Asymmetric 1,4-Hydrosilylations of α,β -Unsaturated Esters

Bruce H. Lipshutz,* Jeff M. Servesko, and Benjamin R. Taft
Department of Chemistry & Biochemistry
University of California
Santa Barbara, CA 93106

Supporting Information

Representative procedure for the asymmetric conjugate reduction of enoates; (*S*)-ethyl 3-phenylbutanoate (Equation 1, entry a; 4, R' = Me). To a 5 mL round bottomed flask, flame dried and purged with argon, was added (Ph₃P)CuH (2 mg, 0.0061 mmol) and (*R*)-DTBM-SEGPHOS (2 mg, 0.0017 mmol). Toluene (0.85 mL) was added and the solution cooled to 0°C. PMHS (110 µL, 1.66 mmol) was introduced *via* syringe followed by *t*-BuOH (89 µL, 0.938 mmol) and enone *Z*-3 (neat, 162 mg, 0.83 mmol). The mixture was stirred at 0°C until complete by TLC (1 h; 5% ethyl acetate/hexanes). The reaction was quenched by pouring into sat. NaHCO₃ and diluted with Et₂O/H₂O and then stirred for 2 h at rt. The aqueous layer was extracted twice with Et₂O and the combined organic layers were washed with brine, dried over anhydrous MgSO₄, filtered, and concentrated by rotary evaporation. The residue was purified by flash chromatography (2% ethyl acetate/hexanes) to afford the title product (152 mg, 92%) as a clear oil. The product^{1,2} (R_f = 0.15, 5% ethyl acetate/hexanes) was analyzed by chiral GC (G-TA 100) which indicated an ee of 99%. IR (neat): 3062, 2968, 1731, 1370, 1173, 910 cm⁻¹; ¹H NMR (500 MHz, C₆D₆): δ 0.87 (t, *J* = 7.1 Hz, 3H), 1.16 (d, *J* = 6.9 Hz, 3H), 2.35 (dd, *J* = 15.1, 8.0 Hz, 1H), 2.47 (dd, *J* = 15.1, 7.1 Hz, 1H), 3.28 (m, 1H), 3.86 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.89 (dq, *J* = 10.8, 7.1 Hz, 1H), 7.11-7.27 (m, 5H); ¹³C NMR (125 MHz, C₆D₆): δ 14.54, 22.28, 37.15, 43.33, 60.34, 126.93, 127.45, 129.05, 146.50, 171.96; EIMS: *m/z* (%): 192(16)[M⁺], 118(65), 105(100), 91(20), 49(24); HREIMS calcd for C₁₂H₁₆O₂: 192.1150; found 192.1155; [α]₅₄₆ = -62° (*c* = 1.01, benzene).

(*R*)-Ethyl 3-phenylpentanoate (Equation 1, entry b; 4, R' = Et). According to the standard procedure, the following amounts were used: Stryker's reagent 1.68 mg (0.0051 mmol), (*R*)-DTBM-SEGPHOS (1.12 mg, 0.0020 mmol), THF (1 mL), PMHS (134 µL, 2.068 mmol), *t*-BuOH (108 µL, 1.13 mmol), enoate *E*-3, R' = Et (neat; 240 mg, 1.0348 mmol). The product ester^{3,4} (217 mg, 90%) was isolated as a clear oil after a reaction time of 4 h; R_f = 0.20 (5% EA/hexanes); Chiracel OD-H (2.0% Et₂O/hexanes, 1 mL/min) showed 95% ee. IR (neat): 3085, 2955, 1740, 1440, 1257, 1165 cm⁻¹; ¹H NMR (400 MHz, C₆D₆) δ 0.85 (t, *J* = 7.4 Hz, 3H), 0.91 (t, *J* = 6.8 Hz, 3H), 1.40-1.50 (m, 1H), 1.51-1.63 (m, 1H), 2.45 (m, 2H), 3.05 (m, 1H), 3.82 (m, 2H), 7.02-7.20 (m, 5H); ¹³C NMR (125 MHz, C₆D₆) δ 12.38, 14.51, 29.72, 41.96, 44.57, 60.31, 126.99, 128.58, 128.97, 144.68, 172.06; EIMS *m/z* (%): 206(34)[M⁺], 161(10), 132(68), 119(64), 91(100), 77(19); HREIMS calcd for C₁₃H₁₈O₂: 206.1307; found 206.1306[M⁺];

