Olefination of aromatic ketones: synthesis of mono- and dihaloalkenes

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A new simple and efficient transformation of various aromatic ketones to the corresponding halo (dihalo) alkenes is described. The reaction proceeds under mild conditions to give the target products in good yields.

Introduction

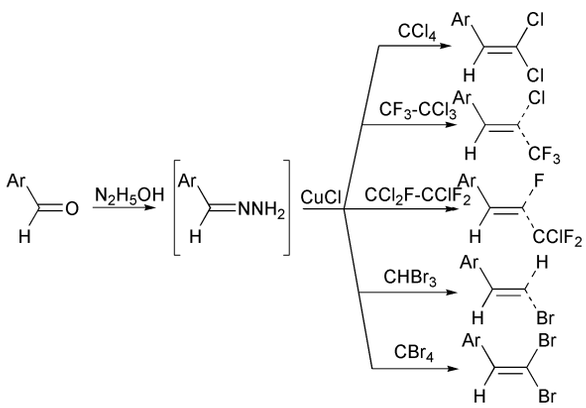
Olefination of carbonyl compounds, that is the $R^1R^2C{=}O$–$R^1R^2C{=}CXY$ transformation is one of the most successful synthetic routes to a wide variety of substituted alkenes.[1] Vinylic mono- ($R^1R^2C{=}CHHal$) and dihalides ($R^1R^2C{=}CHal_2$) have attracted increasing interest in modern organic chemistry as precursors of the corresponding carbenoids $R^1R^2C{=}CHalMet$ (Met = Li, ZnR_2Li, NiL_2Cl, Sm^{III}).[2] Such α-haloorganometallic compounds, possessing both electrophilic and nucleophilic reactivities, are versatile intermediates in C–C bond formation procedures.[3] It is well-known that the Wittig reaction and its modifications are the most common approaches for the synthesis of vinylic halides and dihalides from carbonyl precursors.[2a,b,4] Treatment of carbonyl compounds with trihalomethyllithiums is a key stage in an alternative three-step route to these types of alkenes.[5] However, the need to use equimolar amounts of PPh_3 and/or organometallic reagents is a significant disadvantage of these methods. This problem can be avoided by elaboration of new catalytic routes for the olefination of carbonyl compounds.

Recently we elaborated a novel catalytic, non-Wittig approach to the preparation of substituted alkenes from aldehydes.[6] The proposed approach is based on the new redox reaction between the hydrazones of aromatic and heteroaromatic aldehydes, $Ar(Het)(H)C{=}NNH_2$, and CCl_4 under copper catalysis. This reaction and its synthetic scope are now under intensive investigation in our group. We found that CCl_4,[6a–c] $CHBr_3$,[6d] CBr_4,[6e] and the freons CF_3CCl_3 and CF_2Cl–$CFCl_2$ [6f] can be utilized as C_1 and C_2 units respectively for the preparation of the corresponding haloalkenes in high yields (Scheme 1).

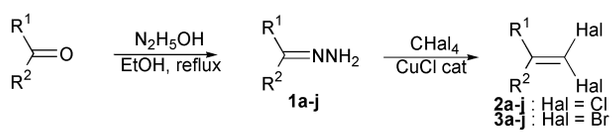
The proposed method represents a new general type of reaction for C=C bond formation. The aim of presented work is to extend the scope of the novel reaction to the olefination of ketones.

Results and discussion

Previously we found the optimal conditions for the reaction between hydrazones of aromatic aldehydes and CCl_4 (solvent, base, quantity and nature of the catalyst).[6b] The reaction proceeds smoothly in DMSO solution at room temperature in the presence of aqueous ammonia as a base and CuCl as a catalyst. Using the same conditions, hydrazones **1**, prepared from corresponding aromatic ketones, were treated with 3 mol equivalents of CCl_4 or CBr_4 in the presence of a copper catalyst (10 mol%). The transformation of **1** into 1,1-dichloroalk-1-enes **2** and 1,1-dibromoalk-1-enes **3**, respectively, takes place (Scheme 2).



