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Supplementary material to the article available at:
https://doi.org/10.5802/crchim.142

Supplementary material: Synthesis and crystal structures of palladium complexes based on α-amino-oximes derived from (*R*)-limonene and their application in allylic alkylation of 1,3-dioxo compounds

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1. General informations

The reactions were performed under nitrogen atmosphere using standard Schlenk line techniques. All reagents were commercial grade materials and were used without any further purification. Previously the solvents were dried and distilled under N_2 and deoxygenated through N_2 bubbling for 20 min.

Conversions were determined by gas chromatography (GC) on Shimadzu 2010 equipped with a HT-5 column (30 m, i.d. = 0.32 mm). The ee's (enantiomeric excess) were determined by HPLC using a column AD-H (hexane/*i*PrOH: 95/5, 1.0 mL/min, 25 °C).

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 300 spectrometer and referenced to TMS with eventually the presence of 1,3,5-trimethoxybenzene (TMB) as internal reference standard for quantitative NMR.

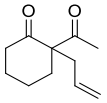
2. NMR spectra of products of the new compounds (Table 3)

The physical state of the following products is liquid after purification by silica gel column chromatography using petroleum ether/ethyl acetate (90/10) as eluent.

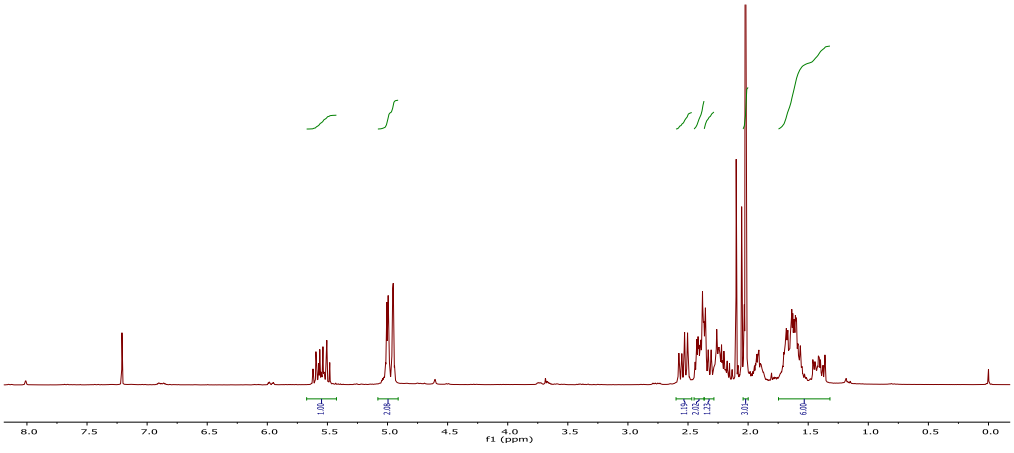
* Corresponding authors.

2.1. *2-acetyl-2-allylcyclohexanone*[1] (***3b***)

Yield: 72%

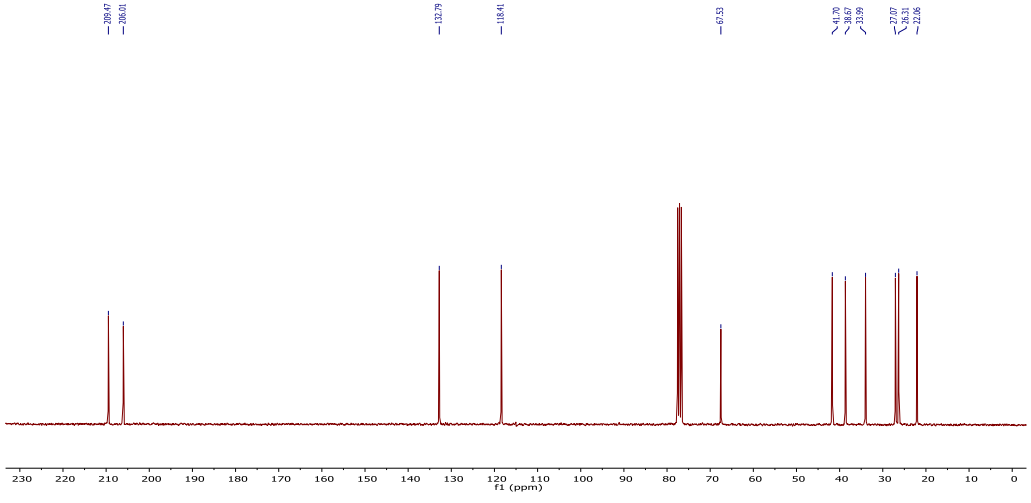


^{1}H NMR (300 MHz, $CDCl_3$): δ 5.68–5.57 (m, 1H, –**CH**=), 5.28–4.99 (m, 2H, **CH$_2$**=CH), 2.57–2.48 (m, J = 5.4 Hz, 1H, –**CH$_2$**–CO), 2.45–2.36 (m, 2H, –**CH$_2$**CH=), 2.35–2.28 (m, 1H, **CH$_2$**–CO), 2.10 (s, 3H, **CH$_3$**), 1.76–1.33 (m, 6H, C**CH$_2$CH$_2$CH$_2$**CH$_2$CO).



Supplementary Figure S1. ^{1}H NMR spectrum of **3b**.

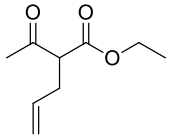
^{13}C NMR (75 MHz, $CDCl_3$) δ 209.47 (**C**=O), 206.01 (**C**=O), 132.79 (**CH**=CH_2), 118.41 (**CH$_2$**=$CHCH_2$), 67.53 (**Cq**–CO), 41.70 (CH_2–**CH$_2$**CO), 38.67 (CH_2=CH**CH$_2$**), 33.99 (**CH$_2$**–CH_2CO), 27.07 (**C**H_3–CO), 26.31 (**CH$_2$**–CqCO), 22.06 (**CH$_2$**–CH_2Cq).



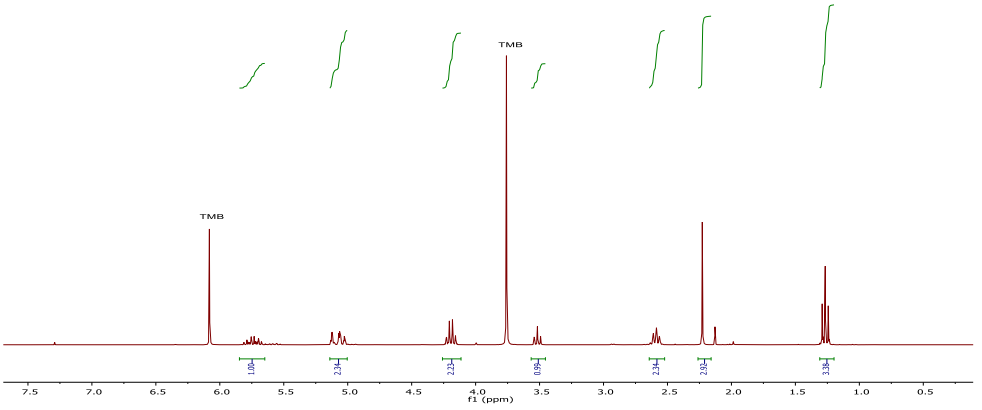
Supplementary Figure S2. ^{13}C NMR spectrum of **3b**.

2.2. *Ethyl 2-acetylpent-4-enoate*[1] (***3c***)

Yield: 42%

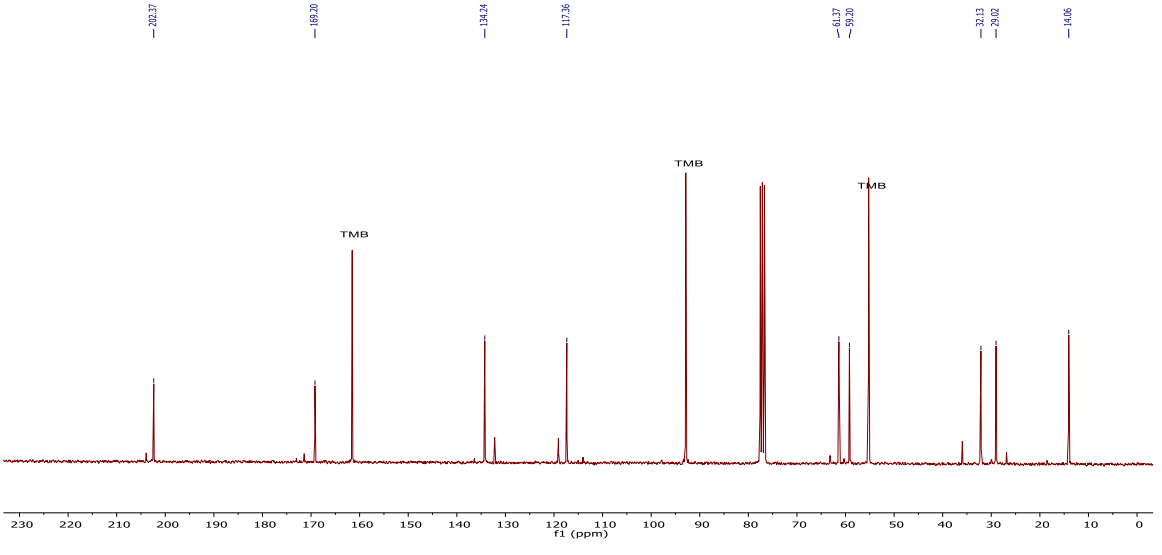


^{1}H NMR (300 MHz, $CDCl_3$) δ 5.74 (m, 1H, –**CH**=), 5.17–4.98 (m, 2H, **CH$_2$**=CH), 4.19 (q, J = 7.1 Hz, 2H, CH_3**CH$_2$**O), 3.52 (t, J = 7.4 Hz, 1H, **CH**–CO), 2.59 (m, J = 7.7, 6.7, 1.6, 0.8, 2H, –**CH$_2$**CH=), 2.23 (s, 3H, **CH$_3$**CO), 1.32–1.20 (t, 3H, **CH$_3$**CH_2O).



