

Supporting information

Abnormal *N*-Heterocyclic Carbene Palladium Complexes for the Copolymerization of Ethylene and Polar Monomers

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1. General Remarks

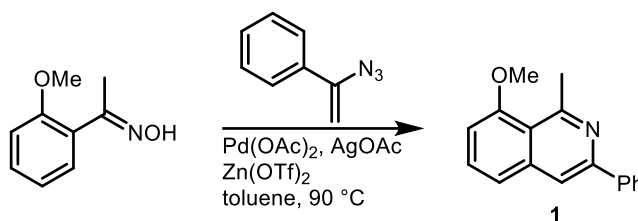
All reactions were carried out under an inert atmosphere of argon by using Schlenk techniques or in a nitrogen-filled Vacuum Atmospheres glovebox with a high-capacity recirculator. Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL spectrometer operating at 400 MHz or 500 MHz for ^1H NMR and at 101 MHz or 126 MHz for ^{13}C NMR. All chemical shifts for ^1H and ^{13}C NMR spectroscopy were referenced to residual signals from chloroform- d (^1H : $\delta = 7.26$ ppm; ^{13}C : $\delta = 77.16$ ppm), dichloromethane- d_2 (^1H : $\delta = 5.32$ ppm; ^{13}C : $\delta = 53.84$ ppm), 1,1,2,2-tetrachloroethane- d_2 (^1H : $\delta = 6.00$ ppm; ^{13}C : $\delta = 73.80$ ppm), or benzene- d_6 (^1H : $\delta = 7.16$ ppm; ^{13}C : $\delta = 128.06$ ppm). Quantitative ^{13}C NMR analyses of polymers were performed in a 5-mm NMR tube on ca. 5–10 wt.% solutions of the polymers in 1,1,2,2-tetrachloroethane with 0.05 M $\text{Cr}(\text{acac})_3$ as a relaxation agent. High-temperature gel permeation chromatography (GPC) was performed on an Agilent PL-GPC 220 instrument equipped with a refractive index detector, two PL-Gel Mixed B columns, and one Guard column. GPC columns were eluted with 1,2,4-trichlorobenzene (TCB) containing 0.0125 wt.% di-*tert*-butylhydroxytoluene at 160 °C, at a run rate of 1.0 mL/min. The samples were prepared in TCB and heated at 160 °C for at least 2–3 hours prior to injection. The GPC data were calibrated with narrow polystyrene standards, and the molecular weights were corrected by universal calibration with the Mark–Houwink parameters described by Rudin et al.¹: $K = 1.75 \times 10^{-2} \text{ cm}^3/\text{g}$ and $\alpha = 0.67$ for polystyrene; $K = 5.90 \times 10^{-2} \text{ cm}^3/\text{g}$ and $\alpha = 0.69$ for LLDPE, $K = 1.56 \times 10^{-2} \text{ cm}^3/\text{g}$ and $\alpha = 0.76$ for polypropylene. Differential scanning calorimetry (DSC) was performed with a DSC Q20 apparatus from TA Instruments. The maximum point endotherm (heating scan) was taken as the melting temperature. High-resolution gas chromatography/mass spectrometry analysis was performed by using a JEOL JMS-700 MStation mass spectrometer.

Tetrahydrofuran (THF), dichloromethane (CH_2Cl_2), N,N-dimethylformamide (DMF) and

diethyl ether (Et₂O) were dried under a positive pressure of dry nitrogen with a J. C. Meyer Solvent Purification System prior to use. Ethanol was dried over 4 Å molecular sieves. Commercial ethylene (99.999%) was purchased from Sinil Gas Co. and purified by passing it through a column packed with BASF catalyst R3-11G, activated carbon, and 4 Å molecular sieves. Commercial propylene (99.99%) was purchased from Daedeok Gas Co. and used as received. The following reagents were distilled from calcium hydride before use: methyl acrylate, allyl acetate, allyl chloride, *tert*-butyl acrylate, allyl ethyl ether, acrylonitrile, butyl vinyl ether, vinyl acetate, toluene and *n*-hexene. The following compounds were prepared according to the procedures reported in literature: 1-(2-methoxyphenyl)ethan-1-one oxime,² 1-azidovinylbenzene,³ 2,6-di(3-pentyl)aniline,⁴ PdClMe(cod),⁵ [PdMeCl(lut)]₂,^{5a,6} PdClMe(Py)⁷. Unless specified, all other chemicals were purchased from Sigma–Aldrich Co., Acros Organics, TCI, Alfa Aesar, or Strem Chemicals Inc. and were used as received without further purification.

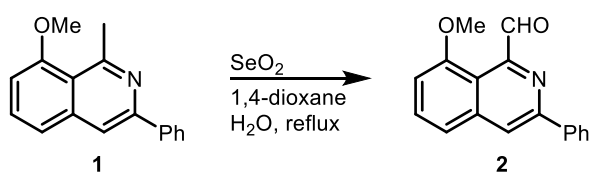
2. Ligands and Catalysts Preparation

Synthesis of 8-methoxy-1-methyl-3-phenylisoquinoline (1)



The procedure was a modified version of that reported by Deng et al.⁸ 1-(2-methoxyphenyl)ethan-1-one oxime (165 mg, 1.0 mmol) and 1-azidovinylbenzene (174 mg, 1.2 mmol), Pd(OAc)₂ (45 mg, 0.2 mmol), AgOAc (83 mg, 0.5 mmol) and Zn(OTf)₂ (73 mg, 0.2 mmol) were added to toluene (6.7 mL). The reaction mixture was stirred at 90 °C for 12 hours. The crude product was cooled to room temperature and concentrated under vacuum. The mixture was purified by flash column chromatography (silica, *n*-hexane: ethylacetate 20:1), and product **1** was obtained as a yellow oil (137 mg, 55%). The ¹H NMR signals of the product were assigned according to the literature.⁹

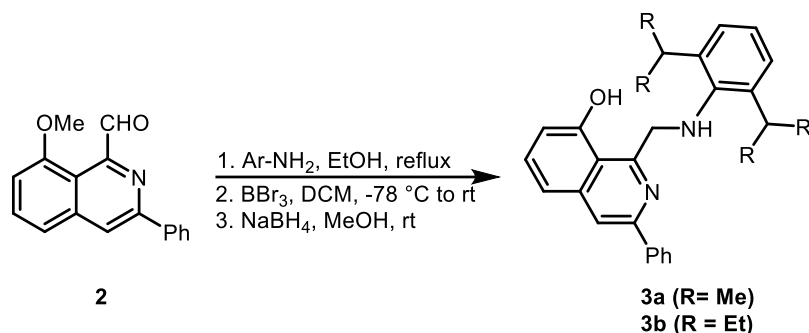
Synthesis of 8-methoxy-3-phenylisoquinoline-1-carbaldehyde (2)



1 (2.30 g, 9.23 mmol) and SeO₂ (3.07 g, 27.7 mmol) were added to 1,4-dioxane (84 mL) and H₂O (3 mL), and the mixture was stirred at 90 °C overnight. The mixture was extracted with dichloromethane and dried over anhydrous Na₂SO₄. The volatiles were removed under vacuum, and the residue was purified by flash chromatography (silica, *n*-hexane:ethyl acetate 6:1) to obtain the product **2** (2.33 g, 96%) as a yellow solid. ¹H NMR (400 MHz, CDCl₃): δ 10.84 (s, 1H), 8.19 – 8.15 (m, 2H), 8.11 (s, 1H), 7.63 (t, *J* = 8.0 Hz, 1H), 7.52 – 7.47 (m, 3H), 7.44 –

7.40 (m, 1H), 6.95 (d, $J = 7.6$ Hz, 1H), 4.03 (s, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 193.8 156.2 154.3, 151.2 139.5 138.5, 131.6 129.1, 128.9, 127.2, 120.1, 118.3, 118.1 106.9, 56.1 pm; HR-MS (EI): calcd. for $\text{C}_{17}\text{H}_{13}\text{NO}_2$ [M] 263.0946 found 263.0943.

Synthesis of Compounds 3a–b

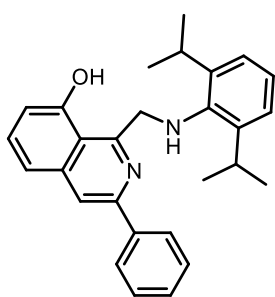


First step: Compound **2** (1.0 equiv.) and substituted aniline (1.0 equiv.) were added to ethanol (0.5 M). The reaction mixture was heated to reflux overnight. A yellow precipitate formed, and the mixture was allowed to cool to room temperature. The precipitate was purified by recrystallization with ethanol or by flash column chromatography (basic silica, *n*-hexane: ethylacetate 15:1) to obtain an imine product.

Second step: The synthesized imine compound (1.0 equiv.) was dissolved in dichloromethane (0.2 M) and cooled to -78°C . Boron tribromide (1.0 M in dichloromethane, 2.5 equiv.) was added dropwise to the cooled solution. The reaction mixture was allowed to warm to room temperature and stirred overnight. Subsequently, water was carefully added and the mixture was neutralized with 2M K_2CO_3 . The organic phase was separated, and the aqueous phase was washed with dichloromethane. The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude product was used in the next step without further purification.

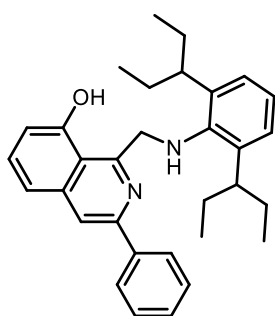
Third step: The imine precursor (1.0 equiv.) was dissolved in methanol (0.12 M) and cooled to 0 °C. Sodium borohydride (excess) was added into the mixture and stirred for 30 min at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 4 h. The reaction was quenched with water, and the mixture was extracted with diethyl ether and dried over anhydrous Na₂SO₄. The mixture was purified by flash column chromatography (silica, *n*-hexane: ethylacetate 20:1) to obtain an amine compound.

1-(((2,6-diisopropylphenyl)amino)methyl)-3-phenylisoquinolin-8-ol (3a)



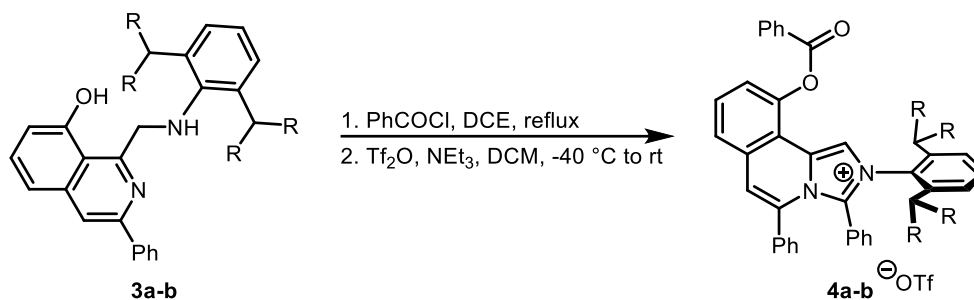
Pale yellow solid, 95% yield (3 steps); ¹H NMR (400 MHz, CDCl₃): δ 8.17 (d, *J* = 7.2 Hz, 2H), 8.06 (s, 1H), 7.62 (t, *J* = 7.9 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 2H), 7.46 – 7.39 (m, 2H), 7.23 (s, 3H), 7.16 (d, *J* = 7.7 Hz, 1H), 4.74 (s, 2H), 3.43 (hept, *J* = 6.8 Hz, 2H), 1.34 (d, *J* = 6.8 Hz, 12H) ppm; ¹³C NMR (101 MHz, CD₂Cl₂): δ 155.9, 143.3 140.0, 138.8 132.4 129.2, 129.2 127.0, 124.9 118.8, 117.7, 113.8, 28.8 24.4 ppm; HR-MS (EI): calcd. for C₂₈H₃₀N₂O [M] 410.2358 found 410.2350.

1-(((2,6-di(pentan-3-yl)phenyl)amino)methyl)-3-phenylisoquinolin-8-ol (3b)



Pale yellow solid, 49% yield (3 steps); ¹H NMR (400 MHz, CD₂Cl₂): δ 8.22 – 8.18 (m, 2H), 8.09 (s, 1H), 7.62 (t, *J* = 7.9 Hz, 1H), 7.52 – 7.38 (m, 4H), 7.24 (dd, *J* = 8.2, 7.2 Hz, 1H), 7.15 – 7.10 (m, 3H), 4.67 (s, 2H), 2.98 (m, 2H), 2.12 (s, 1H), 1.85 – 1.72 (m, 4H), 1.67 – 1.54 (m, 4H), 0.88 – 0.80 (m, 12H) ppm; ¹³C NMR (101 MHz, CDCl₃): δ 155.6, 154.4 148.7 144.0, 142.6, 140.0, 138.9, 131.9, 130.1, 128.8 128.6, 126.7 126.1, 124.6 124.0, 119.3, 118.9, 118.6, 117.2, 114.9, 70.0, 42.5, 29.9, 28.1, 12.3, 12.2 ppm; HR-MS (FAB): calcd. for C₃₂H₃₈N₂O [M] 466.2984 found 466.3002.

Synthesis of Compounds 4a–b



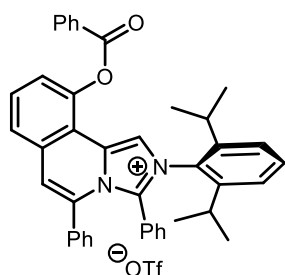
The procedure was a modified version of that reported by Shi group et al.¹⁰

First step: Amine precursors **3a–b** (1.0 equiv.) and benzoyl chloride (2.5 equiv.) were dissolved in 1,2-dichloroethane (0.16 M) and heated to reflux overnight. The crude product was cooled to room temperature and concentrated under vacuum. The mixture was purified by flash column chromatography (silica, *n*-hexane: ethylacetate 6:1) to obtain an amino compound.

Second step: The synthesized amino compound (1.0 equiv.) was added to dichloromethane (0.15 M) and cooled to -40 °C. Triethylamine (1.1 equiv.) was added dropwise into the mixture. After 5 mins, trifluoromethanesulfonic anhydride (1.1 equiv.) was added carefully. The reaction mixture was allowed to warm to room temperature and stirred overnight. The volatiles were removed under vacuum, and the residue was purified by flash chromatography (silica, *n*-hexane:ethyl acetate:dichloromethane:methanol 5:5:5:1) to obtain the product.

10-(benzoyloxy)-2-(2,6-diisopropylphenyl)-3,5-diphenylimidazo[5,1-*a*]isoquinolin-2-ium trifluoromethanesulfonate (**4a**)

White powder, 57% yield (2 steps); ¹H NMR (400 MHz, CD₂Cl₂): δ 8.26 (d, *J* = 7.8 Hz, 2H),



8.07(s, 1H), 7.95 – 7.90 (m, 2H), 7.70 (m, 2H), 7.57 – 7.50 (m, 3H),

7.41 (t, *J* = 7.8 Hz, 1H), 7.26 (d, *J* = 7.0 Hz, 2H), 7.19 – 7.06 (m, 6H),

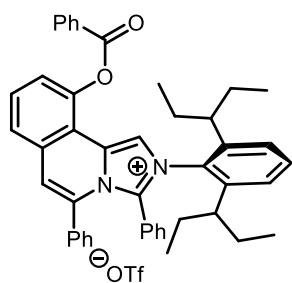
6.97 (t, *J* = 7.8 Hz, 2H), 6.83 (d, *J* = 7.4 Hz, 2H), 2.19 (hept, *J* = 6.8

Hz, 2H), 0.98 (d, *J* = 6.8 Hz, 6H), 0.90 (d, *J* = 6.7 Hz, 6H) ppm; ¹⁹F

NMR (376 MHz, CD₂Cl₂): -78.92 ppm; ¹³C NMR (101 MHz, CD₂Cl₂): δ 164.4, 147.2, 145.4, 139.5, 135.4, 135.0, 132.5, 132.0, 131.8, 131.6, 130.6, 130.5, 130.3, 130.2, 129.8, 129.7, 129.7, 128.8, 128.5, 128.4, 128.2, 126.4, 125.0, 124.7, 123.8, 122.9, 122.0, 119.7, 118.8, 115.5, 29.1, 26.0, 22.0 ppm; HR-MS (FAB): calcd. for C₄₂H₃₇N₂O₂ [M] 601.2850 found 601.2827.

10-(benzoyloxy)-2-(2,6-di(pentan-3-yl)phenyl)-3,5-diphenylimidazo[5,1-a]isoquinolin-2-ium trifluoromethanesulfonate (4b)

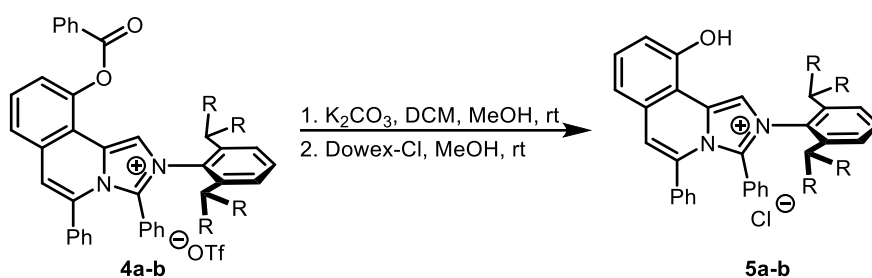
White powder, 47% yield (2 steps); ¹H NMR (400 MHz, CD₂Cl₂): δ 8.23 – 8.18 (m, 2H), 8.16



(d, *J* = 1.1 Hz, 1H), 7.99 – 7.93 (m, 2H), 7.76 – 7.71 (m, 1H), 7.68 (td, *J* = 7.6, 1.2 Hz, 1H), 7.57 (d, *J* = 1.0 Hz, 1H), 7.53 – 7.44 (m, 3H), 7.22 – 7.06 (m, 8H), 6.96 (t, *J* = 7.5 Hz, 2H), 6.84 – 6.78 (m, 2H), 1.65 – 1.56 (m, 3H), 1.51 – 1.38 (m, 2H), 1.25 – 1.16 (m, 3H), 0.86 –

0.76 (m, 2H), 0.72 (t, *J* = 7.2 Hz, 6H), 0.49 (t, *J* = 7.0 Hz, 6H) ppm; ¹⁹F NMR (376 MHz, CD₂Cl₂): -78.87 ppm; ¹³C NMR (101 MHz, CDCl₃): δ 163.9, 146.4, 143.1, 139.0, 135.1, 134.2, 132.0, 131.8, 131.7, 131.4, 131.3, 130.3, 130.1, 129.7, 129.2, 128.7, 128.5, 128.1, 127.8, 127.4, 126.5, 125.5, 124.4, 124.1, 122.4, 121.6, 119.7, 119.2, 114.8, 42.6, 28.6, 27.9, 12.4, 11.8 ppm; HR-MS (FAB): calcd. for C₄₆H₄₅N₂O₂ [M] 657.3476 found 657.3474.

Synthesis of Ligands 5a–b

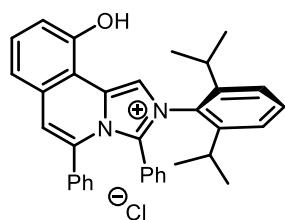


Ligand precursor **4a–b** (1.0 equiv.) and potassium carbonate (excess) were added to a mixture of dichloromethane and methanol (v/v, 2/1). The reaction mixture was stirred at room

temperature overnight. After the mixture had been passed through a plug of Celite, the volatiles were removed under vacuum. The crude product was used in the next step without further purification. The residue was dissolved in methanol, and Dowex-Cl was added into the mixture. The reaction mixture was stirred overnight. The solvent was removed in vacuo, and the residue was purified by flash column chromatography (silica, dichloromethane:methanol 20:1) to obtain the product.

10-hydroxy-2-(2,6-diisopropylphenyl)-3,5-diphenylimidazo[5,1-*a*]isoquinolin-2-ium chloride (5a)

White powder, 69% yield; ¹H NMR (400 MHz, CD₂Cl₂): δ 8.93 (s, 1H), 7.85 (brs, 1H), 7.54

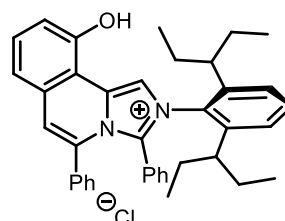


(t, *J* = 7.9 Hz, 1H), 7.49 (t, *J* = 7.9 Hz, 1H), 7.32 (s, 1H), 7.27 – 7.17 (m, 5H), 7.16 – 7.10 (m, 2H), 7.10 – 7.04 (m, 2H), 6.97 (t, *J* = 7.9 Hz, 2H), 6.83 (dd, *J* = 8.3, 1.1 Hz, 2H), 2.28 (hept, *J* = 6.7 Hz, 2H), 1.20

(d, *J* = 6.8 Hz, 6H), 0.98 (d, *J* = 6.8 Hz, 6H) ppm; ¹³C NMR (101 MHz, CDCl₃): δ 145.0, 136.1, 132.6, 132.0, 131.6, 131.2, 130.9, 130.0, 130.0, 129.7, 129.1, 128.5, 128.1, 127.8, 124.3, 122.4, 119.1, 117.1, 109.8, 28.7, 25.8, 22.1 ppm; HR-MS (FAB): calcd. for C₃₅H₃₃N₂O [M] 497.2587 found 497.2601.

10-hydroxy-2-(2,6-di(pentan-3-yl)phenyl)-3,5-diphenylimidazo[5,1-*a*]isoquinolin-2-ium chloride (5b)

White powder 83% yield; ¹H NMR (400 MHz, CD₂Cl₂): δ 12.60 (s, 1H), 8.79 (s, 1H), 8.20 (d,

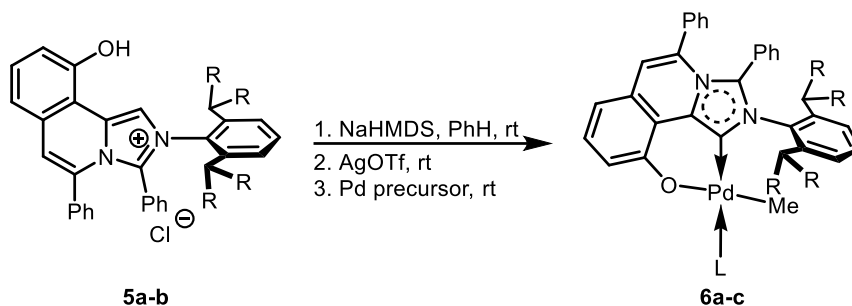


J = 7.4 Hz, 1H), 7.63 (t, *J* = 8.0 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 1H), 7.37 (s, 1H), 7.32 (d, *J* = 7.6 Hz, 1H), 7.21 – 7.04 (m, 8H), 6.94 (t, *J* = 8.0 Hz, 2H), 6.82 (dd, *J* = 8.3, 1.1 Hz, 2H), 1.80 – 1.63 (m, 4H), 1.59 –

1.41 (m, 4H), 0.98 – 0.86 (m, 2H), 0.79 (t, *J* = 7.4 Hz, 6H), 0.70 (t, *J* = 7.4 Hz, 6H) ppm; ¹³C

NMR (101 MHz, CDCl₃): δ 156.1, 143.0, 136.3, 132.4, 132.2, 131.7, 131.4, 131.3, 131.2, 129.6, 129.3, 129.0, 128.5, 128.3, 128.2, 127.8, 125.4, 124.7, 122.2, 120.5, 117.8, 117.4, 109.4, 42.4, 28.3, 26.9, 12.3, 11.2 ppm; HR-MS (FAB): calcd. for C₃₉H₄₁N₂O [M] 553.3213 found 553.3210

Synthesis of *aImPy*-Pd complexes 6a–c

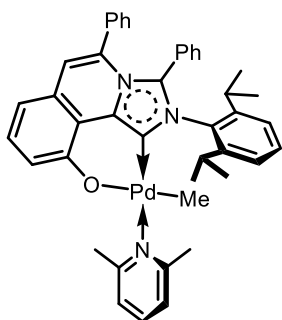


The procedure was a modified version of that reported by Nozaki et al.¹¹ Ligand (1.0 equiv.) and NaHMDS (2.1 equiv.) were dissolved in dry benzene (0.03M). The reaction mixture was stirred at room temperature for 1 h. Silver triflate (1.1 equiv.) was added, and the mixture was stirred for an additional 1 h in the dark. Pd precursor was then added to the mixture, which was stirred for another 3 h in the dark. The resultant mixture was passed through a cotton pad equipped with a syringe filter, and was then evaporated to dryness. The resultant solid was dissolved in the minimum amount of dichloromethane. The solution was filtered through neutral alumina with a mixture of ethyl acetate and dichloromethane. The solvents were removed in vacuo, and the residue was washed with *n*-hexane to give the product.

Note: Similar to the results reported with the Pd/IzQO system,¹¹ an equilibrium with a dimeric species was observed. Thus, the ¹H and ¹³C NMR spectra were recorded in the presence of additional 2,6-lutidine or pyridine.

***aImPy*-Pd complex (6a)**

The use of [PdMeCl(lut)]₂ (0.5 equiv.) as Pd precursor; yellow powder, 55% yield; ¹H NMR

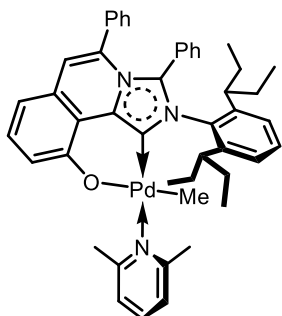


(400 MHz, CD₂Cl₂): δ 7.56 (t, J = 7.7 Hz, 1H), 7.37 (t, J = 7.8 Hz, 1H), 7.20 (t, J = 7.2 Hz, 1H), 7.17 – 6.97 (m, 10H), 6.90 (m, 1H), 6.80 (t, J = 7.7 Hz, 2H), 6.68 (t, J = 8.4 Hz, 4H), 3.12 (s, 6H), 2.57 (m, 2H), 1.46 (d, J = 6.8 Hz, 6H), 0.79 (d, J = 6.9 Hz, 6H), -0.81 (s, 3H) ppm; ¹³C NMR (101 MHz, CD₂Cl₂): δ 160.6, 159.6, 158.0, 145.7, 140.1, 140.1,

137.8, 137.4, 136.6, 135.8, 132.1, 130.5, 130.3, 129.3, 129.2, 128.5, 128.4, 128.3, 128.2, 127.7, 126.5, 125.6, 124.0, 122.7, 122.4, 120.3, 119.3, 116.7, 110.2, 29.1, 28.0, 27.0, 24.6, 23.2, -14.6 ppm; HR-MS (FAB): calcd. for C₄₃H₄₄N₃OPd [M+H] 724.2514 found 724.2485

***aImPy*-Pd complex (6b)**

The use of [PdMeCl(lut)]₂ (0.5 equiv.) as Pd precursor.; yellow powder, 75% yield; ¹H NMR

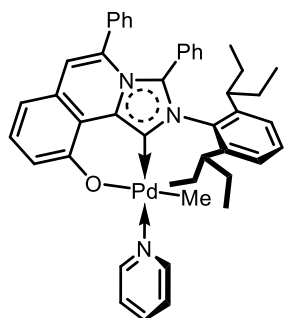


(400 MHz, CD₂Cl₂): δ 7.56 (t, J = 7.7 Hz, 1H), 7.31 (t, J = 7.8 Hz, 1H), 7.79 (t, J = 7.2 Hz, 1H), 7.16 – 6.96 (m, 12H), 6.77 (t, J = 7.2 Hz, 2H), 6.71 – 6.65 (m, 2H), 6.65 – 6.58 (m, 2H), 3.13 (s, 6H), 2.42 – 2.34 (m, 2H), 2.28 (m, 2H), 1.96 – 1.82 (m, 2H), 1.60 – 1.47 (m, 2H), 0.94-0.85 (m, 2H), 0.87 (t, J = 7.4 Hz, 6H), 0.64 (t, J = 7.3 Hz, 6H), -0.83 (s, 3H)

ppm; ¹³C NMR (101 MHz, CD₂Cl₂): δ 159.6, 158.0, 143.4, 140.9, 137.6, 137.4, 136.7, 136.0, 135.2, 132.1, 132.0, 130.3, 129.4, 129.1, 128.6, 128.4, 128.2, 127.6, 126.7, 126.2, 125.7, 122.4, 120.3, 119.3, 116.8, 110.1, 41.1, 26.9, 24.5, 24.4, 11.5, 9.7, -14.5 ppm; HR-MS (FAB): calcd. for C₄₇H₅₁N₃OPd [M] 779.3061 found 779.3057

aImPy-Pd complex (6c)

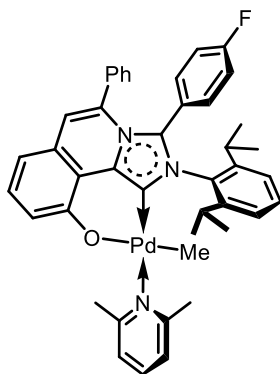
The use of PdMeCl(py)₂ (1.0 equiv.) as Pd precursor.; yellow powder, 35% yield; ¹H NMR



(400 MHz, CD₂Cl₂): δ 8.88 (dd, J = 6.3, 1.4 Hz, 2H), 7.79 (t, J = 7.6 Hz, 1H), 7.42 – 7.32 (m, 4H), 7.16 – 7.10 (m, 3H), 7.07 (d, J = 8.5 Hz, 2H), 7.04 (s, 1H), 7.03 – 6.96 (m, 4H), 6.95 – 6.87 (m, 1H), 6.84 (dd, J = 8.2, 0.8 Hz, 1H), 6.79 (t, J = 7.7 Hz, 2H), 6.74 (d, J = 6.9 Hz, 1H), 6.68 – 6.61 (m, 2H), 2.34 – 2.23 (m, 4H), 1.93 – 1.80 (m, 2H), 1.59 – 1.44 (m, 2H), 0.89 (t, J = 7.3 Hz, 6H), 0.83 (m, 2H), 0.64 (t, J = 7.3 Hz, 6H), -0.47 (s, 3H) ppm; ¹³C NMR (101 MHz, CD₂Cl₂): δ 163.0, 153.4, 151.6, 151.1, 150.2, 143.5, 140.2, 137.9, 137.7, 137.1, 136.2, 135.9, 135.6, 132.3, 132.0, 130.6, 130.3, 129.3, 129.2, 128.7, 128.4, 128.4, 128.2, 127.6, 126.6, 126.2, 125.6, 125.2, 124.5, 124.3, 124.0, 119.5, 116.8, 110.2, 41.1, 24.9, 24.9, 11.7, 9.8, -9.3 ppm; HR-MS (FAB): calcd. for C₄₅H₄₇N₃OPd [M] 751.2748 found 751.2750

aImPy-Pd complex (6d)

Yellow powder, 52% yield; ¹H NMR (400 MHz, CD₂Cl₂): δ 7.56 (td, J = 7.7, 3.7 Hz, 1H), 7.38

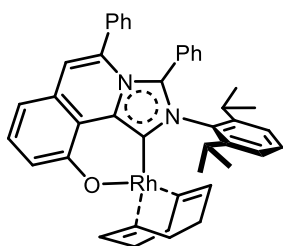


(t, J = 7.8 Hz, 1H), 7.21(t, J = 7.6 Hz, 1H), 7.14 – 7.03 (m, 10H), 6.70 (d, J = 7.4 Hz, 2H), 6.68 – 6.61 (m, 2H), 6.54 – 6.48 (m, 2H), 3.11 (s, 6H), 2.56 (septet, J = 6.8 Hz, 2H), 1.46 (d, J = 6.8 Hz, 6H), 0.82 (d, J = 6.9 Hz, 6H), -0.82 (s, 3H) ppm; ¹⁹F NMR (376 MHz, CD₂Cl₂): -112.61 ppm; ¹³C NMR (101 MHz, CD₂Cl₂): δ 164.0, 163.0, 159.6, 158.0, 145.5, 140.3, 137.5, 136.7, 136.6, 135.6, 134.1, 132.6, 132.5, 132.1, 131.8, 130.4, 129.2, 128.5, 128.4, 128.4, 125.7, 124.1, 122.8, 122.8, 122.7, 122.4, 120.3, 119.4, 116.6, 115.0, 114.7, 110.2, 29.0, 27.0, 24.5, 24.5, 23.3, -14.6 ppm.

Synthesis of [Rh(COD)(NHC)] Catalysts

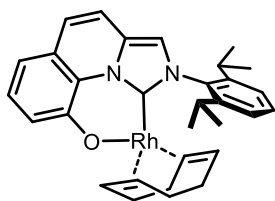
Ligand (1.0 equiv.) and NaHMDS were dissolved in dry benzene (0.03M). The reaction mixture was stirred at room temperature for 1 h. Silver triflate (1.1 equiv.) was added, and the mixture was stirred for an additional 1 h in the dark. [RhCl(COD)]₂ was then added to the mixture, which was stirred for another 3 h in the dark. The resultant mixture was passed through a cotton pad equipped with a syringe filter, and was then evaporated to dryness. The residue was purified by flash column chromatography (silica, *n*-hexane: ethyl acetate 6:1) to obtain the [Rh(COD)NHC] complexes.

[Rh(COD)(*aImPy*)] complex (**7a**)



Following the product **7a** (26%, 8 mg, yellow powder) was obtained from **5a** (0.04 mmol, 14 mg), NaHMDS (0.084 mmol, 15.4 mg), AgOTf (0.044 mmol, 11.3 mg), [RhCl(COD)]₂ (0.02 mmol, 9.9 mg) and benzene (0.8 mL); ¹H NMR (400 MHz, CD₂Cl₂): δ 7.45 (t, J = 7.8 Hz, 1H), 7.33 (dd, J = 8.2, 7.4 Hz, 1H), 7.16 (d, J = 7.8 Hz, 2H), 7.12 (s, 1H), 7.11 – 7.06 (m, 2H), 7.02 – 6.96 (m, 4H), 6.94 – 6.89 (m, 1H), 6.87 (dd, J = 7.4, 0.7 Hz, 1H), 6.78 (t, J = 7.8 Hz, 2H), 6.61 – 6.56 (m, 2H), 4.87 – 4.79 (m, 2H), 3.25-3.24 (m, 2H), 2.46 (hept, J = 6.7 Hz, 2H), 2.29 – 2.09 (m, 4H), 1.83 – 1.68 (m, 4H), 1.48 (d, J = 6.7 Hz, 5H), 0.57 (d, J = 6.8 Hz, 5H) ppm; ¹³C NMR (101 MHz, CD₂Cl₂): δ 161.5, 149.6 (d, J = 53.3 Hz), 145.9, 136.4, 135.9, 135.5, 133.6, 132.5, 130.8, 130.3, 129.5, 129.1, 129.0, 128.5, 128.3 (d, J = 2.0 Hz), 128.1, 127.9, 125.9, 125.6, 124.6, 119.2 (d, J = 1.6 Hz), 115.5 (d, J = 1.2 Hz), 111.7, 93.3 (d, J = 8.5 Hz), 63.2 (d, J = 14.3 Hz), 33.4, 28.9, 28.4, 27.9, 24.3, 24.2 ppm; HR-MS (FAB): calcd. for C₄₃H₄₃N₂ORh [M] 706.2430 found 706.2432.

[Rh(COD)(*n*NHC)] complex (**8a**)



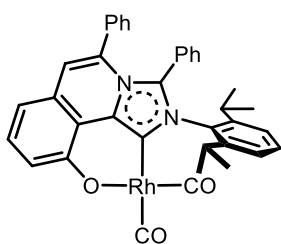
Following the product **8a** (27%, 33 mg, yellow powder) was obtained from 2-(2,6-diisopropylphenyl)imidazo[1,5-a]quinolinium-9-olate (0.2 mmol, 69 mg)¹¹, NaHMDS (0.22 mmol, 40.3 mg), AgOTf (0.22 mmol, 56.5 mg), [RhCl(COD)]₂ (0.1 mmol, 49.3 mg) and benzene (3 mL); ¹H NMR (400 MHz, CD₂Cl₂): δ 7.47 (q, J = 7.8 Hz, 1H), 7.25 (d, J = 7.8 Hz, 2H), 7.17 (dd, J = 8.2, 7.4 Hz, 1H), 7.13 (d, J = 9.4 Hz, 1H), 7.03 (d, J = 9.4 Hz, 1H), 7.00 (s, 1H), 6.93 (dd, J = 8.2, 1.5 Hz, 1H), 6.73 (dd, J = 7.4, 1.5 Hz, 1H), 4.89 – 4.80 (m, 2H), 3.07 – 2.99 (m, 2H), 2.55 (hept, J = 6.9 Hz, 2H), 2.28 – 2.19 (m, 2H), 2.16 – 2.08 (m, 2H), 1.87 – 1.71 (m, 4H), 1.47 (d, J = 6.8 Hz, 6H), 1.06 (d, J = 6.8 Hz, 6H) ppm; ¹³C NMR (101 MHz, CD₂Cl₂): δ 165.7 (d, J = 57.8 Hz), 156.8, 146.2, 136.6, 130.5, 129.0, 128.6, 127.5, 127.3, 126.7, 124.8, 124.1, 120.3, 117.2, 113.8, 112.9, 98.1 (d, J = 8.0 Hz), 65.2 (d, J = 13.7 Hz), 33.3, 28.8, 28.0, 26.1, 23.1 ppm; HR-MS (FAB): calcd. for C₃₁H₃₅N₂ORh [M] 554.1799 found 554.1807

Synthesis of [Rh(CO)₂(NHC)] Catalysts

[Rh(COD)(NHC)] complex and CH₂Cl₂ were added to a 10 mL Schlenk flask equipped with Teflon-valve. The mixture was degassed through three freeze–pump–thaw cycles and CO (1 atm) was charged into the reaction flask. The mixture was stirred for 12 h at room temperature. The solvents were removed in vacuo, and the residue was washed with *n*-hexane to give the product.

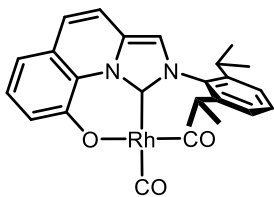
[Rh(CO)₂(*a*ImPy)] complex (**7**)

Following the product **7** (87%, 12 mg, pale yellow powder) was obtained from **7a** (0.02 mmol,



15 mg) and dichloromethane (1 mL); $^1\text{H NMR}$ (400 MHz, CD_2Cl_2): δ 7.45 (t, $J = 7.8$ Hz, 2H), 7.24 – 7.13 (m, 6H), 7.08 – 6.96 (m, 5H), 6.86 (t, $J = 7.8$ Hz, 2H), 6.75 (d, $J = 7.5$ Hz, 2H), 2.28 (hept, $J = 6.7$ Hz, 2H), 1.40 (d, $J = 6.7$ Hz, 6H), 0.85 (d, $J = 6.8$ Hz, 6H) ppm; $^{13}\text{C NMR}$ (101 MHz, CD_2Cl_2): δ 188.3 (d, $J = 71.7$ Hz, CO), 187.1 (d, $J = 54.1$ Hz, CO), 160.1, 155.1 (d, $J = 47.6$ Hz), 146.4, 136.8 (d, $J = 1.99$ Hz), 135.8, 134.6, 132.8, 132.6, 131.5, 130.4, 130.0, 128.8, 128.8, 128.8, 128.5, 127.9, 125.7, 124.9, 124.9, 119.7 (d, $J = 1.79$ Hz), 114.7 (d, $J = 1.49$ Hz), 113.0, 29.0, 25.6, 23.2 ppm; HR-MS (FAB): calcd. for $\text{C}_{37}\text{H}_{32}\text{N}_2\text{O}_3\text{Rh}$ $[\text{M}+\text{H}]^+$ 655.1468 found 655.1463; IR (CH_2Cl_2): $\nu = 1981.15$ (CO), 2059.82 (CO)

[Rh(CO) $_2$ (*n*NHC)] complex (8)



Following the product **8** was obtained from **8a** (0.033 mmol, 20 mg) and dichloromethane (1 mL). However, the complex **8** was confirmed as a crude product without purification. Despite several attempts, an refined complex was not isolated. During purification, we confirmed that the complex was decomposed fastly.; $^1\text{H NMR}$ (400 MHz, C_6D_6): δ 7.64 (d, $J = 8.3$ Hz, 1H), 7.46 – 7.34 (m, 1H), 7.27 (t, $J = 7.8$ Hz, 1 H), 7.24 – 7.18 (m, 2H), 7.08 (d, $J = 7.8$ Hz, 2H), 6.78 – 6.63 (m, 3H), 6.60 (s, 1H), 6.38 (d, $J = 9.4$ Hz, 1H), 2.74 – 2.63 (m, 0.5 H), 2.40 – 2.26 (m, 2H), 1.53 (d, $J = 6.8$ Hz, 2 H), 1.30 (d, $J = 6.8$ Hz, 6H), 1.08 – 1.01 (m, 2 H), 0.94 (d, $J = 6.9$ Hz, 6 H) ppm; $^{13}\text{C NMR}$ (101 MHz, C_6D_6): δ 187.3 (d, $J = 69.2$ Hz, CO), 186.0 (d, $J = 56.2$ Hz, CO), 170.5 (d, $J = 52.6$ Hz), 155.9, 155.6, 146.9, 146.8, 136.6, 131.5, 130.8, 129.7, 129.4, 128.5, 127.3, 127.2, 127.1, 127.0, 126.4, 124.8, 124.6, 122.0 (d, $J = 1.47$ Hz), 120.7 (d, $J = 1.06$ Hz), 115.3 (d, $J = 1.39$ Hz), 114.4 (d, $J = 1.76$ Hz), 114.1, 113.8, 113.4, 112.8, 28.7, 28.7, 25.1, 25.0, 23.8, 23.8 ppm; HR-MS (FAB): calcd. for $\text{C}_{25}\text{H}_{23}\text{N}_2\text{O}_3\text{Rh}$ $[\text{M}]$ 502.0758 found 502.0769; IR (CH_2Cl_2): $\nu = 1992.97$ (CO), 2073.81 (CO).

3. ^1H and ^{13}C NMR Spectra of Ligands and Catalysts

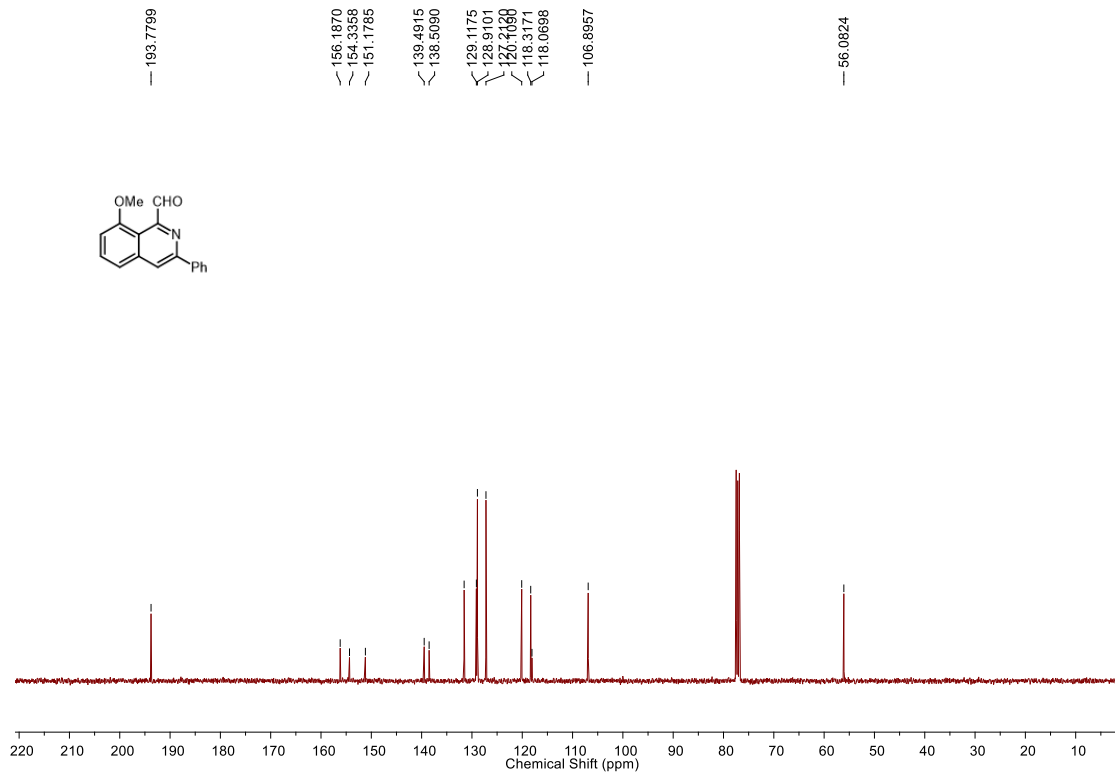
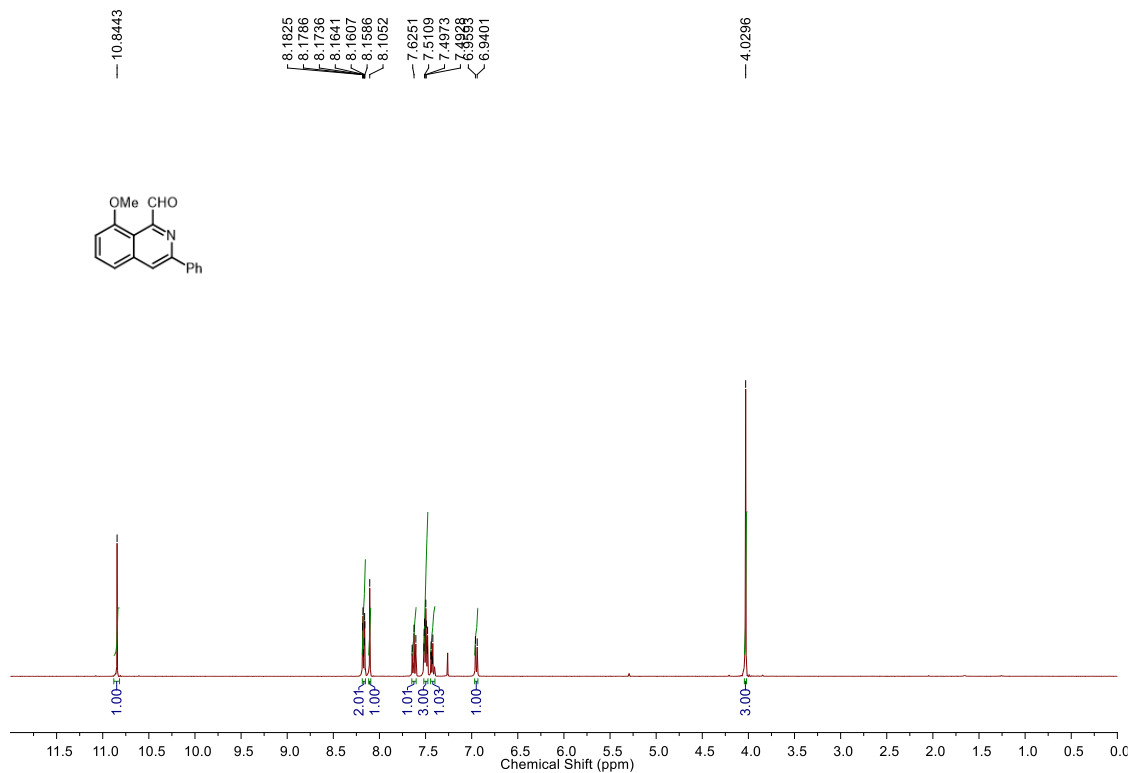


Figure S1 ^1H NMR and ^{13}C NMR spectrum (400 MHz) of compound **2**

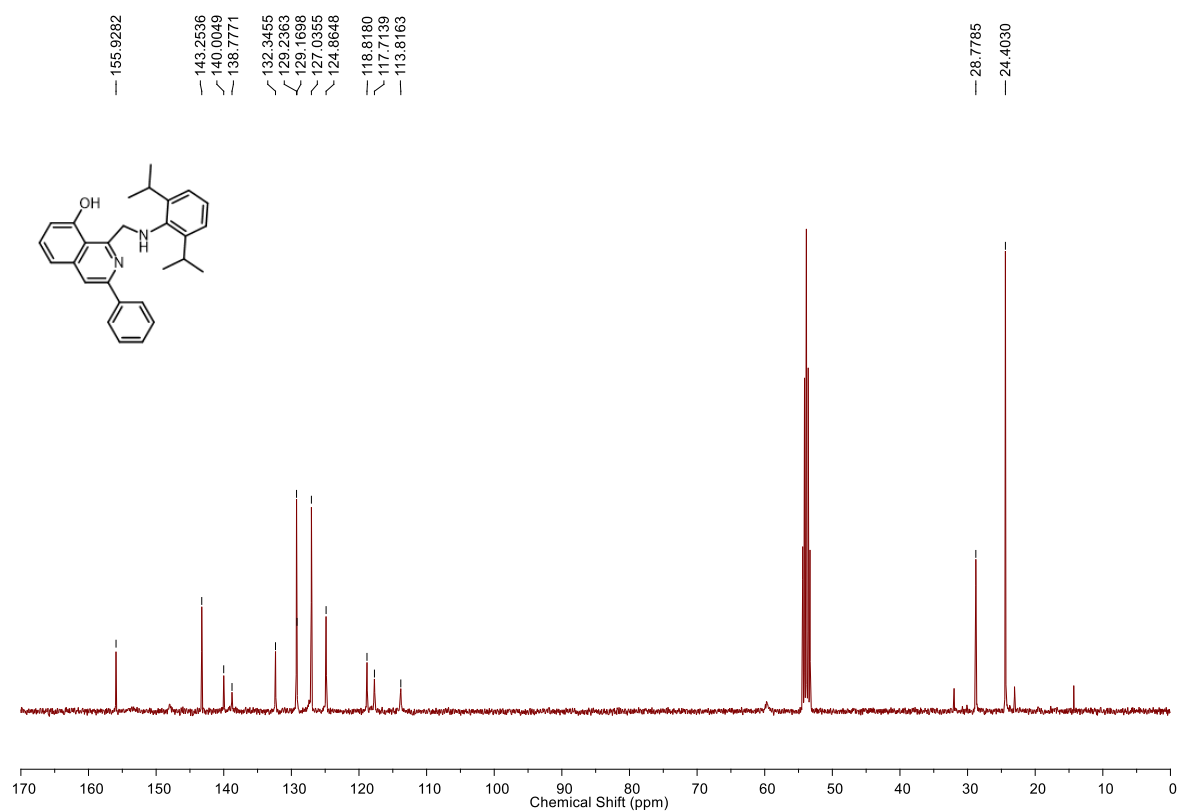
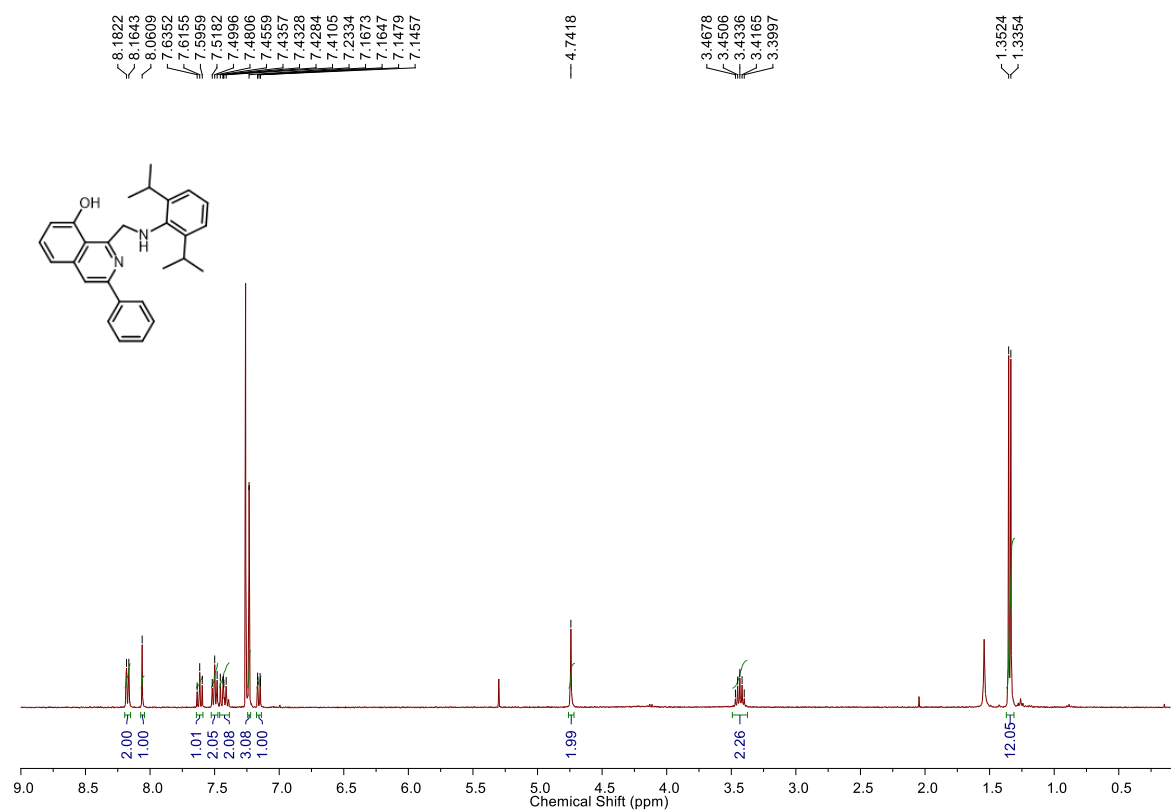


Figure S2 ^1H NMR and ^{13}C NMR spectrum (400 MHz) of compound **3a**

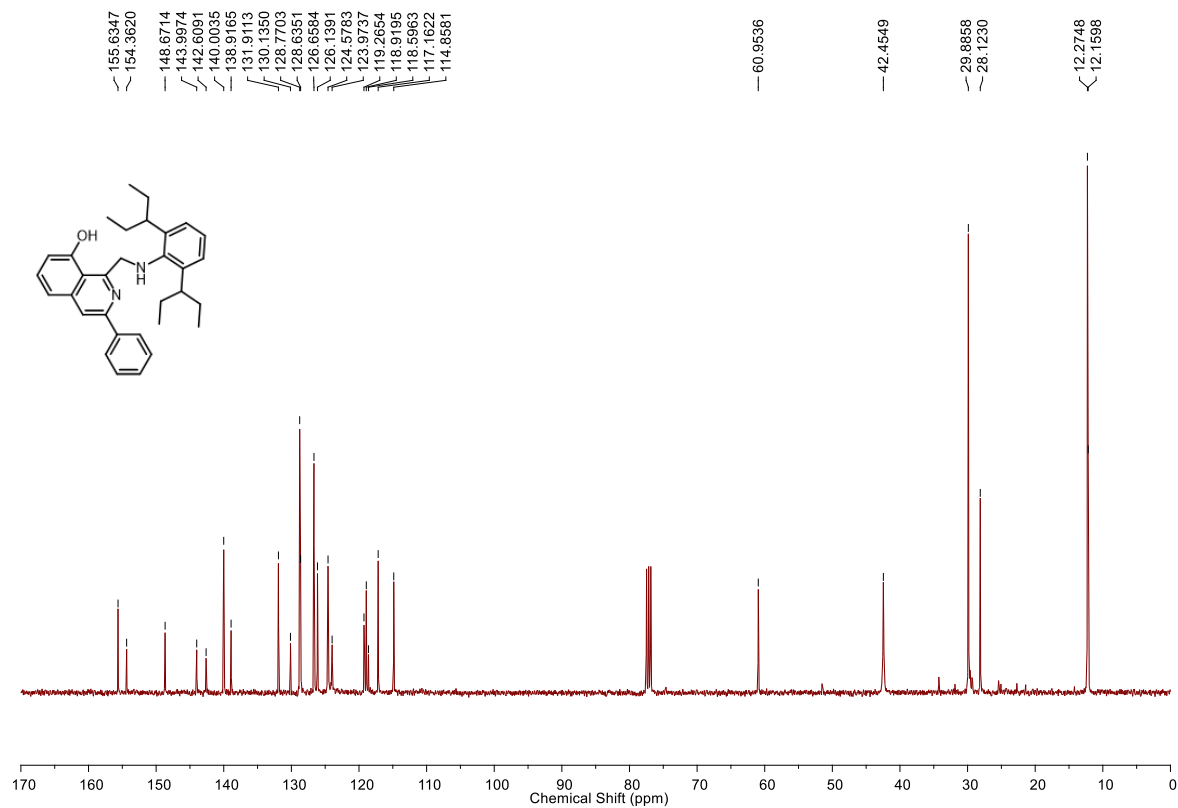
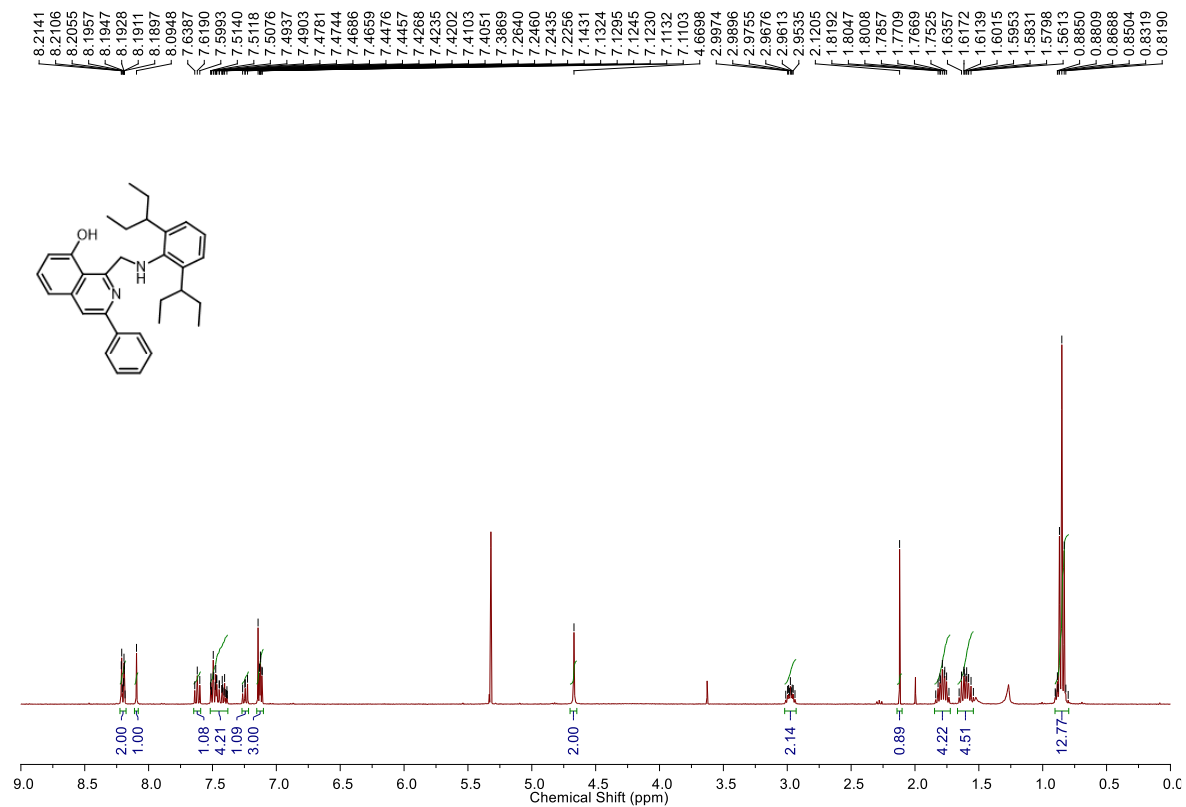


