The mechanism of [2 + 1] and [2 + 2] cycloaddition reactions of 1-phenylseleno-2-(trimethylsilyl)ethene: an isotopic labelling study †

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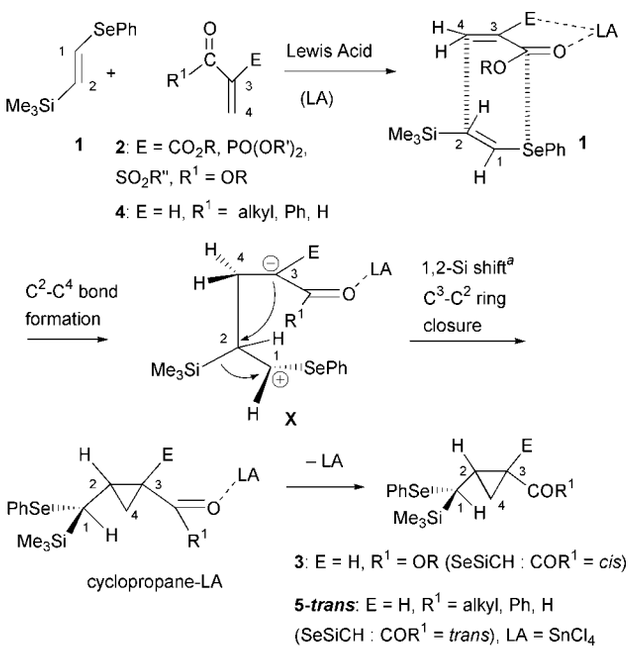
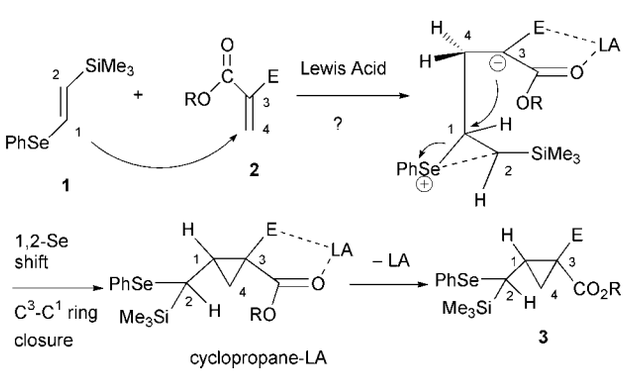
The reactions of deuterio-labelled 1-seleno-2-silylethenes with trimethyl 2-phosphonoacrylate **2** and methyl vinyl ketone **4** in the presence of $SnCl_4$ gave deuterio-substituted cyclopropanes with 1,2-silicon migration. The reaction of deuterio-labelled 1-seleno-2-silylethenes with dimethyl 2,2-dicyanoethene-1,1-dicarboxylate **6** in the presence of $SnCl_4$ and $ZnBr_2$ gave deuterium-substituted cyclobutanes without silicon migration. This labelling study strongly confirms the 1,2-silicon migration for [2 + 1] cycloadditions of **1** and non-1,2-silicon migration for the [2 + 2] cycloaddition reactions, respectively.

Introduction

We have recently reported a novel [2 + 1] cycloaddition method involving reactions of the (*E*)-1-phenylseleno-2-silylethene **1** with electrophilic olefins to afford cyclopropane products with high stereoselectivity in the presence of Lewis acids (Scheme 1).[1] This new approach to cyclopropane construction is based on a 1,2-silicon-migration process. A possible reaction mechanism for the [2 + 1] cycloaddition involves a 1,2-silicon migration in the resulting zwitterionic intermediate. In order to clarify the origin of preferential formation of a cyclopropane instead of a cyclobutane, various theoretical studies have been carried out.[1a,c–f] Recently, higher level calculations have been initiated which promise to unveil the detailed features of this novel cyclopropanation.[2] The theoretical study indicates that silicon migration occurs, rather than selenium migration. Because the possibility of selenium migration instead of silicon migration (Scheme 2) also exists,[3] we wished to make sure experimentally that this mechanism involves not selenium but silicon migration.



Scheme 1 A possible reaction mechanism for [2 + 1] cycloaddition of **1** with electrophilic olefins. The carbon numbering refers to starting olefins **1** and **2**. [a] 1,2-Si shift and C^3-C^2 ring closure could be stepwise rather than concerted.

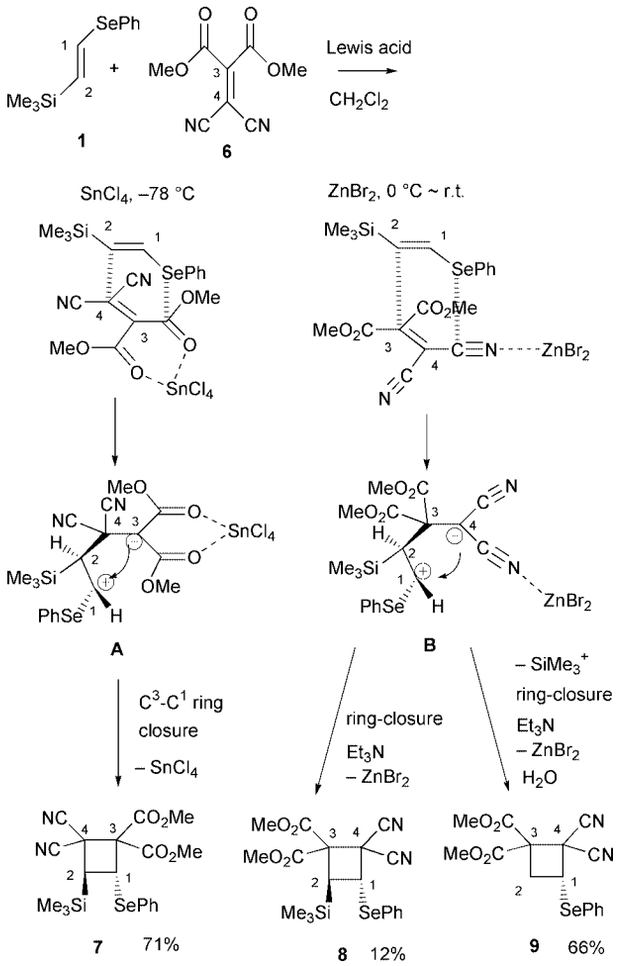


Scheme 2 Alternative mechanism for [2 + 1] cycloaddition of **1**. The carbon numbering of **1** and **2** corresponds to Scheme 1.

