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Palladium-Catalyzed Alkynylation of Morita–Baylis–Hillman Carbonates with (Triisopropylsilyl)acetylene on Water

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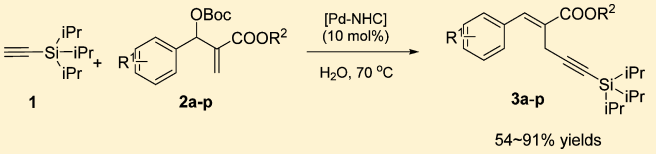
Supporting Information

ABSTRACT: Direct alkynylation of Morita–Baylis–Hillman carbonates with (triisopropylsilyl)acetylene catalyzed by a $Pd(OAc)_2$–NHC complex was developed "on water" to give the corresponding 1,4-enynes. The significant effects of water amount in the solvent on further transformations of 1,4-enynes were investigated.



INTRODUCTION

The Pd-catalyzed allylation of carbon nucleophiles with allylic compounds via π-allylpalladium complexes (Tsuji–Trost reaction) represents one of the most important developments in modern synthetic chemistry.[1] Recently, the Tsuji–Trost reaction of allyl ester with terminal alkynes (or corresponding metal reagent) has received considerable attention because it provides a convenient and direct approach to construct the 1,4-enyne moiety.[2] At the same time, the extensive use of organic solvents has led to concerns regarding their toxicity, hazard, pollution, and waste treatment issues. Water, being cheap, readily available, nontoxic, and nonflammable, has shown extensive potential in organic reactions. In view of sustainable chemistry, the interest in metal-catalyzed processes in aqueous media and air conditions has been increasing dramatically.[3] It is noteworthy that although the aqueous Tsuji–Trost reaction has been developed widely,[4] there has been no example of using a terminal alkyne as a pronucleophile for an aqueous Tsuji–Trost reaction.[5] It is probably attributed to low acidity of terminal alkynes as pronucleophiles, and the Tsuji–Trost reaction is very sensitive to the acidity of the C–H bonds of the pronucleophiles.[5,6] Therefore, the quest for water-stable and more efficient catalyst systems for the coupling of allyl esters with terminal alkynes in water remains a great challenge.

Allylic alkylation of Morita–Baylis–Hillman (MBH) adducts, which possess both allylic hydroxyl and Michael acceptor units in the same molecule, has been widely applied in the synthesis of natural products and bioactive compounds.[7] The reaction of MBH adducts with alkynyl metal could provide allylic substitution products;[8] however, terminal alkynes were seldom directly used as nucleophiles in the alkynylation of MBH adducts.[8d] Very recently, we reported a direct coupling of terminal alkynes with allylic alcohols catalyzed by $Pd(PPh_3)_4$ with a N,P-ligand.[9] Based on our ongoing interest in the transformations of the MBH adducts, as well as organic reactions in aqueous media,[10,11] herein, we wish to report the alkynylation of MBH carbonates with (triisopropylsilyl)-acetylene catalyzed by a [Pd–NHC] complex on water under an air atmosphere.

RESULTS AND DISCUSSION

Initially, the reaction of (triisopropylsilyl)acetylene **1** and MBH carbonate **2a** was investigated under the catalysis of $Pd(PPh_3)_4$ with N,P-ligand **L1** in water alone.[9] However, only 12% yield of the product **3a** was obtained (Table 1). Thus, we turned our attention to more electron-rich ligand to effect the aqueous Tsuji–Trost reaction of (triisopropylsilyl)acetylene. N-Heterocyclic carbene (NHC) ligands have been successfully applied in various transition-metal-catalyzed reactions due to their strong bonding to metal centers and good stability toward air and moisture.[12] As shown in Figure 1 and Table 1, the use of the NHC ligands **L3–L6** in the Pd-catalyzed coupling reaction of terminal alkyne **1** and MBH carbonate **2a** in water provided the desired product **3a** in 38–54% yield, respectively (entries 6–9). It was found that the catalytic activity strongly depended upon the molecular structure of the NHC ligand used. When thiazolyl NHC ligands **L7–L9** were used, 20–21% yield of **3a** was obtained (entries 10–12). The desired product **3a** was obtained in 37% yield in the presence of the Pd catalyst, prepared in situ from $PdCl_2$ and NHC ligand **L2** (Table 1, entry 2). The use of the $Pd(TFA)_2$ with **L2** gave an increased yield (68%, entry 3). In the presence of a base (10 mol %) such as triethylamine (TEA) as additive, the yield of product **3a** was increased to 61% (entry 4). The best result (71% yield, entry 5) was obtained with the combination of $Pd(OAc)_2$ with NHC ligand **L2**.

Notably, no reaction was observed in the absence of $Pd(OAc)_2$ (entry 13). Moreover, when $Pd(OAc)_2$ was employed alone without the use of NHC ligand, a poor yield

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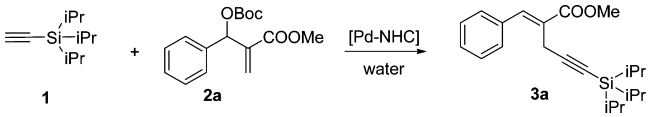
Table 1. Optimization of the NHC Ligands[a]



entry	Pd salts	NHC ligands	yield (%)
1	$Pd(PPh_3)_4$	**L1**	12
2	$PdCl_2$	**L2**	37
3	$Pd(TFA)_2$	**L2**	68
4	$Pd(OAc)_2$	**L2**+TEA	61
5	$Pd(OAc)_2$	**L2**	71
6	$Pd(OAc)_2$	**L3**	38
7	$Pd(OAc)_2$	**L4**	52
8	$Pd(OAc)_2$	**L5**	54
9	$Pd(OAc)_2$	**L6**	38
10	$Pd(OAc)_2$	**L7**	20
11	$Pd(OAc)_2$	**L8**	20
12	$Pd(OAc)_2$	**L9**	21
13		**L2**	NR
14	$Pd(OAc)_2$		14

[a]Reaction conditions: **1** (0.5 mmol), MBH carbonate **2a** (0.2 mmol), [Pd–NHC] catalysts (10 mol %), 2 mL of water, under air atmosphere, 70 °C for 10 h. [Pd–NHC] catalysts were prepared in situ at rt by mixing $Pd(OAc)_2$ (10 mol %), NHC ligands (20 mol %), and *t*-BuOK (24 mol %) in THF (2 mL) for 2 h, followed by the removal of the solvent under reduced pressure.

of **3a** (14%) was obtained (entry 14), suggesting that both $Pd(OAc)_2$ and NHC ligand **L2** are necessary and cooperatively catalyze this reaction.

Subsequently, the solvent effect was examined (Table 2) using the reaction of **1** with **2a** in the presence of Pd(II) catalyst, prepared in situ from $Pd(OAc)_2$ (10 mol %) and NHC ligand **L2** (20 mol %). When organic solvents such as THF, acetone, DMF, and dioxane were used, very little desired product **3a** was isolated (4–23% yield, Table 2, entries 1–4).

