## **Supporting information**

# An insight into regioselectivity in the formation of ruthenacycle

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# 1. Time course for reaction of 1-cyclohexylhex-1-yne (2h) with methyl (*E*)-penta-2,4-dienoate (3a)

1-Cyclohexylhex-1-yne (**2h**) (23.0 µl, 0.119 mmol) was placed in an NMR tube under nitrogen atmosphere, and C<sub>6</sub>D<sub>6</sub> (600 µL) was added. To the solution was added methyl (*E*)-penta-2,4-dienoate (**3a**) (14.0 µL, 0.117 mmol) by a hypodermic syringe at room temperature. [Ru( $\eta^6$ -naphthalene)( $\eta^4$ -1,5-cod)] (**1**) (3.97 mg, 0.0118 mmol) was added in the solution under nitrogen atmosphere. The mixture was allowed to react at room temperature for 210 min, during which the reaction was monitored by H NMR spectroscopy. In order to determine the yield of the product, dibenzyl (5.21 mg, 0.0286 mmol) was added into the solution as an internal standard.

The time course of this reaction was shown Fig S1. The time course curves for the catalytic reaction of **2h** with **3a** the **4ha/5ha** ratio is almost constant. According to these facts, formation of **4ha** and **5ha** was considered to be a parallel reaction.



Figure S1. Time course for reaction of 2h with 3a giving 4ha and 5ha.



Figure S2. <sup>1</sup>H NMR Spectrum of 4aa and 5aa in CDCl<sub>3</sub>.



Figure S3.<sup>13</sup>C{<sup>1</sup>H} NMR Spectrum of 4aa and 5aa in CDCl<sub>3</sub>.



Figure S4. <sup>1</sup>H-<sup>1</sup>H COSY NMR Spectrum of 4aa and 5aa in CDCl<sub>3</sub>.



Figure S5. <sup>1</sup>H-<sup>1</sup>H pNOESY NMR Spectrum of 4aa and 5aa in CDCl<sub>3</sub>.



Figure S6. <sup>13</sup>C-<sup>1</sup>H Correlation Spectrum of 4aa and 5aa in CDCl<sub>3</sub>.



Figure S7-1. HRMS (APCI) data for 4aa and 5aa.



Figure S7-2. HRMS (APCI) data for 4aa and 5aa.



Figure S8. <sup>1</sup>H NMR Spectrum of 4ba in CDCl<sub>3</sub>.



Figure S9. <sup>13</sup>C{<sup>1</sup>H} NMR Spectrum of 4ba in CDCl<sub>3</sub>.



Figure S10. <sup>1</sup>H-<sup>1</sup>H COSY NMR Spectrum of 4ba in CDCl<sub>3</sub>.



Figure S11. <sup>1</sup>H-<sup>1</sup>H pNOESY NMR Spectrum of 4ba in CDCl<sub>3</sub>.



Figure S12-1. HRMS (APCI) data for 4ba.



Figure S12-2. HRMS (APCI) data for 4ba.



Figure S13. <sup>1</sup>H NMR Spectrum of 4ba and 5ba in CDCl<sub>3</sub>.



Figure S14. <sup>13</sup>C{<sup>1</sup>H} NMR Spectrum of 4ba and 5ba in CDCl<sub>3</sub>.



Figure S15. <sup>1</sup>H-<sup>1</sup>H COSY NMR Spectrum of 4ba and 5ba in CDCl<sub>3</sub>.



Figure S16. <sup>1</sup>H-<sup>1</sup>H pNOESY NMR Spectrum of 4ba and 5ba in CDCl<sub>3</sub>.



Figure S17. <sup>13</sup>C-<sup>1</sup>H Correlation Spectrum of 4ba and 5ba in CDCl<sub>3</sub>.



Figure S18. <sup>1</sup>H NMR Spectrum of 4ca and 5ca in CDCl<sub>3</sub>.



Figure S19. <sup>13</sup>C{<sup>1</sup>H} NMR Spectrum of 4ca and 5ca in CDCl<sub>3</sub>.



Figure S20. <sup>19</sup>F{<sup>1</sup>H} NMR Spectrum of 4ca and 5ca in CDCl<sub>3</sub>.



