Tetrahedron 68 (2012) 10573-10576

Contents lists available at SciVerse ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Selenenylations of alkenes with styrene nucleophiles

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ARTICLE INFO

Available online 17 August 2012

Received in revised form 7 August 2012

Article history:

Keywords: Alkenes Diselenides Selenenylation Styrenes

Received 5 July 2012

Accepted 10 August 2012

ABSTRACT

Iodine-mediated addition reactions to alkenes with diphenyl diselenide using the same alkenes as nucleophiles are presented. The transformation proceeds under mild reaction conditions and the addition products were isolated in moderate to good yields.

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1. Introduction

Organoselenium chemistry has been developed as an important synthetic tool¹ after the discovery of the selenoxide elimination in the early 1970s.² Organoselenium reagents have been used for the synthesis of various biologically important synthetic and naturally occurring compounds.³ In the past two decades, addition reactions of selenium electrophiles to alkenes have been received particular attention.⁴ These addition reactions usually consist of two steps involving the formation of seleniranium ion intermediates **3** from alkenes 1 and the selenium electrophile RSeX 2 followed by the attack of nucleophile (Nu⁻) (Scheme 1). Addition reactions of various selenium electrophiles with alkenes have been explored in detail by using internal and external nucleophiles.^{5,6} The addition products **4** of these reactions have been identified as valuable synthetic intermediates also for the synthesis of various natural products.





2. Results and discussion

Herein, we report an iodine-mediated addition reaction of styrenes using the same styrenes as nucleophiles under mild reaction conditions. Intramolecular versions of alkenes as nucleophiles in such reactions have already been reported.⁷ Initially, optimal reaction conditions for the selenenylation of styrenes were established using styrene 5a as model substrate (Scheme 2). The addition reaction was performed in 1,2-dichloroethane using 1 equiv of diphenyl diselenide and 4 equiv of styrene in the presence of 20 mol % iodine at 70 °C for 16 h. The isolated product was characterized as (E)-(2,4-diphenylbut-3-enyl)(phenyl)selane 6a as shown in Scheme 2.

$$(PhSe)_{2} + Ph \xrightarrow{I_{2} (20 \text{ mol}\%)} Ph \xrightarrow{Ph} Se-Ph$$

$$5a \quad 70^{\circ}C, 16 \text{ h} \qquad 6a (55\%)$$

Scheme 2. Selenenylation of styrene 5a with styrene as nucleophile.

In order to optimize the reaction conditions, different solvents have been investigated as shown in Table 1. Initially, the reaction was performed in dichloroethane at room temperature but no reaction took place (Table 1, entry 1). On heating the reaction mixture to 70 °C for 16 h, addition product 6a was isolated in 55% yield (Table 1, entry 2) while the remaining compound was identified to be styrene starting material. The same reaction was also performed for 24 h but the addition product was obtained in identical yields (Table 1, entry 3). Other chlorinated solvents such as dichloromethane and chloroform were also used but the product 6a was



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^{0040-4020/\$ -} see front matter © 2012 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.tet.2012.08.034

Table 1	
Different solvents for the addition reaction of 5a	



^a Reaction performed at 20 °C.

^b Reaction performed at reflux.

isolated in 22% and 15% yields, respectively (Table 1, entries 4 and 5). The reaction also proceeded in tetrahydrofuran and water, but product **6a** was obtained in lower yields (Table 1, entries 6 and 7).

After the solvent optimization, the reaction was performed with smaller amounts of iodine (5 and 10 mol%) but the addition product was obtained in only 18% and 41% yields, respectively. With the optimal reaction conditions, a series of addition reaction of different alkenes **5b**–**g** were successfully performed and addition products **6b**–**g** were isolated in moderate to good yields as shown in Table 2. The addition reactions were working smoothly with styrene systems **5** having electron donating functionality at aromatic ring and the products were isolated in moderate to good yields (Table 2, entries 2–4).

