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膦酰保护基促进选择性 Hay 偶联制备非对称 1,3-二炔

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摘要 报道了芳香末端炔烃与单膦酰基-保护二炔的选择性 Hay 偶联反应. $Ph_2P(O)$的极性使得产物非对称 1,3-二炔易与副产物分离. 单膦酰基-保护二炔的低反应活性减少了自身氧化偶联, 从而提高了目标产物的产率. 很多芳香末端炔烃与单膦酰基-保护二炔都能应用于本 Hay 偶联反应, 且相应非对称 1,3-二炔产物的产率为中等到好. 产物非对称 1,3-二炔能用于合成非对称炔-二炔烃及环多炔烃.

关键词 Hay 偶联; 非对称 1,3-二炔; 末端炔烃; 膦酰保护基

Phosphoryl Protecting Group Enabled Facile Synthesis of Unsymmetrical 1,3-Diynes by Selective Hay Coupling

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Abstract A selective Hay coupling reaction of aromatic terminal acetylenes and monophosphoryl-protected diynes was developed. The polarity of $Ph_2P(O)$ realized facile isolation of the desired unsymmetrical 1,3-diynes from by-products. The low reactivity of monophosphoryl-protected diynes reduced the oxidative homocoupling of itself and enhanced the yields of desired products. A number of aromatic terminal acetylenes and monophosphoryl-protected diynes were tolerated in this reaction, and all the corresponding unsymmetrical 1,3-diynes could be obtained in moderate to good yields. The unsymmetrical 1,3-diynes could be applied to synthesize unsymmetrical yne-diynes and cyclic polyynes.

Keywords Hay coupling; unsymmetrical 1,3-diyne; terminal acetylene; phosphoryl protecting group

1 Introduction

Unsymmetrical 1,3-diynes are important compounds in organic chemistry, and important intermediates in organic synthesis.[1,2] The structural motif of 1,3-diyne, which is a constituent part of natural products,[3] such as panaxydol,[4] panaxytriol,[5] oploxyne,[6] petrosiol[7] and so on, has been recognized as an ubiquitous functionality in organic materials, such as dye for dye sensitized solar cell,[8] fluorophores,[9] liquid crystal[10] and so on.

A number of transition-metal catalyzed oxidative homocoupling reactions of terminal acetylenes, such as Glaser,[11] Eglinton,[12] Hay,[13] Cadiot coupling[14] and their alternative approaches are effective to produce 1,3-diyne structural motif. Although these kind of oxidative homocoupling reactions of an acetylene gave symmetrical 1,3-diynes in good yields, it is difficult to afford unsym-

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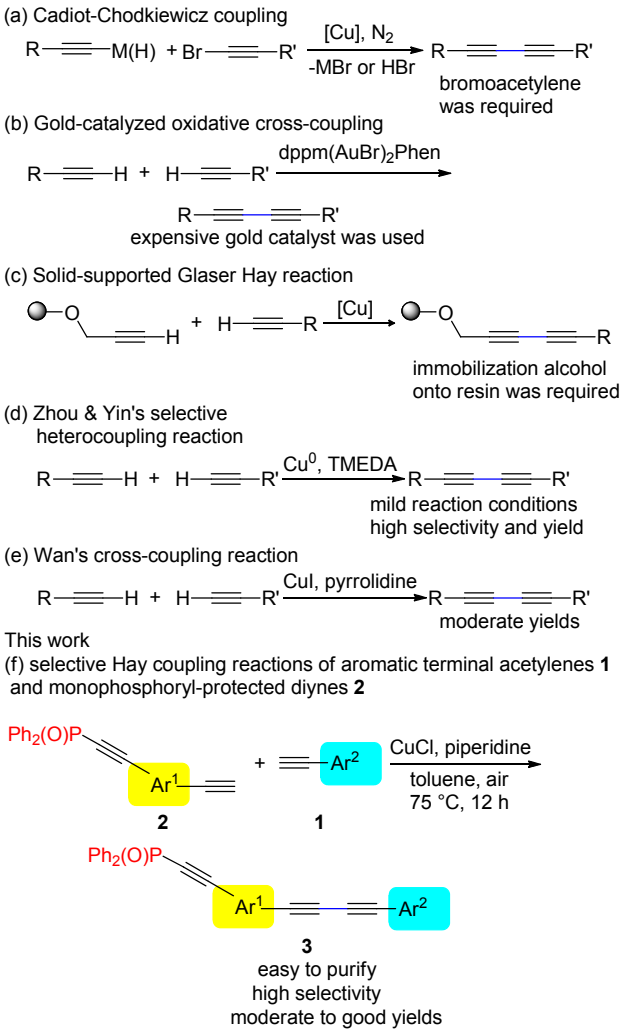
metrical 1,3-diynes by oxidative homocoupling of two different acetylenes for the poor selectivity.[15] Several efforts[16] have been made to enhance the selectivity and synthesize unsymmetrical 1,3-diynes successfully through selective oxidative coupling, such as Cadiot-Chodkiewicz reaction,[17] gold-catalyzed oxidative cross-coupling,[18] solid-supported Glaser Hay reaction,[19] Zhou & Yin's selective heterocoupling reaction,[20] and Wan's cross-coupling reaction,[21] but these methods also have some shortcomings, such as requirement of special substrate like bromoacetylene, the use of expensive catalyst or need to immobilize substrate on resin.

Recently, we developed a new polar protecting group, diphenylphosphoryl group, $Ph_2P(O)$, for terminal acetylenes.[22] High polarity of $Ph_2P(O)$ enabled facile isolation of Sonogashira coupling products.[23,24] Copper acetylides of monophosphoryl-protected diynes exhibited poor nucleophilicity, and the corresponding acetylenes showed low reactivity for the electron-withdrawing effect of $Ph_2P(O)$.[25] A series of unsymmetrical and cyclic aromatic polyynes were synthesized successfully by taking advantage of polar $Ph_2P(O)$ protecting group and low reactive monophosphoryl-protected diynes.

Unlike these previous methods which immobilized the substrates, developed new catalysts or changed reaction conditions to enhance the selectivity for preparation of unsymmetrical 1,3-diynes (Scheme 1, a～e), this paper focused on developing a selective Hay coupling reaction to prepare unsymmetrical 1,3-diynes by taking advantage of the high polarity and electron-withdrawing effect of the $Ph_2P(O)$ protecting group. Although we reported the selective Hay coupling reactions in previous paper,[23] this method is limited to narrow functional group compatibility and need to use large excess amount of terminal alkyne substrates thus leading to environmental pollution problem and high manufacturing cost.

Herein, we report a procedure for preparing unsymmetrical 1,3-diynes by Cu(I)-catalyzed selective Hay coupling reactions of aromatic terminal acetylenes **1** and monophosphoryl-protected diynes **2** (Scheme 1, f). The polarity of $Ph_2P(O)$ realized easy isolation of the desired unsymmetrical 1,3-diynes **3** from by-products. The low reactivity of **2** reduced the oxidative homocoupling of itself and increased the yields of desired products.

