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Selenium-Induced Cyclization of O-Allyl Oximes as a Synthetic Route to N-Alkyl Isoxazolidines

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Abstract: Phenylselenenyl bromide easily reacts with O-allyl oximes to afford cyclic iminium bromides which can be reduced *in situ* with sodium borohydride to produce substituted N-alkyl isoxazolidines in good yield.

Ring-closure reactions which take place by the formation of a carbon-nitrogen bond can be easily effected starting from alkenes containing internal nitrogen nucleophiles under the influence of electrophilic reagents, including metals, iodine, bromine and several phenylselenenyl derivatives. This synthetic process is very useful since it offers an easy access to a wide range of substituted nitrogen heterocycles.¹⁻³ Much attention has been recently devoted to the cyclization reactions of alkenes in which the nitrogen internal nucleophile is that of an imidate,⁴ oxime,⁵⁻⁷ an O-allyl oxime^{8,9} or an imine.^{10,11} In these compounds the imino nitrogen atom is sufficiently nucleophilic to attack the carbon atom of the intermediate formed from the interaction of the electrophilic reagent with the olefinic double bond, e. g. 2 (Scheme 1). Thus, lactams and cyclic nitrones are formed from imidates and oximes, respectively, and cyclic iminium salts, which can evolve in different ways, are produced from O-allyl oximes and from imines.

Scheme 1



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We have recently reported that O-allyl oximes of type 1, when treated with phenylselenenylating agents, give rise to the cyclic iminium salts 3 which, upon treatment with water, afford the N-unsubstituted isoxazolidines 4 (Scheme 1). We report in this paper that the reactions of 1 with PhSeBr afford the bromides 3 which can be reduced with sodium borohydride and give rise to N-alkyl isoxazolidines 5 in good yield. This selenenylation reduction procedure is similar to that employed to convert alkenyl imines into pyrrolidines or piperidines.¹⁰

The O-allyl oximes **1a-f**, employed for the present investigation, are indicated in Table 1. These were conveniently obtained from the corresponding oximes by treatment with NaH in THF and then with the desired allyl halide. The oxime **1e** was constituted by the *syn* isomer and **1f** was an almost equimolecular mixture of the *syn* and *anti* isomers. As indicated in Scheme 1, the geometry of the carbon-carbon double bond was E in every case.

The cyclization reactions were carried out by adding phenylselenenyl bromide to the solution of the O-allyl oximes **1a-f** in dichloromethane at room temperature. The progress of the reaction was monitored by TLC and GC-MS. After 1h, methanol and sodium borohydride were added and the solution was stirred at room temperature for 1h. The reaction mixtures were poured on water and worked up in the usual way. The reaction products **5a-f** were obtained in a pure form by column chromatography on silica gel and were fully characterized by ¹H and ¹³C NMR and GC-MS spectra. The results of these experiments are summarized in Table 1. As indicated in Scheme 1, the reaction proceeds through the initial formation of the seleniranium ion intermediates **2** and the cyclic iminium bromides **3** and hence the isoxazolidines **5** are the result of a stereospecific *trans* addition process. Compounds **5a-f** were in fact obtained as single stereoisomers. The cyclic iminium bromides **3** were not isolated but their presence as reaction intermediates was unambiguosly demonstrated by ¹H and ¹³C NMR spectra (CDCl3) which could be recorded when the reactions of the O-allyl oximes with PhSeBr were carried out in an NMR tube.

