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Supplementary material

Experimental Section

General: All reactions were carried out in the absence of air using standard Schlenk techniques and vacuum-line manipulations. All solvents were dried before use. ^{1}H, ^{13}C, ^{31}P NMR spectra were recorded with Bruker AC 200, AC 250, DPX 300 or AMX 400 spectrometers. References for NMR chemical shifts are $SiMe_4$ for ^{1}H and ^{13}C NMR, 85% H_3PO_4 for ^{31}P NMR. The numbering used for NMR assignments is depicted in a Figure. The ^{31}P NMR spectra of dendrimers G_1, G_2, G_3, G_4 and G_4 one-pot are given, as well as the expanded formula of G_4.

Synthesis of compound 1:

A solution of 4-diphenylphosphino phenol sodium salt freshly prepared from 2.02 g (7.24 mmol) of 4-diphenylphosphino phenol[i] and 0.17 g (7.25 mmol) of sodium hydride in THF (50 mL) was added dropwise to $SPCl_3$ (0.37 mL, 3.62 mmol) in THF (50 mL) at –95°C. The reaction mixture was then allowed to warm to room temperature and stirred overnight. The solvent was partially removed under reduced pressure and the crude oil was poured in chloroform (50 mL). Methylhydrazine (385 µL, 7.24 mmol) in chloroform (20 mL) was then added dropwise to the previous mixture at –60°C under argon and then warmed to room temperature and stirred overnight. The mixture was filtered over Celite and the volatiles removed under reduced pressure. Compound **1** was isolated as a white powder in 92% (2.25 g) yield.

$^{31}P\{^{1}H\}$ NMR (81.015 MHz): δ -6.4 (s, $P'Ph_2$), 67.0 (s, P); ^{1}H NMR (250.133 MHz): δ 3.18 (d, $^{3}J_{PH}$ = 10.7 Hz, 3 H, CH_3), 3.70 (br s, 2 H, NH_2), 7.34 (m, 28 H, H_{Ar}); $^{13}C\{^{1}H\}$ NMR (62.896 MHz): δ 41.0 (d, $^{2}J_{CP}$ = 13.4 Hz, CH_3), 121.1 (dd, $^{3}J_{CP}$ = 7.4 Hz, $^{3}J_{CP}$ = 5.1 Hz, C^{2}), 128.6 (d, $^{3}J_{CP}$ = 6.9 Hz, C^{m}), 128.9 (s, C^{p}), 133.7 (d, $^{2}J_{CP}$ = 19.6 Hz, C^{o}), 135.2 (d, $^{2}J_{CP}$ = 20.6

Hz, C^3), 137.0 (d, $^1J_{CP} = {}^1J_{CP} = 10.8$ Hz, C^i and C^4), 151.5 (d, $^2J_{CP} = 8.0$ Hz, C^1). Anal Calcd for $C_{37}H_{33}N_2O_2P_3S$ (662.66): C, 67.06; H, 5.01; N, 4.22. Found: C, 66.59; H, 4.93, N, 4.13.

Syntheses of dendrimers:

Synthesis of odd generations:

To a solution of $\mathbf{G_n}$ (**n** = 0, 0.100 g, 0.23 mmol; **n** = 2, 0.100 g, 0.10 mmol) in 20 mL of freshly degassed THF was added **1** (**n** = 0, 0.467 g, 0.70 mmol; **n** = 2, 0.200 g, 0.30 mmol). The mixture was then heated to 60°C for 12 h. The solvent was eliminated under reduced pressure and the product was washed twice with 10 mL of degassed diethylether.

Synthesis of even generations:

To a solution of $\mathbf{G_n}$ (**n** = 1, 0.130 g, 0.056 mmol; **n** = 3, 0.200 g, 0.047 mmol) in degassed THF (25 mL) was added a solution of azide **2** (**n** = 0, 0.122 g, 0.35 mmol; **n** =1, 0.420 g, 1.21 mmol). After 5h at 25°C, the solvent was removed under reduced pressure, and the resulting dendrimer was washed twice with 10 mL of diethylether in order to remove the excess of azide.

$\mathbf{G_1}$: $^{31}P\{^1H\}$ NMR (81.015 MHz): δ -6.4 (s, P'_1), 52.4 (s, P_0), 61.6 (s, P_1); ^1H NMR (200.132 MHz): δ 3.36 (d, $^3J_{HP} = 12.0$ Hz, 9H, Me_0), 7.15-7.30 (m, 90H, H_{Ar}), 7.60 (d, $^4J_{HP} = 2.5$ Hz, 3H, CH=N), 7.68 (d, $^3J_{HH} = 8.6$ Hz, 6H, HC_0^3); $^{13}C\{^1H\}$ NMR (62.896 MHz): δ 33.0 (d, $^2J_{CP} = 13.4$ Hz, Me_0), 121.3-121.5 (m, C_0^2, C_1^2), 128.5 (d, $^3J_{CP} = 7.5$ Hz, C_1^m), 128.8 (s, C_1^p and C_0^3), 132.6 (s, C_0^4), 133.7 (d, $^2J_{CP} = 18.5$ Hz, C_1^o), 134.1 (d, $^1J_{CP} = 11.3$ Hz, C_1^4), 135.0 (d, $^2J_{CP} = 20.2$ Hz, C_1^3), 136.9 (d, $^1J_{CP} = 10.7$ Hz, C_1^i), 138.4 (d, $^3J_{CP} = 14.0$ Hz, CH=N), 151.2 (d,

