

## Supporting Information

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### **“Cobalt-catalyzed Hydrovinylation as the Key Step in a Short Synthesis of Moenocinol”**

Synthesis of (*Z*)-ethyl 3-methyl-6-(1-phenyl-1*H*-tetrazol-5-ylsulfonyl)hex-2-enoate (**3**):

#### **a) Nucleophilic substitution / oxidation:**

Synthesis of 5-(1-phenyl-1*H*-tetrazol-5-ylsulfonyl)pentan-2-one

5-Chloropentan-2-one (5.8 mL, 50.0 mmol, 1.0 equiv.), 1-phenyl-1*H*-tetrazol-5-thiol (9.77 g, 55.0 mmol, 1.1 equiv.) and K<sub>2</sub>CO<sub>3</sub> (8.29 g, 60.0 mmol, 1.2 equiv.) were refluxed in acetone (150 mL, abs.) for 18 h. The solvent was removed under reduced pressure and the residue was dissolved in H<sub>2</sub>O und dichloromethane. The layers were separated, the organic layer was washed with aqueous NaOH (1M) and the aqueous layer extracted three times with dichloromethane. The combined organic layers were dried (MgSO<sub>4</sub>) and the solvent removed under reduced pressure. To a cold solution (0 °C) of the residue in dichloromethane (500 mL) *m*CPBA (75%, 23.01 g, 100.0 mmol, 2.0 equiv.) was added. The reaction mixture was allowed to warm to room temperature and stirred for 24 h. After complete conversion (TLC) the solvent was reduced under reduced pressure, the residue was taken up in diethyl ether, washed successively with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (aq., sat.), NaHCO<sub>3</sub> (aq., sat.) and NaCl (aq., sat.) and the aqueous layers were extracted three times with diethyl ether. The combined organic layers were dried (MgSO<sub>4</sub>) and the solvent removed under reduced pressure. The resulting yellow solid was recrystallized from MTBE which gave 12.493 g of 5-(1-phenyl-1*H*-tetrazol-5-ylsulfonyl)pentan-2-one (42.5 mmol, 85%) as a white solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.70-7.57 (m, 5H), 3.83-3.78 (m, 2H), 2.72 (t, *J* = 6.8 Hz, 2H), 2.27-2.18 (m, 2H), 2.16 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 206.3, 153.4, 133.0, 131.5, 129.7, 125.1, 54.9, 40.7, 29.9, 16.5. MS (ESI): m/z = 317 (M<sup>+</sup>+Na, 100), 312 (1), 298 (1). HRMS (ESI): calculated for C<sub>12</sub>H<sub>14</sub>N<sub>4</sub>SO<sub>3</sub>Na: m/z = 317.0679; found: m/z = 317.0680.

#### **b) Peterson olefination**

To a cold solution (-78 °C) of ethyl trimethylsilyl acetate (440 μL, 2.4 mmol, 1.2 equiv.) in THF (5 mL, abs.) was added drop wise LDA (1M in THF, 2.2 mL, 2.2 mmol, 1.2 equiv.) and the resulting yellow solution was stirred for 2 h at -78 °C. A solution of 5-(1-phenyl-1*H*-tetrazol-5-ylsulfonyl)pentan-2-one (589 mg, 2.0 mmol, 1.0 equiv.) in THF (5 mL, abs.) was added slowly and the reaction mixture was allowed to warm to room temperature overnight. The reaction was quenched with NH<sub>4</sub>Cl (aq., sat.) and diethyl ether, the layers were separated and the aqueous layer was extracted three times with ether. The combined organic layers were dried (MgSO<sub>4</sub>) and the solvent was removed under reduced pressure. The residue was purified by column chromatography (pentane/MTBE: 10:1→5:1) which gave 340 mg of (*Z*)-ethyl 3-methyl-6-(1-phenyl-1*H*-tetrazol-5-ylsulfonyl)hex-2-enoate (**3**, 0.9 mmol, 47%) as a colourless oil and 172 mg of (*E*)-ethyl 3-methyl-6-(1-phenyl-1*H*-tetrazol-5-ylsulfonyl)hex-2-enoate (0.5 mmol, 24%) as a white solid. Analytical data of **3**: <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ = 7.68-7.67 (m, 2H), 7.62-7.56 (m, 3H), 5.76 (s, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.76-3.73 (m, 2H), 2.81 (t, *J* = 7.5 Hz, 2H), 2.17-2.12 (m, 2H), 1.90 (d, *J* = 1.4 Hz, 3H), 1.26 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 166.0, 156.5, 153.4, 133.0, 131.4, 129.6, 125.1, 118.3, 59.7,

55.4, 31.0, 24.6, 20.4, 14.2. **MS** (ESI): m/z = 387 (M+Na<sup>+</sup>, 100), 365 (M+H<sup>+</sup>, 5), 295 (2), 257 (1), 245 (2), 213 (2). **HRMS**: calculated for C<sub>16</sub>H<sub>20</sub>N<sub>4</sub>SO<sub>4</sub>Na: m/z = 387.1097; found: m/z = 387.1102. Analytical data of (*E*)-ethyl 3-methyl-6-(1-phenyl-1*H*-tetrazol-5-ylsulfonyl)hex-2-enoate: **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>): δ = 7.69-7.67 (m, 2H), 7.64-7.58 (m, 3H), 5.69 (s, 1H), 4.14 (dq, *J* = 1.7, 7.1 Hz, 2H), 3.72-3.69 (m, 2H), 2.35 (t, *J* = 7.5 Hz, 2H), 2.21-2.15 (m, 5H), 1.27 (dt, *J* = 1.6, 7.1 Hz, 3H). **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>): δ = 166.2, 155.9, 153.3, 133.0, 131.5, 129.7, 125.0, 117.5, 59.7, 55.1, 38.6, 26.9, 19.9, 14.2. **MS** (ESI): m/z = 387 (M+Na<sup>+</sup>, 100), 365 (M+H<sup>+</sup>, 66), 351 (15), 295 (1), 224 (1), 206 (1). **HRMS**: calculated for C<sub>16</sub>H<sub>20</sub>N<sub>4</sub>SO<sub>4</sub>Na: m/z = 387.1097; found: m/z = 387.1100.

#### Synthesis of 2,2-dimethylhex-5-en-1-ol (**4**):

To a cold solution (0 °C) of DTBB (5.59 g, 21.0 mmol, 2.1 equiv.) in THF (35 mL, abs.) lithium pieces (208 mg, 30.0 mmol, 3.0 equiv.) was added and the resulting dark green solution was stirred for 5 h at 0 °C. 3,3-Dimethyloxetane (1.05 mL, 10.0 mmol, 1.0 equiv.) was added and the resulting dark red solution was stirred for further 2 h at 0 °C. A solution of allyl bromide (1.1 mL, 12.0 mmol, 1.2 equiv.) in THF (10 mL, abs.) was added over the course of 15 min. The colour disappeared and the reaction mixture was allowed to warm to room temperature overnight. The reaction was quenched with NH<sub>4</sub>Cl (aq., sat.) and diethyl ether, the layers were separated and the aqueous layer extracted three times with diethyl ether. The combined organic layers were dried (MgSO<sub>4</sub>) and the solvent removed under reduced pressure. The residue was purified by column chromatography (pentane/MTBE: 10:1) which gave 946 mg of 2,2-dimethylhex-5-en-1-ol (7.5 mmol, 75%) as a colourless liquid. **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 300 MHz): δ = 5.83 (ddt, *J* = 16.8, 10.1, 6.5 Hz, 1H), 5.02 (ddd, *J* = 17.2, 3.2, 1.6 Hz), 4.95-4.91 (m, 1H), 3.33 (s, 2H), 2.06-1.98 (m, 2H), 1.37-1.32 (m, 2H), 0.88 (s, 6H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 75 MHz): δ = 139.5, 114.0, 71.6, 37.8, 35.0, 28.3, 23.8.

The data are in accordance with the literature: Mudryk, B.; Cohen, T. *J. Org. Chem.* **1989**, *54*, 5657.

#### Synthesis of (*E*)-2,2,8,12-tetramethyl-5-methylenetrideca-7,11-dien-1-ol (**2**):

Co(dppp)Br<sub>2</sub> (32 mg, 0.05 mmol, 10 mol%), ZnI<sub>2</sub> (32 mg, 0.1 mmol, 10 mol%) und zinc (7 mg, 0.1 mmol, 10 mol%) were suspended in dry dichloromethane (1 mL) under argon atmosphere. 2,2-Dimethylhex-5-en-1-ol (**4**, 128 mg, 1.0 mmol, 1.0 equiv.) and myrcene (209 μL, 1.1 mmol, 1.1 equiv.) were added and the resulting mixture was stirred at room temperature for 16 h. After complete conversion (GC/MS) the reaction mixture was diluted with MTBE and filtered over a small pad of silica (MTBE, 100 mL). The solvent was removed under reduced pressure and the residue purified by column chromatography (pentane/MTBE: 10:1) which gave 238 mg of (*E*)-2,2,8,12-tetramethyl-5-methylenetrideca-7,11-dien-1-ol (**2**, 0.9 mmol, 90%) as a colourless oil. **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 300 MHz): δ = 5.20-5.07 (m, 2H), 4.72 (s, 2H), 3.33 (s, 2H), 2.72 (d, *J* = 7.4 Hz, 2H), 2.10-1.94 (m, 6H), 1.68 (s, 3H), 1.61 (s, 3H), 1.60 (s, 3H), 1.42-1.36 (m, 2H), 0.89 (s, 6H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 75 MHz): δ = 149.8, 136.5, 131.4, 124.3, 121.9, 108.7, 71.9, 39.8, 36.9, 35.0, 35.0, 30.5, 26.7, 25.7, 23.8, 17.7, 15.9.

