Electronic supplementary information

Synthesis of geometry-controlled platinum-containing conjugated polymers bearing optically active bidentate phosphine ligands

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Experimental section

Measurements

Melting points (mp) were measured on a Yanaco micro melting apparatus. IR spectra were measured on a JASCO FT/IR-4100 spectrophotometer. ^{1}H (400 MHz), ^{13}C (100 MHz), and ^{31}P (162 MHz) NMR spectra were acquired using JEOL ECS-400 and ESZ-400 spectrometers. Mass spectrum of **3** was obtained with a SHIMADZU LCMS-IT-TOF mass spectrometer under the following conditions: ionization method, electrospray ionization (ESI); solvent, acetonitrile; mass range, *m*/*z* 100–2000; mode, positive or negative; spray voltage, 4.5 kV (positive mode); nebulizer gas flow rate; 1.5 L/min; CDL temperature, 200 °C; heated block temperature, 200 °C; ion source pressure, 70 Pa; ion trap pressure, 1.7×10^{-2} Pa; TOF pressure, 1.2×10^{-4} Pa; resolution, >10,000, calibrated and tuned using an available standard solution of trifluoroacetic acid. Mass spectra of the other samples were acquired with a BRUKER Compact QTOF spectrometer under the following conditions: ionization method, ESI; solvent, acetonitrile; mass range, *m*/*z* = 300–2000; mode, positive or negative; spray voltage, 4.5 kV (positive mode), –3.5 kV (negative mode); nebulizer gas flow rate; 1.5 L/min; CDL temperature, 200 °C; heated block temperature, 200 °C; ion source pressure, 70 Pa, ion trap pressure, 1.7×10^{-2} Pa; TOF pressure, 1.7×10^{-2} Pa; resolution, >10,000, calibrated and tuned using an available standard solution of Low Concentration Tuning mix (G1969-85000) and sodium formate solution (5 mM) in acetonitrile/water = 1/1 (v/v). Number-average molecular weight (M_n) and polydispersity ($Đ$) values of polymers were determined by size exclusion chromatography (SEC) eluted with LiBr solution (10 mM) in *N,N*-dimethylformamide (DMF) with Shodex TSK polystyrene gel α-M and GMHXL columns calibrated by polystyrene standards at 40 °C using JASCO SEC system consisting of RI-930, UV-4570, PU-4580, DG-2080-53, CO-965, LC-NetII/ADC, and chloroform ($CHCl_3$) with Shodex K-803 and K-804 columns calibrated by polystyrene standards at 40 °C using SEC TOSOH system consisting of RI-930, UV-2075, PU-980, DG-2080-53, CO-4060. CD and UV–vis absorption spectra were recorded on a JASCO J-820

spectropolarimeter. Dynamic light scattering (DLS) measurements were performed using a square glass cell on a Malvern Instruments Zetasizer Nano ZSP at 20 °C. Single crystal X-ray analysis was performed using a Rigaku RAXIS imaging plate area detector with graphite-monochromated MoKα radiation (λ = 0.71075 Å). The crystal was mounted on a nylon loop at –150 °C. The structure was solved and refined using the Olex2[S1] and SHELX[S2,S3] programs. Crystallographic data for **5** was deposited to the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication number CCDC 2245929.

Materials

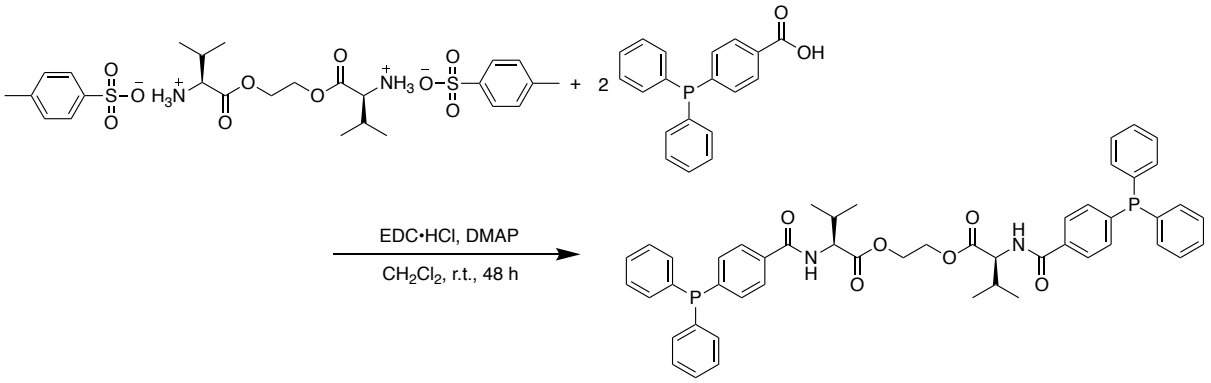
All reagents were commercially obtained from Tokyo Chemical Industry Co., Ltd., Watanabe Chemical Industries, Ltd., Tokuyama, Ltd., FUJIFILM Wako Pure Chemical Co., Apollo Scientific Ltd. and NACALAI TESQUE, INC. Monomers **1** and **5**, and model compound **3** were synthesized according to Schemes S1–S5. Dichloro(1,5-cyclooctadiene)platinum(II) [$PtCl_2$(COD)],[S4] ((4-ethynylphenyl)ethynyl)trimethylsilane,[S5] (2*S*,2'*S*)-1,1'-(ethane-1,2-diylbis(oxy))bis(3-methyl-1-oxobutan-2-aminium) 4-methylbenzenesulfonate,[S6] and tetrakis(triphenylphosphine)palladium(0) [$Pd(PPh_3)_4$][S7] were synthesized according to the literature. 1,4-Diethynylbenzene was purified before use. Solvents used for synthesis under argon were dried over molecular sieves 4A 1/16, and degassed by argon bubbling. The other reagents were used as received without purification.

Computations

DFT and TD-DFT calculations were performed with Gaussian 16:[S8] Fujitsu-Arm-G16 Rev C.01, running on the supercomputer system, Fugaku provided by the RIKEN Center for Computational Science.

Ethane-1,2-diyl (2*S*,2'*S*)-bis(2-(4-(diphenylphosphaneyl)benzamido)-3-methylbutanoate)

A mixture of (2*S*,2'*S*)-1,1'-(ethane-1,2-diylbis(oxy))bis(3-methyl-1-oxobutan-2-aminium) 4-methylbenzenesulfonate (2.59 g, 4.29 mmol), *p*-(diphenylphosphino)benzoic acid (2.50 g, 8.17 mmol), EDC•HCl (1.64 g, 8.58 mmol), DMAP (1.05 g, 8.58 mmol) in CH_2Cl_2 (50 mL) was stirred at room temperature for 48 h. The resulting mixture was sequentially washed with 1 M HCl aq., satd. $NaHCO_3$ aq. and brine. The organic layer was dried over anhydrous $MgSO_4$ and filtered. The solvent was removed by evaporation, and the residual mass was purified by silica gel column chromatography eluted with ethyl acetate/hexane = 2/1 (v/v) to obtain ethane-1,2-diyl (2*S*,2'*S*)-bis(2-(4-(diphenylphosphaneyl)benzamido)-3-methylbutanoate) as a white solid (2.34 g, 2.80 mmol, 68%). Mp: 126–128 °C. IR (KBr): 3427, 3312, 3069, 3052, 2964, 2933, 2874, 1745, 1641, 1597, 1524, 1485, 1434, 1391, 1374, 1312, 1270, 1185, 1156, 1127, 1092, 1068, 1027, 1017, 999, 921, 886, 848, 745, 720, 696, 629, 582 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.73–7.69 (m, 4H, Ar), 7.36–7.28 (m, 24H, Ar), 6.62 (d, J = 8.7 Hz, 2H, –N*H*–), 4.77 (q, J = 4.6 Hz, 2H, –C*H*–), 4.40 (s, 4H, –CH_2–), 2.31–2.23 (m, 2H, –C*H*–), 0.99 (dd, J = 12.1, 7.1 Hz, 12H, –CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.9, 167.2, 142.6, 136.4, 136.3, 134.1, 134.0, 133.9, 133.8, 133.6, 129.2, 128.8, 128.7, 127.1, 127.0, 62.8, 57.5, 31.6, 19.2, 18.0 ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ –4.9 ppm. ESI-MS (*m*/*z*): calcd. 871.2833 ($[C_{50}H_{50}N_2O_6P_2 + Cl]^-$), found 871.3050.



Scheme S1 Synthesis of ethane-1,2-diyl (2*S*,2'*S*)-bis(2-(4-(diphenylphosphaneyl)benzamido)-3-methylbutanoate).

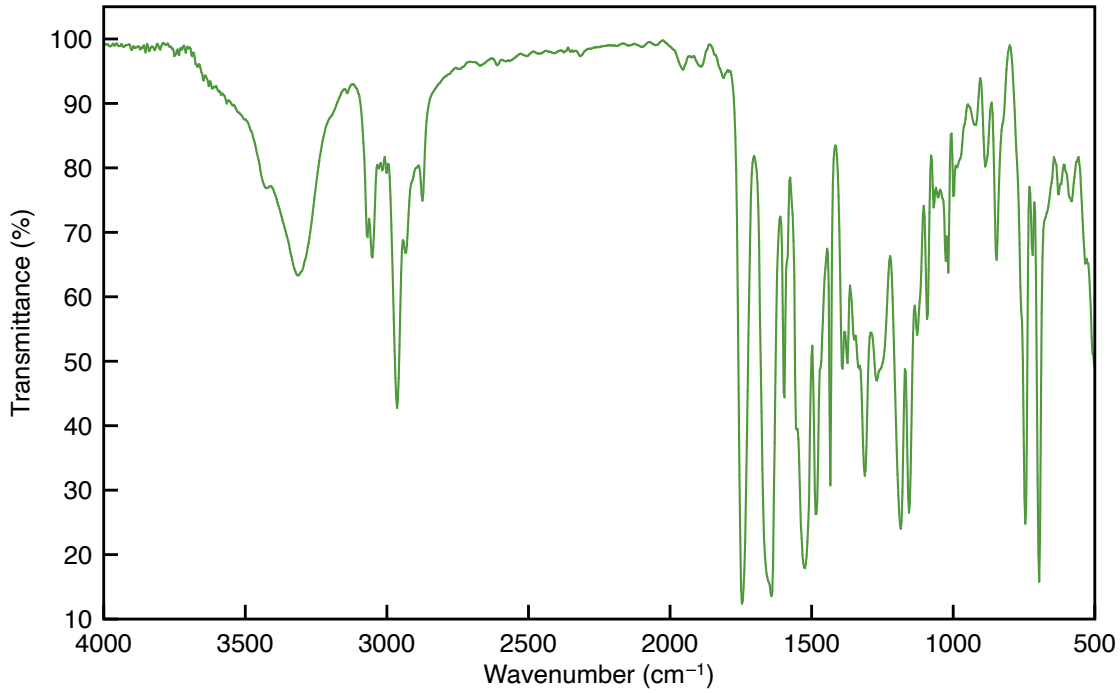


Fig. S1 IR absorption spectrum (KBr pellet) of ethane-1,2-diyl (2*S*,2'*S*)-bis(2-(4-(diphenylphosphaneyl)benzamido)-3-methylbutanoate).

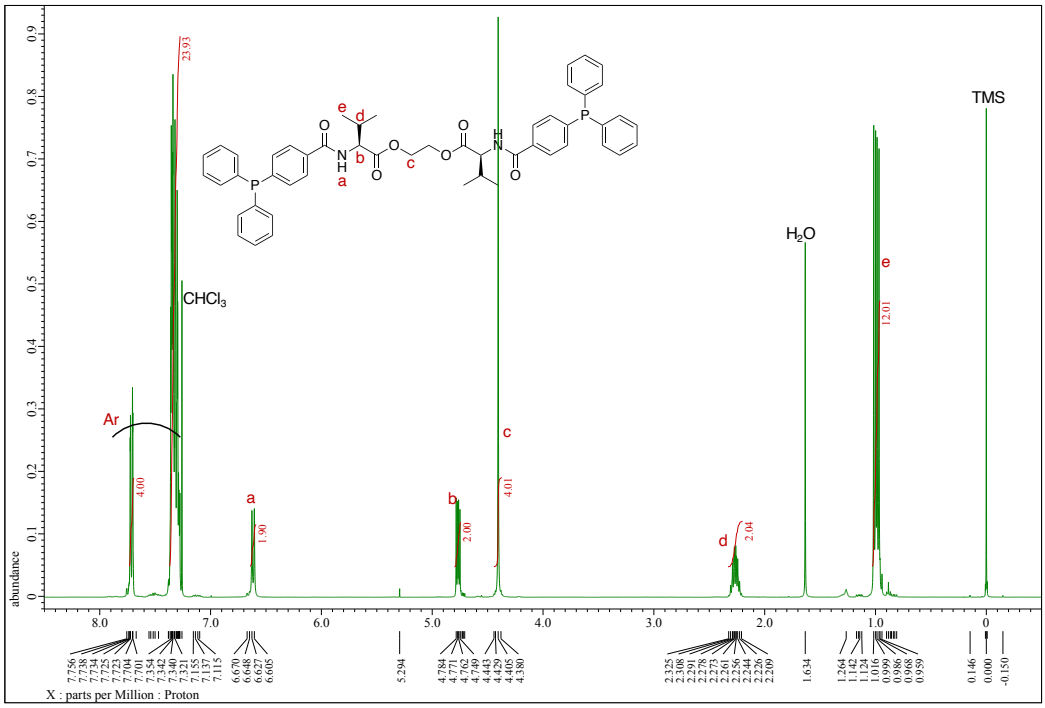


Fig. S2 ^{1}H NMR (400 MHz) spectrum of ethane-1,2-diyl (2*S*,2'*S*)-bis(2-(4-

(diphenylphosphaneyl)benzamido)-3-methylbutanoate) measured in $CDCl_3$.

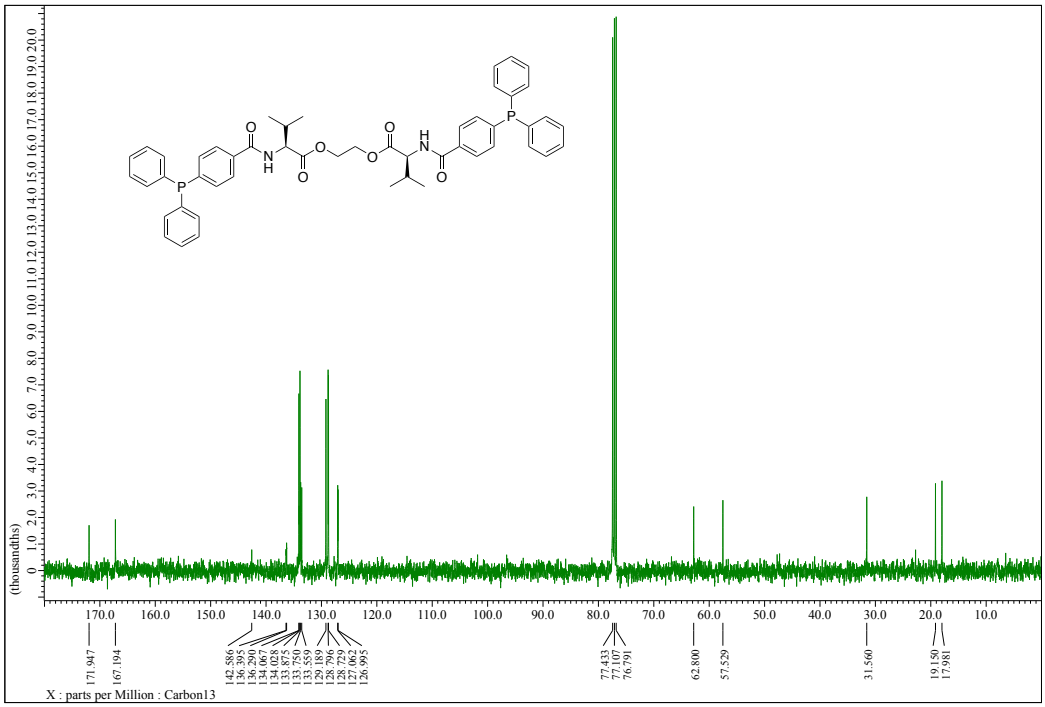


Fig. S3 ^{13}C NMR (100 MHz) spectrum of ethane-1,2-diyl (2*S*,2'*S*)-bis(2-(4-(diphenylphosphaneyl)benzamido)-3-methylbutanoate) measured in $CDCl_3$.

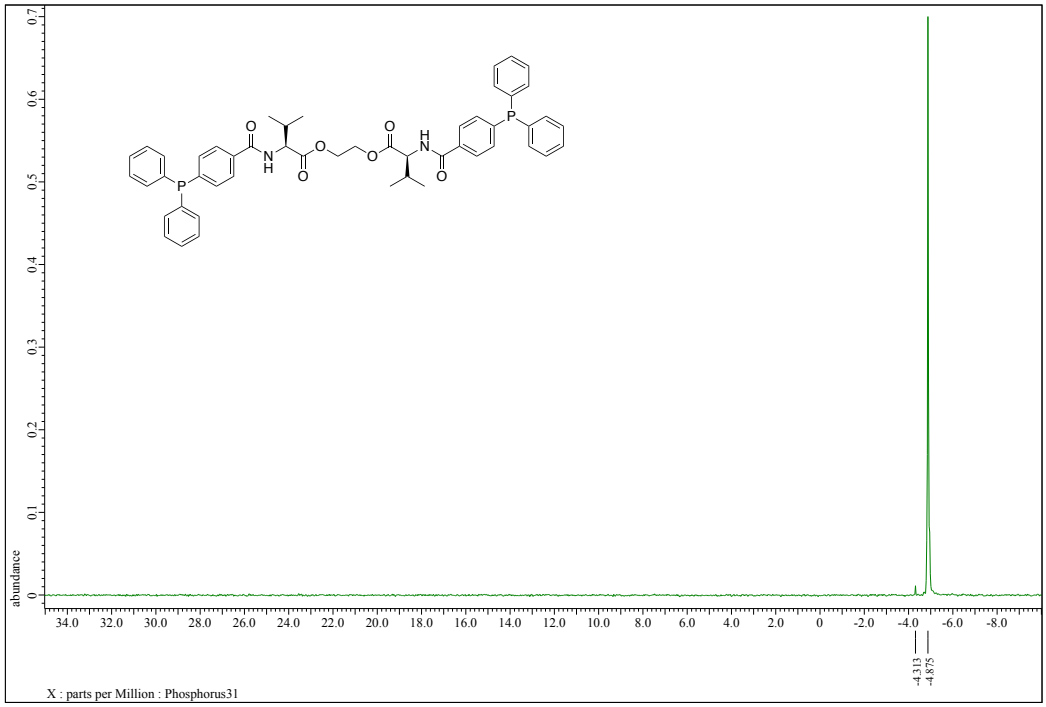


Fig. S4 ^{31}P NMR (162 MHz) spectrum of ethane-1,2-diyl (2*S*,2'*S*)-bis(2-(4-

(diphenylphosphaneyl)benzamido)-3-methylbutanoate) measured in $CDCl_3$.

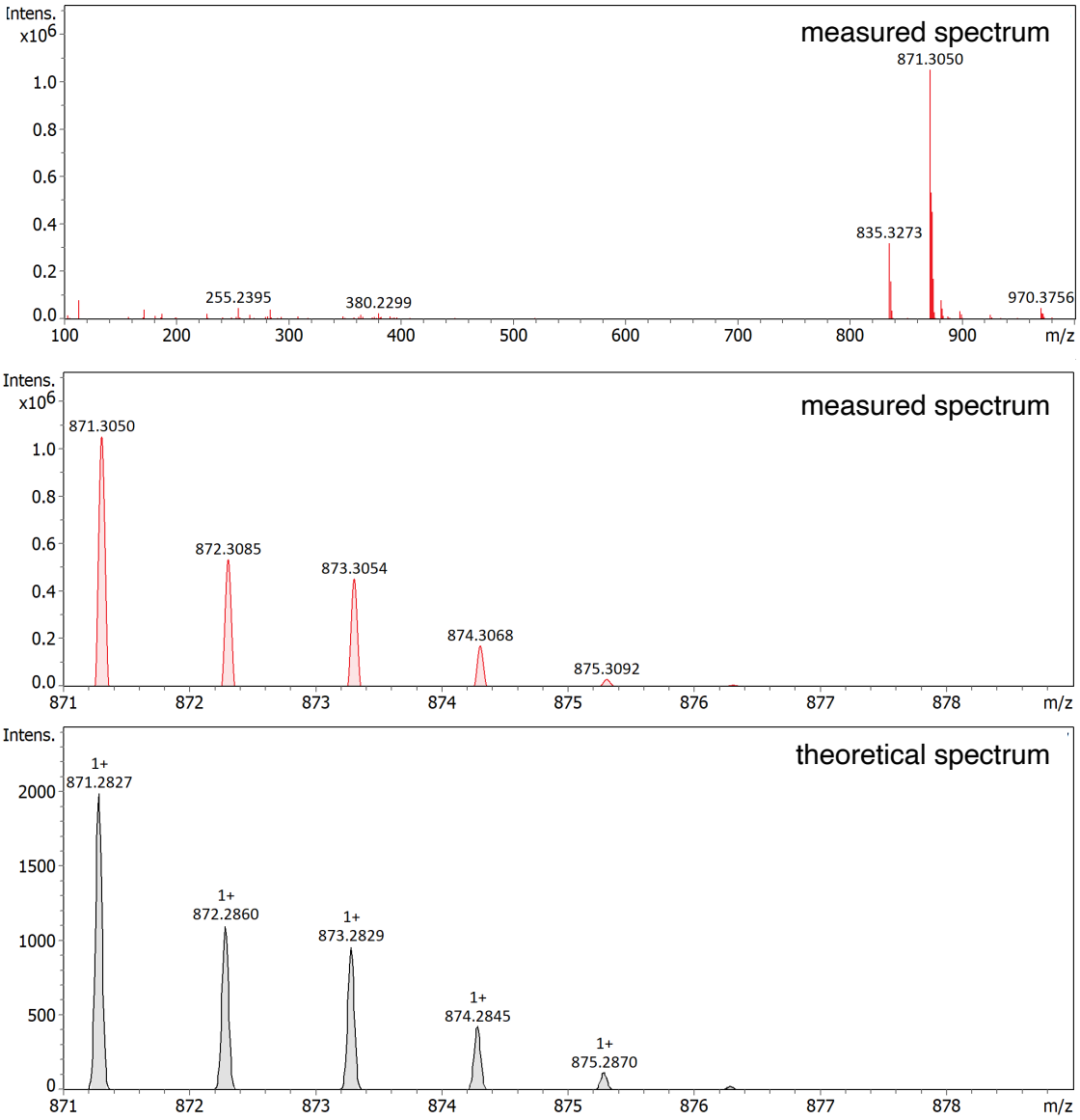
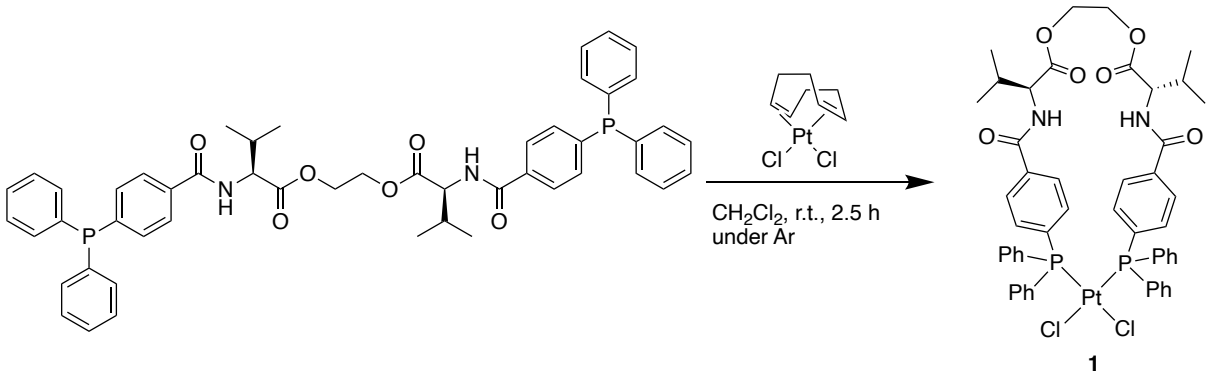


Fig. S5 ESI-MS charts of ethane-1,2-diyl (2*S*,2'*S*)-bis(2-(4-(diphenylphosphaneyl)benzamido)-3-methylbutanoate) measured in acetonitrile.

cis-Dichloro(ethane-1,2-diyl (2*S*,2'*S*)-bis(2-(4-(diphenylphosphaneyl)benzamido)-3-methylbutanoate))platinum(II) (1)

Ethane-1,2-diyl (2*S*,2'*S*)-bis(2-(4-(diphenylphosphaneyl)benzamido)-3-methylbutanoate) (0.835 g, 1.00 mmol), $PtCl_2$(COD) (0.374 g, 1.00 mmol) and CH_2Cl_2 (50 mL) were sequentially fed into a flask filled with argon, and the resulting mixture was stirred at room temperature for

2.5 h. The reaction mixture was removed by evaporation, and the residual mass was purified by preparative HPLC at flow rate of 3.0 mL/min, to obtain **1** as a white solid (0.705 g, 0.639 mmol, 64%). No mp was observed up to 218 °C. IR (KBr): 3440, 3310, 3057, 2964, 2878, 1740, 1658, 1524, 1486, 1441, 1386, 1311, 1271, 1191, 1160, 1095, 1029, 990, 849, 751, 698, 553, 523 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (dd, J = 11.0, 8.2 Hz, 4H, Ar), 7.77 (dd, J = 11.0, 8.2 Hz, 4H, Ar), 7.47 (t, J = 7.3 Hz, 4H, Ar), 7.36 (q, J = 7.2 Hz, 8H, Ar), 7.23 (d, J = 8.2 Hz, 2H, –N*H*–), 7.19 (d, J = 7.3 Hz, 4H, Ar), 6.95 (t, J = 8.9 Hz, 4H, Ar), 4.61 (dd, J = 8.2, 5.9 Hz, 2H, –C*H*–), 4.48 (t, J = 10.5 Hz, 2H, –CH_2–), 4.38 (t, J = 10.7 Hz, 2H, –CH_2–), 2.34–2.26 (m, 2H, –C*H*–), 1.04 (t, J = 6.4 Hz, 12H, –CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.1, 167.9, 136.1, 136.0–135.8 (m), 132.8–132.6 (m), 131.8, 131.6, 128.4–128.1 (m), 126.7–126.5 (m), 62.3, 59.0, 30.8, 19.3, 18.5 ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ 15.0 (s, $J_{P–Pt}$ = 3658 Hz) ppm. ESI-MS (m/z): calcd. 1136.1857 ($[C_{50}H_{50}N_2O_6P_2Cl_2Pt + Cl]^-$), found 1136.2237.



Scheme S2 Synthesis of **1**.

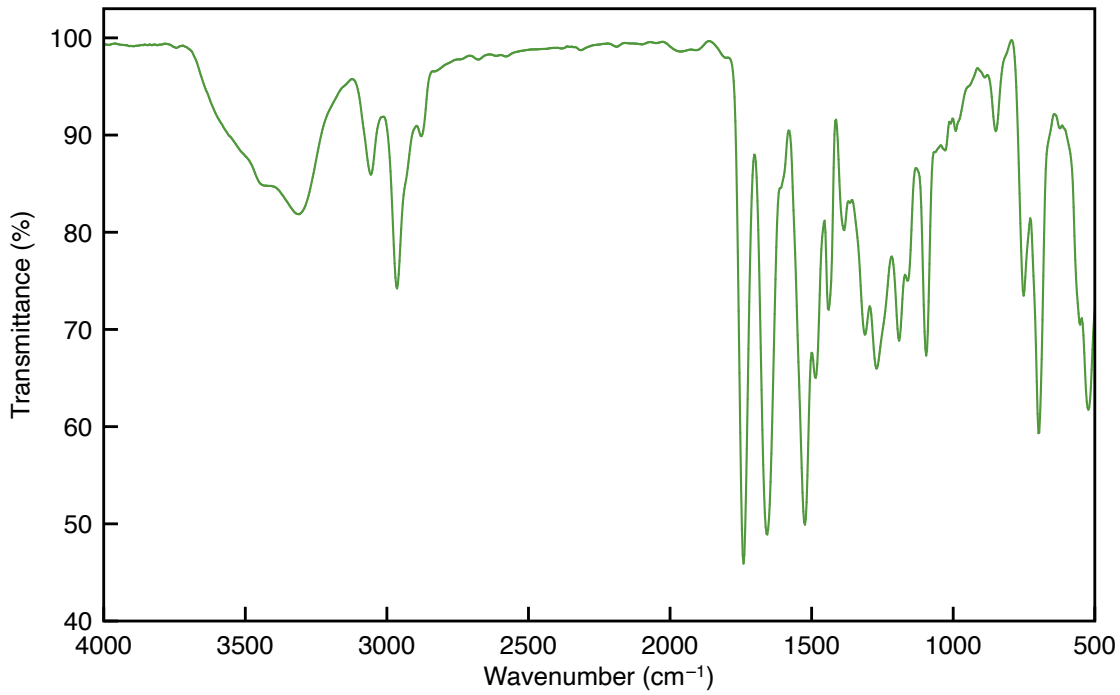


Fig. S6 IR absorption spectrum (KBr pellet) of **1**.

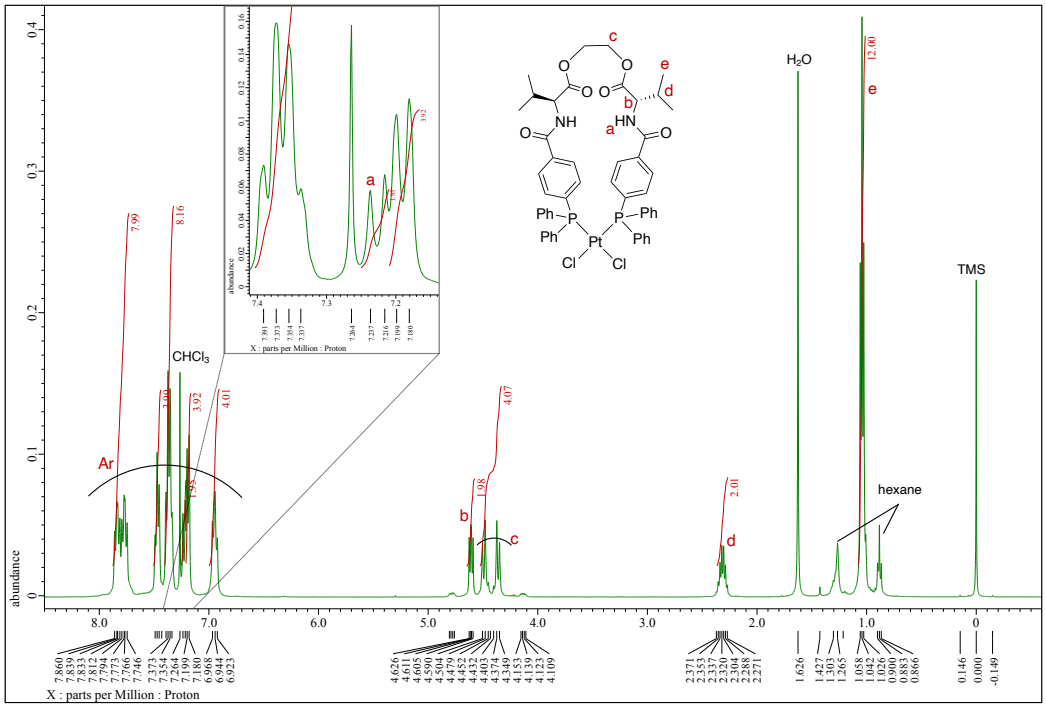


Fig. S7 ^{1}H NMR (400 MHz) spectrum of **1** measured in $CDCl_3$.

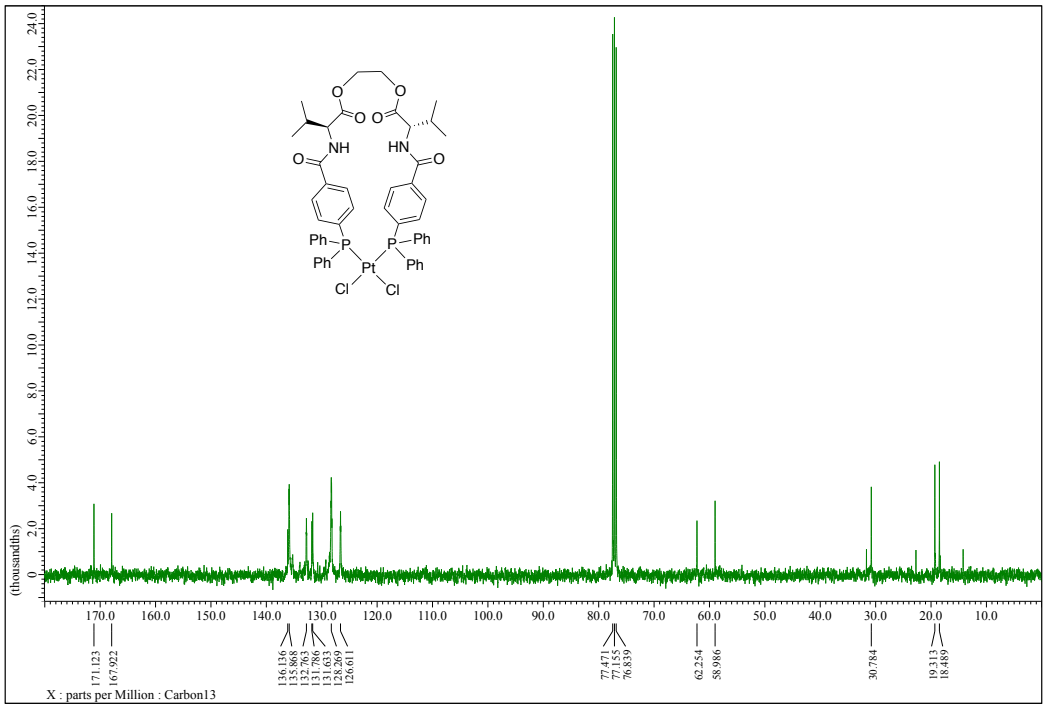


Fig. S8 ^{13}C NMR (100 MHz) spectrum of **1** measured in $CDCl_3$.

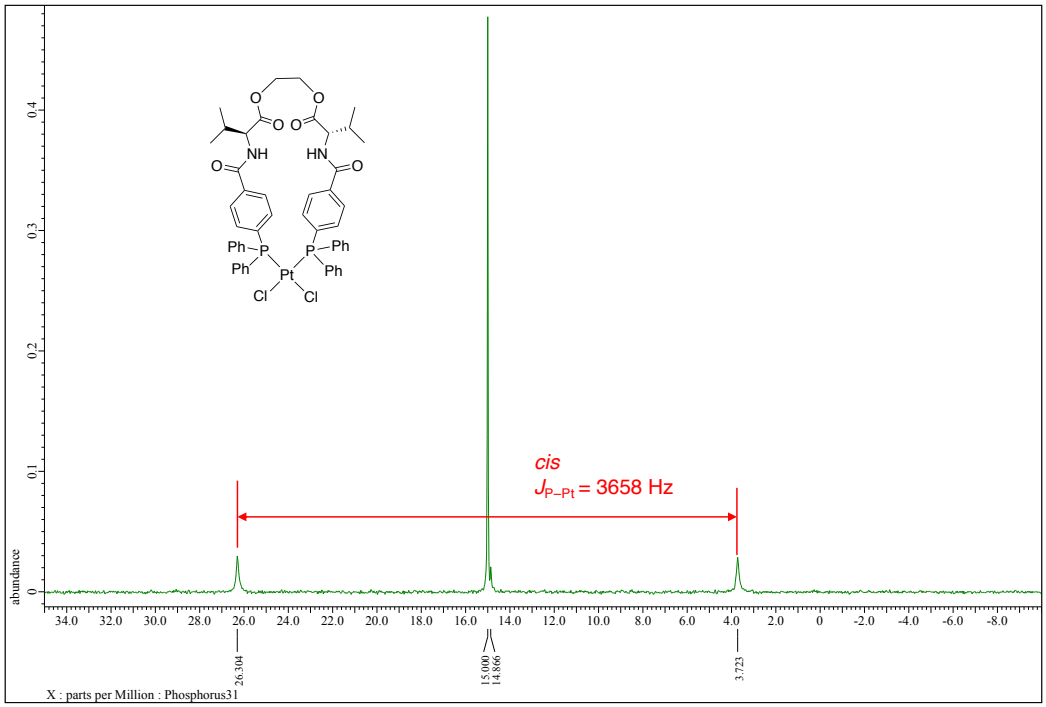


Fig. S9 ^{31}P NMR (162 MHz) spectrum of **1** measured in $CDCl_3$.

