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Supporting Information

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Stereoselective Phosphine-Catalyzed Synthesis of Highly Functionalized Diquinanes**

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I. General

All reactions were carried out in oven-dried glassware under an atmosphere of argon or nitrogen with magnetic stirring, unless otherwise noted. P(*n*-Bu)$_3$ (97%; used as received) was purchased from Aldrich. EtOAc (anhydrous; used as received) was purchased from Fluka. CH_2Cl_2 was purified by passage through neutral alumina.

All NMR spectra were recorded in $CDCl_3$, unless otherwise noted.

II. Phosphine-Catalyzed Cyclizations

General Procedure for Cyclizations: A flask was charged with the substrate, and then it was evacuated and refilled with argon three times. The appropriate volume of CH_2Cl_2:EtOAc (9:1) was added to afford a 0.01 M solution of the substrate. P(*n*-Bu)$_3$ (0.20 equiv) was added by syringe, and the solution was stirred for 20 h at room temperature. Then, the reaction mixture was exposed to air for 1 h, filtered through a short pad of silica gel with Et_2O washings (100 mL), and concentrated. The desired product was purified by flash chromatography.

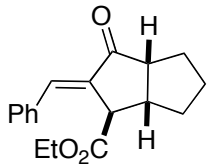


Table 1, entry 1. The general procedure was followed. Ynone (114 mg, 0.400 mmol), P(*n*-Bu)$_3$ (20 μL, 0.080 mmol). Purification by flash chromatography (5→25% Et_2O in hexanes) furnished the product (104 mg, 91%) as a pale-yellow oil.

Second run: Ynone (114 mg, 0.400 mmol), P(*n*-Bu)$_3$ (20 μL, 0.080 mmol). Product: 98.9 mg, 87%.

^{1}H NMR (300 MHz) δ 7.60-7.57 (m, 2H), 7.52 (d, J=1.6 Hz, 1H), 7.44-7.38 (m, 3H), 4.22-4.03 (m, 2H), 3.88 (s, 1H), 3.02 (td, J=9.2 Hz, J=3.7 Hz, 1H), 2.87 (q, J=7.4 Hz, 1H), 2.11-1.86 (m, 3H), 1.61-1.52 (m, 2H), 1.17 (t, J=7.1 Hz, 3H), obscured peak under the triplet at 1.17 (m, 1H).

^{13}C NMR (75 MHz) δ 210.3, 173.4, 137.0, 134.5, 133.5, 131.0, 130.3, 129.0, 61.4, 51.3, 50.5, 44.5, 33.9, 29.9, 26.1, 14.3.

FTIR (thin film) 3057, 3026, 2957, 2871, 1731, 1622, 1575, 1494, 1448, 1367, 1293, 1233, 1173, 1117, 1094, 942 cm^{-1}.

LC-MS calc. for $C_{18}H_{21}O_3$ (M+H) 285.1, found 285.1.

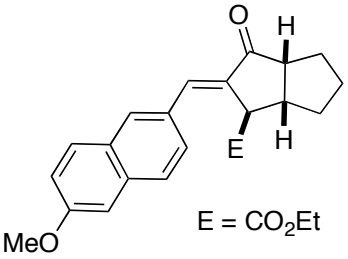


Table 1, entry 2. The general procedure was followed, except CH_2Cl_2:EtOAc (1:1) was used. Ynone (109 mg, 0.300 mmol), P(*n*-Bu)$_3$ (15 μL, 0.060 mmol). Purification by flash chromatography (5→40% Et_2O in hexanes) furnished the product (91.5 mg, 84%) as a yellow solid.

Second run: Ynone (109 mg, 0.300 mmol), P(*n*-Bu)$_3$ (15 μL, 0.060 mmol). Product: 89.6 mg, 82%.

Mp: 87 °C.

^{1}H NMR (300 MHz) δ 8.05 (s, 1H), 7.78 (d, J=9.3 Hz, 1H), 7.74 (d, J=8.9 Hz, 1H), 7.67-7.64 (m, 2H), 7.17 (dd, J=8.9 Hz, J=2.5 Hz, 1H), 7.12 (d, J=2.5 Hz, 1H), 4.22-4.04 (m, 2H), 4.00 (s, 1H), 3.93 (s, 3H), 3.09-3.02 (m, 1H), 2.94-2.86 (m, 1H), 2.12-1.89 (m, 3H), 1.63-1.53 (m, 2H), 1.19 (t, J=7.2 Hz, 3H), 1.33-1.17 (m, 1H).

^{13}C NMR (75 MHz) δ 210.6, 173.7, 159.3, 137.5, 135.5, 132.5, 132.0, 130.6, 129.8, 128.8, 128.1, 127.5, 119.8, 105.8, 61.4, 55.6, 51.4, 50.7, 44.5, 34.0, 29.9, 26.1, 14.4.

FTIR (thin film) 2957, 2870, 1727, 1610, 1482, 1394, 1268, 1249, 1173, 1029 cm^{-1}.

LC-MS calc. for $C_{23}H_{25}O_4$ (M+H) 365.1, found 365.1.

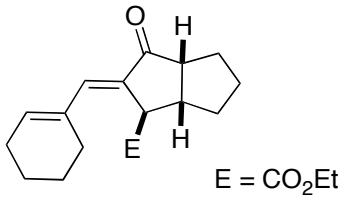


Table 1, entry 3. The general procedure was followed. Ynone (115 mg, 0.400 mmol), P(*n*-Bu)$_3$ (20 μL, 0.080 mmol). Purification by flash chromatography (5→25% Et_2O in hexanes) furnished the product (97.0 mg, 84%) as a pale-yellow oil.

Second run: Ynone (115 mg, 0.400 mmol), P(*n*-Bu)$_3$ (20 μL, 0.080 mmol). Product: 96.3 mg, 83%.

^{1}H NMR (300 MHz) δ 7.01 (s, 1H), 6.28 (t, J=3.9 Hz, 1H), 4.21-4.03 (m, 2H), 3.84 (s, 1H), 2.88 (td, J=9.3 Hz, J=3.6 Hz, 1H), 2.72 (q, J=8.3 Hz, 1H), 2.31-2.24 (m, 2H), 2.24-2.17 (m, 2H), 2.04-1.79 (m, 3H), 1.68-1.49 (m, 6H), 1.20 (t, J=7.1 Hz, 3H), 1.24-1.10 (m, 1H).