It was noteworthy that with the increased proportion of water in a mixture of dioxane/water (>1:1), the yield of **3a** increased despite the reaction system becoming heterogeneous (entries 8–11). For the yield of product **3a**, the heterogeneous system was better than the homogeneous system (entries 4–7 vs 8–11). On the other hand, under the solvent-free conditions, the product **3a** was obtained in 44% yield (entry 15), which was relatively lower than the best result (71% yield) under water-only conditions (entry 11). When the reaction was

Table 2. Optimization of the Solvent and Temperature[a]

entry	solvent	temperature (°C)	yield (%)
1	THF	70	20
2	acetone	70	7
3	DMF	70	4
4	dioxane[b]	70	23
5	dioxane/water (3:1)[b]	70	34
6	dioxane/water (2:1)[b]	70	11
7	dioxane/water (1:1)[b]	70	20
8	dioxane/water (1:2)[c]		44
9	dioxane/water (1:3)[c]	70	45
10	dioxane/water (1:4)[c]	70	64
11	water[c]	70	71
12	water	90	55
13	water	50	48
14	water	30	trace
15		70	44

[a]Reaction conditions: **1** (0.5 mmol), MBH carbonate **2a** (0.2 mmol), [Pd–NHC] catalyst (10 mol %), solvent (2 mL), under air atmosphere, 70 °C for 10 h. [Pd–NHC] catalysts were prepared in situ at rt by mixing $Pd(OAc)_2$ (10 mol %), NHC ligand **L2** (20 mol %), and *t*-BuOK (24 mol %) in THF (2 mL) for 2 h, and then the solvent was removed under reduced pressure. [b]Homogeneous. [c]Heterogeneous.

scaled up 10-fold with the substrates **2a** (2 mmol) and **1** (5 mmol) under the same conditions, the yield of **3a** was increased up to 94%. These interesting results are consistent with the suggestion of the reaction proceeding "on water" put forward by Sharpless.[13] The on water reaction in heterogeneous aqueous media offers better results than the same reactions proceeding in homogeneous aqueous media and under solvent-free conditions.

Screening of different reaction temperatures at 30–90 °C revealed that 70 °C is the optimal temperature, and decreasing or increasing the reaction temperature would result in decreased yields (Table 2, entries 11–14).

With the optimized reaction conditions in hand, various substituted MBH carbonates **2a–r** were reacted with (triisopropylsilyl)acetylene **1** in water, affording the corresponding 1,4-enynes products **3a–r** in good to excellent yields.

The results are summarized in Scheme 1. The substituents, either electron-withdrawing or electron-donating, except CN (**2j**) on the phenyl ring of the MBH carbonates, did not influence the reaction yield significantly. If the ester group was changed from methyl to *t*-butyl or *n*-butyl, the yields of

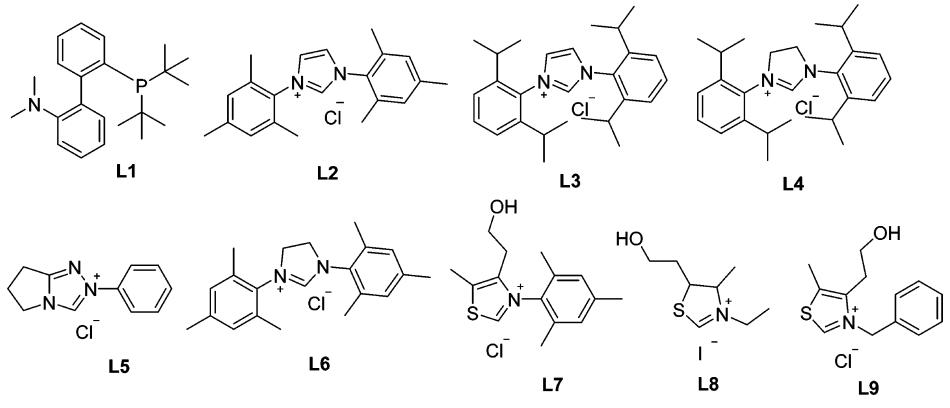


Figure 1. NHC ligands.

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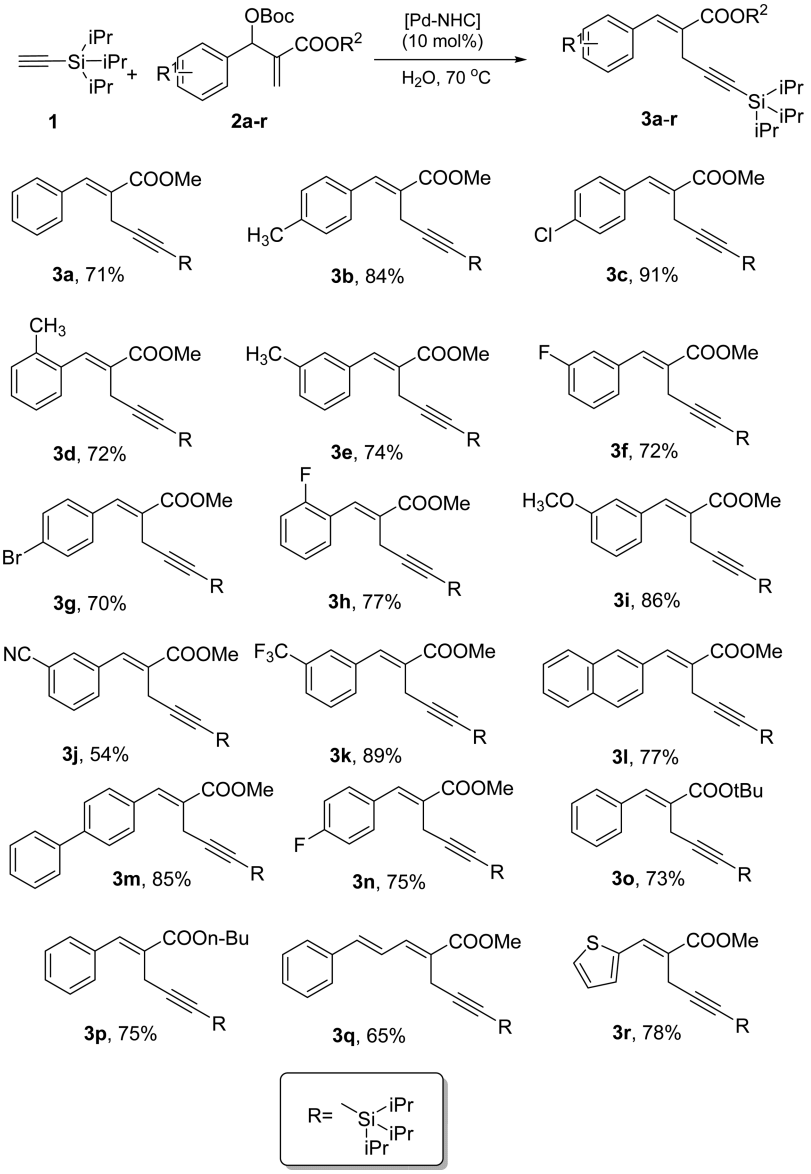
Scheme 1. $Pd(OAc)_2$–L2 Catalyzed Allylation of 1 with MBH Carbonates[a]