The data are in accordance with the literature: R. M. Coates, M. W. Johnson *J. Org. Chem.* **1980**, *45*, 2685.

Synthesis of (*E*)-2,2,8,12-tetramethyl-5-methylenetrideca-7,11-dienal (**7**):

To a solution of (*E*)-2,2,8,12-tetramethyl-5-methylenetrideca-7,11-dien-1-ol (**2**, 264 mg, 1.0 mmol, 1.0 equiv.) in dichloromethane (25 mL, abs.) was added PCC (323 mg, 1.5 mmol, 1.5 equiv.). The reaction mixture was stirred for 16 h at room temperature and then decanted into a separatory funnel. The remaining tar was washed several times with diethyl ether. The combined organic layers were washed twice with KOH (0.1M) and the combined KOH layers were extracted once with diethyl ether. The combined ether solutions were washed once with water, twice with HCl (0.1M), once with water and the aqueous layers were extracted two times with diethyl ether. The combined organic layers were dried ( $\text{MgSO}_4$ ) and the solvent removed under reduced pressure. The residue was purified by column chromatography on silica (pentane/MTBE: 25:1) which gave 248 mg (*E*)-2,2,8,12-tetramethyl-5-methylenetrideca-7,11-dienal (**7**, 0.95 mmol, 95%) as a colourless oil.  **$^1\text{H NMR}$**  ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  = 9.45 (s, 1H), 5.17-5.06 (m, 2H), 4.74 (bs, 1H), 4.72 (bs, 1H), 2.69 (d,  $J$  = 7.3 Hz, 2H), 2.10-2.02 (m, 4H), 1.94-1.88 (m, 2H), 1.67 (s, 3H), 1.64-1.61 (m, 2H), 1.60 (bs, 6H), 1.07 (s, 6H).  **$^{13}\text{C NMR}$**  ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  = 206.0, 148.7, 136.8, 131.4, 124.2, 121.6, 109.3, 45.7, 39.7, 35.6, 34.9, 30.7, 36.6, 25.7, 21.3, 17.7, 15.9. **MS** (EI): m/z = 262 ( $\text{M}^+$ , 1), 244 (1), 193 (9), 175 (20), 163 (2), 147 (2), 133 (7), 123 (20), 109 (31), 93(34), 81 (24), 69 (100), 55 (22). **HRMS**: calculated for  $\text{C}_{18}\text{H}_{30}\text{ONa}$ : m/z = 285.2189; found: m/z = 285.2198.

The data are in accordance with the literature: Coates, R. M.; Johnson; M. W. *J. Org. Chem.* **1980**, *45*, 2685.

Synthesis of (*Z,Z,E,E*)-ethyl 3,8,8,14,18-pentamethyl-11-methylenenonadeca-2,6,13,17-tetraenoate (**9**):

To a cold solution (-78 °C) of (*Z*)-ethyl 3-methyl-6-(1-phenyl-1*H*-tetrazol-5-ylsulfonyl)hex-2-enoate (**3**, 109 mg, 0.30 mmol, 1.2 equiv.) in THF (3 mL, abs.) was added drop wise NaHMDS-solution (2M in THF, 0.15 mL, 0.30 mmol, 1.2 equiv.) and the resulting yellow solution was stirred for 30 min at -78 °C. A solution of (*E*)-2,2,8,12-tetramethyl-5-methylenetrideca-7,11-dienal (**7**, 66 mg, 0.25 mmol, 1.0 equiv.) in THF (2 mL, abs.) was added slowly and the reaction mixture was allowed to warm to room temperature overnight. The reaction was quenched with NH<sub>4</sub>Cl (aq.) and diethyl ether, the layers were separated and the aqueous layer was extracted three times with diethyl ether. The combined organic layers were dried ( $\text{MgSO}_4$ ) and the solvent was removed under reduced pressure. The residue was purified by column chromatography (pentane/MTBE: 100:1) which gave 80 mg of (*Z,Z,E,E*)-ethyl 3,8,8,14,18-pentamethyl-11-methylenenonadeca-2,6,13,17-tetraenoate (**9**, 0.2 mmol, 80%) as a colorless oil.  **$^1\text{H NMR}$**  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 9.45 (s, 1H), 5.17-5.07 (m, 2H), 4.74-4.71 (m, 2H), 2.69 (d,  $J$  = 7.3 Hz, 2H), 2.10-2.00 (m, 4H), 1.99-1.88 (m, 2H), 1.67 (s, 3H), 1.64-1.57 (m, 8H), 1.07 (s, 6H).  **$^{13}\text{C NMR}$**  (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 206.0, 148.7, 136.8, 131.4, 124.2, 121.6, 109.3, 45.7, 39.7, 35.6, 34.9, 30.7, 26.6, 25.7, 21.3, 17.7, 15.9. **MS** (EI): m/z = 400 ( $\text{M}^+$ , 3), 385 (2), 355 (7), 331 (51), 285 (6), 273 (4), 257 (14), 243 (7), 229 (7), 209 (40), 189 (36), 175 (26), 163 (49), 147 (23), 135 (84), 121 (57), 107 (63), 93 (55), 81 (37), 69 (100), 55 (25). **HRMS**: calculated for  $\text{C}_{27}\text{H}_{44}\text{O}_2\text{Na}$ : m/z = 423.3234; found: m/z = 423.3231.

Synthesis of (*Z,Z,E,E*)-3,8,8,14,18-pentamethyl-11-methylenenonadeca-2,6,13,17-tetraen-1-ol (**1**):

To a cold solution (0 °C) of (*Z,Z,E,E*)-ethyl 3,8,8,14,18-pentamethyl-11-methylenenonadeca-2,6,13,17-tetraenoate (**9**, 80 mg, 0.2 mmol, 1.0 equiv.) in diethyl ether (5 mL, abs.) was added DIBAL (1.1M in cyclohexane, 500  $\mu\text{L}$ , 0.55 mmol, 2.75 equiv.) and the resulting

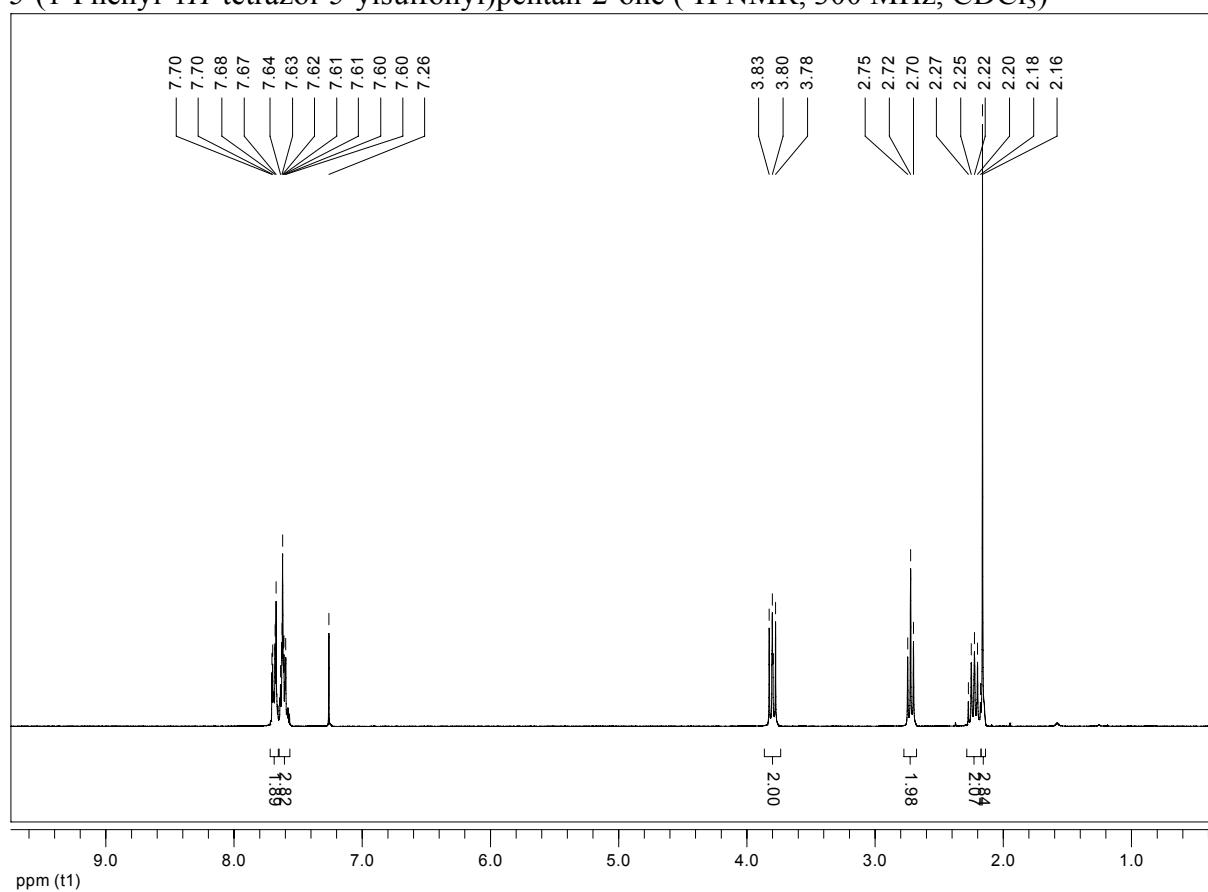
mixture was stirred for 2 h at 0 °C. After complete conversion (GC/MS) the reaction was quenched with KOH (1M, aq.). The layers were separated, the organic layer washed twice with water and the aqueous layers extracted twice with diethyl ether. The combined organic layers were dried ( $\text{MgSO}_4$ ), the solvent was removed under reduced pressure and the residue dried in high vacuum which gave 72 mg of pure moenocinol (**1**, 0.2 mmol, >99%) as a turbid oil.

