Accepted Manuscript

Mukaiyama reagent-promoted metal-free preparation of alkynyl sulfones and phosphonates under mild conditions

Danyang Qi, Wanrong Dong, Zhihong Peng, Yingjun Zhang, Delie An

PII: S0040-4020(19)30707-0

DOI: https://doi.org/10.1016/j.tet.2019.06.035

Reference: TET 30427

To appear in: *Tetrahedron*

Received Date: 9 March 2019

Revised Date: 14 June 2019

Accepted Date: 22 June 2019

Please cite this article as: Qi D, Dong W, Peng Z, Zhang Y, An D, Mukaiyama reagent-promoted metal-free preparation of alkynyl sulfones and phosphonates under mild conditions, *Tetrahedron* (2019), doi: https://doi.org/10.1016/j.tet.2019.06.035.

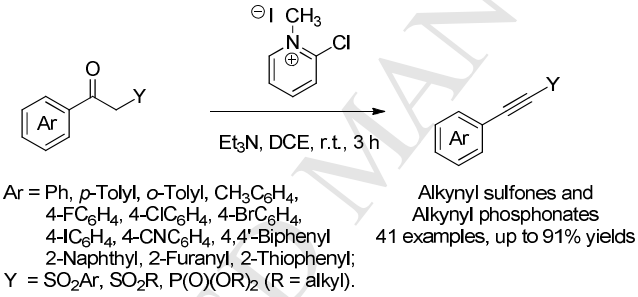
Graphical Abstract

To create your abstract, type over the instructions in the template box below.
Fonts or abstract dimensions should not be changed or altered.

Mukaiyama Reagent-Promoted Metal-free Preparation of Alkynyl Sulfones and Phosphonates under Mild Conditions

Danyang Qi, Wanrong Dong[a,*], Zhihong Peng[a], Yingjun Zhang[b] and Delie An[a,*]
[a]*State Key Laboratory of Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering, Hunan University, Lushan South Rd. 2, Changsha, 410082, P.R. China*
wanrongdong@hnu.edu.cn; deliean@hnu.edu.cn;
[b]*State Key Laboratory of Anti-Infective Drug Development (NO. 2015DQ780357), Sunshine Lake Pharma Co.,Ltd, Dongguan 523871, P. R. China*

A Mukaiyama reagent-mediated protocol towards alkynyl sulfones and alkynyl phosphonates was herein described without participation of any transition metal catalysts. The transformation proceeded under the mild conditions in a one-pot manner from the easily-accessible substrates without carbon-carbon triple bonds, featuring for good functional groups tolerance (up to 41 examples) and high efficiency (up to 91% yields) towards alkynyl sulfones and alkynyl phosphonates at low cost.



Ar = Ph, *p*-Tolyl, *o*-Tolyl, $CH_3C_6H_4$, $4\text{-}FC_6H_4$, $4\text{-}ClC_6H_4$, $4\text{-}BrC_6H_4$, $4\text{-}IC_6H_4$, $4\text{-}CNC_6H_4$, 4,4'-Biphenyl, 2-Naphthyl, 2-Furanyl, 2-Thiophenyl;
Y = SO_2Ar, SO_2R, $P(O)(OR)_2$ (R = alkyl).

Alkynyl sulfones and Alkynyl phosphonates
41 examples, up to 91% yields

Tetrahedron
journal homepage: www.elsevier.com

Mukaiyama Reagent-Promoted Metal-free Preparation of Alkynyl Sulfones and Phosphonates under Mild Conditions

Danyang Qi, Wanrong Dong[a,*], Zhihong Peng[a], Yingjun Zhang[b] and Delie An[a,*]

[a]*State Key Laboratory of Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering, Hunan University, Lushan South Rd. 2, Changsha, 410082, P.R. China*
[b]*State Key Laboratory of Anti-Infective Drug Development (NO. 2015DQ780357), Sunshine Lake Pharma Co.,Ltd, Dongguan 523871, P. R. China.*

ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

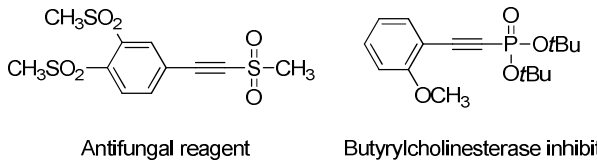
Keywords:
Mukaiyama-reagent
Metal-free
Mild conditions
Alkynyl sulfones
Alkynyl phosphonates

ABSTRACT

An efficient and mild route for the formation sulfur or phosphor-substituted alkynes was herein demonstrated. The Mukaiyama reagent-mediated transformation started from easily-accessible substrates without carbon-carbon triple bonds, and the reaction proceeded under mild conditions (room temperature) in a one-pot manner, requiring for no transition metal-catalysts. The practical protocol featured for good functional groups tolerance (up to 41 examples) and high efficiency (up to 91% yields) towards alkynyl sulfones and alkynyl phosphonates at low cost.

1. Introduction

Heteroatom decorated carbon-carbon triple bonds, such as alkynyl sulfones and alkynyl phosphonates, have aroused broad research interests for the outstanding biological and photo-conductive properties (shown in Scheme 1),[1] as well as versatile intermediates for the preparation of various heterocyclic molecules of great pharmaceutical significance in the field of synthetic and methodology chemistry[2]. Thus, great attempts have been endeavoured for the preparation of the useful compounds. Typically, expensive substrates containing carbon-carbon triple bonds were frequently employed for the construction of alkynyl sulfones and alkynyl phosphonates, transition metal-catalyzed sp-hybridized C-S or C-P cross-coupling protocols were generally applied from acetylenes,[3] acetylenic bromide,[4] arylpropiolic acids,[5] 1,1-dihalo-1-alkenes[6] *etc*.[7] and the corresponding S or P containing coupling partners. However, homo-coupling of the high-cost but instable acetylenic compounds or dibromoalkenes was unavoidable in the presence of palladium and copper catalysts. Therefore, attempts have been devoted to seek the possibilities to form the C-S or C-P bonds in the absence of any transition metal-catalysts for higher efficiency. For example, approaches such as halogenated alkynes coupled with SH reagents or alkynyl lithium reacted with phosphonyl chloride were successfully developed.[8] Zhao also reported a transition metal-free protocol from 1,1-dibromo-1-alkenes and trialkyl phosphites (scheme 1).[9] Yet, research work has been widely embarked for the construction of triple bonds from easier-accessible substrates. One of the pioneering documents was reported by Negishi, using methyl ketones for construction of terminal alkynes with the assistance of LDA and $ClP(O)(OEt)_2$.[10] But the efficient transformation suffered from limited scope of substrates and extremely low reaction temperature (-78 ^oC). Then, methylthiomethyl phenyl sulfone (MP-S) was employed towards acetylenic sulfides with aldehydes.[11] Still, special reagent MP-S restricted the methodology for general applications. As the long-standing interests for the formations of sulfur or selenium-substituted alkynes from our group,[12] we wish to demonstrate a facile transformation of nitrogen or phosphine-substituted acetylenes herein from easily-prepared starting materials.



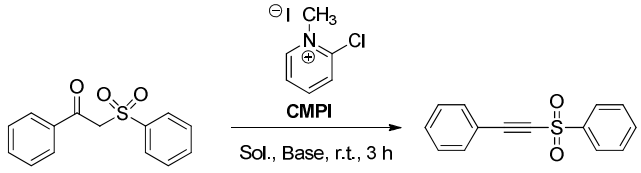
Scheme 1.Biologically active alkynyl sulfone and phosphonate

2. Results and discussions

Initially, 1-phenyl-2-tosylethanone (**1a**) was used as the model substrate for optimization of the dehydration reactions, as shown in Table 1. To our satisfactory, in the presence of Mukaiyama's reagent, 2-chloro-1-methylpyridinium iodide (CMPI), sodium hydroxide made the reaction take place smoothly in dichloromethane (DCM) at room temperature for 3 hours, providing the desired *S*-1-phenylethynyl-*S*-phenyl sulfone (**2a**) in medium yield (52% for entry 1). Sodium carbonate (Na_2CO_3)

allowed the formation of **2a** in only 28% yield (entry 2). However, K_2CO_3 offered the desired alkynyl sulfone **2a** in good 86% yield (entry 3), superior to other potassium salts like KOAc, *t*BuOK did in the system (entries 4 and 5). In the same manner, no improvement was observed when the reaction was conducted in the presence of Cs_2CO_3, and 32% of **2a** was successfully isolated (entry 6). Successively, organic bases such as Et_2HN, Et_3N and pyridine, were turned to for higher efficiency. However, Et_3N distinguished from other organic bases tested, giving the desired alkynyl sulfone **2a** in excellent 92% yield (entries 7 – 9). Furthermore, base was proved of great importance to the useful transformation, for no product was detected in the absence of any bases (entry 10). Subsequently, the effects of different solvents were also tested. Acetonitrile, 1,2-dichloroethane (DCE), *N*,*N*-dimethyl formamide (DMF) ensured the occurrence of the reaction, but in lower yields, up to 85% (entries 11 – 13). Other organic solvents, including 1,4-dioxane, toluene, ethyl acetate were ineffective to the transformation and no reaction was detected after 3 hours (entries 14 – 16). Finally, no decrease was observed at room temperature under the argon atmosphere (entry 17).