Figure S3 ^1H NMR and ^{13}C NMR spectrum (400 MHz) of compound **3b**

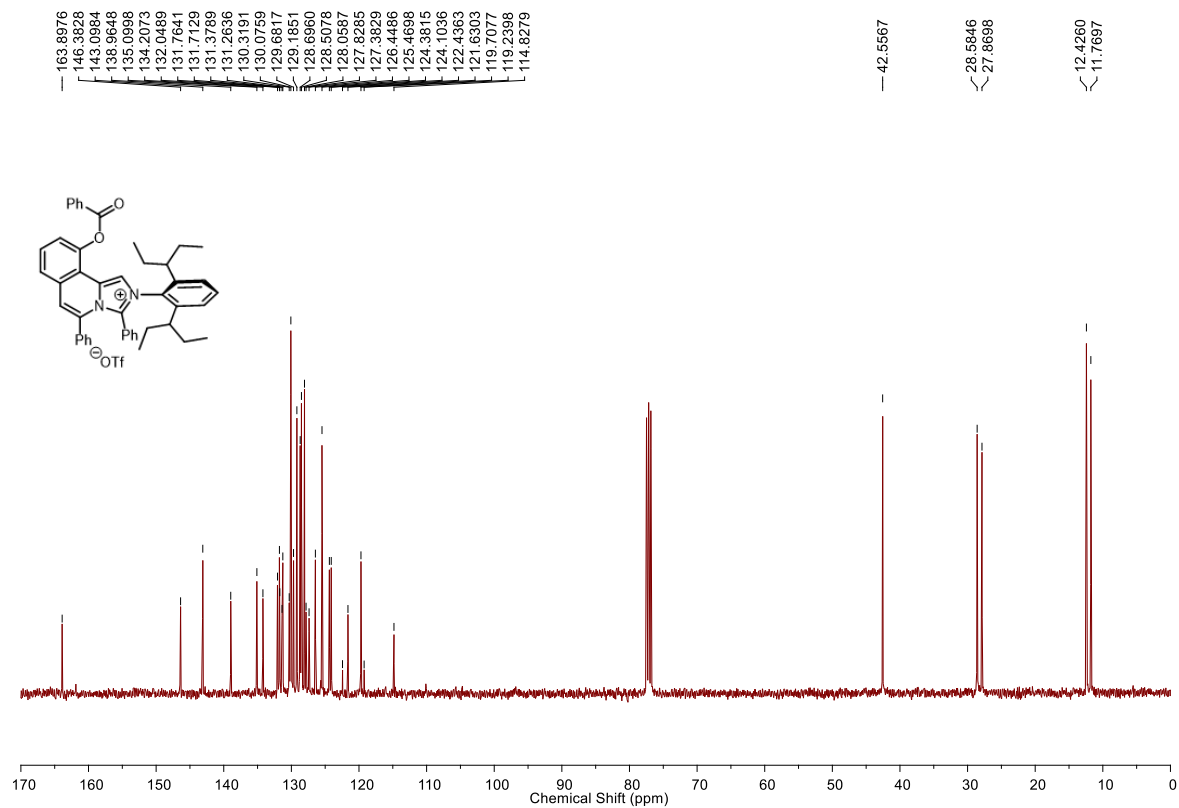
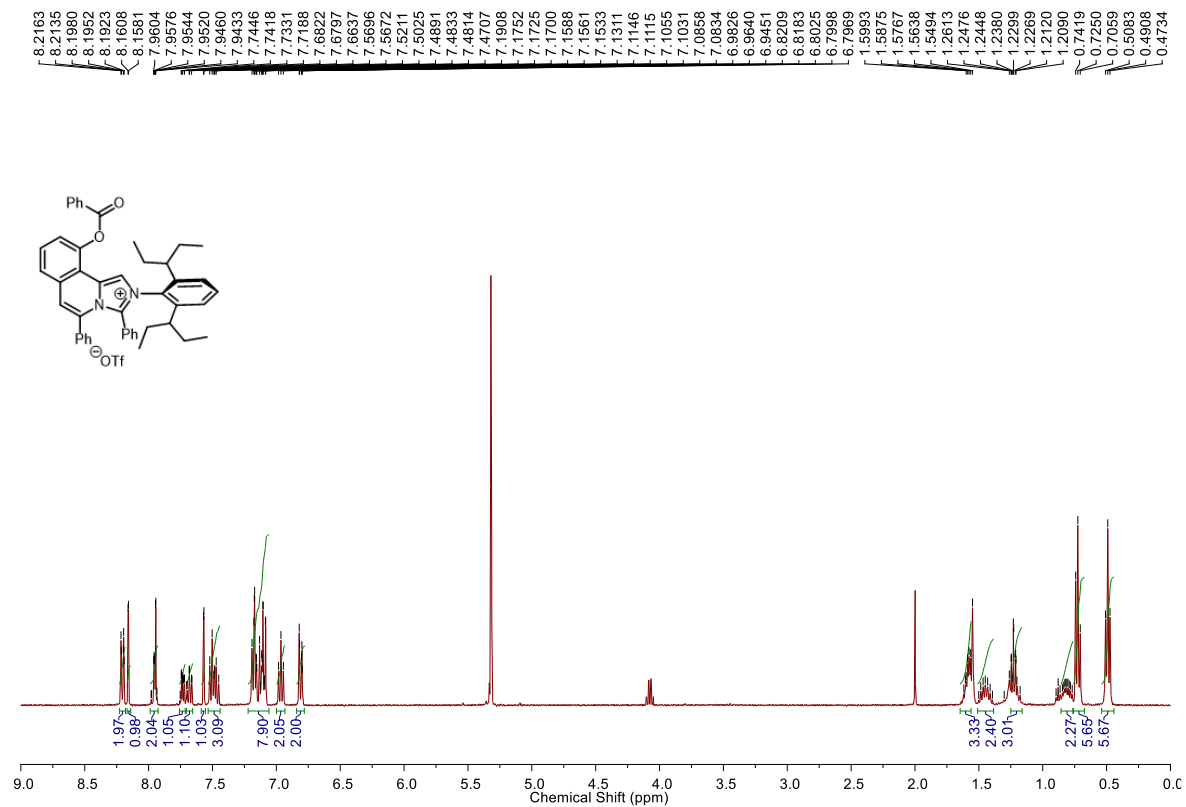


Figure S5 ^1H NMR and ^{13}C NMR spectrum (400 MHz) of compound **4b**

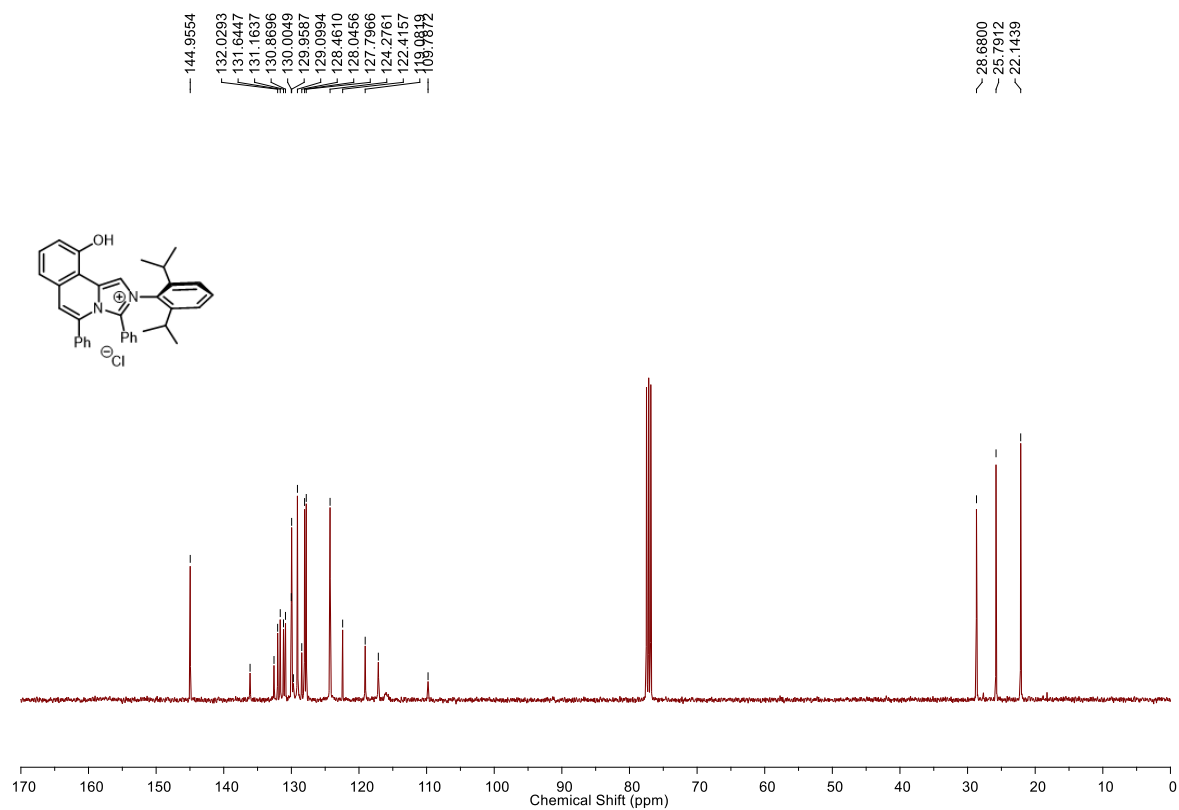
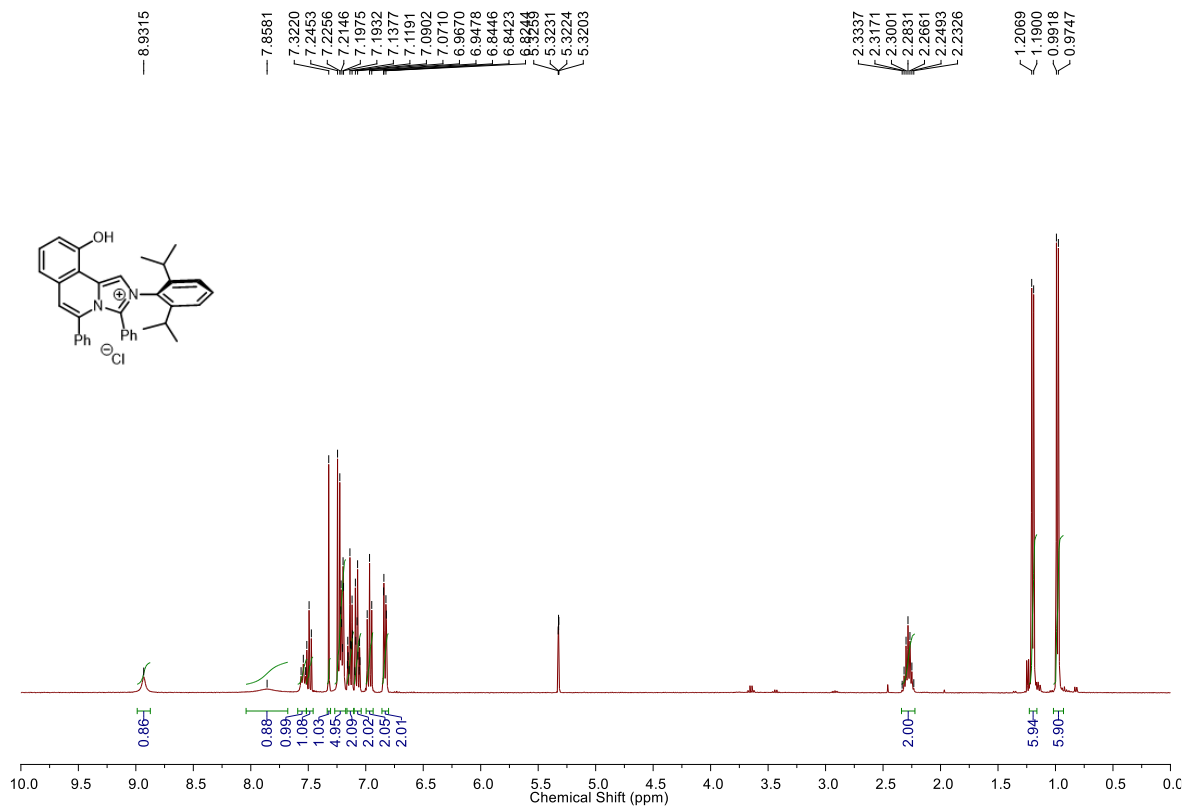


Figure S6 ¹H NMR and ¹³C NMR spectrum (400 MHz) of compound **5a**

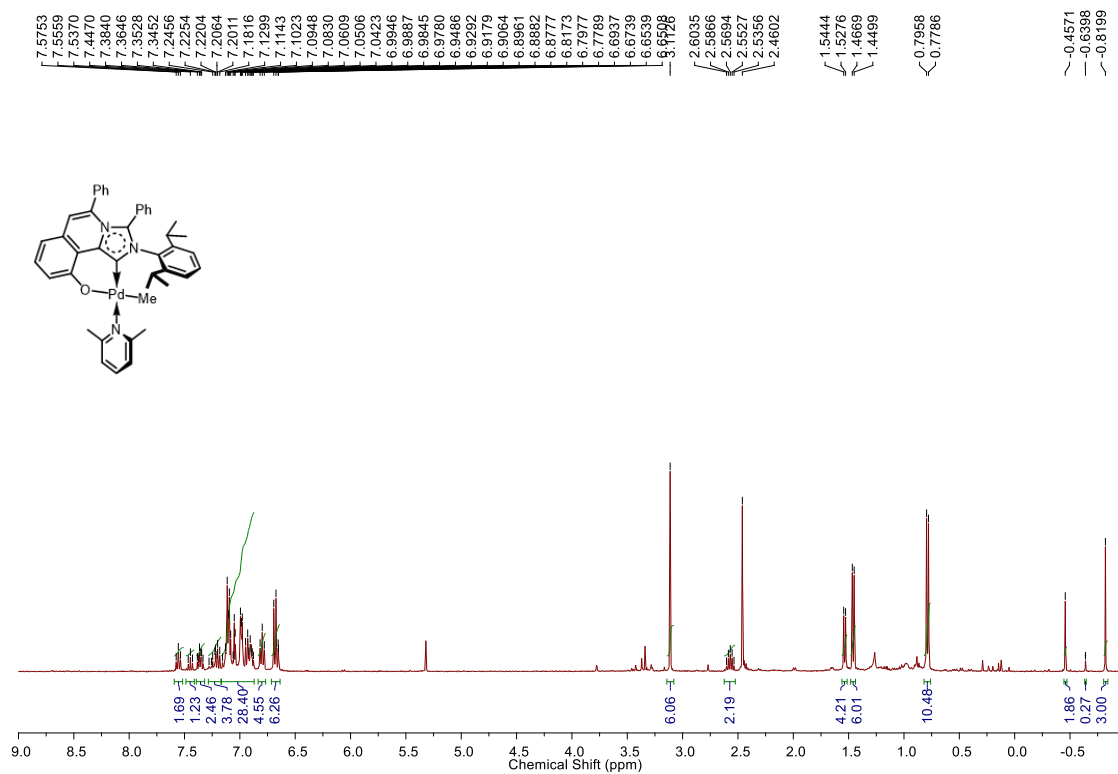


Figure S8 ¹H NMR spectrum (400 MHz) of compound **6a**

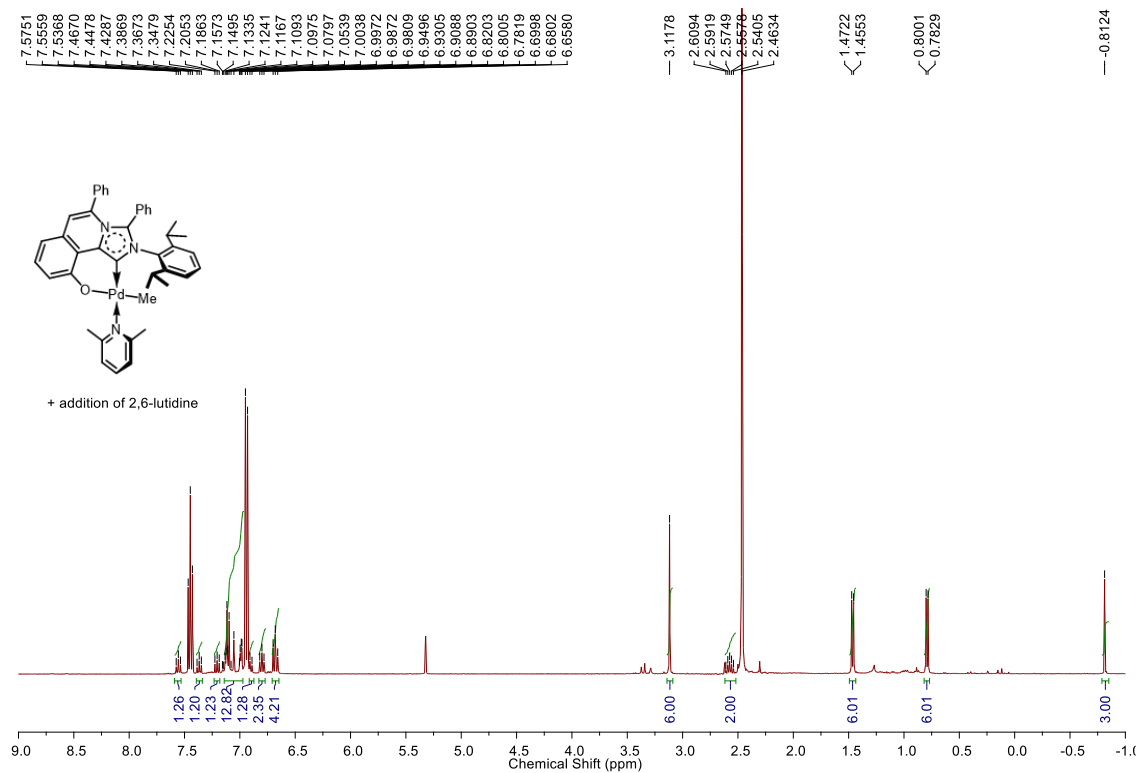


Figure S9 ¹H NMR spectrum (400 MHz) of compound **6a** with 2,6-lutidine

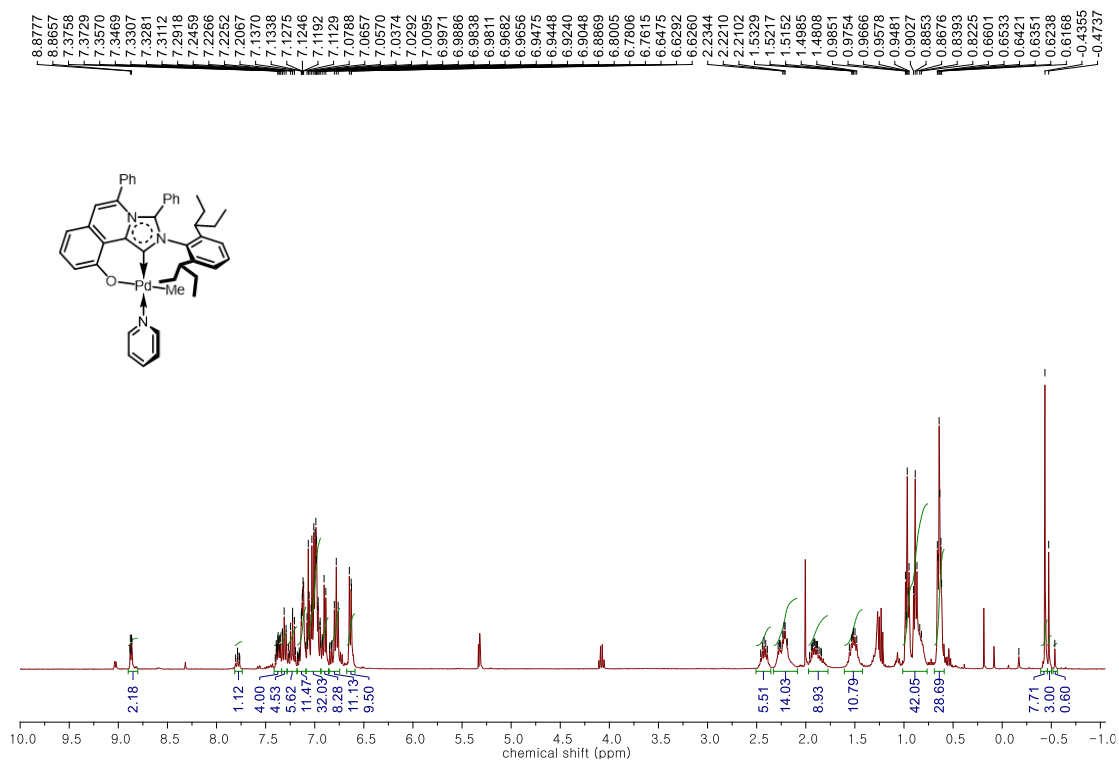


Figure S14 ¹H NMR spectrum (400 MHz) of compound **6c**

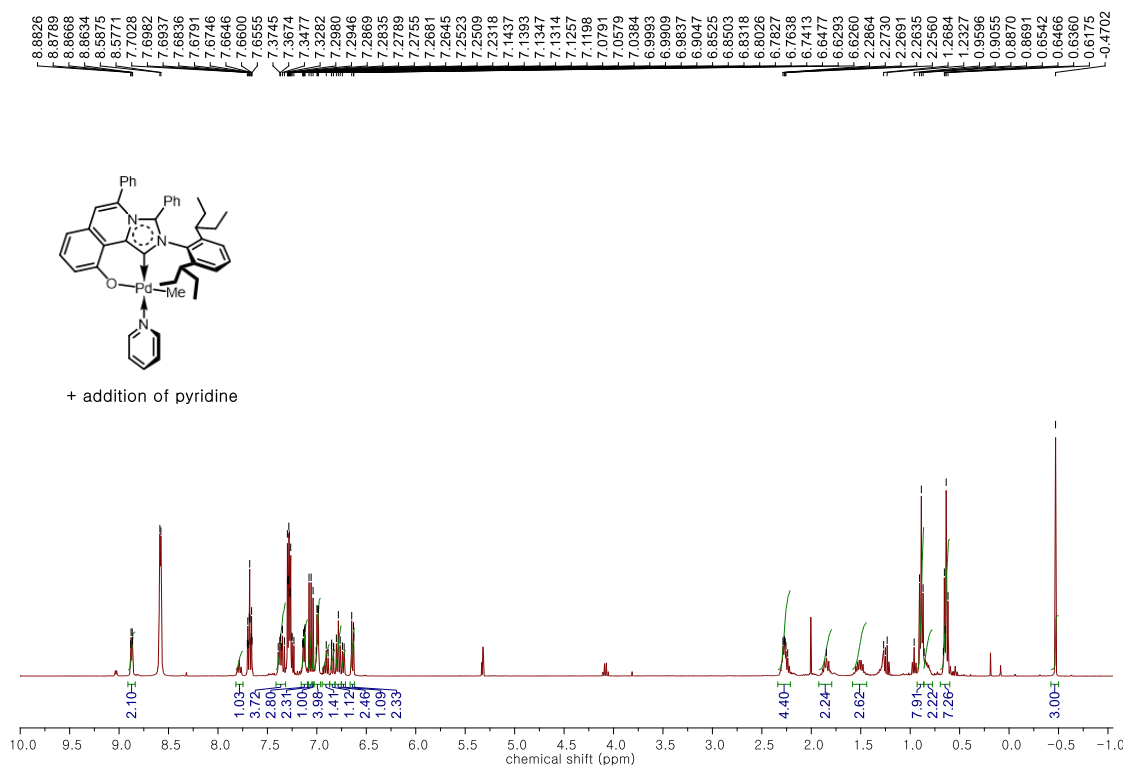


Figure S15 ¹H NMR spectrum (400 MHz) of compound **6c** with pyridine

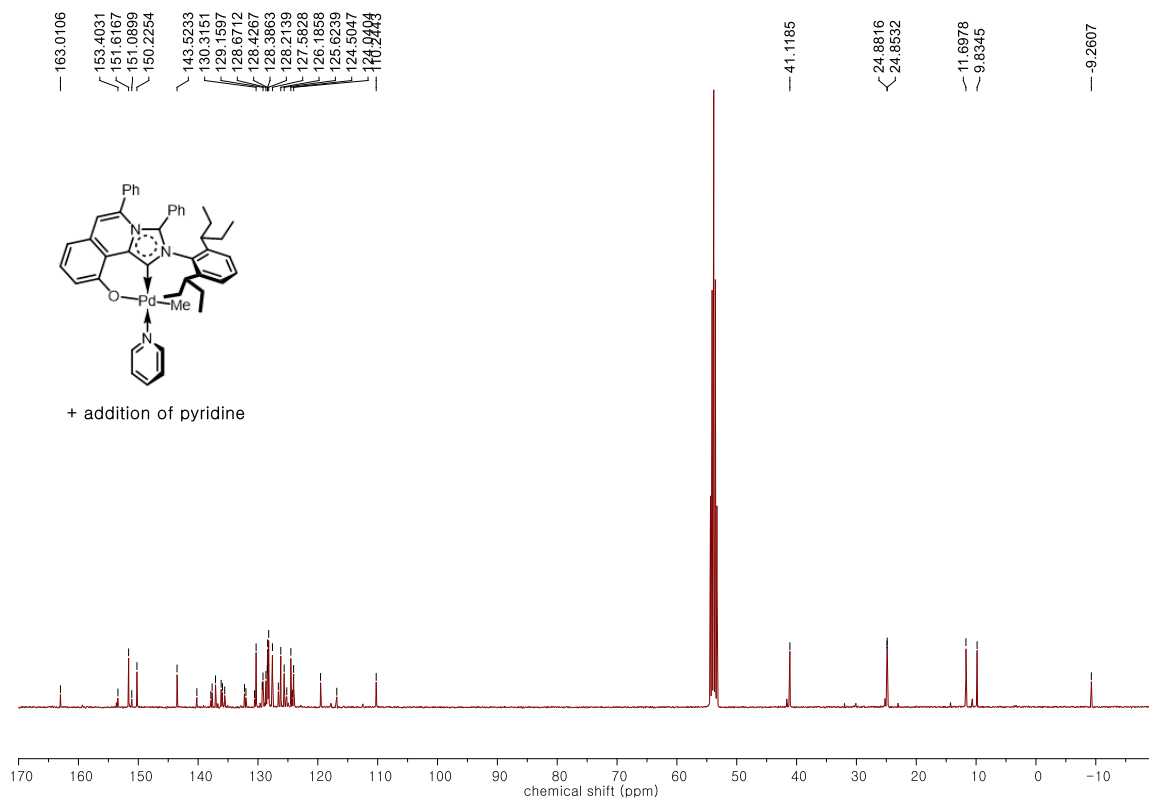


Figure S16 ¹³C NMR spectrum (400 MHz) of compound **6c** with pyridine

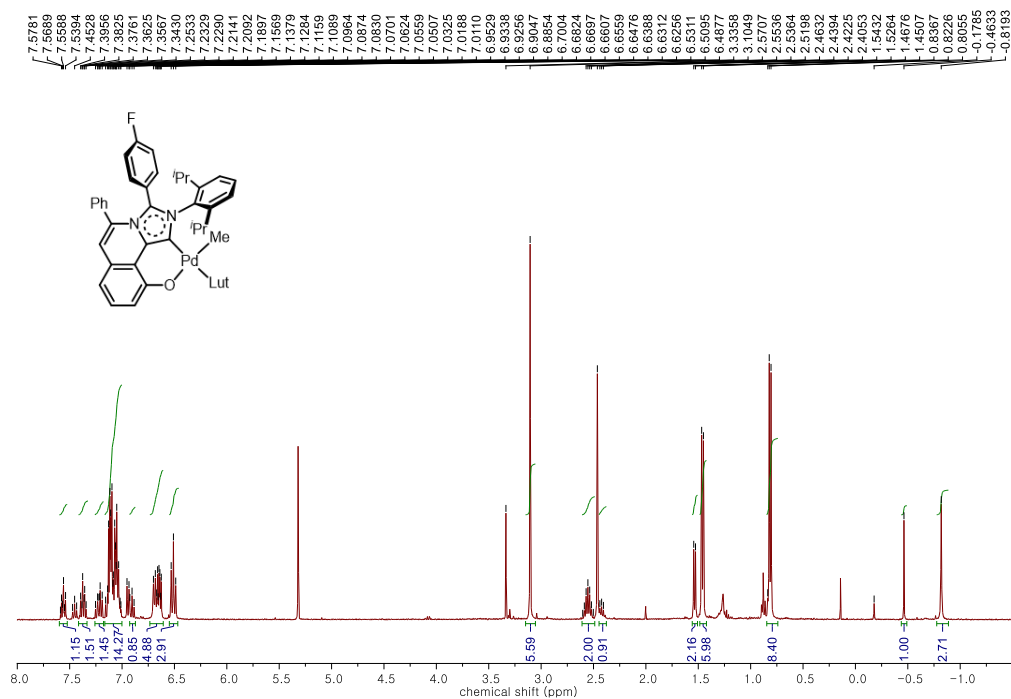


Figure S17 ¹H NMR spectrum (400 MHz) of compound **6d**

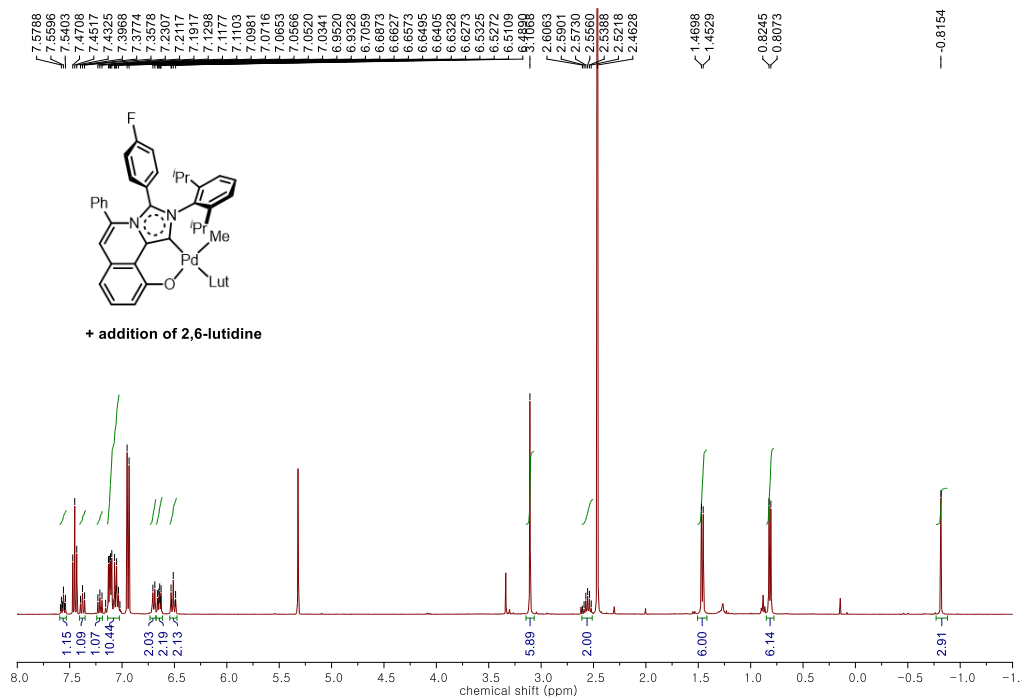


Figure S18 ¹H NMR spectrum (400 MHz) of compound **6d** with 2,6-lutidine

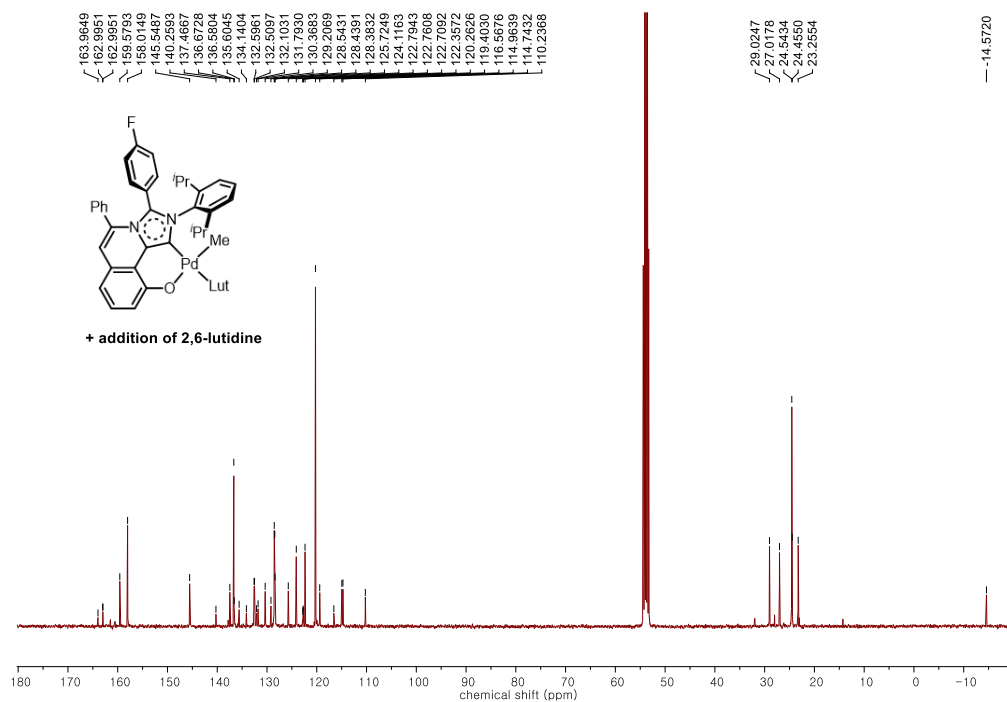


Figure S19 ¹³C NMR spectrum (400 MHz) of compound **6d** with 2,6-lutidine

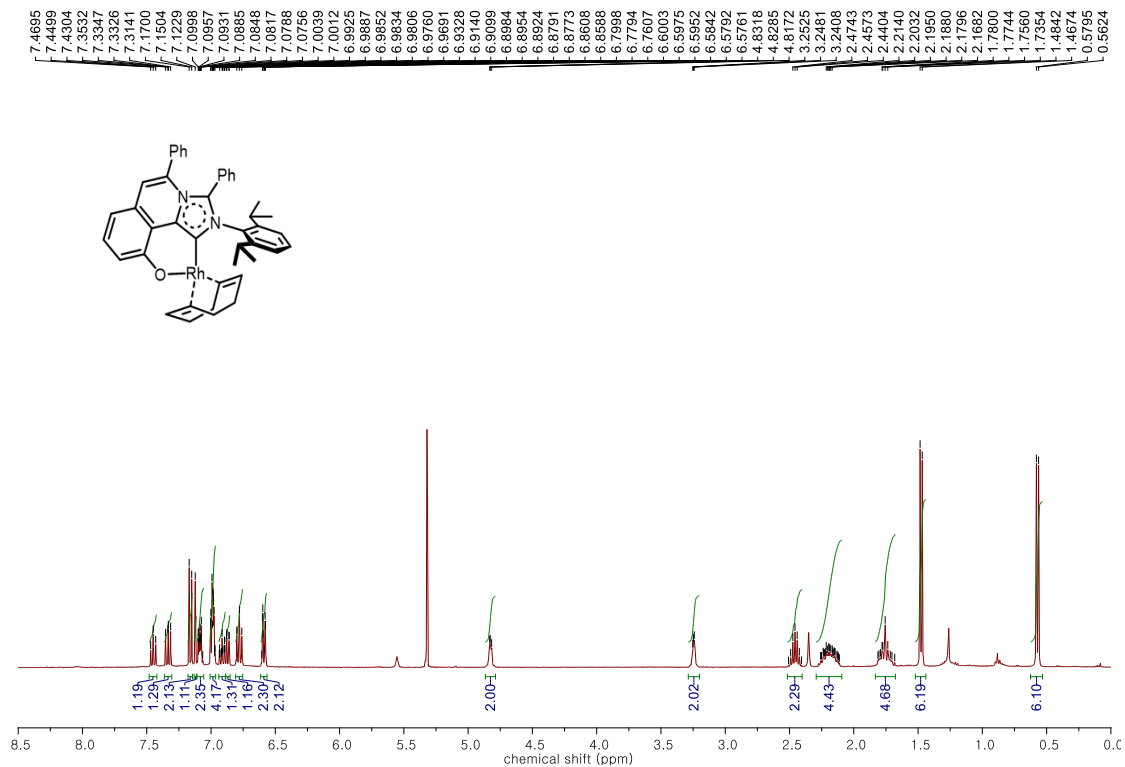


Figure S20 ^1H NMR spectrum (400 MHz) of compound **7a**

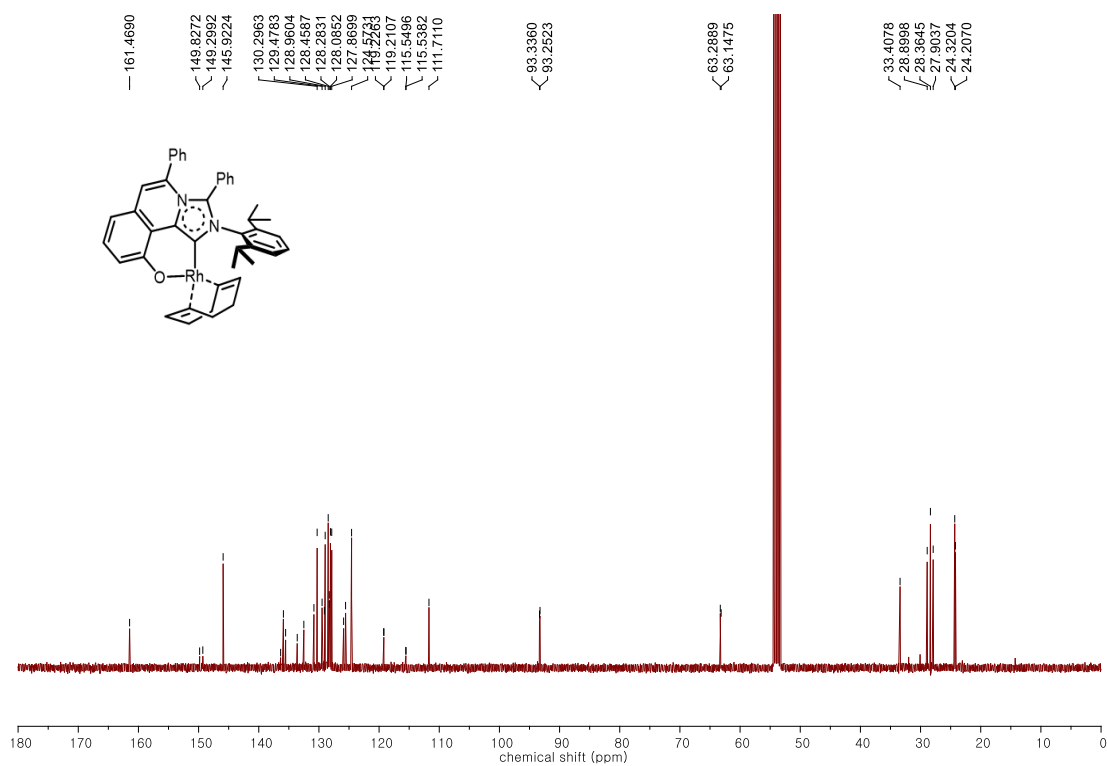


Figure S21 ^{13}C NMR spectrum (400 MHz) of compound **7a**

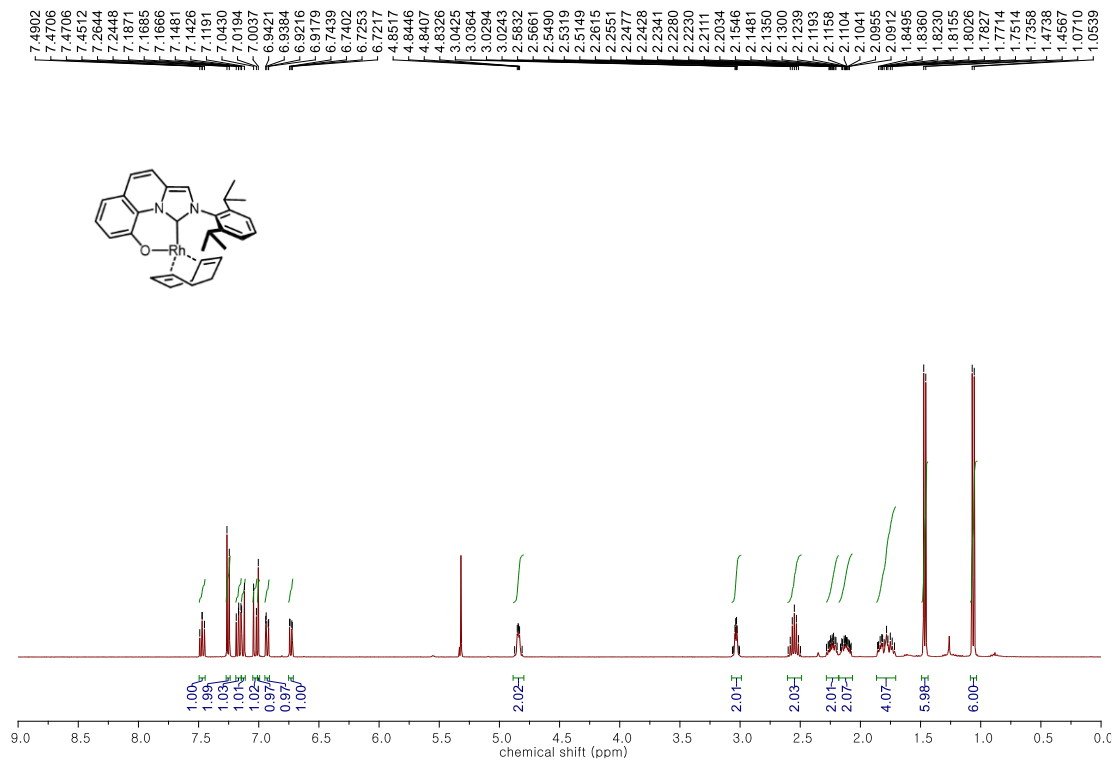


Figure S22 ^1H NMR spectrum (400 MHz) of compound **8a**

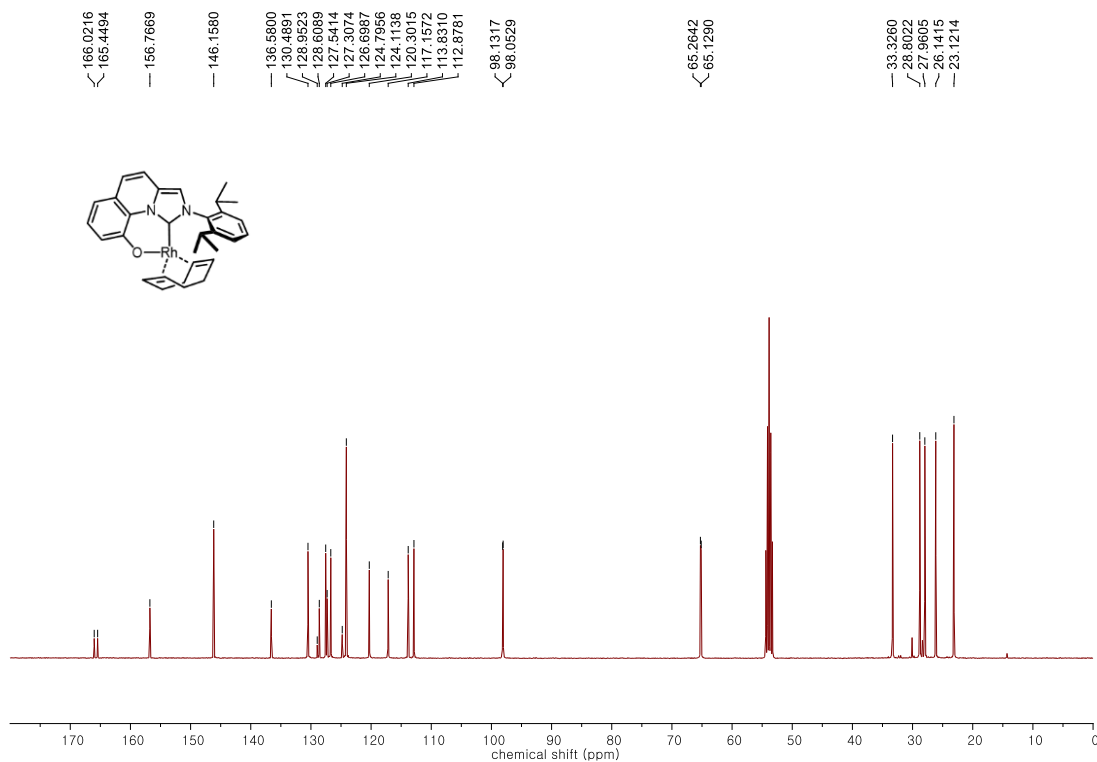


Figure S23 ^{13}C NMR spectrum (400 MHz) of compound **8a**

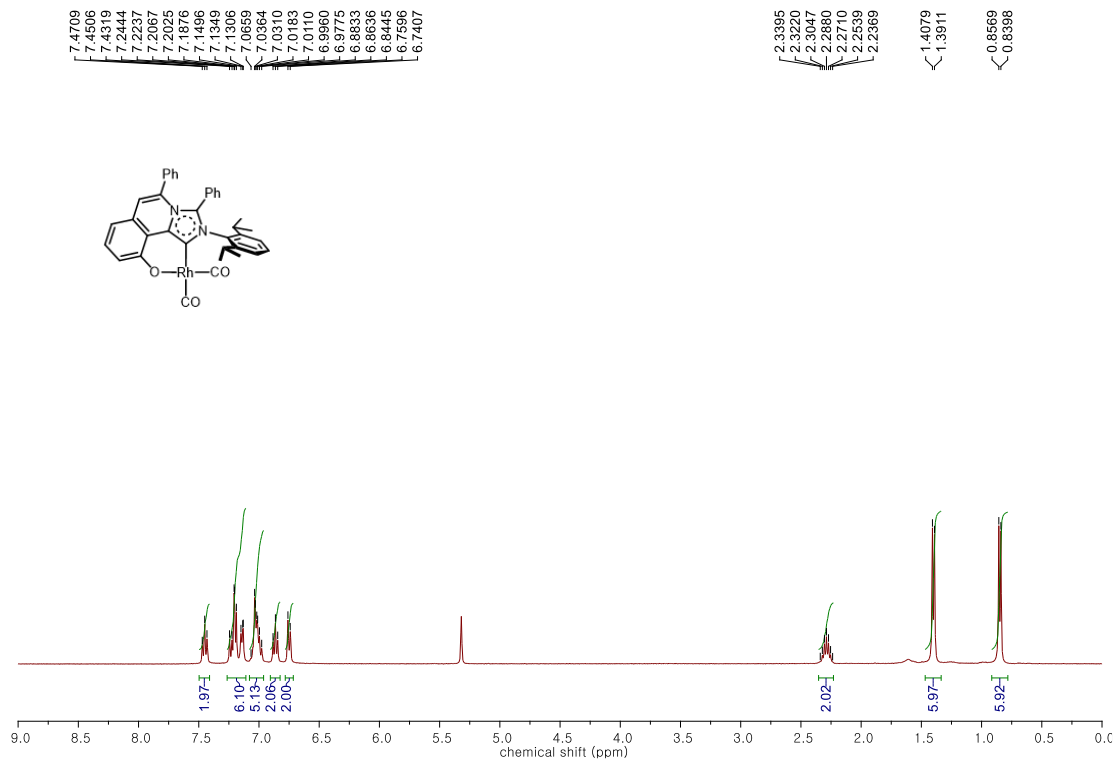


Figure S24 ¹H NMR spectrum (400 MHz) of compound 7

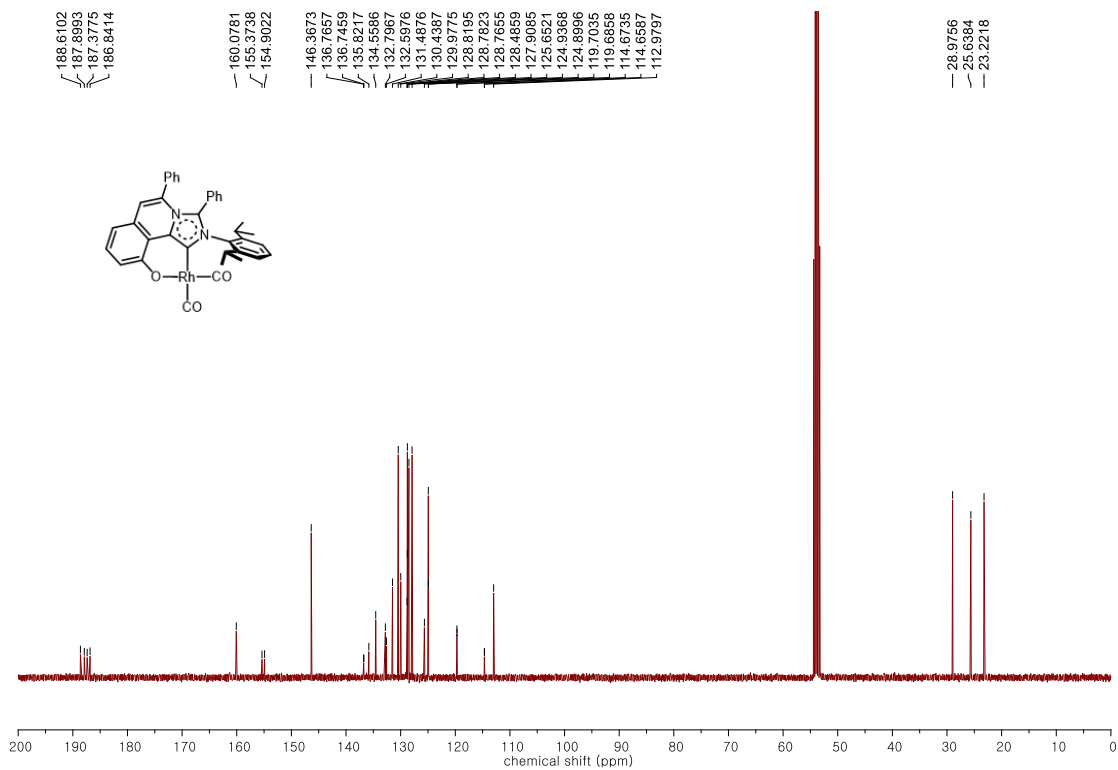


Figure S25 ¹³C NMR spectrum (400 MHz) of compound 7

4. X-ray Analysis for Complex **6c** and **6d**

Reflection data for **6c** and **6d** were collected on a Bruker APEX-II CCD-based diffractometer with graphite-monochromated MoK α radiation ($\lambda = 0.7107 \text{ \AA}$). The hemisphere of reflection data were collected as ω scan frames with $0.5^\circ/\text{frame}$ and an exposure time of 10s/frame. Cell parameters were determined and refined by the SMART program. Data reduction was performed using SAINT software. The data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied using the SADABS program. The structures of the compounds were solved by direct methods and refined by full matrix least-squares methods using the SHELXTL program package with anisotropic thermal parameters for all non-hydrogen atoms.

Note: For complex **6b**, containing 2,6-lutidine instead of pyridine, the molecular structure of **6b** confirmed that the carbene and the methyl group are located *cis* to each other. However, despite several attempts, an adequately refined structure was not obtained, probably as a result of low crystal quality.

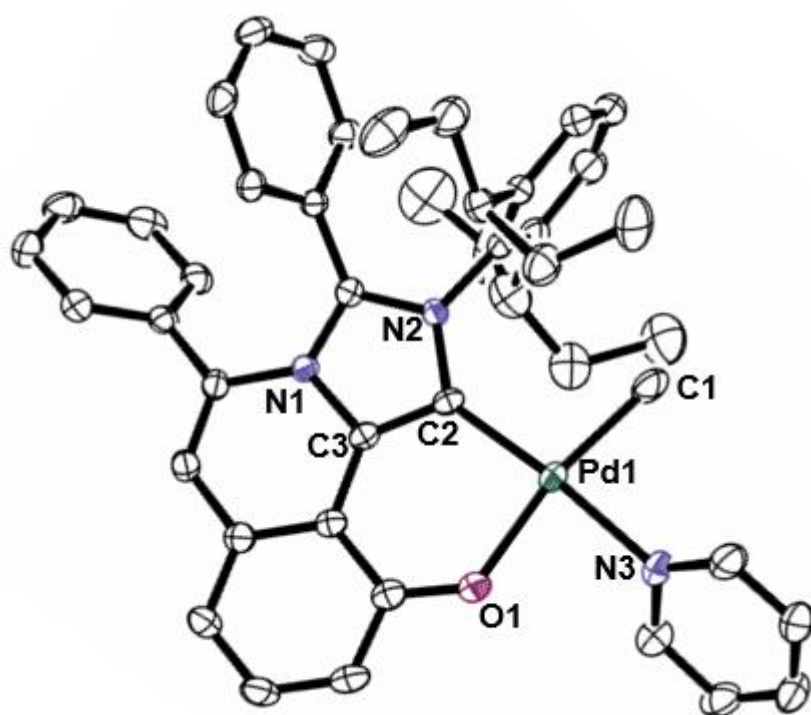


Figure S28 X-ray structure of complex **6c**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Table S1 Crystallographic data and parameters for **6c**

Complex	6c	
CCDC number	1962660	
Empirical formula	C ₄₅ H ₄₇ N ₃ OPd	
Formula weight	756.43	
Temperature	100 (K)	
Wavelength	0.71073	
Crystal system	orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 21.8378(3) Å	$\alpha = 90^\circ$

	$b = 14.1201(2) \text{ \AA}$	$\beta = 90^\circ$
	$c = 23.7032(4) \text{ \AA}$	$\gamma = 90^\circ$
Volume	$7308.93(19) \text{ \AA}^3$	
Z	8	
Density (calculated)	1.375 g cm^{-3}	
Absorption coefficient	0.566 mm^{-1}	
$F(000)$	3143.1	
$F(000)'$	3136.41	
θ range for data collection	2.885 to 26.976°	
Index ranges	$-27 \leq h \leq 27, -17 \leq k \leq 17, -30 \leq l \leq 30$	
Reflections collected	116424	
Independent reflections	7884 [R(int)=0.0698]	
Completeness to $\theta =$ 26.976°	99.3%	
Data / restraints / parameters	7884/1/484	
Goodness-of-fit on F2	1.013	
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0374, wR2 =$ $0.0810[5718]$	
R indices (all data)	$R1 = 0.0610, wR2 = 0.0905$	
Largest diff. peak and hole	0.673 and $-0.652 \text{ e} \cdot \text{\AA}^{-3}$	

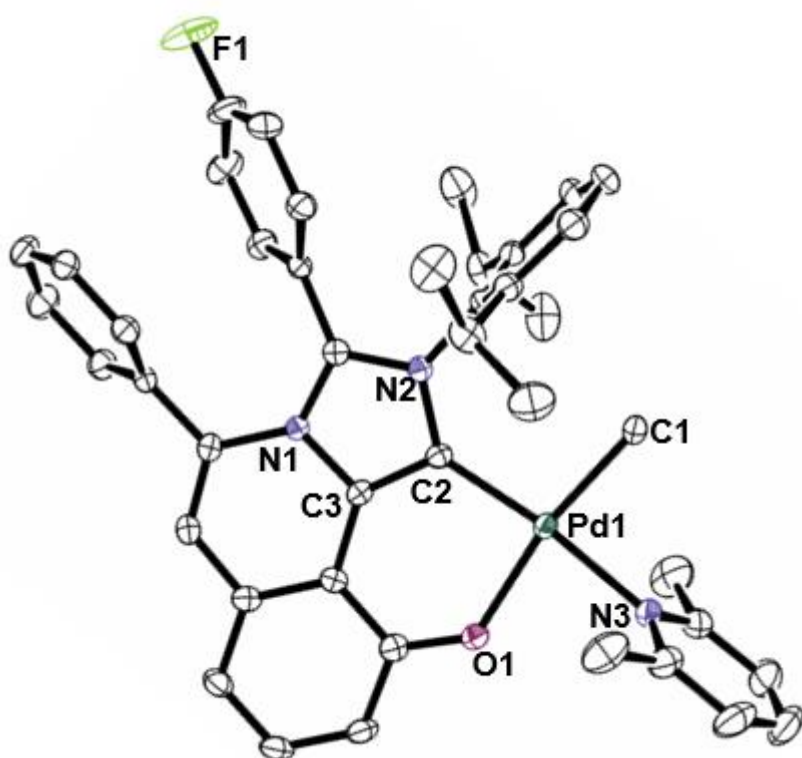


Figure S29 X-ray crystal structure of complex **6d**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Pd(1)–C(2) = 2.001(2), Pd(1)–C(1) = 2.062(3), Pd(1)–O(1) = 2.079(2), Pd(1)–N(3) = 2.119(2); C(3)–C(2)–N(2) = 103.00, C(2)–Pd(1)–O(1) = 90.75(8).

Table S2 Crystallographic data and parameters for **6d**

Complex	6d
CCDC number	1962657
Empirical formula	C ₄₃ H ₄₂ FN ₃ OPd
Formula weight	742.20
Temperature	100 (K)
Wavelength	0.71073
Crystal system	monoclinic

Space group	P 1 21/c 1	
	a = 13.2032(3) Å	$\alpha = 90^\circ$
Unit cell dimensions	b = 12.1088(3) Å	$\beta = 93.7586(13)^\circ$
	c = 21.7900(5) Å	$\gamma = 90^\circ$
Volume	3476.18(14) Å ³	
Z	4	
Density (calculated)	1.418 g cm ⁻³	
Absorption coefficient	0.578 mm ⁻¹	
F(000)	1536.0	
F(000)'	1532.55	
θ range for data collection	2.35 to 25.40 °	
Index ranges	-15 ≤ h ≤ 15, -14 ≤ k ≤ 14, -26 ≤ l ≤ 26	
Reflections collected	51426	
Independent reflections	6387 [R(int) = 0.0422]	
Completeness to $\theta = 25.40^\circ$	99.7%	
Data / restraints / parameters	6387/0/449	
Goodness-of-fit on F2	1.0697	
Final R indices [I > 2σ(I)]	R1 = 0.0307, wR2 = 0.0729[5229]	
R indices (all data)	R1 = 0.0422, wR2 = 0.0806	
Largest diff. peak and hole	0.4223 and -0.4992 e·Å ⁻³	

5. Comparison with Reported Palladium Complexes Bearing Unsymmetrical Bidentate

Ligands

Table S3 Ethylene polymerization by catalysts **6a–6b**, and comparison with reported NHC-palladium catalysts^a

Entry	[Pd] (μmol)	P (bar)	T ($^{\circ}\text{C}$)	Time (h)	Activity ($\text{kgmol}^{-1}\text{h}^{-1}$)	M_n^b (10^3)	PDI ^b	Me br. ^c	T_m^d ($^{\circ}\text{C}$)
1	6a (1.5)	40	80	1	27	31	1.9	-	127
2	6a (1.5)	40	100	1	220	237	1.7	5.5	121
3	6a (1.5)	40	120	1	126	158	1.6	4.6	120
4	6b (1.5)	40	100	1	184	212	1.7	2.2	125
5	6b (1.5)	40	100	0.5	347	151	1.6	-	126
6	6b (1.5)	40	100	2	102	194	1.9	1.9	126
7	6b (1.5)	40	120	1	109	110	1.8	3.4	125

8 ^e	NHC1 (1.0)	40	100	1	690	76	2.4	11.6	-
9 ^e	NHC1-Mes (1.0)	40	100	1	1310	51	2.9	9.2	-
10 ^f	NHC2 (2.5)	30	30	1	44	12	2.1	0	133
11 ^f	NHC2 (2.5)	30	50	1	152	7.2	2.3	0	132
12 ^g	NHC3 (10)	40	100	1	3.6	1.8	3.6	33.3	-

^a A mixture of catalyst and olefin in toluene 20 mL was stirred under conditions mentioned in Table S3. ^b Number-average molecular weights were determined by GPC using polystyrene as an internal standard and corrected by universal calibration. ^c Methyl branches per 1000 C as determined by quantitative ^{13}C NMR analysis. ^d Melting temperatures were determined by DSC. ^e Data from reference 11. ^f 10 mL toluene, data from reference 12. ^g 20 mL toluene, data from reference 13.

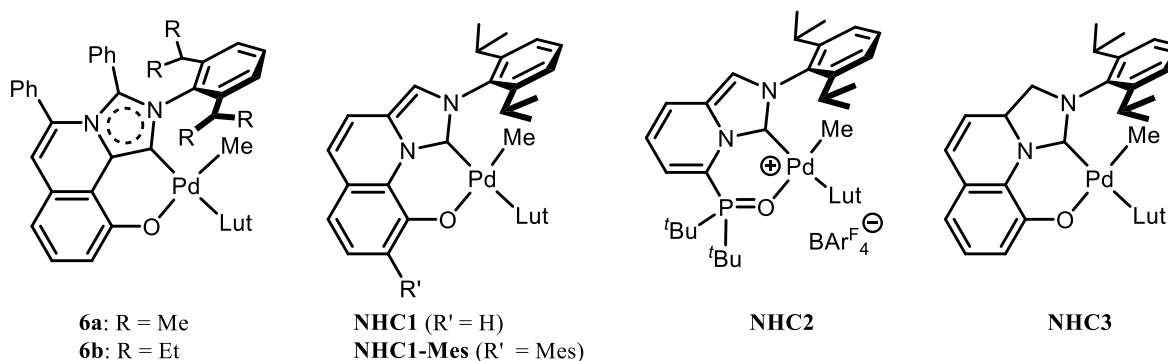


Table S4 Selected examples of high-performance unsymmetrical bidentate Pd catalysts for ethylene polymerization^a

Entry	[Pd] (μmol)	Activity ($\text{kgmol}^{-1}\text{h}^{-1}$)	M_n (gmol^{-1})	ref
1	6a (1.5)	220	237000	
2	6b (1.5)	184	212000	

3	PS1 (10)	205	169000	14
4	PS2 (5.0)	1040	227000	15
5	PP1 (10) + 8 equiv. of $\text{B}(\text{C}_6\text{F}_5)_3$	5700	99200	16
6	PP2 (1.0)	3500	190000	17
7	PP3 (2.5)	2200	240000	18

^a Polymerization conditions: ethylene (40 bar), toluene (20-x mL), 100 °C, 1 h.

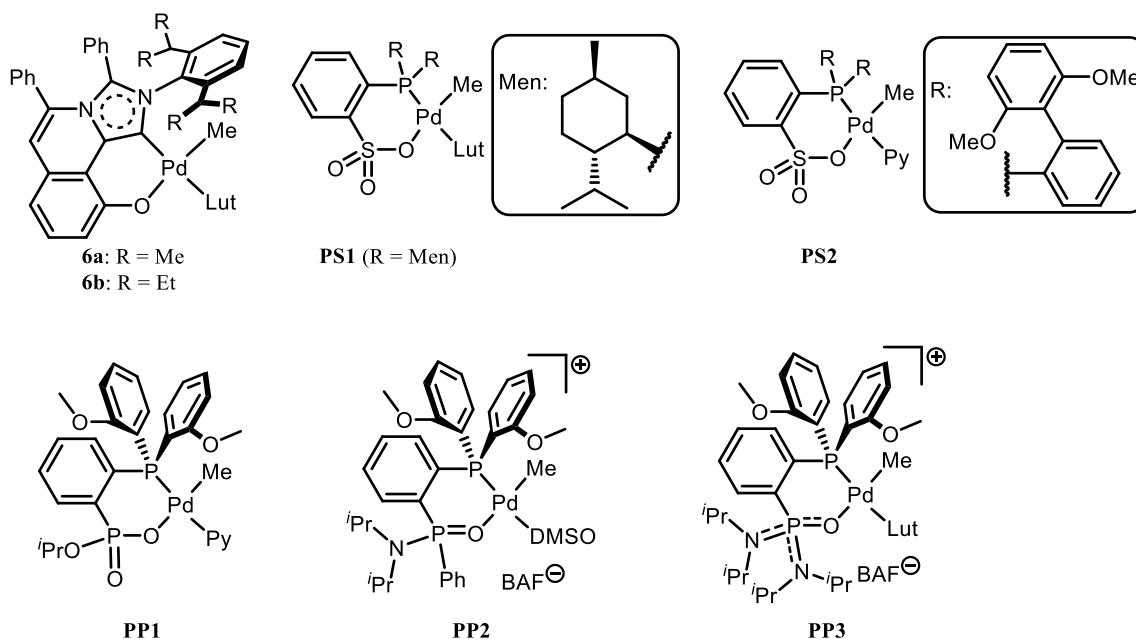


Table S5 Propylene polymerization by catalysts **6a–6b**, and comparison with reported Pd complexes bearing unsymmetrical bidentate ligands^a

Entry	[Pd] (μmol)	Temp ($^{\circ}\text{C}$)	Time (h)	Activity ^b	M_n^c (10^3)	PDI ^c	regio defects ^d (%)
1	6a (3.0)	100	1	36	36	1.3	<0.1
2	6a (3.0)	100	3	19	62	1.6	<0.1
3	6a (3.0)	120	3	9.6	35	1.5	<0.1
4	6b (3.0)	100	3	13	32	1.8	<0.1

5 ^e	NHC1 (2.0)	100	3	34	16	2.2	1.2
6 ^e	NHC1-Mes (2.0)	100	3	52	18	2.5	1.4
7 ^f	PS1 (20)	50	12	9.9	24	2.0	0.9

^a Polymerization conditions: propylene (120 psig), catalyst (3.0 μmol , x mL), toluene (20-x mL). ^b Activity = (kg[PP]·mol[Pd]⁻¹·h⁻¹). ^c Number-average molecular weights were determined by GPC using polystyrene as an internal standard and corrected by universal calibration. ^d Regio defects as determined by quantitative ¹³C NMR. ^e Propylene (10.0 g), data from reference 11. ^f Propylene (5.0 g), toluene (10-x mL), data from reference 19.

