

Supporting Information

**Th(IV) Complexes Possessing Expanded Ring N-heterocyclic iminato
Ligands: Synthesis and Applications**

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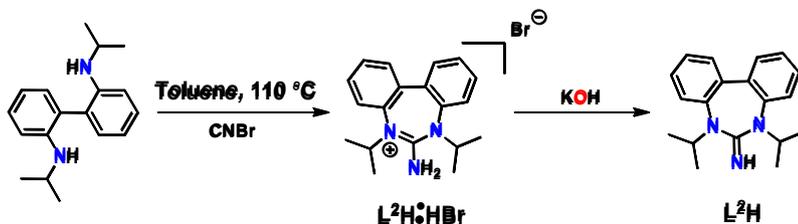
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Contents

Scheme S1. Schematic presentation of Synthesis of L ² H	S3
General procedures and materials	S3
Synthesis of L²H	S4
Synthesis of complex 2 and complex 3	S4-S5
General Procedure for the Catalytic Tishchenko Reaction	S5
Figure S1: Molecular structure of L ² H	S6
Figure S2: ¹ H and ¹³ C NMR spectra of L ² H	S7
Figure S3: ¹ H and ¹³ C NMR spectra of Compound 2	S8
Figure S4: ¹ H and ¹³ C NMR spectra of Compound 3	S9
Table S1: Crystallographic table for L ² H and complexes 2, 3	S10
Table S2: Selected Bond Lengths and Angles for Complexes 2, 3 and L ² H	S11
Characterization of Different Ester	S12-S22
Figure S6: ¹ H NMR spectra of Phthalide	S22
Characterization of Cross Tishchenko Reaction Products	S23-S25
Figure S7: Variation of initial reaction rate with concentration of PhCHO for 2	S26
Figure S8: Variation of initial reaction rate with concentration of precatalyst 2	S26
Figure S9: Eyring plot of the dimerization of PhCHO mediated by complex 2	S27
Figure S10: Arrhenius plot of the dimerization of PhCHO mediated by complex 2	S27
Figure S11: Variation of initial reaction rate with concentration of PhCHO for 3	S28
Figure S12: Variation of initial reaction rate with concentration of precatalyst 3	S28
Figure S13: Kinetic isotopic effect	S29
References:	S30-S31



Scheme S1: Synthesis of L²H

General procedures and materials:

All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware on a high-vacuum line (10^{-5} Torr), or in nitrogen-filled MBraun and Vacuum Atmospheres gloveboxes with a medium capacity recirculator (1–2 ppm oxygen). Argon and nitrogen were purified by passage through a MnO oxygen removal column and a Davison 4 Å molecular sieve column. Analytically pure solvents were dried and stored with Na/K alloy and degassed by three freeze–pump–thaw cycle prior to use (hexane, toluene, benzene-*d*₆). The perimidin-2-iminato (Pr^RN where R = isopropyl) and Th(CH₃)₂(Cp*)₂ were synthesized according to published literature procedures.¹ Benzaldehyde, 2-pyridinylcarboxaldehyde, furfural, 2-thiophencarboxaldehyde, cyclohexylcarboxaldehyde, cyclo-pentylcarbaldehyde, isobutyraldehyde, and 1-naphthaldehyde (Sigma- Aldrich) were distilled over sodium bicarbonate and stored in a glovebox prior to use. 2-Naphthaldehyde, 2,3-naphthylbisaldehyde, phthalaldehyde (Sigma- Aldrich) were dried for 12 h on a high-vacuum line (10^{-5} Torr) and stored in a glovebox prior to use. NMR spectra were recorded on DPX200, Avance 300, and Avance 400 Bruker spectrometers. Chemical shifts for ¹H NMR and ¹³C NMR are reported in ppm and referenced using residual proton or carbon signals of the deuterated solvent relative to tetramethylsilane. MS experiments were performed at 200 °C (source temperature) in Maxis Impact (Bruker) mass spectrometer with an APCI solid probe method.

The single-crystal material was immersed in perfluoropolyalkylether and was quickly fished with a glass rod and mounted on a Kappa CCD diffractometer under a cold stream of nitrogen. Data collection was performed using monochromated Mo K α radiation using φ and ω scans to cover the Ewald sphere.² Accurate cell parameters were obtained with the amount of indicated reflections.³ The structure was solved by SHELXS-97 direct methods⁴ and refined by the SHELXL-97 program package.⁵ The atoms were refined anisotropically. Hydrogen atoms were included using the riding model. Figures were drawn (50 % probability thermal ellipsoids) using Diamond V3.1.⁶

Synthesis of L²H (5,7-diisopropyl-5,7-dihydro-6H-dibenzo[*d,f*][1,3]diazepin-6-imine):

Aqueous KOH (1.00 g, 17.82 mmol) was added to the diethyl ether (40 mL) suspension of L²H•HBr (2.50 g, 7.18 mmol) and the mixture were vigorously stirred for 30 min at ambient temperature. In a separatory funnel the two layers were separated and the aqueous layer was extracted with diethyl ether (3 × 30 mL). The combined organic phases were dried over anhydrous Na₂SO₄. After filtration, the solvent was removed in vacuo to afford an off-white solid. Yield: 1.75 g (90 %). ¹H NMR (400 MHz, CDCl₃): δ = 7.43–7.41 (m, 2H, ArCH), 7.29–7.18 (m, 6H, ArCH), 4.04 (br, 2H, CHMe₂), 1.16 (d, *J* = 8.0 Hz, 6H, CHMe₂), 0.86 (d, *J* = 4.0 Hz, 6H, CHMe₂); ¹³C NMR (100 MHz, CDCl₃): δ = 166.5 (NCN), 143.0 (ArC), 136.9 (ArC), 128.0 (ArC), 125.5 (ArC), 124.4 (ArC), 49.6 (CHMe₂), 23.3 (CHMe₂), 21.6 (CHMe₂) ppm.; ESI-MS, *m/z*: 293.18919, Anal. Calcd for C₁₉H₂₃N₃: C, 77.78; H, 7.90; N, 14.32. Found: C, 77.67; H, 7.81; N, 14.23.

Synthesis of Cp*₂Th(L¹)(Me) (2):

A solution of Cp*₂Th(Me)₂ (500 mg, 0.94 mmol) in toluene (5.0 mL) was treated drop wise with a toluene (10 mL) solution of L¹ (251 mg, 0.94 mmol) inside the glovebox. The pale yellow solution was stirred for 12 h at room temperature. Subsequent removal of the solvent and recrystallization from a concentrated toluene solution afforded **2** as colorless crystals. Yield: 690 mg (94 %). ¹H NMR (300 MHz, C₆D₆): δ = 7.12–7.09 (m, 4H, ArCH), 6.73–6.67 (m, 2H, ArCH), 5.90–5.78 (m, 1H, CHMe₂), 5.70–5.56 (m, 1H, CHMe₂), 1.98 (s, 30H, C₅Me₅), 1.42 (d, 6H, CHMe₂), 1.40 (d, 6H, CHMe₂), 1.95 (s, 15H, C₅Me₂), 0.20 (s, 3H, ThCH₃); ¹³C NMR (75.5 MHz, C₆D₆): δ = 142.4 (C_{ipso}=N), 136.3 (ArC), 136.0 (ArC), 135.1 (ArC), 126.5 (ArC), 126.2 (ArC), 122.0 (ArC), 122.0 (ArC), 118.1 (ArC), 118.1 (ArC), 117.8 (ArC), 116.8 (ArC), 106.1 (ArC), 55.3 (ThCH₃), 46.8 (CHMe₂), 46.3 (CHMe₂), 19.9 (CHMe₂), 18.5 (CHMe₂), 10.9 ((C₅(CH₃)₅) ppm. C₃₈H₅₃N₃Th: C, 58.22; H, 6.81; N, 6.36. Found: C, 58.12; H, 6.75; N, 6.30.

Synthesis of Cp*₂Th(L²)(Me) (3):

Yield 95 % (720 mg, 0.89 mmol); ¹H NMR (300.0 MHz, C₆D₆): δ = 7.46–7.34 (m, 2H, ArCH), 7.18–7.00 (m, 6H, ArCH), 4.48 (br, 1H, CHMe₂), 4.11 (br, 1H, CHMe₂), 2.12 (s, 15H, (C₅(CH₃)₅), 1.91 (s, 15H, (C₅(CH₃)₅), 1.30 (br, 3H, CHMe₂), 1.21 (br, 3H, CHMe₂), 0.85 (br, 3H, CHMe₂), 0.53 (br, 3H, CHMe₂), 0.34 (s, 3H, ThCH₃); ¹³C NMR (75.5 MHz, C₆D₆): δ = 153.4 (C_{ipso}=N), 121.9 (ArC), 121.6 (ArC), 54.3 (ThCH₃), 31.4 (CHMe₂), 13.9 (CHMe₂), 11.1

$((C_5(CH_3)_5)$, 10.9 $((C_5(CH_3)_5)$ ppm. $C_{40}H_{55}N_3Th$: C, 59.31; H, 6.84; N, 5.19. Found: C, 59.40; H, 6.78; N, 5.11.

General Procedure for the Catalytic Tishchenko Reaction

A sealable J. Young NMR tube was loaded with 5.00 mg of complex **2** and **3** from a stock solution in C_6D_6 inside the glovebox. The respective aldehyde (100 equiv) was added, and the reaction was immediately diluted to 500 μ L with C_6D_6 . Solid aldehydes were dissolved in 300 μ L of C_6D_6 before being added to the solution of the precatalyst. The progress of the reaction was monitored by 1H NMR spectroscopy. After 24 h, the tube was opened to air, and the reaction was quenched with methanol. The products were identified by 1H NMR spectroscopy and MS analysis, and the chemical shifts were compared with previously reported literature data.⁷

General Procedure for the Catalytic Crossed Tishchenko Reaction.

A sealable J. Young NMR tube was loaded with 5.00 mg of complex **2** and **3** from a stock solution in C_6D_6 inside the glovebox. The respective aromatic aldehyde and aliphatic aldehyde were added, and the reaction was immediately diluted to 500 μ L with C_6D_6 . Solid aldehydes were dissolved in 300 μ L of C_6D_6 before being added to the catalyst solution. The progress of the reaction was monitored by 1H NMR spectroscopy. After 24 h, the tube was opened to air and the reaction quenched with methanol. The products were identified by 1H NMR spectroscopy and MS analysis, and the values were compared to previous literature.

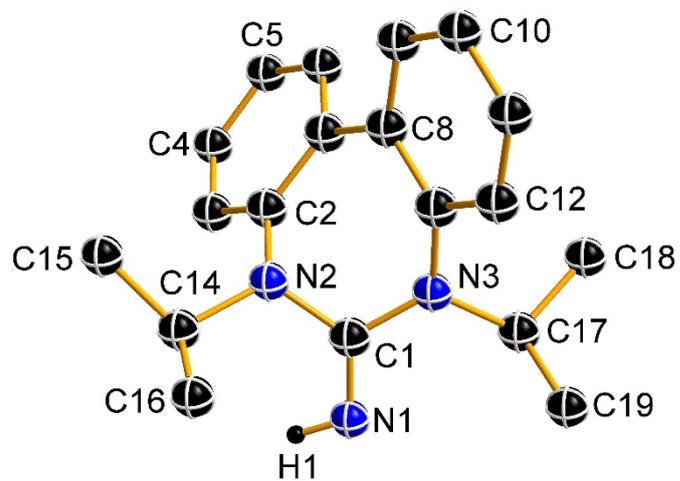


Figure S1. Molecular structure of L²H with thermal ellipsoid set at the 50% probability levels. All Hydrogen atoms (except H1) are omitted for the clarity.

