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ESI

Indole-bridged bisphosphine-monoxide palladium catalysts for ethylene polymerization and copolymerization with polar monomers

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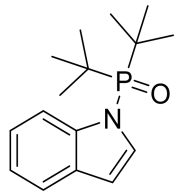
Contents

1. Preparation of Ligands 1a-1g

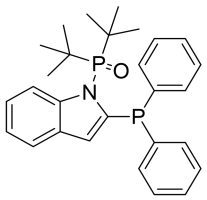
Preparation of S_1:



Indole (1.17 g, 10 mmol, 1.0 equiv) was stirred in tetrahydrofuran (50 mL) and the mixture was cooled to −78 °C. *n*-BuLi (6.56 mL, 1.6 M in hexane, 10.5 mmol, 1.05 equiv) was slowly added and the mixture was stirred for 4 h at -78 °C ensuring the temperature did not change. Di-tert-butylchlorophosphane (1.8 g, 10 mmol, 1.0 equiv) was then added dropwise and the mixture was stirred for 2 h at −78 °C. The reaction mixture was allowed to warm slowly to room temperature and stirred overnight. The salts were removed by extraction with CH_2Cl_2 (30 mL) and distilled water (30 mL). To the organic layer was added H_2O_2 (2 mL, 30 %) and stirred for 3 h. The mixture was concentrated and pure red solid (1.66 g, 6 mmol, 60 %) was obtained by silica gel column chromatography (ethyl acetate: hexane = 1:2).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.50 (d, J = 8.5 Hz, 1H), 7.58 (d, J = 7.6 Hz, 1H), 7.26 – 7.19 (m, 2H), 7.20 – 7.15 (m, 1H), 6.75 – 6.65 (m, 1H).

Preparation of Ligand 1a:

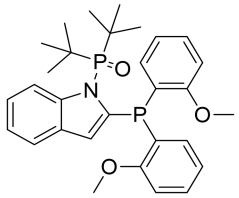


Lithium diisopropylamide (2.16 mL, 2 M in THF/n-heptane ethylbenzene, 4.32 mmol, 2.0 equiv) was slowly added to a solution of **S_1** (0.60 g, 2.16 mmol, 1.0 equiv) in THF (50 mL) at 0 °C. The mixture was stirred for 4 h at 0 °C and then chlorodiphenylphosphine (0.478 g, 2.16 mmol, 1.0 equiv) was added dropwise and the mixture was stirred for 2 h at 0 °C. The reaction mixture was allowed to warm slowly to room temperature and stirred overnight. The salts were removed by extraction with CH_2Cl_2 (30 mL) and distilled water (30 mL) and the organic layer was concentrated under reduced pressure. After purification by column chromatography on silica gel (1:4 ethyl acetate: hexane), white powder product (0.51 g, 1.10 mmol, 51 %) was obtained.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 (d, J_{HH} = 8.4 Hz, 1H), 7.43 (m, 5H), 7.32 (d, J_{HH} = 4.7 Hz, 6H), 7.20 (t, J_{HH} = 7.9 Hz, 1H), 7.13 (t, J_{HH} = 7.4 Hz, 1H), 6.17 (s, 1H), 1.32 (d, J_{HH} = 15.2 Hz, 18H).

^{1}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ 69.47 (P=O), -16.08 (P-aryl).

Preparation of Ligand 1b:

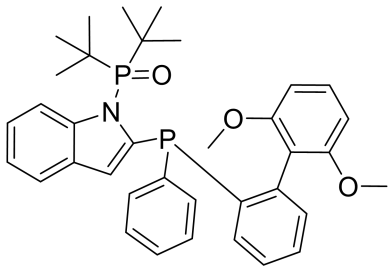


Similar procedure as above was used except that bis(2-methoxyphenyl)chlorophosphine (0.508 g, 1.8 mmol, 1.0 equiv) was used. **1b** was obtained as a light white powder (0.37 g, 40 %).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71 (d, J_{HH} = 8.4 Hz, 1H), 7.39 (d, J_{HH} = 7.8 Hz, 1H), 7.30 – 7.25 (m, 2H), 7.20 – 7.15 (m, 1H), 7.10 (t, J_{HH} = 7.2 Hz, 1H), 6.87 – 6.77 (m, 6H), 6.16 (s, 1H), 3.66 (s, 6H), 1.42 (d, J_{HH} = 15.0 Hz, 18H).

^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ 67.92 (*P*=O), -36.26 (*P*-aryl).

Preparation of Ligand 1c:

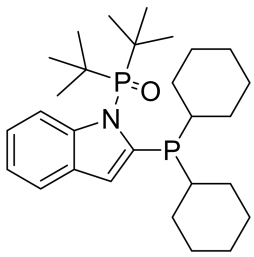


Similar procedure as above was used except that (2', 6'-dimethoxybiphenyl-2-yl)phenylphosphine chloride (0.745 g, 2.09 mmol, 1.0 equiv) was used. The reaction mixture was separated and purified by column chromatography on silica gel (1:2 ethyl acetate: hexane), and **1c** was obtained as a light red solid powder (0.56 g, 45 %).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59 – 7.52 (m, 1H), 7.44 – 7.35 (m, 4H), 7.29 – 7.26 (m, 2H), 7.25 – 7.18 (m, 2H), 7.16 (ddd, J_{HH} = 1.3, 3.9, 7.5 Hz, 1H), 7.13 – 7.05 (m, 3H), 6.90 – 6.84 (m, 1H), 6.56 (dd, J_{HH} = 0.8, 8.3 Hz, 1H), 6.27 – 6.20 (m, 2H), 3.86 (s, 3H), 3.11 (s, 3H), 1.19 (d, J_{HH} = 14.8 Hz, 8H), 1.04 (d, J_{HH} = 15.3 Hz, 8H).

^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ 67.93 (*P*=O), -21.0 (*P*-aryl).

Preparation of Ligand 1d:

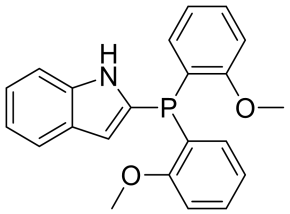


Similar procedure as above was used except that dicyclohexylchlorophosphine (0.41 g, 1.76 mmol, 1.0 equiv) was used. **1d** was obtained as a light white powder (0.33 g, 40 %).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72 – 7.61 (m, 1H), 7.58 – 7.54 (m, 1H), 7.18 – 7.10 (m, 2H), 6.82 (s, 1H), 1.94 – 1.60 (m, 22H), 1.39 (d, J_{HH} = 15.1 Hz, 18H).

^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ 67.18 (*P*=O), -6.40 (*P*-Cy).

Preparation of S_2:

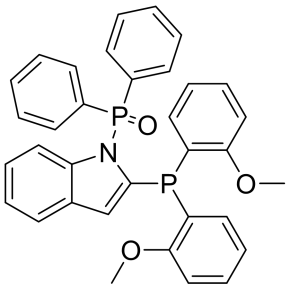


Ligand **1g** (1.0 g, 2 mmol, 1.0 equiv) was stirred in dimethyl sulfoxide (50 mL) and the mixture was heated to 80 °C. Aqueous solution (2.0 M, 32 ml, 16 mmol, 8 equiv) of sodium hydroxide was added and the mixture was stirred for 12 h at 80 °C. The salts were removed by extraction with diethyl ether (150 mL) and distilled water (100 mL) and the organic layer was concentrated under reduced pressure. After purification by column chromatography on silica gel (1:3.5 ethyl acetate: hexane), target compound was obtained as yellow powder (0.5 g, 1.38 mmol, 69 %).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.14 (s, 1H), 7.61 (d, *J* = 7.9 Hz, 1H), 7.39 – 7.33 (m, 2H), 7.30 (d, *J* = 8.1 Hz, 1H), 7.20 – 7.14 (m, 1H), 7.12 – 7.06 (m, 1H), 6.93 – 6.83 (m, 6H), 6.79 – 6.75 (m, 1H), 3.72 (s, 6H).

^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ -45.92.

Preparation of Ligand 1e:

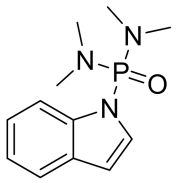


S_2 (0.50 g, 1.4 mmol, 1.0 equiv) was stirred in tetrahydrofuran (50 mL) and the mixture was cooled to −78 °C. *n*-BuLi (0.63 mL, 2.4 M in hexane, 1.5 mmol, 1.1 equiv) was slowly added and the mixture was stirred for 4 h at -78 °C ensuring the temperature did not change. Diphenylphosphinyl chloride (0.36 g, 1.5 mmol, 1.1 equiv) was then added dropwise and the mixture was stirred for 2 h at −78 °C. The reaction mixture was allowed to warm slowly to room temperature and stirred overnight. The salts were removed by extraction with CH_2Cl_2 (30 mL) and distilled water (30 mL) under air and the organic layer was concentrated under reduced pressure. Yellow solid product (0.47 g, 0.84 mmol, 60 %) was obtained after purification by silica gel column chromatography (1:2 ethyl acetate: hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.32 (d, J = 8.3 Hz, 1H), 7.85 – 7.68 (m, 4H), 7.43 – 7.37 (m, 4H), 7.32 – 7.19 (m, 5H), 7.18 – 7.12 (m, 2H), 6.79 (t, J = 7.4 Hz, 2H), 6.74 – 6.72 (m, 2H), 6.66 – 6.64 (m, 2H), 6.26 (dd, J_{HH} = 0.9, 2.6 Hz, 1H), 3.64 (s, 6H).

^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ30.43 (d, J = 3.3 Hz, *P*=O), -44.65 (*P*-aryl).

Preparation of S_3:

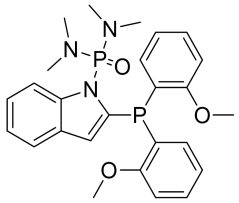


Indole (2.34 g, 20 mmol, 1.0 equiv) was stirred in tetrahydrofuran (50 mL) and the mixture was cooled to −78 °C. *n*-BuLi (8.8 mL, 2.4 M in hexane, 21 mmol, 1.05 equiv) was slowly added and the mixture was stirred for 4 h at -78 °C ensuring the temperature did not change. Bis(dimethylamino)phosphoryl chloride (3.43g, 20 mmol, 1.0 equiv) was then added dropwise and the mixture was stirred for 2 h at −78 °C. The reaction mixture was allowed to warm slowly to room temperature and stirred overnight. CH_2Cl_2 was added and the mixture was washed with distilled water (30 mL). The organic layer was concentrated under reduced pressure, and white powder (2.66 g, 10.6 mmol, 53 %) was obtained.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.92 (d, J = 8.4 Hz, 1H), 7.59 (d, J = 7.7 Hz, 1H), 7.27 – 7.23 (m, 2H), 7.18 (t, J = 7.5 Hz, 1H), 6.62 (t, J = 2.7 Hz, 1H), 2.71 (d, J = 10.2 Hz, 13H).

^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ 14.71 (*P*=O).

Preparation of Ligand 1f:

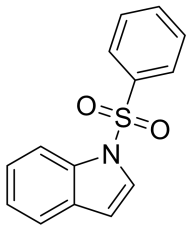


Lithium diisopropylamide (1.99 mL, 2 M in in THF/n-heptane ethylbenzene, 1.99 mmol, 2.0 equiv) was slowly added to a solution of **S₃** (0.50 g, 1.99 mmol, 1.0 equiv) in THF (50 mL) at 0 °C. The mixture was stirred for 4 h at 0 °C and then chlorobis(2-methoxyphenyl)phosphine (0.56 g, 1.99 mmol, 1.0 equiv) was added dropwise and the mixture was stirred for 2 h at 0 °C. The reaction mixture was allowed to warm slowly to room temperature and stirred overnight. CH_2Cl_2 was added and the mixture was washed with distilled water (30 mL). The organic layer was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel (1:2 ethyl acetate: hexane) to afford ligand **1f** as white solid product (0.44 g, 1.10 mmol, 45 %).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.32 (dd, J_{HH} = 1.0, 8.5 Hz, 1H), 7.42 – 7.30 (m, 3H), 7.27 – 7.16 (m, 1H), 7.17 – 7.10 (m, 1H), 6.93 – 6.74 (m, 6H), 6.16 (dd, J_{HH} = 0.8, 2.9 Hz, 1H), 3.71 (s, 6H), 2.52 (d, J_{HH} = 10.0 Hz, 12H).

^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ 16.43 (*P*=O), -43.77 (*P*-aryl).

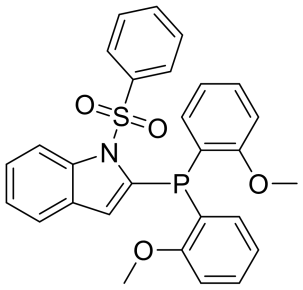
Preparation of S_3:



Indole (2.34 g, 20 mmol, 1.0 equiv) was stirred in tetrahydrofuran (50 mL) and the mixture was cooled to −78 °C. *n*-BuLi (8.8 mL, 2.4 M in hexane, 21 mmol, 1.05 equiv) was slowly added and the mixture was stirred for 4 h at -78 °C ensuring the temperature did not change. Benzenesulfonyl chloride (3.53g, 20 mmol, 1.0 equiv) was then added dropwise and the mixture was stirred for 2 h at −78 °C. The reaction mixture was allowed to warm slowly to room temperature and stirred overnight. The salts were removed by extraction with diethyl ether (30 mL) and distilled water (30 mL) under air and the organic layer was concentrated under reduced pressure. And the mixture was separated and purified by column chromatography on silica gel (1:2 ethyl acetate: hexane) to afford red solid product (3.6 g, 14.0 mmol, 70 %).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.3 Hz, 1H), 7.79 – 7.72 (m, 2H), 7.46 (d, *J* = 3.7 Hz, 1H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.39 – 7.32 (m, 1H), 7.31 – 7.24 (m, 2H), 7.24 – 7.17 (m, 1H), 7.14 – 7.10 (m, 1H), 6.54 (d, *J* = 3.6 Hz, 1H).

Preparation of Ligand 1g:



S₃ (1.78 g, 6.9 mmol, 1.0 equiv) was stirred in tetrahydrofuran (50 mL) and the mixture was cooled to −78 °C. *n*-BuLi (3.16 mL, 2.4 M in hexane, 7.6 mmol, 1.1 equiv) was slowly added and the mixture was stirred for 4 h at -78 °C ensuring the temperature did not change. Chlorobis(2-methoxyphenyl)phosphine (2.14 g, 7.6 mmol, 1.1 equiv) was then added dropwise and the mixture was stirred for 2 h at −78 °C. The reaction mixture was allowed to warm slowly to room temperature and stirred overnight. The salts were removed by extraction with CH_2Cl_2 (30 mL) and distilled water (30 mL) and the organic layer was concentrated under reduced pressure. The mixture was separated and purified by column chromatography on silica gel (1:2 ethyl acetate: hexane) to afford yellow solid product (2.07 g, 4.13 mmol, 60 %).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.27 – 8.20 (m, 3H), 7.56 – 7.51 (m, 1H), 7.49 – 7.41 (m, 2H), 7.40 – 7.27 (m, 4H), 7.21 – 7.15 (m, 1H), 6.92 – 6.87 (m, 4H), 6.87 – 6.82 (m, 2H), 6.09 (s, 1H), 3.69 (s, 6H).

^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ -38.94 (P-aryl).

2. NMR spectra of ligands and complexes

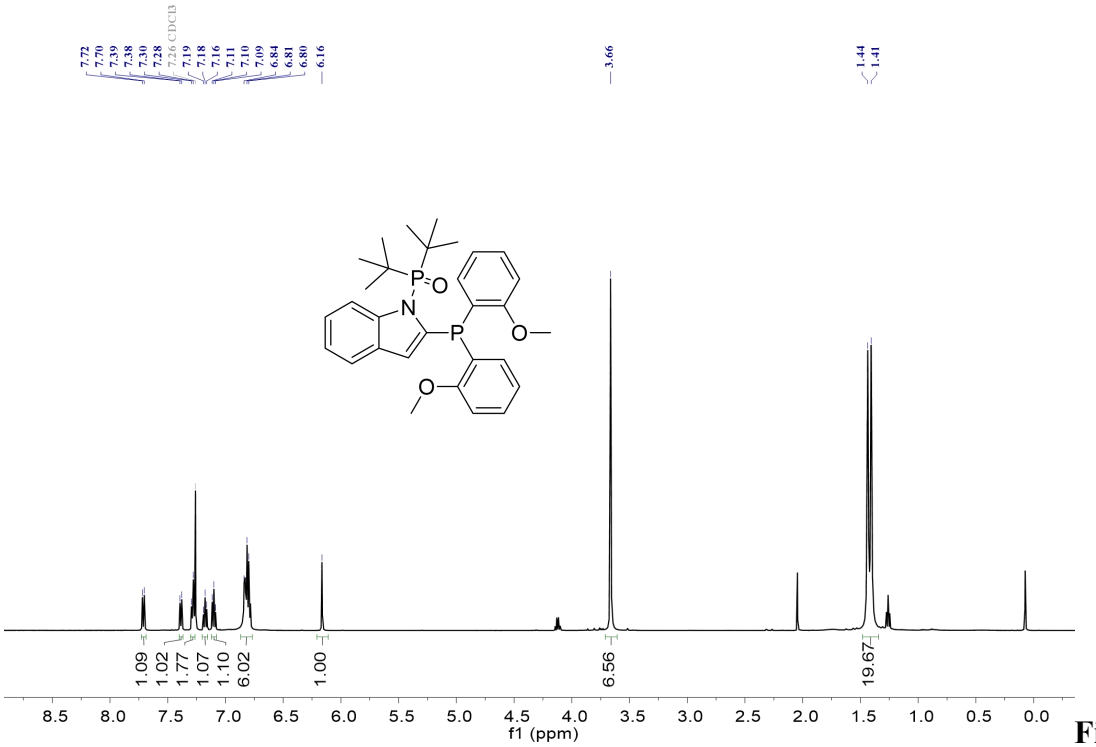


Figure S1. ^{1}H NMR (500 MHz, 298 K, $CDCl_3$) of **1b**.

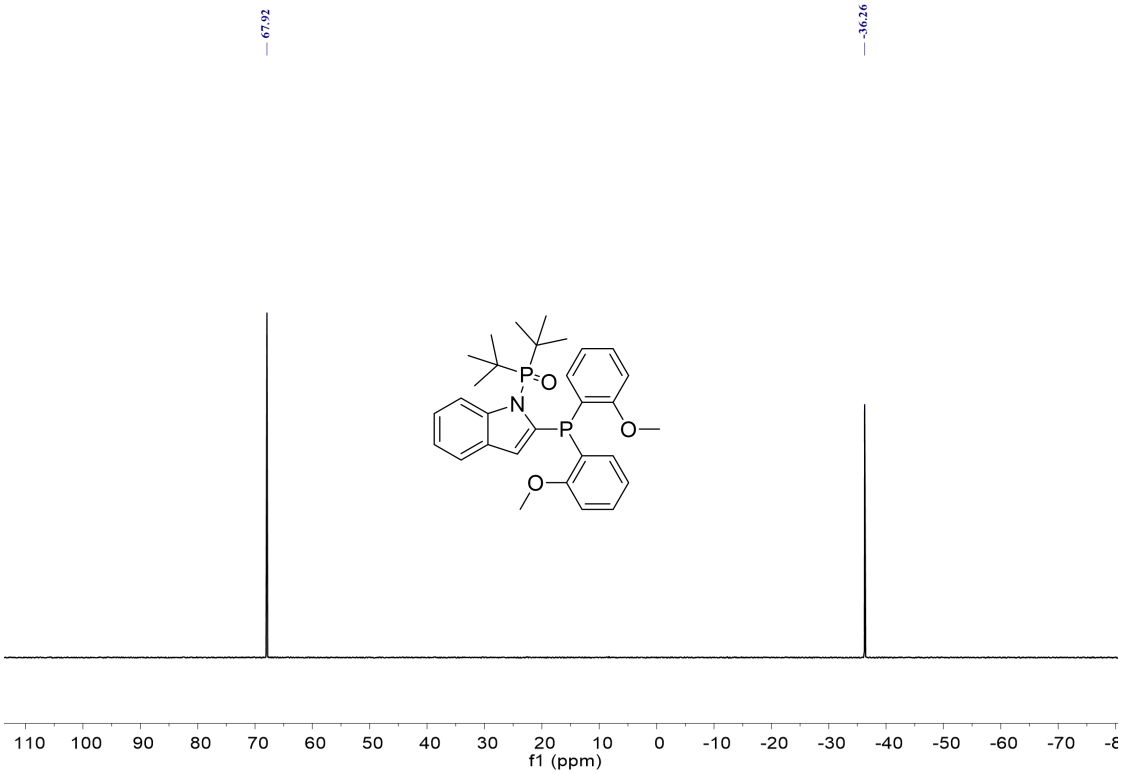


Figure S2. ^{31}P NMR spectrum (202 MHz, 298 K, $CDCl_3$) of **1b**.

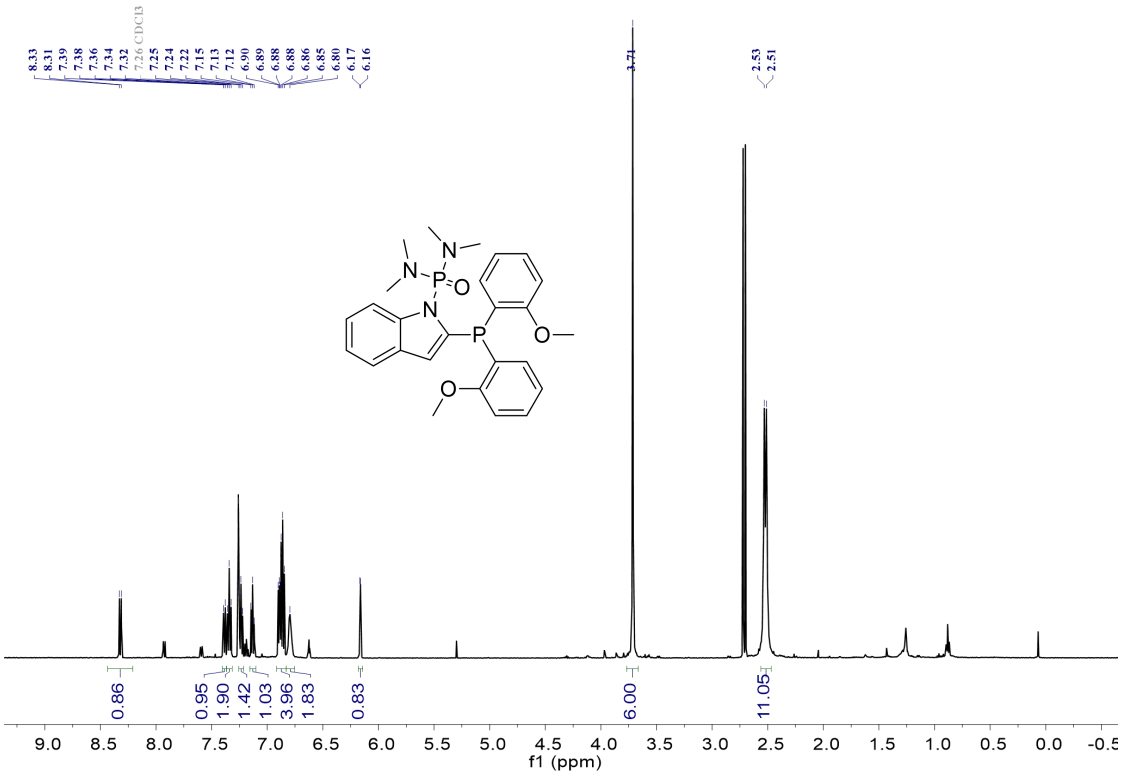


Figure S3. ^{1}H NMR (500 MHz, 298 K, $CDCl_3$) of **1f**.

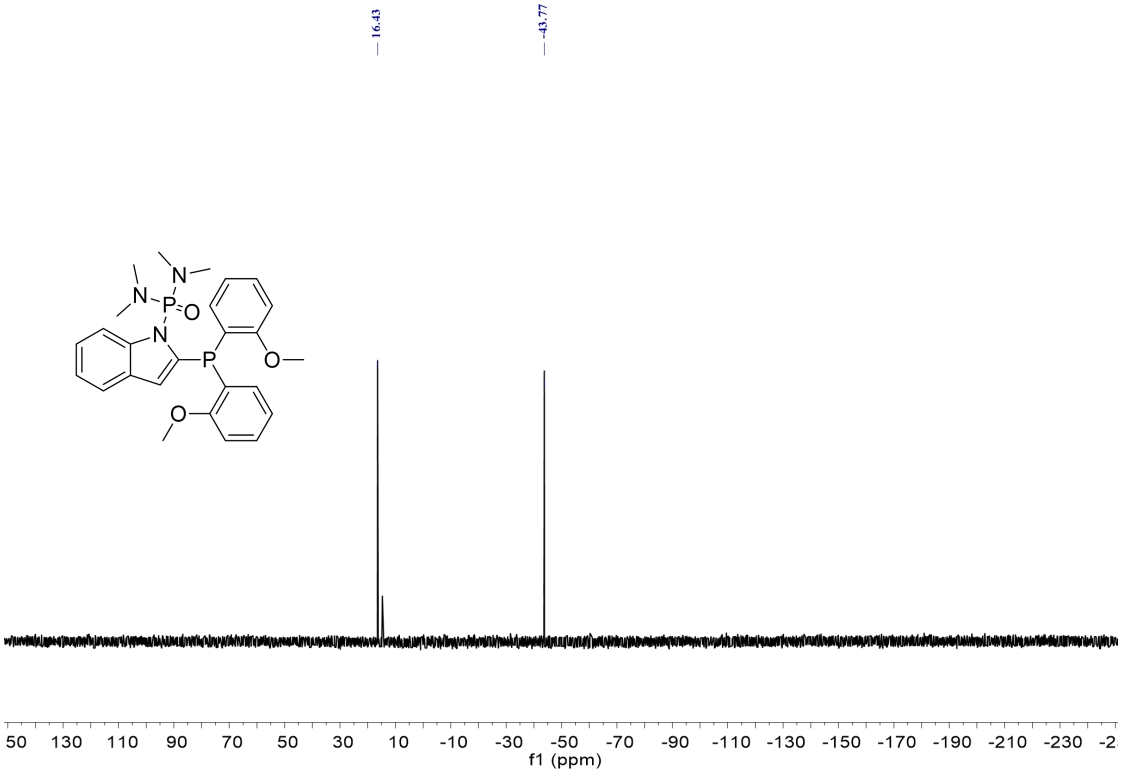


Figure S4. ^{31}P NMR spectrum (202 MHz, 298 K, $CDCl_3$) of **1f.**

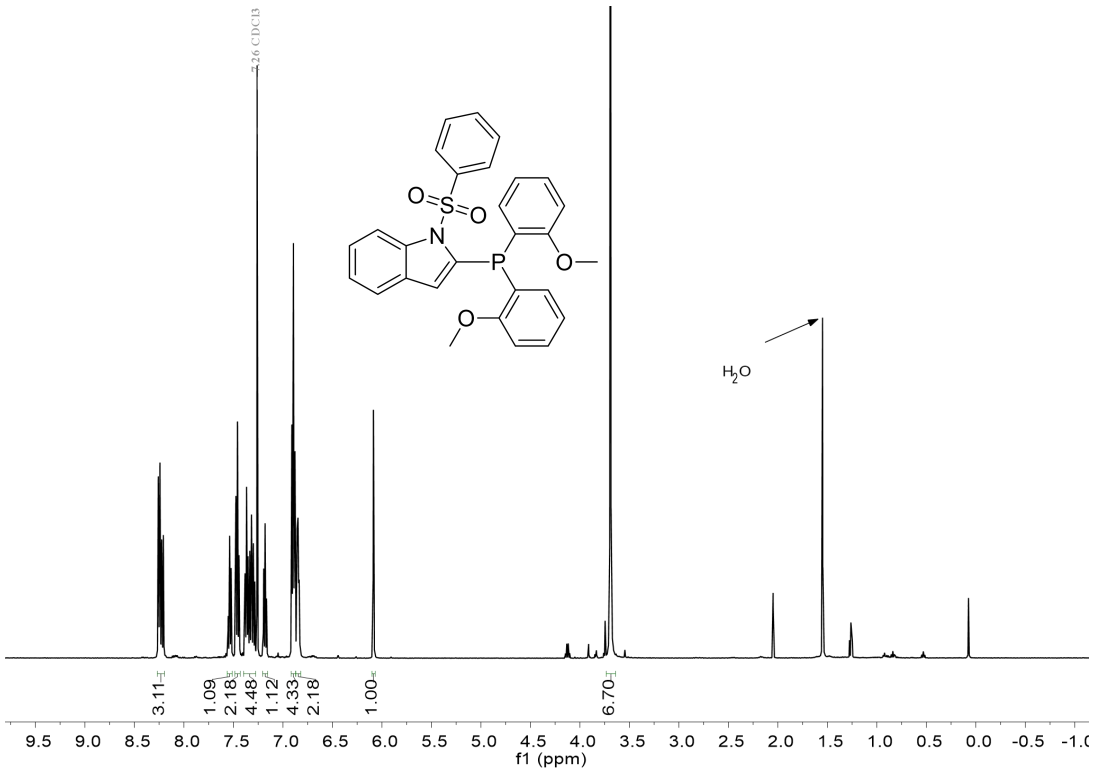


Figure S5. ^{1}H NMR (500 MHz, 298 K, $CDCl_3$) of **1g.**

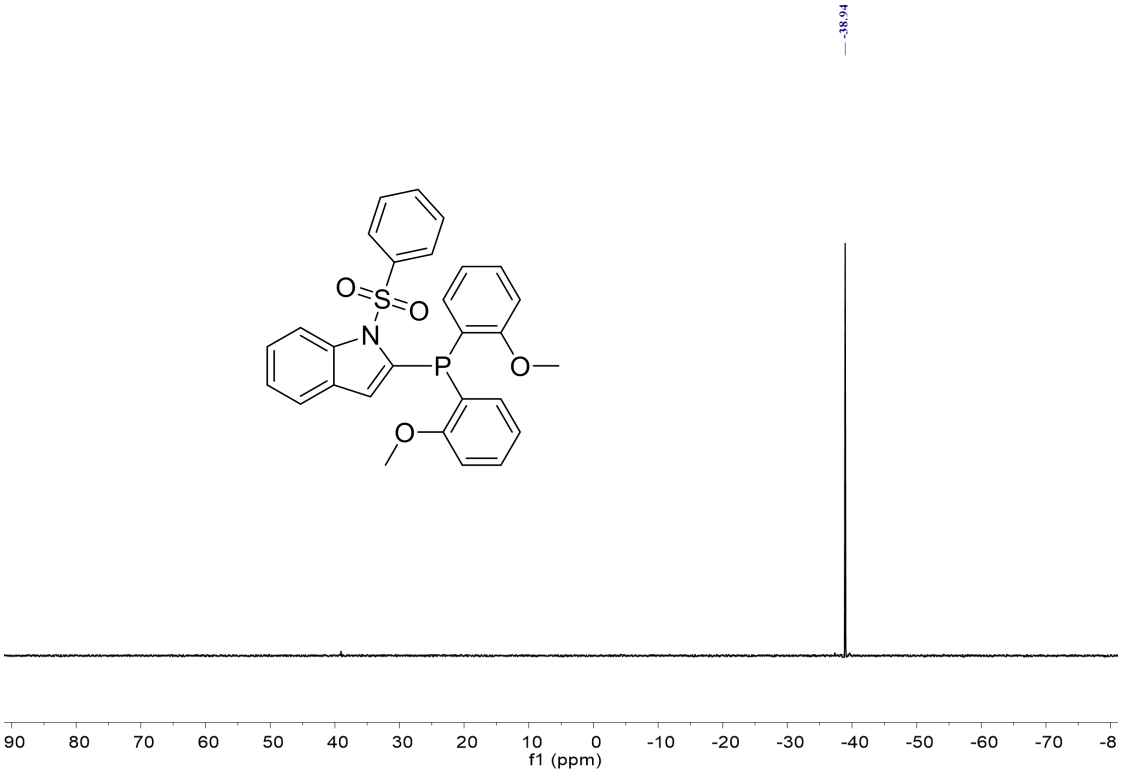


Figure S6. ^{31}P NMR spectrum (202 MHz, 298 K, $CDCl_3$) of **1g**.

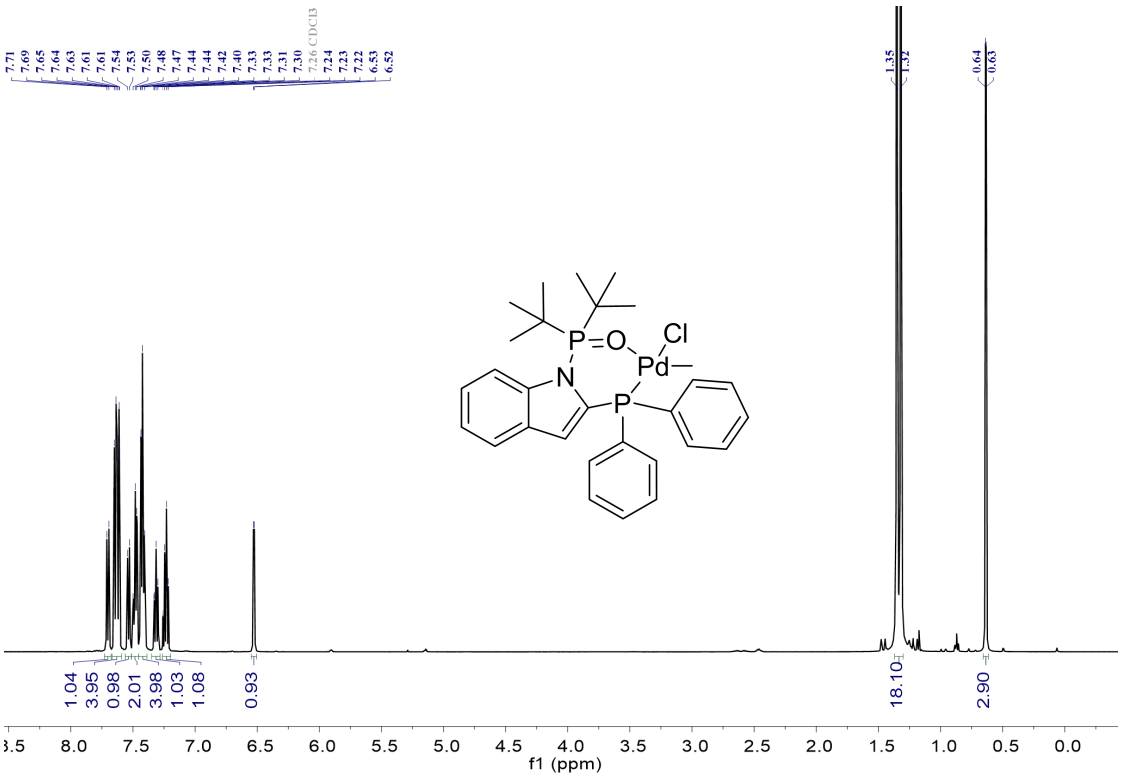


Figure S7. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) of **2a**.