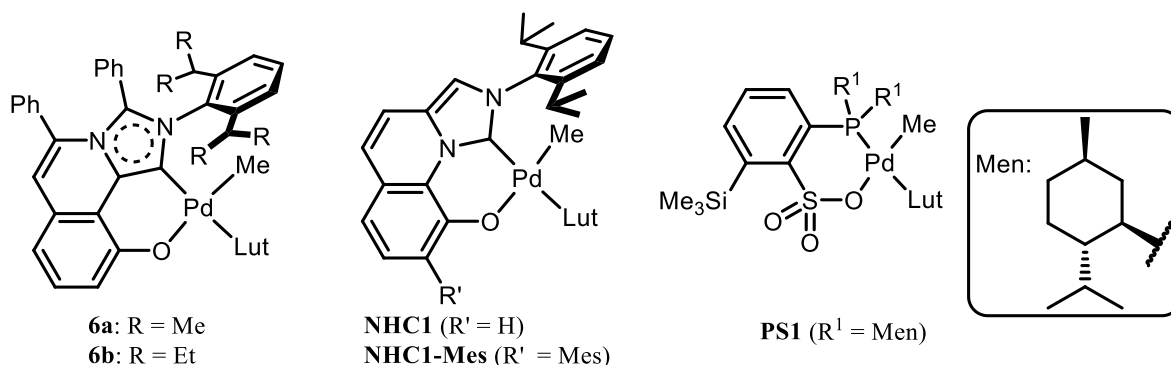


Table S6 Copolymerization of olefins with polar monomers by various NHC-Pd complexes^a

Entry	[Pd] (μmol)	olefins	Comonomer ^b (mL)	Temp. ($^{\circ}\text{C}$)	Time (h)	Activity ($\text{kgmol}^{-1}\text{h}^{-1}$)	M_n^c (10^3)	PDI ^c	Incorp ^d (mol%)
1	6a (10)	ethylene	AC (0.4)	100	3	1.8	5.4	2.0	3.0
2	6a (10)		AAc (1.0)	100	3	2.4	8.3	1.8	2.7
3	6a (10)		MA (0.2)	100	3	3.2	9.9	1.3	2.4
4 ^e	NHC1 (10)		AC (0.4)	100	3	1.3	4.0	2.1	0.5
5 ^e	NHC1 (10)		AAc (1.0)	100	3	4.5	7.4	2.5	1.4
6 ^e	NHC1 (10)		MA (0.2)	100	3	10.6	17	2.0	0.8
7 ^f	NHC2 (5.0)		AC (5.0)	30	3	2.5	6.8	2.1	0.47
8 ^f	NHC2 (5.0)		AAc (5.0)	30	3	4.5	7.4	2.2	0.58
9 ^f	NHC2 (5.0)		MA (5.0)	30	3	1.7	4.8	2.1	0.61

10	6a (10)	propylene	AAc (0.1)	100	6	2.0	14	1.7	3.1
11 ^e	NHC1 (10)		AAc (0.1)	100	6	1.3	3.9	2.2	2.0
12 ^e	NHC1-Mes (10)		AAc (0.1)	100	6	2.8	11	2.3	0.9

^a Polymerization conditions: ethylene (40 bar) or propylene (120 psig), catalyst (10 μmol), comonomer (x mL), toluene (20-x mL), 100 $^{\circ}\text{C}$, 3 h. ^b AC = allyl chloride, AAc = allyl acetate, MA = methyl acrylate. ^c Number-average molecular weights were determined by GPC using polystyrene as an internal standard and corrected by universal calibration. ^d Incorporation ratios of the polar monomers were determined by ^1H NMR or quantitative ^{13}C NMR analysis. ^e Ethylene (4.0 MPa) or propylene (10.0 g), data from reference 11. ^f Ethylene (3.0 MPa), toluene (10-x mL), data from reference 12.

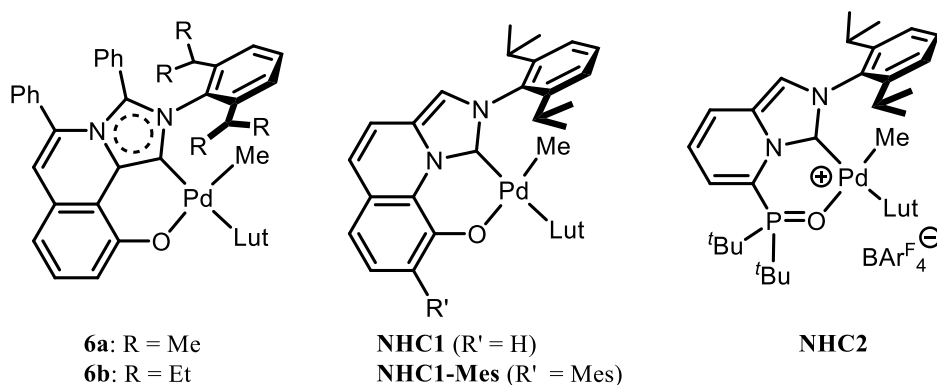
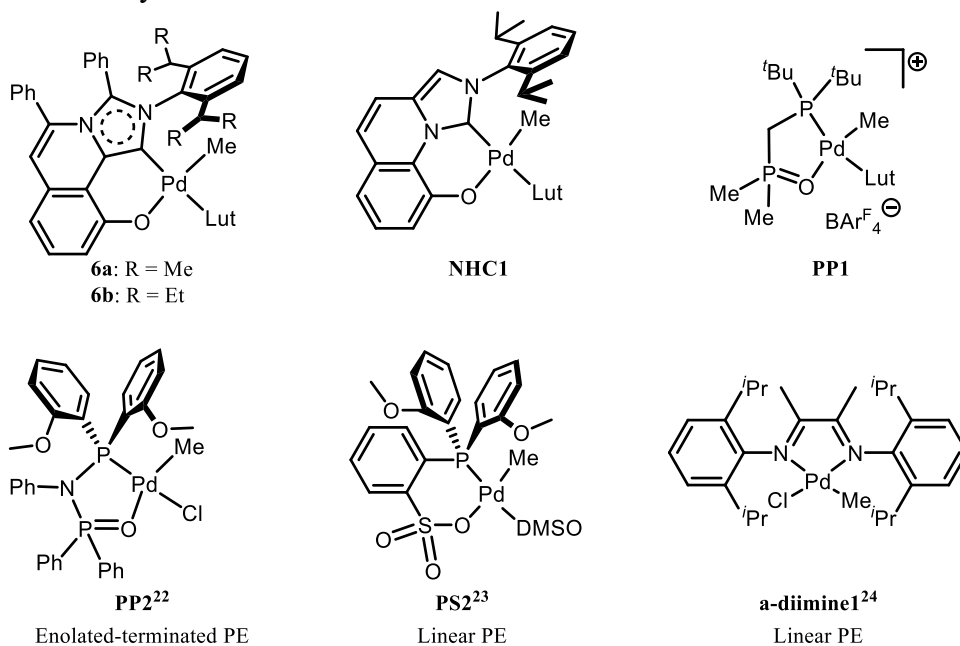


Table S7 Copolymerization of ethylene and MMA by late transition metal complexes^a

Entry	[Pd] (μmol)	MMA (mL)	Toluene (mL)	P (bar)	T ($^{\circ}\text{C}$)	Time (h)	Activity ($\text{kgmol}^{-1}\text{h}^{-1}$)	M_n^b (10^3)	PDI ^b	Incorp ^c (mol%)
1	6a (10)	4.0	4.0	20	120	15	0.31	3.7	2.0	1.4
2	6b (10)	4.0	4.0	20	120	15	0.22	3.3	2.2	1.5
3 ^d	NHC1 (10)	4.0	4.0	20	120	15	0.67	8.6	1.7	0.62
4 ^d	NHC1 (10)	8.0	0	10	120	15	0.16	0.8	2.9	2.5
5 ^e	PP1 (10)	3.0	12	20	100	15	5.9	10	2.7	0.1
6 ^e	PP1 (10)	15	0	10	100	15	0.6	2.2	4.0	0.6

^a The copolymerization of ethylene and MMA (methyl methacrylate) was performed under conditions mentioned in Table S7. ^b Number-average molecular weights were determined by GPC using polystyrene as an internal standard and corrected by universal calibration. ^c Incorporation ratios of the polar monomers were determined by ¹H NMR or quantitative ¹³C NMR analysis. ^d Data from reference 20. ^e Data from reference 21.



6. Activator Screening

Table S8 Ethylene Polymerization by Catalyst **6a** with Addition of Activators at 80 °C^a

Entry	Activator	Yield (mg)	Activity ^b	TOF ^c	M _n ^d (10 ³)	PDI ^d
1	none	41	27	973	31	1.9
2	Ni(cod) ₂ (2.0 equiv.)	13	8.7	309	22	1.4
3	B(C ₆ F ₅) ₃ (2.0 equiv.)	No Rxn.	-	-	-	-
4	Et ₂ AlCl (1000 equiv.)	No Rxn.	-	-	-	-
5	Et ₃ Al (1000 equiv.)	No Rxn.	-	-	-	-

^a Polymerization conditions: ethylene (40 bar), catalyst **6a** (1.5 μmol, x mL), toluene (20-x mL), 80 °C, 1 h. ^b Activity = kg [PE]/(mol [Pd]·h). ^c Turnover frequency (TOF) = mol [ethylene]/(mol [Pd]·h). ^d Number-average molecular weights were determined by GPC using polystyrene as an internal standard and corrected by universal calibration.

7. Yields versus Time for complex **6b** at 100 °C

Table S9 Effect of Time on Ethylene Polymerization with Catalyst **6b** at 100 °C^a

Entry	Time (h)	Yield (mg)	Activity ^b	TOF ^c
1	0.5	260	347	12359
2	1	275	183	6536
3	2	305	102	3624
4	3	333	74	2639
5	5	347	46	1649
6	10	343	23	815

^a Polymerization conditions: ethylene (40 bar), catalyst **6b** (1.5 μmol , x mL), toluene (20-x mL), 100 °C, 1 h. ^b Activity = kg [PE]/(mol [Pd] · h). ^c Turnover frequency (TOF) = mol [ethylene]/(mol [Pd] · h).

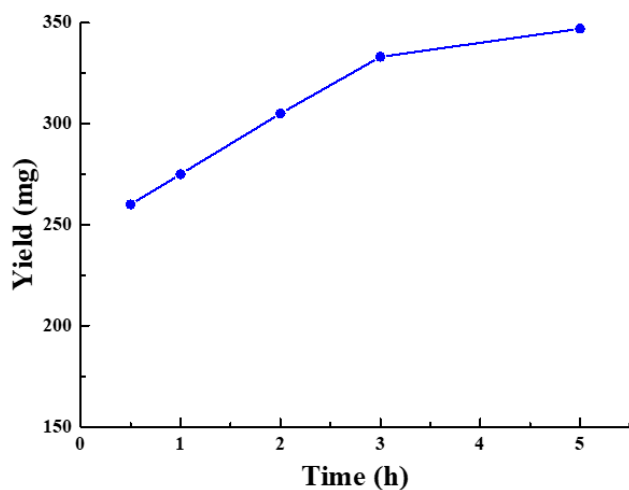


Figure S30 Polymer yield versus time at 100 °C for catalyst **6b**. Polymerization conditions: ethylene (40 bar), catalyst **6b** (1.5 μmol , x mL), toluene (20-x mL).

8. The Buried Volume ($\%V_{\text{bur}}$) for NHC-Pd Complexes

We calculated the % buried volume ($\%V_{\text{bur}}$) and topographic steric maps for two types of NHC-Pd complexes with a diisopropyl aniline group by the SambVca 2.1 program (Figure S31). The *aImPy*-Pd complex **6d** and *n*NHC-Pd complex (IzQO-Pd, **F**), differing in the ligand backbone showed almost similar buried volume value (41.7% and 40.0%, respectively). when comprised to the $\%V_{\text{bur}}$ of east side values, *aImPy*-Pd complex **6d** are higher than that of *n*NHC-Pd complex **F** (54.9% vs 50.9%, respectively). The steric protection around the metal center contributes to suppressing the β -hydride elimination, which could increase the molecular weight of polymer. Furthermore, in propylene polymerization, the insertion mode of propylene could be explained through the steric environment of ligand. In case of IzQO/Pd system, the bulky substituents on the N atom could help the 1,2-insertion of propylene over 2,1-insertion, leading formation of polypropylene with low regiodefects. As shown in IzQO/Pd system, we confirmed that *aImPy*-Pd complexes could prefer 1,2-insertion of propylene over 2,1-insertion, leading to decreasing the regioerrors.

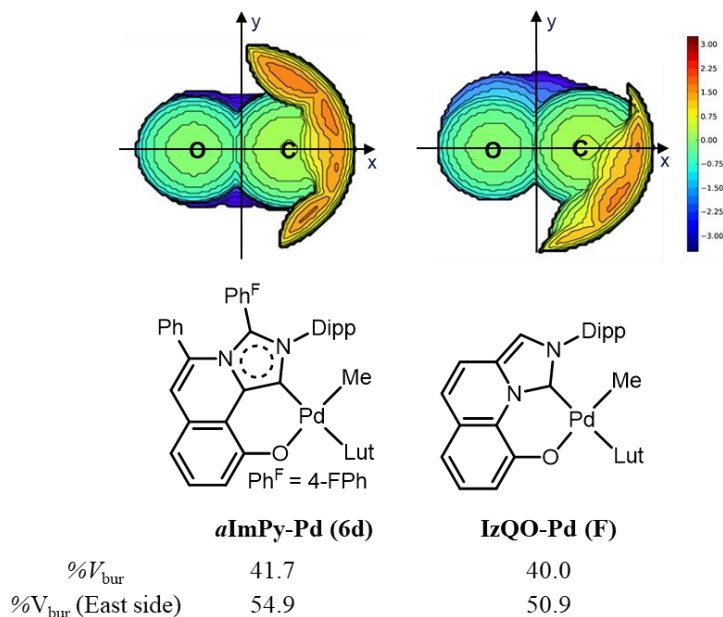


Figure S31 Steric maps of palladium catalysts **6d** and **F** based on bidentate NHC ligands.

9. General Procedure of Polymerization

9.1. General Procedure of Ethylene Polymerization (Table 1)

A 50-mL stainless steel autoclave with a magnetic stirrer bar was dried in an oven at 120 °C, sealed, and evacuated under vacuum until cooled to room temperature. Freshly prepared stock solution of catalyst (1.5 μmol, x mL of a 1.0 mmol/L solution in toluene) and toluene (20-x mL) was added to the autoclave charged with argon. The total volume of toluene was 20 mL. The autoclave was purged three times with ethylene and pressurized to 40 bar. The autoclave mixture was stirred in an oil bath under the given conditions. After the autoclave had cooled to room temperature, the redundant ethylene was vented and the reaction was quenched by addition of ethanol (ca. 20 mL). The formed precipitate was filtered, washed with ethanol, and dried under high vacuum at 120 °C at least for 6 h to afford polyethylene.

9.2. General Procedure of Propylene Polymerization (Table 2)

A 50-mL stainless steel autoclave with a magnetic stirrer bar was dried in an oven at 120 °C, sealed, and evacuated under vacuum until cooled to room temperature. Freshly prepared stock solution of catalyst (3.0 μmol, x mL of a 1.0 mmol/L solution in toluene) and toluene (20-x mL) was added to the autoclave charged with argon. The total volume of toluene was 20 mL. Propylene was then introduced as a gas for reactions at 120 psig at 0 °C with stirring during 5 min. The autoclave mixture was stirred in an oil bath under the given conditions. After the autoclave had cooled to room temperature, the redundant propylene was vented and volatile materials were evaporated. To the resulting mixture was added excess methanol and formed gummy solid was collected. The obtained solid was rubbering washed in methanol two times, and dried under high vacuum at 120 °C at least for 6 hours to afford polypropylene.

9.3. General Procedure of Copolymerization of Ethylene and Polar Monomers (Table 3)

A 50-mL stainless steel autoclave with a magnetic stirrer bar was dried in an oven at 120 °C, sealed, and evacuated under vacuum until cooled to room temperature. Catalyst (10 μmol), a

polar monomer (x mL), and toluene (20-x mL) was added to the autoclave charged with argon. The total volume of toluene was 20 mL. The autoclave was purged three times with ethylene and pressurized to 40 bar. The autoclave mixture was stirred in an oil bath under the given conditions. After the autoclave had cooled to room temperature, the redundant ethylene was vented and the reaction was quenched by addition of ethanol (ca. 20 mL). The formed precipitate was filtered, washed with ethanol, and dried under high vacuum at 120 °C at least for 6 h to afford ethylene/polar monomer copolymers.

9.4. General Procedure of Copolymerization of Ethylene and Methylmethacrylate (Table 4)

A 50-mL stainless steel autoclave with a magnetic stirrer bar was dried in an oven at 120 °C, sealed, and evacuated under vacuum until cooled to room temperature. Catalyst (10 μmol), BHT (200 mg), MMA (4 mL), and toluene (4 mL) were added to the autoclave charged with argon. The autoclave was purged three times with ethylene and pressurized to 20 bar. The autoclave mixture was stirred in an oil bath at 120 °C for 15 h. After the autoclave had cooled to room temperature, the redundant ethylene was vented and the reaction was quenched by addition of ethanol (ca. 20 mL). The formed precipitates were filtered, washed with ethanol and dried under high vacuum at 120 °C at least for 6 h to afford ethylene/methyl methacrylate copolymers.

9.5. General Procedure of Copolymerization of Propylene and Polar Monomers (Scheme 2)

A 50-mL stainless steel autoclave with a magnetic stirrer bar was dried in an oven at 120 °C, sealed, and evacuated under vacuum until cooled to room temperature. Catalyst (10 μmol), a polar monomer (x mL), and toluene (20-x mL) was added to the autoclave charged with argon. Propylene was then introduced as a gas for reactions at 120 psig at 0 °C with stirring during 5 min. The autoclave mixture was stirred in an oil bath at 100 °C for 6 h. After the autoclave had

cooled to room temperature, the redundant propylene was vented and volatile materials were evaporated. To the resulting mixture was added excess methanol and formed gummy solid was collected. The obtained solid was rubbering washed in methanol two times. The resulting gum was dissolved in DCM and passed through a plug of silica-gel with aid of additional DCM. The obtained solution was evaporated and dried under high vacuum at 120 °C at least for 6 hours to afford propylene/polar monomer copolymers.

10. NMR Spectra of Polymers

The observed ^1H and ^{13}C NMR spectra of reported homopolymers and copolymers were assigned according to following literatures; polyethylene,^{11, 25} polypropylene,^{11, 19, 26-27} ethylene/polar monomer,^{12, 28} ethylene/methylmethacrylate²⁰, propylene/allyl acetate.^{11, 19}

10.1. NMR Spectra of polyethylene (Table1)

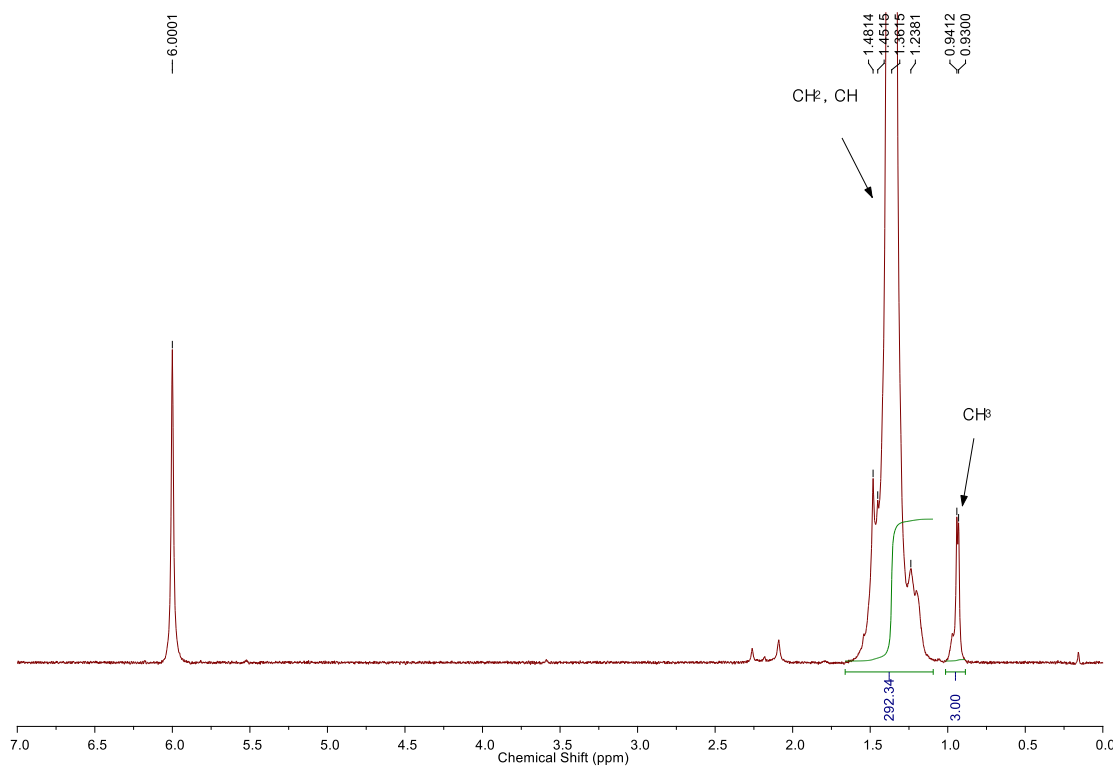


Figure S32 ¹H NMR spectrum (500 MHz, C₂D₂Cl₄, 120 °C) of polyethylene obtained by **6a** at 100 °C (Table 1, entry 2).

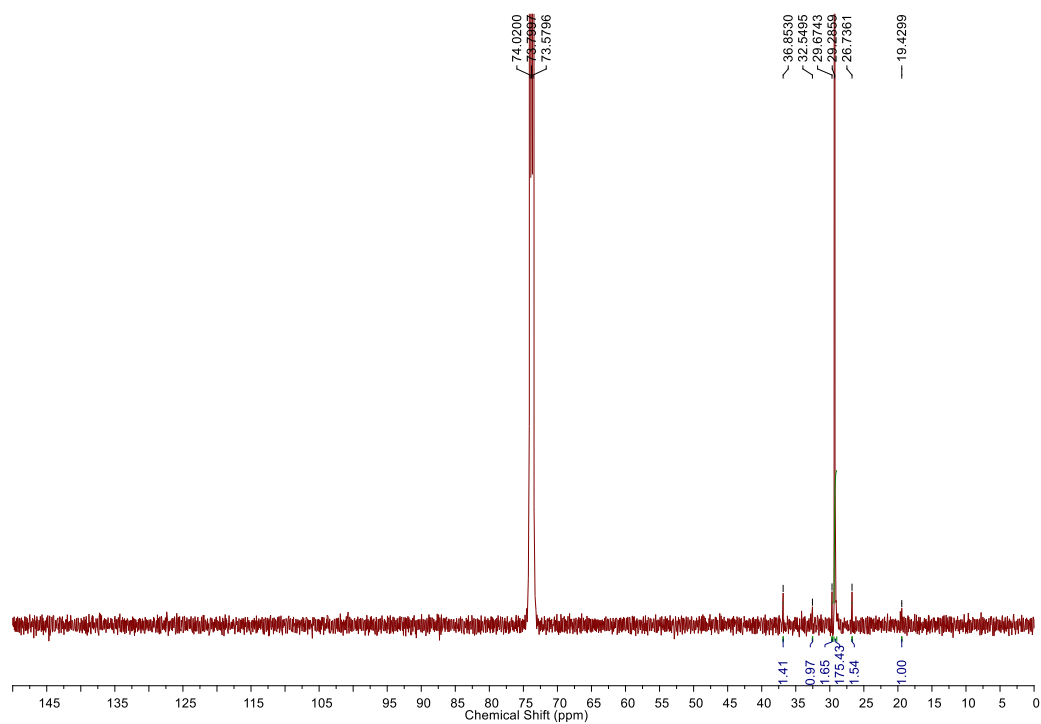


Figure S33 Quantitative ¹³C NMR spectrum (126 MHz, C₂D₂Cl₄, 0.05M Cr(acac)₃, 120 °C) of

polyethylene obtained by **6a** at 100 °C (Table 1, entry 2).

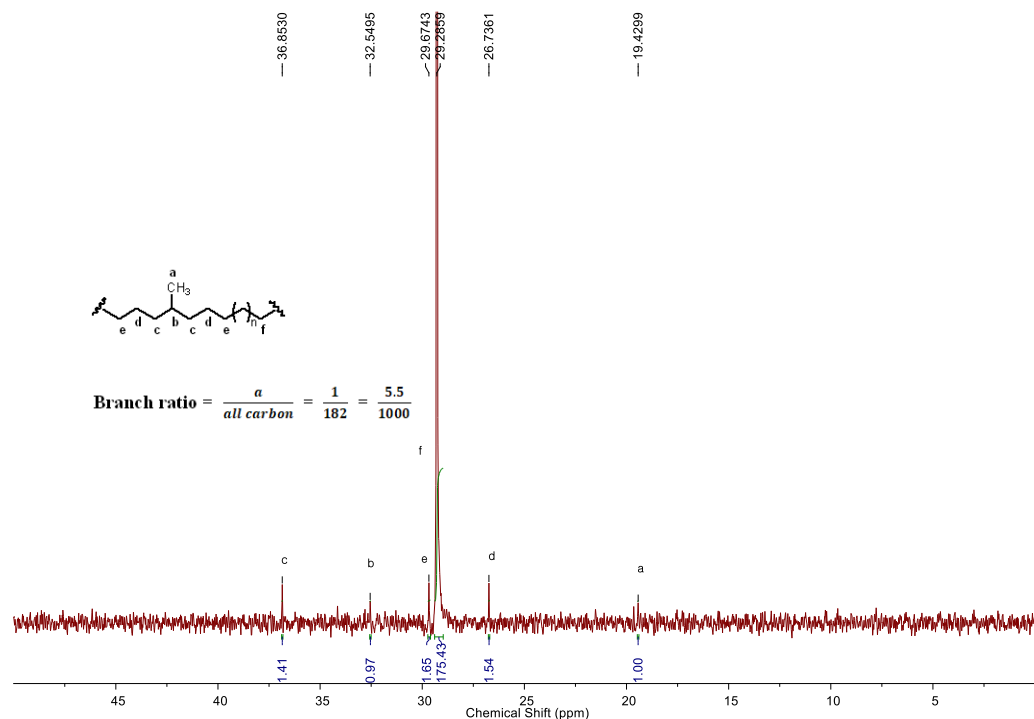


Figure S34 Specific region (0–50 ppm) of quantitative ^{13}C NMR spectrum (126 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 0.05M $\text{Cr}(\text{acac})_3$, 120 °C) of polyethylene obtained by **6a** at 100 °C (Table 1, entry 2).

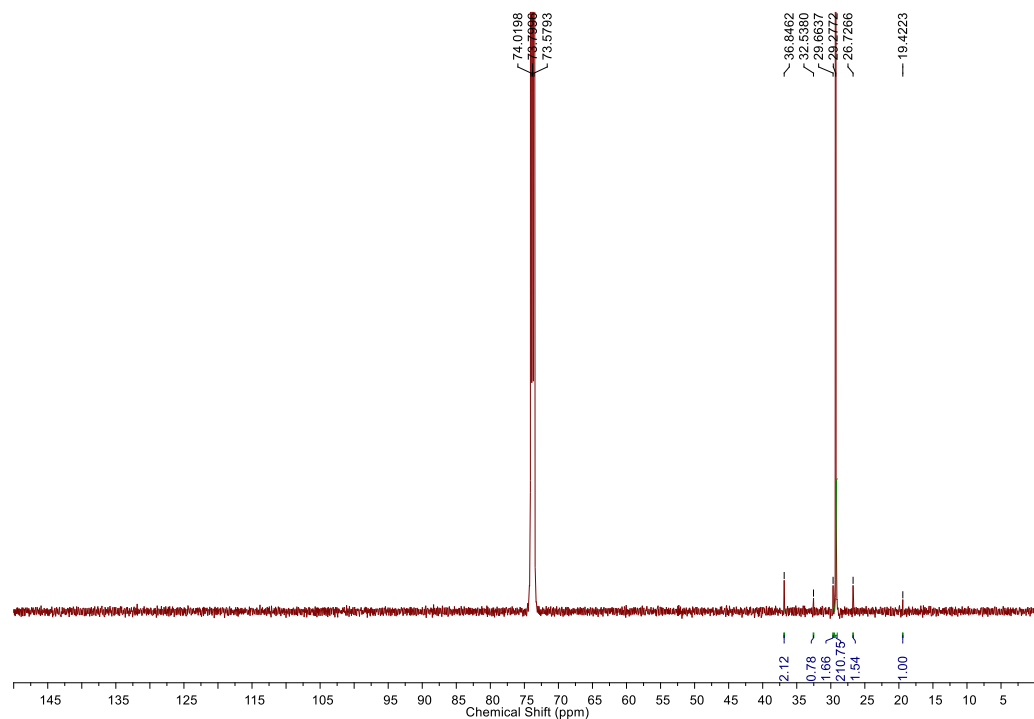


Figure S35 Quantitative ^{13}C NMR spectrum (126 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 0.05M $\text{Cr}(\text{acac})_3$, 120 °C) of polyethylene obtained by **6a** at 120 °C (Table 1, entry 3).

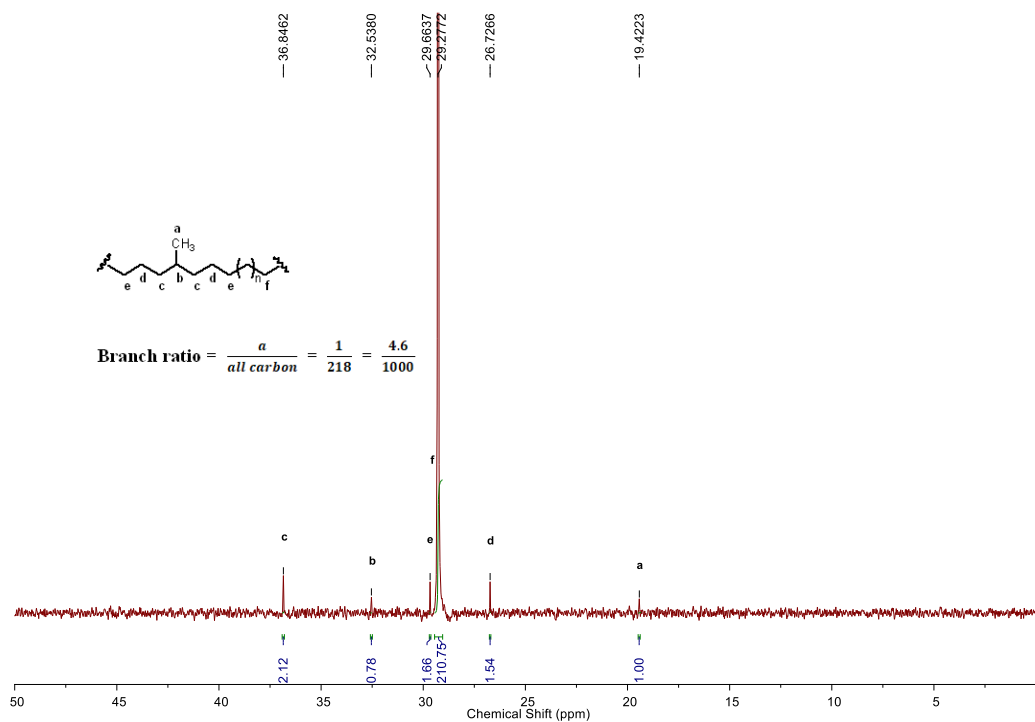


Figure S36 Specific region (0–50 ppm) of quantitative ^{13}C NMR spectrum (126 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 0.05M $\text{Cr}(\text{acac})_3$, 120 °C) of polyethylene obtained by **6a** at 120 °C (Table 1, entry 3).

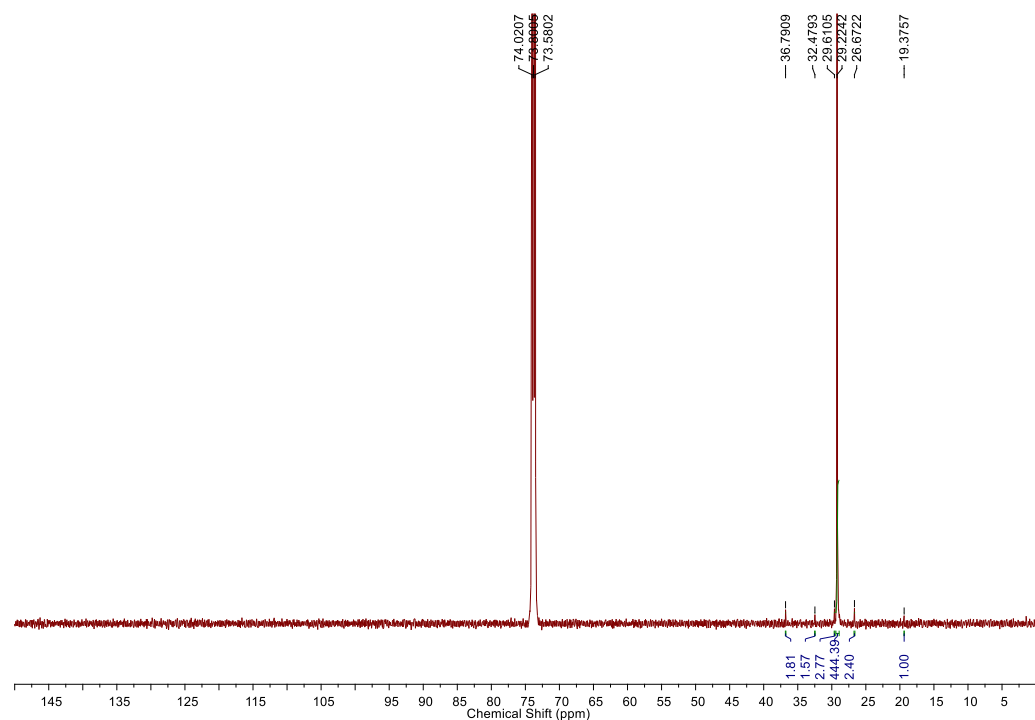


Figure S37 Quantitative ^{13}C NMR spectrum (126 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 0.05M $\text{Cr}(\text{acac})_3$, 120 °C) of polyethylene obtained by **6b** at 100 °C (Table 1, entry 4).

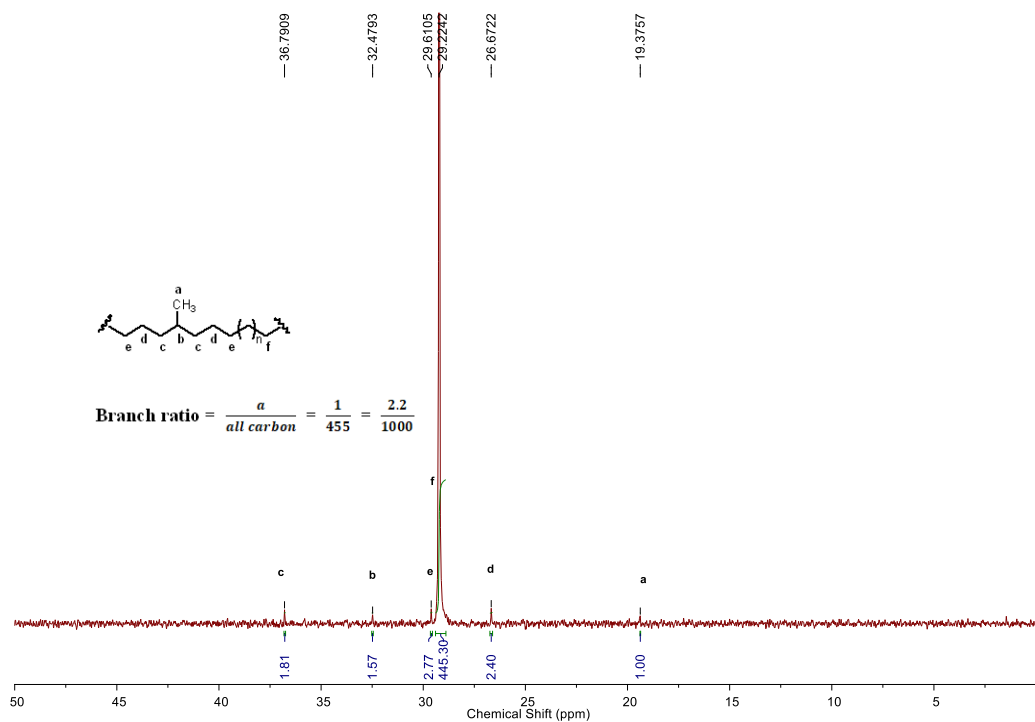


Figure S38 Specific region (0–50 ppm) of quantitative ^{13}C NMR spectrum (126 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 0.05M $\text{Cr}(\text{acac})_3$, 120 °C) of polyethylene obtained by **6b** at 100 °C (Table 1, entry 4).

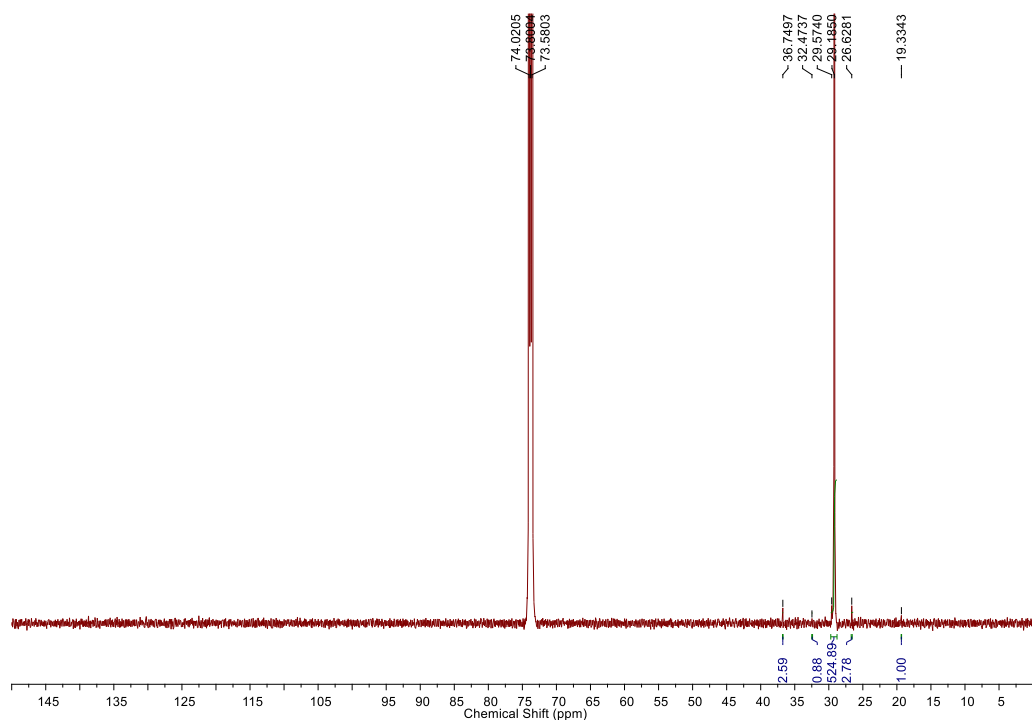


Figure S39 Quantitative ^{13}C NMR spectrum (126 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 0.05M $\text{Cr}(\text{acac})_3$, 120 °C) of polyethylene obtained by **6b** at 100 °C for 2 h (Table 1, entry 6).

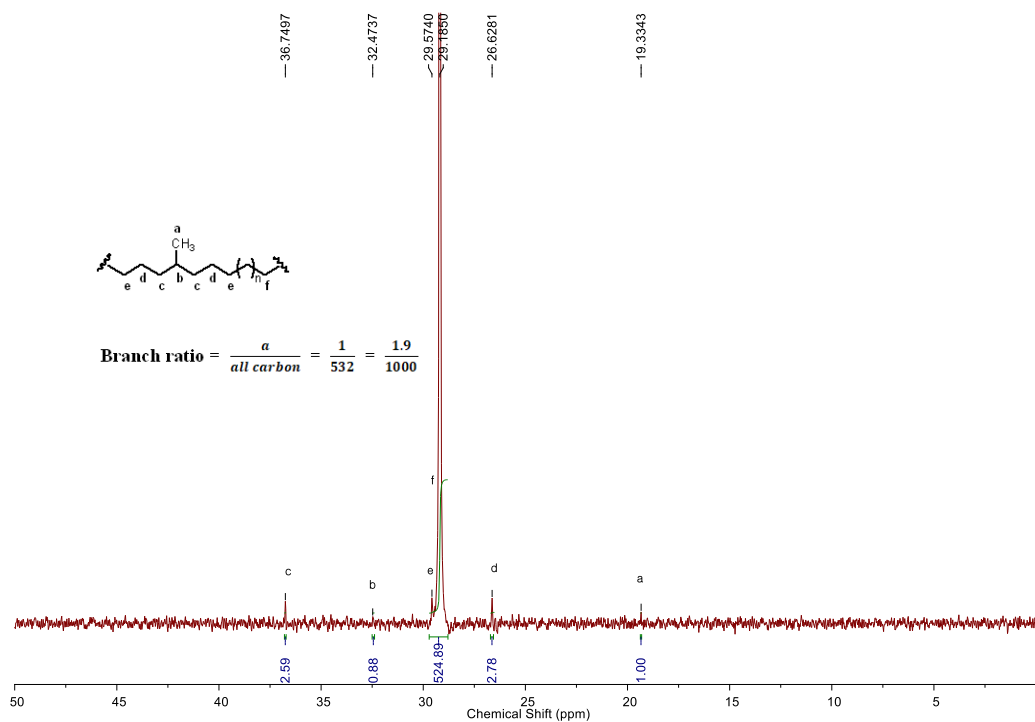


Figure S40 Specific region (0–50 ppm) of quantitative ^{13}C NMR spectrum (126 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 0.05M $\text{Cr}(\text{acac})_3$, 120 °C) of polyethylene obtained by **6b** at 100 °C for 2 h (Table 1, entry 6).

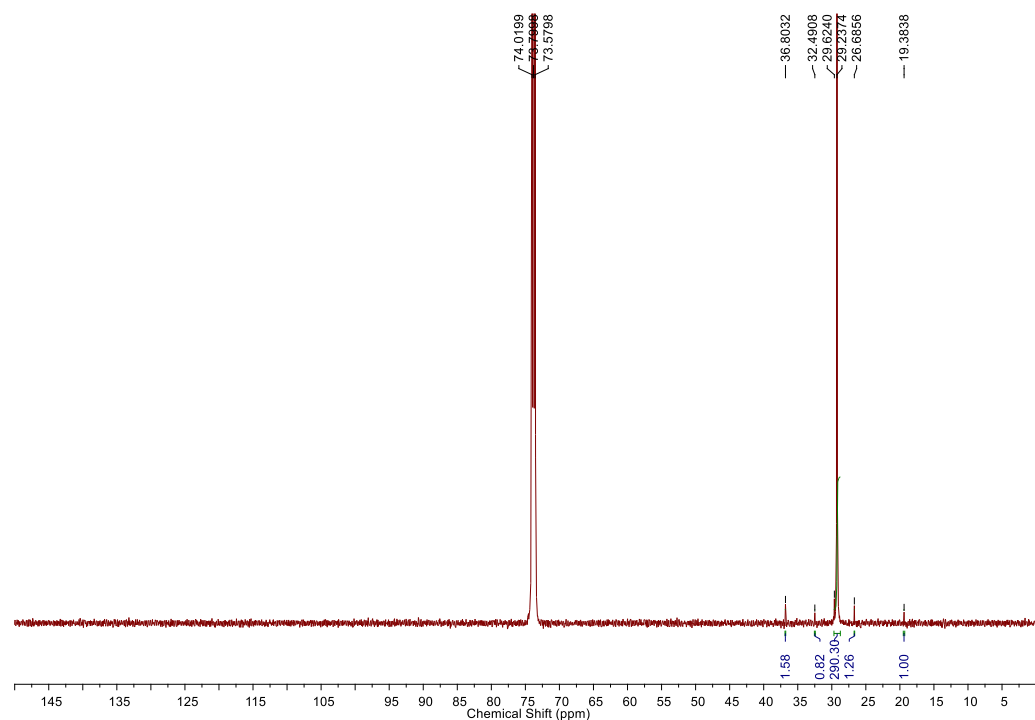


Figure S41 Quantitative ^{13}C NMR spectrum (126 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 0.05M $\text{Cr}(\text{acac})_3$, 120 °C) of polyethylene obtained by **6b** at 120 °C (Table 1, entry 7).

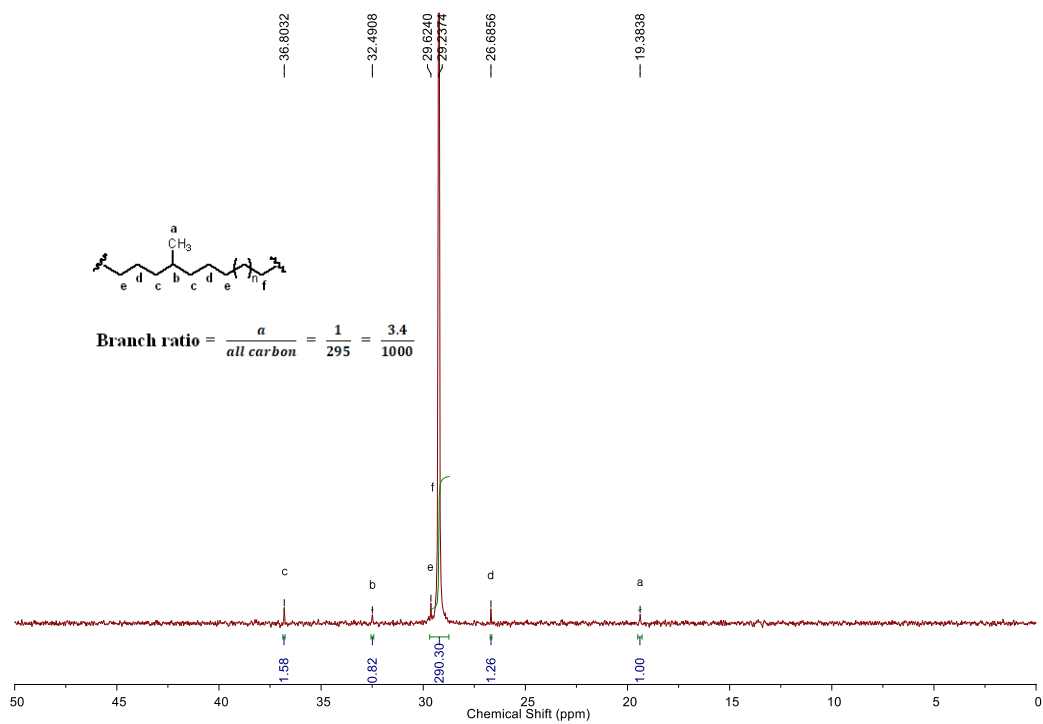


Figure S42 Specific region (0–50 ppm) of quantitative ¹³C NMR spectrum (126 MHz, C₂D₂Cl₄, 0.05M Cr(acac)₃, 120 °C) of polyethylene obtained by **6b** at 120 °C (Table 1, entry 7).

10.2. NMR Spectra of polypropylene (Table 2)

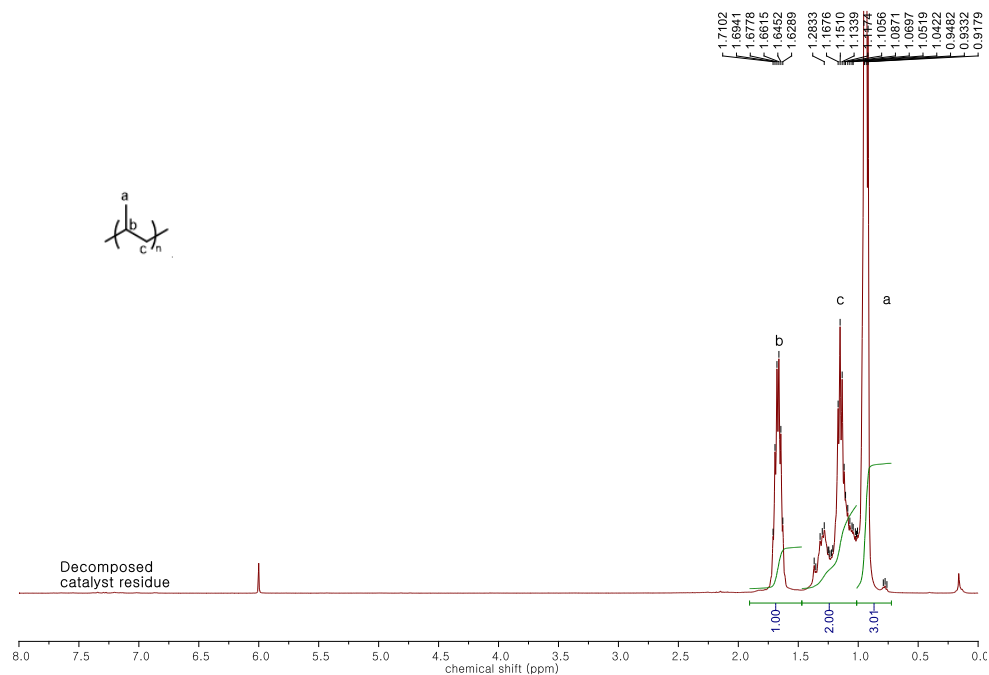


Figure S43 ^1H NMR spectrum (400 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 120 °C) of polypropylene obtained by **6a** at 100 °C for 1 h (Table 2, entry 1).

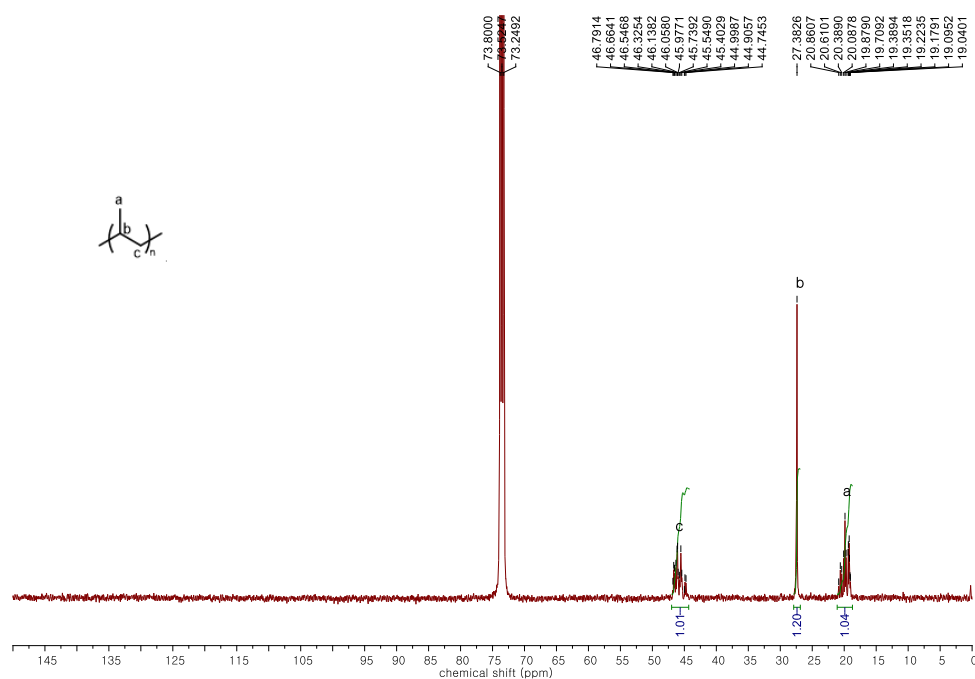


Figure S44 Quantitative ^{13}C NMR spectrum (101 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 0.05M $\text{Cr}(\text{acac})_3$, 120 °C) of polypropylene obtained by **6a** at 100 °C for 1 h (Table 2, entry 1).

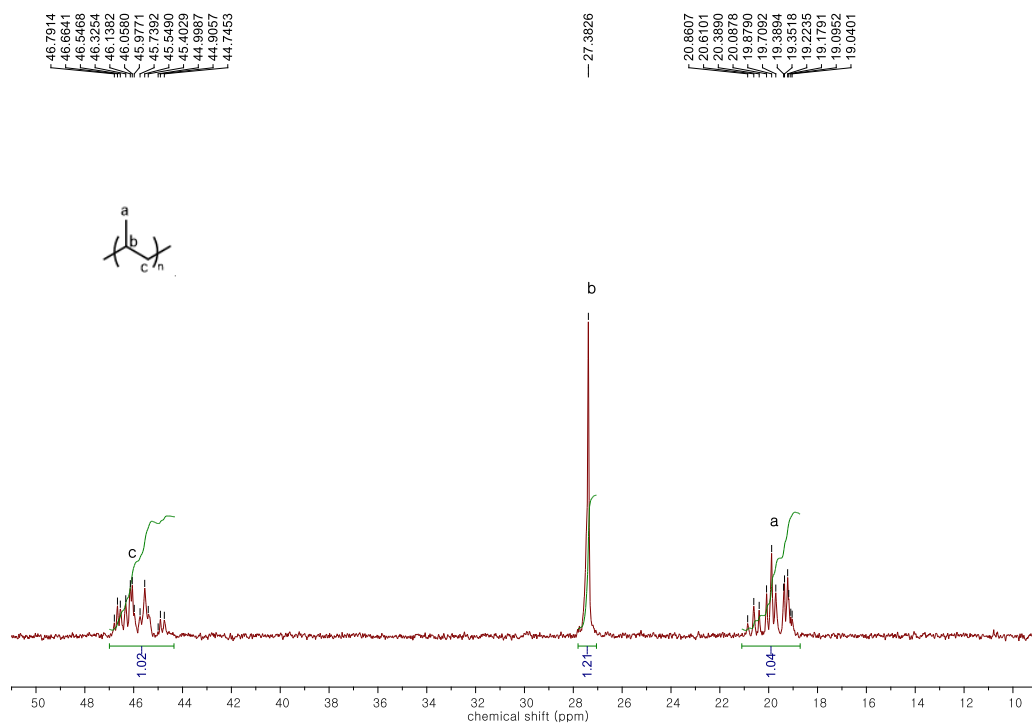


Figure S45 Specific region (0–50 ppm) of quantitative ^{13}C NMR spectrum (101 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 0.05M $\text{Cr}(\text{acac})_3$, 120 °C) of polypropylene obtained by **6a** at 100 °C for 1 h (Table 2, entry 1).

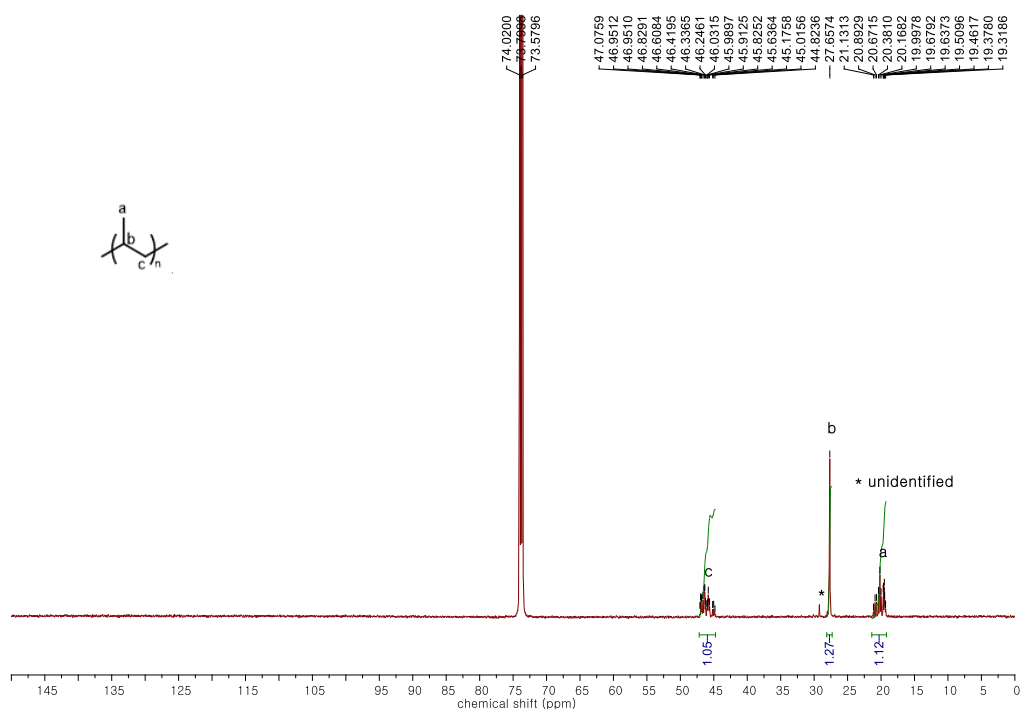


Figure S46 Quantitative ^{13}C NMR spectrum (126 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 0.05M $\text{Cr}(\text{acac})_3$, 120 °C) of polypropylene obtained by **6a** at 100 °C for 3 h (Table 2, entry 2).

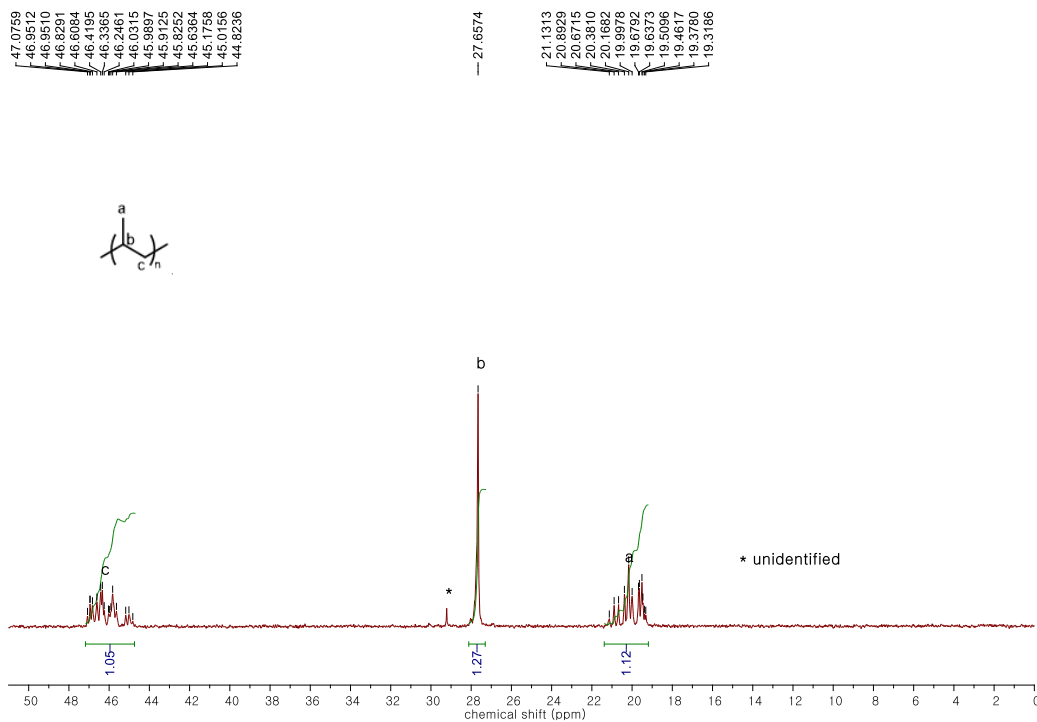


Figure S47 Specific region (0–50 ppm) of quantitative ^{13}C NMR spectrum (126 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 0.05M $\text{Cr}(\text{acac})_3$, 120 °C) of polypropylene obtained by **6a** at 100 °C for 3 h (Table 2, entry 2).

