

Terms & Conditions

Electronic Supporting Information files are available without a subscription to ACS Web Editions. The American Chemical Society holds a copyright ownership interest in any copyrightable Supporting Information. Files available from the ACS website may be downloaded for personal use only. Users are not otherwise permitted to reproduce, republish, redistribute, or sell any Supporting Information from the ACS website, either in whole or in part, in either machine-readable form or any other form without permission from the American Chemical Society. For permission to reproduce, republish and redistribute this material, requesters must process their own requests via the RightsLink permission system. Information about how to use the RightsLink permission system can be found at <http://pubs.acs.org/page/copyright/permissions.html>



ACS Publications

MOST TRUSTED. MOST CITED. MOST READ.

The procedures for the synthesis of the following compounds can be found in the experimental section of this paper.

[1-(Benzotriazol-1-yl)-3-ethoxy-3-(4-chloro)phenyl]propyl phenyl ether (4b): prepared from **1b** following the procedure used to prepare **4a**; 71% yield; white solid; mp 70-72 °C; ¹H NMR (two diastereomers, ratio 1:1) δ 1.09 (t, *J* = 7.0 Hz) and 1.15 (t, *J* = 7.0 Hz) (total 3 H), 2.42-2.99 (m, 2 H), 3.11-3.43 (m, 2 H), 3.86 (dd, *J* = 9.6, 4.4 Hz) and 4.66 (dd, *J* = 10.2, 3.3 Hz) (total 1 H), 6.82-7.52 (m, 12 H), 7.74 (t, 1 H, *J* = 9.0 Hz), 8.01 (d, *J* = 8.5 Hz) and 8.05 (d, *J* = 8.5 Hz) (total 1 H); ¹³C NMR δ 15.1, 42.8 and 43.3, 64.3 and 64.4, 76.7 and 76.8, 85.3 and 85.5, 110.7 and 110.8, 116.4 and 116.7, 120.0 and 120.2, 123.0 and 123.2, 124.2 and 124.3, 127.6 and 127.8, 128.8, 129.4, 129.6 and 129.7, 131.4 and 131.5, 133.6, 139.3 and 139.8, 146.5, 155.8 and 156.2. Anal. Calcd for C₂₃H₂₂ClN₃O₂: C, 67.73; H, 5.44; N, 10.30. Found: C, 67.25; H, 5.44; N, 10.14.

[1-(Benzotriazol-1-yl)-3-methoxy-3-phenyl]propyl phenyl ether (4c): prepared from **1c**, following the procedure of the preparation of compound **4a**, except using 5% PTS as catalyst and diethyl ether (20 mL) as solvent, 60% yield for two diastereomers (ratio 1:1). One of the diastereomer was isolated as a white solid, mp 67-69 °C; ¹H NMR δ 2.66-2.78 (m, 1 H), 2.88-3.03 (m, 1 H), 3.15 (s, 3 H), 3.77 (dd, 1 H, *J* = 9.3, 4.4 Hz), 6.84-7.52 (m, 13 H), 7.77 (d, 1 H, *J* = 8.3 Hz), 8.06 (d, 1 H, *J* = 8.3 Hz); ¹³C NMR δ. 42.9, 55.7, 79.2, 85.5, 110.8, 116.4, 120.2, 123.0, 124.3, 126.5, 127.8, 128.2, 128.6, 129.6, 131.4, 140.1, 146.6, 155.9. Anal. Calcd for C₂₂H₂₁N₃O₂: C, 73.52; H, 5.89; N, 11.69. Found: C, 73.40; H, 5.80; N, 12.36.

[1-(Benzotriazol-1-yl)-3-butoxy-3-phenyl]propyl phenyl ether (4d): prepared from compound **1d** following the procedure used to prepare **4c**; 67% yield; colorless oil; ¹H NMR (two diastereomers, ratio 56:44) δ 0.78 (t, *J* = 7.2 Hz) and 0.87 (t, *J* = 7.2 Hz) (total 3 H), 1.15-1.62 (m, 4 H), 2.43-3.40 (m, 4 H), 3.87 (dd, *J* = 9.4, 4.2 Hz) and 4.69 (dd, *J* = 10.4, 3.0 Hz) (total 1 H), 6.78-7.50 (m, 13 H), 7.73 (t, 1 H, *J* = 7.5 Hz), 7.92-8.11 (m, 1H); ¹³C NMR δ 13.6 and 13.7, 19.1 and 19.2, 31.6 and 31.7, 42.8 and 43.5, 68.4 and 68.6, 77.3 and 77.4, 85.4 and 85.5, 110.7 and 110.8, 116.3 and 116.5, 119.8 and 119.9, 122.8 and 123.0, 124.1 and 124.2, 126.2 and