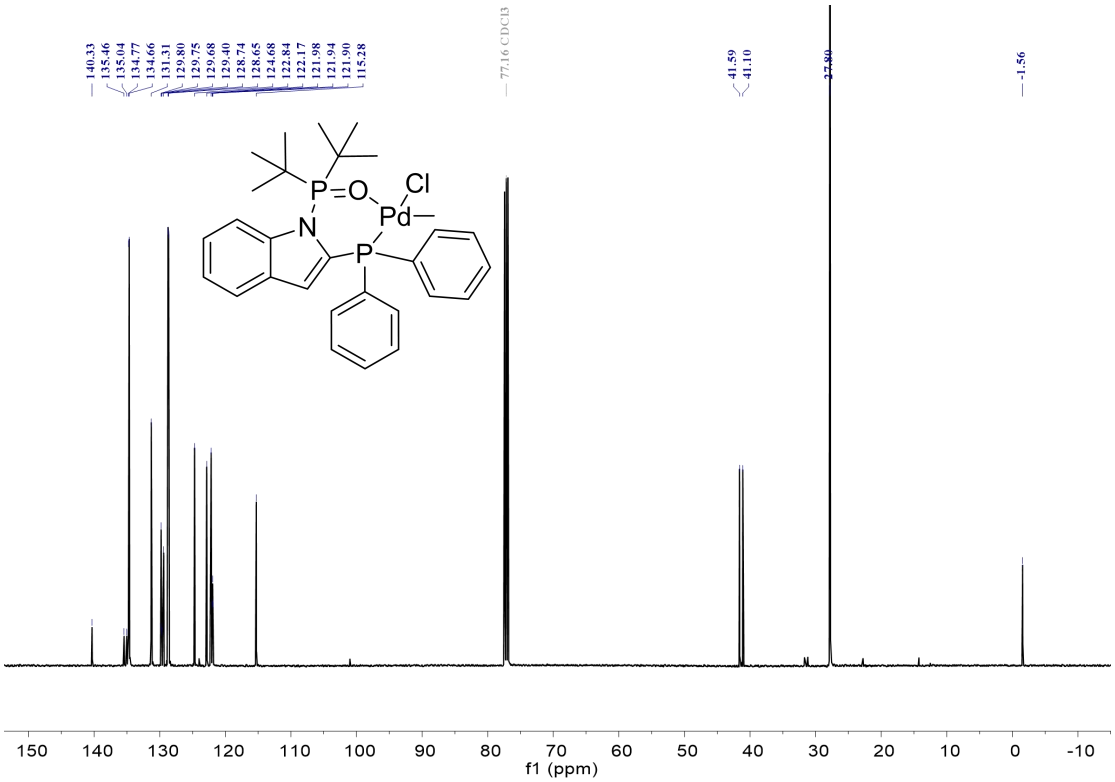


Figure S8. ^{13}C NMR (126 MHz, 298 K, $CDCl_3$) of **2a**.

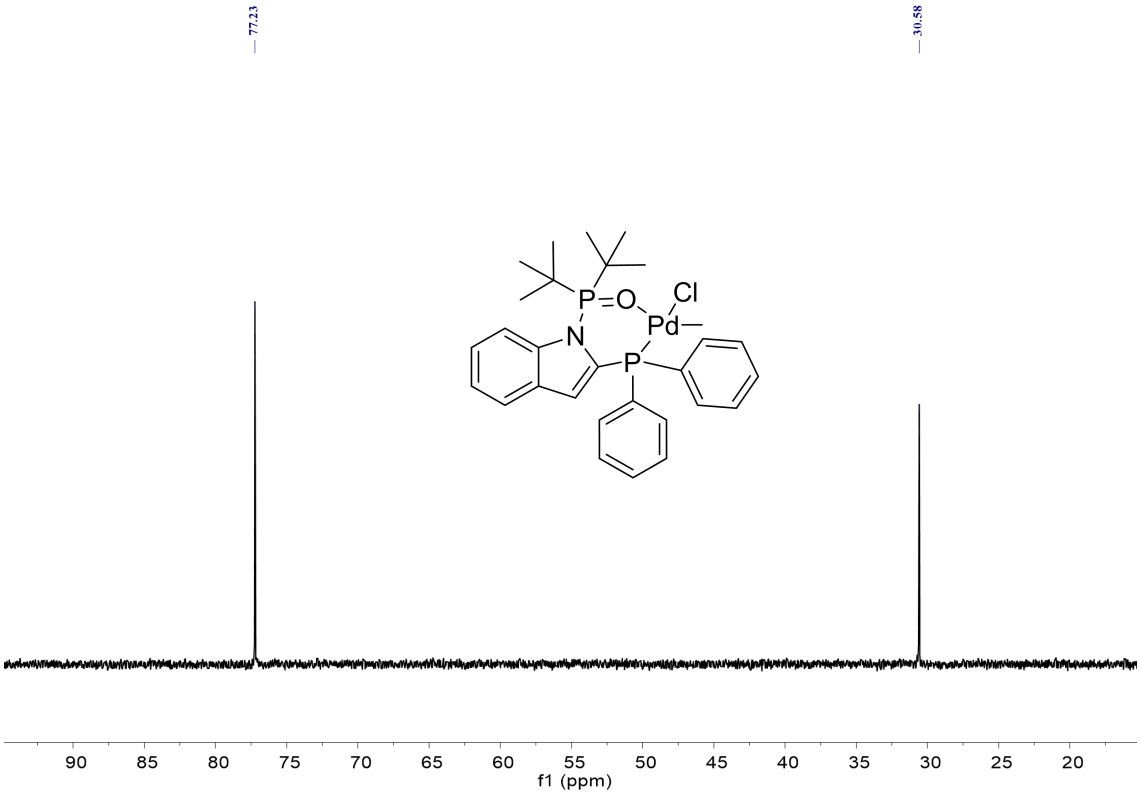


Figure S9. ^{31}P NMR (162 MHz, 298 K, $CDCl_3$) of **2a**.

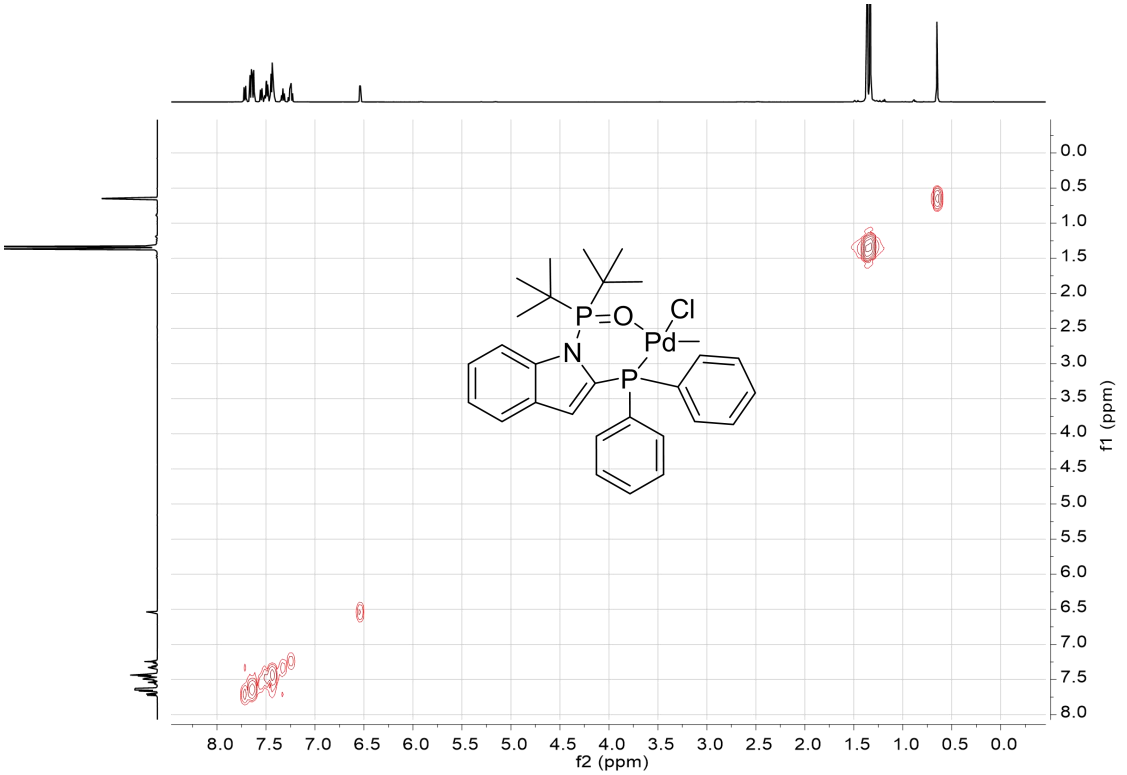


Figure S10. ^{1}H-^{1}H COSY spectrum (500 MHz, 298 K, $CDCl_3$) of **2a**.

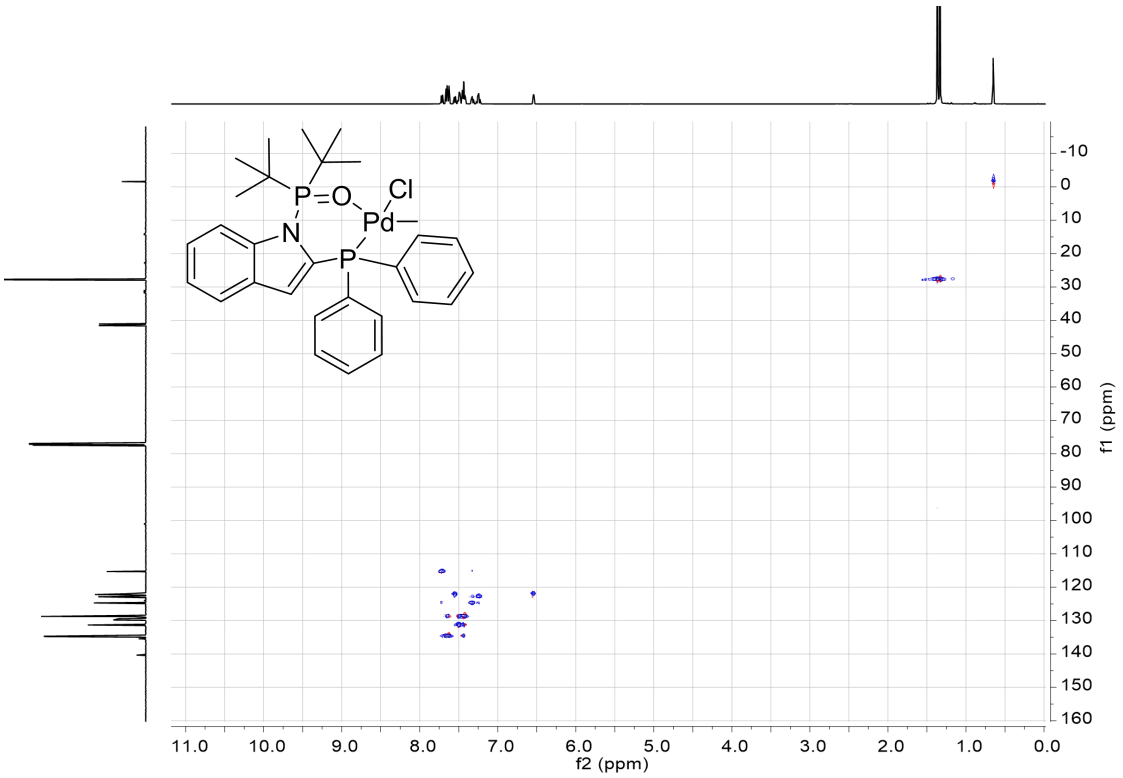


Figure S11. ^{1}H-^{13}C HSQC spectrum (500 MHz, 298 K, $CDCl_3$) of **2a**.

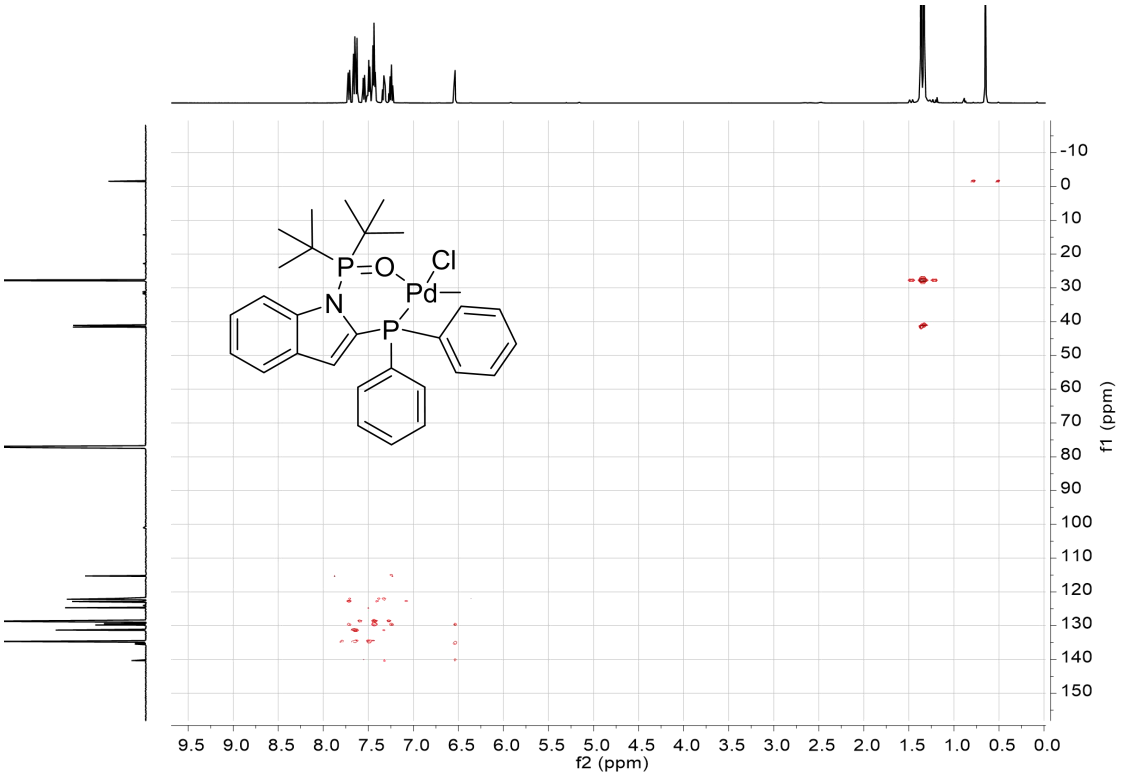


Figure S12. ^{1}H-^{13}C HMBC spectrum (500 MHz, 298 K, $CDCl_3$) of **2a**.

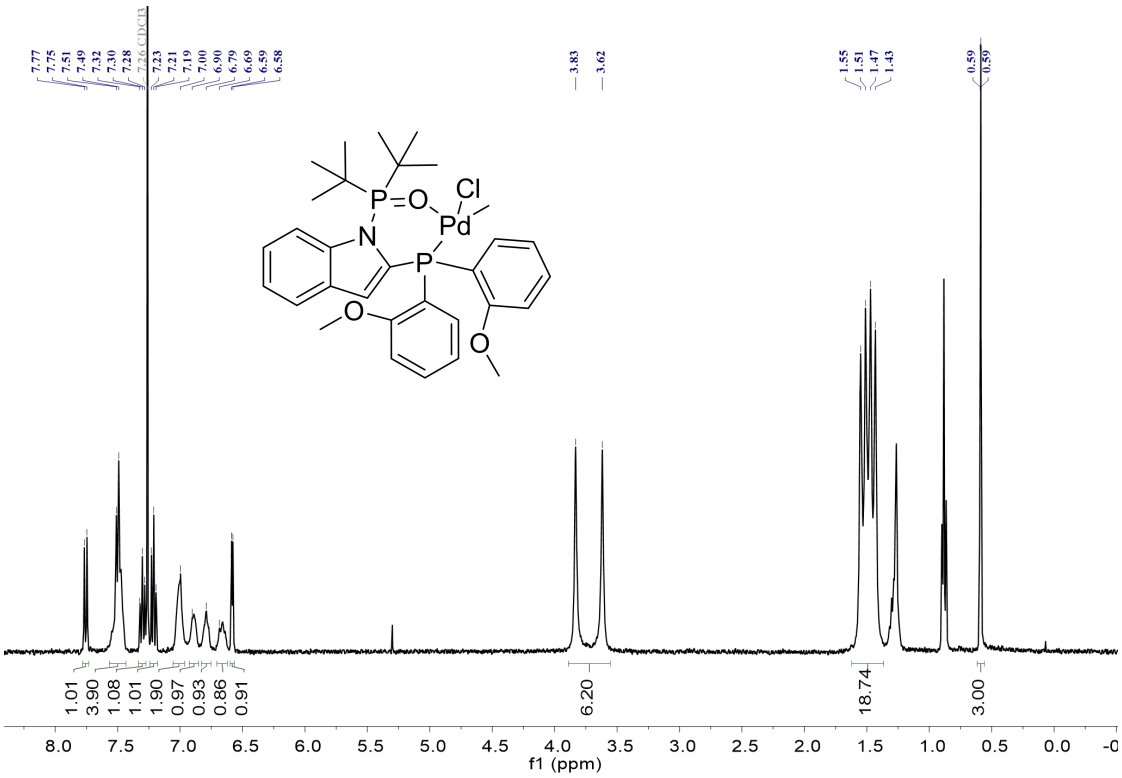


Figure S13. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) of **2b**

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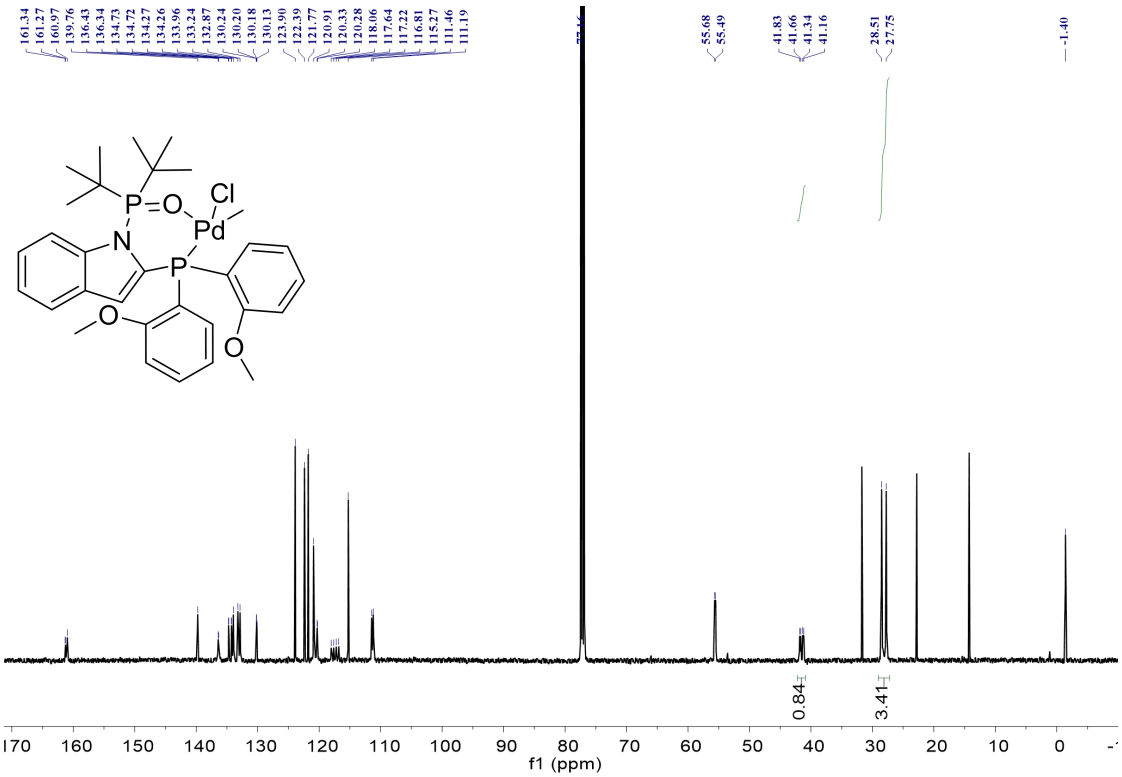


Figure S14. ^{13}C NMR (126 MHz, 298 K, $CDCl_3$) of **2b**.

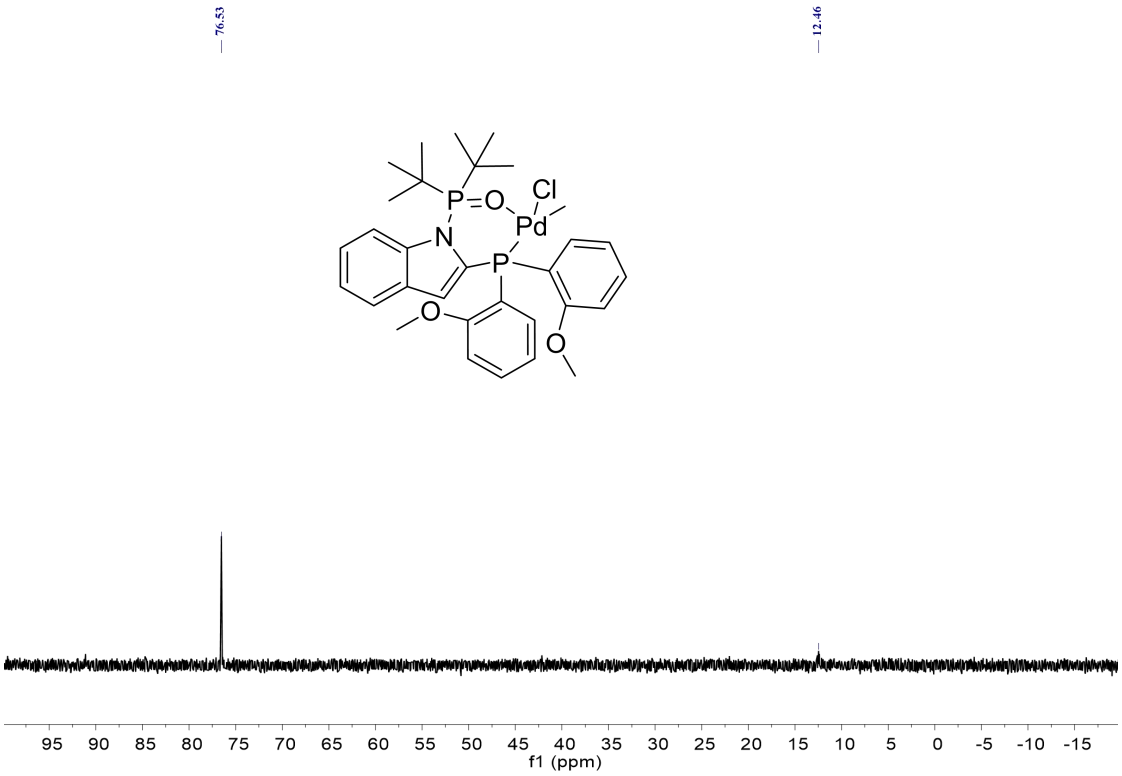


Figure S15. ^{31}P NMR spectrum (162 MHz, 298 K, $CDCl_3$) of **2b**.

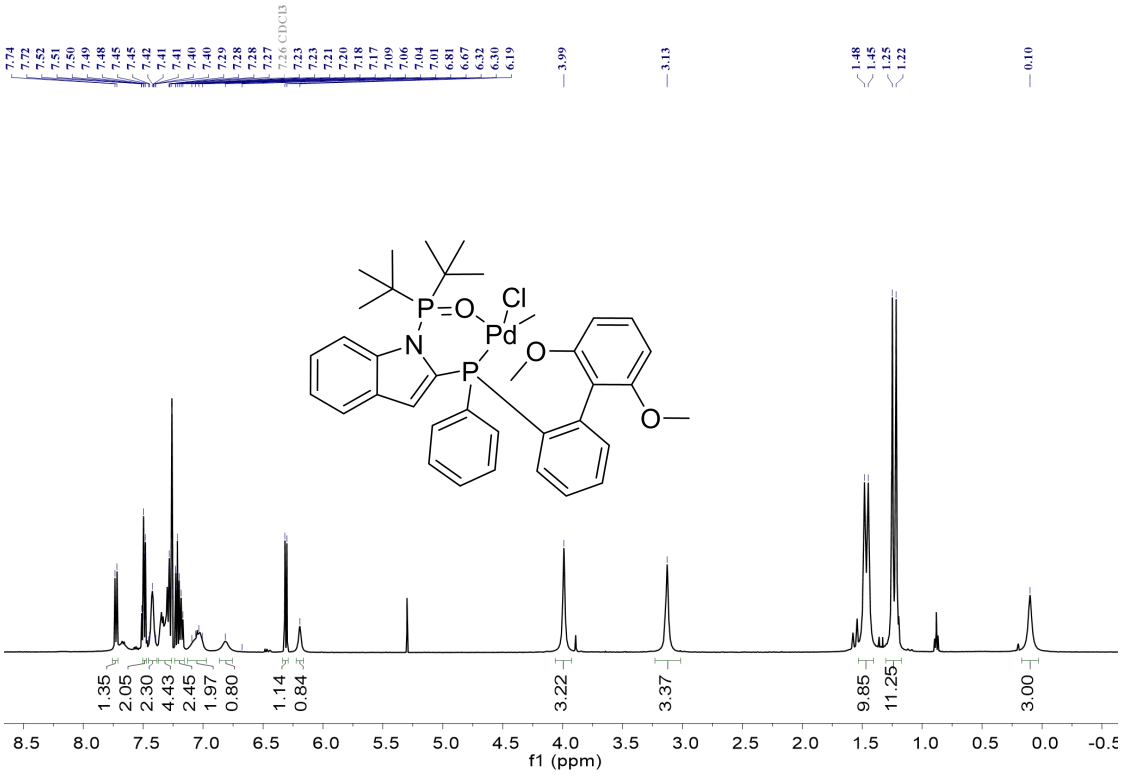


Figure S16. ^{1}H NMR (500 MHz, 298 K, $CDCl_3$) of **2c**.

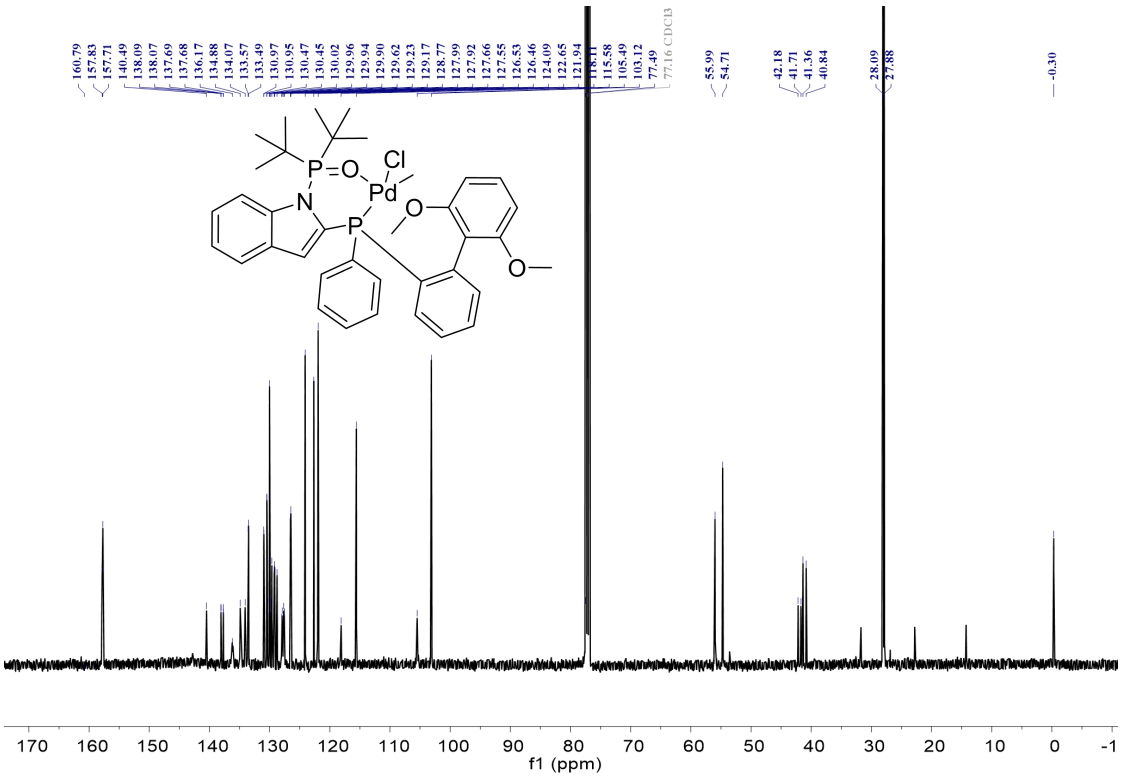


Figure S17. ^{13}C NMR (126 MHz, 298 K, $CDCl_3$) of **2c**.

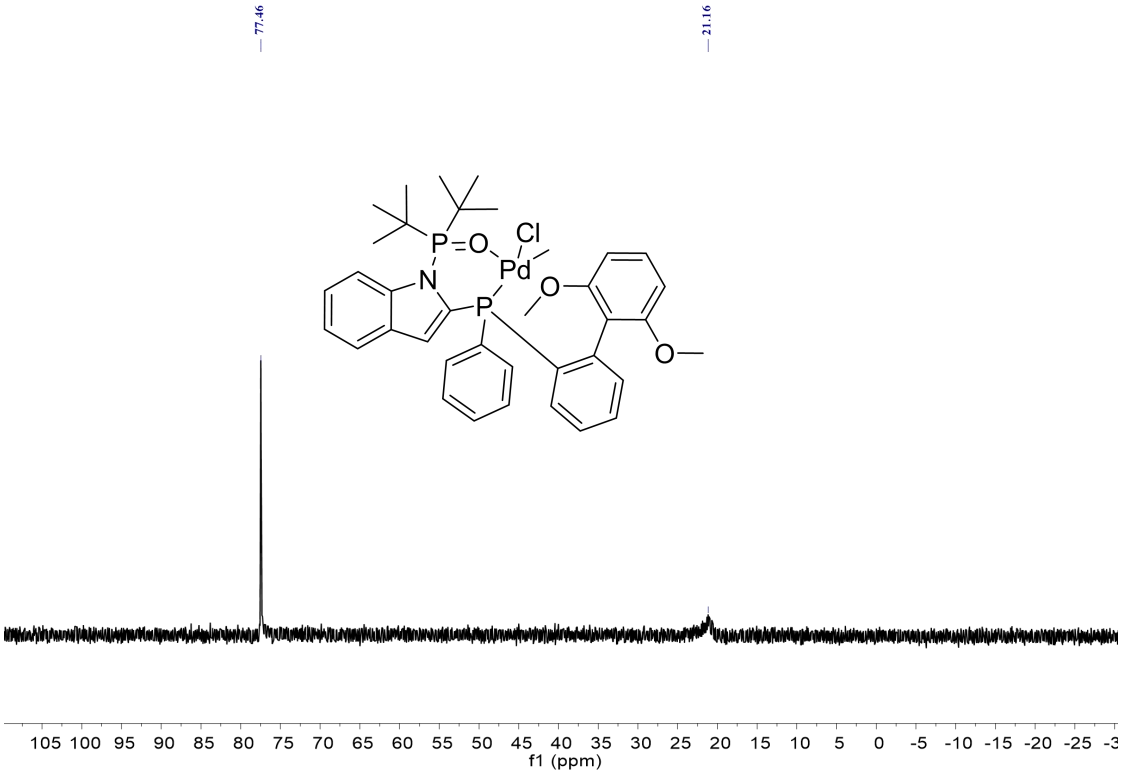


Figure S18. ^{31}P NMR spectrum (202 MHz, 298 K, $CDCl_3$) of **2c**.

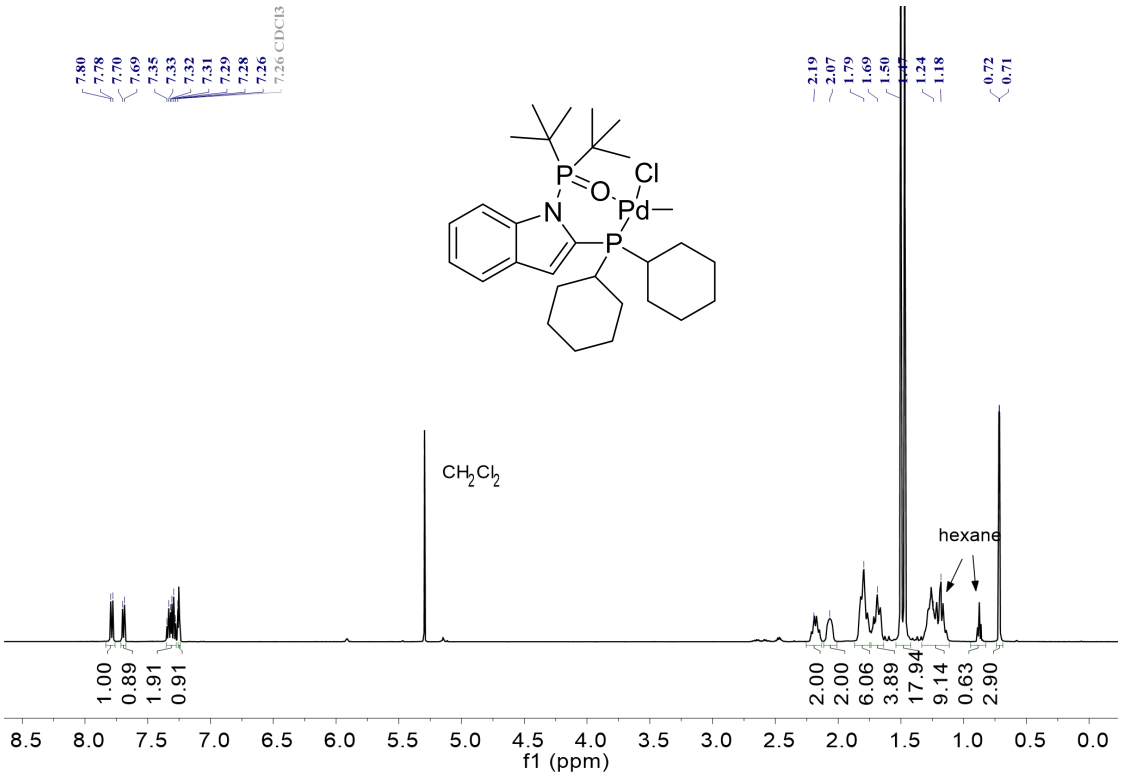


Figure S19. ^{1}H NMR (500 MHz, 298 K, $CDCl_3$) of **2d**.

