Supporting information

Pd(II)-catalyzed ethylene/methyl acrylate copolymerization: toward catalyst recovery and recycle.

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NMR characterization of ligands and complexes

NMR spectra of both ligands and complexes were in agreement to literature.[1-5]

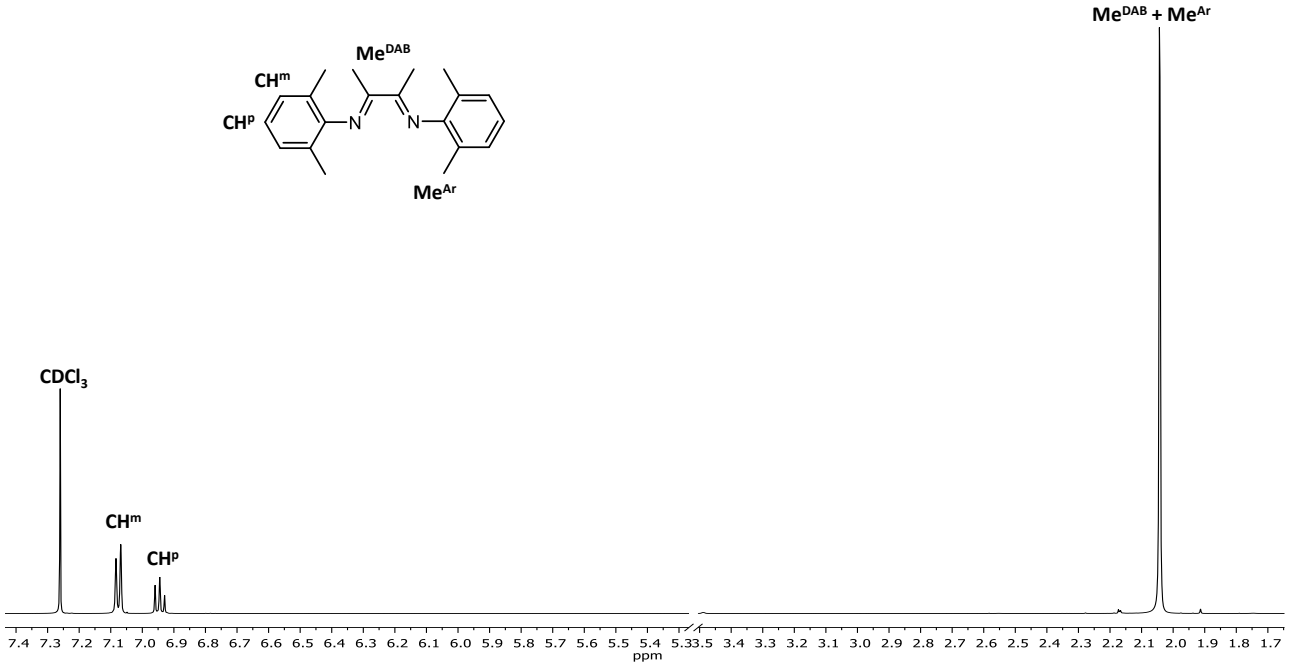


Figure S1 ^{1}H NMR spectrum ($CDCl_3$, 298 K) of **1**.

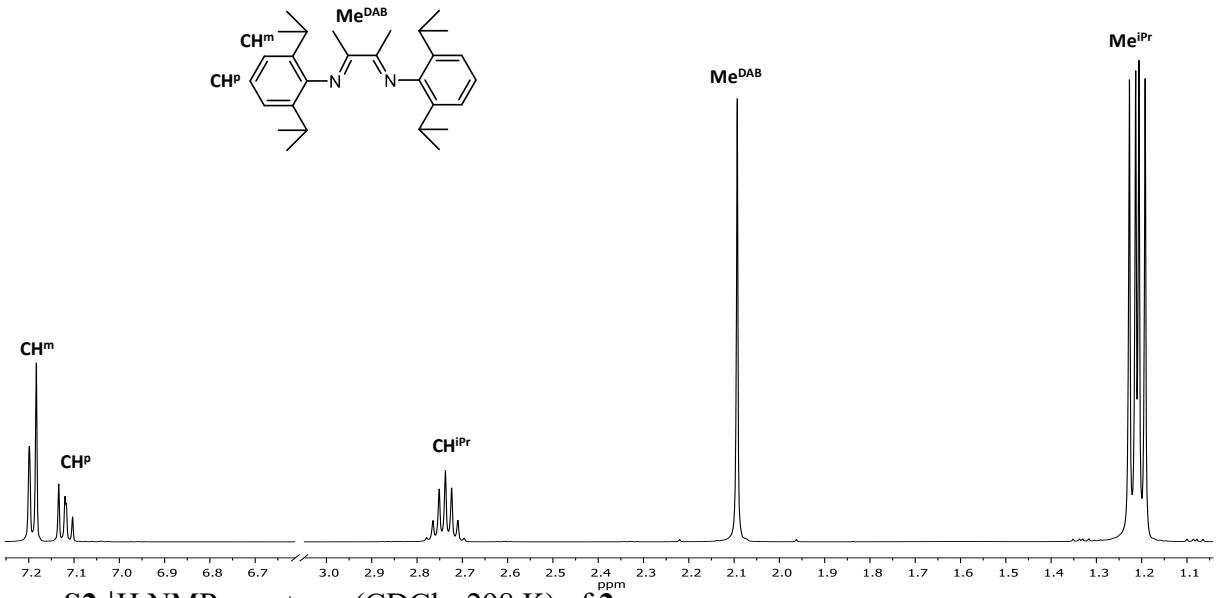


Figure S2 ^{1}H NMR spectrum ($CDCl_3$, 298 K) of **2**.

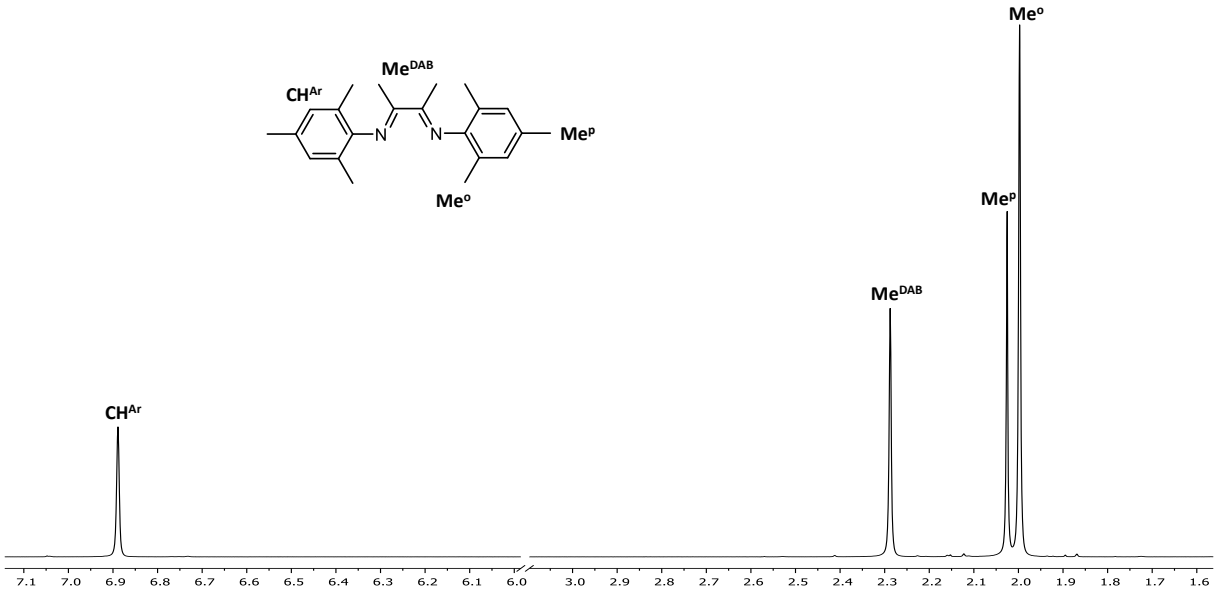


Figure S3 ^{1}H NMR spectrum ($CDCl_3$, 298 K) of **3**.

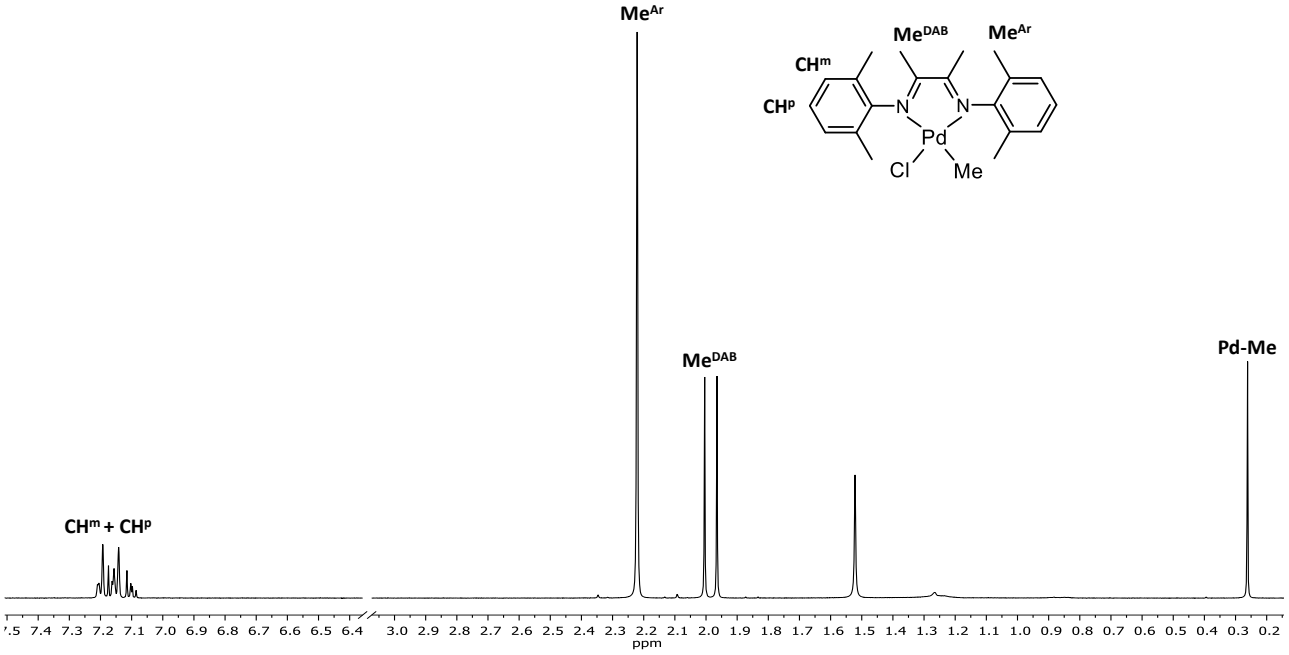


Figure S4 ^{1}H NMR spectrum (CD_2Cl_2, 298 K) of **Pd1a**.

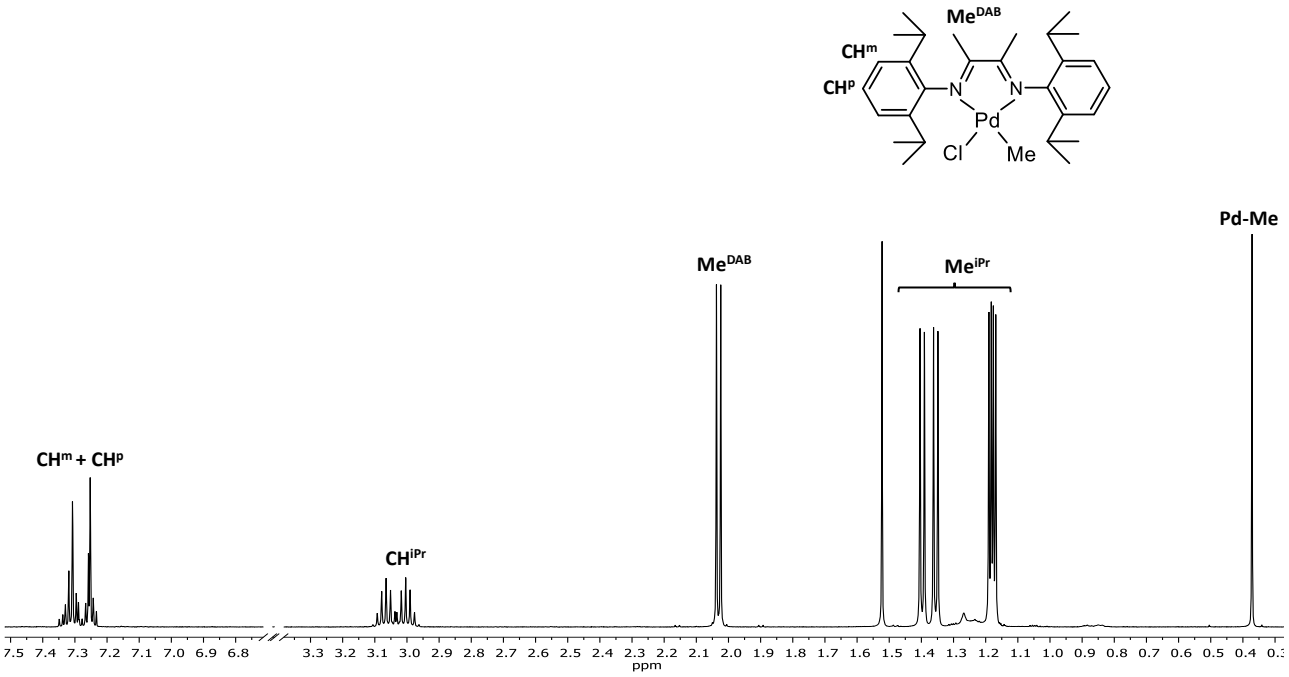


Figure S5 ^{1}H NMR spectrum (CD_2Cl_2, 298 K) of **Pd2a**.

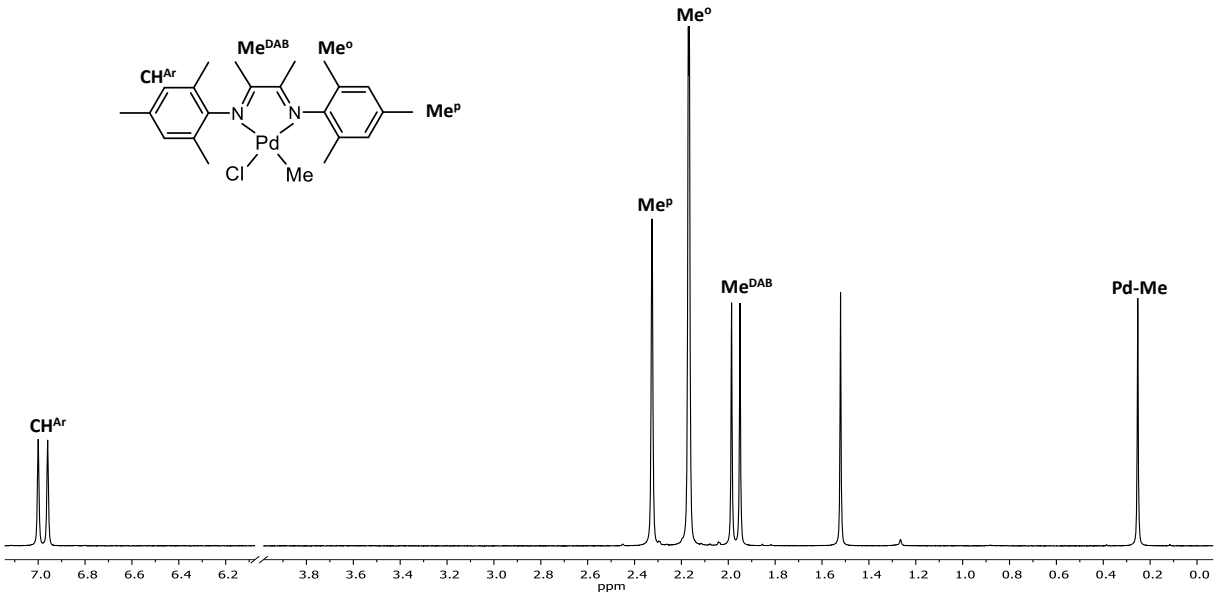


Figure S6 ^{1}H NMR spectrum (CD_2Cl_2, 298 K) of **Pd3a**.