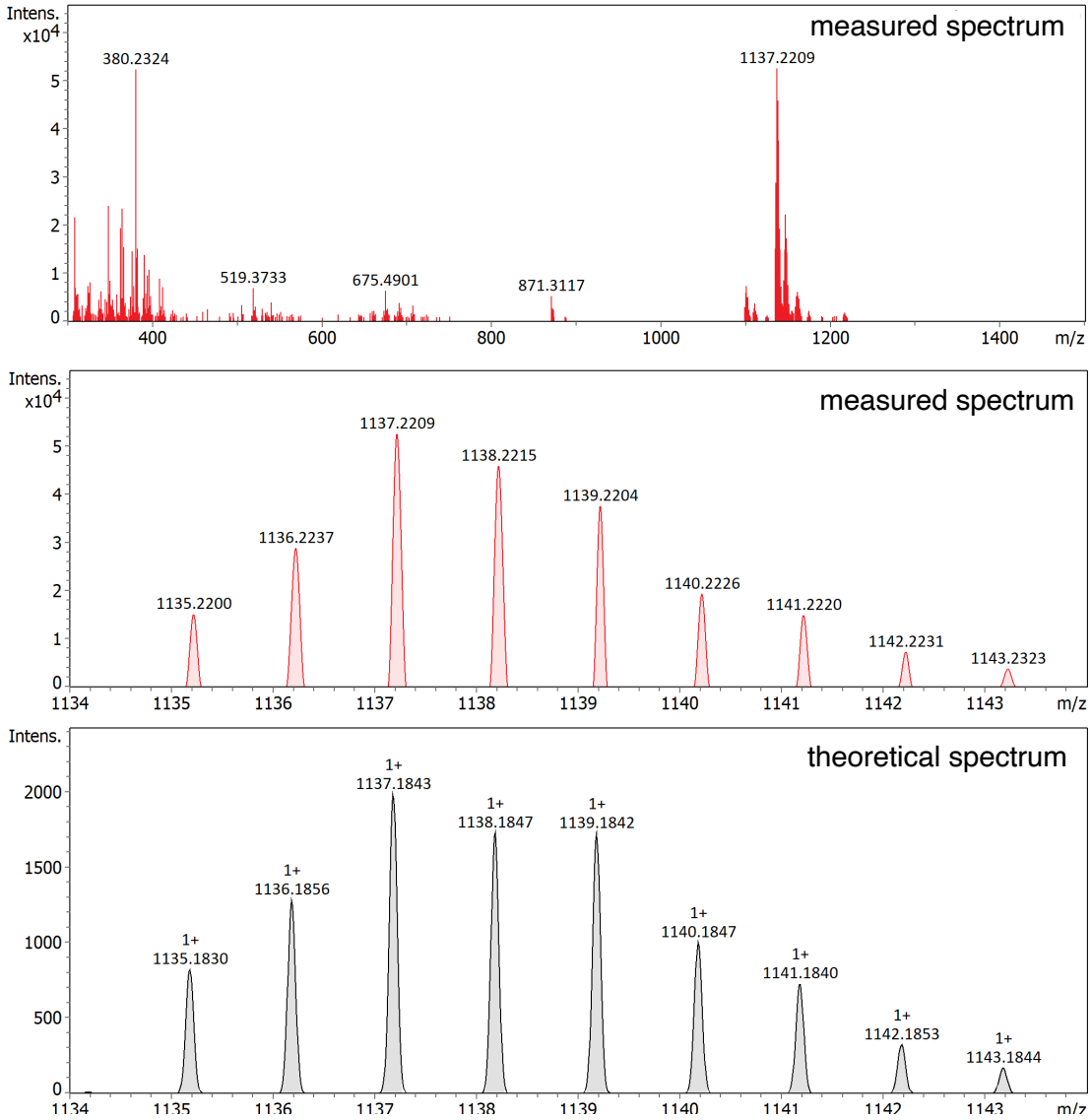
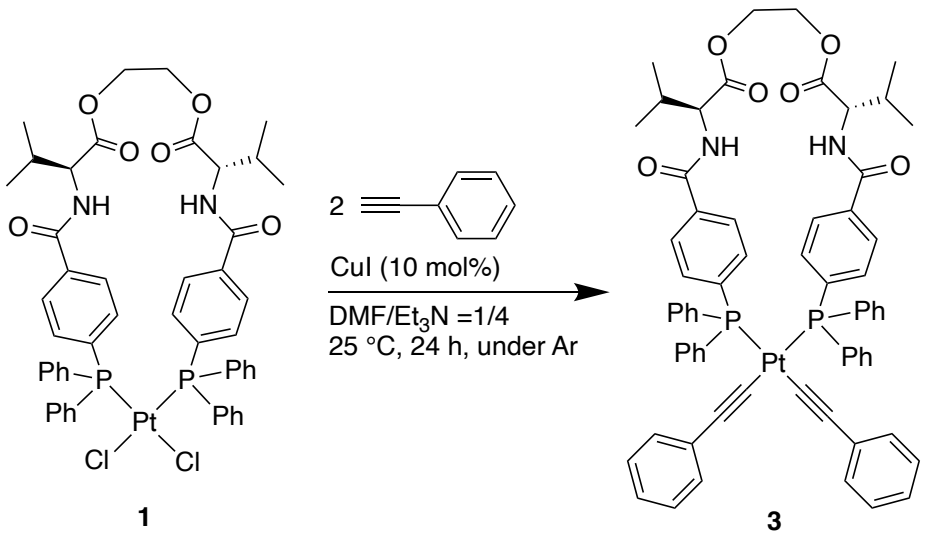


Fig. S10 ESI-MS charts of **1** measured in acetonitrile.

Cis-bis(phenylethynyl)(ethane-1,2-diyl (2*S*,2'*S*)-bis(2-(4-(diphenylphosphaneyl)benzamido)-3-methylbutanoate))platinum(II) (3)

Compound **1** (0.221 g, 0.200 mmol), ethynylbenzene (44.0 μL, 0.4000 mmol), DMF (4.00 mL) and Et_3N (14.0 mL) were sequentially fed into a Schlenk tube filled with argon. A solution of CuI (3.80 mg, 20.0 μmol) in Et_3N (2.00 mL) was added to the Schlenk tube, and the resulting mixture was stirred at 25 °C for 24 h. CH_2Cl_2 (100 mL) was added to the reaction mixture, and the resulting mixture was sequentially washed with satd. NH_4Cl aq. and brine. The organic layer

was dried over anhydrous $MgSO_4$ and filtered. The solvent was removed by evaporation, and the residual mass was purified by silica gel column chromatography eluted with ethyl acetate/hexane = 4/5 (v/v) to obtain **3** as a white solid (0.194 g, 0.157 mmol, 79%). No mp was observed up to 160 °C. IR (KBr): 3432, 3304, 3056, 2964, 2880, 2122, 1741, 1658, 1598, 1522, 1488, 1442, 1384, 1313, 1271, 1193, 1159, 1095, 1025, 967, 909, 847, 753, 696, 618, 520 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.80 (q, J = 9.1 Hz, 8H, Ar), 7.39 (q, J = 6.1 Hz, 4H, Ar), 7.31 (t, J = 7.5 Hz, 8H, Ar), 7.18 (d, J = 6.9 Hz, 4H, Ar), 7.09 (d, J = 8.2 Hz, 2H, –N*H*–), 7.00–6.96 (m, 10H, Ar), 6.77–6.75 (m, 4H, Ar), 4.62 (dd, J = 8.5, 6.2 Hz, 2H, –C*H*–), 4.49 (t, J = 10.7 Hz, 2H, –CH_2–), 4.39 (t, J = 10.7 Hz, 2H, –CH_2–), 2.34–2.26 (m, 2H, –C*H*–), 1.05 (dd, J = 6.9, 4.6 Hz, 12H, –CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3, 168.3, 135.9–135.6 (m), 135.5, 133.0–132.8 (m), 131.7, 130.9, 130.8, 128.3–128.0 (m) 127.1, 126.4–126.2 (m), 125.2, 62.3, 58.7, 30.9, 19.4, 18.3 ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ 17.7 (s, $J_{P–Pt}$ = 2317 Hz) ppm. ESI-MS (*m*/*z*): calcd. 1234.3657 ($[C_{66}H_{60}N_2O_6P_2Pt + H]^+$), found 1234.3593.



Scheme S3 Synthesis of **3**.

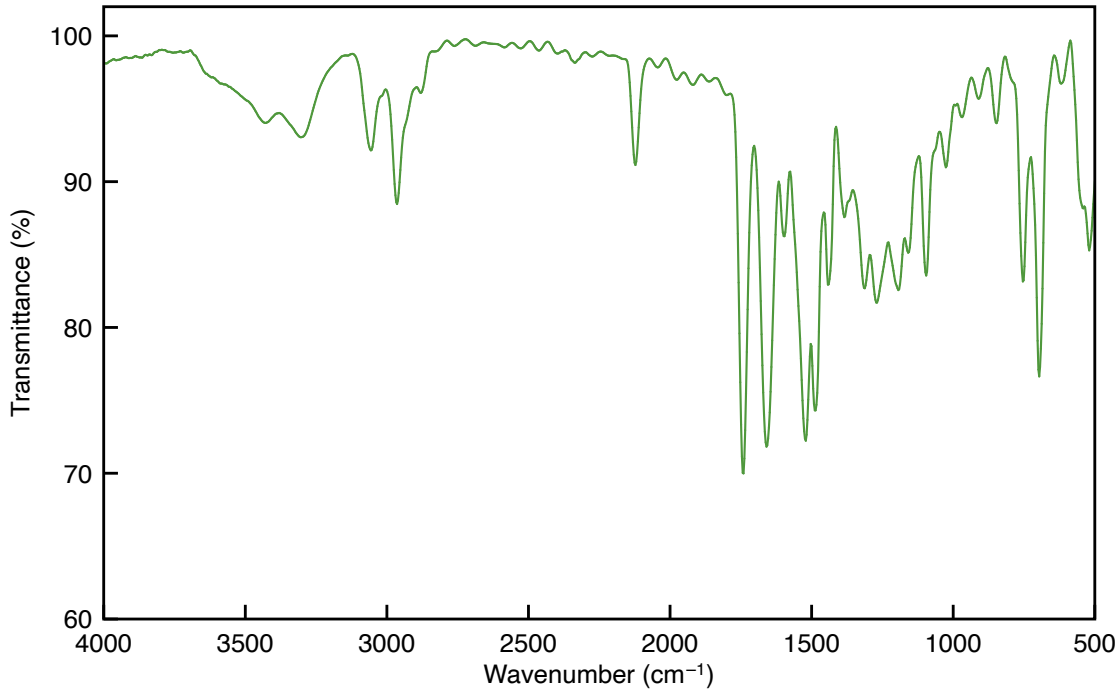


Fig. S11 IR absorption spectrum (KBr pellet) of **3**.

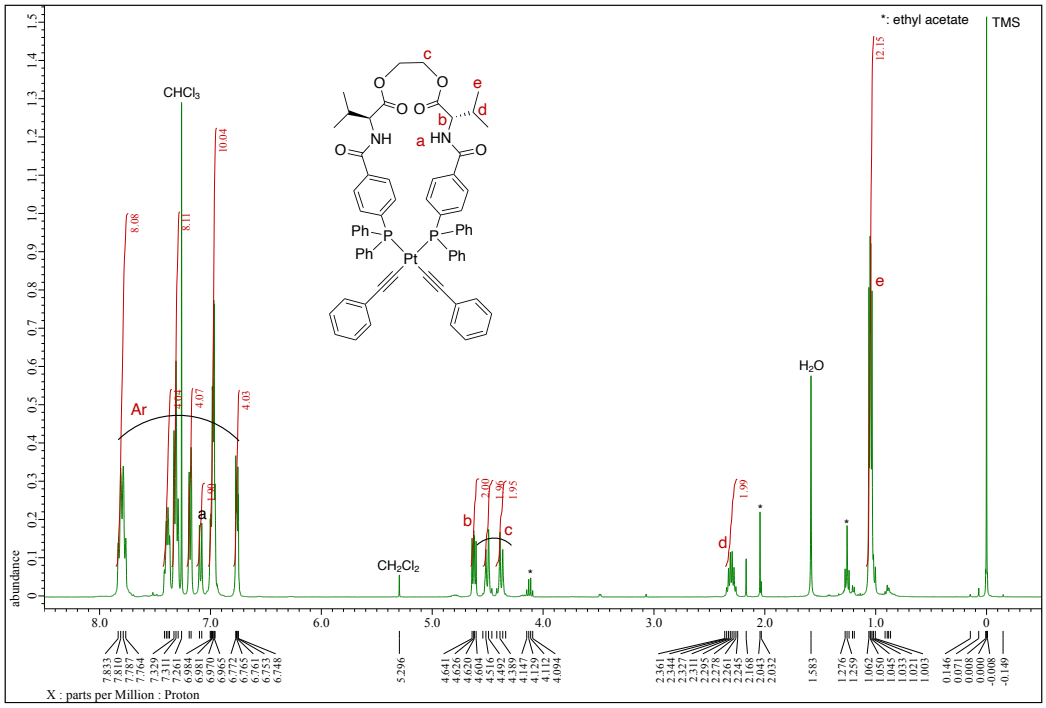


Fig. S12 ^{1}H NMR (400 MHz) spectrum of **3** measured in $CDCl_3$.

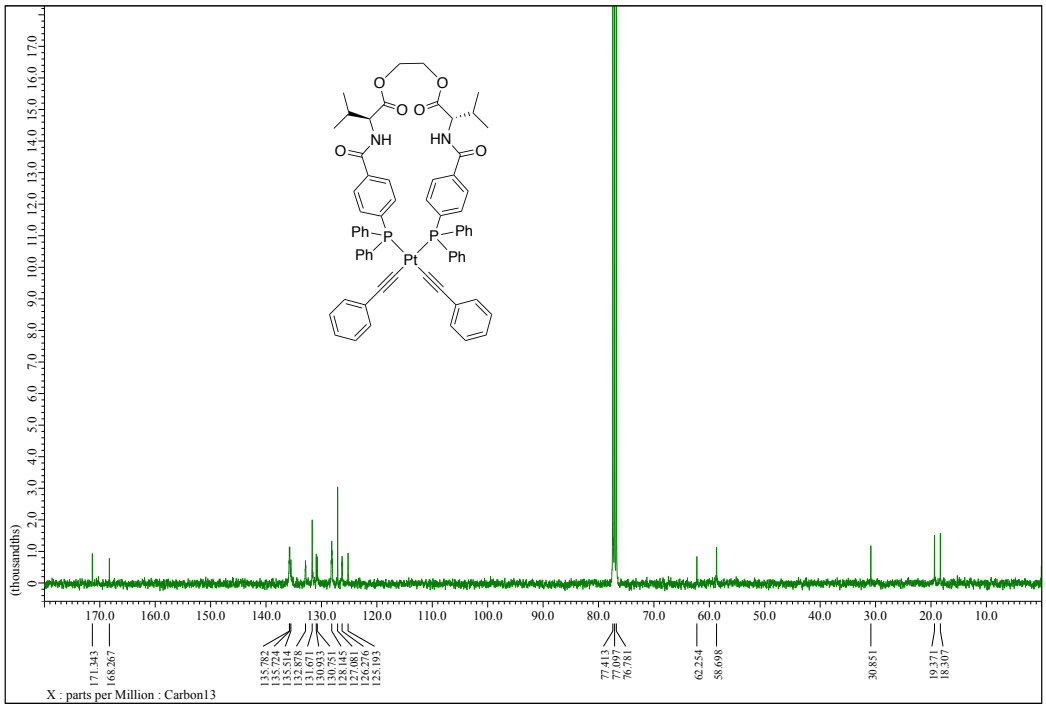


Fig. S13 ^{13}C NMR (100 MHz) spectrum of **3** measured in $CDCl_3$.

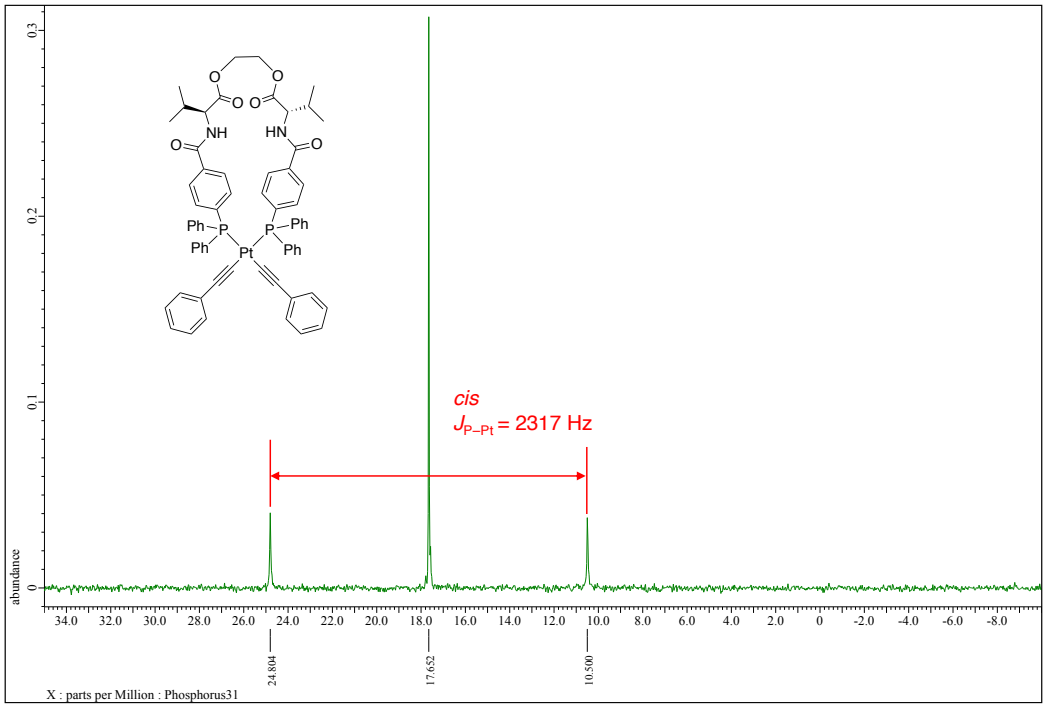


Fig. S14 ^{31}P NMR (162 MHz) spectrum of **3** measured in $CDCl_3$.

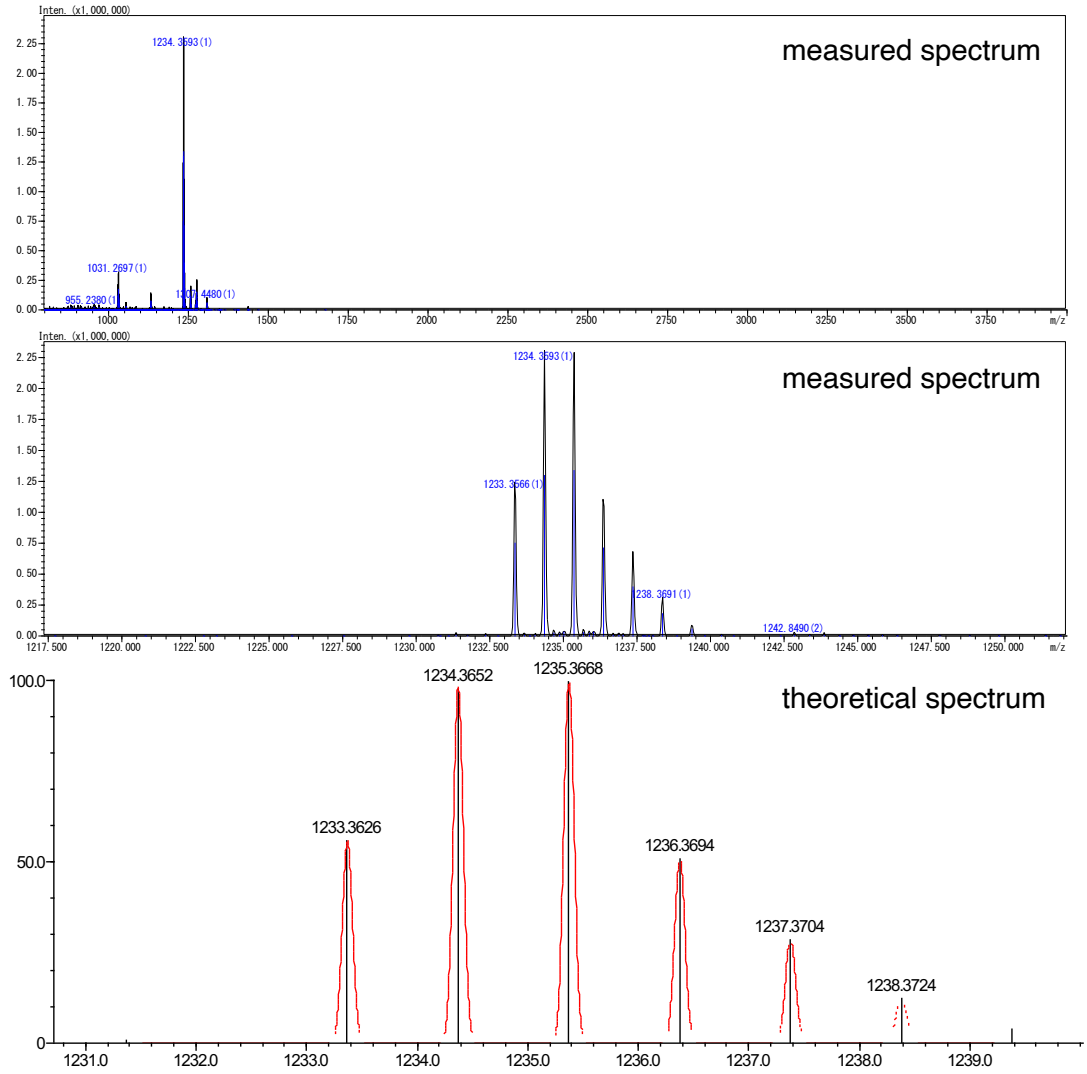
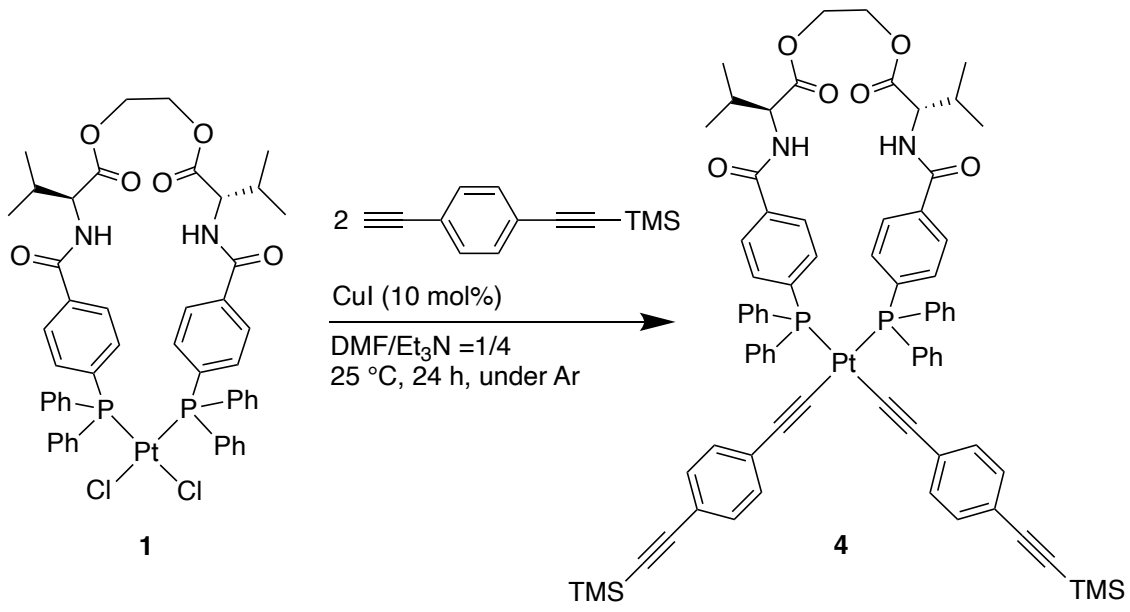


Fig. S15 ESI-MS charts of **3** measured in acetonitrile.

Cis-bis((4-(trimethylsilylethynyl)phenyl)ethynyl)(ethane-1,2-diyl (2S,2'S)-bis(2-(4-(di-phenylphosphaneyl)benzamido)-3-methylbutanoate))platinum(II) (4)

Compound **1** (0.208 g, 0.189 mmol), ((4-ethynylphenyl)ethynyl)trimethylsilane (74.8 mg, 0.377 mmol), DMF (3.72 mL) and Et_3N (13.2 mL) were sequentially fed into a Schlenk tube filled with argon. 1.51 mL of solution of CuI (11.4 mg, 60.0 μmol) in Et_3N (6.00 mL) was added to the Schlenk tube, and the resulting mixture was stirred at 25 °C for 24 h. $CHCl_3$ (50 mL) was added to the reaction mixture, and the resulting mixture was sequentially washed with satd. NH_4Cl aq. and brine. The organic layer was dried over anhydrous $MgSO_4$ and filtered. The

solvent was removed by evaporation, and the residual mass was purified by silica gel column chromatography eluted with ethyl acetate/hexane = 4/5 (v/v) to obtain **4** as a pale yellow solid (0.226 g, 0.158 mmol, 84%). No mp was observed up to 165 °C. IR (KBr): 3439, 3075, 3057, 3031, 2961, 2930, 2898, 2876, 2151, 2119, 1743, 1663, 1599, 1517, 1491, 1437, 1392, 1373, 1311, 1270, 1249, 1221, 1188, 1158, 1097, 1058, 1017, 1000, 970, 864, 839, 761, 724, 695, 634, 601, 574, 747, 520 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$ without TMS): δ 7.76 (dd, J = 18.3, 10.5 Hz, 8H, Ar), 7.38 (q, J = 6.4 Hz, 4H, Ar), 7.29 (t, J = 7.1 Hz, 8H, Ar), 7.18 (d, J = 7.3 Hz, 4H, Ar), 7.08 (d, J = 8.2 Hz, 6H, Ar and –N*H*–), 6.96 (t, J = 9.0 Hz, 4H, Ar), 6.64 (d, J = 8.2 Hz, 4H, Ar), 4.62 (dd, J = 8.2, 5.9 Hz, 2H, –C*H*–), 4.50 (t, J = 10.7 Hz, 2H, –CH_2–), 4.38 (t, J = 10.8 Hz, 2H, –CH_2–), 2.34–2.26 (m, 2H, –C*H*–), 1.04 (dd, J = 6.6, 4.3 Hz, 12H, –CH_3), 0.20 (t, J = 3.4 Hz, 18H, –CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$ without TMS): δ 171.3, 168.2, 135.6, 132.8, 131.4, 131.0, 130.9, 128.4–128.0 (m), 126.3, 119.5, 105.9, 94.2, 62.3, 58.7, 30.9, 19.4, 18.3, 0.1 ppm. ^{31}P NMR (162 MHz, $CDCl_3$ without TMS): δ 17.5 (s, $J_{P–Pt}$ = 2322 Hz) ppm. ESI-MS (*m*/*z*): calcd. 1424.4287 ($[C_{76}H_{76}N_2O_6P_2Si_2Pt - H]^-$), found 1424.4536.



Scheme S4 Synthesis of **4**.

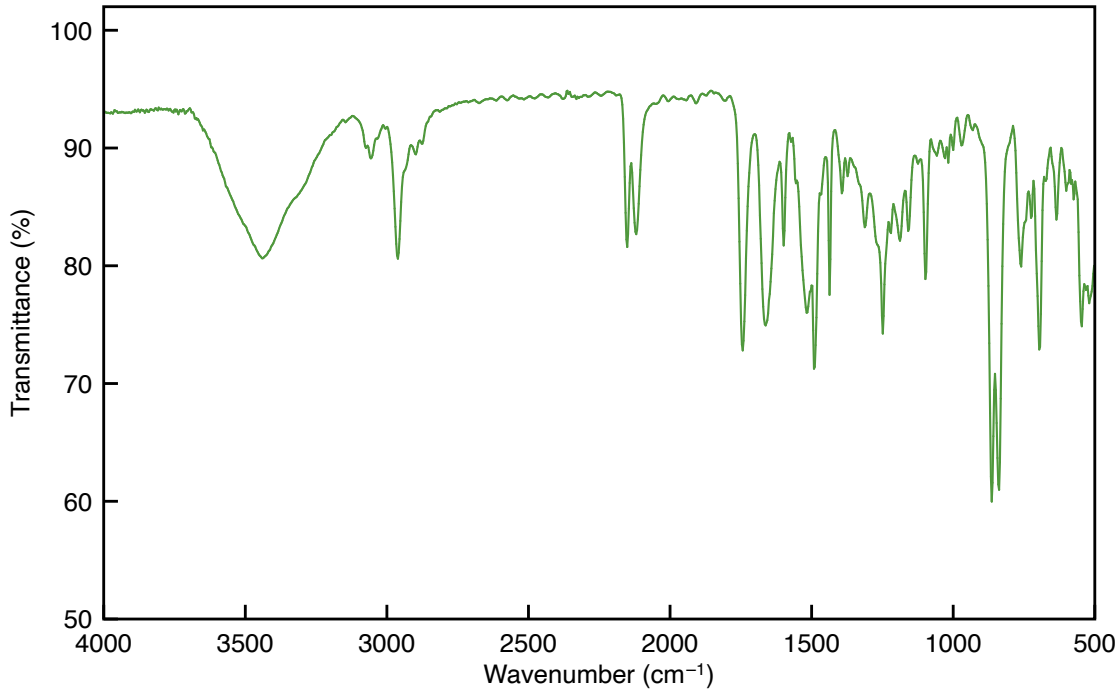


Fig. S16 IR absorption spectrum (KBr pellet) of **4**.

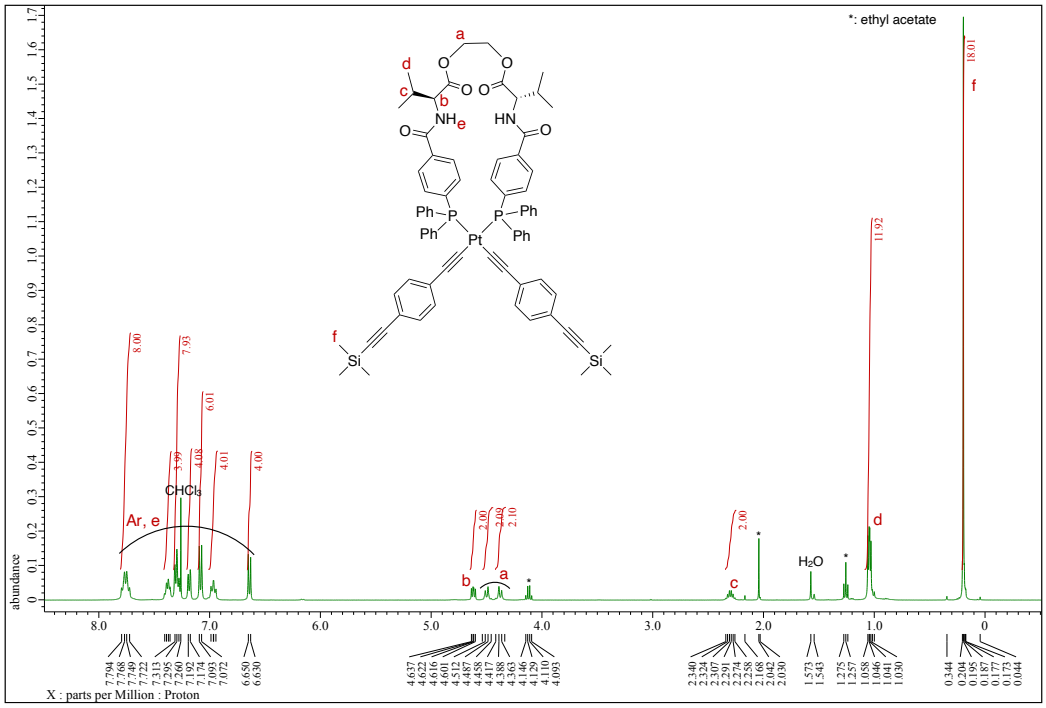


Fig. S17 ^{1}H NMR (400 MHz) spectrum of **4** measured in $CDCl_3$ without TMS.

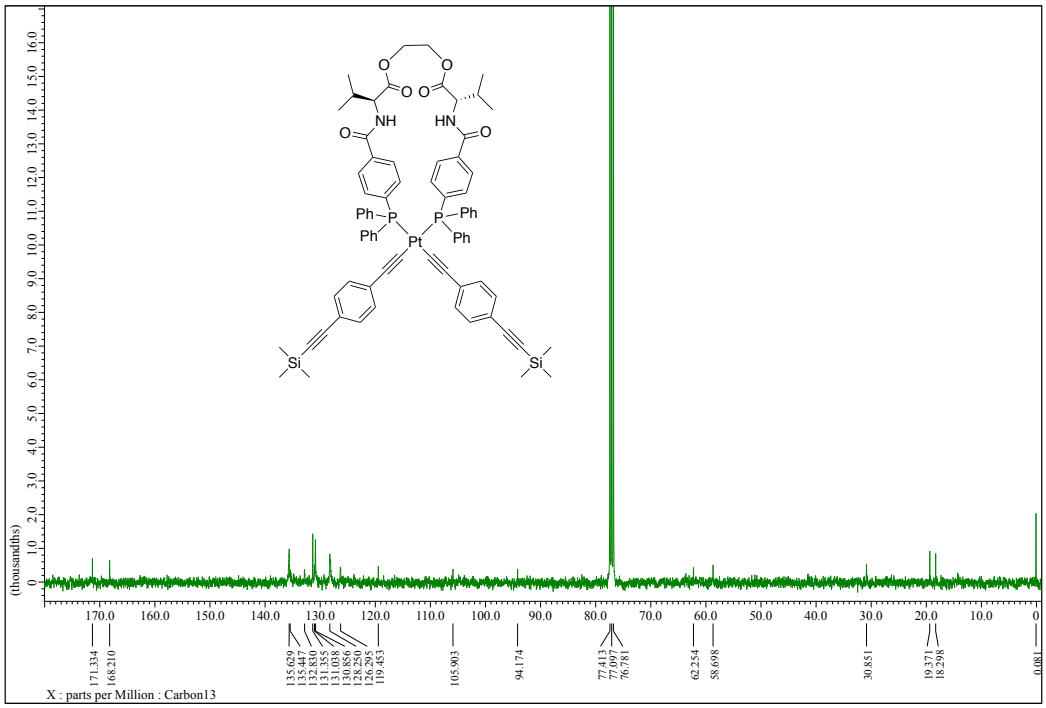


Fig. S18 ^{13}C NMR (100 MHz) spectrum of **4** measured in $CDCl_3$ without TMS.

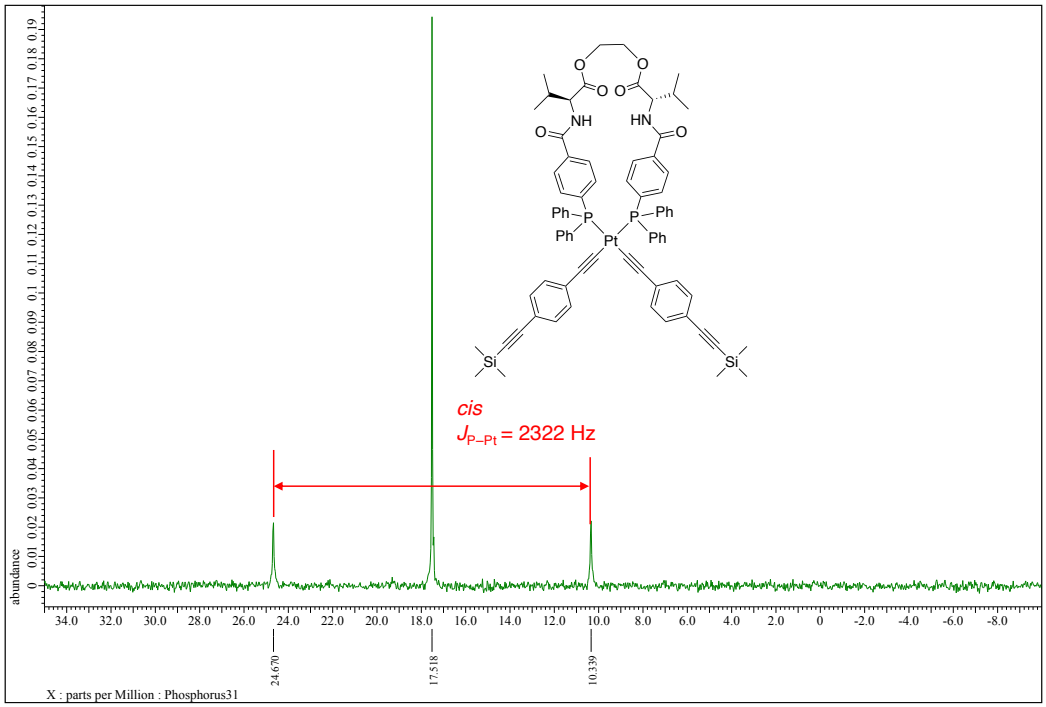


Fig. S19 ^{31}P NMR (162 MHz) spectrum of **4** measured in $CDCl_3$ without TMS.

