Electronic Supplementary Information for

Non-redox metal ions can promote Wacker-type oxidations even better than copper(II): a new opportunity in catalyst design

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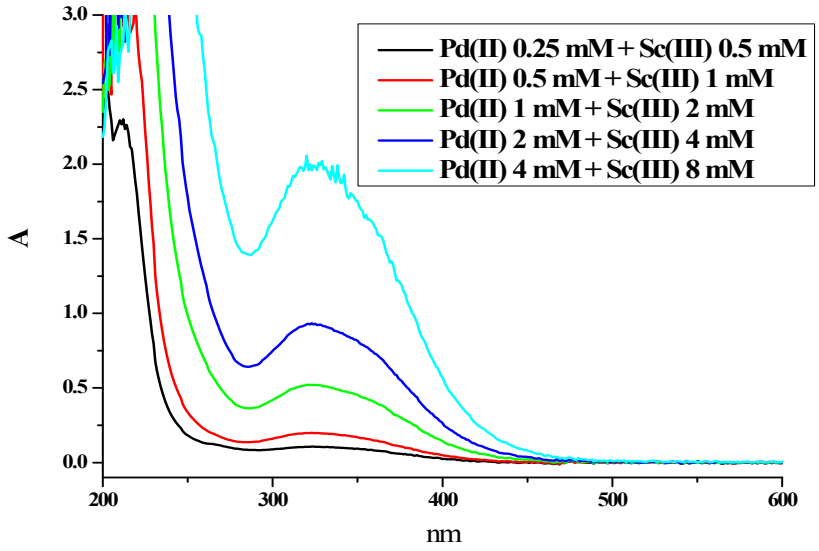


Figure S1. The UV- visible spectra of $Pd(OAc)_2/Sc(OTf)_3$ in acetonitrile under different concentrations.

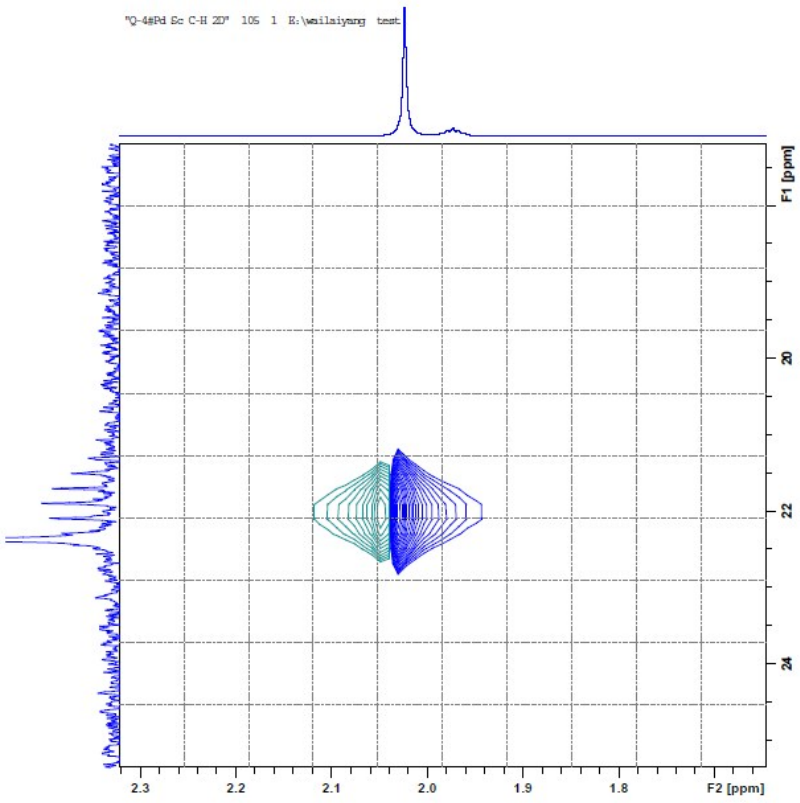


Figure S2. ^{1}H-^{13}C HSQC spectrum of $Pd(OAc)_2$ plus $Sc(OTf)_3$ in CD_3CN.

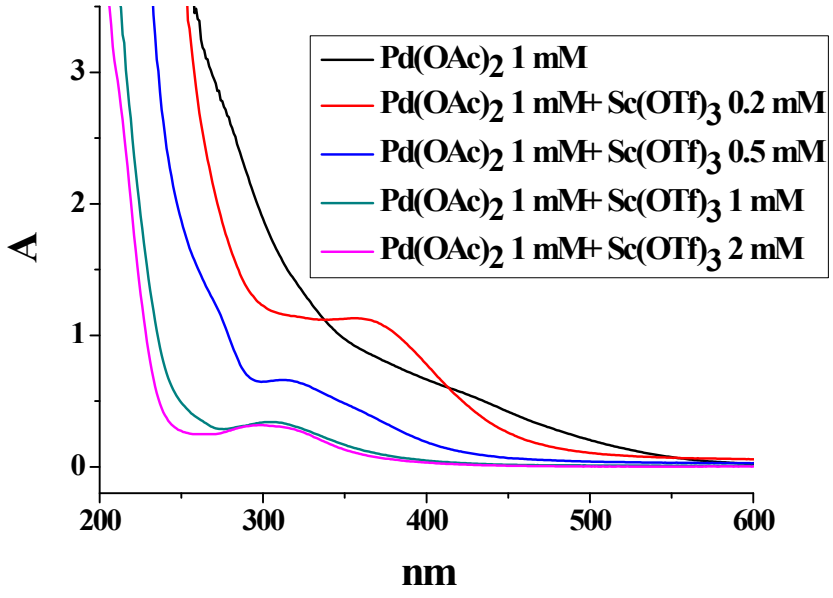


Figure S3. UV- visible spectra of $Pd(OAc)_2$ with different amount of $Sc(OTf)_3$.

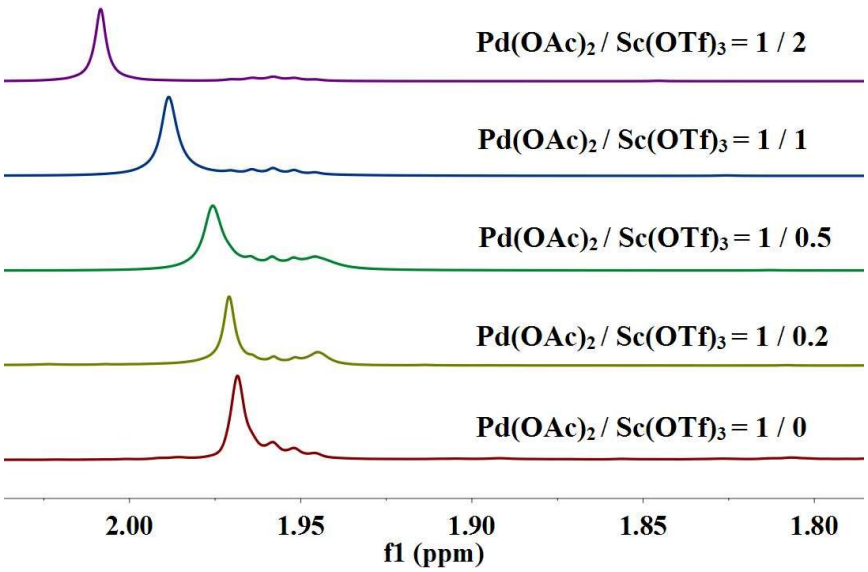


Figure S4. ^{1}H NMR spectra of $Pd(OAc)_2$ with different amount of $Sc(OTf)_3$.

