A water-soluble polyphosphorhydrazone Janus dendrimer built by "click" chemistry as support for Ru-complexes in catalysis

SUPPORTING INFORMATION

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1. General remarks

Commercial reagents were used as received. All reactions were carried out under an atmosphere of nitrogen using standard Schlenk line techniques unless stated otherwise. Dry, oxygen-free solvents (THF and CH_2Cl_2) were obtained from an Innovative technology PureSolv-MD-2 solvent purification system and directly stored under 4 Å. Other solvents (Et_2O and *n*-pentane) were distilled and degassed by freeze-pump-thaw technique before use.

Analytical thin layer chromatography (TLC) was performed on Merck silica gel 60 F_{254} pre-coated aluminum sheets (0.20 mm thickness) that were visualized by observation under UV light (254 nm or 365 nm).

Flash column chromatography was performed using silica gel 60 (230-400 mesh) purchased from Merck.

Melting points (M.p.) were recorded using a Kofler Reichert apparatus, and are uncorrected.

^{1}H NMR spectra were recorded on Agilent Mercury spectrometers (300 MHz, 400 MHz, 600 MHz). Chemical shifts (δ) are reported in parts per million (ppm) downfield from trimethylsilane (TMS) and referred to residual solvent peak: $CDCl_3$ (δ_H = 7.26 ppm) or DCM-d_2 (δ_H = 5.32 ppm) The following abbreviations are used to indicate the multiplicity signal: s (singlet), d (doublet), t (triplet), q (quartet), quin (quintet), sept (septet), dd (doublet of doublets), dt (doublet of triplets), ddd (doublet of doublets), br s (broad singlet), m (multiplet), 2 × s (two singlets), 2 × d (two doublets). The spectra were processed using MestReNova software.

^{13}C NMR spectra were recorded at room temperature. Chemical shifts are reported in parts per million downfield from TMS signal and referred to residual peak solvent: $CDCl_3$ (δ_C = 77.2 ppm) or DCM-d_2 (δ_C = 54.0 ppm). Otherwise stated, the multiplicity refers to ^{1}H decoupled spectra. The spectra were processed using MestReNova software.

^{31}P NMR spectra were recorded at room temperature in $CDCl_3$ or DCM-d_2. Chemical shifts are reported in parts per million relative to H_3PO_4 85% aqueous solution (δ_P = 0.00 ppm) as an external standard. The spectra were processed using MestReNova software.

IR spectra were recorded with on a Bruker Tensor 27 spectrometer fitted with a universal Attenuated Total Reflectance Golden Gate module.

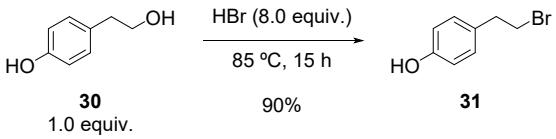
Gas chromatography (GC) chromatograms were recorded on a PerkinElmer Clarus 580 model, using an IntertCap 5MS-Sil column with helium as carrier gas.

High-resolution mass spectra (HR-MS) were measured at the Servicio de Espectrometría de Masas at the Universidad de Zaragoza.

Elemental Analyses and Inductively coupled plasma (ICP-OES) were measured at the Servei d'Anàlisi Química de l'Universitat Autònoma de Barcelona.

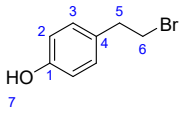
2. Experimental procedures

2.1. Synthesis of 4-(2-bromoethylphenol) 31



30
1.0 equiv.

31



The product was obtained in a 91% yield (3.97 g, 19.7 mmol) as a colorless solid employing previously reported methodologies.[1]

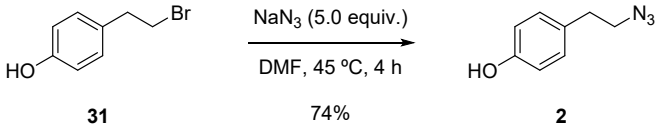
M.p.: 88 – 89 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.08 (d, $^3J_{H,H}$ = 8.6 Hz, 2H, H3), 6.79 (d, $^3J_{H,H}$ = 8.6 Hz, 2H, H2), 4.74 (s, 1H, H7), 3.53 (t, $^3J_{H,H}$ = 7.6 Hz, 2H, H6), 3.09 (t, $^3J_{H,H}$ = 7.6 Hz, 2H, H5).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 154.4 (C1), 131.2 (C4), 129.9 (C3), 115.4 (C2), 38.5 (C5), 33.4 (C6).

IR (ATR) ν (cm^{-1}): 3180, 3020, 2962. 1647, 1610, 1508, 1442, 1365, 1230, 1207, 833, 777.

2.2. Synthesis of 4-(2-azidoethyl)phenol 2



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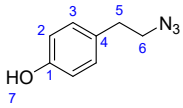


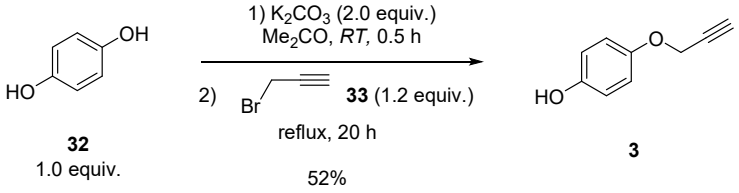
The product was obtained in a 74% yield (1.20 g, 7.35 mmol) as a yellow oil employing previously reported methodologies.[2]

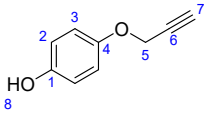
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.10 (d, $^3J_{H,H}$ = 8.6 Hz, 2H, H3), 6.83 (d, $^3J_{H,H}$ = 8.6 Hz, 2H, H2), 3.48 (t, $^3J_{H,H}$ = 7.2 Hz, 2H, H6), 2.85 (t, $^3J_{H,H}$ = 7.2 Hz, 2H, H5).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 154.0 (C1), 130.0 (C4), 129.8 (C3), 115.4 (C2), 52.4 (C6), 34.2 (C5).

IR (ATR) ν (cm^{-1}): 3352, 2927, 2869, 2090, 1613, 1597, 1513, 1443, 1222, 1172, 1105, 827.

2.3. Synthesis of 4-(prop-2-yn-yloxy)phenol 3



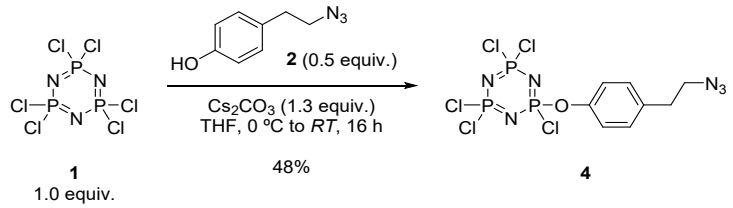


The product was obtained in a 52% yield (1.39 g, 9.39 mmol) as a yellow oil employing previously reported methodologies.[3]

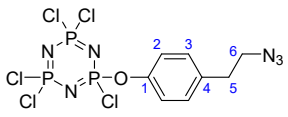
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.88 (d, $^3J_{H,H}$ =9.0 Hz, 2H, H2), 6.78 (d, $^3J_{H,H}$ =9.0 Hz, 2H, H3), 4.84 (s, 1H, H8) 4.63 (d, $^4J_{H,H}$ =2.4 Hz, 2H, H5), 2.50 (t, $^4J_{H,H}$ = 2.4 Hz, 1H, H7).

^{13}C{^{1}H} NMR (161 MHz, $CDCl_3$) δ (ppm): 151.7 (C1), 150.2 (C4), 116.4 (C2), 116.0 (C3), 78.8 (C6), 75.3 (C7), 56.7 (C5).

2.4. Synthesis of 2-(4-(2-azidoethyl)phenoxy)-2,4,4,6,6-pentachlorotriazatriphosphazene 4



In a round bottom Schlenk equipped with a magnetic stirring bar, under nitrogen atmosphere, hexachlorocyclotriphosphazene (**1**) (3.00 g, 8.58 mmol, 1.0 equiv.) and dry cesium carbonate (2.80 g, 11.2 mmol, 1.3 equiv.) were suspended in anhydrous THF (100 mL). Next, the mixture was cooled down to 0 °C, 4-(2-azidoethyl)phenol (**2**) (700 mg, 4.29 mmol, 0.5 equiv.) in anhydrous THF (20 mL) was added dropwise, and the reaction was allowed to warm up to room temperature while stirring for 16 hours. Upon completion, the mixture was filtered, the volatiles were removed, and the crude product was purified by column chromatography on silica (*n*-hexane/EtOAc 9:1 to 1:1) yielding the desired product as a pale-yellow oil (0.93 g, 1.96 mmol, 48% yield).



^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.30 – 7.19 (m, 4H, H2, H3), 3.51 (t, $^3J_{H,H}$ = 7.1 Hz, 2H, H6), 2.90 (t, $^3J_{H,H}$ = 7.1 Hz, 2H, H5).

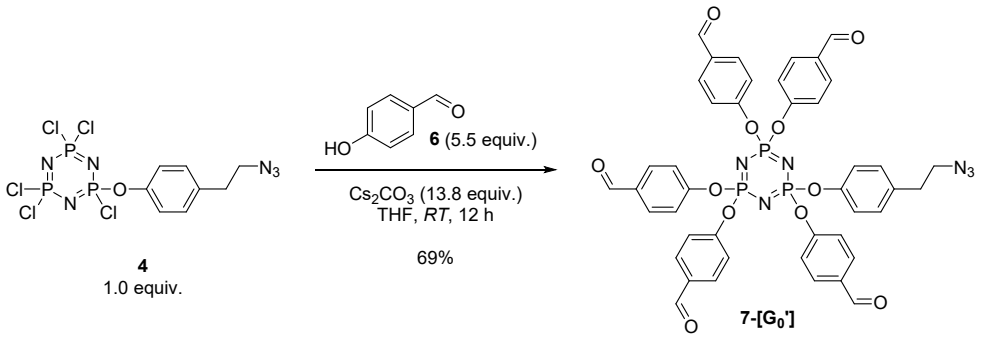
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 148.2 (d, $^2J_{C,P}$ = 10.3 Hz, C1), 136.9 (d, $^5J_{C,P}$ = 2.9 Hz, C4), 130.3 (d, $^3J_{C,P}$ = 2.3 Hz, C2), 121.5 (d, $^4J_{C,P}$ = 5.3 Hz, C3), 52.3 (d, $^7J_{C,P}$ = 1.7 Hz, C6), 34.7 (d, $^6J_{C,P}$ = 0.8 Hz, C5).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ (ppm): 22.4 (d, $^2J_{P,P}$ = 60.9 Hz), 12.3 (t, $^2J_{P,P}$ = 60.9 Hz).

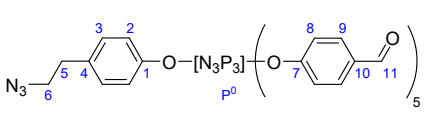
IR (ATR) ν (cm^{-1}): 2928, 2870, 2093, 1504, 1196, 1177, 1153, 976.

Elemental analysis (%) calcd. for $C_8H_8Cl_5N_6OP_3$: C 20.26; H 1.70; N 17.72; found: C 20.26; H 1.74; N 17.33.

2.5. Synthesis of azide dendron 7-[G_0']



In a round bottom Schlenk flask equipped with a magnetic stirring bar, under nitrogen atmosphere, 2-(4-(2-azidoethyl)phenoxy)-2,4,4,6,6-pentachlorotriazatriphosphazene (**4**) (0.52 g, 1.10 mmol, 1.0 equiv.), 4-hydroxybenzaldehyde (**6**) (0.74 g, 6.03 mmol, 5.5 equiv.), and dry cesium carbonate (4.91 g, 15.1 mmol, 13.8 equiv.) were suspended in anhydrous THF (100 mL), and the mixture was stirred at room temperature for 12 h. Upon reaction completion, the mixture was filtered, and the volatiles were removed. The crude product was washed with THF/methanol and purified by column chromatography on silica (*n*-hexane/EtOAc 8:2 to 1:1). The desired product was obtained as a yellow oil (0.68 g, 0.76 mmol, 69% yield).



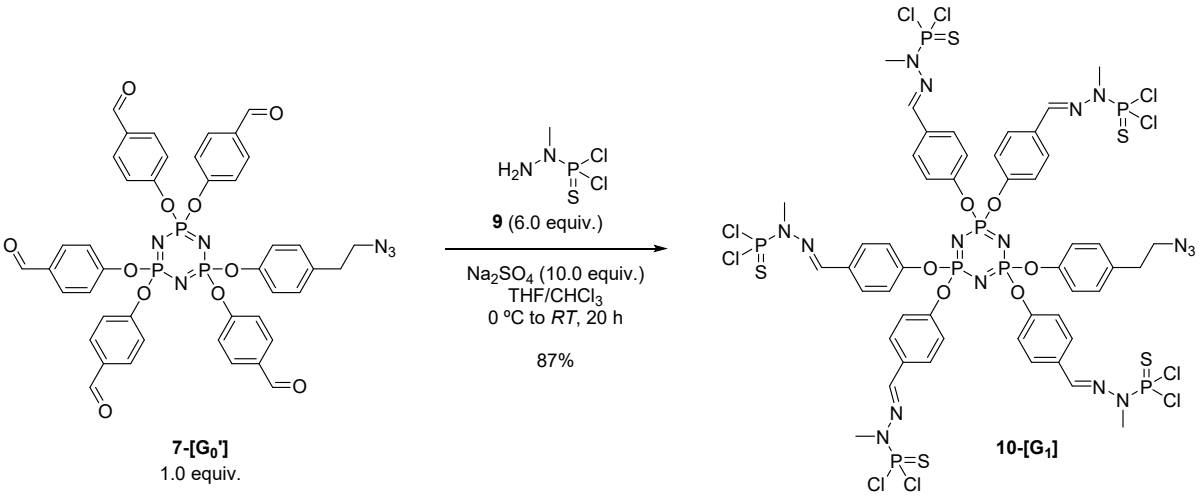
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 9.91 (2 × s, 5H, H11), 7.71 (d, $^3J_{H,H}$ = 8.5 Hz, 10H, H9), 7.17 – 7.07 (m, 10H, H8), 7.05 (d, $^3J_{H,H}$ = 8.6 Hz, 2H, H3), 6.92 (d, $^3J_{H,H}$ = 8.6 Hz, 2H, H2), 3.47 (t, $^3J_{H,H}$ = 6.9 Hz, 2H, H6), 2.82 (t, $^3J_{H,H}$ = 6.9 Hz, 2H, H5).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 190.5 (3 × s, C11), 154.8 (2 × d, $^2J_{C,P}$ = 5.0 Hz, C7), 148.8 (2 × d, $^2J_{C,P}$ = 5.2 Hz, C1), 135.8 (C4), 133.7 (3 × s, C10), 131.4 (2 × s, C9), 130.0 (C3), 121.3 (m, C8), 120.8 (2 × d, $^3J_{C,P}$ = 3.3 Hz ,C2), 52.2 (C6), 34.6 (C5).

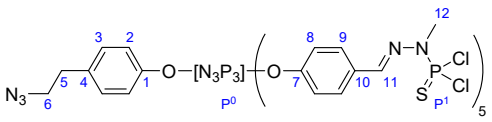
^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ (ppm): 7.4 (s, P^0).

IR (ATR) ν (cm^{-1}): 3068, 2827, 2737, 2097, 1697, 1595, 1501, 1420, 1389, 1267, 1202, 1173, 1148, 1101, 937, 881, 829, 727, 704.

2.6. Synthesis of azide dendron 10-[G_1]^4



In a Schlenk flask equipped with a magnetic stirring bar, under nitrogen atmosphere, **7-[G_0']** dendron (0.30 g, 0.332 mmol, 1.0 equiv.) and anhydrous Na_2SO_4 (0.47 g, 3.32 mmol, 10.0 equiv.) were suspended in anhydrous THF (5 mL). Next, *N*-methyldichlorothiophosphorhydrazide (**9**) (6.7 mL, 1.99 mmol, 6.0 equiv., c = 0.30 mol·L^{-1} in $CHCl_3$) was added dropwise at 0 °C. Upon complete addition, the mixture was allowed to warm up to room temperature while stirring overnight. The mixture was filtered, and the filtrate was concentrated to 3 mL. The product was precipitated from *n*-pentane, the supernatant removed, and the product washed with *n*-pentane/Et_2O (4:1) twice. The volatiles were removed under reduced pressure, and the product was dried to provide a colorless solid (0.49 g, 0.29 mmol, 87% yield).



M.p.: 96 – 97 °C.

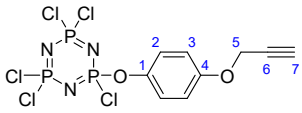
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.67 – 7.54 (m, 15H, H11, H9), 7.09 – 6.97 (m, 12H, H8, H3), 6.93 (d, $^3J_{H,H}$ = 8.2 Hz, 2H, H2), 3.53 – 3.41 (m, 17H, H12, H6), 2.83 (d, $^3J_{H,H}$ = 7.1 Hz, 2H, H5).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 151.9 (2 × d, $^2J_{C,P}$ = 5.0 Hz, C7), 149.3 (2 × d, $^2J_{C,P}$ = 5.2 Hz, C1), 140.8 (2 × d, $^3J_{C,P}$ = 5.0 Hz, C11), 135.3 (C4), 131.4 (C10), 130.0 (C9), 128.8 (C3), 121.5 (m, C8), 121.2 (2 × d, $^3J_{C,P}$ = 3.1 Hz, C2), 52.4 (C6), 34.8 (C5), 32.1 (2 × d, $^3J_{C,P}$ = 12.8 Hz, C12).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ (ppm): 62.4 (s, P^1), 62.4 (s, P^1), 8.3 (s, P^0).

IR (ATR) ν (cm^{-1}): 2929, 2866, 2094, 1601, 1504, 1462, 1267, 1235, 1184, 1175, 1159, 1132, 937, 875, 837, 748, 687.

2.7. Synthesis of 2-(4-(4-(pro-2-yn-yloxy)phenoxy)-2,4,4,6,6-pentachlorotriazatriphosphazene 5



The product was obtained in a 46% yield (773 mg, 1.68 mmol) as a colorless oil employing previously reported methodologies.[5]

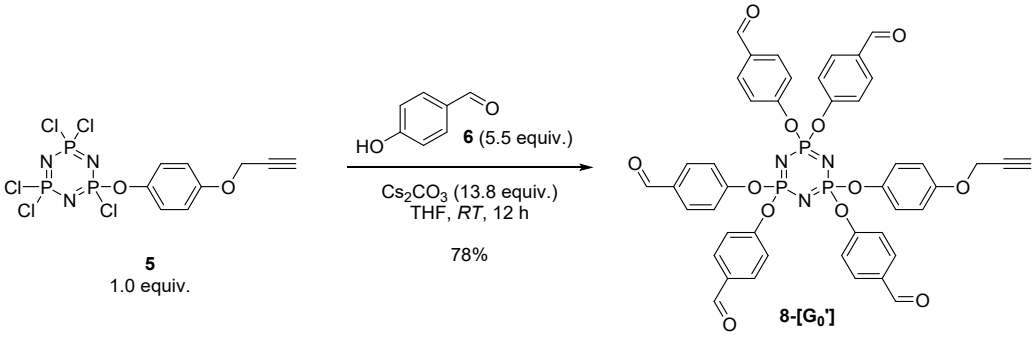
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.21 (dd, $^{3}J_{H,H}$ = 9.1 Hz, $^{5}J_{H,P}$ = 2.2 Hz, 2H, H2), 6.99 (dd, $^{3}J_{H,H}$ = 9.1 Hz, $^{4}J_{H,P}$ = 0.8 Hz, 2H, H3), 4.69 (d, $^{4}J_{H,H}$ = 2.4 Hz, 2H, H5), 2.53 (t, $^{4}J_{H,H}$ = 2.4 Hz, 1H, H7).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 156.0 (d, $^{5}J_{C,P}$ = 2.7 Hz, C4), 143.5 (d, $^{2}J_{C,P}$ = 10.3 Hz, C1), 122.4 (d, $^{3}J_{C,P}$ = 5.0 Hz, C2), 116.1 (d, $^{4}J_{C,P}$ = 2.3 Hz, C3), 78.2 (C6), 76.1 (C7), 56.4 (C5).

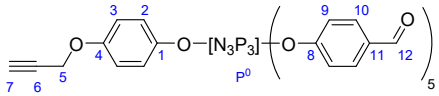
^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ (ppm): 22.4 (d, $^{2}J_{P,P}$ = 59.2 Hz), 13.1 (d, $^{2}J_{P,P}$ = 59.2 Hz).

IR (ATR) ν (cm^{-1}): 3000, 2024, 1594, 1500, 1455, 1194, 1157, 1027, 978, 870, 830, 770.

2.8. Synthesis of acetylene dendron 8-[G_0']



In a round bottom Schlenk flask equipped with a magnetic stirring bar, under nitrogen atmosphere, 2-(4-(4-(pro-2-yn-yloxy)phenoxy)-2,4,4,6,6-pentachlorotriazatriphosphazene (**5**) (0.35 g, 0.76 mmol, 1.0 equiv.), 4-hydroxybenzaldehyde (**6**) (0.51 g, 4.19 mmol, 5.5 equiv.) and dry cesium carbonate (3.41 g, 10.5 mmol, 13.8 equiv.) were suspended in dry THF (100 mL), and the mixture was stirred at room temperature for 12 h. Upon reaction completion, the mixture was filtered, and the volatiles were removed. The crude was dissolved in DCM (50 mL) and washed with a saturated solution of Na_2CO_3 (3 × 50 mL). The organic phase was taken, dried over anhydrous Na_2SO_4, filtered, and the volatiles were removed *in vacuo*. The product was precipitated from *n*-pentane to obtain the desired product as a colorless solid (0.52 g, 0.59 mmol, 78% yield).



M.p.: 66 – 68 °C.

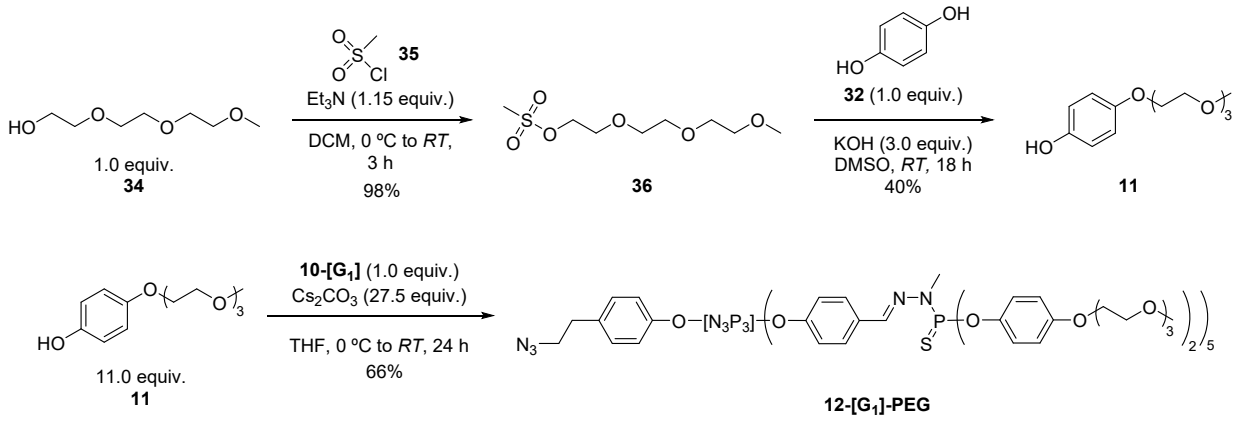
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 9.93 (2 × s, 5H, H12), 7.77 – 7.69 (m, 10H, H10), 7.16 (d, $^{3}J_{H,H}$ = 8.5 Hz, 6H, H9), 7.06 (d, $^{3}J_{H,H}$ = 8.5 Hz, 4H, H9), 6.93 – 6.86 (m, 2H, H2), 6.80 – 6.73 (m, 2H, H3), 4.65 (d, $^{3}J_{H,H}$ = 2.4 Hz, 2H, H5), 2.56 (t, $^{3}J_{H,H}$ = 2.4 Hz, 1H, H7).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ (ppm): 190.71 – 190.45 (m, C12), 155.6 – 154.6 (m, C4, C8), 144.1 (d, $^2J_{C,P}$ = 6.4 Hz, C1), 134.0 – 133.6 (m, C11), 131.5 (d, $^4J_{C,P}$ = 2.3 Hz, C10), 121.8 (d, $^3J_{C,P}$ = 3.9 Hz, C2), 121.5 – 121.3 (m, C9), 115.9 (C3), 78.4 (C6), 76.2 (C7), 56.3 (C5).

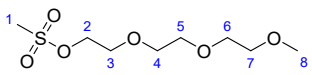
$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ (ppm): 8.7 −6.9 (m, P^0).

IR (ATR) ν (cm^{-1}): 3268, 2924, 2851, 2737, 1770, 1697, 1596, 1499, 1421, 1388, 1298, 1266, 1194, 1171, 1149, 1101, 1013, 939, 882, 828, 725, 705.

2.9. Surface modification of 10-[G_1] azide dendron



2.9.1. Synthesis of 2-(2-(2-methoxyethoxy)ethoxy)ethyl methanesulfonate 36

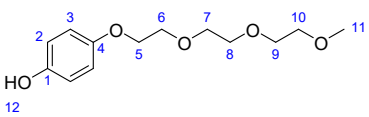


The product was obtained in a 98% yield (2.89 g, 11.9 mmol) as a yellow oil in $CDCl_3$ employing previously reported methodologies.[6]

^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 4.37 – 4.28 (m, 2H, H2), 3.76 – 3.68 (m, 2H, H4), 3.68 – 3.53 (m, 6H, H3, H5, H6), 3.53 – 3.45 (m, 2H, H7), 3.32 (s, 3H, H8), 3.02 (s, 3H, H1).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ (ppm): 71.8 (C7), 70.5 (C4, C5), 70.4 (C6), 69.4 (C3), 68.9 (C2), 58.9 (C8), 37.5 (C1).

2.9.2. 4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenol 11

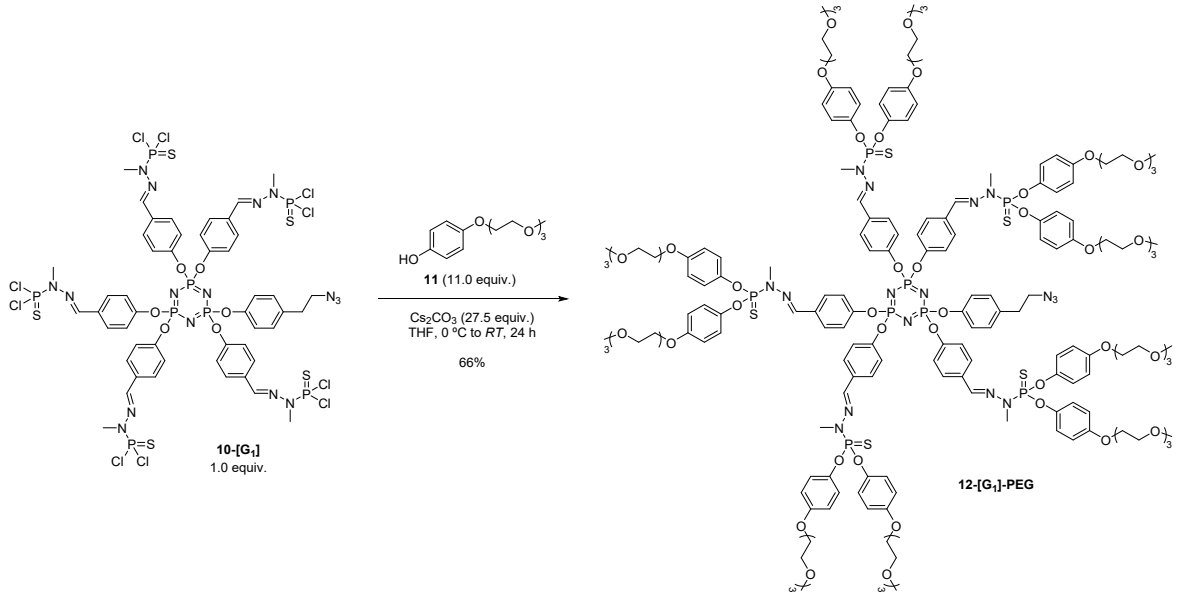


The product was obtained in a 40% yield (2.81 g, 11.0 mmol) as a dark yellow oil employing previously reported methodologies.[6]

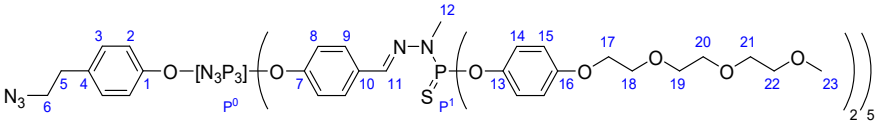
^1H NMR (400 MHz, DCM-d_2) δ (ppm): 6.80 – 6.70 (m, 4H, H2, H3), 5.27 (s, 1H, H12), 4.04 – 3.97 (m, 2H, H5), 3.80 – 3.73 (m, 2H, H7), 3.69 – 3.64 (m, 2H, H6), 3.64 – 3.58 (m, 4H, H8, H9), 3.55 – 3.48 (m, 2H, H10), 3.34 (s, 3H, H11).

$^{13}C\{^1H\}$ NMR (101 MHz, DCM-d_2) δ (ppm): 152.7 (C4), 151.1 (C1), 116.5 (C2), 116.0 (C3), 72.2 (C10), 71.0 (C8), 70.9 (C7), 70.7 (C9), 70.2 (C6), 68.4 (C5), 59.0 (C11).

2.9.3. Synthesis of azide dendron 12-[G_1]-PEG



In a Schlenk flask equipped with a magnetic stirring bar, under nitrogen atmosphere, 4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenol (**11**) (0.50 g, 1.93 mmol, 11.0 equiv.) and cesium carbonate (1.57 g, 4.83 mmol, 27.5 equiv.) were dissolved in dry THF (20 mL), and the mixture was stirred at 0 °C for 2 h. A solution of **10-[G_1]** dendron (0.30 g, 0.18 mmol, 1.0 equiv.) in THF (20 mL) was added dropwise at 0 °C. Upon complete addition, the mixture was let to warm up to room temperature while stirring overnight. THF was then evaporated, the residue was dissolved in DCM, and the mixture was centrifuged. The salts were filtered off, the product concentrated to 5 mL, and precipitated in a *n*-pentane/Et_2O (4:1) mixture thrice. The desired product was obtained as a pale-red oil (0.45 g, 0.12 mmol, 66% yield).



^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.64 – 7.55 (m, 15H, H9, H11), 7.11 – 6.95 (m, 34H, H2, H3, H8, H15), 6.84 – 6.73 (m, 20H, H14), 4.04 – 3.99 (m, 20H, H17), 3.82 – 3.75 (m, 20H, H19), 3.72 – 3.67 (m, 20H, H18), 3.66 – 3.61 (m, 40H, H20, H21), 3.54 – 3.50 (m, 20H, H22), 3.35 (2 × s, 30H, H23), 3.31 – 3.18 (m, 17H, H6, H12), 2.73 (t, $^3J_{H,H}$ = 6.9 Hz, 2H, H5).

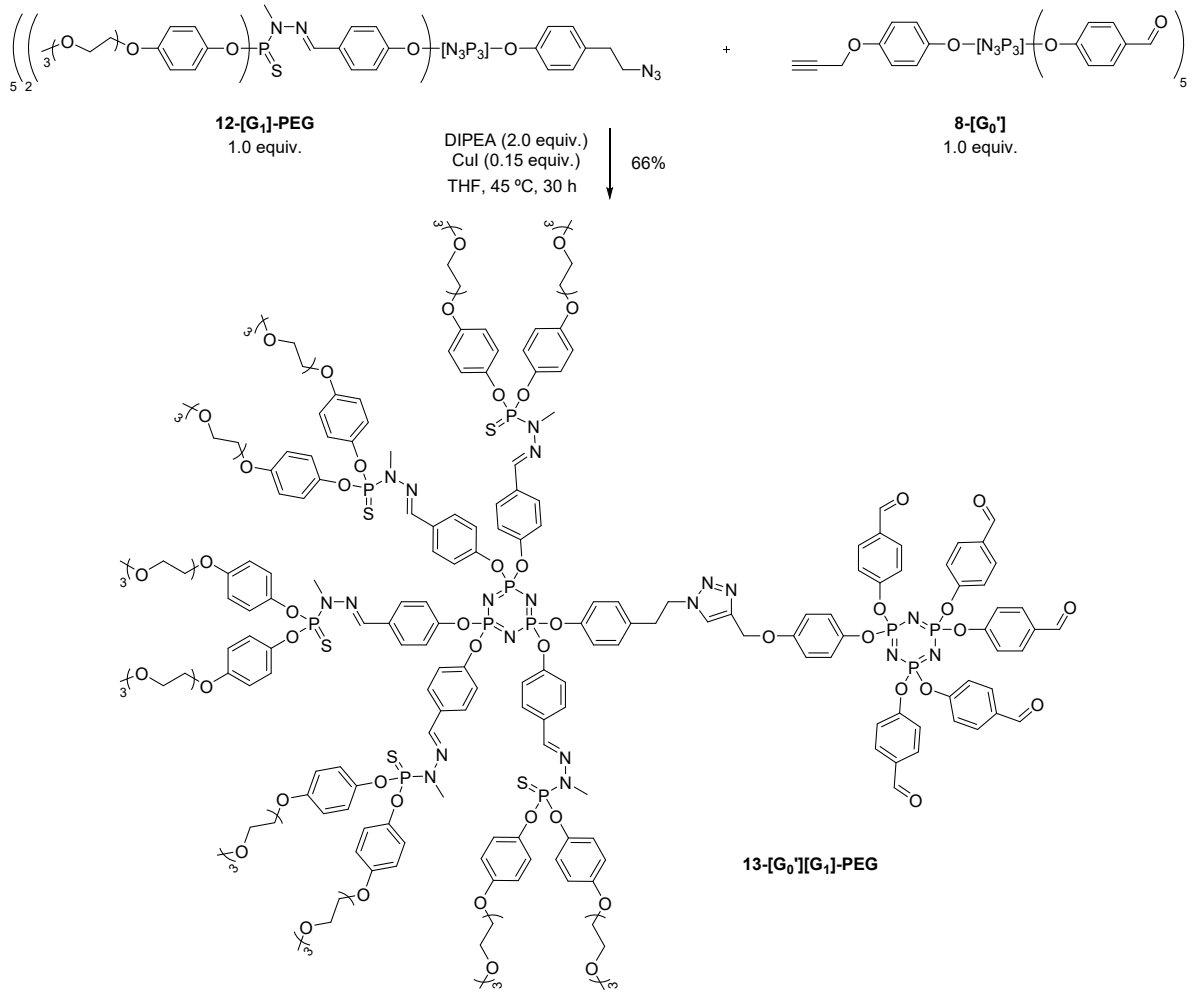
$^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz) δ (ppm): 156.3 – 156.1 (m, C13), 151.4 – 151.1 (m, C7), 148.2 (C1), 144.2 (d, $^3J_{C,P}$ = 7.1 Hz, C11), 138.6 – 138.2 (m, C16), 135.3 (C4), 132.5 – 132.0 (m, C10), 129.9 (C9), 128.5 (d, $^4J_{C,P}$ = 5.6 Hz, C3), 122.3 – 122.2 (m, C14), 121.5 – 121.2 (m, C8), 121.2 – 121.0 (m, C2), 115.2 (C15), 71.9

(C22), 70.8 (C19), 70.7 (C20), 70.6 (C21), 69.7 (C18), 67.8 (C17), 59.0 (C23), 52.2 (C6), 34.5 (C5), 33.1 (d, $^{2}J_{C,P}$ = 11.8 Hz, C12).

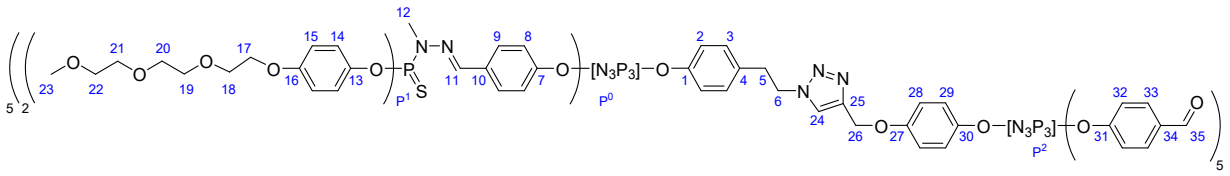
$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz) δ (ppm): 64. 6 (s, P^1), 64.5 (s, P^1), 8.5 (s, P^0).

IR (ATR) ν (cm^{-1}): 2871, 2095, 1602, 1500, 1454, 1352, 1247, 1179, 932, 833, 779.

2.10. Synthesis of 13-[G_0']-[G_1]-PEG



In a Schlenk flask equipped with a magnetic stirring bar, under nitrogen atmosphere, **8-[G_0']** dendron (0.50 g, 0.13 mmol, 1.0 equiv.) and **12-[G_1]-PEG** dendron (0.11 g, 0.13 mmol, 1.0 equiv.) were dissolved in dry, degassed THF (20 mL). DIPEA (45 µL, 0.26 mmol., 2.0 equiv.) and CuI (3.66 mg, 0.02 mmol, 0.15 equiv.) were added, and the mixture was heated at 45 °C for 30 h. The reaction evolution was followed by NMR and IR. Upon reaction completion, the mixture was filtered through Celite®, diluted with NH_4Cl (sat. solution, 30 mL), and the product extracted with THF (3 × 30 mL). The combined organic layers were collected, dried over anhydrous Na_2SO_4, filtered, and the solution was concentrated to 5 mL. The crude was precipitated in *n*-pentane (100 mL) twice, the volatiles removed and the product dried *in vacuo*. The desired product was obtained as a pale-yellow solid (0.41 g, 0.09 mmol, 66% yield).



M.p.: 76 −79 °C.