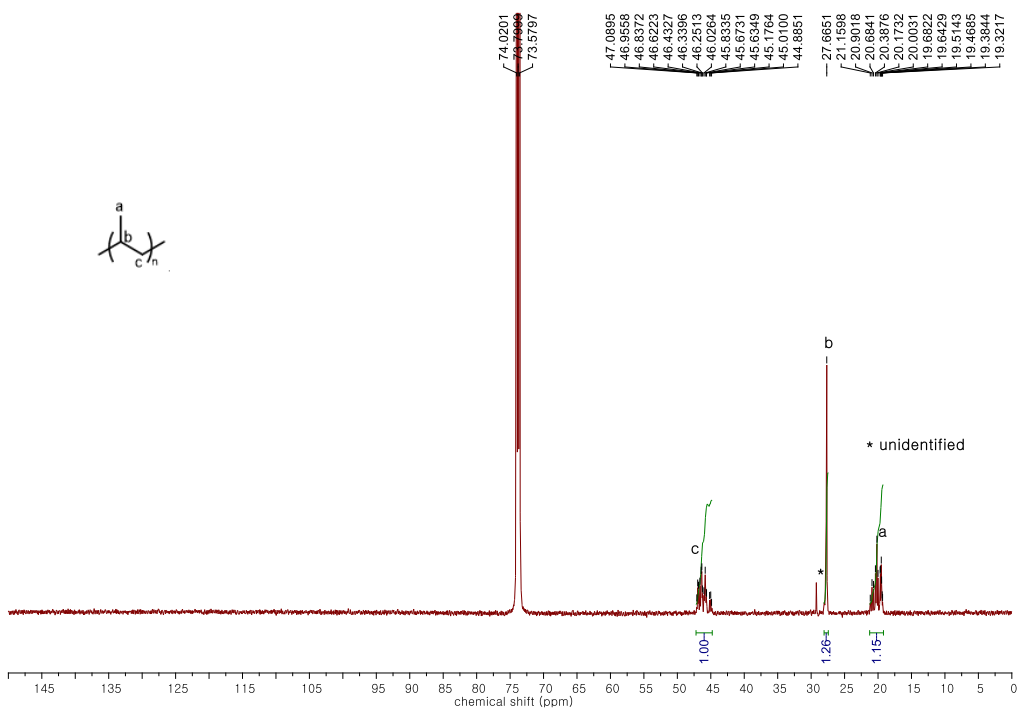


Figure S48 Quantitative ^{13}C NMR spectrum (126 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 0.05M $\text{Cr}(\text{acac})_3$, 120 °C) of polypropylene obtained by **6a** at 120 °C for 3 h (Table 2, entry 3).

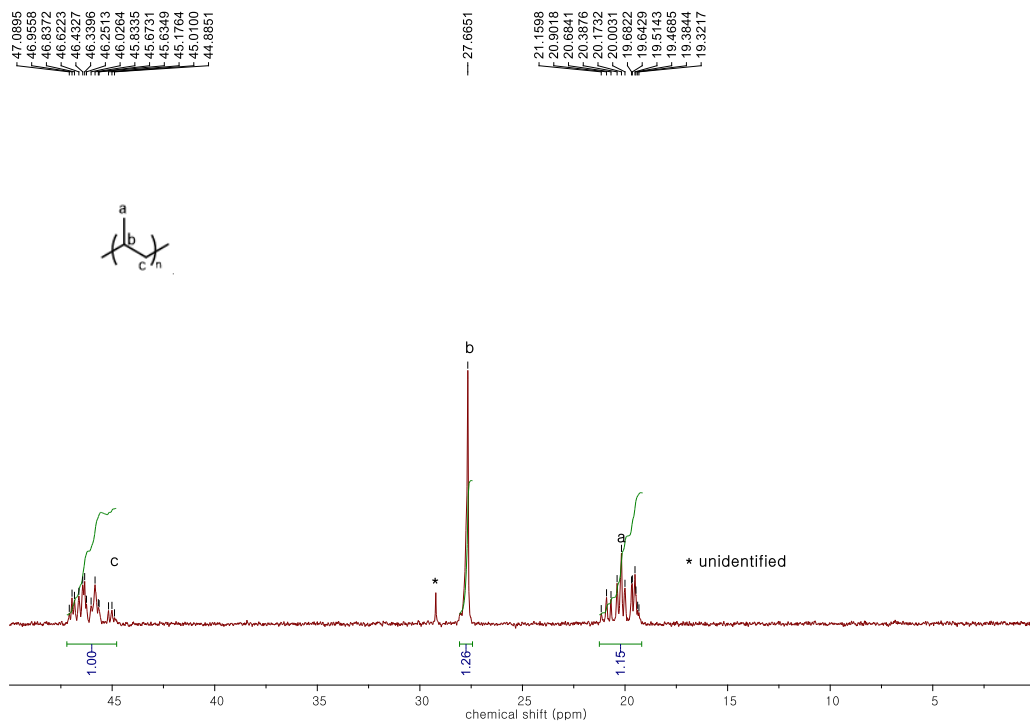


Figure S49 Specific region (0–50 ppm) of quantitative ^{13}C NMR spectrum (126 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 0.05M $\text{Cr}(\text{acac})_3$, 120 °C) of polypropylene obtained by **6a** at 120 °C for 3 h (Table 2, entry 3).

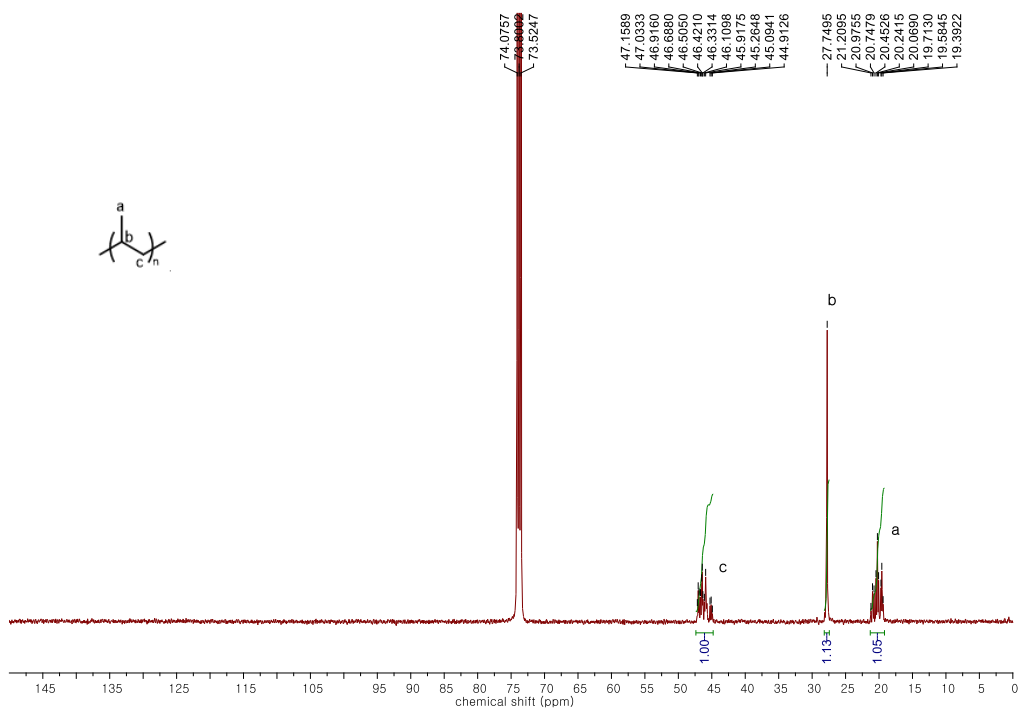


Figure S50 Quantitative ^{13}C NMR spectrum (101 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 0.05M $\text{Cr}(\text{acac})_3$, 120 °C) of polypropylene obtained by **6b** at 100 °C for 3 h (Table 2, entry 4).

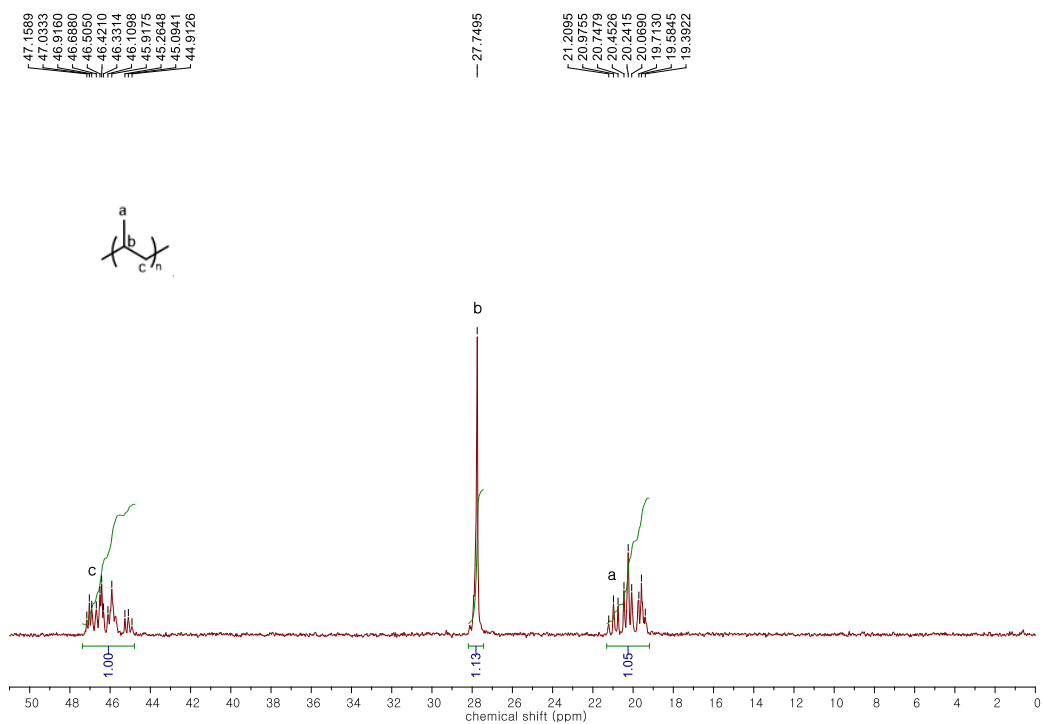


Figure S51 Specific region (0–50 ppm) of quantitative ^{13}C NMR spectrum (101 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 0.05M $\text{Cr}(\text{acac})_3$, 120 °C) of polypropylene obtained by **6b** at 100 °C for 3 h (Table 2, entry 4).

10.3. NMR Spectra of copolymers with ethylene and polar monomers (Table 3)

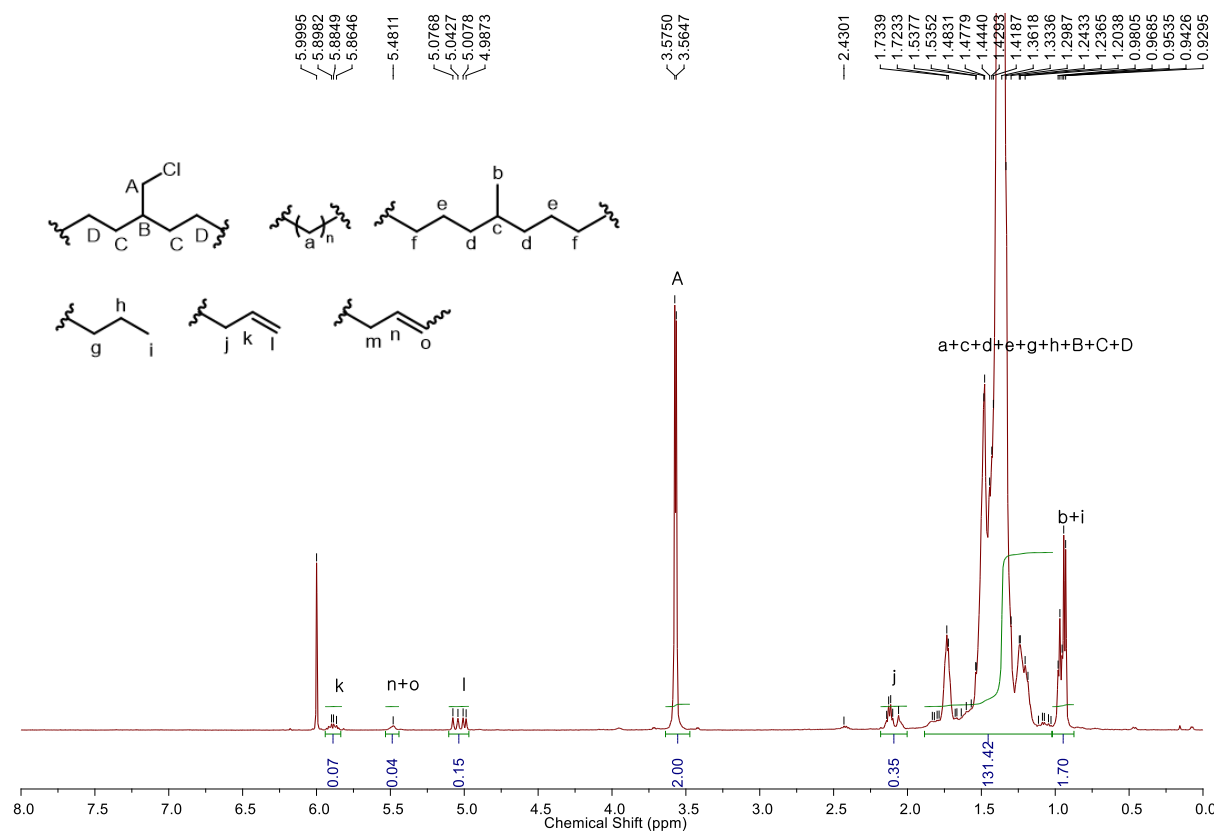


Figure S52 ^1H NMR spectrum (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 120 $^\circ\text{C}$) of poly(ethylene-co-allyl chloride) copolymer obtained by **6a** (Table 3, entry 1).

Note: Calculation of incorporation ratio of allyl chloride

$$\begin{aligned}
 &= \frac{\text{incorporated AC (mol)}}{\text{incorporated PE (mol)} + \text{incorporated AC (mol)}} \times 100 \\
 &= \frac{(\text{protons derived from AC})/5}{(\text{protons derived from PE})/4 + (\text{Protons derived from AC})/5} \times 100 \\
 &= \frac{A/2}{\frac{(\text{protons } 5.9\text{--}4.9 \text{ ppm}) + (\text{protons } 2.2\text{--}0.8 \text{ ppm}) - B - C}{4} + A/2} \times 100 \\
 &= \frac{A/2}{\frac{(\text{protons } 5.9\text{--}4.9 \text{ ppm}) + (\text{protons } 2.2\text{--}0.8 \text{ ppm}) - (A/2) \times 3}{4} + A/2} \times 100 \\
 &= \frac{1}{\frac{0.26 + 133.47 - 3}{4} + 1} \times 100 = 2.97 \approx 3.0
 \end{aligned}$$

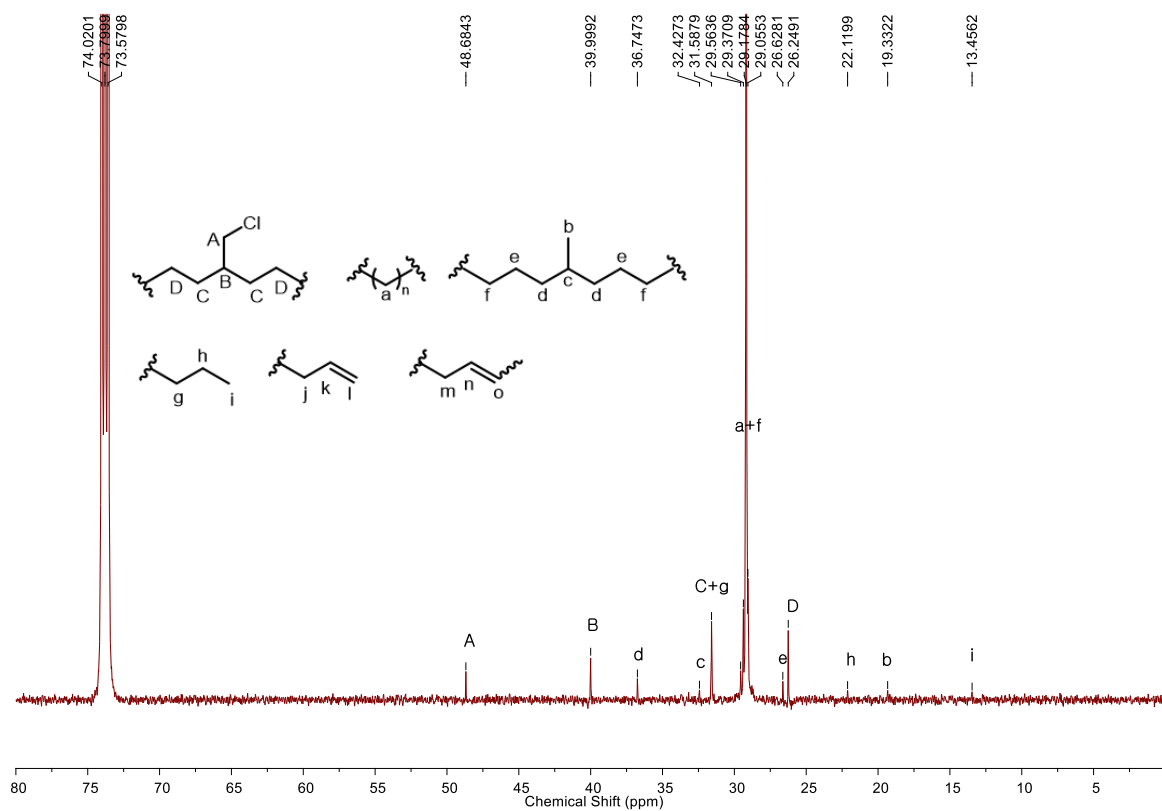


Figure S53 ^{13}C NMR spectrum (126 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 0.05M $\text{Cr}(\text{acac})_3$, 120 °C) of poly(ethylene-co-allyl chloride) copolymer obtained by **6a** (Table 3, entry 1).

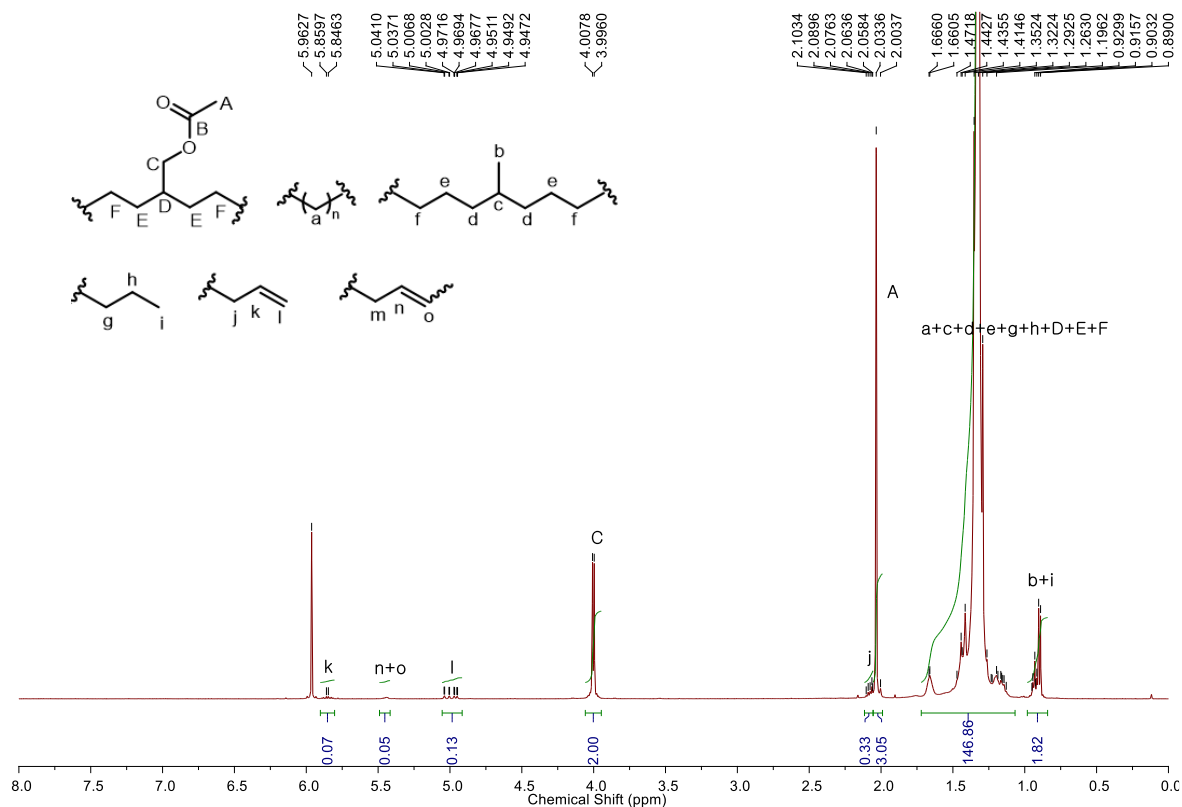


Figure S54 ^1H NMR spectrum (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 120 $^\circ\text{C}$) of poly(ethylene-co-allyl acetate) copolymer obtained by **6a** (Table 3, entry 2).

Note: Calculation of incorporation ratio of allyl acetate

$$\begin{aligned}
 &= \frac{\text{incorporated AAc}(\text{mol})}{\text{incorporated PE}(\text{mol}) + \text{incorporated AAc}(\text{mol})} \times 100 \\
 &= \frac{(\text{protons derived from AAc})/8}{(\text{protons derived from PE})/4 + (\text{Protons derived from AAc})/8} \times 100 \\
 &= \frac{C/2}{\frac{(\text{protons } 5.9\text{--}4.9 \text{ ppm}) + (\text{protons } 2.2\text{--}0.8 \text{ ppm}) - A - D - E}{4} + C/2} \times 100 \\
 &= \frac{C/2}{\frac{(\text{protons } 5.9\text{--}4.9 \text{ ppm}) + (\text{protons } 2.2\text{--}0.8 \text{ ppm}) - (C/2) \times 6}{4} + C/2} \times 100 \\
 &= \frac{1}{\frac{0.25 + 152.06 - 6}{4} + 1} \times 100 = 2.66 \approx 2.7
 \end{aligned}$$

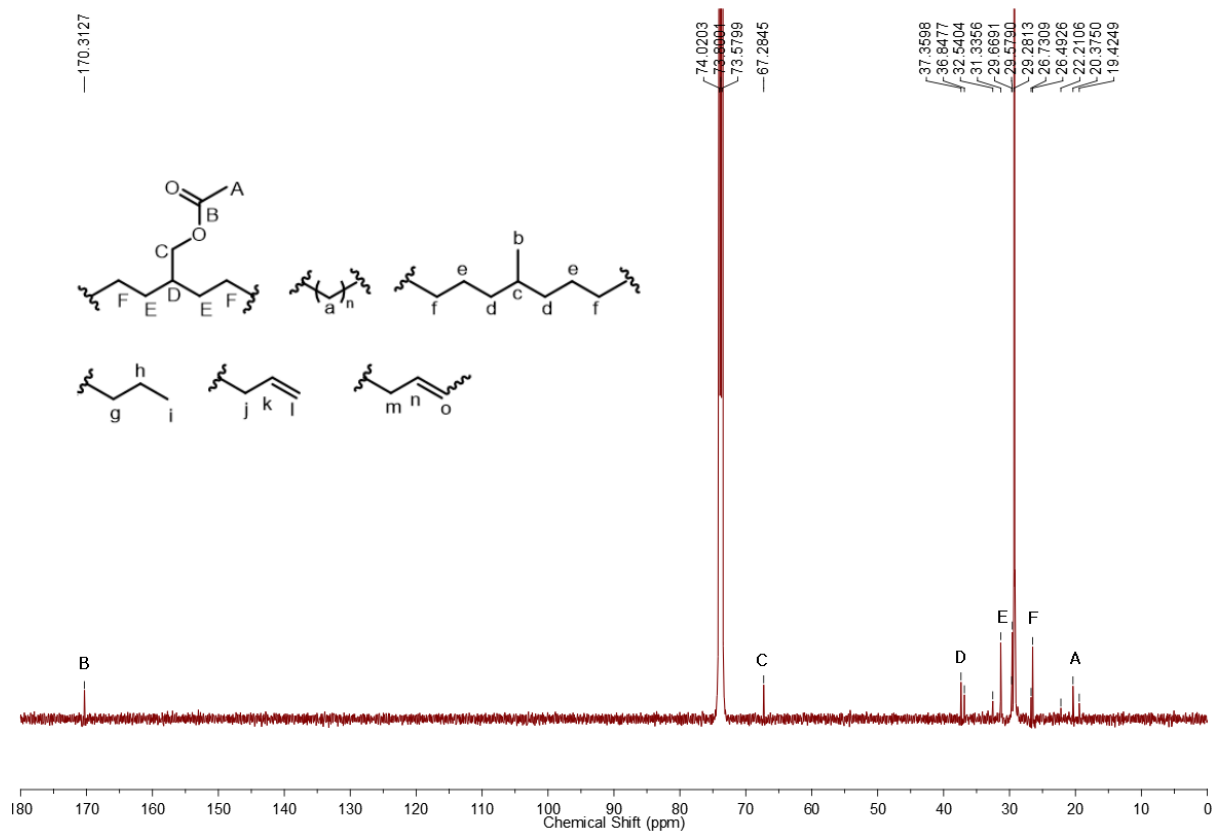


Figure S55 ^{13}C NMR spectrum (126 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 0.05M $\text{Cr}(\text{acac})_3$, 120 $^\circ\text{C}$) of poly(ethylene-co-allyl acetate) copolymer obtained by **6a** (Table 3, entry 2).

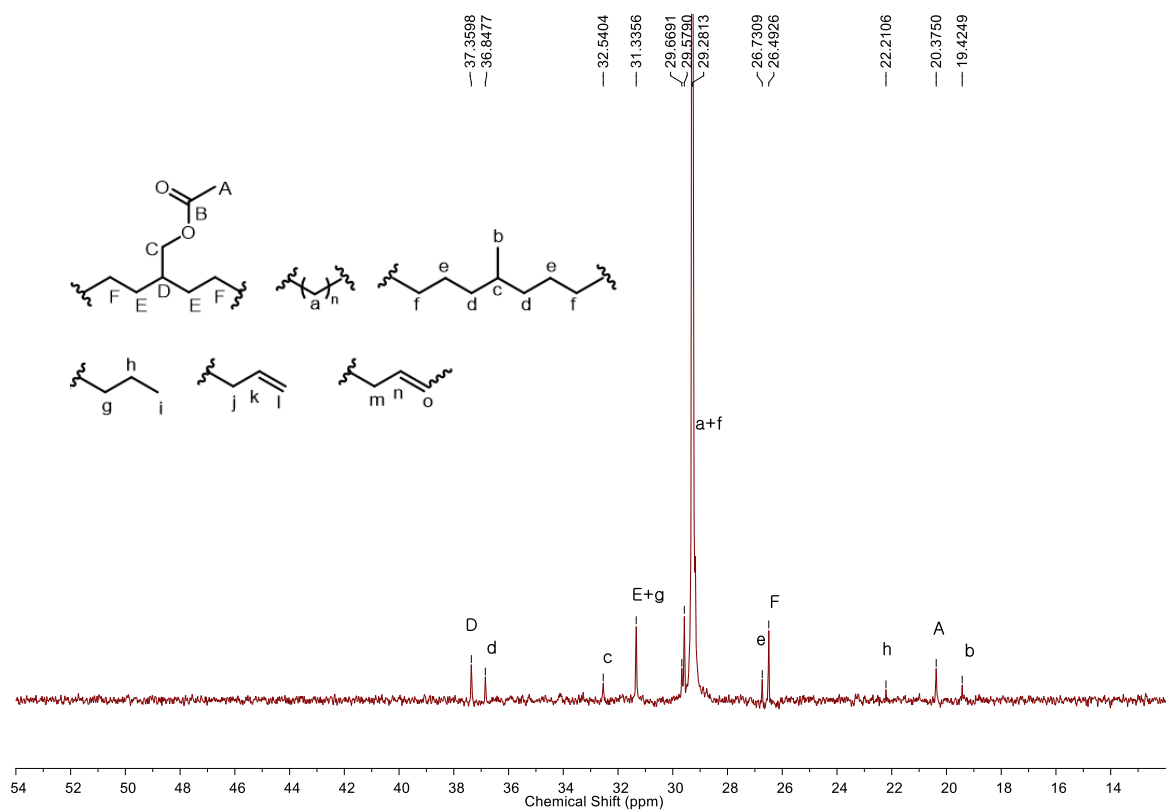


Figure S56 Specific region (12-54 ppm) of ^{13}C NMR spectrum (126 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 0.05M $\text{Cr}(\text{acac})_3$, 120 $^\circ\text{C}$) of poly(ethylene-co-allyl acetate) copolymer obtained by **6a** (Table 3, entry 2).

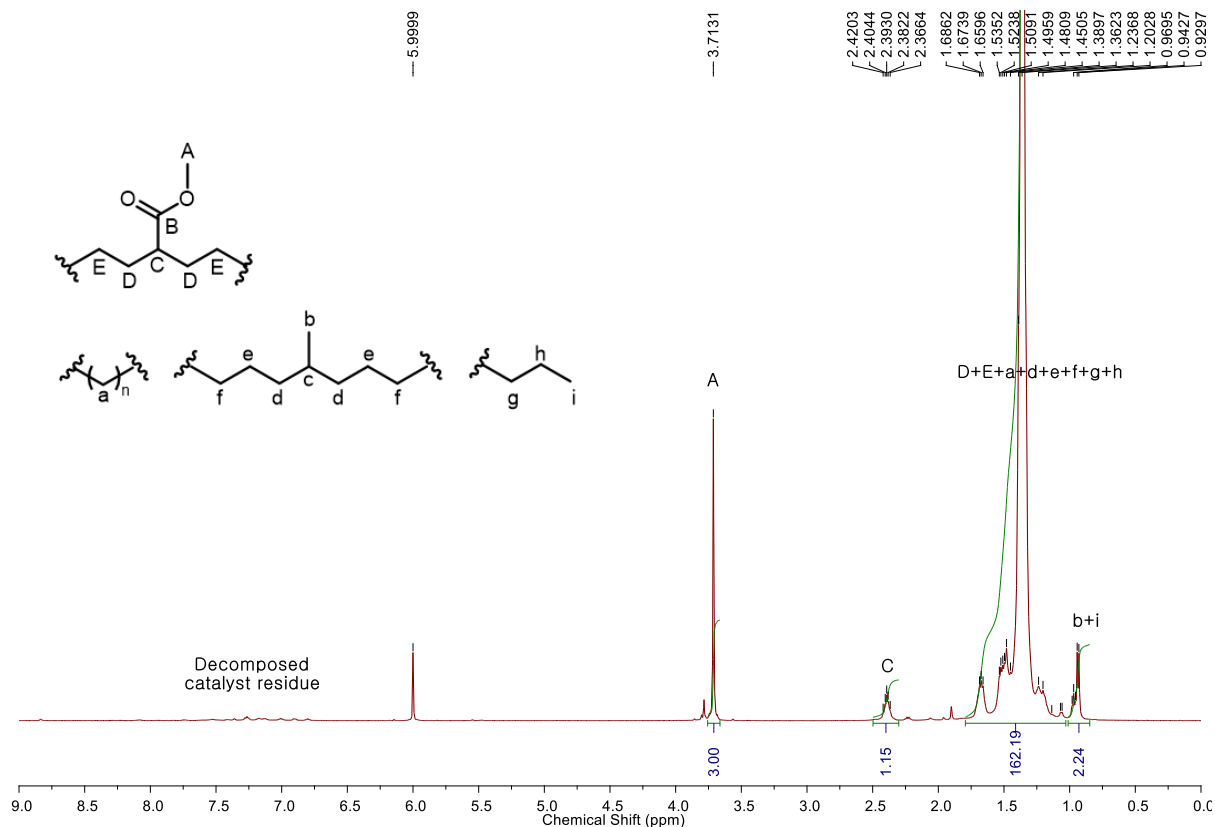


Figure S57 ¹H NMR spectrum (500 MHz, C₂D₂Cl₄, 120 °C) of poly(ethylene-co-methyl acrylate) obtained by **6a** (Table 3, entry 3).

Note: Calculation of incorporation ratio of methyl acrylate

$$\begin{aligned}
 &= \frac{\text{incorporated MA}(\text{mol})}{\text{incorporated PE}(\text{mol}) + \text{incorporated MA}(\text{mol})} \times 100 \\
 &= \frac{(\text{protons derived from MA})/6}{(\text{protons derived from PE})/4 + (\text{Protons derived from MA})/6} \times 100 \\
 &= \frac{A/3}{\frac{(\text{protons } 2.2-0.8 \text{ ppm}) - C - D}{4} + A/3} \times 100 \\
 &= \frac{A/3}{\frac{(\text{protons } 2.2-0.8 \text{ ppm}) - C - (A/3) \times 2}{4} + A/3} \times 100 \\
 &= \frac{1}{\frac{164.43 - 115 - 2}{4} + 1} \times 100 = 2.42 \approx 2.4
 \end{aligned}$$

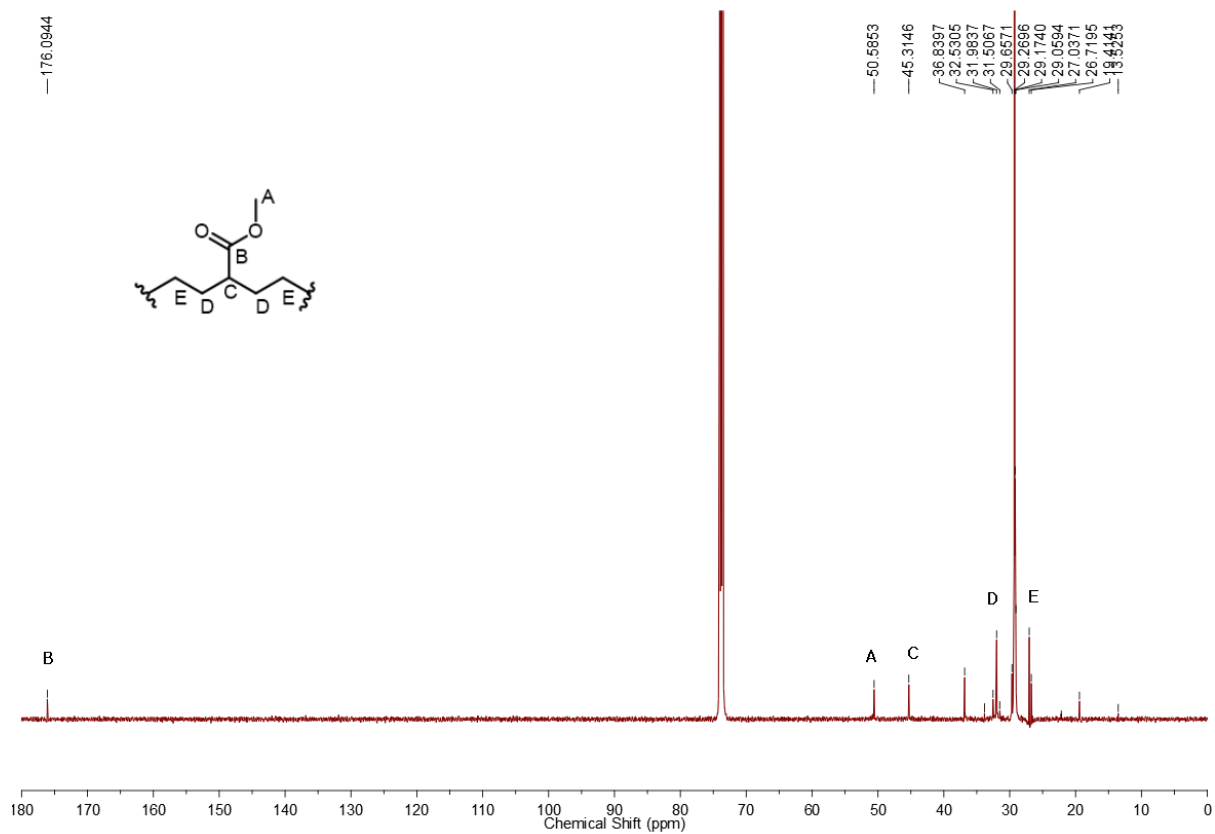


Figure S58 ^{13}C NMR spectrum (126 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 0.05M $\text{Cr}(\text{acac})_3$, 120 $^\circ\text{C}$) of poly(ethylene-co-methyl acrylate) obtained by **6a** (Table 3, entry 3).

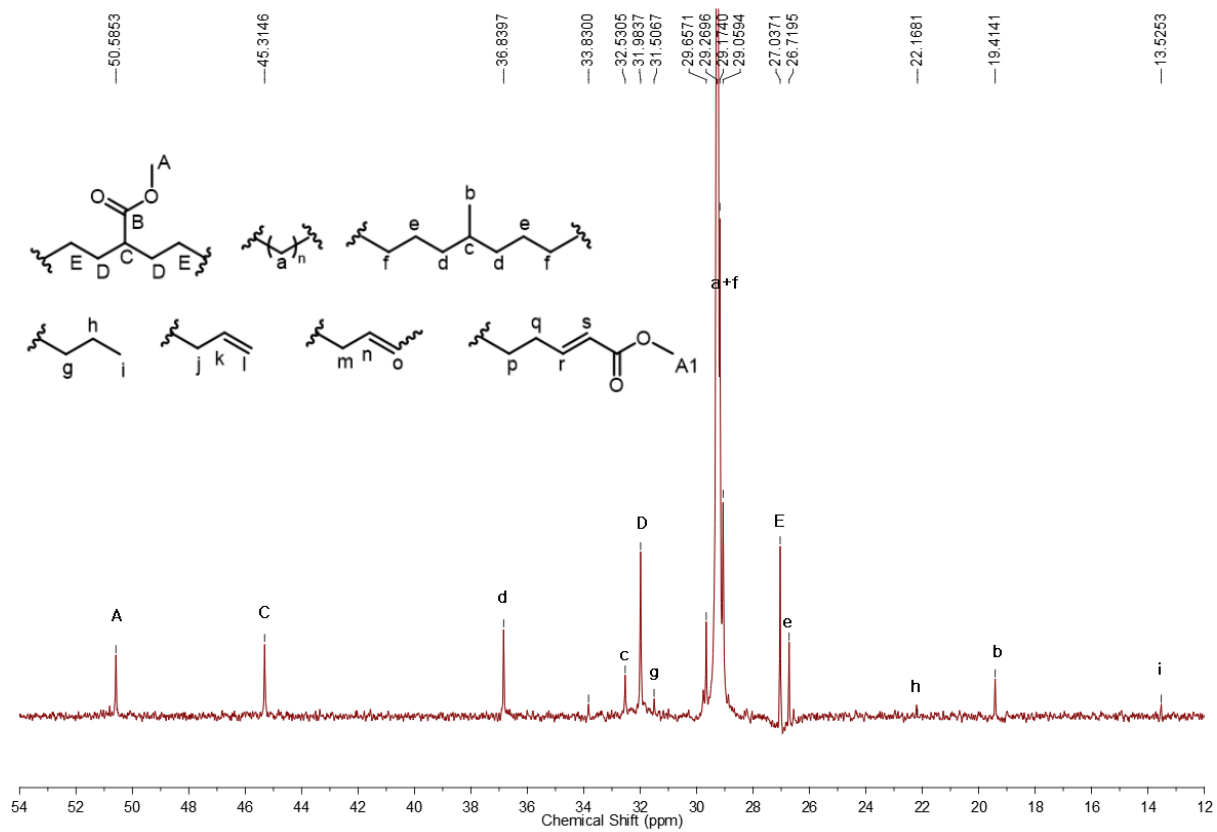


Figure S59 Specific region (12-54 ppm) of ^{13}C NMR spectrum (126 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 0.05M $\text{Cr}(\text{acac})_3$, 120 °C) of poly(ethylene-co-methyl acrylate) obtained by **6a** (Table 3, entry 3).

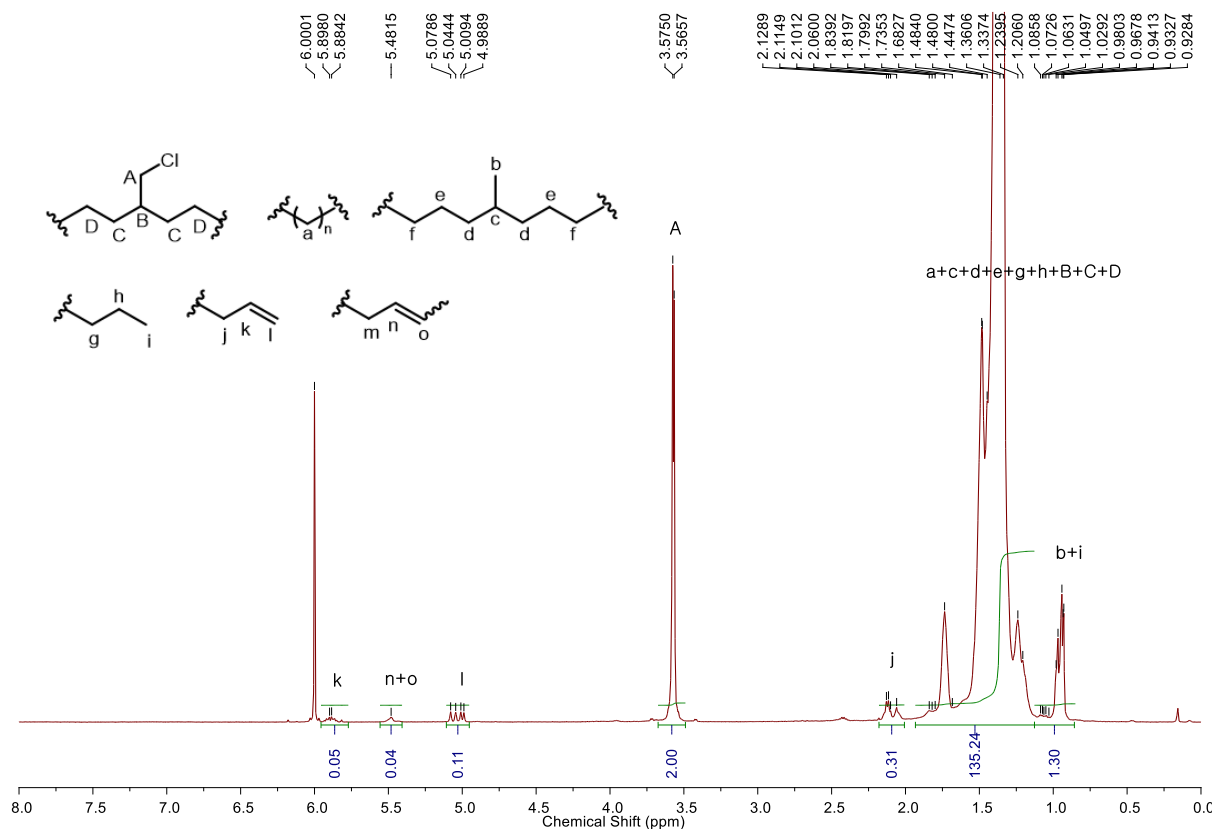


Figure S60 ^1H NMR spectrum (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 120 $^\circ\text{C}$) of poly(ethylene-co-allyl chloride) copolymer obtained by **6b** (Table 3, entry 4).

The incorporation ratio of allyl chloride is calculated as follows:

$$= \frac{A/2}{\frac{(\text{protons } 5.9-4.9 \text{ ppm})+(\text{protons } 2.2-0.8 \text{ ppm})-(A/2)\times 3}{4}+A/2} \times 100$$

$$= \frac{1}{\frac{0.2+136.85-3}{4}+1} \times 100 = 2.90$$

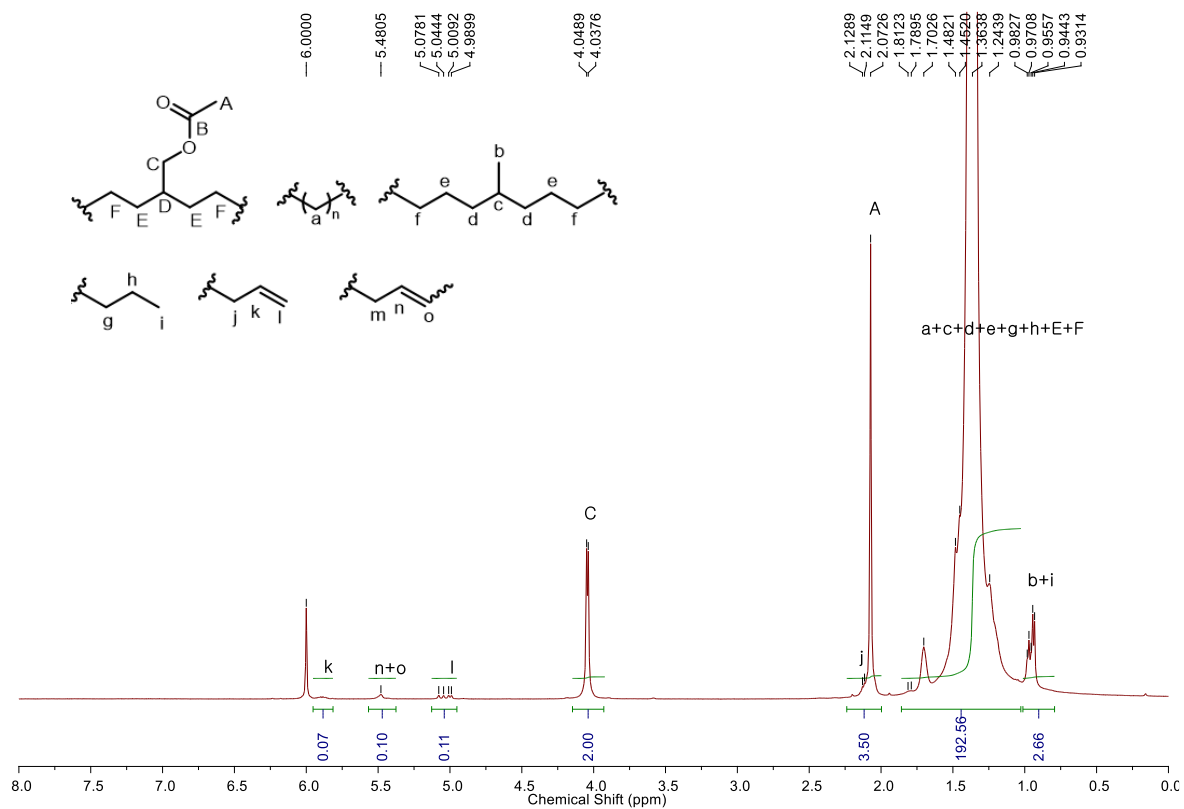


Figure S61 ^1H NMR spectrum (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 120 $^\circ\text{C}$) of poly(ethylene-co-allyl acetate) copolymer obtained by **6b** (Table 3, entry 5).

The incorporation ratio of allyl acetate is calculated as follows:

$$= \frac{C/2}{\frac{(\text{protons } 5.9-4.9 \text{ ppm}) + (\text{protons } 2.2-0.8 \text{ ppm}) - (C/2) \times 6}{4} + C/2} \times 100$$

$$= \frac{1}{\frac{0.28 + 198.72 - 6}{4} + 1} \times 100 = 2.03 \approx 2.0$$

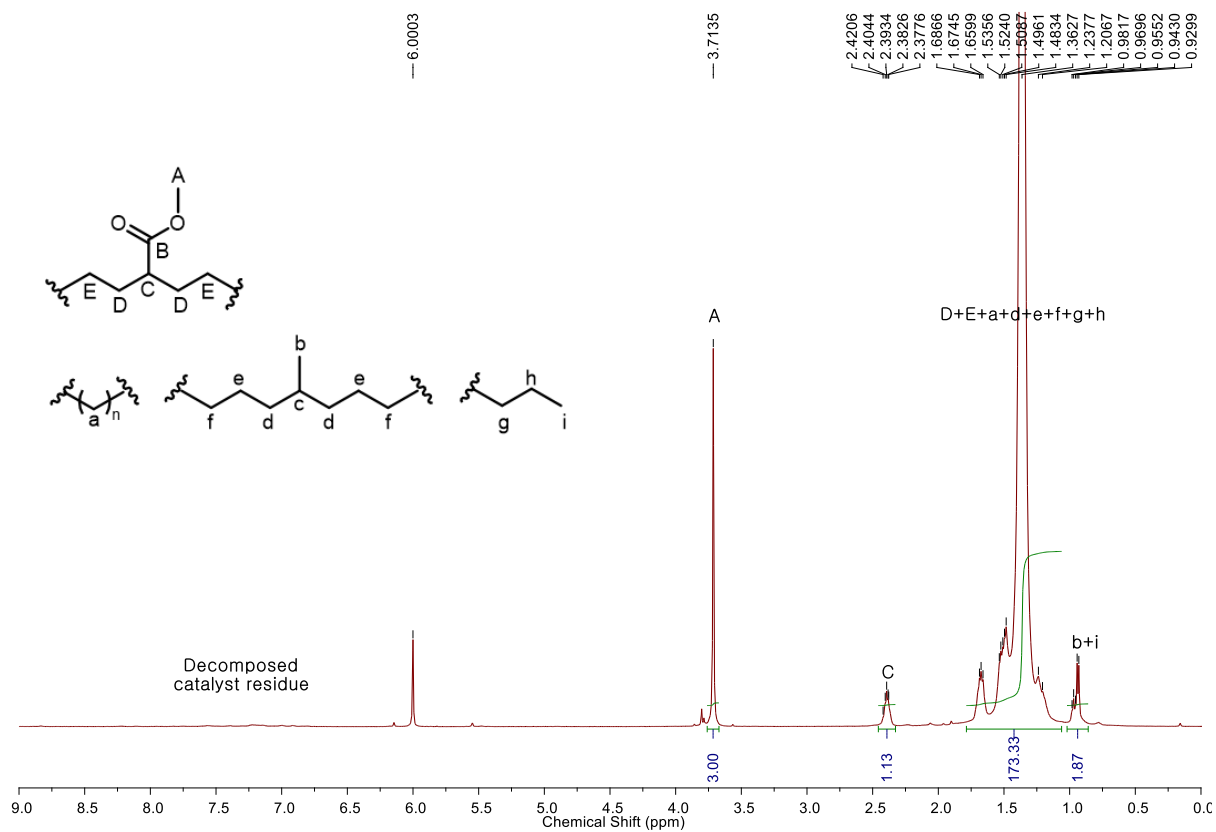


Figure S62 ^1H NMR spectrum (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 120 $^\circ\text{C}$) of poly(ethylene-co-methyl acrylate) copolymer obtained by **6b** (Table 3, entry 6).

The incorporation ratio of methyl methacrylate is calculated as follows:

$$= \frac{A/3}{\frac{(\text{protons } 2.2-0.8 \text{ ppm})-C-(A/3)\times 2}{4}+A/3} \times 100$$

$$= \frac{1}{\frac{175.2-1.13-2}{4}+1} \times 100 = 2.27 \approx 2.3$$

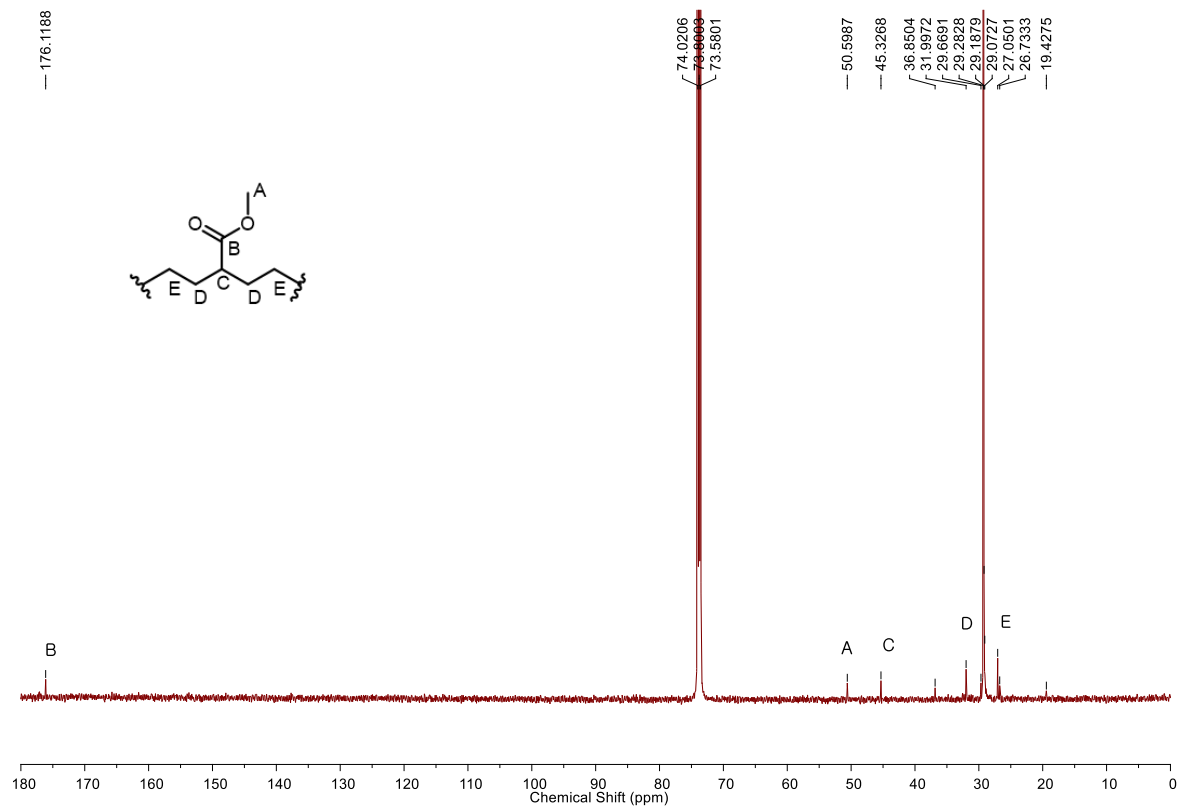


Figure S63 ¹³C NMR spectrum (126 MHz, C₂D₂Cl₄, 0.05M Cr(acac)₃, 120 °C) of poly(ethylene-co-methyl acrylate) copolymer obtained by **6b** (Table 3, entry 6).

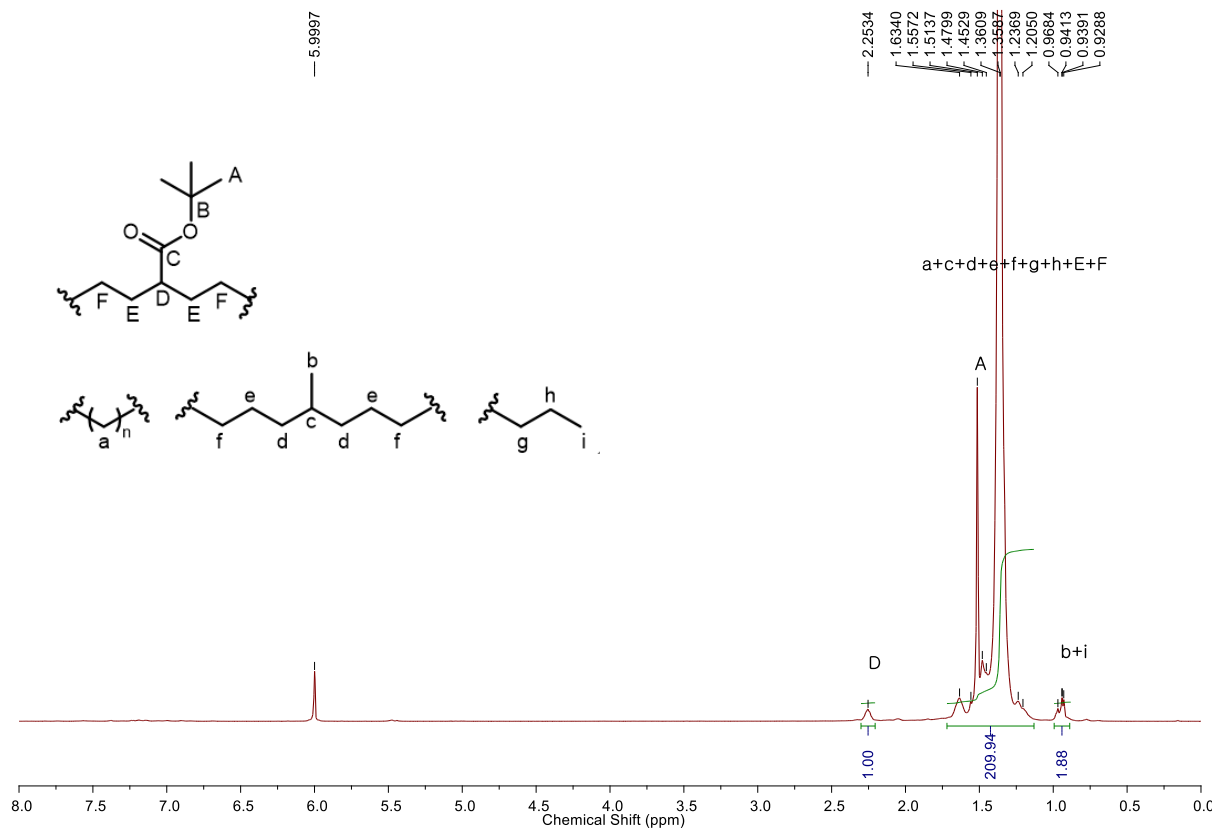


Figure S64 ¹H NMR spectrum (500 MHz, C₂D₂Cl₄, 120 °C) of poly(ethylene-co-*t*-butyl acrylate) copolymer obtained by **6b** (Table 3, entry 7).

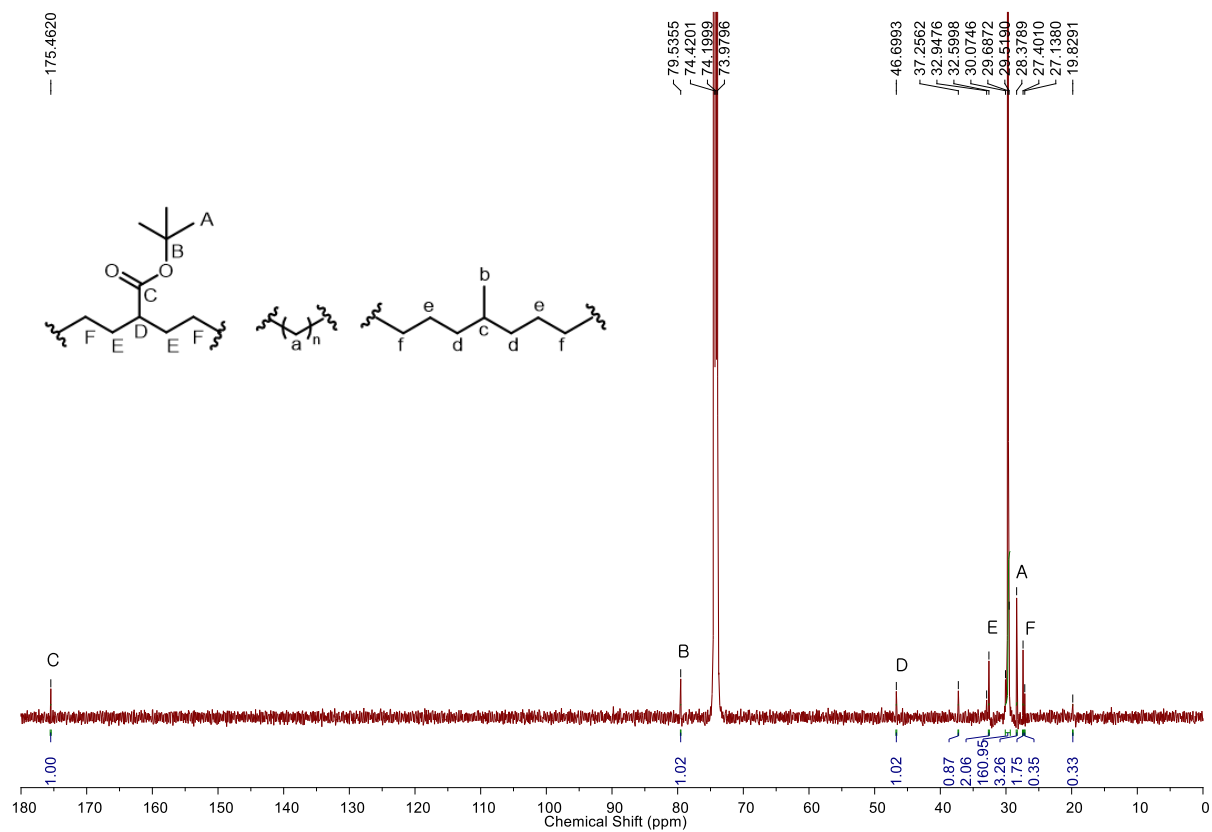


Figure S65 Quantitative ^{13}C NMR spectrum (126 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 0.05M $\text{Cr}(\text{acac})_3$, 120 $^\circ\text{C}$) of poly(ethylene-co-*t*-butyl acrylate) copolymer obtained by **6b** (Table 3, entry 7).