(*R*)-Ethyl 3-phenyl-3-cyclopropylpropanoate (Equation 1, entry c; 4, R' = cyclopropyl). According to the standard procedure, the following amounts were used: Stryker's reagent (2.0 mg, 0.0061 mmol), (*R*)-DTBM-SEGPHOS (2 mg, 0.0017 mmol), PhMe (1 mL), PMHS (112 µL, 1.70 mmol), *t*-BuOH (89 µL, 0.93 mmol), enoate *E*-3, R'' = cyclopropyl (neat) (184 mg, 0.85 mmol). Product ester (180 mg, 97%, clear oil) after a reaction time of 19 h; R_f = 0.25 (20% Et₂O/ligroin). Chiral GC (Chiraldex GTA90, 1 mL) showed 99% ee. IR (neat) 3075, 2981, 1734, 1448, 1255, 1172, 1022, 700 cm⁻¹; ¹H NMR (500 MHz, C₆D₆) δ 0.01-0.07 (m, 1H), 0.16-0.24 (m, 2H), 0.35-0.41 (m, 1H), 0.78-0.84 (m, 1H), 0.86 (t, *J* = 7.1 Hz, 3H), 2.39-2.45 (m, 1H), 2.63 (dd, *J* = 14.8, 7.8 Hz, 1H), 2.67 (dd, *J* = 14.8, 7.2 Hz,

1H), 3.81-3.93 (m, 2H), 7.03-7.16 (m, 5H); ¹³C NMR (125 MHz, C₆D₆) δ 4.69, 5.90, 14.50, 17.92, 42.20, 47.79, 60.37, 127.02, 128.11, 128.95, 144.39, 171.98; EIMS *m/z* (%): 218(33), 144(32), 131(100), 117(45), 105(35), 91(91), 77(24); HREIMS calcd for C₁₄H₁₈O₂: 218.1307; found 218.1312[M⁺].

(*R*)-Ethyl 3-phenylbutanoate (Equation 1, entry d; 4, R' = Me). To a 5 mL round bottomed flask, flame dried and purged with argon, was added CuCl (2 mg, 0.0202 mmol), NaO-*t*-Bu (2 mg, 0.0208 mmol), and (*R*)-DTBM-SEGPPOS (2 mg, 0.002 mmol). Toluene (1.5 mL) was added and the solution stirred at rt for 20 min, and enone *E*-3 (neat, 350 mg, 1.842 mmol) was added. PMHS (239 μL, 3.684 mmol) was introduced *via* syringe followed by *t*-BuOH (205 μL, 2.026 mmol). The mixture was stirred at room temperature until complete by TLC (12 h; 5% ethyl acetate/hexanes). The reaction was quenched by pouring into sat. NaHCO₃ and diluted with Et₂O/H₂O and then stirred for 2 h at rt. The aqueous layer was extracted twice with Et₂O and the combined organic layers were washed with brine, dried over anhydrous MgSO₄, filtered, and concentrated by rotary evaporation. The residue was purified by flash chromatography (2% ethyl acetate/hexanes) to afford the title compound (332 mg, 94%) as a clear oil. The product (R_f = 0.15, 5% ethyl acetate/hexanes) was analyzed by chiral GC (G-TA 100), which indicated an ee of 91%. Spectroscopic data matched those from previous experiments.

(*S*)-Ethyl 3-methyl-5-phenylpentanoate (Equation 2, entry a; 6, R = Ph, R' = Me). According to the standard procedure, the following amounts were used: Stryker's reagent (2.5 mg, 0.007 mmol), (*R*)-DTBM-SEGPPOS (3 mg, 0.002 mmol), PhMe (2 mL), PMHS (286 μL, 4.402 mmol), *t*-BuOH (246 μL, 2.421 mmol), enoate *E*-5, R = Ph, R' = Me (neat) (480 mg, 2.201 mmol). Product ester (464 mg, 96%, clear oil). R_f = 0.25 (5% EtOAc/hexanes) after a reaction time of 6 h. Chiral GC (Chiraldex-GTA 100, 1 mL) showed 90% ee. IR (neat) 3035, 2932, 1734, 1455, 1371, 1155, 1031, 699 cm⁻¹; ¹H NMR (500 MHz, C₆D₆) δ 0.87 (t, *J* = 6.3 Hz, 3H), 0.95 (t, *J* = 7.1 Hz, 3H), 1.28-1.36 (m, 1H), 1.48-1.56 (m, 1H), 1.93-2.02 (m, 2H), 2.12-2.19 (m, 1H), 2.35-2.49 (m, 2H), 3.94 (q, *J* = 7.1, 2H), 7.02-7.16 (m, 5H); ¹³C NMR (125 MHz, CDCl₃) δ 14.69, 20.05, 30.60, 33.96, 39.11, 42.02, 60.25, 126.37, 128.96, 128.98, 142.98, 172.57; EIMS *m/z* (%): 220(5), 174(56), 131(24), 91(100), 65(14); HREIMS calcd for C₁₄H₂₀O₂: 220.1463, found 220.1460[M⁺].

