Supplementary Material (ESI) for Dalton Transactions

Oligomerization and Regioselective Hydrosilylation of Styrenes Catalyzed by Cationic Allyl Nickel Complexes Bearing Allylphosphine Ligands

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ELECTRONIC SUPPLEMENTARY MATERIAL

- **X-Ray Crystal Structure of *trans*-[$NiBr_2(P^iPr_2CH_2CH{=}CH_2)_2$] (3b)**
- **Relevant GPC/SEC chromatograms for the oligomers**

X-Ray Crystal Structure of *trans*-[$NiBr_2(P^iPr_2CH_2CH{=}CH_2)_2$] (3b)

Complexes **3a-b** are easily accessibly in a more direct way by reaction of anhydrous $NiBr_2$ with the corresponding phosphine in ethanol. The X-ray crystal structure of **3b** was determined. The asymmetric unit consist in half a molecule being the Ni atom at a special position. An ORTEP view of the whole molecule is shown in the figure.

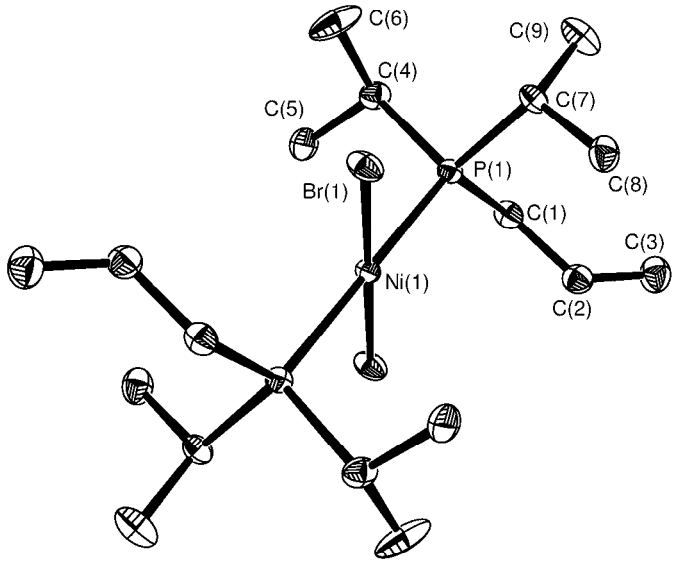


Figure. ORTEP drawing (50 % thermal ellipsoids) of the complex [$NiBr_2(\kappa^1(P)$-$P^iPr_2CH_2CH{=}CH_2)_2$] (**3b**). Selected bond lengths (Å) and angles (º) with estimated standard deviations in parentheses: Ni(1)-P(1) 2.2590(8); Ni(1)-Br(1) 2.3025(5); C(1)-C(2) 1.500(4); C(2)-C(3) 1.312(5); Br(1)-Ni(1)-P(1) 89.34(3); Br(1)-Ni(1)-Br(1)' 180; P(1)-Ni(1)-P(1)' 180.

The structure consists of a packing of discrete [$NiBr_2(\kappa^1(P)$-$P^iPr_2CH_2CH{=}CH_2)_2$] square planar molecules with a *trans* arrangement of bromide and phosphine ligands. This structure is very similar to that adopted by [$NiBr_2(PMe^iPr_2)_2$][§] and other related

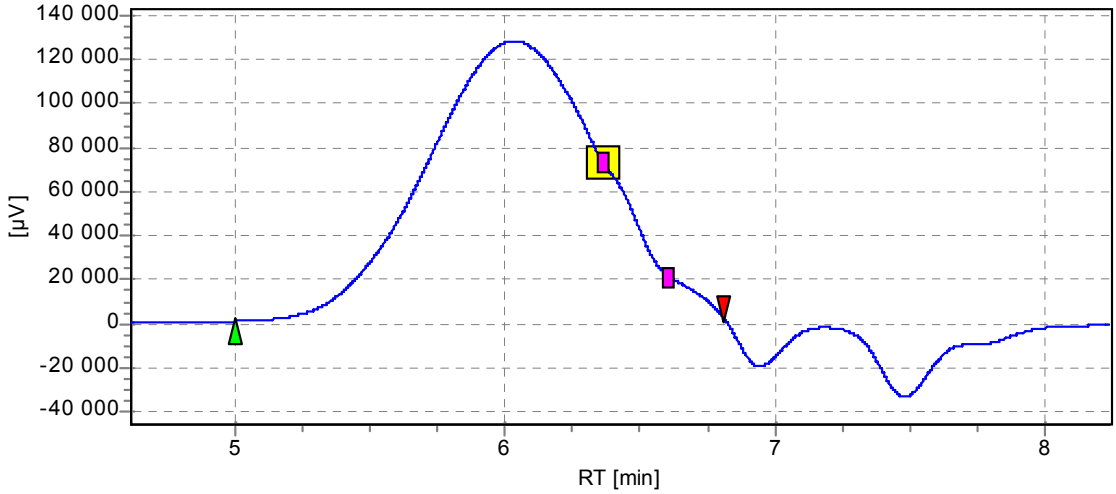
compounds. All distances and angles in this complex are within the expected ranges, being unexceptional and do not require further comment.

