Synthesis of Stable 2*H*-Pyran-5-carboxylates via a Catalyzed Propargyl-Claisen Rearrangement/Oxa-6 π Electrocyclization Strategy

Helge Menz, Stefan F. Kirsch*

Department Chemie, Technische Universität München, Lichtenbergstr. 4, D-85747 Garching, Germany

Supporting Information

Representative experimental procedures for catalytic 2*H*-pyran formation, compound characterization data for **3a–o**, and copies of ^1H and ^{13}C NMR of **3**, **5–7**.

(24 Pages)

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General experimental details: All propargyl vinyl ethers **1** were synthesized by the reaction of the corresponding propargylic alcohols with 2-propynoic acid derivatives in the presence of trimethylphosphine or tributylphosphine.¹ Ethyl 2-butynoate, methyl 2-octynoate, ethyl phenylpropiolate and 3-pentyn-2-ol were purchased from Aldrich. All commercially available chemicals were used without further purification. All the other propargylic alcohols were prepared from the corresponding alkynes by addition to the corresponding aldehyde.² AgSbF₆ and DBU were purchased from Aldrich.

¹ Inanaga, J.; Baba, Y.; Hanamoto, T. *Chem. Lett.* **1993**, 241–244.

² Hashmi, A. S. K.; Haufe, P.; Nass, A. R. *Adv. Synth. Catal.* **2003**, 345, 1237–1241.

^1H NMR spectra were obtained on Bruker 500 MHz FT-NMR, 360 MHz FT-NMR and 250 MHz FT-NMR spectrometers. ^{13}C NMR spectra were recorded at 90.6 MHz. Chemical shifts are reported in ppm relative to solvent signal. Multiplicity is indicated as follows: s (singlet); d (doublet); t (triplet); q (quartet); m (multiplet); dd (doublet of doublets); sep (septet). High resolution mass spectra and EI were determined on a Finnigan MAT 95S and MAT 8200. Flash chromatography was performed with E. Merck silica gel (43–60 μm). The eluent used is reported in parentheses (P = pentanes). Thin-layer chromatography (TLC) was performed on precoated glass-backed plates (Merck Kieselgel 60 F₂₅₄), and components were visualized by observation under UV light or by treating the plates with $\text{KMnO}_4/\text{H}_2\text{SO}_4$ followed by heating.

The 2*H*-pyrans **3** show significant decomposition on silica gel during the purification process. Therefore, it is recommended to use a minimum amount of silica gel for flash chromatography. The use of neutral Al_2O_3 (Aldrich; Brockmann 1) did neither improve the yields nor the purity of the products.

General Procedure for the 2*H*-Pyran Formation starting from Propargyl Vinyl Ethers 1.

Ethyl 6-ethyl-2-methyl-4-phenyl-6*H*-pyran-3-carboxylate (**3a**)

AgSbF_6 (38 mg, 0.11 mmol, 5 mol%) was added to a solution of **1a** (570 mg, 2.1 mmol) in CH_2Cl_2 (10 ml), and the reaction vial was sealed, protected from light, and stirred at room temperature for 60 min. Then, a solution of DBU (17 mg, 0.11 mmol, 5 mol%) in CH_2Cl_2 (0.5 mL) was added, and the reaction mixture was stirred at room temperature for 30 min (until TLC analysis indicated complete conversion). The mixture was concentrated under reduced pressure. Purification of the residue by flash chromatography on silica gel (P/EtOAc = 80/20) gave 2*H*-pyran **3a** as a colorless oil (432 mg, 1.59 mmol, 76%). R_f = 0.65 (P/EtOAc = 80/20); ^1H NMR (360 MHz, CDCl_3) δ 0.72 (t, J = 7.1 Hz, 3 H), 1.04 (t, J = 7.4 Hz, 3 H), 1.74–1.96 (m, 2 H), 2.35 (s, 3 H), 3.81–3.87 (m, 2 H), 4.63 (dt, J = 3.8, 6.4 Hz, 1 H), 5.29 (d, J = 3.8 Hz, 1 H), 7.31–7.34 (m, 3 H), 7.44–7.48 (m, 2 H); ^{13}C NMR (90.6 MHz, CDCl_3) δ 9.6, 13.8, 19.0, 27.3, 60.0, 77.9, 108.3, 116.3, 126.8, 127.3, 128.3, 137.4, 141.1, 166.0, 167.6. LRMS (EI): 272 (10%) [M^+], 199 (100%); HRMS 272.1420 [272.1412 calcd for $\text{C}_{17}\text{H}_{20}\text{O}_3\text{Cl}$ (M^+)].