Supplementary Figure S3. ^{1}H NMR spectrum of **3c**.

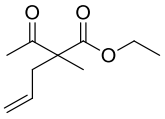
^{13}C NMR (75 MHz, $CDCl_3$) δ 202.37 (**C**=O), 169.20 (**C**=O), 134.24 (CH_2=**CH**–CH_2), 117.36 (CH_2=**CH**–CH_2), 61.37 (CH_3–**CH$_2$**O), 59.20 (**CH**–$COOCH_2CH_3$), 32.13 (CH_2=CH–**CH$_2$**–CH), 29.02 (**C**H_3–CO), 14.06 (**CH$_3$**–CH_2O).



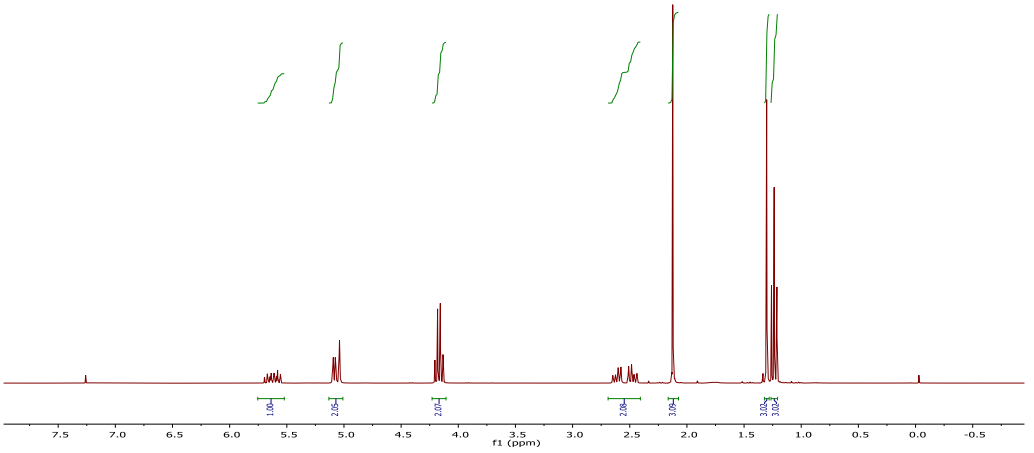
Supplementary Figure S4. ^{13}C NMR spectrum of **3c**.

2.3. *Ethyl 2-acetyl-2-methylpent-4-enoate*[1] (***3d***)

Yield: 61%

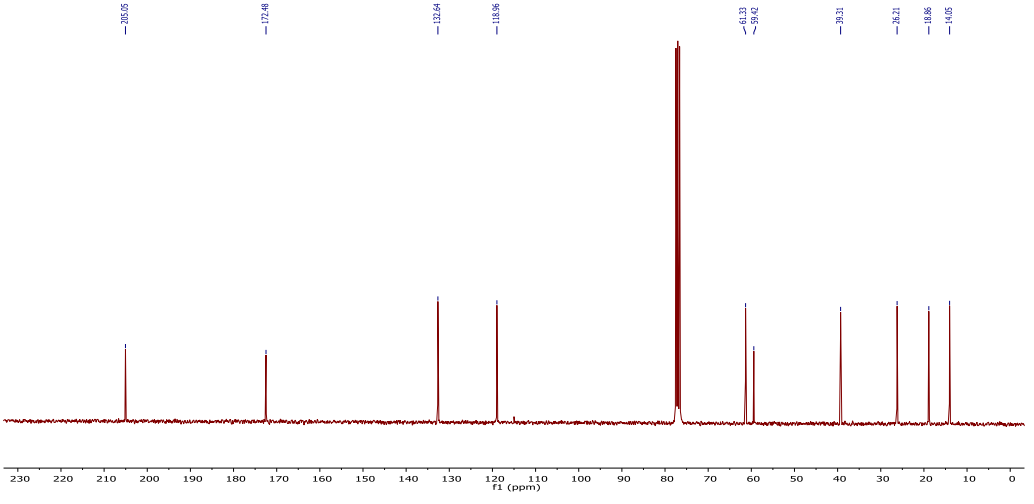


^{1}H NMR (300 MHz, $CDCl_3$) δ 5.72–5.52 (m, 1H, –**CH**=), 5.14–4.99 (m, 2H, **CH$_2$**=CH), 4.17 (q, J = 7.1 Hz, 2H, CH_3**CH$_2$**O), 2.69–2.40 (m, 2H, –**CH$_2$**CH=), 2.12 (s, 3H, **CH$_3$**CO), 1.30 (s, 3H, **CH$_3$**–CCO), 1.24 (t, J = 7.1 Hz, 3H, **CH$_3$**CH_2O).



Supplementary Figure S5. ^{1}H NMR spectrum of **3d**.

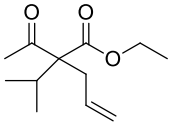
^{13}C NMR (75 MHz, $CDCl_3$) δ 205.05 (**C**=O), 172.48 (**C**=O), 132.64 (CH_2–**CH**=CH_2), 118.96 (**CH$_2$**=CH), 61.33 (CH_3–**CH$_2$**O), 59.42 (**Cq**–CO), 39.31 (=CH–**CH$_2$**Cq), 26.21 (**CH$_3$**–CO), 18.86 (**CH$_3$**–Cq), 14.05 (**CH$_3$**–CH_2O).



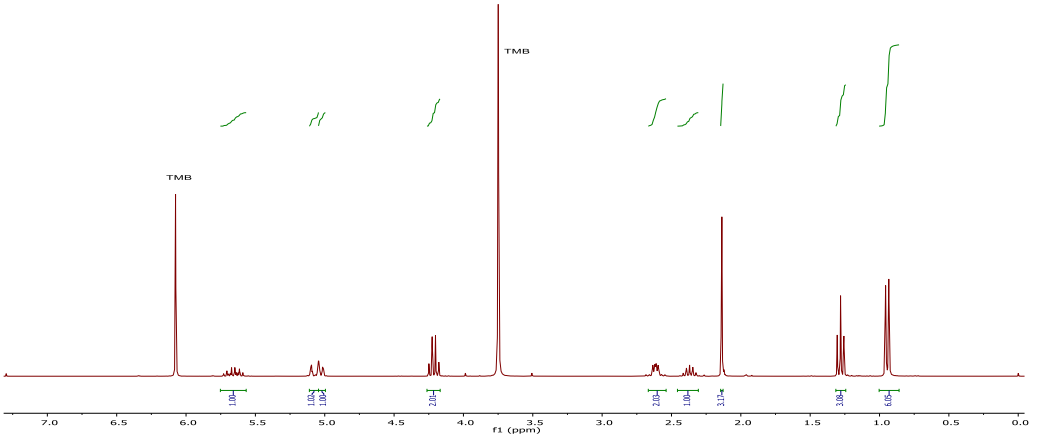
Supplementary Figure S6. ^{13}C NMR spectrum of **3d**.