Table 2

Different alkenes 5 in the selenenylation reaction



Entry	R	Ar	6 Yield (%)	8 Yield (%)
1	7a : H	5a : Ph	6a : 55	_
2	7a : H	5b: 2-MeC ₆ H ₄	6b : 62	_
3	7a : H	5c: 3-MeC ₆ H ₄	6c : 62	_
4	7a : H	5d: 4-MeC ₆ H ₄	6d: 51	_
5	7a : H	5e: 4-PhC ₆ H ₄	6e : 31	8e: 27
6	7a : H	5f: 2-Naphthyl	6f : 33	8f : 26
7 ^a	7a : H	5a : Ph and 5g :	6a and 6g :	_
		$4-ClC_{6}H_{4}(1:1)$	68 (1:1)	
8	7a : H	5h: 4-MeOC ₆ H ₄	6h : 0	_
9 ^b	7b : SO- <i>t</i> -Bu	5a : Ph	6i : 30	_

^a The reaction was performed with the mixture of styrene and 4-chlorostyrene in a 1:1 ratio.

 $^{\rm b}$ The reaction was performed in THF at $-78\,^{\circ}\text{C}$ using equimolar amounts of bromine instead of iodine.

The reaction was successfully performed using methylsubstituted styrenes and the addition products were isolated in good yields (Table 2, entries 2–4). When the same reaction was performed with 4-vinyl-1,1'-biphenyl **5e**, the addition product **6e** was isolated in 31% yield together with the deselenylated product **8e** (Table 2, entry 5). The course of the reaction was similar with 2vinylnaphthalene and the products **6f** along with **8f** were isolated (Table 2, entry 6). The addition reaction was unsuccessful with 4methoxystyrene **5h** (Table 2, entry 8). The addition reaction of styrene was performed with diselenide **7b** (R=SO-*t*-Bu) in THF at -78 °C and the addition product **6i** was obtained in 30% yield, trace amounts of a benzoselenothiine-1-oxide have also been observed as reported earlier (Table 2, entry 9).⁶

Styrenes with electron-withdrawing substituents at the aromatic ring were also used, but the addition reaction was unsuccessful. This is probably due to the fact that electronwithdrawing groups decrease the nucleophilicity of the styrene, which is then unable to react as a nucleophile. Furthermore, we performed the same addition reaction using a 1:1 mixture of styrene **5a** and 4-chlorostyrene **5g** and a mixture of both addition products **6a** and **6g** was obtained in a combined yield of 68% (Table 2, entry 7). Interestingly, 4-chlorostyrene as a single substrate did not produce any product.

Furthermore, the same reaction was performed with α -methylstyrene **9** and the isolated product was characterized as phenyl(2phenylallyl)selane **10** in 87% yield while the expected addition product was not observed (Scheme 3). All reaction products were fully characterized by spectroscopic analysis.



Scheme 3. Selenenylation of α-methylstyrene 9.

We propose a catalytic cycle for the iodine-mediated selenenylation of alkenes using styrene as nucleophile as shown in Scheme 4. The catalytic cycle is initiated by the formation of phenylselenenyl iodide **11** by the reaction of diphenyl diselenide and iodine. Phenylselenenyl iodide **11** then adds to styrene to form the seleniranium intermediate **12**, which could be attacked by the styrene nucleophile to form addition product **13**. The reaction intermediate **13** forms the final reaction product **6** by HI elimination. Finally, HI could further react with diphenyl diselenide to phenylselenenyl iodide **11** to continue the catalytic cycle.



Scheme 4. Proposed mechanism for the selenenylation sequence.

3. Conclusion

In summary, we have demonstrated that iodine-mediated reactions of different styrene derivatives with diaryl diselenides lead to novel addition products. The interesting feature of this reaction is that styrenes are used as nucleophiles. Research studies about the wider scope of this approach are currently in progress.

4. Experimental section

4.1. General

Melting points were obtained in open capillary tubes. ¹H NMR and ¹³C NMR spectra were recorded on an AV-400 Bruker using the solvents indicated with 400 and 100 MHz, respectively, also a DRX-500 Bruker was used in the some cases for 1 H (500 MHz) and 13 C (125 MHz). Mass spectra (m/z) and HRMS were recorded under the conditions of electron impact (EI) and electrospray (ES) and chemical ionization (CI). Infrared spectra were recorded on an ASCO FT/IR-660 Plus spectrophotometer. All reactions were monitored by thin-layer chromatography that was performed on pre-coated sheets of silica gel 60, and flash column chromatography was performed with silica gel 60 (Merck, 230–400 mesh). Eluting solvents are indicated in the text. All experiments were performed under open atmosphere. Dichloroethane was purchased from Sigma--Aldrich Chemicals Limited while THF was used from a solvent purification system. All other purchased chemicals were used without further purification.