^{13}C NMR (75 MHz) δ 210.6, 174.1, 142.3, 140.9, 135.3, 129.4, 61.2, 51.1, 49.9, 44.2, 33.9, 29.8, 27.0, 26.9, 26.1, 22.6, 21.6, 14.3.

FTIR (thin film) 2936, 2866, 1737, 1603, 1447, 1388, 1367, 1308, 1219, 1156, 1116, 1094, 1032 cm^{-1}.

LC-MS calc. for $C_{18}H_{25}O_3$ (M+H) 289.1, found 289.1.

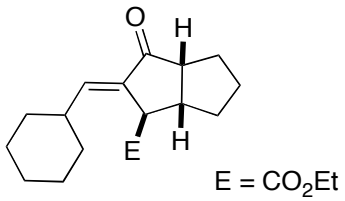


Table 1, entry 4. The general procedure was followed, except 1:1 CH_2Cl_2:EtOAc was used. Ynone (87.1 mg, 0.300 mmol), P(*n*-Bu)$_3$ (15 μL, 0.060 mmol). Purification by flash chromatography (5→25% Et_2O in hexanes) furnished the product (38.1 mg, 44%) as a colorless oil.

Second run: Ynone (87.1 mg, 0.300 mmol), P(*n*-Bu)$_3$ (15 μL, 0.060 mmol). Product: 39.8 mg, 46%.

^{1}H NMR (300 MHz) δ 6.53 (dd, J=10.6 Hz, J=1.9 Hz, 1H), 4.11 (q, J=7.1 Hz, 2H), 3.56 (s, 1H), 3.00-2.92 (m, 1H), 2.84-2.75 (m, 1H), 2.38-2.23 (m, 1H), 2.05-1.51 (m, 10H), 1.32-1.06 (m, 6H), 1.23 (t, J=7.1 Hz, 3H).

^{13}C NMR (75 MHz) δ 209.8, 173.9, 146.4, 133.4, 61.2, 52.4, 48.5, 43.2, 39.2, 33.7, 31.9, 31.5, 29.6, 26.2, 25.9, 25.51, 25.47, 14.3.

FTIR (thin film) 2927, 2853, 1732, 1645, 1448, 1368, 1294, 1266, 1246, 1174, 1031, 935 cm^{-1}.

LC-MS calc. for $C_{18}H_{27}O_3$ (M+H) 291.1, found 291.1.

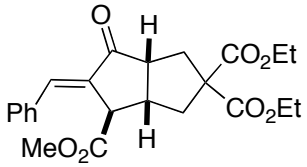


Table 1, entry 5. The general procedure was followed, except 1:1 CH_2Cl_2:EtOAc was used. Ynone (124 mg, 0.300 mmol), P(*n*-Bu)$_3$ (15 μL, 0.060 mmol). Purification by flash chromatography (5→40% Et_2O in hexanes) furnished the product (110 mg, 89%) as a pale-yellow oil.

Second run: Ynone (109 mg, 0.300 mmol), P(*n*-Bu)$_3$ (15 μL, 0.060 mmol). Product: 109 mg, 88%.

^{1}H NMR (300 MHz) δ 7.60-7.56 (m, 3H), 7.46-7.39 (m, 3H), 4.26-4.14 (m, 2H), 4.10 (q, J=7.1 Hz, 2H), 3.91 (s, 1H), 3.67 (s, 3H), 3.19-3.11 (m, 1H), 3.06-2.97 (m, 1H), 2.84 (ddd, J=14.4 Hz, J=10.1 Hz, J=1.5 Hz, 1H), 2.52 (dd, J=13.5 Hz, J=7.0 Hz, 1H), 2.35 (dd, J=14.4 Hz, J=4.3 Hz, 1H), 1.71 (dd, J=13.5 Hz, J=11.5 Hz, 1H), 1.24 (t, J=7.1 Hz, 3H), 1.18 (t, J=7.1 Hz, 3H).

^{13}C NMR (75 MHz) δ 207.9, 173.2, 171.7, 170.9, 138.8, 134.1, 131.9, 131.2, 130.7, 129.2, 62.1, 61.9, 61.1, 52.8, 50.0, 48.9, 43.1, 40.1, 36.1, 14.22, 14.16.

FTIR (thin film) 3057, 2982, 2874, 1731, 1621, 1494, 1448, 1367, 1261, 1097, 1064, 1028, 955 cm^{-1}.

LC-MS calc. for $C_{23}H_{27}O_7$ (M+H) 415.2, found 415.1.

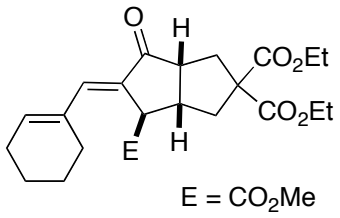


Table 1, entry 6. The general procedure was followed. Ynone (126 mg, 0.300 mmol), P(*n*-Bu)$_3$ (15 μL, 0.060 mmol). Purification by flash chromatography (10→40% Et_2O in hexanes) furnished the product (113 mg, 90%) as a pale-yellow oil.

Second run: Ynone (126 mg, 0.300 mmol), P(*n*-Bu)$_3$ (15 μL, 0.060 mmol). Product: 106 mg, 85%.

^{1}H NMR (300 MHz) δ 7.06 (s, 1H), 6.32 (t, J=3.7 Hz, 1H), 4.23-4.12 (m, 2H), 4.10 (q, J=7.1 Hz, 2H), 3.89 (s, 1H), 3.66 (s, 3H), 3.05-2.98 (m, 1H), 2.91-2.75 (m, 1H), 2.79 (ddd, J=14.3 Hz, J=10.2 Hz, J=1.4 Hz, 1H), 2.49 (dd, J=13.3 Hz, J=7.0 Hz, 1H), 2.29-2.21 (m, 5H), 1.74 (dd, J=13.3 Hz, J=11.5 Hz, 1H), 1.68-1.54 (m, 4H), 1.23 (t, J=7.1 Hz, 3H), 1.19 (t, J=7.1 Hz, 3H).

^{13}C NMR (75 MHz) δ 208.2, 173.9, 171.8, 171.0, 143.6, 142.8, 135.2, 127.8, 62.0, 61.8, 61.1, 52.6, 49.8, 48.3, 42.8, 40.1, 36.1, 27.1, 26.8, 22.5, 21.5, 14.22, 14.18.

FTIR (thin film) 2981, 2935, 2862, 1715, 1603, 1436, 1366, 1222, 1096, 1064, 1028, 941, 860 cm^{-1}.