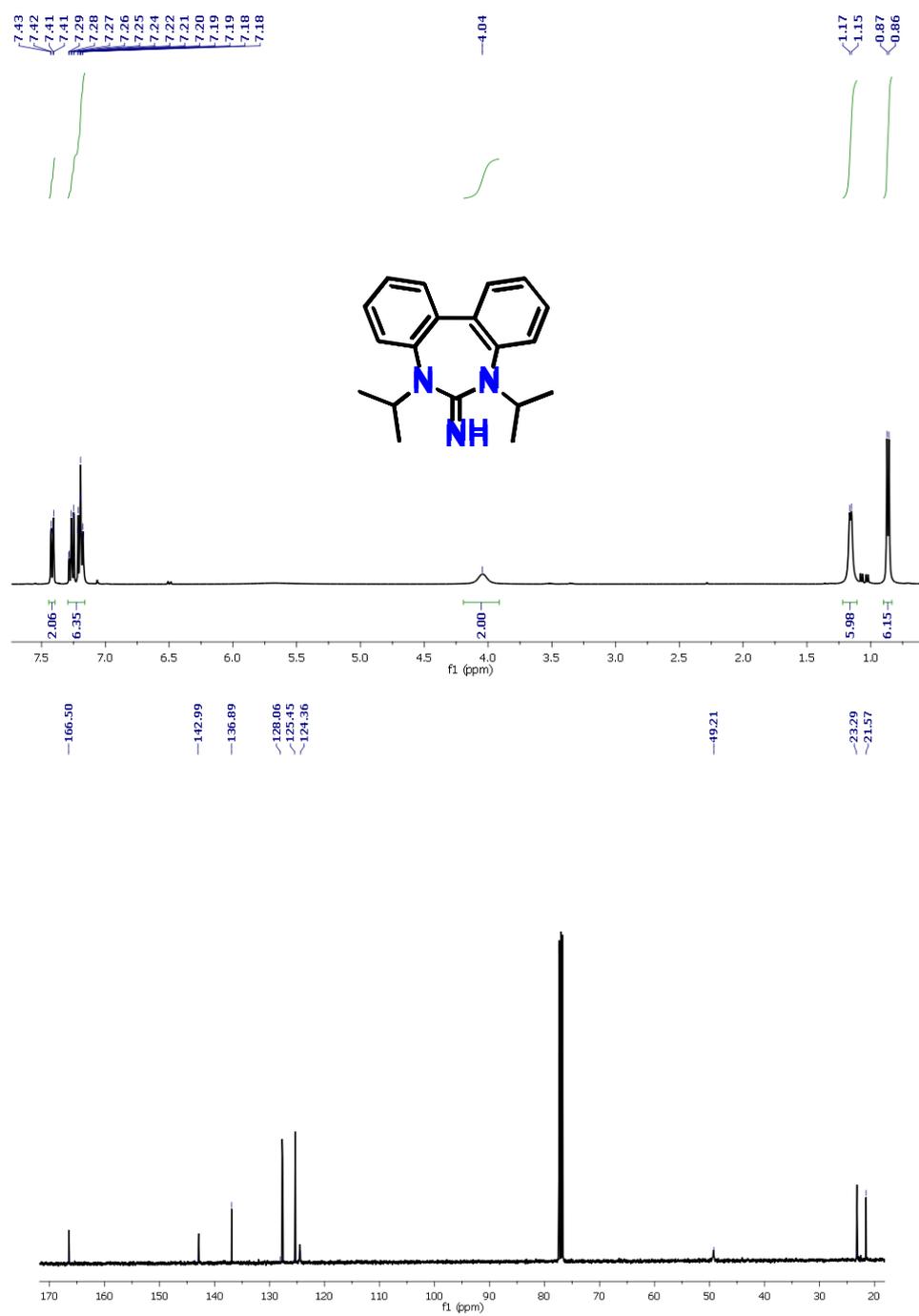


Figure S2. ¹H (top) and ¹³C (below) NMR spectra of 5,7-diisopropyl-5,7-dihydro-6H-dibenzo[*d,f*][1,3]diazepin-6-imine (L²H).

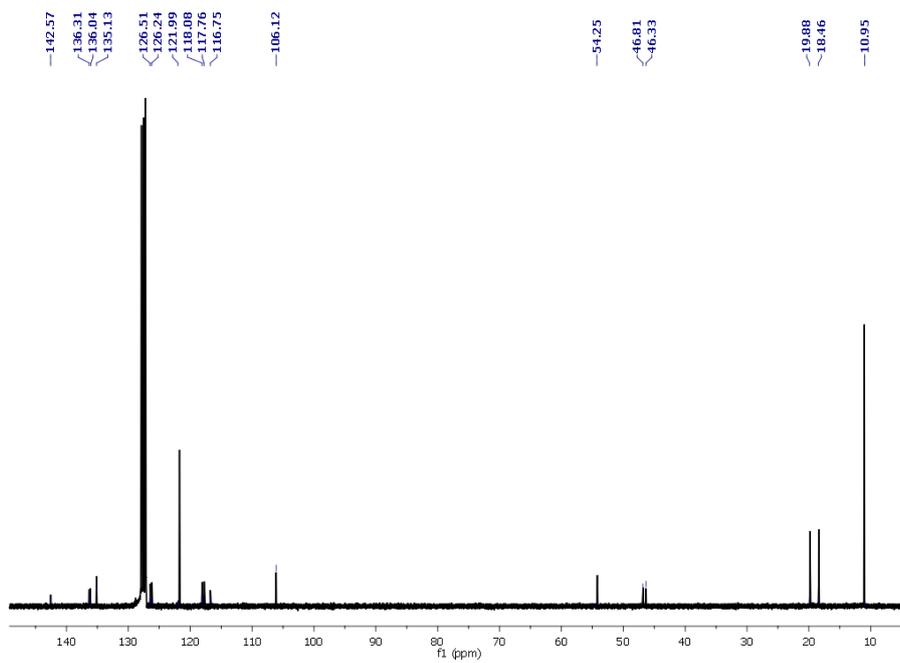
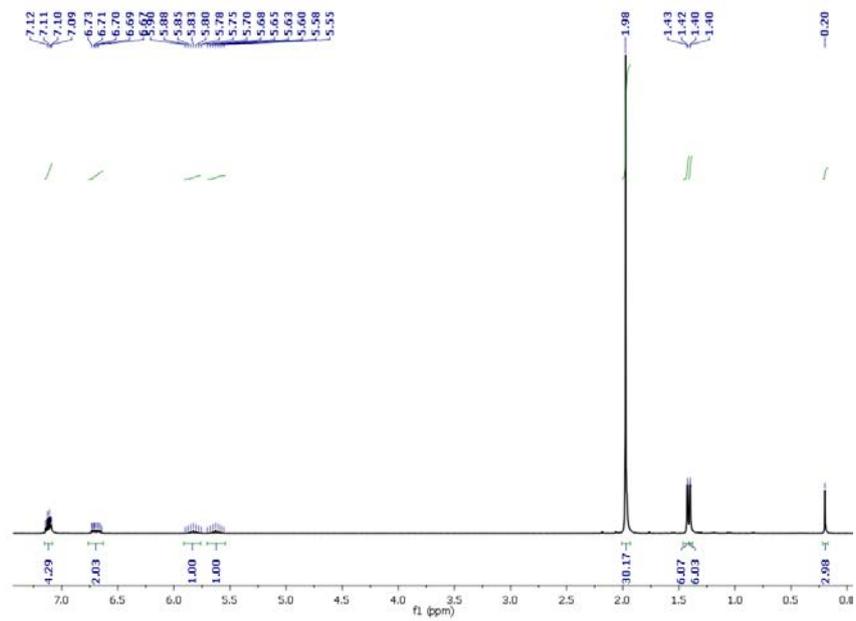


Figure S3. ^1H (top) and ^{13}C (below) NMR spectra of Compound 2.

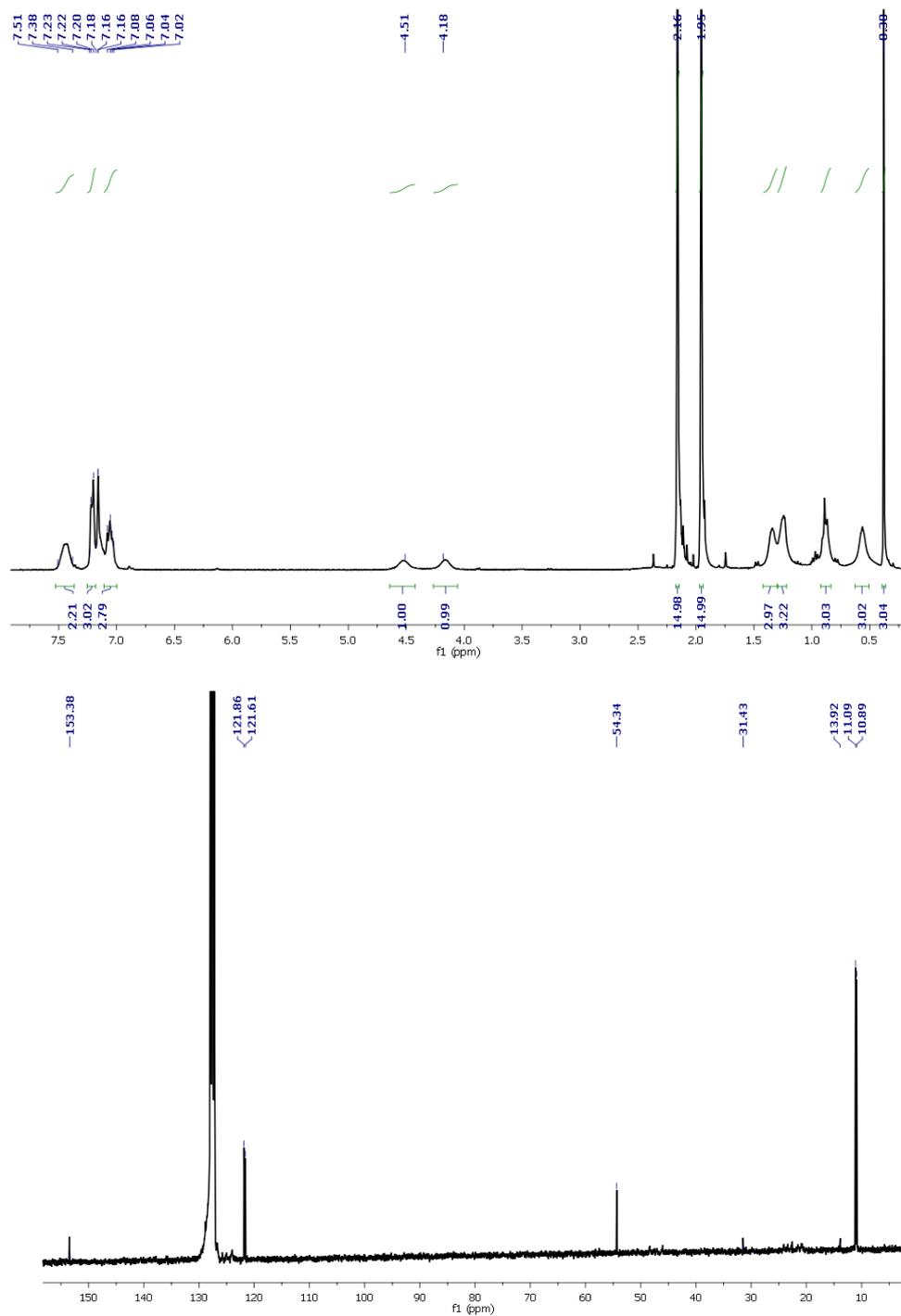


Figure S4. ¹H (top) and ¹³C (below) NMR spectra of Compound 3.