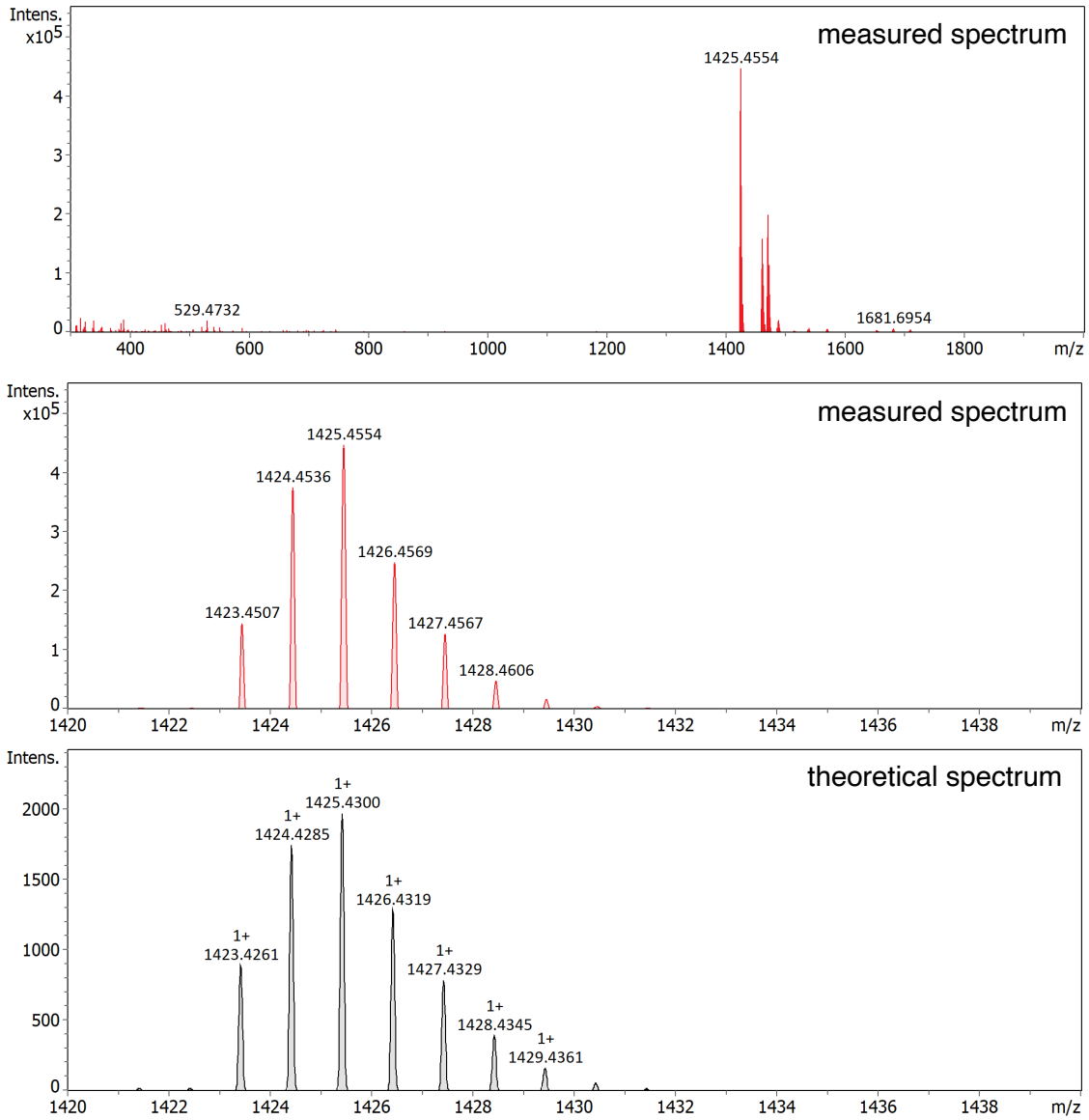
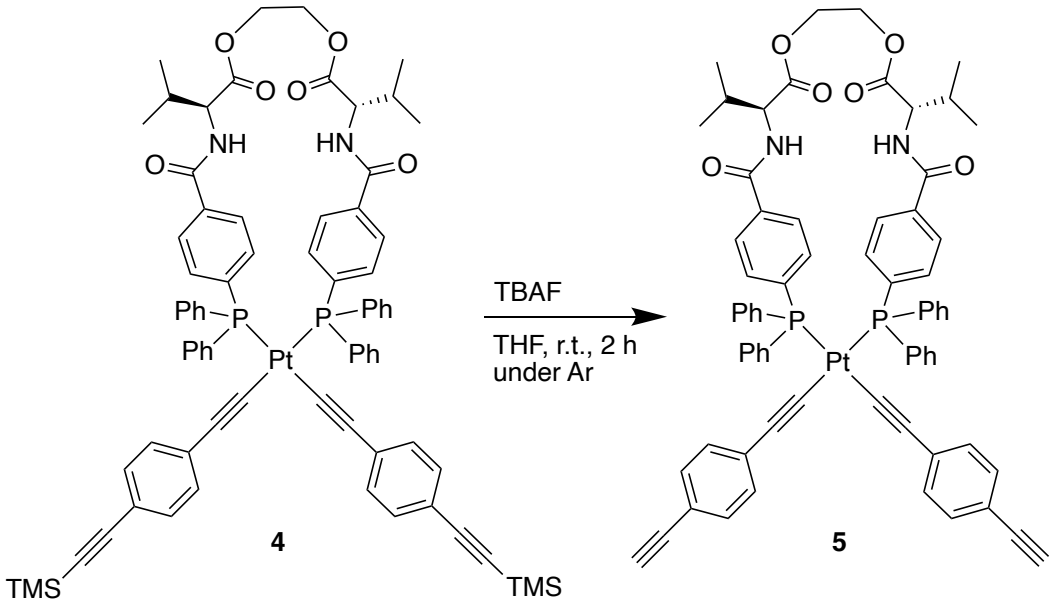


Fig. S20 ESI-MS charts of **4** measured in acetonitrile.

***Cis*-bis((4-ethynylphenyl)ethynyl)(ethane-1,2-diyl (2S,2'S)-bis(2-(4-(diphenylphosphaneyl)benzamido)-3-methylbutanoate))platinum(II) (5)**

Compound **4** (0.208 g, 0.189 mmol), TBAF solution (1.00 mL, 1.00 mmol, c = 1.0 M) and THF (3.00 mL) were sequentially fed into a Schlenk tube filled with argon. The resulting mixture was stirred at room temperature for 2 h. $CHCl_3$ (50 mL) was added to the reaction mixture, and the resulting mixture was sequentially washed with satd. NH_4Cl aq. and brine. The organic layer was dried over anhydrous $MgSO_4$ and filtered. The solvent was removed by evaporation, and

the residual mass was purified by silica gel column chromatography eluted with ethyl acetate/hexane = 2/1 (v/v) to obtain **5** as a pale yellow solid (0.110 g, 0.0858 mmol, 77%). No mp was observed up to 115 °C. IR (KBr): 3436, 3292, 3058, 2963, 2932, 2878, 2166, 1740, 1656, 1603, 1521, 1493, 1442, 1384, 1313, 1265, 1226, 1192, 1162, 1097, 1043, 980, 916, 881, 839, 698, 643, 606, 521 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (dd, J = 18.3, 10.1 Hz, 8H, Ar), 7.39 (q, J = 6.3 Hz, 4H, Ar), 7.31 (t, J = 7.1 Hz, 8H, Ar), 7.19 (d, J = 6.9 Hz, 4H, Ar), 7.11 (d, J = 11.9 Hz, 4H, Ar), 7.08 (d, J = 8.7 Hz, 2H, –N*H*–), 6.97 (dd, J = 9.6, 8.2 Hz, 4H, Ar), 6.67 (d, J = 8.7 Hz, 4H, Ar), 4.62 (dd, J = 8.7, 5.9 Hz, 2H, –CH–), 4.49 (t, J = 10.7 Hz, 2H, –CH_2–), 4.39 (t, J = 10.7 Hz, 2H, –CH_2–), 3.02 (s, 2H, –C≡C–*H*), 2.34–2.24 (m, 2H, –C*H*–), 1.06–1.00 (m, 12H, –CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3, 168.2, 135.8–135.6 (m), 131.4, 131.0, 130.9, 128.4–128.1 (m), 126.4–126.2 (m), 118.4, 62.3, 58.7, 30.9, 19.4, 18.3 ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ 17.5 (s, $J_{P–Pt}$ = 2326 Hz) ppm. ESI-MS (*m*/*z*): calcd. 1316.3263 ($[C_{70}H_{60}N_2O_6P_2Pt + Cl]^-$), found 1316.3287.



Scheme S5 Synthesis of **5**.

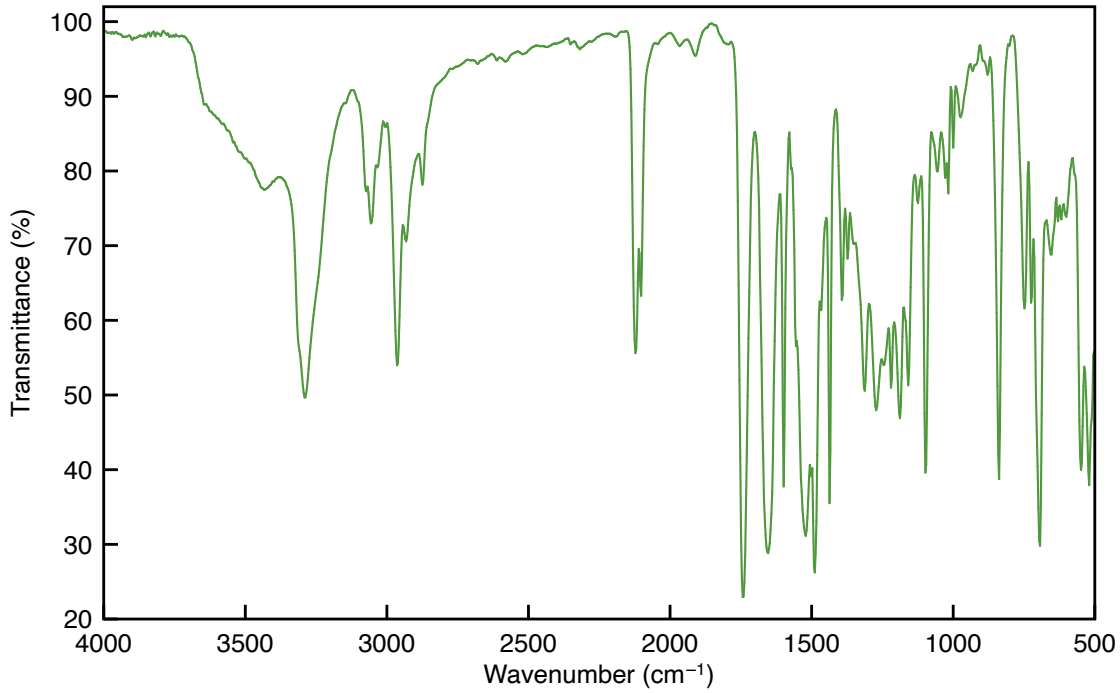


Fig. S21 IR absorption spectrum (KBr pellet) of **5**.

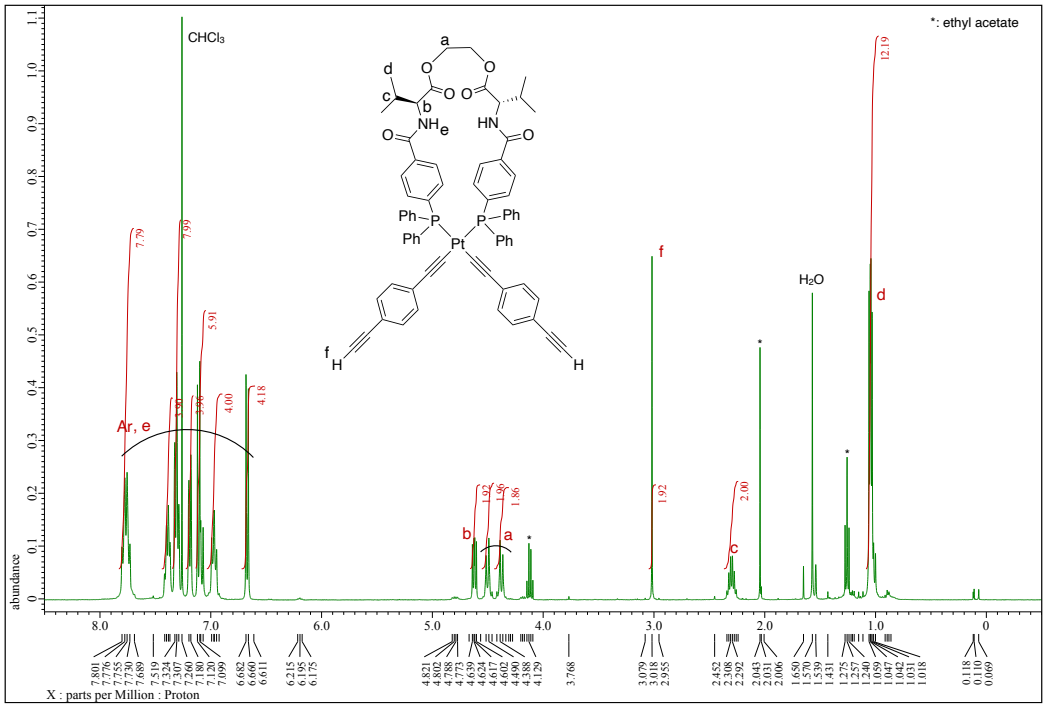


Fig. S22 ^{1}H NMR (400 MHz) spectrum of **5** measured in $CDCl_3$ without TMS.

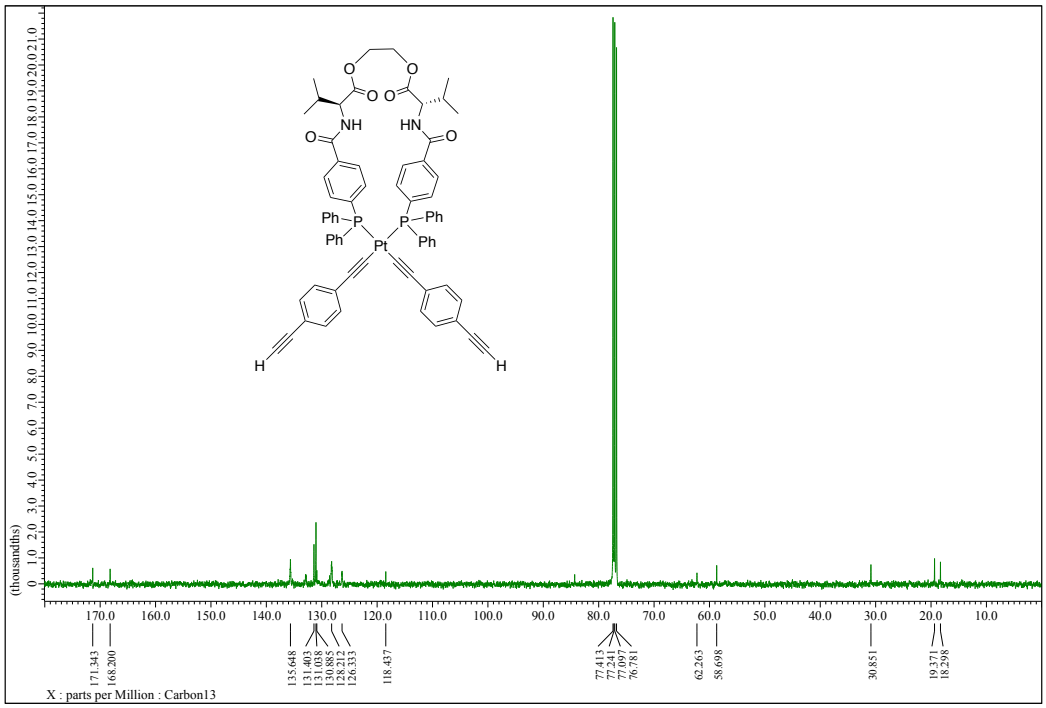


Fig. S23 ^{13}C NMR (100 MHz) spectrum of **5** measured in $CDCl_3$ without TMS.

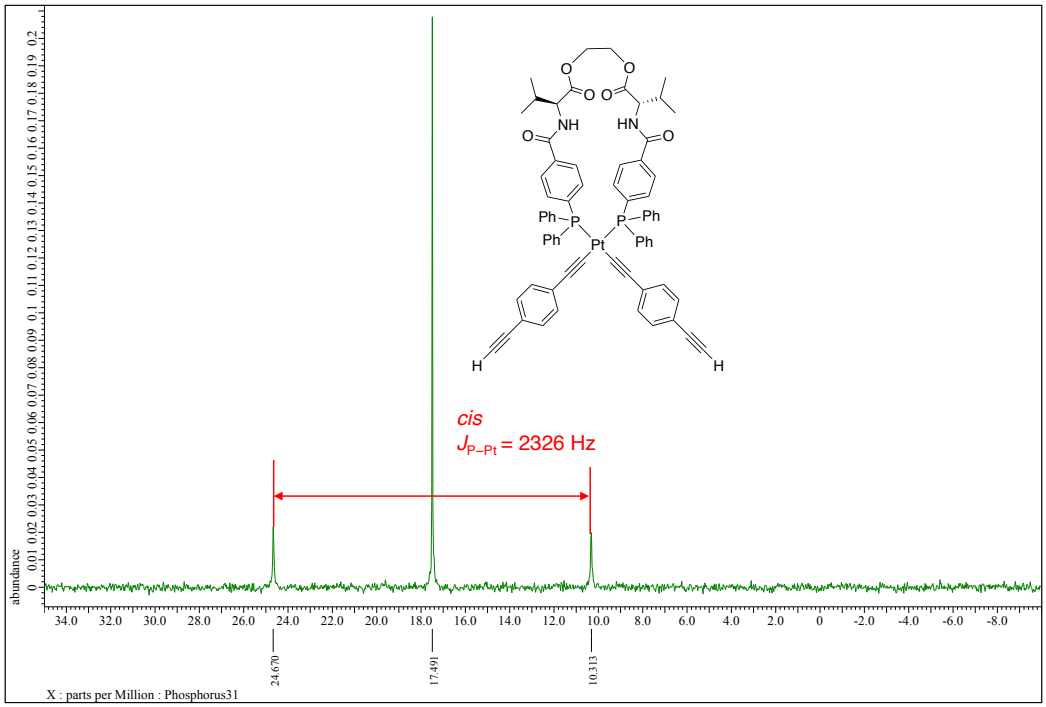


Fig. S24 ^{31}P NMR (162 MHz) spectrum of **5** measured in $CDCl_3$ without TMS.

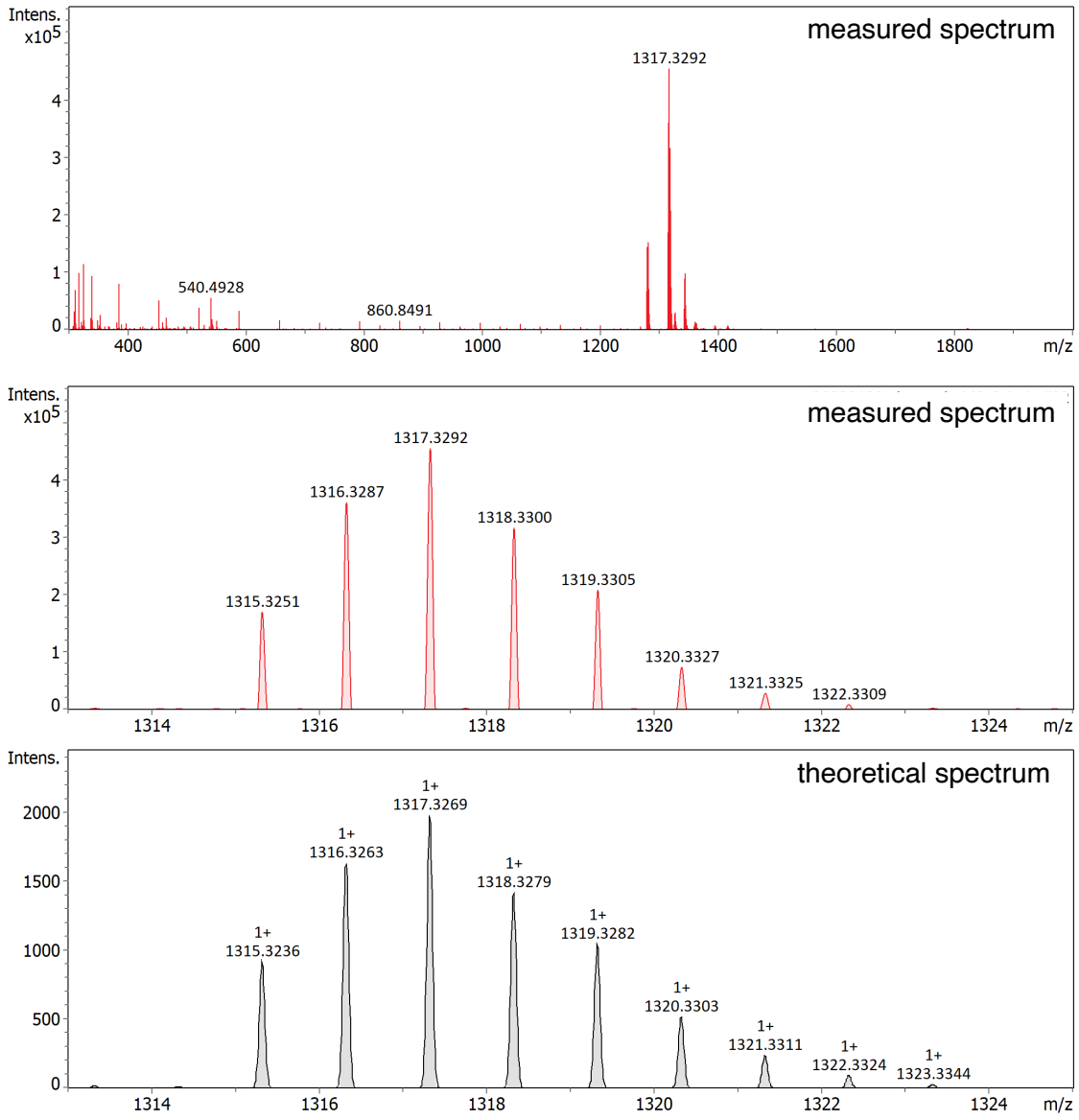
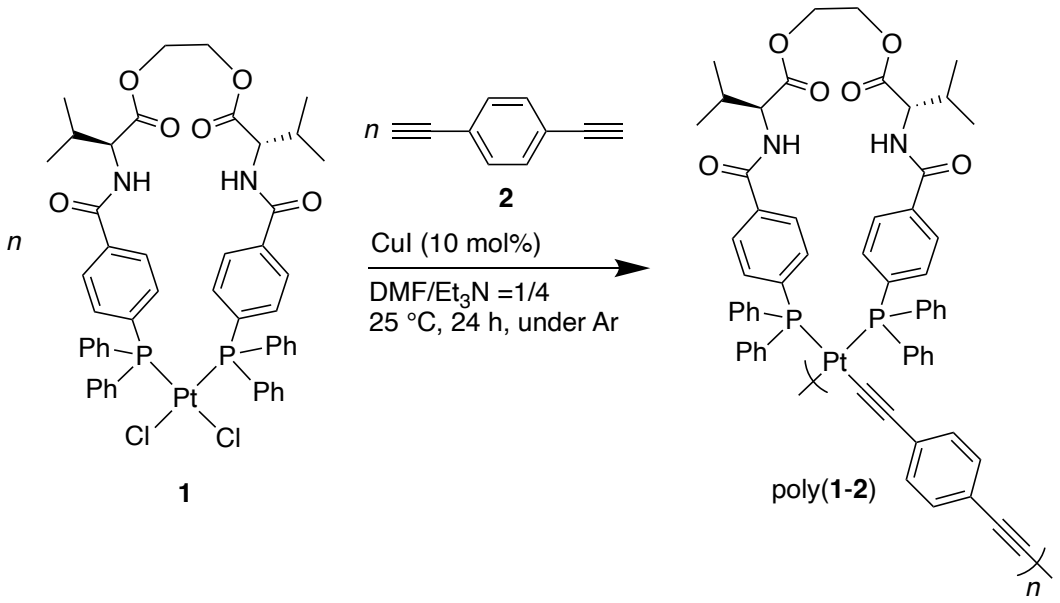


Fig. S25 ESI-MS charts of **5** measured in acetonitrile.

Synthesis of Poly(1-2). Compound **1** (0.110 g, 0.100 mmol), 1,4-diethynylbenzene (12.6 mg, 0.1000 mmol), DMF (2.00 mL) and Et_3N (7.00 mL) were sequentially fed into a Schlenk tube filled with argon. 1.00 mL of solution of CuI (11.4 mg, 60.0 μmol) in Et_3N (6.00 mL) was added to the Schlenk tube, and the resulting mixture was stirred at 25 °C for 24 h. The precipitate was separated by filtration using a membrane filter (ADVANTEC H100A047A) and washed with DMF, MeOH and diethyl ether to obtain $PtCl_2$(COD) as an orange solid (0.107 g, 93%). IR (KBr): 3417, 3311, 3053, 3024, 2961, 2932, 2872, 2109, 1741, 1661, 1599, 1514, 1485, 1435,

1389, 1372, 1309, 1265, 1254, 1185, 1154, 1096, 1026, 1017, 999, 967, 874, 835, 745, 722, 693, 661, 630, 600, 580, 543, 518 cm^{-1}.



Scheme S6 Synthesis of poly(**1**-**2**).

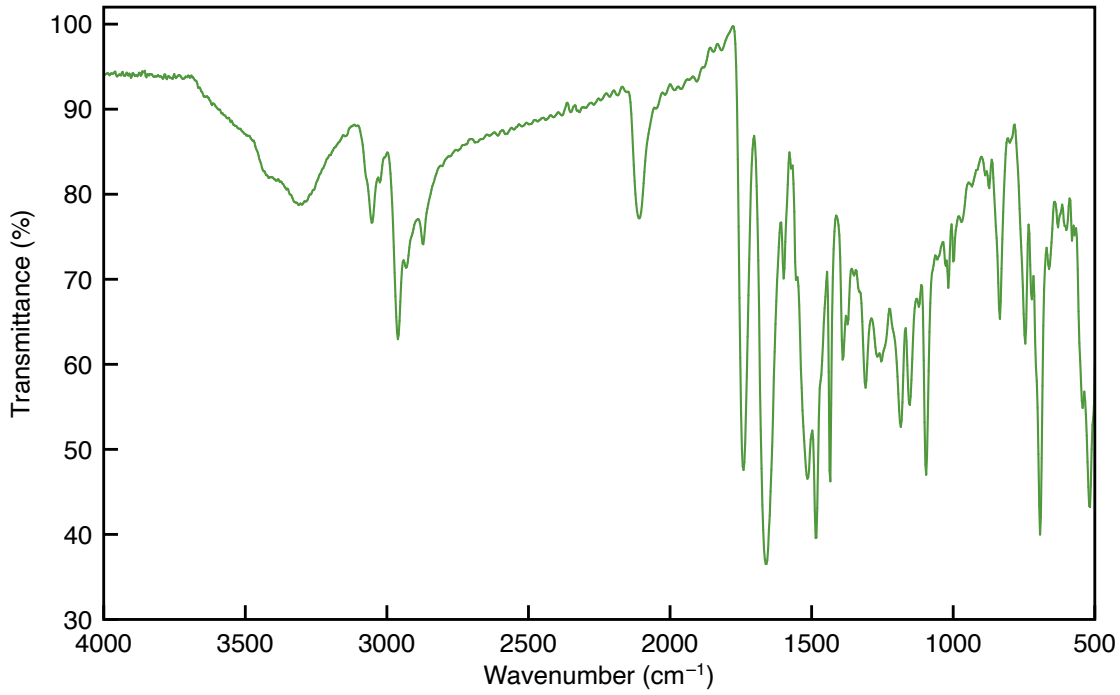
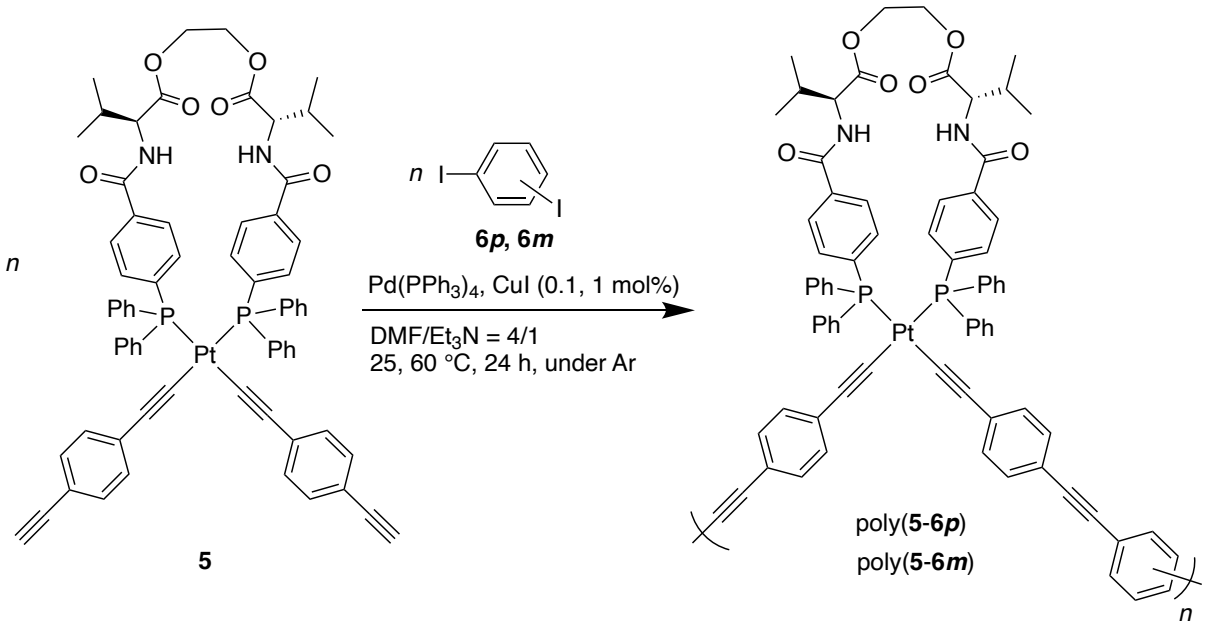


Fig. S26 IR absorption spectrum (KBr pellet) of poly(**1**-**2**).

Synthesis of poly(5-6*p*) and poly(5-6*m*)

Typical procedure: Compound **5** (68.4 mg, 53.3 μmol), **6*p*** (17.6 mg, 53.3 μmol), DMF (0.900 mL) and Et_3N (0.150 mL) were sequentially fed into a Schlenk tube filled with argon. 0.100 mL of solution of CuI (10.2 mg, 53.3 μmol) in Et_3N (100 mL) and 0.100 mL of $Pd(PPh_3)_4$ (12.3 mg, 10.6 μmol) in DMF (20.0 mL) were added to the Schlenk tube, and the resulting mixture was stirred at 25 °C for 24 h. The reaction mixture was poured into MeOH (100 mL) to precipitate a solid. It was separated by filtration using a membrane filter (ADVANTEC H100A047A) to obtain poly(**5-6*p***) (Table 1, run 1) as a yellow solid (3.61 mg, 5%). M_n = 7,800. $Đ$ = 2.0. IR (KBr): 3419, 3298, 3055, 2963, 2930, 2875, 2104, 1743, 1664, 1598, 1516, 1486, 1436, 1391, 1373, 1312, 1271, 1220, 1186, 1158, 1097, 1059, 1018, 998, 936, 838, 780, 746, 725, 696, 661, 624, 613, 600, 582, 567, 552, 542, 533, 508 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.96–6.14 (m, 43*n*H), 4.78–4.23 (m, 6*n*H), 2.42–2.21 (br, 2*n*H), 1.11–0.82 (m, 13*n*H) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ 17.5 (s, $J_{P–Pt}$ = 2328 Hz) ppm. **Poly(5-6*p*)** (Table 1, run 2): Orange solid. Yield 85%, M_n = 15,900. $Đ$ = 10. IR (KBr): 3429, 3300, 3055, 2963, 2933, 2875, 2206, 2111, 1906, 1743, 1666, 1597, 1573, 1515, 1485, 1436, 1391, 1373, 1310, 1268, 1187, 1158, 1123, 1097, 1058, 1028, 1017, 999, 977, 837, 747, 723, 695, 655, 617, 582, 543, 516, 506 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 7.93–6.18 (m, 43*n*H), 4.74–4.26 (m, 6*n*H), 2.38–2.22 (m, 2*n*H), 1.13–0.93 (m, 12*n*H) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ 17.5 (s, $J_{P–Pt}$ = 2335 Hz) ppm. **Poly(5-6*p*)** (Table 1, run 3): Yellow solid. Yield 50%, M_n = 10,200. $Đ$ = 1.9. IR (KBr): 3433, 3302, 3055, 2963, 2878, 2206, 2114, 1912, 1741, 1664, 1599, 1515, 1441, 1386, 1310, 1266, 1190, 1162, 1095, 1056, 1011, 835, 751, 697, 610, 523 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 7.92–6.22 (m, 43*n*H), 4.69–4.28 (m, 6*n*H), 2.37–2.21 (m, 2*n*H), 1.09–0.93 (m, 12*n*H) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ 17.5 (s, $J_{P–Pt}$ = 2309 Hz) ppm. **Poly(5-6*p*)** (Table 1, run 4): Orange solid. Yield 90%, M_n = 17,000. $Đ$ = 5.0. IR (KBr): 3418, 3055, 2963, 2934, 2875, 2203, 2106, 1743, 1666, 1596, 1515, 1485, 1436, 1391, 1373, 1310, 1267, 1186, 1157, 1097, 1060, 1017, 999, 973, 936, 887, 837, 746, 722, 695, 659, 634, 625, 615, 596, 581, 542, 526, 517, 506 cm^{-1}. ^1H NMR (400

MHz, $CDCl_3$): 7.88–6.14 (m, 42*n*H), 4.69–4.23 (m, 6*n*H), 2.32–2.18 (m, 2*n*H), 1.04–0.89 (m, 12*n*H) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ 17.5 (s, $J_{P–Pt}$ = 2326 Hz) ppm. **Poly(5-6*m*)** (Table 1, run 5): Orange solid. Yield 66%, M_n = 9,900. $Đ$ = 2.3. IR (KBr): 3293, 3055, 2963, 2875, 2116, 1741, 1654, 1599, 1521, 1488, 1436, 1394, 1373, 1313, 1261, 1187, 1158, 1096, 1028, 908, 863, 836, 798, 744, 722, 694, 657, 598, 525 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 7.96–6.16 (m, 42*n*H), 4.76–4.24 (m, 6*n*H), 2.42–2.20 (m, 2*n*H), 1.12–0.92 (m, 12*n*H) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ 17.5 (s, $J_{P–Pt}$ = 2322 Hz) ppm. **Poly(5-6*m*)** (Table 1, run 6): Yellow solid. Yield 24%, M_n = 7,300. $Đ$ = 1.8. IR (KBr): 3434, 3302, 3055, 2963, 2932, 2874, 2206, 2116, 1741, 1662, 1598, 1518, 1506, 1488, 1436, 1391, 1372, 1312, 1267, 1187, 1158, 1125, 1097, 1053, 1017, 999, 972, 922, 892, 837, 792, 747, 723, 694, 656, 631, 600, 548, 519, 503 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 7.96–6.20 (m, 42*n*H), 4.77–4.28 (m, 6*n*H), 2.40–2.24 (m, 2*n*H), 1.12–0.94 (m, 12*n*H) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ 17.5 (s, $J_{P–Pt}$ = 2326 Hz) ppm.



Scheme S7. Synthesis of poly(**5**-6***p***) and poly(**5**-6***m***).