[a]Reaction conditions: **1** (0.5 mmol), MBH carbonates **2a–r** (0.2 mmol), [Pd–NHC] catalyst (10 mol %) in water (2 mL) at 70 °C for 10 h. [Pd–NHC] catalysts were prepared in situ at rt by mixing $Pd(OAc)_2$ (10 mol %), NHC ligand **L2** (20 mol %), and *t*-BuOK (24 mol %) in THF (2 mL) for 2 h, and then the solvent was removed under reduced pressure.

products **3o** and **3p** still remained 73 and 75%, respectively. In addition, if the phenyl ring of the MBH carbonates was replaced by cinnamenyl or thienyl, the yields of products **3q** and **3r** were 65 and 78%, respectively. For simple allylic carbonate, *tert*-butyl(1-phenylallyl)carbonate could also react with (triisopropylsilyl)acetylene **1** to afford the corresponding 1,4-enyne product in a low yield (56%).

The proposed mechanism for this coupling reaction is shown in Figure 2. The departure of the OBoc group of MBH carbonate released carbon dioxide and *tert*-butoxide anion and generated a π-allyl palladium intermediate **A** and a hydroxyl anion. Coordination of terminal alkyne to **A** generated intermediate **B**. The hydroxyl anion may help to deprotonate the terminal alkyne to form intermediate **C**. Subsequently, intermediate **C** transformed into 1,4-enyne via reductive elimination.

The significant effects of water amount in the solvent on subsequent desilylation of 1,4-enyne were observed. When **3a** was treated with TBAF in THF without water or 1 equiv of water, 1,3-enyne **4a** was obtained (Table 3, entries 1 and 2).[14] As the amount of water in the system was changed, the product mixtures of rearrangement product **4a**, desilylation product **5a**, and cyclization product **6a** could be obtained in different ratios. If the amount of water was 40 equiv, desilylation product **5a** was obtained in 81% yield exclusively (entry 6). When DBU was added in the reaction of **3a** in the presence of 10 equiv of water in TBAF/THF, cyclization product **6a** was formed in 78% yield and prevented the production of **4a** (entry 4).[15] While the amount of water was increased to 70 equiv, no reaction was observed (entry 7).

Under the optimized conditions, the desilylation products **5a–c** were obtained in good yields by treating 1,4-enynes **3**

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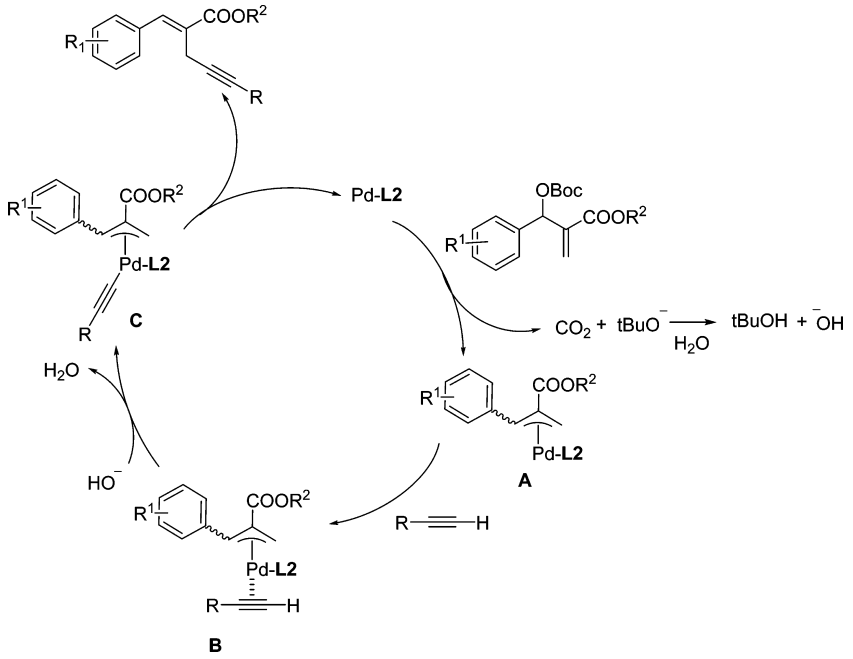
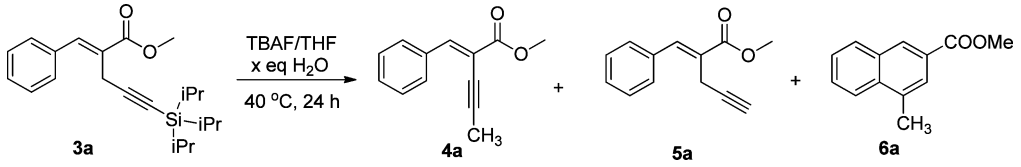


Figure 2. Tentative mechanism for the [Pd−NHC]-catalyzed coupling of MBH carbonates with (triisopropylsilyl)acetylene.

Table 3. Optimization of the Amount of Water in the Conversion of 3a[a]



entry	equiv of H_2O	yield of **4a** (%)	yield of **5a** (%)	yield of **6a** (%)
1	0	75	0	0
2	1	39	0	0
3	10	32	0	61
4[b]	10	0	0	78
5	20	0	52	23
6	40	0	81	0
7	70	0	0	0

[a]Reaction conditions: 1,4-enyne **3a** (0.2 mmol), H_2O (x equiv), TBAF (0.6 mmol) in THF (2 mL) at 40 °C for 24 h. [b]DBU (1 equiv).

with TBAF in the presence of 40 equiv of water in THF (Table 4, entries 1−3).

Corresponding 1,4-enyne products **3** could also be transformed to naphthalene derivatives **6a−g** in high yields by being treated with TBAF in the presence of DBU in THF with a small amount of water (Table 4, entries 4−10).

A proposed mechanism for the conversion of 1,4-enyne is shown in Figure 3. By treating 1,4-enyne with TBAF, intermediate **I** was generated, which was converted to the desilylation product **5a** with slightly large amount of water. Meanwhile, allene intermediate **II** could be formed through 1,3-hydrogen shift of intermediate **I**. From allene intermediate **II**, the cyclization product **6a** through 6-π electron cyclization and product **4a** through 1,3-hydrogen rearrangement were obtained.

CONCLUSION

A direct alkynylation of MBH carbonates with (triisopropylsilyl)acetylene catalyzed by a $Pd(OAc)_2$−NHC complex was developed "on water". The reaction provided the corresponding 1,4-enynes in good yields, which could be further deprotected by the silyl group to access 1,3-enyne derivatives, 1,4-enyne derivatives, and 1-methylnaphthalene derivatives by changing the addition of different amounts of water in a one-pot reaction. The amount of water in the solvent employed strongly influenced the subsequent conversion of 1,4-enyne. Starting from 1,4-enyne, the cyclization products were synthesized in high yields.