126.3, 127.5, 127.7 and 127.8, 128.4 and 128.5, 129.4 and 129.5, 131.3 and 131.4, 140.7 and 141.2, 146.3, 155.8 and 156.2. Anal. Calcd for $C_{25}H_{27}N_3O_2$: C, 74.79; H, 6.78; N, 10.47. Found: C, 74.90; H, 6.99; N, 10.61.

[3-(Benzotriazol-1-yl)-1-phenyl-1-ethoxy]-3-pentyl phenyl ether (7b): obtained from the reaction of **4a** and ethyl iodide (Procedure A) in 82% yield; colorless oil; 1H NMR (two diastereomers, ratio 60:40) δ 0.85 (t, $J = 7.2$ Hz) and 0.89 (t, $J = 6.6$ Hz) (total 3 H), 1.04 (t, $J = 7.2$ Hz) and 1.09 (t, $J = 7.2$ Hz) (total 3 H), 2.74-2.81 (m, 2 H), 2.82-3.25 (m, 4 H), 3.72 (dd, $J = 9.0, 2.7$ Hz) and 4.42 (br d, $J = 9.3$ Hz) (total 1 H), 6.37-6.47 (m, 2 H), 6.86-6.94 (m, 2 H), 7.0-7.09 (m, 3 H), 7.13-7.25 (m, 3 H), 7.33-7.44 (m, 2 H), 7.82-7.98 (m, 1 H), 8.05-8.25 (m, 1 H); ^{13}C NMR δ 7.5 and 7.6, 14.9 and 15.0, 26.7 and 29.3, 42.0 and 44.8, 64.0 and 64.1, 77.1 and 77.3, 97.5 and 97.7, 112.9, 119.1 and 119.2, 119.5 and 119.6, 119.8 and 119.9, 123.1, 124.0 and 124.2, 125.8, 127.3, 127.4 and 127.6, 128.3 and 128.4, 129.3 and 129.5, 132.4 and 132.5, 142.0 and 142.5, 146.7, 153.5 and 153.8. Anal. Calcd for $C_{25}H_{27}N_3O_2$: C, 74.79; H, 6.78; N, 10.47. Found: C, 75.01; H, 7.17; N, 10.22.

[3-(Benzotriazol-1-yl)-1-phenyl-1-methoxy]-3-pentyl phenyl ether (7c): obtained from the reaction of **4c** and ethyl iodide (Procedure A) in 85% yield; colorless oil; 1H NMR (two diastereomers, about 1:1) δ 0.81 (t, $J = 7.3$ Hz) and 1.07 (t, $J = 7.2$ Hz) (total 3 H), 2.71-3.32 (m, 4 H), 2.97 (s) and 3.00 (s) (total 3 H), 3.62 (dd, $J = 8.5, 3.0$ Hz) and 4.31 (d, $J = 8.0$ Hz) (total 1 H), 6.41 (d, $J = 8.2$ Hz) and 6.44 (d, $J = 8.7$ Hz) (total 2 H), 6.82-7.11 (m, 5 H), 7.14-7.98 (m, 5 H), 7.77-7.98 (m, 1 H), 8.04-8.14 (m, 1 H); ^{13}C NMR δ 7.4 and 7.6, 26.8 and 29.6, 41.9 and 44.6, 56.3, 79.0 and 79.2, 97.5 and 97.6, 112.8, 119.1 and 119.5, 119.8 and 119.9, 123.1 and 123.2, 124.0 and 124.1, 125.8, 126.0, 127.4 and 127.6, 128.3 and 128.4, 129.3 and 129.5, 132.4, 141.2 and 141.7, 146.7, 153.5 and 153.8. Anal. Calcd for $C_{24}H_{25}N_3O_2$: C, 74.39; H, 6.50; N, 10.84. Found: C, 74.61; H, 6.82; N, 11.03.