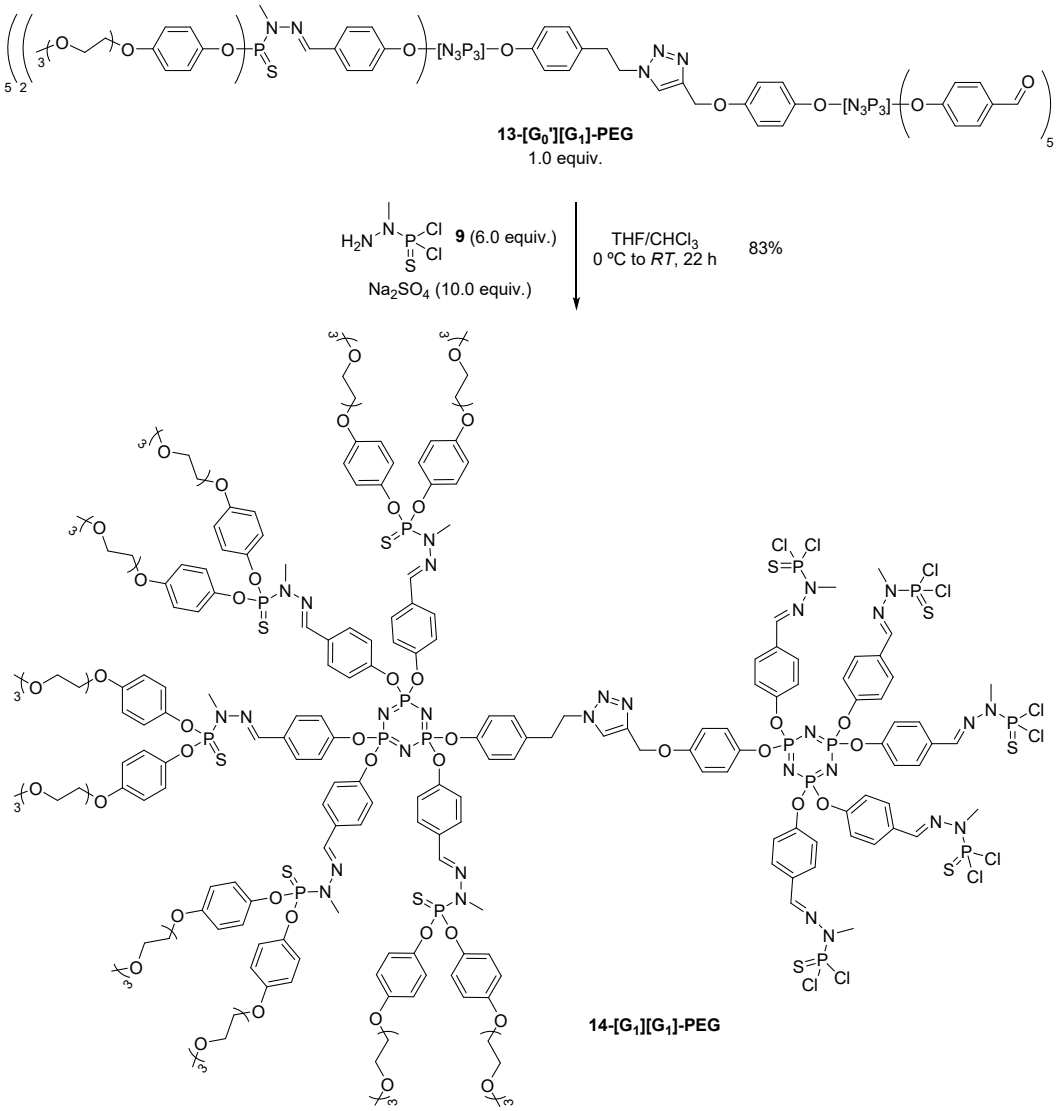
^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 9.94 – 9.87 (m, 5H, H35), 7.75 − 7.65 (m, 10H, H33), 7.64 – 7.54 (m, 16H, H9, H11, H24), 7.15 (d, $^{3}J_{H,H}$ = 8.6 Hz, 6H, H32), 7.11 – 6.94 (m, 40H, H2, H3, H8, H15, H28, H32), 6.82 – 6.73 (m, 22H, H14, H29), 5.01 (s, 2H, H26), 4.39 (t, $^{3}J_{H,H}$ = 7.5 Hz, 2H, H5), 4.07 – 3.97 (m, 20H, H17), 3.82 – 3.75 (m, 20H, H19), 3.71 – 3.58 (m, 60H, H18, H20, H21), 3.55 – 3.48 (m, 20H, H22), 3.34 (s, 30H, H23), 3.30 – 3.18 (m, 17H, H6, H12).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz) δ (ppm): 190.7 – 190.3 (3 × s, C35), 156.2 (d, $^{2}J_{C,P}$ = 2.4 Hz, C13), 154.9 (d, $^{2}J_{C,P}$ = 6.1 Hz, C7), 154.6 (d, $^{2}J_{C,P}$ = 7.6 Hz, C31), 151.2 (C27), 149.4 (C1), 144.2 (d, $^{3}J_{C,P}$ = 7.0 Hz, C11), 143.2 (C25), 138.7 – 138.2 (m, C16), 135.4 (C4), 133.7 (C24), 133.6 (d, $^{2}J_{C,P}$ = 4.2 Hz, C30), 132.3 (C34), 131.7 – 131.0 (m, C10, C33), 129.8 (C9), 128.2 (d, $^{4}J_{C,P}$ = 5.6 Hz, C3), 122.2 (d, $^{4}J_{C,P}$ = 4.2 Hz, C15), 121.8 – 121.6 (m, C29, C32), 121.4 – 121.0 (m, C2, C8), 115.5 (C28), 115.2 (C14), 77.3 (C26), 71.9 (C22), 70.8 (C19), 70.6 (C20), 70.5 (C21), 69.7 (C18), 67.7 (C17), 59.0 (C23), 51.3 (C6), 35.7 (C5), 33.1 (d, $^{2}J_{C,P}$ = 11.9 Hz, C12).

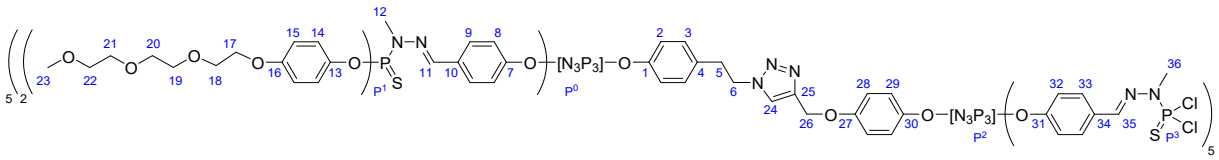
^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz) δ (ppm): 64.7 (2 × s, P^1), 8.5 (s, P^0), 8.0 −7.3 (m, P^2).

IR (ATR) ν (cm^{-1}): 2872, 1699, 1598, 1499, 1367, 1247, 1154, 1100, 932, 885, 831, 780.

2.11. Synthesis of 14-[G_1][G_1]-PEG



In a Schlenk flask equipped with a magnetic stirring bar, under nitrogen atmosphere, **13-[G_0']-[G_1]-PEG** dendrimer (0.45 g, 0.09 mmol, 1.0 equiv.) and anhydrous Na_2SO_4 (0.13 g, 0.94 mmol, 10.0 equiv.) were suspended in dry THF (5 mL), and the mixture was cooled down to 0 °C. Next, *N*-methyldichlorothiophosphorhydrazide **9** (1.9 mL, 0.56 mmol, 6.0 equiv., c = 0.30 mol·L^{-1} in $CHCl_3$) was added dropwise at 0 °C. Upon complete addition, the mixture was allowed to warm up to room temperature while stirring overnight (reaction evolution was followed by $^{31}P\{^1H\}$ NMR). The mixture was filtered by cannula filtration, and the filtrate concentrated to 3 mL. The product was precipitated from *n*-pentane, the supernatant removed, and the product washed with *n*-pentane/Et_2O (4:1) twice. The volatiles were removed and the product dried obtaining a colorless solid (0.44 g, 0.078 mmol, 83% yield).



M.p.: 56 – 60 °C.

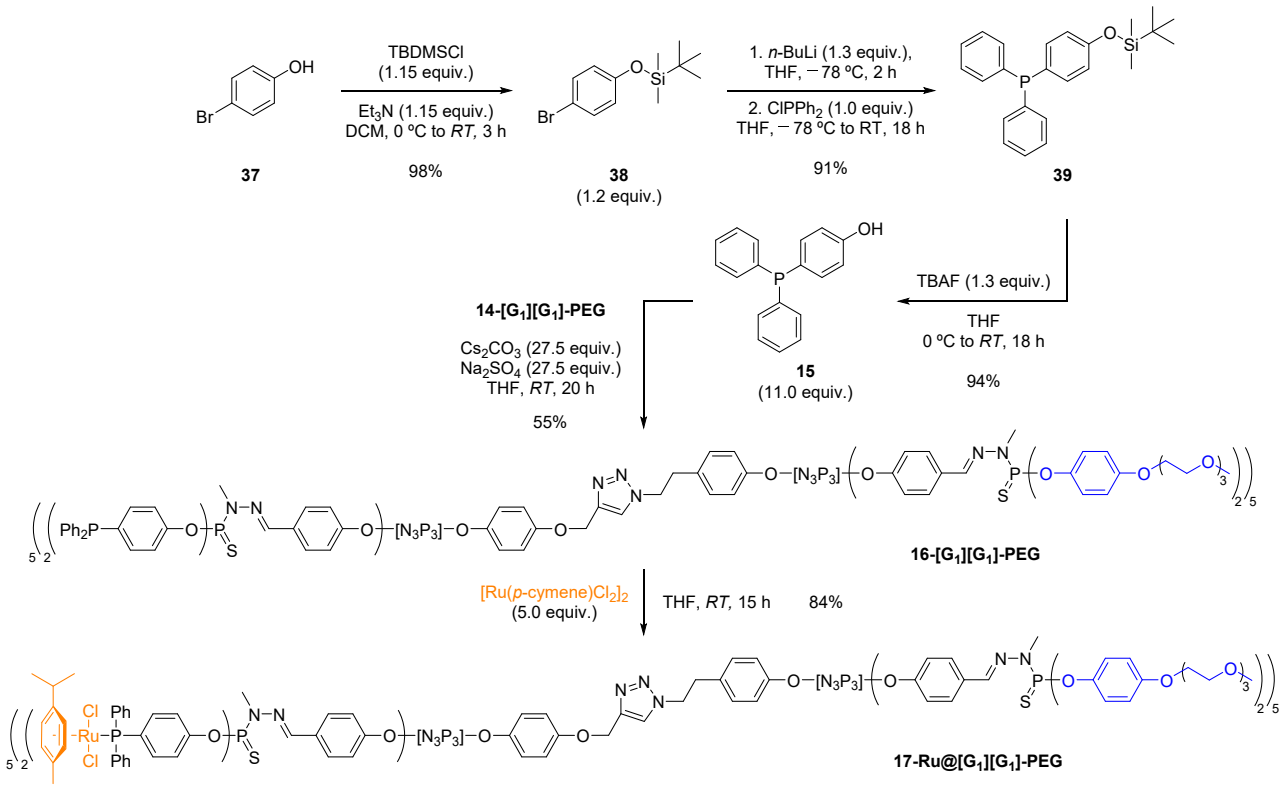
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.66 – 7.52 (m, 26H, H9, H11, H33, H35), 7.09 – 6.90 (m, 33H, H2, H3, H9, H15, H24), 6.86 – 6.68 (m, 40H, H8, H14, H28, H29, H32), 4.95 (s, 2H, H26), 4.42 – 4.34 (m, 2H, H5), 4.06 – °3.98 (m, 20H, H17), 3.83 – 3.75 (m, 20H, H19), 3.70 – 3.59 (m, 60H, H18, H20, H21), 3.55 – 3.48 (m, 20H, H22), 3.34 (2 × s, 30H, H23), 3.29 – 3.19 (m, 32H, H6, H12, H36).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 156.4 – 156.3 (m, C13), 151.5 – 151.2 (m, C7, C31), 144.4 – 144.1 (m, C11, C35), 138.7 – 138.5 (C16), 132.4 (2 × s, C34), 131.5 –131.2 (m, C10), 128.8 – 128.7 (2 × s, C9), 128.5 – 128.2 (C33), 122.4 (d, $^{4}J_{C,P}$ = 4.2 Hz, C15), 122.1 – 122.0 (C8), 121.6 – 121.3 (m, C32), 115.4 (C14), 77.3 (C26), 72.1 (C22) 70.9 (C19), 70.8 (C20), 70.7 (C21), 69.8 (C18), 67.9 (C17), 59.2 (C23), 33.4 – 33.0 (m, C36), 32.3 – 32.0 (2 × d, $^{2}J_{C,P}$ = 13.1 Hz, 12.5 Hz, C12). Carbon signals corresponding to the cores and triazole linker were not detected due to the low concentration and the poor solubility of the compound in deuterated solvents.

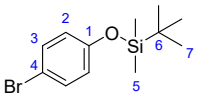
^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ (ppm): 64.5 (s, P^3), 62.7 (s, P^1), 62.5 (s, P^1), 9.5 –7.8 (m, P^0, P^2).

IR (ATR) ν (cm^{-1}): 2874, 1605, 1501, 1461, 1367, 1247, 1179, 1161, 935, 888, 834, 781.

2.12. Synthesis of a Ru(*p*-cymene)@Janus dendrimer system



2.12.1. Synthesis of (4-bromophenoxy)(tert-butyl)dimethylsilane 38

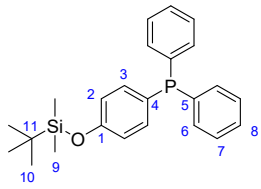


The product was obtained in a 98% yield (1.63 g, 5.67 mmol) as a colorless oil employing previously reported methodologies.[7]

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.32 (d, $^{3}J_{H,H}$ = 8.9 Hz, 2H, H3), 6.72 (d, $^{3}J_{H,H}$ = 8.9 Hz, 2H, H2, 0.98 (s, 9H, H7), 0.19 (s, 6H, H5).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 154.9 (C1), 132.3 (C3), 121.9 (C2), 113.6 (C4), 25.6 (C7), 18.2 (C6), −4.5 (C5).

2.12.2. Synthesis of (4-((*tert*-butyldimethylsilyl)oxy)phenyl)diphenylphosphane 39



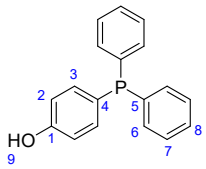
The product was obtained in a 91% yield (0.859 g, 2.19 mmol) as a colorless solid employing previously reported methodologies.[7]

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.37 – 7.15 (m, 12H, H3, H6, H7, H9), 6.83 (d, $^{3}J_{H,H}$ = 8.4, 2H, H2), 0.98 (s, 9H, H12), 0.21 (s, 6H, H9).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ (ppm): 156.8 (C1), 138.1 (d, $^{1}J_{C,P}$ = 10.3 Hz, C5), 135.6 (d, $^{2}J_{C,P}$ = 21.2 Hz, C3), 133.6 (d, $^{2}J_{C,P}$ = 19.1 Hz, C6), 129.3 (C8), 128.6 (C7), 128.5 (d, $^{1}J_{C,P}$ = 6.3 Hz, C4), 120.5 (d, $^{3}J_{C,P}$ = 7.8 Hz, C2), 25.8 (C9), 18.4 (C11), −4.2 (C10).

^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$) δ (ppm): −6.9.

2.12.3. Synthesis of 4-(diphenylphosphoryl)phenol 15



The product was obtained in a 94% yield (398 mg, 1.43 mmol) as a colorless solid employing previously reported methodologies.[7]

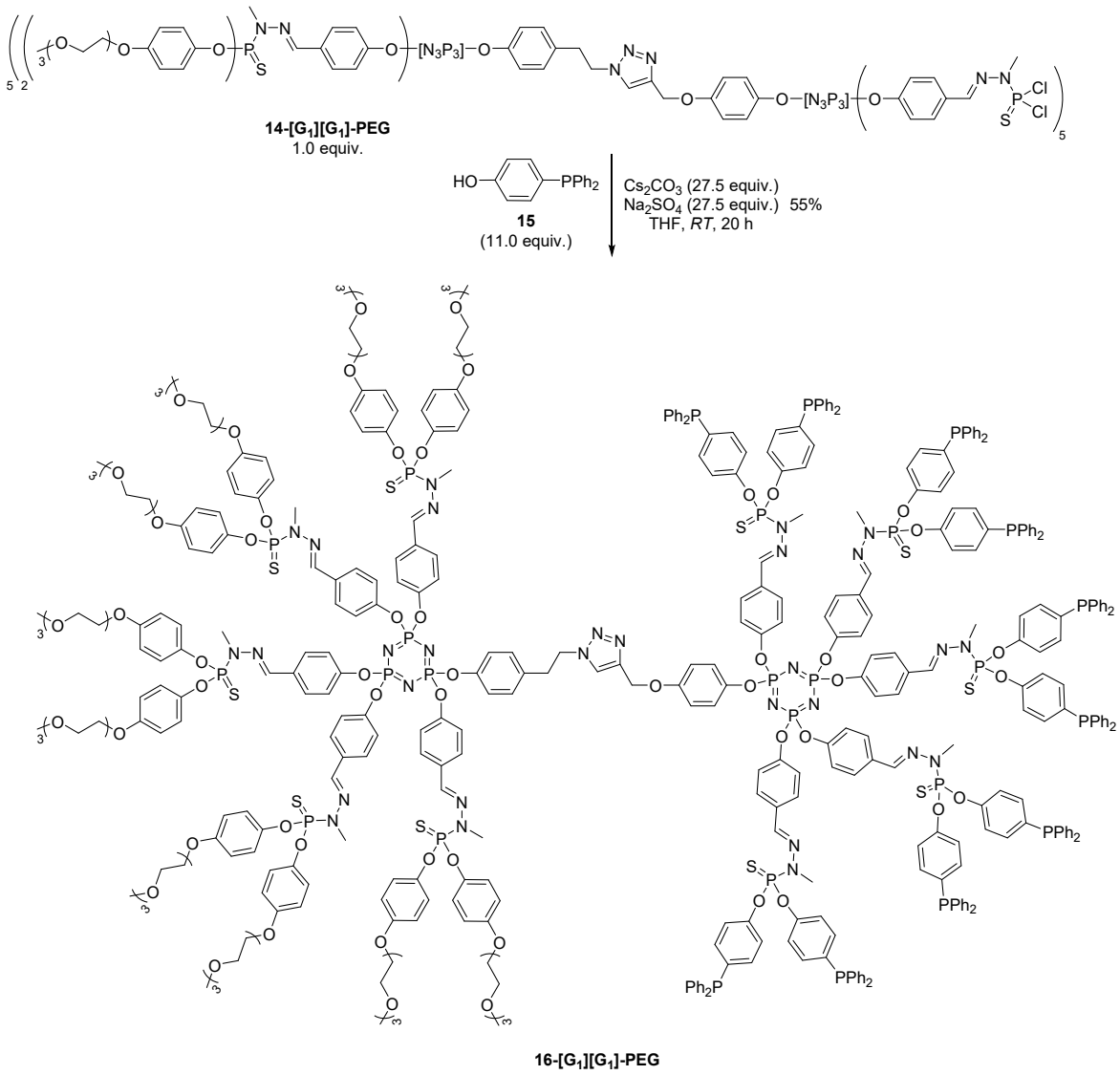
M.p.: 106 – 108 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.29 – 7.12 (m, 12H, H3, H6, H7, H8), 6.74 (d, $^{3}J_{H,H}$ = 8.2, 2H, H2), 4.91 (s, 1H, H9).

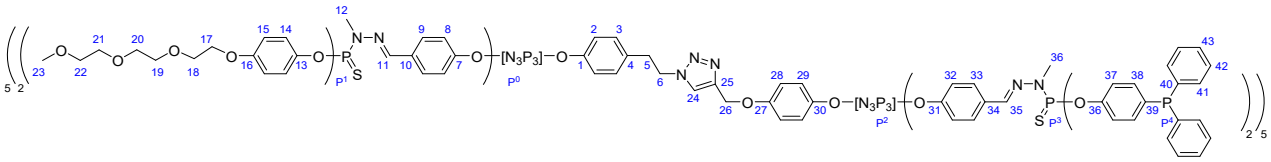
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ (ppm): 156.5 (C1), 137.9 (d, $^{2}J_{C,P}$ = 10.3 Hz, C3), 136.0 (d, $^{1}J_{C,P}$ = 21.3 Hz, C5), 133.6 (d, $^{2}J_{C,P}$ = 19.1 Hz, C6), 128.7 (C8), 128.6 (d, $^{3}J_{C,P}$ = 6.8 Hz, C7), 128.0 (d, $^{1}J_{C,P}$ = 8.1 Hz, C4), 115.9 (d, $^{3}J_{C,P}$ = 8.1 Hz, C2).

^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$) δ (ppm): −7.0.

2.12.4. Synthesis of 16-[G_1][G_1]-PEG



In a Schlenk flask equipped with a magnetic stirring bar, under nitrogen atmosphere, **14-[G_1][G_1]-PEG** dendrimer (93.0 mg, 0.017 mmol, 1.0 equiv.), 4-(diphenylphosphoryl)phenol (**15**) (50.9 mg, 0.183 mmol, 11.0 equiv.), dry cesium carbonate (0.15 g, 0.457 mmol, 27.5 equiv.), and anhydrous Na_2SO_4 (64.9 mg, 0.458 mmol, 27.5 equiv.) were suspended in dry and degassed THF (30 mL), and the mixture was stirred at room temperature overnight. Upon reaction completion (assessed by $^{31}P\{^1H\}$ NMR), the salts were filtered off by cannula filtration, and the crude was concentrated to 5 mL. The product was precipitated from *n*-pentane, the supernatant was removed, and the product washed with *n*-pentane/Et_2O (4:1) thrice. The volatiles were removed and the product was dried obtaining a colorless powder (73.2 mg, 0.091 mmol, 55% yield).



M.p.: 78 – 81 °C.

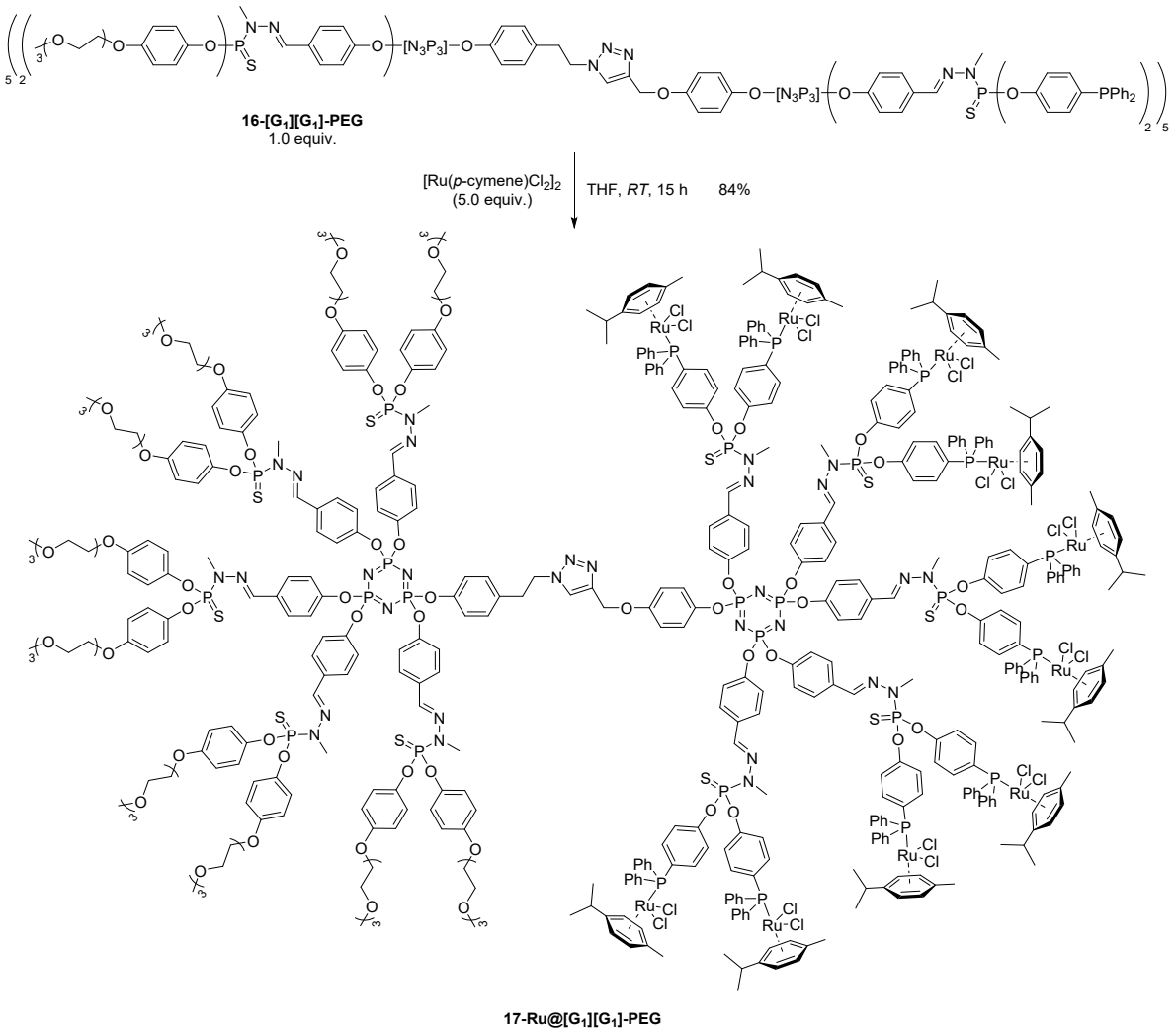
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.65 – 7.52 (m, 26H), 7.50 – 7.41 (m, 15H), 7.27 – 7.09 (m, 118H), 7.07 – 7.01 (m, 24H), 6.97 – 6.88 (m, 16H), 6.78 – 6.73 (m, 20H, H37), 4.88 (s, 2H, H26), 4.32 (m 2H, H5), 4.03 − 3.96 (m, 20H, H17), 3.81 – 3.73 (m, 20H, H19), 3.70 – 3.56 (m, 60H, H18, H20, H21), 3.55 – 3.46 (m, 20H, H19), 3.36 − 3.30 (m, 30H, H23), 3.29 – 3.17 (m, 32H, H6, H12, H36).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 157.0 (C13), 156.4 (C31), 137.0 (d, $^{1}J_{C,P}$ = 10.7 Hz, C40), 135.2 (2 × d, $^{2}J_{C,P}$ = 20.5 Hz, C38), 133.8 (2 × d, $^{2}J_{C,P}$ = 19.7 Hz, C41), 129.0 (C43), 128.8 (d, $^{3}J_{C,P}$ = 7.1 Hz, C42), 128.3 (m, C39), 122.7 − 122.2 (m, C15), 121.8 − 121.3 (m, C32), 115.5 – 115.3 (m, C37), 72.1 (C22) 70.9 (C19), 70.8 (C20), 70.7 (C21), 69.8 (C18), 67.9 (C17), 59.2 (C23). Only the signals from the dendrimer branches can be detected due to the low concentration and poor solubility of the compound in deuterated solvents.

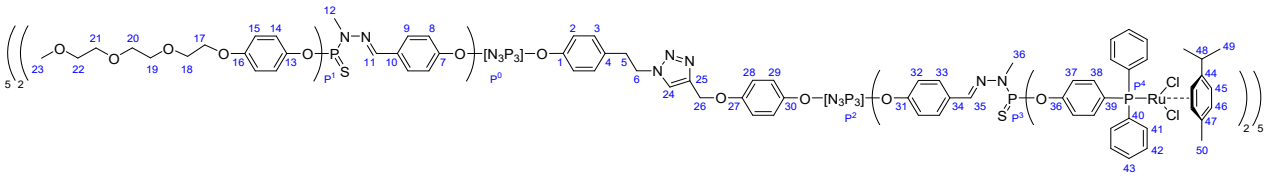
^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ (ppm): 64.5 (s, P^1), 61.5 (s, P^3), 61.1 (s, P^3), 8.7 −8.1 (m, P^0, P^2), −6.6 (s, P^4).

IR (ATR) ν (cm^{-1}): 2872, 1586, 1500, 1434, 1247, 1160, 1095, 913, 832, 781, 742, 695.

2.12.5. Synthesis of 17-Ru@[G_1][G_1]-PEG



In a Schlenk flask equipped with a magnetic stirring bar, under nitrogen atmosphere, **16-[G_1][G_1]-PEG** dendrimer (63.3 mg, 0.008 mmol, 1.0 equiv.) and Ru[(*p*-cymene)Cl_2]$_2$ (24.2 mg, 0.034 mmol, 5.0 equiv.) were dissolved in dry THF (10 mL), and the mixture was stirred at room temperature overnight. The evolution of the reaction was monitored by $^{31}P\{^1H\}$ NMR. Upon reaction completion, the solution was concentrated to 5 mL and the product was precipitated from *n*-pentane. The product was washed thrice with *n*-pentane/CH_2Cl_2 (4:1) to give a dark orange solid (73.2 mg, 0.007 mmol, 84% yield).



M.p.: 113 −117 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.88 – 7.64 (m, 41H), 7.40 – 7.26 (m, 118H), 7.12 – 6.99 (m, 42H), 6.85 – 6.70 (m, 20H), 5.20 (d, $^{3}J_{H,H}$ = 6.0 Hz, 20H, H45), 4.96 (d, $^{3}J_{H,H}$ = 6.0 Hz, 20H, H46), 4.09 – 3.93 (m, 20H, H17), 3.83 – 3.72 (m, 20H, H19), 3.72 – 3.56 (m, 60H, H18, H20, H21), 3.56 – 3.47 (m, 20H, H19), 3.34 (s, 30H, H23), 3.28 – 3.16 (m, 32H, H6, H12, H36), 2.33 – 2.18 (m, 10H, H48), 1.85 (s, 30H, H50), 1.11 (d, $^{3}J_{H,H}$ = 7.0 Hz, 60H, H15).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 134.3 (d, $^{2}J_{C,P}$ = 9.2 Hz, C41), 130.2 (C43), 128.0 (d, $^{3}J_{C,P}$ = 9.8 Hz, C42), 122.4 (C15), 115.4 (C37), 96.2 (C47), 87.3 (C45), 72.1 (C22) 70.9 (C19), 70.8 (C20), 70.7 (C21), 69.8 (C18), 67.9 (C17), 59.2 (C23), 29.9 (C48), 22.1 (C49), 17.9 (C50). Only the signals from the dendrimer branches can be detected due to the low concentration and poor solubility of the compound in deuterated solvents.

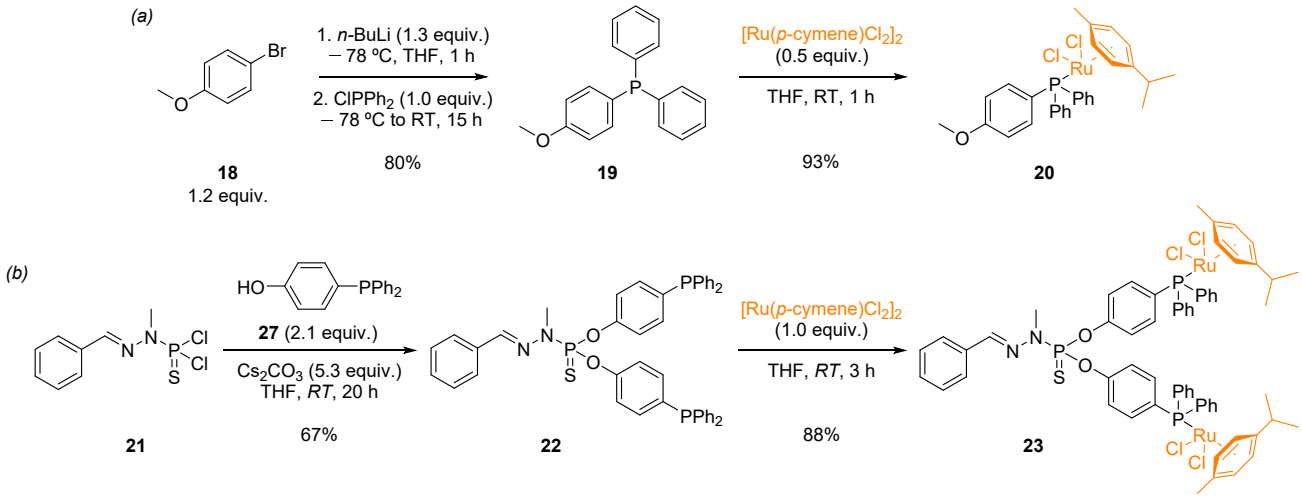
^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ (ppm): 64.6 (s, P^1), 61.0 (br s, P^3), 24.0 (d, $^{1}J_{P,Ru}$ = 37.2 Hz, P^4), 9.0 – 7.7 (m, P^0, P^2).

IR (ATR) ν (cm^{-1}): 2922, 1768, 1587, 1499, 1435, 1247, 1161, 1093, 1030, 941, 835, 796, 695.

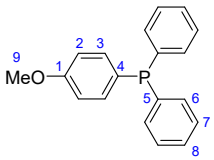
Elemental analysis (%) calcd. for $C_{507}H_{565}Cl_{20}N_{29}O_{73}P_{26}Ru_{10}S_{10}$: C 54.97; H 5.14; N 2.67; S 2.89; Found: C 54.37; H 5.50; N 2.69; S 2.24.

ICP-OES (%) calc. for $C_{507}H_{565}Cl_{20}N_{29}O_{73}P_{26}Ru_{10}S_{10}$: Ru 9.12; Found: Ru 9.1.

2.13. Synthesis of analogous Ru(*p*-cymene) derivatives



2.13.1. Synthesis of diphenyl(4-methoxyphenyl)phosphine 19



The product was obtained in a 80% yield (811 mg, 2.77 mmol) as a colorless powder employing previously reported methodologies.[8]

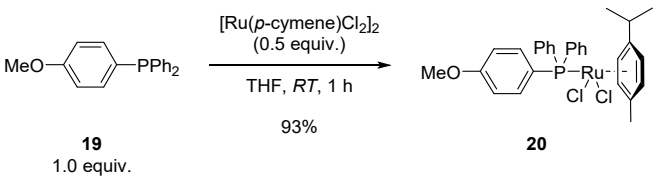
M.p.: 64 – 65 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.44 – 7.33 (m, 12H, H3, H6, H7, H8), 6.97 (dd, $^{3}J_{H,H}$ = 8.9 Hz, $^{4}J_{H,P}$ = 0.9 Hz, 2H, H2), 3.85 (s, 3H, H9).

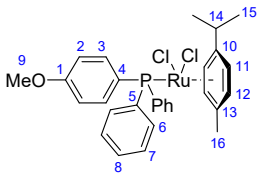
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ (ppm): 160.5 (C1), 138.0 (d, $^{1}J_{C,P}$ = 10.7 Hz, C5), 135.7 (d, $^{2}J_{C,P}$ = 21.5 Hz, C3), 133.5 (d, $^{3}J_{C,P}$ = 19.2 Hz, C6), 128.5 (C8), 128.4 (C7), 127.7 (d, $^{1}J_{C,P}$ = 8.2 Hz, C4), 114.3 (d, $^{3}J_{C,P}$ = 8.1 Hz, C2), 55.2 (C9).

^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$) δ (ppm): −7.0.

2.13.2. Synthesis of monometallic complex 20



In a Schlenk flask equipped with a magnetic stirring bar, under nitrogen atmosphere, diphenyl(4-methoxyphenyl)phosphine (**19**) (0.29 g, 0.98 mmol, 1.0 equiv.) and Ru[(*p*-cymene)Cl_2]$_2$ (0.30 g, 0.49 mmol, 0.5 equiv.) were dissolved in dry THF (10 mL), and the mixture stirred at room temperature until the formation of a precipitate (1 h). The supernatant was removed by cannula filtration, and the residue washed with *n*-hexane (10 mL) twice. The desired product was obtained as an orange powder (0.27 g, 0.46 mmol, 93% yield).



M.p. > 230 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.87 – 7.71 (m, 6H), 7.43 – 7.30 (m, 6H), 6.86 (dd, $^{3}J_{H,H}$ = 7.3 Hz, $^{4}J_{H,P}$ = 1.8 Hz 2H, H2), 5.20 (d, $^{3}J_{H,H}$ = 6.0 Hz, 2H, H11), 4.97 (d, $^{3}J_{H,H}$ = 5.6 Hz, 2H, H12), 3.80 (s, 3H, H9), 2.86 (sept, $^{3}J_{H,H}$ = 6.9 Hz, 1H, H14), 1.86 (s, 3H, H16), 1.10 (d, $^{3}J_{H,H}$ = 6.9 Hz, 6H, H15).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ (ppm): 161.2 (d, $^{4}J_{C,P}$ = 2.3 Hz, C1), 136.5 (d, $^{2}J_{C,P}$ = 11.1 Hz, C3), 134.7 (d, $^{1}J_{C,P}$ = 45.8 Hz, C5),134.2 (d, $^{2}J_{C,P}$ = 9.3 Hz, C6), 130.2 (d, $^{4}J_{C,P}$ = 2.6 Hz, C8), 128.1 (d, $^{3}J_{C,P}$ = 9.9 Hz, C7), 123.9 (d, $^{1}J_{C,P}$ = 50.5 Hz, C4), 113.7 (d, $^{3}J_{C,P}$ = 11.0 Hz, C2), 111.2 (d, $^{3}J_{C,P}$ = 3.5 Hz, C10), 96.0 (C13), 89.1 (d, $^{4}J_{C,P}$ = 3.2 Hz, C12), 87.3 (d, $^{4}J_{C,P}$ = 5.6 Hz, C11), 55.4 (C9), 30.4 (C14), 22.0 (C15), 17.9 (C16).

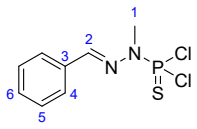
^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$) δ (ppm): 23.2.

