Supporting Information

Zwitterionic Phosphonium Ligands: Synthesis, Characterization and Application in Telomerization of 1,3–Butadiene

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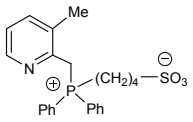
Experimental procedures and characterization of new compounds

General Information: All reactions were carried out under argon atmosphere. Chemicals were purchased from Aldrich, Fluka, Acros, AlfaAsar or Strem and unless otherwise noted were used without further purification. Solvents were additionally purified, degased or distilled under argon atmosphere. All compounds were characterized by ^{1}H NMR, ^{13}C NMR, ^{31}P NMP, FT–IR and HRMS. Melting points were determined automatically on a Mettler Toledo MP90 Melting Point System. No reliable melting points were obtained for ligands L1 and L3 to L10 because of their decomposition generally above 250 °C. ^{1}H NMR spectra were recorded on Bruker AV 300 and AV 400 spectrometers. ^{13}C NMR and ^{31}P NMR spectra were recorded at 75.5 or 101 MHz and 121 or 162 MHz respectively. Chemical shifts are reported in ppm relative to the centre of solvent resonance. GC was performed on Agilent 7890A chromatograph with a 30 m HP5 column. HRMS was performed on MAT 95XP (EI) and Agilent 6210 Time–of–Flight LC/MS (ESI). FT–IR was performed on Bruker Alpha FT–IR Spectrometer with ATR – technic. All yields reported refer to isolated yields. The reaction conditions were not optimized for every single compound.

General procedure for the synthesis of zwitterionic products L1, L3 – L9, L11

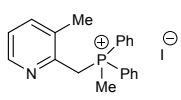
The solution of corresponding phosphine (1 mmol) and 1,4–butane– or 1,3–propanesultone (2.2 eq. or 1.1 eq. in case of monophosphine) in dry dimethylformamide (12 ml) was heated under argon in pressure tube at 140 °C for 20 h (or at 160 °C for 36 h). The resulted heterogeneous mixture was cooled to room temperature, formed product was filtered off and washed with ether. All crude products were recrystallized from water or methanol.

4–(((3–Methylpyridin–2–yl)methyl)diphenylphosphonio)butane–1–sulfonate (**L1**), partially deuterated, crystallographic data on page 31



Yield: 68 %. NMR measurements were performed in D_2O and H_2O at 90 °C. **^{1}H NMR** (400 MHz, Deuterium Oxide) δ 8.94 (d, *J* = 5.1 Hz, 1H), 8.54 – 8.45 (m, 2H), 8.45 – 8.30 (m, 8H), 8.19 (d, *J* = 7.0 Hz, 1H), 7.94 – 7.86 (m, 1H), 4.63 (d, *J* = 14.5 Hz, 4H, only appears if measured in water without lock), 3.79 – 3.66 (m, 2H), 3.55 – 3.46 (m, 2H), 2.67 (s, 3H), 2.60 – 2.48 (m, 2H), 2.48 – 2.35 (m, 2H). **^{13}C NMR** (101 MHz, D_2O) δ 148.53 (d, *J* = 8.3 Hz), 147.48, 140.09, 135.59 (d, *J* = 3.0 Hz, 2C), 134.75 (d, *J* = 6.7 Hz), 133.56 (d, *J* = 9.4 Hz, 4C), 130.65 (d, *J* = 12.5 Hz, 4C), 124.43 (d, *J* = 1.6 Hz), 118.82 (d, *J* = 84.2 Hz, 2C), 50.79, 28.55 (d, *J* = 52.5 Hz, only appears if measured in water without lock), 25.70 (d, *J* = 16.5 Hz), 22.18 (d, *J* = 51.0 Hz), 21.15 (d, *J* = 3.7 Hz), 18.21. **^{31}P NMR** (162 MHz, D_2O) δ 26.98. **HRMS pos.** (**ESI**): Calc for $[M+H]^+$, $C_{23}H_{26}NO_3PS$: 428.1444; found: 428.1445. **HRMS pos. (ESI):** Calc for $[M+Na]^+$, $C_{23}H_{25}NaNO_3PS$: 450.1263; found: 450.1267. **FTIR** (ATR, cm^{-1}): 2914, 2885, 1577, 1438, 1395, 1199, 1186, 1162, 1117, 1105, 1039, 873, 848, 804, 771, 745, 729, 692, 602, 525, 508, 493, 468, 464, 411.

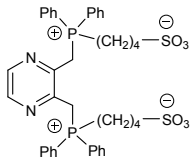
Methyl((3–methylpyridin–2–yl)methyl)diphenylphosphonium iodide (**L2**)



A mixture of 2–((diphenylphosphino)methyl)–3–methylpyridine (250 mg, 0.86 mmol) and iodomethane (122 mg, 0.86 mmol) in toluene (4 mL) was heated at 100 °C for 3 h under argon. The reaction mixture was allowed to

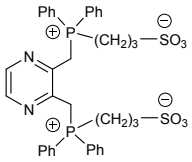
cool down to room temperature and the precipitated white solid collected by filtration, washed successively with toluene, ether and dried. Recrystallization from dichloromethane/heptane gives product as off–white shiny crystalls (**Mp** 252.9 °C) in 89 % **yield**. **^{1}H NMR** (300 MHz, Chloroform–*d*) δ 8.01 (dd, *J* = 5.0, 1.5 Hz, 1H), 7.96 – 7.84 (m, 4H), 7.71 – 7.63 (m, 2H), 7.62 – 7.53 (m, 4H), 7.47 – 7.40 (m, 1H), 7.04 (dd, *J* = 7.7, 4.8 Hz, 1H), 5.09 (d, *J* = 14.0 Hz, 2H), 2.92 (d, *J* = 14.0 Hz, 3H), 2.45 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 149.09 (d, *J* = 7.0 Hz), 145.37, 138.41, 133.97 (d, *J* = 3.4 Hz, 2C), 133.49 (d, *J* = 8.7 Hz), 132.61 (d, *J* = 10.2 Hz, 4C), 129.73 (d, *J* = 12.7 Hz, 4C), 123.05, 121.08 (d, *J* = 88.3 Hz, 2C), 31.86 (d, *J* = 60.4 Hz), 19.46, 10.79 (d, *J* = 58.0 Hz). **^{31}P NMR** (121 MHz, $CDCl_3$) δ 23.65. **HRMS pos.** (**ESI**): Calc for $[M+H]^+$, $C_{20}H_{21}NP$: 306.1406; found: 306.1407. **HRMS neg.** (**ESI**): Calc for $[M]^-$, I: 126.9050; found: 126.9048. **FTIR** (ATR, cm^{-1}): 3056, 3007, 2989, 2957, 2859, 2828, 1588, 1577, 1436, 1112, 1106, 929, 903, 867, 853, 748, 740, 715, 687, 499, 479, 439.

4,4'–((Pyrazine–2,3–diylbis(methylene))bis(diphenylphosphoniumnediyl))bis(butane–1–sulfonate) (**L3**), partially deuterated, crystallographic data on page 32



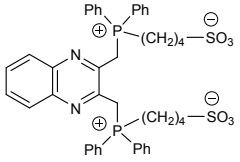
Yield: 73 %. NMR measurements were performed in D_2O and H_2O at 90 °C. **^{1}H NMR** (400 MHz, Deuterium Oxide) δ 9.11 (d, *J* = 2.4 Hz, 2H), 8.57 – 8.49 (m, 4H), 8.42 – 8.34 (m, 16H), 4.05 (d, *J* = 14.5 Hz, 4H, only appears if measured in water without lock), 3.83 – 3.70 (m, 4H), 3.55 – 3.45 (m, 4H), 2.59 – 2.46 (m, 4H), 2.44 – 2.30 (m, 4H). **^{13}C NMR** (101 MHz, D_2O) δ 146.56 (2C), 144.10 (2C), 135.96 (4C), 133.58 (d, *J* = 9.5 Hz, 8C), 130.87 (d, *J* = 12.6 Hz, 8C), 118.22 (d, *J* = 85.2 Hz, 4C), 50.68 (2C), 27.55 (d, *J* = 53.9 Hz, 2C, only appears if measured in water without lock), 25.59 (d, *J* = 16.1 Hz, 2C), 22.40 (d, *J* = 50.3 Hz, 2C), 21.06 (2C). **^{31}P NMR** (162 MHz, D_2O) δ 27.48. **HRMS pos.** (**ESI**): Calc for $[M+H]^+$, $C_{38}H_{42}N_2O_6P_2S_2$: 749.2033; found: 749.2046. **HRMS pos. (ESI):** Calc for $[M+Na]^+$, $C_{38}H_{41}NaN_2O_6P_2S_2$: 771.1852; found: 771.1851. **FTIR** (ATR, cm^{-1}): 3448, 2904, 1540, 1437, 1415, 1297, 1203, 1182, 1159, 1111, 1093, 1035, 996, 878, 791, 744, 709, 690, 600, 509, 500, 485, 450, 430, 416.

3,3'–((Pyrazine–2,3–diylbis(methylene))bis(diphenylphosphoniumnediyl))bis(propane–1–sulfonate) (**L4**), partially deuterated



Yield: 68 %. NMR measurements were performed in D_2O and H_2O at 90 °C. **^{1}H NMR** (300 MHz, Deuterium Oxide) δ 8.45 (s, 2H), 7.89 – 7.60 (m, 20H), 3.33 – 3.16 (m, 4H), 2.96 (t, *J* = 7.0 Hz, 4H), 2.02 – 1.85 (m, 4H). **^{13}C NMR** (101 MHz, D_2O) δ 156.05 (2C), 144.12 (2C), 136.04 (d, *J* = 1.9 Hz, 4C), 133.60 (d, *J* = 9.7 Hz, 8C), 130.89 (d, *J* = 12.3 Hz, 8C), 117.72 (d, *J* = 85.4 Hz, 4C), 51.06 (d, *J* = 16.4 Hz, 2C), 21.82 (d, *J* = 50.2 Hz, 2C), 18.21 (d, *J* = 2.8 Hz, 2C). **^{31}P NMR** (162 MHz, D_2O) δ 27.31. **HRMS pos.** (**ESI**): Calc for $[M+H]^+$, $C_{36}H_{38}N_2O_6P_2S_2$: 721.1719; found: 721.1716. **HRMS pos. (ESI):** Calc for $[M+Na]^+$, $C_{36}H_{37}NaN_2O_6P_2S_2$: 743.1539; found: 743.1536. **FTIR** (ATR, cm^{-1}): 3639, 2902, 1438, 1405, 1218, 1194, 1176, 1152, 1122, 1108, 1095, 1034, 995, 871, 759, 749, 724, 687, 592, 581, 532, 514, 494, 459, 419, 404.

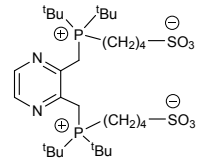
4,4'–((Quinoxaline–2,3–diylbis(methylene))bis(diphenylphosphoniumnediyl))bis(butane–1–sulfonate) (**L5**), partially deuterated



Yield: 55 %. NMR measurements were performed in CD_3OD and CH_3OH at 60 °C. **^{1}H NMR** (400 MHz, Methanol–d_4) δ 8.08 – 7.99 (m, 8H), 7.82 – 7.65 (m, 16H), 5.42 (d, *J* = 13.8 Hz, 4H, only appears if

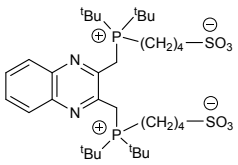
measured in methanol without lock), 3.43 – 3.35 (m, 4H), 2.78 (t, *J* = 6.3 Hz, 4H), 2.02 – 1.82 (m, 8H). **^{13}C NMR** (101 MHz, MeOD) δ without two deuterated carbon atoms: 140. 68 (4C), 135.65 (d, *J* = 2.5 Hz, 4C), 134.17 (d, *J* = 9.7 Hz, 8C), 132.42 (2C), 131.17 (d, *J* = 12.7 Hz, 8C), 128.95 (2C), 121.08 (d, *J* = 86.4 Hz, 4C), 50.96 (2C), 27.63 probably with some of signals at 26.68, 26.53, 23.12, 23.09, 22.74, 22.59, 21.85 and 21.82 (6C). **^{31}P NMR** (162 MHz, MeOD) δ 26.49. **HRMS pos.** (**ESI**): Calc for $[M+H]^+$, $C_{42}H_{44}N_2O_6P_2S_2$: 799.2189; found: 799.2173. **HRMS pos. (ESI):** Calc for $[M+Na]^+$, $C_{42}H_{43}NaN_2O_6P_2S_2$: 821.2008; found: 821.1996. **FTIR** (ATR, cm^{-1}): 3423, 2853, 1485, 1437, 1405, 1334, 1200, 1180, 1111, 1034, 859, 775, 745, 721, 691, 605, 574, 511, 505, 475, 455, 432, 402.

4,4'–((Pyrazine–2,3–diylbis(methylene))bis(di–tert–butylphosphoniumnediyl))bis(butane–1–sulfonate) (**L6**), partially deuterated



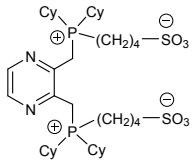
Yield: 74 %. **^{1}H NMR** (300 MHz, Deuterium Oxide) δ 8.71 (s, 2H), 4.30 (d, *J* = 13.6 Hz, 4H, not always appears), 3.04 – 2.96 (m, 4H), 2.76 – 2.63 (m, 4H), 2.08 – 1.93 (m, 8H), 1.45 (d, *J* = 15.4 Hz, 36H). **^{13}C NMR** (75 MHz, Deuterium Oxide) δ 146.24 (t, *J* = 7.4 Hz, 2C), 143.24 (2C), 49.87 (2C), 34.71 (d, *J* = 34.7 Hz, 4C), 27.02 (12C), 25.75 (d, *J* = 15.6 Hz, 2C), 22.29 (d, *J* = 5.8 Hz, 2C), 21.97 (d, *J* = 40.9 Hz, 2C, not always appears), 17.47 (d, *J* = 40.3 Hz, 2C). **^{31}P NMR** (121 MHz, D_2O) δ 52.02. **HRMS pos.** (**ESI**): Calc for $[M+H]^+$, $C_{30}H_{58}N_2O_6P_2S_2$: 669.3284; found: 669.3292. **HRMS pos. (ESI):** Calc for $[M+Na]^+$, $C_{30}H_{57}NaN_2O_6P_2S_2$: 691.3104; found: 691.3109. **FTIR** (ATR, cm^{-1}):3422, 2918, 1648, 1476, 1401, 1378, 1296, 1174, 1094, 1034, 937, 874, 813, 787, 710, 601, 521, 480, 432.

4,4'–((Quinoxaline–2,3–diylbis(methylene))bis(di–tert–butylphosphoniumnediyl))bis(butane–1–sulfonate) (**L7**), partially deuterated



Yield: 77 %. **^{1}H NMR** (400 MHz, Methanol–d_4) δ 8.21 (dt, *J* = 6.6, 3.3 Hz, 2H), 7.96 (dt, *J* = 6.4, 3.3 Hz, 2H), 5.53 (d, *J* = 12.9 Hz, 4H, only appears if measured in methanol without lock), 2.92 (t, *J* = 6.9 Hz, 4H), 2.85 – 2.76 (m, 4H), 2.19 – 2.02 (m, 8H), 1.63 (d, *J* = 15.5 Hz, 36H). **^{13}C NMR** (101 MHz, MeOD) δ 148.81 – 148.59 (m, 2C), 140.81 (2C), 132.87 (2C), 129.09 (2C), 51.24 (2C), 36.88 (d, *J* = 34.7 Hz, 4C), 28.68 (12C), 27.70 (d, *J* = 15.0 Hz, 2C), 26.21 (d, *J* = 43.3 Hz, 2C, only appears if measured in methanol without lock), 23.69 (d, *J* = 5.8 Hz, 2C), 19.72 (d, *J* = 41.5 Hz, 2C). **^{31}P NMR** (162 MHz, MeOD) δ 52.55. **HRMS pos.** (**ESI**): Calc for $[M+H]^+$, $C_{34}H_{60}N_2O_6P_2S_2$: 719.3441; found: 719.3438. **HRMS pos. (ESI):** Calc for $[M+Na]^+$, $C_{34}H_{59}NaN_2O_6P_2S_2$: 741.3260; found: 741.3246. **FTIR** (ATR, cm^{-1}): 3404, 2973, 2878, 1654, 1474, 1399, 1376, 1340, 1297, 1172, 1138, 1122, 1035, 936, 867, 769, 600, 524, 457, 424.

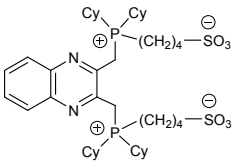
4,4'–((Pyrazine–2,3–diylbis(methylene))bis(dicyclohexylphosphoniumnediyl))bis(butane–1–sulfonate) (**L8**), partially deuterated, crystallographic data on page 33



Yield: 80 %. **^{1}H NMR** (400 MHz, Methanol–d_4) δ 8.62 (s, 2H), 4.33 (dd, *J* = 13.2, 4.9 Hz, 4H), 2.97 – 2.67 (m, 8H), 2.50 (m, 4H), 2.14 – 2.01 (m, 4H), 1.91 (m, 20H), 1.77 (m, 4H), 1.62 (m, 8H), 1.52 – 1.24 (m, 12H). **^{13}C NMR** (75 MHz, MeOD) δ149.44 (dd, *J* = 8.3, 1.1 Hz, 2C), 143.80 (2C), 51.41 (2C), 32.95 (d, *J* = 43.0 Hz, 4C), 27.92 with 27.87, 27.82, 27.77, 27.62, 27.58, 27.52, 27.44, 27.36 and 26.44 (22C), 23.98 (d, *J* = 49.9 Hz, 2C), 22.23 (d, *J* = 4.9 Hz, 2C), 17.95 (d, *J* = 45.2 Hz, 2C). **^{31}P NMR** (121 MHz, MeOD) δ 38.23. **HRMS pos.** (**ESI**): Calc for $[M+H]^+$, $C_{38}H_{66}N_2O_6P_2S_2$: 773.3910; found: 773.3916. **HRMS pos. (ESI):** Calc for

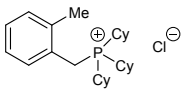
$[M+Na]^+$, $C_{38}H_{65}NaN_2O_6P_2S_2$: 795.3730; found: 795.3735. **FTIR** (ATR, cm^{-1}): 3450, 2929, 2849, 1638, 1446, 1415, 1236, 1176, 1091, 1036, 890, 858, 709, 600, 519, 418.

4,4'–((Quinoxaline–2,3–diylbis(methylene))bis(dicyclohexylphosphoniumnediyl))bis(butane–1–sulfonate) (**L9**), partially deuterated, crystallographic data on page 34



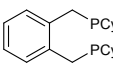
Yield: 84 %. **^{1}H NMR** (300 MHz, Methanol–d_4) δ 8.22 (dd, J = 6.4, 3.4 Hz, 2H), 7.96 (dd, J = 6.4, 3.4 Hz, 2H), 5.42 (d, J = 12.9 Hz, 4H, only appears if measured in methanol without lock), 3.07 – 2.78 (m, 8H), 2.69 – 2.49 (m, 4H), 2.25 – 2.08 (m, 4H), 2.07 – 1.82 (m, 20H), 1.79 – 1.59 (m, 12H), 1.56 – 1.26 (m, 12H). **^{13}C NMR** (101 MHz, MeOD) δ 149.24 (t, J = 7.4 Hz, 2C), 141.25 (2C), 132.72 (2C), 129.32 (2C), 51.38 (2C), 33.40 (d, J = 42.6 Hz, 4C), 28.05 (dd, J = 11.7, 3.8 Hz) with 27.71, 27.60, 27.58, 27.55, 27.47, 27.40 and 26.46 (22C), 24.56 (d, J = 50.0 Hz, 2C, only appears if measured in methanol without lock), 22.27 (d, J = 4.6 Hz, 2C), 18.32 (d, J = 45.1 Hz, 2C). **^{31}P NMR** (121 MHz, MeOD) δ 38.16. **HRMS pos.** (**ESI**): Calc for $[M+H]^+$, $C_{42}H_{68}N_2O_6P_2S_2$: 823.4067; found: 823.4074. **HRMS pos. (ESI):** Calc for $[M+Na]^+$, $C_{42}H_{67}NaN_2O_6P_2S_2$: 845.3886; found: 845.3887. **FTIR** (ATR, cm^{-1}): 3425, 2925, 2889, 2851, 1642, 1448, 1413, 1309, 1209, 1178, 1135, 1118, 1094, 1037, 852, 771, 708, 605, 564, 523, 466, 409.

Tricyclohexyl(2–methylbenzyl)phosphonium chloride (**L10**)



To the stirred solution of tricyclohexylphosphine (561 mg, 2 mmol) in dry toluene (6 ml) 1–(chloromethyl)–2–methylbenzene (366 mg, 2.6 mmol) was added under argon. The light yellow solution was refluxed for 4 h. The resulted heterogeneous mixture was cooled down before ether (~ 10 ml) was added. Solid material was separated, washed with ether. Recrystallization from dichloromethane/ether gives the titled phosphonium salt as white, shiny crystals with 75 % yield. **^{1}H NMR** (400 MHz, Chloroform–d) δ 7.28 – 7.24 (m, 1H), 7.21 – 7.10 (m, 3H), 4.17 (d, J = 14.4 Hz, 2H), 2.85 (tdd, J = 12.2, 9.6, 2.6 Hz, 3H), 2.48 (d, J = 1.4 Hz, 3H), 2.01 – 1.90 (m, 6H), 1.89 – 1.80 (m, 6H), 1.79 – 1.71 (m, 3H), 1.53 – 1.32 (m, 12H), 1.29 – 1.16 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.16 (d, J = 6.9 Hz), 131.63 (d, J = 2.7 Hz), 130.39 (d, J = 3.8 Hz), 128.27, 128.21 (d, J = 3.3 Hz), 126.59 (d, J = 2.7 Hz), 31.55 (d, J = 38.1 Hz, 3C), 27.16 (d, J = 4.2 Hz, 6C), 26.54 (d, J = 11.7 Hz, 6C), 25.41 (3C), 20.86, 20.85 (d, J = 41.3 Hz). **^{31}P NMR** (121 MHz, $CDCl_3$) δ 31.28. **HRMS pos.** (**ESI**): Calc for $[M+H]^+$, $C_{26}H_{42}P$: 385.3019; found: 385.3021. **FTIR** (ATR, cm^{-1}): 2931, 2852, 2842, 2779, 1444, 1009, 867, 854, 782, 773, 757, 747, 732, 519, 507, 477, 424, 405.

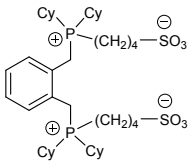
1,2–Bis((dicyclohexylphosphanyl)methyl)benzene



To a solution of o–xylene (1.98 ml, 16.4 mmol) in ether (10 ml) KO^{t}Bu (4.03 g, 36 mmol) was added. Resulted heterogenic mixture cooled to –78 °C before 2.5M *n*–BuLi in hexane (14.4 ml, 36 mmol) was added dropwise. The intensively orange coloured reaction mixture was allowed slowly to warm to RT and then heated under reflux for 2 h. The reaction mixture was again cooled down to –78 °C and an ethereal solution (15 ml) of chlorodicyclohexylphosphine (7.95 ml, 36 mmol) was slowly syringed. After 1h at that temperature, the reaction mixture was allowed to warm slowly to RT. Then, water was slowly added and the product was extracted with CH_2Cl_2 (4x20ml). After drying over Na_2SO_4 and solvent evaporation, the crude product was recrystallized few times from methanol until pure product was obtained as off–white, sensitive solid. **Yield**: 34 %.**^{1}H NMR** (300 MHz, Chloroform–d) δ 7.18 – 7.10 (m, 2H), 7.10 – 7.02 (m, 2H), 3.04 (s, 4H), 1.88 – 1.64 (m,

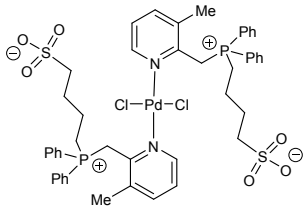
20H), 1.59 – 1.47 (m, 4H), 1.35 – 1.10 (m, 20H). **^{13}C NMR** (75 MHz, Chloroform–*d*) δ 137.58 (dd, *J* = 5.5, 2.7 Hz, 2C), 130.68 (d, *J* = 7.0 Hz, 2C), 125.43 (2C), 33.52 (d, *J* = 15.4 Hz, 4C), 30.06 (d, *J* = 12.1 Hz, 4C), 29.49 (d, *J* = 10.3 Hz, 4C), 27.75 – 27.00 (m, 10C), 26.50 (4C). ^{31}P NMR (121 MHz, $CDCl_3$) δ –2.80. **HRMS pos.** (**ESI**): Calc for $[M+H]^+$, $C_{32}H_{52}P_2$: 499.3617; found: 499.3622. **FTIR** (ATR, cm^{-1}): 2919, 2845, 1597, 1483, 14445, 1416, 1341, 1268, 1207, 1170, 1040, 999, 885, 850, 827, 763, 744, 511, 467.