Note: Calculation of incorporation ratio of *t*-butyl acrylate

$$= \frac{2C}{2C + (\text{all carbon}) - 7C} \times 100$$

$$= \frac{2}{2 + 172.61 - 7} \times 100 = 1.19 \approx 1.2$$

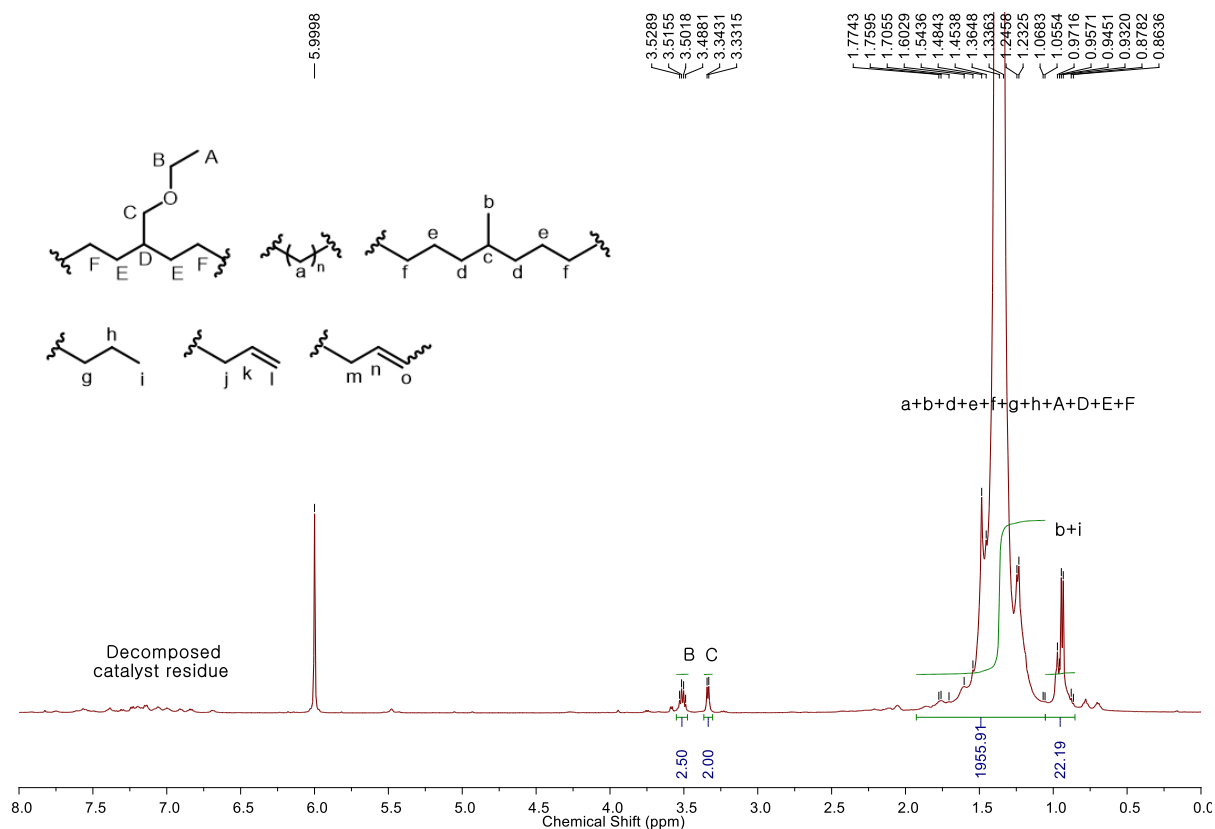


Figure S67 ^1H NMR spectrum (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 120 $^\circ\text{C}$) of poly(ethylene-co-allyl ethyl ether) copolymer obtained by **6b** (Table 3, entry 8).

Note: Calculation of incorporation ratio of allyl ethyl ether

$$\begin{aligned}
 &= \frac{\text{incorporated AEE}(\text{mol})}{\text{incorporated PE}(\text{mol}) + \text{incorporated AEE}(\text{mol})} \times 100 \\
 &= \frac{(\text{protons derived from AEE})/10}{(\text{protons derived from PE})/4 + (\text{Protons derived from AEE})/10} \times 100 \\
 &= \frac{(B+C)/4}{\frac{(\text{protons } 2.2-0.8 \text{ ppm}) - A - D - E}{4} + (B+C)/4} \times 100 \\
 &= \frac{(B+C)/4}{\frac{(\text{protons } 2.2-0.8 \text{ ppm}) - (B+C)/4 \times 6}{4} + (B+C)/4} \times 100 \\
 &= \frac{1.125}{\frac{1955.91 - 6.75}{4} + 1.125} \times 100 = 0.23
 \end{aligned}$$

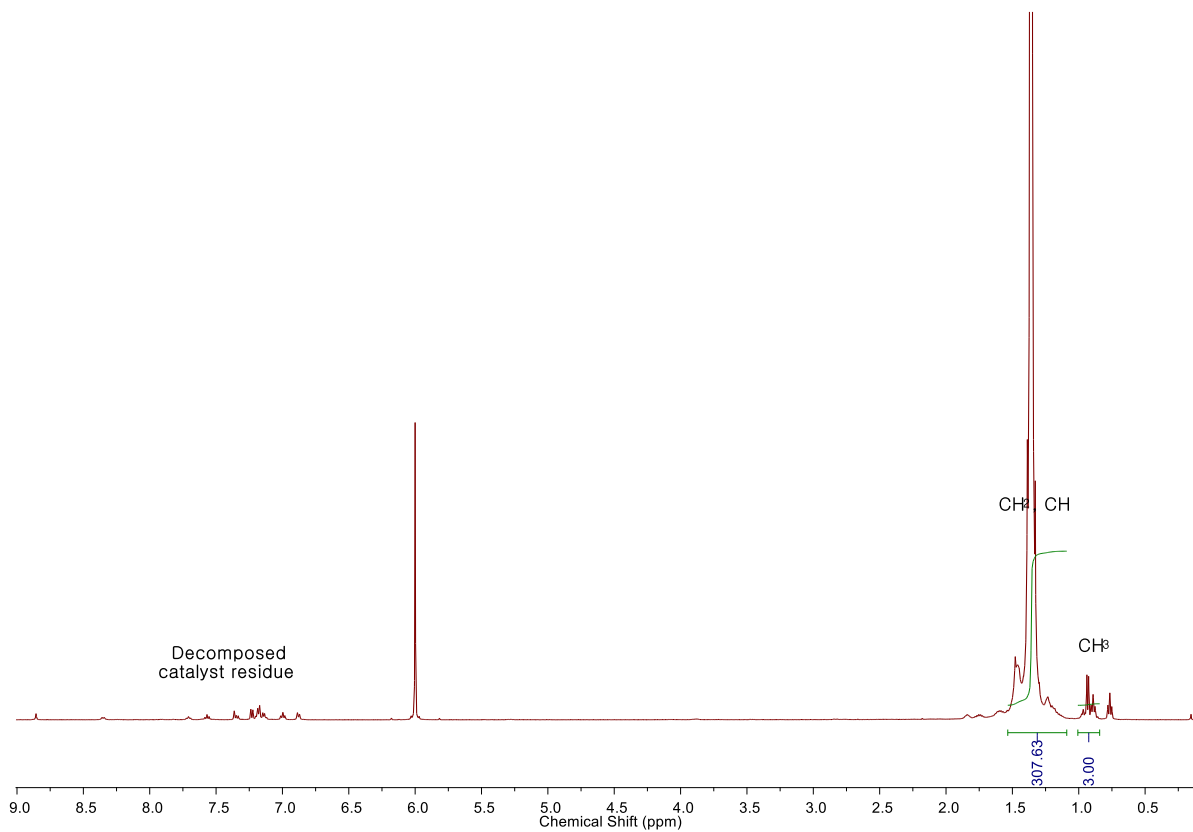


Figure S68 ^1H NMR spectrum (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 120 $^\circ\text{C}$) of poly(ethylene-co-butyl vinyl ether) copolymer obtained by **6b** (Table 3, entry 9).

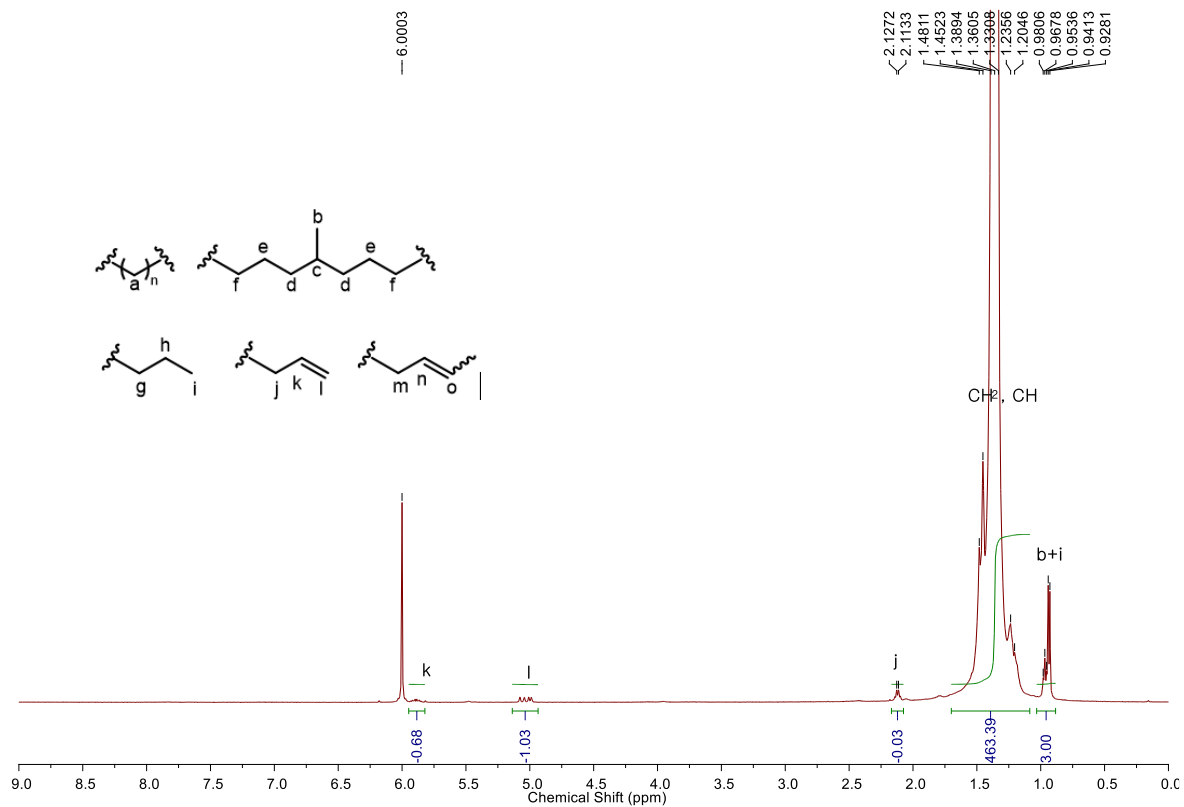


Figure S69 ^1H NMR spectrum (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 120 $^\circ\text{C}$) of poly(ethylene-co-vinyl acetate) copolymer obtained by **6b** (Table 3, entry 10).

10.4. NMR Spectra of copolymers with ethylene and methylmethacrylate (Table 4)

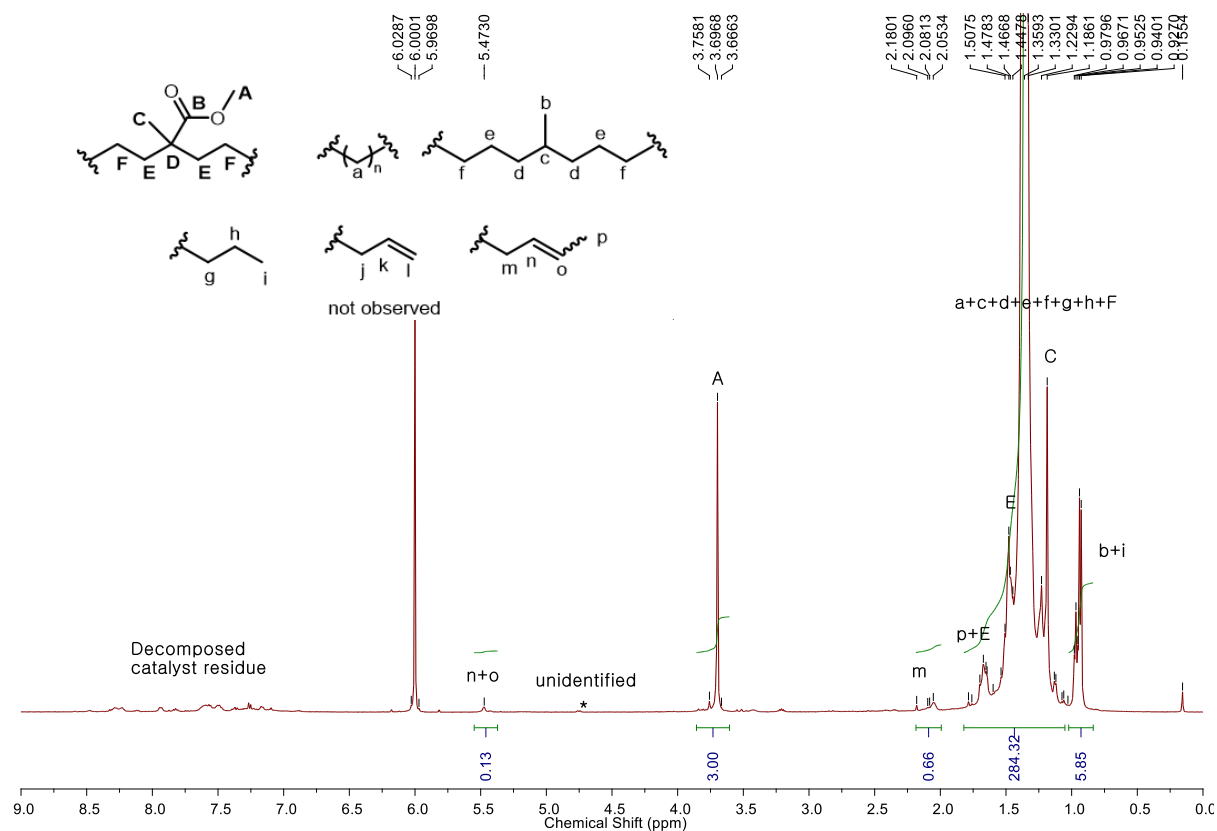


Figure S70 ^1H NMR spectrum (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 120 °C) of poly(ethylene-co-methyl methacrylate) copolymer obtained by **6a** (Table 4, entry 1).

Note: Calculation of incorporation ratio of methyl methacrylate

$$\begin{aligned}
 &= \frac{\text{incorporated MMA}(\text{mol})}{\text{incorporated PE}(\text{mol}) + \text{incorporated MMA}(\text{mol})} \times 100 \\
 &= \frac{(\text{protons derived from MMA})/8}{(\text{protons derived from PE})/4 + (\text{Protons derived from MMA})/8} \times 100 \\
 &= \frac{A/3}{\frac{(\text{protons } 5.9\text{--}4.9 \text{ ppm}) + (\text{protons } 2.2\text{--}0.8 \text{ ppm}) - C - E}{4} + A/3} \times 100 \\
 &= \frac{A/3}{\frac{(\text{protons } 5.9\text{--}4.9 \text{ ppm}) + (\text{protons } 2.2\text{--}0.8 \text{ ppm}) - (A/3) \times 5}{4} + A/3} \times 100 \\
 &= \frac{1}{\frac{290.95 - 5}{4} + 1} \times 100 = 1.38 \approx 1.4
 \end{aligned}$$

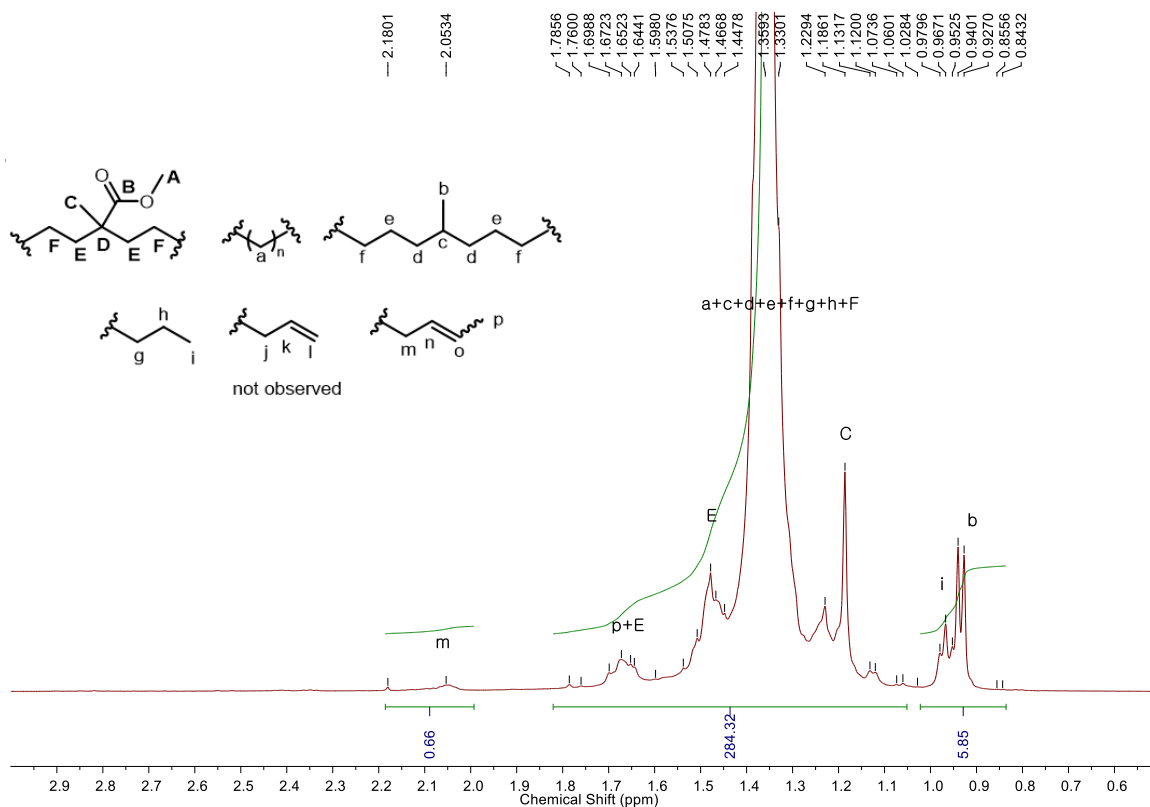


Figure S71 Specific region (0.5-3.0 ppm) of ^1H NMR spectrum (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 120 $^\circ\text{C}$) of poly(ethylene-co-methyl methacrylate) copolymer obtained by **6a** (Table 4, entry 1).

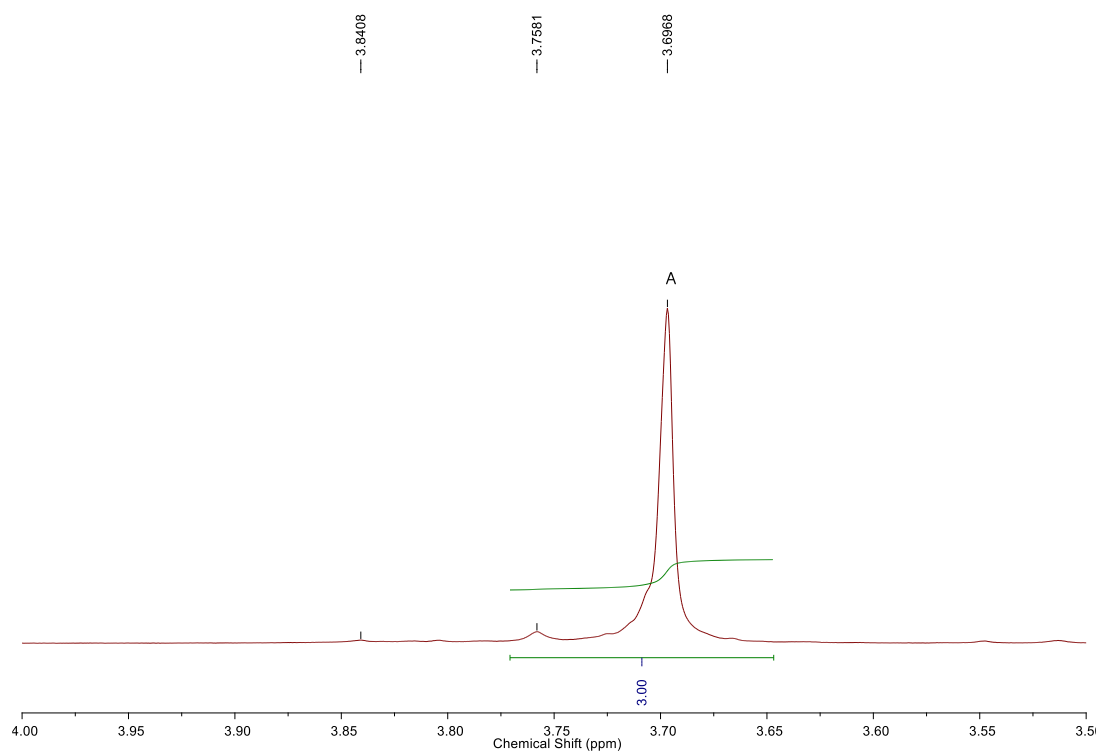


Figure S72 Specific region (3.5-4.0 ppm) of ^1H NMR spectrum (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 120 $^\circ\text{C}$) of poly(ethylene-co-methyl methacrylate) copolymer obtained by **6a** (Table 4, entry 1).

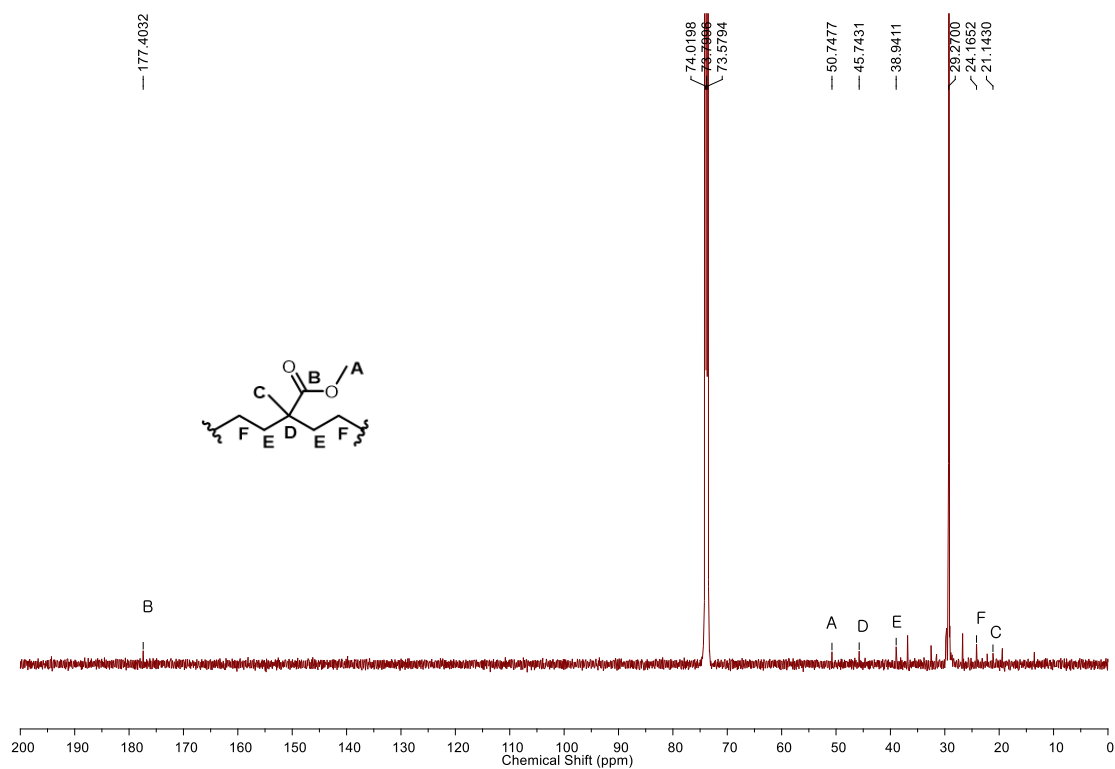


Figure S73 ^{13}C NMR spectrum (126 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 0.05M $\text{Cr}(\text{acac})_3$, 120 $^\circ\text{C}$) of poly(ethylene-co-methyl methacrylate) copolymer obtained by **6a** (Table 4, entry 1).

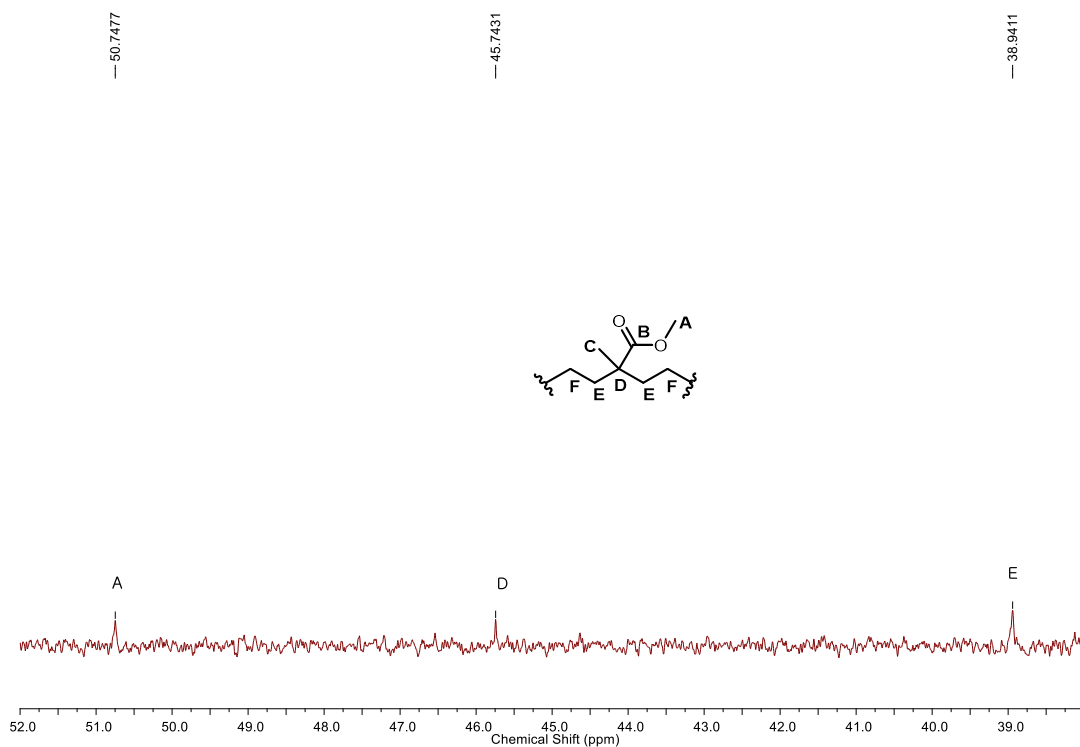


Figure S74 Specific region (38-52 ppm) of ^{13}C NMR spectrum (126 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 0.05M $\text{Cr}(\text{acac})_3$, 120 $^\circ\text{C}$) of poly(ethylene-co-methyl methacrylate) copolymer obtained by **6a** (Table 4, entry 1).

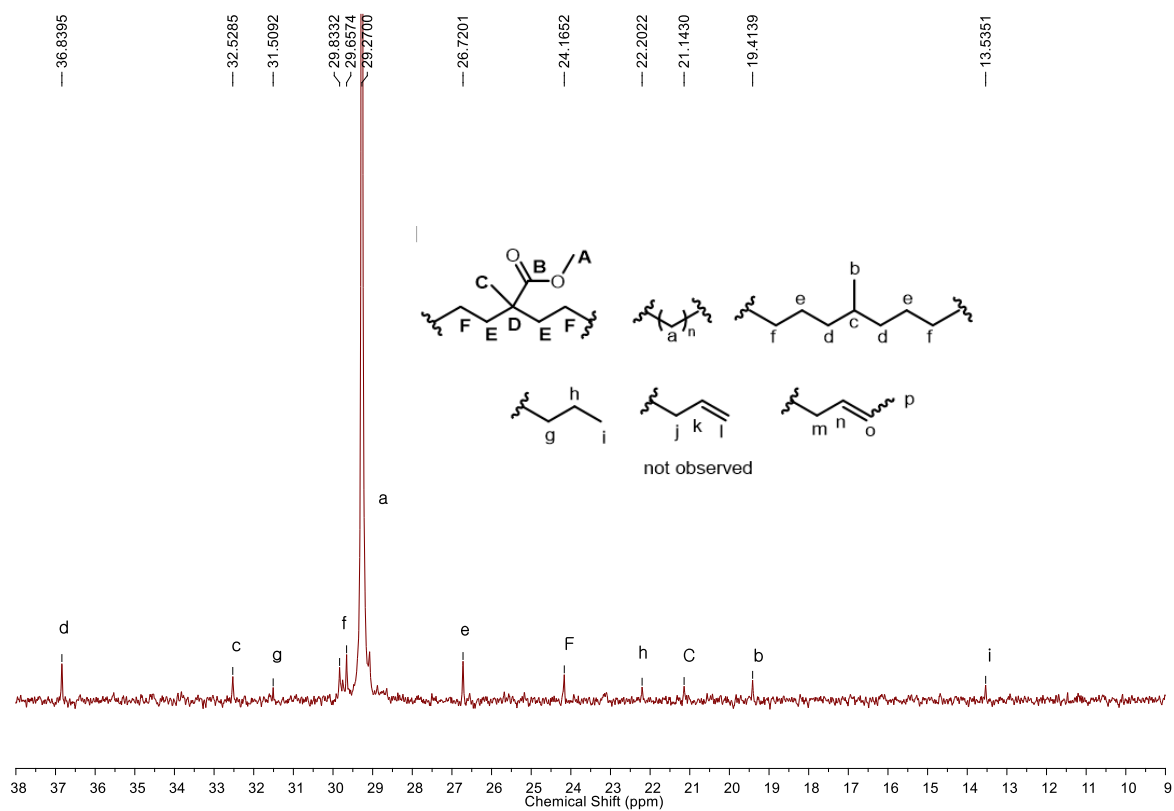


Figure S75 Specific region (9-38 ppm) of ^{13}C NMR spectrum (126 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 0.05M $\text{Cr}(\text{acac})_3$, 120 $^\circ\text{C}$) of poly(ethylene-co-methyl methacrylate) copolymer obtained by **6a** (Table 4, entry 1).

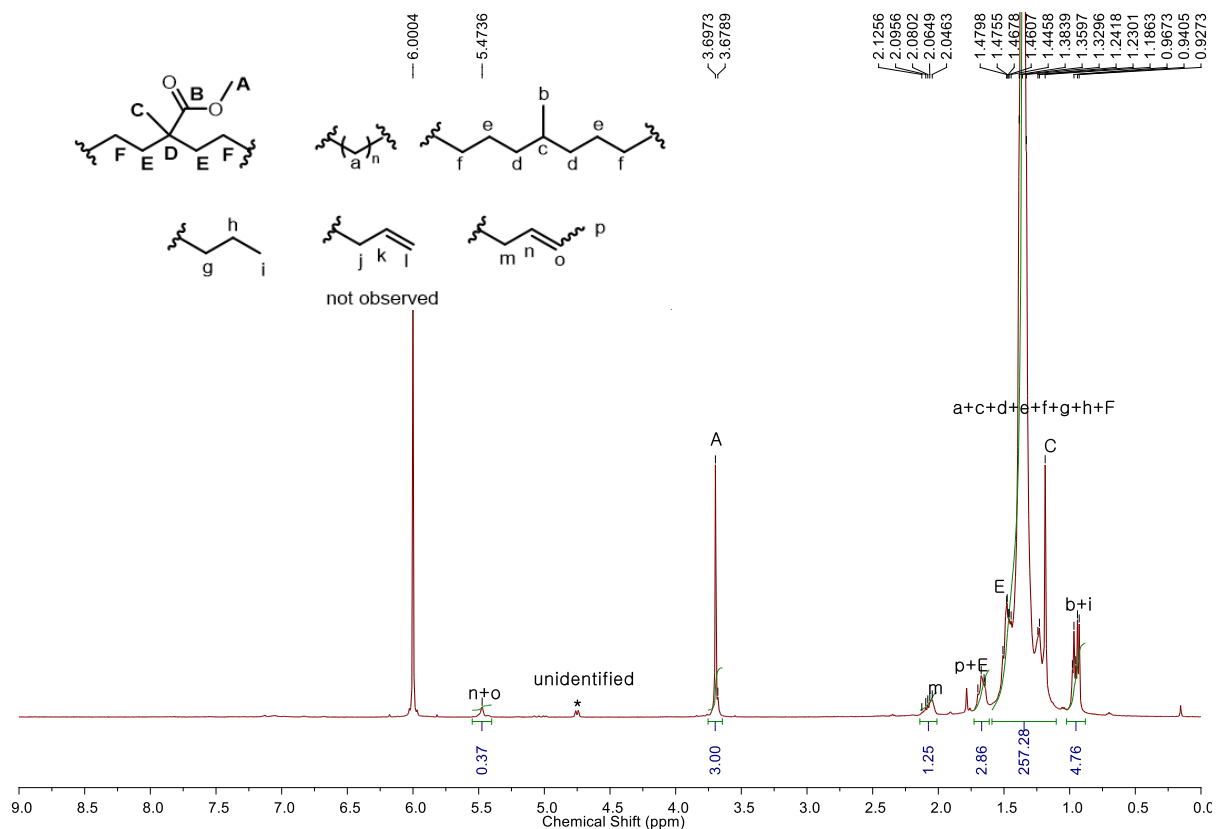


Figure S76 ^1H NMR spectrum (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 120 $^\circ\text{C}$) of poly(ethylene-co-methyl methacrylate) copolymer obtained by **6b** (Table 4, entry 2).

The incorporation ratio of methyl methacrylate is calculated as follows:

$$= \frac{A/3}{\frac{(\text{protons } 5.9-4.9 \text{ ppm}) + (\text{protons } 2.2-0.8 \text{ ppm}) - (A/3) \times 5}{4} + A/3} \times 100$$

$$= \frac{1}{\frac{266.52-5}{4} + 1} \times 100 = 1.51 \approx 1.5$$

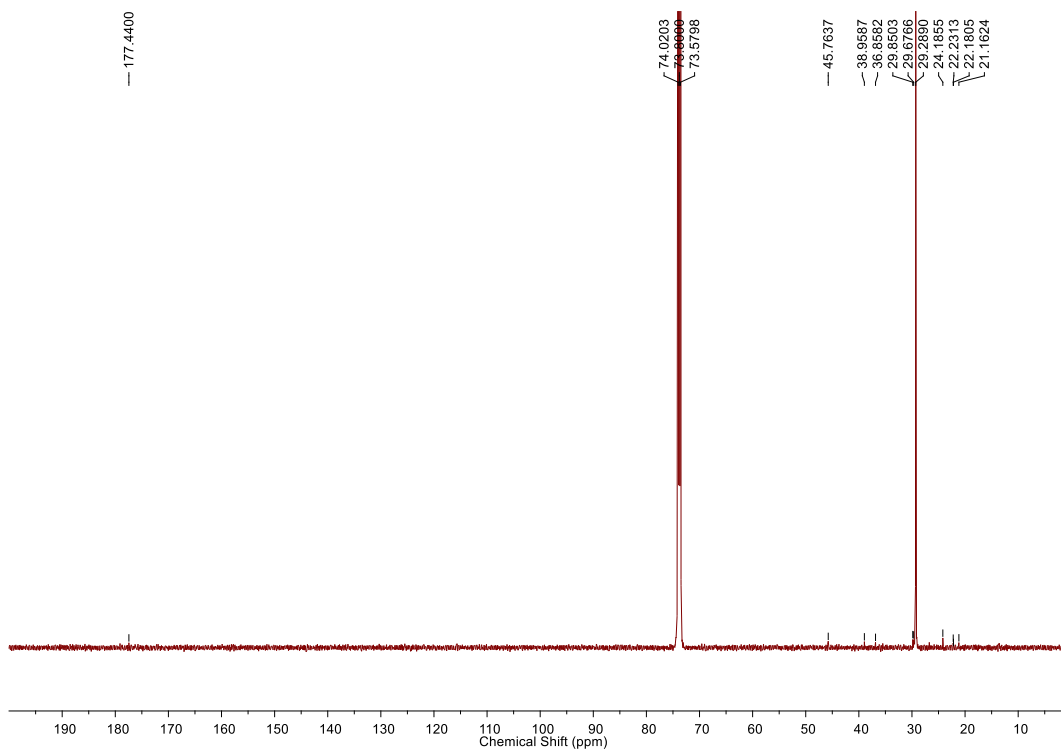


Figure S77 ^{13}C NMR spectrum (126 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 0.05M $\text{Cr}(\text{acac})_3$, 120 $^\circ\text{C}$) of poly(ethylene-co-methyl methacrylate) copolymer obtained by **6b** (Table 4, entry 2).

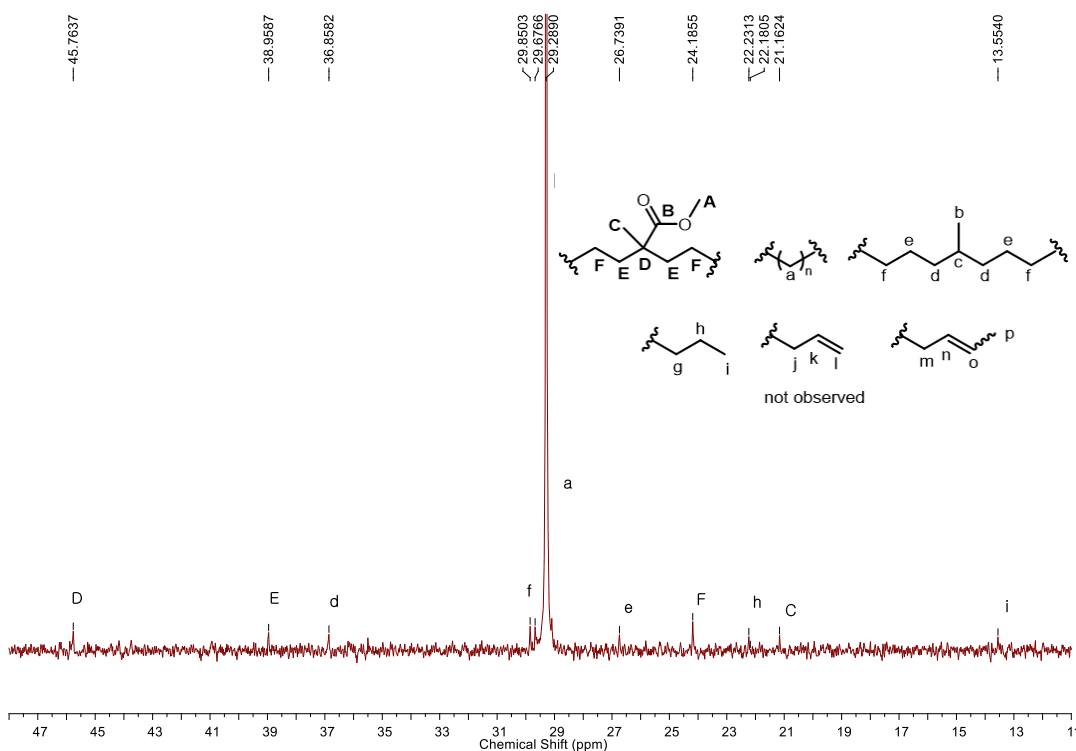


Figure S78 Specific region (48-11 ppm) of ^{13}C NMR spectrum (126 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 0.05M $\text{Cr}(\text{acac})_3$, 120 $^\circ\text{C}$) of poly(ethylene-co-methyl methacrylate) copolymer obtained by **6b** (Table 4, entry 2).

10.5. NMR Spectra of copolymers with propylene and polar monomers (Scheme 2)

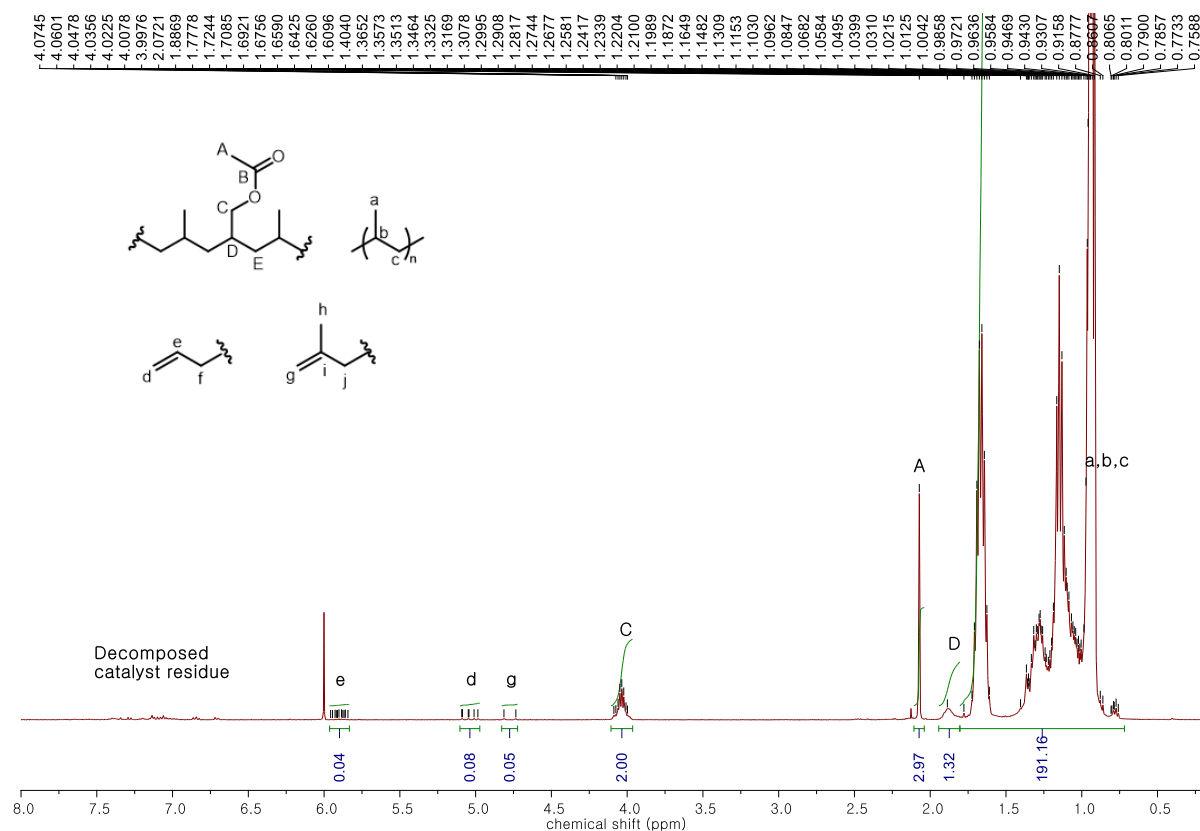


Figure S79 ^1H NMR spectrum (400 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 120 $^\circ\text{C}$) of poly(propylene-co-allyl acetate) copolymer obtained by **6a** (Scheme 2).

Note: Calculation of incorporation ratio of allyl acetate

$$= \frac{c/2}{\{(all\ proton)-C\}/6} \times 100$$

$$= \frac{1}{\frac{197.62-2}{6}} \times 100 = 3.07 \approx 3.1$$

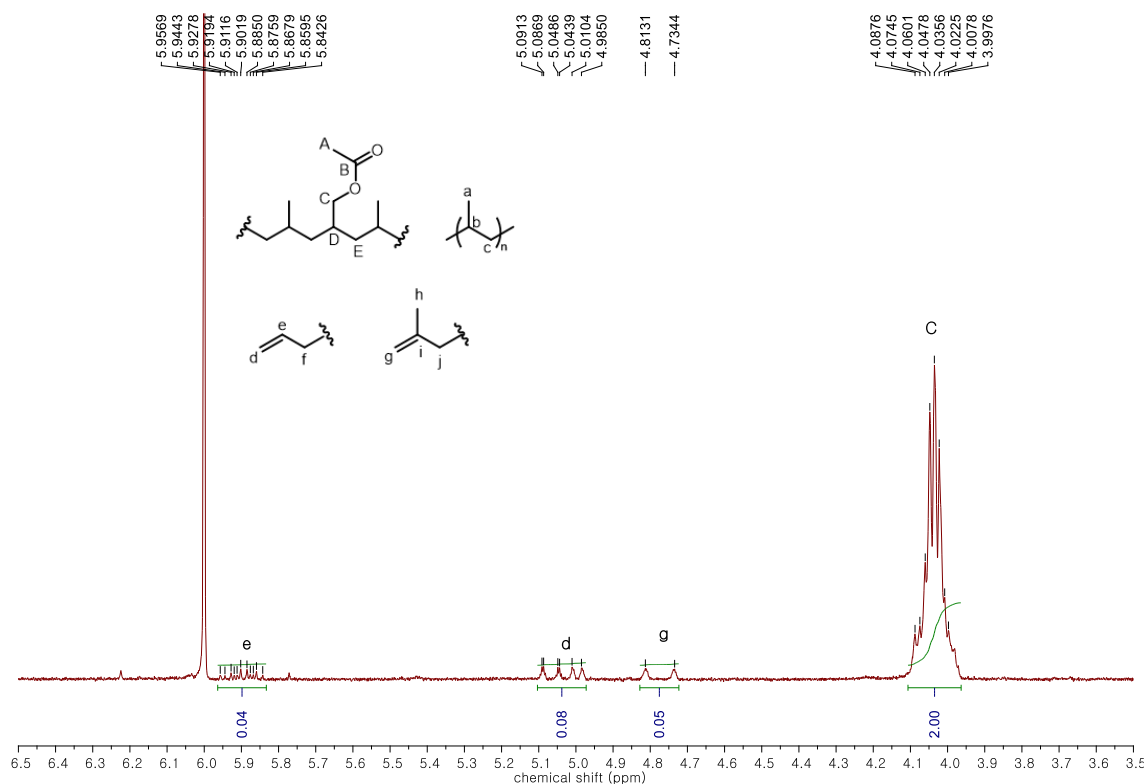


Figure S80 Specific region (6.5-3.5 ppm) of ^1H NMR spectrum (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 120 $^\circ\text{C}$) of poly(propylene-co-allyl acetate) copolymer obtained by **6a** (Scheme 2).

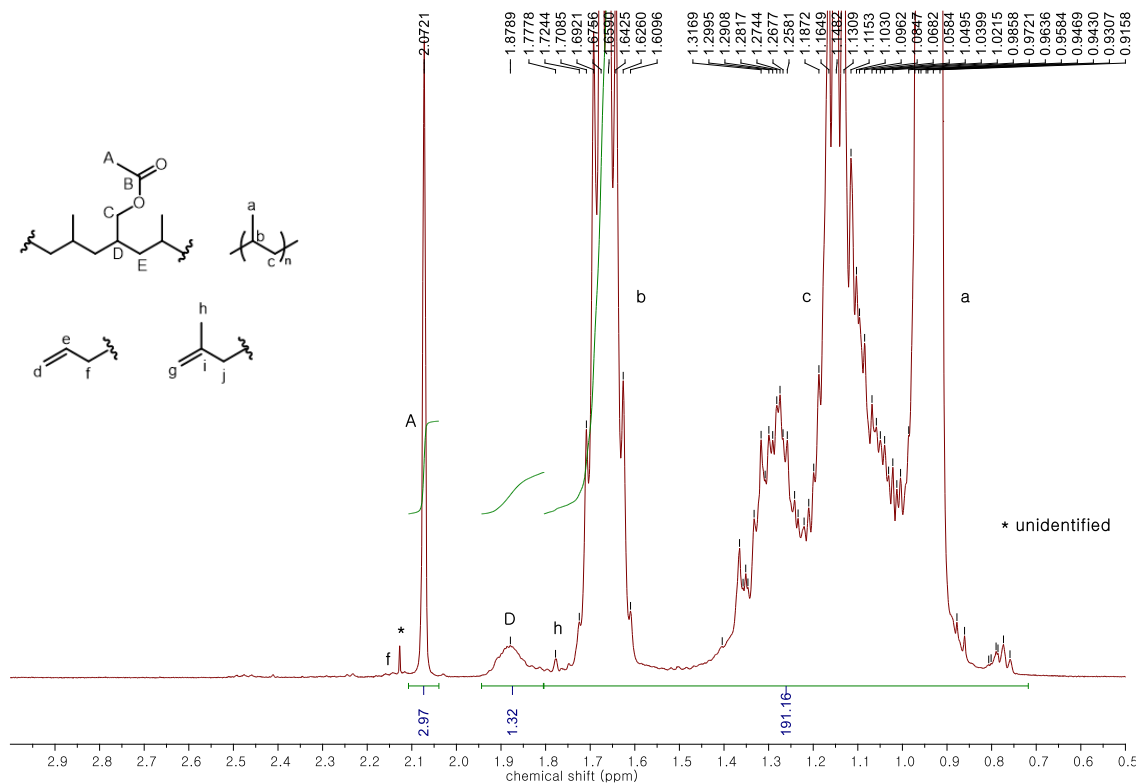


Figure S81 Specific region (3.0-0.5 ppm) of ^1H NMR spectrum (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 120 $^\circ\text{C}$) of poly(propylene-co-allyl acetate) copolymer obtained by **6a** (Scheme 2).

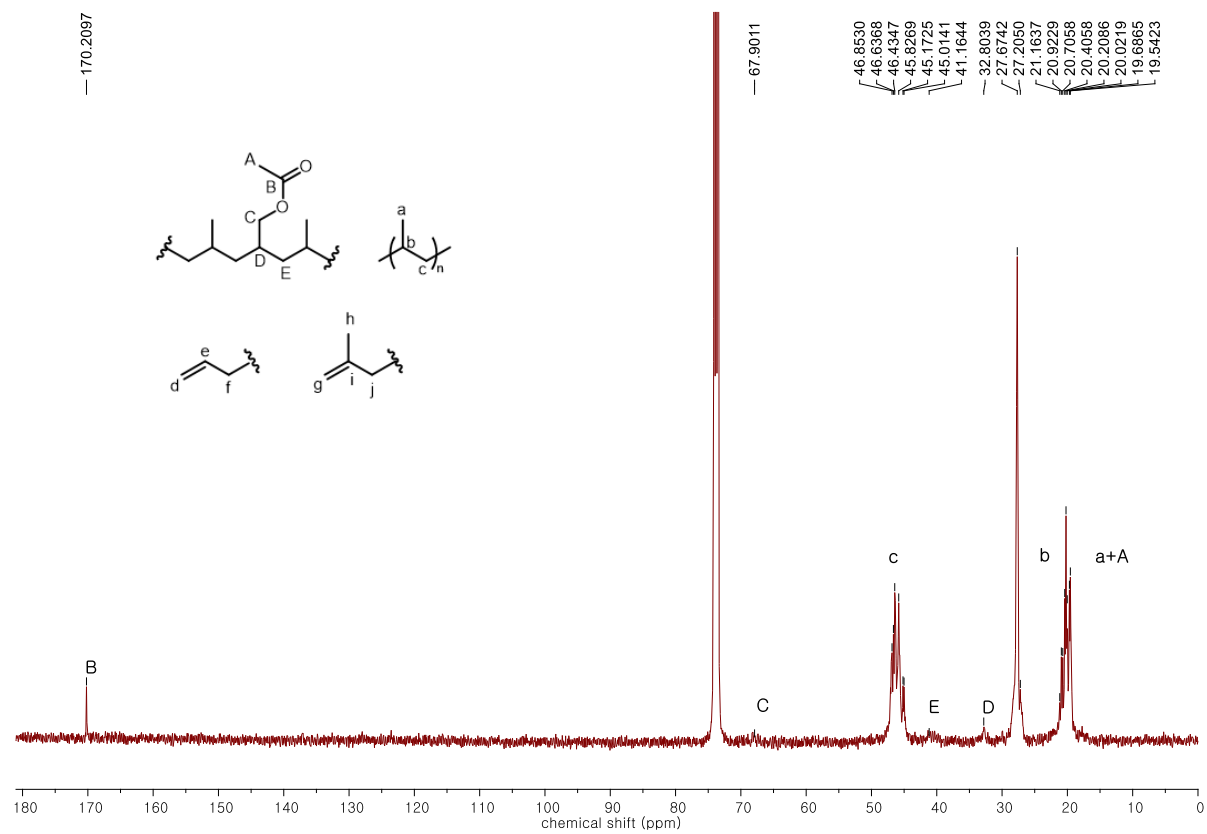


Figure S82 ^{13}C NMR spectrum (101 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 120 °C) of poly(propylene-co-allyl acetate) copolymer obtained by **6a** (Scheme 2).

11. GPC Data of polymers

High Limit MW RT: 10.85 mins

High Limit MW: 8911204

K: 1750.0000

Alpha: 0.6700

FRCF: 1.0000

MW Averages

Mp: 45841

Mn: 31387

Mv: 53186

Mw: 58204

Mz: 101127

Mz+1: 162150

PD: 1.8544

Low Limit MW RT: 16.38 mins

Low Limit MW: 2939

FRM Name:

Flow Marker RT: 0.00 mins

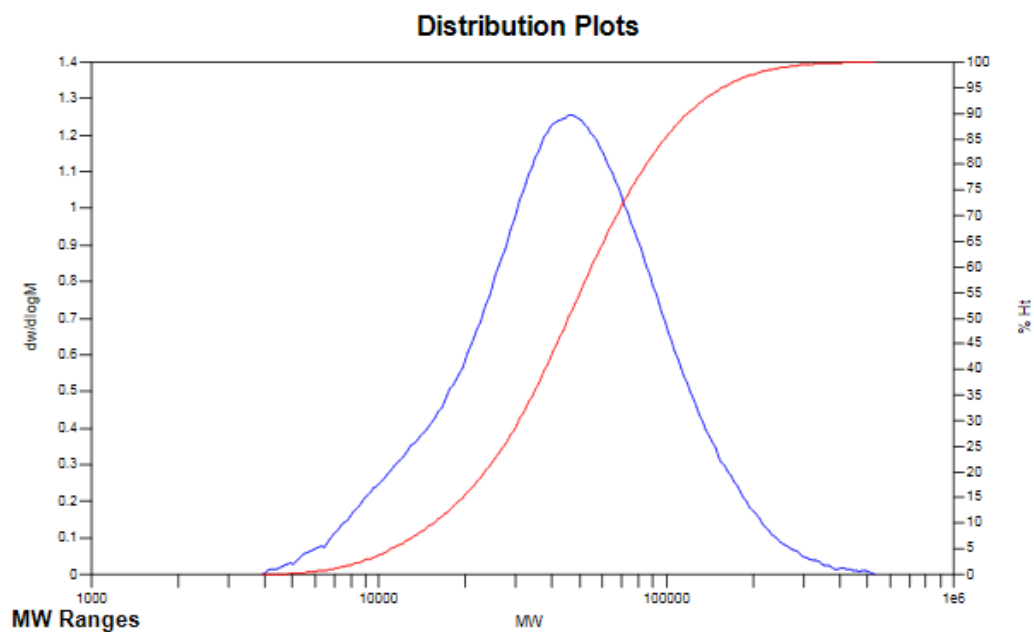


Figure S83 GPC data of polyethylene obtained by **6a** at 80 °C (Table 1, entry 1).

High Limit MW RT: 10.85 mins

High Limit MW: 8911204

K: 1750.0000

Alpha: 0.6700

FRCF: 1.0000

MW Averages

Mp: 384408

Mn: 237228

Mv: 376912

Mw: 401838

Mz: 576058

Mz+1: 757460

PD: 1.6939

Low Limit MW RT: 16.38 mins

Low Limit MW: 2939

FRM Name:

Flow Marker RT: 0.00 mins

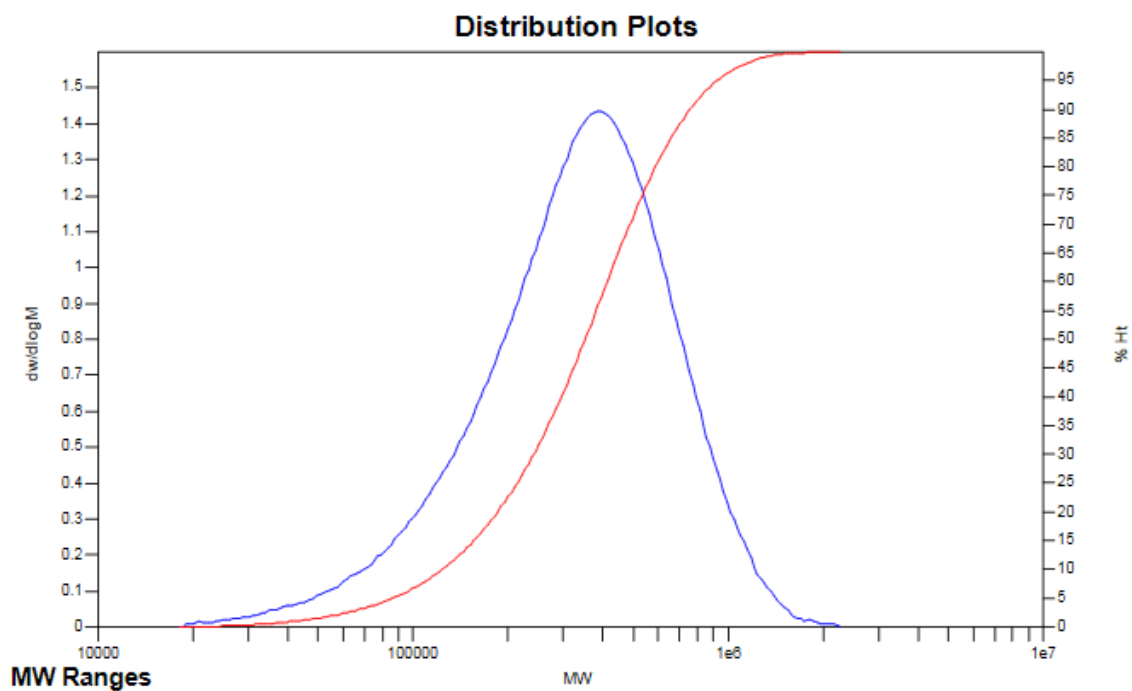


Figure S84 GPC data of polyethylene obtained by **6a** at 100 °C (Table 1, entry 2).

High Limit MW RT: 10.85 mins

High Limit MW: 8911204

K: 1750.0000

Alpha: 0.6700

FRCF: 1.0000

MW Averages

Mp: 244665

Mn: 158120

Mv: 235982

Mw: 250055

Mz: 347193

Mz+1: 444346

PD: 1.5814

Low Limit MW RT: 16.38 mins

Low Limit MW: 2939

FRM Name:

Flow Marker RT: 0.00 mins

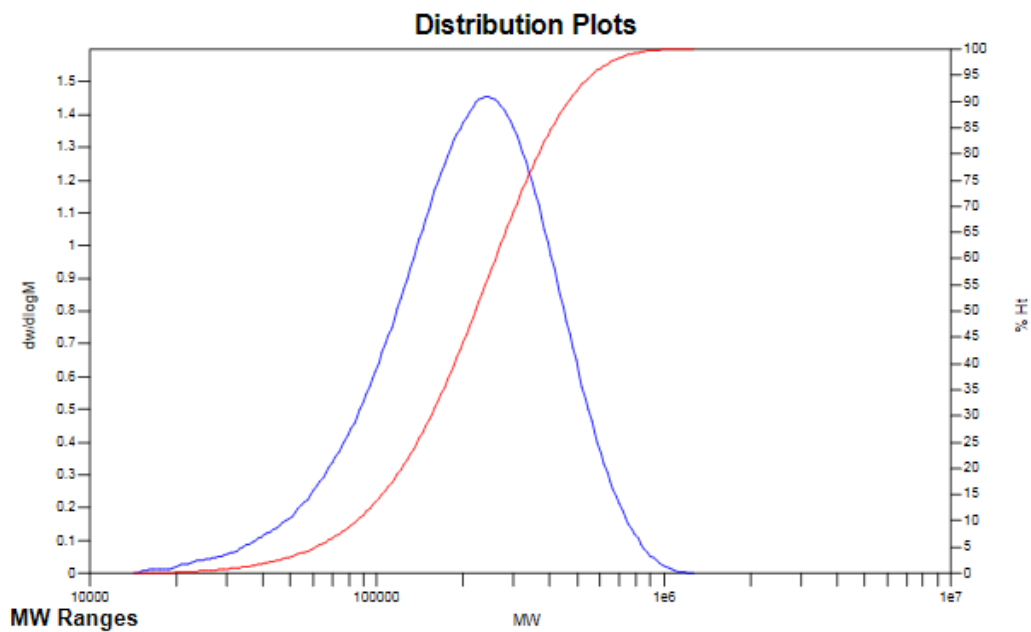


Figure S85 GPC data of polyethylene obtained by **6a** at 120 °C (Table 1, entry 3).

High Limit MW RT: 10.85 mins
High Limit MW: 8911204
K: 1750.0000
Alpha: 0.6700
FRCF: 1.0000

Low Limit MW RT: 16.38 mins
Low Limit MW: 2939
FRM Name:
Flow Marker RT: 0.00 mins

MW Averages

Mp: 356550	Mn: 211758	Mv: 344502	Mw: 367773
Mz: 525100	Mz+1: 673450	PD: 1.7368	

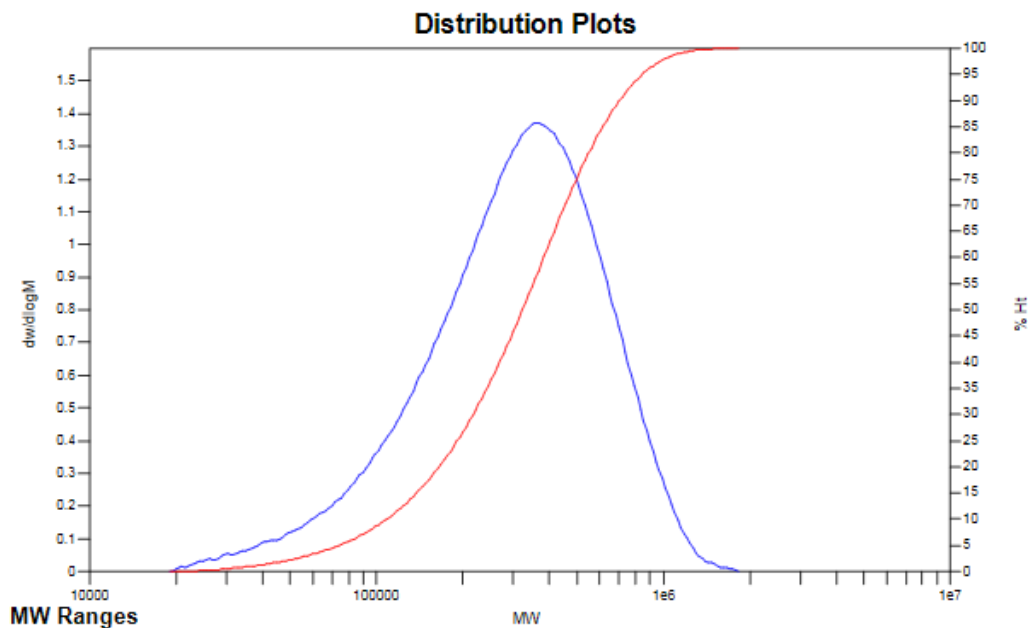


Figure S86 GPC data of polyethylene obtained by **6b** at 100 °C (Table 1, entry 4).

Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	288941	151312	243630	331272	419039	318530	1.61

Peak Information

	Start (mins)	End (mins)
Baseline region 1	7.28333	8.11667
Baseline region 2	8.15000	8.45000
Baseline region 3	15.38333	16.48333
Peak 1	10.66667	14.08333

Peak Trace Information

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	11.78333	3133.279	-46.706

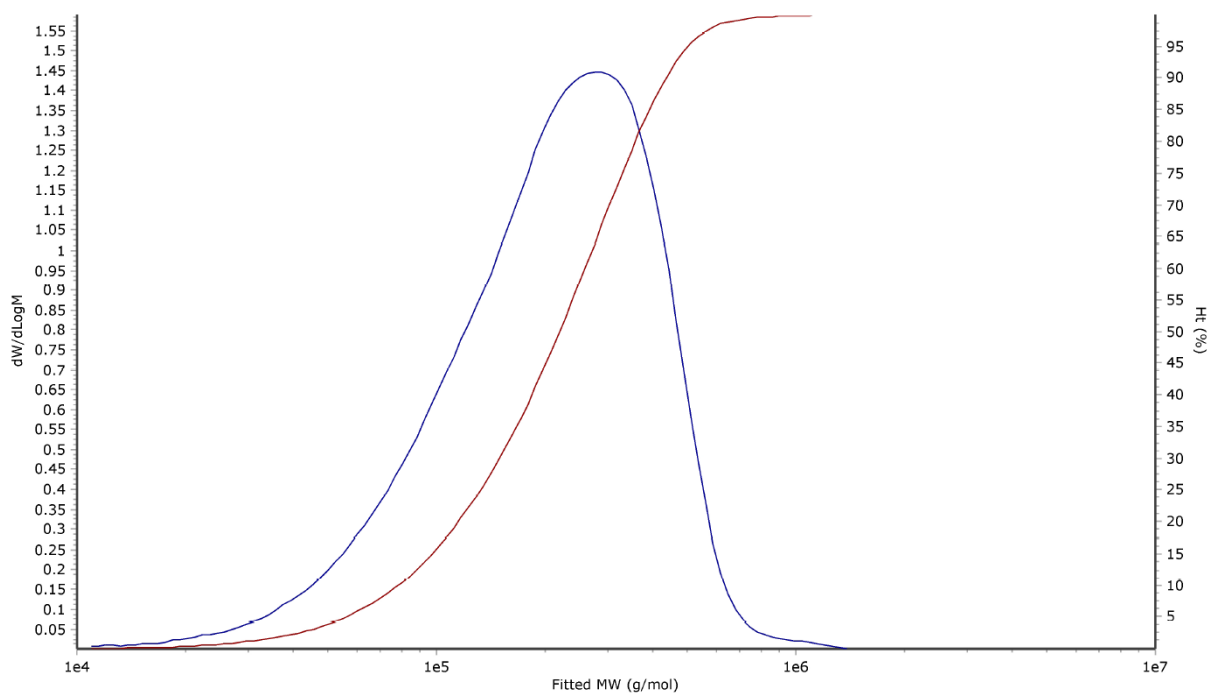


Figure S87 GPC data of polyethylene obtained by **6b** at 100 °C for 0.5 h (Table 1, entry 5).

High Limit MW RT: 10.85 mins
High Limit MW: 8911204
K: 1750.0000
Alpha: 0.6700
FRCF: 1.0000

Low Limit MW RT: 16.38 mins
Low Limit MW: 2939
FRM Name:
Flow Marker RT: 0.00 mins

MW Averages

Mp: 356550	Mn: 193557	Mv: 343034	Mw: 370431
Mz: 569699	Mz+1: 788217	PD: 1.9138	

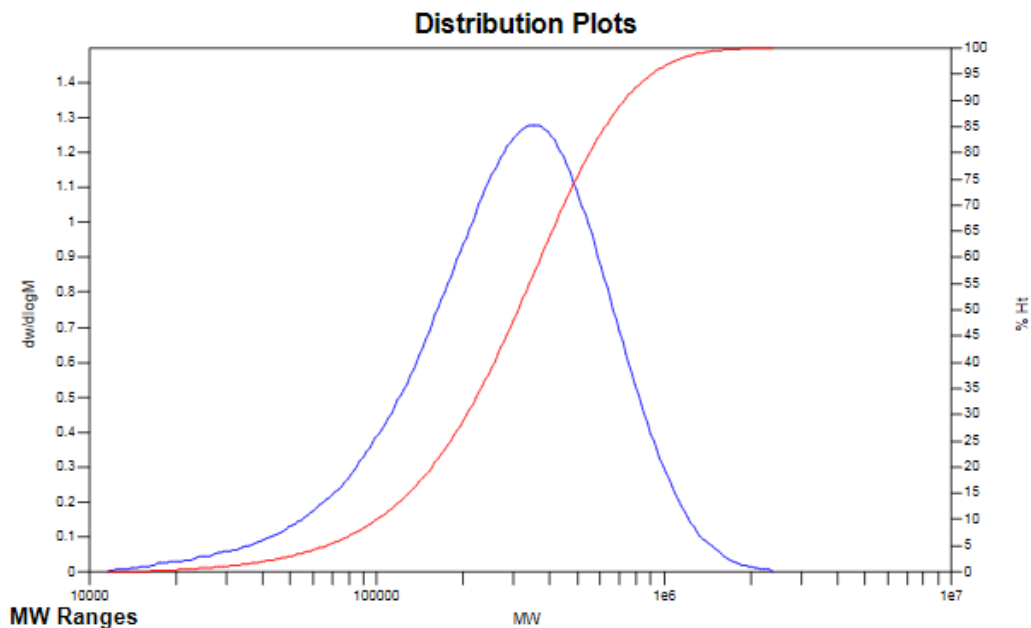


Figure S88 GPC data of polyethylene obtained by **6b** at 100 °C for 2 h (Table 1, entry 6).

High Limit MW RT: 10.85 mins

High Limit MW: 8911204

K: 1750.0000

Alpha: 0.6700

FRCF: 1.0000

MW Averages

Mp: 176498

Mn: 109864

Mv: 179658

Mw: 192444

Mz: 282460

Mz+1: 373446

PD: 1.7517

Low Limit MW RT: 16.38 mins

Low Limit MW: 2939

FRM Name:

Flow Marker RT: 0.00 mins

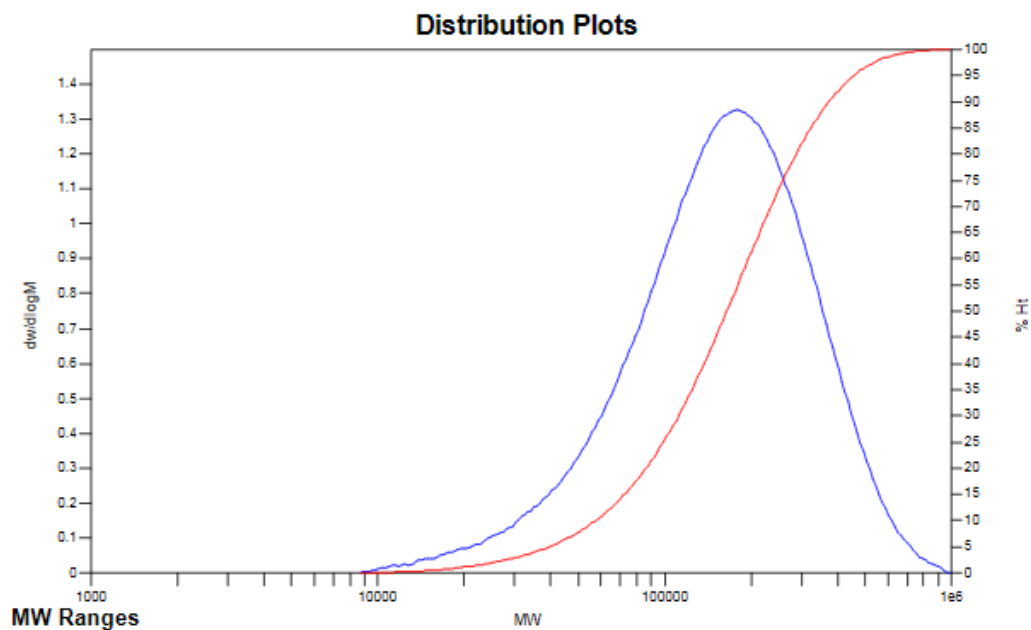


Figure S89 GPC data of polyethylene obtained by **6b** at 120 °C (Table 1, entry 7).

Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	55029	35981	47632	54741	60748	54021	1.324

Peak Information

	Start (mins)	End (mins)
Baseline region 1	8.56667	9.63333
Baseline region 2	16.25000	16.95000
Peak 1	12.35000	15.48333

Peak Trace Information

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	13.18333	3207.971	-94.096

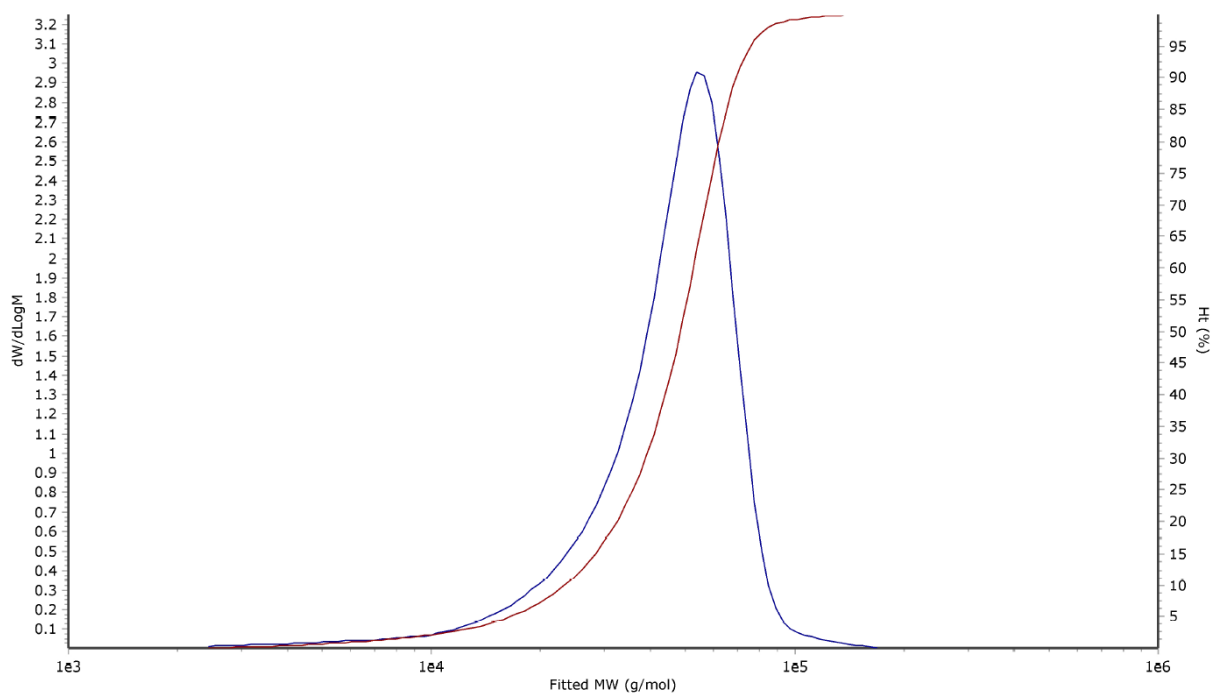


Figure S90 GPC data of polypropylene obtained by **6a** at 100 °C for 1 h (Table 2, entry 1).

Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	95082	61631	97090	130392	159928	126792	1.575

Peak Information

	Start (mins)	End (mins)
Baseline region 1	9.21667	10.13333
Baseline region 2	15.95000	16.33333
Peak 1	11.66667	15.06667

Peak Trace Information

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	12.78333	3136.281	-44.791

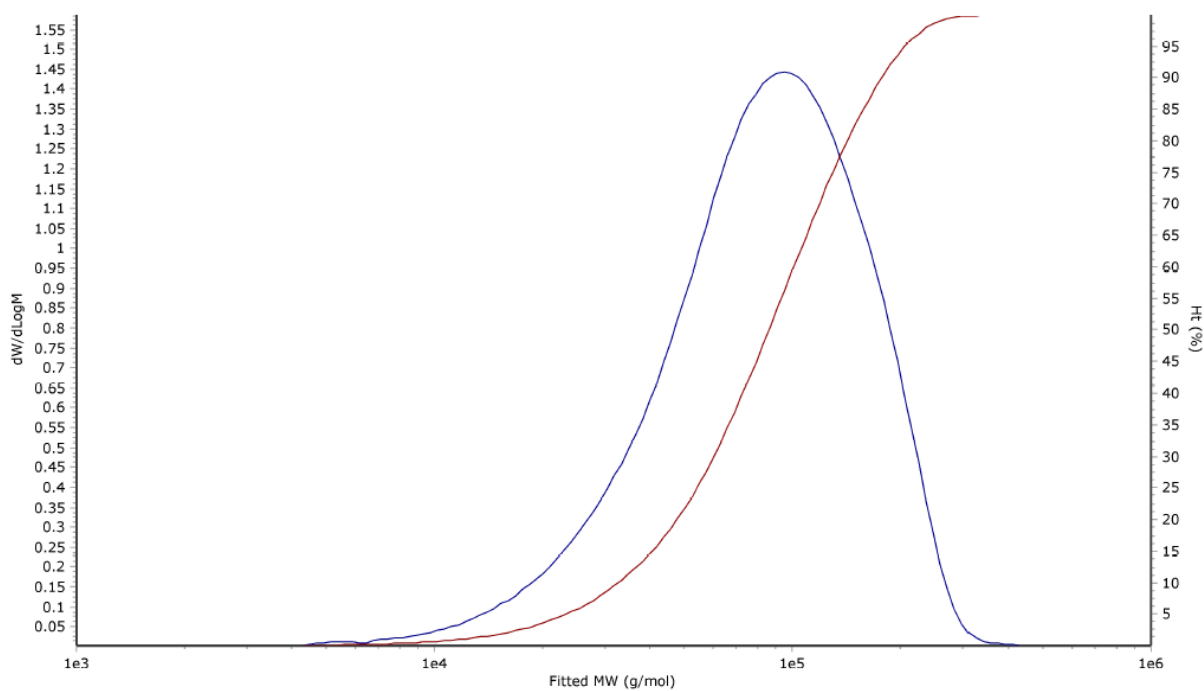


Figure S91 GPC data of polypropylene obtained by **6a** at 100 °C for 3 h (Table 2, entry 2).

Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	55029	35073	53473	71991	90760	69845	1.525

Peak Information

	Start (mins)	End (mins)
Baseline region 1	9.45000	10.33333
Baseline region 2	16.05000	16.73333
Peak 1	11.98333	15.40000

Peak Trace Information

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	13.16667	3307.609	-50.583

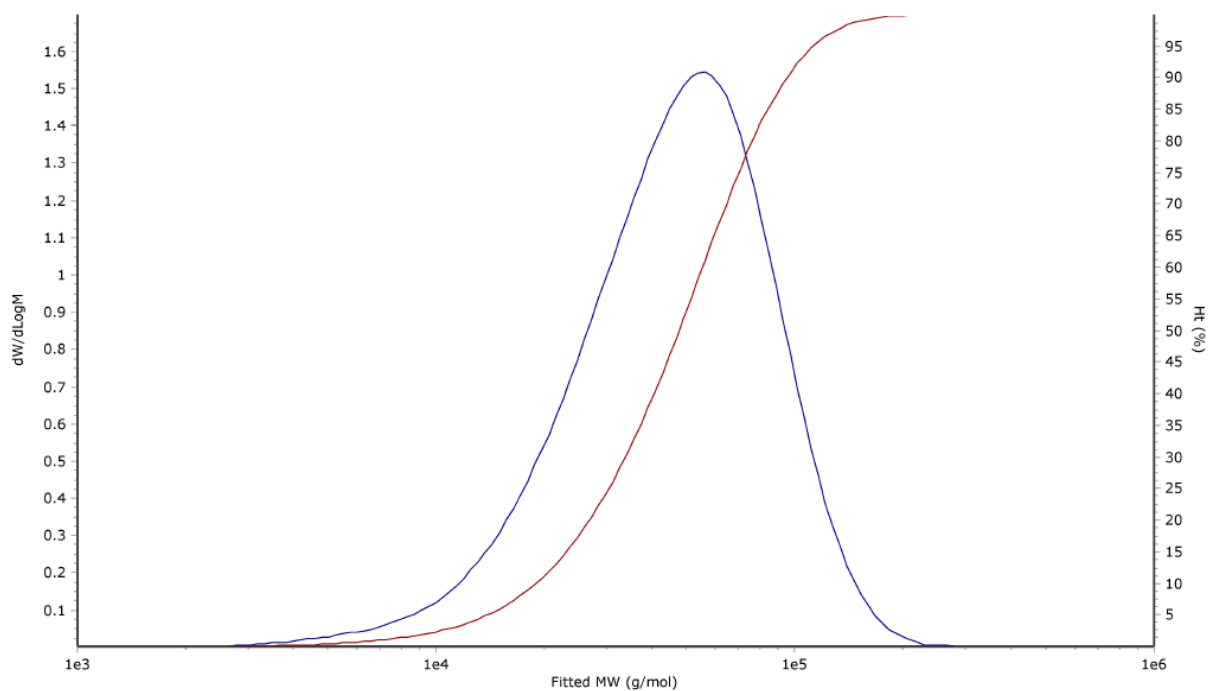


Figure S92 GPC data of polypropylene obtained by **6a** at 120 °C for 3 h (Table 2, entry 3).

Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	55029	31776	56939	82693	109382	79673	1.792

Peak Information

	Start (mins)	End (mins)
Baseline region 1	9.63333	11.20000
Baseline region 2	16.05000	16.51667
Peak 1	11.88333	15.78333

Peak Trace Information

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	13.16667	3364.728	-45.483

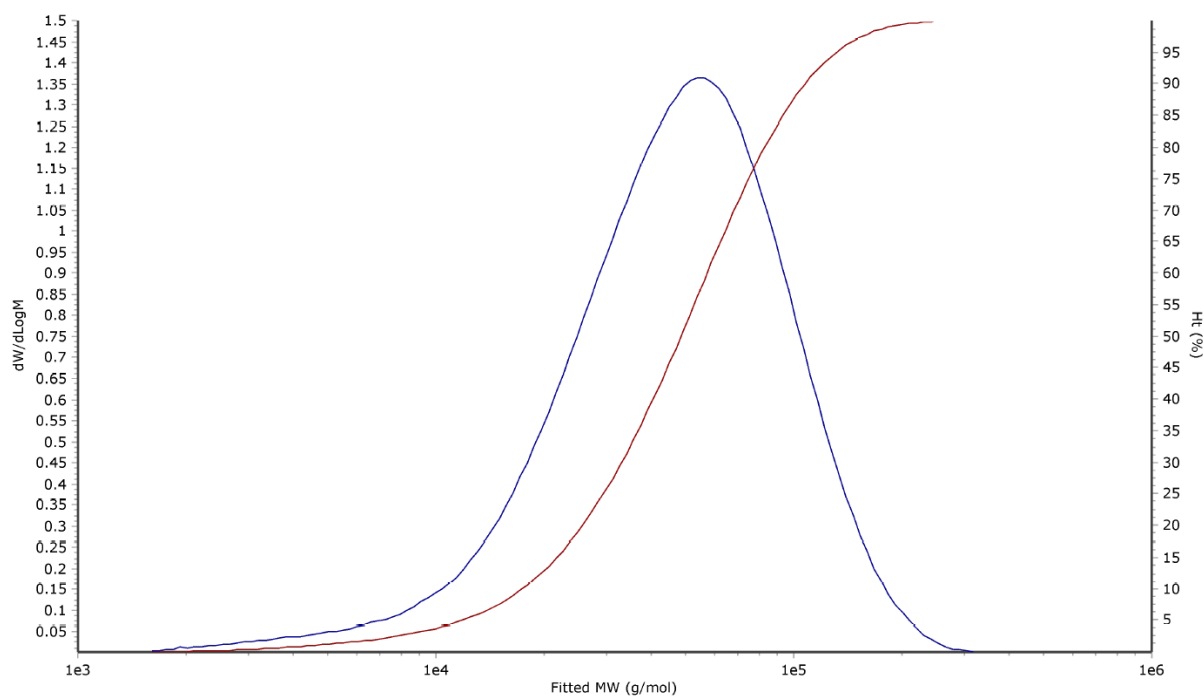


Figure S93 GPC data of polypropylene obtained by **6b** at 100 °C for 3 h (Table 2, entry 4).

High Limit MW RT: 10.85 mins

High Limit MW: 8911204

K: 1750.0000

Alpha: 0.6700

FRCF: 1.0000

MW Averages

Mp: 13605

Mn: 5354

Mv: 10048

Mw: 10962

Mz: 17346

Mz+1: 23206

PD: 2.0474

Low Limit MW RT: 16.38 mins

Low Limit MW: 2939

FRM Name:

Flow Marker RT: 0.00 mins

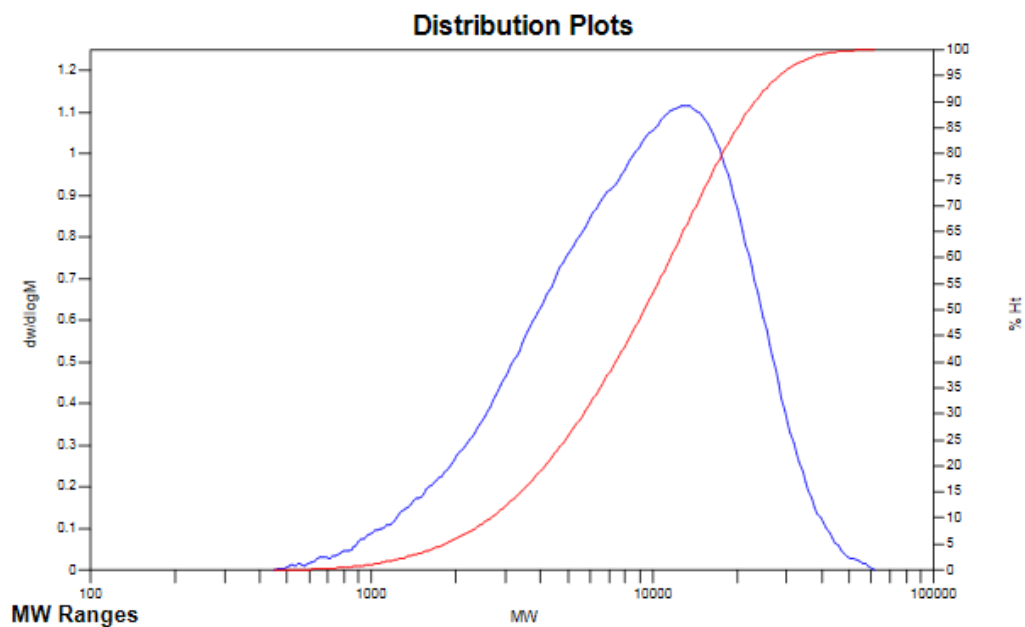


Figure S94 GPC data of poly(ethylene-co-allyl chloride) copolymer obtained by **6a** (Table 3, entry 1).

High Limit MW RT: 10.85 mins

High Limit MW: 8911204

K: 1750.0000

Alpha: 0.6700

FRCF: 1.0000

MW Averages

Mp: 15699

Mn: 8294

Mv: 14152

Mw: 15279

Mz: 23405

Mz+1: 31913

PD: 1.8422

Low Limit MW RT: 16.38 mins

Low Limit MW: 2939

FRM Name:

Flow Marker RT: 0.00 mins

Distribution Plots

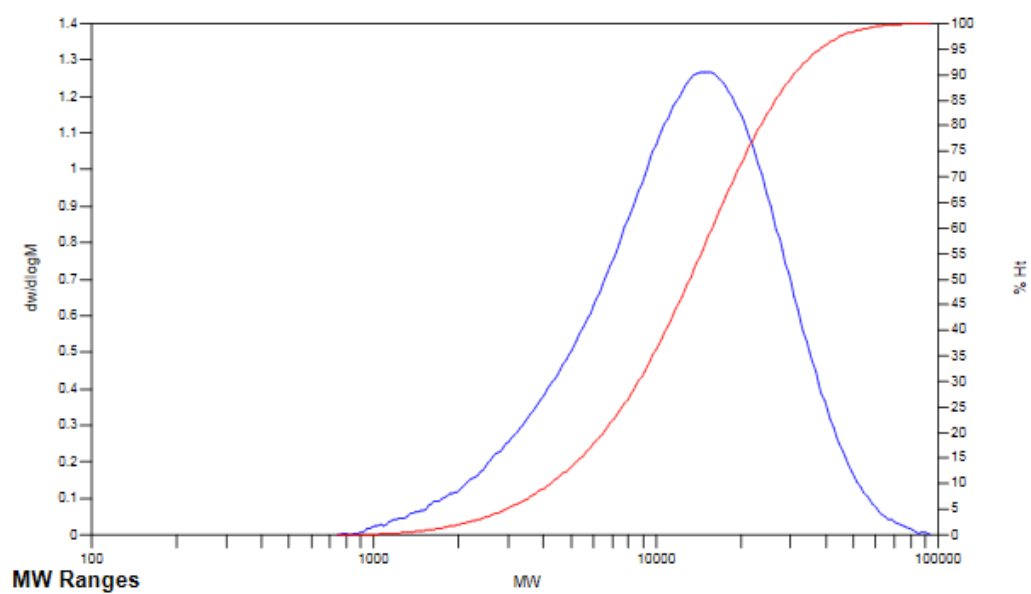


Figure S95 GPC data of poly(ethylene-co-allyl acetate) copolymer obtained by **6a** (Table 3, entry 2).

High Limit MW RT: 10.85 mins

High Limit MW: 8911204

K: 1750.0000

Alpha: 0.6700

FRCF: 1.0000

MW Averages

Mp: 13286

Mn: 9924

Mv: 12779

Mw: 13290

Mz: 16733

Mz+1: 20207

PD: 1.3392

Low Limit MW RT: 16.38 mins

Low Limit MW: 2939

FRM Name:

Flow Marker RT: 0.00 mins

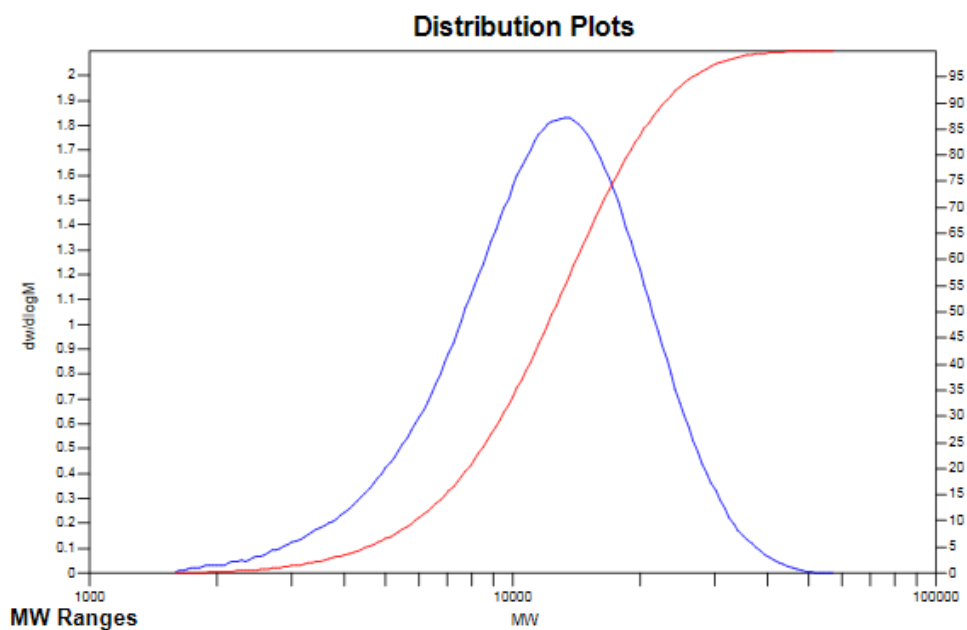


Figure S96 GPC data of poly(ethylene-co-methyl acrylate) copolymer obtained by **6a** (Table 3, entry 3).

High Limit MW RT: 10.85 mins

High Limit MW: 8911204

K: 1750.0000

Alpha: 0.6700

FRCF: 1.0000

MW Averages

Mp: 18572

Mn: 8369

Mv: 15915

Mw: 17415

Mz: 28194

Mz+1: 38764

PD: 2.0809

Low Limit MW RT: 16.38 mins

Low Limit MW: 2939

FRM Name:

Flow Marker RT: 0.00 mins

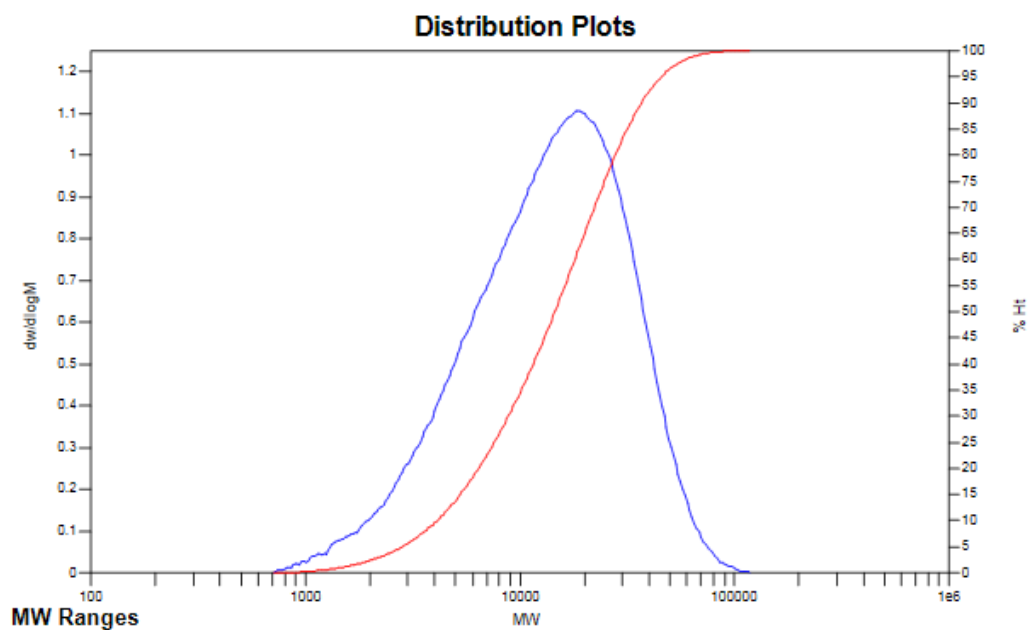


Figure S97 GPC data of poly(ethylene-co-allyl chloride) copolymer obtained by **6b** (Table 3, entry 4).

High Limit MW RT: 10.85 mins

High Limit MW: 8911204

K: 1750.0000

Alpha: 0.6700

FRCF: 1.0000

MW Averages

Mp: 18130

Mn: 9453

Mv: 16833

Mw: 18203

Mz: 27967

Mz+1: 37924

PD: 1.9256

Low Limit MW RT: 16.38 mins

Low Limit MW: 2939

FRM Name:

Flow Marker RT: 0.00 mins

Distribution Plots

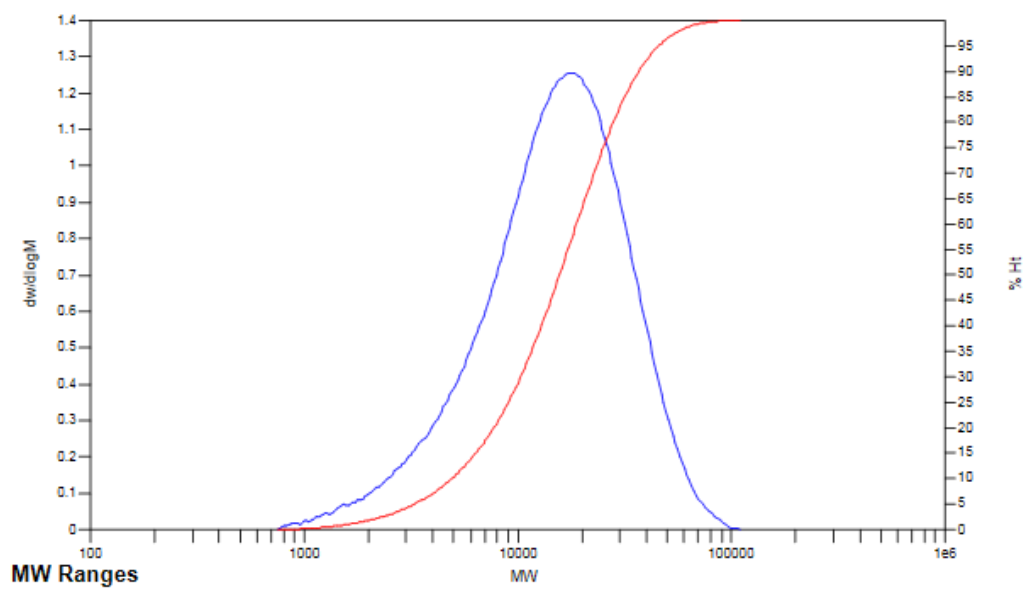


Figure S98 GPC data of poly(ethylene-co-allyl acetate) copolymer obtained by **6b** (Table 3, entry 5).

High Limit MW RT: 10.85 mins

High Limit MW: 8911204

K: 1750.0000

Alpha: 0.6700

FRCF: 1.0000

MW Averages

Mp: 18130

Mn: 14018

Mv: 17687

Mw: 18337

Mz: 22726

Mz+1: 27280

PD: 1.3081

Low Limit MW RT: 16.38 mins

Low Limit MW: 2939

FRM Name:

Flow Marker RT: 0.00 mins

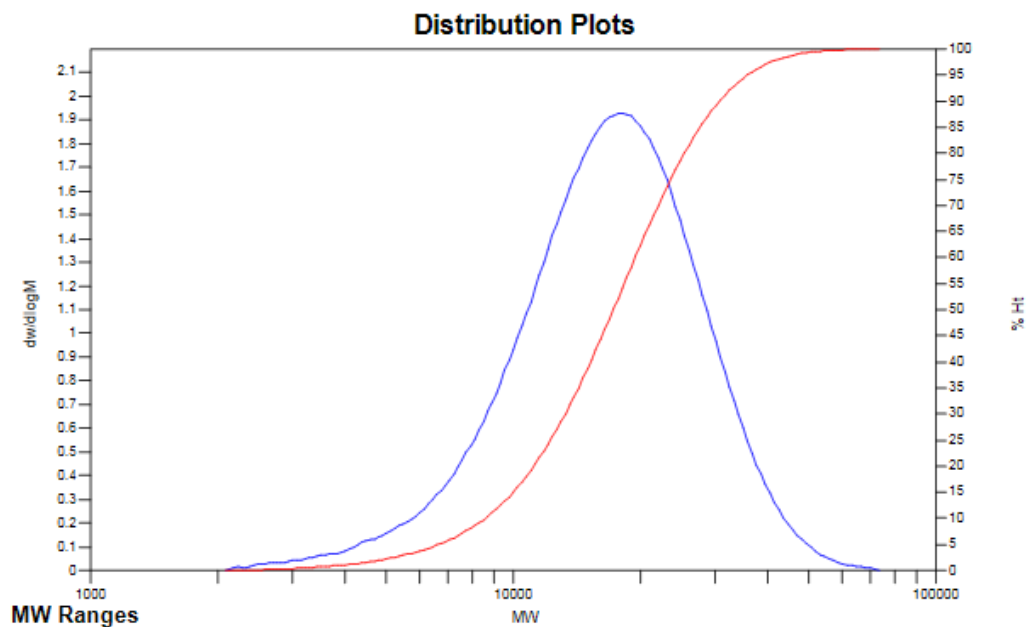


Figure S99 GPC data of poly(ethylene-co-methyl acrylate) copolymer obtained by **6b** (Table 3, entry 6).

High Limit MW RT: 10.85 mins

Low Limit MW RT: 16.38 mins

High Limit MW: 8911204

Low Limit MW: 2939

K: 1750.0000

FRM Name:

Alpha: 0.6700

Flow Marker RT: 0.00 mins

FRCF: 1.0000

MW Averages

Mp: 21992

Mn: 9902

Mv: 17460

Mw: 18867

Mz: 28603

Mz+1: 38018

PD: 1.9054

Distribution Plots

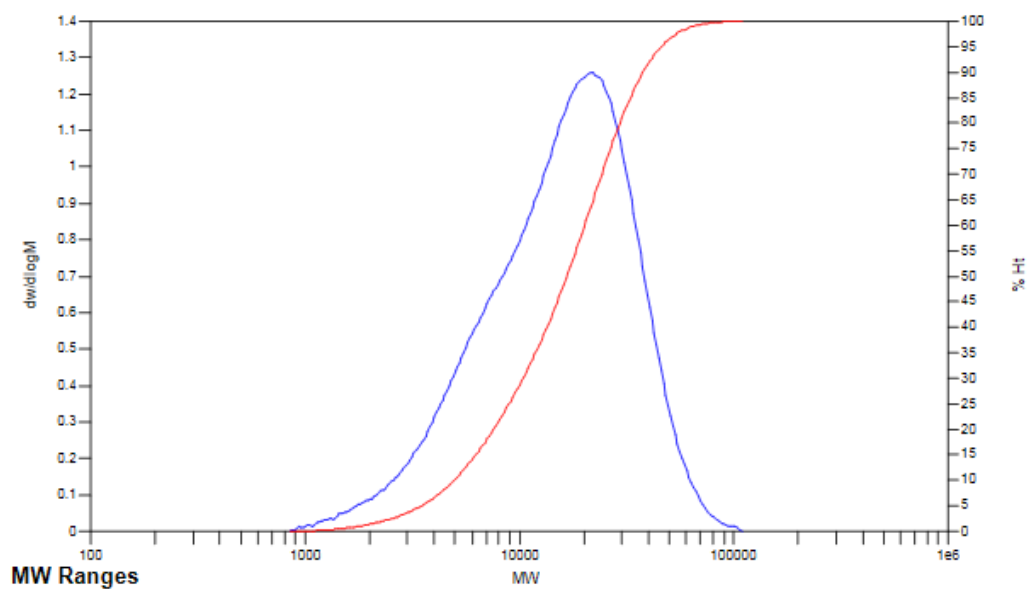


Figure S100 GPC data of poly(ethylene-co-*t*-butyl acrylate) copolymer obtained by **6b** (Table 3, entry 7).

High Limit MW RT: 10.85 mins

High Limit MW: 8911204

K: 1750.0000

Alpha: 0.6700

FRCF: 1.0000

MW Averages

Mp: 26711

Mn: 12808

Mv: 24807

Mw: 27168

Mz: 44509

Mz+1: 62585

PD: 2.1212

Low Limit MW RT: 16.38 mins

Low Limit MW: 2939

FRM Name:

Flow Marker RT: 0.00 mins

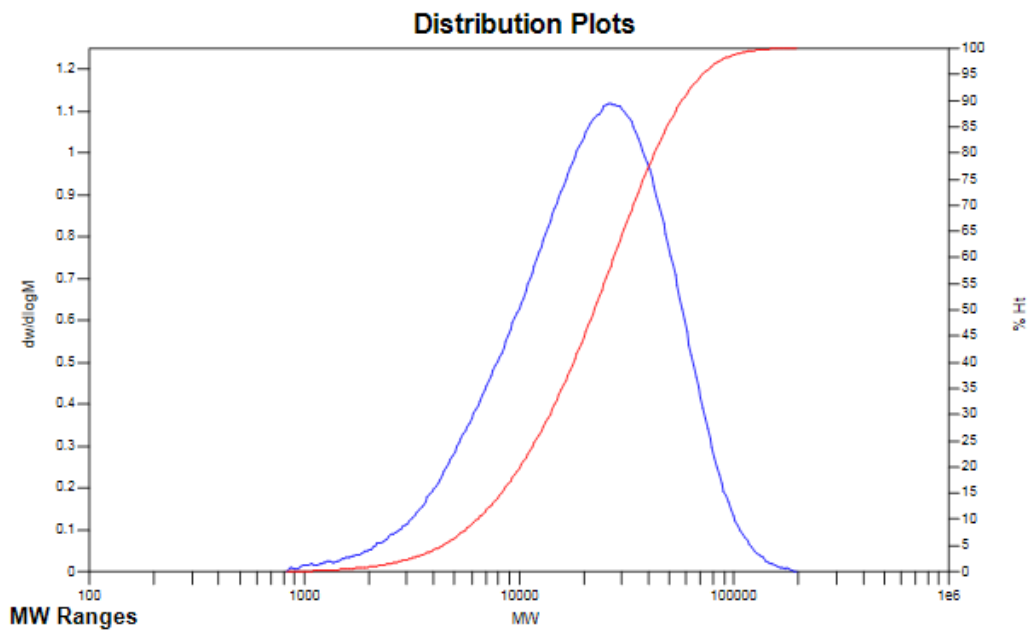


Figure S101 GPC data of poly(ethylene-co-allyl ethyl ether) copolymer obtained by **6b** (Table 3, entry 8).

High Limit MW RT: 10.85 mins

High Limit MW: 8911204

K: 1750.0000

Alpha: 0.6700

FRCF: 1.0000

MW Averages

Mp: 60205

Mn: 26677

Mv: 56478

Mw: 62705

Mz: 110203

Mz+1: 160405

PD: 2.3505

Low Limit MW RT: 16.38 mins

Low Limit MW: 2939

FRM Name:

Flow Marker RT: 0.00 mins

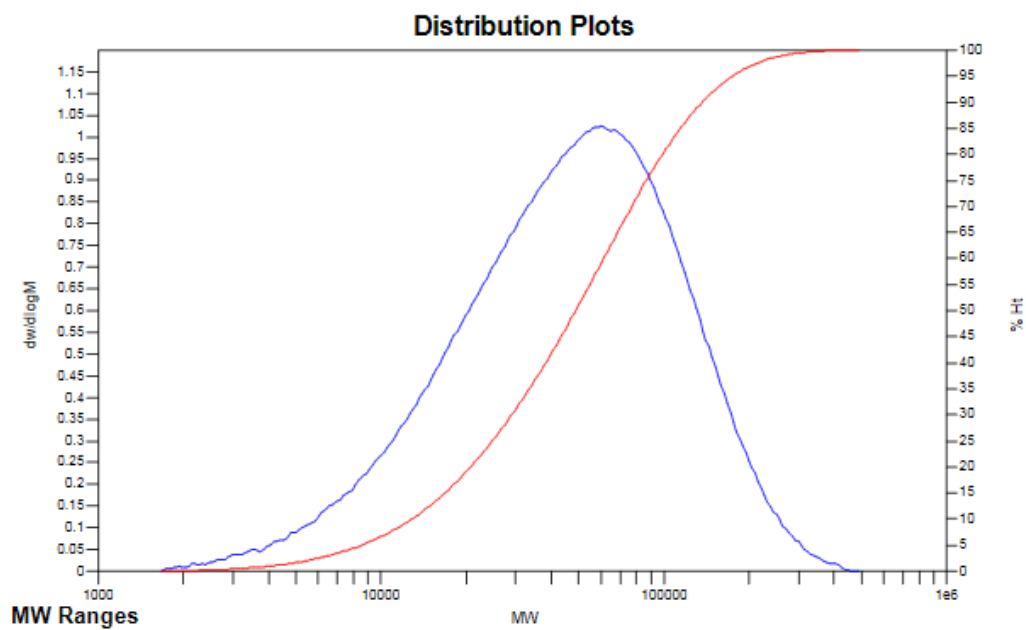


Figure S102 GPC data of poly(ethylene-co-butyl vinyl ether) copolymer obtained by **6b** (Table 3, entry 9).

High Limit MW RT: 10.85 mins

Low Limit MW RT: 16.38 mins

High Limit MW: 8911204

Low Limit MW: 2939

K: 1750.0000

FRM Name:

Alpha: 0.6700

Flow Marker RT: 0.00 mins

FRCF: 1.0000

MW Averages

Mp: 26068

Mn: 11886

Mv: 23864

Mw: 26365

Mz: 44989

Mz+1: 63699

PD: 2.2182

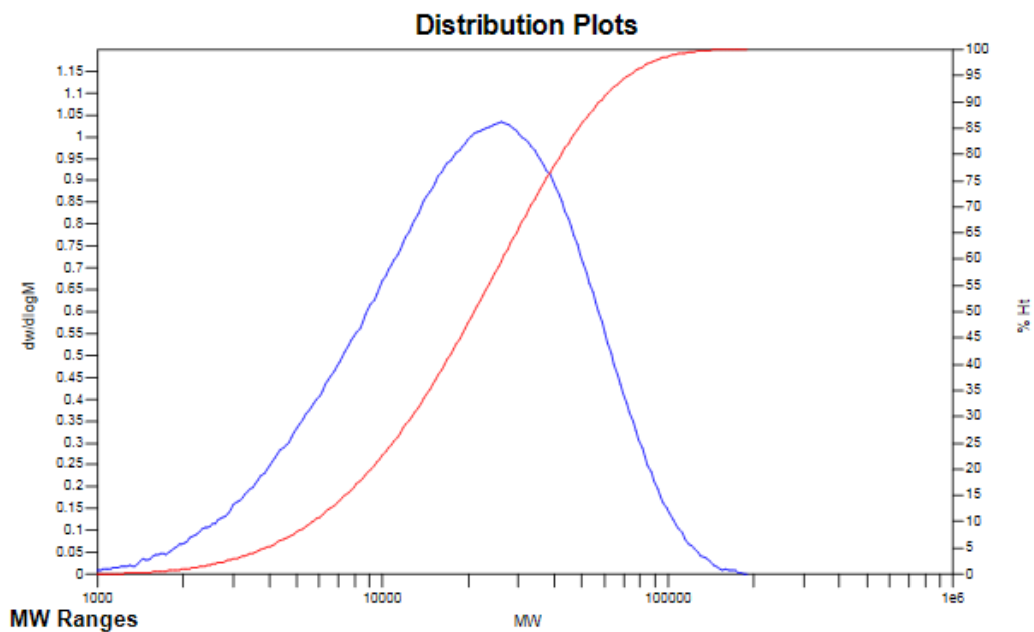


Figure S103 GPC data of poly(ethylene-co-vinyl acetate) copolymer obtained by **6b** (Table 3, entry 10).

High Limit MW RT: 10.85 mins

High Limit MW: 8911204

K: 1750.0000

Alpha: 0.6700

FRCF: 1.0000

MW Averages

Mp: 7567

Mn: 3656

Mv: 6618

Mw: 7247

Mz: 11996

Mz+1: 17127

PD: 1.9822

Low Limit MW RT: 16.38 mins

Low Limit MW: 2939

FRM Name:

Flow Marker RT: 0.00 mins

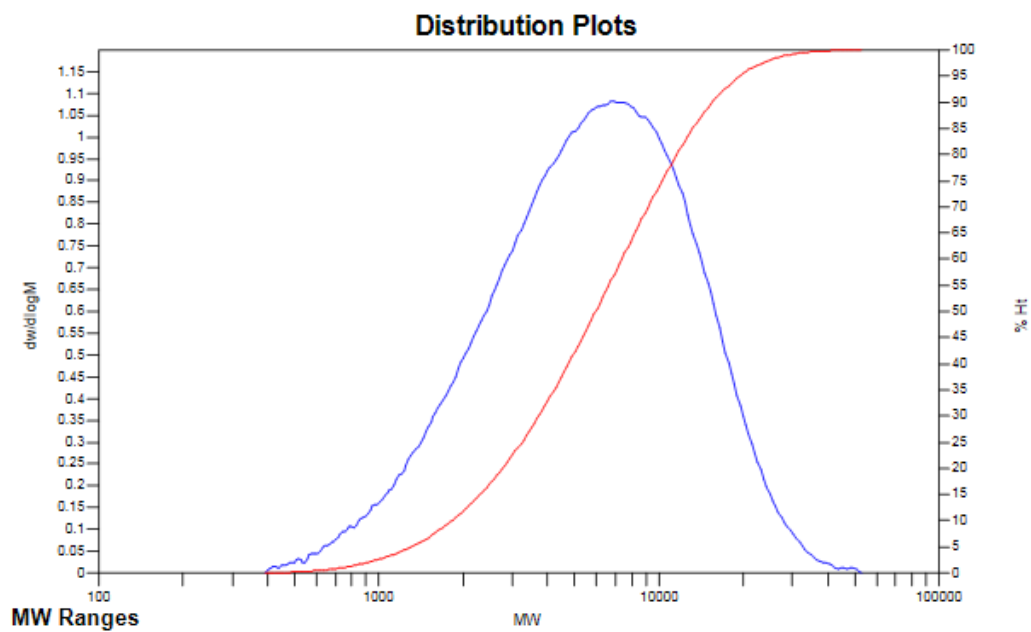


Figure S104 GPC data of poly(ethylene-co-methyl methacrylate) copolymer obtained by **6a** (Table 4, entry 1).

High Limit MW RT: 10.85 mins

Low Limit MW RT: 16.38 mins

High Limit MW: 8911204

Low Limit MW: 2939

K: 1750.0000

FRM Name:

Alpha: 0.6700

Flow Marker RT: 0.00 mins

FRCF: 1.0000

MW Averages

Mp: 7567

Mn: 3288

Mv: 6450

Mw: 7107

Mz: 12005

Mz+1: 17015

PD: 2.1615

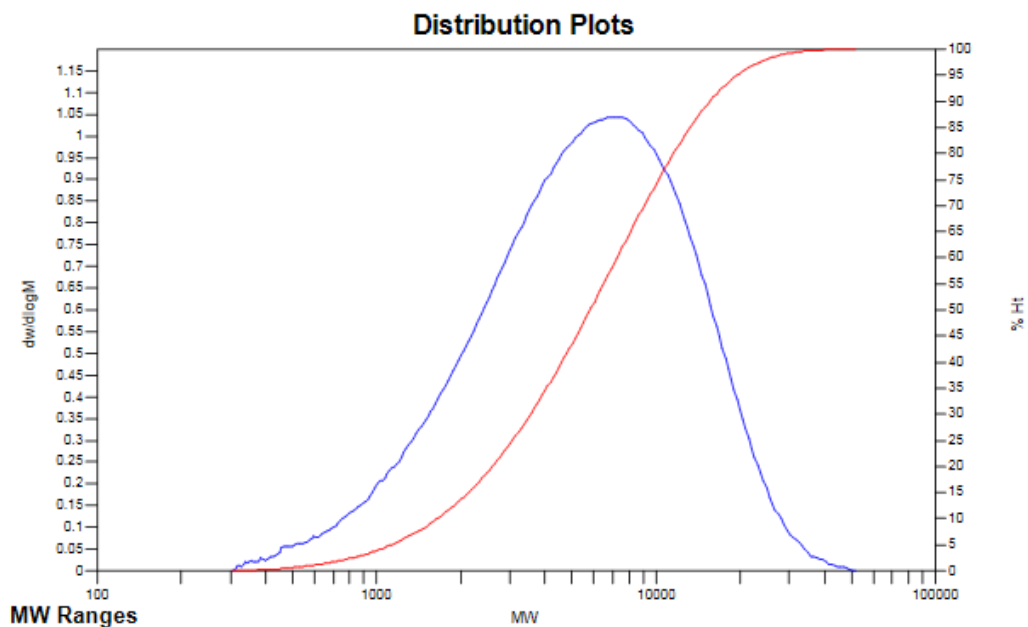


Figure S105 GPC data of poly(ethylene-co-methyl methacrylate) copolymer obtained by **6b** (Table 4, entry 2).

Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	24787	13864	22942	30520	36971	29730	1.655

Peak Information

	Start (mins)	End (mins)
Baseline region 1	9.16667	10.46667
Baseline region 2	16.56667	17.16667
Peak 1	12.83333	16.30000

Peak Trace Information

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	13.76667	2834.467	-43.642

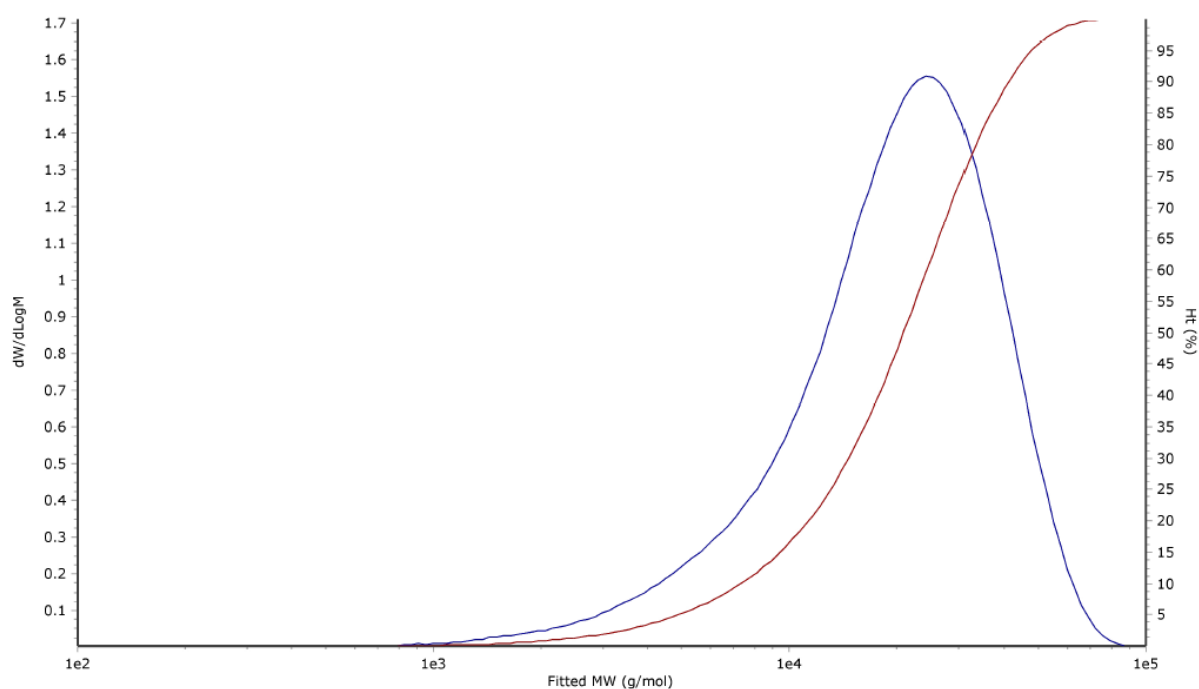


Figure S106 GPC data of poly(propylene-co-allyl acetate) copolymer obtained by **6a** at 100 °C for 6 h (Scheme 2).

Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	20741	21900	30910	46440	71630	43395	1.411

Peak Information

	Start (mins)	End (mins)
Baseline region 1	8.50000	10.01667
Baseline region 2	16.11667	17.00000
Peak 1	11.95000	15.00000

Peak Trace Information

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	13.63333	2079.955	-40.285

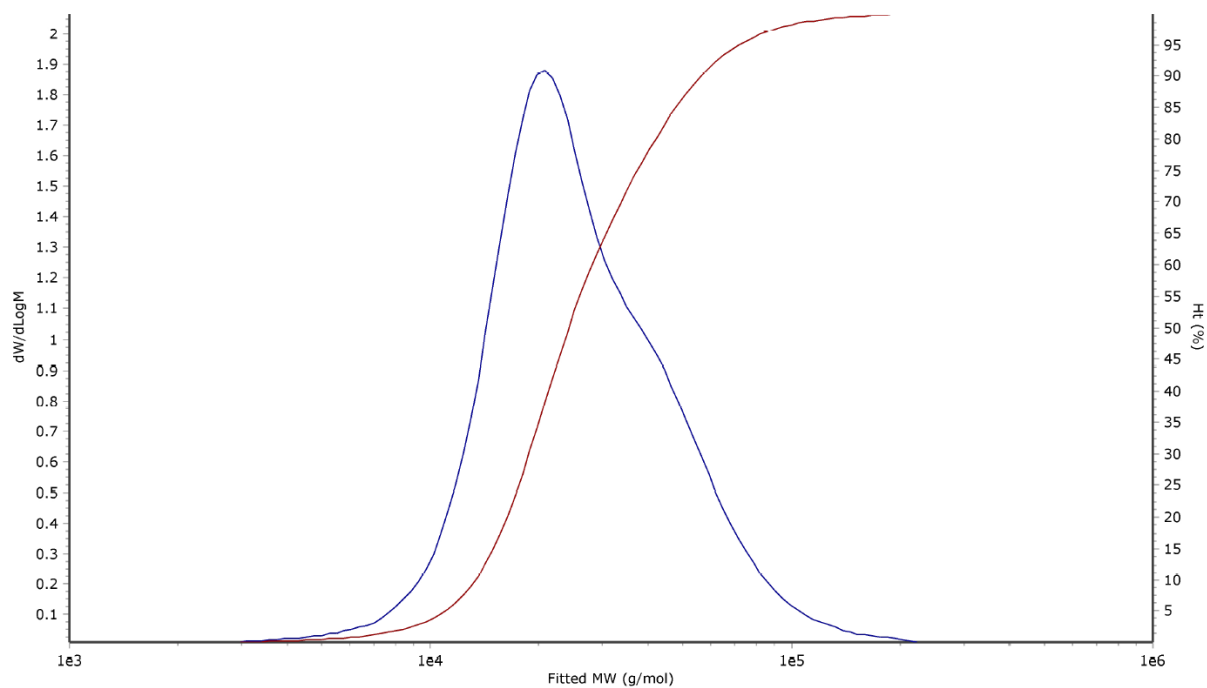


Figure S107 GPC data of polyethylene obtained by **6a** at 80 °C with addition of Ni(cod)₂ (2.0 equiv). (Table S8, entry 2).

11. DSC Data of polymers

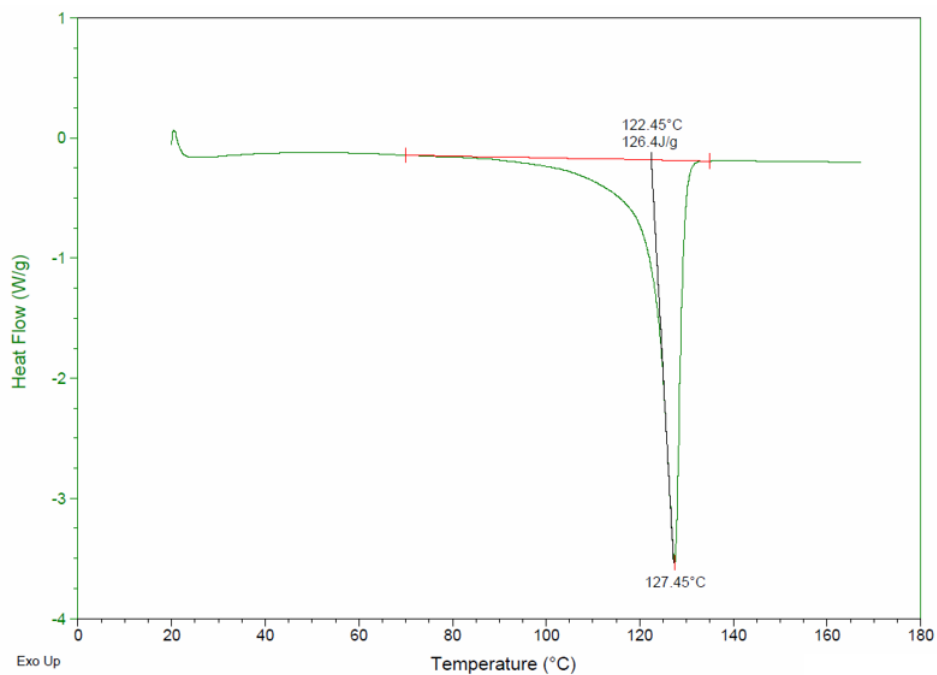


Figure S108 DSC data of polyethylene obtained by **6a** at 80 °C (Table 1, entry 1).

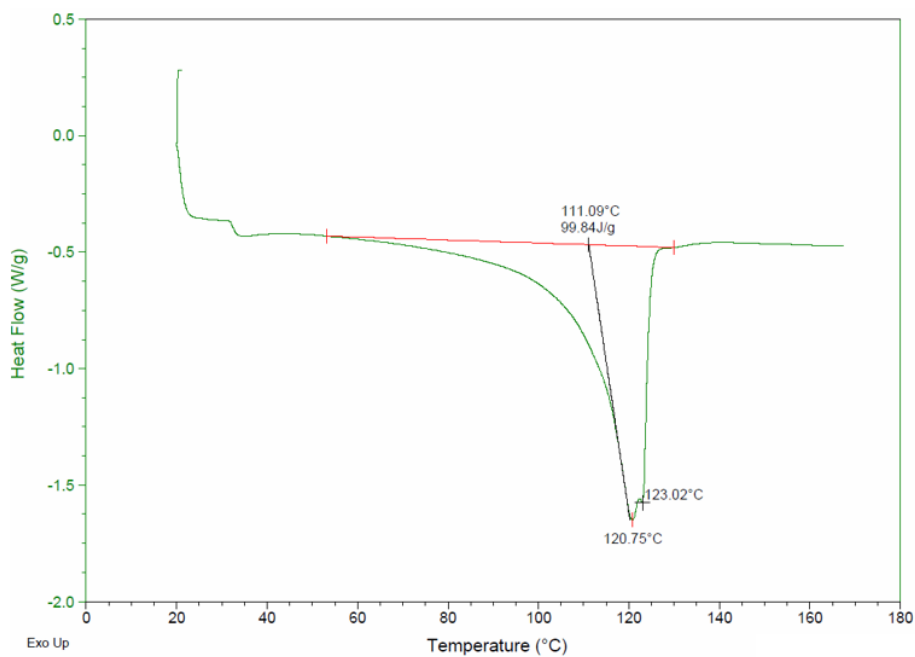


Figure S109 DSC data of polyethylene obtained by **6a** at 100 °C (Table 1, entry 2).

