Supplementary Material

Probing the effect of six membered N-heterocyclic carbene - 6-Mes - on the synthesis, structure and reactivity of $Me_2MOR(NHC)$ (M = Ga, In) complexes.

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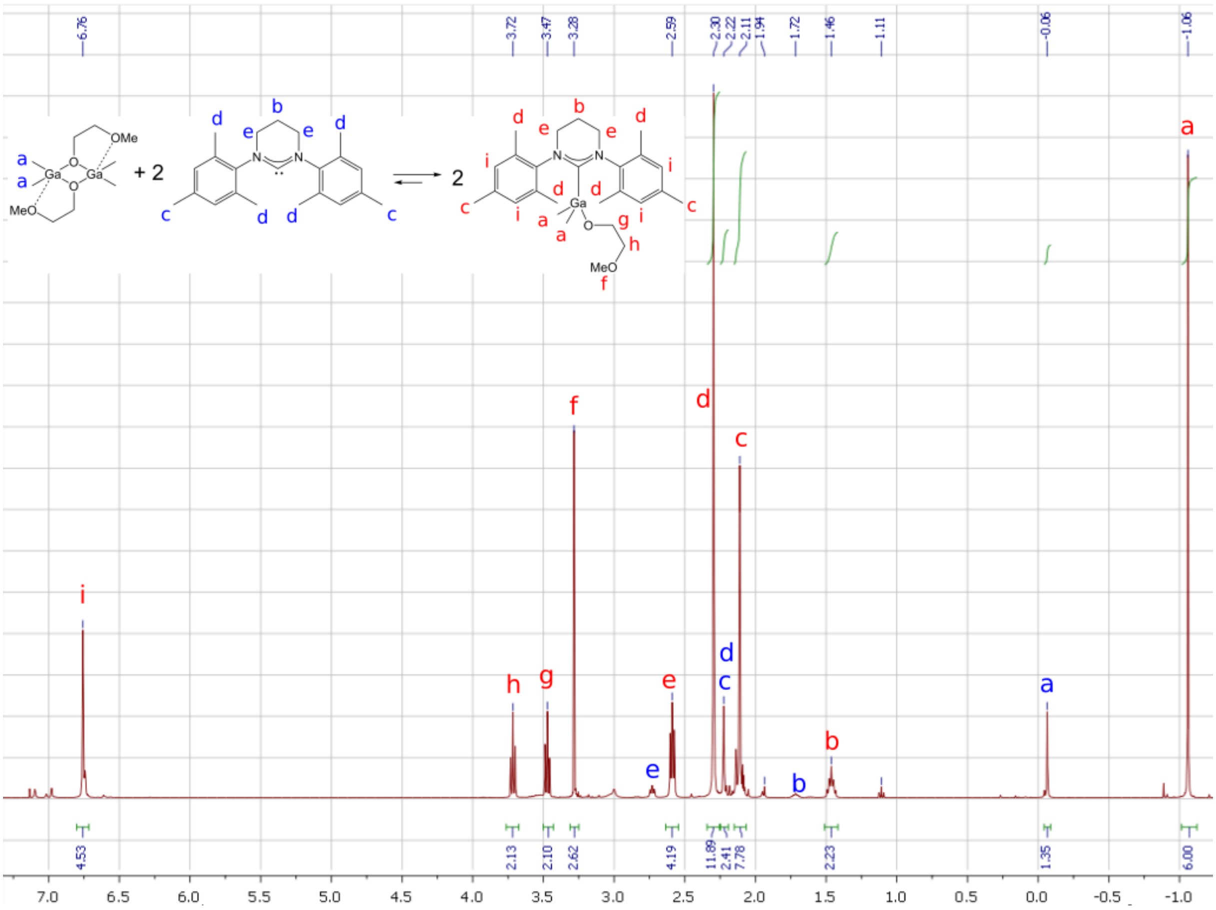


Figure S 1. ^{1}H NMR spectrum of the mixture of $[Me_2Ga(\mu\text{-}OCH_2CH_2OMe)]_2$ and 6-Mes ([Ga]:[6-Mes] = 1:1) in toluene-d_8 (400 MHz).

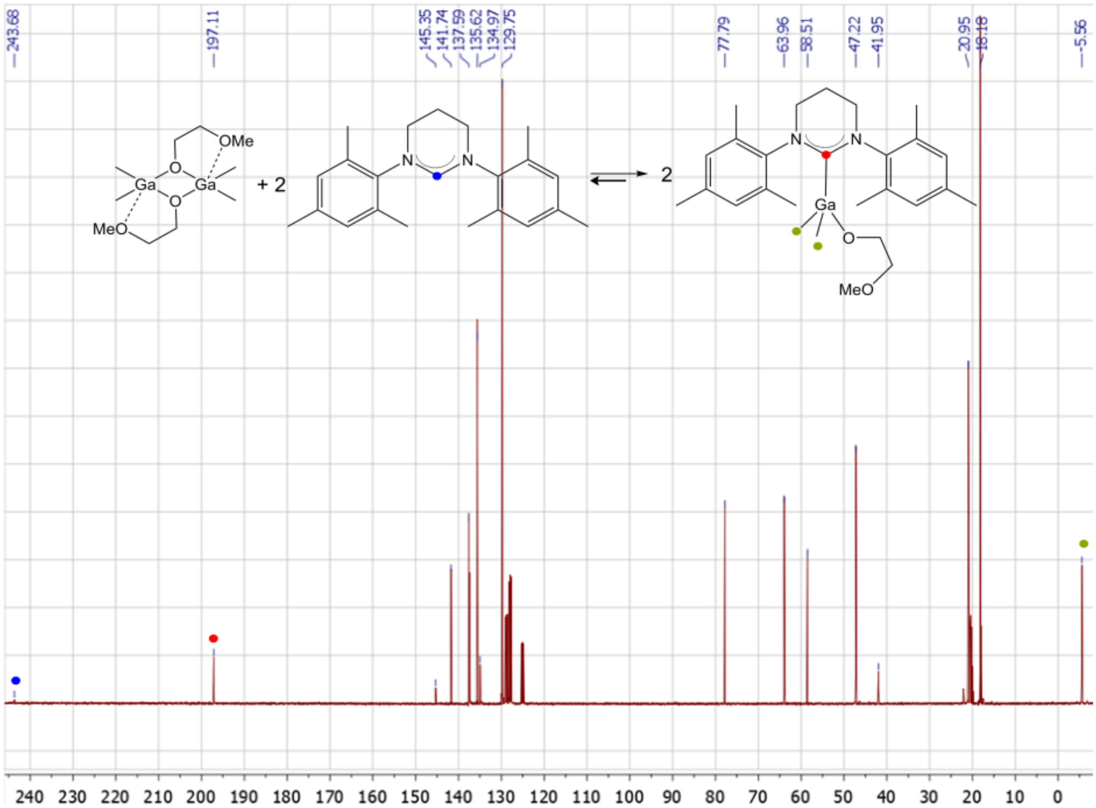


Figure S 2. [13]C NMR spectrum of the mixture of $[Me_2Ga(\mu\text{-}OCH_2CH_2OMe)]_2$ and 6-Mes ([Ga]:[6-Mes] = 1:1) in toluene-d_8 (100 MHz).

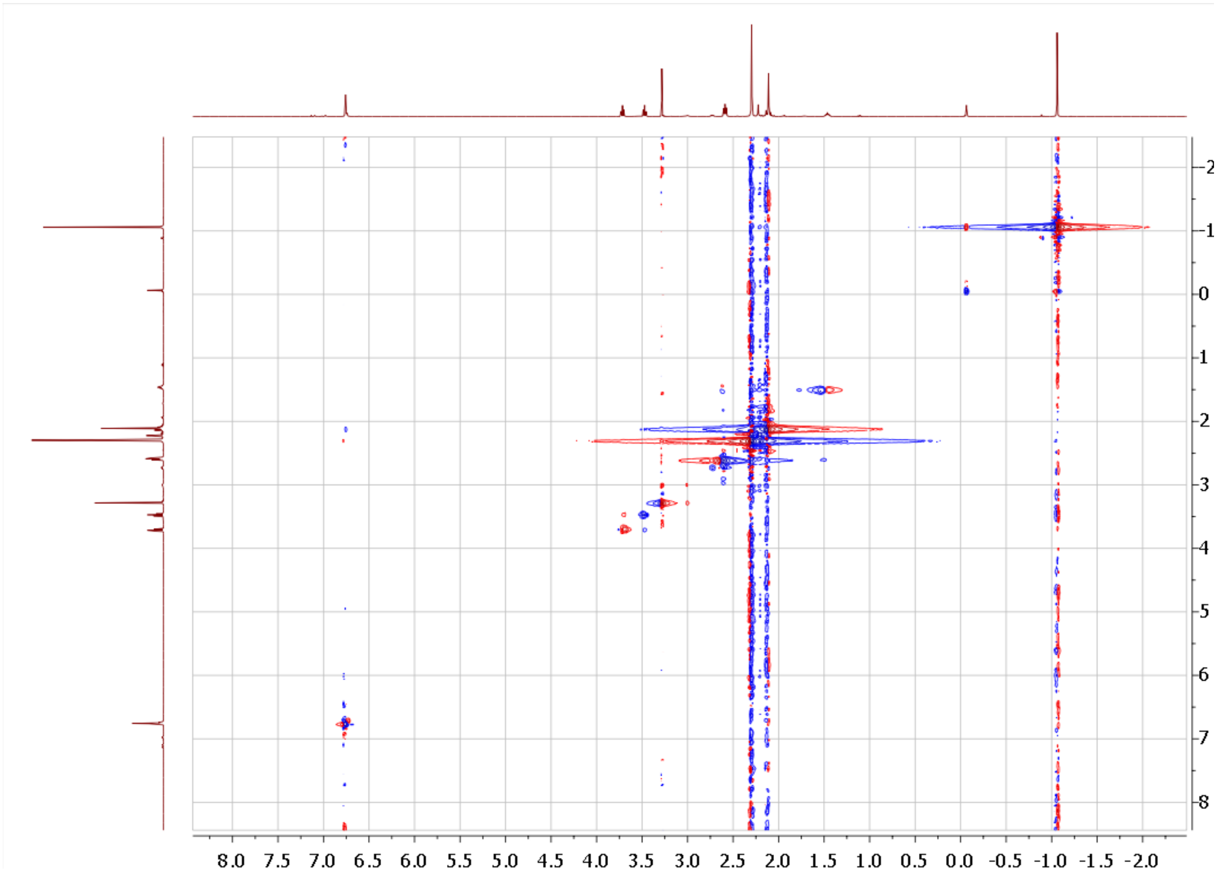


Figure S 3. ROESY NMR of $Me_2Ga(\mu\text{-}OCH_2CH_2OMe)$(6-Mes) (**1**) in toluene-d_8

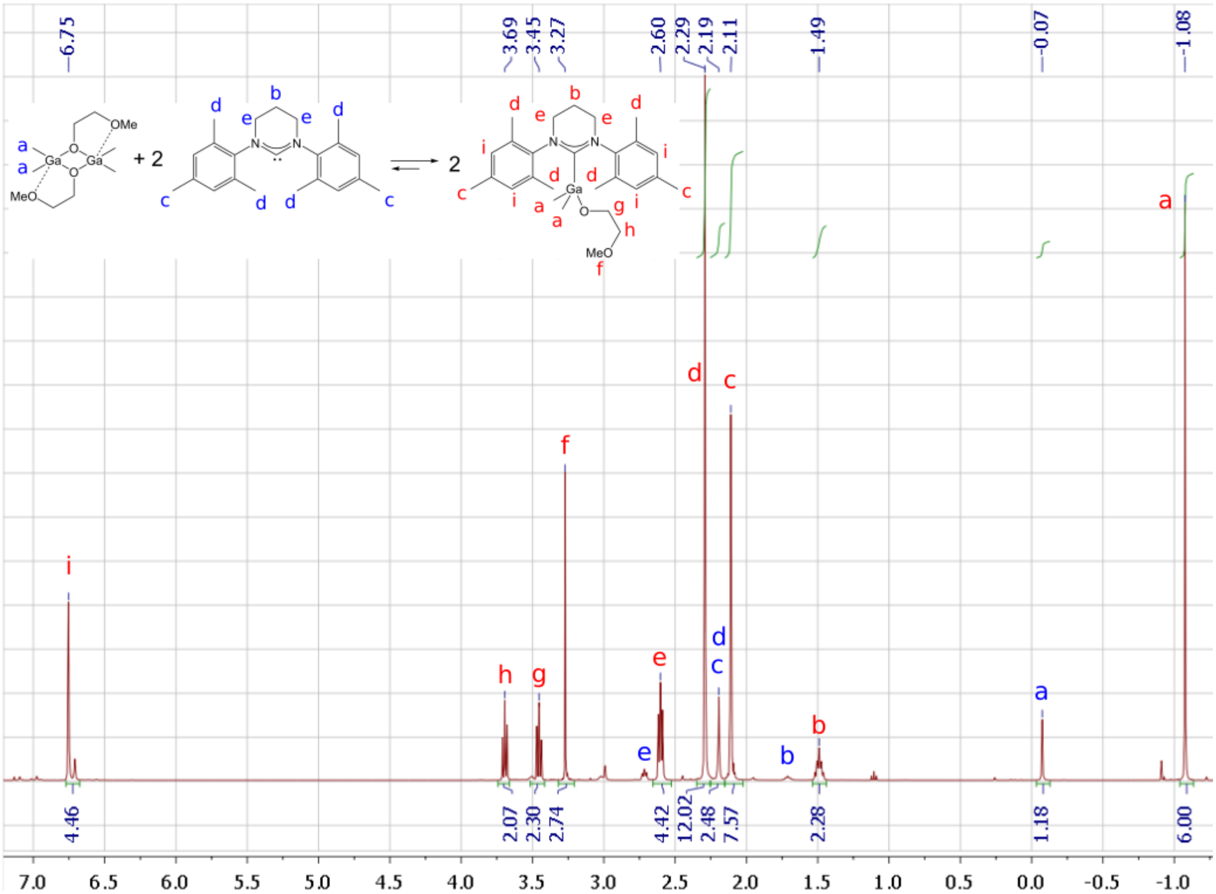


Figure S 4. ^{1}H NMR spectrum of $Me_2Ga(OCH_2CH_2OMe)(6\text{-}Mes)$ (**1**) in toluene-d_8 (400 MHz).

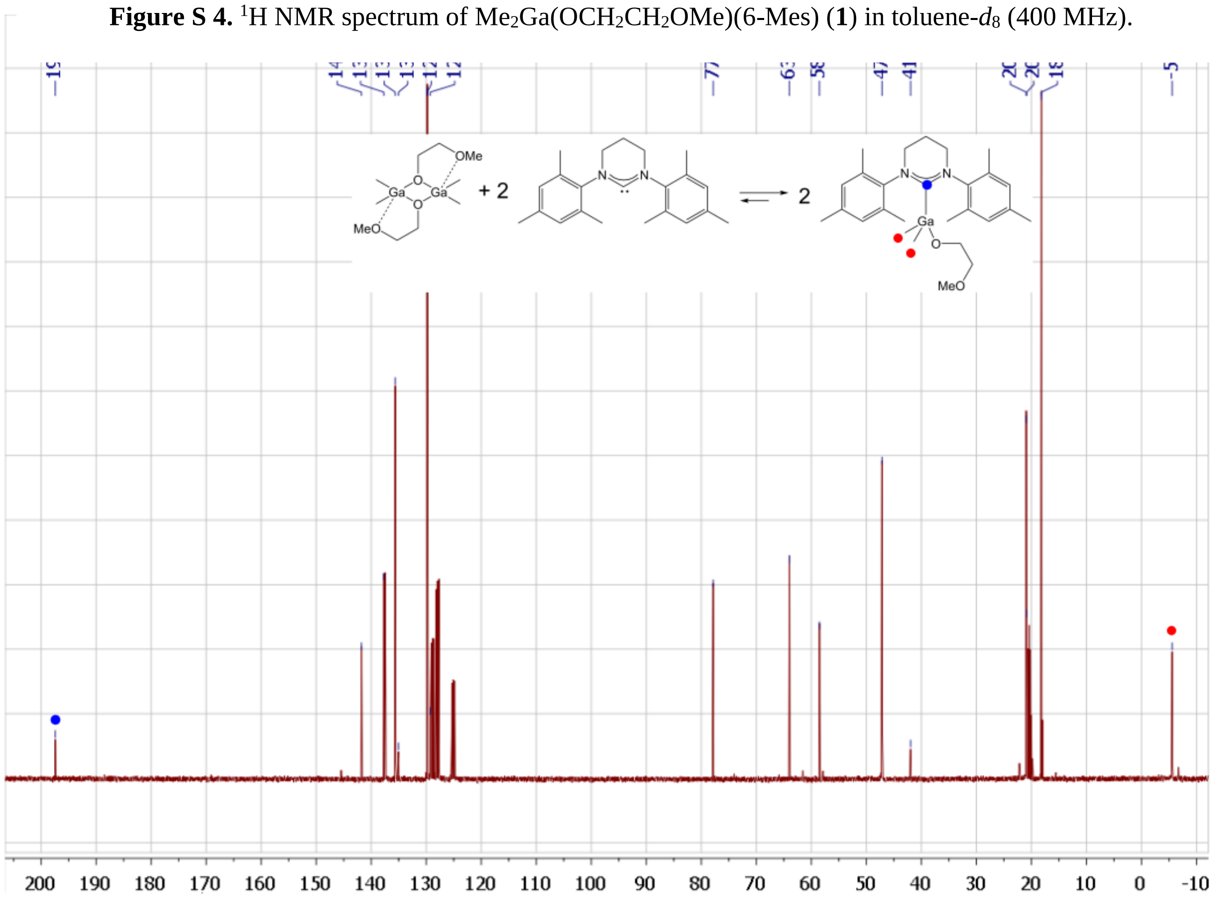


Figure S 5. ^{13}C NMR spectrum of $Me_2Ga(OCH_2CH_2OMe)(6\text{-}Mes)$ (**1**) in toluene-d_8 (100 MHz).

Figure S 6. [1]H NMR spectrum measured 20 minutes after dissolution of $Me_2Ga(OCH_2CH_2OMe)$(6-Mes) (**1**) in

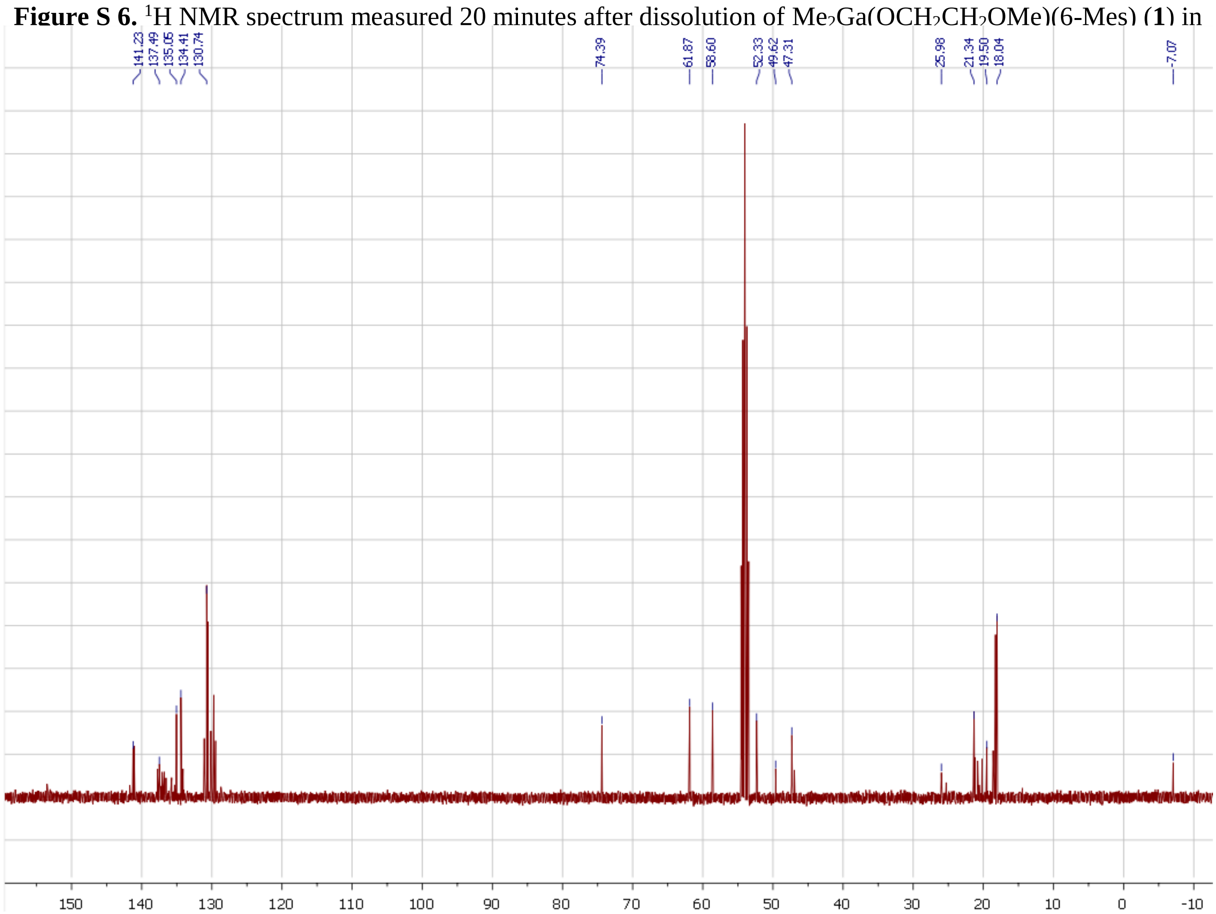


Figure S 7. [13]C NMR spectrum measured 20 minutes after dissolution of $Me_2Ga(OCH_2CH_2OMe)$(6-Mes) (**1**) in CD_2Cl_2.