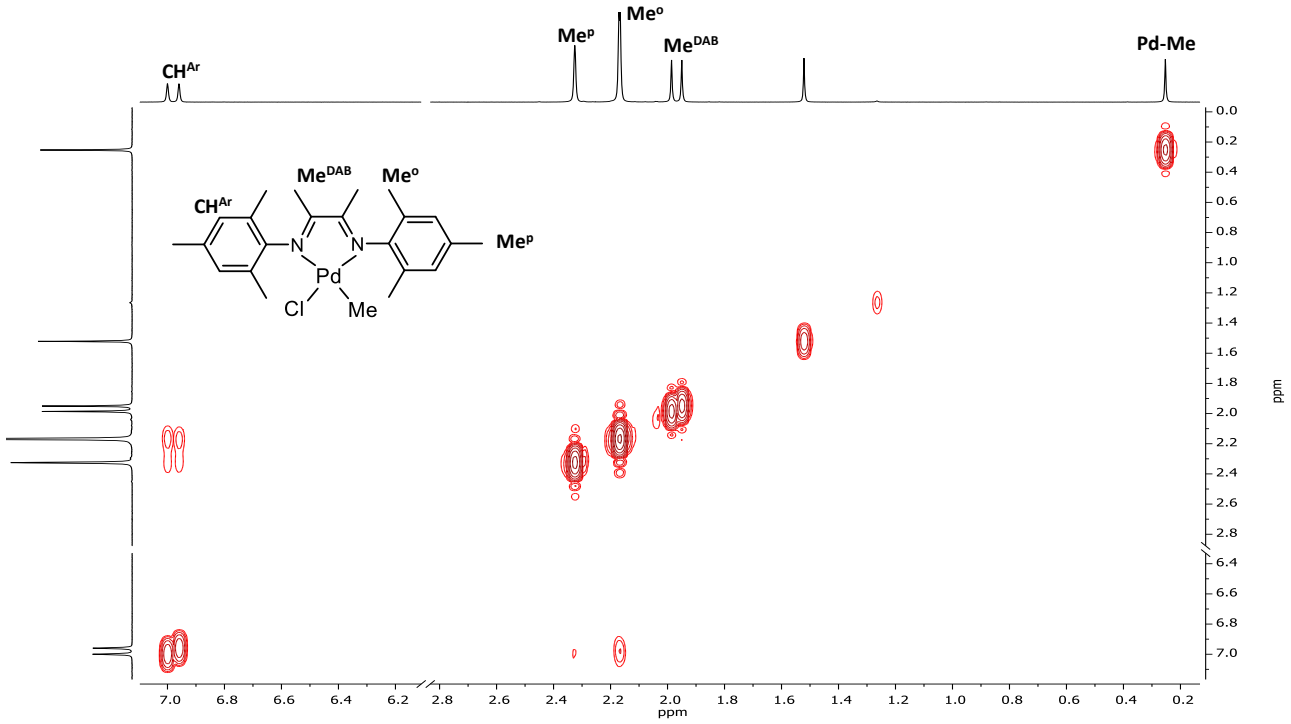


Figure S7 ^{1}H,^{1}H COSY NMR spectrum (CD_2Cl_2, 298 K) of **Pd3a**.

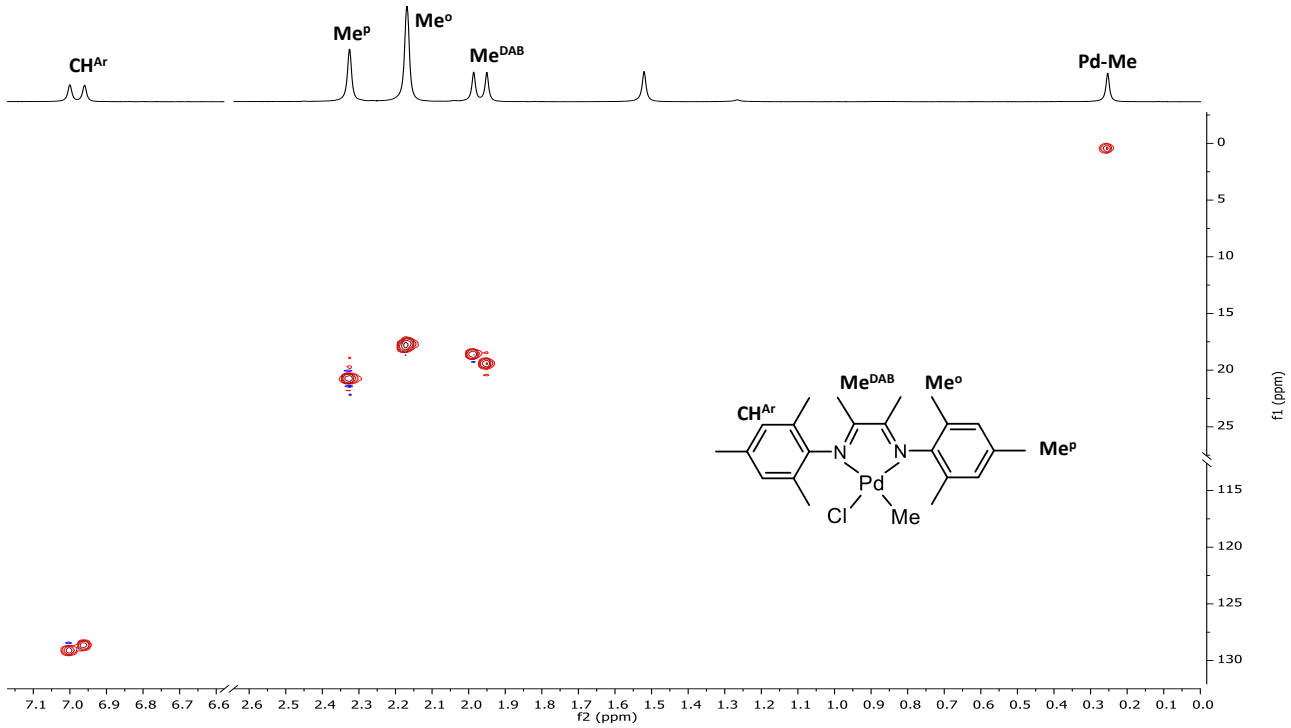


Figure S8 ^{1}H,^{13}C HSQC NMR spectrum (CD_2Cl_2, 298 K) of **Pd3a**.

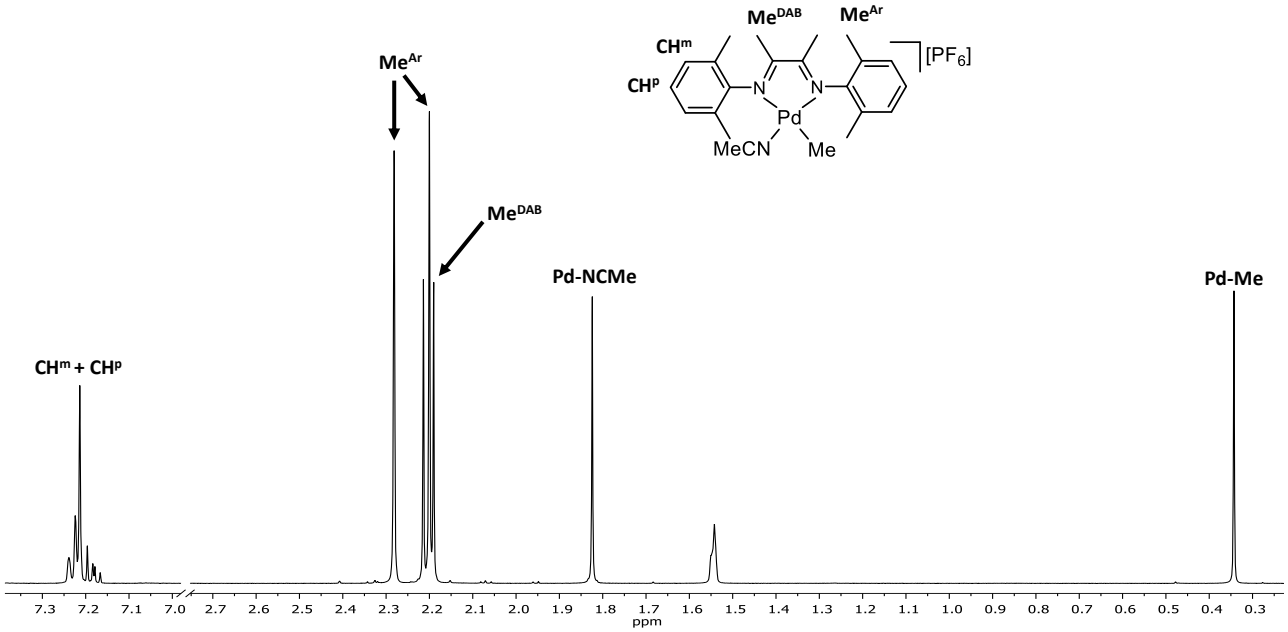


Figure S9 ^{1}H NMR spectrum (CD_2Cl_2, 298 K) of **Pd1b**.

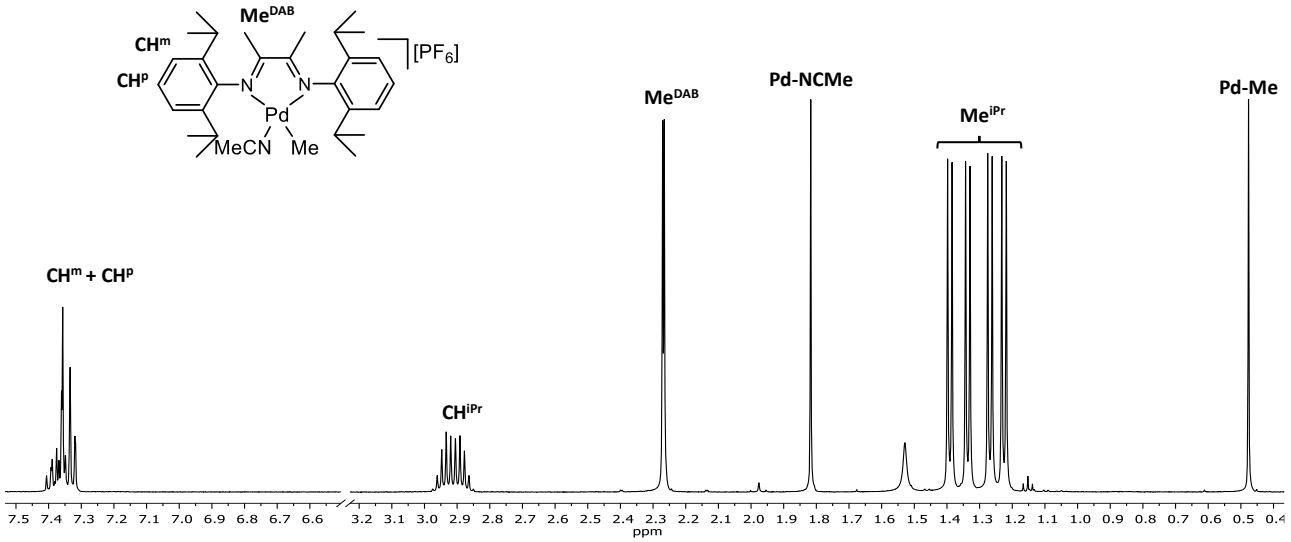


Figure S10 ^{1}H NMR spectrum (CD_2Cl_2, 298 K) of **Pd2b**.

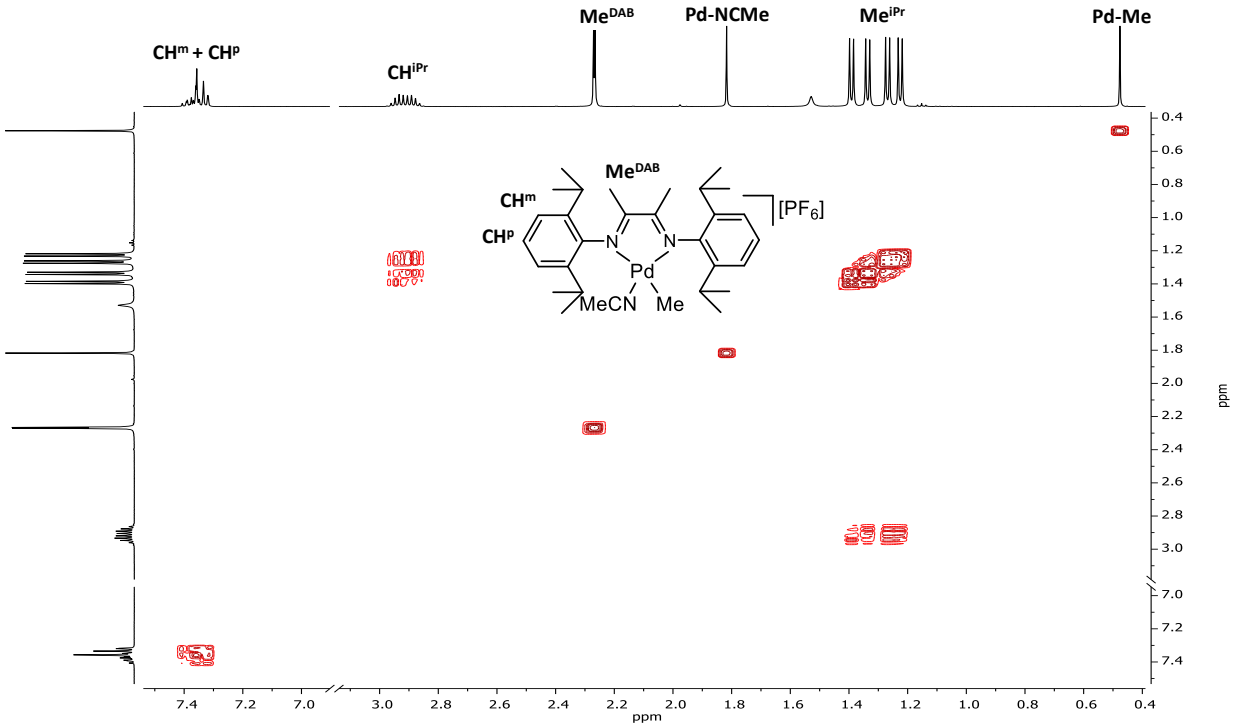


Figure S11 $^{1}H,^{1}H$ COSY NMR spectrum (CD_2Cl_2, 298 K) of **Pd2b**.

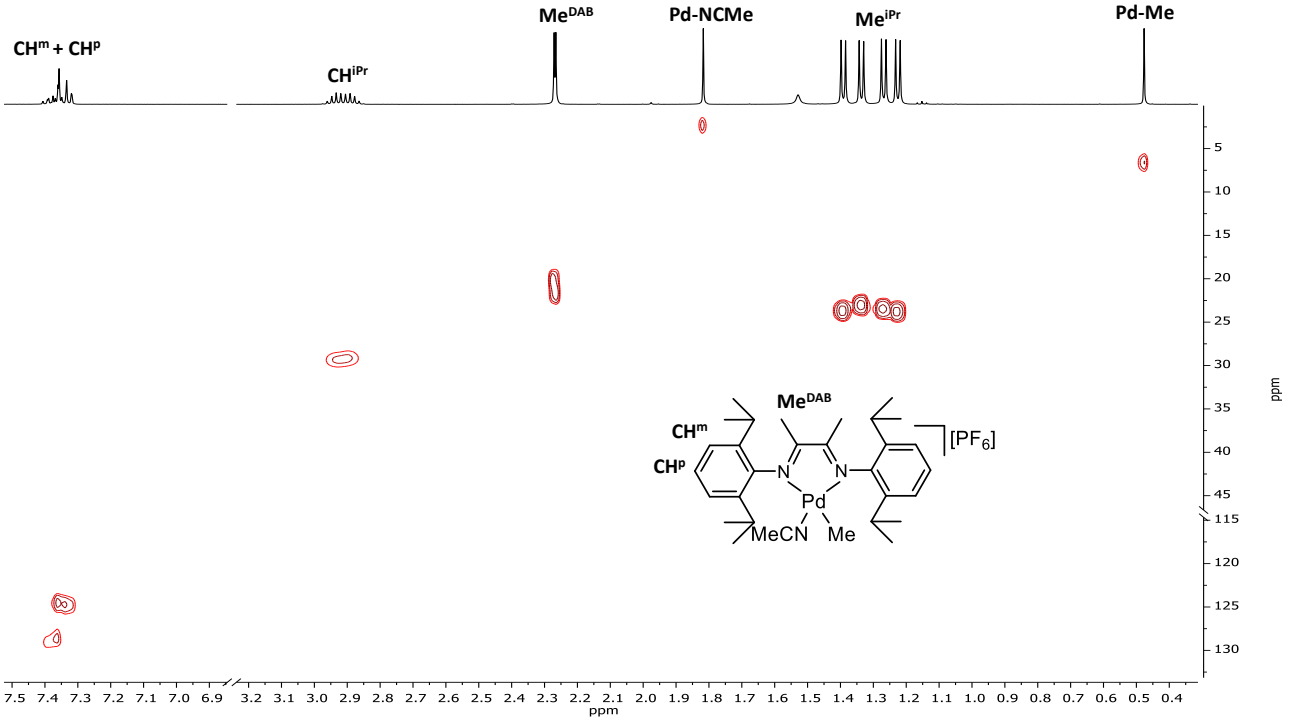


Figure S12 $^{1}H,^{13}C$ HSQC NMR spectrum (CD_2Cl_2, 298 K) of **Pd2b**.

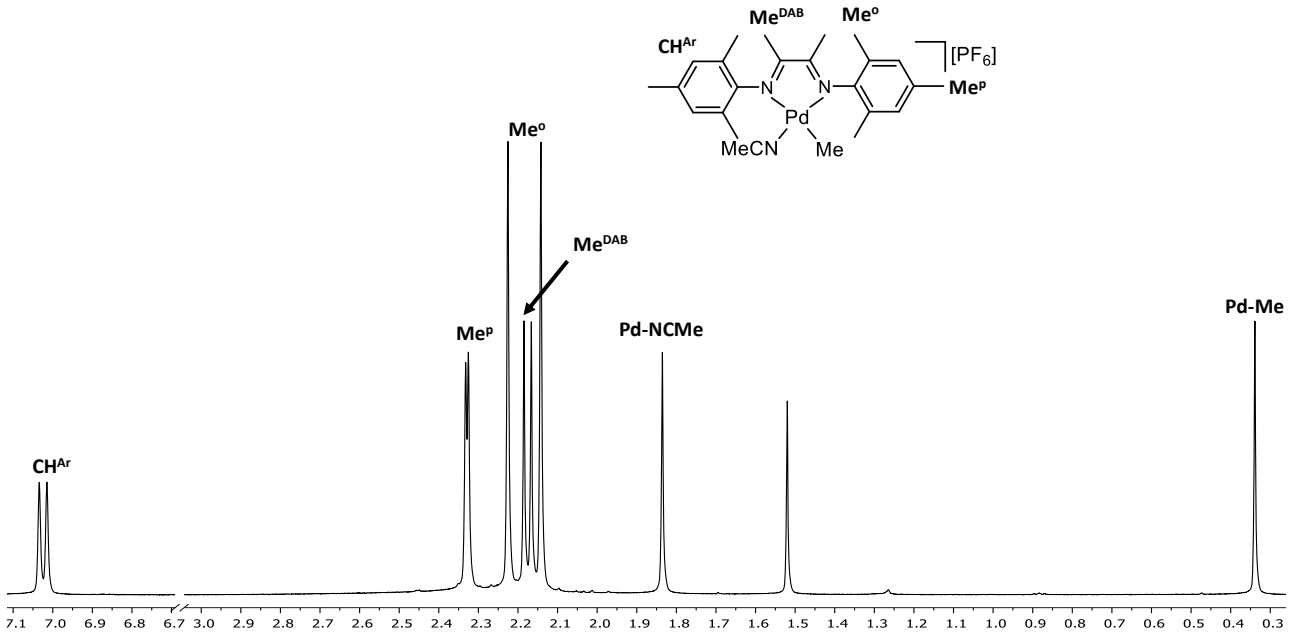


Figure S13 ^{1}H NMR spectrum (CD_2Cl_2, 298 K) of **Pd3b**.

