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PII: S0040-4020(18)31358-9

DOI: https://doi.org/10.1016/j.tet.2018.11.018

Reference: TET 29929

To appear in: *Tetrahedron*

Received Date: 16 September 2018

Revised Date: 7 November 2018

Accepted Date: 9 November 2018

Please cite this article as: Zhang G, Bai R-X, Li C-H, Feng C-G, Lin G-Q, Halogenation of 1,1-diarylethylenes by *N*-halosuccinimides, *Tetrahedron* (2018), doi: https://doi.org/10.1016/j.tet.2018.11.018.

Graphical Abstract

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Halogenation of 1,1-Diarylethylenes by *N*-Halosuccinimides

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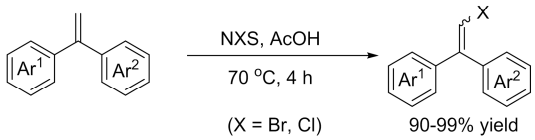
Ge Zhang[a,b] , Rui-Xue Bai [a], Chu-Han Li[a], Chen-Guo Feng[a,c,*], Guo-Qiang Lin[a,b]



- Excellent reaction yields and broad substrate scope
- Scalable reaction (up to 50 g strating material tested)
- Facile experimental operation

Tetrahedron
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Halogenation of 1,1-Diarylethylenes by *N*-Halosuccinimides

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ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

In memory of Professor Wei-Shan Zhou

Keywords:
vinyl halides
halogenation
N-halosuccinimide

ABSTRACT

An efficient method for the preparation of 2,2-diarylvinyl halides from the corresponding 1,1-diarylethylenes has been developed. *N*-Halosuccinimides (*N*-bromosuccinimide or *N*-chlorosuccinimide) were used as the halogenation reagents. The practicability of this method is highlighted by its simple operation, broad substrate scope and capability for large-scale reaction.

1. Introduction

2,2-Diarylvinyl moieties can be found in many organic molecules with wide applications in optical and electronic materials (Fig. 1).[1] Usually, these subunits were introduced by coupling reactions involving 2,2-diarylvinyl bromides or 2,2-diarylvinyl boronates.[1] As the vinyl boronates can be synthesized from the corresponding vinyl bromides, it is of greater importance for the efficient synthesis of 2,2-diarylvinyl bromides. However, only limited examples that scattered in the literatures have been reported, including Hunsdiecker type reaction with α,β-unsaturated acids,[2] $TiCl_4$-Mg promoted coupling of $CHBr_3$ with various aldehydes and ketones,[3] *N*-bromosuccinimide (NBS) promoted elimination and bromination of tertiary alcohols,[4] bromodephosphorylation of α,β-unsaturated phosphonic acid monoesters,[5] and bromination of 1,1-diarylethylenes.[6,7]

The bromination of 1,1-diarylethylenes is the most used method, and conventionally it relies on the use of toxic bromine. The development of more safer and convenient bromination procedure is attractive (Scheme 1a).[6] Recently, a single bromination example with sodium bromide and $PhI(OAc)_2$ was reported by Zhang, Shen, Zhou and co-workers (Scheme 1b).[7] NBS is a widely used bromination reagent and easy to handle. Stavber once proposed 1,1-diarylethylenes as possible intermediates in their NBS promoted preparation of 2,2-diarylvinyl bromides from tertiary alcohols, but they didn't test this hypothesis by experiment.[4] Herein, we reported the bromination and chlorination of 1,1-diarylethylenes by NBS and *N*-chlorosuccinimide (NCS) (Scheme 1c).

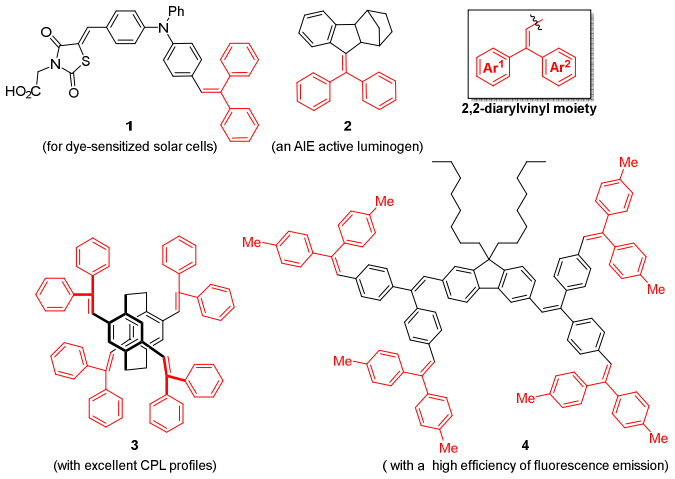
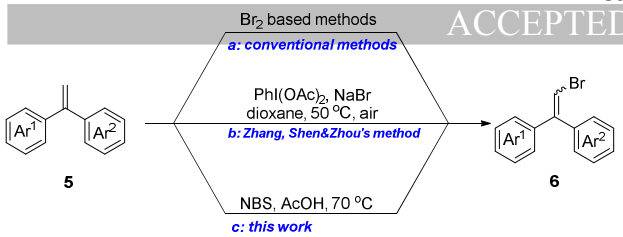