$^2J_{CP}$ = 6.5 Hz, C_0^1, C_1^1). Anal. Calcd for $C_{132}H_{108}N_6O_9P_{10}S_4$ (2232.1): C, 71.03; H, 4.87; N, 3.76. Found: C, 70.85; H, 4.77; N, 3.69.

G_2: $^{31}P\{^1H\}$ NMR (81.015 MHz): δ 14.3 (d, $^2J_{P'1P2}$ = 30.4 Hz, P'_1), 50.2 (d, $^2J_{P2P'1}$ = 30.4 Hz, P_2), 52.5 (s, P_0), 60.8 (s, P_1); ^1H NMR (200.132 MHz): δ 3.36 (d, $^3J_{HP}$ = 10.9 Hz, 9H, Me_0), 7.20-7.70 (m, 123H, H_{Ar} and CH=N), 7.74 (d, $^3J_{HH}$ = 8.2 Hz, 24H, HC_2^3), 9.86 (s, 12H, CHO); $^{13}C\{^1H\}$ NMR (62.896 MHz): δ 33.0 (d, $^2J_{CP}$ = 12.3 Hz, Me_0), 121.6 (d, $^3J_{CP}$ = 5.6 Hz, C_1^2), 121.8 (d, $^3J_{CP}$ = 5.1 Hz, C_0^2), 122.0 (d, $^3J_{CP}$ = 5.6 Hz, C_2^2), 127.8 (dd, $^1J_{CP}$ = 98.4 Hz, $^3J_{CP}$ = 3.2 Hz, C_1^4, C_1^i), 128.8 (s, C_0^3), 128.9 (d, $^3J_{CP}$ = 12.7 Hz, C_1^m), 131.2 (s, C_2^3), 132.6 (d, $^2J_{CP}$ = 10.6 Hz, C_1^o), 132.7 (s, C_0^4, C_2^4), 133.0 (s, C_1^p), 134.7 (d, $^2J_{CP}$ = 12.0 Hz, C_1^3), 139.7 (d, $^1J_{CP}$ = 11.6 Hz, CH=N), 151.4 (d, $^2J_{CP}$ = 7.6 Hz, C_0^1), 153.9 (d, $^2J_{CP}$ = 7.0 Hz, C_1^1), 156.8 (d, $^2J_{CP}$ = 9.2 Hz, C_2^1), 191.05 (s, CHO). IR (KBr): 1700 cm^{-1} ($\nu_{C=O}$). Anal. Calcd for $C_{216}H_{168}N_{12}O_{33}P_{16}S_{10}$ (4276.0): C, 60.67; H, 3.96; N, 3.93. Found: C, 60.51; H, 3.84; N, 3.85.

G_3: $^{31}P\{^1H\}$ NMR (81.015 MHz): δ -6.4 (s, P'_3), 13.2 (d, $^2J_{P'1P2}$ = 29.7 Hz, P'_1), 51.5 (d, $^2J_{P2P'1}$ = 29.7 Hz, P_2), 52.5 (s, P_0), 61.0 (s, P_1), 61.9 (s, P_3); ^1H NMR (200.132 MHz): δ 3.29 (d, $^3J_{PH}$ = 10.9 Hz, 45H, Me_0, Me_2), 7.10-7.70 (m, 495H, H_{Ar}, CH=N); $^{13}C\{^1H\}$ NMR (50.323 MHz): δ 33.0 (d, $^2J_{CP}$ = 13.3 Hz, Me_0, Me_2), 121.3-122.0 (m, C_0^2, C_1^2, C_2^2, C_3^2), 127.8 (dd, $^1J_{CP}$ = 98.4 Hz, $^3J_{CP}$ = 3.2 Hz, C_1^4, C_1^i), 128.5 (d, $^3J_{CP}$ = 7.1 Hz, C_1^m, C_3^m), 128.8 (s, C_0^3, C_2^3, C_3^p), 132.6 (d, $^2J_{CP}$ = 10.5 Hz, C_1^o), 132.7 (s, C_0^4, C_2^4), 133.6 (d, $^2J_{CP}$ = 19.3 Hz, C_3^o), 133.8 (s, C_1^p), 134.7 (d, $^2J_{CP}$ = 12.0 Hz, C_1^3, C_3^4), 135.0 (d, $^2J_{CP}$ = 20.4 Hz, C_3^3), 136.8 (d, $^1J_{CP}$ = 10.8 Hz, C_3^i), 139.4 (d, $^1J_{CP}$ = 14.1 Hz, CH=N), 151.1 (d, $^2J_{CP}$ = 7.3 Hz, C_3^1), 153.0 (br d, $^2J_{CP}$ = 7.0 Hz, C_0^1, C_1^1, C_2^1). Anal. Calcd for $C_{660}H_{540}N_{36}O_{45}P_{52}S_{22}$ (12012): C, 65.99; H, 4.52; N, 4.19. Found: C, 65.75; H, 4.39; N, 4.08.