Scheme 1



Scheme 2

We found that a wide range of aromatic ketones can be converted into alkenes **2** and **3** in good yields (Table 1). The yields of dibromoalkenes were generally higher than the yields of dichloroalkenes, probably because of the higher activity of CBr_4 in comparison with CCl_4.[7] We also investigated the kinetic features of reactions between hydrazones and polyhalogenoalkanes. It was found that their activity diminishes in order $CBr_4 \gg CCl_4 > CHBr_3$.[8]

It should be noted that the proposed olefination procedure is compatible with the presence of both electron-donating (MeO) and electron-withdrawing (NO_2, $MeSO_2$) groups in the aromatic ring. Hydrazones of cyclic compounds **1i** and **1j** and heterocyclic ketone **1g** can also be transformed into the target alkenes.

We also investigated the transformation of ketones into vinyl bromides using $CHBr_3$ as the olefinating agent (Scheme 3). It was demonstrated that the reaction proceeds similarly.

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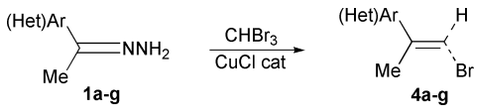


Scheme 3

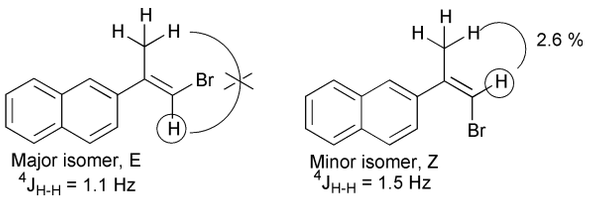
A wide range of hydrazones of aryl(hetaryl) methyl ketones (electron-rich and electron-poor) was converted into the monobromoalkenes **4** in good yields (Table 2).

The bromoalkenes **4** were obtained as a mixture of *E*- and *Z*-isomers (the *E*-isomer is formed predominantly). To determine the structure of isomers we performed NOE experiments on compound **4f** (Scheme 4). It was found that the major isomer has the *E*-configuration.

The structures of the other bromoalkenes can be unambiguously established from their ^{1}H NMR data. For all of the vinyl bromides the allylic ^4J value is larger in the *Z*-isomers of **4** ($^4J_{H-H}$ 1.5–1.7 Hz for the *Z*-isomers and $^4J_{H-H}$ 1.1–1.3 Hz for the *E*-isomers). The olefin proton (marked in Scheme 4) in the *E*-isomers is shifted downfield (0.2–0.4 ppm) compared with the chemical shift of this same proton in the *Z*-isomers.

Table 1 Synthesis of dichloroalkenes **2** and dibromoalkenes **3**

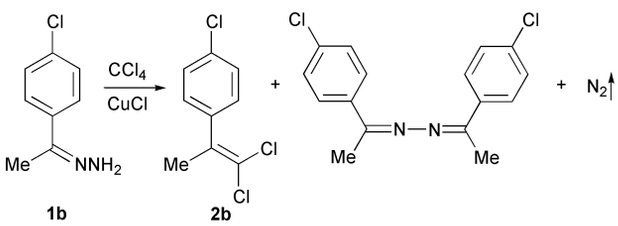
	Starting material		Product yield (%)	
Entry	R^1	R^2	**2**	**3**
1a	4-MeC_6H_4	Me	65	52
1b	4-ClC_6H_4	Me	82	75
1c	4-$MeOC_6H_4$	Me	70	92
1d	4-$O_2NC_6H_4$	Me	58	74
1e	4-$MeSO_2C_6H_4$	Me	33	45
1f	2-Naphthyl	Me	31	41
1g	2-Thienyl	Me	42	62
1h	Ph	Et	57	75
1i	–*o*-C_6H_4–$(CH_2)_2$–		45	51
1j	–*o*-C_6H_4–$(CH_2)_3$–		32	23



Scheme 4

Reaction mechanism

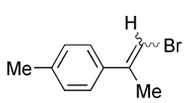
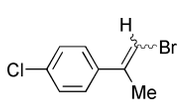
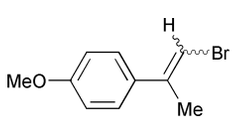
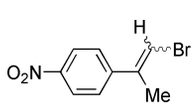
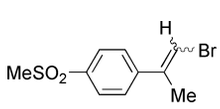
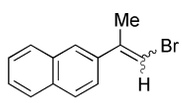
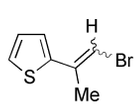
In order to elucidate the mechanistic aspects of the ketone olefination we studied the reaction between hydrazone **1b** and CCl_4 in more detail (Scheme 5). The target dichloroalkene **2b** (82%) and corresponding *sym*-azine of 4-chloroacetophenone (14%) were obtained in 96% total yield, accompanied by the evolution of dinitrogen.



