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Solvent reduced Wittig olefination reactions with halo containing conjugated phosphoranes

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Abstract: The Wittig reaction of carbaldehydes with alkoxycarbonylhalomethylidenetriphenylphosphoranes can be performed with ease in solventless systems. The analogous reaction of carbaldehydes with acylhalomethylidenetriphenylphosphoranes requires a small amount of solvent, such as chloroform, in order for the reaction to proceed. The products of the reaction are versatile precursors for further transformations, such as the Suzuki-Miyaura cross-coupling reaction.

Keywords: Wittig olefination, solventless reaction, Suzuki-Miyaura cross-coupling

1 Introduction

Selected conjugated phosphoranes are stable toward air and moisture [1].Nevertheless, many are still reactive enough to undergo Wittig olefination with carbaldehydes [1]. Typically, such reactions were conducted in aromatic solvents such as benzene [2] and toluene under refluxing conditions [3], where benzoic acid was often used as a catalyst [4]. In recent years, Wittig reactions were performed using solventless systems [5–9], often utilizing non-classical energy sources, such as microwave irradiation [6, 7], or non-classical stirring techniques, such as steel ball-mill mixing [8]. Recently, the authors [9] communicated that certain aldehydes reacted exothermally with alkyl (triphenylphosphoranylidene)acetates and that olefination reactions with the phosphoranes were performed using melts of the starting materials, i.e., in solventless systems. In the current research, the possibilities of using solventless systems or solvent-reduced systems in the reaction of

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(triphenylphosphoranylidene)haloacetates and the related acyl- and phenacylhalomethylidenetriphenylphosphoranes are discussed.

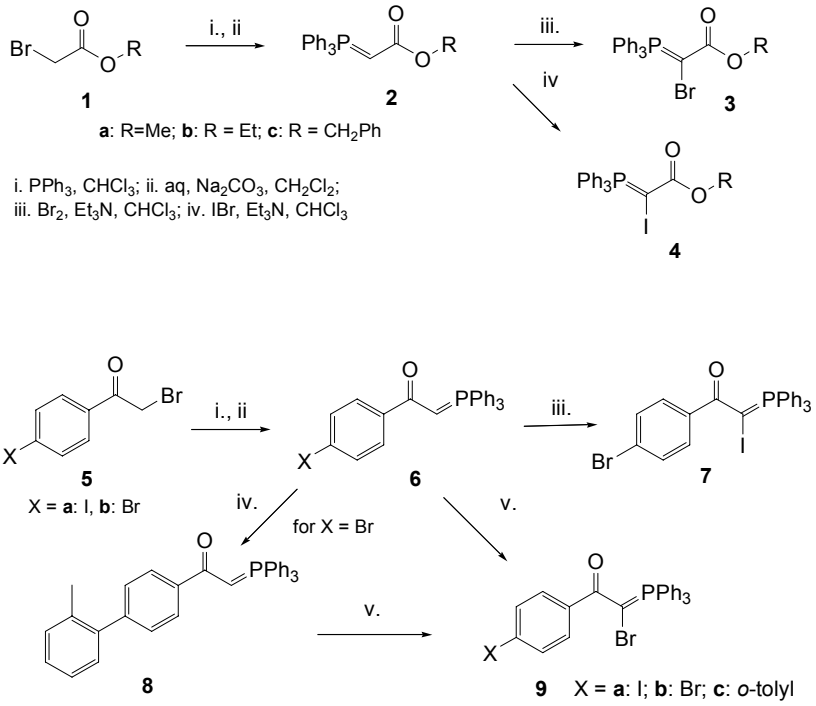
Reducing the solvents used in reaction systems [10] is often worthwhile to pursue, not only because of environmental concerns, but also because such a reduction often simplifies work-up procedures and increased concentrations of the reactive species can shorten reaction times. Solvents are often important in moderating reactions to achieve the selective formation of products [11]. Therefore, it is necessary to evaluate the possibilities of solvent reduction for organic transformations on a case by case basis.

2 Results and discussion

Acyl- and alkyloxycarbonylhalomethylidenetriphenylphosphoranes **3**, **4**, **7**, **9** and **12** were synthesized by halogenation – dehydrohalogenation [12–15] of the corresponding phosphoranes **2**, **6**, **8**, and **11**, where bromine/triethylamine (Et_3N) [13] and *N*-bromosuccinimide (NBS)/K_2CO_3 [bromination – dehydrobromination] [14] and iodomonobromide/Et_3N [iodobromination – dehydrobromination] [15] were used as reagent/base systems (Scheme 1). The halogenated phosphoranes were subjected to flash column chromatography. Phosphoranes, **3**, especially **3c**, and **4,** were least stable. The phosphoranes were stable enough to be recrystallized in air and, when purified, were also stable in the solid state over a long period of time.

Reactions of stabilized halogenated phosphoranes and phosphonates were studied in different solvent systems [16, 17], where the reactions were often conducted in the exclusion of air. Instances are also known in which the phosphoranes were prepared *in situ*. In this manuscript, the possibilities of conducting the reactions of stabilized halo ylides [18] with aldehydes in solventless systems, or solvent-reduced systems, are discussed.

Initially, reactions of the more reactive phosphoranes, such as **3** or **4,** with aldehydes in the absence of solvent were investigated (Scheme 2). Primarily, benzaldehydes that are liquid at rt or have a low melting point, such as *o*-ethoxybenzaldehyde (**13a**), *p*-tolualdehyde (**13f**), 2-furylaldehyde (**13k**) and *p*-anisaldehyde (**13c**), reacted with phosphorane **3**, and also with **4**, in solventless systems at 100°C. In the case of the higher melting carbaldehydes or reactions with phosphoranes **7**, **9**, and **12**, a small amount of chloroform was necessary to solubilize the reactants. The reactions were performed at 100°C with reaction times ranging from 30 min. to 3h. Mixing an aldehyde and a phosphorane, **3,** at rt, can result in an exothermic reaction, such as in the reaction of 5-bromofur-2-ylcarbaldehyde, **13L**, and **3b**. Even aldehydes that did not immediately form homogeneous melts, such as 4-bromobenzaldehyde, **13d**, reacted exothermally with alkoxycarbonylhalomethylidenetriphenylphosphoranes, **3,** when a minimum amount of solvent was added, but overall, these reactions were less exothermic than the corresponding transformations with non-halogenated phosphoranes, **2**. Nevertheless, heating the reaction melts at 100°C was necessary to complete the reactions. In most cases, the Wittig products were isolated in excellent to good yield. In all cases, the dominant isomer formed was the *Z*-isomer. The electron-withdrawing carboxyl group was positioned



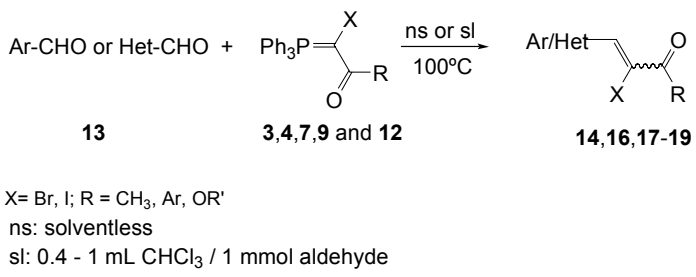
Scheme 1 Preparation of stabilized halomethylidenetriphenylphosphoranes.

trans to the substituent R that was introduced with the aldehyde. Usually, the Z-isomer was the main isomer formed in the Wittig reaction of stabilized halomethylidenetriphenylphosphoranes [12, 15–17]. *E*- and *Z*-isomers were easily distinguished by the low field shift of H(C3) in the *Z*-isomer ($\delta > 8.0$ ppm) as compared to the *E*-isomer ($\delta < 8.0$ ppm). While in most cases the olefinic products were obtained in good yield, a few aldehydes reacted with difficulty under the conditions used. The reaction of quinoline-4-carbaldehyde, **13p**, with methoxycarbonylbromomethylidenetriphenylphosphorane, **3a,** generated the corresponding product, **14w,** in poorer yield. Poor solubility of the carbaldehyde and electronic effects contributed to the result observed. Additionally, 2,4,6-trimethylbenzaldehyde produced no product when allowed to react with the phosphorane, **3b,** in a solventless system (1h, 100°C). A combination of electronic and steric effects may influence the poor reactivity of the aldehyde. Side-products, which were sometimes observed in the reactions, included small amounts of dehalogenated Wittig-product, e.g.

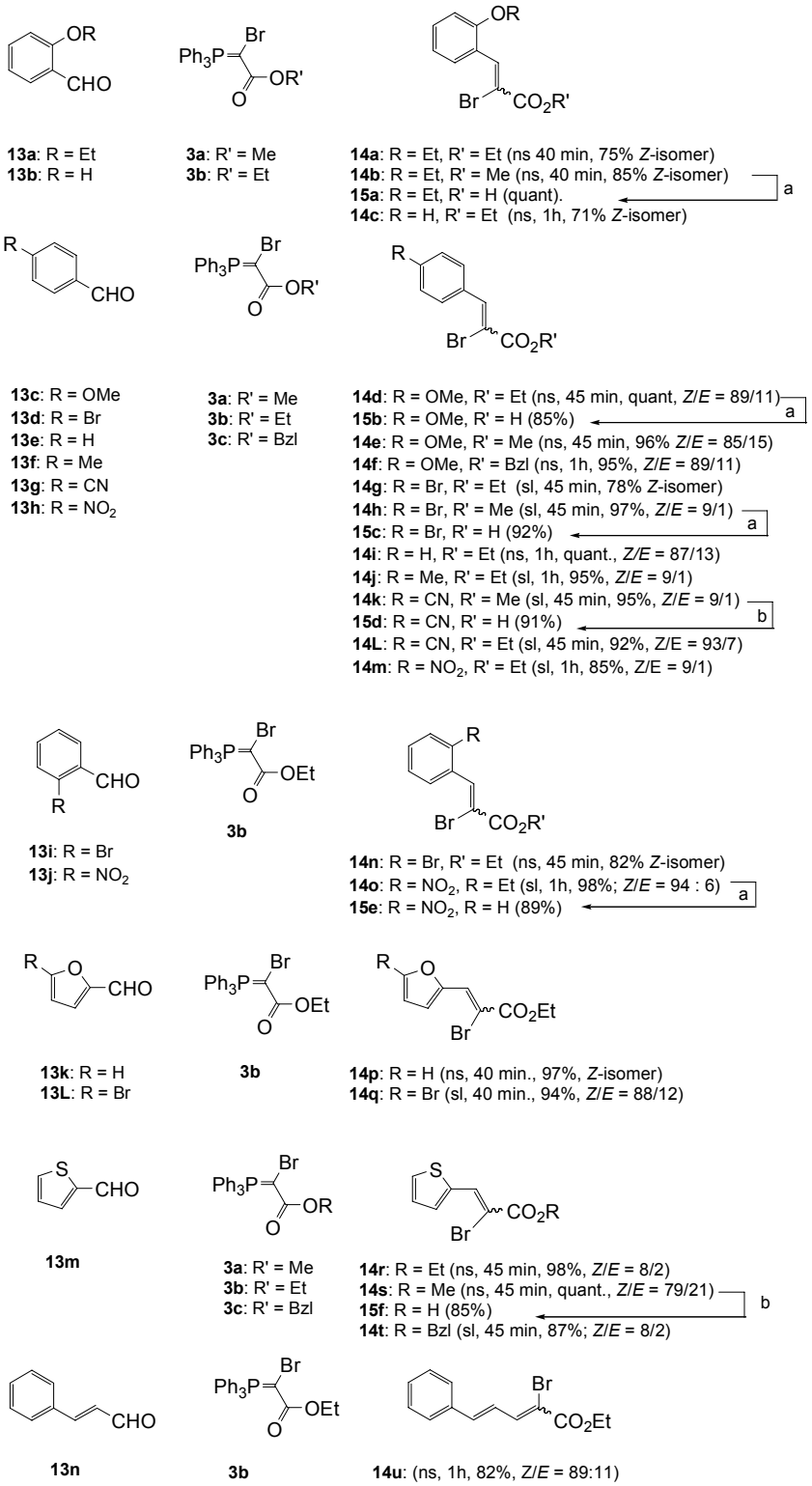
non-halogenated cinnamates, and small amounts of products stemming from the hydrolysis of the halogenated phosphoranes. Thus, small amounts of ethyl bromoacetate and benzyl bromoacetate were formed from phosphoranes, **3b** and **3c**, respectively. Nevertheless, these products were separated with ease using column chromatography, which also isolated the triphenylphosphine oxide formed in the reaction. The esters, **14,** were saponified easily to the corresponding acids, **15,** (see also [17, c]) by reaction with NaOMe or MeOH in aq. H_2O_2 or with NaOMe or MeOH in H_2O.

