **2g** and **2h** proved to be unsuitable reaction partners. The desired α-allyl-β-benzylation products (**4g** and **4h**) were obtained in low yields (entries 7 and 8; 55% and 32%, respectively). Other bromide substrates **1b**–**f** were subsequently examined with **2a** as the activated olefin substrate. The α-allyl-β-benzylation reaction of **2a** with chlorine-containing bromide substrate **1b** proceeded smoothly to provide desired product **4i** in satisfactory yield (entry 9; 67%). However, desired products **4j** and **4k** were obtained in only 47% and 49% yields along with the byproducts **5** and **6** in 31% and 50% yields from the α-allyl-β-benzylation reaction of **2a** with bromide substrates **1c** and **1d**, respectively (entries 10 and 11). Bromide substrates **1e** and **1f** exhibited good reactivity in the α-allyl-β-benzylation reaction of **2a**. Products **4l** and **4m** were obtained in 75% and 87% yields, respectively (entries 12 and 13).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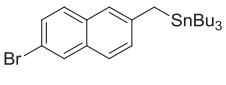
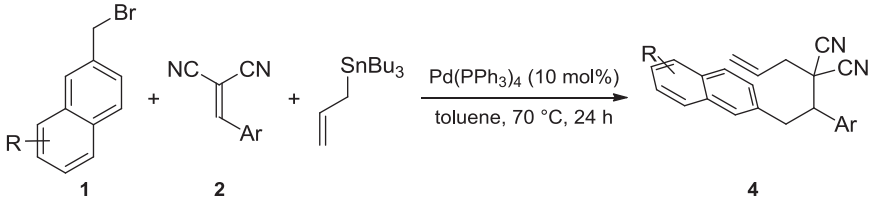

6

A plausible mechanism is presented in Scheme 2. Oxidative addition of **1a** to Pd(0) followed by transmetalation with allyltributylstannane would generate π-benzyl–π-allylpalladium intermediate **A**. Activated olefin **2a** coordinated with Pd(II) to produce intermediate **B** in the absence of PPh_3. The Michael-type nucleophilic addition of an allyl group to **2a** produced intermediate **C**, which subsequently underwent reductive elimination to provide α-benzyl-β-allylation product **3a** and regenerated the Pd(0) species. However, the phosphine ligand PPh_3 coordinated with **A** to produce intermediate **D** in which the π-allyl group still functioned as a ligand. The behavior of the π-allyl group was considered

Table 2
Palladium-catalyzed α-allyl-β-benzylation reaction of arylethylidene malononitriles with 2-(bromomethyl)naphthalenes and allyltributylstannane.[a]



1 **2** **4**

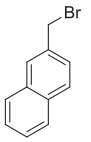
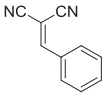
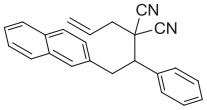
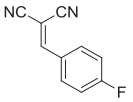
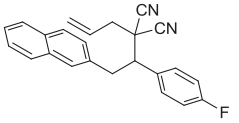
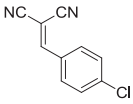
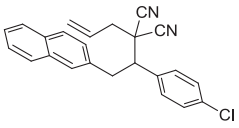
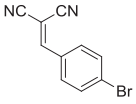
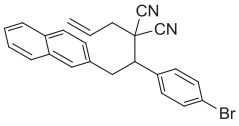
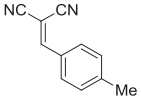
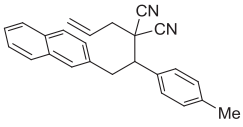
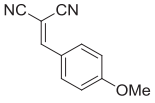
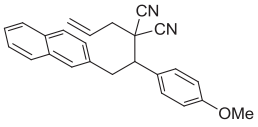
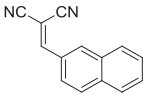
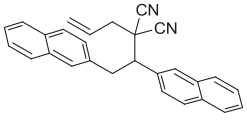
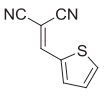
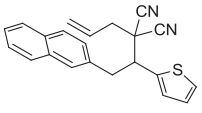
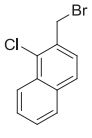
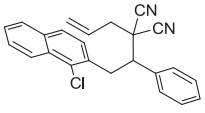
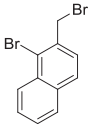
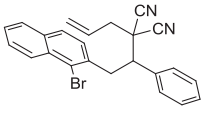
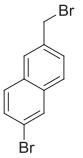
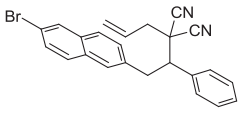
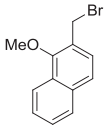
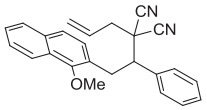
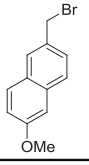
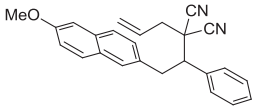
Entry	Bromide **1**	Activated olefin **2**	Product **4**	Yield (%)[b]
1	 **1a**	 **2a**	 **4a**	70
2	**1a**	 **2b**	 **4b**	66
3	**1a**	 **2c**	 **4c**	65
4	**1a**	 **2d**	 **4d**	67
5	**1a**	 **2e**	 **4e**	56
6	**1a**	 **2f**	 **4f**	49[c]
7	**1a**	 **2g**	 **4g**	55[c]
8	**1a**	 **2h**	 **4h**	32[c]
9	 **1b**	**2a**	 **4i**	67
10	 **1c**	**2a**	 **4j**	47

Table 2 (*continued*)

Entry	Bromide **1**	Activated olefin **2**	Product **4**	Yield (%)[b]
11	 **1d**	**2a**	 **4k**	49
12	 **1e**	**2a**	 **4l**	75
13	 **1f**	**2a**	 **4m**	87

[a] Reaction conditions: 2-(bromomethyl)naphthalene (**1**, 0.6 mmol), arylethylidene malononitrile (**2**, 0.5 mmol), allyltributylstanane (0.6 mmol, 198.6 mg), and $Pd(PPh_3)_4$ (10 mol%, 57.8 mg) in toluene (2 mL) at 70 °C for 24 h.
[b] Isolated yield.
[c] Reaction was performed at 90 °C for 36 h.

because of its relatively strong stability. The Michael-type nucleophilic addition of σ-benzyl group to **2a** produced intermediate **E**. Reductive elimination from **E** provided α-allyl-β-benzylation product **4a** and regenerated the Pd(0) species.