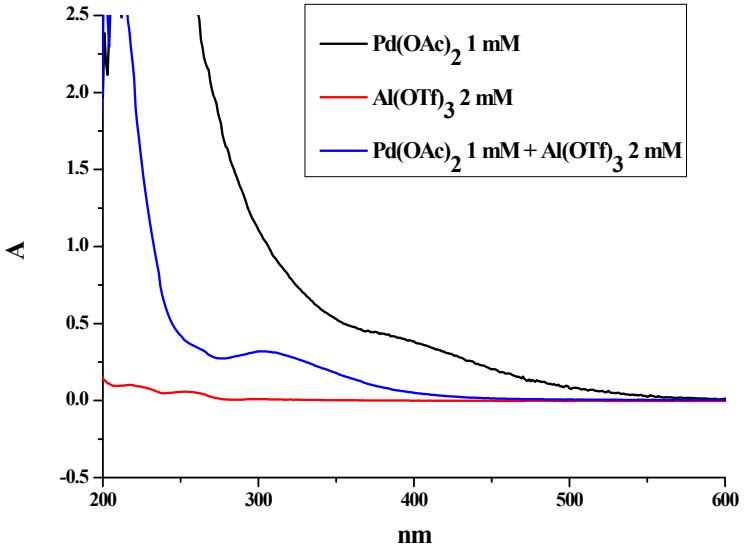


Figure S5. The UV- visible spectra of $Pd(OAc)_2/Al(OTf)_3$ in acetonitrile.

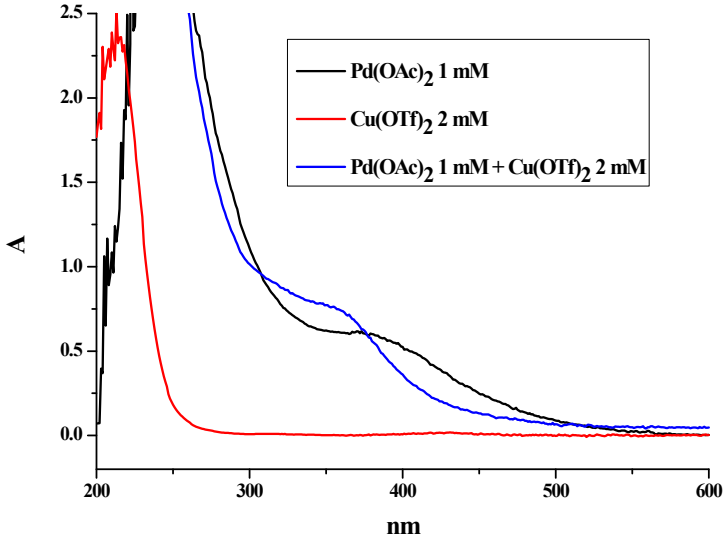
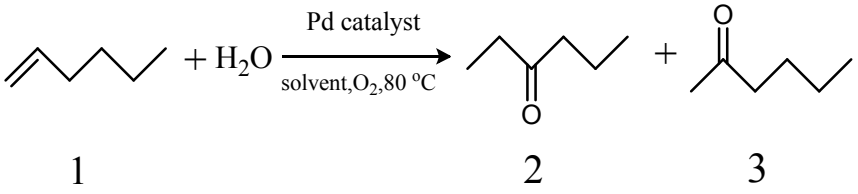


Figure S6 The UV- visible spectra of $Pd(OAc)_2/Cu(OTf)_2$ in acetonitrile.

Table S1 Optimization of Pd(II)-catalyzed 1-hexene oxidation under different solvent conditions[a]



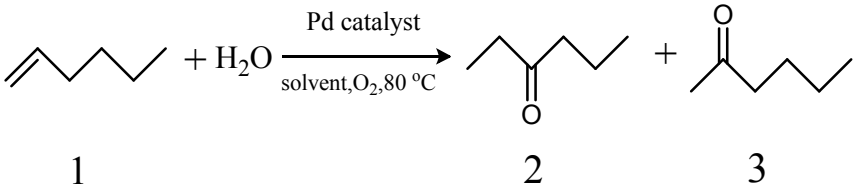
1 2 3

Entries	Catalyst	Additives	Solvent	Conv. [%]	Yield of 2 [%]	Yield of 3 [%]
1	$Pd(OAc)_2$	Sc $(OTf)_3$	DMF	28.3	trace	6.9
2	$Pd(OAc)_2$	Sc $(OTf)_3$	DMSO	23.0	trace	4.5
3	$Pd(OAc)_2$	Cu $(OTf)_2$	DMSO	21.9	trace	4.3
4	$Pd(OAc)_2$	Sc $(OTf)_3$	DMA	21.8	trace	11.8
5[b]	**$Pd(OAc)_2$**	**Sc $(OTf)_3$**	**CH_3CN**	**>99**	**29.3**	**53.1**
6[b]	$PdCl_2$	Sc $(OTf)_3$	CH_3CN	19.7	trace	3.9
7[b]	$Pd(OAc)_2$	Sc $(OTf)_3$	5 mL CH_3CN+ 0.2 mL DMSO	23.6	2.9	11.8
8[b]	$Pd(OAc)_2$	Sc $(OTf)_3$	5 mL CH_3CN+ 0.2 mL DMF	35.1	7.1	13.7
9[b]	$Pd(OAc)_2$	Sc $(OTf)_3$	5 mL CH_3CN+ 0.2 mL DMA	29.4	3.2	9.9

[a] Reaction conditions: solvent (5 mL), H_2O (0.2 mL),1-hexene (2 mmol), Pd(II) catalyst (0.02 mmol), $Sc(OTf)_3$ (0.04 mmol), O_2 (20 atm), 80 °C, 16 h.

[b] Reaction conditions: solvent (5 mL), H_2O (0.2 mL), 1-hexene (2 mmol), Pd(II) catalyst (0.02 mmol), $Sc(OTf)_3$ (0.04 mmol), O_2 (20 atm), 80 °C, 2 h.

Table S2 The influence of water content on Pd(II)/Sc(III)-catalyzed 1-hexene oxidation[a]

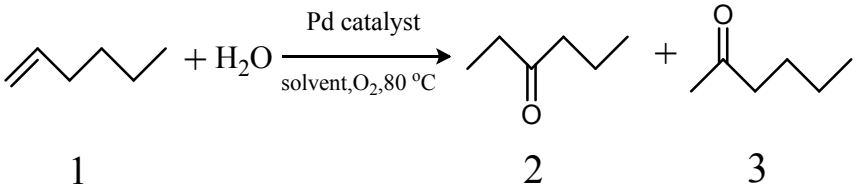


1 2 3

Entries	H_2O (mL)	Conv. [%]	Yield of 2 [%]	Yield of 3 [%]
1	-	15.1	trace	1.4
2	0.05	31.1	2.1	8.3
3	0.1	83.3	21.7	41.2
4	0.2	84.1	24.3	43.2
5	0.3	64.0	13.4	27.5
6	0.4	62.2	14.9	31.1

[a] Reaction conditions: CH_3CN (5 mL), 1-hexene (2 mmol), $Pd(OAc)_2$ (0.02 mmol), $Sc(OTf)_3$ (0.04 mmol), O_2 (20 atm), 60 °C, 5 h.

Table S3 The influence of Pd(II)/Sc(III) ratio on 1-hexene oxidation[a]



1 2 3

Entries	$Sc(OTf)_3$ (equiv)	Conv. (%)	Yield of 2 (%)	Yield of 3 (%)	Pd(0) black formation
1	-	13.7	trace	1.3	a lot
2	0.5	25.7	2.0	8.1	some
3	1	53.7	10.1	23.2	minor
4	2	78.1	20.7	40.9	none
5	3	98.2	28.8	53.3	none
6	4	99.3	29.1	54.2	none

[a] Reaction conditions: CH_3CN (5 mL), H_2O (0.2 mL), 1-hexene (2 mmol), $Pd(OAc)_2$ (0.02 mmol), O_2 (20 atm), 60 °C, 2 h.

Table S4 Lewis acid promoted Pd(II)-catalyzed 1-hexene isomerization under different conditions[a]

Entries	Catalyst	Lewis acid	Time	Conv./%	Internal olefin yield /%
1	$Pd(OAc)_2$	-	1 h	-	-
2	-	$Cu(OTf)_2$	1 h	-	-
3	-	$Sc(OTf)_3$	1 h	-	-
4	$Pd(OAc)_2$	$Sc(OTf)_3$	6 min	98.2	89.5
5	$Pd(OAc)_2$	$Cu(OTf)_2$	6 min	55.8	49.3

[a] Reaction conditions: CD_3CN (0.5 mL), $Pd(OAc)_2$ (4 mM), Lewis acid (8 mM), 1-hexene (40 mM), reaction performed in NMR tube at 25 °C.