IR (ATR) ν (cm^{-1}): 3051, 2972, 1735, 1593, 1568, 1497, 1479, 1460, 1434, 1380, 1305, 1288, 1254, 1181, 1161, 1092, 1060, 1020, 829, 801, 755, 697.

HRMS (ESI TOF *m/z*) calcd. for $C_{29}H_{31}ClOPRu$ $[M\text{-}Cl]^+$: 563.0917; Found: 563.0846.

Elemental analysis (%) calcd. for $C_{29}H_{31}Cl_2OPRu$: C: 58.20; H 5.22; Found: C 58.65; H 5.05.

2.13.3. Synthesis of (2-benzylidene-1-methylhydrazineyl)phosphonothioic dichloride 21



The product was obtained in a 90% yield (2.39 g, 8.96 mmol) as a colorless powder employing previously reported methodologies.[9]

M.p.: 61 − 62 °C.

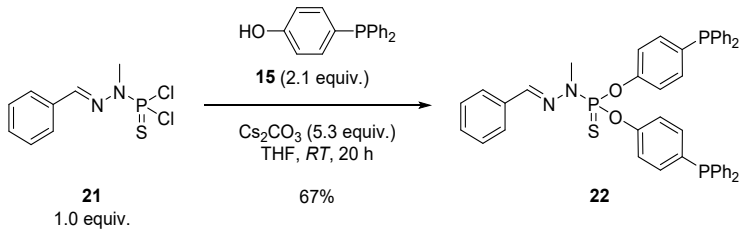
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.79-7.69 (m, 3H, H2, H4), 7.47-7.37 (m, 3H, H5, H6), 3.51 (d, *J* = 14.0 Hz, 3H, H1).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 141.9 (d, $^3J_{C,P}$ = 18.7 Hz, C2), 134.1 (d, $^4J_{C,P}$ = 1.6 Hz, C3), 130.2 (C6), 128.8 (C4), 127.4 (C5), 31.8 (d, $^2J_{C,P}$ = 13.4 Hz, C1).

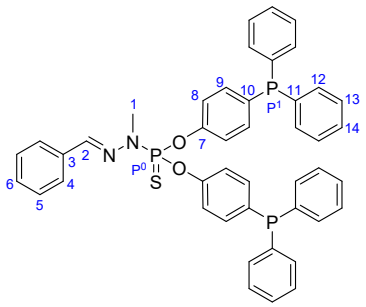
^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ (ppm): 63.4.

IR (ATR) ν (cm^{-1}): 2358, 1737, 1440, 1369, 1238, 1138, 954, 946, 771, 752, 689.

2.13.4. Synthesis of *O,O*-bis(4-(diphenylphosphanyl)phenyl)(2-benzylidene-1-methylhydrazineyl)-phosphonothioate 22



In a Schlenk flask equipped with a magnetic stirring bar, under nitrogen atmosphere, (2-benzylidene-1-methylhydrazineyl)phosphonothioic dichloride (**21**) (0.20 g, 0.749 mmol, 1.0 equiv.), 4-(diphenylphosphoryl)phenol (**15**) (0.44 g, 1.57 mmol, 2.1 equiv.), and cesium carbonate (1.28 g, 3.93 mmol, 5.3 equiv.) were suspended in dry and degassed THF (20 mL), and the mixture was stirred at room temperature overnight. Upon reaction completion (followed by ^{31}P{^{1}H} NMR), the salts were filtered off with cannula, the volatiles removed under reduced pressure, and the product purified by column chromatography on silica (*n*-hexane/EtOAc 8:2 to 1:1). The fractions containing the product were collected and dried *in vacuo* affording a colorless powder (0.38 g, 0.50 mmol, 67% yield).

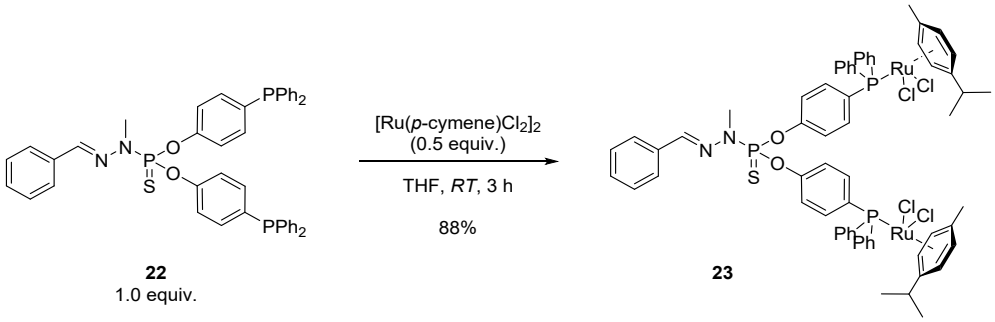


^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.80 – 7.70 (m, 3H, H2, H4), 7.49 – 7.27 (m, 30H, H5, H6, H10, H11, H14, H15), 3.47 (d, $^{3}J_{H,P}$ = 10.7 Hz, 3H, H1).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 151.4 (d, $^{2}J_{C,P}$ = 7.5 Hz, C7), 140.0 (d, $^{3}J_{C,P}$ = 13.7 Hz, C11), 137.2 (d, $^{1}J_{C,P}$ = 10.7 Hz, C12), 135.2 (dd, $J_{C,P}$ = 20.4, 1.5 Hz, C9), 134.9 (C2), 134.1 (d, $^{4}J_{C,P}$ = 2.2 Hz, C14), 133.8 (dd, $^{1}J_{C,P}$ = 19.6, 1.7 Hz, C10), 129.7 (C3), 129.0 (C6), 128.9 (C4), 128.7 (d, $^{3}J_{C,P}$ = 6.9 Hz, C13), 127.2 (C5), 121.7 (dd, $^{3}J_{C,P}$ = 7.3, 4.9 Hz, C8), 33.1 (d, $^{2}J_{C,P}$ = 13.3 Hz, C1).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ (ppm): 61.5 (P^0), −6.4 (P^1).

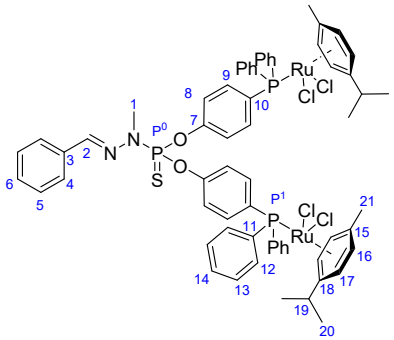
2.13.5. Synthesis of bimetallic complex 23



22
1.0 equiv.

23

In a Schlenk flask equipped with a magnetic stirring bar, under nitrogen atmosphere, *O,O*-bis(4-(diphenylphosphanyl)phenyl)(2-benzylidene-1-methylhydrazineyl)phosphonothioate (**22**) (0.17 g, 0.22 mmol, 1.0 equiv.) and [Ru(*p*-cymene)Cl_2]$_2$ (68.1 mg, 0.11 mmol, 0.5 equiv.) were added to dry and degassed THF (10 mL), and the mixture was stirred at room temperature for 3 h. Upon reaction completion (followed by ^{31}P{^{1}H} NMR), the volatiles were removed under reduced pressure and the crude was purified by column chromatography on silica (EtOAc 100%), affording the desired product as a dark orange powder (0.27 g, 0.20 mmol, 88% yield).



M.p.: 119 – 121 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.81 – 7.73 (m, 12H), 7.66 – 7.59 (m, 3H), 7.41 – 7.30 (m, 15H), 7.17 (d, $^{3}J_{H,H}$ = 8.6 Hz, 4H, H8), 5.17 (d, $^{3}J_{H,H}$ = 5.2 Hz, 4H, H17), 4.96 (d, $^{3}J_{H,H}$ = 5.2 Hz, 4H, H16), 3.34 (d, $^{2}J_{H,P}$ = 10.7 Hz, 3H, H1), 2.80 (sept, $^{3}J_{H,H}$ = 6.9 Hz, 2H, H19), 1.82 (s, 6H, H21), 1.07 (d, $^{3}J_{H,H}$ = 6.9 Hz, 12H, H20).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 152.2 (dd, $^{2}J_{C,P}$ = 7.3 Hz, $^{4}J_{C,P}$ = 2.5 Hz, C7), 140.3 (d, $^{1}J_{C,P}$ = 14.1 Hz, C11), 135.9 (d, $^{2}J_{C,P}$ = 10.3 Hz, C12), 134.6 (s, C2) 134.3 (d, $^{2}J_{C,P}$ = 9.5 Hz, C9), 133.9 (C14), 1335 (C3), 130.4 (C6), 130.0 (C4), 128.8 (C13), 128.1 (d, $^{1}J_{C,P}$ = 9.7 Hz, C10), 127.1 (C5), 120.78 (dd, $^{3}J_{C,P}$ = 10.8, 5.0 Hz, C8), 111.2 (d, $J_{C,P}$ = 3.3 Hz, C18), 96.1 (C15), 89.1 (m, C16), 87.2 (d, $J_{C,P}$ = 5.5 Hz, C17), 53.5 (C1), 30.3 (C19), 21.9 (C20), 17.8 (C21).

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ (ppm): 60.6 (P^0), 23.7 (P^1).

IR (ATR) ν (cm^{-1}): 3653, 3051, 2961, 1588, 1485, 1436,1377, 1205, 1166, 1093, 1019, 912, 840, 795, 770, 695.

HRMS (ESI TOF m/z) calcd. for $C_{64}H_{65}Cl_4N_2NaO_2P_3Ru_2S$ $[M+Na]^+$: 1385.0821; Found: 1385.0717.

Elemental analysis (%) calcd. for $C_{64}H_{65}Cl_4N_2O_2P_3Ru_2S$: C 56.39; H 4.81; N 2.06; S 2.05; Found: C 56.04; H 4.61; N 1.59; S 1.89.

2.14. Activity of [Ru(*p*-cymene)Cl_2]$_2$ derivatives in the isomerization of allyl alcohols

2.14.1. General procedure for the isomerization in THF

To a solution of the corresponding allyl alcohol (**24**, **26**-**29**, **Figure S1**) (1.29 mmol, 1.0 equiv.), Cs_2CO_3 (0.026 mmol, 0.02 equiv.) and 1,3,5-trimethoxybenzene (0.640 mmol, 0.5 equiv., used as an internal standard) in THF (6 mL) and heated up at 75 °C, the appropriate catalyst (1 mol% of "ruthenium" –quantity of ruthenium complexes–; 7.8 mg of monometallic **22**, 8.7 mg of bimetallic **23**, and 13.3 mg of **17-Ru@[G_1][G_1]-PEG**) was added in one portion in nitrogen flow. The resulting mixture was vigorously stirred under given conditions for up to 24 h. An aliquot (0.2 mL) was taken at selected times and the conversion of the substrate was determined by GC by comparing the crude mixtures with original samples.

Upon full conversion (determined by GC), the reaction mixture was allowed to cool down to room temperature, the salts filtered, and the solution concentrated to 2 mL. Later, it was precipitated from *n*-pentane (20 mL), and centrifuged. The supernatant was taken, and the volatiles were removed under reduced pressure. The obtained crude was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc 9:1) affording the desired as colorless oils.

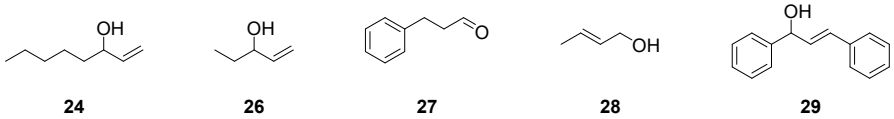


Figure S1. Substrates tested for the isomerization of allyl alcohols.

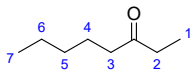
2.14.2. General procedure for the isomerization in H_2O/*n*-heptane

To a solution of the corresponding allyl alcohol (**24**, **26**-**29**, **Figure S1**) (1.29 mmol, 1.0 equiv.), Cs_2CO_3 (0.026 mmol, 0.02 equiv.) and 1,3,5-trimethoxybenzene (0.640 mmol, 0.5 equiv., used as an internal standard) in a *n*-heptane/water 1:1 mixture (6 mL) and heated up at 75 °C, the appropriate catalyst (1 mol% of "ruthenium" –quantity of ruthenium complexes–; 7.8 mg of monometallic **22**, 8.7 mg of bimetallic **23**, and 13.3 mg of **17-Ru@[G_1][G_1]-PEG**) was added in one portion in nitrogen flow. The resulting mixture was vigorously stirred under given conditions for up to 24 h. An aliquot (0.2 mL) was taken at selected times and the conversion of the substrate was determined by GC by comparing the crude mixtures with original samples.

Upon full conversion (determined by GC, or a maximum of 24 h of reaction), the reaction mixture was allowed to cool down to room temperature, and the organic phase taken. The crude was dried over anhydrous Na_2SO_4, filtered, and the volatiles removed under reduced pressure. The desired products were obtained after flash column chromatography on silica gel (*n*-hexane/EtOAc 9:1) affording colorless oils.

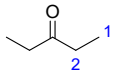
For the recyclability tests, the reaction was performed for 24 h. Upon reaction time, stirring was stopped observing the formation of two layers. The organic layer was recovered and analyzed by GC to assess conversion. Then, fresh *n*-heptane (3.0 mL), 1-octen-3-ol (0.200 mL, 1.29 mmol, 1.0 equiv.) and 1,3,5-trimethoxybenzene (0.640 mmol, 0.5 equiv.) were added to the remaining aqueous phase.

2.14.3. Substrate scope characterization



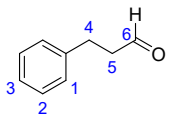
The product was obtained in a 98% yield (162 mg, 1.26 mmol) as a colorless oil, and NMR is in accordance with previously reported procedures.[10]

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.45 – 2.30 (m, 4H, H3, H2), 1.62 – 1.46 (m, 2H, H4), 1.38 – 1.14 (m, 4H, H5, H6), 1.02 (t, $^3J_{H,H}$ = 7.3 Hz, 3H, H1), 0.85 (t, $^3J_{H,H}$ = 7.3 Hz, 3H, H7).



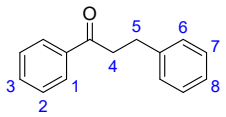
The product was obtained in a 97% yield (107 mg, 1.25 mmol) as a colorless oil, and NMR is in accordance with previously reported procedures.[10]

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.41 (q, $^3J_{H,H}$ = 7.4 Hz, 4H, H2), 1.04 (q, $^3J_{H,H}$ = 7.4 Hz, 6H, H1).



The product was obtained in a 98% yield (169 mg, 1.26 mmol) as a colorless oil, and NMR is in accordance with previously reported procedures.[11]

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 9.85 (t, $^3J_{H,H}$ = 1.4 Hz, 1H, H6), 7.39 – 7.18 (m, 5H, H1, H2, H3), 3.04 – 2.96 (m, 2H, H4), 2.85 – 2.77 (m, 2H, H5).



The product was obtained in a 95% yield (261 mg, 1.24 mmol) as a colorless oil, and NMR is in accordance with previously reported procedures.[12]

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.00 – 7.95 (m, 2H, H1), 7.59 – 7.54 (m, 1H, H3), 7.49 – 7.44 (m, 2H, H2), 7.34 – 7.30 (m, 2H, H7), 7.29 – 7.25 (m, 2H, H6), 7.24 – 7.20 (m, 1H, H8), 3.34 – 3.29 (m, 2H, H4), 3.12 – 3.06 (m, 3H, H5).

3. Spectra and analyses of selected compounds

3.1. Synthesis of 4-(2-bromoethylphenol) 31

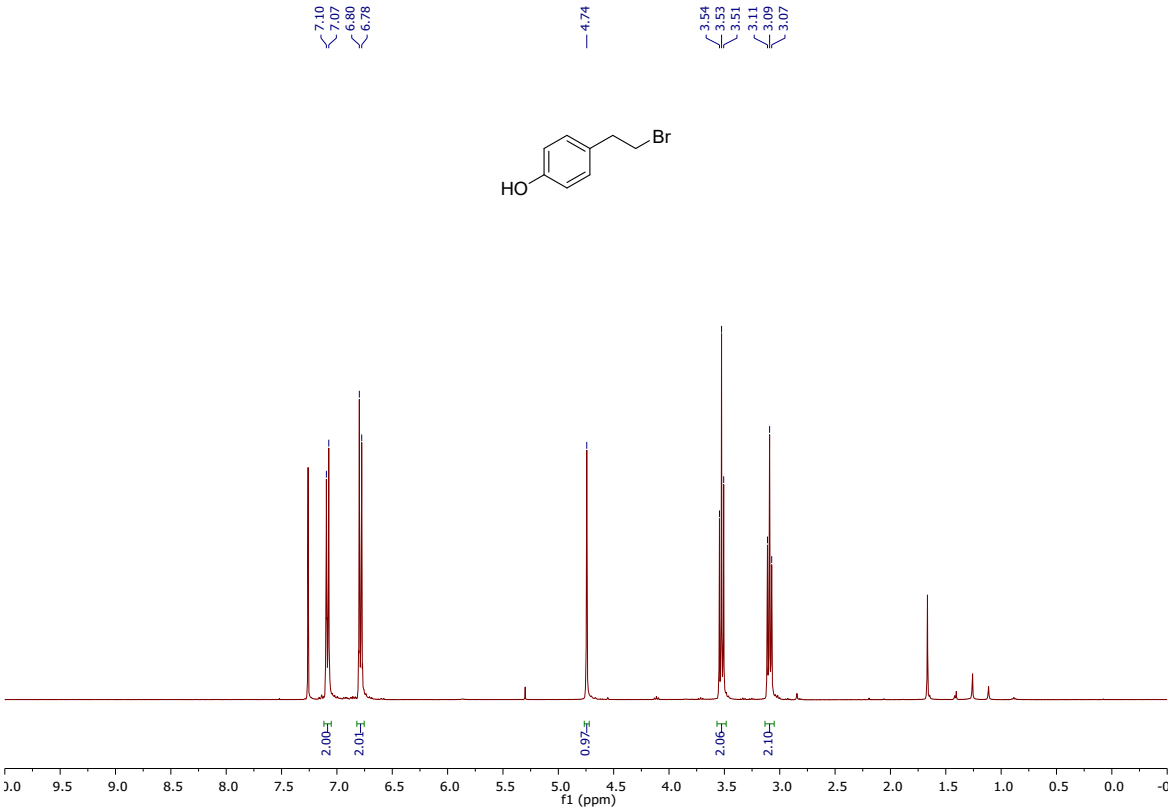


Figure S2.[1]H NMR spectrum of 4-(2-bromoethylphenol) **31** in $CDCl_3$ recorded at room temperature (400 MHz).

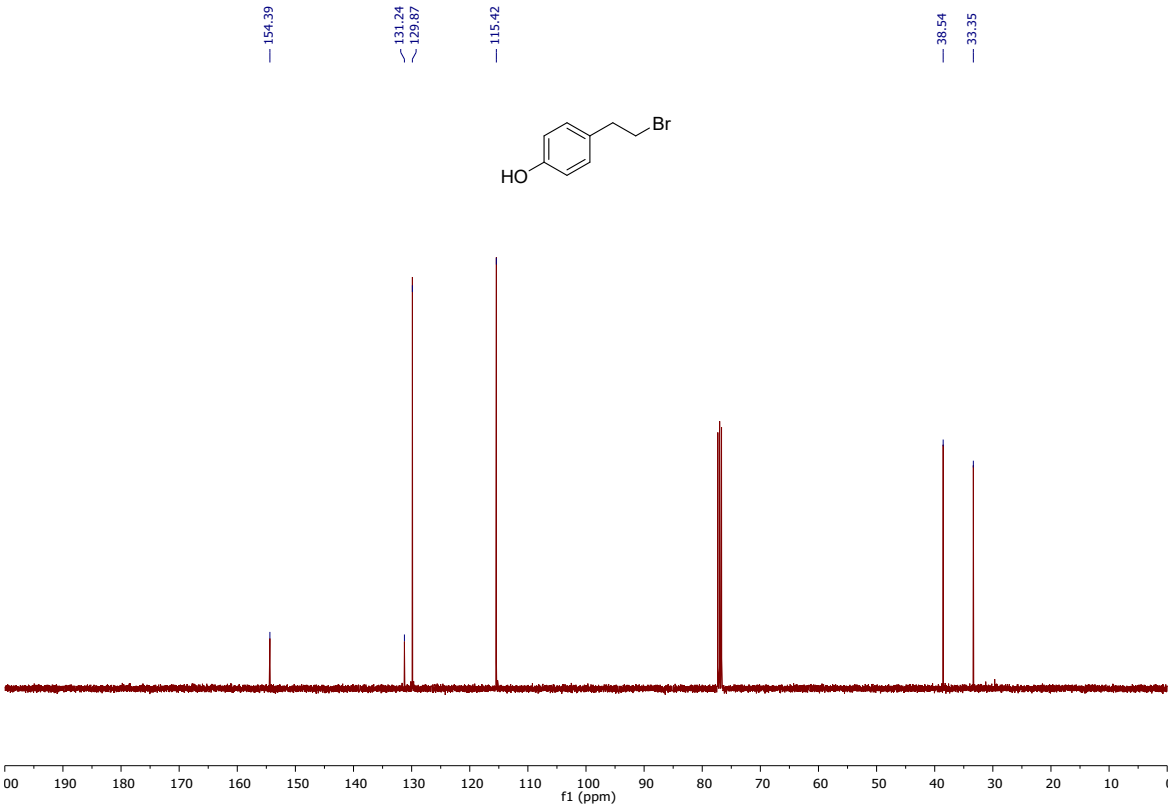


Figure S3. $^{13}C\{^1H\}$ NMR spectrum of 4-(2-bromoethylphenol) **31** in $CDCl_3$ recorded at room temperature (101 MHz).

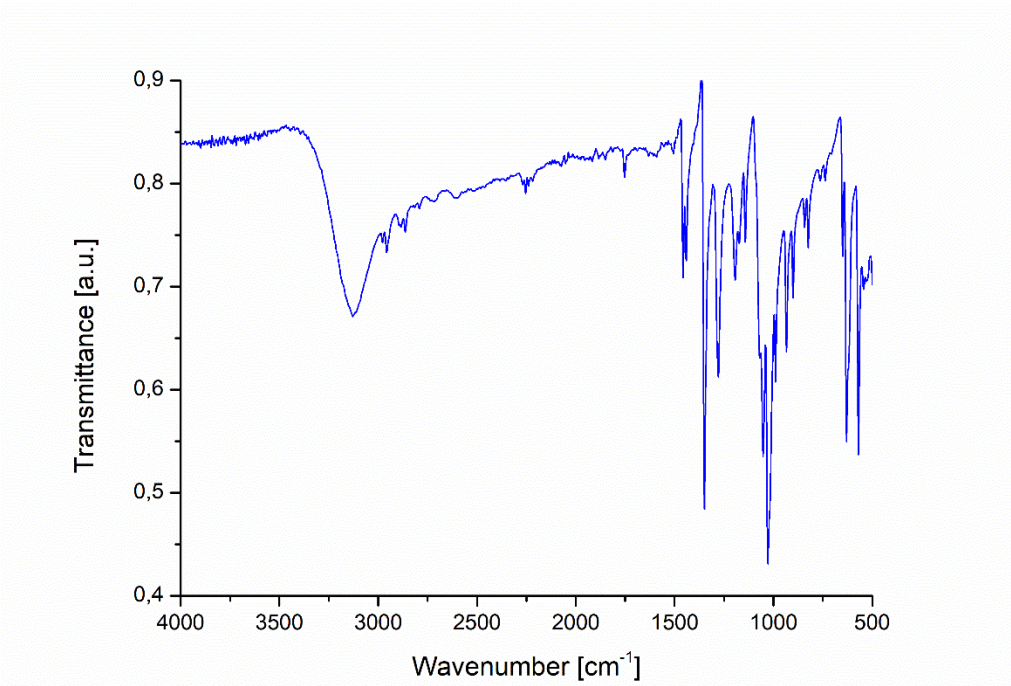


Figure S4. FT-IR spectrum of 4-(2-bromoethylphenol) **31**.

3.2. Synthesis of 4-(2-azidoethyl)phenol 2

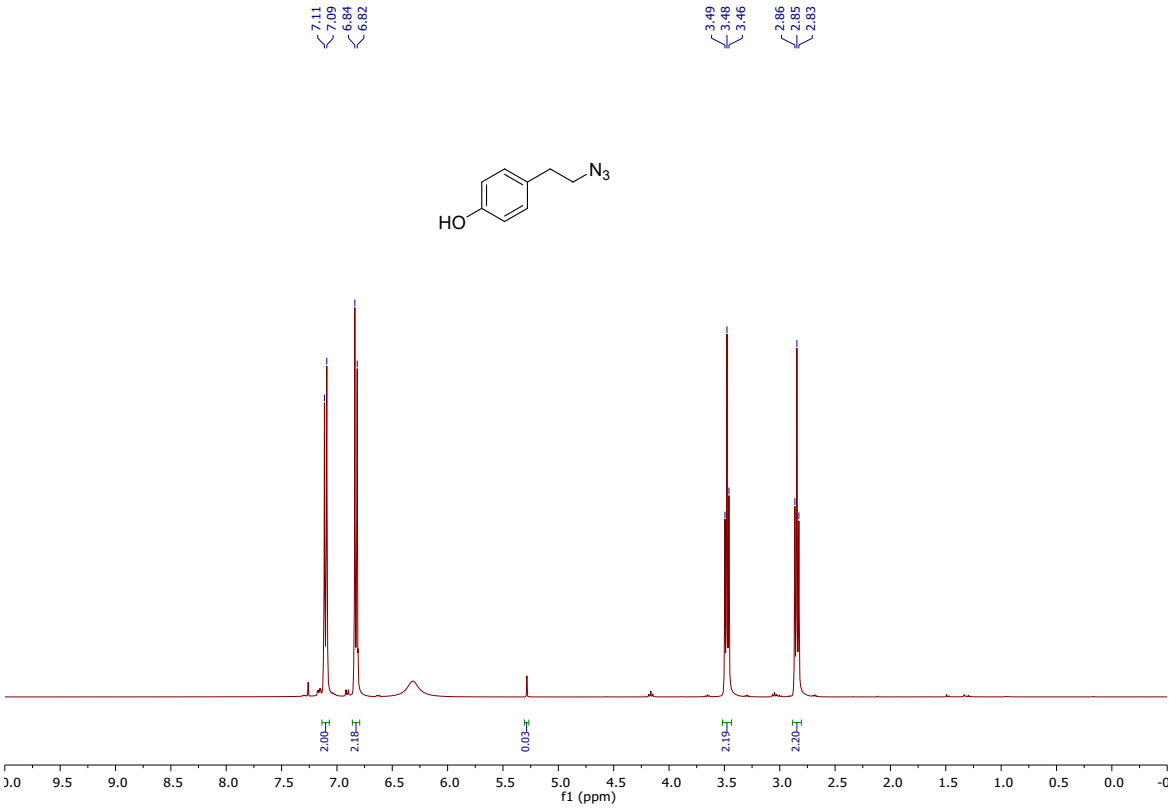


Figure S5. ^{1}H NMR spectrum of 4-(2-azidoethylphenol) **2** in $CDCl_3$ recorded at room temperature (400 MHz).

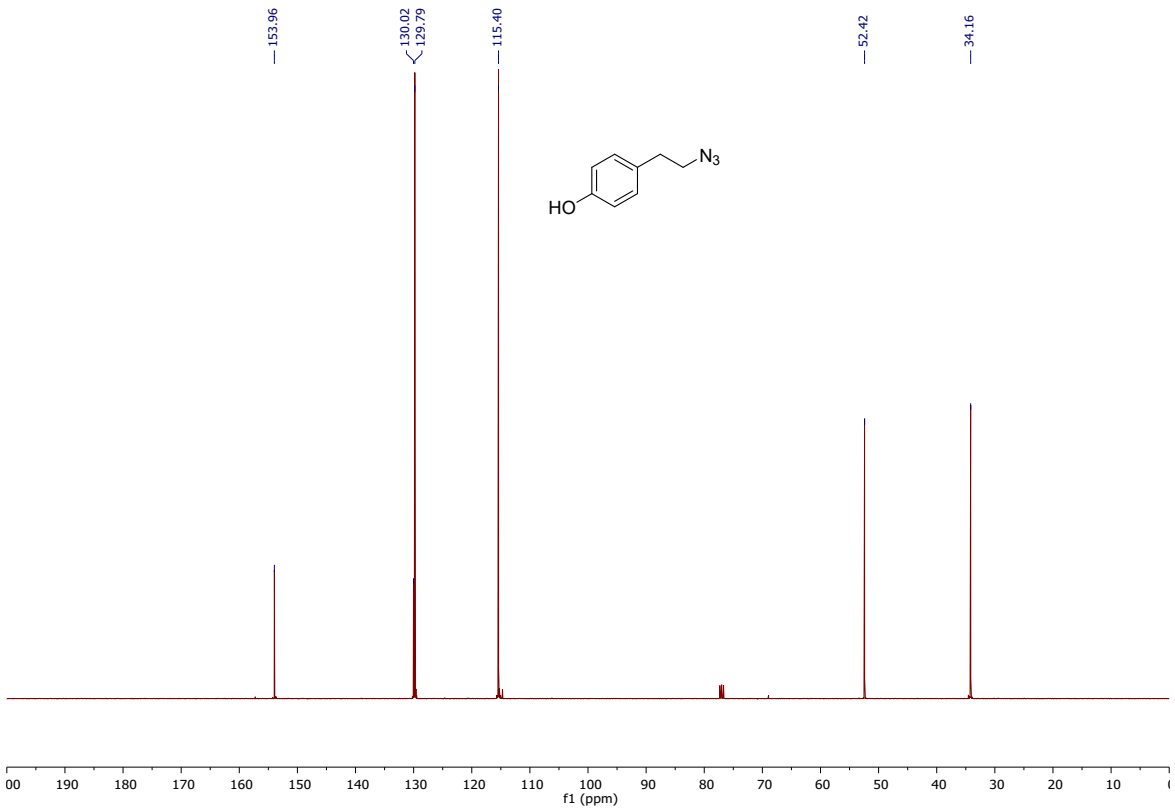


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of 4-(2-azidoethylphenol) **2** in $CDCl_3$ recorded at room temperature (101 MHz).

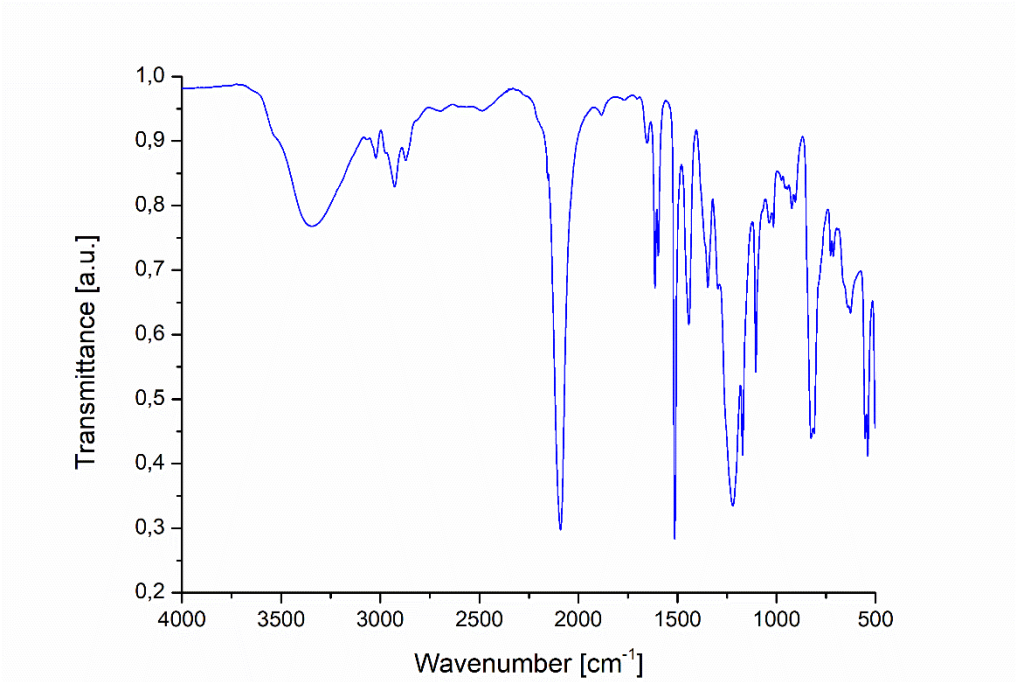


Figure S7. FT-IR spectrum of 4-(2-azidoethylphenol) **2**.

3.3. Synthesis of 4-(prop-2-yn-yloxy)phenol 3

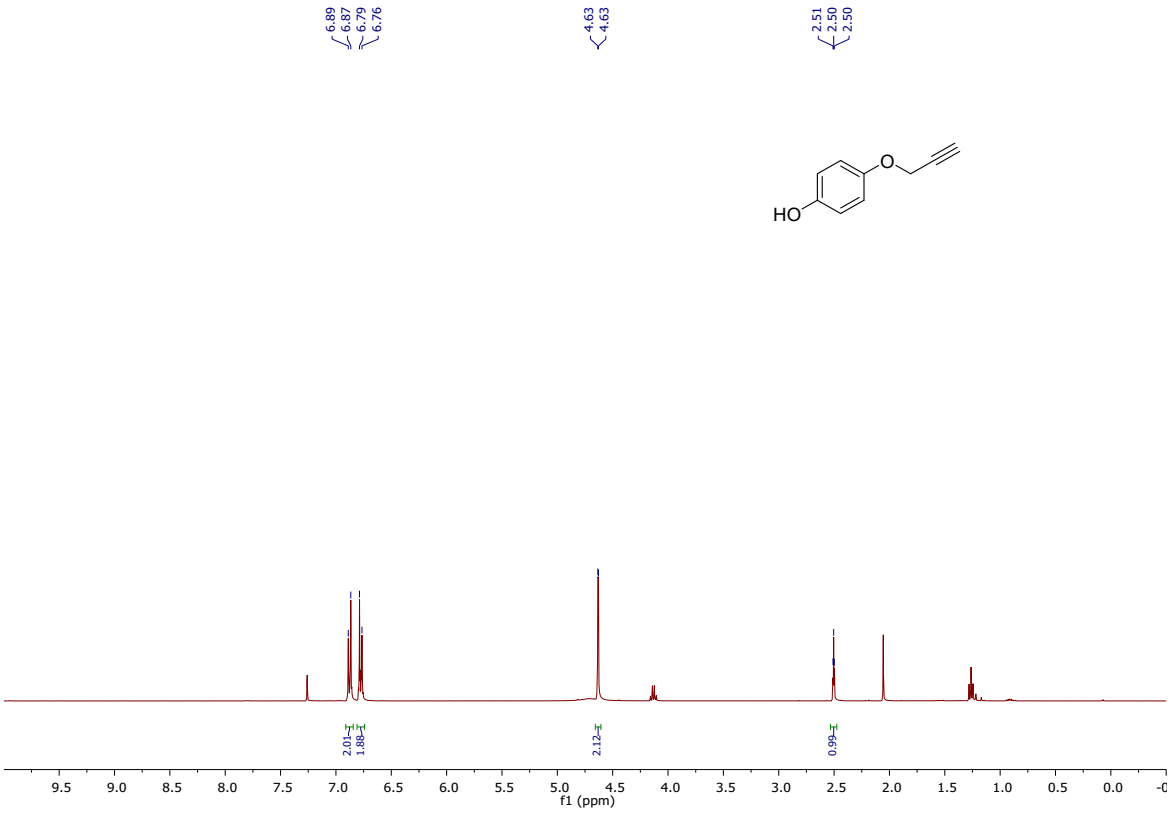


Figure S8. ^{1}H NMR spectrum of 4-(prop-2-yn-yloxy)phenol **3** in $CDCl_3$ recorded at room temperature (400 MHz).

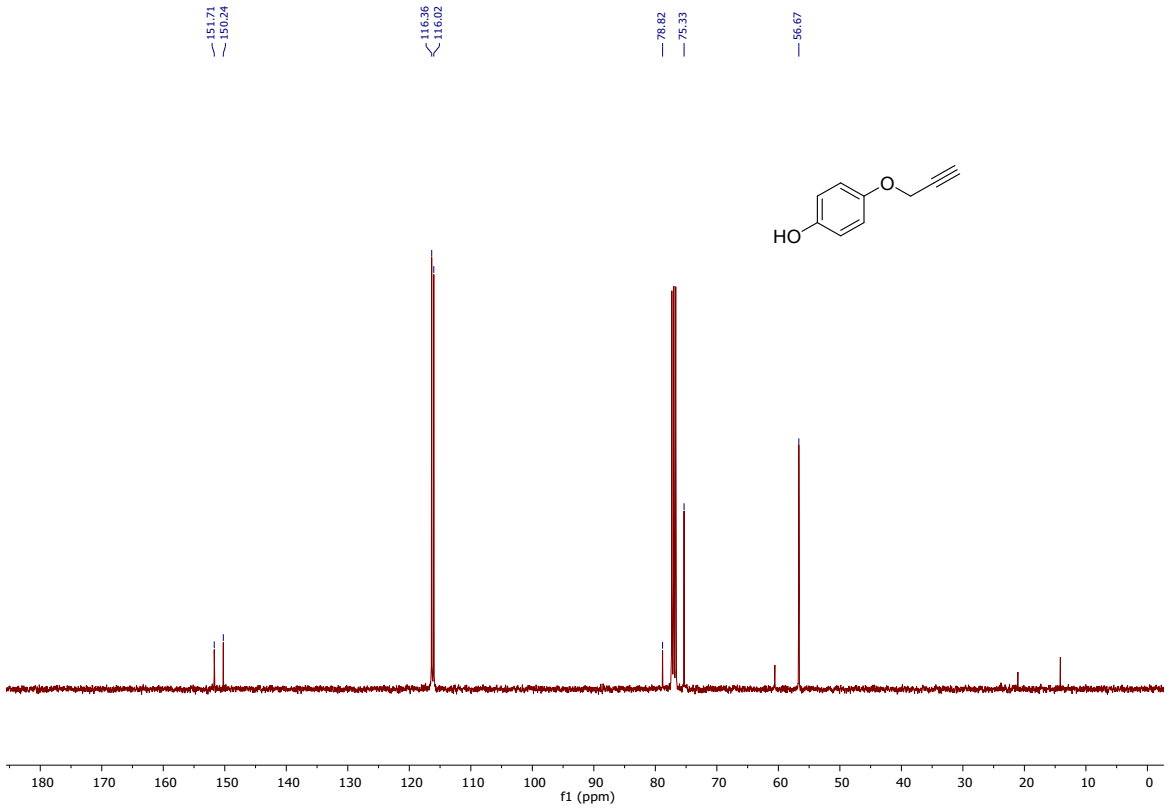


Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum of 4-(prop-2-yn-yloxy)phenol **3** in $CDCl_3$ recorded at room temperature (101 MHz).