G_4: $^{31}P\{^1H\}$ NMR (81.015 MHz): δ 13.5 (d, $^2J_{P'1P2}$ = 29.2 Hz, P'_1), 14.3 (d, $^2J_{P'3P4}$ = 29.4 Hz, P'_3), 50.1 (d, $^2J_{P4P'3}$ = 29.4 Hz, P_4), 51.5 (d, $^2J_{P2P'1}$ = 29.2 Hz, P_2), 52.5 (s, P_0), 61.0 (s, P_1, P_3); ^1H NMR (200.132 MHz): δ 3.32 (d, $^3J_{PH}$ = 10.9 Hz, 45H, Me_0, Me_2), 7.10-7.70 (m, 687H, H_{Ar}, CH=N), 9.83 (s, 48H, CHO); $^{13}C\{^1H\}$ NMR (50.323 MHz): δ 32.9 (d, $^2J_{CP}$ = 13.1 Hz, Me_0, Me_2), 121.3-121.8 (m, C_0^2, C_1^2, C_2^2, C_3^2), 122.0 (d, $^3J_{CP}$ = 5.0 Hz, C_4^2), 127.4 (dd, $^1J_{CP}$ = 74.8 Hz, $^3J_{CP}$ = 4.4 Hz, C_1^4, C_1^i, C_3^4, C_3^i), 128.5 (s, C_0^3, C_2^3), 128.7 (d, $^3J_{CP}$ = 12.3 Hz, C_1^m), 128.8 (d, $^3J_{CP}$ = 13.1 Hz, C_3^m), 131.2 (s, C_4^3), 132.6 (d, $^2J_{CP}$ = 10.9 Hz, C_1^o, C_3^o), 132.5 (s, C_0^4, C_2^4), 132.7 (s, C_4^4), 132.9 (s, C_1^p, C_3^p), 134.6 (d, $^1J_{CP}$ = 11.6 Hz, C_1^3, C_3^3), 140.4 (d, $^1J_{CP}$ = 12.3 Hz, CH=N), 153.2 (br d, $^2J_{CP}$ = 7.0 Hz, C_0^1, C_2^1), 153.9 (br. d, $^2J_{CP}$ = 6.6 Hz, C_1^1, C_3^1), 156.7 (d, $^2J_{CP}$ = 13.1 Hz, C_4^1), 191.0 (s, CHO). IR (KBr): 1700 cm^{-1} ($\nu_{C=O}$). Anal. Calcd for $C_{996}H_{780}N_{60}O_{141}P_{76}S_{46}$ (19674): C, 60.80; H, 3.99; N, 4.27. Found: C, 60.59; H, 3.85; N, 4.15.

Synthesis of G_4 by a one-pot process

The sequence of reactions is identical to those used for the step by step procedure, with a strict control of the stoechiometry, and without any type of purification.

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[i] Herd, O.; Hessler, A.; Hingst, M.; Tepper, M.; Stelzer, O. *J. Organomet. Chem.* **1996**, *522*,69.

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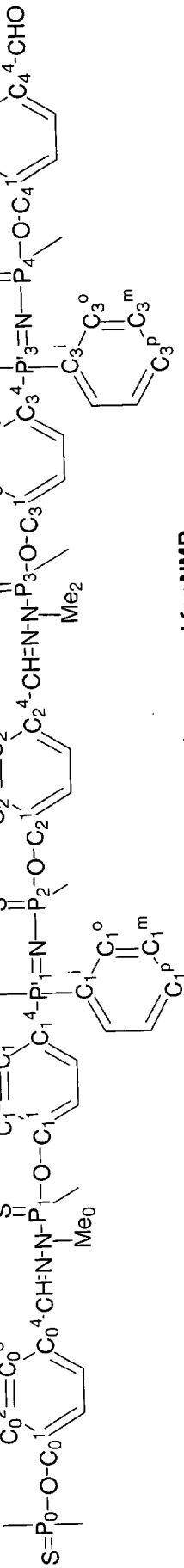
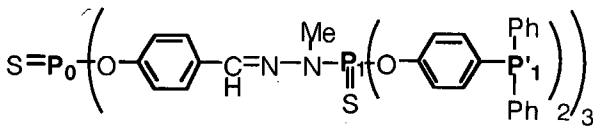