It is interesting to mention that complexes **3a-b** exhibit a NMR spectral behavior very similar to that previously observed for the derivatives *trans*-[$NiBr_2(PR^iPr_2)_2$] (R = Me, Ph).[§] Thus, the ^1H NMR spectra exhibit broad resonances at room temperature, whereas the $^{31}P\{^1H\}$ NMR spectra appear featureless. At low temperatures, the $^{31}P\{^1H\}$ NMR spectra consist of one singlet. This behavior has been interpreted in terms of fast phosphine dissociation, although a rapid exchange between species having square planar or distorted tetrahedral structures in solution can not be excluded.

§ M. Jiménez-Tenorio, M. C. Puerta, I. Salcedo, P. Valerga, S. I. Costa, L. C. Silva and P. T. Gomes, *Organometallics* 2004, **23**, 3139-3146.

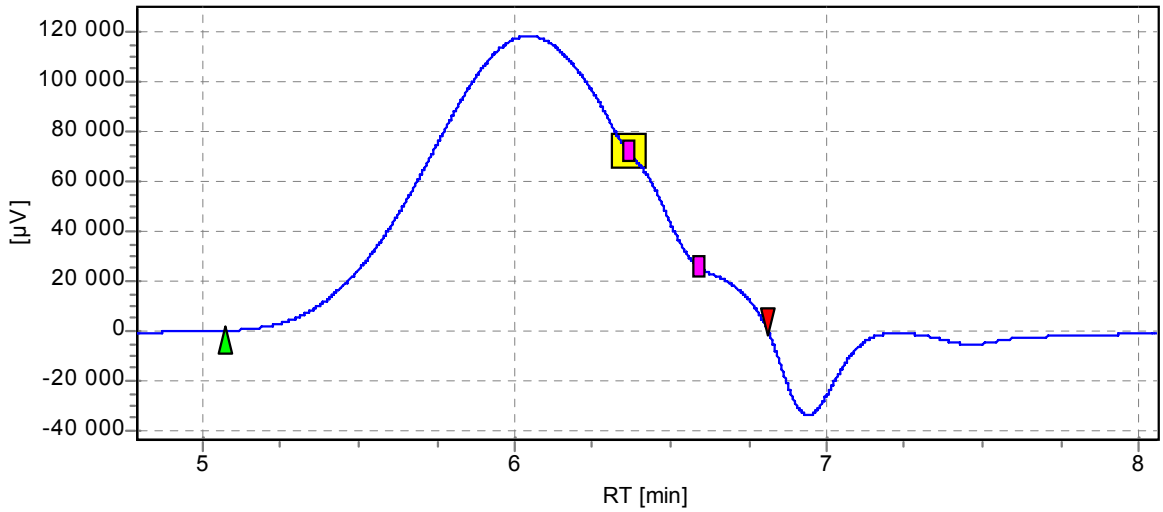
Relevant GPC/SEC chromatograms for the oligomers

Run: Entry 1, Table 1 of the article
Catalyst: 0.5 % [Ni(η^3-CH_2CHCH_2)(κ^1(*P*)-$PPh_2CH_2CH{=}CH_2$)$_2$][BAr'$_4$] (**4a**)
Substrate: Styrene
Temperature: 40 ºC
Reaction time: 30 minutes
Solvent: 1,2-dichloroethane