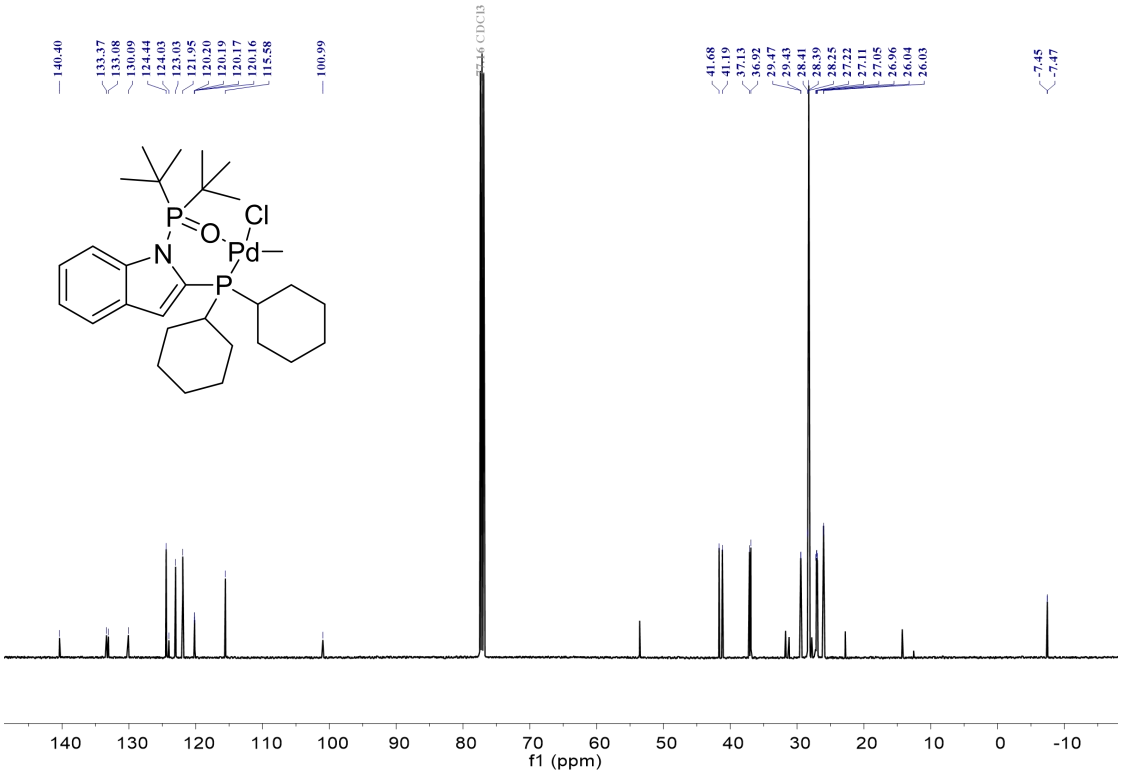


Figure S20.. ^{13}C NMR (126 MHz, 298 K, $CDCl_3$) of **2d**.

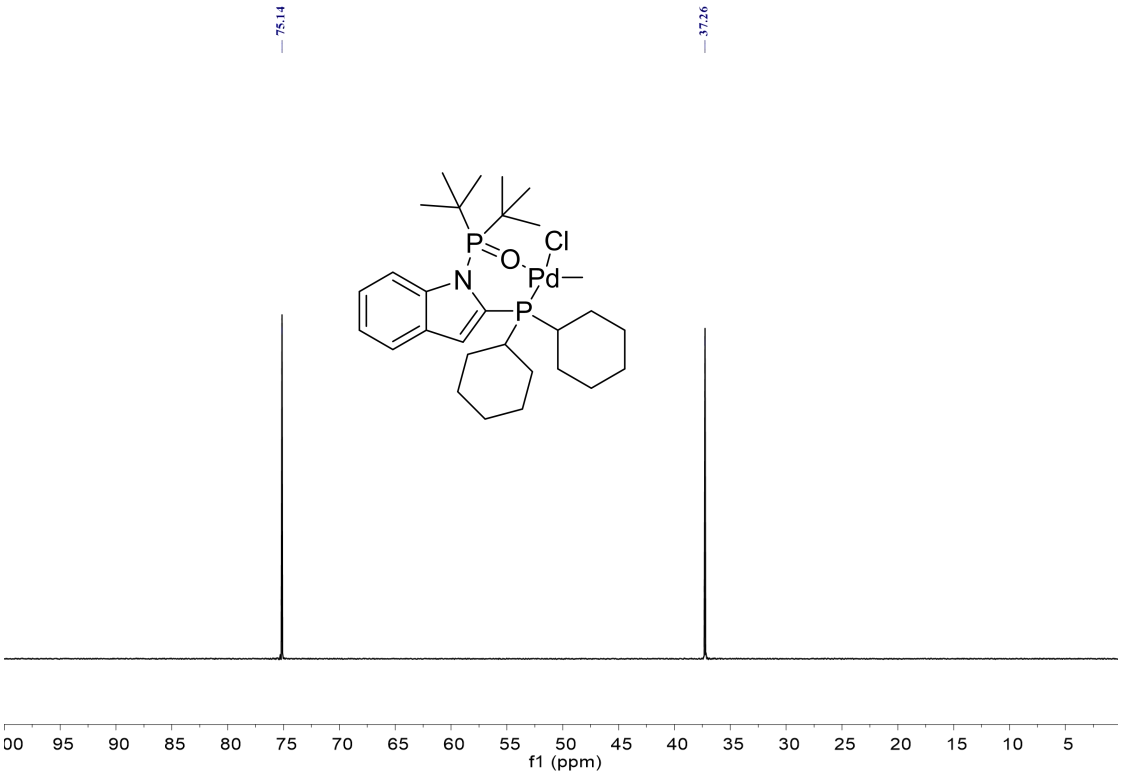


Figure S21. ^{31}P NMR spectrum (202 MHz, 298 K, $CDCl_3$) of **2d**.

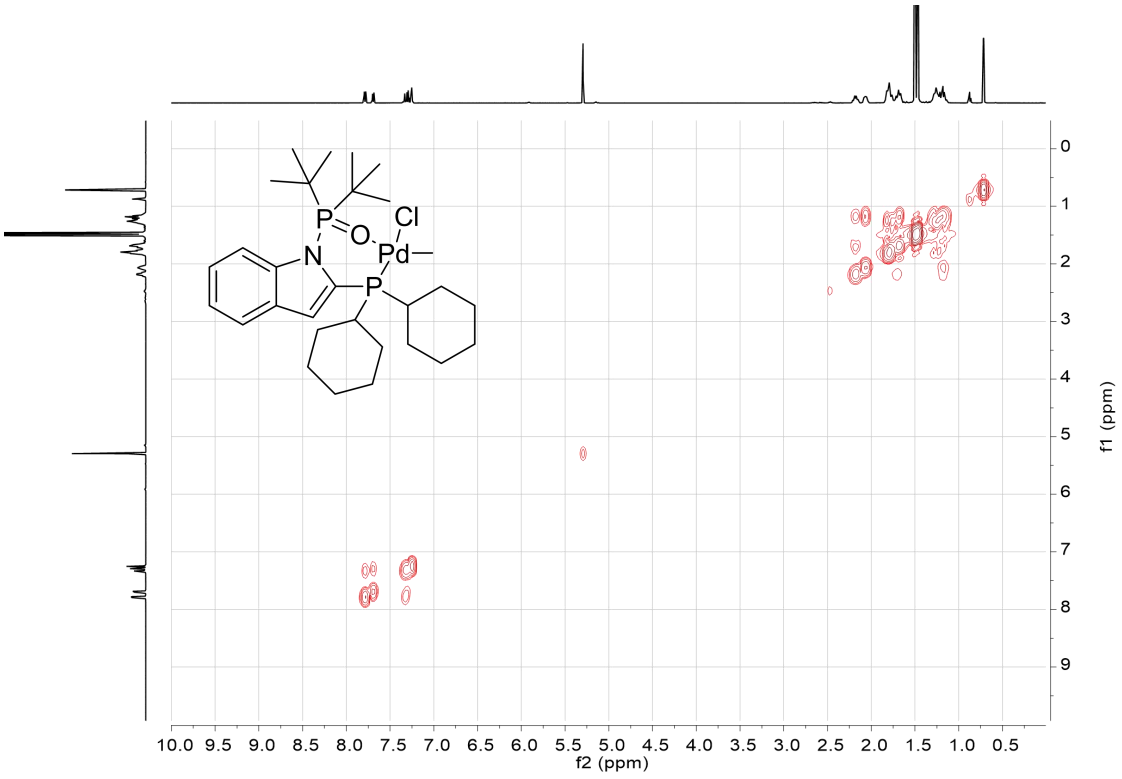


Figure S22. ^{1}H-^{1}H COSY spectrum (500 MHz, 298 K, $CDCl_3$) of **2d**.

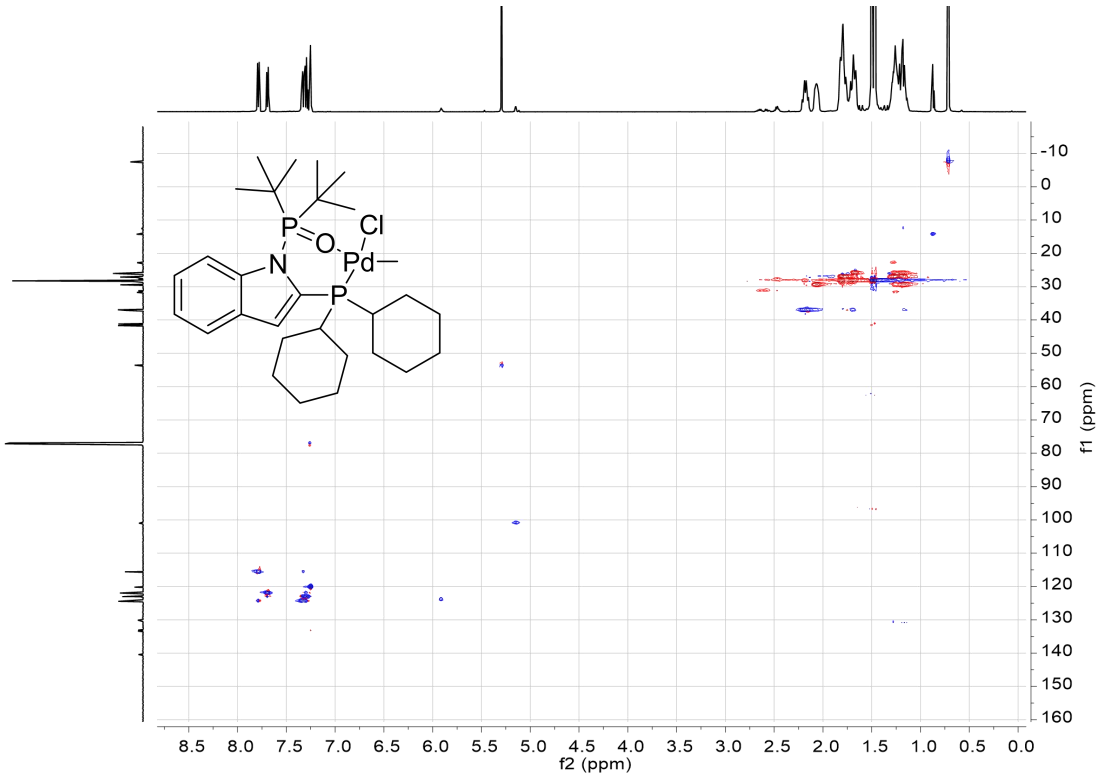


Figure S23. ^{1}H-^{13}C HSQC spectrum (500 MHz, 298 K, $CDCl_3$) of **2d**.

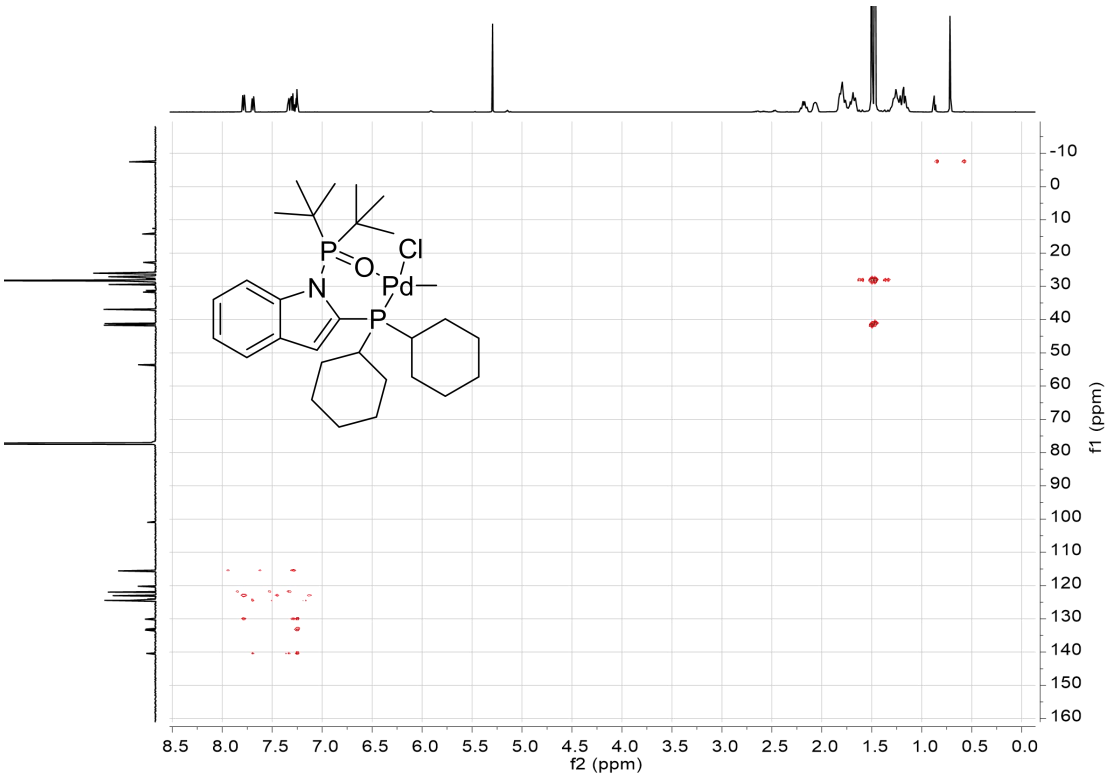


Figure S24. ^{1}H-^{13}C HMBC spectrum (500 MHz, 298 K, $CDCl_3$) of **2d**.

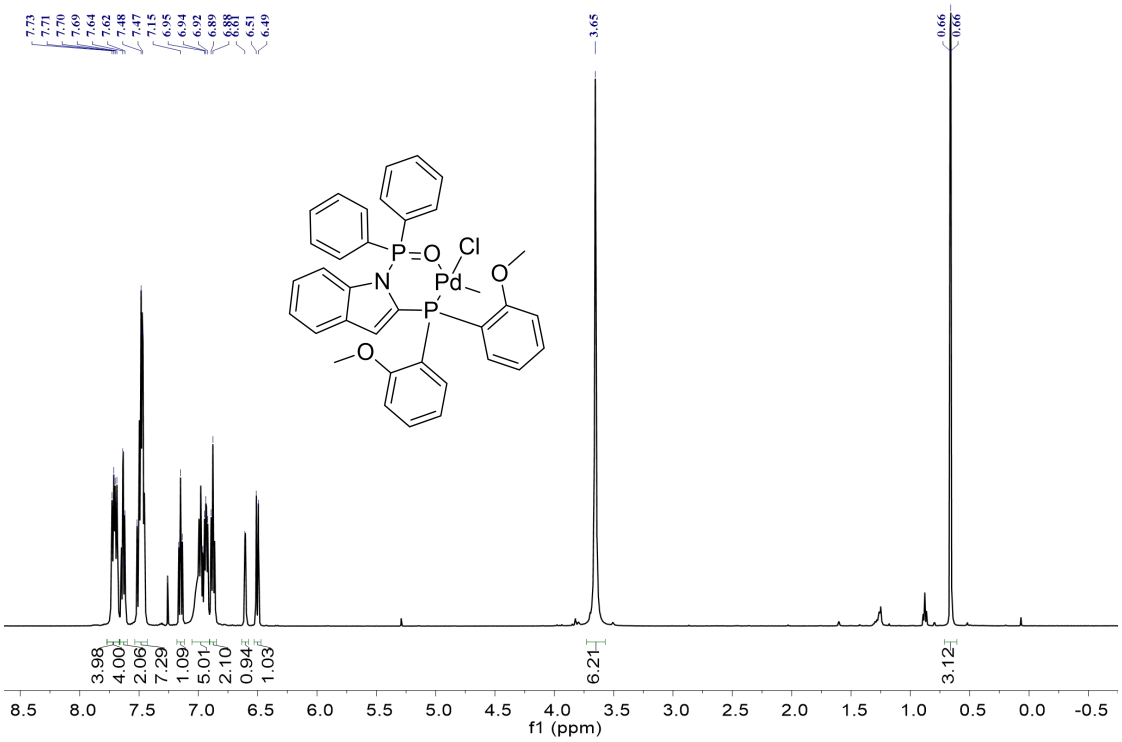


Figure S25. ^{1}H NMR (500 MHz, 298 K, $CDCl_3$) of **2e**.

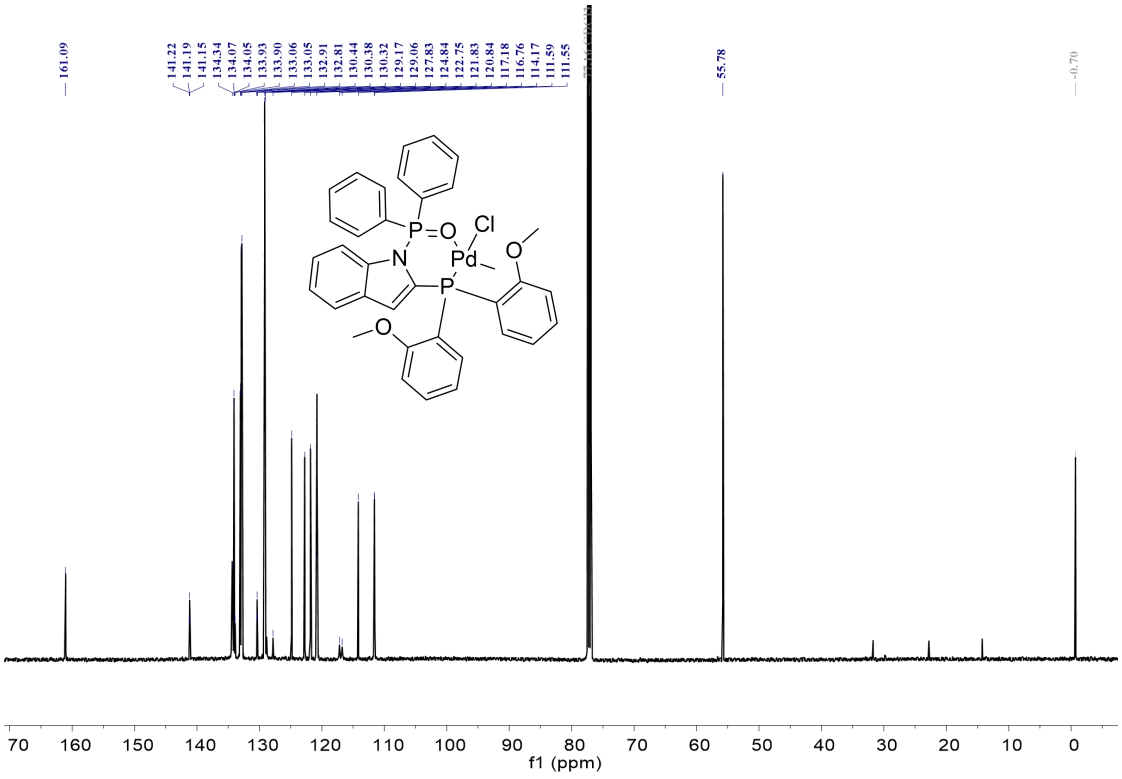


Figure S26. ^{13}C NMR (126 MHz, 298 K, $CDCl_3$) of **2e**.

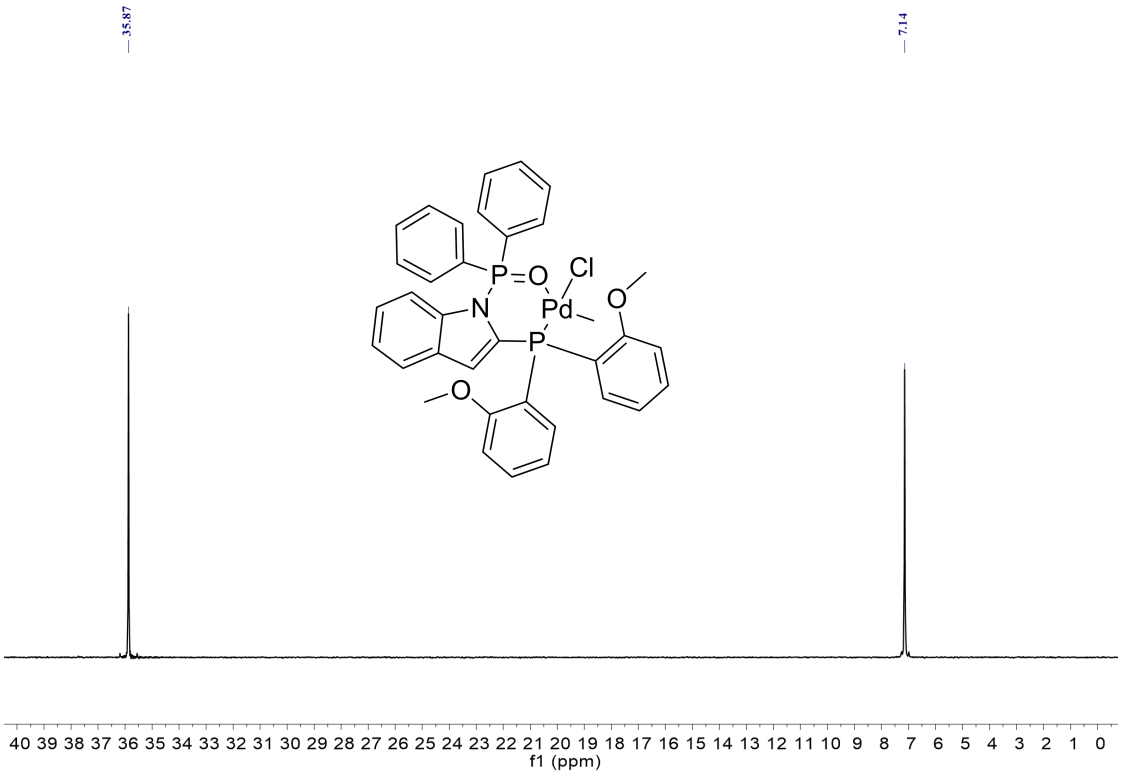


Figure S27. ^{31}P NMR spectrum (202 MHz, 298 K, $CDCl_3$) of **2e**.

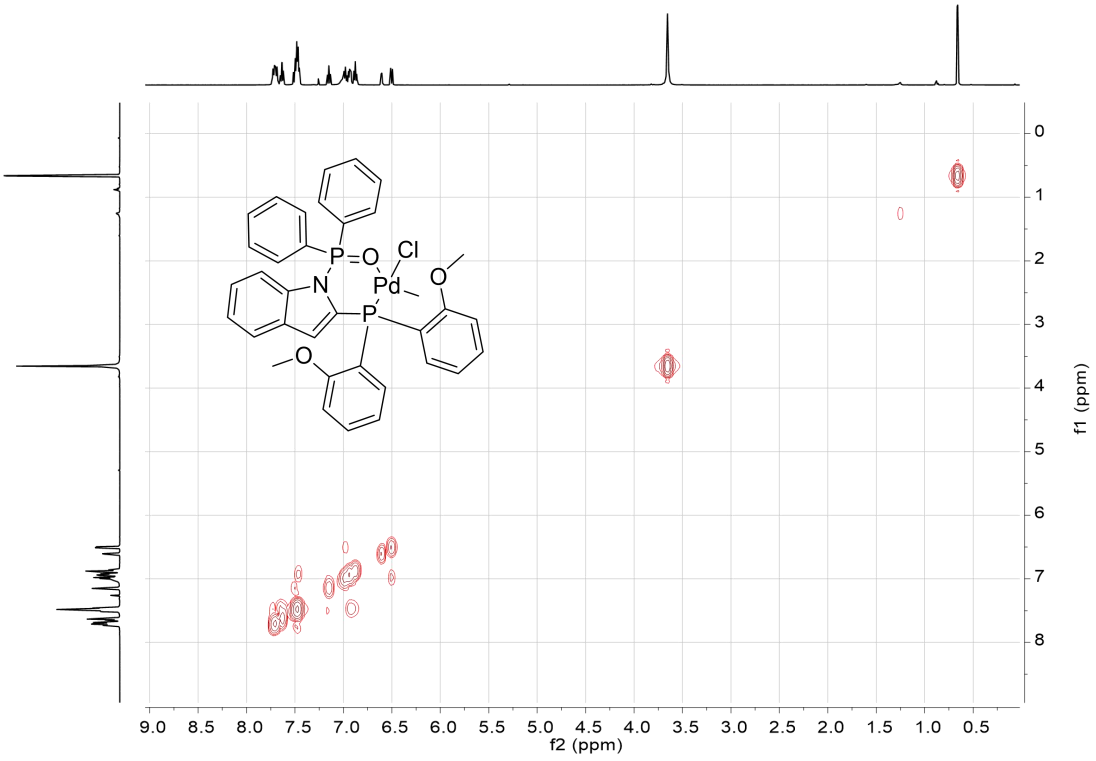


Figure S28. ^{1}H-^{1}H COSY spectrum (500 MHz, 298 K, $CDCl_3$) of **2e**.

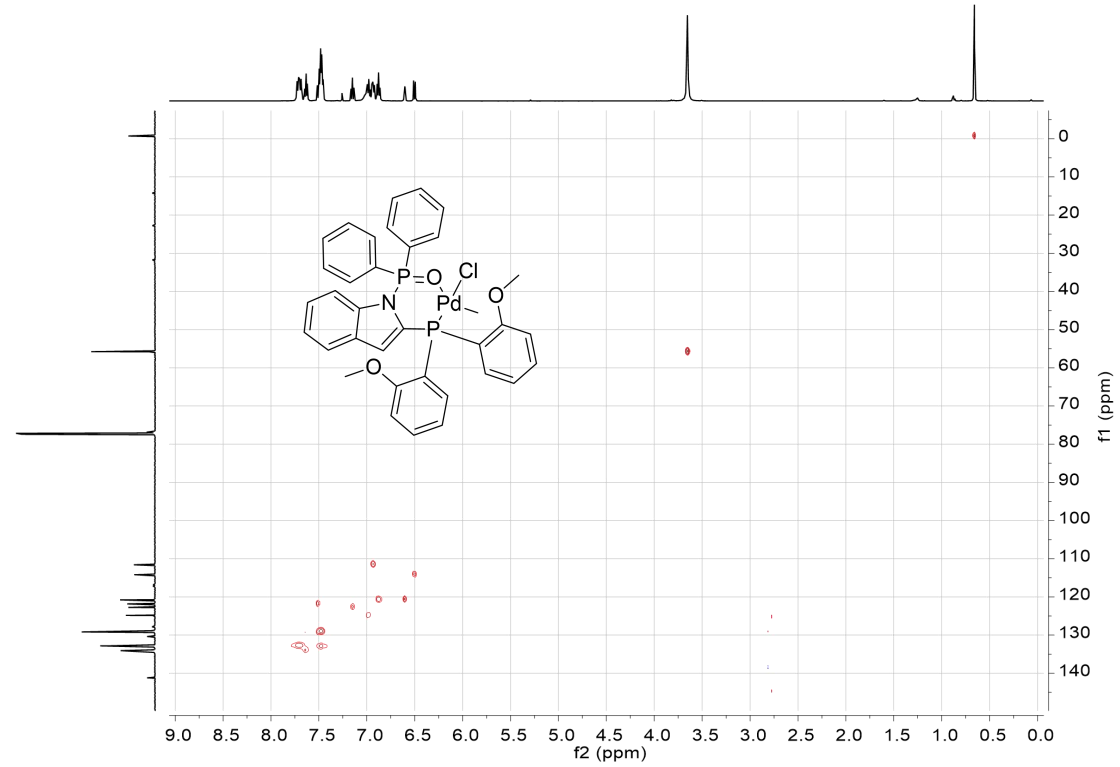


Figure S29. ^{1}H-^{13}C HSQC spectrum (500 MHz, 298 K, $CDCl_3$) of **2e**.

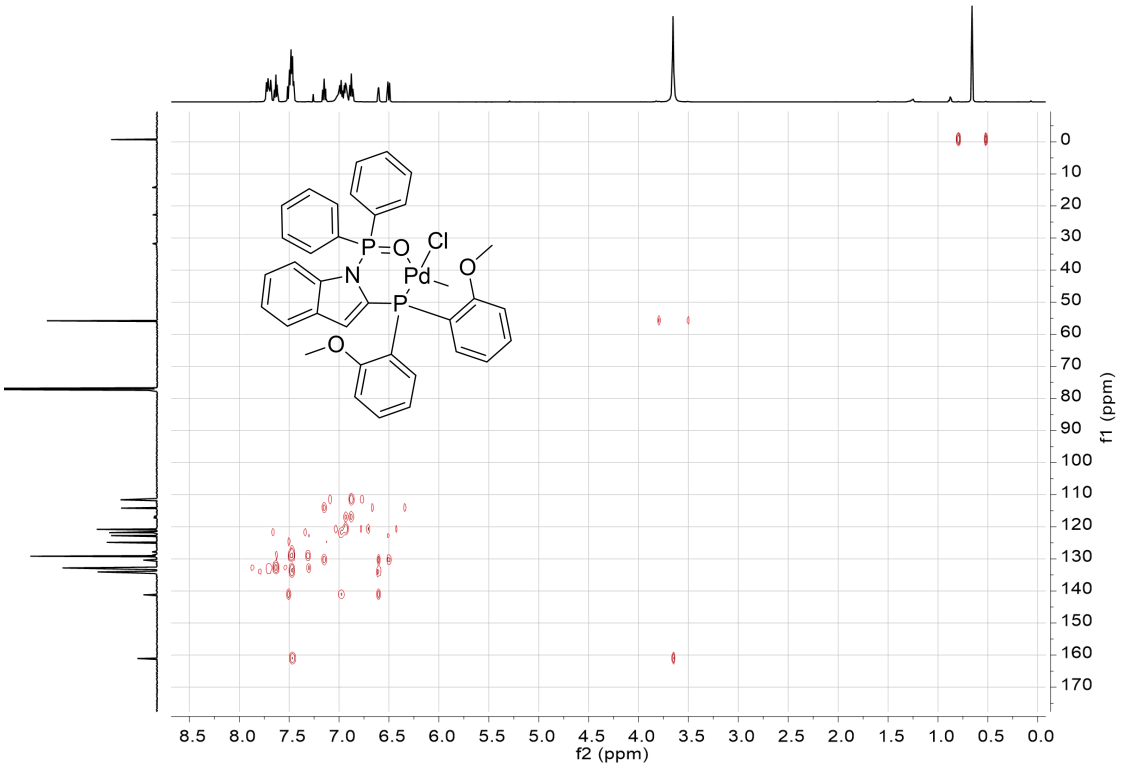


Figure S30. ^{1}H-^{13}C HMBC spectrum (500 MHz, 298 K, $CDCl_3$) of **2e**.

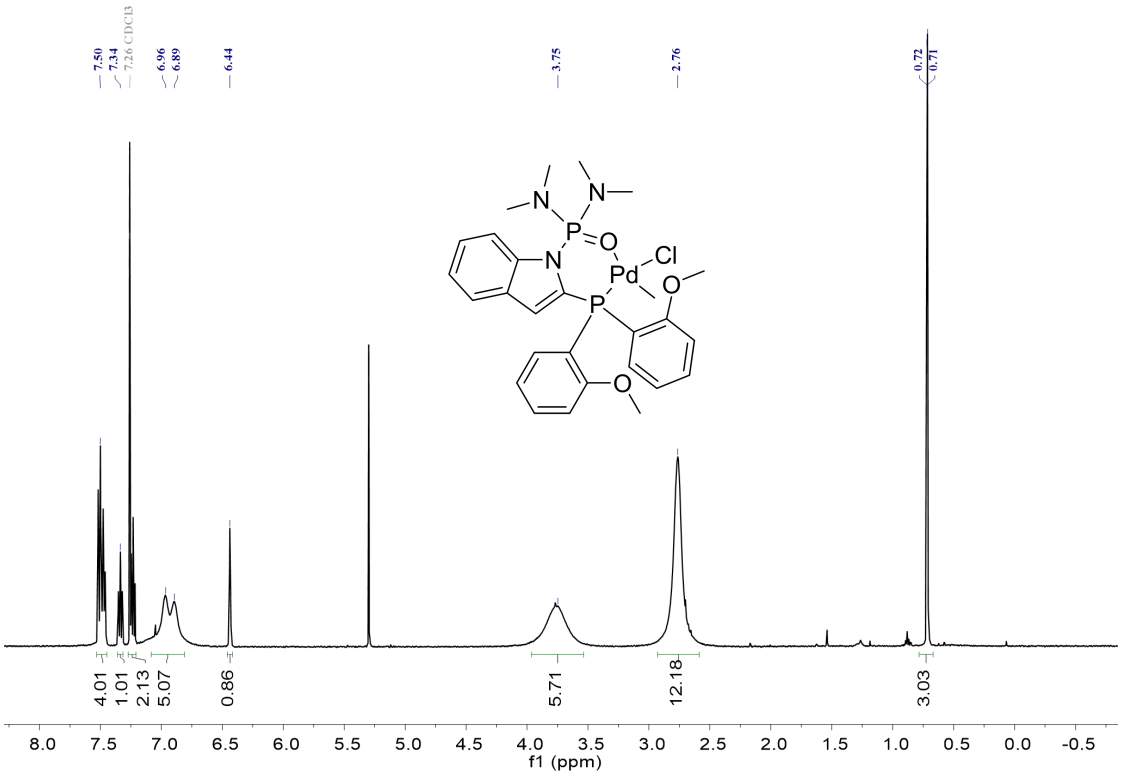


Figure S31. ^{1}H NMR (500 MHz, 298 K, $CDCl_3$) of **2f**.

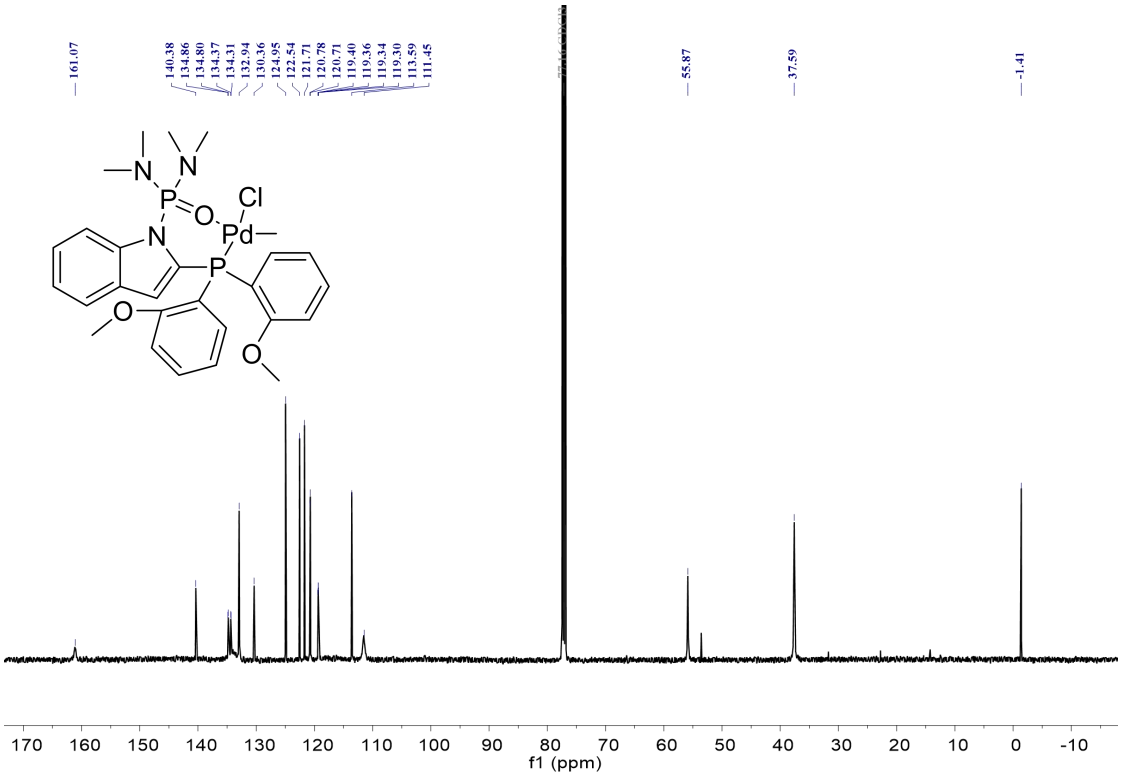


Figure S32. ^{13}C NMR (126 MHz, 298 K, $CDCl_3$) of **2f**.

