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α-Hypervalent Iodine Functionalized Phosphonium and Arsonium Ylides and Their Tandem Reaction as Umpolung Reagents

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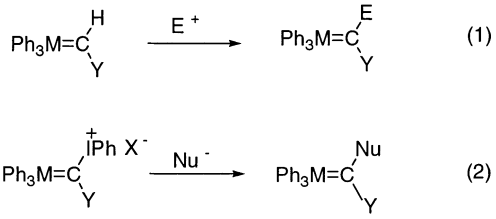
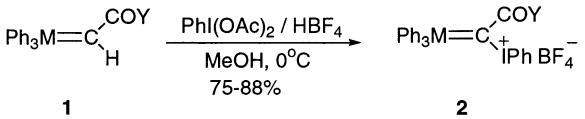
Abstract: α-Hypervalent iodine functionalized phosphonium and arsonium ylides **2** can be used as umpolung ylides to react with nucleophiles to give α-heteroatom substituted ylides **4** in good yields. The nucleophilic substitution−Wittig tandem reaction of **2** can occur smoothly to provide an efficient method for the synthesis of (*Z*)-α-halo-α,*β*-unsaturated enoates or enones **6**, stereoselectively.

Wittig reaction is one of the most important methods for the formation of carbon−carbon double bonds and widely used in the synthesis of natural products.[1−3] Through the Wittig reaction of α-heteroatom substituted ylides, the carbon−carbon double bond with a heteroatom at the α-position can be formed;[3−7] thus, the research on α-heteroatom-substituted ylides is a very important aspect in ylide chemistry. In general, α-heteroatom-substituted ylide can be synthesized via transylidation (eq 1, Scheme 1). Recently, there has been considerable interest demonstrating the synthetic potentials of hypervalent iodine compounds.[8] When a hypervalent iodine group is connected with an unsaturated carbon−carbon bond, the connected carbon can be attacked by nucleophiles. Thus, the polarity of an α-carbon in ylide may be reversed through introducing hypervalent iodine group at the α-carbon of an ylide, which enables the umpolung ylide to react with nucleophiles (eq 2, Scheme 1). In this paper, we wish to report our recent study on synthesis and reaction of α-hypervalent iodine functionalized phosphonium and arsonium ylide.

SCHEME 1



SCHEME 2



2a:M = P, Y =OEt; **2b**: M = P, Y = Me;
2c:M = As, Y = OMe; **2d**: M = As, Y = OEt;

Although the synthesis of α-hypervalent iodine functionalized phosphonium ylides has been reported,[9] it is surprising that the synthesis of α-hypervalent iodine functionalized arsonium ylides and their applications have not been reported so far. Thus, by applying the similar protocol we synthesized new α-hypervalent iodine functionalized phosphonium and arsonium ylides **2b**−**d** in good yields (Scheme 2). In contrast to α-hypervalent iodine functionalized phosphonium ylides, α-hypervalent iodine functionalized arsonium ylides were unstable and should be stored in a refrigerator.

The structure of α-hypervalent iodine functionalized arsonium ylide **2c** was established by its X-ray single-crystal diffraction analysis (Figure 1). The geometry of the As atom is a distorted tetrahedron. The bond length of As−C(5′) (1.852 Å) is almost equal to that of As−C (sp^2) single bond (1.897 Å).[10] The bond length of C(5′)−C(25) (1.422 Å) indicates the partial double bond character. Therefore, ylide **2c** has an enolic structure (Figure 2) and O(1) and I(1) are trans to each other. The fact that the six atoms, i.e., As(1), C(5′), C(25), O(1), O(2), and I(1), reside in the same plane support the enolic structure. The nearest distances from the boron atom of tetrafluoroborate anion to iodine atom and the arsenic cation are 4.291 and 5.269 Å, respectively.