LC-MS calc. for $C_{23}H_{31}O_7$ (M+H) 419.2, found 419.1.

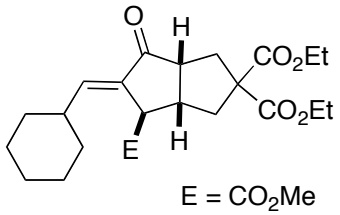


Table 1, entry 7. The general procedure was followed, except 1:1 CH_2Cl_2:EtOAc was used. Ynone (126 mg, 0.300 mmol), P(*n*-Bu)$_3$ (15 μL, 0.060 mmol). Purification by flash chromatography (5→40% Et_2O in hexanes) furnished the product (90.5 mg, 72%) as a colorless oil.

Second run: Ynone (126 mg, 0.300 mmol), P(*n*-Bu)$_3$ (15 μL, 0.060 mmol). Product: 96.0 mg, 76%.

^{1}H NMR (300 MHz) δ 6.60 (dd, J=10.6 Hz, J=1.8 Hz, 1H), 4.21-4.13 (m, 2H), 4.11 (q, J=7.1 Hz, 2H), 3.65 (s, 3H), 3.61-3.59 (m, 1H), 2.98-2.89 (m, 1H), 2.78 (ddd, J=14.3, J=10.2 Hz, J=1.5 Hz, 1H), 2.52-2.45 (m, 1H), 2.33-2.25 (m, 2H), 1.76-1.59 (m, 5H), 1.52-1.44 (m, 1H), 1.36-1.10 (m, 6H), 1.23 (t, J=7.1 Hz, 3H), 1.19 (t, J=7.2 Hz, 3H).

^{13}C NMR (75 MHz) δ 207.2, 173.6, 171.7, 171.0, 148.2, 132.1, 62.0, 61.9, 61.1, 52.5, 51.2, 46.9, 41.8, 39.9, 39.4, 35.8, 31.8, 31.4, 25.9, 25.5, 25.3, 14.23, 14.17.

FTIR (thin film) 2982, 2929, 2853, 1732, 1644, 1447, 1367, 1259, 1185, 1099, 1064, 1028, 932 cm^{-1}.

LC-MS calc. for $C_{23}H_{33}O_7$ (M+H) 421.2, found 421.2.

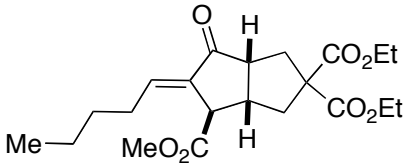


Table 1, entry 8. The general procedure was followed. Ynone (79 mg, 0.20 mmol), P(*n*-Bu)$_3$ (10 μL, 0.040 mmol). Purification by flash chromatography (5→40% Et_2O in hexanes) furnished the product (60.4 mg, 77%) as a colorless oil.

Second run: Ynone (79 mg, 0.20 mmol), P(*n*-Bu)$_3$ (10 μL, 0.040 mmol). Product: 61.0 mg, 77%.

^{1}H NMR (300 MHz) δ 6.78 (td, J=7.7 Hz, J=1.9 Hz, 1H), 4.23-4.12 (m, 2H), 4.11 (q, J=7.1 Hz, 2H), 3.65 (s, 3H), 3.57 (br s, 1H), 3.12-3.04 (m, 1H), 2.98-2.89 (m, 1H), 2.78 (ddd, J=14.4 Hz, J=10.2 Hz, J=1.3 Hz, 1H), 2.49 (dd, J=13.3 Hz, J=7.1 Hz, 1H), 2.27 (dd, J=14.4 Hz, J=4.2 Hz, 1H), 2.26-

2.18 (m, 2H), 1.70 (dd, J=13.4 Hz, J=10.6 Hz, 1H), 1.46-1.20 (m, 4H), 1.23 (t, J=7.1 Hz, 3H), 1.19 (t, J=7.1 Hz, 3H), 0.87 (t, J=7.2 Hz, 3H).

^{13}C NMR (75 MHz) δ 206.6, 173.3, 171.7, 171.0, 144.1, 134.2, 62.0, 61.9, 61.1, 52.5, 51.2, 47.0, 41.8, 39.9, 35.9, 30.5, 29.9, 22.7, 14.23, 14.18, 14.1.

FTIR (thin film) 2958, 2873, 1732, 1645, 1587, 1445, 1367, 1261, 1187, 1100, 1064, 1028, 935, 861 cm^{-1}.

LC-MS calc. for $C_{21}H_{31}O_7$ (M+H) 395.2, found 395.1.

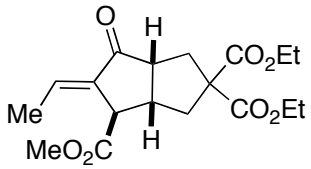


Table 1, entry 9. The general procedure was followed. Ynone (70.5 mg, 0.200 mmol), P(*n*-Bu)$_3$ (10 μL, 0.040 mmol). Purification by flash chromatography (5→40% Et_2O in hexanes) furnished the product (39.8 mg, 56%) as a colorless oil.

Second run: Ynone (70.5 mg, 0.200 mmol), P(*n*-Bu)$_3$ (10 μL, 0.040 mmol). Product: 38.8 mg, 55%.

^{1}H NMR (300 MHz) δ 6.87 (qd, J=7.2 Hz, J=1.8 Hz, 1H), 4.24-4.12 (m, 2H), 4.11 (q, J=7.1 Hz, 2H), 3.66 (s, 3H), 3.59 (s, 1H), 3.12-3.04 (m, 1H), 3.01-2.92 (m, 1H), 2.78 (ddd, J=14.4 Hz, J=10.2 Hz, J=1.4 Hz, 1H), 2.49 (dd, J=13.3 Hz, J=7.1 Hz, 1H), 2.27 (dd, J=14.4 Hz, J=4.0 Hz, 1H), 1.88 (dd, J=7.3 Hz, J=1.0 Hz, 3H), 1.71 (dd, J=13.4 Hz, J=11.4 Hz, 1H), 1.24 (t, J=7.1, 3H), 1.19 (t, J=7.1 Hz, 3H).

^{13}C NMR (75 MHz) δ 206.3, 173.1, 171.7, 171.0, 138.9, 135.4, 62.0, 61.9, 61.1, 52.5, 51.3, 46.9, 41.6, 39.9, 35.9, 15.8, 14.23, 14.17.

FTIR (thin film) 2983, 2875, 1732, 1651, 1585, 1437, 1367, 1262, 1186, 1100, 1064, 1029, 919, 860 cm^{-1}.

