Copper(I)-Catalyzed Disilylation of Alkylidene Malonates Employing a Lewis Base Activation Strategy

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Supporting Information

General Information. All reactions were carried out under an atmosphere of argon or nitrogen in flame-dried glassware with magnetic stirring. THF, Et₂O, CH₂Cl₂, DMF and toluene were purified by passage through a bed of activated alumina.¹ DMI was purified by distillation over calcium hydride under reduced pressure. HMPA and NMP were used from freshly opened bottles from Aldrich without further purification. Reagents were purified prior to use unless otherwise stated following the guidelines of Perrin and Armarego.² Purification of reaction products was carried out by flash chromatography using EM Reagent silica gel 60 (230-400 mesh). Analytical thin layer chromatography was performed on EM Reagent 0.25 mm silica gel 60-F plates. Visualization was accomplished with UV light and anisaldehyde, ceric ammonium nitrate stain, potassium permanganate, or phosphomolybic acid followed by heating. Melting points were obtained on a Melt-temp 3 instrument and are uncorrected. Infrared spectra were recorded on a Perkin Elmer 1600 series FT-IR spectrometer. ¹H-NMR spectra were recorded on a Varian Inova 500 (500 MHz) or Mercury 400 (400 MHz) spectrometer and are reported in ppm using solvent as an internal standard (CDCl₃ at 7.26 ppm). Data are reported as (ap = apparent, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad; coupling constant(s) in Hz; integration. Proton-decoupled ¹³C-NMR spectra were recorded on a Varian Inova 500 (125 MHz) or Mercury 400 (100 MHz) spectrometer and are reported in ppm using solvent as an internal standard (CDCl₃ at 77.0 ppm). Mass spectra data were obtained on a Varian 1200 Quadrupole Mass Spectrometer.

Copper(I) trifluoromethanesulfonate was prepared by a modified method of Kochi and co-workers.³ Alkylidene malonates were prepared according to the general procedure of Evans and co-workers.⁴

(1) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518-1520.

(2) Perrin, D. D. and Armarego, W. L. *Purification of Laboratory Chemicals*; 3rd ed., Pergamon Press, Oxford. 1988.

(3) (a) Salomon, R. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 1889-1897. (b) Cohen, T.; Ruffner, R. J.; Shull, D. W.; Fogel, E. R.; Falck, J. R. *Organic Syntheses*; John Wiley & Sons: New York; Vol. 6.

(4) Evans, D. A.; Rovis, T.; Kozlowski, M. C.; Downey, C. W.; Tedrow, J. S. *J. Am. Chem. Soc.*; **2000**; *122*, 9134-9142 and references cited therein.

General Experimental Procedure for the Copper(I)-Catalyzed Reaction:

Copper(I) triflate benzene complex (6.3 mg, 0.0125 mmol for aryl alkylidene malonates; 19 mg, 0.0375 mmol for all others) and an alkylidene malonate (0.5 mmol) were added to a screw-cap test tube in a nitrogen-filled drybox. The test tube was taken out of the dry box and was put under a positive pressure of nitrogen. To this, toluene (0.5 mL, if applicable) and the ligand (4 equivalents with respect to copper(I) triflate benzene complex) were added *via* syringe, respectively. Finally, the disilane (0.61 mmol) in a strongly coordinating solvent (0.5 mL) was added *via* syringe. The reaction was allowed to stir, heated to 100 °C in an oil bath under nitrogen, for 60 hours, then was allowed to cool to room temperature. Water (2-3 drops) and *p*-toluenesulfonic acid monohydrate (spatula tip) were added, and the reaction stirred for 30 minutes. The reaction mixture was partitioned between water (5 mL) and diethyl ether (5 mL), separated, and the aqueous layer was extracted with ether (2x5 mL). The combined organics were washed twice with water and once with brine, dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. The resulting mixture was purified by flash chromatography on silica gel using the noted elution solvent.