(*R*)-Ethyl 3-methyl-5-phenylpentanoate (Equation 2, entry b; 6, R = Ph, R' = Me). According to the standard procedure, the following amounts were used: Stryker's reagent (4 mg, 0.012 mmol), (*R*)-DTBM-SEGPPOS (5 mg, 0.004 mmol), PhMe (3 mL), PMHS (417 μL, 6.420 mmol), *t*-BuOH (358 μL, 3.531 mmol), enoate *Z*-5, R = Ph, R' = Me (neat) (700 mg, 3.21 mmol). Product ester (656 mg, 93%, clear oil). R_f = 0.25 (5% EtOAc/hexanes) after a reaction time of 6 h. Chiral GC (Chiraldex-GTA 100, 1 mL) showed 65% ee. Spectroscopic data matched previous experiments.

(*S*)-Ethyl 3-methyl-5-phenylpentanoate (Equation 2, entry c; 6, R = Ph, R' = Me). According to the standard procedure, the following amounts were used: Stryker's reagent (2 mg, 0.006 mmol), (*R,S*)-PPF-

P(*t*Bu)₂ (2 mg, 0.003 mmol), PhMe (1 mL), PMHS (178 μ L, 2.752 mmol), *t*-BuOH (153 μ L, 1.51 mmol), enoate *E*-**5**, R = Ph, R' = Me (neat) (300 mg, 1.375 mmol). Product ester (296 mg, 98%, clear oil). *R*_f = 0.25 (5% EtOAc/hexanes) after a reaction time of 6 h. Chiral GC (Chiraldex-GTA 100, 1 mL) showed 99% ee. Spectroscopic data matched previous experiments.

(*R*)-Ethyl 3-methyl-5-phenylpentanoate (Equation 2, entry d; **6, R = Ph, R' = Me).** According to the standard procedure, the following amounts were used: Stryker's reagent (3.2 mg, 0.010 mmol), (*R,S*)-PPF-P(*t*Bu)₂ (2.4 mg, 0.0044 mmol), PhMe (2 mL), PMHS (260 μ L, 4.00 mmol), *t*-BuOH (234 μ L, 2.20 mmol), enoate *Z*-**5**, R = Ph, R' = Me (neat) (436 mg, 2.00 mmol). Product ester^{5,6} (431 mg, 98%, clear oil). *R*_f = 0.25 (5% EtOAc/hexanes) after a reaction time of 6 h. Chiral GC (Chiraldex-GTA 100, 1 mL) showed 93% ee. IR (neat) 3035, 2932, 1734, 1455, 1371, 1155, 1031, 699 cm⁻¹; ¹H NMR (500 MHz, C₆D₆) δ 0.87 (t, *J* = 6.3 Hz, 3H), 0.95 (t, *J* = 7.1 Hz, 3H), 1.28-1.36 (m, 1H), 1.48-1.56 (m, 1H), 1.93-2.02 (m, 2H), 2.12-2.19 (m, 1H), 2.35-2.49 (m, 2H), 3.94 (q, *J* = 7.1, 2H), 7.02-7.16 (m, 5H); ¹³C NMR (125 MHz, CDCl₃) δ 14.69, 20.05, 30.60, 33.96, 39.11, 42.02, 60.25, 126.37, 128.96, 128.98, 142.98, 172.57; EIMS *m/z* (%): 220(5), 174(56), 131(24), 91(100), 65(14); HREIMS calcd for C₁₄H₂₀O₂: 220.1463, found 220.1460[M⁺].