LC-MS calc. for $C_{18}H_{25}O_7$ (M+H) 353.2, found 353.1.

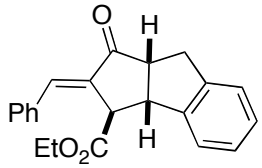


Table 1, entry 10. The general procedure was followed. Ynone (133 mg, 0.400 mmol), P(*n*-Bu)$_3$ (20 μL, 0.080 mmol). Purification by flash chromatography (5→40% Et_2O in hexanes) furnished the product (115 mg, 86%) as a pale-yellow oil.

Second run: Ynone (133 mg, 0.400 mmol), P(*n*-Bu)$_3$ (20 μL, 0.080 mmol). Product: 121 mg, 91%.

^{1}H NMR (300 MHz, C_6D_6) δ 7.60 (d, J=1.6 Hz, 1H), 7.37-7.36 (m, 1H), 7.36-7.33 (m, 1H), 7.02-6.94 (m, 2H), 6.93-6.80 (m, 5H), 4.42 (d, J=1.6 Hz, 1H), 3.99-3.78 (m, 3H), 3.47 (d, J=16.2 Hz, 1H), 3.24-3.17 (m, 1H), 2.90 (dd, J=16.1 Hz, J=8.7 Hz, 1H), 0.81 (t, J=7.1 Hz, 3H).

^{13}C NMR (75 MHz, C_6D_6) δ 208.0, 173.0, 143.4, 143.3, 137.5, 135.0, 133.7, 131.5, 130.4, 129.2, 128.3, 127.9, 125.5, 124.5, 61.6, 52.1, 50.6, 50.1, 36.3, 14.4.

FTIR (thin film) 3068, 3024, 2980, 2936, 2909, 2835, 1715, 1622, 1575, 1448, 1315, 1290, 1222, 1199, 1154, 1095, 1029, 957 cm^{-1}.

LC-MS calc. for $C_{22}H_{21}O_3$ (M+H) 333.1, found 333.1.

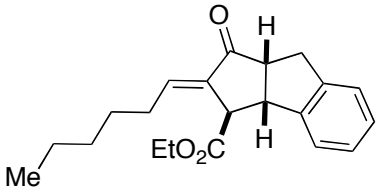


Table 1, entry 11. The general procedure was followed. Ynone (97.9 mg, 0.300 mmol), P(*n*-Bu)$_3$ (15 μL, 0.060 mmol). Purification by flash chromatography (5→40% Et_2O in hexanes) furnished the product (51.3 mg, 52%) as a colorless oil.

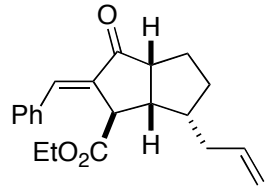
Second run: Ynone (97.9 mg, 0.300 mmol), P(*n*-Bu)$_3$ (15 μL, 0.060 mmol). Product: 55.3 mg, 56%.

^{1}H NMR (300 MHz, C_6D_6) δ 7.01-6.85 (m, 4H), 6.71 (td, J=7.7 Hz, J=1.8 Hz, 1H), 4.02 (s, 1H), 3.98-3.87 (m, 3H), 3.42 (d, J=16.1 Hz, 1H), 3.22 (app t, J=8.1 Hz, 1H), 2.87 (dd, J=16.1 Hz, J=8.6 Hz, 1H), 2.07-1.81 (m, 2H), 1.06-0.84 (m, 6H), 0.90 (t, J=7.1 Hz, 3H), 0.69 (t, J=7.1 Hz, 3H).

^{13}C NMR (75 MHz, C_6D_6) δ 206.3, 172.7, 143.3, 143.2, 141.7, 135.2, 127.9, 127.3, 125.3, 124.1, 61.0, 51.5, 49.9, 48.6, 35.8, 31.7, 29.9, 28.0, 22.7, 14.2, 14.1.

FTIR (thin film) 2929, 2857, 1732, 1645, 1459, 1444, 1367, 1328, 1313, 1269, 1235, 1163, 1133, 1028, 939 cm^{-1}.

LC-MS calc. for $C_{21}H_{27}O_3$ (M+H) 327.2, found 327.2.



Eq 3. The general procedure was followed. Ynone (130 mg, 0.400 mmol), P(*n*-Bu)$_3$ (20 μL, 0.080 mmol). Purification by flash chromatography (5→25% Et_2O in hexanes) furnished the product (93 mg, 72%) as a pale-yellow oil.

Second run: Ynone (130 mg, 0.400 mmol), P(*n*-Bu)$_3$ (20 μL, 0.080 mmol). Product: 98.7 mg, 76%.

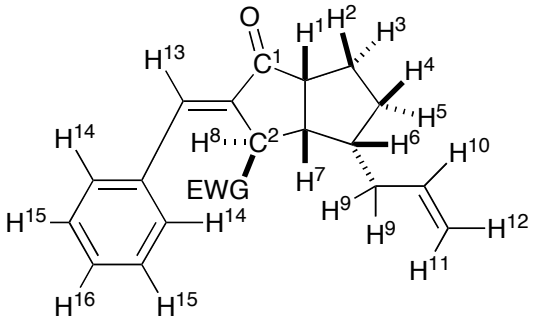
^{1}H NMR (300 MHz) δ 7.63-7.55 (m, 3H), 7.48-7.41 (m, 3H), 5.77 (ddt, J=17.1 Hz, J=10.1 Hz, J=7.0 Hz, 1H), 5.09-4.99 (m, 2H), 4.24-4.06 (m, 2H), 3.91 (s, 1H), 3.13-3.05 (m, 1H), 2.48 (t, J=9.2 Hz, 1H), 2.43-2.34 (m, 1H), 2.22-2.01 (m, 2H), 1.90-1.77 (m, 2H), 1.49-1.25 (m, 2H), 1.20 (t, J=7.2 Hz, 3H).

^{13}C NMR (75 MHz) δ 210.1, 173.2, 137.4, 136.6, 134.5, 133.1, 131.1, 130.4, 129.7, 129.1, 128.7, 116.6, 61.4, 51.3, 50.0, 49.0, 45.9, 37.8, 32.2, 27.8, 14.3.

FTIR (thin film) 3073, 2956, 1716, 1622, 1494, 1448, 1367, 1255, 1159, 1098, 1030, 993, 921 cm^{-1}.