In the reactions of the acetyl- and phenacylhalomethylidenetriphenylphosphoranes, **7**, **9**, and **12** (Schemes 3 and 4), a minimum amount of chloroform was used to solubilize both reactants, when heated. The amount of solvent used in this research comprises about 7% of the solvent used by Speziale and Ratts [16]. The resulting mixture was allowed to stand at 100°C for 1 – 3h. During this time, some chloroform evaporated so that the reaction essentially occurred in a melt of both reactants with a small amount of chloroform still present. The *Z*-/*E*-selectivity of the phosphoranes, **7** and **9,** was more pronounced than for the phosphoranes, **3** and **4**, or for the phosphoranes, **12**. Nevertheless, the phosphoranes **7**, **9**, and **12** were less reactive than **3** and **4** and thus longer reaction times were required. The compound quinoline-4-carbaldehyde, **13p**, was determined to be a poor substrate for the reaction with the phosphorane, **12** (Scheme 3). *Ortho*-substituted benzaldehydes, such as *o*-nitrobenzaldehyde, **13j**, which produced a poor yield in the reaction with *p*-bromophenacyliodomethylidenetriphenylphosphorane, **7** (Scheme 4), and o-ethoxybenzaldehyde, **13a**, reacted poorly with the acetyl and phenacylphosphoranes, **7**, **9**, and **12**. By-products resulting from the αtdebromination of the Wittig olefins were formed in considerable amounts under the conditions used, e.g. the compound **18b**.

The 2-haloacrylates and the 2-halovinylketones are interesting substrates for a large variety of transformations [17, a], [19]. For example, a number of the iodo derivatives were subjected to the Suzuki-Miyaura cross-coupling reaction with *p*-methoxyphenylboronic acid to produce substituted stilbenes (Scheme 5). The reaction system used [$(PPh_3)_2PdCl_2$, PPh_3, 1.5M Na_2CO_3, DME] [20] was similar to the one employed by the authors [21] in the coupling reaction of 3-bromoenaldehydes. *cis*-Stilbenes were formed in good yield. *cis*-Stilbenes were differentiated from *trans*-stilbenes using the chemical shift of H(C3). The ester functionality located in the *cis* position relative to H(C3) produced a low field

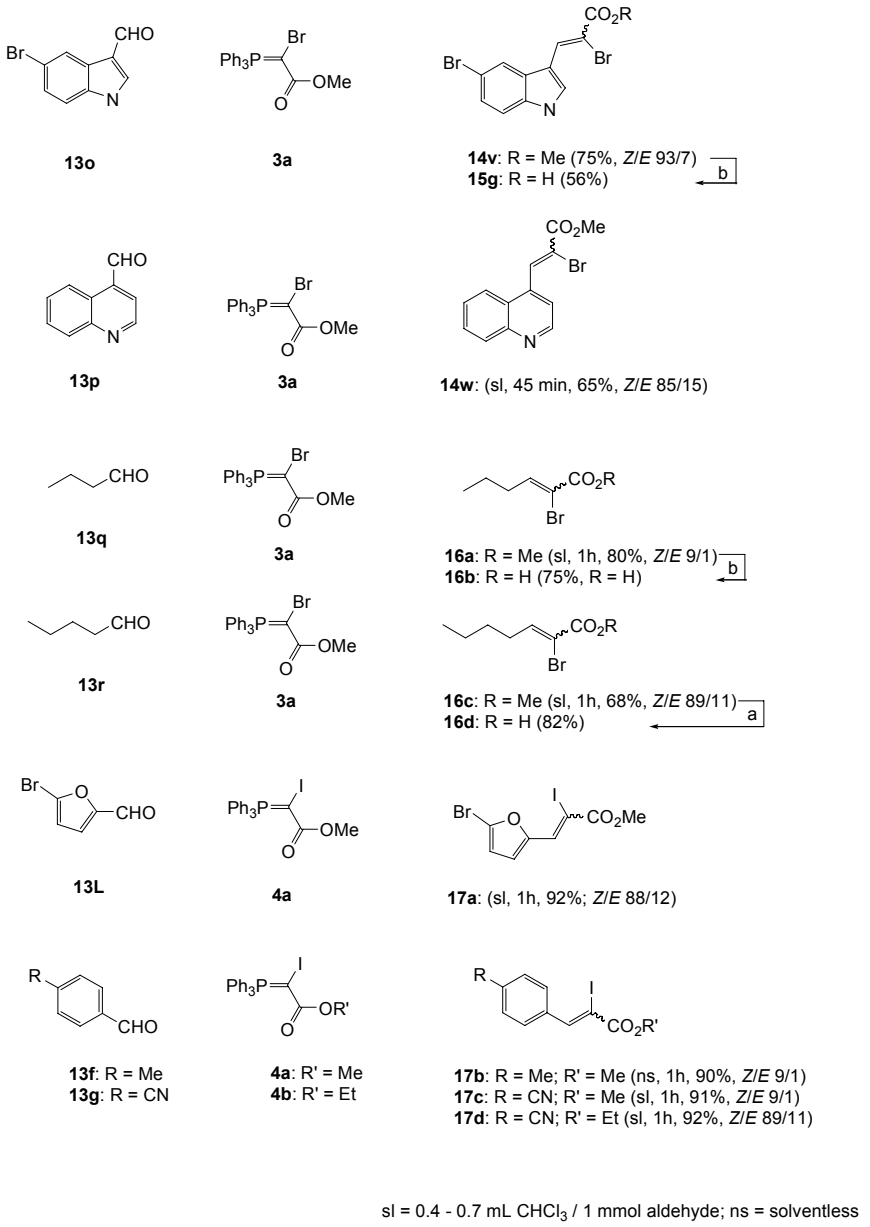


Scheme 2 Wittig olefination with alkoxycarbonylhalomethylidenetriphenylphosphoranes under solventless and solventreduced conditions.



a. NaOMe, 30w% aq. H_2O_2, MeOH, 12h, rt; b. NaOMe, MeOH, H_2O, 12h, rt

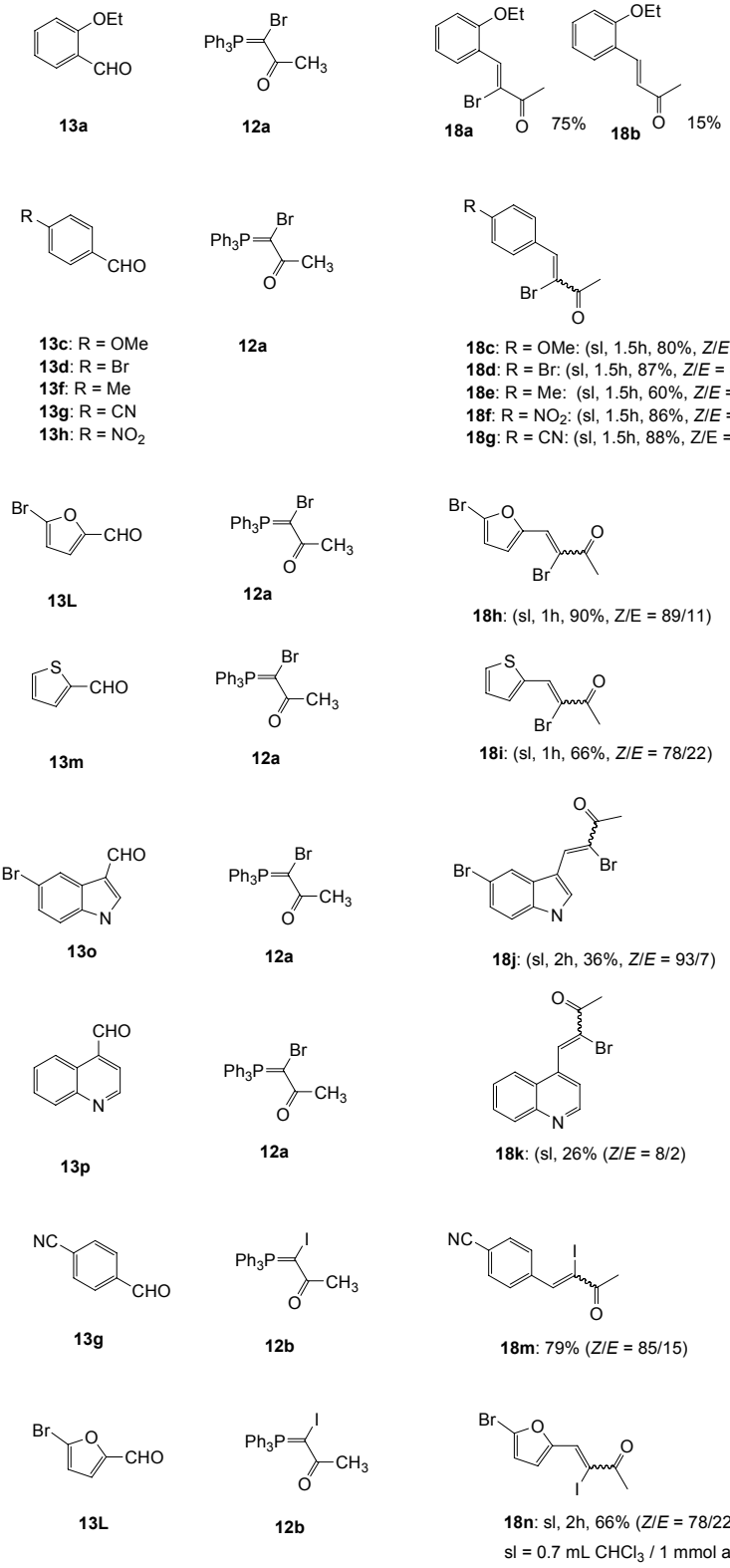
Scheme 2 (continued) Wittig olefination with alkoxycarbonylhalomethylidenetriphenylphosphoranes under solventless and solventreduced conditions.



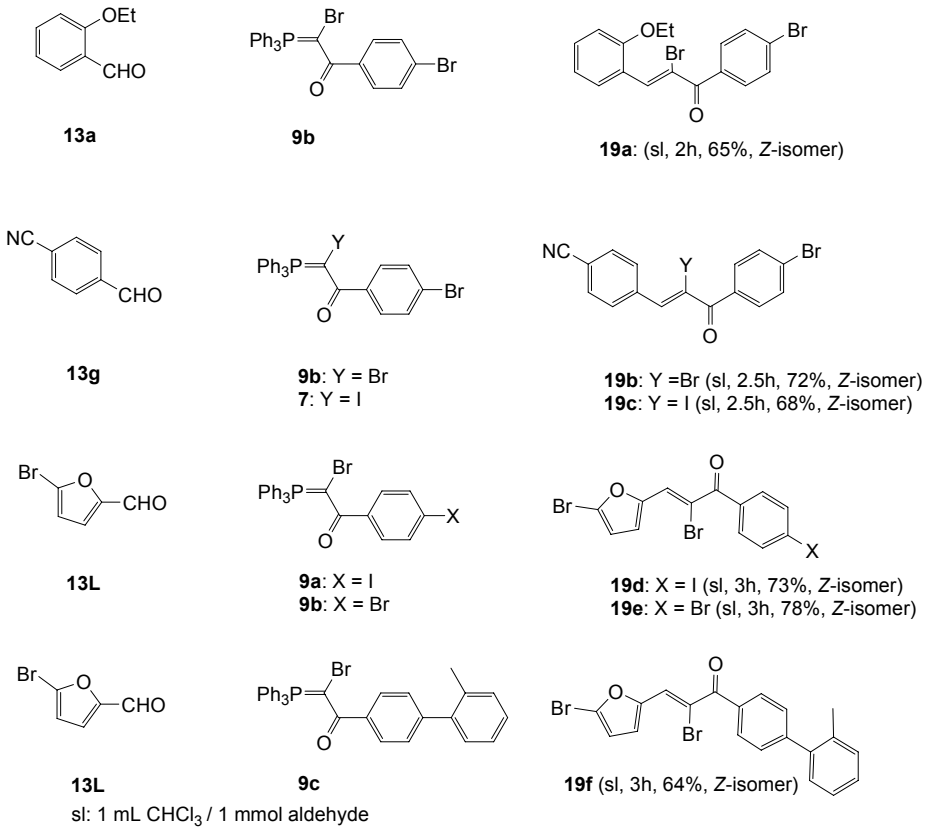
Scheme 2 (continued) Wittig olefination with alkoxycarbonylhalomethylidenetriphenylphosphoranes under solventless and solventreduced conditions.

shift in the signal from H(C3) in ***E*-20** compared to ***Z*-20**. The double bond configuration was also determined by a NOE (Nuclear Overhauser Effect) experiment. Small amounts of side products, such as the *trans*-stilbene, were observed in the reaction of **18m**, with both the *E*- and *Z*-configurations of the dehalogenated cyanophenylbutenone and the *p*-cyanocinnamate, respectively. The side products signified that a small amount of double bond isomerisation occurred. The side products, however, were easily separated using column chromatography of the reaction mixtures.