Figure S21. <sup>1</sup>H-<sup>1</sup>H COSY NMR Spectrum of 4ca and 5ca in CDCl<sub>3</sub>.



Figure S22. <sup>1</sup>H-<sup>1</sup>H pNOESY NMR Spectrum of 4ca and 5ca in CDCl<sub>3</sub>.



Figure S23. <sup>13</sup>C-<sup>1</sup>H Correlation Spectrum of 4ca and 5ca in CDCl<sub>3</sub>.



Figure S24. HRMS (APCI) data for 4ca and 5ca.



Figure S25. <sup>1</sup>H NMR Spectrum of 4da and 5da in CDCl<sub>3</sub>.



Figure S26. <sup>13</sup>C{<sup>1</sup>H} NMR Spectrum of 4da and 5da in CDCl<sub>3</sub>.



Figure S27.<sup>1</sup>H-<sup>1</sup>H COSY NMR Spectrum of 4da and 5da in CDCl<sub>3</sub>.



Figure S28. <sup>1</sup>H-<sup>1</sup>H pNOESY NMR Spectrum of 4da and 5da in CDCl<sub>3</sub>.



Figure S29. <sup>13</sup>C-<sup>1</sup>H Correlation Spectrum of 4da and 5da in CDCl<sub>3</sub>.



Figure S30. HRMS (APCI) data for 4da and 5da.



Figure S31. <sup>1</sup>H NMR Spectrum of 4ea and 5ea in CDCl.



Figure S32. <sup>13</sup>C{<sup>1</sup>H} NMR Spectrum of 4ea and 5ea in CDCl<sub>3</sub>.



Figure S33. <sup>1</sup>H-<sup>1</sup>H COSY NMR Spectrum of 4ea and 5ea in CDCl<sub>3</sub>.



Figure S34. <sup>1</sup>H-<sup>1</sup>H pNOESY NMR Spectrum of 4ea and 5ea in CDCl<sub>3</sub>.



Figure S35. <sup>13</sup>C-<sup>1</sup>H Correlation Spectrum of 4ea and 5ea in CDCl<sub>3</sub>.



Figure S36. HRMS (APCI) data for 4ea and 5ea in CDCl<sub>3</sub>.



Figure S37. <sup>1</sup>H NMR Spectrum of 4ab and 5ab in C<sub>6</sub>D<sub>6</sub>.



Figure S38. <sup>13</sup>C{<sup>1</sup>H} NMR Spectrum of 4ab and 5ab in C<sub>6</sub>D<sub>6</sub>.



Figure S39. <sup>1</sup>H-<sup>1</sup>H COSY NMR Spectrum of 4ab and 5ab in C<sub>6</sub>D<sub>6</sub>.



Figure S40. <sup>1</sup>H-<sup>1</sup>H pNOESY NMR Spectrum of 4ab and 5ab in C<sub>6</sub>D<sub>6</sub>.



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Figure S41. HRMS (APCI) data for 4ab and 5ab.



Figure S42. <sup>1</sup>H NMR Spectrum of 4bb and 5bb in C<sub>6</sub>D<sub>6</sub>.



Figure S43. <sup>13</sup>C{<sup>1</sup>H} NMR Spectrum of 4bb and 5bb in C<sub>6</sub>D<sub>6</sub>.



Figure S44. <sup>1</sup>H-<sup>1</sup>H COSY NMR Spectrum of 4bb and 5bb in C<sub>6</sub>D<sub>6</sub>.



Figure S45. <sup>1</sup>H-<sup>1</sup>H pNOESY NMR Spectrum of 4bb and 5bb in C<sub>6</sub>D<sub>6</sub>.



Figure S46. HRMS (APCI) data for 4bb and 5bb.



Figure S47. <sup>1</sup>H NMR Spectrum of 4db and 5db in C<sub>6</sub>D<sub>6</sub>.



Figure S48. <sup>13</sup>C{<sup>1</sup>H} NMR Spectrum of 4db and 5db in C<sub>6</sub>D<sub>6</sub>.



Figure S49. <sup>1</sup>H-<sup>1</sup>H COSY NMR Spectrum of 4db and 5db in C<sub>6</sub>D<sub>6</sub>.