(*S*)-Methyl 3-methylheptanoate (Equation 2, entry e; **6, R = Et, R' = Me).** According to the standard procedure, the following amounts were used: Stryker's reagent 3.5 mg (0.0112 mmol), (*R,S*)-PPF-P(*t*Bu)₂ (2.43 mg, 0.004 mmol), Et₂O (2 mL), PMHS (291 μ L, 4.486 mmol), *t*-BuOH (234 μ L, 2.46 mmol), enoate *E*-**5**, R = Et, R' = Me (neat) 350 mg (2.243 mmol). Product ester^{7,8} (280 mg, 80%, clear oil). *R*_f = 0.20 (10% Et₂O/ligroin) after a reaction time of 1 h. Chiral GC (Chiraldex GTA 60, 1 mL) showed 95% ee. IR (neat) 2925, 2850, 1742, 1427, 1231, 1153 cm⁻¹; ¹H NMR (500 MHz, C₆D₆) δ 0.88 (t, *J* = 7.2 Hz, 3H), 0.91 (d, *J* = 6.4 Hz, 3H), 1.13-1.32 (m, 7H), 1.87-1.98 (m, 1H), 2.07 (dd, *J* = 12.3, 7.5 Hz, 1H), 2.29 (dd, *J* = 12.3, 7.1 Hz, 1H), 3.63 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 14.22, 19.90, 22.95, 29.29, 30.48, 36.57, 41.83, 51.49, 174.00; EIMS *m/z* (%): 127(10), 101(22), 84(9), 74(100), 59(15), 43(32); HREIMS calcd for C₉H₁₉O₂: 159.1385; found 159.1387[M+H⁺]; [α]_D(carboxylic acid) = -4.6 (*c* = 0.55, CHCl₃).

(*S*)-Ethyl 3-ethyl-5-phenylpentanoate (Equation 2, entry f; **6, R = Ph, R' = Et).** According to the standard procedure, the following amounts were used: Stryker's reagent (1.68 mg, 0.005 mmol), (*R,S*)-PPF-P(*t*Bu)₂ (1.12 mg, 0.002 mmol), THF (1 mL), PMHS (134 μ L, 2.068 mmol), *t*-BuOH (108 μ L, 1.13 mmol), enoate *E*-**5** (neat; 240 mg, 1.0348 mmol). The product ester (225 mg, 93%) was isolated as a clear oil; *R*_f = 0.35 (10% Et₂O/ligroin) after a reaction time of 9 h; Chiracel OD-H (2.5% Et₂O/Hexanes, 1 mL/min) showed 99% ee. IR (neat): 3020, 2929, 1734, 1361, 1165, 1035 cm⁻¹; ¹H NMR (500 MHz, C₆D₆) δ 0.84 (t, *J* = 7.4 Hz, 3H), 1.03 (t, *J* = 7.0 Hz, 3H), 1.28-1.42 (m, 2H), 1.58-1.64 (m, 2H), 1.90-1.98 (m, 1H), 2.21(dd, *J* = 15.1, 6.7 Hz, 1H), 2.23 (dd, *J* = 15.1, 6.9 Hz, 1H), 2.51-2.55 (m, 2H), 4.03 (q, *J* = 7.0 Hz, 2H), 7.12-7.25 (m, 5H); ¹³C NMR (125 MHz, C₆D₆) δ 11.21, 14.69, 26.85, 33.67, 36.08,

36.74, 38.92, 60.27, 126.36, 128.97, 128.99, 143.14, 172.86; EIMS m/z (%): 234(3), 188(54), 159(21), 91(100), 69(15); HREIMS calcd for $C_{15}H_{22}O_2$ 234.1620; found 234.1628 $[M^+]$; $[\alpha]_{436} = 12.2$ ($c = 1.6$, $CHCl_3$).

(R)-Ethyl 3-ethyl-5-phenylpentanoate (Equation 2, entry g; 6, R = Ph, R' = Et). According to the standard procedure, the following amounts were used: Stryker's reagent (2.5 mg, 0.007 mmol), (*R,S*)-PPF-P(*t*Bu)₂ (4 mg, 0.007 mmol), PhMe (2 mL), PMHS (280 μ L, 4.31 mmol), *t*-BuOH (240 μ L, 2.370 mmol), enoate *Z*-5 (neat; 500 mg, 2.155 mmol). The product ester (474 mg, 94%) was isolated as a clear oil; $R_f = 0.35$ (10%Et₂O/ligroin) after a reaction time of 9 h; Chiracel OD-H (2.5% Et₂O/hexanes, 1 mL/min) showed 98% ee. Spectroscopic data matched previous experiments.

