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Sterically very bulky aliphatic/aromatic phosphine-sulfonate palladium catalysts for ethylene polymerization and copolymerization with polar monomers

Jian Xia,[a,c,d] Yixin Zhang,[a,*] Xiaoqiang Hu,[a,b] Xin Ma,[a,b] Lei Cui,[a] Jianfu Zhang[a,c,d] and Zhongbao Jian[a,*]

[a]State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Renmin Street 5625, Changchun 130022, China

[b]University of Science and Technology of China, Hefei 230026, China

[c]School of Chemistry and Environmental Engineering, Changchun University of Science and Technology, Changchun, 130022, China

[d]Jilin Provincial Science and Technology Innovation Center of Optical Materials and Chemistry, Changchun, 130022, China

Contents

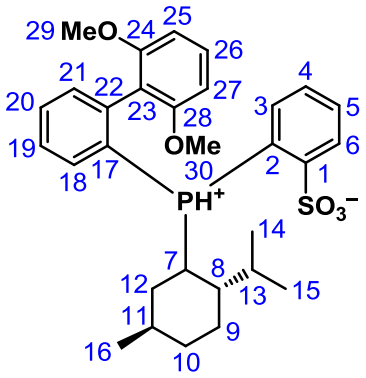
1. General information S2
2. Preparation of ligands and catalysts S3
3. General procedures for the polymerizations S11
4. NMR figures of ligands and catalysts S12
3. NMR figures of (co)polymers S25
4. GPC traces and DSC data of (co)polymers S38
5. Crystallographic data for **L1**, and **3** S58
6. References S58

General Procedures and Materials: All syntheses involving air- and moisture sensitive compounds were carried out using standard Schlenk-type glassware (or in a glove box) under an atmosphere of nitrogen. All solvents were purified from the MBraun SPS system. NMR spectra for the ligands, complexes, and polymers were recorded on a Bruker AV400 (^{1}H: 400 MHz, ^{13}C: 100 MHz, ^{31}P: 162 MHz, ^{19}F: 376 MHz) or a Bruker AV500 (^{1}H: 500 MHz, ^{13}C: 125 MHz, ^{31}P: 202 MHz, ^{19}F: 470 MHz). NMR assignments were confirmed by ^{1}H−^{1}H COSY, ^{1}H−^{13}C HSQC and ^{1}H−^{13}C HMBC experiments when necessary. The molecular weights (M_w) and molecular weight distributions (M_w/M_n) of polyethylenes and copolymers were measured by means of gel permeation chromatography (GPC) on a PL-GPC 220-type high-temperature chromatograph equipped with three PL-gel 10 μm Mixed-B LS type columns at 150 ℃. Melting points (T_m) of polyethylenes and copolymers were measured through DSC analyses, which were carried out on a Q 100 DSC from TA Instruments under a nitrogen atmosphere at heating and cooling rates of 10 ℃/min (temperature range: 20−160 °C). Elemental analysis were performed at the National Analytical Research Centre of Changchun Institute of Applied Chemistry.

X-Ray diffraction: Data collections were performed at −88.5 ℃ on a Bruker SMART APEX diffractometer with a CCD area detector, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The determination of crystal class and unit cell parameters was carried out by the SMART program package.[1] The raw frame data were processed using SAINT and SADABS to yield the reflection data file.[2] All structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2 using SHELXTL 2014.[3] Refinement was performed on F^2 anisotropically for all non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. *Exceptions and special features*: For ligand **L1**, the program SQUEEZE[4] was used to remove mathematically the effect of the solvent. The quoted formula and derived parameters are not included the squeezed solvent molecules.

Materials: MenPCl_2[5], lithium-2,4,6-trimethoxybenzene[6], 2-lithium-2',6'-dimethoxybiphenyl[7] and 2-bromo-2',6'-difluorobiphenyl[8] were prepared according to the literature procedures. All other reagents were commercially available and used as received.

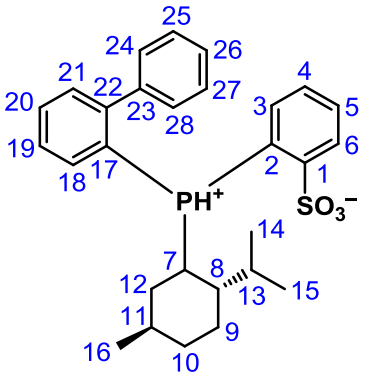
Preparation of Ligands and Catalysts



Preparation of Ligand L1: At 0 ℃ ^{n}BuLi (9.1 mL, 1.6 M in hexane, 14.6 mmol, 2.1 equiv) was added to a solution of benzenesulfonic acid (1.095 g, 6.9 mmol, 1.0 equiv) in THF (50 mL) and the reaction mixture was stirred at 25 ℃ for 30 min. The formed suspension was added at −78 ℃ under vigorous stirring to a solution of $MenPCl_2$ (1.660 g, 6.9 mmol, 1.0 equiv) in THF (50 mL). The mixture was allowed to warm slowly to room temperature. A solution of 2-lithium-2',6'-dimethoxybiphenyl (2.200 g, 6.9 mmol, 1.0 equiv) in THF (30 mL) was added at 0 ℃, and the reaction mixture was stirred at room temperature overnight. Volatiles were removed under vacuum to yield a dark brown solid. Water (100 mL) was slowly added and the resulting mixture was acidified to pH = 2 using a 10% HCl/H_2O solution. The mixture was extracted with CH_2Cl_2 (3 × 50 mL) and the combined organic phase was dried over $MgSO_4$. The solvent was removed in vacuo after filtration to give a pale yellow solid, which was precipitated from a mixture of CH_2Cl_2 and Et_2O to afford the product (2.220 g, 4.1 mmol, 60%).

^{1}H NMR (500 MHz, 298 K, $CDCl_3$, 7.26 ppm): δ =8.38~8.34 (m, 1H, H_6), 8.11~8.03 (m, 1H, H_{18}), 8.08 (dd, $^{1}J_{PH}$ = 547.4 Hz, $^{3}J_{HH}$ = 3.52 Hz, 1H, P-H), 7.81 (tt, $^{3}J_{HH}$ = 7.7 Hz, $^{4}J_{HH}$ = 1.4 Hz, 1H, H_{20}), 7.84~7.79 (m, 2H, H_5 & H_{19}), 7.55 (dddd, $^{3}J_{HH}$ = 7.9 Hz, $^{4}J_{PH}$ = 4.3 Hz, $^{4}J_{HH}$ = 1.4 Hz, 1H, H_{21}), 7.48~7.35 (m, 3H, H_3 & H_4 & H_{26}), 6.68 (d, $^{3}J_{HH}$ = 8.4 Hz, 1H, $H_{25/27}$), 6.49 (d, $^{3}J_{HH}$ = 8.4 Hz, 1H, $H_{25/27}$), 3.83~3.93 (m, 1H, H_7), 3.76 (s, 3H, $H_{29/30}$), 2.80 (s, 3H, $H_{29/30}$), 1.79~1.76 (dbr, 1H, H_{10}), 1.73~1.60 (m, 2H, H_9 & H_{12}), 1.56~1.36 (m, 3H, H_8 & H_{11} & H_{13}), 1.30~1.11 (m, 2H, H_9 & H_{12}), 0.90 (qd, $^{3}J_{HH}$ = 12.9 Hz, $^{4}J_{HH}$ = 3.5 Hz, 1H, H_{10}), 0.82 (d, $^{3}J_{HH}$ = 7.1 Hz, 6H, $H_{14/15}$), 0.63 (d, $^{3}J_{HH}$ = 6.6 Hz, 3H, H_{16}).

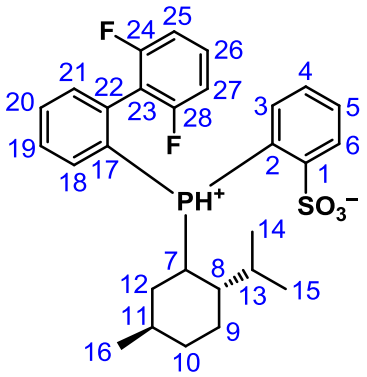
^{13}C{^{1}H} NMR (125 MHz, 298 K, $CDCl_3$, 77.16 ppm): δ = 156.70 ($C_{24/28}$), 156.65 ($C_{24/28}$), 151.41 (d, $^{2}J_{PC}$ = 8.2 Hz, C_1), 141.51 (d, $^{2}J_{PC}$ = 7.3 Hz, C_{22}), 134.77 (d, $^{3}J_{PC}$ = 8.6 Hz, C_{21}), 133.82 (d, $^{4}J_{PC}$ = 1.8 Hz, C_{20}), 133.83 (d, $^{2}J_{PC}$ = 9.1 Hz, C_3), 133.41 (d, $^{4}J_{PC}$ = 3.2 Hz, C_5), 132.99 (d, $^{2}J_{PC}$ = 7.3 Hz, C_{18}), 131.61 (C_{26}), 129.28 (C_6), 129.20 (C_4), 127.58 (d, $^{3}J_{PC}$ = 10.9 Hz, C_{19}), 116.26 (d, $^{1}J_{PC}$ = 81.3 Hz, C_{17}), 112.91 (d, $^{3}J_{PC}$ = 6.1 Hz, C_{23}), 112.86 (d, $^{1}J_{PC}$ = 88.6 Hz, C_2), 103.92 ($C_{25/27}$), 103.68 ($C_{25/27}$), 55.70 ($C_{29/30}$), 54.08 ($C_{29/30}$), 43.70 (d, $^{2}J_{PC}$ = 1.9 Hz, C_8), 36.05 (d, $^{1}J_{PC}$ = 43.6 Hz, C_7), 35.66 (d, $^{3}J_{PC}$ = 3.6 Hz, C_9), 34.10 (C_{10}), 33.21 (d, $^{3}J_{PC}$ = 14.5 Hz, C_{11}), 28.59 (d, $^{3}J_{PC}$ = 6.4 Hz, C_{13}), 24.25 (d, $^{2}J_{PC}$ = 13.6 Hz, C_{12}), 22.04 ($C_{14/15}$), 21.20 (C_{16}), 15.03 ($C_{14/15}$).
^{31}P{^{1}H} NMR (162 MHz, 298 K, $CDCl_3$): δ = −2.34.
Elemental analysis: calc. for $C_{30}H_{37}O_5PS$ (540.65 g mol^{-1}): C, 66.65; H, 6.90. Found: C, 66.24; H, 7.11.



Preparation of Ligand L2: At 0 ℃ ^{n}BuLi (5.5 mL, 1.6 M in hexane, 8.8 mmol, 2.1 equiv) was added to a solution of benzenesulfonic acid (668 mg, 4.2 mmol, 1.0 equiv) in THF (30 mL) and the reaction mixture was stirred at 25 ℃ for 30 min. The formed suspension was added at −78 ℃ under vigorous stirring to a solution of MenPCl$_2$ (1.016 g, 4.2 mmol, 1.0 equiv) in THF (50 mL). The mixture was allowed to warm slowly to room temperature. In a second flask at −78 ℃ ^{n}BuLi (2.8 mL, 1.6 M in hexane, 4.5 mmol, 1.1 equiv) was added to a solution of 2-bromo-biphenyl (980 mg, 4.2 mmol, 1.0 equiv) in THF (30 mL). The mixture was stirred at −78 ℃ for 30 min and then added with the solution in the first flask. The reaction mixture was allowed to warm slowly to room temperature and stirred overnight. Volatiles were removed under vacuum to yield a dark brown solid. Water (100 mL) was slowly added and the resulting mixture was acidified to pH = 2 using a 10% HCl/H$_2$O solution. The mixture was extracted with CH$_2$Cl$_2$ (3 × 50 mL) and the combined organic phase was dried over MgSO$_4$. The solvent was removed in vacuo after filtration to give a pale yellow solid, which was precipitated from a mixture of CH$_2$Cl$_2$ and *n*-hexane to afford the product (1.287 g, 2.7 mmol, 63%).

^{1}H NMR (500 MHz, 298 K, CDCl$_3$, 7.26 ppm): δ = 8.39 (dddd, $^{3}J_{HH}$ = 7.8 Hz, $^{4}J_{PH}$ = 4.9 Hz, $^{4}J_{HH}$ = 1.3 Hz, 1H, H$_6$), 8.09 (dd, $^{1}J_{PH}$ = 551.7 Hz, $^{3}J_{HH}$ = 3.07 Hz, 1H, P-H), 8.01 (ddd, $^{3}J_{PH}$ = 10.0 Hz, $^{3}J_{HH}$ = 7.9 Hz, $^{4}J_{HH}$ = 1.3 Hz, 1H, H$_{18}$), 7.86 (tt, $^{3}J_{HH}$ = 7.6 Hz, $^{4}J_{HH}$ = 1.4 Hz, 1H, H$_{20}$), 7.79~7.72 (m, 2H, H$_5$ & H$_{19}$), 7.62 (dddd, $^{3}J_{HH}$ = 7.8 Hz, $^{4}J_{PH}$ = 4.6 Hz, $^{4}J_{HH}$ = 1.3 Hz, 1H, H$_{21}$), 7.53~7.49 (m, 1H, H$_4$), 7.48~7.38 (m, 4H, H$_3$ & H$_{24/28}$ & H$_{26}$), 7.03 (dbr, 2H, H$_{25/27}$), 3.88~3.77 (m, 1H, H$_7$), 1.74 (m, 2H, H$_9$ & H$_{10}$), 1.66~1.64 (m, 1H, H$_{12}$), 1.54~1.46 (m, 1H, H$_{11}$), 1.31~1.09 (m, 4H, H$_8$ & H$_9$ & H$_{12}$ & H$_{13}$), 0.93~0.83 (m, 1H, H$_{10}$), 0.82 (d, $^{3}J_{HH}$ = 6.5 Hz, 3H, H$_{16}$), 0.72 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, H$_{14/15}$), 0.59 (d, $^{3}J_{HH}$ = 6.6 Hz, 3H, H$_{14/15}$).

^{13}C{^{1}H} NMR (125 MHz, 298 K, CDCl$_3$, 77.16 ppm): δ = 152.13 (d, $^{2}J_{PC}$ = 8.4 Hz, C$_1$), 149.11 (d, $^{2}J_{PC}$ = 7.4 Hz, C$_{22}$), 137.54 (d, $^{3}J_{PC}$ = 5.9 Hz, C$_{23}$), 134.91 (d, $^{4}J_{PC}$ = 3.1 Hz, C$_5$), 134.65 (d, $^{2}J_{PC}$ = 10.0 Hz, C$_3$), 134.49 (d, $^{4}J_{PC}$ = 2.5 Hz, C$_{20}$), 133.75 (d, $^{2}J_{PC}$ = 7.7 Hz, C$_{18}$), 132.92 (d, $^{3}J_{PC}$ = 8.1 Hz, C$_{21}$), 130.26 (d, $^{3}J_{PC}$ = 8.9 Hz, C$_6$), 129.98 (d, $^{3}J_{PC}$ = 12.0 Hz, C$_4$), 129.94 (C$_{26}$), 129.65 (C$_{24/28}$), 128.51 (C$_{25/27}$), 128.30 (d, $^{3}J_{PC}$ = 10.7 Hz, C$_{19}$), 115.52 (d, $^{1}J_{PC}$ = 79.0 Hz, C$_{17}$), 112.45 (d, $^{1}J_{PC}$ = 87.2 Hz, C$_2$), 44.07 (d, $^{3}J_{PC}$ = 2.4 Hz, C$_{13}$), 37.20 (d, $^{1}J_{PC}$ = 43.1 Hz, C$_7$), 36.24 (d, $^{3}J_{PC}$ = 4.0 Hz, C$_9$), 34.30 (d, $^{4}J_{PC}$ = 1.8 Hz, C$_{10}$), 33.33 (d, $^{3}J_{PC}$ = 14.6 Hz, C$_{11}$), 29.49 (d, $^{2}J_{PC}$ = 6.9 Hz, C$_8$), 24.58 (d, $^{2}J_{PC}$ = 13.8 Hz, C$_{12}$), 22.29 (C$_{16}$), 21.15 (C$_{14/15}$), 15.09 (C$_{14/15}$).
^{31}P{^{1}H} NMR (162 MHz, 298 K, CDCl$_3$): δ = −1.19.
Elemental analysis: calc. for C$_{28}$H$_{33}$O$_3$PS (480.60 g mol^{-1}): C, 69.98; H, 6.92. Found: C, 70.14; H, 7.03.



Preparation of Ligand L3: At 0 ℃ ^{n}BuLi (5.5 mL, 1.6 M in hexane, 8.8 mmol, 2.1 equiv) was added to a solution of benzenesulfonic acid (674 mg, 4.3 mmol, 1.0 equiv) in THF (30 mL) and the reaction mixture was stirred at 25 ℃ for 30 min. The formed suspension was added at −78 ℃ under vigorous stirring to a solution of MenPCl$_2$ (1.019 g, 4.2 mmol, 1.0 equiv) in THF (50 mL). The mixture was allowed to warm slowly to room temperature. In a second flask at −78 ℃ ^{n}BuLi (2.9 mL, 1.6 M in hexane, 4.6 mmol, 1.1 equiv) was added to a solution of 2-bromo-2',6'-difluorobiphenyl (1.155 g, 4.3 mmol, 1.0 equiv) in THF (30 mL). The mixture was stirred at −78 ℃ for 30 min and then added with the solution in the first flask. The reaction mixture was allowed to warm slowly to room temperature and stirred overnight. Volatiles were removed under vacuum to yield a dark brown solid. Water (100 mL) was slowly added and the resulting mixture was acidified to pH = 2 using a 10% HCl/H$_2$O solution. The mixture was extracted with CH$_2$Cl$_2$ (3 × 50 mL) and the combined organic phase was dried over MgSO$_4$. The solvent was removed in vacuo after filtration to give a pale yellow solid, which was precipitated from a mixture of THF and *n*-hexane to afford the product (1.330 g, 2.6 mmol, 60%).

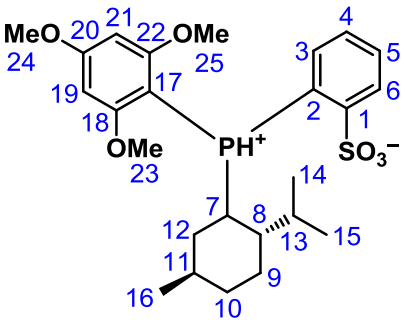
^{1}H NMR (500 MHz, 298 K, CDCl$_3$, 7.26 ppm): δ = 8.28 (t, $^{3}J_{HH}$ = 6.4 Hz, 1H, H$_6$), 8.19 (t, $^{3}J_{HH}$ = 9.0 Hz, 1H, H$_{18}$), 8.14 (dbr, $^{1}J_{PH}$ = 530.9 Hz, 1H, P-H), 7.91 (t, $^{3}J_{HH}$ = 7.7 Hz, 1H, H$_{20}$), 7.84 (t, $^{3}J_{HH}$ = 7.9 Hz, 1H, H$_{19}$), 7.68 (t, $^{3}J_{HH}$ = 7.8 Hz, 1H, H$_5$), 7.59 (br, 1H, H$_{21}$), 7.45~7.39 (m, 2H, H$_4$ & H$_{26}$), 7.21 (dd, $^{2}J_{PH}$ = 14.2 Hz, $^{3}J_{HH}$ = 7.8 Hz, 1H, H$_3$), 7.09 (t, $^{3}J_{HH}$ = 8.7 Hz, 1H, H$_{25/27}$), 6.82 (t, $^{3}J_{HH}$ = 8.6 Hz, 1H, H$_{25/27}$), 3.98 (q, $^{2}J_{PH}$ = $^{3}J_{HH}$ = 13.7 Hz, 1H, H$_7$), 1.79 (d, $^{3}J_{HH}$ = 13.2 Hz, 1H, H$_{10}$), 1.72 (br, 2H, H$_9$ & H$_{12}$), 1.49 (br, 3H, H$_8$ & H$_{11}$ & H$_{13}$), 1.31~1.15 (m, 2H, H$_9$ & H$_{12}$), 0.99~0.92 (m, 1H, H$_{10}$), 0.89 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, H$_{14/15}$), 0.82 (d, $^{3}J_{HH}$ = 6.5 Hz, 3H, H$_{16}$), 0.67 (d, $^{3}J_{HH}$ = 6.6 Hz, 3H, H$_{14/15}$).

^{13}C{^{1}H} NMR (125 MHz, 298 K, CDCl$_3$, 77.16 ppm): δ = 160.41 (dd, $^{1}J_{FC}$ = 60.0 Hz, $^{3}J_{FC}$ = 5.8 Hz, C$_{24/28}$), 158.43 (dd, $^{1}J_{FC}$ = 59.0 Hz, $^{3}J_{FC}$ = 5.9 Hz, C$_{24/28}$), 151.98 (d, $^{2}J_{PC}$ = 8.6 Hz, C$_1$), 136.17 (d, $^{2}J_{PC}$ = 6.8 Hz, C$_{22}$), 134.66 (d, $^{4}J_{PC}$ = 2.4 Hz, C$_{20}$), 134.58 (d, $^{4}J_{PC}$ = 3.0 Hz, C$_5$), 134.50 (d, $^{2}J_{PC}$ = 5.9 Hz, C$_3$), 134.42 (d, $^{3}J_{PC}$ = 2.4 Hz, C$_{21}$), 133.91 (d, $^{2}J_{PC}$ = 7.3 Hz, C$_{18}$), 132.69 (t, $^{3}J_{FC}$ = 10.2 Hz, C$_{26}$), 129.61 (d, $^{3}J_{PC}$ = 6.0 Hz, C$_4$), 129.56 (d, $^{3}J_{PC}$ = 3.6 Hz, C$_{19}$), 129.49 (d, $^{3}J_{PC}$ = 3.3 Hz, C$_6$), 117.99 (d, $^{1}J_{PC}$ = 77.7 Hz, C$_{17}$), 113.68 (td, $^{2}J_{FC}$ = 20.0 Hz, $^{3}J_{PC}$ = 5.9 Hz, C$_{23}$), 112.70 (dd, $^{2}J_{FC}$ = 21.6 Hz, $^{4}J_{FC}$ = 3.5 Hz, C$_{25/27}$), 112.41 (dd, $^{2}J_{FC}$ = 21.8 Hz, $^{4}J_{FC}$ = 3.6 Hz, C$_{25/27}$), 111.65 (d, $^{1}J_{PC}$ = 88.2 Hz, C$_2$), 44.49 (d, $^{3}J_{PC}$ = 2.6 Hz, C$_{13}$), 36.95 (d, $^{1}J_{PC}$ = 42.9 Hz, C$_7$), 35.83 (d, $^{2}J_{PC}$ = 4.0 Hz, C$_{12}$), 34.41 (C$_{10}$), 33.49 (d, $^{3}J_{PC}$ = 14.8 Hz, C$_{11}$), 29.54 (d, $^{2}J_{PC}$ = 6.8 Hz, C$_8$), 24.67 (d, $^{3}J_{PC}$ = 13.8 Hz, C$_9$), 22.26 (C$_{16}$), 21.28 (C$_{14/15}$), 15.15 (C$_{14/15}$).

^{31}P{^{1}H} NMR (202 MHz, 298 K, CDCl$_3$): δ = −2.45.

^{19}F NMR (470 MHz, 298 K, CDCl$_3$): δ = −110.56, −113.36.

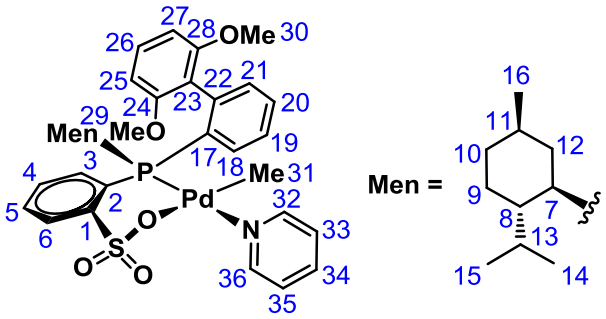
Elemental analysis: calc. for C$_{28}$H$_{31}$F$_2$O$_3$PS (516.58 g mol^{-1}): C, 65.10; H, 6.05. Found: C, 65.47; H, 5.94.



Preparation of Ligand L4: At 0 ℃ ^{n}BuLi (5.7 mL, 1.6 M in hexane, 9.1 mmol, 2.1 equiv) was added to a solution of benzenesulfonic acid (697 mg, 4.4 mmol, 1.0 equiv) in THF (30 mL) and the reaction mixture was stirred at 25 ℃ for 30 min. The formed suspension was added at −78 ℃ under vigorous stirring to a solution of $MenPCl_2$ (1.054 g, 4.4 mmol, 1.0 equiv) in THF (50 mL). The mixture was allowed to warm slowly to room temperature and stirred overnight. A solution of lithium-2,4,6-trimethoxybenzene (764 mg, 4.4 mmol, 1.0 equiv) in THF (15 mL) was added at 0 ℃, and the reaction mixture was stirred at room temperature for 2 h. Volatiles were removed under vacuum to yield a dark brown solid. Water (100 mL) was slowly added and the resulting mixture was acidified to pH = 2 using a 10% HCl/H_2O solution. The mixture was extracted with CH_2Cl_2 (3 × 50 mL) and the combined organic phase was dried over $MgSO_4$. The solvent was removed in vacuo after filtration to give a pale yellow solid, which was twice recrystallized from a mixture of CH_2Cl_2 and *n*-hexane at −35 ℃ to afford the product (500 mg, 1.0 mmol, 23%).

^{1}H NMR (500 MHz, 298 K, $CDCl_3$, 7.26 ppm): δ = 8.88 (dd, $^{1}J_{PH}$ = 560.1 Hz, $^{3}J_{HH}$ = 5.12 Hz, 1H, P-H), 8.33 (dbr, 1H, H_6), 7.66~7.56 (m, 1H, H_5), 7.41~7.33 (m, 2H, H_3 & H_4), 6.25 (d, $^{4}J_{PH}$ = 4.0 Hz, 2H, H_{19} & H_{21}), 3.92 (s, 3H, H_{24}), 3.90 (s, 6H, $H_{23/25}$), 3.85~3.80 (m, 1H, H_7), 1.75 (dbr, 1H, H_{10}), 1.71~1.66 (m, 1H, H_{12}), 1.62~1.50 (m, 2H, H_9 & H_{13}), 1.47~1.39 (m, 2H, H_8 & H_{11}), 1.33~1.27 (m, 1H, H_9), 1.16 (qd, $^{3}J_{PH}$ = 13.0 Hz, $^{3}J_{HH}$ = 3.1 Hz, 1H, H_{12}), 0.92 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, $H_{14/15}$), 0.82 (dbr, 1H, H_{10}), 0.80 (d, $^{3}J_{HH}$ = 6.4 Hz, 3H, H_{16}), 0.67 (d, $^{3}J_{HH}$ = 6.7 Hz, 3H, $H_{14/15}$).

^{13}C{^{1}H} NMR (125 MHz, 298 K, $CDCl_3$, 77.16 ppm): δ = 167.78 (C_{20}), 164.01 ($C_{18/22}$), 151.62 (d, $^{2}J_{PC}$ = 8.9 Hz, C_1), 134.09 (d, $^{2}J_{PC}$ = 9.6 Hz, C_3), 133.81 (d, $^{4}J_{PC}$ = 3.0 Hz, C_5), 129.58 (d, $^{3}J_{PC}$ = 9.2 Hz, C_6), 129.33 (d, $^{3}J_{PC}$ = 12.1 Hz, C_4), 114.41 (d, $^{1}J_{PC}$ = 88.0 Hz, C_2), 91.77 (d, $^{3}J_{PC}$ = 5.9 Hz, $C_{19/21}$), 85.85 (d, $^{1}J_{PC}$ = 87.3 Hz, C_{17}), 56.35 ($C_{23/25}$), 56.09 (C_{24}), 43.69 (d, $^{2}J_{PC}$ = 2.5 Hz, C_8), 35.38 (d, $^{1}J_{PC}$ = 46.3 Hz, C_7), 34.97 (d, $^{3}J_{PC}$ = 3.6 Hz, C_9), 34.47 (d, $^{4}J_{PC}$ = 1.9 Hz, C_{10}), 32.84 (d, $^{3}J_{PC}$ = 15.8 Hz, C_{11}), 30.05 (d, $^{3}J_{PC}$ = 5.8 Hz, C_{13}), 24.80 (d, $^{2}J_{PC}$ = 14.5 Hz, C_{12}), 22.66 (C_{16}), 21.61 ($C_{14/15}$), 15.76 ($C_{14/15}$).
^{31}P{^{1}H} NMR (162 MHz, 298 K, $CDCl_3$): δ = −10.62.
Elemental analysis: calc. for $C_{25}H_{35}O_6PS$ (494.58 g mol^{-1}): C, 60.71; H, 7.13. Found: C, 61.02; H, 7.24.



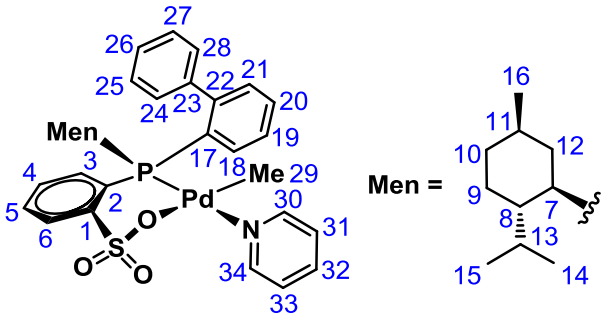
Preparation of complex 1: A solution of $PdMe_2(tmeda)$ (91 mg, 0.4 mmol, 1.0 equiv) in THF (5 mL) was added to a solution of **L1** (196 mg, 0.4 mmol, 1.0 equiv) in THF (5 mL) and the reaction mixture was stirred for 5 h. Pyridine (65 mg, 0.8 mmol, 2.0 equiv) was added and the mixture was stirred for 2 h. Volatiles were removed under vacuum and the residue was precipitated from a mixture of CH_2Cl_2 and *n*-hexane to afford the product (182 mg, 68%).

^{1}H NMR (500 MHz, 298 K, $CDCl_3$, 7.26 ppm): δ = 8.63~8.61 (m, 2H, $H_{32/36}$), 8.18 (dddd, $^4J_{PH}$ = 4.4 Hz, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.4 Hz, 1H, H_6), 8.00~7.96 (m, 1H, H_{18}), 7.79 (tt, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.7 Hz, 1H, H_{34}), 7.64 (t, $^3J_{PH}$ = $^3J_{HH}$ = 8.6 Hz, 1H, H_3), 7.51~7.47 (m, 2H, $H_{19/20}$), 7.39 (t, $^3J_{HH}$ = 6.5 Hz, 2H, $H_{33/35}$), 7.37~7.34 (m, 1H, H_5), 7.25 (br, 1H, H_4), 7.23~7.20 (m, 1H, H_{21}), 7.16 (t, $^3J_{HH}$ = 8.5 Hz, 1H, H_{26}), 6.42 (d, $^3J_{HH}$ = 8.5 Hz, 2H, $H_{25/27}$), 6.40 (d, $^3J_{HH}$ = 8.5 Hz, 1H, $H_{25/27}$), 3.61 (s, 3H, $H_{29/30}$), 3.13 (s, 3H, $H_{29/30}$), 2.73~2.67 (m, 1H, H_7), 2.23 (br, 1H, H_{12}), 1.94~1.82 (m, 3H, H_8 & H_9 & H_{13}), 1.71~1.62 (m, 1H, H_{10}), 1.36~1.28 (m, 2H, H_{11} & H_{12}), 1.23~1.19 (m, 1H, H_9), 0.90~0.86 (m, 1H, H_{10}), 0.83 (d, $^3J_{HH}$ = 5.6 Hz, 3H, H_{16}), 0.58 (d, $^3J_{HH}$ = 6.6 Hz, 3H, $H_{14/15}$), 0.41 (d, $^3J_{HH}$ = 6.3 Hz, 3H, $H_{14/15}$), 0.36 (d, $^3J_{PH}$ = 1.9 Hz, 3H, H_{31}).

^{13}C{^{1}H} NMR (126 MHz, 298 K, $CDCl_3$, 77.16 ppm): δ = 157.85 ($C_{24/28}$), 157.21 ($C_{24/28}$), 150.43 ($C_{32/36}$), 149.23 (d, $^2J_{PC}$ = 12.9 Hz, C_1), 140.52 (d, $^2J_{PC}$ = 10.6 Hz, C_{22}), 137.87 (C_{34}), 134.45 (d, $^3J_{PC}$ = 8.3 Hz, C_{21}), 134.36 (d, $^2J_{PC}$ = 6.7 Hz, C_{18}), 134.24 (C_3), 131.52 (d, $^1J_{PC}$ = 43.3 Hz, C_{17}), 129.97 (d, $^4J_{PC}$ = 2.2 Hz, C_{20}), 129.87 (d, $^4J_{PC}$ = 2.3 Hz, C_5), 129.49 (C_{26}), 129.26 (d, $^3J_{PC}$ = 7.5 Hz, C_6), 129.26 (d, $^1J_{PC}$ = 29.5 Hz, C_2), 128.73 (d, $^2J_{PC}$ = 6.1 Hz, C_4), 126.26 (d, $^3J_{PC}$ = 8.2 Hz, C_{19}), 124.90 (d, $^4J_{PC}$ = 2.3 Hz, $C_{33/35}$), 118.27 (d, $^3J_{PC}$ = 4.3 Hz, C_{23}), 103.85 ($C_{25/27}$), 102.94 ($C_{25/27}$), 55.42 ($C_{29/30}$), 54.81 ($C_{29/30}$), 43.67 (C_8), 42.26 (d, $^1J_{PC}$ = 24.9 Hz, C_7), 38.70 (d, $^2J_{PC}$ = 5.7 Hz, C_{12}), 32.98 (C_{10}), 32.39 (d, $^2J_{PC}$ = 14.1 Hz, C_{16}), 29.03 (d, $^3J_{PC}$ = 5.2 Hz, C_{13}), 24.67 (d, $^3J_{PC}$ = 8.7 Hz, C_9), 23.04 (C_{16}), 21.24 ($C_{14/5}$), 17.04 ($C_{14/15}$), −2.32 (d, $^2J_{PC}$ = 3.1 Hz, C_{31}).

^{31}P{^{1}H} NMR (162 MHz, 298 K, $CDCl_3$): δ = 25.10

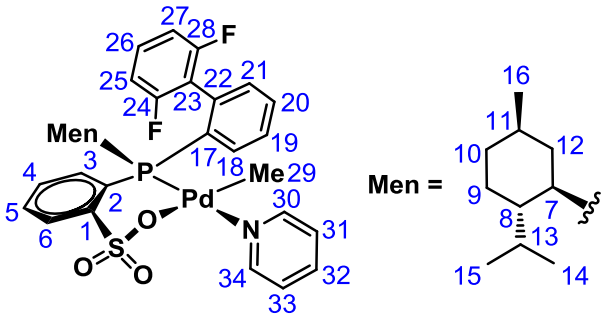
Elemental analysis: calc. for $C_{36}H_{44}NO_5PPdS$ (740.20 g mol^{-1}): C, 58.41; H, 5.99; N, 1.89. Found: C, 58.63; H, 6.08; N, 1.80.



Preparation of complex 2: At −35 ℃ a solution of $PdMe_2$(tmeda) (131 mg, 0.5 mmol, 1.0 equiv) in THF (5 mL) was added to a solution of **L2** (239 mg, 0.5 mmol, 1.0 equiv) in THF (5 mL). The reaction mixture was stirred at −35 ℃ for 1 h and then pyridine (79 mg, 1.0 mmol, 2.0 equiv) was added. The mixture was allowed to warm to room temperature and stirred for 2 h. Volatiles were removed under vacuum and the residue was precipitated from a mixture of THF and *n*-hexane to yield a pale yellow solid. The solid was reprecipitated from a mixture of CH_2Cl_2 and Et_2O, and the solvent of the filtrate was removed in vacuo to afford the product (199 mg, 59%).

