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Reductive α-alkylation of ketones with aldehydes at atmospheric pressure of carbon monoxide: the effect of fluoride activation in ruthenium catalysis

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GENERAL INFORMATION

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification, THF and Et_2O was distilled over sodium/benzophenone, DCM was distilled over calcium hydride, acetone was dried over 3Å MS, MeCN was taken form SPS machine. Carbon monoxide obtained from NII KM (Moscow, Russia).

Purification of the products was performed either via column chromatography (Acros Organic silica gel 0.06–0.2 mm) or using an MPLC machine InterChim PuriFlash with PF-30SIHP- F0012 column. For other details of the chromatographic procedures, see the descriptions of the particular compounds below.

^{1}H and ^{13}C NMR spectra were recorded on Bruker AV-300, AV-400 and Varian Inova-400 spectrometers at ambient temperature. Chemical shifts δ are reported in ppm using the solvent resonance signal as an internal standard. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad; coupling constants are given in Hertz (Hz).

Analytical gas chromatography (GC) was performed using a Chromatec Crystal 5000.2 gas chromatograph fitted with a flame ionization detector (He was used as the carrier gas, 37 ml min^{-1}) and an MS detector. Chromatec CR-5MS (30 meters) capillary column was used. GC settings for the yield determination using the FID detector and the CR5ms column: The injector temperature was 250 °C, the split ratio of 50:1 at the moment of injection, the FID temperature was 250 °C. Column compartment temperature program: 100°C for 2 min, 100°C → 280°C at 30 deg min^{-1}, 280°C for 3 min. GC yields were determined with dodecane internal standard. For GCMS analysis: The injector temperature was 250 °C, split ratio of 75:1 at the moment of injection. Column compartment temperature program: 60°C for 4 min, 60°C → 250°C at 30 deg min^{-1}, 250°C for 12 min. Flow rate 1 mL/min. MSD parameters: ion source temperature 200°C, transfer line temperature 230°C.

ESI-MS spectra were registered using LCMS-2020 (Shimadzu). The voltage on the capillary was 4500 V; the range of scanned masses, m/z 50-2000. Nitrogen as dry gas (15 dm^3 min^{-1}) and nebulizer gas (1.5 dm^3 min^{-1}); interface temperature: 150 °C, heat block temperature 150°C, flow rate 0.1 ml/min (acetonitrile as an eluent, direct connection of LC and MS modules without column).

EXPERIMENTAL SECTION

General procedure for a 10 ml screw-cap Schlenk tube

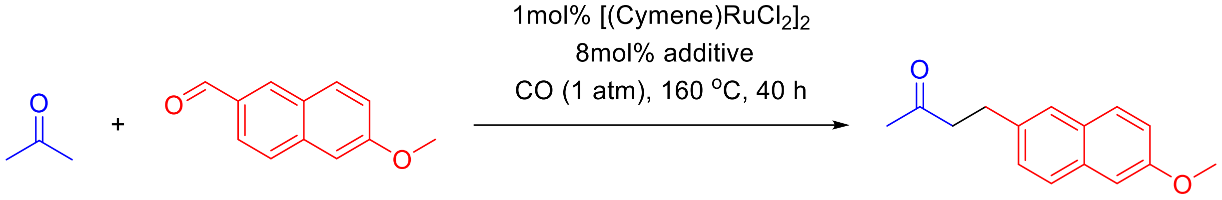
The first GC vial was charged with (*p*-cymene)ruthenium dichloride dimer (6 mg), that was dissolved in dry DCM (1600 μl). Another GC vial was charged with TBAT (28.8 mg)f, that was dissolved in dry DCM (1600 μL). A 10 ml screw-cap Schlenk tube was dried by Schlenk technique and charged with aliquot of the catalyst, followed by aliquot of TBAT. The solution was stirred for 15 minutes, then DCM was evaporated from the Schlenk tube, the tube was filled with carbon monoxide. Other reactants and solvent were added in the carbon monoxide flow. The tube was sealed and placed into a preheated oil bath. After the indicated time, the reactor was cooled to room temperature. Its content was analyzed using NMR or GC, and the product was isolated using chromatography (preparative TLC, column chromatography on silica gel or using flash chromatograph InterChim PuriFlash).

General procedure for a 100 ml screw-cap Schlenk tube

A 100 ml screw-cap Schlenk tube was dried by Schlenk technique and charged with (*p*-cymene)ruthenium dichloride dimer, TBAT, and dry DCM (1 ml). The solution was stirred for 15 minutes, then DCM was evaporated from the Schlenk tube, and was filled with carbon monoxide. Other reactants and solvent were added in the carbon monoxide flow. The Schlenk tube was sealed and placed into a preheated oil bath. After the indicated time, the reactor was cooled to room temperature. Its content was analyzed using NMR or GC, and the product was isolated using chromatography (preparative TLC, column chromatography on silica gel or using flash chromatograph InterChim PuriFlash).

Additive Screening and Conditions Optimization for Nabumetone

Table S1 Investigation of influence of halogen-containing additives

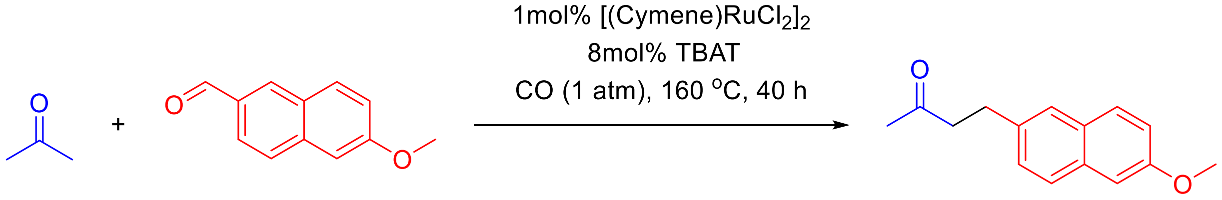


Entry[a]	Additive	Yield[b]
1	-	16
2	$Bu_4N(Ph_3SiF_2)$ (TBAT)	39
3	Bu_4NF	22
4	Bu_4NCl	5
5	Bu_4NBr	7
6	Bu_4NI	8

[a] 6-Methoxy-2-naphthaldehyde (76.0 mg, 0.41 mmol), acetone (3.56 ml, 49.04 mmol), (*p*-cymene)ruthenium dichloride dimer (2.5 mg, 1 mol %), additive (8.6 – 17.7 mg, 8 mol%). The reactions were performed in 100 ml screw-cap Schlenk tube, immersion of the vessel 4/5.

[b] Yields were determined by NMR

Table S2 Investigation of influence of the excess of acetone

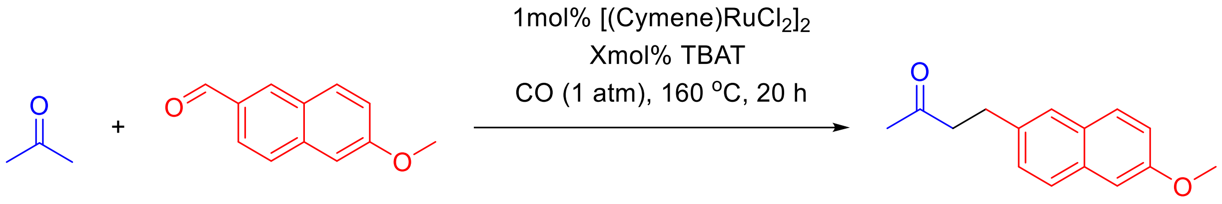


Entry[a]	**Acetone (eq.)**	**Yield[b]**
1	80	31
2	120	39
3	170	29

[a] 6-methoxy-2-naphthaldehyde (76.0 mg, 0.41 mmol), acetone (3.37 – 5.04 ml, 32.69 – 69.46 mmol) acetone, (*p*-cymene)ruthenium dichloride dimer (2.5 mg, 1 mol %), TBAT (17.7 mg, 8 mol%). The reactions were performed in a 100 ml screw-cap Schlenk tube, immersion of the vessel is 4/5.

[b] Yields were determined by NMR

Table S3 Investigation of influence of TBAT loading



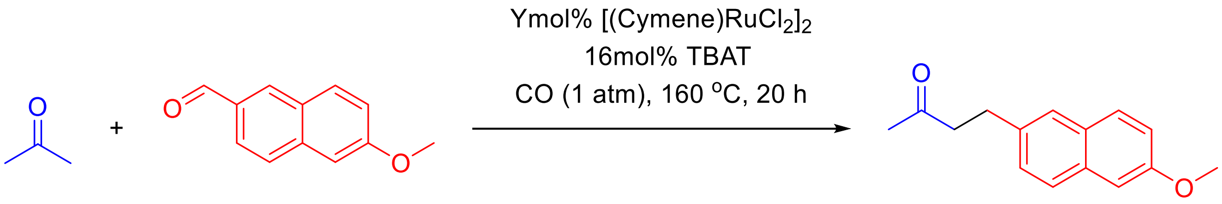
Entry[a]	**TBAT, mol%**	**Yield**[b]
1	0	12
2	1	14
3	4	17
4	8	35
5[c]	16	53

[a] 6-methoxy-2-naphthaldehyde (7.60 mg, 0.04 mmol), acetone (356 µl, 4.92 mmol), (*p*-cymene)ruthenium dichloride dimer (0.25 mg, 1 mol %), TBAT (0–3.54 mg, 0–16 mol%). The reactions were performed in a 10 ml screw-cap Schlenk tube, immersion of the vessel 4/5.