**$^1\text{H}$  NMR** ( $\text{CDCl}_3$ , 600 MHz):  $\delta$  = 5.35 (t,  $J$  = 1.1 Hz, 1H), 5.35 (dt,  $J$  = 15.6, 1.1 Hz, 1H), 5.23 (dt,  $J$  = 15.6, 6.4 Hz, 1H), 5.16-5.14 (m, 1H), 5.09-5.07 (m, 1H), 4.67 (m, 2H), 4.09 (d,  $J$  = 7.1 Hz, 2H), 2.67 (d,  $J$  = 7.3 Hz, 2H), 2.13-2.05 (m, 6H), 2.01-1.99 (m, 2H), 1.89-1.86 (m, 2H), 1.72 (d,  $J$  = 1.0 Hz, 3H), 1.66 (d,  $J$  = 1.0 Hz, 3H), 1.59 (s, 3H), 1.58 (s, 3H), 1.37-1.34 (m, 2H), 1.07 (bs, 1H), 0.94 (s, 6H).  **$^{13}\text{C}$  NMR** ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  = 150.0, 140.7, 139.8, 136.4, 131.4, 125.2, 124.4, 124.3, 122.0, 108.4, 59.1, 41.5, 39.8, 36.9, 35.6, 35.0, 32.3, 31.4, 27.3, 26.7, 25.7, 23.4, 17.7, 15.9. **MS** (EI): m/z = 358 ( $\text{M}^+$ , 1), 340 (1), 325 (1), 271 (7), 229 (1), 215 (2), 203 (4), 189 (4), 175 (3), 161 (5), 147 (11), 133 (9), 123 (20), 107 (32), 93 (40), 81 (33), 69 (100), 55 (21). **HRMS**: calculated for  $\text{C}_{25}\text{H}_{43}\text{O}$ : m/z = 359.3308; found: m/z = 359.3307.

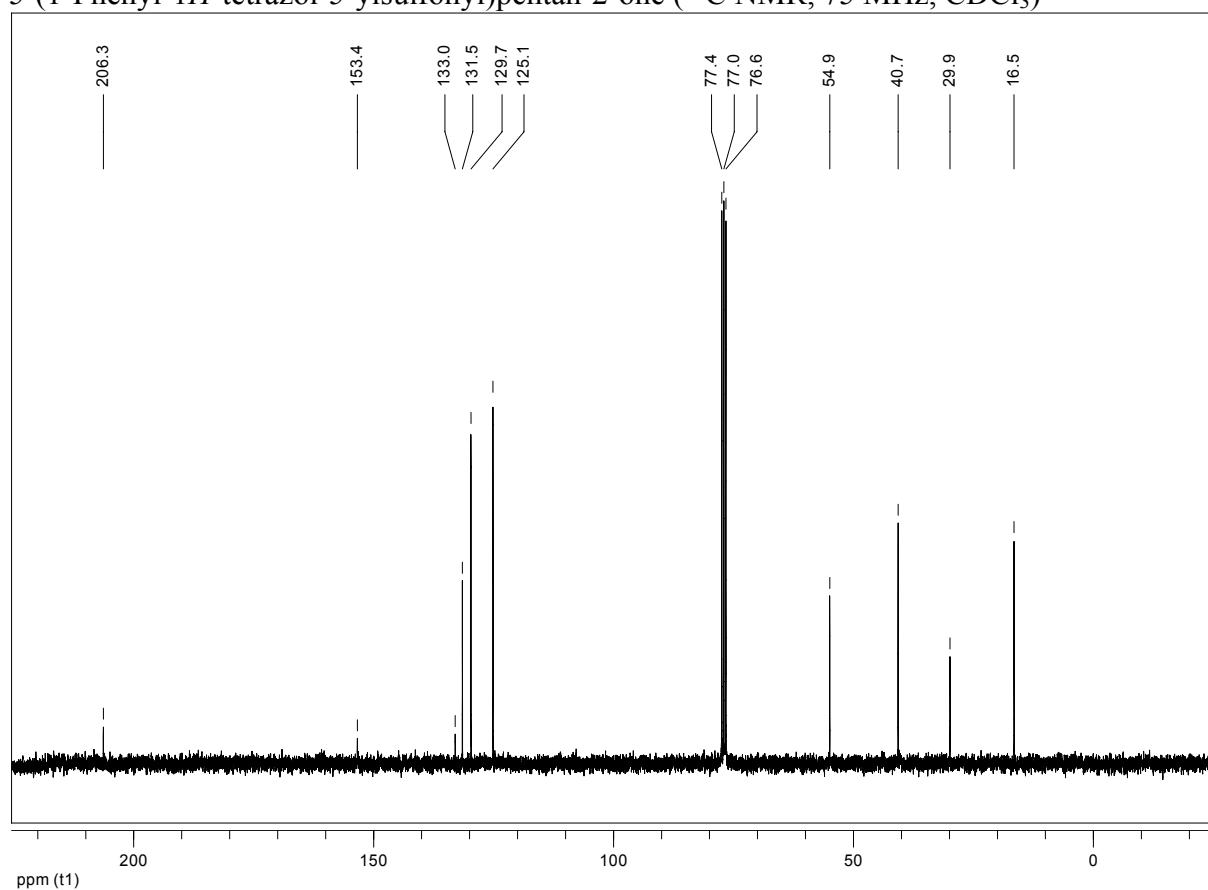
The data are in accordance with the literature: Coates, R. M.; Johnson, M. W. *J. Org. Chem.* **1980**, *45*, 2685.

