Stereoselective Synthesis of (*Z*)- and (*E*)-Allyl Aryl Sulfides and Selenides from *Baylis–Hillman* Acetates under Neutral Conditions Using *β*-Cyclodextrin in Water

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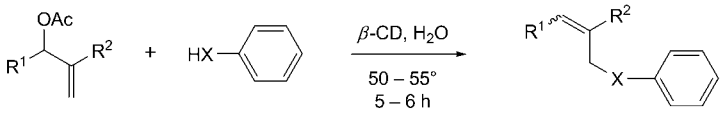
The first example of the stereoselective synthesis of (*Z*)- and (*E*)-allyl aryl sulfides and selenides from *Baylis–Hillman* acetates under neutral conditions in H_2O by supramolecular catalysis involving *β*-cyclodextrin is reported. *β*-Cyclodextrin can be recovered and reused. The reaction is very efficient in providing allyl aryl sulfides and selenides in good-to-excellent yields with clean reaction profiles under mild reaction conditions.

Introduction. – Cyclodextrins [1] (CDs) are cyclic oligosaccharides possessing hydrophobic cavities, which bind substrates selectively and catalyze chemical reactions with high selectivity. Supramolecular catalysis involves the reversible formation of host–guest complexes through non-covalent bonding as seen in enzymes. Earlier, we reported [2] an environmentally benign synthesis of allyl aryl sulfone derivatives by the reaction of sodium benzenesulfinates, which are H_2O-soluble, with *Baylis–Hillman* acetates in H_2O. In continuation of our interest in *Baylis–Hillman* chemistry and to support the concept of sustainability, herein, we report a new protocol to access allyl aryl sulfides/allyl aryl selenides by the addition of H_2O-insoluble benzenethiol/benzeneselenol to *Baylis–Hillman* acetates under biomimetic conditions using *β*-cyclodextrin in H_2O as a solvent at 50–55° (*Scheme*). Here, *β*-CD acts as a supramolecular promoter to facilitate the reaction in H_2O. The H-bonding between SH and OH group of *β*-CD renders the S–H bond weaker, inherently enhancing the nucleophilicity of the S-atom.

Scheme. *Synthesis of Allyl Aryl Sulfides/Selenides from* Baylis–Hillman *Acetates and Benzenethiol/Benzeneselenol*

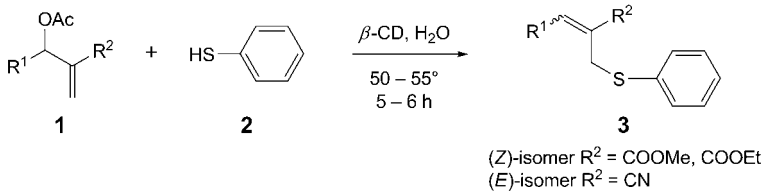


R^1 = Aromatic, heteroaromatic, aliphatic
R^2 = COOMe, COOEt, CN
X = S, Se

(*Z*)-isomer R^2 = COOMe, COOEt
(*E*)-isomer R^2 = CN

Results and Discussion. – In our initial efforts toward the optimization of the present work, *Baylis–Hillman* acetate **1** was reacted with benzenethiol (**2**) using *β*-CD in H_2O at room temperature. Here, the reaction yielded the corresponding allyl sulfide in 54% yield. The same reaction under conventional heating conditions proceeded much better to afford allyl sulfide in 89% in 5–6 h (*Table 1*, *Entry 1*).

Table 1. *Stereoselective Synthesis of (*Z*)- and (*E*)-Allyl Aryl Sulfides Using β-CD*[a])



