Electronic Supplementary Information

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Liberation of methyl esters from metallalactone complexes via M–O ring opening (M = Ni, Pd) with methylation agents

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General procedures

All experiments were performed under an argon atmosphere using standard Schlenk techniques or in a glovebox. Ethanol was dried over CaH_2 and refluxed overnight before distilling. THF was refluxed over sodium/benzophenone and distilled. Diethyl ether, chloroform, dichloromethane, hexane and toluene were purified over activated alumina and dried over 3Å molecular sieves. Reagents were purchased from commercial sources and used without further purification unless otherwise stated. 3-butenoic acid was distilled before use to remove the hydroquinone inhibitor. Nuclear magnetic resonance (NMR) measurements were performed on a Bruker AVANCE 400 MHz and 500 MHz spectrometers. ^{1}H and ^{13}C chemical shifts were referenced to residual solvent resonances ($CDCl_3$: 7.26 ppm, CD_2Cl_2: 5.26 ppm, $(CD_3)_2SO$: 2.50 ppm). Bis-(di-tert-butylphosphino)ethane (dtbpe) ligand was prepared according to published procedures.[S1]

Synthesis of metallalactones

Nickelalactones **2a,**[S2,S3] **2b,**[S2] **2c,**[S2] **2e**[S4]**, 2f**[S5] and palladalactones **7a**[S6] and **7b**[S7] were synthesized according to published procedures; nickelalactone **2d** was prepared from $Ni(COD)_2$, dtbpe ligand, ethylene and CO_2 according to the procedure published by Limbach et al.[12] or according to the following procedure:

Synthesis of nickelalactone **2d, 1-Bis(di-*tert*-butylphosphino)ethan-1-ethylenenickela-2-oxacyclopentan-3-one**: dtbpe (0.64 g, 0.002 mol) was added to a suspension of tmeda-Nickelalactone **2e** (0.12 g, 0.0005 mol) in THF (10 mL). The mixture was stirred for 1 h at room temperature, and the yellow product was filtered, washed with diethyl ether and dried in vacuum to give an orange powder (80 % yield). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.18 (2H, m), 1.35 (18H, J = 9.8 d), 1.38 (18H, J = 9.8 d), 1.48 (2H, m), 1.78 (2H, m), 2.06 (2H, brs). ^{31}P NMR (162 MHz, CD_2Cl_2): 77.7 (d, J = 8.1 Hz) & 80.5 (d, J = 8.1Hz). ^{13}C NMR (100.6 MHz, CD_2Cl_2): 9.77, 18.85, 26.42, 30.47, 30.82, 35.08, 37.14, 189.89. ATR-FTIR: $\nu(C=O)$= 1615 cm^{-1}.

General procedure for the liberation of esters

Nickelalactones **2a-f** (0.1 mmol) were dissolved 0.6 mL CD_2Cl_2 in a J. Young NMR tube and $CHCl_3$ (8 µL, 0.1 mmol) was added as an internal standard. The suitable amount of MeOTf was added and the spectra were recorded at 25°C. Palladalactone **7a**, (0.1mmol) was dissolved in 0.6 mL of $CDCl_3$ and CH_2Cl_2 (6.4 µL, 0.1 mmol) was added as an internal standard. The suitable amount of MeI or MeOTf was added and the spectra were recorded at 25°C. Palladalactone **7b**, (0.1 mmol) was dissolved in 0.6 mL f DMSO-d_6 and $CHCl_3$ (8 µL, 0.1mmol was added as an internal standard. The suitable amount of MeI or MeOTf was added and the spectra were recorded at 25°C.

Reaction of tmeda-Nickelalactone **2e** with MeOTf to form intermediate **6e [(tmeda)Ni(OTf)CH_2CH_2COOMe]**: tmeda-nickelalactone **2e,** (0.0247 g, 0.0001 mol) was dissolved in 0.5 mL of CD_2Cl_2 and MeOTf (11.3 µL, 0.0001 mol) was added in a J. Young NMR tube. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.61 (t, J = 10 Hz, 2H, Ni$CH_2$$CH_2$), 2.20 (t, J = 6.4 Hz, 2H, NiCH_2CH_2), 2.39 (s, 6 H, N$(CH_3)_2$), 2.40 (s, 4H, N(CH_2CH_2)N), 2.56 (s, 6H, N$(CH_3)_2$), 3.72 (s, 3H, C(O)OCH_3). ^{13}C NMR (100.6MHz, CD_2Cl_2): δ -0.35 (NiCH_2CH_2), 36.63 (NiCH_2CH_2), 47.28 (NCH_3), 50.07 (NCH_3), 56.05 (C(O)OCH_3), 56.51 (N(CH_2CH_2)N) , 62.28 N(CH_2CH_2)N, 194.11 (C(O)OCH_3).