4,4'–((1,2–Phenylenebis(methylene))bis(dicyclohexylphosphoniumnediyl))bis(butane–1–sulfonate (**L11**), partially deuterated



Yield: 94.3 %. **^{1}H NMR** (400 MHz, Methanol–d_4) δ 7.61 – 7.43 (m, 4H), 3.98 (dd, *J* = 14.2, 4.2 Hz, 4H), 2.87 (t, *J* = 6.7 Hz, 4H), 2.68 – 2.48 (m, 4H), 2.49 – 2.29 (m, 4H), 1.91 (m, 20H), 1.81 – 1.68 (m, 8H), 1.63 – 1.26 (m, 20H). **^{13}C NMR** (101 MHz, MeOD) δ 133.47 (2C), 130.68 (2C), 130.31 (t, *J* = 8.1 Hz, 2C), 51.03 (2C), 31.83 (d, *J* = 41.3 Hz, 4C), 27.43 with 27.37, 27.30 and 27.22 (16C), 26.42 (6C), 22.75 (d, *J* = 42.7 Hz, 2C), 21.71 (2C), 17.25 (d, *J* = 43.8 Hz, 2C). **^{31}P NMR** (121 MHz, MeOD) δ 35.69. **HRMS pos.** (**ESI**): Calc for $[M+H]^+$, $C_{40}H_{68}O_6P_2S_2$: 771.4005; found: 771.4009. **HRMS pos. (ESI):** Calc for $[M+Na]^+$, $C_{40}H_{67}NaO_6P_2S_2$: 793.3825; found: 793.3835. **FTIR** (ATR, cm^{-1}): 3421, 2922, 2851, 1653, 1448, 1301, 1176, 1078, 1037, 891, 873, 786, 708, 602, 523, 490, 410.

Palladium complex from 4–(((3–Methylpyridin–2–yl)methyl)diphenylphosphonio)butane–1–sulfonate and bis(benzonitrile)palladium(II)chloride as palladium source, crystallographic data on page 35



To the suspension of L1 (0.2 mmol) in dry acetone (5 ml) bis(benzonitrile)palladium(II)chloride (0.1 mmol) was added and red–brown mixture stirred at room temperature for 15 h while the color turned to yellow. Ether was added and yellow solid isolated. Recrystallization from methanol or water led to formation of single crystals along with contaminations of some palladium black and other side products. The complex was not soluble enough under standard conditions and was not stable at elevated temperature for corresponding NMR measurements. Recorded spectra showed only complex mixtures. Attempts to record pure spectra from collected single crystals failed because of further decomposition.

HRMS neg. (**ESI**): Calc for $[M–H]^–$, $C_{46}H_{52}Cl_2N_2O_6P_2PdS_2$: 1028.1102; found: 1028.1108; 1029.1091; found: 1029.1115; 1030.1095; found: 1030.1107; 1031.1080; found: 1031.1082; 1032.1098; found: 1032.1089; 1033.1076; found: 1033.1071. **FTIR** (ATR, cm^{-1}): 3417, 3057, 3023, 2914, 1638, 1587, 1436, 1323, 1177, 1109, 1033, 996, 837, 790, 748, 691, 600, 552, 520, 486, 455.

General procedure for telomerization of 1,3–butadiene with methanol

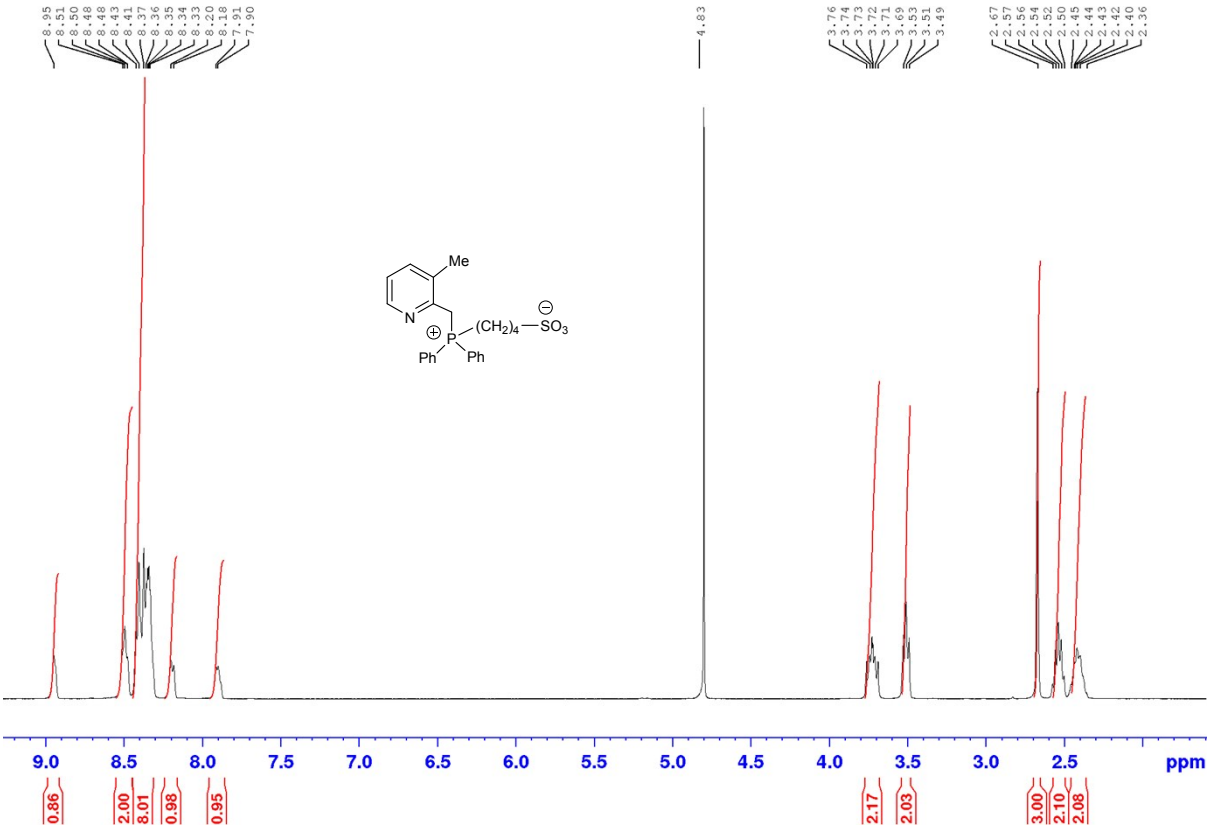
Corresponding ligand (typically 0.016 or 0.032 mol%) and palladium source (typically 0.002 mol%) were dissolved in sodium methanolate (20 ml, 1 mol% relative to butadiene) solution in a Schlenk flask under argon. The resulted yellow–orange solution (only in case of zwitterionic ligands L1, L3–L9) was transferred via syringe into a secured 100 mL stainless steel Parr autoclave under argon. Autoclave cooled down with dry ice before adjusted few seconds under light vacuum. Then 1,3–butadiene (15.0g, 277 mmol, mass control) was

transferred into the cooled autoclave (before was condensed in a separate 75 mL pressure cylinder) and the vessel was warmed to room temperature. After adjusting additional ~20 bar of nitrogen pressure to the autoclave, the reaction mixture was heated to 50 or 60 °C. After 16 or 18 h the autoclave was cooled down to room temperature and the remaining 1,3–butadiene and nitrogen were released. 2,2,4–Trimethylpentane (5 mL) as internal standard was added and the yield of telomerization products was determined by HP 7890A gas chromatograph. In order to isolate the different octadienyl ethers the reaction mixture was distilled in vacuum.

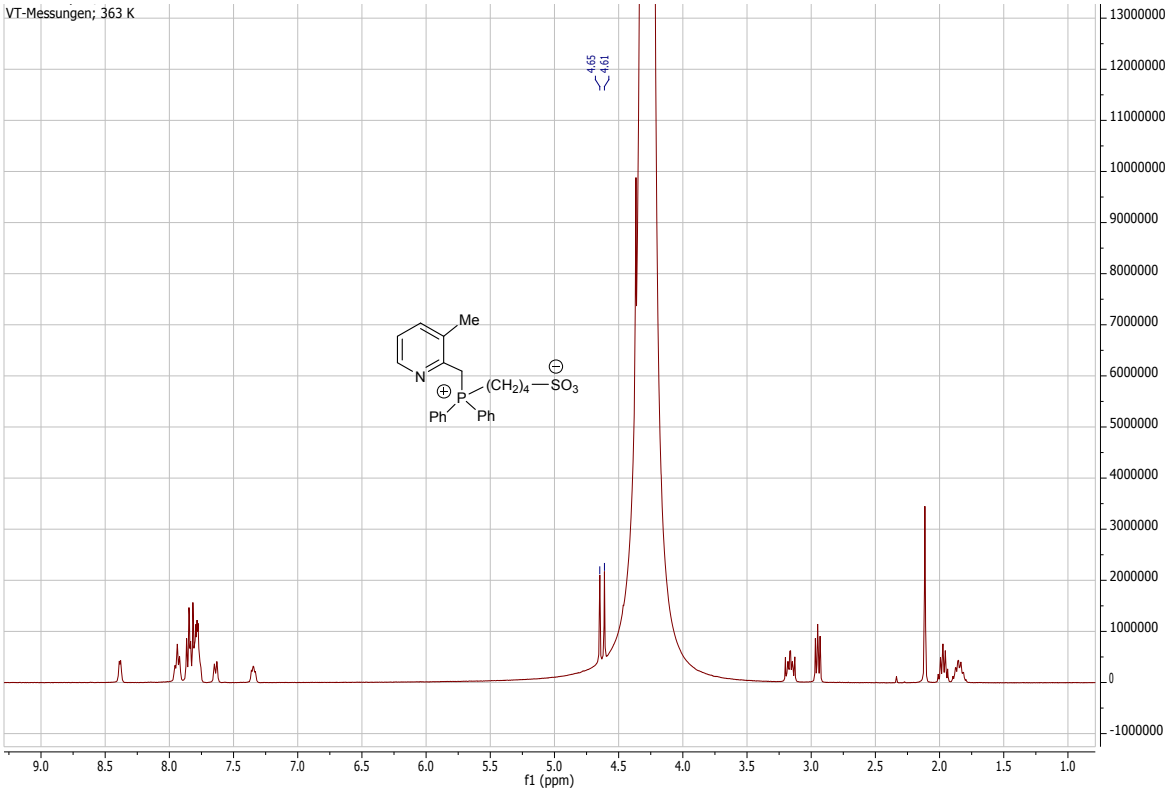
NMR spectra

4–(((3–Methylpyridin–2–yl)methyl)diphenylphosphonio)butane–1–sulfonate (**L1**)

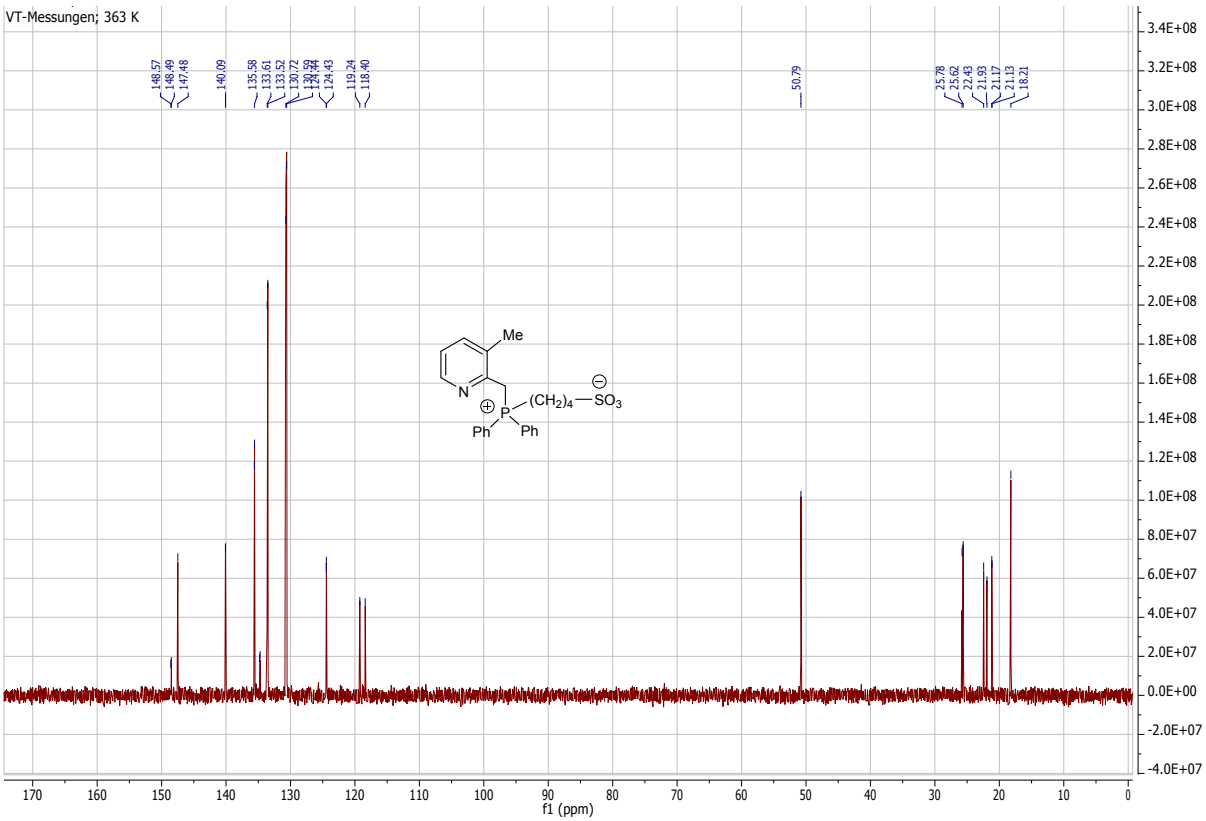
^{1}H–NMR in D_2O at 90 °C



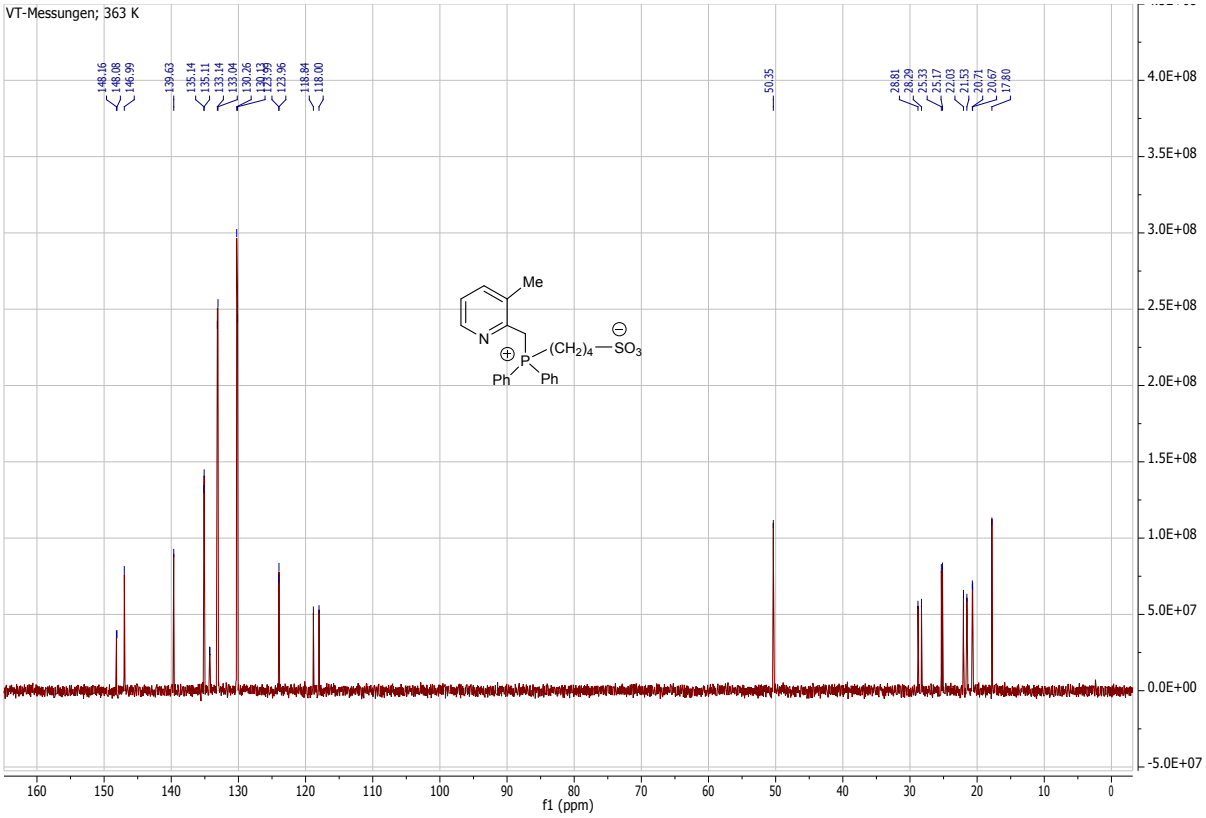
^{1}H–NMR in H_2O at 90 °C



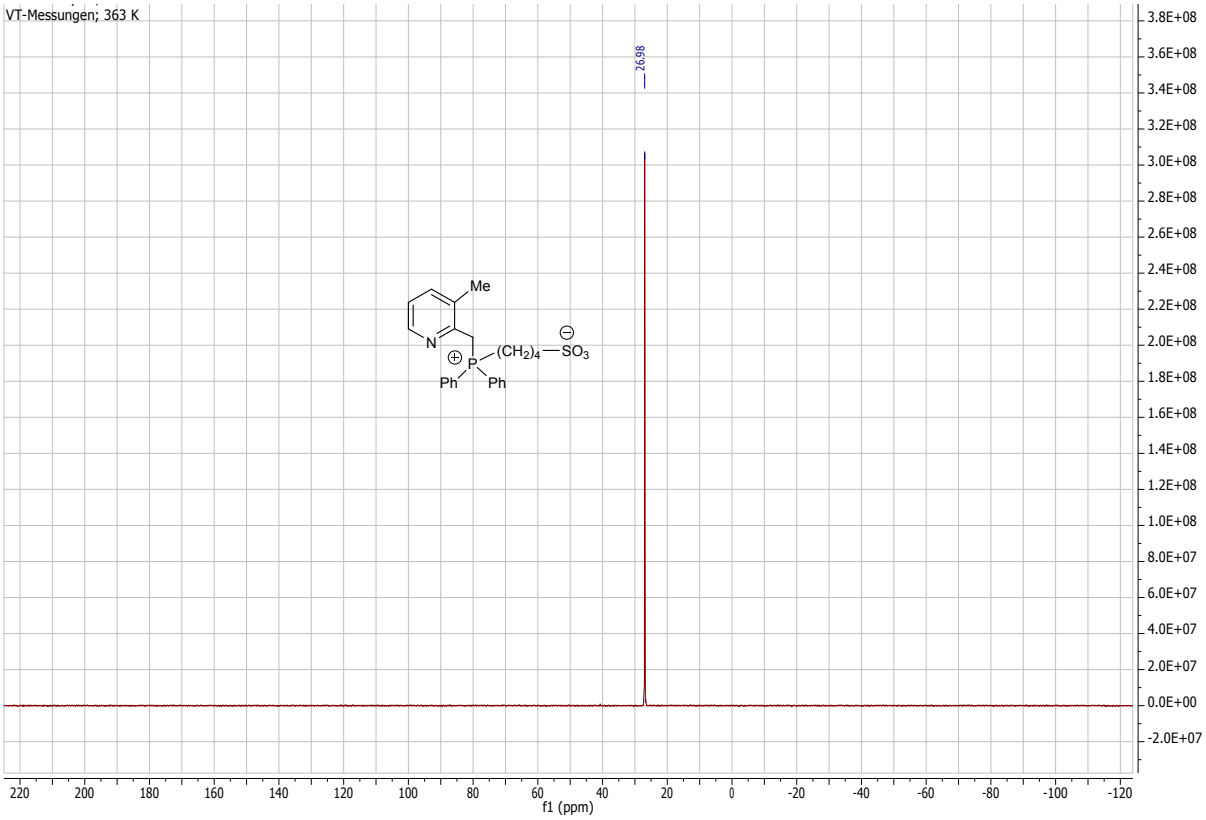
^{13}C–NMR in D_2O at 90 °C



^{13}C–NMR in H_2O at 90 °C

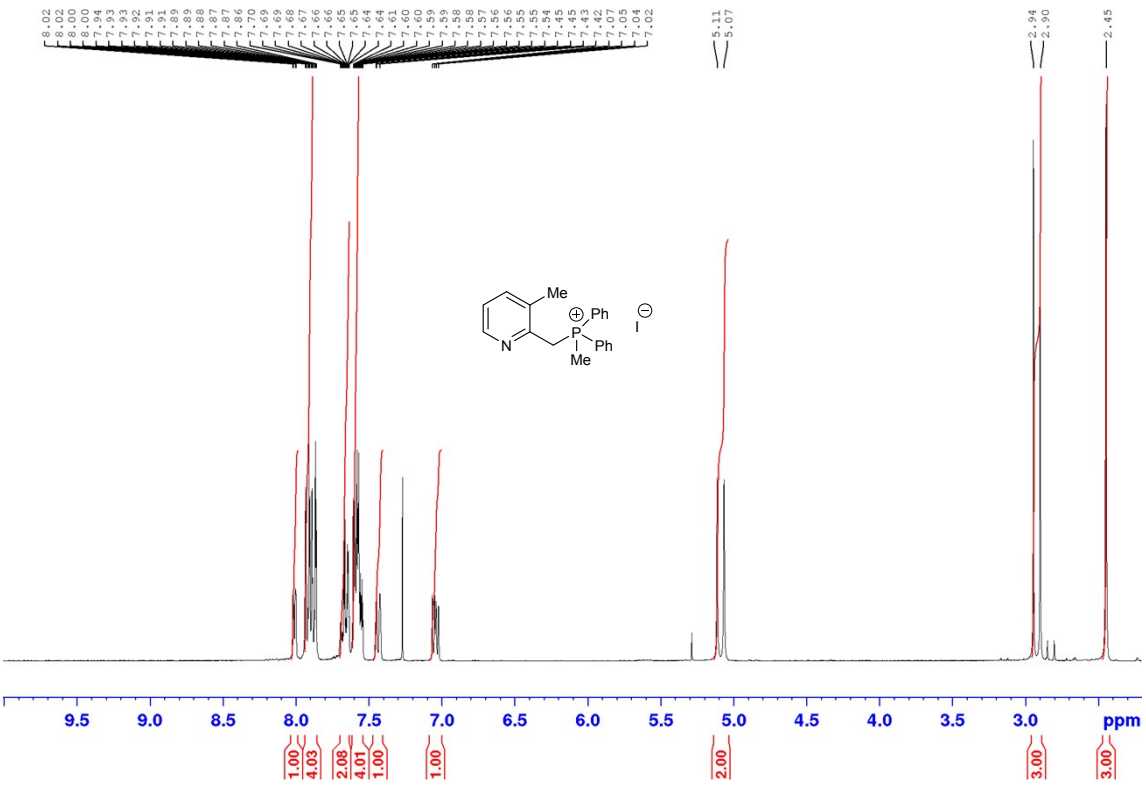


^{31}P–NMR in D_2O at 90 °C

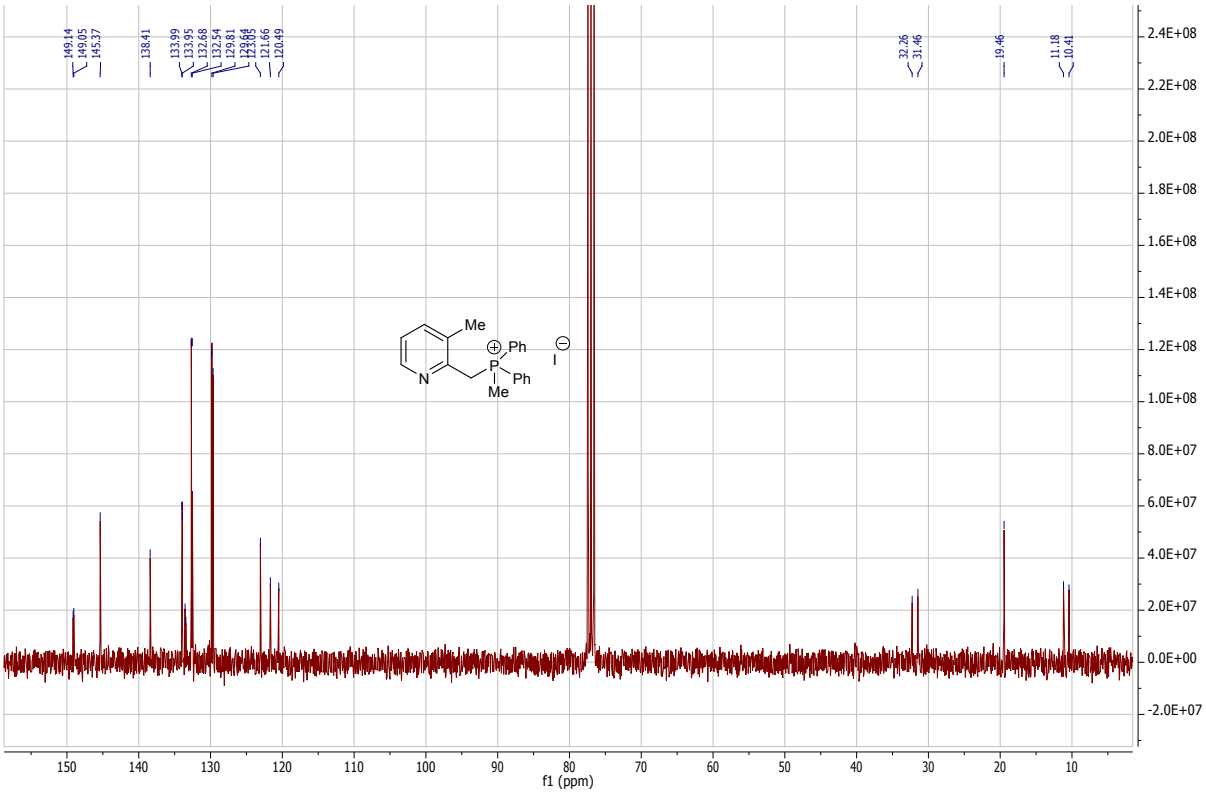


Methyl((3–methylpyridin–2–yl)methyl)diphenylphosphonium iodide (**L2**)