[3-(Benzotriazol-1-yl)-1-phenyl-1-ethoxy]-3-nonyl phenyl ether (7d): obtained from the reaction of **4a** and 1-iodohexane (Procedure A) in 66% yield; colorless oil; 1H NMR (two diastereomers, about 1:1) δ 0.68-0.84 (m, 3 H), 0.90 (t, $J = 7.0$ Hz) and 1.05 (t, $J = 6.9$ Hz) (total

3 H), 1.09-1.79 (m, 8 H), 2.67-2.88 (m, 2 H), 2.89-3.33 (m, 4 H), 3.72 (dd, $J = 8.5, 2.4$ Hz) and 4.43 (d, $J = 8.5$ Hz) (total 1 H), 6.43 (dd, 2 H, $J = 7.8, 2.4$ Hz), 6.81-7.45 (m 10 H), 7.80-7.98 (m, 1 H), 8.02-8.16 (m, 1 H); ^{13}C NMR δ 13.8, 14.9 and 15.0, 22.3 and 22.5, 22.8, 28.8 and 28.9, 31.2 and 33.7, 36.2, 42.6 and 45.4, 63.9 and 64.0, 77.1 and 77.3, 97.1 and 97.4, 112.9, 119.2 and 119.5, 119.7 and 119.9, 123.0 and 123.1, 123.9 and 124.1, 125.8, 127.3, 127.4 and 127.5, 128.2 and 128.3, 129.2 and 129.4, 132.5, 142.1 and 142.4, 146.7, 153.6 and 153.8. Anal. Calcd for $\text{C}_{29}\text{H}_{35}\text{N}_3\text{O}_2$: C, 76.12; H, 7.71; N, 9.18. Found: C, 75.84; H, 7.79; N, 9.39.

1-Phenyl-1-ethoxy-3-pentanone (8b): 91% yield; colorless oil; ^1H NMR δ 1.03 (t, 3 H, $J = 7.3$ Hz), 1.13 (t, 3 H, $J = 7.0$ Hz), 2.28-2.50 (m, 2 H), 2.55 (dd, 1 H, $J = 15.4, 4.5$ Hz), 2.96 (dd, 1 H, $J = 15.6, 9.0$ Hz), 3.27-3.43 (m, 2 H), 4.77 (dd, 1 H, $J = 8.8, 4.4$ Hz), 7.21-7.45 (m, 5 H); ^{13}C NMR δ 7.4, 15.1, 37.1, 50.9, 64.3, 77.8, 126.3, 127.6, 128.4, 141.9, 209.1. Anal. Calcd for $\text{C}_{13}\text{H}_{18}\text{O}_2$: C, 75.69; H, 8.80. Found: C, 75.33; H, 8.64.

1-Phenyl-1-methoxy-3-pentanone (8c): 96% yield; colorless oil; ^1H NMR δ 1.03 (t, 3 H, $J = 7.2$ Hz), 2.28-2.52 (m, 2 H), 2.56 (dd, 1 H, $J = 15.9, 4.3$ Hz), 2.95 (dd, 1 H, $J = 15.7, 8.7$ Hz), 3.19 (s, 3 H), 4.66 (dd, 1 H, $J = 8.9, 4.2$ Hz), 7.21-7.41 (m, 5 H); ^{13}C NMR δ 7.4, 37.0, 50.7, 56.7, 79.6, 126.4, 127.8, 128.5, 141.1, 208.9. Anal. Calcd for $\text{C}_{12}\text{H}_{16}\text{O}_2$: C, 74.97; H, 8.39. Found: C, 75.34; H, 8.77.

