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The reaction of 1,2,3-selenadiazole with olefins

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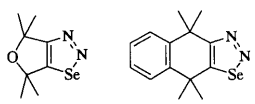
Abstract

When 1,2,3-selenadiazoles synthesized from cyclic ketones were treated with an excess amount of olefins at 130°C, the addition of a vinyl radical, which was generated in situ by the denitrogenation of 1,2,3-selenadiazoles, to a carbon–carbon double bond followed by intramolecular cyclization proceeded efficiently giving the corresponding dihydroselenophenenes in moderate to good yields along with the formation of the corresponding 1,4-diselenins and selenophenes as by-products. In this reaction, the number of carbon atoms on the cyclic ring of the ketones used as the starting materials in the synthesis of the 1,2,3-selenadiazoles plays an important role in the selectivity of the products. In contrast to the reaction of the 1,2,3-selenadiazoles prepared from the cyclic ketones, in the reaction of 1,2,3-selenadiazoles derived from aromatic and linear ketones, the dihydroselenophenene and 1,4-diselenins derivatives were not obtained and the corresponding alkynes were formed as the sole product.

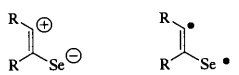
Keywords: 1,2,3-Selenadiazole; Olefins; Thermolysis; Dihydroselenophene

1. Introduction

Recently, the synthesis of heterocyclic compounds containing selenium and the utilization of these compounds in organic synthesis have been steadily increasing [1]. Among selenium-containing heterocyclic compounds, the 1,2,3-selenadiazoles **1** were of interest as versatile intermediates for the preparation of alkynes, because **1** is easily decomposed with the loss of a nitrogen molecule and selenium atom under light irradiation and thermal conditions [2,3]. Ando and Tokitoh et al. have examined the reaction of the sterically protected bicyclic 1,2,3-selenadiazoles **2**–**3** with various organic compounds during light irradiation ($\lambda > 365$ nm and $\lambda = 265$ nm) and assumed the formation of zwitterionic **4** and biradical **5** intermediates [4].



2 **3**



4 **5**

In contrast to the well known reactivity of 1,2,3-selenadiazole under photolysis conditions [5], the reactivity of the intermediate of 1,2,3-selenadiazoles under thermal conditions has not yet been elucidated [6]. We examined the reaction of various 1,2,3-selenadiazoles with olefins in order to elucidate the characteristic features of the intermediates generated in situ by the thermal decomposition of the 1,2,3-selenadiazoles. These results are reported in this paper.

2. Results and discussion

To clarify the characteristic features of the intermediates generated in situ by the decomposition of the 1,2,3-selenadiazoles under thermal conditions, 1,2,3-se-

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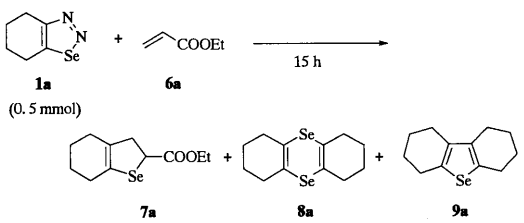
lenadiazole (**1a**) derived from cyclohexanone was first treated with ethyl acrylate **6a** under various reaction conditions and these results are shown in Table 1. When the reaction was carried out in the presence of an excess amount of **6a** (200 equivalents) at 130°C, the denitrogenation of **1a** followed by addition to the unsaturated carbon–carbon double bond of **6a** and subsequent cyclization proceeded to give **7a** in 82% yield along with the formation of 1,4-diselenin **8a** (11%) and selenophenene **9a** (6%) (entry 5) [7]. The decrease in the amounts of **6a** led to a decrease in the selectivity of **7a** (entries 1–5). The conversion of **1a** and the yield of **7a** were affected by the reaction temperature (entries 5–9). When the reaction was carried out at a higher reaction temperature (150°C), **7a** was also formed in 83% yield (entry 8). However, at 180°C, the yield of **7a** was slightly decreased due to the preparation of complex byproducts (entry 9). On the other hand, in the reaction at 80°C, the reaction was significantly decreased to afford **7a** in 17% yield along with the recovery of **1a** (77%) (entry 6).

