**Catalytic Intermolecular Pauson–Khand-type Reaction:
Strong Directing Effect of Pyridylsilyl and Pyrimidylsilyl Groups
and Isolation of Ru Complexes Relevant to Catalytic Reaction**

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Synthetic Scope 1: Ru-Catalyzed Intermolecular Pauson–Khand-type Reaction of Dimethyl(2-pyridyl)(vinyl)silane (1) with Various Alkynes (4). The results using dimethyl(2-pyridyl)(vinyl)silane (1) with various alkynes 4 are depicted in Table S1 and eqs s1 and s2.

Table S1. Ru-Catalyzed Intermolecular PKR of **1** and Various Alkynes

run	alkyne (4)	main product (5)	yield (5/5')	run	alkyne (4)	main product (5)	yield (5/5')
1	$\text{HC}\equiv\text{CC}_6\text{H}_5$ (4a)		55% (>99/1)	8 ^a	$4\text{-MeC}_6\text{H}_4\text{C}\equiv\text{CC}_6\text{H}_4\text{Me-4}$ (4h)		59% (>99/1)
2	$\text{CH}_3\text{C}\equiv\text{CC}_6\text{H}_5$ (4b)		75% (>99/1)	9	$\text{CH}_3\text{C}\equiv\text{CC}_6\text{H}_4\text{Me-4}$ (4i)		78% (>99/1)
3 ^a	$n\text{-C}_3\text{H}_7\text{C}\equiv\text{CC}_3\text{H}_7\text{-}n$ (4c)		59%	10	$\text{CH}_3\text{C}\equiv\text{CC}_6\text{H}_4\text{OMe-4}$ (4j)		59% (>99/1)
4	$\text{HC}\equiv\text{CC}_6\text{H}_4\text{Me-4}$ (4d)		55% (>99/1)	11	$\text{CH}_3\text{C}\equiv\text{CC}_6\text{H}_4\text{Cl-4}$ (4k)		86% (>99/1)
5	$\text{HC}\equiv\text{CC}_6\text{H}_{13}\text{-}n$ (4e)		91% (59/41)	12	$\text{CH}_3\text{C}\equiv\text{CC}_6\text{H}_4\text{CF}_3\text{-4}$ (4l)		74% (>99/1)
6 ^a	$\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5$ (4f)		88%	13 ^a	$n\text{-C}_4\text{H}_9\text{C}\equiv\text{CC}_6\text{H}_5$ (4m)		79% (95/5)
7 ^a	$4\text{-ClC}_6\text{H}_4\text{C}\equiv\text{CC}_6\text{H}_4\text{Cl-4}$ (4g)		72%	14 ^a	$\text{Cl}(\text{CH}_2)_4\text{C}\equiv\text{CC}_6\text{H}_5$ (4n)		67% (87/13)

^a The pretreatment and reaction were performed at 120 °C in xylenes.

As in the case using phenylacetylene **4a** (run 1), substituted phenylacetylene derivative **4d** works equally well giving 2-aryl-substituted cyclopentenone **5d** regioselectivity (run 4). When alkyl-substituted alkyne (**4e**) was employed, substantial decline in regioselectivity was observed (run 5). This trend is in line with the previously reported Co-mediated stoichiometric reactions. Internal alkynes also participate in this catalytic intermolecular PKR with reasonable efficiency. The reactions using tolan (**4f**) and its derivatives (**4g** and **4h**) furnished 2,3-diaryl-2-cyclopentenones in relatively good yields when the pretreatment and reaction were performed at 120 °C in xylenes (runs 6–8). It should be mentioned that the 2,3-diaryl-2-cyclopentenones have proved to be a fertile area for the discovery of selective inhibitors of cyclooxygenase-2 (COX-2). Dialkyl-substituted internal alkyne (**4c**) was also found to participate in this reaction (run 3). Other than symmetrically substituted internal alkynes, unsymmetrically substituted internal alkynes can also be used as substrates (runs 2 and 9–14). When 1-phenyl-1-propyne (**4b**) was employed, cyclopentenone **5b** was obtained in 75% yield with virtually complete regioselectivity (run 2). Other 1-aryl-1-propynes (**4i–4l**) also gave cyclopentenones in good yields with virtually complete regioselectivity (runs 9–12). When 1-phenyl-1-hexyne (**4m**) was employed, the regioselectivity was slightly decreased (95/5; run 13). This may partially due to the high reaction temperature (120 °C). However, when chloroalkyl-substituted alkyne **4n** was employed, substantial decline in regioselectivity was observed (87/13; run 14). Since **4m** and **4n** are sterically and electronically similar, the observed regioselectivity difference may be due to the chloride directing effect, which has been occasionally observed in Ru and other metal complexes. Heteroaryl groups, which are always of interest from synthetical and biological point of view, can be introduced into the cyclopentenone structure. For example, when 1-(3-pyridyl)-1-propyne (**4o**) was employed, cyclopentenone **5o** was obtained in 33% yield with 96% regioselectivity (eq s1). Similarly, thienyl group can also be incorporated with high regioselectivity (eq s2). Although the chemical yields are not satisfactory at this stage, facile entry into the heteroaryl-substituted cyclopentenone should be useful.

Synthetic Scope 2: Ru-Catalyzed Intermolecular Pauson–Khand-type Reaction Using Substituted Vinyl(2-pyridyl)silanes. The results using substituted vinyl(2-pyridyl)silanes are depicted in Table S2.