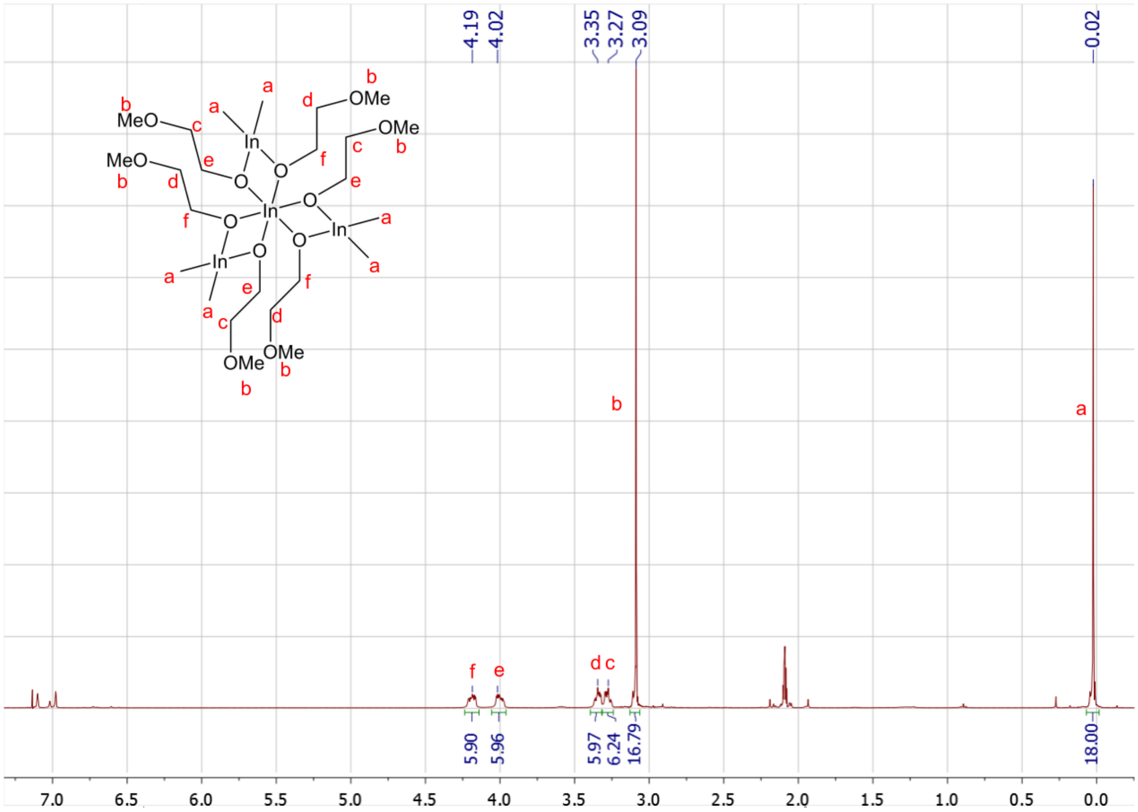


Figure S 8. ^{1}H NMR spectrum of In{$Me_2In(\mu\text{-}OCH_2CH_2OMe)_2$}$_3$ in toluene-d_8 (400 MHz).

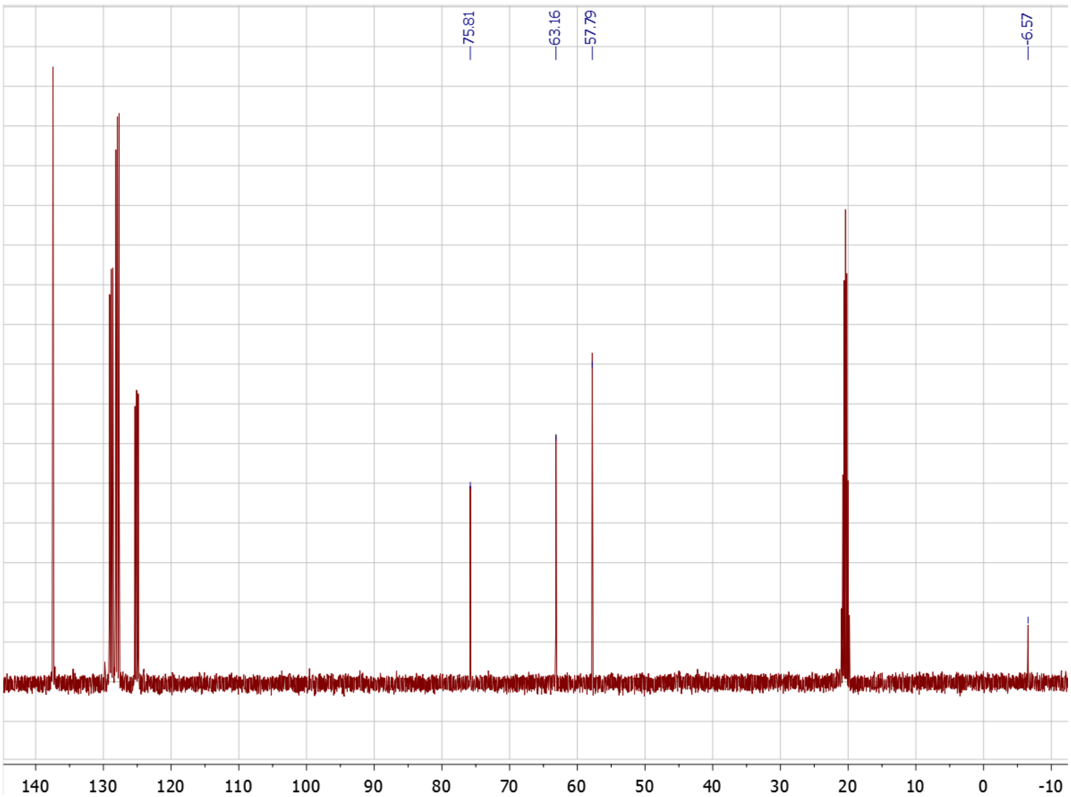


Figure S 9. ^{13}C NMR spectrum of In{$Me_2In(\mu\text{-}OCH_2CH_2OMe)_2$}$_3$ in toluene-d_8 (100 MHz).

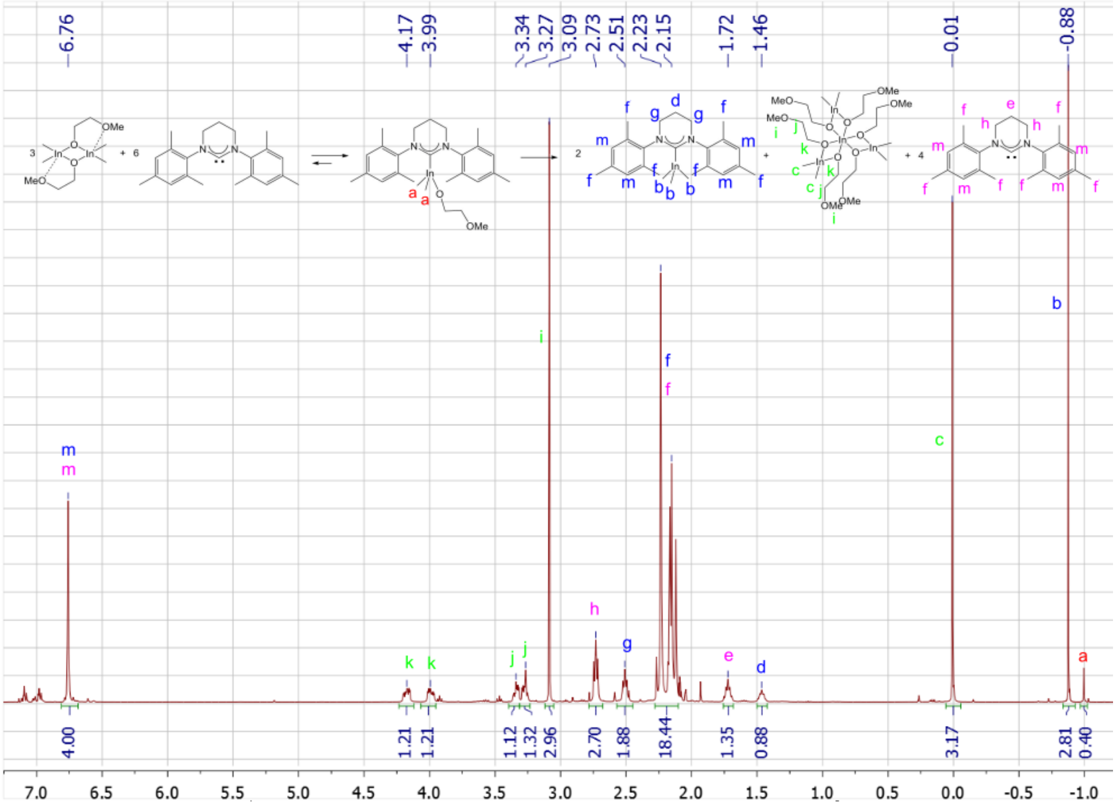


Figure S 10. [1]H NMR spectrum of the mixture of $[Me_2In(\mu\text{-}OCH_2CH_2OMe)]_2$ and 6-Mes ([In]:[6-Mes] = 1:1) in toluene-d_8 (400 MHz).

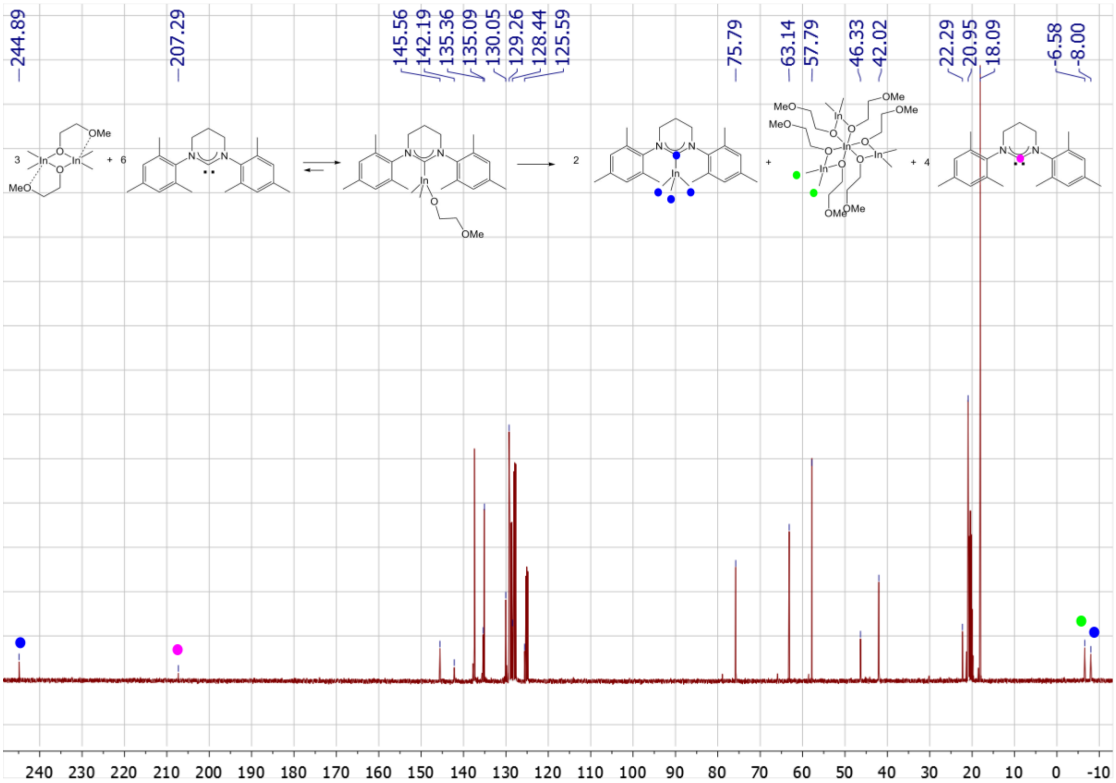


Figure S 11. [13]C NMR spectrum of the mixture of $[Me_2In(\mu\text{-}OCH_2CH_2OMe)]_2$ and 6-Mes ([In]:[6-Mes] = 1:1) in toluene-d_8 (100 MHz).

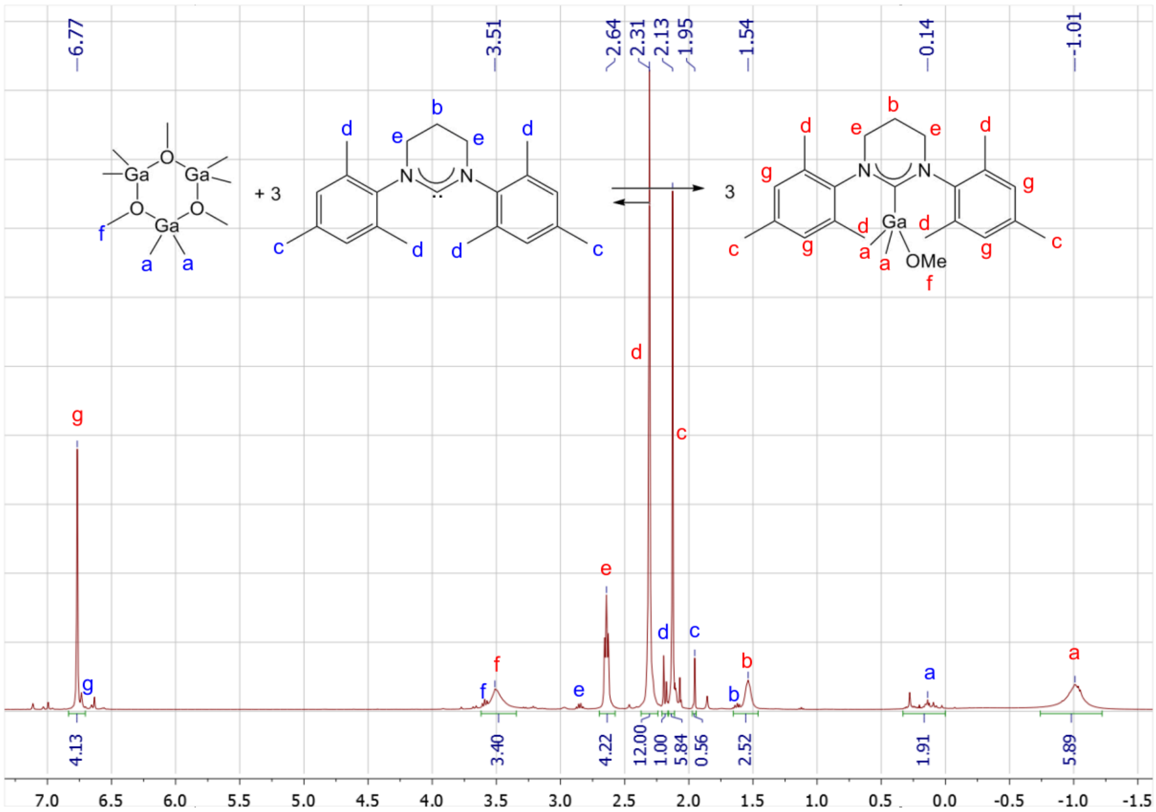


Figure S 12. ^{1}H NMR spectrum of the mixture of $[Me_2Ga(\mu\text{-}OMe)]_3$ and 6-Mes ([Ga]:[6-Mes] = 1:1) in toluene-d_8 (400 MHz).

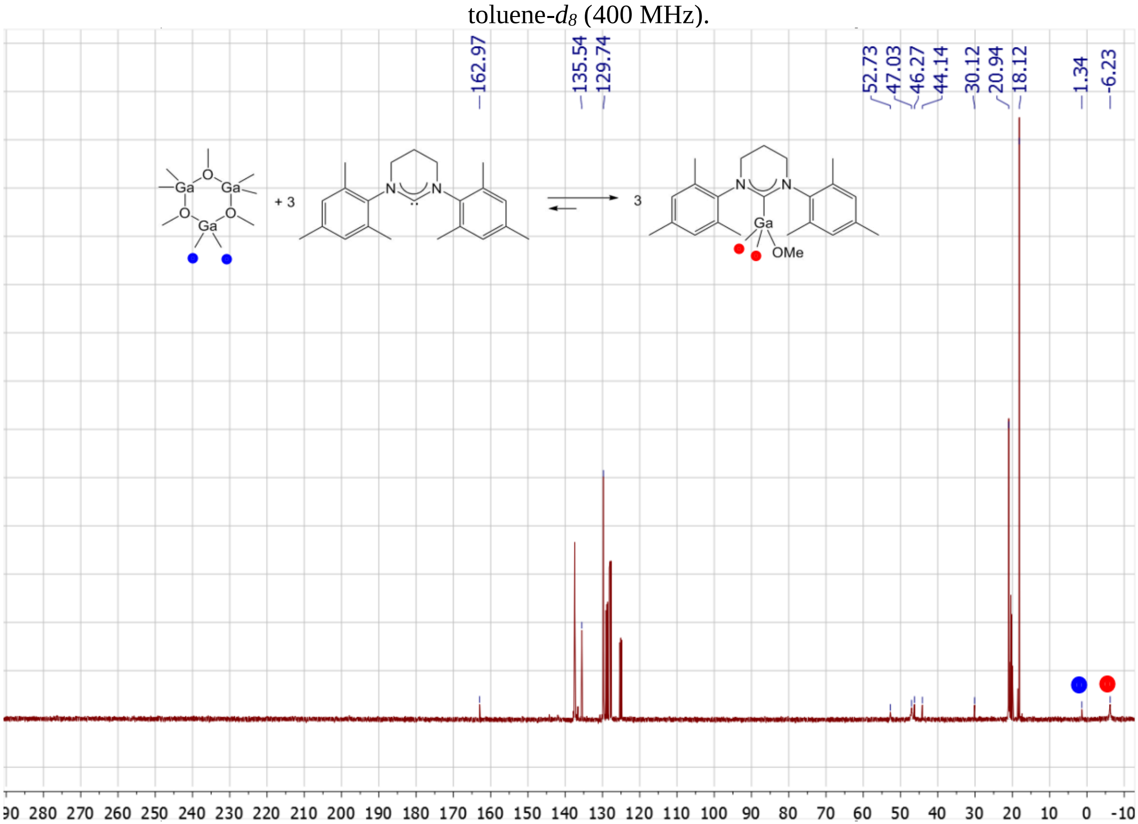


Figure S 13. ^{13}C NMR spectrum of the mixture of $[Me_2Ga(\mu\text{-}OMe)]_3$ and 6-Mes ([Ga]:[6-Mes] = 1:1) in toluene-d_8 (100 MHz).

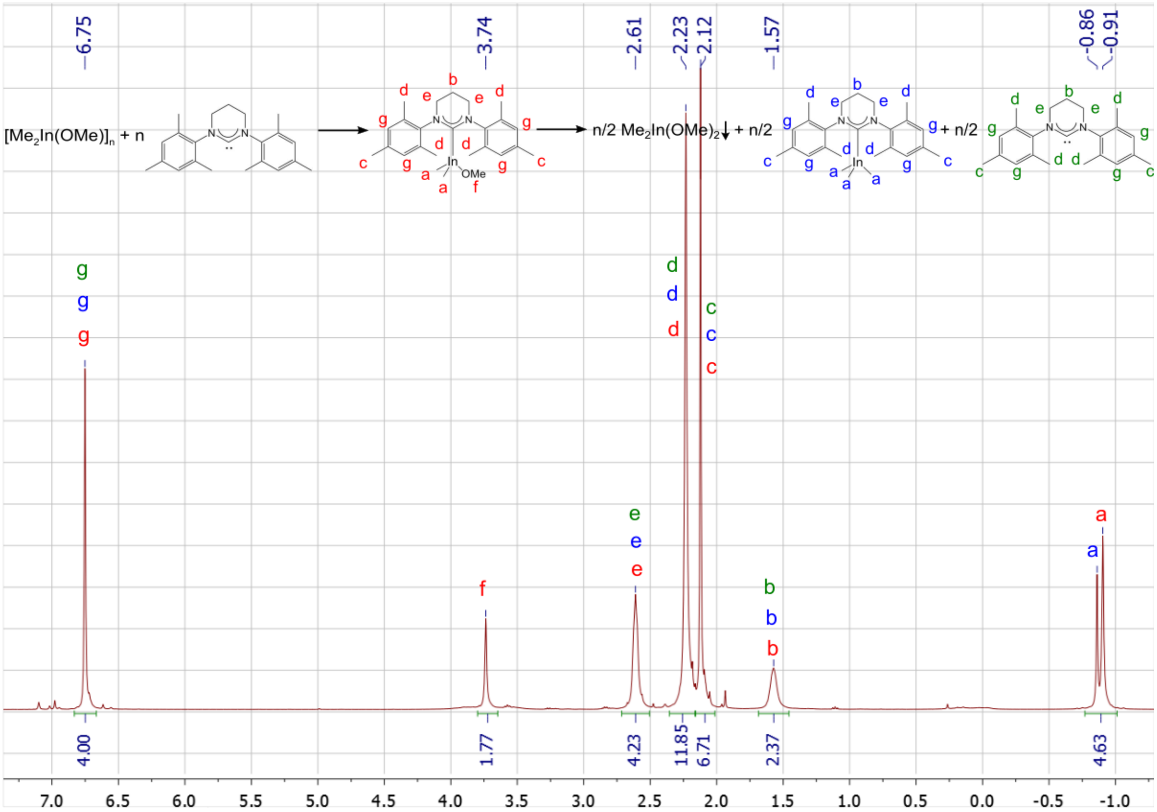


Figure S 14. [1]H NMR spectrum of the mixture of [$Me_2In(\mu$-OMe)]$_n$ and 6-Mes ([In]:[6-Mes] = 1:1) in toluene-d_8 (400 MHz).