^{1}H NMR (500 MHz, 298 K, CD_2Cl_2, 5.32 ppm): δ = 8.50~8.48 (m, 2H, $H_{30/34}$), 8.05 (dddd, $^4J_{PH}$ = 4.3 Hz, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.4 Hz, 1H, H_6), 8.50~8.48 (m, 2H, $H_{30/34}$), 8.00~7.97 (m, 1H, H_{18}), 7.85 (tt, $^3J_{PH}$ = 7.7 Hz, $^4J_{HH}$ = 1.7 Hz, 1H, H_{32}), 7.60~7.54 (m, 2H, $H_{24/28}$), 7.45~7.41 (m, 3H, $H_{31/33}$ & H_5), 7.39~7.36 (m, 2H, $H_{25/27}$), 7.24 (t, $^3J_{PH}$ = 7.6 Hz, 1H, H_4), 7.19 (br, 5H, H_3 & H_{21} & $H_{19/20}$ & H_{26}), 2.93 (q, $^2J_{PH}$ = 13.0 Hz, $^3J_{HH}$ = 11.9 Hz, 1H, H_7), 2.02~1.90 (m, 2H, H_8 & H_{12}), 1.89~1.79 (m, 1H, H_9), 1.75~1.71 (dbr, 1H, H_{10}), 1.59~1.50 (m, 1H, H_{12}), 1.49 (br, 1H, H_{11}), 1.30~1.22 (m, 2H, H_9 & H_{13}), 0.98 (qd, $^3J_{HH}$ = 12.4 Hz, $^4J_{HH}$ = 3.8 Hz, 1H, H_{10}), 0.83 (d, $^3J_{HH}$ = 6.4 Hz, 3H, H_{16}), 0.73 (d, $^3J_{HH}$ = 6.8 Hz, 3H, $H_{14/15}$), 0.64 (br, 3H, $H_{14/15}$), 0.13 (d, $^3J_{PH}$ = 2.3 Hz, 3H, H_{29}).

^{13}C{^{1}H} NMR (125 MHz, 298 K, CD_2Cl_2, 53.84 ppm): δ = 150.13 ($C_{30/34}$), 148.76 (C_1), 147.02 (d, $^2J_{PC}$ = 10.1 Hz, C_{22}), 141.03 (d, $^3J_{PC}$ = 4.1 Hz, C_{23}), 138.10 (C_{32}), 135.46 ($C_{25/27}$), 133.68 (d, $^2J_{PC}$ = 7.6 Hz, C_{18}), 133.08 ($C_{25/27}$), 130.54 (d, $^4J_{PC}$ = 2.3 Hz, C_5), 130.44 (d, $^4J_{PC}$ = 2.2 Hz, $C_{24/28}$), 130.24 ($C_{19/20}$), 129.00 (d, $^1J_{PC}$ = 20.7 Hz, C_{17}), 128.81 (d, $^1J_{PC}$ = 40.4 Hz, C_2), 128.83 (C_4), 128.78 (C_6), 127.83 (C_{26}), 127.14 (C_3 & C_{21}), 126.43 (d, $^4J_{PC}$ = 7.5 Hz, $C_{24/28}$), 124.98 (d, $^4J_{PC}$ = 2.2 Hz, $C_{31/33}$), 44.18 (C_8), 41.23 (d, $^1J_{PC}$ = 22.4 Hz, C_7), 38.63 (C_{12}), 33.56 (C_{10}), 33.00 (d, $^3J_{PC}$ = 13.1 Hz, C_{11}), 28.49 (d, $^3J_{PC}$ = 4.5 Hz, C_{13}), 25.14 (d, $^3J_{PC}$ = 10.3 Hz, C_9), 22.41 (C_{16}), 21.23 ($C_{14/15}$), 15.99 ($C_{14/15}$), 0.14 (d, $^2J_{PC}$ = 2.5 Hz, C_{26}).
^{31}P{^{1}H} NMR (202 MHz, 298 K, CD_2Cl_2): δ = 25.19.
Elemental analysis: calc. for $C_{34}H_{40}NO_3PPdS$ (680.15 g mol^{-1}): C, 60.04; H, 5.93; N, 2.06. Found: C, 60.13; H, 5.98; N, 1.99.



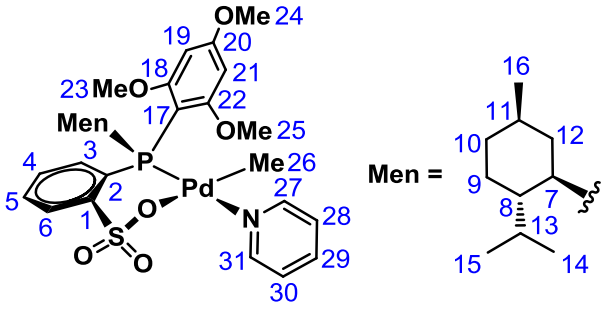
Preparation of complex 3: At −35 ℃ a solution of $PdMe_2$(tmeda) (112 mg, 0.4 mmol, 1.0 equiv) in THF (5 mL) was added to a solution of **L3** (224 mg, 0.4 mmol, 1.0 equiv) in THF (5 mL). The reaction mixture was stirred at −35 ℃ for 1 h and then pyridine (65 mg, 0.8 mmol, 2.0 equiv) was added. The mixture was allowed to warm to room temperature and stirred for 2 h. Volatiles were removed under vacuum and the residue was precipitated from a mixture of THF and *n*-hexane to yield a pale yellow solid. The solid was reprecipitated from a mixture of CH_2Cl_2 and Et_2O, and the solvent of the filtrate was removed in vacuo to afford the product (170 mg, 55%).

^{1}H NMR (500 MHz, 298 K, $CDCl_3$, 7.26 ppm): δ = 8.67~8.65 (m, 2H, $H_{30/34}$), 8.11 (dddd, $^4J_{PH}$ = 4.5 Hz, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 1.4 Hz, 1H, H_6), 7.98~7.94 (m, 1H, H_{18}), 7.81 (tt, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.8 Hz, 1H, H_{32}), 7.60~7.50 (m, 2H, $H_{19/20}$), 7.42~7.36 (m, 4H, H_3 & H_5 & $H_{31/33}$), 7.30~7.22 (m, 2H, H_4 & H_{21}), 7.12~7.06 (m, 1H, H_{26}), 6.76 (td, $^3J_{HH}$ = 8.6 Hz, $^3J_{FH}$ = 1.3 Hz, 1H, $H_{25/27}$), 6.48 (td, $^3J_{HH}$ = 8.5 Hz, $^3J_{FH}$ = 1.2 Hz, 1H, $H_{25/27}$), 2.80~2.74 (m, 1H, H_7), 2.63 (br, 1H, H_{12}), 2.26~2.21 (m, 1H, H_{13}), 1.78~1.72 (m, 1H, H_9), 1.68~1.64 (dbr, 1H, H_{10}), 1.68~1.55 (m, 1H, H_8), 1.51~1.45 (m, 1H, H_{12}), 1.41 (br, 1H, H_{11}), 1.26~1.17 (m, 1H, H_9), 0.91 (d, $^3J_{HH}$ = 6.2 Hz, 3H, H_{16}), 0.83~0.81 (dbr, 1H, H_{10}), 0.77 (d, $^3J_{HH}$ = 6.8 Hz, 3H, $H_{14/15}$), 0.66 (d, $^3J_{HH}$ = 6.6 Hz, 3H, $H_{14/15}$), 0.37 (t, $^3J_{PH}$ = 2.2 Hz, 3H, H_{29}).

^{13}C{^{1}H} NMR (125 MHz, 298 K, $CDCl_3$, 77.16 ppm): δ = 160.49 (dd, $^1J_{FC}$ = 15.0 Hz, $^3J_{FC}$ = 6.9 Hz, $C_{24/28}$), 158.52 (dd, $^1J_{FC}$ = 15.3 Hz, $^3J_{FC}$ = 6.6 Hz, $C_{24/28}$), 150.41 ($C_{30/34}$), 149.36 (d, $^2J_{PC}$ = 13.6 Hz, C_1), 138.03 (C_{32}), 135.26 (d, $^4J_{PC}$ = 3.2 Hz, C_5), 133.85 (d, $^3J_{PC}$ = 7.3 Hz, C_{21}), 133.73 (d, $^2J_{PC}$ = 8.8 Hz, C_{18}), 133.45 (d, $^1J_{PC}$ = 40.6 Hz, C_{17}), 133.14 (d, $^2J_{PC}$ = 6.8 Hz, C_{22}), 130.86 (d, $^2J_{PC}$ = 2.3 Hz, C_3), 130.12 (C_{26}), 130.02 (C_{20}), 128.80 (d, $^3J_{PC}$ = 6.2 Hz, C_6), 127.49 (d, $^3J_{PC}$ = 8.1 Hz, C_4), 127.49 (d, $^3J_{PC}$ = 8.1 Hz, C_{19}), 125.95 (d, $^1J_{PC}$ = 123.3 Hz, C_2), 125.13 ($C_{31/33}$), 117.61 (td, $^2J_{FC}$ = 20.5 Hz, $^3J_{PC}$ = 4.1 Hz, C_{23}), 111.90 (dd, $^2J_{FC}$ = 22.0 Hz, $^4J_{FC}$ = 3.3 Hz, $C_{25/27}$), 111.48 (dd, $^2J_{FC}$ = 22.1 Hz, $^4J_{FC}$ = 3.3 Hz, $C_{25/27}$), 44.39 (C_8), 40.69 (d, $^1J_{PC}$ = 24.0 Hz, C_7), 39.98 (d, $^2J_{PC}$ = 8.1 Hz, C_{12}), 33.75 (d, $^3J_{PC}$ = 11.0 Hz, C_{11}), 33.68 (d, $^4J_{PC}$ = 3.3 Hz, C_{10}), 28.67 (d, $^3J_{PC}$ = 3.1 Hz, C_{13}), 25.46 (d, $^3J_{PC}$ = 9.7 Hz, C_9), 22.73 (C_{16}), 21.55 ($C_{14/15}$), 17.10 ($C_{14/15}$), −0.95 (t, $^2J_{PC}$ = 4.1 Hz, C_{29}).
^{31}P{^{1}H} NMR (202 MHz, 298 K, $CDCl_3$): δ = 29.20.

^{19}F NMR (470 MHz, 298 K, $CDCl_3$): δ = −105.73, −105.91.

Elemental analysis: calc. for $C_{34}H_{38}F_2NO_3PPdS$ (716.13 g mol^{-1}): C, 57.02; H, 5.35; N, 1.96. Found: C, 56.84; H, 5.48; N, 2.03.



Preparation of complex 4: At −35 ℃ a solution of $PdMe_2$(tmeda) (113 mg, 0.4 mmol, 1.0 equiv) in THF (5 mL) was added to a solution of **L4** (203 mg, 0.4 mmol, 1.0 equiv) in THF (5 mL). The reaction mixture was stirred at −35 ℃ for 1 h and then pyridine (65 mg, 0.8 mmol, 2.0 equiv) was added. The mixture was allowed to warm to room temperature and stirred for 2 h. Volatiles were removed under vacuum to yield a pale yellow solid, which was precipitated from a mixture of THF and *n*-hexane to afford the product (216 mg, 75%).

^{1}H NMR (500 MHz, 298 K, $CDCl_3$, 7.26 ppm): δ = 8.96~8.94 (m, 2H, $H_{27/31}$), 8.18~8.15 (m, 1H, H_6), 7.87~7.79 (m, 2H, H_3 & H_{29}), 7.46 (t, $^3J_{PH}$ = 6.6 Hz, 2H, $H_{28/30}$), 7.34 (t, $^3J_{PH}$ = 7.6 Hz, 1H, H_5), 7.22 (t, $^3J_{PH}$ = 7.5 Hz, 1H, H_4), 6.09 (dbr, 2H, $H_{19/21}$), 3.92 (s, 6H, $H_{23/25}$), 3.80 (s, 3H, H_{24}), 3.11~3.04 (m, 1H, H_7), 2.23~2.16 (m, 1H, H_8), 2.08~2.05 (m, 1H, H_{13}), 1.85~1.78 (dbr, 2H, H_9 & H_{10}), 1.77~1.73 (dbr, 1H, H_{12}), 1.49 (br, 1H, H_{11}), 1.49 (qd, $^3J_{PH}$ = 11.8 Hz, $^3J_{HH}$ = 5.7 Hz, 1H, H_{12}), 1.19 (qd, $^3J_{HH}$ = 12.4 Hz, $^4J_{PH}$ = 3.0 Hz, 1H, H_9), 1.06 (qd, $^3J_{HH}$ = 11.9 Hz, $^4J_{HH}$ = 3.2 Hz, 1H, H_{10}), 0.89 (d, $^3J_{HH}$ = 6.5 Hz, 3H, H_{16}), 0.77 (d, $^3J_{HH}$ = 6.7 Hz, 3H, $H_{14/15}$), 0.22 (d, $^3J_{PH}$ = 2.0 Hz, 3H, H_{26}), 0.12 (d, $^3J_{HH}$ = 6.7 Hz, 3H, $H_{14/15}$).

^{13}C{^{1}H} NMR (125 MHz, 298 K, $CDCl_3$, 77.16 ppm): δ = 164.08 (C_{20}), 162.61 (dbr, $C_{18/22}$), 150.66 ($C_{27/31}$), 147.34 (d, $^2J_{PC}$ = 13.3 Hz, C_1), 137.84 (C_{29}), 134.05 (C_3), 132.95 (d, $^1J_{PC}$ = 41.4 Hz, C_2), 130.12 (d, $^4J_{PC}$ = 2.2 Hz, C_5), 129.38 (d, $^3J_{PC}$ = 6.1 Hz, C_4), 128.90 (d, $^3J_{PC}$ = 7.5 Hz, C_6), 125.21 (d, $^4J_{PC}$ = 2.6 Hz, $C_{28/30}$), 99.62 (d, $^1J_{PC}$ = 54.3 Hz, C_{17}), 91.17 (d, $^3J_{PC}$ = 2.6 Hz, $C_{19/21}$), 55.49 ($C_{23/25}$), 55.44 (C_{24}), 49.00 (d, $^2J_{PC}$ = 6.0 Hz, C_8), 43.97 (d, $^1J_{PC}$ = 24.3 Hz, C_7), 40.63 (d, $^2J_{PC}$ = 3.9 Hz, C_{12}), 35.33 (d, $^4J_{PC}$ = 1.8 Hz, C_{10}), 34.07 (d, $^3J_{PC}$ = 13.5 Hz, C_{11}), 27.87 (d, $^3J_{PC}$ = 4.3 Hz, C_{13}), 25.63 (d, $^3J_{PC}$ = 13.8 Hz, C_9), 23.00 ($C_{14/15}$), 21.84 (C_{16}), 14.97 ($C_{14/15}$), −3.22 (d, $^2J_{PC}$ = 2.5 Hz, C_{26}).
^{31}P{^{1}H} NMR (162 MHz, 298 K, $CDCl_3$): δ = 24.30.
Elemental analysis: calc. for $C_{31}H_{42}NO_6PPdS$ (694.13 g mol^{-1}): C, 53.64; H, 6.10; N, 2.02. Found: C, 54.00; H, 6.01; N, 2.05.

A general procedure for the homopolymerization of ethylene.

In a typical experiment, a 300 mL stainless pressure reactor connected with a high pressure gas line was firstly dried at 90 ℃ under vacuum for at least 1 h. The reactor was then adjusted to the desired polymerization temperature. 98 mL of toluene was added to the reactor under N_2 atmosphere, then the desired amount of Pd catalyst in 2 mL of CH_2Cl_2 was injected into the polymerization system via syringe. With a rapid stirring, the reactor was pressurized and maintained at 20 atm of ethylene. After 0.5 h, the pressure reactor was vented and the polymer was precipitated in ethanol, filtered and dried at 50 ℃ for at least 24 h under vacuum.

A general procedure for the copolymerization of polar monomer with ethylene.

In a typical experiment, a 300 mL stainless pressure reactor connected with a high pressure gas line was firstly dried at 90 ℃ under vacuum for at least 1 h. The reactor was then adjusted to the desired polymerization temperature. 98 mL of toluene with 30 mg of BHT was added to the reactor under N_2 atmosphere, then the desired polar monomer and the desired amount of Pd catalyst in 2 mL of CH_2Cl_2 was injected into the polymerization system via syringe subsequently. With a rapid stirring, the reactor was pressurized and maintained at the desired pressure of ethylene. After 1 h, the pressure reactor was vented and the copolymer was precipitated in ethanol, filtered and dried at 50 ℃ for at least 24 h under vacuum.

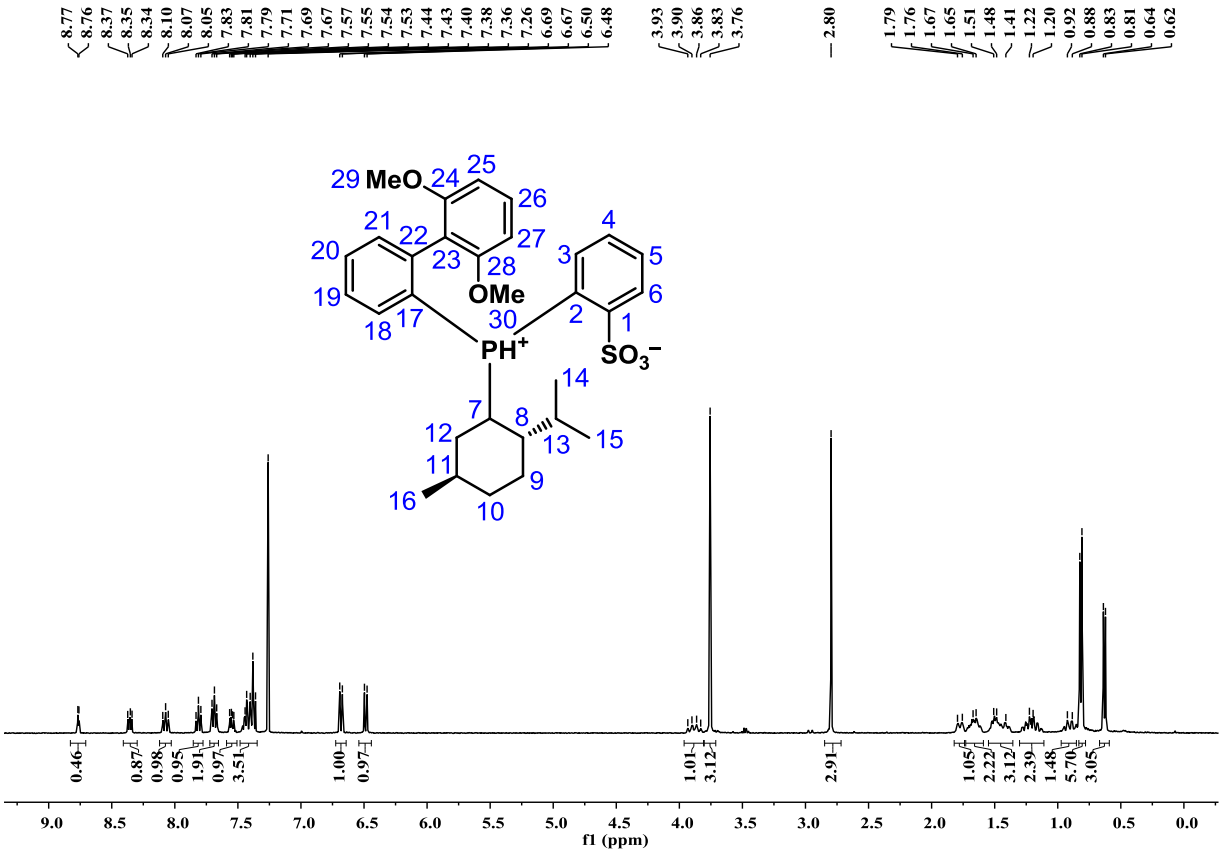


Figure S1. ^{1}H NMR spectrum (500 MHz, 298 K, $CDCl_3$) of **L1**.

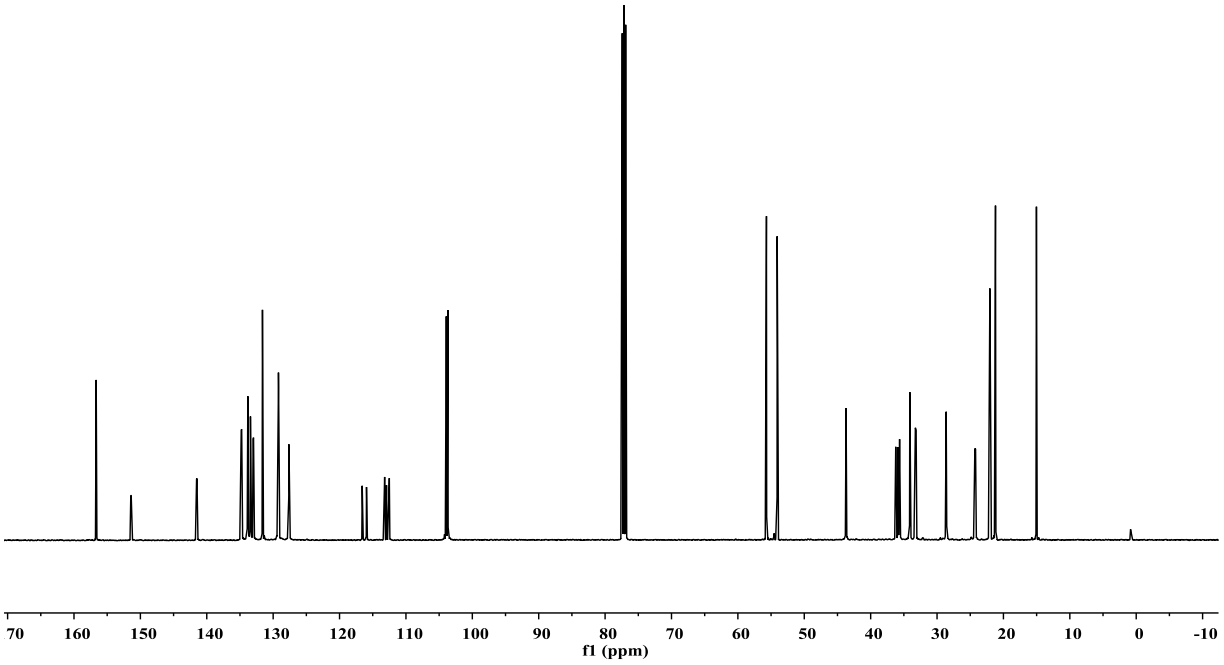


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, 298 K, $CDCl_3$) of **L1**.

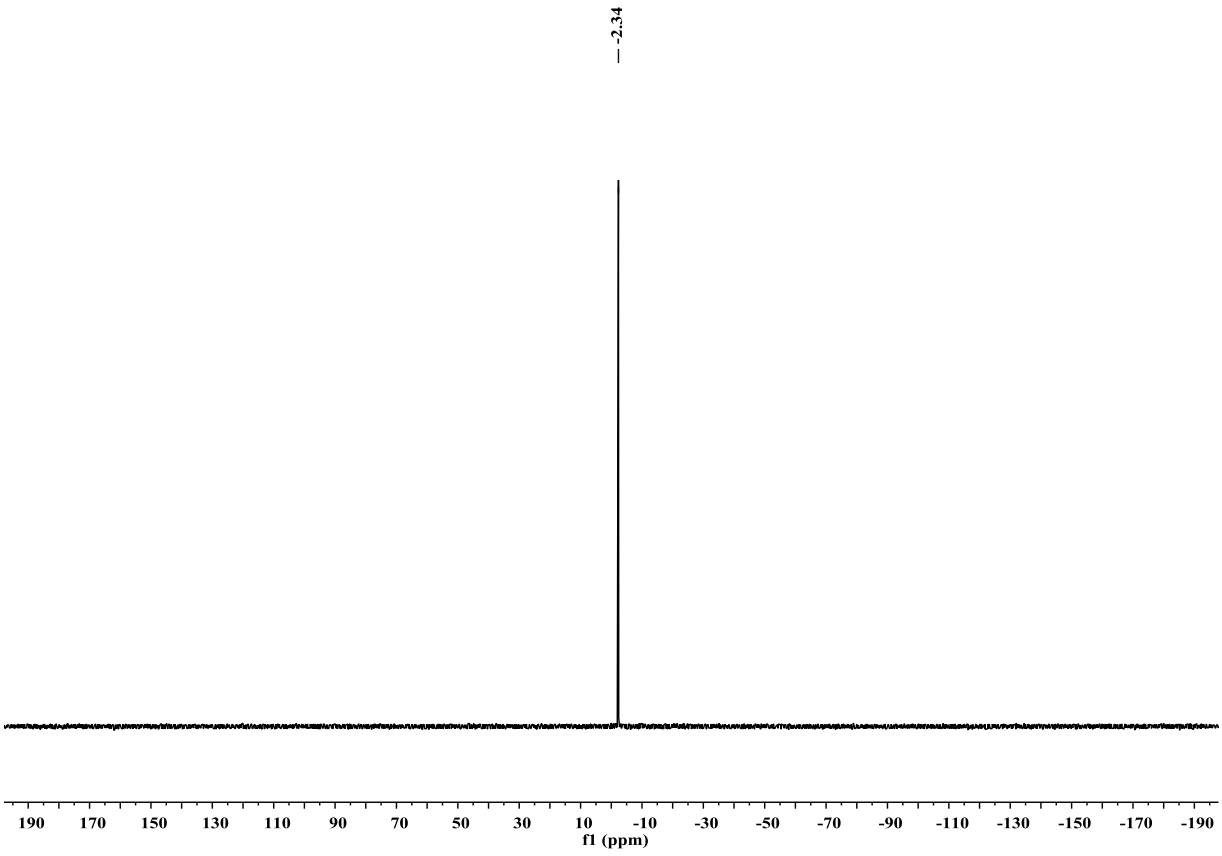


Figure S3. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 298 K, $CDCl_3$) of **L1**.

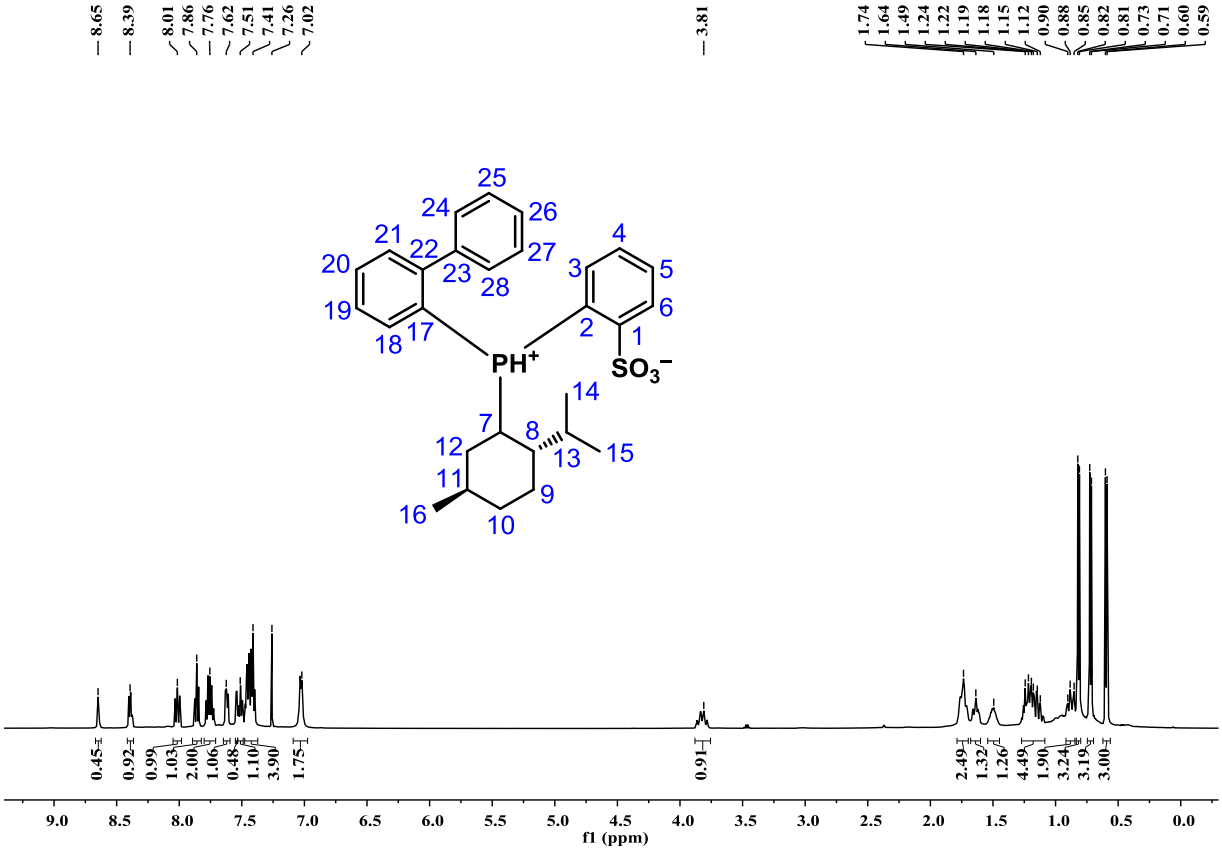


Figure S4. ^{1}H NMR spectrum (500 MHz, 298 K, $CDCl_3$) of **L2**.

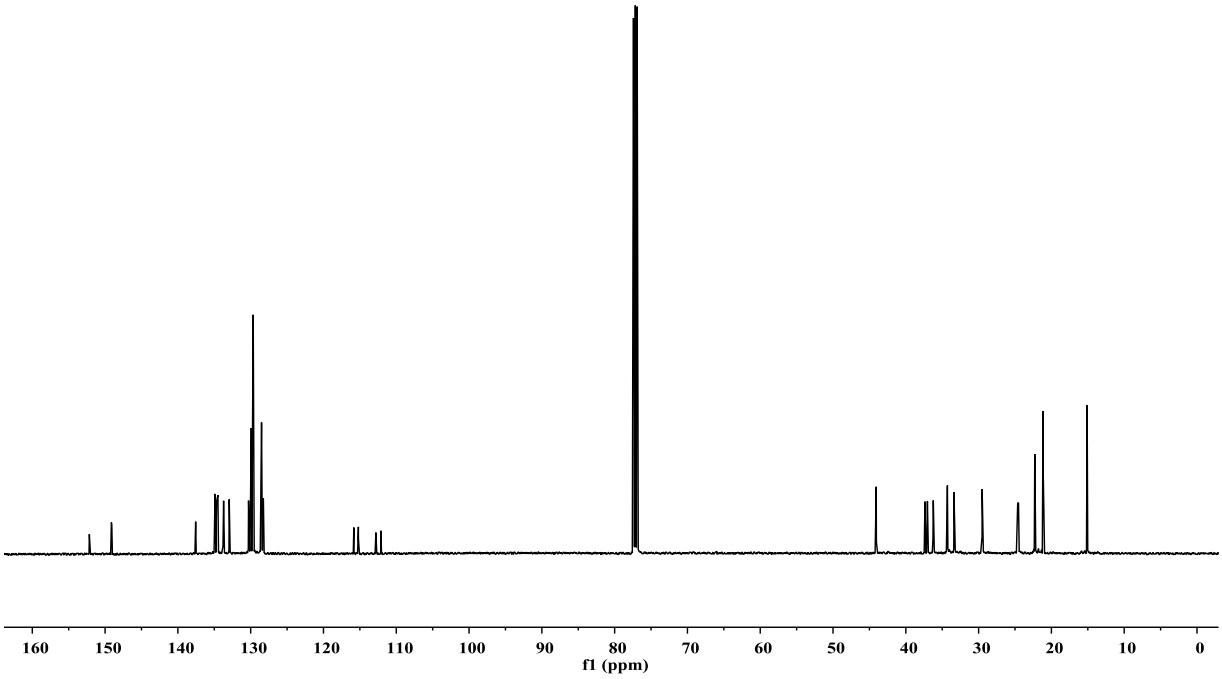


Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, 298 K, $CDCl_3$) of **L2**.

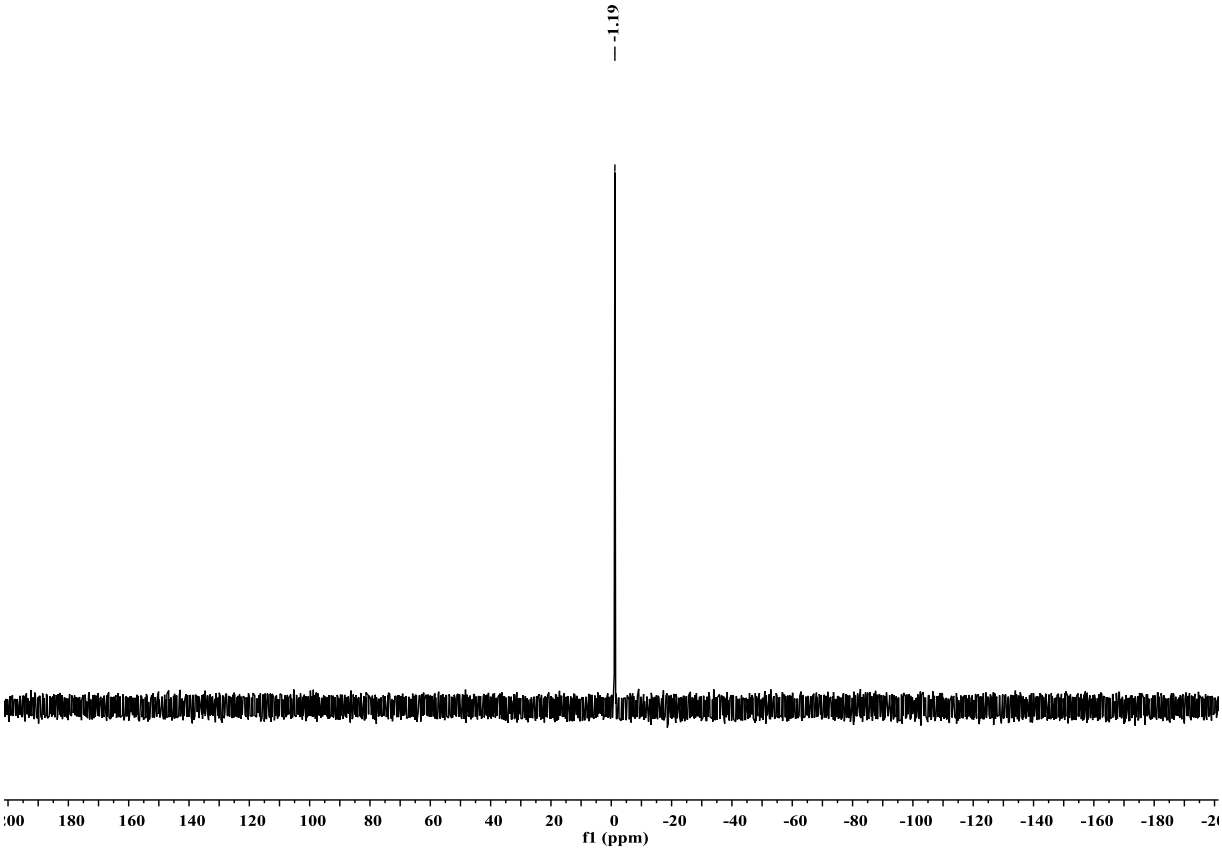


Figure S6. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 298 K, $CDCl_3$) of **L2**.