Table S2. Ru-Catalyzed Intermolecular PKR of Substituted Vinylsilanes and Alkynes

<p> 1a: R¹ = <i>n</i>-C₄H₉, R² = H 1b: R¹ = (CH₂)₄OMe, R² = H 1c: R¹ = H, R² = CH₃ 4a: R³ = H, R⁴ = C₆H₅ 4e: R³ = H, R⁴ = <i>n</i>-C₆H₁₃ 4f: R³ = C₆H₅, R⁴ = C₆H₅ </p>				
run	1	4	products	yield (5/5')
1 ^a	1a	4a	<p>5aa</p>	41% (>99/1)
2 ^b	1a	4e	<p>5ae</p> <p>5'ae</p>	55% (89/11)
3 ^a	1a	4f	<p>5af</p>	44%
4 ^a	1b	4f	<p>5bf</p>	48%
5 ^c	1c	4e	<p>5ce</p> <p>5'ce</p>	40% (62/38)

^a The pretreatment and reaction were performed at 140 °C in xylenes.

^b The pretreatment and reaction were performed at 100 °C in toluene.

^c The pretreatment and reaction were performed at 120 °C in xylenes.

When β-substituted vinylsilane **1a** was employed in the reaction with **4a**, **5aa** was obtained in 41% yield (run 1). The β-substituent (R¹ = *n*-Bu) was exclusively introduced into the 4-position of the cyclopentenone structure and the regioisomers was not observed in the reaction mixture. As was in the case when **4a** was employed in the reaction with **1**, the regioselectivity with respect to the incorporation of alkyne subunit was also complete in this reaction (**5aa/5'aa** = >99/1). When **1a** was employed in the reaction with **4e**, **5ae** and **5'ae** were obtained in 55% combined yield (run 2). The lower regioselectivity

with respect to the alkyne incorporation is similar to that observed when alkyl-substituted alkyne was employed. Yet, the selectivity (89/11) is substantially higher than that observed in the reaction of **1** and **4e** (59/41; Table S1, run 5). This may be due to the presence of β -substituent which is expected to render the formation of **5'** energetically unfavorable (the steric repulsion between R^1 and R^4 in the metallacycle intermediate). Nevertheless, the regioselectivity with respect to the incorporation of alkene subunit was virtually complete in this reaction as well. The regioselective incorporation of alkene subunit was also observed in the reaction of β -substituted vinylsilanes (**1a** and **1b**) with **4f** (runs 3 and 4). When α -substituted vinylsilane **1c** was employed in the reaction with **4e**, **5ce** and **5'ce** were obtained in 40% combined yield (run 5). Although the regioselectivity with respect to alkyne incorporation was moderate (62/38), the regioselectivity with respect to alkene incorporation was virtually complete again (the α -substituent was exclusively introduced into the 5-position of the cyclopentenone structure). Thus, these substituted vinylsilanes not only serve as surrogates for terminal alkenes that were difficult to be applied in the previously reported catalytic PKR, but also enable the complete regioselective incorporation of alkene subunit into the cyclopentenone skeleton.

General Methods. ^1H and ^{13}C NMR spectra were recorded on Varian GEMINI-2000 (^1H 300 MHz, ^{13}C 75 MHz), Varian MERCURYplus-400 (^1H 400 MHz, ^{13}C 100 MHz), and JEOL A-500 (^1H 500 MHz, ^{13}C 125 MHz) spectrometers in CDCl_3 with chemical shifts referenced to internal standards (7.26 ppm ^1H , 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. Alkenyl(2-pyridyl)silanes **1a**,¹ **1b**,² and **1c**² were prepared by the procedure previously reported by us.

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

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solution of *t*-BuLi (48 mmol, 1.38 M solution in pentane) at $-78\text{ }^{\circ}\text{C}$ under argon and the mixture was stirred for 2 h at $-78\text{ }^{\circ}\text{C}$. To this solution was added dimethyl(2-pyridyl)silane (6.86 g, 50 mmol) at $-78\text{ }^{\circ}\text{C}$ 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 Et₂O (2 $\times$ 80 mL), and the combined organic phase was dried over MgSO₄. Removal of solvent under reduced pressure and subsequent distillation (75–78 $^{\circ}\text{C}$ /6.0 mmHg) afforded **1d** (3.58 g, 42%) as a colorless liquid: ¹H 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). ¹³C 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 C₁₀H₁₅NSi: 177.0974, found 177.0974.

Dimethyl(2-pyrimidyl)vinylsilane (**2**).

To a solution of tributyl(2-pyrimidyl)stannane (19.0 g, 51.4 mmol) in THF (50 mL) was added dropwise a hexane solution of BuLi (51.5 mmol) at $-78\text{ }^{\circ}\text{C}$ under argon. The mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for additional 2 h. The resultant solution of 2-pyrimidyllithium was added to the solution of chlorodimethylvinylsilane (6.63 g, 54.9 mmol) in THF (20 mL) at $-78\text{ }^{\circ}\text{C}$. After stirring at room temperature for 2.5 h, H₂O (100 mL) was added to the mixture. The mixture was extracted with Et₂O (3 $\times$ 100 mL), and the combined organic phase was dried over MgSO₄. Removal of solvent under reduced pressure and subsequent distillation (96–98 $^{\circ}\text{C}$ /22.6 mmHg) afforded **2** (4.06 g, 48%) as a colorless liquid: ¹H NMR (300 MHz) δ 0.44 (s, 6H), 5.86 (dd, *J* = 20.1, 3.6 Hz, 1H), 6.11 (dd, *J* = 14.4, 3.6 Hz, 1H), 6.37 (dd, *J* = 20.1, 14.4 Hz, 1H), 7.17 (t, *J* = 5.1 Hz, 1H), 8.75 (d, *J* = 5.1 Hz, 2H). ¹³C NMR (75 MHz) δ -3.9, 119.8, 133.8, 136.0, 155.2, 180.0. IR (neat) 1547, 1393, 1248 cm⁻¹. HRMS (EI) *m/z* calcd for C₈H₁₂N₂Si: 164.0770, found 164.0773.