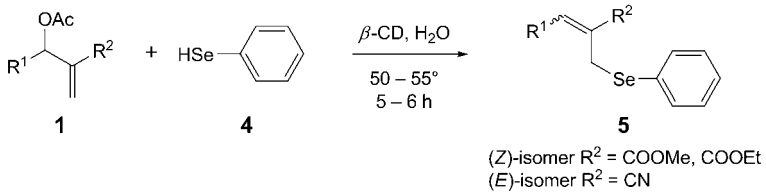
Entry	R^1	R^2	Product **3**	Time [h]	Yield [%][b])
1	Ph	COOMe	**3a** (*Z*)	5	89
2	4-MeO–C_6H_4	COOEt	**3b** (*Z*)	5	87
3	4-F–C_6H_4	COOEt	**3c** (*Z*)	5	84
4	4-Cl–C_6H_4	COOEt	**3d** (*Z*)	5	81
5	3-NO_2–C_6H_4	COOMe	**3e** (*Z*)	5.5	70
6	Pr	COOEt	**3f** (*Z*)	6	72
7	Bu	COOMe	**3g** (*Z*)	6	68
8	Ph	CN	**3h** (*E*)	5	82
9	4-Me–C_6H_4	CN	**3i** (*E*)	5	76
10	4-EtO–C_6H_4	CN	**3j** (*E*)	5	78
11	4-Cl–C_6H_4	CN	**3k** (*E*)	5	78
12	Furan-2-yl	CN	**3l** (*E*)	5.5	71

[a]) Reaction conditions: *Baylis–Hillman* acetate (**1**; 1.0 mmol), benzenethiol (**2**; 1.5 mmol), *β*-CD (1.0 mmol) in H_2O (15 ml), 50–55°, 5–6 h. [b]) Yield of the isolated allyl sulfides.

After having optimized the reaction conditions, various *Baylis–Hillman* acetates, **1**, were synthesized starting from ethyl acrylate or acrylonitrile, and substituted aldehydes [3]. These *Baylis–Hillman* acetates were reacted under optimized conditions to yield corresponding substituted allyl sulfides. In the present study, it was observed that *Baylis–Hillman* acetates **1** derived from benzylaldehydes with 4-MeO, 4-Cl, and 4-F groups afforded substituted allyl sulfides in good yields (*Table 1*, *Entries 2–4*), when compared with *Baylis–Hillman* acetates bearing a 3-NO_2–C_6H_4 group (*Table 1*, *Entry 5*). In the case of *Baylis–Hillman* acetates derived from aliphatic aldehydes, the corresponding allyl sulfides are obtained in moderate yields (*Table 1*, *Entries 6* and *7*).

The scope of this protocol was studied further by replacing benzenethiol (**2**) by benzeneselenol (**4**). The corresponding allyl selenides were obtained in good yields (*Table 2*). *Baylis–Hillman* adducts have proved to be very useful multifunctional synthons in organic chemistry, especially for the stereoselective construction of trisubstituted alkenes.

Table 2. *Stereoselective Synthesis of (*Z*)- and (*E*)-Allyl Aryl Selenides Using β-CD*[a])



Entry	R^1	R^2	Product **5**	Time [h]	Yield [%][b])
1	Ph	COOMe	**5a** (*Z*)	5	88
2	4-MeO–C_6H_4	COOEt	**5b** (*Z*)	5	85
3	4-F–C_6H_4	COOEt	**5c** (*Z*)	5	82
4	4-Cl–C_6H_4	COOEt	**5d** (*Z*)	5	81
5	3-NO_2–C_6H_4	COOMe	**5e** (*Z*)	5.5	68
6	Pr	COOEt	**5f** (*Z*)	6	70
7	4-Cl–C_6H_4	CN	**5g** (*E*)	5	75

[a]) Reaction conditions: *Baylis–Hillman* acetate (**1**; 1.0 mmol), benzeneselenol (**2**; 1.5 mmol), β-CD (1.0 mmol) in H_2O (15 ml), 50–55°, 5–6 h. [b]) Yield of the isolated allyl selenides.

The allylic alcohol functionality is converted to its corresponding acetate to enhance the nucleophilic character and liability to facilitate the formation of (*E*)- and (*Z*)-trisubstituted alkenes. It was observed that (*Z*)-isomer was the only product formed with *Baylis–Hillman* acetates containing an ester moiety, whereas nitrile-containing *Baylis–Hillman* acetates yielded (*E*)-isomers as the predominant products. The configurations of the products were assigned on the basis of ^{1}H-NMR spectroscopy and by comparison with the literature data [4].

In all the cases, the reaction efficiently proceeded at 50–55° without the need of any acid or base catalyst, and in almost quantitative yields and higher selectivities.