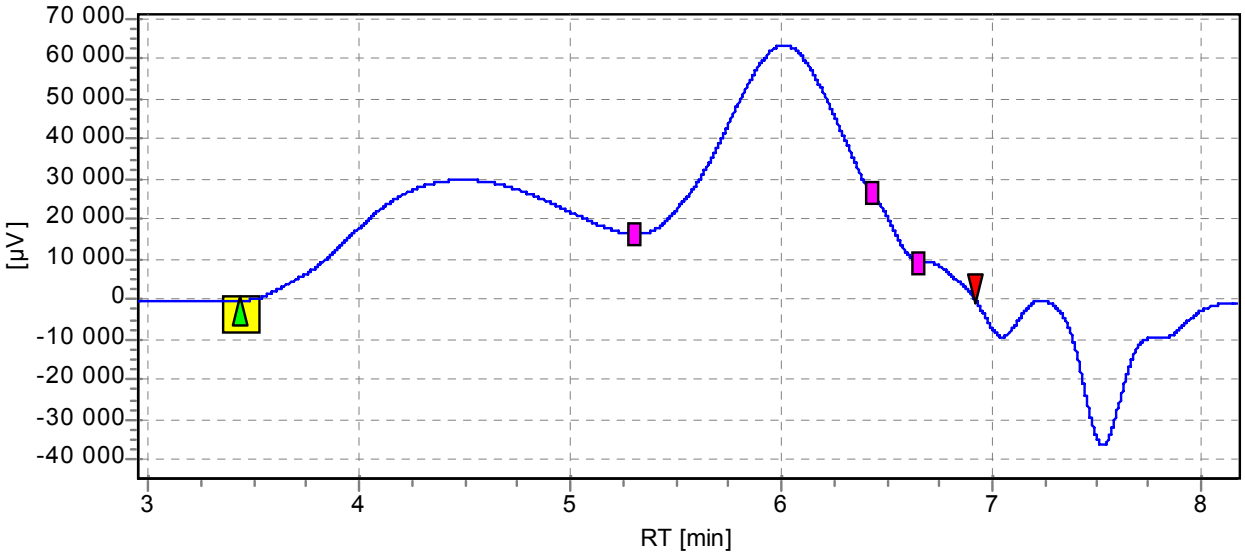
Zone	Start [min]	Stop [min]	M_W	M_n	M_W/M_n	Peak Area %
1 : Division 1 from peak # 1	5.00	6.36	1 008.47	808.49	1.25	86
2 : Division 2 from peak # 1	6.36	6.60	341.55	336.11	1.02	11
3 : Division 3 from peak # 1	6.60	6.81	217.84	215.23	1.01	3

Run: Entry 2, Table 1 of the article
Catalyst: 0.5 % [Ni(η^3-CH_2CHCH_2)(κ^1(*P*)-$PPh_2CH_2CH{=}CH_2)_2$][BAr'$_4$] (**4a**)
Substrate: Styrene
Temperature: 40 ºC
Reaction time: 1 hour
Solvent: 1,2-dichloroethane



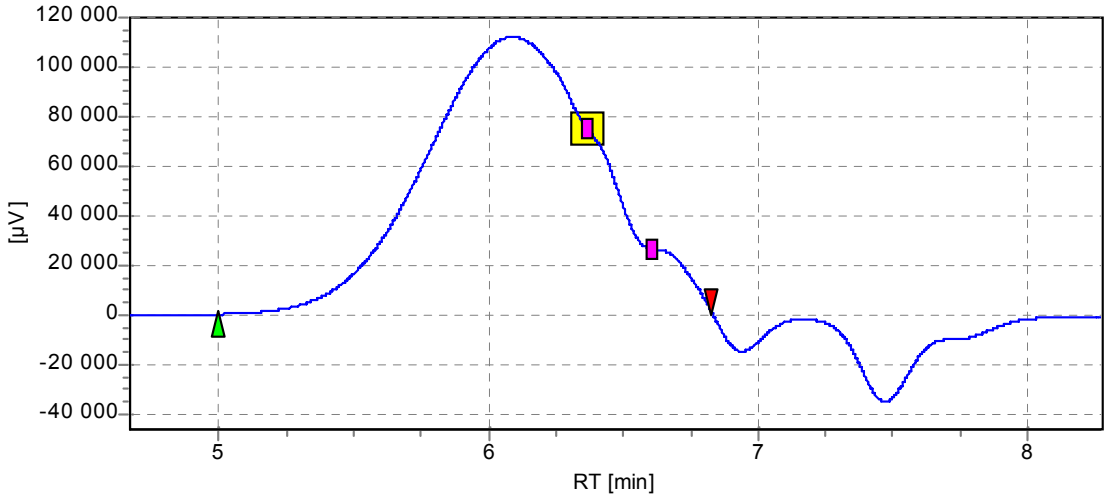
Zone	Start [min]	Stop [min]	M_W	M_n	M_W/M_n	Peak Area %
1 : Division 1 from peak # 1	5.07	6.36	984.74	799.13	1.23	84
2 : Division 2 from peak # 1	6.36	6.59	344.82	339.77	1.01	12
3 : Division 3 from peak # 1	6.59	6.82	222.84	219.94	1.01	4