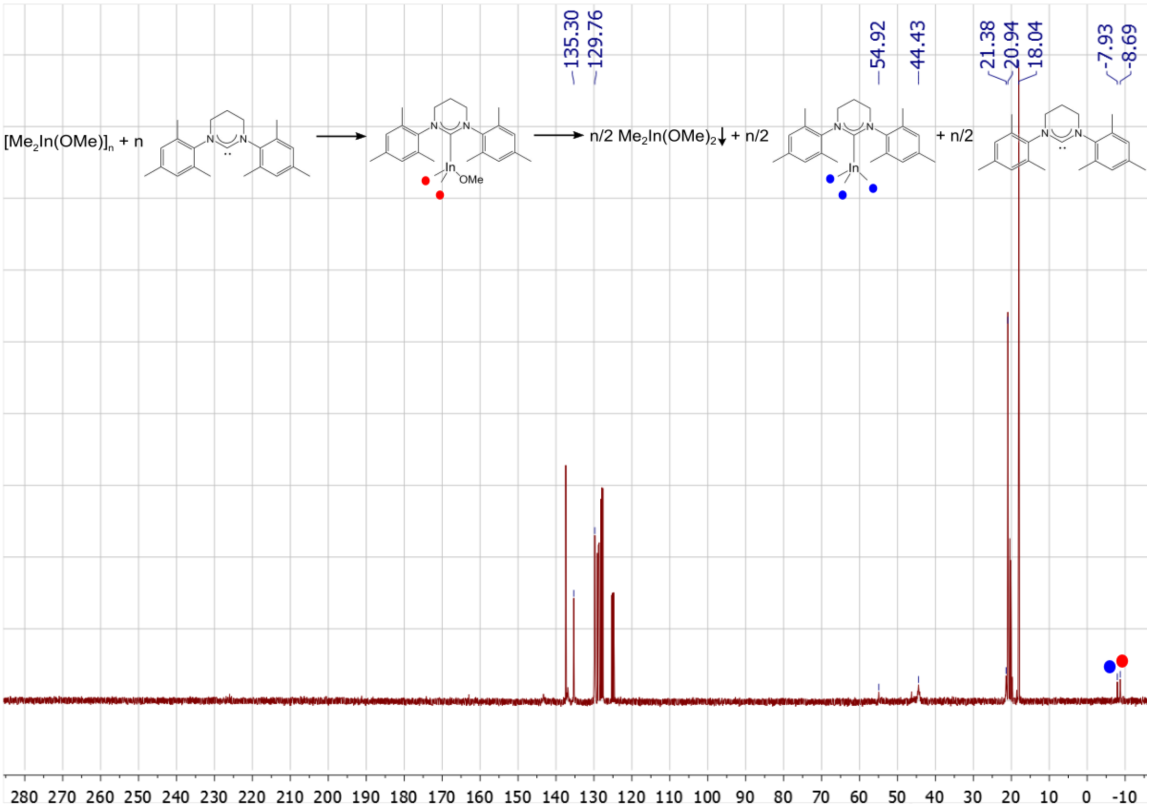


Figure S 12. [13]C NMR spectrum of the mixture of [$Me_2In(\mu$-OMe)]$_n$ and 6-Mes ([In]:[6-Mes] = 1:1) in toluene-d_8 (100 MHz).

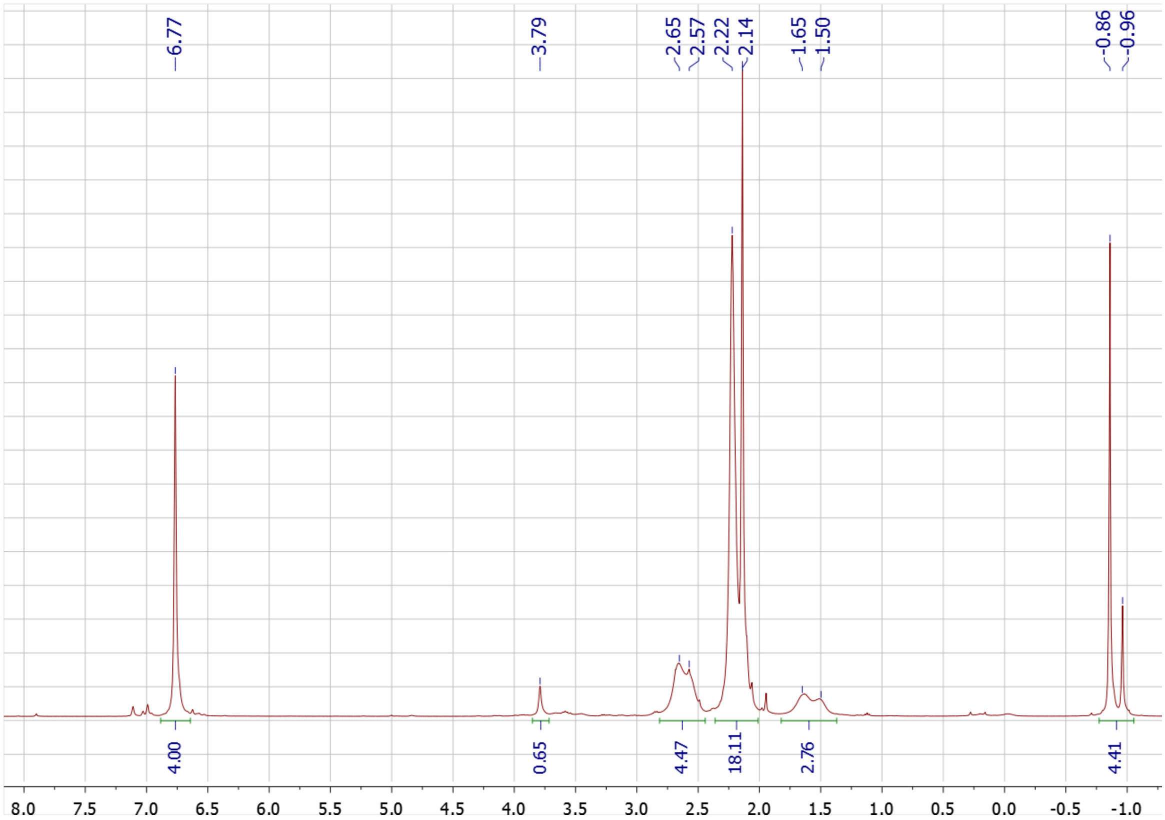


Figure S 16. [1]H NMR spectrum of the mixture of $[Me_2In(\mu\text{-}OMe)]_n$ and 6-Mes ([In]:[6-Mes] = 1:1) in toluene-d_8 (400 MHz), 24h after mixing reagents.

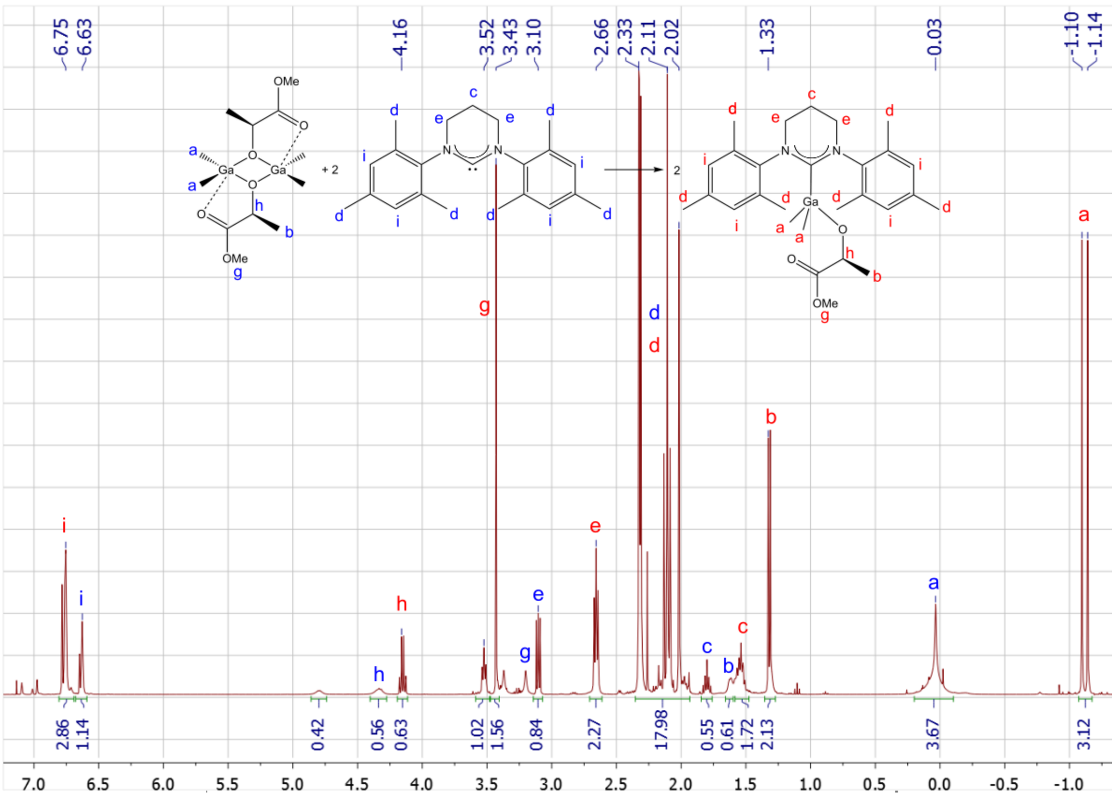


Figure S 17. [1]H NMR spectrum of the mixture of (*S*,*S*)-$[Me_2Ga(OCH(CH_3)COOMe)]_2$ and 6-Mes ([Ga]:[6-Mes] = 1:1) in toluene-d_8 (400 MHz).

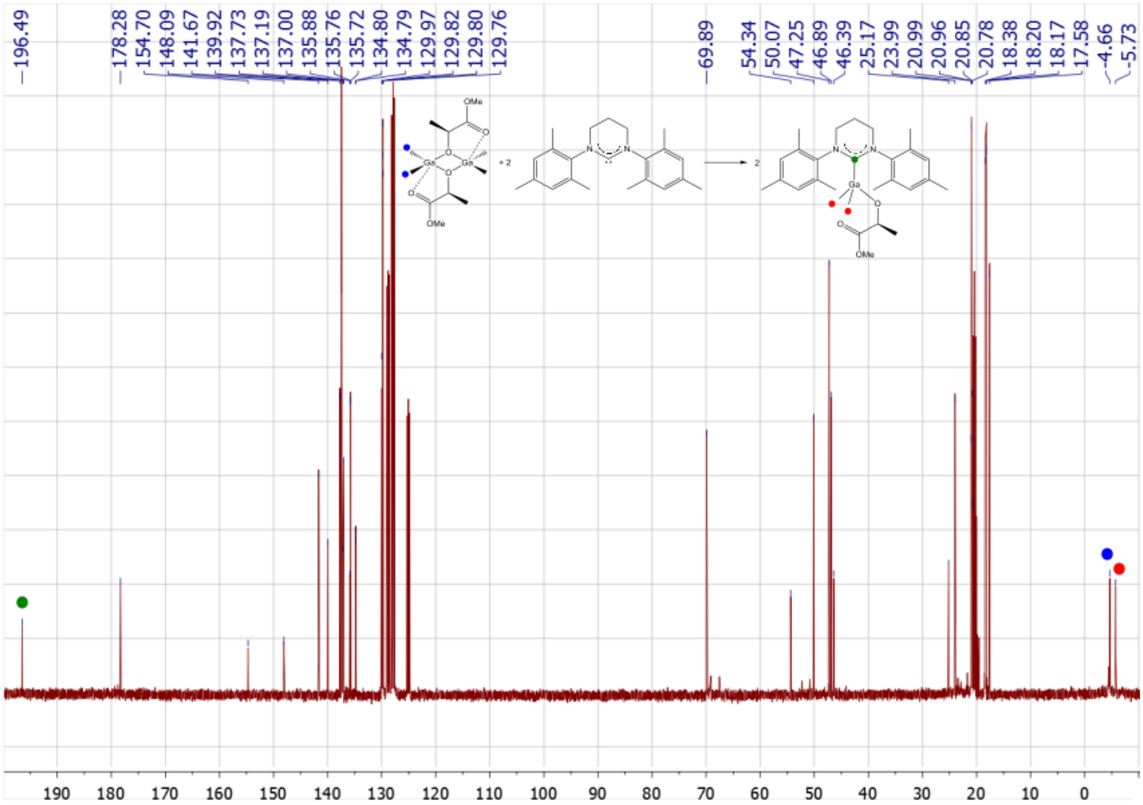


Figure S 18. ^{13}C NMR spectrum of the mixture of (*S*,*S*)-[$Me_2Ga(OCH(CH_3)COOMe)]_2$ and 6-Mes ([Ga]:[6-Mes] = 1:1) in toluene-d_8 (100 MHz).

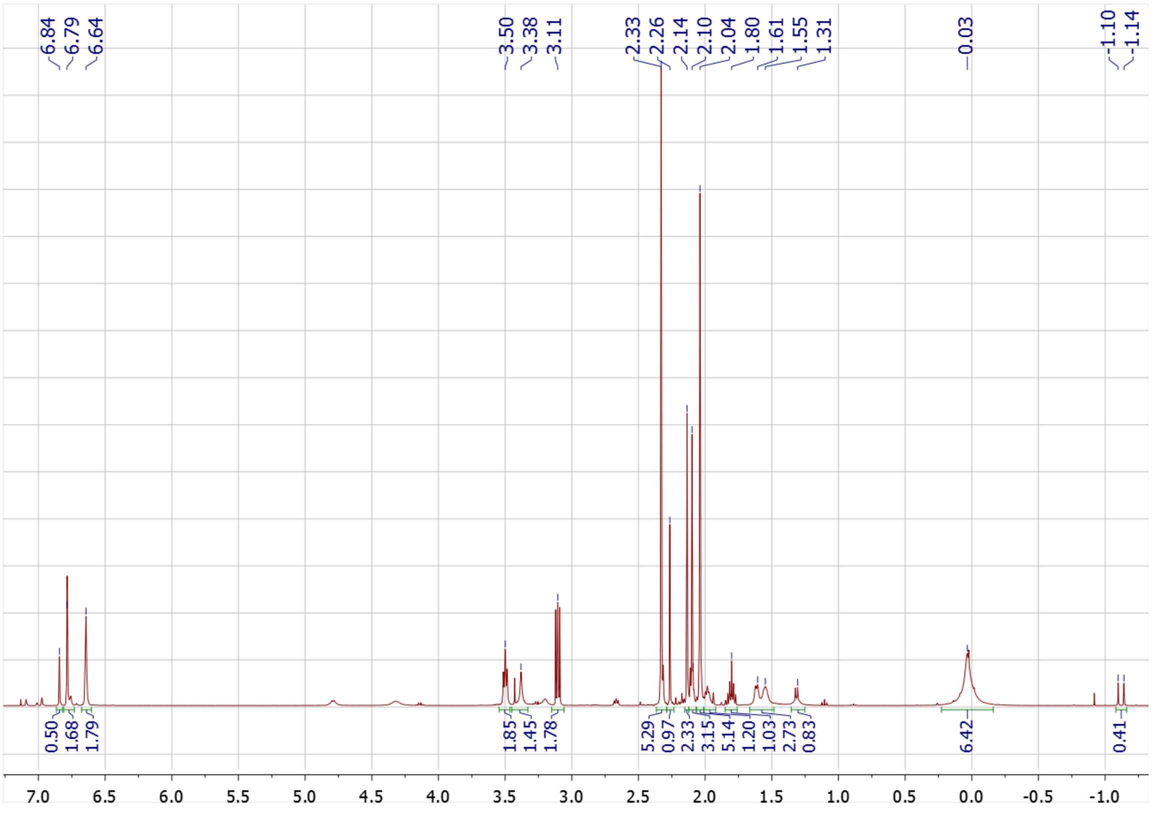


Figure S 19. ^{1}H NMR spectrum of the mixture of (*S*,*S*)-[$Me_2Ga(OCH(CH_3)COOMe)]_2$ and 6-Mes ([Ga]:[6-Mes] = 1:1) 24h after mixing in toluene-d_8 (400 MHz).

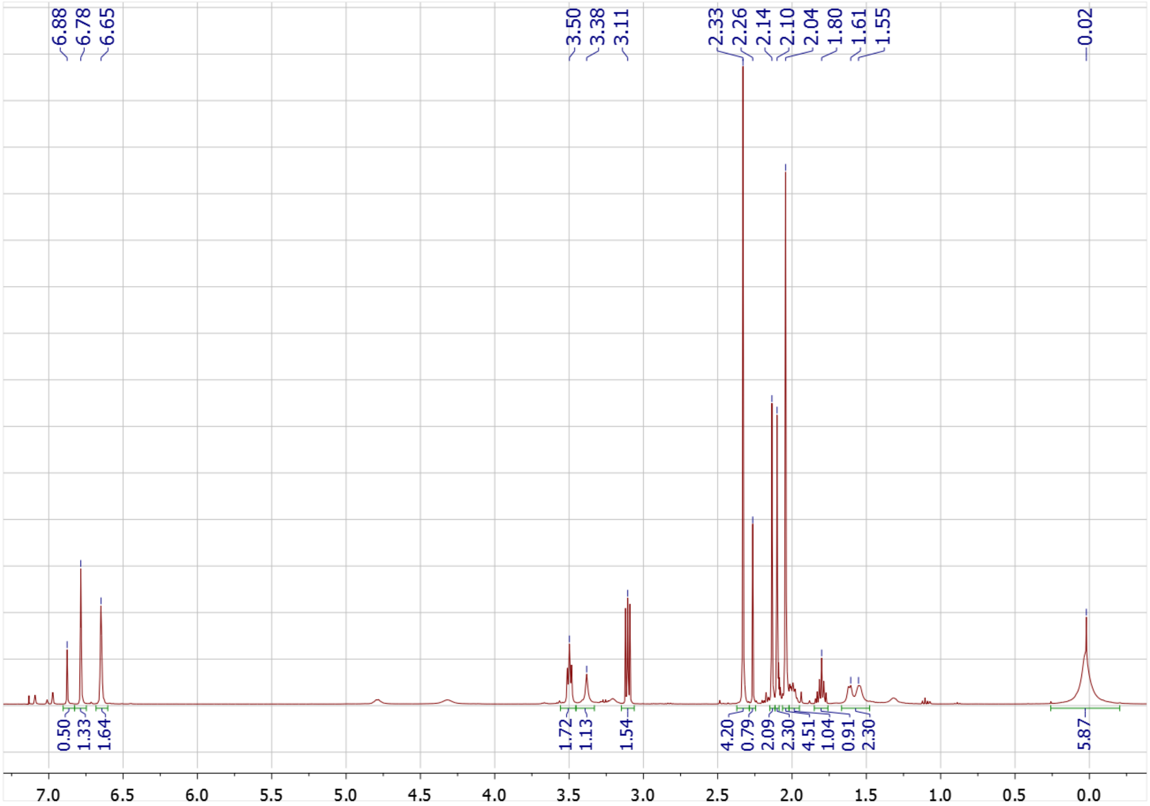


Figure S 20. ^{1}H NMR spectrum of the mixture of (S,S)-[$Me_2Ga(OCH(CH_3)COOMe)$]$_2$ and 6-Mes ([Ga]:[6-Mes] = 1:1) 96h after mixing in toluene-d_8 (400 MHz).

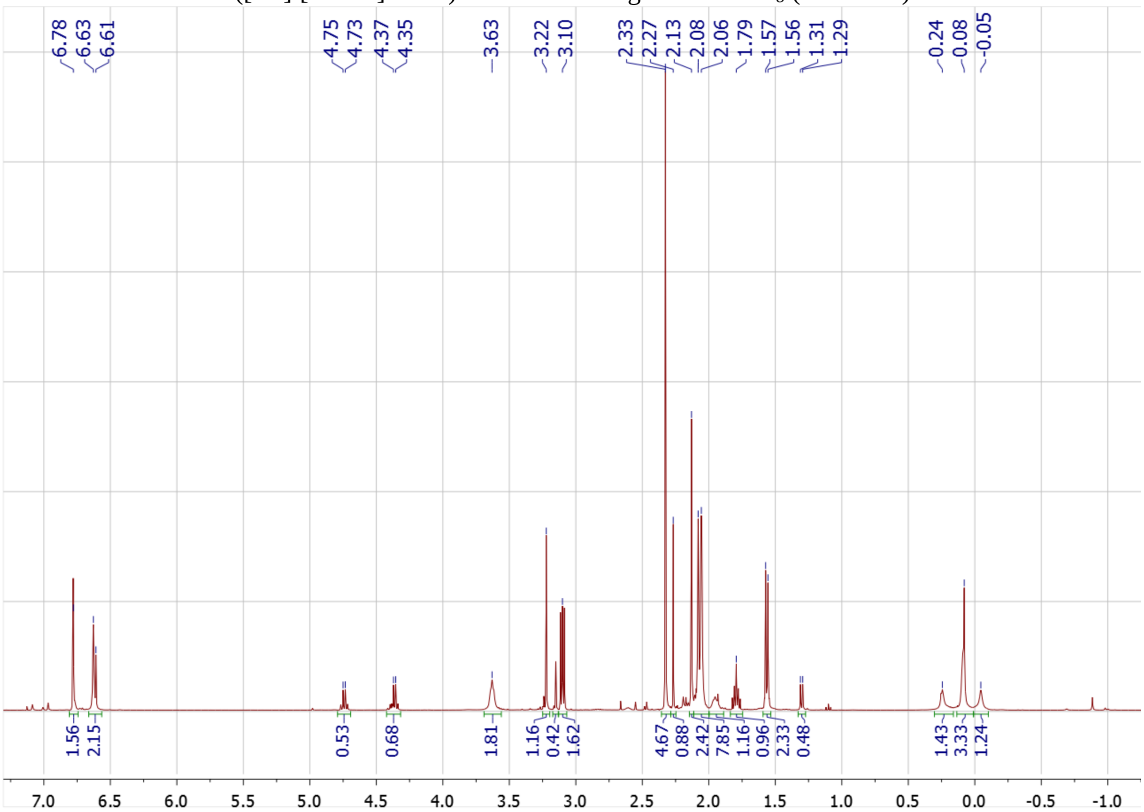


Figure S21. ^{1}H NMR spectrum of the mixture of (S,S)-[$Me_2In(OCH(CH_3)COOMe)$]$_2$ and 6-Mes ([In]:[6-Mes] = 1:1) in toluene-d_8 (400 MHz).