Table 1. Optimization of the reaction conditions[a]



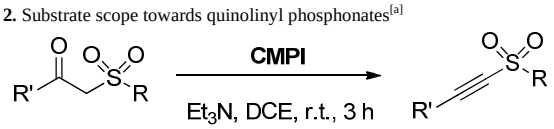
1a **2a**

Entry	Base	Sol.	Yield (%)[b]
1	NaOH	CH_2Cl_2	52
2	Na_2CO_3	CH_2Cl_2	28
3	K_2CO_3	CH_2Cl_2	86
4	KOAc	CH_2Cl_2	20
5	*t*BuOK	CH_2Cl_2	20
6	Cs_2CO_3	CH_2Cl_2	32
7	Et_2NH	CH_2Cl_2	n.d.
8	Et_3N	CH_2Cl_2	92
9	Pyridine	CH_2Cl_2	n.d.
10	--	CH_2Cl_2	n.d.
11	Et_3N	CH_3CN	85
12	Et_3N	1,2-dichloroethane	80
13	Et_3N	DMF	60
14	Et_3N	1,4-dioxane	n.d.
15	Et_3N	toluene	n.d.
16	Et_3N	Ethyl acetate	n.d.
17	Et_3N	CH_2Cl_2	90[c]

a) Conditions: **1a** (0.3 mmol), CMPI (0.36 mmol), Base (0.6 mmol) in Sol. (3.0 mL) at room temperature for 3 hours. b) Isolated yields. c) the yield was obtained under the argon atmosphere.

Subsequently, the functional groups compatibilities were also examined in the mild transformation as shown in Table 2. To our delight, **1b** underwent the dehydration protocol smoothly, affording the desired sulfonyl alkyne **2b** in 90% yield (entry 2). In the same manner, **2c** was successfully isolated in 89% yield after the treatment with CMPI (entry 3). Moreover, electron-sufficient aryl groups were also tested in the system, which was exemplified by the formation of the alkynyl sulfones **2d** and **2e** in 88% and 85% yields, respectively (entries 4 and 5). Generally, however, halo substituted substrates gave inferior performance to alkoxyl-decorated substrates, which probably was attributed to the inductive effect. For example, **2f, 2g**, **2h, 2i** and **2j** were smoothly separated after column in yields from 70% to 79% (entries 5 – 9). And 4-cyanophenylethynyl phenyl sulfone (**2k**) was offered in 76% yield (entry 10). Polyaryl substituted substrates like 4,4'-biphenyl and 1-(7-methoxy-2-naphthyl substrates (**1l** and **1m**) offerred the desired triple carbon-carbon bond decorated sulfones **2l** and **2m** in 80% and 79% yields (entries 11 and 12). Subsequently, functional groups on sulfonic part were also examined in the transformation, and general lower efficiency was acknowledged in the protocol. **1n** was smoothly transformed into the corresponding alkynyl sulfone **2n** in acceptable 60% yield (entry 13). Other electron-rich aryl group, showed positive effect to the transformation and 1-phenylethynyl 4-methoxyphenyl sulfone (**2o**) was formed in 68% yield (entry 14). 1-Phenylethynyl 3-chlorophenyl sulfone (**2p**) and 1-phenylethynyl 4-iodophenyl sulfone (**2q**) were furnished favorably in 52% and 60% yields (entries 15 and 16). Electron-deficient aryl substituents, such as 1-phenylethynyl 4-triflormethylphenyl sulfone (**2r**) and 1-phenylethynyl 4-nitrophenyl sulfone (**2s**) were provided in 48% and 45% yields, separately (entries 17 and 18). Polyaryl, such as 2-naphthyl sulfonyl alkynyl (**2t**) was generated in 72% yield (entry 19). Worthy of note, phenylethynyl cyclopropyl sulfone (**2u**) was observed in 68% yield after the treatment of CMPI at room temperature (entry 20). Moreover, chained alkyl like 4-phenyl-butynyl phenyl sulfone **2v** was obtained in 70% yield (entry 21).

Table 2. Substrate scope towards quinolinyl phosphonates[a]



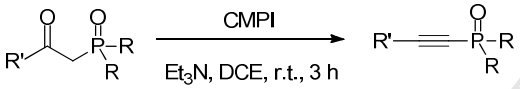
1b - 1t **2b - 2t**

Entry	**2**	R'	R	Yield (%)[b]
1	**2b**	*p*-Tolyl	Ph	90
2	**2c**	*o*-Tolyl	Ph	89
3	**2d**	4-$CH_3OC_6H_4$	Ph	88
4	**2e**	3,4-$CH_2O_2C_6H_3$	Ph	85
5	**2f**	4-FC_6H_4	Ph	72
6	**2g**	4-ClC_6H_4	Ph	79
7	**2h**	3,4-$Cl_2C_6H_4$	Ph	70
8	**2i**	4-BrC_6H_4	Ph	76
9	**2j**	4-IC_6H_4	Ph	70
10	**2k**	4-CNC_6H_4	Ph	76
11	**2l**	4-PhC_6H_4	Ph	80
12	**2m**	2-(7-CH_3ONaphthyl)	Ph	79
13	**2n**	Ph	4-*t*BuC_6H_4	60
14	**2o**	Ph	4-$CH_3OC_6H_4$	68
15	**2p**	Ph	3-ClC_6H_4	52
16	**2q**	Ph	4-IC_6H_4	60
17	**2r**	Ph	4-$CF_3C_6H_4$	48
18	**2s**	Ph	4-$NO_2C_6H_4$	45
19	**2t**	Ph	2-Naphthyl	72
20	**2u**	Ph	Cyclo-C_3H_5	68
21	**2v**	PhC_2H_4	Ph	70

a) Conditions: **1** (0.5 mmol), CMPI (0.6 mmol), Et_3N (1.0 mmol) in DCE (5.0 mL) at room temperature for 3 hours. b) Isolated yields.

Based on the successful formation of the carbon-carbon triple bond decorated sulfones, the evaluation of the substrate scope was then extended on the construction of alkynyl phosphonates, as shown in Table 3. To our delight, *P*-phenylethynyl-*P*,*P*-diethyl phosphonate (**4a**) was successfully furnished under the standard conditions in 91% yield (entry 1). In an analogous pattern, formations of *P*-(4-methylphenylethynyl)-*P*,*P*-diethyl phosphonate (**4b**), *P*-(2-methylphenylethynyl)-*P*,*P*-diethyl phosphonate (**4c**) and *P*-(3,4-dimethylphenylethynyl)-*P*,*P*-diethyl phosphonate (**4d**) were achieved by the facile protocol, and a range of 80% - 89% yields were obtained (entries 2 – 4). Similarly, electron-rich aryl groups were also found compatible in the system, and various alkynyl phosphonates **4e** – **4g** were also smoothly provided in yields from 70% - 79% (entries 5 – 7). Tolerance of haloaryl groups was also examined and gratifyingly, corresponding products **4h** – **4k** were successfully isolated in yields from 72% to 80% (entries 8 – 11). Polyaryl substrates were also readily separated, allowing the formation of the polyarylalkynyl diethyl phosphonates **4l** – **4n** in yields from 76% to 85% (entries 12 – 14). It was noteworthy that heteroaryl substituted starting materials **3o** and **3p** underwent the dehydration procedure, and 2-furanyl and 2-thiophenyl substituted alkynyl phosphonates **4o** and **4p** in acceptable 64% and 71% yields (entries 15 and 16). Successively, different functional groups tolerance was also tested in the transformation and *P*-(1-phenylethynyl)-*P*-dimethyl phosphonate (**4q**), *P*-(1-phenylethynyl)-*P*-diisopropyl phosphonate (**4r**), *P*-(1-phenylethynyl)-*P*-dibutyl phosphonate (**4s**) were readily furnished in yields from 80% to 89% yields (entries 17 – 19). Surprisingly, *P*-(2,2-dimethylbutynyl)-*P*-diethyl phosphonate (**4t**) was successfully furnished in acceptable yield, up to 56% (entry 20).

Table 3. Substrates scope towards triazolyl phosphonates[a)]

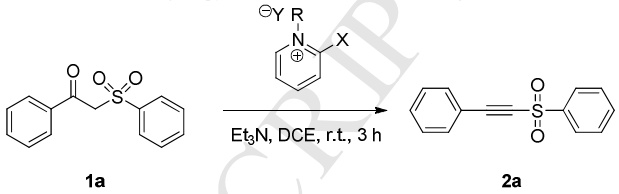


	3a - 3s		4a - 4s	
Entry	**4**	R'	R	Yield (%)[b]
1	**4a**	Ph	Et	91
2	**4b**	4-$CH_3C_6H_4$	Et	89
3	**4c**	2-$CH_3C_6H_4$	Et	85
4	**4d**	3,4-$(CH_3)_2C_6H_3$	Et	80
5	**4e**	4-$CH_3OC_6H_4$	Et	79
6	**4f**	2,5-$(CH_3O)_2C_6H_3$	Et	75
7	**4g**	3,4-$CH_2O_2C_6H_3$	Et	70
8	**4h**	4-FC_6H_4	Et	78
9	**4i**	4-ClC_6H_4	Et	80
10	**4j**	4-BrC_6H_4	Et	76
11	**4k**	4-IC_6H_4	Et	72
12	**4l**	4-PhC_6H_4	Et	78
13	**4m**	2-Naphthyl	Et	85
14	**4n**	6-CH_3O-2-Naphthyl	Et	76
15	**4o**	2-Furanyl	Et	64
16	**4p**	2-Thiophenyl	Et	71
17	**4q**	Ph	Me	88
18	**4r**	Ph	*i*Pr	89
19	**4s**	Ph	*n*Bu	80
20	**4t**	*t*Bu	Et	56

a) Conditions: **3** (0.5 mmol), CMPI (0.6 mmol), Et_3N (1.0 mmol) in DCE (5.0 mL) at room temperature for 3 hours. b) Isolated yields.

To have a better understanding of the dehydration protocol, the reactivities of other pyridinium halides were further examined by the reaction between **1a** and **2a** at room temperature, as summarized in the table 4. 2-chloro-1-ethylpyridinium iodide offered a decreased yield of **2a** under the mild conditions (40% yield for entry 1). By comparison, 2-bromo-1-methylpyridinium iodide allowed the formation of the desired product **2a** in the same 40% yield (entry 2). Other different salts, such as 2-chloro-1-methylpyridinium tetrafluoroborate and 2-bromo-1-methylpyridinium triflate furnished the alkynyl sulfone 2a in higher yields, up to 85% (entries 3 and 4). However, no pyridinium salts gave better performance than CMPI did under the mild conditions.