Ethyl 4-(4-*tert*-butylphenyl)-6-ethyl-2-methyl-6*H*-pyran-3-carboxylate (3b)

Following the general procedure, **3b** was obtained as a colorless oil (77%) after flash chromatography on silica gel (P/EtOAc = 80/20).

R_f = 0.78 (P/EA = 80/20); ^1H NMR (360 MHz, CDCl_3) δ 0.65 (t, J = 7.1 Hz, 3 H), 1.02 (t, J = 7.4 Hz, 3 H), 1.30 (s, 9 H), 1.73–1.94 (m, 2 H), 2.33 (s, 3 H), 3.76–3.90 (m, 2 H), 4.61 (dt, J = 3.8, 6.4 Hz, 1 H), 5.28 (d, J = 3.8 Hz, 1 H), 7.11 (d, J = 8.5 Hz, 2 H), 7.29 (d, J = 8.5 Hz, 2 H); ^{13}C NMR (90.6 MHz, CDCl_3) δ 9.6, 13.5, 18.9, 27.3, 31.7, 34.8, 60.0, 77.9, 108.6, 115.7, 125.2, 126.5, 137.1, 138.1, 150.4, 165.8, 167.8. LRMS (EI): 328 (4%) [M^+], 271 (48%), 161 (100%); HRMS 328.2030 [328.2038 calcd for $\text{C}_{21}\text{H}_{28}\text{O}_3(\text{M}^+)$].

Ethyl 6-ethyl-2-methyl-4-(4-phenoxyphenyl)-6*H*-pyran-3-carboxylate (3c)

Following the general procedure, **3c** was obtained as a colorless solid (63%) after flash chromatography on silica gel (P/EtOAc = 80/20).

R_f = 0.59 (P/EA = 95/5); ^1H NMR (360 MHz, CDCl_3) δ 0.85 (t, J = 7.2 Hz, 3 H), 1.04 (t, J = 7.4 Hz, 3 H), 1.74–1.96 (m, 2 H), 2.34 (s, 3 H), 3.87–3.94 (m, 2 H), 4.61 (dt, J = 3.6, 6.6 Hz, 1 H), 5.28 (d, J = 3.6 Hz, 1 H), 6.93 (d, J = 8.6 Hz, 2 H), 6.99 (d, J = 7.5 Hz, 2 H), 7.09 (t, J = 7.5 Hz, 1 H), 7.17 (d, J = 8.6 Hz, 2 H), 7.32 (t, J = 7.5 Hz, 2 H); ^{13}C NMR (90.6 MHz, CDCl_3) δ 9.6, 14.0, 19.1, 27.2, 60.1, 77.9, 108.5, 116.0, 188.9, 119.0, 123.5, 128.2, 130.1, 136.3, 136.7, 156.7, 157.7, 166.1, 167.6. LRMS (EI): 364 (8%) [M^+], 291 (100%), 235 (95%), 198 (48%), 142 (68%); HRMS 364.1674 [364.1675 calcd for $\text{C}_{23}\text{H}_{24}\text{O}_4(\text{M}^+)$].

Ethyl 6-ethyl-2-methyl-4-(thiophen-3-yl)-6*H*-pyran-3-carboxylate (3d)

Following the general procedure, **3d** was obtained as a colorless solid (90%) after flash chromatography on silica gel (P/EtOAc = 80/20).

R_f = 0.54 (P/EA = 80/20); ^1H NMR (360 MHz, CDCl_3) δ 0.88 (t, J = 7.1 Hz, 3 H), 1.02 (t, J = 7.4 Hz, 3 H), 1.73–1.91 (m, 2 H), 2.30 (s, 3 H), 3.93 (dq, J = 1.9, 7.1 Hz, 2 H), 4.58 (dt, J = 3.7, 6.8 Hz, 1 H), 5.35 (d, J = 3.6 Hz, 1 H), 6.93 (dd, J = 1.4, 5.0 Hz, 1 H), 7.07 (dd, J = 1.4, 3.0 Hz, 1 H), 7.21 (dd, J = 3.0, 5.0 Hz, 1 H); ^{13}C NMR (90.6 MHz, CDCl_3) δ 9.6, 13.9, 19.0, 27.2, 60.2, 77.7, 108.6, 115.7, 120.75, 125.2, 127.2, 132.1, 141.5, 165.4, 167.7. LRMS (EI): 278 (5%) [M^+], 205 (82%), 149 (100%), 134 (60%); HRMS 278.0971 [278.0977 calcd for $\text{C}_{15}\text{H}_{18}\text{O}_3\text{S}(\text{M}^+)$].