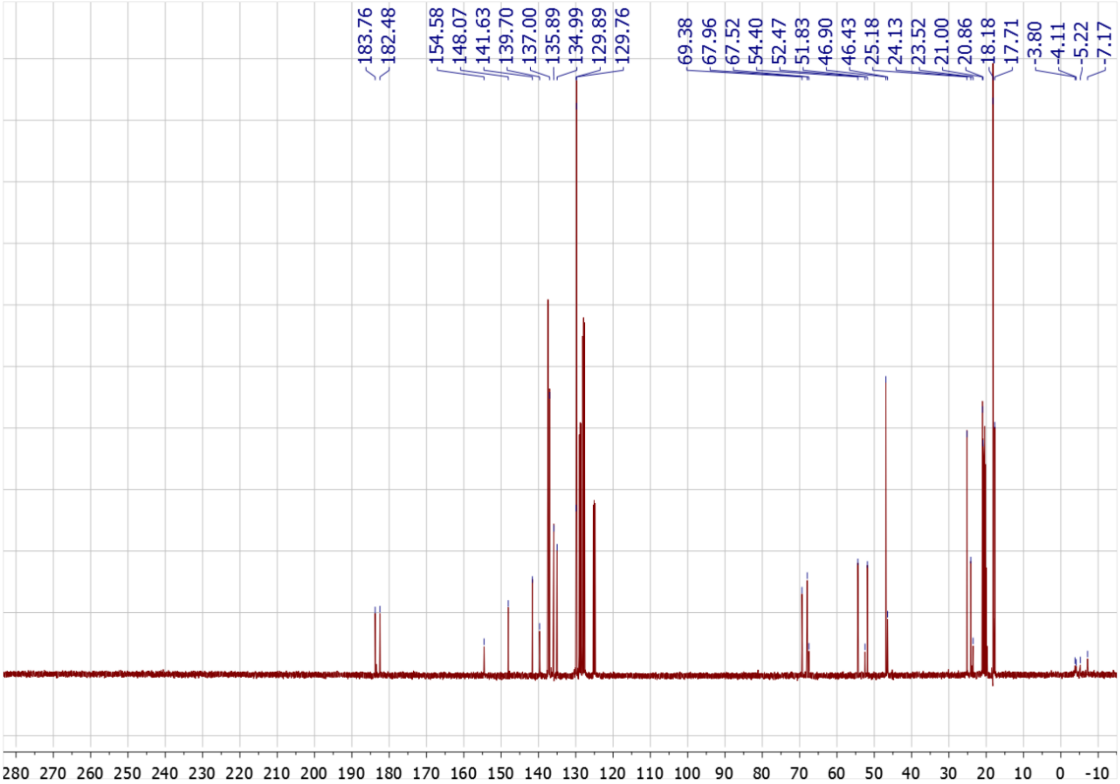


Figure S 22. ^{13}C NMR spectrum of mixture of the mixture of (*S*,*S*)-[$Me_2In(OCH(CH_3)COOMe)]_2$ and 6-Mes ([In]:[6-Mes] = 1:1) in toluene-d_8 (100 MHz).

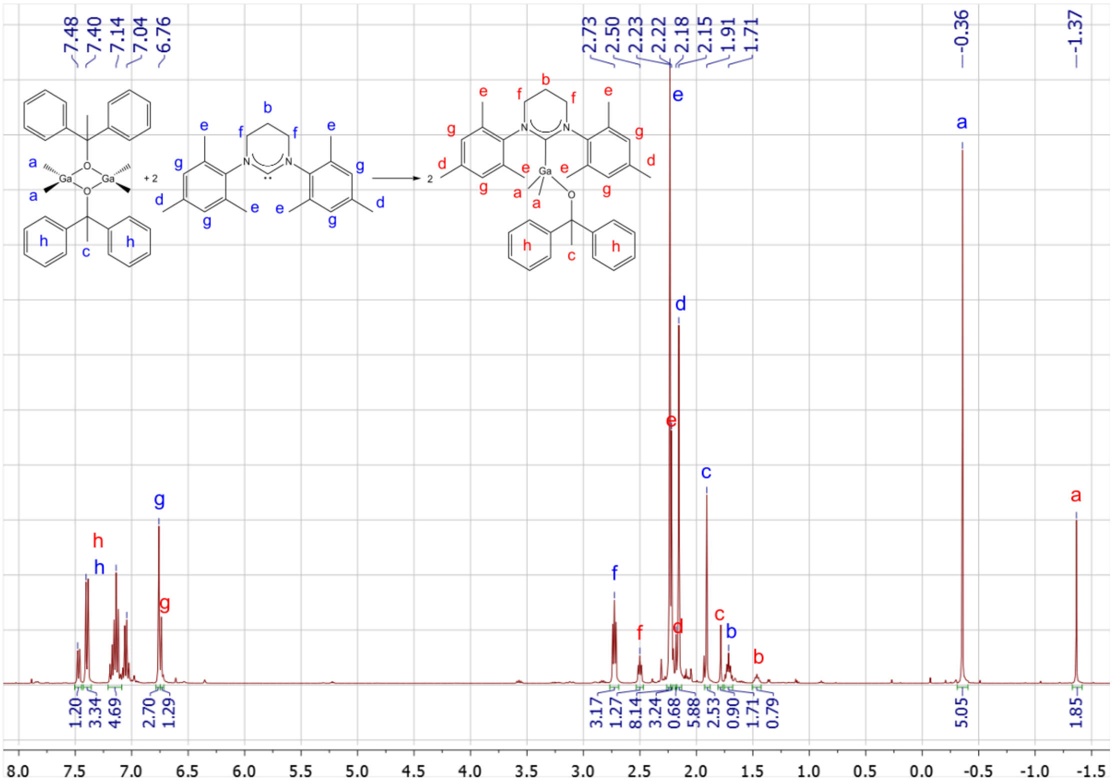


Figure S 23. ^{1}H NMR spectrum of the mixture of (*S*,*S*)-[$Me_2Ga(OCPh_2CH_3)]_2$ and 6-Mes ([Ga]:[6-Mes] = 1:1) in toluene-d_8 (400 MHz).

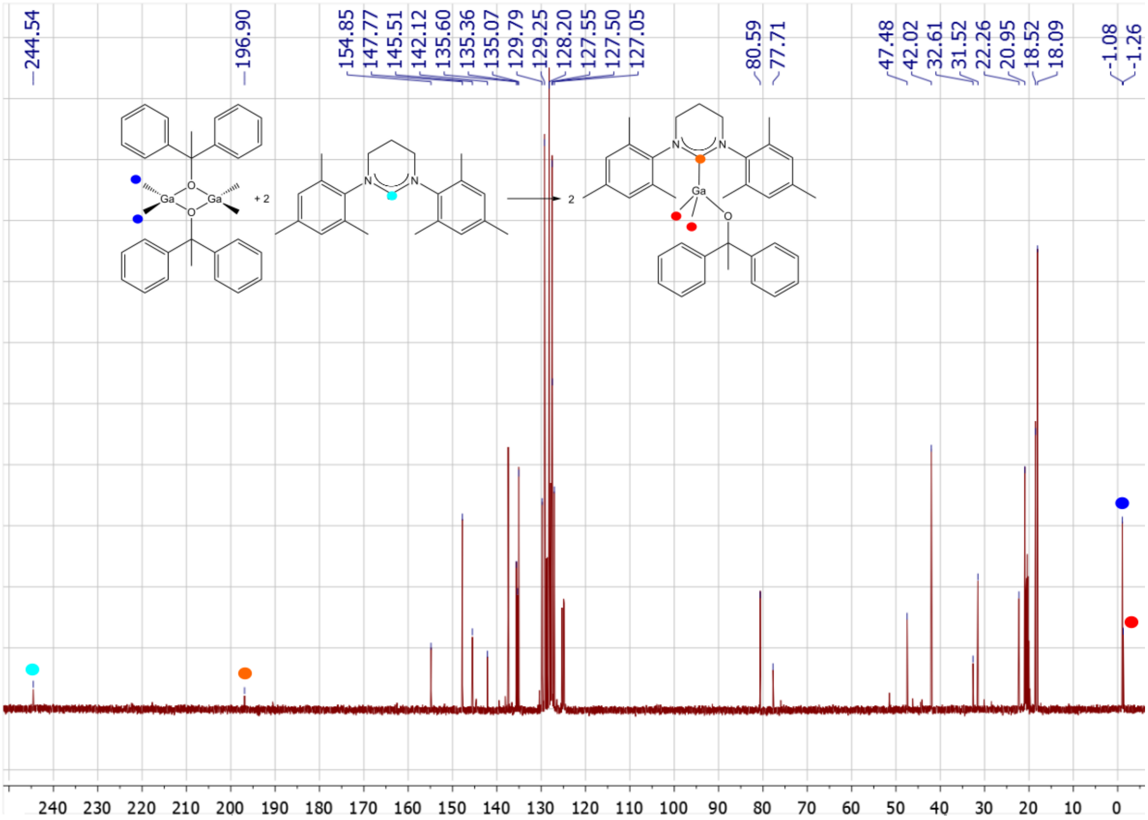


Figure S 24. ^{13}C NMR spectrum of the mixture of (*S*,*S*)-$[Me_2Ga(OCPh_2CH_3)]_2$ and 6-Mes ([Ga]:[6-Mes] = 1:1) in toluene-d_8 (100 MHz).

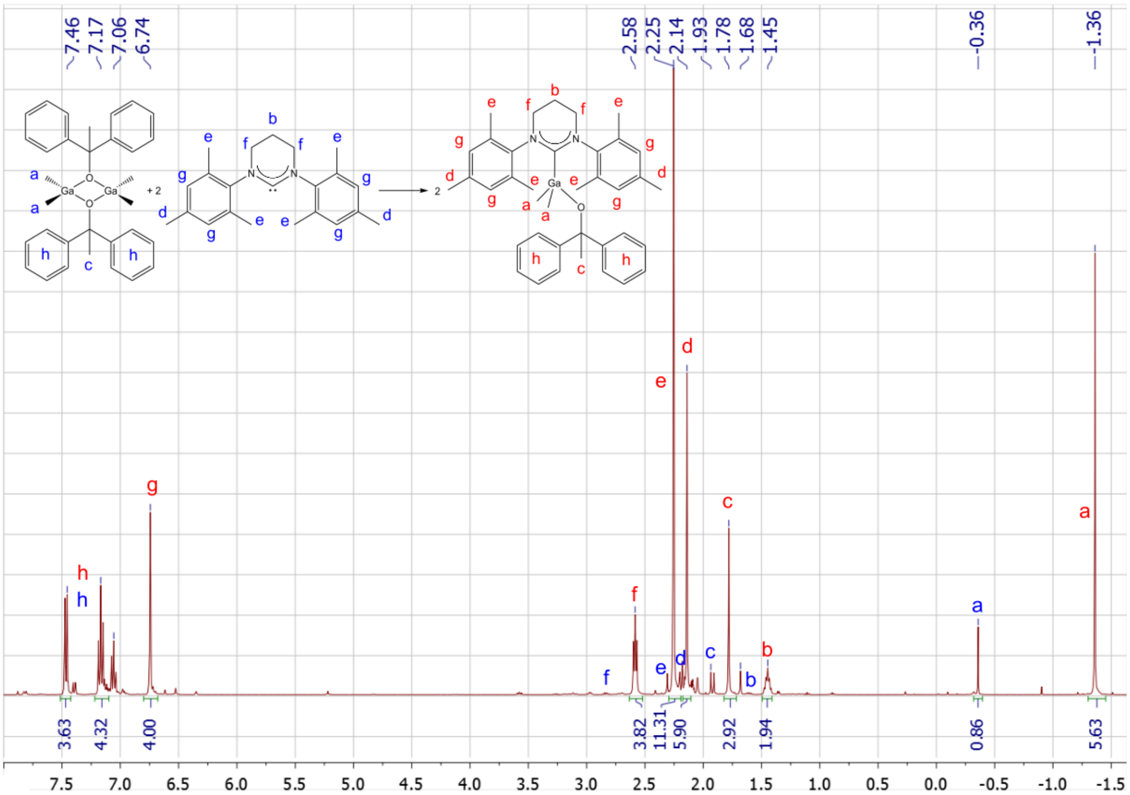


Figure S 25. ^{1}H NMR spectrum of the mixture of (*S*,*S*)-$[Me_2Ga(OCPh_2CH_3)]_2$ and 6-Mes ([Ga]:[6-Mes] = 1:1) 24h after mixing in toluene-d_8 (400 MHz).

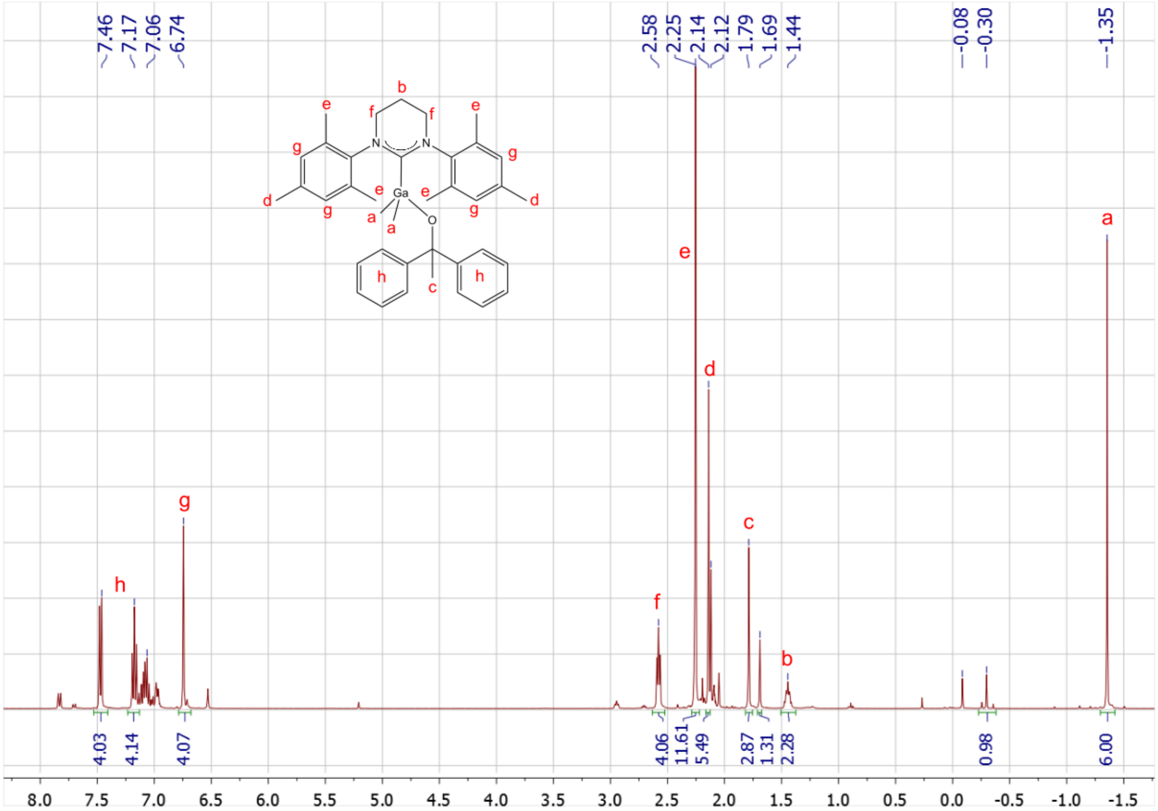


Figure S 26. ^{1}H NMR spectrum of $Me_2Ga(OCPh_2CH_3)(6\text{-}Mes)$ (**3**) in toluene-d_8 (400 MHz).

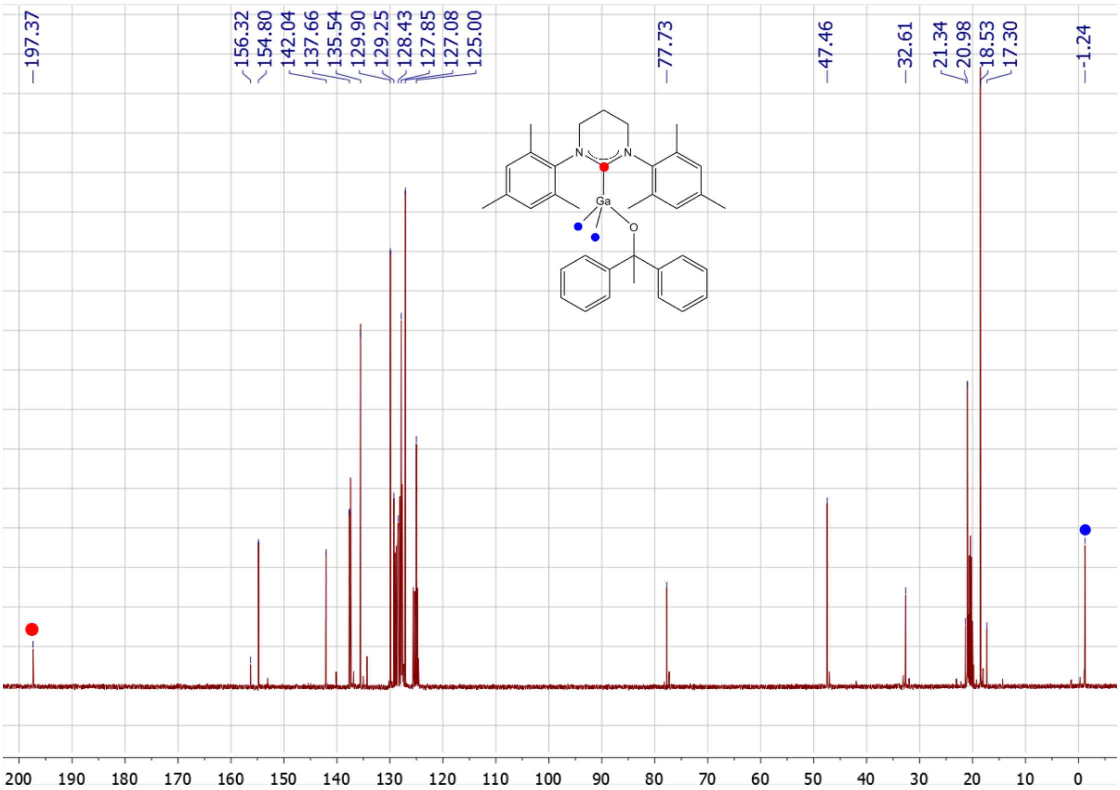


Figure S 27. ^{13}C NMR spectrum of $Me_2Ga(OCPh_2CH_3)(6\text{-}Mes)$ (**3**) in toluene-d_8 (100 MHz).

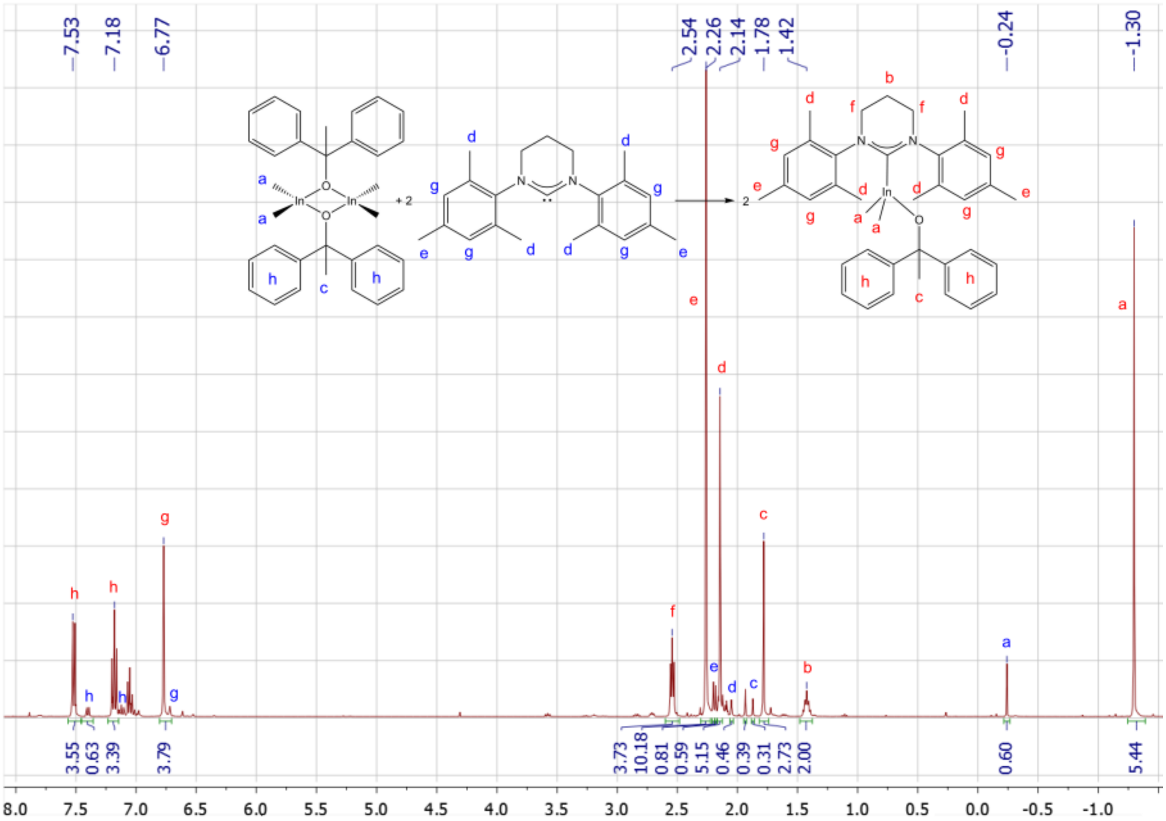


Figure S 28. [1]H NMR spectrum of the mixture of (*S*,*S*)-[$Me_2In(OCPh_2CH_3)]_2$ and 6-Mes ([In]:[6-Mes] = 1:1) in toluene-d_8 (400 MHz).

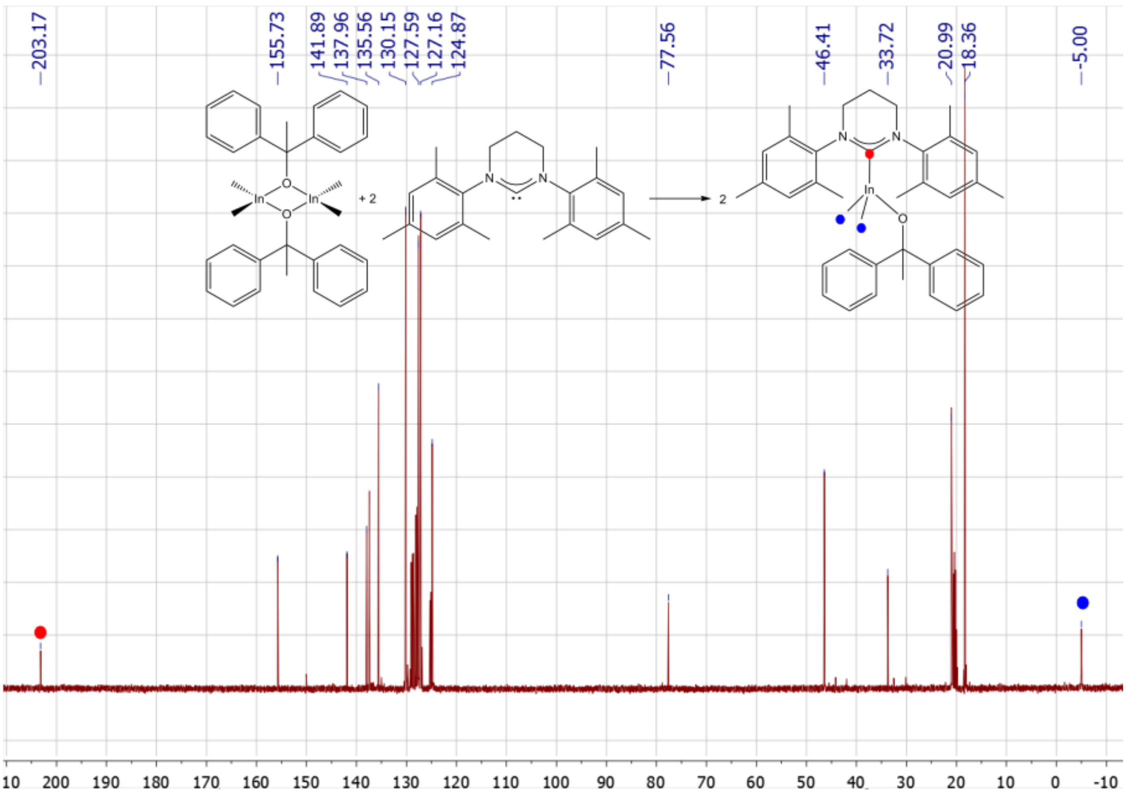


Figure S 29. [13]C NMR spectrum of the mixture of (*S*,*S*)-[$Me_2In(OCPh_2CH_3)]_2$ and 6-Mes ([In]:[6-Mes] = 1:1) in toluene-d_8 (100 MHz).