**NMR-Spectra of compounds 1-9:**

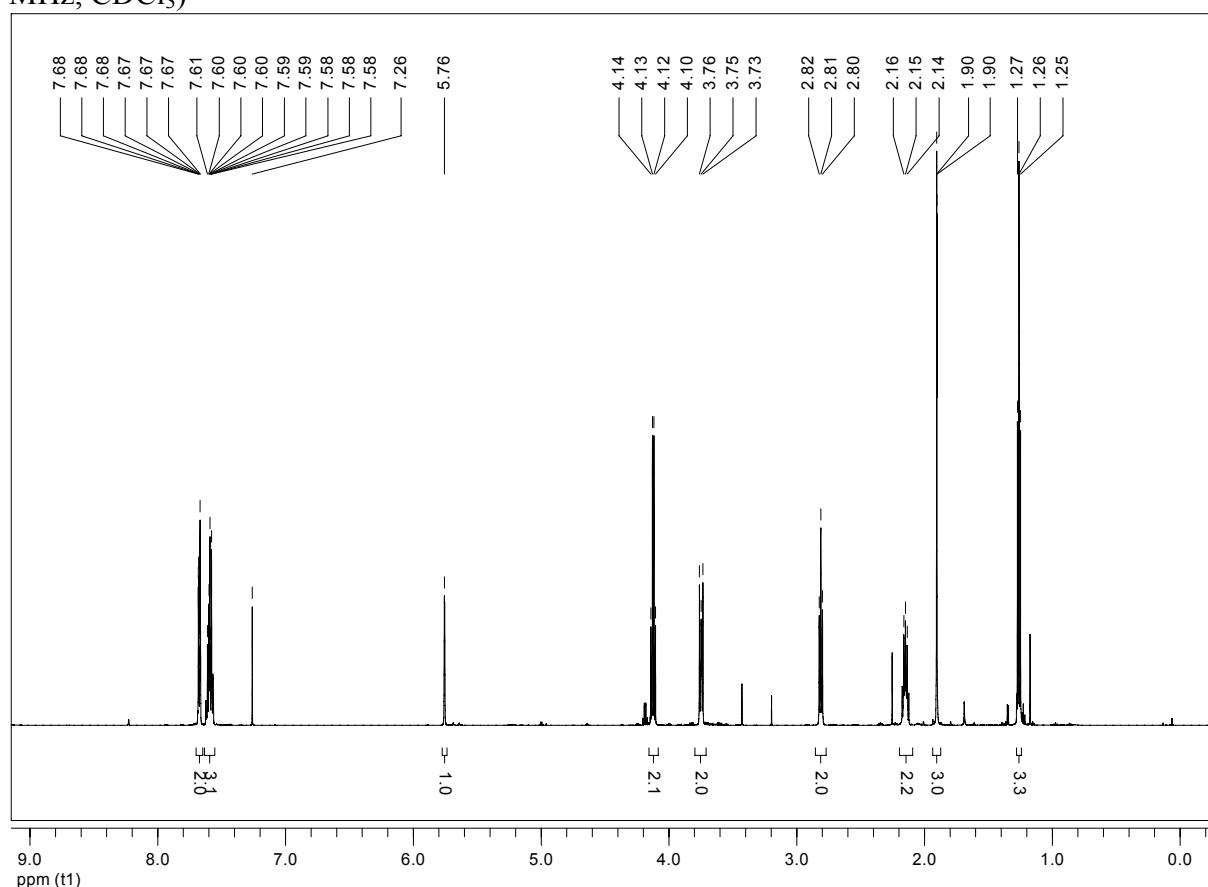
5-(1-Phenyl-1*H*-tetrazol-5-ylsulfonyl)pentan-2-one ( $^1\text{H}$  NMR, 300 MHz,  $\text{CDCl}_3$ )



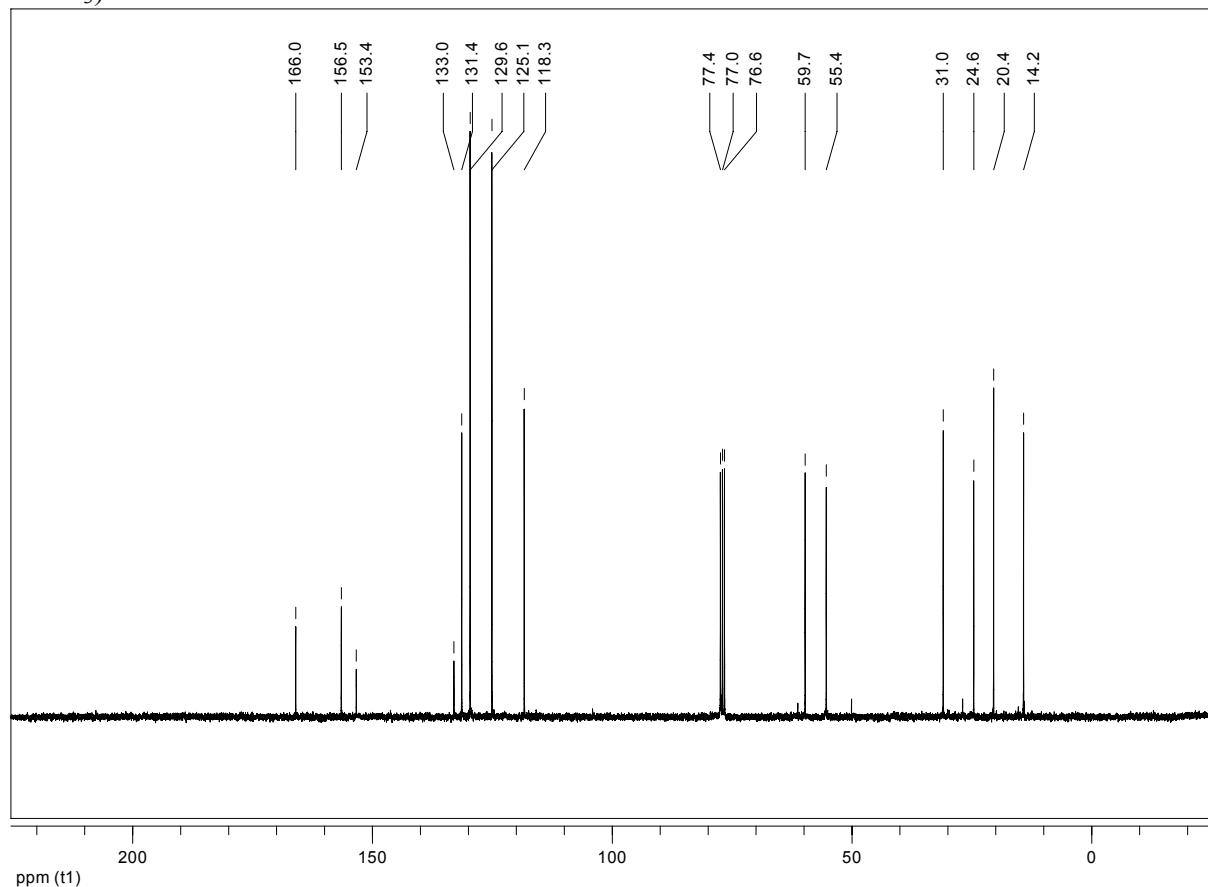
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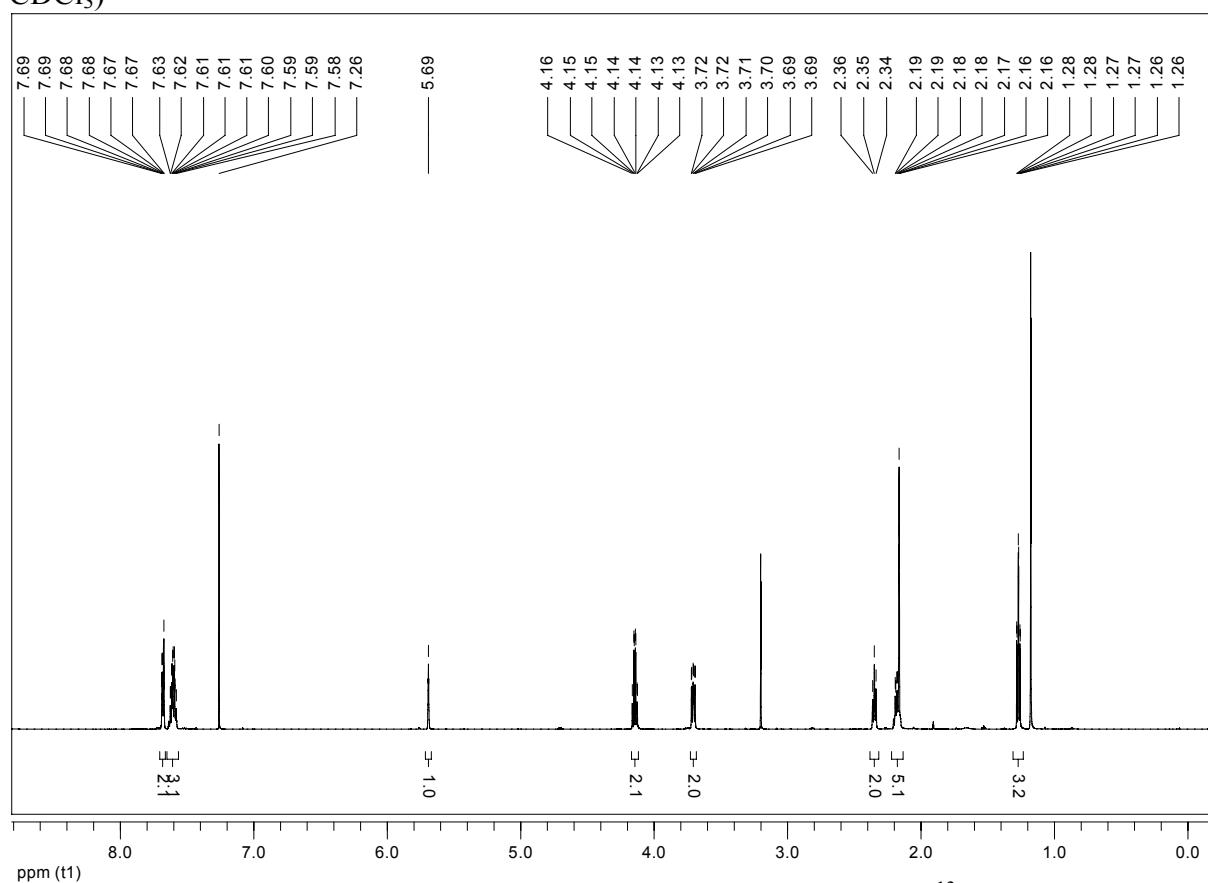
(Z)-Ethyl 3-methyl-6-(1-phenyl-1*H*-tetrazol-5-ylsulfonyl)hex-2-enoate (**3**,  $^1\text{H}$  NMR, 600 MHz,  $\text{CDCl}_3$ )