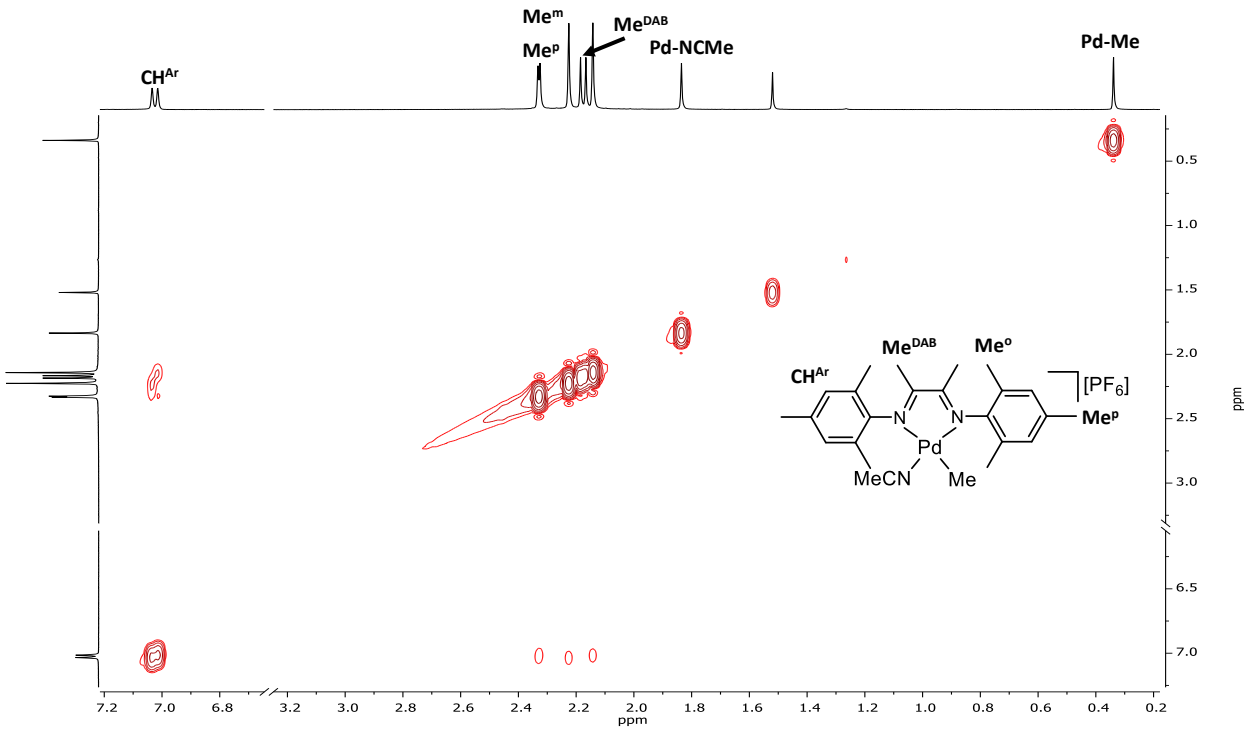


Figure S14 ^{1}H,^{1}H COSY NMR spectrum (CD_2Cl_2, 298 K) of **Pd3b**.

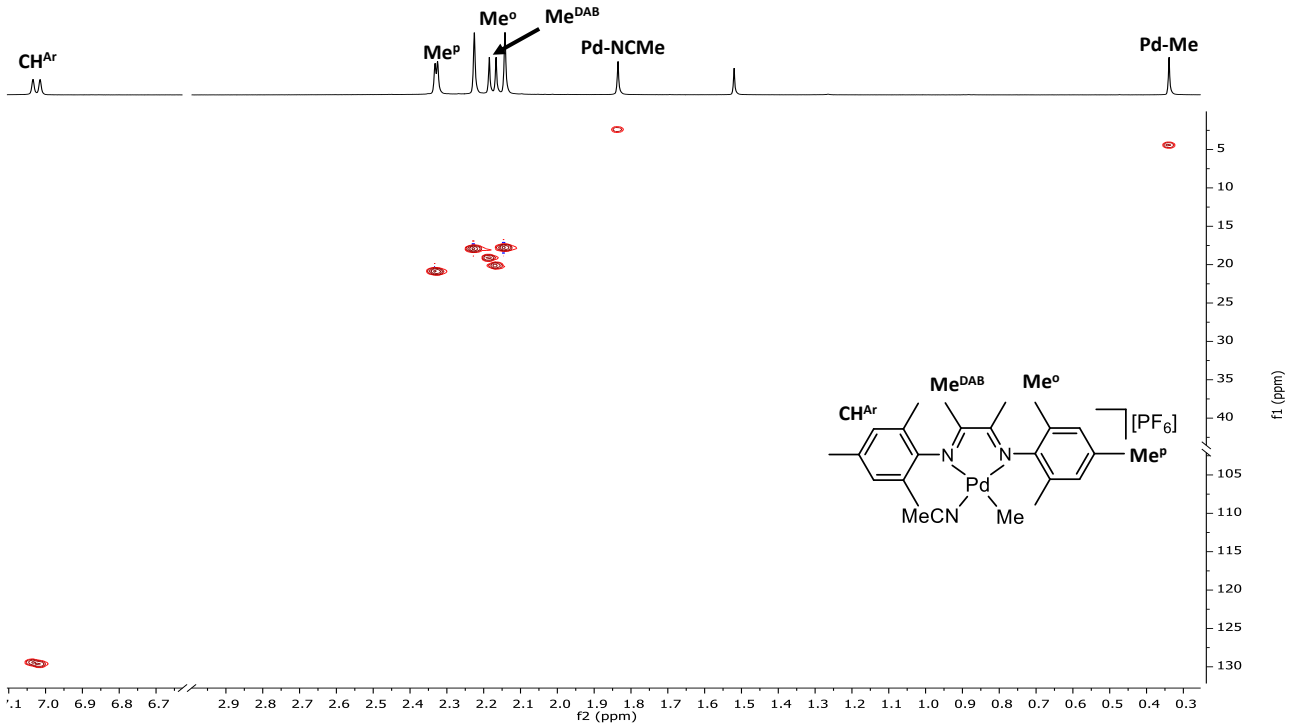


Figure S15 $^{1}H,^{13}C$ HSQC NMR spectrum (CD_2Cl_2, 298 K) of **Pd3b**.

Ethylene/methyl acrylate copolymerization experiments

Table S1 Ethylene/methyl acrylate copolymerization: effect of solvent composition.[a] Precatalyst: [Pd(**1**)(Me)(MeCN)][PF_6] **Pd1b**.

entry	χ_{TFE}[b]	yield [g]	kg CP/mol Pd[c]	mol % MA[d]	M(MA):T(MA)[e]	M_n[f] [kDa] (M_w/M_n)	Bd[g]
1[h]	0.00	1.04	49.4	4.8	12:88	5.0 (2.00)	93
2	0.09	2.42	114.9	3.0	14:85	16.6 (1.69)	99
3	0.17	2.97	141.8	2.4	15:85	18.2 (1.72)	101
4	0.26	2.67	126.9	2.8	13:87	18.2 (1.70)	102
5	0.35	1.89	89.7	4.1	10:90	18.8 (1.53)	99
6	0.47	2.86	136.1	2.3	18:82	18.5 (1.54)	104
7	0.59	2.41	115.1	2.4	21:79	19.3 (1.60)	103
8	0.79	1.94	92.3	2.9	26:74	23.2 (1.70)	100
9	0.89	1.61	76.6	2.8	28:72	24.3 (1.75)	100
10[h]	1.00	1.02	48.8	4.0	40:60	23.4 (1.19)	93

[a]Reaction conditions: $n_{Pd} = 2.1 \cdot 10^{-5}$ mol, $V_{sol} = 21$ mL, $V_{MA} = 2.26$ mL, [MA]/[Pd] = 1188, T = 308 K, $P_E = 5$ bar, t = 6 h; [b]$\chi_{TFE} = n_{TFE}/(n_{DCM} + n_{TFE})$; [c]productivity as kg CP/mol Pd = kilograms of copolymer per mol of palladium; [d]calculated by ^{1}H NMR spectroscopy on isolated product; [e]calculated by ^{13}C NMR spectroscopy on isolated product; [f]molecular weight (M_n and M_w) and molecular weight distribution (M_w/M_n) were measured by GPC; [g]Bd = branching degree as branches per 1000 carbon atoms, calculated by ^{1}H NMR spectroscopy on isolated product; [h]from reference 4.

Table S2 Ethylene/methyl acrylate copolymerization: effect of solvent composition.[a]

Precatalyst: [Pd(**3**)(Me)(MeCN)][PF_6] **Pd3b**.

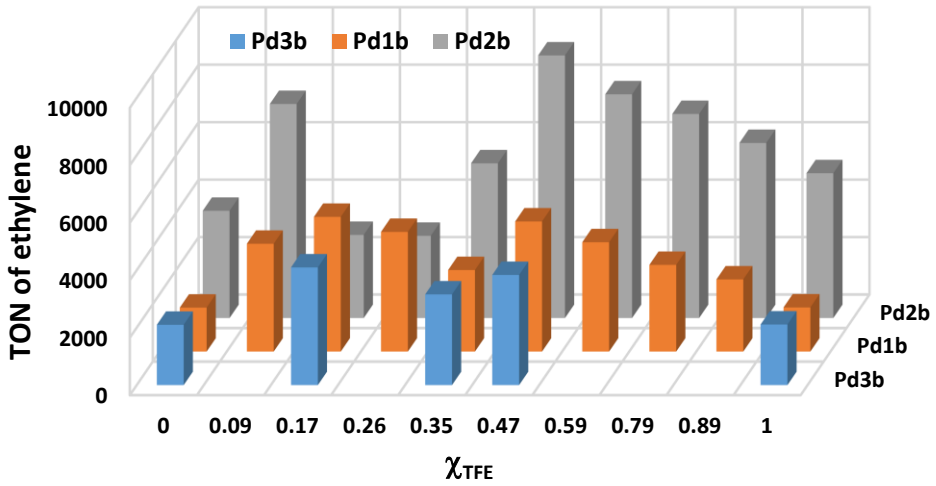
entry	χ_{TFE}[b]	yield [g]	kg CP/mol Pd[c]	mol % MA[d]	M(MA):T(MA)[e]	M_n[f] [kDa] (M_w/M_n)	Bd[g]
1	0.00	1.39	66.0	3.9	22:78	14.1 (1.68)	91
2	0.17	2.61	124.3	2.6	21:79	19.5 (1.80)	100
3	0.35	2.06	98.3	3.4	15:85	19.8 (1.83)	99
4	0.47	2.45	116.9	2.7	24:76	20.5 (1.87)	100
5	1.00	1.38	50.1	3.5	49:51	27.5 (1.98)	100

[a]Reaction conditions: $n_{Pd} = 2.1 \cdot 10^{-5}$ mol, $V_{sol} = 21$ mL, $V_{MA} = 2.26$ mL, [MA]/[Pd] = 1188, T = 308 K, $P_E = 5$ bar, t = 6 h; [b]$\chi_{TFE} = n_{TFE}/(n_{DCM} + n_{TFE})$; [c]productivity as kg CP/mol Pd = kilograms of copolymer per mol of palladium; [d]calculated by ^{1}H NMR spectroscopy on isolated product; [e]calculated by ^{13}C NMR spectroscopy on isolated product; [f]molecular weight (M_n and M_w) and molecular weight distribution (M_w/M_n) were measured by GPC; [g]Bd = branching degree as branches per 1000 carbon atoms, calculated by ^{1}H NMR spectroscopy on isolated product.

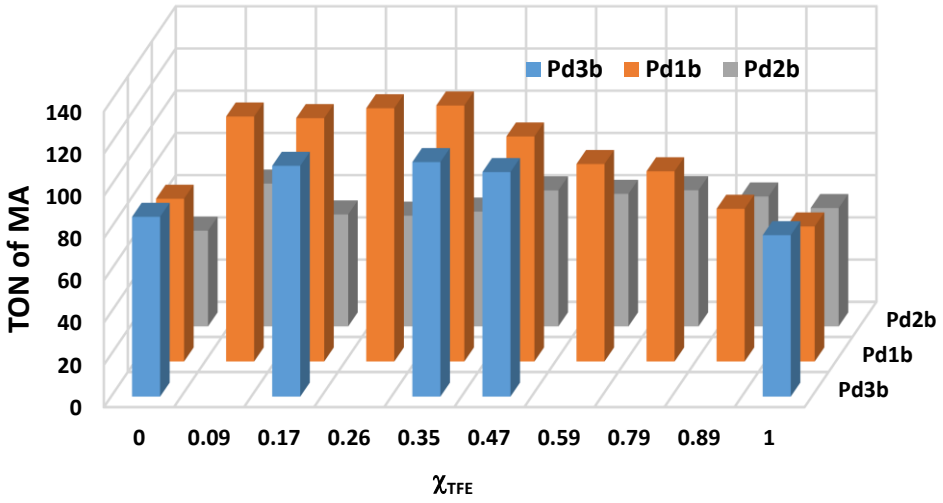
Table S3 Ethylene/methyl acrylate copolymerization: effect of solvent composition.[a] Precatalyst: [Pd(**2**)(Me)(MeCN)][PF_6] **Pd2b**.

entry	χ_{TFE}[b]	yield [g]	kg CP/mol Pd[c]	mol % MA[d]	M(MA):T(MA)[e]	M_n[f] [kDa] (M_w/M_n)	Bd[g]
1	0.00	2.28	108.2	1.2	13:87	2.9 (1.88)	89
2	0.09	4.51	215.4	0.9	12:88	18.4 (1.67)	95
3	0.17	1.80	85.9	1.8	6:94	38.8 (1.38)	93
4	0.26	1.78	85.1	1.8	7:93	39.3 (1.80)	93
5	0.35	3.27	155.8	1.0	12:88	40.0 (1.56)	95
6	0.47	5.50	262.3	0.7	17:83	43.5 (1.51)	96
7	0.59	4.70	224.4	0.8	17:83	71.4 (1.66)	96
8	0.79	4.30	204.5	0.9	24:76	105.2 (1.96)	97
9	0.89	3.70	175.7	1.0	21:79	102.4 (1.87)	98
10	1.00	3.07	146.2	1.1	28:72	101.2 (1.72)	100

[a]Reaction conditions: $n_{Pd} = 21 \cdot 10^{-5}$ mol, $V_{sol} = 21$ mL, $V_{MA} = 2.26$ mL, [MA]/[Pd] = 1188, T = 308 K, $P_E = 5$ bar, t = 6 h; [b]$\chi_{TFE} = n_{TFE}/(n_{DCM} + n_{TFE})$; [c]productivity as kg CP/mol Pd = kilograms of copolymer per mol of palladium; [d]calculated by ^{1}H NMR spectroscopy on isolated product; [e]calculated by ^{13}C NMR spectroscopy on isolated product; [f]molecular weight (M_n and M_w) and molecular weight distribution (M_w/M_n) were measured by GPC; [g]Bd = branching degree as branches per 1000 carbon atoms, calculated by ^{1}H NMR spectroscopy on isolated product.



a)



b)

Figure S16 Ethylene/methyl acrylate copolymerization: effect of the reaction medium composition on TON (Turnover Number = mol of comonomer converted per mol of palladium) of: a) ethylene; b) methyl acrylate. Reaction conditions: see Table S1.

GPC characterization of the synthesized E/MA copolymers

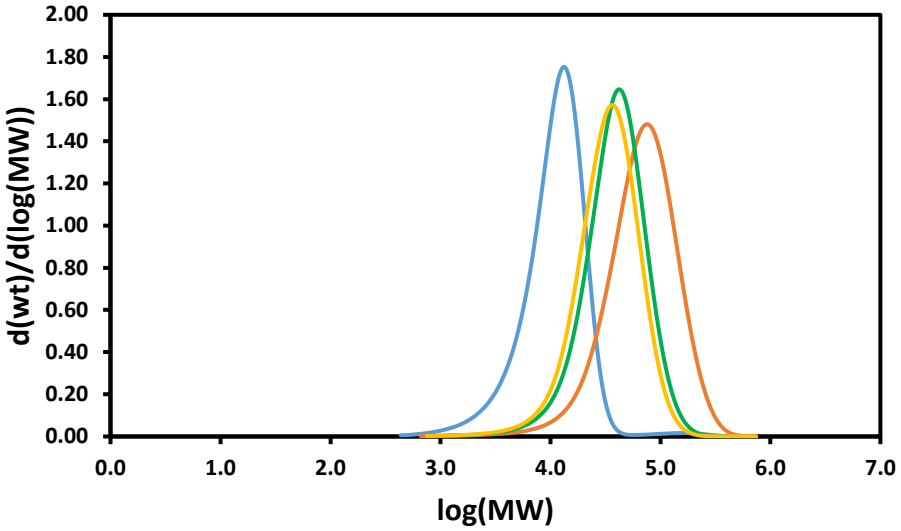


Figure S17 GPC curves of the ethylene/methyl acrylate copolymers obtained with **Pd1b** in: neat DCM (blue trace), neat TFE (orange trace), DCM/TFE mixture χ_{TFE} = 0.17 (green trace), DCM/TFE mixture χ_{TFE} = 0.47 (yellow trace). Reaction conditions: Table S1.