Dimethyl 2-((dimethylphenylsilyl)(phenyl)methyl)malonate (3a):

Purified with 10% EtOAc/hexanes, yielding varying amounts of 3a as a colorless oil. R_f = 0.40 (15% EtOAc/hexanes); IR (film) 3025, 2953, 1736,

1598, 1493, 1431, 1250, 1163, 838, 701 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.41 (m, 2H), 7.36 (m, 3H), 7.18 (t, J = 7 Hz, 2H), 7.09 (t, J = 7 Hz, 1H), 6.94 (d, J = 7 Hz, 2H), 3.95 (d, J = 12 Hz, 1H), 3.39 (s, 3H), 3.38 (s, 3H), 3.22 (d, J = 12 Hz, 1H), 0.16 (s, 3H), 0.13 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 169.2, 169.1, 140.2, 136.5, 134.6, 129.5, 128.5, 128.3, 127.8, 125.7, 54.2, 52.6, 52.5, 36.5, -2.6, -4.5. LRMS (electrospray): Mass calcd for $\text{C}_{20}\text{H}_{24}\text{NaO}_4\text{Si}$ $[\text{M}+\text{Na}]^+$, 379.13. Found 379.

Dimethyl 2-((dimethylvinylsilyl)(phenyl)methyl)malonate (3b):

Purified with 10% EtOAc/hexanes, yielding 50 mg (35%) of 3b as a colorless oil; R_f = 0.45 (15% EtOAc/hexanes); IR (film) 2951, 1759, 1735, 1433, 1249 cm^{-1} ;

^1H NMR (500 MHz, CDCl_3) δ 7.23 (t, J = 8 Hz, 2H), 7.12 (t, J = 8 Hz, 1H), 7.08 (d, J = 8 Hz, 2H), 6.02 (m, 2H), 5.65 (dd, J = 6, 18 Hz, 1H), 3.99 (d, J = 12 Hz, 1H), 3.75 (s, 3H), 3.45 (s, 3H), 3.06 (d, J = 12 Hz, 1H), 0.01 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 169.4, 169.3, 140.4, 136.7, 133.4, 128.4, 128.3, 125.7, 54.2, 52.8, 52.5, 36.3, -3.3, -4.5. LRMS (electrospray): Mass calcd for $\text{C}_{16}\text{H}_{18}\text{NaO}_4\text{Si}$ $[\text{M}+\text{Na}]^+$, 329.12. Found 329.

Dimethyl 2-((4-chlorophenyl)(dimethylphenylsilyl)methyl)malonate

(4): Purified with 10% EtOAc/hexanes, yielding 170 mg (87%) of **4** as a colorless oil; $R_f = 0.42$ (15% EtOAc/hexanes); IR (film) 3069, 2954, 2901, 1738, 1491, 1433, 1250, 1014, 845 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.36 (m, 5H), 7.14 (d, $J = 8$ Hz, 2H), 6.85 (d, $J = 8$ Hz, 2H), 3.89 (d, $J = 12$ Hz, 1H), 3.42 (s, 6H), 3.19 (d, $J = 12$ Hz, 1H), 0.25 (s, 3H), 0.18 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 168.9, 168.8, 138.8, 135.9, 134.5, 131.3, 129.7, 128.4, 127.9, 54.0, 52.8, 52.7, 36.1, -2.8, -4.4. LRMS (electrospray): Mass calcd for $\text{C}_{20}\text{H}_{23}\text{ClNaO}_4\text{Si}$ $[\text{M}+\text{Na}]^+$, 413.10. Found 413.

Dimethyl 2-((4-fluorophenyl)(dimethylphenylsilyl)methyl)malonate

(5): Purified with 10% EtOAc/hexanes, yielding 100 mg (53%) of **5** as a colorless oil; $R_f = 0.34$ (15% EtOAc/hexanes); IR (film) 3071, 2955, 1731, 1509, 1435, 1223, 845 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.36 (m, 5H), 6.87 (d, $J = 7$ Hz, 4H), 3.88 (d, $J = 12$ Hz, 1H), 3.43 (s, 3H), 3.41 (s, 3H), 3.19 (d, $J = 12$ Hz, 1H), 0.25 (s, 3H), 0.18 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.0, 168.9, 161.1 (d, $J = 243$ Hz), 136.1, 135.7, 134.5, 129.8 (d, $J = 7$ Hz), 129.6, 127.9, 115.2 (d, $J = 21$ Hz), 54.2, 52.7, 52.6, 35.8, -2.7, -4.3. LRMS (electrospray): Mass calcd for $\text{C}_{20}\text{H}_{23}\text{FNaO}_4\text{Si}$ $[\text{M}+\text{Na}]^+$, 397.12. Found 397.

