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Supporting Information

Pyridylsilyl Group Expands the Scope of Catalytic Intermolecular Pauson-Khand-type Reaction

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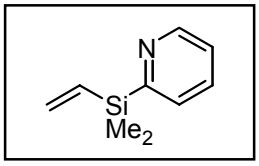
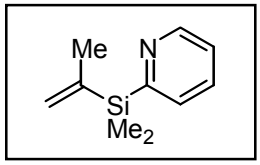
General. ^{1}H and ^{13}C NMR spectra were recorded on Varian GEMINI-2000 (^{1}H 300 MHz, ^{13}C 75 MHz) and JEOL A-500 (^{1}H 500 MHz, ^{13}C 125 MHz) spectrometers in $CDCl_3$ with chemical shifts referenced to internal standards (7.26 ppm ^{1}H, 77.0 ppm ^{13}C). EI mass spectra were recorded on a JMS-SX102A spectrometer. FAB mass spectra were recorded on a JMS-HX110A spectrometer. Infrared spectra were recorded on a Shimadzu FTIR-8100 spectrophotometer. Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. Toluene and xylenes were dried over CaH_2 under argon. Compounds **1a**,[1] **1b**,[2] **1c**,[2] and **5**[3] were prepared according to the literature procedures.



Dimethyl(2-pyridyl)(vinyl)silane (1a).[1] To a solution of 2-bromopyridine (23.7 g, 150 mmol) in Et_2O (100 mL) was added dropwise a solution of BuLi (144 mmol, 1.50 M in hexane) at –78 °C under argon. The mixture was stirred at –78 °C for additional 1.5 h. The resultant solution of 2-pyridyllithium was added to a solution of chlorodimethyl(vinyl)silane (18.9 g, 149 mmol) in Et_2O (50 mL) at –78 °C. After stirring at room temperature for 1 h, *sat.* $NaHCO_3$ aqueous solution (100 mL) was added to the mixture. Aqueous phase was extracted with Et_2O (5 × 100 mL) and the combined organic phase was dried over $MgSO_4$. Removal of the solvent under reduced pressure and subsequent distillation afforded **1a** (20.4 g, 87%) as a pale yellow liquid: Bp 80-84 °C/14 mmHg. ^{1}H NMR (300 MHz) δ 0.39 (s, 6H), 5.80 (dd, *J* = 20.1, 3.6 Hz, 1H), 6.08 (dd, *J* = 14.4, 3.6 Hz, 1H), 6.33 (dd, *J* = 20.1, 14.4 Hz, 1H), 7.16 (ddd, *J* = 7.5, 4.8, 1.7 Hz, 1H), 7.49 (ddd, *J* = 7.5, 1.7, 1.1 Hz,

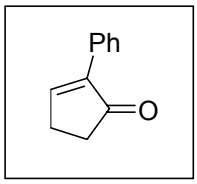
(1) K.Itami, K. Mitsudo, T. Kamei, T. Koike, T. Nokami, J. Yoshida, *J. Am. Chem. Soc.* **2000**, *122*, 12013.
(2) K. Itami, K. Mitsudo, A. Nishino, J. Yoshida, *J. Org. Chem.* **2002**, *67*, 2645.
(3) B. M. Trost, A. B. Pinkerton, *J. Org. Chem.* **2001**, *66*, 7714.

1H), 7.55 (td, *J* = 7.5, 1.7 Hz, 1H), 8.77 (ddd, *J* = 4.8, 1.7, 1.1 Hz, 1H); ^{13}C NMR (75 MHz) δ -3.8, 122.8, 129.4, 133.5, 134.0, 137.0, 150.3, 166.9. IR (neat) 1574, 1561, 1418, 1246 cm^{-1}. HRMS (EI) *m/z* calcd for $C_9H_{13}NSi$: 163.0817, found 163.0824.