Table S1. Crystallographic data and pertinent refinement parameters for complexes 2 – 3 .and Ligand L²H .			
	2	3	L²H
Empirical formula	C ₃₈ H ₅₃ N ₃ Th	C ₄₀ H ₅₅ N ₃ Th	C ₃₅ H ₇₄ N ₆ Si ₆ U
Formula Weight	783.87	809.91	985.57
Crystal System	monoclinic	monoclinic	Orthorhombic
Space Group	<i>P</i> 21/ <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> bca
a (Å)	16.366(15)	35.983(5)	12.812(4)
b (Å)	13.578(4)	9.933(3)	23.795(8)
c (Å)	15.865(11)	22.307(3)	31.24(2)
α (deg)	90.00	90.00	90.00
β (deg)	104.34(3)	112.310(15)	90.00
γ (deg)	90.00	90.00	90.00
V (Å ³)	3416(4)	7376(3)	9524(9)
Z	4	8	8
ρ _{calcd} (g cm ⁻³)	1.524	1.459	1.375
μ (mm ⁻¹)	4.395	4.073	3.589
F(000)	1568	3248	4016
Reflections Collected	5070	6261	7081
Independent	5070	6261	7081
Observed [<i>I</i> > 2σ(<i>I</i>)]	4331	4970	5302
No. of variables	394	412	455
GooF	1.211	1.114	1.054
R _{int}	0.0860	0.0890	0.0800
Final R indices	R1 = 0.0475	R1 = 0.0507	R1 = 0.0338
[<i>I</i> > 2σ(<i>I</i>)] ^a	wR2 = 0.0722	wR2 = 0.1160	wR2 = 0.0802
R indices (all data) ^a	R1 = 0.0606	R1 = 0.0706	R1 = 0.0538
	wR2 = 0.0755	wR2 = 0.1226	wR2 = 0.0902
CCDC No:	1548353	1548354	1548355

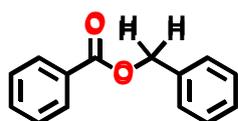
Table S2. Selected Bond Lengths (Å) and Angles (°) for Complexes **2**, **3** and **L²**

	L²H	Complex 2	Complex 3
Th–N1	—	2.225(5)	2.217(7)
Th–CH ₃	—	2.488(7)	2.492(9)
Th–C _{cent1}	—	2.570	2.555
Th–C _{cent2}	—	2.560	2.582
Th–C _{av1}	—	2.836	2.849
Th–C _{av2}	—	2.826	2.822
C1–N1	1.267(2)	1.277(8)	1.268(10)
C1–N2	1.365(2)	1.413(8)	1.449(10)
C1–N3	1.415(2)	1.413(8)	1.395(10)
Th–N1–C1	—	173.4(5)	173.9(6)
N1–Th–C _{av1}	—	109.5	108.7
N1–Th–C _{av2}	—	107.7	107.7
N1–Th–CH ₃	—	97.7(2)	97.2(3)
C _{cent2} –Th–C _{cent1}	—	135.1	133.5
C _{cent1} –Th–CH ₃	—	99.5	102.3
C _{cent2} –Th–CH ₃	—	99.7	100.9
C _{iso} –N–N'–C _{iso}	76.8(3)	26.7(1)	102.3(1)

Esterification of benzaldehyde

Benzyl benzoate⁸, was prepared according to the general procedure with the two catalysts: Complex **2** (4 mg, ~0.005 mmol) and benzaldehyde (52.1 μ L, 0.510 mmol) were added to the NMR tube, the mixture was allowed to react at room temperature for 24h. The benzyl benzoate was obtained exclusively in 96% yield.

Catalyst **3** (4 mg, ~0.005 mmol) and benzaldehyde (48.9 μ L, 0.494 mmol) was added to the NMR tube, the mixture was allowed to react at room temperature for 24h. The benzyl benzoate was obtained exclusively in 90% yield.



Benzyl benzoate: ¹H NMR (300 MHz, C₆D₆): δ 8.07 – 8.03 (m, 2H), 7.18 – 6.94 (m, 8H), 5.12 (s, 2H). ¹³C NMR (75.5 MHz, C₆D₆): δ 168.8, 136.5, 133.5, 132.5, 129.5, 129.2, 128.5, 128.1, 66.5. MS: m/z 213.11

(M⁺), 92.09 (PhCH₂⁺).

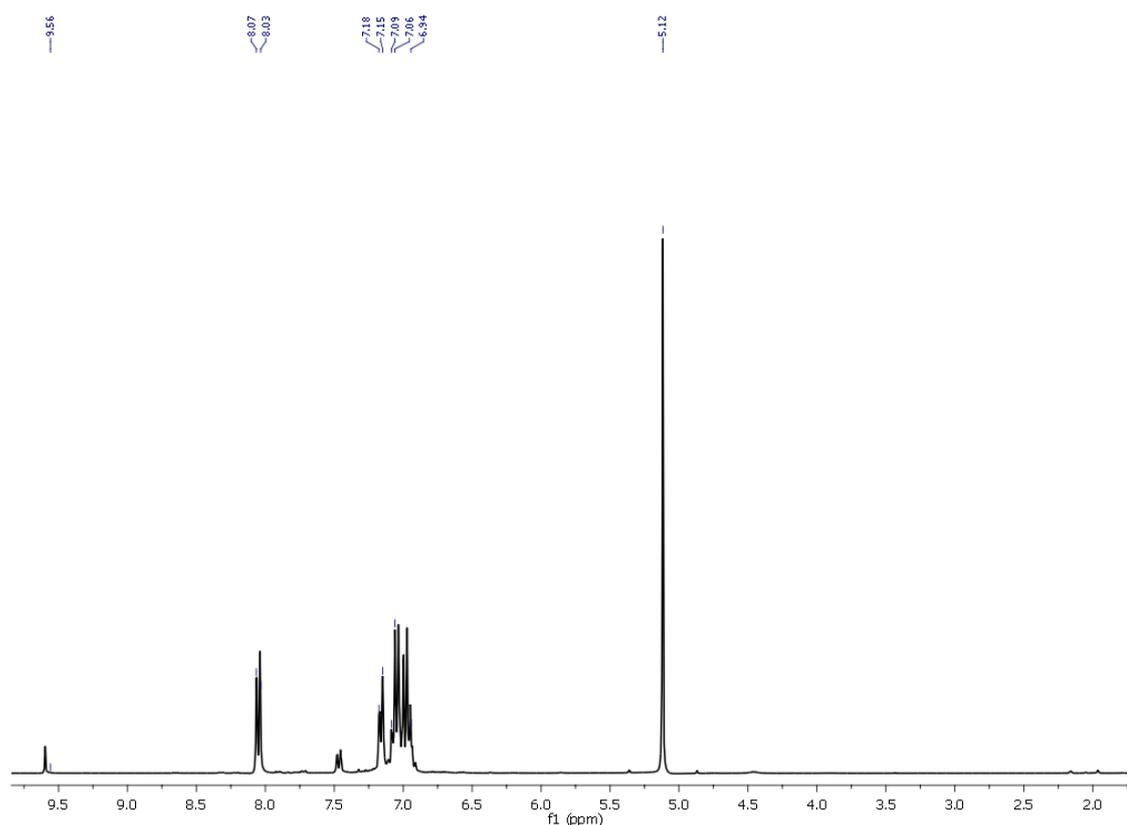


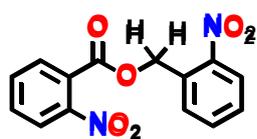
Figure S5. ¹H NMR spectra of Compound Benzyl benzoate

Esterification of o-nitrobenzaldehyde

2'-nitrobenzyl 2-nitrobenzoate⁹, was prepared according to the general procedure with the two catalysts:

Complex **2** (4 mg, ~0.005 mmol) and o-nitrobenzaldehyde (77.2 mg, 0.510 mmol) were added to the NMR tube, the mixture was allowed to react at room temperature for 24h. The 2'-nitrobenzyl 2-nitrobenzoate was obtained exclusively in 56 % yield.

Complex **3** (4 mg, ~0.005 mmol) and o-nitrobenzaldehyde (74.6 mg, 0.494 mmol) were added to the NMR tube, the mixture was allowed to react at room temperature for 24h. The 2'-nitrobenzyl 2-nitrobenzoate was obtained exclusively in 55 % yield.



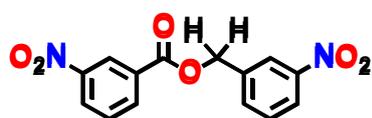
2'-nitrobenzyl 2-nitrobenzoate: ¹H NMR (300 MHz, C₆D₆): δ 8.15 – 8.12 (d, 1H, *J* = 9.0 Hz), 7.95 – 7.92 (d, 1H, *J* = 9.0 Hz), 7.78 – 7.62 (m, 6H), 5.74 (s, 2H). ¹³C NMR (75.5 MHz, C₆D₆): δ 165.4, 149.1, 147.9, 135.7, 132.1, 132.9, 128.7, 65.7. MS: *m/z*: 303.23 (M⁺), 137.9 (ArCH₂⁺)

Esterification of m-nitrobenzaldehyde

3'-nitrobenzyl 3-nitrobenzoate, was prepared according to the general procedure with the two catalysts:

Complex **2** (4 mg, ~0.005 mmol) and m-nitrobenzaldehyde (77.5 mg, 0.512 mmol) were added to the NMR tube, the mixture was allowed to react at room temperature for 24h. The 3'-nitrobenzyl 3-nitrobenzoate was obtained exclusively in 95 % yield.

Complex **3** (4 mg, ~0.005 mmol) and m-nitrobenzaldehyde (74.6 mg, 0.496 mmol) were added to the NMR tube, the mixture was allowed to react at room temperature for 24h. The 3'-nitrobenzyl 3-nitrobenzoate was obtained exclusively in 85 % yield.