Dimethyl 2-((furan-2-yl)(dimethylphenylsilyl)methyl)malonate (7):

Purified with 10% EtOAc/hexanes, yielding 138 mg (80 %) of **7** as a colorless oil. $R_f = 0.37$ (15% EtOAc/hexanes); IR (film) 3001, 2954, 2903, 2845, 1739, 1584, 1503, 1434, 1260, 1159, 1012, 839, 735 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.40 (m, 2H), 7.29 (m, 3H), 7.20 (d, $J = 2$ Hz, 1H), 6.17 (dd, $J = 2, 2$ Hz, 1H), 5.82 (d, $J = 2$ Hz, 1H), 3.73 (d, $J = 11$ Hz, 1H), 3.46 (s, 3H), 3.30 (s, 3H), 3.28 (d, $J = 12$ Hz, 1H), 0.26 (s, 3H), 0.19 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 169.3, 168.7, 154.2, 141.1, 136.5, 134.4, 129.5, 127.8, 110.6, 106.0, 52.8, 52.7, 52.5, 29.7, -2.8, -4.2. LRMS (electrospray): Mass calcd for $\text{C}_{18}\text{H}_{22}\text{NaO}_5\text{Si}$ $[\text{M}+\text{Na}]^+$, 369.11. Found 369.

Dimethyl 2-((4-methoxyphenyl)(dimethylphenylsilyl)methyl)

malonate (8): Purified with 10% EtOAc/hexanes, yielding 130 mg (67%) of **8** as a colorless oil. $R_f = 0.29$ (15% EtOAc/hexanes); IR (film) 3002, 2954, 2904, 2838, 1758, 1737, 1511, 1433, 1251, 1033, 842 cm^{-1} ;

^1H NMR (400 MHz, CDCl_3) δ 7.37 (m, 2H), 7.30 (m, 3H), 6.83 (d, $J = 8$ Hz, 2H), 6.69 (d, $J = 8$ Hz, 2H), 3.85 (d, $J = 12$ Hz, 1H), 3.72 (s, 3H), 3.37 (s, 3H), 3.34 (s, 3H), 3.11 (d, $J = 12$ Hz, 1H), 0.22 (s, 3H), 0.12 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.2, 169.0, 157.5, 136.5, 134.5, 131.8, 129.4, 127.7, 113.7, 55.3, 54.3, 52.6, 52.5, 35.5, -2.6, -4.4. LRMS (electrospray): Mass calcd for $\text{C}_{21}\text{H}_{26}\text{NaO}_5\text{Si}$ $[\text{M}+\text{Na}]^+$, 409.14. Found 409.

Dimethyl 2-((2-methoxyphenyl)(dimethylphenylsilyl)methyl)malonate

(9): Purified with 15% EtOAc/hexanes, yielding 124 mg (64%) of **9** as a colorless oil. $R_f = 0.35$ (15% EtOAc/hexanes); IR (film) 3069, 3000, 2953, 2838, 1738, 1585, 1492, 1435, 1246 cm^{-1} ;

^1H NMR (400 MHz, CDCl_3) δ 7.45 (m, 2H), 7.33 (m, 3H), 7.11 (t, $J = 8$ Hz, 1H), 6.94 (d, $J = 7$ Hz, 1H), 6.84 (t, $J = 7$ Hz, 1H), 6.76 (d, $J = 8$ Hz, 1H), 4.13 (d, $J = 12$ Hz, 1H), 3.77 (s, 3H), 3.60 (bm, 1H), 3.41 (s, 3H), 3.39 (s, 3H), 0.24 (s, 3H), 0.20 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.6, 169.5, 157.0, 137.6, 134.5, 129.1, 127.6, 126.8, 120.5, 110.4, 55.1, 53.4, 52.5, 52.3, -2.5, -4.0. LRMS (electrospray): Mass calcd for $\text{C}_{21}\text{H}_{26}\text{NaO}_5\text{Si}$ $[\text{M}+\text{Na}]^+$, 409.14. Found 409.