Table 4. Effects of analogous pyridinium salts[a)]

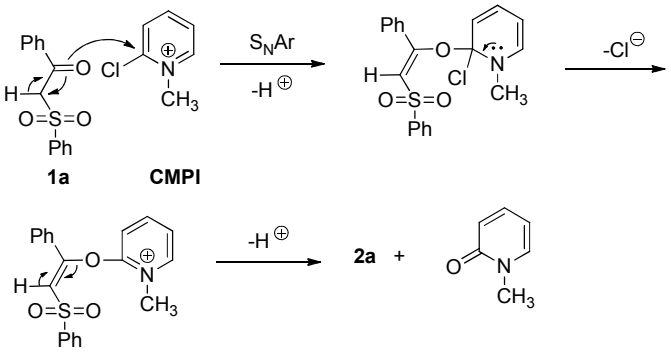


1a **2a**

Entry	R	X	Y	Yield (%)[b]
1	Et	Cl	I	40
2	Me	Br	I	40
3	Me	Cl	BF_4	70
4	Me	Br	OTf	85

a) Conditions: **1a** (0.5 mmol), pyridinium salt (0.6 mmol), Et_3N (1.0 mmol) in DCE (5.0 mL) at room temperature for 3 hours. b) Isolated yields.

Based on the previous demonstrations,[13] a plausible mechanism was proposed for the mild dehydration transformation, which was described by the reaction between **1a** and **2a** as shown in Scheme 2. Firstly, nucleophilic addition reaction took place between the substrate **1a** and **CMPI**, forming a key intermediate with a loss of a hydrogen cation. Then, removal of chloride anion gave an access to another pyridinium intermediate, which could be transformed easily into the desired alkynyl sulfone **2a**.



Scheme 2. Proposed mechanism

3. Conclusion

In conclusion, an effective and practical transformation of alkynyl sulfones and alkynyl phosphonates was successfully achieved under the mild conditions without the participation of any transition metal-catalysts. The methodology offered an facile access to S or P-substituted alkynes from easily-prepared substrates of different structure with high efficiency and in low cost, which made a significant contribution to the development of the topic.

4. Experimental section

4.1 General remarks

All reagents were purchased from commercial companies and used without further purification.^{1}H and ^{13}C NMR spectra were recorded on a Varian INOVA-400 spectrometer in deuterated chloroform at 25 °C with residue solvent peaks as internal standards (δ = 7.26 ppm for ^{1}H-NMR and δ = 77.16 ppm for ^{13}C-NMR). Chemical shifts (δ) are reported in ppm, and spin-spin coupling constants (*J*) are given in Hz, while multiplicities are abbreviated by s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). Mass spectra were recorded on a ThermoFinnigan MAT95XP microspectrometer and High resolution mass spectra (HRMS) were recorded on an Agilent Technologies Accurate Mass Q-TOF 6530 microspectrometer. Infrared (IR) spectra were reported in reciprocal centimeter (cm^{-1}). Melting points were recorded on a national standard melting point apparatus (Model: Taike XT-4) and were uncorrected.

4.2 General Procedure

*4.2.1 Preparations of starting materials **1** and **3***

A sealed tube (35 mL) equipped with a stirring bar was loaded with 2-bromoethanones (1.0 mmol), then sodium benzenesulfinate (1.2 mmol) in DMF (20 ml) or phosphite (1.0 mmol) in toluene (20 ml) was added to the tube and the mixtures were stirred at room temperature till the 2-bromoethanones was totally consumed as indicated by TLC analysis (ca. 12 hours for **1** and 24 hours for **3**). Then, the mixture was diluted with water (20 mL) and extracted with CH_2Cl_2 (30mL × 3). Next, the organic phase was combined and dried over anhydrous Na_2SO_4 . The solvent was removed by rotary evaporation and the oily mixture was purified with flash chromatograph column (elute: mixture of ethyl acetate and n-hexane), giving the desired products. And the ^{1}H-NMR spectra of the purified substrates were in accordance with the known literatures.[14]

*4.2.2 Preparations of alkynyl sulfones **2** or phosphonates **4***

A sealed tube (35 mL) equipped with a stirring bar was loaded with the substrates **1** or **3** (0.5 mmol) in DCM (5.0 mL), then CMPI (0.6 mmol, 1.2 equiv.) and Et_3N was added to the solution in one portion. After addition, the tube was sealed and the mixture was stirred at room temperature for another 3 h. After the completion of the reaction (monitored by TLC), the mixture was then washed with dichloromethane (15 mL × 3). The organic phase was combined and then concentrated. The oily crude product was purified by column chromatography using silica gel (200-300 mesh) as stationary phase and a mixture of petroleum and ethyl acetate as eluent to give the desired product in noted yields.

4.2.3 S-(1-Phenylethynyl)-S-phenyl sulfone (2a)

Yellow solid (65.4 mg, 90% yield). Melting point: 74-75 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.08 (d, *J* = 7.6 Hz, 2H), 7.69 (t, *J* = 7.3 Hz, 1H), 7.60 (t, *J* = 7.5 Hz, 2H), 7.52 (d, *J* = 7.6 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 141.9, 134.3, 132.9, 131.7, 129.5, 128.82, 127.5, 118.0, 93.6, 85.4 ppm. MS (EI): *m*/*z* (%) = 77.04 (51), 89.03 (38), 125.00 (49), 178.06 (100), 241.99 (30). IR (KBr): ν = 2169, 1651, 1455, 1323, 1155, 1081, 866, 756, 720, 688, 653, 569 cm^{-1}. HRMS (EI): Calcd. for $[C_{14}H_{10}O_2S]^+$: 242.0402, Found 242.0398.

4.2.4 S-(1-4-Methylphenylethynyl)-S-phenyl sulfone (2b)

Yellow solid (115.3 mg, 90% yield). Melting point: 82-83 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.08 (d, *J* = 7.8 Hz, 2H), 7.68 (t, *J* = 7.3 Hz, 1H), 7.60 (t, *J* = 7.3 Hz, 2H), 7.42 (d, *J* = 7.4 Hz, 2H), 7.17 (d, *J* = 7.6 Hz, 2H), 2.37 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 142.6, 142.1, 134.2, 132.9, 129.6, 129.5, 127.5, 114.9, 94.37, 85.0, 21.9 ppm. MS (EI): *m*/*z* (%) = 77.04 (48), 103.05 (48), 125.00 (29), 165.06 (20), 192.07 (97), 256.00 (100). IR (KBr): ν = 2962, 2177, 1604, 1508, 1443, 1334, 1155, 1083, 1023, 857, 813, 779, 720, 685, 619, 569, 512 cm^{-1}. HRMS (EI): Calcd. for $[C_{15}H_{12}O_2S]^+$: 256.0558, Found 256.0556.

4.2.5 S-(1-2-Methylphenylethynyl)-S-phenyl sulfone (2c)

Yellow solid (114.1 mg, 89% yield). Melting point: 47-48 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.08 (d, *J* = 7.9 Hz, 2H), 7.68 (t, *J* = 7.2 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 2H), 7.43 (d, *J* = 7.7 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.23 – 7.12 (m, 2H), 2.35 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 142.6, 142.3, 134.2, 133.2, 131.7, 130.1, 129.5, 127.4, 126.1, 117.8, 93.3, 89.1, 20.5 ppm. MS (EI): *m*/*z* (%) = 77.04 (93), 103.05 (57), 115.05 (100),125.00 (37), 165.06 (31), 191.07 (91), 256.00 (66). IR (KBr): ν = 3059, 2179, 1651, 1325, 1157, 1082, 850, 755, 727, 688, 653, 572, 541 cm^{-1}. HRMS (EI): Calcd. for $[C_{15}H_{12}O_2S]^+$: 256.0558, Found 256.0561.

4.2.6 S-(1-4-Methoxyphenylethynyl)-S-phenyl sulfone (2d)

Yellow solid (119.8 mg, 88% yield). Melting point: 84-85 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.07 (d, *J* = 7.5 Hz, 2H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 2H), 7.46 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 3.82 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.3, 142.2, 134.8, 134.1, 129.4, 127.4, 114.6, 109.6, 94.8, 84.7, 55.6 ppm. MS (EI): *m*/*z* (%) = 77.04 (100), 131.05 (88), 207.23 (98), 272.32 (21). IR (KBr): ν = 2939, 2168, 1670, 1598, 1510, 1441, 1321, 1263, 1172, 1153, 1089, 1023, 798, 739, 686, 554, 521 cm^{-1}. HRMS (EI): Calcd. for $[C_{15}H_{12}O_3S]^+$: 272.3190, Found 272.3195.

4.2.7 S-(1-3,4-Methylenedioxyphenylethynyl)-S-phenyl sulfone (2e)

Yellow solid (121.7 mg, 85% yield). Melting point: 102-103 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.06 (d, *J* = 7.8 Hz, 2H), 7.68 (t, *J* = 7.3 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 2H), 7.09 (d, *J* = 8.1 Hz, 1H), 6.92 (s, 1H), 6.78 (d, *J* = 8.1 Hz, 1H), 6.01 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 150.9, 147.9, 142.1, 134.2, 129.5, 129.0, 127.5, 112.2, 110.8, 109.0, 102.1, 94.3, 84.3 ppm. MS (EI): *m*/*z* (%) = 77.04 (23), 133.02 (54), 163.04 (31), 222.04 (35), 285.97 (100). IR (KBr): ν = 2964, 2169, 1789, 1651, 1504, 1255, 1161, 1085, 1035, 810, 667 cm^{-1}. HRMS (EI): Calcd. for $[C_{15}H_{10}O_4S]^+$: 286.0300, Found 286.0294.