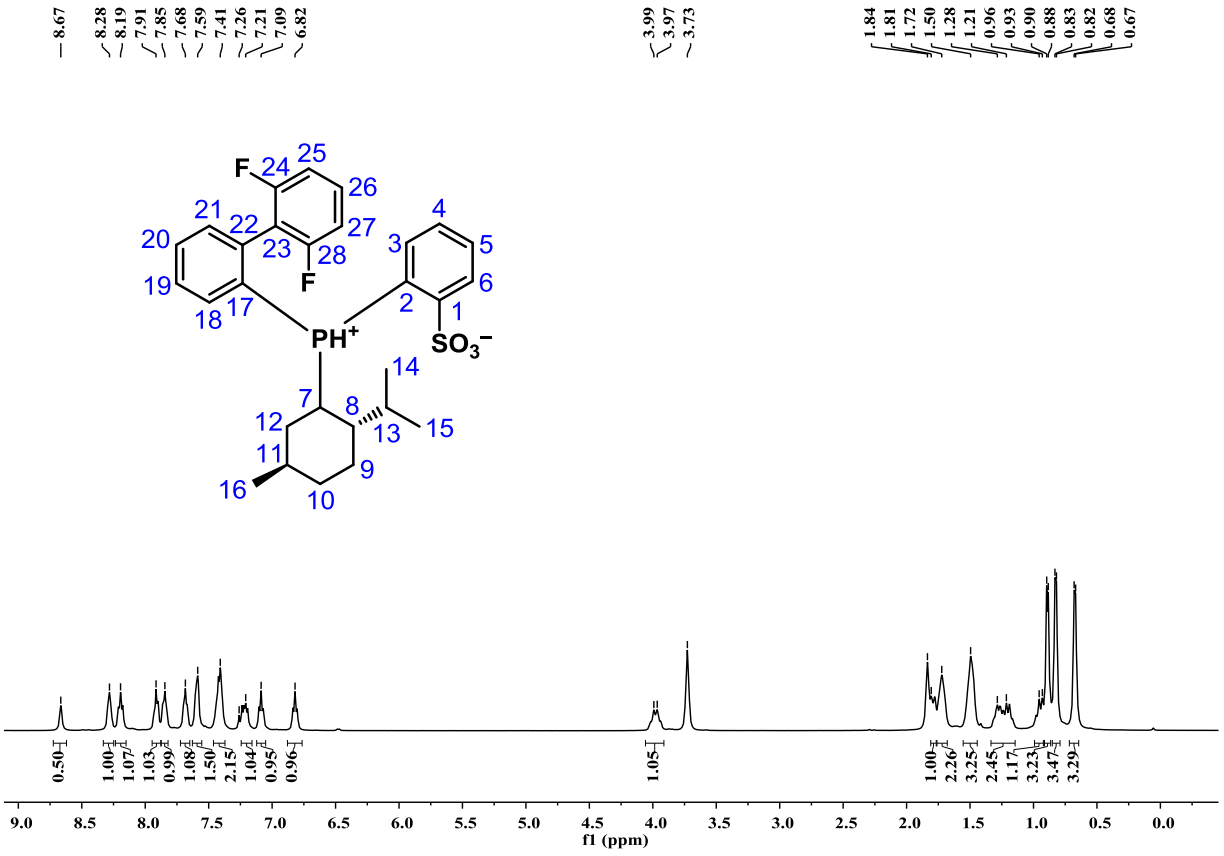


Figure S7. ^{1}H NMR spectrum (500 MHz, 298 K, $CDCl_3$) of **L3**.

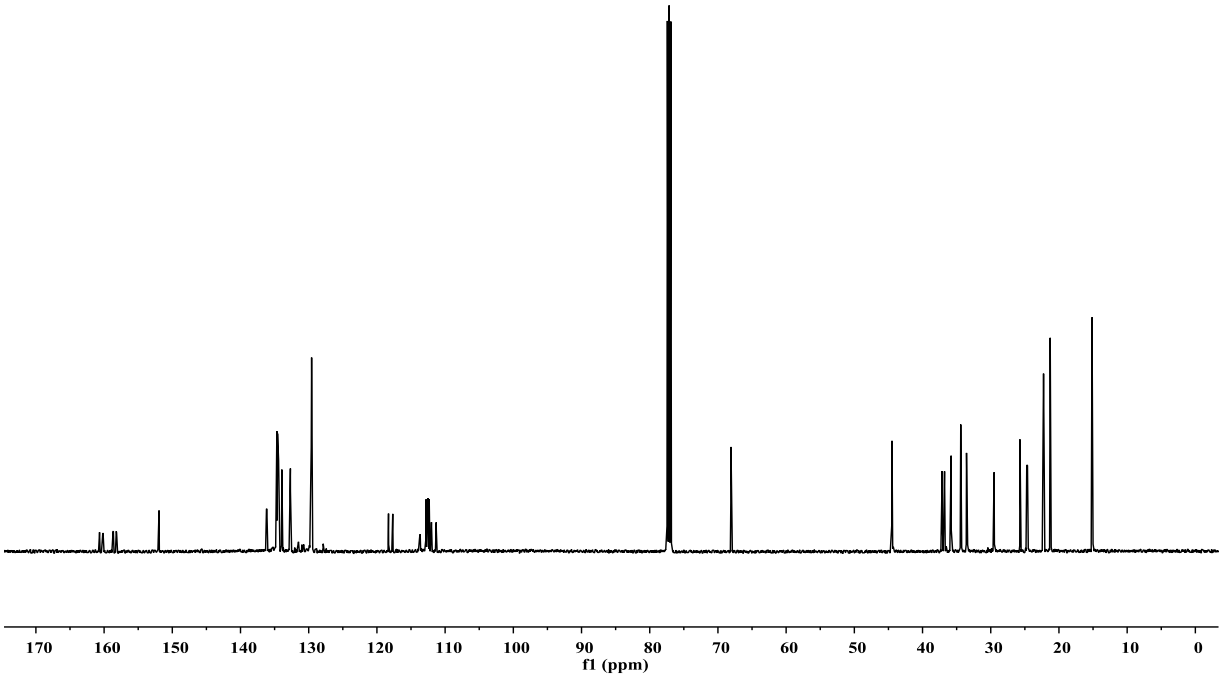


Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, 298 K, $CDCl_3$) of **L3**.

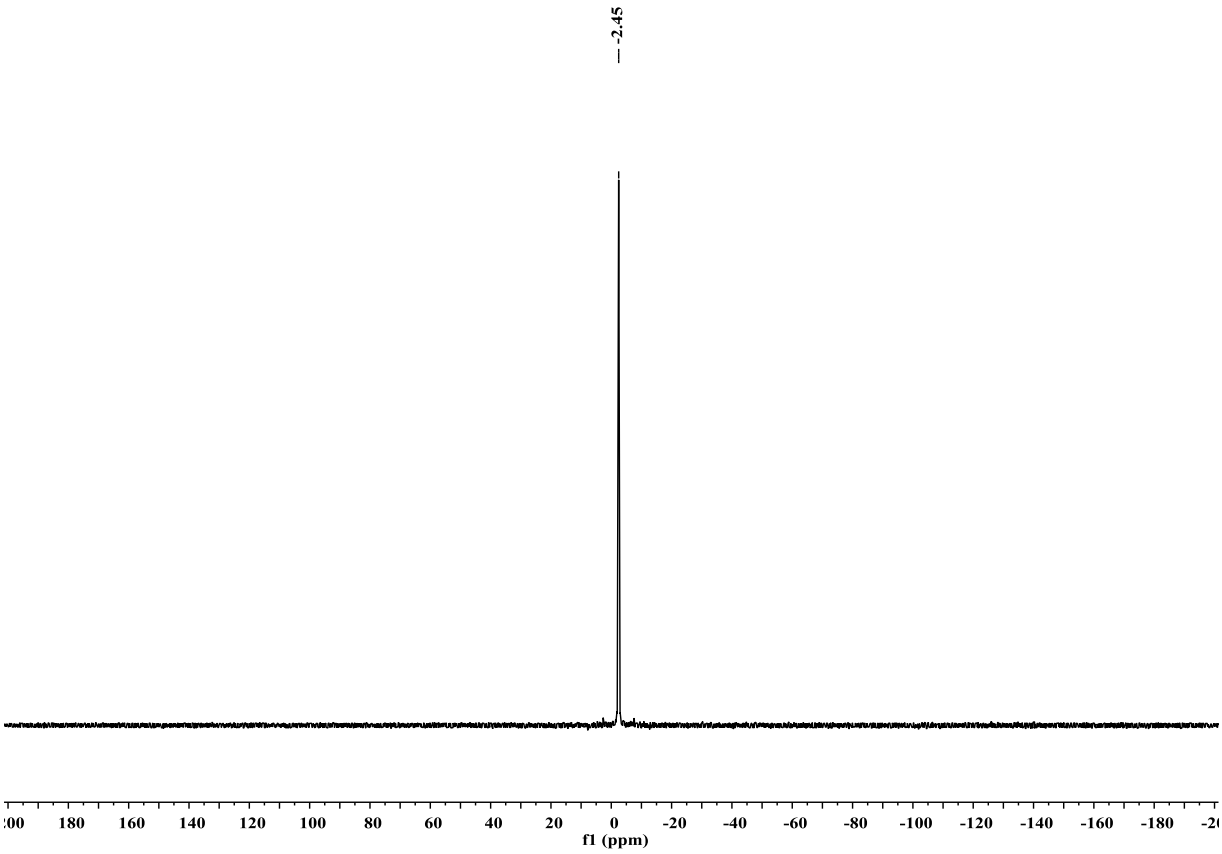


Figure S9. $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, 298 K, $CDCl_3$) of **L3**.

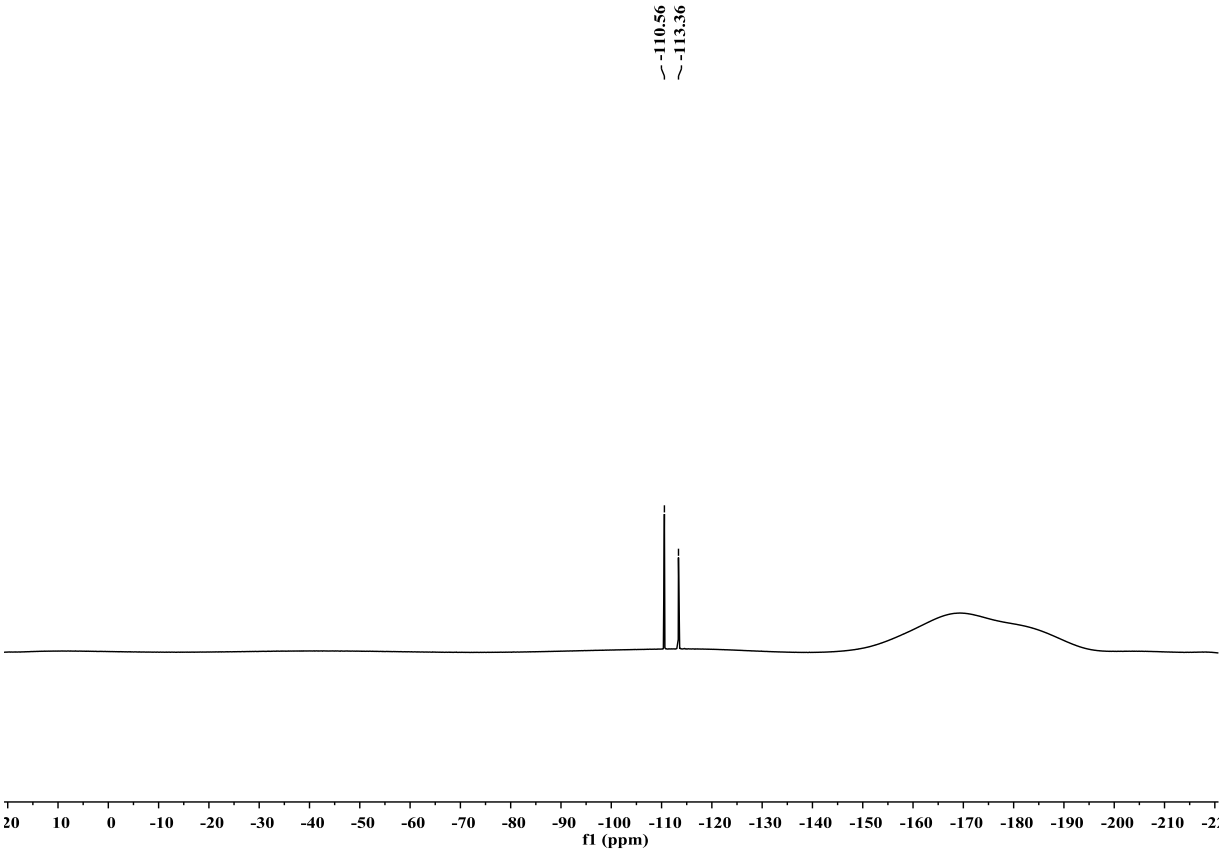


Figure S10. ^{19}F NMR spectrum (470 MHz, 298 K, $CDCl_3$) of **L3**.

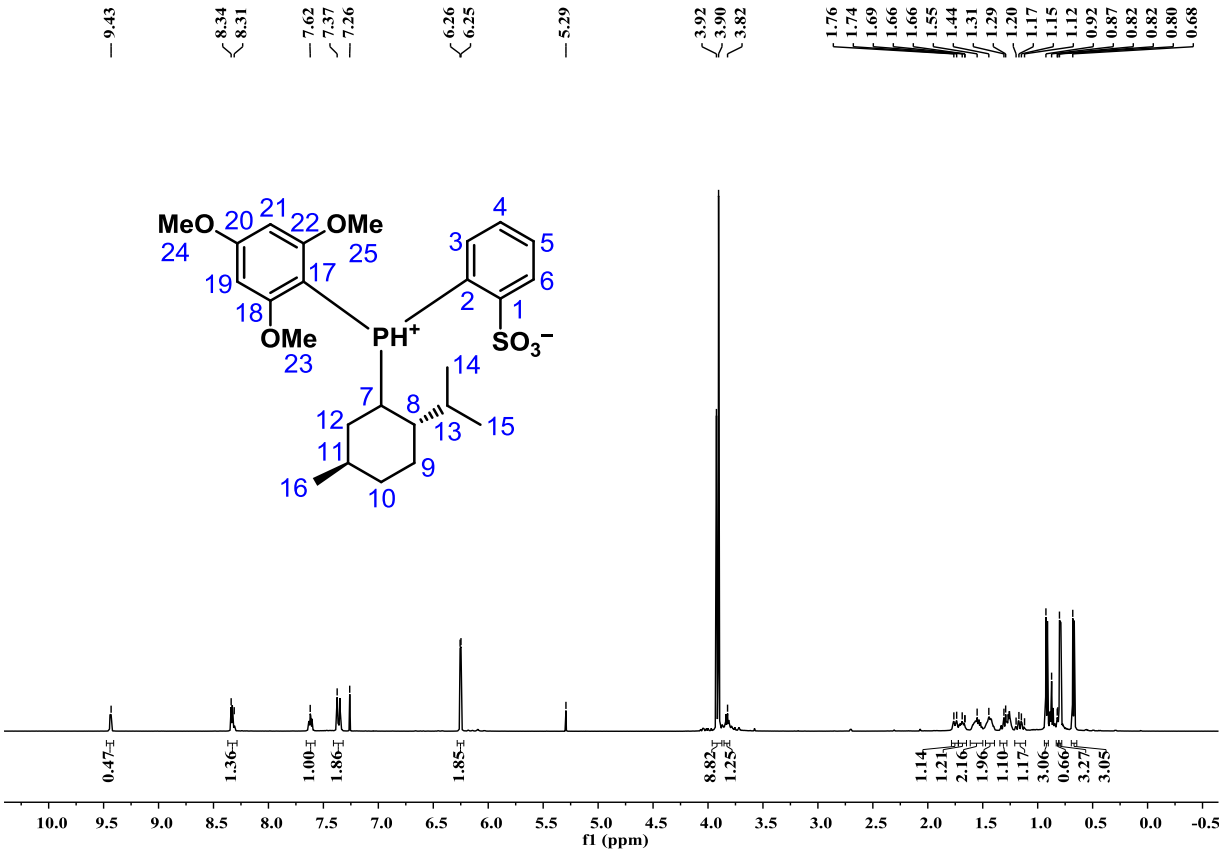


Figure S11. ^{1}H NMR spectrum (500 MHz, 298 K, $CDCl_3$) of **L4**.

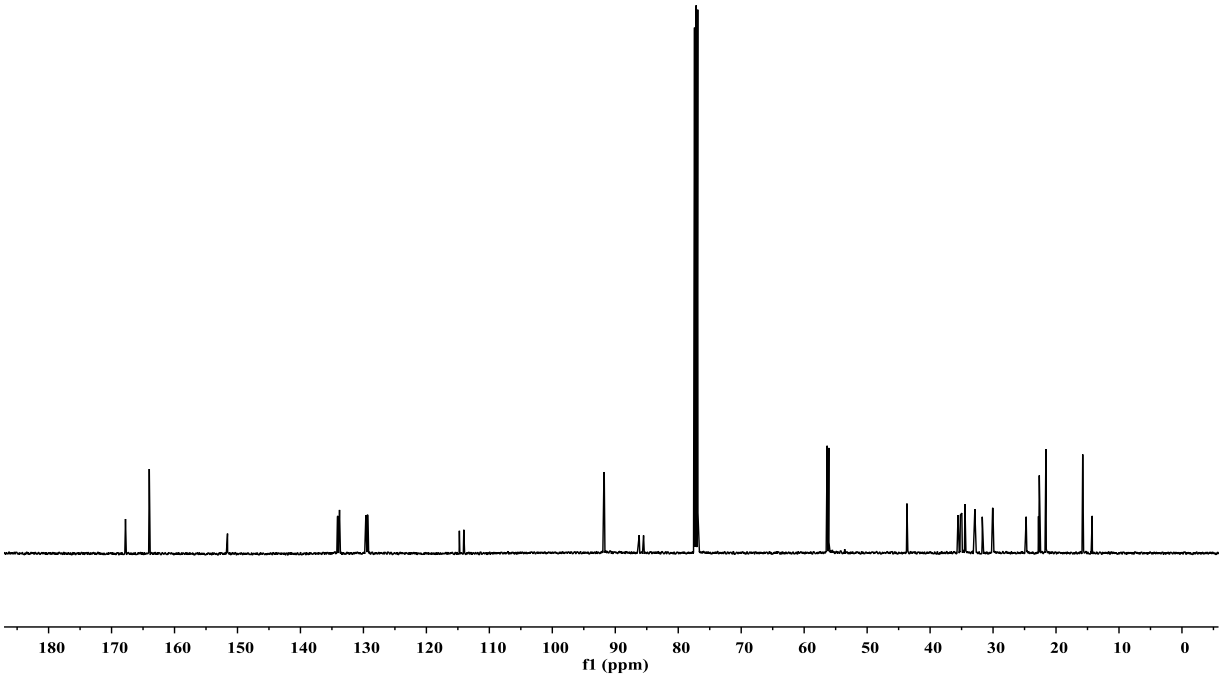


Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, 298 K, $CDCl_3$) of **L4**.

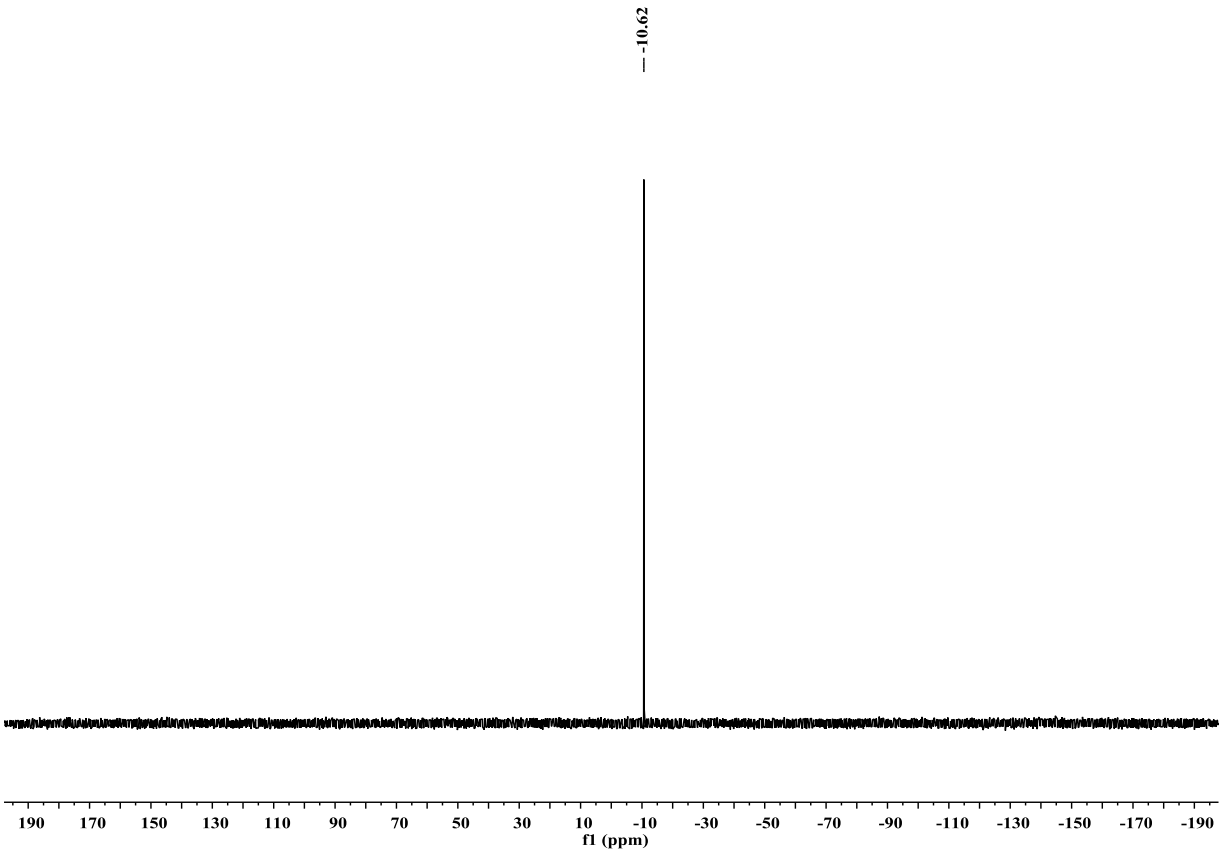


Figure S13. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 298 K, $CDCl_3$) of L4.

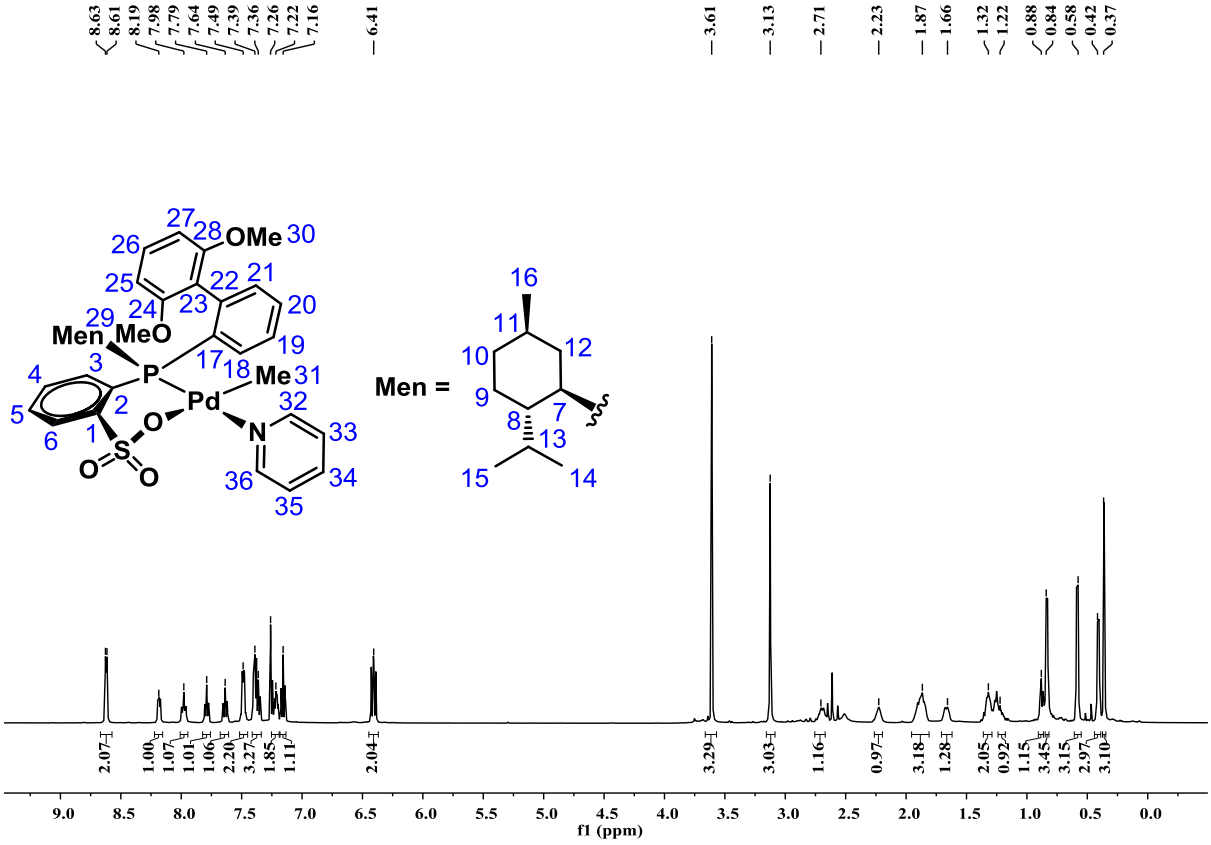


Figure S14. ^{1}H NMR spectrum (500 MHz, 298 K, $CDCl_3$) of complex **1**.

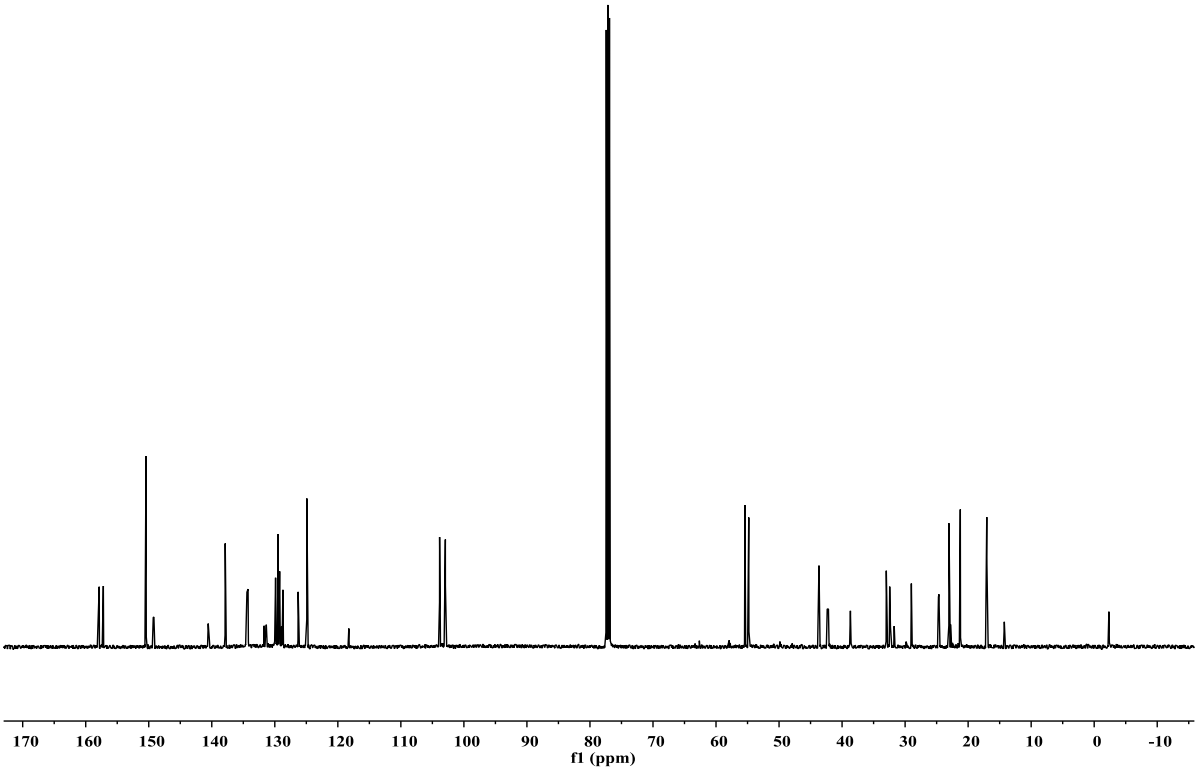


Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, 298 K, $CDCl_3$) of complex **1.**

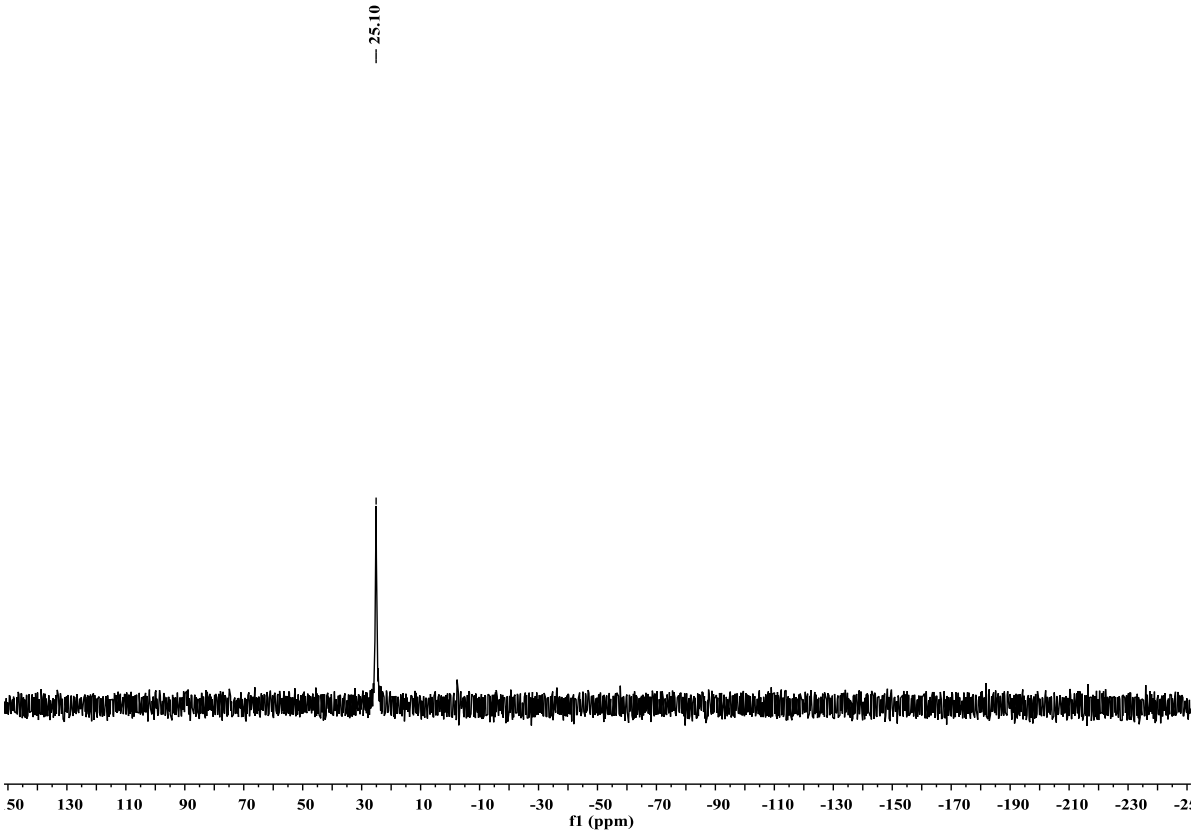


Figure S16. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 298 K, $CDCl_3$) of complex **1**.

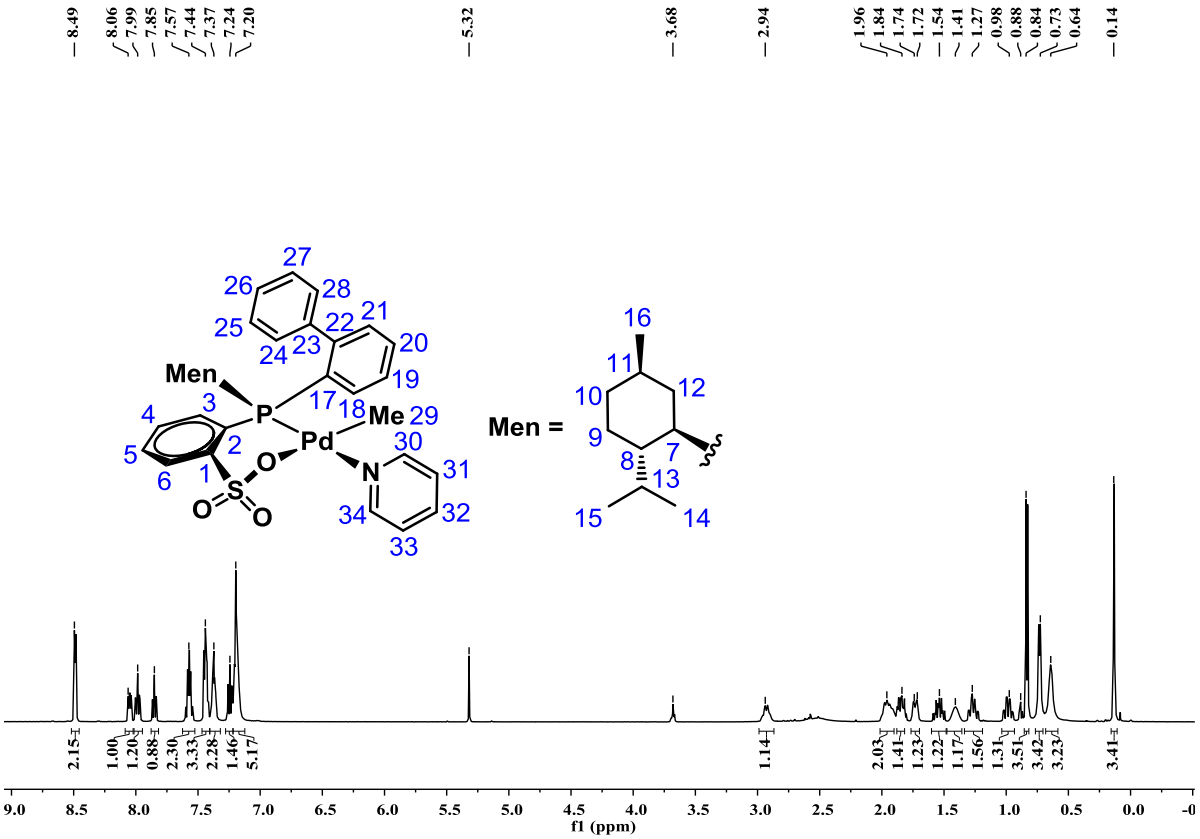


Figure S17. ^{1}H NMR spectrum (500 MHz, 298 K, CD_2Cl_2) of complex **2**.