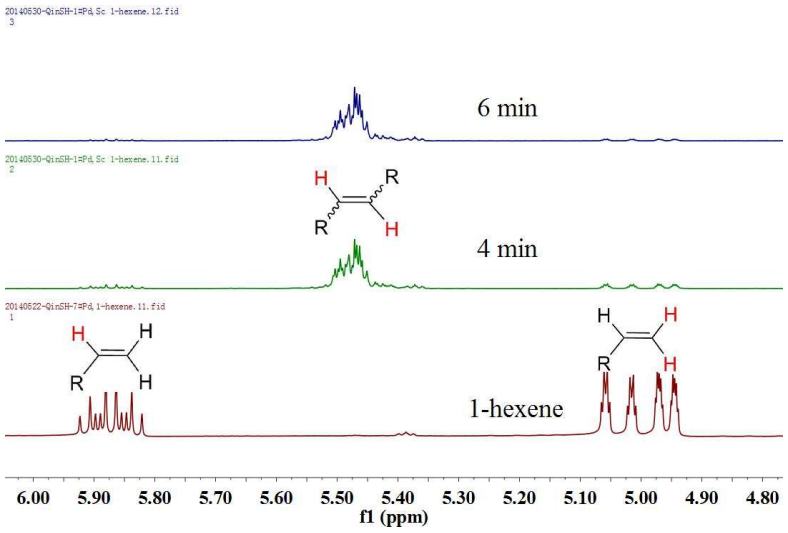


Figure S7-1 The ^1H NMR kinetics of olefinic bond in 1-hexene isomerization at 25 °C (0.5 mL of acetonitrile-d_3 containing 4 mM $Pd(OAc)_2$, 8 mM $Sc(OTf)_3$ and 40 mM 1-hexene).

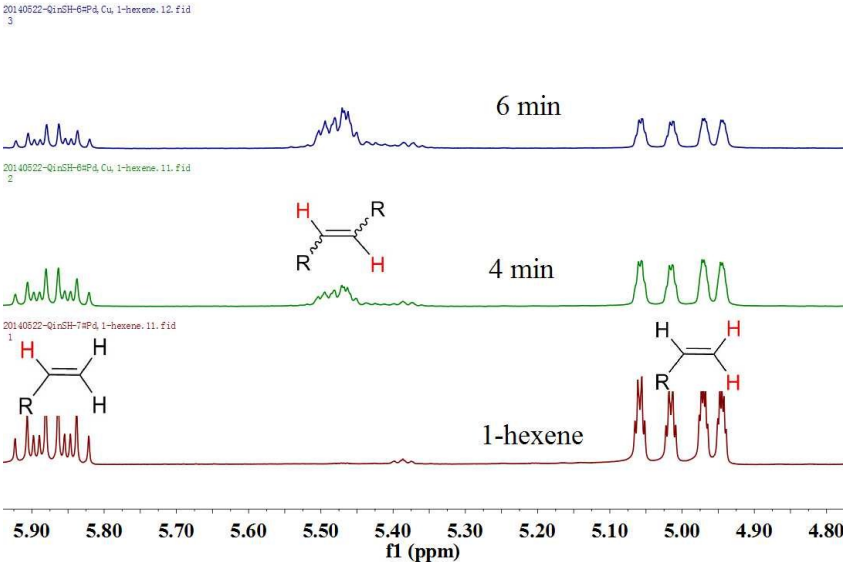


Figure S7-2 The ^{1}H NMR kinetics of olefinic bond in 1-hexene isomerization 25 ^{o}C (0.5 mL of acetonitrile-d_3 containing 4 mM $Pd(OAc)_2$, 8 mM $Cu(OTf)_2$ and 40 mM 1-hexene).

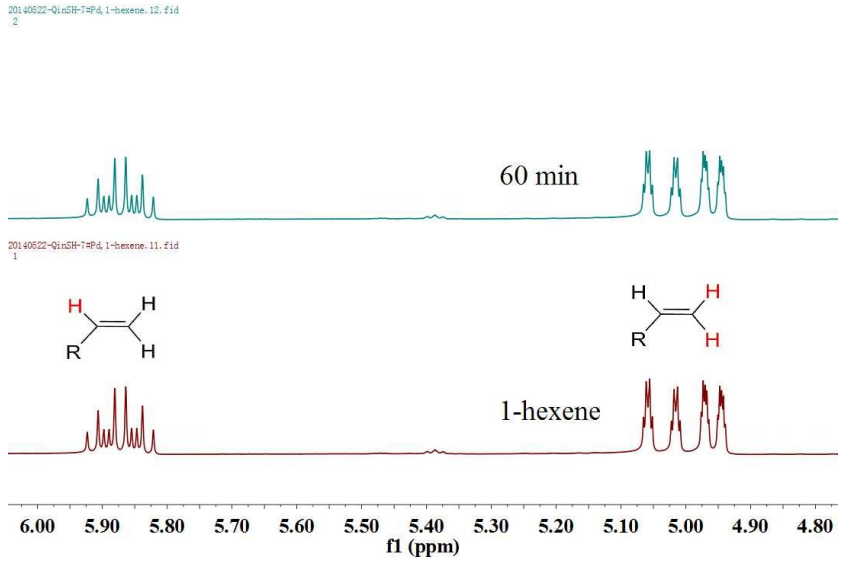


Figure S7-3 The ^{1}H NMR kinetics of olefinic bond in 1-hexene isomerization 25 ^{o}C (0.5 mL of acetonitrile-d_3 containing 4 mM $Pd(OAc)_2$ and 40 mM 1-hexene).

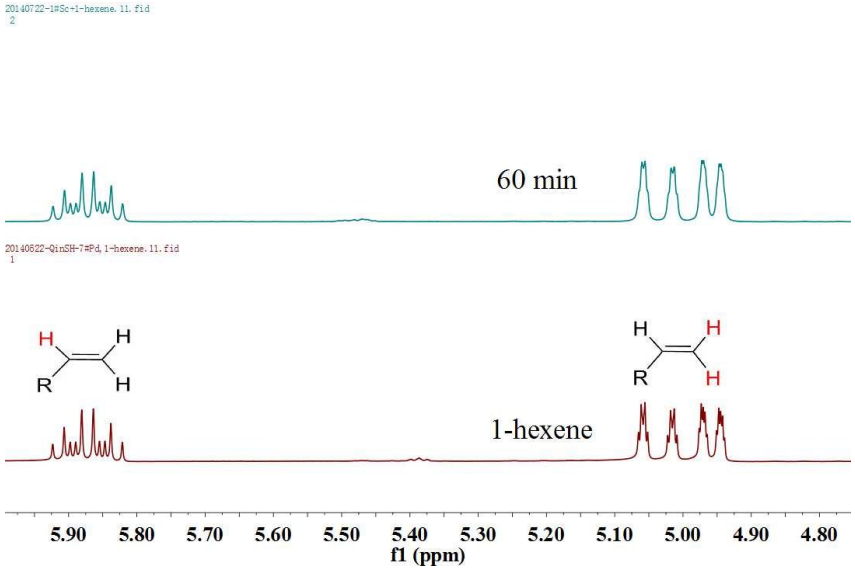


Figure S7-4 The ^{1}H NMR kinetics of olefinic bond in 1-hexene isomerization 25 ^{o}C (0.5 mL of acetonitrile-d_3 containing 8 mM $Sc(OTf)_3$ and 40 mM 1-hexene).