[b] Yields were determined by NMR

[c] Yields are given as average of two experiments

Table S4 Investigation of influence of the catalyst loading



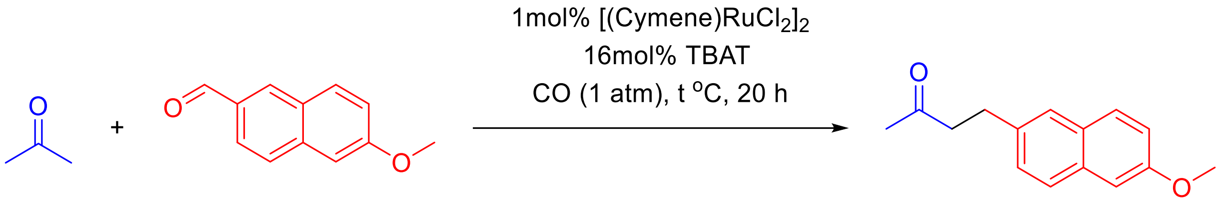
Entry[a]	**[Ru] mol%**	**Yield**[b]
1	0	0
2	0.5	49
3[c]	1	53
4	2	26

[a] 6-methoxy-2-naphthaldehyde (7.60 mg, 0.04 mmol), acetone (356 µl, 4.92 mmol), (*p*-cymene)ruthenium dichloride dimer (0.00 – 0.50 mg, 0 – 1 mol %), TBAT (3.54 mg, 16 mol%). The reactions were performed in a 10 ml screw-cap Schlenk tube, immersion of the vessel 4/5.

[b] Yields were determined by NMR

[c] Yields are given as average of two experiments

Table S5 Investigation of influence of temperature



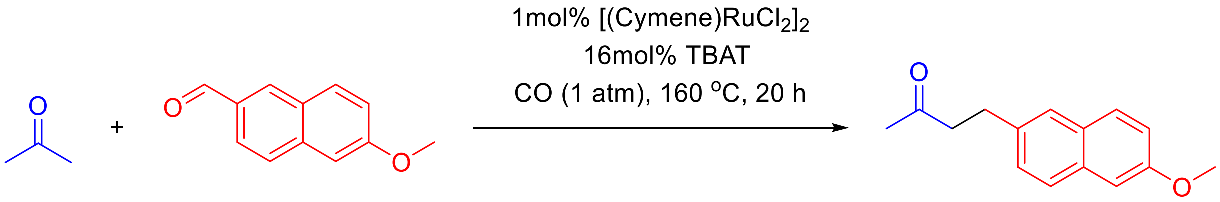
Entry[a]	*T*/°C	Yield[b]
1	140	46
2	150	52
3[c]	160	53
4	170	43

[a] 6-methoxy-2-naphthaldehyde (7.60 mg, 0.04 mmol), acetone (356 μl, 4.92 mmol), (*p*-cymene)ruthenium dichloride dimer (0.25 mg, 1 mol %), TBAT (3.54 mg, 16 mol%). The reactions were performed in a 10 ml screw-cap Schlenk tube, immersion of the vessel 4/5.

[b] Yields were determined by NMR

[c] Yields are given as average of two experiments

Table S6 Investigation of influence of the degree of immersion of the vessel in an oil bath



Entry[a]	Immersion of the tube	Yield[b]
1	1/5	80
2	3/5	92
3[c]	4/5	58

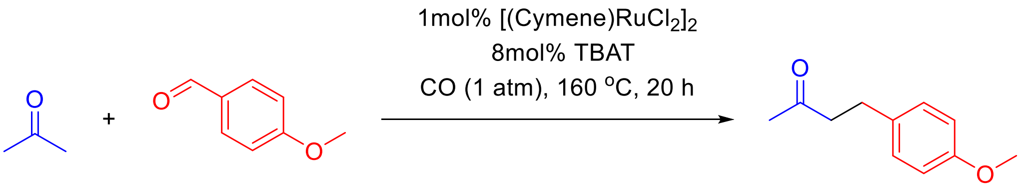
[a] 6-methoxy-2-naphthaldehyde (76.0 mg, 0.41 mmol), acetone (3.56 ml, 49.90 mmol), (*p*-cymene)ruthenium dichloride dimer (2.5 mg, 1 mol %), TBAT (35.4 mg, 16 mol%). The reactions were performed in a 100 ml screw-cap Schlenk tube

[b] Yields were determined by NMR

[c] 1,5-bis(6-methoxynaphthalen-2-yl)pentan-3-one is detected as a major side product

Influence of volume of the vessel

Table S7 Investigation of influence of volume of the vessel



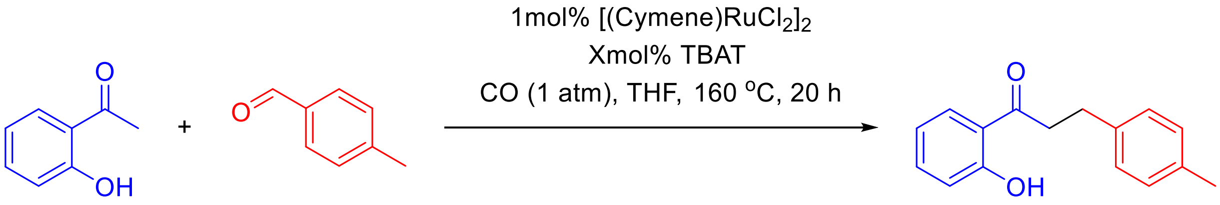
Entry[a]	**Volume of the tube (ml)**	**Yield**[b]
1	10	0
2	25	5
3	100	18
4	250	5

[a] 4-methoxybenzaldehyde (55.0 mg, 0.40 mmol), acetone (2.35 ml, 32.35 mmol), (*p*-cymene)ruthenium dichloride dimer (2.5 mg, 1 mol %), TBAT (35.4 mg, 16 mol%). The reactions were performed in a screw-cap Schlenk tube, immersion of vessels 4/5.

[b] Yields were determined by NMR as average of two experiments

Optimization for 1-(2-hydroxyphenyl)-3-(p-tolyl)propan-1-one

Table S8 Investigation of influence of TBAT loading

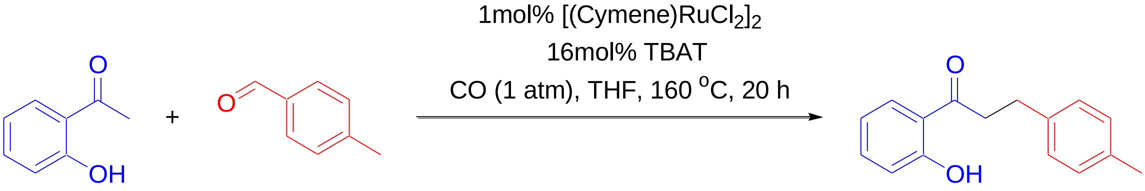


Entry[a]	**TBAT (mol%)**	**Yield**[b]
1	16	10
2	8	18
3	0	0

[a] 4-methylbenzaldehyde (47.0 µl, 0.40 mmol), 1-(2-hydroxyphenyl)ethan-1-one (144.00 µl, 1.20 mmol), (p-cymene)ruthenium dichloride dimer (2.5 mg, 1 mol%), TBAT (0 – 35.4 mg, 0 – 16 mol%), THF (3.5 ml). The reactions were performed in a 100 ml screw-cap Schlenk tube, immersion of the vessel 2/3.

[b] Yields were determined by NMR

Table S9 Investigation of influence of solvent amount and immersion of the vessel

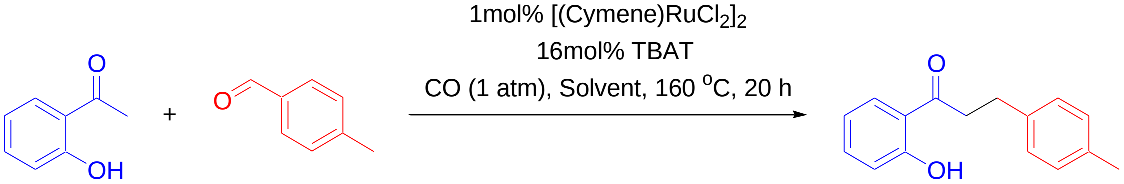


Entry[a]	Solvent (ml)	Immersion of the tube	Yield[b]
1	THF (3.5)	2/3	10
2	THF (1.5)	2/3	59
3	THF (1)	2/3	50
4	THF (1.5)	4/5	70

[a] 4-methylbenzaldehyde (47.0 µl, 0.40 mmol), 1-(2-hydroxyphenyl)ethan-1-one (144.00 µl, 1.20 mmol), (*p*-cymene)ruthenium dichloride dimer (2.5 mg, 1 mol%), TBAT (35.4 mg, 16 mol%). The reactions were performed in a 100 ml screw-cap Schlenk tube.

[b] Yields were determined by NMR

Table S10 Investigation of the influence of the experimental procedure



Entry[a]	Procedure	Yield[b]
1	**A** (with pre-mix in DCM)	70
2	**B** (without pre-mix in DCM)	70

[a] 4-methylbenzaldehyde (47.0 µl, 0.40 mmol), 1-(2-hydroxyphenyl)ethan-1-one (144.00 µl, 1.20 mmol), (*p*-cymene)ruthenium dichloride dimer (2.5 mg, 1 mol%), TBAT (35.4 mg, 16 mol%), THF (1.5 ml). The reactions were performed in a 100 ml screw-cap Schlenk tube, immersion of the tube is 4/5

[b] Yields were determined by NMR as average of 2 experiments.