Diphenyl(2-pyridyl)vinylsilane (**3**).

To a solution of 2-bromopyridine (3.12 g, 19.7 mmol) in dry Et₂O (20 mL) was added dropwise a solution of BuLi (20 mmol, 1.56 M solution in hexane) at -78 °C under argon and the mixture was stirred for 1 h at -78 °C. The resultant solution of 2-pyridyllithium was added to a solution of chlorodiphenylvinylsilane (4.90 g, 20 mmol) in dry Et₂O (20 mL). After stirring the mixture for 2 h at room temperature, H₂O (50 mL) was added to the mixture. The mixture was extracted with Et₂O (3 × 50 mL), and the combined organic phase was dried over MgSO₄. Removal of solvent under reduced pressure and subsequent gel permeation chromatography (CHCl₃) afforded **3** (725 mg, 13%) as a colorless liquid: ¹H NMR (300 MHz) δ 5.95 (dd, *J* = 20.1, 3.6 Hz, 1H), 6.43 (dd, *J* = 14.4, 3.6 Hz, 1H), 6.83 (dd, *J* = 20.1, 14.4 Hz, 1H), 7.22–7.30 (m, 1H), 7.39–7.51 (m, 6H), 7.53–7.63 (m, 2H), 7.67–7.72 (m, 4H), 8.94 (d, *J* = 4.8 Hz, 1H). ¹³C NMR (75 MHz) δ 123.0, 127.8, 129.6, 131.5, 133.0, 133.3, 134.0, 135.9, 137.4, 150.4, 163.4. HRMS (EI) *m/z* calcd for C₁₉H₁₇NSi: 287.1130, found 287.1132.

Typical Procedure for Catalytic Intermolecular Pauson–Khand-type Reaction of Alkenyldimethyl(2-pyridyl)silane and Alkyne.

To a suspension of Ru₃(CO)₁₂ (16 mg, 0.025 mmol, 5 mol %) in dry toluene (1.5 mL) was added dimethyl(2-pyridyl)vinylsilane (**1**: 81 mg, 0.50 mmol) and the mixture was stirred at 100 °C for 10 min under CO (1 atm). To this mixture was added 1-phenylpropyne (**4b**: 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 Et₂O (3 × 2 mL). Aqueous phase was neutralized by adding NaHCO₃ and then was extracted with Et₂O (3 × 2 mL). The combined organic phase was dried over MgSO₄ 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 **5b** (64 mg, 75%) as pale yellow oil.

2-Phenyl-2-cyclopenten-1-one (5a).³ ¹H 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). ¹³C 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 C₁₁H₁₀O: 158.0732, found 158.0732.

3-Methyl-2-phenyl-2-cyclopenten-1-one (5b).⁴ ¹H 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). ¹³C NMR (75 MHz) δ 18.3, 31.7, 34.8, 127.5, 128.2, 129.0, 131.7, 140.3, 171.8, 207.6.

2,3-Bis(1-propyl)-2-cyclopenten-1-one (5c).⁴ ¹H 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). ¹³C 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.

2-(4-Methylphenyl)-2-cyclopenten-1-one (5d). ¹H NMR (400 MHz) δ 2.37 (s, 3H), 2.58–2.61 (m, 2H), 2.69–2.72 (m, 2H), 7.19 (d, J = 7.6 Hz, 2H), 7.60 (d, J = 7.6 Hz, 2H), 7.77–7.80 (m, 1H). ¹³C NMR (100 MHz) δ 21.4, 26.2, 35.8, 126.7, 128.6, 128.9, 138.0, 143.1, 157.8, 207.3. IR (neat) 1698, 1509, 1302, 1129 cm⁻¹. HRMS (EI) m/z calcd for C₁₂H₁₂O: 172.0888, found 172.0888.

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2-Hexyl-2-cyclopenten-1-one (5e).⁵ ^1H 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 (5e').⁶ ^1H 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 (5f).⁴ ^1H 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.

2,3-Bis(4-chlorophenyl)-2-cyclopenten-1-one (5g). mp 113.2–115.5 °C. ^1H NMR (300 MHz) δ 2.67–2.72 (m, 2H), 3.00–3.04 (m, 2H), 7.14 (dm, J = 8.7 Hz, 2H), 7.26 (dm, J = 1.5 Hz, 4H), 7.31 (dm, J =

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8.7 Hz, 2H). ^{13}C NMR (125 MHz) δ 29.4, 34.6, 128.79, 128.80, 129.2, 130.2, 130.7, 133.7, 133.9, 135.9, 138.9, 166.9, 206.8; IR (KBr) 1618, 1590, 1347 cm^{-1} . HRMS (EI) m/z calcd for $\text{C}_{17}\text{H}_{12}\text{Cl}_2\text{O}$: 302.0265, found 302.0267.

2,3-Bis(4-methylphenyl)-2-cyclopenten-1-one (5h).⁷ ^1H NMR (300 MHz) δ 2.34 (s, 3H), 2.35 (s, 3H), 2.66–2.71 (m, 2H), 3.00–3.05 (m, 2H), 7.07–7.17 (m, 6H), 7.23–7.28 (m, 2H). ^{13}C NMR (75 MHz) δ 21.2, 21.3, 29.2, 34.6, 127.9, 129.0, 129.1, 129.2, 129.5, 132.8, 137.4, 139.1, 140.0, 167.3, 207.7.

3-Methyl-2-(4-methylphenyl)-2-cyclopenten-1-one (5i).⁸ ^1H NMR (300 MHz) δ 2.17 (s, 3H), 2.36 (s, 3H), 2.51–2.58 (m, 2H), 2.62–2.67 (m, 2H), 7.16–7.24 (m, 4H). ^{13}C NMR (75 MHz) δ 18.3, 21.2, 31.7, 34.7, 128.7, 128.9, 137.2, 140.1, 171.3, 207.7.