The hypervalent iodine(III) is an electron-withdrawing group and, thus, can stablize the negativly charged α-carbon atom of α-hypervalent iodine functionalized phosphonium and arsonium ylides leading to the dramatic decrease of the nucleophilicity or even the reverse of the polarity of the α-carbon atom. As expected, no reaction was observed between α-hypervalent iodine functionalized phosphonium or arsonium ylides and aldehydes. On the other hand, α-hypervalent iodine functionalized phosphonium and arsonium ylides **2** can react with nucleophiles giving the corresponding α-heteroatom-substituted ylides **4** in good yields (Scheme 3) (see Table 1). The nucleophilic substitution reaction has

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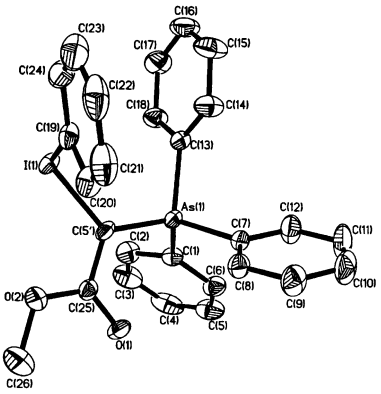


FIGURE 1. X-ray structure of the cationic part of **2c**.

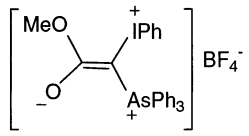
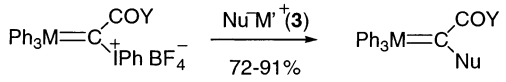


FIGURE 2.

SCHEME 3



2 **4**

M = P, As, Y=OMe, OEt

NuM' = Me_4NCl, *n*-Bu_4NBr, PhSK, 4-$CH_3C_6H_4SK$, PhSeNa.

TABLE 1. Nucleophilic Substitution Reaction of Umpolung Ylides

	2			yield of **4**
entry	M	Y	NuM′	(%)
1	P	OC_2H_5	Me_4NCl	87 (**4a**)
2	P	OC_2H_5	*n*-Bu_4NBr	91 (**4b**)
3	P	OC_2H_5	C_6H_5SH	84 (**4c**)
4	P	OC_2H_5	C_6H_5SeNa	85 (**4d**)
5	As	OCH_3	C_6H_5SH	86 (**4e**)
6	As	OC_2H_5	4-$CH_3C_6H_4SH$	80 (**4f**)
7	As	OCH_3	C_6H_5SeNa	72 (**4g**)

the advantages of simpler manipulation and milder reaction conditions as compared to the previous electrophilic protocols.[11]

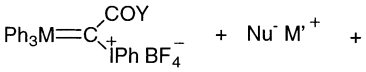
We also observed that the nucleophilic substitution reaction of α-hypervalent iodine phosphonium ylide **2a** took place more easily than that of arsonium analogue **2c**. For example, α-hypervalent iodine phosphonium ylide **2a** could react with Bu_4NCl to form the expected α-chloro phosphonium ylide **4a** (entry 1, Table 1), while α-hypervalent iodine arsonium ylide **2d** could not.

Since α-hypervalent iodine ylides **2** cannot react directly with an aldehyde, a tandem reaction of nucleophilic substitution and Wittig reaction leading to α-halo-α,*β*-unsaturated enoates or enones was designed (Scheme 4). The results of the one-pot reaction of an α-hypervalent iodine ylide, a nucleophile, and an aldehyde are summarized in Table 2.

From Table 2, it can be seen that the tandem reaction took place smoothly to form the desired (*Z*)-α-halo-α,*β*-unsaturated enoates or enones **6** stereoselectively (Table 2). The ratios of *Z*/*E* isomers were determined by the ^{1}H NMR spectra. It was reported that the signals of vinyl and ethyl proton of (*Z*)-α-halo-α,*β*-unsaturated enoates were in lower field than those of the corresponding (*E*) compounds. For example, ^{1}H NMR spectrum shows that the chemical shifts of vinyl and the methyl in ester proton of ethyl 2-bromo-3-(4-methoxyphenyl)-2(*Z*)-propenoate are 7.80 and 1.35 ppm, respectively, while the corresponding chemical shifts of ethyl 2-bromo-3-(4-methoxyphenyl)-2(*E*)-propenoate compound are 7.07 and 1.23 ppm, respectively.[12] The result is in accordance with our results.

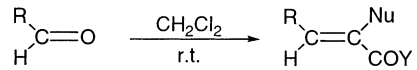
It was also observed that the α-hypervalent iodine arsonium ylide reacts much slower than the corresponding phosphonium ylide (such as entries 4 vs 16 and 7 vs 19, Table 2), which is in good agreement with the results of the nucleophilic substitution reaction, indicating the nucleophilicity of α-hypervalent iodine functionalized phosphonium ylide is stronger than that of the corresponding arsonium ylide.