LC-MS calc. for $C_{21}H_{25}O_3$ (M+H) 325.2, found 325.1.

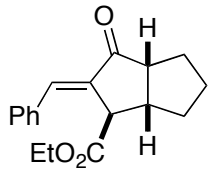
Structure determination: The protons were assigned on the basis of a gCOSY experiment.



Stereochemistry of the allyl group: There is a NOESY cross peak between H^8 and H^9. The relative volume of the cross peaks (H^8,H^9):(H^8,H^7) is 781:432, which indicates that there is direct transfer from H^8 to H^9. H^7 is an apparent triplet, indicating that $J_{H^7H^1} \cong J_{H^7H^6}$, which is consistent with the proposed structure.

Olefin geometry: There are NOESY cross peaks between H^8 and H^{14}. The gHMBC relative cross peak volume for H^{13},C^1:H^{13},C^2 is 3.7:4.4, so H^{13} is 180° from C^2 and 0° from C^1.

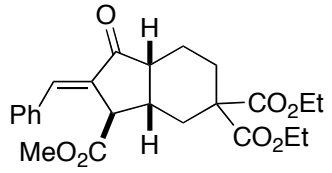
The ^{1}H NMR spectra for all of the other [3.3.0] systems are similar with regard to chemical shifts and splitting patterns, and the structures are therefore assigned by analogy with the above.



Eq 7. In a nitrogen-filled glove box, a flask was charged with the substrate (170 mg, 0.600 mmol), CH_2Cl_2:EtOAc (9:1; 60 mL), and phosphepine (*S*)-**3** (44 mg, 0.12 mmol, 0.20 equiv). Then, the flask was sealed and removed from the glove box. The reaction mixture was stirred for 72 h at room temperature. Then, it was exposed to air for 1 h, filtered through a short pad of silica gel with Et_2O washings (20 mL), and concentrated. The desired product was purified by flash chromatography (5→20% EtOAc in hexanes), which furnished a pale-yellow oil (129 mg, 76%).

HPLC analysis of the product: Daicel CHIRALPAK IC column; 5.0% *i*-PrOH in hexanes; 1.0 mL/min; retention times: 38.8 min (minor), 43.5 min (major).

$[\alpha]_D^{22}$ = +176 (c = 1.02, $CHCl_3$; 60% ee).



Eq 8. The general procedure was followed. Ynone (128 mg, 0.300 mmol), P(*n*-Bu)$_3$ (15 μL, 0.060 mmol). Purification by flash chromatography (5→40% Et_2O in hexanes) furnished the product (73.0 mg, 57%) as a colorless oil.

Second run: Ynone (128 mg, 0.300 mmol), P(*n*-Bu)$_3$ (15 μL, 0.060 mmol). Product: 79.8 mg, 62%.

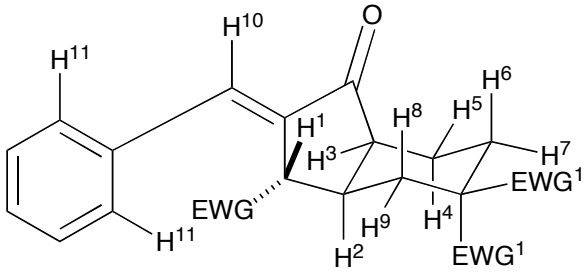
^{1}H NMR (300 MHz) δ 7.66 (d, J=1.2 Hz, 1H), 7.57-7.54 (m, 2H), 7.46-7.39 (m, 3H), 4.23 (q, J=7.2 Hz, 2H), 4.08 (qd, J=7.1 Hz, J=1.2 Hz, 2H), 3.72 (s, 3H), 3.71 (s, 1H), 3.04-2.95 (m, 1H), 2.85-2.81 (m, 1H), 2.44-2.32 (m, 2H), 2.21-2.12 (m, 1H), 1.70-1.58 (m, 1H), 1.49-1.38 (m, 1H), 1.27 (t, J=7.1 Hz, 3H), 1.17 (t, J=7.2 Hz, 3H), 1.10 (t, J=13.0 Hz, 1H).

^{13}C NMR (75 MHz) δ 205.4, 172.8, 171.7, 170.5, 137.7, 134.2, 132.1, 131.0, 130.5, 129.2, 61.8, 61.6, 54.2, 52.7, 51.0, 45.3, 36.3, 34.5, 27.3, 19.1, 14.3, 14.2.

FTIR (thin film) 2980, 2954, 1732, 1627, 1448, 1367, 1315, 1229, 1175, 1127, 1050, 1018 cm^{-1}.

LC-MS calc. for $C_{24}H_{29}O_7$ (M+H) 429.2, found 429.1.

Structure determination: The protons were assigned on the basis of a gCOSY experiment and J couplings.

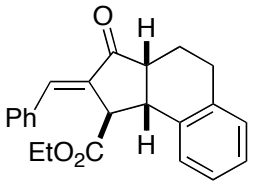


The relative stereochemistry of H^1 to H^2 is based on the lack of a J coupling. H^1 appears as a singlet and shows no cross peak in the gCOSY, indicating a dihedral angle of 80-90°, which is consistent with the assigned structure.

The relative stereochemistry of H^2 to H^3 is based upon a strong NOESY cross peak. Moreover, H^2 has a large J coupling to H^8, which is an apparent triplet ($J_{H^2H^8}=J_{H^8H^9}$; $J_{H^{axial}H^{axial}}=J_{geminal}$). H^2 must be in an axial-axial relationship with H^8. So, if H^3 were axial (it is not, it is equatorial), H^2 should be an apparent td (two $J_{H^{axial}H^{axial}}$, one $J_{H^{axial}H^{eq}}$).

The olefin geometry is based on a NOESY cross peak between H^1 and H^{11}.

The structure of the other [4.3.0] system is assigned by analogy with the above.



Eq 9. The general procedure was followed. Ynone (66.5 mg, 0.192 mmol), P(*n*-Bu)$_3$ (9.5 μL, 0.038 mmol). Purification by flash chromatography (5→30% Et_2O in hexanes) furnished the product (48.0 mg, 72%) as a pale-yellow oil.