3. Conclusion

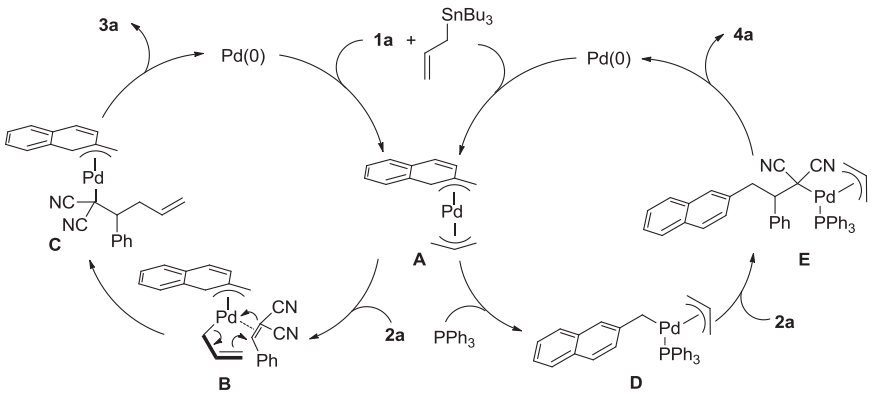
In conclusion, regioselective control in the three-component reaction of 2-(bromomethyl)naphthalenes, arylethylidene malononitriles, and allyltributylstannane was successfully achieved with a catalyst switch. The α-benzyl-β-allylation reaction proceeds smoothly with palladium nanoparticles as a catalyst, whereas the regioselectivity of the three-component reaction was completely overturned with $Pd(PPh_3)_4$ as the catalyst instead of palladium nanoparticles. The α-allyl-β-benzylation reaction provides a novel and general method for the bisfunctionalization of activated olefin compounds.

4. Experimental section

4.1. General information

All reactions were carried out under a nitrogen atmosphere unless otherwise noted. Solvents were purified by standard techniques without special instructions. ^1H and ^{13}C NMR spectra were recorded on either a Varian Inova-400 spectrometer (400 MHz for ^1H, 100 MHz for ^{13}C) or a Bruker Avance II-400 spectrometer (400 MHz for ^1H, 100 MHz for ^{13}C); $CDCl_3$ and TMS were used as a solvent and an internal standard, respectively. The chemical shifts are reported in ppm downfield (δ) from TMS, the coupling constants J are given in Hz. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. IR spectra were recorded on a NEXUS FT-IR spectrometer. High resolution mass spectra were recorded on a GC-TOF mass spectrometry. TLC was carried out on SiO_2 (silica gel 60 F_{254}, Merck), and the spots were located with UV light, iodoplatinate reagent or 1% aqueous $KMnO_4$. Flash chromatography was carried out on either SiO_2 (silica gel 60, 200–300 mesh) or basic alumina (Al_2O_3 90, 100–200 mesh). Melting points were determined using a micro-melting point apparatus and are uncorrected.

The allyltributylstannane is commercially available. The starting materials 2-(bromomethyl)naphthalene (**1a**) [17], 2-(bromomethyl)-1-chloronaphthalene (**1b**) [18], 1-bromo-2-(bromomethyl) naphthalene (**1c**) [19], 2-(bromomethyl)-1-methoxynaphthalene (**1e**) [20], and 2-(bromomethyl)-6-methoxynaphthalene (**1f**) [21] were prepared according to the literature procedures. The



Scheme 2. Proposed mechanism for regioselective palladium-catalyzed benzylallylation of arylethylidene malononitriles.

arylethylidene malononitriles **2** were prepared by Knoevenagel condensation.

4.2. Preparation of starting material 2-bromo-6-(bromomethyl) naphthalene (*1d*)

To a solution of (6-bromonaphthalen-2-yl)methanol (1.19 g, 5 mmol) in anhydrous Et_2O (40 mL) at 0 °C, PBr_3 (1.52 g, 22 mmol) was added dropwise, and the resulting solution was stirred at room temperature for 3 h. The resultant mixture was neutralized with an aq. $NaHCO_3$, and the product was extracted with Et_2O (40 mL × 2). The organic layers were dried over Na_2SO_4, filtered and concentrated. Then, the crude product was purified by flash silica gel chromatography (eluent: petroleum ether) to afford **1d** (1.27 g, 85% yield) as a white solid.

Mp 124–125 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.80 (s, 1H), 7.75 (d, J = 8.6 Hz, 1H), 7.69 (d, J = 8.7 Hz, 1H), 7.58–7.52 (m, 2H), 4.64 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 135.8, 134.2, 131.7, 130.1, 130.0, 129.7, 128.0, 127.9, 120.8, 33.8; IR (KBr) ν (cm^{-1}) 3448, 1637, 1587, 1211, 1132, 1061, 898, 887, 824, 736, 668; HRMS (EI) Calcd for $C_{11}H_8Br_2$ 297.8993 $[M]^+$, found 297.9002.

4.3. Representative procedure for the α-benzyl-β-allylation reaction of arylethylidene malononitriles

An oven-dried reaction tube (25 mL) was charged with $Pd_2(dba)_3$ (22.9 mg, 0.025 mmol), arylethylidene malononitrile (**2**, 0.5 mmol), and 2-(bromomethyl)naphthalene (**1**, 0.6 mmol). The tube was evacuated and purged with nitrogen gas for three times. Then, TBAB (248 mg, 0.75 mmol), freshly distilled THF (2 mL), and allyltributylstannane (198.6 mg, 0.6 mmol) were sequentially added. The reaction mixture was heated to 60 °C for 24 h. After the reaction completed, the resultant mixture was evaporated in vacuo to give the crude product, which was then purified via basic Al_2O_3 chromatography (eluent: ethyl acetate/petroleum ether = 1:30 to 1:20) to afford α-benzyl-β-allylation products **3**.

4.3.1. 2-(Naphthalen-2-ylmethyl)-2-(1-phenylbut-3-en-1-yl) malononitrile (*3a*)

White solid (134.5 mg, 80% yield); mp 134–136 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85–7.82 (m, 3H), 7.77 (s, 1H), 7.51–7.48 (m, 2H), 7.45–7.41 (m, 6H), 5.57–5.47 (m, 1H), 5.10 (d, J = 17.0 Hz, 1H), 4.99 (d, J = 10.2 Hz, 1H), 3.23–3.18 (m, 2H), 3.02–2.92 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.3, 133.6, 133.3, 133.2, 129.83, 129.79, 129.4, 129.3, 129.2, 128.8, 128.2, 127.9, 127.6, 126.7, 126.6, 118.7, 115.6, 114.5, 52.6, 45.4, 42.6, 36.5; IR (KBr) ν (cm^{-1}) 3058, 2925, 2246, 1642, 1600, 1508, 1495, 1455, 989, 936, 856, 820, 751, 702; HRMS (EI) Calcd for $C_{24}H_{20}N_2$ 336.1626 $[M]^+$, found 336.1630.