4.2. General procedure for the synthesis of (*E*)-(2,4-diarylbut-3-enyl)(phenyl)selanes 6a–g and 10

The mixture of styrene derivative (1.0 mmol), diphenyl diselenide (78 mg, 0.25 mmol), and iodine (12.7 mg, 0.05 mmol) in 1,2-dichloroethane (2 mL) was stirred at 70 °C for 16–20 h. The reaction was monitored by thin-layer chromatography. After the completion of reaction, the solvent was removed under vacuum and the reaction was quenched by the addition of 10% aq $Na_2S_2O_3$ solution. The reaction mixture was extracted with dichloromethane (3×10 mL). The combined organic layers were dried over MgSO₄, filtered, and evaporated under vacuum. Finally, the crude product was purified by column chromatography using hexane as eluent.

4.2.1. (*E*)-(2,4-*Diphenylbut*-3-*enyl*)(*phenyl*)*selane* (**6a**). Yellow oil; yield: 55% (100 mg, 0.27 mmol); ¹H NMR (400 MHz, CDCl₃): δ =3.30–3.38 (m, 2H, CH₂), 3.76 (q, J=6 Hz, 1H, CH), 6.33–6.42 (m, 2H, CH=CH), 7.17–7.28 (m, 9H, ArH), 7.29–7.32 (m, 4H, ArH), 7.45–7.47 (m, 2H, ArH) ppm; ¹³C NMR (100 MHz, CDCl₃): δ =34.2, 49.4, 126.4 (2C), 126.9, 127.0, 127.4, 127.6 (2C), 128.5 (2C), 128.7 (2C), 129.1 (2C), 130.8, 130.9, 132.2, 132.8 (2C), 137.2, 143.2 ppm; IR (film): ν =3027, 2360, 1635, 1557, 1494, 1477, 1452, 1073, 1022, 963, 734 cm⁻¹; HRMS (ES⁺): *m*/*z* [M+H]⁺ calculated for C₂₂H₂₁⁸⁰Se: 365.0808; found 365.0824.

4.2.2. (*E*)-(2,4-*Di*-o-tolylbut-3-enyl)(phenyl)selane (**6b**). Yellow oil; yield: 62% (120 mg, 0.30 mmol); ¹H NMR (400 MHz, CDCl₃): δ =2.18 (s, 3H, Me), 2.21 (s, 3H, Me), 3.25 (d, *J*=7.6 Hz, 2H, CH₂), 3.92 (q, *J*=7.6 Hz, 1H, CH), 6.10 (dd, *J*₁=7.6 Hz, *J*₂=15.6 Hz, 1H, CH), 6.50 (d, *J*=15.6 Hz, 1H, CH), 7.02-7.19 (m, 10H, ArH), 7.25-7.28 (m, 1H, ArH), 7.39-7.42 (m, 2H, ArH) ppm; ¹³C NMR (100 MHz, CDCl₃): δ =19.6, 19.9, 33.6, 45.0, 125.8, 126.1, 126.5 (2C), 126.7, 127.0, 127.3, 128.9, 129.2 (2C), 130.2, 130.7 (2C), 133.0 (2C), 133.3, 135.3, 135.9, 136.5, 141.4 ppm; IR (film): *v*=3058, 3018, 2968, 2925, 2738, 1799, 1601, 1578, 1486, 1478, 1460, 1436, 1379, 1022, 964 cm⁻¹; HRMS (ES⁺): *m*/*z* [M+H]⁺ calculated for C₂₄H₂₅⁸⁰Se: 393.1121; found 393.1115.

4.2.3. (*E*)-(2,4-*Di*-*m*-tolylbut-3-enyl)(phenyl)selane (**6**c). Yellow oil; yield: 62% (120 mg, 0.30 mmol); ¹H NMR (400 MHz, CDCl₃): δ =2.25 (s, 3H, Me), 2.26 (s, 3H, Me), 3.27 (d, *J*=7.2 Hz, 2H, CH₂), 3.66 (q, *J*=7.2 Hz, 1H, CH), 6.29–6.34 (m, 2H, CH), 6.94–7.19 (m, 11H, ArH), 7.39–7.42 (m, 2H, ArH) ppm; ¹³C NMR (100 MHz, CDCl₃): δ =19.9, 20.1, 34.1, 49.4, 123.5, 124.6, 126.8 (2C), 127.0, 127.6, 128.1, 128.3, 128.4, 128.6, 129.1 (2C), 130.8 (2C), 132.1, 132.7 (2C), 137.1, 138.0, 143.2 ppm; IR (film): *v*=2918, 2849, 1605, 1579, 1477, 1436, 1377,