Table 2 shows the results of the treatment of 1,2,3-selenadiazole **1a** synthesized from cyclohexanone with various olefins. When **1a** was allowed to react with methyl acrylate **6b** and acrylonitrile **6c**, in which electron withdrawing groups were substituted on the carbon–carbon double bond, the corresponding dihydroselenophenes were formed in 76 and 74% yields, respectively (entries 1 and 2). In the case of methyl vinyl ketone, the yield of the addition product was significantly decreased due to the preparation of complex byproducts (entry 3). For this reaction, the alkyl substituted on the carbon–carbon double bond has a significant influence on the selectivity between dihydroselenophene **7** and 1,4-dihydroselenin **8a**. Ethyl methacrylate **6e** also gave the corresponding dihydroselenophene **7e** in 63% yield. In contrast to the reaction of **6e**, when methyl crotonate **6f**, in which the methyl group was substituted at the β-position, was treated with **1a** under the same reaction condition as that of **6e**, the addition reaction of the vinyl radical species generated in situ with **6f** was reduced and **7f** was formed in 23% yield with the formation of 58% yield of **8a**. In the case of butyl vinyl ether **6g** or 1-octene **6h**, **8a** was also formed as the main product.

Next, various 1,2,3-selenadiazols derived from cyclic ketones were treated with an excess amount of methyl acrylate (**6a**) (200 equivalents) at 130°C for 15 h, the results are shown in Table 3. In the case of the 1,2,3-selenadiazoles prepared from the 2- and 4-methylcyclohexanones, the methyl substituent had no influence on the reactivity for producing the corresponding dihydroselenophenes (entries 4 and 5). On the other hand, the yield of **7** and the selectivity of **7** and **8** were influenced by the number of carbon atoms in the cyclic ketones used for the synthesis of the 1,2,3-selanadiazoles (entries 1–3). In the reaction of the 1,2,3-selenadiazoles prepared from 4-heptanone and acetophenone, dihydroselenophene and 1,4-dihydroselenine were not

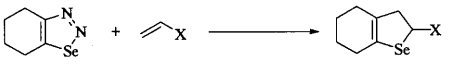
Table 1
Reaction of 1,2,3-selenadiazole with ethyl acrylate under various reaction conditions



entry	**6a** (equiv.)	temp. / °C	yield / %[a]		
			7a	**8a**	**9a**
1	10	130	24	62	6
2	30	130	35	46	8
3	50	130	48	40	6
4	100	130	58	27	6
5	200	130	82	11	6
6[b]	200	80	17	3	1
7	200	100	70	8	5
8	200	150	83	10	6
9	200	180	69	10	5

a) Yields were determined by GC. b) **1a** was recovered in 77 % yield.

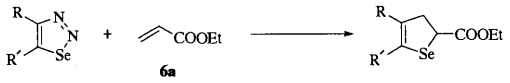
Table 2
Reaction of **1a** with various olefins

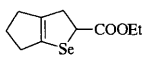
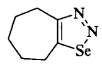
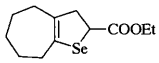
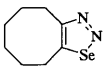
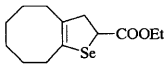
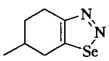
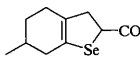
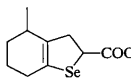


entry	olefin	product	yield / %[b,c]
1	X = COOMe (**6b**)	(**7b**)	76
2	X = CN (**6c**)	(**7c**)	74
3	X = COMe (**6d**)	(**7d**)	25
4	(**6e**)	(**7e**)	63
5	(**6f**)	(**7f**)	23 (58)
6	(**6g**)	(**7g**)	12 (74)
7	(**6h**)	(**7h**)	16 (71)

a) Reaction conditions: **1a** (0.25 mmol) and olefin (50 mmol) at 130 °C for 15 h. b) Isolated yield based on **1a**. c) The number in parenthesis indicates the yield of 1,4-diselenine (**8a**).