SCHEME 4



2 **3**

M = P, As Y = OCH_3, OCH_2CH_3, CH_3



5 **6**

TABLE 2. Tandem Reaction of α-Hypervalent Iodine Ylides 2

	2			**5**	time	isolated yield of	
entry	Y	M	NuM′	R	(h)	**6**[a] (%)	*Z*/*E*[b]
1	OC_2H_5	P	Me_4NCl	4-ClC_6H_4	10	93 (*Z*-**6a**)	85/15
2	OC_2H_5	P	Me_4NCl	C_6H_5	24	78 (*Z*-**6b**)	89/11
3	OC_2H_5	P	Me_4NCl	4-$CH_3C_6H_4$	26	84 (*Z*-**6c**)	85/15
4	OC_2H_5	P	*n*-Bu_4NBr	4-$NO_2C_6H_4$	8	97 (*Z*-**6d**)	86/14
5	OC_2H_5	P	*n*-Bu_4NBr	4-ClC_6H_4	10	86 (*Z*-**6e**)	93/7
6	OC_2H_5	P	*n*-Bu_4NBr	4-$CH_3OC_6H_4$	20	70 (*Z*-**6f**)	90/10
7	OC_2H_5	P	Et_4NI	4-$NO_2C_6H_4$	10	90 (*Z*-**6g**)	86/14
8	OC_2H_5	P	Et_4NI	4-FC_6H_4	10	92 (*Z*-**6h**)	91/9
9	OC_2H_5	P	Et_4NI	$CH_3CH_2CH_2$	48	61 (*Z*-**6i**)	90/10
10	CH_3	P	Me_4NCl	4-$NO_2C_6H_4$	16	95 (*Z*-**6j**	100/0
11	CH_3	P	Me_4NCl	4-FC_6H_4	24	90 (*Z*-**6k**)	93/7
12	CH_3	P	*n*-Bu_4NBr	4-$NO_2C_6H_4$	12	96 (*Z*-**6l**)	99/1
13	CH_3	P	*n*-Bu_4NBr	C_6H_5	36	77 (*Z*-**6m**)	100/0
14	CH_3	P	Et_4NI	4-$NO_2C_6H_4$	16	75 (*Z*-**6n**)	98/2
15	OCH_3	As	*n*-Bu_4NBr	4-$NO_2C_6H_4$	24	82 (*Z*-**6o**)	90/10
16	OC_2H_5	As	*n*-Bu_4NBr	4-$NO_2C_6H_4$	24	81 (*Z*-**6d**)	85/15
17	OCH_3	As	*n*-Bu_4NBr	4-ClC_6H_4	28	73 (*Z*-**6p**)	85/15
18	OCH_3	As	Et_4NI	4-$NO_2C_6H_4$	18	76 (*Z*-**6q**)	91/9
19	OC_2H_5	As	Et_4NI	4-$NO_2C_6H_4$	18	74 (*Z*-**6g**)	84/16

[a] Isolated yield of purified (*Z*)-**6** based on aldehyde. [b] The ratios of *Z*-isomer to *E*-isomer were determined by ^{1}H NMR spectra (400 or 200 MHz in $CDCl_3$).

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In conclusion, the preparation and the structure of the α-hypervalent iodine functionalized phosphonium and arsonium ylides **2** are reported. These ylides **2** can be used as umpolung ylides to react with nucleophiles **3**, giving α-heteroatom substituted ylides **4** in good yields. The present new type of tandem sequence of nucleophilic substitution−Wittig reaction provides an efficient method for the synthesis of (*Z*)-α-halo-α,*β*-unsaturated enoates or enones **6** stereoselectively in moderate to excellent yields. The discovery on the umpolung ylides **2** would enrich the contents of ylide chemistry.

Experimental Section

All reactions were carried out in Schlenk tubes under nitrogen atmosphere. Mass spectra were obtained by EI method. IR spectra were taken the neat forus (liquid samples) or KBr disks (solid samples). Melting points were uncorrected.

General Procedure for the Synthesis of α-Hypervalent Iodine Functionalized Phosphonium and Arsonium Ylides 2a−d. A solution of $PhI(OAc)_2$ (5 mmol) and HBF_4 (5 mmol) in MeOH (5 mL) was added dropwise to the ice bath-cooled solution of ylide **1** (5 mmol) in MeOH (5 mL) for 20 min with stirring. During the addition, a lot of precipitate was formed. Upon complete addition, the reaction mixture was stirred at 0 °C for additional 1.5 h. After filtration, the precipitate was washed with Et_2O (5 mL × 3), recrystallized from CH_2Cl_2−MeOH, and dried under vacuum to give **2a**−**d**.