Run: Entry 3, Table 1 of the article
Catalyst: 0.5 % [Ni(η^3-CH_2CHCH_2)(κ^1(*P*)-$PPh_2CH_2CH{=}CH_2)_2$][BAr'$_4$] (**4a**)
Substrate: Styrene
Temperature: 15 ºC
Reaction time: 24 hour
Solvent: 1,2-dichloroethane



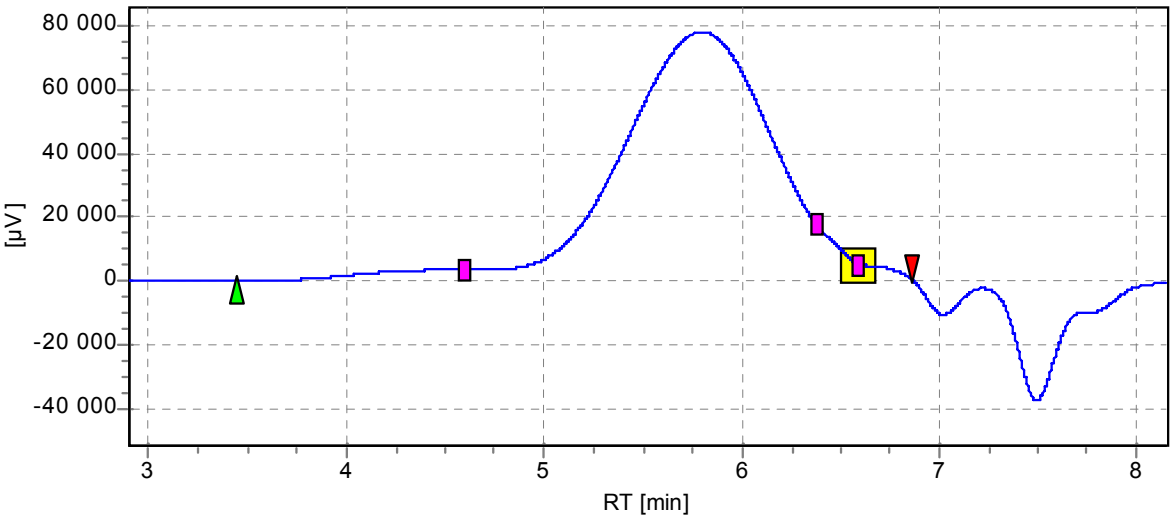
Zone	Start [min]	Stop [min]	M_W	M_n	M_W/M_n	Peak Area %
1 : Division 1 from peak # 1	3.43	5.31	17 653.06	9 841.78	1.79	41
2 : Division 2 from peak # 1	5.31	6.43	1 058.76	813.15	1.30	47
3 : Division 3 from peak # 1	6.43	6.65	304.98	300.58	1.01	10
4 : Division 4 from peak # 1	6.65	6.92	191.17	187.68	1.02	2

Run: Entry 4, Table 1 of the article
Catalyst: 0.5 % [Ni(η^3-$CH_2C(CH_3)CH_2$)(κ^1(*P*)-$PPh_2CH_2CH{=}CH_2)_2$][BAr'$_4$] (**4b**)
Substrate: Styrene
Temperature: 25 ºC
Reaction time: 5 minutes
Solvent: 1,2-dichloroethane



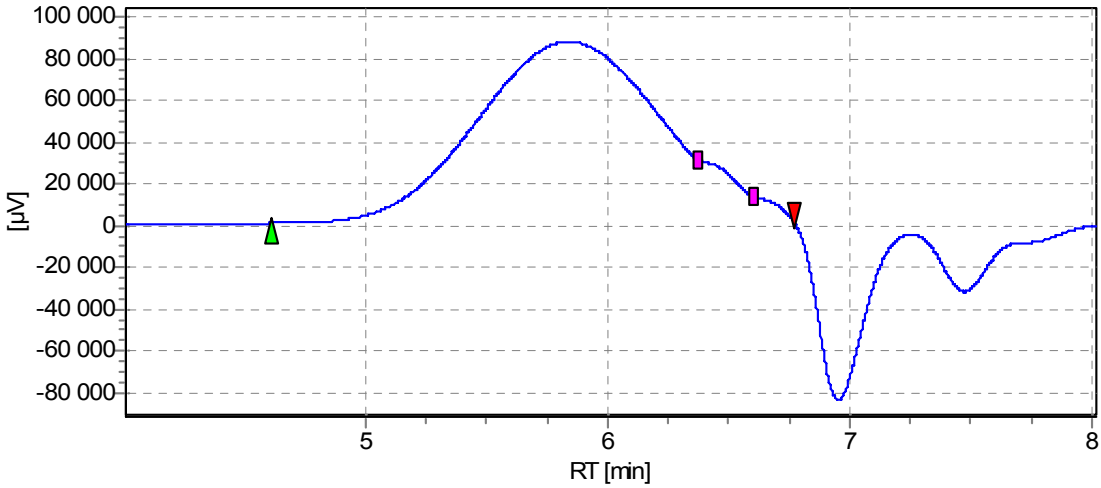
Zone	Start [min]	Stop [min]	M_W	M_n	M_W/M_n	Peak Area %
1 : Division 1 from peak # 1	5.00	6.36	937.11	765.09	1.22	81
2 : Division 2 from peak # 1	6.36	6.60	342.92	337.33	1.02	15
3 : Division 3 from peak # 1	6.60	6.83	217.01	214.22	1.01	4