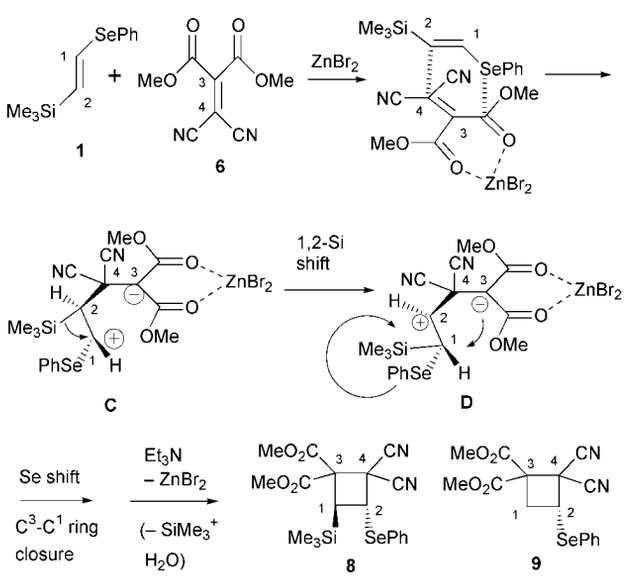
In addition to **2** and **4**, (*E*)-1-phenylseleno-2-silylethenes such as **1** react with some electrophilic olefins such as dimethyl 2,2-dicyanoethene-1,1-dicarboxylate **6**[4] to afford cyclobutane products without 1,2-silicon migration (Scheme 3).[5] The dependency of the regiochemistry on Lewis acids for cyclobutane formation with **1** has also been observed. In the $ZnBr_2$ case, the involvement of both silicon migration and selenium migration as an alternative mechanism cannot be completely ruled out (Scheme 4).

In order to gain more insight into the mechanism of these transformations, reactions using one-deuterium-labelled 1-seleno-2-silylethenes **1**-1-d or **1**-2-d are required. The labelled nucleophilic olefins **1**-1-d and **1**-2-d were readily prepared

† NOESY spectra for **3**-1-d and **9**-2-d and HMBC spectra for **7**-1-d and **8**-1-d are available as supplementary data. For direct electronic access see http://www.rsc.org/suppdata/p1/a9/a909919k/



Scheme 3 A possible mechanism for [2 + 2] cycloaddition of **1** and **6** in the presence of $SnCl_4$ or $ZnBr_2$. The carbon numbering refers to starting olefins **1** and **6**.

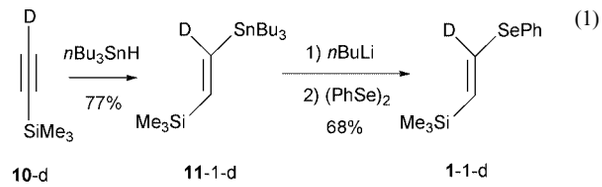


Scheme 4 Alternative mechanism for cyclobutane formation with $ZnBr_2$. The carbon numbering of **1** and **6** corresponds to Scheme 3.

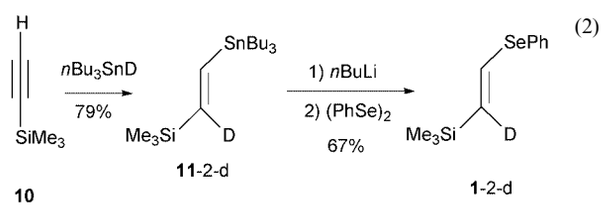
by straightforward methods and their [2 + 1] and [2 + 2] reactions were examined. As a result, the cyclopropanation sequence in Scheme 1, rather than that in Scheme 2, is strongly supported by the labelling study reported herein. For cyclobutane formation, the possibility of silicon–selenium double migration was eliminated, and it was unequivocally shown that the metal-coordination site depends on the Lewis acid, and controls the regiochemistry, as suggested before.[5]

Results and discussion

The deuterium-labelled selenosilylethenes **1**-1-d and **1**-2-d were prepared by treatment of the corresponding (*E*)-1- and -2-deuterio-1-tributylstannyl-2-(trimethylsilyl)ethenes with *n*-butyllithium followed by diphenyl diselenide, according to the preparation method of non-labelled substrate **1** [equations (1) and (2)].[1a] The precursors, (*E*)-1- and -2-deuterio-1-tributyl-



(1)

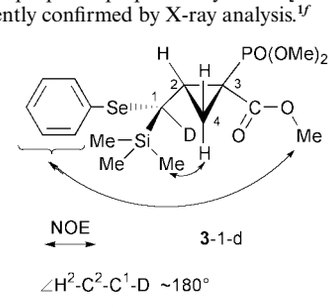


(2)

stannyl-2-(trimethylsilyl)ethenes **11**-1-d and **11**-2-d were obtained by the reaction of (deuterioethynyl)trimethylsilane[6] **10**-d and tri-*n*-butyltin hydride, and the reaction of (ethynyl)trimethylsilane **10** and tri-*n*-butyltin deuteride,[7] respectively.

There are various electrophilic olefins that give cyclopropanes in their reaction with 1-seleno-2-silylethenes. Amongst them, the reaction of trimethyl 2-phosphonoacrylate **2** with deuterium-labelled **1** was examined first because it affords cyclopropanes chemoselectively, stereoselectively and in high yield. The reaction of 1-deuterio-1-phenylseleno-2-(trimethylsilyl)ethene **1**-1-d with phosphonoacrylate **2** in the presence of $SnCl_4$ at −78 °C gave a C-1 deuterio-substituted cyclopropane product **3**-1-d in 76% yield [equation (3)].‡ Similarly, reaction