2-(4-Methoxyphenyl)-3-methyl-2-cyclopenten-1-one (5j).⁹ ^1H NMR (300 MHz) δ 2.16 (s, 3H), 2.49–2.54 (m, 2H), 2.60–2.65 (m, 2H), 3.80 (s, 3H), 6.93 (dm, $J = 7.0$ Hz, 2H), 7.23 (dm, $J = 7.0$ Hz, 2H). ^{13}C NMR (75 MHz) δ 18.3, 31.6, 34.7, 55.1, 113.6, 124.0, 130.2, 139.6, 158.9, 170.9, 207.9.

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2-(4-Chlorophenyl)-3-methyl-2-cyclopenten-1-one (5k).⁸ ¹H NMR (300 MHz) δ 2.13 (s, 3H), 2.47–2.52 (m, 2H), 2.59–2.65 (m, 2H), 7.20 (dm, J = 8.3 Hz, 2H), 7.33 (dm, J = 8.3 Hz, 2H). ¹³C NMR (75 MHz) δ 18.2, 31.6, 34.6, 128.3, 130.1, 130.3, 133.2, 138.9, 172.3, 207.1.

2-(4-Trifluoromethylphenyl)-3-methyl-2-cyclopenten-1-one (5l). mp 71.9–73.0 °C (dec). ¹H NMR (300 MHz) δ 2.19 (s, 3H), 2.54–2.59 (m, 2H), 2.67–2.72 (m, 2H), 7.40 (d, J = 8.6 Hz, 2H), 7.65 (d, J = 8.6 Hz, 2H). ¹³C NMR (75 MHz) δ 18.2, 31.9, 34.7, 124.1 (q, J_{C-F} = 270 Hz), 125.1 (q, J_{C-F} = 3.4 Hz), 129.4, 129.5 (q, J_{C-F} = 32.3 Hz), 135.5, 139.2, 173.2, 207.0. IR (KBr) 1698, 1325, 1111 cm⁻¹. HRMS (EI) m/z calcd for C₁₃H₁₁OF₃: 240.0762, found 240.0762. Anal. Calcd for C₁₃H₁₁OF₃: C, 65.00; H, 4.62. Found: C, 64.86; H, 4.75.

3-Butyl-2-phenyl-2-cyclopenten-1-one (5m).¹⁰ ¹H NMR (300 MHz) δ 0.88 (t, J = 7.2 Hz, 3H), 1.32 (sextet, J = 7.2 Hz, 2H), 1.49–1.61 (m, 2H), 2.48–2.57 (m, 4H), 2.63–2.69 (m, 2H), 7.23 (dt, J = 7.2, 1.5 Hz, 2H), 7.30 (tt, J = 7.2, 1.5 Hz, 1H), 7.40 (tt, J = 7.2, 1.5 Hz, 2H). ¹³C NMR (75 MHz) δ 13.7, 22.6, 28.9, 29.7, 31.3, 34.6, 127.4, 128.1, 129.0, 131.9, 140.3, 175.8, 207.8.

3-(4-Chloro-1-butyl)-2-phenyl-2-cyclopenten-1-one (5n). ¹H 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 $\text{C}_{15}\text{H}_{17}\text{OCl}$: 248.0968, found 248.0966.

2-(4-Chloro-1-butyl)-3-phenyl-2-cyclopenten-1-one (5n'). ^1H 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 $\text{C}_{15}\text{H}_{17}\text{OCl}$: 248.0968, found 248.0967.

3-Methyl-2-(3-pyridyl)-2-cyclopenten-1-one (5o). ^1H NMR (300 MHz) δ 2.23 (s, 3H), 2.56–2.62 (m, 2H), 2.69–2.76 (m, 2H), 7.34–7.43 (m, 1H), 7.68–7.78 (m, 1H), 8.53 (s, 1H), 8.57 (d, $J = 4.2$ Hz, 1H). ^{13}C NMR (75 MHz) δ 18.3, 32.0, 34.7, 123.2, 127.8, 136.6, 137.1, 148.6, 149.7, 173.3, 207.1. IR (neat) 1694, 1638, 1140 cm^{-1} . HRMS (EI) m/z calcd for $\text{C}_{11}\text{H}_{11}\text{NO}$: 173.0841, found 173.0840.

3-Methyl-2-(3-thienyl)-2-cyclopenten-1-one (5p). ^1H NMR (400 MHz) δ 2.19 (s, 3H), 2.43–2.45 (m, 2H), 2.56–2.58 (m, 2H), 7.18–7.20 (m, 1H), 7.25–7.27 (m, 1H), 7.42–7.46 (m, 1H). ^{13}C NMR (100 MHz) δ 19.3, 32.5, 35.1, 124.4, 125.1, 127.8, 132.1, 135.3, 170.7, 207.4. IR (neat) 1690, 1402, 1123 cm^{-1} . HRMS (EI) m/z calcd for $\text{C}_{10}\text{H}_{10}\text{OS}$: 178.0452, found 178.0453.

4-(1-Butyl)-2-phenyl-2-cyclopenten-1-one (5aa). ^1H 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 $\text{C}_{15}\text{H}_{18}\text{O}$: 214.1358, found 214.1360.

4-(1-Butyl)-2-(1-hexyl)-2-cyclopenten-1-one (5ae). ^1H 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 $\text{C}_{15}\text{H}_{26}\text{O}$: 222.1984, found 222.1986.

4-(1-Butyl)-3-(1-hexyl)-2-cyclopenten-1-one (5'ae). ^1H 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 $\text{C}_{15}\text{H}_{26}\text{O}$: 222.1984, found 222.1988.