2.4. *Ethyl 2-acetyl-3-isopropylpent-4-enoate (**3e**)*

Yield: 24%

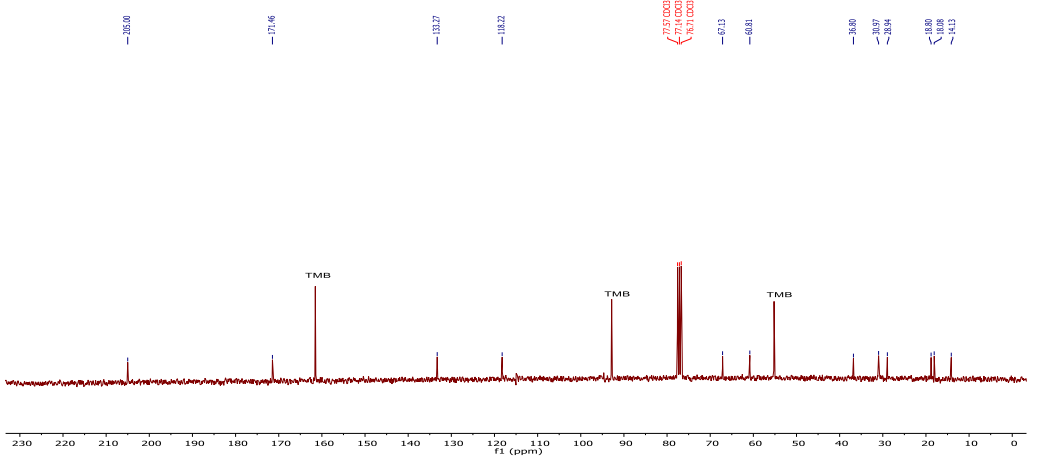


^{1}H NMR (300 MHz, $CDCl_3$) δ 5.66 (m, 2H, J = 17.3, 10.1, 7.3 Hz, –C**H**=), 5.04–4.99 (m, 2H, **CH$_2$**=), 4.24 (q, J = 7.1 Hz, 2H, CH_3**CH$_2$**O), 2.69–2.55 (m, 2H, –**CH$_2$**CH=), 2.37 (m, 1H, **CH**^{isopro}), 2.13 (s, 3H, **CH$_3$**–CO), 1.28 (t, J = 7.1 Hz, 3H, **CH$_3$**CH_2O), 0.94 (d, J = 6.8 Hz, 6H, **CH$_3^{isopro}$**).



Supplementary Figure S7. ^{1}H NMR spectrum of **3e**.

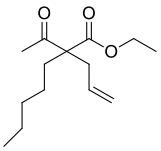
^{13}C NMR (75 MHz, $CDCl_3$) δ 205.00 (**C**=O), 171.46 (**C**=O), 133.27 (CH_2–**CH**=CH_2), 118.22 (**CH$_2$**=CH), 67.13 (**Cq**–CH–$(CH_3)_2$), 60.81 (CH_3–**CH$_2$**O), 36.80 (CH_2=CH–**CH$_2$**Cq), 30.97 (**CH$_3$**–CO), 28.94 (**CH**^{isopro}), 18.80 (**CH$_3$**–CHC), 18.08 (**CH$_3$**–CHC), 14.13 (**CH$_3$**–CH_2O).



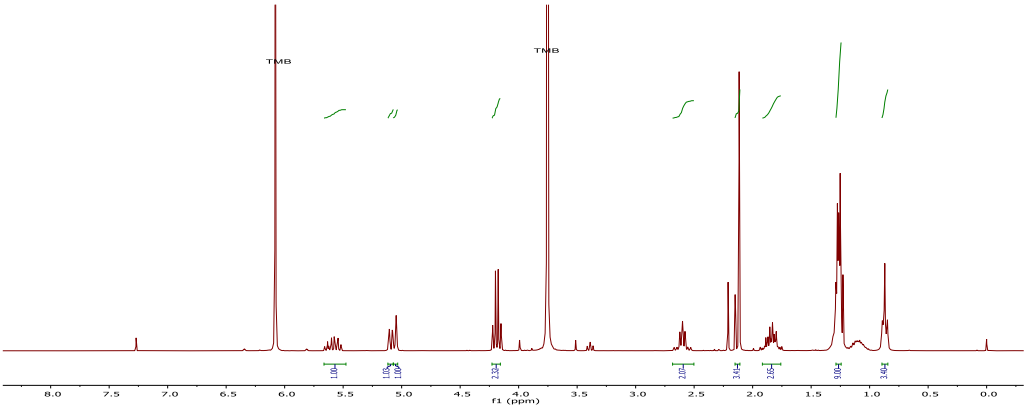
Supplementary Figure S8. ^{13}C NMR spectrum of **3e**.

2.5. *Ethyl 2-acetyl-2-allylheptanoate*[1] (***3f***)

Yield: 20%

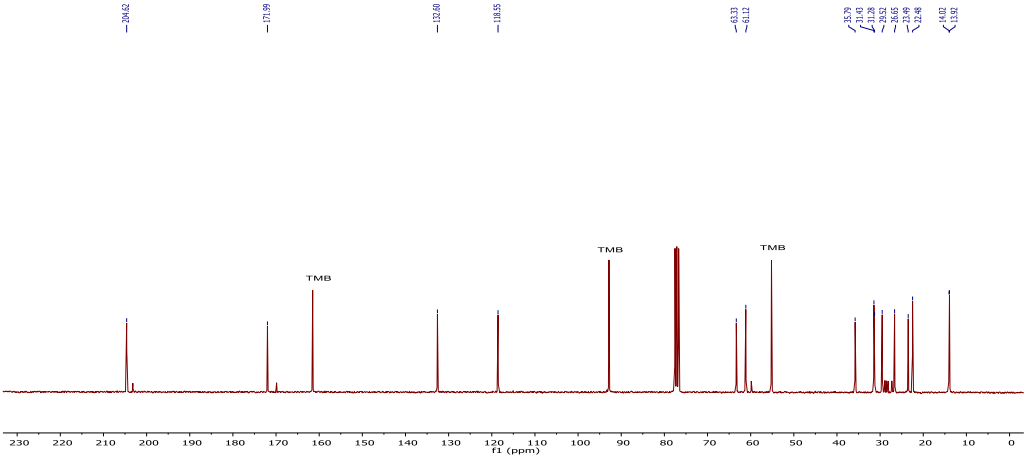


^{1}H NMR (300 MHz, $CDCl_3$) δ 5.66–5.48 (m, 1H, –C**H**=), 5.12–5.02 (m, 2H, **CH$_2$**=), 4.23–4.16 (q, J = 7.1 Hz 2H, CH_3**CH$_2$**O), 2.60 (m, J = 7.3, 6.0 Hz, 2H, –**CH$_2$**CH=), 2.15 (s, 3H, **CH$_3$**–CO), 1.92–1.76 (m, 2H, (**CH$_2$**)^{hept}CCO), 1.29–1.24 (m, 9H, –(**CH$_2$**)$_3$–CH_3 and **CH$_3$**CH_2O), 0.90–0.82 (m, 3H, **CH$_3^{hept}$**).



Supplementary Figure S9. ^{1}H NMR spectrum of **3f**.

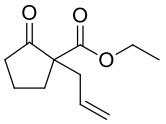
^{13}C NMR (75 MHz, $CDCl_3$) δ 204.62 (**C**=O), 171.99 (**C**=O), 132.60 (**CH**=CH_2), 118.55 (CH=**CH$_2$**), 63.33 (**Cq**–CO), 61.12 (CH_3–**CH$_2$**O), 35.79 (**CH$_2$**CH=CH_2), 31.36 (**CH$_3$**–CO), 29.52 (Cq**CH$_2$**$CH_2CH_2CH_2CH_3$), 26.65 ($CqCH_2CH_2$–**CH$_2$**–CH_2CH_3), 23.49 ($CqCH_2$–**CH$_2$**–$CH_2CH_2CH_3$), 22.48 ($CqCH_2CH_2CH_2$–**CH$_2$**–CH_3), 14.02 (**CH$_3$**–CH_2O), 13.92 (**CH$_3$**–$CH_2CH_2CH_2CH_2$Cq).



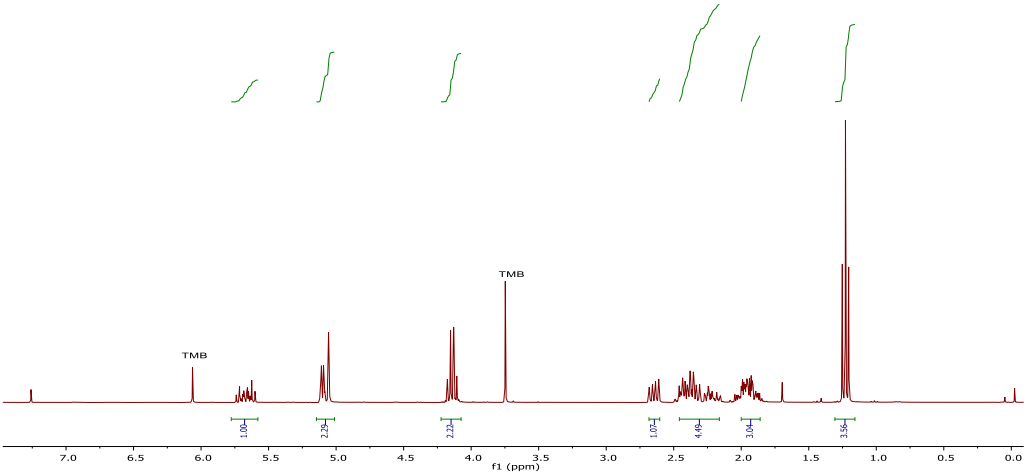
Supplementary Figure S10. ^{13}C NMR spectrum of **3f**.