The N-alkyl isoxazolidines 5 can also be obtained, in similar good yield, from the selenium induced cyclization of the O-allyl hydroxylamines,¹² which can be easily obtained from the O-allyl oximes 1 by reduction, at room temperature, with sodium cyanoborohydride and hydrochloric acid in methanol. Thus these two methods are complementary and represent new and very convenient syntheses of this interesting class of heterocyclic compounds.¹³ However, a substantial difference was observed in the stereochemical course of the two reactions. In fact, it was observed that in the O-allyl hydroxylamine 6 (Scheme 2) the presence of a methyl substituent has no influence on the course of the reaction, the two possible stereoisomers 7 and 8 being obtained in equimolecular amounts (90% yield). On the contrary, when the synthesis was effected starting from the O-allyl oxime 9, according to the procedure described in this paper, the isoxazolidines 7 and 8 were obtained in a 95:5 ratio (75% yield). The stereoselectivity observed in this case indicates that steric requirements for the selenium-induced cyclization of the O-allyl oximes are much greater than those for the corresponding O-allyl hydroxylamines.

The stereochemistry of 7 and 8 was demonstrated by the results of differential NOE and NOESY experiments.¹²

O-Allyl Oxime		Iminium Bromide ^a		Isoxazolidine		% Yield ^b
1a		F 3a	^h Se N+ Me Me	5a	PhSe Me	50
1b	Me	F 3b	hSe Me	5b	PhSe Me	73
1c	Ph N Me	F 3c	PhSe Ph Nt Me Me	F 5c	PhSe Ph N Me	80
1d	Ph -N -n-Pr n-Pr	F 3d	hSe Ph , Ph , Ph , Ph , Ph , Ph , Ph	F 5d	PhSe Ph 	93
1e	Ph O ^N Ph	F 3e	Ph Ph N N Ph	f 5e	PhSe Ph ON Ph	71
1f	Ph O ^N Me	F 3f	hSe Ph , , , , , , , , , , , , ,	5f	PhSe Ph	95

Table 1. Conversion of O-Allyl Oximes into N-Alkyl Isoxazolidines

a. Identified by NMR spectra.

b. Calculated on isolated products after column chromatography.





In conclusion, a general and straightforward synthesis of N-substituted isoxazolidines from electrophilic selenium-induced cyclization of O-allyl oximes has been developed. Because of the easy access to the starting material and of the extremely simple procedure, this method, as well as that in which O-allyl hydroxylamines are used as starting materials,¹² can find a large application. The isoxazolidine is a very important heterocyclic system which can be formed in several ways; however its production by a cyclization reaction involving the formation of a carbon-nitrogen bond is very uncommon.¹³

EXPERIMENTAL

GLC analyses and MS spectra were carried out with an HP 5890 gaschromatograph (dimethyl silicone column, 12.5 m) equipped with an HP 5971 Mass Selective Detector. ¹H and ¹³C NMR spectra were recorded at 200 and 50.32 MHz, respectively, on a Bruker AC 200 instrument; CDCl₃ was used as solvent and TMS as standard. Elemental analyses were carried out on a Carlo Erba 1106 Elemental Analyzer and were in good agreement with the calculated values. All new compounds were fully characterized by MS, ¹H, and ¹³C-NMR spectroscopy.

Synthesis of O-Allyl Oximes. General Procedure. Acetone oxime, acetaldoxime and *syn*-benzaldehyde oxime were commercially available. 4-Heptanone oxime was prepared from the ketone by standard procedure.

A mixture of the oxime (0.05 mol) and sodium hydride (0.055 mol) in tetrahydrofuran (50 ml) was stirred at room temperature for about 1h. Crotyl bromide, cinnamyl bromide or 1-phenyl-3-bromo-1-butene (0.06 mol) was added and the mixture stirred at room temperature for 4-12 h. The progress of the reaction was

monitored by TLC and GC-MS. The reaction mixture was poured on water and worked up in the usual way. The reaction product was obtained in a pure form by column chromatography on silica gel. Reaction yields are reported in parentheses. Physical and spectral data are reported below.

O-Crotyl acetone oxime 1a. Oil (69%). ¹H NMR δ 5.8-5.4 (m, 2 H), 4.45 (m, 2 H), 1.9 (s, 3 H), 1.89 (s, 3 H), 1.7 (d, 3 H, J = 5.0 Hz); ¹³C NMR δ 160.0, 128.8, 127.4, 73.8, 21.6, 17.6, 15.3; MS *m/z* (relative intensity) 127 (7), 112 (19), 73 (10), 55 (100), 41 (10).