Ethyl 4-[2-(*tert*-butyldimethylsilanyloxy)ethyl]-6-ethyl-2-methyl-6*H*-pyran-3-carboxylate (3e)

Following the general procedure, **3e** was obtained as a colorless oil (82%) after flash chromatography on silica gel (P/EtOAc = 80/20).

R_f = 0.79 (P/EA = 80/20); ^1H NMR (360 MHz, CDCl_3) δ 0.01 (s, 6 H), 0.87 (s, 9 H), 0.97 (t, J = 7.1 Hz, 3 H), 1.31 (t, J = 7.4 Hz, 3 H), 1.63–1.80 (m, 2 H), 2.17 (s, 3 H), 2.46–2.61 (m, 2 H), 3.61 (dt, J =

1.2, 6.8 Hz, 2 H), 4.21 (q, $J = 7.1$ Hz, 2 H), 4.41–4.46 (m, 1 H), 5.09 (d, $J = 3.4$ Hz, 1 H); ^{13}C NMR (90.6 MHz, CDCl_3) δ –5.0, 9.5, 14.6, 18.7, 19.9, 26.3, 27.5, 37.1, 60.3, 62.9, 77.5, 108.3, 116.1, 132.3, 164.6, 167.7. LRMS (EI): 354 (2%) [M^+], 297 (42%), 89 (100%); HRMS 354.2217 [354.2226 calcd for $\text{C}_{19}\text{H}_{34}\text{O}_4\text{Si}(\text{M}^+)$].

Ethyl 4-(cyclohexylmethyl)-6-ethyl-2-methyl-6*H*-pyran-3-carboxylate (3f)

Following the general procedure, **3f** was obtained as a colorless oil (75%) after flash chromatography on silica gel (P/EtOAc = 80/20).

$R_f = 0.58$ (P/EA = 95/5); ^1H NMR (360 MHz, CDCl_3) δ 0.96 (t, $J = 7.5$ Hz, 3 H), 1.11–1.21 (m, 5 H), 1.31 (t, $J = 7.2$ Hz, 3 H), 1.62–1.80 (m, 8 H), 2.05–2.11 (m, 1 H), 2.17 (s, 3 H), 2.26–2.30 (m, 1 H), 4.21 (dq, $J = 2.4, 7.1$ Hz, 2 H), 4.43–4.48 (m, 1 H), 4.97 (d, $J = 3.4$ Hz, 1 H); ^{13}C NMR (90.6 MHz, CDCl_3) δ 9.5, 14.7, 19.7, 26.6, 26.7, 27.0, 27.6, 33.2, 33.8, 36.7, 41.9, 60.3, 77.5, 108.3, 115.6, 133.6, 164.1, 168.1. LRMS (EI): 292 (7%) [M^+], 249 (100%), 219 (69%); HRMS 292.2041 [292.2038 calcd for $\text{C}_{18}\text{H}_{28}\text{O}_3(\text{M}^+)$].

Ethyl 2,6-dimethyl-4-phenyl-6*H*-pyran-3-carboxylate (3g)

Following the general procedure, **3g** was obtained as a colorless solid (72%) after flash chromatography on silica gel (P/EtOAc = 80/20).

$R_f = 0.56$ (P/EA = 95/5); ^1H NMR (360 MHz, CDCl_3) δ 0.72 (t, $J = 7.1$ Hz, 3 H), 1.49 (d, $J = 6.6$ Hz, 3 H), 2.34 (s, 3 H), 3.80–3.87 (m, 2 H), 4.81 (dq, $J = 3.8, 6.6$ Hz, 1 H), 5.26 (d, $J = 3.5$ Hz, 1 H), 7.18–7.20 (m, 2 H), 7.24–7.30 (m, 3 H); ^{13}C NMR (90.6 MHz, CDCl_3) δ 13.7, 19.0, 20.2, 60.0, 73.0, 108.5, 117.5, 126.8, 127.3, 128.3, 137.2, 141.0, 166.0, 167.5. LRMS (EI): 258 (32%) [M^+], 243 (100%), 215 (22%); HRMS 258.1251 [258.1256 calcd for $\text{C}_{16}\text{H}_{18}\text{O}_3(\text{M}^+)$].