Figure S50. <sup>1</sup>H-<sup>1</sup>H NOESY NMR Spectrum of 4db and 5db in C<sub>6</sub>D<sub>6</sub>.



Figure S51. <sup>13</sup>C-<sup>1</sup>H Correlation Spectrum of 4db and 5db in C<sub>6</sub>D<sub>6</sub>.



Figure S52. HRMS (APCI) data for 4db and 5db.



Figure S53. <sup>1</sup>H NMR Spectrum of 4eb and 5eb in C<sub>6</sub>D<sub>6</sub>.



Figure S54. <sup>13</sup>C{<sup>1</sup>H} NMR Spectrum of 4eb and 5eb in C<sub>6</sub>D<sub>6</sub>.



Figure S55. <sup>1</sup>H-<sup>1</sup>H COSY NMR Spectrum of 4eb and 5eb in C<sub>6</sub>D<sub>6</sub>.



Figure S56. <sup>1</sup>H-<sup>1</sup>H NOESY NMR Spectrum of 4eb and 5eb in C<sub>6</sub>D<sub>6</sub>.

	M	ass Spectrum	SmartFormu	la Report		
Analysis Info Analysis Name Method Sample Name Comment	D:\Data\HiranoLab\SAY1555.d apci_pos_wide_low_140605.m SAY1555		Acquisition Date Operator Instrument / Ser#	6/11/2019 1:48:59 Pf BDAL micrOTOF-Q II	10323	
Acquisition Paramet Source Type Focus Scan Begin Scan End	APCI Not active 100 miz 2000 m/z	ion Polarity Set Capillary Set End Plate Offset Set Collision Cell RF	Positive 4500 V -500 V 150.0 Vpp	Set Nebulizer Set Dry Heater Set Dry Gas Set Divert Valve	1.6 Bar 200 °C 3.0 l/min Waste	
197,0989	353,1905					+MS, 0.9min #52

Meas. m/z # Formula Score m/z err [mDa] err [ppm] mSigma rdb e Conf N-Rule 353.1905 1 C 26 H 25 O 100.00 353.1900 -0.5 -1.5 3.7 14.5 even ok

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Figure S57. HRMS (APCI) data for 4eb and 5eb.



Figure S58. <sup>1</sup>H NMR Spectrum of 4ga and 5ga in CDCl<sub>3</sub>.



Figure S59. <sup>13</sup>C{<sup>1</sup>H} NMR Spectrum of 4ga and 5ga in CDCl<sub>3</sub>.



Figure S60. <sup>1</sup>H-<sup>1</sup>H COSY NMR Spectrum of 4ga and 5ga in CDCl<sub>3</sub>.



Figure S61. <sup>1</sup>H-<sup>1</sup>H pNOESY NMR Spectrum of 4ga and 5ga in CDCl<sub>3</sub>.



Figure S62. <sup>13</sup>C-<sup>1</sup>H Correlation Spectrum of 4ga and 5ga in CDCl<sub>3</sub>.



Figure S63. HRMS (APCI) data for 4ga and 5ga.



Figure S64. <sup>1</sup>H NMR Spectrum of 4ha and 5ha in C<sub>6</sub>D<sub>6</sub>.



Figure S65. <sup>13</sup>C{<sup>1</sup>H} NMR Spectrum of 4ha and 5ha in C<sub>6</sub>D<sub>6</sub>.



Figure S66. <sup>13</sup>C-<sup>1</sup>H Correlation Spectrum of 4ea and 5ea in C<sub>6</sub>D<sub>6</sub>.



Figure S67. <sup>1</sup>H-<sup>1</sup>H pNOESY NMR Spectrum of 4ha and 5ha in C<sub>6</sub>D<sub>6</sub>.



Figure S68. <sup>13</sup>C-<sup>1</sup>H Correlation Spectrum of 4ha and 5ha in C<sub>6</sub>D<sub>6</sub>.



Figure S69. HRMS (APCI) data for 4ha and 5ha.



Figure S70. <sup>1</sup>H NMR Spectrum of 4ia and 5ia in C<sub>6</sub>D<sub>6</sub>.