Compound **2a**: yield 88%; mp 185−186 °C (lit.[9] mp 185−187 °C); ^{1}H NMR (200 MHz, $CDCl_3$) *δ* 7.62−7.54 (m, 20H), 4.32 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H); IR ν_{max} 1601, 1436, 1284, 1065, 740, 694 cm^{-1}.

Compound **2b**: yield 81%; mp 174−178 °C dec; ^{1}H NMR (200 MHz, $CDCl_3$) *δ* 7.62−7.54 (m, 20H), 3.67 (s, 3H); IR ν_{max} 1560, 1484, 1363, 1055, 740, 693 cm^{-1}. Anal. Calcd for $C_{27}H_{23}BF_4IOP$: C, 53.32; H, 3.81; I, 20.87. Found: C, 53.07; H, 3.83; I, 20.75.

Compound **2c**: yield 75%; mp 109−111 °C dec; ^{1}H NMR (200 MHz, $CDCl_3$) *δ* 7.62−7.54 (m, 20H), 3.67 (s, 3H); IR ν_{max} 1600, 1445, 1310, 1060, 740, 690 cm^{-1}. Anal. Calcd for $C_{27}H_{23}AsBF_4IO_2$: C, 48.54; H, 3.47; I, 18.99. Found: C, 48.45; H, 3.58; I, 18.79. Crystallographic data for the structure (**2c**) reported has been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 189966.

Compound **2d**: yield 82%; mp 109−110 °C dec; ^{1}H NMR (200 MHz, $CDCl_3$) *δ* 7.70−7.40 (m, 20H), 4.06 (q, *J* = 7 Hz, 2H), 1.03 (t, *J* = 7 Hz, 3H); IR ν_{max} 1600, 1445, 1290, 1055, 740, 685 cm^{-1}. Anal. Calcd for $C_{28}H_{25}AsBF_4IO_2$: C, 49.30; H, 3.69; I, 18.60. Found: C, 49.21; H, 3.59; I, 18.70.

General Procedure for the Synthesis of α-Heteroatom-Substituted Phosphonium and Arsonium Ylides 4a−g by the Nucleophilic Substitution of Umpolung Ylide 2. Method A. A solution of a nucleophile (for tetramethylamomnium chloride or tetrabutylammonium bromide, CH_2Cl_2 was used as the solvent; for sodium selenolate, MeOH was used as the solvent) was added dropwise to the solution of α-hypervalent iodine functionalized phosphonium or arsonium ylides **2** (2 mmol) in CH_2Cl_2 (6 mL) within 30 min with stirring. The reaction mixture was then stirred overnight. The solvent was evaporated and the residue was extracted with C_6H_6 (15 mL × 3). After filtration the filtrate was evaporated to obtain a solid. Recrystallization of this solid from acetone-hexane gave the pure α-heteroatom substituted phosphonium and arsonium ylides **4a**−**g**.

Method B. A solution of thiophenol (2 mmol) in CH_3CN (3 mL) was added dropwise to an ice-bath cooled mixture of α-hypervalent iodine functionalized phosphonium or arsonium ylides **2** (2 mmol) and K_2CO_3 (2 mmol) in CH_3CN (6 mL) within 30 min with stirring. The reaction mixture was then stirred overnight. α-Heteroatom-substituted phosphonium and arsonium ylides **4c** and **4e**,**f** were obtained after the workup similar to that in method A.

Compound **4a**: mp 146−148 °C (lit.[11] mp 151−152 °C); ^{1}H NMR (200 MHz, $CDCl_3$) *δ* 7.62−7.54 (m, 15H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H); IR ν_{max} 1665, 1445, 1260, 1105, 740, 690 cm^{-1}.

Compound **4b**: mp 155−156 °C (lit.[11] mp 157−158 °C); ^{1}H NMR (200 MHz, $CDCl_3$) *δ* 7.62−7.53 (m, 15H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H); IR ν_{max} 1651, 1435, 133, 1184, 744, 693 cm^{-1}.