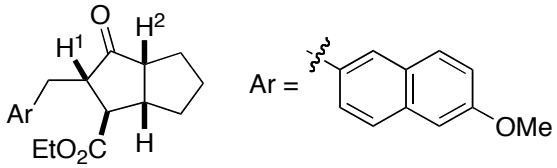
^{1}H NMR (300 MHz) δ 7.57 (d, J=1.8 Hz, 1H), 7.53-7.49 (m, 2H), 7.42-7.36 (m, 4H), 7.19 (td, J=7.5 Hz, J=1.3 Hz, 1H), 7.11 (td, J=7.4 Hz, J=0.8 Hz, 1H), 7.03 (d, J=7.5 Hz, 1H), 4.26-4.16 (m, 3H), 3.95 (d, J=8.8 Hz, 1H), 3.20-3.14 (m, 1H), 2.72-2.56 (m, 2H), 2.48-2.34 (m, 1H), 1.95-1.83 (m, 1H), 1.23 (t, J=7.1 Hz, 3H).

^{13}C NMR (75 MHz) δ 207.3, 173.1, 137.6, 137.0, 136.7, 134.3, 132.9, 131.0, 130.4, 129.32, 129.30, 129.0, 126.9, 126.8, 61.7, 55.0, 46.0, 42.2, 26.4, 22.1, 14.3.

FTIR (thin film) 3059, 3023, 2980, 2934, 1723, 1622, 1575, 1493, 1449 cm^{-1}.

LC-MS calc. for $C_{23}H_{23}O_3$ (M+H) 347.2, found 347.1.

III. Derivatizations



Eq 4. A solution of the enone (43 mg, 0.12 mmol) in MeOH (1.5 mL) was added to a flask that contained Pd/C (5 mg; 5% Pd by weight). The flask was purged with a balloon of H_2, and then a second balloon of H_2 was attached and the mixture was stirred vigorously for 3 h at room temperature. Next, the mixture was filtered through a pad of silica gel with Et_2O washings (60 mL), and the filtrate was concentrated to yield 41 mg (95%) of a clear oil that was determined to be a 7:1 mixture of diastereomers by ^{1}H NMR analysis. A pure sample of the major isomer could be obtained by column chromatography (5→30% Et_2O in hexanes).

Second run: Enone (39 mg, 0.11 mmol), Pd/C (5 mg). Product: 38 mg, 97% (8:1 dr).

^{1}H NMR (500 MHz, C_6D_6) δ 7.52-7.50 (m, 2H), 7.45 (d, J=8.9 Hz, 1H), 7.33 (dd, J=8.5 Hz, J=1.6 Hz, 1H), 7.12 (obscured by solvent peak, 1H), 6.86 (d, J=2.3 Hz, 1H), 3.71-3.58 (m, 2H), 3.33 (s, 3H), 3.24 (dd, J=13.9 Hz, J=5.3 Hz, 1H), 3.09-3.04 (m, 1H), 2.95 (dd, J=13.9 Hz, J=6.5 Hz, 1H),

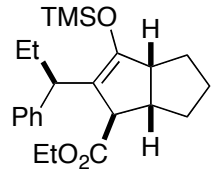
2.55-2.49 (m, 1H), 2.39-2.35 (m, 1H), 2.17 (dd, J=12.1 Hz, J=8.9 Hz, 1H), 1.83-1.77 (m, 1H), 1.45 (dd, J=12.6 Hz, J=6.4 Hz, 1H), 1.35-1.20 (m, 2H), 1.16-1.09 (m, 1H), 0.90-0.78 (m, 1H), 0.73 (t, J=7.1 Hz, 3H).

^{13}C NMR (125 MHz) δ 218.8, 174.9, 157.5, 134.0, 133.4, 129.2, 129.1, 128.5, 128.0, 127.0, 118.9, 105.8, 61.0, 55.7, 55.5, 51.7, 50.9, 43.5, 31.1, 32.9, 29.4, 25.2, 14.2.

FTIR (thin film) 2954, 2868, 1738, 1732, 1634, 1606, 1506, 1484, 1264, 1227 cm^{-1}.

LC-MS calc. for $C_{23}H_{27}O_4$ (M+H) 367.1, found 367.0.

The stereochemical assignment is based on addition to the convex face of the diquinane, on an nOe between H^1 and H^2, and on the lack of vicinal coupling between the proton α to the ketone and the proton α to the ester.



Eq 5. EtMgBr (63 μL, 0.19 mmol; 3.0 M solution in Et_2O) was added to a solution of HMPA (22 μL, 0.13 mmol) and $CuBr{\cdot}SMe_2$ (1.3 mg, 0.0060 mmol) in THF (0.75 mL) at –78 °C. Next, a solution of the enone (18 mg, 0.063 mmol) and TMSCl (16 μL, 0.13 mmol) in THF (0.75 mL) was added dropwise. The resulting solution was stirred at –78 °C for 2 h, and then it was diluted with Et_2O (10 mL) and quenched with a saturated solution of NH_4Cl (1 mL). The mixture was allowed to warm to room temperature, and then the layers were separated. The aqueous layer was extracted with Et_2O (3x10 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated to yield a clear oil (18.5 mg, 70%; ^{1}H NMR analysis showed >10:1 dr).

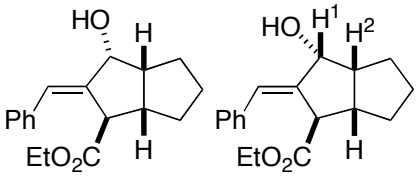
^{1}H NMR (300 MHz) δ 7.25-7.04 (m, 5H), 3.64-3.48 (m, 2H), 3.45 (app t, J=8.0 Hz, 1H), 3.11-3.03 (m, 1H), 2.90 (s, 1H), 2.49-2.42 (m, 1H), 1.87-1.74 (m, 2H), 1.74-1.66 (m, 2H), 1.56-1.42 (m, 3H), 1.36-1.26 (m, 1H), 0.96 (t, J=7.0 Hz, 3H), 0.81 (t, J=9.3 Hz, 3H), 0.23 (s, 9H).

^{13}C NMR (100 MHz) δ 175.9, 152.3, 143.6, 128.0, 127.7, 126.7, 117.3, 59.9, 54.5, 49.4, 44.4, 43.2, 34.7, 29.6, 25.3, 25.1, 13.8, 12.6, 0.8.

FTIR (thin film) 3028, 2958, 2871, 1733, 1669, 1456, 1339, 1036 cm^{-1}.

LC-MS calc. for $C_{23}H_{35}O_3Si$ [M+H]: 387.2, found: 387.2.

The stereochemical assignment is based on addition to the convex face of the diquinane.