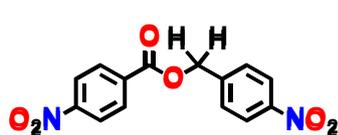
3'-nitrobenzyl 3-nitrobenzoate: ¹H NMR (300 MHz, C₆D₆): δ 8.65 (s, 1H), 7.86 – 7.83 (d, 1H, *J* = 9.0 Hz), 7.75 – 7.65 (m, 2H), 7.36 – 7.33 (d, 1H, *J* = 9.0 Hz), 7.03 – 7.00 (d, 1H, *J* = 9.0 Hz), 6.72 – 6.53 (m, 2H), 4.79 (s, 2H). ¹³C NMR (75.5 MHz, C₆D₆): δ 163.2, 137.1, 134.3, 133.2, 129.2, 129.0, 65.3. MS: *m/z*: 303.23 (M⁺), 137.9 (ArCH₂⁺)

Esterification of p-nitrobenzaldehyde

4'-nitrobenzyl 4-nitrobenzoate, was prepared according to the general procedure with the two catalysts:

Complex **2** (4 mg, ~0.005 mmol) and p-nitrobenzaldehyde (77.2 mg, 0.512 mmol) were added to the NMR tube, the mixture was allowed to react at room temperature for 24h. The 4'-nitrobenzyl 4-nitrobenzoate⁸ was obtained exclusively in 95 % yield.

Complex **3** (4 mg, ~0.005 mmol) and p-nitrobenzaldehyde (74.7 mg, 0.496 mmol) were added to the NMR tube, the mixture was allowed to react at room temperature for 24h. The 4'-nitrobenzyl 4-nitrobenzoate was obtained exclusively in 85 % yield.



4'-nitrobenzyl 4-nitrobenzoate: ¹H NMR (300 MHz, C₆D₆): δ 7.76 – 7.73 (d, 2H, *J* = 9.0 Hz), 7.57 – 7.53 (d, 2H, *J* = 9.0 Hz), 7.02 – 6.99 (d, 2H, *J* = 9.0 Hz), 6.71 – 6.68 (d, 2H, *J* = 9.0 Hz), 4.72 (s, 2H). ¹³C NMR (75.5 MHz, C₆D₆): δ 165.2, 137.3, 134.6, 134.1, 133.8, 130.5, 129.4, 129.0, 64.3. MS: *m/z*: 303.23 (M⁺), 137.9 (ArCH₂⁺)

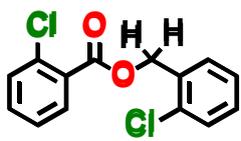
Esterification of o-chlorobenzaldehyde

2'-chlorobenzyl 2-chlorobenzoate⁹, was prepared according to the general procedure with the two catalysts:

Complex **2** (4 mg, ~0.005 mmol) and o-chlorobenzaldehyde (71.8 mg, 0.511 mmol) were added to the NMR tube, the mixture was allowed to react at room temperature for 24h. The 2'-chlorobenzyl 2-chlorobenzoate was obtained exclusively in 90 % yield.

Complex **3** (4 mg, ~0.005 mmol) and o-chlorobenzaldehyde (69.4 mg, 0.514 mmol) were added to the NMR tube, the mixture was allowed to react at room temperature for 24h. The 2'-chlorobenzyl 2-chlorobenzoate was obtained exclusively in 86 % yield.

2'-chlorobenzyl 2-chlorobenzoate: ¹H NMR (300 MHz, C₆D₆): δ 7.82 – 7.75 (m, 1H), 7.52 – 7.49 (d, 1H, *J* = 9.0 Hz), 7.35 – 7.24 (m, 2H), 7.19 – 7.11 (m, 4H), 5.27 (s, 2H). ¹³C NMR (75.5 MHz, C₆D₆): δ 165.8, 134.1, 132.0, 131.4, 130.7, 129.9, 128.9, 126.5, 64.1.



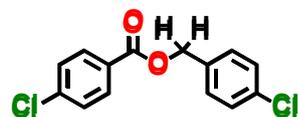
Esterification of p-chlorobenzaldehyde

4'-chlorobenzyl 4-chlorobenzoate⁹, was prepared according to the general procedure with the two catalysts:

Complex **2** (4 mg, ~0.005 mmol) and p-chlorobenzaldehyde (144.2 mg, 0.511 mmol) were added to the NMR tube, the mixture was allowed to react at room temperature for 24h. The 4'-chlorobenzyl 4-chlorobenzoate was obtained exclusively in 80 % yield.

Complex **3** (4 mg, ~0.005 mmol) and p-chlorobenzaldehyde (144.1 mg, 0.511 mmol) were added to the NMR tube, the mixture was allowed to react at room temperature for 24h. The 4'-chlorobenzyl 4-chlorobenzoate was obtained exclusively in 88 % yield.

4'-chlorobenzyl 4-chlorobenzoate: ^1H NMR (300 MHz, C_6D_6): δ 7.98 – 7.95 (d, 1H, $J = 9.0$



Hz), 7.83 – 7.80 (d, 1H, $J = 9.0$ Hz), 7.70 – 7.59 (m, 4H), 7.55 – 7.52 (d, 1H, $J = 9.0$ Hz), 7.36 – 7.33 (d, 1H, $J = 9.0$ Hz), 5.32 (s, 2H). ^{13}C NMR (75.5 MHz, C_6D_6): δ 166.8, 140.9, 134.4, 129.4, 128.8, 128.4,

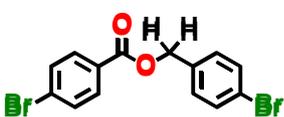
65.4.

Esterification of p-bromobenzaldehyde

4'-bromobenzyl 4-bromobenzoate⁹, was prepared according to the general procedure with the two catalysts:

Complex **2** (4 mg, ~0.005 mmol) and p-bromobenzaldehyde (94.5 mg, 0.511 mmol) were added to the NMR tube, the mixture was allowed to react at room temperature for 12h. The 4'-bromobenzyl 4-bromobenzoate was obtained exclusively in >99 % yield.

Complex **3** (4 mg, ~0.005 mmol) and p-bromobenzaldehyde (91.4 mg, 0.511 mmol) were added to the NMR tube, the mixture was allowed to react at room temperature for 12h. The 4'-bromobenzyl 4-bromobenzoate was obtained exclusively in 95 % yield.



4'-bromobenzyl 4-bromobenzoate: ^1H NMR (300 MHz, C_6D_6): δ 7.90 – 7.87 (d, 2H, $J = 9.0$ Hz), 7.57 – 7.48 (m, 4H), 7.30 – 7.27 (d, 2H, $J = 9.0$ Hz), 5.30 (s, 2H). ^{13}C NMR (75.5 MHz, C_6D_6): δ 165.8,

135.5, 131.4, 130.9, 129.7, 128.4, 66.5.

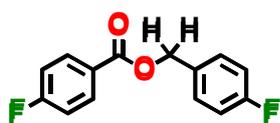
Esterification of p-fluorobenzaldehyde

4'-fluorobenzyl 4-fluorobenzoate, was prepared according to the general procedure with the two catalysts:

Complex **2** (4 mg, ~0.005 mmol) and p-fluorobenzaldehyde (53.8 μL , 0.511 mmol) were added to the NMR tube, the mixture was allowed to react at room temperature for 24h. The 4'-fluorobenzyl 4-fluorobenzoate was obtained exclusively in 25 % yield.

Complex **3** (4 mg, ~0.005 mmol) and p-fluorobenzaldehyde (52.0 μL , 0.511 mmol) were added to the NMR tube, the mixture was allowed to react at room temperature for 24h. The 4'-fluorobenzyl 4-fluorobenzoate was obtained exclusively in 20 % yield.

4'-fluorobenzyl 4-fluorobenzoate: ^1H NMR (300 MHz, C_6D_6): δ 7.72 – 7.69 (d, 2H, $J = 9.0$



Hz), 7.22 – 7.19 (m, 4H), 6.84 – 6.81 (d, 2H, $J = 9.0$ Hz), 4.94 (s, 2H).

^{13}C NMR (75.5 MHz, C_6D_6): δ 166.1, 133.1, 132.5, 131.9, 130.7, 130.4, 68.5.

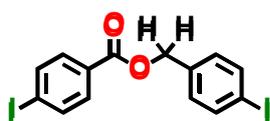
Esterification of p-iodobenzaldehyde

4'-iodobenzyl 4-iodobenzoate, was prepared according to the general procedure with the two catalysts:

Complex **2** (4 mg, ~ 0.005 mmol) and p-iodobenzaldehyde (118.5 mg, 0.511 mmol) were added to the NMR tube, the mixture was allowed to react at room temperature for 24h. The 4'-iodobenzyl 4-iodobenzoate was obtained exclusively in 95 % yield.

Complex **3** (4 mg, ~ 0.005 mmol) and p-iodobenzaldehyde (114.7 mg, 0.511 mmol) were added to the NMR tube, the mixture was allowed to react at room temperature for 24h. The 4'-iodobenzyl 4-iodobenzoate was obtained exclusively in 20 % yield.

4'-iodobenzyl 4-iodobenzoate: ^1H NMR (300 MHz, C_6D_6): δ 7.52 – 7.49 (d, 2H, $J = 9.0$ Hz),



7.36 – 7.24 (m, 4H), 6.60 – 6.57 (d, 2H, $J = 9.0$ Hz), 4.80 (s, 2H). ^{13}C

NMR (75.5 MHz, C_6D_6): δ 164.8, 137.8, 137.5, 137.4, 135.3, 130.8, 130.2, 129.8, 65.4.

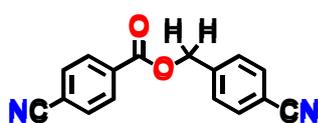
Esterification of p-cyanobenzaldehyde

4'-cyanobenzyl 4-cyanobenzoate, was prepared according to the general procedure with the two catalysts:

Complex **2** (4 mg, ~ 0.005 mmol) and p-cyanobenzaldehyde (66.9 mg, 0.511 mmol) were added to the NMR tube, the mixture was allowed to react at room temperature for 12h. The 4'-fluorobenzyl 4-fluorobenzoate was obtained exclusively in >99 % yield.

Complex **3** (4 mg, ~ 0.005 mmol) and p-cyanobenzaldehyde (64.7 mg, 0.511 mmol) were added to the NMR tube, the mixture was allowed to react at room temperature for 12h. The 4'-cyanobenzyl 4-cyanobenzoate was obtained exclusively in >98 % yield.

4'-cyanobenzyl 4-cyanobenzoate: ^1H NMR (300 MHz, C_6D_6): δ 7.60 – 7.57 (d, 2H, $J = 9.0$



Hz), 7.00 – 6.85 (m, 4H), 6.69 – 6.66 (d, 2H, $J = 9.0$ Hz), 4.72 (s,

2H). ^{13}C NMR (75.5 MHz, C_6D_6): δ 164.5, 139.5, 133.5, 132.9, 128.7, 118.8, 117.4, 116.9, 112.4, 66.2.