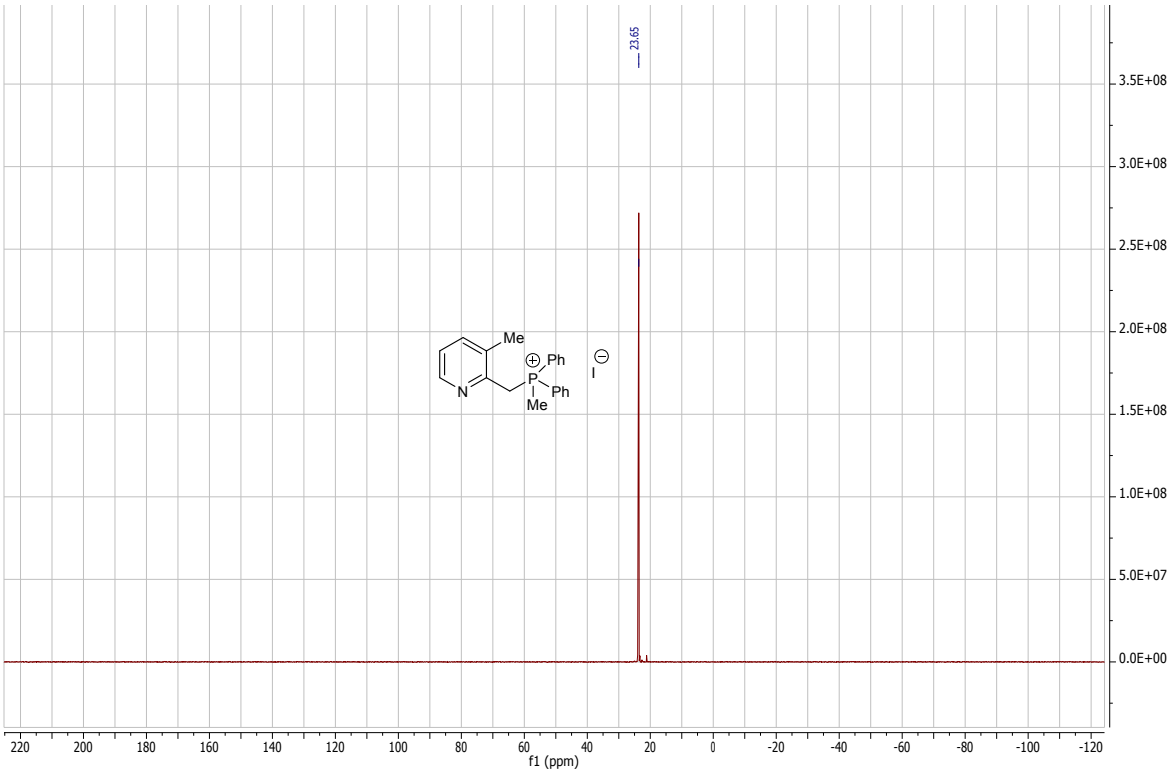
^{1}H–NMR in $CDCl_3$



^{13}C–NMR in $CDCl_3$

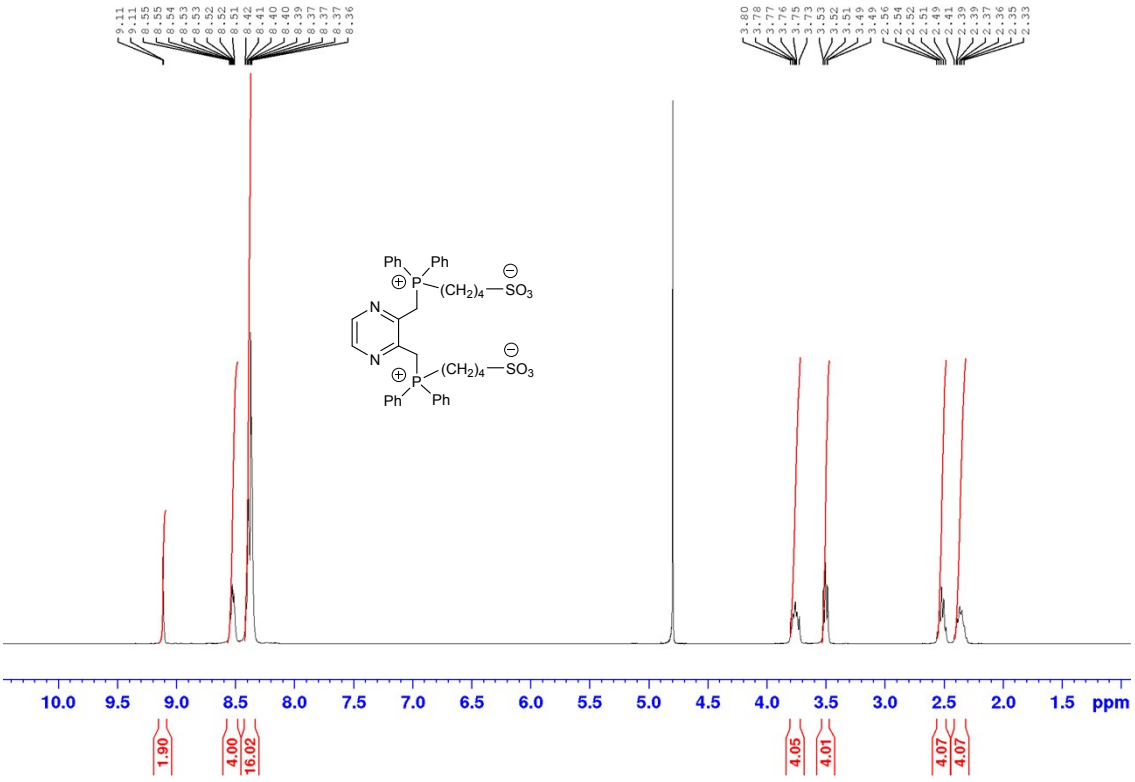


^{31}P–NMR in $CDCl_3$

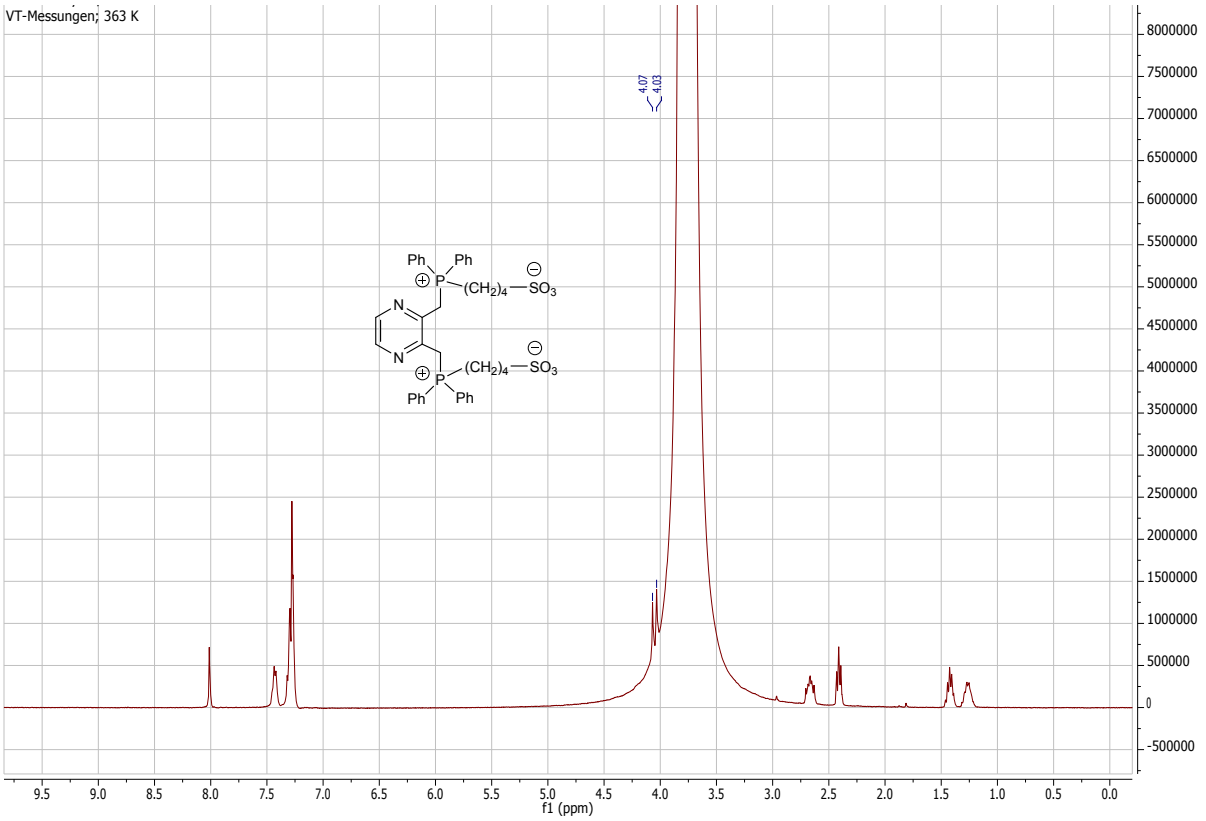


4,4'–((Pyrazine–2,3–diylbis(methylene))bis(diphenylphosphoniumnediyl))bis(butane–1–sulfonate) (**L3**)

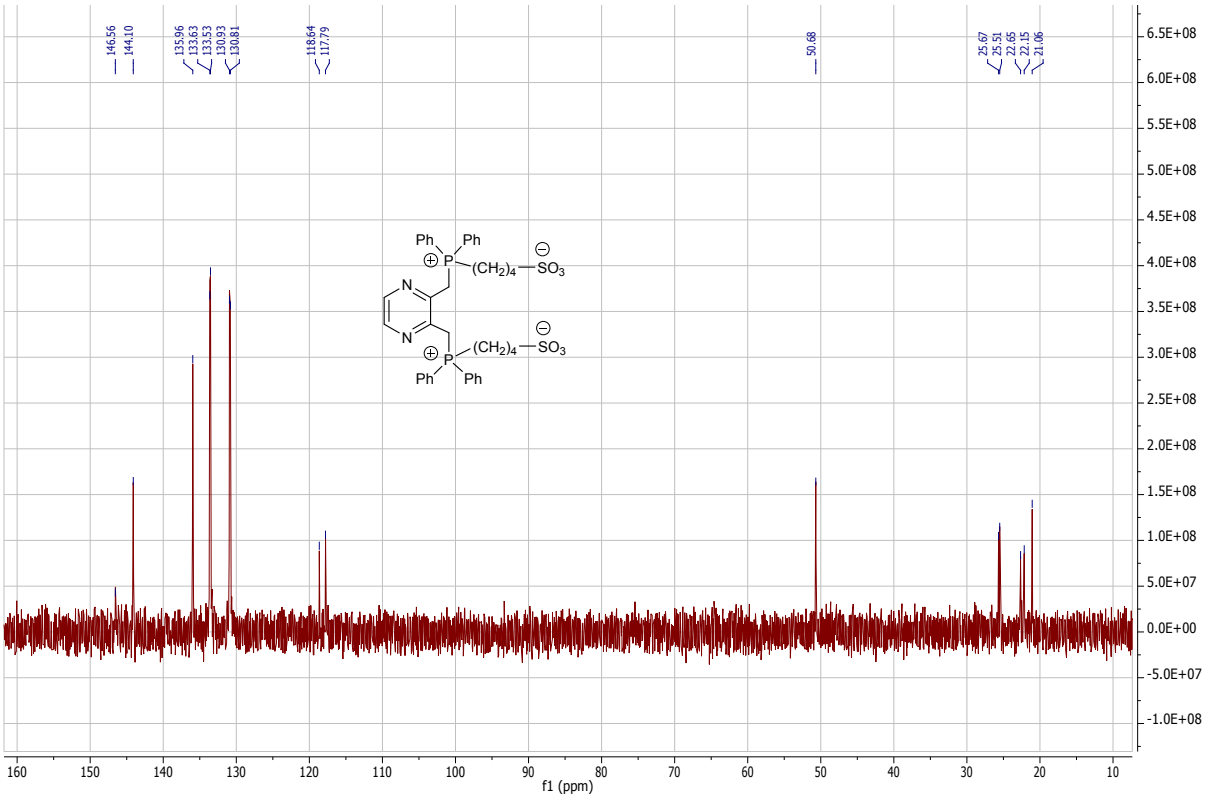
^{1}H–NMR in D_2O at 90 °C



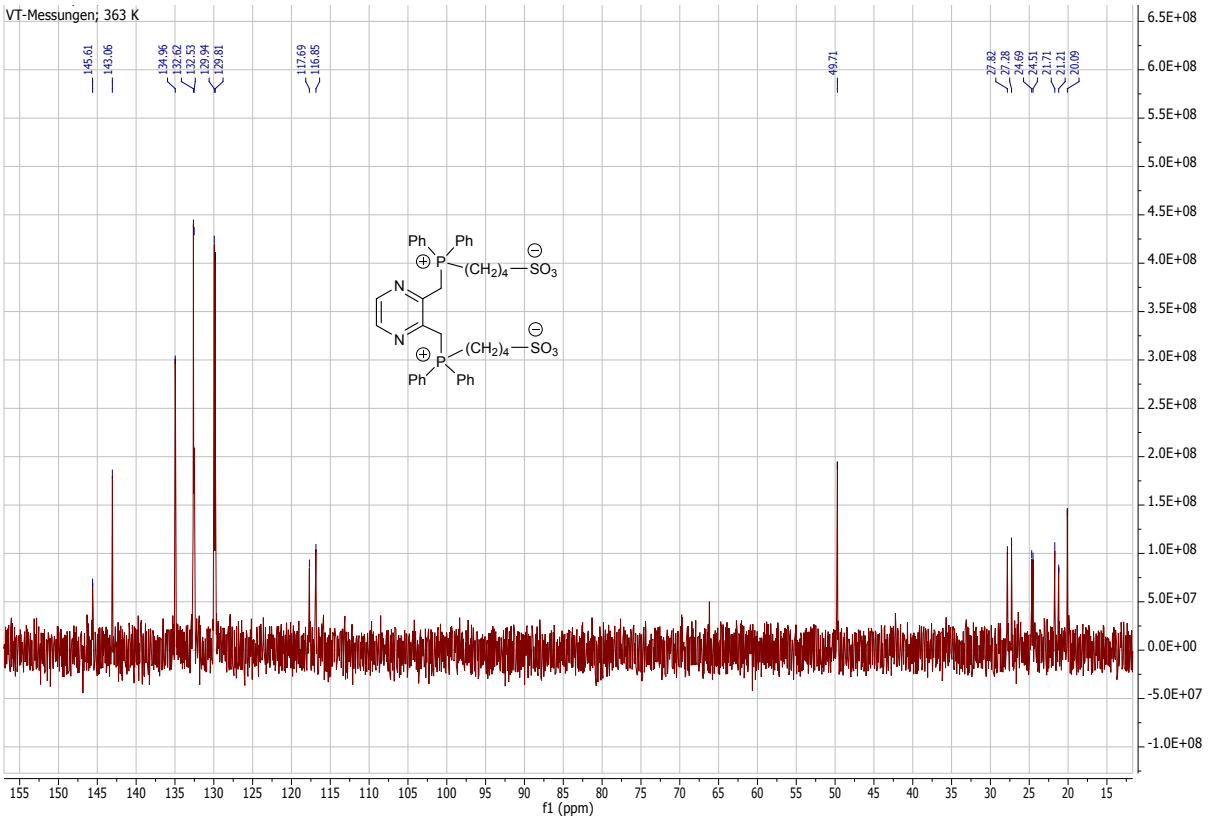
^{1}H–NMR in H_2O at 90 °C



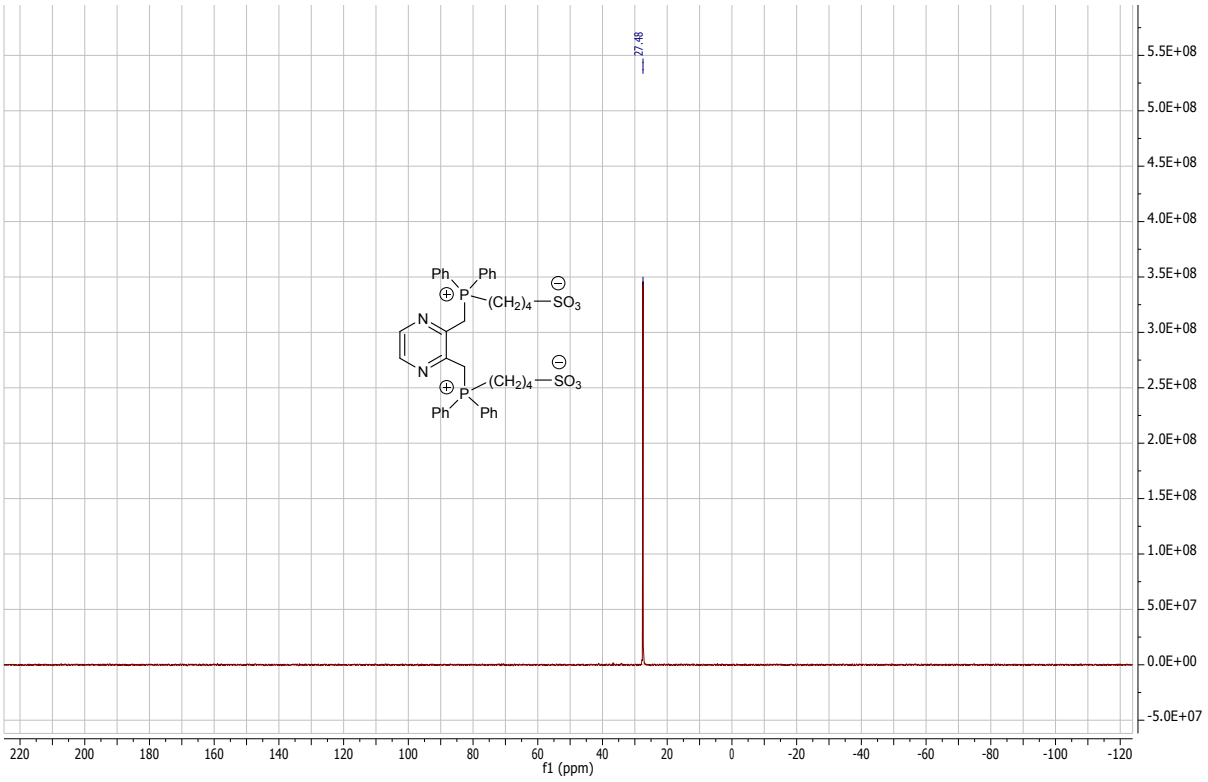
^{13}C–NMR in D_2O at 90 °C



^{13}C–NMR in H_2O at 90 °C

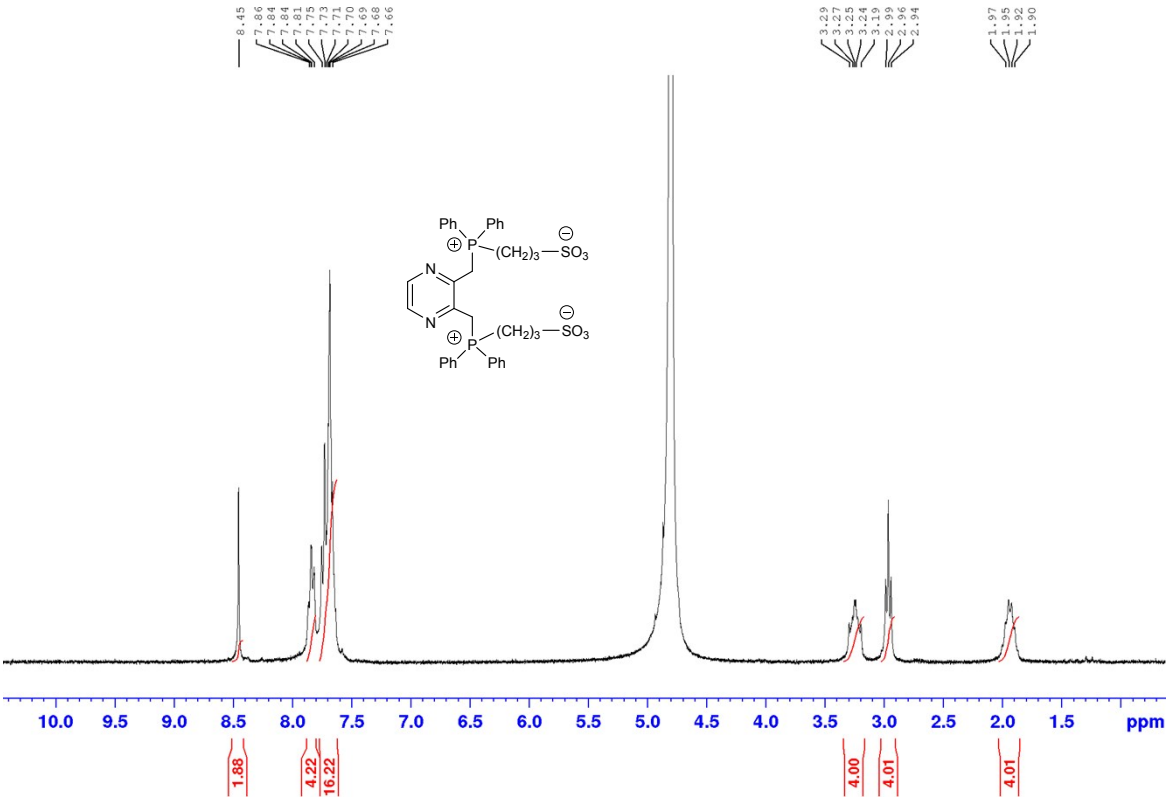


^{31}P–NMR in D_2O at 90 °C

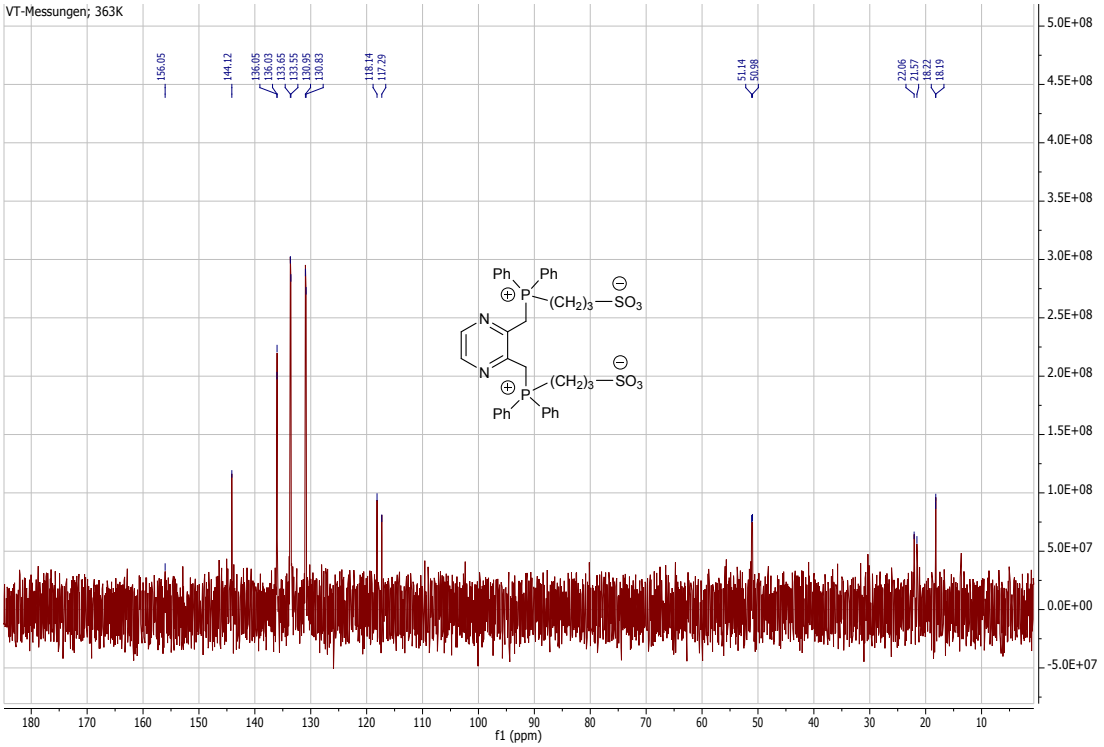


3,3'–((Pyrazine–2,3–diylbis(methylene))bis(diphenylphosphoniumnediyl))bis(propane–1–sulfonate) (**L4**)