NMR Spectra of 6e

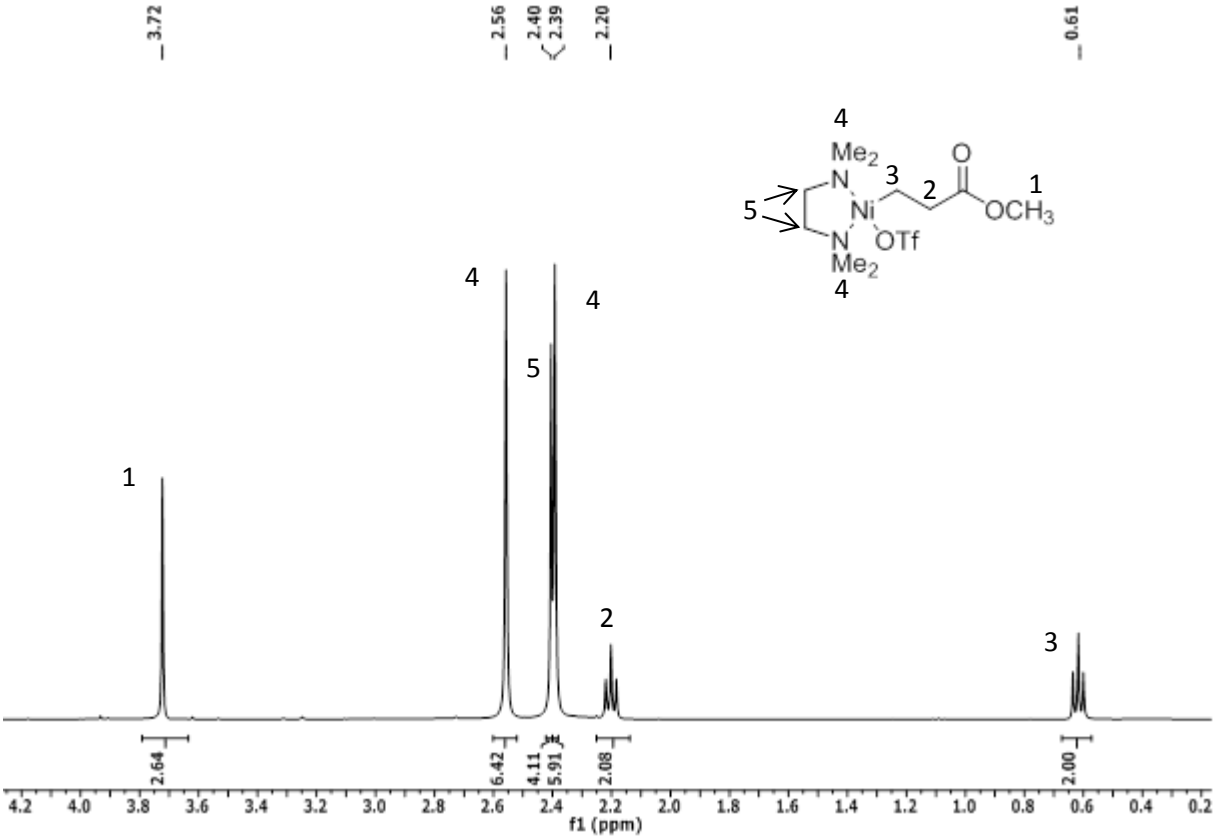

Figure S1. ^{1}H NMR spectrum of **6e** (CD_2Cl)

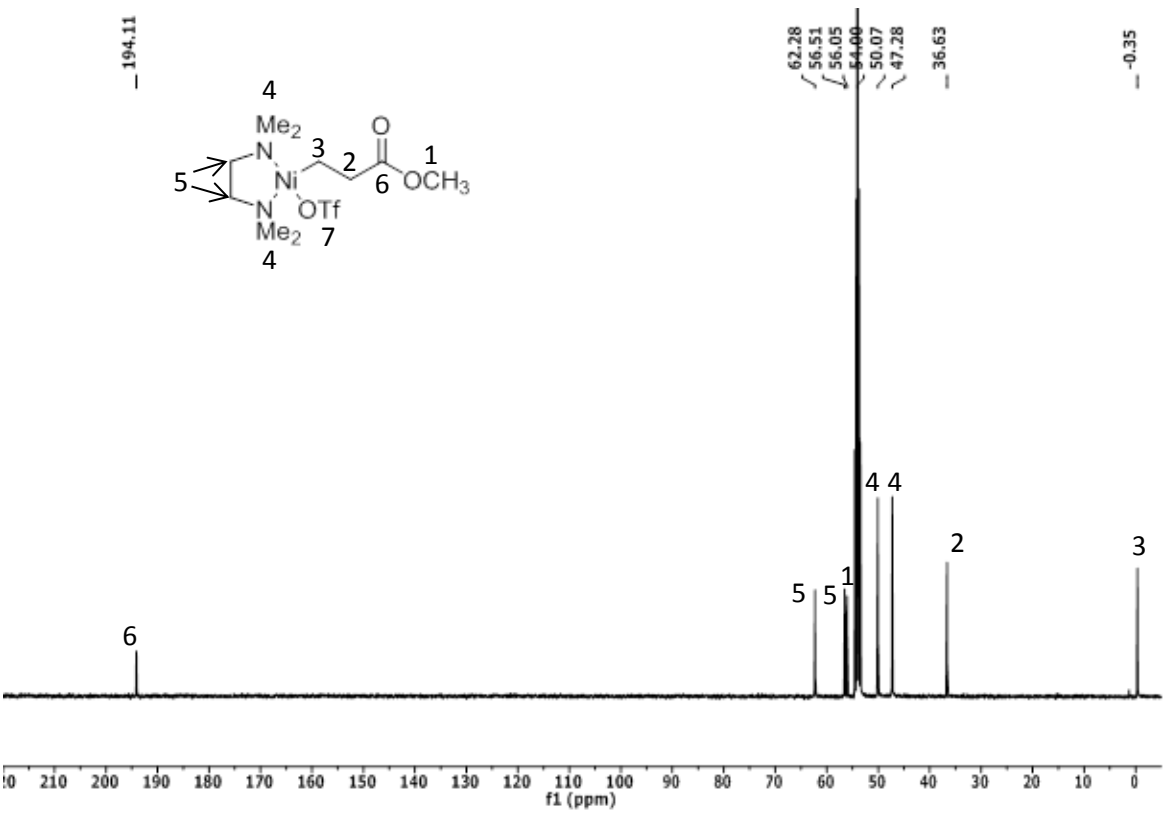

Figure S2. ^{13}C NMR spectrum of **6e** (CD_2Cl_2)

	δH (ppm)	δC (ppm)
1	3.72	56.05
2	2.20	36.63
3	0.61	-0.35
4	2.39, 2.56	50.07, 47.28
5	2.40	62.28, 56.51