4.2.8 S-(1-4-Fluorophenylethynyl)-S-phenyl sulfone (2f)

Yellow solid (93.7 mg, 72% yield). Melting point: 54-55 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.07 (d, *J* = 7.6 Hz, 2H), 7.70 (t, *J* = 7.4 Hz, 1H), 7.60 (t, *J* = 7.5 Hz, 2H), 7.56 – 7.50 (m, 2H), 7.07 (t, *J* = 8.1 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.5 ($J_{C\text{-}F}$ = 255.4 Hz), 141.8, 135.3 ($J_{C\text{-}F}$ = 9.1 Hz), 134.4, 129.6, 127.6, 116.5 ($J_{C\text{-}F}$ = 22.5 Hz), 114.1 ($J_{C\text{-}F}$ = 3.6 Hz), 92.5, 85.4 ppm. ^{19}F NMR (375 MHz, $CDCl_3$) δ = -104.33 ppm. MS (EI): *m*/*z* (%) = 77.04 (20), 107.02 (20), 125.00 (30), 196.04 (100), 259.98 (36). IR (KBr): ν = 2181, 1602, 1504, 1336, 1155, 1085, 839, 794, 723, 684, 617, 568 cm^{-1}. HRMS (EI): Calcd. for $[C_{14}H_9FO_2S]^+$: 260.0307, Found 260.0301.

4.2.8 S-(1-4-Chlorophenylethynyl)-S-phenyl sulfone (2g)

Yellow solid (109.3 mg, 79% yield). Melting point: 91-92 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.08 (d, *J* = 7.6 Hz, 2H), 7.70 (t, *J* = 7.3 Hz, 1H), 7.61 (t, *J* = 7.5 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 7.9 Hz, 2H) ppm.^{13}C NMR (100 MHz, $CDCl_3$) δ = 141.7, 138.3, 134.5, 134.1, 129.6, 129.4, 127.6, 116.5 ppm. MS (EI): *m*/*z* (%) = 77.04 (55), 124.99 (97), 176.04 (38), 212.01 (100), 275.94 (48). IR (KBr): ν = 2351, 2179, 1789, 1651, 1556,

1340, 1158, 1085, 1013, 852, 802, 732, 697, 587, 417 cm^{-1}. HRMS (EI): Calcd. for $[C_{14}H_9ClO_2S]^+$: 276.0012, Found 276.0009.

4.2.9 S-(1-4-Chlorophenylethynyl)-S-phenyl sulfone (2h)

Yellow solid (108.9 mg, 70% yield). Melting point: 88-89 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.07 (d, *J* = 8.0 Hz, 2H), 7.71 (t, *J* = 7.3 Hz, 1H), 7.64 – 7.58 (m, 3H), 7.46 (d, *J* = 8.3 Hz, 1H), 7.35 (d, *J* = 8.3 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 141.4, 136.7, 134.6, 134.3, 133.5, 131.8, 131.1, 129.6, 127.7, 117.9, 90.3, 86.9 ppm. MS (EI): *m/z* (%) = 77.04 (36), 125.00 (67), 176.05 (42), 245.95 (100), 309.92 (58). IR (KBr): ν = 2351, 1652, 1539, 1456, 1339, 1163, 1085, 910, 744, 689, 594 cm^{-1}. HRMS (EI): Calcd. for $[C_{14}H_8C_{l2}O_2S]^+$: 309.9622, Found 309.9625.

4.2.10 S-(1-4-Bromophenylethynyl)-S-phenyl sulfone (2i)

Yellow solid (122.0 mg, 76% yield). Melting point: 116-117 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.07 (d, *J* = 8.0 Hz, 2H), 7.70 (t, *J* = 7.4 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 141.7, 134.5, 134.1, 132.3, 129.6, 127.6, 126.7, 116.9, 92.2, 86.4 ppm. MS (EI): *m/z* (%) = 77.04 (77), 125 (100), 176.04 (55), 255.94 (64), 321.90 (35). IR (KBr): ν = 2351, 1645, 1506, 1336, 1260, 1162, 1085, 1016, 800, 686, 434 cm^{-1}. HRMS (EI): Calcd. for $[C_{14}H_9ClO_2S]^+$: 321.9486, Found 321.9480.

4.2.11 S-(1-4-Iodophenylethynyl)-S-phenyl sulfone (2j)

Yellow solid (128.9 mg, 70% yield). Melting point: 134-135 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.08 (d, *J* = 7.6 Hz, 2H), 7.70 (t, *J* = 7.3 Hz, 1H), 7.61 (t, *J* = 7.5 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 7.9 Hz, 2H) ppm.^{13}C NMR (100 MHz, $CDCl_3$) δ = 141.7, 138.3, 134.5, 134.1, 129.6, 129.4, 127.6, 116.5 ppm. MS (EI): *m/z* (%) = 77.04 (55), 124.99 (97), 176.04 (38), 212.01 (100), 275.94 (48). IR (KBr): ν = 2351, 2179, 1789, 1651, 1556, 1340, 1158, 1085, 1013, 852, 802, 732, 697, 587, 417 cm^{-1}. HRMS (EI): Calcd. for $[C_{14}H_9ClO_2S]^+$: 276.0012, Found 276.0009.

4.2.12 S-(1-4-Cyanophenylethynyl)-S-phenyl sulfone (2k)

Yellow solid (101.6 mg, 76% yield). Melting point: 107-108 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.08 (d, *J* = 7.9 Hz, 2H), 7.73 (t, *J* = 7.4 Hz, 1H), 7.69 – 7.61 (m, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 141.2, 134.8, 133.3, 132.4, 129.7, 127.8, 122.8, 117.7, 115.1, 90.1, 88.6 ppm. MS (EI): *m/z* (%) = 77.04 (36), 125 (100), 203.05 (100), 266.98 (34). IR (KBr): ν = 2230, 2185, 1681, 1499, 1449, 1338, 1159, 1081, 854, 745, 682, 603, 554, 431 cm^{-1}. HRMS (EI): Calcd. for $[C_{15}H_9NO_2S]^+$: 267.0354, Found 267.0349.

4.2.13 S-(1-4,4'-Biphenylethynyl)-S-phenyl sulfone (2l)

Yellow solid (127.4 mg, 80% yield). Melting point: 92-93 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.11 (d, *J* = 7.7 Hz, 2H), 7.70 (t, *J* = 7.2 Hz, 1H), 7.64 – 7.56 (m, 8H), 7.46 (t, *J* = 7.3 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 144.5, 142.0, 139.6, 134.3, 133.4, 129.5, 129.2, 128.5, 127.6, 127.4, 127.3, 116.6, 93.8, 86.0 ppm. MS (EI): *m/z* (%) = 77.04 (20), 165.06 (36), 254.06 (61), 318.02 (100). IR (KBr): ν = 3062, 2177, 1600, 1481, 1445, 1328, 1163, 1085, 1005, 856, 765, 743, 718, 686, 640, 576, 551 cm^{-1}. HRMS (EI): Calcd. for $[C_{20}H_{14}O_2S]^+$: 318.0715, Found 318.0716.

4.2.14 S-(1-7-Methoxy-2-naphthylethynyl)-S-phenyl sulfone (2m)

Yellow solid (127.3 mg, 79% yield). Melting point: 59-60 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.11 (d, *J* = 7.7 Hz, 2H), 8.02 (s, 1H), 7.72 – 7.67 (m, 3H), 7.61 (t, *J* = 7.5 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 1H), 7.19 (d, *J* = 9.0 Hz, 1H), 7.10 (s, 1H), 3.93 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.8, 142.2, 136.0, 134.3, 134.2, 130.0, 129.5, 128.4, 128.0, 127.5, 127.5, 120.4, 112.4, 106.0, 95.0, 85.1, 55.6 ppm. MS (EI): *m/z* (%) = 77.04 (35), 126.04 (37), 139.05 (31), 169.05 (55), 215.06 (44), 322.01 (100). IR (KBr): ν = 2964, 2167, 1867, 1651, 1622, 1327, 1241, 1157, 1085, 1027, 940, 853, 773, 731, 645, 584 cm^{-1}. HRMS (EI): Calcd. for $[C_{19}H_{14}O_3S]^+$: 322.0664, Found 322.0669.

4.2.15 S-(1-Phenylethynyl)-S-(4-tert-butylphenyl) sulfone (2n)

Yellow solid (89.5 mg, 60% yield). Melting point: 76-77 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99 (d, *J* = 7.7 Hz, 2H), 7.60 (d, *J* = 7.7 Hz, 2H), 7.53 (d, *J* = 7.7 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 2H), 1.36 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.4, 138.9, 132.9, 131.6, 128.8, 127.5, 126.6, 118.2, 93.1, 85.7, 35.5, 31.2 ppm. MS (EI): *m/z* (%) = 77.04 (31), 91.05 (32), 149.00 (52), 283.01 (100), 298.05 (25). IR (KBr): ν = 2964, 2181, 1593, 1489, 1332, 1161, 1111, 1082, 850, 755, 669, 617, 562, 547, 517 cm^{-1}. HRMS (EI): Calcd. for $[C_{18}H_{18}O_2S]^+$: 298.1028, Found 298.1033.

4.2.16 S-(1-Phenylethynyl)-S-(p-methoxyphenyl) sulfone (2o)

Yellow solid (92.6 mg, 68% yield). Melting point: 70-71 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.00 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 7.6 Hz, 2H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 3.90 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.3, 133.6, 132.8, 131.5, 130.0, 128.8, 118.3, 114.7, 92.6, 86.0, 55.9 ppm. MS (EI): *m/z* (%) = 77.04 (20), 165.06 (36), 193.04 (46), 208.06 (100), 272.01 (48). IR (KBr): ν = 2945, 2179, 1593, 1496, 1442, 1330, 1263, 1151, 1082, 1020, 848, 755, 682, 642, 558 cm^{-1}. HRMS (EI): Calcd. for $[C_{15}H_{12}O_3S]^+$: 272.0507, Found 272.0504.