4.3.2. 2-(1-(4-Fluorophenyl)but-3-en-1-yl)-2-(naphthalen-2-ylmethyl)malononitrile (*3b*)

White solid (141.7 mg, 80% yield); mp 124–126 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87–7.82 (m, 3H), 7.78 (s, 1H), 7.52–7.49 (m, 2H), 7.43–7.38 (m, 3H), 7.15 (dd, J = 8.4, 8.4 Hz, 2H), 5.55–5.45 (m, 1H), 5.09 (d, J = 17.0 Hz, 1H), 5.01 (d, J = 10.1 Hz, 1H), 3.24–3.19 (m, 2H), 3.05–2.99 (m, 2H), 2.94–2.86 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1 (d, $^1J_{C-F}$ = 247.5 Hz), 133.4, 133.3, 131.2 (d, $^4J_{C-F}$ = 3.1 Hz), 131.1, 131.0, 129.8, 129.6, 128.9, 128.2, 127.9, 127.6, 126.8 (d, $^3J_{C-F}$ = 9.1 Hz), 119.0, 116.47 (d, $^2J_{C-F}$ = 21.4 Hz), 115.4, 114.4, 51.7, 45.5, 42.6, 36.5; IR (KBr) ν (cm^{-1}) 3428, 3058, 2927, 2244, 1643, 1603, 1511, 1442, 1229, 1162, 991, 922, 840, 822, 751; HRMS (EI) Calcd for $C_{24}H_{19}FN_2$ 354.1532 $[M]^+$, found 354.1542.

4.3.3. 2-(1-(4-Chlorophenyl)but-3-en-1-yl)-2-(naphthalen-2-ylmethyl)malononitrile (*3c*)

White solid (152.0 mg, 82% yield); mp 92–94 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85–7.81 (m, 3H), 7.77 (s, 1H), 7.50–7.48 (m, 2H), 7.42–7.40 (m, 3H), 7.34 (d, J = 8.5 Hz, 2H), 5.53–5.43 (m, 1H), 5.08 (dd, J = 17.0, 1.3 Hz, 1H), 5.00 (dd, J = 10.2, 0.8 Hz, 1H), 3.21–3.16 (m, 2H), 3.03–2.98 (m, 2H), 2.93–2.84 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.3, 135.3, 133.9, 133.4, 133.2, 130.7, 129.9, 129.7, 129.6, 128.9, 128.2, 127.9, 127.6, 126.9, 126.8, 119.2, 115.3, 114.4, 51.8, 45.4, 42.5, 36.3; IR (KBr) ν (cm^{-1}) 3398, 3055, 2924, 2247, 1642, 1599, 1508, 1493, 1437, 1414, 1095, 1014, 989, 936, 857, 835, 818, 779, 762, 740; HRMS (EI) Calcd for $C_{24}H_{19}ClN_2$ 370.1237 $[M]^+$, found 370.1241.

4.3.4. 2-(1-(4-Bromophenyl)but-3-en-1-yl)-2-(naphthalen-2-ylmethyl)malononitrile (*3d*)

White solid (178.5 mg, 86% yield); mp 123–125 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87–7.84 (m, 3H), 7.78 (s, 1H), 7.59 (d, J = 8.4 Hz, 2H), 7.52–7.50 (m, 2H), 7.42 (dd, J = 8.5, 1.7 Hz, 1H), 7.30 (d, J = 8.4 Hz, 2H), 5.53–5.44 (m, 1H), 5.10 (dd, J = 16.8, 0.8 Hz, 1H), 5.02 (dd, J = 10.4, 1.0 Hz, 1H), 3.23–3.16 (m, 2H), 3.06–2.99 (m, 2H), 2.94–2.86 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.4, 133.3, 133.1, 132.6, 131.0, 129.5, 128.9, 128.2, 127.9, 127.5, 126.8, 126.7, 123.5, 119.1, 115.3, 114.3, 51.9, 45.2, 42.5, 36.3; IR (KBr) ν (cm^{-1}) 3054, 2924, 2246, 1642, 1600, 1508, 1489, 1438, 1410, 1076, 1010, 989, 937, 856, 832, 818, 777, 762, 738; HRMS (EI) Calcd for $C_{24}H_{19}BrN_2$ 414.0732 and 416.0711 $[M]^+$, found 414.0728 and 416.0716.

4.3.5. 2-(Naphthalen-2-ylmethyl)-2-(1-(p-tolyl)but-3-en-1-yl) malononitrile (*3e*)

White solid (136.6 mg, 77% yield); mp 116–118 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85–7.81 (m, 3H), 7.77 (s, 1H), 7.50–7.48 (m, 2H), 7.42 (dd, J = 8.4, 1.3 Hz, 1H), 7.30 (d, J = 8.1 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 5.58–5.47 (m, 1H), 5.10 (d, J = 17.0 Hz, 1H), 4.99 (d, J = 9.9 Hz, 1H), 3.20–3.16 (m, 2H), 3.01–2.90 (m, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.7, 133.3, 133.2, 132.1, 130.1, 130.0, 129.8, 129.2, 128.8, 128.2, 127.9, 127.7, 126.7, 126.6, 118.6, 115.7, 114.6, 52.3, 45.5, 42.6, 36.5, 21.4; IR (KBr) ν (cm^{-1}) 3410, 3055, 2923, 2244, 1642, 1600, 1514, 1437, 1384, 989, 935, 856, 818, 779, 763, 746; HRMS (EI) Calcd for $C_{25}H_{22}N_2$ 350.1783 $[M]^+$, found 350.1785.

4.3.6. 2-(1-(4-Methoxyphenyl)but-3-en-1-yl)-2-(naphthalen-2-ylmethyl)malononitrile (*3f*)

White solid (139.2 mg, 76% yield); mp 126–128 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85–7.81 (m, 3H), 7.77 (s, 1H), 7.50–7.48 (m, 2H), 7.42 (d, J = 8.5 Hz, 1H), 7.33 (d, J = 8.6 Hz, 2H), 6.97 (d, J = 8.7 Hz, 2H), 5.57–5.47 (m, 1H), 5.10 (d, J = 17.0 Hz, 1H), 4.99 (d, J = 10.2 Hz, 1H), 3.84 (s, 3H), 3.19–3.16 (m, 2H), 3.03–2.88 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 133.7, 133.3, 133.2, 130.4, 130.0, 129.8, 128.8, 128.2, 127.8, 127.6, 127.0, 126.7, 126.6, 118.5, 115.7, 114.7, 114.6, 55.4, 51.9, 45.7, 42.5, 36.5; IR (KBr) ν (cm^{-1}) 3057, 2934, 2246, 1642, 1610, 1514, 1441, 1302, 1254, 1181, 1032, 991, 915, 835, 821, 751, 734; HRMS (EI) Calcd for $C_{25}H_{22}N_2O$ 366.1732 $[M]^+$, found 366.1741.

4.3.7. 2-(1-(Naphthalen-2-yl)but-3-en-1-yl)-2-(naphthalen-2-ylmethyl)malononitrile (*3g*)

White solid (154.6 mg, 80% yield); mp 94–96 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.6 Hz, 1H), 7.89–7.78 (m, 6H), 7.74 (s, 1H), 7.58–7.52 (m, 3H), 7.48–7.45 (m, 2H), 7.40 (dd, J = 8.4, 1.1 Hz, 1H), 5.57–5.47 (m, 1H), 5.11 (d, J = 16.9 Hz, 1H), 4.95 (d, J = 10.1 Hz, 1H), 3.40–3.36 (m, 1H), 3.22 (d, J = 13.7 Hz, 1H), 3.11–3.07 (m, 2H), 3.00 (d, J = 13.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.5, 133.4, 133.3, 133.2, 132.7, 129.8, 129.4, 129.3, 128.8, 128.1, 127.9, 127.8, 127.6, 127.0, 126.9, 126.7, 126.6, 125.9, 118.8, 115.7, 114.5, 52.7, 45.4, 42.6, 36.6; IR (KBr) ν (cm^{-1}) 3434, 3056, 2976, 2244,

1642, 1618, 1600, 1509, 1439, 1272, 1127, 991, 922, 859, 820, 779, 752, 477; HRMS (EI) Calcd for $C_{28}H_{22}N_2$ 386.1783 $[M]^+$, found 386.1788.