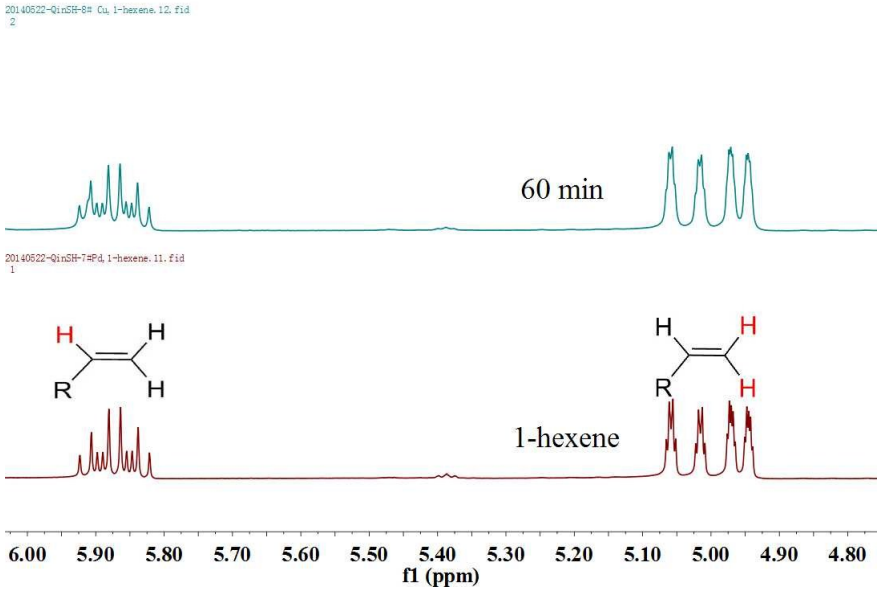


Figure S7-5 The ^{1}H NMR kinetics of olefinic bond in 1-hexene isomerization 25 ^{o}C (0.5 mL of acetonitrile-d_3 containing 8 mM $Cu(OTf)_2$ and 40 mM 1-hexene).

Table S5 Lewis acid promoted Pd(II)-catalyzed 1-octene isomerization under different conditions[a]

Entries	Catalyst	Lewis acid	Time	Conv./%	Internal olefin yield /%
1	$Pd(OAc)_2$	-	1 h	-	-
2	-	$Cu(OTf)_2$	1 h	-	-
3	-	$Sc(OTf)_3$	1 h	-	-
4	$Pd(OAc)_2$	$Sc(OTf)_3$	4 min	94.5	90.3
5	$Pd(OAc)_2$	$Cu(OTf)_2$	6 min	75.7	63.2

[a] Reaction conditions: CD_3CN (0.5 mL), $Pd(OAc)_2$ catalyst (4 mM), Lewis acid (8 mM), 1-octene (40 mM), reaction performed in NMR tube at 25 °C.

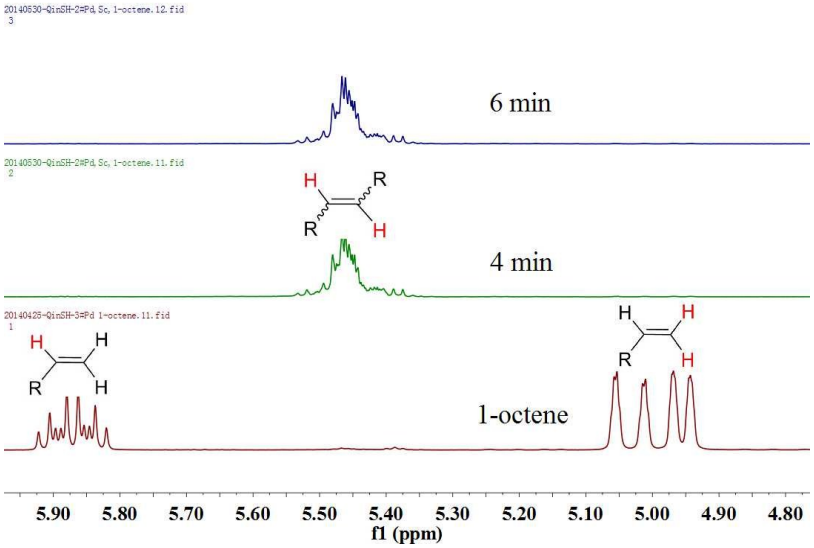


Figure S8-1 The ^1H NMR kinetics of olefinic bond in 1-octene isomerization 25 °C (0.5 mL of acetonitrile-d_3 containing 4 mM $Pd(OAc)_2$, 8 mM $Sc(OTf)_3$ and 40 mM 1-octene).

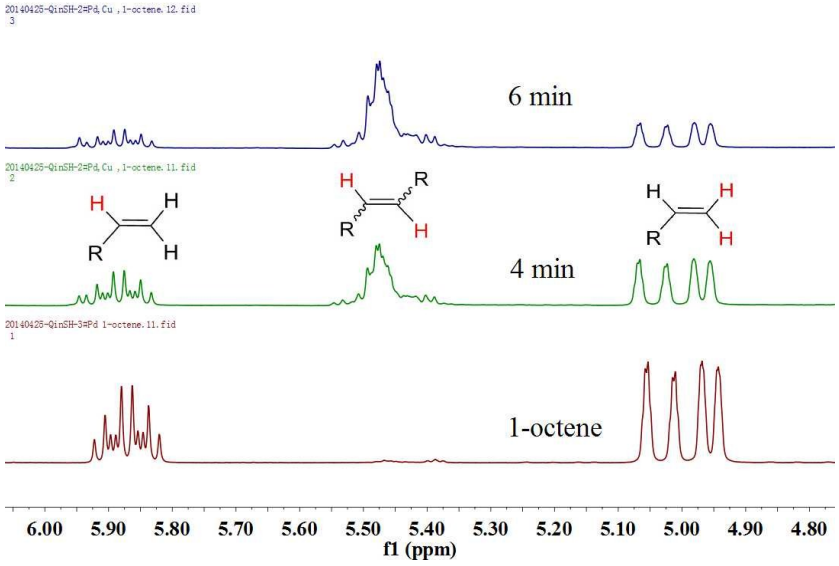


Figure S8-2 The ^{1}H NMR kinetics of olefinic bond in 1-octene isomerization 25 ^{o}C (0.5 mL of acetonitrile-d_3 containing 4 mM $Pd(OAc)_2$, 8 mM $Cu(OTf)_2$ and 40 mM 1-octene).

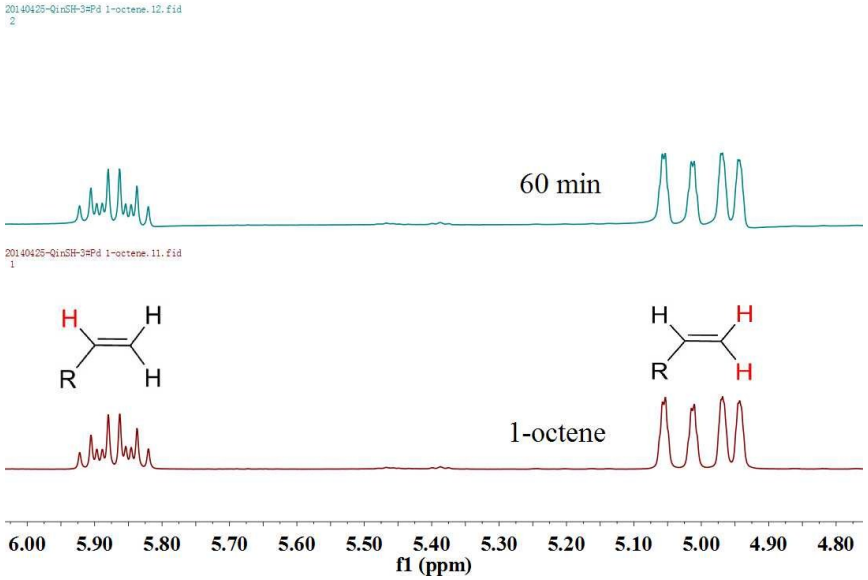


Figure S8-3 The ^{1}H NMR kinetics of olefinic bond in 1-octene isomerization 25 ^{o}C (0.5 mL of acetonitrile-d_3 containing 4 mM $Pd(OAc)_2$ and 40 mM 1-octene).