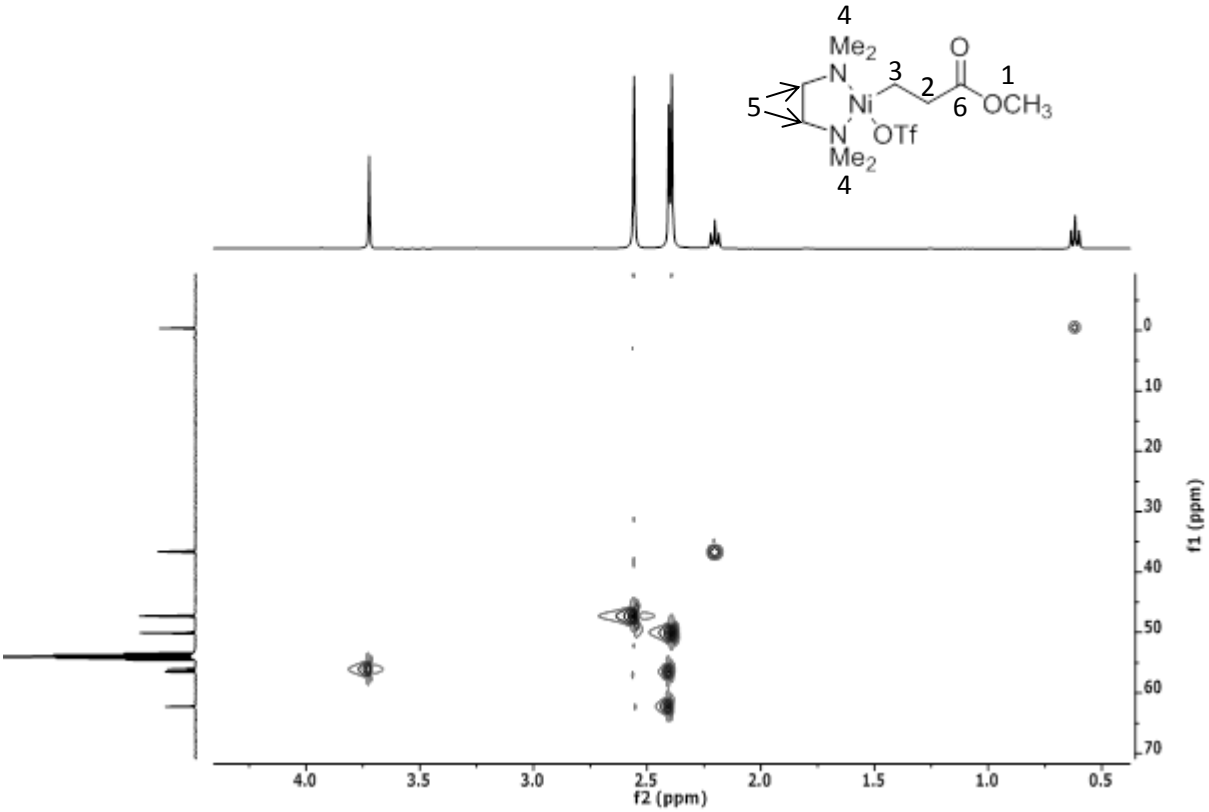

Figure S3. ^{1}H-^{13}C HSQC NMR of intermediate **6e** (CD_2Cl_2)

NMR Spectra of 2d

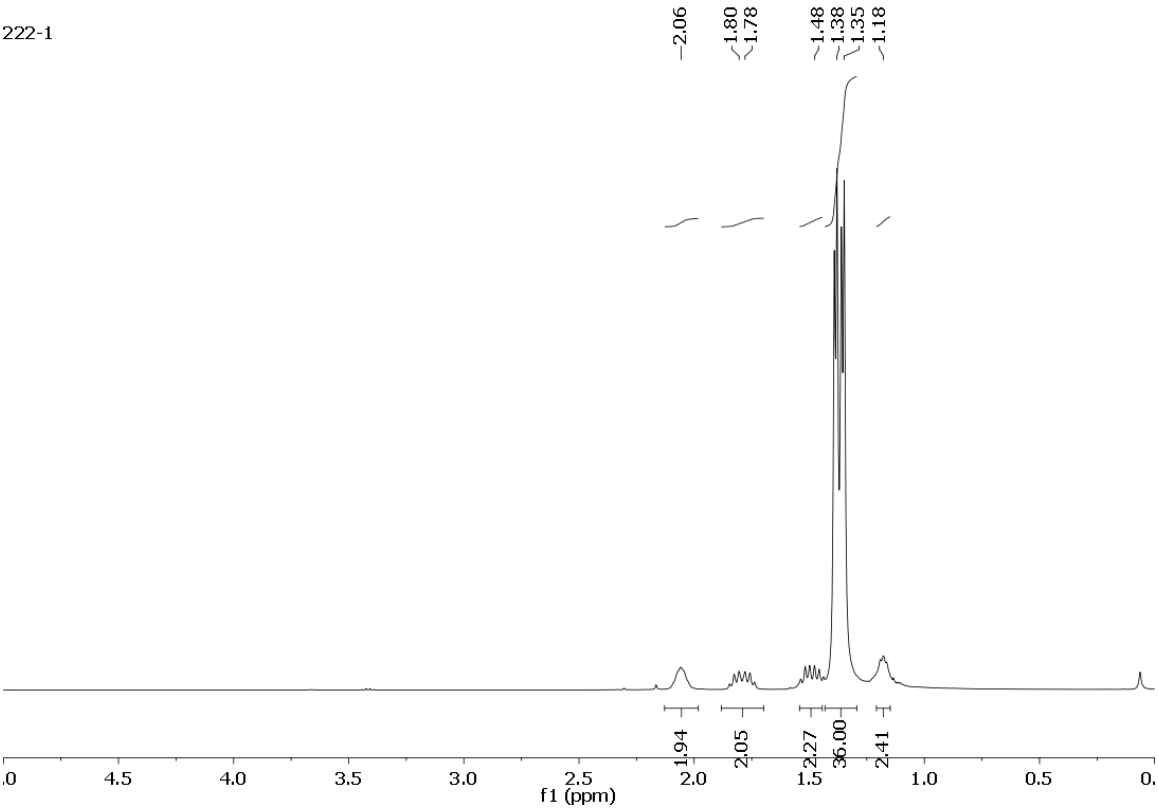

Figure S4. ^{1}H NMR spectrum of nickelalactone **2d** (CD_2Cl_2)

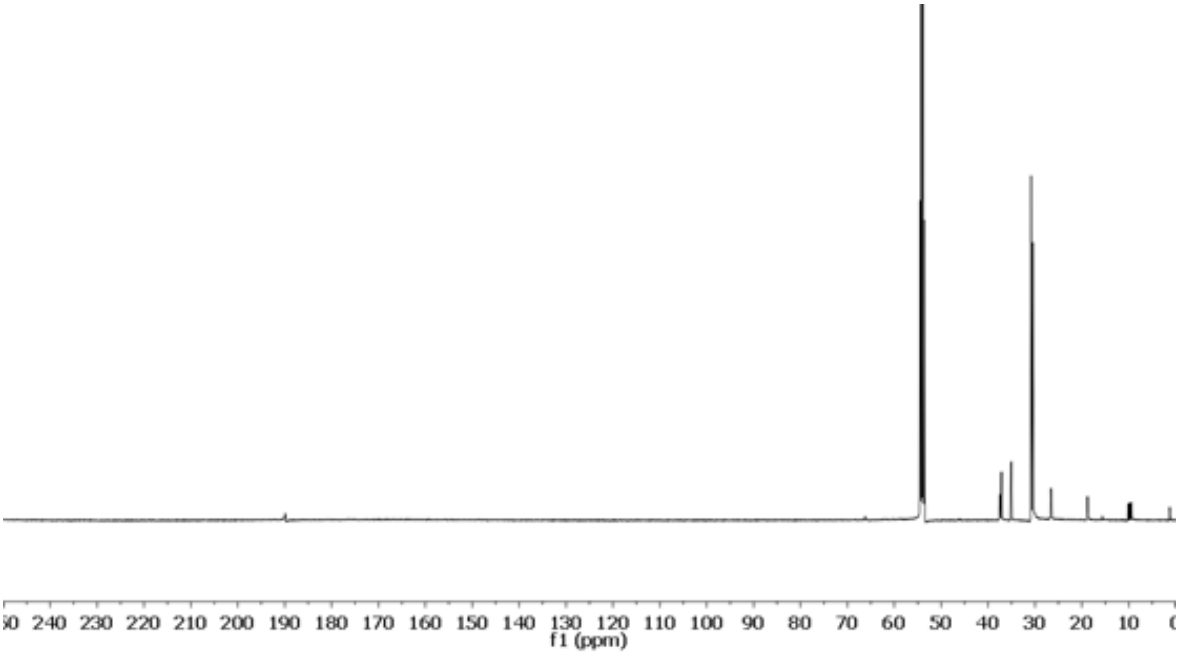

Figure S5. ^{13}C NMR spectrum of nickelalactone **2d** (CD_2Cl_2)