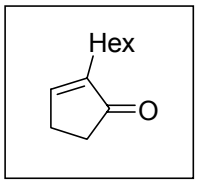


Dimethyl(2-pyridyl)(2-propenyl)silane (1d). To a solution of 2-bromopropene (6.05 g, 50 mmol) in dry Et_2O (50 mL) was added dropwise a solution of *t*-BuLi (48 mmol, 1.38 M solution in pentane) at –78 °C under argon and the mixture was stirred for 2 h at –78 °C. To this solution was added dimethyl(2-pyridyl)silane (6.86 g, 50 mmol) at –78 °C and the mixture was gradually warmed to room temperature. After stirring the mixture for 2 h at room temperature, brine (80 mL) was added to the mixture. The mixture was extracted with Et_2O (2 × 80 mL), and the combined organic phase was dried over $MgSO_4$. Removal of solvent under reduced pressure and subsequent distillation (75–78 °C/6.0 mmHg) afforded **1d** (3.58 g, 42%) as a colorless liquid: ^{1}H NMR (300 MHz) δ 0.42 (s, 6H), 1.85 (t, *J* = 1.5 Hz, 3H), 5.39 (dq, *J* = 3.0, 1.5 Hz, 1H), 5.72 (dq, *J* = 3.0, 1.5 Hz, 1H), 7.21 (ddd, *J* = 7.5, 4.8, 1.5 Hz, 1H), 7.51 (dt, *J* = 7.5, 1.5 Hz, 1H), 7.59 (td, *J* = 4.8, 1.5 Hz, 1H), 8.79 (ddd, *J* = 4.8, 1.5, 1.2 Hz, 1H); ^{13}C NMR (75 MHz) δ –4.1, 22.6, 122.8, 127.1, 129.4, 134.0, 145.1, 150.2, 166.4. IR (neat) 1574, 1559, 1451, 1418, 1246 cm^{-1}. HRMS (EI) *m/z* calcd for $C_{10}H_{15}NSi$: 177.0974, found 177.0974.

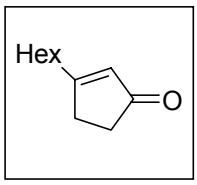
Typical Procedure for Catalytic Intermolecular Pauson-Khand-type Reaction of Alkenyldimethyl(2-pyridyl)silane (1) and Alkyne (2). To a suspension of $Ru_3(CO)_{12}$ (16 mg, 0.025 mmol, 5 mol %) and dimethyl(2-pyridyl)(vinyl)silane **1a** (81 mg, 0.50 mmol) in toluene (1.5 mL) under CO (1 atm) was added 1-phenylpropyne (87 mg, 0.75 mmol) over 3 h at 100 °C and the mixture was stirred for 24 h. After being cooled to room temperature, 1 N *aq* HCl (1 mL) was added to the mixture and the organic phase was extracted with Et_2O (3 × 2 mL). Aqueous phase was neutralized by adding $NaHCO_3$ and then was extracted with Et_2O (3 × 2 mL). The combined organic phase was dried over $MgSO_4$ and removal of solvents under reduced pressure afforded the crude product. The residue was chromatographed on silica gel (hexane/EtOAc = 20/1 → 10/1 → 5/1 → 1/1) to afford **3ae** (64 mg, 75%) as pale yellow oil.



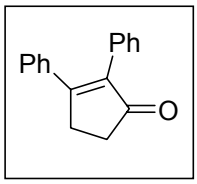
2-Phenyl-2-cyclopenten-1-one (3aa).[4] ^{1}H NMR (300 MHz) δ 2.57–2.62 (m, 2H), 2.67–2.73 (m, 2H), 7.29–7.42 (m, 3H), 7.65–7.71 (m, 2H), 7.82 (t, *J* = 3.0 Hz, 1H); ^{13}C NMR (75 MHz) δ 26.1, 35.7, 127.0, 128.26, 128.33, 131.6, 143.3, 159.1, 207.6. HRMS (EI) *m/z* calcd for $C_{11}H_{10}O$: 158.0732, found 158.0732.