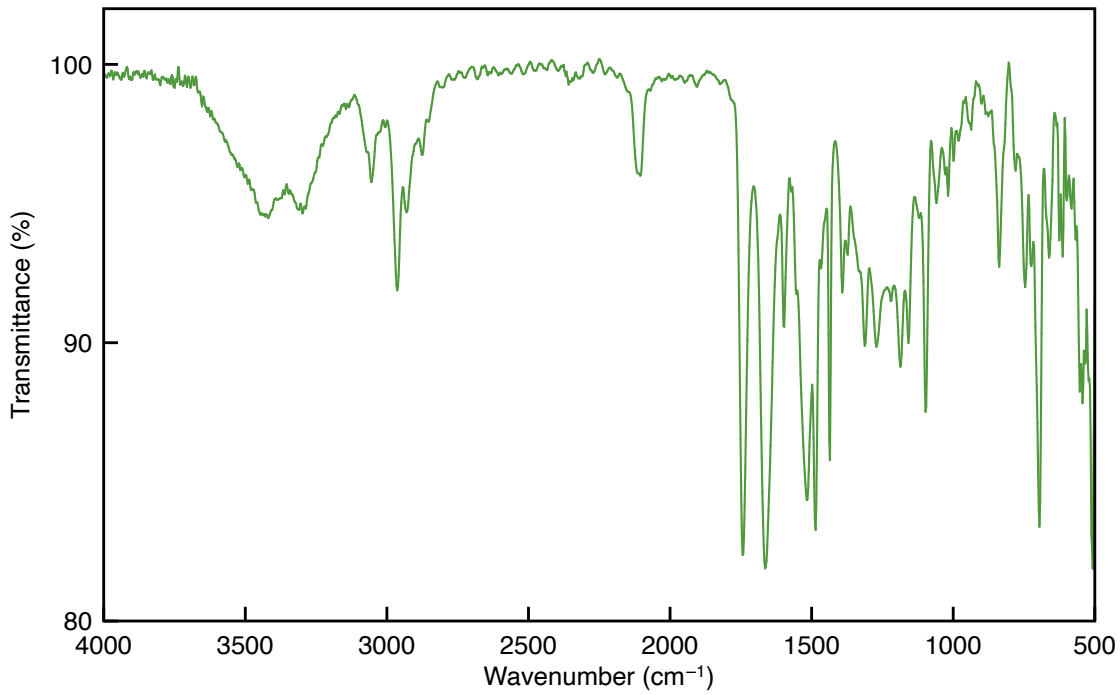


Fig. S27 IR absorption spectrum (KBr pellet) of poly(**5**-**6*p***) (Table 1, run 1).

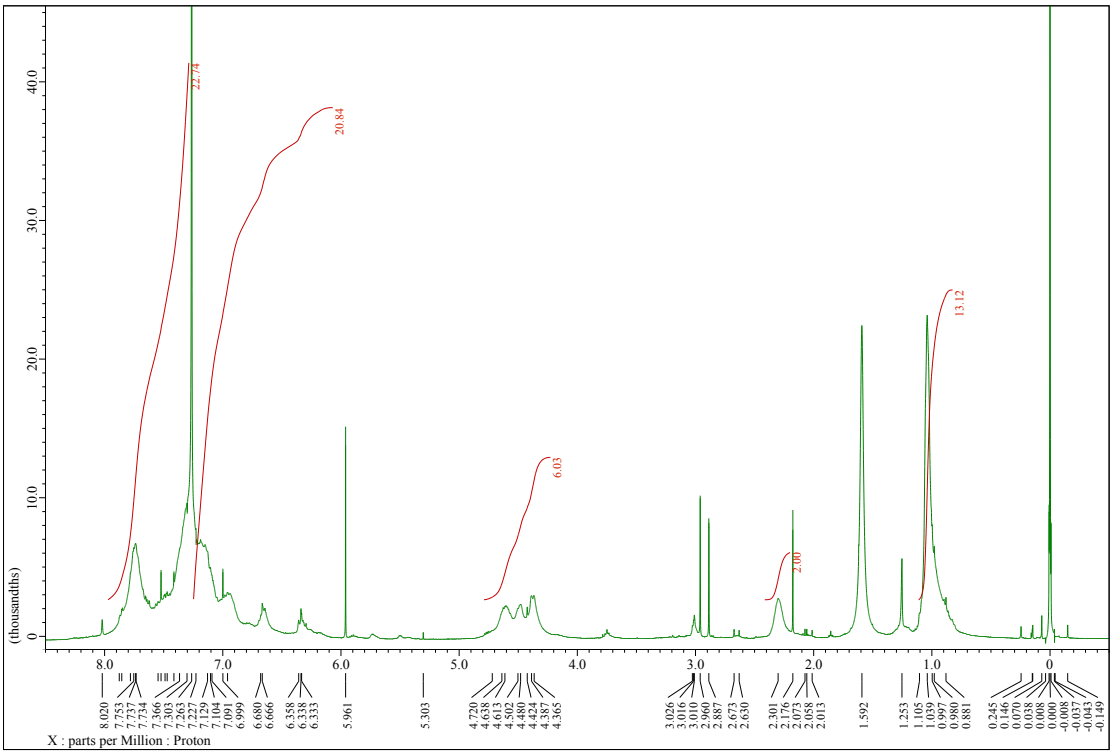


Fig. S28 ^{1}H NMR (400 MHz) spectrum of poly(**5**-**6*p***) (Table 1, run 1) measured in $CDCl_3$.

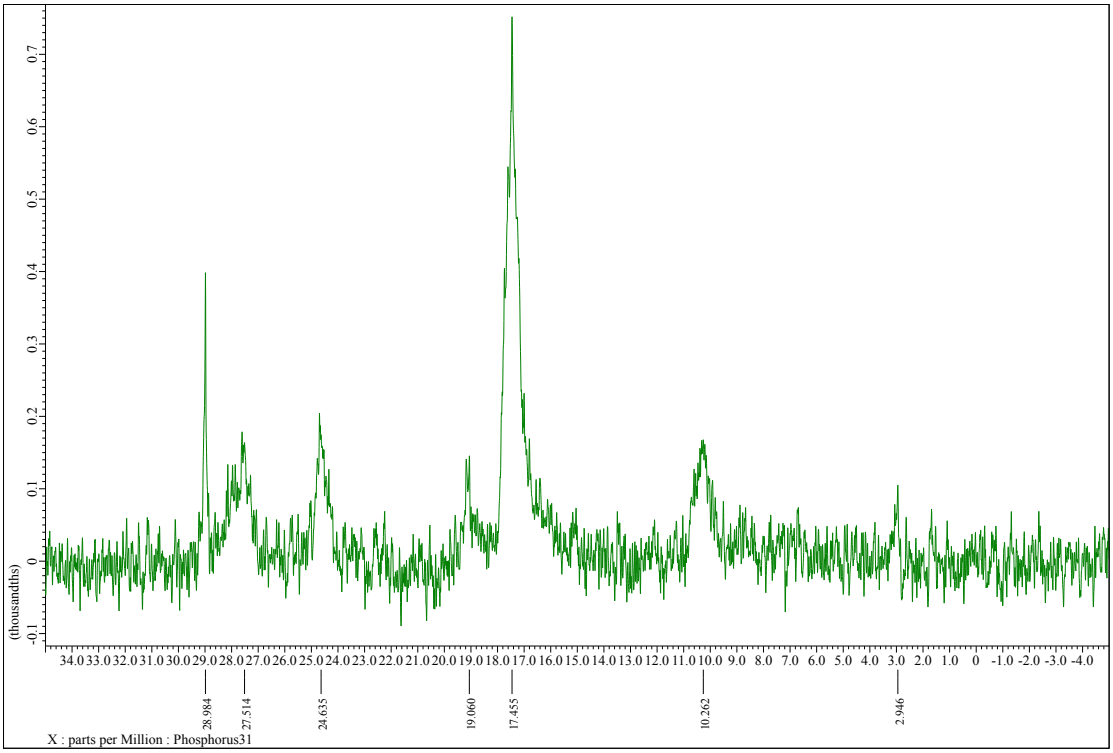


Fig. S29 ^{31}P NMR (162 MHz) spectrum of poly(**5**-**6*p***) (Table 1, run 1) measured in $CDCl_3$.

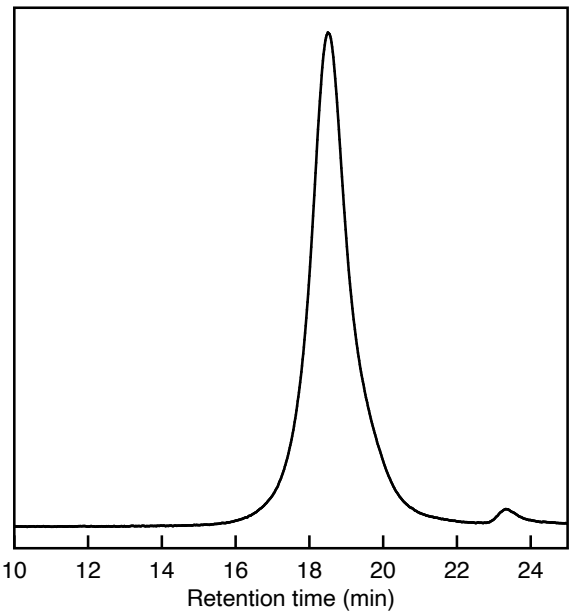


Fig. S30 SEC chart of poly(**5**-**6*p***) (Table 1, run 1) eluted with DMF (10 mM LiBr).

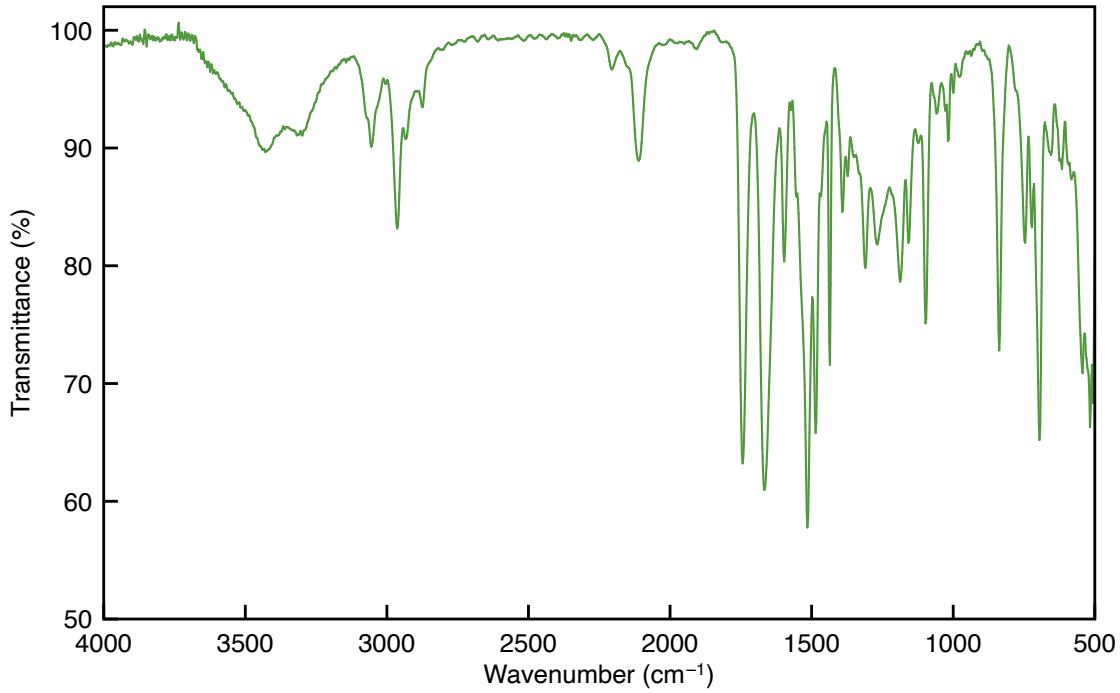


Fig. S31 IR absorption spectrum (KBr pellet) of poly(**5**-**6*p***) (Table 1, run 2).

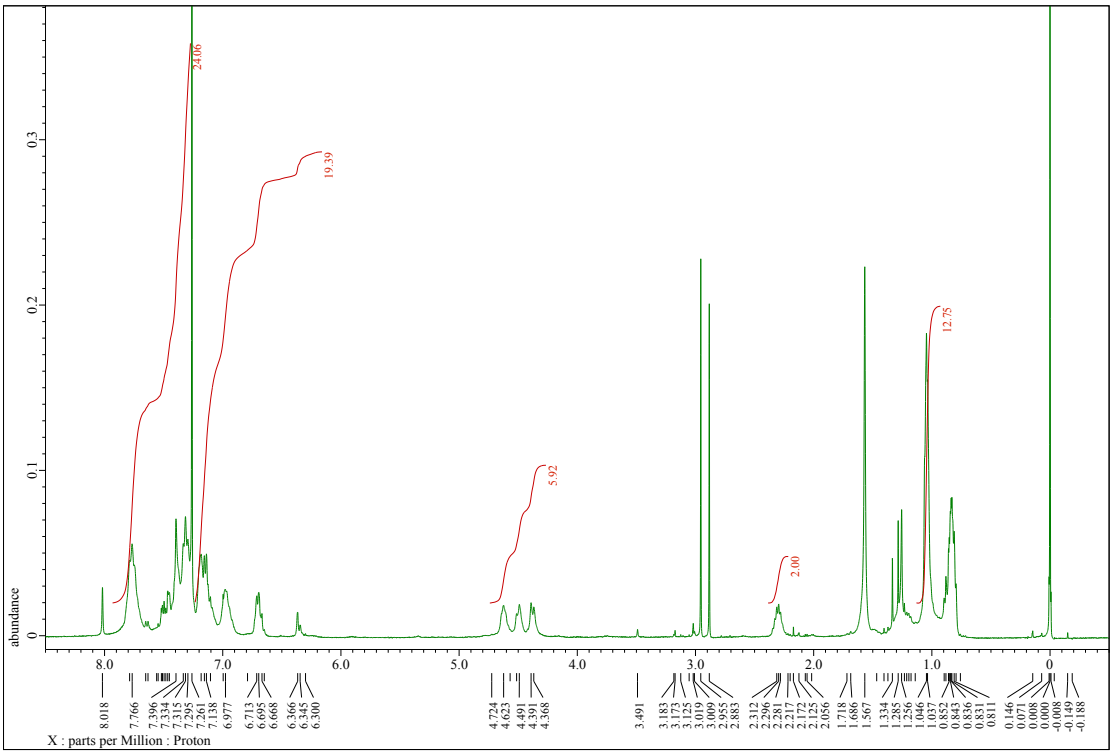


Fig. S32 ^{1}H NMR (400 MHz) spectrum of poly(**5**-**6*p***) (Table 1, run 2) measured in $CDCl_3$.

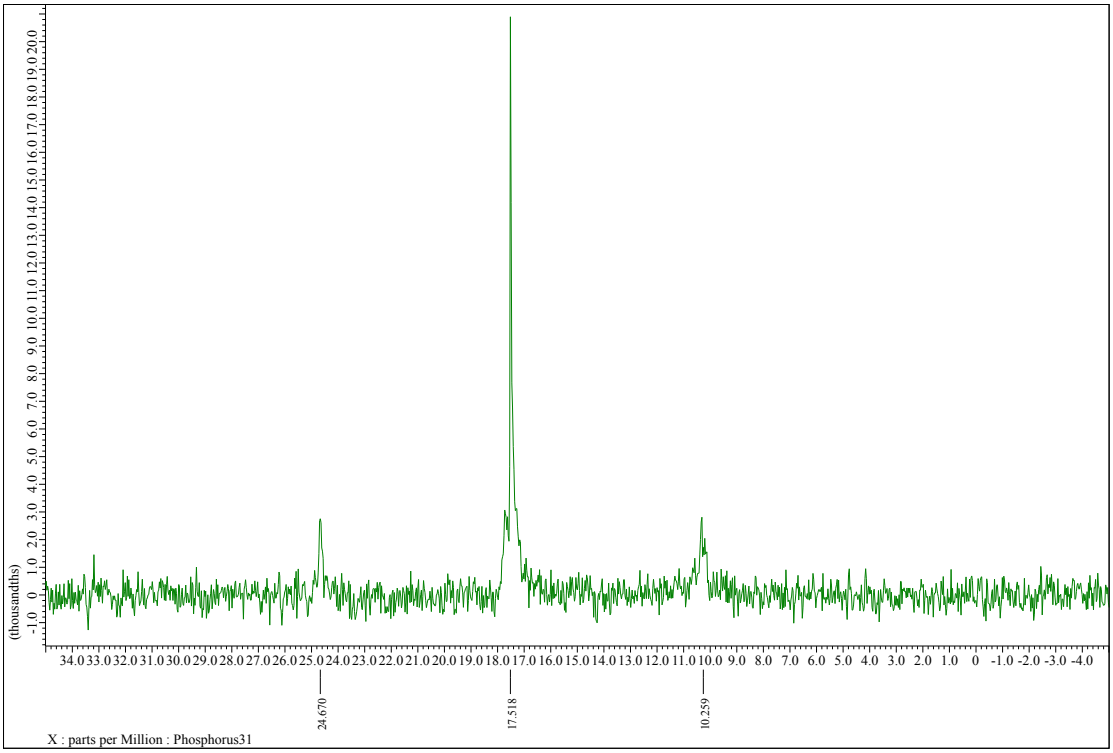


Fig. S33 ^{31}P NMR (162 MHz) spectrum of poly(**5**-**6*p***) (Table 1, run 2) measured in $CDCl_3$.

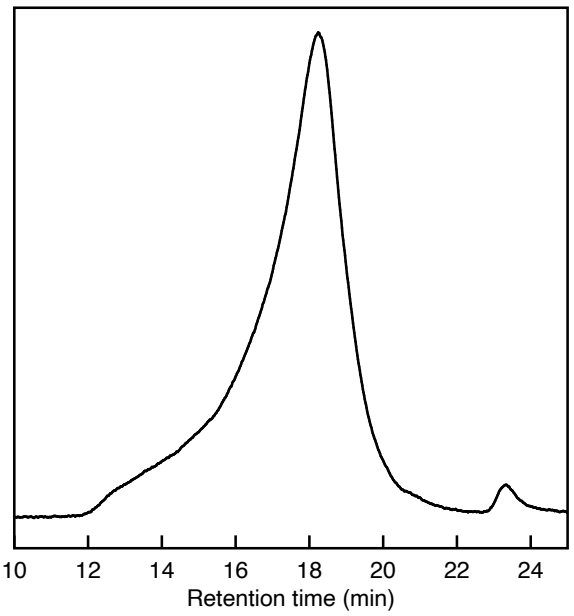


Fig. S34 SEC chart of poly(**5**-**6*p***) (Table 1, run 2) eluted with DMF (10 mM LiBr).

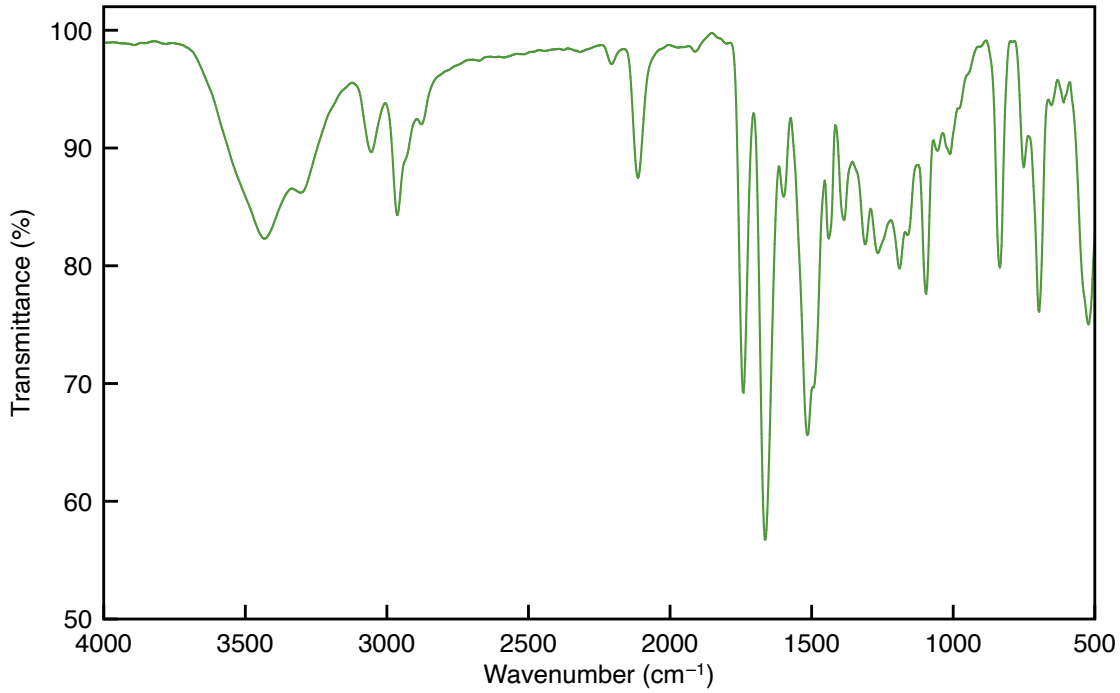


Fig. S35 IR absorption spectrum (KBr pellet) of poly(**5**-**6*p***) (Table 1, run 3).

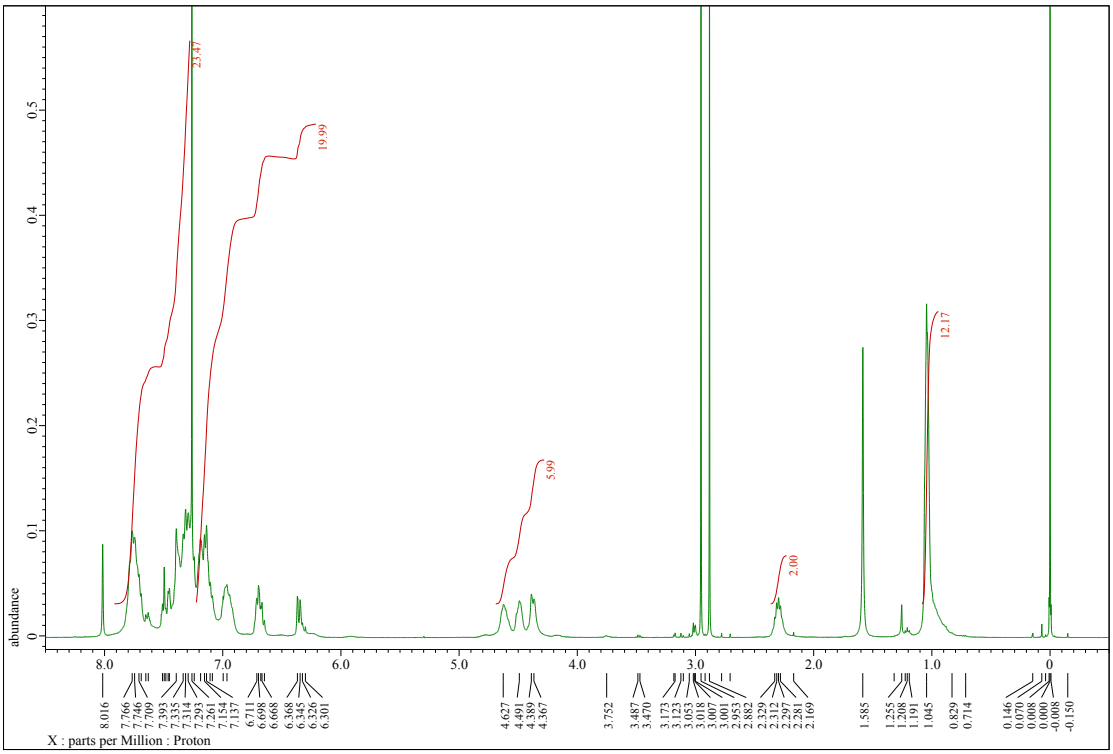


Fig. S36 ^{1}H NMR (400 MHz) spectrum of poly(**5**-**6*p***) (Table 1, run 3) measured in $CDCl_3$.

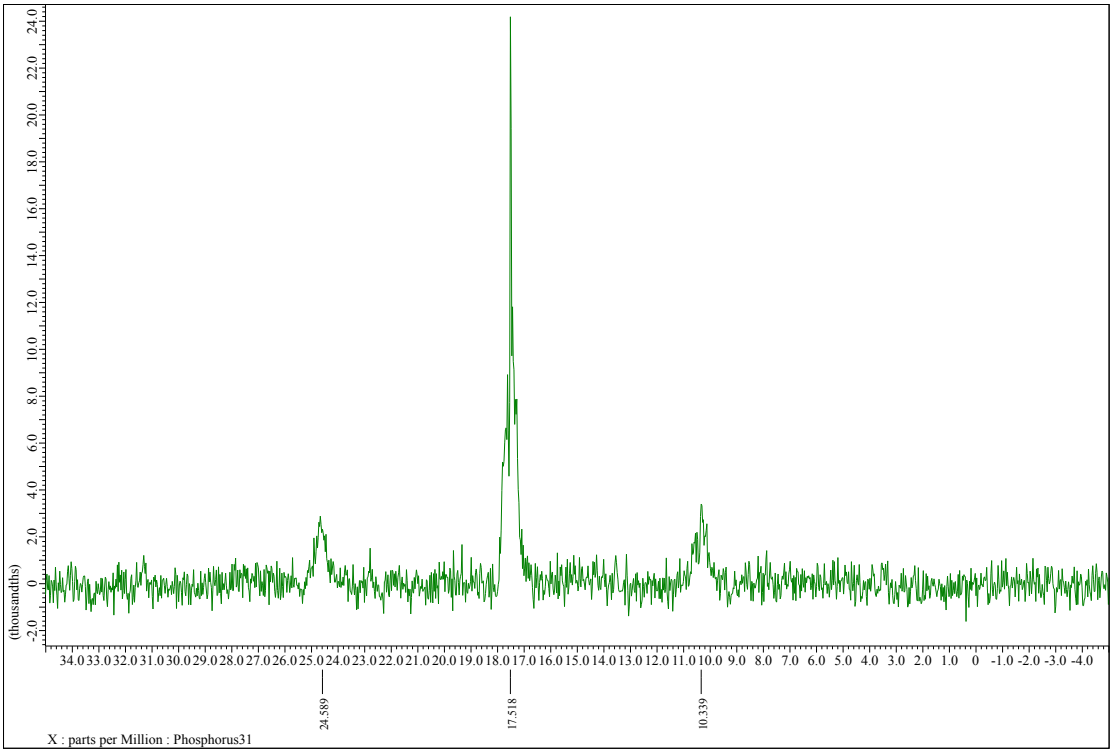


Fig. S37 ^{31}P NMR (162 MHz) spectrum of poly(**5**-**6*p***) (Table 1, run 3) measured in $CDCl_3$.

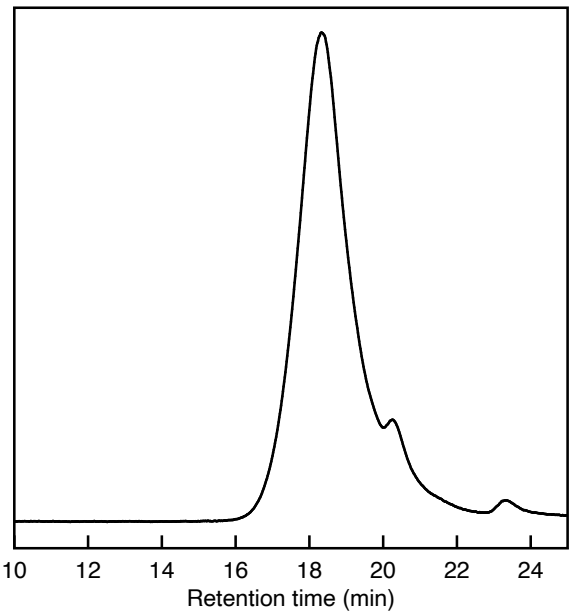


Fig. S38 SEC chart of poly(**5**-**6*p***) (Table 1, run 3) eluted with DMF (10 mM LiBr).

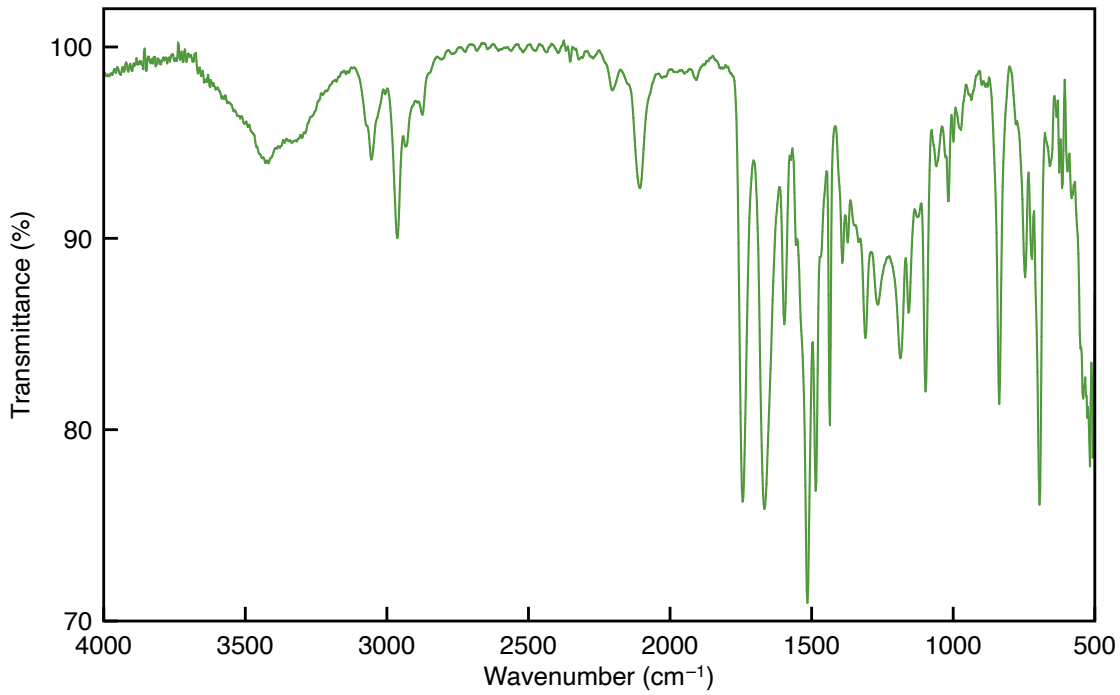


Fig. S39 IR absorption spectrum (KBr pellet) of poly(**5**-**6*p***) (Table 1, run 4).

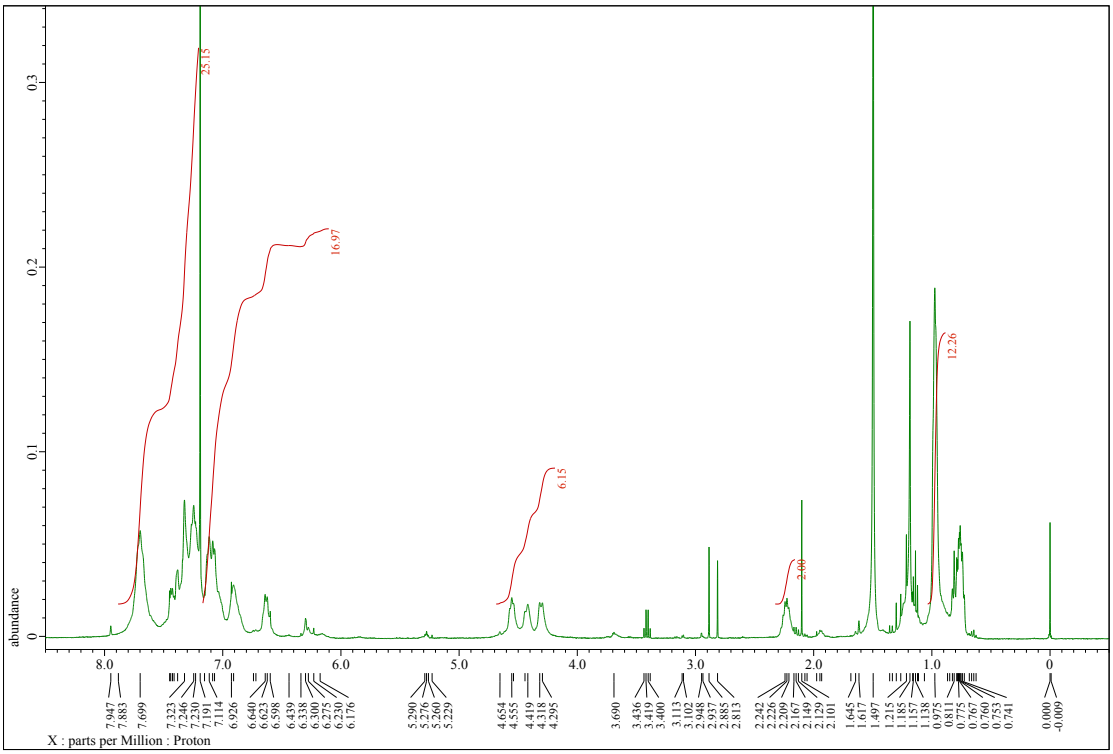


Fig. S40 ^{1}H NMR (400 MHz) spectrum of poly(**5**-**6*p***) (Table 1, run 4) measured in $CDCl_3$.

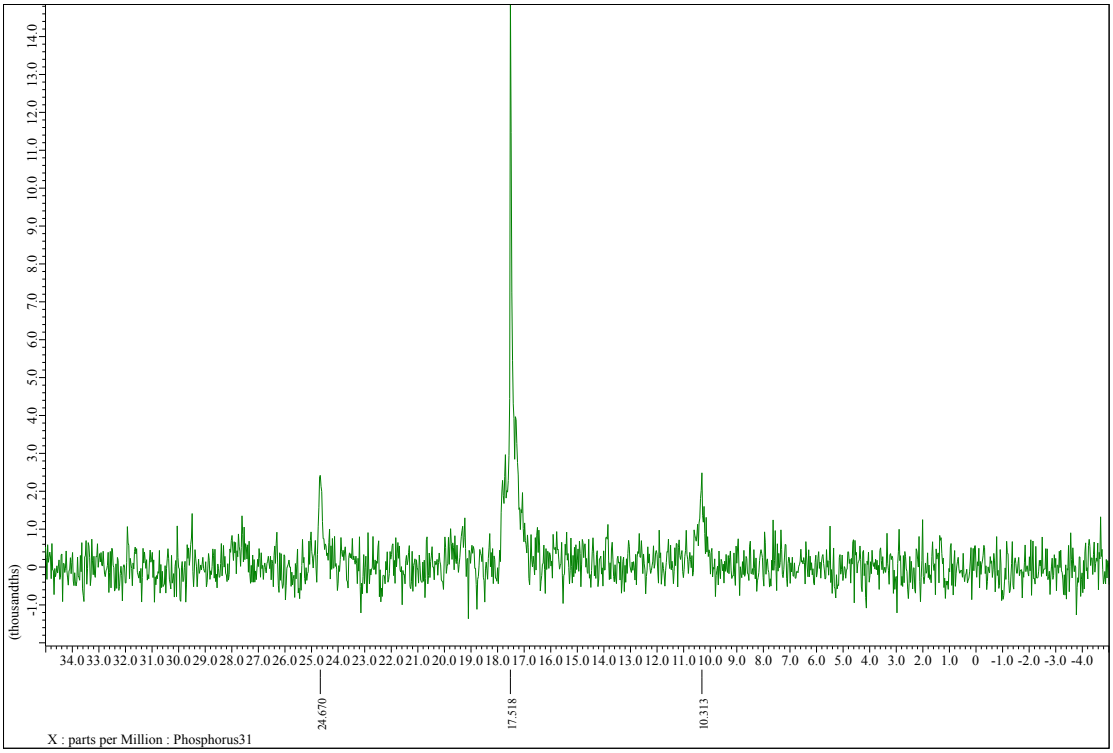


Fig. S41 ^{31}P NMR (162 MHz) spectrum of poly(**5**-**6*p***) (Table 1, run 4) measured in $CDCl_3$.

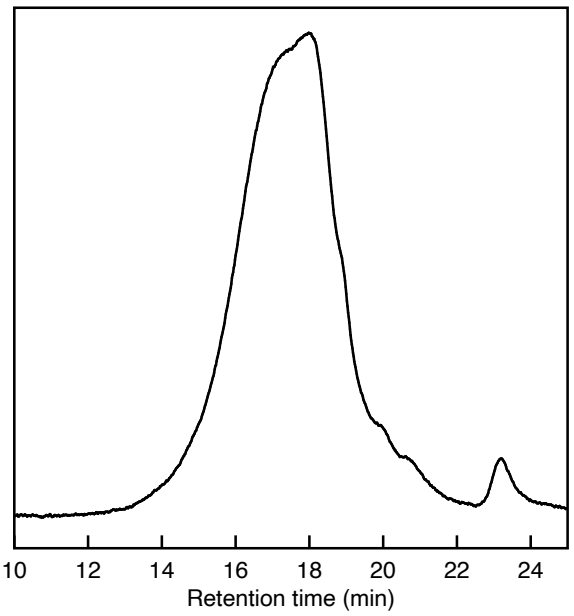


Fig. S42 SEC chart of poly(**5**-**6*p***) (Table 1, run 4) eluted with DMF (10 mM LiBr).