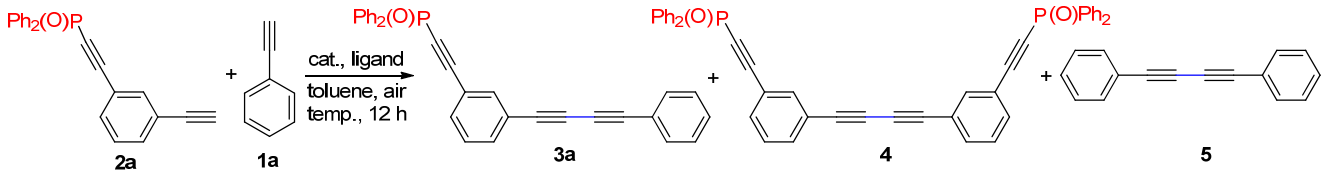


Scheme 1 Selective Hay coupling reactions of aromatic terminal acetylenes and monophosphoryl-protected diynes

2 Results and discussion

Initially, the selective Hay coupling of phenylacetylene **1a** and *meta*-monophosphoryl-protected diyne **2a** was carried out to optimize the reaction conditions (Table 1). Treatment of **2a** with **1a** (1.5 equiv.), CuI (10 mol%) and tetramethylethylenediamine (TMEDA, 50 mol%) in toluene at room temperature under air gave the desired product **3a** in 12% yield (Table 1, Entry 1). To increase the reaction efficiency, a series of other copper salts were investigated (Entries 2～5). The results revealed that CuCl was a superior catalyst with a 23% yield (Entry 3). When piperidine was used as a ligand instead of TMEDA, the yield was improved to 29% (Entry 6). With increasing the reaction temperature, the yield of the **3a** reached the maximum at a temperature of 75 ℃ (Entry 7). Further raising the temperature has a negative impact on the reaction (Entries 8～10). The investigation on the optimal amount of **1a** (Entries 11～15) indicated that 3.5 equiv. of **1a** (Entry 14) was an appropriate amount. Considering the cost of alkyne substrates and the separation difficulty of organic compounds, the amount of cheap CuCl was explored (Entries 16～21). To our delight, the amount of **1a** could be decreased to 2.0 equiv. by increasing the amount of CuCl to 30 mol% (Entry 20). However, further increasing the amount of CuCl to 50 mol% was not beneficial for the reaction (Entry 21). By varying the ligand loading to 60, 40, 30 mol%, the desired product **3a** was obtained with 78%, 80%, 71% yields (Entries 22～24). Control experiments (Entries 25 and 26) revealed that both the catalyst and ligand were essential for this new selective Hay coupling reaction. Therefore, the optimum conditions are 1.0 mmol of **2a**, 2.0 mmol of **1a**, 30 mol% of CuCl, 40 mol% of piperidine in toluene at 75 ℃ under air for 12 h.

Table 1 Optimization of the reaction conditions[a]



Entry	Cat.(mol%)	Ligand (mol%)	Temp./℃	Amount of **1a**/equiv.	Yield[b]/%		
					4	**3a**	**5**
1	CuI (10)	TMEDA (50)	r.t.	1.5	9	12	89
2	CuBr (10)	TMEDA (50)	r.t.	1.5	13	18	85
3	CuCl (10)	TMEDA (50)	r.t.	1.5	16	23	81
4	Cu_2O (10)	TMEDA (50)	r.t.	1.5	＜5	Trace	72
5	$Cu(OAc)_2$ (10)	TMEDA (50)	r.t.	1.5	＜5	Trace	Trace
6	CuCl (10)	Piperidine (50)	r.t.	1.5	19	29	78
7	CuCl (10)	Piperidine (50)	75	1.5	43	52	61
8	CuCl (10)	Piperidine (50)	85	1.5	45	49	69
9	CuCl (10)	Piperidine (50)	95	1.5	47	45	73
10	CuCl (10)	Piperidine (50)	105	1.5	49	42	74
11	CuCl (10)	Piperidine (50)	75	2.0	29	66	60
12	CuCl (10)	Piperidine (50)	75	2.5	26	69	67
13	CuCl (10)	Piperidine (50)	75	3.0	19	74	72
14	CuCl (10)	Piperidine (50)	75	3.5	16	78	71
15	CuCl (10)	Piperidine (50)	75	3.8	17	76	77
16	CuCl (15)	Piperidine (50)	75	2.5	18	70	60
17	CuCl (20)	Piperidine (50)	75	2.5	15	79	56
18	CuCl (20)	Piperidine (50)	75	2.2	16	79	52
19	CuCl (20)	Piperidine (50)	75	2.0	28	68	50
20	CuCl (30)	Piperidine (50)	75	2.0	16	80	49
21	CuCl (50)	Piperidine (50)	75	1.8	27	67	54
22	CuCl (30)	Piperidine (60)	75	2.0	20	78	58
23	CuCl (30)	Piperidine (40)	75	2.0	15	80	50
24	CuCl (30)	Piperidine (30)	75	2.0	17	71	60
25	CuCl (10)	—	75	2.0	0	0	Trace
26	—	Piperidine (50)	75	2.0	0	0	0

[a] Reaction conditions: monophosphoryl-protected diyne **2a** (1.0 mmol), toluene (10 mL). [b] Isolated yields, yields of **4** and **3a** based on **2a**, yields of **5** based on **1a**.

In the above reactions, *meta*-monophosphoryl-protected diyne **2a** showed lower reactivity than **1a** for the electron-withdrawing effect of $Ph_2P(O)$ group. Therefore the selective oxidative Hay coupling of **1a** and **2a** could be favored and the yield of desired product **3a** could increase. The polarity of $Ph_2P(O)$ enabled facile isolation of desired product **3a** from by-products **4** and **5** by column chromatography on silica gel for their different R_f values (R_f= 0.55 for **3a**, 0.24 for **4**, and 0.97 for **5** in AcOEt).

In sharp contrast to *meta*-monophosphoryl-protected diyne **2a**, the selective Hay coupling of phenylacetylene **1a** and *meta*-monosilyl-protected diyne **2b** gave a mixture of the desired product **3b**, by-products **6** and **5**. The yield of **3b** was lower for the similar reactivity of **1a** and **2b**. And **3b** was difficult to purify by column chromatography on silica gel for the similar R_f values of **3b**, **6** and **5** (R_f=0.49 for **3b**, 0.56 for **5**, and 0.43 for **6** in hexane) (Eq. 1).

To demonstrate the efficiency of this selective Hay coupling reaction, we explored the generality of our method extending the conditions to various aromatic terminal acetylenes and monophosphoryl-protected diynes, and the results are summarized in Table 2 and Scheme 2.