4-(1-Butyl)-2,3-diphenyl-2-cyclopenten-1-one (5af). ^1H 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 $\text{C}_{21}\text{H}_{22}\text{O}$: 290.1671, found 290.1671.

4-(4-Methoxy-1-butyl)-2,3-diphenyl-2-cyclopenten-1-one (5bf). ^1H 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 $\text{C}_{22}\text{H}_{24}\text{O}_2$: 320.1776, found 320.1776.

2-(1-Hexyl)-5-methyl-2-cyclopenten-1-one (5ce).¹¹ ^1H 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.

3-(1-Hexyl)-5-methyl-2-cyclopenten-1-one (5'ce).⁶ ^1H 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.

Ru(vinylsilane) Complex 6. To a suspension of Ru₃(CO)₁₂ (662.7 mg, 1.04 mmol) in dry toluene (20 mL) was added a solution of **1** (791.2 mg, 5.00 mmol) in dry toluene (10 mL). After the mixture was stirred at 100 °C for 24 h, the solvent was removed under vacuum. The subjection of the crude mixture to gel permeation chromatography (CHCl₃) afforded **6** (639.5 mg, 59%) as a pale yellow oil. ¹H NMR (300 MHz) δ 0.38 (s, 3H), 0.41 (s, 3H), 1.18 (dd, *J* = 13.2, 1.5 Hz, 1H), 1.77 (dd, *J* = 13.2, 11.1 Hz, 1H), 2.62 (dd, *J* = 11.1, 1.5 Hz, 1H), 7.05 (ddd, *J* = 7.8, 5.7, 1.5 Hz, 1H), 7.35 (ddd, *J* = 7.8, 1.5, 0.9 Hz, 1H), 7.56 (td, *J* = 7.8, 1.5 Hz, 1H), 8.72 (dt, *J* = 5.7, 1.2 Hz, 1H). ¹³C NMR (75 MHz) δ -2.0, 0.7, 27.6, 34.9, 123.8, 131.4, 135.2, 155.4, 172.4, 201.3, 203.3, 205.1. IR (neat) 1945, 1460, 1281, 1248 cm⁻¹. HRMS (FAB) *m/z* calcd for C₁₂H₁₃NO₃SiRu: 348.9711, found 348.9707.

X-ray data for **6**: C₁₂H₁₃NO₃SiRu, *M* = 348.40, triclinic, space group *P*-1 (No. 2), *a* = 8.9301 Å, *b* = 9.493(1) Å, *c* = 9.7181(1) Å, α = 71.094(8)°, β = 82.6320(3)°, γ = 73.3640(4)°, *V* = 746.20(7) Å³, *Z* = 2, *D*_c = 1.55 g/cm³, μ = 11.29 cm⁻¹. Intensity data were measured on a Rigaku RAXIS imaging plate area detector with graphite-monochromated Mo-Kα radiation. The data were collected at 23 ± 1 °C to a maximum 2θ value of 54.9°. A total of 3102 reflections were collected. The structure was solved by heavy-atom Patterson methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. The final cycle of full-matrix least-squares refinement on *F* was based on 2534 observed reflections (*I* > 3.00σ(*I*)) and 177 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of *R* = 0.059 (*R*_w = 0.066). All calculations were performed using the CrystalStructure crystallographic software package.

Ru(vinylsilane) Complex 7. The Ru(vinylsilane) complex **7** was prepared according to the procedure used for the preparation of **6**. Yield: 46%. ¹H NMR (300 MHz) δ 0.42 (s, 3H), 0.43 (s, 3H), 1.29 (dd, *J* = 13.2, 2.1 Hz, 1H), 1.83 (dd, *J* = 13.2, 11.1 Hz, 1H), 2.68 (dd, *J* = 11.1, 2.1 Hz, 1H), 7.05 (t, *J* = 6.0 Hz, 1H), 8.67–8.71 (m, 1H), 8.73–8.78 (m, 1H). ¹³C NMR (75 MHz) δ -3.3, 0.2, 26.2, 35.0, 119.6, 155.7, 159.3, 185.3, 200.6, 203.0, 204.1. IR (neat) 2965, 1574, 1402 cm⁻¹. HRMS (FAB) *m/z* calcd for C₁₁H₁₂N₂O₃SiRu: 349.9661, found 349.9663.

Ru(vinylsilane) Complex 8. The Ru(vinylsilane) complex **8** was prepared according to the procedure used for the preparation of **6**. Yield: 68%. ¹H NMR (300 MHz) δ 1.55 (dd, *J* = 12.9, 1.8 Hz, 1H), 2.02 (dd, *J* = 12.9, 10.5 Hz, 1H), 2.89 (dd, *J* = 10.5, 1.8 Hz, 1H), 7.10 (ddd, *J* = 7.5, 5.4, 1.5 Hz, 1H), 7.34–7.48 (m, 7H), 7.52–7.59 (m, 3H), 7.62–7.67 (m, 2H), 8.79 (dt, *J* = 5.4, 1.5 Hz, 1H). ¹³C NMR (100 MHz) δ 23.2, 35.3, 124.1, 127.7, 127.9, 129.6, 129.7, 133.3, 134.9, 135.2, 135.4, 135.5, 137.1, 155.6, 169.1, 200.6, 202.46, 202.53. HRMS (FAB) *m/z* calcd for C₂₂H₁₇NO₃SiRu: 473.0021, found 473.0018.

