Supporting Information for:

Ethylene Polymerization and Copolymerization by Palladium and Nickel Catalysts Containing Naphthalene Bridged Phosphine-Sulfonate Ligands

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1. Spectra Data

1.1 ^{1}H, ^{13}C, ^{31}P of Compound L1-L4, Complexes 1-3.

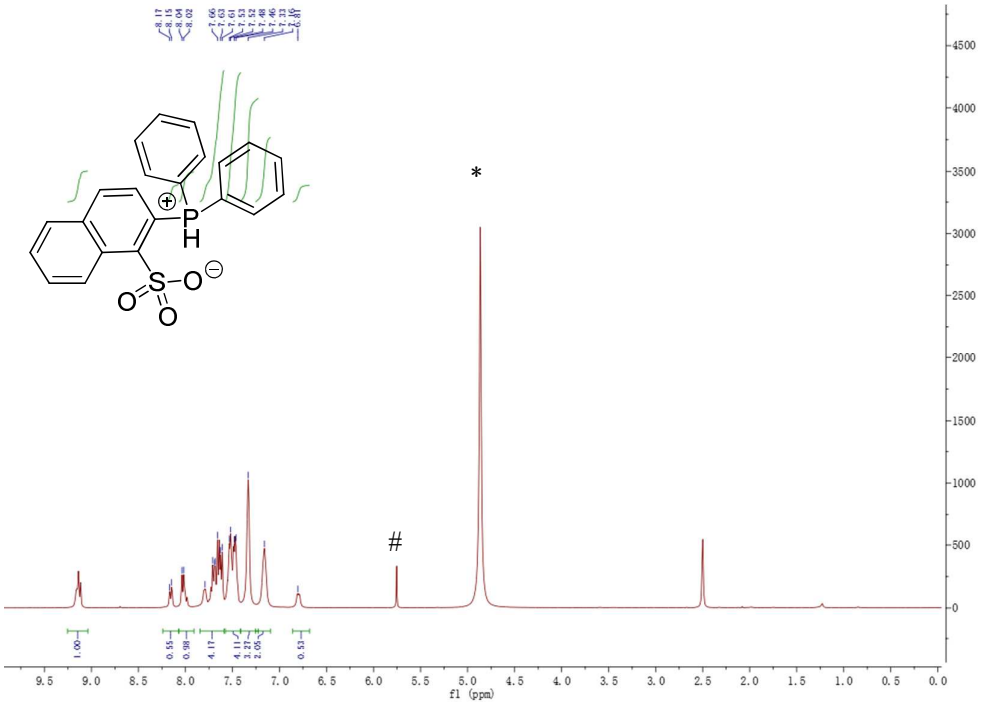

Figure S1. ^{1}H NMR spectrum (400 MHz, [D_6]DMSO) of **L1**. * H_2O from solvent [D $_6$]DMSO, # CH_2Cl_2.

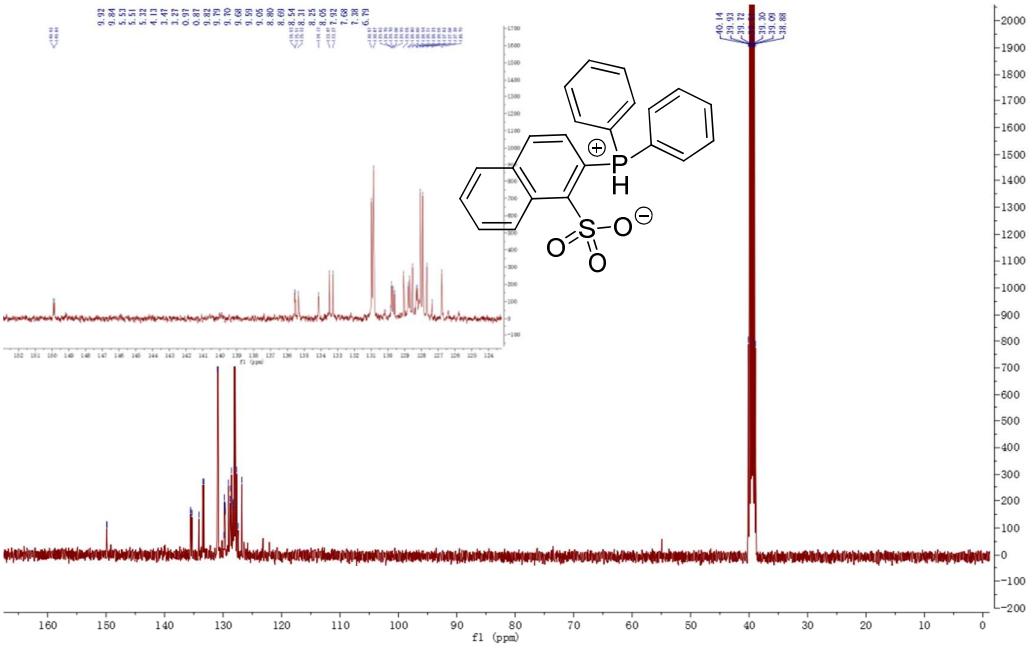

Figure S2. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **L1**.

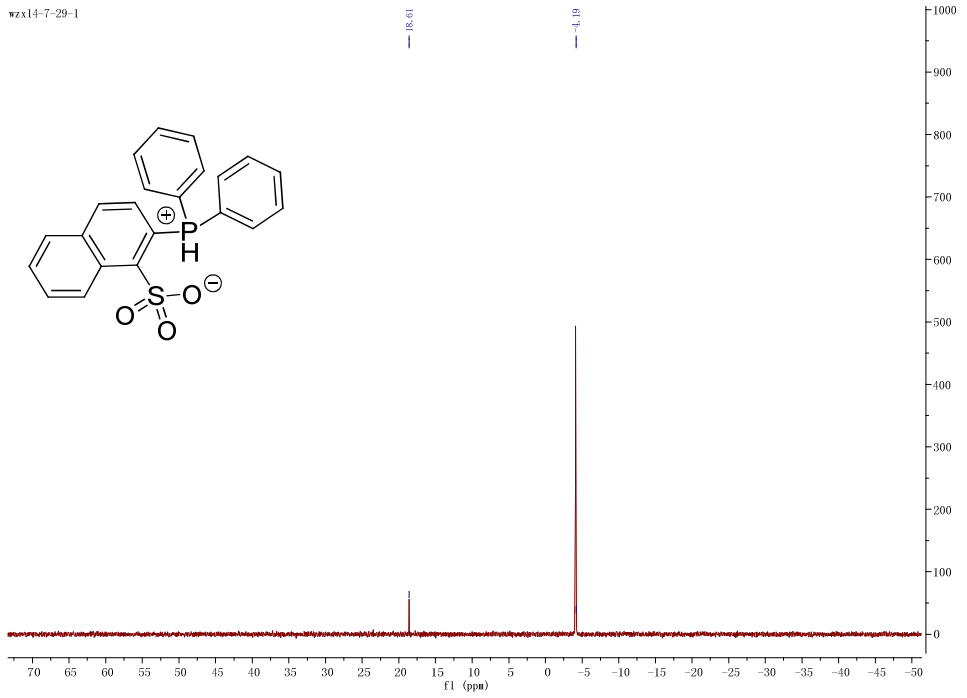

Figure S3. ^{31}P NMR spectrum (162 MHz, [D_6]DMSO) of **L1**.

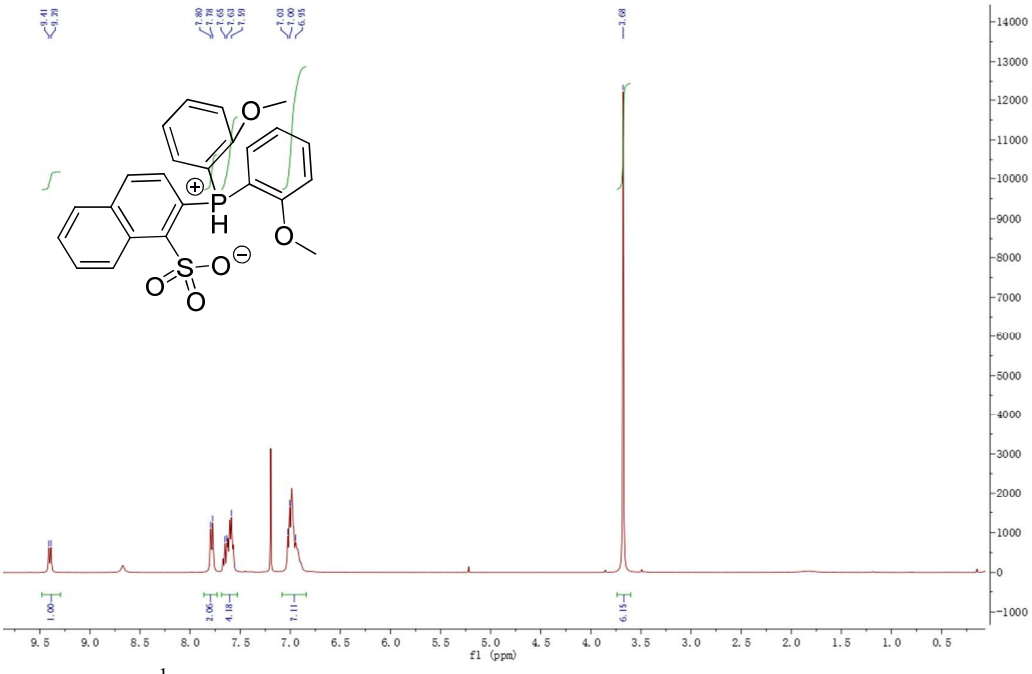

Figure S4. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **L2**.

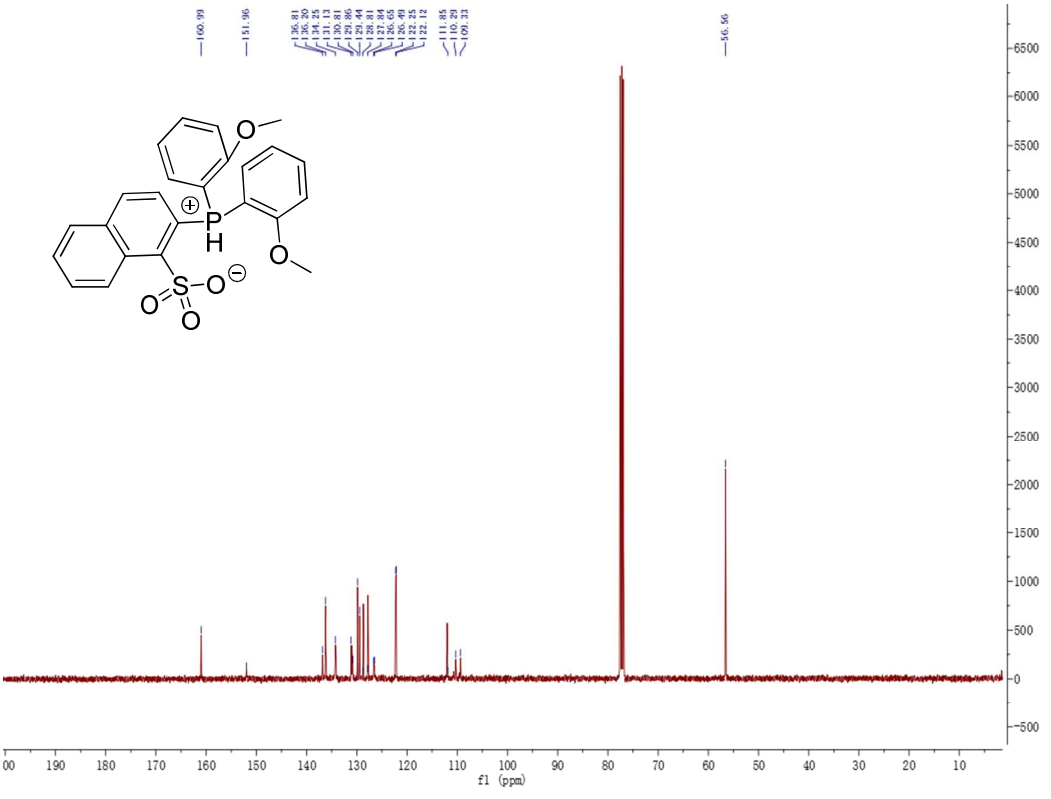

Figure S5. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **L2**.