Table 3
The reaction of various 1,2,3-selenadiazoles with COOEt

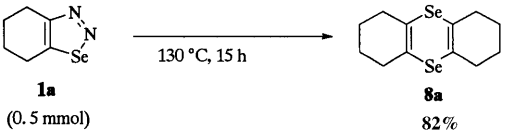


entry	1,2,3-selenadiazole	product	yield / %[b,c]
1	 (1b)	 (7i)	75 (21)
2	 (1c)	 (7j)	47 (32)
3	 (1d)	 (7k)	35 (27)
4	 (1e)	 (7l)	76 (17)
5	 (1f)	 (7m)	76 (17)

a) Reaction conditions: 1,2,3-selenadiazole (0.25 mmol) and 6a (50 mmol) at 130 °C for 15 h. b) Isolated yield based on **1a**. c) The number in parenthesis indicates the yield of 1,4-diselenine (**8**).

formed, but the corresponding alkyne was predominantly formed (Scheme 1).

We cannot explain the decomposition reaction pathways of the 1,2,3-selenadiazoles under thermal conditions in detail, however, possible reaction pathways are shown in Scheme 2. In the case of the 1,2,3-selnadiazoles derived from cyclic ketones, the results of the reaction of **1** with olefins would suggest a reaction pathway that involved the generation of a vinyl radical **11** (path 1). In the presence of olefins, the vinyl radical **10**, which was generated via the homolytic cleavage of the N–Se bond of **1** and the subsequent denitrogenation, was added to the carbon–carbon double bond and subsequently cyclized giving the corresponding dihydroselenophenen **7**. The formation of **8** was also explained by the attack of the vinyl radical **11** on the selenium atom of another molecule of the 1,2,3-selenadiazole following by dinitrogenation and the subsequent intramolecular cyclization pathway. In fact, when **1a** was treated in the absence of an olefin at 150°C for 15 h, 1.4-diselenine was formed in 82% yield (Eq. 1).

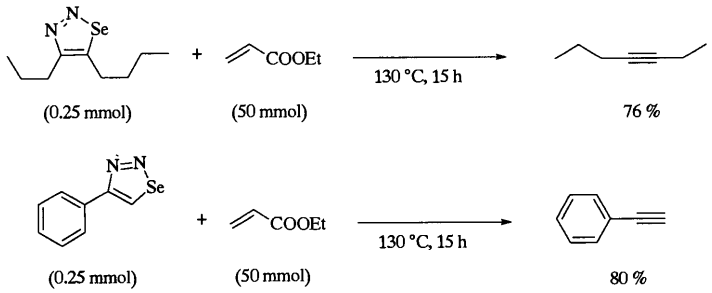


1a (0.5 mmol) — 130 °C, 15 h — **8a** 82% (1)

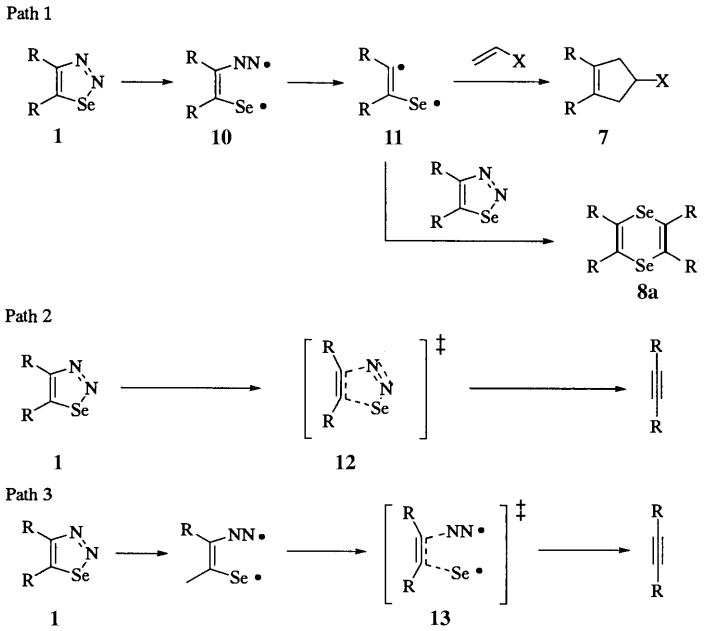
On the other hand, in the case of the 1,2,3-selenadiazoles derived from linear and aromatic ketones, dihydroselenophenen **7**, 1,4-diselenide **8** and selenophene **9** were not formed and the corresponding alkynes as the sole product were formed in good yields. Therefore, the reaction of the 1,2,3-selenadiazole derived from linear and aromatic ketones appears to contain another reaction pathway via the retro [2 + 3] addition reaction (path 2) or the concerted elimination of moleculer nitrogen and selenium atom from the radical intermediate **10** (path 3).