2-Hexyl-2-cyclopenten-1-one (3ab).[5] ^{1}H NMR (300 MHz) δ 0.85 (t, *J* = 6.6 Hz, 3H), 1.20–1.50 (m, 8H), 2.13 (tm, *J* = 7.8 Hz, 2H), 2.34–2.38 (m, 2H), 2.50–2.56 (m, 2H), 7.26–7.29 (m, 1H); ^{13}C NMR (75 MHz) δ 14.0, 22.5, 24.7, 26.4, 27.6, 29.0, 31.5, 34.5, 146.5, 157.3, 210.1.



3-Hexyl-2-cyclopenten-1-one (4ab).[6] ^{1}H NMR (300 MHz) δ 0.87 (t, *J* = 6.6 Hz, 3H), 1.23–1.39 (m, 6H), 1.50–1.62 (m, 2H), 2.35–2.42 (m, 4H), 2.53–2.58 (m, 2H), 5.92 (quintet, *J* = 1.5 Hz, 1H); ^{13}C NMR (125 MHz) δ 14.0, 22.5, 27.0, 28.9, 31.45, 31.47, 33.5, 35.2, 129.3, 183.3, 210.1.



2,3-Diphenyl-2-cyclopenten-1-one (3ac).[7] ^{1}H NMR (300 MHz) δ 2.69–2.75 (m, 2H), 3.03–3.10 (m, 2H), 7.19–7.38 (m, 10H); ^{13}C NMR (75 MHz) δ 29.5, 34.7, 127.8, 128.0, 128.37, 128.41, 129.4, 129.8, 132.3, 135.7, 139.9, 168.0, 207.5.

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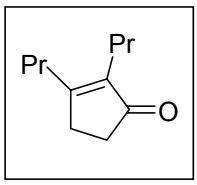
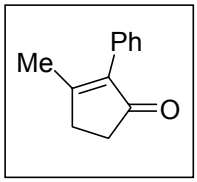
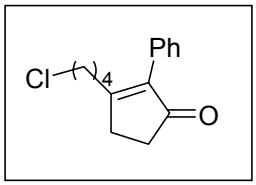
(4) J. G. Donkervoort, A. R. Gordon, C. Johnstone, W. J. Kerr, U. Lange, *Tetrahedron* **1996**, *52*, 7391.
(5) E. Negishi, Z. Tan, S. Y. Liou, B. Liao, *Tetrahedron* **2000**, *56*, 10197.
(6) N. Iwasawa, T. Matsuo, M. Iwamoto, T. Ikeno, *J. Am. Chem. Soc.* **1998**, *120*, 3903.
(7) T. Takahashi, Z. Xi, Y. Nishihara, S. Huo, K. Kasai, K. Aoyagi, V. Denisov, E. Negishi, *Tetrahedron* **1997**, *53*, 9123.



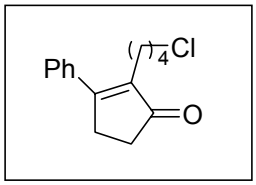
2,3-Dipropryl-2-cyclopenten-1-one (3ad).[7] ^{1}H NMR (300 MHz) δ 0.86 (t, *J* = 7.2 Hz, 3H), 0.94 (t, *J* = 7.5 Hz, 3H), 1.37 (qt, *J* = 7.2, 6.0 Hz, 2H), 1.54 (qt, *J* = 7.5, 6.0 Hz, 2H), 2.08–2.15 (m, 2H), 2.31–2.41 (m, 4H), 2.43–2.49 (m, 2H); ^{13}C NMR (75 MHz) δ 14.08, 14.13, 20.8, 21.8, 25.0, 28.8, 33.1, 34.2, 140.4, 173.9, 210.1.



3-Methyl-2-phenyl-2-cyclopenten-1-one (3ae).[7] ^{1}H NMR (300 MHz) δ 2.19 (s, 3H), 2.54–2.58 (m, 2H), 2.64–2.70 (m, 2H), 7.26–7.35 (m, 3H), 7.38–7.44 (m, 2H); ^{13}C NMR (75 MHz) δ 18.3, 31.7, 34.8, 127.5, 128.2, 129.0, 131.7, 140.3, 171.8, 207.6.