Analyzing Table 2, we observed that the reaction is not sensitive to the positions of $Ph_2P(O)$-ethynyl group presenting at benzene ring of monophosphoryl-protected diynes. Both *m*-$Ph_2P(O)$-ethynyl- (**3c**～**3f**, **3l**), *o*-$Ph_2P(O)$-ethynyl- (**3g**, **3h**, **3j**, **3m**, **3o**) and *p*-$Ph_2P(O)$-ethynyl-substituted monophosphoryl-protected diynes (**3i**, **3k**, **3n**) gave the desired products in moderate to good yields. A closer inspections of the results revealed that the reaction worked well for various aromatic terminal acetylenes. Both phenyl-substituted acetyelenes (**3c**, **3e**, **3j**～**3i**, **3k**) and polycyclic aromatic acetylenes (**3d**, **3f**) gave the corresponding products in moderate to good yields. And 2-ethynylthiophene also afforded the desired product in moderate yield (**3j**). The functional groups substituted to benzene ring of aromatic terminal acetylenes influenced the selective Hay coupling slightly, both electron-donating (**3h**, **3k**, 70%, 71%) and electron-withdrawing functional groups (**3c**, **3e**, **3g**, **3i**, 70%～82%) substituted aromatic

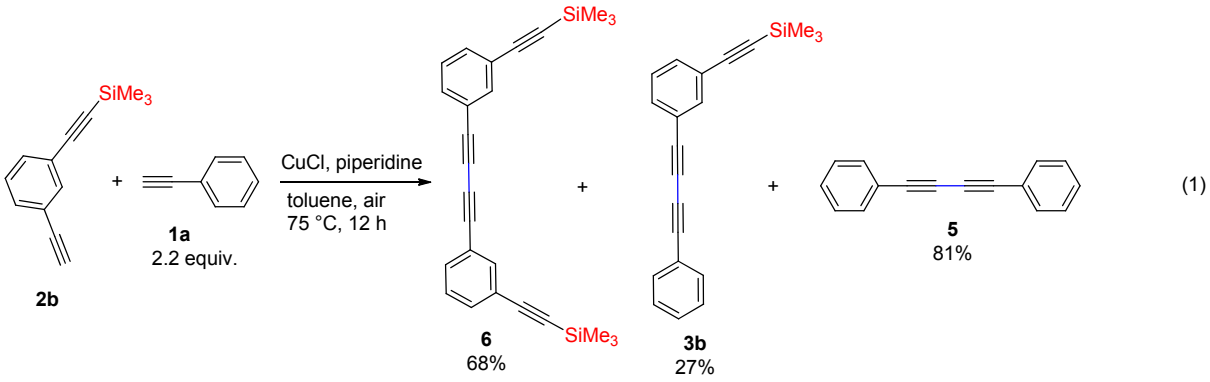
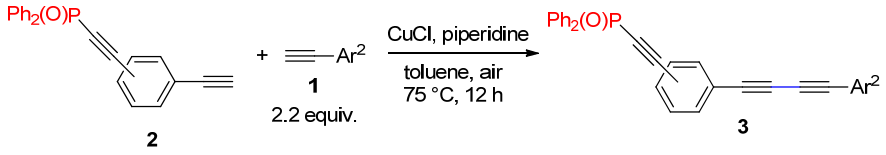
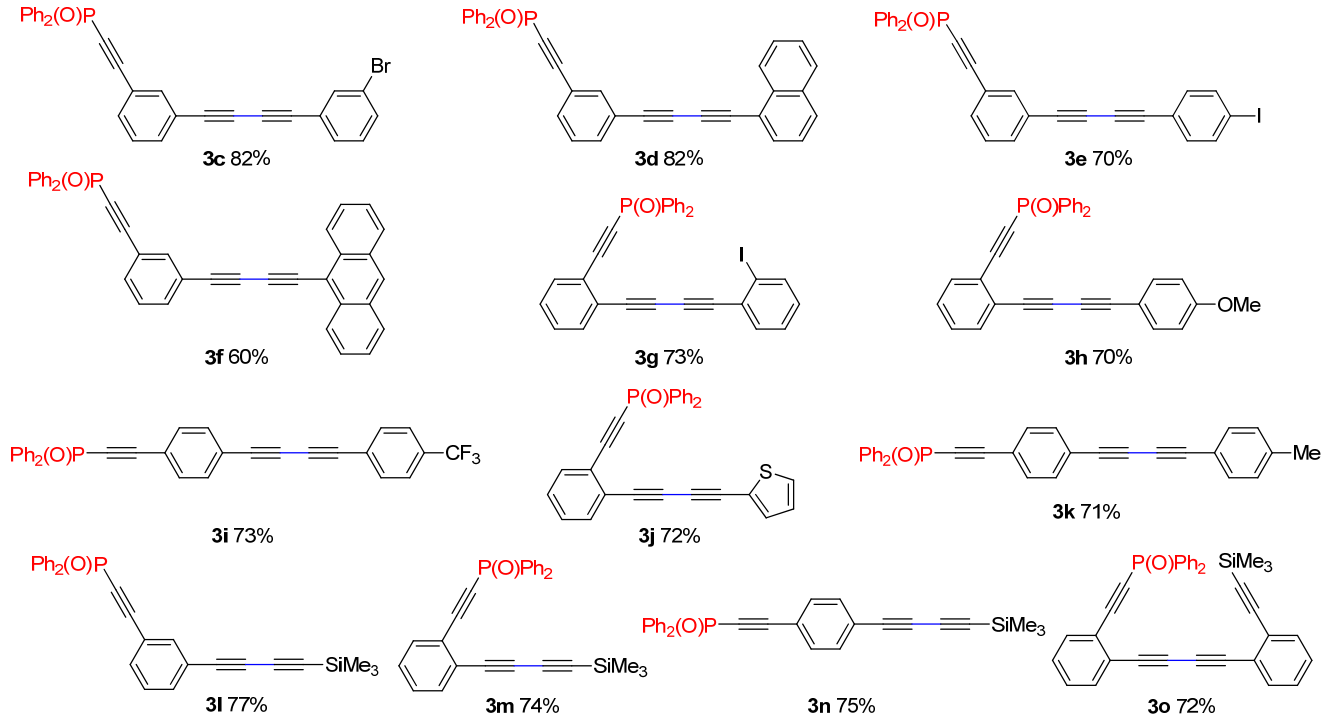
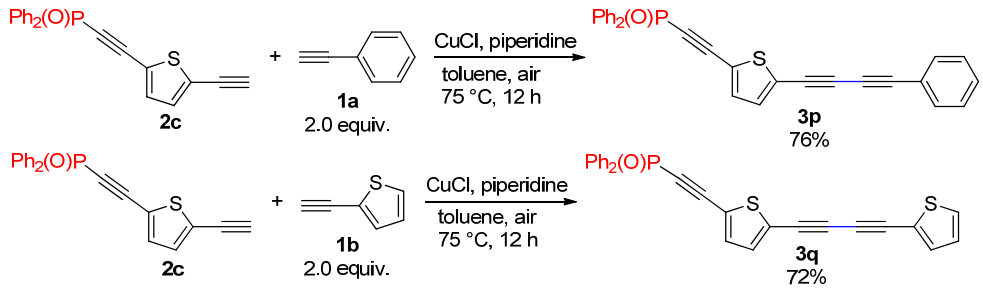


Table 2 Oxidative homocoupling reaction of monophosphoryl-protected phenyl-substituted diynes with various aromatic acetylenes[a]





[a] Reaction conditions: **2** (1.0 mmol), **1** (2.0 mmol), CuCl (30 mol%), piperidine (40 mol%), toluene (10 mL).



Scheme 2 Oxidative homocoupling reaction of monophosphoryl-protected thienyl-substituted diyne **2c**

terminal acetyelenes gave the desired products in good yields. Trimethylsilylacetylene was also suitable for this reaction, and the corresponding selective Hay coupling products were obtained in moderate yields (**3l**～**3o**, 72%～77%).