Determination of conversion for palladalactones

The conversion of the metallalactones to unsaturated esters was calculated from the ^{1}H NMR of the reaction mixture based on the ratio between the integral of the olefinic proton(s) of the ester products and the peak of an internal standard ($CHCl_3$ or CH_2Cl_2) which initial concentration is known. For nickelalactones **2a-f**, the amount of methyl acrylate liberated was calculated as already reported in the experimental part of Ref. 13a. For palladalactone **7a**, the formation of methyl crotonate (**8a**, CAS 623-43-8) in $CDCl_3$ was consistent with the appearance of the vinylic protons at 6.96 ppm (m, 1H) and at 5.83 ppm (m, 1H) and of the methyl ester at 3.65 ppm (s, 3H), (Fig. S6, S7); the formation of 3-butenoic acid methyl ester (**8b**, CAS 3724-55-8),[S8] was consistent with the appearance of the vinylic protons at 5.89 ppm (m, 1H) and at 5.09 ppm (m, 2H) and of the methylene protons at 3.05 ppm (d, 2H), (Fig. S6, S7). For **7b**, the formation of dimethyl fumarate (**8c**) in $(CD_3)_2SO$ (6.67 ppm, s, 2H) was proved by comparison with a pure sample of **8b** in $(CD_3)_2SO$ (Fig S8).

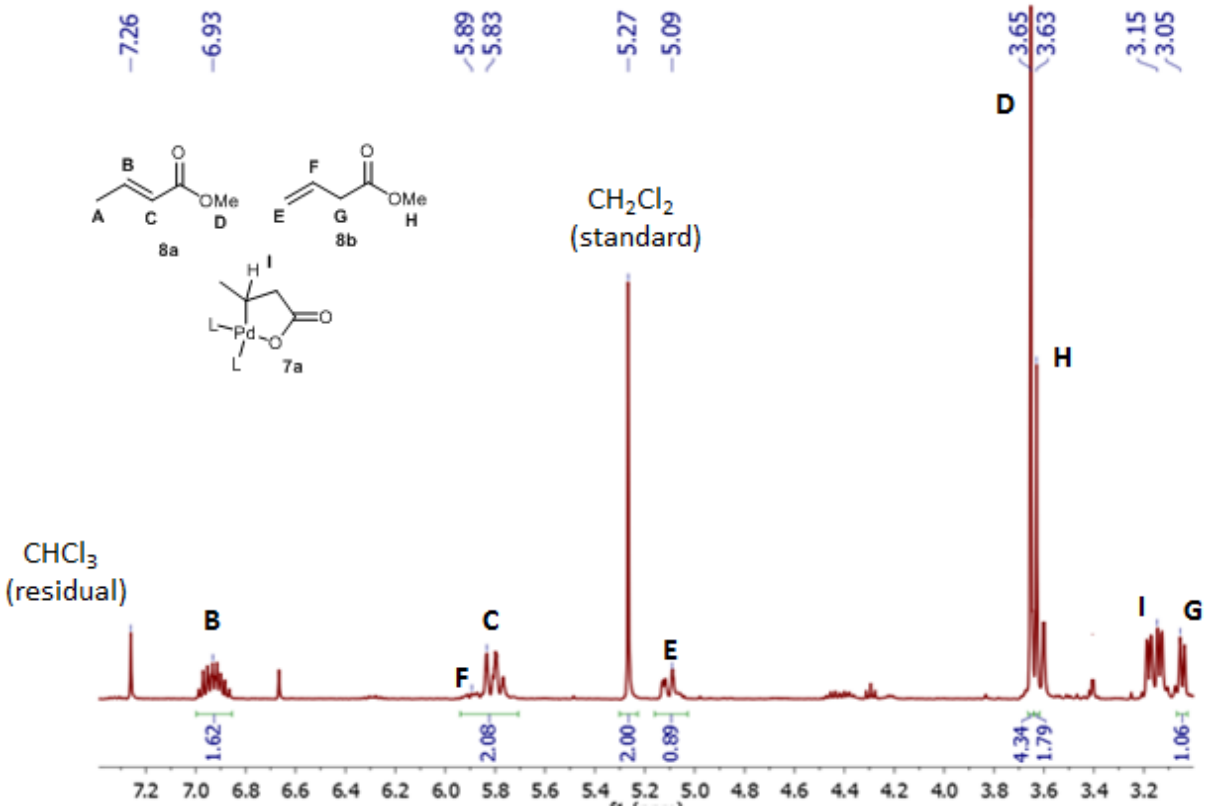

Figure S6. ^{1}H NMR of the reaction between **7a** and MeI (100 equiv. MeI, 3 h, in $CDCl_3$ with CH_2Cl_2 as internal standard, the concentration of the standard is 1/3 of the initial concentration of **7a**) to afford **8a** and **8b**.