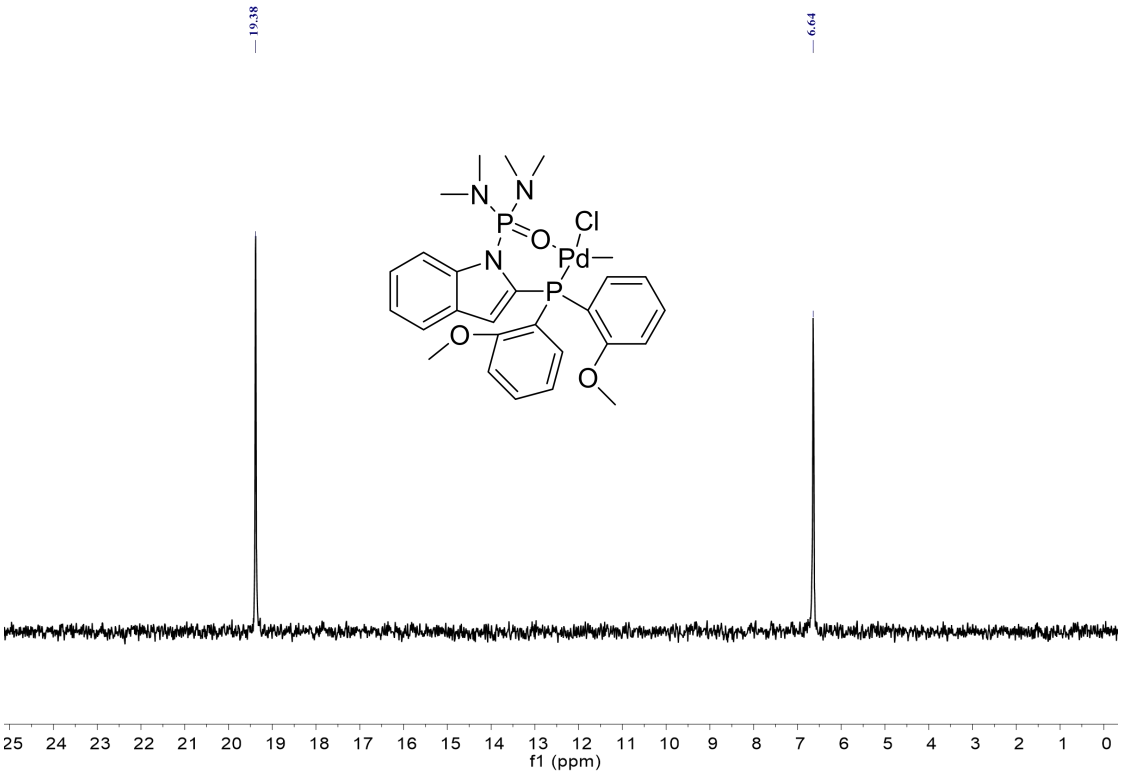


Figure S33. ^{31}P NMR spectrum (202 MHz, 298 K, $CDCl_3$) of **2f**.

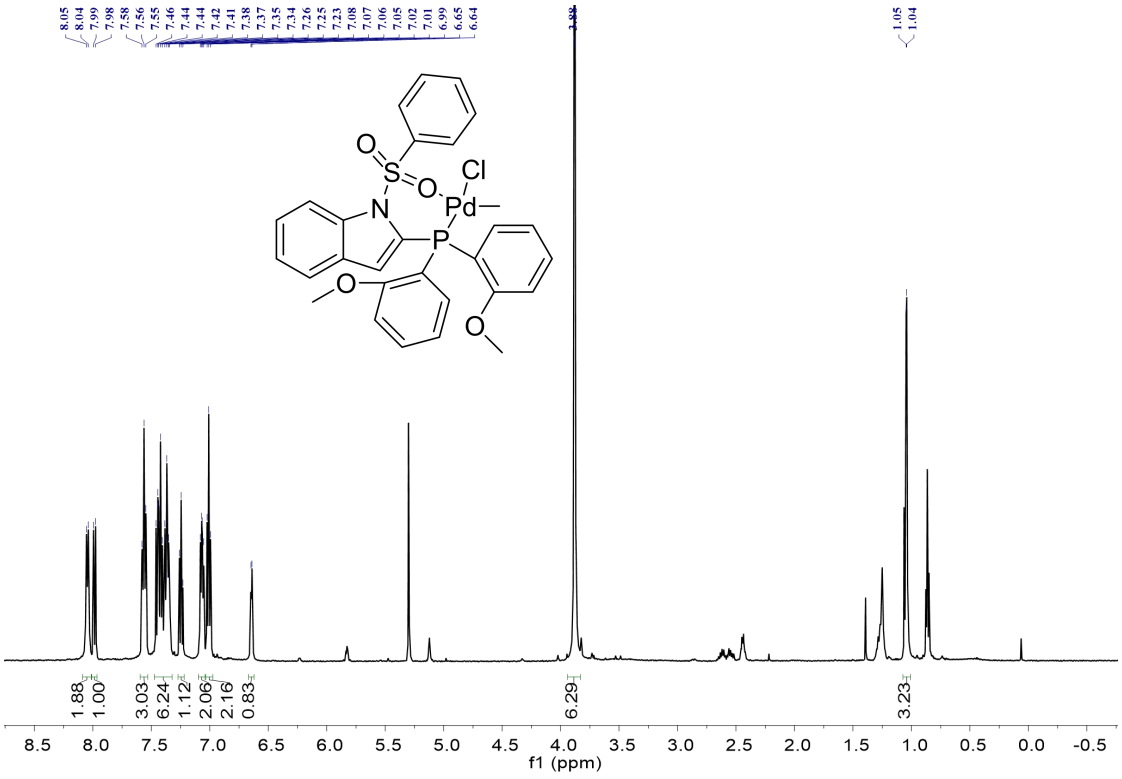


Figure S34. ^{1}H NMR (500 MHz, 298 K, $CDCl_3$) of **2g**.

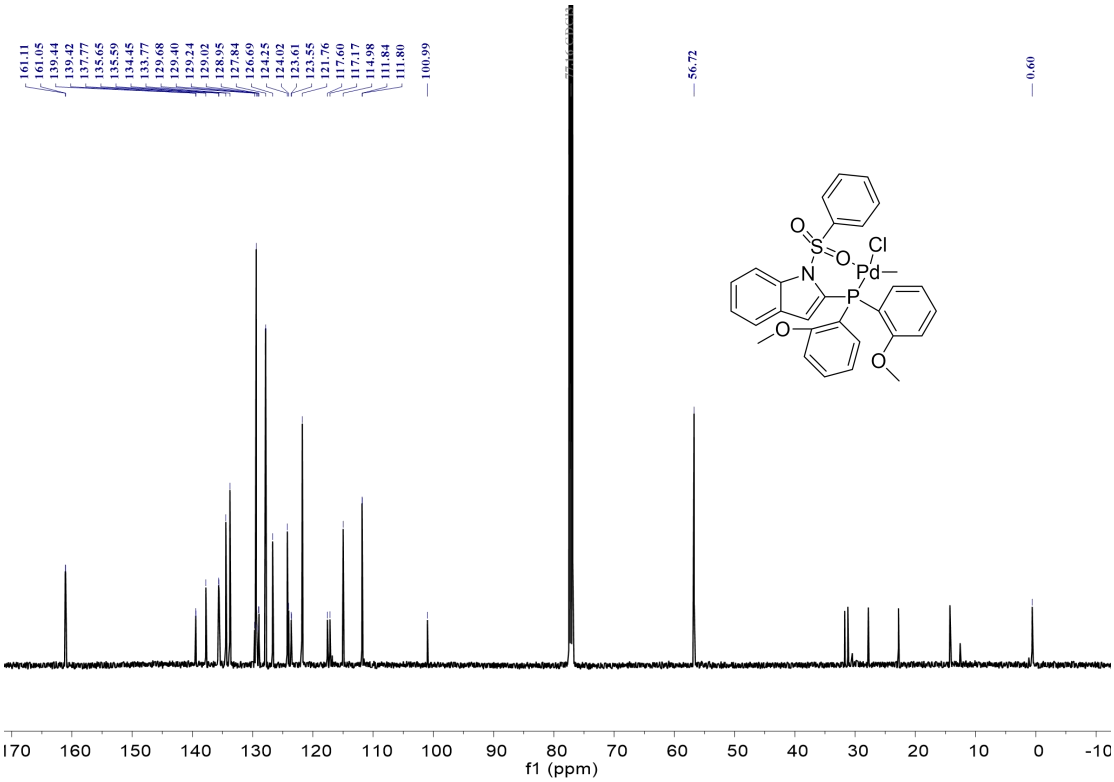


Figure S35. ^{13}C NMR (126 MHz, 298 K, $CDCl_3$) of **2g**.

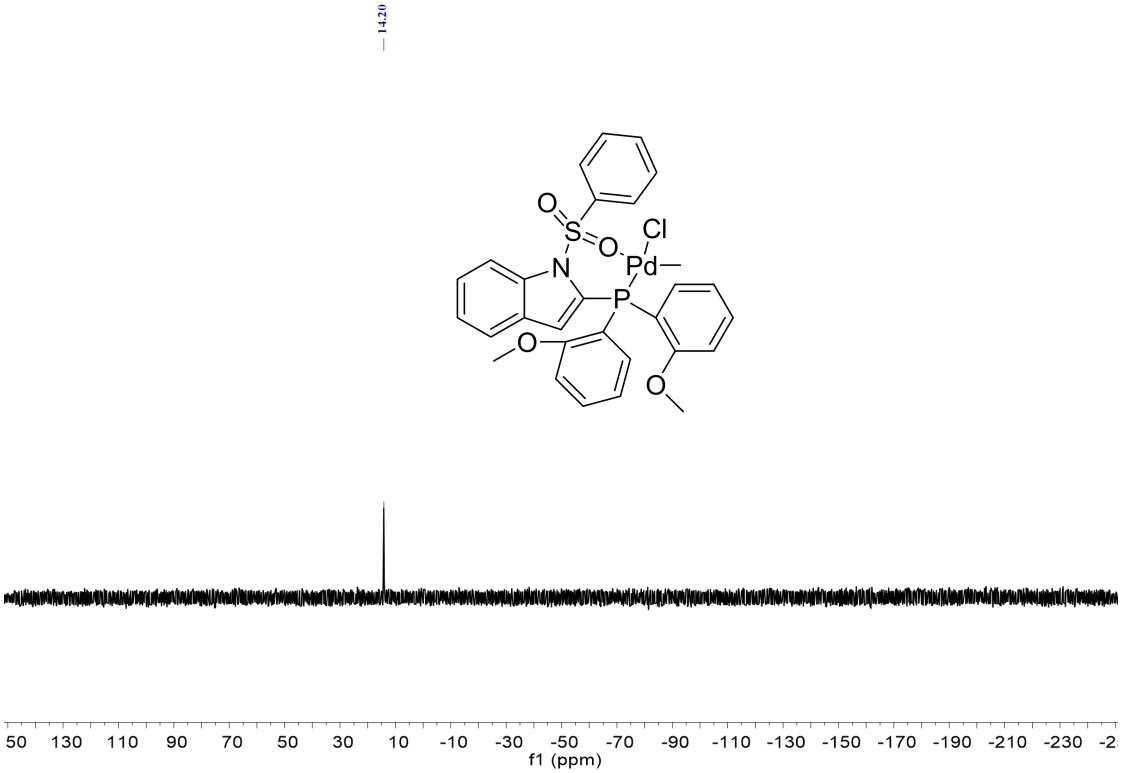


Figure S36. ^{31}P NMR spectrum (202 MHz, 298 K, $CDCl_3$) of **2g**.

3. NMR spectra of (co)polymers

Calculation of Me Branches/ 1000C

$$\text{Me Branches (doublet)/ 1000C} = \frac{(I_1 - \frac{I_4 + I_5}{2} \times 3) / 3}{(I_1 + I_2 + I_3 + I_4 + I_5)/2} \times 1000$$

I_1: overall integral of Me groups

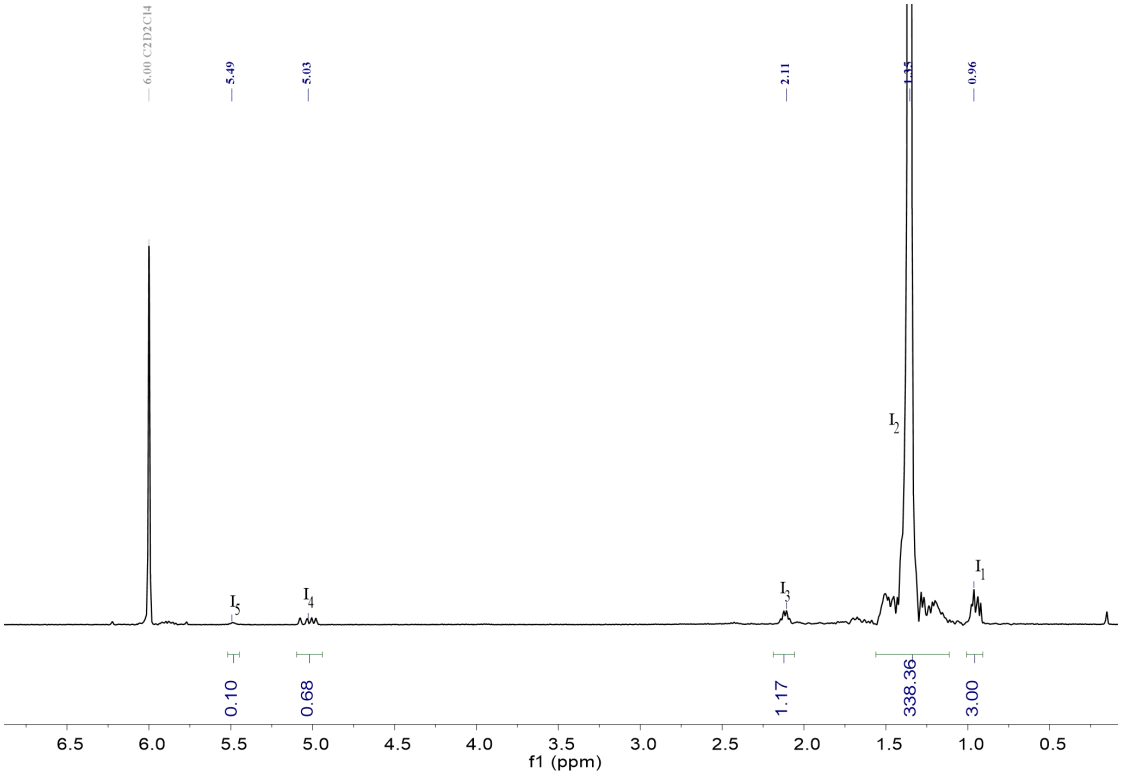
I_2: Integral of main-chain CH_2 signals

I_3: Integral of allylic group

I_4: Integral of CH_2 signals of chain-end double bonds

I_5: Integral of CH signals of inner double bonds

Figure S40 as an example



$$\text{Me Branches/ 1000C} = \frac{\left(3.0 - 3 \times \frac{0.68 + 0.10}{2}\right) / 3}{(3.0 + 338.36 + 1.17 + 0.68)/2} \times 1000 = 3.6$$

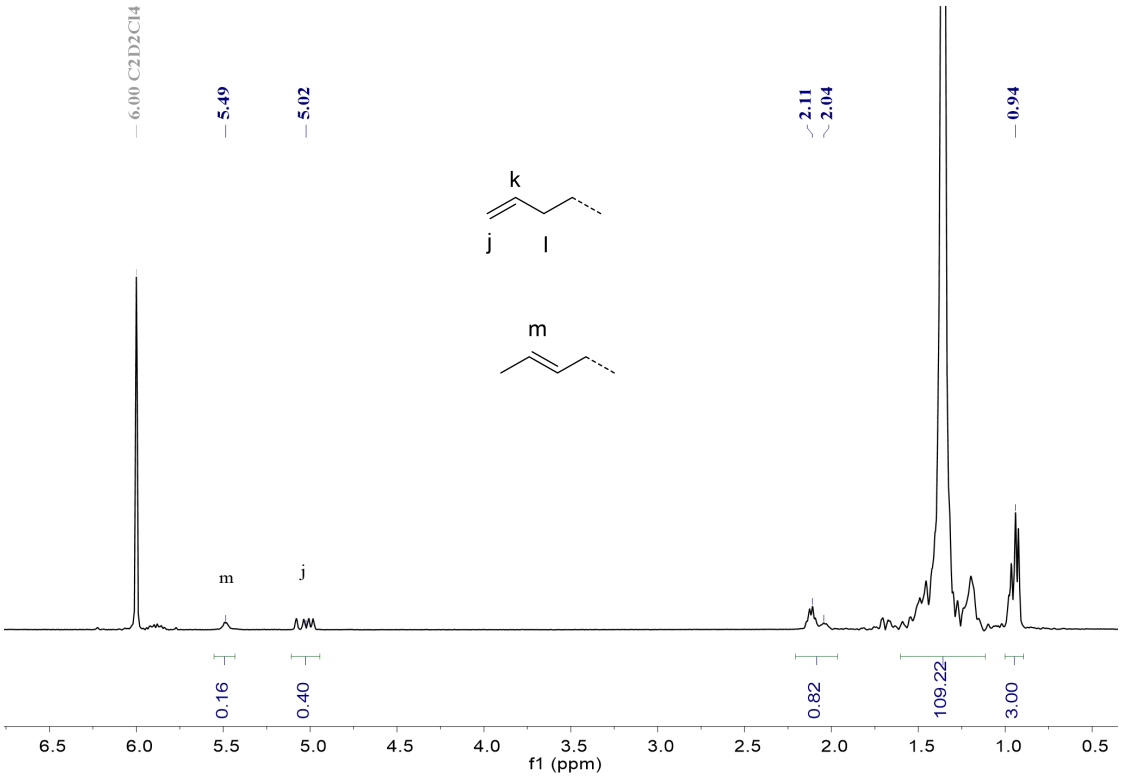


Figure S37. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 °C) of the polymer from table 1, entry 2.

$$\text{Me Branches/ 1000C} = \frac{\left(3.0 - 3\times\frac{0.40+0.16}{2}\right)/3}{(3.0+109.22+0.82+0.40+0.16)/2} \times 1000 = 12.7$$

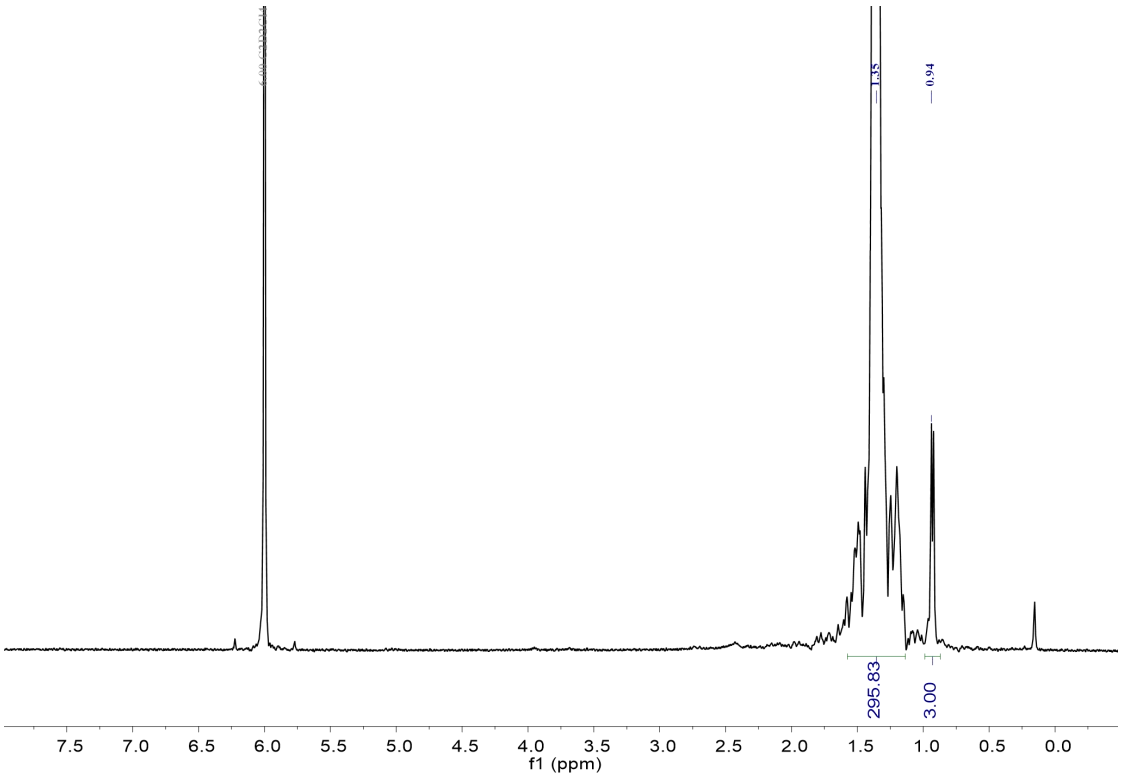


Figure S38. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 °C) of the polymer from table 1, entry 4.

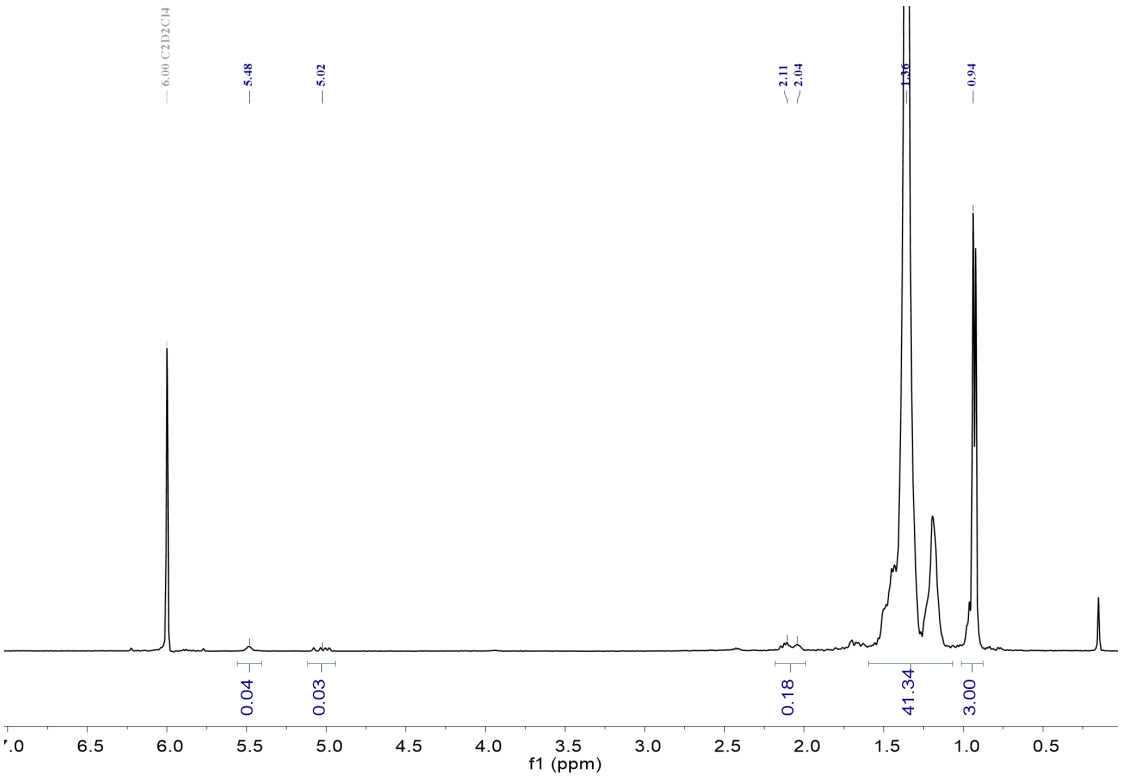


Figure S39. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 °C) of the polymer from table 1, entry 8.

$$\text{Me Branches/ 1000C} = \frac{\left(3.0 - 3\times\frac{0.03+0.04}{2}\right)/3}{(3.0+41.34+0.18+0.21+0.03+0.04)/2} \times 1000 = 41.9$$

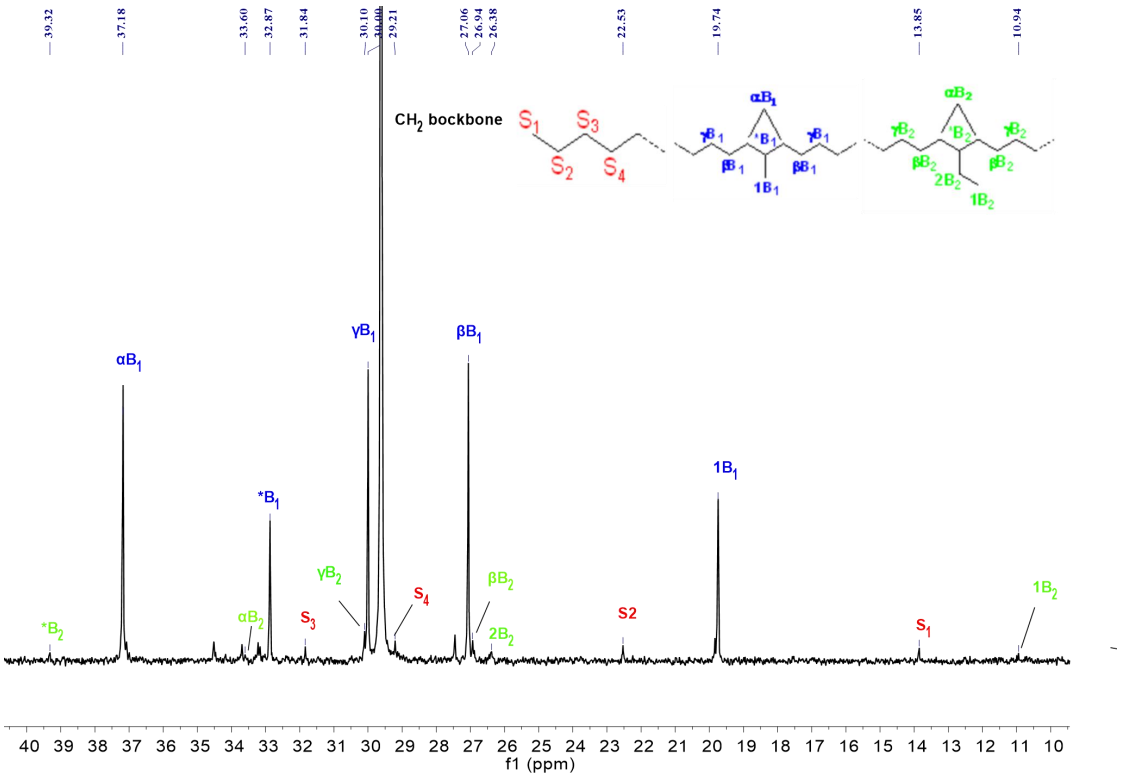


Figure S40. ^{13}C NMR spectrum (101 MHz, $C_2D_2Cl_4$, 110 °C) of the polymer from table 1, entry 8.

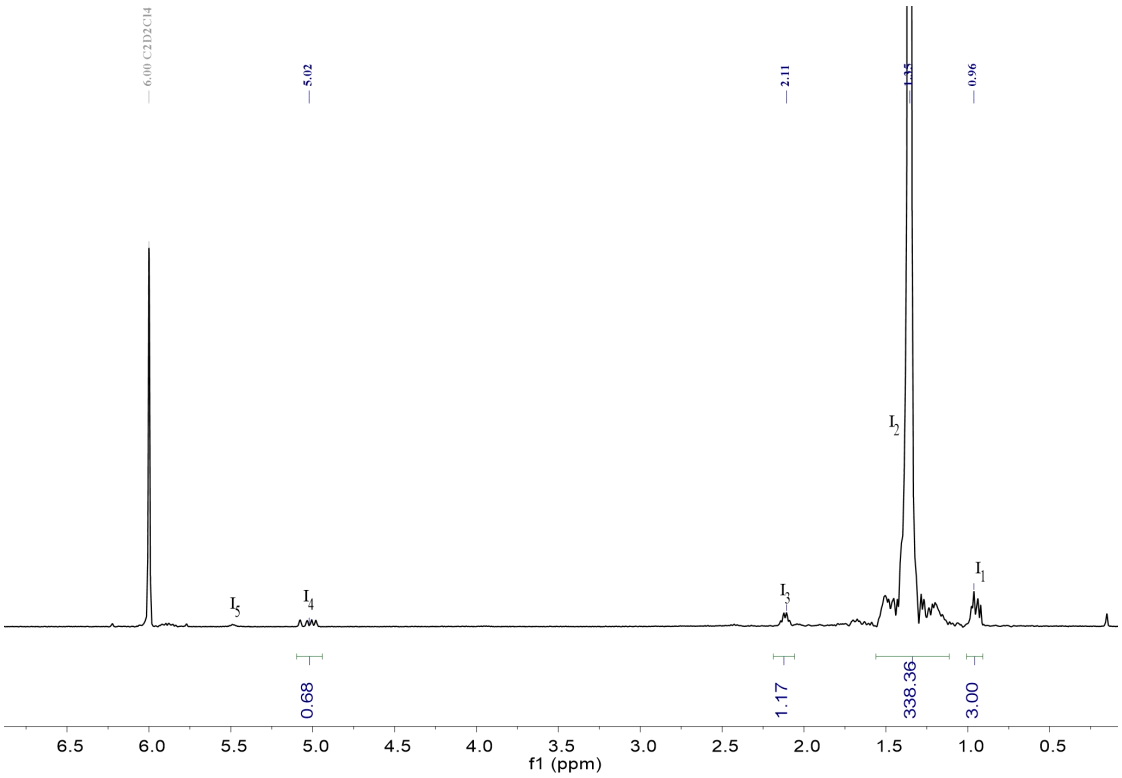


Figure S41. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 °C) of the polymer from table 1, entry 10.

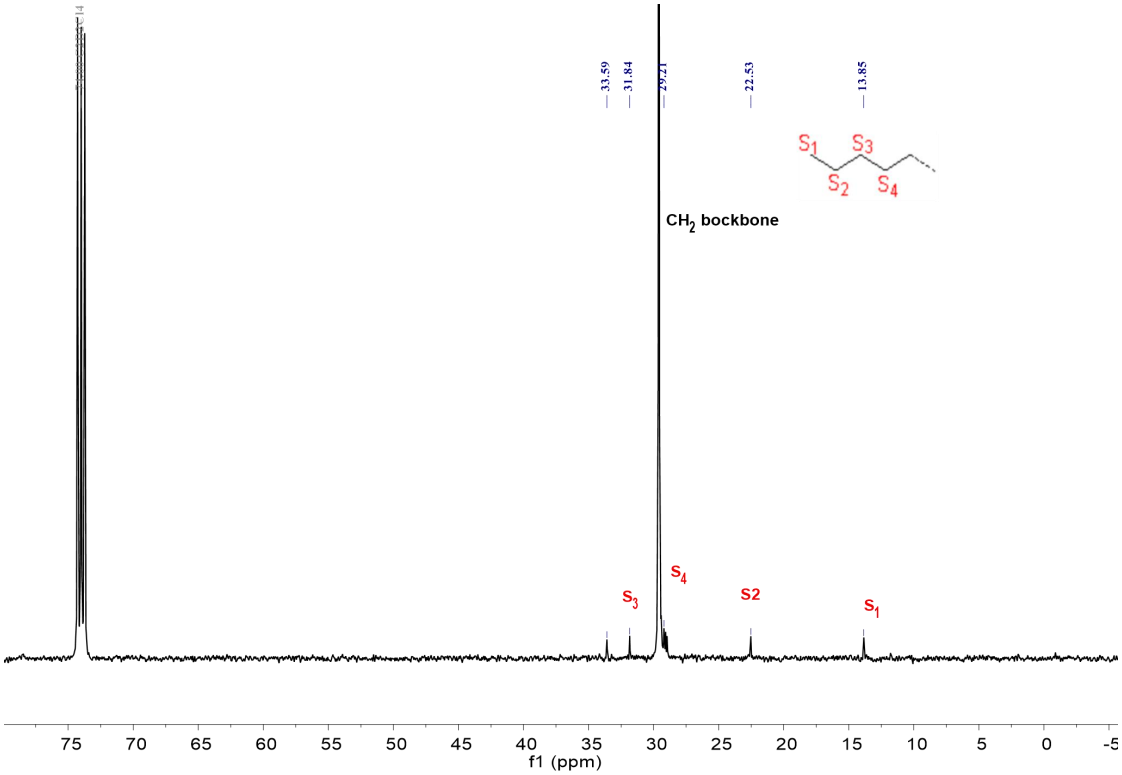


Figure S42. ^{13}C NMR spectrum (101 MHz, $C_2D_2Cl_4$, 110 °C) of the polymer from table 1, entry 12.

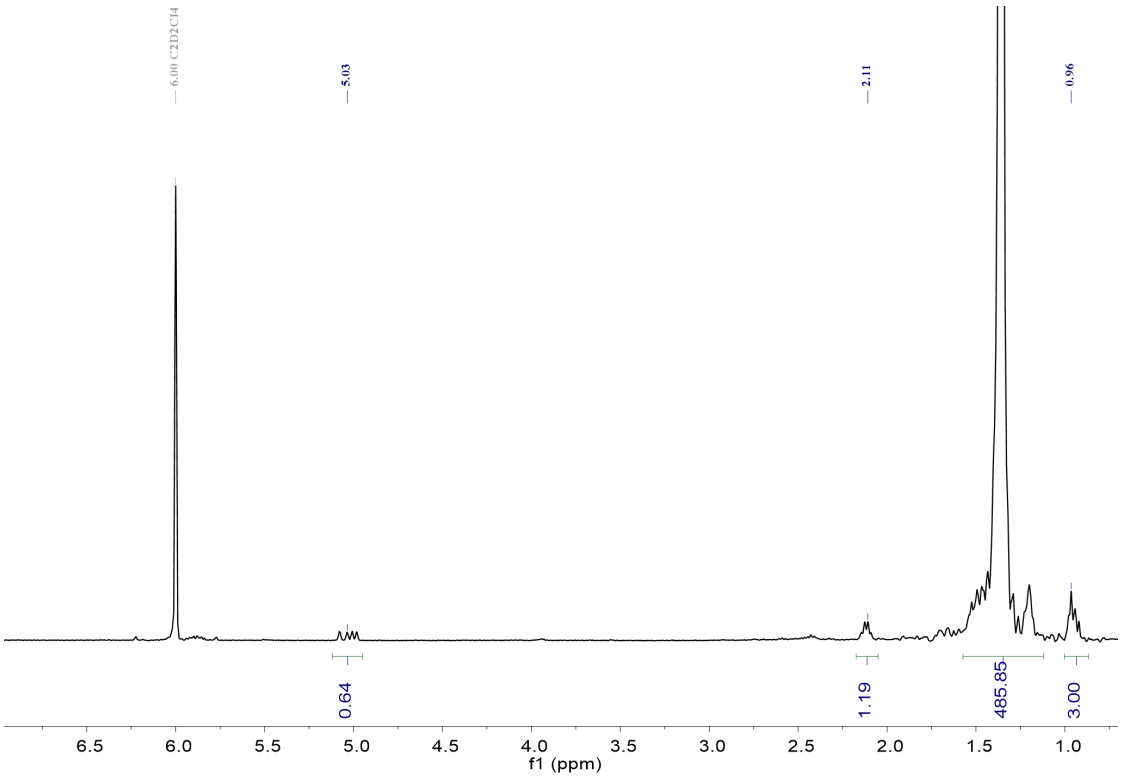


Figure S43. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 °C) of the polymer from table 1, entry 14.