Numbering scheme used for NMR

^{31}P NMR spectrum of G_1



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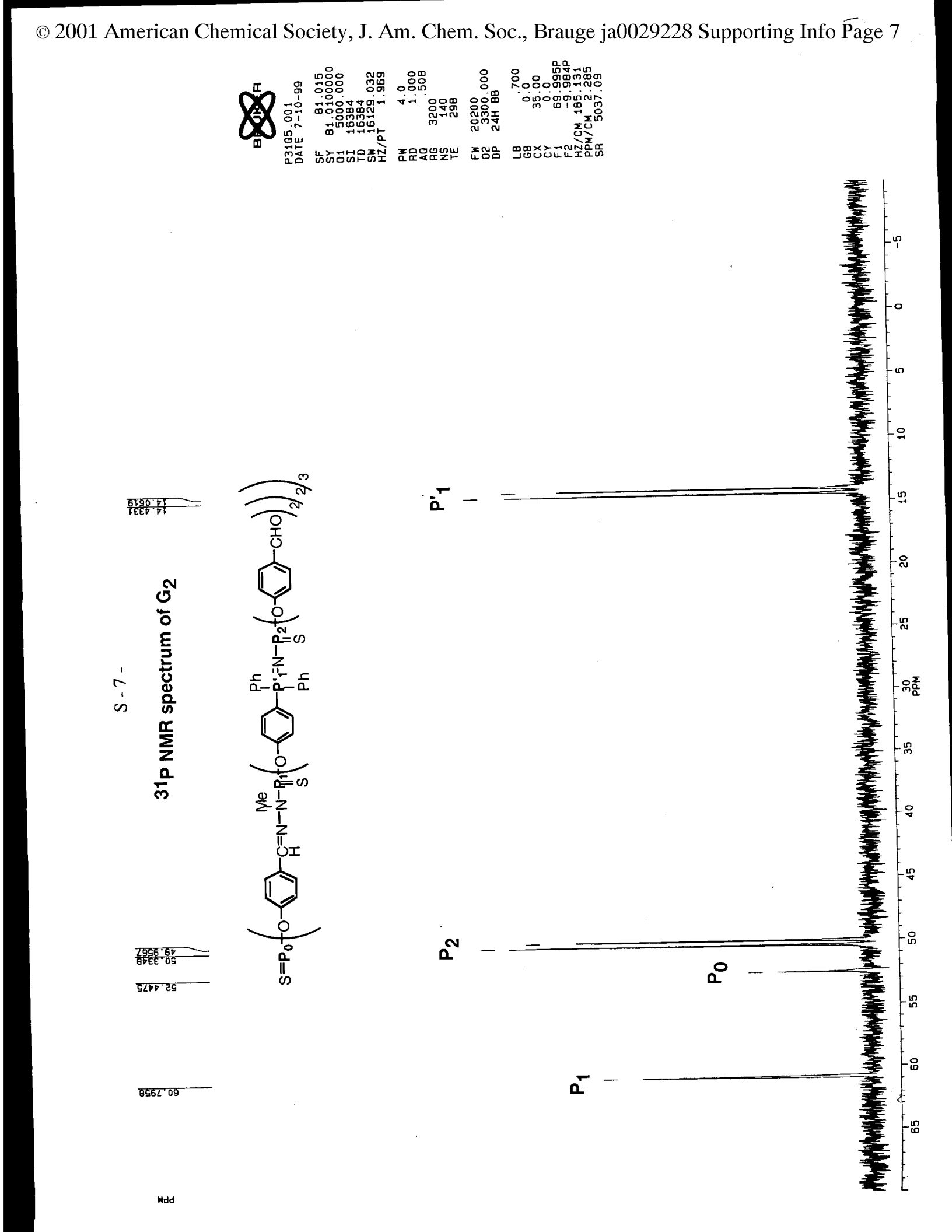