Fig. 1. Selected molecules bearing 2,2-diarylvinyl moieties in the research of optical and electronic materials

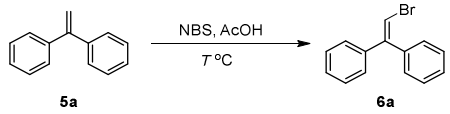


Scheme 1. Bromination of 1,1-diarylethylenes

2. Results and discussion

Initially, 1,1-diphenylethene **5a** and NBS were mixed and heated in AcOH at 110 °C. To our delight, the desired bromination product was obtained in 97% yield (Table 1, Entry 1). Attempts to decrease the reaction temperature have been made, and found that the reaction can run at lower reaction temperature, but an obvious loss in reaction yield took place below 70 °C (Entries 4 and 5). DBDMH is also competent bromination reagent, albeit in slightly reduced reaction yield.

Table 1
Temperature effect in the bromination of 1, 1-diphenylethene[a]



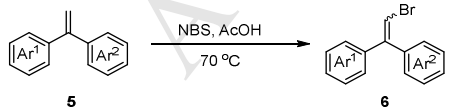
Entry	T (°C)	Yield (%)[b]
1	110	97
2	90	96
3	80	96
4	70	97
5	60	89
6	50	75
7[c]	70	90

[a] Reaction Conditions: 1,1-diarylethene **5a** (0.20 mmol), NBS (1.0 equiv), AcOH (2 mL), 4 h.

[b] Isolated yield.

[c] NBS was replaced by DBDMH (1,3-dibromo-5,5-dimethylhydantoin).

Table 2
Synthesis of 2,2-diarylvinyl bromides from 1, 1-diarylethenes[a]



Entry	Ar^1	Ar^2	Product	Yield[b]	Z/E isomer ratio[c]
1	Ph	Ph	**6a**	97	-
2	4-$MeOC_6H_4$	Ph	**6b**	91	1:1
3	4-PhC_6H_4	Ph	**6c**	99	2:1
4	4-ClC_6H_4	Ph	**6d**	99	1:1
5	4-$CF_3C_6H_4$	Ph	**6e**	95	3:2
6	3-ClC_6H_4	Ph	**6f**	93	1:1
7	3,4-$Me_2C_6H_3$	Ph	**6g**	96	1:1
8	2-MeC_6H_4	Ph	**6h**	94	4:1
9	2-FC_6H_4	Ph	**6i**	94	3:1
10	2-naphthyl	Ph	**6j**	99	3:2
11	4-MeC_6H_4	4-MeC_6H_4	**6k**	95	-
12	4-FC_6H_4	4-FC_6H_4	**6l**	98	-
13	4-ClC_6H_4	4-ClC_6H_4	**6m**	96	-
14	4-$CF_3C_6H_4$	4-$CF_3C_6H_4$	**6n**	90	-

[a] Reaction conditions: 1,1-diarylethenes **5** (0.2 mmol), NBS (1.0 equiv), AcOH (2 mL), 4 h.

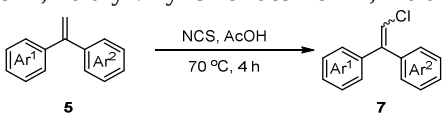
[b] Isolated yield.

[c] Determined by ^{1}H NMR analysis.

Having the optimized reaction conditions in hand, the substrate scope was then explored (Table 2). Excellent yields were observed when either electron-donating or –withdrawing groups were introduced to one of the phenyl rings at different positions. Normally, an 1:1 *E*/*Z* isomer ratio was obtained. While a *para*-CF_3 substitution gave a 3:2 isomer ratio (Entry 5), an *ortho*-methyl substitution afforded a 4:1 ratio (Entry 8), which shows the effect of the electronic and steric factors to this reaction. An equally high reaction yield was afforded by replacing the phenyl ring by a naphthyl group (Entry 10). Excellent yields were also observed when electron-donating or –withdrawing substitution was introduced to the both phenyl ring at the same time (Entries 11-14).

Encouraged by the success of the above bromination results, we decided to extend this system to the chlorination reaction. Although several methods have been reported for the preparation of 2,2-diarylvinyl chlorides,[8] a practical and facile protocol is still highly desirable. Replacing NBS by NCS, the corresponding chlorination product can be generated under the same reaction conditions. A variety of substrates with different substitutions on different positions were examined, and excellent reaction yields were obtained for all these tested examples (Table 3). Notably, heteroaryl group like 2-thienyl group was also well tolerated in this reaction (Entry 11), which may very useful in the material science. The effect of substation to the *E*/*Z* ratio shows a different trend compared to the bromination process. The steric factor seems to be diminished, which may be attributed to the smaller atomic radius of chlorine. Replacing NCS by DCDMH also generates the desired product in 91% yield (Entry 2).