O-Crotyl 4-heptanone oxime 1b. Oil (80%). ¹H NMR δ 5.83-5.51 (m, 2 H), 4.48-4.39 (m, 2 H), 2.26 (t, 2 H, J = 7.3 Hz), 2.12 (t, 2 H, J = 7.3 Hz), 1.7 (d, 3 H, J = 5.0 Hz), 1.52 (sextet, 1 H, J = 7.3 Hz), 1.51 (sextet, 1 H, J = 7.3 Hz), 0.93 (t, 3 H, J = 7.3 Hz), 0.92 (t, 3 H, J = 7.3 Hz); ¹³C NMR δ 160.2, 128.4, 127.6, 73.7, 36.0, 29.9, 19.7, 19.1, 17.5, 14.0, 13.5; MS *m/z* (relative intensity) 183 (3), 166 (17), 114 (14), 101 (18), 73 (38), 70 (19), 55 (100), 43 (15).

O-Cinnamyl acetone oxime 1c. Oil (79%). ¹H NMR δ 7.43-7.11 (m, 5 H), 6.6 (d, 1 H, J = 16.0 Hz), 6.35 (dt, 1 H, J = 6.0 and 16.0 Hz), 4.68 (dd, 2 H, J = 1.1 and 6.0 Hz), 1.87 (s, 3 H), 1.86 (s, 3 H); ¹³C NMR δ 154.2, 136.6, 132.2, 128.2, 127.3, 126.3, 125.8, 73.6, 21.5, 15.3; MS *m/z* (relative intensity) 189 (2), 118 (15), 117 (100), 115 (38), 91 (13), 77 (9), 51 (6).

O-Cinnamyl 4-heptanone oxime 1d. Oil (92%). ¹H NMR δ 7.42-7.19 (m, 5 H), 6.6 (d, 1 H, *J* = 16.0 Hz), 6.35 (dt, 1 H, *J* = 5.8 and 16.0 Hz), 4.66 (dd, 2 H, *J* = 1.2 and 5.8 Hz), 2.3 (t, 2 H, *J* = 7.3 Hz), 2.12 (t, 2 H, *J* = 7.3 Hz), 1.52 (sextet, 4 H, *J* = 7.3 Hz), 0.94 (t, 3 H, *J* = 7.3 Hz), 0.93 (t, 3 H, *J* = 7.3 Hz); ¹³C NMR δ 161.1, 136.8, 132.0, 128.3, 127.3, 126.3, 126.1, 73.6, 36.0, 29.9, 19.8, 19.1, 14.2, 13.7; MS *m*/*z* (relative intensity) 245 (1), 117 (100), 115 (14), 91 (6), 77 (4), 41 (6).

O-Cinnamyl syn-benzaldehyde oxime 1e. Oil (85%). ¹H NMR δ 8.1 (s, 1 H), 7.6-7.5 (m, 2 H), 7.4-7.1 (m, 8 H), 6.65 (d, 1 H, J = 16.0 Hz), 6.4 (dt, 1 H, J = 6.0 and 16.0 Hz), 4.8 (dd, 2 H, J = 1.05 and 6.0 Hz); ¹³C NMR δ 148.7, 137.0, 133.3, 132.3, 129.6, 128.5, 128.4, 127.7, 127.0, 126.6, 125.2, 74.8; MS m/z (relative intensity) 237 (1), 117 (100), 91 (7), 77 (8).