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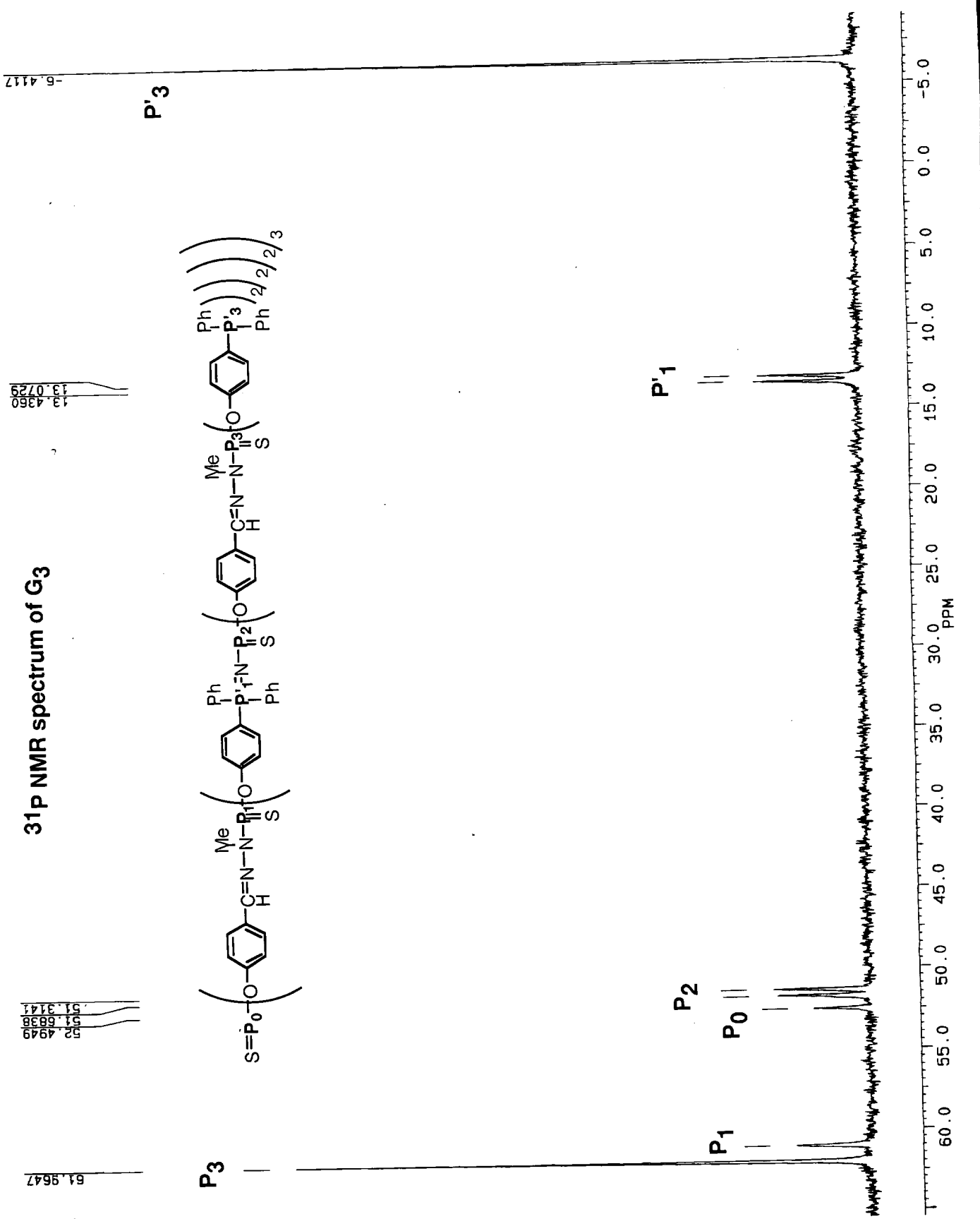