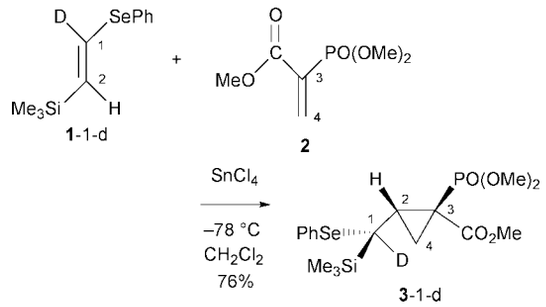
‡ The chemical shifts of our deuterium-labelled cyclopropanes and cyclobutanes are essentially the same as for the non-deuterium-labelled products which were reported previously, except at the deuterium-labelled positions.[1,5] Therefore, the stereochemistry of these cycloadducts is assigned as the same as the non-deuterium products reported previously. An example of the determination of the stereochemistry for the deuterium-labelled cyclopropane **3**-1-d by NMR is as follows. In **3**-1-d, NOEs [between $SiMe_3$ and H-4 (*cis* to CSeSi group) and between CO_2Me and Ph] were observed. These NOEs are also seen in the non-deuterium-labelled cyclopropanes **3** [*e.g.*, E = $PO(OMe)_2$, R = Me].[1e] In the non-deuterium-labelled cyclopropanes **3**, $J_{1,2}$ is 12.5 Hz. The large coupling constant, together with considerations of molecular models, suggests that the favoured dihedral angle ∠H-1–C-1–C-2–H-2 is close to 180°. By a combination of the suggested favoured structure and observed NOEs, the relative stereochemistry of C-2,C-1 was assigned as (*R*,*R*) or (*S*,*S*). The relative stereochemistry for a sulfone-substituted cyclopropane prepared by this [2 + 1] cycloaddition method was recently confirmed by X-ray analysis.[1f]



∠H^2-C^2-C^1-D ~180°

On the regiochemistry of cyclobutanes, for example, the HMBC correlations of H-2 · · · *C*N for **7**-1-d and H-2 · · · *C*O_2Me for **8**-1-d were observed. The stereochemistry of the Me_3Si and PhSe groups of cyclobutanes **7**-1-d, **8**-1-d, **7**-2-d and **8**-2-d was deduced as *trans* according to the assignment of non-deuterium-labelled cyclobutanes by NOESY spectra.[5]

of 1-deuterio-2-phenylseleno-1-(trimethylsilyl)ethene **1**-2-d with phosphonoacrylate **2** gave a C-2 deuterio-substituted cyclopropane product **3**-2-d in 78% yield [equation (4)]. Thus,



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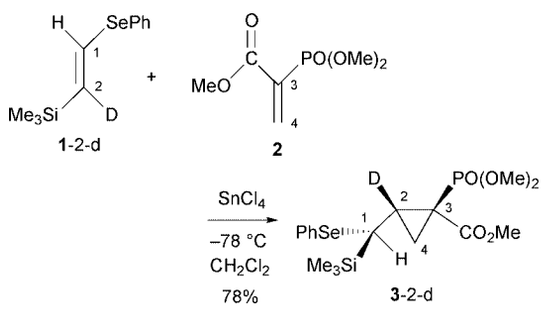
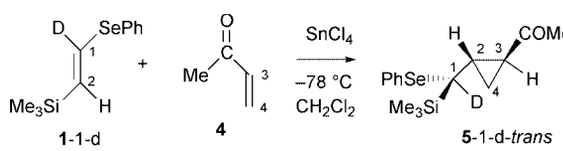


(4)

phenylseleno-group migration as an alternative to silicon migration is completely ruled out.

Reaction of vinyl ketones with **1** in the presence of $SnCl_4$ led to *trans*-cyclopropanes preferentially (Scheme 1). The reaction of 1-deuterio-1-phenylseleno-2-(trimethylsilyl)ethene **1**-1-d with methyl vinyl ketone **4** in the presence of $SnCl_4$ at −78 °C gave the C-1 deuterio-substituted *trans*-cyclopropane product **5**-1-d in 59% yield [equation (5)]. The reaction of 1-deuterio-2-phenylseleno-1-(trimethylsilyl)ethene **1**-2-d with **4** gave the C-2 deuterio-substituted cyclopropanes **5**-2-d-*trans* and **5**-2-d-*cis* in 48% yield (3.8 : 1 *trans* : *cis* ratio) [equation (6)]. Thus, phenylseleno-group migration instead of silicon migration is ruled out



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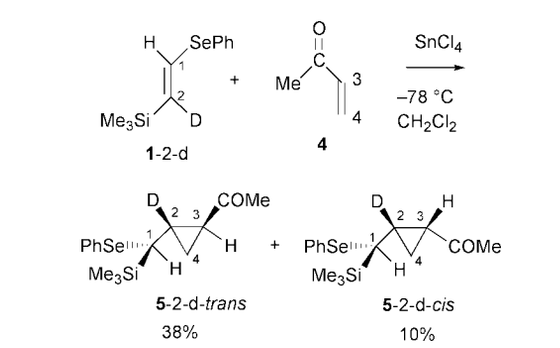

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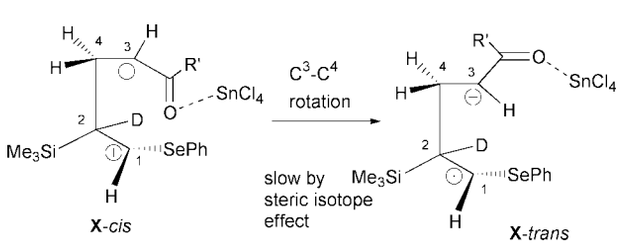
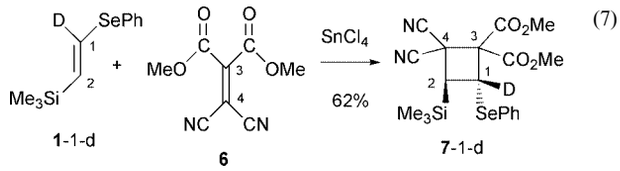


in this case as well. The formation of *cis*-cyclopropane **5**-2-d-*cis* as a minor product may be explained by a steric isotope effect[8] in C–C bond rotation in the zwitterion intermediate **X** (see Scheme 1).