2.6. *Ethyl 1-allyl-2-oxocyclopentanecarboxylate*[1] (***3g***)

Yield: 64%

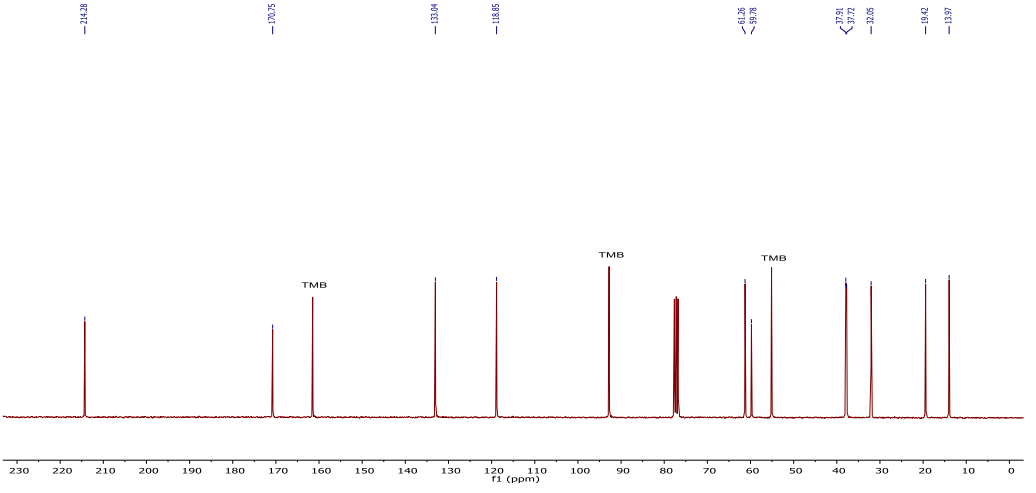


^{1}H NMR (300 MHz, $CDCl_3$): δ 5.75–5.64 (m, 1H, –C**H**=), 5.28–5.07 (m, 2H, **CH$_2$**=CH), 4.15 (q, J = 7.1 Hz, 2H, O**CH$_2$**), 2.73–1.80 (m, 8H, **CH$_2$CH$_2$CH$_2$** and –**CH$_2$**CH=), 1.24 (t, J = 7.1 Hz, **CH$_3$**CH_2O).



Supplementary Figure S11. ^{1}H NMR spectrum of **3g**.

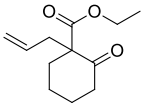
^{13}C NMR (75 MHz, $CDCl_3$) δ 214.28 (**C**=O), 170.75 (**C**=O), 133.04 (CH_2=**CH**–CH_2), 118.85 (**CH$_2$**=CH–CH_2), 61.26 (CH_3–**CH$_2$**O), 59.78 (**Cq**–CO), 37.91 (=CH–**CH$_2$**), 37.72 (**CH$_2$**–CO), 32.05 (**CH$_2$**–CqCO), 19.42 (**CH$_2$**–CH_2CO), 13.97 (**CH$_3$**–CH_2O).



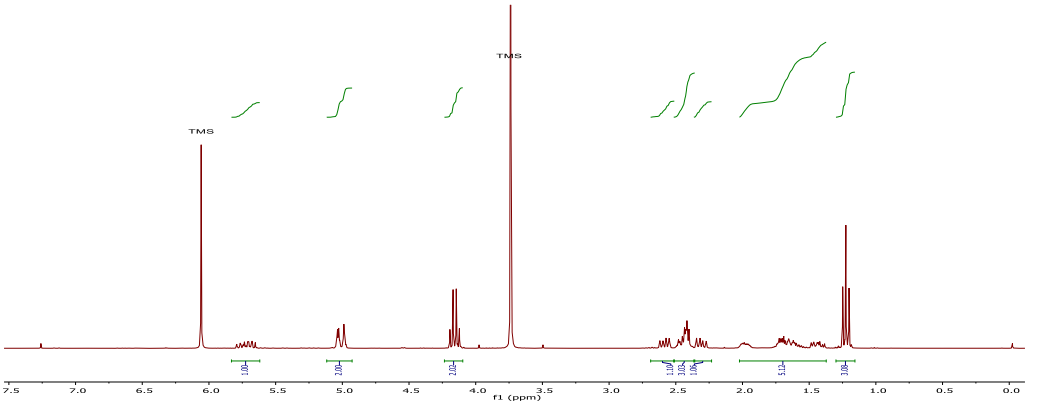
Supplementary Figure S12. ^{13}C NMR spectrum of **3g**.

2.7. *Ethyl 1-allyl-2-oxocylohexanecarboxylate*[1] (***3h***)

Yield: 75%

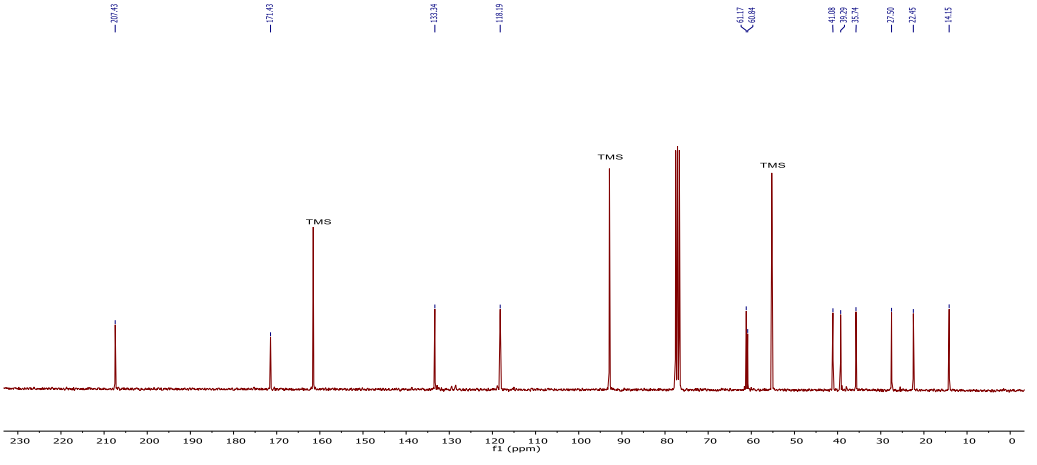


^{1}H NMR (300 MHz, $CDCl_3$) δ 5.82–5.62 (m, 1H, –**CH**=), 5.08–4.94 (m, 2H, **CH$_2$**=CH), 4.16 (q, J = 7.1 Hz, 2H, O**CH$_2$**), 2.58 (m, J = 13.9, 7.0, 1.3 Hz, 1H, –**CH$_2$**CH=), 2.31 (m, J = 13.9, 7.8, 1.1 Hz, 1H, –**CH$_2$**CH=), 2.49–1.35 (m, 8H, **CH$_2$CH$_2$CH$_2$CH$_2$**CO), 1.22 (t, J = 7.1 Hz, 3H, **CH$_3$**).



Supplementary Figure S13. ^{1}H NMR spectrum of **3h**.

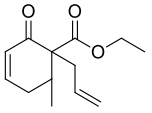
^{13}C NMR (75 MHz, $CDCl_3$) δ 207.43 (**C**=O), 171.43 (**C**=O), 133.34 (CH_2=**CH**), 118.19 (**CH$_2$**=CH), 61.01 (CH_3–**CH$_2$**O), 60.84 (**Cq**), 41.08 (**CH$_2$**–COCq), 39.29 (**CH$_2$**–CqCO), 35.74 (**CH$_2$**–CH=), 27.50 (**CH$_2$**–CH_2CO), 22.45 ($CqCH_2$–**CH$_2$**), 14.15 (**CH$_3$**–CH_2O).



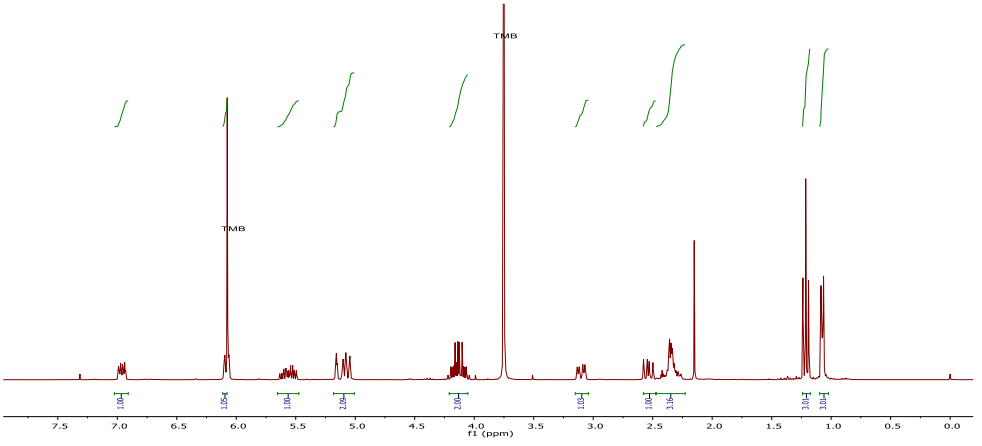
Supplementary Figure S14. ^{13}C NMR spectrum of **3h**.