Scheme 5

Mass spectrometric study of the reaction mixture confirmed these results. Dichloroalkene **2b** (*m*/*z* = 220) and azine (*m*/*z* = 304) were detected by GCMS of the reaction mixture

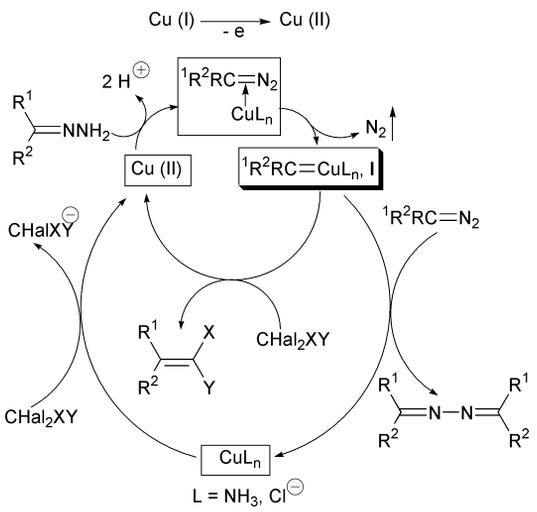
Table 2 Synthesis of bromoalkenes **4**

	Starting material	Product, **4**	Yield (%)	*E* : *Z* ratio [a]
1a			55	5 : 4
1b			73	4 : 3
1c			54	2 : 1
1d			47	5 : 4
1e			21	1 : 1
1f			39	3 : 1
1g			60	2 : 1

[a] Ratio *E* : *Z* of isomers was determined by ^{1}H NMR spectroscopy.

as the main reaction product (more than 90%). Traces of side products 4-chloroacetophenone (*m*/*z* = 154) and stilbene $ClC_6H_4(CH_3)C{=}C(CH_3)C_6H_4Cl$ (*m*/*z* = 276) were also observed.

Similar results were previously obtained in the reaction between hydrazones of aldehydes and polyhalogenoalkanes.[6] Therefore we believe that the proposed mechanism of olefination (ref. 6*f*) can be extended to the reaction of aromatic ketones. The catalytic cycle illustrating the reaction mechanism and formation of all of the reaction products is given in Scheme 6.



Scheme 6

In the initial step copper(I) is oxidized to copper(II) by CCl_4 in DMSO solution.[6] The Cu^{2+} species formed oxidizes hydrazones to the corresponding diazoalkanes. Earlier we postulated the copper–carbene complex **I** as a key intermediate of the olefination reaction.[6d,f] This complex is formed in the copper-catalysed decomposition of diazoalkane. Similar copper–carbene complexes are universally accepted as labile intermediates in the copper-catalysed decomposition of diazoalkanes and consequent carbene-transfer processes.[9]

Two possible routes for the further transformation of **I** are usually observed. Labile intermediate **I** reacts with a molecule of polyhaloalkane giving the target alkene with regeneration of copper(II) (the target route). A competitive reaction between **I** and another molecule of diazoalkane gives the corresponding *sym*-azine. Stilbene is likely formed by the coupling of two copper–carbene species in line with a similar reaction of Pt(0)– and Au(I)–carbene complexes.[10]

In conclusion, we have studied the catalytic transformation of ketones into mono- and dihalo-alkenes. The presented reaction proceeds under mild conditions using readily available reagents. The simplicity of the experimental technique and good yields of the target alkenes are the remarkable features of the method.

Experimental

General procedures

Melting points were determined in sealed capillaries and are uncorrected. NMR spectra were recorded on Varian VXR-400 and Bruker AM 400C spectrometers in $CDCl_3$ or DMSO-d_6 with TMS as an internal standard. *J* values are given in Hz. The IR spectra were obtained with a UR-20 spectrometer. Silica gel Merck 60 and Merck $60F_{254}$ plates were used for conventional and analytical (TLC) chromatography, respectively. Mass spectra were recorded on an HP5890 mass spectrometer (70 eV) with a 5989x-G detector.

Hydrazones of ketones **1a**,[11] **1b**,[11] **1c**,[12] **1d**,[13] **1f**,[14] **1g**,[15] **1h**,[16] **1i**[16] and **1j**[17] were prepared according to literature procedures.