In conclusion, the stabilized, halo-ylides, **3** and **4,** having ester functional groups,



Scheme 3 Wittig olefination with acetylhalomethylidenetriphenylphosphoranes under solvent-reduced conditions.



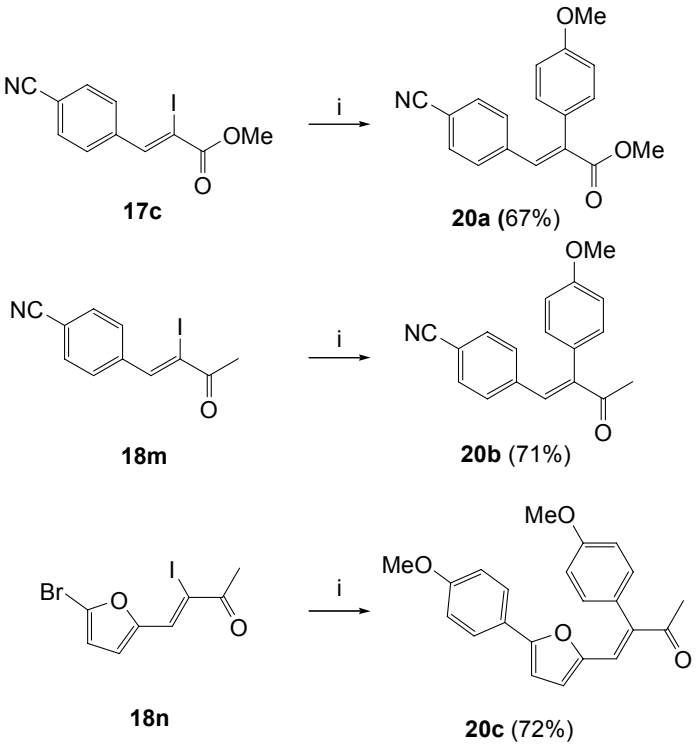
Scheme 4 Wittig olefination with aroylhalomethylidenetriphenylphosphoranes under solventreduced conditions.

were demonstrated to react with a number of carbaldehydes under solventless conditions. Small amounts of chloroform were sufficient for the reaction of **3** and **4,** as well as for the stabilized phosphoranes, **7**, **9**, and **12,** to undergo olefination with aldehydes. The products formed were interesting substrates for further reactions. Thus, the iodoalkenones, **18m** and **18n,** as well as the iodoacrylate, **17c,** yielded substituted *cis*-stilbenes, **20,** when subjected to a Suzuki-Miyaura type cross-coupling reaction.

3 Experimental section

3.1 General remarks

Melting points were measured on a Yanaco microscopic hotstage instrument and are uncorrected. Infrared spectra were measured with JASCO IR-700 and Nippon Denshi JIR-AQ2OM instruments. ^{1}H and ^{13}C NMR spectra were recorded with a JEOL EX-270 spectrometer (^{1}H at 270 MHz, ^{13}C at 67.8 MHz). The chemical shifts were reported relative to TMS (solvent $CDCl_3$, unless otherwise noted). Assignments of ^{13}C signals were aided by DEPT (Distortionless Enhancement by Polarisation Transfer) measurements; where (+) denoted primary and tertiary carbons, and (-) denoted secondary and quater-



i. *p*-MeOPhB(OH)$_2$, Pd(PPh$_3$)$_2$Cl$_2$, PPh$_3$, 1.5M aq. Na$_2$CO$_3$, DME, 70ºC, 9h

Scheme 5 C-C coupling reaction with 3-iodo-but-3-en-2-ones.

nary carbons (C_{quat}). Mass spectra were measured using a JMS-01-SG-2 spectrometer. Column chromatography was performed on Wakogel 300. For experiments requiring heating, an electric oven, EYELA NDO-450N, preheated at 100 °C, was used. Alternatively, submersion of the reaction vessel in an oil bath was used.

Phosphoranes were prepared according to procedures published in the literature: **2a** [22, a], **2b** [22, a], **2c** [22, b,c], **6** [22, d], and **11** [22, e]. The extended phosphorane, **8,** was prepared by Suzuki coupling of bromophenacylmethylidenetriphenylphosphorane, **6b,** with *o*-tolylboronic acid [23]. Compounds **3**, **9**, and **12** were prepared by bromination/dehydrobromination of **2**: **3a**, **3b**, **3c** [22, b,c] and **12a** (all utilizing Et_3N/Br_2[13]), or **9a**, **9b** and **9c** (all utilizing NBS, K_2CO_3, THF [14]). Compounds **4**, **7** and **12b** were prepared by iodobromination and dehydrobromination (all utilizing IBr, Et_3N [15]).

Ethyl (*Z*)-3-(furan-2-yl)-2-bromoacrylate (***Z*-14p**). [15, 24] – General Procedure A (solventless Wittig olefination reaction) – A mixture of 2-furaldehyde (**13k**) (480 mg, 5.0 mmol) and the phosphorane **3b** (2.98 g, 7.0 mmol) was heated at 100°C for 40 min. Thereafter, the mixture was subjected to column chromatography on silica gel (hexane/ether/ $CHCl_3$ 3:1:1) to yield ***Z*-14p** (1.21 g, quant.) as a colorless oil; IR (neat) ν 3150, 2984, 1719, 1621, 1473, 1205, 1175, 1146, 1091, 1043, 943, 886, 750 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.37 (t, 3H, CH_3, ^3J 7.3 Hz), 4.33 (q, 2H, OCH_2, ^3J 7.3 Hz), 6.58 (dd, 1H, ^3J 3.2 Hz, ^4J 1.9 Hz), 7.44 (d, 1H, ^3J 3.2 Hz), 7.61 (d, 1H, ^4J 1.9 Hz), 8.16 (s,

1H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 14.21, 62.67, 109.65, 112.50, 116.73, 129.07, 144.95, 150.01, 163.05; MS (EI, 70 eV) *m/z* (%) 246 ([^{81}Br]M^+, 39), 244 ([^{79}Br]M^+, 40), 165 (51), 137 (100). HRMS Found: 243.9728; Calcd. for $C_9H_9O_3^{79}Br$: 243.9735.

Ethyl (*E*)- and (*Z*)-2-bromo-3-(5-bromofuran-2-yl)acrylate (**14q**). – General Procedure B (solvent-reduced Wittig olefination) – A mixture of 5-bromofur-2-ylaldehyde (**13L**) (875 mg, 5.0 mmol) and the phosphorane **3b** (2.98 g, 7.0 mmol) in chloroform (2 mL) was added to a flat-bottomed flask sealed with Saran Wrap. The mixture was heated to 100°C. A small amount of chloroform was lost due to evaporation and a homogeneous melt formed. The ensuing mixture was kept at 100°C for 1h. After cooling to rt, the mixture was subjected directly to column chromatography on silica gel (hexane/ether/$CHCl_3$, 4:1:1) to yield ***E*-14q** [25] (184 mg, 11%) and ***Z*-14q** [25] (1.35 g, 83%), for an overall yield of 94%.

(*Z*)-3-(2-Ethoxyphenyl)-2-bromoacrylic acid (**15a**) – General Procedure C (Saponification) – To an ice-cooled mixture of **14b** (437 mg, 1.5 mmol) and NaOMe (400 mg, 7.4 mmol) in MeOH (5 mL), 30 wt % aq. H_2O_2 (0.4 mL, 3.5 mmol) was added. The solution was stirred at rt for 6h. Subsequently, it was neutralized with 4N HCl. The precipitate formed was filtered and dried to yield **15a** (405 mg, quant.) as colorless needles, mp. 174°C; IR (KBr) ν 3452 (bs, OH), 1682, 1597, 1411, 1246, 1164, 1118, 1038, 995, 744 cm^{-1}; ^{1}H NMR (270 MHz, DMSO-d^6) δ 1.34 (t, 3H, ^3J 6.7 Hz, CH_3), 4.10 (q, 2H, ^3J 6.7 Hz, OCH_2), 6.99 – 7.10 (m, 2H), 7.42 (dd, 1H, ^3J 7.8 Hz, ^3J 7.5 Hz), 7.95 (d, 1H, ^3J 7.8 Hz), 8.34 (s, 1H), 13.55 (bs, OH); ^{13}C NMR (67.8 MHz, DMSO-d^6) δ 14.55 (+, CH_3), 63.81 (-, OCH_2), 112.18 (+, CH), 114.75 (C_{quat}), 119.88 (+, CH), 122.19 (C_{quat}), 129.14 (+, CH), 131.74 (+, CH), 135.58 (+, CH), 156.74 (C_{quat}), 164.20 (C_{quat}, CO); MS (EI, 70 eV) *m/z* (%) 272 ([^{81}Br]M^+, 59), 270 ([^{79}Br]M^+, 60), 226 (33), 224 (32), 198 (32), 196 (33), 163 (78), 145 (100). HRMS Found: 269.9895. Calcd. for $C_{11}H_{11}O_3^{79}Br$: 269.9892. Calcd. for $C_{11}H_{11}BrO_3$: C, 48.72; H, 4.09%. Found: C, 48.61; H, 4.04%.

(*E*)-3-(*p*-Methoxyphenyl)-4-[5-(*p*-methoxyphenyl)fur-2-yl]but-3-en-2-one (**20c**) – General Procedure D (Suzuki-Miyaura coupling with 2-iodoprop-2-enones) – A mixture of **18n** (156 mg, 0.45 mmol), *p*-methoxyphenylboronic acid (222 mg, 1.46 mmol), $Pd(PPh_3)_2Cl_2$ (6.3 mg, $9{\cdot}10^{-6}$ mol) and PPh_3 (4.7 mg, $1.8{\cdot}10^{-5}$ mol) in DME (6 mL) and aq. Na_2CO_3 (1.5 M, 3.5 mL) was held at 70 °C for 9h. Thereafter, the cooled mixture was diluted with chloroform (15 mL) and poured into water (15 mL). The mixture was extracted with chloroform (2 x 10 mL) and the organic phase was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was subjected to column chromatography on silica gel (hexane/ether/$CHCl_3$, 3:1:1) to yield **20c** (112 mg, 72%) as a yellow solid; mp. 139°C; IR (KBr) νg096, 3004, 1657, 1605, 1505, 1470, 1368, 1250, 1227, 1179, 1028, 833, 803 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.30 (s, 3H, CH_3), 3.82 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 6.13 (d, 1H, ^3J 3.8 Hz), 6.44 (d, 1H, ^3J 3.8 Hz), 6.84 (d, 2H, 3J 8.9 Hz), 7.02 (d, 2H, ^3J 8.6 Hz), 7.16 (d, 2H, ^3J 8.6 Hz), 7.32 (d, 2H, ^3J 8.9 Hz), 7.54 (s, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 27.68 (+, CH_3), 55.32 (2C, +, OCH_3), 106.24 (+, CH), 114.12 (2C, +, CH), 114.36 (+, 2C, CH), 118.70 (+, CH), 122.74 (C_{quat}), 125.72 (2C, +,

CH), 126.27 (+, CH), 129.78 (C_{quat}), 130.34 (2C, +, CH), 135.97 (C_{quat}), 149.96 (C_{quat}), 156.06 (C_{quat}), 159.28 (C_{quat}), 159.76 (C_{quat}), 198.49 (C_{quat}, CO); MS (EI, 70 eV) *m/z* (%) 348 (M^+, 100), 305 (24). HRMS Found: 348.1361. Calcd. for $C_{22}H_{20}O_4$: 348.1362. Calcd. for $C_{22}H_{20}O_4$: C, 75.84; H, 5.79%. Found: C, 75.45; H, 5.77%.