The striking differences observed between the reaction of the 1,2,3-selenadiazoles (**1**) derived from cyclic ketones and the reaction of **1** derived from the linear ketones appears to be explained in terms of the difference in these geometries. In the case of **1** derived from the cyclic ketones, the formation of an alkyne via the retro [2 + 3] reaction (path 2) or concerted elimination (path 3) path was suppressed due to the difficulty in the formation of the transition states **12** and **13** due to the cyclic ring, therefore, the homolytic cleavage of N–Se of **1** and subsequent elimination of the nitrogen molecule predominantly proceeded to generate the vinyl radical **11**.

In summary, we examined the reaction of 1,2,3-selenadiazoles with an excess amount of olefins at 130°C. In the case of the 1,2,3-selenadiazole derived from cyclic ketones, the addition of a vinyl radical, which was generated in situ by the denitrogenation of the 1,2,3-selenadiazoles, to a carbon–carbon double bond followed by intramolecular cyclization proceeded efficiently giving the corresponding dihydroselenophenenes in moderate to good yields. In contrast to the reaction of the 1,2,3-selenadiazoles prepared from cyclic ketones, in the reaction of the 1,2,3-selenadiazoles derived from aromatic and linear ketones, the corresponding alkynes were formed as the sole product.



Scheme 1.



Scheme 2. Plausible reaction pathways.

3. Experimental

^{1}H (400 MHz) and ^{13}C (99.5 MHz) NMR spectra were recorded on a JEOL JNM-GSX-400 spectrometer. The ^{1}H and ^{13}C chemical shifts are referenced to external Me_4Si in $CDCl_3$ as the solvent. FT-IR spectra were obtained using a Perkin–Elmer model Paragon 1000 spectrophotometer. Mass spectra were measured on a Shimadzu model Qp-5050A. Gas chromatography (GC) was carried out on Shimadzu GC-14A equipped with a flame ionizing detector using a capillary column (Hicap-CBP-1-S25-0.25, 0.25 mm × 25 m). Column chromatography was performed using a 5742 (Aldrich). Selenium dioxide, semicarbazide hydrochloride and acetic acid were commercially available high grade products and were used without purification. 1,2,3-Selenadiazoles were prepared by the reaction of selenium dioxide with semicarbazone [8]. The other reagents and solvents were purified by the usual methods before use.

3.1. General procedure for the reaction of 1,2,3-selenadiazole with olefins

In a 50 ml stainless steel autoclave were placed 1,2,3-selenadiazole (0.5 mmol), and olefins (100 mmol). The autoclave was heated by a mantle heater and maintained at 130°C with magnetic stirring for 13 h. The remaining olefin was removed under reduced pressure and purified by column chromatography on silica gel (C_6H_{14}:$CHCl_3$ = 10:1 as the eluate) to give dihydroselenophene, 1,4-diselenin and selenophenene. The structures of the products were assigned based on the ^{1}H, ^{13}C-NMR, IR amd GC mass spectra.