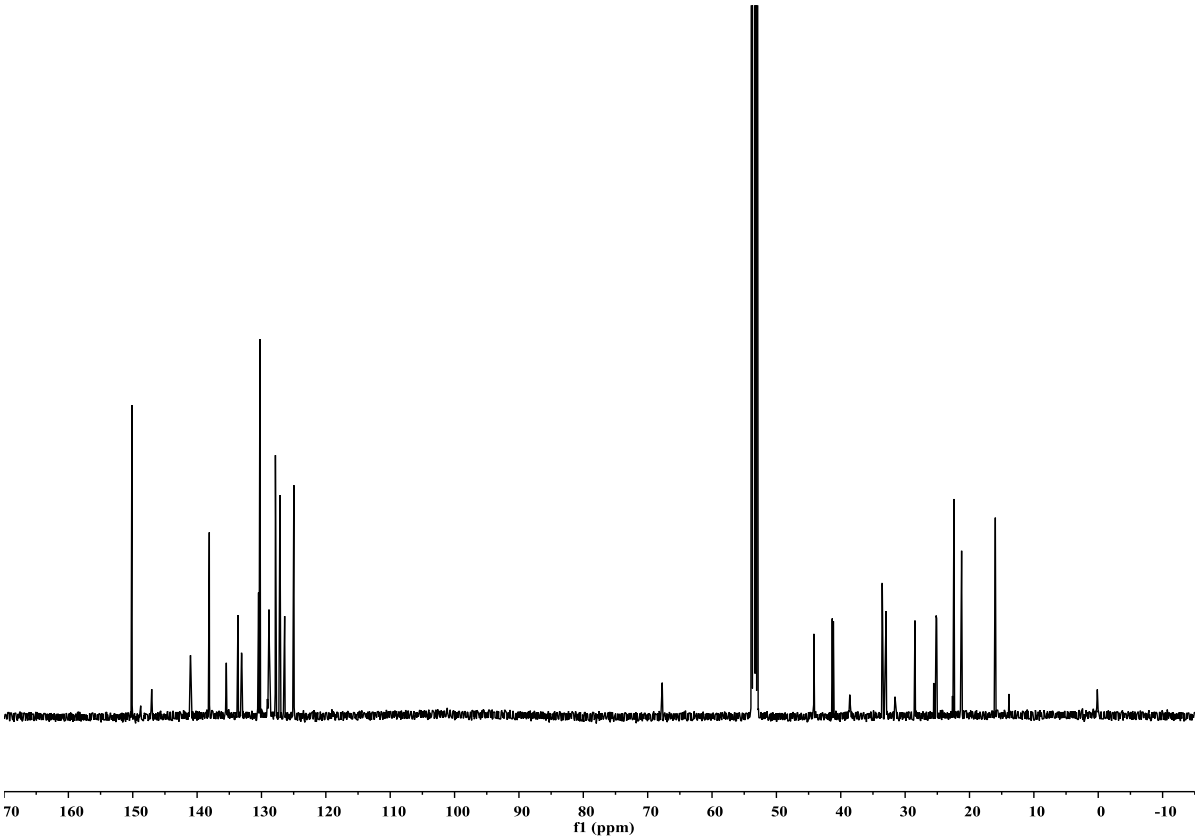


Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, 298 K, CD_2Cl_2) of complex **2**.

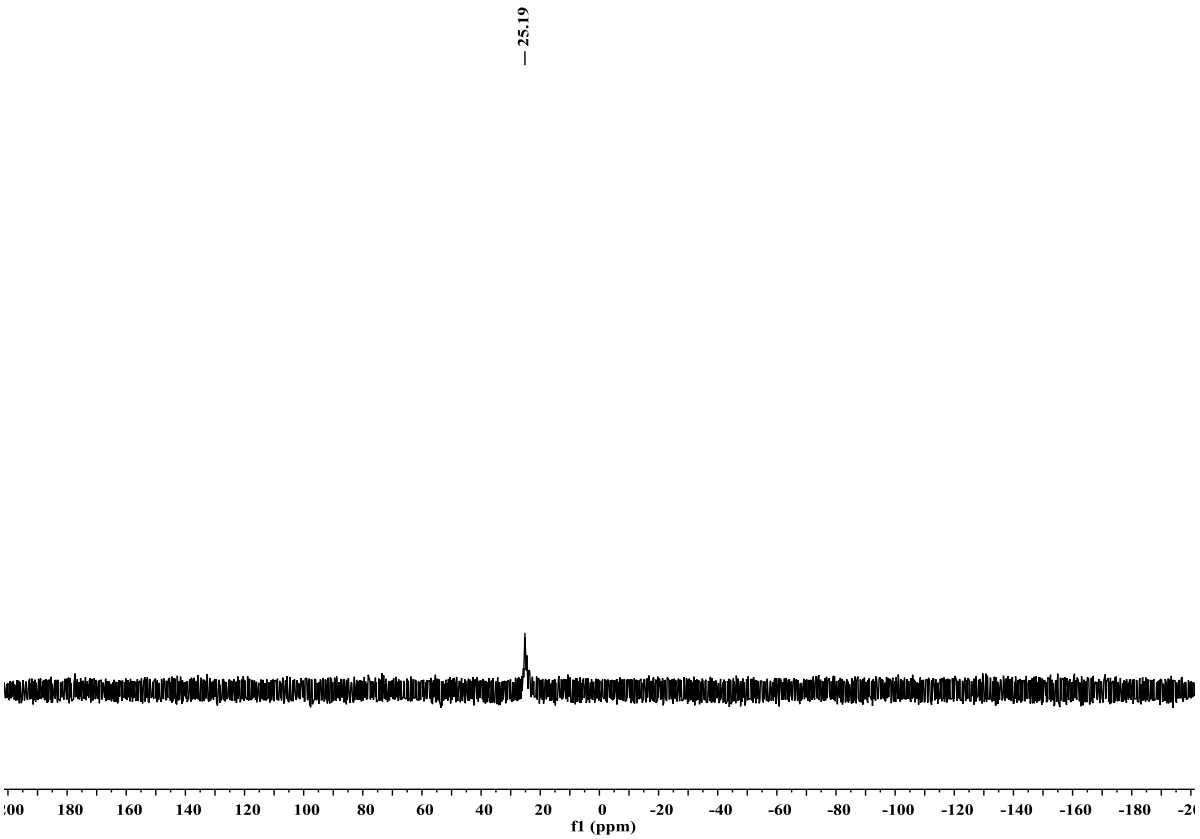


Figure S19. $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, 298 K, CD_2Cl_2) of complex **2**.

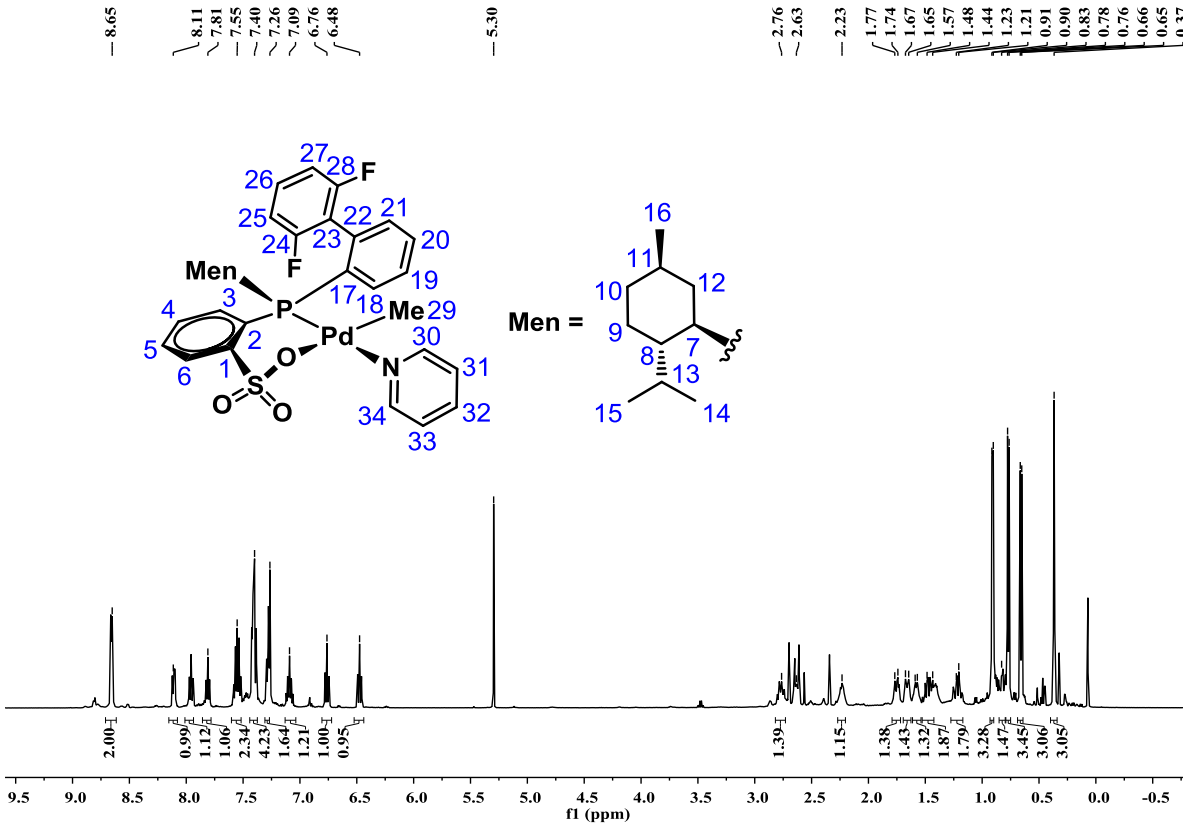


Figure S20. ^{1}H NMR spectrum (500 MHz, 298 K, $CDCl_3$) of complex **3**.

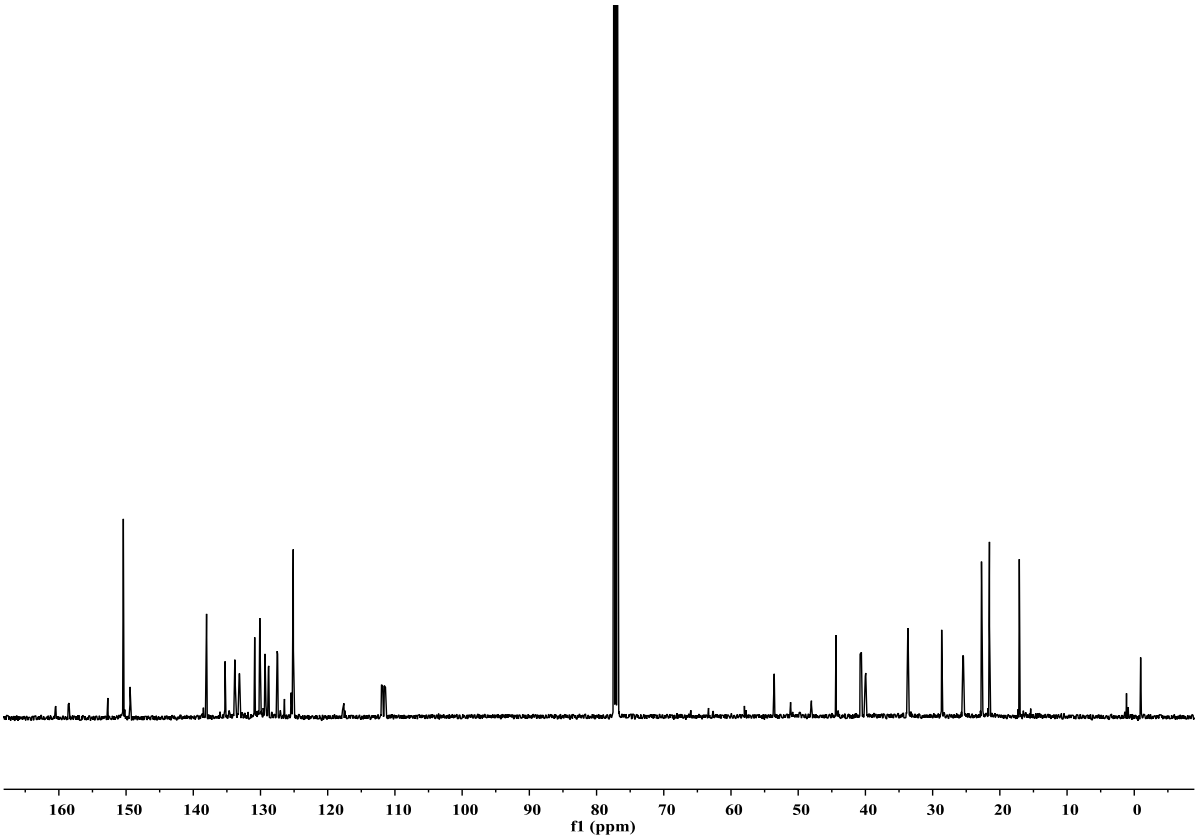


Figure S21. $^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, 298 K, $CDCl_3$) of complex **3**.

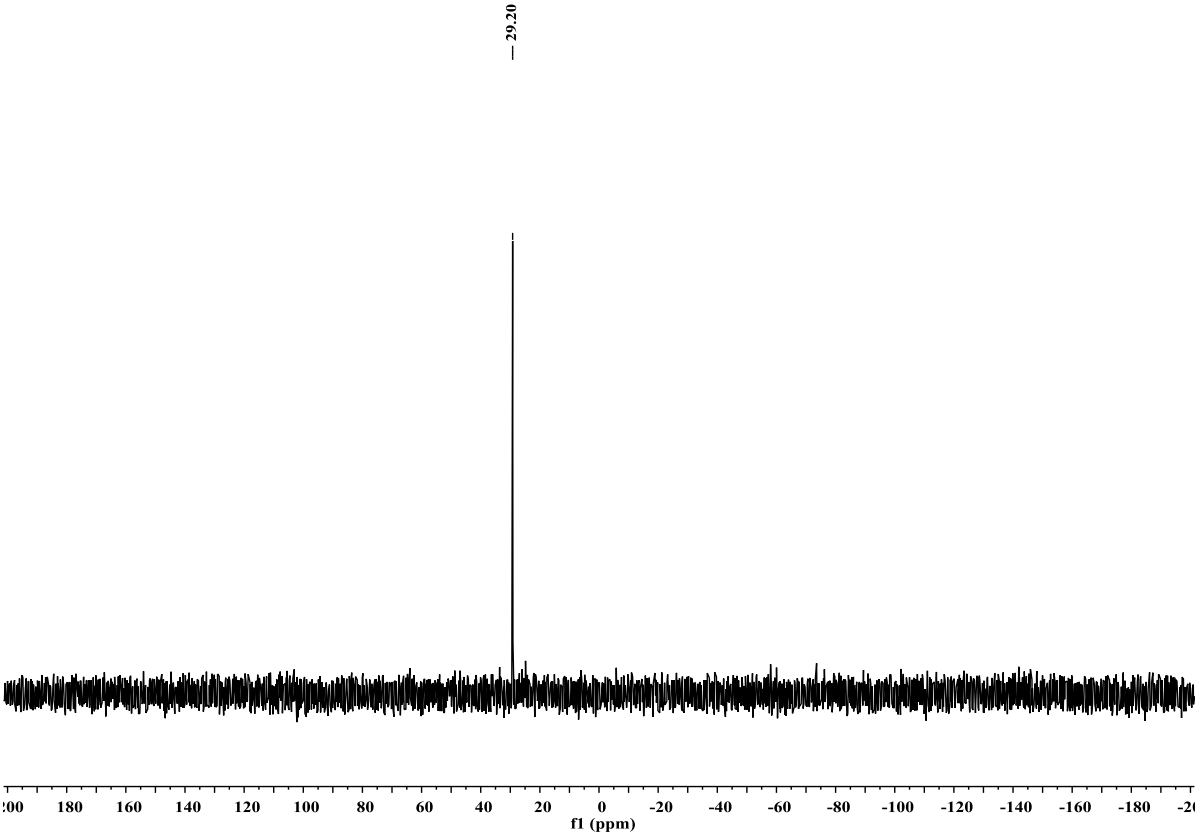


Figure S22. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 298 K, $CDCl_3$) of complex **3**.

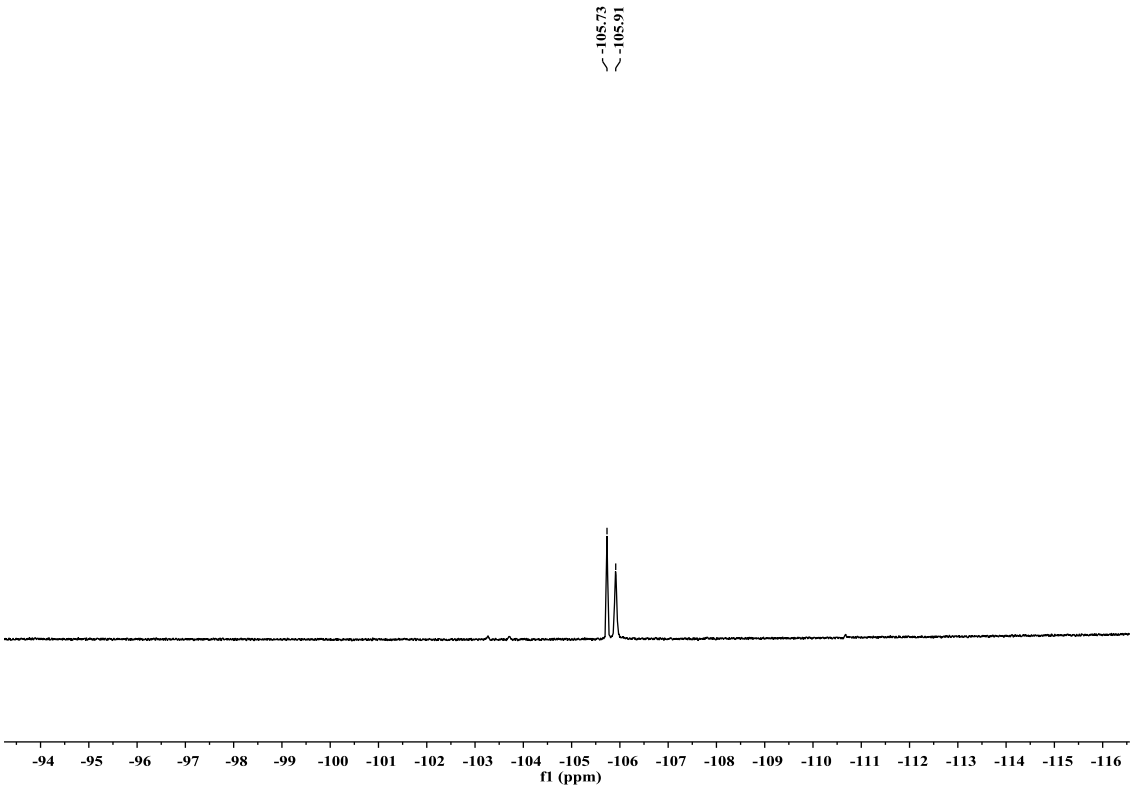


Figure S23. ^{19}F NMR spectrum (376 MHz, 298 K, $CDCl_3$) of complex **3**.

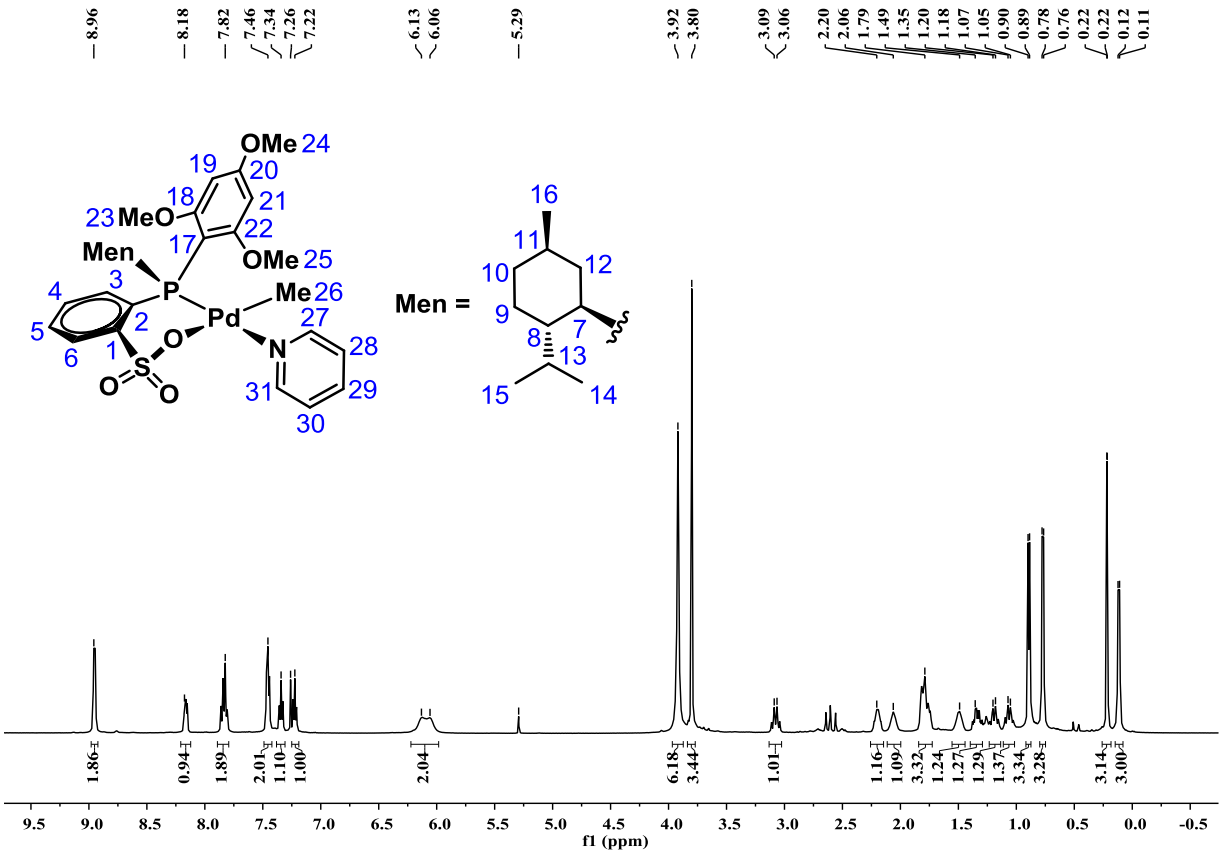


Figure S24. ^{1}H NMR spectrum (500 MHz, 298 K, $CDCl_3$) of complex **4**.

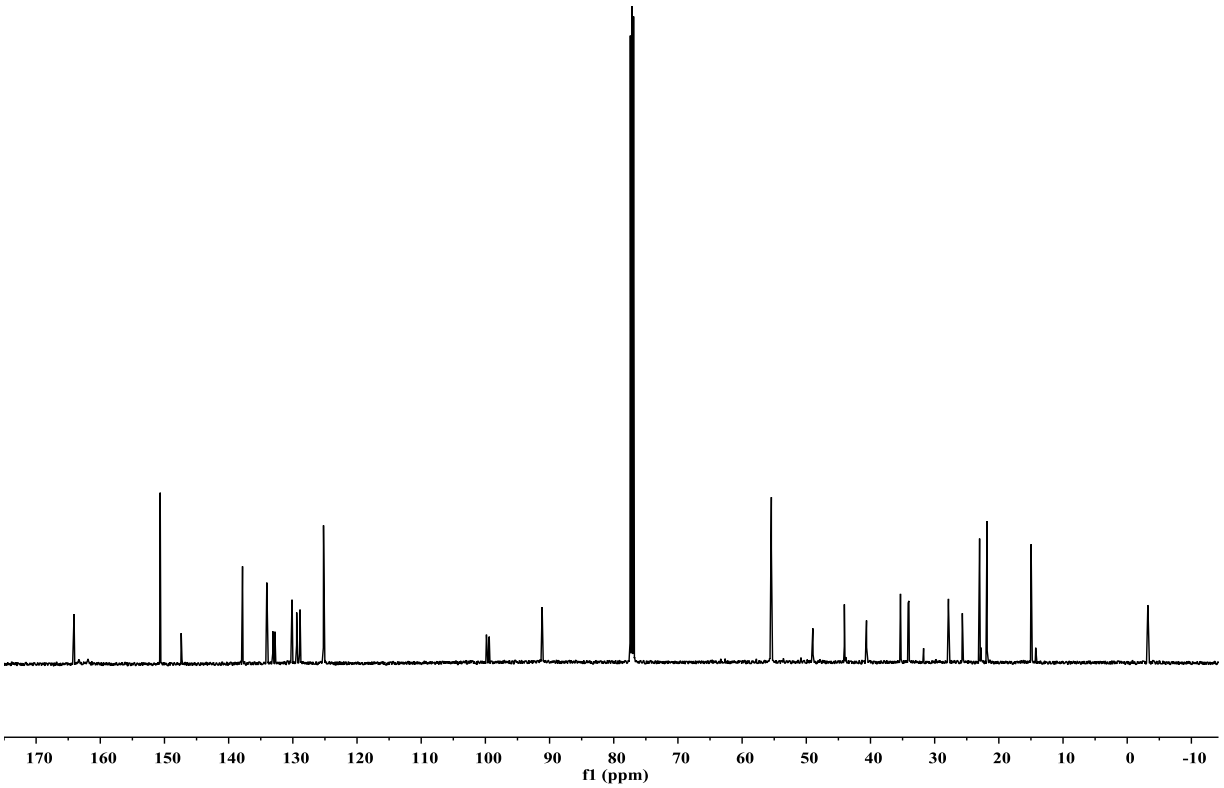


Figure S25. $^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, 298 K, $CDCl_3$) of complex **4**.

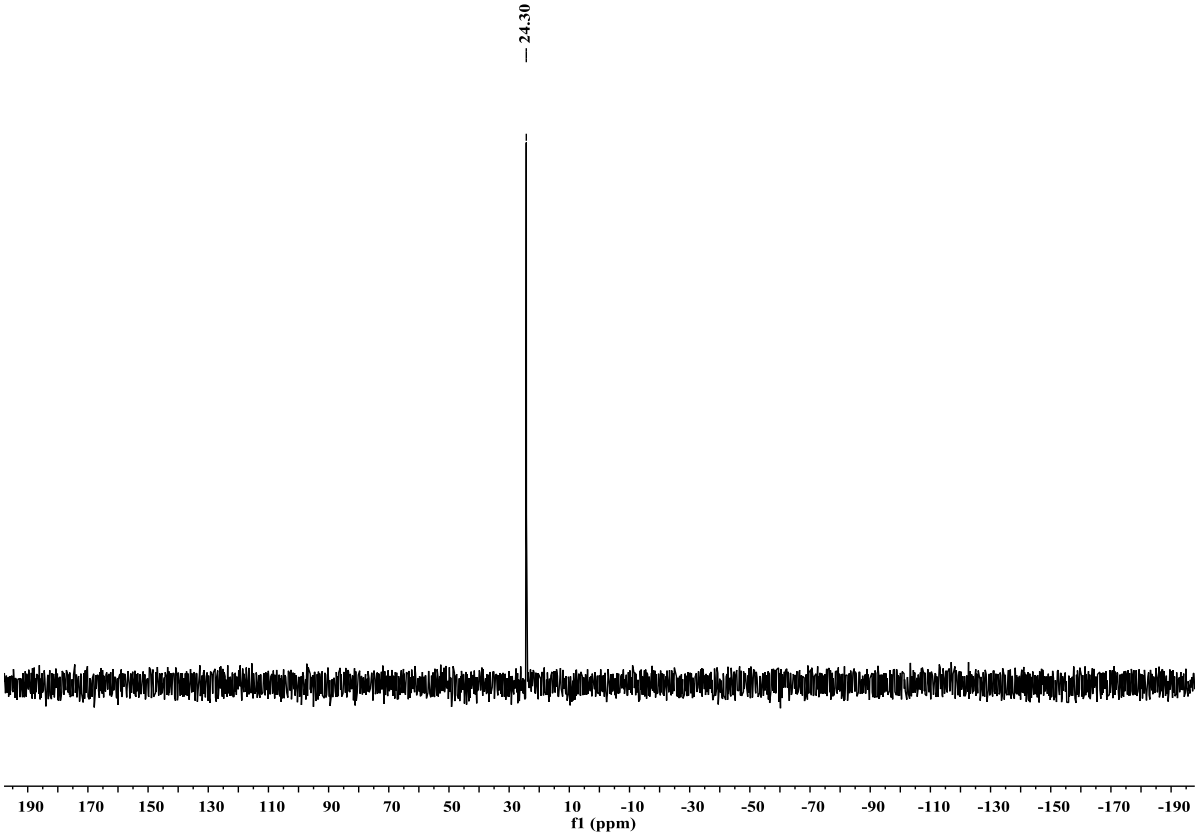


Figure S26. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 298 K, $CDCl_3$) of complex **4**.

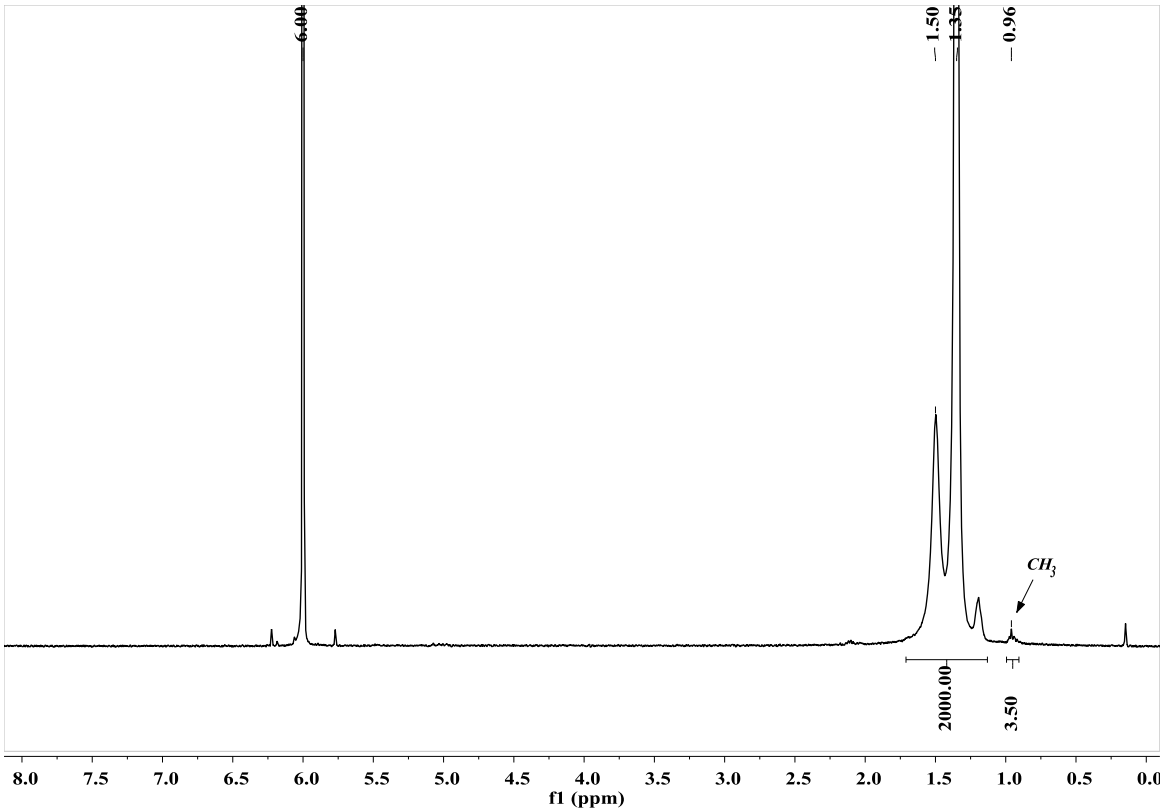


Figure S27. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 100 ℃) of the polymer from table 1, entry 1.

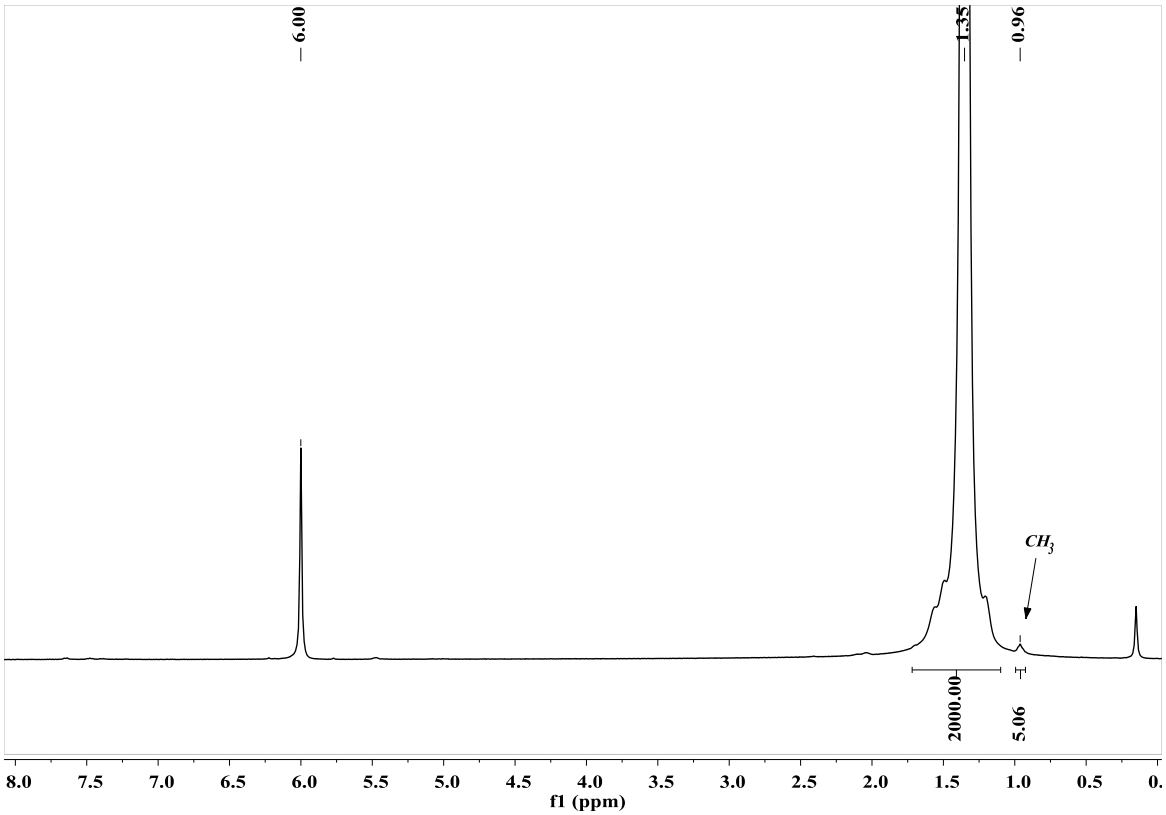


Figure S28. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 100 ℃) of the polymer from table 1, entry 2.