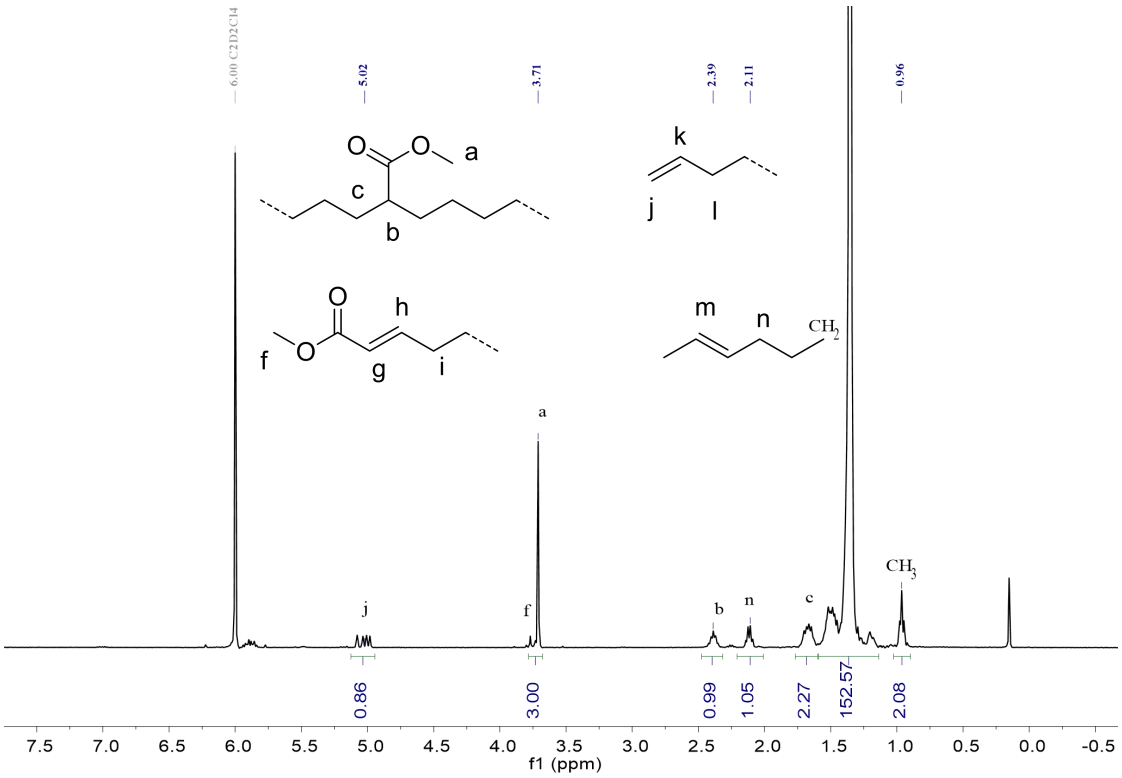


Figure S44. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 100 °C) of the E-MA copolymer from table 2, entry 2. (Signal assignments: JACS. 2009, 131, 422)

$$\text{MA (\%)} = \frac{(a+f)/3}{\frac{(CH_3+CH_2)}{4}+\frac{(a+f)}{3}} \times 100\% = \frac{3/3}{\frac{152.57+2.08}{4}+\frac{3}{3}} \times 100\% = 2.5\ \%$$

$$\text{Me Branches/ 1000C} = \frac{(I_{CH_3}-\frac{j}{2}\times 3)\ /\ 3}{\frac{CH_3}{3}+\frac{CH_2+n+c+j}{2}+\frac{a+f}{3}} \times 1000 = \frac{\left(2.08-\frac{0.86}{2}X3\right)/3}{\frac{2.08+3}{3}+\frac{152.57+2.27+1.05+0.86}{2}} = 3.3$$

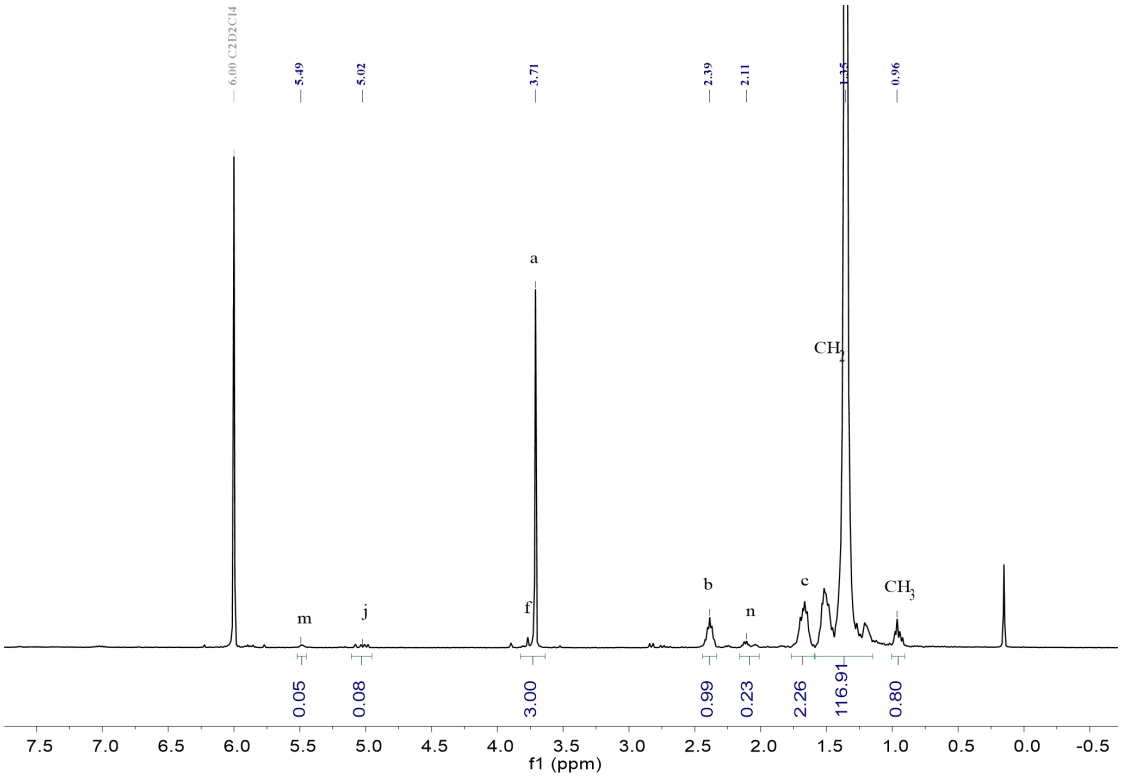


Figure S45. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 100 °C) of the E-MA copolymer from table 2, entry 3. (Signal assignments: JACS. 2009, 131, 422)

$$\text{MA (\%)} = \frac{(a+f)/3}{\frac{(CH_3+CH_2)}{4}+\frac{(a+f)}{3}} \times 100\% = \frac{3/3}{\frac{116.91+0.80}{4}+\frac{3}{3}} \times 100\% = 3.3\ \%$$

$$\text{Me Branches/ 1000C} = \frac{\left(I_{CH_3}-\frac{j+m}{2}\times 3\right)/3}{\frac{CH_3}{3}+\frac{CH_2+n+c+j}{2}+\frac{a+f}{3}} \times 1000 = \frac{\left(0.80-\frac{0.08+0.05}{2}X3\right)/3\times 1000}{\frac{0.80+3}{3}+\frac{116.91+2.26+0.23+0.08}{2}} = 3.3$$

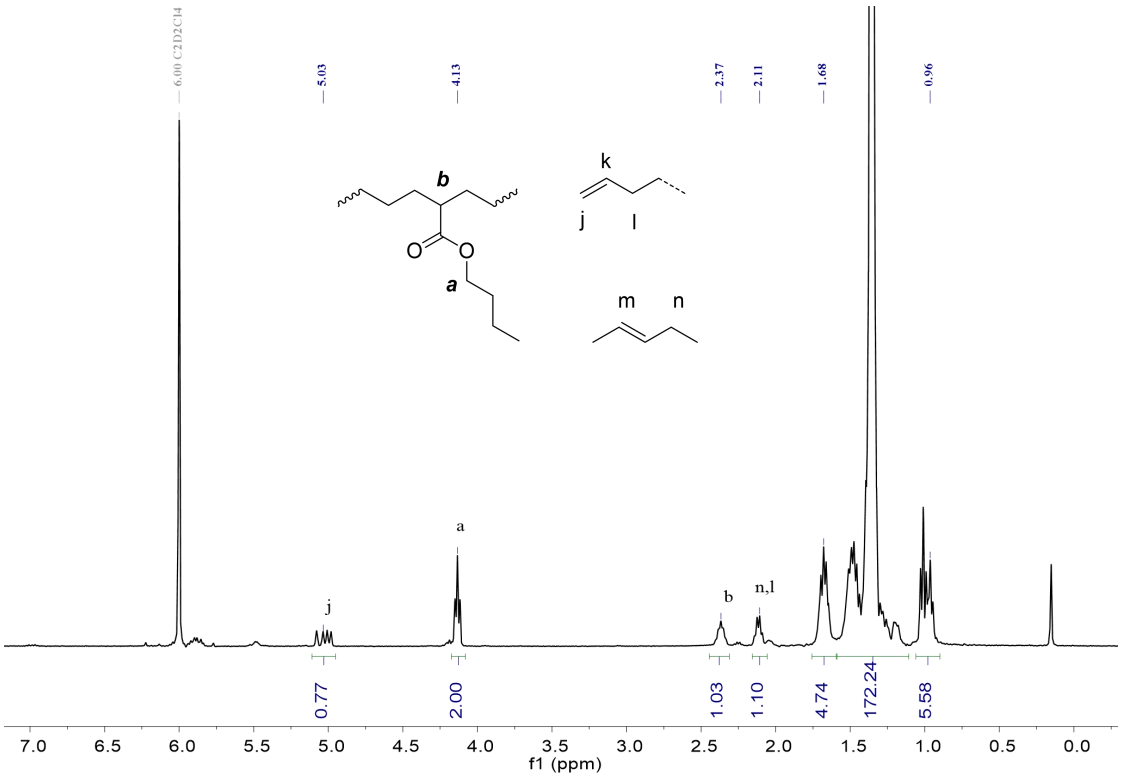


Figure S46. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 100 °C) of the E-*n*BuA copolymer from table 2, entry 5. (assignments: ACS Catal. 2018, 8, 5963)

$$n\text{BuA (\%)} = \frac{a/2}{\frac{CH3+CH_2-\frac{a}{2}\times 9}{4}+a/2}\times 100\% = \frac{1}{\frac{5.58+172.27+4.74-\frac{2}{2}\times 9}{4}+1}\times 100\% = 2.3\%$$

$$\text{Me Branches/ 1000C} = \frac{\left(I_{CH_3}-\frac{j}{2}\times 3-\frac{a}{2}\times 3\right)/3}{\frac{CH_3}{3}+\frac{CH_2+n+l+j-\frac{a}{2}\times 7}{2}+\frac{a}{2}}\times 1000$$

$$= \frac{\left(5.58-\frac{0.77}{2}\times 3-\frac{2}{2}\times 3\right)/3}{\frac{5.58}{3}+\frac{172.24+4.74+1.10+0.77-7}{2}+1}\times 1000 = 5.4$$

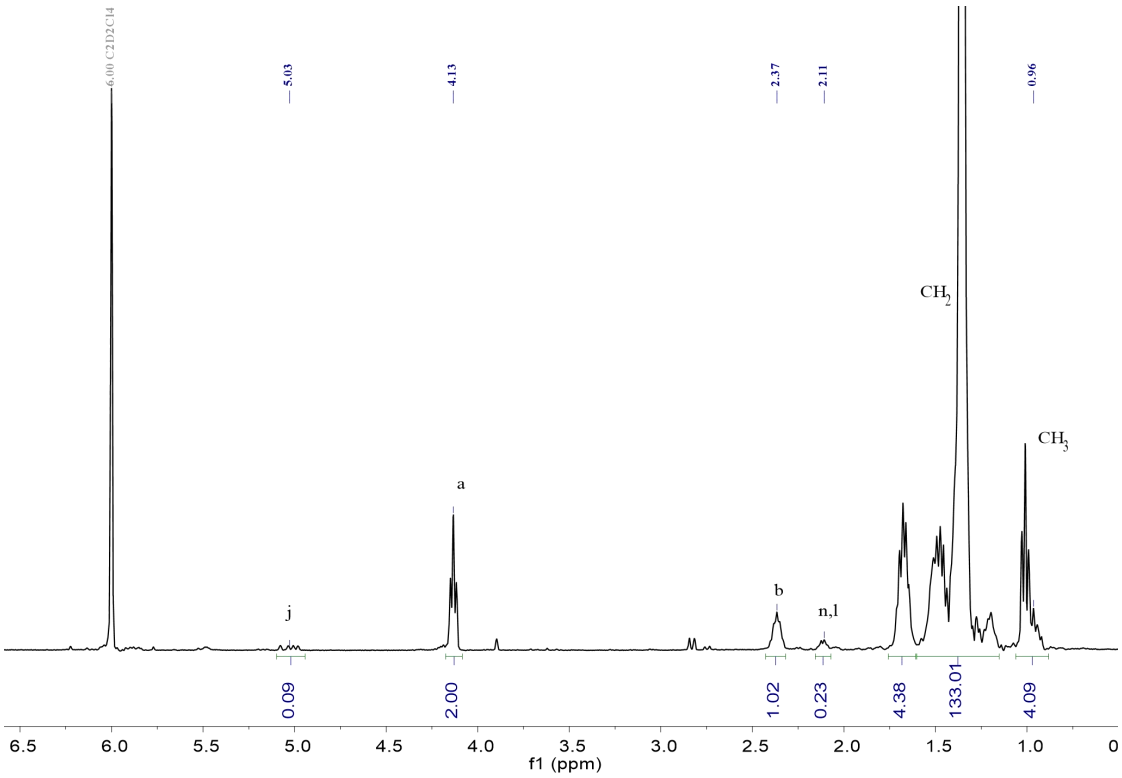


Figure S47. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 100 °C) of the E-*n*BuA copolymer from table 2, entry 6. (assignments: ACS Catal. 2018, 8, 5963)

$$n\text{BuA (\%)} = \frac{a/2}{\frac{CH3+CH_2-\frac{a}{2}\times 9}{4}+a/2} \times 100\% = \frac{1}{\frac{4.09+133.01+4.38-\frac{2}{2}\times 9}{4}+1} \times 100\% = 2.9\%$$

$$\text{Me Branches/ 1000C} = \frac{\left(I_{CH_3}-\frac{j}{2}\times 3-\frac{a}{2}\times 3\right)}{\frac{CH_3}{3}+\frac{CH_2+n+l+j-\frac{a}{2}\times 7}{2}+\frac{a}{2}} \times 1000$$

$$= \frac{\left(4.09-\frac{0.09}{2}\times 3-\frac{2}{2}\times 3\right)/3}{\frac{4.09}{3}+\frac{133.01+4.38+0.23+0.09-7}{2}+1} \times 1000 = 4.7$$

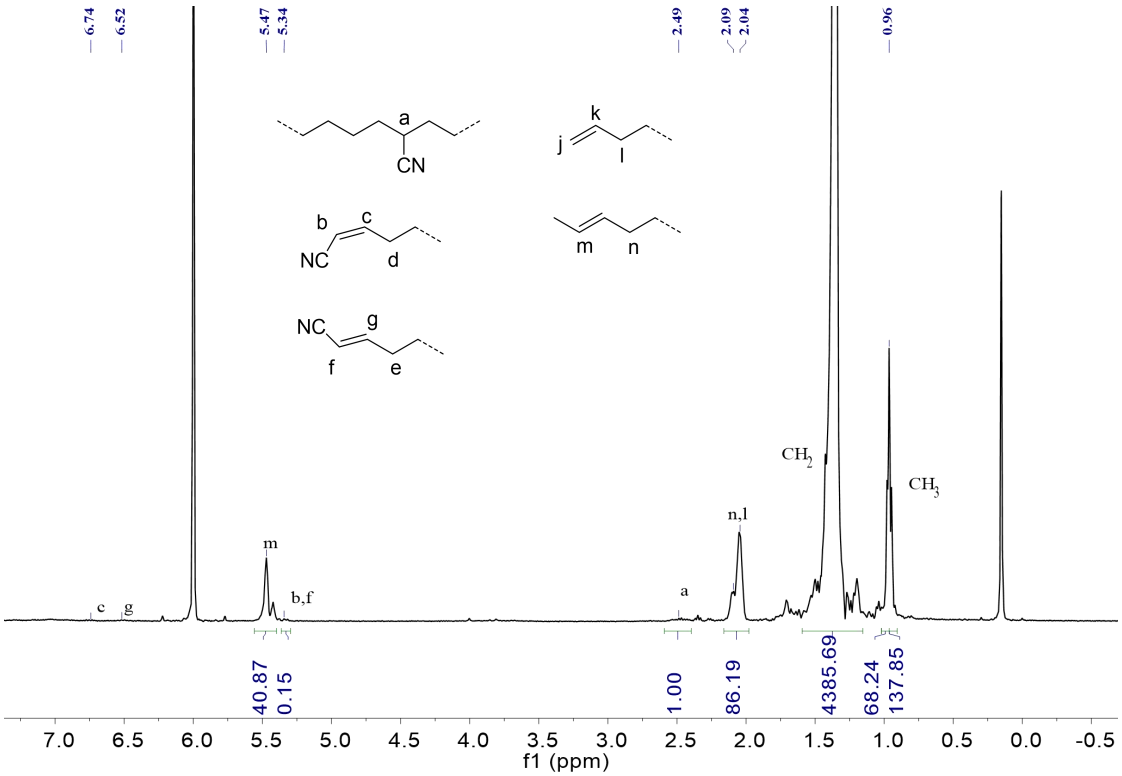


Figure S48. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 °C) of the E-AN copolymer from table 2, entry 7.

$$\text{AN}(\%)=\frac{a/1}{\frac{(CH_3+CH_2-2a)}{4}+a/1}\times 100\% = \frac{1}{\frac{(137.85+4385.69-2)}{4}+1}\times 100\% = 0.09\%$$

$$\text{Me Branches/ 1000C} = \frac{1000\times(I_{CH_3}-I_{CH_3}'\times 2)/3}{\frac{I_{CH_3}}{3}+\frac{I_{CH2+n+l+m}}{2}}\times 1000 = \frac{1000\times(137.85-68.24\times 2)/3}{\frac{137.85}{3}+\frac{4385.69+86.19+40.87}{2}} = 0.2$$

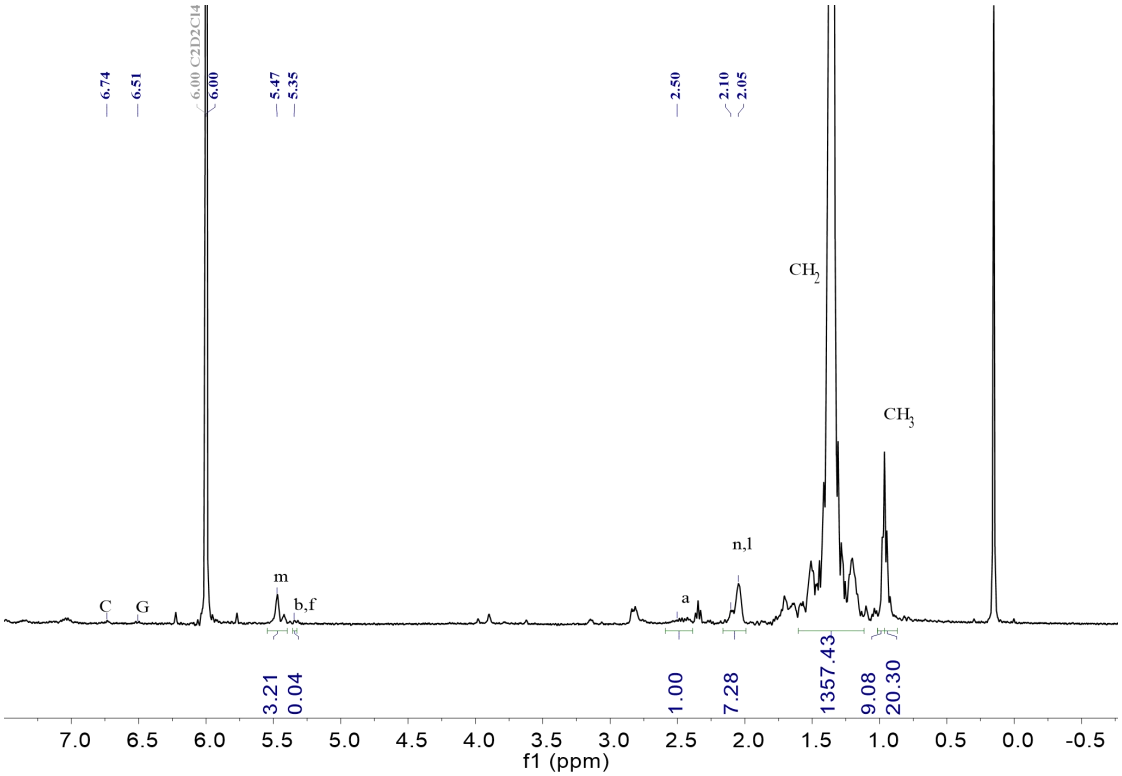


Figure S49. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 °C) of the E-AN copolymer from table 2, entry 8.

$$\text{AN}(\%) = \frac{a/1}{\frac{(CH_3+CH_2-2a)}{4}+a/1} \times 100\% = \frac{1}{\frac{(20.30+1357.43-2)}{4}+1} \times 100\% = 0.29\%$$

$$\text{Me Branches/ 1000C} = \frac{1000\times(I_{CH_3}-I_{CH_3}'\times 2)/3}{\frac{I_{CH_3}}{3}+\frac{I_{CH2+n+l}}{2}} \times 1000 = \frac{1000\times(20.03-9.08\times 2)/3}{\frac{20.03}{3}+\frac{1357.43+7.28}{2}} = 1.0$$

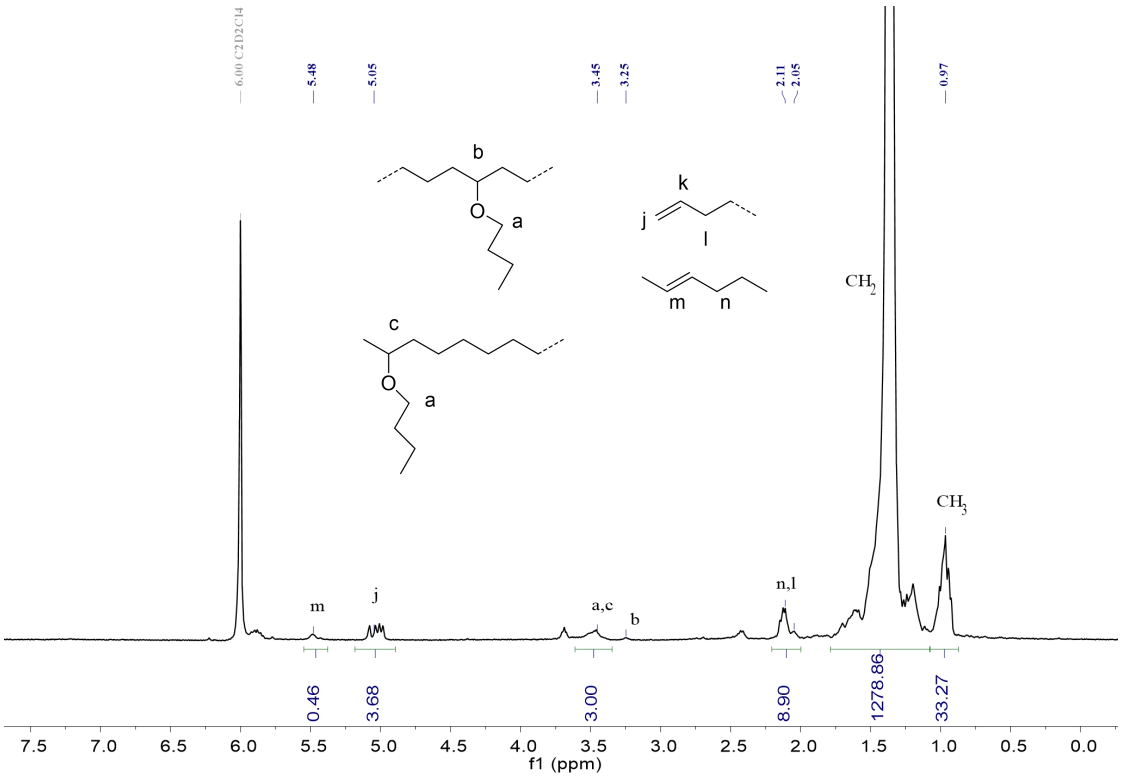


Figure S50. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 100 °C) of the E-*n*BuVE copolymer from table 2, entry 9. (assignments: JACS. 2007, 129, 8946)

$$n\text{BuVE (\%)} = \frac{(a+b+c)/3}{\frac{\left(CH3+CH_2-\frac{(a+b+c)}{3}\times 9\right)}{4}+(a+b+c)/3} = \frac{3/3}{\frac{(33.27+1278.86-9)}{4}+1} = 0.3\%$$

$$\text{Me Branches/ 1000C} = \frac{\left[I_{CH_3}-\frac{j+m}{2}\times 3-\left(\frac{a+b+c}{3}\right)\times 3\right]/3}{\frac{CH_3}{3}+\frac{CH_2+n+l+j-8\times(a+b+c)/3}{2}+\frac{a+b+c}{3}} \times 1000$$

$$= \frac{\left(33.27-\frac{3.68+0.46}{2}\times 3-\frac{3}{3}\times 3\right)/3}{\frac{33.27}{3}+\frac{1278.86+8.90+3.68+0.46-8}{2}+1} \times 1000 = 12.2$$

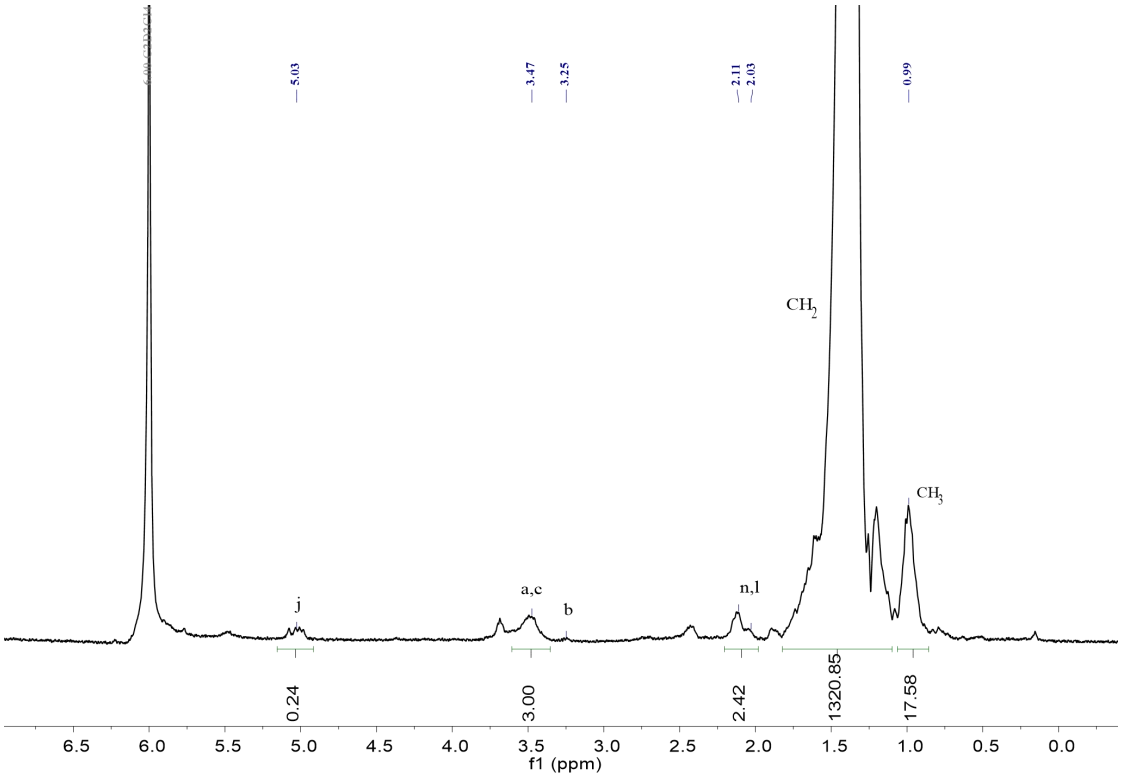


Figure S51. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 °C) of the E-*n*BuVE copolymer from table 2, entry 10.

$$n\text{BuVE (\%)} = \frac{(a+b+c)/3}{\frac{(CH3+CH_2-(a+b+c)\div 3\times 9)}{4}+(a+b+c)/3} \times 100\% = \frac{3/3}{\frac{(17.58+1320.85-9)}{4}+1} = 0.3\%$$

$$\text{Me Branches/ 1000C} = \frac{\left[I_{CH_3}-\frac{j}{2}\times 3-\left(\frac{a+b+c}{3}\right)\times 3\right]/3}{\frac{CH_3}{3}+\frac{CH_2+n+l+j-8\times(a+b+c)/3}{2}+\frac{a+b+c}{3}} \times 1000$$

$$= \frac{\left(17.58-\frac{0.24}{2}\times 3-\frac{3}{3}\times 3\right)/3}{\frac{17.58}{3}+\frac{1320.85+2.42+0.24-8}{2}+1} \times 1000 = 7.1$$

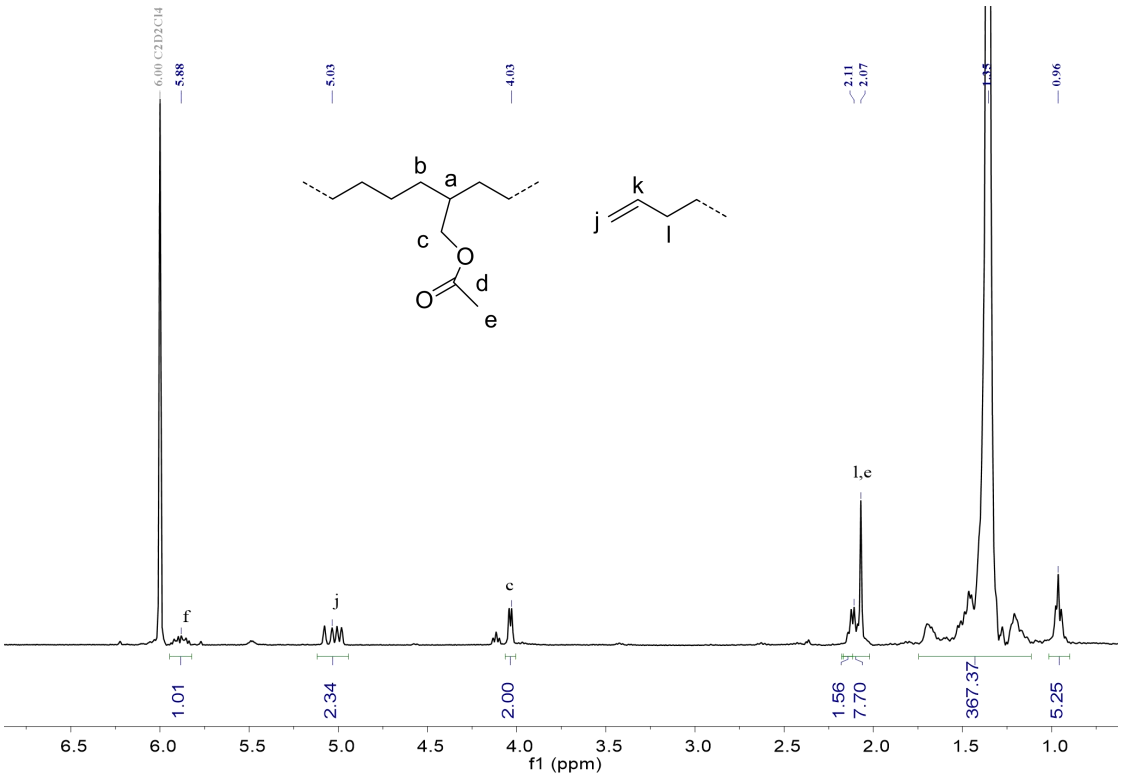


Figure S52. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 °C) of the E-AAC copolymer from table 2, entry 11.

$$\text{AAc (\%)} = \frac{c/2}{\frac{\left(I_{CH_3}+I_{CH_2}-3a\right)}{4}+\frac{c}{2}} \times 100\% = \frac{2/2}{\frac{(5.25+367.37-1.5\times2)}{4}+\frac{2}{2}} \times 100\% = 1.1\%$$

$$\text{Me Branches/ 1000C} = \frac{(I_{CH_3}-\frac{j}{2}\times3)/3}{\frac{I_{CH_3}}{3}+\frac{I_{CH_2}+l+j-a}{2}+\frac{c}{2}} \times 1000 = \frac{\left(5.25-\frac{2.34}{2}\times3\right)/3\times1000}{\frac{5.25}{3}+\frac{367.37+2.34+7.70-4}{2}+1} = 3.1$$