Ru Complex 9. To a solution of **6** (343.2 mg, 0.98 mmol) in dry toluene (6 mL) was added a solution of 1-phenylpropyne (**4b**; 117.6 mg, 1.01 mmol) in dry toluene (4 mL). The resultant yellow solution was stirred at 50 °C for 1.5 h. Removal of solvent and remaining **4b** under reduced pressure afforded **9** (456 mg, >99%). ¹H NMR (400 MHz) δ 0.22 (s, 3H), 0.39 (s, 3H), 1.41 (s, 3H), 1.69 (dd, *J* = 8.8, 1.3 Hz, 1H), 2.80 (d, *J* = 17.4 Hz, 1H), 3.13 (dd, *J* = 17.4, 8.8, 1.3 Hz, 1H), 6.93 (tm, *J* = 7.3 Hz, 1H), 7.00–7.15 (m, 2H), 7.04 (ddd, *J* = 7.3, 5.7, 1.6 Hz, 1H), 7.25–7.40 (m, 2H), 7.46 (dm, *J* = 7.5 Hz, 1H), 7.62 (td, *J* = 7.5, 1.6 Hz, 1H), 8.25 (dm, *J* = 5.7 Hz, 1H). ¹³C NMR (100 MHz) δ –2.1, –0.4, 17.6, 19.5, 47.6, 123.1, 124.3, 126.6, 128.3, 129.1, 129.5, 134.9, 145.6, 154.1, 156.5, 178.3, 190.6, 194.7, 199.7. IR (neat) 2064, 1998, 1979, 1592, 1244 cm^{–1}. HRMS (FAB) *m/z* calcd for C₂₁H₂₁NO₃SiRu: 465.0334, found 465.0339.

X-ray Data for Ru(vinylsilane) Complex 6.

Table 1. Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	B_{eq}
Ru(1)	0.22508(9)	0.45043(8)	0.22893(8)	4.86(2)
Si(1)	0.3209(3)	0.7312(3)	0.2875(3)	5.13(6)
O(1)	0.247(1)	0.276(1)	0.011(1)	10.3(3)
O(2)	-0.1184(9)	0.573(1)	0.3231(9)	9.0(2)
O(3)	0.258(1)	0.1474(8)	0.4726(8)	8.1(2)
N(1)	0.2102(8)	0.6728(7)	0.0627(7)	4.7(2)
C(1)	0.469(1)	0.442(1)	0.246(1)	6.0(2)
C(2)	0.378(1)	0.521(1)	0.337(1)	5.4(2)
C(3)	0.158(1)	0.801(1)	0.411(1)	7.0(3)
C(4)	0.477(1)	0.828(1)	0.281(1)	6.9(3)
C(5)	0.253(1)	0.7876(9)	0.0980(9)	5.0(2)
C(6)	0.244(1)	0.931(1)	-0.010(1)	6.1(2)
C(7)	0.194(1)	0.961(1)	-0.148(1)	7.4(3)
C(8)	0.150(1)	0.848(1)	-0.178(1)	6.8(3)
C(9)	0.160(1)	0.709(1)	-0.072(1)	5.8(2)
C(10)	0.237(1)	0.345(1)	0.088(1)	6.8(3)
C(11)	0.009(1)	0.527(1)	0.287(1)	6.1(2)
C(12)	0.245(1)	0.266(1)	0.378(1)	5.8(2)
H(1)	0.502(1)	0.489(1)	0.148(1)	7.0(3)
H(2)	0.546(1)	0.331(1)	0.281(1)	7.0(3)
H(3)	0.406(1)	0.460(1)	0.407(1)	6.5(2)
H(4)	0.196(1)	0.776(1)	0.506(1)	8.6(3)
H(5)	0.077(1)	0.753(1)	0.417(1)	8.6(3)
H(6)	0.120(1)	0.909(1)	0.373(1)	8.6(3)
H(7)	0.515(1)	0.802(1)	0.376(1)	8.7(3)
H(8)	0.561(1)	0.794(1)	0.219(1)	8.7(3)
H(9)	0.438(1)	0.937(1)	0.244(1)	8.7(3)
H(10)	0.294(1)	1.015(1)	0.001(1)	7.2(3)
H(11)	0.184(1)	1.058(1)	-0.231(1)	8.5(3)
H(12)	0.126(1)	0.863(1)	-0.267(1)	8.1(3)
H(13)	0.122(1)	0.632(1)	-0.082(1)	6.9(3)

$$B_{eq} = 8/3\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos \gamma + 2U_{13}(aa^*cc^*)\cos \beta + 2U_{23}(bb^*cc^*)\cos \alpha$$

Table 2. Anisotropic Displacement Parameters

atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Ru(1)	0.0700(5)	0.0544(4)	0.0662(4)	-0.0240(3)	0.0008(3)	-0.0205(3)
Si(1)	0.075(2)	0.061(1)	0.067(1)	-0.026(1)	-0.006(1)	-0.021(1)
O(1)	0.19(1)	0.098(6)	0.121(7)	-0.050(6)	0.011(6)	-0.060(5)
O(2)	0.078(5)	0.142(7)	0.099(6)	-0.018(5)	0.017(4)	-0.023(5)
O(3)	0.133(7)	0.070(4)	0.097(5)	-0.031(4)	-0.012(5)	-0.010(4)
N(1)	0.070(4)	0.062(4)	0.054(4)	-0.024(3)	0.002(3)	-0.023(3)
C(1)	0.067(5)	0.066(5)	0.091(7)	-0.017(4)	-0.003(5)	-0.017(5)
C(2)	0.071(5)	0.059(5)	0.074(6)	-0.018(4)	-0.008(4)	-0.018(4)
C(3)	0.100(8)	0.089(7)	0.084(7)	-0.029(6)	0.007(6)	-0.035(6)
C(4)	0.090(7)	0.086(7)	0.100(8)	-0.037(6)	-0.014(6)	-0.031(6)
C(5)	0.072(5)	0.056(4)	0.070(5)	-0.025(4)	0.005(4)	-0.025(4)
C(6)	0.087(6)	0.060(5)	0.080(6)	-0.027(5)	-0.004(5)	-0.005(4)
C(7)	0.104(8)	0.080(7)	0.087(7)	-0.023(6)	-0.009(6)	-0.011(6)
C(8)	0.107(8)	0.084(7)	0.065(6)	-0.021(6)	-0.003(5)	-0.024(5)
C(9)	0.081(6)	0.073(6)	0.065(5)	-0.014(5)	-0.004(5)	-0.024(4)
C(10)	0.123(9)	0.068(6)	0.081(6)	-0.039(6)	0.003(6)	-0.032(5)
C(11)	0.078(6)	0.086(6)	0.069(6)	-0.030(5)	-0.008(5)	-0.014(5)
C(12)	0.089(7)	0.061(5)	0.080(6)	-0.024(5)	-0.002(5)	-0.028(5)