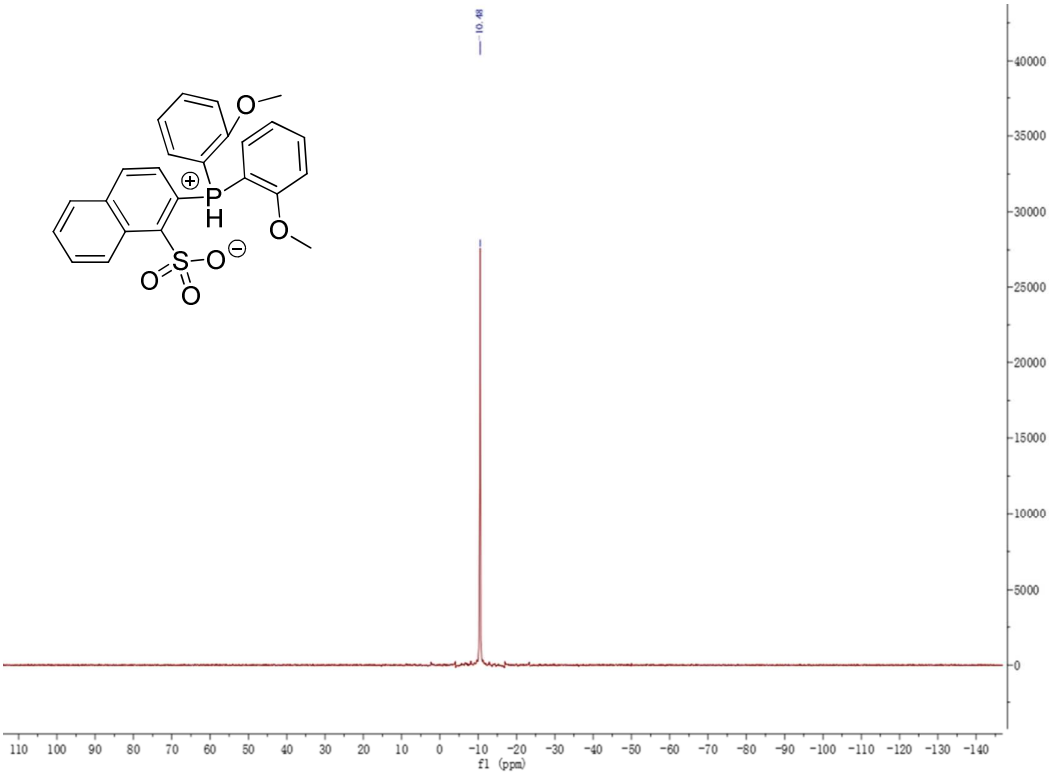

Figure S6.^{31}P NMR spectrum (162 MHz, $CDCl_3$) of **L2**.

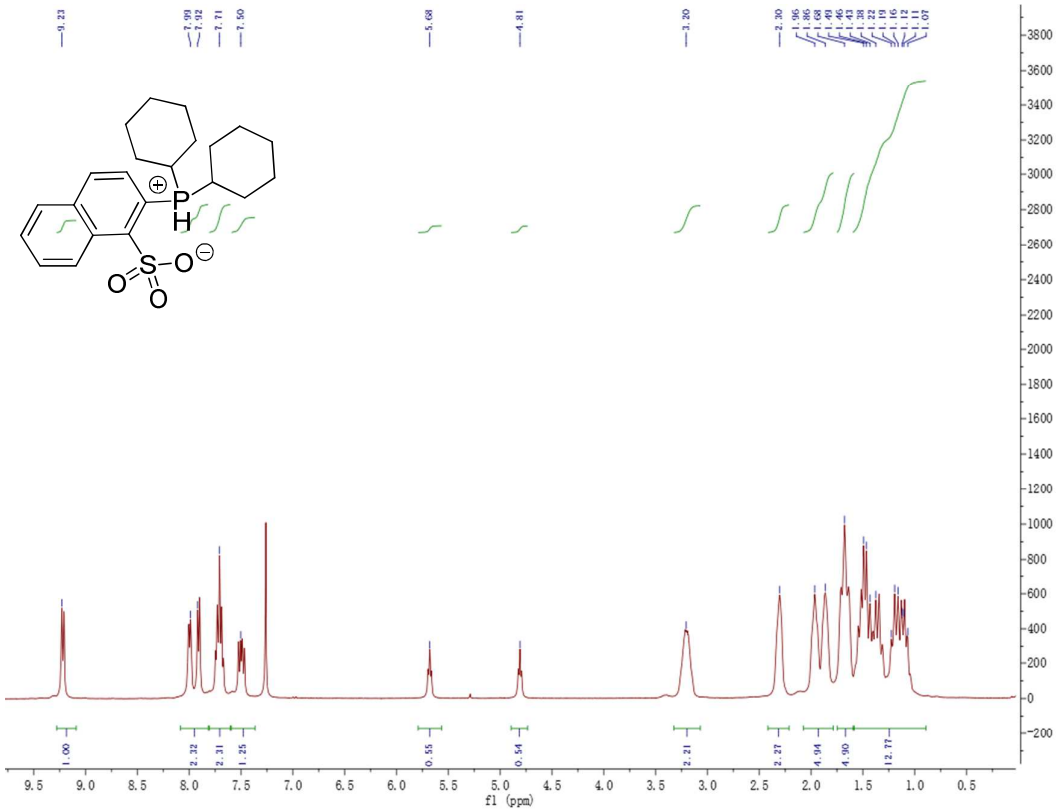

Figure S7.[1]H NMR spectrum (400 MHz, $CDCl_3$) of **L3**.

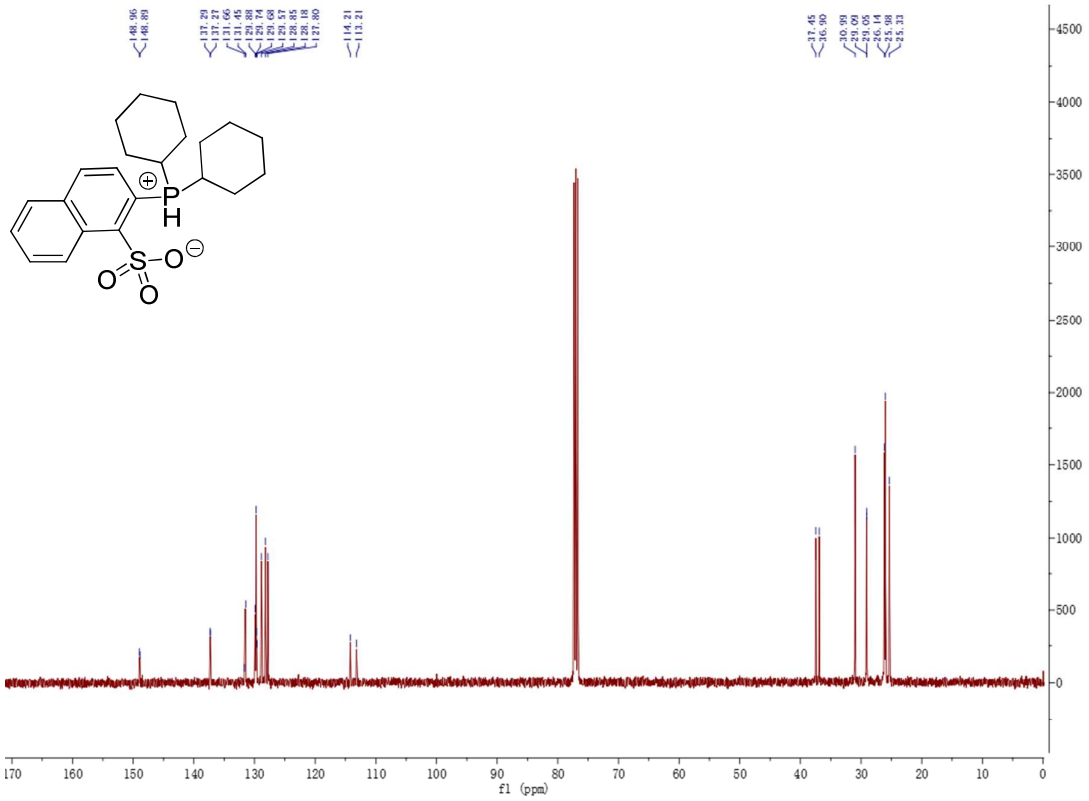

Figure S8. [13]C NMR spectrum (100 MHz, $CDCl_3$) of **L3**.

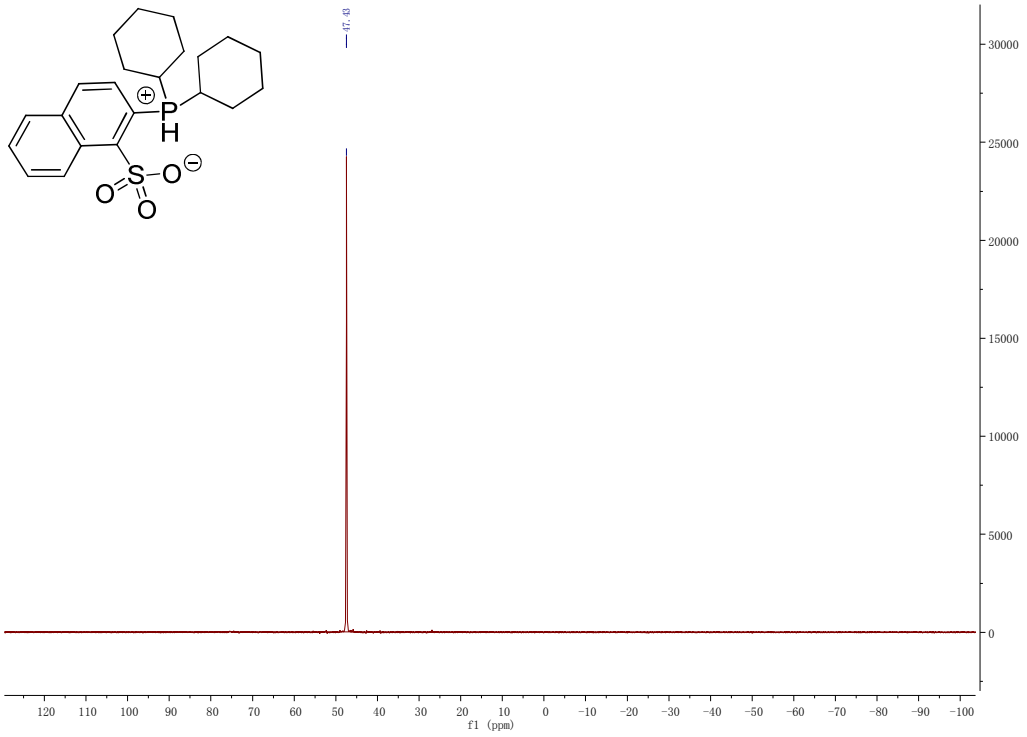

Figure S9. ^{31}P NMR spectrum (162 MHz, $CDCl_3$) of **L3**.