1-[4-(Methylsulfonyl)phenyl]ethanone hydrazone 1e

1-[4-(Methylsulfonyl)phenyl]ethanone (9.90 g, 50 mmol) was dissolved in EtOH (100 cm^3) and added dropwise to a solution of 100% hydrazine hydrate (7.5 cm^3, 150 mmol) in EtOH (100 cm^3). The reaction mixture was refluxed (3 hours) and evaporated *in vacuo*. The residue of crude hydrazone was recrystallized from EtOH to give colourless crystals (8.30 g, 78%); mp 132–133 °C (from EtOH). Found: C, 51.14; H, 5.87. Calc. for $C_9H_{12}N_2O_2S$: C, 50.92; H, 5.70%; ν_{max}(Nujol)/cm^{-1} 1630 (C=N); δ_H (400 MHz; DMSO-d_6; Me_4Si) 2.14 (3 H, s, Me-C=N), 3.05 (3 H, s, $MeSO_2$), 5.62 (2 H, br s, NH_2), 7.82 (2 H, d, *J* 8.5, Ar), 7.89 (d, 2 H, *J* 8.5, Ar); δ_C (100 MHz; DMSO-d_6; Me_4Si) 11.11 (Me), 43.66 ($MeSO_2$), 125.06, 126.89, 138.41, 139.38, 144.58.

Preparation of halo (dihalo) alkenes

1,1-Dichloroalk-1-enes 2. A 25% aqueous solution of ammonia (3.33 cm^3) and freshly purified CuCl[18] (100 mg, 1 mmol) were added to a solution of freshly prepared hydrazone **1a**–**j** (10 mmol) in DMSO (10 cm^3). Then CCl_4 (2.89 cm^3, 30 mmol) was added dropwise over 10 min, maintaining the temperature at 20 °C (water bath). The reaction mixture was stirred for 24 h and quenched with water (300 cm^3). The reaction products were extracted with CH_2Cl_2 (50 cm^3 × 3). The extracts were dried over sodium sulfate, CH_2Cl_2 was evaporated and the residue was purified by column chromatography (eluents: hexane, CH_2Cl_2 or a mixture).

1,1-Dibromoalk-1-enes **3** and 1-bromoalk-1-enes **4** were prepared similarly by reaction of **1** with 3 mol equivalents of CBr_4 (9.95 g, 30 mmol) and $CHBr_3$ (2.62 cm^3, 30 mmol), respectively. CBr_4 was added to hydrazone **1** in DMSO (20 cm^3) solution.

The known compounds **2a**,[4b] **2b**,[4b] **2c**,[4b] **2d**,[19] **2f**,[20,21] **2g**,[4a] **2h**,[2b] **2i**,[21] **2j**,[21] **3g**,[21] **3h**,[5] **3j**,[2c] **4a**[2a] and **4b**[22] were identified by their ^1H NMR spectra and/or by comparison of the spectral data and physical constants with literature data.

1-(2,2-Dichloro-1-methylvinyl)-4-(methylsulfonyl)benzene 2e. Colourless crystals (0.88 g, 33%); mp 54–55 °C (from EtOH); R_f (CH_2Cl_2) 0.70. Found: C, 45.52; H, 3.66. Calc. for $C_{10}H_{10}Cl_2O_2S$: C, 45.30; H, 3.80%; ν_{max}(Nujol)/cm^{-1} 1610 (C=C); δ_H (400 MHz; $CDCl_3$; Me_4Si) 2.22 (3 H, s, Me), 3.09 (3 H, s, $MeSO_2$), 7.48 (2 H, d, *J* 8.5, Ar), 7.96 (2 H, d, *J* 8.5, Ar); δ_C (100 MHz; $CDCl_3$; Me_4Si) 22.64 (Me), 44.29 ($MeSO_2$), 118.67 (CCl_2), 127.41, 128.82, 134.01, 139.60, 145.46.