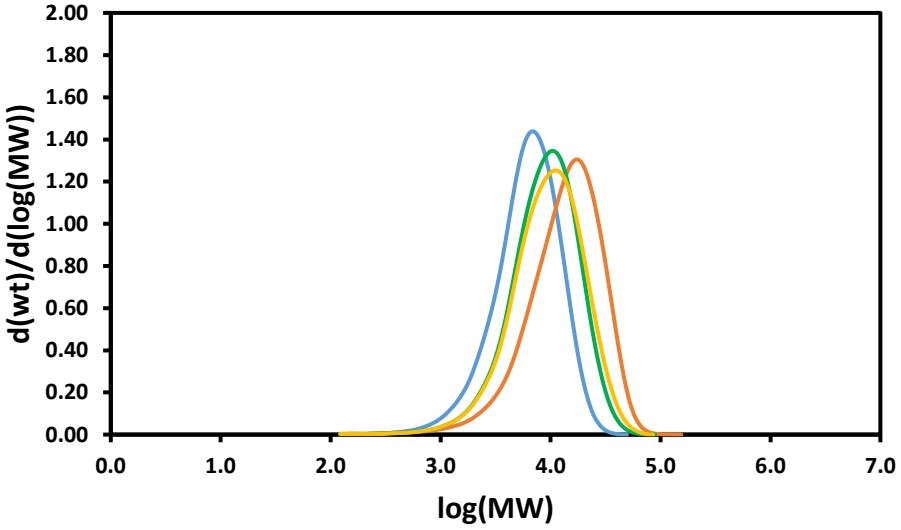


Figure S18 GPC curves of the ethylene/methyl acrylate copolymers obtained with **Pd3b** in: neat DCM (blue trace), neat TFE (orange trace), DCM/TFE mixture χ_{TFE} = 0.17 (green trace), DCM/TFE mixture χ_{TFE} = 0.47 (yellow trace). Reaction conditions: Table S2.

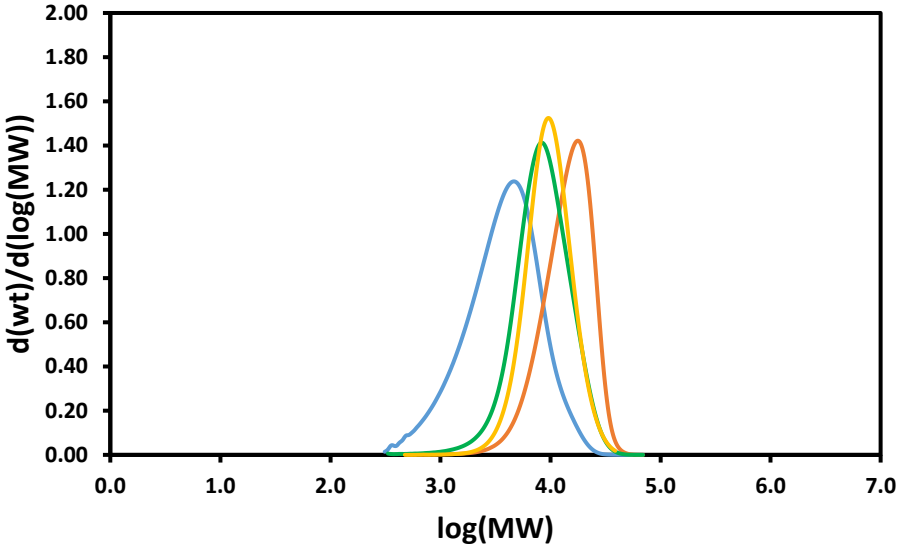


Figure S19 GPC curves of the ethylene/methyl acrylate copolymers obtained with **Pd2b** in: neat DCM (blue trace), neat TFE (orange trace), DCM/TFE mixture χ_{TFE} = 0.09 (green trace), DCM/TFE mixture χ_{TFE} = 0.47 (yellow trace). Reaction conditions: Table S3.

NMR characterization of the synthesized E/MA copolymers

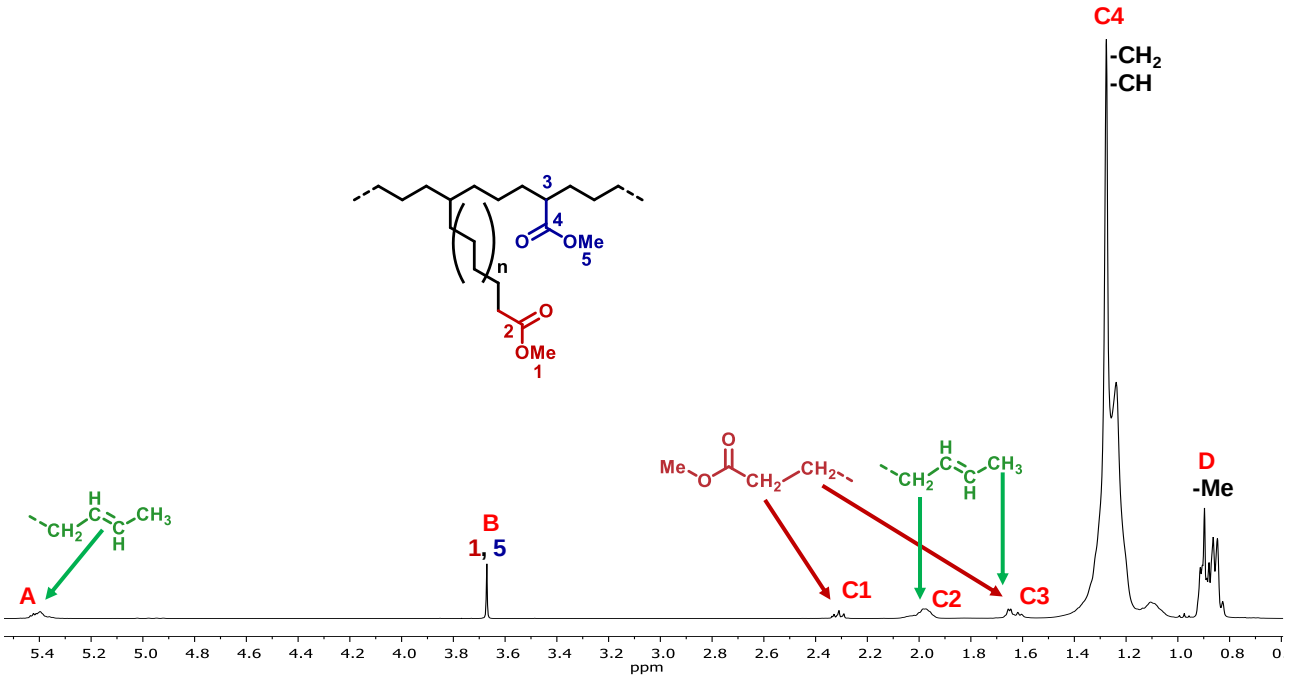


Figure S20 ^{1}H NMR spectrum ($CDCl_3$, 298 K) of ethylene/methyl acrylate copolymer obtained with **Pd2b** in neat DCM (Table S3, entry 1).

Formulas used to calculate the amount of inserted MA and branching degree.

$$\%\,\mathrm{MA} = \frac{\frac{1}{3}B}{[\frac{1}{4}(A + C + D - B) + \frac{1}{3}B]} \cdot 100$$

$$\mathrm{C} = \mathrm{C1} + \mathrm{C2} + \mathrm{C3} + \mathrm{C4}$$

$$\frac{\mathrm{Branches}}{1000\mathrm{C}} = \frac{\mathrm{I_{CH}} \times 1000}{\frac{\mathrm{D}}{3} + \frac{\mathrm{C4}}{2} + \mathrm{I_{CH}} + \frac{\mathrm{C2}}{2} + \mathrm{A}}$$

$$\mathrm{I_{CH}} = \frac{\mathrm{D} - \frac{3\mathrm{A}}{2}}{3}$$

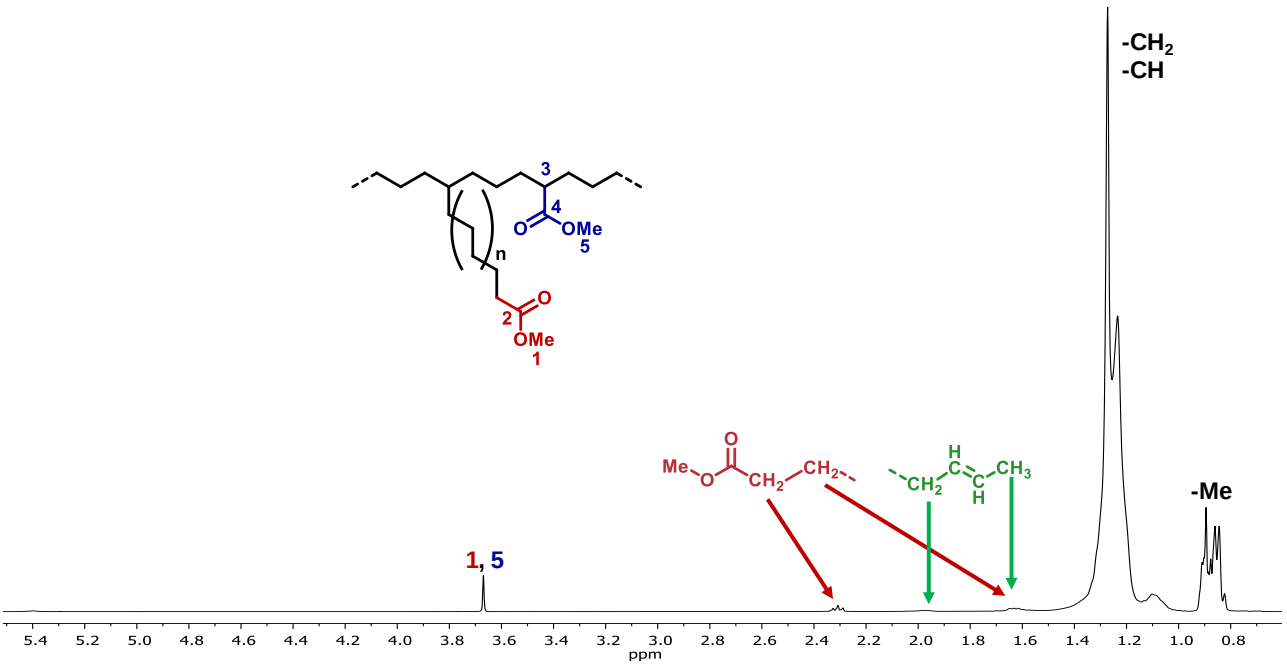


Figure S21 ^{1}H NMR spectrum ($CDCl_3$, 298 K) of ethylene/methyl acrylate copolymer obtained with **Pd2b** in DCM/TFE mixture of χ_{TFE} = 0.09 (Table S3, entry 2).

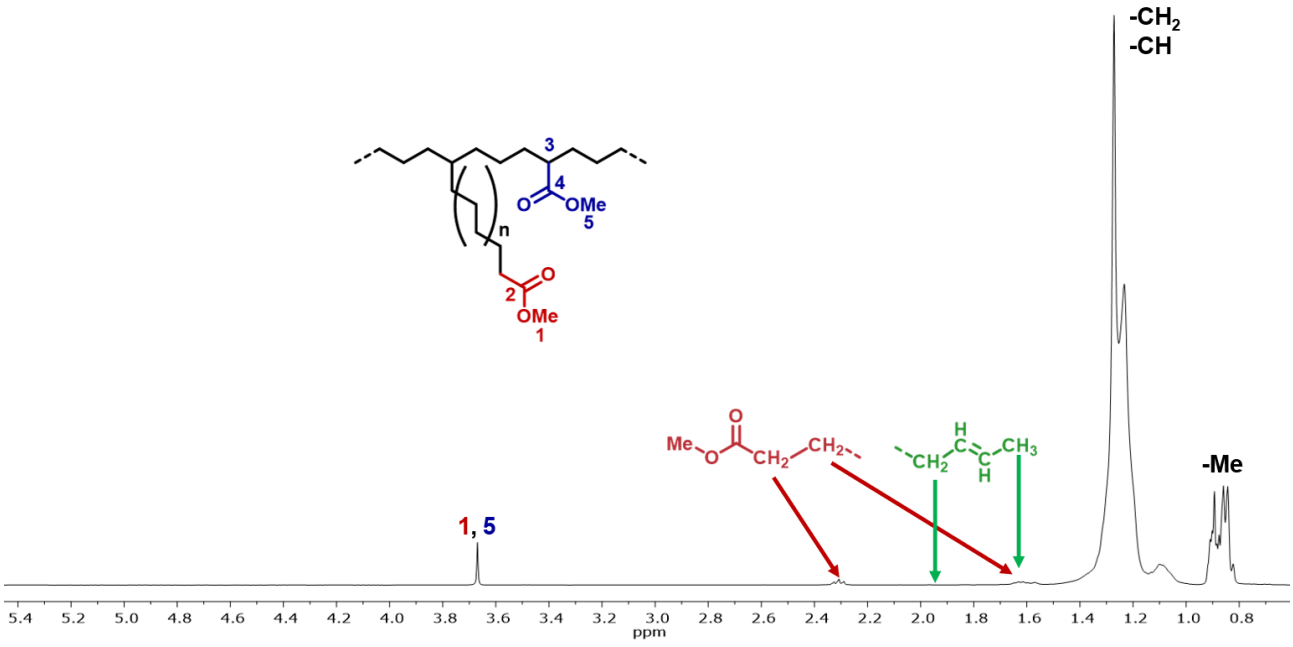


Figure S22 ^{1}H NMR spectrum ($CDCl_3$, 298 K) of ethylene/methyl acrylate copolymer obtained with **Pd2b** in neat TFE (Table S3, entry 10).

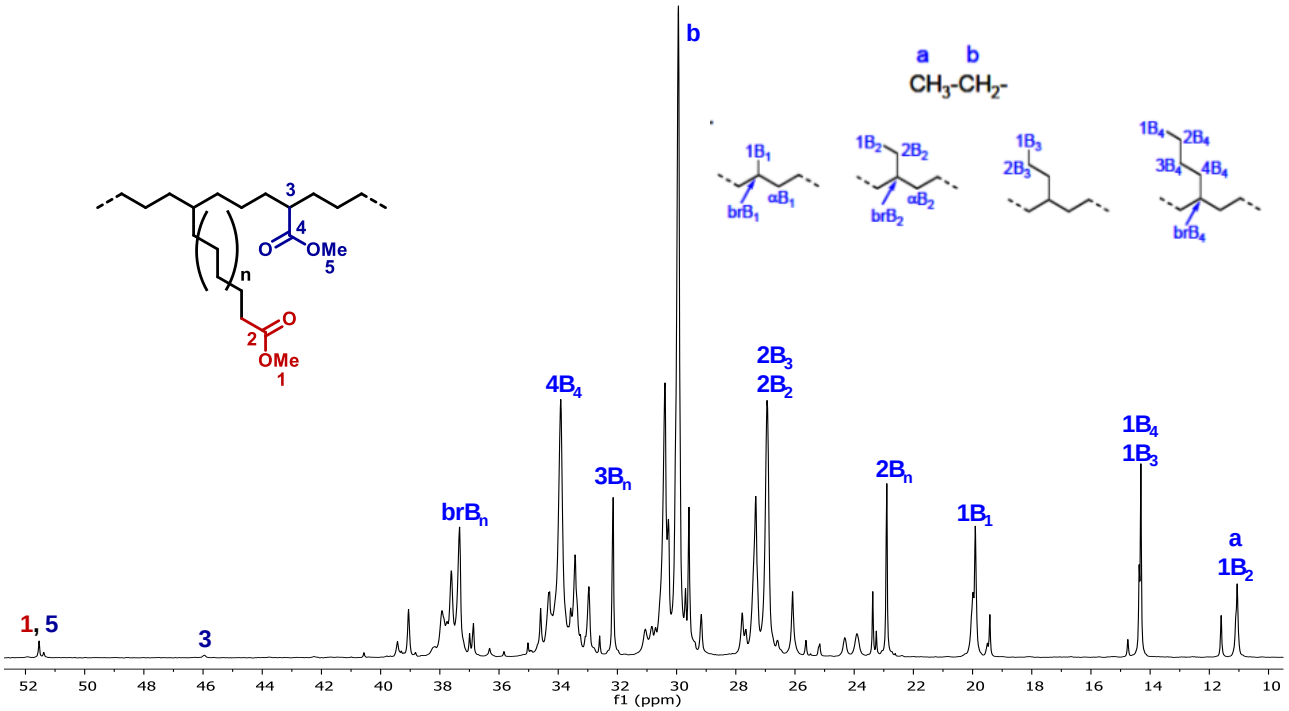


Figure S23 ^{13}C NMR spectrum ($CDCl_3$, 298 K) of ethylene/methyl acrylate copolymer obtained with **Pd2b** in neat TFE (Table S3, entry 10). Aliphatic region.