O-Cinnamyl acetaldoxime 1f. Oil (65%). ¹H NMR (isomer a+b) δ 7.43 (q, 1 H (a), J = 5.8 Hz), 7.40-7.13 (m, 10 H), 6.75 (q, 1 H (b), J = 5.5 Hz), 6.61 (d, 2 H, (a+b), J = 16.0 Hz), 6.34 (dt, 1 H (b), J = 6.0 and 16.0 Hz), 6.32 (dt, 1 H (a), J = 6.0 and 16.0 Hz), 4.69 (dd, 2 H (b), J = 6.0 and 13.0 Hz), 4.67 (dd, 2 H (a), J = 6.0 and 13.0 Hz), 1.84 (d, 3 H (b), J = 5.5 Hz), 1.82 (d, 3 H (a), J = 5.8 Hz); ¹³C NMR δ 146.5, 136.7, 132.8, 132.6, 128.3, 127.4, 126.4, 125.7, 125.5, 74.1, 73.8, 14.8, 11.6; MS *m/z* (relative intensity) isomer a: 175 (2), 118 (10), 117 (100), 115 (28), 91 (9), 77 (9), 51 (4); isomer b: 175 (2), 118 (10), 117 (100), 115 (29), 91 (10), 77 (9), 51 (5).

O-(1-Phenyl-1-buten-3-yl) acetone oxime 9. Oil (64%). ¹H NMR δ 7.4-7.1 (m, 5 H), 6.5 (d, 1 H, J = 16.1 Hz), 6.25 (dd, 1 H, J = 6.4 and 16.1 Hz), 4.77 (dq, 1 H, J = 0.8 and 6.4 Hz), 1.86 (s, 3 H), 1.85 (s, 3 H), 1.39 (d, 3 H, J = 6.5 Hz); ¹³C NMR δ 154.3, 137.1, 131.7, 130.2, 128.4, 127.4, 126.5, 78.6, 21.7, 20.3, 15.7; MS *m/z* (relative intensity) 203 (1), 132 (11), 131 (100), 91 (24), 77 (5).

Cyclic Iminium Bromide. General Procedure. These compounds were detected by NMR, at room temperature, by dissolving equimolecolar amounts of the oximes **1a-f** and of PhSeBr in CDCl₃. The spectral data are reported below.

3-Methyl-4-(phenylseleno)-N-isopropyliden isoxazolidinium bromide 3a. ¹H NMR δ 7.4-7.2 (m, 5 H), 5.18 (dq, 1 H, J = 2.3 and 6.7 Hz), 5.1 (dd, 1 H, J = 5.9 and 9.2 Hz), 4.72 (dd, 1 H, J = 3.8 and 9.2 Hz), 4.05 (ddd, 1 H, J = 2.3, 3.8 and 5.9 Hz), 2.5 (s, 3 H), 2.3 (s, 3 H), 1.65 (d, 3 H, J = 6.7 Hz); ¹³C NMR δ 166.3, 128.4, 127.4, 126.7, 77.1, 67.8, 41.6, 22.7, 21.0, 17.5.

3-Methyl-4-(phenylseleno)-N-(4-heptyliden) isoxazolidinium bromide 3b. ¹H NMR δ 7.65-7.5 (m, 2 H), 7.35-7.19 (m, 3 H), 4.65-4.22 (m, 3 H), 3.72-3.5 (m, 1 H), 2.31-2.0 (m, 4 H), 1.79 (d, 3 H, J = 6.7 Hz), 1.65-1.38 (m, 4 H), 1.05-0.8 (m, 6 H); ¹³C NMR δ 173.9, 135.7, 130.0, 129.4, 76.6, 69.6, 43.8, 37.3, 35.1, 20.3, 20.1, 19.3, 14.4, 14.3.

3-Phenyl-4-(phenylseleno)-N-isopropyliden isoxazolidinium bromide 3c. ¹H NMR δ 7.49-7.12 (m, 10 H), 6.1 (d, 1 H, *J* = 7.2 Hz), 4.9 (dd, 1 H, *J* = 7.3 and 8.5 Hz), 4.8 (dd, 1 H, *J* = 8.5 and 8.8 Hz), 3.9 (ddd, 1 H, *J* = 7.2, 7.3 and 8.8 Hz), 2.5 (s, 3 H), 2.1 (s, 3 H); ¹³C NMR δ 171.0, 134.9, 132.6, 129.8, 129.4, 128.7, 128.5, 126.1, 77.0, 75.4, 47.2, 23.8, 23.2.