Table 3
Synthesis of 1,1-diarylvinyl chlorides from 1, 1-diarylethenes[a]



Entry	Ar^1	Ar^2	Product	Yield[b]	Z/E isomer ratio[c]
1	Ph	Ph	**7a**	95	-
2[d]	Ph	Ph	**7a**	91	-
3	4-$MeOC_6H_4$	Ph	**7b**	93	5:4
4	4-MeC_6H_4	Ph	**7c**	97	3:2
5	4-PhC_6H_4	Ph	**7d**	98	1:1

6	4-ClC_6H_4	Ph	**7e**	97	1:1
7	2-FC_6H_4	Ph	**7f**	92	3:1
8	3-ClC_6H_4	Ph	**7g**	96	3:2
9	3,4-$Me_2C_6H_3$	Ph	**7h**	99	1:1
10	2-MeC_6H_4	Ph	**7i**	90	2:1
11	2-naphthyl	Ph	**7j**	94	1:1
12	2-thienyl	Ph	**7k**	91	1:1
13	4-MeC_6H_4	4-MeC_6H_4	**7l**	98	-
14	4-FC_6H_4	4-FC_6H_4	**7m**	93	-
15	4-ClC_6H_4	4-ClC_6H_4	**7n**	94	-

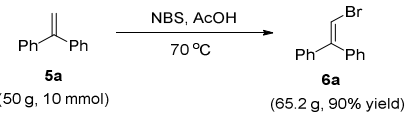
[a] Reaction conditions: 1,1-diarylethene **5** (0.2 mmol), NCS (1.0 equiv), AcOH (2 mL), 4 h.

[b] Isolated yield.

[c] Determined by ^{1}H NMR analysis.

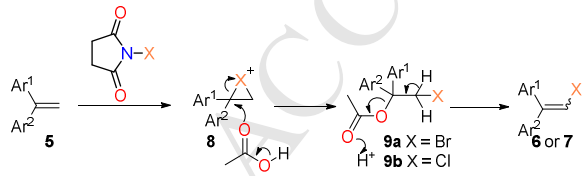
[d] NBS was replaced by DCDMH(1,3-Dichloro-5,5-dimethylhydantoin).

To demonstrate the practicability of this reaction, a 50-gram-scale reaction was carried out (Scheme 2). The reaction proceeded very well, albeit in a slightly reduced reaction yield compared with the small-scale reaction.



Scheme 2. A scaled-up reaction with 50 grams starting material

A plausible reaction pathway was proposed (Scheme 3). The halonium ion **8** was first generated by the treatment of *N*-halosuccinimides (NXS), and followed by a regioselective addition of acetic acid to give compound **9**. In the presence of acid, the acetoxy group can be easily cleaved to produce carbocation intermediates, and then trigger the elimination of α-hydrogen to give product **6** or **7**. These two steps were assumed to proceed in a concerted pattern, which will require a proper molecular configuration and are in accordance with the observation for the difference of *E*/*Z* ratio with NBS and NCX. To our delight, the intermediate **9a** was observed when alkene **5** was treated by NBS at room temperature, which offers a strong evidence for the proposed mechanism.[9,10]



Scheme 3. Proposed Reaction Pathway

3. Conclusion

In conclusion, the halogenation of 1,1-diarylethylenes by *N*-halosuccinimides has been developed for the efficient synthesis of 2,2-diarylvinyl bromides or chlorides.[11] Excellent reaction yields and broad substrate scope were observed. The practicability of this protocol is also demonstrated by a 50-gram-scale reaction. A possible reaction mechanism was demonstrated and the key intermediate was identified.

4. Experimental section

4.1. General

Commercially available NBS, NCS, DBDMH and DCDMH were used as received. 1,1-Diarylethenes **5** were synthesized from commercially available 1,1-diarylmethanone by Wittig reactions (see Supplementary Material for details). Chromatography was performed on silica gel 300-400 mesh. ^{1}H and ^{13}C NMR spectra were recorded on a Brüker Avance-400 HD spectrometer at ambient temperature. High-resolution mass spectra were determined on a JMS-HX 110 spectrometer.

4.2. Typical procedure for the synthesis of 6 and 7

To a suspension of 1, 1-diphenylethene **5** (0.20 mmol) in AcOH (2 mL) was added NBS (0.2 mmol, 35 mg) or NCS (0.2 mmol, 27 mg). The resulting mixture was stirred at 70 ℃ for 4 h. After cooling down to room temperature naturally, the reaction was neutralized by slowly adding NaOH/$NaHCO_3$ (1:1) and extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel flash chromatography (petroleum ether/EtOAc = 100:1) to afford the corresponding 2,2-diarylvinyl bromides **6** or 2,2-diarylvinyl chlorides **7**.