EXPERIMENTAL SECTION

Typical Procedure for [Pd−NHC]-Catalyzed Alkynylation of Morita−Baylis−Hillman Carbonates with (Triisopropylsilyl)-acetylene. $Pd(OAc)_2$ (0.0045 g, 0.02 mmol, 10 mol %), NHC ligand **L2** (0.0136 g, 0.04 mmol, 20 mol %), and *t*-BuOK (0.0054 g, 0.048 mmol, 24 mol %) were added to a dried Schlenk tube under N_2 atmosphere. THF (2 mL) was added, and the solution was deoxygenated (three vacuum−argon cycles) at room temperature. The mixture was stirred at room temperature for 2 h, and then the solvent was removed under reduced pressure. Then, (triisopropylsilyl)acetylene (0.091 g, 0.5 mmol), MBH carbonates **2a−r** (0.2 mmol), and 2 mL of water were added under air

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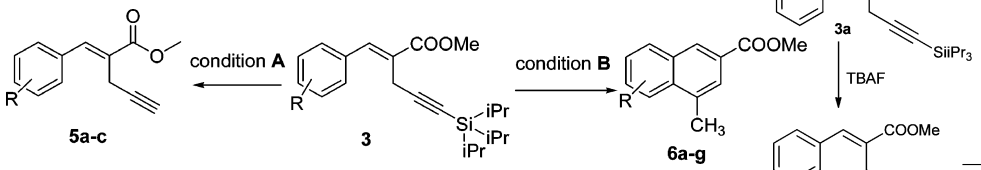
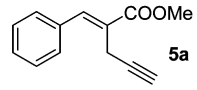
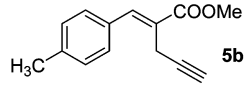
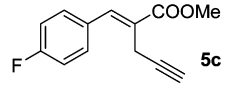
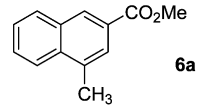
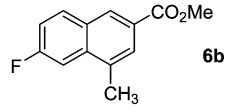
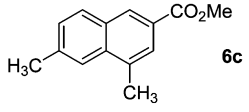
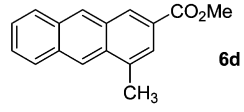
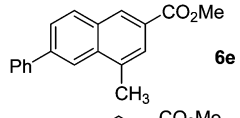
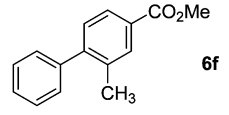
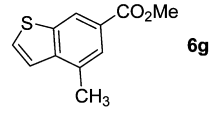
Table 4. Conversion of 1,4-Enynes 3 to 5 and 6[a,b]



Entry	1,4-Enyne	Condition	Product	Yield (%)
1	3a	A	 5a	81
2	3b	A	 5b	86
3	3n	A	 5c	52
4	3a	B	 6a	78
5	3n	B	 6b	55
6	3b	B	 6c	83
7	3l	B	 6d	85
8	3m	B	 6e	83
9	3q	B	 6f	82
10	3r	B	 6g	80

[a]Reaction conditions **A**: **3** (0.2 mmol), H_2O (40 equiv), TBAF (0.6 mmol) in THF (2 mL) at 40 °C for 24 h. [b]Reaction conditions **B**: **3** (0.2 mmol), H_2O (10 equiv), TBAF (0.6 mmol), and DBU (1 equiv) in THF (2 mL) at 40 °C for 24 h.

atmosphere at room temperature and heated at 70 °C for 10 h. The reaction mixture was cooled to room temperature and extracted with dichloromethane (150 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give the crude product. The products **3a**−**r** were isolated from the dark crude mixture by flash column chromatography (the eluent used was 30:1 petroleum ether/ethyl acetate).

Conversion of 1,4-Enynes 3 into Desilylation Derivatives 5. The 1,4-enyne **3a** (0.0712 g, 0.2 mmol) was dissolved in anhydrous THF (2 mL) under argon atmosphere in a 25 mL Schlenk flask. Then, H_2O (144 mg, 8 mmol) and TBAF (0.4 mL, 0.4 mmol, 1 M in THF)

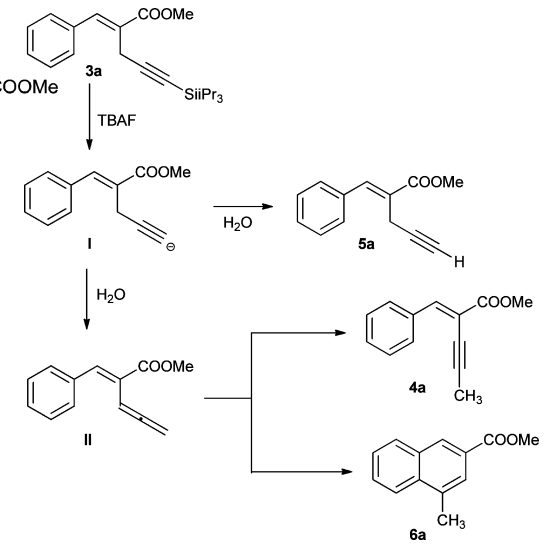


Figure 3. Proposed mechanism for the conversion of 1,4-enyne.

were added into the solution, and the mixture was stirred for 24 h at 40 °C. The reaction mixture was poured into water (100 mL) and extracted with dichloromethane (150 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give the crude product. The product **5** was isolated from the crude mixture by flash column chromatography (the eluent used was 30:1 petroleum ether/ethyl acetate).

Conversion of 1,4-Enynes 3 into 1-Methylnaphthalene Derivatives 6. The 1,4-enyne **3a** (0.0712 g, 0.2 mmol) was dissolved in anhydrous THF (2 mL) under argon atmosphere in a 25 mL Schlenk flask. Then, H_2O (36 mg, 2 mmol), DBU (30.4 mg, 0.2 mmol), and TBAF (0.4 mL, 0.4 mmol, 1 M in THF) were added into the solution, and the mixture was stirred for 24 h at 40 °C. The reaction mixture was poured into water (100 mL) and extracted with dichloromethane (150 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give the crude product. The product **6** was isolated from the crude mixture by flash column chromatography (the eluent used was 30:1 petroleum ether/ethyl acetate).

***(E)*-Methyl-2-benzylidene-5-(triisopropylsilyl)pent-4-ynoate (3a):** Colorless oil, 50.4 mg, yield 71%; ^{1}H NMR (300 MHz, $CDCl_3$-d_1) δ 7.76 (s, 1H), 7.59 (d, J = 6.8 Hz, 2H), 7.40 (td, 3H), 3.85 (s, 3H), 3.43 (s, 2H), 1.06 (d, 21H) ppm; ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$-d_1) δ 167.7, 140.3, 134.9, 129.7, 128.9, 128.5, 127.9, 105.6, 81.4, 52.2, 19.4, 18.6, 11.2 ppm; HRMS-EI (m/z) calcd for $C_{22}H_{32}O_2Si$, $[M]^+$ 356.2172; found, 356.2177.