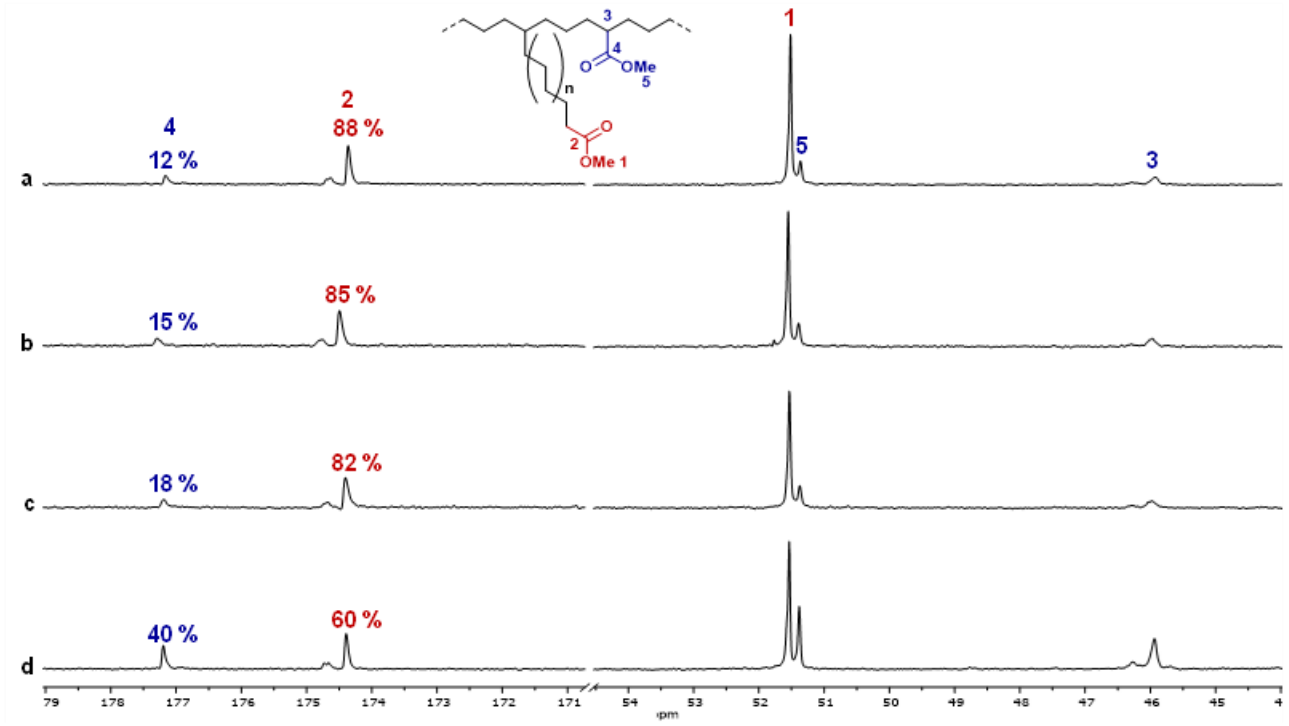


Figure S24 ^{13}C NMR spectra ($CDCl_3$, 298 K) of the macromolecules obtained with **Pd1b** in different reaction media: a) χ_{TFE} = 0.00, b) χ_{TFE} = 0.17, c) χ_{TFE} = 0.47, d) χ_{TFE} = 1.00 (Figure 1b; Table S1; carbonyl and aliphatic regions are not in scale).

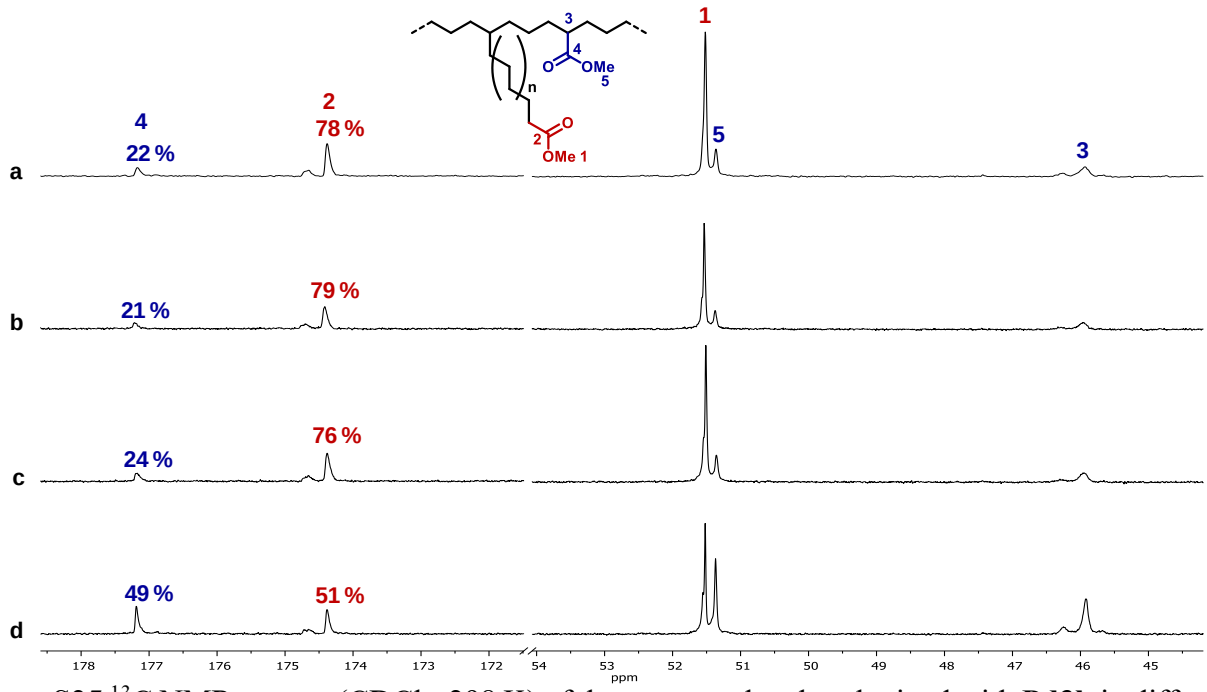


Figure S25 ^{13}C NMR spectra ($CDCl_3$, 298 K) of the macromolecules obtained with **Pd3b** in different reaction media: a) χ_{TFE} = 0.00, b) χ_{TFE} = 0.17, c) χ_{TFE} = 0.47, d) χ_{TFE} = 1.00 (Figure 1b; Table S2; carbonyl and aliphatic regions are not in scale).

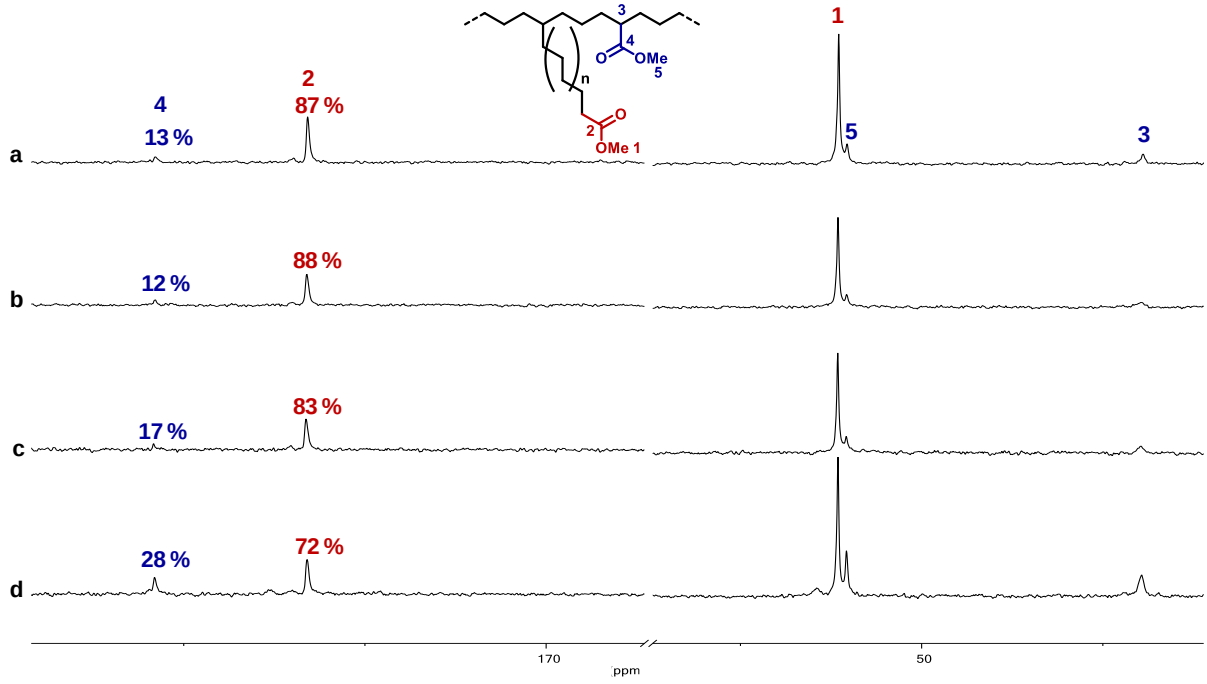


Figure S26 ^{13}C NMR spectra ($CDCl_3$, 298 K) of the macromolecules obtained with **Pd2b** in different reaction media: a) χ_{TFE} = 0.00, b) χ_{TFE} = 0.09, c) χ_{TFE} = 0.47, d) χ_{TFE} = 1.00 (Figure 1b; Table S3; carbonyl and aliphatic regions are not in scale).

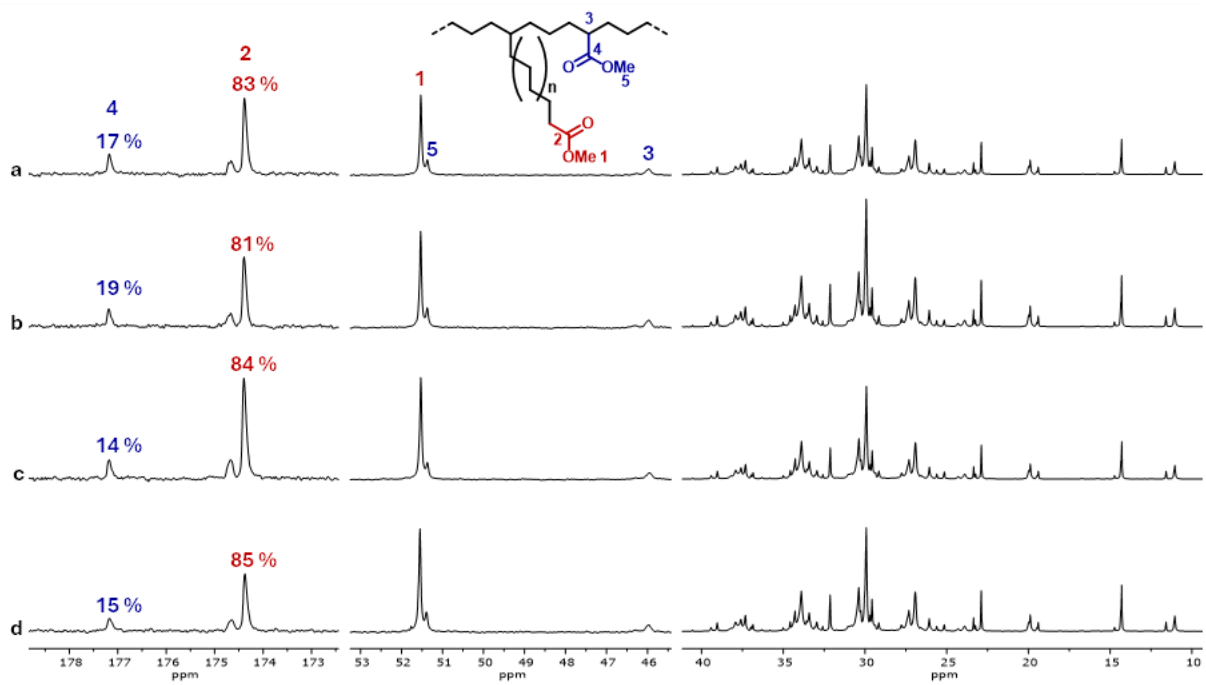


Figure S27 ^{13}C NMR spectra ($CDCl_3$, 298 K) of E/MA copolymers obtained with **Pd1b**. Catalyst recycle experiments of Table 1, entries: a) 1, b) 2, c) 3, d) Ref1 (carbonyl and aliphatic regions are not in scale).

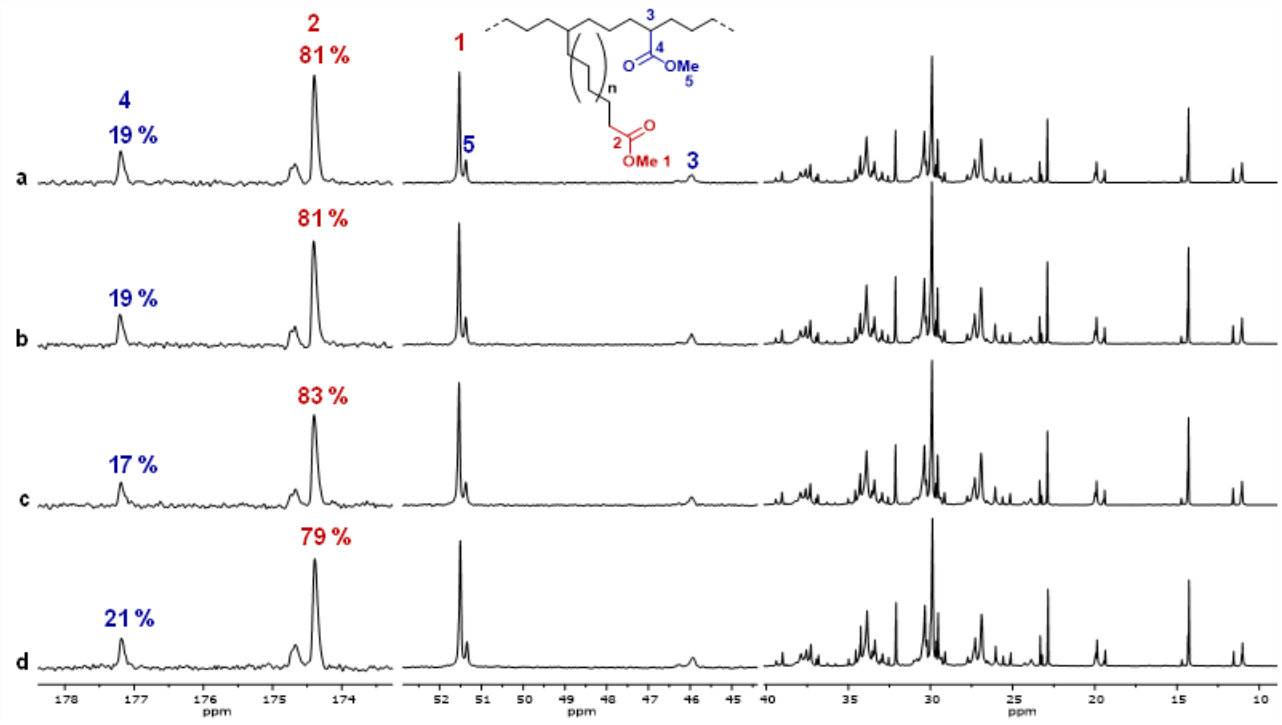


Figure S28 ^{13}C NMR spectra ($CDCl_3$, 298 K) of E/MA copolymers obtained with **Pd3b**. Catalyst recycle experiments of Table 1, entries: a) 4, b) 5, c) 6, d) Ref3 (carbonyl and aliphatic regions are not in scale).

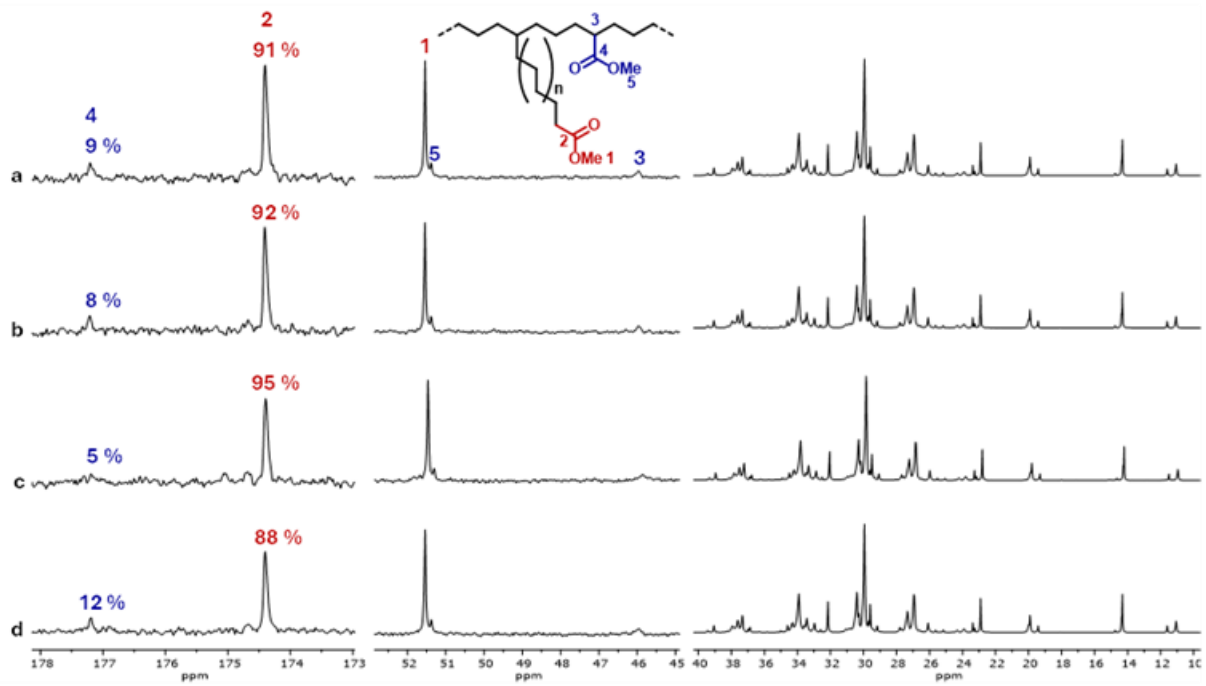


Figure S29 ^{13}C NMR spectra ($CDCl_3$, 298 K) of E/MA copolymers obtained with **Pd2b**. Catalyst recycle experiments of Table 1, entries: a) 7, b) 8, c) 9, d) Ref2 (carbonyl and aliphatic regions are not in scale).