Procedure **A**

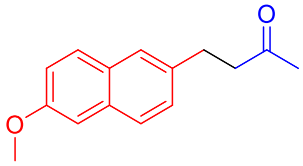
A 100 ml screw-cap Schlenk tube was dried by Schlenk technique and charged with (*p*-cymene)ruthenium dichloride dimer (2.5 mg, 1 mol%), TBAT (34.6 mg, 16 mol%), and dry DCM (1 ml). The solution was stirred for 15 min, then DCM was evaporated from the Schlenk tube, and it was filled with carbon monoxide. 4-Methylbenzaldehyde (47.00 µl, 0.40 mmol), 1-(2-hydroxyphenyl)ethan-1-one (144.00 µl, 1.20 mmol), and dry THF (1.5 ml) were added in the carbon monoxide flow. The Schlenk tube was sealed and placed merged on 4/5 into a preheated oil bath on to 160 °C. After 20 hours, the reactor was cooled to room temperature. The reaction mixture was transferred into a flask and the Schlenk tube was washed with dichloromethane (2x3ml), the solvents were removed on a rotary evaporator to give 70% yield by NMR.

Procedure **B**

A 100 ml screw-cap Schlenk tube was dried by Schlenk technique and charged with (*p*-cymene)-ruthenium dichloride dimer (2.5 mg, 1 mol%), TBAT (34.6 mg, 16 mol%), then it was filled with carbon monoxide. 4-Methylbenzaldehyde (47.00 µl, 0.40 mmol), 1-(2-hydroxyphenyl)ethan-1-one (144.00 µl, 1.20 mmol) and dry THF (1.5 ml) were added in the carbon monoxide flow. The Schlenk tube was sealed and placed merged on 4/5 into a preheated oil bath on to 160 °C. After 20 hours, the reactor was cooled to room temperature. The reaction mixture was transferred into a flask and the Schlenk tube was washed with dichloromethane (2x3ml), the solvents were removed on a rotary evaporator to give 70% yield by NMR.

Spectroscopic and analytical data

Nabumetone, 4-(6-methoxynaphthalen-2-yl)butan-2-one (3aa)



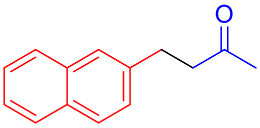
A 100 mL screw-cap Schlenk tube was dried by Schlenk technique and charged with (*p*-cymene)ruthenium dichloride dimer (2.5 mg, 1 mol%), TBAT (35.4 mg, 16 mol%), and dry DCM (1 ml). The solution was stirred for 15 minutes, then DCM was evaporated from the Schlenk tube, and was filled with carbon monoxide. 6-Methoxy-2-naphthaldehyde (76.0 mg, 0.41 mmol) and acetone (4.74 ml, 65.38 mmol) were added in the carbon monoxide flow. The Schlenk tube was sealed and placed merged on 3/5 into a preheated oil bath on to 160 °C. After 20 hours, the reactor was cooled to room temperature. The reaction mixture was transferred into a flask and the Schlenk tube was washed with dichloromethane (2x3mL), solvents were removed on a rotary evaporator to give 94% yield by NMR. The residue was purified by preparative thin-layer chromatography (eluent: hexane: ethyl acetate 3:1; R_f=0.63) to afford 83.0 mg (89%) of the product as yellow crystals.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (m appears as d, J = 8.5 Hz, 2H), 7.55 (broad s, 1H), 7.29 (m appears as d, J = 8.3, 1H), 7.19 – 7.07 (m, 2H), 3.90 (s, 3H), 3.03 (t, J = 7.6 Hz, 2H), 2.83 (t, J = 7.6 Hz, 2H), 2.15 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 208.1, 157.3, 136.2, 133.1, 129.1, 129.0, 127.60, 127.0, 126.3, 118.9, 105.7, 55.3, 45.3, 30.2, 29.8.

NMR spectra are in agreement with the literature data[S1].

4-(Naphthalen-2-yl)butan-2-one (3ab)



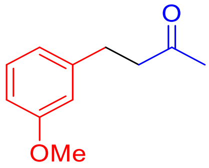
A 100 ml screw-cap Schlenk tube was dried by Schlenk technique and charged with (*p*-cymene)-ruthenium dichloride dimer (2.5 mg, 1 mol%), TBAT (34.9 mg, 16 mol%) dry DCM (1 ml). The solution was stirred for 15 minutes, then DCM was evaporated from the Schlenk tube, and was filled with carbon monoxide. 2-Naphthaldehyde (63.0 mg, 0.40 mmol) and acetone (4.69 ml, 64.61 mmol) were added in the carbon monoxide flow. The Schlenk tube was sealed and placed merged on 3/5 into a preheated oil bath on to 160 °C. After 20 hours, the reactor was cooled to room temperature. The reaction mixture was transferred into a flask and the Schlenk tube was washed with dichloromethane (2x3mL), solvents were removed on a rotary evaporator to give 68% yield by NMR. The residue was purified by preparative thin-layer chromatography (eluent: hexane: ethyl acetate 7:2; Rf=0.60) to afford 48.1 mg (60%) of the product as a yellow oil.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.84 – 7.75 (m, 3H), 7.64 (s, 1H), 7.46 (m appear as p, J = 6.7 Hz, 2H), 7.34 (d, J = 8.3 Hz, 1H), 3.07 (t, J = 7.6 Hz, 2H), 2.85 (t, J = 7.6 Hz, 2H), 2.16 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 208.0, 138.6, 133.7, 132.2, 128.2, 127.7, 127.5, 127.1, 126.5, 126.1, 125.4, 45.1, 30.2, 30.0.

NMR spectra are in agreement with the literature data[S2].

4-(3-Methoxyphenyl)butan-2-one (3ac)



Procedure A

A 100 ml screw-cap Schlenk tube was dried by Schlenk technique and charged with (*p*-cymene)-ruthenium dichloride dimer (2.5 mg, 1 mol%), TBAT (34.6 mg, 16 mol%) and dry DCM (1 ml). The solution was stirred for 15 minutes, then DCM was evaporated from the Schlenk tube, and was filled with carbon monoxide. 3-Methoxybenzaldehyde (31.00 µl, 0.40 mmol) and acetone (4.50 ml, 62.08 mmol) were added in the carbon monoxide flow. The Schlenk tube was sealed and placed merged on 3/5 into a preheated oil bath on to 160 °C. After 20 hours, the reactor was cooled to room temperature. The reaction mixture was transferred into a flask and the Schlenk tube was washed with dichloromethane (2x3ml), solvents were removed on a rotary evaporator to give 75% yield by GC. The product is a highly volatile substance.

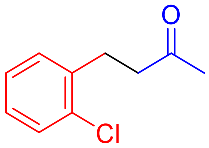
Procedure B

A 100 ml screw-cap Schlenk tube was dried by Schlenk technique and charged with (*p*-cymene)-ruthenium dichloride dimer (2.5 mg, 1 mol%), TBAT (34.6 mg, 16 mol%), then it as filled with carbon monoxide. 3-Methoxybenzaldehyde (31.00 µl, 0.40 mmol) and acetone (4.50 ml, 62.08 mmol) were added in the carbon monoxide flow. The Schlenk tube was sealed and placed merged on 4/5 into a preheated oil bath on to 160 °C. After 20 hours, the reactor was cooled to room temperature. The reaction mixture was transferred into a flask and the Schlenk tube was washed with dichloromethane (2x3ml), solvents were removed on a rotary evaporator to give 71% yield by NMR.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 (t, *J* = 8.3 Hz, 1H), 6.80 – 6.71 (singlet and two doublets, 3H), 3.79 (s, 3H), 2.87 (t, *J* = 7.7 Hz, 2H), 2.76 (t, *J* = 7.7 Hz, 2H), 2.15 (s, 3H).

NMR spectra are in agreement with the literature data[S3].

4-(2-Chlorophenyl)butan-2-one (3ad)



Procedure A

A 100 ml screw-cap Schlenk tube was dried by Schlenk technique and charged with (*p*-cymene)-ruthenium dichloride dimer (2.5 mg, 1 mol%), TBAT (34.6 mg, 16 mol%) and dry DCM (1 ml). The solution was stirred for 15 minutes, then DCM was evaporated from the Schlenk tube, and was filled with carbon monoxide. 2-Chlorobenzaldehyde (43.00 µl, 0.40 mmol) and acetone (4.50 ml, 62.00 mmol) were added in the carbon monoxide flow. The Schlenk tube was sealed and placed merged on 3/5 into a preheated oil bath on to 160 °C. After 20 hours, the reactor was cooled to room temperature. The reaction mixture was transferred into a flask and the Schlenk tube was washed with dichloromethane (2x3mL), solvents were removed on a rotary evaporator to give 66% yield by GC.

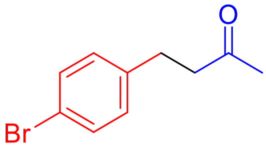
Procedure B

A 100 ml screw-cap Schlenk tube was dried by Schlenk technique and charged with (*p*-cymene)-ruthenium dichloride dimer (2.5 mg, 1 mol%), TBAT (34.6 mg, 16 mol%), then it was filled with carbon monoxide. 2-Chlorobenzaldehyde (43.00 µl, 0.40 mmol) and acetone (4.50 ml, 62.00 mmol) were added in the carbon monoxide flow. The Schlenk tube was sealed and placed merged on 4/5 into a preheated oil bath on to 160 °C. After 20 hours, the reactor was cooled to room temperature. The reaction mixture was transferred into a flask and the Schlenk tube was washed with dichloromethane (2x3ml), solvents were removed on a rotary evaporator to give 60% yield by NMR.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.8 Hz, 1H), 7.10-7.25 (m, 3H), 3.00 (t, *J* = 7.6 Hz, 2H), 2.77 (t, *J* = 7.6 Hz, 2H), 2.15 (s, 3H).