3-Phenyl-4-(phenylseleno)-N-(4-heptyliden) isoxazolidinium bromide 3d. ¹H NMR δ 7.5-7.2 (m, 5 H), 6.49 (d, 1 H, *J* = 7.4 Hz), 4.49 (d, 2 H, *J* = 8.3 Hz), 4.05 (dt, 1 H, *J* = 7.4 and 8.3 Hz), 2.9-2.3 (m, 4 H), 1.8-1.4 (m, 3 H), 1.05 (t, 3 H, *J* = 7.2 Hz), 1.0-0.8 (m, 1 H), 0.6 (t, 3 H, *J* = 7.0 Hz); ¹³C NMR δ 176.7, 130.0, 129.5, 128.8, 128.4, 126.6, 77.3, 75.8, 47.7, 37.3, 35.6, 19.2, 18.6, 14.2, 13.8.

3-Phenyl-4-(phenylseleno)-N-benzyliden isoxazolidinium bromide 3e. ¹H NMR δ 9.3 (s, 1 H), 7.6-7.2 (m, 15 H), 6.75 (d, 1 H, *J* = 12.7 Hz), 5.3 (dd, 1 H, *J* = 7.1 and 8.5 Hz), 4.9 (t, 1 H, *J* = 8.5 Hz), 4.25 (ddd, 1 H, *J* = 7.1, 8.5 and 12.7 Hz); ¹³C NMR δ 148.9, 132.0, 130.5, 130.2, 130.0, 129.7, 129.5, 129.3, 129.2, 128.5, 128.1, 79.4, 78.1, 42.6.

3-Phenyl-4-(phenylseleno)-N-ethyliden isoxazolidinium bromide 3f. ¹H NMR δ 7.52-7.15 (m, 11 H), 5.95 (d, 1 H, J = 10.7 Hz), 5.13 (dd, 1 H, J = 7.4 and 8.4 Hz), 4.73 (dd, 1 H, J = 8.4 and 10.3 Hz), 4.45-4.15 (m, 1 H), 3.4 (d, 3 H, J = 5.0 Hz); ¹³C NMR δ 155.0, 135.9, 131.0, 129.9, 129.5, 129.3, 129.0, 77.9, 77.2, 42.5, 16.1.

Conversion of O-Allyl Oximes into Isoxazolidines. General Procedure. Crystalline phenylselenenyl bromide (5.5 mmol) was added portionwise to the solution of the O-allyl oxime (5 mmol) in dichloromethane (20 ml) at room temperature. The progress of the reaction was monitored by TLC and GC-MS. After 1h, methanol (10 ml) and sodium borohydride (7.5 mmol) were added and the solution was stirred at room temperature for 1h. The reaction mixture was poured on water and worked up in the usual way. The reaction product was obtained in a pure form by column chromatography on silica gel. Reaction yields are reported in Table 1. Physical and spectral data are reported below. In the mass spectra only the peaks of the most abundant ⁸⁰Se isotope are reported.

3-Methyl-4-(phenylseleno)-N-isopropyl isoxazolidine 5a. ¹H NMR δ 7.6-7.5 (m, 2 H), 7.35-7.2 (m, 3 H), 4.21 (dd, 1 H, *J* = 7.4 and 8.8 Hz), 3.86 (dd, 1 H, *J* = 7.4 and 8.8 Hz), 3.5 (dt, 1 H, *J* = 6.6 and 7.4 Hz), 3.7 (dq, 1 H, *J* = 6.3 and 6.6 Hz), 2.99 (septet, 1 H, *J* = 6.3 Hz), 1.28 (d, 3 H, *J* = 6.3 Hz), 1.27 (d, 3 H, *J* = 6.3 Hz), 1.09 (d, 3 H, *J* = 6.3 Hz); ¹³C NMR δ 134.3, 129.1, 127.8, 71.7, 64.0, 54.2, 49.4, 20.6, 19.2, 18.2; MS *m/z* (relative intensity) 285 (12), 186 (10), 184 (58), 158 (30), 157 (16), 128 (11), 113 (13), 91 (14), 86 (12), 84 (15), 77 (17), 55 (100), 43 (29).