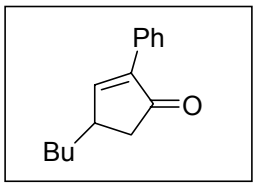


3-(4-Chlorobutyl)-2-phenyl-2-cyclopenten-1-one (3af). ^{1}H NMR (300 MHz) δ 1.66–1.81 (m, 4H), 2.51–2.58 (m, 4H), 2.65–2.70 (m, 2H), 3.48 (t, *J* = 6.3 Hz, 2H), 7.21 (dt, *J* = 7.5, 1.8 Hz, 2H), 7.31 (tt, *J* = 7.5, 1.8 Hz, 1H), 7.40 (tt, *J* = 7.5, 1.8 Hz, 2H); ^{13}C NMR (75 MHz) δ 24.6, 28.9, 30.6, 32.0, 34.6, 44.3, 127.6, 128.3, 128.9, 131.7, 140.8, 174.4, 207.7. IR (neat) 1700, 762, 702 cm^{-1}. HRMS (EI) *m/z* calcd for $C_{15}H_{17}OCl$: 248.0968, found 248.0966.

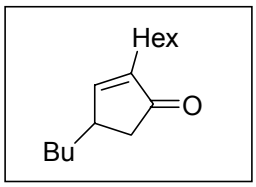


2-(4-Chlorobutyl)-3-phenyl-2-cyclopenten-1-one (4af). ^{1}H NMR (300 MHz) δ 1.57–1.68 (m, 2H), 1.72–1.83 (m, 2H), 2.40 (tm, *J* = 7.5 Hz, 2H), 2.50–2.56 (m, 2H), 2.88–2.93 (m, 2H), 3.50 (t, *J* = 6.6 Hz, 2H), 7.38–7.51 (m, 5H); ^{13}C NMR (75 MHz) δ 23.1, 25.3, 29.9, 32.5, 34.2, 44.6, 127.1, 128.7, 129.5, 136.4,

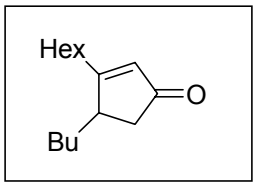
140.4, 167.9, 209.6. IR (neat) 1696, 762, 698 cm^{-1}. HRMS (EI) *m/z* calcd for $C_{15}H_{17}OCl$: 248.0968, found 248.0967.



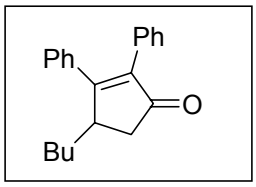
4-Butyl-2-phenyl-2-cyclopenten-1-one (3ba). ^{1}H NMR (300 MHz) δ 0.97 (t, *J* = 7.5 Hz, 3H), 1.42 (sextet, *J* = 7.5 Hz, 2H), 1.58–1.69 (m, 2H), 2.49 (t, *J* = 7.5 Hz, 2H), 2.69 (dm, *J* = 18.6 Hz, 1H), 3.13 (ddm, *J* = 18.6, 7.5 Hz, 1H), 3.61 (dd, *J* = 7.5, 3.0 Hz, 1H), 6.03 (quintet, *J* = 1.5 Hz, 1H), 7.11–7.16 (m, 2H), 7.20–7.35 (m, 3H); ^{13}C NMR (75 MHz) δ 13.8, 22.4, 29.1, 33.2, 41.3, 52.2, 126.8, 127.5, 128.4, 128.8, 139.8, 182.4, 209.1. IR (neat) 1703, 1617, 1173, 700 cm^{-1}. HRMS (EI) *m/z* calcd for $C_{15}H_{18}O$: 214.1358, found 214.1360.