4.3.8. 2-(Naphthalen-2-ylmethyl)-2-(1-(thiophen-2-yl)but-3-en-1-yl)malononitrile (**3h**)

White solid (126.6 mg, 70% yield); mp 156–158 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87–7.84 (m, 3H), 7.81 (s, 1H), 7.52–7.50 (m, 2H), 7.45 (dd, J = 8.5, 1.3 Hz, 1H), 7.40 (d, J = 5.1 Hz, 1H), 7.19 (d, J = 3.2 Hz, 1H), 7.12–7.10 (m, 1H), 5.65–5.55 (m, 1H), 5.15 (d, J = 17.2 Hz, 1H), 5.06 (d, J = 10.2 Hz, 1H), 3.54 (dd, J = 11.7, 3.5 Hz, 1H), 3.25 (d, J = 13.7 Hz, 1H), 3.14 (d, J = 13.7 Hz, 1H), 3.08–3.02 (m, 1H), 2.91–2.83 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.7, 137.6, 133.4, 133.1, 129.9, 129.8, 128.9, 128.2, 127.9, 127.6, 126.8, 126.7, 126.6, 126.5, 119.2, 119.1, 115.3, 114.3, 48.3, 45.8, 42.4, 38.4; IR (KBr) ν (cm^{-1}) 3411, 3057, 2927, 2245, 1642, 1600, 1509, 1438, 1370, 1247, 991, 924, 820, 750, 707; HRMS (EI) Calcd for $C_{22}H_{18}N_2S$ 342.1191 $[M]^+$, found 342.1198.

4.3.9. 2-((1-Chloronaphthalen-2-yl)methyl)-2-(1-phenylbut-3-en-1-yl)malononitrile (**3i**)

White solid (129.8 mg, 70% yield); mp 126–128 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, J = 8.5 Hz, 1H), 7.85 (d, J = 8.3 Hz, 1H), 7.78 (d, J = 8.5 Hz, 1H), 7.63–7.54 (m, 2H), 7.52 (d, J = 8.5 Hz, 1H), 7.47–7.42 (m, 5H), 5.60–5.50 (m, 1H), 5.12 (d, J = 17.0 Hz, 1H), 5.01 (d, J = 10.1 Hz, 1H), 3.55 (d, J = 14.0 Hz, 1H), 3.30 (dd, J = 11.6, 4.0 Hz, 1H), 3.26 (d, J = 14.0 Hz, 1H), 3.08–2.95 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.2, 134.3, 133.6, 133.1, 131.2, 129.4, 129.3, 129.2, 128.3, 128.1, 127.8, 127.7, 127.6, 127.4, 125.4, 118.8, 115.4, 114.4, 53.2, 44.0, 39.6, 36.4; IR (KBr) ν (cm^{-1}) 3065, 3033, 2927, 2247, 1642, 1495, 1455, 1440, 1336, 991, 913, 819, 753, 735, 710, 702; HRMS (EI) Calcd for $C_{24}H_{19}ClN_2$ 370.1237 $[M]^+$, found 370.1238.

4.3.10. 2-((1-Bromonaphthalen-2-yl)methyl)-2-(1-phenylbut-3-en-1-yl)malononitrile (**3j**)

White solid (135.0 mg, 65% yield); mp 142–144 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 8.6 Hz, 1H), 7.85–7.82 (m, 2H), 7.63–7.60 (m, 1H), 7.57–7.54 (m, 2H), 7.48–7.44 (m, 5H), 5.61–5.51 (m, 1H), 5.13 (dd, J = 17.1, 1.2 Hz, 1H), 5.02 (dd, J = 9.9, 1.0 Hz, 1H), 3.60 (d, J = 14.0 Hz, 1H), 3.35–3.30 (m, 2H), 3.07–2.95 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.1, 134.3, 133.5, 132.6, 130.5, 129.4, 129.3, 128.4, 128.3, 128.0, 127.6, 127.3, 126.6, 118.7, 115.4, 114.3, 53.2, 44.0, 42.3, 36.4; IR (KBr) ν (cm^{-1}) 3441, 3030, 2928, 2248, 1640, 1495, 1455, 1384, 991, 925, 823, 757, 697; HRMS (EI) Calcd for $C_{24}H_{19}BrN_2$ 414.0732 and 416.0711 $[M]^+$, found 414.0734 and 416.0719.

4.3.11. 2-((6-Bromonaphthalen-2-yl)methyl)-2-(1-phenylbut-3-en-1-yl)malononitrile (**3k**)

White solid (149.5 mg, 72% yield); mp 129–131 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.79–7.69 (m, 3H), 7.57 (dd, J = 8.7, 1.8 Hz, 1H), 7.45–7.41 (m, 6H), 5.57–5.47 (m, 1H), 5.11 (dd, J = 17.0, 1.2 Hz, 1H), 5.00 (dd, J = 10.1, 1.0 Hz, 1H), 3.24–3.16 (m, 2H), 3.02–2.95 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.2, 134.3, 133.5, 131.7, 130.4, 130.1, 129.9, 129.8, 129.7, 129.5, 129.3, 128.7, 127.9, 120.8, 118.8, 115.5, 114.4, 52.7, 45.3, 42.6, 36.6; IR (KBr) ν (cm^{-1}) 3442, 3069, 2927, 2252, 1639, 1590, 1494, 1455, 1399, 1063, 917, 891, 810, 761, 702; HRMS (EI) Calcd for $C_{24}H_{19}BrN_2$ 414.0732 and 416.0711 $[M]^+$, found 414.0738 and 416.0720.

4.3.12. 2-((1-Methoxynaphthalen-2-yl)methyl)-2-(1-phenylbut-3-en-1-yl)malononitrile (**3l**)

White solid (135.6 mg, 74% yield); mp 70–72 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09–8.07 (m, 1H), 7.85–7.82 (m, 1H), 7.63 (d, J = 8.5 Hz, 1H), 7.53–7.49 (m, 3H), 7.44–7.39 (m, 5H), 5.58–5.48 (m, 1H), 5.09 (dd, J = 17.0, 1.4 Hz, 1H), 4.98 (dd, J = 10.2, 1.3 Hz, 1H), 3.78 (s, 3H), 3.31 (d, J = 13.7 Hz, 1H), 3.23 (dd, J = 11.7, 3.7 Hz, 1H), 3.18 (d, J = 13.8 Hz, 1H), 3.08–3.02 (m, 1H), 2.99–2.91 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5, 135.6, 135.2, 133.7, 129.3, 129.2, 129.1, 128.4, 127.7, 127.5, 126.8, 126.5, 124.8, 122.7, 121.4, 118.5, 115.9, 114.7, 62.6, 52.4, 44.4, 36.2, 35.8; IR (KBr) ν (cm^{-1}) 3065, 3032, 2939, 2249, 1642, 1598, 1573, 1508, 1455, 1372, 1261, 1089, 987, 912, 820, 754, 734, 714; HRMS (EI) Calcd for $C_{25}H_{22}N_2O$ 366.1732 $[M]^+$, found 366.1743.