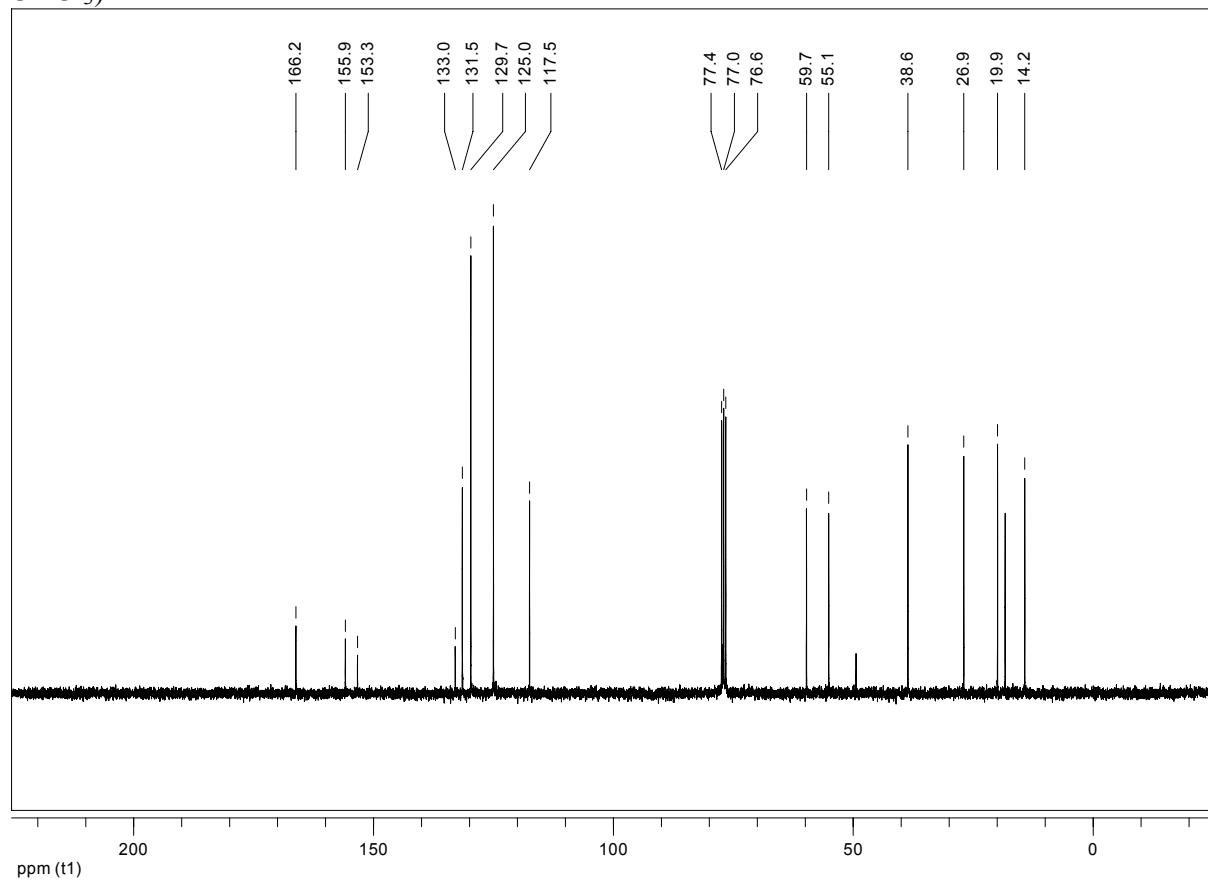
(Z)-Ethyl 3-methyl-6-(1-phenyl-1*H*-tetrazol-5-ylsulfonyl)hex-2-enoate (**3**,  $^{13}\text{C}$  NMR, 75 MHz,  $\text{CDCl}_3$ )



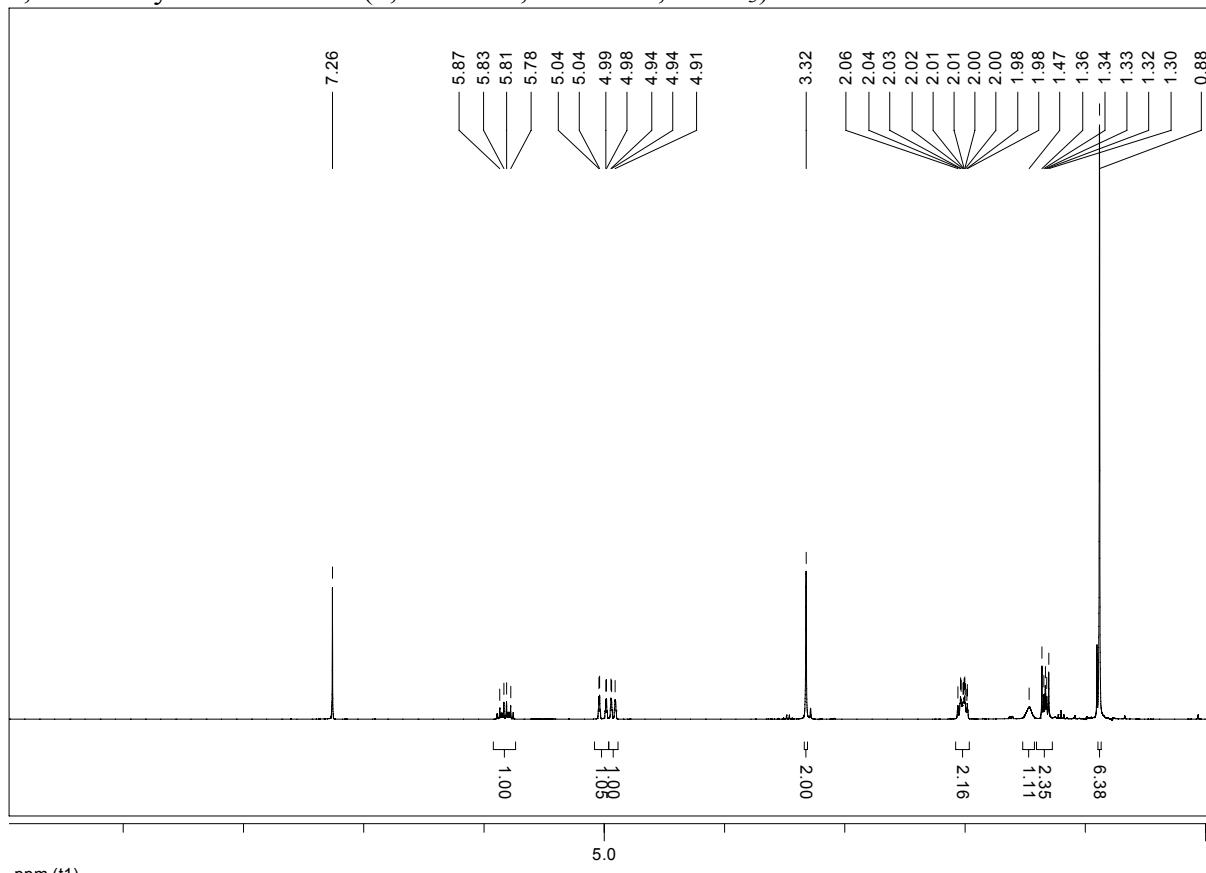
(*E*)-Ethyl 3-methyl-6-(1-phenyl-1*H*-tetrazol-5-ylsulfonyl)hex-2-enoate ( $^1\text{H}$  NMR, 600 MHz,  $\text{CDCl}_3$ )