Figure S71.  $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$  NMR Spectrum of 4ia and 5ia in  $\mathrm{C}_{6}\mathrm{D}_{6}.$ 



Figure S72. <sup>1</sup>H-<sup>1</sup>H COSY NMR Spectrum of 4ia and 5ia in C<sub>6</sub>D<sub>6</sub>.



Figure S73. <sup>1</sup>H-<sup>1</sup>H pNOESY NMR Spectrum of 4ia and 5ia in C<sub>6</sub>D<sub>6</sub>.



Figure S74. <sup>13</sup>C-<sup>1</sup>H Correlation Spectrum of 4ia and 5ia in C<sub>6</sub>D<sub>6</sub>.

Analysis Info Analysis Name Method Sample Name Comment	D:Data\HiranoLab\SAY1485R-1.d apci_pos_wide_low_140605.m SAY1485R		anoLab\SAY1485R-1.d iride_low_140605.m		6/11/2019 2:00:24 Pf BDAL micrOTOF-Q II	M 10323
Acquisition Paramet Source Type Focus Scan Begin Scan End	er APCI Not active 100 m/z 2000 m/z	ion Polarity Set Capillary Set End Plate Offset Set Collision Cell RF	Positive 4500 ∨ -500 ∨ 150.0 ∨pp	Set Nebulizer Set Dry Heater Set Dry Gas Set Divert Valve	1.6 Bar 200 °C 3.0 l/min Waste	+MS, 1.0mi
227.10	85 335 1632					

 Meas. m/z
 # Formula
 Score
 m/z
 err [mDa]
 err [ppm]
 mSigma
 rdb
 e<sup>-</sup> Conf
 N-Rule

 251.2014
 1
 C 16 H 27 O 2
 100.00
 251.2006
 -0.8
 -3.2
 32.6
 3.5
 even
 ok

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Figure S75-1. HRMS (APCI) data for 4ia and 5ia.



Figure S75-2. HRMS (APCI) data for 4ia and 5ia.



Figure S76. <sup>1</sup>H NMR Spectrum of 4ja and 5ja in C<sub>6</sub>D<sub>6</sub>.



Figure S77. <sup>13</sup>C{<sup>1</sup>H} NMR Spectrum of 4ja and 5ja in C<sub>6</sub>D<sub>6</sub>.



Figure S78. <sup>1</sup>H-<sup>1</sup>H COSY NMR Spectrum of 4ja and 5ja in C<sub>6</sub>D<sub>6</sub>.



Figure S79. <sup>1</sup>H-<sup>1</sup>H pNOESY NMR Spectrum of 4ja and 5ja in C<sub>6</sub>D<sub>6</sub>.



Figure S80. <sup>13</sup>C-<sup>1</sup>H Correlation Spectrum of 4ja and 5ja in C<sub>6</sub>D<sub>6</sub>.



Figure S81. HRMS (APCI) data for 4ja and 5ja.



Figure S82. <sup>1</sup>H NMR Spectrum of 4ka and 5ka in C<sub>6</sub>D<sub>6</sub>.



Figure S83. <sup>13</sup>C{<sup>1</sup>H} NMR Spectrum of 4ka and 5ka in C<sub>6</sub>D<sub>6</sub>.



Figure S84. <sup>1</sup>H-<sup>1</sup>H COSY NMR Spectrum of 4ka and 5ka in C<sub>6</sub>D<sub>6</sub>.



Figure S85. <sup>1</sup>H-<sup>1</sup>H pNOESY NMR Spectrum of 4ka and 5ka in C<sub>6</sub>D<sub>6</sub>.



Figure S86. <sup>13</sup>C-<sup>1</sup>H Correlation Spectrum of 4ka and 5ka in C<sub>6</sub>D<sub>6</sub>.