3.4. Synthesis of 2-(4-(2-azidoethyl)phenoxy)-2,4,4,6,6-pentachlorotriazatriphosphazene 4

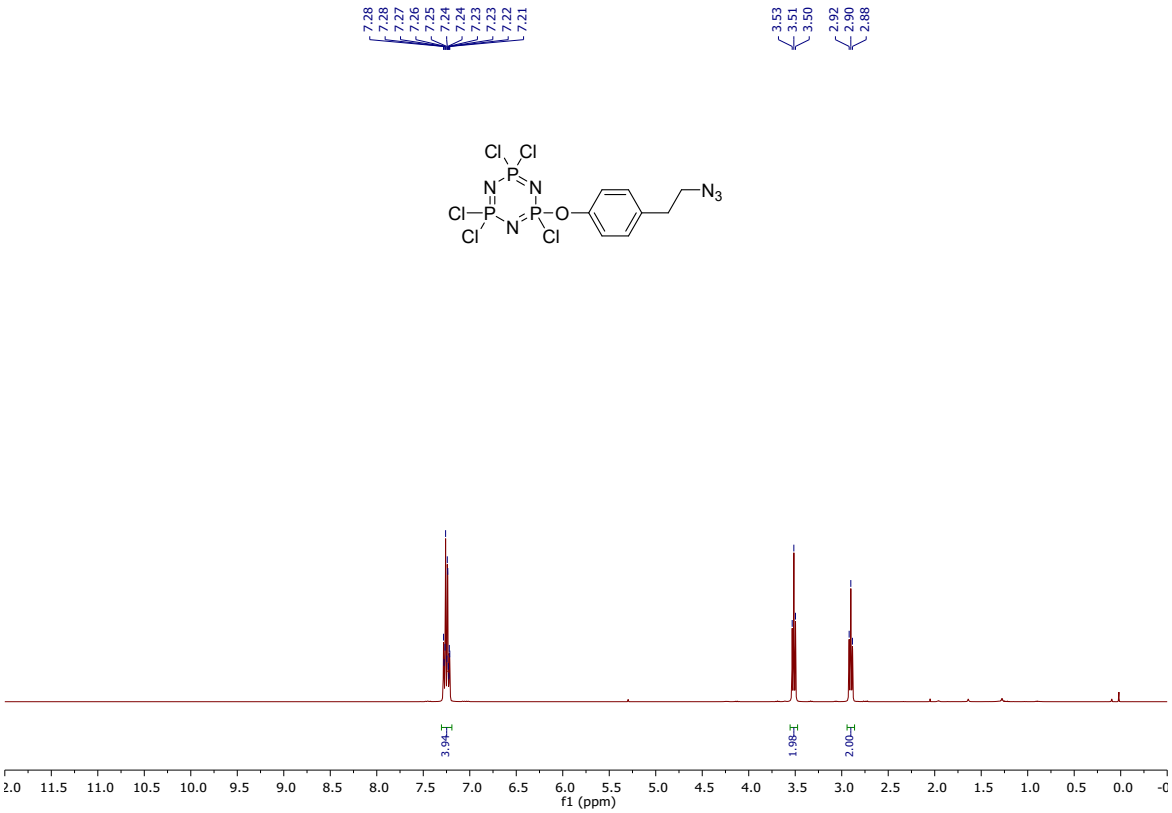


Figure S10. ^{1}H NMR spectrum of 2-(4-(2-azidoethyl)phenoxy)-2,4,4,6,6-pentachlorotriazatriphosphazene **4** in $CDCl_3$ recorded at room temperature (400 MHz).

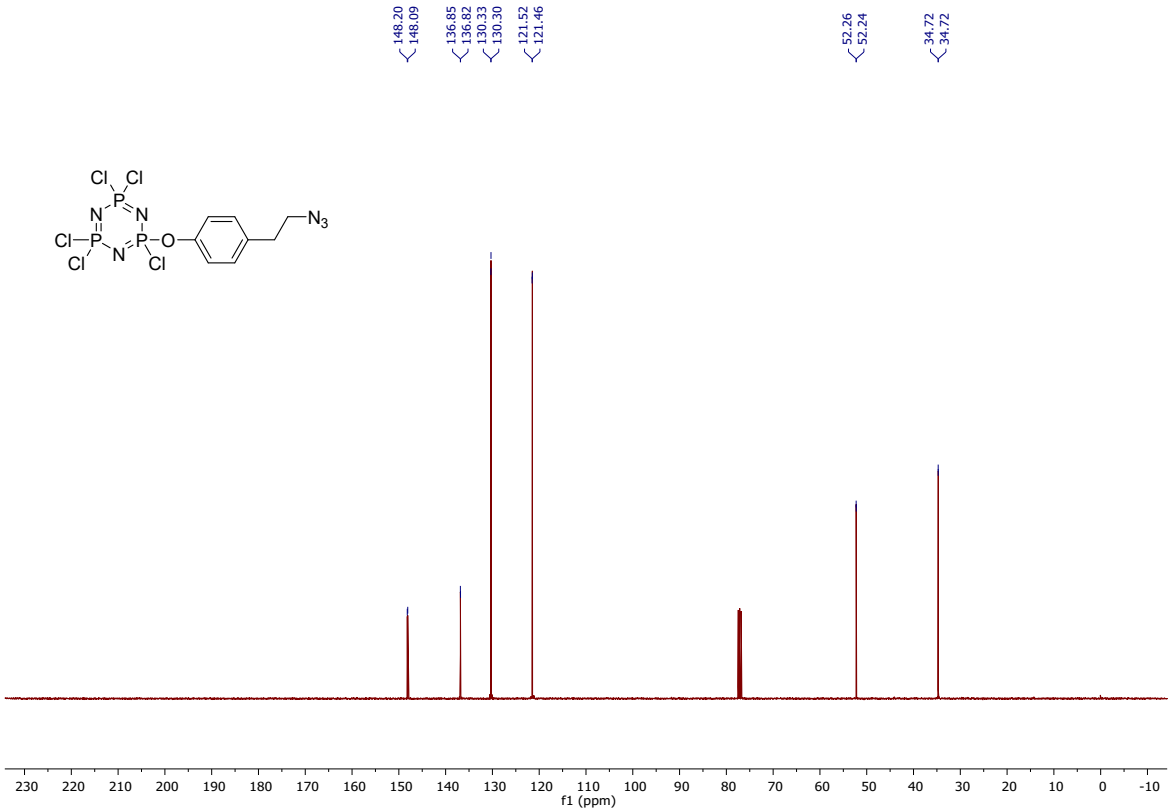


Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of 2-(4-(2-azidoethyl)phenoxy)-2,4,4,6,6-pentachlorotriazatriphosphazene **4** in $CDCl_3$ recorded at room temperature (101 MHz).

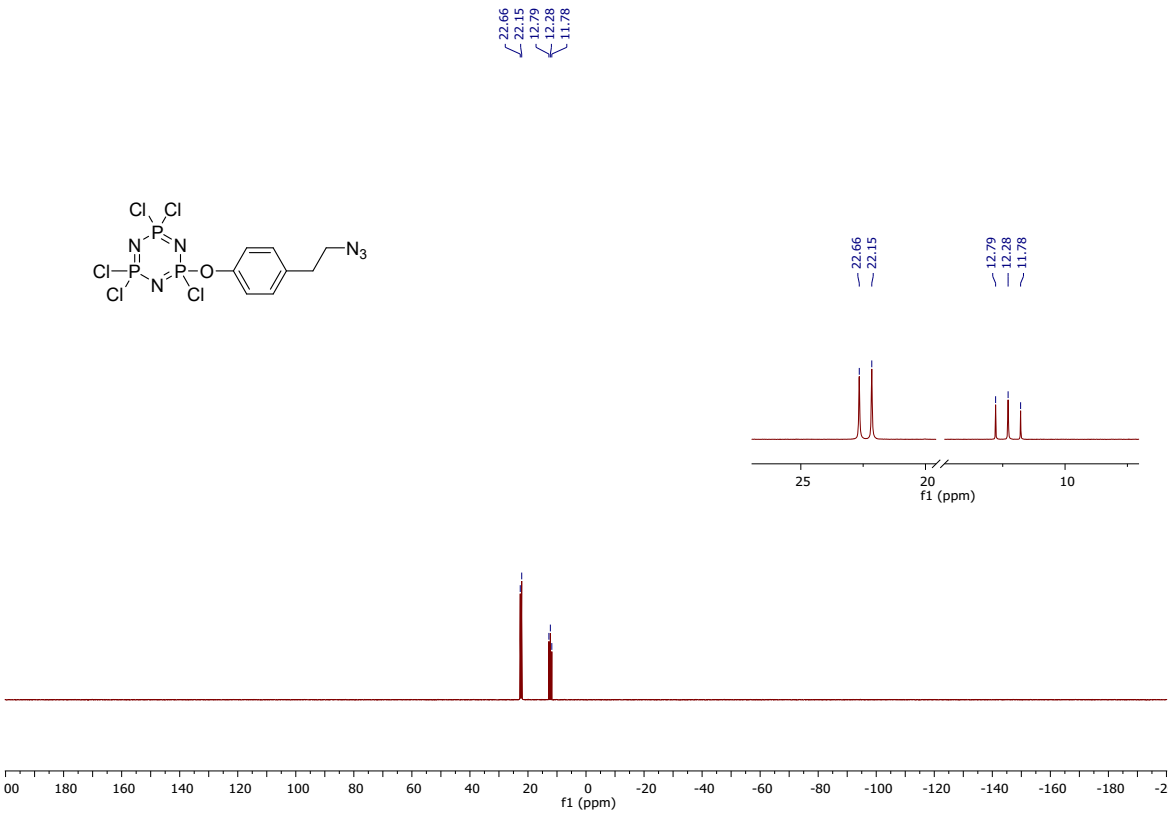


Figure S12. $^{31}P\{^{1}H\}$ NMR spectrum of 2-(4-(2-azidoethyl)phenoxy)-2,4,4,6,6-pentachlorotriazatriphosphazene **4** in $CDCl_3$ recorded at room temperature (162 MHz).

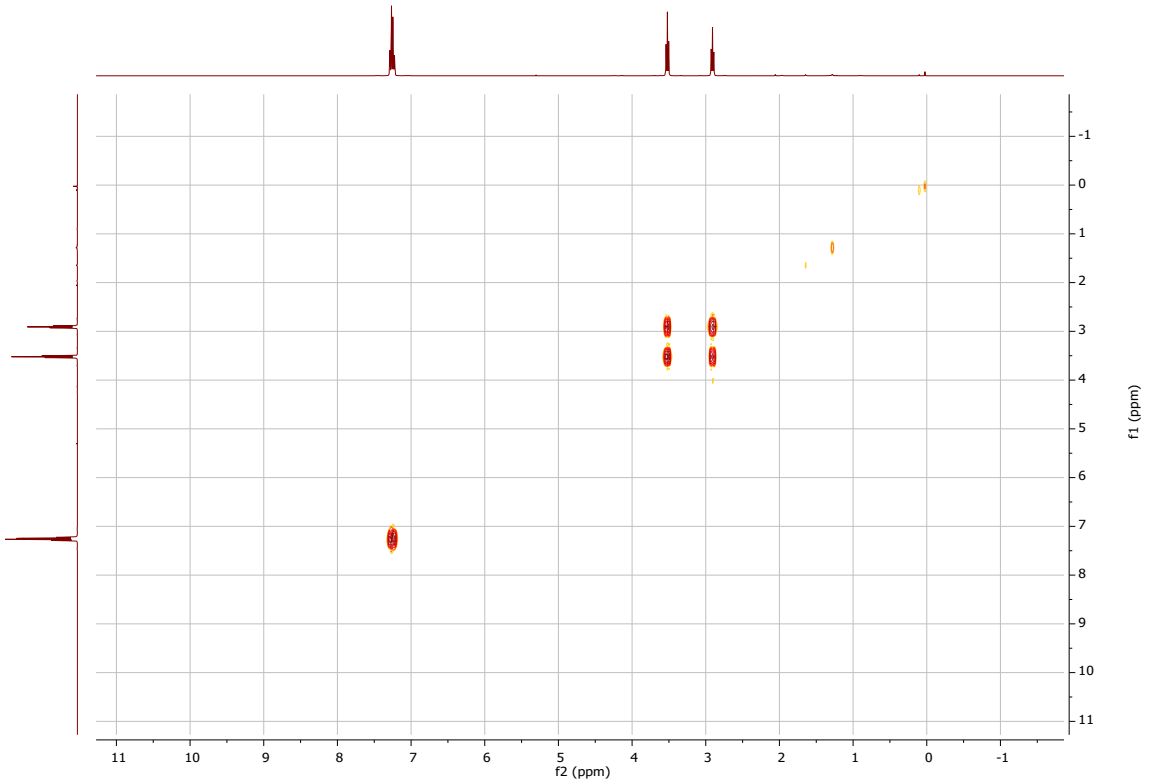


Figure S13. ^{1}H-^{1}H COSY spectrum of 2-(4-(2-azidoethyl)phenoxy)-2,4,4,6,6-pentachlorotriazatriphosphazene **4** in $CDCl_3$ recorded at room temperature (400 MHz).

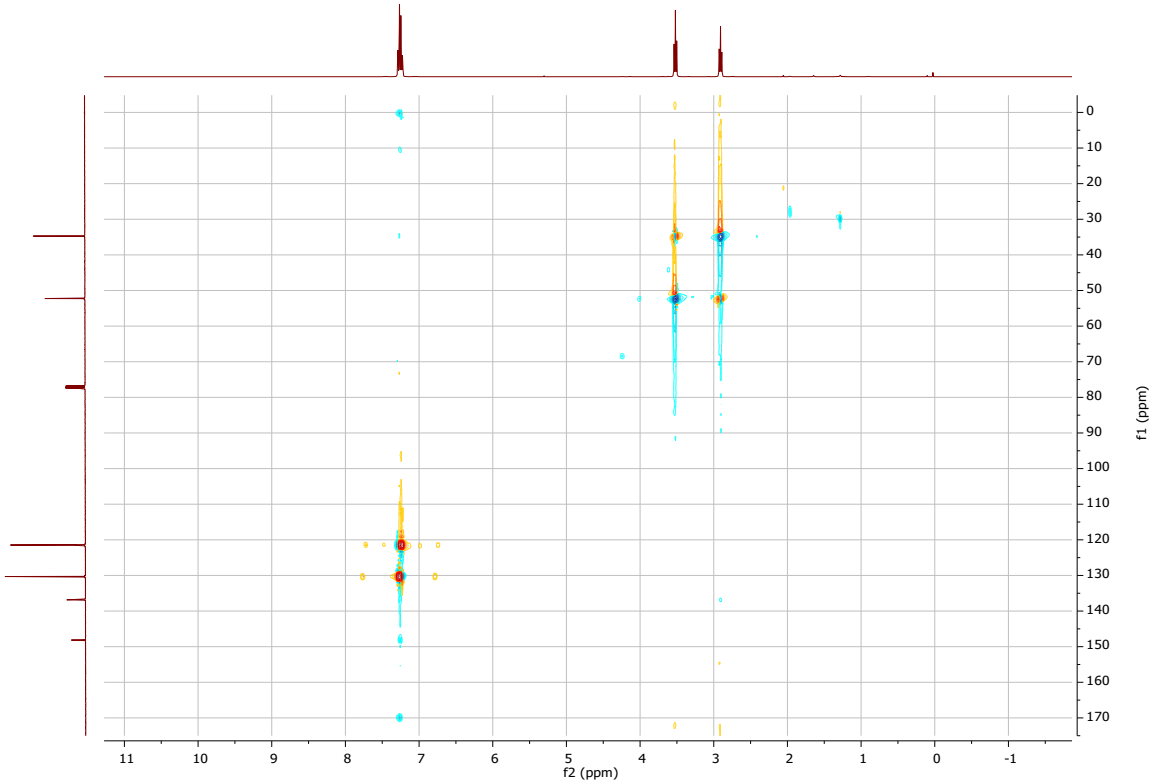


Figure S14. ^{1}H-$^{13}C\{^{1}H\}$ HSQC spectrum of 2-(4-(2-azidoethyl)phenoxy)-2,4,4,6,6-pentachlorotriazatriphosphazene **4** in $CDCl_3$ recorded at room temperature (400 MHz, 101 MHz).

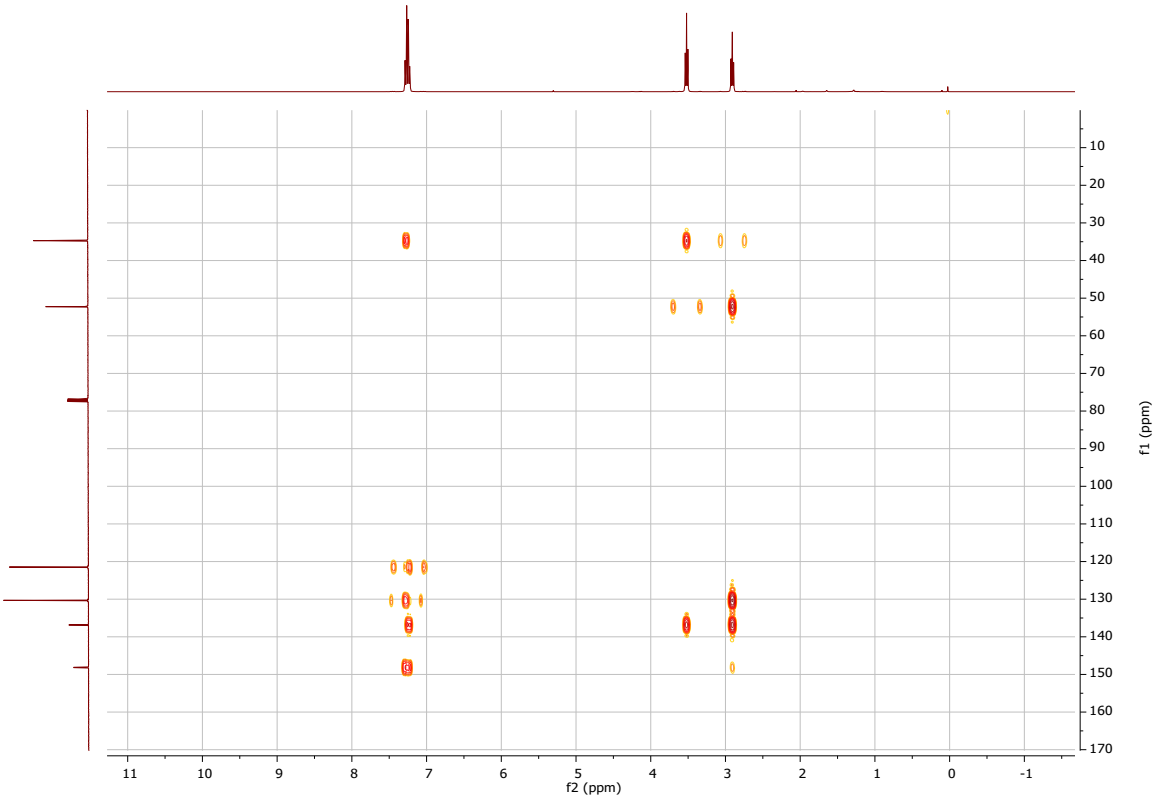


Figure S15. ^{1}H-$^{13}C\{^{1}H\}$ HMBC spectrum of 2-(4-(2-azidoethyl)phenoxy)-2,4,4,6,6-pentachlorotriazatri-phosphazene **4** in $CDCl_3$ recorded at room temperature (400 MHz, 101 MHz).

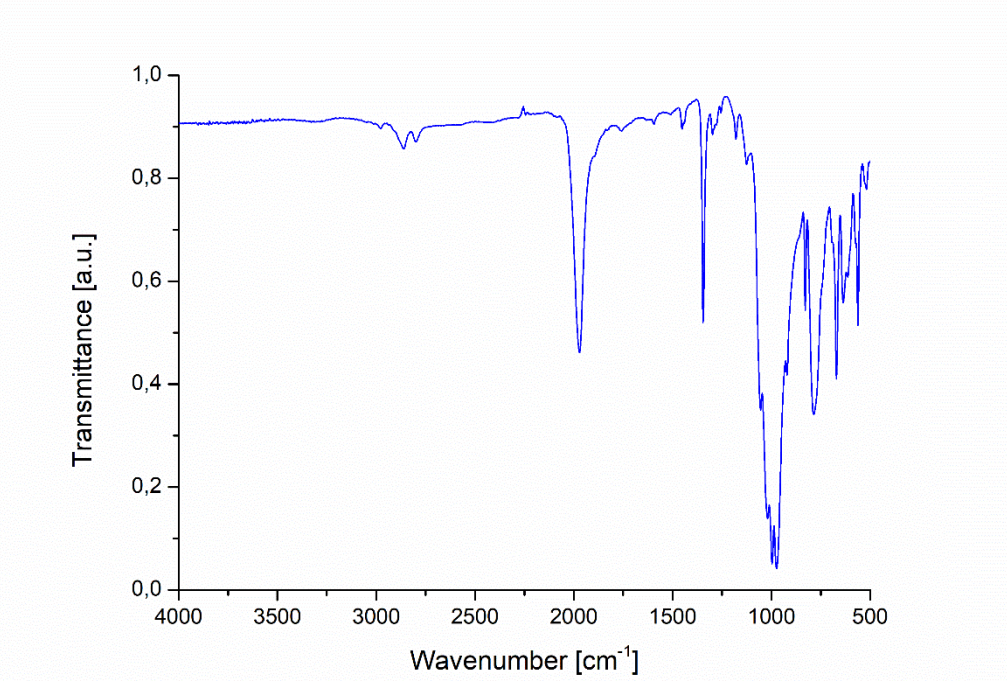


Figure S16. FT-IR spectrum of 2-(4-(2-azidoethyl)phenoxy)-2,4,4,6,6-pentachlorotriazatriphosphazene **4**.

Codi SAQ	Ref. mostra	%C	%H	%N	%S
23AE038/004	JCS2-AB1-azide	20,26	1,74	17,33	<0.1

Figure S17. Elemental analysis of 2-(4-(2-azidoethyl)phenoxy)-2,4,4,6,6-pentachlorotriazatriphophazene **4**.

3.5. Synthesis of azide dendron 7-[G_0']

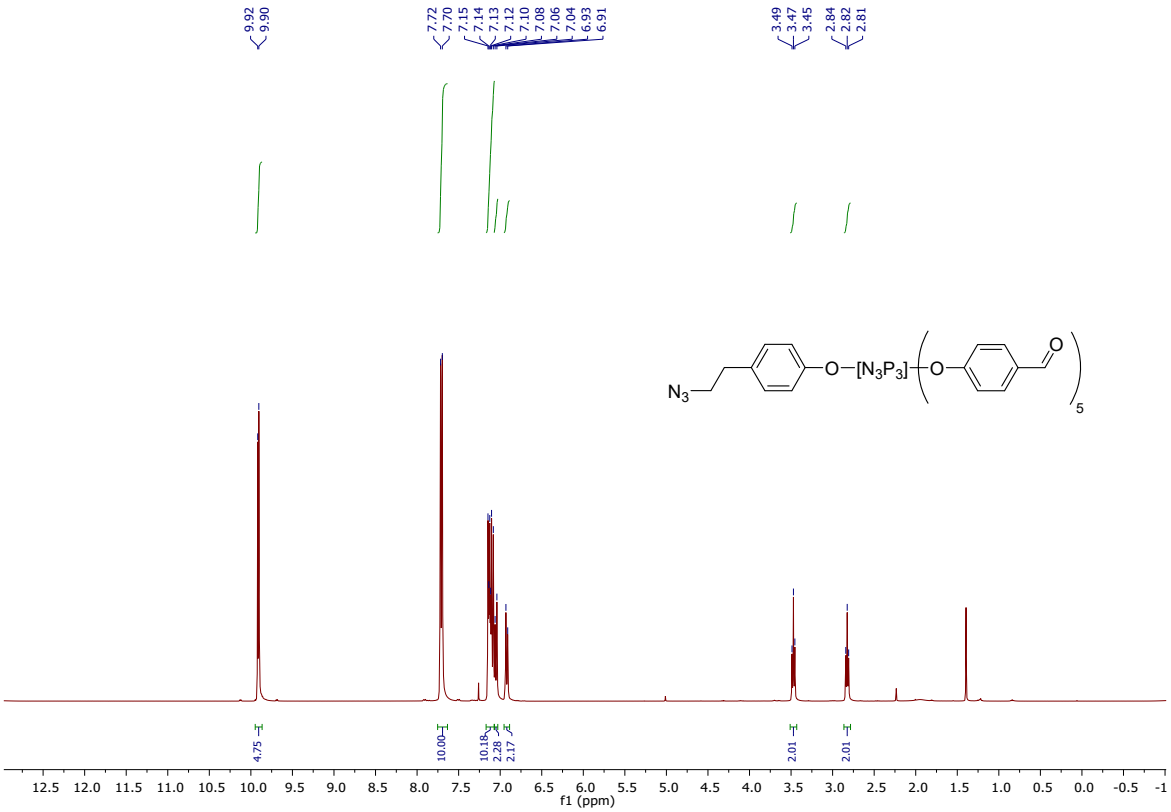


Figure S18. ^{1}H NMR spectrum of **7-[G_0']** in $CDCl_3$ recorded at room temperature (400 MHz).

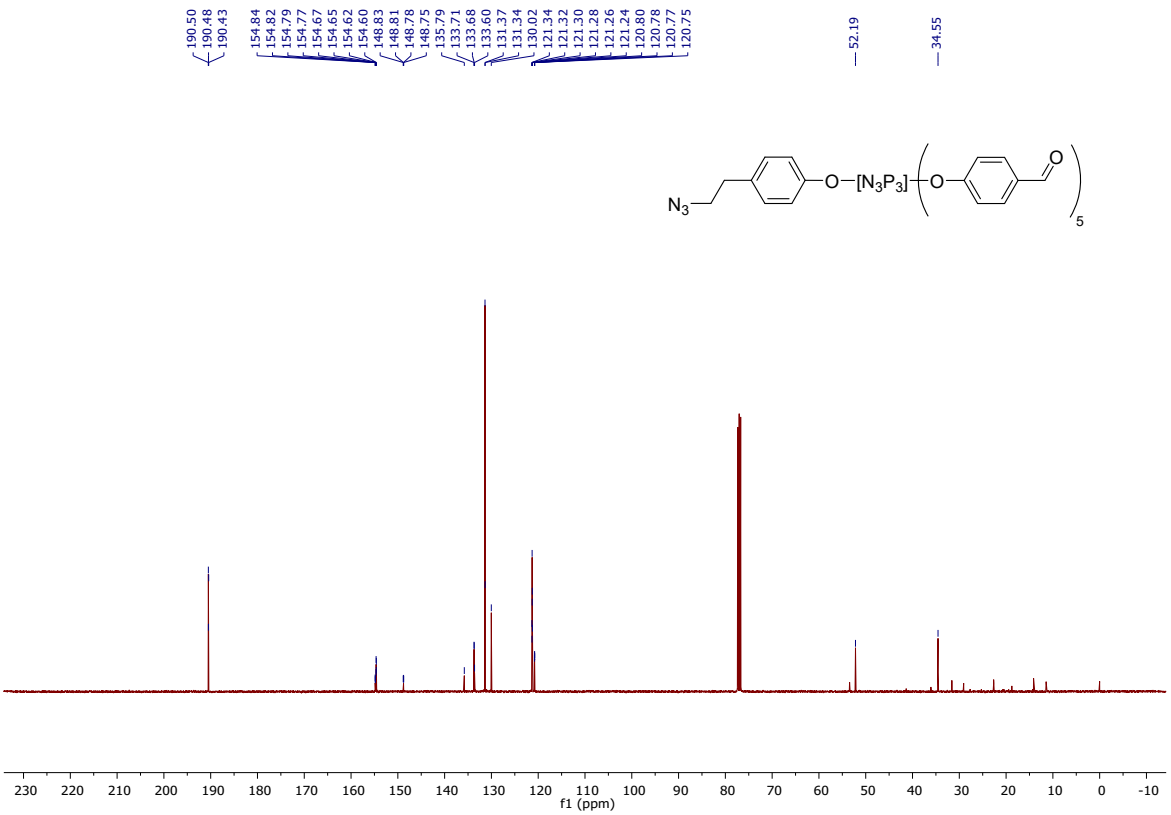


Figure S19. $^{13}C\{^{1}H\}$ NMR spectrum of **7-[G_0']** azide dendron in $CDCl_3$ recorded at room temperature (101 MHz).

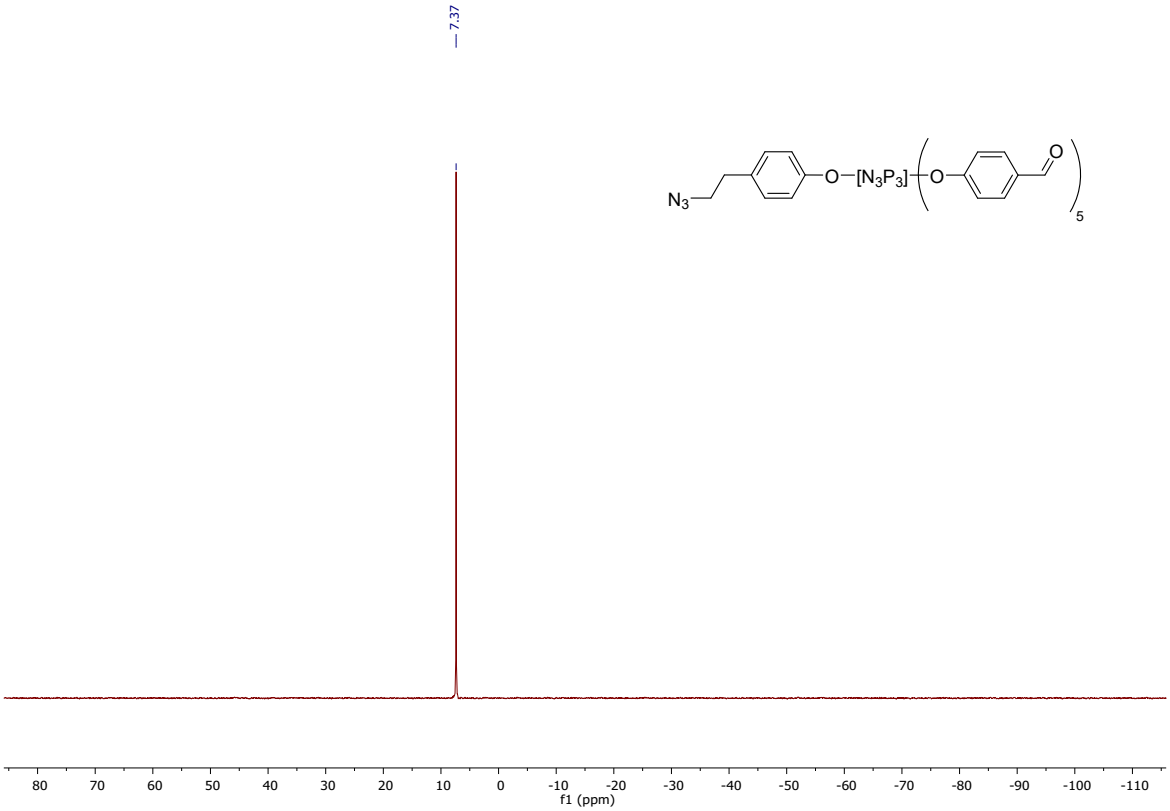


Figure S20. $^{31}P\{^{1}H\}$ NMR spectrum of **7-[G_0']** azide dendron in $CDCl_3$ recorded at room temperature (162 MHz).

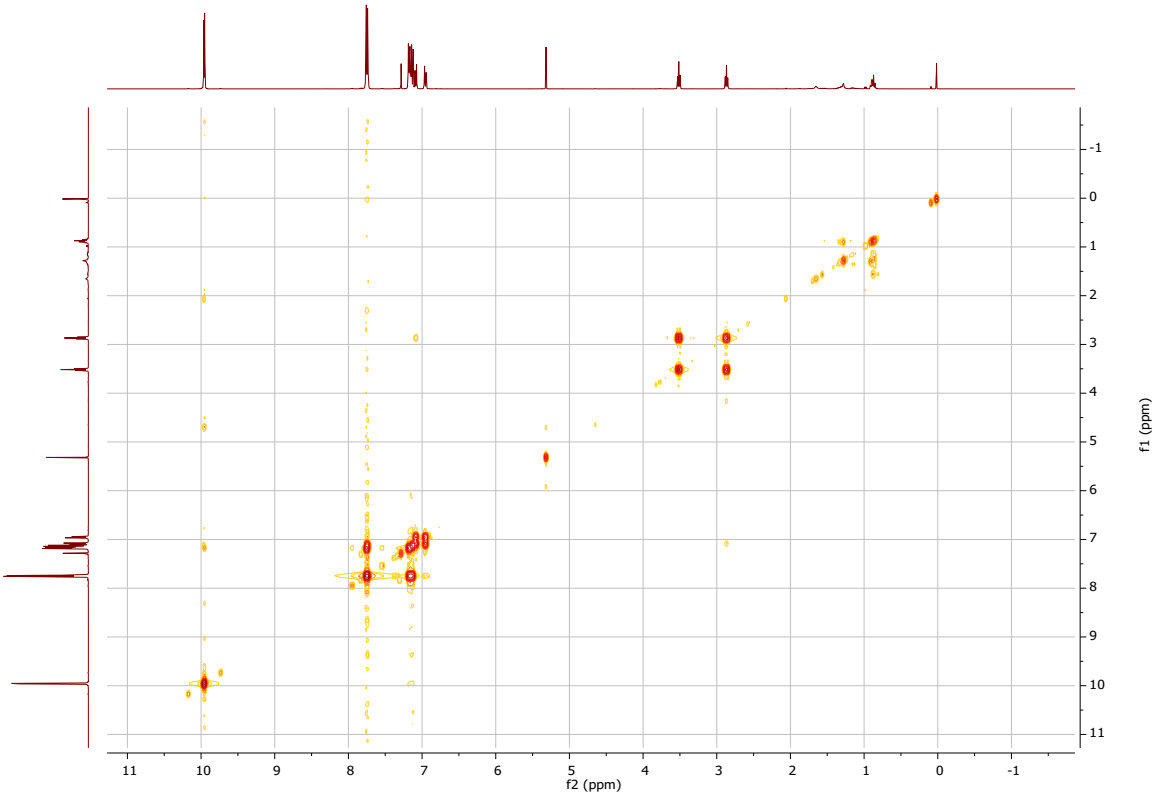


Figure S21. ^{1}H-^{1}H COSY spectrum of **7-[G_0']** azide dendron in $CDCl_3$ recorded at room temperature (400 MHz).

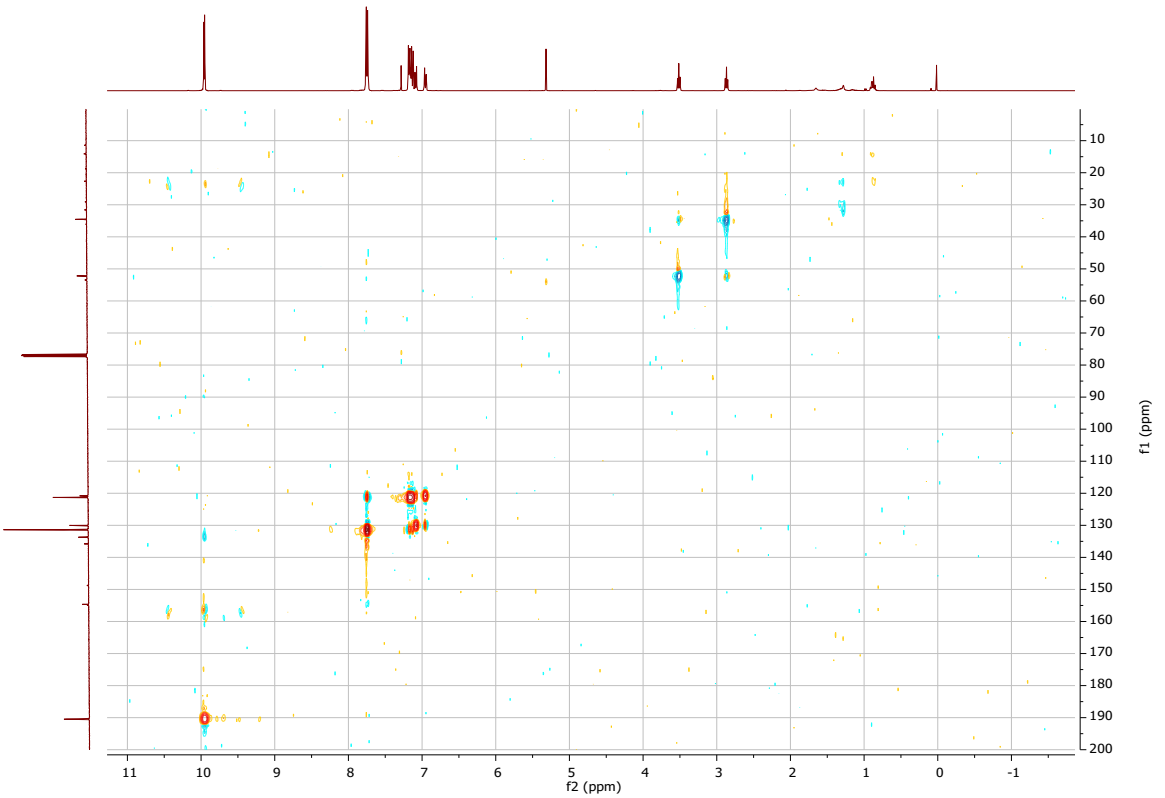


Figure S22. ^{1}H-$^{13}C\{^{1}H\}$ HSQC spectrum **7-[G_0']** azide dendron in $CDCl_3$ recorded at room temperature (400 MHz, 101 MHz).