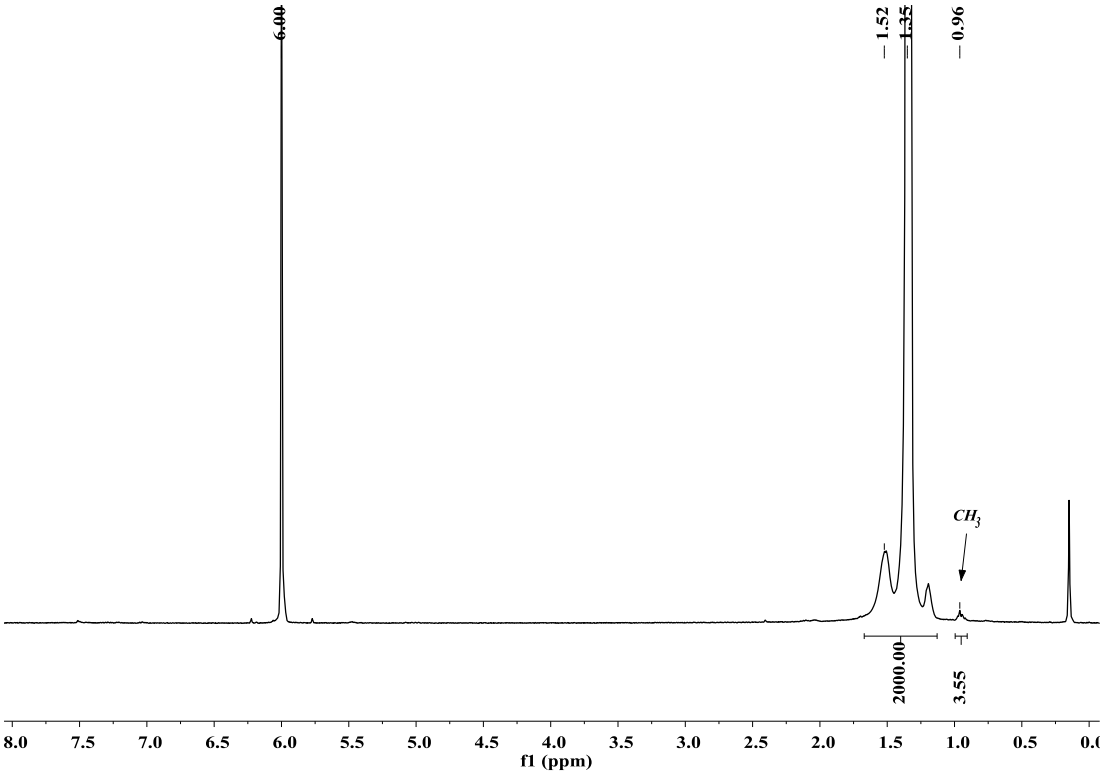


Figure S29. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 100 ℃) of the polymer from table 1, entry 5.

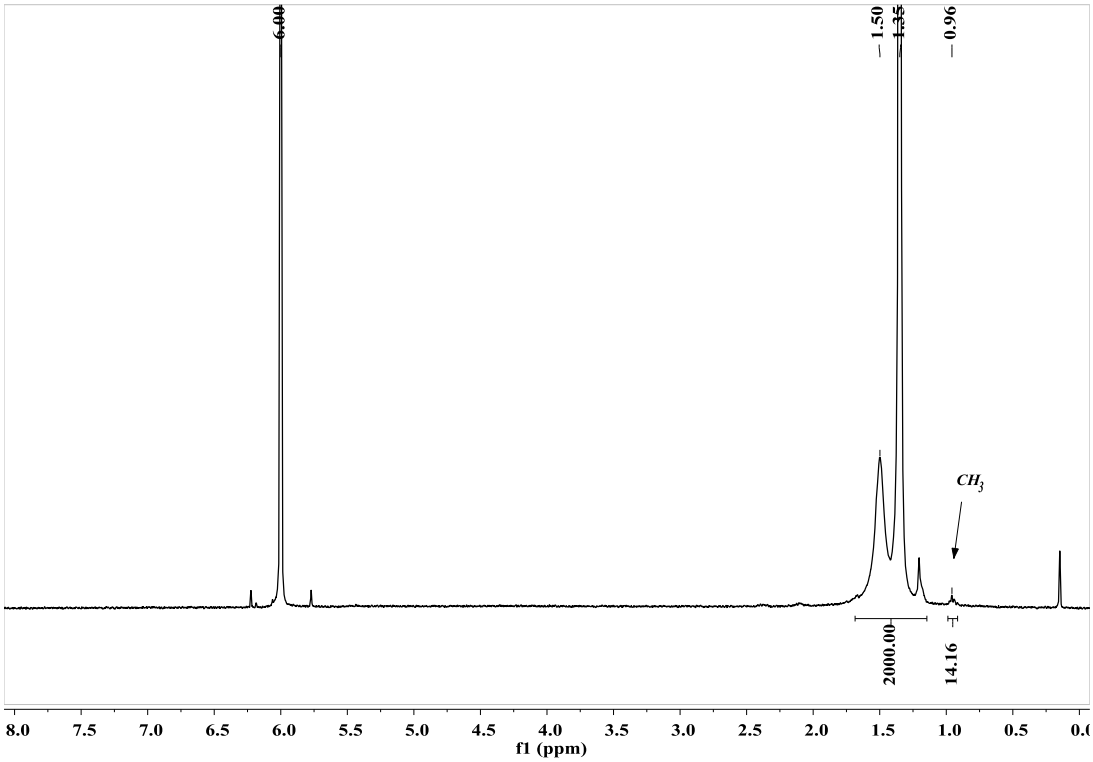


Figure S30. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 100 ℃) of the polymer from table 1, entry 6.

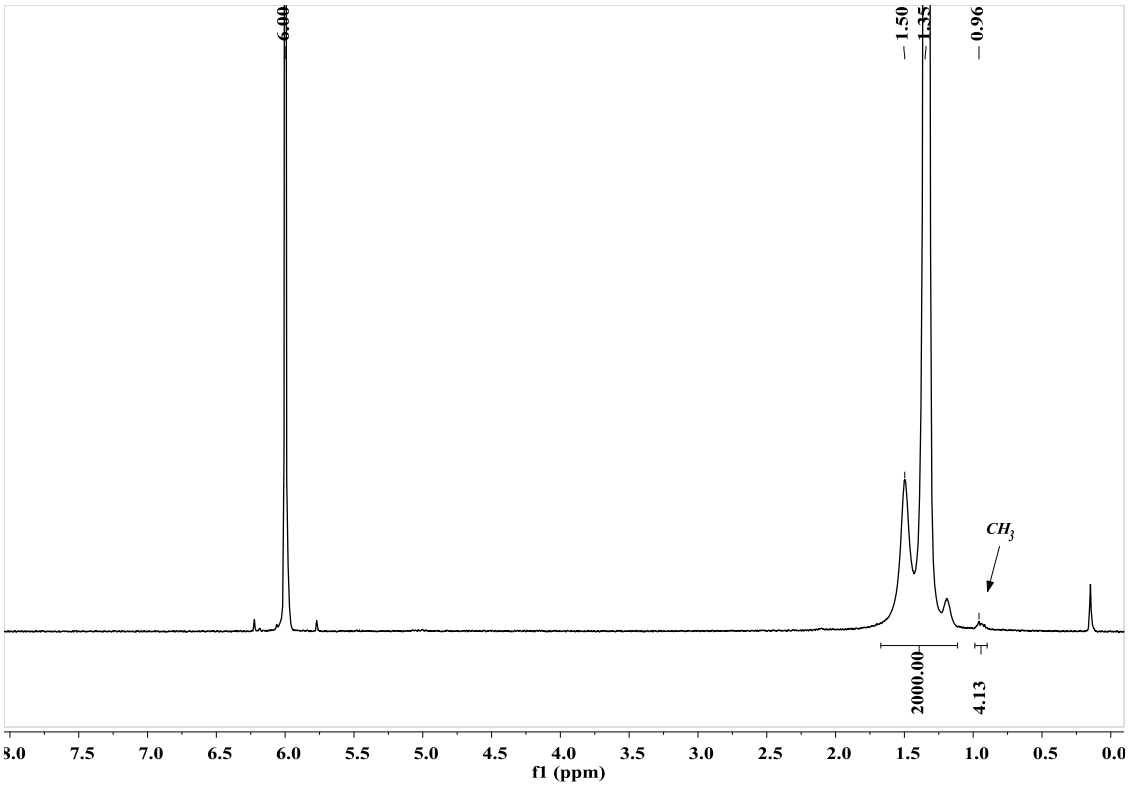


Figure S31. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 100 ℃) of the polymer from table 1, entry 7.

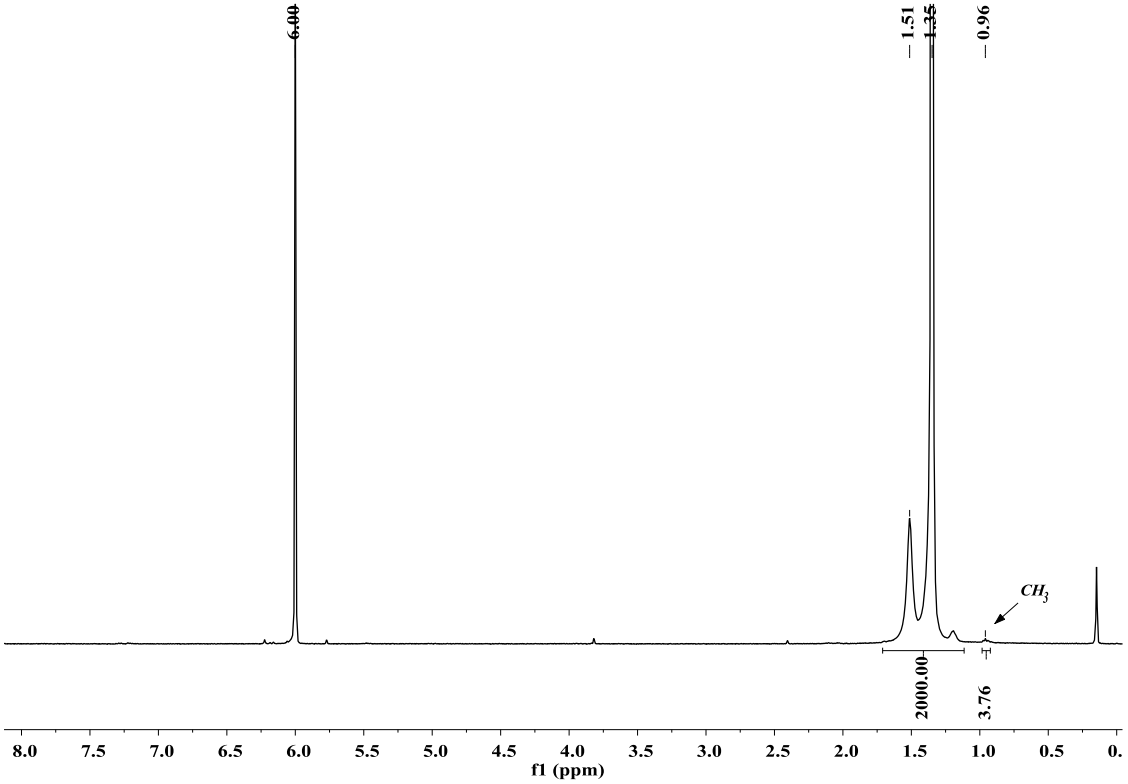


Figure S32. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 100 ℃) of the polymer from table 1, entry 8.

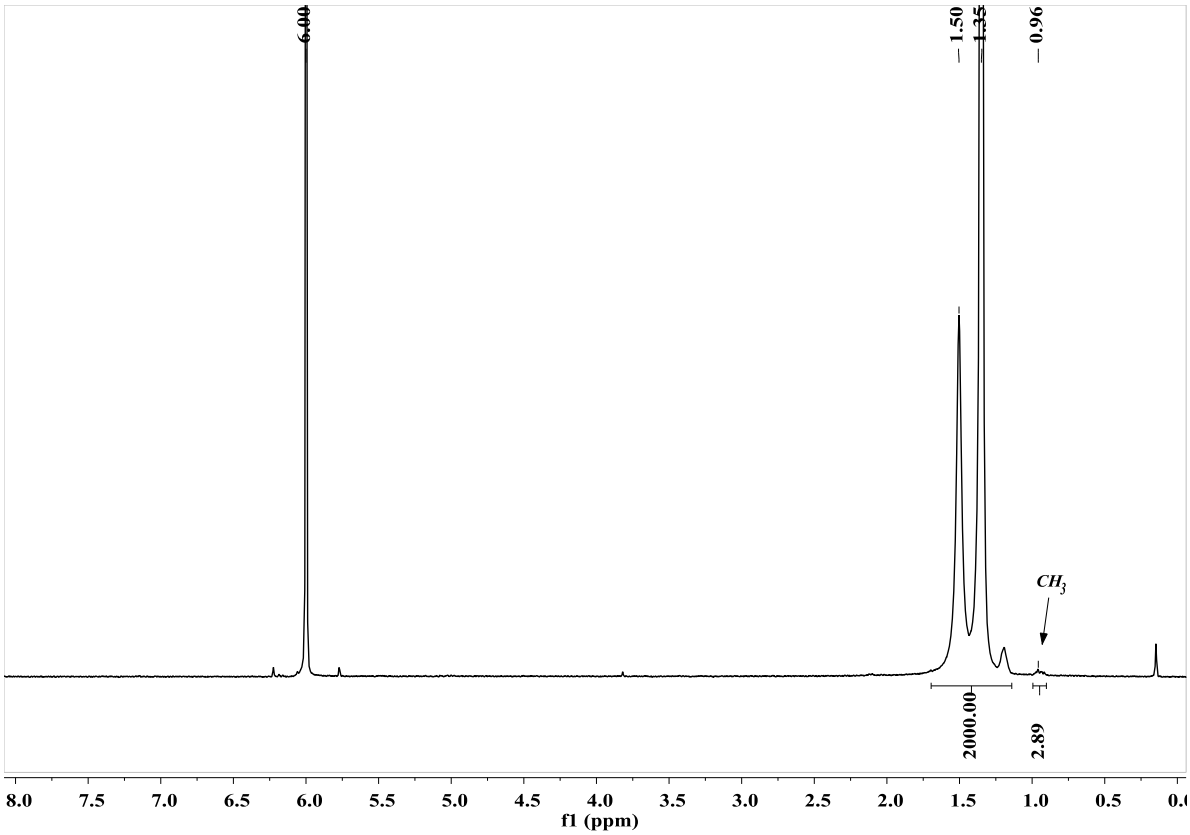


Figure S33. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 100 ℃) of the polymer from table 1, entry 9.

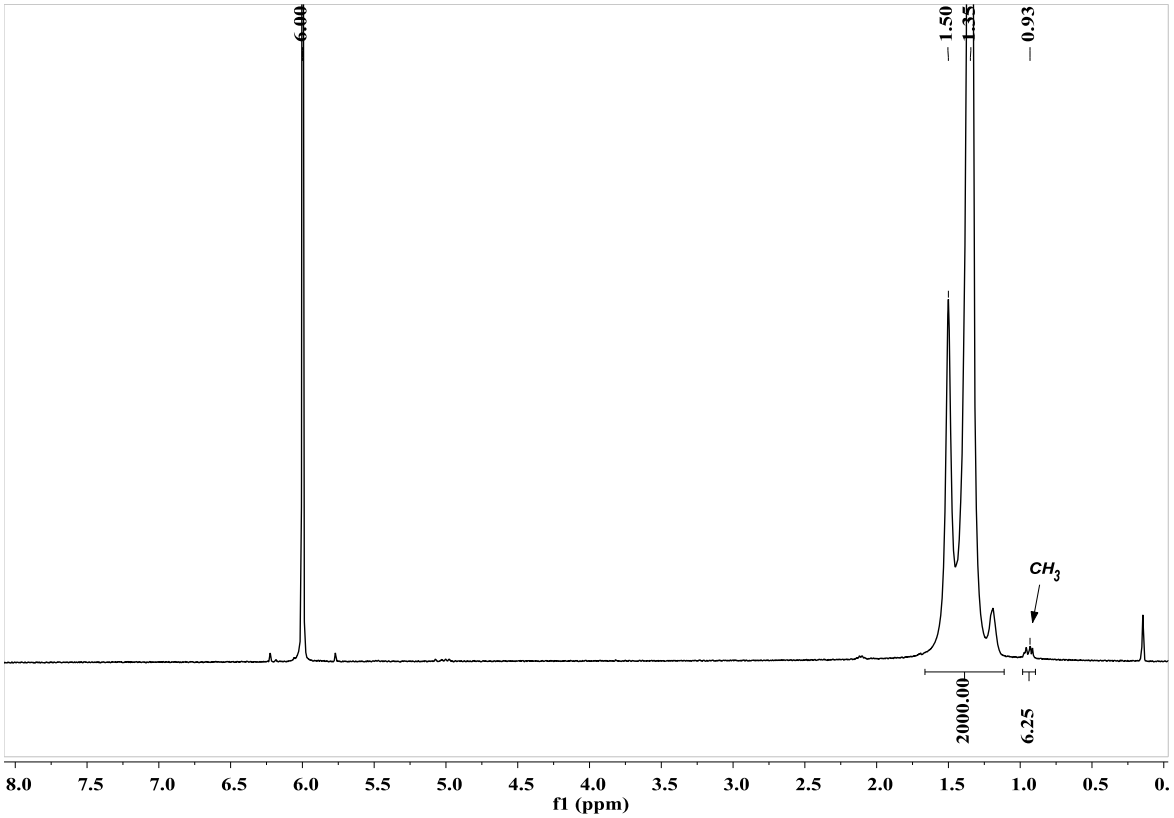


Figure S34. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 100 ℃) of the polymer from table 1, entry 10.

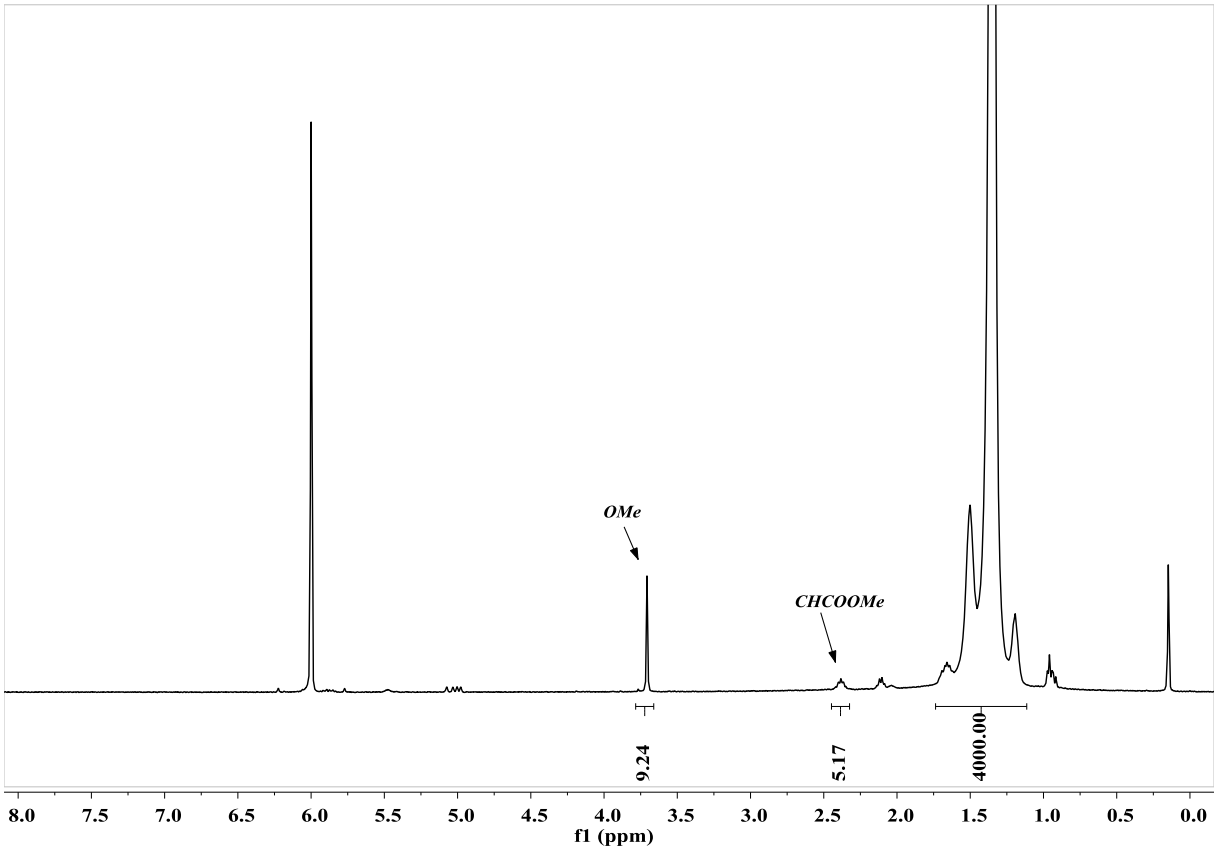


Figure S35. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 100 ℃) of the E-MA copolymer from table 2, entry 1.

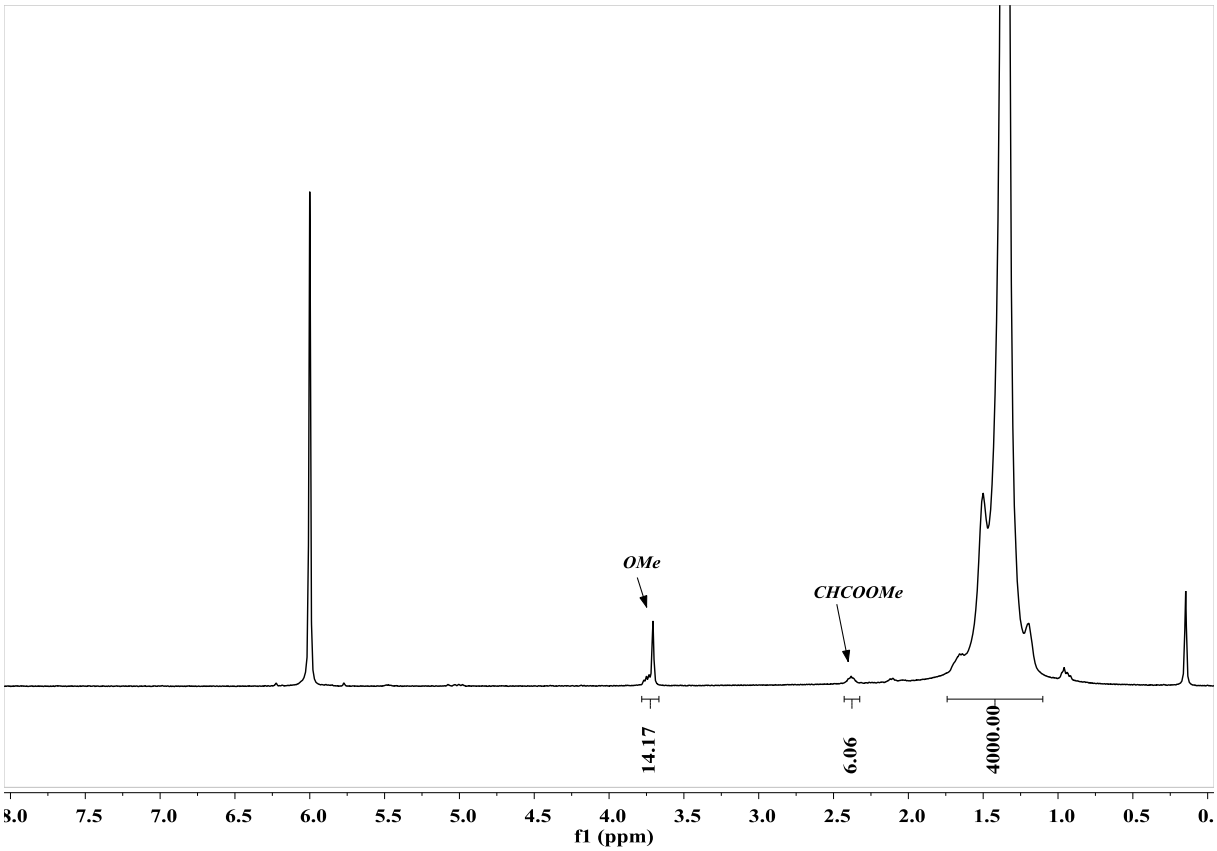


Figure S36. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 100 ℃) of the E-MA copolymer from table 2, entry 2.

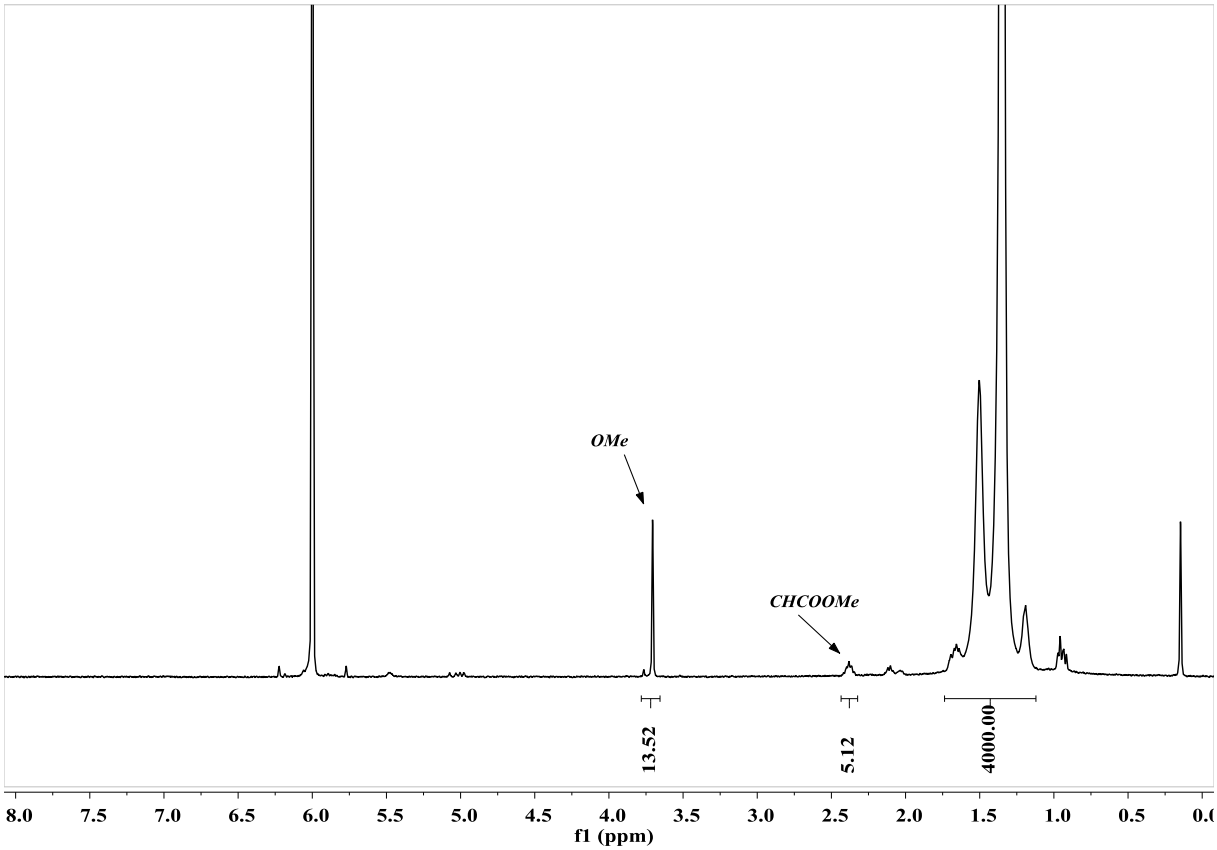


Figure S37. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 100 ℃) of the E-MA copolymer from table 2, entry 3.

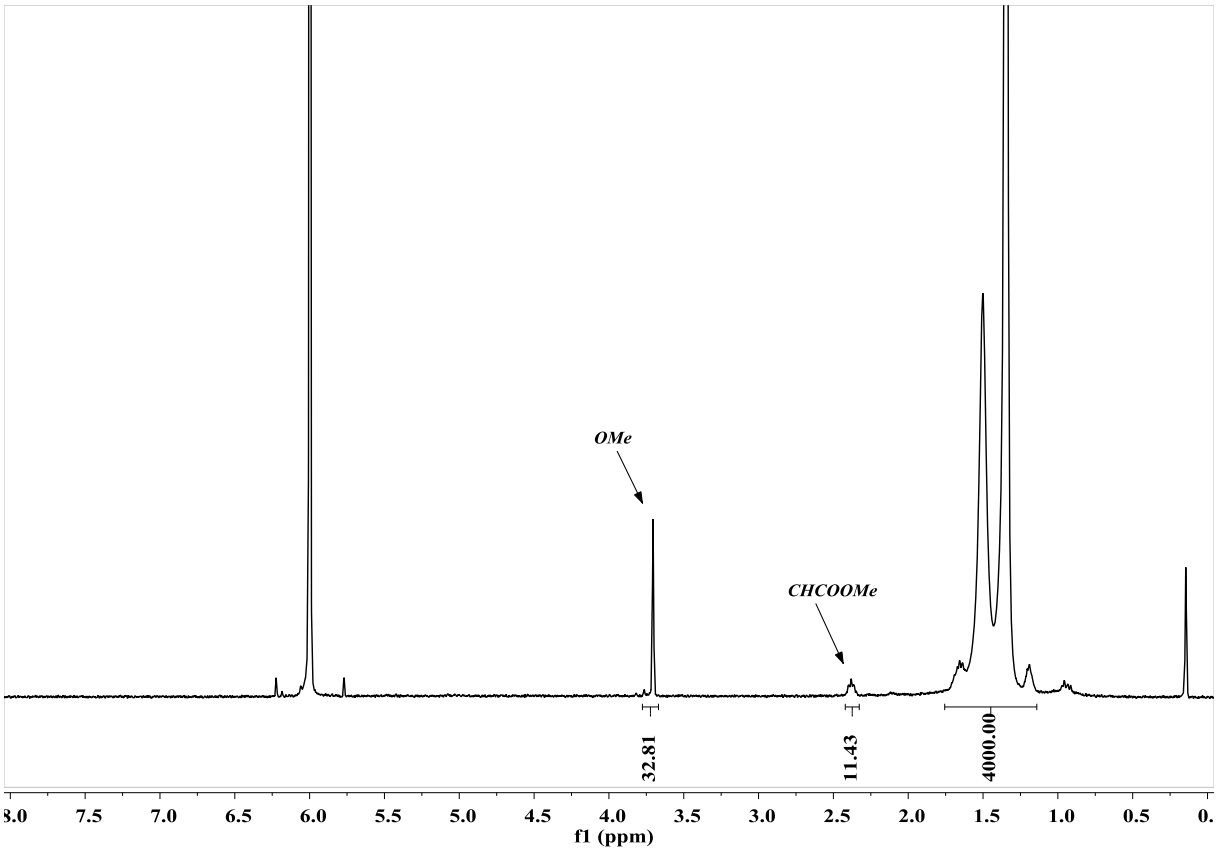


Figure S38. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 100 ℃) of the E-MA copolymer from table 2, entry 4.

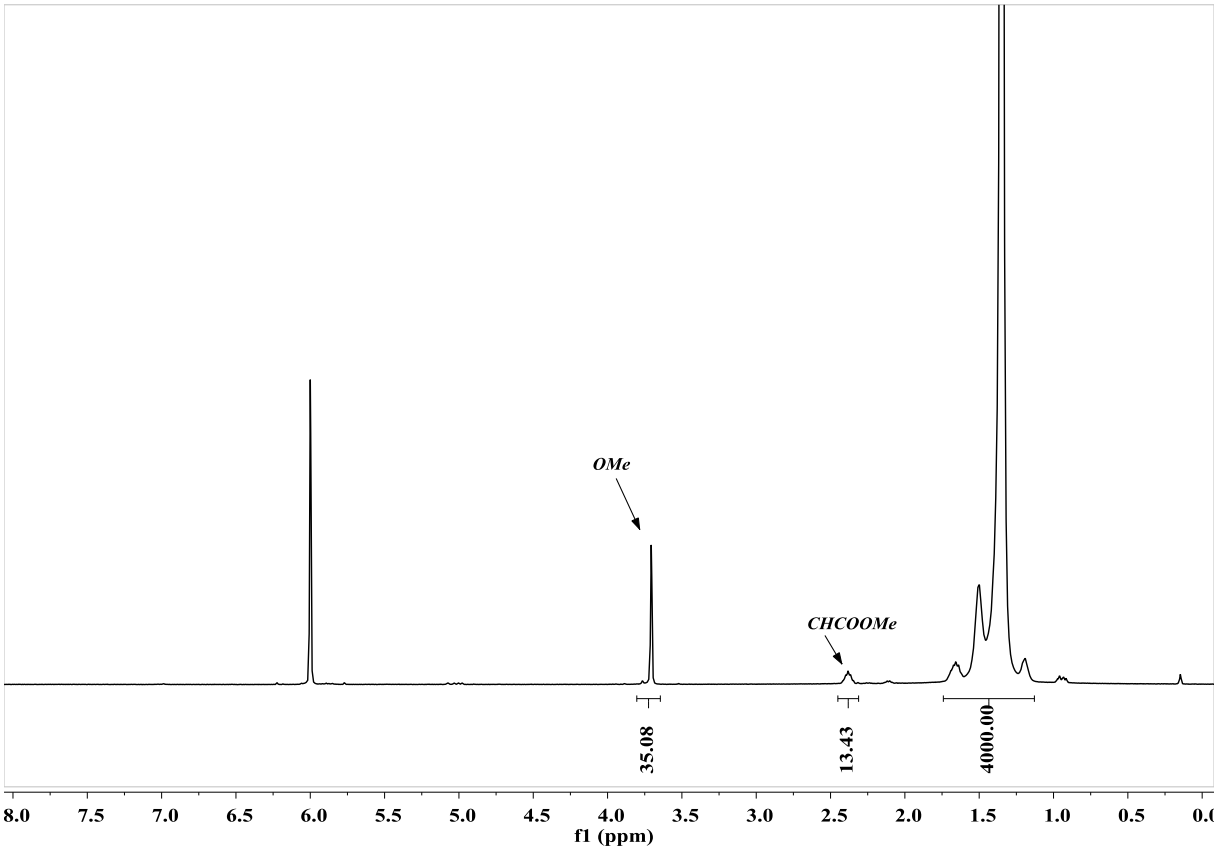


Figure S39. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 100 ℃) of the E-MA copolymer from table 2, entry 5.

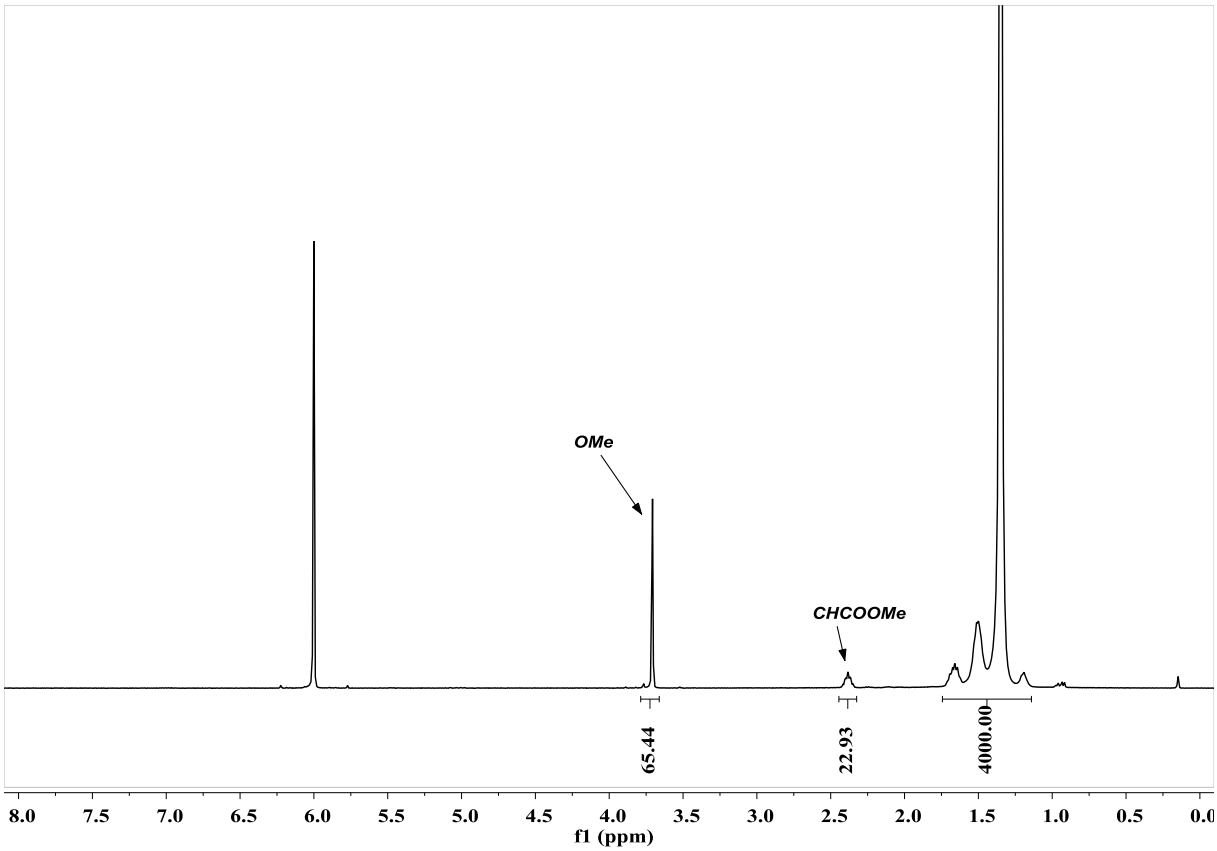


Figure S40. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 100 ℃) of the E-MA copolymer from table 2, entry 6.