To demonstrate the efficacy and recyclability of β-CD, after completion of the reaction, the mixture was allowed to cool to 0°, and β-CD was filtered, washed with ice-cold water, and dried under reduced pressure. The recovered β-CD was re-used with the same substrates and found to be effective even after three cycles (*Table 3*).

Table 3. *Recyclability of β-CD*[a])

Cycle	Yield [%]	Catalyst recovered [%]
Native	89	90
1	86	88
2	84	85
3	81	82

[a]) All reactions were carried out with methyl 2-[(acetoxy)(phenyl)methyl]acrylate (**1a**; 1.0 mmol), benzenethiol (**2**; 1.5 mmol), and β-CD (1.0 mmol) in H_2O (15 ml).

Conclusions. – We have developed an environmentally benign procedure for the transformation of *Baylis–Hillman* acetates into trisubstituted alkenes using H_2O as reaction medium under supramolecular conditions. β-Cyclodextrin, apart from being non-toxic, is also considered as metabolically safe and environmentally benign. This straightforward methodology may find widespread applications in synthetic organic and medicinal chemistry.

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Experimental Part

General. TLC: Precoated silica-gel plates *60 F_{254}* (SiO_2; 0.2-mm layer, *E. Merck*). Column chromatography (CC): SiO_2, 60–120 mesh. M.p.: *Fischer–Johns* apparatus; uncorrected. IR Spectra: *Thermo Nicolet Nexus 670* FT-IR spectrophotometer; in KBr; $\tilde{\nu}$ in cm^{-1}. ^1H- and ^{13}C-NMR spectra: *Bruker Avance 300*, and *Innova 400* MHz instrument; in $CDCl_3$; δ in ppm rel. to Me_4Si as internal standard, *J* in Hz. ESI-MS: *Finnigan MAT 1020* mass spectrometer; in *m/z*.

General Procedure for the Synthesis of Allyl Aryl Sulfides/Selenides: β-CD (1.0 mmol) was dissolved in H_2O (15 ml) by warming to 50–55°, until a clear soln. was obtained. Then, *Baylis–Hillman* acetate (1.0 mmol) was added portionwise, followed by benzenethiol or benzeneselenol (**1** or **4**, resp. 1.5 mmol), resp. The mixture was stirred at 50–55° until the reaction was complete (as monitored by TLC). The product was extracted with AcOEt, and the extract was filtered. The org. layer was dried (Na_2SO_4), and the solvent was removed under reduced pressure. The crude product was purified by CC (SiO_2 (60–120 mesh; AcOEt/hexane 1:9). The aq. layer was cooled to 5° to recover β-CD by filtration.

Methyl (2Z)-3-Phenyl-2-[(phenylsulfanyl)methyl]prop-2-enoate (**3a**; *Table 1*, *Entry 1*): IR (KBr): 3058, 2948, 1714. ^1H-NMR (300 MHz, $CDCl_3$): 3.76 (*s*, 3 H); 4.02 (*s*, 2 H); 7.10–7.42 (*m*, 10 H); 7.75 (*s*, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 167.6; 141.5; 134.7; 132.5; 130.8; 129.4; 129.0; 128.9; 128.6; 128.2; 126.7; 52.3; 32.2. ESI-MS: 285 ($[M + H]^+$).

Ethyl (2Z)-3-(4-Methoxyphenyl)-2-[(phenylsulfanyl)methyl]prop-2-enoate (**3b**; *Table 1*, *Entry 2*): IR (KBr): 2932, 1705, 1603. ^1H-NMR (300 MHz, $CDCl_3$): 1.30 (*t*, *J* = 6.9, 3 H); 3.78 (*s*, 3 H); 4.07 (*s*, 2 H); 4.24 (*q*, *J* = 6.9, 2 H); 6.87 (*d*, *J* = 8.6, 2 H); 7.12–7.29 (*m*, 3 H); 7.39 (*d*, *J* = 8.6, 2 H); 7.44 (*d*, *J* = 8.6, 2 H); 7.73 (*s*, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 167.1; 160.1; 141.0; 136.1; 131.3; 130.2; 128.6; 127.0; 126.3; 125.7; 113.9; 60.8; 55.0; 32.0; 14.0. ESI-MS: 329 ($[M + H]^+$).