Monophosphoryl-protected thienyl-substituted diyne **2c** also worked well for this selective Hay coupling (Scheme 3). Selective Hay coupling reaction of **2c** and **1a** produced the desired product **3p** in 76% yield. Similarly, treatment of **2c**, 2-ethynylthiophene with CuCl/piperidine catalysts also gave the desired unsymmetrical 1,3-diyne **3q** in 72% yield. However monophosphoryl-protected pyridyl-substituted diyne was not suitable for this selective Hay coupling because of the low stability, and decomposition of monophosphoryl-protected pyridyl-substituted diyne occurred in this reaction. And selective Hay coupling between **2a** and alkyl alkynes (such as but-1-yne) also did not produce the desired unsymmetrical 1,3-diynes.

With unsymmetrical 1,3-diynes **3j**, **3a** and **3p** in hand, we succeeded in synthesis of unsymmetrical yne-diynes by one-pot deprotection/Sonogashira coupling. Treatment of **3j** with Grignard reagent MeMgBr gave the magnesium acetylide intermediate, without isolation and purification the magnesium acetylide, *in situ* addition of 1-bromo-3-nitrobenzene and [Pd]/[Cu] catalysts into the resulted magnesium acetylide reaction mixture afforded the desired Sonogashira coupling product **4a** in 76% yield. Unsymmetrical yne-diynes **4b** and **4c** were prepared successfully through the similar one-pot deprotection/Sonogashira coupling procedure (Scheme 3).

Unsymmetrical 1,3-diynes **3g** and **3o** are important intermediates for the synthesis of cyclic polyynes. Through Sonogashira coupling and one-pot deprotection/Eglinton coupling, **3g** could be transformed to cyclic pentayne.[23] Cyclic octayne would be synthesized from **3o** by tetrabutylammonium fluoride-catalyzed desilylatin, Hay coupling and one-pot deprotection/Eglinton coupling.[24]

Compared with the previous reported,[23] this present work showed the following outstanding features: (i) the amount of aromatic terminal acetylenes **1** was reduced from 3.0 equiv. to 2.0 equiv. by optimizing the reaction conditions, and then the yield of by-products from homocoupling of **1** was reduced, and the amount of eluent required to purify the desired unsymmetrical 1,3-diynes decreased (for example, the amount of eluent decreased from 608 to 420 mL/mmol in Hay coupling of **1a** and **2a**); (ii) the yields of unsymmetrical 1,3-diynes also increased effectively (for example, the yield of **3i** increased from 60% to 73%); (iii) wide functional group tolerance.

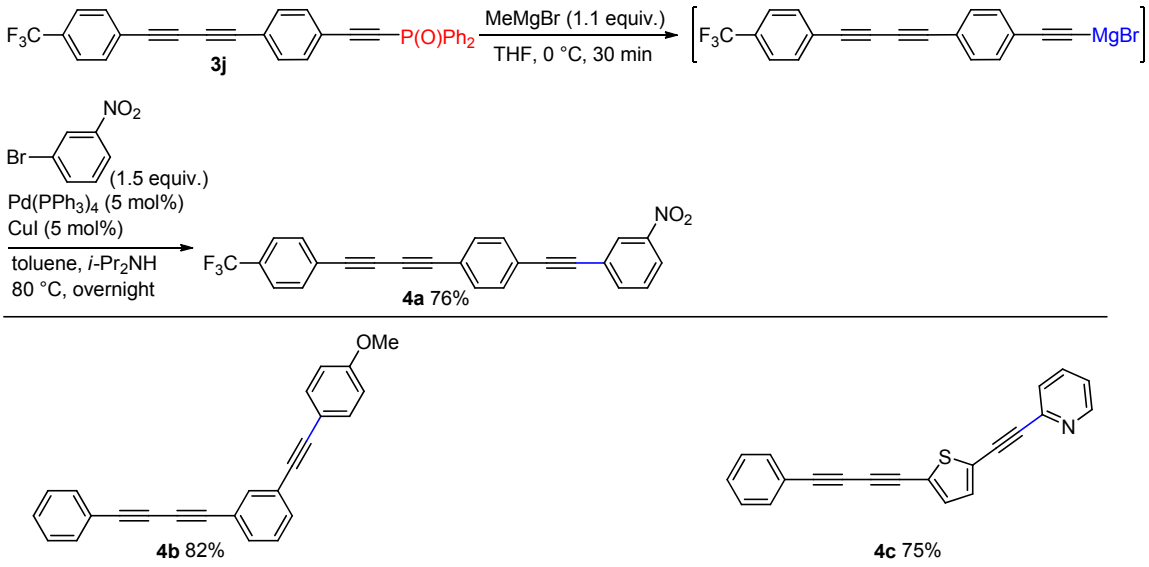
3 Conclusions

In conclusion, a method for the synthesis of unsymmetrical 1,3-diynes from aromatic terminal acetylenes and monophosphoryl-protected diynes through selective Hay coupling was developed. The polarity of $Ph_2P(O)$ enabled facile isolation of the desired unsymmetrical 1,3-diynes from by-products. The low reactivity of monophosphoryl-protected diynes reduced the oxidative homocoupling of itself and enhanced the yields of desired products. A broad range of aromatic terminal acetylenes and monophosphoryl-protected diynes were tolerated in this reaction, and all the corresponding unsymmetrical 1,3-diynes could be obtained in moderate to good yields. Unsymmetrical yne-diynes and aromatic cyclic polyynes could be synthesized by invoking this selective Hay coupling.

4 Experimental section

4.1 Instruments and reagents

^{1}H NMR and ^{13}C NMR spectra were recorded using residue solvent peaks as internal standards ($CHCl_3$, δ 7.26 for ^{1}H; $CDCl_3$, δ 77.0 for ^{13}C). Coupling constants are given in hertz. High resolution mass spectra (HRMS) were



Scheme 3 Synthesis of unsymmetrical yne-diynes

measured on an electrospray ionization (ESI) apparatus using time-of-flight (ToF) mass spectrometry. Melting points were measured on a SGW X-4 (INESA) melting point apparatus and are uncorrected. All reactions were carried out under an atmosphere of air with freshly distilled solvents, unless otherwise noted. Toluene and tetrahydrofuran (THF) were distilled from sodium. Aromatic terminal acetylenes **1** and monophosphoryl-protected diynes **2** were prepared according to the reported procedure.[1] Other materials were purchased from commercial sources and used without additional purification.

4.2 General Procedure for the preparation of unsymmetrical 1,3-diynes 3a and 3c～3n

A mixture of monophosphoryl-protected diynes **2** (1.0 mmol), terminal acetylenes **1** (2.0 mmol), CuCl (29.7 mg, 0.3 mmol), piperidine (40.0 μL, 0.4 mmol) and toluene (10 mL) in an atmosphere of air was stirred at 75 ℃ for 12 h. After workup with CH_2Cl_2 and NH_4Cl (aq.), the organic layer was washed with brine, and dried over $MgSO_4$. After filtration, the solvents were evaporated. The crude product was subjected to column chromatography on silica gel (AcOEt) to afford **3** in a pure form.