Compound **4c**: mp 197−199 °C (lit.[13] mp 199 °C); ^{1}H NMR (200 MHz, $CDCl_3$) *δ* 8.11−7.01 (m, 20H), 4.32 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H); IR ν_{max} 1657, 1450, 1320, 1009, 742, 691 cm^{-1}.

Compound **4d**: mp 184−186 °C (lit.[14] mp 184−186 °C); ^{1}H NMR (200 MHz, $CDCl_3$) *δ* 7.62−7.54 (m, 20H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H); IR ν_{max} 1653, 1485, 1310, 1060, 743, 692 cm^{-1}.

Compound **4e**: mp 185−186 °C; ^{1}H NMR (200 MHz, $CDCl_3$) *δ* 7.37−7.07 (m, 20H), 3.63 (s, 3H); IR ν_{max} 1600, 1485, 1300, 760, 720 cm^{-1}; MS *m*/*z* (rel intensity) 486 (M^+, 24), 306 (14), 227 (36), 152 (100), 109 (8), 77 (7). Anal. Calcd for $C_{27}H_{23}AsO_2S$: C, 66.67; H, 4.77. Found: C, 66.49; H, 4.89.

Compound **4f**: mp 163−164 °C; ^{1}H NMR (200 MHz, $CDCl_3$) *δ* 7.81−7.66 (m, 19H), 3.94 (q, *J* = 7 Hz, 2H), 2.11 (s, 3H), 0.98 (t, *J* = 7 Hz, 3H); IR ν_{max} 1605, 1500, 1290, 800, 745, 690 cm^{-1}; MS *m*/*z* (rel intensity) 514 (M^+, 11), 416 (32), 306 (74), 229 (39), 152 (100), 91 (11), 77 (15). Anal. Calcd for $C_{29}H_{27}AsO_2S$: C, 67.70; H, 5.29. Found: C, 67.40; H, 5.40.

Compound **4g**: mp 202−203 °C (lit.[15] mp 203−205 °C); ^{1}H NMR (200 MHz, $CDCl_3$) *δ* 7.70−7.09 (m, 20H), 3.41 (s, 3H); IR ν_{max} 1600, 1445, 1300, 750, 690 cm^{-1}.

General Procedure for the Stereoseletive Synthesis of (*Z*)-α-Halo-α,*β*-unsaturated Esters 6 by the Tandem Reaction of Umpolung Ylides 2. A mixture of α-hypervalent iodine functionalized phosphonium or arsonium ylides **2** (2 mmol), tetrakisalkylammonium halide **3** (2 mmol), and aldehyde **5** (2 mmol) in CH_2Cl_2 (20 mL) was stirred at room temperature for 8−48 h. After the reaction was complete, the organic phase was washed with water (10 mL × 2) and dried over magnesium sulfate. After evaporation of the solvent, the crude product was purified by preparative TLC (silica gel, hexanes−ethyl acetate as eluent) to give α-halo-α,*β*-unsaturated enoate or enone **6**.

Ethyl 2-chloro-3-(4-chlorophenyl)-2-propenoate (6a): oil (lit.[16] oil); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.85 (s, 1H), 7.77 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H); IR ν_{max} 2983, 1728, 1618, 1491, 1262, 1198, 823 cm^{-1}; MS *m*/*z* (rel intensity) 244 (M^+, 31), 185 (36), 138 (37), 136 (100), 135 (31), 75 (36).

Ethyl 2-chloro-3-phenyl-2-propenoate (6b): oil (lit.[17] 95/0.2 mm); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.9 (s, 1H), 7.85−7.83 (m, 2H), 7.43−7.41 (m, 3H), 4.36 (q, *J* = 7.1 Hz, 2H), 1.39 (t, 3H, *J* = 7.1 Hz); IR ν_{max} 2982, 1723, 1611, 1447, 1258, 1182, 765, 691 cm^{-1}; MS *m*/*z* (rel intensity) 212 ($M^+ + 2$, 33), 210 (M^+, 100), 175 (37), 147 (55), 102 (86).

Ethyl 2-chloro-3-(4-methylphenyl)-2-propenoate (6c): oil (lit.[18] bp 150−152 °C/3 mm); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.74 (d, *J* = 8.0 Hz, 2H), 7.56 (s, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H); IR ν_{max} 2982, 1726, 1608, 1511, 1263, 1183, 1044, 813 cm^{-1}; MS *m*/*z* (rel intensity) 226 ($M^+ + 2$, 37), 225 ($M^+ + 1$, 45), 224 (M^+, 100), 179 (23), 115 (68), 116 (43).