Run: Entry 5, Table 1 of the article
Catalyst: 0.5 % [Ni(η^3-CH_2CHCH_2)(κ^1(*P*)-P^{i}Pr$_2$$CH_2CH{=}CH_2$)$_2$][BAr'$_4$] (**5a**)
Substrate: Styrene
Temperature: 40 ºC
Reaction time: 1 hour
Solvent: 1,2-dichloroethane



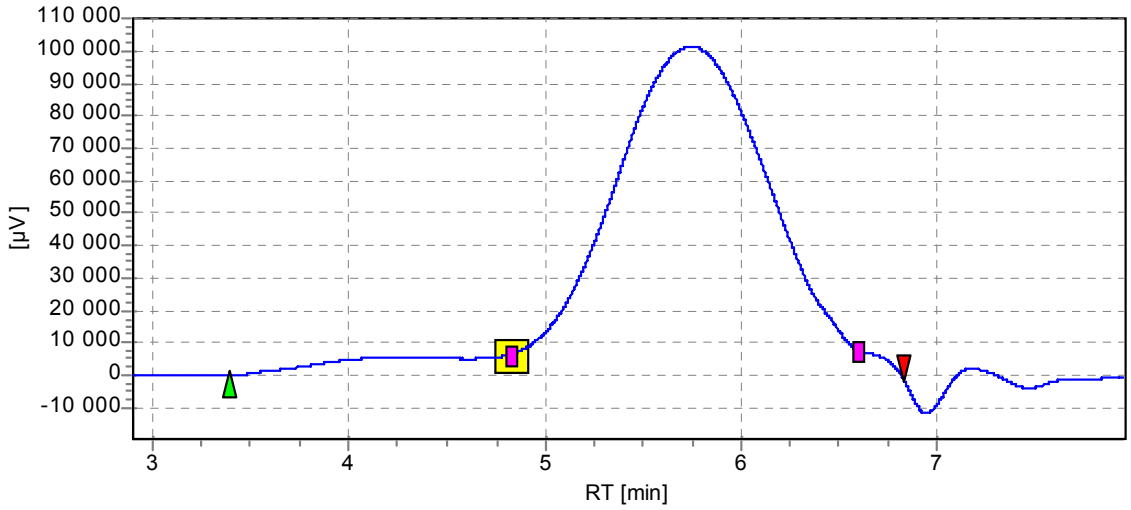
Zone	Start [min]	Stop [min]	M_W	M_n	M_W/M_n	Peak Area %
1 : Division 2 from peak # 1	4.60	6.37	1 677.56	1 128.10	1.49	95
2 : Division 3 from peak # 1	6.37	6.59	340.35	335.71	1.01	4
3 : Division 4 from peak # 1	6.59	6.86	211.85	207.66	1.02	1

Run: Entry 6, Table 1 of the article
Catalyst: 0.5 % [Ni(η^3-$CH_2C(CH_3)CH_2$)(κ^1(*P*)-P^{i}Pr$_2$$CH_2CH{=}CH_2$)$_2$][BAr'$_4$] (**5b**)
Substrate: Styrene
Temperature: 40 ºC
Reaction time: 1 hour
Solvent: 1,2-dichloroethane