4-((3-((Diphenylphosphoryl)ethynyl)phenyl)buta-1,3-diyn-1-yl)benzene-1-ylium (**3a**): pale-yellow powder, m.p. 166～167 ℃ (Lit.[23] 166～167 ℃); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.33～7.42 (m, 4H), 7.49～7.54 (m, 6H), 7.55～7.58 (m, 4H), 7.74 (s, 1H), 7.88～7.92 (m, 4H).

((3-((3-Bromophenyl)buta-1,3-diyn-1-yl)phenyl)ethynyl)diphenylphosphine oxide (**3c**): white powder, m.p. 105～106 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.22 (t, J=7.9 Hz, 1H), 7.38 (t, J=7.9 Hz, 1H), 7.46 (d, J=7.9 Hz, 1H), 7.49～7.53 (m, 5H), 7.56～7.60 (m, 4H), 7.67 (s, 1H), 7.74 (s, 1H), 7.88～7.92 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 74.69, 74.91, 80.36, 80.52, 83.94 (d, J=166.0 Hz), 103.62 (d, J=29.1 Hz), 120.62 (d, J=4.0 Hz), 122.22, 122.41, 123.45, 128.70 (d, J=13.6 Hz), 128.91, 129.89, 130.95 (d, J=11.5 Hz), 131.07, 132.36 (d, J=3.1 Hz), 132.62, 132.70 (d, J=122.2 Hz), 133.04 (d, J=1.8 Hz), 134.38, 135.10, 136.12 (d, J=1.9 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ: 6.38; HRMS calcd for $C_{30}H_{18}BrOP$ 504.0279 found 504.0281.

((3-(Naphthalen-1-ylbuta-1,3-diyn-1-yl)phenyl)ethynyl)diphenylphosphine oxide (**3d**): white powder, m.p. 92～93 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.40 (t, J=7.8 Hz, 1H), 7.45 (t, J=7.8 Hz, 1H), 7.51～7.54 (m, 4H), 7.55～7.64 (m, 6H), 7.79～7.80 (m, 2H), 7.87～7.93 (m, 6H), 8.35 (d, J=8.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 75.47, 78.02, 80.62, 80.78, 83.81 (d, J=166.3 Hz), 103.72 (d, J=29.5 Hz), 118.97, 120.50 (d, J=4.0 Hz), 122.67, 125.11, 125.87, 126.67, 127.24, 128.41, 128.66 (d, J=13.6 Hz), 128.86, 129.96, 130.89 (d, J=11.2 Hz), 132.14, 132.32 (d, J=2.8 Hz), 132.66 (d, J=122.2 Hz), 132.79 (d, J=1.9 Hz), 132.97, 133.78, 134.29, 136.01; ^{31}P NMR (121 MHz, $CDCl_3$) δ: 6.20; HRMS calcd for $C_{34}H_{21}OP$ 476.1330, found 476.1333.

((3-((4-Iodophenyl)buta-1,3-diyn-1-yl)phenyl)ethynyl)diphenylphosphine oxide (**3e**): white powder, m.p. 180～181 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.24 (d, J=8.6 Hz, 2H), 7.37 (t, J=7.8 Hz, 1H), 7.49～7.53 (m, 4H), 7.56～7.60 (m, 4H), 7.70 (d, J=8.6 Hz, 2H), 7.74 (s, 1H), 7.87～7.91 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 74.83, 75.08, 80.32, 81.33, 83.91 (d, J=166.3 Hz), 95.82, 103.65 (d, J=29.2 Hz), 120.61 (d, J=4.1 Hz), 120.90, 122.51, 128.70 (d, J=13.6 Hz), 128.91, 130.95 (d, J=11.2 Hz), 132.37 (d, J=2.8 Hz), 132.69 (d, J=122.3 Hz), 132.99, 133.83, 134.34, 136.09, 137.69; ^{31}P NMR (121 MHz, $CDCl_3$) δ: 6.26; HRMS calcd for $C_{30}H_{18}IOP$ 552.0140, found 552.0145.

((3-(Anthracen-9-ylbuta-1,3-diyn-1-yl)phenyl)ethynyl)diphenylphosphine oxide (**3f**): white powder, m.p. 94～95 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.41 (t, J=7.8 Hz, 1H), 7.50～7.54 (m, 6H), 7.56～7.64 (m, 5H), 7.68 (d, J=7.6 Hz, 1H), 7.84 (s, 1H), 7.90～7.94 (m, 4H), 8.03 (d, J=8.2 Hz, 2H), 8.48 (s, 1H), 8.56 (d, J=8.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 75.78, 79.78, 82.44, 83.89 (d, J=166.3 Hz), 84.22, 103.79 (d, J=29.5 Hz), 115.16, 120.64 (d, J=4.0 Hz), 122.87, 125.91, 126.43, 127.36, 128.73 (d, J=13.4 Hz), 128.90, 128.96, 129.19 (d, J=3.5 Hz), 130.92 (d, J=11.2 Hz), 131.01, 132.38 (d, J=2.8 Hz), 132.76 (d, J=122.3 Hz), 132.88 (d, J=2.2 Hz), 134.11, 134.30, 136.05; ^{31}P NMR (121 MHz, $CDCl_3$) δ: 6.50; HRMS calcd for $C_{38}H_{23}OP$ 527.1487, found 527.1452.

((2-((2-Iodophenyl)buta-1,3-diyn-1-yl)phenyl)ethynyl)diphenylphosphine oxide (**3g**): yellow powder, m.p. 129～131 ℃ (Lit.[23] 129～131 ℃); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.07 (dt, J=1.2 Hz, J=7.6 Hz, 1H) 7.32 (t, J=7.6 Hz, 1H), 7.36～7.41 (m, 1H), 7.42～7.44 (m, 2H), 7.48～7.50 (m, 6H), 7.60～7.62 (m, 2H), 7.85 (d, J=7.9 Hz 1H), 8.00～8.04 (m, 4H).

((2-((4-Methoxyphenyl)buta-1,3-diyn-1-yl)phenyl)ethynyl)diphenylphosphine oxide (**3h**): white powder, m.p. 204～205 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.84 (s, 3H), 6.87 (d, J=8.8 Hz, 2H), 7.36 (t, J=7.5 Hz, 1H), 7.40～7.43 (m, 3H), 7.48～7.49 (m, 6H), 7.56～7.61 (m, 2H), 8.00～8.04 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 55.36 (d, J=4.6 Hz), 72.70, 78.69, 79.21, 83.82, 86.72 (d, J=167.0 Hz), 102.86 (d, J=29.5 Hz), 113.23, 114.21, 114.30, 123.49 (d, J=4.1 Hz), 125.78 (d, J=2.0 Hz), 128.68 (d, J=12.9 Hz), 130.21 (d, J=2.6 Hz), 131.08 (d, J=11.3 Hz), 132.10, 132.97(d, J=12.8 Hz), 132.98 (d, J=122.0 Hz), 134.15, 134,21, 160.63; ^{31}P NMR (121 MHz, $CDCl_3$) δ: 6.41; HRMS calcd for $C_{31}H_{21}O_2P$ 457.1279, found 457.1285.