1-Phenyl-1-ethoxy-3-nonanone (8d): 93% yield; colorless oil; ^1H NMR δ 0.87 (t, 3 H, $J = 6.9$ Hz), 1.13 (t, 3 H, $J = 7.0$ Hz), 1.18-1.38 (m, 6 H), 1.45-1.53 (m, 2 H), 2.26-2.29 (m, 2 H), 2.54 (dd, 1 H, $J = 15.4, 4.4$ Hz), 2.95 (dd, 1 H, $J = 15.7, 9.0$ Hz), 3.26-3.43 (m, 2 H), 4.76 (dd, 1 H, $J = 8.8, 4.4$ Hz), 7.22-7.42 (m, 5 H); ^{13}C NMR δ 13.9, 15.1, 22.4, 23.3, 28.7, 31.5, 44.0, 51.2, 64.2, 77.8, 126.3, 127.6, 128.4, 141.9, 208.8. Anal. Calcd for $\text{C}_{17}\text{H}_{26}\text{O}_2$: C, 77.82; H, 9.99. Found: C, 77.82; H, 9.94.

1-[1-(Benzotriazol-1-yl)-1-phenoxy-3-phenyl-3-ethoxy]propyl-1-cyclohexanol (9b): obtained from the reaction of **4a** and cyclohexanone (Procedure A, except the reaction mixture was warmed to rt before being quenched) in 92% yield based on 49% conversion of **4a**, 51% of **4a** recovered; white microcrystals, mp 195-198 °C; ^1H NMR (two diastereomers, 60:40) δ 0.67-

1.03 (m, 2 H), 1.11 (t, $J = 7.1$ Hz) and 1.23 (t, $J = 7.1$ Hz) (total 3 H), 1.30-1.90 (m, 6 H), 2.05-2.24 (m, 1 H), 2.30-2.51 (m, 1 H), 2.82-3.02 (m) and 3.80-3.93 (m) (total 2 H), 3.15-3.38 (m, 2 H), 4.57 (d, $J = 9.1$ Hz) and 5.72 (t, $J = 5.8$ Hz) (total 1 H), 4.69 (s), and 5.36 (s) (total 1 H), 6.42-6.70 (m, 3 H), 6.87-7.43 (m, 9 H), 7.70-7.86 (m, 1 H), 7.95-8.13 (m, 1 H); ^{13}C NMR δ 14.7 and 14.9, 21.3, 21.2 and 21.5, 25.3 and 25.4, 31.4 and 31.9, 32.0 and 32.3, 41.4 and 44.1, 63.7 and 64.2, 76.9 and 77.6, 78.3 and 78.8, 101.3 and 101.4, 114.7 and 115.2, 119.4 and 119.5, 120.0 and 120.7, 123.2 and 123.5, 123.8, 125.5 and 126.3, 127.4 and 127.5, 127.6 and 127.7, 128.3 and 128.5, 129.2 and 129.7, 134.2 and 134.5, 141.3 and 142.3, 145.4, 153.8 and 154.4. Anal. Calcd for $\text{C}_{29}\text{H}_{33}\text{N}_3\text{O}_3$: C, 73.86; H, 7.05; N, 8.91. Found: C, 74.03; H, 7.28; N, 8.94.