Dimethyl 2-((dimethylphenylsilyl)(naphthalen-1-yl)methyl)malonate (10):

Purified with 10 % EtOAc/hexanes, yielding 170 mg (84%) of **10** as a colorless solid. $R_f = 0.34$ (15% EtOAc/hexanes); mp = 95 $^\circ\text{C}$; IR (film) 3047, 2953, 1737, 1434, 1249, 1024 cm^{-1} ;

^1H NMR (400 MHz, CDCl_3) δ 8.24 (d, $J = 8$ Hz, 1H), 7.80 (d, $J = 8$ Hz, 1H), 7.62 (d, $J = 8$ Hz, 1H), 7.5-7.2 (m, 8H), 7.01 (d, $J = 7$ Hz, 1H), 4.21 (d, $J = 13$ Hz, 1H), 4.13 (d, $J = 13$ Hz, 1H), 3.40 (s, 3H), 3.24 (s, 3H), 0.17 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.1, 169.0, 137.4, 136.5, 134.6, 134.1,

132.3, 129.5, 128.9, 127.8, 126.2, 126.0, 125.7, 125.1, 124.0, 55.1, 52.7, 52.5, 29.7, -2.1, -4.5.
LRMS (electrospray): Mass calcd for $C_{24}H_{26}NaO_4Si$ $[M+Na]^+$, 429.15. Found 429.

Dimethyl 2-((dimethylphenylsilyl)(naphthalen-2-yl)methyl)malonate

(11): Purified with 15% EtOAc/hexanes, yielding 170 mg (84%) of **11** as a white crystalline solid. R_f = 0.24 (15% EtOAc/hexanes); mp = 92 °C; IR (film) 3052, 2953, 2901, 1737, 1631, 1599, 1432, 1251 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 8 Hz, 1H), 7.68 (d, J = 8 Hz, 2H), 7.45-7.32 (m, 8H), 7.13 (d, J = 7 Hz, 1H), 4.07 (d, J = 12 Hz, 1H), 3.42 (s, 3H), 3.41 (d, J = 12 Hz, 1H), 3.35 (s, 3H), 0.28 (s, 3H), 0.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 169.2, 138.2, 136.5, 134.8, 133.7, 132.1, 129.7, 128.0, 127.9, 127.8, 126.4, 126.23, 125.5, 54.4, 52.8, 52.7, 36.8, -2.42, -4.3. LRMS (electrospray): Mass calcd for $C_{24}H_{26}NaO_4Si$ $[M+Na]^+$, 429.15. Found 429.

Dimethyl 2-(1-(dimethylphenylsilyl)hexyl)malonate (12):

Purified with 8% EtOAc/hexanes, yielding 83 mg (60% based on 80% pure starting material by 1H NMR)⁵ of **12** as a colorless oil. R_f = 0.53 (15% EtOAc/hexanes); IR (film) 3069, 2954, 2929, 2858, 1373, 1435, 1250, 1152, 819 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 7.52 (m, 2H), 7.34 (m, 3H), 3.62 (s, 3H), 3.60 (s, 3H), 3.52 (d, J = 7 Hz, 1H), 1.6-1.1 (m, 8H), 0.81 (t, J = 7 Hz, 3H), 0.34 (s, 3H), 0.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 170.4, 138.7, 134.3, 129.2, 127.9, 52.9, 52.4, 52.3, 32.0, 29.1, 28.7, 26.5, 22.6, 14.2, -2.9, -3.2. LRMS (electrospray): Mass calcd for $C_{19}H_{30}NaO_4Si$ $[M+Na]^+$, 373.13. Found 373.

Dimethyl 2-(1-(dimethylphenylsilyl)-3-phenylpropyl)malonate (13):

Purified with 15% EtOAc/hexanes, yielding 50 mg (37%, based on 70% pure starting malonate by 1H NMR)⁶ of **13** as a colorless oil. R_f = 0.34 (15%

(5) All attempts to isolate dimethyl 2-hexylidenemalonate with greater than 80% purity (via distillation and/or silica gel chromatography) were unsuccessful. Currently, methods to obtain this malonate in greater purity are under investigation.

(6) Similarly, attempts to isolate dimethyl 2-(3-phenylpropylidene)malonate (via distillation and/or silica gel chromatography) with greater than 70% purity were unsuccessful.

EtOAc/hexanes); IR (film) 3025, 2953, 2861, 1736, 1434, 1250, 1155, 1111 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.53 (m, 3H), 7.36 (m, 2H), 7.23 (t, $J = 7$ Hz, 2H), 7.15 (t, $J = 7$ Hz, 1H), 7.01 (d, $J = 7$ Hz, 2H), 3.65 (s, 3H), 3.63 (s, 3H), 3.60 (d, $J = 6$ Hz, 1H), 2.58 (m, 1H), 2.46 (m, 1H), 1.81 (m, 2H), 1.72 (m, 1H), 0.38 (s, 3H), 0.34 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 170.6, 170.2, 142.3, 138.4, 134.3, 129.3, 128.5, 128.0, 126.0, 52.8, 52.5, 35.9, 31.1, 26.3, -2.9, -3.5. LRMS (electrospray): Mass calcd for $\text{C}_{22}\text{H}_{28}\text{NaO}_4\text{Si}$ $[\text{M}+\text{Na}]^+$, 407.17. Found 407.