NMR spectra are in agreement with the literature data[S4].

4-(4-Bromophenyl)butan-2-one (3ae)



Procedure A

A 100 ml screw-cap Schlenk tube was dried by Schlenk technique and charged with (*p*-cymene)-ruthenium dichloride dimer (2.5 mg, 1 mol%), TBAT (35 mg, 16 mol%) and dry DCM (1 ml). The solution was stirred for 15 minutes, then DCM was evaporated from the Schlenk tube, and was filled with carbon monoxide. 4-Bromobenzaldehyde (75.0 mg, 0.41 mmol) and acetone (4.70 ml, 64.86 mmol) were added in the carbon monoxide flow. The Schlenk tube was sealed and placed merged on 3/5 into a preheated oil bath on to 160 °C. After 20 hours, the reactor was cooled to room temperature. The reaction mixture was transferred into a flask and the Schlenk tube was washed with dichloromethane (2x3ml), solvents were removed on a rotary evaporator to give 64% yield by GC.

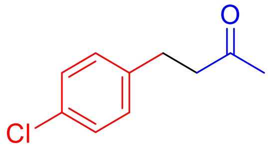
Procedure B

A 100 ml screw-cap Schlenk tube was dried by Schlenk technique and charged with (*p*-cymene)-ruthenium dichloride dimer (2.5 mg, 1 mol%), TBAT (34.6 mg, 16 mol%), then it was filled with carbon monoxide. 4-Bromobenzaldehyde (75.0 mg, 0.41 mmol) and acetone (4.50 ml, 62.00 mmol) acetone were added in the carbon monoxide flow. The Schlenk tube was sealed and placed merged on 4/5 into a preheated oil bath on to 160 °C. After 20 hours, the reactor was cooled to room temperature. The reaction mixture was transferred into a flask and the Schlenk tube was washed with dichloromethane (2x3mL), solvents were removed on a rotary evaporator to give 58% yield by NMR.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.1 Hz, 2H), 7.06 (d, *J* = 8.1 Hz, 1H), 2.85 (t, *J* = 7.8 Hz, 2H), 2.74 (t, *J* = 7.8 Hz, 2H), 2.14 (s, 3H).

NMR spectra are in agreement with the literature data[S5].

4-(4-Chlorophenyl)butan-2-one (3af)



Procedure A

A 100 ml screw-cap Schlenk tube was dried by Schlenk technique and charged with (*p*-cymene)-ruthenium dichloride dimer (2.5 mg, 1 mol%), TBAT (34.6 mg, 16 mol%) and dry DCM (1 ml). The solution was stirred for 15 minutes, then DCM was evaporated from the Schlenk tube, and was filled with carbon monoxide. 4-Chlorobenzaldehyde (56.00 mg, 0.40 mmol) and acetone (4.50 ml, 62.00 mmol) were added in the carbon monoxide flow. The Schlenk tube was sealed and placed merged on 3/5 into a preheated oil bath on to 160 °C. After 20 hours, the reactor was cooled to room temperature. The reaction mixture was transferred into a flask and the Schlenk tube was washed with dichloromethane (2x3mL), solvents were removed on a rotary evaporator to give 62% yield by GC and NMR.

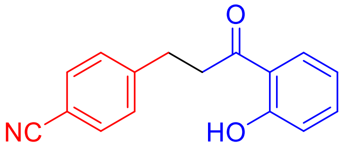
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 8.1 Hz, 2H), 2.86 (t, *J* = 7.4 Hz, 2H), 2.74 (t, *J* = 7.4 Hz, 2H), 2.14 (s, 3H).

NMR spectra are in agreement with the literature data[S6].

Procedure B

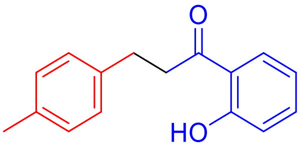
A 100 ml screw-cap Schlenk tube was dried by Schlenk technique and charged with (*p*-cymene)-ruthenium dichloride dimer (2.5 mg, 1 mol%), TBAT (34.6 mg, 16 mol%), then it was filled with carbon monoxide. 4-Chlorobenzaldehyde (56.00 mg, 0.40 mmol) and acetone (4.50 ml, 62.00 mmol) were added in the carbon monoxide flow. The Schlenk tube was sealed and placed merged on 4/5 into a preheated oil bath on to 160 °C. After 20 hours, the reactor was cooled to room temperature. The reaction mixture was transferred into a flask and the Schlenk tube was washed with dichloromethane (2x3mL), solvents were removed on a rotary evaporator to give 60% yield by GC.

4-(3-(2-Hydroxyphenyl)-3-oxopropyl)benzonitrile (3bg)



A 100 ml screw-cap Schlenk tube was dried by Schlenk technique and charged with (*p*-cymene)-ruthenium dichloride dimer (2.5 mg, 1 mol%), TBAT (34.6 mg, 16 mol%), then it was filled with carbon monoxide. 4-Formylbenzonitrile (52.5 mg, 0.40 mmol), 1-(2-hydroxyphenyl)ethan-1-one (144.00 µl, 1.20 mmol) and dry THF (1.5 ml) were added in the carbon monoxide flow. The Schlenk tube was sealed and placed merged on 4/5 into a preheated oil bath on to 160 °C. After 20 hours, the reactor was cooled to room temperature. The reaction mixture was transferred into a flask and the Schlenk tube was washed with dichloromethane (2x3mL), solvents were removed on a rotary evaporator to give 52 % yield by GC.

1-(2-Hydroxyphenyl)-3-(*p*-tolyl)propan-1-one (3bh)



Procedure A

A 100 ml screw-cap Schlenk tube was dried by Schlenk technique and charged with (*p*-cymene)-ruthenium dichloride dimer (2.5 mg, 1 mol%), TBAT (34.6 mg, 16 mol%), and dry DCM (1 ml). The solution was stirred for 15 minutes, then DCM was evaporated from the Schlenk tube, and was filled with carbon monoxide. 4-Methylbenzaldehyde (47.00 µl, 0.40 mmol), 1-(2-hydroxyphenyl)ethan-1-one (144.00 µl, 1.20 mmol) and dry THF (1.5 ml) were added in the carbon monoxide flow. The Schlenk tube was sealed and placed merged on 4/5 into a preheated oil bath on to 160 °C. After 20 hours, the reactor was cooled to room temperature. The reaction mixture was transferred into a flask and the Schlenk tube was washed with dichloromethane (2x3ml), solvents were removed on a rotary evaporator to give 70 % yield by GC.

Procedure B

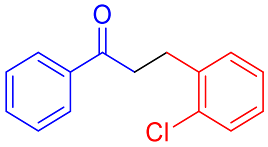
A 100 ml screw-cap Schlenk tube was dried by Schlenk technique and charged with (*p*-cymene)-ruthenium dichloride dimer (2.5 mg, 1 mol%), TBAT (34.6 mg, 16 mol%), then it was filled with carbon monoxide. 4-Methylbenzaldehyde (47.00 µl, 0.40 mmol), 1-(2-hydroxyphenyl)ethan-1-one (144.00 µl, 1.20 mmol) and dry THF (1.5 ml) were added in the carbon monoxide flow. The Schlenk tube was sealed and placed merged on 4/5 into a preheated oil bath on to 160 °C. After 20 hours, the reactor was cooled to room temperature. The reaction mixture was transferred into a flask and the Schlenk tube was washed with dichloromethane (2x3mL), solvents were removed on a rotary evaporator to give 70 % yield by NMR. The residue was purified by flash chromatograph InterChim PuriFlash, following elution was applied: isocratic hexane: ethyl acetate 98:2 for 20 min., R_f=0.24 in hexane: ethyl acetate 98:2 mixture) to afford 60.5 mg (63%) of the product as a colorless oil. The product is volatile.

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.35 (br. s, 1H), 7.76 (d, J = 7.8 Hz, 1H), 7.48 (dd app. as t, J = 7.9 Hz, 1H), 7.15 (d, J = 3.2 Hz, 4H), 7.00 (d, J = 8.3 Hz, 1H), 6.89 (dd app. as t, J = 7.5 Hz, 1H), 3.32 (t, J = 7.7 Hz, 2H), 3.05 (t, J = 7.7 Hz, 2H), 2.35 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 205.6, 162.6, 137.7, 136.4, 136.0, 130.0, 129.4, 128.4, 119.4, 119.0, 118.66, 40.3, 29.7, 21.1.

NMR spectra are in agreement with the literature data[S7].

3-(2-Chlorophenyl)-1-phenylpropan-1-one (3cd)



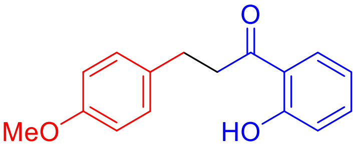
A 100 ml screw-cap Schlenk tube was dried by Schlenk technique and charged with (*p*-cymene)-ruthenium dichloride dimer (2.5 mg, 1 mol%), TBAT (34.6 mg, 16 mol%), then it was filled with carbon monoxide. 2-Chlorobenzaldehyde (45.0 µl, 0.40 mmol), acetophenone (140.00 µl, 1.20 mmol) and dry THF (1.5 ml) were added in the carbon monoxide flow. The Schlenk tube was sealed and placed merged on 4/5 into a preheated oil bath on to 160 °C. After 20 hours, the reactor was cooled to room temperature. The reaction mixture was transferred into a flask and the Schlenk tube was washed with dichloromethane (2x3ml), solvents were removed on a rotary evaporator to give 70 % yield by NMR. The residue was purified by flash chromatograph InterChim PuriFlash, following elution was applied: isocratic hexane: ethyl acetate 97:3 for 20 min., R_f=0.30 in hexane: ethyl acetate 97:3 mixture) to afford 61.0 mg (63%) of the product as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.98 (d, J = 7.1 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.7 Hz, 2H), 7.34 (m app. as dd, J = 18.7, 7.5 Hz, 2H), 7.25 – 7.12 (m, 1H), 3.32 (t, J = 7.8 Hz, 2H), 3.19 (t, J = 7.8 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-d) δ 199.1, 138.9, 136.8, 134.0, 133.2, 130.9, 129.7, 128.7, 128.5, 127.9, 127.1, 38.6, 28.4.