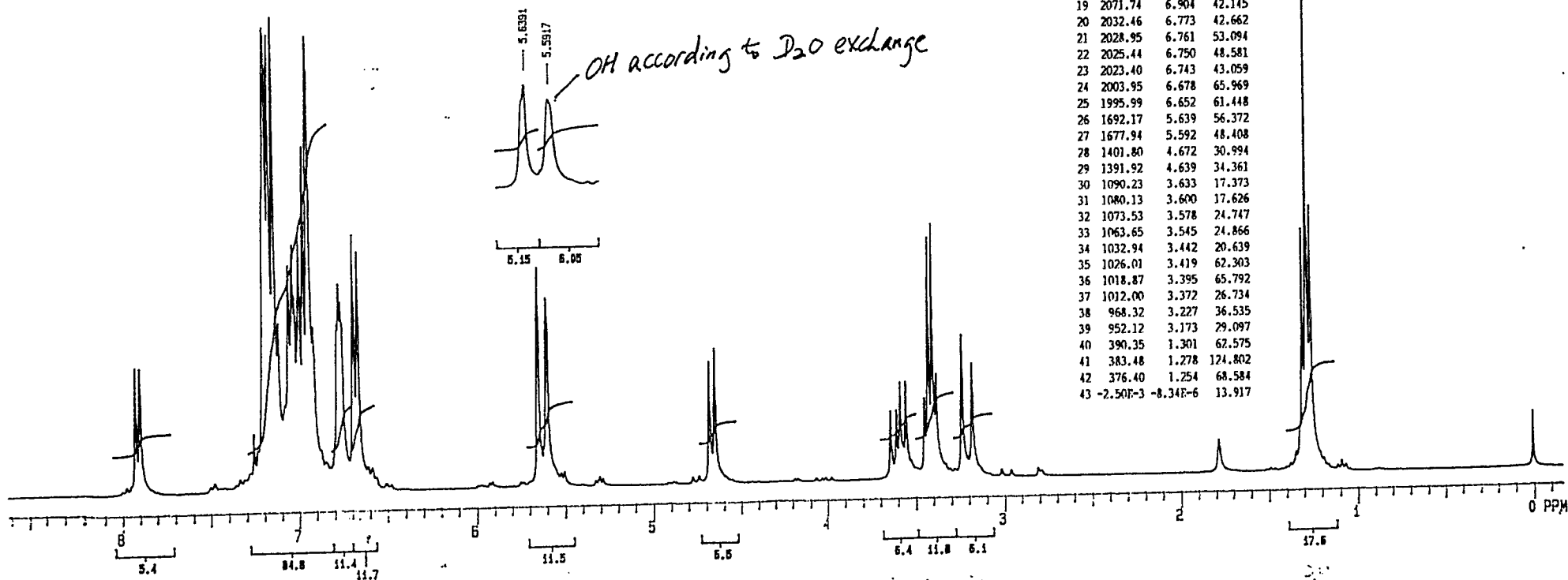
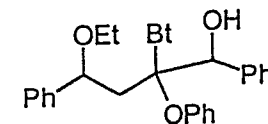
1-Phenyl-1-butoxy-3-(benzotriazol-1-yl)-3-phenoxy-4-methyl-4-pentanol (9c): obtained from the reaction of **4d** and acetone (similar to **9b**) in 54% yield based on 45% conversion of **4d**, 55% of **4d** recovered; white microcrystals, mp 107-110 °C; ^1H NMR (two diastereomers, 1:1) δ 0.98-1.20 (m, 3 H), 1.39-1.94 (m, 10 H), 3.08-3.25 (m, 2 H), 3.34-3.60 (m, 2 H), 4.82 (d, $J = 9.3$ Hz) and 5.93 (dd, $J = 8.3, 2.7$ Hz) (total 1 H), 5.34 (s) and 5.99 (s) (total 1 H), 6.65-6.90 (m, 2 H), 7.08-7.70 (m, 10 H), 7.97-8.13 (m, 1 H), 8.21-8.34 (m, 1 H); ^{13}C NMR δ 13.8, 19.1, 19.2, 24.9, 25.6, 26.2, 26.3, 31.5, 31.6, 41.9, 44.6, 68.2, 68.7, 76.8, 76.9, 77.6, 78.9, 100.5, 100.6, 114.6, 115.1, 119.5, 119.8, 120.6, 123.3, 123.6, 123.9, 126.0, 126.2, 126.4, 127.4, 127.5, 127.7, 128.4, 128.5, 129.1, 129.3, 129.7, 129.8, 133.8, 134.1, 141.3, 142.2, 145.5, 145.6, 153.7, 154.4. Anal. Calcd for $\text{C}_{28}\text{H}_{33}\text{N}_3\text{O}_3$: C, 73.18; H, 7.24; N, 9.14. Found: C, 73.19; H, 7.42; N, 9.11.

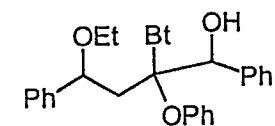
1-(1-Hydroxycyclohexyl)-3-phenyl-3-ethoxypropan-1-one (10b): obtained from the hydrolysis of **9b** (Procedure B) in 90% yield; colorless oil; ^1H NMR δ 1.13 (t, 3 H, $J = 6.9$ Hz), 1.19-1.42 (m, 2 H), 1.46-1.86 (m, 8 H), 2.52 (dd, 1 H, $J = 14.8, 4.2$ Hz), 3.23-3.46 (m, 3 H), 3.85 (s, 1 H), 4.76 (dd, 1 H, $J = 9.3, 4.1$ Hz), 7.22-7.46 (m, 5 H); ^{13}C NMR δ 15.1, 20.9, 21.0, 25.3, 33.2, 33.5, 45.2, 64.5, 78.2, 78.8, 126.4, 127.9, 128.5, 141.4, 213.2. Anal. Calcd for $\text{C}_{17}\text{H}_{24}\text{O}_3$: C, 73.88; H, 8.75. Found: C, 73.83; H, 9.10.