7a: ^{1}H-NMR ($CDCl_3$) δ 1.26 (t, J = 7.3 Hz, 3H), 1.61–1.72 (m, 4H), 1.96–2.22 (m, 4H), 2.72–2.82 (m, 1H), 3.10–3.18 (m, 1H), 4.17 (q, J = 7.3 Hz, 1H), 4.18 (q, J = 7.3 Hz, 1H), 4.41 (dd, J = 5.9, 9.5 Hz, 1H); ^{13}C-NMR ($CDCl_3$) δ 14.2, 22.2, 23.5, 27.3, 27.7, 38.3, 43.1, 61.4, 125.2, 131.4, 174.0; IR (neat) 857, 1045, 1096, 1155, 1181, 1207, 1261, 1298, 1324, 1367, 1442, 1733, 2834, 2931, 2979 cm^{-1}.

8a: ^{1}H-NMR ($CDCl_3$) δ 1.69–1.74 (m, 8H), 2.45–2.48 (m, 8H); ^{13}C-NMR ($CDCl_3$) δ 23.7, 34.0, 129.7; IR (neat) 553, 762, 816, 846, 940, 1070, 1110, 1133, 1170, 1263, 1321, 1431, 1560, 2827, 2857, 2922 cm^{-1}.

9a: ^{1}H-NMR ($CDCl_3$) δ 1.75–1.84 (m, 8H), 2.17–2.37 (m, 8H), 2.76–2.77 (m, 4H); ^{13}C-NMR ($CDCl_3$) δ 22.7, 24.2, 25.7, 27.6, 136.5, 137.3; IR (neat) 795, 1005, 1105, 1132, 1237, 1289, 1333, 1441, 1525, 2835, 2852, 2926 cm^{-1}.

7b: ^{1}H-NMR ($CDCl_3$) δ 1.63–1.80 (m, 4H), 1.96–2.22 (m, 4H), 2.76–2.84 (m, 1H), 3.10–3.15 (m, 1H), 3.72 (s, 3H), 4.42 (dd, J = 5.9, 9.5 Hz, 1H); ^{13}C-NMR ($CDCl_3$) δ 22.2, 23.5, 27.3, 27.7, 38.0, 43.2, 52.6, 125.3, 131.4, 174.5; IR (neat) 844, 983, 1055, 1155, 1172, 1209, 1262, 1293, 1329, 1435, 1737, 2835, 2855, 2930 cm^{-1}.

7c: ^{1}H-NMR ($CDCl_3$) δ 1.61–1.79 (m, 4H), 1.98–2.32 (m, 4H), 2.91–3.07 (m, 2H), 4.24 (dd, J = 5.5, 8.8 Hz, 1H); ^{13}C-NMR ($CDCl_3$) δ 21.0, 22.0, 23.4, 27.4, 27.6, 46.0, 121.6, 127.6, 129.8; IR (neat) 822, 997, 1062, 1156, 1200, 1262, 1307, 1350, 1437, 1655, 2231, 2834, 2855, 2928 cm^{-1}.

7d: ^{1}H-NMR ($CDCl_3$) δ 1.61–1.73 (m, 4H), 1.95–2.23 (m, 4H), 2.26 (s, 3H), 2.64–2.75 (m, 1H), 3.05–3.11 (m, 1H), 4.40 (dd, J = 3.7, 9.2 Hz, 1H); ^{13}C-NMR ($CDCl_3$) δ 22.2, 23.6, 27.2, 27.4, 27.8, 41.5, 47.6, 124.7,

132.3, 203.9; IR (neat) 827, 994, 1062, 1168, 1201, 1239, 1263, 1317, 1353, 1438, 1705, 2833, 2855, 2928 cm^{-1}.

7e: ^{1}H-NMR ($CDCl_3$) δ 1.62–1.72 (m, 4H), 1.82 (s, 3H), 1.98–2.09 (m, 4H), 2.11–2.22 (m, 2H), 2.41–2.46 (m, 1H), 3.35–3.41 (m, 1H), 3.73 (s, 3H); ^{13}C-NMR ($CDCl_3$) δ 22.3, 23.6, 27.5, 28.0, 28.2, 51.6, 52.3, 52.8, 125.8, 130.5, 175.9; IR (neat) 720, 767, 822, 995, 1063, 1097, 1136, 1154, 1211, 1239, 1260, 1274, 1307, 1349, 1373, 1436, 1732, 2856, 2928 cm^{-1}.