Ethyl 2-bromo-3-(4-nitrophenyl)-2-propenoate (6d): mp 154−156 °C (lit.[11b] mp 154−156 °C); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.29 (m, 3H), 7.94 (d, *J* = 8.6 Hz, 2H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H); IR ν_{max} 3050, 1710, 1610, 1511,

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1349, 1262, 1199, 861 cm^{-1}; MS *m*/*z* (rel intensity) 301 (M$^+$ + 2, 21), 299 (M$^+$, 20), 220 (100), 192 (86), 101 (31), 75 (29).

Ethyl 2-bromo-3-(4-chlorophenyl)-2-propenoate (6e): oil (lit.[19] oil); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.80 (d, J = 8.5 Hz, 2H), 7.42 (d, J = 8.5 Hz, 2H), 4.36 (q, J = 7.1 Hz, 2H), 1.39 (t, J = 7.1 Hz, 3H); IR ν_{max} 2982, 1718, 1612, 1490, 1257, 1199, 822 cm^{-1}; MS *m*/*z* (rel intensity) 290 (M$^+$ + 2, 79), 288 (M$^+$, 56), 209 (100), 211 (50), 181 (76), 136(59), 101 (43).

Ethyl 2-bromo-3-(4-methoxyphenyl)-2-propenoate (6f): oil (lit.[19] oil); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.77 (d, J = 8.2 Hz, 2H), 7.22 (d, J = 8.2 Hz, 2H), 4.34 (q, J = 7.1 Hz, 2H), 3.83 (s, 3H), 1.38 (t, J = 7.1 Hz, 3H); IR ν_{max} 2981, 1723, 1606, 1510, 1182, 1040, 813 cm^{-1}; MS *m*/*z* (rel intensity) 286 (M$^+$ + 2, 27), 284 (M$^+$, 27), 205 (82), 177 (84), 115 (100), 91 (38).

Ethyl 2-iodine-3-(4-nitrophenyl)-2-propenoate (6g): mp 98−100 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30−8.28 (m, 3H), 7.87−7.85 (m, 2H), 4.38 (q, 2H, J = 7.1 Hz), 1.40 (t, J = 7.1 Hz); IR ν_{max} 1708, 1589, 1519, 1348, 1250, 1201, 852 cm^{-1}; MS *m*/*z* (rel intensity) 347 (44), 220 (68), 192 (100), 101 (40), 89 (25), 75 (39).

Ethyl 2-iodine-3-(4-flurophenyl)-2-propenoate (6h): oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.79−7.82 (m, 2H), 7.10−7.14 (m, 2H), 4.35 (q, J = 7.1 Hz, 2H), 1.38 (t, J = 7.1 Hz, 3H); IR ν_{max} 2982, 1714, 1600, 1507, 1238, 1190, 1036, 832 cm^{-1}; MS *m*/*z* (rel intensity) 320 (M$^+$, 67), 193 (93), 165 (92), 149 (70), 120 (100), 101 (56). Anal. Calcd for $C_{11}H_{10}FIO_2$: C, 40.62; H, 3.38. Found: C, 40.89; H, 3.12.

Ethyl 2-iodine-2-hexenoate (6i): oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (t, J = 7.0 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 2.30 (q, J = 7.6 Hz, 2H), 1.60−1.52 (m, 2H), 1.32 (t, J = 7.1 Hz, 3H), 1.01 (t, J = 7.4 Hz, 3H); IR ν_{max} 2924, 1715, 1596, 1509, 1249, 1182, 1037, 812 cm^{-1}; MS *m*/*z* (rel intensity) 268 (M$^+$, 100), 198 (51), 113 (47), 95 (48), 67 (69), 55 (40). Anal. Calcd for $C_8H_{13}IO_2$: C, 35.84; H, 4.89. Found: C, 35.72; H, 4.93.