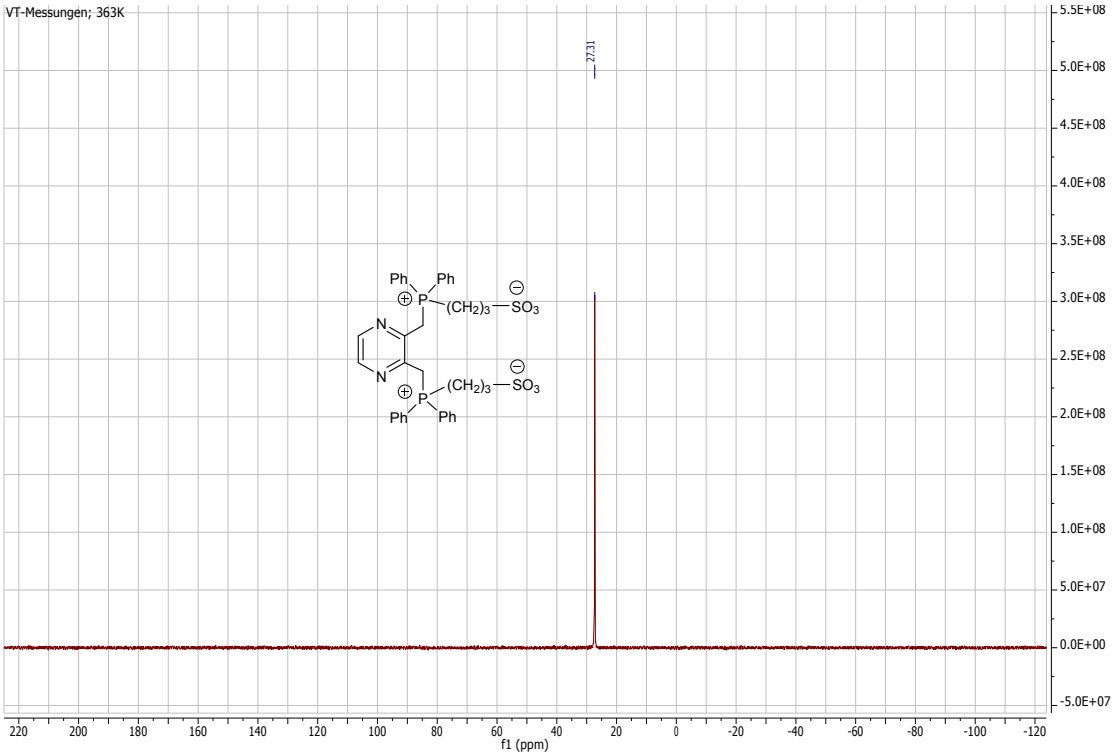
^{1}H–NMR in D_2O at 90 °C



^{13}C–NMR in D_2O at 90 °C

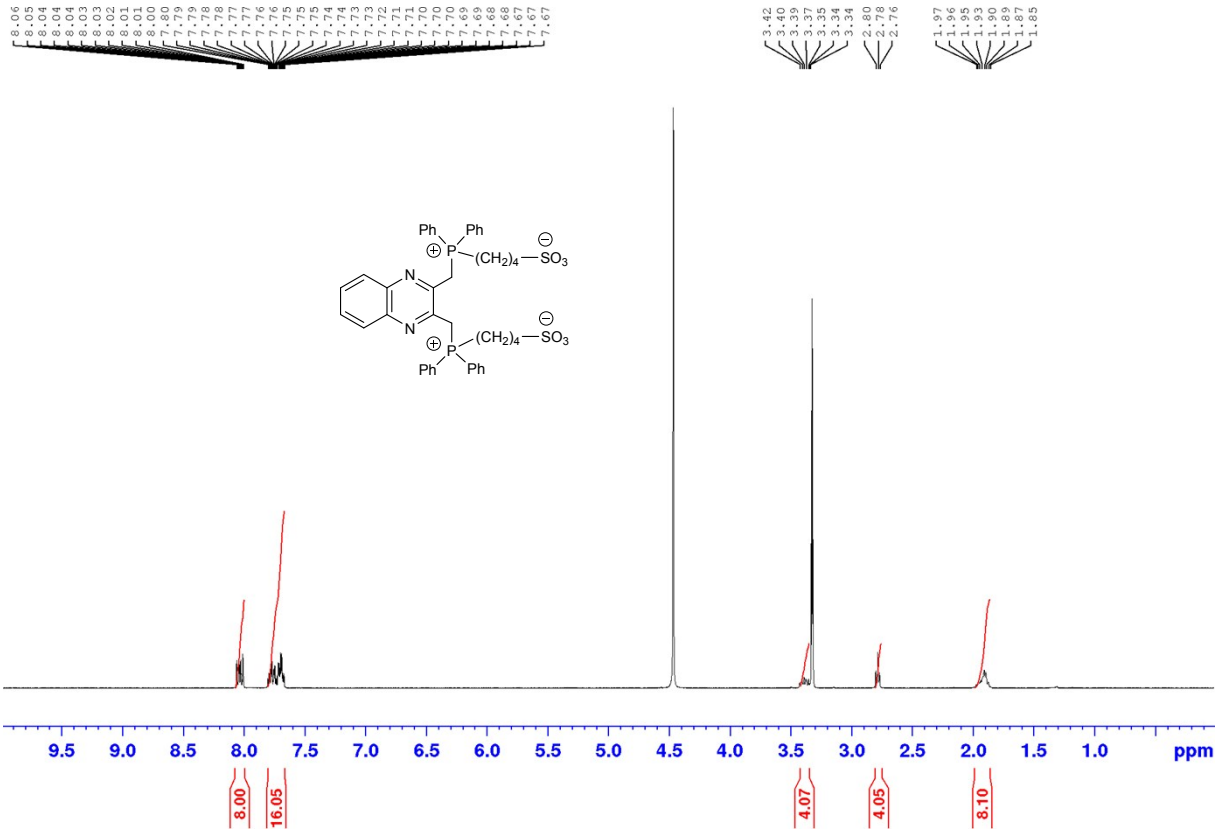


^{31}P–NMR in D_2O at 90 °C

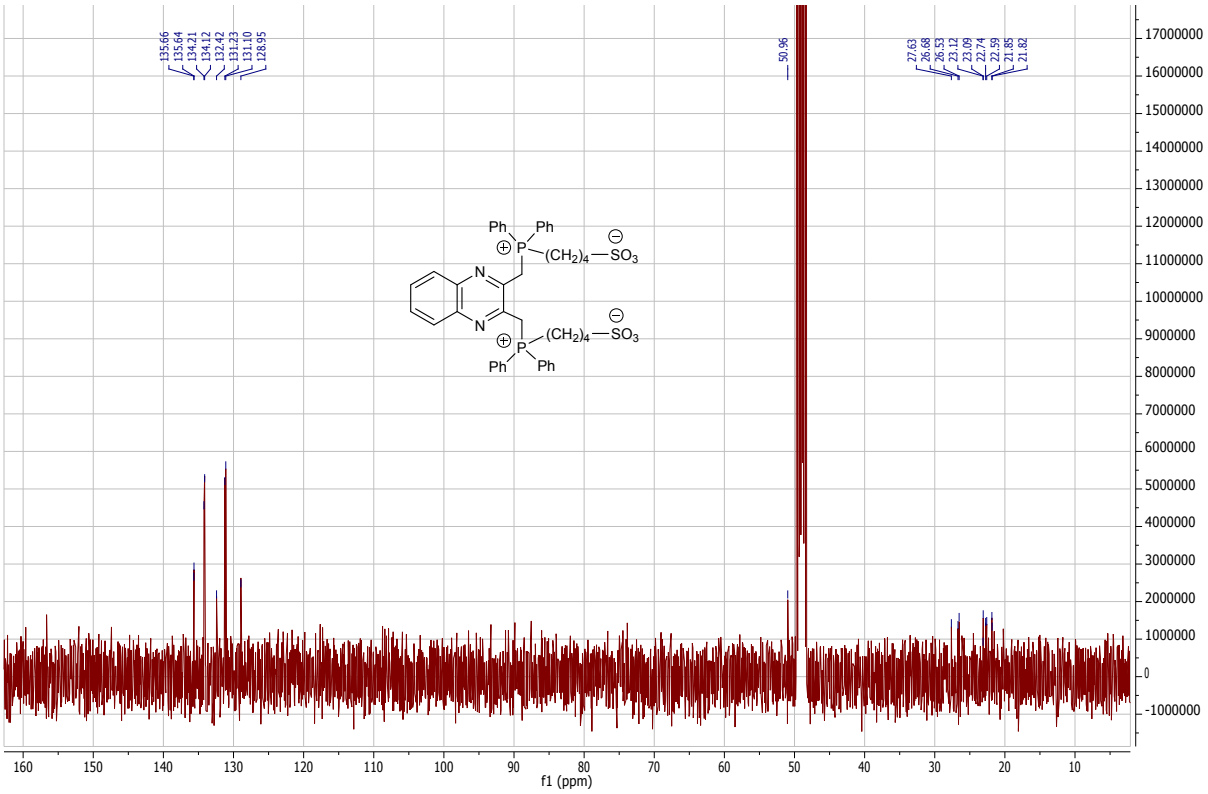


4,4'–((Quinoxaline–2,3–diylbis(methylene))bis(diphenylphosphoniumnediyl))bis(butane–1–sulfonate) (**L5**)