Next, [2 + 2] cycloaddition reactions of deuterium-labelled **1** with dimethyl 2,2-dicyanoethene-1,1-dicarboxylate **6** were examined [equations (7) and (8)]. The reaction of 1-deuterio-1-



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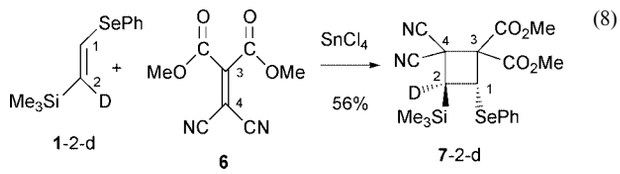

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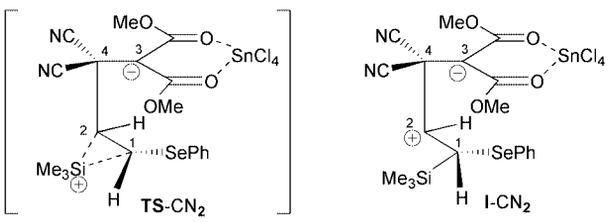


phenylseleno-2-(trimethylsilyl)ethene **1**-1-d with **6** in the presence of $SnCl_4$ at −78 °C gave C-1 deuterium-substituted cyclobutane **7**-1-d in 62% yield.‡ The reaction of 1-deuterio-2-phenylseleno-1-(trimethylsilyl)ethene **1**-2-d with **6** in the presence of $SnCl_4$ gave C-2 deuterium-substituted cyclobutane **7**-2-d exclusively in 56% yield. Thus, the mechanism is in complete agreement with that proposed previously (Scheme 3). In contrast to the [2 + 1] cycloaddition described above, [2 + 2] cycloaddition proceeds without silicon migration. This result can be explained by destabilization of the corresponding intermediate after silicon migration (**I**-CN_2) and/or the silicon-migration transition state (**TS**-CN_2) by the two electron-withdrawing cyano groups next to the cationic centre (at C-4).

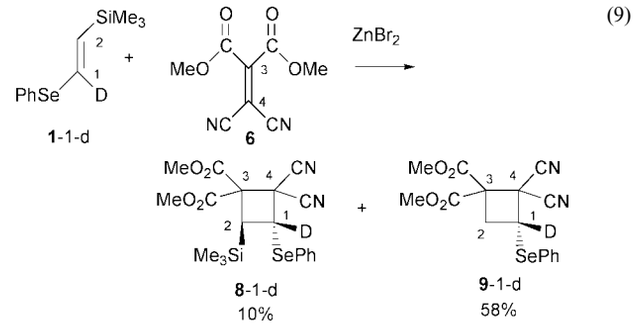
The reaction of deuterium-substituted **1** and **6** in the presence of $ZnBr_2$ was also examined [equations (9) and (10)]. As a result, the deuterium atoms on **1**-1-d and **1**-2-d stayed on the original carbons adjacent to the heteroatoms. It was confirmed that no silicon and selenium double migration as depicted in Scheme 4 occurred. Thus, the regioselectivity was controlled by the Lewis acid coordination sites as previously predicted.[5]

In summary, this labelling study strongly supports the previously proposed 1,2-silicon migration for [2 + 1] cycloaddition of **1** and non-1,2-silicon migration for [2 + 2] cycloaddition, respectively. The deuterium-substituted cyclopropanes and cyclobutanes were stereoselectively prepared.

Experimental

General methods

Mps were measured on a Yamato MP-21 melting point apparatus and are uncorrected. IR spectra were recorded with a JASCO FT-IR 5000 spectrophotometer. NMR spectra were recorded on a Varian INOVA 400 spectrometer. Chemical shifts are reported in ppm relative to Me_4Si or residual non-deuterated solvent. *J*-Values are given in Hz. ^{13}C multiplicities were determined by DEPT and HSQC. Mass spectra were recorded on a JEOL JMS-01SG-2 spectrometer at an ionizing



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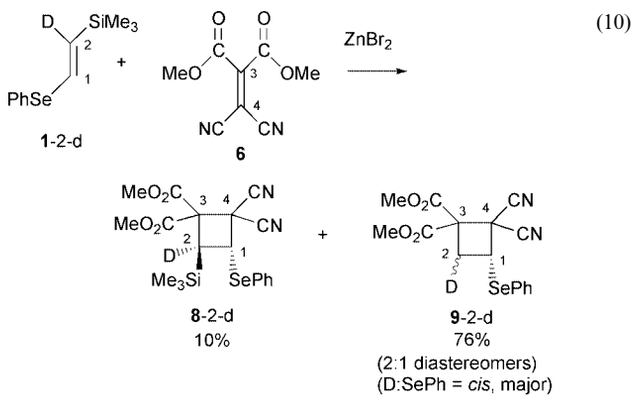

(10)

The carbon numbering corresponds to Scheme 3

voltage of 70 eV by EI. All reactions were carried out under a nitrogen atmosphere.

(*E*)-1-Tributylstannyl-2-(trimethylsilyl)[1-^{2}H]ethene 11-1-d §

A neat solution of *n*-Bu_3SnH (6.36 g, 22.9 mmol) and ([^{2}H]-ethynyl)trimethylsilane[6] **10**-d [prepared from (trimethylsilyl)-ethynylmagnesium bromide and D_2O (CEA, 99.9% D)] (2.90 g, 2.93 mmol) was heated at 100 °C for 24 h. The reaction mixture was cooled and the product was distilled directly to give **11**-1-d (6.87 g, 77%) as a colourless oil; bp 105–110 °C/1 mmHg; δ_H (400 MHz, $CDCl_3$) 0.056 (9H, s, $SiMe_3$), 0.862–0.924 (15H, m), 1.26–1.37 (6H, m), 1.46–1.54 (6H, m) and 6.60 (1H, t, J_{HD} 3.4, H-2). ^{1}H NMR analysis indicated 99% D incorporation; δ_C (100.6 MHz; $CDCl_3$) −1.39 ($SiMe_3$), 9.49 (CH_2), 13.79 (CH_3), 27.35 (CH_2), 29.19 (CH_2), 149.5 (t, J_{CD} 22, C-1) and 155.0 (C-2); ν_{max}/cm^{-1} (neat) 2960, 2928, 2874, 1464, 1247, 861 and 837; *m*/*z* (EI) 334 (M^+ − 55, 100%), 276 (13) and 73 (22).

(*E*)-2-Tributylstannyl-1-(trimethylsilyl)[1-^{2}H]ethene 11-2-d

11-2-d was prepared from *n*-Bu_3SnD[7] [prepared from Bu^n_3SnCl and $LiAlD_4$ (Aldrich, 98% D)] and ethynyltrimethylsilane by the same procedure as for **11**-1-d in 79% yield as a colourless oil; bp 100–110 °C/1 mmHg; δ_H (400 MHz, $CDCl_3$) 0.056 (9H, s, $SiMe_3$), 0.862–0.923 (15H, m), 1.26–1.35 (6H, m), 1.46–1.54 (6H, m) and 6.95 (1H, t, J_{HD} 3.4, H-1). Non-deuterium-labelled compound was not detected by ^{1}H NMR analysis; δ_C (100.6 MHz, $CDCl_3$) −1.40 ($SiMe_3$), 9.50 (CH_2), 13.80 (CH_3), 27.35 (CH_2), 29.19 (CH_2), 149.8 (C-1) and 154.7 (t, J_{CD} 21, C-2); ν_{max}/cm^{-1} (neat) 2960, 2928, 2874, 2856, 1526, 1464, 1377, 1247 and 837; *m*/*z* (EI) 334 (M^+ − 55, 100%), 278 (20) and 73 (20).