3-Methyl-4-(phenylseleno)-N-(4-heptyl) isoxazolidine 5b. ¹H NMR δ 7.6-7.48 (m, 2 H), 7.3-7.2 (m, 3 H), 4.16 (dd, 1 H, *J* = 7.6 and 8.7 Hz), 3.83 (dd, 1 H, *J* = 6.7 and 8.7 Hz), 3.47 (q, 1 H, *J* = 7.1 Hz), 3.02 (quint, 1 H, *J* = 6.4 Hz), 2.65-2.43 (m, 1 H), 1.58-1.23 (m, 8 H), 1.21 (d, 3 H, *J* = 6.3 Hz), 0.89 (t, 6 H, *J* = 7.0 Hz); ¹³C NMR δ 134.5, 129.1, 128.7, 127.8, 71.9, 62.7, 61.8, 49.6, 34.5, 30.8, 20.0, 19.2, 18.1, 14.4, 14.2; MS *m/z* (relative intensity) 341 (13), 298 (100), 184 (39), 157 (31), 98 (34), 91 (16), 86 (19), 84 (19), 78 (18), 77 (16), 70 (25), 57 (46), 55 (80), 43 (55).

3-Phenyl-4-(phenylseleno)-N-isopropyl isoxazolidine 5c. ¹H NMR δ 7.5-7.38 (m, 4 H), 7.35-7.11 (m, 6 H), 4.38 (dd, 1 H, J = 7.1 and 9.0 Hz), 4.01 (dd, 1 H, J = 6.0 and 9.0 Hz), 3.91 (d, 1 H, J = 6.8 Hz), 3.78 (dd, 1 H, J = 6.0, 6.8 and 7.1 Hz), 2.9 (septet, 1 H, J = 6.3 Hz), 1.03 (d, 3 H, J = 6.3 Hz), 0.92 (d, 3 H, J = 6.3 Hz); ¹³C NMR δ 140.7, 134.3, 129.0, 128.4, 127.7, 127.4, 127.3, 73.1, 72.3, 55.1, 52.4, 20.9, 18.4; MS *m/z* (relative intensity) 347 (3), 163 (34), 162 (15), 157 (6), 132 (13), 121 (17), 117 (100), 115 (19), 104 (14), 91 (22), 77(19).

3-Phenyl-4-(phenylseleno)-N-(4-heptyl) isoxazolidine 5d. ¹H NMR δ 7.5-7.1 (m, 10 H), 4.36 (dd, 1 H, *J* = 7.2 and 8.9 Hz), 4.0 (dd, 1 H, *J* = 5.3 and 8.9 Hz), 3.93 (d, 1 H, *J* = 7.2 Hz), 3.77 (dt, 1 H, *J* = 5.3 and 7.2 Hz), 2.61-2.47 (m, 1 H), 1.64-1.03 (m, 8 H), 0.82 (t, 3 H, *J* = 7.0 Hz), 0.73 (t, 3 H, *J* = 6.9 Hz); ¹³C NMR δ 139.7, 134.3, 128.9, 128.5, 128.3, 127.6, 127.5, 72.5, 71.6, 61.6, 52.2, 34.1, 30.4, 19.9, 19.1, 14.2, 13.9; MS *m*/*z* (relative intensity) 403 (3), 360 (23), 202 (23), 176 (33), 160 (78), 157 (17), 132 (17), 117 (100), 115 (28), 104 (21), 91 (74), 77 (34), 57 (19), 43 (30).