2.8. *Ethyl 1-allyl-6-methyl-2-oxocyclohex-3-enecarboxylate (**3i**)*

Yield: 38%

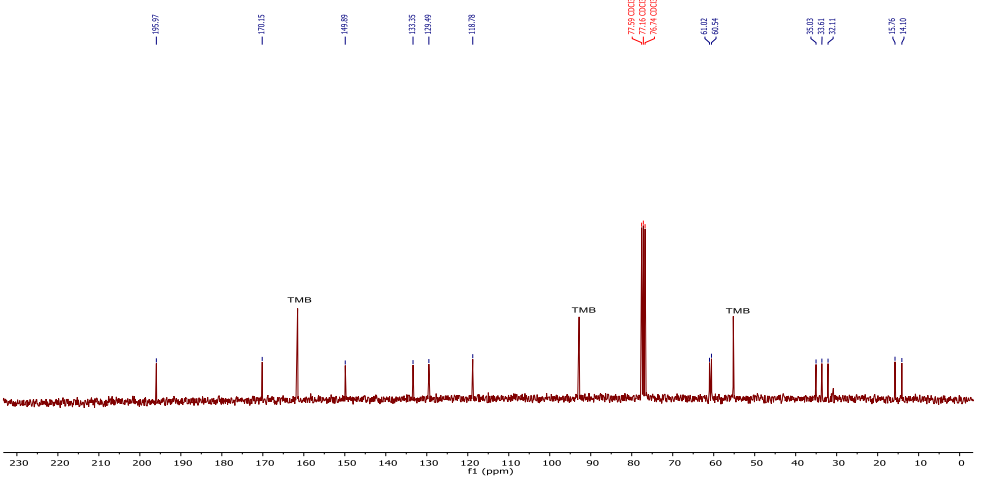


^{1}H NMR (300 MHz, $CDCl_3$) δ 7.00–6.89 (m, 1H, **CH**=CHCO), 6.10 (d, 1H, CH=**CH**CO), 5.65–5.48 (m, 1H, –C**H**=), 5.18 (J = 2.7 Hz, m, 1H, **CH$_2$**=CH), 5.09 (J = 2.4 Hz, m, 1H, **CH$_2$**=), 4.13 (q, J = 7.1 Hz, 2H, CH_3**CH$_2$**O), 3.10 (dd, J = 14.2, 5.2 Hz, 1H, CH_3**CH**C), 2.54 (J = 14.2, 9.4 Hz, m, 1H, –**CH$_2$**–CH=), 2.34 (m, J = 7.5, 4.0 Hz, 3H, –**CH$_2$**CH=CH_2 and **CH**–CH_3), 1.26–1.16 (t, J = 7.1 Hz, 3H, **CH$_3$**CH_2O), 1.08 (d, J = 6.5 Hz, 3H, **CH$_3$**CHCCO).



Supplementary Figure S15. ^{1}H NMR spectrum of **3i**.

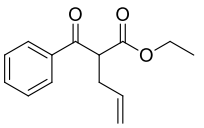
^{13}C NMR (75 MHz, $CDCl_3$) δ 195.97 (**C**=O), 170.15 (**C**=O), 149.89 (**CH**=CHCO), 133.35 (CH_2=**CH**CH_2), 129.49 (CH=**CH**CO), 118.78 (**CH$_2$**=$CHCH_2$), 61.02 (CH_3–**CH$_2$**O), 60.54 (CH_3–**CH$_2$**-O), 35.03 (**CH$_2$**–CH=CH), 33.61 (**CH$_2$**–CH=CH), 32.11 (**CH$_3$**–CHCCO), 15.76 (**CH$_3$**–CHCCO), 14.10 (**CH$_3$**–CH_2O).



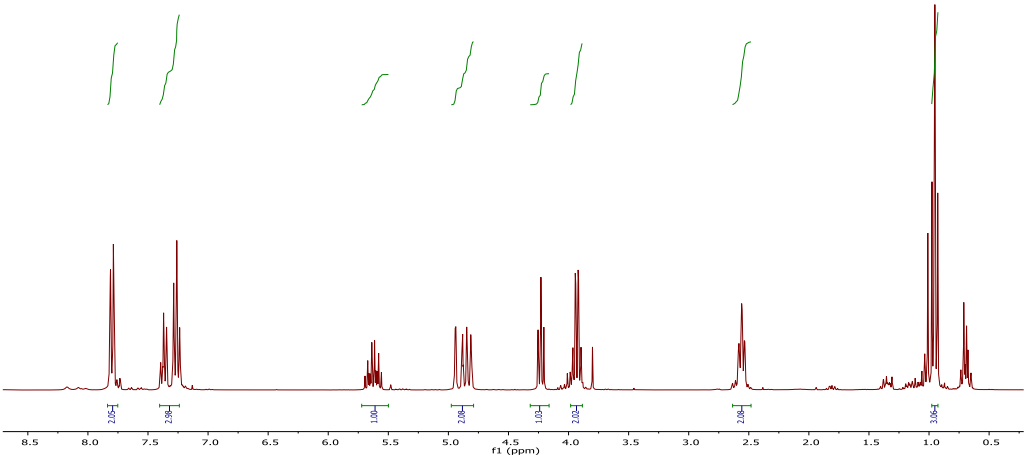
Supplementary Figure S16. ^{13}C NMR spectrum of **3i**.

2.9. *Ethyl 2-benzoylpent-4-enoate*[1] ***(3j)***

Yield: 31%

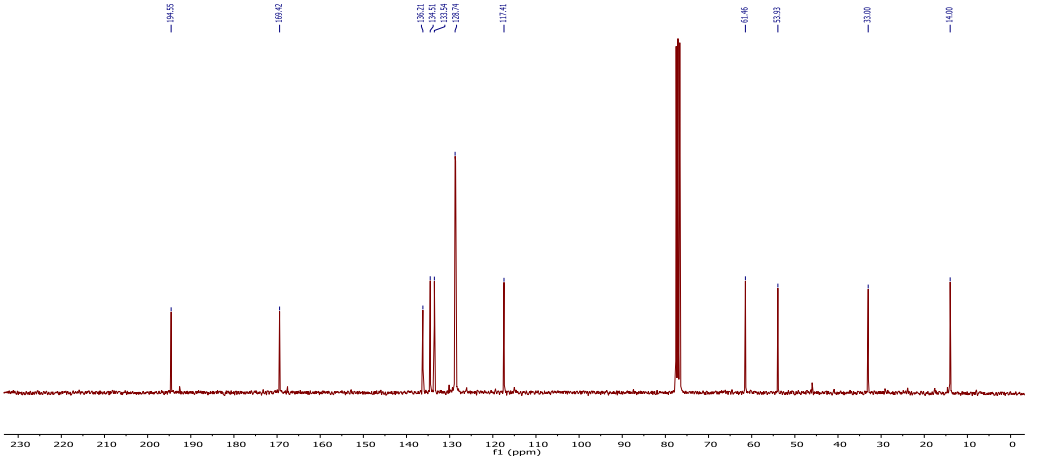


^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88–7.20 (m, 5H, **C$_6$H$_5$**), 5.63 (m, J = 17.0, 10.1, 6.8 Hz, 1H, m, –C**H**=), 5.02–4.75 (m, 2H, **CH$_2$**=), 4.23 (t, J = 7.2 Hz, 1H, –**CH**CO), 3.93 (q, J = 7.1, 2H, CH_3**CH$_2$**O), 2.56 (m, J = 9.5, 6.9, 1.4 Hz, 2H, –**CH$_2$**–CH=CH), 1.07–0.90 (t, J = 7.1, 3H, **CH$_3$**CH_2O).



Supplementary Figure S17. ^{1}H NMR spectrum of **3j**.

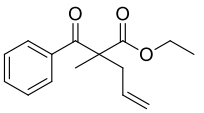
^{13}C NMR (75 MHz, $CDCl_3$) δ 194.55 (**C**=O), 169.42 (**C**=O), 136.21 (**Cq**–CO), 134.51 (CH_2=**CH**CH_2), 133.54 (**CH**^{para}), 128.74 (**CH**^{aromatic}), 117.41 (**CH$_2$**=CH), 61.46 (CH_3–**CH$_2$**O), 53.93 (**CH**–CO), 33.00 (**CH$_2$**–CH=), 14.00 (**CH$_3$**–CH_2O).



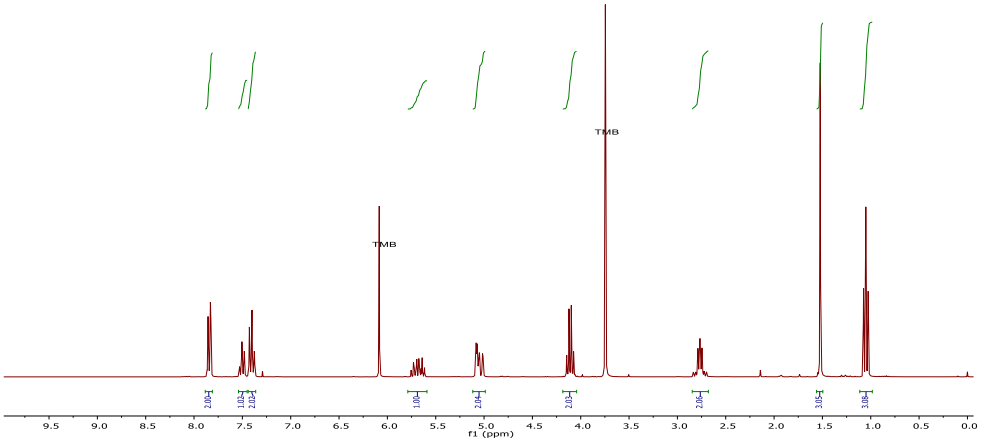
Supplementary Figure S18. ^{13}C NMR spectrum of **3j**.