(*E*)-1-Phenylseleno-2-(trimethylsilyl)[1-^{2}H]ethene 1-1-d

A solution of 1.42 M *n*-BuLi (9.0 mL, 12.8 mmol) in hexane was added to a pre-cooled (−78 °C) solution of (*E*)-1-tributylstannyl-2-(trimethylsilyl)[1-^{2}H]ethene **11**-1-d (5.0 g, 12.8 mmol) in THF (37 mL) with stirring. The solution was allowed to warm to −30 °C slowly. After 2 h at −30 °C, the solution was re-cooled to −78 °C. To the solution was added diphenyl diselenide (4.0 g, 12.8 mmol). The mixture was stirred at −78 °C for 1 h, and then was allowed to warm to room temperature and was stirred for 1.5 h. After the addition of water, the mixture was extracted with hexane–diethyl ether (1:1). The organic layer was dried over anhydrous $MgSO_4$. The solvent was removed at reduced pressure, and column chromatography (silica gel; hexane) of the residue gave **1**-1-d (2.2 g, 68%) (R_f 0.5). **1**-1-d: Pale yellow oil; δ_H (400 MHz, $CDCl_3$) 0.076 (9H, s, $SiMe_3$), 6.18 (1H, t, J_{HD} 2.7, H-2), 7.31–7.34 (3H, m, *m,p*-H of Ph) and 7.51–7.55 (2H, m, *o*-H of Ph). Non-deuterium-labelled compound was not detected by ^{1}H NMR analysis; δ_C (100.6 MHz, $CDCl_3$) −1.19 ($SiMe_3$), 127.7 (CH), 129.3 (CH), 129.4 (CH), 133.8 (CH), 134.1 (CH) and 134.2 (t, J_{CD} 28, C-1); ν_{max}/cm^{-1} (neat) 2958, 1524, 1479, 1249, 861 and 837; *m*/*z* (EI) 257 (M^+); exact mass M^+, 257.0222 ($C_{11}H_{15}D^{80}Se^{28}Si$ requires *M*, 257.0250) (Found: C, 51.65; H + D, 6.2%. Calc. for $C_{11}H_{15}$DSeSi: C, 51.55; H + D, 6.3%).

(*E*)-2-Phenylseleno-1-(trimethylsilyl)[1-^{2}H]ethene 1-2-d

1-2-d was prepared from **11**-2-d by the same procedure as for **1**-2-d in 67% yield as a pale yellow oil; δ_H (400 MHz, $CDCl_3$) 0.070 (9H, s, $SiMe_3$), 7.00 (1H, t, J_{HD} 2.7, H-1), 7.30–7.34 (3H, m, *m,p*-H of Ph) and 7.51–7.55 (2H, m, *o*-H of Ph). ^{1}H NMR analysis indicated 99% D incorporation; δ_C (100.6 MHz, $CDCl_3$) −1.20 ($SiMe_3$), 127.8 (CH), 129.37 (C), 129.42 (CH), 133.8 (CH), 133.9 (t, J_{CD} 21, C-2) and 134.4 (CH); ν_{max}/cm^{-1} (neat) 2958, 1580, 1533, 1479, 1249, 967 and 841; *m*/*z* (EI) 257 (M^+) (Found: C, 51.5; H + D, 6.3%. Calc. for $C_{11}H_{15}$DSeSi: C, 51.55; H + D, 6.3%).

Methyl *r*-1-(dimethoxyphosphoryl)-*c*-2-[(phenylseleno)(trimethylsilyl)[^{2}H]methyl]cyclopropanecarboxylate 3-1-d §¶

To a solution of **1**-1-d (256 mg, 1.00 mmol) in dichloromethane (2.5 mL) was added $SnCl_4$ (0.176 mL, 391 mg, 1.50 mmol), followed by 2-phosphonoacrylate **2** (0.202 mL, 252 mg, 1.30 mmol) at −78 °C. The mixture was stirred at −78 °C for 3 h. The reaction mixture was quenched by triethylamine (0.36 mL, 260 mg, 2.6 mmol) and then with saturated aq. $NaHCO_3$. The mixture was extracted with dichloromethane and the organic phase was washed with water, dried (Na_2SO_4), and evaporated *in vacuo*. The residue was purified by column chromatography over silica gel and eluting with CH_2Cl_2–diethyl ether (2:1) to give **3**-1-d (340 mg, 76%) (R_f 0.5) as a pale yellow oil; δ_H (400 MHz, $CDCl_3$) 0.104 (9H, s, $SiMe_3$), 1.62 (1H, ddd, *J* 9.9, 8.1 and 4.5, H-4), 1.86 (1H, ddd, *J* 14.1, 8.7 and 4.5, H-4), 2.23 (1H, ddd, *J* 14.2, 8.7 and 8.1, H-2), 3.40 (3H, s, CO_2Me), 3.80 (3H, d, *J* 11.0, POMe), 3.89 (3H, d, *J* 11.0, POMe), 7.19–7.23 (3H, m, *m,p*-H of Ph) and 7.49–7.51 (2H, m, *o*-H of Ph); δ_C (100.6 MHz, $CDCl_3$) −1.87 ($SiMe_3$), 24.01 (d, J_{CP} 3.1, C-4), 25.43 (d, J_{CP} 191, C-3), 28.65 (t, J_{CD} 20, CD), 33.42 (d, J_{CP} 2.3, C-2), 52.66 (CO_2*Me*), 53.55 (d, J_{CP} 6.1, POMe), 53.66 (d, J_{CP} 6.1, POMe), 127.1 (CH), 128.9 (CH), 130.6 (C), 133.8 (CH) and 168.9 (d, J_{CP} 7.6, CO); ν_{max}/cm^{-1} (neat) 2958, 1721, 1578, 1479, 1437, 1307, 1251, 1036 and 841; *m*/*z* (EI) 456; exact mass M^+, 451.0576 ($C_{17}H_{26}DO_5P^{80}Se^{28}Si$ requires *M*, 451.0592).