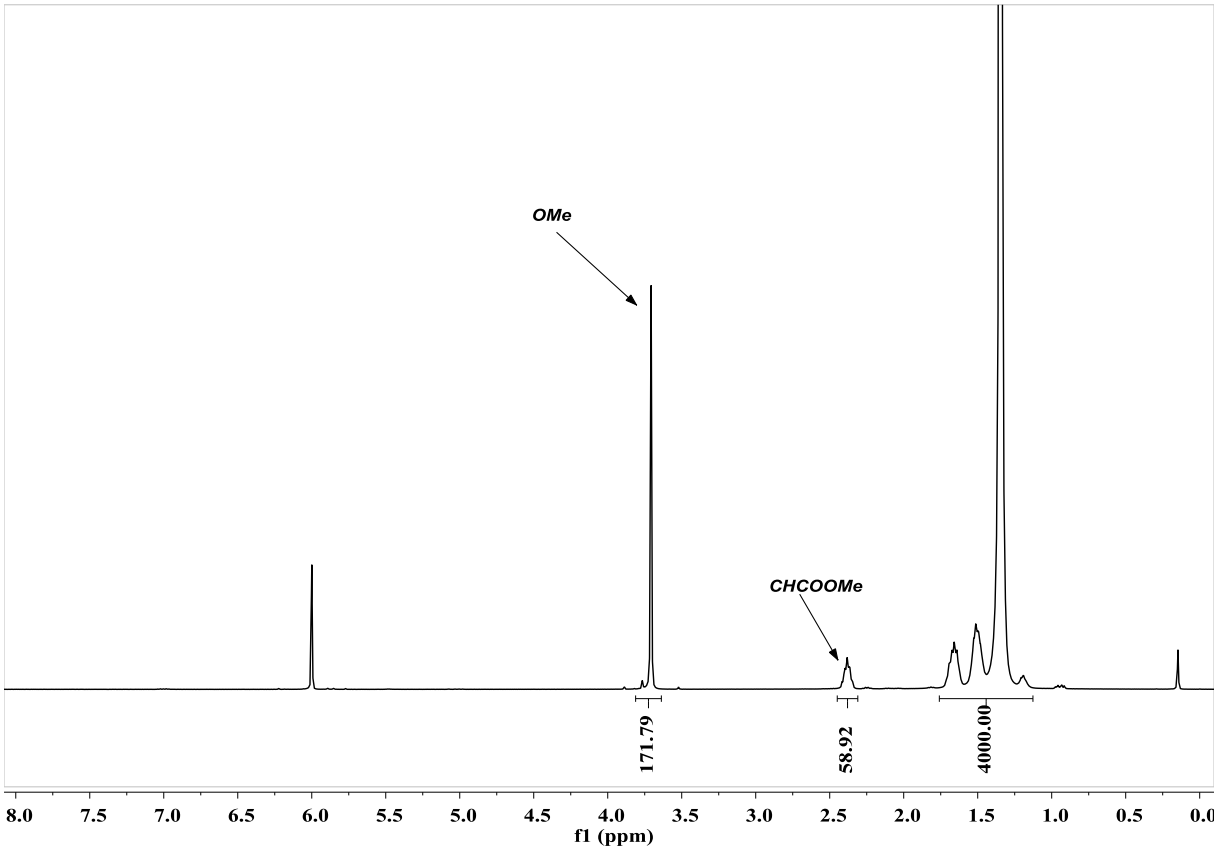


Figure S41. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 100 ℃) of the E-MA copolymer from table 2, entry 7.

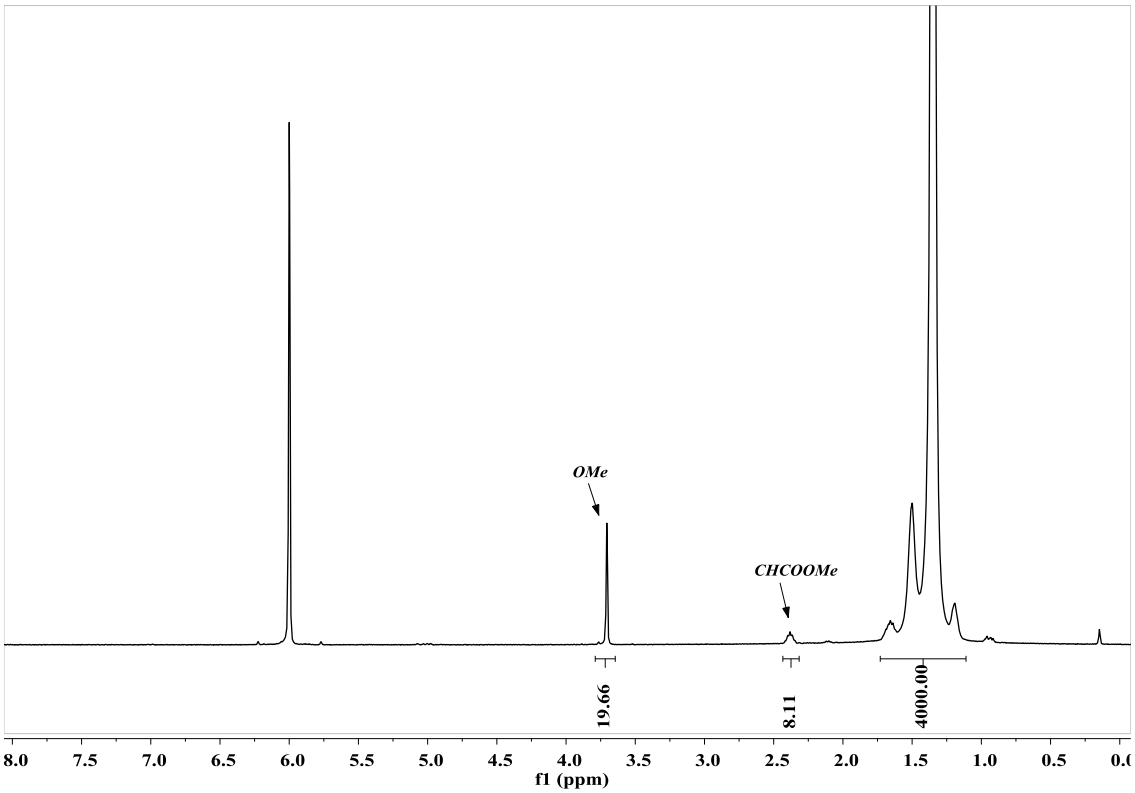


Figure S42. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 100 ℃) of the E-MA copolymer from table 2, entry 8.

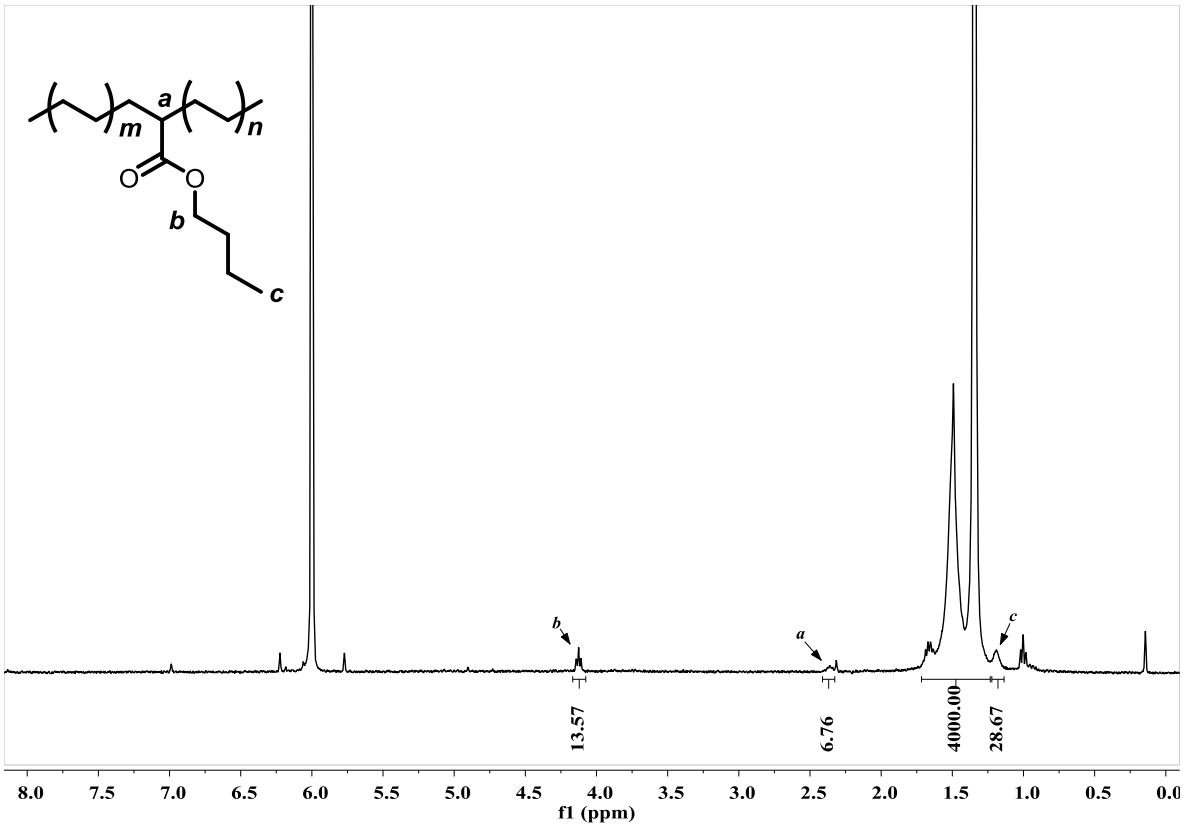


Figure S43. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 100 ℃) of the E-*n*BuA copolymer from table 2, entry 9.

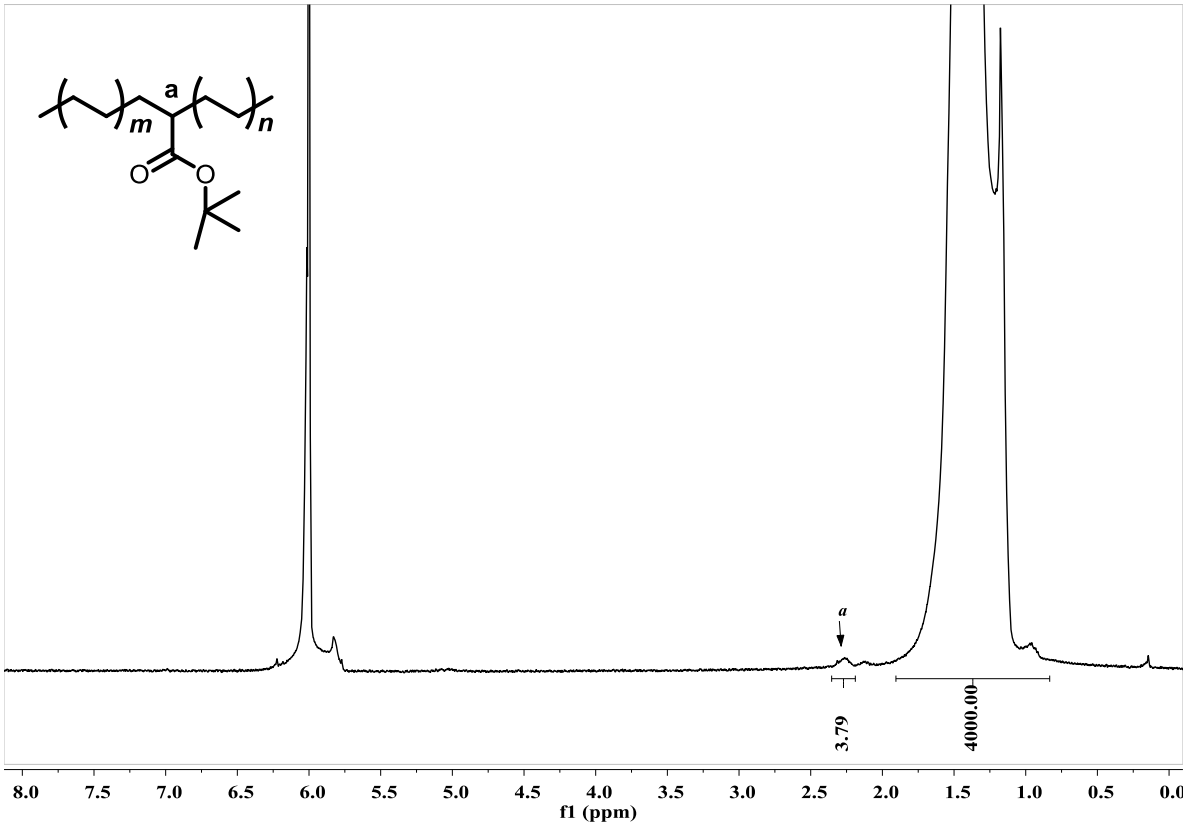


Figure S44. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 100 ℃) of the E-*t*BuA copolymer from table 2, entry 10.

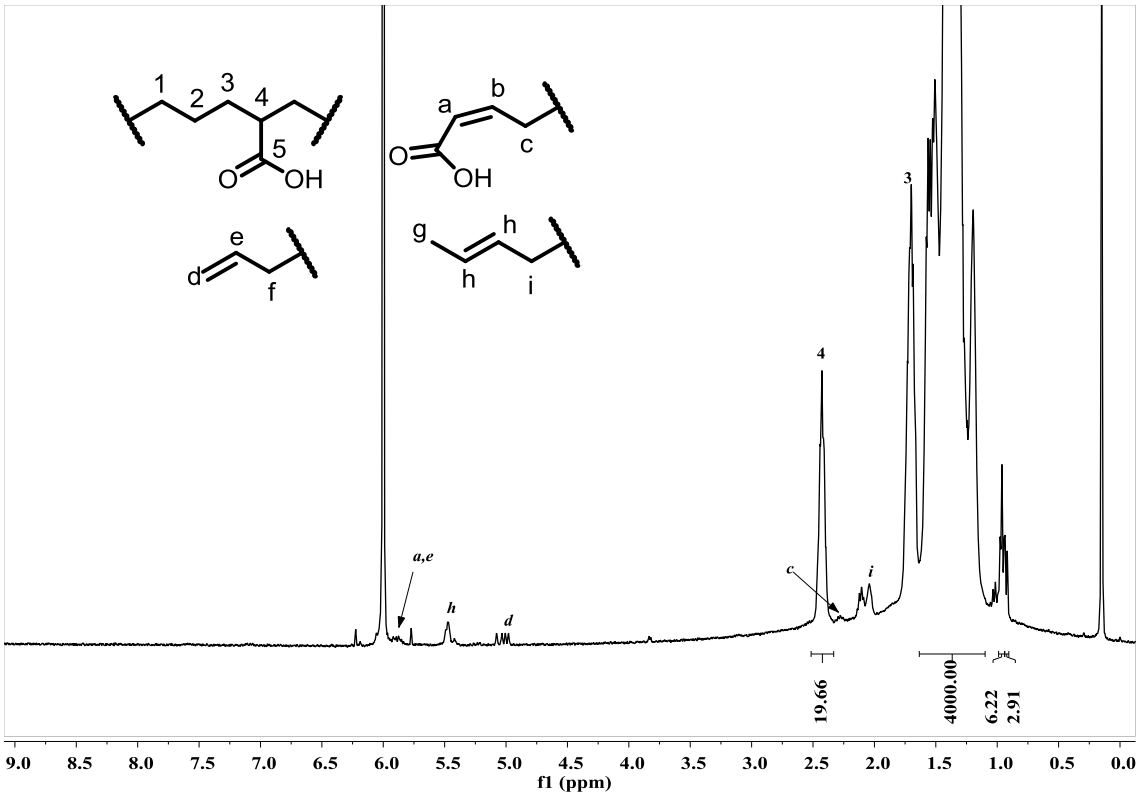


Figure S45. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 100 ℃) of the E-AA copolymer from table 2, entry 12.

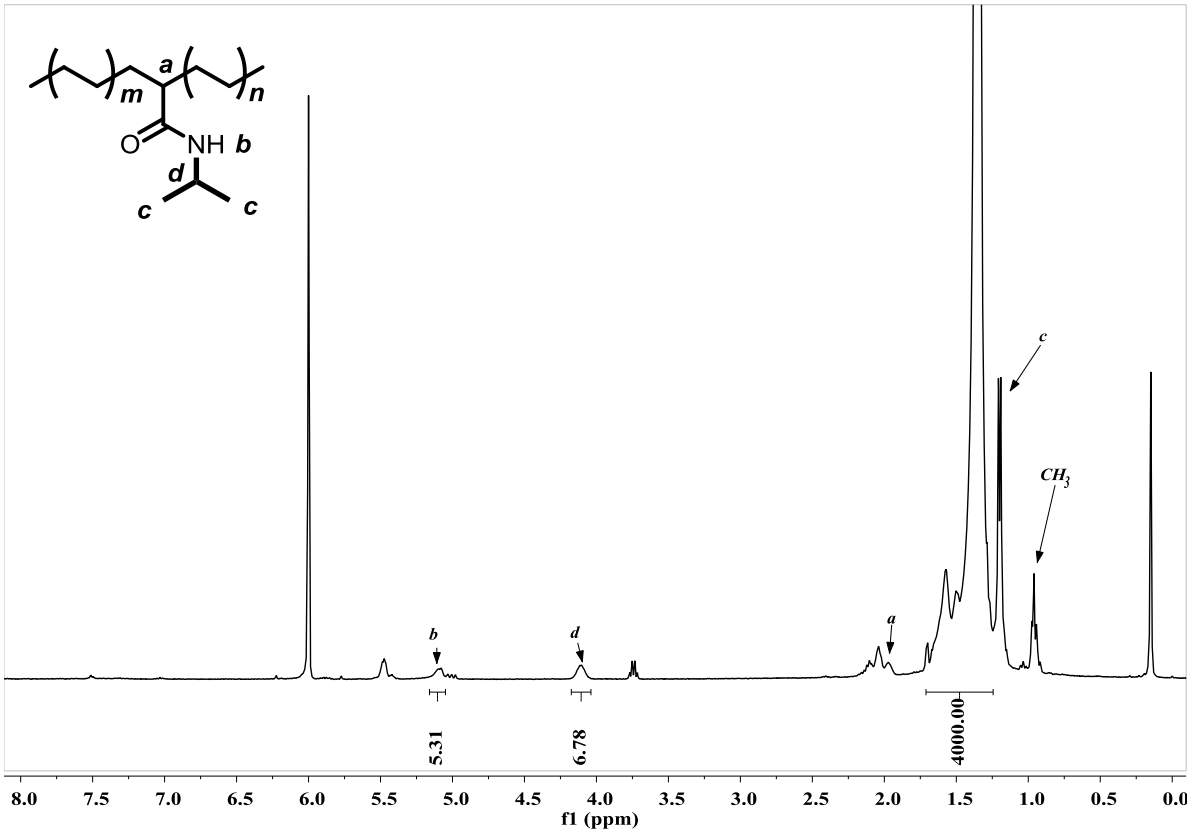


Figure S46. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 100 ℃) of the E-NIPAA copolymer from table 2, entry 13.

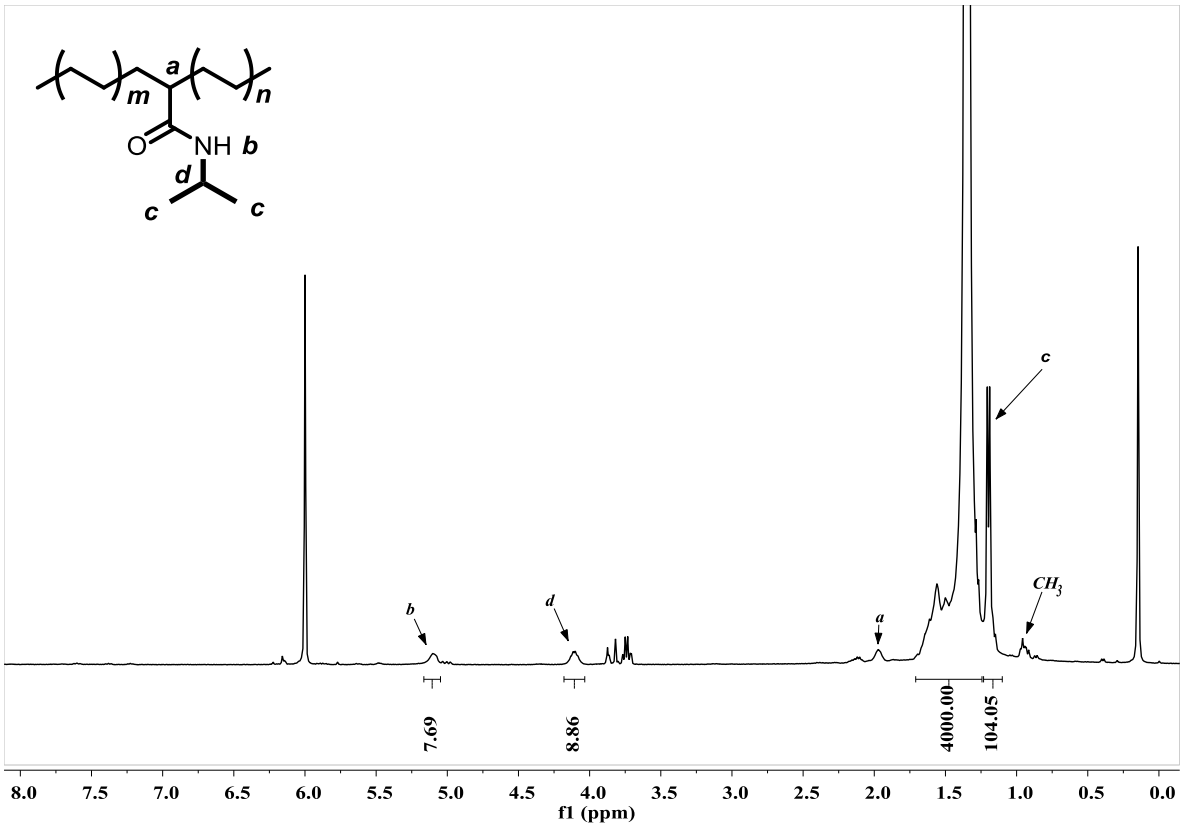


Figure S47. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 100 ℃) of the E-NIPAA copolymer from table 2, entry 14.

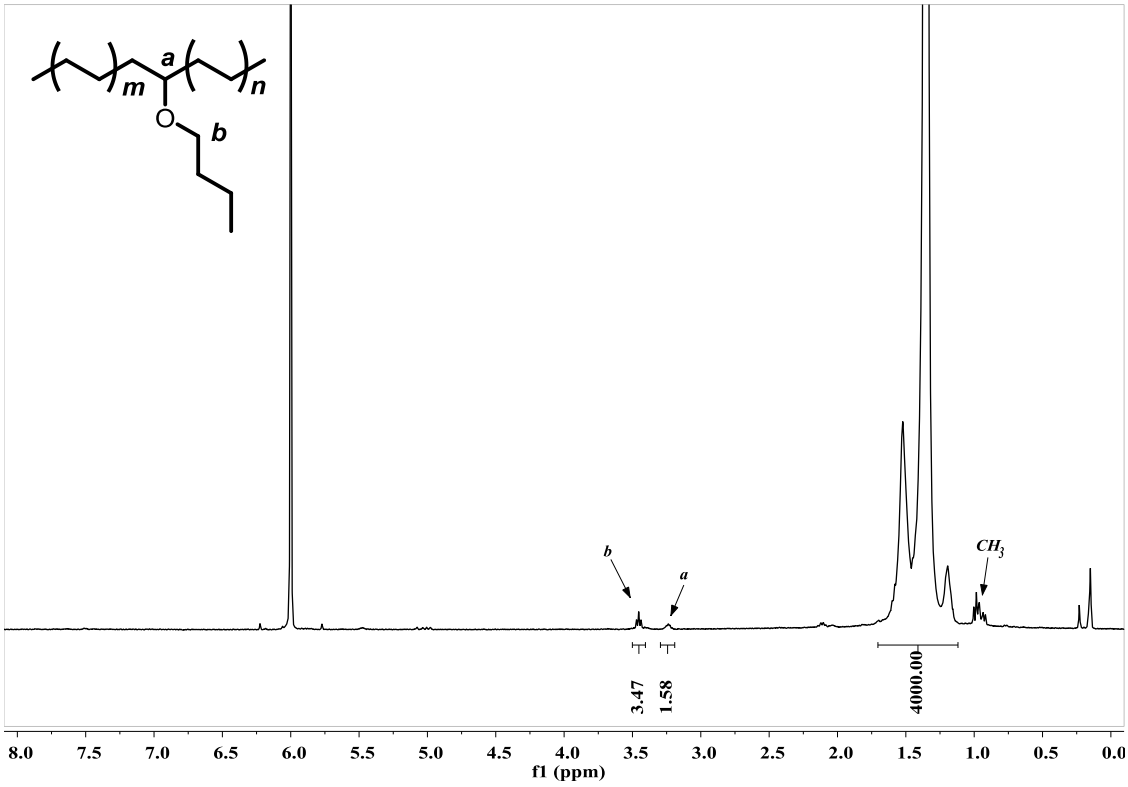


Figure S48. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 100 ℃) of the E-BVE copolymer from table 2, entry 15.

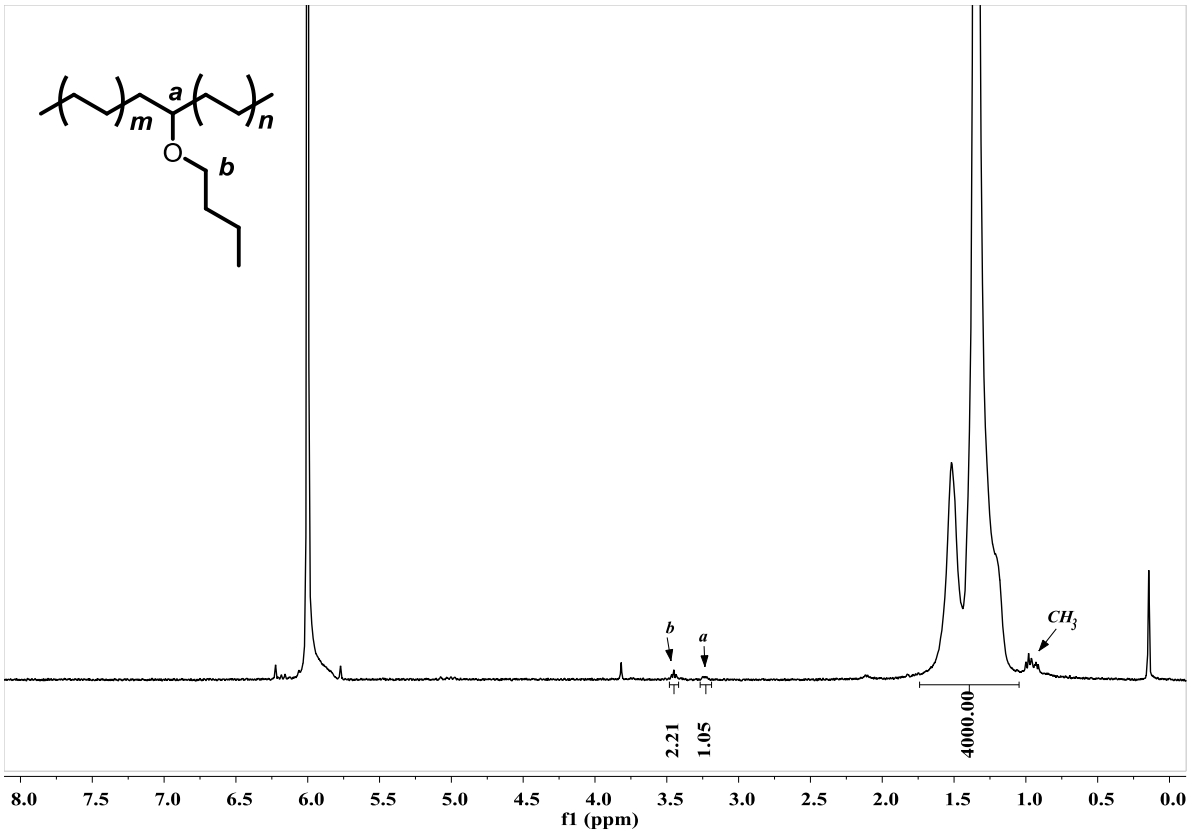


Figure S49. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 100 ℃) of the E-BVE copolymer from table 2, entry 16.

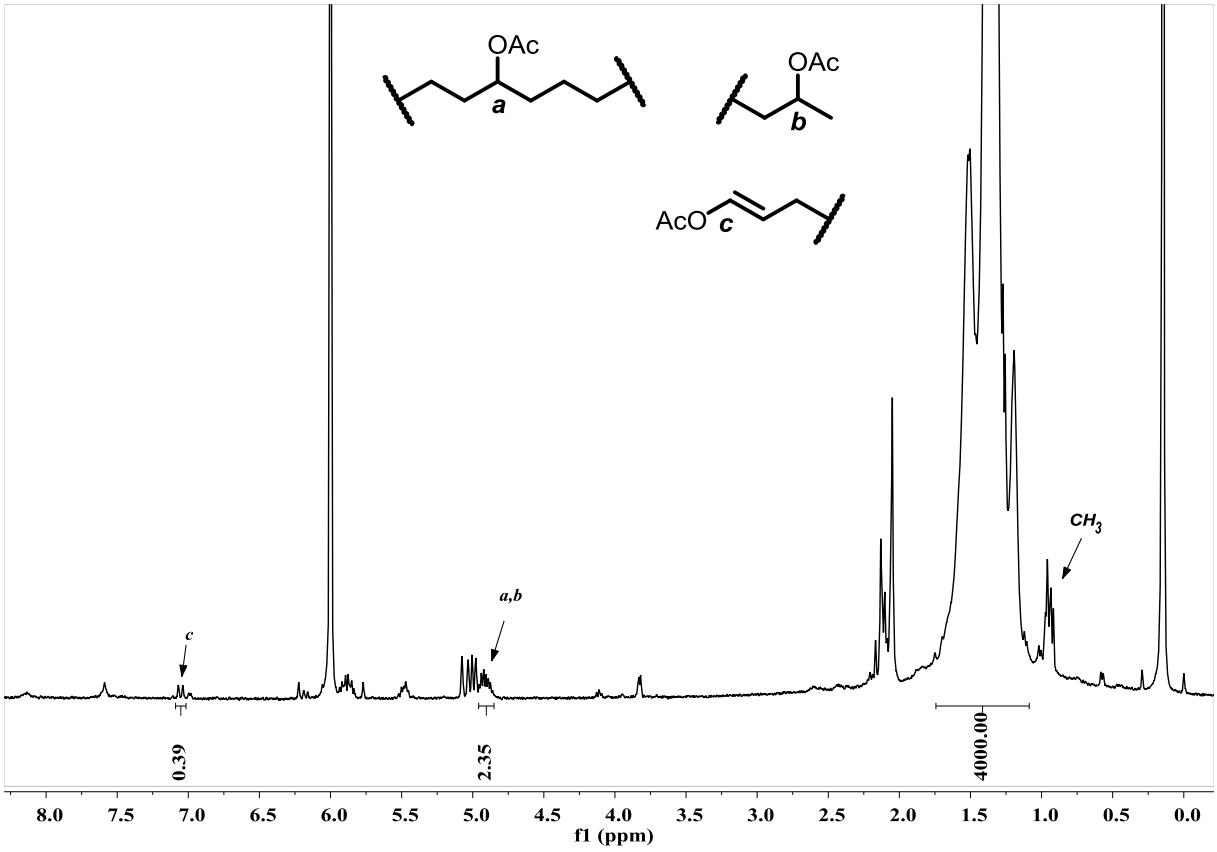


Figure S50. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 100 ℃) of the E-VA copolymer from table 2, entry 18.

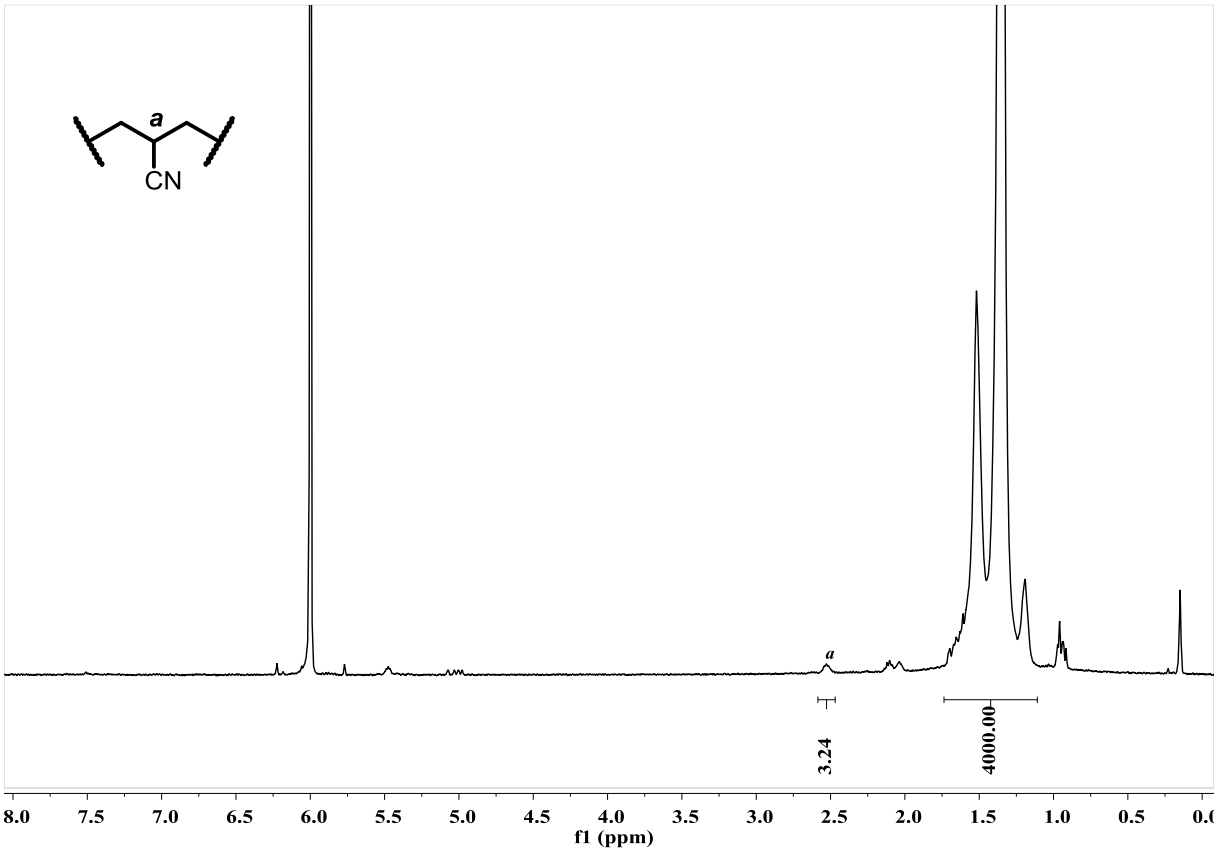


Figure S51. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 100 ℃) of the E-AN copolymer from table 2, entry 19.