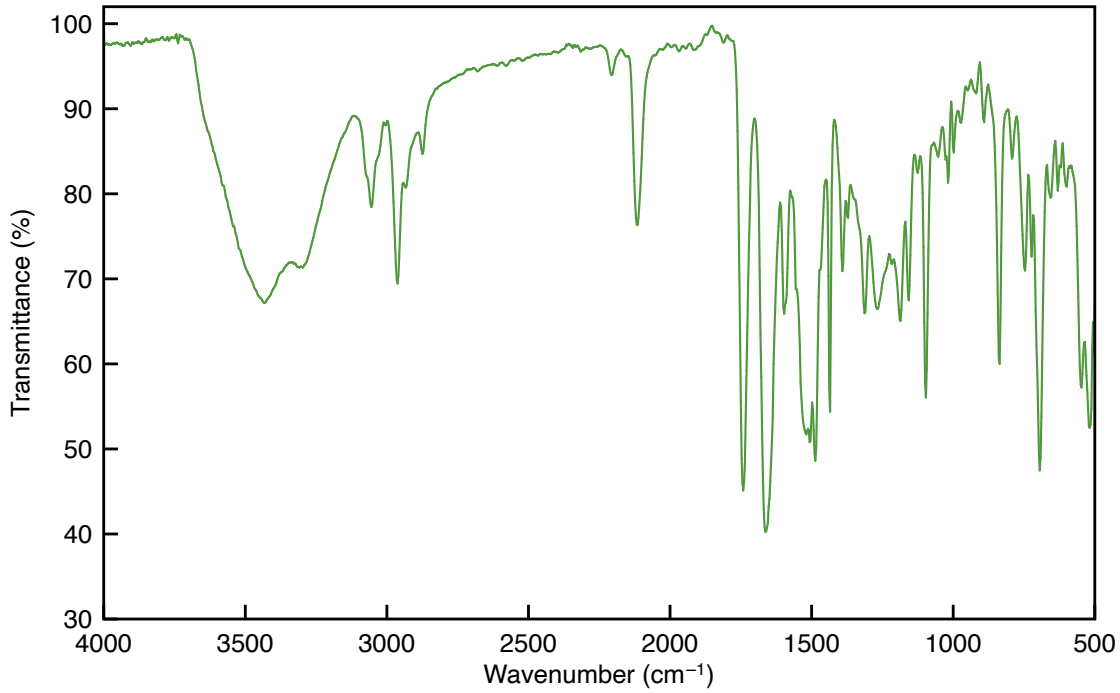


Fig. S43 IR absorption spectrum (KBr pellet) of poly(**5**-**6*m***) (Table 1, run 5).

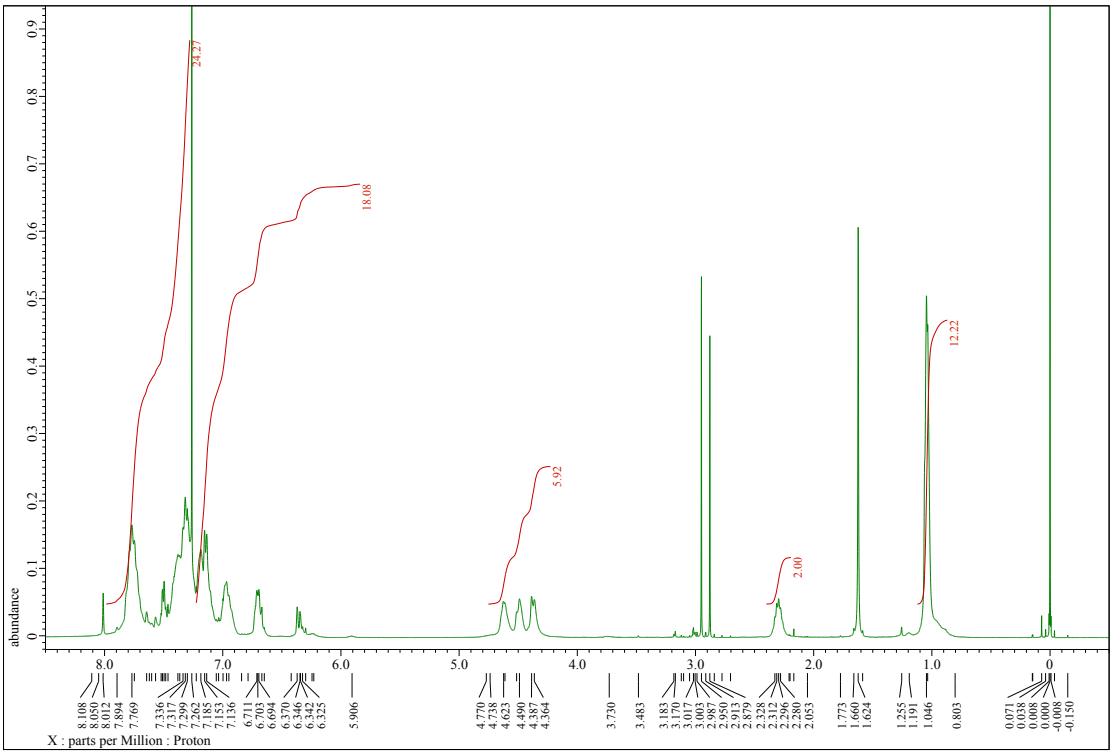


Fig. S44 ^{1}H NMR (400 MHz) spectrum of poly(**5**-**6*m***) (Table 1, run 5) measured in $CDCl_3$.

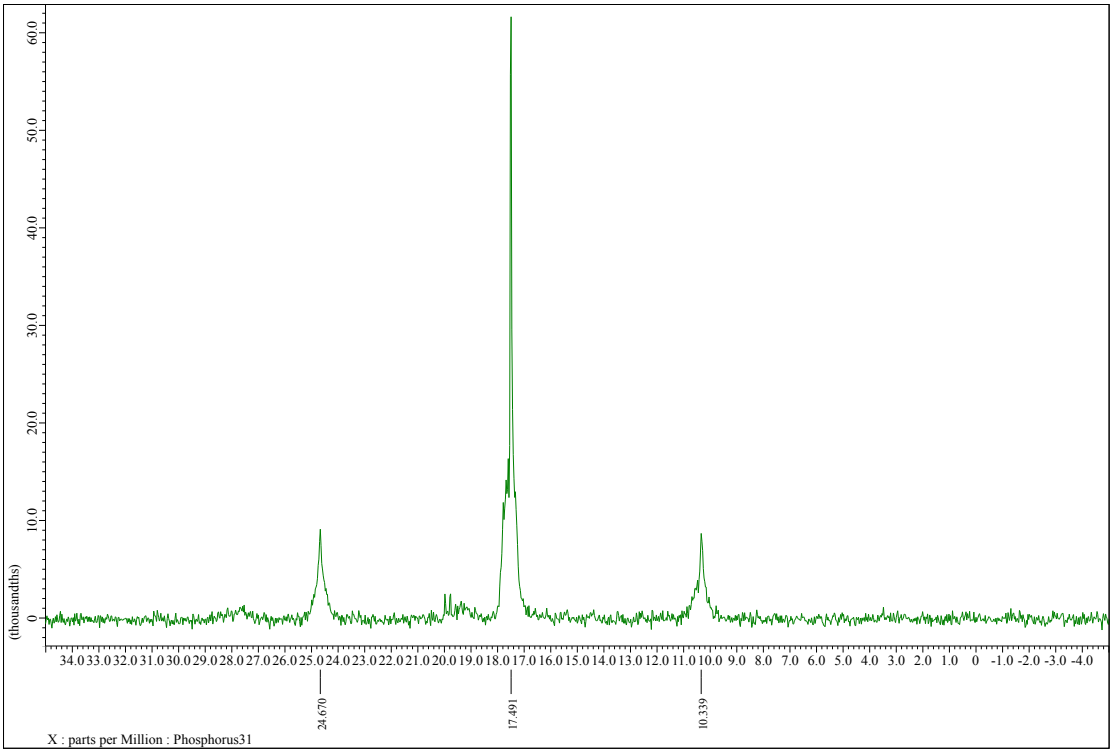


Fig. S45 ^{31}P NMR (162 MHz) spectrum of poly(**5**-**6*m***) (Table 1, run 5) measured in $CDCl_3$.

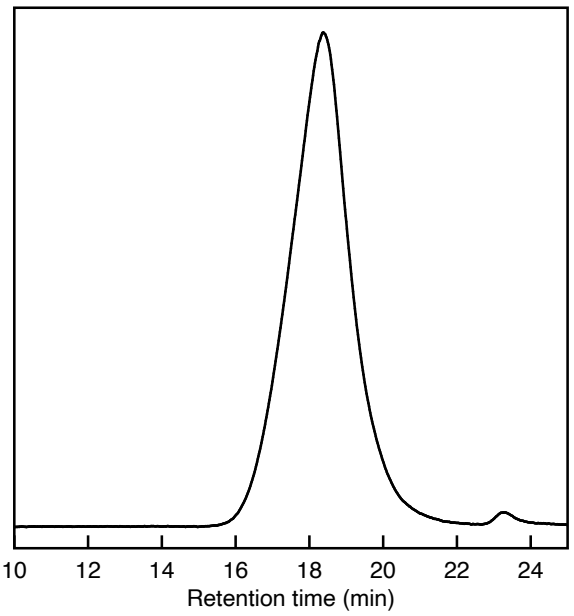


Fig. S46 SEC chart of poly(**5**-**6*m***) (Table 1, run 5) eluted with DMF (10 mM LiBr).

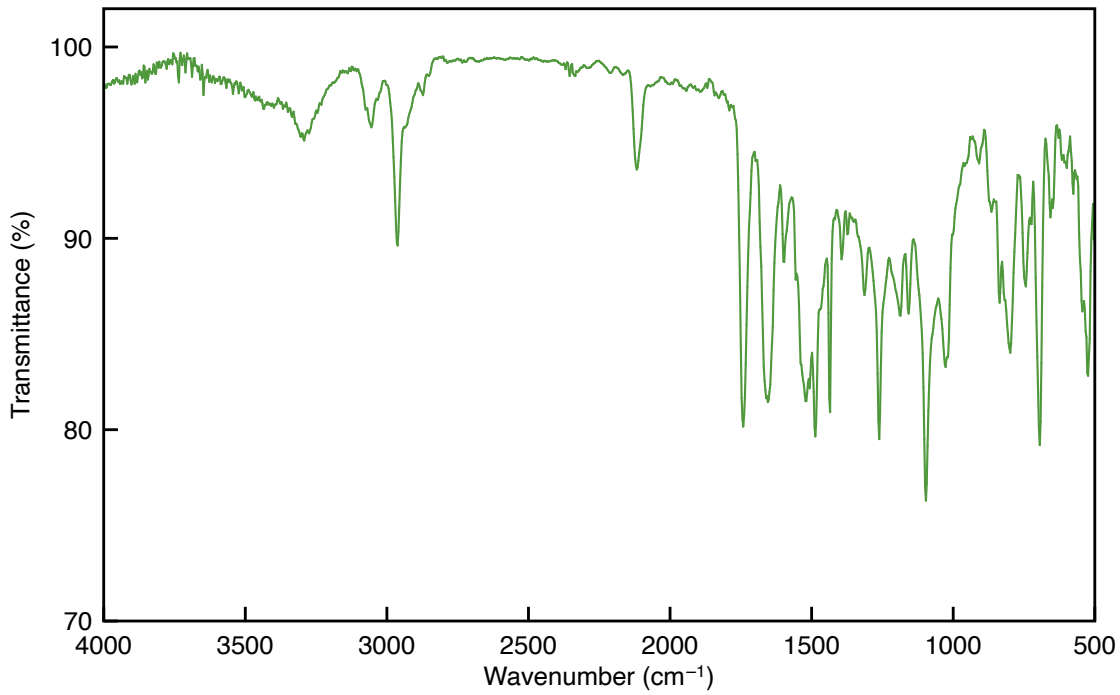


Fig. S47 IR absorption spectrum (KBr pellet) of poly(**5**-**6*m***) (Table 1, run 6).

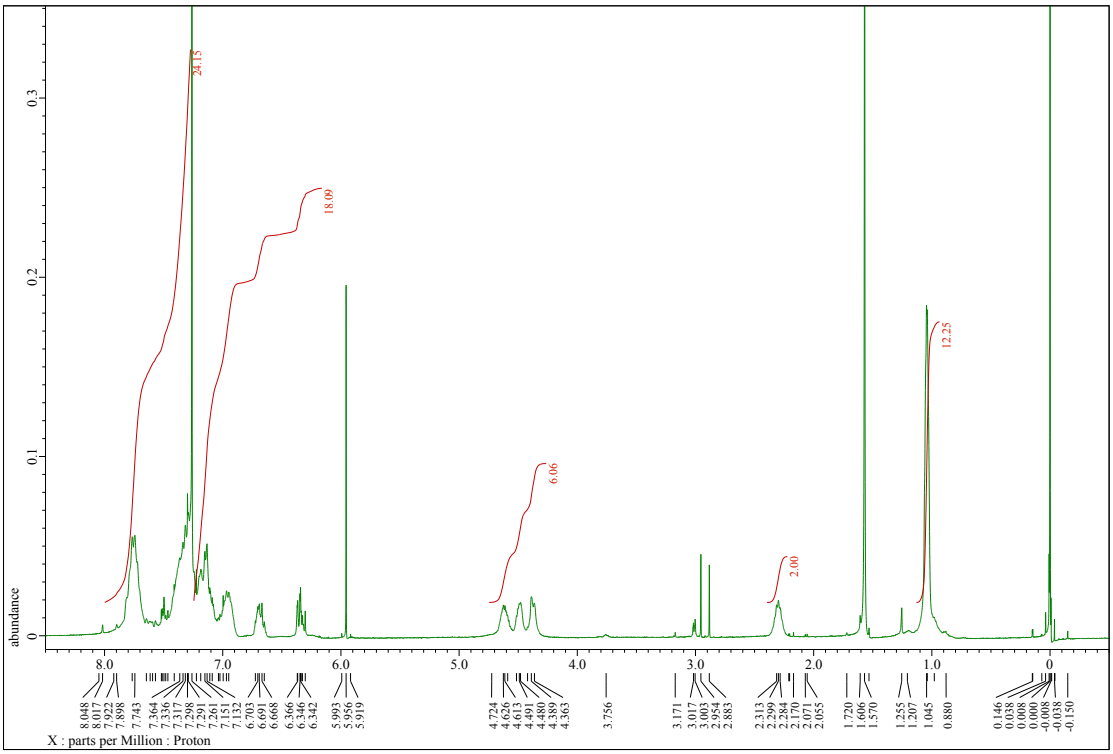


Fig. S48 ^{1}H NMR (400 MHz) spectrum of poly(**5**-**6*m***) (Table 1, run 6) measured in $CDCl_3$.

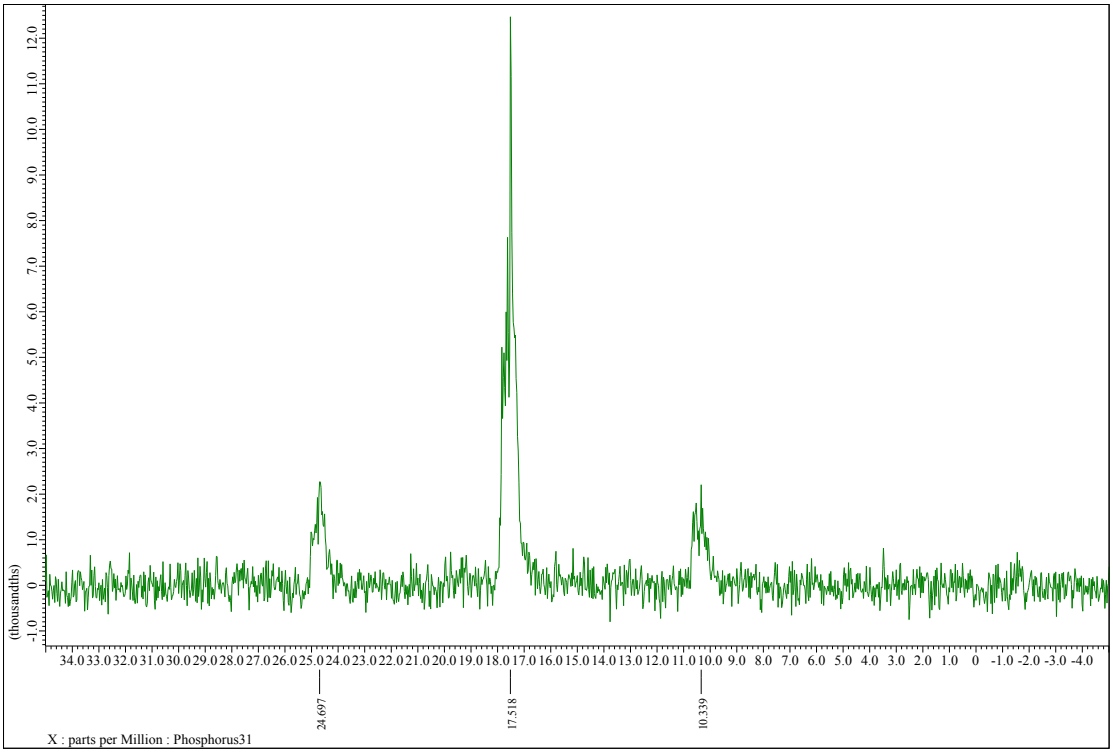


Fig. S49 ^{31}P NMR (162 MHz) spectrum of poly(**5**-**6*m***) (Table 1, run 6) measured in $CDCl_3$.

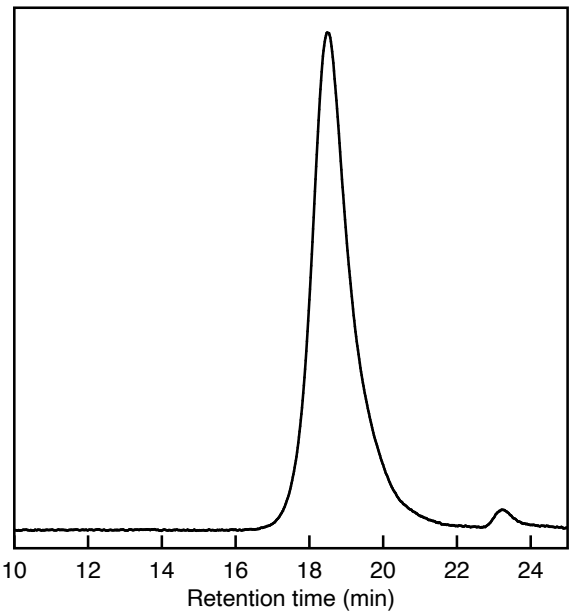


Fig. S50 SEC chart of poly(**5**-**6*m***) (Table 1, run 6) eluted with DMF (10 mM LiBr).

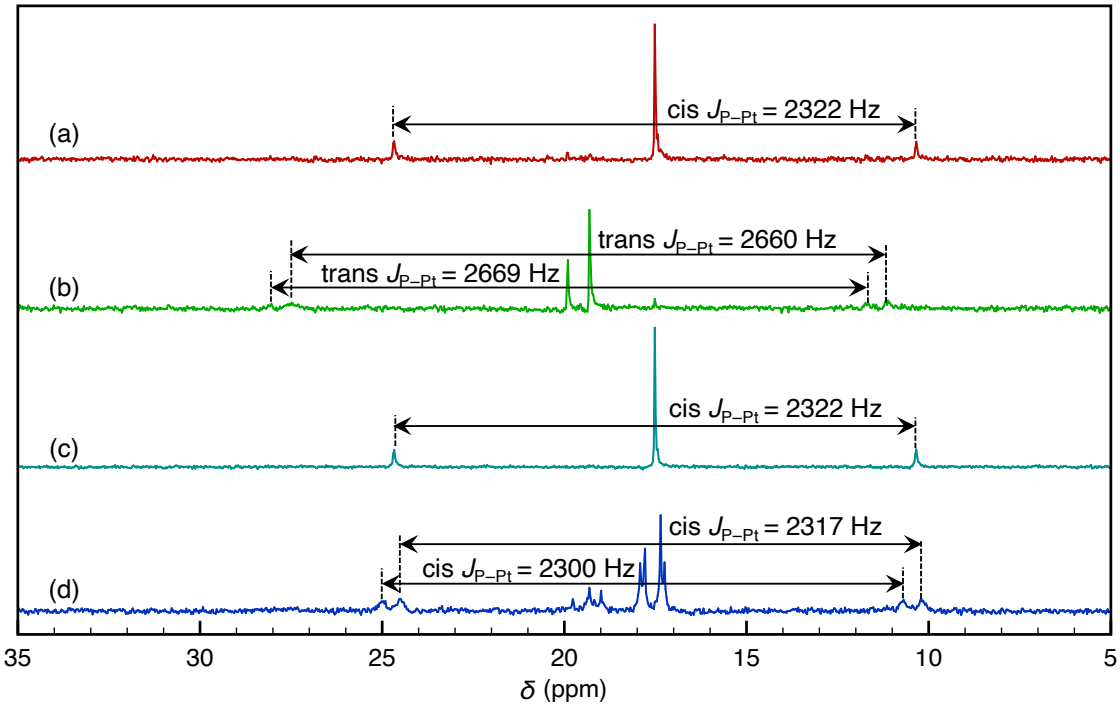


Fig. S51 ^{31}P NMR (162 MHz) spectra of the products in the first step of Scheme 3 measured in $CDCl_3$. (a) Before purification, (b) 1st fraction after column chromatographic purification, (c) 2nd fraction, (d) 3rd fraction. Ratio of 1st:2nd:3rd fractions = 2:89:9.

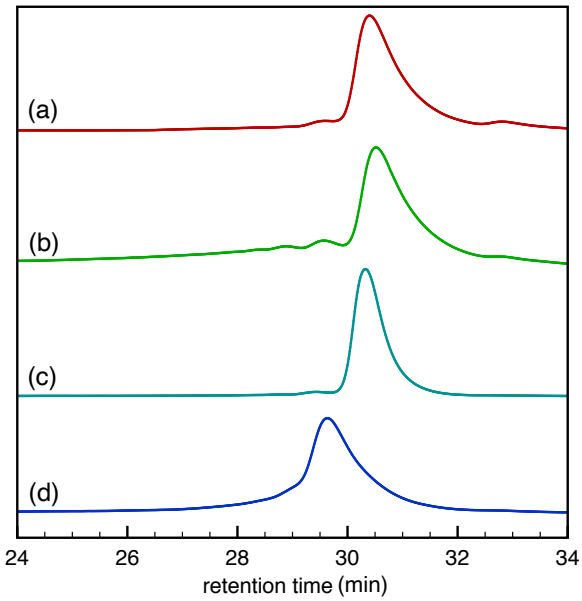


Fig. S52 SEC charts of the products in the first step of Scheme 3 (eluent: $CHCl_3$). (a) Before purification, (b) 1st fraction after column chromatographic purification, (c) 2nd fraction, (d) 3rd fraction. Ratio of 1st:2nd:3rd fractions = 2:89:9.

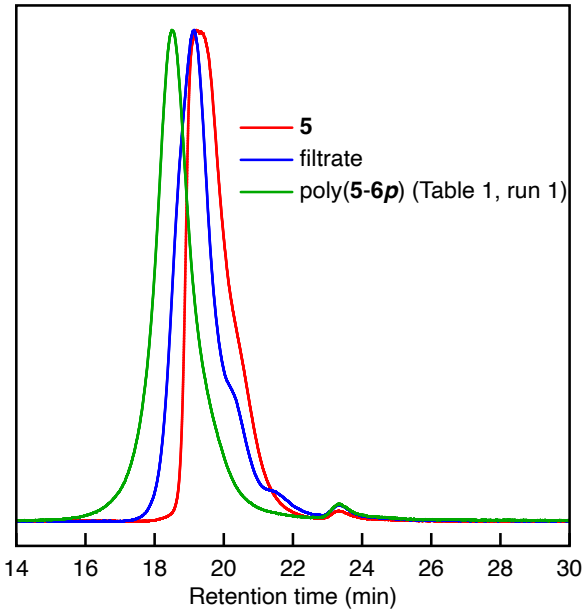


Fig. S53 SEC charts of **5**, filtrate (Table 1, run 1) and poly(**5**-**6*p***) (Table 1, run 1) eluted with DMF (10 mM LiBr).

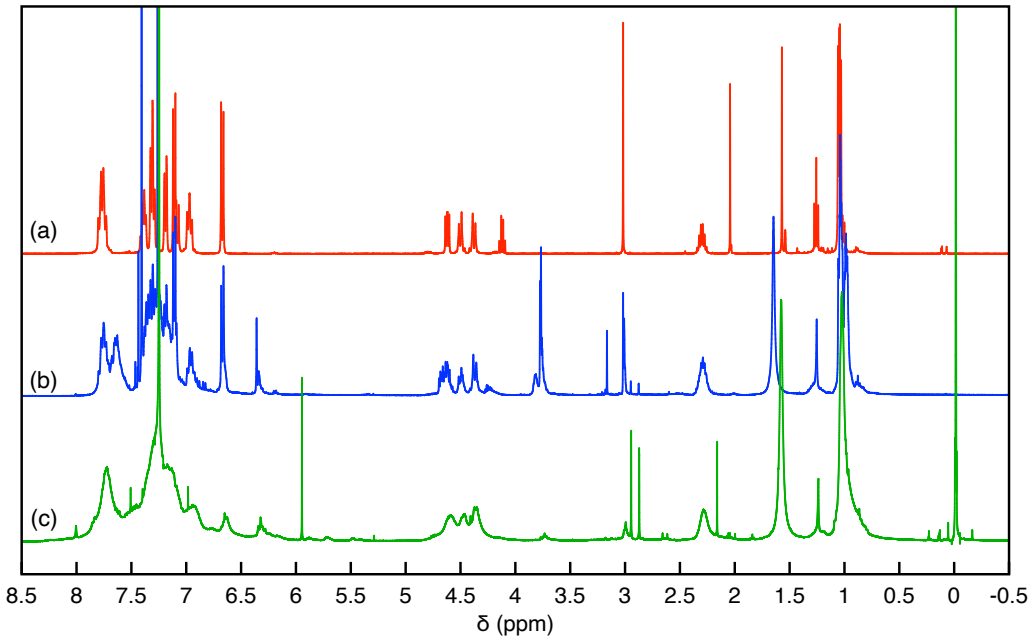


Fig. S54 ^{1}H NMR (400 MHz) spectra of the products measured in $CDCl_3$. (a) **5**, (b) filtrate (Table 1, run 1), (c) poly(**5**-**6*p***) (Table 1, run 1).

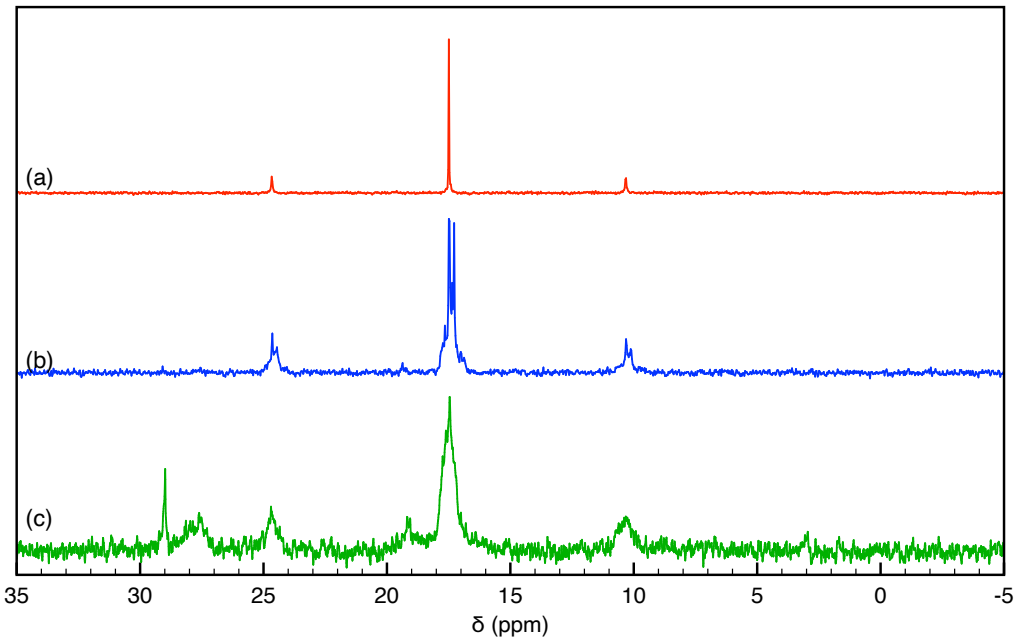


Fig. S55 ^{31}P NMR (162 MHz) spectra of the products measured in $CDCl_3$. (a) **5**, (b) filtrate (Table 1, run 1), (c) poly(**5**-**6*p***) (Table 1, run 1).

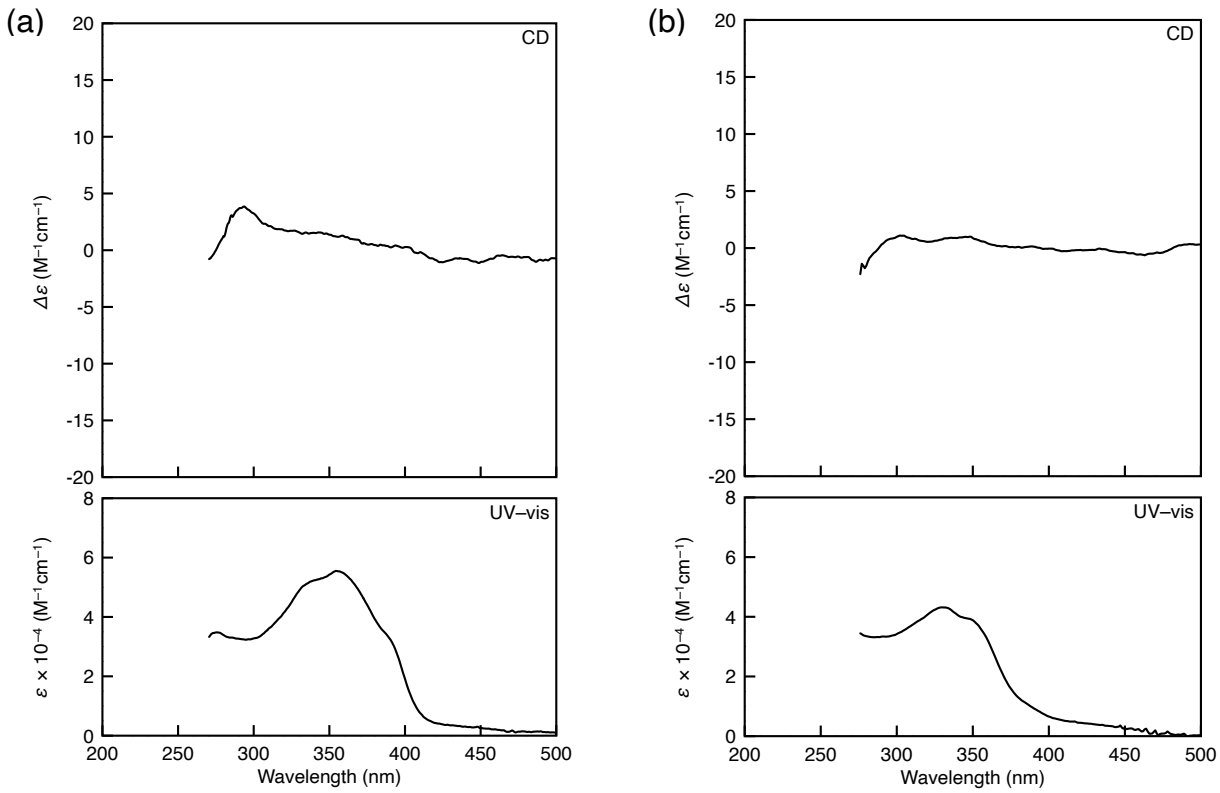


Fig. S56 CD and UV–vis absorption spectra of (a) poly(**5**-**6*p***) and (b) poly(**5**-**6*m***) measured in DMF (c = 0.01 mM) at 25 °C.

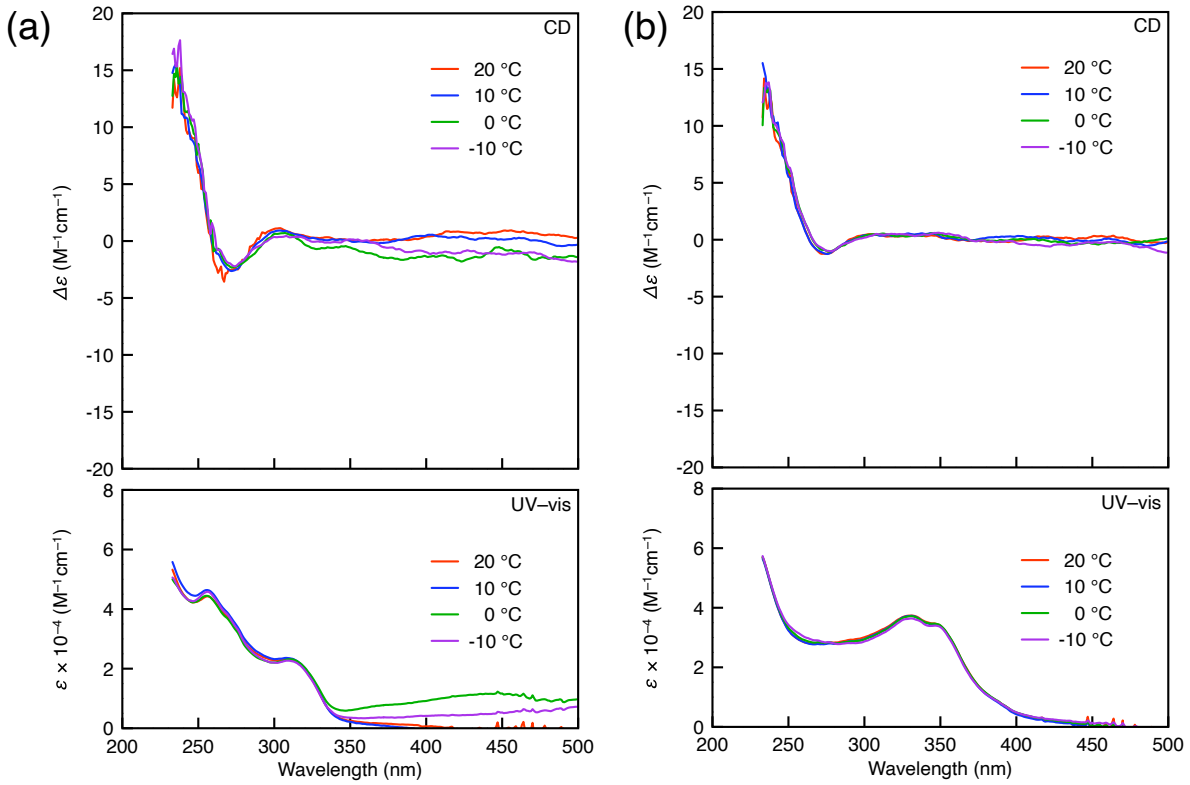


Fig. S57 CD and UV–vis absorption spectra of (a) **3** and (b) poly(**5**-**6*m***) measured in CH_2Cl_2 (c = 0.01 mM) at –10–20 °C.