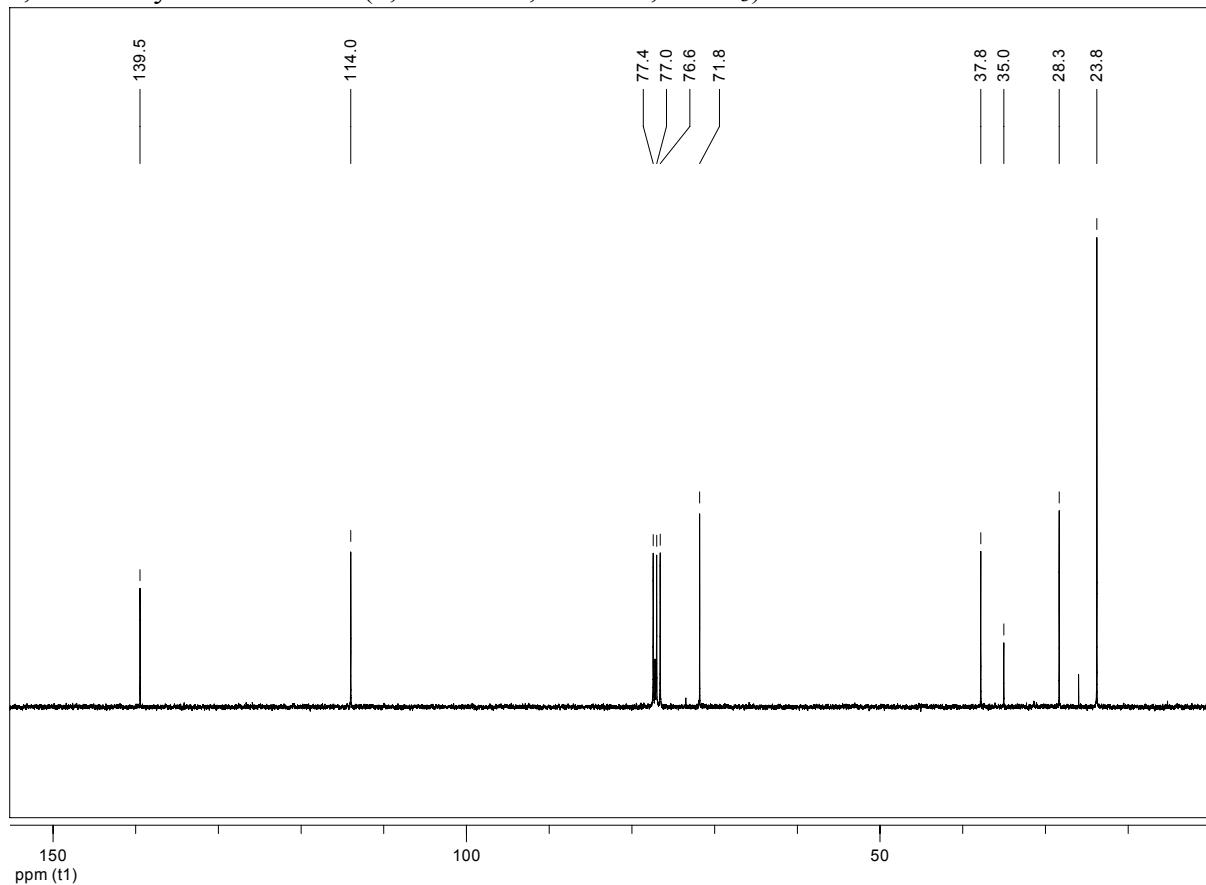
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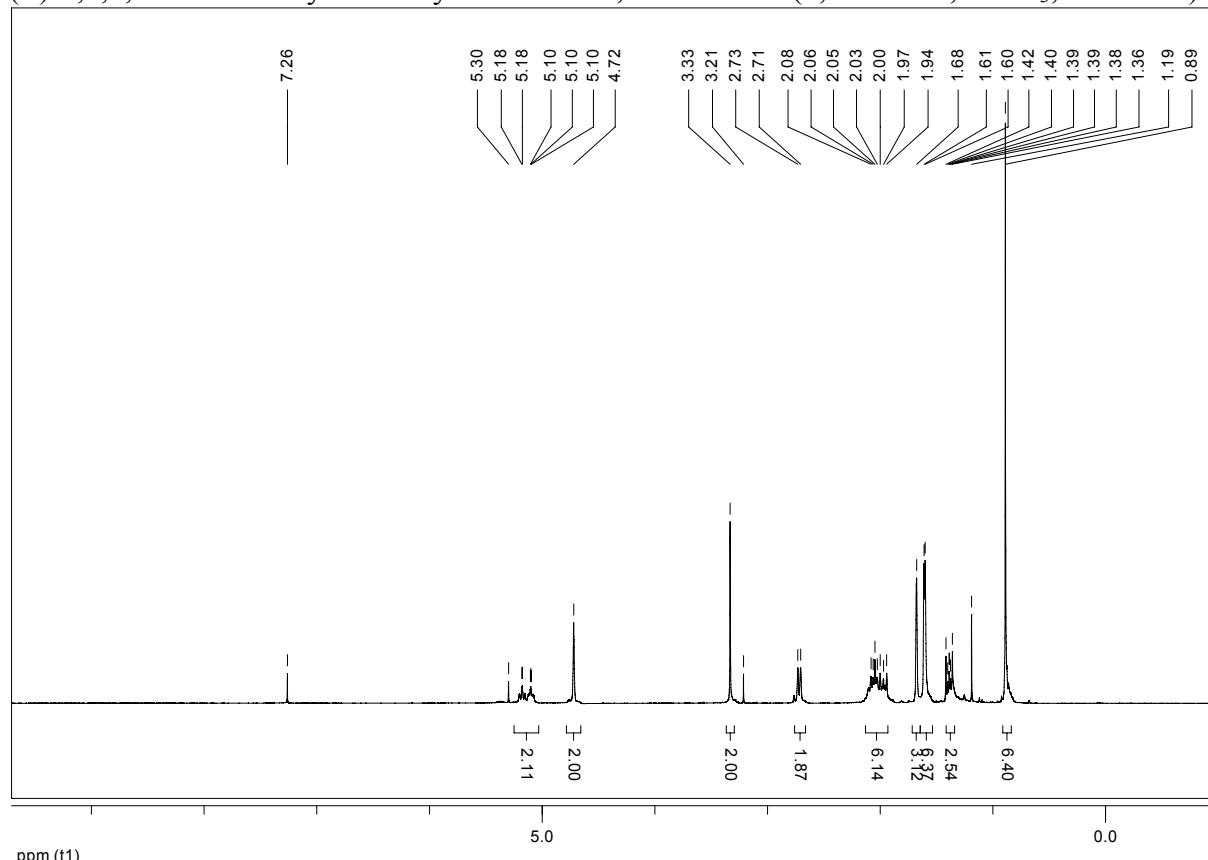
2,2-Dimethylhex-5-en-1-ol (**4**,  $^1\text{H}$  NMR, 300 MHz,  $\text{CDCl}_3$ )



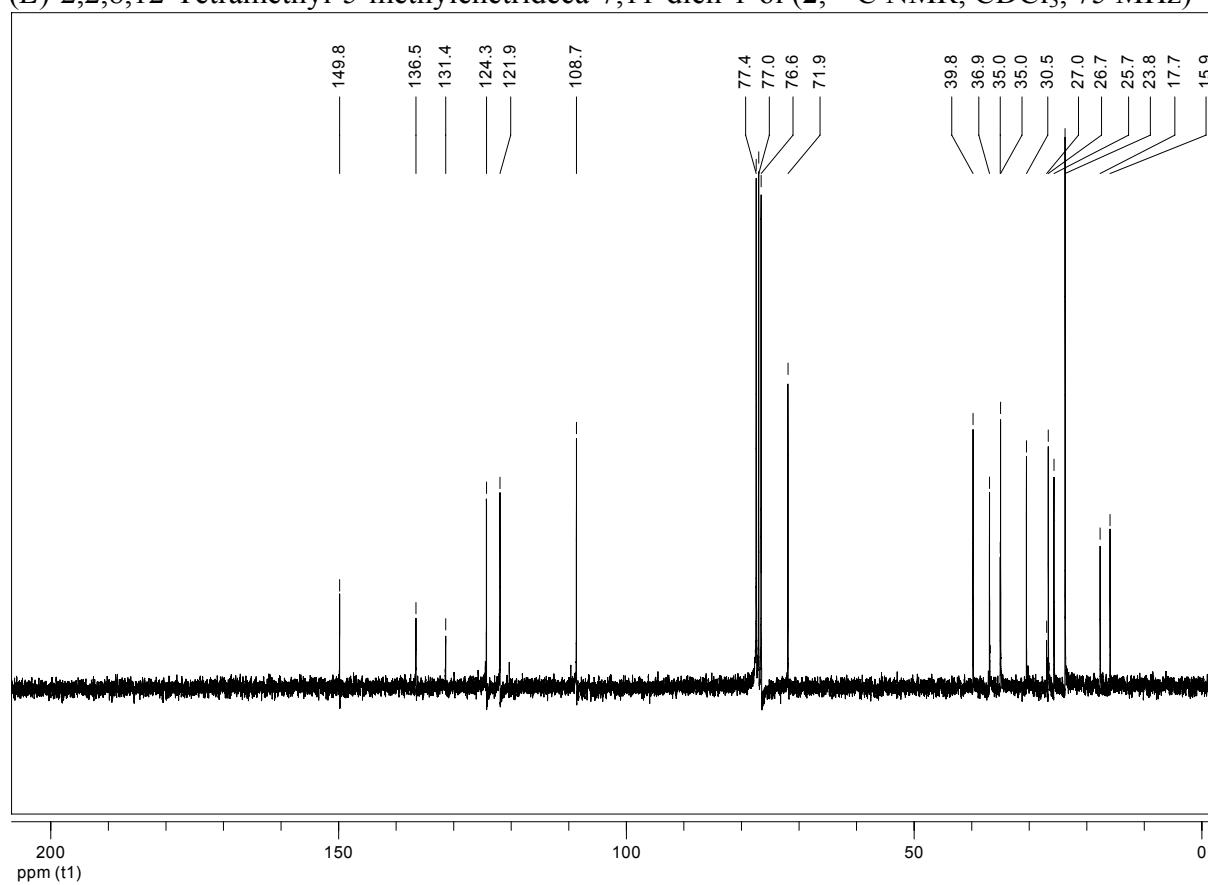
2,2-Dimethylhex-5-en-1-ol (**4**,  $^{13}\text{C}$  NMR, 75 MHz,  $\text{CDCl}_3$ )