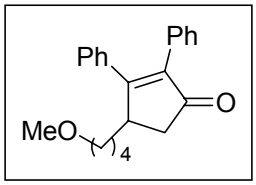
4-Butyl-2-hexyl-2-cyclopenten-1-one (3bb). ^{1}H NMR (300 MHz) δ 0.85 (t, *J* = 6.9 Hz, 3H), 0.89 (t, *J* = 6.9 Hz, 3H), 1.22–1.56 (m, 14H), 1.99 (dd, *J* = 18.9, 2.1 Hz, 1H), 2.08–2.16 (m, 2H), 2.54 (dd, *J* = 18.9, 6.0 Hz, 1H), 2.69–2.80 (m, 1H), 7.19 (quintet, *J* = 1.2 Hz, 1H); ^{13}C NMR (75 MHz) δ 13.9, 14.0, 22.5, 22.7, 24.6, 27.6, 29.0, 29.8, 31.5, 34.8, 38.7, 41.6, 145.6, 161.3, 209.6. IR (neat) 1707, 1632, 1466 cm^{-1}. HRMS (EI) *m/z* calcd for $C_{15}H_{26}O$: 222.1984, found 222.1986.



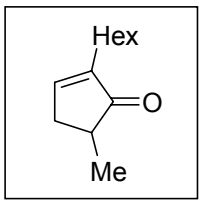
4-Butyl-3-hexyl-2-cyclopenten-1-one (4bb). ^{1}H NMR (300 MHz) δ 0.87 (t, *J* = 6.8 Hz, 3H), 0.93 (t, *J* = 7.4 Hz, 3H), 1.23–1.43 (m, 12H), 1.50–1.62 (m, 2H), 1.73–1.82 (m, 1H), 2.24 (dm, *J* = 18.3 Hz, 1H), 2.39 (t, *J* = 7.7 Hz, 2H), 2.73 (ddt, *J* = 18.3, 6.9, 0.9 Hz, 1H), 5.90 (quintet, *J* = 1.5 Hz, 1H); ^{13}C NMR (75 MHz) δ 13.8, 14.1, 22.4, 22.6, 27.2, 29.1, 29.3, 31.5, 31.7, 33.2, 38.3, 46.3, 128.7, 181.7, 212.4. IR (neat) 1703, 1619, 1466 cm^{-1}. HRMS (EI) *m/z* calcd for $C_{15}H_{26}O$: 222.1984, found 222.1988.



4-Butyl-2,3-diphenyl-2-cyclopenten-1-one (3bc). ^{1}H NMR (500 MHz): δ 0.85 (t, *J* = 7.2 Hz, 3H), 1.17–1.34 (m, 5H), 1.59–1.67 (m, 1H), 2.40 (dd, *J* = 18.9, 2.0 Hz, 1H), 2.85 (dd, *J* = 18.9, 6.8 Hz, 1H), 3.39–3.44 (m, 1H), 7.14–7.33 (m, 10H); ^{13}C NMR (125 MHz): δ 13.9, 22.5, 29.1, 33.2, 40.8, 41.3, 127.6, 128.1 (five carbons), 128.4 (two carbons), 129.1, 129.5 (two carbons), 131.7, 134.9, 139.8, 173.2, 206.9. IR (neat) 1705, 1445, 1350, 1157, 938, 696 cm^{-1}. HRMS (EI) *m/z* calcd for $C_{21}H_{22}O$: 290.1671, found 290.1671.

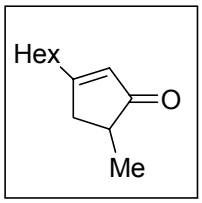


4-(4-Methoxybutyl)-2,3-diphenyl-2-cyclopenten-1-one (3cc). ^{1}H NMR (300 MHz): δ 1.15–1.71 (m, 6H), 2.42 (dd, *J* = 18.9, 2.1 Hz, 1H), 2.87 (dd, *J* = 18.9, 6.6 Hz, 1H), 3.29 (s, 3H), 3.30 (td, *J* = 6.0, 0.9 Hz, 2H), 3.38–3.46 (m, 1H), 7.13–7.33 (m, 10H); ^{13}C NMR (125 MHz): δ 23.8, 29.5, 33.4, 40.8, 41.2, 58.5, 72.4, 127.6, 128.1 (four carbons), 128.4 (two carbons), 129.2, 129.5 (two carbons), 131.7, 134.9, 139.8, 172.8, 206.6; IR (neat) 1700, 1350, 1119, 733, 696 cm^{-1}. HRMS (EI) *m/z* calcd for $C_{22}H_{24}O_2$: 320.1776, found 320.1776.