4.3.13. 2-((6-Methoxynaphthalen-2-yl)methyl)-2-(1-phenylbut-3-en-1-yl)malononitrile (**3m**)

White solid (148.4 mg, 81% yield) mp 133–135 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74–7.71 (m, 2H), 7.69 (s, 1H), 7.45–7.41 (m, 5H), 7.38 (dd, J = 8.5, 1.8 Hz, 1H), 7.16 (dd, J = 8.8, 2.4 Hz, 1H), 7.13 (d, J = 2.1 Hz, 1H), 5.57–5.47 (m, 1H), 5.10 (dd, J = 17.0, 1.5 Hz, 1H), 4.99 (dd, J = 10.2, 1.5 Hz, 1H), 3.92 (s, 3H), 3.22–3.15 (m, 2H), 3.02–2.95 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 135.4, 134.5, 133.6, 129.7, 129.6, 129.4, 129.3, 129.2, 128.8, 128.2, 127.6, 127.4, 119.6, 118.7, 115.7, 114.6, 105.7, 55.5, 52.5, 45.5, 42.5, 36.5; IR (KBr) ν (cm^{-1}) 3061, 3030, 2936, 2245, 1634, 1607, 1484, 1393, 1267, 1176, 1030, 992, 917, 719, 700; HRMS (EI) Calcd for $C_{25}H_{22}N_2O$ 366.1732 $[M]^+$, found 366.1737.

4.4. Representative procedure for the α-allyl-β-benzylation reaction of arylethylidene malononitriles

An oven-dried reaction tube (25 mL) was charged with $Pd(PPh_3)_4$ (57.8 mg, 0.05 mmol), arylethylidene malononitrile (**2**, 0.5 mmol), and 2-(bromomethyl)naphthalene (**1**, 0.6 mmol). The tube was evacuated and purged with nitrogen gas for three times. Then, freshly distilled toluene (2 mL) and allyltributylstannane (198.6 mg, 0.6 mmol) were sequentially added. The reaction mixture was heated to 70 °C for 24 h. After the reaction completed, the resultant mixture was evaporated in a vacuum to give the crude product, which was then purified via basic Al_2O_3 chromatography (eluent: ethyl acetate/petroleum ether = 1:30 to 1:20) to afford α-allyl-β-benzylation products **4**.

4.4.1. 2-Allyl-2-(2-(naphthalen-2-yl)-1-phenylethyl)malononitrile (**4a**)

White solid (117.7 mg, 70% yield); mp 110–112 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74–7.71 (m, 1H), 7.66–7.62 (m, 2H), 7.42–7.37 (m, 3H), 7.29 (s, 5H), 7.06 (d, J = 12.4 Hz, 1H), 5.97–5.86 (m, 1H), 5.41 (d, J = 10.1 Hz, 1H), 5.32 (d, J = 16.9 Hz, 1H), 3.69 (dd, J = 13.4, 2.9 Hz, 1H), 3.52 (dd, J = 13.0, 12.0 Hz, 1H), 3.35 (dd, J = 11.6, 3.0 Hz, 1H), 2.53 (dd, J = 14.0, 7.3 Hz, 1H), 2.43 (dd, J = 14.0, 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.8, 134.7, 133.3, 132.2, 129.1, 129.0, 128.9, 128.7, 128.1, 127.8, 127.6, 127.5, 127.0, 126.1, 125.7, 123.2, 115.7, 114.6, 53.6, 43.3, 40.6, 38.9; IR (KBr) ν (cm^{-1}) 3449, 3084, 3030, 2926, 2248, 1643, 1601, 1508, 1494, 1455, 989, 934, 858, 834, 821, 748, 699; HRMS (EI) Calcd for $C_{24}H_{20}N_2$ 336.1626 $[M]^+$, found 336.1630.

4.4.2. 2-Allyl-2-(1-(4-fluorophenyl)-2-(naphthalen-2-yl)ethyl) malononitrile (**4b**)

White solid (116.9 mg, 66% yield); mp 92–94 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72–7.69 (m, 1H), 7.65–7.61 (m, 2H), 7.41–7.36 (m, 3H), 7.26–7.22 (m, 2H), 7.03 (d, J = 8.4 Hz, 1H), 6.95 (dd, J = 8.5, 8.5 Hz, 2H), 5.95–5.84 (m, 1H), 5.39 (d, J = 10.2 Hz, 1H), 5.30 (d, J = 16.9 Hz, 1H), 3.65 (dd, J = 12.8, 2.2 Hz, 1H), 3.41 (dd, J = 12.7, 11.9 Hz, 1H), 3.34 (dd, J = 11.8, 2.4 Hz, 1H), 2.52 (dd, J = 14.0, 7.3 Hz, 1H), 2.42 (dd, J = 14.0, 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0 (d, $^1J_{C-F}$ = 247.3 Hz), 133.2, 133.1, 131.0 (d, $^4J_{C-F}$ = 3.4 Hz), 130.9, 130.8, 129.7, 129.5, 128.8, 128.0, 127.7, 127.4, 126.6 (d, $^3J_{C-F}$ = 9.1 Hz), 118.8, 116.3 (d, $^2J_{C-F}$ = 21.4 Hz), 115.2, 114.2, 51.6, 45.3,

42.4, 36.3; IR (KBr) ν (cm^{-1}) 3055, 2959, 2927, 2246, 1604, 1511, 1448, 1371, 1230, 1162, 1015, 988, 960, 857, 841, 819, 784, 764, 747; HRMS (EI) Calcd for $C_{24}H_{19}FN_2$ 354.1532 $[M]^+$, found 354.1542.

4.4.3. 2-Allyl-2-(1-(4-chlorophenyl)-2-(naphthalen-2-yl)ethyl) malononitrile (**4c**)

White solid (120.5 mg, 65% yield); mp 87–89 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.75–7.73 (m, 1H), 7.69–7.65 (m, 2H), 7.45–7.40 (m, 3H), 7.29–7.23 (m, 4H), 7.06 (dd, J = 8.4, 1.6 Hz, 1H), 5.97–5.87 (m, 1H), 5.44 (d, J = 14.0 Hz, 1H), 5.34 (d, J = 17.0 Hz, 1H), 3.69 (dd, J = 13.2, 2.6 Hz, 1H), 3.45 (dd, J = 13.0, 11.9 Hz, 1H), 3.36 (dd, J = 11.8, 2.8 Hz, 1H), 2.55 (dd, J = 13.9, 7.3 Hz, 1H), 2.47 (dd, J = 14.0, 7.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.0, 134.3, 133.4, 133.3, 132.2, 130.3, 129.4, 128.4, 128.3, 127.8, 127.6, 127.5, 126.8, 126.3, 125.9, 123.5, 115.3, 114.4, 52.5, 43.2, 40.5, 38.7; IR (KBr) ν (cm^{-1}) 3055, 2958, 2928, 2246, 1701, 1643, 1599, 1508, 1493, 1438, 1414, 1370, 1095, 1014, 989, 960, 939, 892, 857, 836, 818, 780, 762, 743; HRMS (EI) Calcd for $C_{24}H_{19}ClN_2$ 370.1237 $[M]^+$, found 370.1241.