7f (mixture of stereoisomers): ^{1}H-NMR ($CDCl_3$) δ 1.12 (d, $J = 7.0$ Hz, 2.7H), 1.45 (d, $J = 7.0$ Hz, 0.3H), 1.54–1.74 (m, 4H), 1.95–2.25 (m, 4H), 2.98–3.06 (m, 0.1H), 3.20–3.28 (m, 0.9H), 3.72 (s, 0.3H), 3.73 (s, 2.7H), 3.97 (d, $J = 5.5$ Hz, 0.9H), 4.58 (d, $J = 7.7$ Hz, 0.1H); ^{13}C-NMR ($CDCl_3$) δ 17.7, 22.2, 22.3, 23.5, 23.6, 26.7, 27.5, 46.5, 49.5, 52.6, 124.4, 135.5, 174.2; IR (neat) 735, 780, 811, 911, 1019, 1064, 1145, 1175, 1199, 1272, 1341, 1434, 1736, 2835, 2929 cm^{-1}.

7g: ^{1}H-NMR ($CDCl_3$) δ 0.91 (t, $J = 7.3$ Hz, 3H), 1.30–1.43 (m, 2H), 1.52–1.78 (m, 6H), 1.99–2.36 (m, 4H), 2.79–2.83 (m, 1H), 3.00–3.04 (m, 1H), 3.27 (dt, $J = 6.6$, 9.2 Hz, 1H), 3.58 (dt, $J = 6.6$, 9.2 Hz, 1H), 5.72 (dd, $J = 1.5$, 6.6 Hz, 1H); ^{13}C-NMR ($CDCl_3$) δ 14.0, 19.6, 22.4, 23.8, 27.7, 28.2, 31.3, 50.2, 70.0, 86.4, 125.5, 130.2; IR (neat) 717, 827, 904, 1010, 1045, 1079, 1115, 1150, 1209, 1262, 1301, 1328, 1378, 1438, 1654, 1735, 2871, 2929 cm^{-1}.

7h: ^{1}H-NMR ($CDCl_3$) δ 0.88 (t, $J = 7.0$ Hz, 3H), 1.20–1.40 (m, 10H), 1.47–1.69 (m, 4H), 1.98–2.03 (m, 2H), 2.18–2.22 (m, 2H), 2.39–2.43 (m, 1H), 2.78–2.80 (m, 1H), 3.88–3.90 (m, 1H); ^{13}C-NMR ($CDCl_3$) δ 14.3, 22.6, 22.8, 23.9, 28.0, 28.2, 29.2, 29.9, 32.0, 38.2, 45.2, 48.6, 126.4, 131.7; IR (neat) 724, 998, 1165, 1261, 1376, 1457, 1541, 1654, 1734, 2854, 2925 cm^{-1}.

7i: ^{1}H-NMR ($CDCl_3$) δ 1.27 (t, $J = 7.0$ Hz, 3H), 2.19–2.34 (m, 4H), 2.35–2.45 (m, 4H), 2.62–2.67 (m, 1H), 2.95–3.01 (m, 1H), 4.18 (q, $J = 7.0$ Hz, 1H), 4.19 (q, $J = 7.0$ Hz, 1H), 4.91 (dd, $J = 5.9$, 9.5 Hz, 1H); ^{13}C-NMR ($CDCl_3$) δ 14.2, 28.0, 31.0, 31.7, 34.4, 46.8, 61.5, 132.0, 142.6, 173.7; IR (neat) 857, 1046, 1193, 1325, 1368, 1444, 1733, 2847, 2955 cm^{-1}.