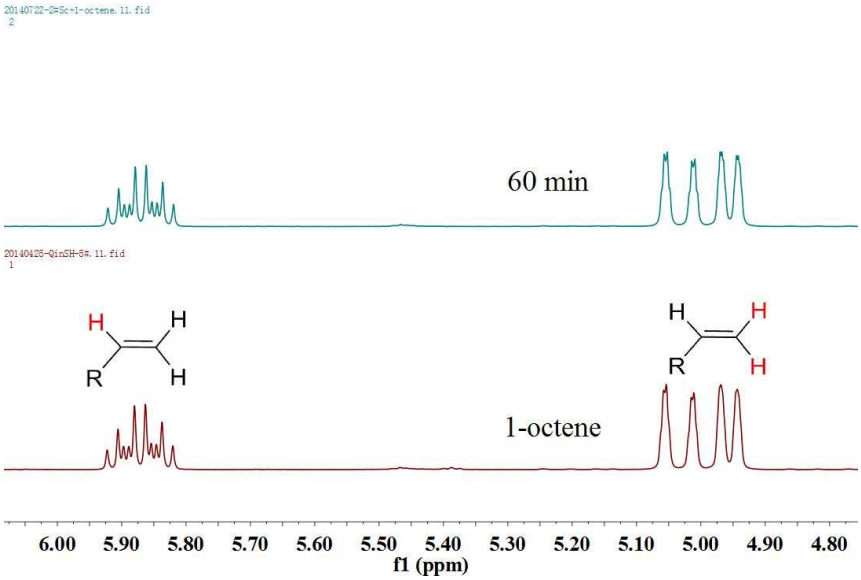


Figure S8-4 The ^{1}H NMR kinetics of olefinic bond in 1-octene isomerization 25 ^{o}C (0.5 mL of acetonitrile-d_3 containing 8 mM $Sc(OTf)_3$ and 40 mM 1-octene).

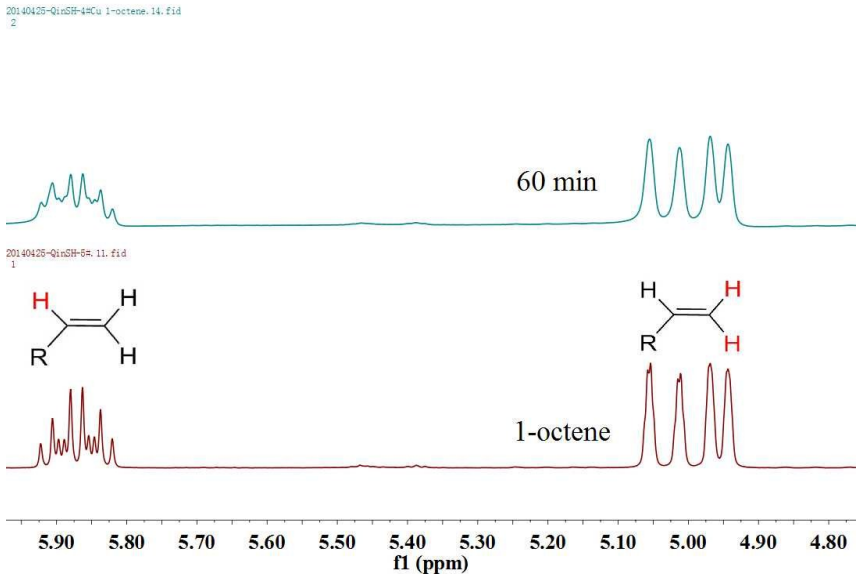


Figure S8-5 The ^{1}H NMR kinetics of olefinic bond in 1-octene isomerization 25 ^{o}C (0.5 mL of acetonitrile-d_3 containing 8 mM $Cu(OTf)_2$ and 40 mM 1-octene).

Table S6 Lewis acid promoted Pd(II)-catalyzed 1-dodecene isomerization under different conditions[a]

Entries	Catalyst	Lewis acid	Time	Conv./%	Internal olefin yield /%
1	$Pd(OAc)_2$	-	1 h	-	-
2	-	$Cu(OTf)_2$	1 h	-	-
3	-	$Sc(OTf)_3$	1 h	-	-
4	$Pd(OAc)_2$	$Sc(OTf)_3$	6 min	99.6	84.4
5	$Pd(OAc)_2$	$Cu(OTf)_2$	6 min	48.4	41.4

[a] Reaction conditions: CD_3CN (0.5 mL), $Pd(OAc)_2$ (4 mM), Lewis acid (8 mM), 1-dodecene (40 mM), reaction performed in NMR tube at 25 °C.

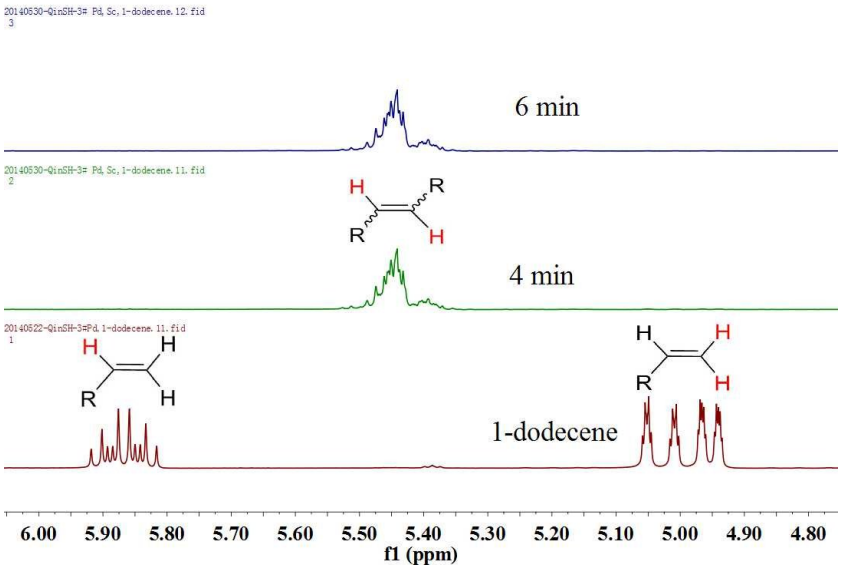


Figure S9-1 The ^1H NMR kinetics of olefinic bond in 1-dodecene isomerization 25 °C (0.5 mL of acetonitrile-d_3 containing 4 mM $Pd(OAc)_2$, 8 mM $Sc(OTf)_3$ and 40 mM 1-dodecene).

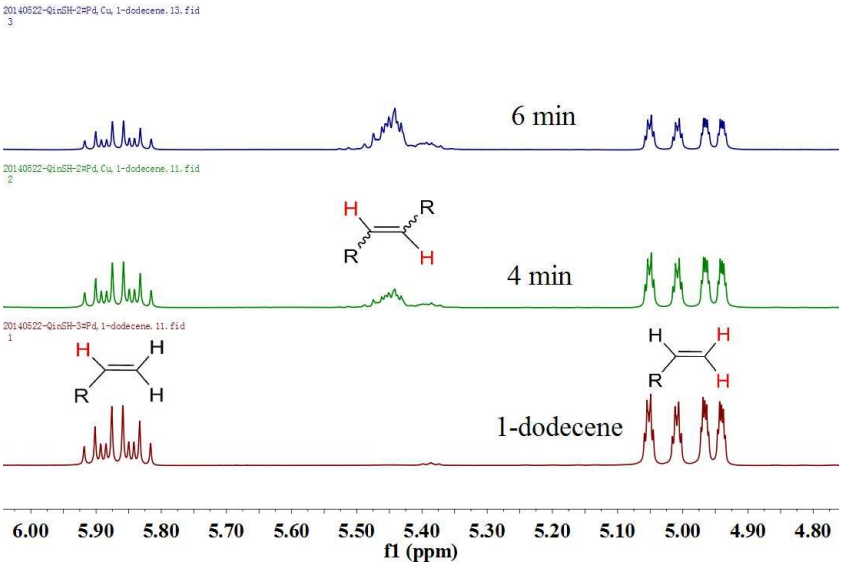


Figure S9-2 The ^{1}H NMR kinetics of olefinic bond in 1-dodecene isomerization 25 ^{o}C (0.5 mL of acetonitrile-d_3 containing 4 mM $Pd(OAc)_2$, 8 mM $Cu(OTf)_2$ and 40 mM 1-dodecene).