4.4.4. 2-Allyl-2-(1-(4-bromophenyl)-2-(naphthalen-2-yl)ethyl) malononitrile (**4d**)

White solid (139.1 mg, 67% yield); mp 81–83 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.74–7.72 (m, 1H), 7.68–7.64 (m, 2H), 7.43–7.39 (m, 5H), 7.17 (d, J = 8.1 Hz, 2H), 7.05 (dd, J = 8.4, 1.2 Hz, 1H), 5.96–5.85 (m, 1H), 5.43 (d, J = 10.1 Hz, 1H), 5.33 (d, J = 16.9 Hz, 1H), 3.68 (dd, J = 13.2, 2.8 Hz, 1H), 3.43 (dd, J = 13.0, 11.9 Hz, 1H), 3.34 (dd, J = 11.8, 2.8 Hz, 1H), 2.54 (dd, J = 14.0, 7.3 Hz, 1H), 2.45 (dd, J = 13.9, 7.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.4, 134.0, 133.4, 132.4, 130.8, 128.6, 128.5, 128.0, 127.8, 127.7, 126.9, 126.4, 126.0, 123.7, 123.3, 115.5, 114.5, 53.0, 43.2, 40.7, 38.8; IR (KBr) ν (cm^{-1}) 3054, 2955, 2925, 2246, 1698, 1643, 1600, 1590, 1508, 1489, 1438, 1410, 1371, 1272, 1076, 1010, 989, 960, 937, 857, 832, 818, 777, 762, 743, 720; HRMS (EI) Calcd for $C_{24}H_{19}BrN_2$ 414.0732 and 416.0711 $[M]^+$, found 414.0731 and 416.0718.

4.4.5. 2-Allyl-2-(2-(naphthalen-2-yl)-1-(p-tolyl)ethyl) malononitrile (**4e**)

White solid (98.1 mg, 56% yield); mp 104–106 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.74–7.72 (m, 1H), 7.67–7.62 (m, 2H), 7.44–7.39 (m, 3H), 7.18 (d, J = 7.6 Hz, 2H), 7.10–7.06 (m, 3H), 5.96–5.86 (m, 1H), 5.41 (d, J = 9.8 Hz, 1H), 5.32 (d, J = 17.0 Hz, 1H), 3.67 (dd, J = 13.8, 3.0 Hz, 1H), 3.50 (dd, J = 13.5, 11.7 Hz, 1H), 3.33 (dd, J = 11.5, 3.2 Hz, 1H), 2.52 (dd, J = 14.2, 7.4 Hz, 1H), 2.43 (dd, J = 14.0, 7.2 Hz, 1H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 135.1, 133.5, 132.3, 131.8, 129.9, 129.0, 128.9, 128.2, 127.9, 127.7, 127.2, 126.2, 125.8, 123.3, 115.9, 114.8, 53.4, 43.6, 40.7, 39.0, 21.3; IR (KBr) ν (cm^{-1}) 3450, 3057, 3025, 2926, 2248, 1644, 1632, 1516, 1444, 989, 935, 856, 834, 823, 779, 765, 742; HRMS (EI) Calcd for $C_{25}H_{22}N_2$ 350.1783 $[M]^+$, found 350.1787.

4.4.6. 2-Allyl-2-(1-(4-methoxyphenyl)-2-(naphthalen-2-yl)ethyl) malononitrile (**4f**)

White solid (95.3 mg, 49% yield); mp 120–122 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.74–7.71 (m, 1H), 7.68–7.62 (m, 2H), 7.44–7.39 (m, 3H), 7.26–7.20 (m, 2H), 7.07 (d, J = 8.3 Hz, 1H), 6.81 (d, J = 8.1 Hz, 2H), 5.96–5.86 (m, 1H), 5.41 (d, J = 10.2 Hz, 1H), 5.32 (dd, J = 16.9, 10.2 Hz, 1H), 3.74 (s, 3H), 3.66 (dd, J = 13.4, 2.9 Hz, 1H), 3.47 (dd, J = 13.2, 11.9 Hz, 1H), 3.32 (dd, J = 11.7, 2.9 Hz, 1H), 2.52 (dd, J = 14.0, 7.4 Hz, 1H), 2.43 (dd, J = 14.0, 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.1, 133.5, 132.3, 130.3, 128.9, 128.2, 127.9, 127.7, 127.2, 126.7, 126.2, 125.8, 123.3, 115.9, 114.8, 114.5, 55.4, 53.0, 43.7, 40.7, 39.0; IR (KBr) ν (cm^{-1}) 3448, 3054, 3012, 2933, 2246, 1611, 1514, 1463, 1440, 1305, 1254, 1181, 1033, 989, 936, 857, 836, 812, 783, 745; HRMS (EI) Calcd for $C_{25}H_{22}N_2O$ 366.1732 $[M]^+$, found 366.1741.

4.4.7. 2-Allyl-2-(1,2-di(naphthalen-2-yl)ethyl)malononitrile (**4g**)

White solid (106.3 mg, 55% yield); mp 121–123 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.84–7.79 (m, 2H), 7.76–7.74 (m, 1H), 7.70–7.67 (m, 1H), 7.64–7.57 (m, 2H), 7.51–7.45 (m, 5H), 7.38–7.36 (m, 2H), 7.07 (dd, J = 8.4, 1.3 Hz, 1H), 5.98–5.87 (m, 1H), 5.41 (dd, J = 10.1, 0.4 Hz, 1H), 5.30 (dd, J = 16.9, 0.9 Hz, 1H), 3.78 (dd, J = 13.4, 3.0 Hz, 1H), 3.67 (dd, J = 13.4, 11.5 Hz, 1H), 3.54 (dd, J = 11.3, 3.0 Hz, 1H), 2.56 (dd, J = 14.2, 7.3 Hz, 1H), 2.42 (dd, J = 13.9, 7.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.9, 133.4, 133.2, 132.3, 129.2, 129.1, 128.8, 128.3, 128.2, 127.9, 127.8, 127.7, 127.1, 126.9, 126.8, 126.2, 125.8, 123.4, 115.9, 114.7, 114.6, 54.0, 43.6, 40.8, 39.1; IR (KBr) ν (cm^{-1}) 3450, 3053, 2923, 2250, 1642, 1600, 1508, 1440, 1375, 990, 936, 861, 830, 813, 782, 750, 743, 478; HRMS (EI) Calcd for $C_{28}H_{22}N_2$ 386.1783 $[M]^+$, found 386.1784.