			Mas	s Spec	ctrum S	SmartF	orn	nula F	Report				
Analysis Info Analysis Name Method Sample Name Comment	D:\Data\HiranoL apci_pos_wide_ SAY1493R-1	.ab\SAY14 low_1406	193R-1.d 05.m						Acquisitio Operator Instrumer	n Date nt / Ser#	6/11/2019 2: BDAL micrOTOF-C	:17:33 PN 2 II	10323
Acquisition Paramete Source Type Socue Scan Begin Scan End	r APCI Not active 100 m/z 2000 m/z		k S S	on Polarity et Capillary et End Plate et Collision C	Offset ell RF	Positive 4500 V -500 V 150.0 V	e /pp			et Nebulizer et Dry Heater et Dry Gas et Divert Valve		1.6 Bar 200 °C 3.0 l/min Waste	
167.0879	011 335.1658												
Meas. m/z 251.2011	# Formula 1 C16H27O2 2 C12H23N6	Score 100.00 11.10	m/z 251.2006 251.1979	ет [mDa] -0.6 -3.2	err [ppm] -2.2 -12.9	mSigma 16.0 25.1	rdb 3.5 4.5	e <sup>-</sup> Conf even even	N-Rule ok ok				
ruker Compass Data/	Analysis 4.0				printed:	6/11/	/2019	2:22:08	PM			Page 1	of 2

Figure S87. HRMS (APCI) data for 4ka and 5ka.



Figure S88. <sup>1</sup>H NMR Spectrum of 4ma in C<sub>6</sub>D<sub>6</sub>.



Figure S89. <sup>13</sup>C{<sup>1</sup>H} NMR Spectrum of 4ma in C<sub>6</sub>D<sub>6</sub>.

		mass spectrum	SmartFormu	па кероп		
Analysis Info			Acquisition Date	6/11/2019 1:23:38 P	M	
Analysis Name Method Sample Name Comment	D:\Data\HiranoLab\SAY1 apci_pos_wide_low_140 SAY1531R-B-2	531R-B-2.d 605.m	Operator Instrument / Ser#	BDAL micrOTOF-Q II	10323	
Acquisition Parame	ter	ine Beladiu	Destitue	Calible built are	16.8%	
Focus Scan Begin Scan End	Not active 100 miz 2000 miz	Set Capillary Set End Plate Offset Set Collision Cell RF	4500 V -500 V 150.0 Vpp	Set Dry Heater Set Dry Gas Set Divert Valve	200 °C 3.0 limin Waste	
						466, 2000 910
167.0887	335.1634					

Meas. m/z # Formula Score m/z err [mDa] err [ppm] mSigma rdb e Conf N-Rule 259.1320 1 C 16 H 19 O 3 100.00 259.1329 0.9 3.4 133.9 7.5 even ox

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Figure S90-1. HRMS (APCI) data for 4ma.



Figure S90-2. HRMS (APCI) data for 4ma.



Figure S91. <sup>1</sup>H NMR Spectrum of 5ma in C<sub>6</sub>D<sub>6</sub>.



Figure S92. <sup>13</sup>C{<sup>1</sup>H} NMR Spectrum of 5ma in C<sub>6</sub>D<sub>6</sub>.



Figure S93-1. HRMS (APCI) data for 5ma.



Figure S93-2. HRMS (APCI) data for 5ma.



Figure S94. <sup>1</sup>H NMR Spectrum of 4na and 5na in CDCl<sub>3</sub>.



Figure S95. <sup>1</sup>H NMR Spectrum of 4na and 5na in C<sub>6</sub>D<sub>6</sub>.



Figure S96. <sup>13</sup>C{<sup>1</sup>H} NMR Spectrum of 4na and 5na in C<sub>6</sub>D<sub>6</sub>.



Figure S97. <sup>1</sup>H-<sup>1</sup>H COSY NMR Spectrum of 4na and 5na in CDCl<sub>3</sub>.



Figure S98. <sup>1</sup>H-<sup>1</sup>H COSY NMR Spectrum of 4na and 5na in C<sub>6</sub>D<sub>6</sub>.



Figure S99. <sup>1</sup>H-<sup>1</sup>H pNOESY NMR Spectrum of 4na and 5na in CDCl<sub>3</sub>.



Figure S100. <sup>1</sup>H-<sup>1</sup>H pNOESY NMR Spectrum of 4na and 5na in C<sub>6</sub>D<sub>6</sub>.



Figure S101. <sup>13</sup>C-<sup>1</sup>H Correlation Spectrum of 4na and 5na in C<sub>6</sub>D<sub>6</sub>.



#### Figure S102. HRMS (APCI) data for 4na and 5na