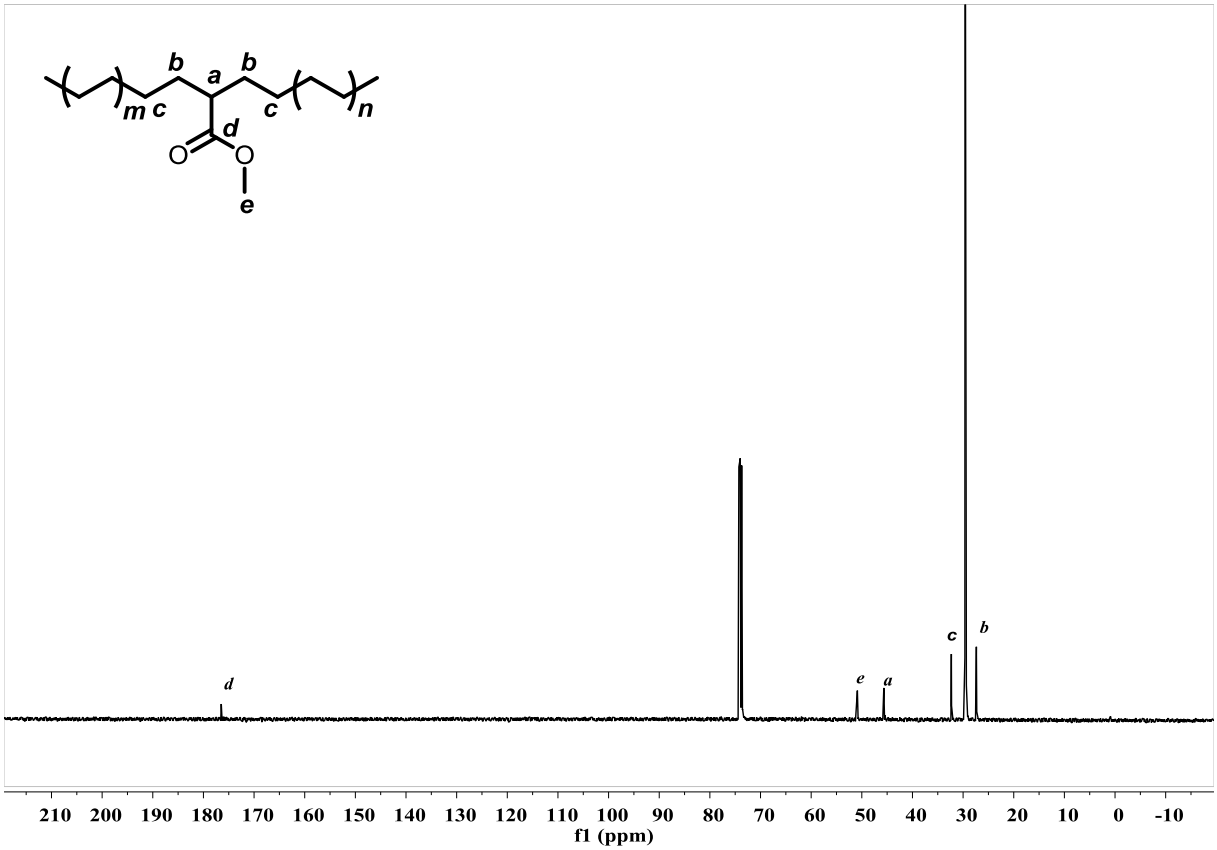
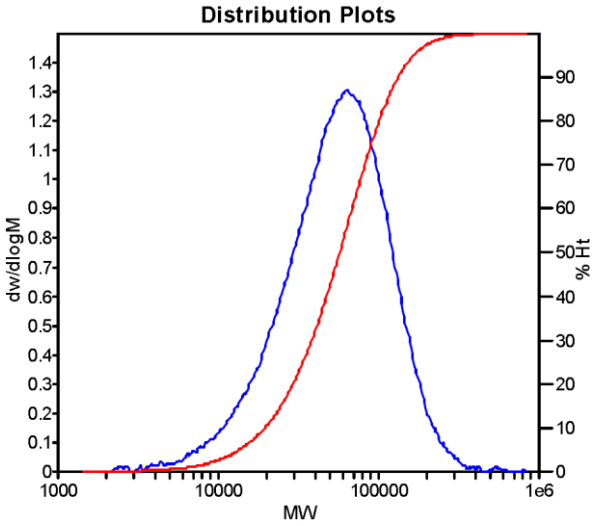


Figure S52. ^{13}C NMR spectrum (400 MHz, $C_2D_2Cl_4$, 100 ℃) of the E-MA polymer from table 2, entry 7.



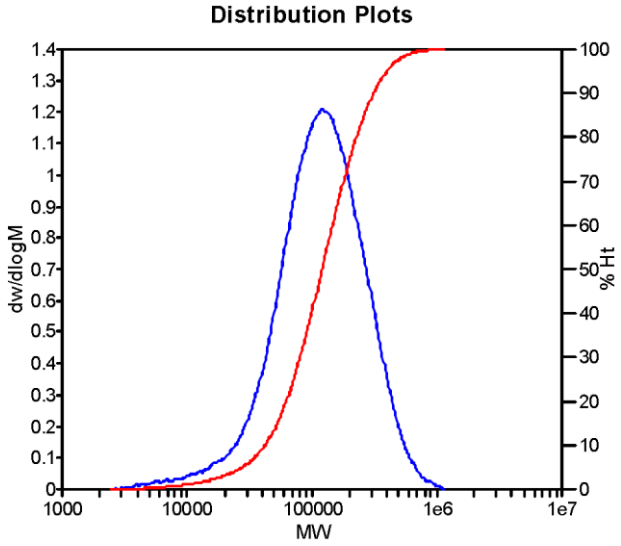
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	62867	37742	68729	108200	165766	64267	1.82102

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		17.05	19.68	23.53	-5.43008	100	587.485	100

Figure S53. GPC trace of the polymer from table 1, entry 1.



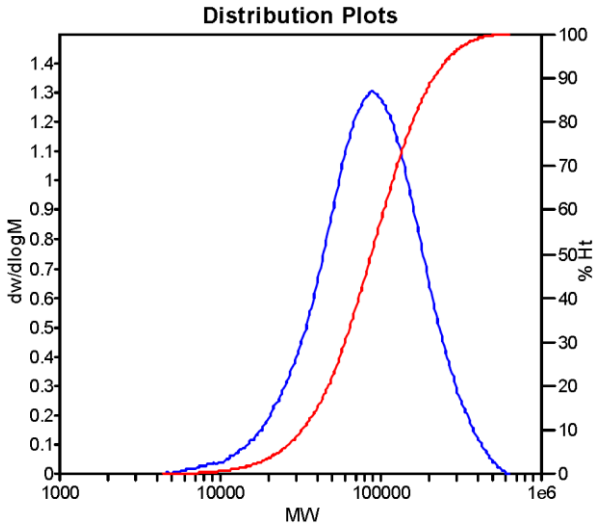
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	119459	74658	153803	252963	372953	141543	2.0601

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		16.92	19.20	23.12	-11.5689	100	1334.23	100

Figure S54. GPC trace of the polymer from table 1, entry 3.



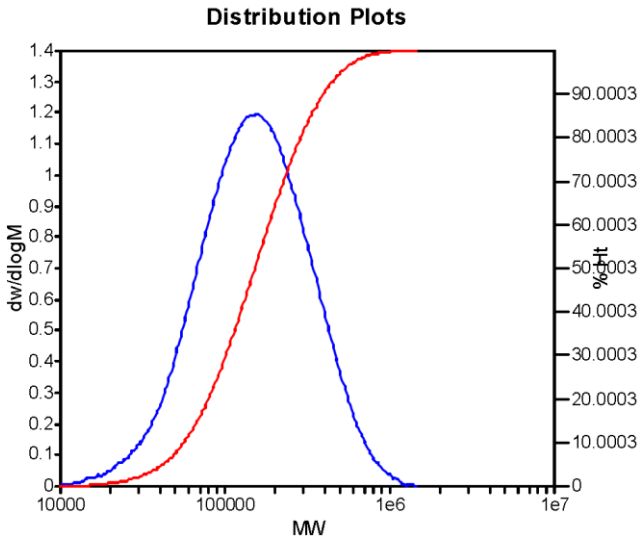
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	87255	62249	107799	166303	232324	100348	1.73174

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		17.52	19.52	22.52	-12.5168	100	1336.38	100

Figure S55. GPC trace of the polymer from table 1, entry 5.



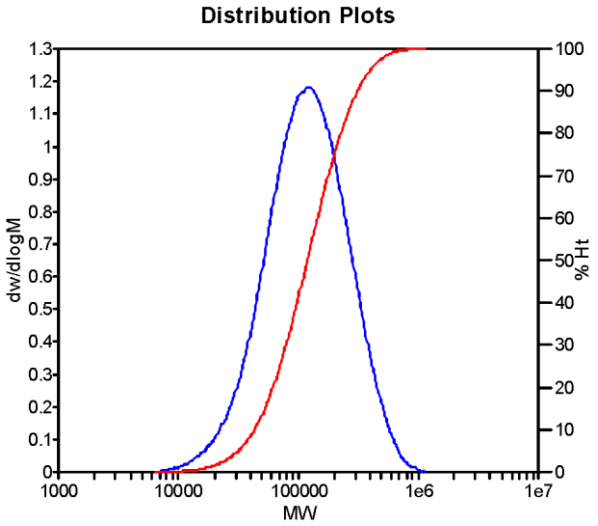
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	153083	110225	194422	314577	456721	179714	1.76386

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		16.68	18.95	21.73	-11.1337	100	1296.89	100

Figure S56. GPC trace of the polymer from table 1, entry 6.



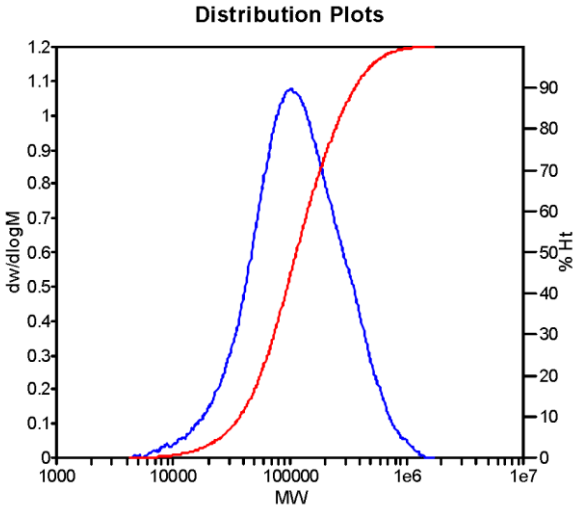
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	125534	84850	153315	250493	365453	141423	1.80689

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		16.92	19.15	22.15	-12.4246	100	1463.52	100

Figure S57. GPC trace of the polymer from table 1, entry 7.



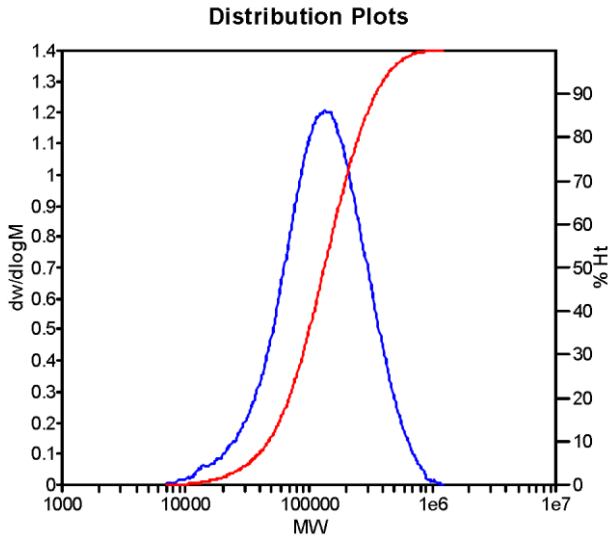
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	102498	74937	164803	318430	512866	149194	2.19922

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		16.32	19.18	22.43	-7.87008	100	1032.89	100

Figure S58. GPC trace of the polymer from table 1, entry 8.



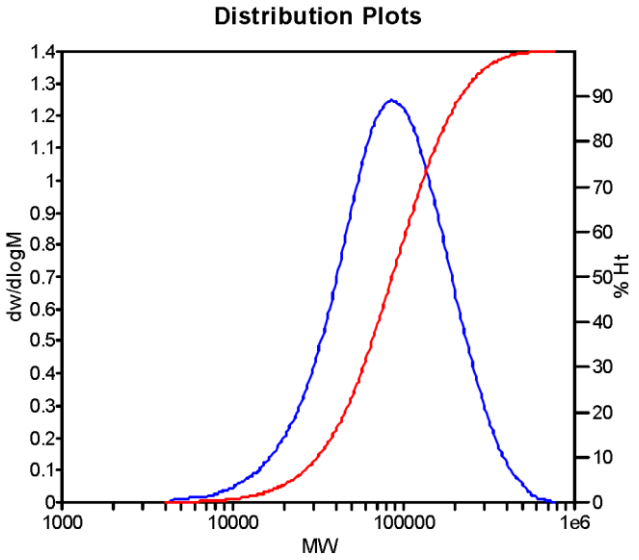
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	136353	91648	171042	279284	404951	157659	1.86629

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		16.87	19.07	22.07	-7.05129	100	814.459	100

Figure S59. GPC trace of the polymer from table 1, entry 9.



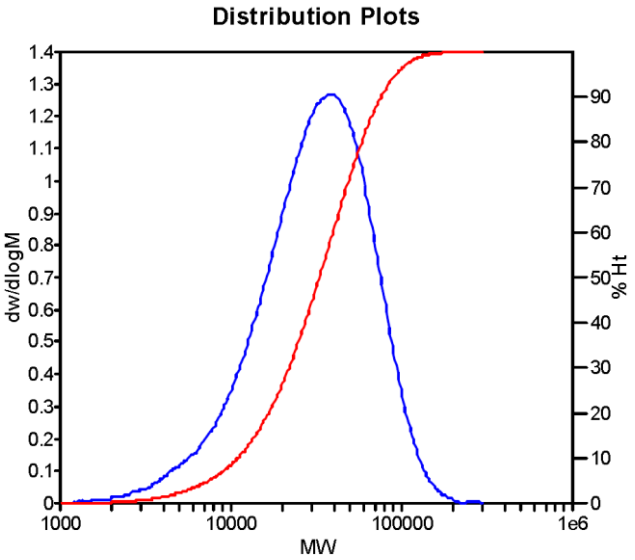
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	85824	60147	107757	171339	246123	99839	1.79156

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		17.33	19.53	22.62	-12.9058	100	1437.59	100

Figure S60. GPC trace of the polymer from table 1, entry 10.



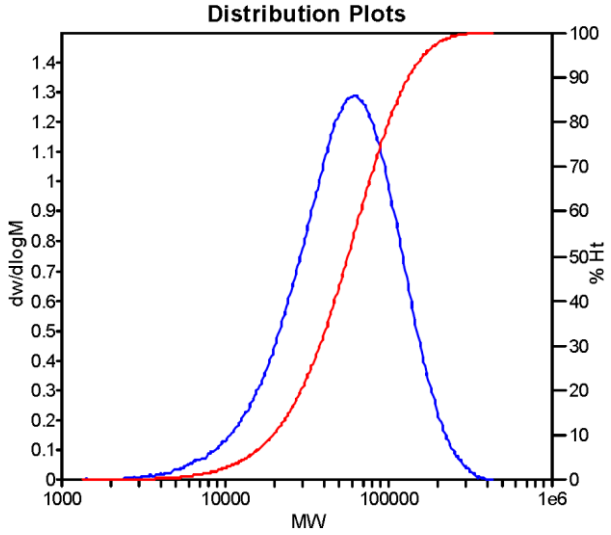
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	37323	21259	38954	58377	79352	36541	1.83235

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		18.10	20.22	23.90	-9.62565	100	1072.78	100

Figure S61. GPC trace of the polymer from table 2, entry 1.



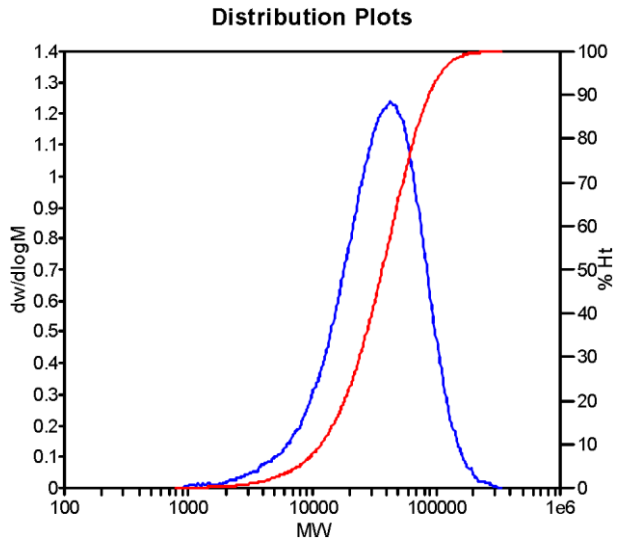
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	62867	37850	67617	102000	138813	63423	1.78645

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		17.70	19.68	23.62	-9.73975	100	1067.74	100

Figure S62. GPC trace of the polymer from table 2, entry 2.



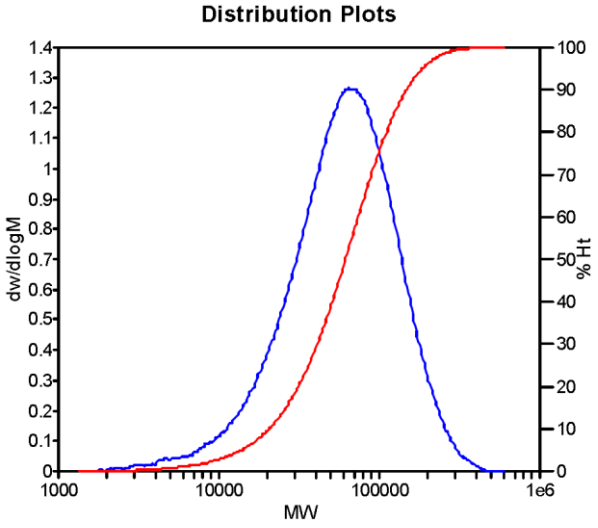
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	42519	22311	44495	69494	98044	41487	1.99431

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		17.97	20.08	24.13	-8.68718	100	992.075	100

Figure S63. GPC trace of the polymer from table 2, entry 3.



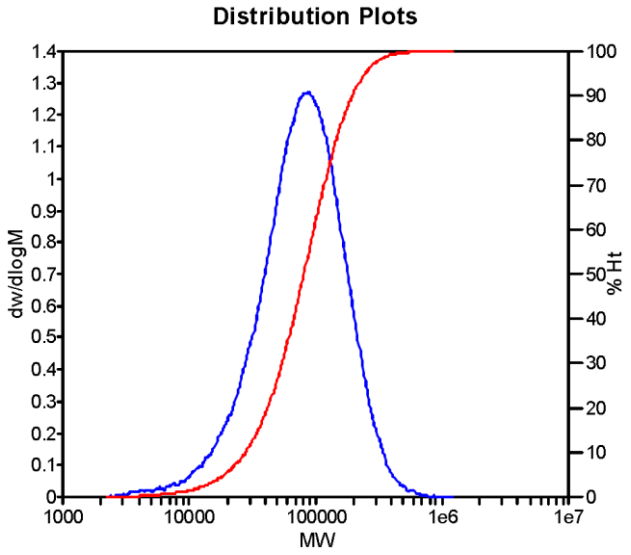
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	64949	38929	74839	116371	162548	69859	1.92245

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		17.38	19.65	23.62	-8.46316	0	946.193	100

Figure S64. GPC trace of the polymer from table 2, entry 4.



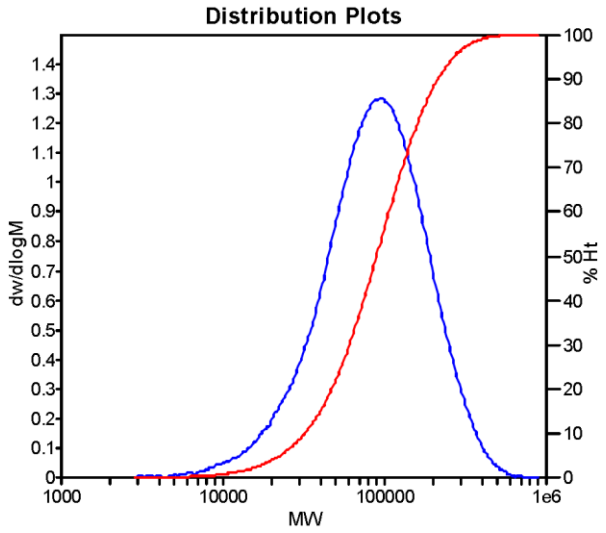
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	87086	52537	99460	158639	236248	92726	1.89314

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		16.67	19.35	23.08	-8.63715	0	959.32	100

Figure S65. GPC trace of the polymer from table 2, entry 9.



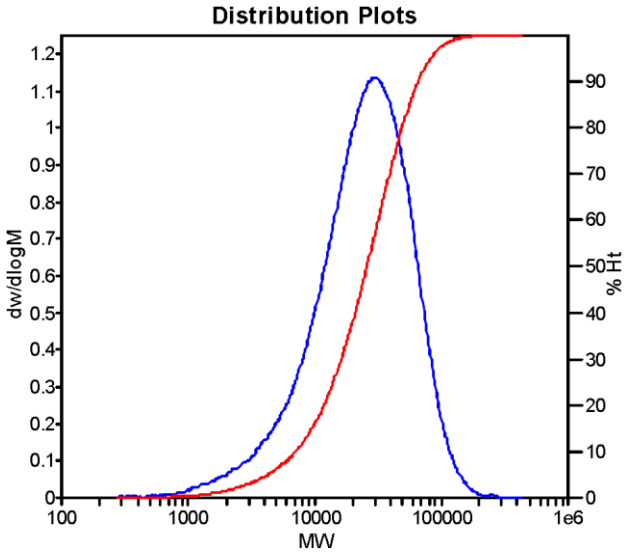
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	94478	61357	108699	166622	232360	101833	1.77158

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		16.98	19.27	22.85	-10.3084	100	1135.27	100

Figure S66. GPC trace of the polymer from table 2, entry 10.



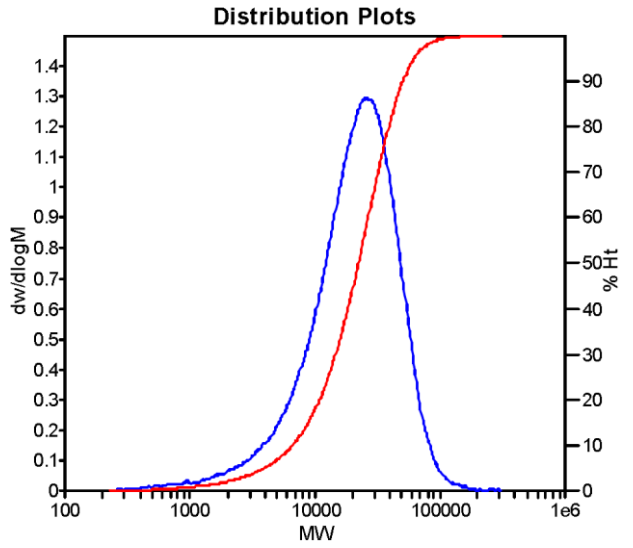
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	29230	13478	32161	53378	78984	29649	2.38618

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		17.70	20.47	25.23	-9.56305	100	1190.11	100

Figure S67. GPC trace of the polymer from table 2, entry 12.



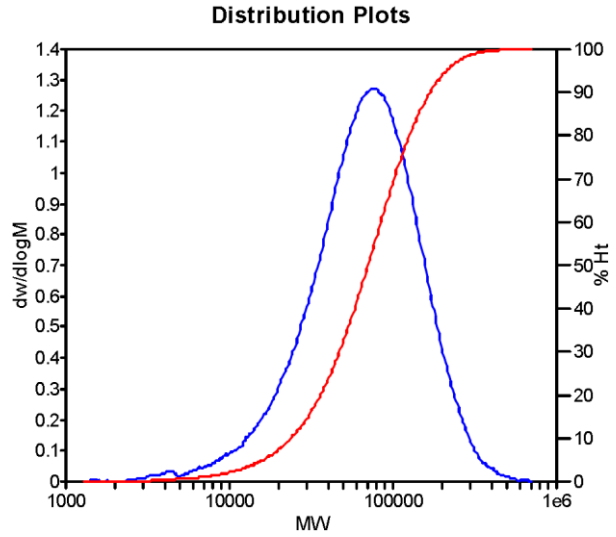
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	25657	11534	26252	41147	62022	24474	2.27605

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		18.05	20.60	25.42	-9.74733	100	1061.71	100

Figure S68. GPC trace of the polymer from table 2, entry 14.



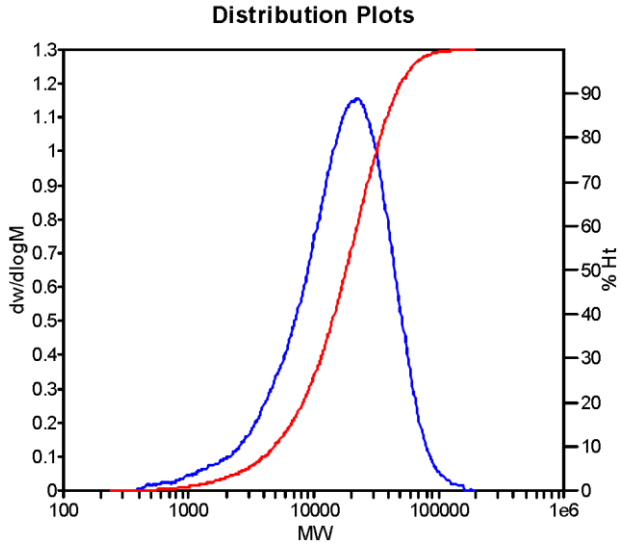
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	75207	44580	85877	135308	195922	80115	1.92636

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		17.20	19.50	23.67	-9.07076	0	1007.27	100

Figure S69. GPC trace of the polymer from table 2, entry 16.



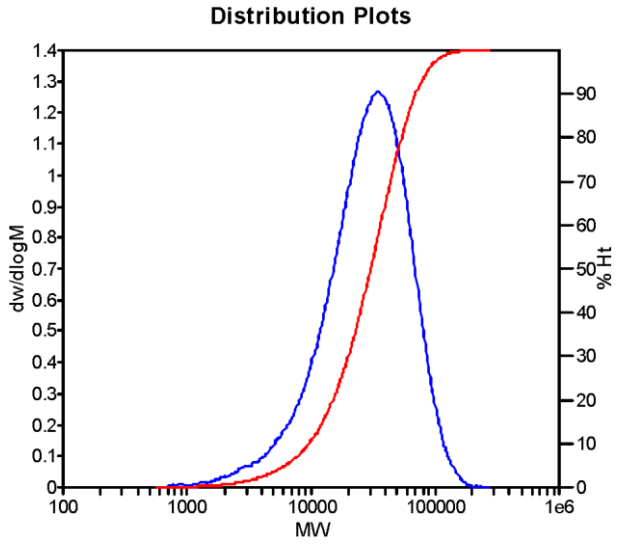
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	22892	9460	22504	37162	53982	20751	2.37886

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		18.55	20.72	25.37	-8.18232	100	1001.31	100

Figure S70. GPC trace of the polymer from table 2, entry 18.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	34968	18088	35765	53863	72486	33480	1.97728

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		18.18	20.28	24.48	-10.1198	100	1128.67	100

Figure S71. GPC trace of the polymer from table 2, entry 19.

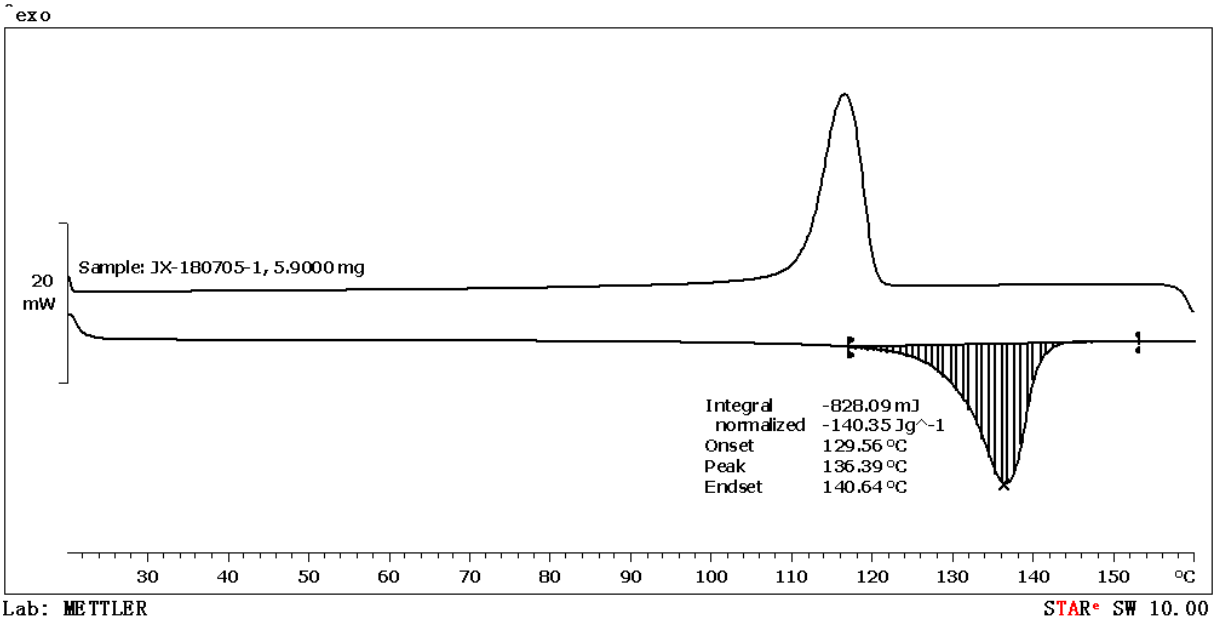


Figure S72. DSC data of the polymer from table 1, entry 1.

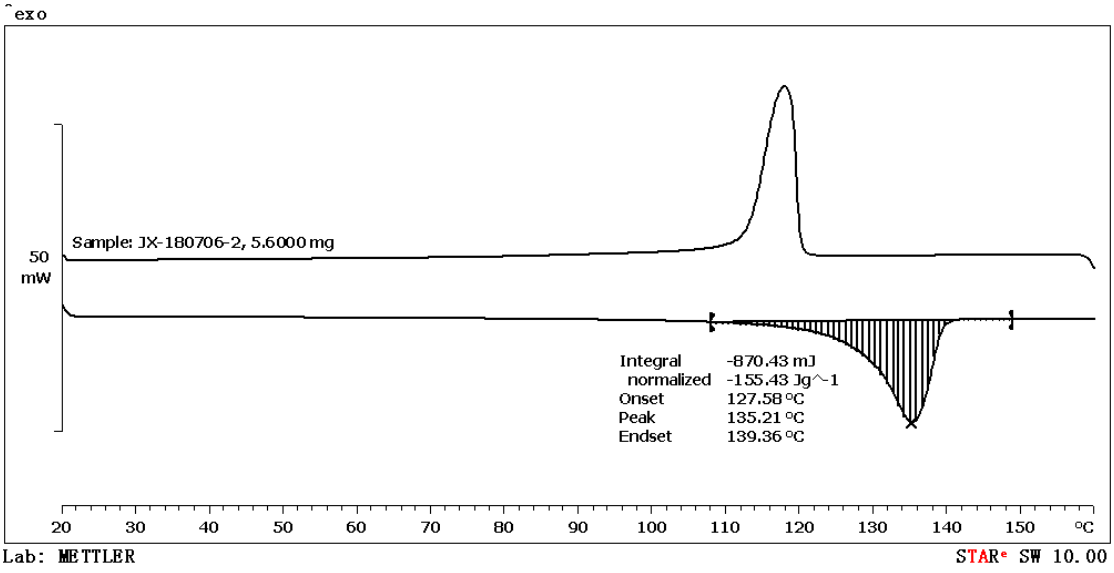


Figure S73. DSC data of the polymer from table 1, entry 3.

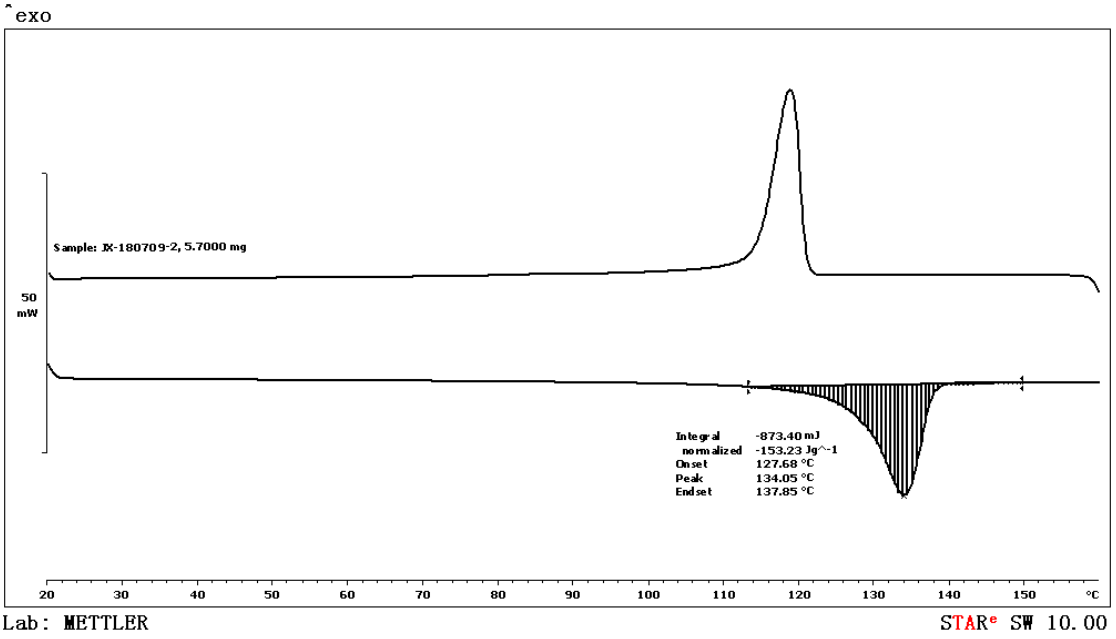


Figure S74. DSC data of the polymer from table 1, entry 5.