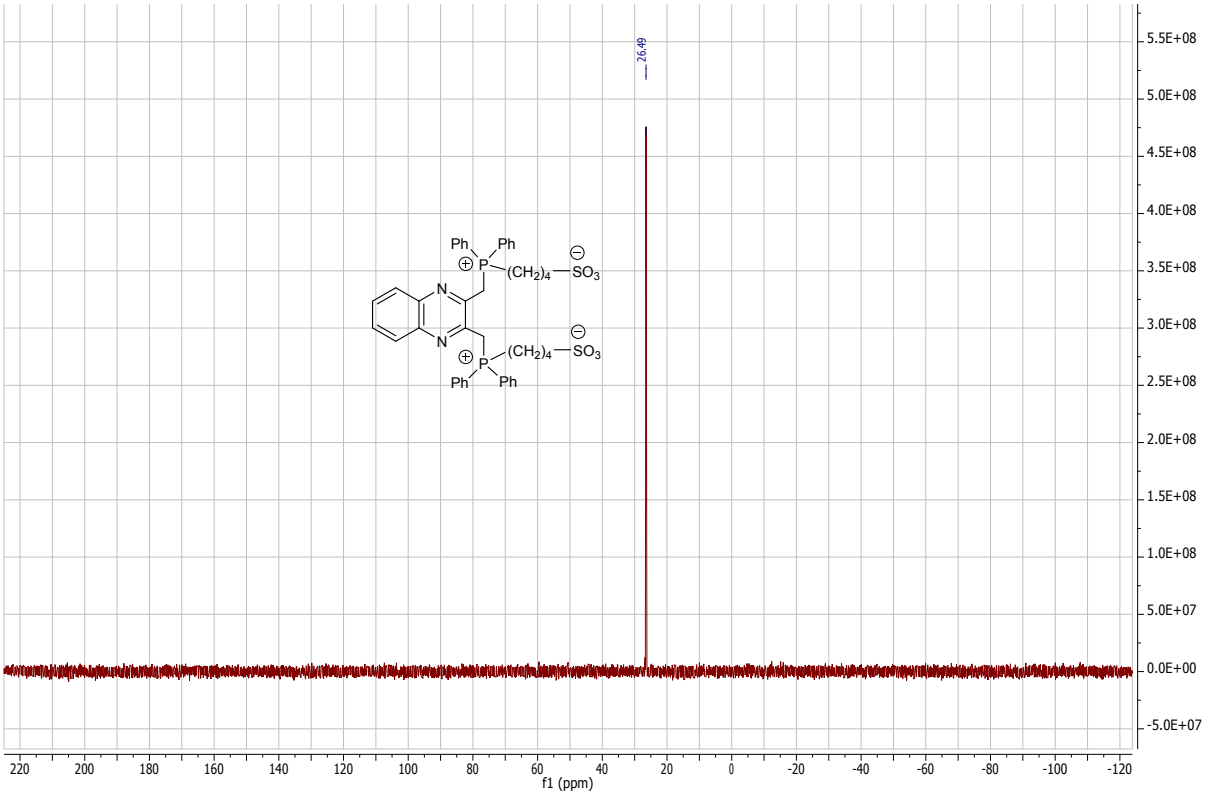
^{1}H–NMR in methanol–d_4 at 60 °C



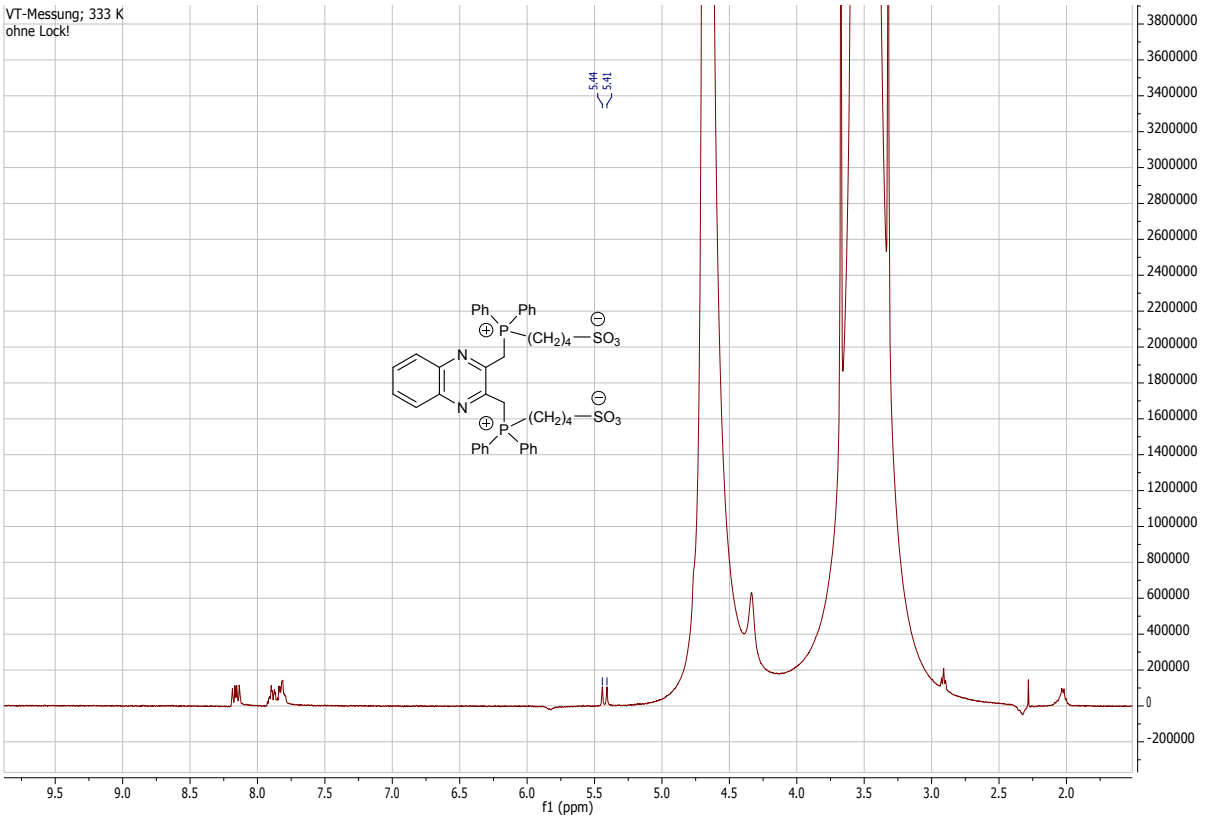
^{13}C–NMR in methanol–d_4 at 60 °C



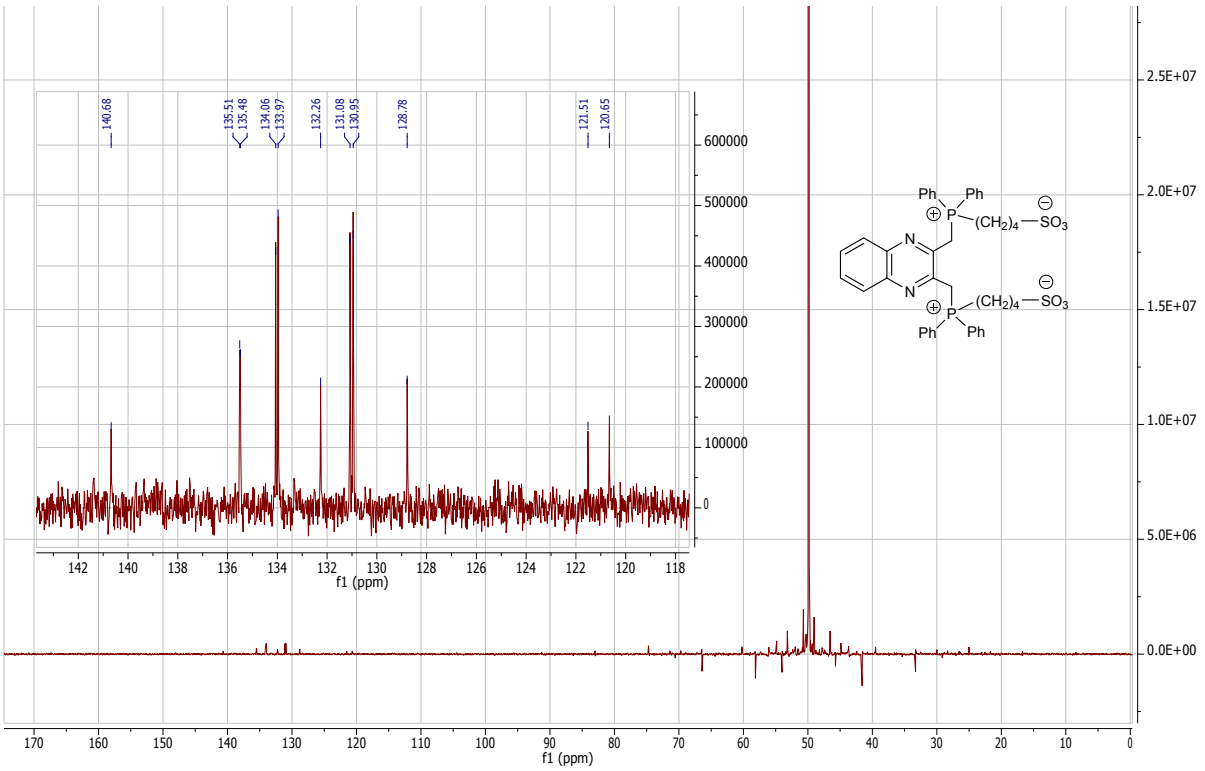
^{31}P–NMR in methanol–d_4 at 60 °C



^{1}H–NMR in methanol at 60 °C

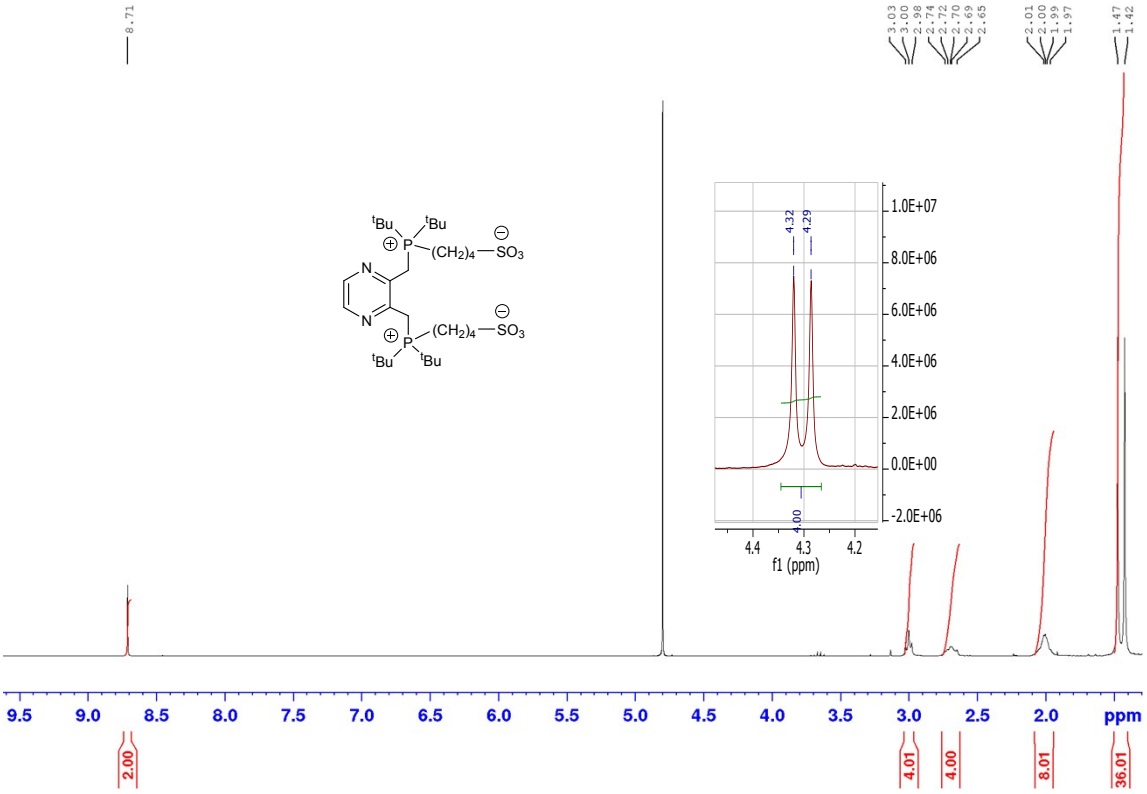


^{13}C–NMR in methanol at 60 °C and NS 4096

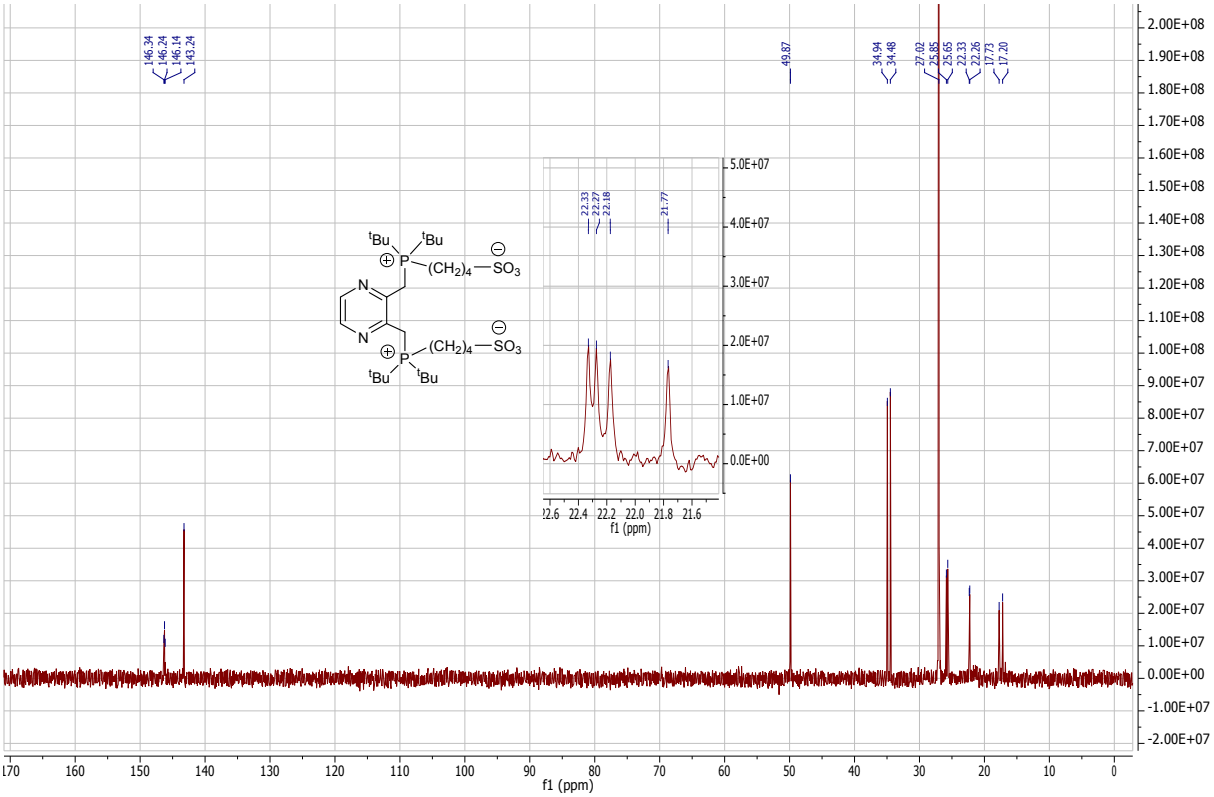


4,4'–((Pyrazine–2,3–diylbis(methylene))bis(di–tert–butylphosphoniumnediyl))bis(butane–1–sulfonate) (**L6**)

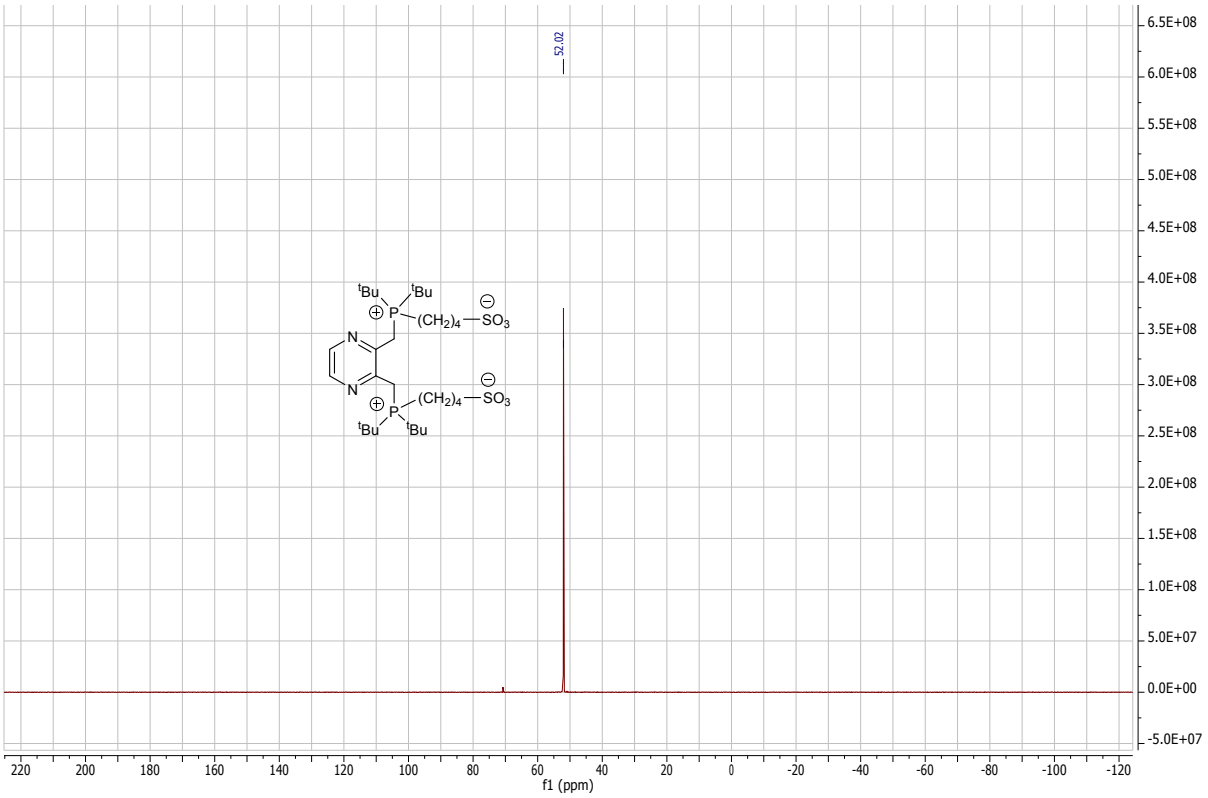
^{1}H–NMR in D_2O



^{13}C–NMR in D_2O

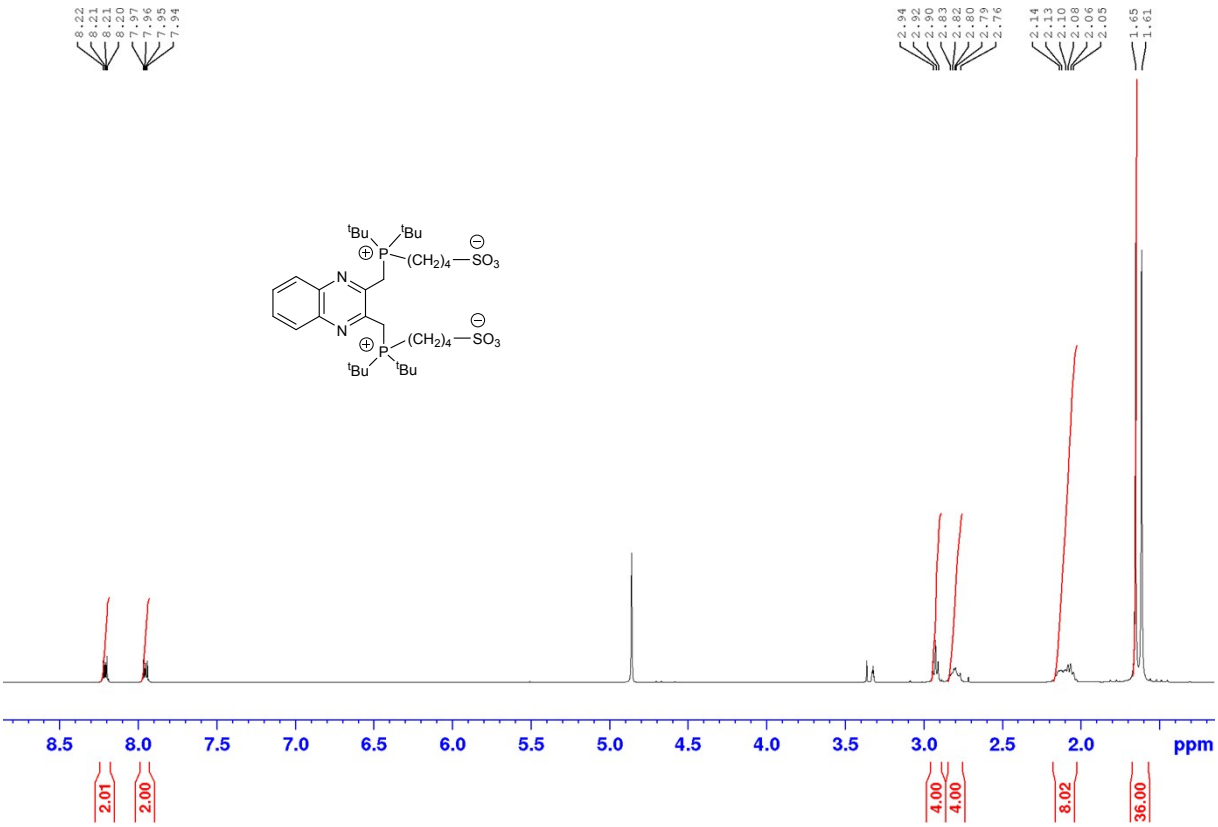


^{31}P–NMR in D_2O

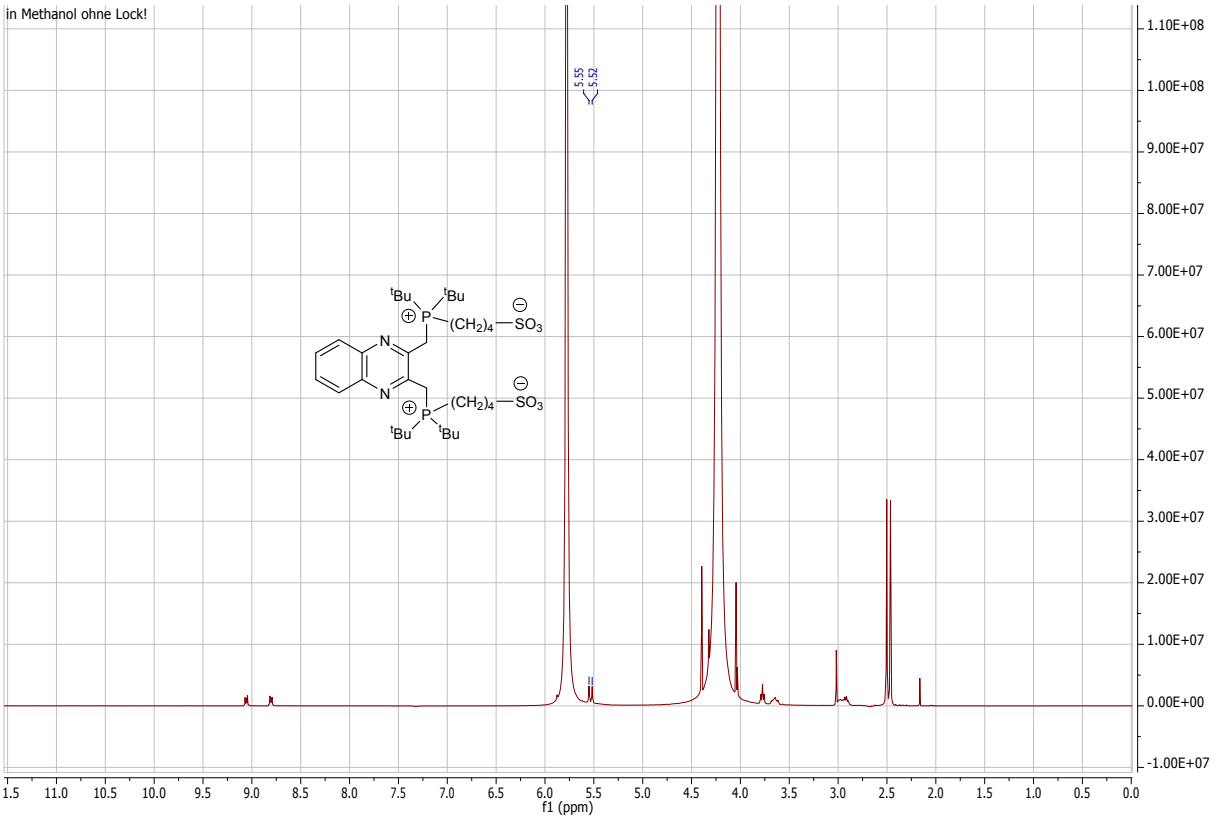


4,4'–((Quinoxaline–2,3–diylbis(methylene))bis(di–tert–butylphosphoniumnediyl))bis(butane–1–sulfonate) (**L7**)