Ethyl 6-*iso*-propyl-2-methyl-4-phenyl-6*H*-pyran-3-carboxylate (3h)

Following the general procedure, **3h** was obtained as a colorless solid (80%) after flash chromatography on silica gel (P/EtOAc = 80/20).

$R_f = 0.54$ (P/EA = 95/5); ^1H NMR (250 MHz, CDCl_3) δ 0.71 (t, $J = 7.1$ Hz, 3 H), 1.01 (d, $J = 6.6$ Hz, 3 H), 1.03 (d, $J = 6.8$ Hz, 3 H), 2.05–2.19 (m, 1 H), 2.35 (s, 3 H), 3.83 (q, $J = 7.1$ Hz, 2 H), 4.40 (dd, $J = 3.9, 6.4$ Hz, 1 H), 5.33 (d, $J = 3.8$ Hz, 1 H), 7.18–7.21 (m, 2 H), 7.23–7.29 (m, 3 H); ^{13}C NMR (62.9 MHz, CDCl_3) δ 13.7, 18.3, 18.3, 19.0, 31.8, 60.0, 81.6, 108.4, 115.0, 126.8, 127.3, 128.3, 137.5, 141.3, 166.1, 167.7.

Ethyl 6-benzyl-2-methyl-4-phenyl-6*H*-pyran-3-carboxylate (3i)

Following the general procedure, **3i** was obtained as a colorless solid (50%) after flash chromatography on silica gel (P/EtOAc = 80/20).

$R_f = 0.50$ (P/Ea = 95/5); ^1H NMR (360 MHz, CDCl_3) δ 0.73 (t, $J = 7.2$ Hz, 3 H), 2.34 (s, 3 H), 3.03 (dd, $J = 6.8, 13.6$ Hz, 1 H), 3.21 (dd, $J = 7.3, 13.6$ Hz, 1 H), 3.85 (q, $J = 7.2$ Hz, 2 H), 4.95 (dt, $J = 4.1, 7.0$ Hz, 1 H), 5.32 (d, $J = 4.1$ Hz, 1 H), 7.17–7.20 (m, 2 H), 7.26–7.31 (m, 6 H), 7.33–7.38 (m, 2 H); ^{13}C NMR (90.6 MHz, CDCl_3) δ 13.7, 19.1, 40.4, 60.1, 77.1, 108.7, 115.8, 126.8, 127.0, 127.4, 128.3, 128.8, 129.9, 137.1, 137.2, 141.0, 165.0, 167.5. LRMS (EI): 334 (2%) [M^+], 243 (100%), 215 (18%); HRMS 334.1559 [334.1569 calcd for $\text{C}_{22}\text{H}_{22}\text{O}_3$ (M^+)].

Ethyl 2-methyl-4-phenyl-6*H*-pyran-3-carboxylate (3j)

Following the general procedure, **3j** was obtained as a colorless solid (61%) after flash chromatography on silica gel (P/EtOAc = 80/20).

$R_f = 0.45$ (P/Ea = 95/5); ^1H NMR (360 MHz, CDCl_3) δ 0.74 (t, $J = 7.1$ Hz, 3 H), 2.37 (s, 3 H), 3.86 (q, $J = 7.1$ Hz, 2 H), 4.67 (d, $J = 4.6$ Hz, 2 H), 5.45 (t, $J = 4.6$ Hz, 1 H), 7.19–7.22 (m, 2 H), 7.26–7.30 (m, 3 H); ^{13}C NMR (90.6 MHz, CDCl_3) δ 13.7, 18.7, 60.1, 66.1, 109.2, 111.7, 126.8, 127.4, 128.4, 137.9, 140.8, 166.9, 167.4. LRMS (EI): 244 (5%) [M^+], 201 (9%), 171 (28%), 115 (100%); HRMS 244.1097 [244.1099 calcd for $\text{C}_{15}\text{H}_{16}\text{O}_3$ (M^+)].