4.4.8. 2-Allyl-2-(2-(naphthalen-2-yl)-1-(thiophen-2-yl)ethyl) malononitrile (**4h**)

White solid (54.8 mg, 32% yield); mp 110–112 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.76–7.74 (m, 1H), 7.70–7.67 (m, 2H), 7.48 (s, 1H), 7.45–7.40 (m, 2H), 7.24 (d, J = 7.0 Hz, 1H), 7.12 (d, J = 8.4 Hz, 1H), 6.99 (d, J = 3.2 Hz, 1H), 6.93 (dd, J = 4.9, 3.7 Hz, 1H), 5.99–5.88 (m, 1H), 5.44 (d, J = 10.1 Hz, 1H), 5.38 (d, J = 16.8 Hz, 1H), 3.73 (dd, J = 13.0, 2.7 Hz, 1H), 3.68 (dd, J = 11.5, 2.8 Hz, 1H), 3.42 (dd, J = 12.7, 11.8 Hz, 1H), 2.63–2.53 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.0, 134.5, 133.5, 132.4, 128.7, 128.3, 128.2, 128.0, 127.7, 127.4, 126.9, 126.4, 126.3, 125.9, 123.7, 115.4, 114.5, 49.4, 43.9, 40.8, 40.5; IR (KBr) ν (cm^{-1}) 3447, 2957, 2923, 2853, 2252, 1636, 1508, 1458, 1442, 1295, 1076, 992, 935, 859, 833, 785, 746, 702; HRMS (EI) Calcd for $C_{22}H_{18}N_2S$ 342.1191 $[M]^+$, found 342.1199.

4.4.9. 2-Allyl-2-(2-(1-chloronaphthalen-2-yl)-1-phenylethyl) malononitrile (**4i**)

White solid (124.2 mg, 67% yield); mp 94–96 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, J = 8.5 Hz, 1H), 7.69 (d, J = 8.1 Hz, 1H), 7.57–7.53 (m, 1H), 7.47–7.40 (m, 2H), 7.27 (s, 5H), 6.83 (d, J = 8.4 Hz, 1H), 5.98–5.88 (m, 1H), 5.40 (d, J = 10.1 Hz, 1H), 5.32 (d, J = 16.9 Hz, 1H), 3.95 (dd, J = 20.0, 10.5 Hz, 1H), 3.58–3.51 (m, 2H), 2.59 (dd, J = 13.9, 7.4 Hz, 1H), 2.47 (dd, J = 14.0, 7.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.0, 133.5, 132.5, 131.3, 131.1, 129.1, 129.0, 128.8, 128.5, 128.1, 127.3, 126.6, 126.5, 124.5, 123.4, 115.3, 114.7, 51.0, 43.2, 40.8, 37.6; IR (KBr) ν (cm^{-1}) 3061, 3035, 2929, 2248, 1643, 1598, 1560, 1496, 1455, 1334, 1227, 992, 935, 910, 818, 771, 753, 733, 705; HRMS (EI) Calcd for $C_{24}H_{19}ClN_2$ 370.1237 $[M]^+$, found 370.1242.

4.4.10. 2-Allyl-2-(2-(1-bromonaphthalen-2-yl)-1-phenylethyl) malononitrile (**4j**)

White solid (97.6 mg, 47% yield); mp 104–106 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, J = 8.6 Hz, 1H), 7.68 (d, J = 8.1 Hz, 1H), 7.58–7.54 (m, 1H), 7.48–7.43 (m, 2H), 7.28 (s, 5H), 6.81 (d, J = 8.4 Hz, 1H), 5.99–5.89 (m, 1H), 5.41 (d, J = 10.2 Hz, 1H), 5.33 (d, J = 16.8 Hz, 1H), 3.98 (dd, J = 24.1, 14.0 Hz, 1H), 3.64–3.55 (m, 2H), 2.61 (dd, J = 13.9, 7.4 Hz, 1H), 2.48 (dd, J = 14.0, 7.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.9, 134.7, 133.5, 132.4, 129.2, 129.1, 129.0, 128.9, 128.8, 128.1, 127.6, 127.4, 127.3, 126.5, 124.5, 123.4, 115.3, 114.7, 50.8, 43.1, 40.8, 40.3; IR (KBr) ν (cm^{-1}) 3061, 3034, 2930, 2248, 1643, 1597, 1557, 1497, 1455, 1330, 1257, 1224, 978, 936, 908, 819, 769, 753, 733, 704; HRMS (EI) Calcd for $C_{24}H_{19}BrN_2$ 414.0732 and 416.0711 $[M]^+$, found 414.0721 and 416.0720.

4.4.11. 2-Allyl-2-(2-(6-bromonaphthalen-2-yl)-1-phenylethyl) malononitrile (**4k**)

White solid (101.7 mg, 49% yield); mp 94–96 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.55–7.51 (m, 2H), 7.47 (dd, J = 8.8, 1.8 Hz, 1H), 7.38 (s, 1H), 7.29 (s, 5H), 7.08 (dd, J = 8.6, 1.6 Hz, 1H),

5.96–5.86 (m, 1H), 5.42 (d, J = 10.5 Hz, 1H), 5.32 (d, J = 17.0 Hz, 1H), 3.67 (dd, J = 13.4, 3.0 Hz, 1H), 3.50 (dd, J = 11.6, 11.6 Hz, 1H), 3.32 (dd, J = 11.5, 3.2 Hz, 1H), 2.52 (dd, J = 13.7, 7.3 Hz, 1H), 2.43 (dd, J = 13.5, 7.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.4, 134.8, 133.4, 131.8, 129.7, 129.6, 129.32, 129.27, 129.2, 129.1, 128.8, 128.2, 127.9, 127.3, 123.5, 119.8, 115.7, 114.6, 53.6, 43.4, 40.7, 39.1; IR (KBr) ν (cm^{-1}) 3032, 2924, 2246, 1590, 1498, 1455, 1062, 989, 936, 879, 807, 731, 706; HRMS (EI) Calcd for $C_{24}H_{19}BrN_2$ 414.0732 and 416.0711 $[M]^+$, found 414.0721 and 416.0722.

4.4.12. 2-Allyl-2-(2-(1-methoxynaphthalen-2-yl)-1-phenylethyl) malononitrile (**4l**)

White solid (137.4 mg, 75% yield); mp 110–112 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.4 Hz, 1H), 7.72 (d, J = 8.3 Hz, 1H), 7.50–7.47 (m, 1H), 7.44–7.40 (m, 1H), 7.33–7.26 (m, 6H), 6.84 (d, J = 8.4 Hz, 1H), 5.98–5.88 (m, 1H), 5.40 (d, J = 10.0 Hz, 1H), 5.31 (d, J = 16.8 Hz, 1H), 3.99 (s, 3H), 3.79 (dd, J = 13.0, 2.8 Hz, 1H), 3.58 (dd, J = 13.0, 2.8 Hz, 1H), 3.41 (dd, J = 12.7, 12.7 Hz, 1H), 2.53 (dd, J = 13.9, 7.3 Hz, 1H), 2.41 (dd, J = 14.0, 7.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 135.3, 134.4, 129.1, 129.0, 128.9, 128.5, 128.2, 128.0, 126.1, 126.0, 124.0, 123.3, 122.1, 115.9, 114.8, 62.3, 52.1, 43.6, 40.7, 34.3; IR (KBr) ν (cm^{-1}) 3063, 2937, 2247, 1643, 1597, 1573, 1507, 1495, 1455, 1371, 1260, 1246, 1080, 990, 935, 911, 820, 754, 732, 702; HRMS (EI) Calcd for $C_{25}H_{22}N_2O$ 366.1732 $[M]^+$, found 366.1732.