4.2.17 S-(1-Phenylethynyl)-S-(3-chlorophenyl) sulfone (2p)

Yellow oil (71.9 mg, 52% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.06 (s, 1H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.52 (m, 5H), 7.39 (t, *J* = 7.5 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 143.5, 135.7, 134.5, 133.0, 132.0, 130.9, 128.9, 127.7, 125.7, 117.7, 94.5, 85.0 ppm. MS (EI): *m/z* (%) = 77.04 (20), 151.05 (26), 176.05 (100), 212.03 (72), 276.03 (57). IR (KBr): ν = 2179, 1681, 1575, 1338, 1165, 1118, 1078, 854, 794, 754, 680, 576 cm^{-1}. HRMS (EI): Calcd. for $[C_{14}H_9ClO_2S]^+$: 276.0012, Found 276.0018.

4.2.18 S-(1-Phenylethynyl)-S-(4-iodophenyl) sulfone (2q)

Yellow solid (110.5 mg, 60% yield). Melting point: 106-107 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.96 (d, *J* = 7.7 Hz, 2H), 7.78 (d, *J* = 7.5 Hz, 2H), 7.50 (m, 3H), 7.38 (t, *J* = 7.5 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 141.7, 138.9, 133.0, 131.9, 128.9, 128.9, 117.8, 102.4, 94.2, 85.2 ppm. MS (EI): *m/z* (%) = 77.04 (20), 176.04 (25), 250.85 (62), 303.92 (74), 367.86 (100). IR (KBr): ν = 2179, 1867, 1681, 1506, 1338, 1157, 1085, 1005, 850, 734, 659, 590, 536 cm^{-1}. HRMS (EI): Calcd. for $[C_{14}H_9IO_2S]^+$: 837.9368, Found 367.9375.

4.2.19 S-(1-Phenylethynyl)-S-(4-trifloromethylphenyl) sulfone (2r)

Yellow solid (74.5 mg, 48% yield). Melting point: 56-57 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.22 (d, *J* = 8.1 Hz, 2H), 7.87 (d, *J* = 8.1 Hz, 2H), 7.52 (m, 3H), 7.39 (t, *J* = 7.6 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 145.4, 135.9 (J_{C-F} = 33.3 Hz), 133.0, 132.1, 128.9, 128.2, 126.7 (J_{C-F} = 3.6 Hz), 123.2 (J_{C-F} = 271.5 Hz), 117.6, 95.1, 84.8 ppm. ^{19}F NMR (375 MHz, $CDCl_3$) δ = -63.24 ppm. MS (EI): *m/z* (%) = 77.04 (46), 89.03 (41), 105.03

(99), 145.02 (100), 246.02 (83), 309.98 (40). IR (KBr): ν = 2181, 1732, 1681, 1405, 1321, 1163, 1064, 852, 758, 715, 663, 591, 533, 431 cm^{-1}. HRMS (EI): Calcd. for $[C_{15}H_9F_3O_2S]^+$: 310.0275, Found 310.0277.

4.2.20 S-(1-Phenylethynyl)-S-(4-nitrophenyl) sulfone (2s)

Yellow solid (64.7 mg, 45% yield). Melting point: 120-121 °C. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.44 (d, *J* = 8.3 Hz, 2H), 8.28 (d, *J* = 8.3 Hz, 2H), 7.53 (m, 3H), 7.40 (t, *J* = 7.5 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 151.1, 147.3, 133.1, 132.3, 129.0, 129.0, 124.8, 117.3, 96.0, 84.5 ppm. MS (EI): *m/z* (%) = 77.04 (33), 89.03 (100), 165.06 (20), 176.05 (38), 193.05 (21), 223.04 (29), 286.97 (70). IR (KBr): ν = 2179, 1685, 1533, 1348, 1159, 1085, 848, 740, 685, 598, 532, 463 cm^{-1}. HRMS (EI): Calcd. for $[C_{14}H_9NO_4S]^+$: 287.0252, Found 287.0245.

4.2.21 S-(1-Phenylethynyl)-S-(2-naphthyl) sulfone (2t)

Yellow solid (105.2 mg, 72% yield). Melting point: 90-91 °C. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.65 (s, 1H), 8.04 (d, *J* = 7.4 Hz, 3H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.68 (m, 2H), 7.52 (d, *J* = 7.6 Hz, 2H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 138.8, 135.7, 132.9, 132.3, 131.7, 130.0, 129.8, 129.8, 129.4, 128.8, 128.2, 128.0, 122.3, 118.1, 93.9, 85.7 ppm. MS (EI): *m/z* (%) = 77.04 (20), 127.05 (30), 228.07 (100), 292.00 (27). IR (KBr): ν = 2360, 2177, 1843, 1716, 1648, 1543, 1508, 1338, 1155, 1070, 860, 812, 751, 680, 551, 434 cm^{-1}. HRMS (EI): Calcd. for $[C_{18}H_{12}O_2S]^+$: 292.0558, Found 292.0560.

4.2.22 S-(1-Phenylethynyl)-S-cyclopropyl sulfone (2u)

Brown oil (70.1 mg, 68% yield). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.59 (d, *J* = 7.6 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 2H), 2.89 – 2.74 (m, 1H), 1.52 – 1.41 (m, 2H), 1.18 (q, *J* = 6.4 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 132.9, 131.7, 128.9, 118.0, 91.3, 84.2, 35.3, 6.5 ppm. MS (EI): *m/z* (%) = 89.05 (28), 115.06 (26), 141.07 (100), 206.03 (70). IR (KBr): ν = 3057, 2183, 1681, 1488, 1445, 1330, 1143, 888, 850, 757, 713, 652, 547, 532 cm^{-1}. HRMS (EI): Calcd. for $[C_{11}H_{10}O_2S]^+$: 206.0402, Found 206.0399.

4.2.22 S-(1-Phenylbutynyl)-S-phenyl sulfone (2v)

Yellow solid (94.6 mg, 70% yield). Melting point: 54-55 °C. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.92 (d, *J* = 8.0 Hz, 1H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 1H), 7.27 (m, 2H), 7.19 (t, *J* = 8.0 Hz, 1H), 4.00 (s, 1H), 3.55 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 137.8, 135.7, 134.1, 129.1, 128.9, 128.6, 128.0, 126.9, 86.4, 69.9, 49.1, 25.2 ppm. MS (EI) *m/z* (%) = 77.04 (51), 117.17 (38), 125.00 (49), 129.30 (100), 165.06 (35), 205.25 (24), 270.35 (M^+, 45). **HRMS** (EI) Calcd. for $[C_{14}H_{10}O_2S]^+$: 270.3462, Found 270.3460.

4.2.23 P-(1-Phenylethynyl)-P,P-diethyl phosphonate (4a)

Colorless oil (108.4 mg, 91% yield). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.55 (d, *J* = 7.1 Hz, 2H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 7.4 Hz, 2H), 4.26 – 4.18 (m, 4H), 1.40 (t, *J* = 7.0 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 132.8, 132.7, 130.8, 128.7, 119.7, 119.6, 99.4, 98.9, 80.0, 77.0, 63.4, 63.3, 16.3, 16.2 ppm. ^{31}P NMR (160 MHz, $CDCl_3$) δ = -5.92 ppm. MS (EI): *m/z* = 89.1 (12), 102.1 (100), 165.0 (27), 182.0 (11), 195.0 (18), 210.0 (24), 238.1 (M^+, 16). IR (KBr): ν = 3058, 2986, 2934, 2908, 2187, 1489, 1444, 1390, 1265, 1163, 1024, 974, 857, 760, 690, 650 cm^{-1}. HRMS (EI): calcd. for $[C_{12}H_{15}O_3P]^+$: 238.0759, found 238.0753.

4.2.24 P-(1-p-Tolylethynyl)-P,P-diethyl phosphonate (4b)

Colorless oil (112.3 mg, 89% yield). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.44 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 4.25 – 4.16 (m, 4H), 2.37 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 141.5, 132.7, 132.7, 129.4, 116.5, 116.5, 100.1, 99.5, 79.3, 76.3, 63.3, 63.3, 21.8, 16.3, 16.2 ppm. ^{31}P NMR (160 MHz, $CDCl_3$) δ = -4.59 ppm. MS (EI): *m/z* = 103.1 (5), 116.1 (100), 179.1 (31), 196.1 (11), 209.1 (48), 224.1 (38), 237.1 (8), 252.1 (M^+, 46). IR (KBr): ν = 2985, 2934, 2905, 2184, 1508, 1266, 1158, 1023, 973, 863, 815, 788, 739, 608 cm^{-1}. HRMS (EI): calcd. for $[C_{13}H_{17}O_3P]^+$: 252.0915, found 252.0910.

4.2.25 P-(1-o-Tolylethynyl)-P,P-diethyl phosphonate (4c)

Colorless oil (107.2 mg, 85% yield). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.50 (d, *J* = 7.6 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 4.26 – 4.17 (m, 4H), 2.46 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 141.9, 141.9, 133.19, 133.16, 130.8, 129.9, 125.9, 119.5, 119.4, 104.2, 98.7, 98.2, 83.5, 80.5, 63.4, 63.3, 20.6, 16.3, 16.2 ppm. ^{31}P NMR (160 MHz, $CDCl_3$) δ = -5.87 ppm. MS (EI): *m/z* = 103.1 (10), 115.1 (100), 178.1(18), 196.1 (39), 224.1 (5), 252.1 (M^+, 45). IR (KBr): ν = 2985, 2938, 2911, 2182, 1480, 1453, 1388, 1265, 1161, 1024, 974, 868, 785, 762, 647 cm^{-1}. HRMS (EI): calcd. for $[C_{13}H_{17}O_3P]^+$: 252.0907, found 252.0910.

4.2.26 P-(1-(3,4-Dimethylphenyl)ethynyl)-P,P-diethyl phosphonate (4d)

Colorless oil (106.5 mg, 80% yield). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.32 (s, 1H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.11 (d, *J* = 7.8 Hz, 1H), 4.24 – 4.16 (m, 4H), 2.26 (s, 3H), 2.23 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 140.3, 137.2, 133.63, 133.60, 130.27, 130.25, 129.9, 116.7, 116.7, 100.4, 99.8, 78.9, 75.9, 63.31, 63.25, 20.1, 19.6, 16.24, 16.17 ppm. ^{31}P NMR (160 MHz, $CDCl_3$) δ = -4.48 ppm. MS (EI): *m/z* = 115.1 (39), 130.1 (100), 193.1 (10), 223.1 (29), 238.1 (17), 251.1 (4), 266.1 (M^+, 21). IR (KBr): ν = 2985, 2938, 2905, 2177, 1450, 1451, 1393, 1268, 1164, 1024, 972, 803, 624 cm^{-1}. HRMS (EI): calcd. for $[C_{14}H_{19}O_3P]^+$: 266.1072, found 266.1066.