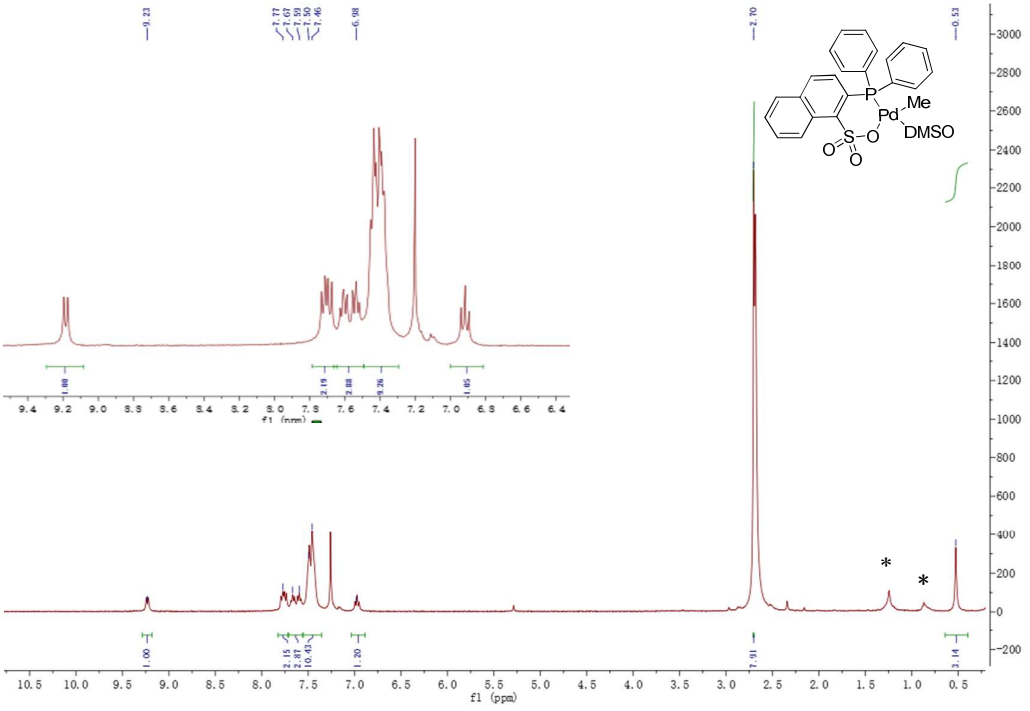

Figure S10. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1**. (Insert: the region of δ 9.4 – 6.4). * hexane.

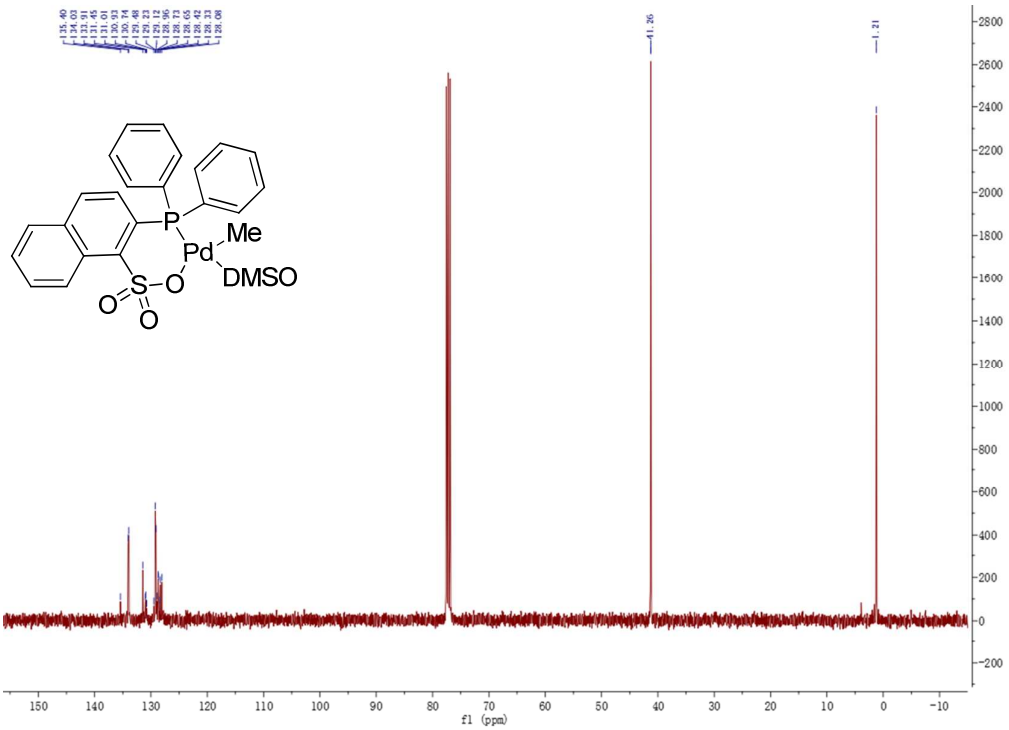

Figure S11. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **1**.

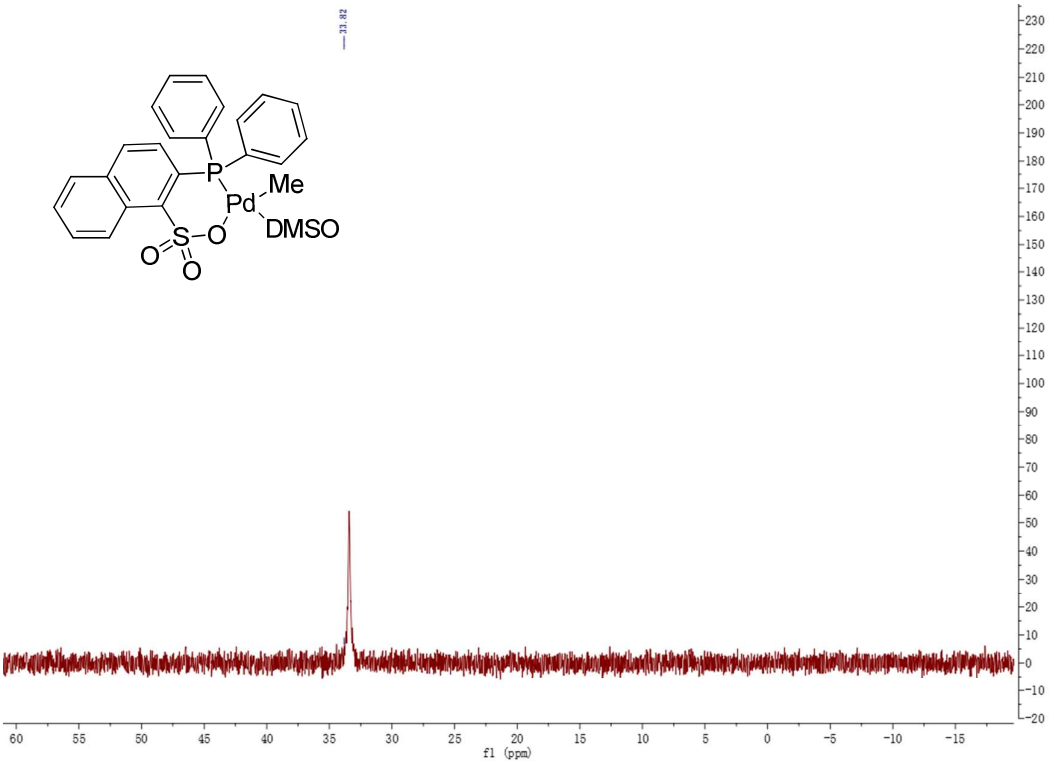

Figure S12. ^{31}P NMR spectrum (162 MHz, $[D_6]$DMSO) of **1**.

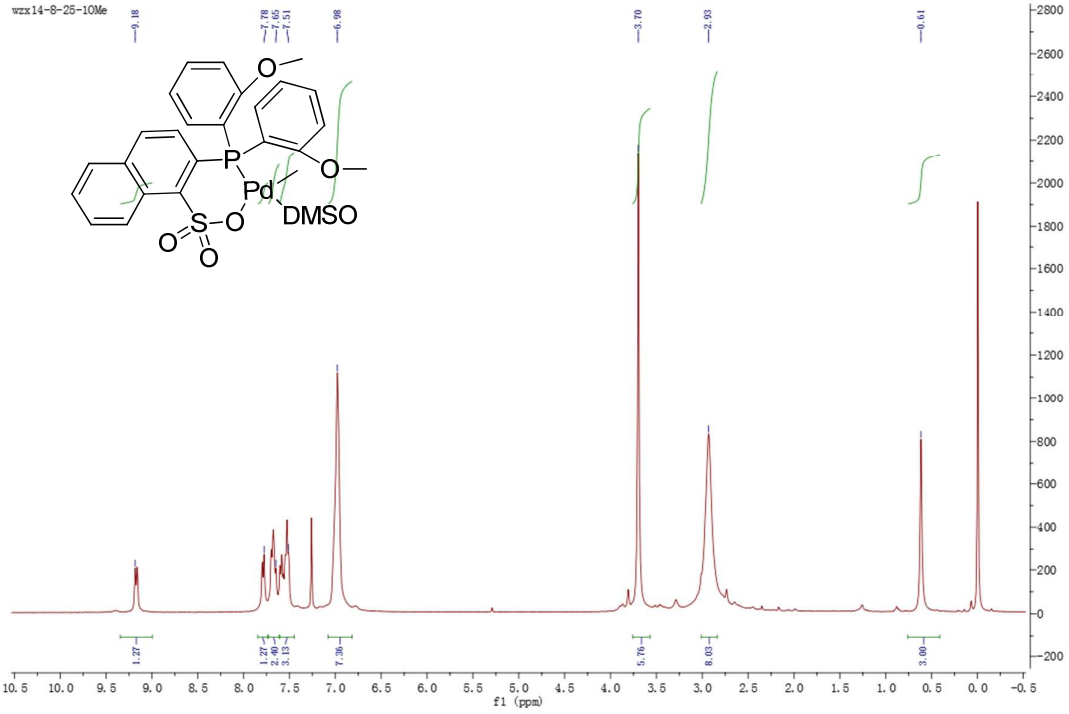

Figure S13. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2**.

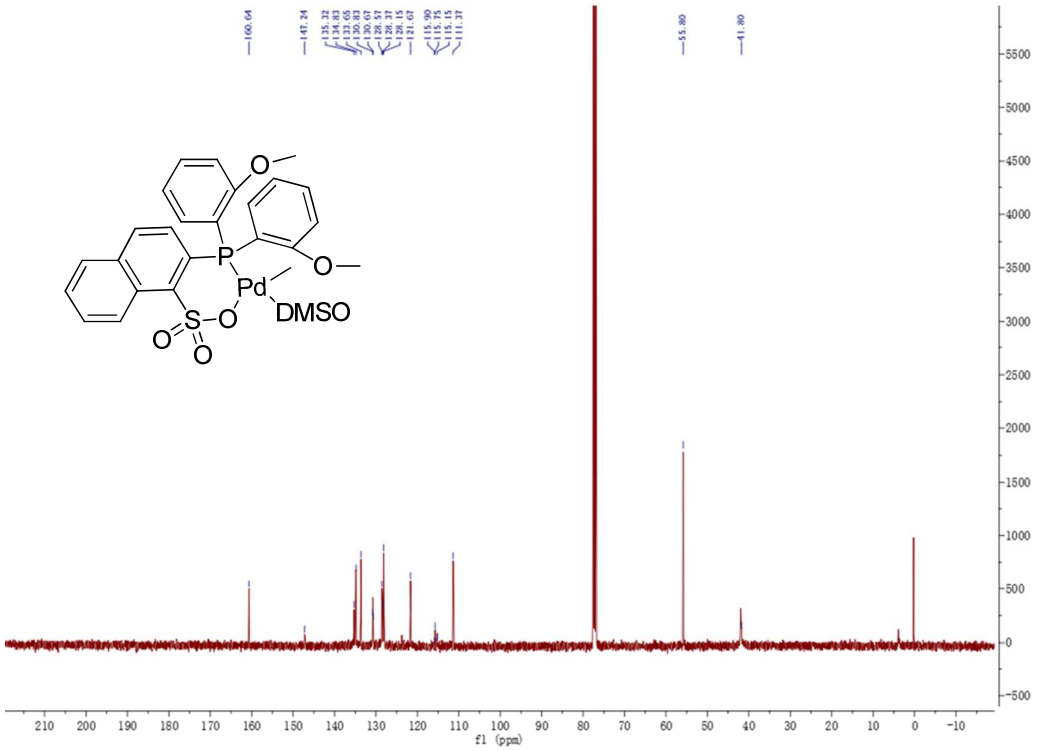

Figure S14. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **2**.