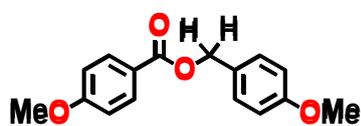
Esterification of p-methoxybenzaldehyde

4'-methoxybenzyl 4-methoxybenzoate⁹ was prepared according to the general procedure with the two catalysts:

Complex **2** (4 mg, ~0.005 mmol) and p-methoxybenzaldehyde (69.5 mg, 0.511 mmol) were added to the NMR tube, the mixture was allowed to react at room temperature for 24h. The 4-methoxybenzyl 4-methoxybenzoate was obtained exclusively in 30 % yield.

Complex **3** (4 mg, ~0.005 mmol) and p-methoxybenzaldehyde (67.2 mg, 0.511 mmol) were added to the NMR tube, the mixture was allowed to react at room temperature for 24h. The 4'-methoxybenzyl 4-methoxybenzoate was obtained exclusively in 15 % yield.

4'-methoxybenzyl 4-methoxybenzoate: ¹H NMR (300 MHz, C₆D₆): δ 8.10 – 8.07 (d, 2H, *J* = 9.0 Hz), 7.85 – 7.82 (d, 2H, *J* = 9.0 Hz), 7.18 – 7.11 (m, 2H), 6.70 – 6.67 (d, 2H, *J* = 9.0 Hz), 5.26 (s, 2H), 3.23 (s, 3H), 3.14 (s, 3H). ¹³C NMR (75.5 MHz, C₆D₆): δ 165.5, 138.2, 136.3, 134.5, 133.9, 129.2, 120.1, 118.4, 116.9, 112.4, 66.2, 55.6, 55.2.



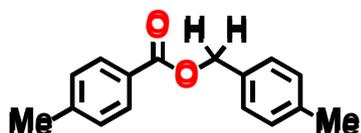
Esterification of p-Tolualdehyde

4'-methylbenzyl 4-methylbenzoate⁹ was prepared according to the general procedure with the two catalysts:

Complex **2** (4 mg, ~0.005 mmol) and p-tolualdehyde (60.5 μL, 0.511 mmol) were added to the NMR tube, the mixture was allowed to react at room temperature for 24h. The 4-methylbenzyl 4-methylbenzoate was obtained exclusively in 66 % yield.

Complex **3** (4 mg, ~0.005 mmol) and p-tolualdehyde (58.1 μL, 0.511 mmol) were added to the NMR tube, the mixture was allowed to react at room temperature for 24h. The 4'-methylbenzyl 4-methylbenzoate was obtained exclusively in 60 % yield.

4'-methylbenzyl 4-methylbenzoate: ¹H NMR (300 MHz, C₆D₆): δ 8.08 – 8.05 (d, 2H, *J* = 9.0 Hz), 7.74 – 7.71 (d, 1H, *J* = 9.0 Hz), 7.35 – 7.32 (d, 1H, *J* = 9.0 Hz), 7.15 – 7.11 (m, 2H), 6.90 – 6.87 (d, 1H, *J* = 9.0 Hz), 6.77 – 6.74 (d, 1H, *J* = 9.0 Hz), 5.17 (s, 2H), 2.01 (s, 3H), 1.89 (s, 3H). ¹³C NMR (75.5 MHz, C₆D₆): δ 159.5, 143.2, 134.2, 133.5, 129.6, 129.0, 128.9, 128.3, 120.1, 66.4, 20.9, 20.6.



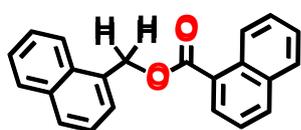
Esterification of 1-naphthaldehyde

1-naphthylmethyl 1-naphthoate¹⁰ was prepared according to the general procedure with the two catalysts:

Complex **2** (4 mg, ~0.005 mmol) and 1-naphthaldehyde (69.4 μ L, 0.511 mmol) were added to the NMR tube, the mixture was allowed to react at room temperature for 24h. The 1-Naphthylmethyl 1-naphthoate was obtained exclusively in 96 % yield.

Complex **3** (4 mg, ~0.005 mmol) and 1-naphthaldehyde (67.1 μ L, 0.511 mmol) were added to the NMR tube, the mixture was allowed to react at room temperature for 24h. The 1-naphthylmethyl 1-naphthoate was obtained exclusively in 90 % yield.

1-naphthylmethyl 1-naphthoate: ¹H NMR (300 MHz, C₆D₆): δ 8.43 – 8.40 (d, 1H, *J* = 9.0



Hz), 8.06 – 8.03 (d, 1H, *J* = 9.0 Hz), 7.95 – 7.92 (d, 1H, *J* = 9.0 Hz), 7.56 – 7.28 (m, 7H), 7.23 – 7.08 (m, 4H), 6.84 (t, 1H, *J* = 9.0 Hz), 5.68 (s, 2H). ¹³C NMR (75.5 MHz, C₆D₆): δ 167.1, 134.8, 134.1,

133.5, 132.2, 131.3, 130.4, 129.7, 129.1, 128.9, 128.2, 128.0, 127.8, 127.1, 126.8, 126.4, 126.3, 126.0, 125.9, 125.2, 124.9, 123.1, 65.7.

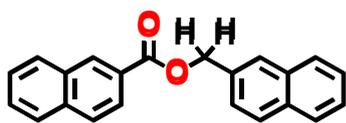
Esterification of 2-naphthaldehyde

2-naphthylmethyl 2-naphthoate¹⁰ was prepared according to the general procedure with the two catalysts:

Complex **2** (4 mg, ~0.005 mmol) and 1-naphthaldehyde (79.8 mg, 0.511 mmol) were added to the NMR tube, the mixture was allowed to react at room temperature for 24h. The 2-naphthylmethyl 2-naphthoate was obtained exclusively in 75 % yield.

Complex **3** (4 mg, ~0.005 mmol) and 2-naphthaldehyde (77.2 μ L, 0.511 mmol) were added to the NMR tube, the mixture was allowed to react at room temperature for 24h. The 2-naphthylmethyl 2-naphthoate was obtained exclusively in 50 % yield.

2-naphthylmethyl 2-naphthoate: ¹H NMR (300 MHz, C₆D₆): δ 8.72 (s, 1H), 8.16 – 8.13 (d,



1H, *J* = 9.0 Hz), 7.98 – 7.90 (m, 7H), 7.67 – 7.58 (m, 5H), 7.23 – 7.08 (m, 4H), 5.63 (s, 2H). ¹³C NMR (75.5 MHz, C₆D₆): δ

166.5, 135.9, 134.1, 133.7, 132.7, 131.6, 131.2, 129.9, 129.0, 128.8, 128.3, 128.0, 127.9, 127.2, 126.7, 126.3, 126.0, 125.9, 125.4, 124.8, 123.5, 67.2.

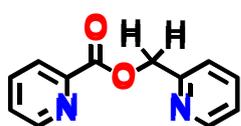
Esterification of 2-pyridinecarboxaldehyde

2-pyridylmethyl-2-picolinate¹¹ was prepared according to the general procedure with the two catalysts:

Complex **2** (4 mg, ~0.005 mmol) and 2-Pyridinecarboxaldehyde (49.6 μ L, 0.511 mmol) were added to the NMR tube, the mixture was allowed to react at room temperature for 24h. The 2-pyridylmethyl-2-picolinate was obtained exclusively in 78 % yield.

Complex **3** (4 mg, ~0.005 mmol) and 2-pyridinecarboxaldehyde (46.9 μ L, 0.511 mmol) were added to the NMR tube, the mixture was allowed to react at room temperature for 24h. The 2-pyridylmethyl-2-picolinate was obtained exclusively in 70 % yield.

Pyridin-2-ylmethyl picolinate: ¹H NMR (300 MHz, C₆D₆): δ 8.43 – 8.40 (m, 2H), 7.89 –



7.86 (m, 2H), 7.26 – 7.23 (m, 2H), 7.09 – 7.05 (m, 2H), 5.46 (s, 2H).

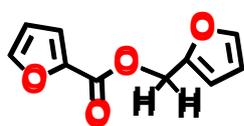
¹³C NMR (75.5 MHz, C₆D₆): δ 162.9, 153.2, 149.4, 149.1, 147.3, 142.9, 126.2, 124.9, 122.2, 121.0, 67.3.

Esterification of furfural

2'-furylmethyl-2-furancarboxylate⁹ was prepared according to the general procedure with the two catalysts:

Complex **2** (4 mg, ~0.005 mmol) and furfural (42.3 μ L, 0.511 mmol) were added to the NMR tube, the mixture was allowed to react at room temperature for 24h. The 2-furylmethyl-2-furancarboxylate was obtained exclusively in 20 % yield.

Complex **3** (4 mg, ~0.005 mmol) and furfural (40.9 μ L, 0.511 mmol) were added to the NMR tube, the mixture was allowed to react at room temperature for 24h. The 2-furylmethyl-2-furancarboxylate was obtained exclusively in 18 % yield.



2'-furylmethyl-2-furancarboxylate: ¹H NMR (300 MHz, C₆D₆): δ 7.54 –

7.20 (m, 3H), 6.96 – 6.60 (m, 3H). ¹³C NMR (75.5 MHz, C₆D₆): δ 159.1,

50.7, 147.6, 143.4, 121.6, 114.2, 112.0, 79.9, 77.5, 75.3, 60.5. MS: m/z

193.15 (M⁺), 125.96 (ArCOOCH₂⁺)

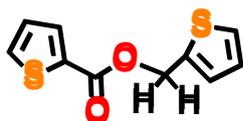
Esterification of 2-thiophencarboxaldehyde

2'-thiophenylmethyl-2-thiophencarboxylate¹⁰ was prepared according to the general procedure with the two catalysts:

Complex **2** (4 mg, ~0.005 mmol) and 2-thiophencarboxaldehyde (47.7 μL , 0.511 mmol) were added to the NMR tube, the mixture was allowed to react at room temperature for 24h. The 2'-thiophenylmethyl-2-thiophencarboxylate was obtained exclusively in 30 % yield.

Complex **3** (4 mg, ~0.005 mmol) and 2-thiophencarboxaldehyde (46.2 μL , 0.511 mmol) were added to the NMR tube, the mixture was allowed to react at room temperature for 24h. The 2-thiophenylmethyl-2-thiophencarboxylate was obtained exclusively in 18 % yield.

2'-thiophenylmethyl-2-thiophencarboxylate: ^1H NMR (300 MHz, C_6D_6): δ 7.87 – 7.83 (m,



2H), 7.67 – 7.63 (m, 2H), 7.39 – 7.36 (m, 2H), 5.39 (s, 2H). ^{13}C NMR (75.5 MHz, C_6D_6): δ 158.1, 133.4, 132.2, 128.2, 127.4, 126.7, 126.5, 125.7, 124.5, 66.8.

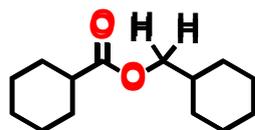
Esterification of cyclohexanecarboxaldehyde

Cyclohexylmethyl cyclohexanecarboxylate¹² was prepared according to the general procedure with the two catalysts:

Complex **2** (4 mg, ~0.005 mmol) and cyclohexanecarboxaldehyde (61.9 μL , 0.511 mmol) were added to the NMR tube, the mixture was allowed to react at room temperature for 2h. The Cyclohexylmethyl cyclohexanecarboxylate was obtained exclusively in 100 % yield.