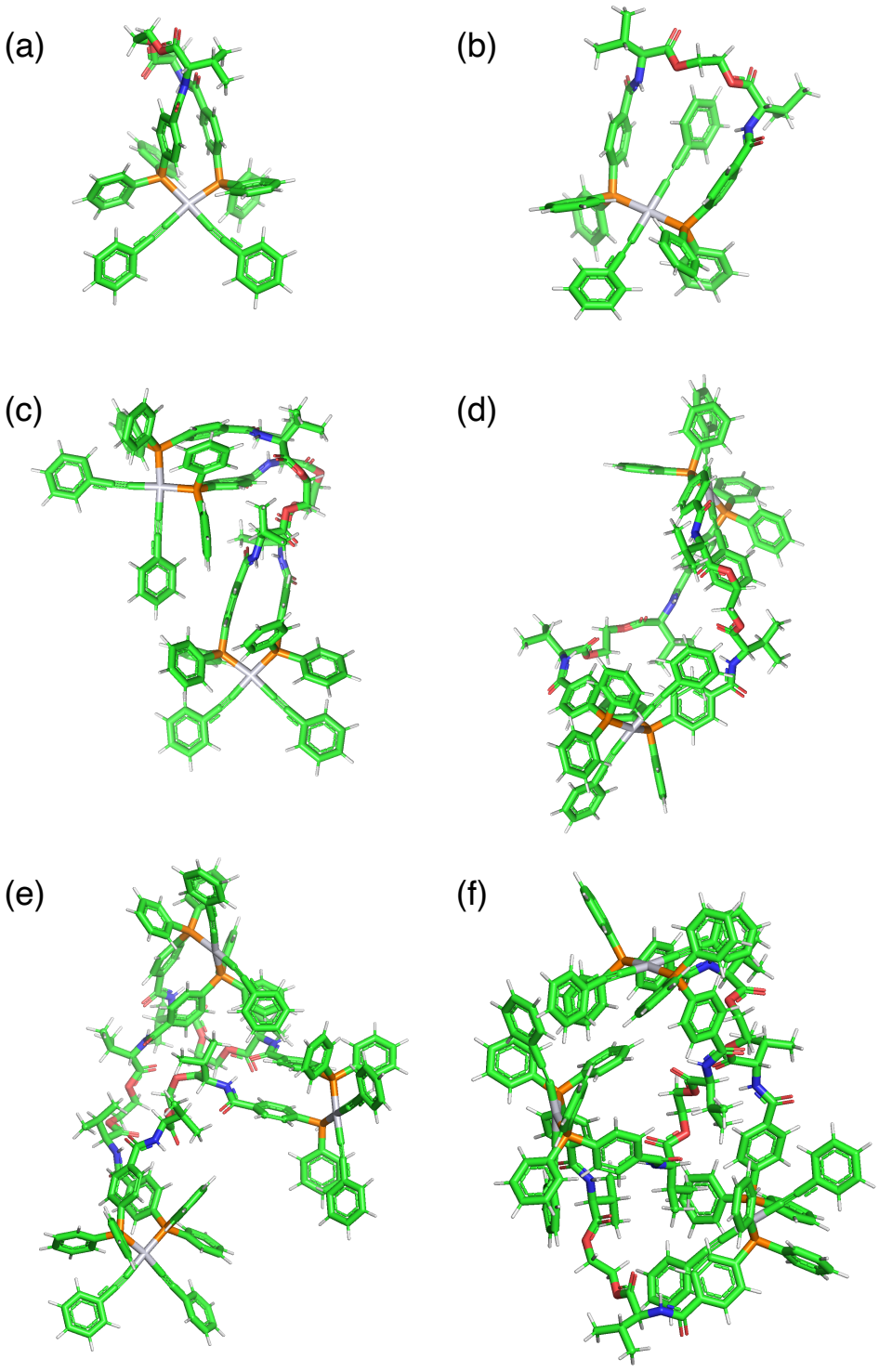


Fig. S58 Possible conformers of cyclic Pt compounds shown in Scheme 2. The geometries were optimized by the DFT method using the ωB97X-D functional with 6-31G* (H, C, N, O, P) and LANL2DZ (Pt) basis sets. (a) cyclic *cis*-Pt monomeric compound (**3**), (b) cyclic *trans*-Pt monomeric compound, (c) cyclic *cis*-Pt dimeric compound, (d) cyclic *trans*-Pt dimeric compound, (e) cyclic *cis*-Pt trimeric compound and (f) cyclic *trans*-Pt trimeric compound.

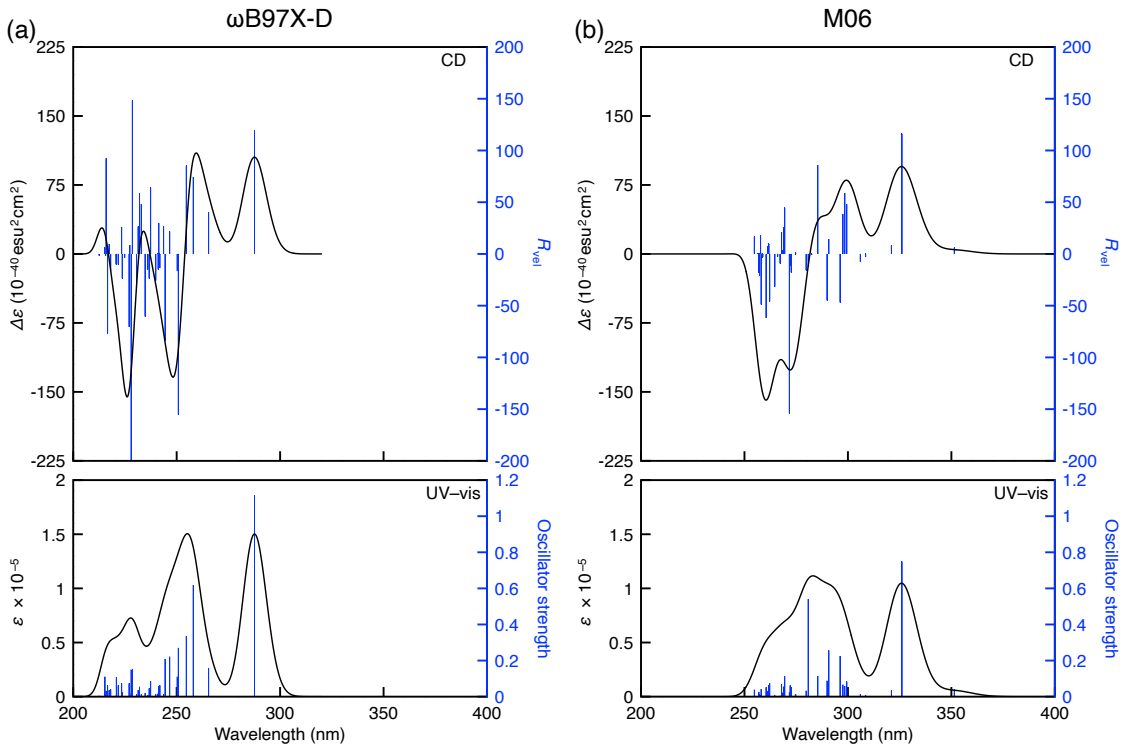


Fig. S59 CD and UV–vis absorption spectra of **5** simulated by the TD-DFT method using (a) ωB97X-D and (b) M06 functionals, with 6-31G* (C, H, N, O, P) and LANL2DZ (Pt) basis sets, and SCRF-IEFPCM (solvent CH_2Cl_2), nstates = 40, plotted with peak half-width at half-height = 0.1 eV using GaussView 6. Black and blue lines in the charts represent the spectrum and oscillator strength, respectively. The geometries of H atoms were optimized by the DFT method using the same functional and basis sets as those of the TD-DFT method, while those of C, N, O, P and Pt atoms were obtained from the single crystal X-ray analysis of **5** and frozen without optimization.

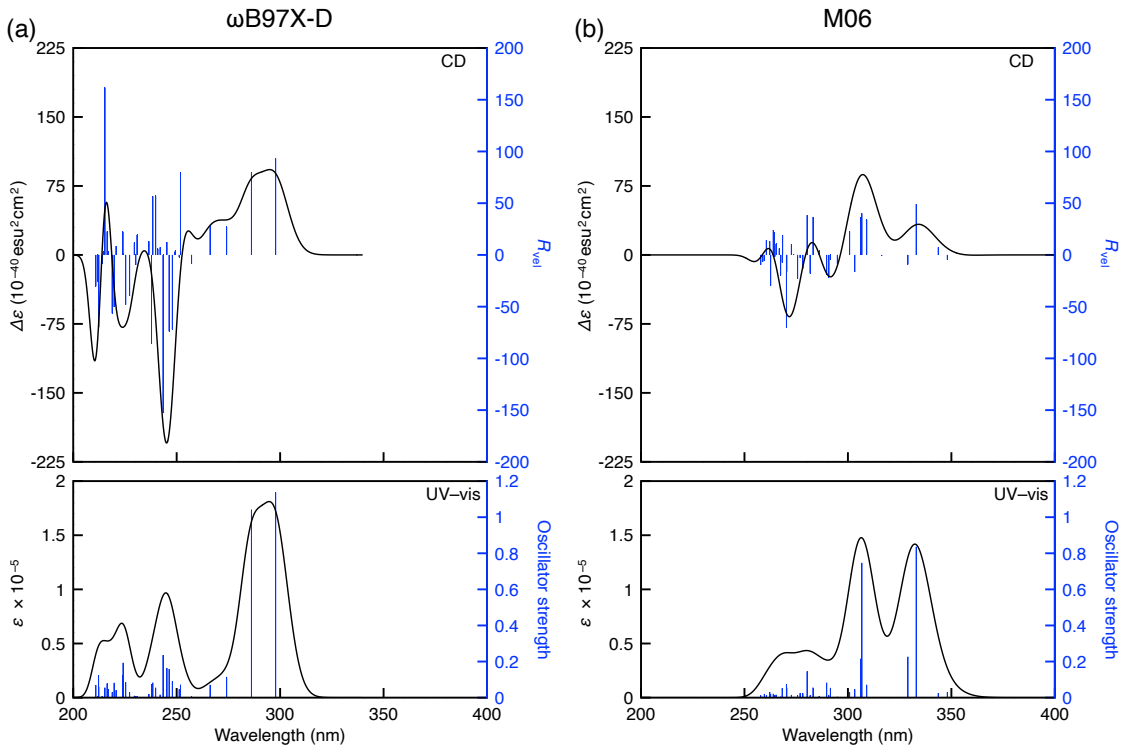


Fig. S60 CD and UV–vis absorption spectra of **5** simulated by the TD-DFT method using (a) ωB97X-D and (b) M06 functionals, with 6-31G* (C, H, N, O, P) and LANL2DZ (Pt) basis sets, and SCRF-IEFPCM (solvent CH_2Cl_2), nstates = 40, plotted with peak half-width at half-height = 0.1 eV using GaussView 6. Black and blue lines in the charts represent the spectrum and oscillator strength, respectively. The geometries were fully optimized by the DFT method using the same functional and basis sets as those of the TD-DFT method, starting from the geometries obtained by the single crystal X-ray analysis of **5**.

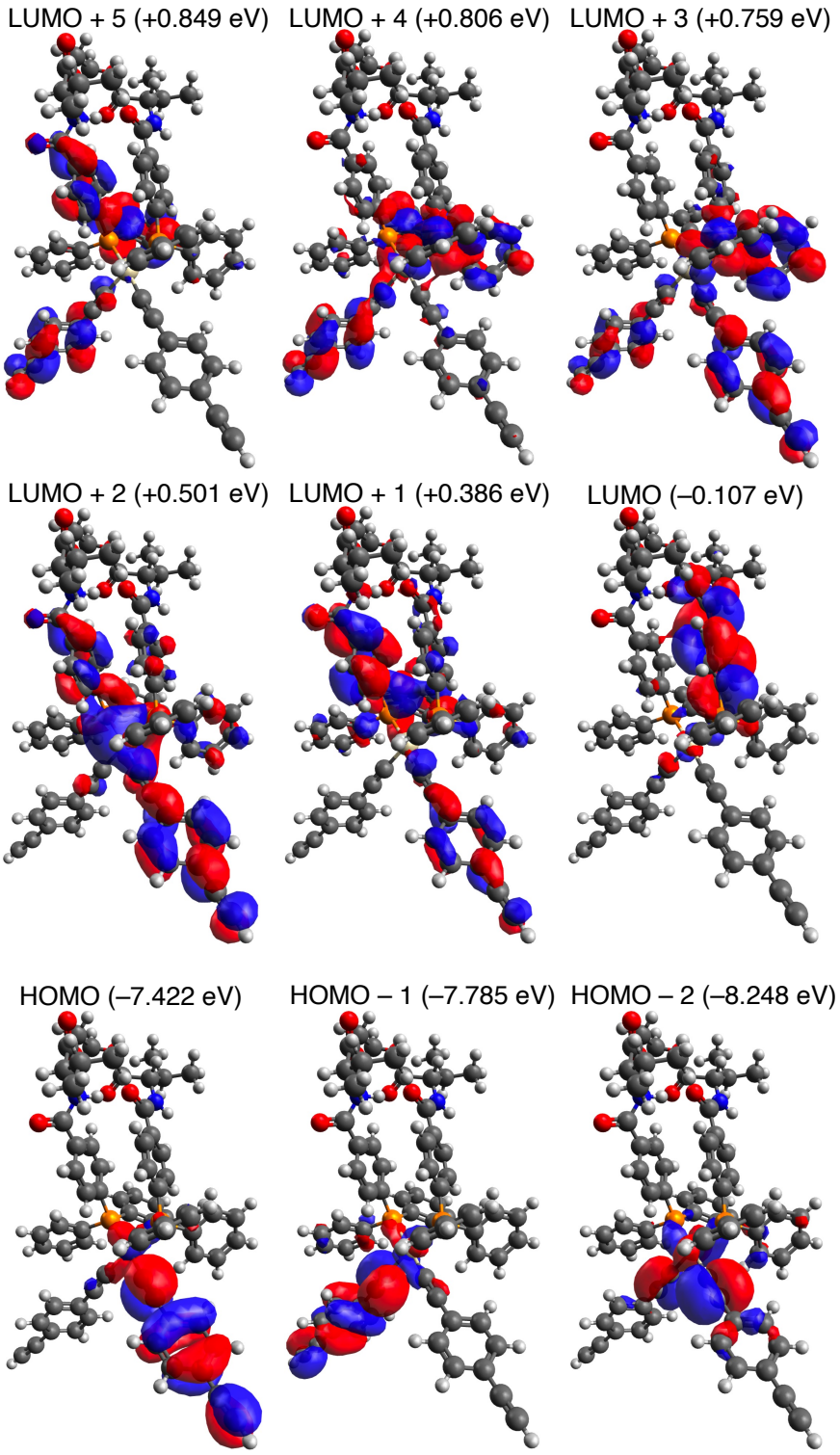


Fig. S61 Shapes and energy levels from LUMO + 5 to HOMO – 2 of S_0 state of **5**. The geometries of H atoms were optimized by the DFT method using the ωB97X-D functional with 6-31G* (C, H, N, O, P) and LANL2DZ (Pt) basis sets, and SCRF-IEFPCM (solvent CH_2Cl_2), while those of C, N, O, P and Pt atoms were obtained by the single crystal X-ray analysis of **5** and frozen without optimization.

Excitation Energies and Oscillator Strengths for S_0 state of **5** calculated by the TD-DFT method using the ωB97X-D functional with 6-31G* (C, H, N, O, P) and LANL2DZ (Pt) basis sets, and SCRF-IEFPCM (solvent CH_2Cl_2), nstates = 40. The geometries were same as those of Fig. S61.

Correspondence of MOs

301 LUMO + 5

300 LUMO + 4

299 LUMO + 3

298 LUMO + 2

297 LUMO + 1

296 LUMO

295 HOMO

294 HOMO – 1

293 HOMO – 2

Excited State 1: Singlet-A 4.3107 eV 287.62 nm *f*=1.1139 <S**2>=0.000

295 -> 297 0.31048

295 -> 298 0.54420

295 -> 299 0.19018

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-DFT) = -4064.83313429

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 4.6713 eV 265.42 nm *f*=0.1591 <S**2>=0.000

292 -> 297 -0.10385

292 -> 298 -0.17720

293 -> 297 0.29542

293 -> 298 0.49858

293 -> 299 0.13640

293 -> 325 -0.10753

Excited State 3: Singlet-A 4.8048 eV 258.04 nm *f*=0.6186 <S**2>=0.000

287 -> 296 -0.11583

289 -> 296 0.14144

294 -> 297 0.10735

294 -> 298 0.22138

294 -> 299 -0.10712

294 -> 300 0.23403

294 -> 301 -0.14390

295 -> 296 0.27510

295 -> 300 -0.19402

295 -> 302 -0.24495

Excited State 4: Singlet-A 4.8684 eV 254.67 nm *f*=0.3344 <S**2>=0.000

294 -> 297 0.11410

294 -> 298 0.19138

294 -> 299 -0.18619

294 -> 300 0.30535

294 -> 301 -0.22944

295 -> 296 -0.22615

295 -> 300 0.17408

295 -> 302 0.23295

Excited State 5: Singlet-A 4.9431 eV 250.82 nm *f*=0.2702 <S**2>=0.000

272 -> 296 -0.11410

285 -> 296 -0.11748

287 -> 296 -0.20311

289 -> 296 0.31355

291 -> 296 0.20069

292 -> 296 -0.12133

294 -> 296 0.10582

294 -> 298 -0.14130

294 -> 302 -0.16159

295 -> 296 0.10701

295 -> 302 0.13208

Excited State 6: Singlet-A 4.9540 eV 250.27 nm *f*=0.1101 <S**2>=0.000

277 -> 297 0.14778

277 -> 317 0.14098

283 -> 297 -0.10275

287 -> 297 0.18452

287 -> 298 -0.12330

288 -> 297 0.11335

289 -> 297 0.22908

289 -> 298 -0.14397

289 -> 301 -0.11609

289 -> 317 0.10299

291 -> 297 0.18164

291 -> 298 -0.10478

Excited State 7: Singlet-A 5.0276 eV 246.61 nm *f*=0.2215 <S**2>=0.000

272 -> 296 -0.12045

289 -> 296 0.15658

291 -> 296 0.11322

294 -> 298 0.13119

294 -> 299 0.14356

294 -> 300 -0.11983

294 -> 301 0.18413

294 -> 302 0.24692

294 -> 304 0.11519

294 -> 307 -0.12393

295 -> 296 -0.15737

Excited State 8: Singlet-A 5.0730 eV 244.40 nm *f*=0.2084 <S**2>=0.000

269 -> 296 -0.11843

279 -> 296 -0.10075

288 -> 296 0.12799

292 -> 296 0.14022

293 -> 296 -0.11865

294 -> 296 -0.12880

295 -> 296 0.29865

295 -> 299 -0.17084

295 -> 302 0.18944

295 -> 304 0.10745

295 -> 315 -0.13104

Excited State 9: Singlet-A 5.0881 eV 243.67 nm *f*=0.0137 <S**2>=0.000

268 -> 296 0.24349

269 -> 296 -0.17425

272 -> 296 -0.17631

278 -> 296 -0.13576

282 -> 296 0.12374

284 -> 296 0.12607

287 -> 296 0.15011

294 -> 307 0.12791

295 -> 296 -0.15036

295 -> 300 -0.10367

295 -> 302 -0.12761

Excited State 10: Singlet-A 5.1255 eV 241.90 nm *f*=0.0626 <S**2>=0.000

286 -> 299 0.13937

286 -> 300 -0.19530

286 -> 301 0.18163

292 -> 298 -0.10184

294 -> 306 -0.10995

294 -> 307 0.39209

294 -> 309 0.12305

Excited State 11: Singlet-A 5.1367 eV 241.37 nm *f*=0.0563 <S**2>=0.000

281 -> 297 -0.11227

281 -> 298 -0.20073

281 -> 299 -0.11420

292 -> 297 -0.13379

292 -> 298 -0.26163

292 -> 300 -0.16578

292 -> 302 -0.11859

292 -> 309 -0.11579

293 -> 300 -0.11322

295 -> 314 0.32018

Excited State 12: Singlet-A 5.1437 eV 241.04 nm *f*=0.0102 <S**2>=0.000

268 -> 296 0.38221

268 -> 315 0.11763

274 -> 296 0.10754

281 -> 298 0.14031

292 -> 298 -0.13199

295 -> 314 -0.24971

Excited State 13: Singlet-A 5.1480 eV 240.84 nm *f*=0.0162 <S**2>=0.000

268 -> 296 0.31831

269 -> 296 0.10739

274 -> 296 0.12407

281 -> 298 -0.13982

282 -> 296 -0.10466

292 -> 298 0.14970

295 -> 314 0.25645

Excited State 14: Singlet-A 5.1683 eV 239.89 nm *f*=0.0130 <S**2>=0.000

271 -> 311 0.31051

271 -> 312 0.34520

289 -> 311 -0.15544

289 -> 312 -0.17092

290 -> 311 0.15655

290 -> 312 0.17055

291 -> 311 0.24698

291 -> 312 0.27122

Excited State 15: Singlet-A 5.2226 eV 237.40 nm *f*=0.0861

<S**2>=0.000

288 -> 296 0.28297

288 -> 297 0.10996

288 -> 315 -0.17930

291 -> 296 0.11270

292 -> 296 0.15158

293 -> 296 0.16314

295 -> 299 0.27165

295 -> 300 0.10583

Excited State 16: Singlet-A 5.2381 eV 236.70 nm *f*=0.0458

<S**2>=0.000

276 -> 299 0.20222

276 -> 300 -0.28166

276 -> 301 0.27922

276 -> 302 0.17112

276 -> 322 0.14789

276 -> 323 -0.11002

283 -> 316 -0.11567

294 -> 307 0.10426

294 -> 316 0.11793

295 -> 299 0.17666

Excited State 17: Singlet-A 5.2525 eV 236.05 nm *f*=0.0093

<S**2>=0.000

276 -> 299 -0.10045

276 -> 300 0.13814

276 -> 301 -0.13504

288 -> 296 -0.11012

293 -> 296 -0.17113

295 -> 296 0.11842

295 -> 299 0.36749

295 -> 300 0.14814

Excited State 18: Singlet-A 5.2818 eV 234.74 nm *f*=0.0201 <S**2>=0.000

291 -> 296 0.10240

292 -> 296 0.26116

292 -> 315 -0.12350

293 -> 296 -0.20571

293 -> 300 0.11084

294 -> 296 0.26821

294 -> 297 0.12420

294 -> 315 -0.10557

Excited State 19: Singlet-A 5.3236 eV 232.89 nm *f*=0.0122 <S**2>=0.000

269 -> 296 0.11594

274 -> 297 -0.11828

277 -> 297 0.11525

279 -> 297 -0.12953

282 -> 297 0.10596

284 -> 297 0.13334

287 -> 298 -0.11386

288 -> 298 0.20931

288 -> 302 0.14294

289 -> 297 -0.11572

291 -> 297 -0.11059

293 -> 296 -0.11333

Excited State 20: Singlet-A 5.3433 eV 232.04 nm *f*=0.0546 <S**2>=0.000

274 -> 297 0.12103

287 -> 297 -0.11106

288 -> 297 0.14981

288 -> 298 0.25148

288 -> 302 0.18942

288 -> 309 0.11200

293 -> 296 -0.14996

Excited State 21: Singlet-A 5.3585 eV 231.38 nm *f*=0.0364 <S**2>=0.000

285 -> 296 0.10220

288 -> 296 -0.22759

288 -> 298 0.19676

288 -> 300 0.12761

288 -> 302 0.14815

288 -> 315 0.11576

292 -> 296 0.16558

293 -> 296 0.27796

293 -> 315 -0.13518

295 -> 296 0.11012

Excited State 22: Singlet-A 5.3763 eV 230.61 nm *f*=0.0130 <S**2>=0.000

273 -> 303 -0.10945

279 -> 299 -0.12157

280 -> 297 -0.10676

280 -> 298 -0.13113

280 -> 299 0.27265

280 -> 300 0.14136

281 -> 299 -0.10379

282 -> 303 0.14321

293 -> 299 -0.16737

293 -> 302 0.11461

Excited State 23: Singlet-A 5.4235 eV 228.60 nm *f*=0.1531 <S**2>=0.000

277 -> 297 -0.10820

285 -> 302 0.12451

285 -> 303 -0.11685

287 -> 296 0.11841

291 -> 296 0.15542

291 -> 297 0.19578

291 -> 298 -0.11226

293 -> 302 -0.11020

295 -> 299 -0.14352

295 -> 303 -0.10422

Excited State 24: Singlet-A 5.4378 eV 228.01 nm *f*=0.1489 <S**2>=0.000

277 -> 297 -0.11177

279 -> 299 -0.11179

282 -> 305 0.11308

285 -> 300 -0.10069

285 -> 302 -0.15247

285 -> 303 0.10644

291 -> 296 0.14467

291 -> 297 0.20378

291 -> 298 -0.12043

295 -> 299 0.11314

295 -> 303 0.10971

Excited State 25: Singlet-A 5.4528 eV 227.38 nm *f*=0.0180 <S**2>=0.000

274 -> 297 -0.12851

274 -> 300 -0.11723

274 -> 301 -0.14813

275 -> 297 0.14966

275 -> 300 0.12658

275 -> 301 0.21695

275 -> 304 -0.15661

278 -> 297 0.18783

278 -> 300 0.17552

278 -> 301 0.20205

284 -> 304 -0.14327

284 -> 309 0.11462

Excited State 26: Singlet-A 5.4618 eV 227.00 nm *f*=0.0733 <S**2>=0.000

291 -> 296 0.10480

292 -> 302 -0.19433

293 -> 296 0.15214

293 -> 299 -0.19915

293 -> 300 0.16143

293 -> 302 0.25798

293 -> 304 0.12338

293 -> 309 0.13037

293 -> 315 -0.11786

294 -> 296 -0.15288

Excited State 27: Singlet-A 5.5134 eV 224.88 nm *f*=0.0037 <S**2>=0.000

292 -> 296 -0.12552

292 -> 297 -0.10137

292 -> 299 -0.17283

292 -> 300 0.24837

292 -> 301 -0.19993

292 -> 302 -0.19836

292 -> 322 0.12436

293 -> 299 -0.10838

293 -> 300 0.10714

293 -> 301 -0.12328

293 -> 302 -0.16322

294 -> 296 0.10567

294 -> 297 0.12897

Excited State 28: Singlet-A 5.5421 eV 223.71 nm *f*=0.0247 <S**2>=0.000

267 -> 306 0.13056

267 -> 308 0.37000

268 -> 308 0.14415

269 -> 308 -0.14312

272 -> 308 0.22130

273 -> 308 0.20734

292 -> 296 -0.10081

293 -> 302 0.10331

294 -> 296 0.12552

Excited State 29: Singlet-A 5.5500 eV 223.39 nm *f*=0.0735 <S**2>=0.000

267 -> 308 -0.23208

272 -> 308 -0.13773

273 -> 308 -0.12291

291 -> 296 -0.13596

292 -> 296 -0.16384

292 -> 299 0.12495

293 -> 302 0.13074

294 -> 296 0.20124

294 -> 297 0.16310

295 -> 296 0.16331

Excited State 30: Singlet-A 5.5910 eV 221.76 nm *f*=0.0621 <S**2>=0.000

288 -> 297 -0.10326

290 -> 300 0.13843

290 -> 305 0.13399

290 -> 310 -0.17221

291 -> 296 0.16949

291 -> 297 -0.10551

294 -> 297 0.11613

294 -> 310 -0.11117

Excited State 31: Singlet-A 5.6134 eV 220.87 nm *f*=0.1074 <S**2>=0.000

277 -> 296 -0.12677

284 -> 296 -0.10096

287 -> 296 0.20512

288 -> 296 0.13667

290 -> 310 0.10079

291 -> 296 0.27963

291 -> 297 -0.15171

Excited State 32: Singlet-A 5.6183 eV 220.68 nm *f*=0.0047 <S**2>=0.000

260 -> 316 0.11128

276 -> 300 -0.13289

276 -> 301 0.13138

282 -> 316 0.14282

283 -> 316 0.35586

290 -> 316 0.15059

294 -> 316 -0.37618

Excited State 33: Singlet-A 5.6847 eV 218.10 nm *f*=0.0397 <S**2>=0.000

276 -> 316 0.11219

283 -> 301 -0.10166

294 -> 296 0.16496

294 -> 297 -0.25120

294 -> 298 0.13588

294 -> 301 -0.11565

295 -> 297 0.30769

295 -> 298 -0.16995

295 -> 303 -0.11691

Excited State 34: Singlet-A 5.7043 eV 217.35 nm *f*=0.0357 <S**2>=0.000

282 -> 299	0.15218
292 -> 299	-0.12577
293 -> 296	0.13129
293 -> 297	-0.11678
293 -> 299	0.26994
293 -> 300	0.12947
295 -> 297	0.10594
295 -> 303	0.23916

Excited State 35: Singlet-A 5.7189 eV 216.80 nm *f*=0.0020 <S**2>=0.000

270 -> 297	0.25007
270 -> 298	0.44443
270 -> 299	0.28096
270 -> 300	-0.10817
270 -> 302	-0.18221
270 -> 325	0.15078
270 -> 328	0.10134

Excited State 36: Singlet-A 5.7240 eV 216.60 nm *f*=0.0616 <S**2>=0.000

276 -> 316	-0.13304
289 -> 297	0.12543

290 -> 301 0.12702

291 -> 297 -0.14064

293 -> 297 -0.10258

294 -> 297 0.19266

294 -> 301 0.11908

295 -> 296 -0.11263

295 -> 297 0.24483

295 -> 298 -0.13211

295 -> 303 -0.21246

295 -> 305 -0.12053

Excited State 37: Singlet-A 5.7428 eV 215.89 nm *f*=0.0316 <S**2>=0.000

276 -> 316 0.15931

283 -> 300 0.12896

284 -> 297 -0.14424

290 -> 297 -0.15487

291 -> 297 -0.12774

291 -> 301 0.10846

292 -> 297 0.10688

294 -> 297 0.18984

294 -> 300 0.14045

295 -> 303 0.12128

Excited State 38: Singlet-A 5.7490 eV 215.66 nm *f*=0.0058 <S**2>=0.000

292 -> 299 0.11243

293 -> 299 -0.29172

293 -> 300 -0.18901

295 -> 297 0.13680

295 -> 298 -0.10565

295 -> 303 0.30668

295 -> 309 0.10842

Excited State 39: Singlet-A 5.7574 eV 215.35 nm *f*=0.1105 <S**2>=0.000

276 -> 316 0.17132

283 -> 300 0.12342

283 -> 301 -0.10463

284 -> 297 0.10342

284 -> 301 0.12603

288 -> 297 -0.11651

290 -> 296 0.11824

290 -> 297 0.28993

290 -> 298 -0.10413

Excited State 40: Singlet-A 5.8353 eV 212.47 nm *f*=0.0053 <S**2>=0.000

272 -> 296 -0.10019

273 -> 296 -0.11963

274 -> 297 -0.10551

284 -> 297 0.10401

289 -> 296	0.25355
289 -> 297	0.19009
289 -> 298	-0.14950
290 -> 296	-0.16573
291 -> 296	-0.16876
292 -> 297	-0.16751
294 -> 301	-0.10387
295 -> 297	-0.14930
295 -> 303	-0.10678

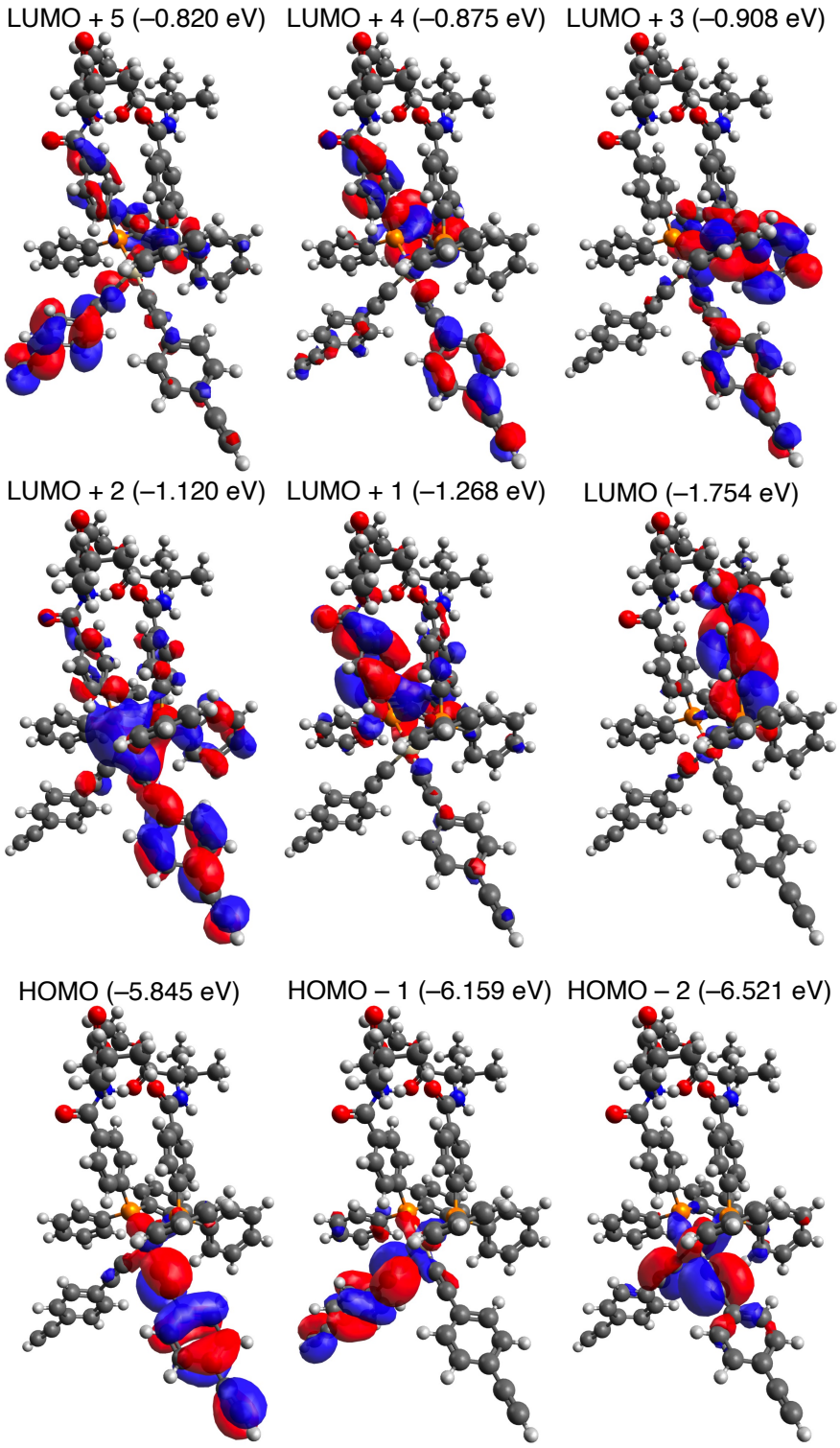


Fig. S62 Shapes and energy levels from LUMO + 5 to HOMO – 2 of S_0 state of **5**. The geometries of H atoms were optimized by the DFT method using the M06 functional with 6-31G* (C, H, N, O, P) and LANL2DZ (Pt) basis sets, and SCRF-IEFPCM (solvent CH_2Cl_2), while those of C, N, O, P and Pt atoms were obtained by the single crystal X-ray analysis of **5** and frozen without optimization.

Excitation Energies and Oscillator Strengths for S_0 state of **5** calculated by the TD-DFT method using the M06 functional with 6-31G* (C, H, N, O, P) and LANL2DZ (Pt) basis sets, and SCRF-IEFPCM (solvent CH_2Cl_2), nstates = 40. The geometries were same as those of Fig. S62.