Ethyl (*Z*)-2-bromo-3-(4-methoxyphenyl)acrylate (***Z*-14d**) [26]; methyl (*E*)-2-bromo-3-(4-methoxyphenyl)acrylate (***E*-14e**) [24, a,b], methyl (*Z*)-2-bromo-3-(4-methoxyphenyl)acrylate (***Z*-14e**) [27], (*E*)- and (*Z*)-methyl 3-(4-bromophenyl)-2-bromoacrylate (**14h**) [27], ethyl (*E*)-2-bromocinnamate (***E*-14i**) [24, a,b]; ethyl (*Z*)-2-bromocinnamate (***Z*-14i**) [17, a], [28]; ethyl (*Z*)-2-bromo-(*p*-tolyl)acrylate (**14j**) [29]; ethyl (*Z*)-2-bromo-(4-nitrophenyl) acrylate (**14m**) [30]; ethyl (*E*)- and (*Z*)-2-bromo-3-(5-bromofuran-2-yl)acrylate (**14q**) [25], ethyl (*Z*)-2-bromo-3-(thien-2-yl)acrylate (***Z*-14r**) [25], [26, a], methyl (*E*)-2-bromo-(3-thien-2-yl)acrylate (***E*-14s**) [28], (*Z*)-methyl 2-bromohept-2-enoate (**16c**)[28]; (*Z*)-methyl 2-bromo-5-phenylpenta-2,4-dienoate (**14u**) [31]; (*Z*)-3-(4-methoxyphenyl)-2-bromoacrylic acid (**15b**) [27],(*Z*)-3-(4-bromophenyl)-2-bromoacrylic acid (**15c**) [27], (*Z*)-3-(4-cyanophenyl)-2-bromoacrylic acid (**15d**) [32], (*Z*)-3-(2-nitrophenyl)-2-bromoacrylic acid (**15e**) [33], (*Z*)-3-(thien-2-yl)-2-bromoacrylic acid (**15f**) [25]; (*Z*)-2-bromo-hex-2-enoic acid (**16b**) [34], (*Z*)-2-bromo-hept-2-enoic acid (**16d**) [34]; (*Z*)-4-(2-ethoxyphenyl)-2-but-3-en-2-one (**18b**) [35]; (*Z*)-4-(4-methoxyphenyl)-3-bromobut-3-en-2-one (**18c**) [36]; (*E*)-4-(4-nitrophenyl)-3-bromobut-3-en-2-one (***E*-18f**) [17, 30] are known compounds.

3.2 Selected spectroscopic and analytical data include

Ethyl (*Z*)-2-bromo-3-(2-ethoxyphenyl)acrylate (**14a**); oil; IR (neat) ν 2970, 1719, 1600, 1235 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.38 (t, 3H, ^3J 7.0 Hz), 1.45 (t, 3H, ^3J 7.0 Hz), 4.12 (q, 2H, ^3J 7.0 Hz), 4.35 (q, 2H, ^3J 7.0 Hz), 6.90 (d, 1H, ^3J 8.1 Hz), 7.00 (dd, 1H, ^3J 7.6 Hz, ^3J 7.6 Hz), 7.39 (ddd, 1H, ^3J 8.1 Hz, ^3J 7.6 Hz, ^4J 1.6 Hz), 8.06 (dd, 1H, ^3J 7.6 Hz, ^4J 1.6 Hz), 8.50 (s, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 14.20 (+, CH_3), 14.72 (+, CH_3), 62.58 (-), 64.07 (-), 111.56 (+, CH), 113.48 (C_{quat}), 119.86 (+, CH), 120.63 (C_{quat}), 129.80 (+, CH), 131.41 (+, CH), 136.69 (+, CH), 157.30 (C_{quat}), 162.35 (C_{quat}, CO); MS (EI, 70 eV) *m/z* (%) 300 ([^{81}Br]M^+, 33), 298 ([^{79}Br]M^+, 34), 191 (37), 173 (50), 163 (47), 145 (85). HRMS Found: 298.0203. Calcd. for $C_{13}H_{15}O_3^{79}Br$: 298.0205.

Methyl (*Z*)-2-bromo-3-(2-ethoxyphenyl)acrylate (**14b**); colorless needles; mp. 59°C; IR (KBr) ν 2970, 1720, 1601, 1490, 1455, 1301, 1263, 1238, 1039, 763 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.42 (t, 3H, ^3J 7.0 Hz), 3.90 (s, 3H, $CO_2C\underline{H}_3$), 4.09 (q, 2H, OCH_2, ^3J 7.0 Hz), 6.90 (d, 1H, ^3J 8.1 Hz), 7.00 (m, 1H), 7.38 (m, 1H), 8.05 (dd, 1H, ^3J 7.8 Hz, ^4J 1.4 Hz), 8.49 (s, 1H);^{13}C NMR (67.8 MHz, $CDCl_3$) δ 14.74 (+, CH_3), 53.47 (+, CH_3), 64.08 (-, CH_2), 111.55 (+, CH), 112.91 (C_{quat}), 119.85 (+, CH), 122.99 (C_{quat}), 129.82 (+, CH), 131.48 (+, CH), 137.09 (+, CH), 157.32 (C_{quat}), 164.08 (C_{quat}, CO); MS (EI, 70 eV) *m/z* (%) 286 ([^{81}Br]M^+, 53), 284 ([^{79}Br]M^+, 53), 177 (90), 173 (42), 145 (100), 89 (49). HRMS Found: 284.0047. Calcd. for $C_{12}H_{13}O_3^{79}Br$: 284.0048. Calcd. for $C_{12}H_{13}BrO_3 0.15H_2O$: C, 50.06; H, 4.62%. Found: C, 49.84; H, 4.51%.

(*Z*)-Ethyl 3-(2-hydroxyphenyl)-2-bromoacrylate (**14c**); slowly crystallizing oil; IR (KBr) ν 3362 (bs, OH), 1688, 1602, 1458, 1363, 1299, 1253, 1187, 1154, 1034, 752 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.38 (t, 3H, CH_3, ^3J 7.0 Hz), 4.36 (q, 2H, OCH_2, ^3J 7.0 Hz), 6.05 (s, 1H, OH), 6.88 (d, 1H, ^3J 7.9 Hz), 6.98 (dd, 1H, ^3J 7.9 Hz, ^3J 7.9 Hz), 7.29 (dd, 1H, ^3J 7.9 Hz, ^3J 7.9 Hz), 8.00 (d, 1H, ^3J 7.9 Hz); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 14.16 (+, CH_3), 60.94 (-, OCH_2), 113.98 (C_{quat}), 115.79 (+, CH), 120.25 (+, CH), 121.32, (C_{quat}), 129.73 (+, CH), 131.49 (+, CH), 136.46 (+,CH), 154.46 (C_{quat}), 163.82 (C_{quat}, CO). MS (EI, 70 eV) *m/z* (%) 272 ([^{81}Br]M$^+$, 22), 270 ([^{79}Br]M$^+$, 23), 226 (98), 224 (100), 198 (39), 196 (40). HRMS Found: 269.9892. Calcd. for $C_{11}H_{10}O_3^{79}Br$: 269.9891.

Benzyl (*Z*)-2-bromo-3-(4-methoxyphenyl)acrylate (**14f**), oil; IR (neat) ν 3064, 3039, 2954, 2836, 1721, 1600, 1511, 1458, 1253, 1173, 1029, 8730, 750, 697 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.85 (s, 3H, OCH_3), 5.32 (s, 2H, OCH_2), 6.95 (d, 2H, ^3J 8.9 Hz), 7.30 – 7.45 (m, 5H), 7.90 (d, 2H, ^3J 8.9 Hz), 8.20 (s, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 55.36 (+, OCH_3), 68.12 (-, OCH_2), 109.80 (C_{quat}), 113.85 (+, CH), 126.08 (C_{quat}), 128.19 (+, CH), 128.37 (+, CH), 128.61 (+, CH), 130.04 (C_{quat}), 132.54 (+, CH), 140.76 (+, CH), 161.25 (C_{quat}), 163.51 (C_{quat}, CO); MS (EI, 70 eV) m/z (%) 348 ([^{81}Br]M$^+$, 36), 346 ([^{79}Br]M$^+$, 37), 249 (23), 160 (28), 129 (29). HRMS Found: 346.0205. Calcd. for $C_{17}H_{15}O_3^{79}Br$: 346.0205.

(*Z*)-Ethyl 3-(4-bromophenyl)-2-bromoacrylate (**14g**); colorless oil; IR (neat) ν 2980, 1722, 1613, 1584, 1487, 1400, 1367, 1260, 1073, 1034, 1010, 818, 754 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.39 (t, 3H, CH_3, ^3J 7.0 Hz), 4.35 (q, 2H, OCH_2, ^3J 7.0 Hz), 7.55 (d, 2H, ^3J 8.4 Hz), 7.72 (d, 2H, ^3J 8.4 Hz), 8.14 (s, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 14.20, 62.91, 113.98, 124.54, 131.65, 131.69, 132.63, 139.46, 163.12; MS (EI, 70 eV) *m/z* (%) 336 ([$^{81}Br_2$]M$^+$, 32), 334 ([^{81}Br^{79}Br]M$^+$, 64), 332 ([$^{79}Br_2$]M$^+$, 32), 289 ([$^{79}Br_2$]M$^+$-OC_2H_5, 14). HRMS Found: 333.9030. Calcd. for $C_{11}H_{10}O_2^{79}Br^{81}Br$: 333.9028.

Methyl (*E*)-2-bromo-(4'-cyanophenyl)acrylate) (***E*-14k**); colorless solid; mp. 72°C; IR (KBr) ν 2924, 2220, 1719, 1233, 1002, 899, 837, 820, 547 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.77 (s, 3H, OCH_3), 7.38 (d, 2H, ^3J 8.1 Hz), 7.40 (s, 1H), 7.64 (d, 2H, ^3J 8.1 Hz); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 53.27 (+, OCH_3), 112.42 (C_{quat}), 114.55 (C_{quat}), 118.34 (C_{quat}), 128.66 (2C, +, CH), 132.18 (2C, +, CH), 138.48 (+, CH), 139.14 (C_{quat}), 164.08 (C_{quat}, CO); MS (EI, 70 eV) *m/z* (%) 267 ([^{81}Br]M$^+$, 17), 265 ([^{79}Br]M$^+$, 17), 236 (9), 234 (9), 208 (7), 206 (7), 186 (100), 154 (27), 127 (38). HRMS Found: 264.9741. Calcd. for $C_{11}H_8O_2N^{79}Br$: 264.9738; and methyl (*Z*)-2-bromo-(4'-cyanophenyl)acrylate (***Z*-14k**); colorless needles, mp. 152°C; IR (KBr) ν 3016, 2224, 1713, 1611, 1505, 1427, 1265, 1198, 1024, 923, 847, 821, 768, 750, 606, 550 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.93 (s, 3H, OCH_3), 7.72 (d, 2H, ^3J 8.4 Hz), 7.90 (d, 2H, ^3J 8.4 Hz), 8.21 (s, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 53.90 (+, OCH_3), 113.31 (C_{quat}), 116.18 (C_{quat}), 118.34 (C_{quat}), 130.44 (2C, +, CH), 132.15 (2C, +, CH), 138.13 (C_{quat}), 138.96 (+, CH), 163.21 (C_{quat}); MS (EI, 70 eV) *m/z* (%) 267 ([^{81}Br]M$^+$, 19), 265 ([^{79}Br]M$^+$, 19), 186 (100), 154 (31), 127 (39). HRMS Found: 264.9737. Calcd. for $C_{11}H_8O_2N^{79}Br$: 264.9738. Calcd. for $C_{11}H_8BrNO_2$: C, 49.65; H, 3.03; N, 5.26%. Found: C, 49.74; H, 3.02; N, 5.23%.