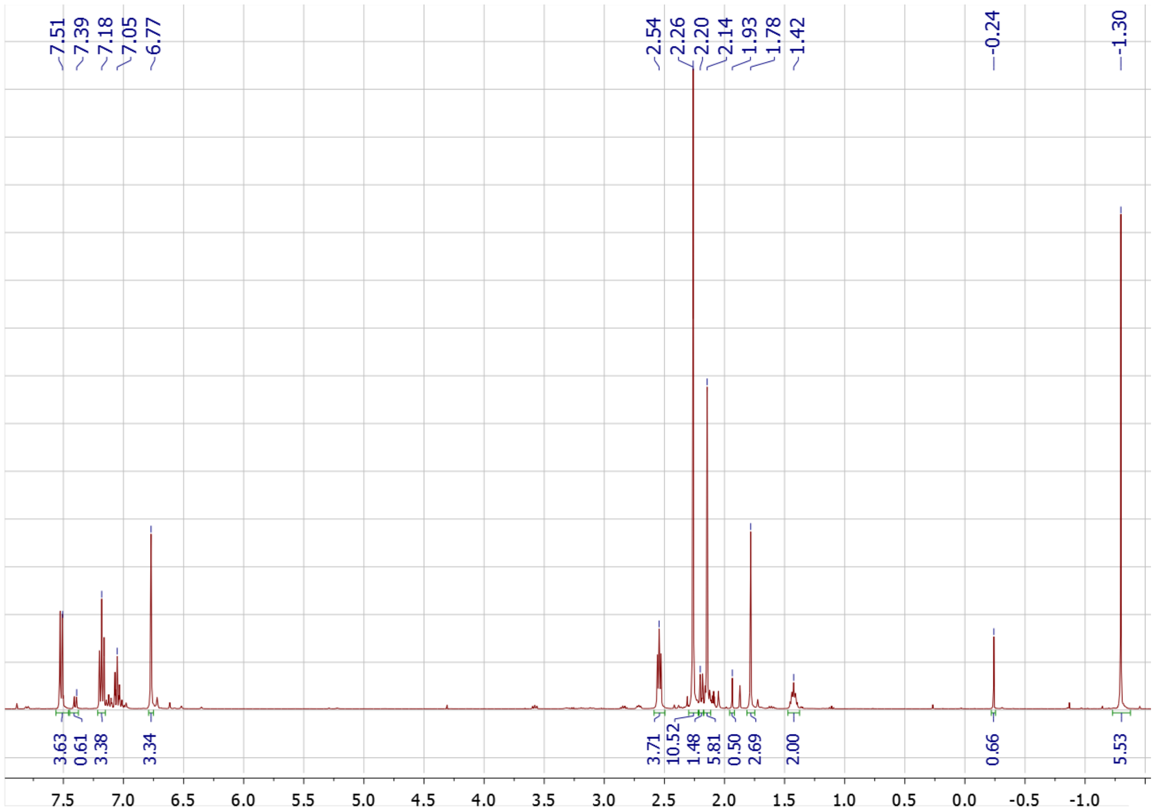


Figure S 30. ^{1}H NMR spectrum of the mixture of (*S*,*S*)-[$Me_2In(OCPh_2CH_3)$]$_2$ and 6-Mes ([In]:[6-Mes] = 1:1) 24h after mixing in toluene-d_8 (400 MHz).

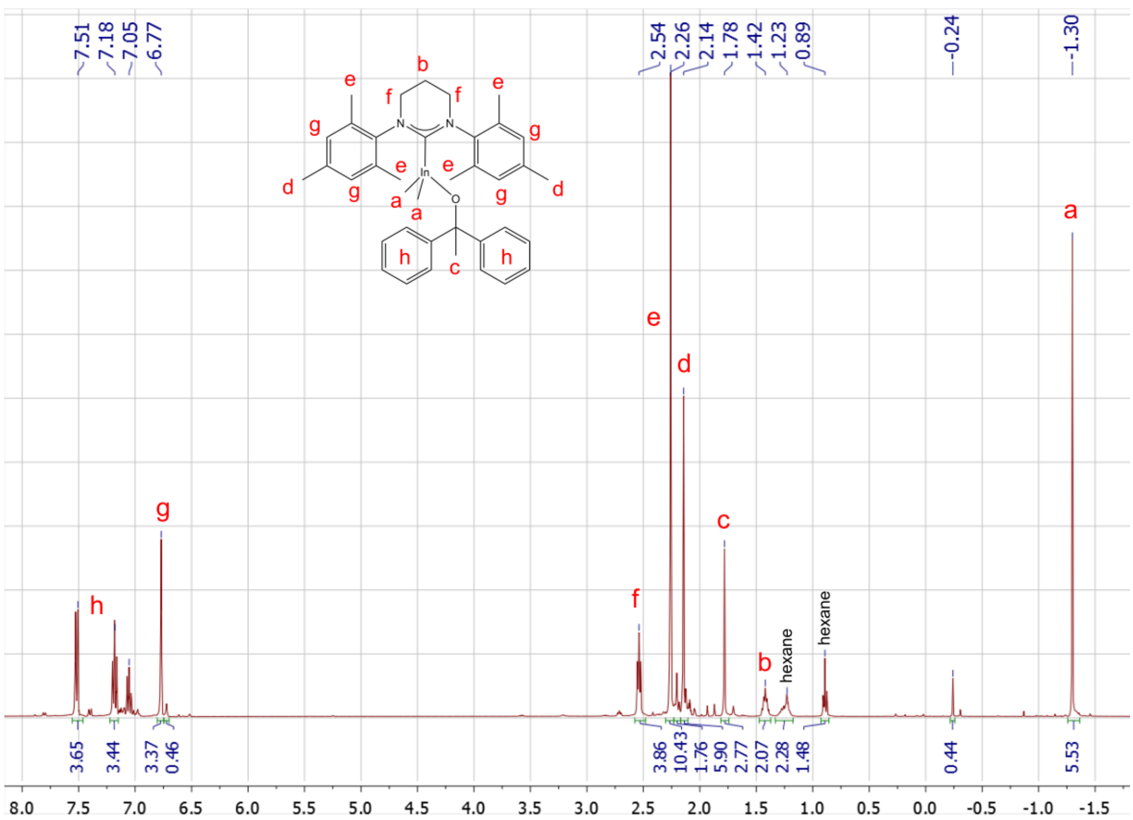


Figure S 31. ^{1}H NMR spectrum of $Me_2In(OCPh_2CH_3)$(6-Mes) (**4**) in toluene-d_8 (400 MHz).

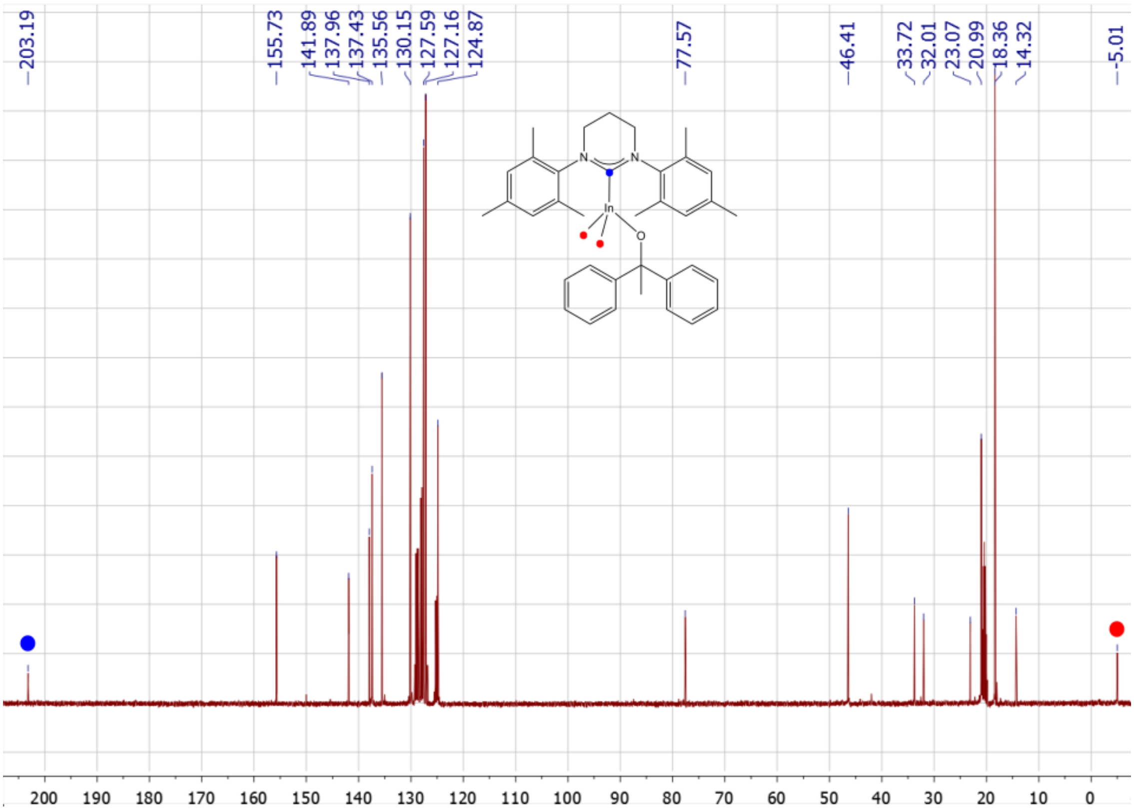


Figure S 32. ^{13}C NMR spectrum of $Me_2In(OCPh_2CH_3)$(6-Mes) (**4**) in toluene-d_8 (100 MHz).

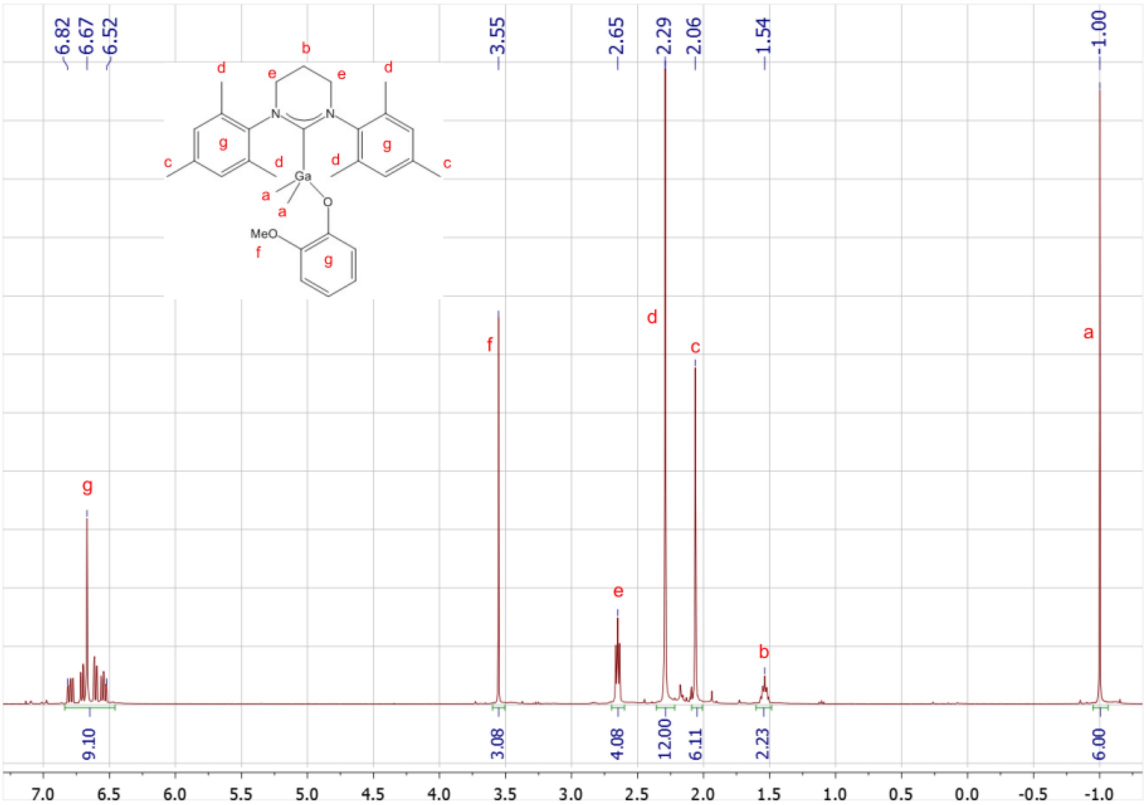


Figure S 33. ^{1}H NMR spectrum of $Me_2Ga(OC_6H_4OMe)$(6-Mes) (**5**) in toluene-d_8 (400 MHz).

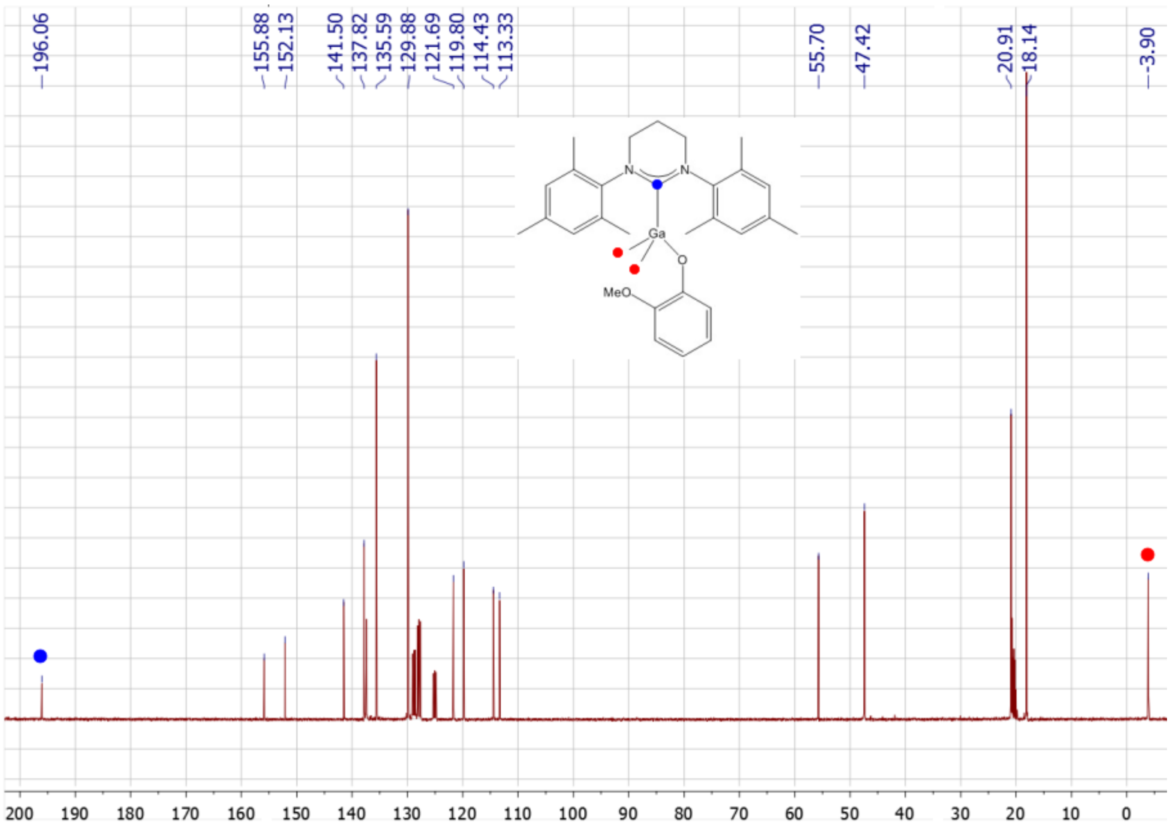


Figure S 34. [13]C NMR spectrum of the mixture of of $Me_2Ga(OC_6H_4OMe)(6\text{-}Mes)$ (**5**) in toluene-d_8 (100 MHz).

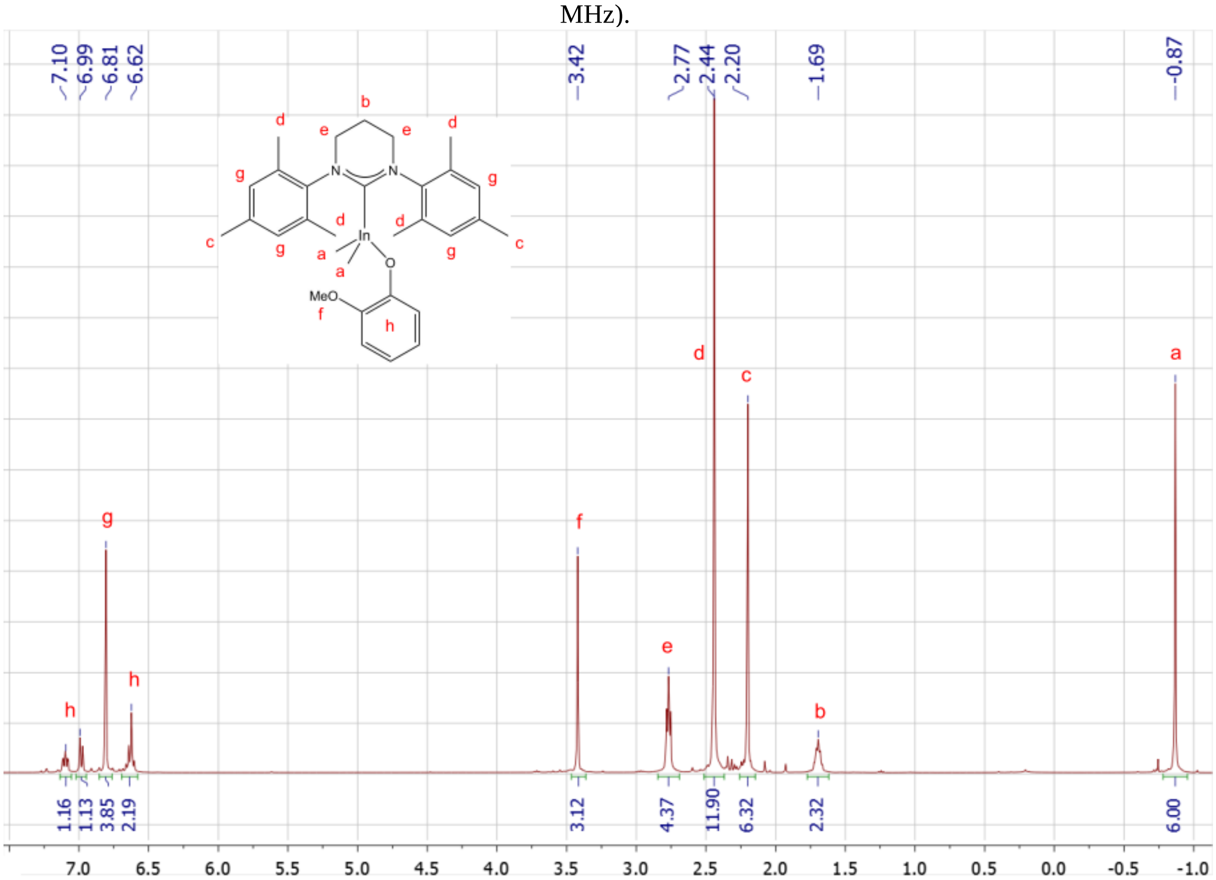


Figure S 35. [1]H NMR spectrum of of $Me_2In(OC_6H_4OMe)(6\text{-}Mes)$ (**6**) in toluene-d_8 (400 MHz).

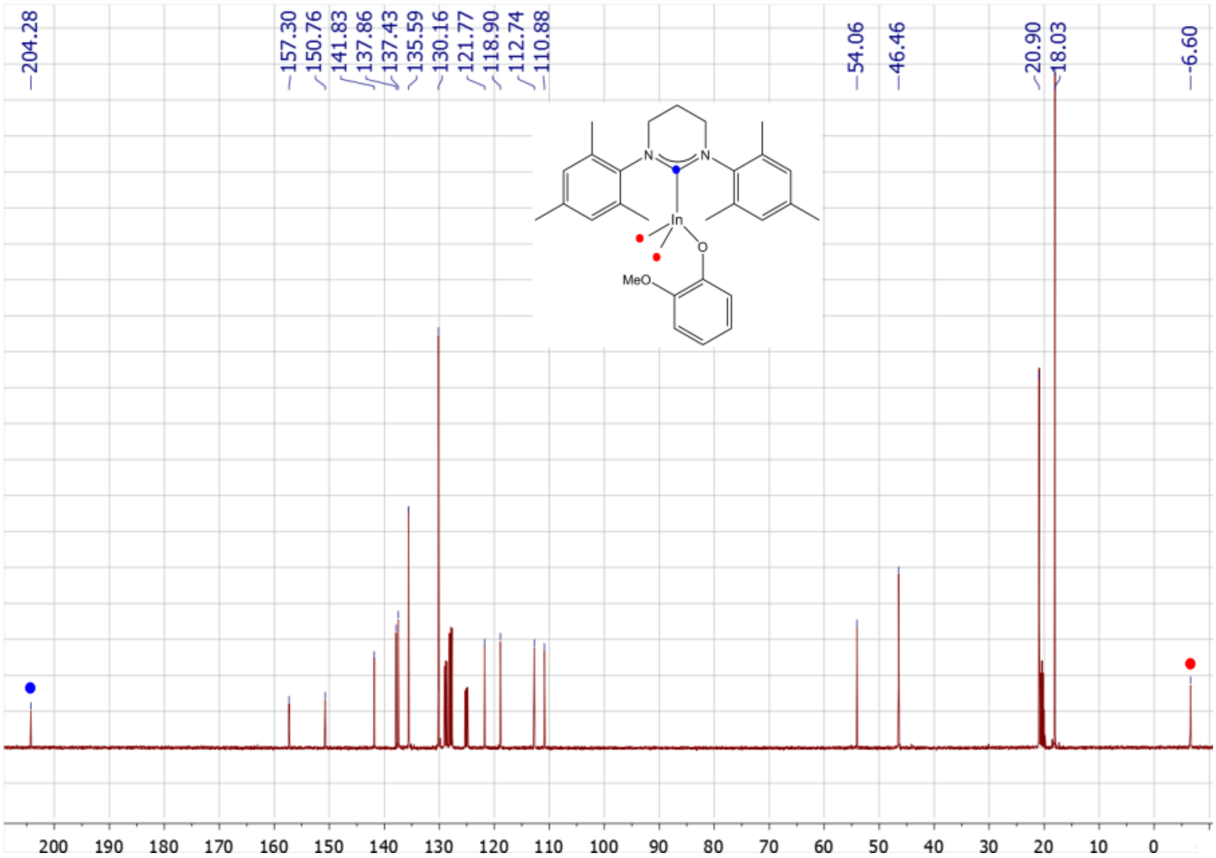


Figure S 36. ^{13}C NMR spectrum of $Me_2In(OC_6H_4OMe)$(6-Mes) (**6**) in toluene-d_8 (100 MHz).