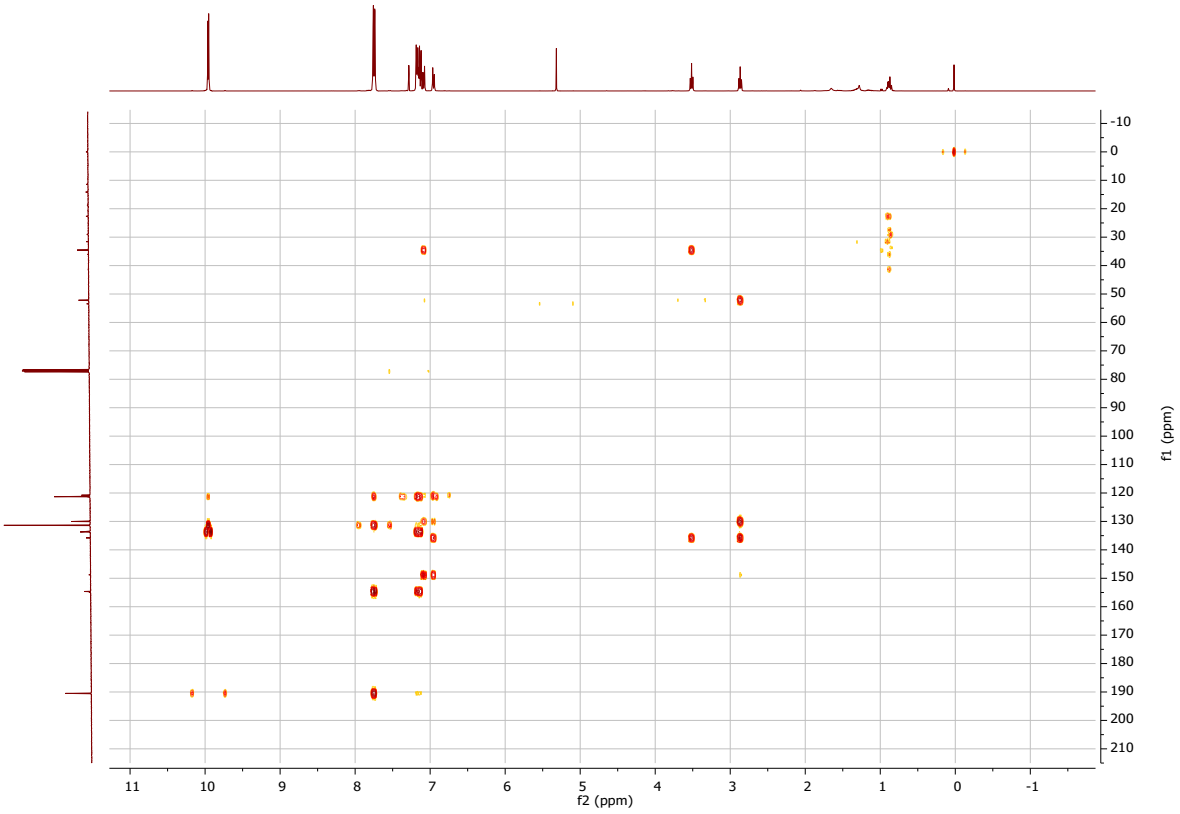


Figure S23. ^{1}H-$^{13}C\{^{1}H\}$ HSQC spectrum **7-[G_0']** azide dendron in $CDCl_3$ recorded at room temperature (400 MHz, 101 MHz).

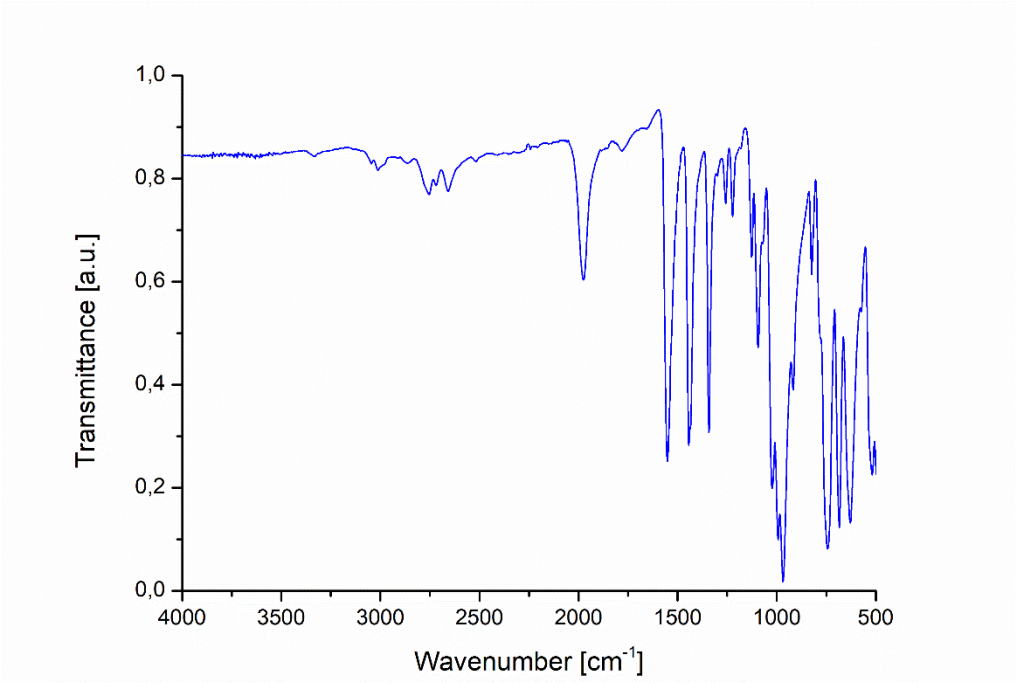


Figure S24. FT-IR spectrum of **7-[G_0']**.

3.6. Synthesis of azide dendron 10-[G_1][4]

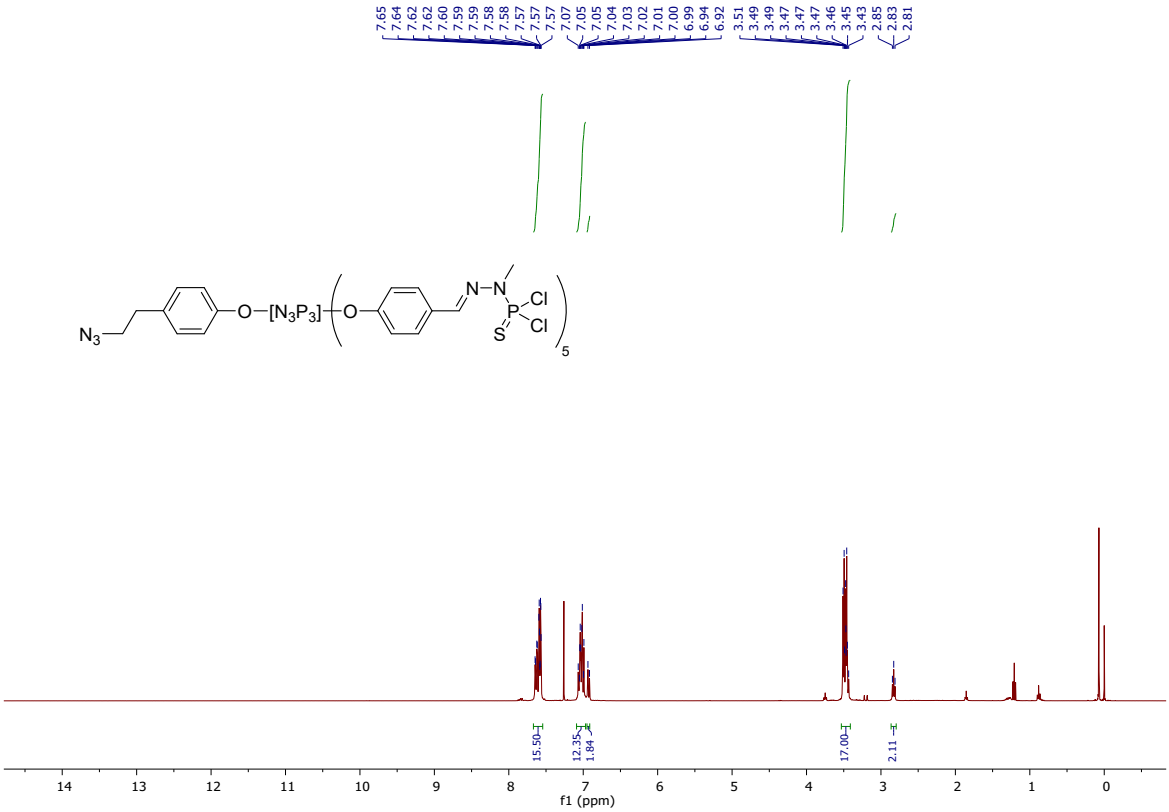


Figure S25. ^{1}H NMR spectrum of **10-[G_1]** in $CDCl_3$ recorded at room temperature (400 MHz).

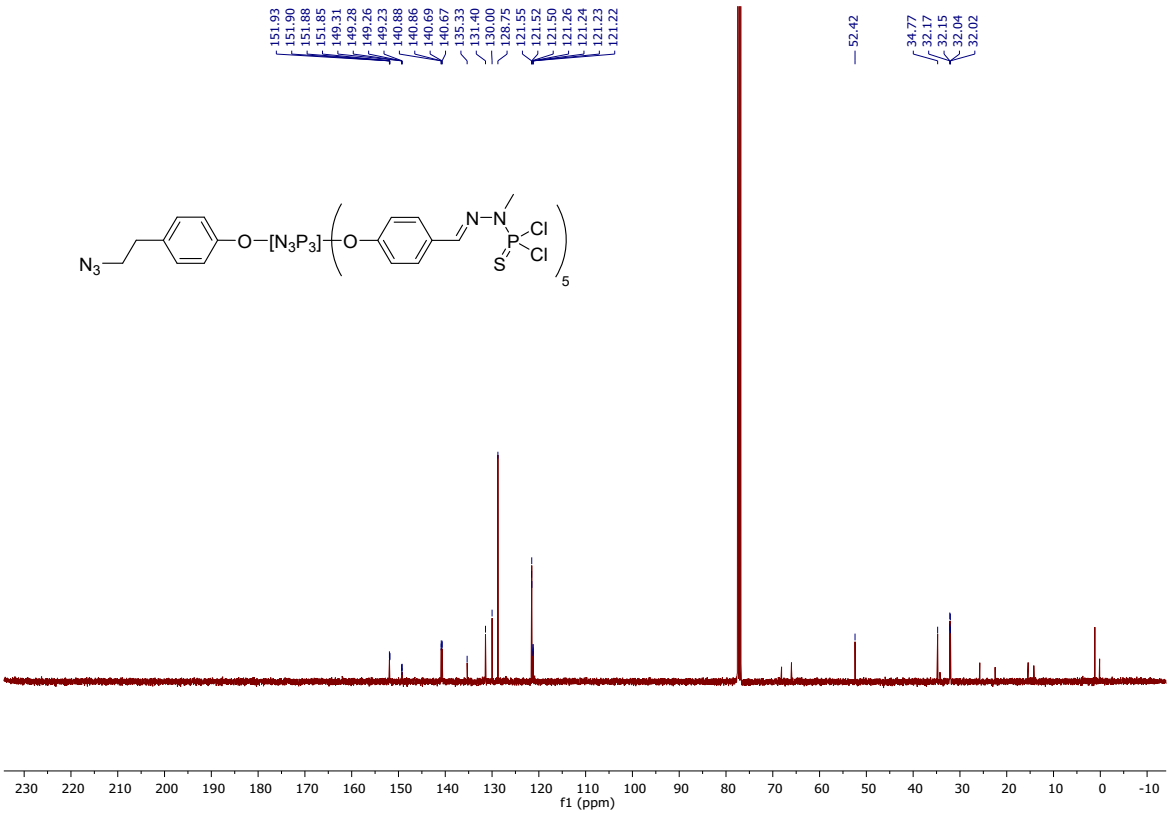


Figure S26. $^{13}C\{^{1}H\}$ NMR spectrum of **10-[G_1]** in $CDCl_3$ recorded at room temperature (101 MHz).

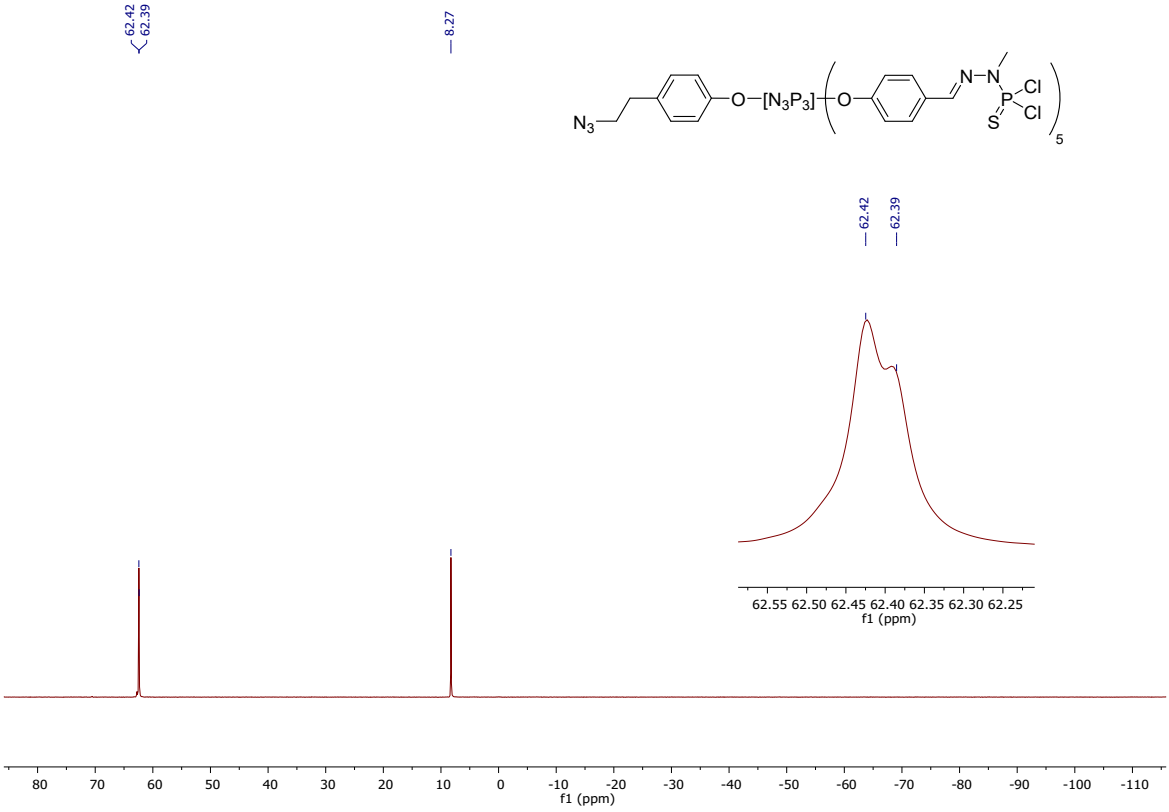
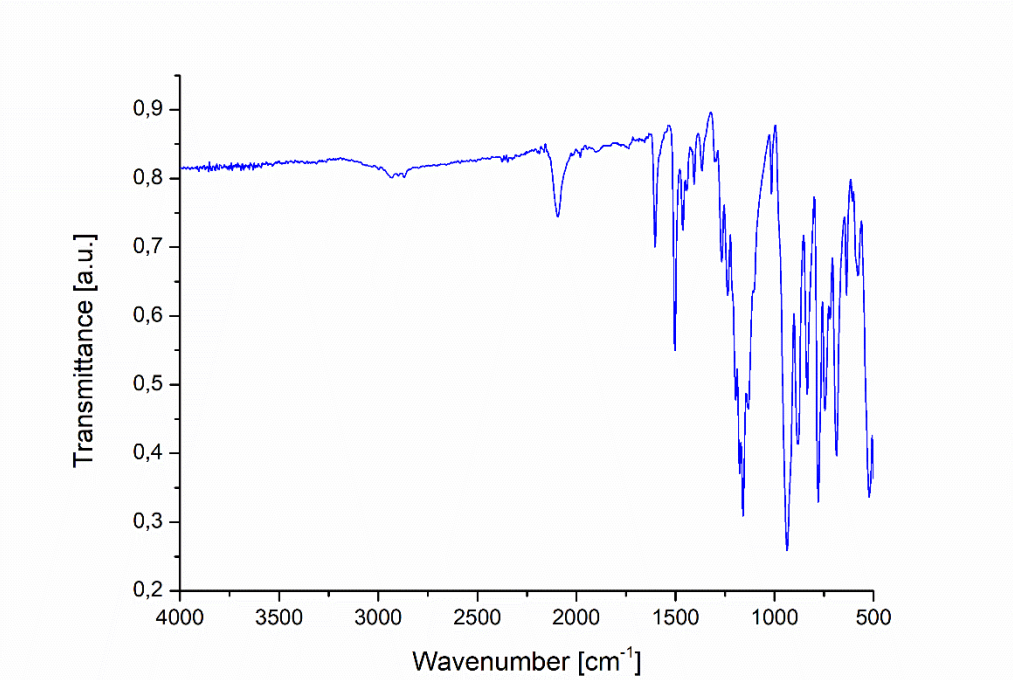


Figure S27. $^{31}P\{^{1}H\}$ NMR spectrum of **10-[G_1]** in $CDCl_3$ recorded at room temperature (162 MHz).



4. Figure S28. FT-IR spectrum of 10-[G_1].

3.7. Synthesis of 2-(4-(4-(pro-2-yn-yloxy)phenoxy)-2,4,4,6,6-pentachlorotriazatri-phosphazene 5

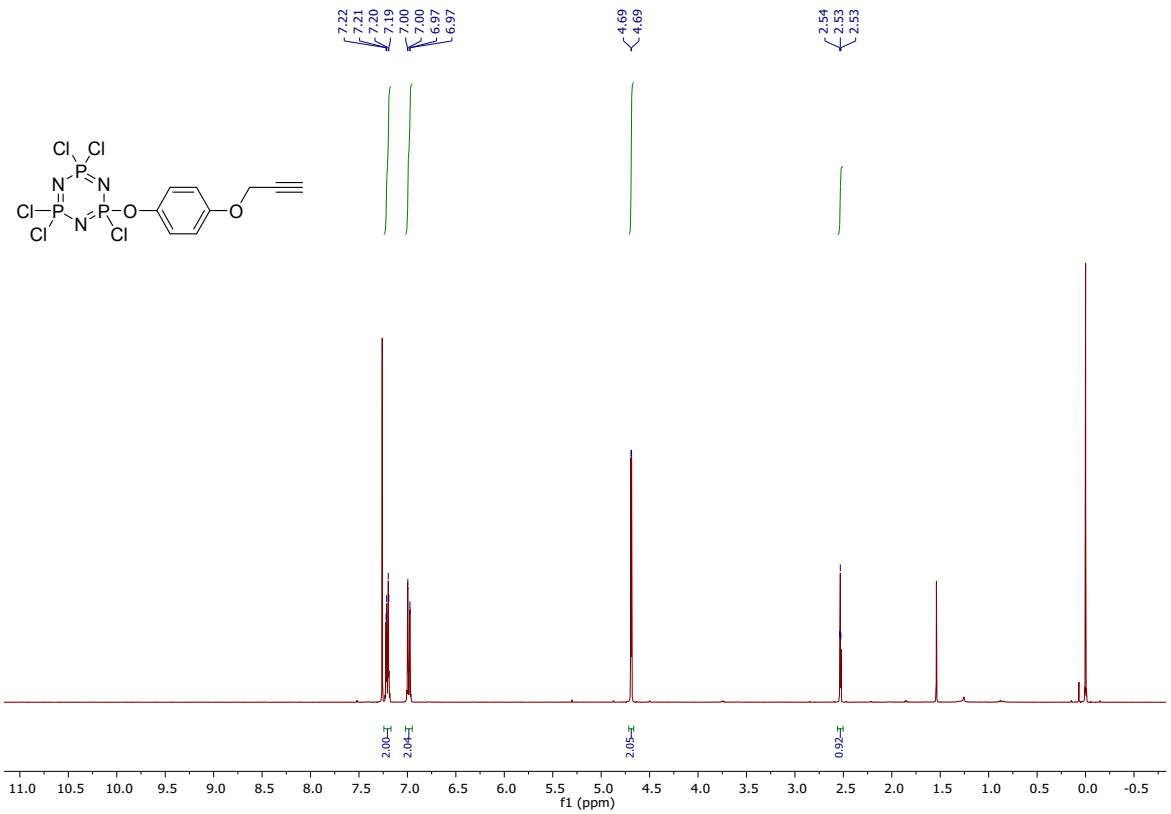


Figure S29. ^{1}H NMR spectrum of 2-(4-(4-(pro-2-yn-yloxy)phenoxy)-2,4,4,6,6-pentachlorotriazatriphosphazene **5** in $CDCl_3$ recorded at room temperature (400 MHz).

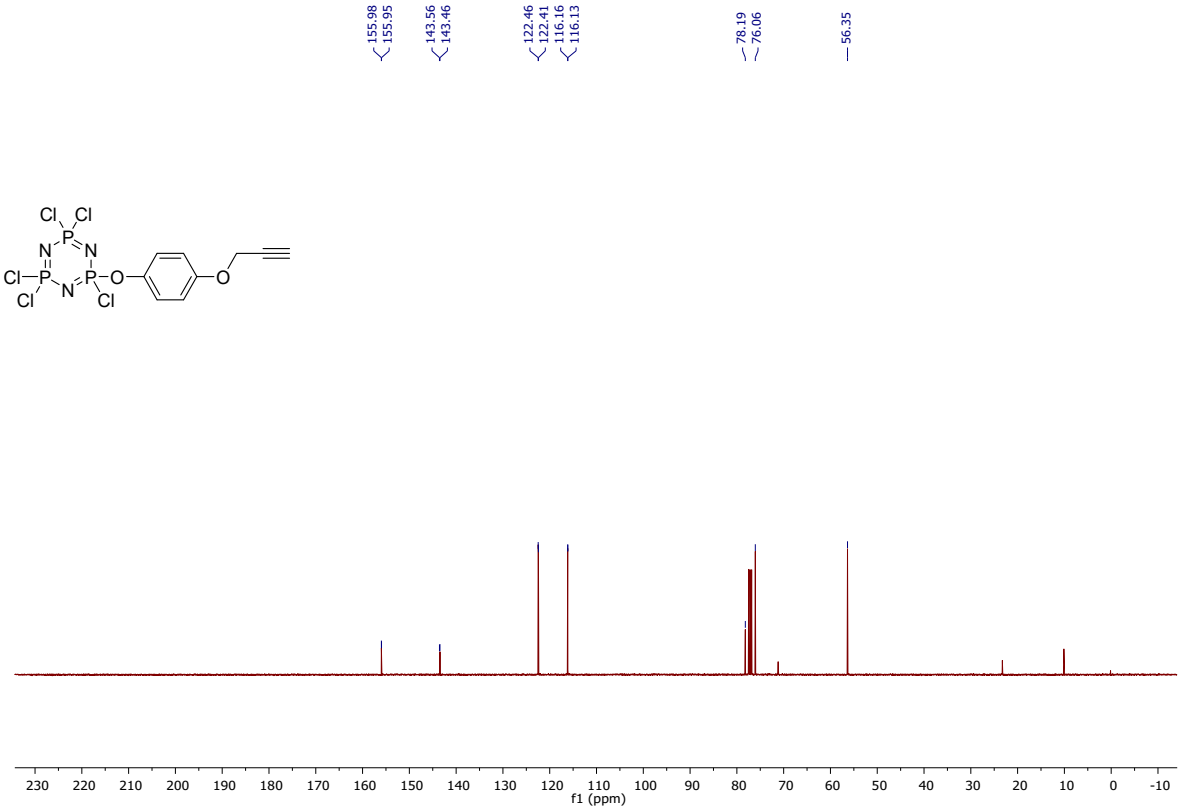


Figure S30. $^{13}C\{^{1}H\}$ NMR spectrum of 2-(4-(4-(pro-2-yn-yloxy)phenoxy)-2,4,4,6,6-pentachlorotriazatriphosphazene **5** in $CDCl_3$ recorded at room temperature (101 MHz).

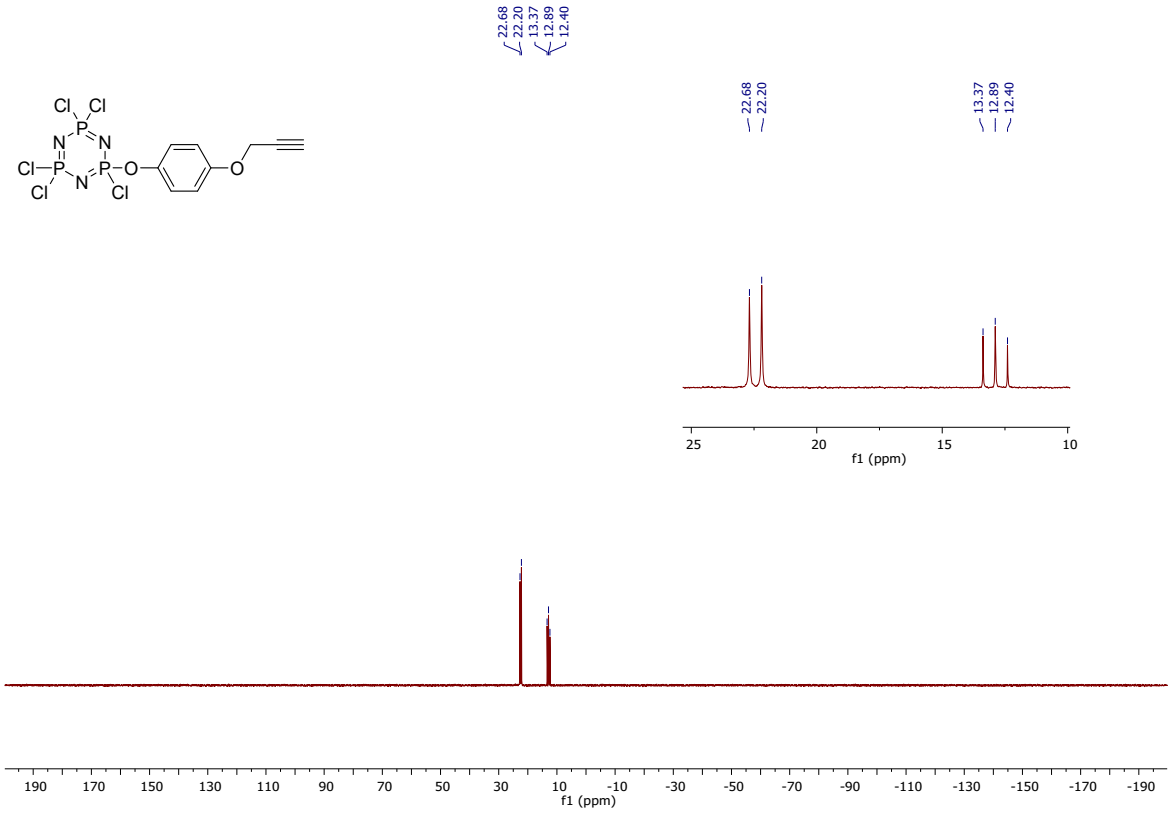


Figure S31. $^{31}P\{^{1}H\}$ NMR spectrum of 2-(4-(4-(pro-2-yn-yloxy)phenoxy)-2,4,4,6,6-pentachlorotriazatriphosphazene **5** in $CDCl_3$ recorded at room temperature (162 MHz).

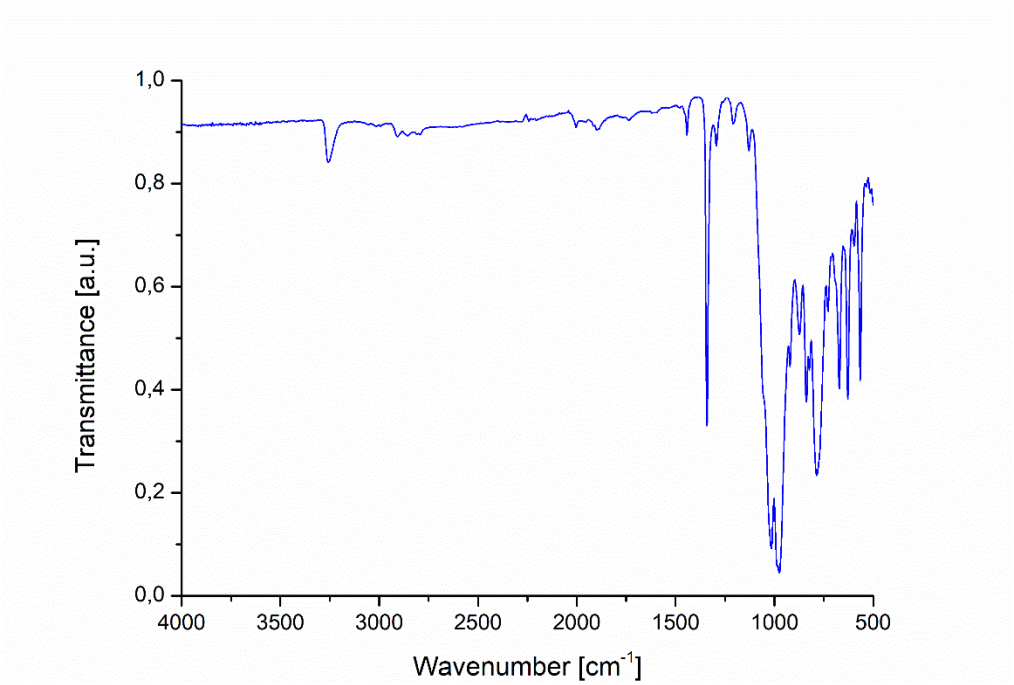


Figure S32. FT-IR spectrum of 2-(4-(4-(pro-2-yn-yloxy)phenoxy)-2,4,4,6,6-pentachlorotriazatriphosphazene **5**.

3.8. Synthesis of acetylene dendron 8-[G_0']

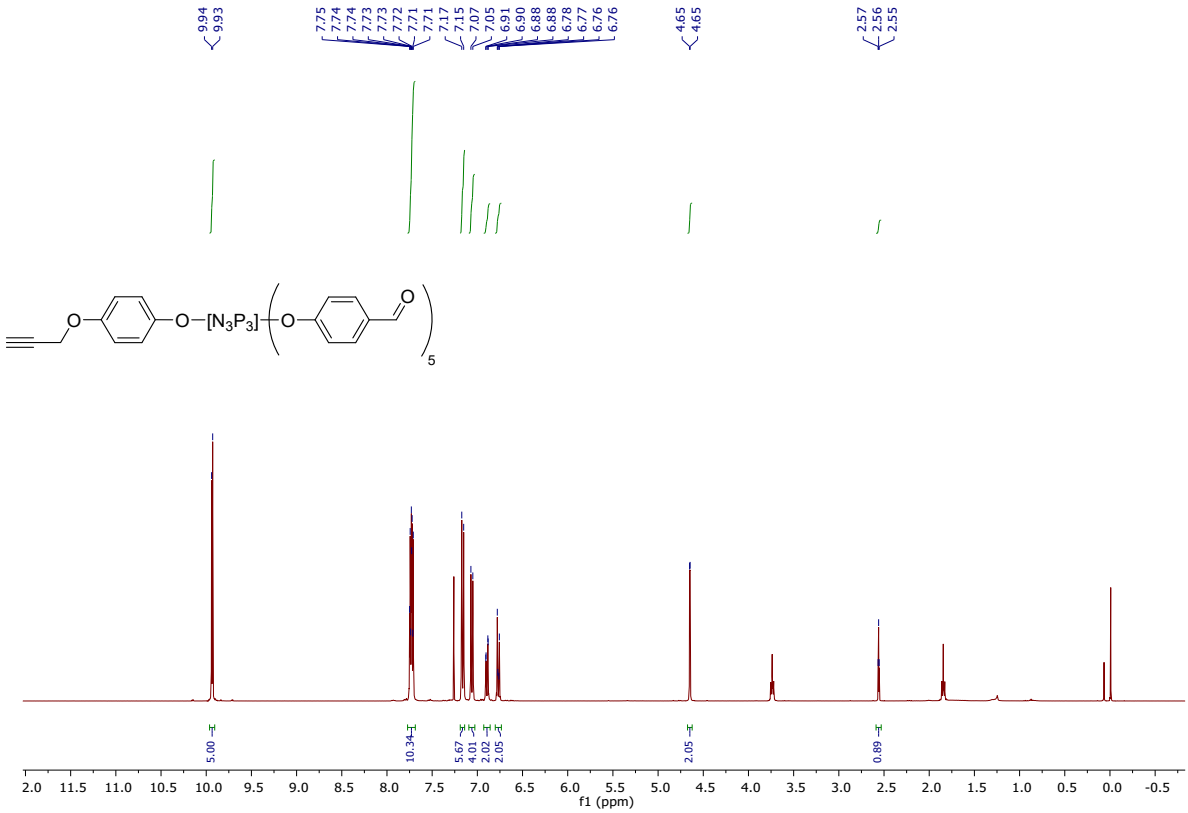


Figure S33. ^{1}H NMR spectrum of **9-[G_0']** in $CDCl_3$ recorded at room temperature (400 MHz).

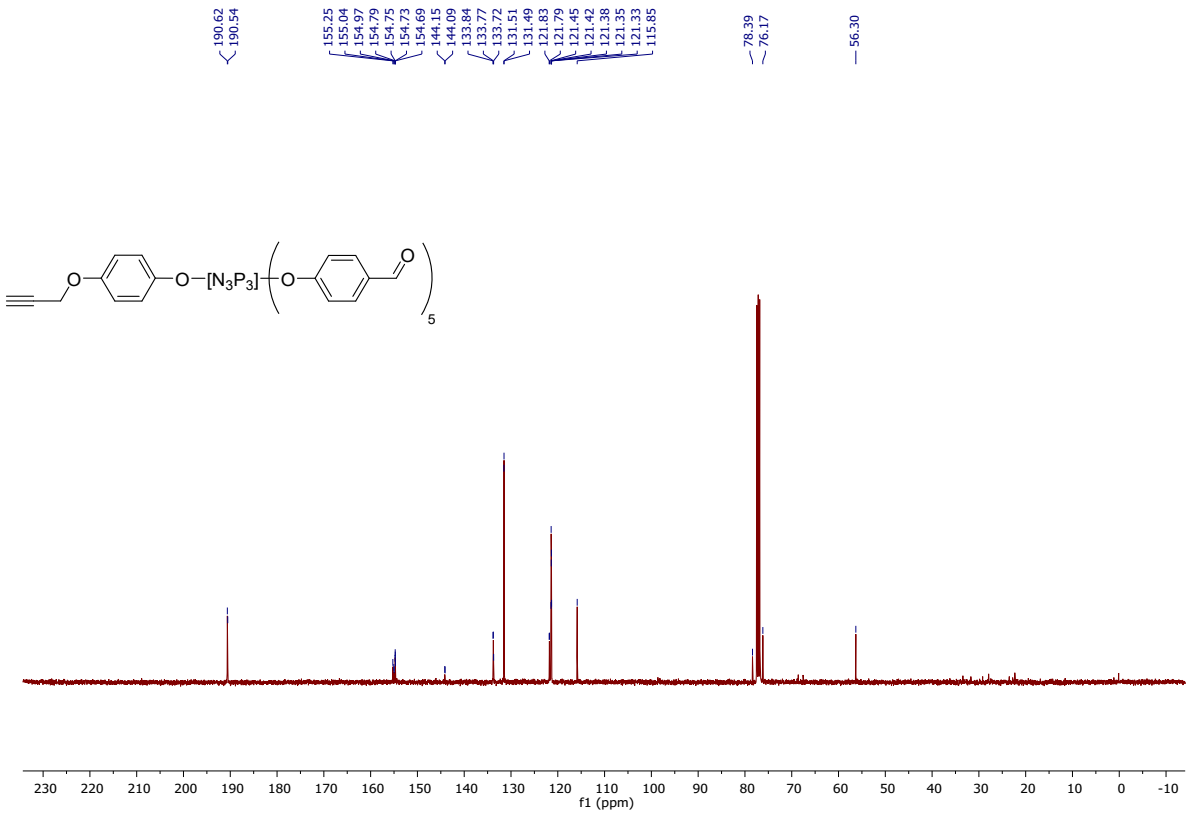


Figure S34. $^{13}C\{^{1}H\}$ NMR spectrum of **9-[G_0']** in $CDCl_3$ recorded at room temperature (101 MHz).