Ethyl (*Z*)-2-bromo-(4'-cyanophenyl)acrylate (**14L**); colorless solid; mp. 97°C; IR (KBr) ν 2224, 1712, 1608, 1263, 1199, 1032, 925, 850, 832, 774, 749, 555 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.40 (t, 3H, ^3J 7.3 Hz, CH_3), 4.37 (q, 2H, ^3J 7.3 Hz, OCH_2), 7.71 (d, 2H, ^3J 8.4 Hz), 7.91 (d, 2H, ^3J 8.4 Hz), 8.20 (s, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 14.18 (+, CH_3), 63.21 (-, OCH_2), 113.22 (C_{quat}), 116.82 (C_{quat}), 118.36 (C_{quat}), 130.43 (+, 2C, CH), 132.13 (+, 2C, CH), 138.26 (C_{quat}), 138.60 (+, CH), 162.66 (C_{quat}, CO); MS (EI, 70 eV) m/z (%) 281 ([^{81}Br]M^+, 21), 279 ([^{79}Br]M^+, 20), 201 (57), 175 (100), 134 (60). HRMS Found: 278.9893. Calcd. for $C_{12}H_{10}^{79}BrNO_2$: 278.9895. Calcd. for $C_{12}H_{10}BrNO_2$: C, 51.45; H, 3.60; N, 5.00%. Found: C, 51.52; H, 3.52; N, 5.00%.

Ethyl (*Z*)-3-(2-bromophenyl)-2-bromoacrylate (**14n**); colorless oil; IR (neat) *n* 2970, 1718 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.26 (ddd, 1H, ^3J 8.1 Hz, ^3J 7.8 Hz, ^4J 1.6 Hz), 7.35 (dd, 1H, ^3J 7.8 Hz, ^3J 7.8 Hz), 7.63 (d, 1H, ^3J 8.1 Hz), 7.81 (dd, 1H, ^3J 7.8 Hz, ^4J 1.6 Hz), 8.29 (s, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 14.17 (+, CH_3), 62.95 (-, OCH_2), 116.64 (C_{quat}), 124.26 (C_{quat}), 126.98 (+, CH), 130.63 (+, CH), 130.77 (+, CH), 132.74 (+, CH), 134.73 (C_{quat}), 140.51 (+, CH), 162.78 (C_{quat}, CO); MS (EI, 70 eV) *m/z* (%) 336 ([$^{81}Br_2$]M^+, 3), 334 ([^{81}Br^{79}Br]M^+, 6), 332 ([$^{79}Br_2$]M^+, 3), 289 ([^{81}Br^{79}Br]M^+-OC_2H_5, 5), 227 (97), 225 (100). HRMS Found: 333.9030. Calcd. for $C_{11}H_{10}O_2^{79}Br^{81}Br$: 333.9028.

Ethyl (*Z*)-2-bromo-(2-nitrophenyl)acrylate (**14o**); colorless solid; mp. 61°C; IR (KBr) ν 2970, 1717, 1625, 1523, 1342, 1264, 1033, 857, 840, 789, 748, 692, 622 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.40 (t, 3H, CH_3, ^3J 7.3 Hz), 4.38, (q, 2H, OCH_2, ^3J 7.3 Hz), 7.56 – 7.76 (m, 3H), 8.21 (dd, 1H, ^3J 8.4 Hz, ^4J 1.4 Hz), 8.48 (s, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 14.14, 63.08, 117.32, 124.82, 129.90, 130.93, 131.18, 133.60, 139.11, 146.93, 162.30. MS (FAB, 3-nitrobenzyl alcohol) m/z (%) 302 (^{81}BrMH$^+$, 4), 300 (^{79}BrMH$^+$, 4). HRMS Found: 299.9875. Calcd. for $C_{11}H_{10}O_4N^{79}Br$: 299.9871. Calcd. for $C_{11}H_{10}BrNO_4$: C, 44.02; H, 3.36; N, 4.67%. Found: C, 44.06; H, 3.35; N, 4.66%.

Benzyl (*E*)-2-bromo-3-(thien-2-yl)acrylate (***E*-14t**); oil; IR (neat) ν 1720, 1615 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 5.85 (s, 2H), 7.03 (dd, 1H, ^3J 5.1 Hz, ^3J 3.8 Hz), 7.29 (dd, 1H, ^3J 3.8 Hz, ^4J 1.0 Hz), 7.34 – 7.49 (m, 5H), 7.50 (dd, 1H, ^3J 5.1 Hz, ^4J 1.0 Hz), 7.68 (s, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 68.19 (-, OCH_2), 109.53 (C_{quat}), 127.05 (+, CH), 128.26 (2C, +, CH), 128.44 (+, CH), 128.64 (+, 2C, CH), 131.36 (+, CH), 134.89 (+, CH), 135.27 (+, CH), 135.45 (C_{quat}), 137.50 (C_{quat}), 163.15 (C_{quat}, CO); MS (EI, 70 eV) *m/z* (%) 324 ([^{81}Br]M^+, 21), 322 ([^{79}Br]M^+, 20), 225 (29), 91 (100). HRMS Found: 321.9662. Calcd. for $C_{14}H_{11}O_2^{79}BrS$: 321.9663; and benzyl (*Z*)-2-bromo-3-(thien-2-yl)acrylate (***Z*-14t**); oil, IR (neat) ν 1718, 1617 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δg.32 (s, 2H), 7.16 (dd, 1H, ^3J 5.1 Hz, ^3J 3.5 Hz), 7.36 – 7.46 (m, 5H), 7.56 (d, 1H, ^3J 3.5 Hz), 7.61 (d, 1H, ^3J 5.1 Hz), 8.48 (s, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 68.19 (-), 109.53 (C_{quat}), 127.05 (+, CH), 128.26 (2C, +, CH), 128.44 (+, CH), 128.64 (2C, +, CH), 131.36 (+, CH), 134.89 (+, CH), 135,27 (+, CH), 135.45 (C_{quat}), 137.50 (C_{quat}), 163.15 (C_{quat}, CO); MS (EI, 70 eV) *m/z* (%) 324 ([^{81}Br]M^+, 21), 322 ([^{79}Br]M^+, 20), 225 (25), 91 (100). HRMS Found: 321.9662. Calcd. for $C_{14}H_{11}O_2^{79}BrS$: 321.9663.

Methyl (*Z*)-3-(5-bromoindol-3-yl)-2-bromoacrylate (***Z*-14v**); off-white solid; mp. 173°C

(dec.); IR (KBr) ν 3280 (NH), 1699, 1600, 1508, 1457, 1420, 1277, 1229, 1053, 882, 767, 741, 716, 617 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 3.93 (s, 3H, OCH_3), 7.39 (dd, 1H, ^3J 8.9 Hz, ^4J 1.6 Hz), 7.32 (d, 1H, ^3J 8.9 Hz), 7.95 (s, 1H), 8.53 (d, 1H, ^4J 1.6 Hz), 8.77 (s, 1H, NH); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 53.40 (+, OCH_3), 108.55 (C_{quat}), 111.19 (C_{quat}), 113.00 (+, CH), 114.88 (C_{quat}), 121.25 (+, CH), 126.49 (+, CH), 128.59 (+, CH), 129.65 (C_{quat}), 132.01 (+, CH), 134.01 (C_{quat}), 164.34 (C_{quat}, CO). Calcd. for $C_{12}H_9Br_2NO_2$: C, 40.15; H, 2.53; N, 3.90%. Found: C, 40.26; H, 2.53; N, 3.90%.

Methyl (*Z*)-3-(quinolin-4-yl)-2-bromoacrylate (***Z*-14w**); colorless rhombic crystals; mp. 105°C; IR (KBr) ν 3040, 2942, 1713, 1621, 1582, 1563, 1431, 1265, 1230, 1153, 1020, 852, 766, 743, 579, 463, 420 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 3.98 (s, 3H, OCH_3), 7.57 – 7.89 (m, 4H), 8.18 (d, 1H, ^3J 8.6 Hz), 8.65 (s, 1H), 8.99 (d, 1H, ^3J 4.3 Hz); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 53.92 (+, OCH_3), 119.21 (C_{quat}), 120.45 (+, CH), 123.93 (+, CH), 125.43 (C_{quat}), 127.23 (+, CH), 129.84 (+, CH), 130.27 (+, CH), 137.79 (+, CH), 140.16 (C_{quat}), 148.33 (C_{quat}), 149.87 (+, CH), 162.85 (C_{quat}, CO); MS (EI, 70 eV) *m/z* (%) 293 ([^{81}Br]M^+, 22), 291 ([^{79}Br]M^+, 22), 212 (50). Calcd. for $C_{13}H_{10}BrNO_2$: C, 53.45; H, 3.45; N, 4.79%. Found: C, 53.50; H, 3.42; N, 4.73%; and methyl (*E*)-3-(quinolin-4-yl)-2-bromoacrylate (***E*-14w**); colorless solid; IR (KBr) ν 2980, 1720, 1335, 1231, 991, 896, 854, 764, 583 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 3.56 (s, 3H, OCH_3), 7.24 – 7.91 (m, 4H), 7.88 (s, 1H), 8.15 (d, 1H, ^3J 8.4 Hz), 8.89 (d, 1H, ^3J 4.3 Hz); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 53.13 (+, OCH_3), 116.46 (C_{quat}), 119.66 (+, CH), 124.11 (+, CH), 125.43 (C_{quat}), 127.21 (+, CH), 129.80 (+, CH), 130.12 (+, CH), 137.39 (+, CH), 141.37 (C_{quat}), 148.37 (C_{quat}), 149.84 (+, CH), 163.41 (C_{quat}, CO); MS (EI, 70 eV) *m/z* (%) 293 ([^{81}Br]M^+, 40), 291 ([^{79}Br]M^+, 39), 212 (100). HRMS Found: 290.9897. Calcd, for $C_{13}H_{10}O_2N^{79}Br$: 290.9895.

(*Z*)-3-(5-Bromoindol-3-yl)-2-bromoacrylic acid (**15g**); colorless solid; mp. > 250°C; IR (KBr) ν 3408 (bs, OH), 1674, 1601, 1520, 1498, 1456, 1283, 1107, 1019, 891, 790 cm^{-1}; ^1H NMR (270 MHz, DMSO-d^6) δ 7.34 (d, 1H, ^3J 8.9 Hz, ^4J 2.7 Hz), 7.46 (d, 1H, ^3J 8.9 Hz), 8.01 (s, 1H), 8.49 (s, 1H), 8.56 (d, 1H, ^4J 2.7 Hz), 12.18 (bs, 1H, NH), 13.14 (bs, 1H, OH); ^{13}C NMR (67.8 MHz, DMSO-d^6) δ 108.46, 109.32, 113.50, 114.30, 120.55, 125.36, 129.27, 130.02, 131.70, 134.34, 164.41; MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 345 ([^{81}Br^{79}Br]M^+, 9). HRMS Found: 344.8835. Calcd. for $C_{11}H_7O_2N^{79}Br^{81}Br$: 344.8823.

Methyl (*E*)-2-bromohex-2-enoate (***E*-16a**); oil; IR (neat) ν 2960, 2870, 1723, 1616, 1434, 1359, 1226, 1132, 1024, 911, 749 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.95 (t, 3H, ^3J 7.8 Hz), 1.51 (m, 2H), 2.48 (dd, 2H, ^3J 7.8 Hz, ^3J 7.6 Hz), 3.82 (s, 3H, $CO_2C\underline{H}_3$), 6.69 (t, 1H, ^3J 7.8 Hz); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 13.67, 22.03, 33.36, 52.82, 110.66, 149.36, 163.42; MS (EI, 70 eV) *m/z* (%) 208 ([^{81}Br]M^+, 1.8), 206 ([^{79}Br]M^+, 1.9), 149 (40), 133 (29). HRMS Found: 205.9941. Calcd. for $C_7H_{11}O_2^{79}Br$: 205.9942; and methyl (*Z*)-2-bromohex-2-enoate (***Z*-16a**); oil; IR (neat) ν 2926, 1730, 1625, 1495, 1260, 1132, 1034, 911, 749 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.98 (t, 3H, ^3J 7.3 Hz), 1.53 (tt, 2H, ^3J 7.3 Hz, ^3J 7.3 Hz), 2.33 (dt, 2H, ^3J 7.3 Hz, ^3J 7.3 Hz), 3.83 (s, 3H, $CO_2C\underline{H}_3$), 7.31 (t, 1H, ^3J 7.3 Hz); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 13.86 (+, CH_3), 20.95 (-), 34.06 (-), 53.25

(-), 115.85 (C_{quat}), 146.58 (+, CH), 163.08 (C_{quat}, CO); MS (EI, 70 eV) *m/z* (%) 208 ([^{81}Br]M^+, 46), 206 ([^{79}Br]M^+, 48). HRMS Found: 205.9943. Calcd. for $C_7H_{11}O_2^{79}Br$: 205.9942.