2.10. *Ethyl 2-benzoyl-2-methylpent-4-enoate (**3k**)*

Yield: 62%

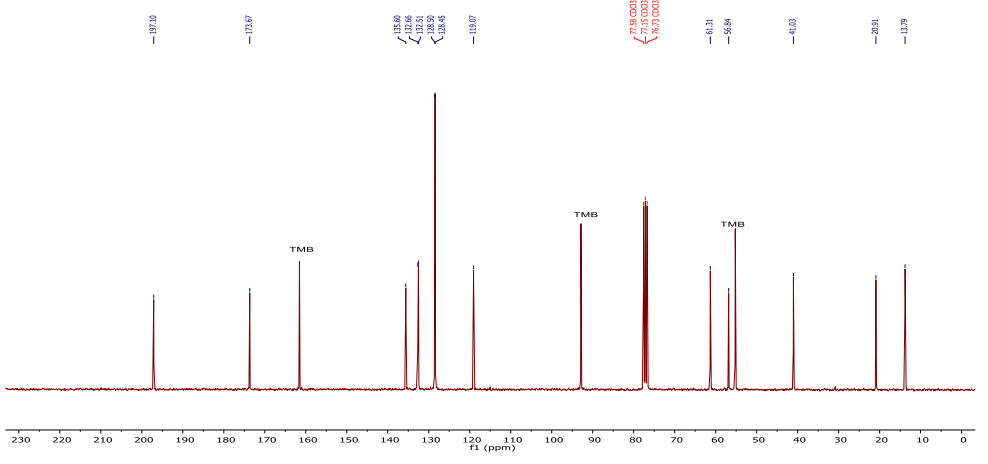


^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90–7.38 (m, 5H, **C$_6$H$_5$**), 5.83–5.59 (m, 1H, –C**H**=), 5.13–4.98 (m, 2H, **CH$_2$**=), 4.11 (q, J = 7.1 Hz, 2H, CH_3**CH$_2$**O), 2.76 (m, J = 7.1 Hz, 2H, Cq**CH$_2$**CH=), 1.52 (s, 3H, **CH$_3$**CCO), 1.05 (t, J = 7.1 Hz, 3H, **CH$_3$**CH_2O).



Supplementary Figure S19. ^{1}H NMR spectrum of **3k**.

^{13}C NMR (75 MHz, $CDCl_3$) δ 197.10 (**C**=O), 173.67 (**C**=O), 135.60 (**Cq**^{aromatic}), 132.66 (**CH**^{aromatic}), 132.51 (**CH**^{aromatic}), 128.50 (**CH**^{aromatic}), 128.45 (**CH**^{aromatic}), 119.07 (**CH$_2$**=), 61.31 (CH_3–**CH$_2$**O), 56.84 (**Cq**–COOEt), 41.03 (**CH$_2$**–CH=CH_2), 20.91 (**CH$_3$**–CCO), 13.79 (**CH$_3$**–CH_2O).

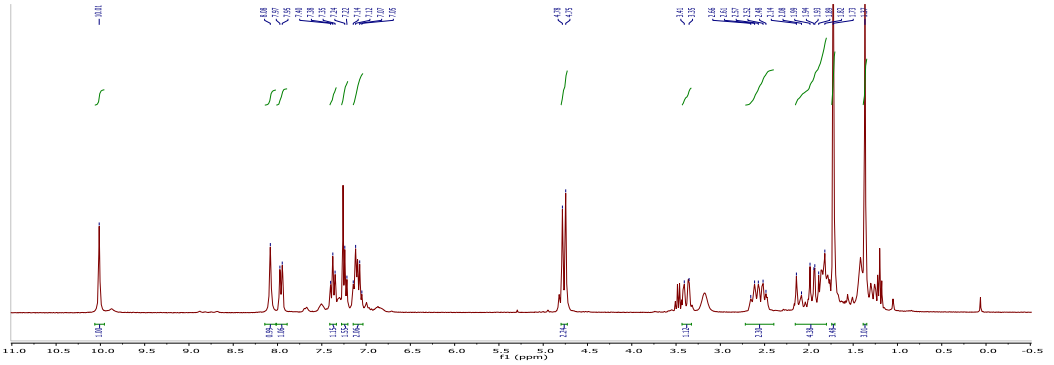


Supplementary Figure S20. ^{13}C NMR spectrum of (**3k**).

3. NMR spectra of PdL_nCl_2 complexes

3.1. ^{1}*H NMR of Pd(L1)Cl$_2$ (**C1**)*

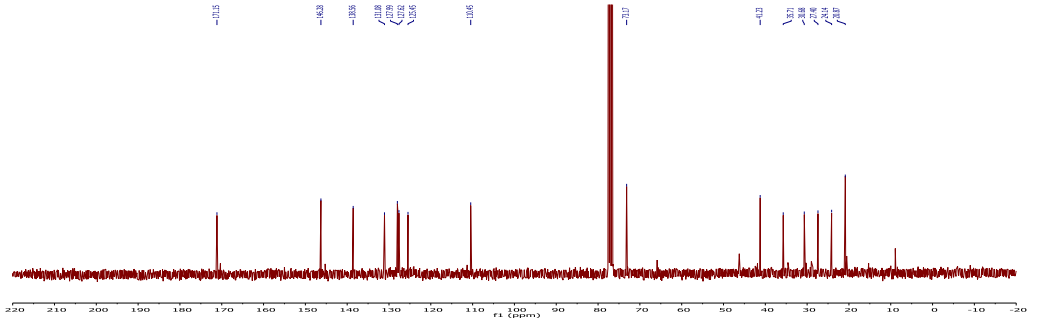
^{1}H NMR (300 MHz, $CDCl_3$) δ 10.01 (s, 1H), 8.08 (s, 1H), 7.96 (d, J = 8.0 Hz, 1H), 7.38 (t, J = 7.6 Hz, 2H), 7.23 (d, J = 7.2 Hz, 1H), 7.17–7.02 (m, 3H), 4.76 (d, J = 11.2 Hz, 3H), 3.38 (d, J = 16.2 Hz, 1H), 2.57 (dt, J = 25.8, 11.4 Hz, 3H), 2.18–1.80 (m, 5H), 1.73 (s, 4H), 1.37 (s, 3H).



Supplementary Figure S21. ^{1}H NMR of Pd(**L1**)Cl_2 in $CDCl_3$.

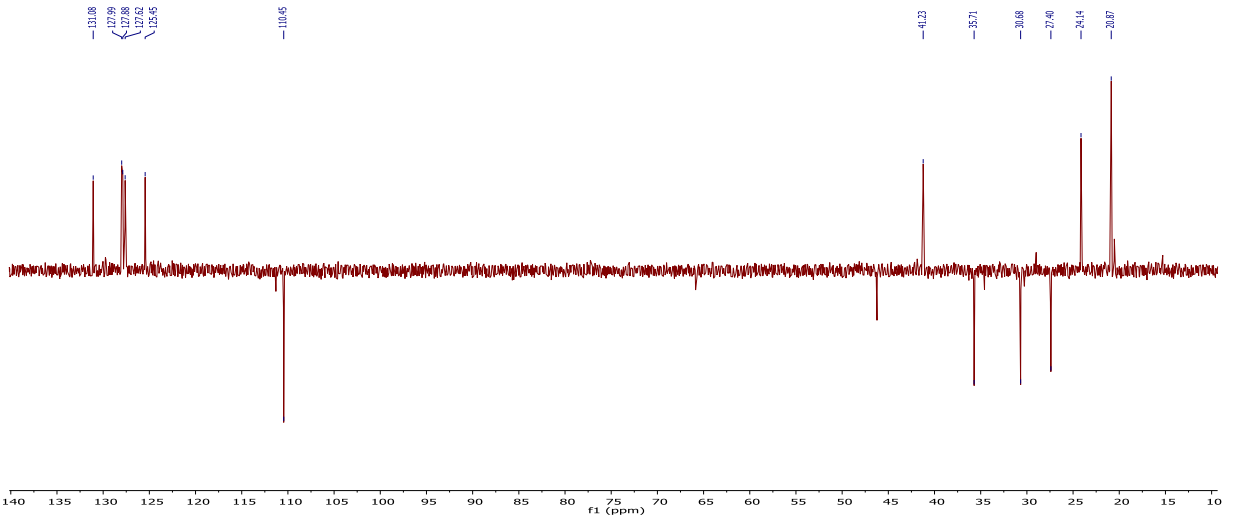
3.2. ^{13}*C NMR of Pd(L1)Cl$_2$ (**C1**)*

^{13}C NMR (75 MHz, $CDCl_3$) δ 171.15 (**Cq**=NOH), 146.28 (**Cq**=CH_2), 138.56 (**Cq**–C_6H_5), 131.08, 127.99, 127.62, 125.45 ($\mathbf{C}_{aromatic}$), 110.45 (**CH_2**=), 73.17 (**Cq**–NH), 41.23 (CH_2–**C***–NH), 35.71 (**CH_2**–CH–Cq), 30.68 (CH_2–C=NOH), 27.40 (**CH_2**–CH–Cq), 24.14 (**CH_3**–(C=CH_2) 20.87 (**CH_3**–(C–NH).