Dimethyl 2-(1-(dimethylphenylsilyl)ethyl)malonate (14): Purified with 10% EtOAc/hexanes, yielding 60 mg (40%)⁷ of **14** as a colorless oil. $R_f = 0.33$ (15% EtOAc/hexanes); IR (film) 3070, 3000, 2954, 1737, 1435, 1251,

1016 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.50 (m, 2H), 7.35 (m, 3H), 3.65 (s, 3H), 3.54 (s, 3H), 3.37 (d, $J = 8$ Hz, 1H), 1.81 (dt, $J = 8, 7$ Hz, 1H), 1.03 (d, $J = 7$ Hz, 3H), 0.31 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.1, 137.5, 134.3, 129.4, 128.0, 54.0, 52.5, 52.3, 10.65, 13.0, -4.1, -4.3. LRMS (electrospray): Mass calcd for $\text{C}_{15}\text{H}_{22}\text{NaO}_4\text{Si}$ $[\text{M}+\text{Na}]^+$, 317.12. Found 317.

Dimethyl 2-((2,2,2-trifluoroacetamido)(dimethylphenylsilyl)

methyl)malonate (15): Purified with 15% EtOAc/ hexanes, yielding 111 mg (57%) of **15** as a colorless oil. $R_f = 0.23$ (15% EtOAc/hexanes); IR (film) 3073, 3012, 2957, 1724, 1529, 1438, 1213, 1162 cm^{-1} ; ^1H NMR (500 MHz,

CDCl_3) δ 7.61 (d, $J = 10$ Hz, 1H), 7.52 (m, 2H), 7.42 (m, 3H), 4.42 (dd, $J = 10, 3$ Hz, 1H), 3.68 (s, 3H), 3.61 (s, 3H), 3.52 (d, $J = 3$ Hz, 1H), 0.45 (s, 3H), 0.43 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 170.0, 168.4, 157.0 (q, $J = 37$ Hz), 134.2, 134.1, 130.5, 128.45, 116.2 (q, $J = 288$ Hz), 53.3, 53.0, 50.9, 40.6, -3.9, -4.8. LRMS (electrospray): Mass calcd for $\text{C}_{16}\text{H}_{20}\text{F}_3\text{NNaO}_5\text{Si}$ $[\text{M}+\text{Na}]^+$, 414.10. Found 414.

(2RS,3RS)-Methyl 2-benzyl-3-(dimethylphenylsilyl)-3-phenylpropanoate (17). Lithium chloride (24 mg, 0.57 mmol) was added to a stirring solution of

(7) Dimethyl 2-ethylidenemalonate appeared to decompose slightly upon distillation at temperature lower than 100 $^{\circ}\text{C}$. Thus, decomposition of the starting material *in situ* could be the reason for a low yield.