$$Yield(\mathbf{8a}) = \frac{1.62}{3} = 54\ \%$$

$$Yield(\mathbf{8b}) = \frac{0.89}{3 \times 2} = 15\ \%$$

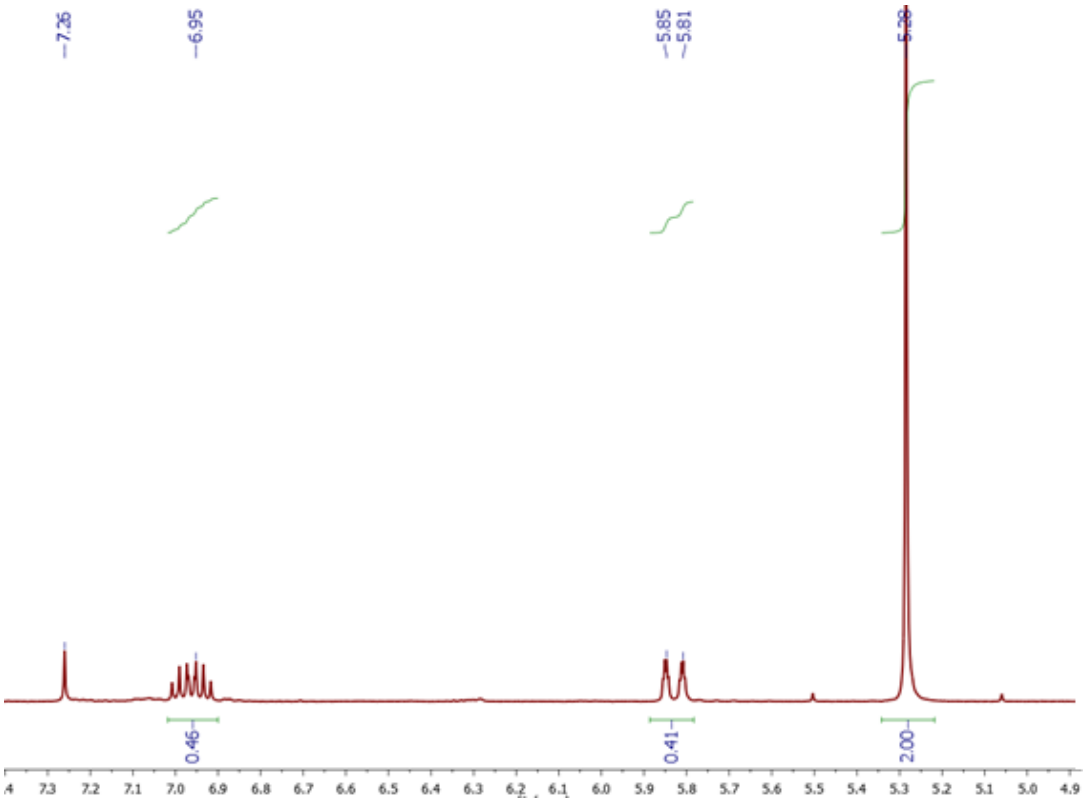

Figure S7. ^{1}H NMR of the reaction between **7a** and MeOTf (100 equiv. MeI, 3 h, in $CDCl_3$ with CH_2Cl_2 as internal standard, the concentration of the standard is 1/2 of the initial concentration of **7a**) to afford **8a** selectively.

$$Yield(\mathbf{8a}) = \frac{0.46}{2} = 23\ \%$$

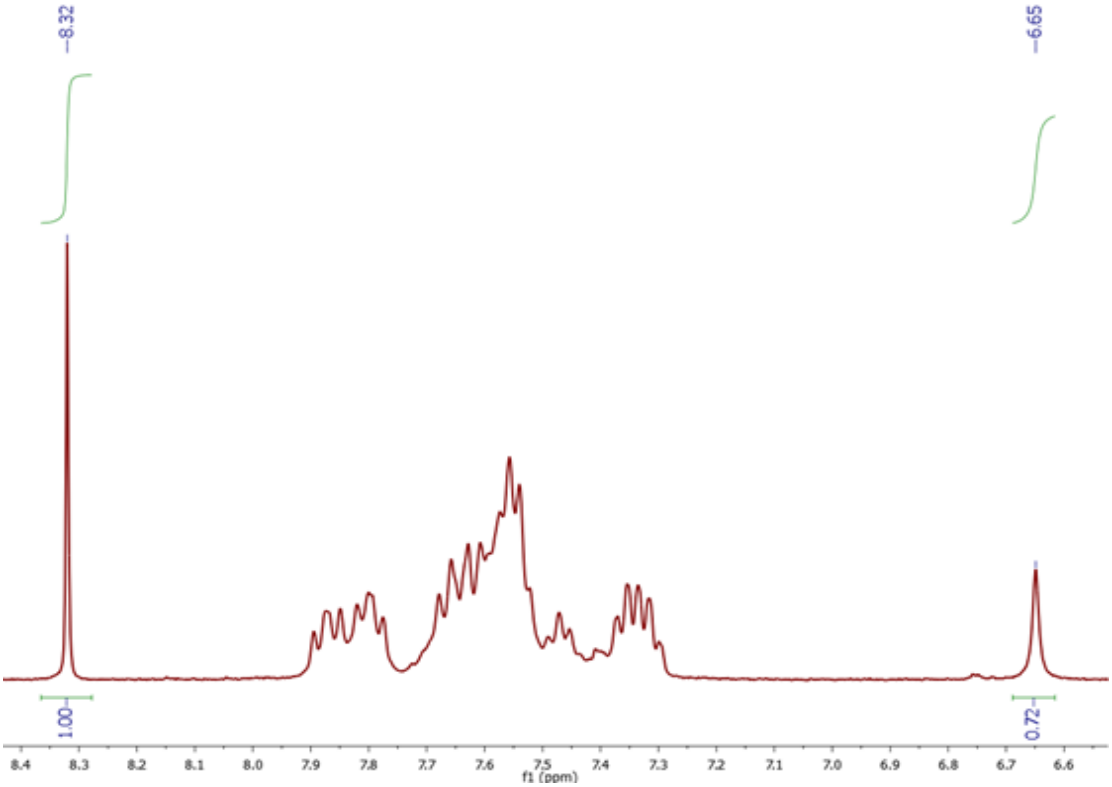

Figure S8. ^{1}H NMR of the reaction between **7b** and MeOTf (2 equiv. MeOTf, 15 min, using CH_3Cl as a standard in DMSO-*d6*, the concentration of the standard is equimolar to the initial concentration of **7b**) to afford **8c**.

$$Yield(\mathbf{8a}) = \frac{0.72}{2} = 36\ \%$$

NMR spectra of the reaction between 2a-d, 7a and MeOTf

The formation of new intermediates following addition of MeOTf to nickelalactones **2a-d** was observed in the ^{1}H NMR and in the ^{13}C NMR of the reaction mixture. Typically, a new signal appears in the carbonyl region at 194-197 ppm (doublet J = 14.1-15.1 Hz) along with the peak of methyl acrylate at 169 ppm, while the carbonyl signals relative to the starting lactones disappear (Fig S9a-S12a). Comparing these observations with what has been discussed for **2e**/**6e** it is possible to assign the new carbonyl signals to the formation of the intermediates of ring opening for lactones **2a-d**. At the same time, new signals are observed in the ^{1}H NMR of the reaction mixture in the -3.8 ppm to -4.7 ppm region that can be attributed to the formation of new Ni-hydride species (Fig. S9b-S12b). Similarly, when MeOTf is added to palladalactone **7a**, the immediate disappearing of the starting material is noticed in the ^{1}H NMR of the mixture, along with the formation of new signals in the methyl ester region (3.65-3.70 ppm), with the peak of the unreacted MeOTf and with the formation of methyl crotonate (Fig. S13).