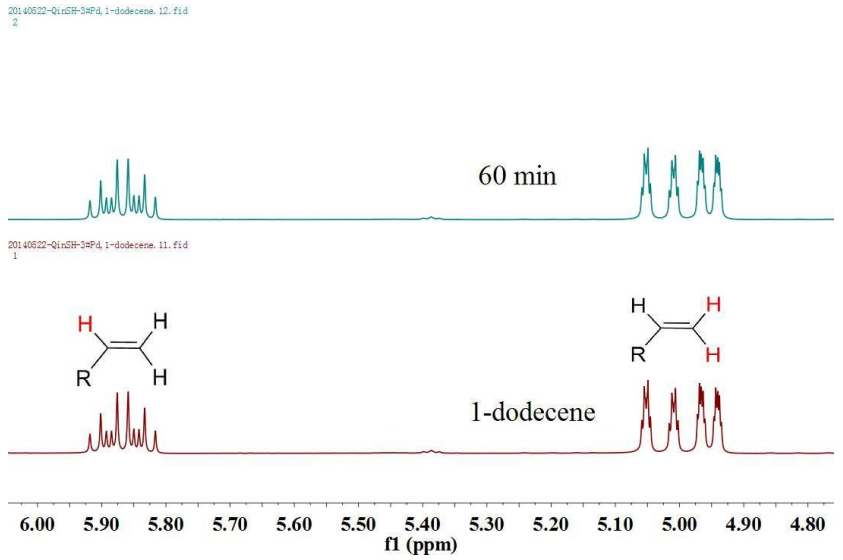


Figure S9-3 The ^{1}H NMR kinetics of olefinic bond in 1-dodecene isomerization 25 ^{o}C (0.5 mL of acetonitrile-d_3 containing 4 mM $Pd(OAc)_2$ and 40 mM 1-dodecene).

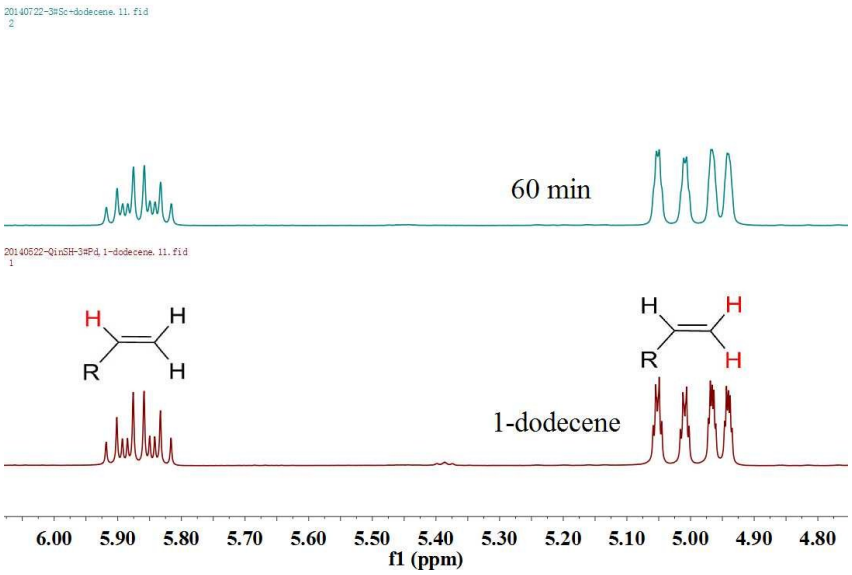


Figure S9-4 The ^{1}H NMR kinetics of olefinic bond in 1-dodecene isomerization 25 ^{o}C (0.5 mL of acetonitrile-d_3 containing 8 mM $Sc(OTf)_3$ and 40 mM 1-dodecene).

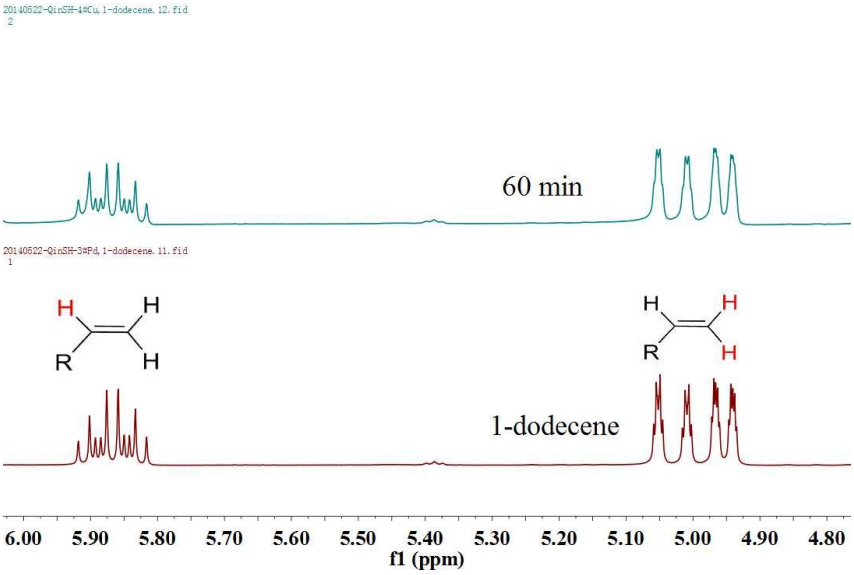
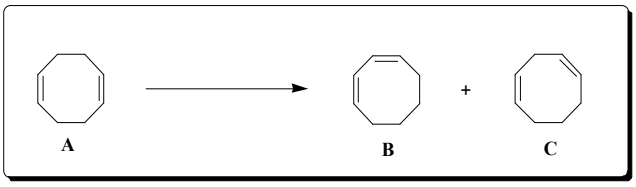


Figure S9-5 The ^{1}H NMR kinetics of olefinic bond in 1-dodecene isomerization 25 ^{o}C (0.5 mL of acetonitrile-d_3 containing 8 mM $Cu(OTf)_2$ and 40 mM 1-dodecene).

Table S7 Lewis acid promoted Pd(II)-catalyzed 1,5-cyclooctadiene isomerization under different conditions[a]



Entries	Catalyst	Lewis acid	Time	Conv./%	Yield B /%	Yield C /%
1	$Pd(OAc)_2$	-	24 h	0.9	-	-
2	-	$Sc(OTf)_3$	24 h	1.1	-	-
3	-	$Cu(OTf)_2$	24 h	1.0	-	-
4	$Pd(OAc)_2$	$Sc(OTf)_3$	24 h	95.2	89.0	4.7
5	$Pd(OAc)_2$	$Cu(OTf)_2$	24 h	93.0	88.0	4.1
6	$Pd(OAc)_2$	$Al(OTf)_3$	22 h	91.6	87.3	3.4
7	$Pd(OAc)_2$	$Mg(OTf)_2$	22 h	88.5	79.6	4.8
8	$Pd(OAc)_2$	$Zn(OTf)_2$	22 h	89.1	80.0	6.5

[a] Reaction conditions: CH_3CN (5 mL), $Pd(OAc)_2$ (4 mM), Lewis acid (8 mM), 1,5-cycloctadiene (0.2 M), 90 ^oC.