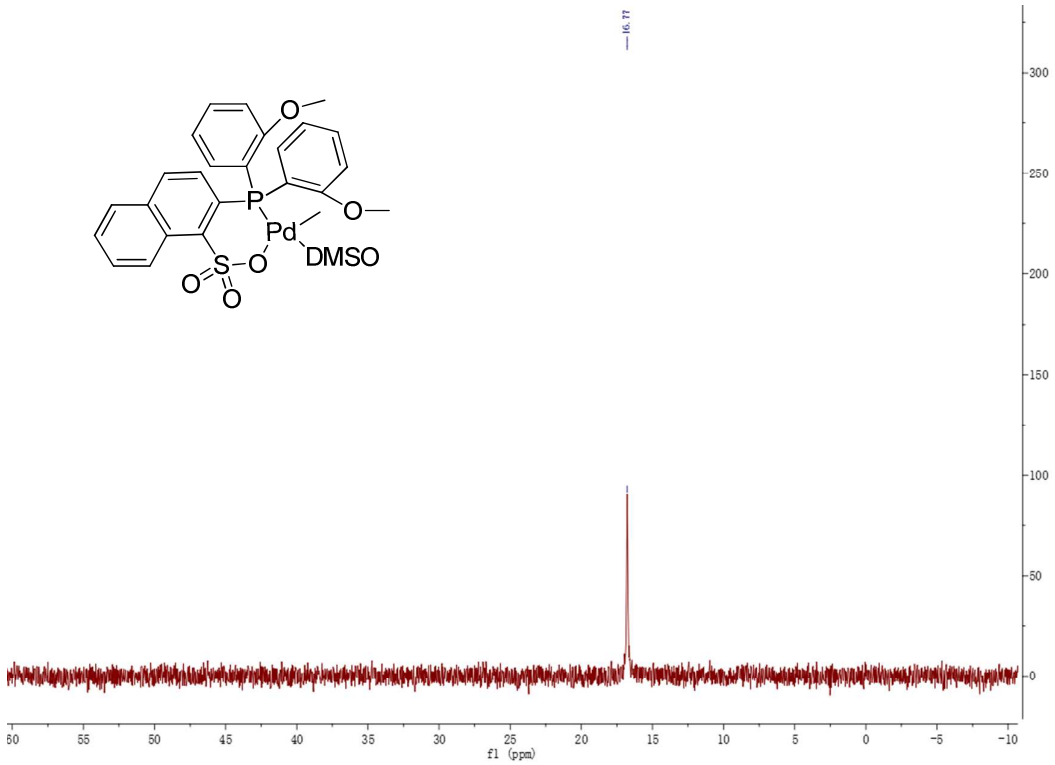

Figure S15. ^{31}P NMR spectrum (162 MHz, [D_6]DMSO) of **2**.

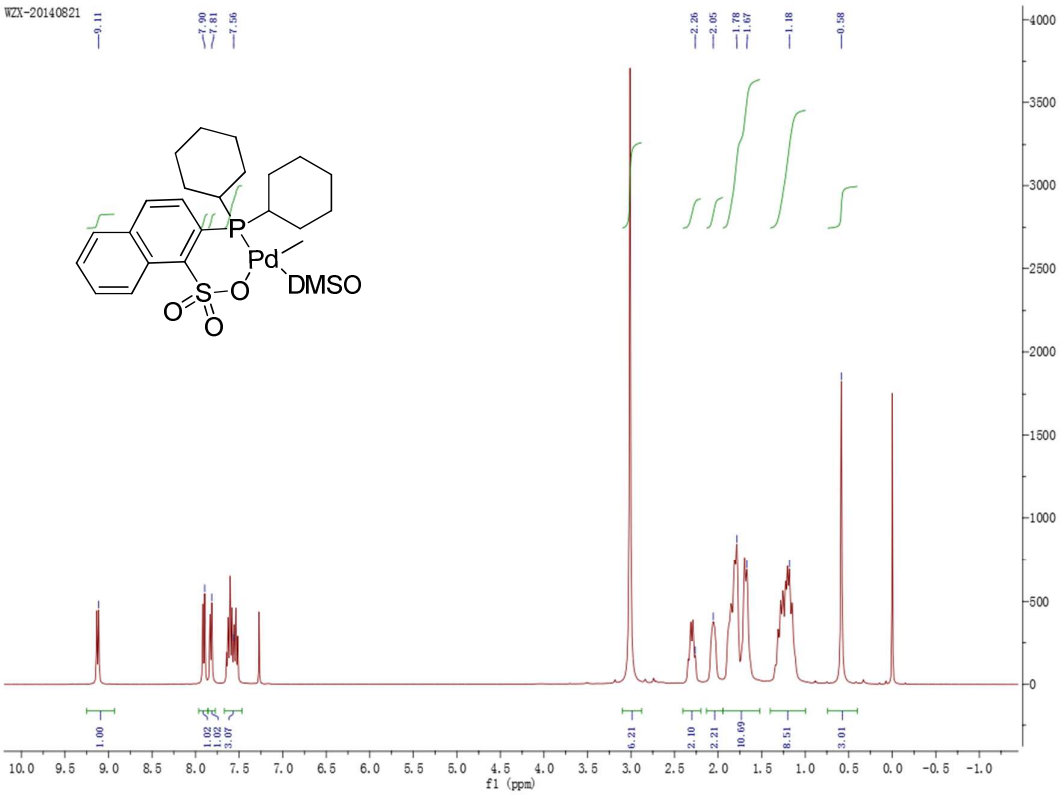

Figure S16. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3**.

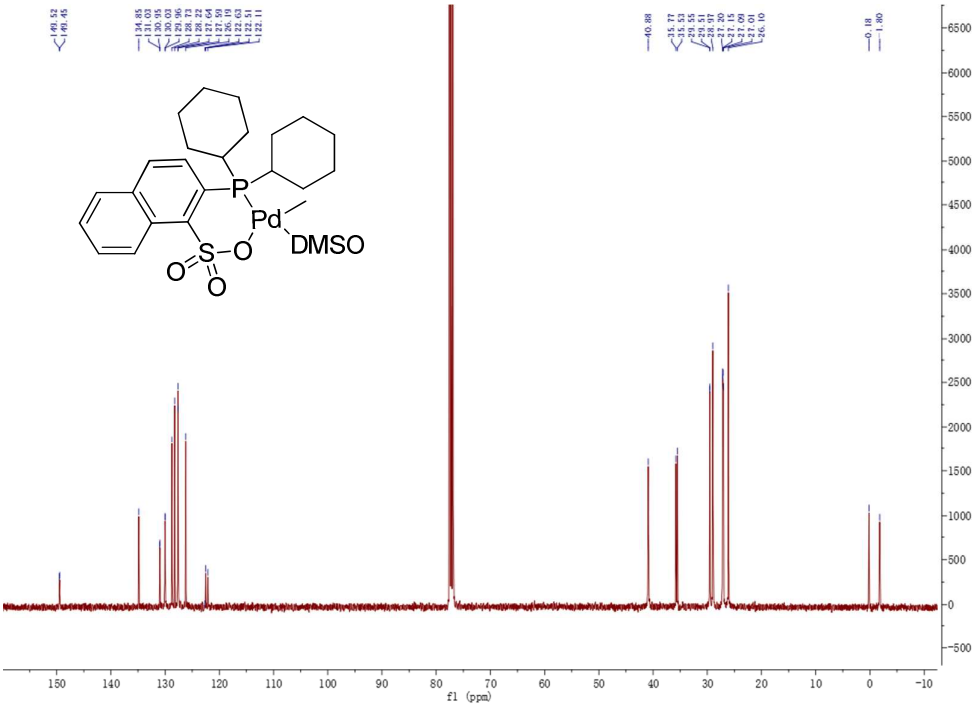

Figure S17. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **3**.

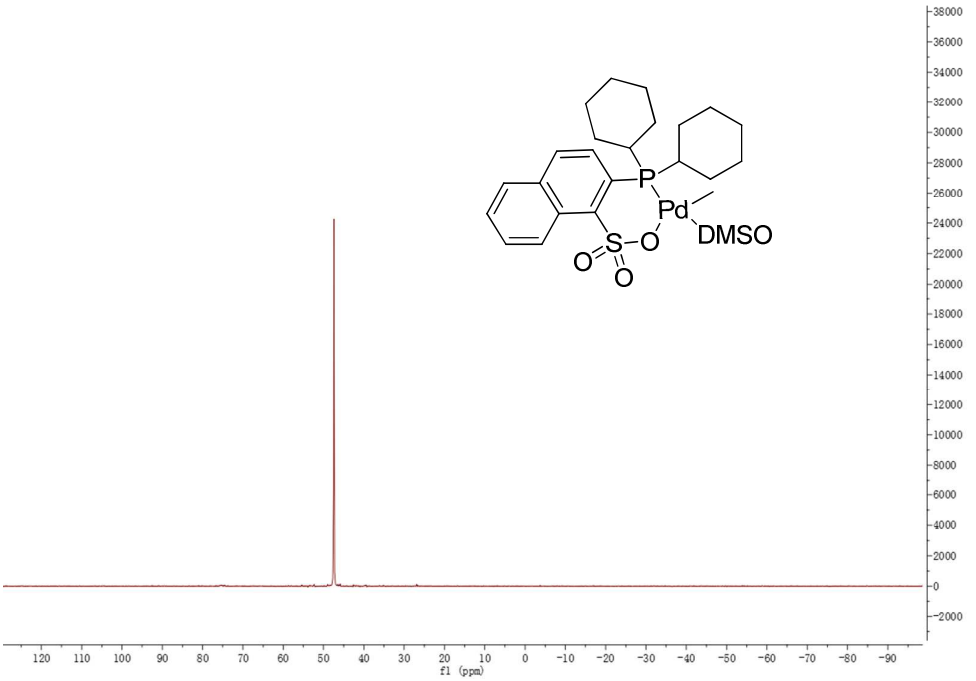

Figure S18. ^{31}P NMR spectrum (162 MHz, $CDCl_3$) of **3**.

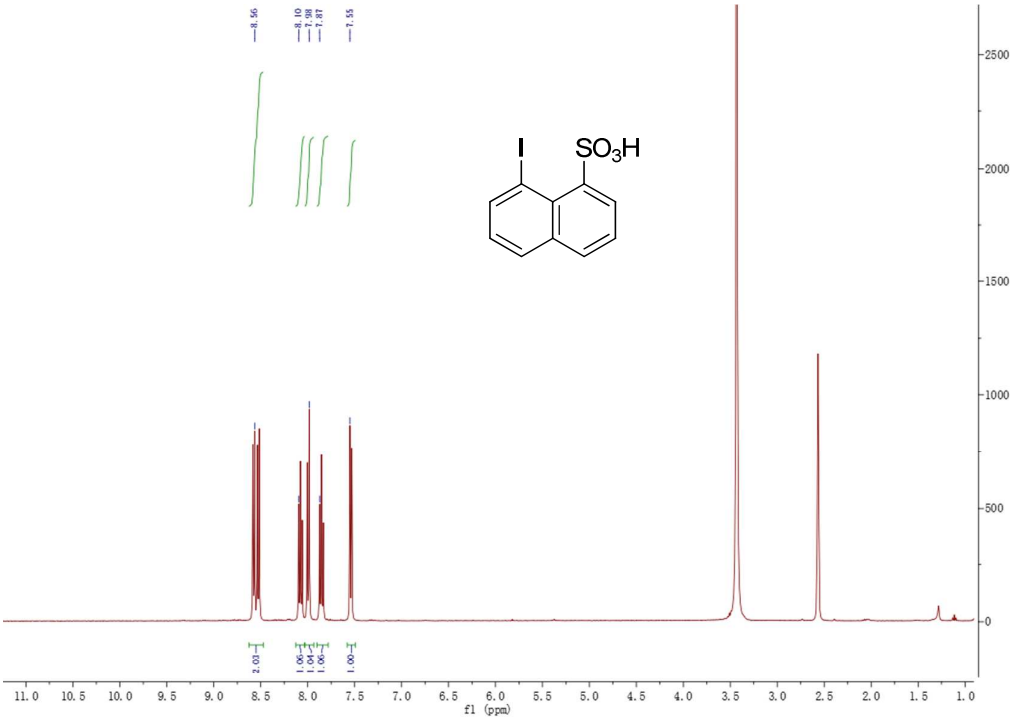

Figure S19. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 8-iodonaphthalene-1-sulfonic acid.