Methyl (*Z*)-2-iodo-3-(5-bromofuran-2-yl)acrylate (**17a**); oil; IR (neat) ν 3010, 2950, 1716, 1606, 1468, 1433, 1250, 1160, 1034, 973, 929, 898, 790, 748 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.88 (s, 3H, COOC<u>H</u>$_3$), 6.52 (d, 1H, ^3J 3.5 Hz), 7.55 (d, 1H, ^3J 3.5 Hz), 8.31 (s, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 53.88 (+, OCH_3), 84.55 (C_{quat}), 114.00 (+, CH), 118.23 (+, CH), 126.22 (C_{quat}), 134.81 (+, CH), 152.89 (C_{quat}), 163.94 (C_{quat}, CO); MS (EI, 70 eV) m/z (%) 358 ([^{81}Br]M^+, 43), 356 ([^{79}Br]M^+, 43), 277 (100). HRMS Found: 355.8550. Calcd. for $C_8H_6O_3^{79}BrI$: 355.8545.

Methyl (*Z*)-2-iodo-(*p*-tolyl)acrylate (**17b**); oil; IR (neat)gν 3024, 2948, 1718, 1599, 1510, 1434, 1233, 1199, 1034, 898, 812, 747, 587 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.38 (s, 3H, CH_3), 3.89 (s, 3H, OCH_3), 7.24 (d, 2H, ^3J 8.4 Hz), 7.73 (d, 2H, ^3J 8.4 Hz), 8.26 (s, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 21.56 (+, CH_3), 53.78 (+, OCH_3), 88.47 (C_{quat}), 129.00 (2C, +, CH), 129.65 (2C, +, CH), 132.37 (C_{quat}), 140.67 (C_{quat}), 148.19 (+, CH), 164.42 (C_{quat}, CO); MS (EI, 70 eV) *m/z* (%) 302 (93), 175 (100). HRMS Found: 301.9800. Calcd. for $C_{11}H_{11}O_2I$: 301.9804.

Methyl (*Z*)-2-iodo-(4-cyanophenyl)acrylate (**17c**); colorless needles; mp. 125°C; IR (KBr) ν 2995, 2222, 1709, 1428, 1257, 1205, 1020, 850, 823, 587, 551 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.92 (s, 3H, COOC<u>H</u>$_3$), 7.71 (d, 2H, ^3J 8.1 Hz), 7.81 (d, 2H, ^3J 8.1 Hz), 8.26 (s, 1H); ^{13}C NMR (67.8 MHz) δ 54.14 (+, OCH_3), 94.19 (C_{quat}), 113.19 (C_{quat}), 118.40 (C_{quat}), 129.72 (2C, +, CH), 132.13 (2C, +, CH), 140.20 (C_{quat}), 146.23 (+, CH), 163.74 (C_{quat}, CO); MS (EI, 70 eV) *m/z* (%) 313 (82), 186 (100). HRMS Found: 312.9604. Calcd. for $C_{11}H_8O_2NI$: 312.9600. Calcd. for $C_{11}H_8INO_2$: C, 42.20; H, 2.58; N, 4.47%. Found: C, 42.95; H, 2.55; N, 4.52%.

Ethyl (*Z*)-2-iodo-(4-cyanophenyl)acrylate (**17d**); colorless solid; mp. 65°C; IR (KBr) ν 2998, 2222, 1706, 1600, 1504, 1244, 1196, 1065, 1022, 853, 825, 757, 587, 553 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.39 (t, 3H, ^3J 7.0 Hz), 4.34 (q, 2H, ^3J 7.0 Hz), 7.62 (d, 2H, ^3J 8.4 Hz), 7.81 (d, 2H, ^3J 8.4 Hz), 8.24 (s, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 14.19 (+, CH_3), 63.43 (-, OCH_2), 95.25 (C_{quat}), 113.12 (C_{quat}), 118.42 (C_{quat}), 129.73 (+, 2C, CH), 132.11 (+, 2C, CH), 140.33 (C_{quat}), 145.85 (+, CH), 163.21 (C_{quat}, CO); MS (EI, 70 eV) *m/z* (%) 327 (M^+, 86), 282 (22), 200 (43), 172 (100), 127 (59). HRMS Found: 326.9752. Calcd. for $C_{12}H_{10}O_2NI$: 326.9756. Calcd. for $C_{12}H_{10}INO_2$: C, 44.06; H, 3.08; N, 4.28%. Found: C, 44.11; H, 3.06; N, 4.27%.

(*Z*)-4-(2-Ethoxyphenyl)-2-bromobut-3-en-2-one (**18a**); oil; IR (neat) ν 2980, 2930, 1687, 1600, 1470, 1456, 1391, 1294, 1248, 1162, 1137, 1043, 927, 754 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.46 (t, 3H, ^3J 7.1 Hz, CH_3), 2.60 (s, 3H, $COCH_3$), 4.10 (q, 2H, ^3J 7.1 Hz, OCH_2), 6.91 (d, 1H, ^3J 8.1 Hz), 7.02 (m, 1H), 7.36 (m, 1H), 8.13 (dd, 1H, ^3J 7.8 Hz, ^4J 1.6 Hz), 8.36 (s, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 14.74 (+, CH_3), 26.65 (+, CH_3, 64.05 (-, OCH_2), 111.59 (+, CH), 120.11 (+, CH), 122.89 (C_{quat}), 124.21 (C_{quat}), 130.02 (+, CH), 131.89 (+, CH), 136.45 (+, CH), 157.46 (C_{quat}), 192.93 (C_{quat}, CO); MS (EI,

70 eV) *m/z* (%) 270 ([^{81}Br]M$^+$, 45), 268 ([^{79}Br]M$^+$, 46), 225 (100), 223 (73), 189 (48), 161 (62). HRMS Found: 268.0093. Calcd. for $C_{12}H_{13}O_2^{79}Br$: 268.0099.

(*E*)-4-(4-Bromophenyl)-3-bromobut-3-en-2-one (***E*-18d**); pale yellow solid; mp. 45°C; IR (neat)gν 1706, 1586, 1486, 1359, 1199, 1173, 1073, 1010, 893, 814 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.32 (s, 3H, $COCH_3$), 7.14 (d, 2H, ^3J 8.4 Hz), 7.20 (s, 1H), 7.48 (d, 2H, ^3J 8.4 Hz); ^{13}C NMR (67.8 MHz, $CDCl_3$) δg9.00 (+, CO$\underline{C}H_3$), 121.35 (C_{quat}), 123.60 (C_{quat}), 129.92 (2C, +, CH), 131.91 (2C, +, CH), 133.47 (C_{quat}), 135.84 (+, CH), 197.45 (C_{quat}, CO); MS (EI, 70 eV) *m/z* (%) 306 ([$^{81}Br_2$]M$^+$, 16), 304 ([^{81}Br^{79}Br]M$^+$, 31), 302 ([$^{79}Br_2$]M$^+$, 16), 225 (99), 223 (100), 182 (23), 180 (22), 101 (27). HRMS Found: 303.8925. Calcd. for $C_{10}H_8O^{79}Br^{81}Br$: 303.8922; and (*Z*)-4-(4-bromophenyl)-3-bromobut-3-en-2-one (***Z*-18d**), colorless plates; mp. 106°C; IR (KBr) ν 1674, 1596, 1487, 1401, 1354, 1275, 1225, 1199, 1003, 889, 808, 654, 608, 563, 520 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.60 (s, 3H, CH_3), 7.58 (d, 2H, ^3J 8.6 Hz), 7.74 (d, 2H, ^3J 8.6 Hz), 7.96 (s, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 27.10 (CO$\underline{C}H_3$), 123.72 (C_{quat}), 124.79 (C_{quat}), 131.78 (2C, +, CH), 131.81 (2C, +, CH), 132.55 (C_{quat}), 138.42 (+, CH), 193.24 (C_{quat}, CO); MS (EI, 70 eV) *m/z* (%) 306 ([$^{81}Br_2$]M$^+$, 15), 304 ([^{81}Br^{79}Br]M$^+$, 30), 302 ([$^{79}Br_2$]M$^+$, 15), 225 (99), 223 (100), 182 (23), 180 (23), 101 (31). HRMS Found: 303.8925. Calcd. for $C_{10}H_8O^{79}Br^{81}Br$: 303.8922; Calcd. for $C_{10}H_8Br_2O$: C, 39.51; H, 2.65%. Found: C, 39.55; H, 2.66%.

(*E*)-4-(4-Methylphenyl)-3-bromobut-3-en-2-one (***E*-18e**); oil; IR (neat) ν 2922, 1703, 1610, 1354, 1254, 1169, 1037, 898, 811, 744 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.27 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 7.15 (s, 4H), 7.31 (s, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 21.36 (+, CH_3), 29.05 (+, CH_3), 120.06 (C_{quat}), 129.39 (2C, +, CH), 129.44 (2C, +, CH), 131.93 (C_{quat}), 137.51 (+, CH), 139.45 (C_{quat}), 197.95 (C_{quat}, CO); MS (EI, 70 eV) *m/z* (%) 240 ([^{81}Br]M$^+$, 28), 238 ([^{79}Br]M$^+$, 29), 225 (72), 223 (76), 163 (100), 124 (88), 78 (33). HRMS Found: 237.9996. Calcd. for $C_{11}H_{11}O^{79}Br$: 237.9993; and (*Z*)-4-(4-methylphenyl)-3-bromobut-3-en-2-one (***Z*-18e**); pale yellow solid; mp. 43°C; IR (KBr) νg032, 1675, 1595, 1283, 1226, 1200, 1183, 1004, 888, 810, 574, 517 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.40 (s, 3H, CH_3), 2.60 (s, 3H, CH_3), 7.25 (d, 2H, ^3J 8.1 Hz), 7.81 (d, 2H, ^3J 8.1 Hz), 8.01 (s, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 21.60 (+, CH_3), 27.00 (+, CH_3), 122.33 (C_{quat}), 129.26 (2C, +, CH), 130.66 (2C, +, CH), 130.82 (C_{quat}), 140.09 (+, CH), 141.13 (C_{quat}), 193.13 (C_{quat}, CO); MS (EI, 70 eV) *m/z* (%) 240 ([^{81}Br]M$^+$, 28), 238 ([^{79}Br]M$^+$, 28), 225 (55), 223 (56), 163 (100), 124 (67), 78 (53). HRMS Found: 237.9991. Calcd. for $C_{11}H_{11}^{79}BrO$: 237.9993. Calcd. for $C_{11}H_{11}BrO$: C, 55.25; H, 4.64%. Found: C, 55.42; H, 4.72%.

(*E*)-4-(4-Cyanophenyl)-3-bromobut-3-en-2-one (***E*-18g**); colorless solid, mp. 70°C; IR (neat) ν 2920, 2220, 1715, 1608, 1500, 1411, 1359, 1255, 1202, 1039, 899, 827, 757 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.38 (s, 3H, CH_3), 7.22 (s, 1H), 7.38 (d, 2H, ^3J 8.1 Hz), 7.63 (d, 2H, ^3J 8.1 Hz); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 28.90 (+, CO$\underline{C}H_3$), 112.51 (C_{quat}), 118.31 (C_{quat}), 123.58 (C_{quat}), 128.91 (2C, +, CH), 132.37 (2C, +, CH), 134.80 (+, CH), 138.89 (Cquat), 196.91 (C_{quat}, CO); MS (EI, 70 eV) *m/z* (%) 251 ([^{81}Br]M$^+$, 12), 249

([^{79}Br]M$^+$, 12), 173 (31), 134 (19). HRMS Found: 248.9787. Calcd. for $C_{11}H_8ON^{79}Br$: 248.9789; and (*Z*)-4-(4-cyanophenyl)-3-bromobut-3-en-2-one (***Z*-18g**); colorless plates, mp. 143°C; IR (KBr) ν 3028, 2224, 1682, 1607, 1498, 1428, 1408, 1359, 1220, 1203, 1007, 901, 826, 573, 555 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.62 (s, 3H, CH_3), 7.73 (d, 2H, ^3J 8.6 Hz), 7.91 (d, 2H, ^3J 8.6 Hz), 8.01 (s, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 26.81 (CO$\underline{C}$H$_3$), 112.96 (C$_{quat}$), 117.93 (C$_{quat}$), 125.31 (C$_{quat}$), 130.14 (2C, +, CH), 131.76 (2C, +, CH), 136.71 (+, CH), 137.83 (C$_{quat}$), 192.44 (C$_{quat}$, CO); MS (EI, 70 eV) *m/z* (%) 251 ([^{81}Br]M$^+$, 42), 249 ([^{79}Br]M$^+$, 43), 173 (100), 134 (54). HRMS Found: 248.9789. Calcd. for $C_{11}H_8ON^{79}Br$: 248.9789. Calcd. for $C_{11}H_8BrNO$: C, 52.83; H, 3.22; N, 5.60%. Found: C, 52.80; H, 3.15; N, 5.57%.