Methyl *r*-1-(dimethoxyphosphoryl)-*c*-2-[(phenylseleno)(trimethylsilyl)methyl][2-^{2}H]cyclopropanecarboxylate 3-2-d

3-2-d was prepared from **1**-2-d by the same procedure for **3**-1-d in 78% yield as a pale yellow oil; δ_H (400 MHz, $CDCl_3$) 0.106 (9H, s, $SiMe_3$), 1.61 (1H, dd, *J* 9.9 and 4.5, H-4), 1.86 (1H, dd, *J* 14.2 and 4.5, H-4), 2.59 (1H, s, CHSeSi), 3.39 (3H, s, CO_2Me), 3.80 (3H, d, *J* 11.0, POMe), 3.89 (3H, d, *J* 11.0, POMe), 7.19–

§ The compound nomenclature in titles is systematic. The ^{1}H and ^{13}C assignments follow the Schemes in the text.

¶ Non-deuterium-labelled compounds were not detected in the products by ^{1}H NMR analysis.

7.23 (3H, m, *m,p*-H of Ph) and 7.49–7.52 (2H, m, *o*-H of Ph); δ_C (100.6 MHz, $CDCl_3$) −1.86 ($SiMe_3$), 23.95 (d, J_{CP} 2.3, C-4), 25.33 (d, J_{CP} 191, C-3), 28.89 (CHSeSi), 33.23 (t, J_{CD} 25, C-2), 52.66 (CO_2*Me*), 53.55 (d, J_{CP} 6.1, POMe), 53.66 (d, J_{CP} 6.1, POMe), 127.1 (CH), 128.9 (CH), 130.7 (C), 133.8 (CH) and 168.9 (d, J_{CP} 6.9, CO); ν_{max}/cm^{-1} (neat) 2956, 1721, 1578, 1479, 1437, 1311, 1284, 1251, 1035, 839 and 741; *m/z* (EI) 451 (M^+); exact mass M^+, 451.0595 ($C_{17}H_{26}DO_5P^{80}Se^{28}Si$ requires *M*, 451.0592).

trans-1-Acetyl-2-{(phenylseleno)(trimethylsilyl)[^{2}H]methyl}-cyclopropane 5-1-d-*trans*

To a solution of **1**-1-d (256 mg, 1.00 mmol) in dichloromethane (2.5 ml) was added $SnCl_4$ (0.176 mL, 391 mg, 1.50 mmol), followed by methyl vinyl ketone **4** (0.108 mL, 91.1 mg, 1.30 mmol) at −78 °C. The mixture was stirred at −78 °C for 3 h. The reaction mixture was quenched by triethylamine (0.36 mL, 260 mg, 2.6 mmol) and then with saturated aq. $NaHCO_3$. The mixture was extracted with dichloromethane and the organic phase was washed with water, dried (Na_2SO_4), and evaporated *in vacuo*. The residue was purified by column chromatography over silica gel and elution with hexane–diethyl ether (4:1) to give **5**-1-d (340 mg, 59%) (R_f 0.5) as a pale yellow oil; δ_H (400 MHz, $CDCl_3$) 0.166 (9H, s, $SiMe_3$), 0.745 (1H, ddd, *J* 8.1, 6.4, and 4.0, H-4), 1.32 (1H, ddd, *J* 8.7, 4.8 and 4.0, H-4), 1.53 (1H, ddd, *J* 8.1, 4.8 and 3.9, H-3), 1.72 (1H, ddd, *J* 8.7, 6.4 and 3.9, H-2), 1.93 (3H, s, COMe), 7.25–7.30 (3H, m, *m,p*-H of Ph) and 7.56–7.58 (2H, m, *o*-H of Ph); δ_C (100.6 MHz, $CDCl_3$) −1.84 ($SiMe_3$), 19.78 (C-4), 29.94 (C-2), 30.00 (C-3), 30.53 (COMe), 35.85 (t, J_{CD} 19, CDSeSi), 127.5 (*p*-C of Ph), 129.1 (*m*-C of Ph), 130.6 (C of Ph), 134.5 (*o*-C of Ph) and 207.9 (CO); ν_{max}/cm^{-1} (neat) 2958, 1698, 1578, 1390, 1249 and 843; *m/z* (EI) 327 (M^+, 24%), 170 (57), 96 (38) and 73 (100); exact mass M^+, 327.0638 ($C_{15}H_{21}DO^{80}Se^{28}Si$ requires *M*, 327.0667) (Found: C, 55.2; H + D, 6.65%. Calc. for $C_{15}H_{21}DOSeSi$: C, 55.2; H + D, 6.8%).

trans-2-Acetyl-1-[(phenylseleno)(trimethylsilyl)methyl][1-^{2}H]-cyclopropane 5-2-d-*trans* and *cis*-2-acetyl-1-[(phenylseleno)-(trimethylsilyl)methyl][1-^{2}H]cyclopropane 5-2-d-*cis*

5-2-d-*trans* and **5**-2-d-*cis* were prepared from **1**-2-d by the same procedure used for **5**-1-d in 38% and 10% yield, respectively. **5**-2-d-*trans* [R_f 0.15 (hexane–diethyl ether 2:1)] was obtained as colourless crystals; mp 40–42 °C; δ_H (400 MHz, $CDCl_3$) 0.166 (9H, s, $SiMe_3$), 0.740 (1H, dd, *J* 8.0 and 4.0, H-4), 1.31 (1H, dd, *J* 4.5 and 4.5, H-4), 1.52 (1H, dd, *J* 8.0 and 5.0, H-3), 1.92 (3H, s, COMe), 2.09 (1H, s, CHSeSi), 7.24–7.29 (3H, m, *m,p*-H of Ph) and 7.56–7.58 (2H, m, *p*-H of Ph); δ_C (100.6 MHz, $CDCl_3$) −1.83 ($SiMe_3$), 19.70 (C-4), 29.71 (t, J_{CD} 25, C-2), 29.92 (C-3), 30.53 (COMe), 36.13 (CHSeSi), 127.5 (CH), 129.1 (CH), 130.6 (C), 134.4 (CH) and 207.9 (CO); ν_{max}/cm^{-1} (KBr) 2960, 1692, 1576, 1383, 1249 and 839; *m/z* (EI) 327; exact mass M^+, 327.0640 ($C_{15}H_{21}DO^{80}Se^{28}Si$ requires *M*, 327.0667) (Found: C, 55.1; H + D, 6.5%. Calc. for $C_{15}H_{21}DOSeSi$: C, 55.2; H + D, 6.8%).