NMR spectra are in agreement with the literature data[S8].

1-(2-Hydroxyphenyl)-3-(4-methoxyphenyl)propan-1-one (3bi)



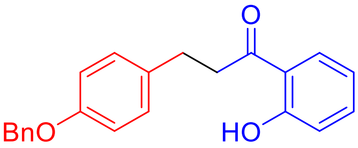
A 100 ml screw-cap Schlenk tube was dried by Schlenk technique and charged with (*p*-cymene)-ruthenium dichloride dimer (2.5 mg, 1 mol%), TBAT (34.6 mg, 16 mol%), then it was filled with carbon monoxide. 4-Methoxybenzaldehyde (49.0 µl, 0.40 mmol), 1-(2-hydroxyphenyl)ethan-1-one (144.00 µl, 1.20 mmol) and dry THF (1.5 ml) were added in the carbon monoxide flow. The Schlenk tube was sealed and placed merged on 4/5 into a preheated oil bath on to 160 °C. After 20 hours, the reactor was cooled to room temperature. The reaction mixture was transferred into a flask and the Schlenk tube was washed with dichloromethane (2x3ml), solvents were removed on a rotary evaporator to give 68 % yield by NMR. The residue was purified by flash chromatograph InterChim PuriFlash, following elution was applied: isocratic hexane: ethyl acetate 95:5 for 15 min., R_f=0.3 in hexane: ethyl acetate 95:5 mixture) to afford 61.8 mg (60%) of the product as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-d) δ 12.34 (s, 1H), 7.75 (d, J = 7.9 Hz, 1H), 7.47 (t, J = 7.8 Hz, 1H), 7.18 (d, J = 8.6 Hz, 2H), 6.99 (d, J = 8.4 Hz, 1H), 6.91 – 6.83 (m, 3H), 3.80 (s, 3H), 3.30 (t, J = 7.7 Hz, 2H), 3.02 (t, J = 7.6 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-d) δ 205.6, 162.5, 158.2, 136.4, 132.8, 129.9, 129.4, 119.4, 119.0, 118.6, 114.1, 55.3, 40.4, 29.3.

NMR spectra are in agreement with the literature data[S9].

3-(4-Benzyloxyphenyl)-1-(2-hydroxyphenyl)propan-1-one (3bj)



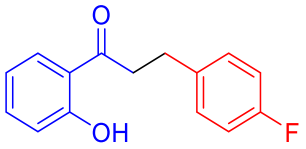
A 100 ml screw-cap Schlenk tube was dried by Schlenk technique and charged with (*p*-cymene)-ruthenium dichloride dimer (2.5 mg, 1 mol%), TBAT (34.6 mg, 16 mol%), then it was filled with carbon monoxide. 4-(Benzyloxy)benzaldehyde (85.0 mg, 0.40 mmol), 1-(2-hydroxyphenyl)ethan-1-one (144.00 µl, 1.20 mmol) and dry THF (1.5 ml) were added in the carbon monoxide flow. The Schlenk tube was sealed and placed merged on 4/5 into a preheated oil bath on to 160 °C. After 20 hours, the reactor was cooled to room temperature. The reaction mixture was transferred into a flask and the Schlenk tube was washed with dichloromethane (2x3mL), solvents were removed on a rotary evaporator to give 62 % yield by NMR. The residue was purified by flash chromatograph InterChim PuriFlash, following elution was applied: isocratic hexane: ethyl acetate 98:2 for 15 min., gradient hexane: ethyl acetate 98:2 → 95:5 for 1 min, isocratic hexane: ethyl acetate 95:5 for 15 min., R_f=0.3 in hexane: ethyl acetate 95:5 mixture) to afford 70.4 mg (53%) of the product as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-d) δ 12.35 (s, 1H), 7.75 (d, J = 7.9 Hz, 1H), 7.50 – 7.32 (m, 6H), 7.18 (d, J = 8.5 Hz, 2H), 7.01 (d, J = 8.4 Hz, 1H), 6.94 (d, J = 8.6 Hz, 2H), 6.92 – 6.87 (m, 1H), 5.06 (s, 2H), 3.31 (t, J = 7.7 Hz, 2H), 3.03 (t, J = 7.6 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-d) δ 205.6, 162.6, 157.4, 137.2, 136.4, 133.1, 130.0, 129.5, 128.7, 128.04, 127.6, 119.4, 119.0, 118.7, 115.1, 70.2, 40.4, 29.3.

NMR spectra are in agreement with the literature data[S10].

3-(4-Fluorophenyl)-1-(2-hydroxyphenyl)propan-1-one (3bk)

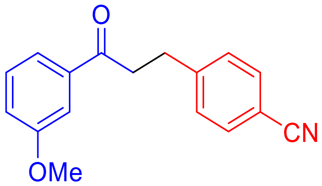


A 100 ml screw-cap Schlenk tube was dried by Schlenk technique and charged with (*p*-cymene)-ruthenium dichloride dimer (2.5 mg, 1 mol%), TBAT (34.6 mg, 16 mol%), then it was filled with carbon monoxide. 4-Fluorobenzaldehyde (42.0 µl, 0.40 mmol), 1-(2-hydroxyphenyl)ethan-1-one (144.00 µl, 1.20 mmol) and dry THF (1.5 ml) were added in the carbon monoxide flow. The Schlenk tube was sealed and placed merged on 4/5 into a preheated oil bath on to 160 °C. After 20 hours, the reactor was cooled to room temperature. The reaction mixture was transferred into a flask and the Schlenk tube was washed with dichloromethane (2x3mL), solvents were removed on a rotary evaporator to give 76 % yield by GC.

^{1}H NMR (400 MHz, Chloroform-d) δ 12.34 (s, 1H), 7.75 (d, J = 7.9 Hz, 1H), 7.47 (dd appears as t, J = 7.8 Hz, 1H), 7.20 (dd, *J* = 8.3, 5.5 Hz, 2H), 6.82-6.99 (m, 4H), 3.30 (t, *J* = 7.6 Hz, 2H), 3.03 (t, *J* = 7.6 Hz, 2H).

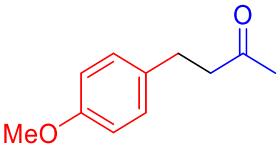
NMR spectra are in agreement with the literature data [9].

4-(3-(3-Methoxyphenyl)-3-oxopropyl)benzonitrile (3dg)



A 100 ml screw-cap Schlenk tube was dried by Schlenk technique and charged with (*p*-cymene)-ruthenium dichloride dimer (2.5 mg, 1 mol%), TBAT (34.6 mg, 16 mol%), then it was filled with carbon monoxide. 4-Formylbenzonitrile (52.4 mg, 0.40 mmol), 1-(3-methoxyphenyl)ethan-1-one (164.00 µl, 1.20 mmol) and dry THF (1.5 ml) were added in the carbon monoxide flow. The Schlenk tube was sealed and placed merged on 4/5 into a preheated oil bath on to 160 °C. After 20 hours, the reactor was cooled to room temperature. The reaction mixture was transferred into a flask and the Schlenk tube was washed with dichloromethane (2x3mL), solvents were removed on a rotary evaporator to give 55% yield by GC.

4-(4-Methoxyphenyl)butan-2-one (3ai)

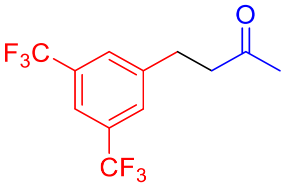


A 100 ml screw-cap Schlenk tube was dried by Schlenk technique and charged with (*p*-cymene)-ruthenium dichloride dimer (2.5 mg, 1 mol%), TBAT (34.6 mg, 16 mol%) and dry DCM (1 ml). The solution was stirred for 15 minutes, then DCM was evaporated from the Schlenk tube, and was filled with carbon monoxide. 4-Methoxybenzaldehyde (49.0 µl, 0.40 mmol) and acetone (4.55 ml, 62.68 mmol) were added in the carbon monoxide flow. The Schlenk tube was sealed and placed merged on 3/5 into a preheated oil bath on to 160 °C. After 20 hours, the reactor was cooled to room temperature. The reaction mixture was transferred into a flask and the Schlenk tube was washed with dichloromethane (2x3ml), solvents were removed on a rotary evaporator to give 60% yield by NMR.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 8.5 Hz, 2H), 6.82 (d, *J* = 8.5 Hz, 2H), 3.78 (s, 3H), 2.84 (d, *J* = 7.4 Hz, 2H), 2.71 (d, *J* = 7.4 Hz, 2H), 2.17 (s, 3H).

NMR spectra are in agreement with the literature data [S6].