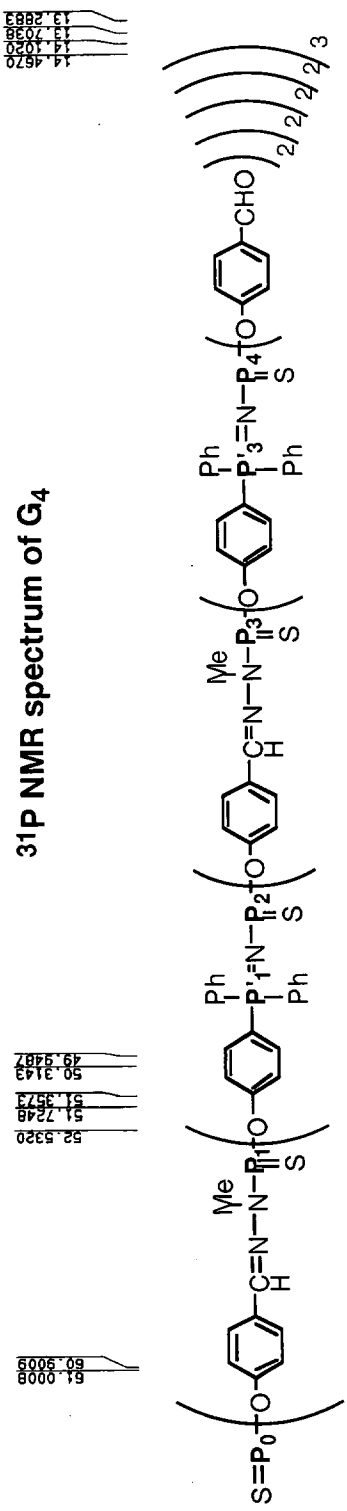
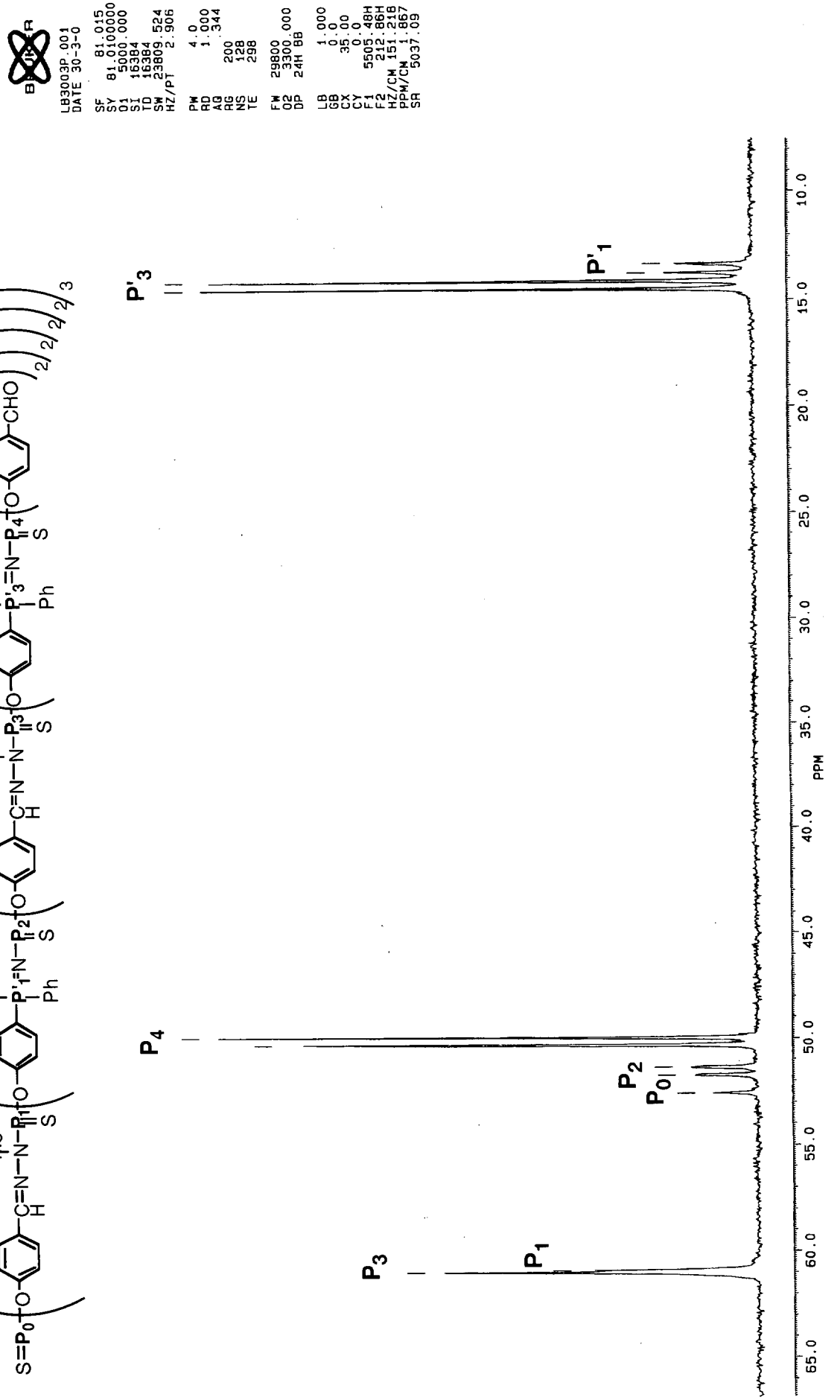
^{31}P NMR spectrum of G_3