Supplementary Figure S22. ^{13}C NMR of Pd(**L1**)Cl_2 in $CDCl_3$.

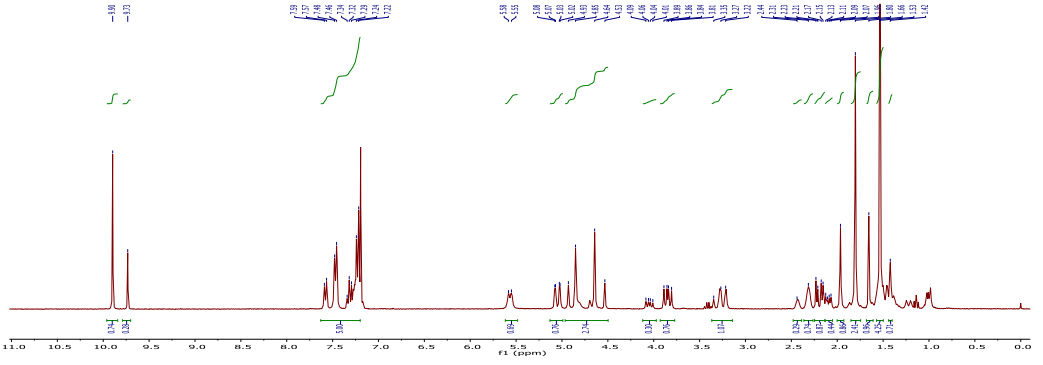
3.3. *DEPT 135 NMR of Pd(L1)Cl_2 (**C1**)*



Supplementary Figure S23. DEPT 135 NMR of Pd(**L1**)Cl_2 in $CDCl_3$.

3.4. ^{1}*H NMR of Pd(L2)Cl_2 (**C2** and **C′2**)*

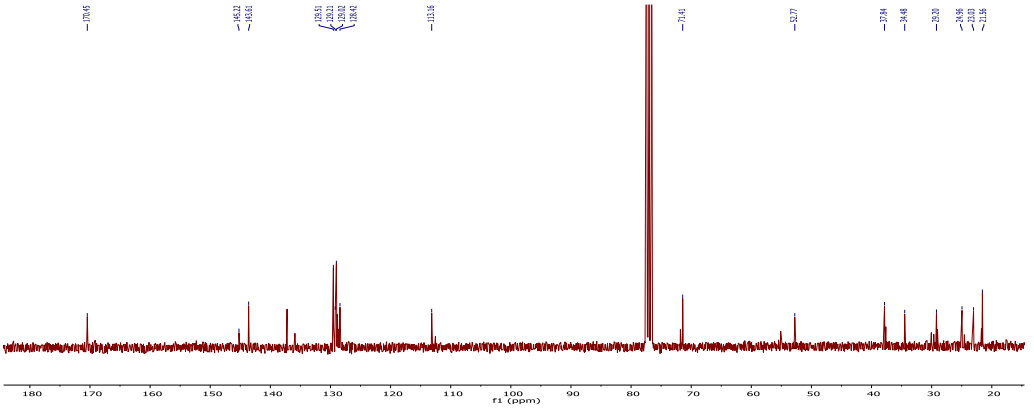
^{1}H NMR (300 MHz, $CDCl_3$) δ 9.90 (s, 1H), 9.73 (s, 1H), 7.66–7.31 (m, 10H), 5.57 (d, J = 9.7 Hz, 1H), 5.04 (dd, J = 14.9, 2.4 Hz, 2H), 4.93–4.52 (m, 4H), 4.05 (dd, J = 14.4, 8.3 Hz, 1H), 3.85 (dd, J = 15.0, 10.0 Hz, 1H), 3.24 (d, J = 15.5 Hz, 2H), 2.31 (s, 1H), 2.28–2.13 (m, 1H), 1.96 (s, 1H), 1.80 (s, 6H), 1.65 (s, 1H), 1.44 (s, 1H), 1.53 (s, 3H), 1.42 (m, 1H).



Supplementary Figure S24. ^{1}H NMR of Pd(**L2**)Cl_2 in $CDCl_3$.

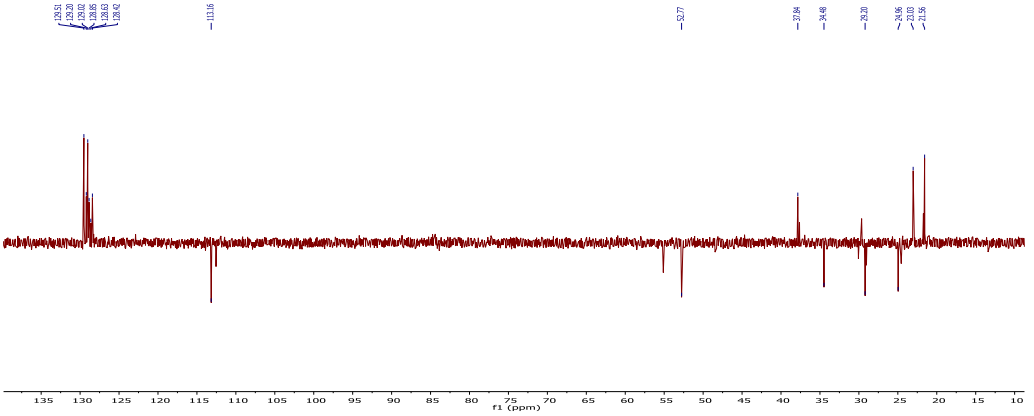
3.5. ^{13}C *NMR of Pd(L2)Cl$_2$ (**C2**)*

^{13}C NMR (75 MHz, $CDCl_3$) δ 170.45 (**Cq**=N–OH), 143.61 (**Cq**=CH_2), 137.22 (**Cq**–C_6H_5), 129.51 (**C**$_{aromatic}$), 129.20, 129.02, 128.85, 113.16 (**CH$_2$**=), 71.41 (**Cq**–NH), 52.68 (**CH$_2$**–(C_6H_5)), 37.84 (**CH***), 34.48 (**CH$_2$**–(C*–NH)), 29.20 (**CH$_2$**–C–NOH), 24.96 (**CH$_2$**–CH–Cq), 23.03 (**CH$_3$**–(C=CH_2)), 21.56 (**CH$_3$**–(C–NH)).



Supplementary Figure S25. ^{13}C NMR of Pd(**L2**)Cl_2 in $CDCl_3$.

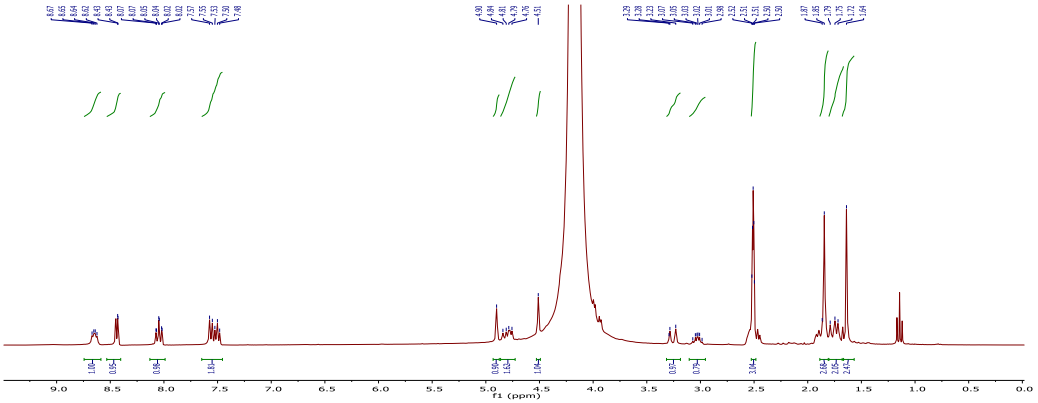
3.6. *DEPT 135 NMR of Pd(L2)Cl$_2$ (**C2**)*



Supplementary Figure S26. DEPT 135 NMR of Pd(**L2**)Cl_2 in $CDCl_3$.