4-(3,5-Bis(trifluoromethyl)phenyl)butan-2-one (3al)

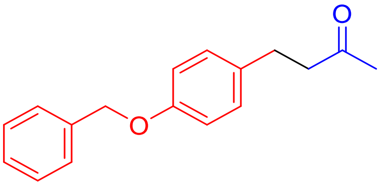


A 100 ml screw-cap Schlenk tube was dried by Schlenk technique and charged with (*p*-cymene)-ruthenium dichloride dimer (2.5 mg, 1 mol%), TBAT (34.6 mg, 16 mol%) and dry DCM (1 ml). The solution was stirred for 15 minutes, then DCM was evaporated from the Schlenk tube, and was filled with carbon monoxide. 3,5-Bis(trifluoromethyl)benzaldehyde (66.00 µl, 0.40 mmol) and acetone (4.50 ml, 62.08 mmol) acetone were added in the carbon monoxide flow. The Schlenk tube was sealed and placed merged on 3/5 into a preheated oil bath on to 160 °C. After 20 hours, the reactor was cooled to room temperature. The reaction mixture was transferred into a flask and the Schlenk tube was washed with dichloromethane (2x3ml), solvents were removed on a rotary evaporator to give 66% yield by GC. The product is a highly volatile substance.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.65 (s, 2H), 3.01 (t, *J* = 7.3 Hz, 2H), 2.83 (t, *J* = 7.3 Hz, 2H), 2.17 (s, 3H).

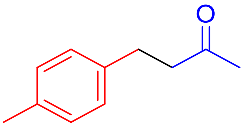
NMR spectra are in agreement with the literature data [S11]

4-(4-Benzyloxyphenyl)butan-2-one (3aj)



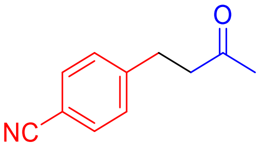
A 100 ml screw-cap Schlenk tube was dried by Schlenk technique and charged with (*p*-cymene)-ruthenium dichloride dimer (2.5 mg, 1 mol%), TBAT (34.6 mg, 16 mol%) and dry DCM (1 ml). The solution was stirred for 15 minutes, then DCM was evaporated from the Schlenk tube, and was filled with carbon monoxide. 4-(benzyloxy)benzaldehyde (85.0 mg, 0.40 mmol) and acetone (4.65 ml, 64.15 mmol) acetone were added in the carbon monoxide flow. The Schlenk tube was sealed and placed merged on 3/5 into a preheated oil bath on to 160 °C. After 20 hours, the reactor was cooled to room temperature. The reaction mixture was transferred into a flask and the Schlenk tube was washed with dichloromethane (2x3ml), solvents were removed on a rotary evaporator to give 52% yield by GC.

4-(*p*-Tolyl)butan-2-one (3ah)



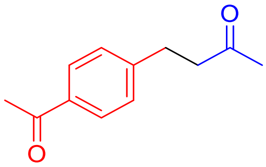
A 100 ml screw-cap Schlenk tube was dried by Schlenk technique and charged with (*p*-cymene)-ruthenium dichloride dimer (2.5 mg, 1 mol%), TBAT (34.6 mg, 16 mol%) and dry DCM (1 ml). The solution was stirred for 15 minutes, then DCM was evaporated from the Schlenk tube, and was filled with carbon monoxide. 4-Methylbenzaldehyde (49.00 µl, 0.41 mmol) and acetone (4.73 ml, 65.33 mmol) acetone were added in the carbon monoxide flow. The Schlenk tube was sealed and placed merged on 3/5 into a preheated oil bath on to 160 °C. After 20 hours, the reactor was cooled to room temperature. The reaction mixture was transferred into a flask and the Schlenk tube was washed with dichloromethane (2x3ml), solvents were removed on a rotary evaporator to give 50% yield by GC.

4-(3-Oxobutyl)benzonitrile (3ag)



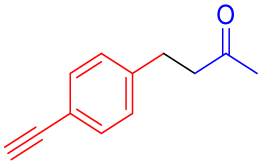
A 100 ml screw-cap Schlenk tube was dried by Schlenk technique and charged with (*p*-cymene)-ruthenium dichloride dimer (2.5 mg, 1 mol%), TBAT (34.6 mg, 16 mol%) and dry DCM (1 ml). The solution was stirred for 15 minutes, then DCM was evaporated from the Schlenk tube, and was filled with carbon monoxide. 4-Formylbenzonitrile (53.0 mg, 0.41 mmol) and acetone (4.69 ml, 64.73 mmol) were added in the carbon monoxide flow. The Schlenk tube was sealed and placed merged on 3/5 into a preheated oil bath on to 160 °C. After 20 hours, the reactor was cooled to room temperature. The reaction mixture was transferred into a flask and the Schlenk tube was washed with dichloromethane (2x3ml), solvents were removed on a rotary evaporator to give 47% yield by GC.

4-(4-Acetylphenyl)butan-2-one (3am)



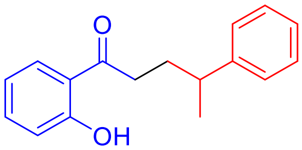
A 100 ml screw-cap Schlenk tube was dried by Schlenk technique and charged with (*p*-cymene)-ruthenium dichloride dimer (2.5 mg, 1 mol%), TBAT (34.6 mg, 16 mol%) and dry DCM (1 ml). The solution was stirred for 15 minutes, then DCM was evaporated from the Schlenk tube, and was filled with carbon monoxide. 4-Acetylbenzaldehyde (60.00 mg, 0.41 mmol) and acetone (4.56 ml, 62.83 mmol) were added in the carbon monoxide flow. The Schlenk tube was sealed and placed merged on 3/5 into a preheated oil bath on to 160 °C. After 20 hours, the reactor was cooled to room temperature. The reaction mixture was transferred into a flask and the Schlenk tube was washed with dichloromethane (2x3ml), solvents were removed on a rotary evaporator to give 23% yield by GC.

4-(4-Ethynylphenyl)butan-2-one (3an)



A 100 ml screw-cap Schlenk tube was dried by Schlenk technique and charged with (*p*-cymene)-ruthenium dichloride dimer (2.5 mg, 1 mol%), TBAT (34.6 mg, 16 mol%) and dry DCM (1 ml). The solution was stirred for 15 minutes, then DCM was evaporated from the Schlenk tube, and was filled with carbon monoxide. 4-Ethynylbenzaldehyde (52.00 µl, 0.40 mmol) and acetone (4.64 ml, 64.00 mmol) were added in the carbon monoxide flow. The Schlenk tube was sealed and placed merged on 3/5 into a preheated oil bath on to 160 °C. After 20 hours, the reactor was cooled to room temperature. The reaction mixture was transferred into a flask and the Schlenk tube was washed with dichloromethane (2x3ml), solvents were removed on a rotary evaporator to give 0% yield by GC.

1-(2-Hydroxyphenyl)-4-phenylpentan-1-one (3bo)

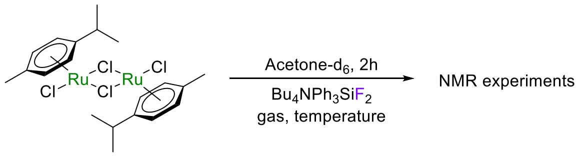


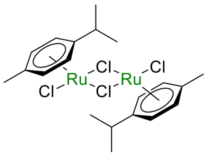
A 100 ml screw-cap Schlenk tube was dried by Schlenk technique and charged with (*p*-cymene)-ruthenium dichloride dimer (2.5 mg, 1 mol%), TBAT (34.6 mg, 16 mol%), then it was filled with carbon monoxide. 2-Phenylpropanal (54.0 µl, 0.40 mmol), 1-(2-hydroxyphenyl)ethan-1-one (144.00 µl, 1.20 mmol) and dry THF (1.5 ml) were added in the carbon monoxide flow. The Schlenk tube was sealed and placed merged on 4/5 into a preheated oil bath on to 160 °C. After 20 hours, the reactor was cooled to room temperature. The reaction mixture was transferred into a flask and the Schlenk tube was washed with dichloromethane (2x3ml), solvents were removed on a rotary evaporator to give 0 % yield by GC.

Control experiments for the mechanism elucidation

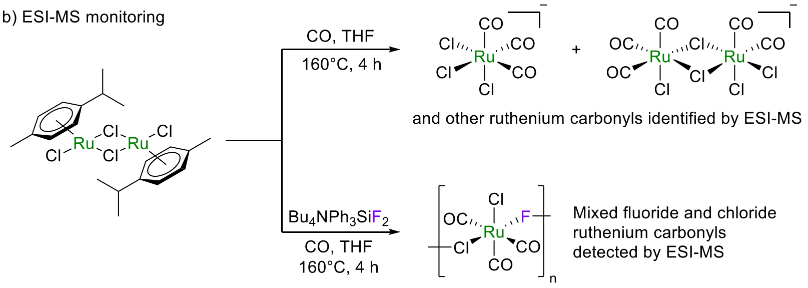
NMR experiments were carried out (Scheme S1, *a*). After premixing of the [(*p*-cymene)RuCl$_2$]$_2$ with TBAT at 45°C under argon atmosphere, no reaction occurred within 2 hours. In the presence of CO signals of [(*p*-cymene)RuCl$_2$]$_2$ disappear immediately, however, no TBAT was consumed according to ^{1}H and ^{19}F data. The heating of these mixtures at 160°C for two hours leads to the full transformation of [(*p*-cymene)RuCl$_2$]$_2$ to the ruthenium complex without cymene ligand, and TBAT fully converts to Ph$_3$SiF thus releasing the F$^-$, that we assume to be bound by the ruthenium.

a) NMR monitoring



	Bu$_4$NPh$_3$SiF$_2$	
Ar, 45°C	Starting material	Starting material
CO, 45°C	Starting material	Full conversion
Ar, 160°C	Full conversion	Full conversion
CO, 160°C	Full conversion	Full conversion

b) ESI-MS monitoring

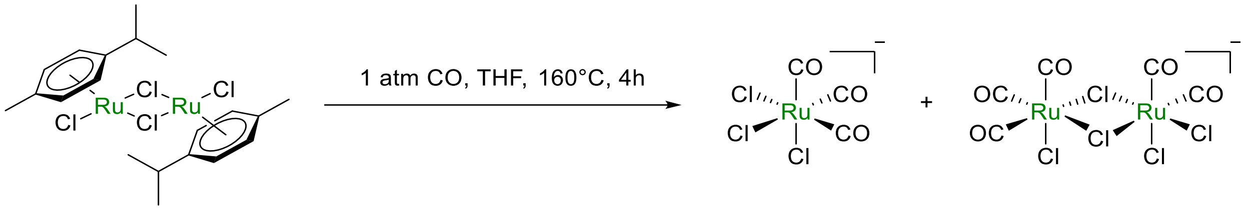


Scheme S1. Control experiments for the mechanism elucidation.