Correspondence of MOs

301 LUMO + 5

300 LUMO + 4

299 LUMO + 3

298 LUMO + 2

297 LUMO + 1

296 LUMO

295 HOMO

294 HOMO – 1

293 HOMO – 2

Excited State 1: Singlet-A 3.5279 eV 351.43 nm *f*=0.0399 <S**2>=0.000

295 -> 296 0.69599

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-DFT) = -4063.46791406

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.8018 eV 326.12 nm *f*=0.7487 <S**2>=0.000

295 -> 297 0.25708

295 -> 298 0.60812

295 -> 299 0.10919

Excited State 3: Singlet-A 3.8621 eV 321.03 nm *f*=0.0348 <S**2>=0.000

294 -> 296 0.68695

Excited State 4: Singlet-A 4.0183 eV 308.55 nm *f*=0.0080 <S**2>=0.000

295 -> 297 0.60803

295 -> 298 -0.20058

295 -> 299 -0.18850

295 -> 301 -0.12062

295 -> 302 -0.13567

Excited State 5: Singlet-A 4.0518 eV 306.00 nm *f*=0.0128 <S**2>=0.000

293 -> 296 0.62339

293 -> 297 0.13432

293 -> 298 0.21371

Excited State 6: Singlet-A 4.1406 eV 299.43 nm *f*=0.0833 <S**2>=0.000

293 -> 296 -0.18712

293 -> 298 0.20259

294 -> 297 0.24155

294 -> 298 0.37505

294 -> 301 0.13239

295 -> 297 -0.12146

295 -> 298 0.12314

295 -> 299 -0.30183

295 -> 301 -0.10235

Excited State 7: Singlet-A 4.1538 eV 298.48 nm *f*=0.0589 <S**2>=0.000

294 -> 297 0.13754

294 -> 298 0.26232

295 -> 297 0.13239

295 -> 298 -0.16779

295 -> 299 0.53654

295 -> 301 0.10806

Excited State 8: Singlet-A 4.1663 eV 297.59 nm *f*=0.0664 <S**2>=0.000

292 -> 296 -0.21325

292 -> 298 -0.11644

293 -> 296 -0.22050

293 -> 297 0.17006

293 -> 298 0.43022

293 -> 299 0.12347

294 -> 297 -0.14953

294 -> 298 -0.22723

294 -> 301 -0.12687

Excited State 9: Singlet-A 4.1856 eV 296.21 nm *f*=0.2249 <S**2>=0.000

292 -> 296 0.61342

293 -> 298 0.20101

Excited State 10: Singlet-A 4.2641 eV 290.76 nm *f*=0.2556 <S**2>=0.000

292 -> 296 -0.11566

294 -> 297 -0.31466

294 -> 298 0.17962

294 -> 301 0.17909

295 -> 299 -0.13582

295 -> 300 0.31418

295 -> 301 0.23179

295 -> 302 0.33092

Excited State 11: Singlet-A 4.2769 eV 289.90 nm *f*=0.0882 <S**2>=0.000

292 -> 296 -0.10002

294 -> 297 0.52090

294 -> 298 -0.22418

295 -> 300 0.20509

295 -> 301 0.16990

295 -> 302 0.19960

Excited State 12: Singlet-A 4.3437 eV 285.44 nm *f*=0.1146

<S**2>=0.000

288 -> 296	-0.19843
289 -> 296	0.24508
290 -> 296	-0.41949
291 -> 296	0.42408

Excited State 13: Singlet-A 4.3890 eV 282.49 nm *f*=0.0028

<S**2>=0.000

288 -> 296	0.44246
289 -> 296	0.44109
290 -> 296	-0.11350
291 -> 296	-0.15169
292 -> 296	-0.10138

Excited State 14: Singlet-A 4.4150 eV 280.82 nm *f*=0.5406

<S**2>=0.000

278 -> 316	-0.11601
294 -> 298	-0.14287
294 -> 299	-0.15916
294 -> 300	0.16044
294 -> 301	0.43214
294 -> 302	-0.27741
295 -> 300	-0.21446

Excited State 15: Singlet-A 4.4311 eV 279.80 nm *f*=0.0327

<S**2>=0.000

294 -> 301 0.13240

295 -> 299 0.16792

295 -> 300 0.51458

295 -> 301 -0.32620

295 -> 302 -0.19353

Excited State 16: Singlet-A 4.5125 eV 274.76 nm *f*=0.0131

<S**2>=0.000

288 -> 296 -0.22110

289 -> 296 0.32712

290 -> 296 0.27329

292 -> 298 0.13726

292 -> 301 0.10722

295 -> 301 -0.29928

295 -> 302 0.27451

295 -> 303 -0.14057

Excited State 17: Singlet-A 4.5149 eV 274.61 nm *f*=0.0134

<S**2>=0.000

288 -> 296 -0.25588

289 -> 296 0.27704

290 -> 296 0.30387

294 -> 301 0.10892

295 -> 301 0.28733

295 -> 302 -0.28348

295 -> 303 0.18386

Excited State 18: Singlet-A 4.5485 eV 272.58 nm *f*=0.0528 <S**2>=0.000

286 -> 296 0.12640

292 -> 297 0.29259

292 -> 298 0.34032

292 -> 301 0.13149

293 -> 297 0.27528

293 -> 300 0.12507

293 -> 301 0.10743

295 -> 301 0.14458

295 -> 302 -0.11683

295 -> 303 0.17631

Excited State 19: Singlet-A 4.5572 eV 272.07 nm *f*=0.0616 <S**2>=0.000

285 -> 296 -0.10612

286 -> 296 -0.12817

292 -> 298 -0.11050

293 -> 297 0.54391

293 -> 298 -0.22782

293 -> 301 -0.11252

295 -> 303 -0.17921

Excited State 20: Singlet-A 4.5632 eV 271.71 nm *f*=0.0227

<S**2>=0.000

285 -> 296 0.25466

286 -> 296 0.31587

286 -> 297 0.11700

288 -> 296 -0.13289

288 -> 297 0.11027

289 -> 297 -0.18429

291 -> 296 -0.10300

291 -> 297 -0.15635

292 -> 297 -0.11902

292 -> 298 -0.15128

293 -> 297 0.10897

293 -> 298 -0.10046

294 -> 301 0.10366

295 -> 303 -0.10203

Excited State 21: Singlet-A 4.6016 eV 269.44 nm *f*=0.1123

<S**2>=0.000

292 -> 297 -0.12111

292 -> 298 -0.12732

293 -> 297 0.11592

294 -> 300 0.13240

295 -> 301 -0.17231

295 -> 302 0.20452

295 -> 303 0.53241

Excited State 22: Singlet-A 4.6110 eV 268.89 nm *f*=0.0554

<S**2>=0.000

286 -> 296	0.10277
288 -> 296	-0.12517
288 -> 297	-0.15451
289 -> 297	0.14783
290 -> 296	-0.18685
291 -> 296	-0.27032
291 -> 297	0.10665
294 -> 299	0.20369
294 -> 300	0.32223
295 -> 302	-0.10076
295 -> 303	-0.18492

Excited State 23: Singlet-A 4.6188 eV 268.44 nm *f*=0.0221

<S**2>=0.000

288 -> 297	0.12396
289 -> 297	-0.13179
290 -> 296	0.14783
291 -> 296	0.23034
293 -> 299	0.10063
294 -> 298	-0.11878
294 -> 299	0.38762
294 -> 300	0.33345

Excited State 24: Singlet-A 4.6277 eV 267.92 nm *f*=0.0701

<S**2>=0.000

274 -> 296 -0.10683

276 -> 296 -0.12055

279 -> 296 0.10656

281 -> 296 0.13602

283 -> 296 -0.14374

285 -> 296 0.22463

286 -> 296 0.24829

288 -> 296 0.18480

289 -> 297 0.14852

290 -> 296 0.15266

291 -> 296 0.28374

291 -> 297 0.14206

292 -> 297 0.13252

294 -> 299 -0.11169

Excited State 25: Singlet-A 4.6405 eV 267.18 nm *f*=0.0048

<S**2>=0.000

292 -> 297 0.49891

292 -> 298 -0.18066

292 -> 301 -0.11017

293 -> 299 0.29623

294 -> 299 0.11818

Excited State 26: Singlet-A 4.6602 eV 266.05 nm *f*=0.0011

<S**2>=0.000

292 -> 297 0.19512

292 -> 298 -0.14144

293 -> 299 -0.13500

294 -> 298 0.13393

294 -> 299 -0.30521

294 -> 300 0.37666

294 -> 301 -0.27574

Excited State 27: Singlet-A 4.6845 eV 264.67 nm *f*=0.0078 <S**2>=0.000

292 -> 297 -0.10891

292 -> 298 0.21072

293 -> 298 -0.16186

293 -> 299 0.39273

293 -> 300 -0.16956

293 -> 302 -0.13986

294 -> 298 0.14531

294 -> 299 -0.13105

294 -> 301 -0.15047

294 -> 302 -0.22857

294 -> 304 -0.11372

Excited State 28: Singlet-A 4.7289 eV 262.18 nm *f*=0.0731 <S**2>=0.000

292 -> 299 -0.11336

293 -> 299 0.29346

293 -> 300 0.15049

293 -> 301 0.21151

293 -> 302 0.14315

294 -> 299 -0.21211

294 -> 300 0.12810

294 -> 302 0.22009

294 -> 304 0.10019

294 -> 308 -0.20494

295 -> 304 0.14768

Excited State 29: Singlet-A 4.7358 eV 261.80 nm *f*=0.0636 <S**2>=0.000

281 -> 296 -0.20473

283 -> 296 0.20441

286 -> 296 0.11856

287 -> 296 -0.10324

287 -> 301 -0.12983

291 -> 296 0.10468

292 -> 298 -0.12599

293 -> 302 0.12612

294 -> 299 0.10155

294 -> 302 -0.13416

294 -> 308 0.24192

295 -> 304 0.18305

Excited State 30: Singlet-A 4.7442 eV 261.34 nm *f*=0.0290

<S**2>=0.000

281 -> 296	0.18152
283 -> 296	-0.18110
286 -> 296	-0.14777
287 -> 301	-0.12184
292 -> 302	-0.14776
293 -> 300	0.15114
293 -> 301	0.20247
294 -> 308	0.24758
295 -> 304	0.12697

Excited State 31: Singlet-A 4.7605 eV 260.44 nm *f*=0.0515

<S**2>=0.000

278 -> 301	-0.10820
292 -> 298	-0.11794
292 -> 299	-0.10193
292 -> 300	0.14172
292 -> 301	0.29699
292 -> 302	-0.12854
293 -> 301	0.10371
293 -> 302	-0.27403
294 -> 299	-0.11109
294 -> 302	0.16871
294 -> 308	0.16774
295 -> 304	-0.12533
295 -> 305	0.10935

Excited State 32: Singlet-A 4.7896 eV 258.86 nm *f*=0.0031 <S**2>=0.000

278 -> 301	-0.16538
287 -> 301	0.15013
292 -> 298	-0.11005
292 -> 301	0.16194
293 -> 299	-0.11699
293 -> 302	-0.16503
294 -> 302	-0.24950
294 -> 308	-0.24455
295 -> 304	0.28940
295 -> 309	0.10221

Excited State 33: Singlet-A 4.7951 eV 258.56 nm *f*=0.0033 <S**2>=0.000

279 -> 296	-0.12775
280 -> 296	0.14586
281 -> 296	-0.14409
284 -> 296	0.15894
285 -> 296	0.47431
286 -> 296	-0.25075
287 -> 296	0.22386

Excited State 34: Singlet-A 4.8010 eV 258.25 nm *f*=0.0048 <S**2>=0.000

278 -> 301 0.10040

293 -> 301 -0.10480

294 -> 302 0.16621

295 -> 304 0.38052

295 -> 305 0.37818

295 -> 306 0.17818

295 -> 307 0.12688

295 -> 309 0.14160

Excited State 35: Singlet-A 4.8047 eV 258.05 nm *f*=0.0412 <S**2>=0.000

268 -> 296 0.24774

277 -> 296 0.11455

289 -> 297 -0.22072

291 -> 297 0.45791

295 -> 305 -0.10487

Excited State 36: Singlet-A 4.8099 eV 257.77 nm *f*=0.0068 <S**2>=0.000

282 -> 297 0.10509

282 -> 298 0.27888

282 -> 299 0.12433

282 -> 300 -0.14066

295 -> 305 0.13014

295 -> 314 0.53084

Excited State 37: Singlet-A 4.8185 eV 257.31 nm *f*=0.0112

<S**2>=0.000

268 -> 296	0.46409
271 -> 296	-0.14751
274 -> 296	0.12383
277 -> 296	0.13264
279 -> 296	-0.11089
281 -> 296	-0.20008
291 -> 297	-0.24331

Excited State 38: Singlet-A 4.8243 eV 257.00 nm *f*=0.0260

<S**2>=0.000

278 -> 301	-0.10922
291 -> 297	0.12633
292 -> 298	-0.11031
293 -> 300	0.14132
293 -> 301	0.10321
293 -> 302	0.14655
294 -> 302	-0.16406
295 -> 304	-0.24054
295 -> 305	0.40364
295 -> 306	0.13951
295 -> 307	0.10266
295 -> 314	-0.12566

Excited State 39: Singlet-A 4.8405 eV 256.14 nm *f*=0.0006

<S**2>=0.000

278 -> 300	-0.13311
278 -> 301	-0.44195
278 -> 302	0.24674
278 -> 323	-0.13912
292 -> 301	-0.14675
293 -> 301	-0.13575
294 -> 302	0.13076
294 -> 308	0.10883

Excited State 40: Singlet-A 4.8664 eV 254.78 nm *f*=0.0383

<S**2>=0.000

283 -> 296	-0.10930
286 -> 297	-0.10065
288 -> 297	-0.36808
289 -> 297	-0.23502
289 -> 298	-0.10259
290 -> 297	0.38015
291 -> 297	-0.15393

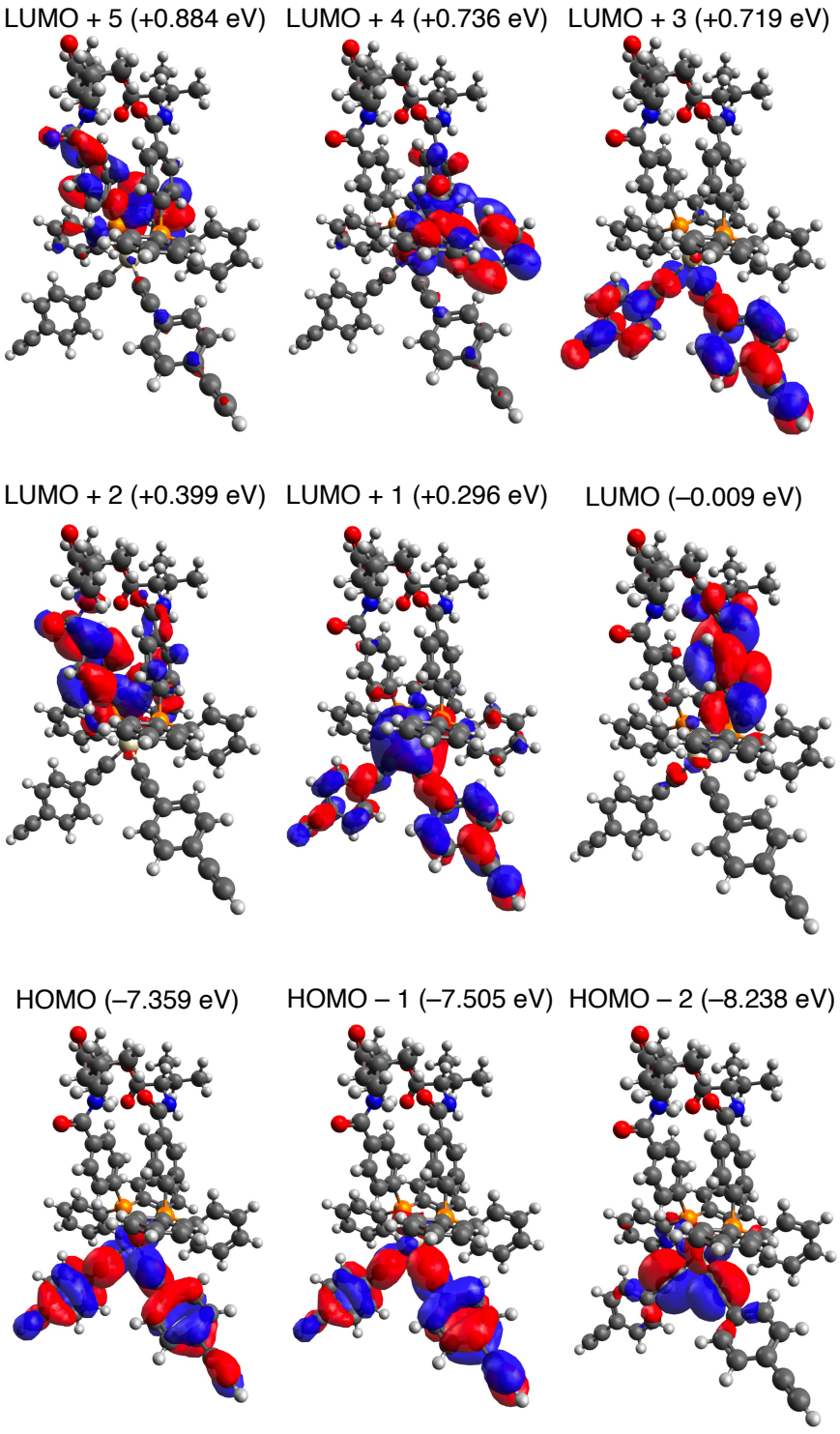


Fig. S63 Shapes and energy levels from LUMO + 5 to HOMO – 2 of S_0 state of **5**. The geometries were fully optimized by the DFT method using the ωB97X-D functional with 6-31G* (C, H, N, O, P) and LANL2DZ (Pt) basis sets, and SCRF-IEFPCM (solvent CH_2Cl_2), starting from the geometries obtained by the single crystal X-ray analysis of **5**.

Excitation Energies and Oscillator Strengths for S_0 state of **5** calculated by the TD-DFT method using the ωB97X-D functional with 6-31G* (C, H, N, O, P) and LANL2DZ (Pt) basis sets, and SCRF-IEFPCM (solvent CH_2Cl_2), nstates = 40. The geometries were same as those of Fig. S63.

Correspondence of MOs

301 LUMO + 5

300 LUMO + 4

299 LUMO + 3

298 LUMO + 2

297 LUMO + 1

296 LUMO

295 HOMO

294 HOMO – 1

293 HOMO – 2

Excited State 1: Singlet-A 4.1631 eV 297.82 nm *f*=1.1376 <S**2>=0.000

294 -> 299 -0.29239

295 -> 297 0.57522

295 -> 298 -0.10127

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-DFT) = -4065.00523383

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 4.3329 eV 286.15 nm *f*=1.0416 <S**2>=0.000

294 -> 297 0.55552

295 -> 299 -0.32741

Excited State 3: Singlet-A 4.5229 eV 274.13 nm *f*=0.1147 <S**2>=0.000

292 -> 299 -0.24277

293 -> 297 0.57510

293 -> 298 -0.10139

293 -> 299 -0.11672

Excited State 4: Singlet-A 4.6581 eV 266.17 nm *f*=0.0706 <S**2>=0.000

292 -> 297 0.53517

293 -> 299 -0.32306

Excited State 5: Singlet-A 4.8207 eV 257.19 nm *f*=0.0075 <S**2>=0.000

281 -> 296 0.10134

295 -> 296 0.45360

295 -> 298 0.11926

295 -> 303 -0.23562

295 -> 315 -0.21073

Excited State 6: Singlet-A 4.9230 eV 251.85 nm *f*=0.0715 <S**2>=0.000

289 -> 296 0.17260

292 -> 296 0.10233

294 -> 296 0.41613

294 -> 298 0.11408

294 -> 303 -0.18430

294 -> 311 0.10380

294 -> 315 -0.16456

Excited State 7: Singlet-A 4.9353 eV 251.22 nm *f*=0.0461 <S**2>=0.000

284 -> 296 0.10863

290 -> 296 0.30975

290 -> 303 -0.13384

290 -> 315 -0.20304

291 -> 296 0.19743

291 -> 303 -0.12537

291 -> 315 -0.16078

293 -> 296 0.10423

294 -> 299 -0.13411

Excited State 8: Singlet-A 4.9733 eV 249.30 nm *f*=0.0026 <S**2>=0.000

282 -> 297 0.14795

282 -> 299 0.14717

284 -> 297 -0.10427

284 -> 299 -0.10394

285 -> 297 0.14094

285 -> 299 0.13299

286 -> 297 0.15126

286 -> 299 0.14237

294 -> 304 -0.10841

294 -> 307 0.10460

294 -> 310 0.27501

294 -> 311 -0.23564

295 -> 310 -0.21425

295 -> 311 0.18103

Excited State 9: Singlet-A 4.9797 eV 248.98 nm *f*=0.0014 <S**2>=0.000

280 -> 299 -0.10879

283 -> 297 0.15754

283 -> 299 -0.19321

288 -> 297 -0.16767

288 -> 299 0.18927

294 -> 309 -0.13389

294 -> 310 0.16734

294 -> 311 0.14738

294 -> 312 -0.13458

295 -> 309 -0.19397

295 -> 310 0.23319

295 -> 311 0.21647

295 -> 312 -0.19243

Excited State 10: Singlet-A 5.0008 eV 247.93 nm *f*=0.0911

<S**2>=0.000

269 -> 296	-0.13138
271 -> 296	-0.13242
273 -> 296	0.27727
276 -> 296	-0.12066
280 -> 296	-0.17060
281 -> 296	-0.13038
283 -> 296	0.12578
287 -> 296	0.11950
288 -> 296	0.10107
289 -> 296	-0.22252
290 -> 296	0.13355
292 -> 296	0.12298

Excited State 11: Singlet-A 5.0324 eV 246.37 nm *f*=0.1588

<S**2>=0.000

277 -> 298	0.11649
280 -> 296	0.16502
284 -> 296	0.10345
285 -> 296	0.18663
285 -> 298	0.19491
286 -> 298	-0.12688
290 -> 296	0.12293
292 -> 296	0.13921
294 -> 299	0.12668

295 -> 299 0.17912

Excited State 12: Singlet-A 5.0546 eV 245.29 nm *f*=0.1639 <S**2>=0.000

275 -> 298 0.13331

277 -> 298 0.15622

285 -> 298 0.29428

285 -> 301 -0.11167

286 -> 298 -0.19042

294 -> 299 -0.15164

295 -> 299 -0.14424

295 -> 304 -0.10123

Excited State 13: Singlet-A 5.0931 eV 243.43 nm *f*=0.2358 <S**2>=0.000

269 -> 296 0.10263

289 -> 296 0.12390

291 -> 296 0.11739

292 -> 296 -0.16397

294 -> 299 0.25952

294 -> 304 -0.15677

295 -> 304 0.17296

Excited State 14: Singlet-A 5.1236 eV 241.99 nm *f*=0.0161 <S**2>=0.000

269 -> 296 0.28569

280 -> 296 -0.10690

289 -> 296 0.11411

290 -> 296 -0.10650

293 -> 296 0.17323

293 -> 303 -0.10893

293 -> 315 -0.10877

294 -> 304 0.15888

295 -> 299 0.22717

Excited State 15: Singlet-A 5.1465 eV 240.91 nm *f*=0.0011 <S**2>=0.000

269 -> 296 -0.14680

293 -> 296 0.35986

293 -> 298 0.10562

293 -> 300 0.10375

293 -> 303 -0.23469

293 -> 315 -0.24708

295 -> 299 -0.12123

Excited State 16: Singlet-A 5.1697 eV 239.83 nm *f*=0.0549 <S**2>=0.000

268 -> 296 -0.10572

269 -> 296 0.41398

274 -> 298 -0.11516

279 -> 298 0.10704

287 -> 296 0.13747

289 -> 296 -0.14520

290 -> 296 0.10326

290 -> 297 0.11638

292 -> 296 0.11490

295 -> 299 -0.11652

Excited State 17: Singlet-A 5.1995 eV 238.46 nm *f*=0.0827 <S**2>=0.000

269 -> 296 -0.13873

274 -> 298 -0.14507

279 -> 298 0.14856

284 -> 297 0.10410

289 -> 296 0.12766

289 -> 298 -0.16336

290 -> 297 0.23013

291 -> 297 0.15081

291 -> 298 -0.11516

292 -> 296 -0.12298

295 -> 299 0.10356

Excited State 18: Singlet-A 5.2129 eV 237.84 nm *f*=0.0748 <S**2>=0.000

274 -> 298 0.17166

279 -> 298 -0.17178

284 -> 297 0.11116

287 -> 297 -0.10216

289 -> 297 0.16072

289 -> 298 0.11415

290 -> 297 0.24402

290 -> 298 -0.12533

291 -> 297 0.24020

Excited State 19: Singlet-A 5.2400 eV 236.61 nm *f*=0.0195 <S**2>=0.000

294 -> 297 0.11477

294 -> 300 0.40731

294 -> 304 -0.11166

295 -> 299 0.11047

295 -> 300 -0.37011

295 -> 304 0.10936

Excited State 20: Singlet-A 5.3712 eV 230.83 nm *f*=0.0087 <S**2>=0.000

276 -> 301 0.14923

278 -> 298 -0.10929

278 -> 301 -0.21467

280 -> 301 -0.16018

281 -> 301 -0.10037

282 -> 301 0.11987

288 -> 302 0.12392

289 -> 305 -0.11836

291 -> 305 0.19349

Excited State 21: Singlet-A 5.3851 eV 230.23 nm *f*=0.0071 <S**2>=0.000

277 -> 300	-0.10329
277 -> 308	0.12231
278 -> 300	-0.20163
278 -> 302	0.13188
278 -> 303	0.12386
281 -> 300	0.18416
286 -> 300	-0.15731
290 -> 307	-0.10739
292 -> 300	0.10769

Excited State 22: Singlet-A 5.3999 eV 229.60 nm *f*=0.0021 <S**2>=0.000

276 -> 300	0.10430
278 -> 300	0.17751
282 -> 304	-0.17002
284 -> 307	0.14639
286 -> 304	0.12884
286 -> 308	-0.10959
290 -> 308	0.10278
292 -> 300	-0.11317
293 -> 300	0.11207
294 -> 300	0.10457

Excited State 23: Singlet-A 5.4014 eV 229.54 nm *f*=0.0101

<S**2>=0.000

276 -> 301	0.10284
276 -> 305	-0.12248
278 -> 301	-0.12679
280 -> 301	-0.13638
288 -> 302	-0.15776
288 -> 303	0.13988
291 -> 309	0.14295
291 -> 312	-0.12819
295 -> 298	0.17338
295 -> 302	-0.11996

Excited State 24: Singlet-A 5.4561 eV 227.24 nm *f*=0.0304

<S**2>=0.000

289 -> 298	0.10342
294 -> 298	0.25304
295 -> 298	0.43049

Excited State 25: Singlet-A 5.5019 eV 225.35 nm *f*=0.0850

<S**2>=0.000

292 -> 299	0.28043
293 -> 297	0.12944
293 -> 299	0.20834
293 -> 302	0.17510
293 -> 304	0.17628

293 -> 305 0.10341

293 -> 306 -0.18248

293 -> 307 0.14023

293 -> 309 -0.11658

Excited State 26: Singlet-A 5.5324 eV 224.11 nm *f*=0.1930 <S**2>=0.000

274 -> 298 -0.10050

275 -> 298 -0.13283

288 -> 298 -0.10882

289 -> 298 0.12914

291 -> 298 0.13722

292 -> 296 -0.15598

292 -> 303 0.10126

294 -> 302 0.10623

294 -> 303 -0.12618

295 -> 296 -0.11955

295 -> 302 0.26923

295 -> 303 -0.14782

Excited State 27: Singlet-A 5.5335 eV 224.06 nm *f*=0.1241 <S**2>=0.000

274 -> 298 0.11427

275 -> 298 0.15660

288 -> 298 0.12205

291 -> 298 -0.20064

294 -> 296 0.10554

295 -> 296 -0.18687

295 -> 298 0.31621

295 -> 302 0.13170

Excited State 28: Singlet-A 5.6179 eV 220.69 nm *f*=0.0406 <S**2>=0.000

289 -> 296 -0.10796

292 -> 296 -0.21437

292 -> 297 0.11870

292 -> 306 -0.10095

293 -> 299 0.22279

294 -> 296 0.11264

294 -> 302 -0.13162

294 -> 303 -0.11188

294 -> 304 0.12587

294 -> 306 0.10697

295 -> 296 0.19302

295 -> 298 -0.10218

295 -> 303 0.14277

295 -> 304 -0.10429

Excited State 29: Singlet-A 5.6416 eV 219.77 nm *f*=0.0819 <S**2>=0.000

292 -> 297 -0.13953

292 -> 298 0.10103

292 -> 299 0.16355

292 -> 304 -0.11891

292 -> 306 0.10128

293 -> 299 -0.19074

294 -> 296 -0.16649

294 -> 298 0.19735

294 -> 302 -0.10673

294 -> 303 -0.11885

294 -> 304 0.15443

295 -> 296 0.10140

295 -> 303 0.13135

295 -> 304 -0.10791

Excited State 30: Singlet-A 5.6653 eV 218.85 nm *f*=0.0294 <S**2>=0.000

285 -> 296 0.11129

292 -> 297 -0.11311

292 -> 299 0.11191

292 -> 303 0.17108

292 -> 304 -0.12787

292 -> 315 0.13925

293 -> 299 -0.14660

294 -> 296 0.30839

294 -> 298 -0.19632

Excited State 31: Singlet-A 5.7168 eV 216.88 nm *f*=0.0444

<S**2>=0.000

278 -> 300	0.12934
279 -> 300	-0.13817
290 -> 300	0.17000
292 -> 300	0.31902
292 -> 302	-0.12608
292 -> 304	-0.11609
293 -> 300	-0.25983
295 -> 296	0.10657
295 -> 300	-0.11492

Excited State 32: Singlet-A 5.7299 eV 216.38 nm *f*=0.0781

<S**2>=0.000

289 -> 298	0.11317
291 -> 296	-0.10075
291 -> 298	-0.14793
291 -> 301	-0.17395
292 -> 300	-0.11723
294 -> 298	0.27463
294 -> 303	0.10442
294 -> 304	-0.15842
295 -> 298	-0.18449
295 -> 302	-0.11722
295 -> 304	0.14188

Excited State 33: Singlet-A 5.7578 eV 215.33 nm *f*=0.0553

<S**2>=0.000

279 -> 296 0.13462

286 -> 296 0.10735

289 -> 296 -0.18947

289 -> 298 -0.15663

291 -> 297 0.12377

291 -> 298 0.26972

291 -> 301 0.22575

292 -> 296 -0.12624

294 -> 298 0.10967

Excited State 34: Singlet-A 5.7718 eV 214.81 nm *f*=0.0003

<S**2>=0.000

270 -> 297 -0.40083

270 -> 299 -0.42427

270 -> 300 0.11171

270 -> 301 0.12020

270 -> 306 -0.12008

270 -> 307 0.12426

270 -> 328 -0.12513

Excited State 35: Singlet-A 5.7805 eV 214.49 nm *f*=0.0001

<S**2>=0.000

272 -> 297 0.36257

272 -> 299 -0.46328

272 -> 304 -0.12966

272 -> 306 0.10290

272 -> 307 -0.10639

272 -> 325 -0.11993

272 -> 327 0.12330

272 -> 328 0.10340

Excited State 36: Singlet-A 5.7945 eV 213.97 nm *f*=0.0083 <S**2>=0.000

292 -> 298 -0.11254

293 -> 300 0.11749

294 -> 298 -0.14427

294 -> 302 0.17518

294 -> 307 -0.10208

295 -> 296 0.21403

295 -> 301 0.25099

295 -> 315 0.16051

Excited State 37: Singlet-A 5.8391 eV 212.33 nm *f*=0.0603 <S**2>=0.000

268 -> 314 -0.12987

275 -> 296 -0.11855

279 -> 296 -0.14906

284 -> 296 -0.11025

286 -> 296 -0.16520

287 -> 298 -0.11995

287 -> 314 0.13834

288 -> 298 0.14339

289 -> 298 -0.18214

291 -> 296 0.18494

295 -> 301 0.12487

Excited State 38: Singlet-A 5.8418 eV 212.24 nm *f*=0.1255 <S**2>=0.000

285 -> 296 0.11331

291 -> 296 0.12039

291 -> 298 -0.14088

291 -> 302 0.23524

291 -> 303 -0.18272

294 -> 298 0.14266

294 -> 300 0.11599

295 -> 300 0.13944

295 -> 305 -0.13605

295 -> 309 0.10759

Excited State 39: Singlet-A 5.8511 eV 211.90 nm *f*=0.0062 <S**2>=0.000

268 -> 314 -0.40808

269 -> 314 -0.12623

287 -> 314 0.39735

288 -> 314 -0.16898

289 -> 314 0.18351

Excited State 40: Singlet-A 5.8780 eV 210.93 nm *f*=0.0696

<S**2>=0.000

287 -> 298	-0.15296
289 -> 298	-0.11447
290 -> 297	0.10119
290 -> 300	0.25290
293 -> 298	-0.15066
293 -> 300	0.23463
293 -> 304	-0.12247
294 -> 302	-0.10210
295 -> 301	-0.14536
295 -> 304	-0.10569

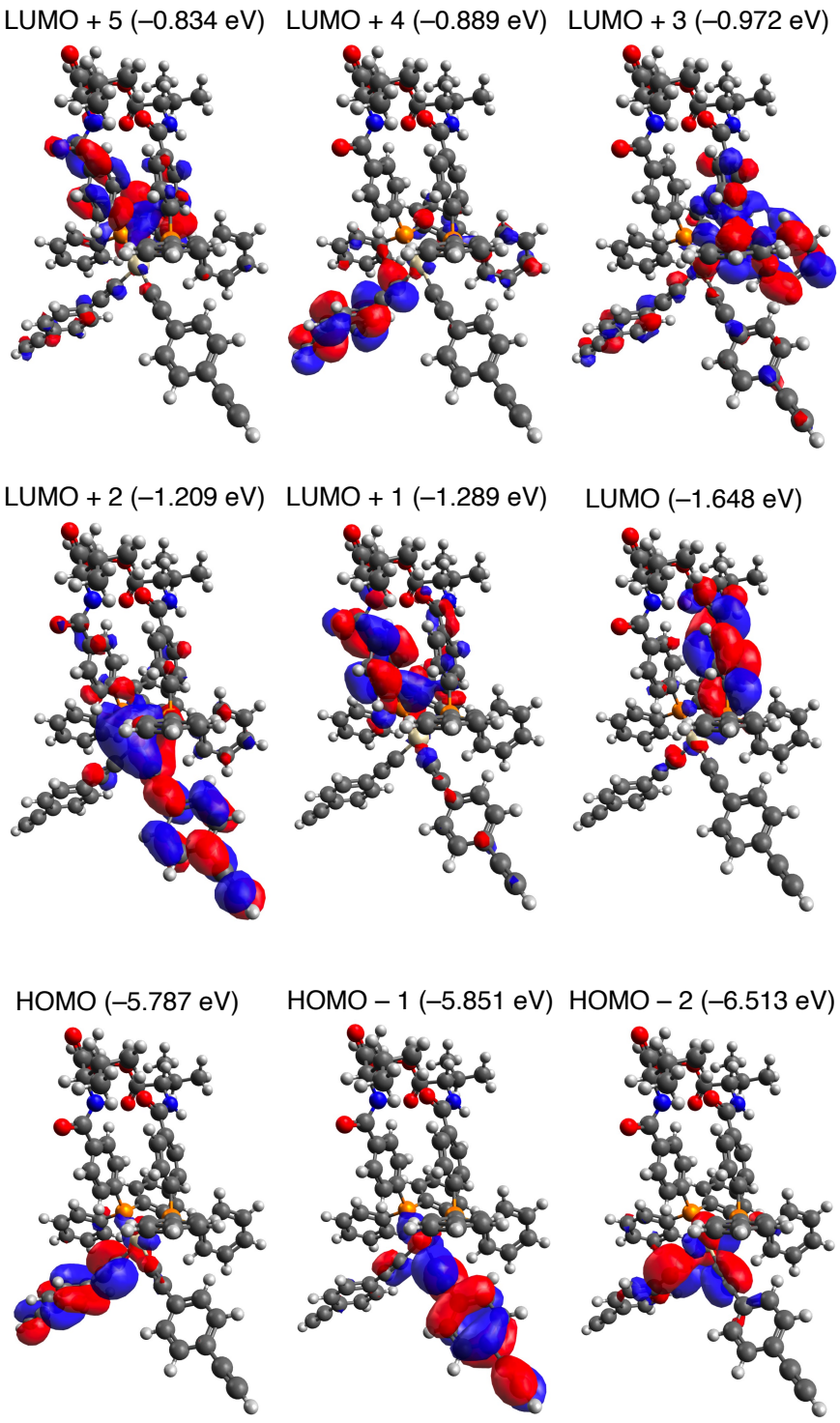


Fig. S64 Shapes and energy levels from LUMO + 5 to HOMO – 2 of S_0 state of **5**. The geometries were fully optimized by the DFT method using the M06 functional with 6-31G* (C, H, N, O, P) and LANL2DZ (Pt) basis sets, and SCRF-IEFPCM (solvent CH_2Cl_2), starting from the geometries obtained by the single crystal X-ray analysis of **5**.

Excitation Energies and Oscillator Strengths for S_0 state of **5** calculated by the TD-DFT method using the M06 functional with 6-31G* (C, H, N, O, P) and LANL2DZ (Pt) basis sets, and SCRF-IEFPCM (solvent CH_2Cl_2), nstates = 40. The geometries were same as those of Fig. S64.