***(E)*-Methyl-2-(4-methylbenzylidene)-5-(triisopropylsilyl)-pent-4-ynoate (3b):** Colorless oil, 62 mg, yield 84%; ^{1}H NMR (300 MHz, $CDCl_3$-d_1) δ 7.74 (s, 1H), 7.50 (d, J = 8.1 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 3.84 (s, 3H), 3.44 (s, 2H), 2.38 (s, 3H), 1.06 (d, J = 2.8 Hz, 21H) ppm; ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$-d_1) δ 167.8, 140.4, 139.2, 132.1, 129.8, 129.2, 127.0, 105.8, 81.2, 52.1, 21.3, 19.4, 18.5, 11.2 ppm; HRMS-APCI (m/z) calcd for $C_{23}H_{35}O_2Si$, $[M + H]^+$ 371.2395; found, 371.2400.

***(E)*-Methyl-2-(4-chlorobenzylidene)-5-(triisopropylsilyl)-pent-4-ynoate (3c):** Colorless oil, 71.0 mg, yield 91%; IR (KBr, cm^{-1}) 2943, 2891, 2865, 2172, 1720, 1636, 1592, 1463, 1219, 1014; ^{1}H NMR (300 MHz, $CDCl_3$-d_1) δ 7.69 (s, 1H), 7.53 (d, J = 8.5 Hz, 2H), 7.37 (d, J = 8.5 Hz, 2H), 3.85 (s, 3H), 3.40 (s, 2H), 1.05 (d, J = 2.5 Hz, 21H) ppm; ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$-d_1) δ 167.4, 138.9, 134.9, 133.4, 131.0, 128.7, 128.5, 105.1, 81.8, 52.3, 19.3, 18.5, 11.2 ppm; HRMS-APCI (m/z) calcd for $C_{22}H_{32}O_2ClSi$, $[M + H]^+$ 391.1853; found, 391.1854.

***(E)*-Methyl-2-(2-methylbenzylidene)-5-(triisopropylsilyl)-pent-4-ynoate (3d):** Colorless oil, 53.3 mg, yield 72%; ^{1}H NMR (300 MHz, $CDCl_3$-d_1) δ 7.81 (s, 1H), 7.56−7.51 (m, 1H), 7.22 (td, J = 7.0, 3.6 Hz, 3H), 3.85 (s, 3H), 3.29 (s, 2H), 2.30 (s, 3H), 1.06 (d, J =

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3.2 Hz, 21H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$-d_1) δ 167.5, 139.3, 137.0, 134.3, 130.0, 128.9, 128.8, 128.8, 125.8, 105.9, 81.2, 52.1, 19.9, 19.4, 18.6, 11.2 ppm; HRMS-APCI (m/z) calcd for $C_{23}H_{35}O_2Si$, $[M + H]^+$ 371.2397; found, 371.2401.

(*E*)-Methyl-2-(3-methylbenzylidene)-5-(triisopropylsilyl)-pent-4-ynoate (3e): Colorless oil, 54.8 mg, yield 74%; ^1H NMR (300 MHz, $CDCl_3$-d_1) δ 7.73 (s, 1H), 7.38 (d, 2H), 7.29 (t, J = 7.5 Hz, 1H), 7.17 (d, J = 7.5 Hz, 1H), 3.84 (s, 3H), 3.42 (s, 2H), 2.38 (s, 3H), 1.06 (d, J = 2.7 Hz, 21H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$-d_1) δ 167.7, 140.4, 138.2, 134.9, 130.2, 129.7, 128.4, 127.7, 126.9, 105.7, 81.2, 52.1, 21.4, 19.4, 18.6, 11.2 ppm; HRMS-APCI (m/z) calcd for $C_{23}H_{35}O_2Si$, $[M + H]^+$ 371.2396; found, 371.2400.

(*E*)-Methyl-2-(3-fluorobenzylidene)-5-(triisopropylsilyl)pent-4-ynoate (3f): Colorless oil, 53.9 mg, yield 72%; IR (KBr, cm^{-1}) 2943, 2865, 2173, 1720, 1637, 1583, 1486, 1286, 1207, 1154; ^1H NMR (300 MHz, $CDCl_3$-d_1) δ 7.70 (s, 1H), 7.41−7.31 (m, 3H), 7.11−7.02 (m, 1H), 3.85 (s, 3H), 3.42 (s, 2H), 1.05 (d, J = 2.4 Hz, 21H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$-d_1) δ 167.3, 164.3, 161.1, 138.9, 138.8, 137.1, 137.0, 130.1, 130.0, 129.1, 125.5, 125.4, 116.5, 116.1, 115.7, 105.0, 81.9, 77.4, 77.0, 76.58, 52.3, 19.3, 18.5, 11.2 ppm; HRMS-APCI (m/z) calcd for $C_{22}H_{32}O_2FSi$, $[M + H]^+$ 375.2145; found, 375.2150.

(*E*)-Methyl-2-(4-bromobenzylidene)-5-(triisopropylsilyl)-pent-4-ynoate (3g): Colorless oil, 60.8 mg, yield 70%; IR (KBr, cm^{-1}) 2942, 2864, 2172, 1720, 1636, 1587, 1488, 1204, 1074; ^1H NMR (300 MHz, $CDCl_3$-d_1) δ 7.67 (s, 1H), 7.55−7.51 (m, 2H), 7.49−7.43 (m, 2H), 3.85 (s, 3H), 3.39 (s, 2H), 1.05 (d, J = 2.6 Hz, 21H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$-d_1) δ 167.4, 138.9, 133.9, 131.7, 131.2, 128.7, 123.3, 105.1, 81.9, 52.3, 19.3, 18.5, 11.2 ppm; HRMS-APCI (m/z) calcd for $C_{22}H_{32}O_2BrSi$, $[M + H]^+$ 435.1347; found, 435.1349.

(*E*)-Methyl-2-(2-fluorobenzylidene)-5-(triisopropylsilyl)pent-4-ynoate (3h): Colorless oil, 57.6 mg, yield 77%; IR (KBr, cm^{-1}) 2943, 2865, 2173, 1723, 1640, 1611, 1578, 1294, 1211, 1102; ^1H NMR (300 MHz, $CDCl_3$-d_1) δ 7.75 (s, 1H), 7.60 (d, J = 7.0 Hz, 2H), 7.40 (dd, J = 12.1, 4.4 Hz, 3H), 4.25 (t, J = 6.5 Hz, 2H), 3.42 (s, 2H), 1.76−1.67 (m, 2H), 1.47 (dd, J = 15.0, 7.4 Hz, 2H), 1.06 (d, J = 2.6 Hz, 21H), 0.97 (t, J = 7.4 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$-d_1) δ 167.1, 162.3, 158.9, 132.8, 132.7, 130.9, 130.8, 130.6, 129.9, 124.1, 124.0, 123.1, 122.9, 115.7, 115.4, 105.2, 81.7, 52.3, 19.6, 18.5, 11.2 ppm; HRMS-APCI (m/z) calcd for $C_{22}H_{32}O_2FSi$, $[M + H]^+$ 375.2145; found, 375.2150.