The general temperature factor expression: $\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table 3. Bond lengths (Å)

atom	atom	distance	atom	atom	distance
Ru(1)	N(1)	2.184(6)	Ru(1)	C(1)	2.182(9)
Ru(1)	C(2)	2.184(8)	Ru(1)	C(10)	1.92(1)
Ru(1)	C(11)	1.94(1)	Ru(1)	C(12)	1.86(1)
C(1)	H(1)	0.96	C(1)	H(2)	1.05
C(2)	H(3)	0.75	C(3)	H(4)	0.95
C(3)	H(5)	0.95	C(3)	H(6)	0.95
C(4)	H(7)	0.95	C(4)	H(8)	0.95
C(4)	H(9)	0.95	C(6)	H(10)	1.06
C(7)	H(11)	0.99	C(8)	H(12)	0.88(1)
C(9)	H(13)	0.93			

Table 4. Bond angles (°)

atom	atom	atom	angle	atom	atom	atom	angle
N(1)	Ru(1)	C(1)	86.5(3)	N(1)	Ru(1)	C(2)	85.2(3)
C(1)	Ru(1)	C(2)	36.8(3)	N(1)	Ru(1)	C(10)	93.1(3)
C(1)	Ru(1)	C(10)	102.9(4)	C(2)	Ru(1)	C(10)	139.7(4)
N(1)	Ru(1)	C(11)	89.0(3)	C(1)	Ru(1)	C(11)	146.8(4)
C(2)	Ru(1)	C(11)	110.0(4)	C(10)	Ru(1)	C(11)	110.2(4)
N(1)	Ru(1)	C(12)	175.9(3)	C(1)	Ru(1)	C(12)	90.6(4)
C(2)	Ru(1)	C(12)	90.8(4)	C(10)	Ru(1)	C(12)	90.3(4)
C(11)	Ru(1)	C(12)	91.9(4)	Ru(1)	N(1)	C(5)	118.6(5)
Ru(1)	N(1)	C(9)	124.3(6)	Ru(1)	C(1)	C(2)	71.7(5)
Ru(1)	C(1)	H(1)	103.8(3)	C(2)	C(1)	H(1)	124.7(5)
Ru(1)	C(1)	H(2)	116.2(2)	C(2)	C(1)	H(2)	124.7(5)
H(1)	C(1)	H(2)	107.10(1)	Ru(1)	C(2)	Si(1)	108.0(4)
Ru(1)	C(2)	C(1)	71.5(5)	Ru(1)	C(2)	H(3)	110.7(2)
Si(1)	C(2)	H(3)	132.0(3)	C(1)	C(2)	H(3)	96.0(5)
Si(1)	C(3)	H(4)	110.1(3)	Si(1)	C(3)	H(5)	109.4(3)
H(4)	C(3)	H(5)	109.47(1)	Si(1)	C(3)	H(6)	108.8(3)
H(4)	C(3)	H(6)	109.47(1)	H(5)	C(3)	H(6)	109.47(1)
Si(1)	C(4)	H(7)	110.5(3)	Si(1)	C(4)	H(8)	108.1(3)
H(7)	C(4)	H(8)	109.5	Si(1)	C(4)	H(9)	109.8(3)
H(7)	C(4)	H(9)	109.47(1)	H(8)	C(4)	H(9)	109.47(1)
C(5)	C(6)	H(10)	122.7(5)	C(7)	C(6)	H(10)	114.2(6)
C(6)	C(7)	H(11)	127.9(6)	C(8)	C(7)	H(11)	114.2(6)
C(7)	C(8)	H(12)	118.5(6)	C(9)	C(8)	H(12)	121.8(6)
N(1)	C(9)	H(13)	111.3(5)	C(8)	C(9)	H(13)	123.4(6)
Ru(1)	C(10)	O(1)	176.6(1)	Ru(1)	C(11)	O(2)	178.6(9)
Ru(1)	C(12)	O(3)	179.5(8)				

Table 5. Torsion Angles(°)