Diphenyl(((4-((4-(trifluoromethyl)phenyl)buta-1,3-diyn-1-yl)phenyl)ethynyl)oxy)phosphane **3i**: white powder, m.p. 253～255 ℃ (Lit.[23] 253～255 ℃); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.49～7.54 (m, 6H), 7.56～7.59 (m, 4H), 7.60～7.64 (m, 4H), 7.87～7.91 (m, 4H).

Diphenyl((2-(thiophen-2-ylbuta-1,3-diyn-1-yl)phenyl)ethynyl)phosphine oxide **3j**: white powder, m.p. 169～170 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.03 (t, J=4.4 Hz, 1H), 7.34 (d, J=3.4 Hz, 1H), 7.36～7.39 (m, 2H), 7.42 (t,

J=7.2 Hz, 1H), 7.51～7.52 (m, 6H), 7.58 (d, *J*=7.6 Hz, 1H), 7.61 (d, *J*=7.6 Hz, 1H), 7.98～8.03 (m, 4H); ^{13}C NMR (125MHz, $CDCl_3$) *δ*: 76.49, 77.80, 78.56, 81.24, 86.95 (d, *J*=166.4 Hz), 102.64 (d, *J*=28.9 Hz), 121.60, 123.54 (d, *J*=4.1 Hz), 125.38 (d, *J*=2.0 Hz), 127.31 (d, *J*=11.9 Hz), 128.70 (d, *J*=11.8 Hz), 129.04 (d, *J*=5.6 Hz), 129.22 (d, *J*=11.3 Hz), 130.25 (d, *J*=5.6 Hz), 131.07 (d, *J*=11.3 Hz), 132.16, 132.89 (d, *J*=121.9 Hz), 133.03 (d, *J*=12.9 Hz), 134.65, 134,74; ^{31}P NMR (121 MHz, $CDCl_3$) *δ*: 6.08; HRMS calcd for $C_{28}H_{17}OPS$ 433.0738, found 433.0746.

Diphenyl(((4-(*p*-tolylbuta-1,3-diyn-1-yl)phenyl)-ethynyl)oxy)phosphane (**3k**): white powder, m.p. 265～266 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 2.37 (s, 3H), 7.16 (d, *J*=7.6 Hz, 2H), 7.43 (d, *J*=8.2 Hz, 2H), 7.49～7.52 (m, 6H), 7.55～7.58 (m, 4H), 7.87～7.91 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ*: 21.64 (d, *J*=7.8 Hz), 72.94, 77.30, 79.99, 83.72, 85.16 (d, *J*=166.4 Hz), 104.41 (d, *J*=28.9 Hz), 118.26, 120.27 (d, *J*=4.1 Hz), 124.46, 128.70 (d, *J*=13.9 Hz), 129.23, 129.31, 130.97 (d, *J*=11.3 Hz), 132.35, 132.45, 132.52, 132.79 (d, *J*=121.9 Hz), 144.00; ^{31}P NMR (121 MHz, $CDCl_3$) *δ*: 6.21; HRMS calcd for $C_{31}H_{21}OP$ 441.1330, found 441.1333.

Diphenyl((3-((trimethylsilyl)buta-1,3-diyn-1-yl)phenyl)-ethynyl)phosphine oxide (**3l**): white powder, m.p. 138～140 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 0.24 (s, 9H), 7.33～7.36 (m, 1H), 7.49～7.59 (m, 8H), 7.70 (s, 1H), 7.86～7.91 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ*: −0.50 (d, *J*=5.6 Hz), 74.74, 75.47, 83.85 (d, *J*=165.8 Hz), 87.27, 91.88, 103.65 (d, *J*=28.9 Hz), 120.54 (d, *J*=4.1 Hz), 122.32, 128.62～128.77 (m), 130.93 (d, *J*=11.3 Hz), 132.36, 132.68 (d, *J*=121.88 Hz), 132.95, 134.50, 136.24; ^{31}P NMR (121 MHz, $CDCl_3$) *δ*: 6.22; HRMS calcd for $C_{27}H_{23}OPSi$ 422.1256, found 422.1259.

Diphenyl((2-((trimethylsilyl)buta-1,3-diyn-1-yl)phenyl)-ethynyl)phosphine oxide (**3m**): white powder, m.p. 138～140 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 0.23 (s, 9H), 7.36～7.41 (m, 2H), 7.50～7.60 (m, 8H), 7.98～8.02 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ*: −0.54～−0.41 (m), 74.25, 78.96, 86.71 (d, *J*=167.9 Hz), 87.53, 92.92, 102.59 (d, *J*=29.4 Hz), 123.71 (d, *J*=4.1 Hz), 125.07, 128.71 (d, *J*=11.8 Hz), 129.07, 130.22, 131.07 (d, *J*=11.8 Hz), 131.10, 132.41, 132.57 (d, *J*=126.65 Hz), 133.38; ^{31}P NMR (121 MHz, $CDCl_3$) *δ*: 6.25; HRMS calcd for $C_{27}H_{23}OPSi$ 422.1256, found 422.1261.

Diphenyl(((4-((trimethylsilyl)buta-1,3-diyn-1-yl)-phenyl)ethynyl)oxy)phosphane (**3n**): white powder, m.p. 138～140 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 0.24 (s, 9H), 7.47～7.59 (m, 10H), 7.86～7.91 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ*: −0.51 (d, *J*=3.0 Hz), 75.37, 77.14, 85.19 (d, *J*=167.0 Hz), 87.24, 92.83, 104.20 (d, *J*=29.4 Hz), 120.49 (d, *J*=4.1 Hz), 123.82, 128.68 (d, *J*=13.4 Hz), 130.92 (d, *J*=10.8 Hz), 132.35, 132.40, 132.61, 132.62 (d, *J*=122.0 Hz), 132.63; ^{31}P NMR (121 MHz, $CDCl_3$) *δ*: 6.23; HRMS calcd for $C_{27}H_{23}OPSi$ 422.1256, found 422.1260.

Diphenyl((2-((2-((trimethylsilyl)ethynyl)phenyl)buta-1,3-diyn-1-yl)phenyl)ethynyl)phosphine oxide (**3o**): yellow powder, m.p. 57～60 ℃ (Lit.[24] 57～60 ℃); ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 0.25 (s, 9H), 7.29～7.30 (m, 1H), 7.33～7.40 (m, 2H), 7.41～7.45 (m, 2H), 7.48～7.52 (m, 7H), 7.58 (d, *J*=7.0 Hz, 1H), 7.62 (d, *J*=7.6 Hz, 1H), 7.99～8.03 (m, 4H).

Diphenyl((5-(phenylbuta-1,3-diyn-1-yl)thiophen-2-yl)-ethynyl)phosphine oxide (**3p**): white powder, m.p. 141～144 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 7.22 (d, *J*=4.0 Hz, 1H), 7.32～7.37 (m, 3H), 7.39～7.40 (m, 1H), 7.39～7.54 (m, 6H), 7.56～7.60 (m, 2H), 7.85～7.89 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ*: 73.01, 73.29, 80.26, 85.17, 88.04 (d, *J*=164.4 Hz), 97.27 (d, *J*=29.4 Hz), 121.11, 121.62 (d, *J*=4.1 Hz), 126.74, 128.51, 128.73 (d, *J*=13.4 Hz), 129.69, 131.00 (d, *J*=11.3 Hz), 132.28, 132.40 (d, *J*=122.5 Hz), 132.50 (d, *J*=12.4 Hz), 133.85 (d, *J*=10.3 Hz), 135.44 (d, *J*=12.4 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) *δ*: 6.12; HRMS calcd for $C_{28}H_{17}OPS$ 432.0738, found 432.0742.