(*E*)-Methyl-2-(3-methoxybenzylidene)-5-(triisopropylsilyl)-pent-4-ynoate (3i): Colorless oil, 66.4 mg, yield 86%; ^1H NMR (300 MHz, $CDCl_3$-d_1) δ 7.73 (s, 1H), 7.31 (t, J = 7.9 Hz, 1H), 7.16 (d, J = 7.6 Hz, 1H), 7.10 (s, 1H), 6.91 (d, J = 8.2 Hz, 1H), 3.84 (s, 3H), 3.83 (s, 3H), 3.44 (s, 2H), 1.05 (d, J = 2.4 Hz, 21H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$-d_1) δ 167.6, 159.6, 140.2, 136.2, 129.5, 128.2, 122.1, 115.1, 114.4, 105.6, 81.3, 55.2, 52.2, 19.5, 18.5, 11.2 ppm; HRMS-APCI (m/z) calcd for $C_{23}H_{35}O_3Si$, $[M + H]^+$ 387.2343; found, 387.2350.

(*E*)-Methyl-2-(3-cyanobenzylidene)-5-(triisopropylsilyl)pent-4-ynoate (3j): Colorless oil, 41.1 mg, yield 54%; IR (KBr, cm^{-1}) 2942, 2864, 2232, 2172, 1720, 1484, 1277, 1232, 1206, 1120; ^1H NMR (300 MHz, $CDCl_3$-d_1) δ 7.85 (s, 1H), 7.80 (d, J = 7.9 Hz, 1H), 7.68 (s, 1H), 7.65 (d, J = 7.8 Hz, 1H), 7.54 (d, J = 7.8 Hz, 1H), 3.86 (s, 3H), 3.39 (s, 2H), 1.04 (s, 21H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$-d_1) δ 166.9, 137.5, 136.2, 133.7, 132.8, 132.2, 130.5, 129.4, 118.2, 113.1, 104.3, 82.5, 52.5, 19.3, 18.5, 11.1 ppm; HRMS-APCI (m/z) calcd for $C_{23}H_{32}O_2NSi$, $[M + H]^+$ 382.2191; found, 382.2196.

(*E*)-Methyl-2-(3-(trifluoromethyl)benzylidene)-5-(triisopropylsilyl)pent-4-ynoate (3k): Colorless oil, 75.5 mg, yield 89%; IR (KBr, cm^{-1}) 2944, 2866, 2173, 1722, 1463, 1437, 1217, 1199, 1076; ^1H NMR (300 MHz, $CDCl_3$-d_1) δ 7.79 (dd, J = 11.7, 5.3 Hz, 3H), 7.62 (d, J = 7.8 Hz, 1H), 7.53 (t, J = 7.7 Hz, 1H), 3.86 (s, 3H), 3.41 (s, 2H), 1.05 (d, J = 2.2 Hz, 21H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$-d_1) δ 167.2, 138.4, 135.7, 132.7, 131.4, 130.9, 129.8, 129.1, 126.3, 126.3, 125.5, 125.4, 122.0, 104.6, 82.1, 52.3, 19.3, 18.5, 11.2 ppm; HRMS-APCI (m/z) calcd for $C_{23}H_{32}O_2F_3Si$, $[M + H]^+$ 425.2112; found, 425.2118.

(*E*)-Methyl-2-(naphthalen-2-ylmethylene)-5-(triisopropylsilyl)pent-4-ynoate (3l): Colorless oil, 62.5 mg, yield 77%; IR (KBr, cm^{-1}) 3056, 2941, 2864, 2172, 1712, 1635, 1595, 1504, 1463, 1257; ^1H NMR (300 MHz, $CDCl_3$-d_1) δ 8.10 (s, 1H), 7.90 (s, 1H), 7.84 (dd, J = 8.6, 4.4 Hz, 3H), 7.64 (dd, J = 8.6, 1.6 Hz, 1H), 7.54−7.47 (m, 2H), 3.87 (s, 3H), 3.51 (s, 2H), 1.08 (d, J = 2.9 Hz, 21H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$-d_1) δ 167.7, 140.3, 133.2, 132.5, 129.6, 128.5, 128.2, 128.2, 127.7, 127.0, 126.9, 126.5, 105.7, 81.5, 52.2, 19.6, 18.6, 11.3 ppm; HRMS-APCI (m/z) calcd for $C_{26}H_{35}O_2Si$, $[M + H]^+$ 407.2397; found, 407.2400.

(*E*)-Methyl-2-([1,1′-biphenyl]-4-ylmethylene)-5-(triisopropylsilyl)pent-4-ynoate (3m): Colorless oil, 73.4 mg, yield 85%; IR (KBr, cm^{-1}) 3056, 3030, 2941, 2864, 2172, 1712, 1633, 1603, 1488, 1205; ^1H NMR (300 MHz, $CDCl_3$-d_1) δ 7.81 (s, 1H), 7.66 (ddd, J = 9.8, 7.1, 5.9 Hz, 6H), 7.51−7.44 (m, 2H), 7.42−7.35 (m, 1H), 3.88 (s, 3H), 3.51 (s, 2H), 1.09 (s, 21H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$-d_1) δ 167.7, 141.8, 140.3, 139.9, 133.9, 130.34, 128.9, 127.9, 19.5, 18.6, 11.3 ppm; HRMS-APCI (m/z) calcd for $C_{28}H_{37}O_2Si$, $[M + H]^+$ 433.2555; found, 433.2557.

(*E*)-Methyl-2-(4-fluorobenzylidene)-5-(triisopropylsilyl)pent-4-ynoate (3n): Colorless oil, 56.1 mg, yield 75%; IR (KBr, cm^{-1}) 2943, 2865, 2172, 1719, 1601, 1509, 1463, 1289, 1201, 1160; ^1H NMR (300 MHz, $CDCl_3$-d_1) δ 7.71 (s, 1H), 7.59 (dd, J = 8.6, 5.5 Hz, 2H), 7.10 (dd, J = 12.0, 5.3 Hz, 2H), 3.85 (s, 3H), 3.41 (s, 2H), 1.05 (d, J = 2.5 Hz, 21H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$-d_1) δ 167.5, 161.3, 139.1, 131.8, 131.7, 131.1, 131.1, 127.8, 115.8, 115.5, 105.3, 81.6, 52.2, 19.3, 18.5, 11.2 ppm; HRMS-APCI (m/z) calcd for $C_{22}H_{32}O_2FSi$, $[M + H]^+$ 375.2146; found, 375.2150.