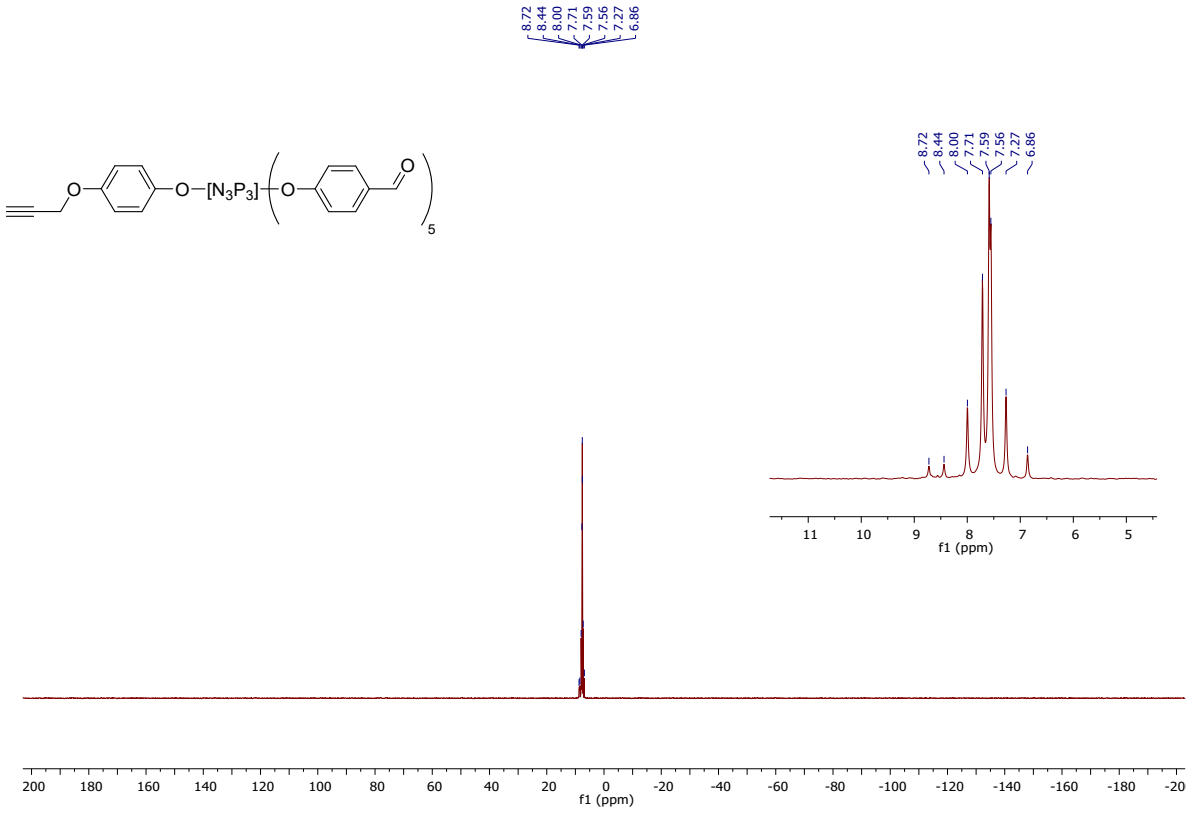


Figure S35. $^{31}P\{^{1}H\}$ NMR spectrum of **9-[G_0']** in $CDCl_3$ recorded at room temperature (162 MHz).

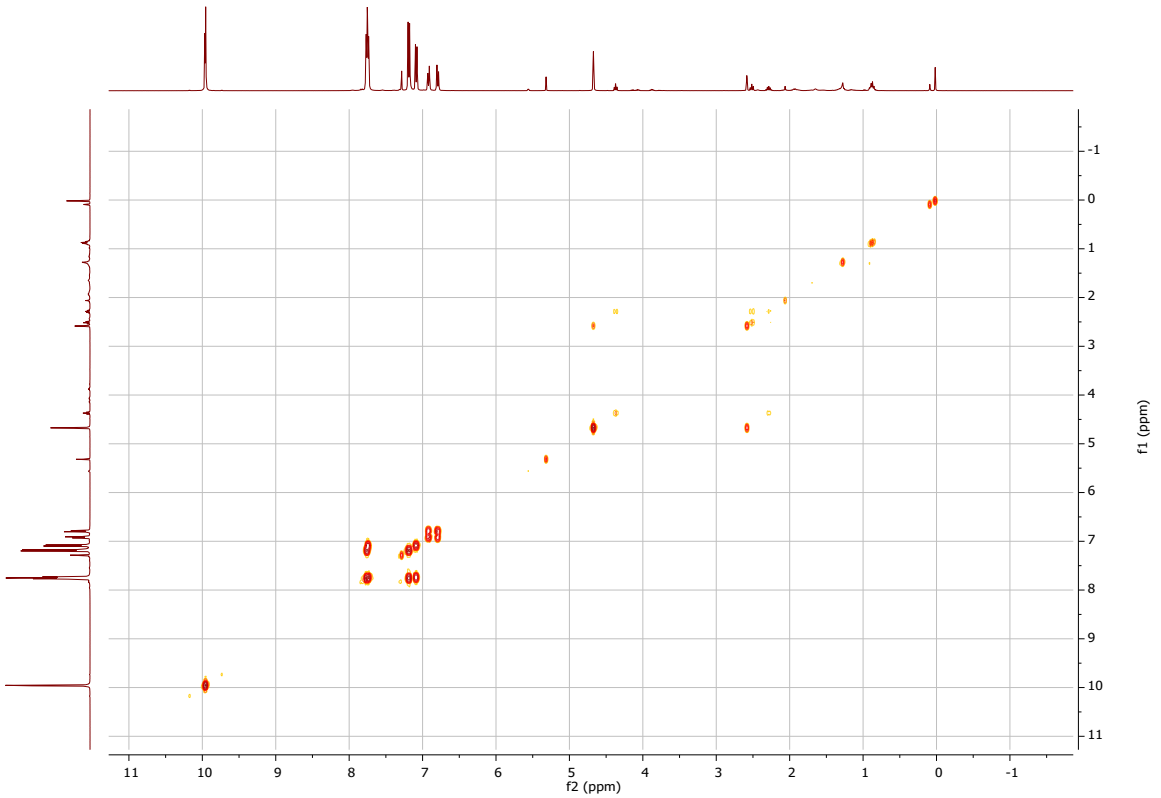


Figure S36. ^{1}H-^{1}H COSY spectrum of **9-[G_0']** in $CDCl_3$ recorded at room temperature (400 MHz).

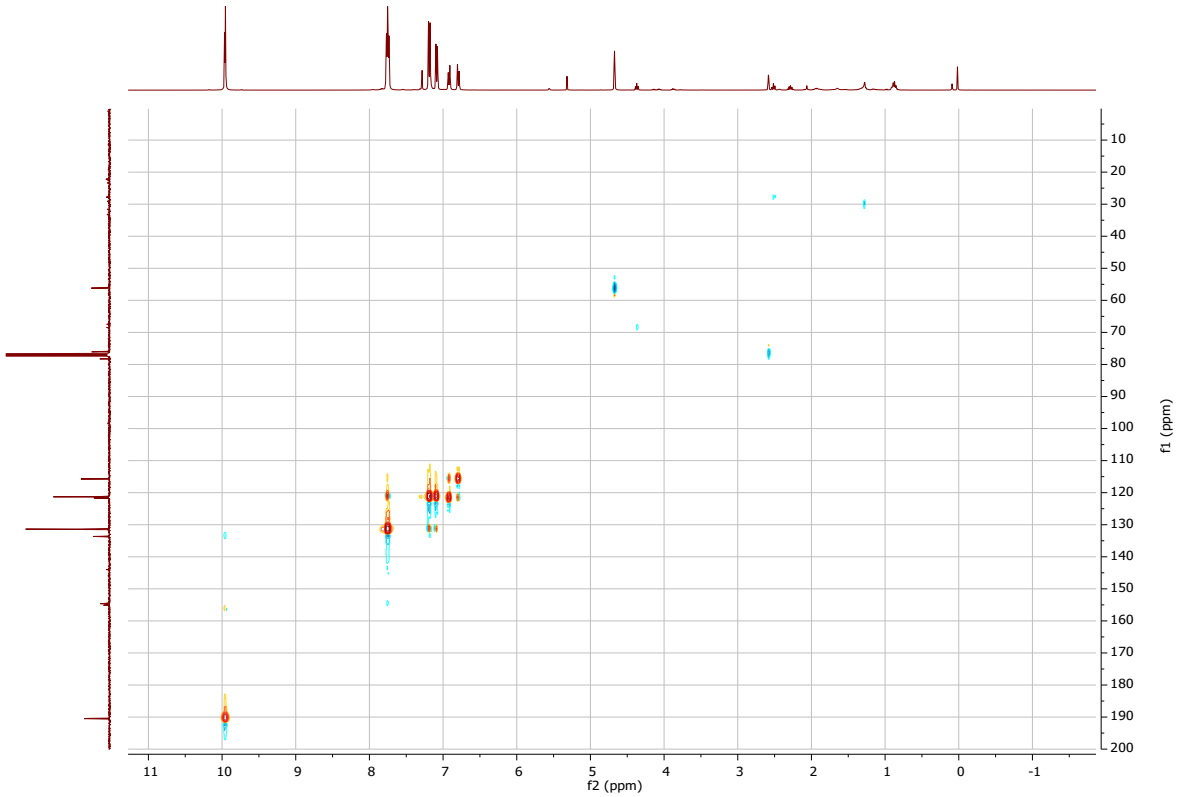


Figure S37. ^{1}H-$^{13}C\{^{1}H\}$ HSQC spectrum of **9-[G_0']** in $CDCl_3$ recorded at room temperature (400 MHz, 101 MHz).

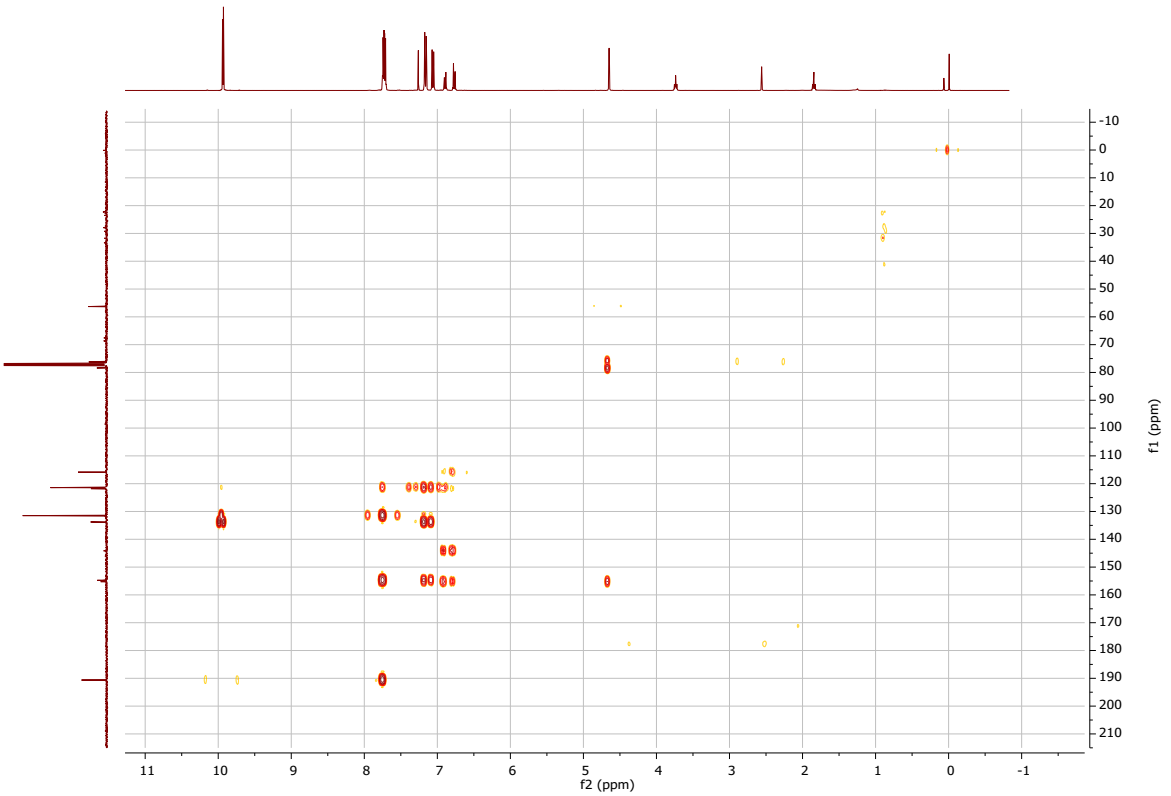


Figure S38. ^{1}H-$^{13}C\{^{1}H\}$ HMBC spectrum of **9-[G_0']** in $CDCl_3$ recorded at room temperature (400 MHz, 101 MHz).

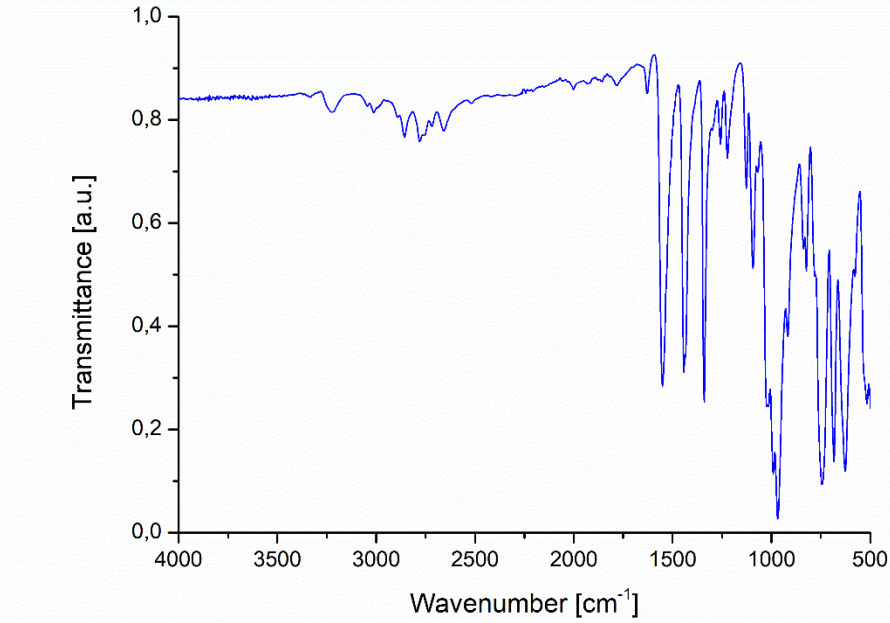


Figure S39. FT-IR spectrum of **9-[G_0']**.

3.9. Synthesis of 2-(2-(2-methoxyethoxy)ethoxy)ethyl methanesulfonate 36

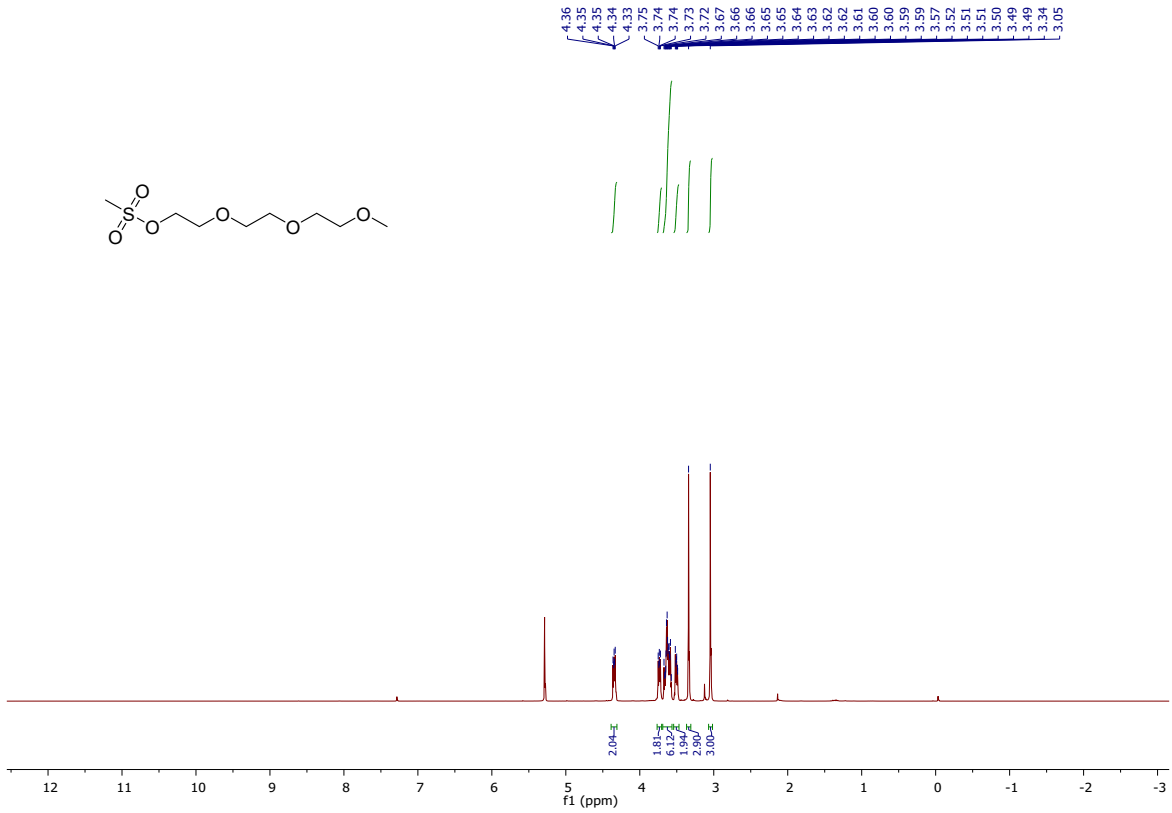


Figure S40. ^{1}H NMR spectrum of (2-(2-methoxyethoxy)ethoxy)ethyl methanesulfonate **36** in $CDCl_3$ recorded at room temperature (300 MHz).

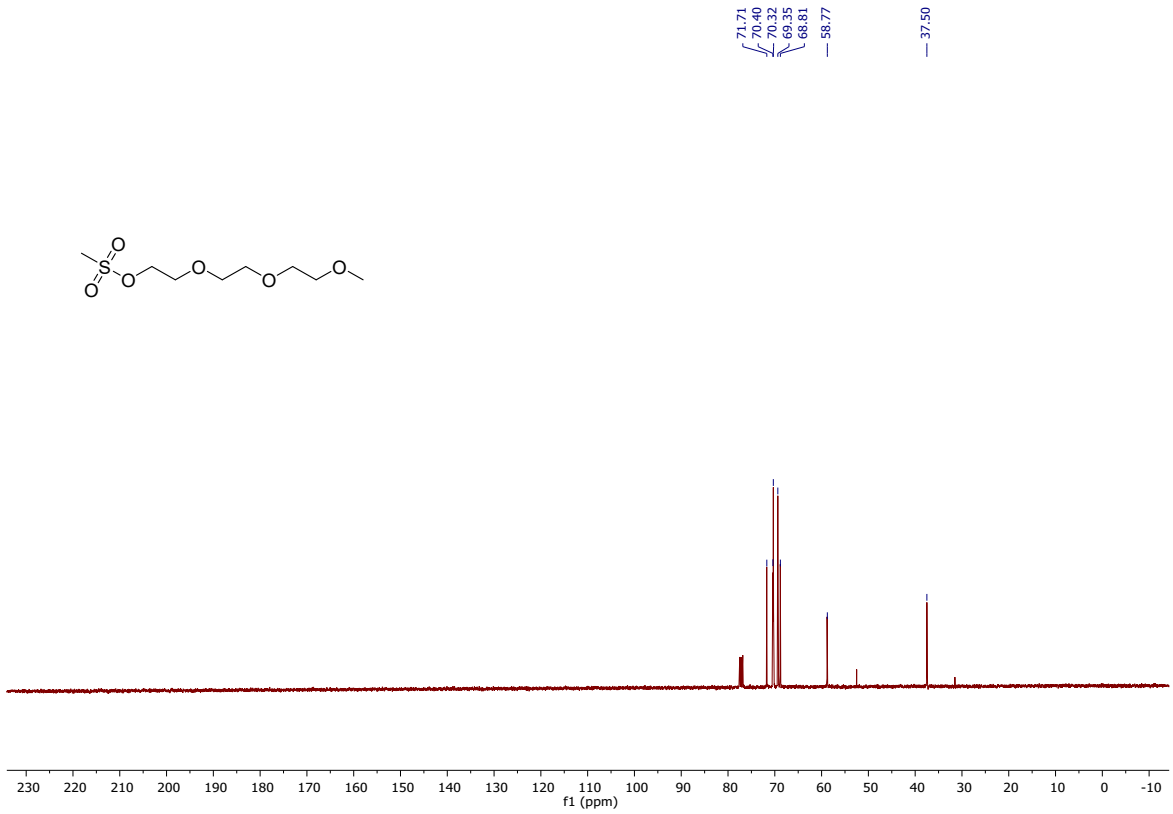


Figure S41.$^{13}C\{^{1}H\}$ NMR spectrum of (2-(2-methoxyethoxy)ethoxy)ethyl methanesulfonate **36** in $CDCl_3$ recorded at room temperature (75 MHz).

3.10. 4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenol 11

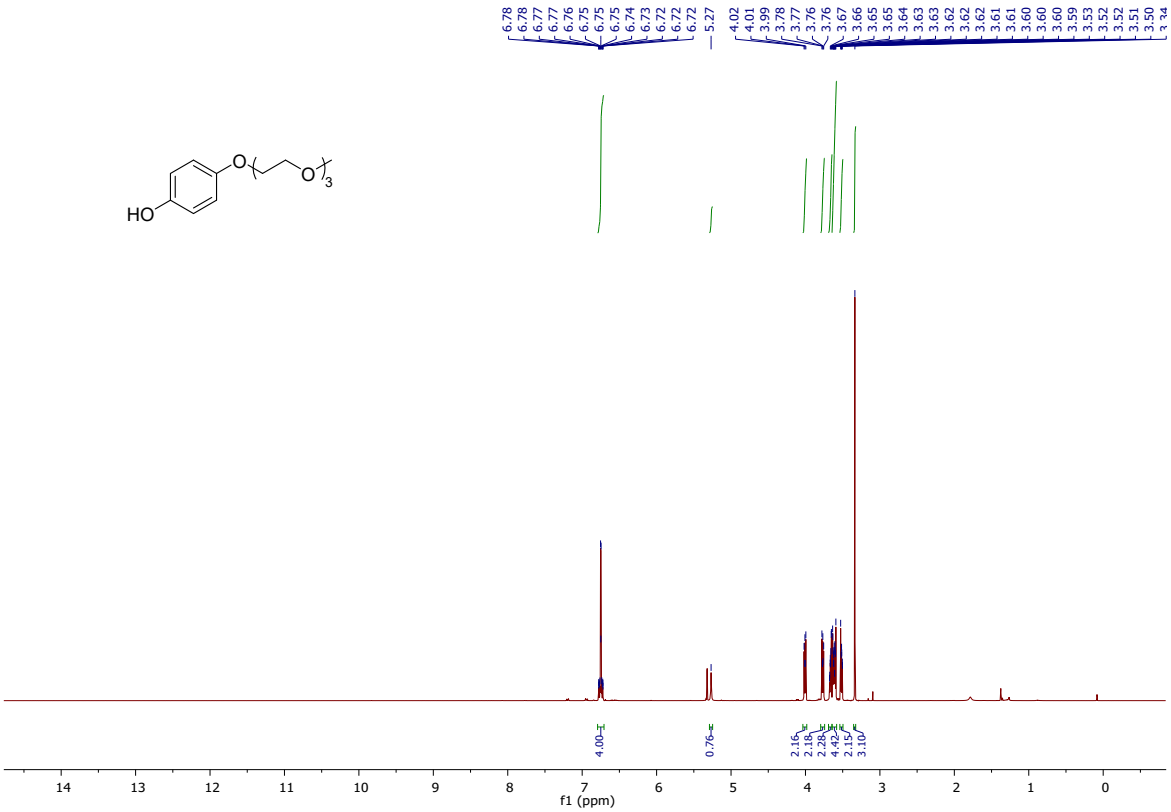


Figure S42. ^{1}H NMR spectrum of 4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenol **11** in DCM-d_2 recorded at room temperature (400 MHz).

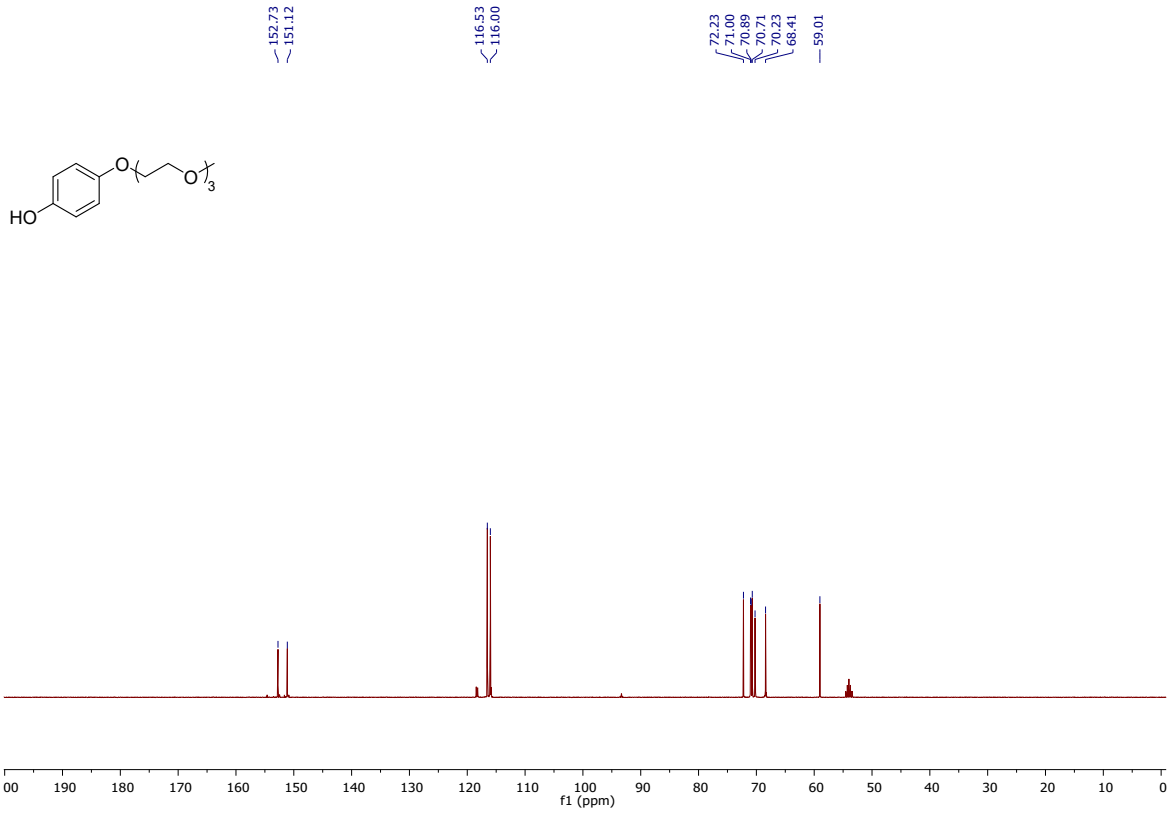


Figure S43. $^{13}C\{^{1}H\}$ NMR spectrum of 4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenol **11** in DCM-d_2 recorded at room temperature (101 MHz).

3.11. Synthesis of azide dendron 12-[G_1]-PEG

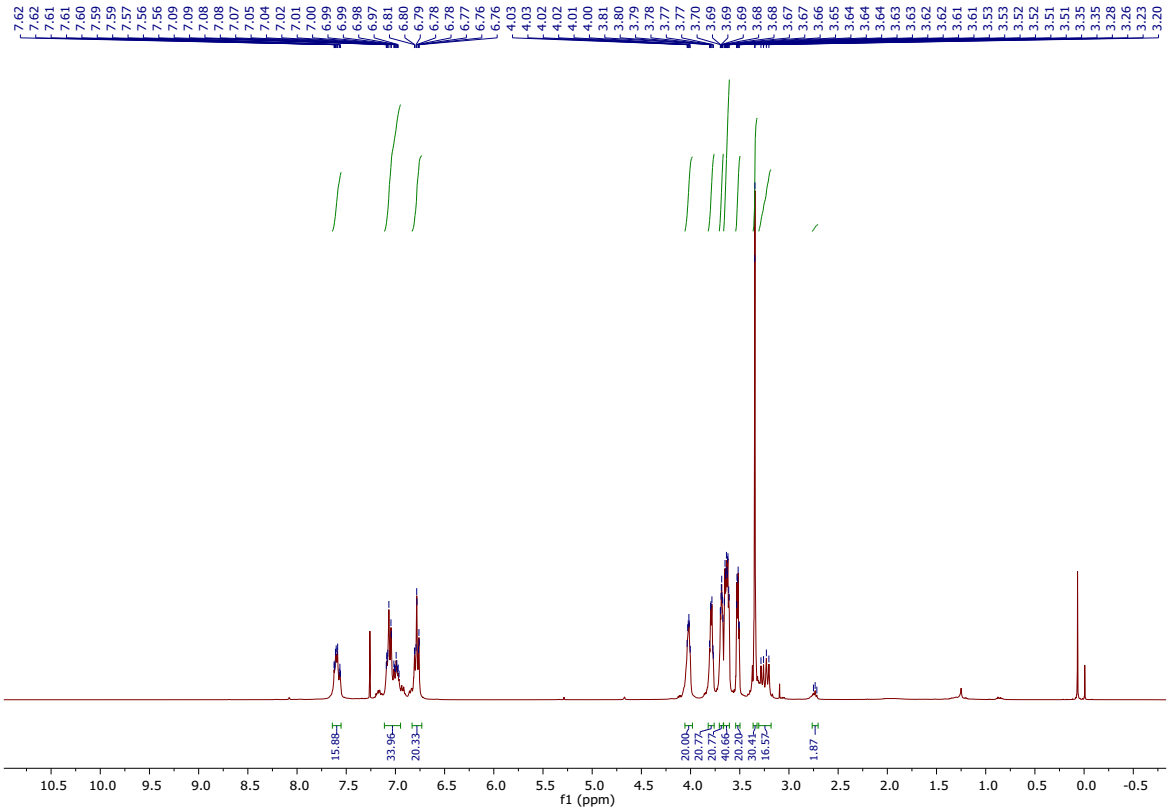


Figure S44. ^{1}H NMR spectrum of **12-[G_1]-PEG** in $CDCl_3$ recorded at room temperature (400 MHz).

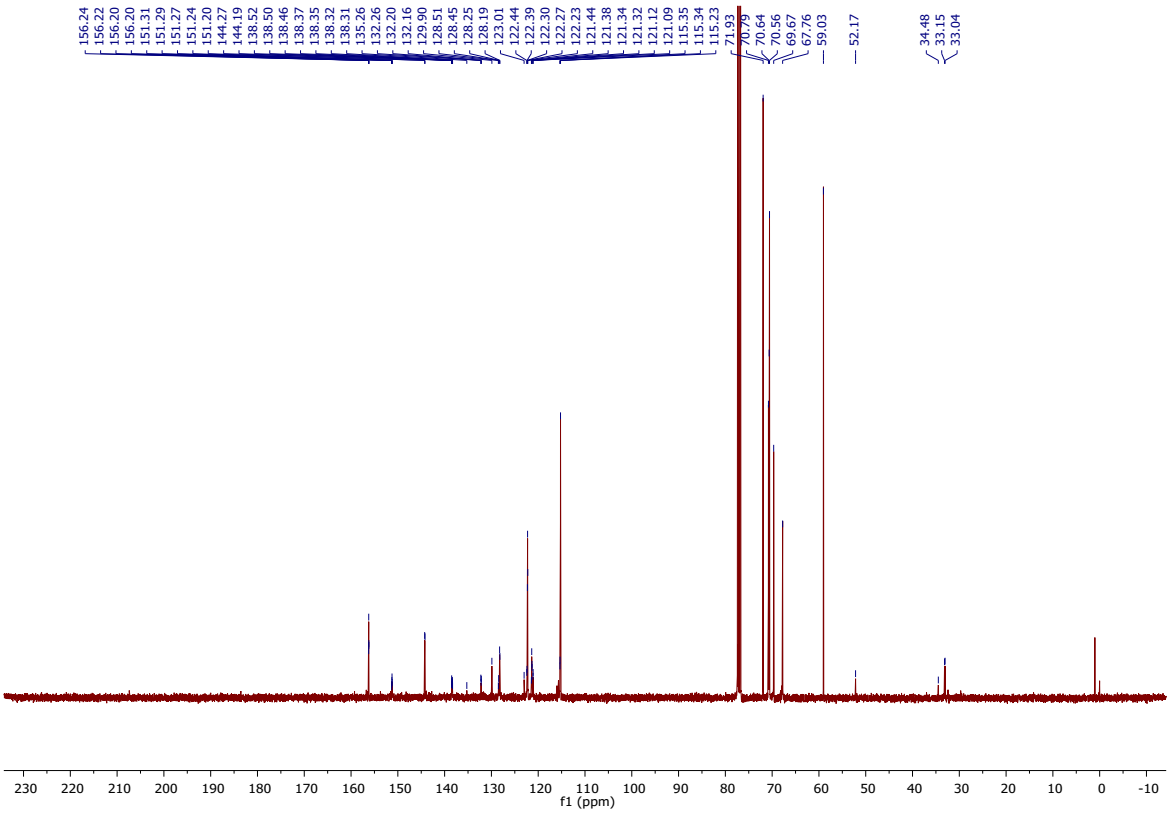


Figure S45. $^{13}C\{^{1}H\}$ NMR spectrum of **12-[G_1]-PEG** in $CDCl_3$ recorded at room temperature (101 MHz).

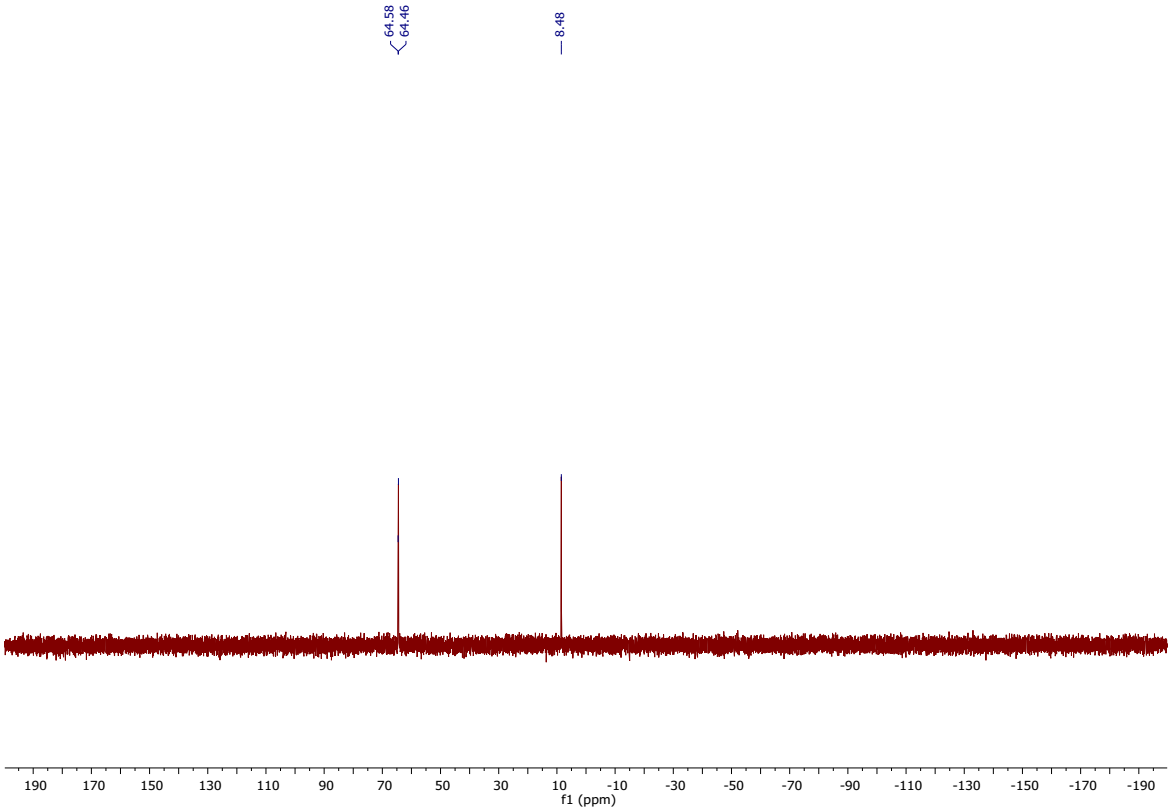


Figure S46. $^{31}P\{^{1}H\}$ NMR spectrum of **12-[G_1]-PEG** in $CDCl_3$ recorded at room temperature (162 MHz).

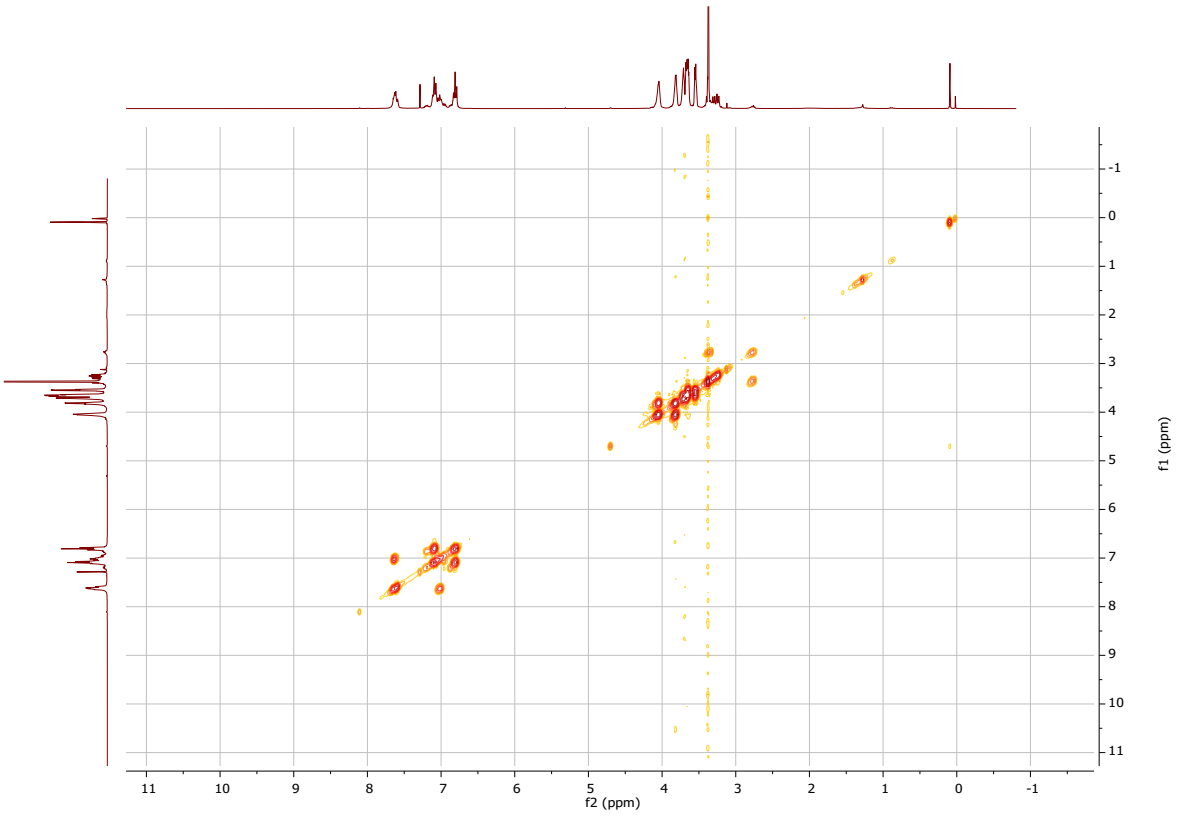


Figure S47. ^{1}H-^{1}H COSY spectrum of **12-[G_1]-PEG** recorded in $CDCl_3$ at room temperature (400 MHz).