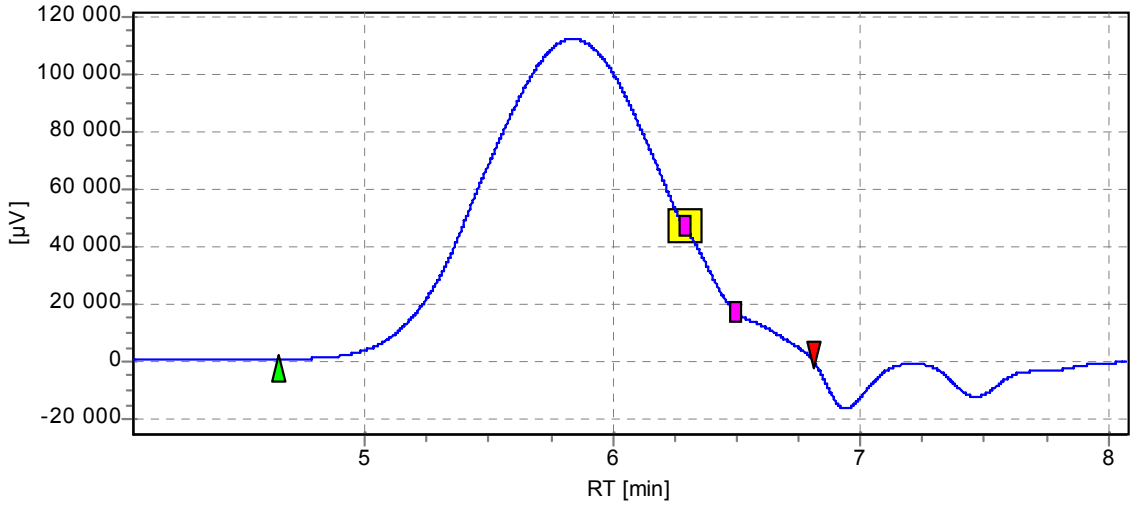
Zone	Start [min]	Stop [min]	M_W	M_n	M_W/M_n	Peak Area %
1 : Division 2 from peak # 1	4,62	6,38	1 472,10	1 030,05	1,43	91
2 : Division 3 from peak # 1	6,38	6,60	331,16	326,31	1,01	7
3 : Division 4 from peak # 1	6,60	6,78	223,55	221,75	1,01	2

Run: Entry 7, Table 1 of the article
Catalyst: 0.5 % [Ni(η^3-$CH_2C(CH_3)CH_2$)(κ^1(*P*)-P^{i}Pr$_2$$CH_2CH{=}CH_2$)$_2$][BAr'$_4$] (**5b**)
Substrate: Styrene
Temperature: 25 ºC
Reaction time: 15 hour
Solvent: 1,2-dichloroethane



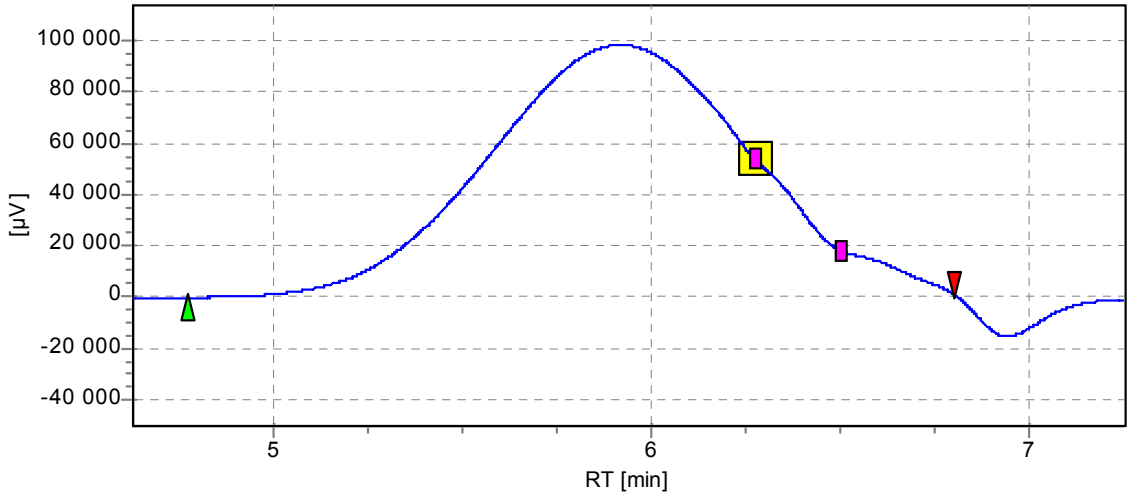
Zone	Start [min]	Stop [min]	M_W	M_n	M_W/M_n	Peak Area %
1 : Division 1 from peak # 1	3.39	4.82	27 028.06	17 903.39	1.51	6
2 : Division 2 from peak # 1	4.82	6.60	1 660.41	1 072.84	1.55	93
3 : Division 3 from peak # 1	6.60	6.83	216.84	214.22	1.01	1

Run: Entry 8, Table 1 of the article
Catalyst: 0.5 % [Ni(η^3-CH_2CHCH_2)(κ^1(*P*)-P^{i}Ph$_2$$CH_2CH$=$CH_2$)$_2$][BAr'$_4$] (**4a**)
Substrate: 4-Methylstyrene
Temperature: 40 ºC
Reaction time: 20 hour
Solvent: 1,2-dichloroethane