*4.2.1. (2-bromoethene-1,1-diyl)dibenzene (**6a**)*

White solid; 50 mg, yield 97%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.32 (m, 8H), 7.23-7.17 (m, 2H), 6.77 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.81, 140.68, 139.04, 129.63, 128.40, 128.20, 128.08, 127.95, 127.59, 105.17; HRMS (EI): m/z calcd for $C_{14}H_{11}Br$: 258.0044; found: 258.0054.

*4.2.2. 1-(2-bromo-1-phenylvinyl)-4-methoxybenzene (**6b**)*

Colorless oil; 52 mg, yield 91%; Z/E isomer ratio: 1:1; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.39-7.35 (m, 1.5H), 7.30-7.19 (m, 4.5H), 7.14 (s, 0.5H), 7.12 (s, 0.5H), 6.93 (s, 0.5H), 6.91 (s, 0.5H), 6.82 (s, 0.5H), 6.80 (s, 0.5H), 6.68 (s, 0.5H), 6.67 (s, 0.5H), 3.83 (s, 1.5H), 3.78 (s, 1.5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.56, 159.21, 146.37, 146.29, 141.16, 139.30, 133.33, 131.25, 131.06, 129.64, 128.79, 128.36, 128.18, 128.05, 127.89, 127.78, 113.77, 113.52, 104.43, 103.34, 55.29, 55.22; HRMS (EI): m/z calcd for $C_{15}H_{13}OBr$: 288.0150; found: 288.0156.

*4.2.3. 4-(2-bromo-1-phenylvinyl)-1,1'-biphenyl (**6c**)*

White solid; 66 mg, yield 99%; Z/E isomer ratio: 2:1; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.66-7.60 (m, 1.33H), 7.57-7.50 (m, 4H), 7.44 -7.21 (m, 8.67H), 6.82 (s, 0.66H), 6.77 (s, 0.33H); 13C NMR (100 MHz,$CDCl_3$) δ 146.41, 140.88, 140.70, 140.33, 139.53, 138.99, 130.15, 129.66, 129.24, 128.79, 128.76, 128.43, 128.35, 128.26, 128.15, 128.00, 127.94, 127.74, 127.48, 127.41, 127.07, 127.01, 126.94, 126.84, 105.22 HRMS (EI): m/z calcd for $C_{20}H_{15}Br$: 334.0357; found: 334.0363.

*4.2.4. 1-(2-bromo-1-phenylvinyl)-4-chlorobenzene (**6d**)*

Colorless oil; 58 mg, yield 99%; Z/E isomer ratio: 1:1; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.37-7.35 (m, 2H), 7.30-7.28 (m, 5H), 7.17 (m, 1H), 7.12 (m, 1H), 6.76 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.74, 145.73, 140.32, 139.16, 138.61, 137.41, 134.11, 133.92, 131.13, 129.59, 128.85, 128.62, 128.53, 128.35, 128.20, 127.60, 105.69, 105.65; HRMS (EI): m/z calcd for $C_{14}H_{10}ClBr$: 291.9654; found: 291.9640.

*4.2.5. 1-(2-bromo-1-phenylvinyl)-4-(trifluoromethyl)benzene (**6e**)*

White solid; 62 mg, yield 95%; Z/E isomer ratio: 3:2; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.68 (s, 0.6H), 7.66 (s, 0.6H), 7.56 (s, 0.4H), 7.54 (s, 0.4H), 7.44-7.41 (m, 2.4H), 7.33-7.28 (m, 3.4H), 7.22-7.09 (m, 1.2H), 6.87 (s, 0.4H), 6.84 (s, 0.6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.73, 144.09, 142.73, 139.93, 138.30, 130.11, 129.56, 128.61, 128.47, 128.44, 128.35, 127.86, 127.52, 125.43, 125.39, 125.30, 125.27, 107.32, 106.28; HRMS (EI): m/z calcd for $C_{15}H_{10}F_3Br$: 325.9918; found: 325.9929.

*4.2.6. 1-(2-bromo-1-phenylvinyl)-3-chlorobenzene (**6f**)*

Colorless oil; 54 mg, yield 93%; Z/E isomer ratio: 1:1; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.41-7.17 (m, 8.5H), 7.08 (d, *J* = 7.6 Hz, 0.5H), 6.79 (s, 0.5H), 6.79 (s, 0.5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.66, 145.64, 142.43, 140.78, 140.04, 138.37, 134.40, 134.14, 129.65, 129.62, 129.56, 128.55, 128.37, 128.36, 128.24, 128.15, 127.92, 127.62, 127.52, 125.77, 112.49, 106.49, 106.03; EI-MS (m/z, %): 169 (M^+, 55.27), 178 (100), 292 (42.34), 213 (40.21); HRMS (EI): m/z calcd for $C_{15}H_{10}ClBr$: 291.9666; found: 291.9660.