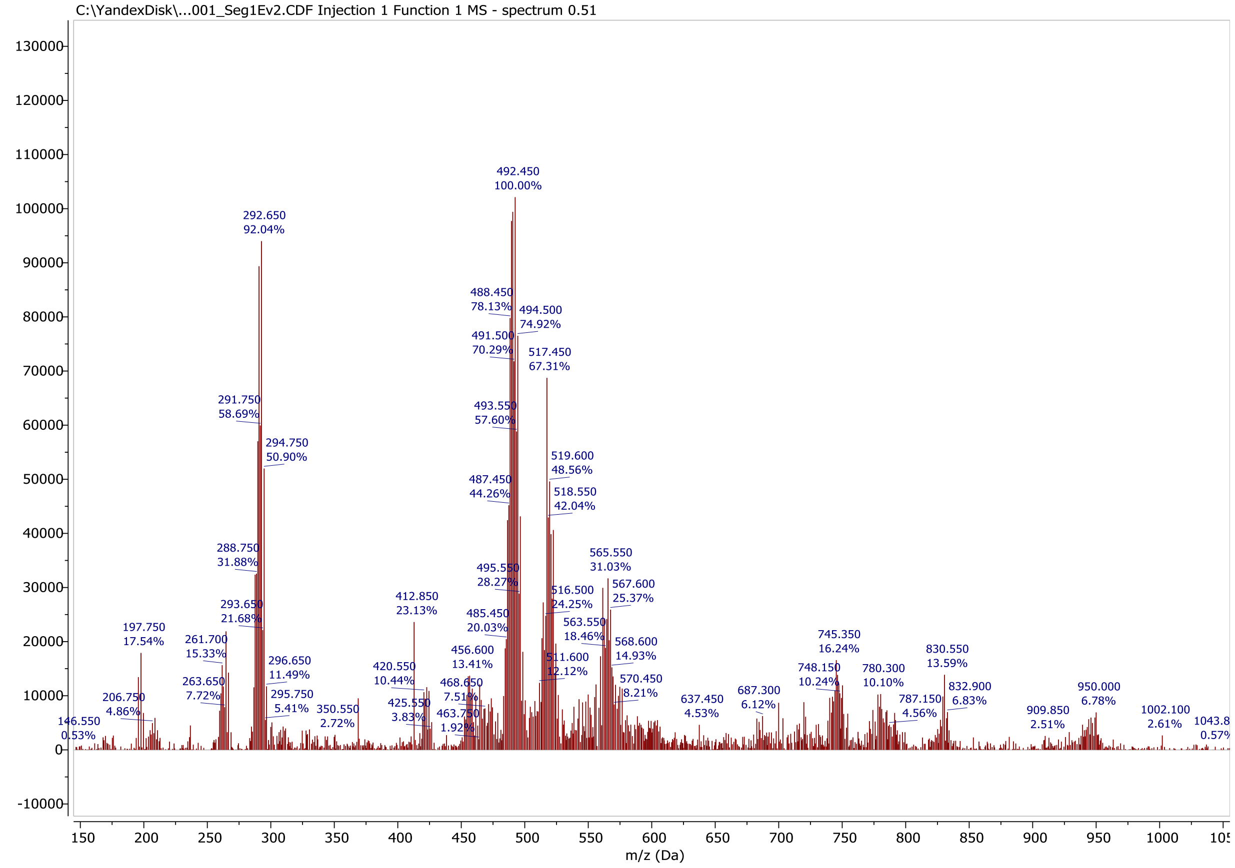
ESI-MS analysis

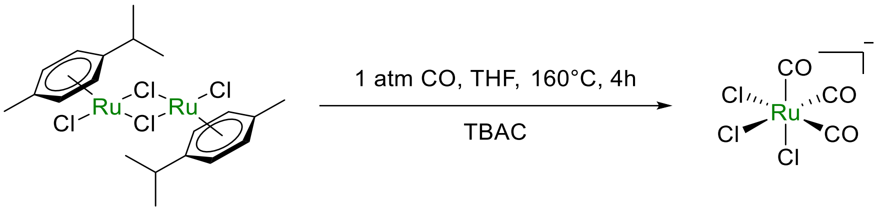
General procedure: A 10 ml screw-cap Schlenk tube was dried by Schlenk technique and charged with (*p*-cymene)ruthenium dichloride dimer (10 mg, 1 equiv.), TBAT or Bu$_4$NCl (8 equiv., if mentioned), then it was filled with carbon monoxide. THF (1 ml) was added, the Schlenk tube was sealed and heated at 160 °C for 4 hours. After that, the reaction mixture was cooled to room temperature, diluted in MeCN to achieve 0.1 mg/mL concentration, and analyzed by ESI-MS in both negative and positive modes. Positive mode mass spectra are blank, ruthenium-containing ions were detected only in negative mode spectra.

ESI-MS analysis of similar reaction mixtures (Scheme S1, *b*) confirms these data. The reaction of [(*p*-cymene)RuCl$_2$]$_2$ with CO without TBAT leads to the formation of a mixture of carbonyl chloride complexes with full consumption of starting material, which is in line with the previously reported data.[S12,S13] The main particle detected in the solution was Ru(CO)$_3$Cl$_3^-$. In contrast, after the addition of TBAT, no signs of this particle were detected, and several mixed halides with 2-4 ruthenium atoms were observed (identified structures are provided in SI). These data well agree with the previous reports about the behavior of the ruthenium fluoride complexes.[S14,S15]

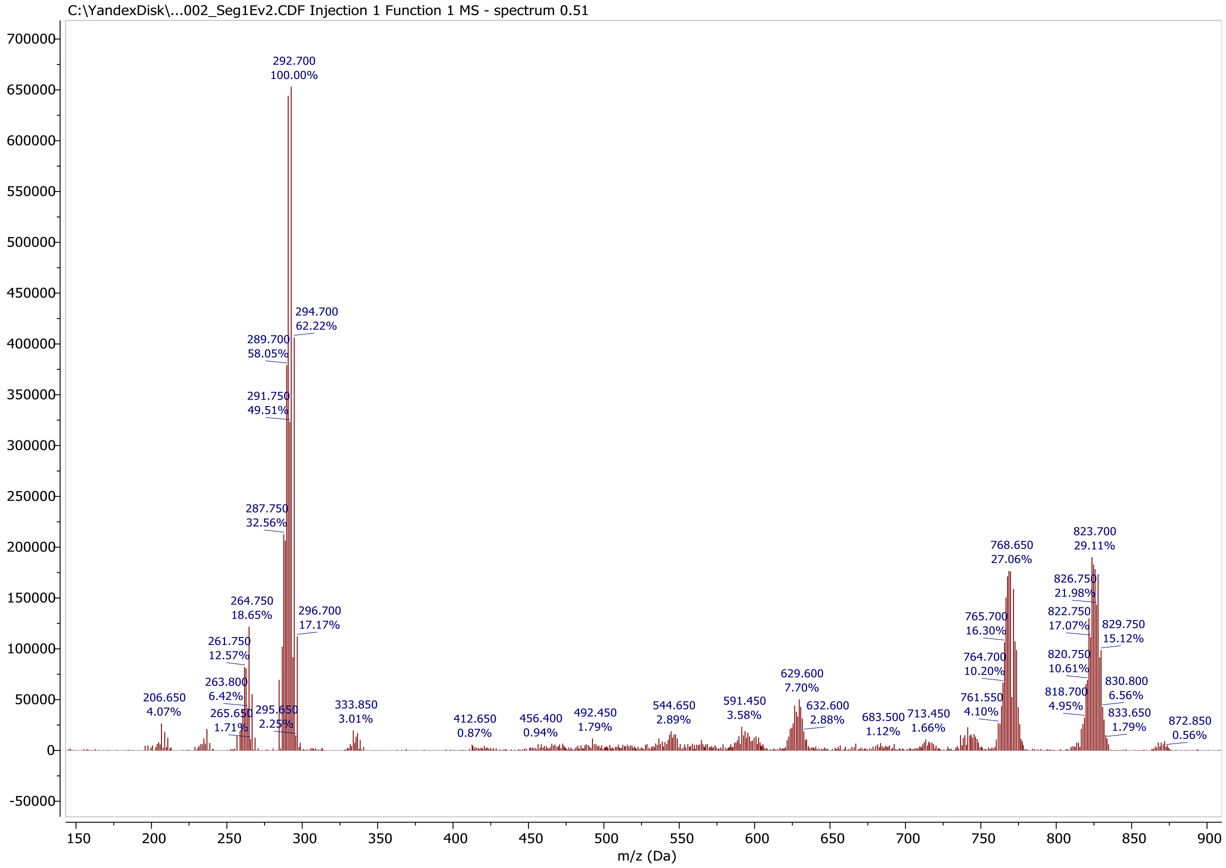


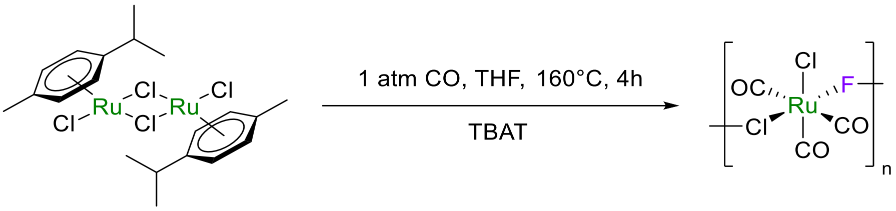
261.700: $Ru(CO)_2Cl_3^-$; 292.650: $Ru(CO)_3Cl_3^-$; 492.450: $Ru_2(CO)_4Cl_5^-$; 519.600: $Ru_2(CO)_5Cl_5^-$; 565.550: $Ru_2Cl_5(MeCN)(THF)_2^-$.