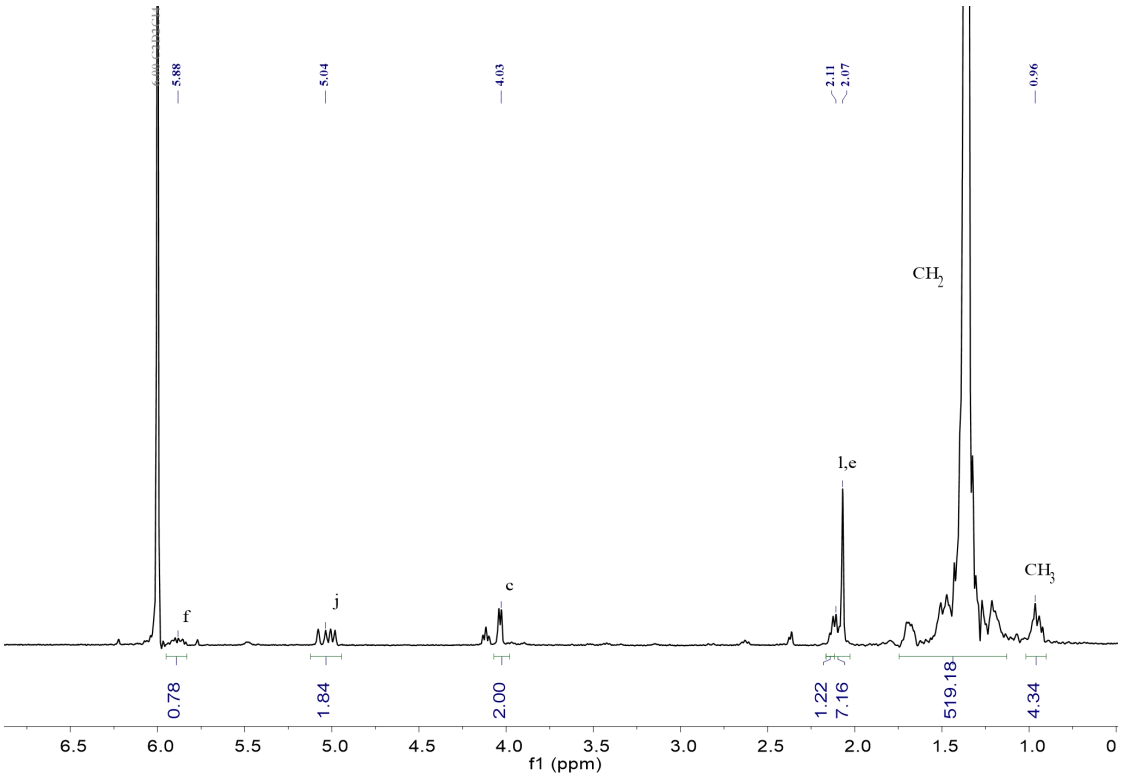


Figure S53. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 °C) of the E-AAC copolymer from table 2, entry 12.

$$\text{AAc (\%)} = \frac{c/2}{\frac{\left(I_{CH_3}+I_{CH_2}-3a\right)}{4}+\frac{c}{2}} \times 100\% = \frac{2/2}{\frac{(4.34+519.18-1.5\times2)}{4}+\frac{2}{2}} \times 100\% = 0.8\%$$

$$\text{Me Branches/ 1000C} = \frac{(I_{CH_3}-\frac{j}{2}\times3)/3}{\frac{I_{CH_3}}{3}+\frac{I_{CH_2}+l+j-a}{2}+\frac{c}{2}} \times 1000 = \frac{\left(4.34-\frac{1.84}{2}\times3\right)/3\times1000}{\frac{4.34}{3}+\frac{519.18+1.84+7.16-4}{2}+1} = 2.0$$

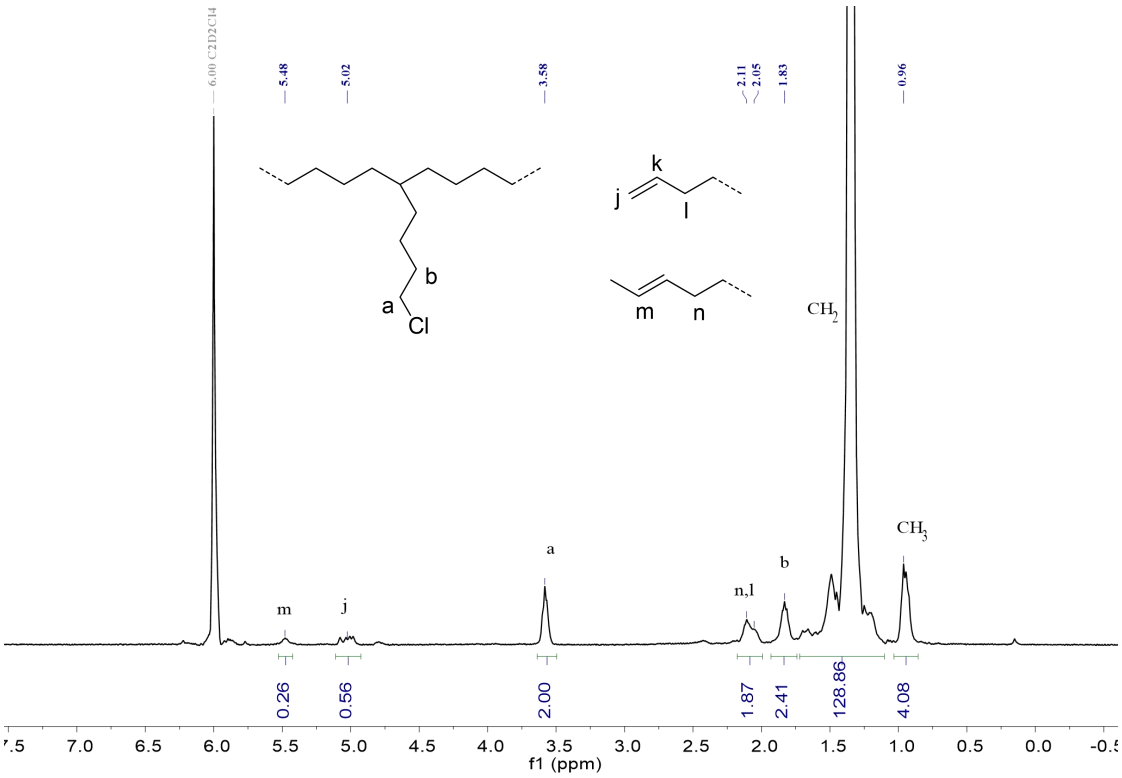


Figure S54. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 °C) of the copolymer from table 2, entry 13.

$$X\% = \frac{a/2}{\frac{\left(I_{CH_3}+I_{CH_2}-3.5a\right)}{4}+a/2} = \frac{2/2}{\frac{(128.86+4.08-3.5\times 2)}{4}+2/2} = 3.1\%$$

$$\text{Me Branches/ 1000C} = \frac{(I_{CH_3}-\frac{j+m}{2}\times 3)/3}{\frac{I_{CH_3}}{3}+\frac{I_{CH_2}+\text{n+l+j+m}-2.5a}{2}+\frac{a}{2}} \times 1000 =$$

$$\frac{1000\times(4.08-3\times\frac{0.56+0.26}{2})/3}{\frac{4.08}{3}+(128.86+1.87+0.56+0.26-2.5\times 2)/2+2/2} = 14.4$$

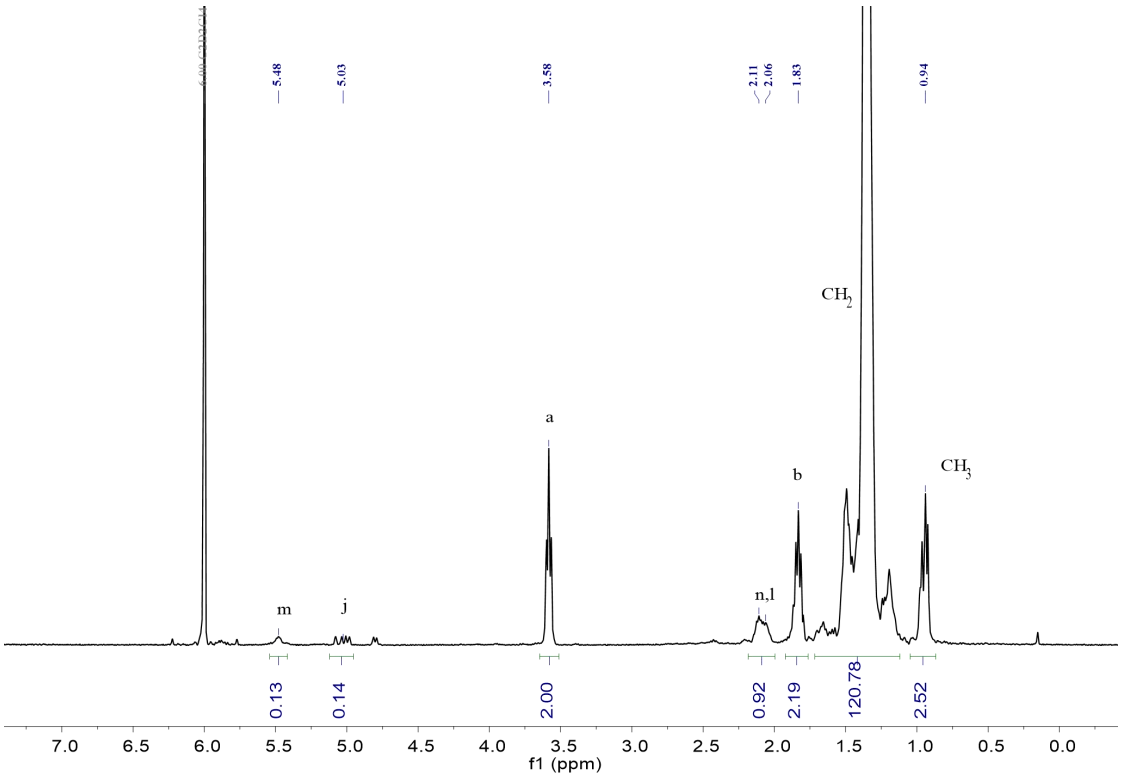


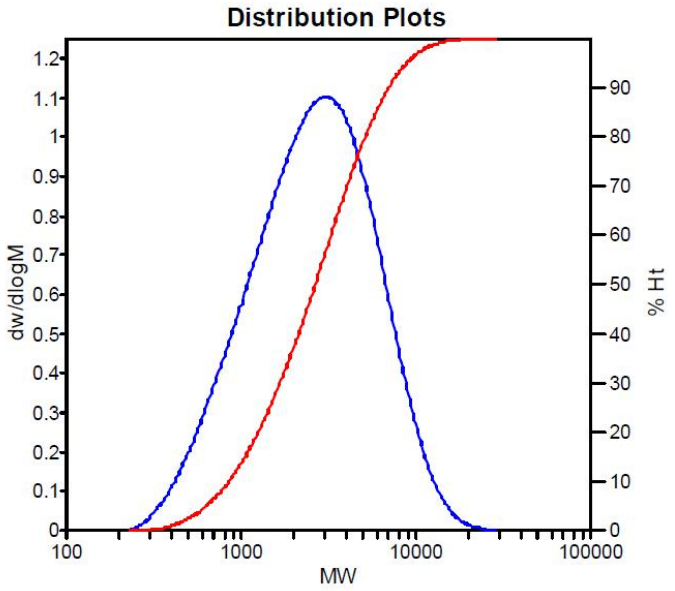
Figure S55. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 °C) of the copolymer from table 2, entry 14.

$$X\% = \frac{a/2}{\frac{\left(I_{CH_3}+I_{CH_2}-3.5a\right)}{4}+a/2} = \frac{2/2}{\frac{(120.78+2.52-3.5\times 2)}{4}+2/2} = 3.3\%$$

$$\text{Me Branches/ 1000C} = \frac{(I_{CH_3}-\frac{j+m}{2}\times 3)/3}{\frac{I_{CH_3}}{3}+\frac{I_{CH_2}+\text{n+l+j+m}-2.5a}{2}+\frac{a}{2}} \times 1000 =$$

$$\frac{1000\times(2.52-3\times\frac{0.14+0.13}{2})/3}{\frac{2.52}{3}+(120.78+0.92+0.14+0.13-2.5\times 2)/2+2/2} = 11.7$$

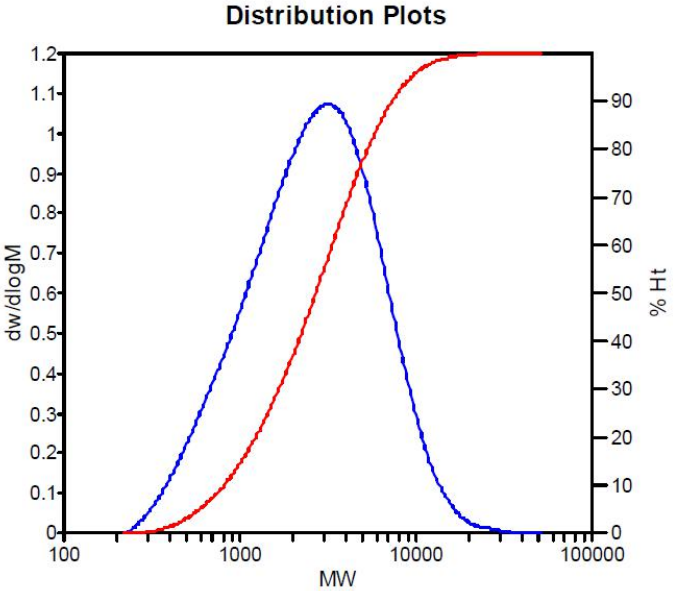
4. GPC traces and DSC data of (co)polymers



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	3087	1817	3394	5598	8102	3141	1.86791

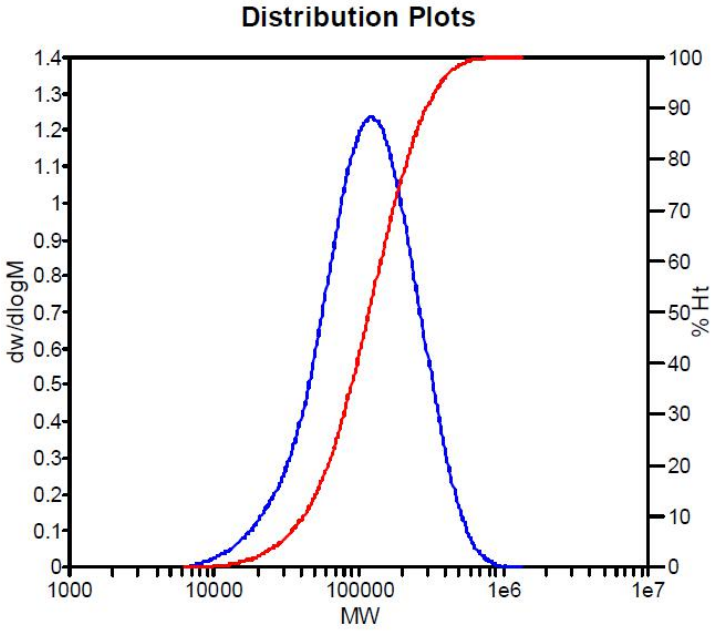
Figure S56. GPC trace of the polymer from table 1, entry 1.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	3188	1783	3530	6197	9794	3242	1.97981

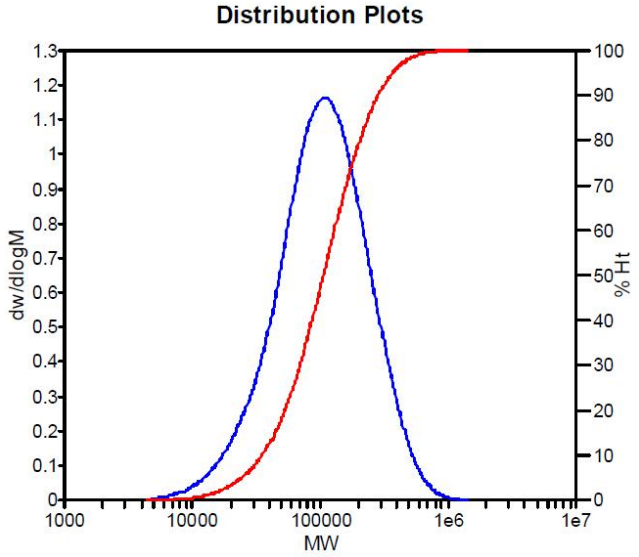
Figure S57. GPC trace of the polymer from table 1, entry 2.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	121886	81635	147137	232076	330162	137257	1.80238

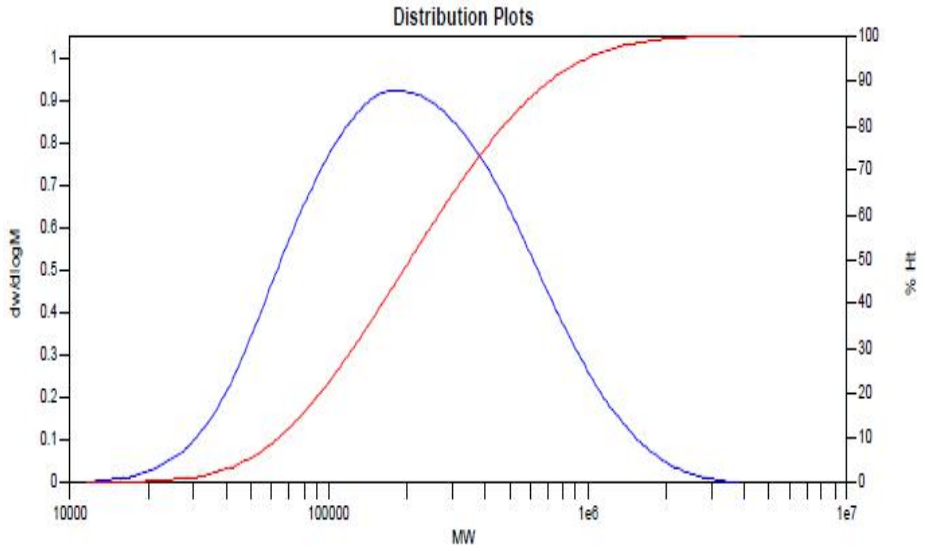
Figure S58. GPC trace of the polymer from table 1, entry 3.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	107138	70831	138707	236935	362665	127968	1.95828

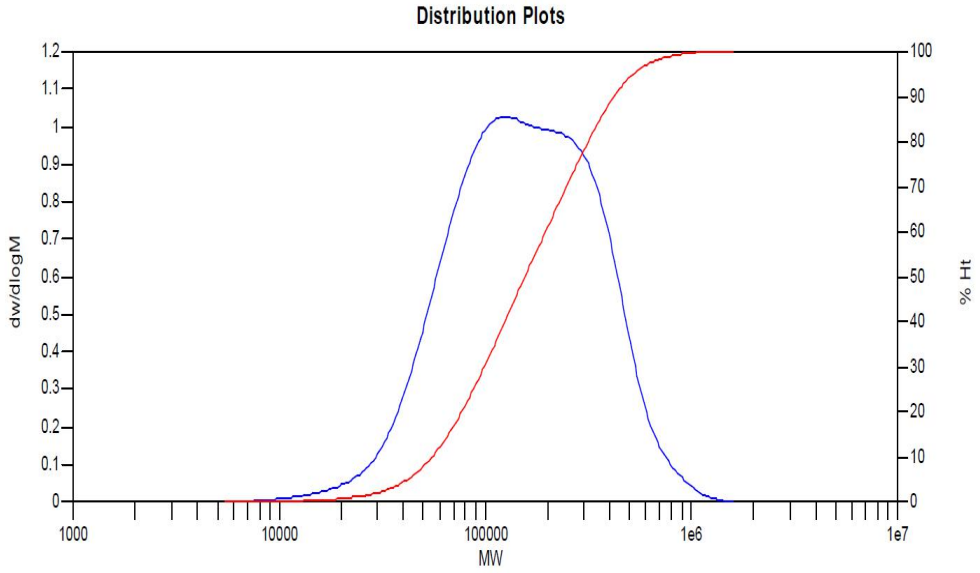
Figure S59. GPC trace of the polymer from table 1, entry 4.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	177085	138105	315020	664270	1124352	281303	2.28102

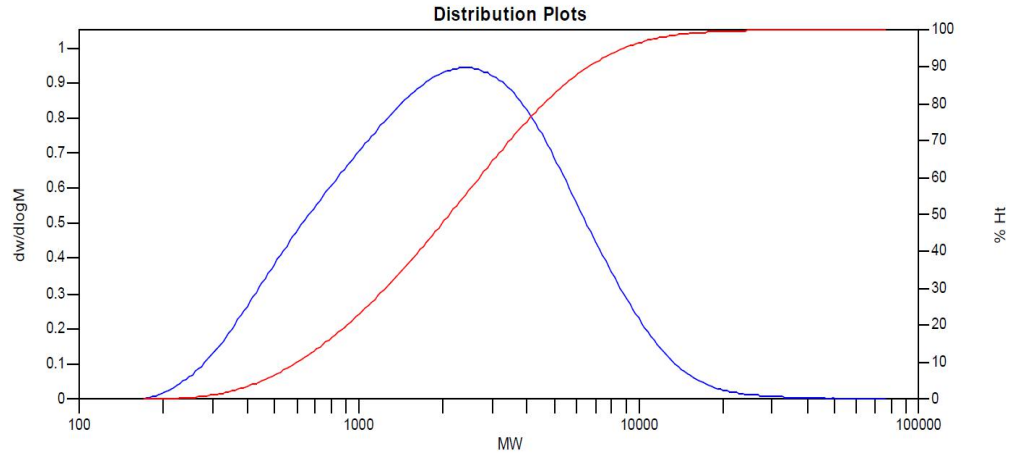
Figure S60. GPC trace of the polymer from table 1, entry 5.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	124811	109658	203064	332207	476023	188165	1.85179

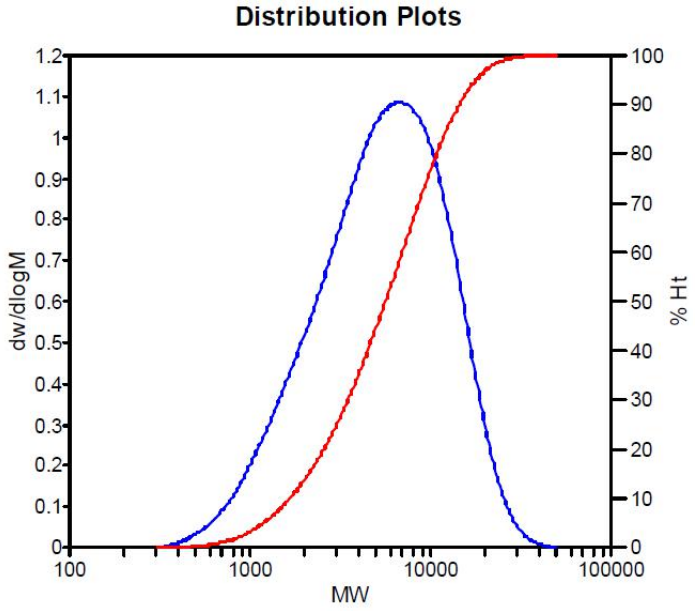
Figure S61. GPC trace of the polymer from table 1, entry 6.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	2468	1361	3025	6263	12287	2720	2.22263

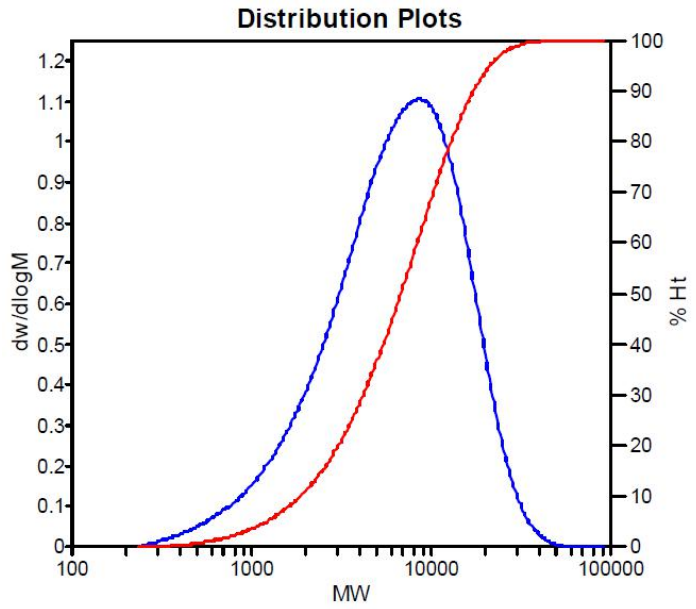
Figure S62. GPC trace of the polymer from table 1, entry 7.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	6803	3604	7021	11218	15428	6508	1.94811

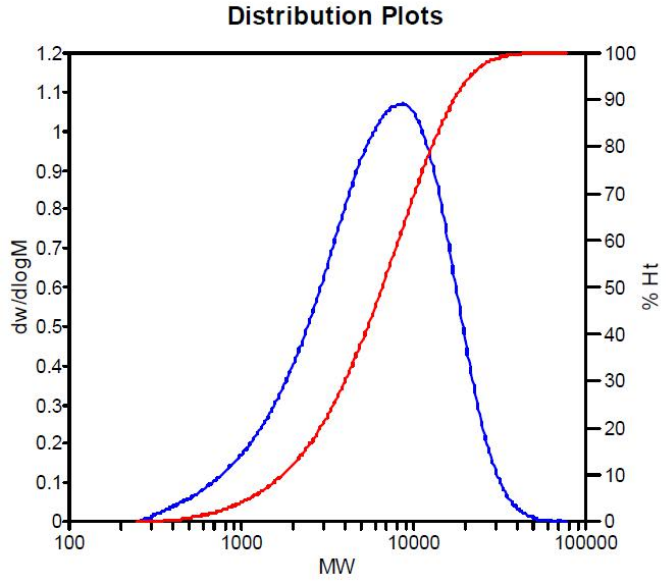
Figure S63. GPC trace of the polymer from table 1, entry 8.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	8389	3921	8379	13505	18982	7750	2.13695

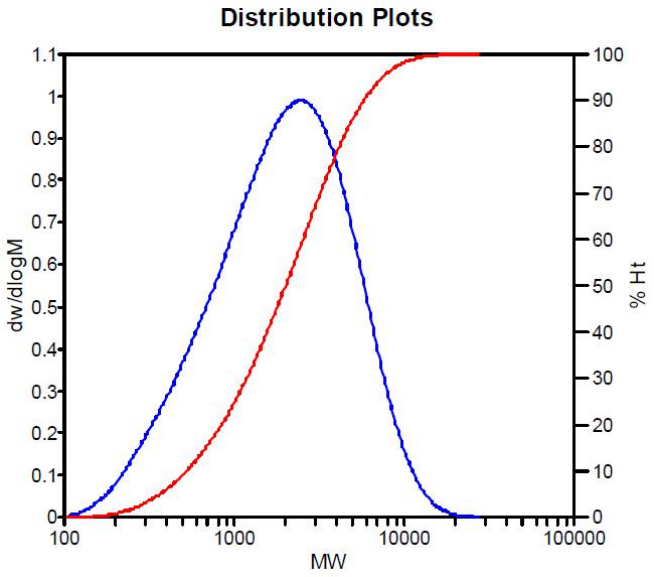
Figure S64. GPC trace of the polymer from table 1, entry 9.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	8664	3725	8262	13665	19427	7608	2.21799

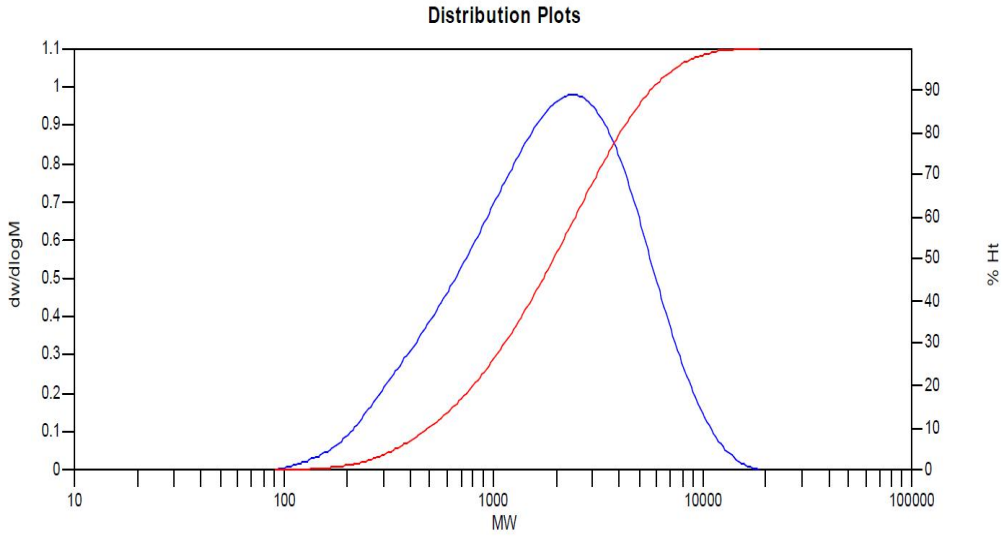
Figure S65. GPC trace of the polymer from table 1, entry 10.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	2424	1193	2694	4835	7264	2452	2.25817

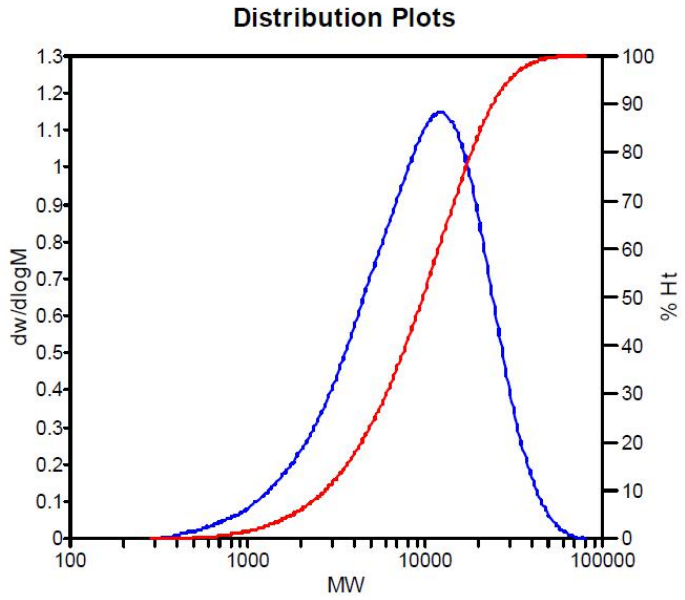
Figure S66. GPC trace of the polymer from table 1, entry 11.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	2407	1128	2579	4557	6577	2349	2.28635

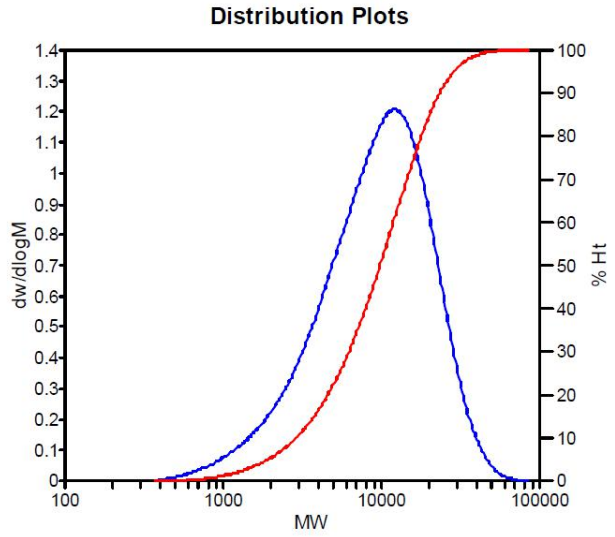
Figure S67. GPC trace of the polymer from table 1, entry 12.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	12155	5664	11898	18905	25910	11027	2.10064

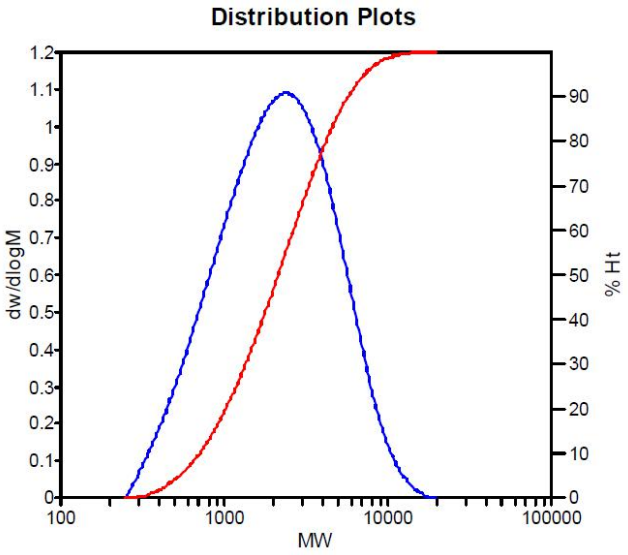
Figure S68. GPC trace of the polymer from table 1, entry 13.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	12155	5946	11746	18156	24677	10944	1.97545

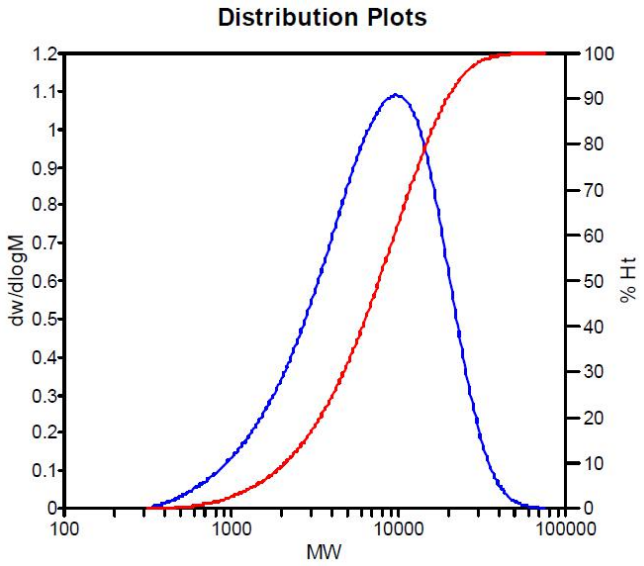
Figure S69. GPC trace of the polymer from table 1, entry 14.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	2388	1509	2755	4507	6403	2553	1.82571

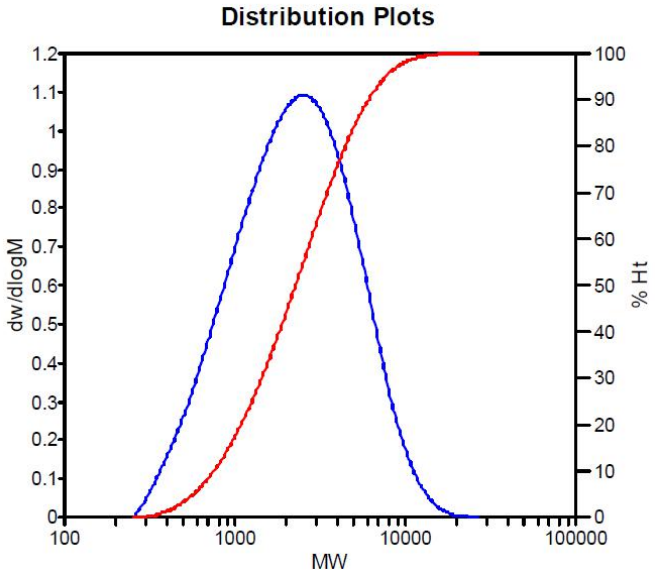
Figure S70. GPC trace of the polymer from table 2, entry 2.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	9717	4503	9518	15414	21431	8794	2.1137

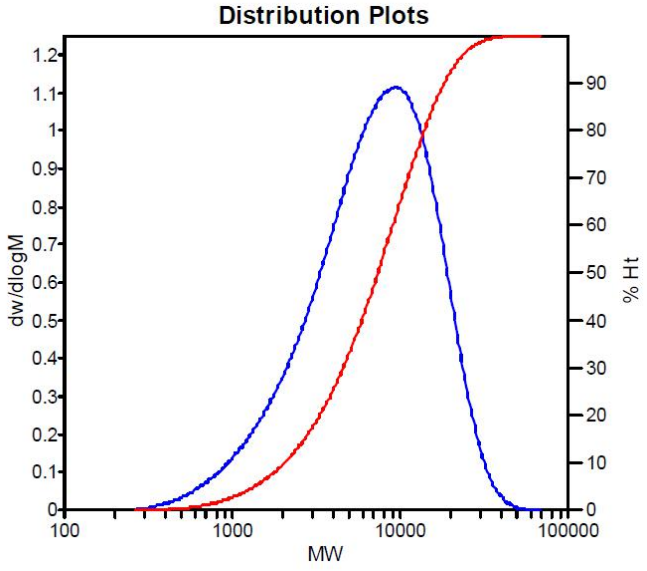
Figure S71. GPC trace of the polymer from table 2, entry 3.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	2587	1602	2937	4879	7154	2718	1.83333