Complex **3** (4 mg, ~0.005 mmol) and cyclohexanecarboxaldehyde (59.8 μL , 0.511 mmol) were added to the NMR tube, the mixture was allowed to react at room temperature for 2h. The Cyclohexylmethyl cyclohexanecarboxylate was obtained exclusively in 100 % yield.

Cyclohexylmethyl cyclohexanecarboxylate: ^1H NMR (300 MHz, C_6D_6): δ 3.82 – 3.80 (d, 2H, J = 6.0 Hz), 2.20 – 2.10 (m, 1H), 1.84 – 1.80 (m, 2H), 1.57 – 1.37 (m, 10H), 1.07 – 0.95 (m, 7H), 0.84 – 0.75 (m, 2H). ^{13}C NMR (75.5 MHz, C_6D_6): δ 176.8, 66.4, 47.2, 40.2, 30.5, 30.1, 29.8, 28.2, 27.4, 26.3, 24.5.



MS: m/z 225.18 ($\text{M}+\text{H}$).

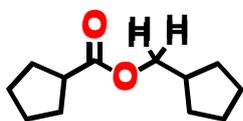
Esterification of cyclopentylcarbaldehyde

Cyclopentylmethyl cyclopentanecarboxylate¹² was prepared according to the general procedure with the two catalysts:

Complex **2** (4 mg, ~0.005 mmol) and cyclopentylcarbaldehyde (61.9 μL , 0.511 mmol) were added to the NMR tube, the mixture was allowed to react at room temperature for 2h. The Cyclopentylmethyl cyclopentanecarboxylate was obtained exclusively in 100 % yield.

Complex **3** (4 mg, ~0.005 mmol) and cyclopentylcarbaldehyde (59.8 μL , 0.511 mmol) were added to the NMR tube, the mixture was allowed to react at room temperature for 2h. The Cyclopentylmethyl cyclopentanecarboxylate was obtained exclusively in 100 % yield.

Cyclopentylmethyl cyclopentanecarboxylate: ^1H NMR (300 MHz, C_6D_6): δ 3.92 – 3.90 (d, 2H, $J = 6.0$ Hz), 2.68 – 2.60 (m, 1H), 2.18 – 2.12 (m, 1H), 1.88 – 1.66 (m, 8H), 1.62 – 1.54 (m, 6H), 1.22 – 1.18 (m, 2H). ^{13}C NMR (75.5 MHz, C_6D_6): δ 175.8, 68.4, 45.2, 39.2, 30.9, 30.1, 29.5, 28.7, 24.5. MS: m/z 197.15 (M+H).

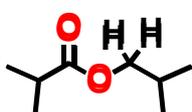


Esterification of isobutyraldehyde

Isobutylisobutyrate¹³ was prepared according to the general procedure with the two catalysts: Complex **2** (4 mg, ~0.005 mmol) and isobutyraldehyde (46.6 μL , 0.511 mmol) were added to the NMR tube, the mixture was allowed to react at room temperature for 2h. The Isobutylisobutyrate was obtained exclusively in 100 % yield.

Complex **3** (4 mg, ~0.005 mmol) and isobutyraldehyde (45.1 μL , 0.511 mmol) were added to the NMR tube, the mixture was allowed to react at room temperature for 2h. The Isobutylisobutyrate was obtained exclusively in 100 % yield.

Isobutylisobutyrate: ^1H NMR (300 MHz, C_6D_6): δ 3.75 – 3.73 (d, 2H, $J = 6.0$ Hz), 2.32 (q, 1H), 1.73 – 1.64 (m, 1H), 1.02 – 0.99 (d, 6H, $J = 6.0$ Hz), 0.71 – 0.68 (d, 6H, $J = 6.0$ Hz). ^{13}C NMR (75.5 MHz, C_6D_6): δ 176.2, 69.9, 34.2, 27.4, 18.7, 18.6, 18.1.

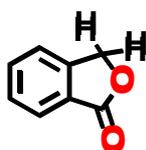


Lactonization of phthalaldehyde

Phthalide¹⁴ was prepared according to the general procedure with the two catalysts:

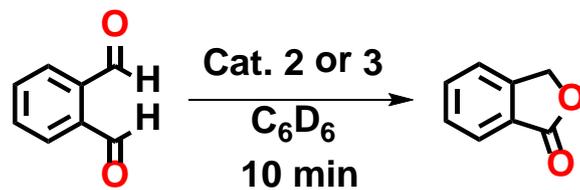
Complex **2** (4 mg, ~0.005 mmol) and phthalaldehyde (46.6 μL , 0.511 mmol) were added to the NMR tube, the mixture was allowed to react at room temperature for 2h. The Phthalide was obtained exclusively in 100 % yield.

Complex **3** (4 mg, ~0.005 mmol) and phthalaldehyde (46.6 μL , 0.511 mmol) were added to the NMR tube, the mixture was allowed to react at room temperature for 2h. The Phthalide was obtained exclusively in 100 % yield.



Phthalide: ^1H NMR (300 MHz, C_6D_6): δ 7.65 – 7.62 (d, 1H, $J = 9.0$ Hz), 7.00 – 6.96 (m, 1H), 6.89 – 6.84 (d, 1H, $J = 6.0$ Hz), 6.59 – 6.57 (d, 1H, $J = 6.0$

Hz), 4.35 (s, 2H). ^{13}C NMR (75.5 MHz, C_6D_6): δ 170.2, 145.6, 134.5, 127.8, 125.2, 121.1, 69.9.



Scheme S2: Lactonization of phthalaldehyde

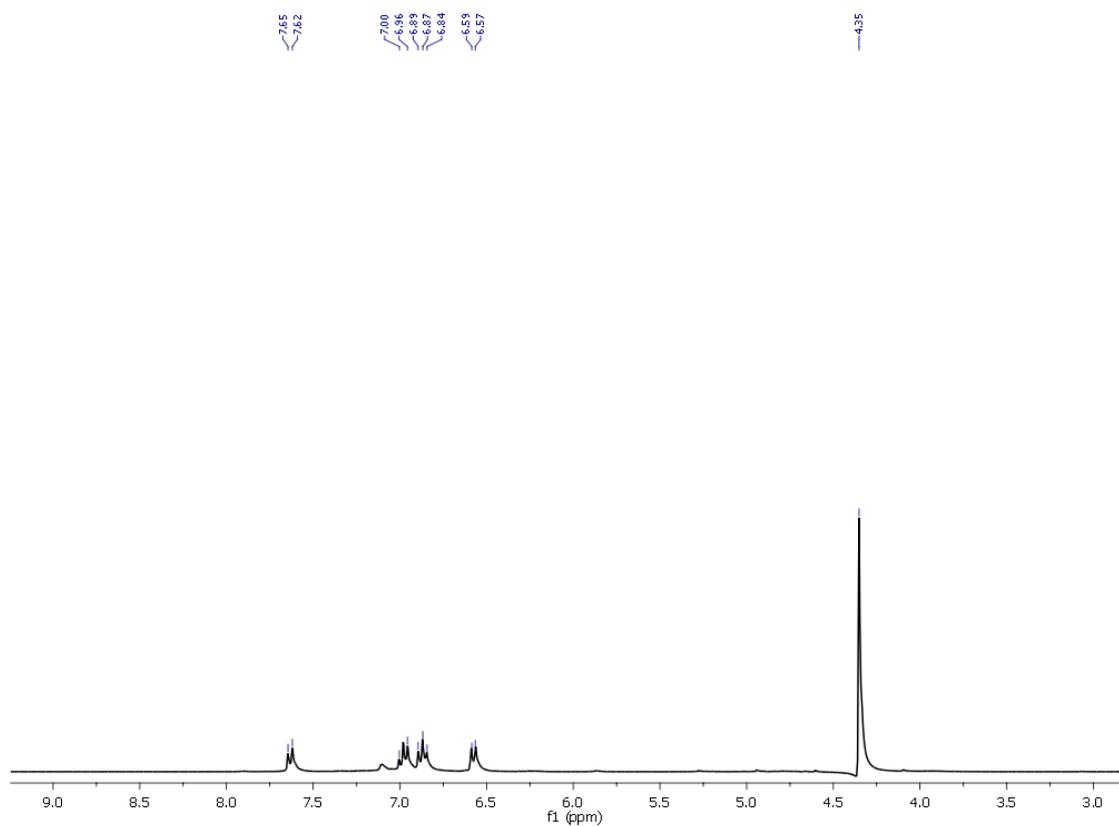


Figure S6. ^1H NMR spectra of Phthalide

Cross esterification of benzaldehyde and 1-naphthaldehyde

The cross-esterification of benzaldehyde (52.1 μL , 0.510 mmol) and 1-naphthaldehyde (69.4 μL , 0.511 mmol) was carried out following the general procedure described above. A mixture of products **I** (17%), **II** (16%), **III** (62%) and **IV** (4%) was obtained (Entry 1, Table 2).

I (17%): $^1\text{H NMR}$ (300 MHz, C_6D_6): δ 8.07 – 8.03 (m, 2H), 7.18 – 6.94 (m, 8H), 5.12 (s, 2H).

II (16%): $^1\text{H NMR}$ (300 MHz, C_6D_6): δ 8.43 – 8.40 (d, 1H, $J = 9.0$ Hz), 8.06 – 8.03 (d, 1H, $J = 9.0$ Hz), 7.95 – 7.92 (d, 1H, $J = 9.0$ Hz), 7.56 – 7.28 (m, 7H), 7.23 – 7.08 (m, 4H), 6.84 (t, 1H, $J = 9.0$ Hz), 5.68 (s, 2H).

III¹⁵ (62%): $^1\text{H NMR}$ (300 MHz, C_6D_6): δ 8.15 – 8.12 (d, 1H, $J = 9.0$ Hz), 8.09 – 8.06 (d, 2H, $J = 9.0$ Hz), 7.95 – 7.92 (d, 1H, $J = 9.0$ Hz), 7.90 – 7.87 (d, 1H, $J = 9.0$ Hz), 7.68 – 7.65 (d, 1H, $J = 9.0$ Hz), 7.60 – 7.45 (m, 4H), 7.42 – 7.35 (m, 2H), 5.83 (s, 2H).

IV¹⁶ (4%): $^1\text{H NMR}$ (300 MHz, C_6D_6): δ 9.03 – 9.00 (d, 1H, $J = 9.0$ Hz), 8.25 – 8.16 (m, 2H), 8.00 – 7.97 (d, 1H, $J = 9.0$ Hz), 7.92 – 7.89 (d, 1H, $J = 9.0$ Hz), 7.68 – 7.63 (m, 1H), 7.60 – 7.48 (m, 4H), 7.44 – 7.38 (m, 2H), 7.34 – 7.29 (m, 1H), 5.52 (s, 2H).

The cross-esterification of benzaldehyde (52.1 μL , 0.510 mmol) and 1-naphthaldehyde (104.1 μL , 0.767 mmol) was carried out following the general procedure described above and **III** was obtained exclusively (Entry 2, Table 2).