Eq 6. $CeCl_3$ (64 mg, 0.26 mmol) was added to a stirred solution of the enone (49 mg, 0.17 mmol) in MeOH (3.5 mL) under argon. This solution was stirred for 10 min at room temperature, and then it was cooled to –10 °C. Next, a solution of $NaBH_4$ (7.6 mg, 0.21 mmol) in MeOH (1.0 mL) was added dropwise. The resulting mixture was stirred at –10 °C for 20 min, and then it was warmed to room temperature and stirred for an additional hour. The reaction was quenched with H_2O (5 mL), and the mixture was extracted with Et_2O (3x10 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated. The crude material was purified by flash chromatography (10→40% EtOAc in hexanes), which provided 44.5 mg (90%) of a clear, colorless oil.

Second run: $CeCl_3$ (68 mg, 0.28 mmol), enone (52 mg, 0.28 mmol), $NaBH_4$ (8.2 mg, 0.22 mmol). Product: 47.1 mg (89%).

^{1}H NMR (300 MHz) δ 7.37-7.23 (m, 5H), 6.62 (s, 1H), 5.02 (d, J=7.1 Hz, 1H), 4.25-4.08 (m, 2H), 3.29 (s, 1H), 2.77-2.66 (m, 2H), 2.06 (br s, 1H), 1.98-1.84 (m, 1H), 1.64-1.52 (m, 1H), 1.49-1.40 (m, 3H), 1.34-1.22 (m, 1H), 1.26 (t, J=7.1 Hz, 3H).

^{13}C NMR (75 MHz) δ 174.5, 143.1, 136.8, 128.8, 128.5, 127.1, 123.7, 76.1, 61.2, 52.0, 45.3, 45.2, 35.4, 26.1, 25.7, 14.4.

FTIR (thin film) 3439 (broad), 2952, 2867, 1715, 1599, 1494, 1446, 1368, 1320, 1259, 1222, 1142, 1029, 921 cm^{-1}.

LC-MS calc. for $C_{18}H_{22}NaO_3$ (M+Na) 309.1, found 309.1.

The stereochemical assignment is based on addition to the convex face of the diquinane and on an nOe between H^1 and H^2.

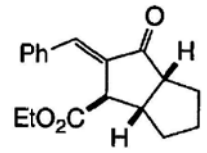
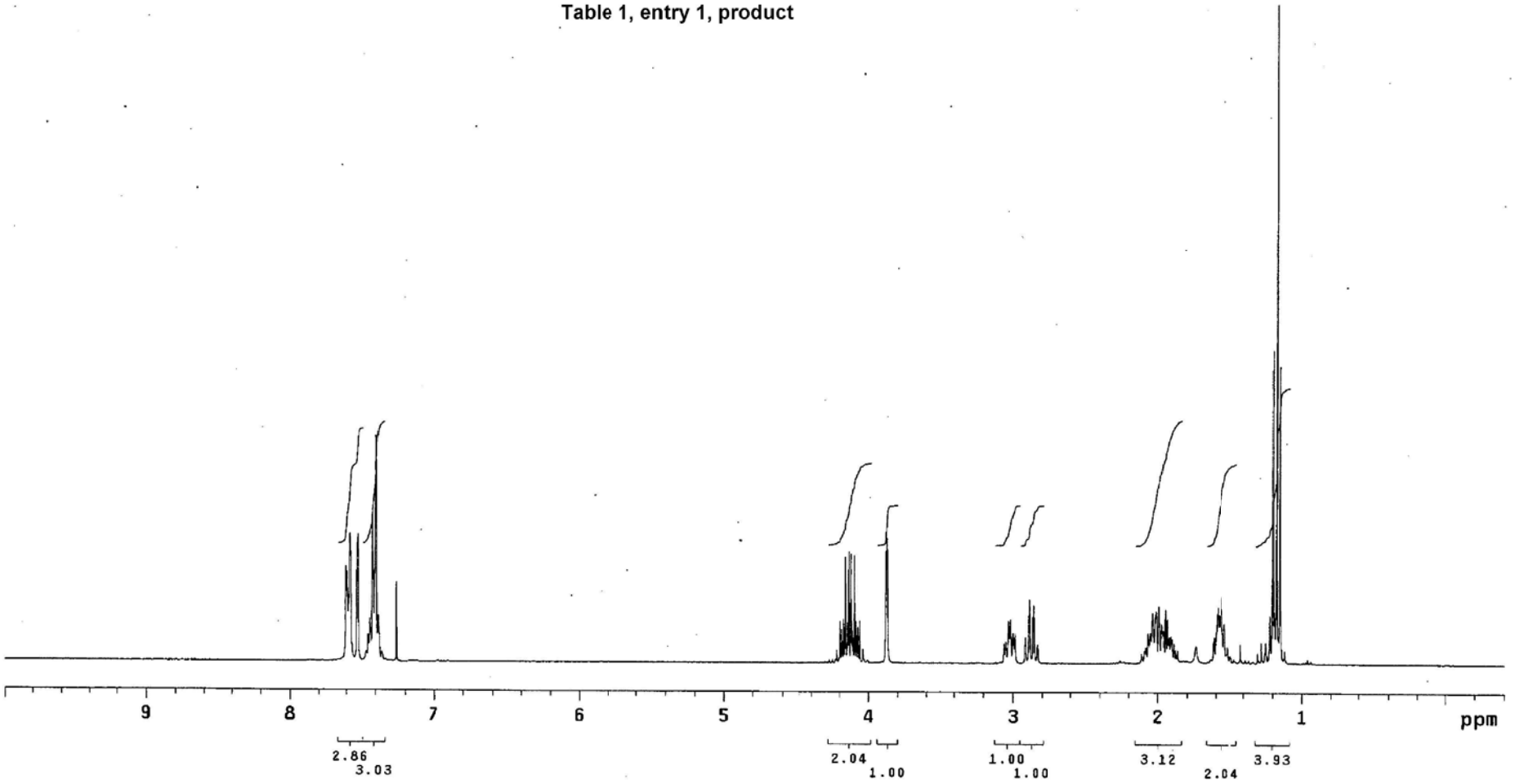
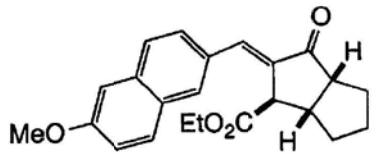


Table 1, entry 1, product





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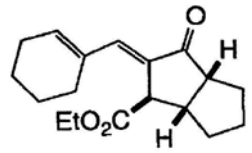

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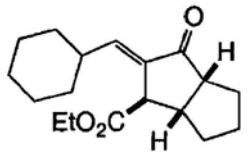