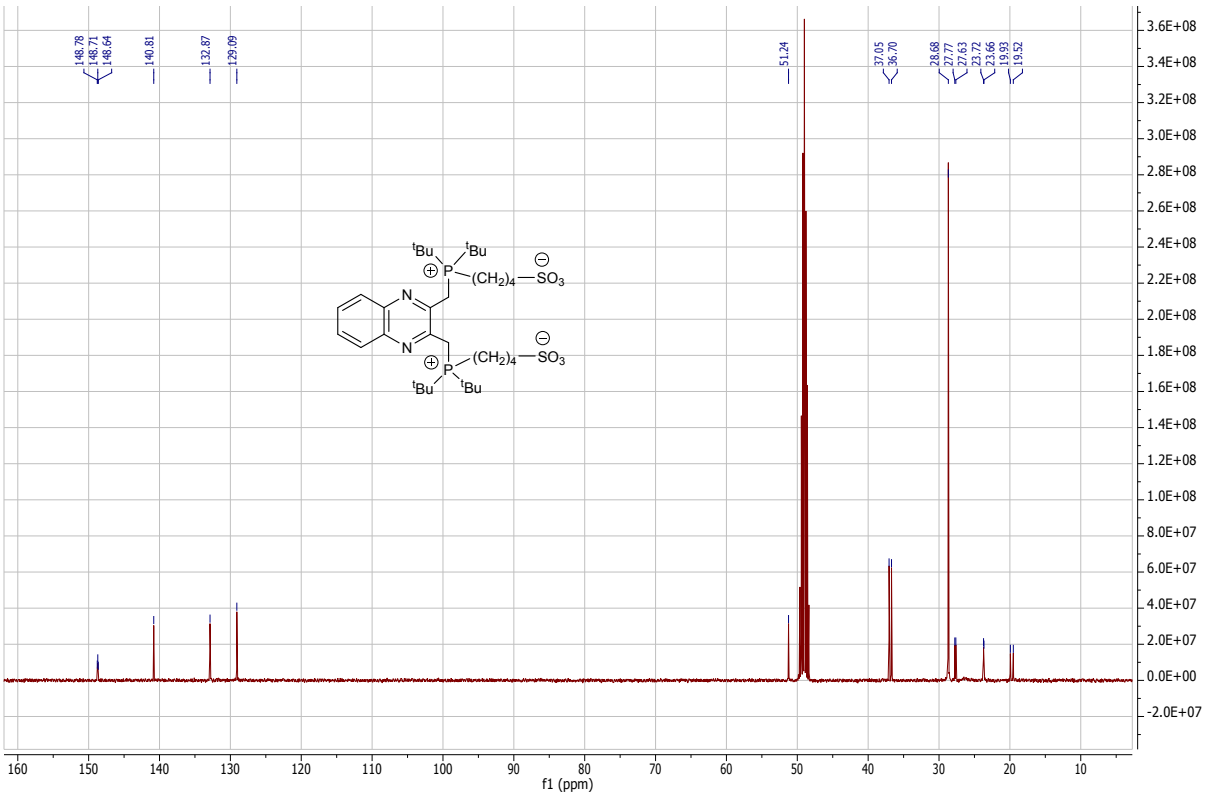
^{1}H–NMR in methanol–d_4



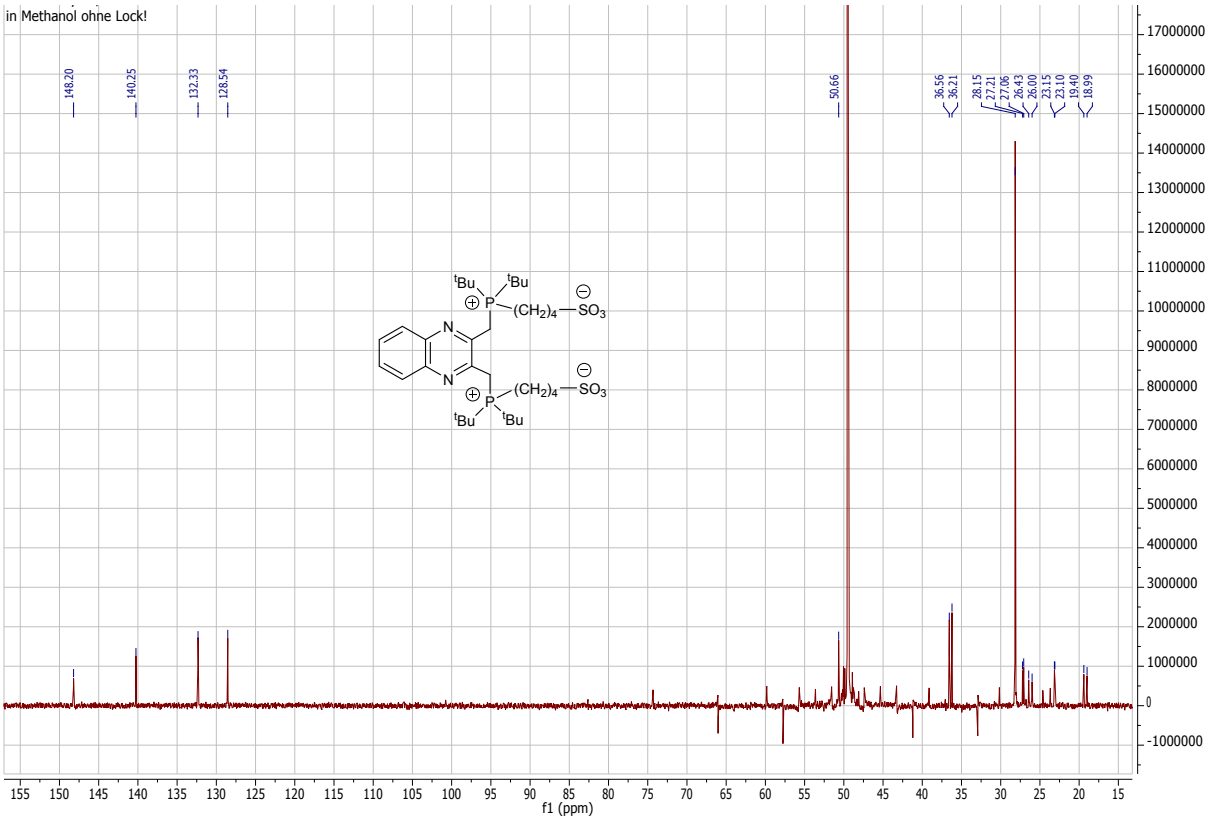
^{1}H–NMR in methanol



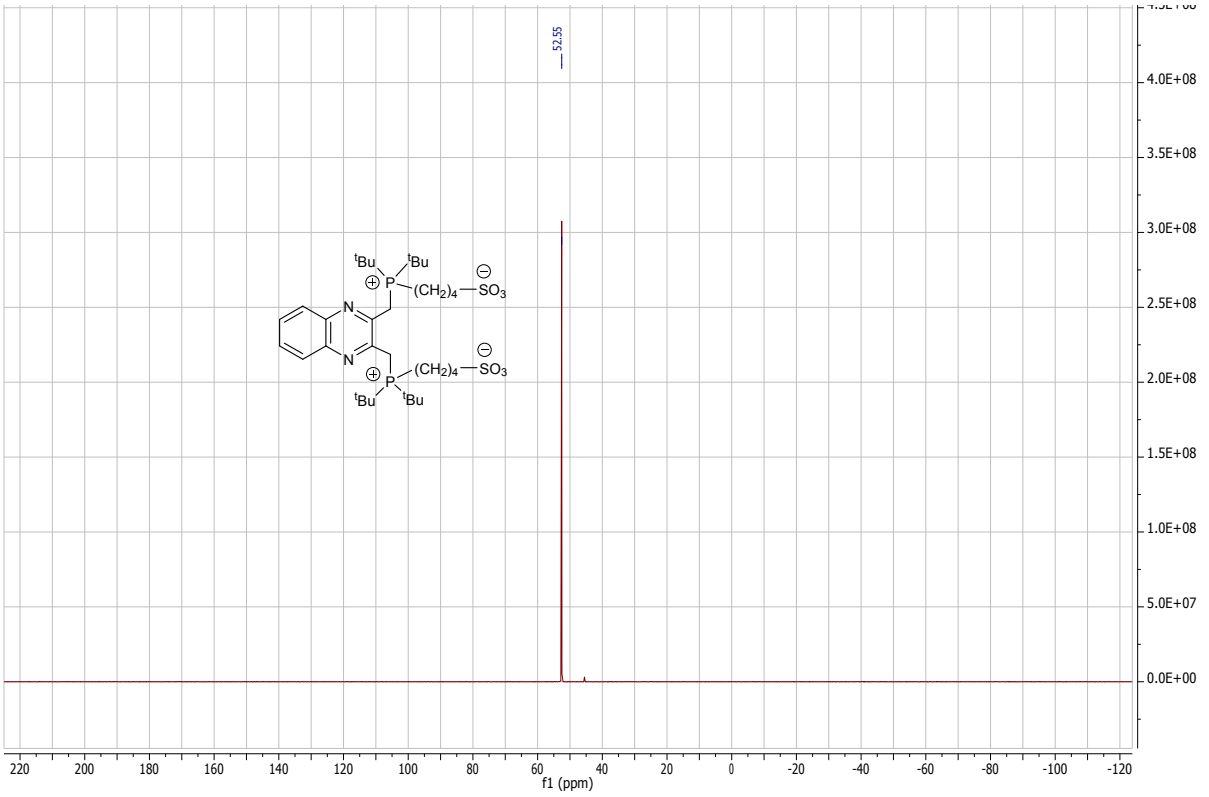
^{13}C–NMR in methanol–d_4



^{13}C–NMR in methanol

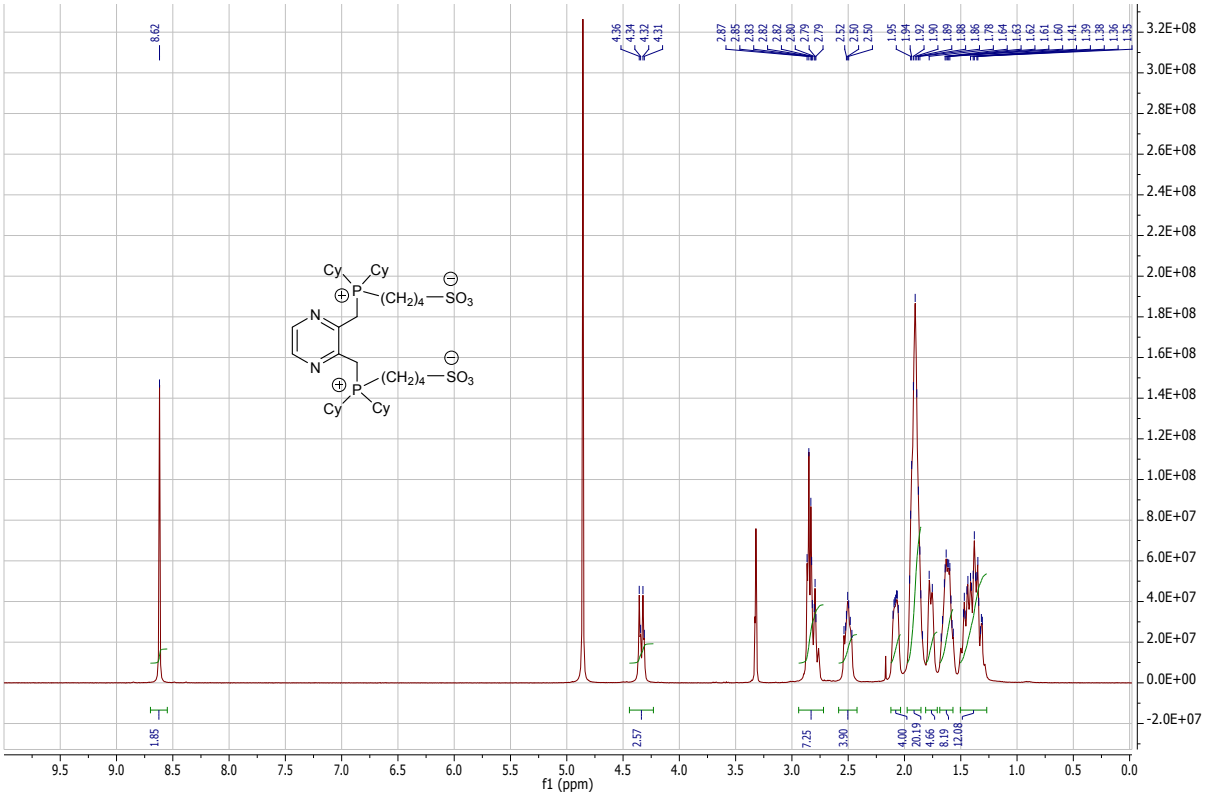


^{31}P–NMR in methanol–d_4

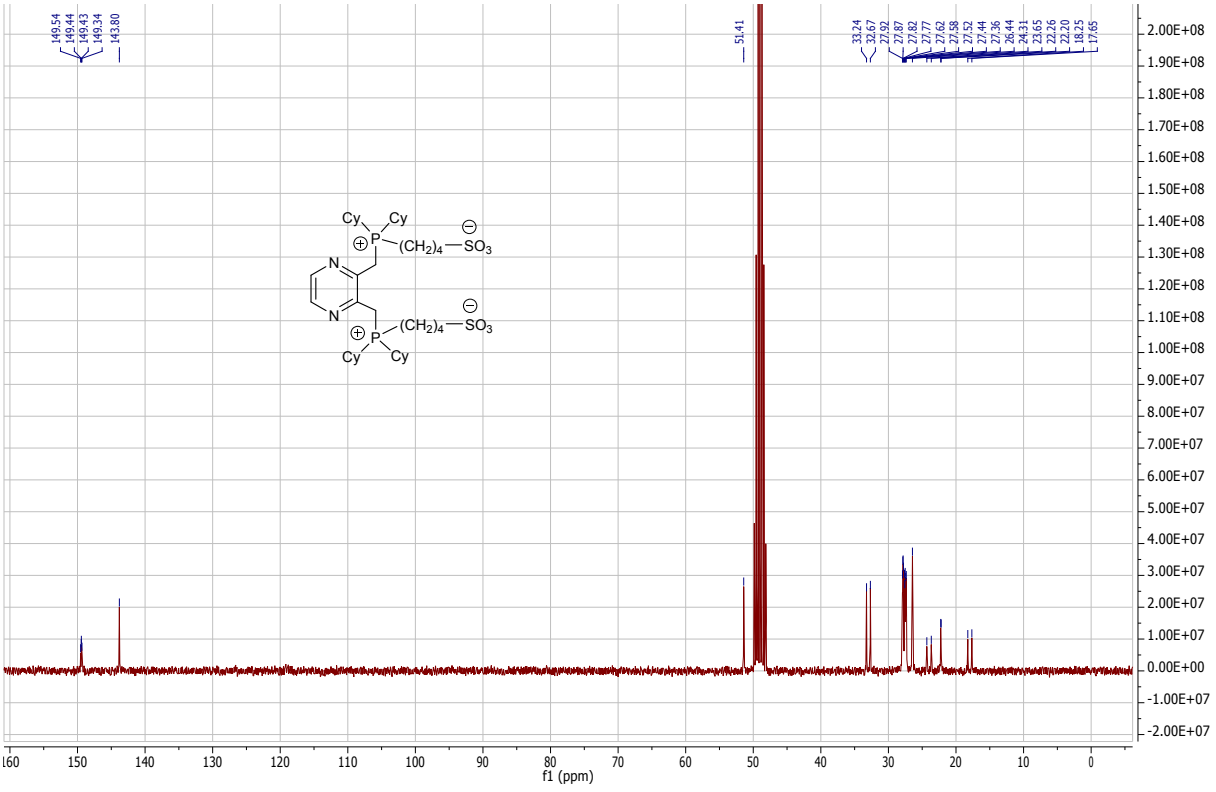


4,4'–((Pyrazine–2,3–diylbis(methylene))bis(dicyclohexylphosphoniumnediyl))bis(butane–1–sulfonate) (**L8**)

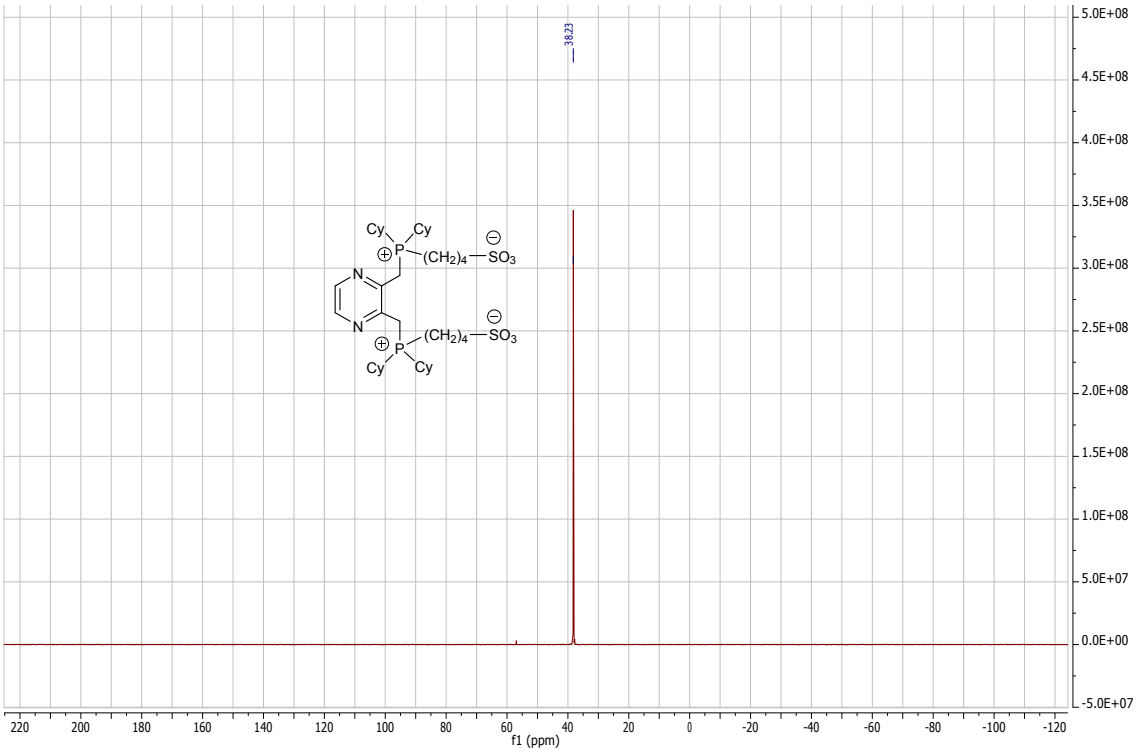
^{1}H–NMR in methanol–d_4



^{13}C–NMR in methanol–d_4

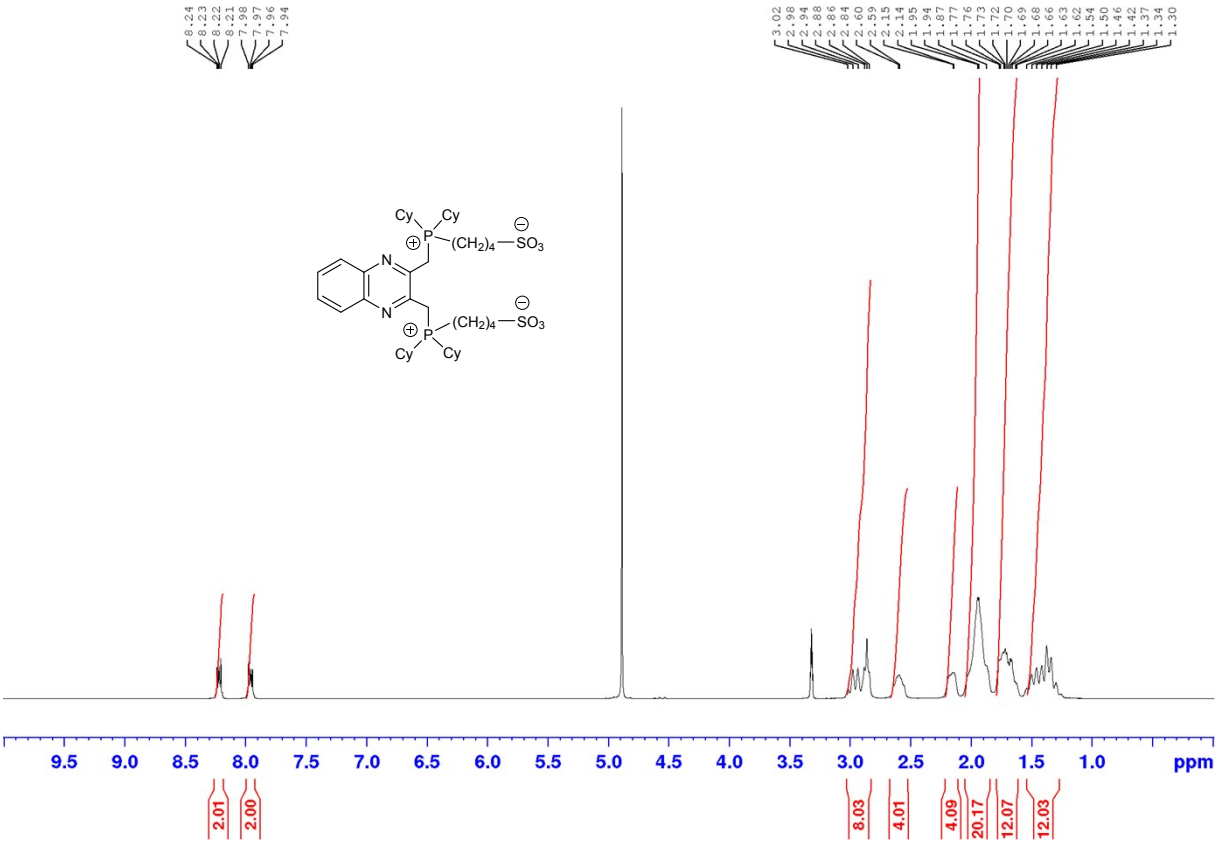


^{31}P–NMR in methanol–d_4

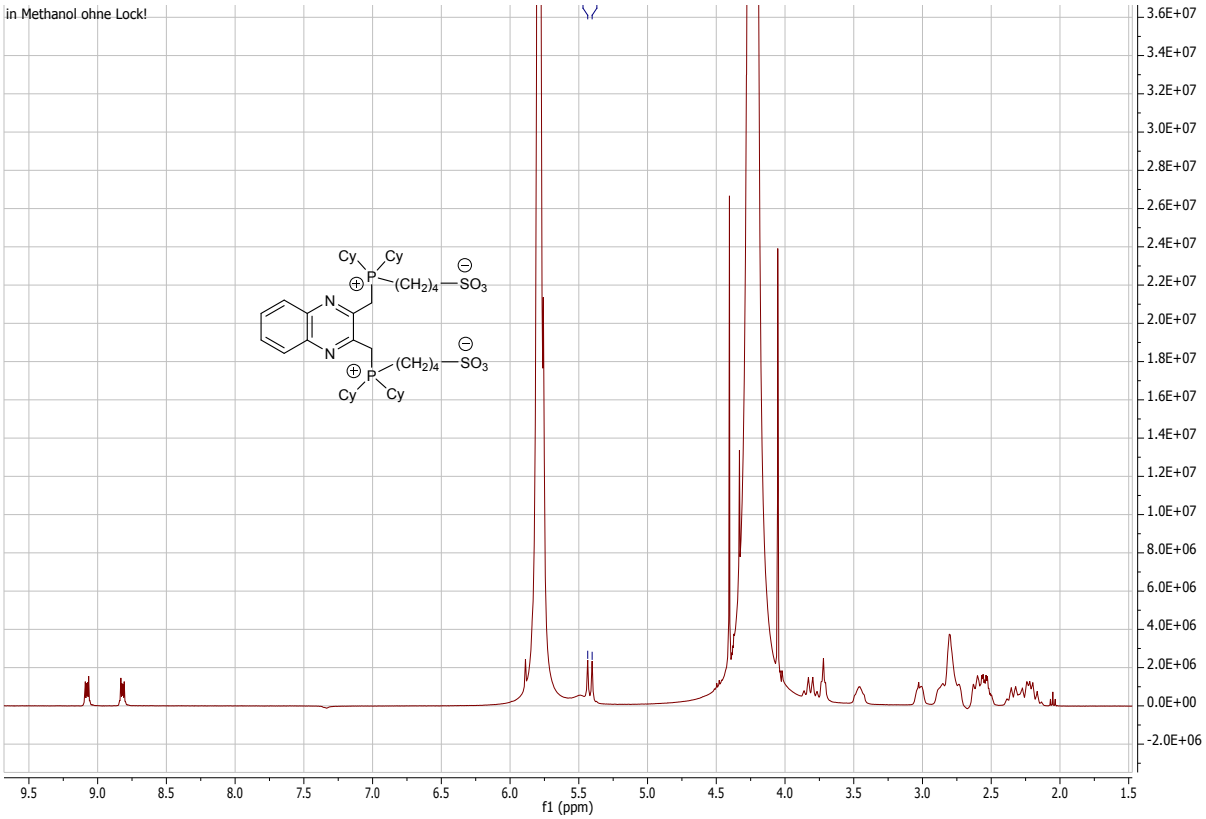


4,4'–((quinoxaline–2,3–diylbis(methylene))bis(dicyclohexylphosphoniumnediyl))bis(butane–1–sulfonate) (**L9**)