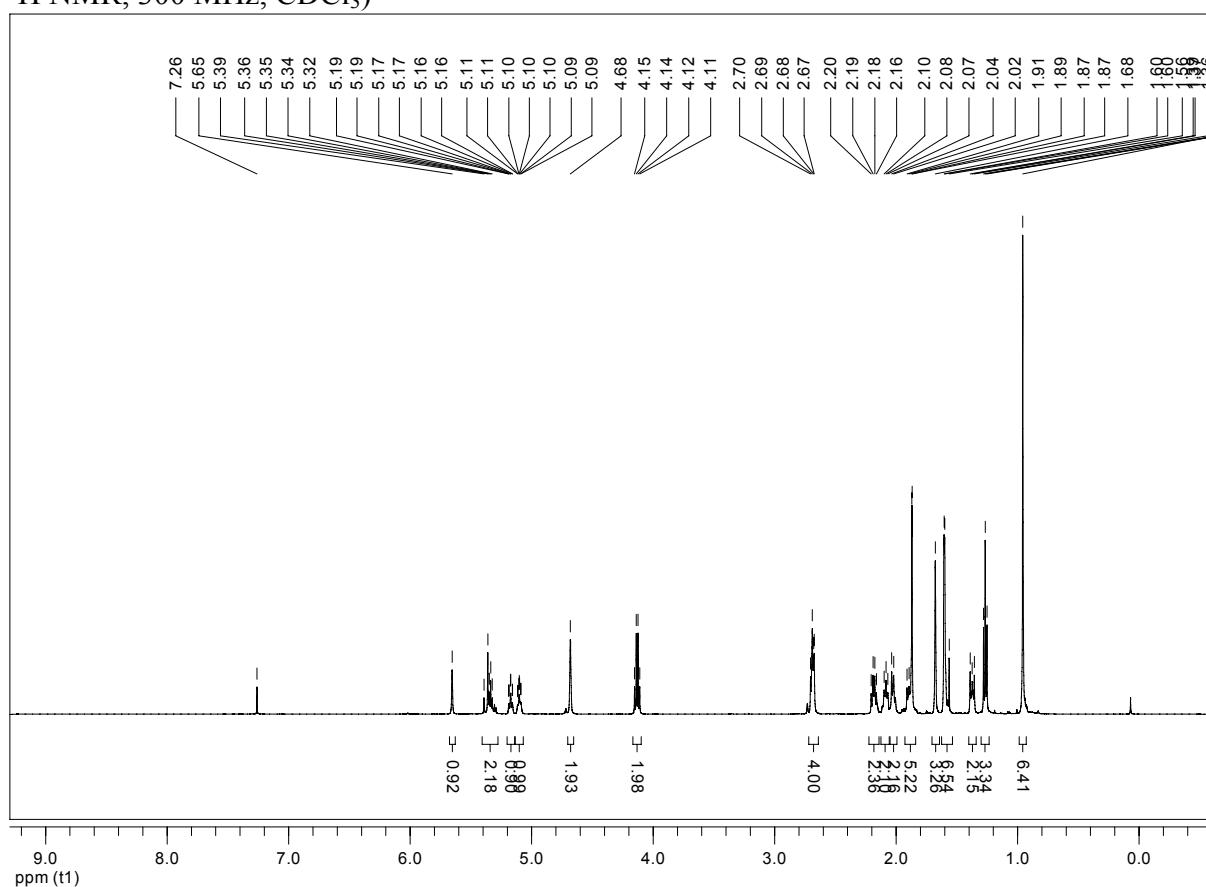
(*E*)-2,2,8,12-Tetramethyl-5-methylenetrideca-7,11-dien-1-ol (**2**,  $^1\text{H}$  NMR,  $\text{CDCl}_3$ , 300 MHz)



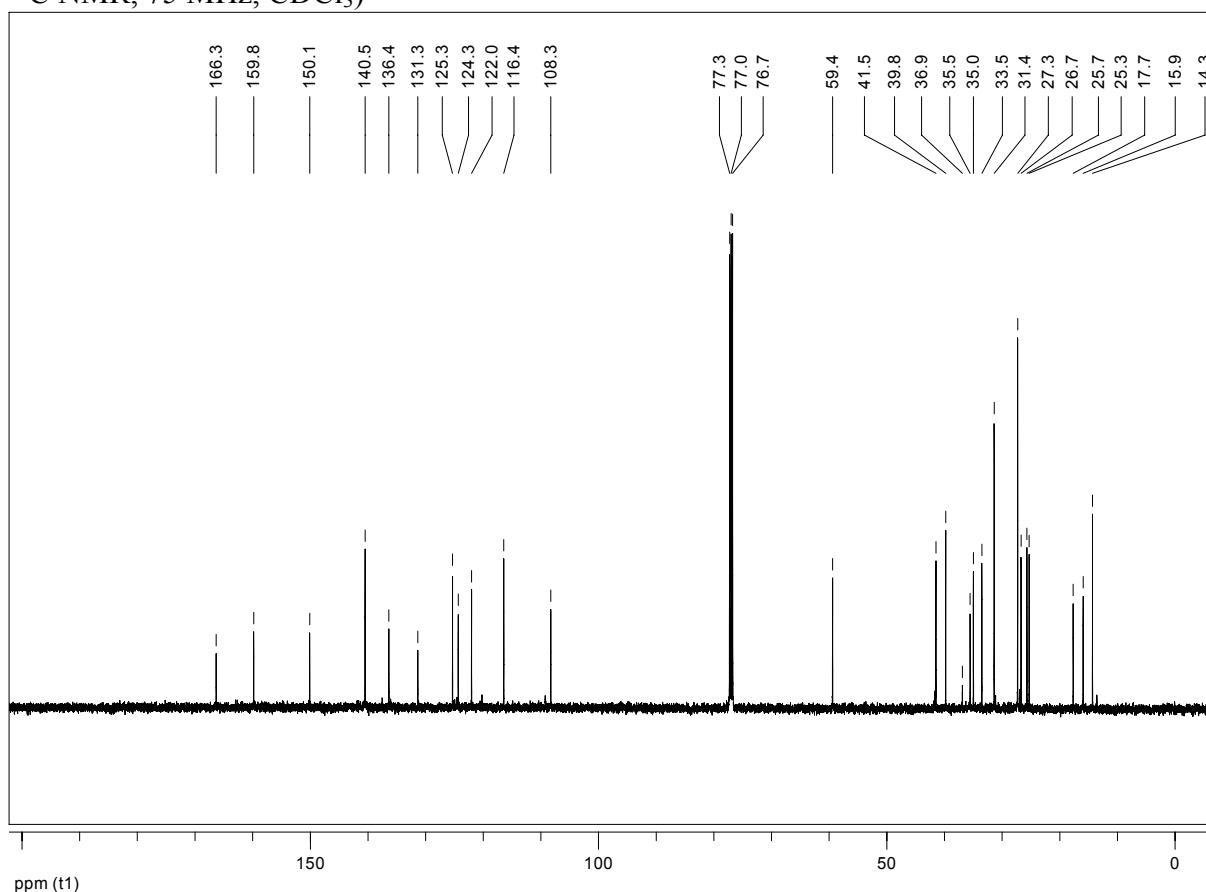
(*E*-2,2,8,12-Tetramethyl-5-methylenetrideca-7,11-dien-1-ol (**2**,  $^{13}\text{C}$  NMR,  $\text{CDCl}_3$ , 75 MHz)