4.2.4. (*E*)-(2,4-*Di*-*p*-tolylbut-3-enyl)(phenyl)selane (**6d**). Yellow oil; yield: 51% (100 mg, 0.255 mmol); ¹H NMR (400 MHz, CDCl₃): δ =2.24 (s, 3H, Me), 2.25 (s, 3H, Me), 3.26 (d, *J*=6.8 Hz, 2H, CH₂), 3.65 (q, *J*=6.8 Hz, 1H, CH), 6.17–6.34 (m, 2H, CH), 6.94–7.06 (m, 6H, ArH), 7.12–7.17 (m, 5H, ArH), 7.38–7.42 (m, 2H, ArH) ppm; ¹³C NMR (100 MHz, CDCl₃): δ =21.1, 21.2, 34.3, 48.9, 126.2 (2C), 126.8, 127.5 (2C), 129.1 (2C), 129.2 (129.2), 129.4 (2C), 130.5, 130.8, 131.4, 132.7 (2C), 134.4, 136.5, 137.1, 140.2 ppm; IR (film): *v*=3019, 2919, 2860, 1578, 1511, 1478, 1437, 1180, 1073, 1021, 963, 913, 815, 797 cm⁻¹; HRMS (ES⁺): *m*/z [M+H]⁺ calculated for C₂₄H₂₅⁸⁰Se: 393.1121; found 393.1121.

4.2.5. (*E*)-(2,4-*Di*(*biphenyl*-4-*yl*)*but*-3-*enyl*)(*phenyl*)*selane* (*6e*). Yellow oil; yield: 31% (79 mg, 0.155 mmol); ¹H NMR (400 MHz, CDCl₃): δ =3.34 (d, J=7.6 Hz, 2H, CH₂), 3.79 (q, *J*=7.6 Hz, 1H, CH), 6.38–6.45 (m, 2H, CH), 7.34–7.38 (m, 7H, ArH), 7.42–7.46 (m, 5H, ArH), 7.47–7.53 (m, 11H, ArH) ppm; ¹³C NMR (125 MHz, CDCl₃): δ =34.1, 49.2, 126.2 (2C), 126.9 (3C), 127.1 (2C), 127.2 (2C), 127.3, 127.5 (2C), 128.1 (2C), 128.79 (3C), 128.81 (2C), 129.1 (2C), 130.6, 130.7, 132.3, 132.9 (2C), 136.2, 139.9, 140.2, 140.8, 140.9, 142.3 ppm; IR (film): ν =1653, 1635, 1485, 913, 743 cm⁻¹; HRMS (ES⁺): *m*/*z* [M+H]⁺ calculated for C₃₄H₂₈⁷⁶Se: 513.1456; found 513.1445.

4.2.6. (*E*)-(2,4-*D*i(*naphthalen*-2-*y*l)*but*-3-*enyl*)(*phenyl*)*selane* (*6f*). Yellow oil; yield: 33% (76 mg, 0.165 mmol); ¹H NMR (400 MHz, CDCl₃): δ =3.42 (d, *J*=7.6 Hz, 2H, CH₂), 3.93 (q, *J*=7.6 Hz, 1H, CH), 6.47–6.56 (m, 2H, CH), 7.38–7.41 (m, 3H, ArH), 7.45–7.50 (m, 4H, ArH), 7.53–7.61 (m, 7H, ArH) ppm; ¹³C NMR (125 MHz, CDCl₃): δ =34.4, 50.1, 124.0, 126.1 (2c), 126.2, 126.4 (2C), 126.59 (2C), 128.61, 126.64, 127.4, 128.06, 128.11, 128.2, 128.4 (2C), 128.5, 128.9, 129.5 (2C), 131.6, 132.6, 133.0 (2C), 133.3, 134.0, 134.9, 140.9 ppm; IR (film): *v*=3054, 2961, 2924, 1599, 1507, 1271, 1022, 913, 855, 816, 743 cm⁻¹; HRMS (ES⁺): *m/z* [M+H]⁺ calculated for C₃₀H₂₅⁸⁰Se: 465.1121; found 466.1117.