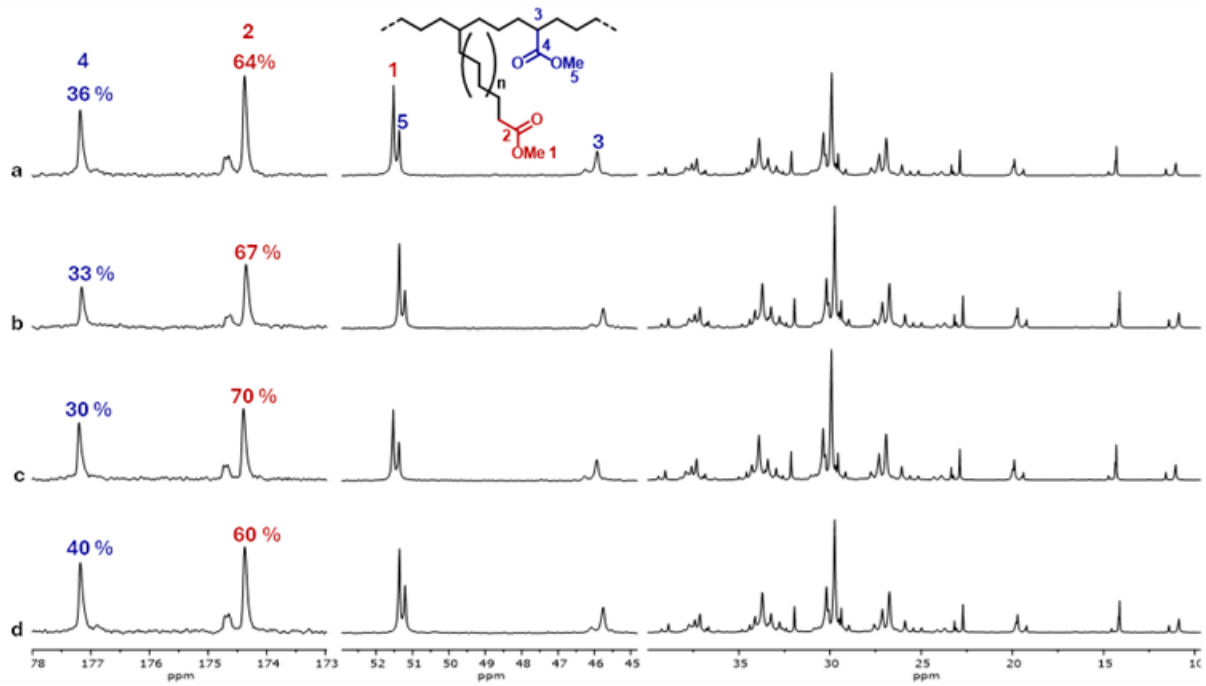
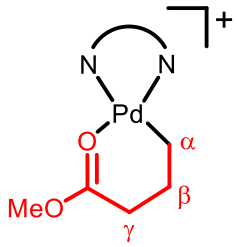
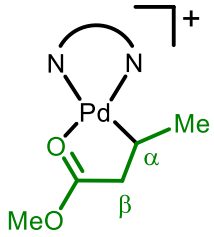


Figure S30 ^{13}C NMR spectra ($CDCl_3$, 298 K) of E/MA copolymers obtained with **Pd1b**. Catalyst recycle experiments of Table 2, entries: a) 1, b) 2, c) 3, d) Ref1 (carbonyl and aliphatic regions not in scale).

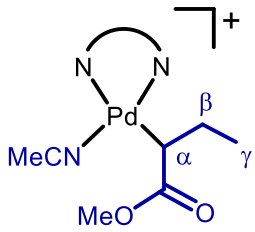
NMR assignments for the palladium organometallic compounds (MC6, MC5 and OC1) present in the solution of the reaction between Pd1b and MA carried out in the CD_2Cl_2/TFE-d_3 mixture of $\chi_{TFE} = 0.17$.



MC6: the signals of the CH_2 groups were assigned on the basis of $^1H,^1H$ COSY and $^1H,^{13}C$ HSQC spectra (Figures S33 and S34): in particular βCH_2 falls at 0.71 ppm, while αCH_2 and γCH_2 are at 1.29 and 2.41 ppm, respectively. The OCH_3 resonates at 3.12 ppm (based on $^1H,^1H$ COSY, Figure S33). Thanks to the correlation peaks in the $^1H,^{13}C$ HMBC spectrum (Figure S35) between the signal of the CH_2 group close to the carbonyl moiety and the OMe group of inserted MA, we established that the carbon atom of the C=O group resonates at 183.3 ppm.



MC5: the signal at 0.32 ppm was assigned to the methyl group. Starting from this peak, on the basis of $^1H,^1H$ COSY spectrum (Figure S33), it was possible to assign the signal at 1.41 ppm to αCH. The signal at 3.54 ppm, related to the methoxy group, was assigned based on on literature data.[4]



OC1: the signals of the CH_2 groups were assigned on the basis of $^1H,^1H$ COSY and $^1H,^{13}C$ HSQC spectra (Figures S33 and S34, respectively): γMe falls at 0.58 ppm, the signals related to βCH_2 are at 1.20 and 1.31 ppm, while the signal of αCH_2 is found at 1.84 ppm. The OCH_3 resonates at 3.52 ppm (based on $^1H,^1H$ COSY, Figure S33). Thanks to the correlation peaks in the $^1H,^{13}C$ HMBC spectrum (Figure S35), we established that the carbon atom of the C=O group resonates at 179.3 ppm. Finally, the singlet of coordinated acetonitrile (Pd-NCMe) is found at 1.76 ppm.

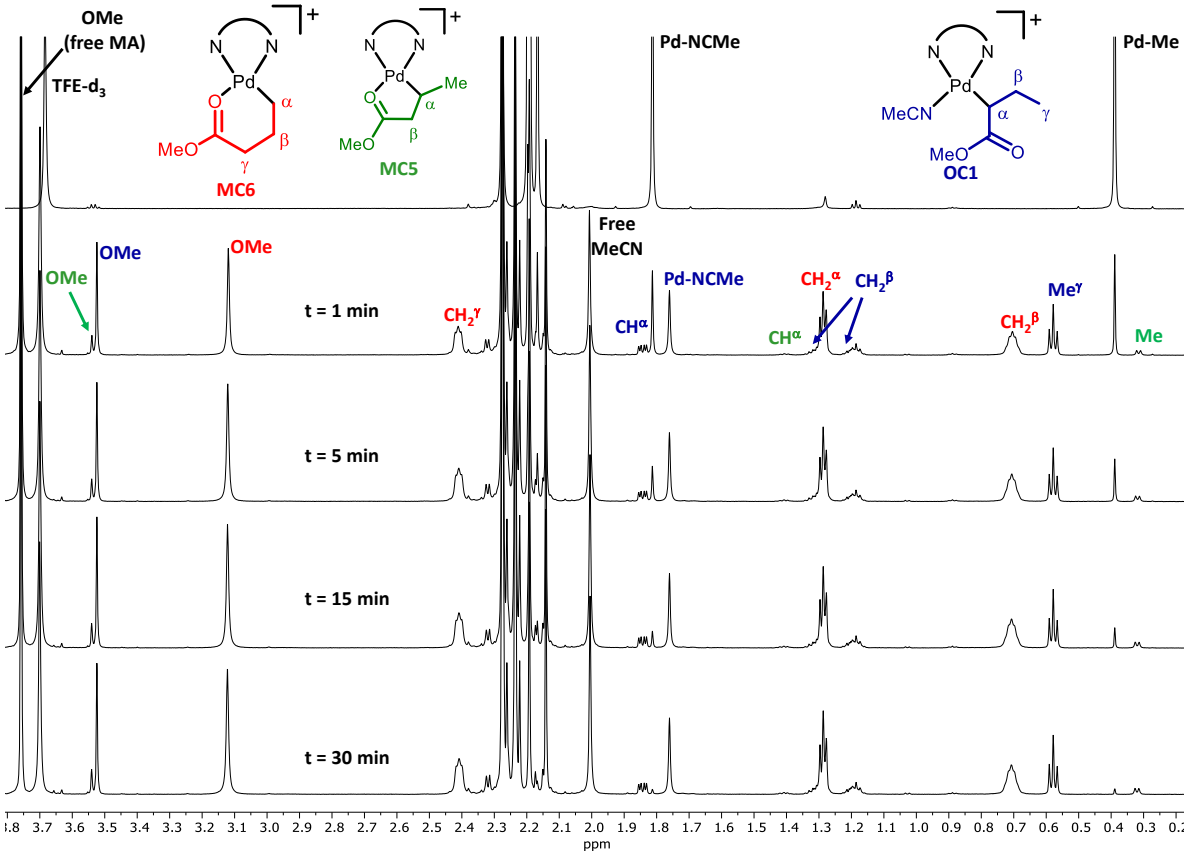


Figure S31. ^{1}H NMR spectra (CD_2Cl_2/TFE-d_3 mixture at χ_{TFE} = 0.17, T = 298 K) of **Pd1b** (top spectrum) and of **Pd1b** after the addition of methyl acrylate at different reaction times. Region of aliphatic protons.

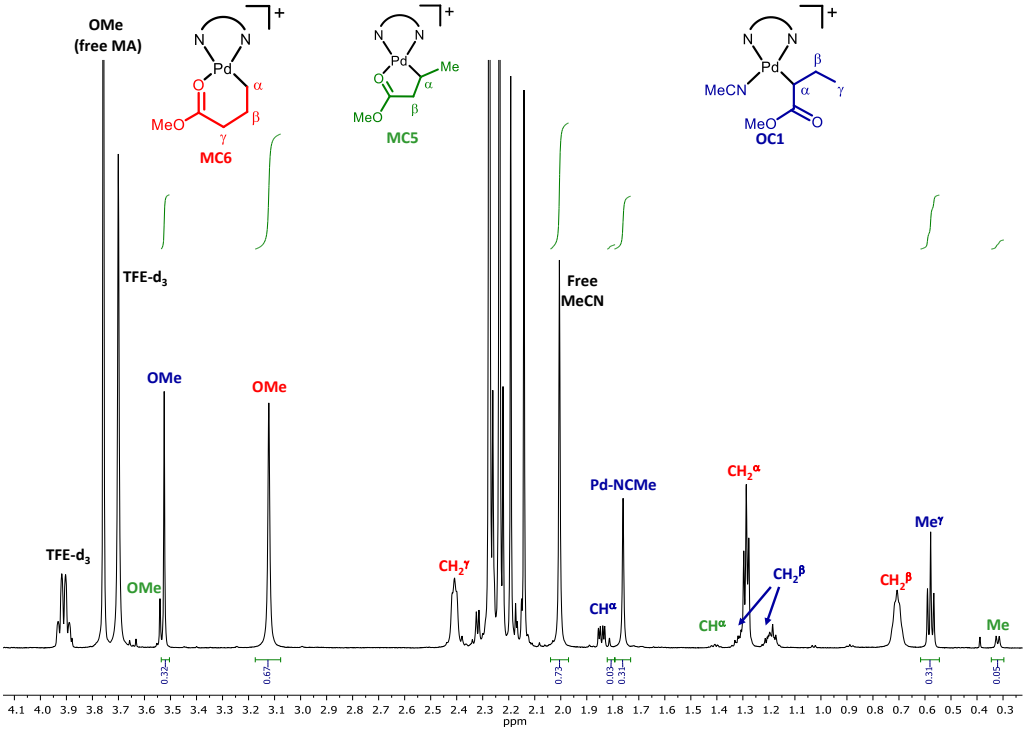


Figure S32. ^{1}H NMR spectrum (CD_2Cl_2/TFE-d_3 mixture at χ_{TFE} = 0.17, T = 298 K) of the reaction mixture of **Pd1b** with methyl acrylate at t = 30 min. Region of aliphatic protons.

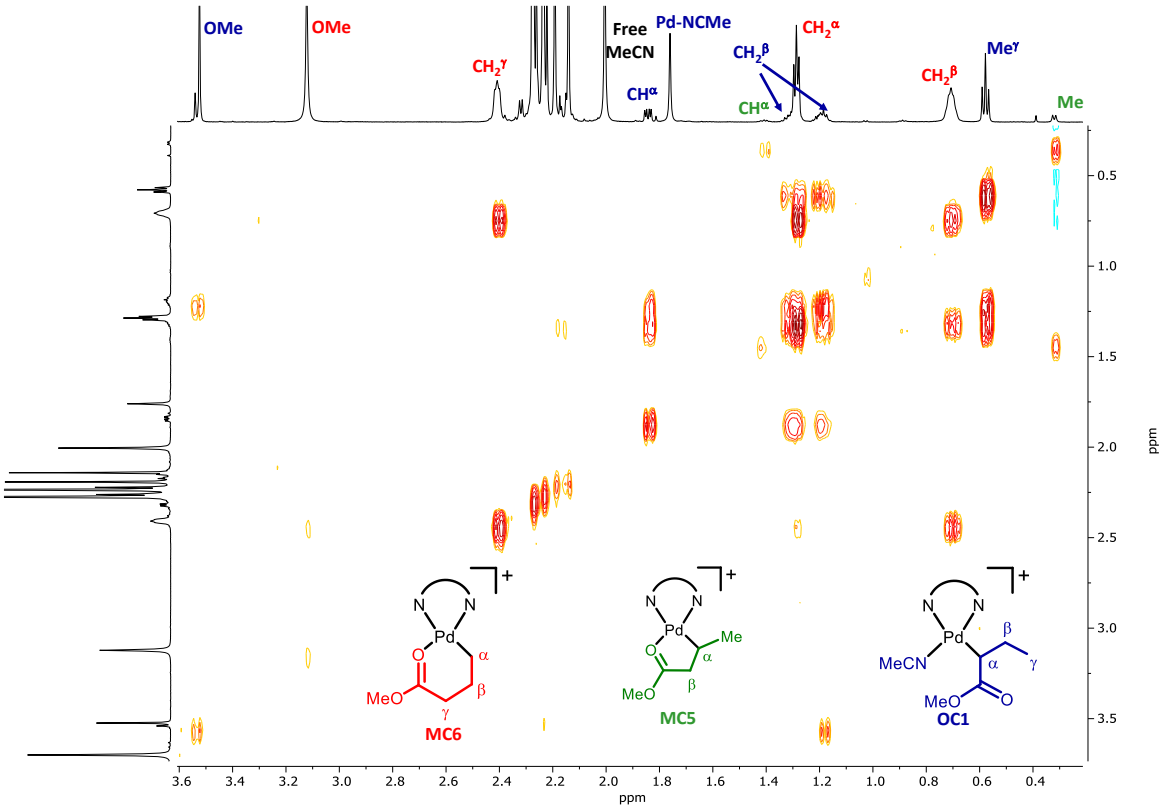


Figure S33. $^{1}H,^{1}H$ COSY spectrum (CD_2Cl_2/TFE-d_3 mixture at $\chi_{TFE} = 0.17$, T = 298 K) of the reaction mixture of **Pd1b** with methyl acrylate at t = 30 min. Region of aliphatic protons.