5-2-d-*cis* [R_f 0.3 (hexane–diethyl ether 2:1)] was obtained as a colourless oil; δ_H (400 MHz, $CDCl_3$) 0.058 (9H, s, $SiMe_3$), 1.21 (2H, d, *J* 6.4, H-4), 2.07 (3H, s, COMe), 2.15 (1H, dd, *J* 6.4 and 6.4, H-3), 2.66 (1H, s, CHSeSi), 7.19–7.23 (3H, m, *m,p*-H of Ph) and 7.49–7.52 (2H, m, *o*-H of Ph); δ_C (100.6 MHz, $CDCl_3$) −1.74 ($SiMe_3$), 18.60 (C-4), 27.21 (CH), 28.43 (CH), 29.24 (t, J_{CD} 25, C-2), 32.30 (COMe), 127.2 (CH), 128.9 (CH), 129.9 (C), 134.7 (CH) and 206.9 (CO); ν_{max}/cm^{-1} (neat) 2958, 1692, 1578, 1479, 1381, 1249, 1176, 874 and 837; *m/z* (EI) 327; exact mass M^+, 327.0652 ($C_{15}H_{21}DO^{80}Se^{28}Si$ requires *M*, 327.0667).

Dimethyl 3,4-*trans*-2,2-dicyano-4-phenylseleno-3-(trimethylsilyl)[4-^{2}H]cyclobutane-1,1-dicarboxylate 7-1-d

To a solution of **1**-1-d (256 mg, 1.00 mmol) in dichloromethane (1.2 mL) was added $SnCl_4$ (0.176 mL, 391 mg, 1.50 mmol), followed by a solution of dimethyl 2,2-dicyanoethene-1,1-dicarboxylate **6**[4] (252 mg, 1.30 mmol) in CH_2Cl_2 (1.2 mL) at −78 °C. The mixture was stirred at −78 °C for 1 h. The reaction mixture was quenched by triethylamine (0.32 mL, 233 mg, 2.3 mmol) and then with saturated aq. $NaHCO_3$. The mixture was extracted with dichloromethane and the organic phase was washed with water, dried (Na_2SO_4), and evaporated *in vacuo*. The residue was purified by column chromatography over silica gel and elution with hexane–diethyl ether (2:1) to give **7**-1-d (279 mg, 62%) (R_f 0.7) as colourless crystals; mp 78–80 °C; δ_H (400 MHz, $CDCl_3$) 0.239 (9H, s, $SiMe_3$), 2.89 (1H, s, H-2), 3.85 (3H, s, CO_2Me), 3.97 (3H, s, CO_2Me), 7.30–7.38 (3H, m, *m,p*-H of Ph) and 7.60–7.64 (2H, m, *o*-H of Ph); δ_C (100.6 MHz, $CDCl_3$) −2.57 ($SiMe_3$), 33.29 (C-3), 38.91 (C-2), 41.91 (t, J_{CD} 24, C-1), 53.73 (CO_2*Me*), 53.84 (CO_2*Me*), 67.96 (C-4), 112.6 (CN), 113.9 (CN), 128.7 (CH), 128.7 (C), 129.5 (CH), 134.5 (CH), 165.1 (CO) and 165.7 (CO); ν_{max}/cm^{-1} (KBr) 2960, 2250, 1744, 1578, 1301, 1253 and 847; *m/z* (EI) 451; exact mass M^+, 451.0563 ($C_{19}H_{21}DN_2O_4{}^{80}Se^{28}Si$ requires *M*, 451.0576) (Found: C, 50.8; H + D, 4.7; N, 6.2%. Calc. for $C_{19}H_{21}DN_2O_4SeSi$: C, 50.7; H + D, 4.9; N, 6.2%).

Dimethyl 3,4-*trans*-2,2-dicyano-4-phenylseleno-3-(trimethylsilyl)[3-^{2}H]cyclobutane-1,1-dicarboxylate 7-2-d

7-2-d was prepared from **1**-2-d by the same procedure used for **7**-1-d in 56% yield [R_f 0.7 (hexane–diethyl ether 2:1)] as colourless crystals; mp 78–81 °C; δ_H (400 MHz, $CDCl_3$) 0.240 (9H, s, $SiMe_3$), 3.85 (3H, s, CO_2Me), 3.97 (3H, s, CO_2Me), 4.31 (1H, s, H-1), 7.31–7.38 (3H, m, *m,p*-H of Ph) and 7.61–7.64 (2H, m, *o*-H of Ph); δ_C (100.6 MHz, $CDCl_3$) −2.59 ($SiMe_3$), 33.21 (C-3), 38.54 (t, J_{CD} 21, C-2), 42.12 (C-1), 53.73 (CO_2*Me*), 53.85 (CO_2*Me*), 68.04 (C-4), 112.6 (CN), 113.9 (CN), 128.71 (CH), 128.74 (C), 129.5 (CH), 134.5 (CH), 165.1 (CO) and 165.7 (CO); ν_{max}/cm^{-1} (KBr) 2960, 2370, 2334, 2248, 1744, 1578, 1296, 845 and 743; *m/z* (EI) 451; exact mass M^+, 451.0536 ($C_{19}H_{21}DN_2O_4{}^{80}Se^{28}Si$ requires *M*, 451.0576) (Found: C, 50.8; H + D, 4.9; N, 6.2%. Calc. for $C_{19}H_{21}DN_2O_4SeSi$: C, 50.7; H + D, 4.9; N, 6.2%).

Reaction of 1-1-d and 6 with $ZnBr_2$

To a solution of **1**-1-d (255 mg, 1.00 mmol) in dichloromethane (1.2 mL) was added $ZnBr_2$ (338 mg, 1.50 mmol), followed by a solution of dimethyl 2,2-dicyanoethene-1,1-dicarboxylate **6** (252 mg, 1.30 mmol) in CH_2Cl_2 (1.2 mL) at 0 °C. The mixture was stirred at 0 °C for 5 h, then at room temperature for 2 h. The reaction mixture was quenched by triethylamine (0.32 mL, 233 mg, 2.3 mmol) and then with saturated aq. $NaHCO_3$. The mixture was extracted with dichloromethane and the organic phase was washed with water, dried (Na_2SO_4), and evaporated *in vacuo*. The residue was purified by column chromatography over silica gel and elution with hexane–diethyl ether (2:1) to give **8**-1-d (43 mg, 10%) (R_f 0.7) and **9**-1-d (220 mg, 58%) (R_f 0.6).