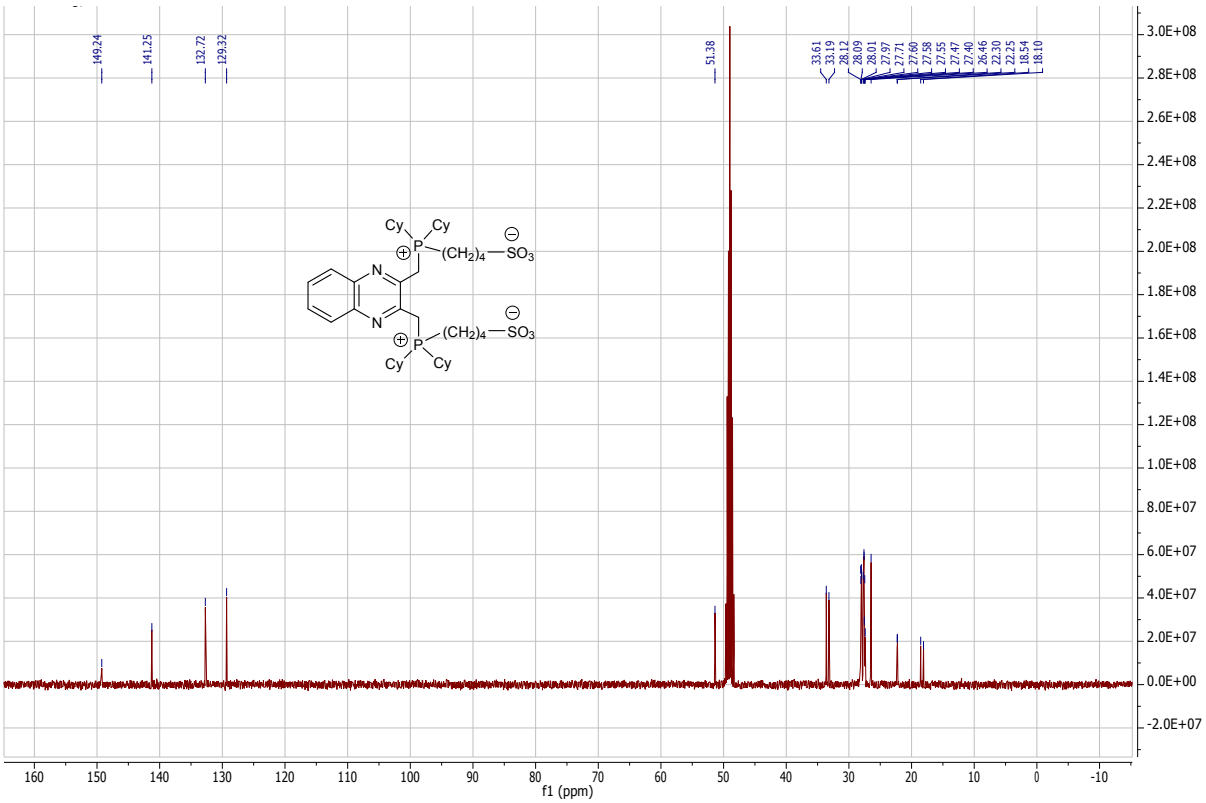
^{1}H–NMR in methanol–d_4



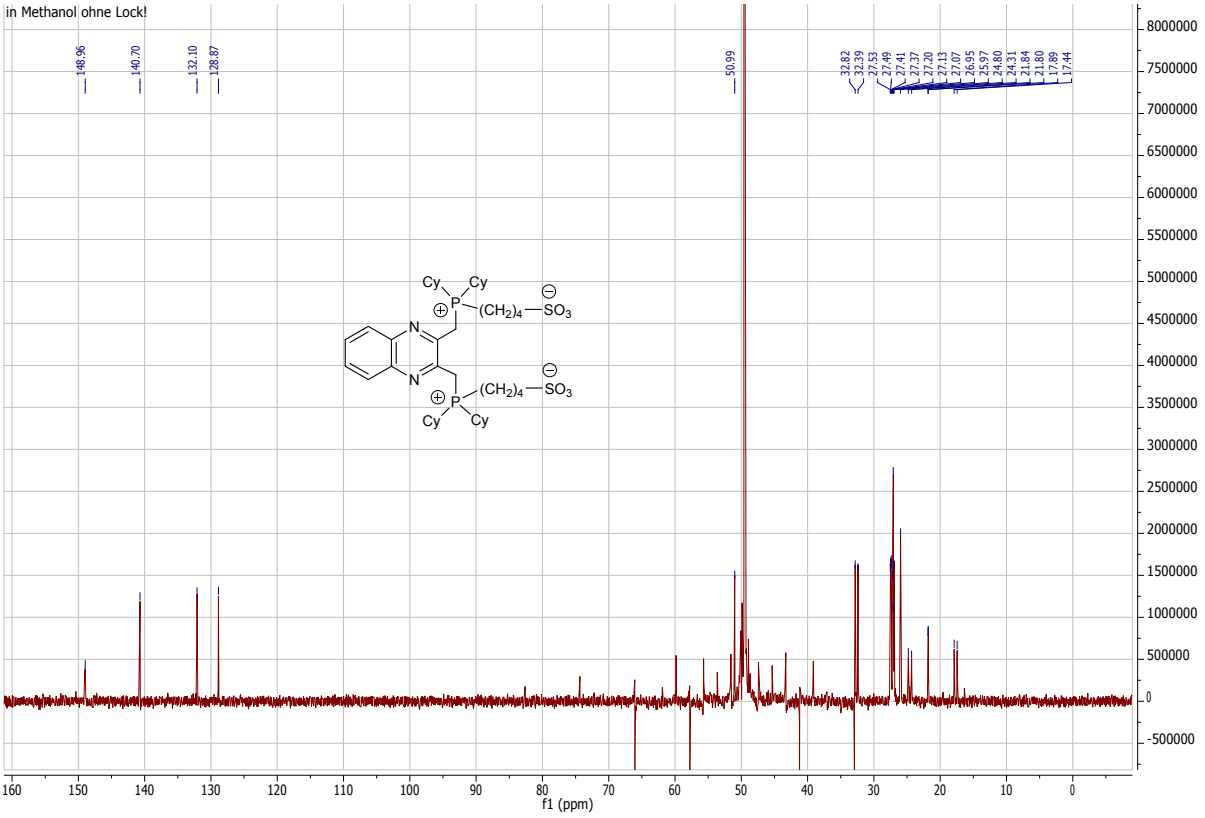
^{1}H–NMR in methanol



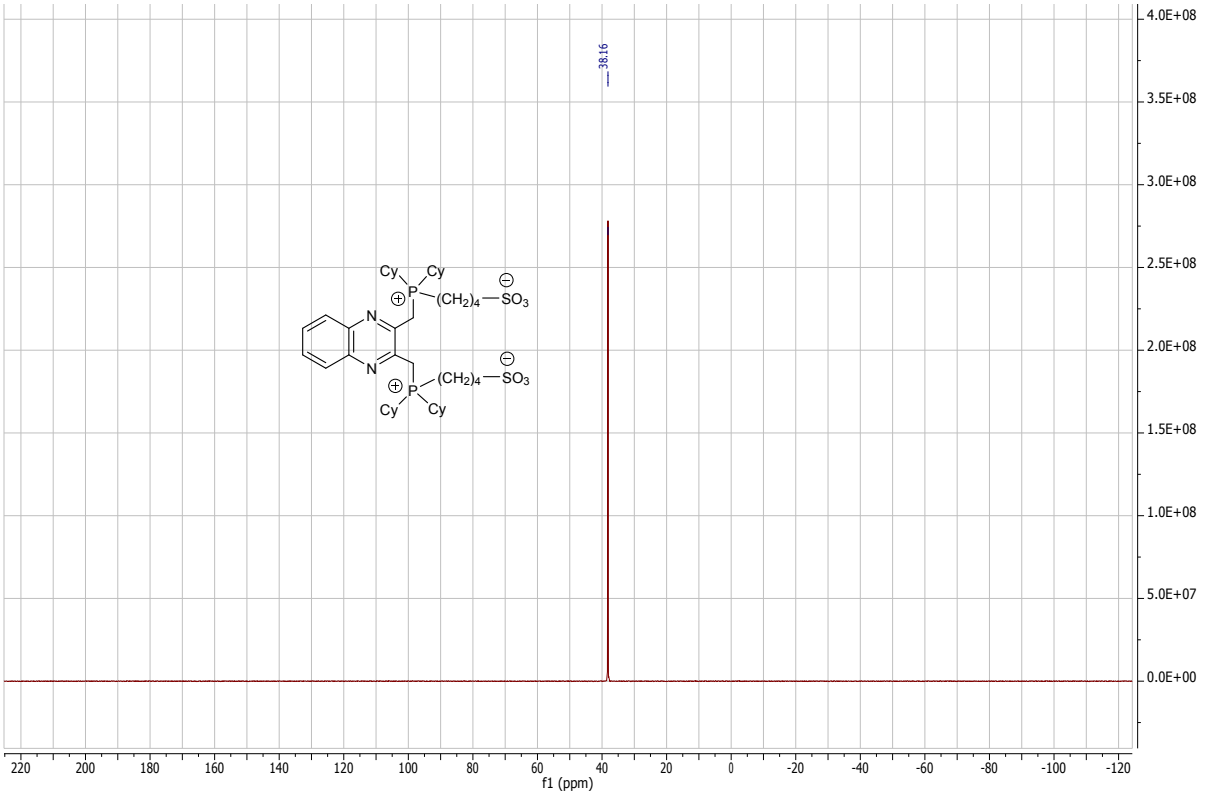
^{13}C–NMR in methanol–d_4



^{13}C–NMR in methanol

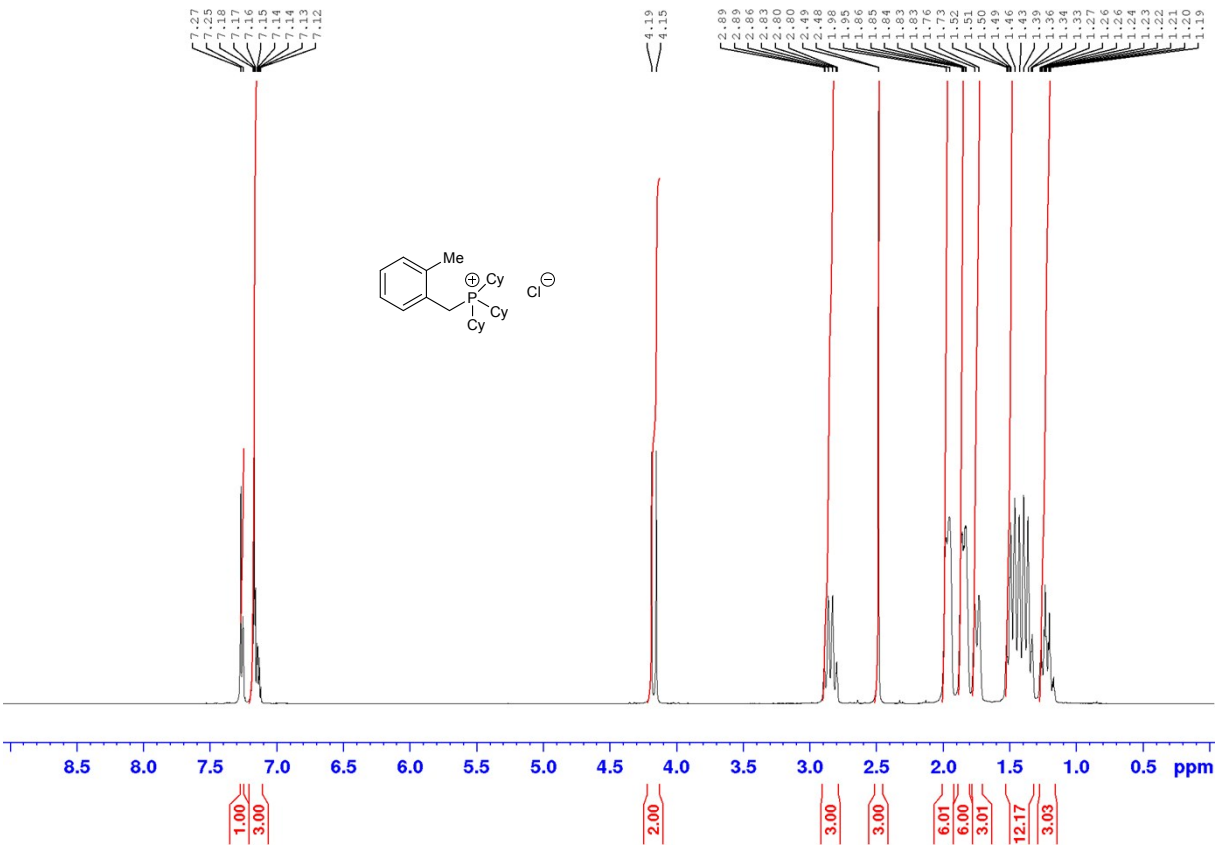


^{31}P–NMR in methanol–d_4

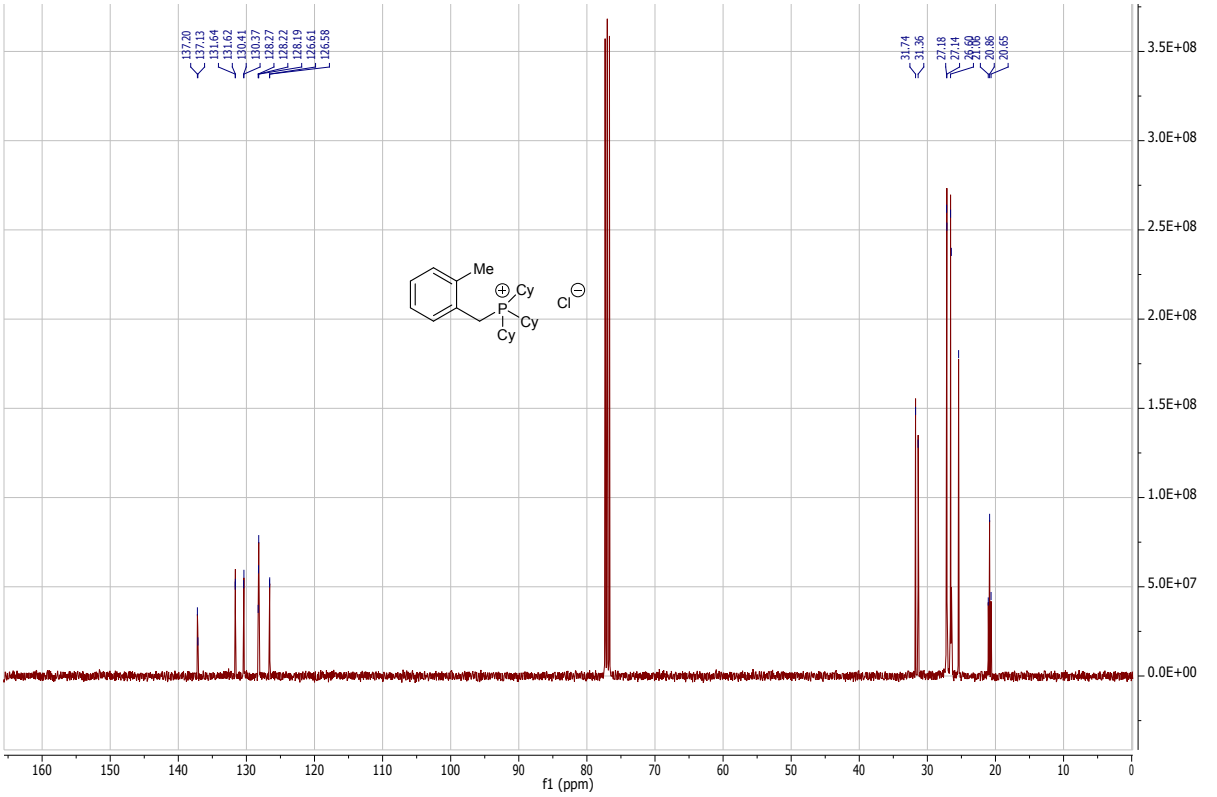


Tricyclohexyl(2–methylbenzyl)phosphonium chloride (**L10**)

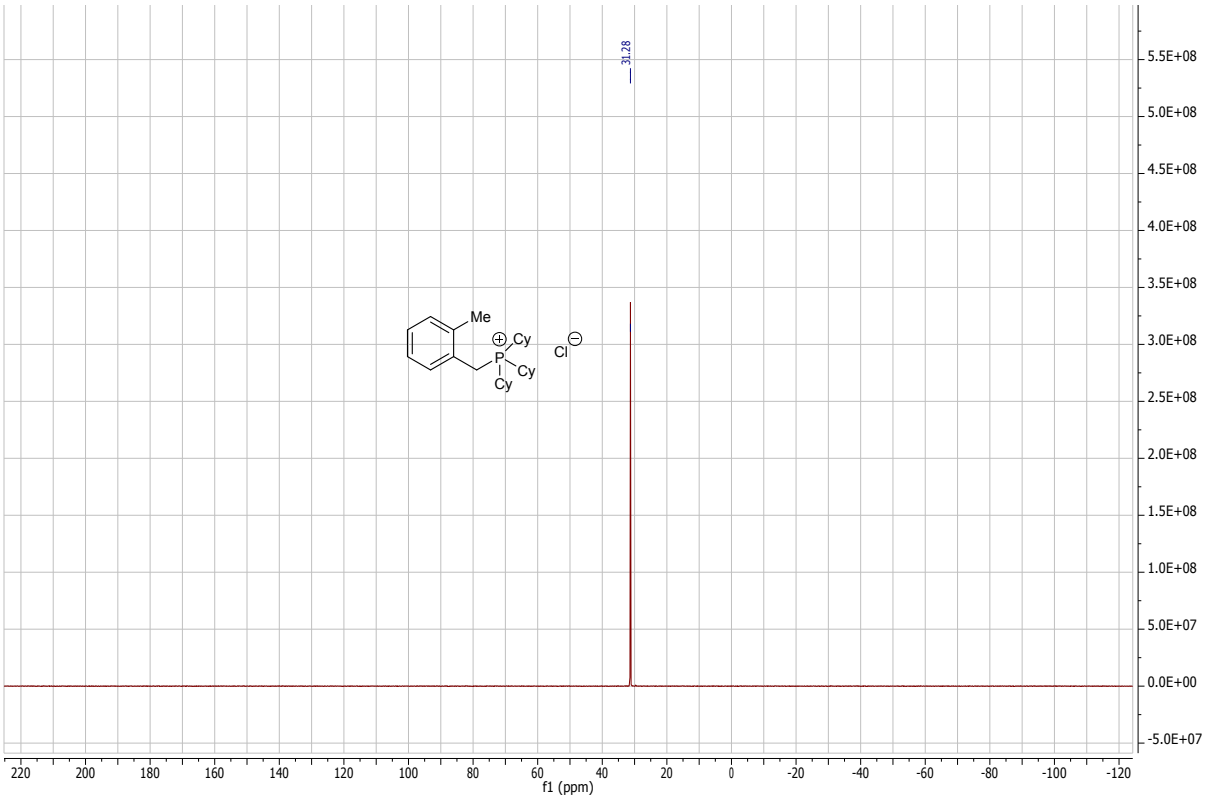
^{1}H–NMR in $CDCl_3$



^{13}C–NMR in $CDCl_3$

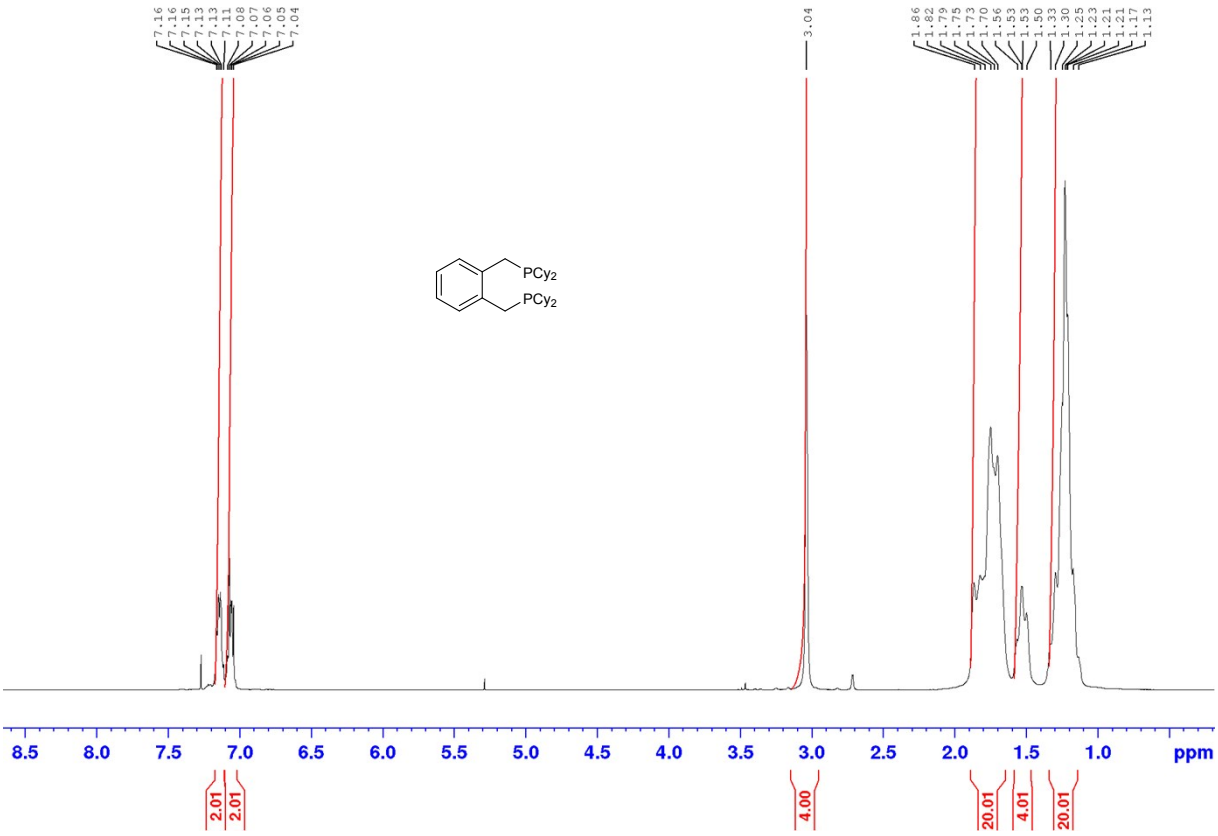


^{31}P–NMR in $CDCl_3$

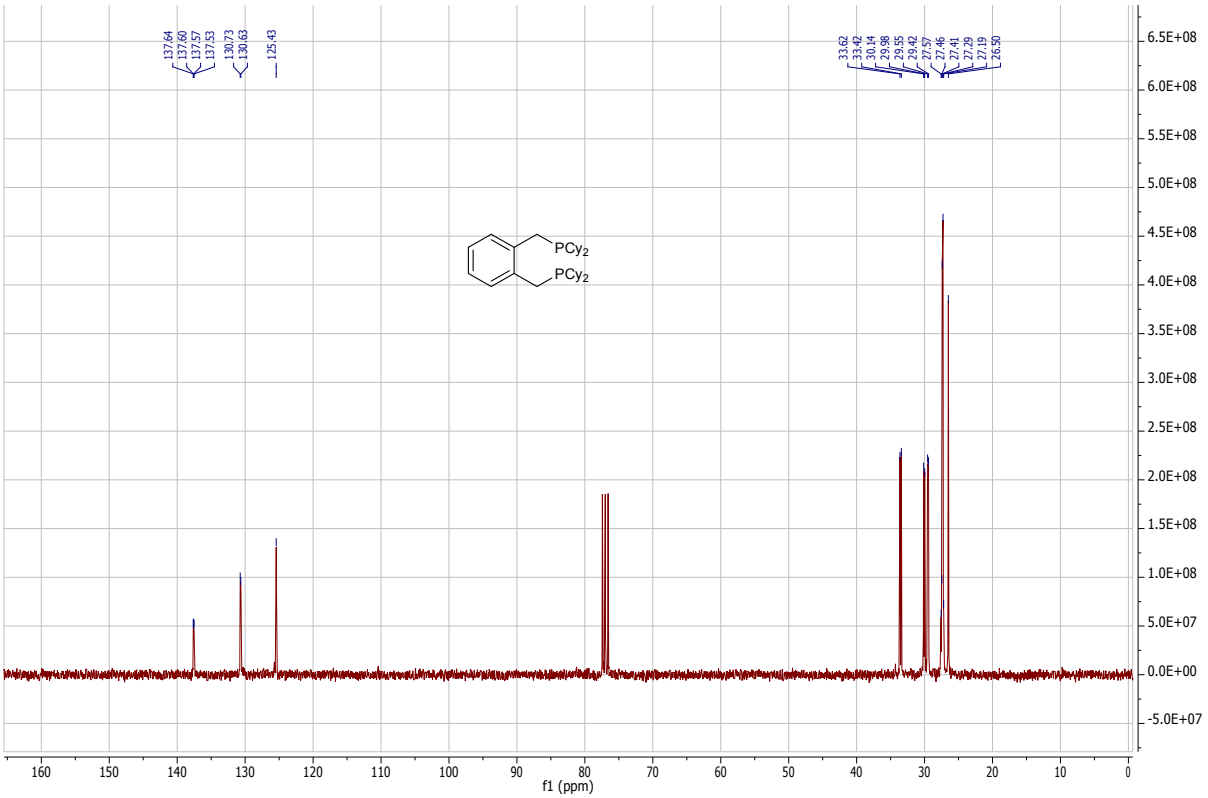


1,2–Bis((dicyclohexylphosphanyl)methyl)benzene

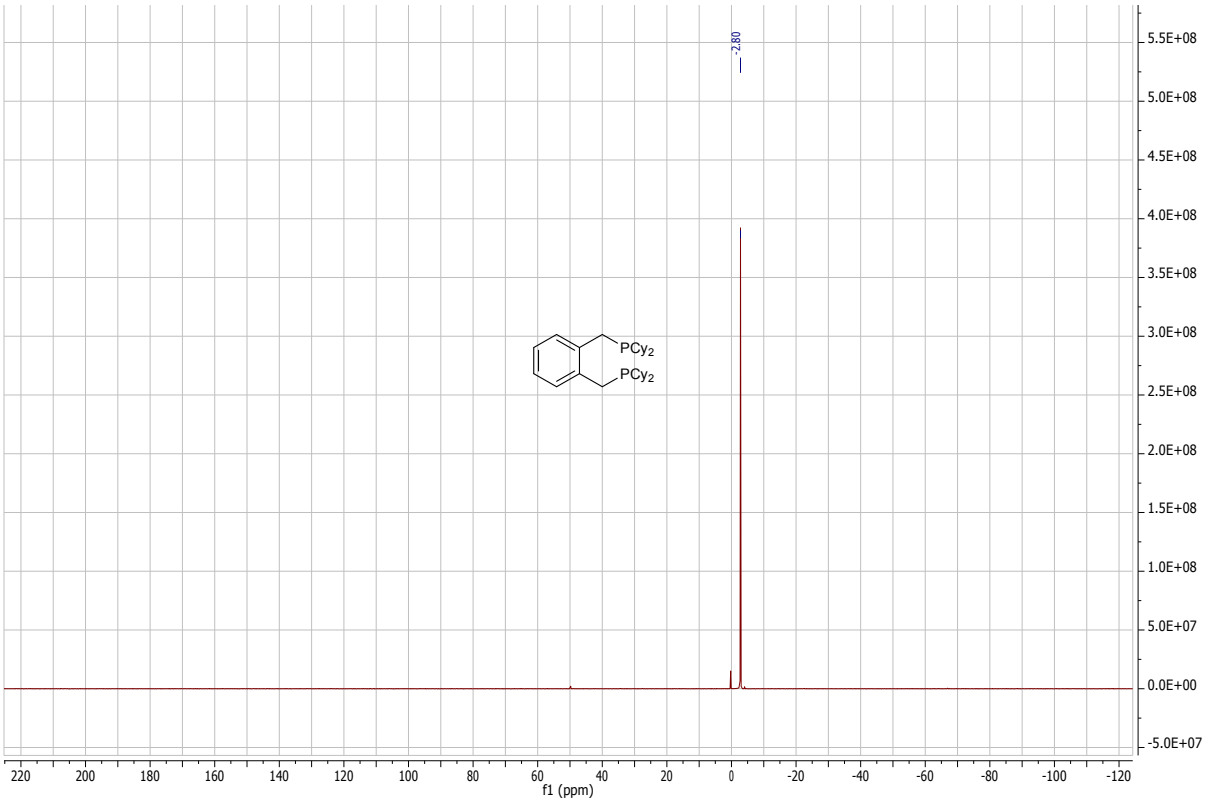
^{1}H–NMR in $CDCl_3$



^{13}C–NMR in $CDCl_3$

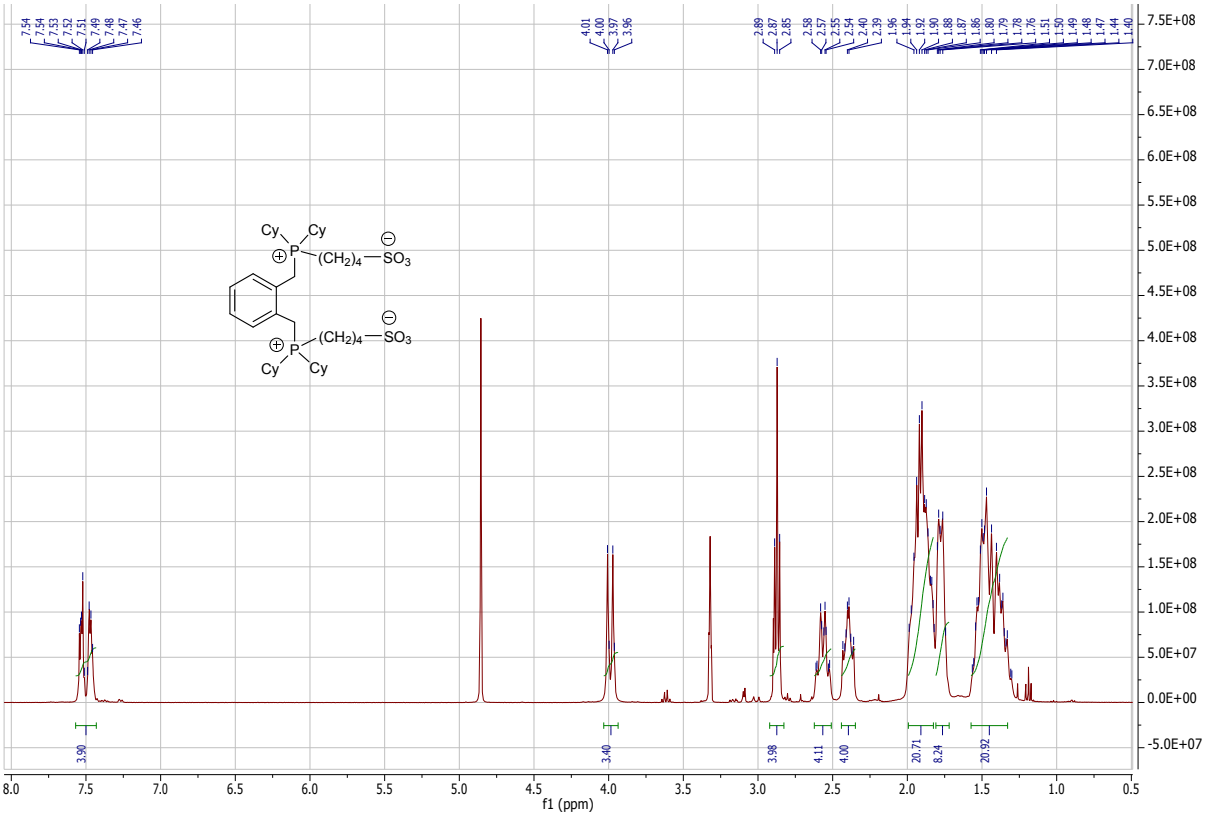


^{31}P–NMR in $CDCl_3$

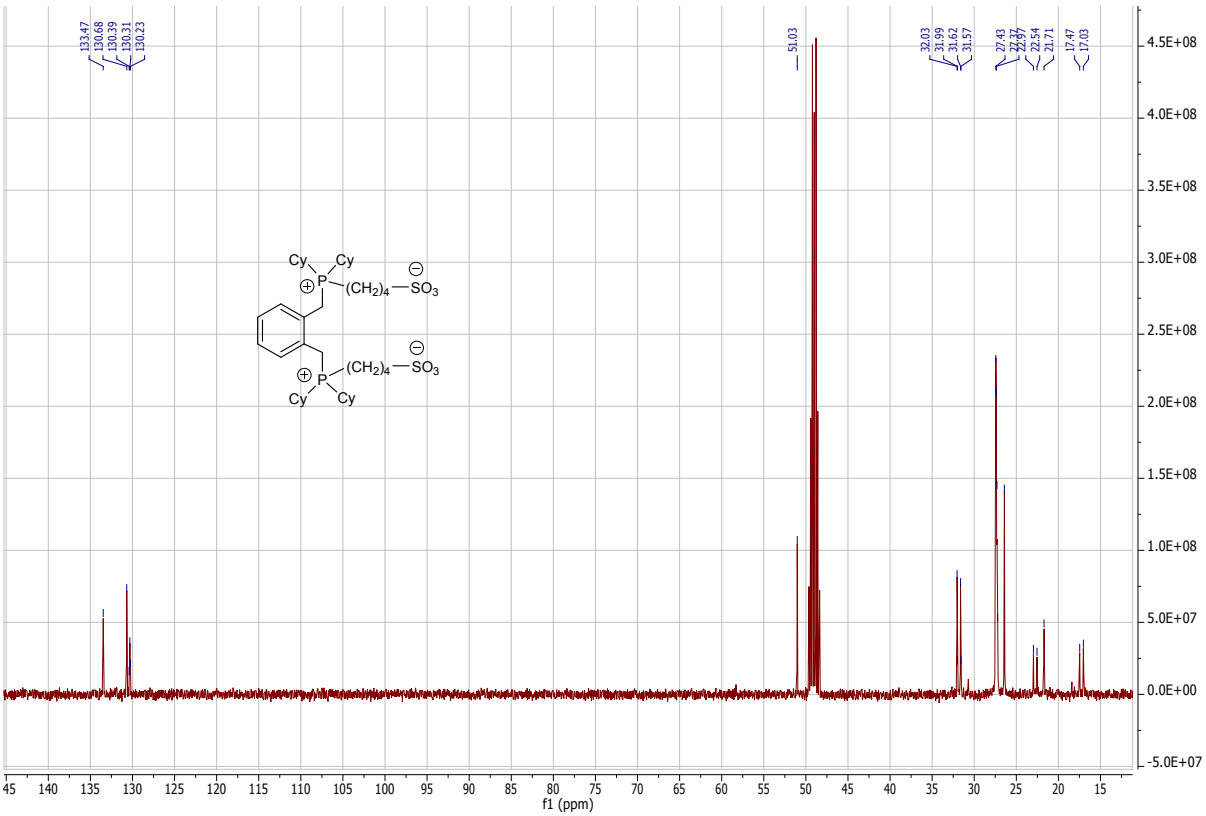


4,4'–((1,2–phenylenebis(methylene))bis(dicyclohexylphosphoniumnediyl))bis(butane–1–sulfonate) (**L11**)