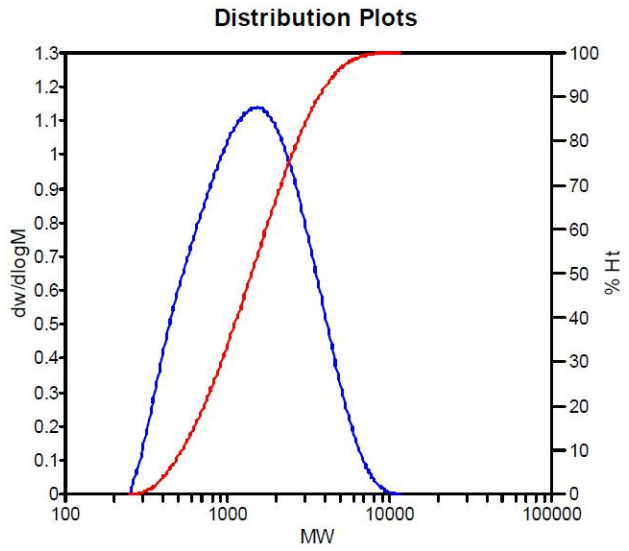
Figure S72. GPC trace of the polymer from table 2, entry 5.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	9563	4356	8999	14164	19129	8348	2.06589

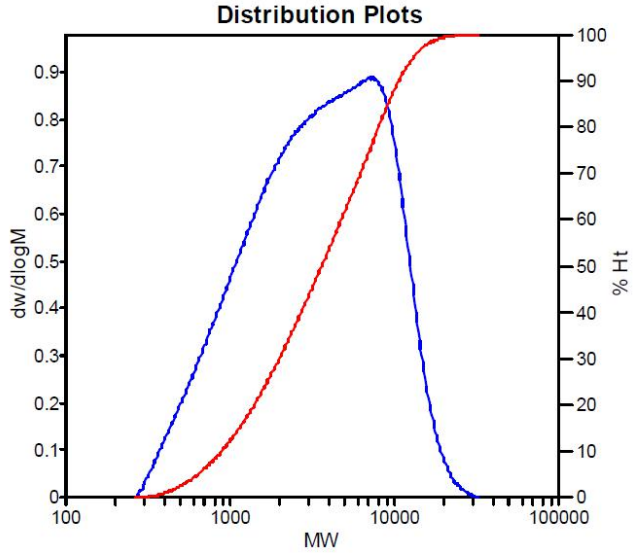
Figure S73. GPC trace of the polymer from table 2, entry 6.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1553	1082	1794	2804	3886	1677	1.65804

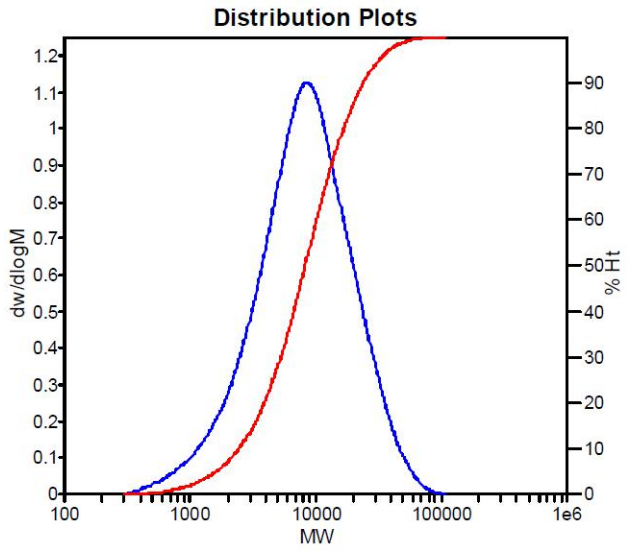
Figure S74. GPC trace of the polymer from table 2, entry 7.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	7293	2110	4843	8306	11306	4412	2.29526

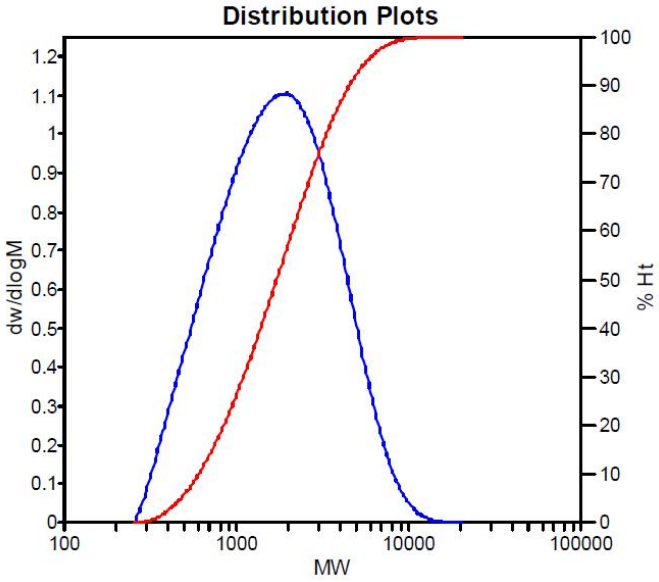
Figure S75. GPC trace of the polymer from table 2, entry 9.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	8691	5072	11255	20561	32036	10259	2.21905

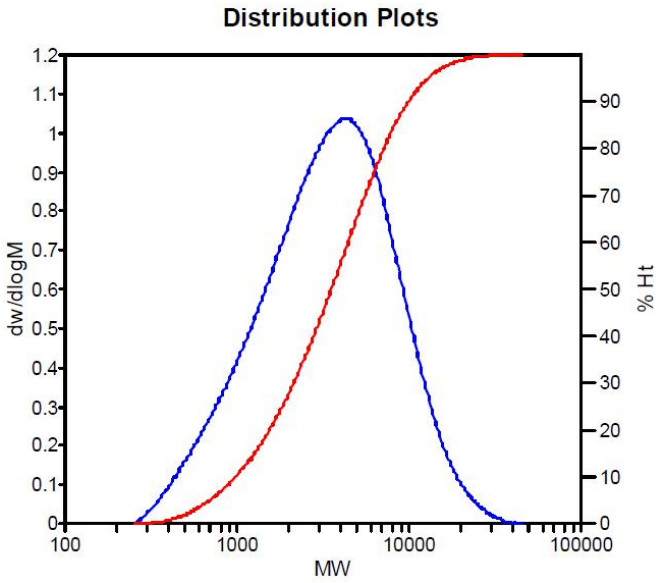
Figure S76. GPC trace of the polymer from table 2, entry 10.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1941	1269	2206	3566	5106	2050	1.73838

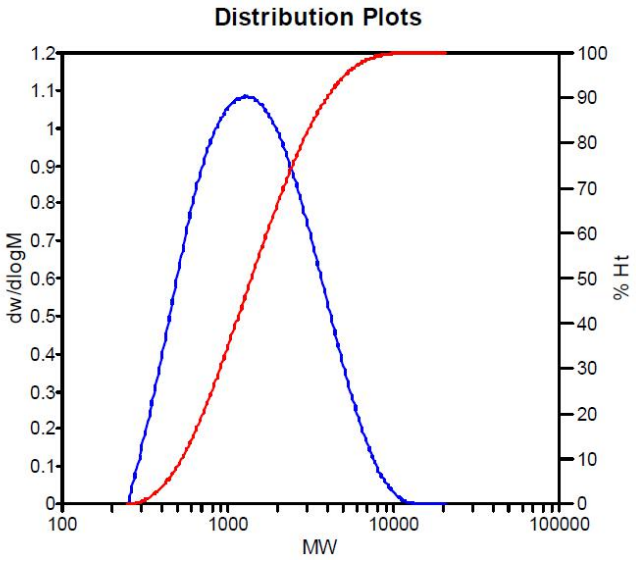
Figure S77. GPC trace of the polymer from table 2, entry 11.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	4240	2209	4712	8476	13016	4300	2.13309

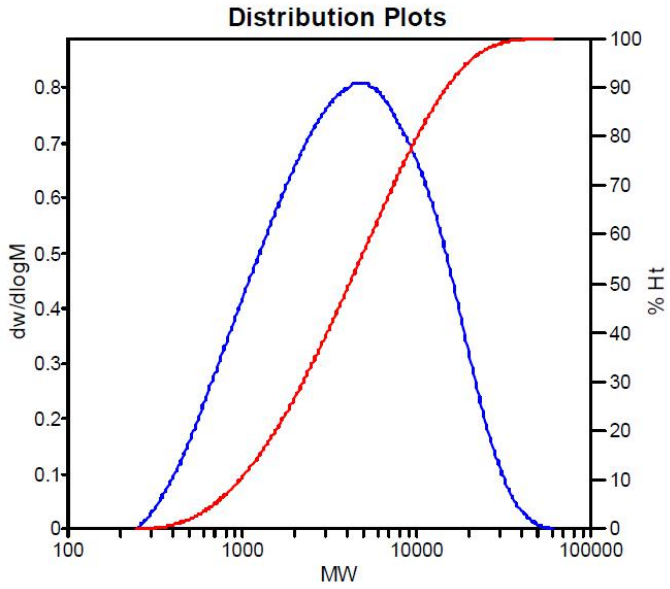
Figure S78. GPC trace of the polymer from table 2, entry 12.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1262	1080	1877	3160	4634	1737	1.73796

Figure S79. GPC trace of the polymer from table 2, entry 13.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	4895	2341	6332	12911	19600	5617	2.70483

Figure S80. GPC trace of the polymer from table 2, entry 14.

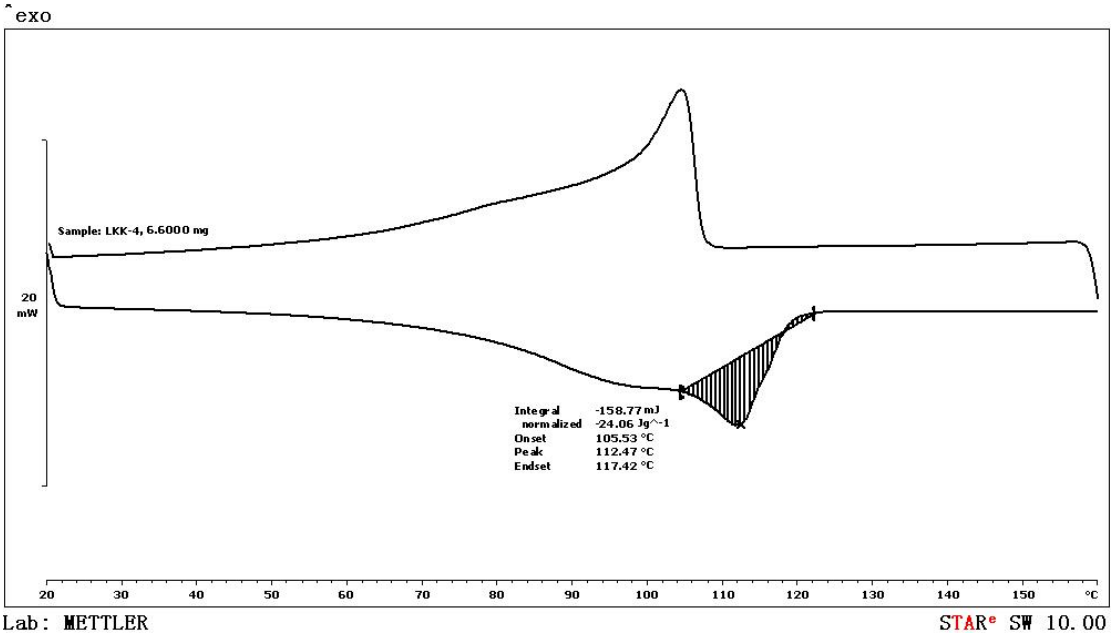


Figure S81. DSC data of the polymer from table 1, entry 1.

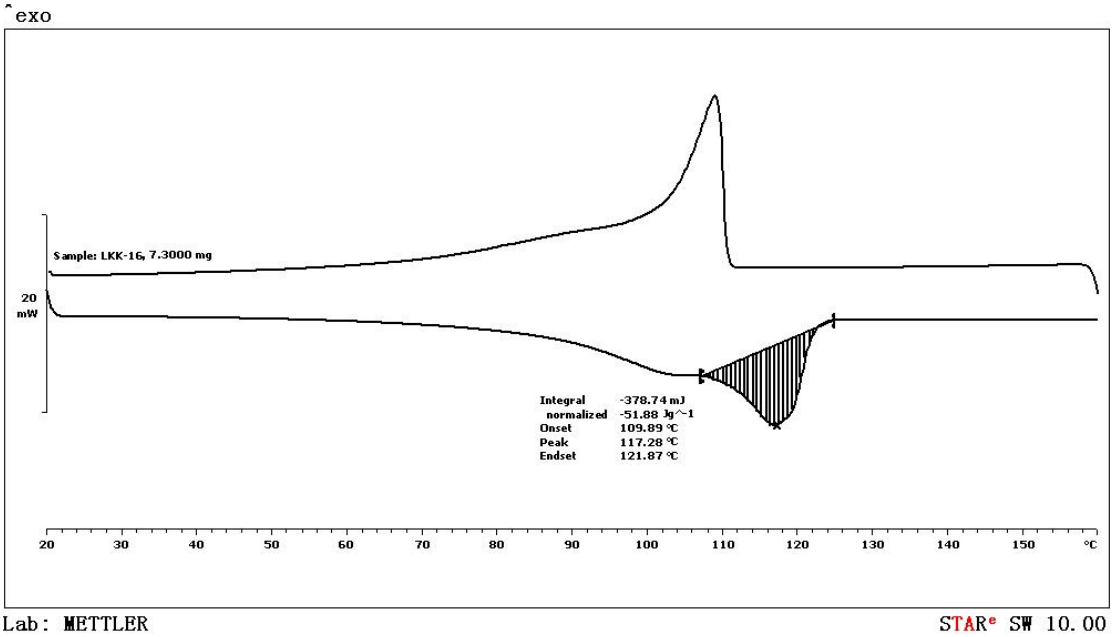


Figure S82. DSC data of the polymer from table 1, entry 2.

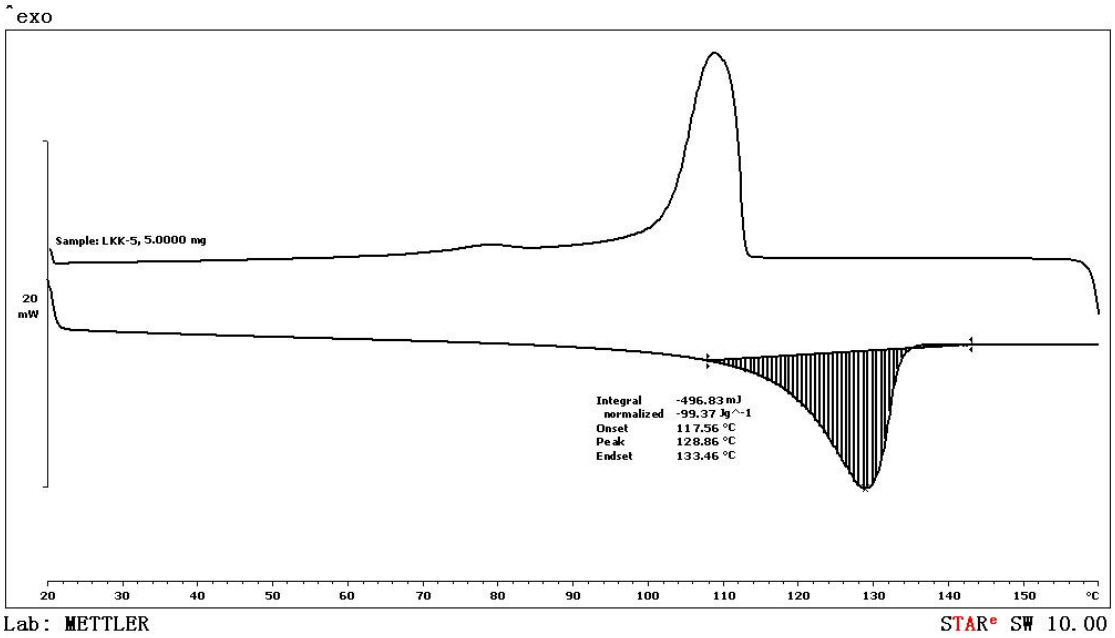


Figure S83. DSC data of the polymer from table 1, entry 3.

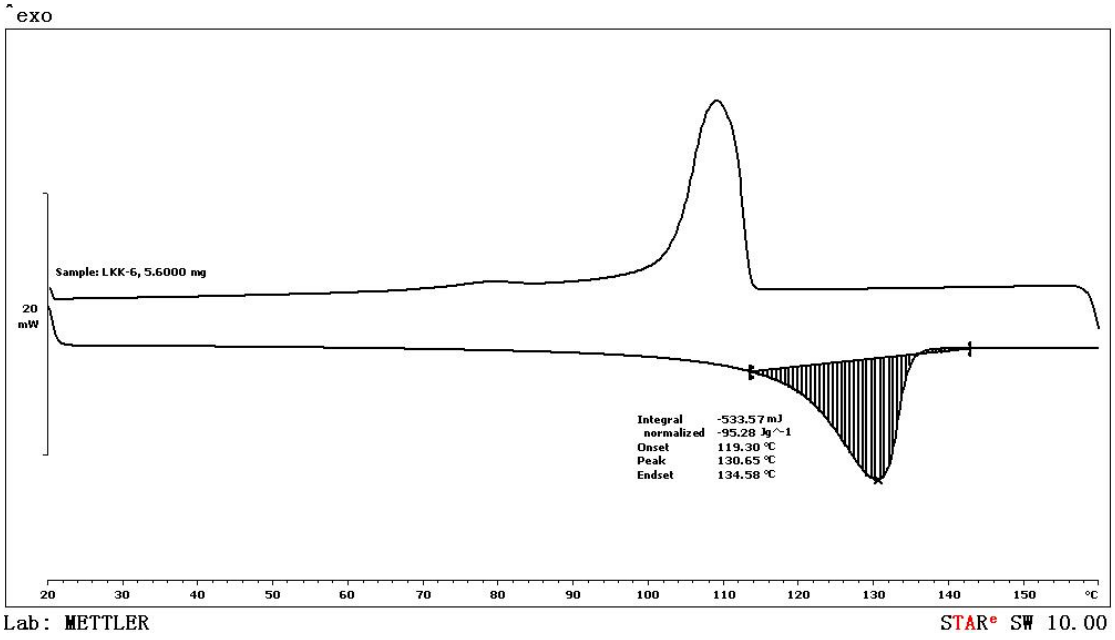


Figure S84. DSC data of the polymer from table 1, entry 4.

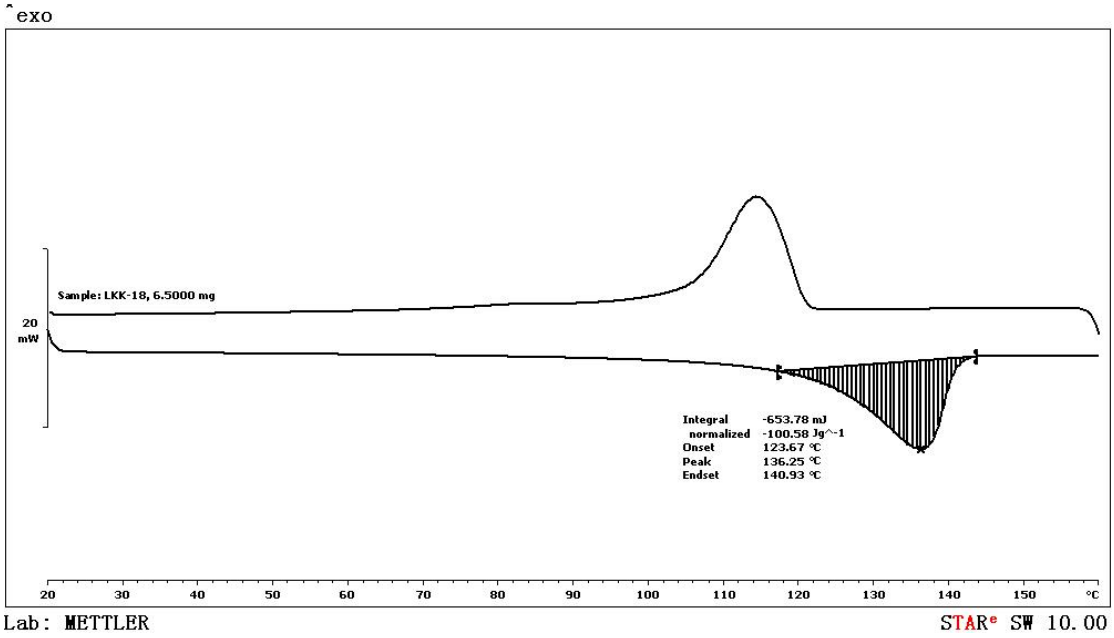


Figure S85. DSC data of the polymer from table 1, entry 5.

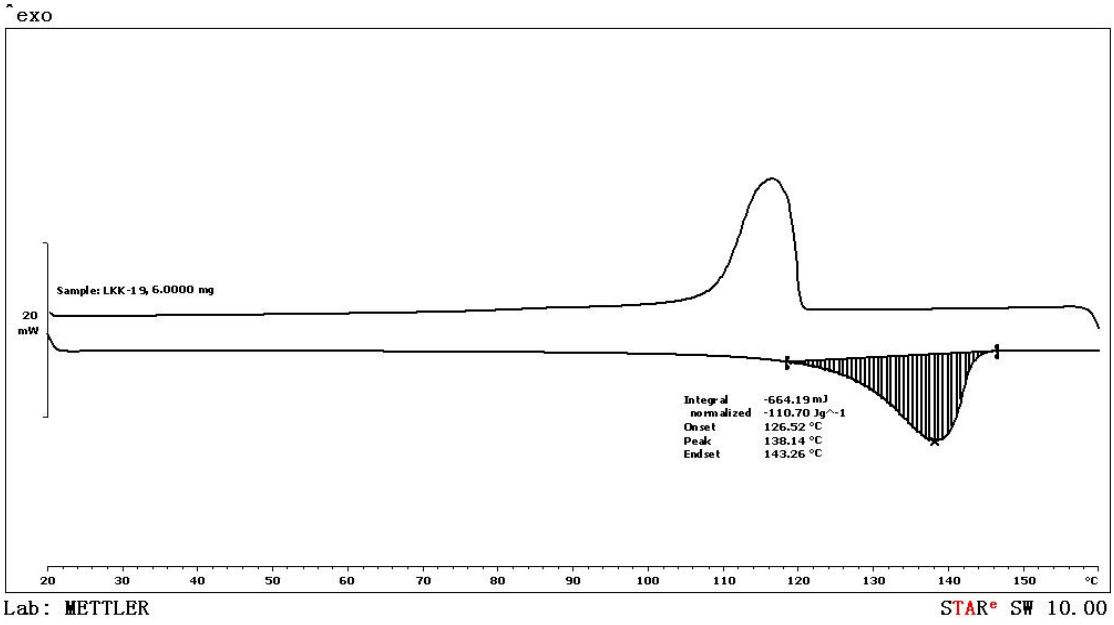


Figure S86. DSC data of the polymer from table 1, entry 6.

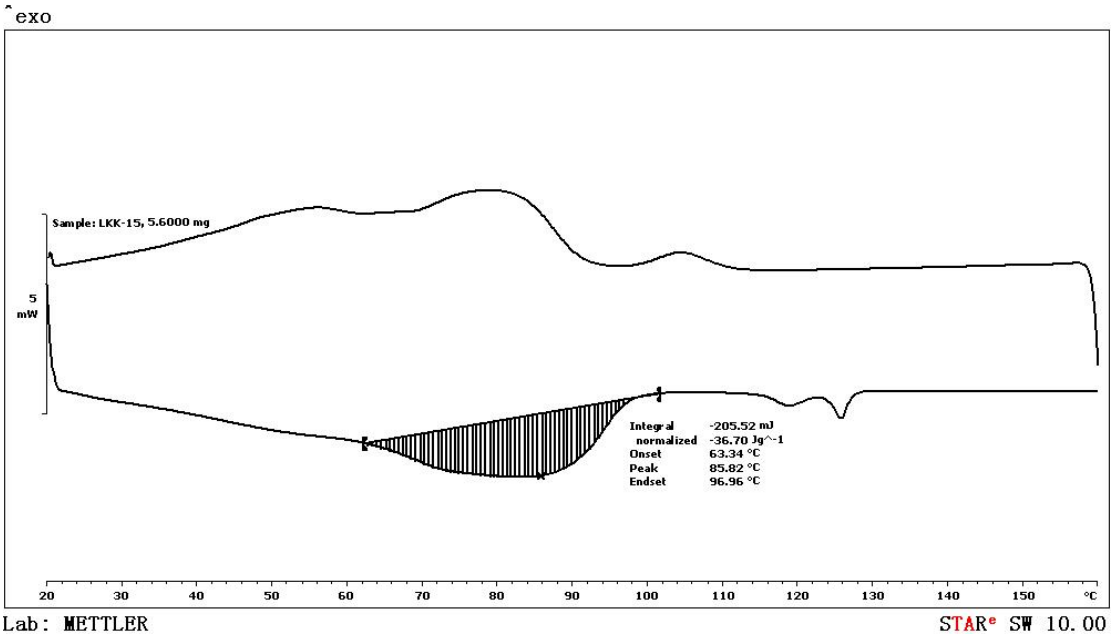


Figure S87. DSC data of the polymer from table 1, entry 8.

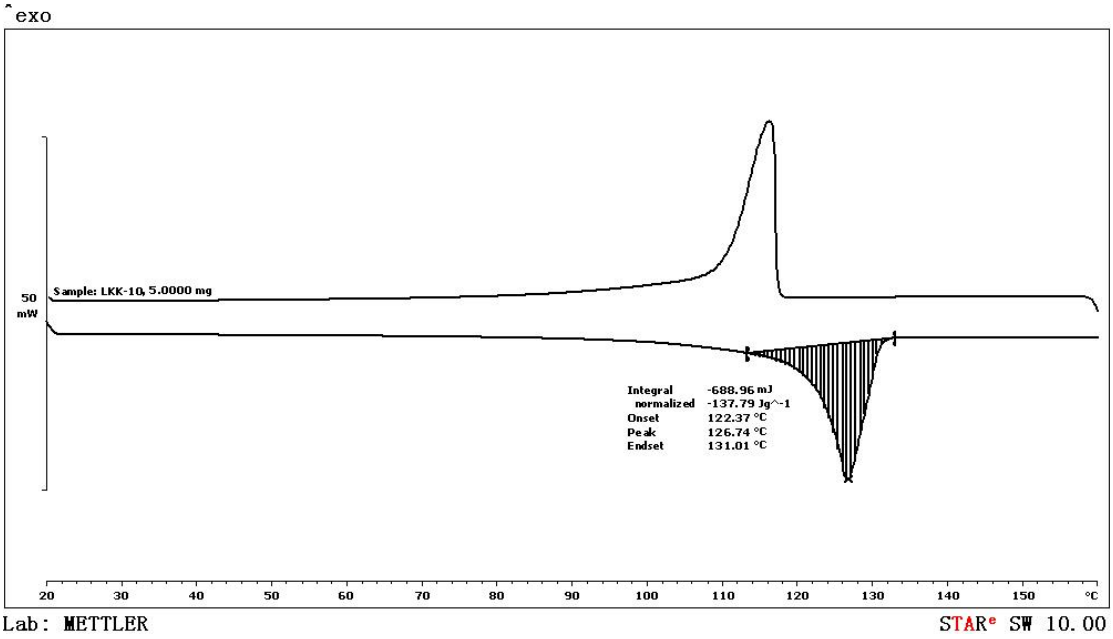


Figure S88. DSC data of the polymer from table 1, entry 9.

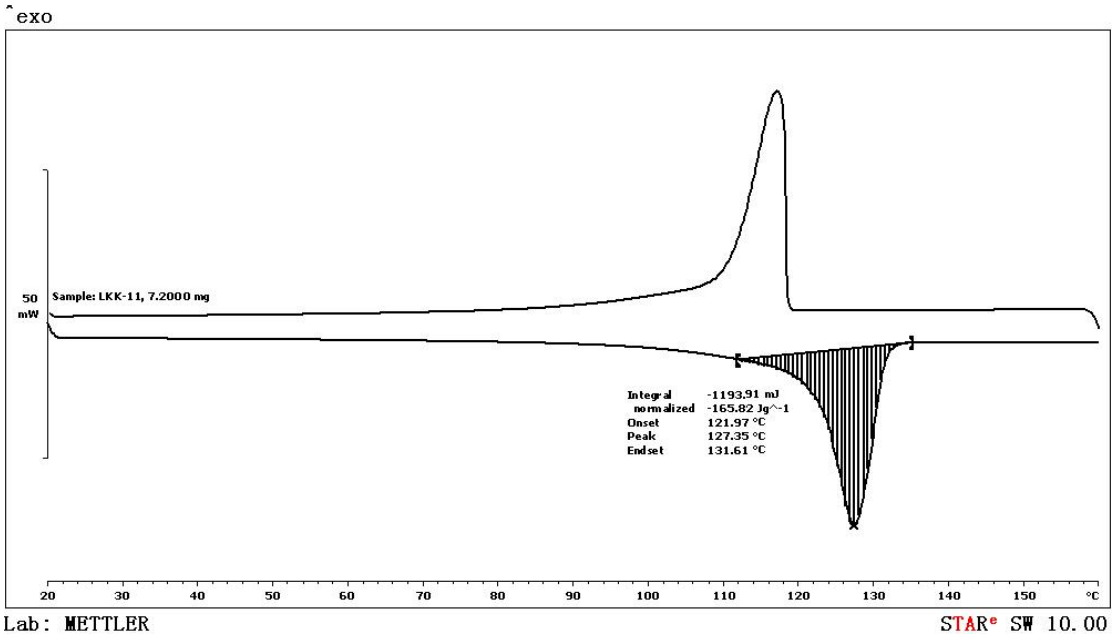


Figure S89. DSC data of the polymer from table 1, entry 10.

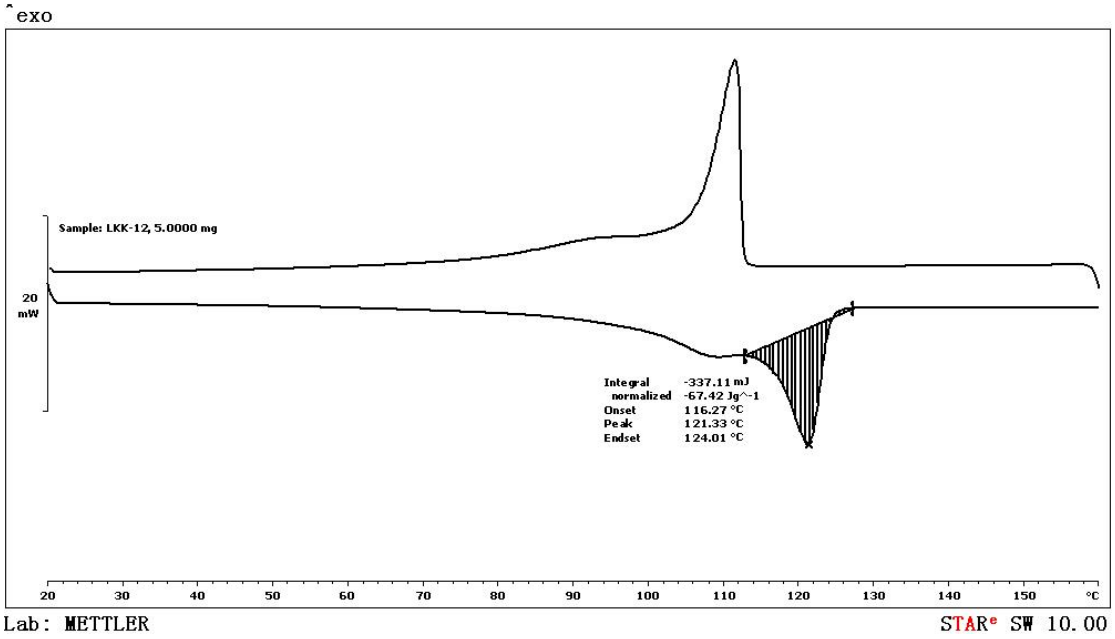


Figure S90. DSC data of the polymer from table 1, entry 11.

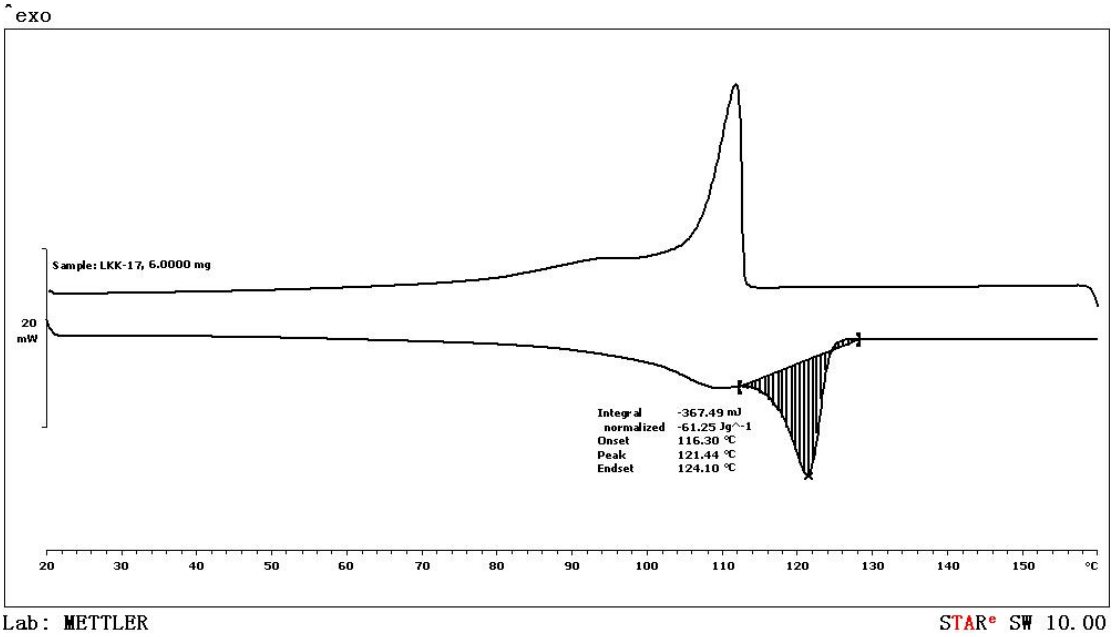


Figure S91. DSC data of the polymer from table 1, entry 12.