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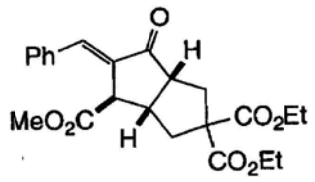

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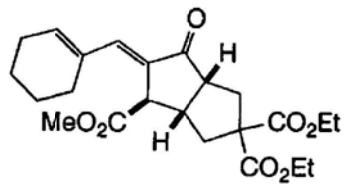

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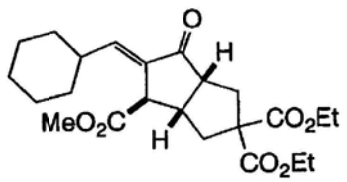

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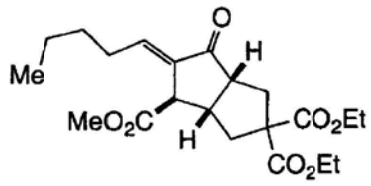

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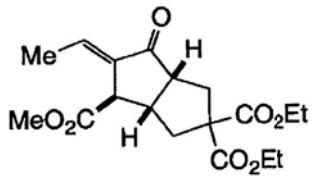

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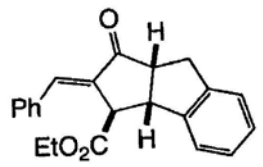

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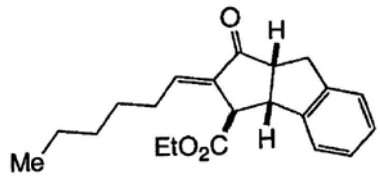

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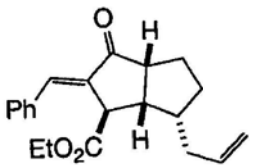
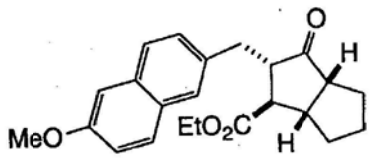
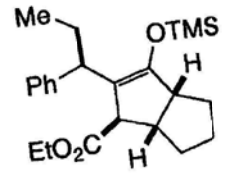


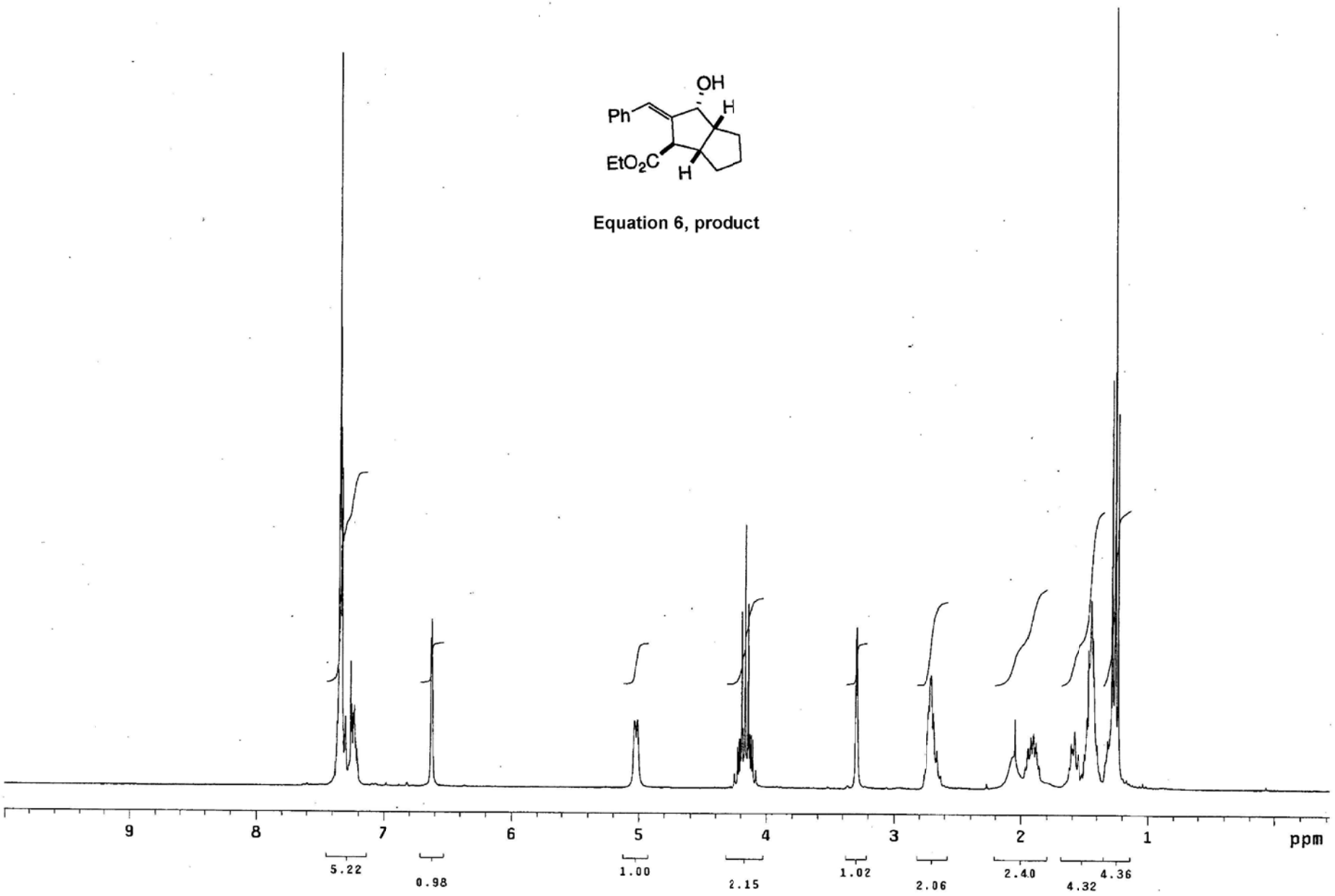
Equation 3, product



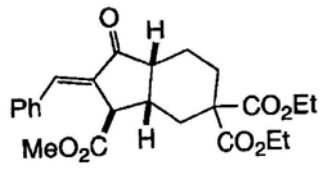
Equation 4, product



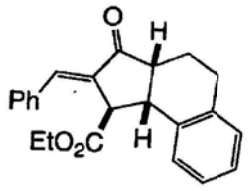
Equation 5, product



Equation 6, product



Equation 8, product



Equation 9, product