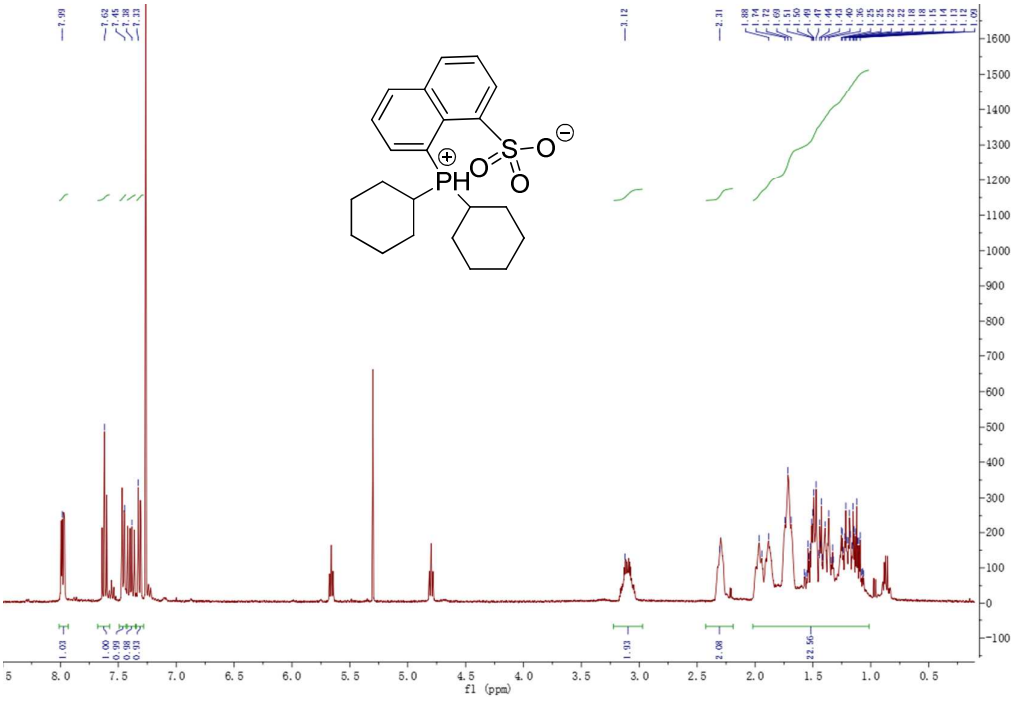

Figure S20. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **L4**.

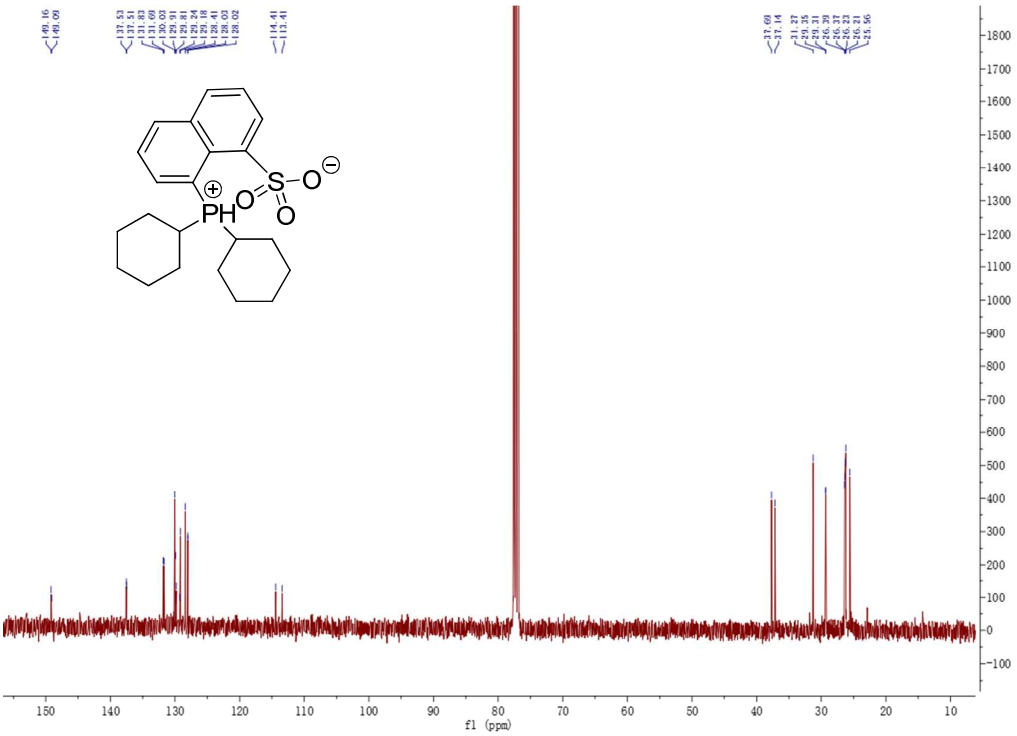

Figure S21. ^{12}C NMR spectrum (100 MHz, $CDCl_3$) of **L4**.

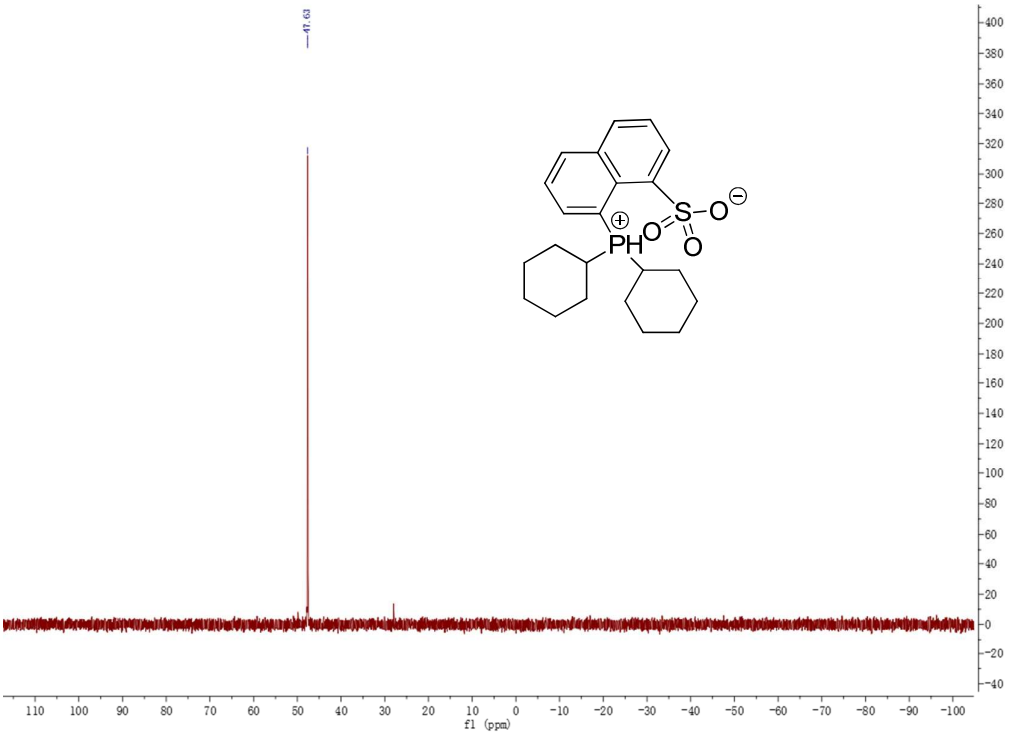

Figure S22. ^{31}P NMR spectrum (162 MHz, $CDCl_3$) of **L4**.