Cross esterification of benzaldehyde and 2-pyridylcarboxaldehyde

The cross-esterification of benzaldehyde (52.1 μL , 0.510 mmol) and 2-pyridinecarboxaldehyde (49.6 μL , 0.511 mmol) was carried out following the general procedure described above. A mixture of products **I** (3%), **II** (6%), **III** (80%) and **IV** (10%) was obtained (Entry 3, Table 3).

I (3%): $^1\text{H NMR}$ (300 MHz, C_6D_6): δ 8.07 – 8.03 (m, 2H), 7.18 – 6.94 (m, 8H), 5.12 (s, 2H).

II (6%): $^1\text{H NMR}$ (300 MHz, C_6D_6): δ 8.43 – 8.40 (m, 2H), 7.89 – 7.86 (m, 2H), 7.26 – 7.23 (m, 2H), 7.09 – 7.05 (m, 2H), 5.46 (s, 2H).

III¹⁷ (80%): $^1\text{H NMR}$ (300 MHz, C_6D_6): δ 8.63 – 8.59 (m, 1H), 8.13 – 8.09 (m, 1H), 8.07 (s, 2H), 7.72 – 7.60 (m, 2H), 7.46 – 7.43 (d, 1H, $J = 9.0$ Hz), 7.26 – 7.20 – 7.43, 5.44 (s, 2H).

IV¹⁸ (10%): $^1\text{H NMR}$ (300 MHz, C_6D_6): δ 8.71 – 8.67 (m, 1H), 8.15 – 8.12 (m, 1H), 7.85 – 7.81 (m, 3H), 7.46 – 7.43 (d, 1H, $J = 9.0$ Hz), 7.36 – 7.20 (m, 3H), 5.46 (s, 2H).

The cross-esterification of benzaldehyde (52.1 μL , 0.510 mmol) and 2-pyridinecarboxaldehyde (74.4 μL , 0.765 mmol) was carried out following the general procedure described above and **III** was obtained exclusively (Entry 4, Table 2).

Cross esterification of benzaldehyde and cyclohexyl-carboxaldehyde

The cross-esterification of benzaldehyde (52.1 μL , 0.510 mmol) and cyclohexyl-carboxaldehyde (61.9 μL , 0.511 mmol) was carried out following the general procedure described above. A mixture of products **I** (27%), **II** (46%), and **IV** (26%) was obtained (Entry 5, Table 3).

I (27%): $^1\text{H NMR}$ (300 MHz, C_6D_6): δ 8.07 – 8.03 (m, 2H), 7.18 – 6.94 (m, 8H), 5.12 (s, 2H).

II (46%): $^1\text{H NMR}$ (300 MHz, C_6D_6): δ 3.82 – 3.80 (d, 2H, $J = 6.0$ Hz), 2.20 – 2.10 (m, 1H), 1.84 – 1.80 (m, 2H), 1.57 – 1.37 (m, 10H), 1.07 – 0.95 (m, 7H), 0.84 – 0.75 (m, 2H).

IV¹⁸ (26%): $^1\text{H NMR}$ (300 MHz, C_6D_6): δ 7.48 – 7.45 (d, 2H, $J = 9.0$ Hz), 7.11 – 6.92 (m, 3H), 5.11 (s, 2H), 2.61 – 2.45 (m, 1H), 2.19 – 2.04 (m, 2H), 1.91 – 1.71 (m, 3H), 1.67 – 1.50 (m, 5H).

The cross-esterification of benzaldehyde (78.2 μL , 0.765 mmol) and cyclohexyl-carboxaldehyde (61.9 μL , 0.511 mmol) was carried out following the general procedure described above. A mixture of products **I** (20%), **II** (35%), and **IV** (40%) was obtained (Entry 6, Table 3).

Cross esterification of benzaldehyde and isobutyraldehyde

The cross-esterification of benzaldehyde (52.1 μL , 0.510 mmol) and isobutyraldehyde (46.6 μL , 0.511 mmol) was carried out following the general procedure described above. A mixture of products **I** (18%), **II** (55%), **III** (6%) and **IV** (25%) was obtained (Entry 7, Table 3).

I (18%): $^1\text{H NMR}$ (300 MHz, C_6D_6): δ 8.07 – 8.03 (m, 2H), 7.18 – 6.94 (m, 8H), 5.12 (s, 2H).

II (55%): $^1\text{H NMR}$ (300 MHz, C_6D_6): δ 3.75 – 3.73 (d, 2H, $J = 6.0$ Hz), 2.32 (m, 1H), 1.73 – 1.64 (m, 1H), 1.02 – 0.99 (d, 6H, $J = 6.0$ Hz), 0.71 – 0.68 (d, 6H, $J = 6.0$ Hz).

III¹⁹ (6%): $^1\text{H NMR}$ (300 MHz, C_6D_6): δ 8.07 – 8.03 (m, 2H), 7.18 – 6.91 (m, 3H), 4.03 – 4.01 (d, 2H, $J = 6.0$ Hz), 1.78 – 1.71 (m, 1H), 0.78 (d, 6H, $J = 6.0$ Hz).

IV²⁰ (25%): $^1\text{H NMR}$ (300 MHz, C_6D_6): δ 7.41 – 7.35 (m, 5H), 5.12 (s, 2H), 7.11 – 6.92 (m, 3H), 5.11 (s, 2H), 2.52 (m, 1H), 1.21 (d, 6H, $J = 6.0$ Hz).

The cross-esterification of benzaldehyde (78.2 μL , 0.765 mmol) and isobutyraldehyde (46.6 μL , 0.511 mmol) was carried out following the general procedure described above. A mixture of products **I** (46%), **II** (28%), **III** (11%) and **IV** (15%) was obtained (Entry 8, Table 3).

The cross-esterification of benzaldehyde (52.1 μL , 0.510 mmol) and isobutyraldehyde (69.9 μL , 0.765 mmol) was carried out following the general procedure described above. A mixture of products **II** (77%) and **IV** (24%) was obtained (Entry 9, Table 3).

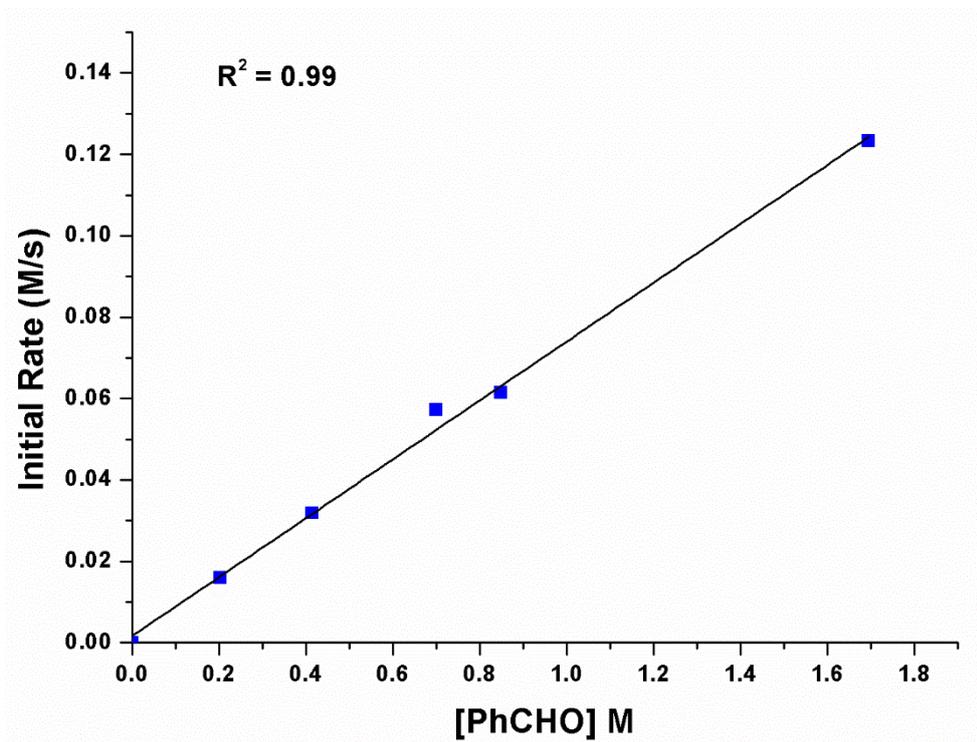


Figure S7. Observed aldehyde concentration-dependent initial reaction rate for precatalyst **2**.

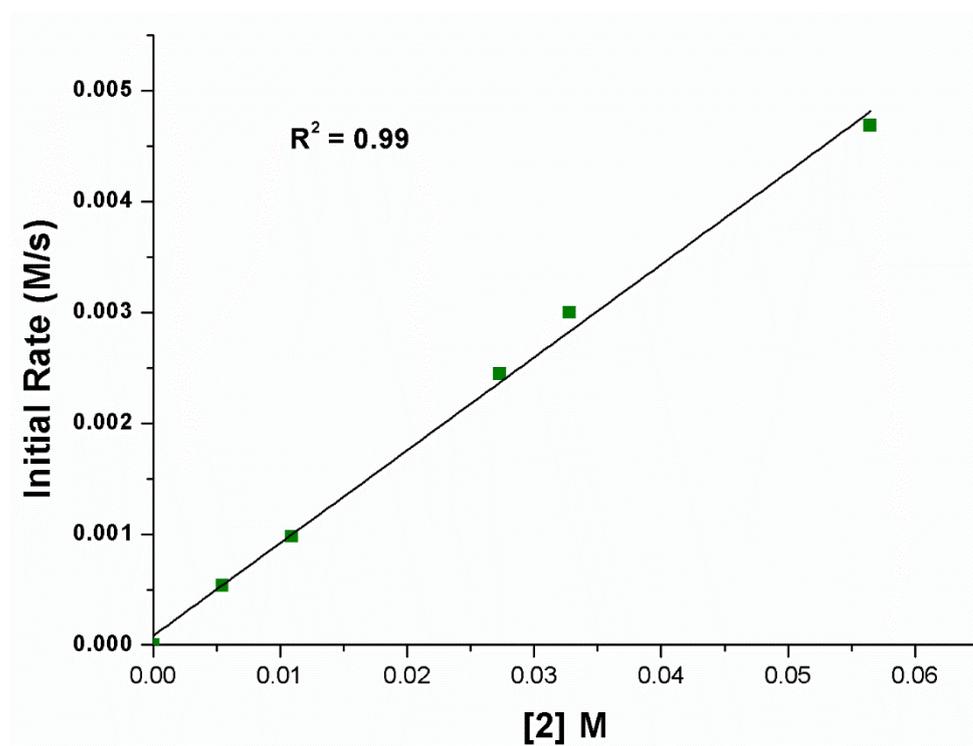


Figure S8. Variation of the reaction initial rate with concentration of precatalyst **2**.