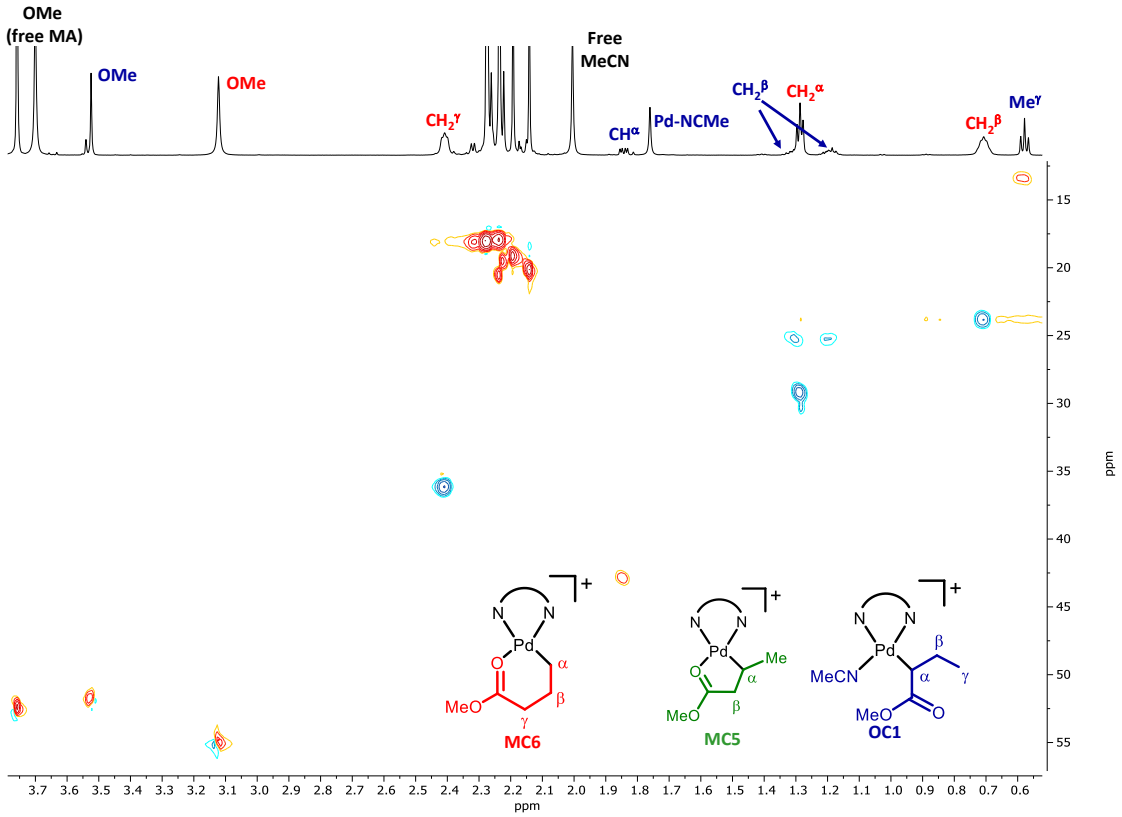


Figure S34. $^{1}H,^{13}C$ HSQC spectrum (CD_2Cl_2/TFE-d_3 mixture at χ_{TFE} = 0.17, T = 298 K) of the reaction mixture of **Pd1b** with methyl acrylate at t = 30 min. Red cross peaks are due to CH_3 and CH, light blue cross peaks are due to CH_2. Region of aliphatic protons.

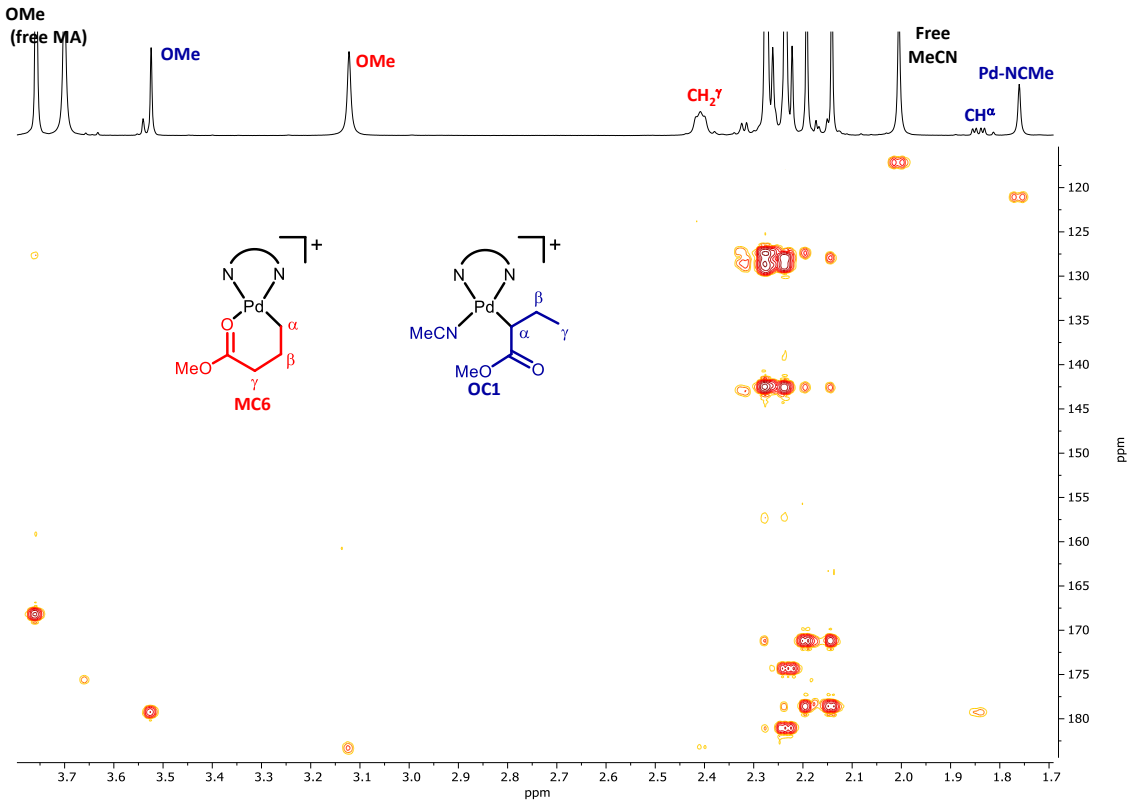


Figure S35. $^{1}H,^{13}C$ HMBC spectrum (CD_2Cl_2/TFE-d_3 mixture at χ_{TFE} = 0.17, T = 298 K) of the reaction mixture of **Pd1b** with methyl acrylate at t = 30 min. Region of aliphatic protons.

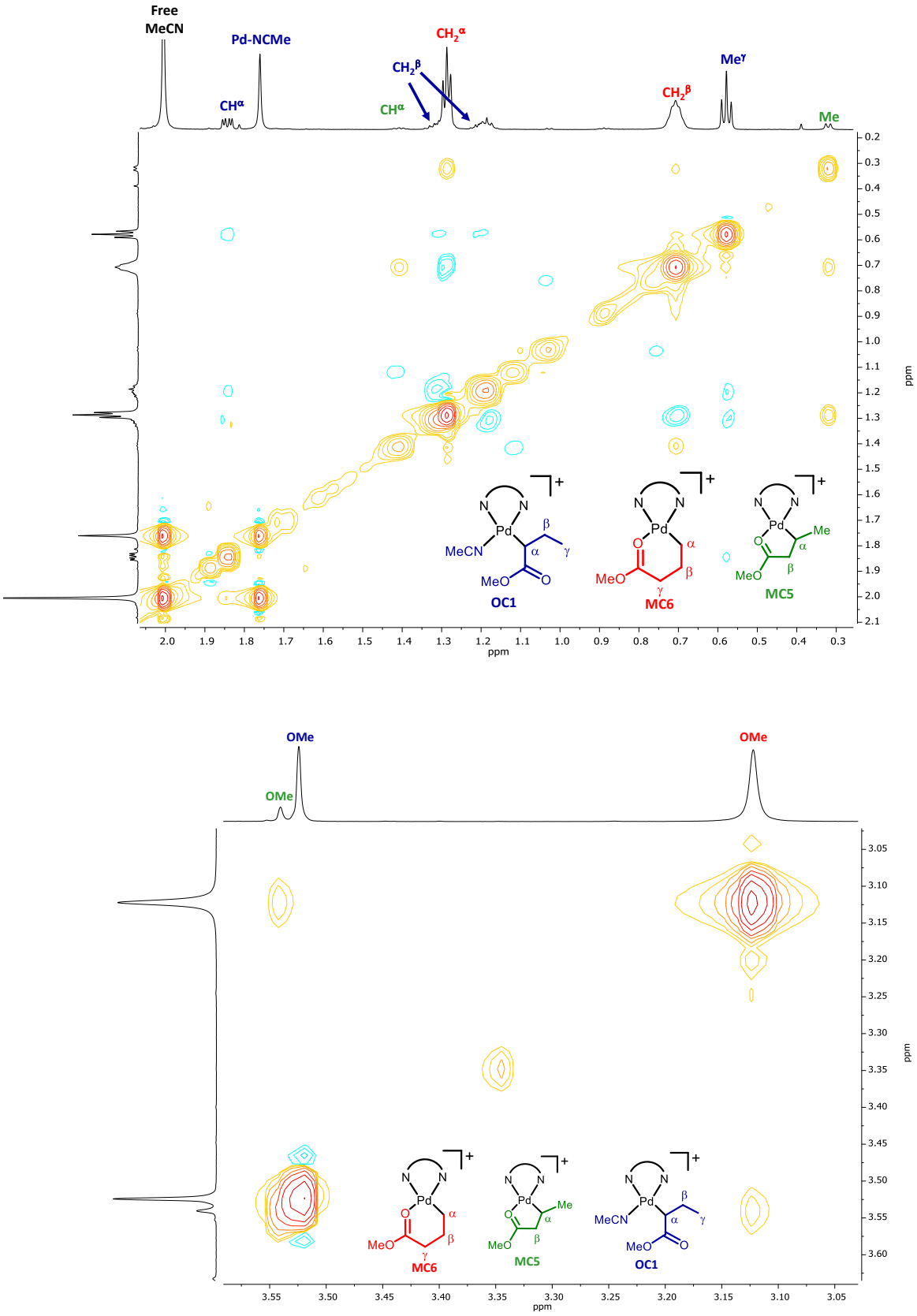
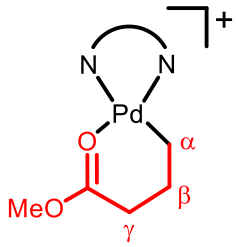
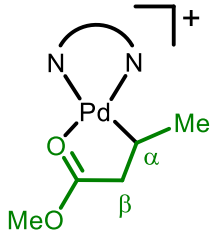


Figure S36. ^{1}H,^{1}H NOESY spectrum (CD_2Cl_2/TFE-d_3 mixture at χ_{TFE} = 0.17, T = 298 K) of the reaction mixture of **Pd1b** with methyl acrylate at t = 30 min. Yellow cross peaks are due to exchange process, light blue cross peaks are due to nuclear Overhauser effect. Top spectrum: region of aliphatic protons; bottom spectrum: region of methoxy groups.

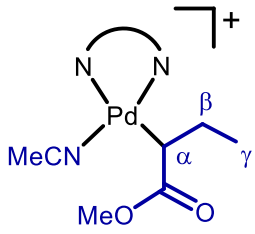
NMR assignments for the palladium organometallic compounds (MC6, MC5 and OC1) present in the solution of the reaction between Pd1b and MA carried out in the CD_2Cl_2/TFE-d_3 mixture of χ_{TFE} = 0.79.



MC6: the signals of the CH_2 groups were assigned on the basis of $^1H,^1H$ COSY and $^1H,^{13}C$ HSQC spectra (Figures S39 and S40): in particular βCH_2 falls at 0.69 ppm, while αCH_2 and γCH_2 are at 1.32 and 2.37 ppm, respectively. The signal of the methoxy group of inserted MA, found at 3.11 ppm, was assigned based on literature data.[4]



MC5: the signal at 0.34 ppm was assigned to the methyl group. Starting from this peak, on the basis of $^1H,^1H$ COSY spectrum (Figure S39), it was possible to assign the signal at 1.43 ppm to αCH. The signal at 3.51 ppm, related to the methoxy group, was assigned based on literature data.[4]



OC1: the signals of the CH_2 groups were assigned on the basis of $^1H,^1H$ COSY and $^1H,^{13}C$ HSQC spectra (Figures S39 and S40, respectively): γMe falls at 0.59 ppm, the signals related to βCH_2 are at 1.24 and 1.34 ppm, while the signal of αCH_2 is found at 1.92 ppm. Thanks to the correlation peaks in the $^1H,^{13}C$ HMBC spectrum (Figure S41), we established that the carbon atom of the C=O group resonates at 179.0 ppm. The singlet in the ^1H NMR spectrum that shows the same correlation with the C=O group, assigned to the methoxy group, is found at 3.54 ppm. The singlet due to coordinated acetonitrile (Pd-NCMe) is found at 1.71 ppm.

Table S4. The relative amount, in mol%, of the palladium organometallic compounds present in solution in the reaction of **Pd1b** with MA carried out in CD_2Cl_2/TFE-d_3 mixtures of different composition, at the time of complete reaction of **Pd1b**.

Time required for complete reaction of Pd1b (min)	χ_{TFE}[a]	MC6	MC5	MC4	OC1
120[b]	0	67	5	28	n.d.[c]
30	0.17	65	5	n.d.[c]	30
5	0.79	53	4	n.d.[c]	43
1[b]	1	61	n.d.[c]	n.d.[c]	39

[a]Molar fraction of TFE-d_3 in the mixture CD_2Cl_2/TFE-d_3. [b]Values from reference 4. [c]n.d. = not detected.

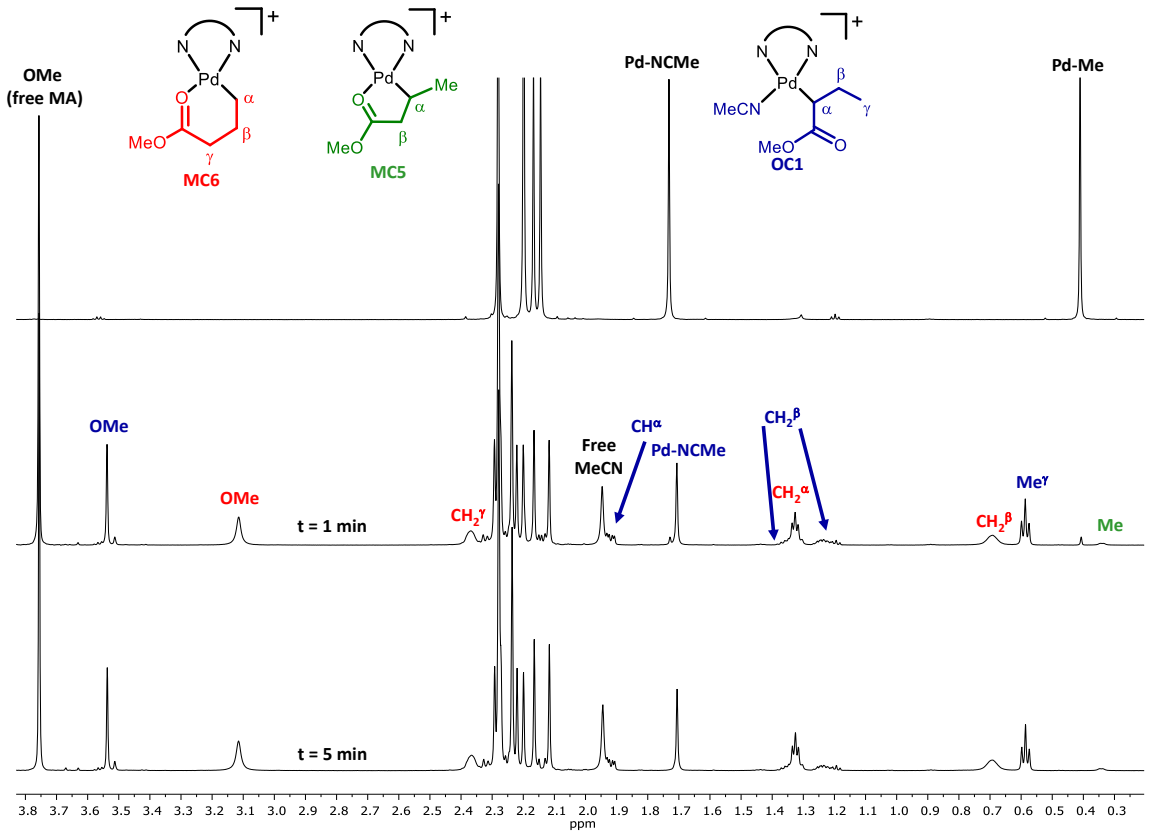


Figure S37. ^{1}H NMR spectra (CD_2Cl_2/TFE-d_3 mixture at χ_{TFE} = 0.79, T = 298 K) of **Pd1b** (top spectrum) and of **Pd1b** after the addition of methyl acrylate at different reaction times. Region of aliphatic protons.

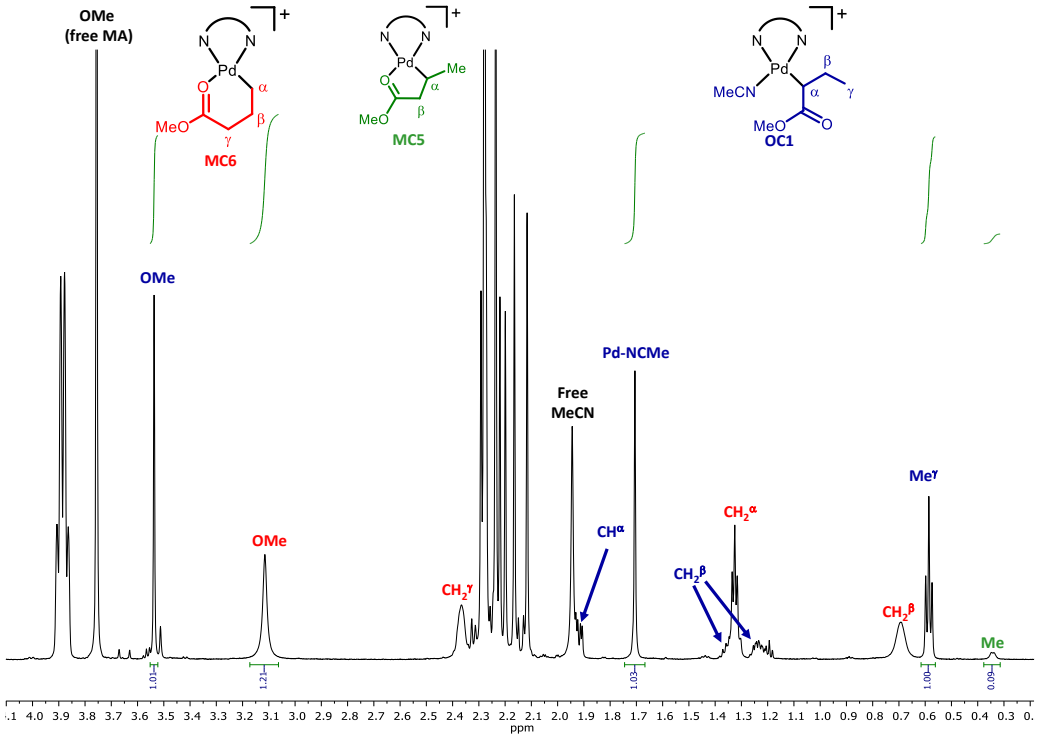


Figure S38. ^{1}H NMR spectrum (CD_2Cl_2/TFE-d_3 mixture at χ_{TFE} = 0.79, T = 298 K) of the reaction mixture of **Pd1b** with methyl acrylate at t = 5 min. Region of aliphatic protons.