1.2 ESI-MS of L1-L3

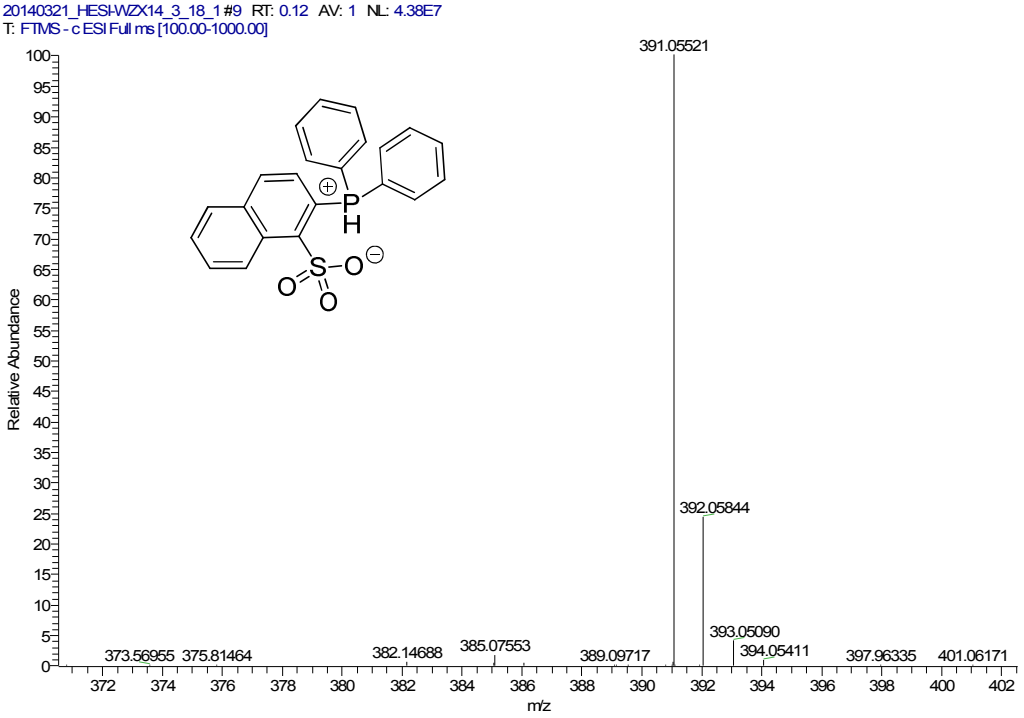

Figure S23. ESI-MS of **L1.**

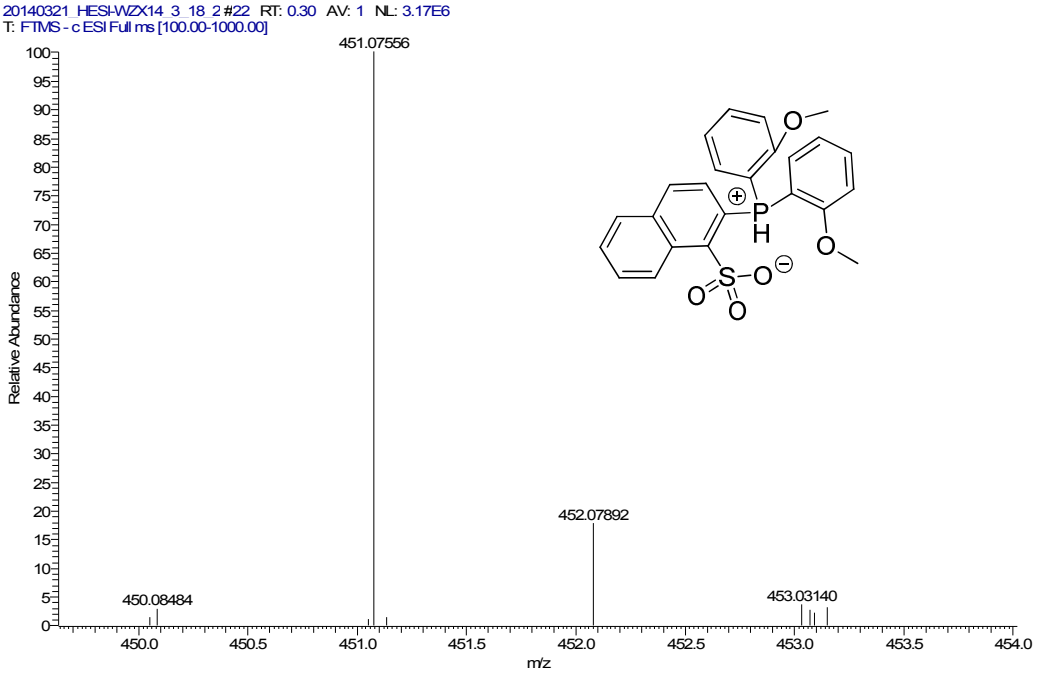

Figure S24. ESI-MS of **L2.**

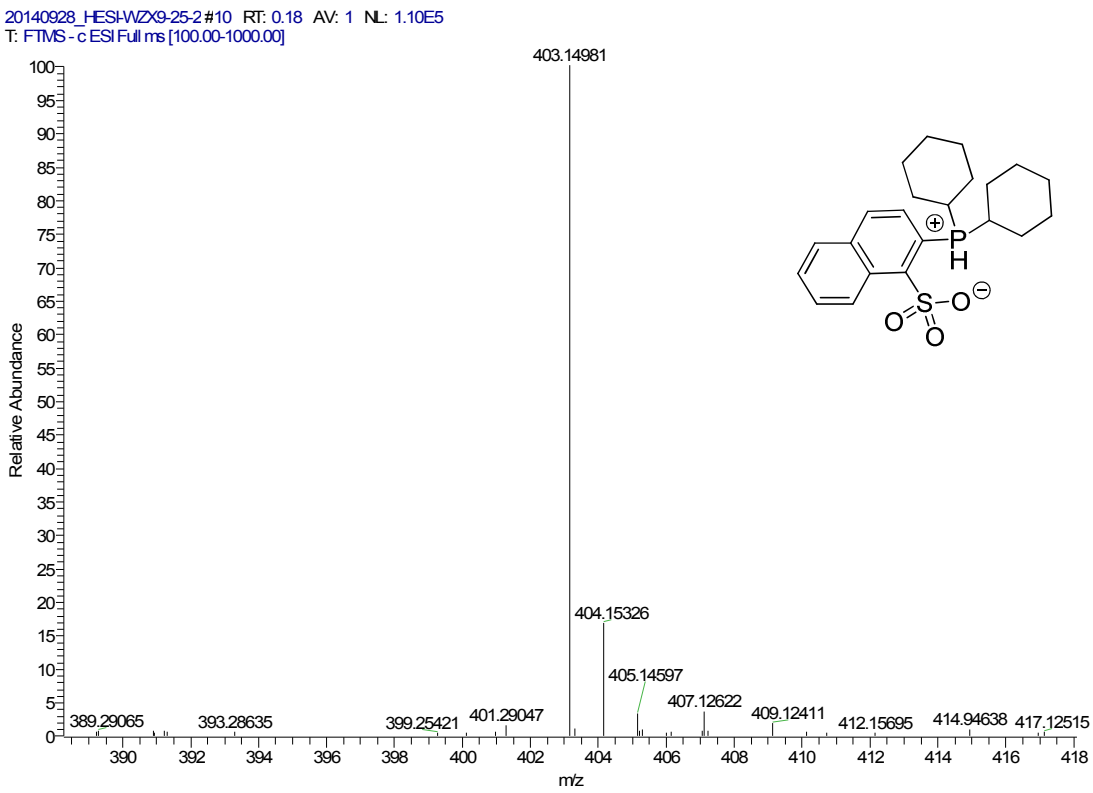

Figure S25. ESI-MS of **L3.**

1.3 ^{1}H and ^{13}C NMR of polymer

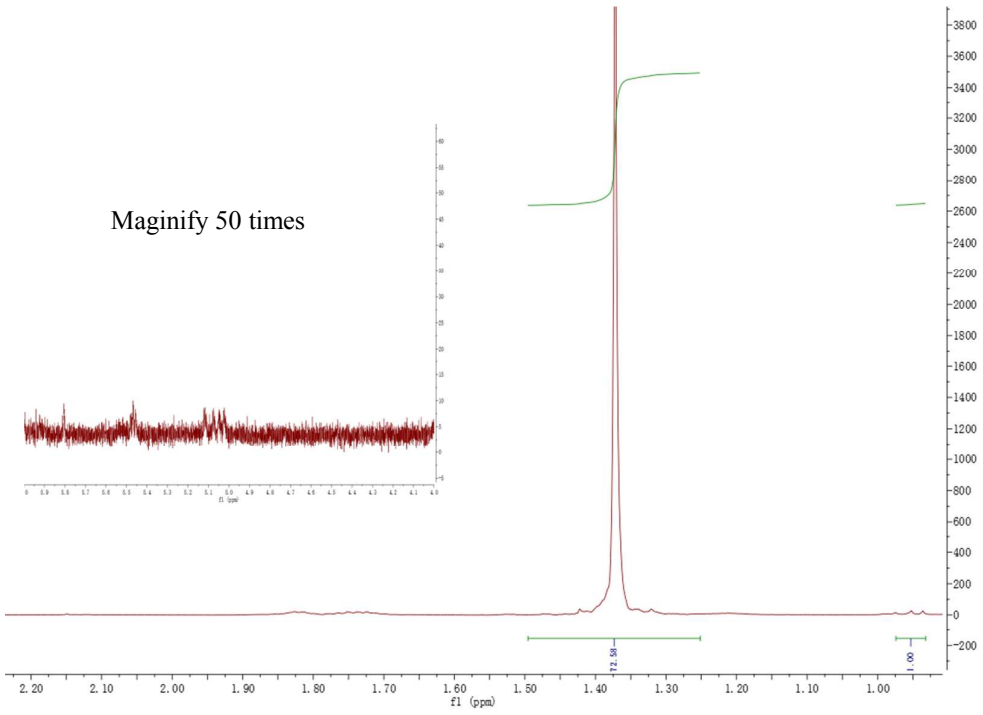

Figure S26. ^{1}H NMR spectrum of the polymer from table 1, entry 5 (Insert: the regi on of δ 5.5-4.0, magnify 50 times). ($C_2D_2Cl_4$, 120 ^{o}C).

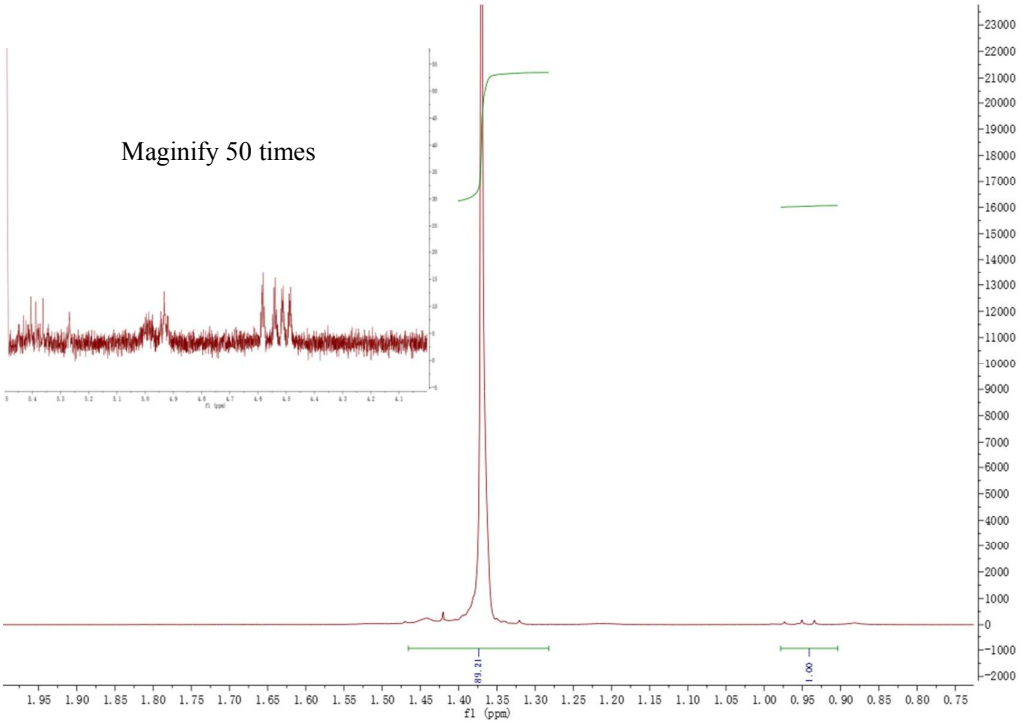

Figure S27. ^{1}H NMR spectrum of the polymer from table 1, entry 11 (Insert: the reg ion of δ 5.5-4.0, magnify 50 times). ($C_2D_2Cl_4$, 120 ^{o}C).

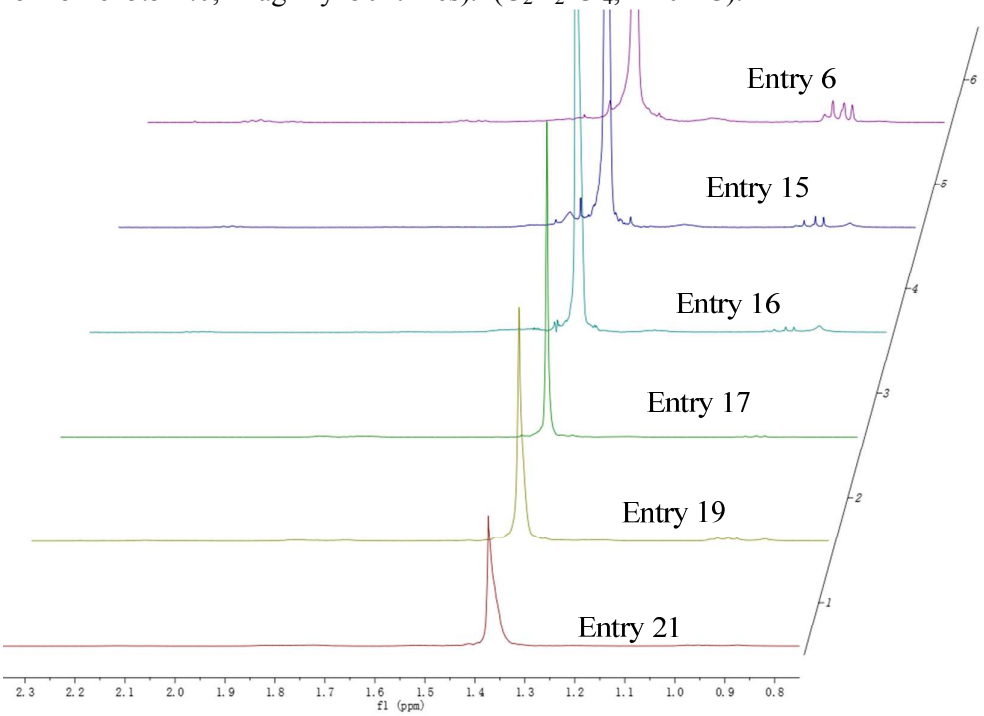

Figure S28. ^{1}H NMR spectrum of the polymer from table 1. ($C_2D_2Cl_4$, 120 ^{o}C).