4.2.27 P-(1-(4-Methoxyphenyl)ethynyl)-P,P-diethyl phosphonate (4e)

Colorless oil (105.9 mg, 79% yield). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.47 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.9 Hz, 2H), 4.23 – 4.13 (m, 4H), 3.80 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.5, 134.50, 134.48, 114.3, 111.4, 111.3, 100.2, 99.6, 78.7, 75.7, 63.23, 63.17, 55.5, 16.23, 16.16 ppm. ^{31}P NMR (160 MHz, $CDCl_3$) δ = -5.43 ppm. MS (EI): *m/z* = 107 (1), 119 (4), 132 (100), 195 (8), 225 (15), 240 (16), 268 (M^+, 19). IR (KBr): ν = 2982, 2938, 2905, 2182, 1603, 1509, 1295, 1257, 1172, 1024, 973, 866, 837, 787 cm^{-1}. HRMS (EI): calcd. for $[C_{13}H_{17}O_4P]^+$: 268.0864, found 268.0859.

4.2.28 P-(1-(2,5-Dimethoxyphenyl)ethynyl)-P,P-diethyl phosphonate (4f)

Bright yellow oil (111.9 mg, 75% yield). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.00 (d, *J* = 3.1 Hz, 1H), 6.95 (dd, *J* = 9.1, 3.1 Hz, 1H), 6.81 (d, *J* = 9.1 Hz, 1H), 4.27 – 4.18 (m, 4H), 3.81 (s, 3H), 3.75 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.23, 156.21, 153.1, 118.9, 118.48, 118.45, 112.3, 109.3, 109.2, 96.6, 96.1, 83.5, 80.6, 63.4, 63.3, 56.4, 56.0, 16.24, 16.17 ppm. ^{31}P NMR (160 MHz, $CDCl_3$) δ = -5.78 ppm. MS (EI): *m/z* = 147 (59), 161 (100), 224 (24), 242 (68), 270 (23), 283 (9), 298 (M^+, 77). IR (KBr): ν = 2985, 2938, 2905, 2837, 2181, 1501, 1463, 1267, 1234, 1166, 1024, 962, 804, 724, 662, 611 cm^{-1}. HRMS (EI): calcd. for $[C_{14}H_{19}O_5P]^+$: 298.0970, found 298.0965.

4.2.29 P-(1-(3,4-Methylenedioxyphenyl)ethynyl)-P,P-diethyl phosphonate (4g)

Colorless oil (98.8 mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.10 (d, *J* = 8.0 Hz, 1H), 6.95 (s, 1H), 6.77 (d, *J* = 8.1 Hz, 1H), 5.99 (s, 2H), 4.23 – 4.15 (m, 4H), 1.37 (t, *J* = 7.1 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 150.1, 147.7, 128.43, 128.41, 112.61, 112.55, 112.18, 112.16, 108.8, 101.9, 99.8, 99.3, 78.4, 75.4, 63.32, 63.27, 16.24, 16.17 ppm. ^{31}P NMR (160 MHz, $CDCl_3$) δ = -5.70 ppm. MS (EI): *m*/*z* = 133.1 (4), 146.1 (100), 209.0 (9), 239.0 (9), 254.1 (15), 282.1 (M^+, 39). IR (KBr): ν = 2986, 2907, 2179, 1604, 1505, 1489, 1443, 1339, 1253, 1207, 1131, 1101, 1029, 974, 822, 754, 664, 593 cm^{-1}. HRMS (EI): calcd. for $[C_{13}H_{15}O_5P]^+$: 282.0657, found 282.0652.

4.2.30 P-(1-(4-Fluorophenyl)ethynyl)-P,P-diethyl phosphonate (4h)

Colorless oil (99.8 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.54 (dd, *J* = 8.6, 5.4 Hz, 2H), 7.05 (t, *J* = 8.6 Hz, 2H), 4.25 – 4.15 (m, 4H), 1.38 (t, *J* = 7.1 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.2, 162.7, 135.04, 135.01, 134.95, 134.9, 116.3, 116.1, 115.84, 115.80, 115.78, 115.7, 98.3, 97.7, 79.9, 77.0, 63.4, 63.3, 16.24, 16.18 ppm. ^{19}F NMR (370 MHz, $CDCl_3$): δ = -122.2 (ppm) ^{31}P NMR (160 MHz, $CDCl_3$) δ = -6.18 ppm. MS (EI): *m*/*z* = 107.1 (15), 120.1 (100), 183.1 (20), 200.1 (7), 213.1 (16), 228.1 (16), 256.1 (M^+, 10). IR (KBr): ν = 2985, 2935, 2905, 2189, 1599, 1508, 1267, 1236, 1160, 1024, 975, 867, 843, 800, 742 cm^{-1}. HRMS (EI): calcd. for $[C_{12}H_{14}FO_3P]^+$: 256.0665, found 256.0659.

4.2.31 P-(1-(4-Chlorophenyl)ethynyl)-P,P-diethyl phosphonate (4i)

Colorless oil (109.1 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.47 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.3 Hz, 2H), 4.25 – 4.15 (m, 4H), 1.38 (t, *J* = 7.0 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 137.2, 133.92, 133.89, 130.9, 129.1, 118.1, 118.0, 98.0, 97.4, 81.0, 78.0, 63.44, 63.38, 16.24, 16.17 ppm. ^{31}P NMR (160 MHz, $CDCl_3$) δ = -5.31 ppm. MS (EI): *m*/*z* = 123.1 (10), 136.1 (100), 199.9 (19), 229.0 (20), 244.0 (18), 272.1 (M^+, 17). IR (KBr): ν = 2986, 2935, 2908, 2189, 1587, 1488, 1393, 1267, 1092, 1022, 975, 858, 832, 762, 701 cm^{-1}. HRMS (EI): calcd. for $[C_{12}H_{14}ClO_3P]^+$: 272.0369, found 272.0364.

4.2.32 P-(1-(4-Bromophenyl)ethynyl)-P,P-diethyl phosphonate (4j)

Bright yellow oil (120.5 mg, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.50 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 4.25 – 4.16 (m, 4H), 1.39 (t, *J* = 7.1 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 134.1, 134.0, 132.1, 125.6, 118.61, 118.56, 98.0, 97.5, 81.2, 78.2, 63.5, 63.4, 16.3, 16.2 ppm. ^{31}P NMR (160 MHz, $CDCl_3$) δ = -6.39 ppm. MS (EI): *m*/*z* = 101.1 (29), 169.0 (10), 180.0 (100), 260 (9), 273.0 (22), 290.1 (17), 316.1 (M^+, 16). IR (KBr): ν = 2985, 2938, 2905, 2187, 1483, 1391, 1265, 1164, 1025, 976, 857, 823, 761, 680 cm^{-1}. HRMS (EI): calcd. for $[C_{12}H_{14}BrO_3P]^+$: 315.9864, found 315.9858.

4.2.33 P-(1-(4-Iodophenyl)ethynyl)-diethyl phosphonate (4k)

Yellow solid (131.1 mg, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.70 (dd, *J* = 10.1, 8.4 Hz, 2H), 7.24 (dd, *J* = 11.3, 5.9 Hz, 2H), 4.23 – 4.13 (m, 4H), 1.37 (m, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 138.1, 138.0, 133.92, 133.90, 130.8, 119.1, 119.0, 98.2, 97.7, 81.4, 78.4, 63.5, 63.4, 16.3, 16.2 ppm. ^{31}P NMR (160 MHz, $CDCl_3$) δ = -5.30 ppm. MS (EI): *m*/*z* = 89.1 (11), 101.1 (32), 164.1 (6), 193.1 (4), 209.1 (15), 228.0 (100), 290.9 (16), 321.0 (20), 336.0 (25), 364.0 (M^+, 27). IR (KBr): ν = 2984, 2938, 2902, 2187, 1479, 1392, 1263, 1024, 975, 856, 820, 760, 668 cm^{-1}. HRMS (EI): calcd. for $[C_{12}H_{14}IO_3P]^+$: 363.9725, found 363.9720.

4.2.34 P-(1-Biphenylethynyl)-P,P-diethyl phosphonate (4l)

Colorless oil (122.6 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.64 – 7.55 (m, 6H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 1H), 4.28 – 4.19 (m, 4H), 1.41 (t, *J* = 7.1 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 143.5, 139.7, 133.2, 133.1, 129.0, 128.3, 127.3, 127.2, 118.3, 118.2, 99.4, 99.0, 80.5, 77.4, 63.4, 63.3, 16.3, 16.2 ppm. ^{31}P NMR (160 MHz, $CDCl_3$) δ = -5.93 ppm. MS (EI): *m*/*z* = 165.1(15), 178.1 (100), 241.1 (7), 271.1 (14), 286.1 (19), 314.2 (M^+, 38). IR (KBr): ν = 3036, 2982, 2938, 2908, 2184, 1485, 1265, 1023, 974, 861, 765, 695, 635 cm^{-1}. HRMS (EI): calcd. for $[C_{18}H_{19}O_3P]^+$: 314.1072, found 314.1066.