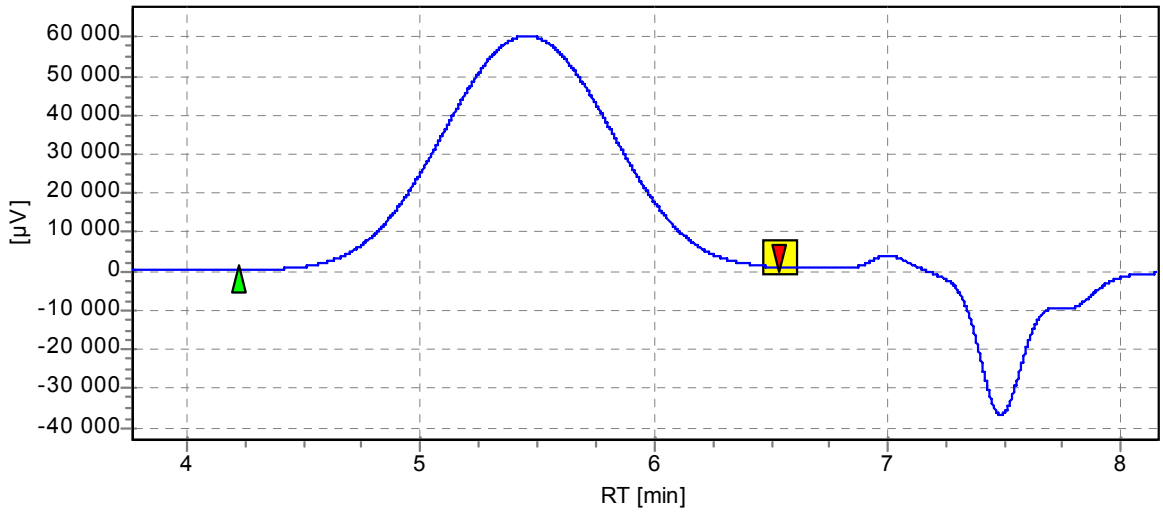
Zone	Start [min]	Stop [min]	M_W	M_n	M_W/M_n	Peak Area %
1 : Division 1 from peak # 1	4.65	6.29	1 452.61	1 089.42	1.33	90
2 : Division 2 from peak # 1	6.29	6.49	403.12	398.23	1.01	7
3 : Division 3 from peak # 1	6.49	6.81	255.75	249.57	1.02	3

Run: Entry 9, Table 1 of the article
Catalyst: 0.5 % [Ni(η^3-$CH_2C(CH_3)CH_2$)(κ^1(*P*)-P^i$Ph_2CH_2CH{=}CH_2)_2$][BAr'$_4$] (**4b**)
Substrate: 4-Methylstyrene
Temperature: 25 ºC
Reaction time: 5 minutes
Solvent: 1,2-dichloroethane



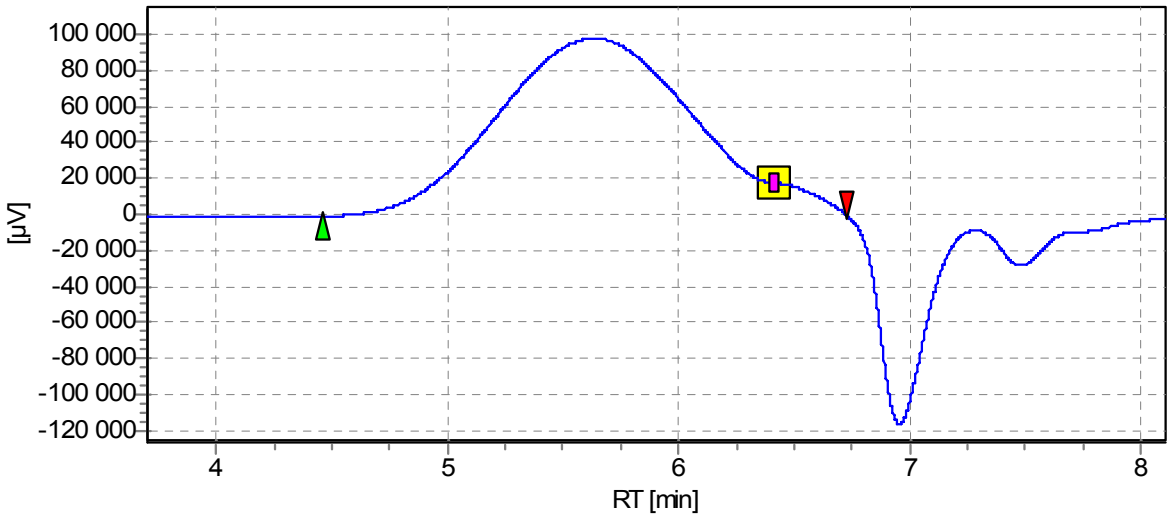
Zone	Start [min]	Stop [min]	M_W	M_n	M_W/M_n	Peak Area %
1 : Division 1 from peak # 1	4.77	6.27	1 263.33	998.89	1.26	86
2 : Division 2 from peak # 1	6.27	6.50	409.58	403.42	1.02	10
3 : Division 3 from peak # 1	6.50	6.81	252.94	247.31	1.02	4