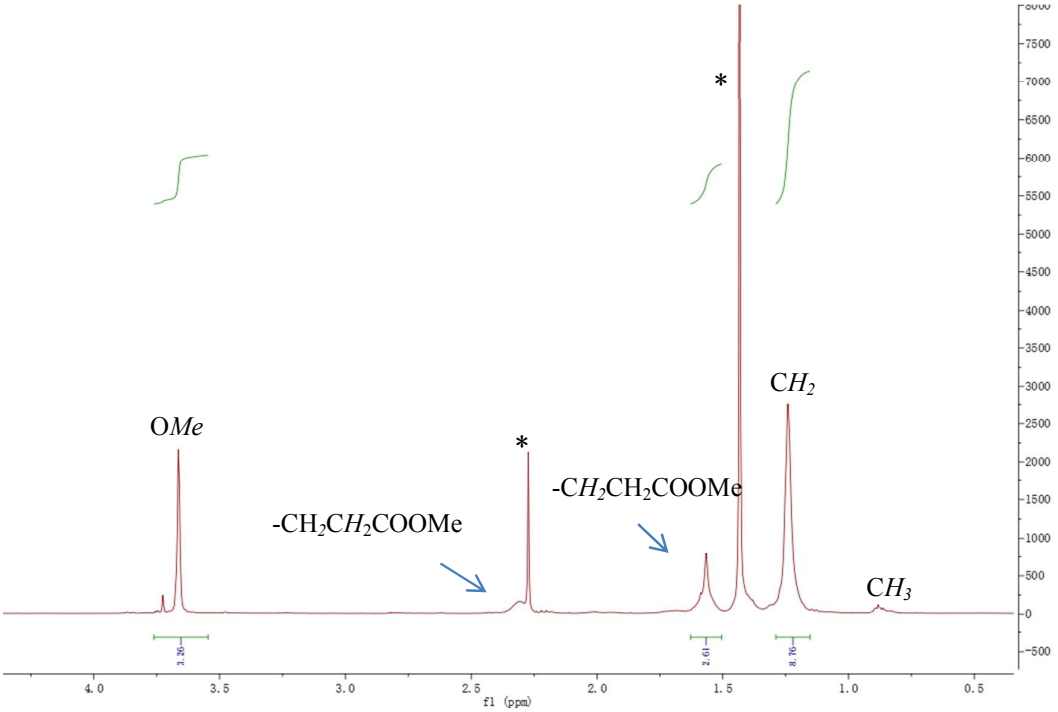

Figure S29. ^{1}H NMR spectrum of the E-MA copolymer generated by complex **2** at 85 ^{o}C from table 2, entry 3 in $CDCl_3$. * BHT

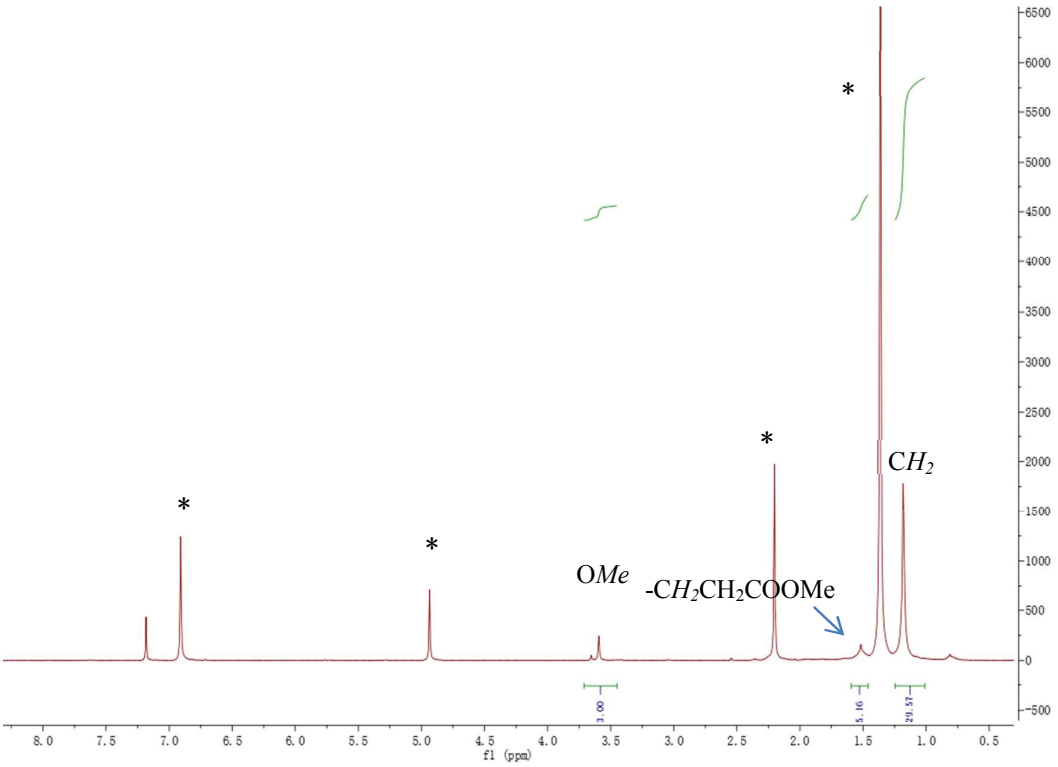

Figure S30. ^{1}H NMR spectrum of the E-MA copolymer generated by complex **2'** at 85 ^{o}C from table 2, entry 5 in $CDCl_3$. * BHT

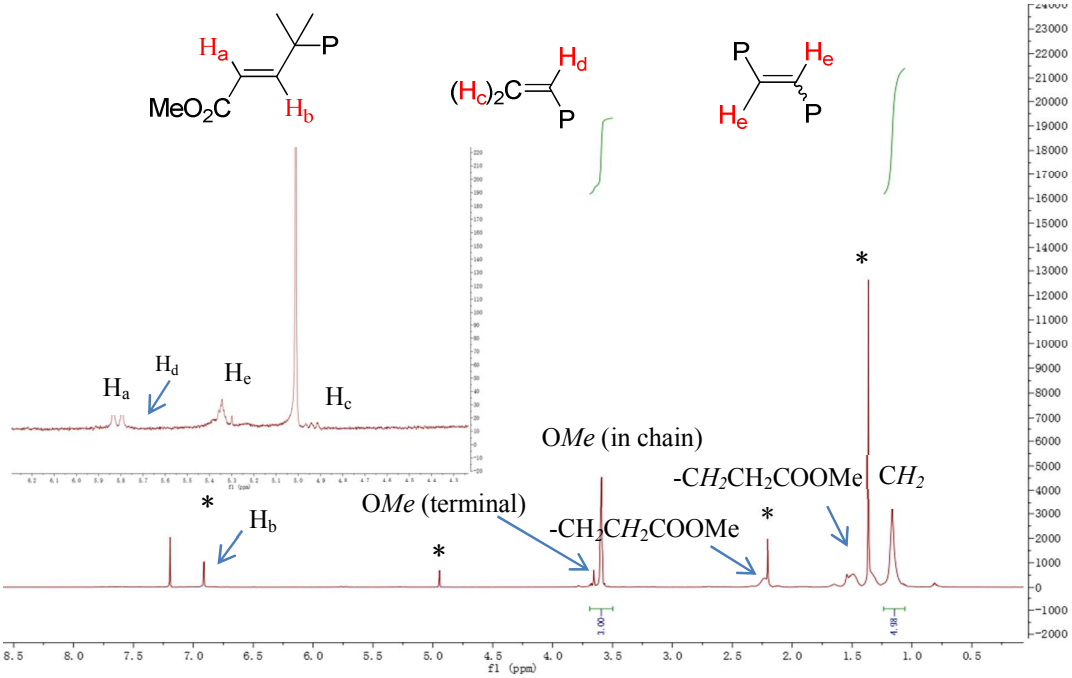

Figure S31. ^{1}H NMR spectrum of the E-MA copolymer generated by complex **2** at 85 ^{o}C from table 2, entry 4 in $CDCl_3$. * BHT. (Insert: the region of δ 6.0-4.0, magnify 50 times).

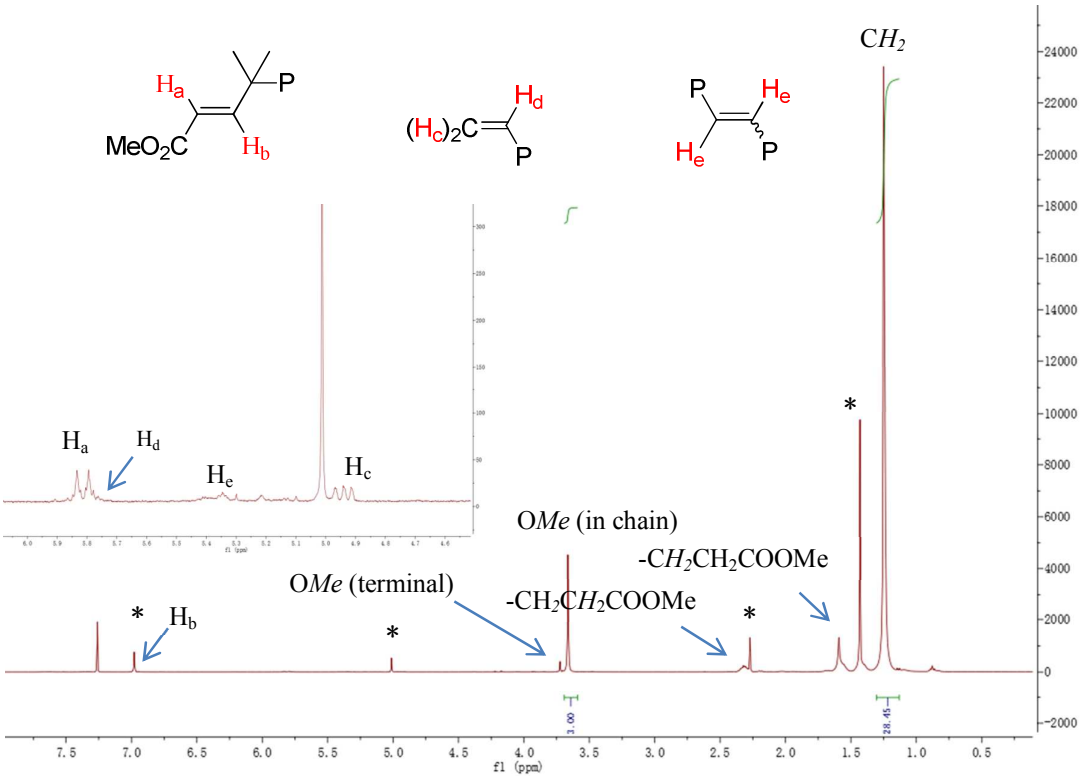

Figure S32. ^{1}H NMR spectrum of the E-MA copolymer generated by complex **2'** at 85 ^{o}C from table 2, entry 6 in $CDCl_3$. * BHT. (Insert: the region of δ 6.0-4.0, magnify 50 times).