4.2.7. (*E*)-(2,4-*Bis*(4-*chlorophenyl*)*but*-3-*enyl*)(*phenyl*)*selane* (**6g**). This compound was isolated as inseparable mixture with compound **6a** in 1:1 ratio in overall 68% yield. Orange oil; ¹H NMR (400 MHz, CDCl₃): δ =3.17–3.28 (m, 4H, 2×CH₂), 3.63–3.70 (m, 2H, 2×CH), 6.20–6.33 (m, 4H, 4×CH), 7.08 (d, *J*=8.4 Hz, 2H, ArH), 7.12–7.25 (m, 22H, ArH), 7.36–7.40 (m, 4H, ArH) ppm; ¹³C NMR (100 MHz, CDCl₃): δ =34.3, 34.4, 49.2, 49.9, 126.8 (2C), 127.37, 127.44, 127.5, 127.96 (3C), 127.99 (2C), 129.0 (2C), 129.1 (2C), 129.19 (2C), 129.22 (2C), 129.5 (2C), 125.5 (2C), 129.6 (2C), 130.1, 130.8, 131.0, 131.5, 132.1, 133.0, 133.2 (2C), 133.2, 133.34 (2C), 133.4, 136.0, 137.3, 141.9, 143.4 ppm; IR (film): *v*=3057, 3026, 2918, 2849, 1578, 1490, 1477, 1451, 1437, 1403, 1091, 1073, 1012, 820, 734 cm⁻¹; HRMS (ES⁺): *m/z* [M]⁺ calculated for C₂₂H₁₈Cl₂⁷⁶Se: 427.9972; found 427.9971.

4.3. Procedure for the synthesis of (*rac*)-2-(*tert*-butylsulfinyl) phenyl-(*E*)-2,4-diphenylbut-3-enyl selenide (6i)

Bis[2-(*tert*-butylsulfinyl)phenyl]diselenide (520 mg, 1.0 mmol) was dissolved in dry tetrahydrofuran (40 mL) under argon, cooled to -78 °C, and treated with bromine (1.0 mmol, 1.0 mL of a 1 M solution in CCl₄). After 20 min silver triflate (540 mg, 2.1 mmol) was added and the mixture was stirred for 25 min at -78 °C. The reaction mixture was treated with styrene (229 mg, 2.20 mmol). The mixture was further stirred at -78 °C and warmed to -10 °C overnight. Then MeOH (1 mL) was added and the mixture was stirred for 2,4,6-collidine (1 mL)

was added, followed by water (40 mL). After extraction of the reaction mixture with dichloromethane (3×50 mL), drying of the combined organic phases with MgSO₄, and removal of the solvent under reduced pressure; the residue was purified by flash column chromatography on silica gel, yielding the addition products as pale yellow oils. The diastereomers could not be separated by flash chromatography (ethyl acetate/hexanes, 1:5); yield 30% (309 mg, 0.30 mmol), pale yellow oil.

4.3.1. (*rac*)-2-(*tert-Butylsulfinyl*)*phenyl*-(*E*)-2,4-*diphenylbut-3-enyl selenide* (**6***i*). Yellow oil; yield: 33% (309 mg, 0.66 mmol); ¹H NMR (500 MHz, CDCl₃): δ =1.12 (s, 9H, C(CH₃)₃), 3.30 (m, 2H, CH₂), 3.69 (q, *J*=7.4 Hz, 1H, CH), 6.27 (ddd, *J*₁=1.9 Hz, *J*₂=7.6 Hz, *J*₃=15.8 Hz, 1H, CH), 6.37 (dd, *J*₁=15.9 Hz, *J*₂=20.4 Hz, 1H, CH), 7.16–7.24 (m, 11H, ArH), 7.33–7.37 (m, 1H, ArH), 7.45 (td, *J*₁=1.2 Hz, *J*₂=7.6 Hz, 1H, ArH), 7.73 (ddd, *J*₁=1.4 Hz, *J*₂=3.7 Hz, *J*₃=7.8 Hz, 1H, ArH) ppm; ¹³C NMR (125 MHz, CDCl₃): δ =23.3, 35.8, 35.9, 49.0, 49.1, 58.1, 58.2, 122.5, 126.3, 126.9, 127.0, 127.4, 127.5, 127.6, 128.4, 128.7, 130.9, 131.1, 131.4, 131.7, 131.8, 133.6, 133.7, 136.8, 136.9, 142.6, 142.7, 143.4 ppm; IR (film): *v*=3057, 3026, 2966, 2926, 1599, 1569, 1494, 1443, 1426, 1362, 1326, 1217, 1148, 1091, 965, 749, 699 cm⁻¹; HRMS (ES⁺): *m*/*z* [M+H]⁺ calculated for C₂₆H₂₉OS⁷⁴Se: 463.1158; found 463.1163.