Ethyl (2Z)-3-(4-Fluorophenyl)-2-[(phenylsulfanyl)methyl]prop-2-enoate (**3c**; *Table 1*, *Entry 3*): IR (KBr): 3064, 2982, 1710. ^1H-NMR (300 MHz, $CDCl_3$): 1.31 (*t*, *J* = 6.7, 3 H); 3.99 (*s*, 2 H); 4.25 (*q*, *J* = 6.7, 2 H); 7.01 (*t*, *J* = 8.3, 2 H); 7.14–7.29 (*m*, 3 H); 7.32–7.42 (*m*, 4 H); 7.69 (*s*, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 166.9; 164.5; 161.2; 139.9; 131.5; 131.4; 131.0; 128.9; 126.8; 115.8; 115.5; 61.8; 32.2; 14.2. ESI-MS: 317 ($[M + H]^+$).

Ethyl (2Z)-3-(4-Chlorophenyl)-2-[(phenylsulfanyl)methyl]prop-2-enoate (**3d**; *Table 1*, *Entry 4*): IR (neat): 3059, 2982, 1710. ^1H-NMR (300 MHz, $CDCl_3$): 1.29 (*t*, *J* = 6.9, 3 H); 3.94 (*s*, 2 H); 4.23 (*q*, *J* = 6.9, 2 H); 7.09–7.40 (*m*, 9 H); 7.63 (*s*, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 166.1; 144.9; 144.3; 136.2; 132.1; 130.5; 129.6; 128.8; 128.4; 121.8; 61.6; 21.5; 14.0. ESI-MS: 333 ($[M + H]^+$).

Methyl (2Z)-3-(3-Nitrophenyl)-2-[(phenylsulfanyl)methyl]prop-2-enoate (**3e**; *Table 1*, *Entry 5*): IR (KBr): 3070, 2924, 1718, 1530. ^1H-NMR (300 MHz, $CDCl_3$): 3.84 (*s*, 3 H); 3.92 (*s*, 2 H); 7.14–7.24 (*m*, 3 H); 7.28–7.39 (*m*, 2 H); 7.49 (*d*, *J* = 7.5, 1 H); 7.56 (*d*, *J* = 7.5, 1 H); 7.67 (*s*, 1 H); 8.13 (*d*, *J* = 7.5, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 166.7; 147.2; 138.7; 137.5; 136.4; 134.4; 130.0; 128.9; 128.5; 125.3; 122.8; 121.5; 52.1; 32.1. ESI-MS: 330 ($[M + H]^+$).

Ethyl (2Z)-2-[(Phenylsulfanyl)methyl]hex-2-enoate (**3f**; *Table 1*, *Entry 6):* IR (KBr): 3010, 2965, 2815, 1610. ^1H-NMR (300 MHz, $CDCl_3$): 0.86 (*t*, *J* = 7.5, 3 H); 1.22–1.39 (*m*, 5 H); 1.93 (*q*, *J* = 7.5, 2 H); 3.75 (*s*, 2 H); 4.19 (*q*, *J* = 7.5, 2 H); 6.76 (*t*, *J* = 7.5, 1 H); 7.15–7.29 (*m*, 3 H); 7.39 (*d*, *J* = 7.5, 2 H).

^{13}C-NMR (75 MHz, $CDCl_3$): 167.1; 144.7; 136.1; 132.2; 128.7; 126.9; 60.5; 31.5; 30.6; 22.0; 14.4; 14.0. ESI-MS: 265 ($[M + H]^+$).

Methyl (2Z)-2-[(Phenylsulfanyl)methyl]hept-2-enoate (**3g**; *Table 1*, *Entry 7*): IR (KBr): 3010, 2965, 1595. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.86 (*t*, *J* = 7.5, 3 H); 1.20–1.28 (*m*, 4 H); 1.94 (*q*, *J* = 7.5, 2 H); 3.74 (*s*, 3 H); 3.77 (*s*, 2 H); 6.79 (*t*, *J* = 7.5, 1 H); 7.17–7.32 (*m*, 3 H); 7.41 (*d*, *J* = 6.0, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 166.5; 144.9; 136.4; 131.3; 129.2; 127.7; 126.2; 52.2; 31.8; 30.2; 29.2; 22.2; 14.2. ESI-MS: 265 ($[M + H]^+$).