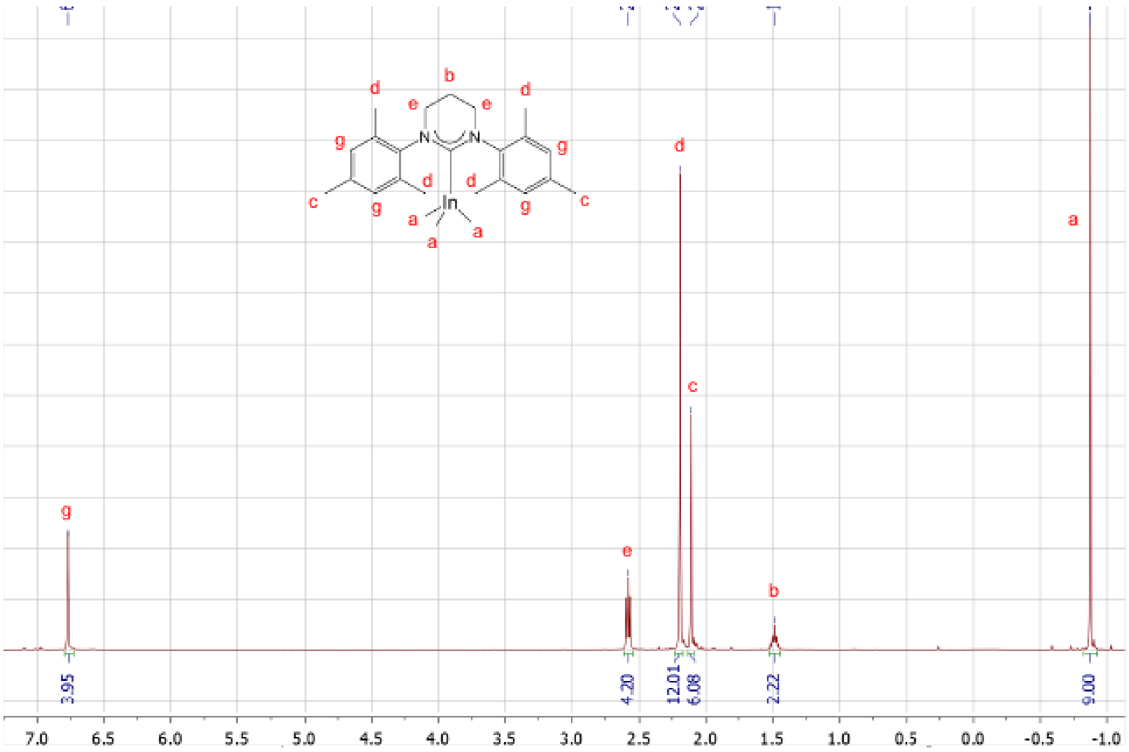


Figure S 37. ^{1}H NMR spectrum of Me_3In(6-Mes) (**2**) in toluene-d_8 (400 MHz).

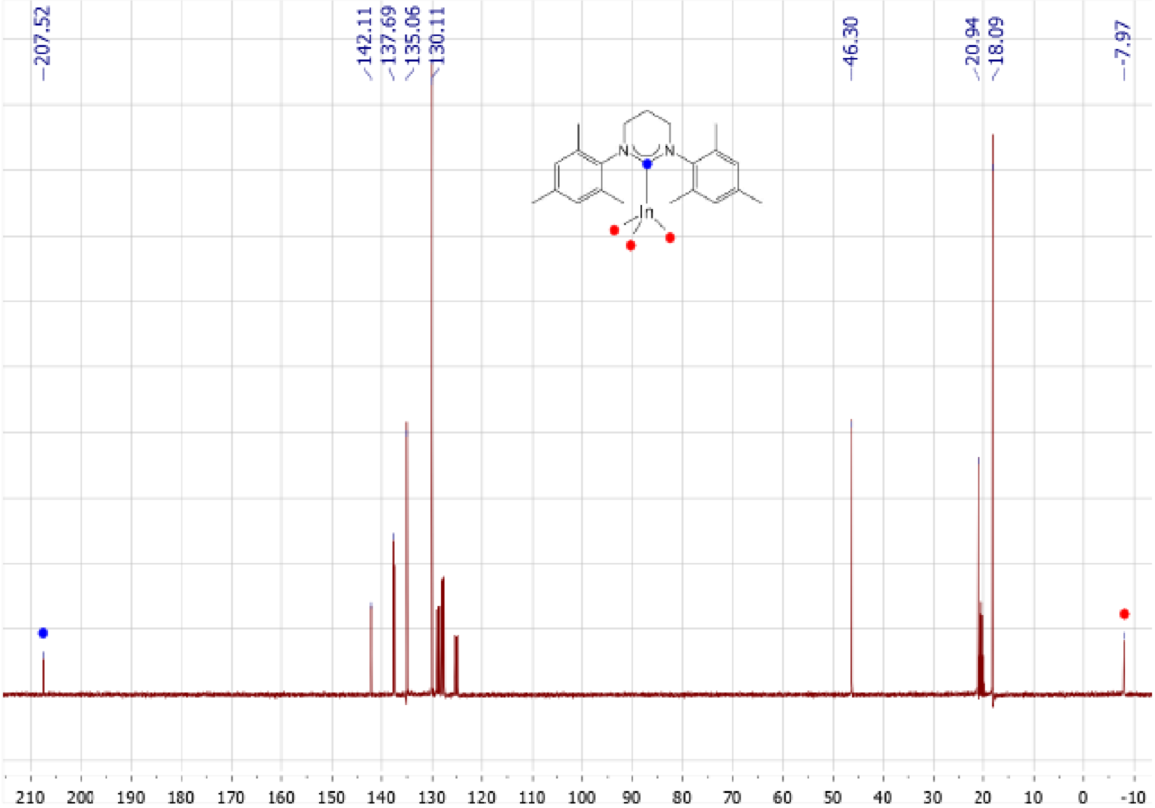


Figure S 3. [13]C NMR spectrum of Me_3In(6-Mes) (**2**) in toluene-d_8 (100 MHz).

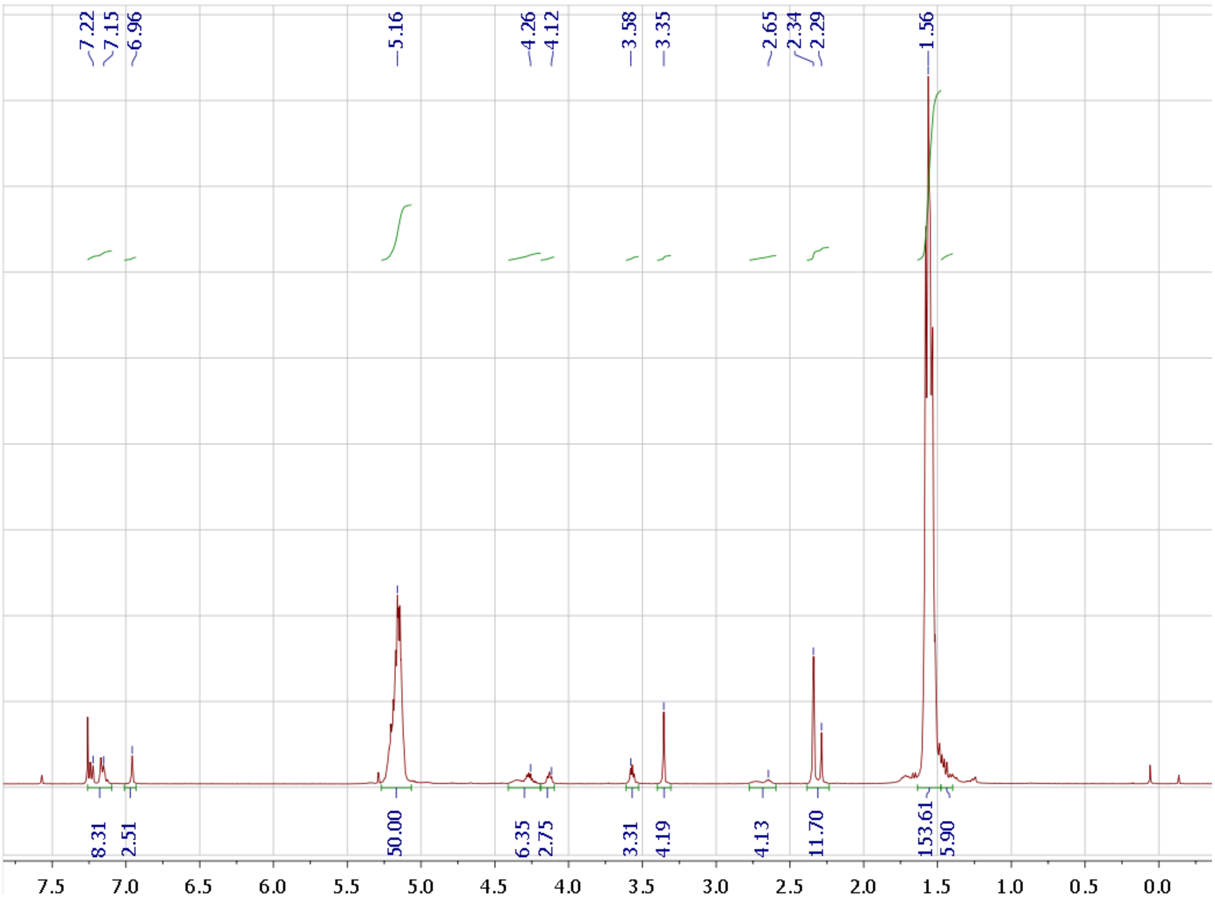


Figure S 39. [1]H NMR spectrum of PLA prepared by polymerization of *rac*-LA with **1** (toluene, rt, 10 min.); $CDCl_3$.

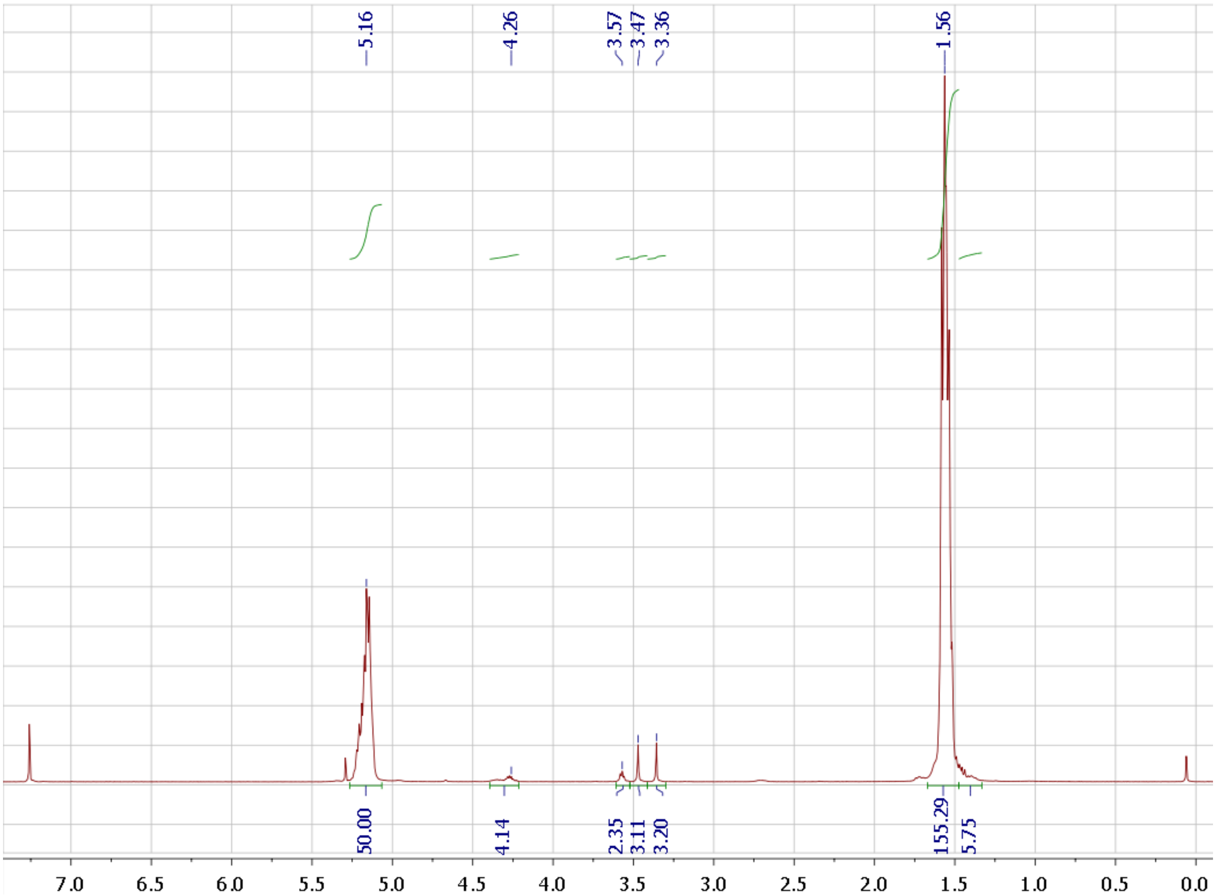


Figure S 40. ^{1}H NMR spectrum of precipitated PLA prepared by polymerization of *rac*-LA with **1** as catalyst

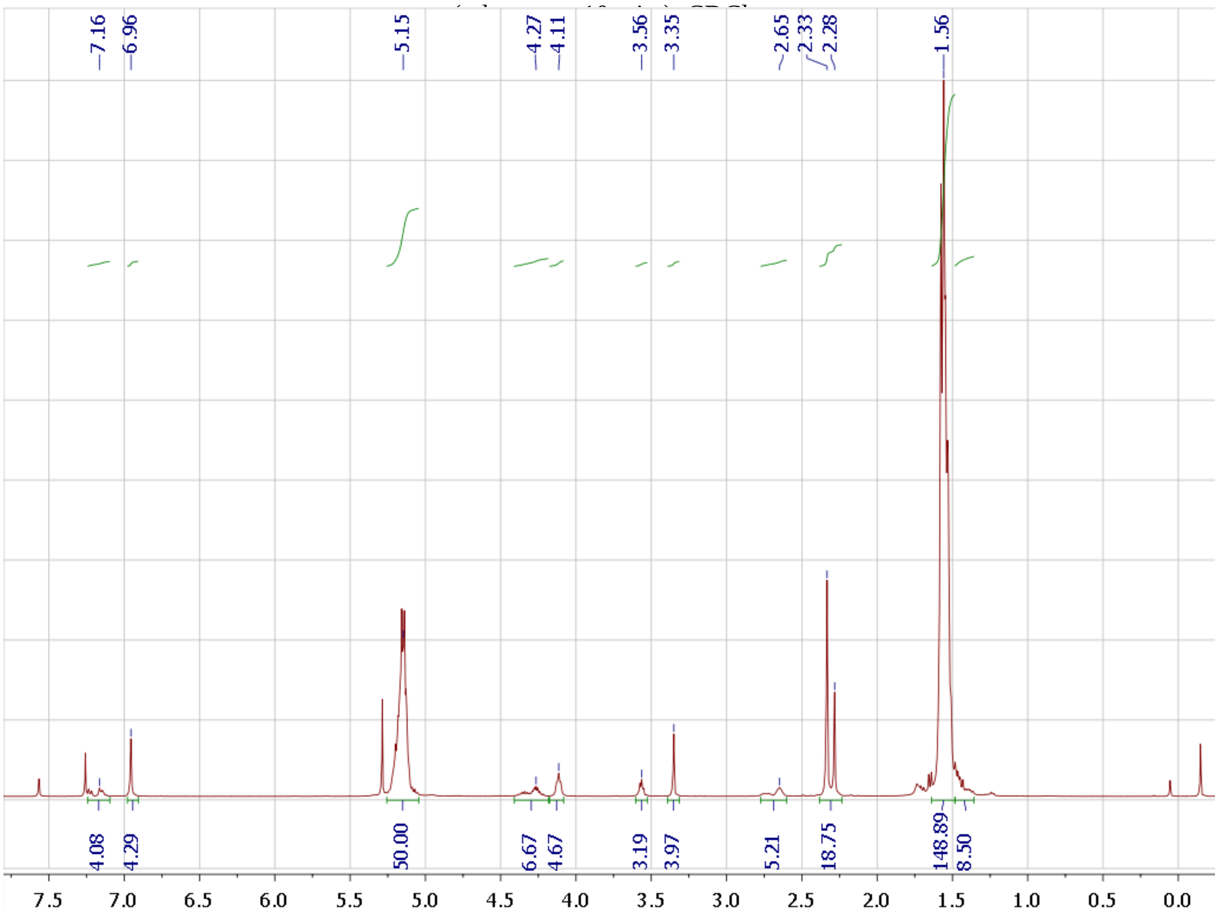


Figure S 41. ^{1}H NMR spectrum of PLA prepared by polymerization of *rac*-LA with **1** (toluene, -20°C, 12h); $CDCl_3$.

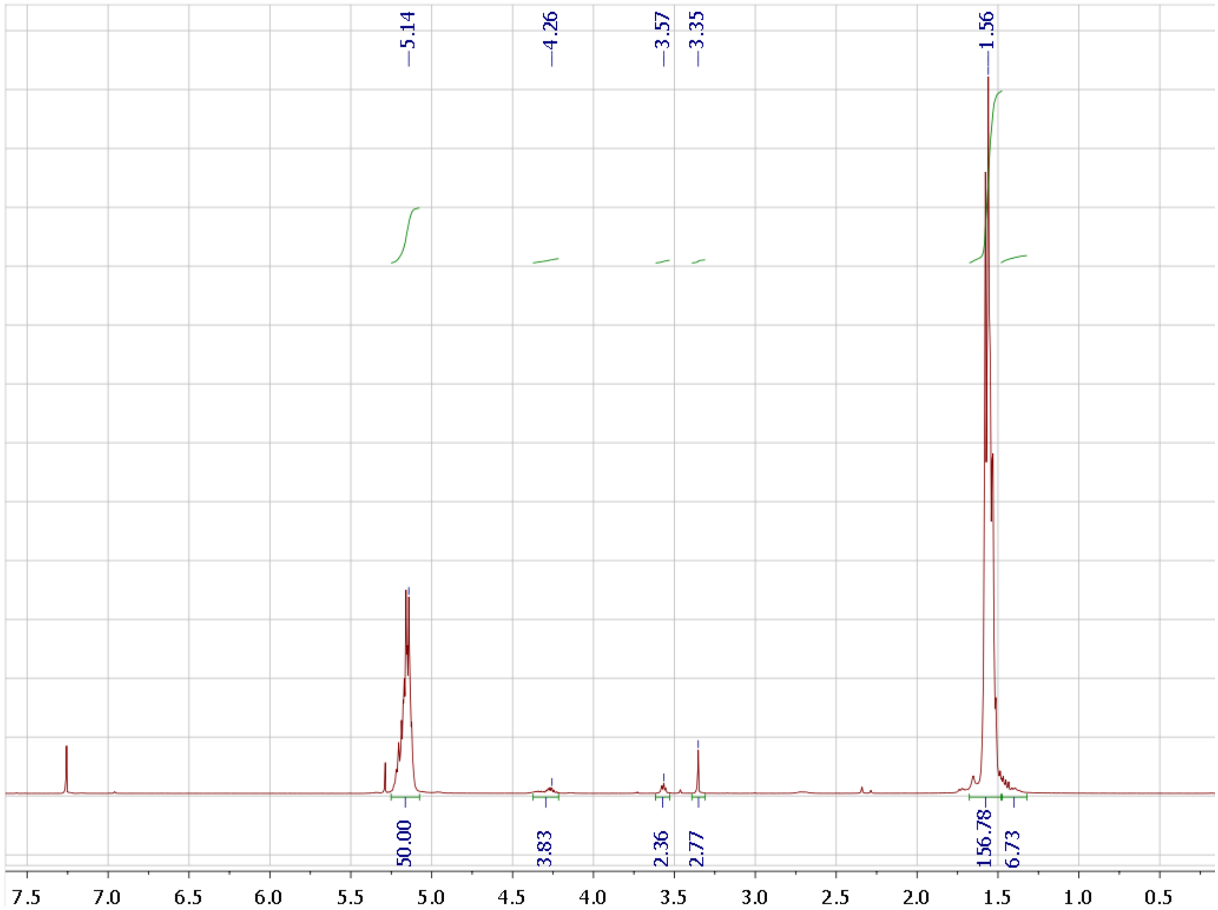


Figure S 42. ^{1}H NMR spectrum of precipitated PLA prepared by polymerization of *rac*-LA with **1** as catalyst (toluene, -20°C, 12h); $CDCl_3$.