Diphenyl((5-(thiophen-2-ylbuta-1,3-diyn-1-yl)thiophen-2-yl)ethynyl)phosphine oxide (**3q**): white powder, m.p. 136～137 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 7.01～7.03 (m, 1H), 7.22 (d, *J*=3.7 Hz, 1H), 7.32 (d, *J*=3.6 Hz, 1H), 7.36～7.38 (m, 2H), 7.49～7.53 (m, 4H), 7.56～7.59 (m, 2H), 7.85～7.89 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ*: 75.10, 77.34, 78.22, 80.02, 88.15 (d, *J*=163.8 Hz), 97.08 (d, *J*=30.0 Hz), 121.31, 121.79 (d, *J*=4.6 Hz), 126.54, 127.30 (d, *J*=8.8 Hz), 128.72 (d, *J*=13.9 Hz), 129.49 (d, *J*=8.3 Hz), 130.98 (d, *J*=11.4 Hz), 132.38 (d, *J*=122.5 Hz), 132.44, 133.91 (d, *J*=9.8 Hz), 134.93 (d, *J*=8.3 Hz), 135.44 (d, *J*=10.3 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) *δ*: 7.19; HRMS calcd for $C_{26}H_{15}OPS_2$ 438.0302, found 438.0305.

4.3 General Procedure for the preparation of unsymmetrical yne-diynes 4a～4c

To a THF solution (20.0 mL) of **3** (0.5 mmol) was added MeMgBr (0.55 mmol). After the mixture was stirred for 30 min under nitrogen at room temperature, THF solvent was evaporated under vacuum. To the concentrated reaction mixture were added 1-bromo-3-nitrobenzene (0.75 mmol), $Pd(PPh_3)_4$ (28.9 mg, 0.025 mmol), CuI (4.8 mg, 0.025 mmol), toluene (10.0 mL) and diisopropylamine (0.25 mL), and the mixture was stirred under nitrogen at 80 ℃ for 15 h. After workup with CH_2Cl_2 and NH_4Cl (aq.), the organic layer was washed with brine, and dried over $MgSO_4$. After filtration, the solvents were evaporated. The crude product was subjected to column chromatography on silica gel [*V*(hexane)∶*V*(CH_2Cl_2)=7∶1] to give **4** in a pure form (128.8 mg, 62% yield).

1-Nitro-3-((4-((4-(trifluoromethyl)phenyl)buta-1,3-diyn-1-yl)phenyl)ethynyl)benzene (**4a**): white powder, m.p. 159～161 ℃ (Lit.[23] 159～161 ℃); ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 7.52～7.57 (m, 5H), 7.62 (q, *J*=8.6 Hz, 4H), 7.83 (d, *J*=7.9 Hz, 1H), 8.19～8.21 (m, 1H), 8.38 (s, 1H).

1-((4-Methoxyphenyl)ethynyl)-3-(phenylbuta-1,3-diyn-1-yl)benzene (**4b**):[23] ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 3.83

(s, 3H), 6.89 (d, J=8.8 Hz, 2H), 7.29～7.40 (m, 4H), 7.45～7.50 (m, 4H), 7.54 (d, J=6.7 Hz, 2H), 7.67 (s, 1H).

2-((5-(Phenylbuta-1,3-diyn-1-yl)thiophen-2-yl)ethynyl)-pyridine (**4c**): white powder, m.p. 90～92 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.23～7.28 (m, 3H), 7.33～7.40 (m, 3H), 7.52～7.54 (m, 3H), 7.70 (t, J=7.0 Hz, 1H), 8.63 (d, J=3.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 73.54, 73.80, 79.29, 81.93, 84.59, 93.39, 121.36, 123.16, 124.34, 124.68, 127.16, 128.48, 129.52, 132.51, 133.09, 134.04, 136.27, 142.68, 150.22; HRMS calcd for $C_{21}H_{11}NS$ 309.0612, found 309.0616.

Supporting Information ^{1}H NMR and ^{13}C NMR spectra. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn/.

References

[1] Stang, P. J.; Diederich, F. *Modern Acetylene Chemistry*, VCH, Weinheim, **1995**.

[2] Shi, W.; Lei, A.-W. *Tetrahedron Lett*. **2014**, *55*, 2763.

[3] (a) Ito, A.; Cui, B.; Chavez, D.; Chai, H. B.; Shin,Y. G.; Kawanishi, K.; Kardono, L. B.; Riswan, S.; Farnsworth, N. R.; Cordell, G. A.; Pezzuto, J. M.; Kinghorn, A. D. *J. Nat. Prod.* **2001**, *64*, 246.
(b) Evano, G.; Blanchard, N. *Copper-Mediated Cross-Coupling Reactions*, John Wiley & Sons, Inc., Hoboken, NJ, **2014**.
(c) Siemsen, P.; Livingston, R. C.; Diederich, F. *Angew. Chem. Int. Ed.* **2000**, *39*, 2632.

[4] Guo, L.; Song, L.; Wang, Z.; Zhao, W.; Mao, W.; Yin, M. *Chem. Biol. Interact.* **2009**, *181*, 138.

[5] (a) Katano, M.; Yamamoto, H.; Matsunaga, H.; Mori, M.; Takata, K.; Nakamura, M. *Gan to Kagaku Ryoho* **1990**, *17*, 1045.
(b) Matsunaga, H.; Saita, T.; Naguo, F.; Mori, M.; Katano, M. *Cancer Chemother. Pharmacol.* **1995**, *35*, 291.

[6] (a) Yadav, J. S.; Kumaraswamy, B.; Sathish Reddy, A.; Srihari, P.; Janakiram, R. V.; Kalivendi, S. V. *J. Org. Chem.* **2011**, *76*, 2568.
(b) Srihari, P.; Sathish Reddy, A.; Deepthi, Y.; Kalivendi, S. *Tetrahedron Lett.* **2013**, *54*, 5616.

[7] Gangadhar, P.; Reddy, S. A.; Srihari, P. *Tetrahedron* **2016**, *72*, 5807.

[8] (a) Fang, J.-K.; Sun, T.-X.; Tian, Y.; Zhang, Y.-J.; Jin, C.-F.; Xu, Z.-M.; Hu, X.-Y.; Wang, H.-B. *Mater. Chem. Phys*. **2017**, *195*, 1.
(b) Peng, L.-F.; Wang, B.-H.; Wang, M.; Tang, Z.-L.; Jiang, Y.-Z.; Jiao, Y.-C.; Xu, X.-H. *J. Chem. Res.* **2018**, *42*, 235.
(c) Peng, L.-F.; Lei, J.-Y.; Wu, L.; Tang, Z.-L.; Luo, Z.-P.; Jiao, Y.-C.; Xu, X.-H. *J. Chem. Res.* **2018**, *42*, 271.