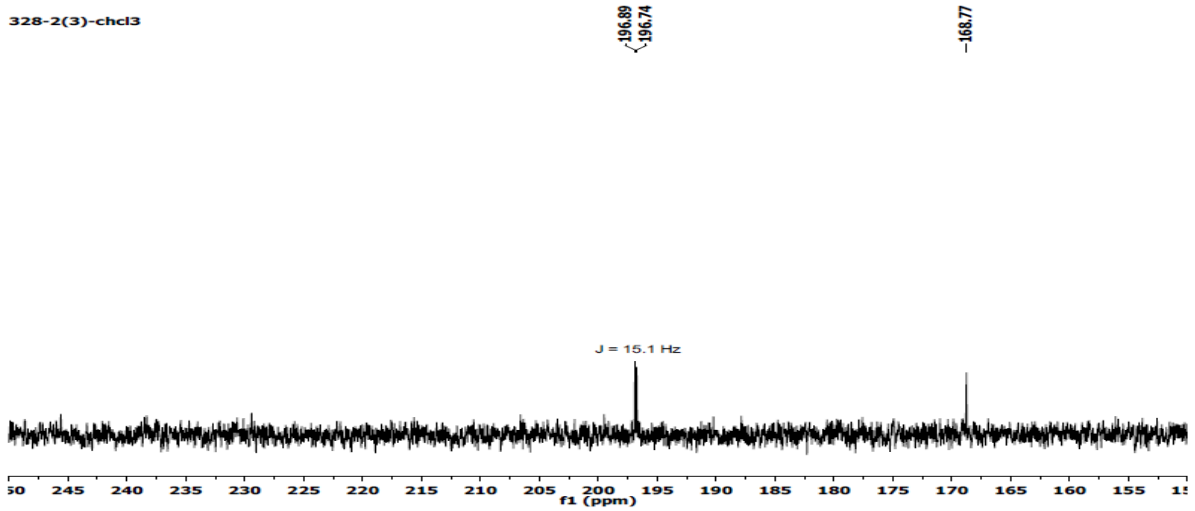

Figure S9a. ^{13}C NMR spectrum (CD_2Cl_2) of the reaction between MeOTf and **2a** in the carbonyl region showing the appearance of a new signal at 196.7 ppm along with the signal of methyl acrylate at 168.8 ppm, following the addition of MeOTf.

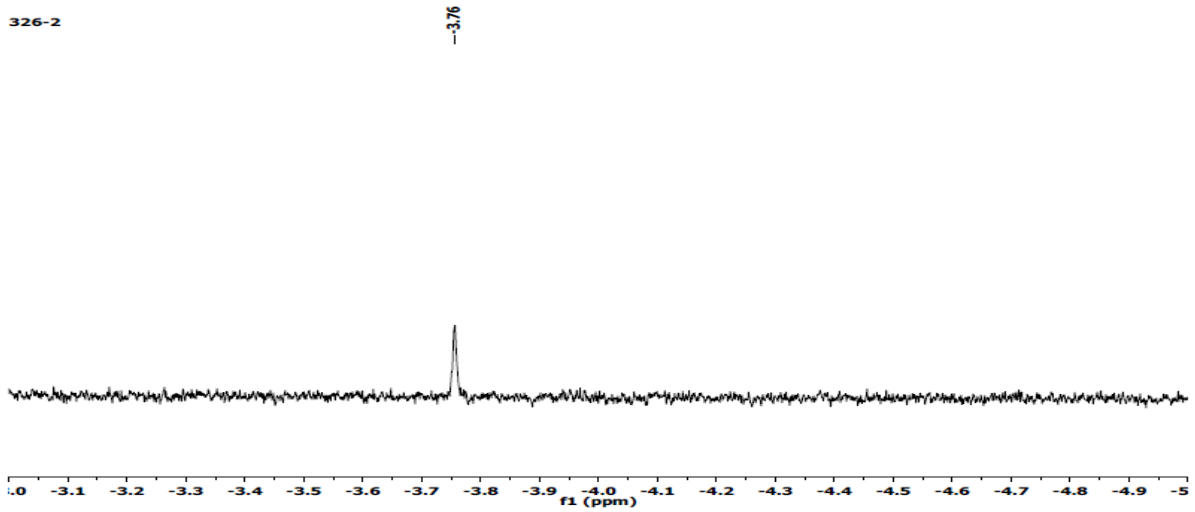

Figure S9b. Appearance of a new Ni-hydride species in the ^{1}H NMR spectrum (CD_2Cl_2) of the reaction of MeOTf with **2a**.

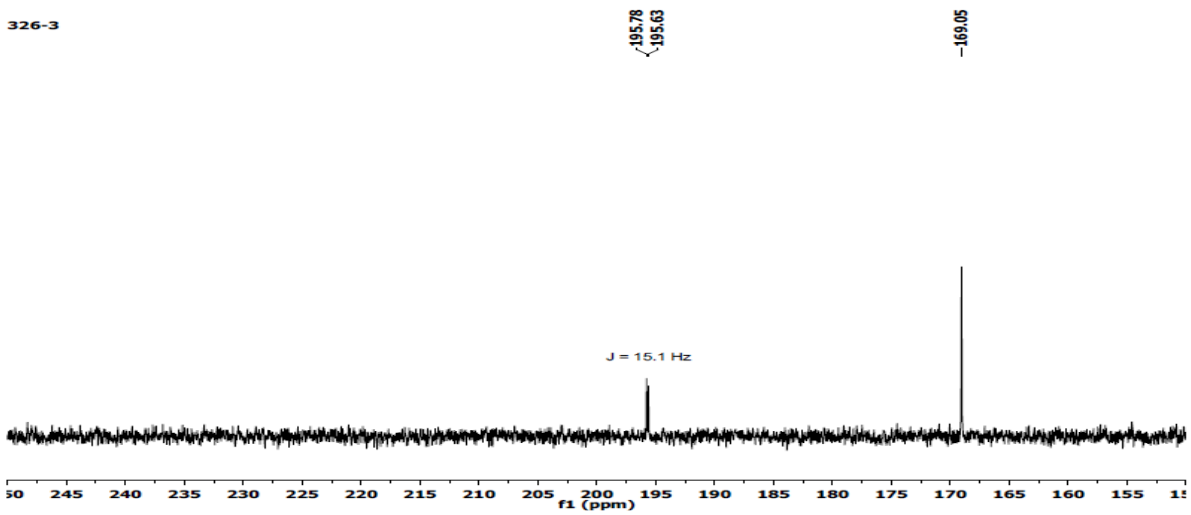

Figure S10a. ^{13}C NMR spectrum (CD_2Cl_2) of the reaction between MeOTf and **2b** in the carbonyl region showing the appearance of a new signal at 195.7 ppm along with the signal of methyl acrylate at 169.0 ppm, following the addition of MeOTf.