Ethyl 4-(2-methoxyphenyl)-2-methyl-6*H*-pyran-3-carboxylate (3k)

Following the general procedure, **3k** was obtained as a colorless solid (59%) after flash chromatography on silica gel (P/EtOAc = 80/20).

$R_f = 0.49$ (P/Ea = 95/5); ^1H NMR (250 MHz, CDCl_3) δ 0.75 (t, $J = 7.1$ Hz, 3 H), 2.33 (s, 3 H), 3.73 (s, 3 H), 3.82 (q, $J = 7.1$ Hz, 2 H), 4.68 (d, $J = 4.3$ Hz, 2 H), 5.42 (t, $J = 4.3$ Hz, 1 H), 6.80 (d, $J = 8.0$ Hz, 1 H), 6.92 (t, $J = 7.4$ Hz, 1 H), 7.13–7.27 (m, 2 H); ^{13}C NMR (62.9 MHz, CDCl_3) δ 13.7, 19.2, 55.7, 59.7, 65.8, 109.6, 110.3, 120.9, 128.7, 129.6, 130.4, 134.8, 156.7, 164.8, 167.2. LRMS (EI): 274 (10%) [M^+], 201 (82%), 145 (100%); HRMS 274.1197 [274.1205 calcd for $\text{C}_{16}\text{H}_{18}\text{O}_4$ (M^+)].

Ethyl 2-methyl-4-(thiophen-3-yl)-6*H*-pyran-3-carboxylate (3l)

Following the general procedure, **3l** was obtained as a colorless solid (53%) after flash chromatography on silica gel (P/EtOAc = 80/20).

$R_f = 0.47$ (P/Ea = 95/5); ^1H NMR (360 MHz, CDCl_3) δ 0.88 (t, $J = 7.1$ Hz, 3 H), 2.31 (s, 3 H), 3.93 (q, $J = 7.1$ Hz, 2 H), 4.61 (d, $J = 4.6$ Hz, 2 H), 5.49 (t, $J = 4.6$ Hz, 1 H), 6.94 (dd, $J = 1.4, 5.0$ Hz, 1 H), 7.09 (dd, $J = 1.4, 3.0$ Hz, 1 H), 7.24 (dd, $J = 3.0, 5.0$ Hz, 1 H); ^{13}C NMR (90.6 MHz, CDCl_3) δ 13.9, 18.7, 60.3, 65.8, 109.3, 111.1, 120.9, 125.3, 127.1, 132.6, 141.2, 166.2, 167.5. LRMS (EI): 250 (6%) [M^+], 177 (44%), 121 (100%); HRMS 250.0657 [250.0664 calcd for $\text{C}_{13}\text{H}_{14}\text{O}_3\text{S}$ (M^+)].

Methyl 6-ethyl-2-pentyl-4-phenyl-6*H*-pyran-3-carboxylate (3m)

Following the general procedure, **3m** was obtained as a colorless solid (72%) after flash chromatography on silica gel (P/EtOAc = 80/20).

$R_f = 0.60$ (P/Ea = 95/5); ^1H NMR (360 MHz, CDCl_3) δ 0.91 (t, $J = 7.1$ Hz, 3 H), 1.04 (t, $J = 7.4$ Hz, 3 H), 1.35–1.37 (m, 4 H), 1.62–1.64 (m, 2 H), 1.77–1.91 (m, 2 H), 2.60–2.68 (m, 1H), 2.77–2.86 (m, 1H), 3.34 (s, 3 H), 4.58 (dq, $J = 3.8, 6.8$ Hz, 1 H), 5.31 (d, $J = 3.8$ Hz, 1 H), 7.18–7.20 (m, 2 H), 7.24–7.30 (m, 3 H); ^{13}C NMR (90.6 MHz, CDCl_3) δ 9.7, 14.3, 22.8, 27.3, 27.9, 31.9, 32.1, 51.1, 77.9, 108.2, 116.4, 126.6, 127.4, 128.4, 137.2, 140.8, 168.0, 169.3. LRMS (EI): 314 (5%) [M^+], 299 (32%), 103 (100%); HRMS 314.1878 [314.1882 calcd for $\text{C}_{20}\text{H}_{26}\text{O}_3$ (M^+)].

Ethyl 6-ethyl-2,4-diphenyl-6*H*-pyran-3-carboxylate (3n) / 3n:trans-4n:cis-4n = 20:30:50

Following the general procedure, the product mixture was obtained as a colorless oil (90%) after flash chromatography on silica gel (P/EtOAc = 80/20). The ratio 3n:trans-4n:cis-4n = 20:30:50 was determined by ^1H NMR of the purified compound.