3a (50 mg, 0.14 mmol) and water (1 drop) in DMSO (2 mL). The reaction was heated in an oil bath to 140 °C for 3.5 hours. It was diluted with 100 mL of water, and was extracted with EtOAc (3x50 mL). The combined organics were washed with water and brine, dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. The residue was purified by flash chromatography over silica gel (7% EtOAc/hexanes) to give 30 mg (72%) of a colorless oil that was identical by ¹H NMR and TLC to previously reported methyl 3-(dimethylphenylsilyl)-3-phenylpropanoate.⁸ To a solution of diisopropylamine (335 μL, 2.4 mmol) in THF (2.5 mL) cooled to –78 °C was added butyllithium (1.6 M in hexanes, 1.5 mL, 2.4 mmol). It was allowed to warm to 0 °C and stir for 10 minutes, then was cooled to –78 °C. To this, a solution of methyl 3-(dimethylphenylsilyl)-3-phenylpropanoate (500 mg, 1.68 mmol) in THF (5 mL) was added *via* cannula. It was allowed to stir for 30 minutes, and then benzyl bromide (250 μL, 2.1 mmol) was added *via* syringe. The reaction was warmed to room temperature and allowed to react for 10 hours. Saturated ammonium chloride (15 mL) was added, and it was extracted with EtOAc (2x30 mL). The organics were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. The unpurified reaction mixture contained a single diastereomer by ¹H NMR (500 Mhz). Coupling constants matched data reported for similar *anti* diastereomers.⁹ The residue was purified by flash chromatography over silica gel (7% EtOAc/hexanes) to give 560 mg (86%) of **17** as a colorless solid. *R*_f = 0.51 (15% EtOAc/hexanes); mp = 65 °C; IR (film) 3023, 2947, 1733, 1489, 1450 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.5-7.1 (m, 11H), 7.04 (d, *J* = 7 Hz, 2H), 6.98 (d, *J* = 7 Hz, 2H), 3.18 (m, 1H), 3.17 (s, 3H), 2.75 (d, *J* = 12 Hz, 2H), 2.59 (dd, *J* = 12, 13 Hz, 1 H), 0.33, (s, 3H), 0.13 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 175.2, 141.0, 139.6, 137.2, 134.6, 129.3, 128.9, 128.8, 128.6, 128.4, 127.7, 126.4, 125.6, 51.2, 49.6, 39.8, 39.6, –2.4, –4.6. LRMS (electrospray): Mass calcd for C₂₅H₂₈NaO₂Si [M+Na]⁺, 411.18. Found 411.

(2*RS*,3*SR*)-Methyl 2-benzyl-3-hydroxy-3-phenylpropanoate (18) :

Tetrafluoroboric acid diethyl ether complex (0.1 mL) was added to a stirring solution of **17** (206 mg, 0.5 mmol) in dichloromethane (1 mL) at room

(8) Fleming, I.; Newton, T. W. *J. Chem. Soc., Perkin Trans. 1*, **1984**, 1805-1808.

(9) Fleming, I.; Waterson, D. *J. Chem. Soc., Perkin Trans. 1*, **1984**, 1809-1815.

temperature. The reaction was allowed to stir for two hours. It was quenched with water (10 mL), and the mixture was extracted with EtOAc (2x15 mL). The combined organics were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. The residue was dissolved in diethyl ether (1 mL) and cooled to 0 °C. *m*-Chloroperbenzoic acid (350 mg, 2.0 mmol) was added, followed by dropwise addition of triethylamine (84 µL, 0.60 mmol) in ether (0.5 mL). The mixture was warmed to room temperature, and stirred for 2.25 hours. The reaction was quenched by the addition of saturated sodium sulfite (7 mL). The organic layer was separated, washed with saturated sodium sulfite and 0.5% aqueous hydrochloric acid, and concentrated *in vacuo*. The residue was taken up in methanol (5 mL), and concentrated hydrochloric acid (2-3 drops) was added. After 15 minutes, it was concentrated again, taken up in ether, washed with saturated sodium bicarbonate and saturated sodium chloride, dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo* to give 120 mg (89%) of **18** as a white solid. The product was ≥95% pure by ¹H and ¹³C NMR and identical to spectra previously reported for known compound **18**.¹⁰

(10) Ranu, B. C.; Saha, M.; Bhar, S. *Synth. Commun.* **1997**, 27, 3065-3078.

Selected ^1H NMR Spectra: STANDARD ^1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl_3

Ambient temperature

File: 1H-CTC-149.2

INOVA-500 "wakko"

PULSE SEQUENCE

Relax. delay 1.000 sec

Pulse 70.6 degrees

Acq. time 0.998 sec

Width 5000.0 Hz

8 repetitions

OBSERVE H1, 400.1658659 MHz

DATA PROCESSING

Line broadening 1.0 Hz

FT size 16384

Total time 0 min, 16 sec

H1 stdpar 25C idpfg_5mm inova500

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

User: 1-15-87

File: 1H-CTC-vinylpure

INOVA-500 "wakko"

PULSE SEQUENCE

Relax. delay 1.000 sec

Pulse 65.5 degrees

Acq. time 1.003 sec

Width 5997.0 Hz

16 repetitions

OBSERVE H1, 499.5765818 MHz

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 0 min, 32 sec

STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: 1H-CTC-p-Fclean

INOVA-500 "wakko"

PULSE SEQUENCE

Relax. delay 1.000 sec

Pulse 70.6 degrees

Acq. time 0.998 sec

Width 5000.0 Hz

16 repetitions

OBSERVE H1, 400.1658648 MHZ

DATA PROCESSING

Line broadening 1.0 Hz

FT size 16384

Total time 0 min, 32 sec

STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: 1H-CTC-181.2

INOVA-500 "wakko"