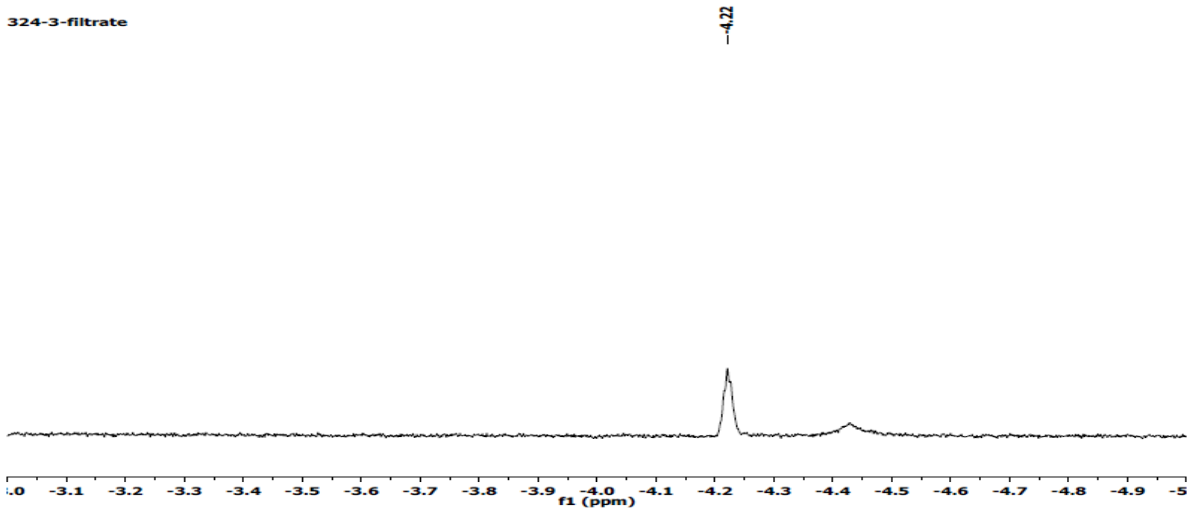

Figure S10b. Appearance of a new Ni-hydride species in the ^{1}H NMR spectrum (CD_2Cl_2) reaction of MeOTf with **2b**.

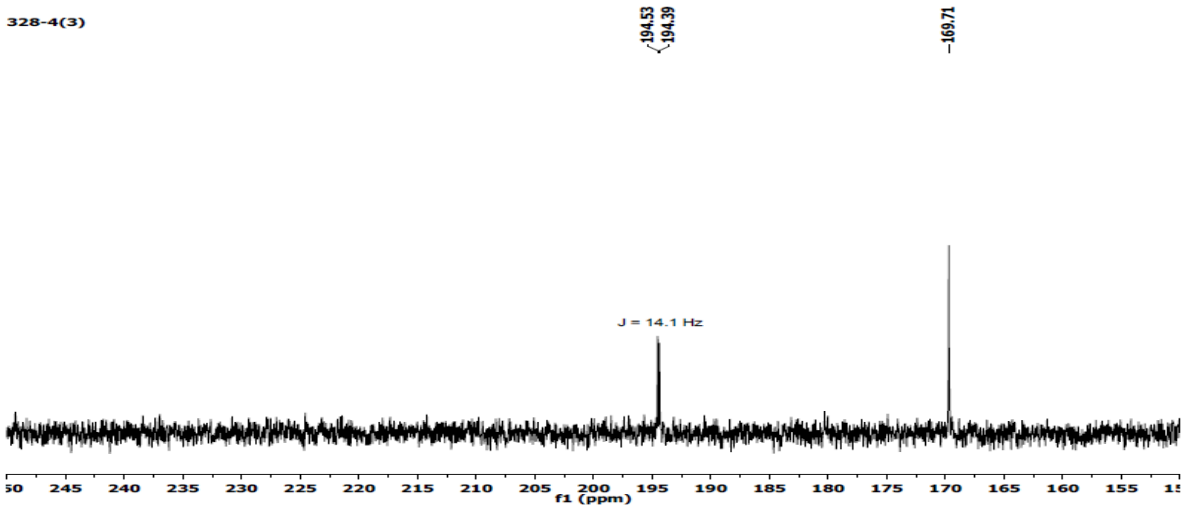

Figure S11a. ^{13}C NMR spectrum (CD_2Cl_2) of the reaction between MeOTf and **2c** in the carbonyl region showing the appearance of a new signal at 194.4 ppm along with the signal of methyl acrylate at 169.7 ppm, following the addition of MeOTf.

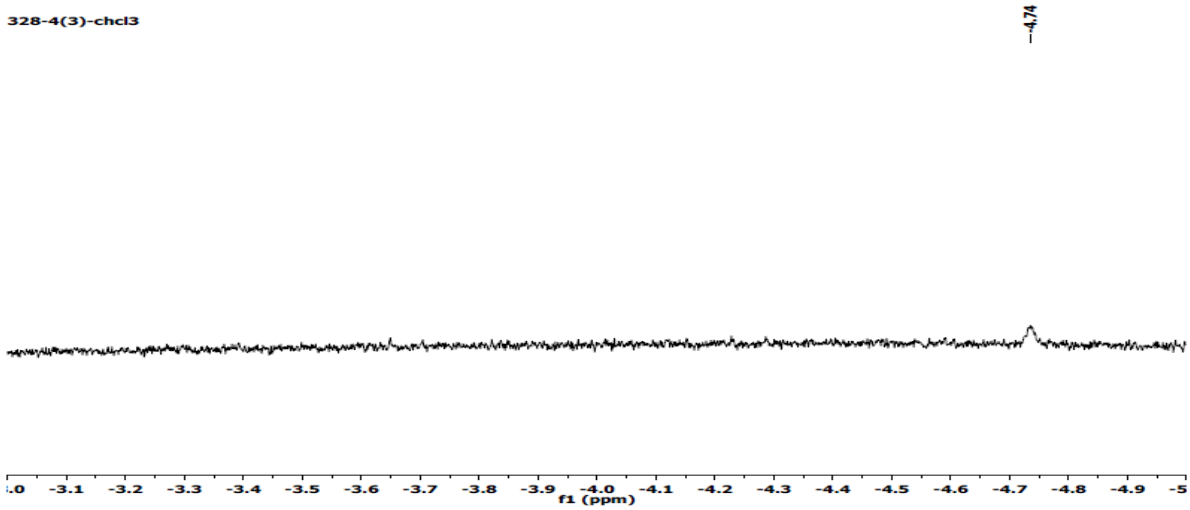

Figure S11b. Appearance of a new Ni-hydride species in the ^{1}H NMR spectrum (CD_2Cl_2) reaction of MeOTf with **2c**.