1-(2,2-Dibromo-1-methylvinyl)-4-methylbenzene 3a. Colourless oil (1.51 g, 52%); R_f (hexane) 0.65. Found: C, 41.25; H, 3.67. Calc. for $C_{10}H_{10}Br_2$: C, 41.42; H, 3.48%; ν_{max}(Nujol)/cm^{-1} 1605 (C=C); δ_H (400 MHz; $CDCl_3$; Me_4Si) 2.17 (3 H, s, *Me*-C=C), 2.33 (3 H, s, Me-Ar), 7.10 (2 H, d, *J* 8.2, Ar), 7.15 (2 H, d, *J* 8.2, Ar); δ_C (100 MHz; $CDCl_3$; Me_4Si) 21.24 (Me-Ar), 26.14 (*Me*-C=C), 87.24 (CBr_2), 127.28, 129.03, 137.49, 139.02, 143.00.

1-Chloro-4-(2,2-dibromo-1-methylvinyl)benzene 3b. Colourless oil (2.33 g, 75%); R_f (hexane) 0.65. Found: C, 35.12; H, 2.44. Calc. for $C_9H_7Br_2Cl$: C, 34.82; H, 2.27%; ν_{max}(Nujol)/cm^{-1} 1615 (C=C); δ_H (400 MHz; $CDCl_3$; Me_4Si) 2.17 (3 H, s, Me), 7.16 (2 H, d, *J* 8.8, Ar), 7.32 (2 H, d, *J* 8.8, Ar); δ_C (100 MHz; $CDCl_3$; Me_4Si) 25.98 (Me), 88.29 (CBr_2), 128.59, 128.83, 133.53, 140.21, 141.82.

1-(2,2-Dibromo-1-methylvinyl)-4-methoxybenzene 3c. Colourless crystals (2.82 g, 92%); mp 56–57 °C; R_f (hexane–CH_2Cl_2, 2 : 1) 0.70. Found: C, 39.28; H, 3.19. Calc. for $C_{10}H_{10}Br_2O$: C, 39.25; H, 3.29%; ν_{max}(Nujol)/cm^{-1} 1620 (C=C); δ_H (400 MHz; $CDCl_3$; Me_4Si) 2.15 (3 H, s, *Me*-C=C), 3.75 (3 H, s, MeO), 6.84

(2 H, d, *J* 8.2, Ar), 7.13 (2 H, d, *J* 8.2, Ar); δ_C (100 MHz; $CDCl_3$; Me_4Si) 26.07 (*Me*-C=C), 55.11 (MeO), 87.13 (CBr_2), 113.58, 128.66, 133.97, 142.53, 158.85.

1-(2,2-Dibromo-1-methylvinyl)-4-nitrobenzene 3d. Colourless crystals (2.38 g, 74%); mp 84–85 °C; R_f (hexane–CH_2Cl_2, 2 : 1) 0.70. Found: C, 33.43; H, 2.01. Calc. for $C_9H_7Br_2NO_2$: C, 33.68; H, 2.20%; ν_{max}(Nujol)/cm^{-1} 1600 (C=C); δ_H (400 MHz; $CDCl_3$; Me_4Si) 2.21 (3 H, s, Me), 7.40 (2 H, d, *J* 8.8, Ar), 8.21 (2 H, d, *J* 8.8, Ar); δ_C (100 MHz; $CDCl_3$; Me_4Si) 25.80 (Me), 89.47 (CBr_2), 123.67, 128.61, 141.17, 146.92, 148.30.

1-(2,2-Dibromo-1-methylvinyl)-4-(methylsulfonyl)benzene 3e. Colourless crystals (1.59 g, 45%); mp 100–101 °C (from EtOH); R_f (CH_2Cl_2) 0.70. Found: C, 34.17; H, 2.96. Calc. for $C_{10}H_{10}Br_2O_2S$: C, 33.92; H, 2.85%; ν_{max}(Nujol)/cm^{-1} 1600 (C=C); δ_H (400 MHz; $CDCl_3$; Me_4Si) 2.19 (3 H, s, Me), 3.07 (3 H, s, $MeSO_2$), 7.43 (2 H, d, *J* 8.8, Ar), 7.93 (2 H, d, *J* 8.8, Ar); δ_C (100 MHz; $CDCl_3$; Me_4Si) 25.79 (Me), 44.27 ($MeSO_2$), 89.18 (CBr_2), 127.48, 128.45, 139.54, 141.25, 147.35.