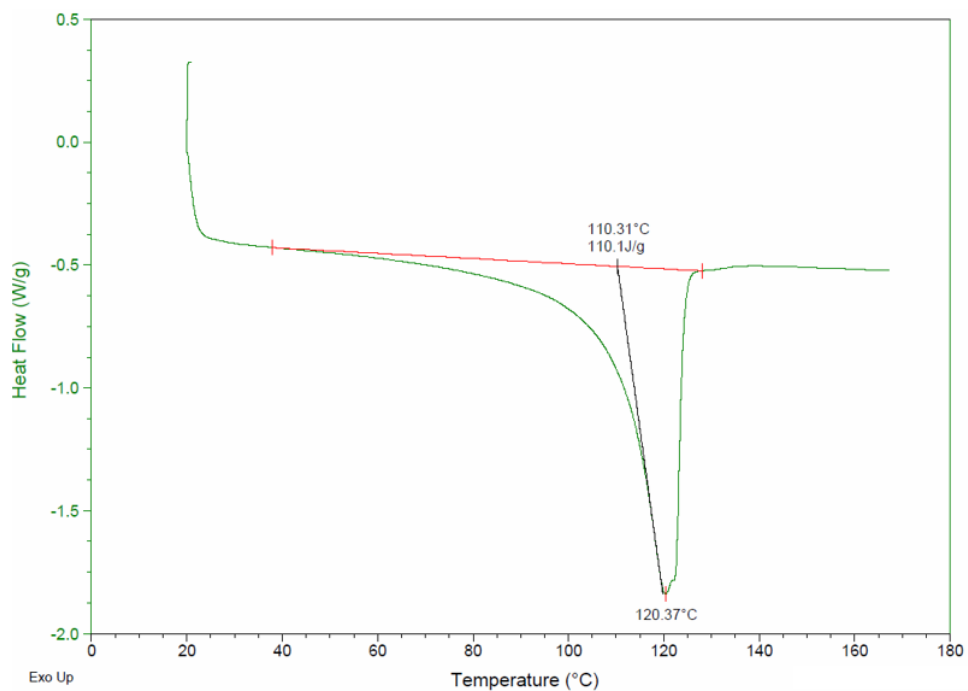


Figure S110 DSC data of polyethylene obtained by **6a** at 120 °C (Table 1, entry 3).

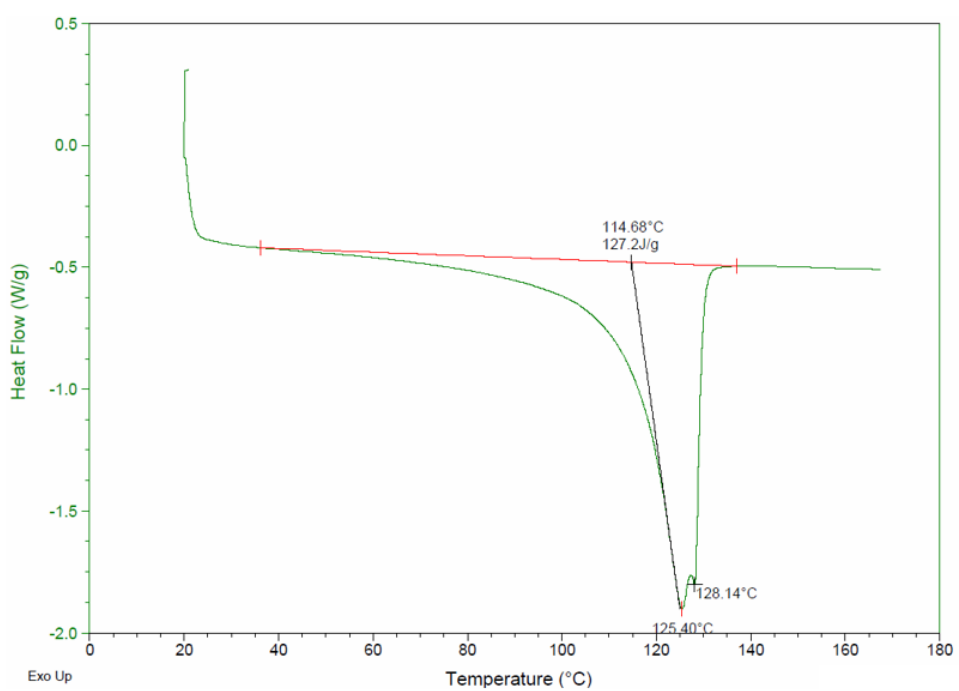


Figure S111 DSC data of polyethylene obtained by **6b** at 100 °C (Table 1, entry 4).

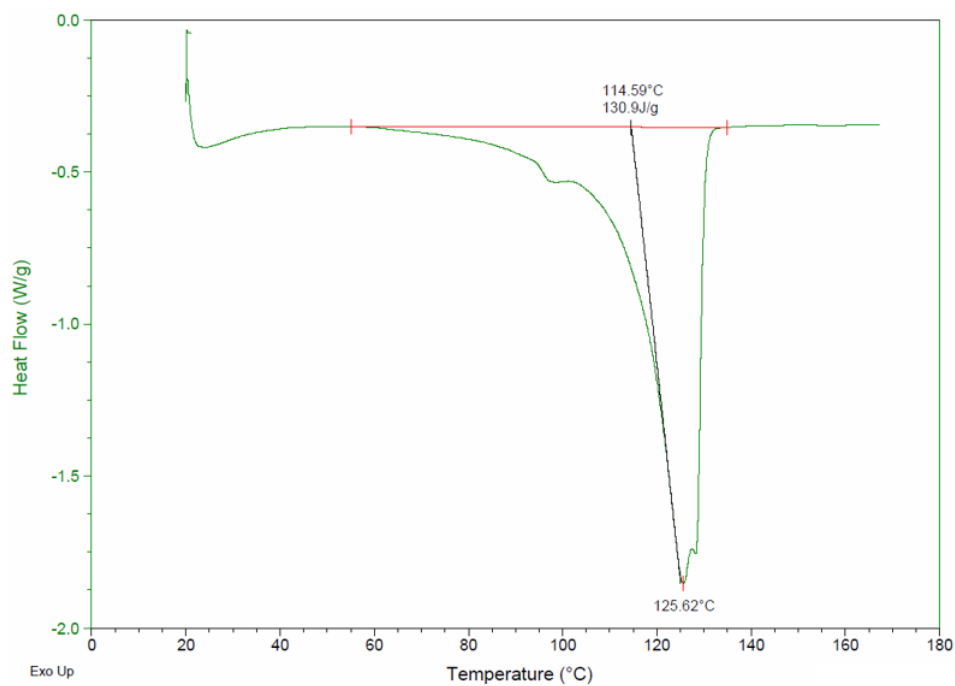


Figure S112 DSC data of polyethylene obtained by **6b** at 100 °C for 0.5 h (Table 1, entry 5).

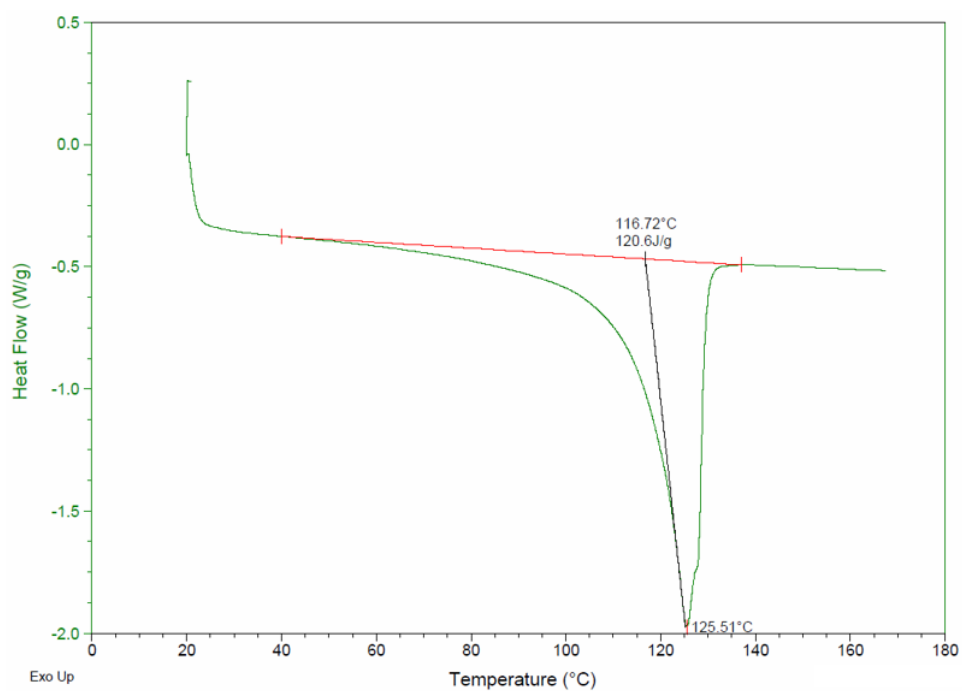


Figure S113 DSC data of polyethylene obtained by **6b** at 100 °C for 2h (Table 1, entry 6).

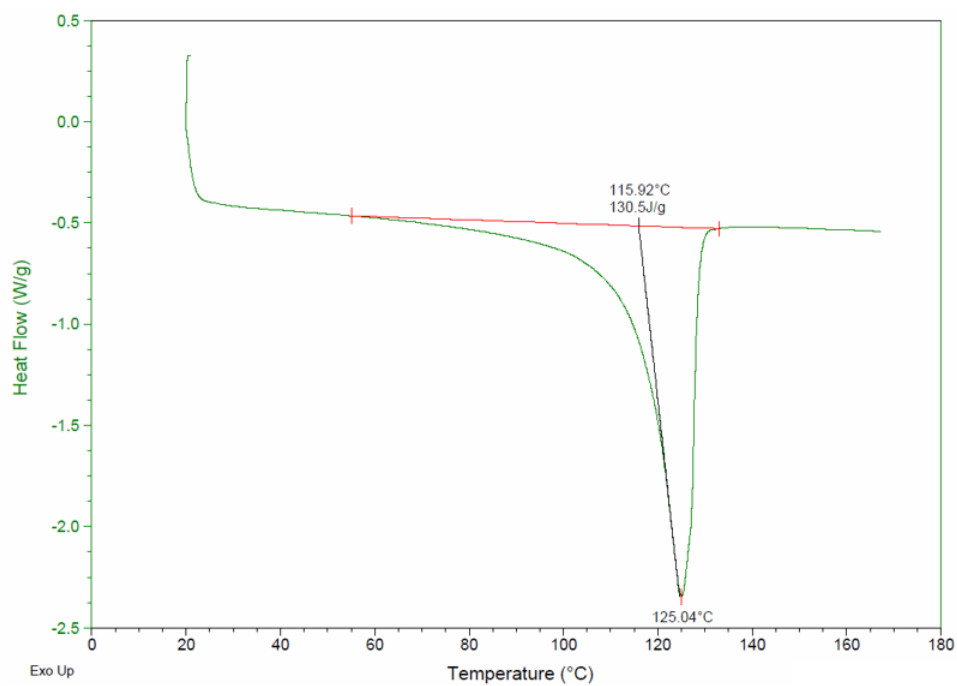


Figure S114 DSC data of polyethylene obtained by **6b** at 120 °C (Table 1, entry 7).

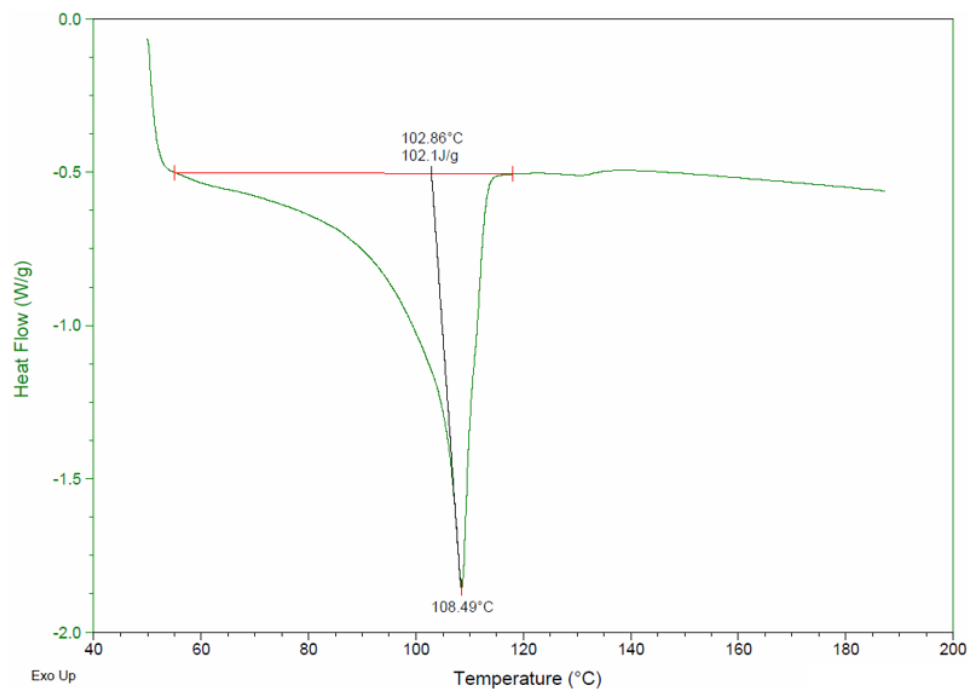


Figure S115 DSC data of copolymer with allyl chloride obtained by **6a** (Table 3, entry 1).

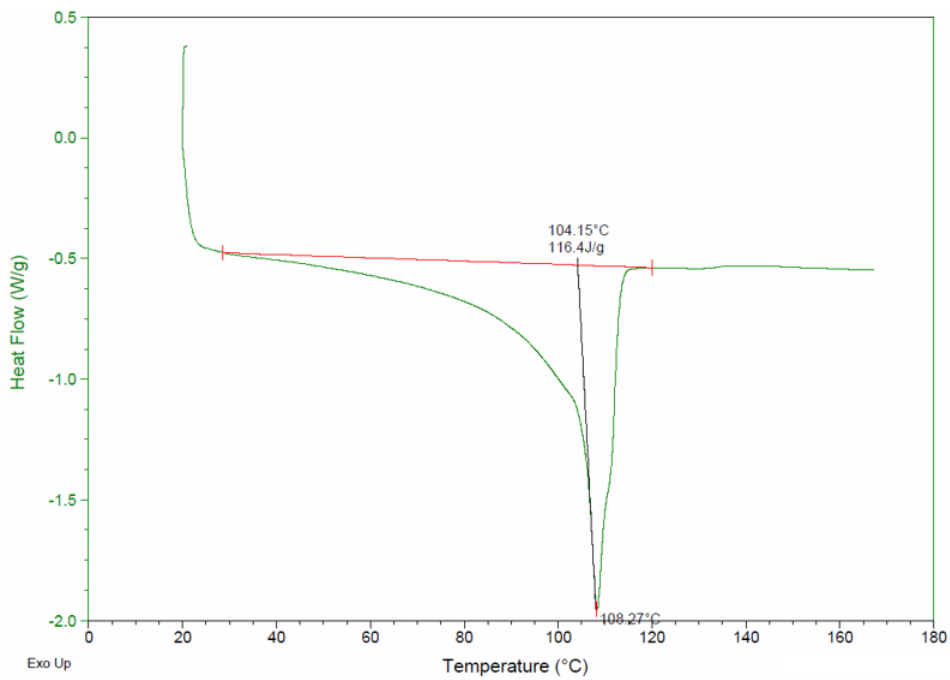


Figure S116 DSC data of copolymer with allyl acetate obtained by **6a** (Table 3, entry 2).

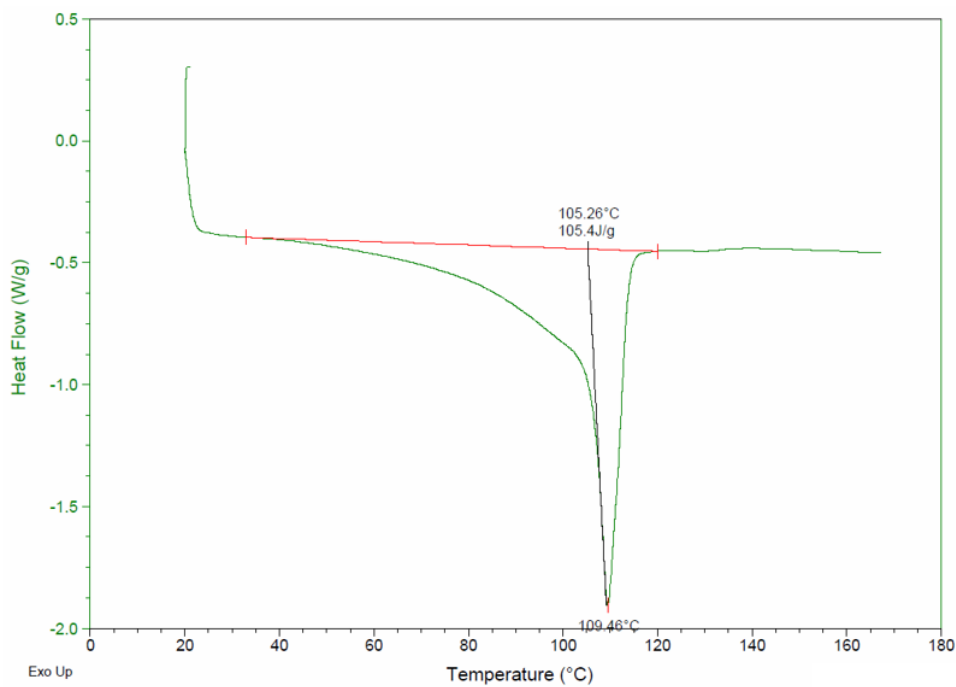


Figure S117 DSC data of copolymer with methyl acrylate obtained by **6a** (Table 3, entry 3).

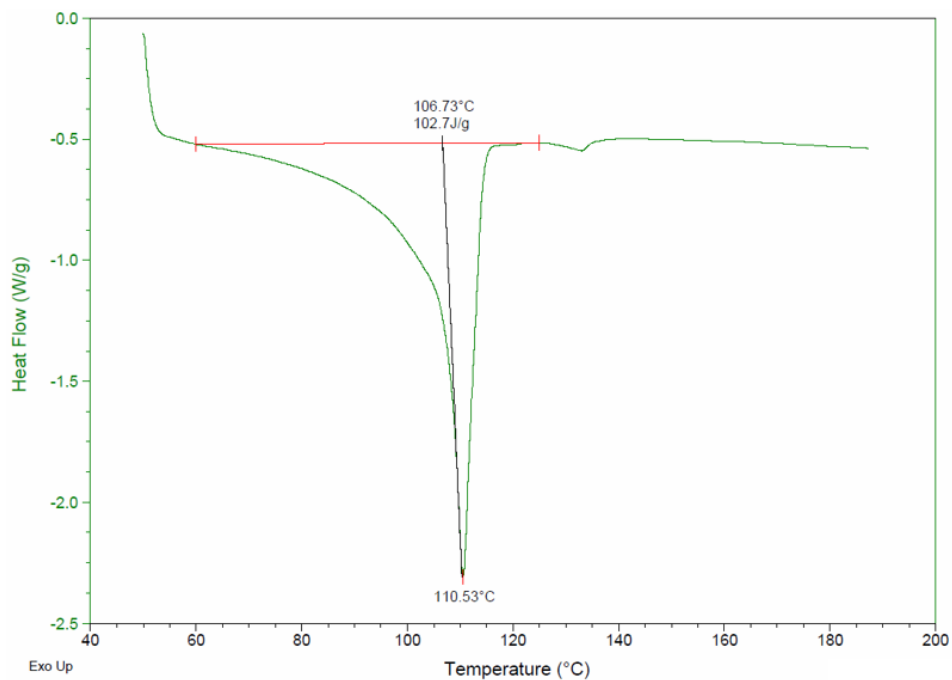


Figure S118 DSC data of copolymer with allyl chloride obtained by **6b** (Table 3, entry 4).

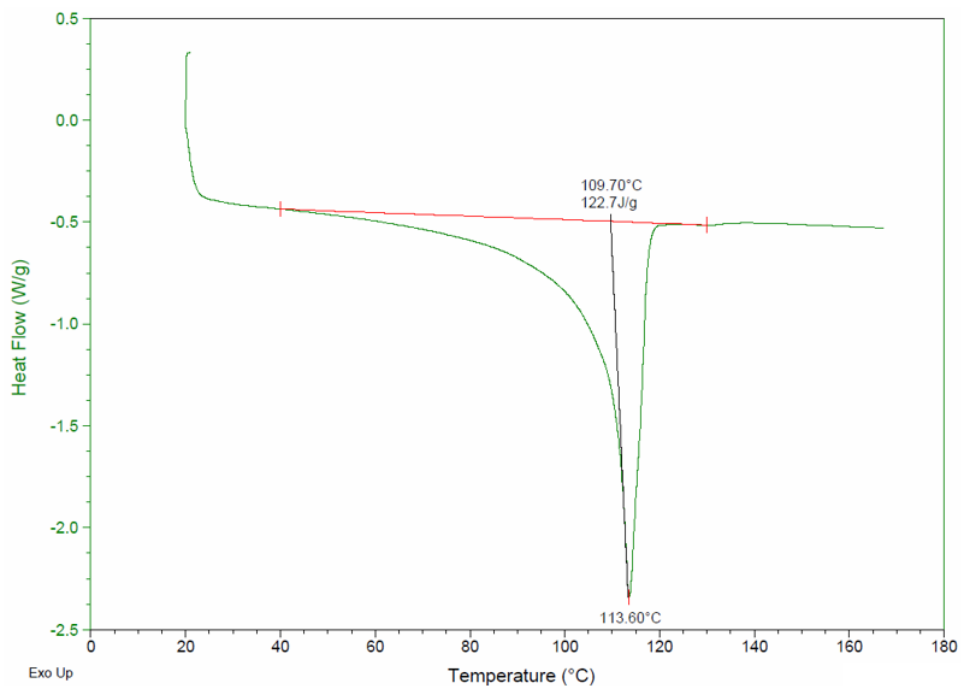


Figure S119 DSC data of copolymer with allyl acetate obtained by **6b** (Table 3, entry 5).

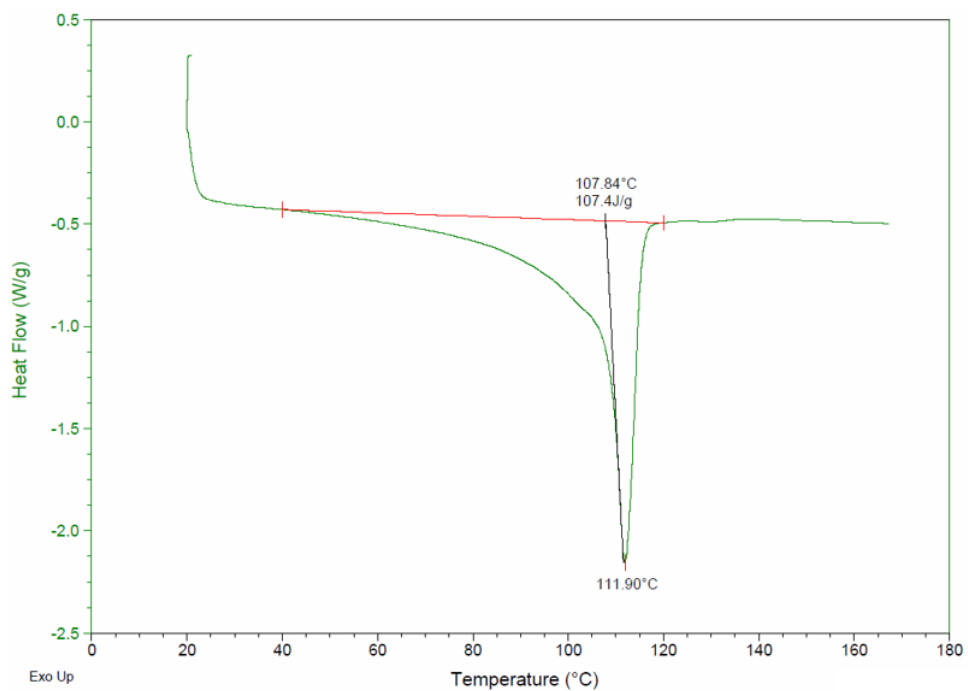


Figure S120 DSC data of copolymer with methyl acrylate obtained by **6b** (Table 3, entry 6).

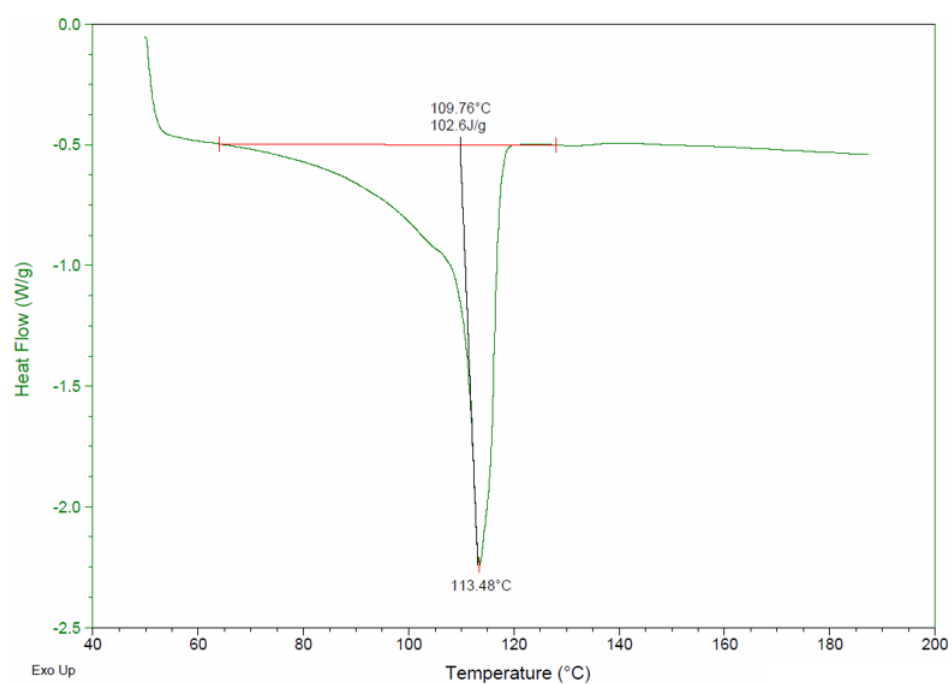


Figure S121 DSC data of copolymer with *t*-butyl acrylate obtained by **6b** (Table 3, entry 7).

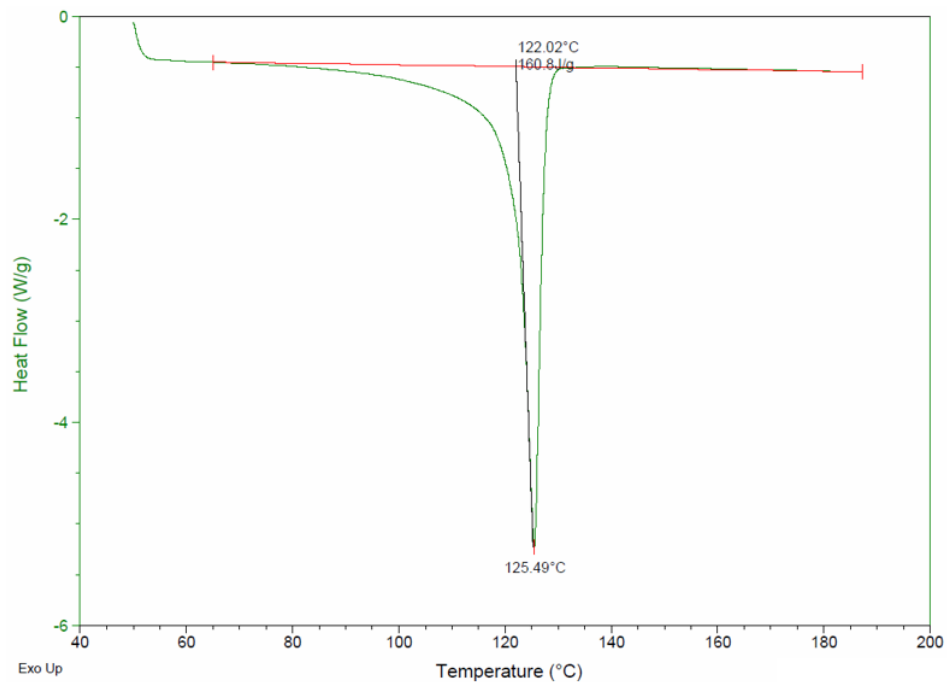


Figure S122 DSC data of copolymer with allyl ethyl ether obtained by **6b** (Table 3, entry 8).

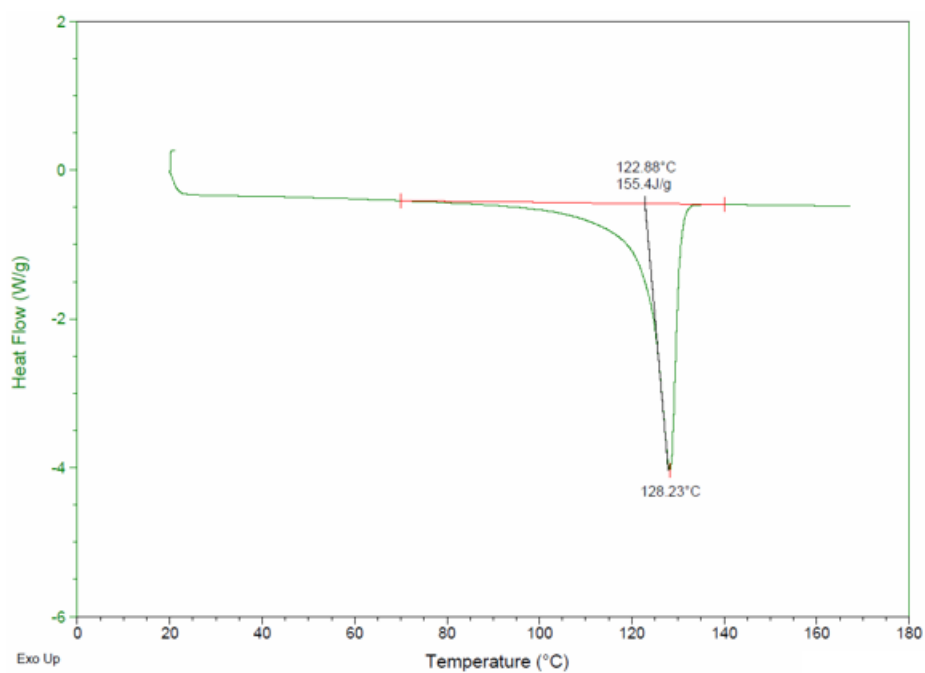


Figure S123 DSC data of copolymer with butyl vinyl ether obtained by **6b** (Table 3, entry 9).

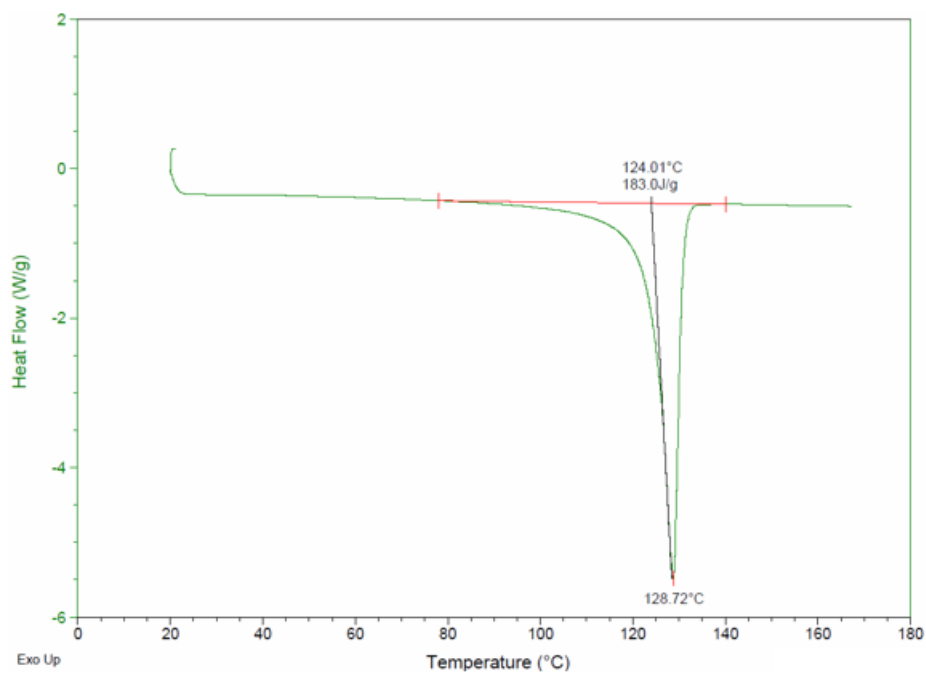


Figure S124 DSC data of copolymer with vinyl acetate obtained by **6b** (Table 3, entry 10).

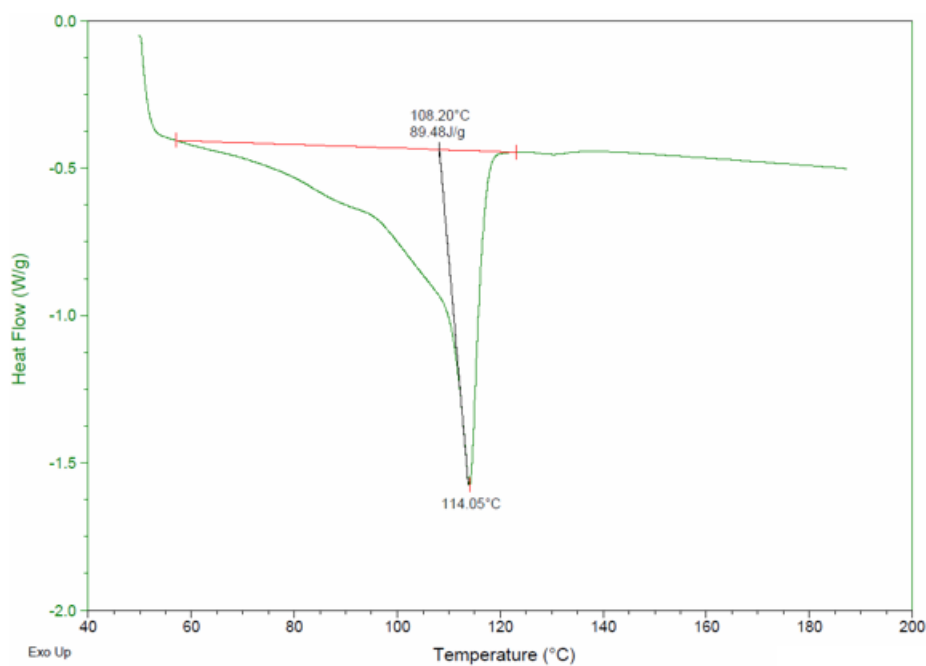


Figure S125 DSC data of copolymer with methyl methacrylate obtained by **6a** (Table 4, entry 1).

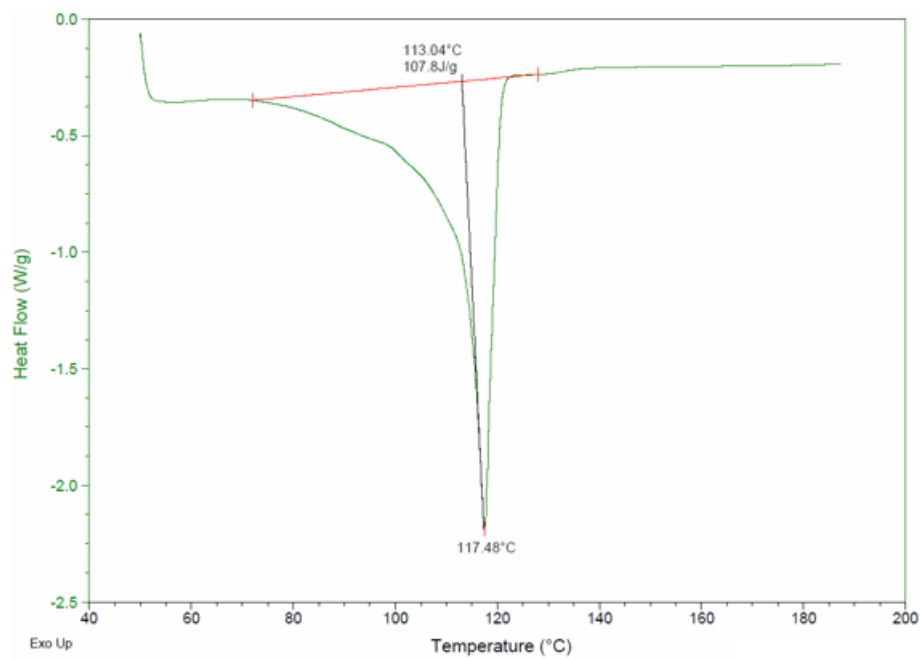


Figure S126 DSC data of copolymer with methyl methacrylate obtained by **6b** (Table 4, entry 2).

13. Computational Study for *aImPy*-Pd Catalyst **6a** on Ethylene Polymerization

13.1. Computational details

All DFT calculations were carried out with Gaussian 09 program.²⁹ All structures were optimized by the functional B3LYP-D3³⁰ with the basis sets of Los Alamos National Laboratory double ζ (LanL2DZ) and its corresponding effective core potential (ECP) basis set³¹ for Pd atom and 6-31G(d) basis set for all other atoms, which was one of the standard combinations for optimization of metal complexes, the SMD model³² with the parameters for toluene was used to account for solvent effects. Thermodynamic parameters including Gibbs free energies at 298 K were obtained by frequency calculations. Gibbs free reaction energies and enthalpies were calculated for standard conditions ($p = 1$ atm, $T = 298$ K) and are unscaled. Gibbs free reaction energies and enthalpies were calculated for standard conditions ($p = 1$ atm, $T = 298$ K) and are unscaled.

13.2. Energy profiles for NHC-Pd complexes on ethylene polymerization.

The calculated energy profile tendency for *aImPy*-Pd **6a** was similar to previously reported group-10-metal catalysts bearing unsymmetrical bidentate ligands. Ethylene insertion occurs exclusively from *trans*-(C[^]O)Pd(R)(ethylene) intermediate **1'** (R is *trans* to the C atom of carbene), leading to the alkyl chain being found *cis*- to carbon (Intermediate **2**) immediately after insertion. In general pathway for β -hydride elimination proceeds along the formation of β -agostic intermediate **4'** from *trans*-C,R-(C[^]O)Pd(R) intermediate **1'**. The opposite pathway from *cis*-C,R-(C[^]O)Pd(R) intermediate **1** rarely occurs through β -hydride elimination pathway because of the thermodynamic instability of intermediate **5**.

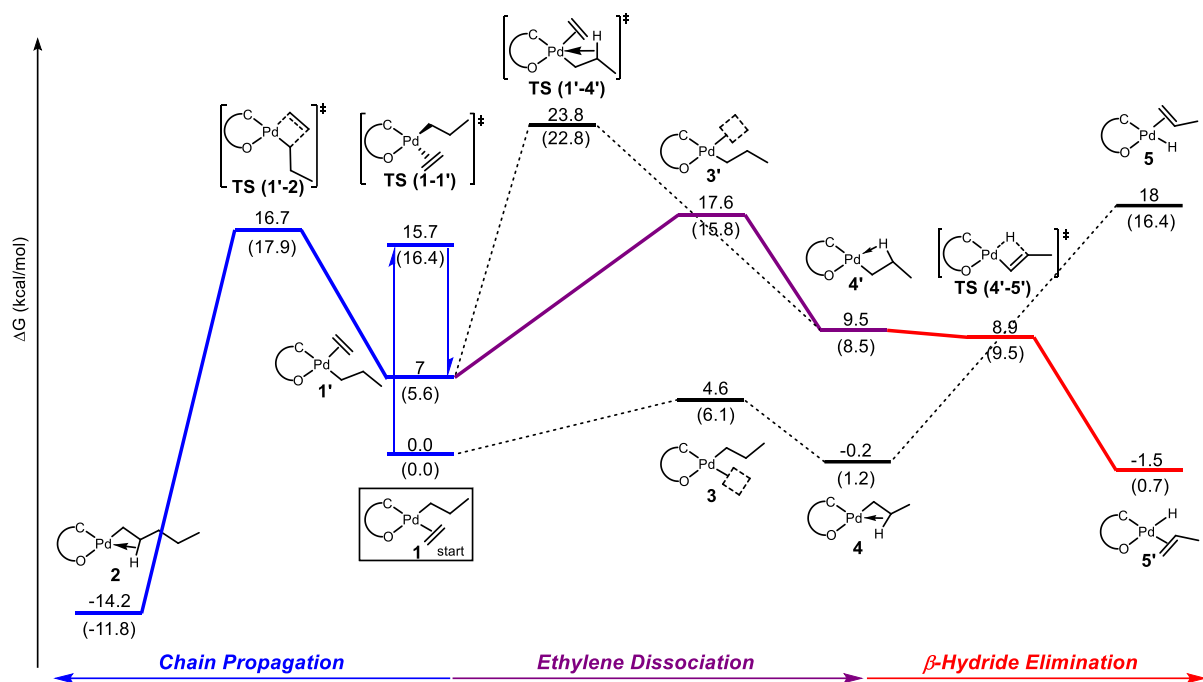


Figure S127 The energy profile for *aImPy*-Pd catalyst **6a** in chain propagation and β -hydride elimination. Free energies are relative to the energy sum of corresponding catalyst and monomer. The values in parentheses refer to IzQO/Pd complex (**F**)¹¹

13.3. Cartesian Coordinates

aImPy-Pd (6a) int 3

O 1				C	11.91027	14.89443	1.758285
O	8.614132	8.597271	1.98758	C	12.51414	16.14186	1.890979
N	9.242918	12.78478	2.825322	C	11.7464	17.26208	2.219768
N	10.15229	12.47577	0.867944	C	10.3702	17.12582	2.415784
C	9.070288	11.42966	2.570895	C	9.759653	15.88095	2.273524
C	9.655169	11.22709	1.316195	C	8.682583	13.48935	3.952676
C	9.923286	13.41576	1.827375	C	7.324716	13.85295	3.877747
C	9.838681	10.05316	0.510914	C	6.769899	14.48008	4.999735
C	9.310925	8.774004	0.908462	C	7.543824	14.75143	6.126701
C	9.584026	7.67533	0.052699	C	8.896593	14.41939	6.146972
C	10.31231	7.814318	-1.12498	C	9.500325	13.78067	5.056571
C	10.80184	9.057189	-1.52297	C	6.478972	13.6212	2.626272
C	10.56212	10.17579	-0.70949	C	5.412593	12.53298	2.840012
C	10.95876	11.49137	-1.1314	C	5.827255	14.92702	2.133585
C	10.73244	12.62402	-0.41796	C	10.98271	13.42791	5.098272
C	10.95809	13.96453	-1.00867	C	11.27813	12.32065	6.126408
C	12.1975	14.26867	-1.59099	C	11.84133	14.67742	5.367171
C	12.40806	15.50303	-2.20641	H	9.194459	6.7076	0.355932
C	11.38413	16.45105	-2.24341	H	10.49378	6.939452	-1.74538
C	10.14298	16.15217	-1.67372	H	11.35085	9.175189	-2.45286
C	9.928776	14.91811	-1.06474	H	9.492643	14.64969	7.024932
C	10.52327	14.75234	1.938746	H	7.092173	15.23473	6.988964

H	5.720702	14.76012	4.989235	H	11.68141	15.06311	6.38125
H	8.690938	15.78466	2.41821	H	12.9055	14.43078	5.27257
H	9.766093	17.99142	2.672576	H	12.21871	18.23473	2.325327
H	13.58595	16.23702	1.743004	C	7.971077	10.69164	5.462355
H	12.51011	14.02384	1.51449	H	8.434628	9.849815	6.019377
H	8.960407	14.69049	-0.62919	H	8.513717	11.59426	5.732128
H	9.338418	16.8817	-1.70559	C	6.497827	10.81915	5.85428
H	11.54995	17.41654	-2.71346	H	6.436625	10.98861	6.943147
H	13.37619	15.72662	-2.6464	H	6.070657	11.71442	5.39207
H	13.00031	13.5382	-1.54277	C	5.63959	9.598457	5.500374
H	11.38482	11.60632	-2.12318	H	6.056925	8.681585	5.939497
H	7.137807	13.26628	1.828398	H	4.61166	9.70434	5.869697
H	5.879057	11.57526	3.087111	H	5.583438	9.450582	4.413122
H	4.723329	12.80533	3.648305	Pd	8.313924	9.91769	3.597776
H	4.822764	12.39939	1.925001				
H	5.090873	15.30929	2.849879	<i>aImPy-Pd (6a) int 3'</i>			
H	6.567846	15.71722	1.964093	0 1			
H	5.303442	14.74934	1.186836	C	1.454425	-3.88827	0.407851
H	11.27014	13.03976	4.117656	C	2.774102	-3.68074	0.1541
H	10.9647	12.61817	7.134464	C	3.36156	-2.40117	-0.15094
H	10.76093	11.3916	5.868419	C	2.514246	-1.25682	-0.13153
H	12.35477	12.11311	6.156845	C	0.072248	-0.56076	0.106174
H	11.6131	15.47934	4.658529	C	-0.76716	-2.6756	0.387839

H	3.436429	-4.53478	0.256705	H	-1.62292	-0.65294	-4.09216
C	4.737659	-2.27585	-0.39874	H	-2.94467	0.367823	-3.49186
C	3.059835	0.052692	-0.36172	H	-1.34761	0.433612	-2.7163
C	4.451452	0.121596	-0.61824	C	-3.45639	-2.35498	-2.89772
H	4.868147	1.107962	-0.79978	H	-3.7508	-3.15275	-2.20756
C	5.265658	-1.00921	-0.63315	H	-4.36674	-1.86141	-3.25773
H	6.32893	-0.89355	-0.83026	H	-2.96951	-2.81772	-3.76456
H	5.369444	-3.15966	-0.40131	C	-2.06825	-0.12536	2.737388
O	2.405303	1.193055	-0.35274	H	-1.21211	-0.79831	2.632081
N	-1.05163	-1.34392	0.298934	C	-1.50991	1.289738	2.979882
C	-2.37529	-0.77109	0.270918	H	-0.92254	1.320527	3.905394
C	-3.08115	-0.77145	-0.94595	H	-0.84919	1.596888	2.157144
C	-2.86973	-0.16634	1.441647	H	-2.31929	2.025217	3.06289
C	-4.33854	-0.15537	-0.96166	C	-2.88923	-0.601	3.949259
C	-4.12931	0.441653	1.369912	H	-2.25229	-0.64514	4.84038
C	-4.85948	0.443671	0.183215	H	-3.71804	0.080886	4.171723
H	-4.90935	-0.1346	-1.88507	H	-3.31415	-1.59855	3.787021
H	-4.53921	0.923367	2.252545	C	0.746788	3.496516	-0.41329
H	-5.83533	0.920841	0.148652	H	1.0999	3.64109	-1.44436
Pd	0.374185	1.488505	-0.15258	H	-0.27175	3.92329	-0.31604
C	-2.49643	-1.36062	-2.22324	C	1.717339	4.092697	0.591133
H	-1.58934	-1.91283	-1.96451	H	1.329797	3.960665	1.612449
C	-2.0794	-0.23373	-3.18727	H	2.657552	3.52844	0.535401

N	-0.61073	-1.34571	0.292182	C	-1.59564	0.847315	3.28963
C	-2.04005	-1.19466	0.403884	H	-0.98606	0.95506	4.195094
C	-2.82972	-1.39672	-0.73931	H	-1.12718	1.432159	2.492922
C	-2.57082	-0.82423	1.653165	H	-2.58578	1.271559	3.497145
C	-4.20804	-1.18495	-0.61179	C	-2.20413	-1.4778	4.081429
C	-3.95438	-0.62228	1.724864	H	-1.50956	-1.38775	4.925
C	-4.76473	-0.79471	0.604039	H	-3.18816	-1.14224	4.42888
H	-4.84995	-1.32266	-1.47681	H	-2.28634	-2.54055	3.826428
H	-4.40104	-0.32237	2.668254	C	-0.62632	-3.85271	0.302991
H	-5.83605	-0.62821	0.680309	C	-0.22701	-4.75322	-0.70074
Pd	-0.02349	1.636934	-0.30163	C	-1.6858	-4.20581	1.152614
C	-2.23607	-1.82509	-2.07569	C	-0.86217	-5.98473	-0.83598
H	-1.17936	-2.05936	-1.92217	H	0.578903	-4.48168	-1.37453
C	-2.29641	-0.68331	-3.10613	C	-2.32664	-5.43462	1.005676
H	-1.8855	-1.01695	-4.06692	H	-2.0041	-3.52053	1.927962
H	-3.32866	-0.35391	-3.27739	C	-1.91442	-6.33016	0.016248
H	-1.71121	0.17715	-2.76645	H	-0.53901	-6.67176	-1.61276
C	-2.91096	-3.10218	-2.6075	H	-3.14421	-5.69437	1.672225
H	-2.88193	-3.90594	-1.86458	H	-2.41103	-7.29036	-0.0921
H	-3.9589	-2.92482	-2.87714	C	2.329411	-4.4858	0.998928
H	-2.394	-3.45247	-3.50885	C	2.937813	-5.5783	0.36302
C	-1.7006	-0.63694	2.893499	C	1.639176	-4.6993	2.203221
H	-0.68831	-0.9777	2.655887	C	2.8484	-6.85805	0.911638

H	3.465263	-5.42099	-0.5737	C	3.910539	-2.6142	0.09656
C	1.545784	-5.97851	2.745988	C	4.12319	-1.19532	0.225479
H	1.17366	-3.86053	2.711985	C	2.988762	-0.34123	0.126658
C	2.146336	-7.06345	2.100599	C	0.448979	-0.37481	-0.09368
H	3.318228	-7.6954	0.402734	C	0.224908	-2.65537	-0.09458
H	1.004491	-6.12855	3.676068	H	4.782009	-3.26096	0.062249
H	2.067018	-8.06137	2.523032	C	5.41192	-0.66271	0.388075
C	1.526931	-0.88377	0.034061	C	3.13769	1.089402	0.198028
N	1.363046	-2.26809	0.28099	C	4.461819	1.570654	0.364713
C	-1.7619	3.39456	-0.61296	H	4.587848	2.648213	0.421605
H	-2.08741	4.069427	0.18825	C	5.56221	0.720787	0.456267
H	-0.63467	3.580965	-0.6323	H	6.553668	1.149906	0.583556
C	-2.2876	3.848688	-1.97853	H	6.268734	-1.32743	0.454405
H	-1.97392	4.871709	-2.21733	O	2.171591	1.966929	0.127763
H	-1.91978	3.186353	-2.77044	N	-0.41783	-1.45353	-0.15485
H	-3.38337	3.814539	-1.99167	C	-1.84761	-1.26876	-0.18027
C	-2.03548	1.941154	-0.2695	C	-2.47196	-1.04852	-1.42231
H	-2.50254	1.780444	0.702022	C	-2.53797	-1.21785	1.042741
H	-2.58377	1.398106	-1.04113	C	-3.84454	-0.77126	-1.41232
				C	-3.91088	-0.94439	0.996907
				C	-4.55833	-0.72011	-0.21586
<i>aImPy-Pd (6a) int 4'</i>				H	-4.35851	-0.58793	-2.35095
0 1				H	-4.47432	-0.8957	1.923956
C	2.696334	-3.20557	-0.06578				

H	-5.62313	-0.50247	-0.22959	H	-0.79773	-1.68656	2.189276
Pd	0.12398	1.652435	0.043917	C	-1.81047	-0.08787	3.173355
C	-0.52411	3.637838	0.22542	H	-1.2827	-0.22425	4.125079
H	-0.21227	4.244283	-0.62675	H	-1.29264	0.694777	2.607234
H	-0.23687	4.054309	1.191277	H	-2.82518	0.263603	3.397895
C	-1.82941	2.963927	0.129427	C	-2.47182	-2.54552	3.201488
H	-2.40304	2.970914	1.062306	H	-1.90358	-2.70569	4.125688
C	-2.7	3.249941	-1.09488	H	-3.50485	-2.31223	3.48585
H	-2.10254	3.210701	-2.01105	H	-2.47793	-3.48524	2.63906
H	-3.51754	2.526619	-1.18655	C	-0.44132	-3.94019	0.141578
H	-3.13294	4.253433	-1.01042	C	-1.47667	-4.38027	-0.69774
H	-1.64839	1.747882	0.050143	C	-0.08752	-4.71873	1.257703
C	-1.69581	-1.06489	-2.7348	C	-2.14032	-5.57609	-0.42962
H	-0.71106	-1.50135	-2.54081	H	-1.75187	-3.78976	-1.56373
C	-1.46621	0.369309	-3.24861	C	-0.74594	-5.91857	1.515192
H	-0.89454	0.353331	-4.18467	H	0.702379	-4.37939	1.919603
H	-2.42146	0.87221	-3.4426	C	-1.77485	-6.3508	0.673605
H	-0.90531	0.961188	-2.51754	H	-2.93839	-5.90575	-1.08899
C	-2.37954	-1.92463	-3.81265	H	-0.45858	-6.51336	2.377543
H	-2.5812	-2.94222	-3.45817	H	-2.28886	-7.28601	0.87768
H	-3.33289	-1.49078	-4.13573	C	2.569097	-4.65428	-0.34926
H	-1.7365	-1.99568	-4.69766	C	1.887952	-5.11831	-1.48623
C	-1.83737	-1.40857	2.3816	C	3.187304	-5.58569	0.498385

C	1.813191	-6.48259	-1.75641	H	4.95857	2.166345	-0.5263
H	1.415027	-4.407	-2.15632	C	5.609833	0.144566	-0.92225
C	3.116623	-6.95184	0.222957	H	6.645261	0.433148	-1.08837
H	3.708391	-5.23275	1.383983	H	5.969706	-1.96769	-1.23865
C	2.423721	-7.40465	-0.90111	O	2.508314	1.802872	-0.06705
H	1.278203	-6.82687	-2.6372	N	-0.60159	-1.2278	-0.07567
H	3.593964	-7.66152	0.893347	C	-1.98618	-0.94875	0.217419
H	2.359413	-8.46877	-1.11142	C	-2.90334	-0.80567	-0.83951
C	1.705173	-0.95353	-0.01798	C	-2.35125	-0.8194	1.573996
N	1.558621	-2.36151	-0.04551	C	-4.21159	-0.42994	-0.50542

aImPy-Pd (6a) int 5

0 1				H	-4.9438	-0.29726	-1.2963
C	2.224457	-3.35068	-0.56281	H	-3.98476	-0.30952	2.88047
C	3.49403	-2.92629	-0.79148	H	-5.60322	0.076607	1.054782
C	3.897562	-1.54679	-0.80169	Pd	0.456383	1.898373	0.091469
C	2.917119	-0.55821	-0.4977	C	-1.53766	2.554795	0.825369
C	0.389177	-0.24778	-0.09473	H	-1.42108	3.527891	1.294181
C	-0.12326	-2.48443	-0.30149	H	-1.89333	1.754476	1.461003
H	4.263766	-3.68637	-0.88149	C	-1.61699	2.431885	-0.55105
C	5.239392	-1.19489	-1.01576	H	-2.0037	1.497881	-0.93752
C	3.304591	0.817574	-0.37707	C	-1.59917	3.577901	-1.52495
C	4.670389	1.122359	-0.60882	H	-2.62338	3.760454	-1.88362

H	-1.21841	4.49499	-1.06695	C	-0.94642	-3.66081	-0.60849
H	-0.98323	3.350229	-2.40181	C	-0.73375	-4.359	-1.81034
H	0.704606	3.466019	0.209665	C	-1.9747	-4.07893	0.249881
C	-2.54444	-1.09682	-2.29495	C	-1.52031	-5.46127	-2.1335
H	-1.50036	-1.41769	-2.33316	H	0.048579	-4.03333	-2.48785
C	-2.67313	0.135795	-3.20819	C	-2.76791	-5.17569	-0.08339
H	-2.49482	-0.15242	-4.25098	H	-2.14586	-3.5509	1.179568
H	-3.67483	0.578351	-3.15155	C	-2.5399	-5.87377	-1.27145
H	-1.94238	0.907794	-2.95035	H	-1.3402	-5.99469	-3.06237
C	-3.40752	-2.25728	-2.82909	H	-3.55826	-5.4899	0.592503
H	-3.05681	-2.56381	-3.82161	H	-3.15421	-6.73303	-1.52571
H	-3.36262	-3.12745	-2.1685	C	1.922188	-4.78434	-0.33905
H	-4.45811	-1.95767	-2.92598	C	2.355195	-5.74146	-1.26872
C	-1.37883	-1.12372	2.714311	C	1.273388	-5.21727	0.828721
H	-0.51445	-1.64228	2.28847	C	2.135573	-7.10068	-1.04231
C	-0.84807	0.148613	3.399423	H	2.850752	-5.4117	-2.17761
H	-0.27068	0.764704	2.704778	C	1.049064	-6.57384	1.049992
H	-1.67093	0.752834	3.801763	H	0.944108	-4.48777	1.562368
H	-0.19134	-0.12152	4.235212	C	1.476156	-7.52068	0.114228
C	-2.00731	-2.06482	3.759947	H	2.471301	-7.82929	-1.77532
H	-1.24415	-2.38135	4.480327	H	0.541881	-6.89316	1.956301
H	-2.80412	-1.56875	4.325994	H	1.296075	-8.57814	0.287488
H	-2.43541	-2.96451	3.303331	N	1.226612	-2.3544	-0.42128

C	1.556359	-0.9769	-0.32358	C	4.042917	-0.65615	1.529643
				C	4.263609	-0.36109	-0.85761
<i>α</i>ImPy-Pd (6a) int 5'				C	4.824229	-0.35012	0.417227
O 1				H	4.486585	-0.62923	2.520759
C	-2.00726	-3.52827	-0.60843	H	4.877417	-0.10639	-1.7165
C	-3.30647	-3.14168	-0.70326	H	5.872804	-0.09441	0.545862
C	-3.76565	-1.7847	-0.56777	Pd	-0.29231	1.538431	0.399203
C	-2.80558	-0.7814	-0.25042	C	-0.32738	3.621274	1.389616
C	-0.27448	-0.42586	0.055415	H	0.616015	3.747528	1.915851
C	0.323425	-2.58067	-0.40597	H	-1.21856	3.497059	1.999251
H	-4.04917	-3.92526	-0.81713	C	-0.42432	3.850665	0.043993
C	-5.12826	-1.46868	-0.67913	H	-1.41784	3.859125	-0.40216
C	-3.22084	0.582671	-0.03349	C	0.706959	4.312923	-0.83218
C	-4.61135	0.844438	-0.16486	H	1.677065	4.180694	-0.34328
H	-4.93185	1.870683	-0.00771	H	0.720781	3.768702	-1.78301
C	-5.53329	-0.14959	-0.4778	H	0.578786	5.379007	-1.07075
H	-6.58644	0.109361	-0.56337	H	1.260328	1.527798	0.491499
H	-5.84657	-2.24925	-0.91339	C	1.845145	-1.27739	2.629762
O	-2.41732	1.557837	0.262033	H	0.842873	-1.56892	2.303238
N	0.765114	-1.33658	-0.07517	C	2.306543	-0.6416	-2.44496
C	2.159703	-1.00287	0.089993	H	1.287149	-1.03285	-2.38846
C	2.689787	-0.9879	1.393025	C	2.203599	0.814379	-2.93588
C	2.915116	-0.68495	-1.04985	H	1.723276	0.852757	-3.92149

C	1.146227	2.57519	-0.32675	H	-2.57727	-3.02405	1.026787
H	-2.65724	5.080951	-0.84519	H	-1.19194	-4.07013	0.60821
C	-4.37045	3.02121	-0.85979	C	-2.44122	-3.52407	-1.0843
C	-3.14548	0.516535	-0.21249	C	0.965167	-2.52142	1.077909
C	-4.54366	0.650511	-0.40693	H	0.616551	-3.54679	-0.79242
H	-5.14026	-0.2501	-0.29312	H	1.688721	-2.05445	-0.8762
C	-5.1393	1.868375	-0.72257	H	-3.01714	-2.64953	-1.40895
H	-6.21735	1.916402	-0.85876	H	-1.65846	-3.68926	-1.84032
H	-4.82754	3.979335	-1.09089	C	-3.36494	-4.7533	-1.0491
O	-2.68241	-0.66219	0.097227	H	1.611352	-1.80511	1.56652
N	1.212959	1.242228	-0.04882	H	0.527303	-3.28315	1.716816
C	2.45298	0.544438	0.180904	H	-4.18384	-4.60442	-0.33361
C	3.172553	0.043975	-0.91826	H	-3.81087	-4.95109	-2.03324
C	2.880427	0.388754	1.516075	H	-2.81719	-5.65428	-0.74218
C	4.314243	-0.7207	-0.64085	C	2.801308	0.367914	-2.36349
C	4.026834	-0.38443	1.735502	H	1.921583	1.016316	-2.35322
C	4.724839	-0.95114	0.669326	C	2.434591	-0.87516	-3.19346
H	4.890157	-1.13385	-1.46377	H	2.274159	-0.59072	-4.24024
H	4.380711	-0.54293	2.749419	H	3.232937	-1.62667	-3.17143
H	5.607313	-1.5555	0.86172	H	1.512228	-1.34045	-2.83279
Pd	-0.74806	-1.42356	0.205967	C	3.947878	1.150744	-3.03448
C	-1.80883	-3.22582	0.270283	H	4.249217	2.014058	-2.43391
C	1.008323	-2.66309	-0.29671	H	4.828846	0.514138	-3.1816