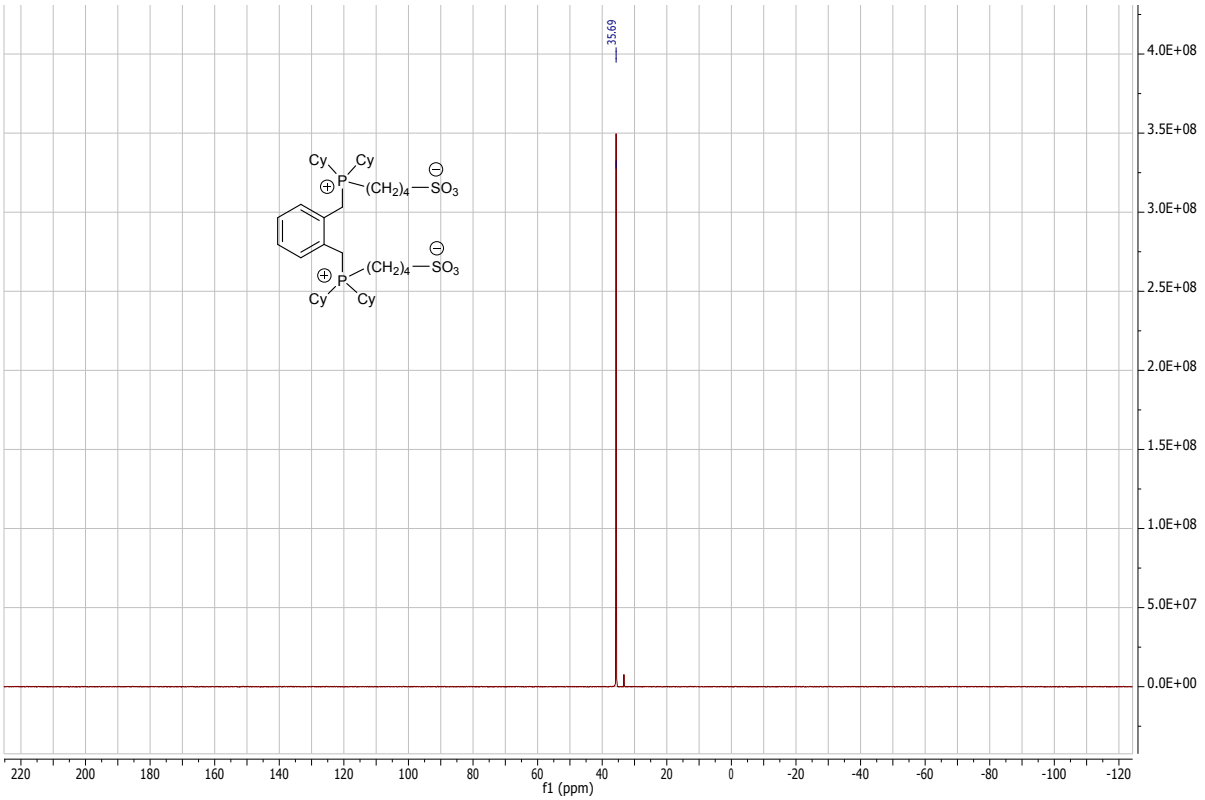
^{1}H–NMR in methanol–d_4



^{13}C–NMR in methanol–d_4



^{31}P–NMR in methanol–d_4



X–ray structures and crystallographic data

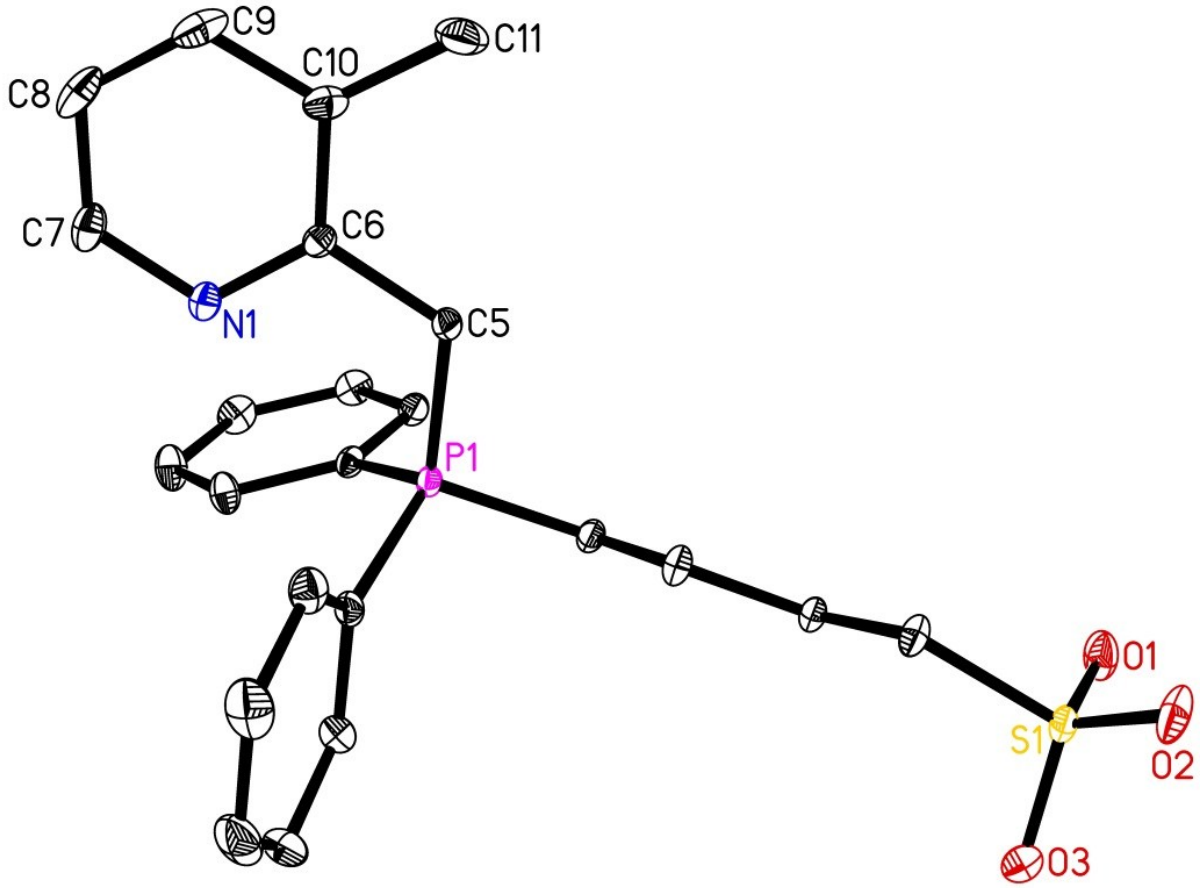
Data were collected on a Bruker Kappa APEX II Duo diffractometer. The structures were solved by direct methods (SHELXS–97: Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112.) and refined by full–matrix least–squares procedures on F^2 ((SHELXL–97: Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112. and SHELXL–2014: G. M. Sheldrick, *Acta Cryst.* **2015**, *C71*, 3., resp.). XP (Bruker AXS) was used for graphical representations.

All ligands were found to have cocrystallized with solvent molecules (water). Contributions of further water molecules were removed from the diffraction data of **L1** and **L9** with PLATON/SQUEEZE (Spek, A. L. *Acta Cryst.* **2009**, *D*65, 148). For **palladium complex of L1** contributions of solvent molecules were also removed from the diffraction data with the PLATON/SQUEEZE procedure.

CCDC 1455278–1455282 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

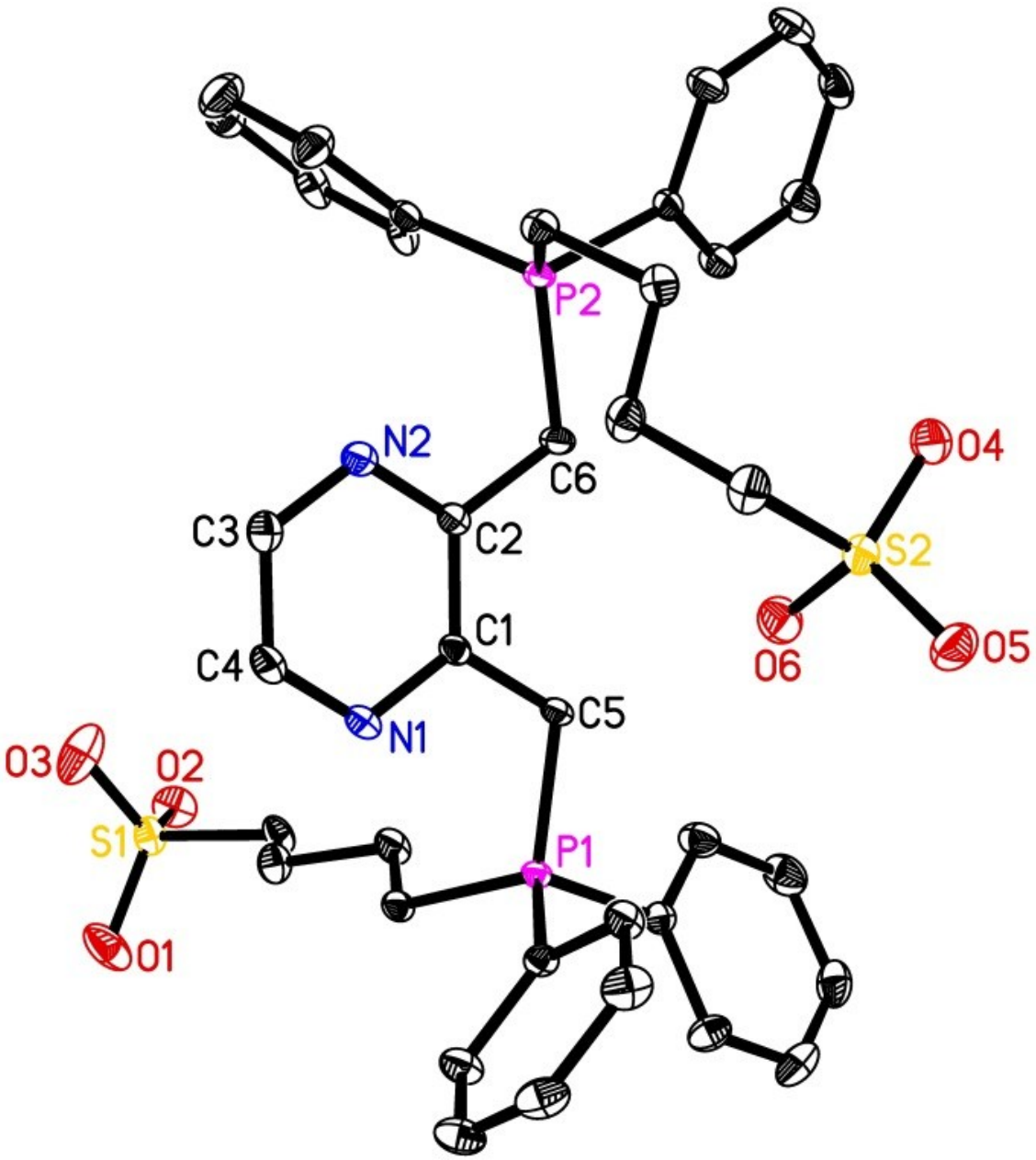
Crystallographic data of L1

Crystal data for **L1**: $C_{23}H_{35}NO_{7.5}PS$, M = 508.55, triclinic, space group $P\bar{1}$, a = 8.2742(4), b = 10.4756(5), c = 15.3061(7) Å, α = 85.733(1), β = 80.041(1), γ = 85.762(1)°, V = 1300.56(11) Å^3, T = 150(2) K, Z = 2, 23040 reflections measured, 6272 independent reflections (R_{int} = 0.0313), final R values ($I > 2\sigma(I)$): R_1 = 0.0382, wR_2 = 0.0974, final R values (all data): R_1 = 0.0529, wR_2 = 0.1073, GOF on F^2: 1.018, 326 parameters, CCDC 1455279.



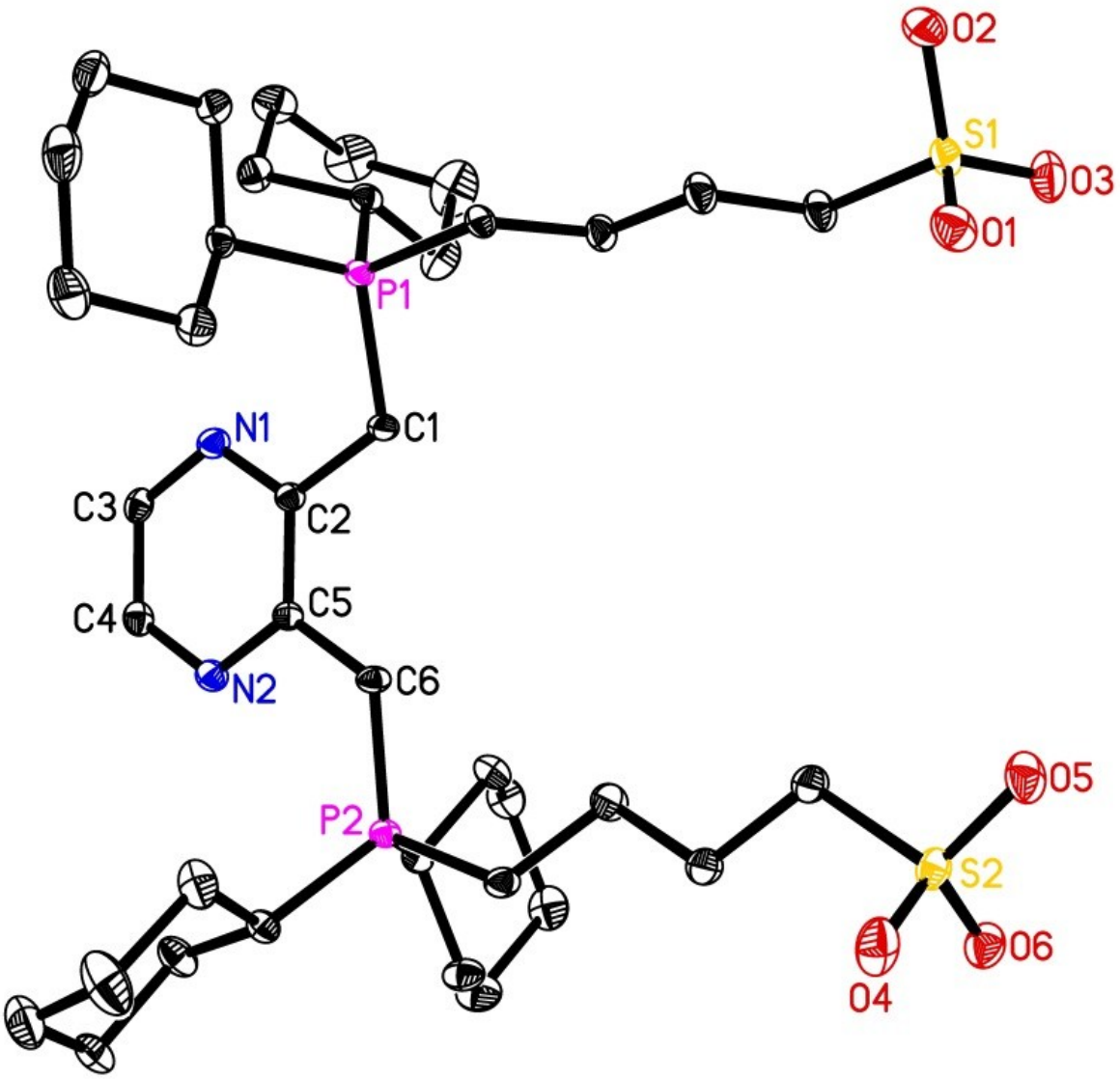
Crystallographic data of L3

Crystal data for **L3**: $C_{38}H_{48}N_2O_9P_2S_2$, M = 802.84, monoclinic, space group $P2_1/n$, a = 12.1680(7), b = 16.4620(9), c = 20.5828(12) Å, β = 106.522(1)°, V = 3952.7(4) Å^3, T = 150(2) K, Z = 4, 17159 reflections measured, 7729 independent reflections (R_{int} = 0.0166), final R values ($I > 2\sigma(I)$): R_1 = 0.0421, wR_2 = 0.1078, final R values (all data): R_1 = 0.0518, wR_2 = 0.1175, GOF on F^2: 1.022, 496 parameters, CCDC 1455278.



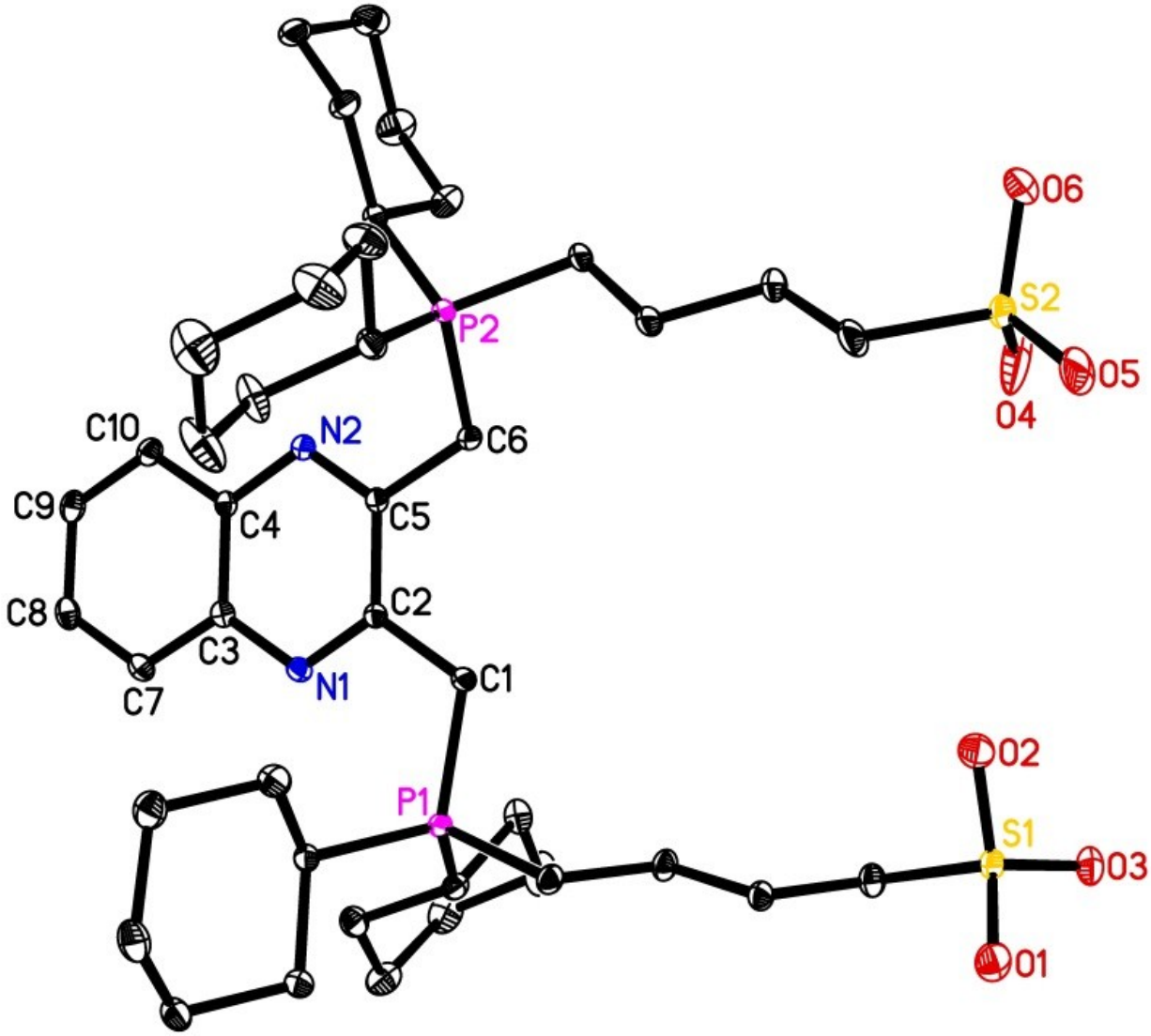
Crystallographic data of L8

Crystal data for **L8**: $C_{38}H_{96}N_2O_{21}P_2S_2$, M = 1043.22, triclinic, space group $P\bar{1}$, a = 13.1432(6), b = 14.2603(6), c = 16.3102(7) Å, α = 99.7610(15), β = 104.0954(15), γ = 96.6406(16)°, V = 2882.3(2) Å^3, T = 220(2) K, Z = 2, 119639 reflections measured, 13880 independent reflections (R_{int} = 0.0371), final R values ($I > 2\sigma(I)$): R_1 = 0.0584, wR_2 = 0.1650, final R values (all data): R_1 = 0.0701, wR_2 = 0.1708, GOF on F^2: 1.087, 652 parameters, CCDC 1455280.



Crystallographic data of L9

Crystal data for **L9**: $C_{42}H_{84}N_2O_{14}P_2S_2$, M = 967.17, triclinic, space group $P\bar{1}$, a = 11.5658(3), b = 15.1397(4), c = 17.4884(5) Å, α = 104.2545(8), β = 97.3596(8), γ = 110.6962(8)°, V = 2697.17(13) Å^3, T = 150(2) K, Z = 2, 96936 reflections measured, 13001 independent reflections (R_{int} = 0.0363), final R values ($I > 2\sigma(I)$): R_1 = 0.0475, wR_2 = 0.1290, final R values (all data): R_1 = 0.0586, wR_2 = 0.1360, GOF on F^2: 1.087, 583 parameters, CCDC 1455281.



Crystallographic data of palladium complex of L1

Crystal data for **palladium complex with L1**: $C_{46}H_{52}Cl_2N_2O_6P_2PdS_2$, M = 1032.25, orthorhombic, space group *Ccca*, a = 24.1441(7), b = 29.7358(9), c = 16.0452(5) Å, V = 11519.6(6) Å^3, T = 150(2) K, Z = 8, 118459 reflections measured, 6959 independent reflections (R_{int} = 0.0319), final R values ($I > 2\sigma(I)$): R_1 = 0.0346, wR_2 = 0.0920, final R values (all data): R_1 = 0.0401, wR_2 = 0.0953, GOF on F^2: 1.073, 278 parameters, CCDC 1455282.