2-(2,2-Dibromo-1-methylvinyl)naphthalene 3f. Colourless oil (1.34 g, 41%); R_f (hexane) 0.60. Found: C, 48.14; H, 3.27. Calc. for $C_{13}H_{10}Br_2$: C, 47.89; H, 3.09%; ν_{max}(Nujol)/cm^{-1} 1600 (C=C); δ_H (400 MHz; $CDCl_3$; Me_4Si) 2.23 (Me), 7.28 (1 H, dd, *J* 8.5, *J* 1.8, Naphth), 7.42–7.45 (2 H, m, Naphth), 7.64 (1 H, d, *J* 1.8, Naphth), 7.74–7.79 (3 H, m, Naphth); δ_C (100 MHz; $CDCl_3$; Me_4Si) 26.25 (CH_3), 87.90 (CBr_2), 125.70, 126.62, 126.76, 126.79, 127.90, 128.24, 128.34, 132.52, 133.02, 139.22, 143.64.

1-(Dibromomethylene)indane 3i. Colourless oil (1.47 g, 51%); R_f (hexane) 0.60. Found: C, 41.46; H, 2.55. Calc. for $C_{10}H_8Br_2$: C, 41.71; H, 2.80%; ν_{max}(Nujol)/cm^{-1} 1610 (C=C); δ_H (400 MHz; $CDCl_3$; Me_4Si) 2.85–2.92 (2 H, m, CH_2), 2.95–3.02 (2 H, m, CH_2), 7.20–7.35 (3 H, m, Ar), 8.28–8.33 (1 H, m, Ar); δ_C (100 MHz; $CDCl_3$; Me_4Si) 31.14 (CH_2), 33.26 (CH_2), 85.94 (CBr_2), 124.88, 125.93, 126.77, 131.15, 133.62, 137.28, 145.77.

1-(2-Bromo-1-methylvinyl)-4-methylbenzene 4a. Obtained as a mixture of *E*–*Z* isomers 5 : 4 (after purification); colourless oil (1.16 g, 55%); R_f (hexane) 0.65. *E*-Isomer: δ_H (400 MHz; $CDCl_3$; Me_4Si) 2.16 (3 H, d, *J* 1.3, *Me*-C=C), 2.29 (3 H, s, Me-Ar), 6.37 (1 H, q, *J* 1.3, -CH=), 7.07–7.22 (4 H, m, Ar). *Z*-Isomer: δ_H (400 MHz; $CDCl_3$; Me_4Si) 2.05 (3 H, d, *J* 1.6, *Me*-C=C), 2.32 (3 H, s, Me-Ar), 6.15 (1 H, q, *J* 1.6, -CH=), 7.07–7.22 (4 H, m, Ar).

1-(2-Bromo-1-methylvinyl)-4-chlorobenzene 4b. Obtained as a mixture of *E*–*Z* isomers 4 : 3 (after purification); colourless oil (1.69 g, 73%); R_f (hexane) 0.70. *E*-Isomer: δ_H (400 MHz; $CDCl_3$; Me_4Si) 2.17 (3 H, d, *J* 1.3, *Me*-C=C), 6.42 (1 H, q, *J* 1.3, -CH=), 7.19–7.33 (4 H, m, Ar). *Z*-Isomer: δ_H (400 MHz; $CDCl_3$; Me_4Si) 2.06 (3 H, d, *J* 1.6, *Me*-C=C), 6.21 (1 H, q, *J* 1.6, -CH=), 7.19–7.33 (4 H, m, Ar).

1-(2-Bromo-1-methylvinyl)-4-methoxybenzene 4c. was obtained as a mixture of *E*–*Z* isomers 2 : 1 (after purification); colourless oil (1.23 g, 54%); R_f (hexane–CH_2Cl_2, 2 : 1) 0.55. Found: C, 53.17; H, 5.16. Calc. for $C_{10}H_{11}BrO$: C, 52.89; H, 4.88%; ν_{max}(Nujol)/cm^{-1} 1600 (C=C). *E*-Isomer: δ_H (400 MHz; $CDCl_3$; Me_4Si) 2.21 (3 H, d, *J* 1.3, *Me*-C=C), 3.82 (3 H, s, MeO), 6.38 (1 H, q, *J* 1.3, -CH=), 6.88 (2 H, d, *J* 8.9, Ar), 7.27 (2 H, d, *J* 8.9, Ar). *Z*-Isomer: δ_H (400 MHz; $CDCl_3$; Me_4Si) 2.11 (3 H, d, *J* 1.6, *Me*-C=C), 3.83 (3 H, s, MeO), 6.19 (1 H, q, *J* 1.6, -CH=), 6.93 (2 H, d, *J* 8.9, Ar), 7.19 (2 H, d, *J* 8.9, Ar). For the mixture of isomers: δ_C ($CDCl_3$) 19.53 (Me), 24.84 (Me), 55.09 (MeO), 55.17 (MeO), 100.72 (=CHBr), 103.68 (=CHBr), 113.38, 113.75, 126.97, 128.87, 132.13, 133.30, 140.69, 158.85, 159.22.