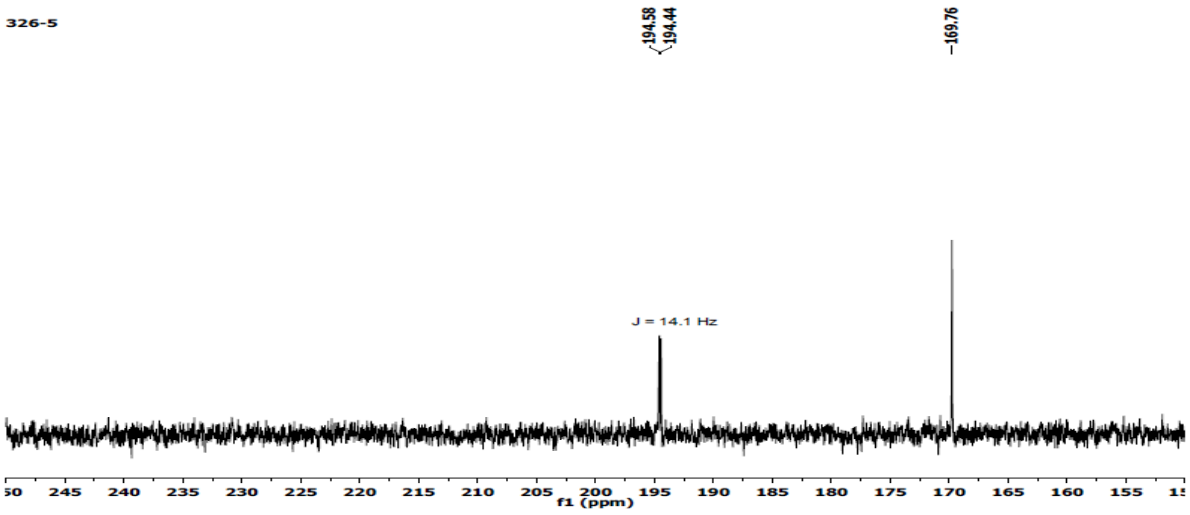

Figure S12a. ^{13}C NMR spectrum (CD_2Cl_2) of the reaction between MeOTf and **2d** in the carbonyl region, showing the appearance of a new signal at 194.5 ppm along with the signal of methyl acrylate at 169.8 ppm, following the addition of MeOTf.

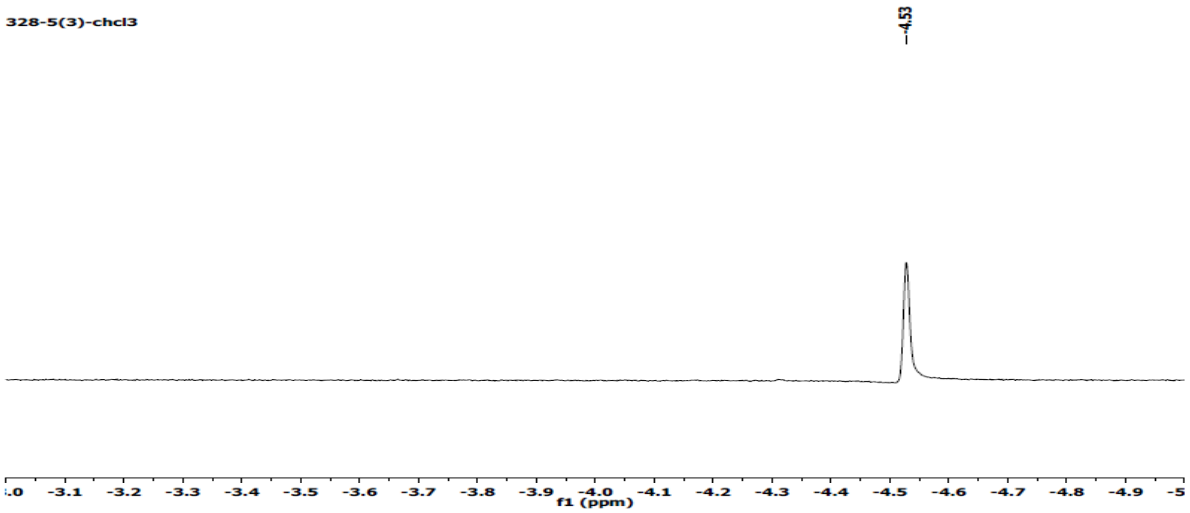

Figure S12b. Appearance of a new Ni-hydride species in the ^{1}H NMR spectrum (CD_2Cl_2) reaction of MeOTf with **2d**.

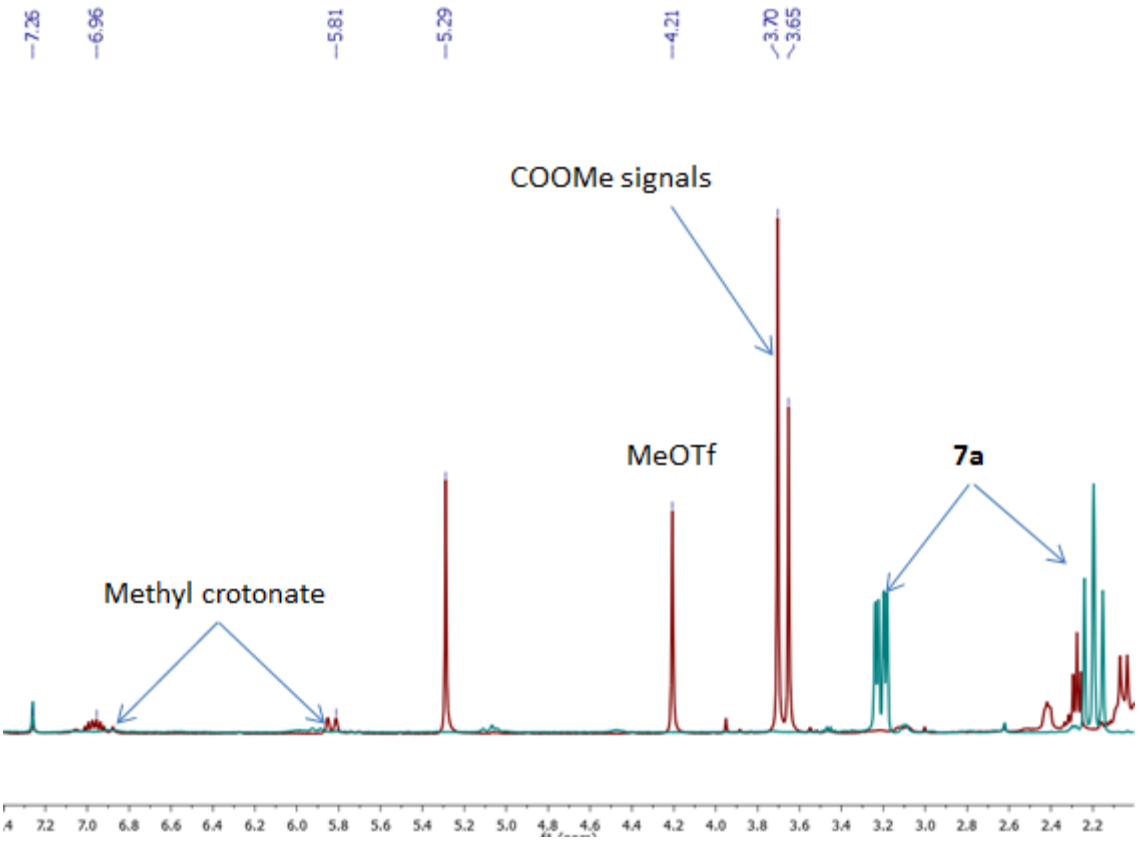

Figure S13. ^{1}H NMR spectrum of the reaction between MeOTf (1 equiv) and **7a** after 15 min in $CDCl_3$; the signals relative to the starting material (blue) disappear to form methyl crotonate and new signals in the methyl ester region as expected following the ring opening of the lactone. The residual peak of the unreacted MeOTf is visible at 4.21 ppm.

References

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