*4.2.7. 4-(2-bromo-1-phenylvinyl)-1,2-dimethylbenzene (**6g**)*

Colorless oil; 55 mg, yield 96%; Z/E isomer ratio: 1:1; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.41-7.34 (m, 1.5H), 7.32-7.25 (m, 2.5H), 7.19-7.23 (m, 1H), 7.16 (d, *J* = 8.2 Hz, 0.5H), 7.03-7.06 (m, 1.5H), 6.98 (s, 0.5H), 6.94-6.90 (m, 0.5H), 6.71 (d, *J* = 1.0 Hz, 1H), 2.29 (s, 1.5H), 2.26 (s, 1.5H), 2.23 (s, 1.5H), 2.21 (s, 1.5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.87, 146.78, 141.00, 139.26, 138.34, 136.73, 136.58, 136.48, 136.39, 130.62, 129.63, 129.42, 128.71, 128.66, 128.32, 128.25, 128.12, 127.96, 127.81, 127.64, 127.11, 125.12, 104.63, 104.16, 19.78, 19.75, 19.65, 19.48; HRMS (EI): m/z calcd for $C_{16}H_{15}Br$: 286.0357; found: 286.0362.

*4.2.8. 1-(2-bromo-1-phenylvinyl)-2-methylbenzene (**6h**)*

Colorless oil; 51 mg, yield 94%; Z/E isomer ratio: 4:1; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.29-7.18 (m, 8H), 7.12-7.15 (m, 1H), 6.92 (s, 0.8H), 6.46 (s, 0.2H), 2.13 (s, 2.4H), 2.03 (s, 0.6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ146.45, 146.19, 141.08, 139.08, 138.77, 138.34, 136.33, 135.99, 130.52, 130.27, 130.06, 129.34, 129.24, 128.60, 128.21, 128.05, 127.94, 127.90, 126.50, 125.89, 125.79, 106.55, 105.43, 20.19, 19.42; HRMS (EI): m/z calcd for $C_{15}H_{13}Br$: 272.0201; found: 272.0194.

*4.2.9. 1-(2-bromo-1-phenylvinyl)-2-fluorobenzene (**6i**)*

Colorless oil; 51 mg, yield 94%; Z/E isomer ratio: 3:1; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.38-7.11 (m, 9H), 6.93 (s, 0.75H), 6.80 (s, 0.25H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.01, 160.64, 158.53, 158.17, 141.62, 140.86, 139.21, 138.70, 131.42, 131.38, 131.11, 131.07, 131.04, 130.10, 130.02, 129.75, 129.66, 129.12, 128.56, 128.43, 128.32, 128.24, 128.13, 127.99, 126.84, 126.65, 124.17, 124.09, 124.05, 124.00, 116.18, 116.06, 115.96, 115.84, 108.52, 108.46, 108.09; ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.27, -113.61; EI-MS (m/z, %): 276 (M^+, 74.43), 197 (100), 196 (84.29), 276 (74.43); HRMS (EI): m/z calcd for $C_{14}H_{10}FBr$: 275.9950; found: 275.9942.

*4.2.10. 2-(2-bromo-1-phenylvinyl)naphthalene (**6j**)*

White solid; 61 mg, yield 99%; Z/E isomer ratio: 3:2; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.80 (m, 3.8H), 7.63 (s, 0.6H), 7.56-7.20 (m, 7.6H), 6.90 (s, 0.6H), 6.85 (s, 0.4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.80, 140.71, 139.00, 138.04, 136.48, 133.17, 133.09, 132.92, 132.86, 129.76, 129.03, 128.45, 128.28, 128.22, 128.17, 128.06, 128.03, 127.84, 127.73, 127.58, 127.40, 127.01, 126.43, 126.37, 126.19, 125.24, 105.60, 105.49; HRMS (EI): m/z calcd for $C_{18}H_{13}Br$: 308.0201; found: 308.0207.

*4.2.11. 4,4'-(2-bromoethene-1,1-diyl)bis(methylbenzene) (**6k**)*

White solid; 54 mg, yield 95%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.19 (s, 4H), 7.09 (s, 4H), 6.68 (s, 1H), 2.38 (s, 3H), 2.32 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.6, 138.2, 138.0, 137.7, 136.2, 129.6, 129.7, 128.9, 127.6, 103.9, 21.4, 21.2; HRMS (EI): m/z calcd for $C_{16}H_{15}Br$: 286.0357; found: 286.0364.