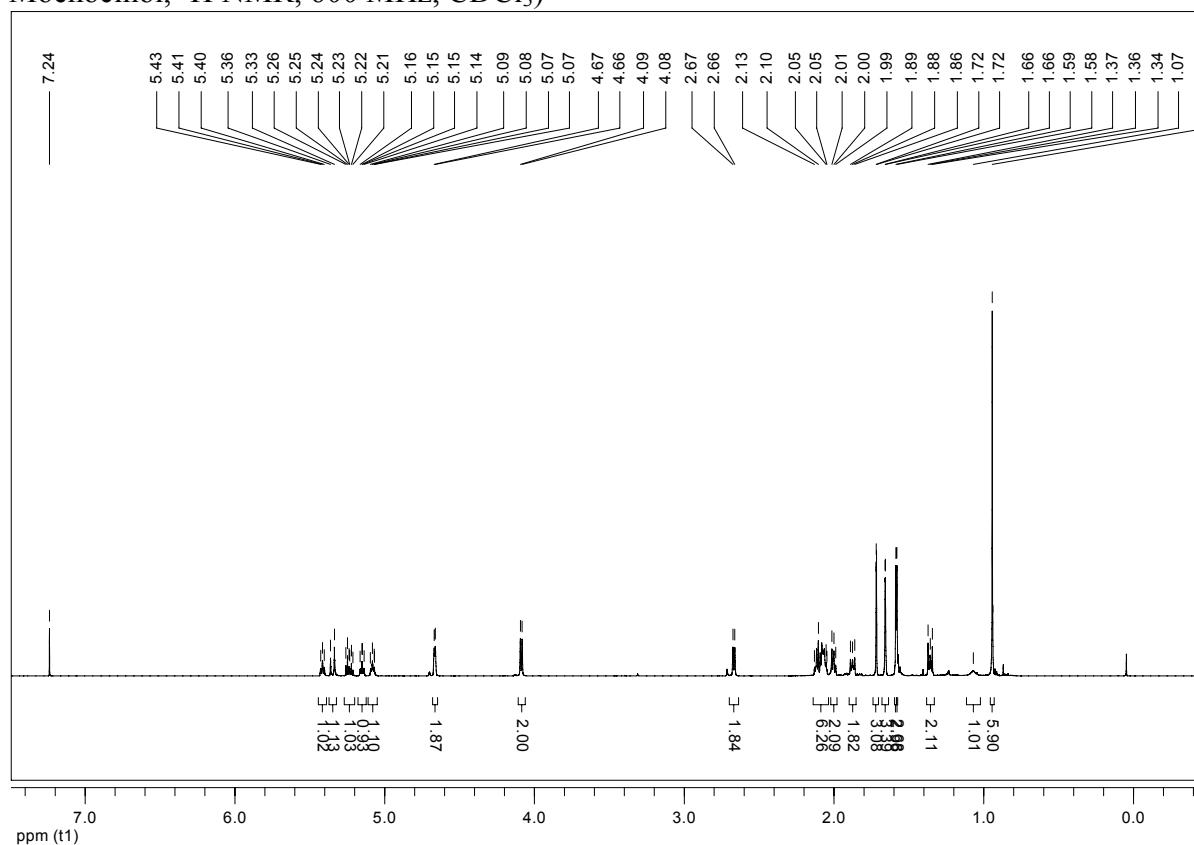
(2Z,6E,13E)-Ethyl 3,8,8,14,18-pentamethyl-11-methylenenonadeca-2,6,13,17-tetraenoate (**9**,  
 $^1\text{H}$  NMR, 300 MHz,  $\text{CDCl}_3$ )



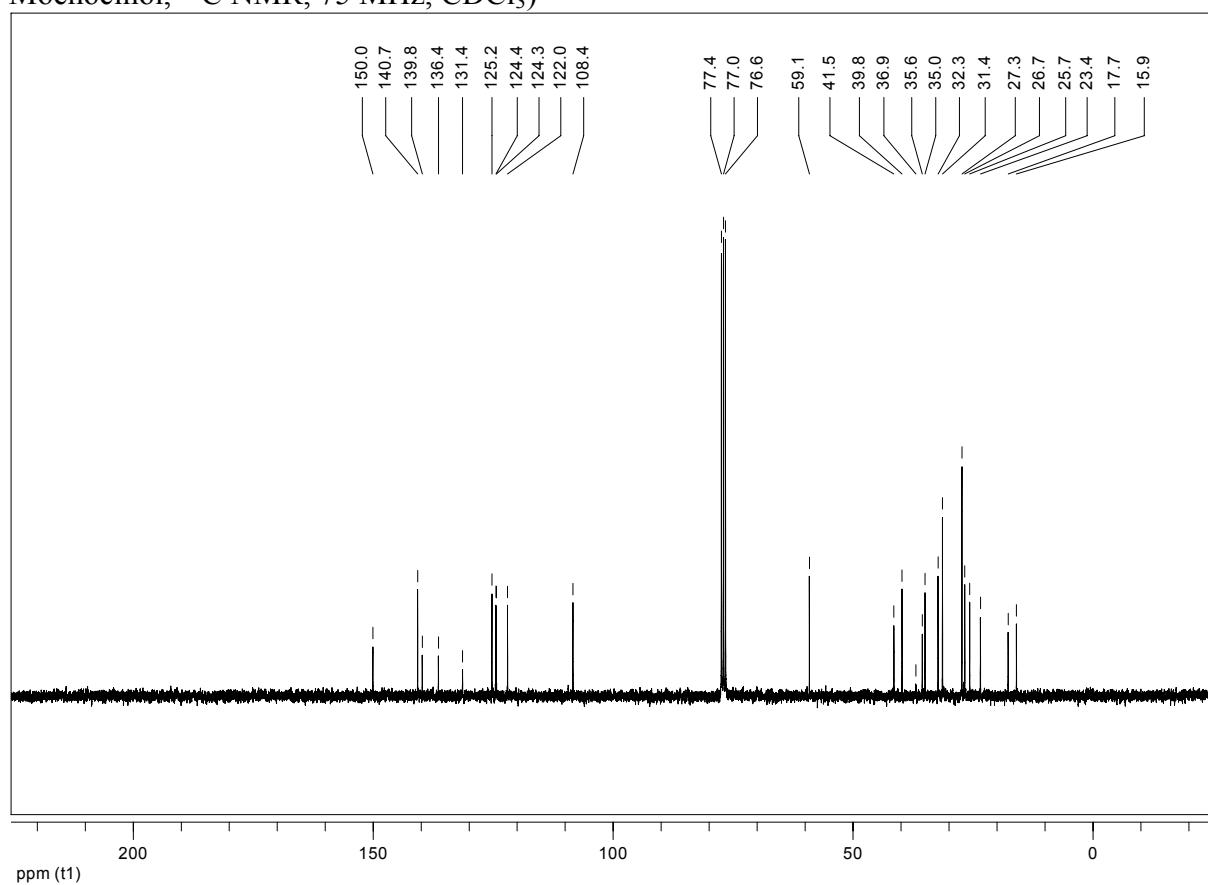
(2Z,6E,13E)-Ethyl 3,8,8,14,18-pentamethyl-11-methylenenonadeca-2,6,13,17-tetraenoate (**9**,  
 $^{13}\text{C}$  NMR, 75 MHz,  $\text{CDCl}_3$ )



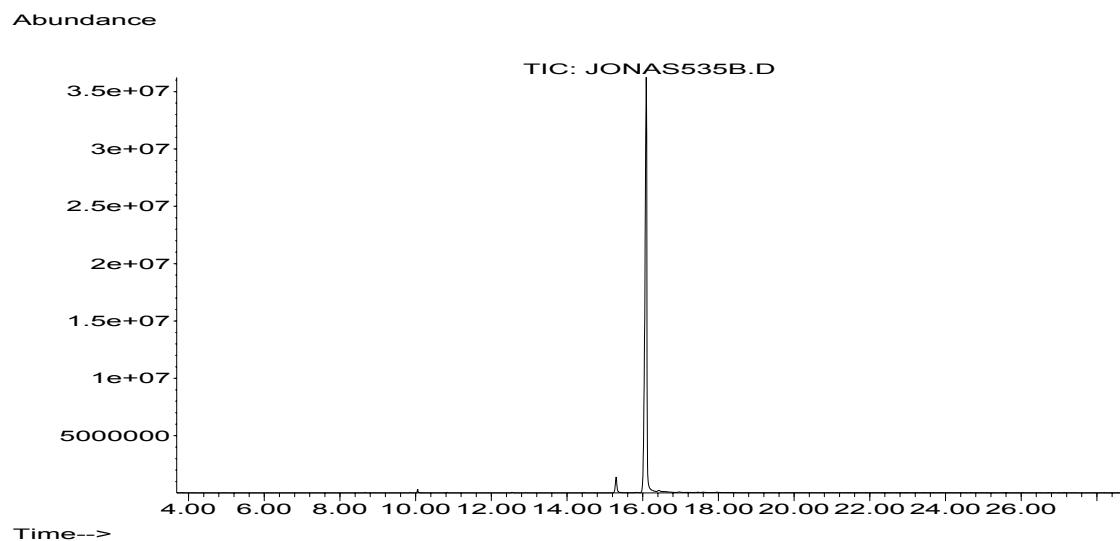
(2Z,6E,13E)-3,8,8,14,18-Pentamethyl-11-methylenenonadeca-2,6,13,17-tetraen-1-ol (**1**,  
Moenocinol,  $^1\text{H}$  NMR, 600 MHz,  $\text{CDCl}_3$ )



(2Z,6E,13E)-3,8,8,14,18-Pentamethyl-11-methylenenonadeca-2,6,13,17-tetraen-1-ol (**1**,  
Moenocinol,  $^{13}\text{C}$  NMR, 75 MHz,  $\text{CDCl}_3$ )



(2Z,6E,13E)-3,8,8,14,18-Pentamethyl-11-methylenenonadeca-2,6,13,17-tetraen-1-ol (**1**,  
Moenocinol, GC)



(2Z,6E,13E)-3,8,8,14,18-Pentamethyl-11-methylenenonadeca-2,6,13,17-tetraen-1-ol (**1**,  
Moenocinol, GC-MS)