(*E*)-*tert*-Butyl-2-benzylidene-5-(triisopropylsilyl)pent-4-ynoate (3o): Colorless oil, 58.1 mg, yield 73%; IR (KBr, cm^{-1}) 2958, 2943, 2892, 2865, 2172, 1716, 1635, 1463, 1217, 1199; ^1H NMR (300 MHz, $CDCl_3$-d_1) δ 7.67 (s, 1H), 7.57 (d, J = 7.0 Hz, 2H), 7.43−7.33 (m, 3H), 3.36 (s, 2H), 1.56 (s, 9H), 1.08 (d, J = 3.2 Hz, 21H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$-d_1) δ 166.2, 139.1, 135.42, 129.8, 129.6, 128.6, 128.4, 106.1, 81.0, 80.8, 28.1, 19.5, 18.6, 11.3 ppm; HRMS-APCI (m/z) calcd for $C_{25}H_{38}O_2NaSi$, $[M + Na]^+$ 421.2531; found, 421.2533.

(*E*)-Butyl-2-benzylidene-5-(triisopropylsilyl)pent-4-ynoate (3p): Colorless oil, 59.7 mg, yield 75%; IR (KBr, cm^{-1}) 2943, 2892, 2865, 2173, 1711, 1636, 1463, 1391, 1216, 1162; ^1H NMR (300 MHz, $CDCl_3$-d_1) δ 7.75 (s, 1H), 7.60 (d, J = 7.0 Hz, 2H), 7.40 (dd, J = 12.1, 4.4 Hz, 3H), 4.25 (t, J = 6.5 Hz, 2H), 3.42 (s, 2H), 1.76−1.67 (m, 2H), 1.47 (dd, J = 15.0, 7.4 Hz, 2H), 1.06 (d, J = 2.6 Hz, 21H), 0.97 (t, J = 7.4 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$-d_1) δ 167.3, 140.1, 135.1, 129.7, 128.9, 128.5, 128.3, 105.8, 81.2, 65.0, 30.8,19.4, 19.3, 18.6, 13.8, 11.2 ppm; HRMS-APCI (m/z) calcd for $C_{25}H_{39}O_2Si$, $[M + H]^+$ 399.2707; found, 399.2714.

(2*E*,4*E*)-Methyl-5-phenyl-2-(3-(triisopropylsilyl)prop-2-yn-1-yl)penta-2,4-dienoate (3q): Colorless oil, 45.8 mg, yield 60%; IR (KBr, cm^{-1}) 2941, 2864, 2171, 1711, 1623, 1462, 1383, 1202, 1075; ^1H NMR (300 MHz, $CDCl_3$-d_1) δ 7.42 (d, J = 7.5 Hz, 2H), 7.34 (d, J = 11.5 Hz, 1H), 7.30−7.22 (m, 3H), 7.16 (dd, J = 11.5, 7.5 Hz, 1H), 6.83 (d, J = 15.3 Hz, 1H), 3.73 (s, 3H), 3.41 (s, 2H), 0.93 (s, 21H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$-d_1) δ 167.6, 140.7, 140.1, 136.3, 129.0, 128.7, 127.3, 126.4, 123.6, 105.5 81.1, 52.1, 18.5, 18.0, 11.2 ppm; HRMS-APCI (m/z) calcd for $C_{48}H_{68}O_4NaSi_2$, $[2M+Na]^+$ 787.4548; found, 787.4536.

(*E*)-Methyl-2-(thiophen-2-ylmethylene)-5-(triisopropylsilyl)-pent-4-ynoate (3r): Colorless oil, 56.5 mg, yield 78%; IR (KBr, cm^{-1}) 2943, 2864, 2172, 1713, 1623, 1463, 1421, 1273, 1207, 1088; ^1H NMR (300 MHz, $CDCl_3$-d_1) δ 7.78 (s, 1H), 7.45 (d, 1H), 7.38 (d, 1H), 7.07−7.02 (m, 1H), 3.76 (s, 3H), 3.54 (s, 2H), 0.93 (s, 21H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$-d_1) δ 167.7, 137.7, 132.6, 132.1, 129.8, 127.7, 124.6, 104.2, 80.9, 52.3, 19.4, 18.6, 11.2 ppm; HRMS-APCI (m/z) calcd for $C_{40}H_{60}O_4NaS_2Si_2$, $[2M + Na]^+$ 747.3363; found, 747.3358.

(*E*)-Methyl-2-benzylidenepent-3-ynoate (4a): Colorless oil, 30.0 mg, yield 75%; IR (KBr, cm^{-1}) 3025, 2951, 2851, 2227, 1721, 1597, 1447, 1434, 1261, 1207, 1141; ^1H NMR (300 MHz, $CDCl_3$-d_1) δ 8.00 (dd, J = 6.6, 3.0 Hz, 2H), 7.85 (s, 1H), 7.46−7.34 (m, 3H), 3.86

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(s, 3H), 2.17 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$-d_1) δ 166.6, 144.7, 134.5, 130.3, 130.1, 128.4, 113.2, 95.6, 75.4, 52.7, 5.0 ppm; HRMS-APCI (m/z) calcd for $C_{26}H_{24}O_4Na$, $[2M + Na]^+$ 423.1567; found, 423.1565.

(*E*)-Methyl-2-benzylidenepent-4-ynoate (5a): Colorless oil, 32.4 mg, yield 81%; IR (KBr, cm^{-1}) 3294, 2951, 2863, 2119, 1715, 1635, 1435, 1271, 1222, 1090; ^1H NMR (300 MHz, $CDCl_3$-d_1) δ 7.79 (s, 1H), 7.53 (d, J = 7.3 Hz, 2H), 7.41 (dt, J = 8.5, 6.9 Hz, 3H), 3.87 (s, 3H), 3.38 (d, J = 2.6 Hz, 2H), 2.08 (t, J = 2.7 Hz, 1H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$-d_1) δ 167.5, 140.9, 134.8, 129.5, 129.1, 128.6, 127.3, 81.6, 68.8, 52.3, 17.9 ppm; HRMS-APCI (m/z) calcd for $C_{26}H_{24}O_4Na$, $[2M + Na]^+$ 423.1567; found, 423.1567.

(*E*)-Methyl 2-(4-methylbenzylidene)pent-4-ynoate (5b): Colorless oil, 36.8 mg, yield 86%; IR (KBr, cm^{-1}) 3295, 2951, 2864, 2120, 1716, 1635, 1512, 1463, 1270, 1117; ^1H NMR (300 MHz, $CDCl_3$-d_1) δ 7.76 (s, 1H), 7.43 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 3.86 (s, 3H), 3.39 (d, J = 2.5 Hz, 2H), 2.39 (s, 3H), 2.07 (t, J = 2.5 Hz, 1H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$-d_1) δ 167.7, 141.0, 139.4, 132.0, 129.7, 129.4, 126.4, 81.8, 68.7, 52.3, 21.4, 17.9 ppm; HRMS-APCI (m/z) calcd for $C_{14}H_{15}O_2$, $[M + H]^+$ 215.1066; found, 215.1068.