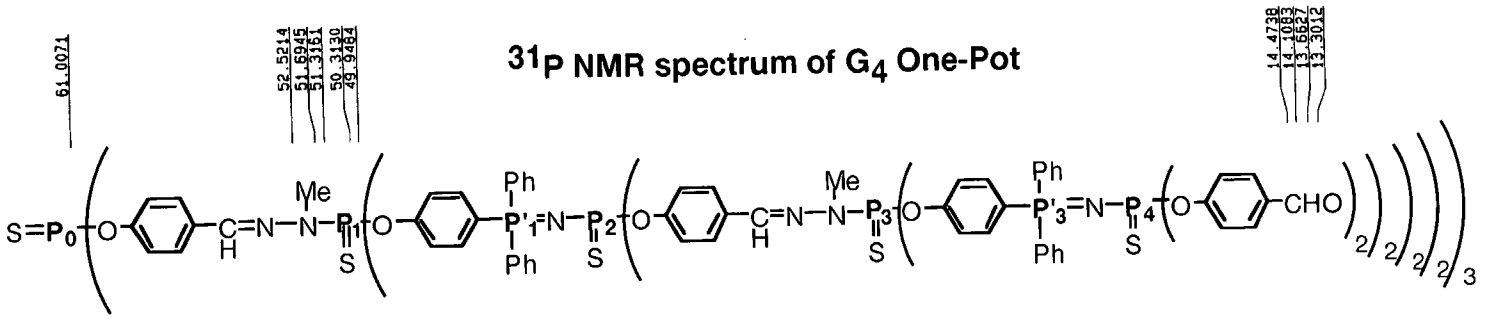
S - 9 -

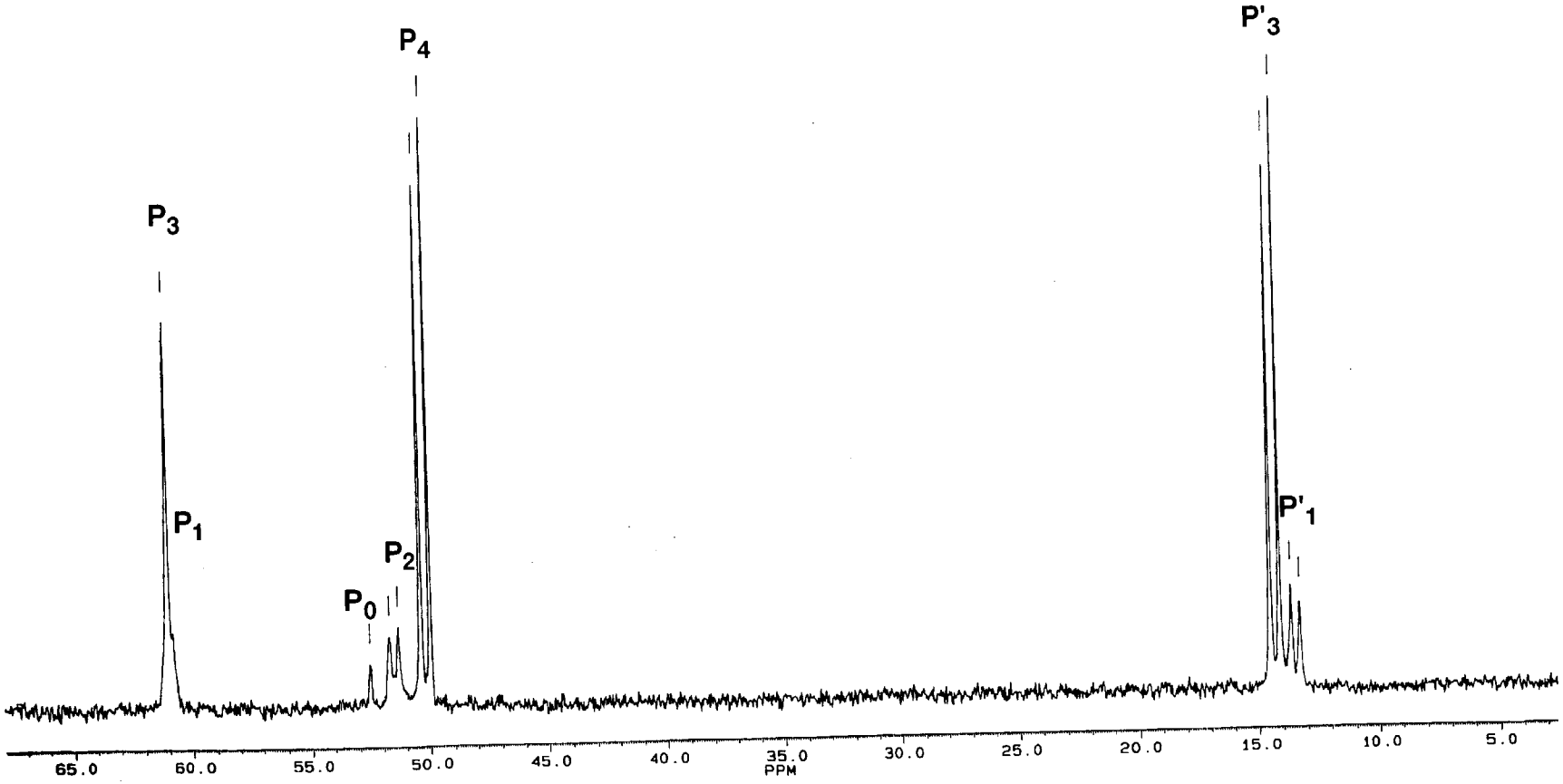
^{31}P NMR spectrum of G_4





^{31}P NMR spectrum of G_4 One-Pot