1-(2-Bromo-1-methylvinyl)-4-nitrobenzene 4d. Obtained as a mixture of *E*–*Z* isomers 5 : 4 (after purification); colourless oil (1.14 g, 47%); R_f (hexane–CH_2Cl_2, 2 : 1) 0.60. Found: C, 44.42; H, 3.09. Calc. for $C_9H_8BrNO_2$: C, 44.66; H, 3.33%; ν_{max}(Nujol)/cm^{-1} 1620 (C=C). *E*-Isomer: δ_H (400 MHz; $CDCl_3$; Me_4Si) 2.26 (3 H, d, *J* 1.3, *Me*-C=C), 6.66 (1 H, q, *J* 1.3, -CH=), 7.49 (2 H, d, *J* 9.0, Ar), 8.17 (2 H, d, *J* 9.0, Ar). *Z*-Isomer: δ_H (400 MHz; $CDCl_3$; Me_4Si) 2.15 (3 H, d, *J* 1.6, *Me*-C=C), 6.36 (1 H, q, *J* 1.6, -CH=), 6.93 (2 H, d, *J* 8.7, Ar), 7.48 (2 H, d, *J* 8.7, Ar). For the mixture of isomers: δ_C (100 MHz; $CDCl_3$; Me_4Si) 19.32 (Me), 24.49 (Me), 103.76 (=CHBr), 109.18 (=CHBr), 123.46, 123.75, 126.55, 128.71, 139.75, 146.88; *m*/*z* (EI) 243 (M^+, 57%), 213 ($M^+ - NO$, 10), 115 ($M^+ - NO_2 - Br - H$, 100).

1-(2-Bromo-1-methylvinyl)-4-(methylsulfonyl)benzene 4e. Obtained as a mixture of *E*–*Z* isomers 1 : 1 (after purification); colourless oil (0.58 g, 21%); R_f (CH_2Cl_2) 0.70. Found: C, 43.65; H, 4.03. Calc. for $C_{10}H_{11}BrO_2S$: C, 43.65; H, 4.03%; ν_{max}(Nujol)/cm^{-1} 1620 (C=C). *E*-Isomer: δ_H (400 MHz; $CDCl_3$; Me_4Si) 2.17 (3 H, d, *J* 1.3, *Me*-C=C), 3.79 (3 H, s, $MeSO_2$), 6.33 (1 H, q, *J* 1.3, -CH=), 6.88 (2 H, d, *J* 8.8, Ar), 7.28 (2 H, d, *J* 8.8, Ar). *Z*-Isomer: δ_H (400 MHz; $CDCl_3$; Me_4Si) 2.07 (3 H, d, *J* 1.7, *Me*-C=C), 3.77 (3 H, s, $MeSO_2$), 6.15 (1 H, q, *J* 1.7, -CH=), 6.82 (2 H, d, *J* 8.8, Ar), 7.25 (2 H, d, *J* 8.8, Ar). For the mixture of isomers: δ_C (100 MHz; $CDCl_3$; Me_4Si) 19.84 (Me), 25.18 (Me), 37.61 (MeO), 38.01 (MeO), 99.87 (=CHBr), 101.54 (=CHBr), 113.16, 113.69, 123.72, 124.43, 138.13, 138.30, 143.69, 143.83, 152.58, 153.22.