4.2.35 P-(1-(2-Naphthyl)ethynyl)-P,P-diethyl phosphonate (4m)

Colorless oil (122.5 mg, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.10 (s, 1H), 7.84 – 7.78 (m, 3H), 7.56 – 7.49 (m, 3H), 4.29 – 4.21 (m, 4H), 1.41 (t, *J* = 7.1 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 133.89, 133.86, 133.85, 132.5, 128.5, 128.1, 128.0, 127.94, 127.92, 127.89, 127.1, 116.73, 116.67, 99.8, 99.3, 80.0, 77.1, 63.4, 63.3, 16.3, 16.2 ppm. ^{31}P NMR (160 MHz, $CDCl_3$) δ = -5.94 ppm. MS (EI): *m*/*z* = 139.1(14), 152.1 (100), 215.1 (7), 245.1 (10), 260.1 (16), 288.1 (M^+, 34). IR (KBr): ν = 3057, 2985, 2932, 2908, 2185, 1266, 1159, 1024, 964, 905, 861, 792, 750, 632, 592 cm^{-1}. HRMS (EI): calcd. for $[C_{16}H_{17}O_3P]^+$: 288.0915, found 288.0910.

4.2.36 P-(1-(6-Methoxy-2-naphthalenyl)ethynyl)-P,P-diethyl phosphonate (4n)

Bright yellow oil (120.9 mg, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.02 (s, 1H), 7.68 (dd, *J* = 8.5, 5.1 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 1H), 7.16 (d, *J* = 9.0 Hz, 1H), 7.09 (s, 1H), 4.29 – 4.19 (m, 4H), 3.90 (s, 3H), 1.41 (t, *J* = 7.0 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.4, 135.5, 133.7, 133.6, 129.7, 128.7, 128.6, 128.0, 127.2, 120.1, 114.2, 114.1, 105.9, 100.5, 99.9, 79.4, 76.4, 63.34, 63.29, 55.5, 16.3, 16.2 ppm. ^{31}P NMR (160 MHz, $CDCl_3$) δ = -5.65 ppm. MS (EI): *m*/*z* = 139.1 (21), 182.1 (100), 244.1 (9), 275.1 (7), 290.1 (19), 318.1 (M^+, 61). IR (KBr): ν = 2985, 2935, 2905, 2179, 1625, 1480, 1391, 1263, 1262, 1162, 1024, 970, 941, 784, 703, 638 cm^{-1}. HRMS calcd. for $[C_{17}H_{19}O_4P]^+$: 318.1021, found 318.1015.

4.2.37 P-(1-(2-Furanyl)ethynyl)-P,P-diethyl phosphonate (4o)

Bright yellow oil (73.1 mg, 64% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.45 (d, *J* = 0.8 Hz, 1H), 6.85 (d, *J* = 3.5 Hz, 1H), 6.42 (dd, *J* = 3.4, 1.7 Hz, 1H), 4.23 – 4.14 (m, 4H), 1.36 (t, *J* = 7.1 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 145.9, 134.6, 134.5, 120.24, 120.22, 111.4, 88.9, 88.3, 85.1, 82.2, 63.6, 63.5, 16.2, 16.1 ppm. ^{31}P NMR (160 MHz, $CDCl_3$) δ = -6.79 ppm. MS (EI): *m*/*z* = 92.1 (100), 155.1 (15), 172.1 (7), 185.1 (17), 200.1 (8), 228.1 (M^+, 19). IR (KBr): ν = 3122, 2987, 2938, 2908, 2183, 1471, 1391, 1267, 1215, 1162, 1024, 977, 944, 811, 757 cm^{-1}. HRMS (EI): calcd. for $[C_{10}H_{13}O_4P]^+$: 228.0546, found 228.0546.

4.2.38 P-(1-(2-Thiophenyl)ethynyl)-P,P-diethyl phosphonate (4p)

Bright yellow oil (86.7 mg, 71% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.42 (d, *J* = 5.2 Hz, 2H), 7.01 (t, *J* = 4.3 Hz, 1H), 4.19 (m, 4H), 1.37 (t, *J* = 7.0 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 136.1, 136.0, 130.7, 127.5, 119.33, 119.27, 92.8, 92.3, 84.0, 81.0, 63.44, 63.38, 16.23, 16.16 ppm. ^{31}P NMR (160 MHz, $CDCl_3$) δ = -6.27 ppm. MS (EI): *m*/*z* = 95.1 (6), 108.1 (100), 171.0 (12), 201.0 (15), 216.1 (12), 244.1 (M^+, 13). IR (KBr): ν = 3077, 2986, 2938, 2908, 2174, 1263, 1174, 1023, 976,

852, 801, 715, 638 cm^{-1}. HRMS (EI): calcd. for $[C_{10}H_{13}O_3PS]^+$: 244.0319, found 244.0318.

4.2.39 P-(1-Phenylethynyl)-P,P-dimethyl phosphonate (4q)

Bright yellow oil (92.5 mg, 88% yield). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.54 (d, *J* = 7.5 Hz, 2H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 2H), 3.83 (d, *J* = 12.3 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 132.8, 132.7, 130.9, 128.7, 119.30, 119.28, 100.3, 99.8, 78.4, 75.4, 53.53, 53.47 ppm. ^{31}P NMR (160 MHz, $CDCl_3$) δ = -2.77 ppm. MS (EI): *m/z* = 89 (9), 102 (100), 115 (48), 179 (6), 195 (6), 210 (M^+, 22). IR (KBr): ν = 3063, 3000, 2956, 2852, 2187, 1492, 1450, 1271, 1179, 1033, 861, 840, 765, 689, 647 cm^{-1}. HRMS (EI) calcd. for $[C_{10}H_{11}O_3P]^+$: 210.0448, found 210.0440.

4.2.40 P-(1-Phenylethynyl)-P,P-diisopropyl phosphonate (4r)

Bright yellow oil (118.5 mg, 89% yield). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.51 (d, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 2H), 4.84 – 4.71 (m, 2H), 1.37 (d, *J* = 6.1 Hz, 12H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 132.53, 132.50, 130.6, 128.6, 119.9, 119.8, 98.4, 97.9, 81.4, 78.4, 72.40, 72.35, 24.0, 23.9, 23.7, 23.6 ppm. ^{31}P NMR (160 MHz, $CDCl_3$) δ = -8.60 ppm. MS (EI): *m/z* = 89 (17), 102 (100), 165 (55), 183 (78), 209 (80), 225 (69), 266 (M^+, 3). IR (KBr): ν = 3063, 3000, 2956, 2852, 2187, 1492, 1450, 1271, 1179, 1033, 861, 840, 765, 689, 647 cm^{-1}. HRMS (EI) calcd. for $[C_{14}H_{19}O_3P]^+$: 266.1061, found 266.1066.

4.2.41 P-(1-Phenylethynyl)-P,P-dibutyl phosphonate (4s)

Bright yellow oil (1127.7 mg, 80% yield). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.53 (d, *J* = 7.1 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 2H), 4.13 (dd, *J* = 14.2, 6.7 Hz, 4H), 1.74 – 1.65 (m, 4H), 1.48 – 1.38 (m, 4H), 0.92 (t, *J* = 7.4 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 132.7, 132.6, 130.7, 128.6, 119.7, 119.6, 99.4, 98.8, 79.9, 76.9, 70.0, 66.9, 32.3, 32.2, 18.8, 13.6 ppm. ^{31}P NMR (160 MHz, $CDCl_3$) δ = -5.60 ppm. MS (EI): *m/z* = 89 (6), 102 (36), 165 (30), 183 (100), 209 (7), 223 (6), 239 (27), 294 (M^+, 1.5). IR (KBr): ν = 2961, 2935, 2869, 2187, 1465, 1271, 1066, 1025, 992, 900, 858, 761, 695, 653 cm^{-1}. HRMS (EI) calcd. for $[C_{16}H_{23}O_3P]^+$: 294.1374, found 294.1379.

4.2.42 P-(2,2-Dimethylbutynyl)-P,P-diethyl phosphonate (4t)

Colorless oil (61.1 mg, 56% yield). ^1H NMR (400 MHz, $CDCl_3$) δ = 4.15 – 4.06 (m, 4H), 1.33 (t, *J* = 7.1 Hz, 6H), 1.25 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 110.6, 110.1, 70.3, 67.3, 63.0, 62.9, 29.98, 29.96, 28.1, 28.0, 16.2, 16.1 ppm. ^{31}P NMR (160 MHz, $CDCl_3$) δ = -5.65 ppm. MS (ESI) *m/z* (%): 218 (M^+, 100). IR (KBr) ν = 2976, 2935, 2908, 2873, 2215, 2181, 1455, 1392, 1368, 1261, 1164, 1099, 1027, 972, 792, 605 cm^{-1}. **HRMS** (ESI) calcd. for $[C_{10}H_{19}O_3P](M+H^+)$: 219.1072, found 219.1078.

Acknowledgments

The authors are grateful for the financial support from the National Natural Science Foundation of China (NSFC) (grant number 21806033), the Natural Science Foundation of Hunan Province (No. 2017JJ3027), the Fundamental Research Funds for Hunan University (No. 531107040840).

Supplementary Material

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.xx.