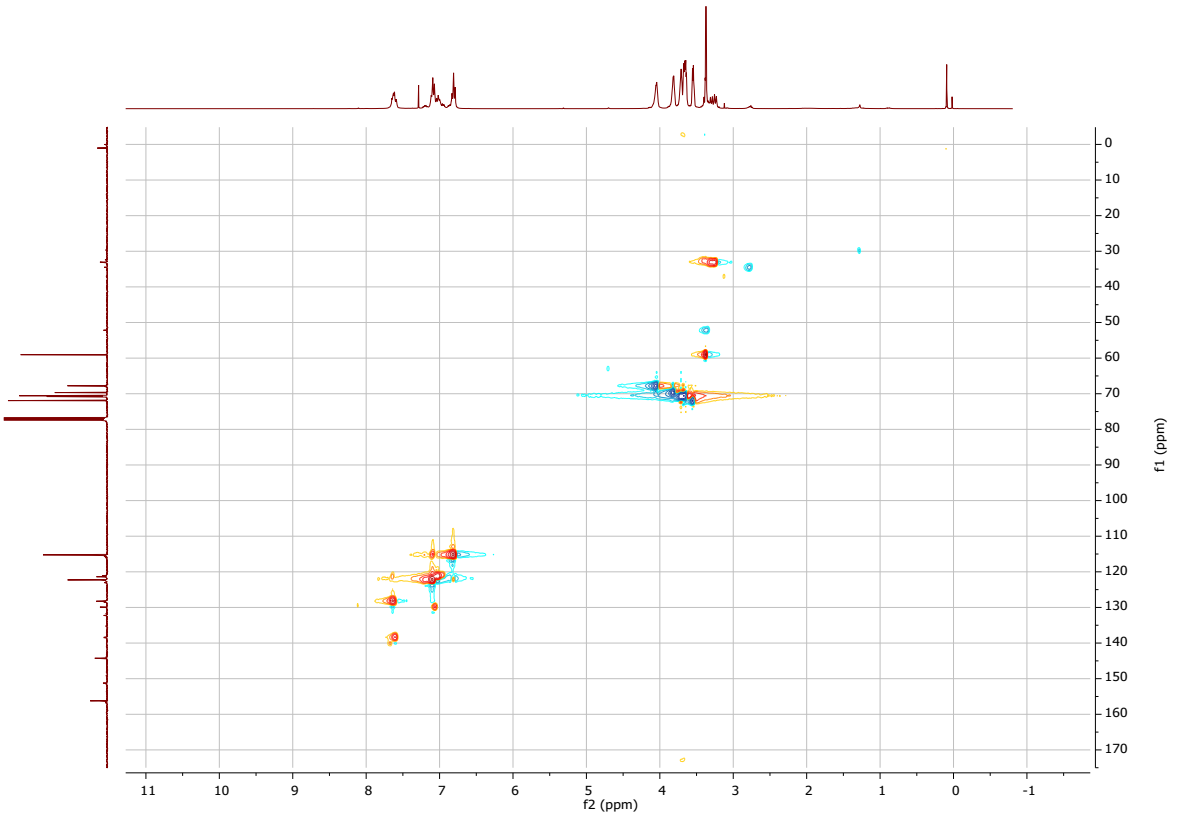


Figure S48. ^{1}H-$^{13}C\{^{1}H\}$ HSQC spectrum of **12-[G_1]-PEG** recorded in $CDCl_3$ at room temperature (400 MHz, 101 MHz).

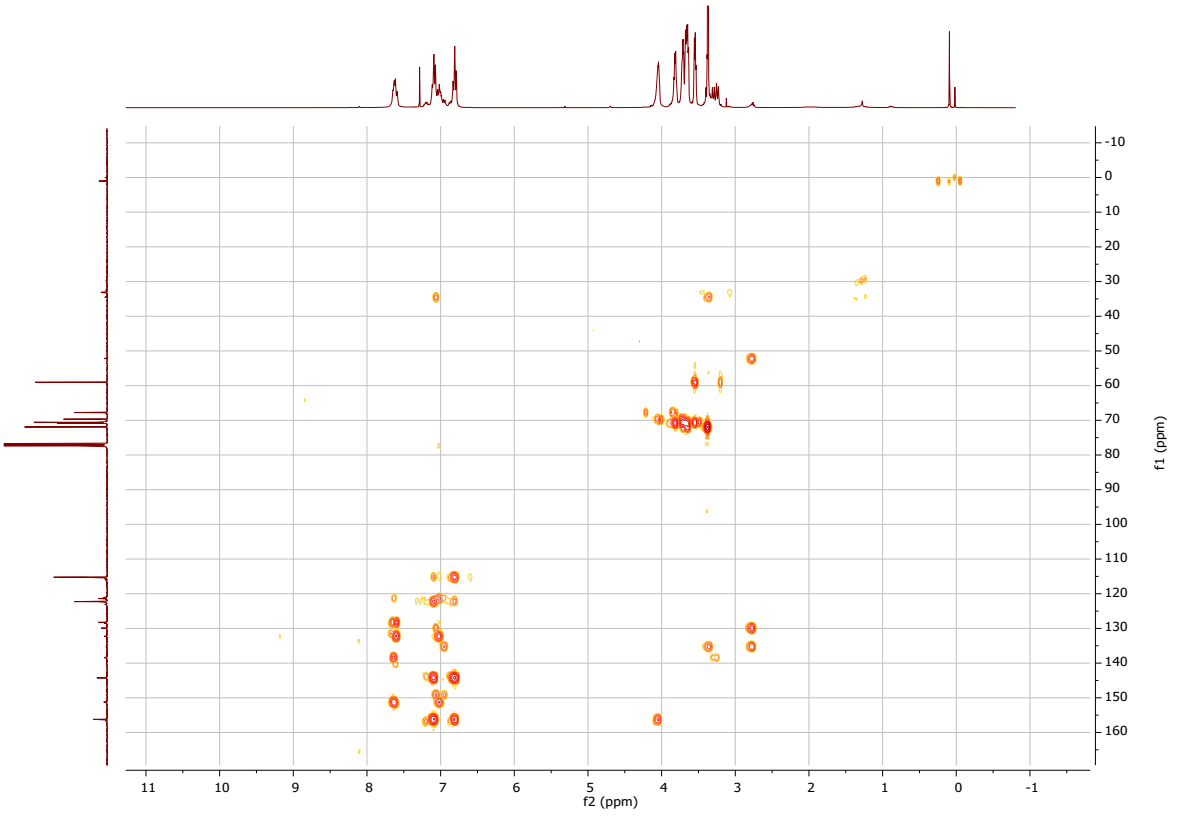


Figure S49. ^{1}H-$^{13}C\{^{1}H\}$ HMBC spectrum of **12-[G_1]-PEG** recorded in $CDCl_3$ at room temperature (400 MHz, 101 MHz).

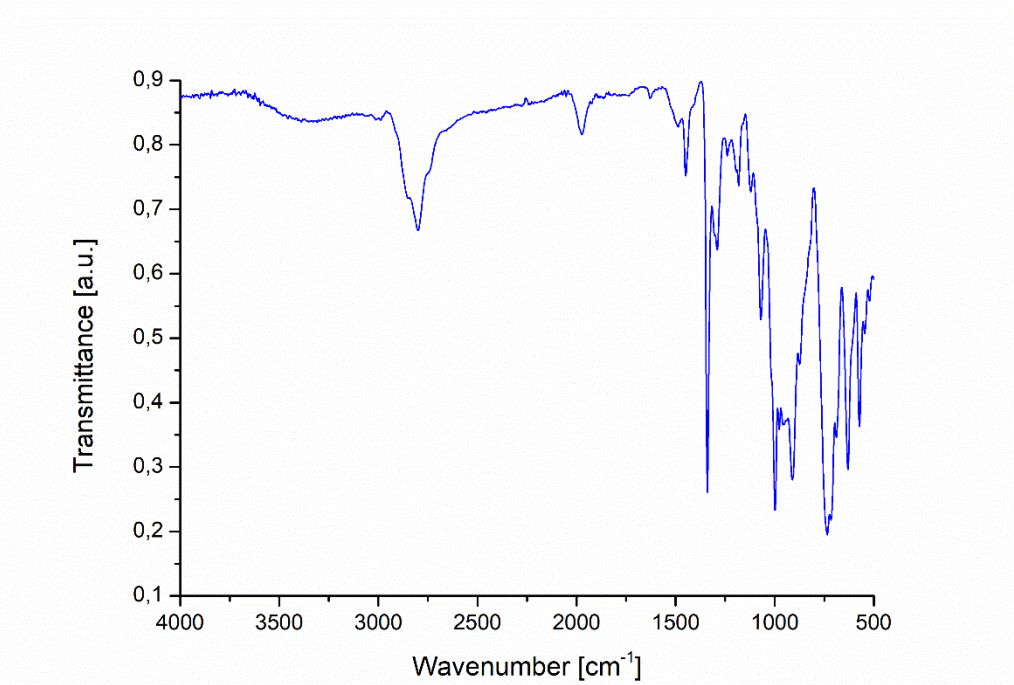


Figure S50. FT-IR spectrum of **12-[G_1]-PEG**.

3.12. Synthesis of 13-[G_0']-[G_1]-PEG

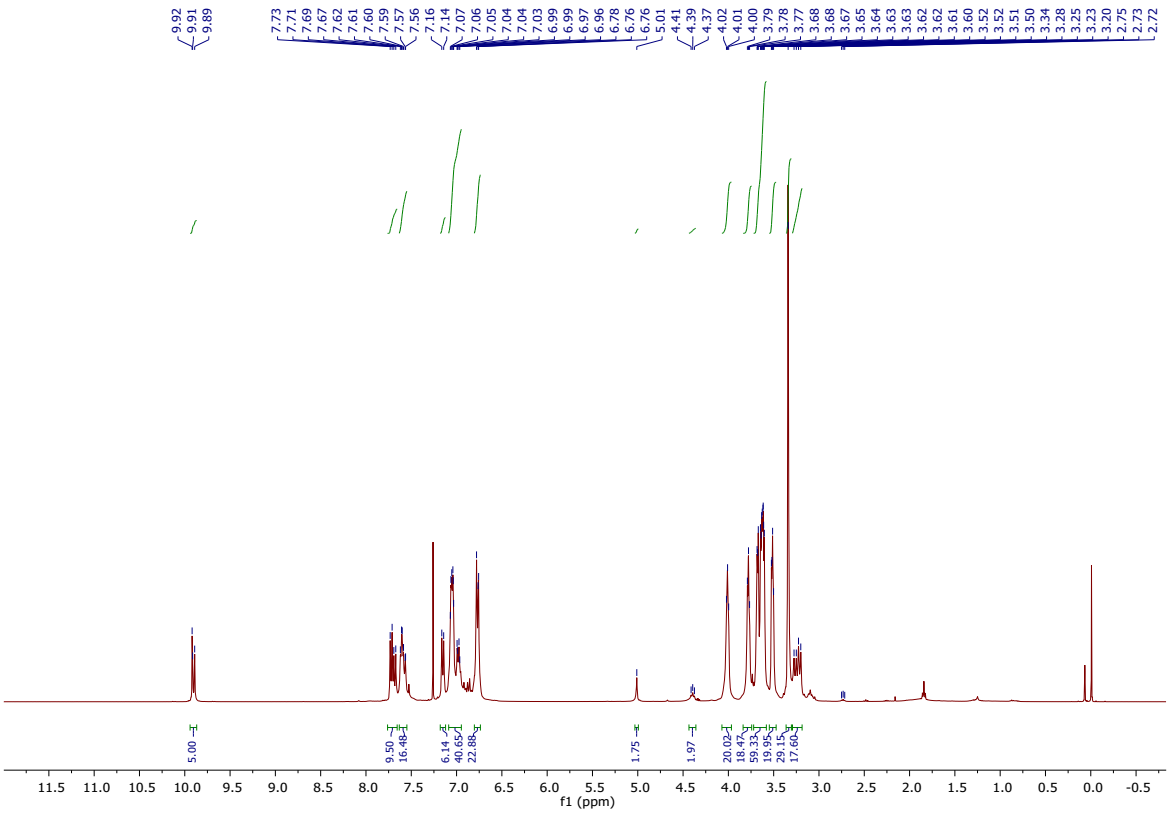


Figure S51. ^{1}H NMR spectrum of **13-[G_0']-[G_1]-PEG** in $CDCl_3$ recorded at room temperature (400 MHz).

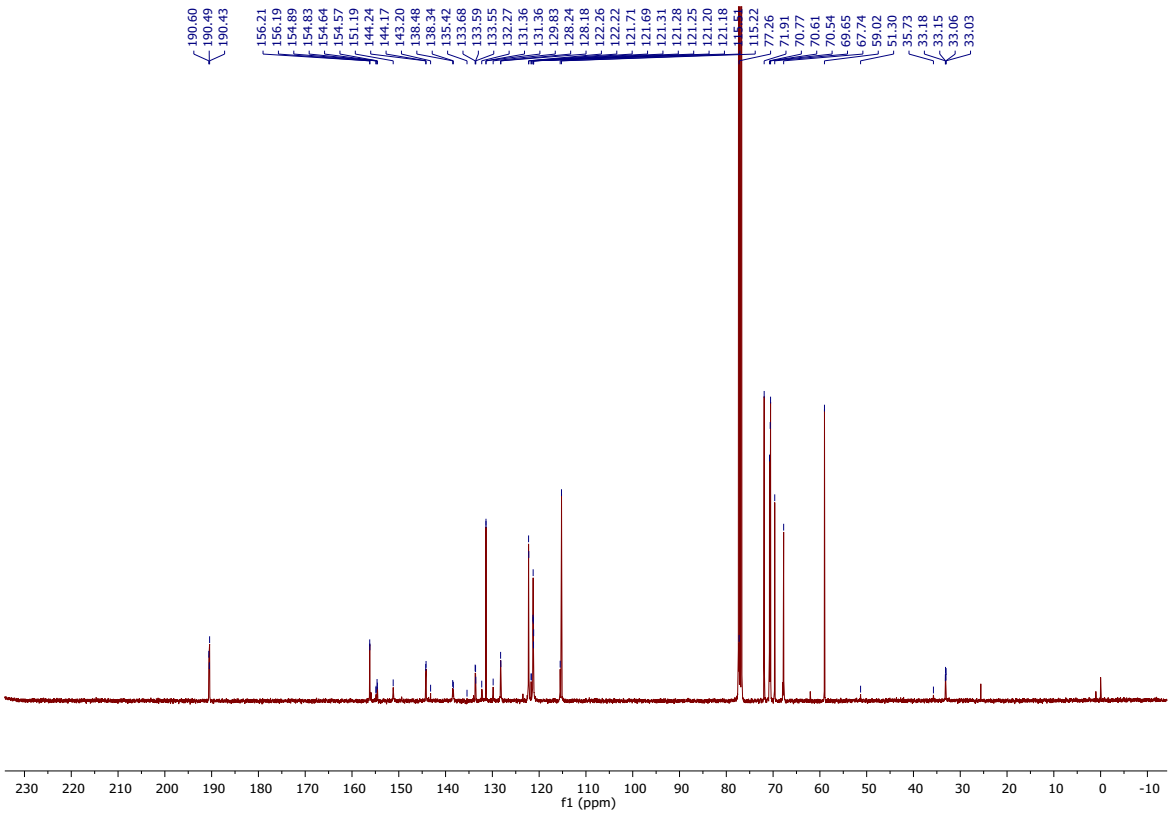


Figure S52. $^{13}C\{^{1}H\}$ NMR spectrum of **13-[G_0'][G_1]-PEG** in $CDCl_3$ recorded at room temperature (101 MHz).

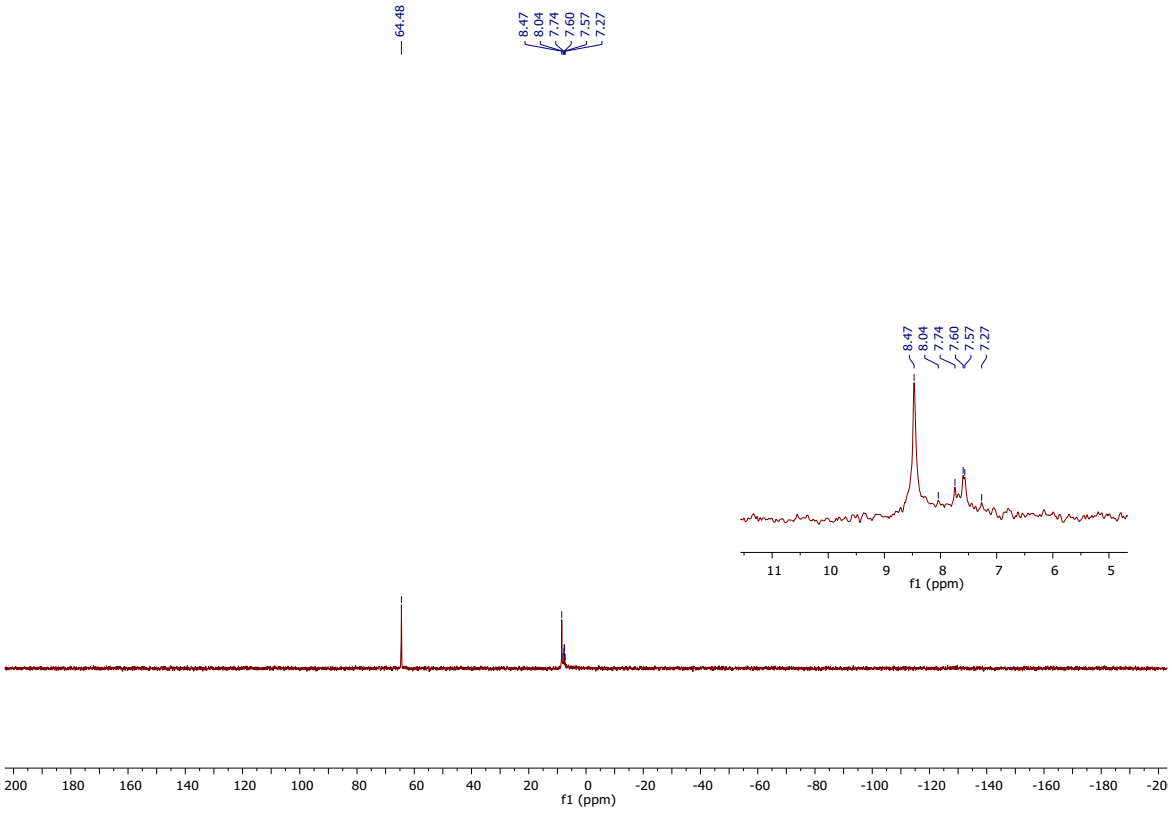


Figure S53. $^{31}P\{^{1}H\}$ NMR spectrum of **13-[G_0'][G_1]-PEG** in $CDCl_3$ recorded at room temperature (162 MHz).

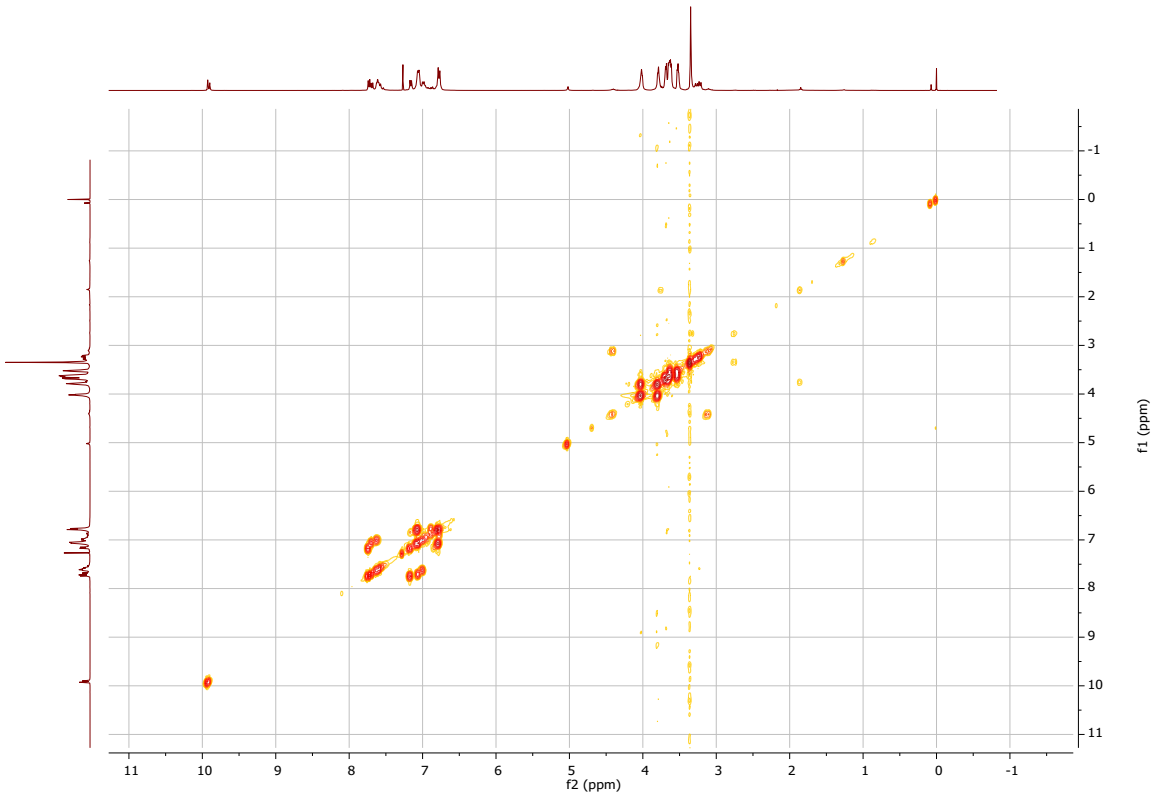


Figure S54. ^{1}H-^{1}H COSY spectrum of **13-[G_0'][G_1]-PEG** recorded in $CDCl_3$ at room temperature (400 MHz).

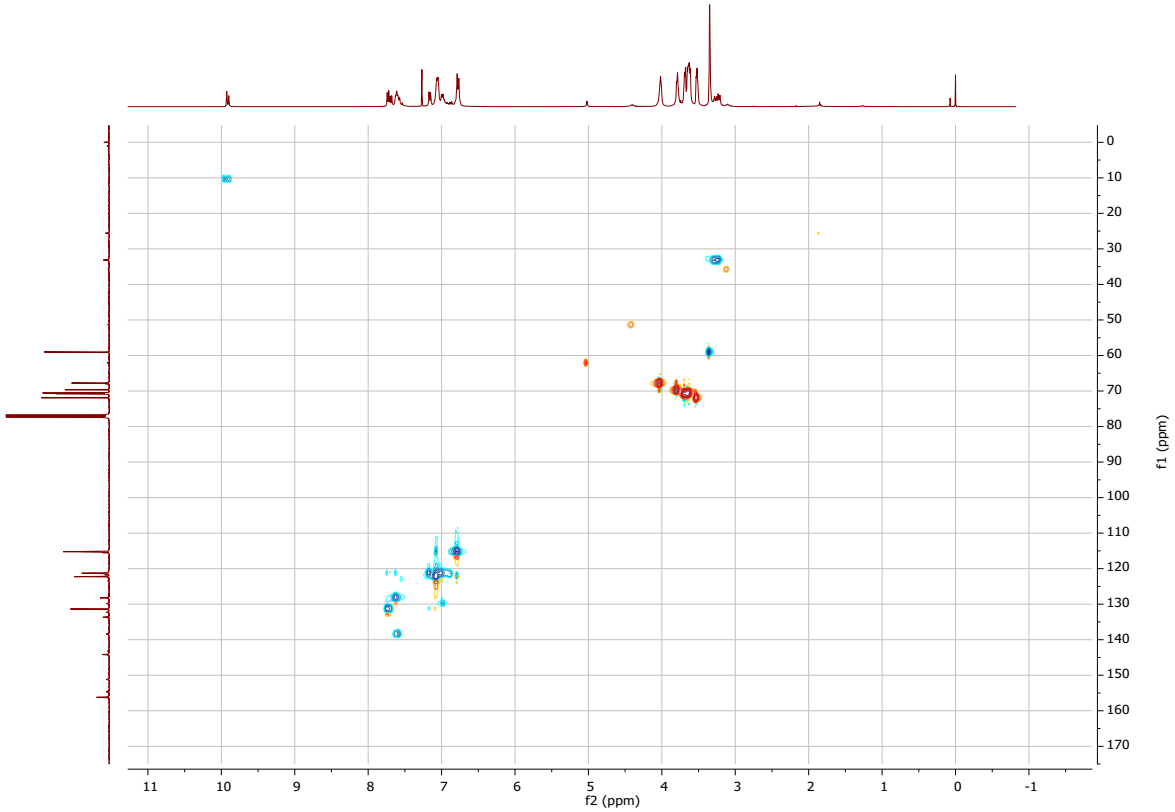


Figure S55. ^{1}H-^{13}C{^{1}H} HSQC spectrum of **13-[G_0'][G_1]-PEG** recorded in $CDCl_3$ at room temperature (400 MHz, 101 MHz).

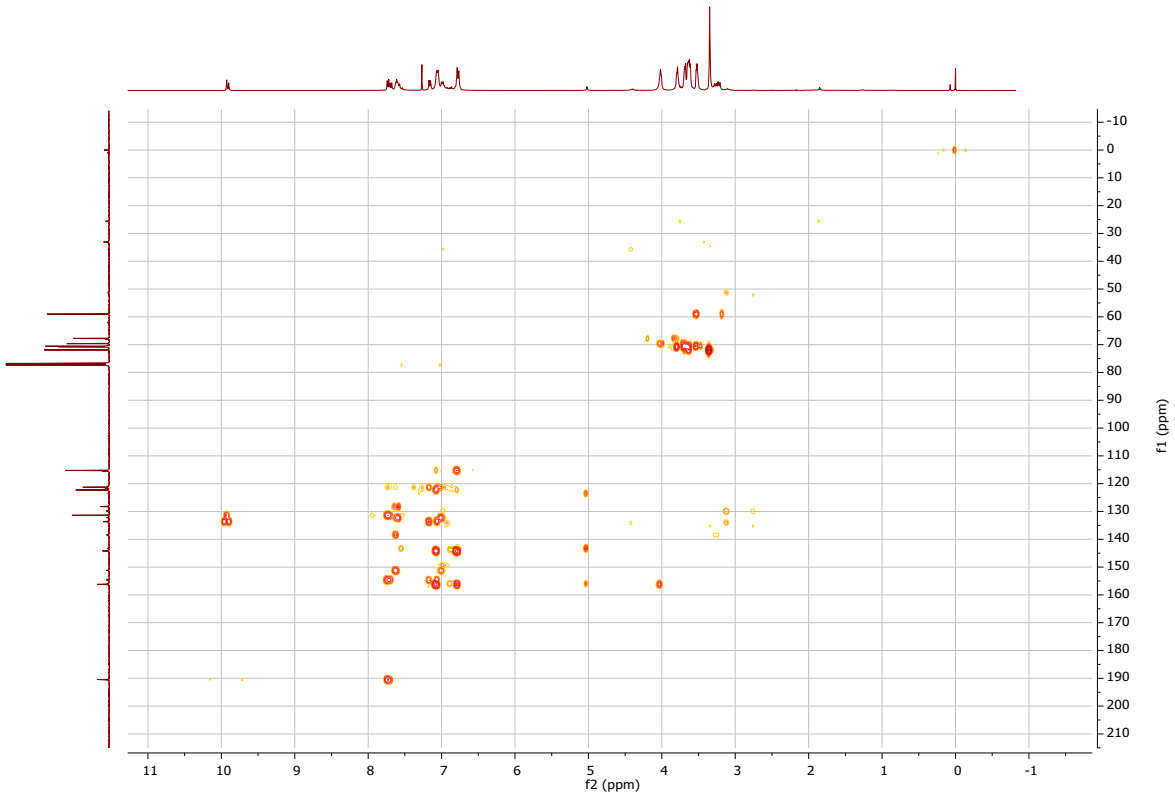


Figure S56. ^{1}H-$^{13}C\{^{1}H\}$ HMBC spectrum of **13-[G_0'][G_1]-PEG** recorded in $CDCl_3$ at room temperature (400 MHz, 101 MHz).

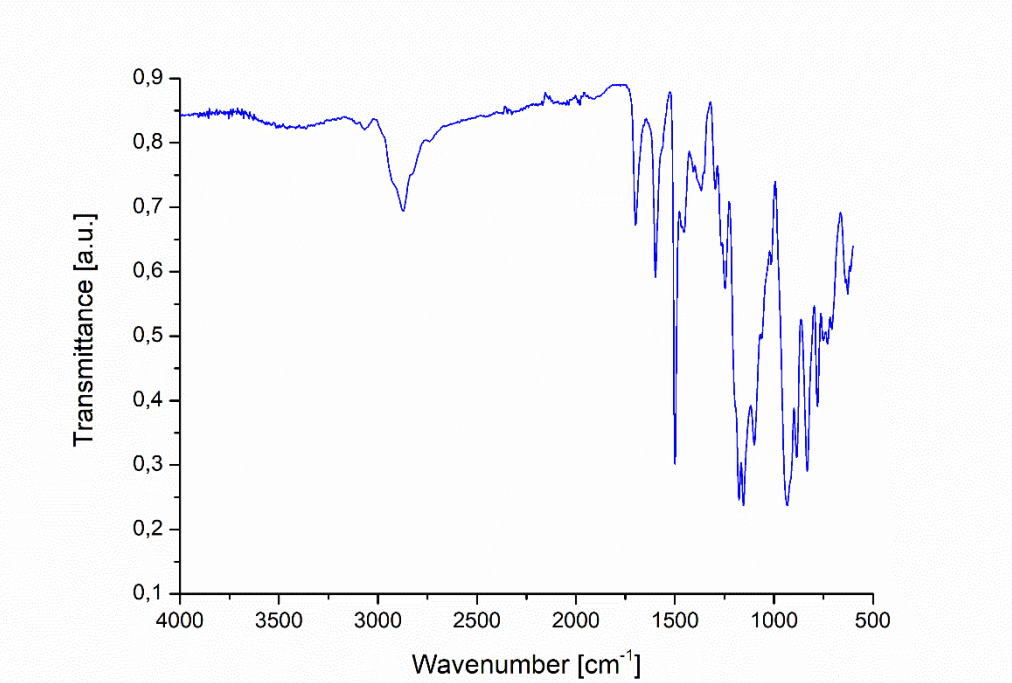


Figure S57. FT-IR spectrum of **13-[G_0'][G_1]-PEG**.

3.13. Synthesis of 14-[G_1][G_1]-PEG

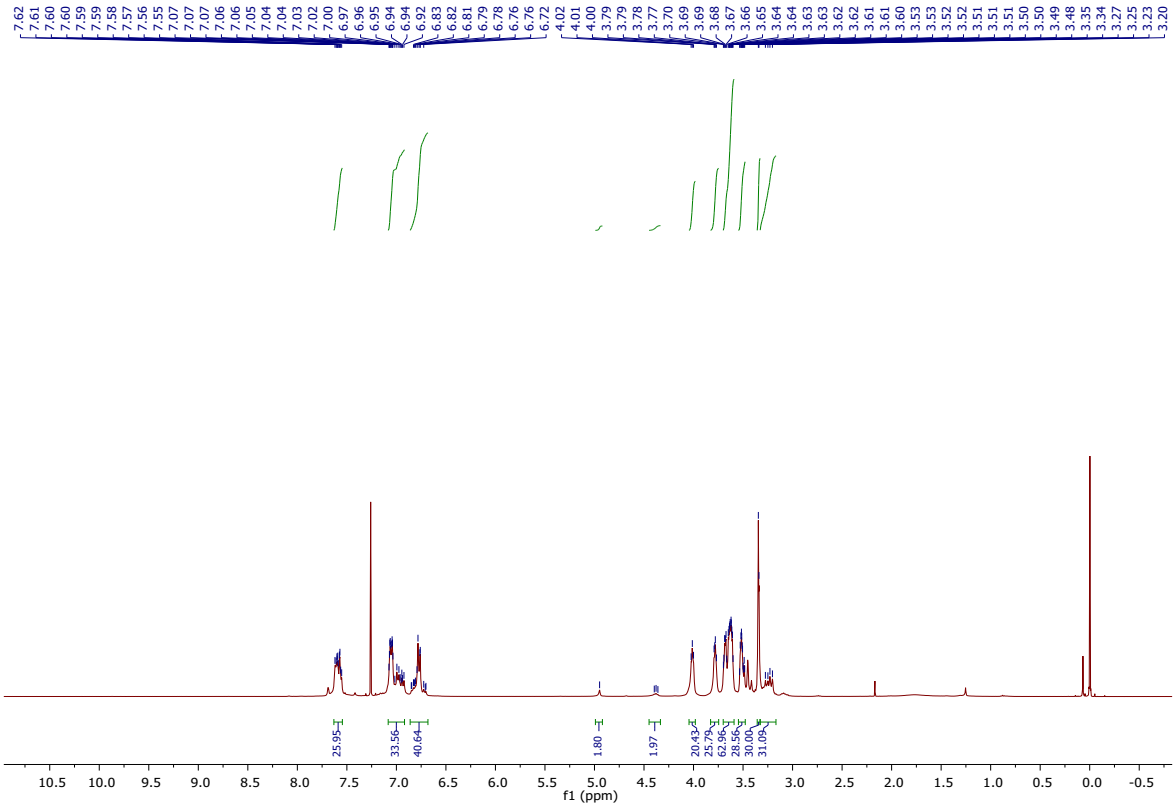


Figure S58. ^{1}H NMR spectrum of **14-[G_1][G_1]-PEG** in $CDCl_3$ recorded at room temperature (400 MHz).

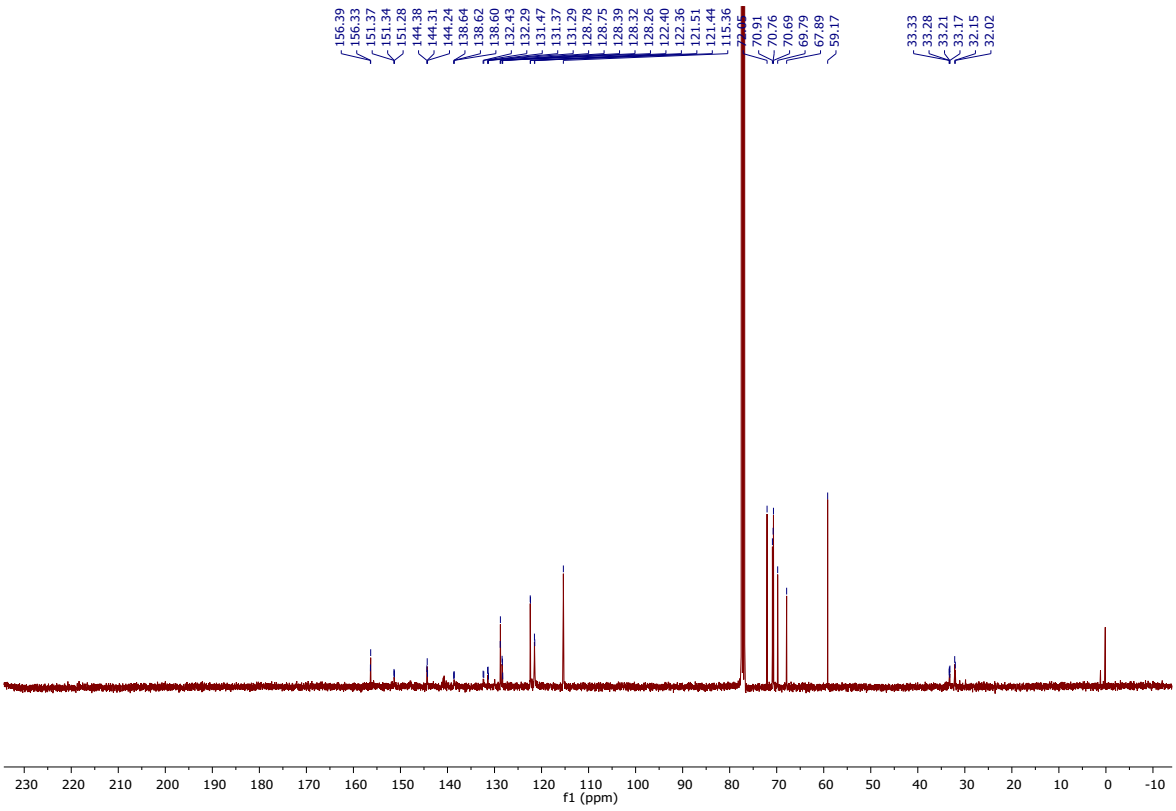


Figure S59. $^{13}C\{^{1}H\}$ NMR spectrum of **14-[G_1][G_1]-PEG** in $CDCl_3$ recorded at room temperature (101 MHz).