[9] Pati, A. K.; Mohapatra, M.; Ghosh, P.; Gharpure, S. J.; Mishra, A. K. *J. Phys. Chem. A* **2013**, *117*, 6548.

[10] (a) Wan,W. B.; Brand, S. C.; Pak, J. J.; Haley, M. M. *Chem.-Eur. J.* **2005**, *6*, 2044.
(b) Peng, L.-F.; Jiang, J.; Peng, C.; Dai, N.-N.; Tang, Z.-L.; Jiao, Y.-C.; Chen, J.-Y.; Xu, X.-H. *Chin. J. Org. Chem.* **2017**, *37*, 3013 (in Chinese).
(彭丽芬, 蒋娟, 彭超, 代宁宁, 唐子龙, 焦银春, 陈锦杨, 许新华, 有机化学, **2017**, *37*, 3013.)
(c) Peng, L.-F.; Zhang, S.-W.; Wang, B.-H.; Xun, M.-S.; Tang, Z.-L.; Jiao, Y.-C.; Xu, X.-H. *Chin. J. Org. Chem.* **2018**, *38*, 519 (in Chinese).
(彭丽芬, 张思维, 王丙昊, 寻梦硕, 唐子龙, 焦银春, 许新华, 有机化学, **2018**, *38*, 519.)

[11] (a) Li, Y.-N.; Wang, J.-L.; He, L.-N. *Tetrahedron Lett.* **2011**, *52*, 3485.
(b) Yadav, J. S.; Reddy, B. V. S.; Reddy, K. B.; Gayathri, K. U.; Prasad, A. R. *Tetrahedron Lett*. **2003**, *44*, 6493.

[12] (a) Hay, A. *J. Org. Chem.* **1960**, *25*, 1275.
(b) Abe, H.; Kurokawa, H.; Chida, Y.; Inouye, M. *J. Org. Chem.* **2011**, *76*, 309.

[13] (a) Hay, A. S. *J. Org. Chem*. **1962**, *27*, 3320.
(b) Montierth, J. M.; DeMario, D. R.; Kurth, M. J.; Schore, N. E. *Tetrahedron* **1998**, *54*, 11741.

[14] (a) Bandyopadhyay, A.; Varghese, B.; Sankararaman, S. *J. Org. Chem.* **2006**, *71*, 4544.
(b) Cahiez, G.; Moyeux, A. *Chem. Rev.* **2010**, *110*, 1435.

[15] (a) Allen, S. E.; Walvoord, R. R.; Padilla-Salinas, R.; Kozlowski, M. C. *Chem. Rev.* **2013**, *113*, 6234.
(b) Siemsen, P.; Livingston, R. C.; Diederich, F. *Angew. Chem., Int. Ed.* **2000**, *39*, 2632.
(c) Stefani, H. A.; Guarezemini, A. S.; Cella, R. *Tetrahedron* **2010**, *66*, 7871.
(d) Jia, X.; Yin, K.; Li, C.; Li, J.; Bian, H. *Green Chem*. **2011**, *13*, 2175.
(e) Kamata, K.; Yamaguchi, S.; Kotani, M.; Yamaguchi, K.; Mizuno, N. *Angew. Chem., Int. Ed.* **2008**, *47*, 2407.
(f) Crowley, J. D.; Goldup, S. M.; Gowans, N. D.; Leigh, D. A.; Ronaldson, V. E.; Slawin, A. M. Z. *J. Am. Chem. Soc*. **2010**, *132*, 6243.
(g) Gao, H.-Y.; Wagner, H.; Zhong, D.; Franke, J.-H.; Studer, A.; Fuchs, H. *Angew. Chem., Int. Ed*. **2013**, *52*, 4024.
(h) Zhang, S.; Liu, X.; Wang, T. *Adv. Synth. Catal*. **2011**, *353*, 1463.
(i) Balamurugan, R.; Naveen, N.; Manojveer, S.; Nama, M. V. *Aust. J. Chem.* **2011**, *64*, 567.
(j) Wong, W.-Y.; Lu, G.-L.; Choi, K.-H.; Guo, Y.-H. *J. Organomet. Chem.* **2005**, *690*, 177.
(k) Navale, B. S.; Bhat, R. G. *RSC Adv.* **2013**, *3*, 5220.
(l) Liu, Y.; Wang, C.; Wang, X.; Wan, J.-P. *Tetrahedron Lett*. **2013**, *54*, 3953.

[16] (a) Yin, W.; He, C.; Chen, M.; Zhang, H.; Lei, A. *Org. Lett.* **2009**, *11*, 709.
(b) Suarez, J. R.; Collado-Sanz, D.; Cardenas, D. J.; Chiara, J. L. *J. Org. Chem.* **2015**, *80*, 1098.
(c) Balaraman, K.; Kesavan, V. *Synthesis* **2010**, 3461.
(d) Lampkowski, J. S.; Durham, C. E.; Padilla, M. S.; Young, D. D. *Org. Biomol. Chem*. **2015**, *13*, 424.

[17] (a) Cadiot, P.; Chodkiewicz, W. *Chemistry of Acetylenes*, Marcel Dekker, New York, **1969**.
(b) Sindhu, K. S.; Thankachan, A. P.; Sajitha, P. S.; Anilkumar, G. *Org. Biomol. Chem*. **2015**, *13*, 6891.
(c) Yu, M.; Pan, D.; Jia, W.; Chen, W.; Jiao, N. *Tetrahedron Lett.* **2010**, *51*, 1287.

[18] (a) Peng, H.-H.; Xi, Y.-M.; Ronaghi, N.; Dong, B.-L.; Akhmedov, N. G.; Shi, X.-D. *J. Am. Chem. Soc*. **2014**, *136*, 13174.
(b) Vilhanová, B.; Václavík, J.; Artiglia, L.; Ranocchiari, M.; Togni, A.; Bokhoven, J. A. *ACS Catal*. **2017**, *7*, 3414.

[19] Lampkowski, J. S.; Uthappa, D. M.; Halonski, J. F.; Maza, J. C.; Young, D. D. *J. Org. Chem*. **2016**, *81*, 12520.

[20] Su, L.-B.; Dong, J.-Y.; Liu, L.; Sun, M.-L.; Qiu, R.-H.; Zhou, Y.-B.; Yin, S.-F. *J. Am. Chem. Soc*. **2016**, *138*, 12348.

[21] Wan, J.-P.; Cao, S.; Jing, Y.-F. *Appl. Organomet. Chem.* **2014**, *28*, 631.

[22] Yang, X.; Matsuo, D.; Suzuma, Y.; Fang, J.-K.; Xu, F.; Orita, A.; Otera, J. *Synlett* **2011**, 2402.

[23] Peng, L.-F.; Xu, F.; Suzuma, Y.; Orita, A.; Otera, J. *J. Org. Chem*. **2013**, *78*, 12802.

[24] Peng, L.-F.; Xu, F.; Shinohara, K.; Orita, A.; Otera, J. *Chem. Lett*. **2014**, *43*, 1610.

[25] Peng, L.-F.; Xu, F.; Shinohara, K.; Orita, A.; Otera, J. *Org. Chem. Front*. **2015**, *2*, 248.

(Cheng, F.)