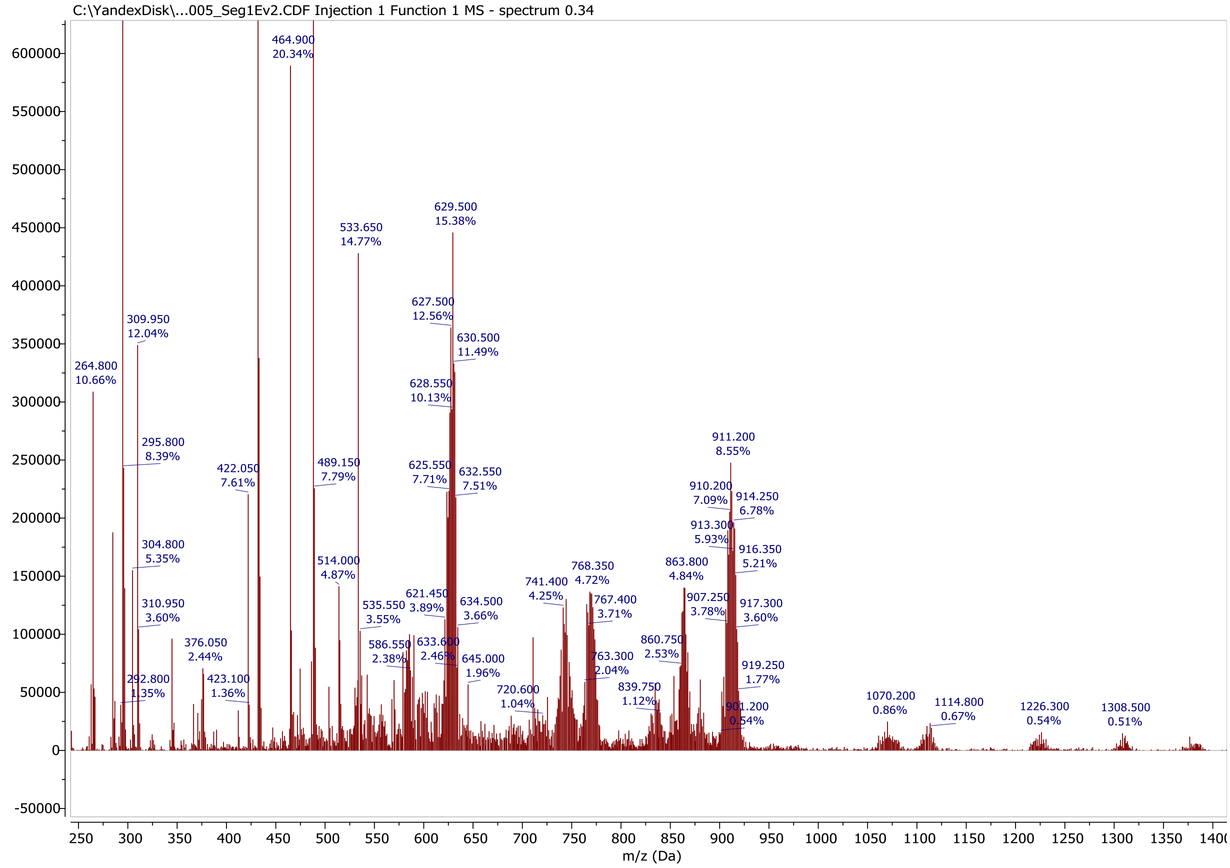


206.650: $RuCl_3^-$; 264.750: $Ru(CO)_2Cl_3^-$; 292.700: $Ru(CO)_3Cl_3^-$; 333.850: $Ru(CO)_3Cl_3(MeCN)^-$ + $Ru(CO)_2Cl_3(THF)^-$; 629.600: $Ru_2(CO)_6Cl_5(MeCN)_2^-$; 768.650: $Ru_2(CO)_4Cl_6(Bu_4N)^-$; 823.700: $Ru_2(CO)_6Cl_6(Bu_4N)^-$



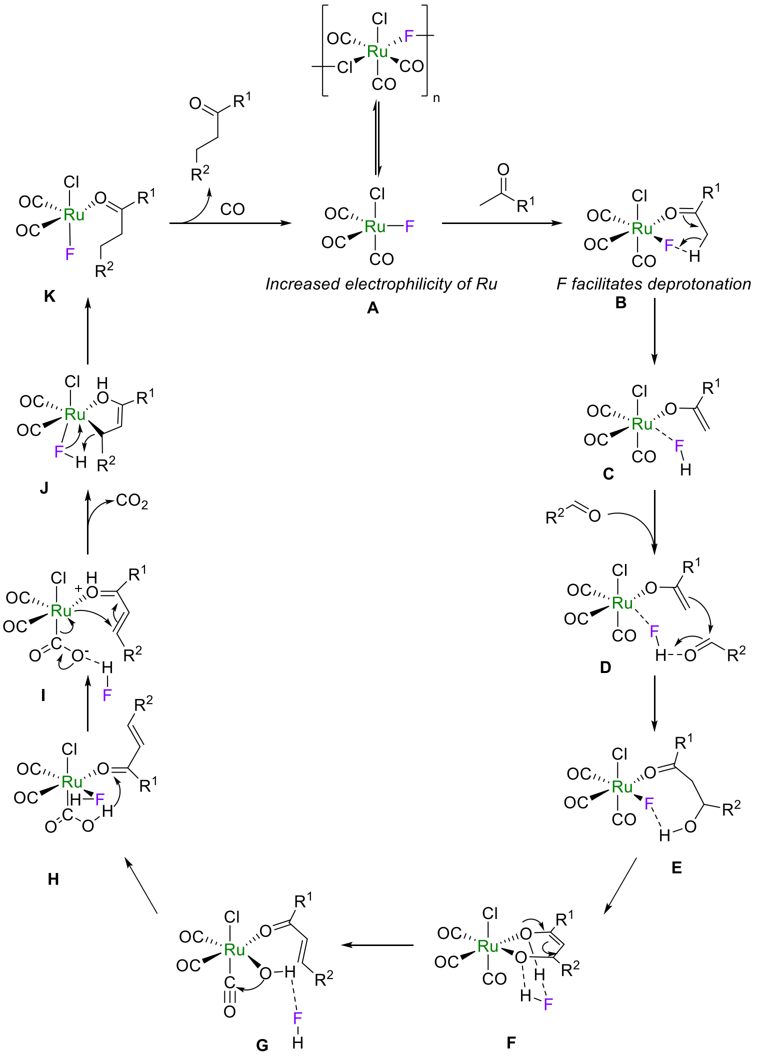


Some identified particles: 629.500: $Ru_2(CO)_8Cl_4F_1(MeCN)^-$; 741.400: $Ru_3(CO)_4Cl_5F_2(MeCN)(THF)^-$; 768.350: $Ru_3(CO)_2Cl_5F_2(MeCN)_3(THF)^-$; 863.600: $Ru_3(CO)_5F_7(MeCN)_7^-$; 911.200: $Ru_4(CO)_3Cl_6F_3(MeCN)_2(THF)^-$



Proposed mechanism

Based on these data and our previous results as well as the literature reports we propose the possible mechanism for the reaction and the explanation of the fluorine role in this process (Scheme S2). We assume that the oligomeric ruthenium halide complexes with 18e configuration are the catalyst resting states. Their depolymerization gives the catalytically active 16e complex **A**. Due to the fluorine coordination, the electrophilicity of the ruthenium center is increased, facilitating the ketone coordination to the metal center. In the resulting particle **B** fluoride ligand acts as a hydrogen bond acceptor[S16,S17] as well as a π-donor helping to deprotonate the ketone in the α-position to give an intermediate **C**. In the next stages, fluoride serves as a proton-transfer mediator or as a hydrogen bond acceptor for the precoordination of different molecules. In the intermediate **D**, the aldehyde is coordinated to HF followed by an attack of enolate to give an intermediate **E**. The resulting aldol coordinates the ruthenium in a bidentate mode with HF transfer to the outer sphere to give **F**. HF-assisted H_2O elimination gives the intermediate **G** in which the inner-sphere CO to COOH oxidation followed by CO_2 evolution and cyclometallation step leads to the particle **J**. In the presence of HF this complex is transformed to **K**, and the latter after the product to CO exchange regenerates the starting particle **A**. Noteworthy that as we see the mixture of ruthenium species in our reaction mixtures, the proposed catalytic cycle is only an illustration of the principle, and other ruthenium species may also contribute to the reaction.[S18]



Scheme S2. Proposed mechanism for the ruthenium-catalyzed reductive alkylation

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