References

1. (a) Viehe, H. G. Chemistry of Acetylenes; Marcel Dekker: New York, 1969; Chapter 12, pp 861-912;
(b) Ficini, J. Tetrahedron 1976, 32, 448;
(c) Pitacco, G.; Valentin, E. Chemistry of Functional Groups; 1979; chapter 15, pp 623-714;
(d) Collard-Motte, J.; Janousek, Z. Top. Curr. Chem. 1986, 130, 89;
(e) Himbert, G. In Methoden Der Organischen Chemie (Houben-Weyl); Kropf, H., Schaumann, E., Eds.; Georg Thieme Verlag: Stuttgart, 1993; p 3267;
(f) Zificsak, C. A.; Mulder, J. A.; Rameshkumar, C.; Wei, L.-L.; Hsung, R. P. Tetrahedron 2001, 57, 7575;
(g) Chauvin, R.; Lepetit, C. Theoretical Studies on Acetylenic Scaffolds, Acetylene Chemistry-Chemistry, Biology and Material Science; Wiley-VCH, 2005.
(h) Iorga, B.; Eymery, F.; Carmichael, D.; Savignac, P. *Eur. J. Org. Chem*. **2000**, 3103;
(i) Lei, A.; Srivastava, M.; Zhang, X. *J. Org. Chem.* **2002**, *67*, 1969;
(j) Szafert, S.; Gladysz, J. A. *Chem. Rev.* **2006**, *106*, 1.
(k) Selling, H. A.; Tempel, A. *Pestic. Sci.* **1976**, *7*, 19.
(l) Cavallaro, V.; Moglie, Y. F.; Murray, A. P.; Radivoy, G. E., *Bioorg. Chem.* **2018**, *77*, 420.
(m) Lu, L.-H.; Wang, Z.; Xia, W.; Cheng, P.; Zhang, B.; Cao, Z.; He, W.-M. *Chin. Chem. Lett.* **2019,** , https://doi.org/10.1016/j.cclet.2019.04.033.
(n) Wang, Z.; Yang, L.; Liu, H. L; Tan, Y. Z.; Bao, W. H.; Wang, M.; Tang, Z. L.; He, W. M. *Chin. J. Org. Chem.* **2018**, *38*, 2639.
(o) Wu, C.; Xin, X.; Fu, Z.-M.; Xie, L.-Y.; Liu, K.-J.; Wang, Z.; Li, W.; Yuan, Z.-H.; He, W.-M. *Green Chem.* **2017**, *19*, 1983.
2. a) Couty, S.; Meyer, C.; Cossy, J. *Angew. Chem. Int. Ed.* **2006**, *45*, 6726;
(b) Tanaka, K.; Takeishi, K.; Noguchi, K. *J. Am. Chem. Soc.* **2006**, *128*, 4586;
(c) Ashburn, B. O.; Carter, R. G.; Zakharov, L. N. *J. Am. Chem. Soc.* **2007**, *129*, 9109;
(d) Nishida, G.; Noguchi, K.; Hirano, M.; Tanaka, K. *Angew. Chem. Int. Ed.* **2007**, *46*, 3951;
(e) Zhang, Y.; DeKorver, K. A.; Lohse, A. G.; Zhang, Y. S.; Huang, J.; Hsung, R. P. *Org. Lett.* **2009**, *11*, 899;
(f) Dooleweerdt, K.; Ruhland, T.; Skrydstrup, T. *Org. Lett.* **2009**, *11*, 221;
(g) Gourdet, B.; Lam, H. W. *J. Am. Chem. Soc.* **2009**, *131*, 3802;
(h) Kee, J. M.; Villani, B.; Carpenter, L. R.; Muir, T. W. *J. Am. Chem. Soc.* **2010**, *132*, 14327;
(i) Mo, J.; Kang, D.; Eom, D.; Kim, S. H.; Lee, P. H. *Org. Lett.* **2013**, *15*, 26;
(j) Huang, H.; He, G.; Zhu, G.; Zhu, X.; Qiu, S.; Zhu, H. *J. Org. Chem.* **2015**, *80*, 3480;
(k) Huang, H.; Zhu, X.; He, G.; Liu, Q.; Fan, J.; Zhu, H. *Org. Lett.* **2015**, *17*, 2510;
(l) Kim, J.; Stahl, S. S. *J. Org. Chem.* **2015**, *80*, 2448.
(m) Wu, C.; Lu, L.-H.; Peng, A.-Z.; Jia, G.-K.; Peng, C.; Cao, Z.; Tang, Z.; He, W.-M.; Xu, X. *Green Chem.* **2018**, *20*, 3683.
(n) Wu, C.; Xiao, H.-J.; Wang, S.-W.; Tang, M.-S.; Tang, Z.-L.; Xia, W.; Li, W.-F.; Cao, Z.; He, W.-M. *ACS Sustainable Chem. Eng.* **2019**, *7*, 2169.
(o) Lu, L.-H.; Zhou, S.-J.; Sun, M.; Chen, J.-L.; Xia, W.; Yu, X.; Xu, X.; He, W.-M. *ACS Sustainable Chem. Eng.* **2019**, *7*, 1574.
(p) Li, W.; Yin, G.; Huang, L.; Xiao, Y.; Fu, Z.; Xin, X.; Liu, F.; Li, Z.; He, W. *Green Chem.* **2016**, *18*, 4879.
(q) Wu, C.; Wang, Z.; Hu, Z.; Zeng, F.; Zhang, X.-Y.; Cao, Z.; Tang, Z.; He, W.-M.; Xu, X.-H. *Org. Biomol. Chem.* **2018**, *16*, 3177.
(r) Wu, C.; Yang, P.; Fu, Z.; Peng, Y.; Wang, X.; Zhang, Z.; Liu, F.; Li, W.; Li, Z.; He, W. *J. Org. Chem.* **2016**, *81*, 10664.
3. (a) Hamada, T.; Ye, X.; Stahl, S. S. *J. Am. Chem. Soc.* **2008**, *130*, 833;
(b) Gao, Y.; Wang, G.; Chen, L.; Xu, P.; Zhao, Y.; Zhou, Y.; Han, L. B. *J. Am. Chem. Soc.* **2009**, *131*, 7956 and the references cited therein;
(c) Wang, L.; Huang, H.; Priebbenow, D. L.; Pan, F. F.; Bolm, C. *Angew. Chem. Int. Ed.* **2013**, *52*, 3478;
(d) Liu, L.; Wu, Y.; Wang, Z.; Zhu, J.; Zhao, Y. *J. Org. Chem.* **2014**, *79*, 6816; (e) Nandi, G. C.; Kota, S. R.; Naicker, T.; Govender, T.; Kruger, H. G.; Arvidsson, P. I. *Eur. J. Org. Chem.* **2015**, 2861;

(4) (a) Zhang, Y.; Hsung, R. P.; Tracey, M. R.; Kurtz, K. C.; Vera, E. L. *Org. Lett.* **2004**, *6*, 1151;
(b) Laroche, C.; Li, J.; Freyer, M. W.; Kerwin, S. M. *J. Org. Chem.* **2008**, *73*, 6462;
(c) Yao, B.; Liang, Z.; Niu, T.; Zhang, Y. *J. Org. Chem.* **2009**, *74*, 4630;
(d) Burley, G. A.; Davies, D. L.; Griffith, G. A.; Lee, M.; Singh, K. *J. Org. Chem.* **2010**, *75*, 980;
(e) Chen, X. Y.; Wang, L.; Frings, M.; Bolm, C. *Org. Lett.* **2014**, *16*, 3796;
(5) (a) Jia, W.; Jiao, N. *Org. Lett.* **2010,** *12*, 2000;
(b) Priebbenow, D. L.; Becker, P.; Bolm, C. *Org. Lett.* **2013**, *15*, 6155;
(c) Li, X.; Yang, F.; Wu, Y.; Wu, Y. *Org. Lett.* **2014**, *16*, 992.
(6) (a) Lera, M.; Hayes, C. J. *Org. Lett.* **2000**, *2*, 3873;
(b) Berciano, B. P.; Lebrequier, S.; Besselievre, F.; Piguel, S. *Org. Lett.* **2010**, *12*, 4038;
(c) Das, B.; Salvanna, N.; Reddy, G. C.; Balasubramanyam, P. *Tetrahedron Lett.* **2011**, *52*, 6497.
(7) (a) Lodaya, J. S.; Koser, G. F. *J. Org. Chem.* **1990**, *55*, 1513;
(b) Yatsumonji, Y.; Ogata, A.; Tsubouchi, A.; Takeda, T. *Tetrahedron Lett.* **2008**, *49*, 2265;
(c) Jouvin, K.; Couty, F.; Evano, G. *Org. Lett.* **2010**, *12*, 3272;
(d) Jouvin, K.; Veillard, R.; Theunissen, C.; Alayrac, C.; Gaumont, A. C.; Evano, G. *Org. Lett.* **2013**, *15*, 4592.
(8) (a) David, W. M.; Kerwin, S. M. *J. Am. Chem. Soc.* **1997**, *119*, 1464;
(b) Wei, C. H.; Wu, C. E.; Huang, Y. L.; Kultyshev, R. G.; Hong, F. E. *Chem. Eur. J.* **2007**, *13*, 1583.
(9) Wang, Y.; Gan, J.; Liu, L.; Yuan, H.; Gao, Y.; Liu, Y.; Zhao, Y. *J. Org. Chem.* **2014**, *79*, 3678;
(10) Negishi, E.; King, A. O.; Klima, W. L.; Patterson, W.; Silveira, A. *J. Org. Chem.* **1980**, *45*, 2526.
(11) (a) Orita, A.; Yoshioka, N.; Struwe, P.; Braier, A.; Beckmann, A.; Otera, J. *Chem. Eur. J.* **1999**, *5*, 1355.
(b) Orita, A.; An, D. L.; Nakano, T.; Yaruva, J.; Ma, N.; Otera, J. *Chem. Eur. J.* **2002**, *8*, 2005.
(12) (a) Su, Q.; Zhao, Z.-J.; Xu, F.; Lou, P.-C.; Zhang, K.; Xie, D.-X.; Shi, L.; Cai, Q.-Y.; Peng, Z.-H.; An, D.-L. *Eur. J. Org. Chem.* **2013**, 1551.
(b) Su, Q.; Yan, H.; Gao, S.-C.; Xie, D.-X.; Cai, Q.-Y.; Shao, G.; Peng, Z.-H.; An, D.-L. *Synth. Commun.* **2013,** *43*, 2648;
(c) Zhu, Y.-X.; Zhao, Z.-J.; Zhang, Y.; Su, Q.; Peng, Z.-H.; An, D.-L. *Heteroat. Chem* **2015**, *26*, 35.
(13) Huang, H.; Mukaiyama, T.; Chem. Lett., 1984, 13 (8), 1465
(14) (a) Perrin, D. D.; Armarego, W. L. F.; In Purification of Laboratory Chemicals, 3rd ed.; Pergamon Press: New York, 1988.
(b) Cons, B. D.; Bunt A. J.; Bailey, C. D. and Willi L. *Org. Lett.*, **2013**, *15*, 2946