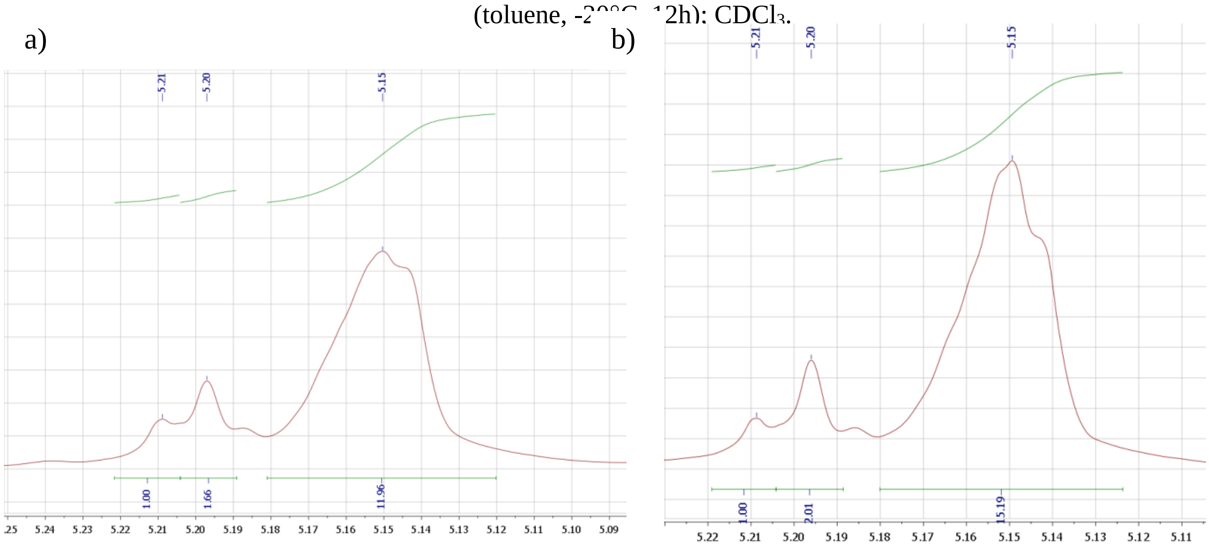


Figure S 43. Homonuclear decoupled ^{1}H NMR ($CDCl_3$, 400MHz,) spectra of the methine region of polylactide prepared by polymerization of *rac*-LA with **1** a) in toluene, rt, 10 min.; $P_m = 0.63$; b) in toluene, -20°C, 12h; $P_m = 0.66$.

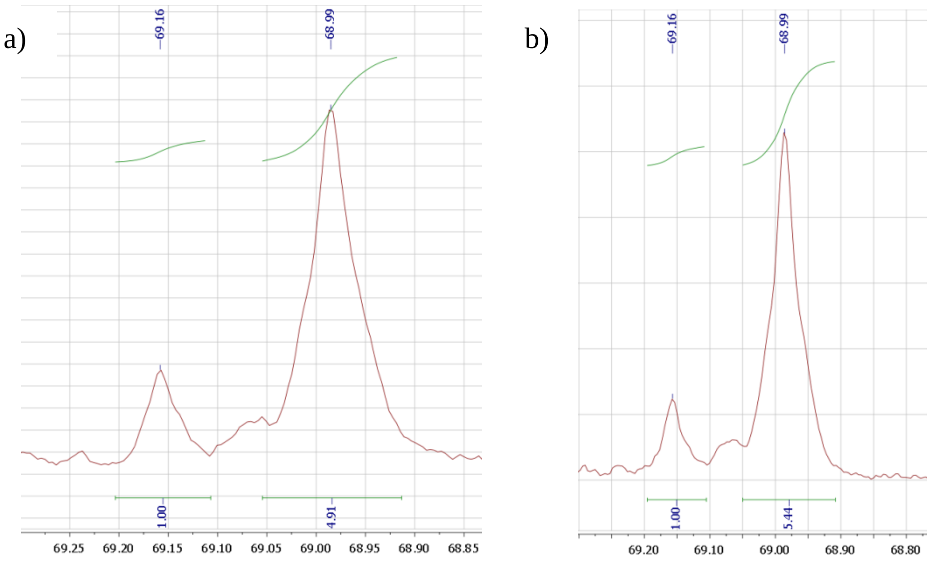


Figure S 44. ^{13}C NMR ($CDCl_3$, 100MHz,) spectra of the methine region of polylactide prepared by polymerization of *rac*-LA with **1** a) in toluene, rt, 10 min., $P_m = 0.66$; b) in toluene, -20°C, 12h, $P_m = 0.69$.

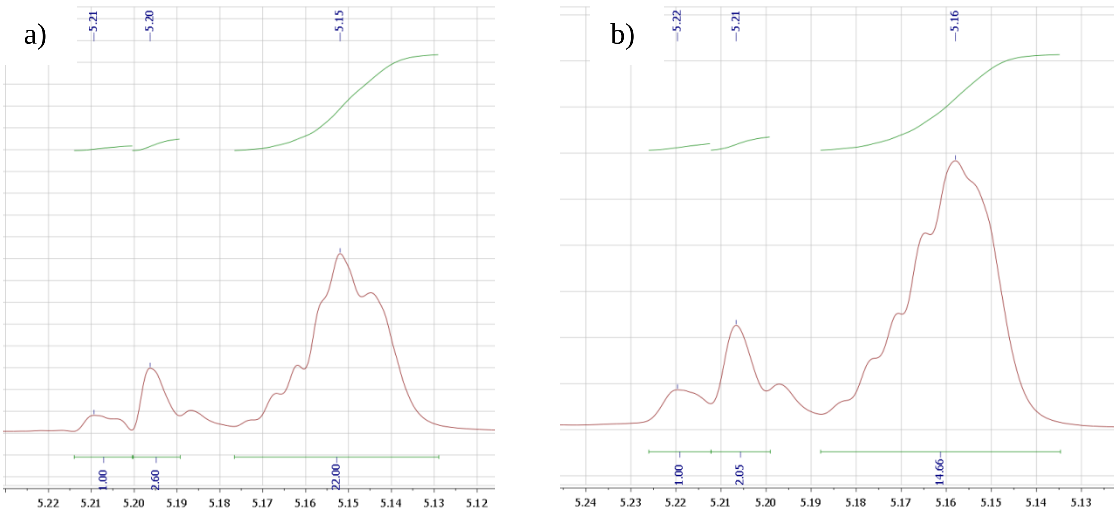


Figure S 45. Homonuclear decoupled ^{1}H NMR ($CDCl_3$, 400MHz,) spectra of the methine region of polylactide prepared by polymerization of *rac*-LA with a) **6**, in methylene chloride, -20°C, 3h, $P_m = 0.72$; b) **4**, in methylene chloride, -20°C, 3h, $P_m = 0.67$.

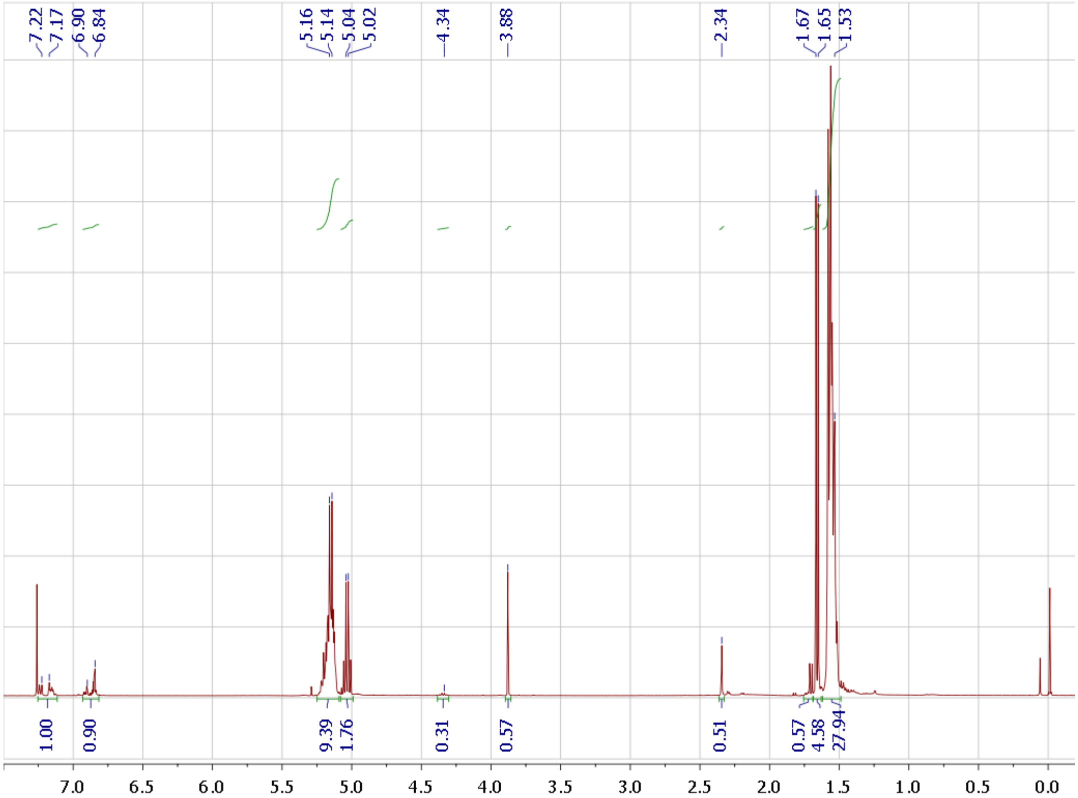


Figure S 46. [1]H NMR spectrum of PLA prepared by polymerization of *rac*-LA with **6** as catalyst (CH_2Cl_2, -20˚C, 3h); $CDCl_3$.

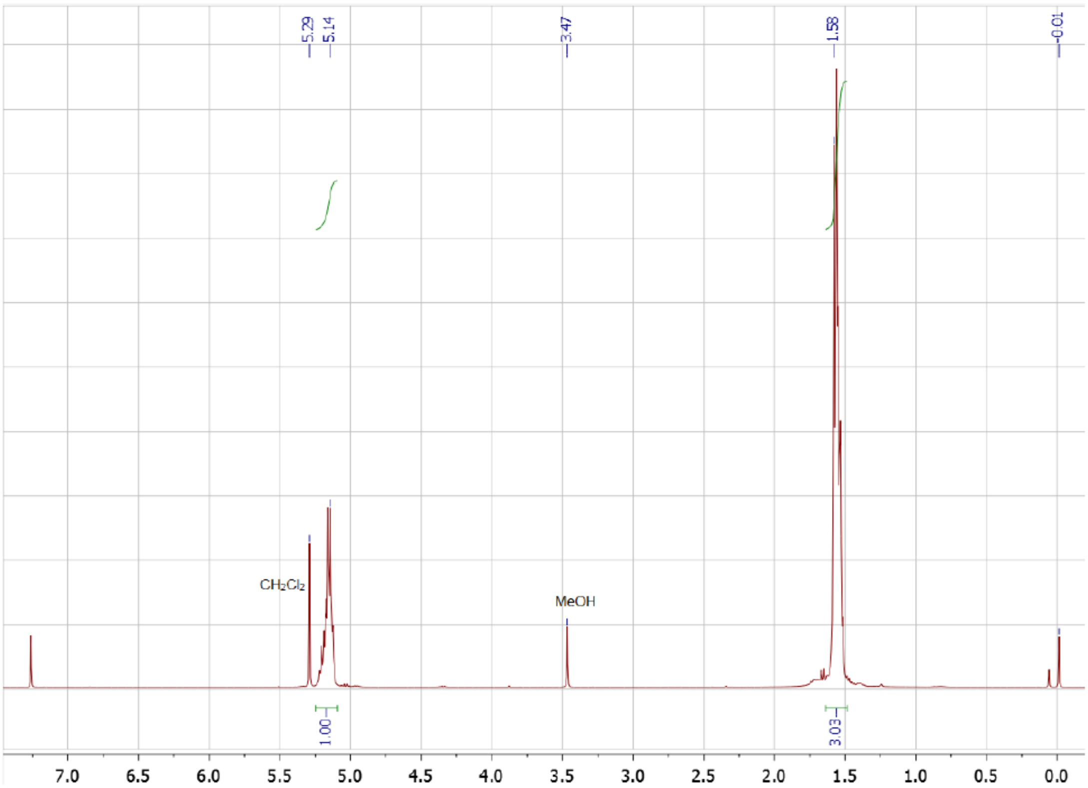


Figure S 47. [1]H NMR spectrum of precipitated PLA prepared by polymerization of *rac*-LA with **6** as catalyst (CH_2Cl_2, -20˚C, 3h); $CDCl_3$.

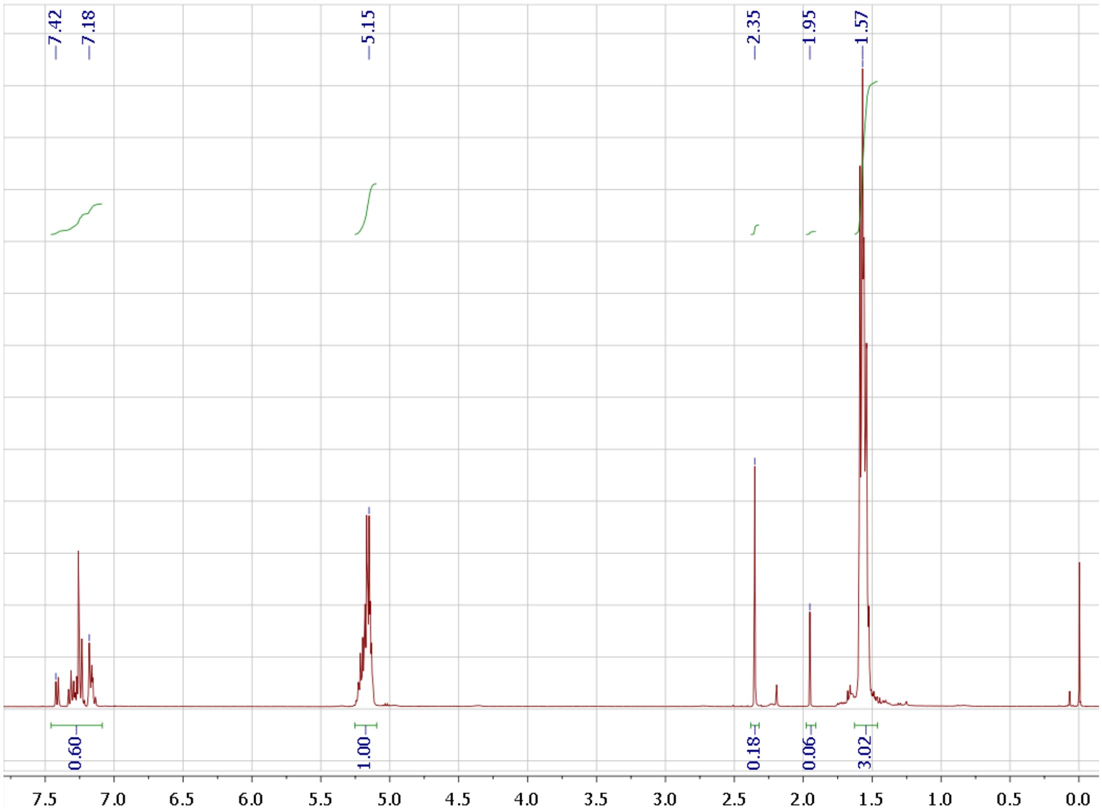


Figure S 48. [1]H NMR spectrum of PLA prepared by polymerization of *rac*-LA with **4** as catalyst (CH_2Cl_2, -20˚C, 3h); $CDCl_3$.

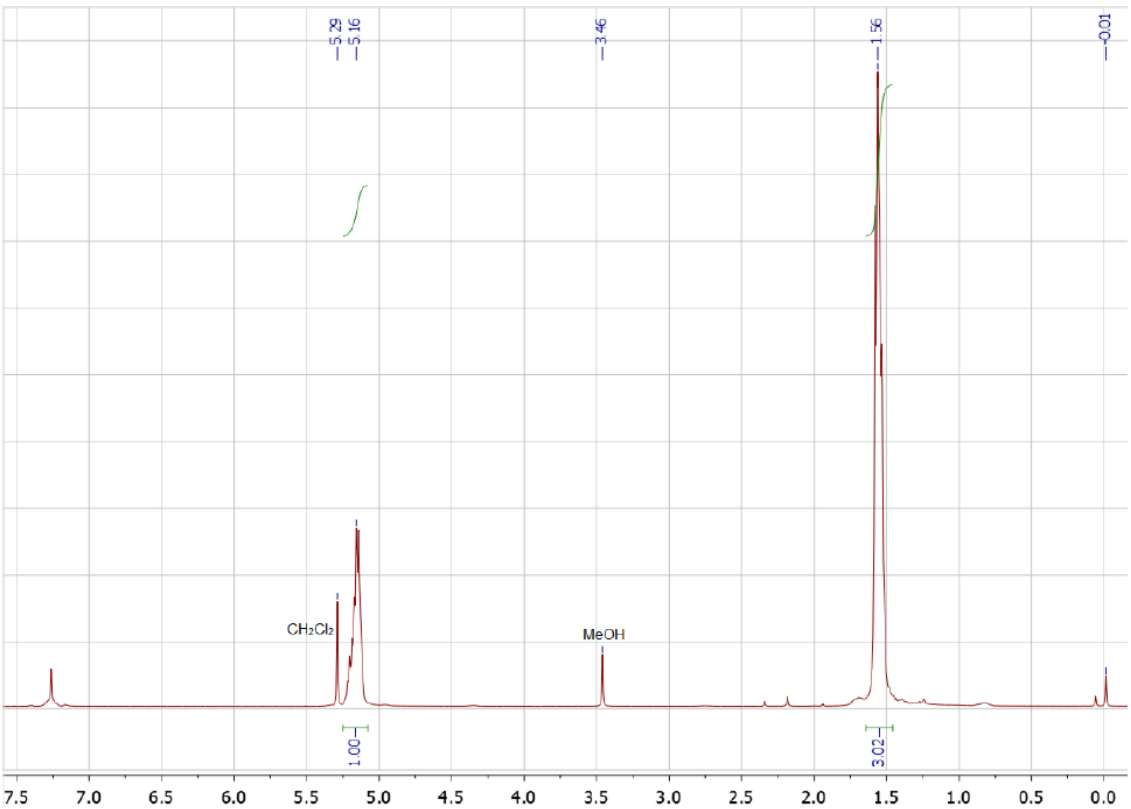


Figure S 49. [1]H NMR spectrum of precipitated PLA prepared by polymerization of *rac*-LA with **4** as catalyst (CH_2Cl_2, -20˚C, 3h); $CDCl_3$.

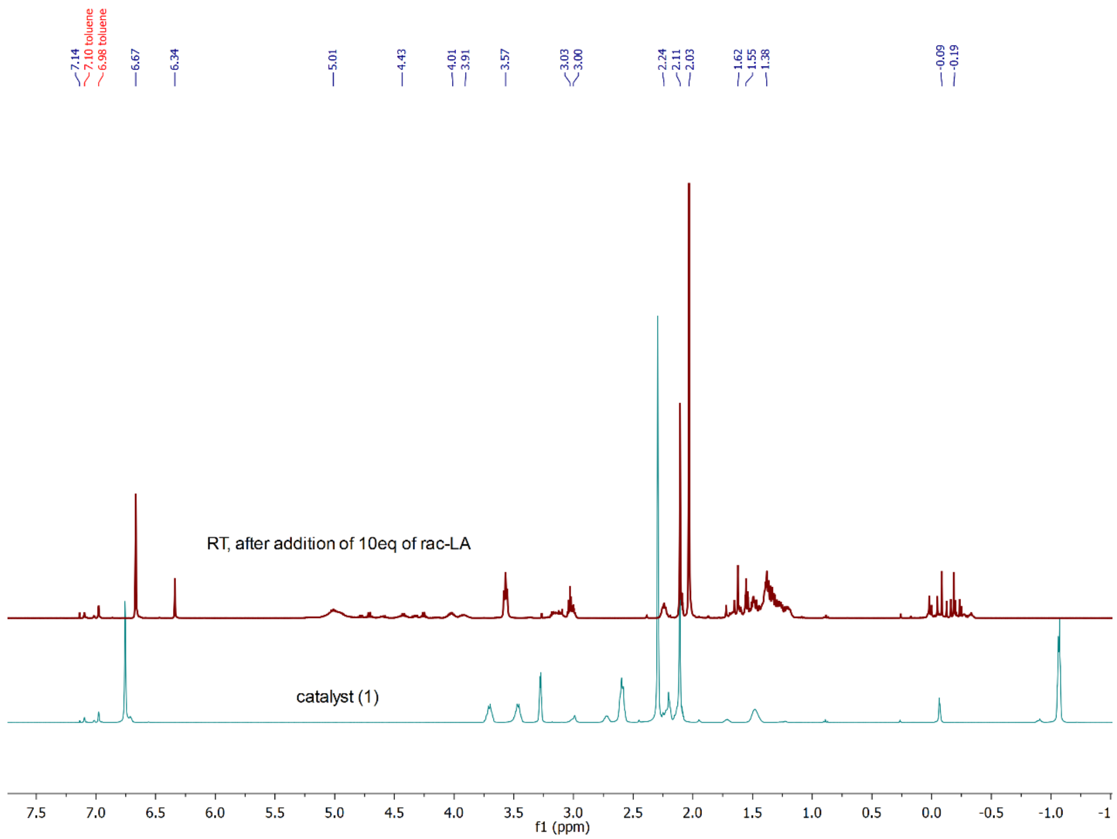


Figure S 50. ^{1}H NMR spectrum of the reaction of **1** with 10 eq of *rac*-LA at room temperature (red), compared to the spectrum of the catalyst (**1**, green) (toluene-d_8, 400 MHz).