*(2*E*)-3-Phenyl-2-[(phenylsulfanyl)methyl]prop-2-enenitrile* (**3h**; *Table 1*, *Entry 8*): IR (KBr): 3012, 2928, 2215, 1591. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.60–7.18 (*m*, 10 H); 6.58 (*s*, 1 H); 3.74 (*s*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 144.1; 136.2; 134.5; 130.6; 129.0; 128.4; 125.9; 118.6; 106.2; 31.2. ESI-MS: 274 ($[M + Na]^+$).

*(2*E*)-3-(4-Methylphenyl)-2-[(phenylsulfanyl)methyl]prop-2-enenitrile* (**3i**; *Table 1*, *Entry 9*): IR (KBr): 3025, 2923, 2213, 1608. ^{1}H-NMR (300 MHz, $CDCl_3$): 2.34 (*s*, 3 H); 3.75 (*s*, 2 H): 6.56 (*s*, 1 H); 7.02–7.31 (*m*, 6 H); 7.34–7.53 (*m*, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 145.7; 144.3; 140.5; 132.7; 131.8; 129.3; 128.9; 128.6; 127.7; 117.7; 106.3; 41.0; 21.4. ESI-MS: 288 ($[M + Na]^+$).

*(2*E*)-3-(4-Ethoxyphenyl)-2-[(phenylsulfanyl)methyl]prop-2-enenitrile* (**3j**; *Table 1*, *Entry 10*): IR (KBr): 3021, 2925, 2216, 1615. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.39 (*t*, *J* = 6.7, 3 H); 3.67 (*s*, 2 H); 3.99 (*q*, *J* = 6.7, 2 H); 6.52 (*s*, 1 H); 6.80 (*d*, *J* = 9.6, 2 H); 7.18–7.28 (*m*, 3 H); 7.38 (*d*, *J* = 6.7, 2 H); 7.53 (*d*, *J* = 8.6, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 160.5; 144.0; 132.6; 130.4; 128.9; 127.6; 125.4; 114.5; 104.2; 63.3; 41.0; 14.7. ESI-MS: 296 ($[M + H]^+$).

*(2*E*)-3-(4-Chlorophenyl)-2-[(phenylsulfanyl)methyl]prop-2-enenitrile* (**3k**; *Table 1*, *Entry 11*): IR (KBr): 3060, 2923, 2215, 1589. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.71 (*s*, 2 H); 6.55 (*s*, 1 H); 7.21–7.46 (*m*, 7 H); 7.49 (*d*, *J* = 8.4, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 144.5; 143.1; 132.9; 132.3; 130.1; 129.8; 129.1; 129.0; 128.0; 117.6; 108.2; 41.0. ESI-MS: 286 ($[M + H]^+$).

*(2*E*)-3-(Furan-2-yl)-2-[(phenylsulfanyl)methyl]prop-2-enenitrile* (**3l**; *Table 1*, *Entry 12*): IR (KBr): 3015, 2975, 2210. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.11 (*s*, 2 H); 6.52 (*d*, *J* = 3.7, 1 H); 6.77 (*s*, 1 H); 7.16–7.27 (*m*, 3 H); 7.42–7.49 (*m*, 4 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 150.6; 144.1; 142.3; 135.9; 130.0; 128.5; 124.4; 117.3; 111.8; 109.5; 108.4; 41.3. ESI-MS: 242 ($[M + H]^+$).

Methyl (2Z)-3-Phenyl-2-[(phenylselanyl)methyl]prop-2-enoate (**5a**; *Table 2*, *Entry 1*): IR (KBr): 3058, 2950, 1710. ^{1}H-NMR (300 MHz, $CDCl_3$): 2.12 (*s*, 2 H); 3.82 (*s*, 3 H); 7.11–7.48 (*m*, 10 H); 7.69 (*s*, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 167.4; 140.2; 134.9; 132.7; 130.8; 129.2; 129.0; 128.7; 128.5; 127.7; 126.5; 52.1; 26.2. ESI-MS: 333 ($[M + H]^+$).