(*E*)-4-(5-Bromofuran-2-yl)-3-bromobut-3-en-2-one (***E*-18h**); pale yellow oil; IR (neat) ν 3030, 2920, 1684, 1604, 1560, 1459, 1371, 1331, 1217, 1187, 1024, 968, 928, 915, 793, 717 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.53 (s, 3H, CH_3), 6.39 (d, 1H, ^3J 3.8 Hz), 7.04 (s, 1H), 7.24 (d, 1H, ^3J 3.8 Hz); ^{13}C NMR (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135) δ 29.42 (+, CH_3), 114.41 (+, CH), 116.50 (C$_{quat}$), 117.95 (+, CH), 125.15 (C$_{quat}$), 126.13 (+, CH), 151.75 (C$_{quat}$), 195.41 (C$_{quat}$, CO); MS (EI, 70 eV) *m/z* (%) 296 ([$^{81}Br_2$]M$^+$, 13), 294 ([^{81}Br^{79}Br]M$^+$, 26), 292 ([$^{79}Br_2$]M$^+$, 14), 215 (76), 213 (80). HRMS Found: 293.8717. Calcd. for $C_8H_6O_2^{79}Br^{81}Br$: 293.8735; and (*Z*)-4-(5-bromofuran-2-yl)-3-bromobut-3-en-2-one (***Z*-18h**); colorless solid; mp. 82°C; IR (KBr) ν 3036, 1674, 1611, 1464, 1231, 1016, 957, 928, 876, 788, 630, 596, 568 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.56 (s, 3H, CH_3), 6.54 (d, 1H, ^3J 3.8 Hz), 7.48 (d, 1H, ^3J 3.8 Hz), 7.93 (s, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135) δ 26.42 (+, CH_3), 114.71 (+, CH), 119.57 (+, CH), 119.91 (C$_{quat}$), 126.70 (C$_{quat}$), 127.16 (+, CH), 151.98 (C$_{quat}$), 191.76 (C$_{quat}$, CO); MS (EI, 70 eV) *m/z* (%) 296 ([$^{81}Br_2$]M$^+$, 6.7), 294 ([^{81}Br^{79}Br]M$^+$, 13), 292 ([$^{79}Br_2$]M$^+$, 6.7), 215 (80), 213 (81), 58 (100). HRMS Found: 293.8711. Calcd. for $C_8H_6O_2^{79}Br^{81}Br$: 293.8735. Calcd. for $C_8H_6O_2^{79}Br^{81}Br$: 293.8735. Calcd. for $C_8H_6Br_2O_2$: C, 32.69; H, 2.06%. Found: C, 32.71; H, 2.07%.

(*E*)-4-(Thien-2-yl)-3-bromobut-3-en-2-one (***E*-18i**); oil; IR (neat) ν 3100, 2972, 2920, 1677, 1592, 1550, 1417, 1380, 1354, 1322, 1247, 1216, 1195, 1173, 1058, 977, 928, 895, 856, 749, 716 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.56 (s, 3H, CH_3), 7.06 (dd, 1H, ^3J 5.3 Hz, ^3J 3.4 Hz), 7.34 (d, 1H, ^3J 3.4 Hz), 7.49 (d, 1H, ^3J 5.3 Hz), 7.50 (s, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 29.97 (+, CH_3), 115.27 (C$_{quat}$), 127.08 (+, CH), 131.61 (+, CH), 134.96 (+, CH), 135.82 (+, CH), 137.21 (C$_{quat}$), 195.85 (C$_{quat}$, CO), MS (EI, 70 eV) *m/z* (%) 232 ([^{81}Br]M$^+$, 2.9), 230 ([^{79}Br]M$^+$, 3.0), 97 (56), 95 (56), 78 (100). HRMS Found: 229.9393. Calcd. for $C_8H_7O^{79}BrS$: 229.9401; and (*Z*)-4-(thien-2-yl)-3-bromobutenone (***Z*-18i**); oil; IR (neat) ν 2928, 1668, 1599, 1417, 1359, 1246, 1194, 1095, 1000, 892, 856, 713 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.59 (s, 3H, CH_3), 7.19 (dd, 1H, ^3J 5.3 Hz, ^3J 3.6 Hz), 7.61 (d, 1H, ^3J 3.6 Hz), 7.65 (d, 1H, ^3J 5.3 Hz), 8.30 (s, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 26.90 (+, CH_3), 120.17 (C$_{quat}$), 127.21 (+, CH), 131.83 (+, CH), 133.60 (+, CH), 135.77 (+, CH), 137.66 (C$_{quat}$), 192.28 (C$_{quat}$, CO); MS (EI, 70 eV) *m/z* (%) 232 ([^{81}Br]M$^+$, 34), 230 ([^{79}Br]M$^+$, 34), 151 (100), 108 (41); HRMS Found: 229.9408. Calcd. for $C_8H_7O^{79}BrS$: 229.9401.

(*Z*)-4-(5-Bromoindol-3-yl)-but-3-en-2-one (**18j**); colorless solid; mp. > 250°C; IR (KBr) ν 3248, 1658, 1592, 1566, 1503, 1454, 1331, 1273, 1223, 1136, 1122, 1002, 880, 743, 622 cm^{-1}; ^1H NMR (270 MHz, DMSO-d^6) δ 2.63 (s, 3H, CH_3), 7.35 (d, 1H, ^3J 8.9 Hz), 7.47 (d, 1H, ^3J 8.9 Hz), 8.34 (s, 1H), 8.56 (s, 1H), 8.67 (s, 1H), 12.26 (bs, NH); ^{13}C NMR (67.8 MHz, DMSO-d^6) δ 25.91, 109.78, 113.66, 114.25, 119.62, 121.26, 125.48, 129.49, 130.85, 134.06, 134.43, 191.08; MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 343 ([$^{79}Br^{81}Br$]M^+, 1.6). HRMS Found: 342.9035. Calcd. for $C_{12}H_9ON^{79}Br^{81}Br$: 342.9031. Calcd. for $C_{12}H_9Br_2NO$: C, 42.02; H, 2.64; N, 4.08%. Found: C, 42.02; H, 2.64; N, 4.01%.

4-(Quinolin-4-yl)-3-bromobut-3-en-2-one (**18k**). IR (neat) ν 2924, 1692, 1582, 1388, 1359, 1214, 762 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 2.70 (s, 3H, CH_3), 7.58 – 7.87 (m, 4H), 8.18 (d, 1H, ^3J 8.4 Hz), 8.46 (s, 1H), 9.00 (d, 1H, ^3J 4.6 Hz); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 27.43 (+, CH_3), 120.45 (+, CH), 123.88(+, CH), 125.47 (C_{quat}), 127.30 (+, CH), 129.02 (C_{quat}), 129.91 (+, CH) 130.37 (+, CH), 135.64 (+, CH), 140.38 (C_{quat}), 148.34 (C_{quat}), 149.87 (+, CH), 192.65 (C_{quat}, CO); MS (EI, 70 eV) *m/z* (%) 277 ([^{81}Br]M^+, 48), 275 ([^{79}Br]M^+, 49), 196 (91), 154 (100). HRMS Found: 274.9940. Calcd. for $C_{13}H_{10}ON^{79}Br$: 274.9946.

(*E*)-4-(4-Cyanophenyl)-3-iodobut-3-en-2-one (***E*-18m**); colorless solid, mp. 108°C; IR (KBr) ν 2228, 1691, 1600, 1358, 1167, 875, 822, 555 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$)gδ 2.32 (s, 3H, CH_3), 7.22 (s, 1H), 7.32 (d, 2H, ^3J 8.4 Hz), 7.63 (d, 2H, ^3J 8.4 Hz); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 27.65 (+, CH_3), 100.85 (C_{quat}), 112.51 (C_{quat}), 118.20 (C_{quat}), 128.55 (2C, +, CH), 132.50 (2C, +, CH), 140.15 (C_{quat}), 140.68 (+, CH), 199.96 (C_{quat}, CO); MS (EI, 70 eV) *m/z* (%) 297 (M^+, 100), 282 (22), 170 (98), 127 (55). HRMS Found: 296.9651. Calcd. for $C_{11}H_8ONI$: 296.9651. Calcd. for $C_{11}H_8INO$: C, 44.47; H, 2.71; N, 4.71%. Found: C, 44.65; H, 2.71; N, 4.70%; and (*Z*)-4-(4-cyanophenyl)-3-iodobut-3-en-2-one (***Z*-18m**); pale yellow rhombic crystals; mp. 158°C; IR (KBr) ν 3008, 2220, 1674, 1595, 1202, 1004, 896, 822, 555 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 2.68 (s, 3H, CH_3), 7.73 (d, 2H, ^3J 8.6 Hz), 7.82 (d, 2H, ^3J 8.6 Hz), 8.00 (s, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 26.08 (+, CH_3), 110.65 (C_{quat}), 113.30 (C_{quat}), 118.34 (C_{quat}), 129.81 (+, 2C, CH), 132.17 (+, 2C, CH), 140.39 (C_{quat}), 145.12 (+, CH), 193.35 (C_{quat}, CO); MS (EI, 70 eV) *m/z* (%) 297 (M^+, 100), 282 (20), 170 (82), 127 (48). HRMS Found: 296.9652. Calcd. for $C_{11}H_8ONI$: 296.9651. Calcd. for $C_{11}H_8INO$: C, 44.47; H, 2.71; N, 4.71%. Found: C, 44.51; H, 2.72; N, 4.70%.

(*E*)-4-(5-Bromofuran-2-yl)-3-iodobut-3-en-2-one (***E*-18n**); oil; IR (neat) ν 3134, 2922, 1703, 1597, 1461, 1354, 1161, 1022, 789, 732 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 2.52 (s, 3H, CH_3), 6.33 (d, 1H, ^3J 4.0 Hz), 6.64 (d, 1H, ^3J 4.0 Hz), 7.49 (s, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 27.84 (+, CH_3), 92.47 (C_{quat}), 113.79 (+, CH), 115.32 (+, CH), 124.78 (C_{quat}), 129.57 (+, CH), 152.74 (C_{quat}), 204.83 (C_{quat}, CO); MS (EI, 70 eV) *m/z* (%) 342 ([^{81}Br]M^+, 23), 340 ([^{79}Br]M^+, 23), 261 (100). HRMS Found: 339.8599. Calcd. for $C_8H_6O_2^{79}BrI$: 339.8596; and (*Z*)-4-(5-bromofuran-2-yl)-3-iodobut-3-en-2-one (***Z*-18n**); colorless solid; mp. 98°C; IR (KBr) ν 3018, 1661, 1603, 1530, 1455, 1364, 1221, 1194, 1016, 998, 954, 925, 892, 789, 615, 549 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 2.62 (s, 3H,

CH_3), 6.56 (d, 1H, ^3J 3.7 Hz), 7.74 (d, 1H, ^3J 3.7 Hz), 8.07 (s, 1H); ^{13}C NMR (67.8 MHz) δ 25.05 (+, CH_3), 102.10 (C_{quat}), 114.28 (+, CH), 118.91 (+, CH), 126.89 (C_{quat}), 134.43 (+, CH), 153.01 (C_{quat}), 192.57 (C_{quat}); MS (EI, 70 eV) *m/z* (%) 342 ([^{81}Br]M$^+$, 8), 340 ([^{79}Br]M$^+$, 8), 261 (100). HRMS Found: 339.8595. Calcd. for $C_8H_6O_2^{79}BrI$: 339.8596. Calcd. for $C_8H_6BrIO_2$: C, 28.18; H, 1.77%. Found: C, 28.37; H, 1.66%.