3.7. ^{1}H *NMR Pd(L3)Cl$_2$*

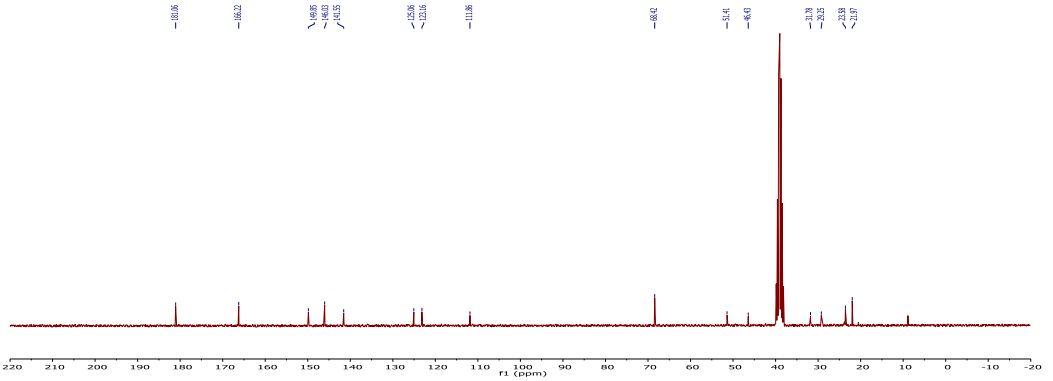
^{1}H NMR (300 MHz, DMSO-d_6) δ 8.65 (dd, J = 8.9, 4.9 Hz, 1H), 8.47–8.40 (m, 1H), 8.05 (td, J = 7.8, 1.5 Hz, 1H), 7.61–7.46 (m, 2H), 4.90 (s, 1H), 4.80 (dd, J = 16.2, 9.1 Hz, 2H), 4.51 (s, 1H), 3.34–3.19 (m, 1H), 3.10–2.95 (m, 1H), 2.51 (dt, J = 3.4, 1.7 Hz, 3H), 1.85 (s, 3H), 1.82–1.70 (m, 2H), 1.64 (s, 3H).



Supplementary Figure S27. ^{1}H NMR of Pd(**L3**)Cl$_2$ in DMSO-d_6.

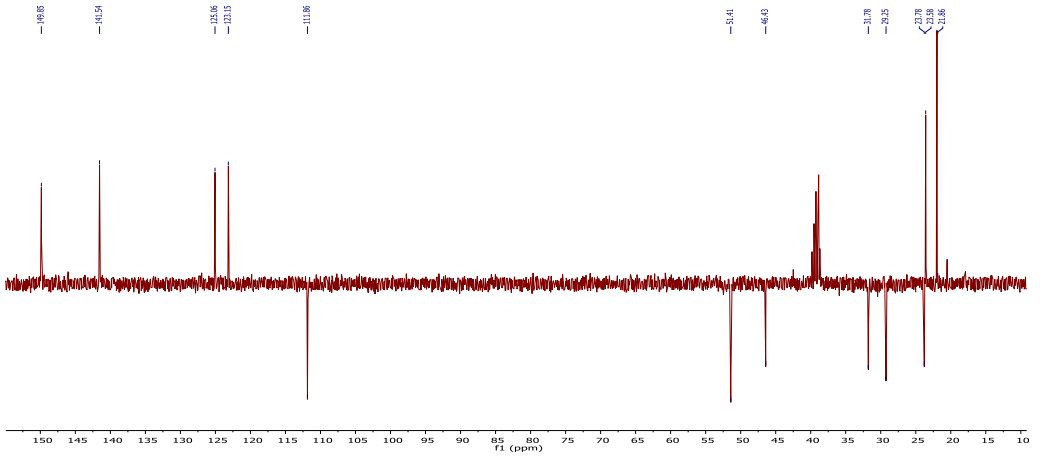
3.8. ^{13}C *NMR of Pd(L3)Cl$_2$*

^{13}C NMR (75 MHz, DMSO) δ 181.06 (**Cq**=N–OH), 166.22 (**Cq**–(py)), 149.85 (**CH**), 146.03 (**Cq**–CH_3), 141.55 **CH**(py), 125.06 **CH** (py), 123.16 **CH** (py), 111.86 (**CH$_2$**=), 68.42 (**Cq**–NH), 51.41 (**CH$_2$**–NH), 46.43 (**CH$_2$**), 31.78 (**CH$_2$**–C=NOH), 29.25 (**CH$_2$**), 23.58 (**CH$_3$**–CNH), 21.97 (**CH$_3$**–C=CH_2).



Supplementary Figure S28. ^{13}C NMR of Pd(**L3**)Cl$_2$ in DMSO-d_6.

3.9. *DEPT 135 of $Pd(L3)Cl_2$*



Supplementary Figure S29. DEPT 135 NMR of PdL_3 in DMSO-d_6.

4. Diffraction studies

4.1. *Crystal data and structure refinement for complexes **C1** and **C2***

Parameter	**C1**	**C2**
Crystal data		
Formula	$4(C_{16}H_{22}Cl_2N_2OPd)\cdot C_4H_{10}O$	$PdCl_2C_{17}H_{24}N_2O$
Molecular weight	1816.74	449.68
Crystal colour	Orange	Orange
Crystal size (mm)	$0.44 \times 0.39 \times 0.26$	$0.23 \times 0.19 \times 0.11$
Temperature (K)	100	100
Crystal system	Trigonal	Orthorhombic
Space group	P 3_1	P $2_12_12_1$
a (Å)	13.1530(4)	8.6502 (3)
b (Å)	13.1530(4)	11.3195 (4)
c (Å)	38.2924(12)	18.1538 (6)
α (°)	90	90
β (°)	90	90
γ (°)	120	90
V (Å^3)	5737.1(4)	1777.55(11)
D_{calc} (mg/m^3); Z	1.578; 3	1.680; 4
F(0 0 0)	2766	912
μ (mm^{-1})	1.26	1.35

(continued on next page)

Parameter	**C1**	**C2**
Data collection		
Instrument	Bruker APEX-II CCD	Bruker APEX-II CCD
Θ range for data collection (deg)	1.86 to 36.29	2.12 to 33.12
Index ranges	$-21 \le h \le 21$	$-13 \le h \le 11$
	$-21 \le k \le 21$	$-17 \le k \le 17$
	$-63 \le l \le 63$	$-22 \le l \le 27$
Number of measured reflections	198742	45344
Number of independent reflections	36836	6736
Number of reflections with $I > 2\sigma(I)$	35926	6627
R_{int}	0.043	0.038
Refinement		
Refinement method	Full matrix least square on F^2	Full matrix least square on F^2
$R[F^2 > 2\sigma(F^2)]$	0.030	0.018
$wR(F^2)$	0.065	0.043
S	1.09	1.04
Data/restraints/parameters	36836/7/861	6736/0/218
$\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}$ [e Å^{-3}]	1.25/−0.60	0.79/−0.60
Absolute structure Flack parameter	−0.007(4)	−0.011(8)

4.2. *Selected bond lengths d and bond angles ω in complex* ***C1***

Bond	d (Å)
Pd(1)–Cl(1)	2.288(1)
Pd(1)–Cl(2)	2.307(8)
Pd(1)–N(1)	2.071(3)
Pd(1)–N(2)	1.981(4)
N(1)–C(1)	1.458(5)
N(1)–C(7)	1.543(6)
N(2)–O(1)	1.382(6)
N(2)–C(12)	1.289(4)

Angle	ω (deg)
Cl(1)–Pd(1)–Cl(2)	91.80(4)
N(2)–Pd(1)–Cl(2)	91.43(1)
N(1)–Pd(1)–Cl(1)	96.50(8)
N(1)–Pd(1)–N(2)	80.1(1)
O(1)–N(2)–Pd(1)	123.4(3)
O(1)–N(2)–C(12)	116.2(3)
Pd(1)–N(1)–C(7)	109.3(2)
Pd(1)–N(1)–C(1)	121.4(2)
N(2)–C(12)–C(7)	115.5(3)
N(2)–C(12)–C(11)	123.7(3)
C(1)–N(1)–C(7)	112.2(3)
N(1)–C(1)–C(6)	120.1(3)

4.3. *Selected bond lengths d and angles ω in Complex* ***C2***

Angle	ω (deg)
Cl(2)–Pd(1)–Cl(1)	94.56(2)
N(1)–Pd(1)–Cl(1)	92.20(4)
N(1)–Pd(1)–Cl(2)	172.79(4)
N(1)–Pd(1)–N(2)	80.60(6)
N(2)–Pd(1)–Cl(1)	172.79(4)
N(2)–Pd(1)–Cl(2)	92.64(4)
O(1)–N(1)–Pd(1)	124.1(1)
C(1)–N(1)–Pd(1)	119.3(1)
C(1)–N(1)–O(1)	116.6(1)

Bond	d (Å)
Pd(1)–Cl(1)	2.3187(5)
Pd(1)–Cl(2)	2.2886(5)
Pd(1)–N(1)	1.990(1)
Pd(1)–N(2)	2.046(1)
N(1)–O(1)	1.383(2)
N(1)–C(1)	1.285(2)
N(2)–C(6)	1.530(2)
N(2)–C(11)	1.512(2)