1-Phenyl-1-butoxy-4-hydroxy-4-methyl-3-pentanone (10c): prepared from the hydrolysis of **9c** (Procedure B) in 94% yield; colorless oil; ^1H NMR δ 0.86 (t, 3 H, $J = 7.3$ Hz),

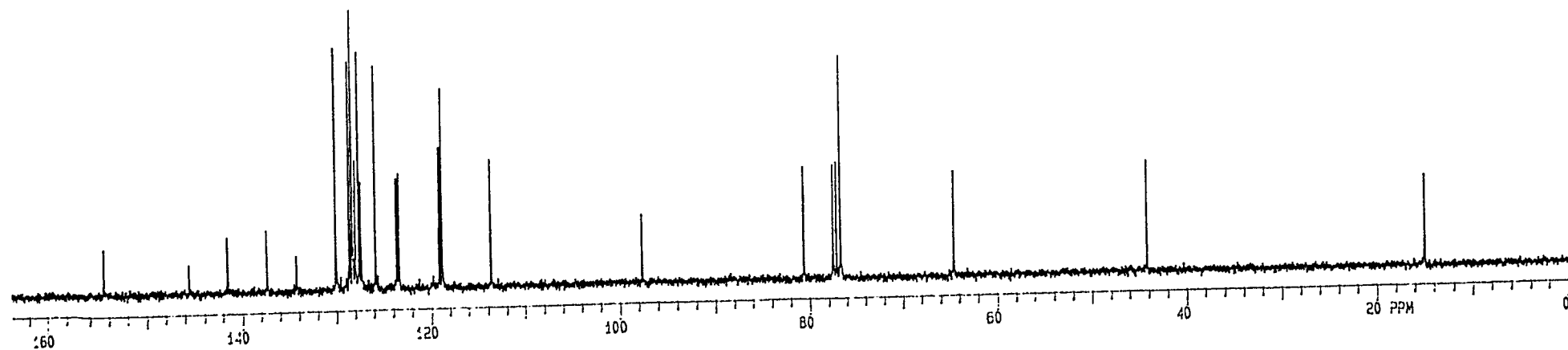
1.25 (s, 3 H), 1.22-1.35 (m, 2 H), 1.36 (s, 3 H), 1.42-1.56 (m, 2 H), 2.53 (dd, 1 H, $J = 15.0, 4.2$ Hz), 3.17-3.36 (m, 3 H), 4.04 (s, 1 H), 4.77 (dd, 1 H, $J = 9.4, 4.3$ Hz), 7.22-7.44 (m, 5 H); ^{13}C NMR δ 13.8, 19.2, 25.8, 26.0, 31.8, 45.0, 68.9, 76.4, 78.7, 126.4, 127.9, 128.6, 141.3, 212.8.
Anal. Calcd for $\text{C}_{16}\text{H}_{24}\text{O}_3$: C, 72.69; H, 9.15. Found: C, 72.80; H, 9.59.