*4.2.12. 4,4'-(2-bromoethene-1,1-diyl)bis(fluorobenzene) (**6l**)*

White solid; 58 mg, yield 98%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.30-7.26 (m, 2H), 7.17 (m, 2H), 7.09 (m, 2H), 6.99 (m, 2H), 6.71 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.92, 163.60, 161.45, 161.14, 144.87, 136.71, 134.68, 131.52, 131.44, 129.33, 129.25, 115.56, 115.47, 115.35, 115.25, 105.16; GC-MS(EI) (m/z, %): 294 (M^+); HRMS (EI): m/z calcd for $C_{14}H_9F_2Br$: 293.9856; found: 293.9861.

*4.2.13. 4,4'-(2-bromoethene-1,1-diyl)bis(chlorobenzene) (**6m**)*

White solid; 62 mg, yield 96%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.38 (d, *J* = 8.6 Hz, 2H), 7.2-7.22 (m, 4H), 7.12 (d, *J* = 8.6 Hz, 2H), 6.77 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.69, 138.74, 136.93, 134.35, 134.16, 131.04, 128.81, 128.73, 128.65, 106.14; HRMS (EI): m/z calcd for $C_{14}H_9Cl_2Br$: 325.9265; found: 325.9268.

*4.2.14. 4,4'-(2-bromoethene-1,1-diyl)bis((trifluoromethyl)benzene) (**6n**)*

White solid; 70.9 mg, yield 90%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.1 Hz, 2H), 7.58 (d, *J* = 7.9 Hz, 2H), 7.43 (d, *J* = 7.9 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 6.96 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.64, 143.27, 141.93, 130.61, 130.29, 130.06, 127.80, 125.65, 125.62, 125.55, 125.51, 122.55, 108.52; HRMS (EI): m/z calcd for $C_{16}H_9F_6Br$: 393.9792; found: 393.9795.

*4.2.15. (2-chloroethene-1,1-diyl)dibenzene (**7a**)*

Yellow oil; 41 mg, yield 95%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.41-7.26 (m, 8H), 7.21-7.18 (m, 2H), 6.58 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.84, 140.09, 137.55, 129.83, 128.40, 128.18, 128.04, 127.94, 127.69, 115.85; EI-MS (m/z, %): 214 (M^+, 80.78), 178 (100), 179 (90.88), 214 (80.78); HRMS (EI): m/z calcd for $C_{14}H_{11}Cl$: 214.0549; found: 214.0545.

*4.2.16. 1-(2-chloro-1-phenylvinyl)-4-methoxybenzene (**7b**)*

Colorless oil; 45 mg, yield 93%; Z/E isomer ratio: 1:1;^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.39-7.24 (m, 5.5H), 7.24-7.17 (m, 1.1H), 7.12 (d, *J* = 8.8 Hz, 1.1H), 6.92 (d, *J* = 8.8 Hz, 1.1H), 6.82 (m, 1.2H), 6.50 (m, 1H), 3.83 (s, 1.5H), 3.78 (s, 1.5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.50, 159.15, 143.34, 143.30, 140.50, 137.76, 132.65, 131.21, 129.81, 129.74, 128.84, 128.34, 128.13, 127.99, 127.85, 115.06, 114.16, 113.75, 113.49, 55.26, 55.19; HRMS (EI): m/z calcd for $C_{14}H_{10}Cl_2$: 244.0655; found: 244.0653.

*4.2.17. (2-chloro-1-phenylvinyl)-4-methylbenzene (**7c**)*

Colorless oil; 44 mg, yield 97%; Z/E isomer ratio: 3:2; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.39-7.28 (m, 4H), 7.21 (m, 3H), 7.09 (m, 2H), 6.56 (s, 1H), 2.40 (s, 1.2H), 2.35 (s, 1.8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.57, 143.51, 140.14, 137.80, 137.80,

137.60, 137.52, 137.10, 129.66, 129.57, 128.92, 128.71, 128.18, 128.16, 128.01, 127.89, 127.78, 127.59, 115.48, 115.07, 21.16, 20.96; EI-MS (m/z, %): 228 (M^+, 94.28), 178 (100), 193 (33.26), 230 (31.28); HRMS (EI): m/z calcd for $C_{15}H_{13}Cl$: 228.0706; found: 228.0702.

*4.2.18. 4-(2-chloro-1-phenylvinyl)-1,1'-biphenyl (**7d**)*

White solid; 48 mg, yield 98%; Z/E isomer ratio: 1:1 ^1H NMR ($CDCl_3$, 400 MHz) δ 7.63-7.47 (m, 4H), 7.47-7.25 (m, 9H), 6.64 (s, 0.5H), 6.58 (s, 0.5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ143.45, 143.42, 140.82, 140.66, 140.56, 140.32, 140.12, 138.93, 137.44, 136.42, 130.32, 129.84, 128.78, 128.75, 128.41, 128.22, 128.09, 128.01, 127.98, 127.83, 127.45, 127.40, 127.05, 126.93, 126.81, 115.87, 115.85; EI-MS (m/z, %): 290 (M^+, 100), 292 (34.73), 252 (25.06), 253 (24.11); HRMS (EI): m/z calcd for $C_{20}H_{15}Cl$: 290.0862; found: 290.0860.