Representative procedure for larger scale reduction; (S)-ethyl 3-phenylbutanoate (Equation 3). To a 25 mL round bottomed flask, flame dried and purged with argon, was added CuCl (10 mg, 0.101 mmol), NaO-*t*-Bu (12 mg, 0.125 mmol), and (*R*)-DTBM-SEPHOS (2 mg, 0.002 mmol). Toluene (0.85 mL) was added and the solution stirred at rt for 20 min, then cooled to 0°C and enone *Z*-3 (neat, 2.47 g, 13.020 mmol) was added. PMHS (1.7 mL, 26 mmol) was introduced *via* syringe followed by *t*-BuOH (1.45 mL, 14.30 mmol). The mixture was stirred at 0°C until complete by TLC (12 h; 5% ethyl acetate/hexanes). The reaction was quenched by pouring into sat. NaHCO₃ and diluted with Et₂O/H₂O and then stirred for 2 h at rt. The aqueous layer was extracted twice with Et₂O and the combined organic layers were washed with brine, dried over anhydrous MgSO₄, filtered, and concentrated by rotary evaporation. The residue was purified by flash chromatography (2% ethyl acetate/hexanes) to afford the title compound (2.29 g, 92%) as a clear oil. The product ($R_f = 0.15$, 5% ethyl acetate/hexanes) was analyzed by chiral GC (G-TA 100), which indicated an ee of 98%. Spectroscopic data matched those from the previous (smaller scale) experiment (*vide supra*).

(R)-Ethyl 3-methyl-5-phenylpentanoate (Equation 4). According to the standard procedure, the following amounts were used: Stryker's reagent (2 mg, 0.006 mmol), (*S,R*)-PPF-P(*t*Bu)₂ (2 mg, 0.003 mmol), PhMe (1 mL), PMHS (178 μ L, 2.752 mmol), *t*-BuOH (153 μ L, 1.51 mmol), enoate *E*-5, R = Ph, R' = Me (neat) (300 mg, 1.375 mmol). Product ester (292 mg, 96%, clear oil) after a reaction time of 6 h; $R_f = 0.25$ (5% EtOAc/hexanes). Chiral GC (Chiraldex-GTA 100, 1 mL) showed 98% ee. Spectroscopic data matched previous experiments.

Ethyl 3-[(4*S*)-2,2-dimethyl-1,3-dioxolan-4-yl]-(3*R*)-butanoate (8; Equation 5). According to the standard procedure, the following amounts were used: Stryker's reagent (1.6 mg, 0.0050 mmol), (*R,S*)-PPF-P(*t*Bu)₂ (1.2 mg, 0.0022 mmol), PhMe (1 mL), PMHS (130 μ L, 2.00 mmol), *t*-BuOH (105 μ L, 1.10 mmol), enoate 7 (neat) (214 mg, 1.00 mmol). Product ester (194 mg, 91%, clear oil) after a reaction time of 22 h; $R_f = 0.25$ (20% Et₂O/ligroin). GC (50° C, 5 min, 20° ramp) showed 98.0% de. IR (neat) 3461, 2984, 2868, 1734, 1461, 1371, 1264, 1048, 860 cm^{-1} ; ¹H NMR (400 MHz, C₆D₆) δ 0.93 (t, $J = 6.4$ Hz, 3H), 0.95 (d, $J = 7.1$ Hz, 3H), 1.26 (s, 3H), 1.36 (s, 3H), 1.96 (dd, $J = 14.9, 8.5$ Hz, 1H), 2.11-2.21 (m, 1H), 2.24 (dd, $J = 14.9, 5.0$ Hz, 1H), 3.37 (dd, $J = 7.9, 7.3$ Hz, 1H), 3.66 (dd, $J = 7.9, 6.4$ Hz, 1H),

3.74-3.79 (m, 1H), 3.92 (q, $J = 7.1$ Hz, 2H); ^{13}C NMR (125 MHz, C_6D_6) δ 14.12, 15.28, 25.14, 26.26, 32.89, 37.46, 60.27, 66.66, 78.68, 108.81, 172.52; EIMS m/z (%): 201(42), 171(10), 113(76), 101(44), 72(47), 49(43); HREIMS calcd for $\text{C}_{11}\text{H}_{20}\text{O}_4\text{Na}$: 239.1259, found 239.1250 $[\text{M}+\text{Na}^+]$.