Ethyl (2Z)-3-(4-Methoxyphenyl)-2-[(phenylselanyl)methyl]prop-2-enoate (**5b**; *Table 2*, *Entry 2*): IR (KBr): 2923, 1705, 1605. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.31 (*t*, *J* = 6.7, 3 H); 3.80 (*s*, 3 H); 4.07 (*s*, 2 H); 4.23 (*q*, *J* = 6.7, 2 H), 6.83 (*d*, *J* = 9.0, 2 H); 7.18–7.25 (*m*, 3 H); 7.35 (*d*, *J* = 8.3, 2 H); 7.52–7.56 (*m*, 2 H); 7.61 (*s*, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 167.3; 160.0; 139.6; 133.9; 131.4; 130.3; 128.9; 127.4; 127.3; 114.0; 60.9; 55.1; 25.2; 14.3. ESI-MS: 377 ($[M + H]^+$).

Ethyl (2Z)-3-(4-Fluorophenyl)-2-[(phenylselanyl)methyl]prop-2-enoate (**5c**; *Table 2*, *Entry 3*): IR (KBr): 3064, 2982, 1710. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.34 (*t*, *J* = 6.7, 3 H); 2.14 (*s*, 2 H); 4.24 (*q*, *J* = 6.7, 2 H); 6.96 (*t*, *J* = 8.3, 2 H); 7.16–7.28 (*m*, 5 H); 7.50 (*d*, *J* = 8.3, 2 H); 7.56 (*s*, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 166.7; 161.5; 139.7; 132.0; 131.0; 130.6; 130.2; 128.9; 126.6; 115.5; 61.8; 26.1; 14.0. ESI-MS: 365 ($[M + H]^+$).

Ethyl (2Z)-3-(4-Chlorophenyl)-2-[(phenylselanyl)methyl]prop-2-enoate (**5d**; *Table 2*, *Entry 4*): IR (KBr): 2930, 1710, 1610. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.33 (*t*, *J* = 7.1, 3 H), 3.99 (*s*, 2 H); 4.26 (*q*, *J* = 7.1, 2 H); 7.18–7.31 (*m*, 7 H); 7.51 (*d*, *J* = 7.7, 2 H); 7.58 (*s*, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 166.6; 141.0; 132.9; 132.5; 130.8; 129.4; 128.9; 128.8; 127.5; 61.5; 26.5; 14.0. ESI-MS: 381 ($[M + H]^+$).

Methyl (2Z)-3-(3-Nitrophenyl)-2-[(phenylselanyl)methyl]prop-2-enoate (**5e**; *Table 2*, *Entry 5*): IR (KBr): 3070, 2924, 1715, 1510. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.84 (*s*, 3 H); 3.95 (*s*, 2 H); 7.12–7.26 (*m*, 3 H); 7.40–7.49 (*m*, 4 H); 7.58 (*s*, 1 H); 8.03 (*s*, 1 H); 8.09 (*d*, *J* = 6.7, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 166.9; 148.2; 136.4; 136.2; 135.2; 134.6; 132.4; 131.4; 129.3; 128.9; 128.0; 123.7; 122.9; 52.4; 24.5. ESI-MS: 378 ($[M + H]^+$).

Ethyl (2Z)-2-[(Phenylselanyl)methyl]hex-2-enoate (**5f**; *Table 2*, *Entry 6*): IR (KBr): 3010, 2965, 2815, 1710. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.87 (*t*, *J* = 7.5, 3 H); 1.21–1.32 (*m*, 5 H); 1.63 (*q*, *J* = 7.5, 2 H);

2.15 (*s*, 2 H); 3.76 (*q*, *J* = 7.5, 2 H); 6.74 (*t*, *J* = 7.7, 1 H); 7.25 – 7.38 (*m*, 5 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 167.0; 144.5; 132.7; 131.2; 129.0; 128.7; 127.1; 60.7; 30.2; 25.8; 22.1; 14.1. ESI-MS: 313 ($[M + H]^+$).

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