Dimethyl 3,4-*trans*-2,2-dicyano-3-phenylseleno-4-(trimethylsilyl)[3-^{2}H]cyclobutane-1,1-dicarboxylate 8-1-d. Colourless oil; δ_H (400 MHz, $CDCl_3$) 0.112 (9H, s, $SiMe_3$), 2.70 (1H, s, H-2), 3.85 (3H, s, CO_2Me), 3.89 (3H, s, CO_2Me), 7.34–7.40 (3H, m, *m,p*-H of Ph) and 7.65–7.67 (2H, m, *o*-H of Ph); δ_C (100.6 MHz, $CDCl_3$) −2.17 ($SiMe_3$), 37.37 (C-2), 43.82 (t, J_{CD} 25, C-1), 44.81 (C-3), 53.84 (CO_2*Me*), 53.91 (CO_2*Me*), 60.78 (C-4), 111.8 (CN), 112.8 (CN), 127.1 (C), 129.3 (CH), 129.9 (CH), 135.1 (CH), 166.3 (CO) and 166.4 (CO); ν_{max}/cm^{-1} (neat) 2958, 2270, 1754, 1736 and 1294; *m/z* (EI) 451; exact mass M^+, 451.0517 ($C_{19}H_{21}DN_2O_4{}^{80}Se^{28}Si$ requires *M*, 451.0576) (Found: C, 50.7; H + D, 4.8; N, 6.1%. Calc. for $C_{19}H_{21}DN_2O_4SeSi$: C, 50.7; H + D, 4.9; N, 6.2%).

Dimethyl 2,2-dicyano-3-(phenylseleno)[3-^{2}H]cyclobutane-1,1-dicarboxylate 9-1-d. Colourless oil; δ_H (400 MHz, $CDCl_3$) 2.84 (1H, d, *J* 12.9, H-2), 2.91 (1H, d, *J* 12.9, H-2), 3.88 (3H, s,

CO_2Me), 3.90 (3H, s, CO_2Me), 7.33–7.42 (3H, m, *m,p*-H of Ph) and 7.64–7.67 (2H, m, *o*-H of Ph); δ_C (100.6 MHz, $CDCl_3$) 33.93 (C-2), 40.22 (t, J_{CD} 24, C-1), 42.17 (C-3), 54.00 (CO_2*Me*), 54.56 (CO_2*Me*), 58.01 (C-4), 111.79 (CN), 111.82 (CN), 126.3 (C), 129.4 (CH), 129.8 (CH), 135.4 (CH), 165.5 (CO) and 166.1 (CO); ν_{max}/cm^{-1} (neat) 2962, 2344, 2250, 1746, 1578, 1437, 1288, 743 and 692; *m/z* (EI) 379 (Found: C, 50.85; H + D, 3.8; N, 7.2%. Calc. for $C_{16}H_{13}DN_2O_4Se$: C, 50.8; H + D, 3.7; N, 7.4%).

Reaction of **1**-2-d and **6** with $ZnBr_2$ by the same procedure as used for **1**-1-d gave **8**-2-d and **9**-2-d in 10% and 76% yield, respectively.

Dimethyl 3,4-*trans*-2,2-dicyano-3-phenylseleno-4-(trimethylsilyl)[4-^{2}H]cyclobutane-1,1-dicarboxylate 8-2-d. [R_f 0.7 (hexane–diethyl ether 2 : 1)]; colourless crystals; mp 65–68 °C; δ_H (400 MHz, $CDCl_3$) 0.000 (9H, s, $SiMe_3$), 3.85 (3H, s, CO_2Me), 3.89 (3H, s, CO_2Me), 4.50 (1H, s, H-1), 7.34–7.40 (3H, m, *m,p*-H of Ph) and 7.65–7.67 (2H, m, *o*-H of Ph); δ_C (100.6 MHz, $CDCl_3$) −2.20 ($SiMe_3$), 37.04 (t, J_{CD} 19, C-2), 44.04 (C-1), 44.87 (C-3), 53.83 (CO_2*Me*), 53.91 (CO_2*Me*), 60.69 (C-4), 111.8 (CN), 112.8 (CN), 127.2 (C), 129.3 (CH), 129.9 (CH), 135.0 (CH), 166.3 (CO) and 166.4 (CO); ν_{max}/cm^{-1} (KBr) 2960, 2348, 1750, 1738, 1439, 1296, 1255 and 845; *m/z* (EI) 451; exact mass M^+, 451.0548 ($C_{19}H_{21}DN_2O_4{}^{80}Se^{28}Si$ requires *M*, 451.0576) (Found: C, 50.5; H + D, 4.8; N, 6.3%. Calc. for $C_{19}H_{21}DN_2O_4SeSi$: C, 50.7; H + D, 4.9; N, 6.2%).

Dimethyl 2,2-dicyano-3-(phenylseleno)[4-^{2}H]cyclobutane-1,1-dicarboxylate 9-2-d. 2 : 1 Diastereomixture (D : SePh = *cis*, major). The observed NOEs were between δ 4.58 and 2.91 and between δ 4.58 and 7.64–7.67. [R_f 0.6 (hexane–diethyl ether 2 : 1)]. Pale yellow oil; δ_H (400 MHz, $CDCl_3$) 2.84 (0.33H, d, *J* 11.4, H-2), 2.91 (0.69H, d, *J* 9.0, H-2), 3.88 (3H, s, CO_2Me), 3.90 (3H, s, CO_2Me), 4.58 (1H, br d, *J* 9.2, H-1), 7.33–7.42 (3H, m, *m,p*-H of Ph) and 7.64–7.67 (2H, m, *o*-H of Ph); δ_C (100.6 MHz, $CDCl_3$) 33.66 (t, J_{CD} 22, C-2), 40.39 (C-1), 42.20 (C-3), 53.98 (CO_2*Me*), 54.55 (CO_2*Me*), 57.86 (C-4), 111.76 (CN), 111.80 (CN), 126.3 (C), 129.4 (CH), 129.8 (CH), 135.4 (CH), 165.4 (CO) and 166.1 (CO); ν_{max}/cm^{-1} (neat) 2962, 1744, 1578, 1437, 1280, 743 and 692; *m/z* (EI) 379; exact mass M^+, 379.0159 ($C_{16}H_{13}DN_2O_4{}^{80}Se$ requires *M*, 379.0181) (Found: C, 50.7; H + D, 3.6; N, 7.15%. Calc. for $C_{16}H_{13}DN_2O_4Se$: C, 50.8; H + D, 3.7; N, 7.4%).

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