7j: ^{1}H-NMR ($CDCl_3$) δ 1.26 (t, $J = 7.3$ Hz, 3H), 1.48–1.77 (m, 6H), 2.08–2.30 (m, 4H), 2.99 (dd, $J =$ 9.5, 16.5 Hz, 1H), 3.28 (dd, $J = 5.9$, 16.5 Hz, 1H), 4.17 (q, $J = 7.3$ Hz, 1H), 4.18 (q, $J = 7.3$ Hz, 1H), 4.37 (dd, $J = 5.9$, 9.5 Hz, 1H); ^{13}C-NMR ($CDCl_3$) δ 14.2, 26.6, 27.0, 30.5, 30.9, 31.0, 39.0, 46.8, 61.4, 127.9, 135.2, 173.9; IR (neat) 755, 858, 969, 1023, 1097, 1178, 1207, 1325, 1367, 1444, 1732, 2848, 2920, 2978 cm^{-1}.

7k: ^{1}H-NMR ($CDCl_3$) δ 1.27 (t, $J = 7.1$ Hz, 3H), 1.35–1.59 (m, 3H), 2.11–2.38 (m, 4H), 2.92 (dd, $J =$ 9.5, 16.1 Hz, 1H), 3.20 (dd, $J = 4.8$, 16.1 Hz, 1H), 4.17 (q, $J = 7.1$ Hz, 1H), 4.18 (q, $J = 7.1$ Hz, 1H), 4.34 (dd, $J = 4.8$, 9.5 Hz, 1H); ^{13}C-NMR ($CDCl_3$) δ 14.3, 25.9, 26.4, 28.2, 28.6, 28.7, 29.2, 38.3, 43.6, 61.4, 127.7, 133.7, 174.2; IR (neat) 688, 736, 859, 1040, 1068, 1096, 1179, 1206, 1326, 1367, 1445, 1462, 1731, 2849, 2922, 2978 cm^{-1}.

7l (mixture of stereoisomers): ^{1}H-NMR ($CDCl_3$) δ 1.03 (d, $J = 7.2$ Hz, 1.76 H), 1.08 (d, $J = 7.2$ Hz, 1.24 H),1.25 (t, $J = 7.2$ Hz, 3H), 1.25–1.40 (m, 1H), 1.58–1.67 (m, 1H), 1.72–1.82 (m, 2H), 2.13–2.17 (m, 2H), 2.18–2.34 (m, 1H), 2.64–2.75 (m, 0.5 H), 2.92–3.12 (m, 1H), 3.24–3.35 (m, 0.5H), 4.15–4.21 (m, 2H), 4.37 (dd, $J = 3.2$, 7.2 Hz, 0.58H), 4.40 (dd, $J = 3.2$, 7.2 Hz, 0.42H); ^{13}C-NMR ($CDCl_3$) δ 14.3, 19.9, 20.0, 21.4, 21.6, 27.7, 30.7, 30.8, 32.9, 33,0. 38.1, 38.5, 41.2, 41.3, 61.5, 125.7, 125.8, 135.8, 135.9, 174.1; IR (neat) 1180,1209, 1318, 1322, 1732, 2852, 2927, 2957 cm^{-1}.

7m (mixture of stereoisomers): ^{1}H-NMR ($CDCl_3$) δ 0.97 (t, $J = 7.2$ Hz, 1.5H), 0.98 (t, $J = 7.2$ Hz, 1.5H), 1.26 (t, $J = 7.2$ Hz, 3H), 1.24–1.30 (m, 1H), 1.70–1.87 (m, 3H), 1.98–2.15 (m, 2H), 2.18–2.23 (m, 1H), 2.72–2.88 (m, 1H), 3.04–3.18 (m, 1H), 1.61–1.73 (m, 4H), 4.12–4.21 (m, 2H), 4.43 (dt, $J = 4.0$, 7.2 Hz, 1H); ^{13}C-NMR ($CDCl_3$) δ 14.2, 21.4, 21.5, 27.5, 27.6, 29.9, 30.0, 30.5, 30.6, 35.4, 35.5, 38.6, 38.7, 42.7, 42.8, 61.4, 61.5, 124.9, 125.0, 131.1, 131.2, 174.0, 174.1; IR (neat) 1153, 1179, 1204, 1324, 1368, 1733, 2832, 2850, 2921, 2951 cm^{-1}.

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