4.3.2. (*E*)-4,4'-(*But-1-ene-1*,3-*diyl*)*dibiphenyl* (**8***e*). Colorless solid; mp: 105–107 °C; yield: 27% (49 mg, 0.135 mmol); ¹H NMR (400 MHz, CDCl₃): δ =1.45 (d, *J*=6.8 Hz, 3H, Me), 3.64 (q, *J*=7.6 Hz, 1H, CH), 6.36–6.45 (m, 2H, CH), 7.24–7.30 (m, 4H, ArH), 7.34–7.38 (m, 6H, ArH), 7.46–7.53 (m, 8H, ArH) ppm; ¹³C NMR (125 MHz, CDCl₃): δ =21.3, 42.4, 126.6 (2C), 126.9 (2C), 127.08 (2C), 127.1, 127.2 (3C), 127.3 (2C), 127.8 (2C), 128.2, 128.7 (2C), 128.8 (2C), 135.3, 136.6, 139.3, 139.9, 140.8, 141.1, 144.7 ppm; IR (film): ν =3026, 1485, 1449, 1407, 761 cm⁻¹; HRMS (ES⁺): *m*/*z* [M]⁺ calculated for C₂₈H₂₄: 360.1873; found 360.1868.

4.3.3. (*E*)-2,2'-(*But*-1-*ene*-1,3-*diyl*)*dinaphthalene* (**8***f*). Orange oil; yield: 26% (40 mg, 0.13 mmol); ¹H NMR (400 MHz, CDCl₃): δ =1.61 (d, *J*=6.8 Hz, 3H, Me), 3.88 (q, *J*=6.8 Hz, 1H, CH), 6.56–6.66 (m, 2H, CH), 7.40–7.49 (m, 5H, ArH), 7.60 (d, *J*=8.4 Hz, 1H, ArH), 7.71–7.79 (m, 5H, ArH), 7.83 (d, *J*=8.0 Hz, 3H, ArH) ppm; ¹³C NMR (100 MHz, CDCl₃): δ =21.2, 42.8, 123.6, 125.3, 125.4, 125.6, 125.8, 126.0, 126.2, 126.4, 127.6 (3C), 127.7, 127.9, 128.1 (2C), 129.0 (2C), 132.8, 133.7, 135.02, 135.6, 143.0 ppm; IR (film): *v*=3051, 2961, 2864, 1569, 1507, 913, 810, 743 cm⁻¹; HRMS (ES⁺): *m*/*z* [M+H]⁺ calculated for C₂₄H₁₉: 307.1487; found 307.1483.

4.3.4. *Phenyl*(2-*phenylallyl*)*selane* (**10**). Yellow oil; yield: 87% (119 mg, 0.435 mmol); ¹H NMR (400 MHz, CDCl₃): δ =3.88 (s, 2H,

CH₂), 4.93 (d, *J*=1.6 Hz, 1H, CH), 5.20 (d, *J*=1.6 Hz, 1H, CH), 7.14–7.29 (m, 6H, ArH), 7.35–7.42 (m, 4H, ArH) ppm; ¹³C NMR (100 MHz, CDCl₃): δ =33.0, 115.0, 126.3 (2C), 127.4, 127.9, 128.4 (2C), 129.0 (2C), 130.5, 134.0 (2C), 139.5, 144.2 ppm; IR (film): *v*=3055, 3030, 2932, 1623, 1577, 1476, 1445, 1436, 1301, 1185, 1072, 1022, 900, 859, 775, 717 cm⁻¹; HRMS (ES⁺): *m/z* [M+H]⁺ calculated for C₁₅H₁₄⁷⁴Se: 269.0393; found 269.0390.

Acknowledgements

Financial support by the EU, FP7 IIF Marie Curie Grant and the School of Chemistry, Cardiff University, is gratefully acknowledged. We thank the EPSRC National Mass Spectrometry Service Centre, Swansea, for mass spectrometric data.

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