*4.2.19. 1-chloro-4-(2-chloro-1-phenylvinyl)benzene (**7e**)*

Colorless oil; 47 mg, yield 97%; Z/E isomer ratio: 1:1; ^1H NMR (400 MHz, $CDCl_3$) δ 7.41-7.35 (m, 2H), 7.33-7.24 (m, 5H), 7.19-7.12 (m, 2H), 6.59 (s, 0.5H), 6.58 (s, 0.5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.78, 142.76, 139.66, 138.54, 137.07, 135.89, 134.03, 133.86, 131.28, 129.76, 128.93, 128.60, 128.50, 128.47, 128.30, 128.27, 128.16, 127.68, 116.31, 116.30; HRMS (EI): m/z calcd for $C_{14}H_{10}Cl_2$: 244.0655; found: 244.0653.

*4.2.20. 1-(2-chloro-1-phenylvinyl)-2-fluorobenzene (**7f**)*

Colorless oil; 43 mg, yield 92%; Z/E isomer ratio: 3:1; ^1H NMR (400 MHz, $CDCl_3$) δ 7.39-6.99 (m, 9H), 6.93 (s, 0.75H), 6.80 (s, 0.25H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.23, 160.91, 158.75, 158.44, 138.54, 138.44, 137.90, 137.17, 131.56, 131.52, 131.22, 131.19, 130.09, 130.01, 129.71, 129.63, 129.24, 128.54, 128.18, 128.11, 127.96, 126.65, 125.18, 125.02, 124.06, 124.03, 118.97, 118.92, 118.50, 116.13, 116.01, 115.91, 115.80; GC-MS(EI) (m/z, %): 232 (M^+).

*4.2.21. 1-chloro-3-(2-chloro-1-phenylvinyl)benzene (**7g**)*

Colorless oil; 47 mg, yield 96%; Z/E isomer ratio: 1:1; ^1H NMR (400 MHz, $CDCl_3$) δ 7.42-7.05 (m, 9H), 6.61 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.70, 142.64, 141.85, 139.39, 139.26, 136.83, 134.37, 134.10, 129.82, 129.74, 129.62, 129.50, 128.54, 128.33, 128.31, 128.22, 128.12, 128.09, 127.70, 127.61, 125.86, 117.08, 116.70; HRMS (EI): m/z calcd for $C_{14}H_{10}Cl_2$: 244.0160; found: 244.0158.

*4.2.22. 4-(2-chloro-1-phenylvinyl)-1,2-dimethyl-benzene (**7h**)*

Colorless oil; 48 mg, yield 99%; Z/E isomer ratio: 3:2; ^1H NMR (400 MHz, $CDCl_3$) δ 7.42-7.25 (m, 5.4H), 7.24-7.12 (m, 1.6H), 7.09-7.02 (m, 1.8H), 7.0(s, 0.6H), 6.94-6.89 (m, 0.6H), 6.54 (s, 0.6H), 6.53 (s, 0.4H), 2.29 (s, 1.2H), 2.25 (s, 1.2H), 2.24 (s, 1.8H), 2.21 (s, 1.8H). HRMS (EI): m/z calcd for $C_{16}H_{15}Cl$: 242.0862; found: 242.0864.

*4.2.23. 1-(2-chloro-1-phenylvinyl)-2-methylbenzene (**7i**)*

Colorless oil; 41 mg, yield 90%; Z/E isomer ratio: 2:1; ^1H NMR (400 MHz, $CDCl_3$) δ 7.43-7.12 (m, 9H), 6.76 (s, 0.6H), 6.32 (s, 0.3H), 2.15 (s, 2H), 2.03 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.42, 143.06, 140.16, 138.52, 137.10, 136.72, 136.32, 130.49, 130.28, 130.25, 129.52, 129.32, 128.59, 128.20, 128.04, 128.00, 127.97, 127.84, 126.42, 125.87, 125.77, 116.85, 116.42, 20.17, 19.45; HRMS (EI): m/z calcd for $C_{15}H_{13}Cl$:228.0706; found: 228.0711.

*4.2.24. 2-(2-chloro-1-phenylvinyl)naphthalene (**7j**)*

White solid; 50 mg, yield 94%; Z/E isomer ratio: 1:1; ^1H NMR (400 MHz, $CDCl_3$) δ 7.81-7.73 (m, 4H), 7.64 (s, 0.5H), 7.53-7.21 (m, 7.5H), 6.73 (s, 0.5H), 6.68 (s, 0.5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.97, 143.78, 140.04, 137.44, 137.39, 134.94, 133.13, 133.04, 132.87, 132.81, 129.90, 129.20, 128.40, 128.21, 128.13, 128.09, 128.00, 127.75, 127.65, 127.52, 126.96, 126.40, 126.36, 126.32, 126.28, 126.22, 126.13, 125.33, 124.02, 116.23, 116.14; GC-MS(EI) (m/z, %): 264(M^+); HRMS (EI): m/z calcd for $C_{18}H_{13}Cl$: 264.0706; found: 264.0702.