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
C(1)	Ru(1)	N(1)	C(5)	-55.0(1)	C(1)	Ru(1)	N(1)	C(9)	126.2(1)
C(2)	Ru(1)	N(1)	C(5)	-18.2(1)	C(2)	Ru(1)	N(1)	C(9)	163.1(1)
C(10)	Ru(1)	N(1)	C(5)	-157.8(1)	C(10)	Ru(1)	N(1)	C(9)	23.4(2)
C(11)	Ru(1)	N(1)	C(5)	92.0(1)	C(11)	Ru(1)	N(1)	C(9)	-86.8(2)
C(12)	Ru(1)	N(1)	C(5)	-10.4(2)	C(12)	Ru(1)	N(1)	C(9)	170.8(2)
N(1)	Ru(1)	C(1)	C(2)	86.5(1)	C(2)	Ru(1)	C(1)	C(2)	0.0(7)
C(10)	Ru(1)	C(1)	C(2)	178.9(2)	C(11)	Ru(1)	C(1)	C(2)	3.7(3)
C(12)	Ru(1)	C(1)	C(2)	-90.6(1)	N(1)	Ru(1)	C(2)	Si(1)	28.9(1)
N(1)	Ru(1)	C(2)	C(1)	-90.7(1)	C(1)	Ru(1)	C(2)	Si(1)	119.6(2)
C(1)	Ru(1)	C(2)	C(1)	0.0(8)	C(10)	Ru(1)	C(2)	Si(1)	118.0(2)
C(10)	Ru(1)	C(2)	C(1)	-1.6(2)	C(11)	Ru(1)	C(2)	Si(1)	-58.3(2)
C(11)	Ru(1)	C(2)	C(1)	-177.8(2)	C(12)	Ru(1)	C(2)	Si(1)	-150.6(1)
C(12)	Ru(1)	C(2)	C(1)	89.8(1)	N(1)	Ru(1)	C(10)	O(1)	156.3(3)
C(1)	Ru(1)	C(10)	O(1)	69.2(3)	C(2)	Ru(1)	C(10)	O(1)	70.1(3)
C(11)	Ru(1)	C(10)	O(1)	-113.6(3)	C(12)	Ru(1)	C(10)	O(1)	-21.5(3)
N(1)	Ru(1)	C(11)	O(2)	-83.3(7)	C(1)	Ru(1)	C(11)	O(2)	-1.3(7)
C(2)	Ru(1)	C(11)	O(2)	1.1(7)	C(10)	Ru(1)	C(11)	O(2)	-176.3(7)
C(12)	Ru(1)	C(11)	O(2)	92.7(7)	N(1)	Ru(1)	C(12)	O(3)	-140.9(2)
C(1)	Ru(1)	C(12)	O(3)	-96.4(2)	C(2)	Ru(1)	C(12)	O(3)	-133.2(2)
C(10)	Ru(1)	C(12)	O(3)	6.5(2)	C(11)	Ru(1)	C(12)	O(3)	116.7(2)
C(3)	Si(1)	C(2)	Ru(1)	85.8(1)	C(3)	Si(1)	C(2)	C(1)	165.1(1)
C(4)	Si(1)	C(2)	Ru(1)	-150.3(1)	C(4)	Si(1)	C(2)	C(1)	-71.0(2)
C(5)	Si(1)	C(2)	Ru(1)	-32.8(1)	C(5)	Si(1)	C(2)	C(1)	46.5(2)
C(2)	Si(1)	C(5)	N(1)	21.4(2)	C(2)	Si(1)	C(5)	C(6)	-157.7(1)
C(3)	Si(1)	C(5)	N(1)	-97.4(2)	C(3)	Si(1)	C(5)	C(6)	83.5(2)
C(4)	Si(1)	C(5)	N(1)	145.3(1)	C(4)	Si(1)	C(5)	C(6)	-33.9(2)
Ru(1)	N(1)	C(5)	Si(1)	0.5(9)	Ru(1)	N(1)	C(5)	C(6)	179.7(8)
C(9)	N(1)	C(5)	Si(1)	179.4(1)	C(9)	N(1)	C(5)	C(6)	-1.4(2)
Ru(1)	N(1)	C(9)	C(8)	-179.9(9)	C(5)	N(1)	C(9)	C(8)	1.3(2)
Ru(1)	C(1)	C(2)	Ru(1)	0.00(6)	Ru(1)	C(1)	C(2)	Si(1)	-99.9(9)
Si(1)	C(5)	C(6)	C(7)	179.5(9)	N(1)	C(5)	C(6)	C(7)	0.4(2)
C(5)	C(6)	C(7)	C(8)	0.8(2)	C(6)	C(7)	C(8)	C(9)	-1.0(2)
C(7)	C(8)	C(9)	N(1)	-0.1(2)

**¹³C NMR of 1d
(75 MHz, CDCl₃)**

¹³C NMR of 2
(75 MHz, CDCl₃)

¹³C NMR of 3
(75 MHz, CDCl₃)

¹³C NMR of 5a
(75 MHz, CDCl₃)

**¹³C NMR of 5b
(75 MHz, CDCl₃)**

**¹³C NMR of 5c
(75 MHz, CDCl₃)**

**¹³C NMR of 5d
(100 MHz, CDCl₃)**

**¹³C NMR of 5e
(75 MHz, CDCl₃)**

¹³C NMR of 5e'
(125 MHz, CDCl₃)

**¹³C NMR of 5f
(75 MHz, CDCl₃)**

**¹³C NMR of 5h
(75 MHz, CDCl₃)**

**¹³C NMR of 5i
(75 MHz, CDCl₃)**

**¹³C NMR of 5j
(75 MHz, CDCl₃)**

**¹³C NMR of 5k
(75 MHz, CDCl₃)**

**¹³C NMR of 5I
(75 MHz, CDCl₃)**

**¹³C NMR of 5m
(75 MHz, CDCl₃)**

¹³C NMR of 5n
(75 MHz, CDCl₃)

¹³C NMR of 5n'
(75 MHz, CDCl₃)

¹³C NMR of 5o
(75 MHz, CDCl₃)

¹³C NMR of 5p
(100 MHz, CDCl₃)

**¹³C NMR of 5aa
(75 MHz, CDCl₃)**

**¹³C NMR of 5ae
(75 MHz, CDCl₃)**

**¹³C NMR of 5'ae
(75 MHz, CDCl₃)**

¹³C NMR of 5af
(125 MHz, CDCl₃)

**¹³C NMR of 5bf
(125 MHz, CDCl₃)**

**¹³C NMR of 5ce
(75 MHz, CDCl₃)**

**¹³C NMR of 5'ce
(75 MHz, CDCl₃)**

¹³C NMR of 6
(75 MHz, CDCl₃)

**¹³C NMR of 7
(75 MHz, CDCl₃)**

¹³C NMR of 8
(100 MHz, CDCl₃)