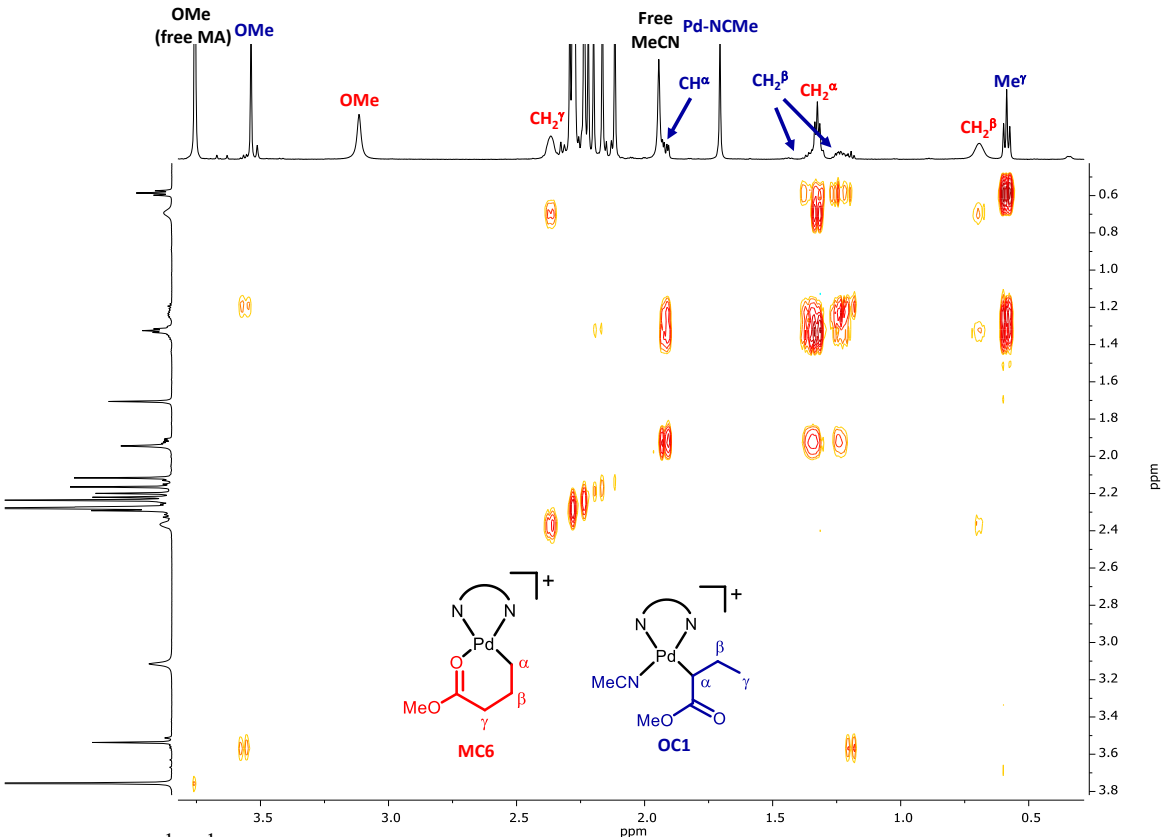


Figure S39. $^{1}H,^{1}H$ COSY spectrum (CD_2Cl_2/TFE-d_3 mixture at $\chi_{TFE} = 0.79$, T = 298 K) of the reaction mixture of **Pd1b** with methyl acrylate at t = 5 min. Region of aliphatic protons.

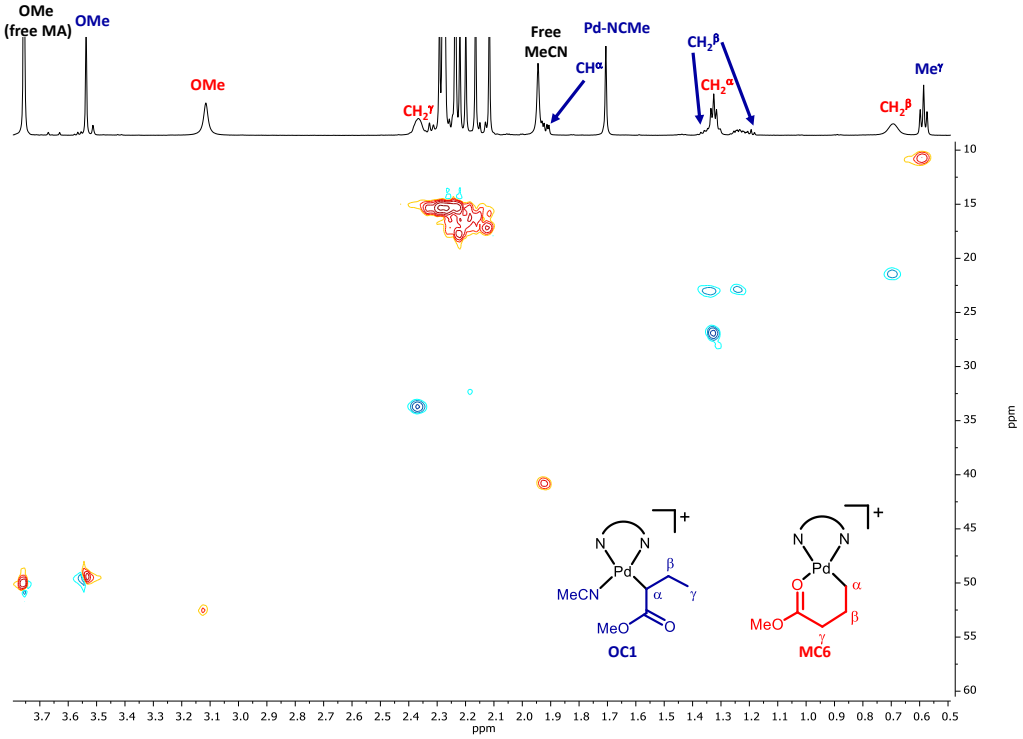


Figure S40. $^{1}H,^{13}C$ HSQC spectrum (CD_2Cl_2/TFE-d_3 mixture at χ_{TFE} = 0.79, T = 298 K) of the reaction mixture of **Pd1b** with methyl acrylate at t = 5 min. Red cross peaks are due to CH_3 and CH, light blue cross peaks are due to CH_2. Region of aliphatic protons.

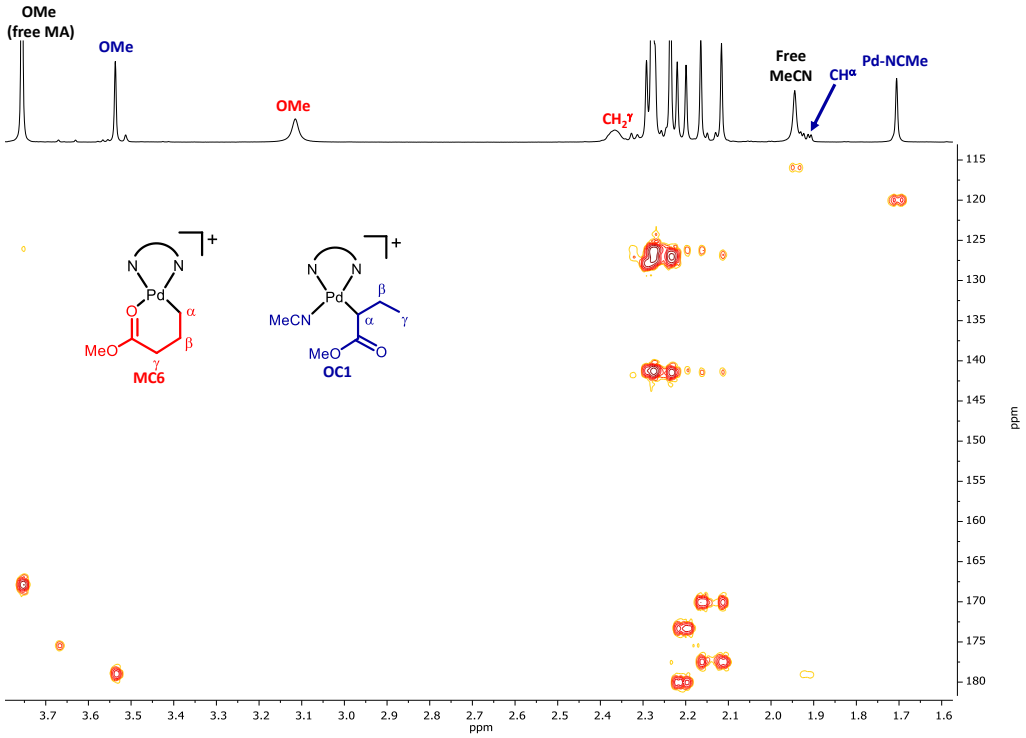


Figure S41. $^{1}H,^{13}C$ HMBC spectrum (CD_2Cl_2/TFE-d_3 mixture at χ_{TFE} = 0.79, T = 298 K) of the reaction mixture of **Pd1b** with methyl acrylate at t = 5 min. Region of aliphatic protons.

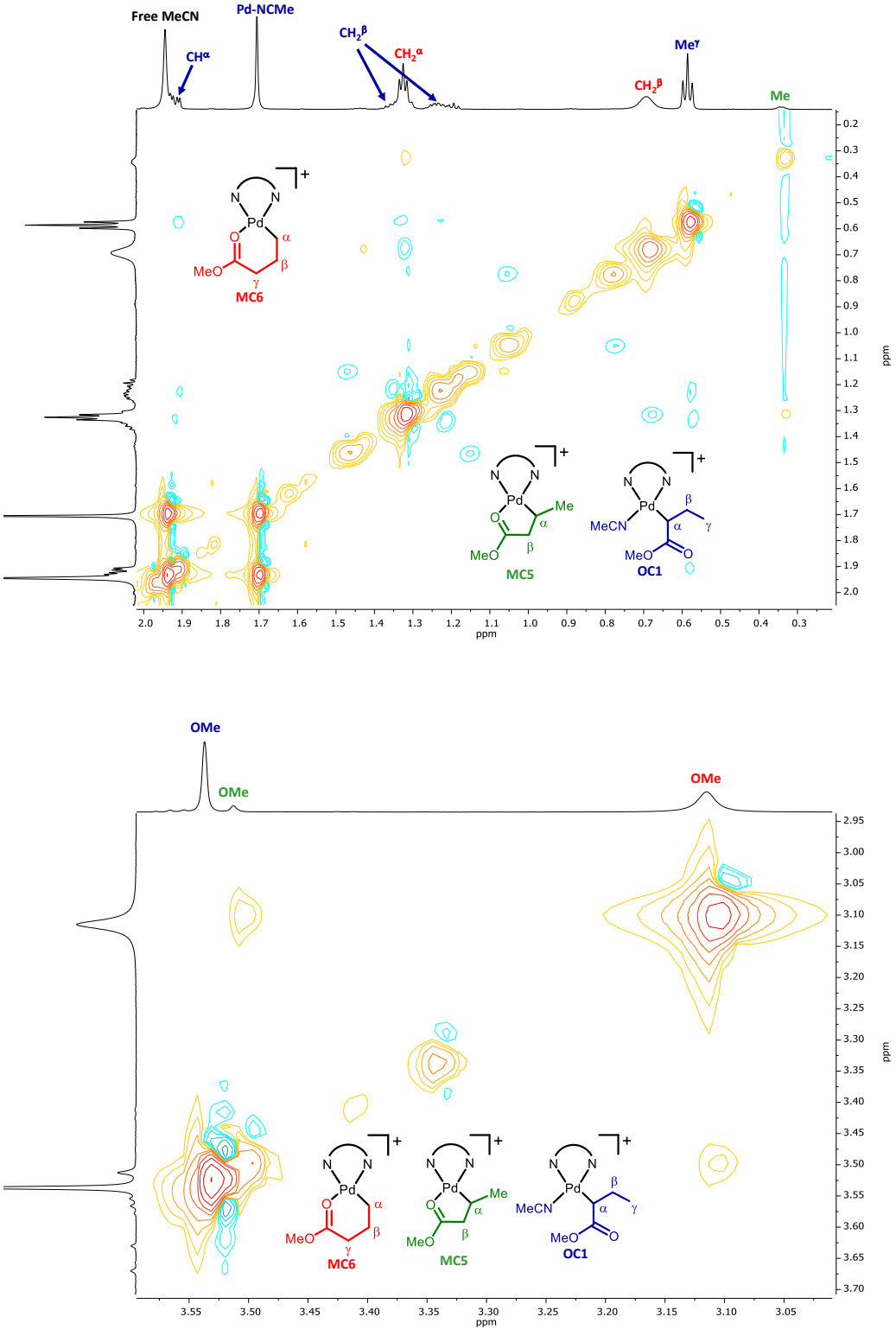


Figure S42. ^{1}H,^{1}H NOESY spectrum (CD_2Cl_2/TFE-d_3 mixture at χ_{TFE} = 0.79, T = 298 K) of the reaction mixture of **Pd1b** with methyl acrylate at t = 5 min. Yellow cross peaks are due to exchange process, light blue cross peaks are due to nuclear Overhauser effect. Top spectrum: region of aliphatic protons; bottom spectrum: region of methoxy groups.

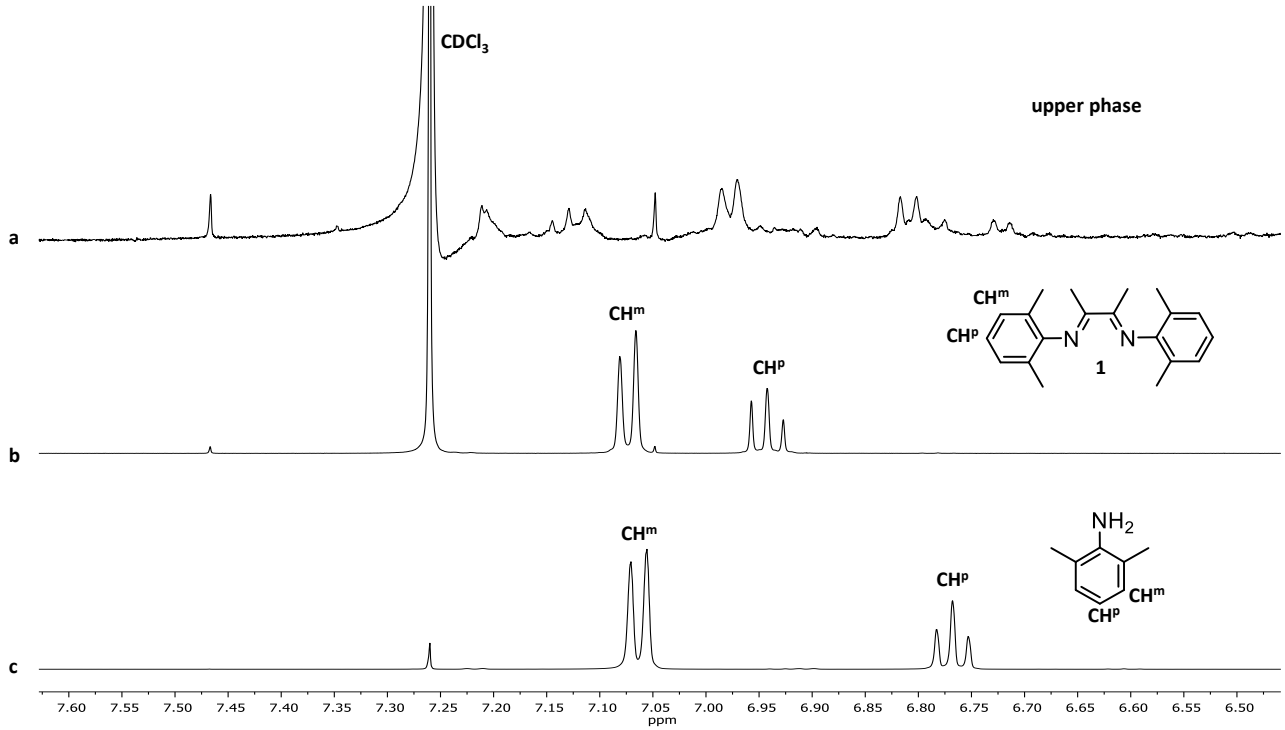


Figure S43. ^{1}H NMR spectra ($CDCl_3$, T = 298 K) of: a) lower phase of the reaction mixture at the end of the catalytic run with **Pd1b** at χ_{TFE} = 0.17; b) ligand **1**; c) 2,6-dimethyl aniline. Region of aromatic protons.

References

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2. H. A. Zhong, J. A. Labinger and J. E. Bercaw, *J. Am. Chem. Soc.*, 2002, **124**, 1378-1399.
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5. L. Guo, J. Li, W. Zhao, P. Wei, Y. Ju, X. Cui, L. Yuan, M. Ji and Z. Liu, *Inorg. Chem.*, 2024, **63**, 17809-17827.