Run: Entry 10, Table 1 of the article
Catalyst: 0.5 % [Ni(η^3-CH_2CHCH_2)(κ^1(*P*)-P^{i}Pr$_2$$CH_2CH{=}CH_2$)$_2$][BAr'$_4$] (**5a**)
Substrate: 4-Methylstyrene
Temperature: 40 ºC
Reaction time: 5 hours
Solvent: 1,2-dichloroethane



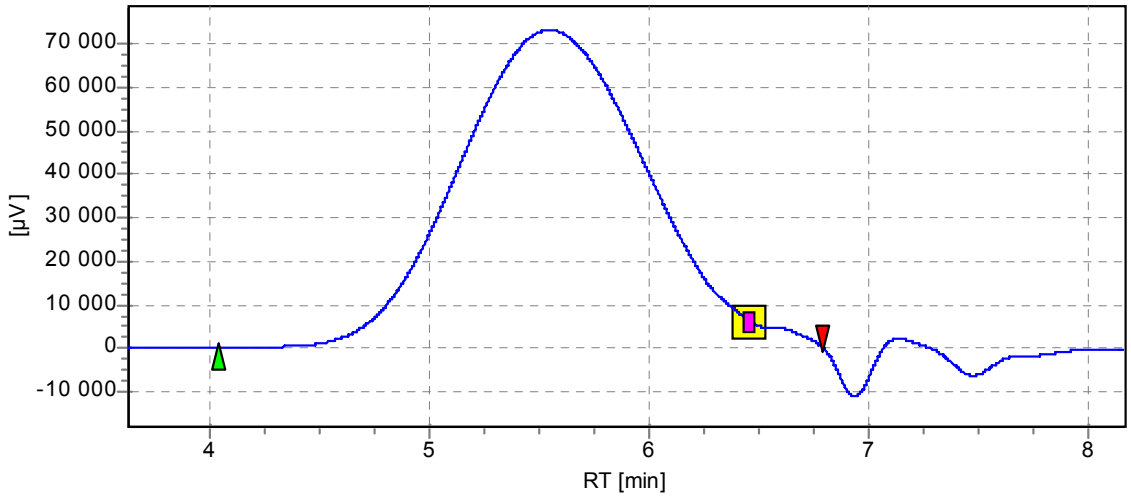
Zone	Start [min]	Stop [min]	M_W	M_n	M_W/M_n	Peak Area %
1 : Peak # 1	4.22	6.53	2 813.92	1 844.44	1.53	100

Run: Entry 11, Table 1 of the article
Catalyst: 0.5 % [Ni(η^3-$CH_2C(CH_3)CH_2$)(κ^1(*P*)-P^{i}Pr$_2$$CH_2CH=CH_2$)$_2$][BAr'$_4$] (**5b**)
Substrate: 4-Methylstyrene
Temperature: 40 ºC
Reaction time: 1 hour
Solvent: 1,2-dichloroethane



Zone	Start [min]	Stop [min]	M_W	M_n	M_W/M_n	Peak Area %
1 : Division 1 from peak # 1	4,47	6,41	2 056,83	1 334,00	1,54	97
2 : Division 2 from peak # 1	6,41	6,73	299,61	293,06	1,02	3

Run: Entry 12, Table 1 of the article
Catalyst: 0.5 % [Ni(η^3-$CH_2C(CH_3)CH_2$)(κ^1(*P*)-P^{i}Pr$_2$$CH_2CH{=}CH_2$)$_2$][BAr'$_4$] (**5b**)
Substrate: 4-Methylstyrene
Temperature: 25 ºC
Reaction time: 22 hour
Solvent: 1,2-dichloroethane



Zone	Start [min]	Stop [min]	M_W	M_n	M_W/M_n	Peak Area %
1 : Division 1 from peak # 1	4.04	6.45	2 456.08	1 501.55	1.64	98
2 : Division 2 from peak # 1	6.45	6.79	269.68	262.06	1.03	2