Correspondence of MOs

301 LUMO + 5

300 LUMO + 4

299 LUMO + 3

298 LUMO + 2

297 LUMO + 1

296 LUMO

295 HOMO

294 HOMO – 1

293 HOMO – 2

Excited State 1: Singlet-A 3.5622 eV 348.06 nm *f*=0.0296 <S**2>=0.000

294 -> 296 -0.29998

295 -> 296 0.60631

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-DFT) = -4063.63256358

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.6076 eV 343.68 nm *f*=0.0252 <S**2>=0.000

294 -> 296 0.61577

295 -> 296 0.29734

Excited State 3: Singlet-A 3.7230 eV 333.03 nm *f*=0.8358 <S**2>=0.000

294 -> 297 0.18790

294 -> 298 0.52184

295 -> 297 -0.15685

295 -> 298 -0.34148

Excited State 4: Singlet-A 3.7689 eV 328.97 nm *f*=0.2264 <S**2>=0.000

294 -> 297 0.14324

294 -> 298 0.36085

295 -> 297 0.24963

295 -> 298 0.47082

Excited State 5: Singlet-A 3.9188 eV 316.39 nm *f*=0.0031 <S**2>=0.000

295 -> 296 -0.10452

295 -> 297 0.62883

295 -> 298 -0.28680

Excited State 6: Singlet-A 4.0117 eV 309.05 nm *f*=0.0710 <S**2>=0.000

294 -> 297 0.64023

294 -> 298 -0.20430

295 -> 300 0.14085

Excited State 7: Singlet-A 4.0423 eV 306.72 nm *f*=0.7467 <S**2>=0.000

292 -> 298 -0.23434

293 -> 296 -0.11674

293 -> 298 0.13979

294 -> 298 0.12769

295 -> 299 0.20822

295 -> 300 0.51787

295 -> 301 0.10205

Excited State 8: Singlet-A 4.0502 eV 306.12 nm *f*=0.2152 <S**2>=0.000

292 -> 297 0.16282

292 -> 298 0.51102

293 -> 298 -0.25275

295 -> 299 0.12474

295 -> 300 0.24143

Excited State 9: Singlet-A 4.0880 eV 303.29 nm *f*=0.0465 <S**2>=0.000

292 -> 296 0.11120

293 -> 296 0.62993

294 -> 299 0.10556

Excited State 10: Singlet-A 4.1218 eV 300.80 nm *f*=0.0290

<S**2>=0.000

294 -> 299 0.61893

294 -> 300 -0.13213

294 -> 302 -0.11434

295 -> 299 -0.22141

Excited State 11: Singlet-A 4.2042 eV 294.91 nm *f*=0.0050

<S**2>=0.000

292 -> 296 -0.25789

294 -> 299 0.16162

295 -> 296 -0.11727

295 -> 299 0.41889

295 -> 301 -0.18412

295 -> 303 -0.29528

295 -> 304 0.18599

Excited State 12: Singlet-A 4.2527 eV 291.54 nm *f*=0.0539

<S**2>=0.000

291 -> 296 -0.11566

292 -> 296 0.47179

293 -> 296 -0.10145

293 -> 299 0.10386

293 -> 300 0.23707

294 -> 300 0.22976

295 -> 299 0.12781

295 -> 300 -0.17472

295 -> 303 -0.10485

Excited State 13: Singlet-A 4.2638 eV 290.78 nm *f*=0.0121 <S**2>=0.000

291 -> 296 0.11925

292 -> 296 -0.30011

292 -> 300 0.11518

293 -> 299 0.11792

293 -> 300 0.36633

294 -> 300 0.38747

Excited State 14: Singlet-A 4.2796 eV 289.71 nm *f*=0.0825 <S**2>=0.000

290 -> 296 0.25182

291 -> 296 0.52452

291 -> 297 0.10303

291 -> 315 -0.11234

292 -> 296 0.19622

Excited State 15: Singlet-A 4.3343 eV 286.05 nm *f*=0.0081 <S**2>=0.000

295 -> 299 0.27490

295 -> 300 -0.23439

295 -> 301 0.56181

295 -> 303 0.11729

Excited State 16: Singlet-A 4.3788 eV 283.15 nm *f*=0.0551 <S**2>=0.000

295 -> 299	0.27970
295 -> 301	-0.31324
295 -> 302	-0.28552
295 -> 303	0.37151
295 -> 304	-0.18221
295 -> 306	0.10486

Excited State 17: Singlet-A 4.4006 eV 281.74 nm *f*=0.0129 <S**2>=0.000

294 -> 301	-0.39269
294 -> 302	0.25114
294 -> 304	0.43239
295 -> 303	-0.13191

Excited State 18: Singlet-A 4.4235 eV 280.29 nm *f*=0.1453 <S**2>=0.000

292 -> 297	0.12187
292 -> 298	0.24315
293 -> 297	0.32076
293 -> 298	0.47236
294 -> 301	0.10739

Excited State 19: Singlet-A 4.4563 eV 278.22 nm *f*=0.0232

<S**2>=0.000

293 -> 300 0.18626

294 -> 300 -0.34524

294 -> 301 0.42059

294 -> 302 0.14653

294 -> 303 0.20844

294 -> 304 0.17221

Excited State 20: Singlet-A 4.4782 eV 276.86 nm *f*=0.0244

<S**2>=0.000

293 -> 297 -0.14827

293 -> 299 -0.11273

293 -> 300 -0.29666

294 -> 299 0.13195

294 -> 300 0.33046

294 -> 301 0.18449

294 -> 302 0.22303

294 -> 303 0.28897

294 -> 304 0.12266

Excited State 21: Singlet-A 4.4976 eV 275.67 nm *f*=0.0127

<S**2>=0.000

293 -> 296 -0.10193

293 -> 297 0.55603

293 -> 298 -0.32958

293 -> 300 -0.11986

Excited State 22: Singlet-A 4.5270 eV 273.88 nm *f*=0.0040 <S**2>=0.000

294 -> 301	0.14535
294 -> 302	-0.14796
294 -> 304	0.31149
295 -> 298	-0.13257
295 -> 302	0.38150
295 -> 303	0.21195
295 -> 305	0.23528
295 -> 307	0.10228
295 -> 309	0.11644

Excited State 23: Singlet-A 4.5468 eV 272.69 nm *f*=0.0150 <S**2>=0.000

294 -> 300	-0.11335
294 -> 301	-0.14632
294 -> 302	0.34171
294 -> 303	0.17683
294 -> 304	-0.25767
294 -> 305	0.14093
295 -> 298	-0.11192
295 -> 302	0.21510
295 -> 303	0.16212
295 -> 304	0.12598
295 -> 305	0.19528

295 -> 307 0.10719

Excited State 24: Singlet-A 4.5848 eV 270.42 nm *f*=0.0553 <S**2>=0.000

287 -> 296 -0.11819

288 -> 296 0.29624

289 -> 296 0.22081

292 -> 297 0.11969

294 -> 301 -0.17206

294 -> 302 -0.25844

294 -> 303 0.32534

295 -> 303 -0.13085

295 -> 304 -0.12549

Excited State 25: Singlet-A 4.5869 eV 270.30 nm *f*=0.0740 <S**2>=0.000

287 -> 296 0.12968

288 -> 296 -0.29859

289 -> 296 -0.23439

294 -> 301 -0.14038

294 -> 302 -0.21308

294 -> 303 0.36065

295 -> 304 0.11001

Excited State 26: Singlet-A 4.6190 eV 268.42 nm *f*=0.0089 <S**2>=0.000

283 -> 300 0.14108

286 -> 296 0.14973

286 -> 297 0.12403

289 -> 300 0.10742

294 -> 303 -0.11073

295 -> 302 -0.19762

295 -> 303 -0.13218

295 -> 305 0.22173

295 -> 306 0.16306

295 -> 311 0.35426

295 -> 312 0.11113

Excited State 27: Singlet-A 4.6217 eV 268.26 nm *f*=0.0531 <S**2>=0.000

277 -> 297 0.10277

284 -> 296 0.10777

284 -> 297 0.13416

286 -> 296 0.27560

286 -> 297 0.25613

288 -> 296 0.14325

289 -> 296 0.10862

290 -> 296 -0.22250

291 -> 296 0.10936

295 -> 303 0.12564

295 -> 305 -0.10673

295 -> 306 -0.10119

295 -> 311 -0.20097

Excited State 28: Singlet-A 4.6355 eV 267.46 nm *f*=0.0054 <S**2>=0.000

288 -> 296 0.15080

290 -> 296 0.11025

294 -> 304 0.11075

294 -> 310 -0.16358

295 -> 302 -0.19249

295 -> 303 0.18851

295 -> 304 0.46074

295 -> 306 -0.10441

Excited State 29: Singlet-A 4.6466 eV 266.83 nm *f*=0.0008 <S**2>=0.000

282 -> 298 -0.13849

285 -> 298 -0.28267

294 -> 302 -0.11646

294 -> 303 0.11609

294 -> 304 0.11928

294 -> 310 0.49915

295 -> 304 0.11682

Excited State 30: Singlet-A 4.6744 eV 265.24 nm *f*=0.0156 <S**2>=0.000

280 -> 296 -0.12019

284 -> 296 0.10689

286 -> 296 0.12100

286 -> 297 0.11566

289 -> 296 -0.14318

290 -> 296 0.32026

291 -> 296 -0.12889

291 -> 297 -0.22220

292 -> 297 0.32916

292 -> 298 -0.11687

295 -> 304 -0.10231

Excited State 31: Singlet-A 4.6832 eV 264.74 nm *f*=0.0105 <S**2>=0.000

290 -> 296 -0.19486

291 -> 296 0.17582

291 -> 297 -0.17799

292 -> 297 0.37903

292 -> 299 0.16655

293 -> 299 -0.17008

295 -> 304 0.14589

295 -> 305 -0.18758

295 -> 311 0.14942

295 -> 312 0.12406

Excited State 32: Singlet-A 4.6909 eV 264.31 nm *f*=0.0130 <S**2>=0.000

286 -> 297 -0.12477

290 -> 296 -0.19560

291 -> 296 0.11372

292 -> 297 0.21803

292 -> 298 -0.10289

295 -> 302 -0.19165

295 -> 305 0.38886

295 -> 311 -0.17993

295 -> 312 -0.17639

Excited State 33: Singlet-A 4.6974 eV 263.94 nm *f*=0.0209 <S**2>=0.000

277 -> 296 0.10608

277 -> 297 0.10042

278 -> 296 -0.11620

280 -> 296 0.13171

286 -> 296 -0.13143

286 -> 297 0.22008

287 -> 296 -0.10899

292 -> 299 0.19352

293 -> 299 -0.20760

295 -> 302 -0.17399

295 -> 305 0.23217

Excited State 34: Singlet-A 4.7207 eV 262.64 nm *f*=0.0205 <S**2>=0.000

291 -> 296 -0.12469

291 -> 297 0.46672

292 -> 299 0.19492

293 -> 299 -0.26376

Excited State 35: Singlet-A 4.7283 eV 262.21 nm *f*=0.0315 <S**2>=0.000

286 -> 296 -0.14178

286 -> 297 0.10705

287 -> 296 -0.12571

290 -> 298 0.11229

291 -> 297 0.29559

291 -> 298 0.16140

292 -> 297 0.22371

292 -> 298 -0.11069

293 -> 299 0.29567

293 -> 303 -0.12697

295 -> 305 -0.10610

Excited State 36: Singlet-A 4.7580 eV 260.58 nm *f*=0.0112 <S**2>=0.000

290 -> 297 0.14665

290 -> 298 0.24528

291 -> 297 -0.13005

291 -> 298 0.50860

292 -> 297 -0.12211

292 -> 299 0.10888

Excited State 37: Singlet-A 4.7756 eV 259.62 nm *f*=0.0207 <S**2>=0.000

287 -> 296 -0.12217

291 -> 298 0.12614

292 -> 299 -0.16641

293 -> 299 -0.21625

293 -> 303 0.11675

294 -> 302 -0.12448

294 -> 305 0.43083

294 -> 306 -0.18400

294 -> 307 0.12213

Excited State 38: Singlet-A 4.7892 eV 258.88 nm *f*=0.0044 <S**2>=0.000

292 -> 299 0.42446

293 -> 301 -0.15878

293 -> 303 -0.18786

293 -> 304 0.11851

294 -> 305 0.26170

294 -> 306 -0.11160

295 -> 306 0.16340

Excited State 39: Singlet-A 4.8039 eV 258.09 nm *f*=0.0041 <S**2>=0.000

269 -> 296 0.10007

279 -> 296 -0.10005

282 -> 296 0.11575

284 -> 296 -0.13015

287 -> 296 0.34430

290 -> 296 0.14910

295 -> 304 0.10134

295 -> 306 0.41037

295 -> 312 -0.13463

Excited State 40: Singlet-A 4.8082 eV 257.86 nm *f*=0.0113 <S**2>=0.000

269 -> 296 -0.10646

282 -> 296 -0.11820

284 -> 296 0.11906

287 -> 296 -0.33982

288 -> 296 -0.10093

290 -> 296 -0.15003

294 -> 305 -0.18316

295 -> 306 0.38884

295 -> 312 -0.12987

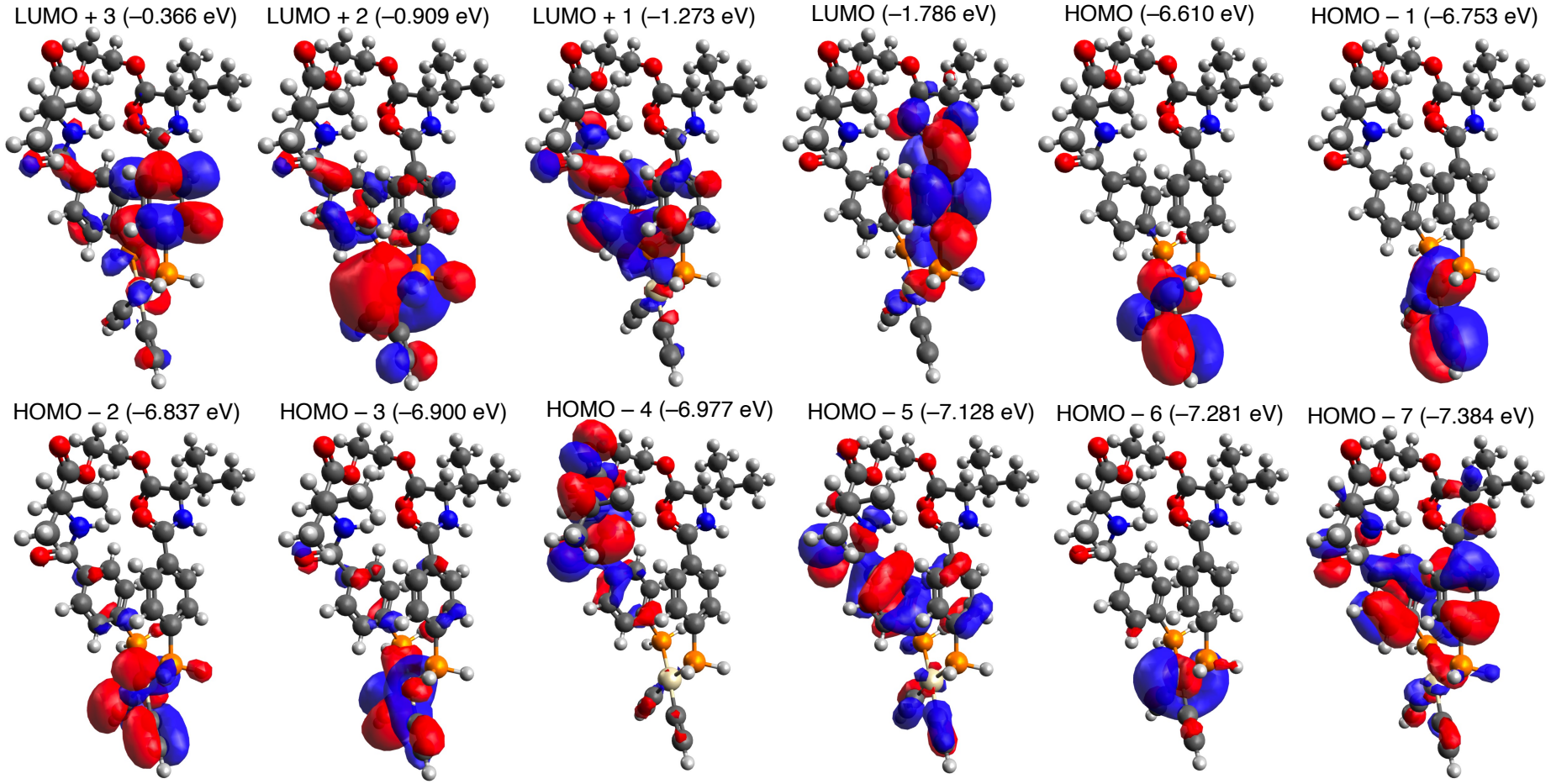


Fig. S65 Shapes and energy levels from LUMO + 3 to HOMO – 3 of S0 state of **5'**. The geometries of H atoms were optimized by the DFT method using the M06 functional with 6-31G* (C, H, N, O, P) and LANL2DZ (Pt) basis sets, and SCRF-IEFPCM (solvent CH_2Cl_2), while those of C, N, O, P and Pt atoms were obtained from the single crystal X-ray analysis of **5** and frozen without optimization.

Excitation Energies and Oscillator Strengths for S_0 state of **5'** calculated by the TD-DFT method using the M06 functional with 6-31G* (C, H, N, O, P) and LANL2DZ (Pt) basis sets, and SCRF-IEFPCM (solvent CH_2Cl_2), nstates = 40. The geometries were same as those of Fig. S65.

Correspondence of MOs

167 LUMO + 3

166 LUMO + 2

165 LUMO + 1

164 LUMO

163 HOMO

162 HOMO – 1

161 HOMO – 2

160 HOMO – 3

159 HOMO – 4

158 HOMO – 5

157 HOMO – 6

156 HOMO – 7

Excited State 1: Singlet-A 4.1102 eV 301.65 nm *f*=0.0061 <S**2>=0.000

163 ->164 0.68206

163 ->170 0.10895

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-DFT) = -2526.10599506

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 4.2569 eV 291.26 nm *f*=0.0275

<S**2>=0.000

162 ->164 0.67042

Excited State 3: Singlet-A 4.2865 eV 289.24 nm *f*=0.0042

<S**2>=0.000

161 ->164 0.65967

161 ->170 0.10700

Excited State 4: Singlet-A 4.3826 eV 282.90 nm *f*=0.1217

<S**2>=0.000

156 ->164 -0.11800

158 ->164 0.27083

159 ->164 -0.32012

160 ->164 0.50130

161 ->164 -0.13248

Excited State 5: Singlet-A 4.4267 eV 280.08 nm *f*=0.0013

<S**2>=0.000

162 ->164 0.11178

162 ->165 -0.26148

162 ->166 0.56633

162 ->167 -0.11318

163 ->165 0.11473

163 ->166 -0.15577

Excited State 6: Singlet-A 4.4589 eV 278.06 nm *f*=0.0121

<S**2>=0.000

159 ->164 0.56970

160 ->164 0.34760

Excited State 7: Singlet-A 4.5171 eV 274.47 nm *f*=0.0528

<S**2>=0.000

157 ->164 0.25944

162 ->166 -0.17608

163 ->165 0.43620

163 ->166 -0.37882

Excited State 8: Singlet-A 4.5522 eV 272.36 nm *f*=0.0164

<S**2>=0.000

156 ->165 0.11210

158 ->164 0.55966

158 ->165 0.18680

159 ->164 0.19179

160 ->164 -0.19503

160 ->166 0.10347

Excited State 9: Singlet-A 4.5711 eV 271.23 nm *f*=0.0239

<S**2>=0.000

155 ->165 -0.11817

156 ->164 -0.13118

156 ->165 -0.11246

157 ->164 0.36894

158 ->165 -0.35117

158 ->166 -0.10572

160 ->165 -0.17816

161 ->165 -0.12457

163 ->165 -0.24580

Excited State 10: Singlet-A 4.5981 eV 269.64 nm *f*=0.0500 <S**2>=0.000

155 ->165 0.11516

157 ->164 0.44658

157 ->170 0.10187

158 ->164 -0.19219

158 ->165 0.32420

160 ->165 0.14222

163 ->165 -0.16197

163 ->166 0.10904

Excited State 11: Singlet-A 4.6299 eV 267.79 nm *f*=0.0018 <S**2>=0.000

160 ->165 -0.26748

160 ->166 0.51259

160 ->167 -0.10737

161 ->165 0.20777

161 ->166 -0.19575

162 ->166 -0.11035

Excited State 12: Singlet-A 4.6795 eV 264.95 nm *f*=0.2166

<S**2>=0.000

154 ->164 -0.13162

155 ->164 -0.12600

156 ->164 0.60490

158 ->165 -0.11450

163 ->165 -0.14030

163 ->166 -0.12105

Excited State 13: Singlet-A 4.7042 eV 263.56 nm *f*=0.0255

<S**2>=0.000

156 ->164 0.16351

163 ->165 0.39047

163 ->166 0.47408

Excited State 14: Singlet-A 4.7233 eV 262.50 nm *f*=0.0250

<S**2>=0.000

158 ->164 0.13904

158 ->165 -0.12437

160 ->164 -0.13730

160 ->165 0.10654

160 ->166 -0.19792

161 ->165 0.49375

161 ->166 -0.27487

Excited State 15: Singlet-A 4.8036 eV 258.10 nm *f*=0.0093 <S**2>=0.000

149 ->164	-0.12967
150 ->164	0.44076
151 ->164	0.11022
152 ->164	0.13562
153 ->164	-0.16024
154 ->164	-0.19569
155 ->164	0.19277
159 ->165	0.23559
162 ->165	0.17006

Excited State 16: Singlet-A 4.8227 eV 257.09 nm *f*=0.0249 <S**2>=0.000

150 ->164	-0.24512
156 ->165	0.11868
159 ->165	0.13301
161 ->165	0.14087
162 ->165	0.52379
162 ->166	0.21615

Excited State 17: Singlet-A 4.8498 eV 255.65 nm *f*=0.1548 <S**2>=0.000

150 ->164	-0.18268
156 ->165	0.12060
159 ->165	0.41125

160 ->165 -0.12438

160 ->166 -0.10144

161 ->165 -0.23051

161 ->166 -0.31851

162 ->165 -0.15704

Excited State 18: Singlet-A 4.8771 eV 254.22 nm *f*=0.0649 <S**2>=0.000

150 ->164 -0.12866

154 ->164 -0.19495

156 ->165 0.13051

157 ->165 -0.12605

159 ->165 0.17038

160 ->165 -0.24862

161 ->165 0.25743

161 ->166 0.39132

162 ->165 -0.14498

Excited State 19: Singlet-A 4.9185 eV 252.08 nm *f*=0.0779 <S**2>=0.000

151 ->164 -0.15623

154 ->164 0.33966

156 ->164 0.13568

156 ->165 -0.22049

156 ->167 0.11073

159 ->165 0.39625

161 ->166 0.17152

Excited State 20: Singlet-A 4.9670 eV 249.61 nm *f*=0.0396 <S**2>=0.000

154 ->164 -0.29644

156 ->165 -0.15877

159 ->165 0.13948

160 ->165 0.45326

160 ->166 0.26058

162 ->165 -0.10716

Excited State 21: Singlet-A 5.0199 eV 246.98 nm *f*=0.0394 <S**2>=0.000

157 ->165 0.54495

157 ->166 -0.36865

Excited State 22: Singlet-A 5.0522 eV 245.41 nm *f*=0.0019 <S**2>=0.000

152 ->171 -0.22381

153 ->171 -0.28682

156 ->165 0.10177

159 ->165 -0.10451

159 ->171 0.54700

Excited State 23: Singlet-A 5.0551 eV 245.27 nm *f*=0.0100 <S**2>=0.000

154 ->164 0.21606

154 ->165 -0.14498

155 ->164 -0.18176

155 ->165 -0.10748

156 ->165 0.39375

157 ->165 -0.13038

158 ->165 -0.16894

158 ->169 0.14029

159 ->171 -0.12755

160 ->165 0.20292

160 ->166 0.11953

Excited State 24: Singlet-A 5.0932 eV 243.43 nm *f*=0.0920 <S**2>=0.000

151 ->164 -0.17978

152 ->164 -0.15361

153 ->164 0.19199

154 ->164 -0.16700

154 ->165 -0.11503

155 ->164 0.48682

156 ->165 0.16124

158 ->165 -0.14338

Excited State 25: Singlet-A 5.1825 eV 239.24 nm *f*=0.0137 <S**2>=0.000

157 ->164 -0.11020

157 ->165 0.30746

157 ->166 0.44891

157 ->170 0.14950

163 ->170 0.32281

Excited State 26: Singlet-A 5.1977 eV 238.54 nm *f*=0.0525 <S**2>=0.000

150 ->164 -0.15683

151 ->164 0.19608

152 ->164 0.18369

153 ->164 -0.10439

154 ->164 0.24795

154 ->165 0.22905

155 ->164 0.21575

155 ->165 0.20217

156 ->165 0.12305

158 ->165 -0.23128

158 ->166 0.19958

159 ->166 -0.10448

Excited State 27: Singlet-A 5.2348 eV 236.84 nm *f*=0.0269 <S**2>=0.000

157 ->165 -0.13144

157 ->166 -0.29859

163 ->164 -0.10057

163 ->168 0.14900

163 ->170 0.53642

Excited State 28: Singlet-A 5.2765 eV 234.97 nm *f*=0.0112 <S**2>=0.000

150 ->164 0.22045

151 ->164 -0.13754

152 ->164 -0.29258

153 ->164 0.17669

155 ->164 -0.25608

155 ->165 0.30456

158 ->165 -0.18120

158 ->166 0.21227

159 ->166 -0.11422

Excited State 29: Singlet-A 5.3346 eV 232.41 nm *f*=0.0254 <S**2>=0.000

151 ->164 0.34535

152 ->164 -0.30182

152 ->168 0.10893

153 ->164 0.22971

154 ->165 0.14705

155 ->165 -0.24363

162 ->170 -0.17647

Excited State 30: Singlet-A 5.3601 eV 231.31 nm *f*=0.0228 <S**2>=0.000

151 ->164 0.10899

155 ->165 -0.11826

158 ->166 0.14559

159 ->166 -0.11019

160 ->170 0.20350

162 ->165 -0.10674

162 ->168 0.13672

162 ->170 0.51086

Excited State 31: Singlet-A 5.3877 eV 230.12 nm *f*=0.0343 <S**2>=0.000

154 ->165 -0.22680

155 ->165 -0.15504

155 ->166 -0.12215

156 ->166 -0.11843

158 ->166 0.35046

159 ->166 -0.26419

161 ->170 0.28085

162 ->170 -0.17144

Excited State 32: Singlet-A 5.3959 eV 229.78 nm *f*=0.0383 <S**2>=0.000

154 ->165 0.11452

158 ->166 -0.16380

159 ->166 0.13531

161 ->164 -0.11276

161 ->168 0.14516

161 ->170 0.53849

162 ->170 0.10709

Excited State 33: Singlet-A 5.4809 eV 226.21 nm *f*=0.0827 <S**2>=0.000

149 ->164 -0.15656

149 ->168 0.24102

150 ->168 0.10742

151 ->164 -0.17448

151 ->168 0.17230

152 ->164 -0.14669

152 ->168 -0.21358

153 ->168 0.18585

154 ->165 0.28386

155 ->165 -0.24116

156 ->165 0.16538

Excited State 34: Singlet-A 5.5251 eV 224.40 nm *f*=0.0502 <S**2>=0.000

149 ->168 -0.13965

151 ->164 -0.20415

152 ->164 0.40435

152 ->168 0.11655

153 ->164 0.29581

153 ->168 -0.11253

154 ->165 0.17947

155 ->165 -0.17310

156 ->165 0.12529

Excited State 35: Singlet-A 5.5344 eV 224.02 nm *f*=0.0225 <S**2>=0.000

149 ->168 0.18956

151 ->164 0.19848

151 ->168 0.12952

152 ->164 0.18991

152 ->168 -0.18140

153 ->164 0.46611

153 ->168 0.14535

154 ->165 -0.12990

155 ->165 0.11079

Excited State 36: Singlet-A 5.5553 eV 223.18 nm *f*=0.0044 <S**2>=0.000

163 ->166 0.10619

163 ->167 0.66287

Excited State 37: Singlet-A 5.5716 eV 222.53 nm *f*=0.0031 <S**2>=0.000

156 ->166 -0.10314

158 ->166 0.34494

159 ->165 -0.10518

159 ->166 0.56457

159 ->167 0.10962

Excited State 38: Singlet-A 5.6053 eV 221.19 nm *f*=0.0004 <S**2>=0.000

156 ->166 -0.21919

157 ->164 -0.14964

157 ->165 -0.16778

157 ->166 -0.10257

157 ->168 0.14179

157 ->170 0.54296

157 ->177 -0.11347

Excited State 39: Singlet-A 5.6151 eV 220.81 nm *f*=0.0254 <S**2>=0.000

154 ->165 0.14335

155 ->166 -0.16334

156 ->166 0.54146

157 ->166 -0.14693

157 ->170 0.18087

158 ->166 0.14250

Excited State 40: Singlet-A 5.6874 eV 218.00 nm *f*=0.0087 <S**2>=0.000

160 ->170 0.18325

162 ->166 0.13880

162 ->167 0.63025

Table S1 Representative excitation of S_0 state of **5** and the assignment [a]

Functional	Excited state [b]	Wavelength [nm]	f [c]	Main transition [d]	CI coefficient [e]	Assignment
ωB97X-D	1	287.62	1.1139	HOMO → LUMO + 2	0.54420	(HC≡C–C_6H_4–C≡C)Pt → (HC≡C–C_6H_4–C≡C)Pt[$P(Ph)_2$–C_6H_4–CO–]
	3	258.04	0.6186	HOMO → LUMO	0.27510	(HC≡C–C_6H_4–C≡C)Pt → $P(Ph)_2$–C_6H_4–CONH–
	4	254.67	0.3344	HOMO – 1 → LUMO + 4	0.30535	(HC≡C–C_6H_4–C≡C)Pt → (HC≡C–C_6H_4–C≡C)Pt[$P(Ph)_2$–C_6H_4–]$_2$
M06	2	326.12	0.7487	HOMO → LUMO + 2	0.60812	(HC≡C–C_6H_4–C≡C)Pt → (HC≡C–C_6H_4–C≡C)Pt[$P(Ph)_2$–C_6H_4–]$_2$
	14	280.82	0.5406	HOMO – 1 → LUMO + 5	0.43214	(HC≡C–C_6H_4–C≡C)Pt → (HC≡C–C_6H_4–C≡C)Pt[$P(Ph)_2$–C_6H_4–CO–]

[a] Corresponding to Figs. S61 and S62 calculated by the TD-DFT method [ωB97X-D and M06/6-31G* (C, H, N, O, P) and LANL2DZ (Pt)/ SCRF-IEFPCM (solvent CH_2Cl_2)]. The geometries of H atoms were optimized by the DFT method using the same functional and basis sets as those of the TD-DFT method, while those of C, N, O, P and Pt atoms were obtained from the single crystal X-ray analysis of **5** and frozen without optimization.

[b] Excited states with an oscillator strength (*f*) value larger than 0.3 are listed.

[c] Oscillator strength.

[d] Transition with the largest CI coefficient was listed.

[e] Configuration Interaction coefficient of the wavefunction.

Table S2 Representative excitation of S_0 state of **5** and the assignment [a]

Functional	Excited state [b]	Wavelength [nm]	f [c]	Main transition [d]	CI coefficient [e]	Assignment
ωB97X-D	1	297.82	1.1376	HOMO → LUMO + 1	0.57522	$(HC{\equiv}C–C_6H_4–C{\equiv}C)_2Pt$ → $(HC{\equiv}C–C_6H_4–C{\equiv}C)_2Pt(P–)_2$
	2	286.15	1.0416	HOMO – 1 → LUMO + 1	0.55552	$(HC{\equiv}C–C_6H_4–C{\equiv}C)_2Pt$ → $(HC{\equiv}C–C_6H_4–C{\equiv}C)_2Pt(P–)_2$
M06	3	333.03	0.8358	HOMO – 1 → LUMO + 2	0.52184	$(HC{\equiv}C–C_6H_4–C{\equiv}C)Pt$ → $(HC{\equiv}C–C_6H_4–C{\equiv}C)Pt(P–)_2$
	7	306.72	0.7467	HOMO → LUMO + 4	0.51787	$(HC{\equiv}C–C_6H_4–C{\equiv}C)Pt$ → $HC{\equiv}C–C_6H_4–C{\equiv}C–$

[a] Corresponding to Figs. S63 and S64 calculated by the TD-DFT method [ωB97X-D and M06/6-31G* (C, H, N, O, P) and LANL2DZ (Pt)/ SCRF-IEFPCM (solvent CH_2Cl_2)]. The geometries were fully optimized by the DFT method using the same functional and basis sets as those of the TD-DFT method, starting from the geometries obtained by the single crystal X-ray analysis of **5**.

[b] Excited states with an oscillator strength (*f*) value larger than 0.3 are listed.

[c] Oscillator strength.

[d] Transition with the largest CI coefficient was listed.

[e] Configuration Interaction coefficient of the wavefunction.

Table S3 Representative excitation of S_0 state of **5'** and the assignment [a]

Excited state [b]	Wavelength [nm]	*f* [c]	Main transition [d]	CI coefficient [e]	Assignment
4	282.90	0.1217	HOMO – 3 → LUMO	0.50130	$(HC{\equiv}C)_2Pt(P–)_2$ → $Pt[P(Ph)_2–C_6H_4–CONH–]$
12	264.95	0.2166	HOMO – 7 → LUMO	0.60490	$(HC{\equiv}C)_2Pt[P(Ph)_2–C_6H_4–CONH–]_2$ → $Pt[P(Ph)_2–C_6H_4–CONH–]$
17	255.65	0.1548	HOMO – 4 → LUMO + 1	0.41125	$\{–C_6H_4–CONH–C^*H[CH(CH_3)_2]–COO–\}$ → $Pt[P(Ph)_2–C_6H_4–CONH–]$

[a] Corresponding to Fig. S65 calculated by the TD-DFT method [M06/6-31G* (C, H, N, O, P) and LANL2DZ (Pt)/ SCRF-IEFPCM (solvent CH_2Cl_2)]. The geometries of H atoms were optimized by the DFT method using the M06 functional with 6-31G* (C, H, N, O, P) and LANL2DZ (Pt) basis sets, and SCRF-IEFPCM (solvent CH_2Cl_2), while those of C, N, O, P and Pt atoms were obtained from the single crystal X-ray analysis of **5** and frozen without optimization.

[b] Excited states with an oscillator strength (*f*) value larger than 0.1 are listed.

[c] Oscillator strength.

[d] Transition with the largest CI coefficient was listed.

[e] Configuration Interaction coefficient of the wavefunction.

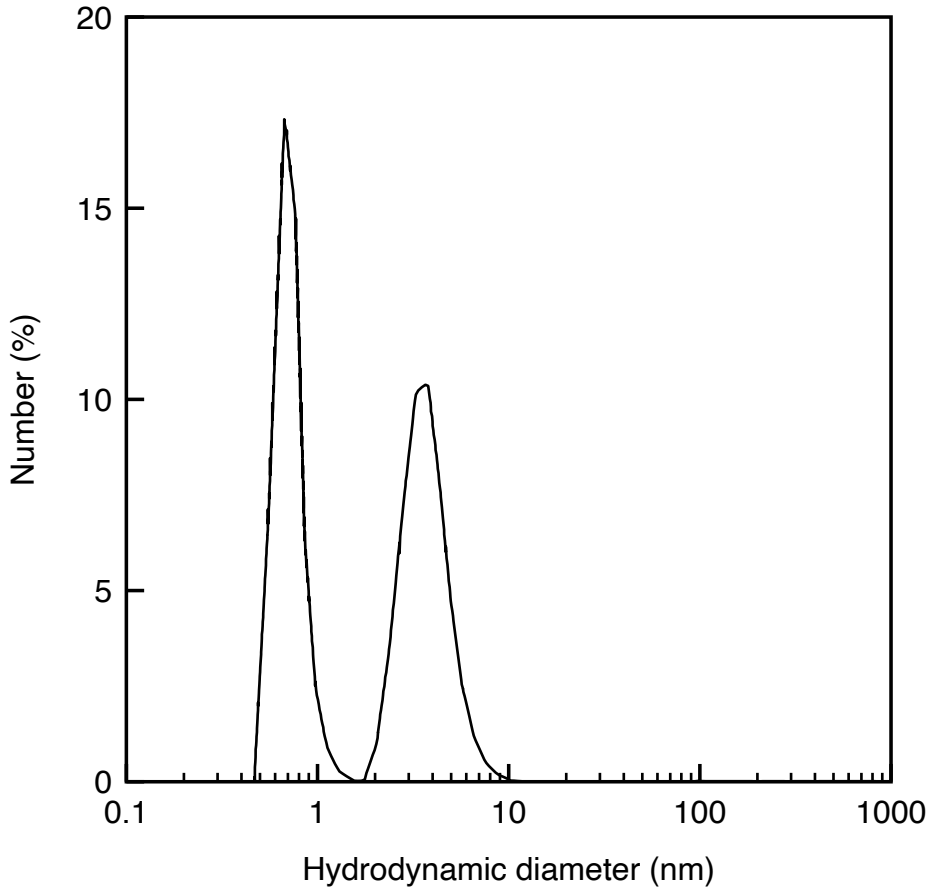


Fig. S66 DLS chart of poly(**5**-**6*m***) measured in DMF (c = 0.01 mM) at room temperature.

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