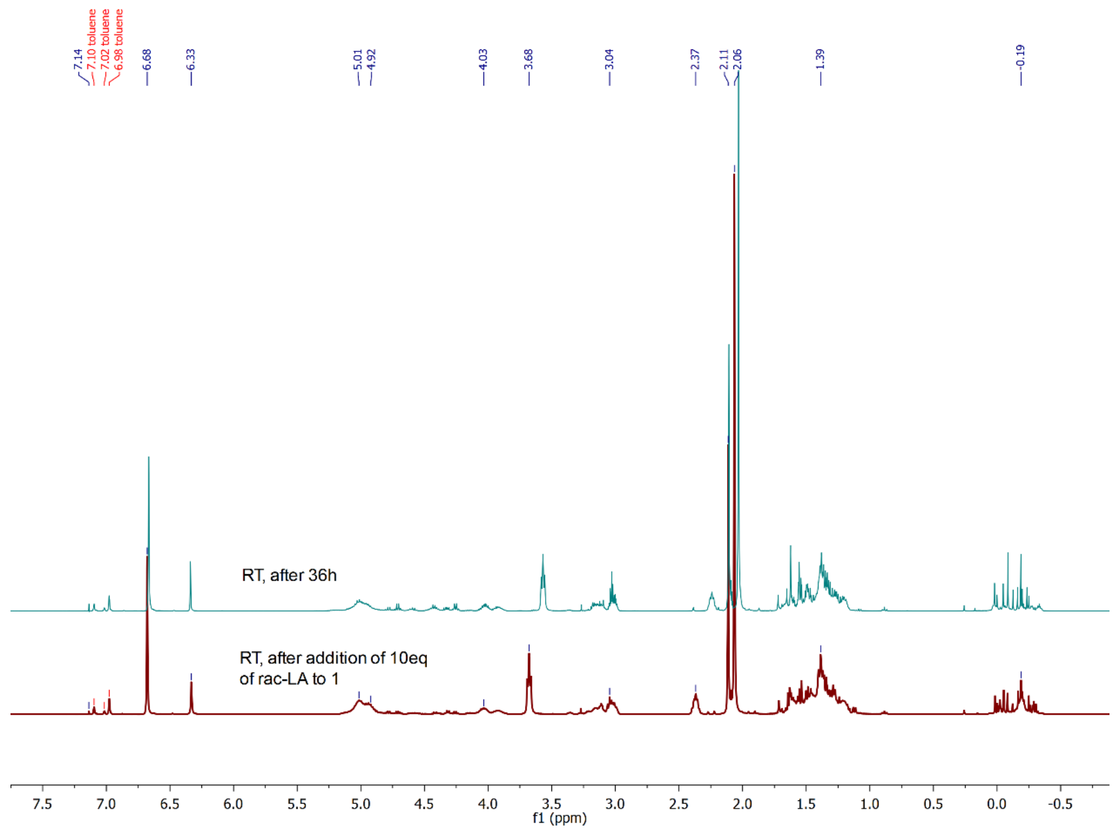


Figure S 51. ^{1}H NMR spectrum of the reaction of **1** with 10 eq of *rac*-LA at room temperature (red), and the same reaction mixture after 36 hours (green) (toluene-d_8, 400 MHz).

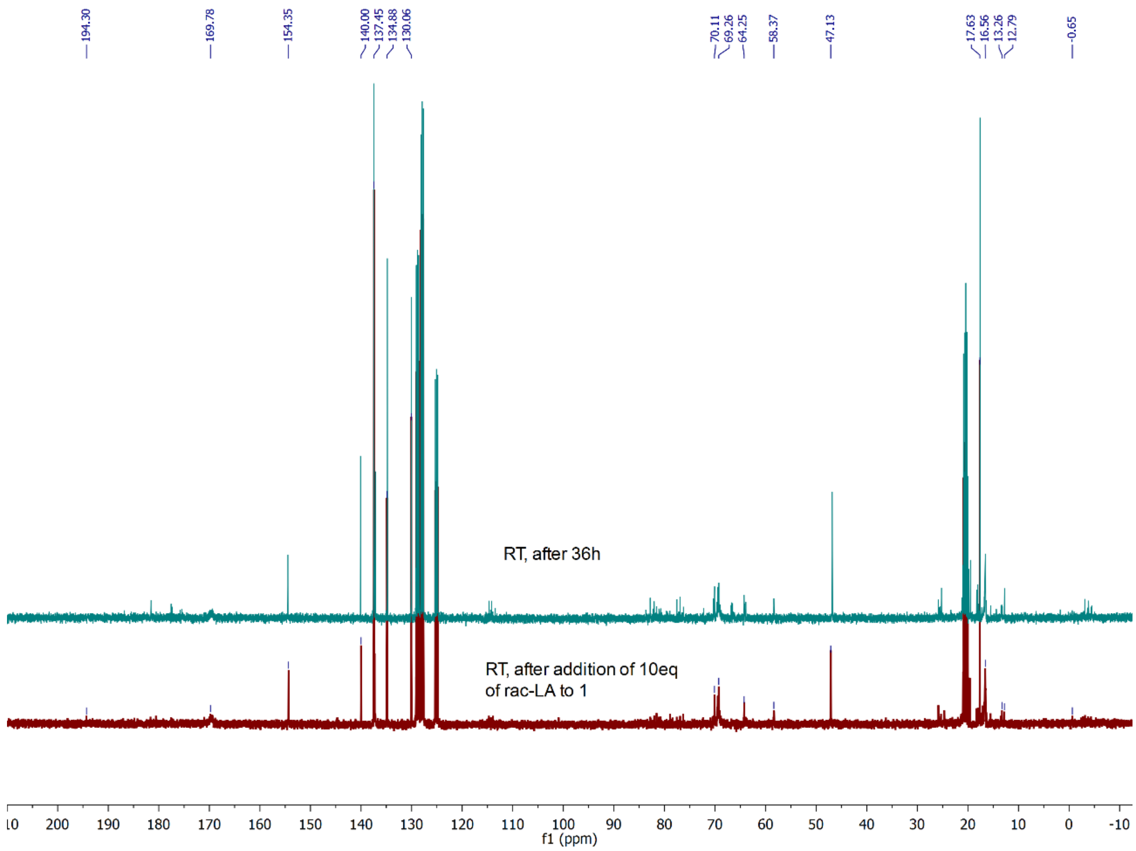


Figure S 52. ^{13}C NMR spectrum of the reaction of **1** with 10 eq of *rac*-LA at room temperature (red), and the same reaction mixture after 36 hours (green) (toluene-d_8, 100 MHz).

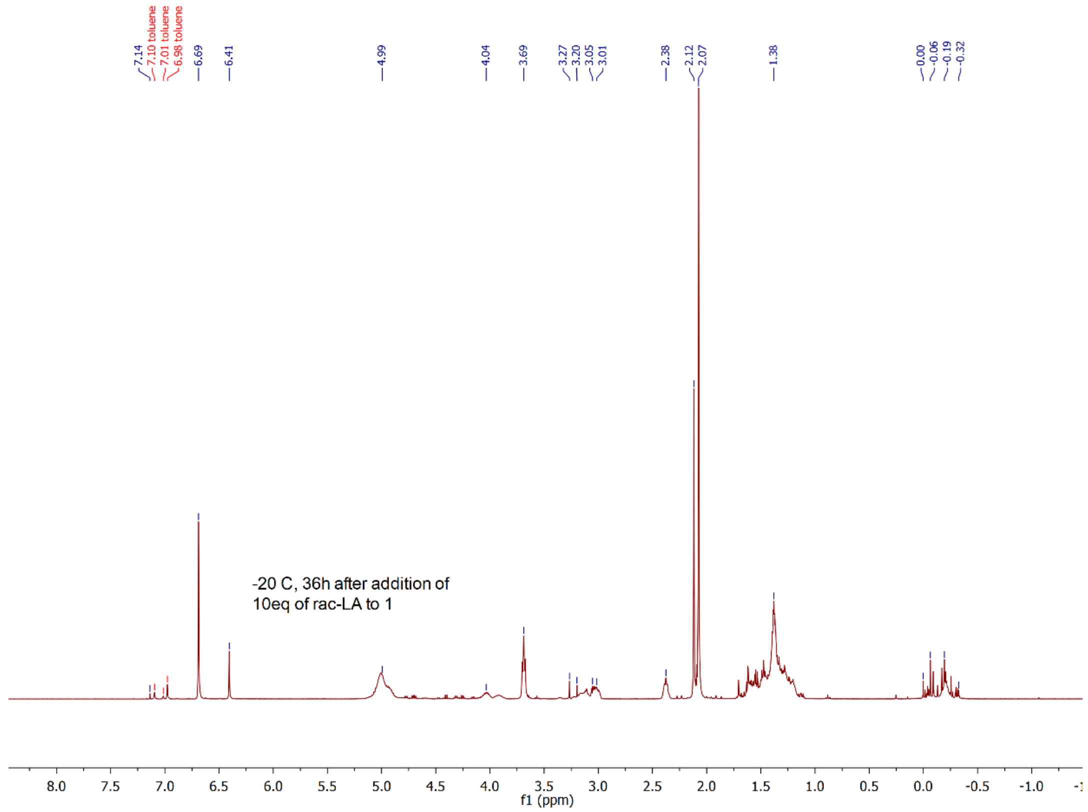


Figure S 53. ^{1}H NMR spectrum of the reaction of **1** with 10 eq of *rac*-LA at -20°C, after 36 hours (toluene-d_8, 400 MHz).

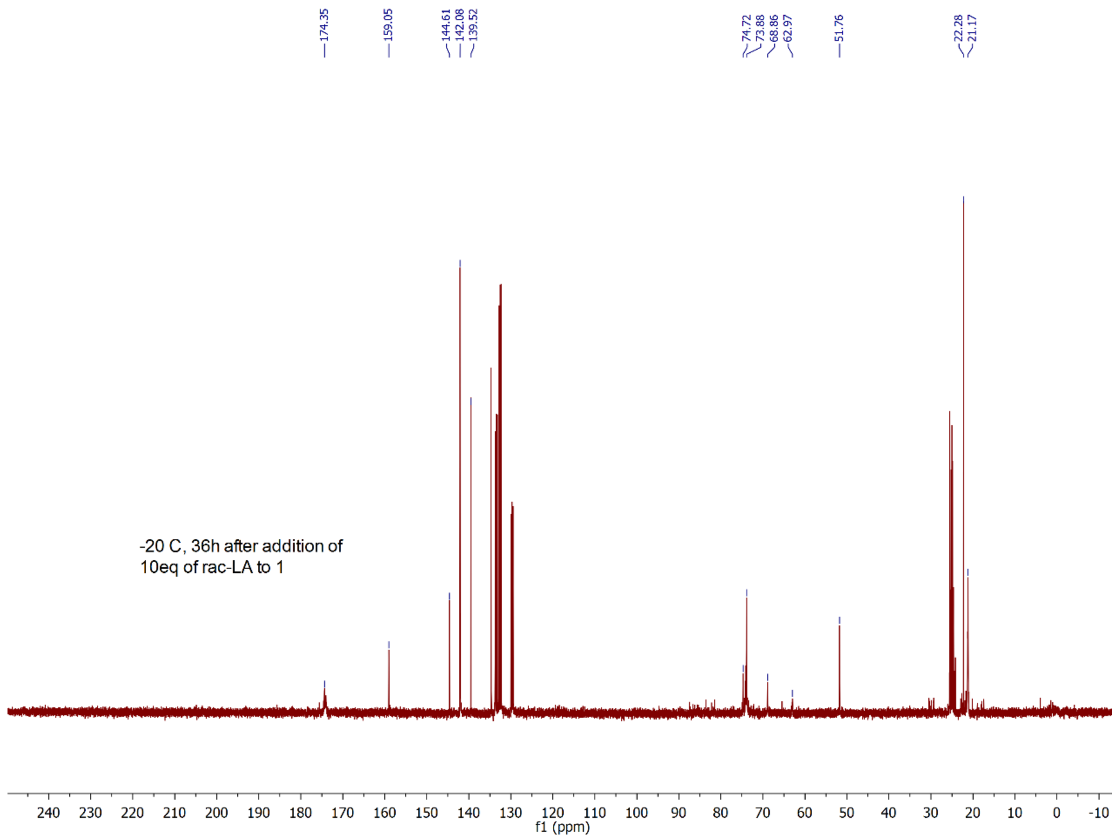
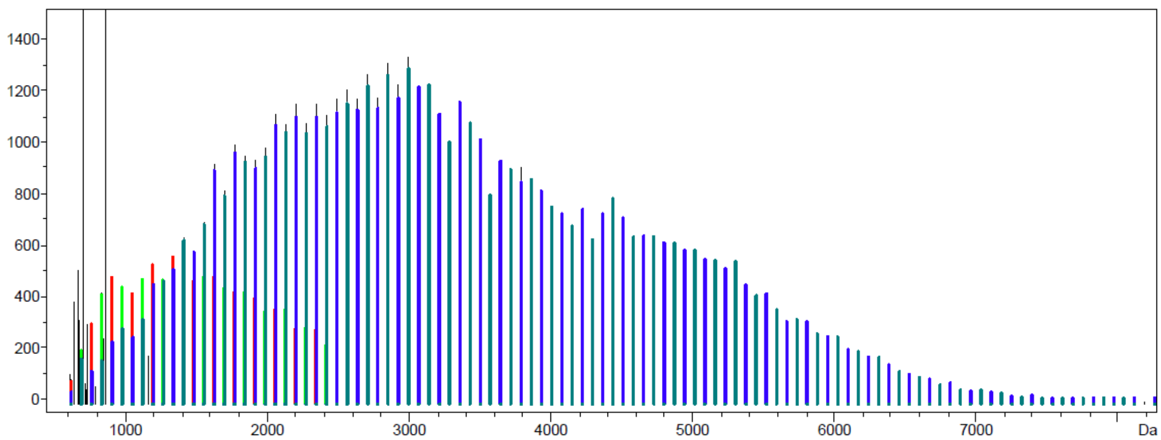


Figure S 54. ^{13}C NMR spectrum of the reaction of **1** with 10 eq of *rac*-LA at at -20°C, after 36 hours (toluene-d_8, 100 MHz).



n	ser.	rep.unit	resid.	end1	end2	cation	Mn	Mw	pd	DP	% I.	cnt
1	1	144.018	0.19804			38.9637	1479.65	1645.97	1.11240	10.2741	7	14
2	2	144.018	4.06095			38.9637	3298.42	3879.97	1.17631	22.9028	38.3	57
3	3	144.018	72.2133			38.9637	1508.88	1685.37	1.11697	10.4770	6.8	14
4	4	144.018	76.0900			38.9637	3295.54	3877.57	1.17661	22.8828	37.9	52

Figure S 55. MALDI-TOF spectrum of PLA (T-2-(3-(4-*t*-butyl-phenyl)-2-methyl-2-propenylidene) malononitrile (DCTB) was used as a matrix) obtained by polymerization of 25 equiv. of *rac*-LA with 1as initiator, in toluene, rt, 10 min.

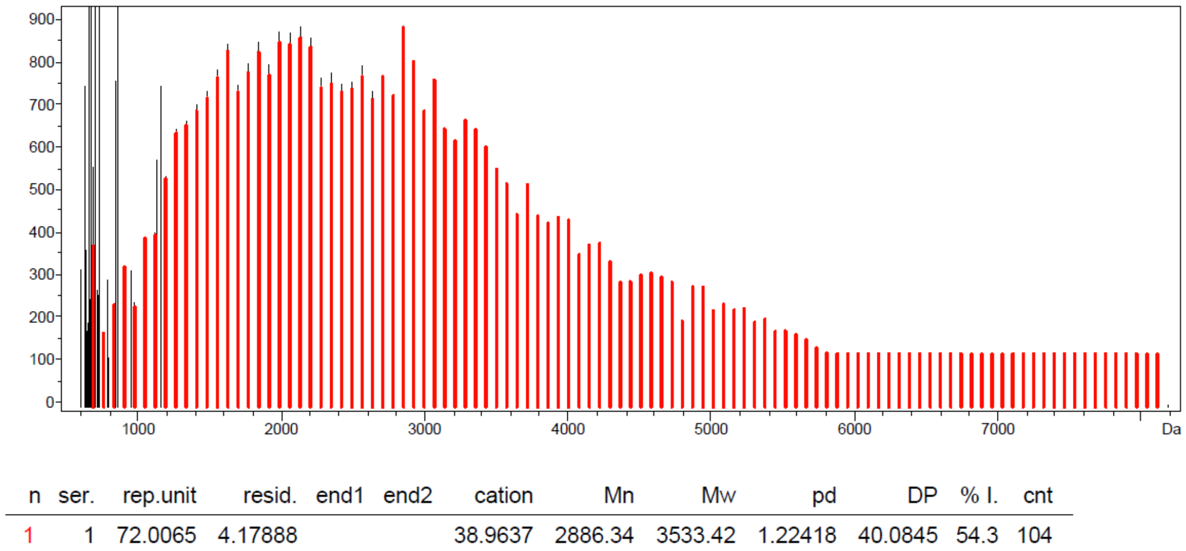


Figure S 56. MALDI-TOF spectrum of PLA (T-2-(3-(4-*t*-butyl-phenyl)-2-methyl-2-propenylidene) malononitrile (DCTB) was used as a matrix) obtained by polymerization of 25 equiv. of *rac*-LA with 1as initiator, in toluene, -20°C, 12h.

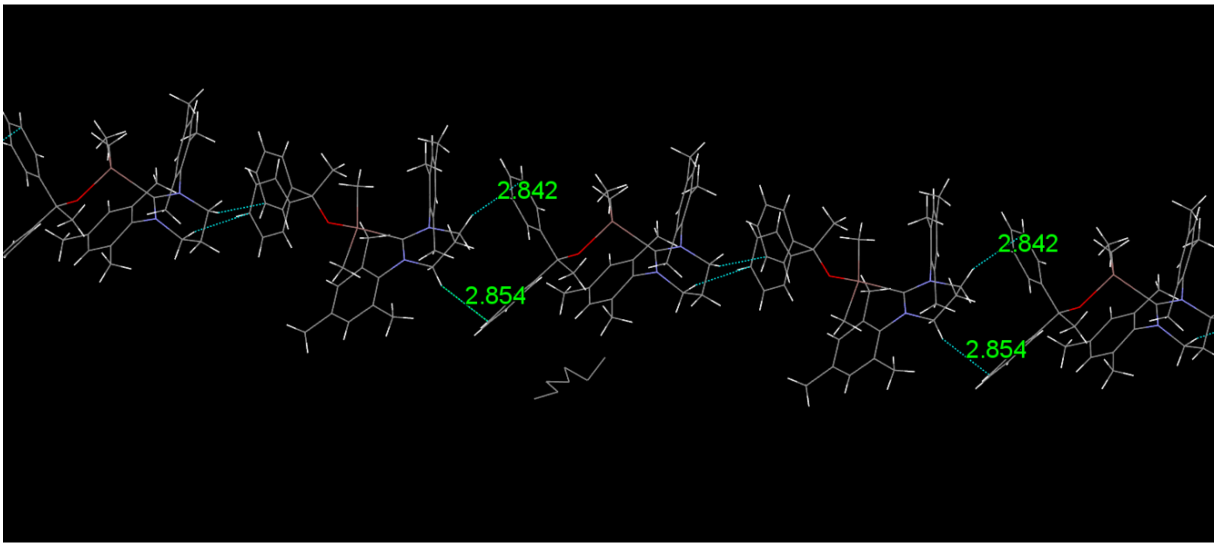


Figure S 57. Weak intermolecular interactions within the crystal structure of $Me_2In(OPh_2Me)$(6-Mes) (4).

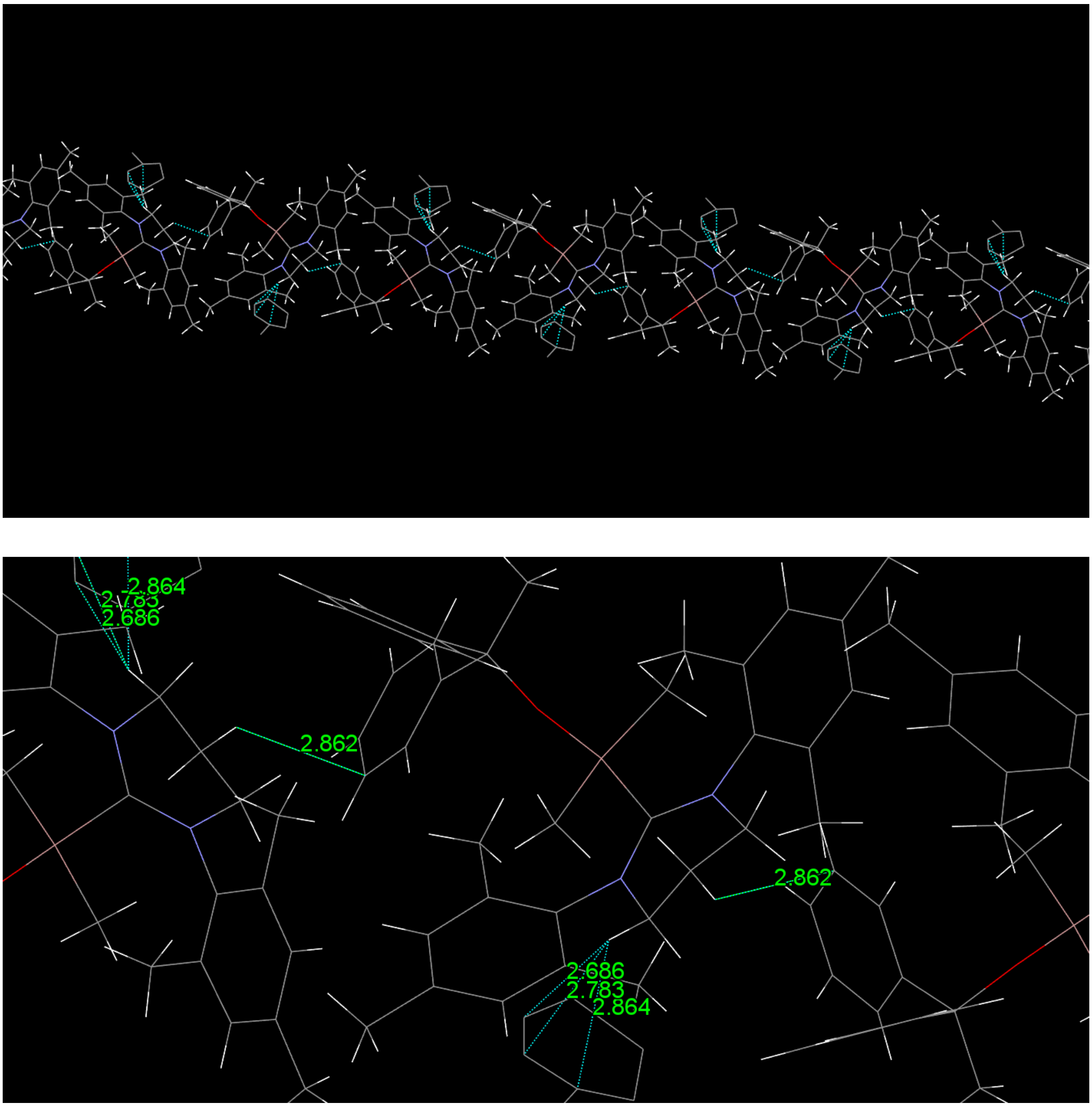


Figure S 58. Weak intermolecular interactions within the crystal structure of $Me_2Ga(OPh_2Me)(6\text{-}Mes)$ (3).