(*E*)-Methyl 2-(4-fluorobenzylidene)pent-4-ynoate (5c): Colorless oil, 22.7 mg, yield 52%; IR (KBr, cm^{-1}) 3294, 2951, 2865, 2119, 1715, 1601, 1509, 1463, 1289, 1087; ^1H NMR (300 MHz, $CDCl_3$-d_1) δ 7.74 (s, 1H), 7.53 (dd, J = 8.6, 5.5 Hz, 2H), 7.12 (t, J = 8.6 Hz, 2H), 3.87 (s, 3H), 3.36 (d, J = 2.6 Hz, 2H), 2.09 (t, J = 2.7 Hz, 1H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$-d_1) δ 167.4, 164.7, 161.4, 139.7, 131.7, 131.6, 130.9, 130.9, 127.2, 127.1, 115.9, 115.7, 81.4, 69.0, 52.4, 17.8 ppm; HRMS-APCI (m/z) calcd for $C_{13}H_{12}O_2F$, $[M + H]^+$ 219.0816; found, 219.0818.

Methyl-4-methyl-2-naphthoate (6a): Colorless oil, 31.2 mg, yield 78%; ^1H NMR (300 MHz, $CDCl_3$-d_1) δ 8.47 (s, 1H), 8.02 (d, J = 8.1 Hz, 1H), 7.96 (d, J = 8.1 Hz, 1H), 7.91 (s, 1H), 7.64 (t, J = 7.3 Hz, 1H), 7.55 (t, J = 7.3 Hz, 1H), 3.98 (s, 3H), 2.73 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$-d_1) δ 167.4, 134.8, 134.8, 132.7, 130.0, 129.5, 128.1, 126.9, 126.3, 125.6, 124.1, 52.2, 19.4 ppm; HRMS-APCI (m/z) calcd for $C_{13}H_{13}O_2$, $[M + H]^+$ 201.0910; found, 201.0908.

Methyl-6-fluoro-4-methyl-2-naphthoate (6b): Colorless oil, 24.0 mg, yield 55%; IR (KBr, cm^{-1}) 2951, 2864, 1719, 1636, 1508, 1437, 1234, 1200, 1103, 1003; ^1H NMR (300 MHz, $CDCl_3$-d_1) δ 8.45 (s, 1H), 8.04−7.85 (m, 2H), 7.60 (dd, J = 10.8, 2.1 Hz, 1H), 7.32 (td, J = 8.7, 2.1 Hz, 1H), 3.97 (s, 3H), 2.67 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$-d_1) δ 167.2, 163.8, 160.5, 136.0, 134.2, 132.6, 132.5, 129.6, 129.3, 126.5, 116.8, 116.5, 108.2, 107.9, 52.2, 19.3 ppm; HRMS-APCI (m/z) calcd for $C_{13}H_{12}O_2F$, $[M + H]^+$ 219.0816; found, 219.0818.

Methyl-4,6-dimethyl-2-naphthoate (6c): Colorless oil, 35.5 mg, yield 83%; ^1H NMR (300 MHz, $CDCl_3$-d_1) δ 8.42 (s, 1H), 7.88 (s, 1H), 7.85 (d, J = 8.3 Hz, 1H), 7.78 (s, 1H), 7.38 (d, J = 8.3 Hz, 1H), 3.97 (s, 3H), 2.70 (s, 3H), 2.57 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$-d_1) δ 167.5, 138.2, 135.0, 134.0, 130.8, 129.8, 129.3, 128.5, 126.1, 125.7, 123.3, 52.1, 22.2, 19.4 ppm; HRMS-APCI (m/z) calcd for $C_{14}H_{15}O_2$, $[M + H]^+$ 215.1066; found, 215.1068.

Methyl-4-methylanthracene-2-carboxylate (6d): Colorless oil, 42.5 mg, yield 85%; IR (KBr, cm^{-1}) 3051, 2978, 2929, 1712, 1466, 1453, 1301, 1274, 1226, 1107; ^1H NMR (300 MHz, $CDCl_3$-d_1) δ 8.99−8.90 (m, 1H), 8.47 (s, 1H), 8.11 (s, 1H), 7.99−7.90 (m, 1H), 7.81−7.75 (m, 2H), 7.71−7.62 (m, 2H), 4.00 (s, 3H), 3.19 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$-d_1) δ 167.1, 136.0, 134.3, 133.3, 133.2, 131.1, 130.7, 129.4, 128.9, 128.3, 127.9, 127.8, 126.9, 126.0, 52.2, 27.4 ppm; HRMS-APCI (m/z) calcd for $C_{17}H_{15}O_2$, $[M + H]^+$ 251.1066; found, 251.1070.

Methyl-4-methyl-6-phenyl-2-naphthoate (6e): Colorless oil, 45.8 mg, yield 83%; IR (KBr, cm^{-1}) 3029, 2979, 2931, 2864, 1710, 1608, 1487, 1373, 1256, 1107; ^1H NMR (300 MHz, $CDCl_3$-d_1) δ 8.49 (s, 1H), 8.18 (s, 1H), 8.03 (d, J = 8.5 Hz, 1H), 7.94 (s, 1H), 7.81 (dd, J = 8.5, 1.3 Hz, 1H), 7.74 (d, J = 7.5 Hz, 2H), 7.52 (t, J = 7.5 Hz, 2H), 7.43 (d, J = 7.5 Hz, 1H), 3.99 (s, 3H), 2.78 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$-d_1) δ 167.4, 141.1, 140.9, 135.0, 135.0, 131.8, 130.6, 129.3, 129.0, 127.8, 127.6, 126.9, 126.1, 126.1, 122.2, 52.2, 19.5 ppm; HRMS-APCI (m/z) calcd for $C_{19}H_{17}O_2$, $[M + H]^+$ 277.1223; found, 277.1226.

Methyl-2-methyl-[1,1′-biphenyl]-4-carboxylate (6f): Colorless oil, 37.1 mg, yield 82%; ^1H NMR (300 MHz, $CDCl_3$-d_1) δ 7.89 (s, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.37 (t, J = 7.2 Hz, 2H), 7.31 (d, J = 7.2 Hz, 1H), 7.27−7.17 (m, 3H), 3.87 (s, 3H), 2.25 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$-d_1) δ 167.2, 146.6, 141.0, 135.7, 131.5, 129.9, 128.9, 128.2, 127.4, 127.0, 100.0, 52.1, 20.5 ppm; HRMS-APCI (m/z) calcd for $C_{15}H_{15}O_2$, $[M + H]^+$ 227.1066; found, 227.1064.

Methyl-4-methylbenzo[*b*]thiophene-6-carboxylate (6g): Colorless oil, 33.0 mg, yield 80%; ^1H NMR (300 MHz, $CDCl_3$-d_1) δ 8.45 (s, 1H), 7.82 (s, 1H), 7.64 (d, J = 5.5 Hz, 1H), 7.43 (d, J = 5.5 Hz, 1H), 3.95 (s, 3H), 2.65 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$-d_1) δ 167.3, 142.5, 139.3, 132.8, 129.8, 126.0, 125.2, 122.3, 122.0, 52.1, 19.6 ppm; HRMS-APCI (m/z) calcd for $C_{11}H_{11}O_2S$, $[M + H]^+$ 207.0474; found, 207.0473.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Characterization data. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b00728.

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Notes

The authors declare no competing financial interest.

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