Ethyl 3-[(4*S*)-2,2-dimethyl-1,3-dioxolan-4-yl]-(3*S*)-butanoate (using (*S,R*)-PPF- $\text{P}(t\text{Bu})_2$). According to the standard procedure, the following amounts were used: Stryker's reagent (1.6 mg, 0.0050 mmol), (*S,R*)-PPF- $\text{P}(t\text{Bu})_2$ (1.2 mg, 0.0022 mmol), PhMe (1 mL), PMHS (130 μL , 2.00 mmol), *t*-BuOH (105 μL , 1.10 mmol), enoate **7** (neat) (214 mg, 1.00 mmol). Product ester analyzed by GC (70% conversion at 36 h); $R_f = 0.15$ (20% Et_2O /ligroin). GC (50° C, 5 min, 20° ramp) showed -40.0% de.

(*R*)-Dihydro-4-phenyl-(3*H*)-furan-2-one (10). According to the standard procedure, the following amounts were used: Stryker's reagent 2.8 mg (0.009 mmol), (*R*)-DTBM-SEPHOS (2.0 mg, 0.0017 mmol), THF (1 mL), PMHS (224 μL , 3.36 mmol), *t*-BuOH (173 μL , 1.81 mmol), butenolide **9** (270 mg, 1.68 mmol) in THF (1 mL). The product lactone^{9,10} (263 mg, 96%) was isolated as a white solid after a reaction time of 2 h; mp 59-60 °C; $R_f = 0.2$ (30% Et_2O /ligroin); Chiral GC (Chiraldex GTA160, 1 mL) showed 99% ee; IR (nujol): 3059, 2924, 1772, 1456, 1163, 1011; ^1H NMR (500 MHz, CDCl_3) δ 2.68 (dd, $J = 17.4, 9.1$ Hz, 1H), 2.93 (dd, $J = 17.4, 8.7$ Hz, 1H), 3.79 (m, 1H), 4.28 (dd, $J = 9.0, 7.9$ Hz, 1H), 4.68 (dd, $J = 9.0, 7.8$ Hz, 1H), 7.22-7.40 (m, 5H); ^{13}C NMR (125 MHz, CDCl_3) δ 35.85, 41.26, 74.18, 126.85, 127.89, 129.30, 139.56, 176.52; EIMS m/z (%): 162(24), 104(100), 71(34), 57(50); HREIMS calcd for $\text{C}_{10}\text{H}_{10}\text{O}_2$ 162.0681: found 162.0677 $[\text{M}^+]$; $[\alpha]_D = -67.2$ ($c = 2.0$, CHCl_3).

(4*R*,5*S*)-Dihydro-5-hydroxymethyl-4-methyl-(3*H*)-furan-2-one (cf. ref 9). Ethyl 3-[(4*S*)-2,2-dimethyl-1,3-dioxolan-4-yl]-(3*R*)-butanoate (50 mg, 0.23 mmol) was added to a 5 mL RBF to which was added 1,4-dioxane (2 mL) and a 2% H_2SO_4 (aq.) solution (1 mL). The mixture was refluxed gently for 2 h, quenched with NaHCO_3 , diluted with H_2O , extracted twice with EtOAc, washed with brine, dried over anhydrous MgSO_4 , concentrated *in vacuo*, and purified by flash chromatography (20% EtOAc/hexanes) to produce the title compound^{11,12} as a clear oil (26 mg, 88%). ^1H NMR and NOE studies conclusively show *cis* stereochemistry. IR(neat) 3412, 2941, 1753, 1179, 1022 cm^{-1} ; ^1H NMR (500 MHz, C_6D_6) δ 0.56 (d, $J = 6.9$ Hz, 3H), 1.78-1.87 (m, 1H), 1.97 (dd, $J = 17.0, 8.4$ Hz, 1H), 2.02 (dd, $J = 17.0, 9.3$ Hz, 1H), 2.22 (bs, 1H), 3.25 (dd, $J = 12.4, 4.3$ Hz, 1H), 3.37 (dd, $J = 12.4, 3.1$ Hz, 1H), 3.79-3.82 (m, 1H); ^{13}C NMR (125 MHz, C_6D_6) δ 13.74, 32.40, 36.88, 62.01, 82.67, 176.69; EIMS m/z (%): 99(100), 84(12), 71(35), 43(66); HREIMS calcd for $\text{C}_6\text{H}_{11}\text{O}_3$: 131.1708, found 131.0707 $[\text{M}+\text{H}^+]$.

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