3-Phenyl-4-(phenylseleno)-N-benzyl isoxazolidine 5e. ¹H NMR δ 7.5-7.1 (m, 15 H), 4.48 (dd, 1 H, J = 7.7 and 8.9 Hz), 4.1 (dd, 1 H, J = 4.9 and 8.9 Hz), 3.95 (d, 1 H, J = 13.9 Hz), 3.85 (ddd, 1 H, J = 4.9, 7.7 and 9.0 Hz), 3.77 (d, 1 H, J = 13.9 Hz), 3.75 (d, 1 H, J = 9.0 Hz); ¹³C NMR δ 138.4, 137.4, 134.4, 129.1, 128.9, 128.6, 128.1, 128.0, 127.9, 127.7, 127.1, 76.7, 73.1, 60.0, 51.6.

3-Phenyl-4-(phenylseleno)-N-ethyl isoxazolidine 5f. ¹H NMR δ 7.4-7.1 (m, 10 H), 4.45 (dd, 1 H, J = 7.7 and 9.0 Hz), 4.08 (dd, 1 H, J = 5.2 and 9.0 Hz), 3.84 (dt, 1 H, J = 5.2 and 7.7 Hz), 3.58 (d, 1 H, J = 7.7 Hz), 2.74 (q, 2 H, J = 7.1 Hz), 1.1 (t, 3 H, J = 7.1 Hz); ¹³C NMR δ 138.5, 134.1, 128.9, 128.7, 128.4, 127.6, 127.5, 77.0, 72.6, 51.6, 50.8, 12.7; MS *m*/*z* (relative intensity) 333 (6), 184 (22), 182 (12), 176 (11), 157 (6), 149 (61), 148 (41), 118 (15), 117 (100), 115 (20), 104 (13), 91 (30), 77 (21).

3,5-Dimethyl-4-(phenylseleno)-N-isopropyl isoxazolidine 7 and 8. (7): ¹H NMR δ 7.5-7.4 (m, 4 H), 7.3-7.1 (m, 6 H), 4.17 (dq, 1 H, J = 5.9 and 8.9 Hz), 4.04 (d, 1 H, J = 8.0 Hz), 3.23 (dd, 1 H, J = 8.0 and 8.9 Hz), 2.91 (septet, 1 H, J = 6.2 Hz), 1.3 (d, 3 H, J = 5.9 Hz), 1.08 (d, 3 H, J = 6.2 Hz), 0.9 (d, 3 H, J = 6.2 Hz); ¹³C NMR δ 135.5, 129.0, 128.4, 128.2, 127.3, 78.7, 73.9, 59.2, 55.7, 20.6, 19.2, 17.3; MS m/z

(relative intensity) 361 (7), 198 (26), 195 (13), 164 (16), 157 (6), 132 (22), 131 (100), 104 (11), 91 (34), 77 (18), 43 (17). (8): ¹H NMR δ 7.4-7.1 (m, 10 H), 4.6 (quintet, 1 H, *J* = 6.2 Hz), 3.92 (d, 1 H, *J* = 6.7 Hz), 3.85 (dd, 1 H, *J* = 6.2 and 6.7 Hz), 2.97 (septet, 1 H, *J* = 6.5 Hz), 1.36 (d, 3 H, *J* = 6.2 Hz), 1.1 (d, 3 H, *J* = 6.5 Hz), 0.92 (d, 3 H, *J* = 6.5 Hz); ¹³C NMR δ 140.6, 133.6, 129.0, 128.4, 127.6, 127.5, 127.2, 74.8, 74.7, 60.5, 55.7, 21.0, 18.2, 17.8; MS *m/z* (relative intensity) 361 (11), 198 (31), 164 (23), 157 (8), 146 (22), 131 (100), 91 (39), 77 (22), 43 (31).

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