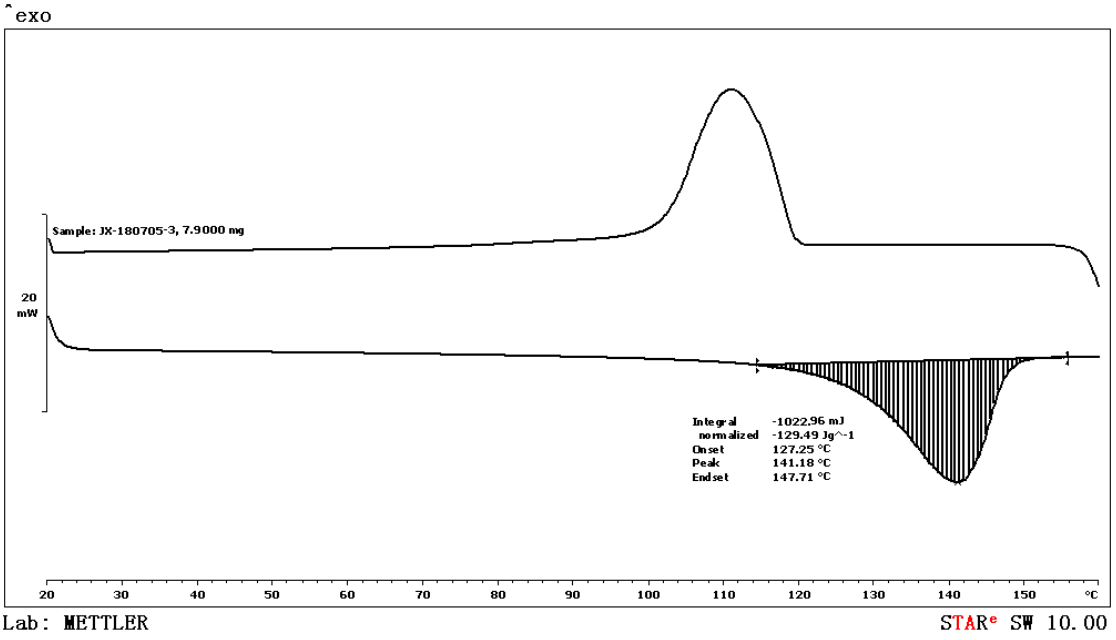


Figure S75. DSC data of the polymer from table 1, entry 6.

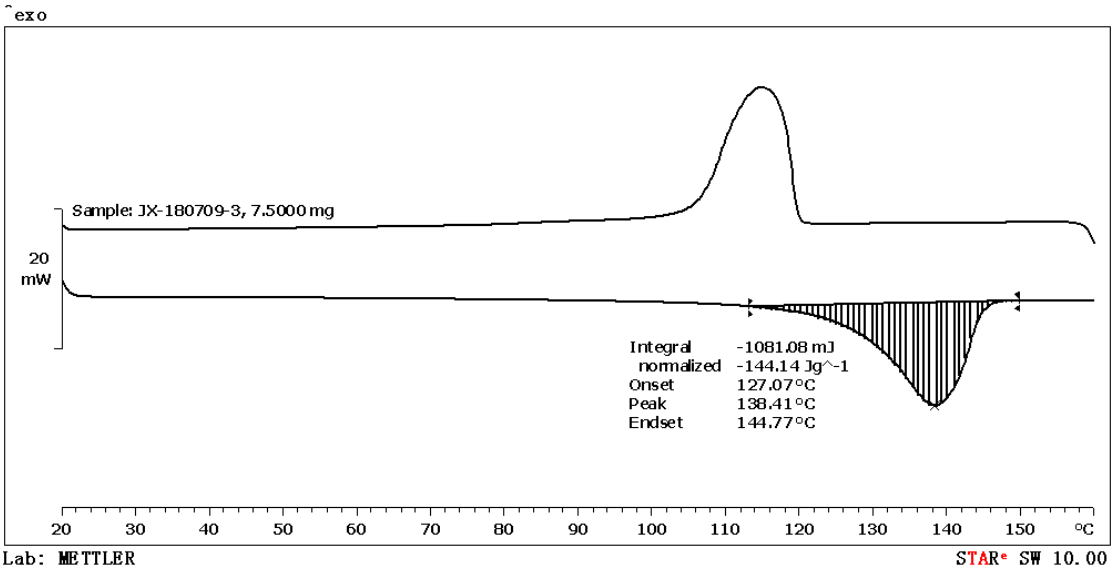


Figure S76. DSC data of the polymer from table 1, entry 7.

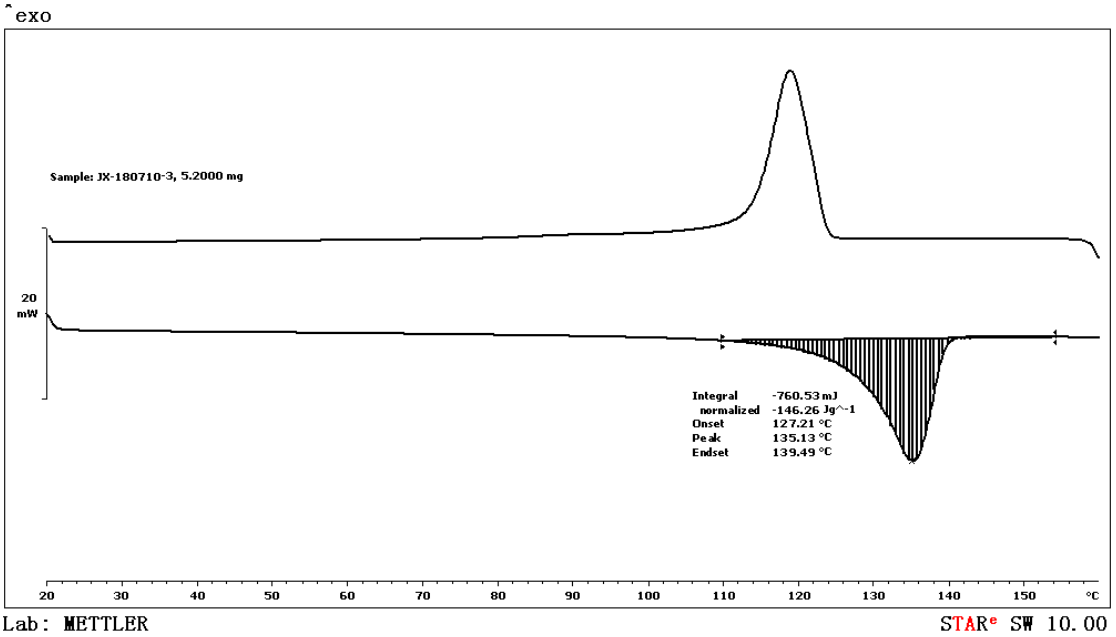


Figure S77. DSC data of the polymer from table 1, entry 8.

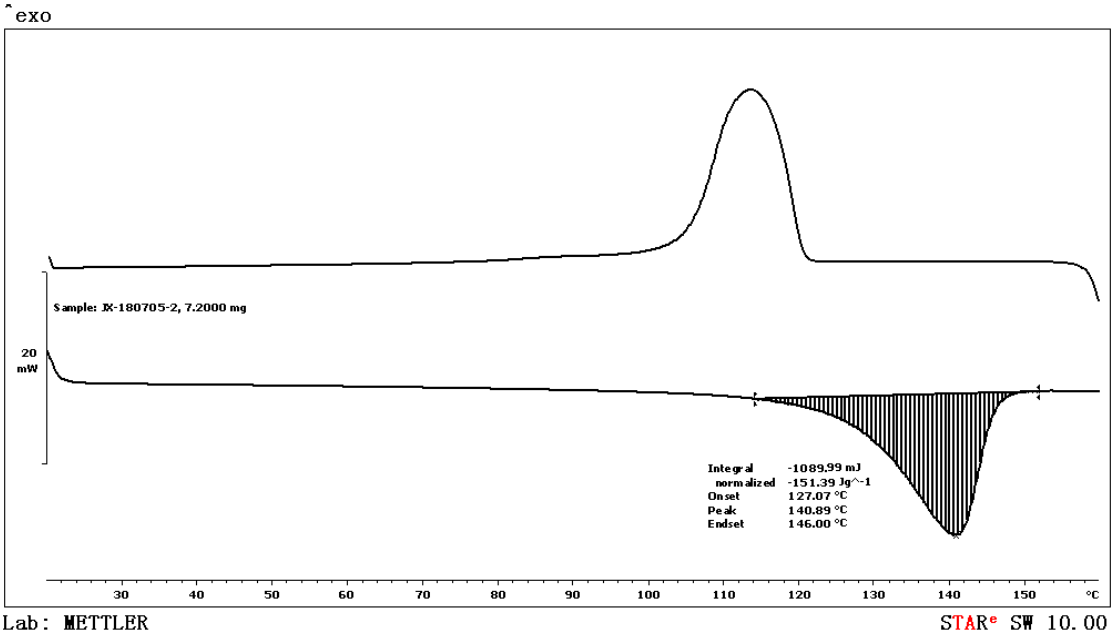


Figure S78. DSC data of the polymer from table 1, entry 9.

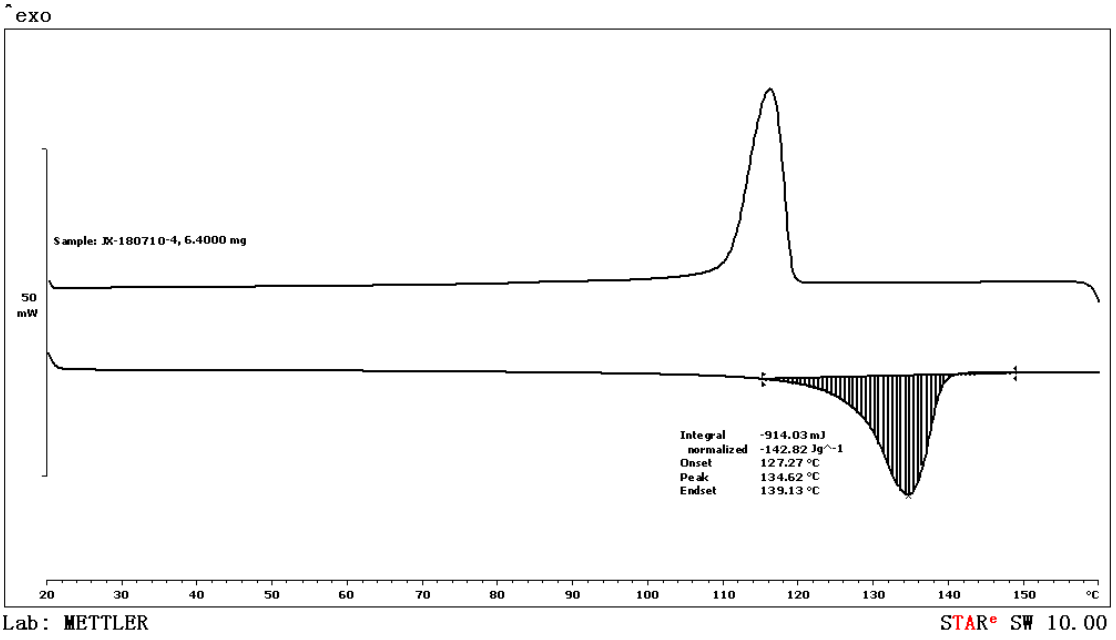


Figure S79. DSC data of the polymer from table 1, entry 10.

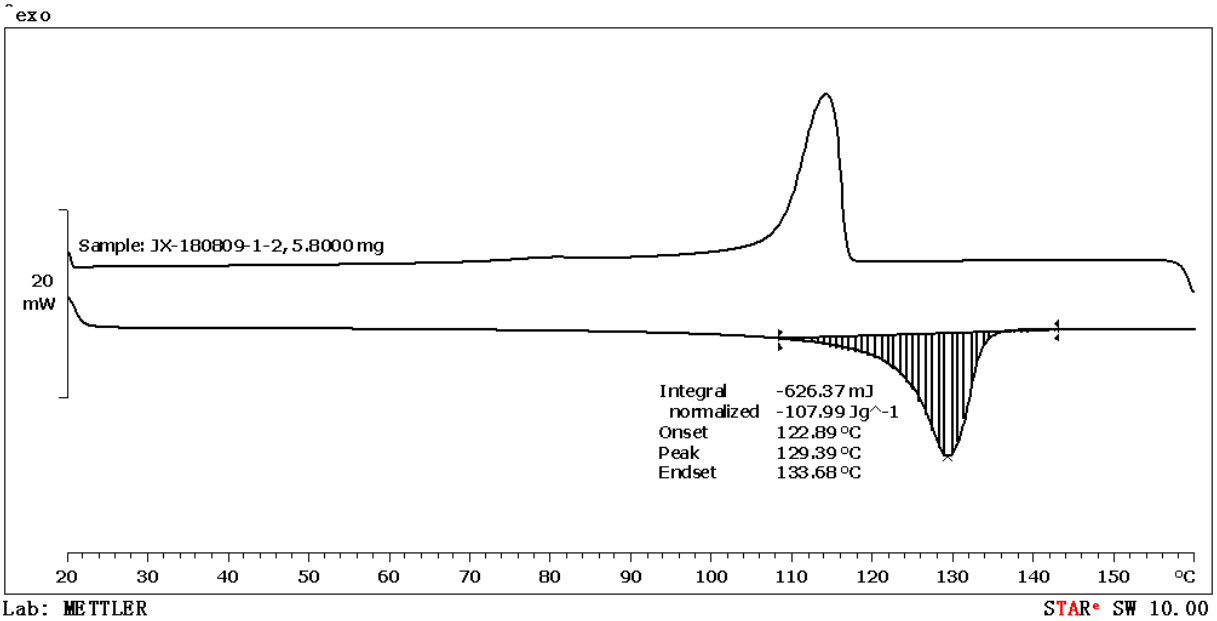


Figure S80. DSC data of the polymer from table 2, entry 2.

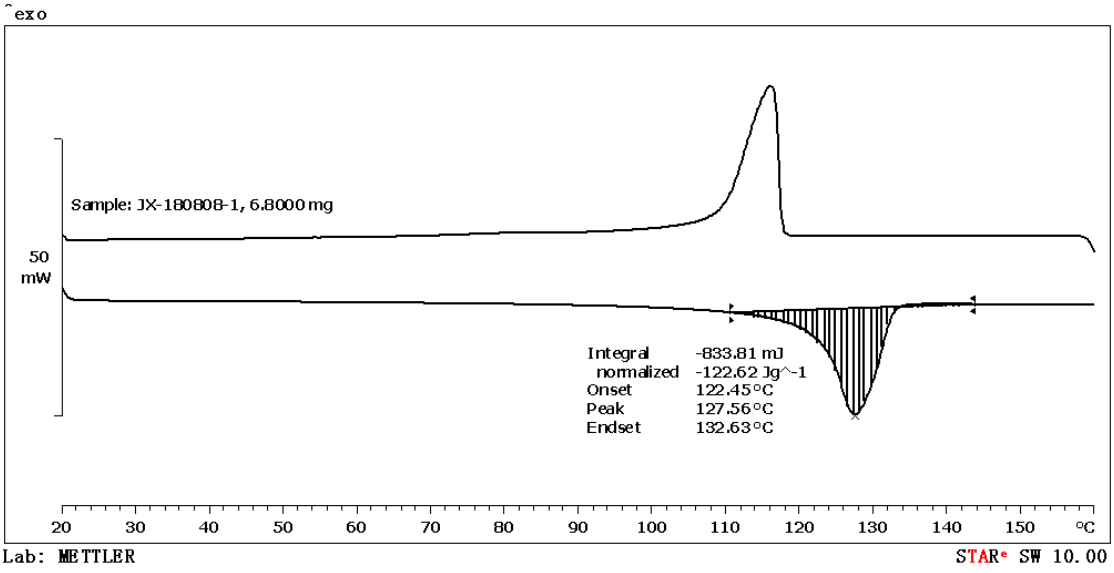


Figure S81. DSC data of the polymer from table 2, entry 3.

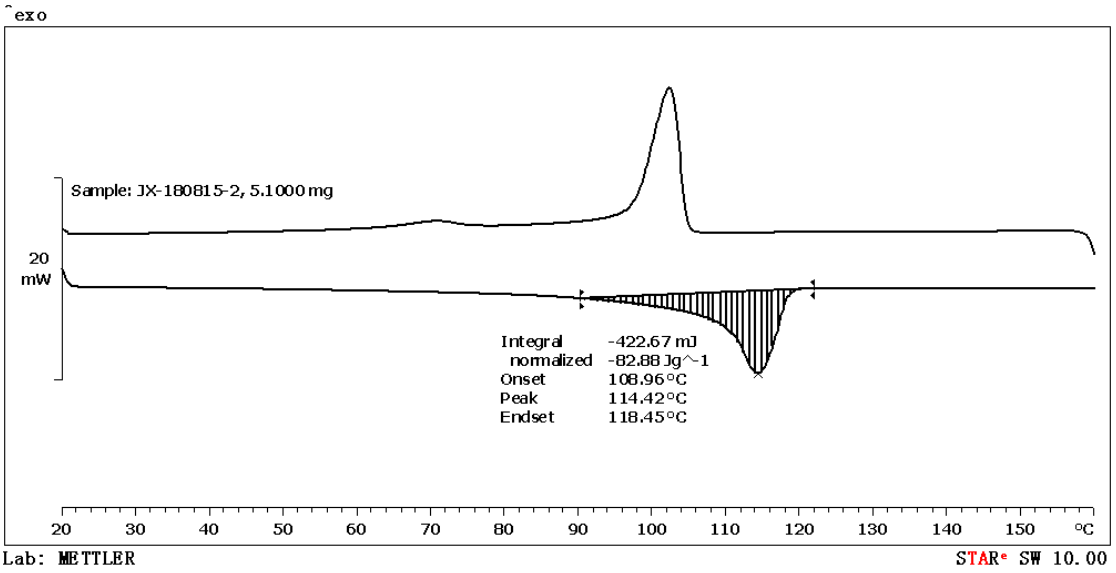


Figure S82. DSC data of the polymer from table 2, entry 6.

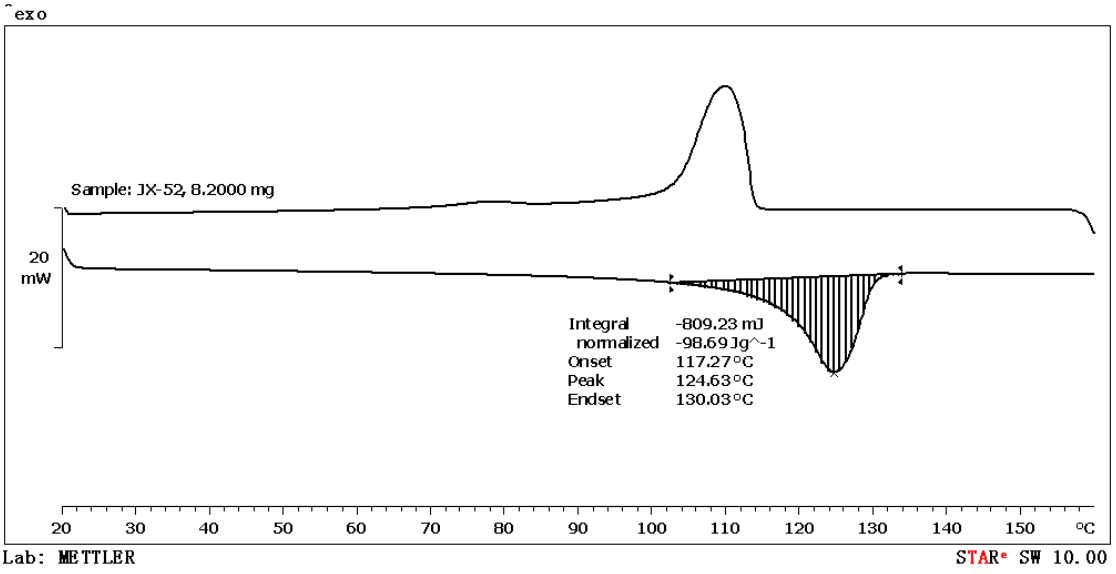


Figure S83. DSC data of the polymer from table 2, entry 9.

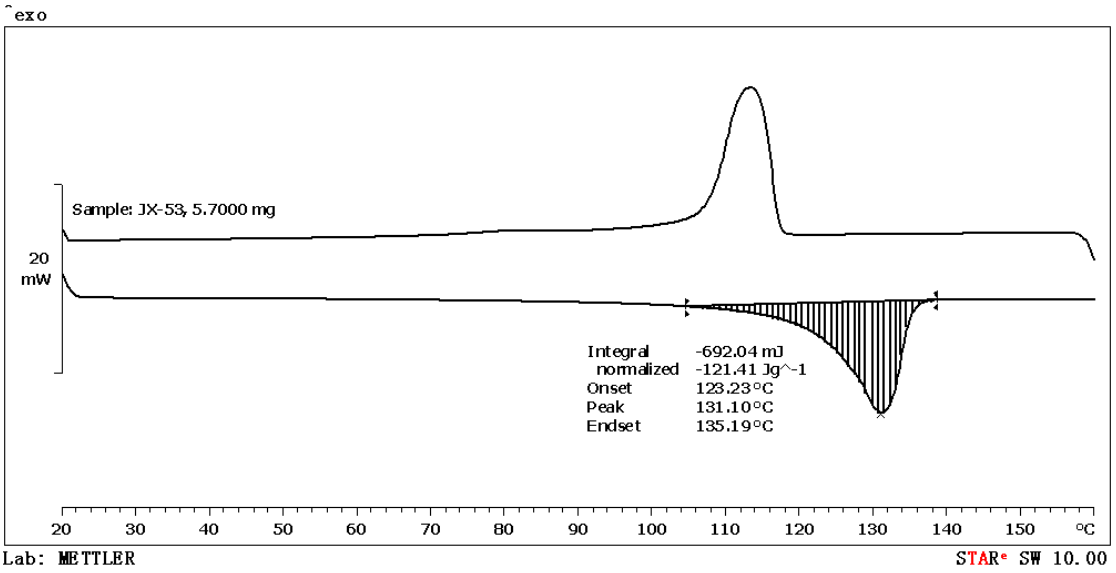


Figure S84. DSC data of the polymer from table 2, entry 10.

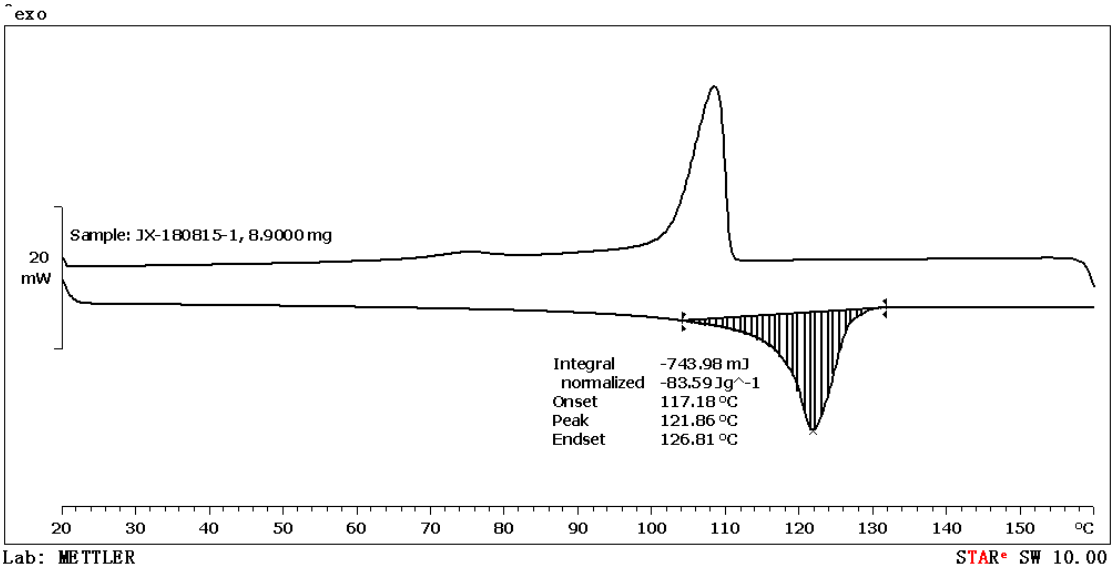


Figure S85. DSC data of the polymer from table 2, entry 12.

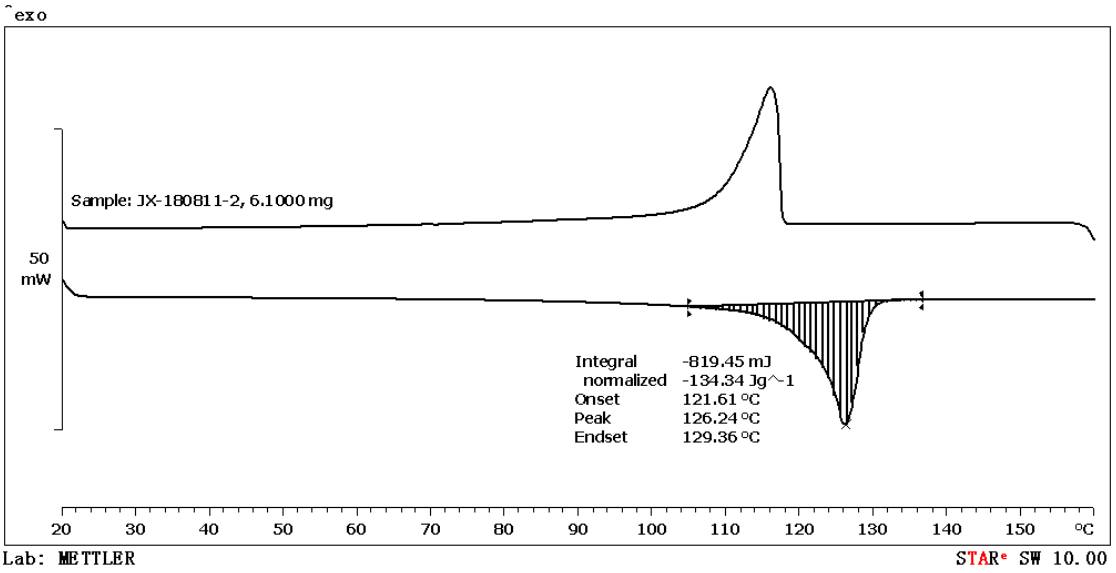


Figure S86. DSC data of the polymer from table 2, entry 13.

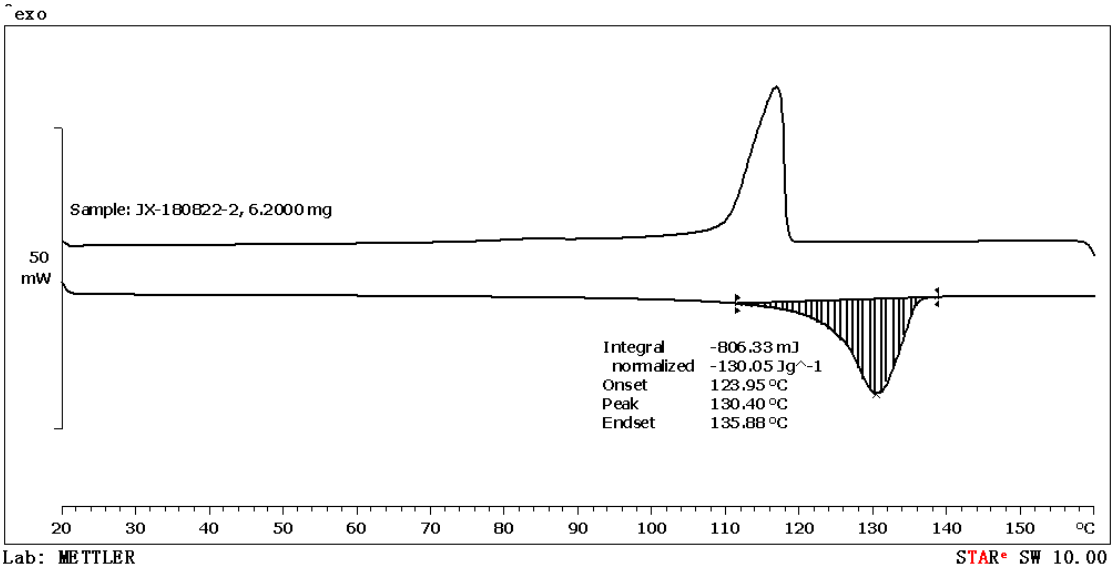


Figure S87. DSC data of the polymer from table 2, entry 16.

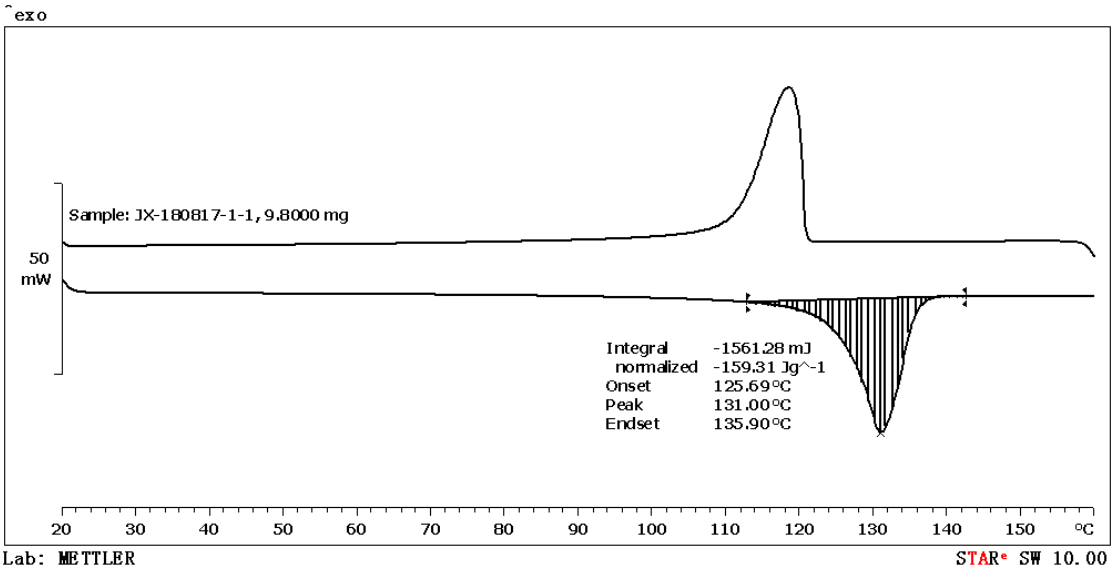


Figure S88. DSC data of the polymer from table 2, entry 18.

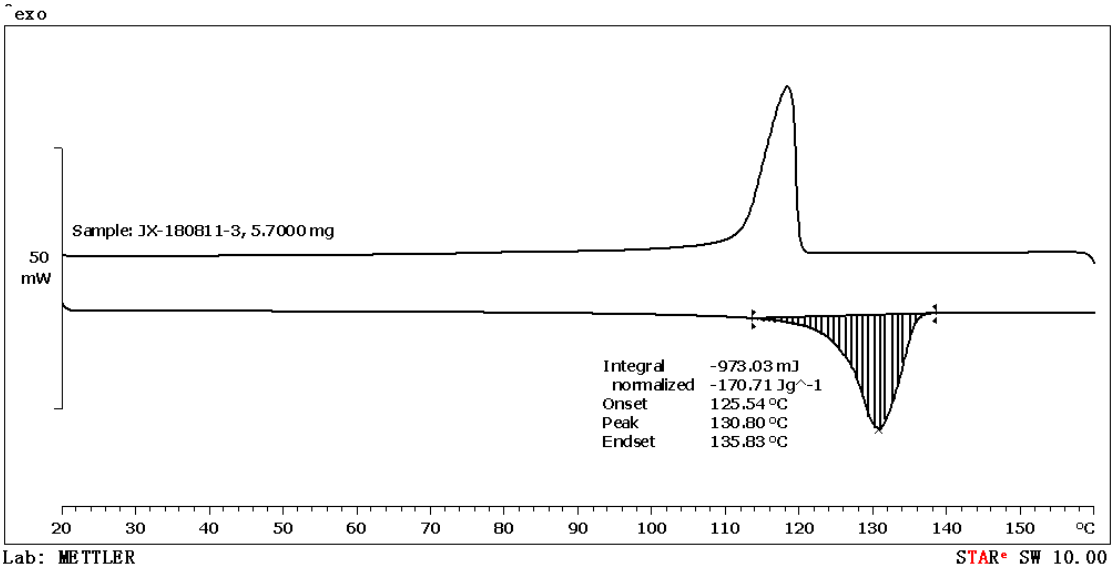


Figure S89. DSC data of the polymer from table 2, entry 19.

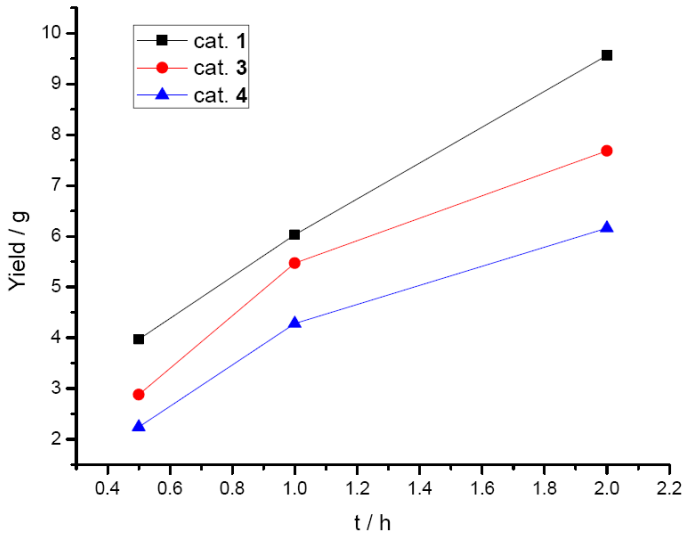


Figure S90. Time-dependence studies of catalysts towards ethylene polymerization.

Table S1. Crystallographic data for **L1**, and **3**.

	L1	**3**
Formula	$C_{31}H_{38}Cl_2O_5PS$	$C_{34}H_{38}F_2NO_3PPdS$
Formula weight	624.54	716.08
Crystal dimensions (mm^3)	0.32 × 0.11 × 0.08	0.31 × 0.20 × 0.05
Crystal system	hexagonal	orthorhombic
Space group	P 65	P 21 21 21
a (Å)	22.6855(8)	9.1697(6)
b (Å)	22.6855(8)	9.5203(6)
c (Å)	10.7563(7)	36.333(2)
α (°)	90	90
β (°)	90	90
γ (°)	120	90
Volume ($Å^3$)	4793.9(5)	3171.9(4)
Z	6	4
T (K)	298(2)	298(2)
D_{calcd} (g cm^{-3})	1.298	1.500
μ (mm^{-1})	0.356	0.749
F (000)	1974	1472
No. of rflns. collected	24765	16352
No. of indep. rflns. /R_{int}	5002 / 0.0598	5595 / 0.0751
No. of obsd. rflns. [$I_0 > 2\sigma(I_0)$]	4358	4534
Data / restraints / parameters	5002 / 1 / 365	5595 / 0 / 388
R_1 / wR_2 [$I_0 > 2\sigma(I_0)$]	0.0514 / 0.1419	0.0468 / 0.0837
R_1 / wR_2 (all data)	0.0623 / 0.1592	0.0662 / 0.0898
GOF (on F^2)	0.934	0.964
Largest diff. peak and hole (e $Å^{-3}$)	0.312 / –0.436	0.674 / –0.412
CCDC No.	1868503	1868504

(1) SMART, version 5.054; Bruker AXS Inc.: Madison, WI, 2000.

(2) SAINT and SADABS, version 6.22; Bruker AXS Inc.: Madison, WI, 2000.

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