H	3.632051	1.513761	-4.01974	C	-0.21512	6.398348	-1.40692
C	2.15292	1.059281	2.682194	C	0.741337	5.656114	0.685186
H	1.52522	1.854681	2.267725	C	0.436178	7.624644	-1.26987
C	1.214887	0.094495	3.431632	H	-0.83093	6.20158	-2.28012
H	0.738646	0.612542	4.272945	C	1.396021	6.87833	0.817377
H	0.424089	-0.28228	2.777175	H	0.855141	4.895797	1.45181
H	1.771523	-0.76026	3.835815	C	1.249155	7.866067	-0.16106
C	3.132644	1.721419	3.668345	H	0.316275	8.386077	-2.0359
H	2.57703	2.327906	4.392887	H	2.020517	7.061473	1.687455
H	3.702987	0.97818	4.237279	H	1.764725	8.816933	-0.05774
H	3.851167	2.375241	3.160432	N	-0.17983	2.872014	-0.40532
C	2.282207	3.410215	-0.73617	C	-0.92085	1.672177	-0.23431
C	2.238768	4.073723	-1.97523				
C	3.434245	3.522193	0.057197				
C	3.318034	4.843394	-2.40048	<i>aImPy-Pd (6a) int 1</i>			
H	1.357416	3.980612	-2.60114	0 1			
C	4.517856	4.28314	-0.37857	C	-2.30467	3.576342	0.082299
H	3.476363	3.023857	1.017641	C	-3.5629	3.208398	-0.2689
C	4.461861	4.949735	-1.60461	C	-3.95541	1.85874	-0.56592
H	3.268186	5.354805	-3.35745	C	-2.97321	0.833205	-0.45177
H	5.40246	4.362494	0.247101	C	-0.41517	0.480141	-0.17719
H	5.304729	5.548202	-1.939	C	0.048285	2.701966	0.178933
C	-0.0657	5.3981	-0.43444	H	-4.33786	3.966011	-0.20669
				C	-5.29846	1.552632	-0.83731

C	-3.37097	-0.54693	-0.53698	H	1.941354	-3.8559	-0.2262
C	-4.74088	-0.80286	-0.81602	C	3.850855	-2.92013	-0.56438
H	-5.03608	-1.84568	-0.89438	H	4.345667	-1.95326	-0.41565
C	-5.67363	0.217036	-0.97096	H	4.417039	-3.67955	-0.0082
H	-6.71054	-0.03445	-1.18328	H	3.918053	-3.16724	-1.63208
H	-6.02798	2.353772	-0.91544	H	-1.75913	-3.64112	0.625983
O	-2.56249	-1.54246	-0.36102	C	-0.81577	-3.77996	0.106737
N	0.559689	1.443121	0.091438	H	0.026613	-4.12155	0.700041
C	1.947959	1.168002	0.383154	C	-0.76215	-3.72079	-1.25698
C	2.929135	1.433615	-0.58927	H	-1.66237	-3.54509	-1.83878
C	2.251102	0.645459	1.655464	H	0.130112	-4.01129	-1.80477
C	4.25621	1.13094	-0.26082	C	2.602523	1.998641	-1.96708
C	3.591967	0.343649	1.92255	H	1.544319	2.271995	-1.9867
C	4.585913	0.582794	0.976199	C	2.820169	0.947162	-3.07114
H	5.038397	1.312871	-0.99138	H	3.858698	0.594743	-3.08378
H	3.860199	-0.07769	2.886884	H	2.17087	0.078895	-2.92861
H	5.621072	0.34331	1.204639	H	2.599649	1.381742	-4.05388
Pd	-0.41681	-1.56308	-0.45117	C	3.417208	3.272521	-2.25719
C	1.594973	-1.80447	-0.8795	H	3.070655	3.736928	-3.18798
H	2.107879	-0.853	-0.8002	H	3.316971	4.005647	-1.45202
H	1.564459	-2.07008	-1.94814	H	4.483049	3.045772	-2.38023
C	2.38517	-2.85925	-0.10417	C	1.194013	0.425368	2.734966
H	2.360263	-2.63485	0.969353	H	0.239047	0.811104	2.368344

C	0.98763	-1.07103	3.026518	H	-2.91453	5.950701	-1.02981
H	0.229842	-1.20382	3.808496	C	-1.24658	6.345697	2.445254
H	0.643965	-1.59152	2.126924	H	-1.11321	4.198585	2.457367
H	1.915785	-1.54248	3.372008	C	-1.66303	7.480066	1.742118
C	1.535479	1.19169	4.026782	H	-2.60151	8.210652	-0.05816
H	2.455418	0.817264	4.490511	H	-0.77649	6.449856	3.419269
H	1.667367	2.264599	3.843055	H	-1.51225	8.469603	2.164865
H	0.726081	1.074036	4.757083	N	-1.29732	2.580303	0.016808
C	0.843705	3.93803	0.20325	C	-1.60702	1.214025	-0.21645
C	0.648133	4.903296	-0.79954				
C	1.823059	4.16155	1.183117				
C	1.400609	6.074823	-0.80686	<i>aImPy-Pd (6a) int 2</i>			
H	-0.09466	4.730881	-1.57137	0 1			
C	2.582253	5.330231	1.165347	C	2.466282	-3.0818	0.388379
H	1.98705	3.422694	1.958179	C	3.678722	-2.54228	0.096987
C	2.369678	6.292884	0.175863	C	3.894502	-1.15955	-0.23568
H	1.233457	6.814498	-1.58446	C	2.77513	-0.27977	-0.19725
H	3.334921	5.49081	1.932064	C	0.213738	-0.26398	0.116339
H	2.95746	7.206561	0.168314	C	0.009343	-2.52347	0.403901
C	-2.03357	4.921302	0.643869	H	4.546096	-3.18687	0.200629
C	-2.45691	6.063996	-0.05098	C	5.181708	-0.67608	-0.51703
C	-1.43373	5.076086	1.904038	C	2.948994	1.130815	-0.43884
C	-2.2748	7.334674	0.495801	C	4.27209	1.563242	-0.72299
				H	4.410615	2.62425	-0.91167

C	5.351855	0.686126	-0.76165	H	-4.02366	-2.86157	-2.81916
H	6.344025	1.073424	-0.98335	H	-2.46319	-3.35577	-3.48769
H	6.024416	-1.3615	-0.53365	C	-1.70217	-0.68783	2.97321
O	1.983368	1.995552	-0.41316	H	-0.69092	-1.01474	2.712897
N	-0.64539	-1.33025	0.342743	C	-1.60319	0.78805	3.400768
C	-2.07426	-1.195	0.477923	H	-0.983	0.880274	4.300758
C	-2.87843	-1.37864	-0.65817	H	-1.14908	1.394115	2.611633
C	-2.5895	-0.85543	1.742312	H	-2.59371	1.199933	3.630211
C	-4.25674	-1.18368	-0.50563	C	-2.18071	-1.55877	4.149818
C	-3.97356	-0.66751	1.838429	H	-1.47369	-1.48185	4.984288
C	-4.79881	-0.82476	0.72633	H	-3.16156	-1.23848	4.519819
H	-4.91025	-1.308	-1.36392	H	-2.25893	-2.61628	3.872758
H	-4.40921	-0.39133	2.79419	C	-0.63801	-3.8364	0.292477
H	-5.87039	-0.6703	0.82185	C	-0.24683	-4.70884	-0.73885
Pd	-0.09859	1.670815	-0.1891	C	-1.68129	-4.21943	1.149315
C	-2.30021	-1.76583	-2.01386	C	-0.8734	-5.94237	-0.89436
H	-1.23879	-1.99241	-1.88256	H	0.54604	-4.41393	-1.41823
C	-2.38752	-0.5974	-3.01221	C	-2.31386	-5.44995	0.982158
H	-1.9885	-0.90109	-3.98785	H	-1.99416	-3.55599	1.945771
H	-3.42531	-0.27352	-3.15848	C	-1.90953	-6.31757	-0.03501
H	-1.80501	0.259253	-2.65846	H	-0.55652	-6.60733	-1.69263
C	-2.97007	-3.03517	-2.56974	H	-3.11897	-5.73289	1.654406
H	-2.92171	-3.85815	-1.84921	H	-2.39966	-7.27919	-0.15914

C	2.337373	-4.46031	0.916368	H	-0.78057	5.279226	-2.27552
C	2.945665	-5.52626	0.236781	H	-2.21248	5.971894	-1.5226
C	1.671291	-4.7181	2.125635	C	-2.39986	5.665613	-3.65674
C	2.880685	-6.82286	0.747839	H	-3.49726	5.670837	-3.68128
H	3.454261	-5.33473	-0.70398	H	-2.05542	6.67091	-3.92734
C	1.602181	-6.01406	2.631038	H	-2.05451	4.973692	-4.43551
H	1.205686	-3.90085	2.668094				
C	2.203197	-7.07203	1.942706	<i>α</i>ImPy-Pd (6a) TS (1'-2)			
H	3.350469	-7.63896	0.205471	0	1		
H	1.079432	-6.19833	3.565576	C	-0.82424	4.108623	-0.61299
H	2.143039	-8.08297	2.336371	C	-2.1627	4.086296	-0.84171
C	1.483294	-0.84045	0.065152	C	-2.96598	2.894491	-0.82042
N	1.336759	-2.2324	0.278666	C	-2.33176	1.666649	-0.47861
C	-1.84345	3.405378	-0.48788	C	-0.01207	0.616639	-0.02424
H	-2.18363	4.094737	0.295915	C	1.148713	2.583553	-0.29884
H	-0.71438	3.599442	-0.48712	H	-2.66197	5.041923	-0.96846
C	-2.33953	3.842926	-1.87232	C	-4.34989	2.953037	-1.05259
H	-1.99326	3.11196	-2.61588	C	-3.11017	0.466979	-0.3468
H	-3.43776	3.795824	-1.87586	C	-4.50264	0.577044	-0.60028
C	-2.11306	1.956645	-0.12994	H	-5.08999	-0.33244	-0.50901
H	-2.56214	1.801171	0.85112	C	-5.10253	1.785296	-0.9442
H	-2.67214	1.407174	-0.88859	H	-6.17479	1.815409	-1.12548
C	-1.8797	5.246486	-2.27899	H	-4.81461	3.902216	-1.30429

O	-2.61593	-0.68505	-0.01301	H	0.255453	-3.84187	1.509812
N	1.228315	1.250887	-0.0268	H	0.374576	-4.17166	-0.28487
C	2.485477	0.580033	0.187539	H	-4.29122	-3.8579	-0.90987
C	3.198951	0.1165	-0.93026	H	-3.72979	-4.48433	-2.4713
C	2.929187	0.405373	1.511959	H	-3.32602	-5.34429	-0.97239
C	4.381274	-0.59369	-0.68607	C	2.728953	0.362371	-2.36005
C	4.116726	-0.31181	1.699933	H	1.883727	1.05456	-2.32854
C	4.830299	-0.81552	0.613438	C	2.222997	-0.93172	-3.02327
H	4.953922	-0.98032	-1.52392	H	1.933298	-0.73574	-4.0629
H	4.485574	-0.48196	2.706748	H	3.00058	-1.70563	-3.03113
H	5.746456	-1.37567	0.781265	H	1.346807	-1.32519	-2.4978
Pd	-0.59695	-1.35355	0.173139	C	3.830886	1.027569	-3.20451
C	-1.77581	-3.32324	0.169738	H	4.213428	1.931673	-2.72001
C	1.259485	-2.31046	0.3712	H	4.674634	0.348596	-3.37592
H	-2.50959	-2.74113	0.73199	H	3.432426	1.310212	-4.18626
H	-1.65776	-4.28527	0.669243	C	2.152902	0.950165	2.708886
C	-2.17085	-3.50811	-1.28761	H	1.426584	1.679381	2.33544
C	0.406331	-3.43533	0.513291	C	1.356199	-0.16063	3.41929
H	1.832683	-2.21118	-0.54516	H	0.823467	0.250971	4.285344
H	1.766485	-1.93886	1.254996	H	0.61726	-0.60869	2.748683
H	-2.33823	-2.53208	-1.75386	H	2.025712	-0.9518	3.7799
H	-1.35885	-4.00049	-1.84205	C	3.063519	1.680015	3.713181
C	-3.45229	-4.34878	-1.41798	H	2.453435	2.164244	4.484558

C	-2.46499	-1.0523	-1.41949	H	-2.40281	0.846327	-3.46679
C	-2.54917	-1.20375	1.046025	H	-0.90157	0.95024	-2.52007
C	-3.83995	-0.78739	-1.4222	C	-2.35378	-1.9502	-3.80198
C	-3.92432	-0.94449	0.987491	H	-2.55907	-2.96452	-3.44044
C	-4.56364	-0.7332	-0.23172	H	-3.30397	-1.51942	-4.13833
H	-4.34873	-0.61818	-2.36629	H	-1.70255	-2.02951	-4.68029
H	-4.49588	-0.89776	1.909725	C	-1.85998	-1.38896	2.391368
H	-5.63034	-0.52579	-0.25564	H	-0.81262	-1.64372	2.208944
Pd	0.124636	1.649621	0.05587	C	-1.86903	-0.07574	3.195357
C	-0.46587	3.721682	0.228772	H	-1.34762	-0.21043	4.150881
H	-0.06921	4.256922	-0.633	H	-1.36296	0.721931	2.640287
H	-0.11645	4.060975	1.201788	H	-2.89308	0.251655	3.41403
C	-1.72484	3.071205	0.121197	C	-2.48152	-2.5462	3.192895
H	-2.29643	2.961498	1.044465	H	-1.92138	-2.70485	4.122339
C	-2.58061	3.221869	-1.12475	H	-3.52221	-2.33494	3.466559
H	-1.96088	3.251121	-2.02553	H	-2.46321	-3.48019	2.62134
H	-3.30116	2.40439	-1.2261	C	-0.44012	-3.91593	0.165323
H	-3.1381	4.165172	-1.05966	C	-1.4831	-4.36195	-0.66099
H	-1.49758	1.570945	0.042538	C	-0.07075	-4.69054	1.27915
C	-1.67989	-1.07926	-2.72681	C	-2.13983	-5.55901	-0.38195
H	-0.69566	-1.51208	-2.52184	H	-1.77026	-3.77533	-1.52531
C	-1.44831	0.349596	-3.25364	C	-0.72234	-5.8917	1.547601
H	-0.86411	0.324472	-4.18179	H	0.725654	-4.34662	1.930935

C	-1.75953	-6.32946	0.71921	C	-2.34316	1.691586	-0.26044
H	-2.94417	-5.89298	-1.03146	C	-0.02749	0.667196	0.190388
H	-0.4232	-6.48308	2.408281	C	1.149081	2.609353	-0.18693
H	-2.26826	-7.26566	0.931743	H	-2.67691	5.05384	-0.85106
C	2.551244	-4.63888	-0.37251	C	-4.37037	2.979075	-0.81636
C	1.859982	-5.08383	-1.51102	C	-3.12685	0.494906	-0.09832
C	3.171637	-5.58498	0.457046	C	-4.52226	0.613334	-0.32473
C	1.777605	-6.44376	-1.8002	H	-5.11279	-0.29115	-0.20969
H	1.385657	-4.361	-2.16772	C	-5.12669	1.819872	-0.66815
C	3.093567	-6.94668	0.162431	H	-6.20294	1.85116	-0.82269
H	3.700415	-5.24695	1.343885	H	-4.8344	3.925954	-1.07794
C	2.390673	-7.38054	-0.96289	O	-2.67487	-0.68068	0.251464
H	1.234926	-6.77312	-2.682	N	1.214115	1.28791	0.147751
H	3.57294	-7.66782	0.818996	C	2.438578	0.570462	0.392919
H	2.320585	-8.44124	-1.18811	C	3.060929	-0.08583	-0.68022
C	1.713023	-0.93546	-0.00265	C	2.937625	0.535498	1.71084
N	1.558096	-2.34216	-0.03735	C	4.187171	-0.86853	-0.39021
<i>aImPy-Pd (6a) TS (1'-4')</i>				C	4.072088	-0.25001	1.944593
0 1				C	4.679333	-0.96112	0.908455
C	-0.8282	4.13352	-0.52107	H	4.687543	-1.39917	-1.19517
C	-2.17442	4.103098	-0.70217	H	4.486158	-0.31246	2.945589
C	-2.9816	2.915055	-0.61709	H	5.552362	-1.57467	1.114871
				Pd	-0.7055	-1.34003	0.214691

C	-1.40641	-3.23348	-0.16585	H	4.041301	1.670745	-2.53713
C	1.392982	-2.83171	2.279703	H	4.562659	0.063532	-3.07784
H	-2.17557	-3.14218	-0.93844	H	3.319192	0.940107	-3.98358
H	-1.81952	-3.68713	0.738766	C	2.270985	1.327065	2.833989
C	-0.08315	-3.78437	-0.64112	H	1.758973	2.179209	2.373465
C	0.151978	-2.84885	2.77539	C	1.192551	0.497029	3.554728
H	1.825876	-3.70631	1.799831	H	0.689211	1.108318	4.313778
H	2.022625	-1.95007	2.325947	H	0.438774	0.139914	2.847914
H	0.706181	-2.99148	-0.48948	H	1.6367	-0.36913	4.059386
H	0.269912	-4.60274	0.000683	C	3.278535	1.901049	3.843088
C	-0.0495	-4.18687	-2.119	H	2.766365	2.585459	4.529138
H	-0.28645	-1.98561	3.267963	H	3.738892	1.116369	4.454442
H	-0.46976	-3.73916	2.726632	H	4.083909	2.456493	3.34772
H	-0.39258	-3.36012	-2.75175	C	2.285586	3.411663	-0.65687
H	0.960552	-4.4654	-2.44323	C	2.232645	3.98899	-1.93865
H	-0.71317	-5.04113	-2.29846	C	3.449832	3.567374	0.111669
C	2.590108	0.084398	-2.11932	C	3.313393	4.715426	-2.4311
H	1.736691	0.767708	-2.12023	H	1.341992	3.861528	-2.54523
C	2.104714	-1.2396	-2.73007	C	4.534294	4.284929	-0.39082
H	1.804895	-1.09086	-3.77445	H	3.502834	3.138662	1.104748
H	2.887406	-2.00775	-2.71145	C	4.469174	4.864586	-1.65972
H	1.238361	-1.6192	-2.18211	H	3.255108	5.158767	-3.42109
C	3.696594	0.728587	-2.97581	H	5.428176	4.398301	0.216246

H	5.313488	5.428898	-2.04588	H	-2.75212	4.729891	-0.50909
C	-0.08347	5.412494	-0.44919	C	-4.27776	2.530754	-0.70566
C	-0.23553	6.364138	-1.46882	C	-2.81873	0.067638	-0.33202
C	0.728539	5.723921	0.653346	C	-4.23278	0.112067	-0.53071
C	0.417273	7.595059	-1.39406	H	-4.74613	-0.84568	-0.55339
H	-0.85409	6.125287	-2.32947	C	-4.93386	1.298262	-0.70712
C	1.384533	6.950523	0.723437	H	-6.01142	1.263894	-0.85615
H	0.845129	5.001708	1.455647	H	-4.82155	3.459349	-0.85524
C	1.234592	7.889512	-0.3014	O	-2.22036	-1.06545	-0.22181
H	0.295363	8.318266	-2.19599	N	1.443357	1.215794	0.084668
H	2.012675	7.175216	1.581111	C	2.733228	0.58741	0.22977
H	1.751778	8.843554	-0.24689	C	3.380595	0.117305	-0.92392
N	-0.18008	2.894654	-0.30085	C	3.27686	0.460751	1.523102
C	-0.91726	1.70013	-0.09774	C	4.638764	-0.47739	-0.76048

aImPy-Pd (6a) TS (1-1')

0 1				C	5.217243	-0.59298	0.500122
C	-0.82856	3.920963	-0.35677	H	5.166707	-0.85368	-1.63172
C	-2.17688	3.809427	-0.48326	H	4.998996	-0.24419	2.606363
C	-2.88877	2.558808	-0.51192	H	6.196331	-1.05249	0.607457
C	-2.15042	1.356635	-0.29526	Pd	-0.02804	-1.53274	0.404018
C	0.250094	0.508629	0.138463	C	1.422752	-3.1242	0.709014
C	1.268539	2.531057	-0.23352	C	0.196799	-3.73553	0.427809
				H	2.176272	-2.99196	-0.06628

H	1.811984	-3.09016	1.724263	C	-0.16303	5.231458	-0.17068
H	-0.40062	-4.18494	1.216065	C	-0.44266	6.288386	-1.04979
H	-0.03623	-4.07406	-0.58126	C	0.707718	5.459264	0.907573
C	2.753002	0.219475	-2.30815	C	0.140806	7.541695	-0.86133
H	1.825215	0.791349	-2.22536	H	-1.10468	6.11579	-1.89375
C	2.373229	-1.17561	-2.83666	C	1.29377	6.709251	1.090923
H	1.899141	-1.09563	-3.82225	H	0.923502	4.654522	1.60388
H	3.254827	-1.82051	-2.93618	C	1.015881	7.754679	0.205327
H	1.666211	-1.66983	-2.16016	H	-0.08023	8.347601	-1.55601
C	3.665778	0.968079	-3.29484	H	1.967546	6.868112	1.928485
H	3.931323	1.959222	-2.91356	H	1.478815	8.727456	0.346854
H	4.594099	0.416459	-3.48569	C	2.286735	3.400236	-0.83952
H	3.155092	1.097958	-4.25644	C	1.976642	4.065036	-2.04247
C	2.526208	0.943774	2.761447	C	3.586794	3.523874	-0.3204
H	1.459822	0.901792	2.529184	C	2.928136	4.849105	-2.68781
C	2.763017	0.045771	3.987064	H	0.989512	3.953226	-2.47763
H	2.04654	0.298709	4.776862	C	4.538809	4.302732	-0.97648
H	2.639692	-1.01418	3.742393	H	3.860612	3.01054	0.591133
H	3.768222	0.180133	4.404662	C	4.214451	4.974253	-2.15675
C	2.860726	2.40747	3.10886	H	2.665383	5.355253	-3.6124
H	2.334775	2.709267	4.022832	H	5.537626	4.386202	-0.55727
H	3.936652	2.536737	3.280391	H	4.958063	5.584663	-2.66146
H	2.558916	3.093259	2.311587	N	-0.08733	2.716919	-0.28359

C	-0.73226	1.46486	-0.12327	C	-0.2905	4.9249	-0.1409
C	-0.31996	-1.2314	2.420289	H	-0.23322	6.00771	-0.20571
H	0.581158	-1.58941	2.923223	C	0.949138	4.183455	-0.06102
H	-0.41833	-0.15527	2.564746	C	2.17143	4.873277	0.002966
C	-1.58075	-1.95961	2.854714	H	2.170808	5.95676	-0.0719
H	-2.41832	-1.65888	2.218242	C	3.355097	4.165882	0.192271
H	-1.46454	-3.0429	2.740554	H	4.302715	4.696865	0.242109
C	-1.8941	-1.63569	4.327587	C	3.334534	2.784656	0.338448
H	-1.06921	-1.93241	4.98811	H	4.248394	2.225044	0.515355
H	-2.06739	-0.56163	4.468478	C	2.133987	2.030587	0.283707
H	-2.79604	-2.16665	4.656011	C	0.931217	2.764081	0.028367

IzQO-Pd (F) int 3

0 1

C	-0.63276	0.775143	-0.13316	C	-4.41341	-2.71732	0.244046
N	-1.99905	0.715459	-0.09714	H	-5.03462	-3.60463	0.33304
C	-2.55456	1.977606	-0.03103	C	-3.65922	-2.28487	1.331103
H	-3.61903	2.131795	0.011703	H	-3.70185	-2.83524	2.266397
C	-1.52515	2.873607	-0.03436	C	-2.85241	-1.14326	1.2452
C	-1.48886	4.300482	-0.08605	C	-3.56964	-0.11255	-2.42784
H	-2.43066	4.838576	-0.10268	H	-2.67127	0.51321	-2.45301

C	-3.52332	-1.0446	-3.65275	H	-0.63337	-3.15371	-2.90701
H	-4.47296	-1.57367	-3.79511	H	-0.67328	-1.39843	-2.97459
H	-2.73151	-1.79305	-3.56692	C	1.31247	-2.23632	-3.05561
H	-3.34183	-0.45614	-4.5597	H	1.889203	-3.06923	-2.63106
C	-4.80042	0.811174	-2.53619	H	1.347091	-2.33024	-4.14815
H	-4.77941	1.366882	-3.48143	H	1.826823	-1.30321	-2.78843
H	-4.84751	1.538905	-1.72018	Pd	0.757405	-0.61818	-0.19118
H	-5.72561	0.222537	-2.51013				
C	-2.08308	-0.67254	2.474296	IzQO-Pd (F) int 3'			
H	-1.50222	0.212652	2.205627	0 1			
C	-3.04968	-0.26101	3.600433	C	0.64497	-2.82232	0.409846
H	-3.73832	0.523878	3.266035	C	1.544857	-3.92069	0.56468
H	-2.48814	0.123344	4.460345	C	2.87607	-3.69263	0.467112
H	-3.65123	-1.11021	3.946106	C	3.416651	-2.37073	0.221665
C	-1.08306	-1.73596	2.959389	C	2.541177	-1.25786	0.074661
H	-1.5917	-2.65046	3.287276	C	0.137051	-0.62864	0.028735
H	-0.50464	-1.35126	3.807792	C	-0.72002	-2.69988	0.431413
H	-0.38136	-2.00141	2.161029	H	1.136885	-4.90842	0.751566
O	2.178364	0.746292	0.487834	H	3.581702	-4.51143	0.576615
C	-0.24938	-2.19248	-1.01116	H	-1.49494	-3.43405	0.583379
H	0.364987	-2.99661	-0.55149	C	4.806094	-2.18917	0.13636
H	-1.27891	-2.34501	-0.68692	C	3.057072	0.05802	-0.14733
C	-0.13048	-2.24458	-2.53529	C	4.468111	0.170969	-0.23149

H	4.859512	1.168479	-0.40651	C	-3.23283	-2.07635	-3.23653
C	5.320253	-0.91732	-0.0919	H	-3.6392	-2.90671	-2.64749
H	6.394662	-0.76704	-0.16223	H	-4.07661	-1.50018	-3.63346
H	5.461229	-3.04784	0.250563	H	-2.69339	-2.49826	-4.09251
O	2.389645	1.188556	-0.27019	C	-2.10999	-0.25088	2.636077
N	1.15201	-1.52617	0.163824	H	-1.26519	-0.93935	2.542101
N	-0.99362	-1.36324	0.19835	C	-1.53498	1.144256	2.949568
C	-2.30054	-0.7631	0.129854	H	-0.97365	1.127275	3.891525
C	-2.94119	-0.68676	-1.12191	H	-0.85094	1.475614	2.156915
C	-2.85496	-0.2247	1.306924	H	-2.33535	1.888632	3.042771
C	-4.18921	-0.05259	-1.16975	C	-2.98849	-0.75929	3.792033
C	-4.10465	0.399322	1.203687	H	-2.39169	-0.84291	4.707793
C	-4.76626	0.482736	-0.01981	H	-3.82055	-0.07802	4.00423
H	-4.70905	0.032378	-2.1192	H	-3.40978	-1.7465	3.569287
H	-4.55885	0.83381	2.088969	C	0.630971	3.407758	-0.71984
H	-5.73399	0.97389	-0.07892	H	1.033732	3.508119	-1.73791
Pd	0.361424	1.407657	-0.34864	H	-0.41785	3.766962	-0.70812
C	-2.28483	-1.20445	-2.396	C	1.49928	4.132465	0.293292
H	-1.43358	-1.8305	-2.11277	H	1.057427	4.045346	1.296814
C	-1.73478	-0.02697	-3.22424	H	2.474033	3.628887	0.333829
H	-1.2338	-0.39251	-4.12872	C	1.706779	5.621405	-0.03413
H	-2.54178	0.649757	-3.531	H	2.346585	6.110697	0.71217
H	-1.00331	0.553695	-2.64667	H	2.182294	5.742747	-1.01589

H	0.750142	6.159399	-0.06037	N	-0.41632	-1.27373	0.249121
				C	-1.84705	-1.12451	0.240919
IzQO-Pd (F) int 4				C	-2.53819	-1.36152	-0.95984
0 1				C	-2.48732	-0.75754	1.437893
C	1.549858	-2.24427	0.474535	C	-3.92594	-1.173	-0.94908
C	2.678419	-3.09057	0.691825	C	-3.87582	-0.58098	1.393998
C	3.920466	-2.57564	0.549535	C	-4.58723	-0.77716	0.211796
C	4.128067	-1.19414	0.176281	H	-4.49203	-1.33392	-1.86204
C	3.015927	-0.33393	-0.05136	H	-4.40369	-0.28196	2.294909
C	0.485089	-0.2863	-0.02609	H	-5.66383	-0.62878	0.1974
C	0.203716	-2.46646	0.553299	Pd	0.203009	1.616289	-0.52162
H	2.501211	-4.12434	0.969222	C	-1.81223	1.932969	-0.52954
H	4.797696	-3.19532	0.712521	H	-2.30157	1.784462	0.432985
H	-0.35264	-3.35648	0.799363	H	-2.34337	1.390993	-1.31131
C	5.437223	-0.70558	0.035124	C	-1.49762	3.378345	-0.85378
C	3.214819	1.033564	-0.43274	H	-1.87605	3.66734	-1.84164
C	4.563719	1.462917	-0.55689	C	-1.89556	4.391253	0.22449
H	4.710964	2.500052	-0.84398	H	-1.47496	4.10484	1.194962
C	5.643809	0.621604	-0.3301	H	-1.54337	5.401183	-0.01514
H	6.655829	1.004213	-0.43983	H	-2.98662	4.423385	0.325166
H	6.272679	-1.37628	0.213549	H	-0.36676	3.506971	-0.99823
O	2.267744	1.889884	-0.6702	C	-1.83038	-1.80474	-2.23586
N	1.714777	-0.88778	0.11231	H	-0.77273	-1.95969	-2.00504

C	-1.90276	-0.724	-3.32939	C	4.000861	-2.5886	-0.1508
H	-1.40573	-1.07451	-4.24206	C	4.152786	-1.14956	-0.08472
H	-2.94163	-0.48142	-3.58448	C	3.002982	-0.31222	-0.03418
H	-1.40397	0.194679	-3.00468	C	0.513862	-0.36753	-0.00098
C	-2.38805	-3.14717	-2.74333	C	0.271403	-2.62946	-0.11093
H	-2.3247	-3.92231	-1.97051	H	2.664845	-4.26096	-0.21801
H	-3.43823	-3.06173	-3.04688	H	4.905665	-3.18894	-0.18812
H	-1.81736	-3.48848	-3.61515	H	-0.26602	-3.56329	-0.14985
C	-1.72366	-0.54471	2.740837	C	5.436912	-0.58181	-0.07318
H	-0.68328	-0.84216	2.581663	C	3.127525	1.114323	0.025914
C	-1.71165	0.938347	3.153811	C	4.454333	1.620137	0.034746
H	-1.17857	1.063171	4.104148	H	4.553573	2.700628	0.081285
H	-1.20577	1.548774	2.399257	C	5.57535	0.801424	-0.01308
H	-2.72951	1.325578	3.285435	H	6.566109	1.249397	-0.00312
C	-2.28341	-1.43116	3.868134	H	6.305244	-1.2332	-0.1117
H	-1.67097	-1.32602	4.771476	O	2.161026	1.997733	0.070754
H	-3.31099	-1.15389	4.131166	N	1.741152	-0.95894	-0.04836
H	-2.28522	-2.48887	3.579416	N	-0.3681	-1.40535	-0.04246
				C	-1.79276	-1.206	-0.01857
				C	-2.46682	-1.0341	-1.24184
				C	-2.43936	-1.12267	1.228267
				C	-3.84122	-0.76867	-1.18952
				C	-3.81451	-0.85603	1.225289
IzQO-Pd (F) int 4'							
0 1							
C	1.61592	-2.36476	-0.11568				
C	2.78473	-3.18386	-0.16772				

C	-4.50945	-0.67962	0.030442	H	-3.41247	-1.69893	-3.86118
H	-4.39081	-0.62081	-2.1142	H	-1.81265	-2.10531	-4.49319
H	-4.34363	-0.7786	2.170534	C	-1.69097	-1.27732	2.546683
H	-5.57566	-0.46942	0.049743	H	-0.65435	-1.54422	2.323326
Pd	0.142171	1.649687	0.145184	C	-1.66256	0.052256	3.323634
C	-0.56359	3.605834	0.337231	H	-1.1091	-0.06717	4.262823
H	-0.32878	4.21029	-0.54056	H	-1.16995	0.838004	2.739762
H	-0.22839	4.046512	1.276555	H	-2.67577	0.392404	3.571019
C	-1.85242	2.890109	0.336236	C	-2.28223	-2.41002	3.404782
H	-2.36061	2.890562	1.306304	H	-1.68724	-2.54416	4.315868
C	-2.81203	3.139169	-0.8284	H	-3.31234	-2.19233	3.710977
H	-2.27717	3.112574	-1.7828	H	-2.28813	-3.36093	2.859184
H	-3.6098	2.389732	-0.86046				
H	-3.26889	4.129494	-0.71941				
H	-1.63681	1.686512	0.253226	IzQO-Pd (F) int 5			
C	-1.73962	-1.07459	-2.58069	0 1			
H	-0.72366	-1.44096	-2.40772	C	1.26655	-2.34304	-0.31711
C	-1.62047	0.342429	-3.17319	C	2.290848	-3.30707	-0.56406
H	-1.07789	0.314251	-4.12598	C	3.574128	-2.88835	-0.65257
H	-2.61006	0.777239	-3.35926	C	3.935641	-1.50372	-0.43818
H	-1.07599	1.006466	-2.49255	C	2.929911	-0.53468	-0.16102
C	-2.40949	-2.03773	-3.57601	C	0.440284	-0.22034	-0.04085
H	-2.50212	-3.04589	-3.15546	C	-0.09241	-2.43452	-0.2162
				H	2.005154	-4.34606	-0.69014

H	4.373098	-3.59527	-0.85748	H	-1.72961	3.523712	0.674326
H	-0.74457	-3.29176	-0.23676	H	-2.17747	1.739556	0.798075
C	5.288984	-1.12882	-0.44812	C	-1.33267	2.351852	-1.08272
C	3.283988	0.805187	0.183777	H	-1.53432	1.385899	-1.53289
C	4.666343	1.121804	0.152167	C	-1.04864	3.467445	-2.05069
H	4.928938	2.145852	0.400206	H	-1.92394	3.611567	-2.7017
C	5.643392	0.18521	-0.1594	H	-0.83779	4.408162	-1.53471
H	6.689347	0.481957	-0.16693	H	-0.19761	3.227653	-2.69736
H	6.043444	-1.87944	-0.66501	H	0.655063	3.482262	0.333225
O	2.464659	1.756306	0.555273	C	-2.43696	-1.07328	-2.30584
N	1.579066	-0.97282	-0.17781	H	-1.3571	-0.9008	-2.37132
N	-0.56668	-1.14633	-0.05766	C	-3.12105	-0.14545	-3.32604
C	-1.9554	-0.87125	0.210063	H	-2.65731	-0.27314	-4.31077
C	-2.86646	-0.81165	-0.8644	H	-4.18617	-0.37895	-3.43708
C	-2.34928	-0.71281	1.553069	H	-3.03934	0.910169	-3.04772
C	-4.20623	-0.54307	-0.55846	C	-2.70226	-2.5436	-2.68931
C	-3.70042	-0.43576	1.801194	H	-2.3709	-2.73642	-3.71669
C	-4.61858	-0.34625	0.758187	H	-2.17565	-3.24003	-2.02972
H	-4.93644	-0.48512	-1.3592	H	-3.77382	-2.77004	-2.62986
H	-4.03378	-0.29288	2.824837	C	-1.37438	-0.84167	2.719272
H	-5.66212	-0.13046	0.971551	H	-0.3951	-1.12102	2.322719
Pd	0.468063	1.912941	0.159131	C	-1.20066	0.494846	3.462295
C	-1.67903	2.526971	0.24528	H	-0.8054	1.269089	2.796159

H	-2.15217	0.850151	3.876582	C	-5.55749	-0.14352	-0.01126
H	-0.4959	0.375801	4.293759	H	-6.6137	0.113712	0.017264
C	-1.81179	-1.96186	3.681005	H	-5.90207	-2.24643	-0.38657
H	-1.06699	-2.08955	4.475425	O	-2.39688	1.585287	0.363191
H	-2.77223	-1.73551	4.159029	N	-1.45594	-1.17108	-0.14095
H	-1.91571	-2.91861	3.155758	N	0.711628	-1.27858	-0.14412
IzQO-Pd (F) int 5'				C	2.108885	-0.93507	-0.07016
0 1				C	2.738521	-0.96157	1.186397
C	-1.09908	-2.51996	-0.36063	C	2.778124	-0.58984	-1.25704
C	-2.10026	-3.52094	-0.541	C	4.097172	-0.62569	1.231069
C	-3.40252	-3.15745	-0.50245	C	4.136003	-0.26316	-1.15751
C	-3.80218	-1.78591	-0.27518	C	4.790028	-0.28066	0.072544
C	-2.82016	-0.77173	-0.08366	H	4.615346	-0.62677	2.185654
C	-0.32632	-0.4033	-0.01048	H	4.683402	0.016165	-2.05319
C	0.268776	-2.56562	-0.35641	H	5.843962	-0.02086	0.129174
H	-1.78332	-4.54511	-0.70699	Pd	-0.29953	1.565489	0.31547
H	-4.18606	-3.89731	-0.63956	C	-0.15553	3.648431	1.300917
H	0.946617	-3.3938	-0.48575	H	0.858683	3.760224	1.676678
C	-5.16761	-1.46026	-0.23808	H	-0.94366	3.532312	2.040688
C	-3.20738	0.588533	0.160205	C	-0.4551	3.885847	-0.01257
C	-4.60461	0.846898	0.181542	H	-1.50491	3.90298	-0.30206
H	-4.89601	1.87747	0.362899	C	0.534051	4.332771	-1.05227
				H	1.566194	4.180424	-0.72222

C	2.423372	0.492964	0.113635	H	-4.25888	-4.58054	0.304351
C	3.231315	0.116404	-0.97841	H	-4.47137	-4.67919	-1.45435
C	2.791759	0.254627	1.452548	H	-3.12467	-5.52853	-0.67137
C	4.430797	-0.54765	-0.69257	C	2.850689	0.443084	-2.41944
C	3.996826	-0.42296	1.680408	H	1.766245	0.595143	-2.45362
C	4.806496	-0.82335	0.620683	C	3.199505	-0.68224	-3.41048
H	5.078071	-0.85762	-1.5066	H	2.748624	-0.46889	-4.38636
H	4.301633	-0.6384	2.700136	H	4.281465	-0.76526	-3.56544
H	5.737362	-1.34846	0.817967	H	2.836207	-1.65838	-3.07329
Pd	-0.76116	-1.43424	0.134274	C	3.522848	1.755301	-2.87315
C	-1.78949	-3.23871	0.281978	H	3.239779	2.600489	-2.23846
C	0.688619	-2.44608	-1.16217	H	4.615101	1.660422	-2.83895
H	-2.26619	-3.16354	1.268267	H	3.234912	1.996536	-3.90344
H	-1.11651	-4.1069	0.280348	C	1.928308	0.685996	2.633152
C	-2.83654	-3.36285	-0.81982	H	1.09628	1.284117	2.253282
C	1.141604	-2.60505	0.133578	C	1.32324	-0.53398	3.351638
H	0.141182	-3.23581	-1.66965	H	0.696325	-0.209	4.190505
H	1.086938	-1.66292	-1.79672	H	0.696768	-1.12109	2.671245
H	-3.46844	-2.46705	-0.81776	H	2.10703	-1.19026	3.749639
H	-2.34868	-3.40504	-1.80536	C	2.715953	1.57457	3.612855
C	-3.72345	-4.60823	-0.65329	H	2.052263	1.939645	4.405535
H	1.913671	-1.9643	0.539229	H	3.53469	1.026713	4.094273
H	0.944793	-3.5189	0.686198	H	3.14692	2.444483	3.103472

IzQO-Pd (F) int 1

				C	1.868027	1.02647	0.456
				C	2.84177	1.392599	-0.49522
0	1			C	2.196192	0.460412	1.702435
C	-1.36393	2.528767	0.129315	C	4.182466	1.157119	-0.16952
C	-2.38576	3.522103	0.028508	C	3.552979	0.227525	1.966735
C	-3.65993	3.129405	-0.20186	C	4.536559	0.571158	1.044134
C	-4.02178	1.728983	-0.24392	H	4.958799	1.429	-0.87817
C	-3.02112	0.728027	-0.1094	H	3.838773	-0.22151	2.913472
C	-0.51638	0.4121	-0.05786	H	5.582994	0.38626	1.271671
C	-0.01042	2.602753	0.296235	Pd	-0.52139	-1.59845	-0.37647
H	-2.10186	4.565557	0.11538	C	1.320001	-1.64909	-1.31486
H	-4.45332	3.863504	-0.31062	H	1.632192	-0.6282	-1.5298
H	0.632069	3.448721	0.475408	H	1.097632	-2.12423	-2.28246
C	-5.37535	1.360331	-0.32841	C	2.444184	-2.39931	-0.60232
C	-3.37487	-0.65028	0.060861	H	2.63087	-1.94994	0.379246
C	-4.75871	-0.95551	-0.03461	H	2.155389	-3.44262	-0.41892
H	-5.0286	-2.00188	0.076693	C	3.75259	-2.39193	-1.41001
C	-5.73024	0.017959	-0.23359	H	4.105956	-1.36753	-1.57042
H	-6.77622	-0.27289	-0.29772	H	4.5481	-2.94119	-0.88878
H	-6.12885	2.134874	-0.43753	H	3.612557	-2.85781	-2.39441
O	-2.53333	-1.60679	0.323228	H	-1.41222	-3.8105	0.886206
N	-1.66784	1.161343	-0.03687	C	-0.65827	-3.8772	0.106664
N	0.48189	1.317472	0.179739	H	0.33011	-4.21357	0.404381

C	1.1239	-1.9695	0.2527	H	2.3694	-2.9447	-3.6839
C	1.6624	-2.5274	-0.9199	H	1.7866	-1.29	-3.4212
C	1.8766	-1.7574	1.4198	C	0.3823	-4.2567	-2.2194
C	3.0165	-2.8803	-0.8993	H	0.1615	-4.5567	-1.317
C	3.2304	-2.1138	1.3835	H	1.2617	-4.9053	-2.3142
C	3.7947	-2.6699	0.2377	H	0.2681	-4.4353	-3.0836
H	3.4692	-3.3181	-1.7835	C	1.2731	-1.1428	2.6771
H	3.8478	-1.9516	2.2622	H	0.1948	-1.0396	2.5248
H	4.8468	-2.9421	0.2302	C	1.8322	0.2709	2.9261
Pd	0.1166	1.2807	-0.5953	H	1.3936	0.6986	3.8354
C	2.0713	0.7978	-0.9256	H	1.5937	0.9322	2.0876
H	2.617	0.4049	-0.0677	H	2.9214	0.2505	3.0527
H	2.2062	0.1496	-1.7919	C	1.4758	-2.0506	3.904
C	2.2902	2.273	-1.1867	H	0.9702	-1.6235	4.7775
H	2.6393	2.4707	-2.2086	H	2.5369	-2.1603	4.1565
C	3.1481	3.0063	-0.1473	H	1.0679	-3.0524	3.7278
H	2.7798	2.7501	0.8553	C	3.1589	4.5288	-0.3171
H	4.1738	2.6167	-0.2103	H	2.1275	4.9045	-0.2543
H	1.2784	2.8206	-1.1923	H	3.5167	4.7796	-1.326
C	0.8012	-2.7745	-2.1523	C	4.027	5.2354	0.7289
H	0.1081	-2.1743	-2.0513	H	4.0185	6.3223	0.5895
C	1.4824	-2.3406	-3.4609	H	5.0693	4.8978	0.67
H	0.7866	-2.4604	-4.299	H	3.6673	5.0251	1.7437

IzQO-Pd (F) TS (1'-2)

				C	2.419163	0.556851	-0.00552
				C	3.145395	0.292098	-1.18243
0 1				C	2.898121	0.234364	1.277188
C	-0.29617	2.869102	-0.30424	C	4.389052	-0.33599	-1.04395
C	-1.01603	4.082218	-0.52796	C	4.142095	-0.40508	1.358141
C	-2.36805	4.047761	-0.55223	C	4.87989	-0.68949	0.211387
C	-3.0962	2.826131	-0.28699	H	4.978504	-0.55585	-1.92862
C	-2.39412	1.616492	-0.02885	H	4.536054	-0.6798	2.332392
C	-0.08183	0.602212	-0.02959	H	5.843833	-1.18438	0.296172
C	1.037058	2.575753	-0.27902	Pd	-0.60646	-1.36718	0.179435
H	-0.45176	4.994187	-0.69243	C	1.168186	-2.30379	-0.40678
H	-2.941	4.951198	-0.7414	C	0.405649	-3.46536	-0.10161
H	1.901935	3.211416	-0.37373	H	1.349958	-2.06408	-1.45189
C	-4.50013	2.849574	-0.22645	H	1.979234	-2.03735	0.263849
C	-3.09288	0.435214	0.372001	H	0.649287	-3.99699	0.814228
C	-4.50952	0.521505	0.408475	H	0.068761	-4.10198	-0.91515
H	-5.03782	-0.38248	0.697574	H	-4.45791	-3.78727	0.418593
C	-5.19557	1.692834	0.112736	C	-3.90595	-4.25542	-0.40537
H	-6.28207	1.705328	0.158253	C	-2.64603	-3.44197	-0.74537
H	-5.02205	3.780129	-0.43009	H	-4.57921	-4.31659	-1.26986
O	-2.52763	-0.68292	0.723555	H	-3.65324	-5.27978	-0.10194
N	-0.97539	1.644996	-0.11744	C	-1.70318	-3.3655	0.446732
N	1.141311	1.208987	-0.11646	H	-2.94755	-2.43571	-1.05191

C	-3.79805	-2.6765	1.286685	C	4.634308	-0.95992	0.031047
C	-4.0518	-1.42882	0.597522	H	4.586627	0.40134	1.684727
C	-2.96857	-0.62465	0.141107	H	4.413925	-2.34443	-1.59077
C	-0.46095	-0.48682	0.118829	H	5.706788	-0.85631	-0.11153
C	-0.08525	-2.48642	1.157898	C	1.702621	-2.79754	-1.6158
H	-2.33729	-4.06147	2.017242	H	0.830827	-3.18456	-1.07893
H	-4.65645	-3.25705	1.612829	C	1.17411	-1.92098	-2.76943
H	0.507996	-3.28515	1.573211	H	0.552401	-2.51666	-3.44888
C	-5.37828	-1.02956	0.364082	H	0.568349	-1.09412	-2.38815
C	-3.21707	0.588525	-0.57971	H	2.004932	-1.50005	-3.34884
C	-4.57937	0.939043	-0.77172	C	2.468387	-4.01169	-2.16302
H	-4.76191	1.863973	-1.31087	H	3.26917	-3.71829	-2.85188
C	-5.63199	0.154603	-0.31919	H	2.913933	-4.6078	-1.35807
H	-6.65597	0.472102	-0.50087	H	1.782717	-4.657	-2.72398
H	-6.18935	-1.65794	0.720548	C	1.930108	0.36613	2.406567
O	-2.32771	1.392861	-1.10698	H	0.931989	0.660835	2.066125
N	-1.65392	-1.09525	0.416028	C	1.751161	-0.57893	3.612263
N	0.480938	-1.3669	0.571686	H	1.23998	-0.05947	4.431777
C	1.901739	-1.21265	0.389599	H	1.156587	-1.45966	3.35048
C	2.617982	-0.36263	1.25516	H	2.72529	-0.92268	3.98197
C	2.517829	-1.94588	-0.64584	C	2.656886	1.646394	2.843979
C	3.998407	-0.24751	1.045227	H	3.596459	1.426359	3.365249
C	3.902772	-1.80297	-0.80202	H	2.887262	2.295919	1.992949

H	2.024755	2.209552	3.539041	C	-3.17411	2.776273	1.656427
Pd	-0.35377	1.512015	-0.53729	C	-3.5678	1.585957	0.932631
C	-0.35122	3.552561	-0.7695	C	-2.58859	0.791118	0.272006
H	-1.27112	3.941454	-0.32457	C	-0.10846	0.530188	0.000958
H	-0.26293	3.846097	-1.81759	C	0.489742	2.447059	1.073033
C	0.887239	3.694848	0.073793	H	-1.58013	4.079508	2.247905
H	1.725809	4.119621	-0.49342	H	-3.9573	3.360455	2.131859
C	0.682899	4.418568	1.408371	H	1.165304	3.196006	1.452962
H	1.267716	2.648322	0.320791	C	-4.92783	1.243837	0.848226
H	-0.11357	3.935868	1.986565	C	-2.96936	-0.32248	-0.56503
H	0.388911	5.460404	1.235428	C	-4.36544	-0.61716	-0.58364
C	2.492415	1.46154	-2.05056	H	-4.66042	-1.46745	-1.19245
C	1.510299	1.756489	-2.90857	C	-5.312	0.135141	0.097654
H	3.103339	2.237084	-1.59463	H	-6.3631	-0.13816	0.033783
H	2.728116	0.439317	-1.77695	H	-5.6621	1.859164	1.360155
H	1.289589	2.780789	-3.19685	O	-2.1655	-1.03318	-1.28392
H	0.908006	0.985493	-3.38145	N	-1.2308	1.183528	0.430115
H	1.593825	4.418137	2.017147	N	0.926095	1.320265	0.404765
				C	2.305036	1.015451	0.122643
IzQO-Pd (F) TS (1-1')				C	2.826447	1.373208	-1.1333
0 1				C	3.064404	0.34827	1.102705
C	-0.87756	2.36996	1.113906	C	4.165089	1.050477	-1.39326
C	-1.88331	3.178324	1.725266	C	4.401035	0.063352	0.799394

C	4.947046	0.409627	-0.43554	C	2.921462	-1.43988	2.915041
H	4.596699	1.302478	-2.35736	H	3.972068	-1.44142	3.228476
H	5.020042	-0.44525	1.531611	H	2.325054	-1.75758	3.778123
H	5.984905	0.171957	-0.65381	H	2.806945	-2.18976	2.124814
Pd	0.046323	-1.35441	-0.91451	C	2.774213	1.010092	3.520679
C	-0.32268	-2.18216	0.934888	H	3.85671	1.106925	3.669721
C	1.861774	-2.46905	-1.24151	H	2.383563	1.993799	3.239631
C	0.833268	-3.11716	-1.94548	H	2.322936	0.72902	4.480027
H	-0.82666	-1.39336	1.495887	C	1.976837	2.043041	-2.20661
H	0.652303	-2.38877	1.37993	H	1.021576	2.332164	-1.75993
C	-1.20323	-3.40977	0.798859	C	1.670431	1.052286	-3.34505
H	2.552961	-1.79463	-1.74499	H	2.590476	0.723667	-3.84375
H	2.238229	-2.88243	-0.30801	H	1.159143	0.159551	-2.96357
H	0.39926	-4.0429	-1.57963	H	1.021006	1.515904	-4.09696
H	0.698452	-2.93771	-3.01223	C	2.631753	3.324986	-2.74966
H	-2.07272	-3.17368	0.1773	H	2.851007	4.032135	-1.94126
H	-0.65958	-4.22553	0.311065	H	3.570233	3.114324	-3.27574
C	-1.67155	-3.87231	2.191761	H	1.959205	3.819288	-3.46052
H	-2.27031	-3.09643	2.683788				
H	-2.29156	-4.7731	2.108139				
H	-0.82093	-4.10783	2.843844				
C	2.463021	-0.04889	2.445535				
H	1.376349	-0.08965	2.322395				

Reference

1. Grinshpun, V.; Rudin, A., Measurement of Mark-Houwink constants by size exclusion chromatography with a low angle laser light scattering detector. *Macromol. Rapid Commun.* **1985**, *6*, 219-223.
2. Mo, X.; Morgan, T. D. R.; Ang, H. T.; Hall, D. G., Scope and Mechanism of a True Organocatalytic Beckmann Rearrangement with a Boronic Acid/Perfluoropinacol System under Ambient Conditions. *J. Am. Chem. Soc.* **2018**, *140*, 5264-5271.
3. (a) Donthiri, R. R.; Pappula, V.; Reddy, N. N. K.; Bairagi, D.; Adimurthy, S., Copper-Catalyzed C–H Functionalization of Pyridines and Isoquinolines with Vinyl Azides: Synthesis of Imidazo Heterocycles. *J. Org. Chem.* **2014**, *79*, 11277-11284. (b) Xiang, L.; Niu, Y.; Pang, X.; Yang, X.; Yan, R., I₂-catalyzed synthesis of substituted imidazoles from vinyl azides and benzylamines. *Chem. Commun.* **2015**, *51*, 6598-6600.
4. Meiries, S.; Le Duc, G.; Chartoire, A.; Collado, A.; Speck, K.; Arachchige, K. S. A.; Slawin, A. M. Z.; Nolan, S. P., Large yet Flexible *N*-Heterocyclic Carbene Ligands for Palladium Catalysis. *Chem. Eur. J.* **2013**, *19*, 17358-17368.
5. (a) Ladipo, F. T.; Anderson, G. K., Convenient Method for the Synthesis of Chloro-Bridged Methyl- and Acetyl-palladium(II) Dimers. *Organometallics* **1994**, *13*, 303-306. (b) Salo, E. V.; Guan, Z., Late-Transition-Metal Complexes with Bisazaferrocene Ligands for Ethylene Oligomerization. *Organometallics* **2003**, *22*, 5033-5046.
6. Zhou, X.; Lau, K.-C.; Petro, B. J.; Jordan, R. F., cis/trans Isomerization of o-Phosphino-Arenesulfonate Palladium Methyl Complexes. *Organometallics* **2014**, *33*, 7209-7214.
7. Owen, G. R.; Haddow, M. F., Trans-Chloromethyldipyridinepalladium(II). *Acta Crystallogr. Sect. Sect. E: Struct. Rep. Online* **2005**, *E61*, m2651-m2652.
8. Zhu, Z.; Tang, X.; Li, X.; Wu, W.; Deng, G.; Jiang, H., Palladium-Catalyzed C-H

- Functionalization of Aromatic Oximes: A Strategy for the Synthesis of Isoquinolines. *J. Org. Chem.* **2016**, *81*, 1401-1409.
9. Zhou, S.; Wang, M.; Wang, L.; Chen, K.; Wang, J.; Song, C.; Zhu, J., Bidentate Directing-Enabled, Traceless Heterocycle Synthesis: Cobalt-Catalyzed Access to Isoquinolines. *Org. Lett.* **2016**, *18*, 5632-5635.
10. Zhang, J.; Fu, J.; Su, X.; Wang, X.; Song, S.; Shi, M., Synthesis of Various Saturated and Unsaturated N-Heterocyclic Carbene Precursors by Triflic Anhydride Mediated Intramolecular Cyclization. *Chem. Asian J.* **2013**, *8*, 552-555.
11. Nakano, R.; Nozaki, K., Copolymerization of Propylene and Polar Monomers Using Pd/IzQO Catalysts. *J. Am. Chem. Soc.* **2015**, *137*, 10934-10937.
12. Tao, W.; Akita, S.; Nakano, R.; Ito, S.; Hoshimoto, Y.; Ogoshi, S.; Nozaki, K., Copolymerisation of ethylene with polar monomers by using palladium catalysts bearing an N-heterocyclic carbene-phosphine oxide bidentate ligand. *Chem. Commun.* **2017**, *53*, 2630-2633.
13. Akita, S.; Nakano, R.; Ito, S.; Nozaki, K., Synthesis and Reactivity of Methylpalladium Complexes Bearing a Partially Saturated IzQO Ligand. *Organometallics* **2018**, *37*, 2286-2296.
14. Ota, Y.; Ito, S.; Kuroda, J. I.; Okumura, Y.; Nozaki, K., Quantification of the steric influence of alkylphosphine-sulfonate ligands on polymerization, leading to high-molecular-weight copolymers of ethylene and polar monomers. *J. Am. Chem. Soc.* **2014**, *136*, 11898-11901.
15. Skupov, K. M.; Marella, P. R.; Simard, M.; Yap, G. P. A.; Allen, N.; Conner, D.; Goodall, B. L.; Claverie, J. P., Palladium Aryl Sulfonate Phosphine Catalysts for the Copolymerization of Acrylates with Ethene. *Macromol. Rapid Commun.* **2007**, *28*, 2033-2038.
16. Johnson, A. M.; Contrella, N. D.; Sampson, J. R.; Zheng, M.; Jordan, R. F., Allosteric Effects in Ethylene Polymerization Catalysis. Enhancement of Performance of Phosphine-Phosphinate and Phosphine-Phosphonate Palladium Alkyl Catalysts by Remote Binding of

B(C₆F₅)₃. *Organometallics* **2017**, *36*, 4990-5002.

17. Sui, X.; Dai, S.; Chen, C., Ethylene Polymerization and Copolymerization with Polar Monomers by Cationic Phosphine Phosphonic Amide Palladium Complexes. *ACS Catal.* **2015**, *5*, 5932-5937

18. Zhang, W.; Waddell, P. M.; Tiedemann, M. A.; Padilla, C. E.; Mei, J.; Chen, L.; Carrow, B. P., Electron-Rich Metal Cations Enable Synthesis of High Molecular Weight, Linear Functional Polyethylenes. *J. Am. Chem. Soc.* **2018**, *140*, 8841-8850.

19. Ota, Y.; Ito, S.; Kobayashi, M.; Kitade, S.; Sakata, K.; Tayano, T.; Nozaki, K., Crystalline Isotactic Polar Polypropylene from the Palladium-Catalyzed Copolymerization of Propylene and Polar Monomers. *Angew. Chem. Int. Ed.* **2016**, *55*, 7505-7509.

20. Yasuda, H.; Nakano, R.; Ito, S.; Nozaki, K., Palladium/IzQO-Catalyzed coordination-insertion copolymerization of ethylene and 1,1-disubstituted ethylenes bearing a polar functional group. *J. Am. Chem. Soc.* **2018**, *140*, 1876-1883.

21. Mitsushige, Y.; Yasuda, H.; Carrow, B. P.; Ito, S.; Kobayashi, M.; Tayano, T.; Watanabe, Y.; Okuno, Y.; Hayashi, S.; Kuroda, J.; Okumura, Y.; Nozaki, K., Methylene-Bridged Bisphosphine Monoxide Ligands for Palladium-Catalyzed Copolymerization of Ethylene and Polar Monomers. *ACS Macro Lett.* **2018**, *7*, 305-311.

22. Chen, M.; Chen, C., A Versatile Ligand Platform for Palladium- and Nickel-Catalyzed Ethylene Copolymerization with Polar Monomers. *Angew. Chem. Int. Ed.* **2018**, *57*, 3094-3098.

23. Rünzi, T.; Guironnet, D.; Göttker-Schnetmann, I.; Mecking, S., Reactivity of methacrylates in insertion polymerization. *J. Am. Chem. Soc.* **2010**, *132*, 16623-16630.

24. Borkar, S.; Yennawar, H.; Sen, A., Methacrylate Insertion into Cationic Diimine Palladium(II)-Alkyl Complexes and the Synthesis of Poly(alkene-mocfc-alkene/carbon monoxide) Copolymers. *Organometallics* **2007**, *26*, 4711-4714.

25. Cotts, P. M.; Guan, Z.; McCord, E.; McLain, S., Novel branching topology in polyethylenes as revealed by light scattering and ^{13}C NMR. *Macromolecules* **2000**, *33*, 6945-6952.
26. Ruiz-Orta, C.; Fernandez-Blazquez, J. P.; Anderson-Wile, A. M.; Coates, G. W.; Alamo, R. G. Isotactic Polypropylene with (3,1) Chain-Walking Defects: Characterization, Crystallization, and Melting Behaviors. *Macromolecules*. **2011**, *44*, 3436–3451.
27. Small, B. L.; Brookhart, M., Polymerization of Propylene by a New Generation of Iron Catalysts: Mechanisms of Chain Initiation, Propagation, and Termination. *Macromolecules*. **1999**, *32*, 2120–2130.
28. (a) Drent, E.; Dijk, R. v.; Ginkel, R. v.; Oort, B. v.; Pugh, R. I., Palladium catalysed copolymerisation of ethene with alkylacrylates: Polar comonomer built into the linear polymer chain. *Chem. Commun.* **2002**, 744-745. (b) Ito, S.; Kanazawa, M.; Munakata, K.; Kuroda, J.-i.; Okumura, Y.; Nozaki, K., Coordination-insertion copolymerization of allyl monomers with ethylene. *J. Am. Chem. Soc.* **2011**, *133*, 1232-1235. (c) Jian, Z.; Mecking, S., Insertion Homo- and Copolymerization of Diallyl Ether. *Angew. Chem. Int. Ed.* **2015**, *54*, 15845-15849. (d) Tao, W.-j.; Nakano, R.; Ito, S.; Nozaki, K., Copolymerization of Ethylene and Polar Monomers by Using Ni/IzQO Catalysts. *Angew. Chem. Int. Ed.* **2016**, *55*, 2835-2839.
29. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T. M.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.;

Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, revision E.01; Gaussian, Inc.: Wallingford CT, 2013.

30. Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H., A Consistent and Accurate Ab Initio Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H-Pu. *J. Chem. Phys.* **2010**, *132*, No. 154104.

31. (a) Hay, P. J.; Wadt, W. R., Ab Initio Effective Core Potentials for Molecular Calculations. Potentials for K to Au Including the Outermost Core Orbitals. *J. Chem. Phys.* **1985**, *82*, 299-310. (b) Wadt, W. R.; Hay, P. J., Ab Initio Effective Core Potentials for Molecular Calculations. Potentials for Main Group Elements Na to Bi. *J. Chem. Phys.* **1985**, *82*, 284-298. (c) Hay, P. J.; Wadt, W. R., Ab Initio Effective Core Potentials for Molecular Calculations. Potentials for the Transition Metal Atoms Sc to Hg. *J. Chem. Phys.* **1985**, *82*, 270-283.

32. Marenich, A. V.; Cramer, C. J.; Truhlar, D. G., Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. *J. Phys. Chem. B* **2009**, *113*, 6378-6396.