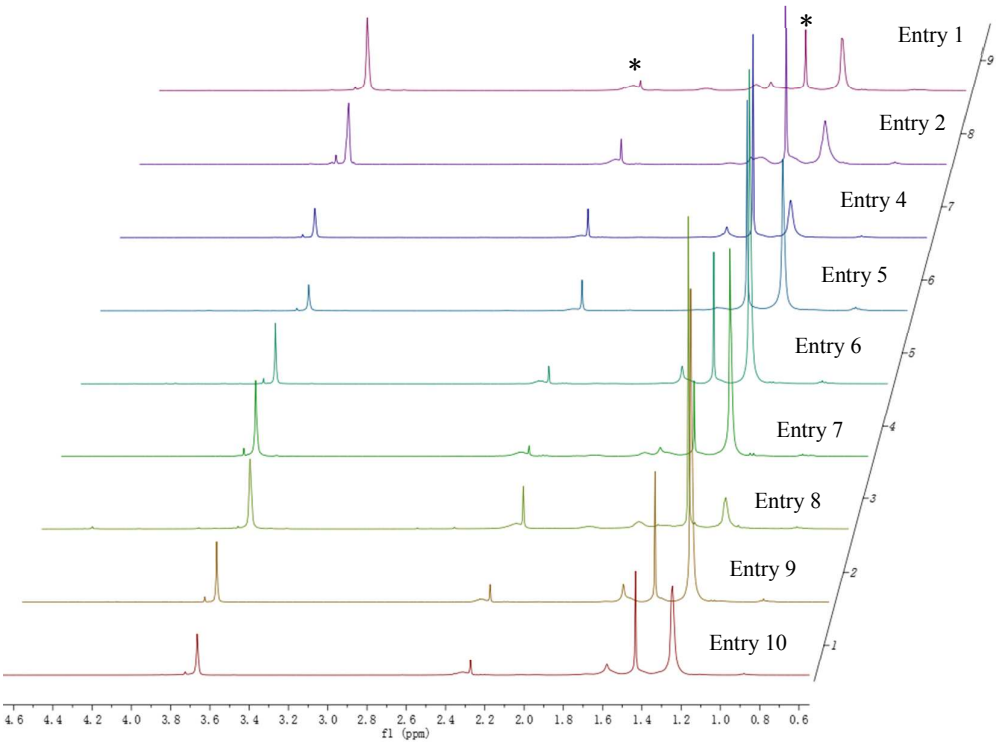

Figure S33. ^{1}H NMR spectrum of the E-MA copolymer from table 2. * BHT

2.4 DSC of polymer and copolymer.

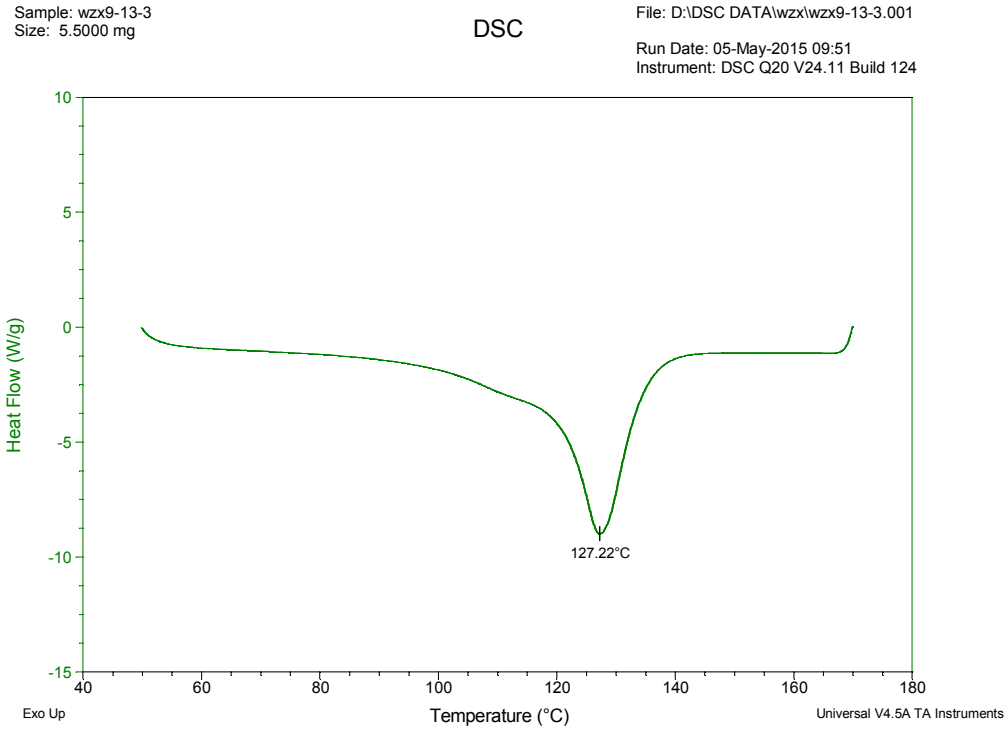

Figure S34. DSC of the polymer from table 1, entry 3.

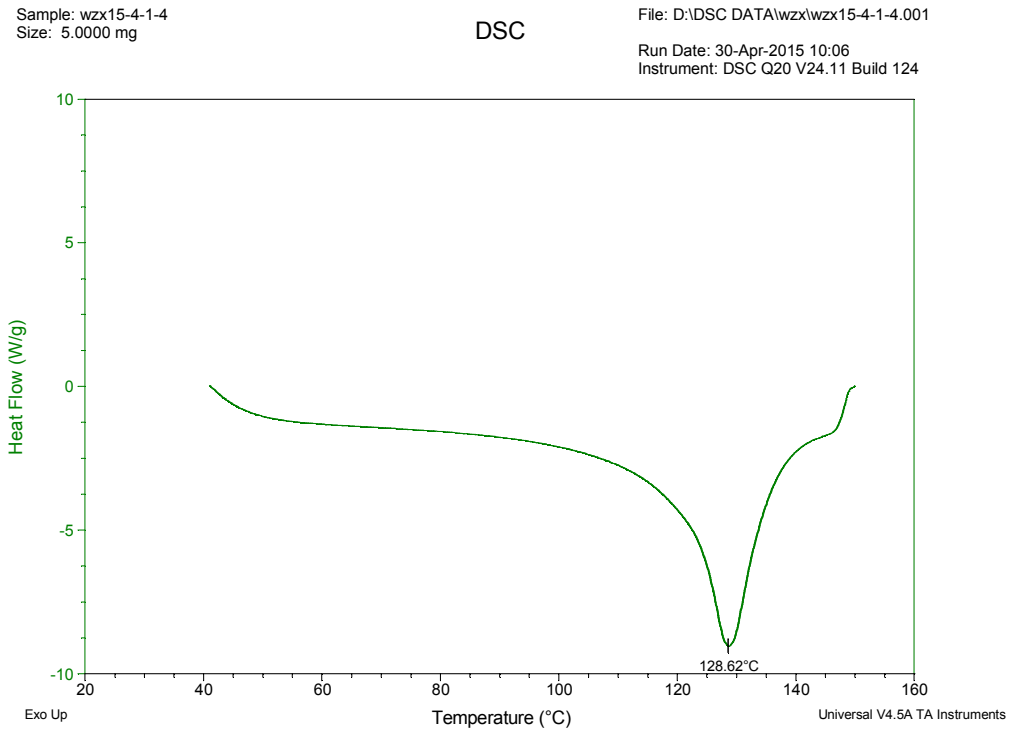

Figure S35. DSC of the polymer from table 1, entry 16.

2.Picture of the polyethylene.

Figure S36. The polyethylene generated by complex **2** (left) and complex **2'** (left).

3. X-ray Crystallography of 1, 3.

Experimental for 1

Single crystals of $C_{25}H_{25}O_4PPdS_2$ **1** were **yellow**. A suitable crystal was selected and **mounted** on a diffractometer. The crystal was kept at 290(2) K during data collection. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimisation.

Crystal structure determination of 1

Crystal Data for $C_{25}H_{25}O_4PPdS_2$ (M = 590.94 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 10.73190(10) Å, b = 9.79140(10) Å, c = 24.6354(3) Å, β = 96.1360(10)°, V = 2573.87(5) Å^3, Z = 4, T = 290(2) K, μ(CuKα) = 8.159 mm^{-1}, $Dcalc$ = 1.525 g/cm^3, 10113 reflections measured (8.286° ≤ 2Θ ≤ 139.164°), 4724 unique (R_{int} = 0.0253, R_{sigma} = 0.0349) which were used in all calculations. The final R_1 was 0.0334 (I > 2σ(I)) and wR_2 was 0.0935 (all data).

Refinement model description

Number of restraints - 0, number of constraints - unknown.
Details:
N/A

This report has been created with Olex2, compiled on 2015.01.26 svn.r 3150 forOlexSys. Please let us know if there are any errors or if you would like to have additional features.

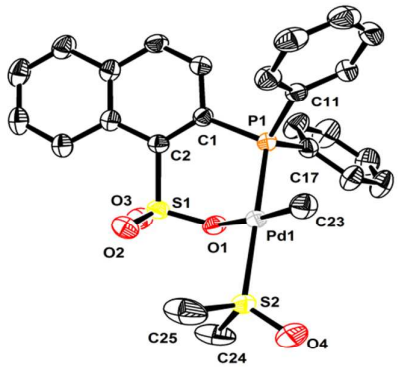

Figure S37. Molecular structure of **1.**

Table S1. Crystal data and structure refinement for **1**.

data	**1**
Identification code	wu-ph
Empirical formula	C25H25O4PPdS2
Formula weight	590.94
Temperature/K	290(2)
Crystal system	monoclinic
Space group	P21/c
a/Å	10.73190(10)
b/Å	9.79140(10)
c/Å	24.6354(3)
α/°	90
β/°	96.1360(10)
γ/°	90
Volume/Å3	2573.87(5)
Z	4
ρcalcg/cm3	1.525
μ/mm‐1	8.159
F(000)	1200.0
Crystal size/mm3	0.410 × 0.400 × 0.360
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.286 to 139.164
Index ranges	-13 ≤ h ≤ 12, -7 ≤ k ≤ 11, -26 ≤ l ≤ 29
Reflections collected	10113
Independent reflections	4724 [Rint = 0.0253, Rsigma = 0.0349]
Data/restraints/parameters	4724/0/301
Goodness-of-fit on F2	1.037
Final R indexes [I>=2σ (I)]	R1 = 0.0334, wR2 = 0.0910
Final R indexes [all data]	R1 = 0.0357, wR2 = 0.0935
Largest diff. peak/hole / e Å-3	0.53/-0.73

Experimental for 3

Single crystals of $C_{25}H_{37}O_4PPdS_2$ **3** were **yellow**. A suitable crystal was selected and **mounted** on a diffractometer. The crystal was kept at 291(2) K during data collection. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimisation.

Crystal structure determination of 3

Crystal Data for $C_{25}H_{37}O_4PPdS_2$ (M =603.03 g/mol): monoclinic, space group I2/a (no. 15), a = 21.5627(6) Å, b = 12.9662(4) Å, c = 19.8892(7) Å, β = 103.413(4)°, V = 5409.1(3) Å^3, Z = 8, T = 291(2) K, μ(CuKα) = 7.766 mm^{-1}, $Dcalc$ = 1.481 g/cm^3, 9193

reflections measured (8.016° ≤ 2Θ ≤ 139.318°), 4960 unique (R_{int} = 0.0311, R_{sigma} = 0.0459) which were used in all calculations. The final R_1 was 0.0698 (I > 2σ(I)) and wR_2 was 0.2060 (all data).

Refinement model description

Number of restraints - 0, number of constraints - unknown.

Details:

N/A

This report has been created with Olex2, compiled on 2015.01.26 svn.r3150 for OlexSys. Please let us know if there are any errors or if you would like to have additional features.

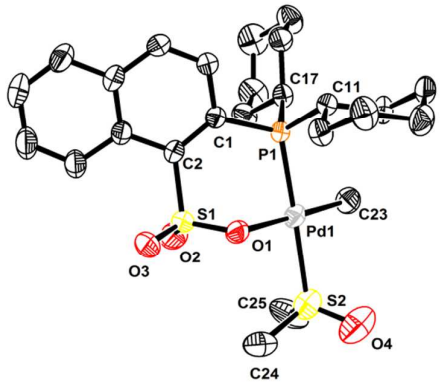

Figure S38. Molecular structure of **3.**

Table S2. Crystal data and structure refinement for **3**.

data	**3**
Identification code	wu-cy
Empirical formula	$C_{25}H_{37}O_4PPdS_2$
Formula weight	603.03
Temperature/K	291(2)
Crystal system	monoclinic
Space group	I2/a
a/Å	21.5627(6)
b/Å	12.9662(4)
c/Å	19.8892(7)
α/°	90
β/°	103.413(4)
γ/°	90
Volume/Å3	5409.1(3)
Z	8
ρcalcg/cm3	1.481
μ/mm⍰1	7.766
F(000)	2496.0

Crystal size/mm3	0.360 × 0.320 × 0.310
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.016 to 139.318
Index ranges	-24 ≤ h ≤ 26, -15 ≤ k ≤ 12, -24 ≤ l ≤ 22
Reflections collected	9193
Independent reflections	4960 [Rint = 0.0311, Rsigma = 0.0459]
Data/restraints/parameters	4960/0/301
Goodness-of-fit on F2	1.045
Final R indexes [I>=2σ (I)]	R1 = 0.0698, wR2 = 0.1904
Final R indexes [all data]	R1 = 0.0812, wR2 = 0.2060

References

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. G. M. Sheldrick, SHELXL 97, Programs for structure refinement, Universität Göttingen, 1997.
3. Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.