*4.2.25. 2-(2-chloro-1-phenylvinyl)thiophene (**7k**)*

Colorless oil; 40 mg, yield 91%; Z/E isomer ratio: 1:1; ^1H NMR (400 MHz, $CDCl_3$) 7.46-7.30 (m, 5.5H), 7.21 (dd, *J* = 5.1, 0.9 Hz, 0.5H), 7.08 (dd, *J* = 3.7, 0.9 Hz, 0.5H), 7.02 (dd, *J* = 5.1, 3.7 Hz, 0.5H), 6.93 (dd, *J* = 5.1, 3.7 Hz, 0.5H), 6.74 (dd, *J* = 3.7, 0.9 Hz, 0.5H), 6.70 (s, 0.5H), 6.27 (s, 0.5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.07, 140.16, 139.29, 137.95, 137.17, 136.85, 130.08, 129.48, 129.20, 128.87, 128.32, 128.29, 128.27, 127.31, 127.16, 126.36, 126.21, 125.23, 114.89, 114.85; HRMS (EI): m/z calcd for $C_{12}H_9SCl$: 220.0113; found: 220.0105.

*4.2.26. 4,4'-(2-chloroethene-1,1-diyl)bis(methyl-benzene) (**7l**)*

Colorless oil; 47 mg, yield 98%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.20 (s, 4H), 7.09 (s, 4H), 6.51(s, 1H)2.37 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.58, 137.89, 137.67, 137.48, 134.71, 129.74, 129.04, 128.83, 127.61, 114.65, 21.33, 21.12; HRMS (EI): m/z calcd for $C_{16}H_{15}Cl$: 242.9862; found: 242.0867.

*4.2.27. 4,4'-(2-chloroethene-1,1-diyl)bis(fluoro-benzene) (**7m**)*

White solid; 47 mg, yield 93%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33-7.26 (m, 2H), 7.20-7.12 (m, 2H), 7.08 (t, *J* = 8.7 Hz, 2H), 6.99 (t, *J* = 8.7 Hz, 2H), 6.52(s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.90, 136.09, 136.06, 133.22, 133.18, 131.70, 131.62, 129.42, 129.34, 115.85, 115.56, 115.45, 115.35, 115.21; HRMS (EI): m/z calcd for $C_{14}H_9F_2Cl$: 250.0361; found: 250.0359.

*4.2.28. 4,4'-(2-chloroethene-1,1-diyl)bis(chloro-benzene) (**7n**)*

White solid; 53 mg, yield 94%; ^1H NMR (400 MHz, $CDCl_3$) 7.37 (d, *J* = 13.8 Hz, 2H), 7.26 (dd, *J* = 13.8, 8.5 Hz, 4H), 7.11 (d, *J* = 8.6 Hz, 2H), 6.58 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.73, 138.12, 135.43, 134.30, 134.12, 131.22, 128.92, 128.73, 128.60, 116.79; HRMS (EI): m/z calcd for $C_{14}H_9Cl_3$: 281.9770; found: 281.9772.

4.3. Procedure for 50-gram-scale synthesis of 6a

To a suspension of 1, 1-diphenylethene **5a** (50 g, 278 mmol) in AcOH (300 mL) was added NBS (50 g, 278 mmol). The resulting mixture was stirred at 70 ℃ for 4 h. After cooling down to room temperature naturally, the reaction was neutralized by slowly adding NaOH/$NaHCO_3$ (1:1) and extracted with EtOAc (3 × 200 mL). The combined organic layers were dried over $MgSO_4$, and concentrated under vacuum. The residue was purified by silica gel flash chromatography (petroleum ether/EtOAc = 100:1) to afford the vinyl bromide **6** (65.2 g, 90% yield).

5. Acknowledgments

This work was supported by the National Natural Science Foundation of China (21472212, 21772216), the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB 20020100), the 973 Program (2015CB856600) and The Key Research Program of Frontier Science (QYZDY-SSW-SLH026).

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10. Intermediate **9a** can be obtained by reaction of **5a** and NBS in acetic acid at rt. It is unstable and failed to be purified by silica gel flash chromatography, but can be determined by ^{1}H NMR and GC-MS analysis of the crude product. Heating **9a** in acetic acid can generate the bromination product **6a** in 90% yield.
11. NIS (*N*-iodosuccinimide) was also tested in this reaction, and the desired iodination product can be obtained in 21% yield (determined by NMR analysis) and confirmed by GC-MS. However, the obtained vinyl iodide is rather unstable in silica gel purification. See Supplementary Material for details.

Supplementary Material

Supplementary data associated with this article can be found, in t

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