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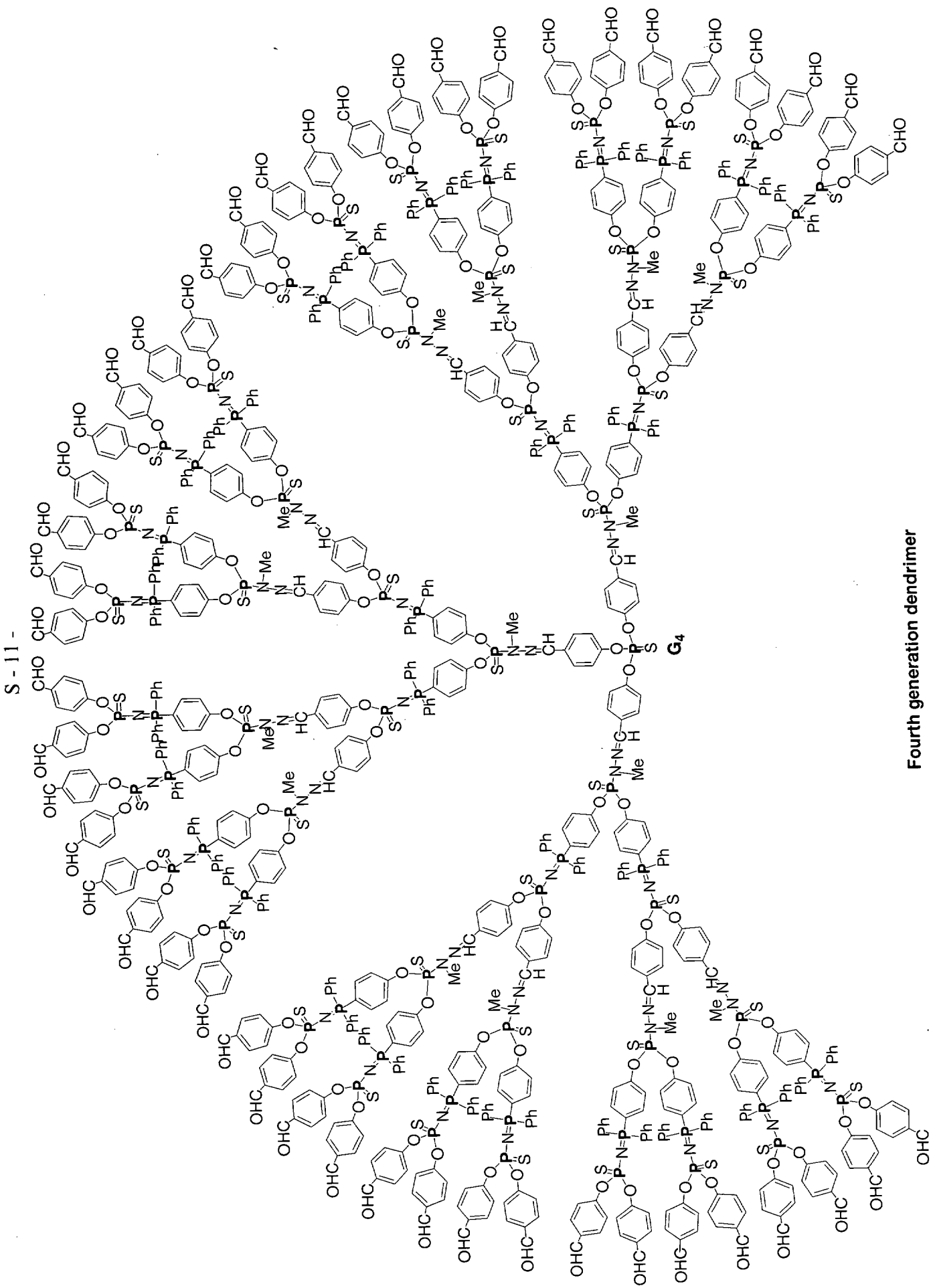
G4
Fourth generation dendrimer

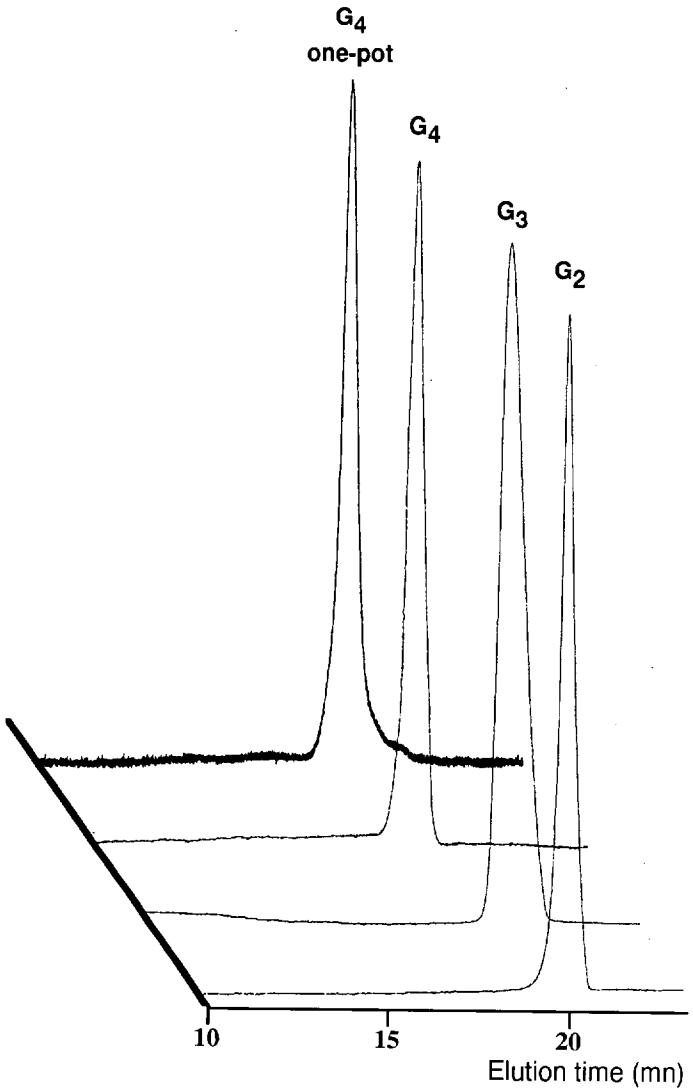

Figure 1