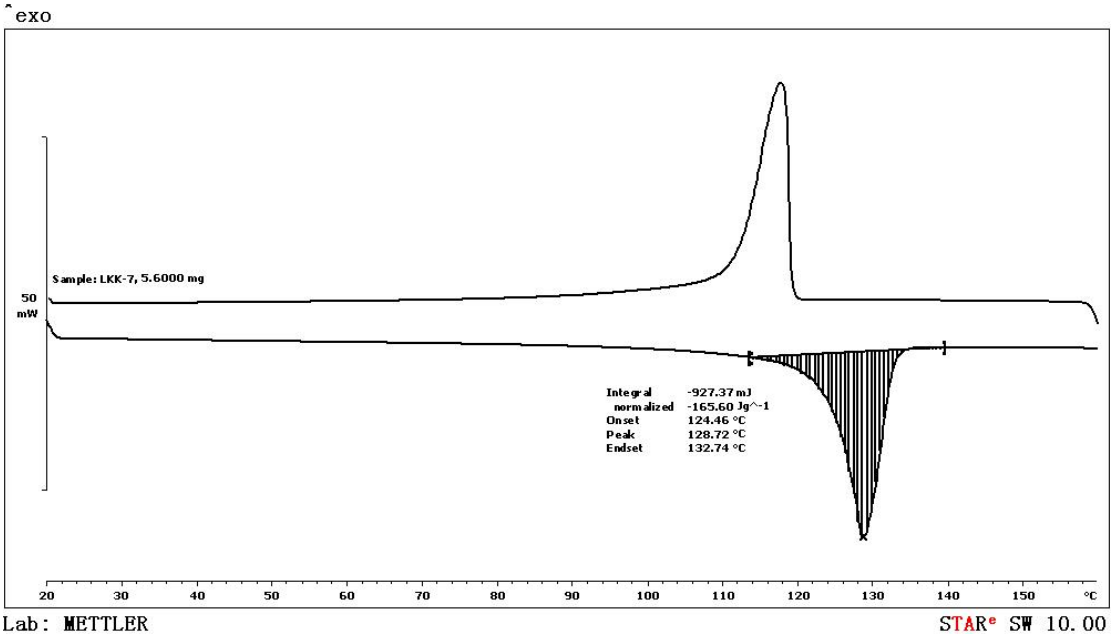


Figure S92. DSC data of the polymer from table 1, entry 13

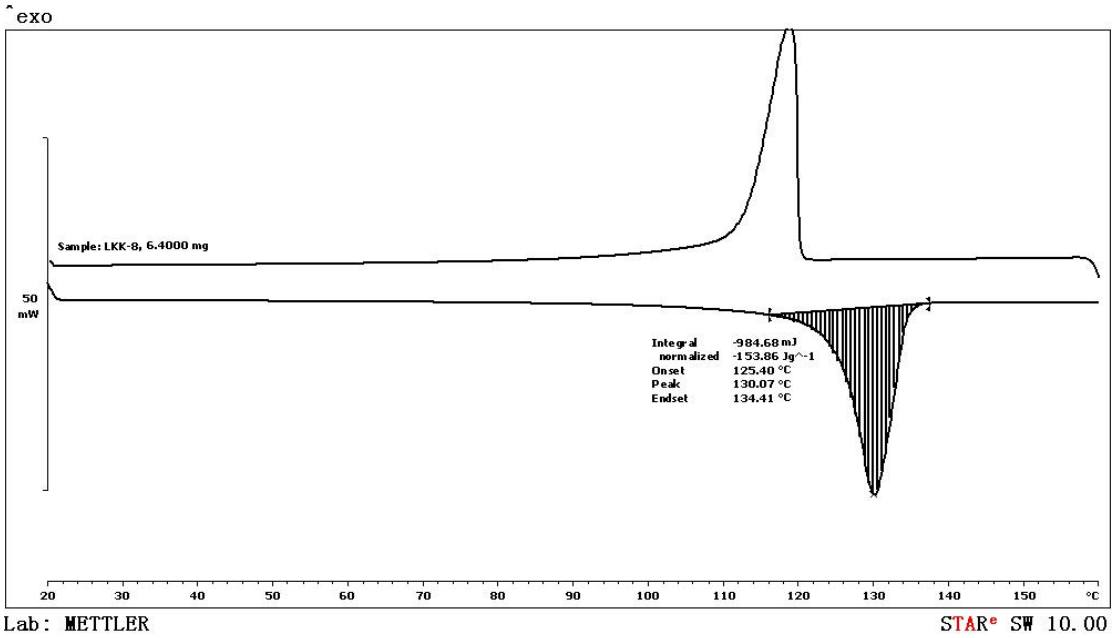


Figure S93. DSC data of the polymer from table 1, entry 14.

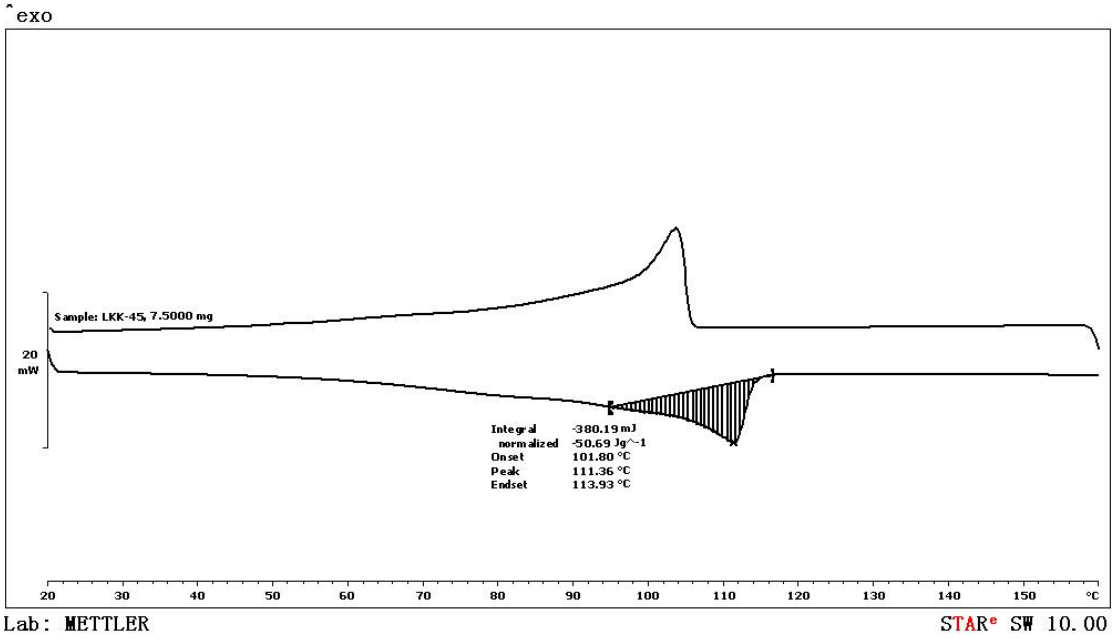


Figure S94. DSC data of the polymer from table 2, entry 2.

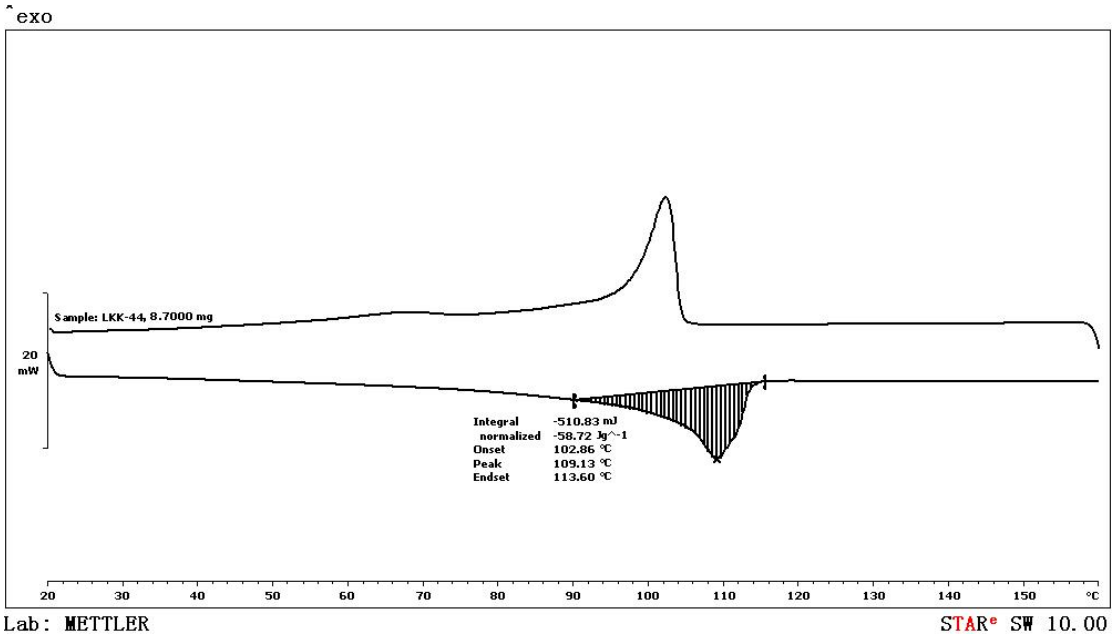


Figure S95. DSC data of the polymer from table 2, entry 3.

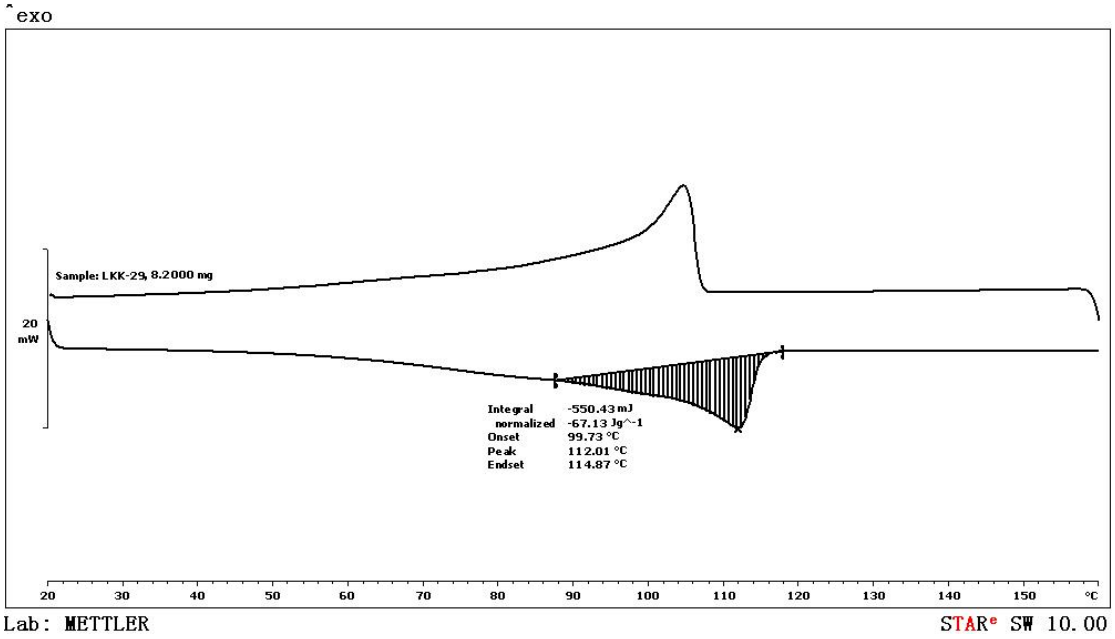


Figure S96. DSC data of the polymer from table 2, entry 5.

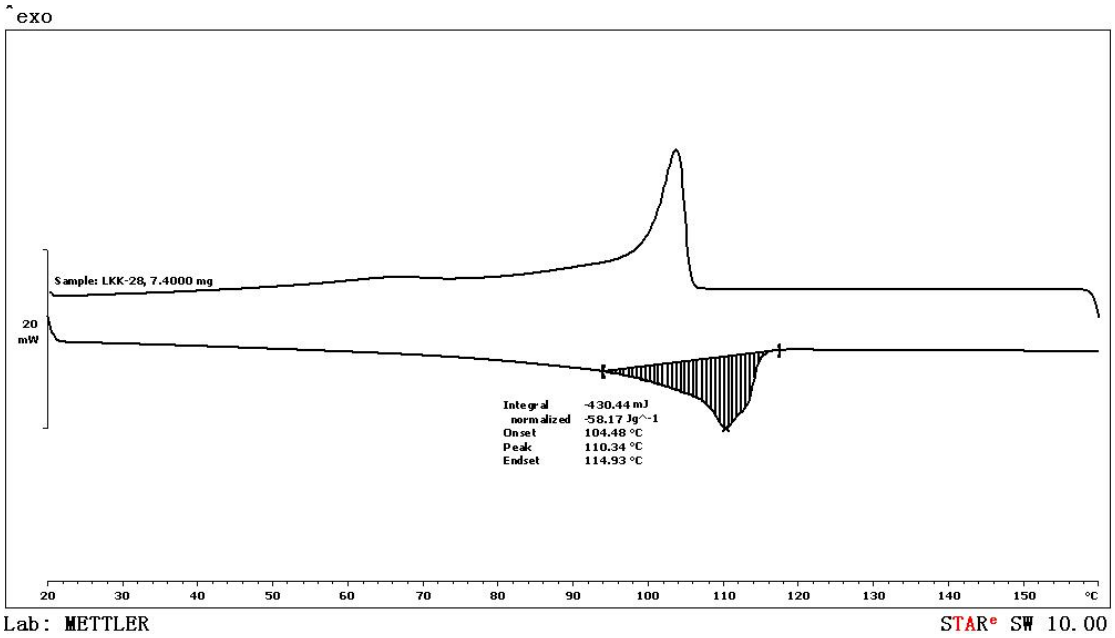


Figure S97. DSC data of the polymer from table 2, entry 6.

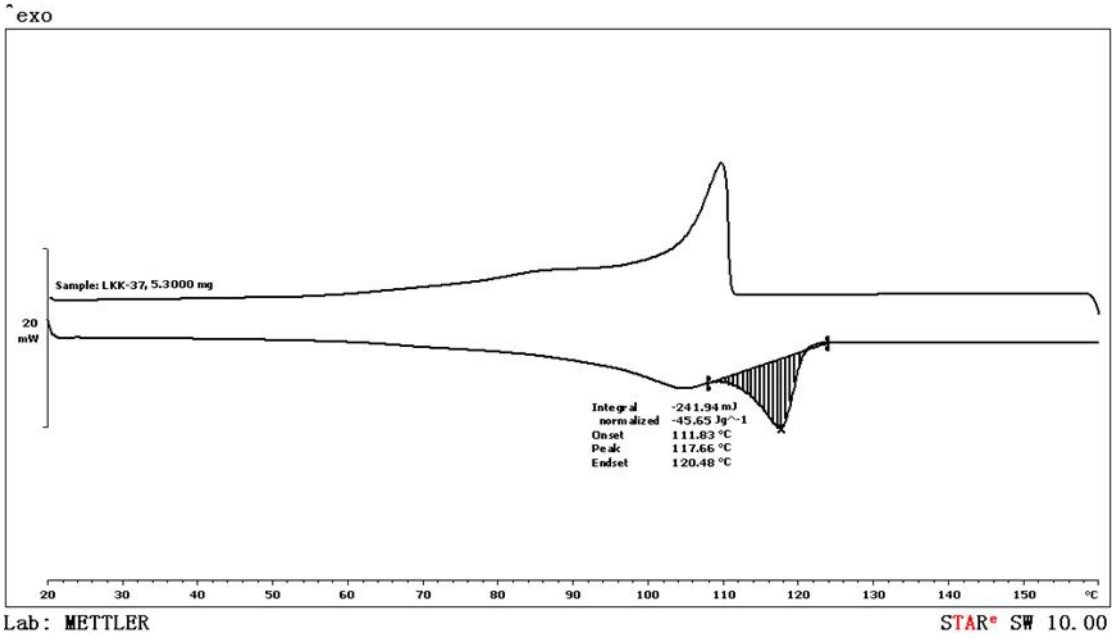


Figure S98. DSC data of the polymer from table 2, entry 7.

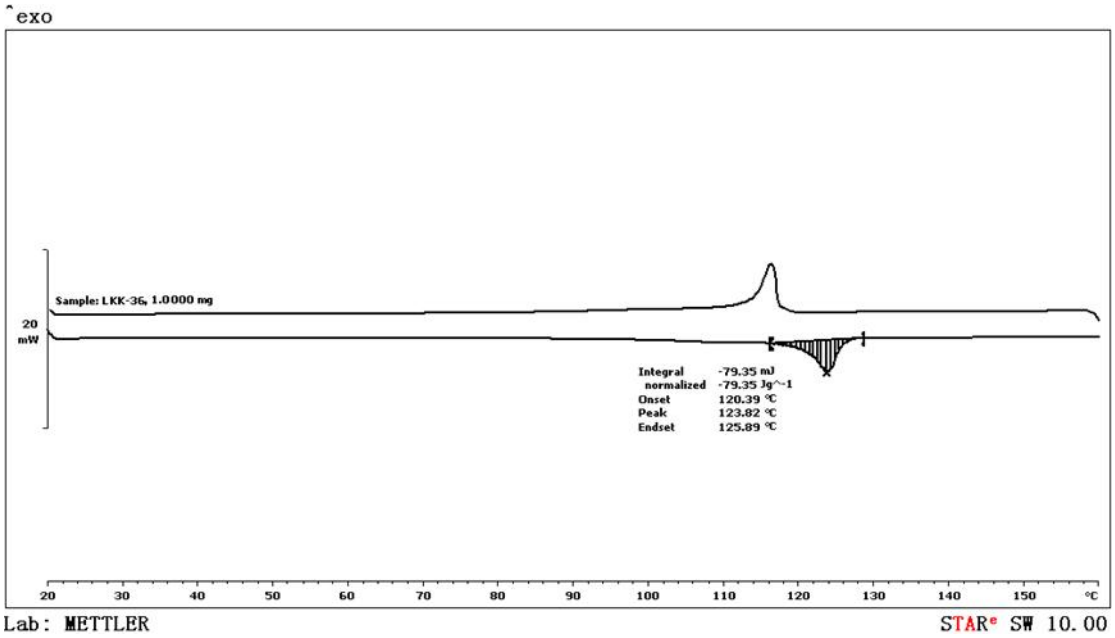


Figure S99. DSC data of the polymer from table 2, entry 8.

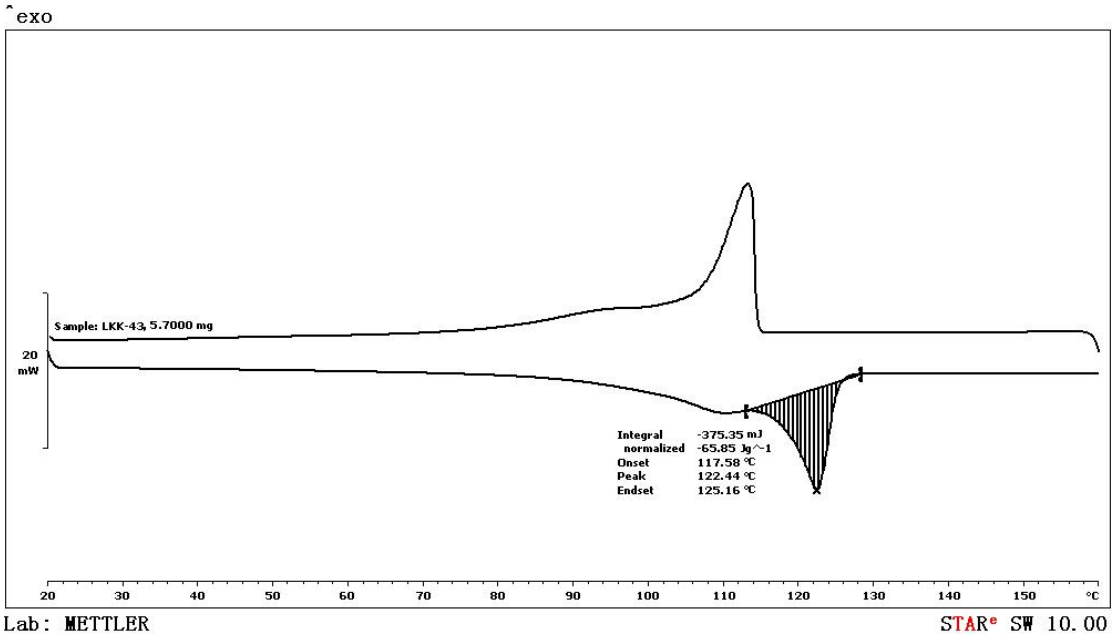


Figure S100. DSC data of the polymer from table 2, entry 9.

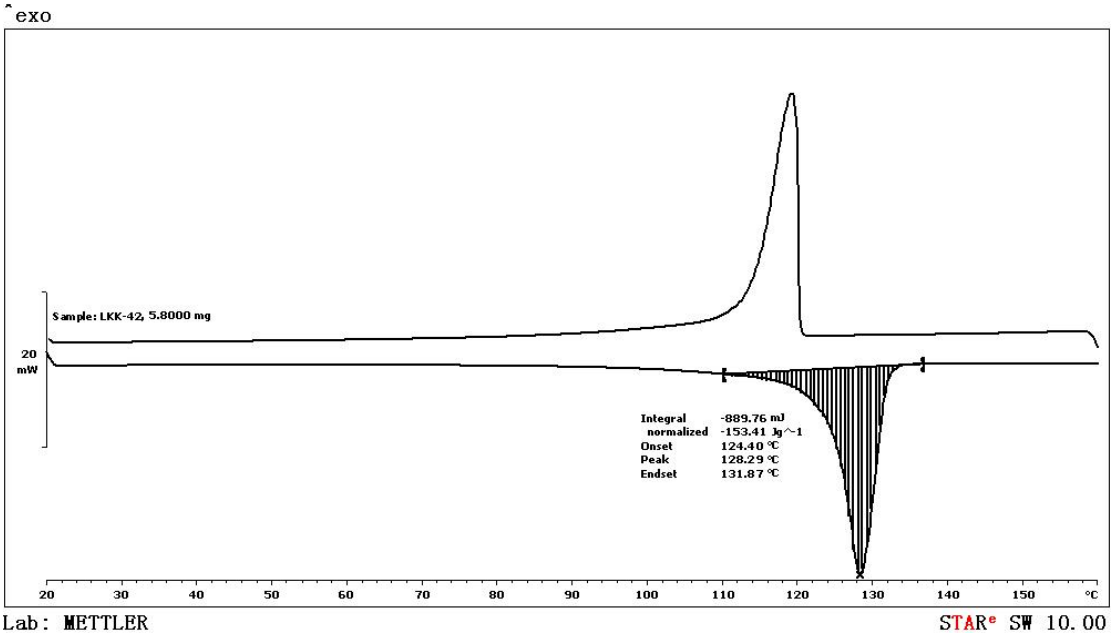


Figure S101. DSC data of the polymer from table 2, entry 10.

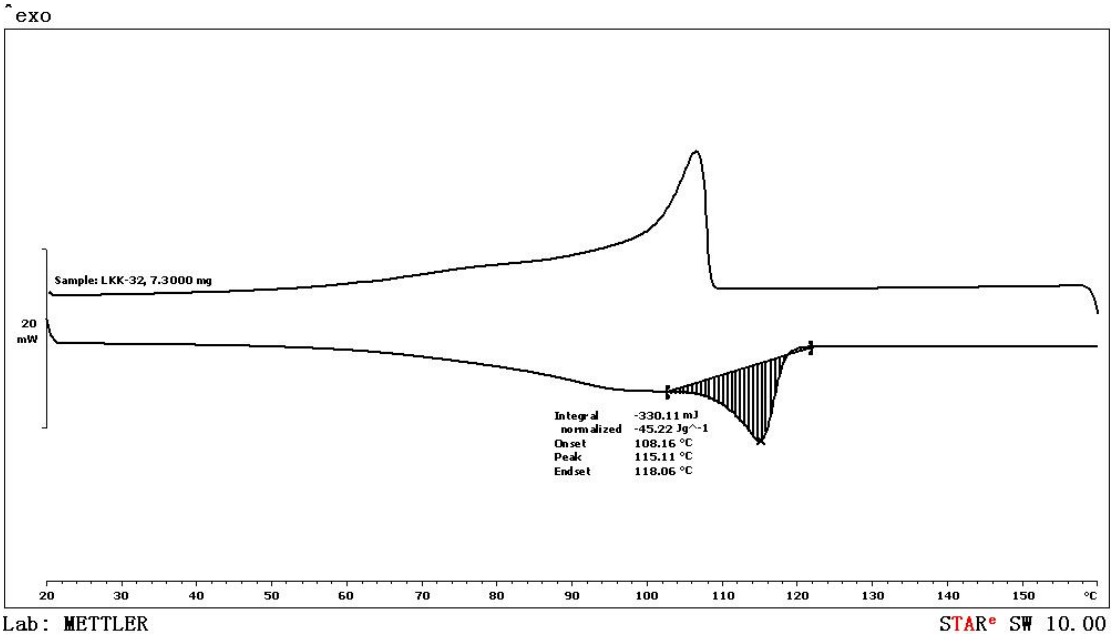


Figure S102. DSC data of the polymer from table 2, entry 11.

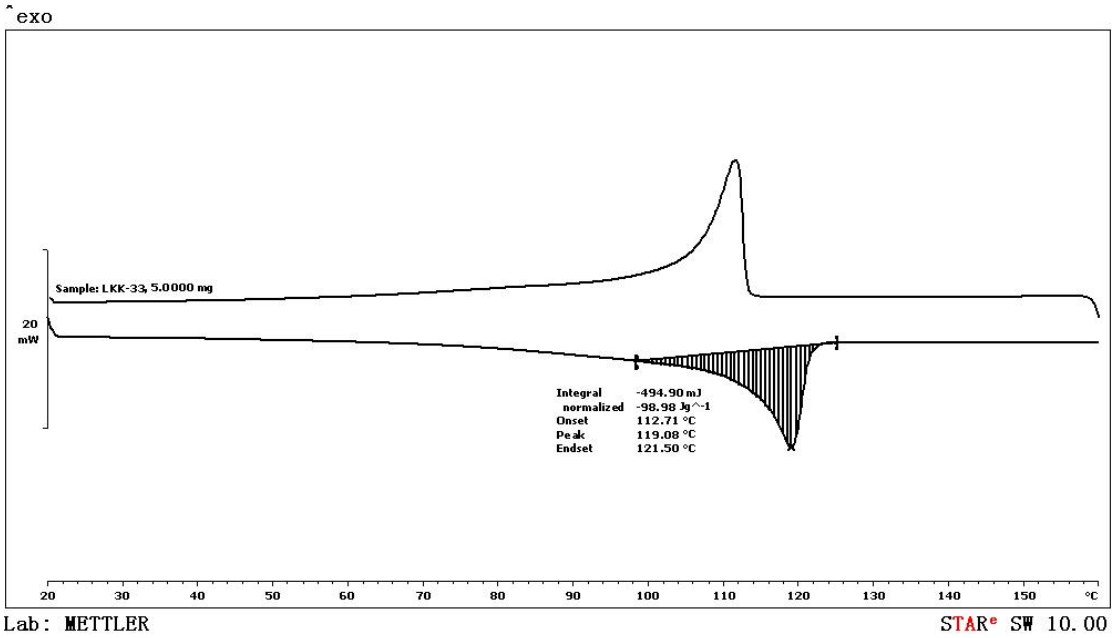


Figure S103. DSC data of the polymer from table 2, entry 12.

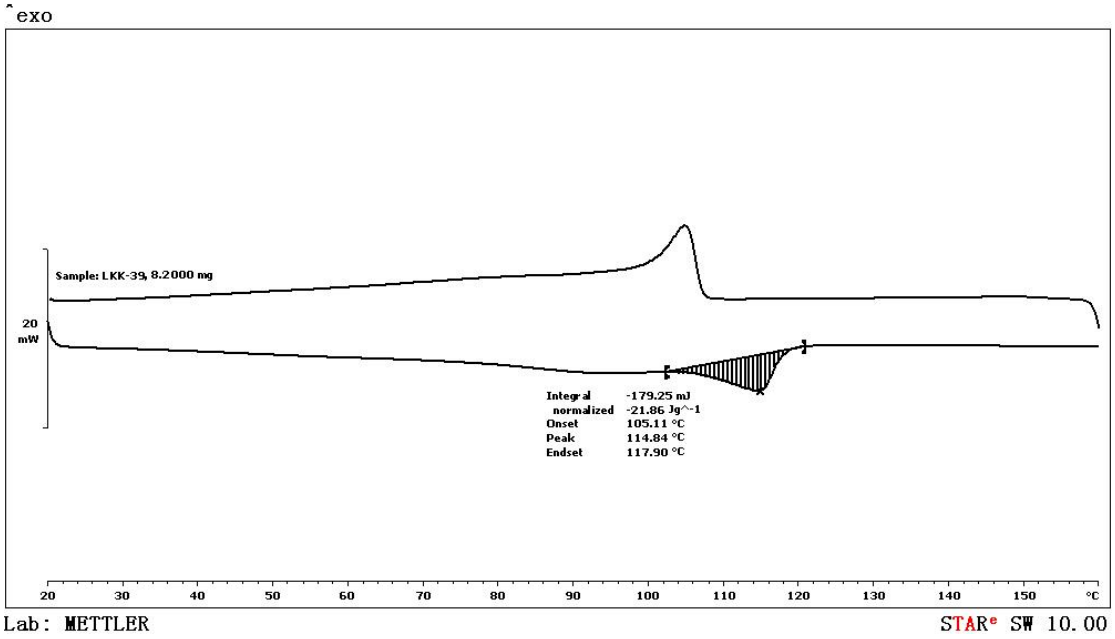


Figure S104. DSC data of the polymer from table 2, entry 13.

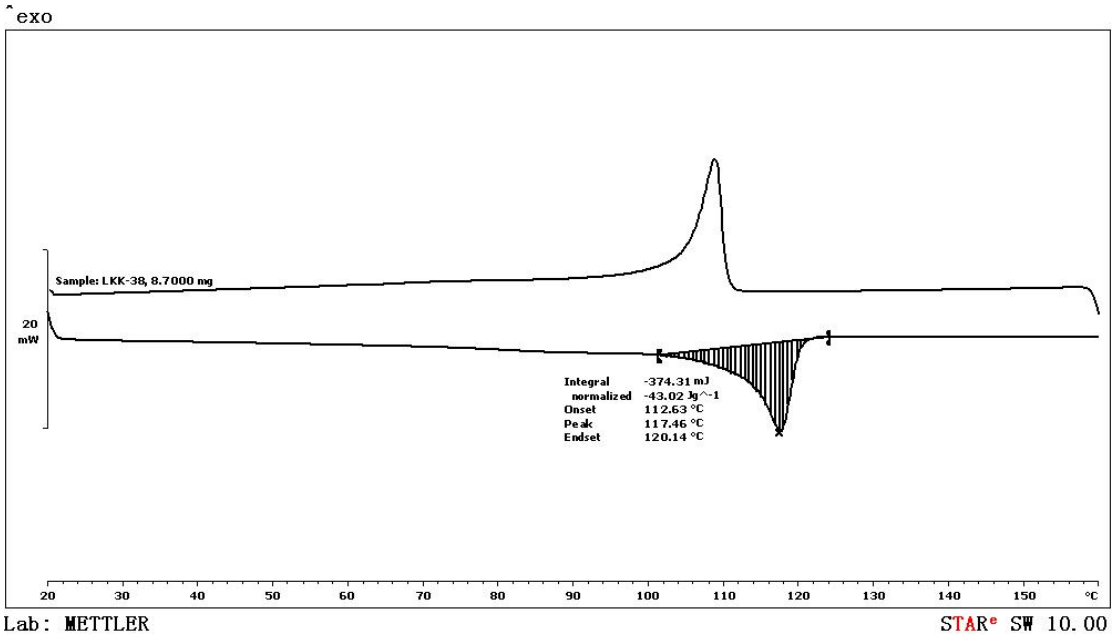


Figure S105. DSC data of the polymer from table 2, entry 14.

5. **Topographic steric maps of palladium catalysts 2e and G**

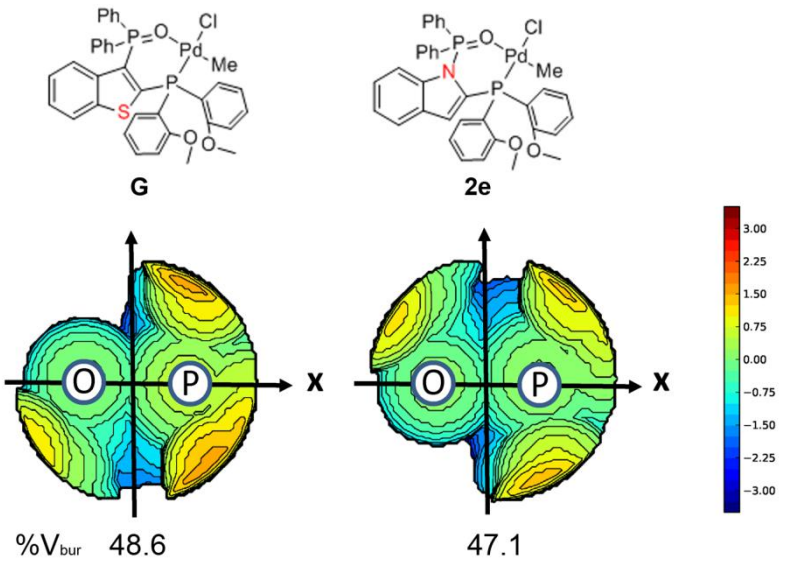


Figure S106. Topographic steric maps of palladium catalysts **2e** and **G**.

6. Table S1. Crystallographic data for **2c**, **2e** and **2f**.

	2c	**2e**	**2f**
Formula	$C_{38}H_{45}Cl_4NO_3P_2Pd$	$C_{35}H_{32}ClNO_3P_2Pd$	$C_{27}H_{34}ClN_3O_3P_2Pd+CHCl_3$
Formula weight	873.89	718.40	771.73
Crystal dimensions (mm^3)	0.20 × 0.10 × 0.10	0.30 × 0.23 × 0.10	0.36 × 0.20 × 0.11
Crystal system	triclinic	triclinic	triclinic
Space group	P^{-1}	P^{-1}	P^{-1}
a (Å)	10.2352(4)	11.0648(4)	11.2563(6)
b (Å)	14.3325(5)	12.5473(5)	12.7674(7)
c (Å)	14.8170(5)	15.4261(5)	14.3032(8)
α (º)	65.2480(10)	78.2720(10)	67.146(2)
β (º)	83.2000(10)	71.1550(10)	74.271(2)
γ (º)	79.8140(10)	88.7090(10)	78.535(2)
Volume ($Å^3$)	1940.40(12)	1982.39(13)	1813.12(17)
Z	2	2	2
T (K)	173(2)	173(2)	173(2)
D_{calcd} (g cm^{-3})	1.496	1.204	1.414
μ (mm^{-1})	7.468	5.393	7.93
F (000)	896	732	784
No. of rflns. collected	12056	13025	10880
No. of indep. rflns. /R_{int}	5422 /0.0407	5418 / 0.0415	5023 / 0.0176
No. of obsd. rflns. [$I_0 > 2\sigma(I_0)$]	4935	5255	4789
Data / restraints / parameters	5422 / 0 / 451	5418 / 0 / 391	5023 / 12 / 371
R_1 / wR_2 [$I_0 > 2\sigma(I_0)$]	0.0542 / 0.1532	0.0463 /0.1246	0.0564 / 0.1462
R_1 / wR_2 (all data)	0.0587 /0.1606	0.0473 / 0.1257	0.0589 / 0.1517
GOF (on F^2)	1.147	1.065	1.041
Largest diff. peak and hole (e $Å^{-3}$)	0.837 / -1.249	0.872 / -1.207	1.703 / –1.796
CCDC No.	1955275	1955170	1962725