PULSE SEQUENCE

Relax. delay 1.000 sec

Pulse 70.6 degrees

Acq. time 0.998 sec

Width 5000.0 Hz

16 repetitions

OBSERVE H1, 400.1658750 MHz

DATA PROCESSING

Line broadening 1.0 Hz

FT size 16384

Total time 0 min, 32 sec

STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: 1H-CTC-175.2

INOVA-500 "wakko"

PULSE SEQUENCE

Relax. delay 1.000 sec

Pulse 70.6 degrees

Acq. time 0.998 sec

Width 5000.0 Hz

16 repetitions

OBSERVE H1, 400.1658788 MHz

DATA PROCESSING

Line broadening 1.0 Hz

FT size 16384

Total time 0 min, 32 sec

H1 stdpar 25C idpfg_5mm inova500

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

User: 1-15-87

File: 1H-CTC-180.3

INOVA-500 "wakko"

PULSE SEQUENCE

Relax. delay 1.000 sec

Pulse 65.5 degrees

Acq. time 1.003 sec

Width 5997.0 Hz

4 repetitions

OBSERVE H1, 499.5765818 MHz

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 0 min, 8 sec

STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: 1H-CTC-140.2

INOVA-500 "wakko"

PULSE SEQUENCE

Relax. delay 1.000 sec

Pulse 70.6 degrees

Acq. time 0.998 sec

Width 5000.0 Hz

16 repetitions

OBSERVE H1, 400.1658659 MHz

DATA PROCESSING

Line broadening 1.0 Hz

Ft size 16384

Total time 0 min, 32 sec

H1 stdpar 25C idpfg_5mm inova500

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

User: 1-15-87

File: 1H-CTC-2nappure

INOVA-500 "wako"

PULSE SEQUENCE

Relax. delay 1.000 sec

Pulse 65.5 degrees

Acq. time 1.003 sec

Width 5997.0 Hz

32 repetitions

OBSERVE H1, 499.5674628 MHz

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 1 min, 4 sec

STANDARD ¹H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

File: 1H-CTC-pentylpure

INOVA-500 "wakko"

PULSE SEQUENCE

Relax. delay 1.000 sec

Pulse 70.6 degrees

Acq. time 0.998 sec

Width 5000.0 Hz

16 repetitions

OBSERVE H1, 400.1658659 MHz

DATA PROCESSING

Line broadening 1.0 Hz

Ft size 16384

Total time 0 min, 32 sec

STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: 1H-CTC-197.2

INOVA-500 "wakko"

PULSE SEQUENCE

Relax. delay 1.000 sec

Pulse 70.6 degrees

Acq. time 0.998 sec

Width 5000.0 Hz

16 repetitions

OBSERVE H1, 400.1658659 MHz

DATA PROCESSING

Line broadening 1.0 Hz

FT size 16384

Total time 0 min, 32 sec

STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: 1H-CTC-198.2

INOVA-500 "wakko"

PULSE SEQUENCE

Relax. delay 1.000 sec

Pulse 70.6 degrees

Acq. time 0.998 sec

Width 5000.0 Hz

16 repetitions

OBSERVE H1, 400.1658659 MHz

DATA PROCESSING

Line broadening 1.0 Hz

FT size 16384

Total time 0 min, 32 sec

H1 std RT spin=0 INOVA-400 DB_5mm
pw90=9.2us@58dB LK sample cdc13

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: 1H-CTC-200.2

INOVA-500 "wakko"

PULSE SEQUENCE

Relax. delay 1.000 sec

Pulse 78.3 degrees

Acq. time 1.000 sec

Width 4799.3 Hz

16 repetitions

OBSERVE H1, 399.9417506 MHz

DATA PROCESSING

Line broadening 1.0 Hz

FT size 16384

Total time 0 min, 32 sec

H1 stdpar 25C idpfg_5mm inova500

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

User: 1-15-87

File: 1H-CTC-alkylationpure

INOVA-500 "wakko"

PULSE SEQUENCE

Relax. delay 1.000 sec

Pulse 65.5 degrees

Acq. time 1.003 sec

Width 5997.0 Hz

16 repetitions

OBSERVE HL, 499.5765818 MHz

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 0 min, 32 sec