^1H NMR (360 MHz, CDCl_3) δ 0.75–0.86 (m, 3n+trans-4n+cis-4n), 1.09–1.13 (m, 3n+trans-4n+cis-4n), 1.59–1.67 (m, 3n+trans-4n+cis-4n), 1.91–2.03 (m, 3n+trans-4n+cis-4n), 3.73–3.80 (m, 0.4 H, 3n), 3.87 (q, $J = 7.1$ Hz, 0.6 H, trans-4n), 4.09–4.21 (m, 1 H, cis-4n), 4.80–4.85 (m, 0.2 H, 3n), 5.41 (d, $J = 3.9$ Hz, 0.2 H, 3n), 5.63–5.73 (m, 0.3 H, trans-4n), 5.86 (td, $J = 7.5, 11.8$ Hz, 0.5 H, cis-4n), 6.31 (d, $J = 15.2$ Hz, 0.3 H, trans-4n), 6.77 (td, $J = 1.6, 11.7$ Hz, 0.5 H, cis-4n), 7.09–7.16 (m, 3n+trans-4n+cis-4n), 7.25–7.33 (m, 3n+trans-4n+cis-4n), 7.40–7.51 (m, 3n+trans-4n+cis-4n), 7.57–7.65 (m, 3n+trans-4n+cis-4n), 7.75–7.77 (m, 3n+trans-4n+cis-4n), 7.99–8.02 (m, A+B+C); ^{13}C NMR (the signals are not assigned to structures; 90 MHz, CDCl_3) δ 9.8, 13.0, 13.6, 13.8, 13.9, 14.2, 14.5, 23.1, 26.7, 27.4, 61.3, 127.4, 127.5, 127.6, 128.0, 128.2, 128.3, 128.5, 128.6, 128.9, 128.9, 129.0, 129.1, 129.2, 129.3, 129.4, 129.5, 129.9, 130.2, 131.7, 133.1, 133.8, 137.8, 138.0, 139.5, 142.1, 147.8, 152.6, 153.1, 165.4, 165.5, 195.0, 195.0.

Ethyl 2-acetyl-3-cyclohexylmethyl-5-phenylpenta-2,4-dienecarboxylate (4o) / 3o:trans-4o:cis-4o = 0:100:0

Following the general procedure, 4o was obtained as a colorless oil (36%) after flash chromatography on silica gel (P/EtOAc = 80/20).

$R_f = 0.41$ (P/Ea = 95/5); ^1H NMR (360 MHz, CDCl_3) δ 0.98–1.07 (m, 2 H), 1.11–1.21 (m, 3 H), 1.32 (t, $J = 7.1$ Hz, 3 H), 1.57–1.76 (m, 6 H), 2.37 (s, 3 H), 2.73 (d, $J = 7.0$ Hz, 2 H), 4.27 (q, $J = 7.1$ Hz, 2 H), 6.99 (d, $J = 16.1$ Hz, 1 H), 7.14 (d, $J = 16.1$ Hz, 1 H), 7.30–7.37 (m, 3 H), 7.45–7.48 (m, 2 H); ^{13}C NMR (90.6 MHz, CDCl_3) δ 14.5, 26.7, 26.8, 31.7, 33.8, 36.5, 39.1, 61.3, 126.7, 127.8, 129.1, 129.4, 133.8, 136.7, 137.3, 151.2, 166.3, 201.4. LRMS (EI): 340 (11%) [M^+], 243 (100%), 168 (40%), 105 (48%); HRMS 340.2037 [340.2039 calcd for $\text{C}_{22}\text{H}_{28}\text{O}_3$ (M^+)].

S11

$C_{19}H_{34}O_4Si$
M = 354,56

S12

$C_{18}H_{28}O_3$
M = 292,41

$C_{16}H_{18}O_4$
M = 274,31

6.7915	5.8962	5.7121	4.8477
6.7865	5.8754	5.6932	4.8370
6.7821	5.8641	5.6743	4.8313
6.7587	5.8546	5.6503	4.8212
6.7543	5.8426	5.6320	4.8124
6.7493	5.8218	5.4132	4.8016
6.3306		5.4025	
6.2884			

S20