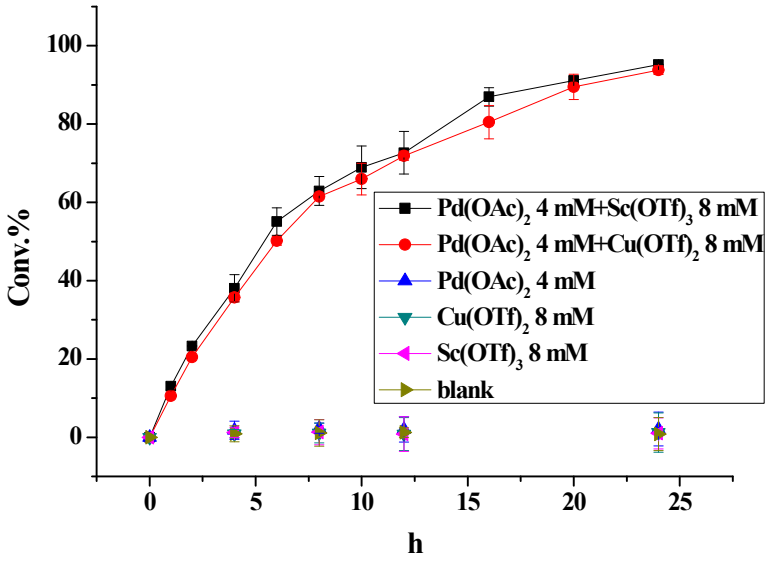


Figure S10 Isomerization kinetics of 1,5-cyclooctadiene. Conditions: CH_3CN (5 mL), $Pd(OAc)_2$ (4 mM), Lewis acid (8 mM), 1,5-cyclooctadiene (0.2 M), 90 °C.

GC-MS data for catalytic oxidation of 1-octene by $Pd(OAc)_2$ plus $Sc(OTf)_3$. Conditions: CH_3CN (5 mL), water (0.2 mL), $Pd(OAc)_2$ (0.02 mmol), $Sc(OTf)_3$ (0.04 mmol), 1-octene (2 mmol), O_2 (20 atm), temperature 80 °C, reaction time 12 h. The measurements were conducted with auto sampler, HP-5 capillary column and a flame ionization detector.

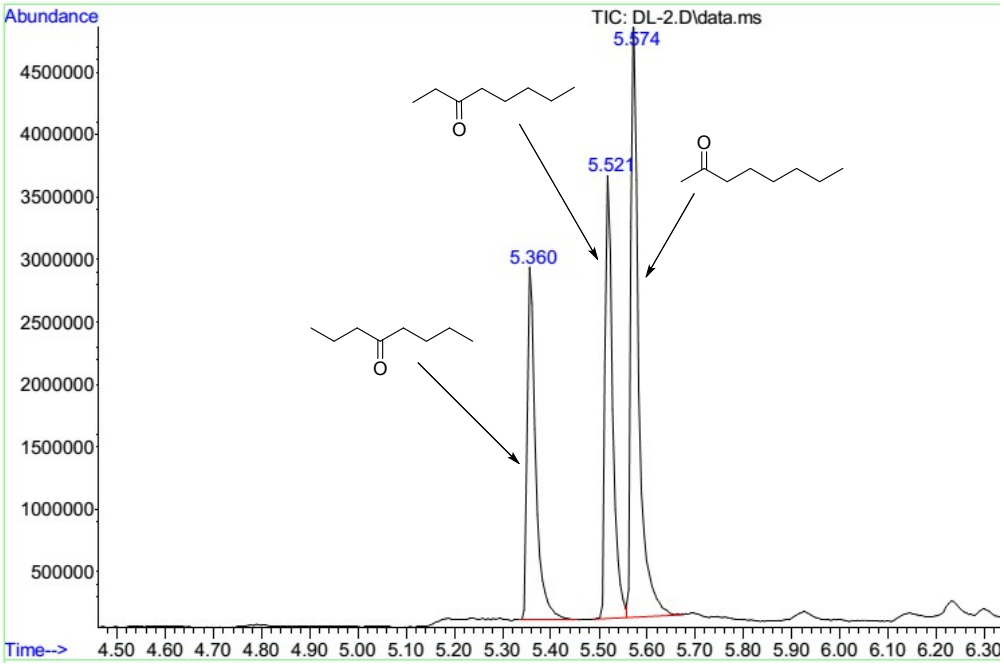


Figure S11. GC-MS graph of 1-octene oxidation by $Pd(OAc)_2$ plus $Sc(OTf)_3$.

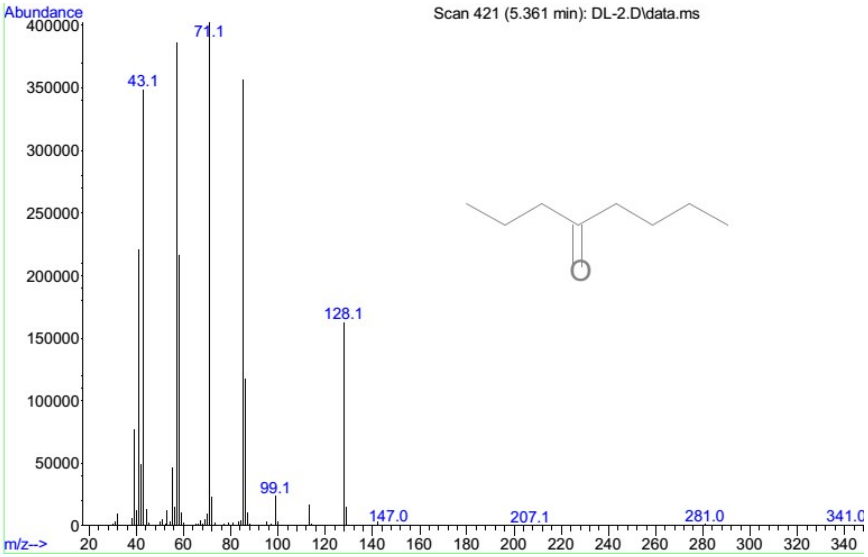


Figure S11-1. MS graph of 4-octanone in GC-MS analysis.

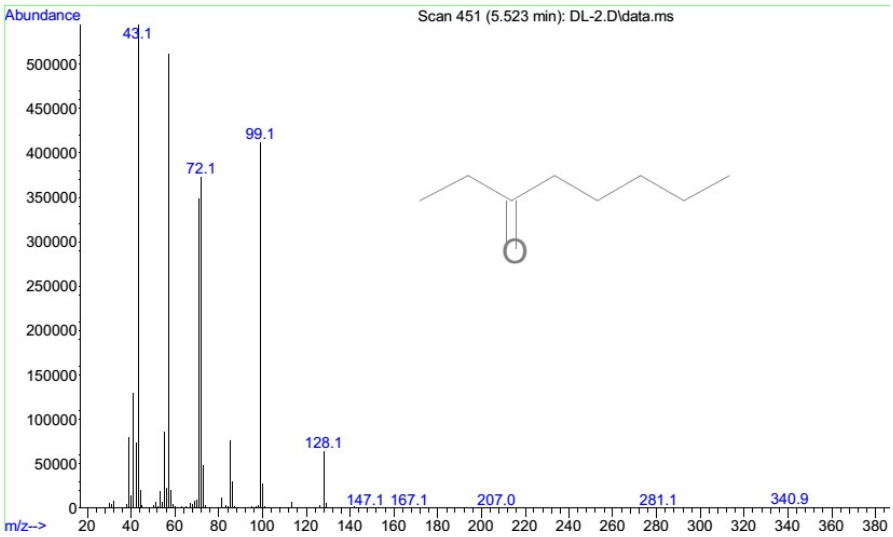


Figure S11-2. MS graph of 3-octanone in GC-MS analysis.

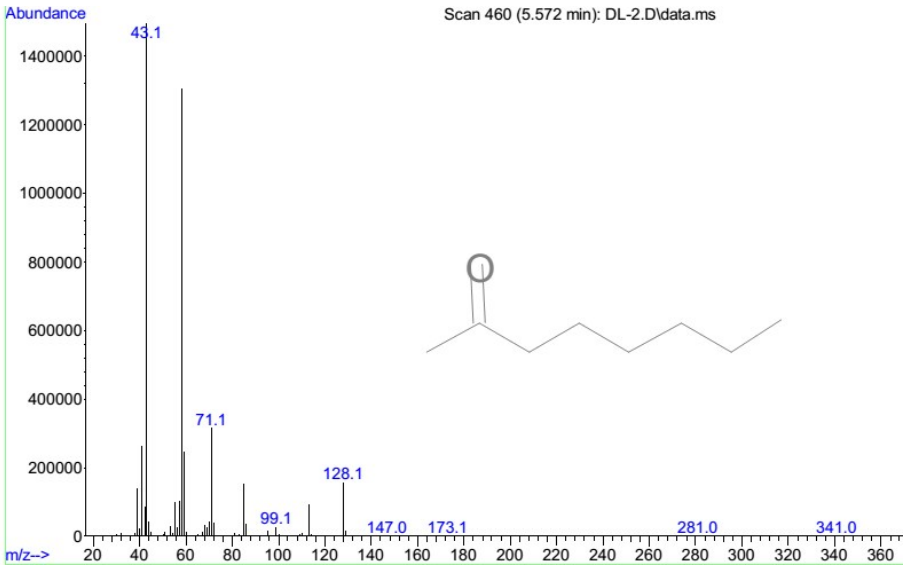


Figure S11-3. MS graph of 2-octanone in GC-MS analysis.