| INDEX | FREQ | PPM | INTENSITY |
|-------|----------|----------|-----------|
| 01 | 2375.08 | 7.915 | 32.274 |
| 02 | 2366.83 | 7.887 | 32.021 |
| 03 | 2174.33 | 7.246 | 14.839 |
| 04 | 2157.51 | 7.190 | 78.279 |
| 05 | 2153.94 | 7.178 | 119.718 |
| 06 | 2151.53 | 7.170 | 117.928 |
| 07 | 2146.25 | 7.152 | 117.931 |
| 08 | 2138.83 | 7.128 | 122.402 |
| 09 | 2131.41 | 7.103 | 43.243 |
| 10 | 2121.19 | 7.069 | 22.083 |
| 11 | 2119.54 | 7.063 | 21.713 |
| 12 | 2113.83 | 7.044 | 58.350 |
| 13 | 2106.20 | 7.019 | 63.641 |
| 14 | 2103.06 | 7.008 | 50.378 |
| 15 | 2095.37 | 6.983 | 66.270 |
| 16 | 2087.74 | 6.957 | 89.127 |
| 17 | 2080.04 | 6.932 | 117.264 |
| 18 | 2078.46 | 6.926 | 108.540 |
| 19 | 2071.74 | 6.904 | 42.145 |
| 20 | 2032.46 | 6.773 | 42.662 |
| 21 | 2028.95 | 6.761 | 53.094 |
| 22 | 2025.44 | 6.750 | 48.581 |
| 23 | 2023.40 | 6.743 | 43.059 |
| 24 | 2003.95 | 6.678 | 65.969 |
| 25 | 1995.99 | 6.652 | 61.448 |
| 26 | 1692.17 | 5.639 | 56.372 |
| 27 | 1677.94 | 5.592 | 48.408 |
| 28 | 1401.80 | 4.672 | 30.994 |
| 29 | 1391.92 | 4.639 | 34.361 |
| 30 | 1090.23 | 3.633 | 17.373 |
| 31 | 1080.13 | 3.600 | 17.626 |
| 32 | 1073.53 | 3.578 | 24.747 |
| 33 | 1063.65 | 3.545 | 24.866 |
| 34 | 1032.94 | 3.442 | 20.639 |
| 35 | 1026.01 | 3.419 | 62.303 |
| 36 | 1018.87 | 3.395 | 65.792 |
| 37 | 1012.00 | 3.372 | 26.734 |
| 38 | 968.32 | 3.227 | 36.535 |
| 39 | 952.12 | 3.173 | 29.097 |
| 40 | 390.35 | 1.301 | 62.575 |
| 41 | 383.48 | 1.278 | 124.802 |
| 42 | 376.40 | 1.254 | 68.584 |
| 43 | -2.50E-3 | -8.34E-6 | 13.917 |





| INDEX | FREQ | PPM | INTENSITY |
|-------|---------|---------|-----------|
| 01 | 11650.2 | 154.385 | 22.019 |
| 02 | 10974.8 | 145.434 | 13.091 |
| 03 | 10666.7 | 141.352 | 25.667 |
| 04 | 10353.3 | 137.199 | 24.953 |
| 05 | 10119.3 | 134.098 | 17.050 |
| 06 | 9800.4 | 129.872 | 99.202 |
| 07 | 9695.6 | 128.483 | 93.958 |
| 08 | 9671.5 | 128.164 | 53.259 |
| 09 | 9666.3 | 128.095 | 114.444 |
| 10 | 9643.5 | 127.793 | 53.052 |
| 11 | 9614.1 | 127.404 | 95.650 |
| 12 | 9597.2 | 127.179 | 42.375 |
| 13 | 9483.5 | 125.672 | 98.410 |
| 14 | 9318.3 | 123.483 | 46.255 |
| 15 | 9301.2 | 123.257 | 44.972 |
| 16 | 8978.2 | 118.976 | 58.098 |
| 17 | 8954.9 | 118.667 | 91.719 |
| 18 | 8567.0 | 113.528 | 50.866 |
| 19 | 7358.9 | 97.518 | 28.832 |
| 20 | 6072.7 | 80.473 | 47.556 |
| 21 | 5842.9 | 77.428 | 49.069 |
| 22 | 5810.9 | 77.005 | 51.117 |
| 23 | 5778.5 | 76.575 | 87.014 |
| 24 | 4866.8 | 64.493 | 45.407 |
| 25 | 3332.2 | 44.158 | 45.378 |
| 26 | 1128.9 | 14.960 | 38.364 |



SPEC: 1583ci-c1

Samp: F5

Comm: POS CI/METHANE

Mode: CI +VE +LMR BSCAN (EXP) UP HR

Oper: MPO

Client: ARK

Base: 135.1

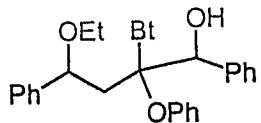
Inten: 347711

Norm: 135.1

RIC: 1410325

Peak: 1000.00 mmu

Data: +21-15>16 (CMASS : converted |CMASS : converted |CMASS : conver



02-Jul-97

DERIVED SPECTRUM

#9

Start: 17:39:27

30

Inlet:

Masses: 60 > 700

#peaks: 92