3-Chloro-(4-nitrophenyl)-3-buten-2-one (6j): mp 111−113 °C (lit.[20] mp 113−115 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.24 (d, 2H, J = 8.6 Hz), 7.96 (d, 2H, J = 8.6 Hz), 7.76 (s, 1H), 2.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.09, 148.08, 133.05, 132.39, 131.24, 123.68, 26.89; IR ν_{max} 1676, 1607, 1512, 1345 cm^{-1}; MS *m*/*z* (rel intensity) 227 (M$^+$ + 2, 1), 225 (M$^+$, 4), 208 (24), 210 (9), 75 (10), 73 (100).

3-Chloro-4-(4-fluorophenyl)-3-buten-2-one (6k): mp 62−64 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.85−7.80 (m, 2H), 7.70 (s, 1H), 7.12−7.08 (m, 2H), 2.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.40, 164.84, 162.32, 134.25, 133.05, 132.97, 129.77, 129.75, 129.07, 129.04, 115.92, 115.70, 26.77; IR ν_{max} 1675, 1500, 1209 cm^{-1}; MS *m*/*z* (rel intensity) 200 (M$^+$ + 2, 12), 198 (M$^+$, 38), 163 (31), 147 (23), 120 (41), 43 (100). Anal. Calcd for $C_{10}H_8ClFO$: C, 60.47; H, 4.06. Found: C, 60.35; H, 4.11.

3-Bromo-4-(4-nitrophenyl)-3-buten-2-one (6l): mp 115−117 °C (lit.[21] mp 115−117 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.24 (d, J = 8.7 Hz, 2H), 8.03 (s, 1H), 7.95 (d, J = 8.7 Hz, 2H), 2.61 (s, 3H); IR ν_{max} 1675, 1510, 1345, 1215 cm^{-1}; MS *m*/*z* (rel intensity) 271 (M$^+$ + 2, 2), 269 (M$^+$, 2), 190 (26), 75 (14), 43 (100), 28 (17), 18 (57).

3-Bromo-4-phenyl-3-buten-2-one (6m): oil (lit.[22] oil); ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.80−7.76 (m, 2H), 7.43−7.40 (m, 3H), 2.58 (s, 3H); IR ν_{max} 1670, 1590, 1220, 765, 691 cm^{-1}; MS *m*/*z* (rel intensity) 226 (M$^+$ + 2, 28), 224 (M$^+$, 28), 145 (73), 102 (73), 43 (100).

3-Iodine-4-(4-nitrophenyl)-3-buten-2-one (6n): mp 117−119 °C (lit.[23] mp 117.5−119 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.30 (d, J = 8.7 Hz, 2H), 8.01 (s, 1H), 7.85 (d, J = 8.7 Hz, 2H), 2.67 (s, 3H); IR ν_{max} 1669, 1585, 1511, 1539, 1204, 856 cm^{-1}; MS *m*/*z* (rel intensity) 317 (M$^+$, 10), 300 (19), 190 (43), 101 (20), 75 (85), 43 (100).

Methyl 2-bromo-3-(4-nitrophenyl)-2-propenoate (6o): mp 124−125 °C (lit.[24] mp 126.5−127 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (m, 3H), 7.95 (d, J = 8.9 Hz, 2H), 3.94 (s, 3H); IR ν_{max} 1715, 1593, 1514, 1350, 1277, 1190, 850 cm^{-1}; MS *m*/*z* (rel intensity) 287 (M$^+$ + 2, 18), 285 (M$^+$, 17), 206 (100), 174 (24), 101 (47).

Methyl 2-bromo-3-(4-chlorophenyl)-2-propenoate (6p): mp 72−74 °C (lit.[24] mp 74−75 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16(s, 1H), 7.79 (d, J = 8.5 Hz, 2H), 7.42 (d, J = 8.5 Hz, 2H), 3.94 (s, 3H); IR ν_{max} 1715, 1607, 1490, 1255, 1190, 822 cm^{-1}; MS *m*/*z* (rel intensity) 276 (M$^+$ + 2, 14), 274 (M$^+$, 13), 197 (30), 195 (100), 136 (49), 75 (24).

Methyl 2-iodine-3-(4-nitrophenyl)-2-propenoate (6q): mp 104−106 °C (lit.[23] mp 105−106 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (m, 3H), 7.87 (d, J = 8.5 Hz, 2H), 3.95 (s, 3H); IR ν_{max} 1705, 15899, 1522, 1349, 1273, 1201, 852 cm^{-1}; MS *m*/*z* (rel intensity) 333 (M$^+$, 72), 302 (16), 206 (100), 101 (40), 75 (39).

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