(*Z*)-2-Bromo-1-(4-bromophenyl)-3-(2-ethoxyphenyl)propenone (**19a**); colorless solid; mp. 105°C; IR (KBr) νg978, 1655, 1586, 1243, 1116, 1076, 1037, 1011, 830, 815, 750 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.39 (t, 3H, ^3J 6.9 Hz), 4.05 (q, 2H, ^3J 6.9 Hz), 6.89 (d, 1H, ^3J 8.2 Hz), 7.04 (dd, 1H, ^3J 8.3 Hz, ^3J 8.3 Hz), 7.42 (dd, 1H, ^3J 8.3 Hz, ^3J 8.2 Hz), 7.63 (d, 2H, ^3J 8.3 Hz), 7.73 (d, 2H, ^3J 8.3 Hz), 8.03 (s, 1H), 8.13 (d, 1H ^3J 7.6 Hz); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 14.79, 63.87, 111.27, 120.03, 122.57, 122.69, 127.37, 129.72, 131.37 (2C), 131.59 (2C), 131.88, 135.59, 139.82, 157.19, 190.58; MS (70 eV) *m/z* 412 ([$^{81}Br_2$]M$^+$, 13), 410 ([^{81}Br^{79}Br]M$^+$, 26), 408 ([$^{79}Br_2$]M$^+$, 14), 367 (20), 365 (40), 363 (21), 331 (29), 329 (30), 185 (98), 183 (100). HRMS Found: 409.9341. Calcd. for $C_{17}H_{14}O_2^{79}Br^{81}Br$: 409.9341.

(*Z*)-4-[2-Bromo-3-(4-bromophenyl)-3-oxopropenyl]benzonitrile (**19b**); colorless needles; mp. 105°C; IR (KBr) ν 2226, 1659, 1611, 1581, 1258, 1174, 1071, 1052, 1007, 885, 823, 755, 549 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.66 (d, 2H, ^3J 8.6 Hz), 7.71 (d, 2H, ^3J 8.6 Hz), 7.74 (d, 2H, ^3J 8.3 Hz), 7.91 (d, 2H, ^3J 8.3 Hz), ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 113.43 (C_{quat}), 118.26 (C_{quat}), 124.59 (C_{quat}), 128.50 (C_{quat}), 130.34 (2C, +, CH), 131.28 (2C, +, CH), 132.03 (2C, +, CH), 132.23 (2C, +, CH), 134.23 (C_{quat}), 137.83 (C_{quat}), 139.01 (+, CH), 189.91 (C_{quat}, CO); MS (EI, 70 eV) *m/z* (%) 393 ([$^{81}Br_2$]M$^+$, 15), 391 ([^{81}Br^{79}Br]M$^+$, 30), 389 ([$^{79}Br_2$]M$^+$, 15), 312 (50), 310 (50), 185 (98), 183 (100). HRMS Found: 390.9036. Calcd. for $C_{16}H_9ON^{79}Br^{81}Br$: 390.9031. Calcd. for $C_{16}H_9Br_2NO$: C, 49.14; H, H, 2.32; N, 3.58%. Found: C, 49.21; H, 2.26; N, 3.69%.

(*Z*)-4-[3-(4-Bromophenyl)-2-iodo-3-oxopropenyl]benzonitrile (**19c**); semi-solid; IR (melt) ν 3086, 2922, 2224, 1657, 1580, 1499, 1480, 1397, 1247, 1179, 1068, 1007, 864, 827, 749, 670 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.65 (d, 2H, ^3J 8.4 Hz), 7.73 (d, 2H, ^3J 8.1 Hz), 7.75 (d, 2H, ^3J 8.4 Hz), 7.84 (d, 2H, ^3J 8.1 Hz); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 105.37 (C_{quat}), 113.32 (C_{quat}), 118.33 (C_{quat}), 128.60 (2C, +, CH), 129.65 (C_{quat}), 131.50 (2C, +, CH), 132.09 (2C, +, CH), 132.22 (2C, +, CH), 133.26 (C_{quat}), 139.71 (C_{quat}), 144.88 (+, CH), 191.47 (C_{quat}, CO); MS (FAB, 3-nitrobenzyl alcohol) m/z (%) 440 ([^{81}Br]MH$^+$, 25), 438 ([^{79}Br]MH$^+$, 25). HRMS Found: 437.8990. Calcd. for $C_{16}H_{10}ON^{79}BrI$: 437.8991.

(*Z*)-2-Bromo-3-(5-bromofur-2-yl)-1-(4-iodophenyl)propenone (**19d**); pale yellow needles; mp. 153°C; IR (KBr) ν 1664, 1603, 1457, 1247, 1076, 1024, 1006, 959, 845, 817, 791, 736 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.56 (d, 1H, ^3J 3.8 Hz), 7.43 (d, 2H, ^3J 8.6 Hz), 7.55 (d, 1H, ^3J 3.8 Hz), 7.63 (s, 1H), 7.85 (d, 2H, ^3J 8.6 Hz); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 99.86 (C_{quat}), 114.85 (+, CH), 119.59 (C_{quat}), 119.80 (+, CH), 127.02 (C_{quat}), 130.72 (2C, +, CH), 131.00 (+, CH), 135.75 (C_{quat}), 137.82 (2C, +, CH), 151.61 (C_{quat}), 189.69 (C_{quat}, CO); MS (FAB, 3-nitrobenzyl alcohol) m/z (%) 485 ([$^{81}Br_2$]MH$^+$, 3.8),

483 ([^{81}Br^{79}Br]MH$^+$, 7.3), 481 ([^{79}Br$_2$]MH$^+$, 3.9), 403 (7.8), 401 (7.8). HRMS Found: 482.7914. Calcd. for $C_{13}H_8O_2^{79}Br^{81}BrI$: 482.7916. Calcd. for $C_{13}H_7Br_2IO_2$: C, 32.40; H, 1.46%. Found: C, 32.55; H, 1.44%.

(*Z*)-2-Bromo-3-(5-bromofur-2-yl)-1-(4-bromophenyl)propenone (**19e**); colorless needles; mp. 130°C; IR (KBr) ν 1666, 1603, 1581, 1461, 1248, 1078, 1065, 1025, 1010, 959, 926, 851, 816, 792, 738, 679 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.56 (d, 1H, ^3J 3.6 Hz), 7.55 – 7.66 (m, 5H), 7.62 (s, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 113.56 (+, CH), 119.79 (C_{quat}), 120.02 (+, CH), 127.24 (C_{quat}), 127.64 (C_{quat}), 131.09 (+, CH, 2C), 131.19 (+, CH), 132.11 (+, CH, 2C), 135.41 (C_{quat}), 151.88 (C_{quat}), 189.65 (C_{quat}, CO); MS (EI, 70 ev) *m/z* (%) 438 ([^{81}Br$_3$]M$^+$, 2.0), 436 ([^{81}Br$_2^{79}$Br]M$^+$, 5.9), 434 ([^{81}Br^{79}Br$_2$]M$^+$, 6.0), 432 ([^{79}Br$_3$]M$^+$, 2.0), 357 (50), 355 (100), 353 (51). HRMS Found: 433.7975. Calcd. for $C_{13}H_7O_2^{79}Br_2^{81}Br$: 433.7976. Calcd. for $C_{13}H_7Br_3O_2$: C, 35.90; H, H, 1.62%. Found: C, 36.08; H, 1.58%.

(*Z*)-2-Bromo-3-(5-bromofur-2-yl)-1-(2-methylbiphenyl-4-yl)propenone (**19f**); IR (neat) ν 3144, 3058, 2954, 2924, 1663, 1600, 1459, 1256, 1074, 1020, 788, 752, 702 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.31 (s, 3H, CH_3), 6.57 (d, 1H, ^3J 3.8 Hz), 7.04 – 7.31 (m, 4H), 7.45 (d, 2H ^3J 8.4 Hz), 7.58 (d, 1H, ^3J 3.8 Hz), 7.77 (s, 1H), 7.78 (d, 2H, ^3J 8.4 Hz); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 20.46, 114.75, 119.44, 120.25, 125.96, 126.58, 127.95, 129.34, 129.43, 129.56, 130.54, 130.78, 134.75, 135.20, 140.57, 146.43, 151.83, 190.16; MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 449 ([^{81}Br$_2$]MH$^+$, 5.5), 447 ([^{81}Br^{79}Br]MH$^+$, 11), 445 ([^{79}Br$_2$]MH$^+$, 5.6), 367, 365. HRMS Found: 446.9421. Calcd. for $C_{20}H_{15}O_2^{79}Br^{81}Br$: 446.9420.

Methyl (*E*)-3-(*p*-cyanophenyl)-2-(*p*-methoxyphenyl)acrylate (**20a**); colorless solid; mp. 128°C; IR (KBr) ν 3040, 2940, 2842, 2222, 1706, 1614, 1512, 1293, 1249, 1024, 847, 512 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.82 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 6.90 (d, 2H, ^3J 8.6 Hz), 7.09 (d, 2H, ^3J 8.6 Hz), 7.15 (d, 2H, ^3J 8.4 Hz), 7.45 (d, 2H, ^3J 8.4 Hz), 7.75 (s, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 55.64 (+, OCH_3), 55.23 (+, OCH_3), 111.88 (C_{quat}), 114.28 (2C, +, CH), 118.58 (C_{quat}), 126.67 (C_{quat}), 130.69 (2C, +, CH), 130.87 (2C, +, CH), 131.87 (2C, +, CH), 135.39 (C_{quat}), 137.56 (+, CH), 139.55 (C_{quat}), 159.64 (C_{quat}), 167.90 (C_{quat}, CO); MS (EI, 70 eV) *m/z* (%) 293 (M$^+$, 100), 234 (46), 190 (29), 146 (29). HRMS Found: 293.1049. Calcd. for $C_{18}H_{15}O_3N$: 293.1052.

(*Z*)-4-(*p*-Cyanophenyl)-3-(*p*-methoxyphenyl)-but-3-en-2-one (***Z*-20b**); slowly crystallizing oil; IR (neat) ν 2924, 2224, 1702, 1600, 1510, 1460, 1358, 1250, 1184, 1033, 828 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.26 (s, 3H, CH_3), 3.84 (s, 3H, OCH_3), 6.81 (s, 1H), 6.93 (d, 2H, ^3J 8.6 Hz), 7.35 (d, 2H,^3J 8.6 Hz), 7.42 (d, 2H, ^3J 8.1 Hz), 7.63 (d, 2H, ^3J 8.1 Hz); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 31.40 (+, CH_3), 55.39 (+, OCH_3), 111.21 (C_{quat}), 114.44 (2C, +, CH), 118.63 (C_{quat}), 124.58 (+, CH), 127.93 (2C, +, CH), 128.30 (Cquat), 128.93 (2C, +, CH), 132.37 (2C, +, CH), 140.48 (C_{quat}), 146.55 (C_{quat}), 160.40 (C_{quat}), 206.69 (C_{quat}, CO); MS (EI, 70 eV) *m/z* (%) 277 (M$^+$, 59), 234 (100), 190 (30). HRMS Found: 277.1102. Calcd. for $C_{18}H_{15}NO_2$: 277.1103; and (*E*)-4-(*p*-cyanophenyl)-3-(*p*-methoxyphenyl)-but-3-en-2-one (***E*-20b**); colorless solid; mp. 136°C; IR (KBr) ν 3000,

2954, 2836, 2224, 1669, 1607, 1512, 1354, 1291, 1245, 1179, 1033, 827, 794, 614 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 2.31 (s, 3H, CH_3), 3.85 (s, 3H, OCH_3), 6.93 (d, 2H, ^3J 8.9 Hz), 7.05 (d, 2H, ^3J 8.9 Hz), 7.14 (d, 2H, ^3J 8.4 Hz), 7.45 (d, 2H, ^3J 8.4 Hz), 7.53 (s, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 28.01 (+, CH_3), 55.25 (+, OCH_3), 111.97 (C_{quat}), 114.70 (2C, +, CH), 115.99 (+, CH), 127.64 (C_{quat}), 130.54 (2C, +, CH), 130.89 (2C, +, CH), 131.88 (2C, +, CH), 135.69 (C_{quat}), 139.53 (C_{quat}), 143.26 (C_{quat}), 159.67 (C_{quat}), 199.63 (C_{quat}, CO); MS (EI, 70 eV) *m/z* (%) 277 (M^+, 34), 234 (60), 190 (18). HRMS Found: 277.1101. Calcd. for $C_{18}H_{15}O_2N$: 277.1103. Calcd. for $C_{18}H_{15}NO_2$: C, 77.96; H, 5.45; N, 5.05 %. Found: C, 77.55; H, 5.49; N, 4.92 %.

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