GC-MS data for catalytic isomerization of 1,5-cyclooctadiene by $Pd(OAc)_2$ plus $Sc(OTf)_3$. Conditions: CH_3CN (5 mL), $Pd(OAc)_2$ (0.02 mmol), $Sc(OTf)_3$ (0.04 mmol), 1,5-cyclooctadiene (1 mmol), temperature 90 °C; reaction time 24 h. The measurements were conducted with auto sampler, HP-5 capillary column and a flame ionization detector.

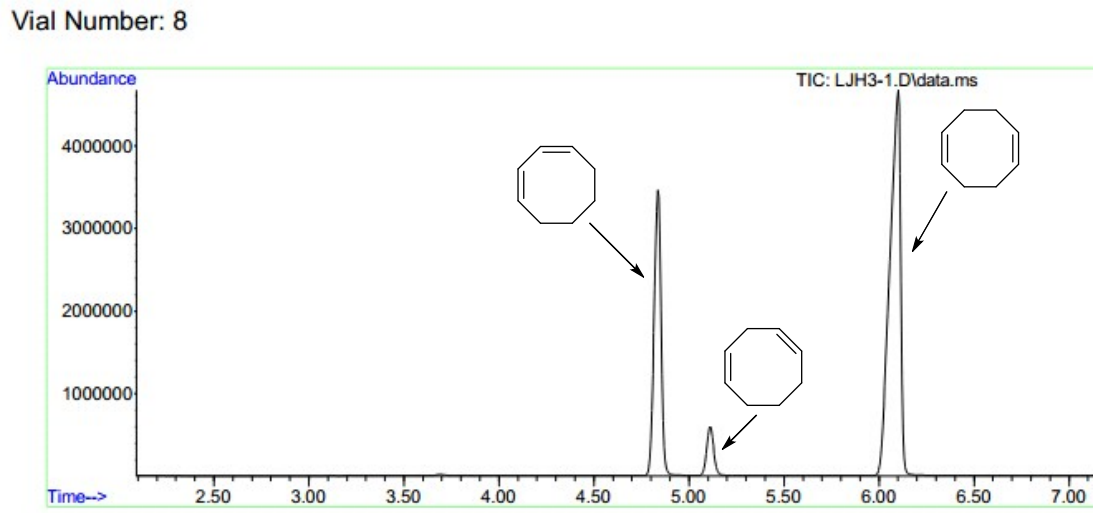


Figure S12. GC-MS graph of 1,5-cyclooctadiene isomerization by $Pd(OAc)_2$ plus $Sc(OTf)_3$.

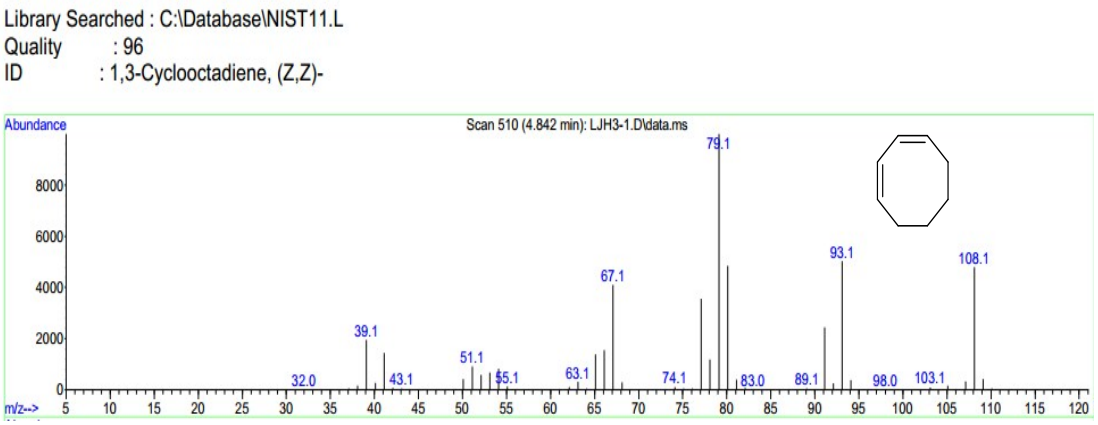


Figure S12-1. MS graph of 1,3-cyclooctadiene in GC-MS analysis.

Library Searched : C:\Database\NIST11.L
Quality : 97
ID : 1,4-Cyclooctadiene, (Z,Z)-

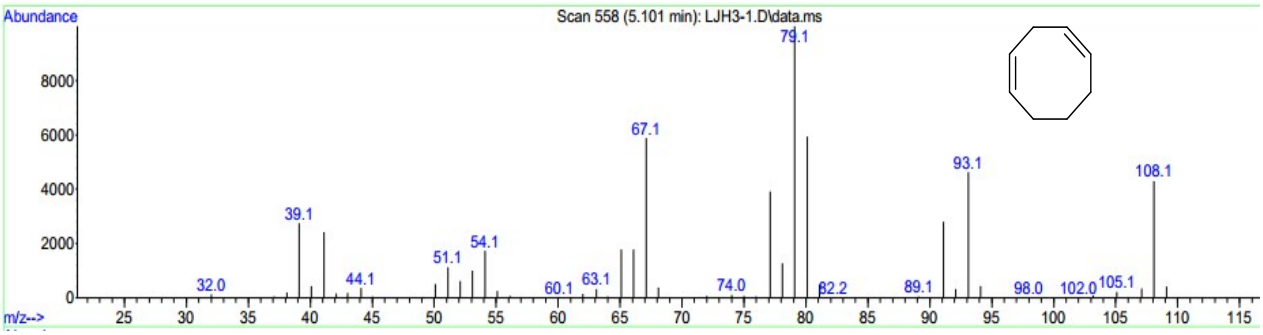


Figure S12-2. MS graph of 1,4-cyclooctadiene in GC-MS analysis.

Library Searched : C:\Database\NIST11.L
Quality : 90
ID : 1,5-Cyclooctadiene

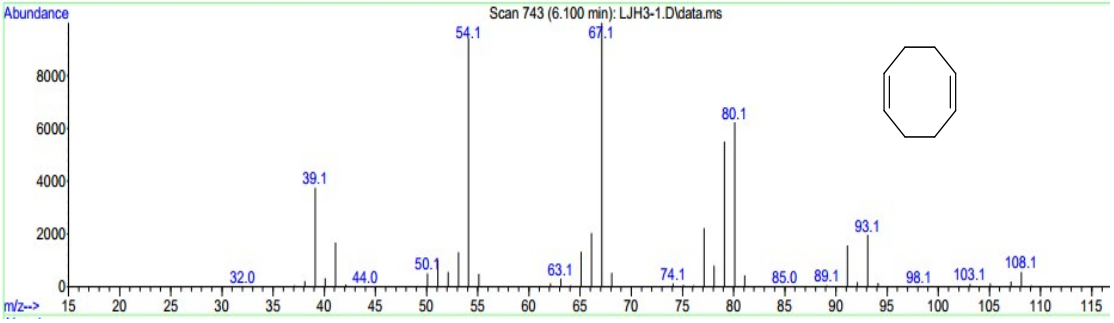


Figure S12-3. MS graph of 1,5-cyclooctadiene in GC-MS analysis.