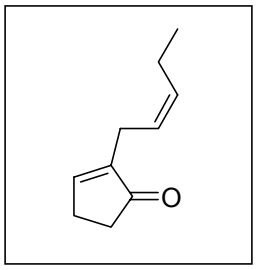


2-Hexyl-5-methyl-2-cyclopenten-1-one (3db).[8] ^{1}H NMR (300 MHz) δ 0.87 (t, *J* = 6.6 Hz, 3H), 1.17 (d, *J* = 7.5 Hz, 3H), 1.23–1.35 (m, 6H), 1.40–1.52 (m, 2H), 2.08–2.19 (m, 3H), 2.31–2.42 (m, 1H), 2.74–2.86 (m, 1H), 7.20–7.24 (m, 1H); ^{13}C NMR (75 MHz) δ 14.0, 16.4, 22.5, 24.9, 27.6, 29.0, 31.6, 35.5, 39.9, 145.3, 155.5, 212.5.

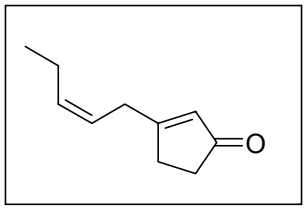
(8) K. Tanaka, G. C. Fu, *J. Am. Chem. Soc.* **2001**, *123*, 11492.



3-Hexyl-5-methyl-2-cyclopenten-1-one (4db).[6] ^{1}H NMR (300 MHz) δ 0.89 (t, *J* = 6.9 Hz, 3H), 1.17 (t, *J* = 7.5 Hz, 3H), 1.24–1.40 (m, 6H), 1.51–1.62 (m, 2H), 2.17 (dm, *J* = 18.3 Hz, 1H), 2.34–2.42 (m, 2H), 2.81 (ddm, *J* = 18.3, 6.6 Hz, 1H); ^{13}C NMR (75 MHz) δ 14.0, 16.5, 22.5, 27.0, 29.0, 31.5, 33.5, 40.3, 40.7, 128.1, 181.5, 212.8.



2-(3-*cis*-Pentenyl)-2-cyclopenten-1-one (6).[9] ^{1}H NMR (300 MHz): δ 0.97 (t, *J* = 7.5 Hz, 3H), 2.02 (qdm, *J* = 7.5, 6.0 Hz, 2H), 2.38–2.42 (m, 2H), 2.52–2.59 (m, 2H), 2.82–2.87 (m, 2H), 5.38–5.59 (m, 2H), 7.29–7.32 (m, 1H); ^{13}C NMR (75 MHz): δ 13.7, 25.5, 26.5, 28.0, 34.6, 124.7, 134.4, 145.5, 158.0, 209.6; IR (neat) 1705, 1634, 791, 733 cm^{-1}. HRMS (EI) *m/z* calcd for $C_{10}H_{14}O$: 150.1045, found 150.1047.



3-(3-*cis*-Pentenyl)-2-cyclopenten-1-one.[9] ^{1}H NMR (300 MHz): δ 0.99 (t, *J* = 7.5 Hz, 3H), 2.05 (qdm, *J* = 7.5, 6.6 Hz, 2H), 2.38–2.43 (m, 2H), 2.55–2.60 (m, 2H), 3.08 (d, *J* = 6.6 Hz, 2H), 5.51 (dtt, *J* = 21.6, 6.6, 1.5 Hz, 1H), 5.56 (dtt, *J* = 21.6, 6.6, 1.5 Hz, 1H), 5.95 (quintet, *J* = 1.5 Hz, 1H); ^{13}C NMR (75 MHz): δ 13.6, 25.5, 31.2, 35.4, 36.7, 123.1, 129.7, 136.1, 181.9, 210.1; IR (neat) 1709, 1674, 1617, 733 cm^{-1}. HRMS (EI) *m/z* calcd for $C_{10}H_{14}O$: 150.1045, found 150.1045.

(9) A. Rudolph, A. C. Weedon, *Can. J. Chem.* **1990**, *68*, 1590.