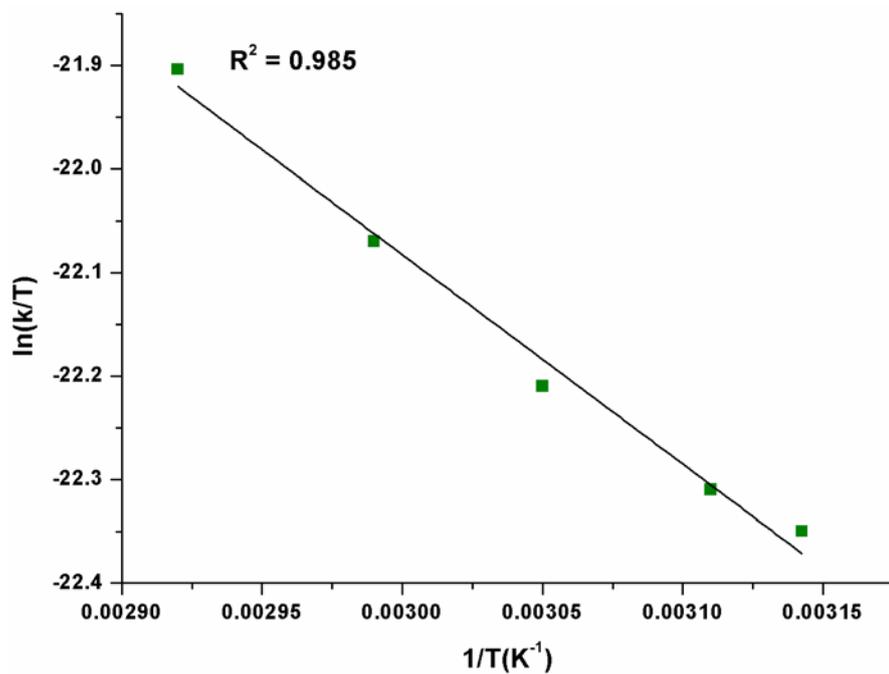


Figure S9. Eyring plot of the dimerization of PhCHO mediated by complex 2.

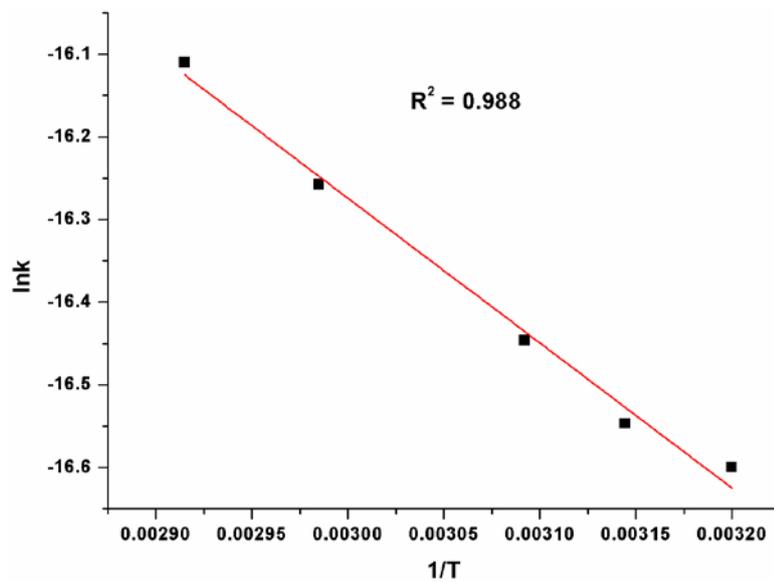


Figure S10. Arrhenius plot of the dimerization of PhCHO mediated by complex 2.

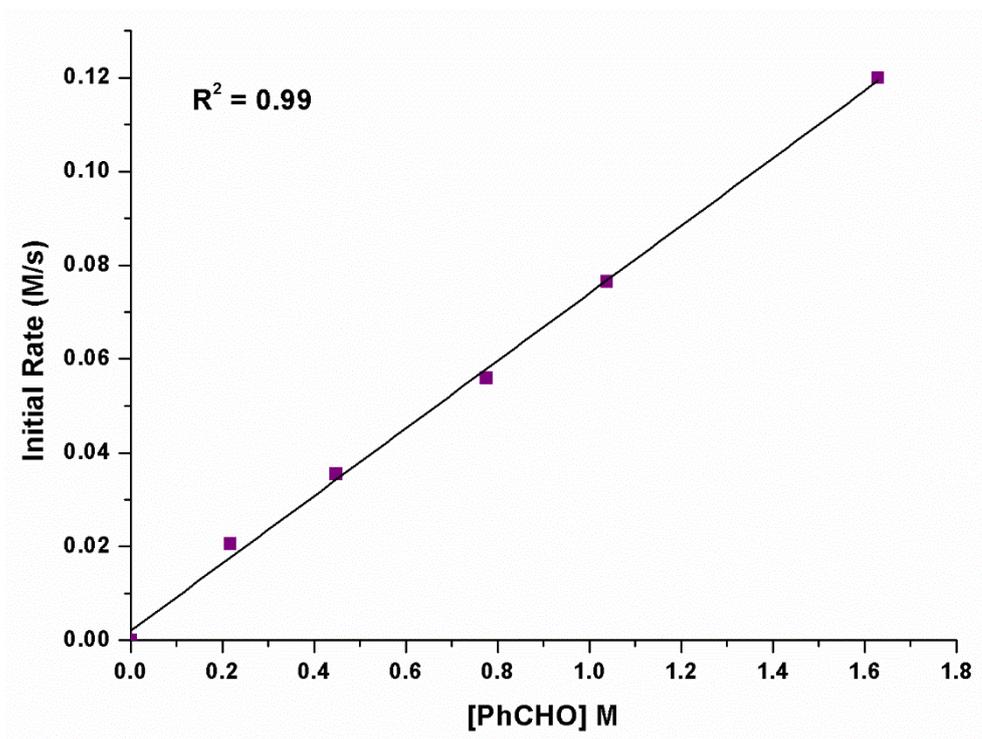


Figure S11. Observed aldehyde concentration-dependent initial reaction rate for precatalyst 3.

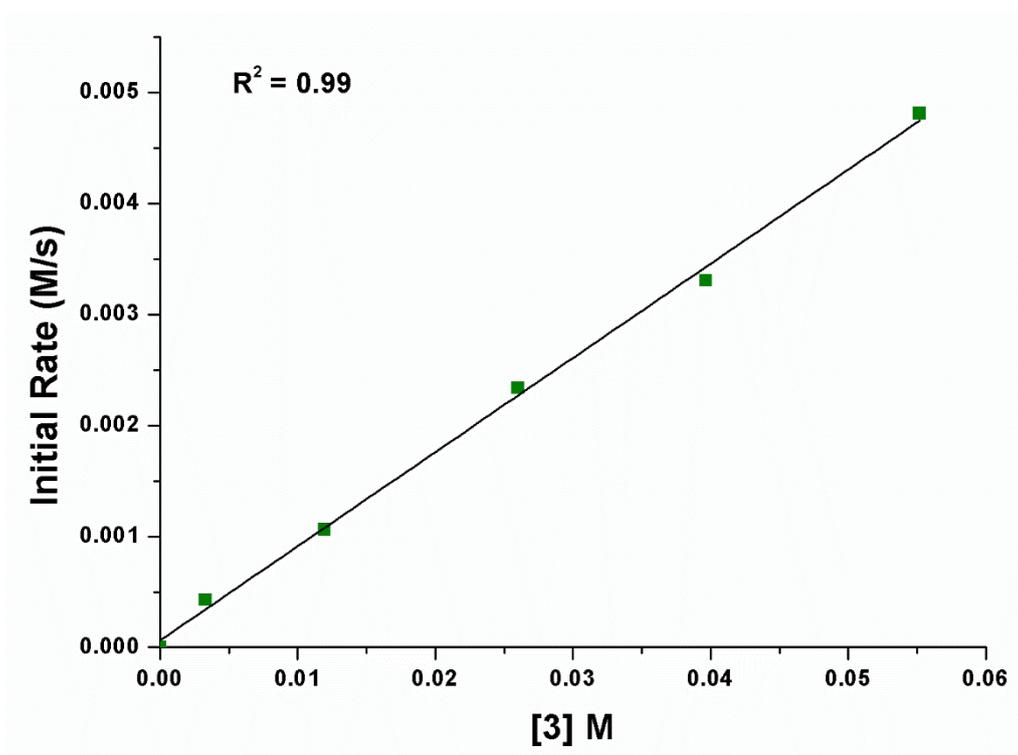


Figure S12. Variation of initial reaction rate with concentration of precatalyst 3.

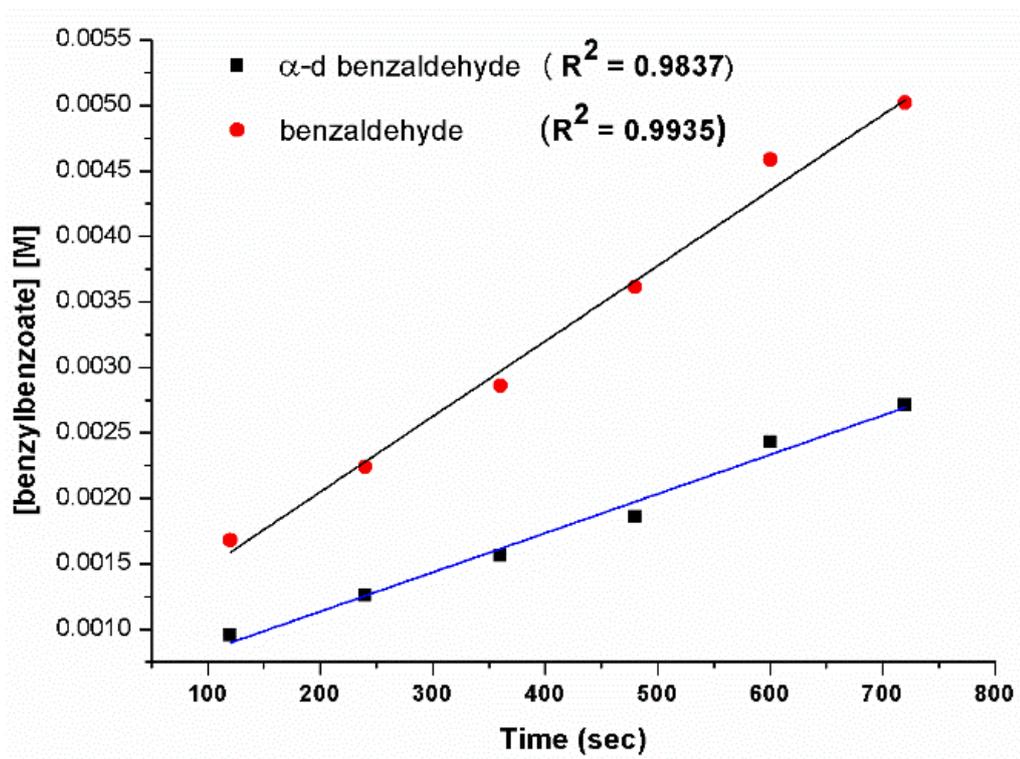


Figure S13. Kinetic isotopic effect on the Tishchenko reaction of benzaldehyde and α -d-benzaldehyde promoted by complex **2**.

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