4.4.13. 2-Allyl-2-(2-(6-methoxynaphthalen-2-yl)-1-phenylethyl) malononitrile (**4m**)

White solid (159.4 mg, 87% yield); mp 110–112 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, J = 9.5, 9.5 Hz, 2H), 7.34 (s, 1H), 7.29 (s, 5H), 7.08 (dd, J = 8.8, 2.5 Hz, 1H), 7.00–7.03 (m, 2H), 5.86–5.96 (m, 1H), 5.41 (d, J = 10.2 Hz, 1H), 5.31 (d, J = 17.0 Hz, 1H), 3.87 (s, 3H), 3.65 (dd, J = 13.6, 3.3 Hz, 1H), 3.48 (dd, J = 13.3, 11.6 Hz, 1H), 3.32 (dd, J = 11.5, 3.2 Hz, 1H), 2.52 (dd, J = 14.1, 7.5 Hz, 1H), 2.42 (dd, J = 14.0, 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 135.1, 133.4, 132.5, 129.2, 129.0, 128.9, 128.8, 127.8, 127.7, 127.0, 123.4, 119.1, 115.8, 114.7, 105.6, 55.4, 53.8, 43.4, 40.8, 38.9; IR (KBr) ν (cm^{-1}) 3060, 3032, 3006, 2956, 2246, 1635, 1606, 1484, 1392, 1266, 1232, 1197, 1031, 989, 936, 852, 724, 701; HRMS (EI) Calcd for $C_{25}H_{22}N_2O$ 366.1732 $[M]^+$, found 366.1738.

4.4.14. ((1-Bromonaphthalen-2-yl)methyl)tributylstannane (**5**)

Colorless oil (94.8 mg, 31% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 8.4 Hz, 1H), 7.73 (d, J = 8.0 Hz, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.52 (dd, J = 7.6, 7.2 Hz, 1H), 7.37 (dd, J = 7.6, 6.8 Hz, 1H), 7.20 (d, J = 8.4 Hz, 1H), 2.69 (s, 2H), 1.46–1.38 (m, 6H), 1.25–1.20 (m, 6H), 0.87–0.79 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 133.0, 131.8, 128.1, 127.6, 127.4, 127.3, 126.5, 124.6, 29.2, 27.5, 22.3, 13.8, 10.5; IR (neat) ν (cm^{-1}) 3049, 2955, 2921, 2869, 2849, 1620, 1595, 1498, 1462, 1374, 1329, 1257, 1220, 1078, 968, 812, 744.

4.4.15. ((6-Bromonaphthalen-2-yl)methyl)tributylstannane (**6**)

Colorless oil (153.0 mg, 50% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.56 (d, J = 8.4 Hz, 1H), 7.52 (d, J = 8.6 Hz, 1H), 7.44 (dd, J = 8.4, 2.0 Hz, 1H), 7.35 (s, 1H), 7.16 (dd, J = 8.4, 1.6 Hz, 1H), 2.45 (s, 2H), 1.46–1.38 (m, 6H), 1.29–1.20 (m, 6H), 0.86–0.79 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 132.6, 131.7, 129.7, 129.2, 128.5, 128.4, 127.0, 123.5, 29.2, 27.5, 19.0, 13.9, 9.7; IR (neat) ν (cm^{-1}) 3049, 2955, 2923, 2869, 2851, 1586, 1495, 1462, 1194, 1064, 896, 875, 810, 799.

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Appendix A. Supplementary data

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References

[1] I. Nakamura, Y. Yamamoto, Chem. Rev. 104 (2004) 2127–2198.
[2] N.T. Patil, Y. Yamamoto, Synlett 13 (2007) 1994–2005.
[3] B.M. Trost, C.-J. Li, Tetrahedron Lett. 34 (1993) 2271–2274.
[4] H. Nakamura, J.G. Shim, Y. Yamamoto, J. Am. Chem. Soc. 119 (1997) 8113–8114.
[5] N. Solin, S. Narayan, K.J. Szabó, J. Org. Chem. 66 (2001) 1686–1693.
[6] S.C. George, J. John, S. Anas, J. John, Y. Yamamoto, E. Suresh, K.V. Radhakrishnan, Eur. J. Org. Chem. (2010) 5489–5497.
[7] H. Nakamura, K. Shimizu, Tetrahedron Lett. 52 (2011) 426–429.
[8] S.C. George, S. Thulasi, K.V. Radhakrishnan, Y. Yamamoto, Org. Lett. 13 (2011) 4984–4987.
[9] L. Adak, S. Bhadra, K. Chattopadhyay, B.C. Ranu, New J. Chem. 35 (2011) 430–437.
[10] M. Jeganmohan, M. Shanmugasundaram, C.-H. Cheng, J. Org. Chem. 69 (2004) 4053–4062 (and references therein).
[11] J.G. Shim, H. Nakamura, Y. Yamamoto, J. Org. Chem. 120 (1998) 8470–8474.
[12] H. Nakamura, M. Sekido, M. Ito, Y. Yamamoto, J. Am. Chem. Soc. 120 (1998) 6838–6839.
[13] H. Nakamura, H. Shibata, Y. Yamamoto, Tetrahedron Lett. 41 (2000) 2911–2914.
[14] K. Aoyagi, H. Nakamura, Y. Yamamoto, J. Org. Chem. 67 (2002) 5977–5980.
[15] J.-G. Shim, J.C. Park, C.S. Cho, S.C. Shim, Y. Yamamoto, J. Chem. Soc. Chem. Commun. (2002) 852–853.
[16] X. Zhang, X. Feng, X. Yu, R. He, M. Bao, Org. Biomol. Chem. 11 (2013) 4016–4024.
[17] C. Bazzini, S. Brovelli, T. Caronna, Eur. J. Org. Chem. (2005) 1247–1257.
[18] C.T. Goralski, J.R. McCarthy, W.R. Kracht, J. Lab. Com Rad. (1987) 852–858.
[19] G. Chouhan, H. Alper, J. Org. Chem. 74 (2009) 6181–6189.
[20] N. Kongkathip, B. Kongkathip, P. Siripong, Bioorg. Med. Chem. 11 (2003) 3179–3191.
[21] R.W. Hartmann, A. Palusczak, F. Lacan, G. Ricci, R. Ruzziconi, J. Enzym. Inhib. 19 (2004) 145–155.