2-(2-Bromo-1-methylvinyl)naphthalene 4f. Obtained as a mixture of *E*–*Z* isomers 3 : 1 (after purification); colourless oil (0.96 g, 39%); R_f (hexane) 0.70. Found: C, 63.46; H, 4.73. Calc. for $C_{13}H_{11}Br$: C, 63.18; H, 4.49%; ν_{max}(Nujol)/cm^{-1} 1605 (C=C). *E*-Isomer: δ_H (400 MHz; $CDCl_3$; Me_4Si) 2.39 (3 H, d, *J* 1.1, *Me*-C=C), 6.67 (1 H, q, *J* 1.1, -CH=), 7.50–7.56 (3 H, m), 7.83–7.93 (4 H, m). *Z*-Isomer: δ_H (400 MHz; $CDCl_3$; Me_4Si) 2.27 (3 H, d, *J* 1.5, *Me*-C=C), 6.37 (1 H, q, *J* 1.5, -CH=), other signals are overlapped by those of the *E*-isomer. For the mixture of isomers: δ_C (100 MHz; $CDCl_3$; Me_4Si) 20.73 (Me), 22.26 (Me), 100.37 (=CHBr), 103.18 (=CHBr), 123.62, 123.94, 127.32, 127.76, 129.58, 129.90, 130.54, 130.79, 131.81, 132.52, 133.02, 137.42, 144.17, 144.27.

2-(2-Bromo-1-methylvinyl)thiophene 4g. Obtained as a mixture of *E*–*Z* isomers 2 : 1 (after purification); colourless oil (1.22 g, 60%); R_f (hexane) 0.65. Found: C, 41.54; H, 3.68. Calc. for C_7H_7BrS: C, 41.40; H, 3.47%; ν_{max}(Nujol)/cm^{-1} 1610 (C=C). *E*-Isomer: δ_H (400 MHz; $CDCl_3$; Me_4Si) 2.23 (3 H, d, *J* 1.1, *Me*-C=C), 6.62 (1 H, q, *J* 1.1, -CH=), 6.98 (1 H, dd, *J* 5.1, *J* 3.6, Th), 7.04 (1 H, dd, *J* 3.6, *J* 1.3, Th), 7.18 (1 H, dd, *J* 5.1, *J* 1.3, Th). *Z*-Isomer: 2.24 (3 H, d, *J* 1.5, *Me*-C=C), 6.22 (1 H, q, *J* 1.5, -CH=), 7.02 (1 H, dd, *J* 5.1, *J* 3.8, Th), 7.24 (1 H, dd, *J* 3.8, *J* 1.2, Th), 7.33 (1 H, dd, *J* 5.1, *J* 1.2, Th). For the mixture of isomers: δ_C (100 MHz; $CDCl_3$; Me_4Si) 19.38 (Me), 24.57 (Me), 100.43 (=CHBr), 104.16 (=CHBr), 123.62, 124.50, 126.02, 126.23, 127.31, 127.46, 134.83.

GCMS analysis of the reaction mixture

A 25% aqueous solution of ammonia (0.33 cm^3) and freshly purified CuCl[18] (10 mg, 0.1 mmol) were added to a solution of freshly prepared hydrazone **1b** (169 mg, 1 mmol) in DMSO (1 cm^3). Then CCl_4 (0.29 cm^3, 3 mmol) was added dropwise over 10 min, with the temperature maintained at 20 °C (water bath). The reaction mixture was stirred for 24 h and quenched with water (50 cm^3). The reaction products were extracted with CH_2Cl_2 (10 cm^3 × 3). The extracts were dried over sodium sulfate, CH_2Cl_2 was evaporated and the residue was analysed by GCMS. The following products were detected in the reaction mixture.

1-Chloro-4-(2,2-dichloro-1-methylvinyl)benzene 2b. *m*/*z* (EI) 220 (M^+, 100%), 185 ($M^+ - Cl$, 17), 149 ($M^+ - 2\ Cl$, 92), 112 ($M^+ - 2\ Cl - C_3H_3$, 50).

***sym*-Azine of 4-chloroacetophenone.** *m*/*z* (EI) 304 (M^+, 49%), 289 ($M^+ - CH_3$, 100), 152 [$ClC_6H_4C(CH_3)=N$].

4-Chloroacetophenone. *m*/*z* (EI) 154 (M^+, 33%), 139 ($M^+ - CH_3$, 100), 111 ($M^+ - CH_3CO$, 47).

1-Chloro-4-[2-(4-chlorophenyl)-1-methylprop-1-enyl]benzene, $ClC_6H_4(CH_3)C=C(CH_3)C_6H_4Cl$. *m*/*z* (EI) 276 ($M^+$, 100%), 261 ($M^+ - CH_3$, 10), 226 ($M^+ - CH_3 - Cl$, 28).

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