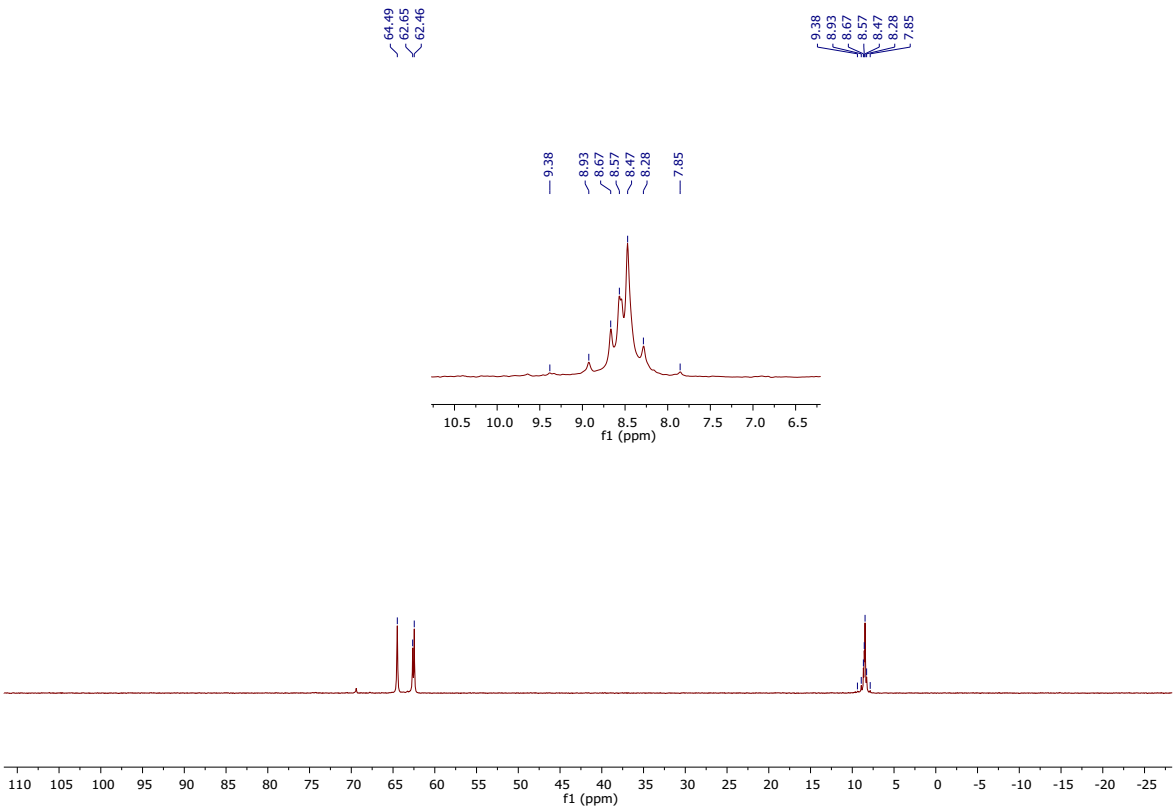


Figure S60. $^{31}P\{^{1}H\}$ NMR spectrum of **14-[G_1][G_1]-PEG** in $CDCl_3$ recorded at room temperature (162 MHz).

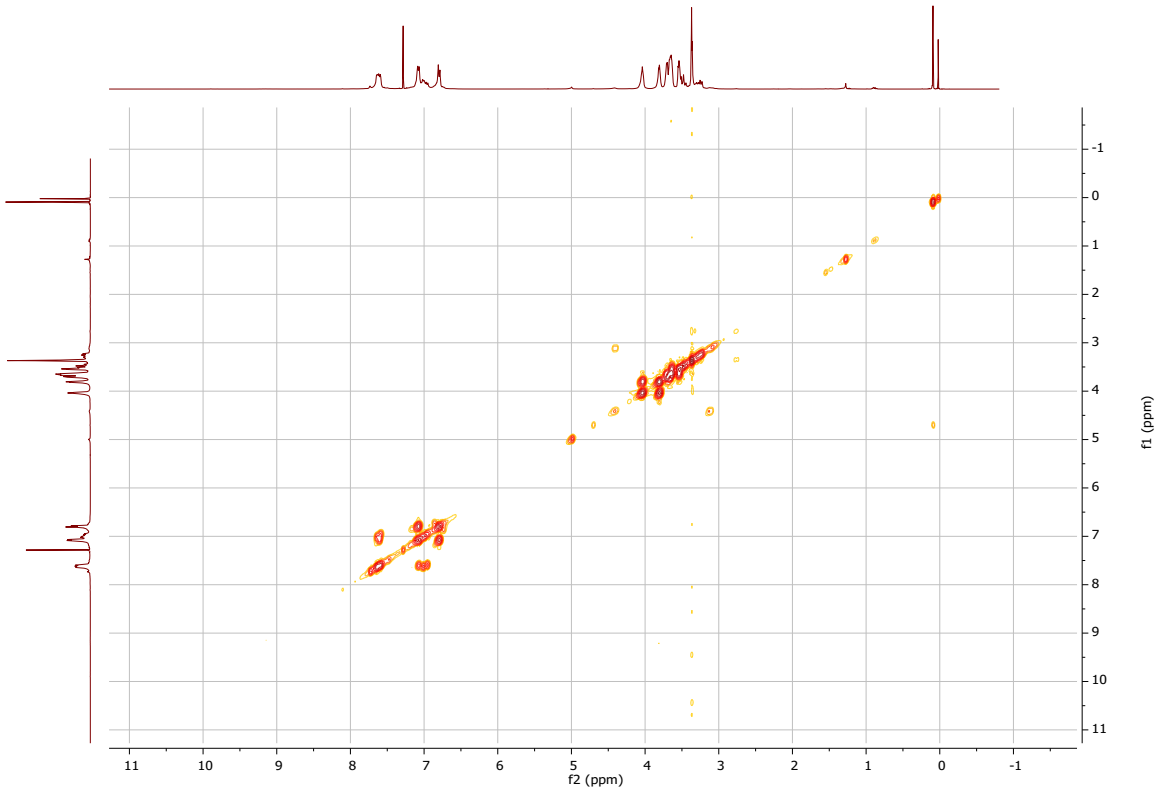


Figure S61. ^{1}H-^{1}H COSY spectrum of **14-[G_1][G_1]-PEG** recorded in $CDCl_3$ at room temperature (400 MHz).

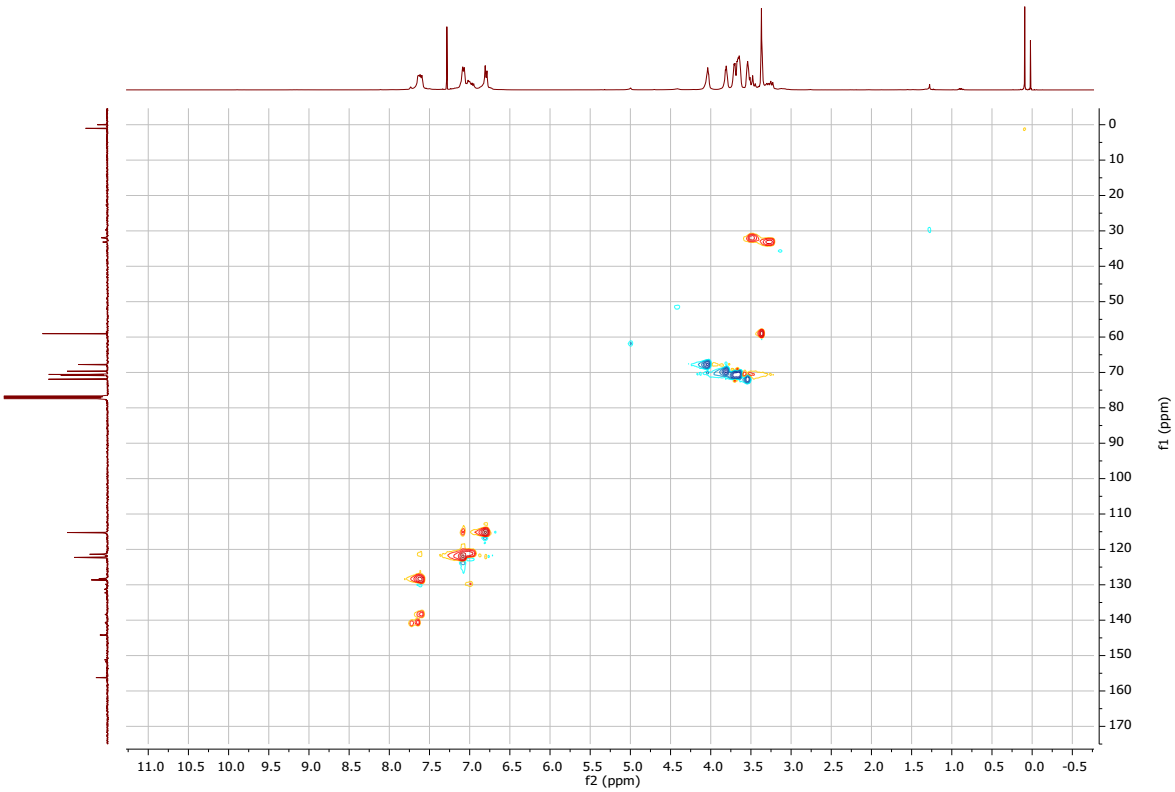


Figure S62. ^{1}H-$^{13}C\{^{1}H\}$ HSQC spectrum of **14-[G_1][G_1]-PEG** recorded in $CDCl_3$ at room temperature (400 MHz, 101 MHz).

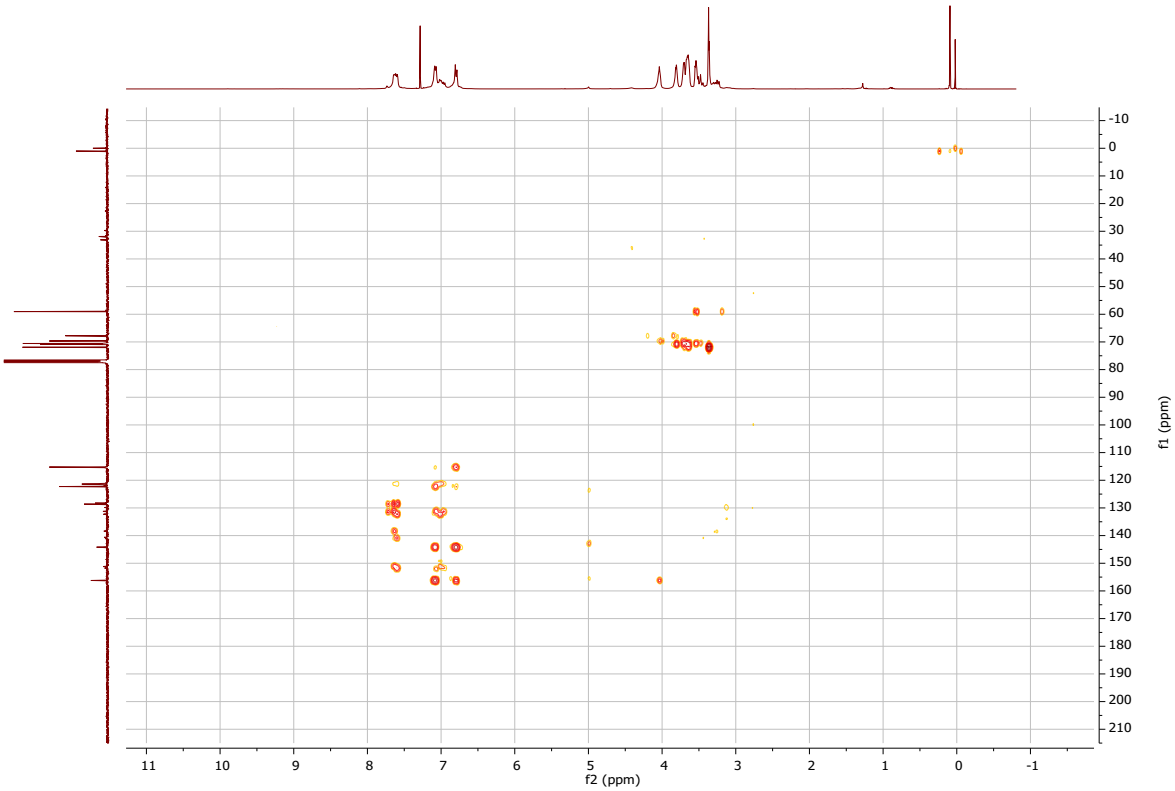


Figure S63. ^{1}H-$^{13}C\{^{1}H\}$ HMBC spectrum of **14-[G_1][G_1]-PEG** recorded in $CDCl_3$ at room temperature (400 MHz, 101 MHz).

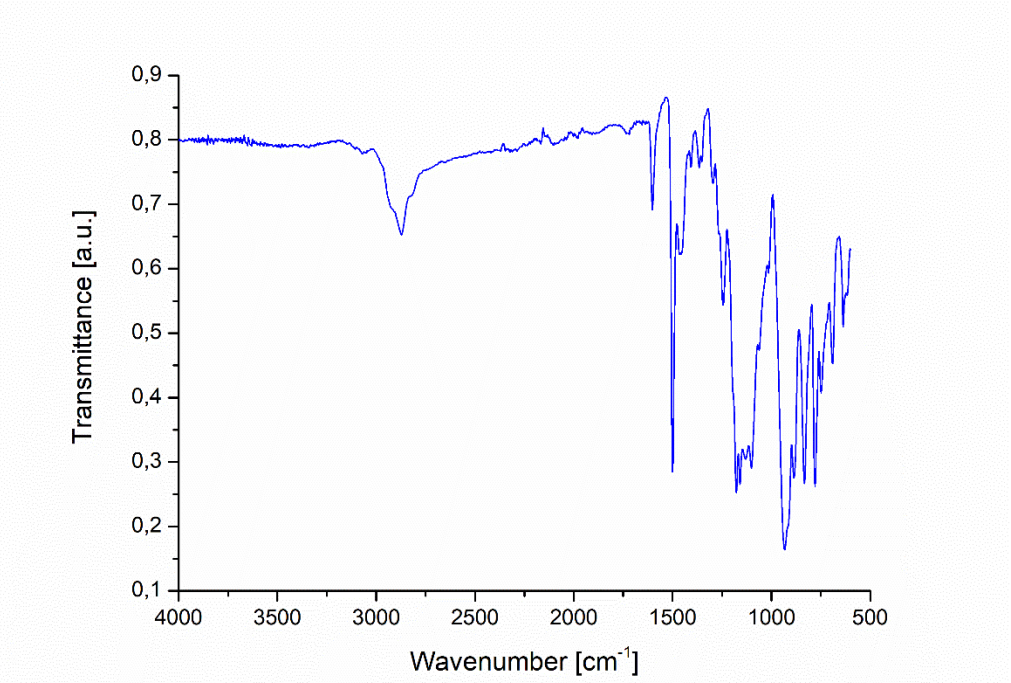


Figure S64. FT-IR spectrum of **14-[G_1][G_1]-PEG**.

3.14. Synthesis of (4-bromophenoxy)(tert-butyl)dimethylsilane 38

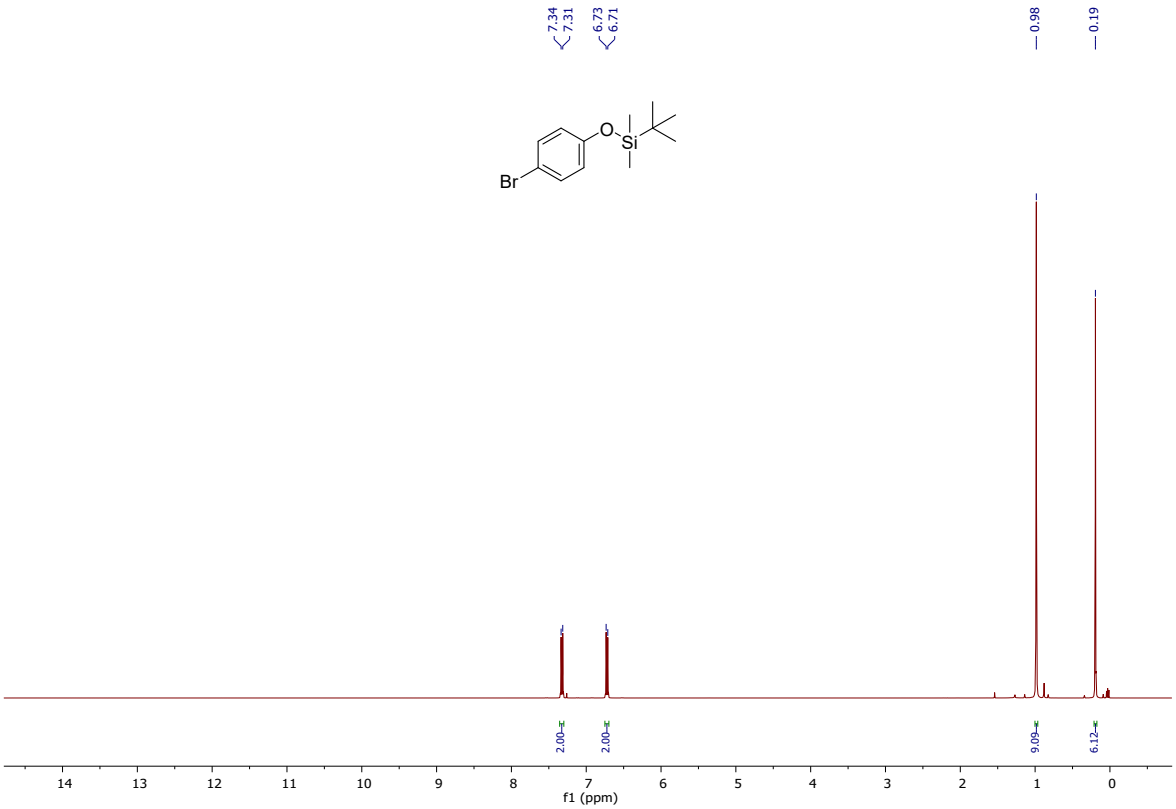


Figure S65. ^{1}H NMR spectrum of (4-bromophenoxy)(tert-butyl)dimethylsilane **38** in $CDCl_3$ recorded at room temperature (400 MHz).

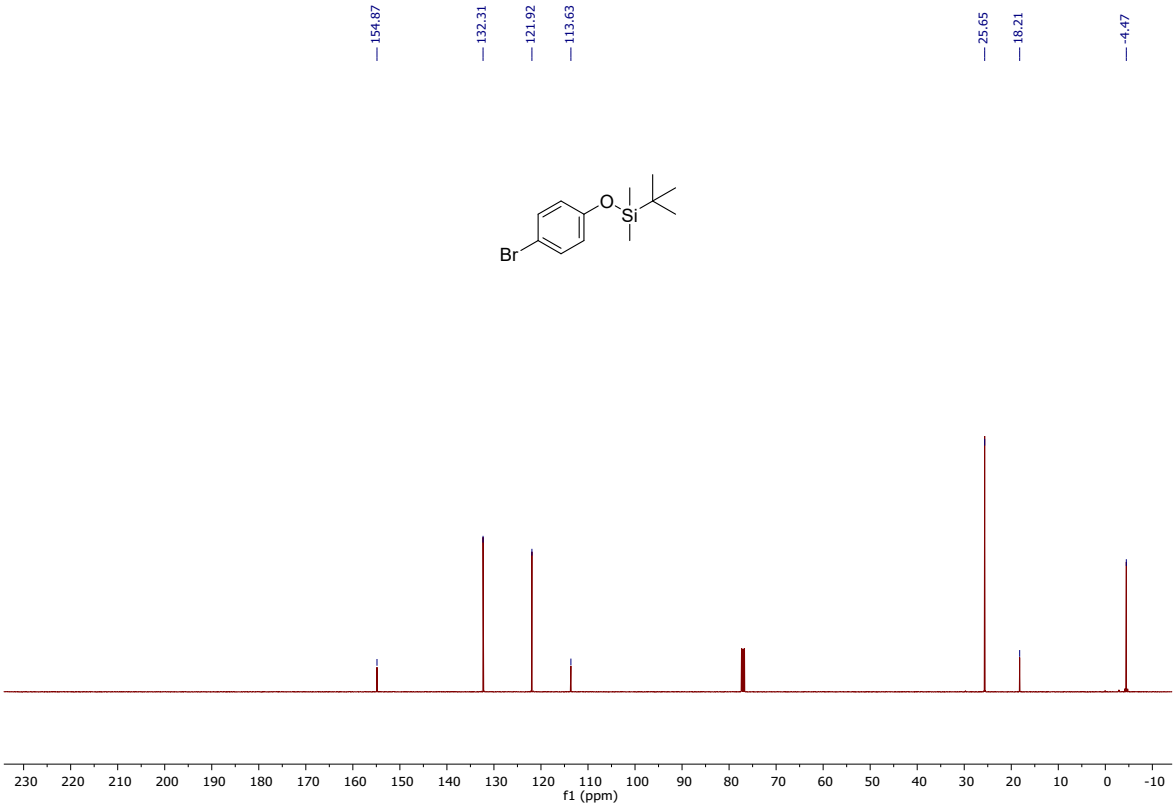


Figure S66. $^{13}C\{^{1}H\}$ NMR spectrum of (4-bromophenoxy)(tert-butyl)dimethylsilane **38** in $CDCl_3$ recorded at room temperature (101 MHz).

3.15. Synthesis of (4-((*tert*-butyldimethylsilyl)oxy)phenyl)diphenylphosphane 39

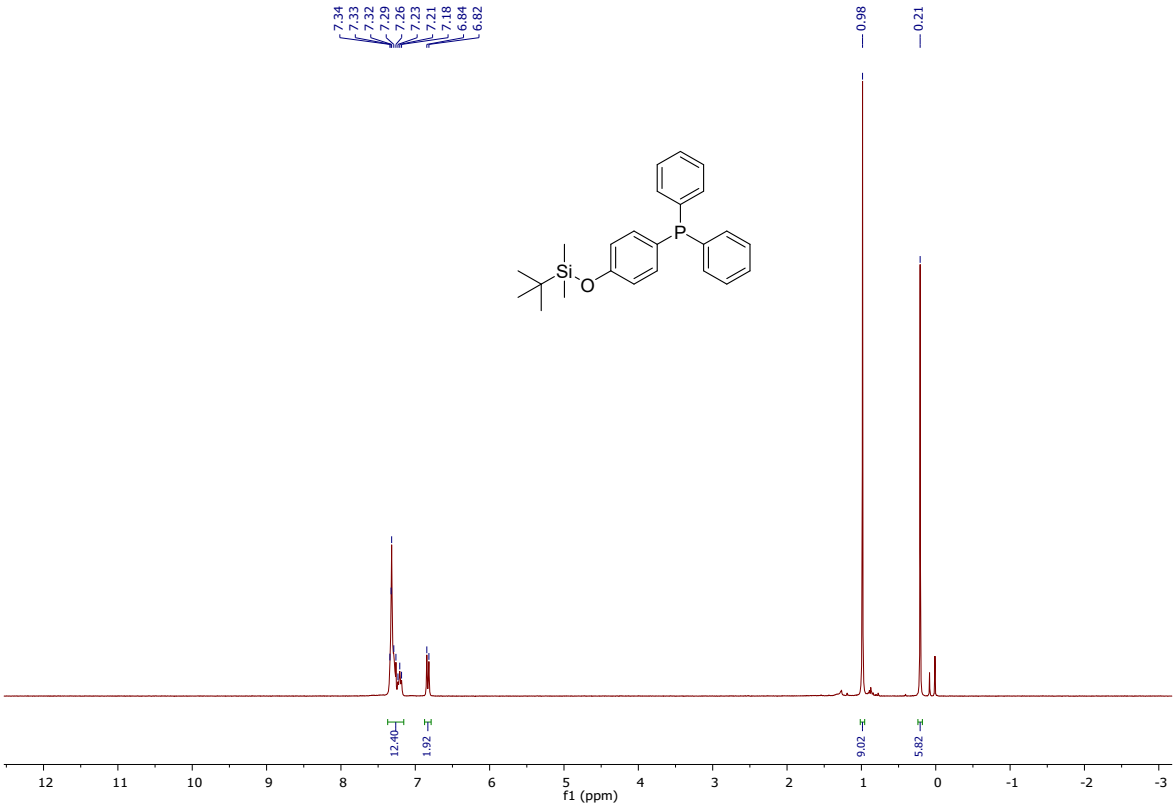


Figure S67. ^{1}H NMR spectrum of (4-((tert-butyldimethylsilyl)oxy)phenyl)diphenylphosphane **39** recorded at room temperature in $CDCl_3$ (300 MHz).

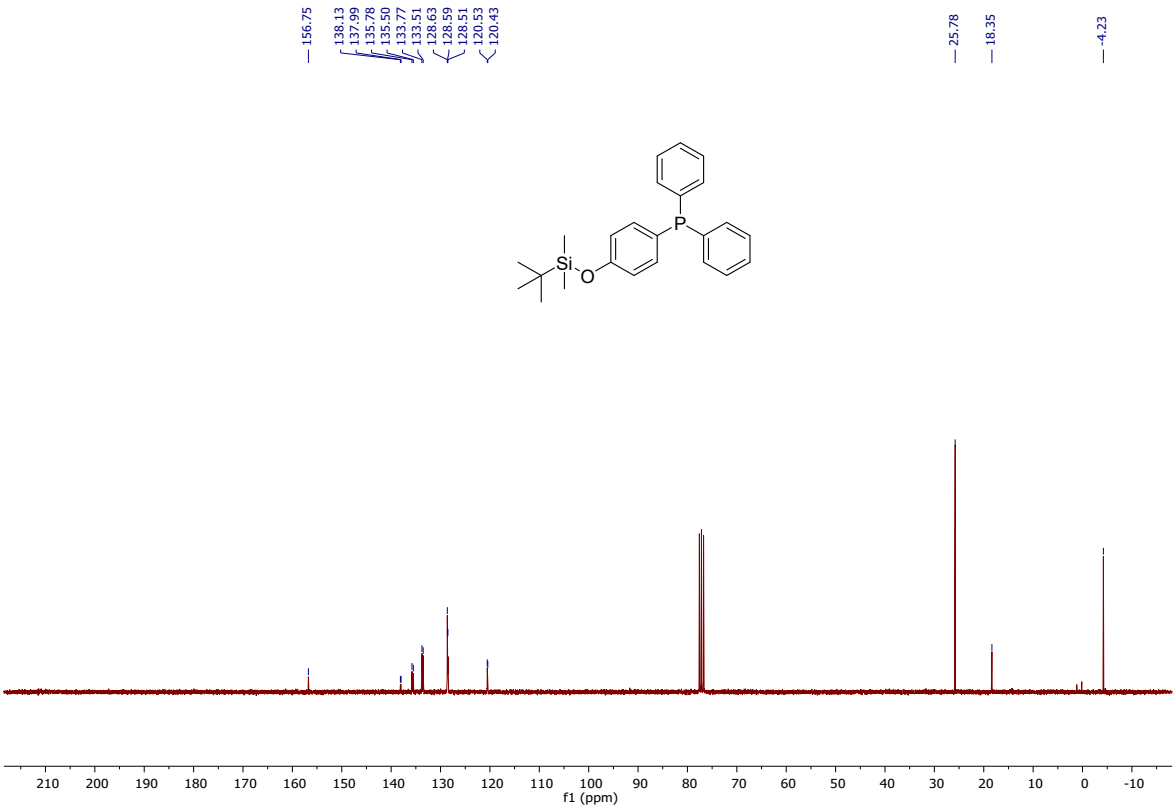


Figure S68. $^{13}C\{^{1}H\}$ NMR spectrum of (4-((tert-butyldimethylsilyl)oxy)phenyl)diphenylphosphane **39** recorded at room temperature in $CDCl_3$ (75 MHz).

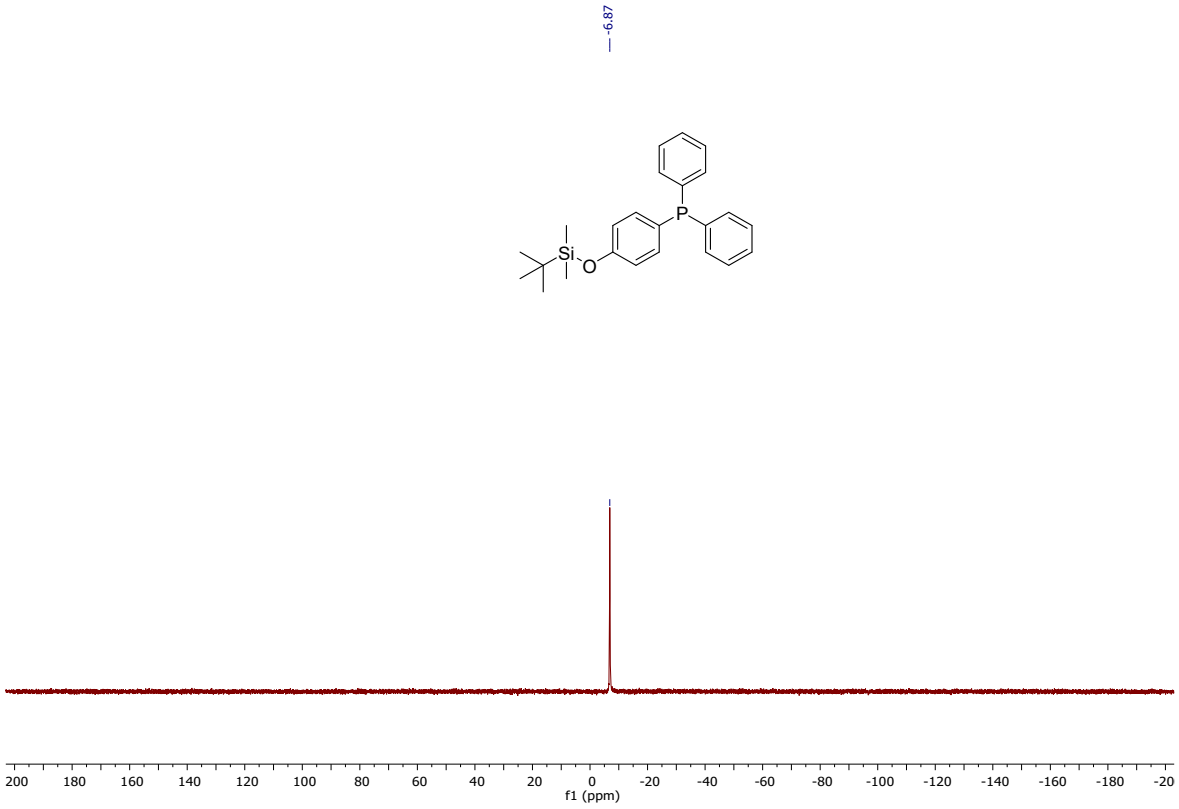


Figure S69. $^{31}C\{^{1}H\}$ NMR spectrum of (4-((tert-butyldimethylsilyl)oxy)phenyl)diphenylphosphane **39** recorded at room temperature in $CDCl_3$ (121 MHz).

3.16. Synthesis of 4-(diphenylphosphoryl)phenol 15

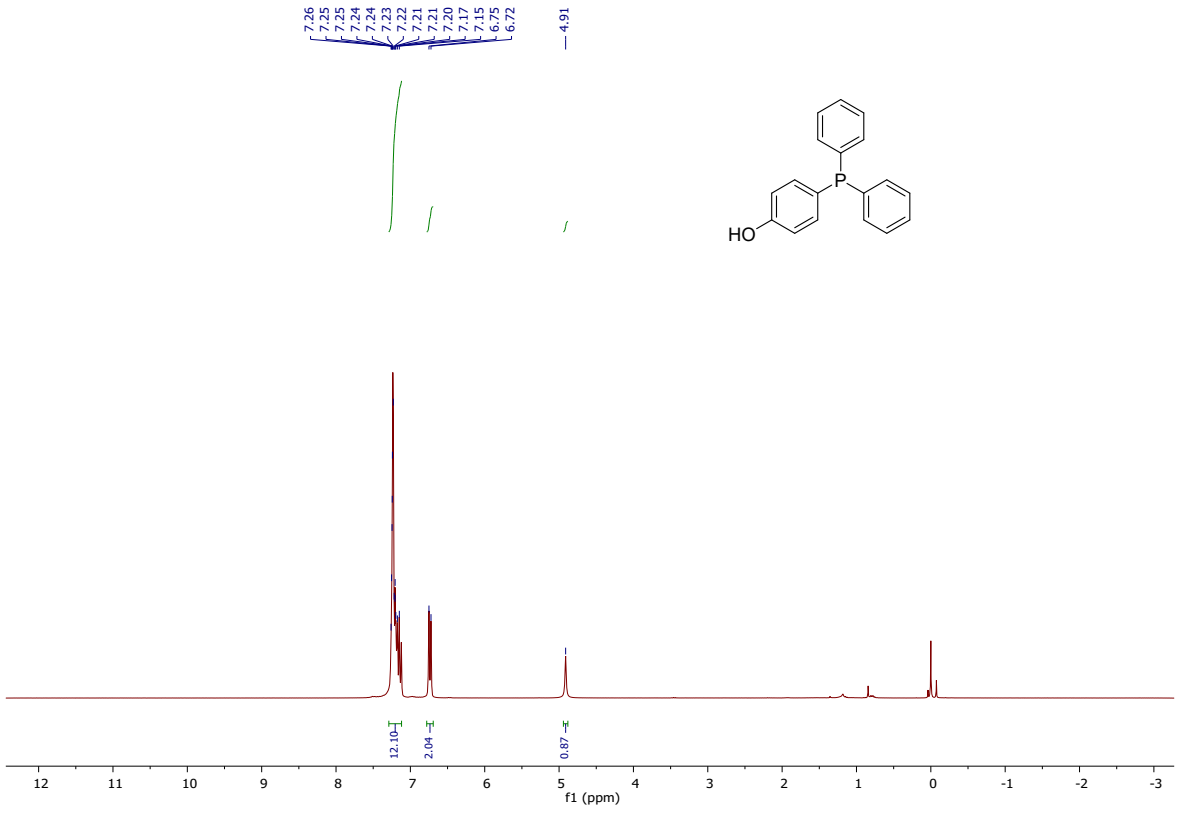


Figure S70. ^{1}H NMR spectrum of 4-(diphenylphosphoryl)phenol **15** in $CDCl_3$ recorded at room temperature (400 MHz).

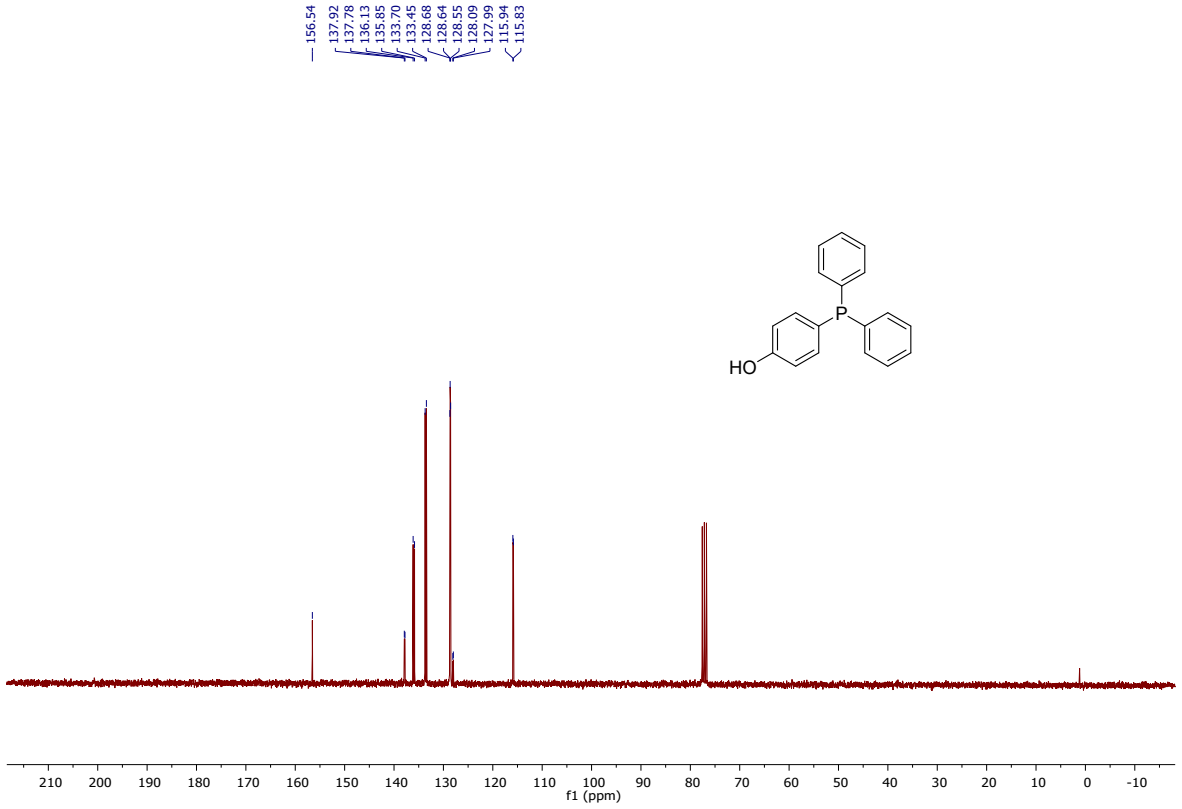


Figure S71. $^{13}C\{^{1}H\}$ NMR spectrum of 4-(diphenylphosphoryl)phenol **15** in $CDCl_3$ recorded at room temperature (101 MHz).

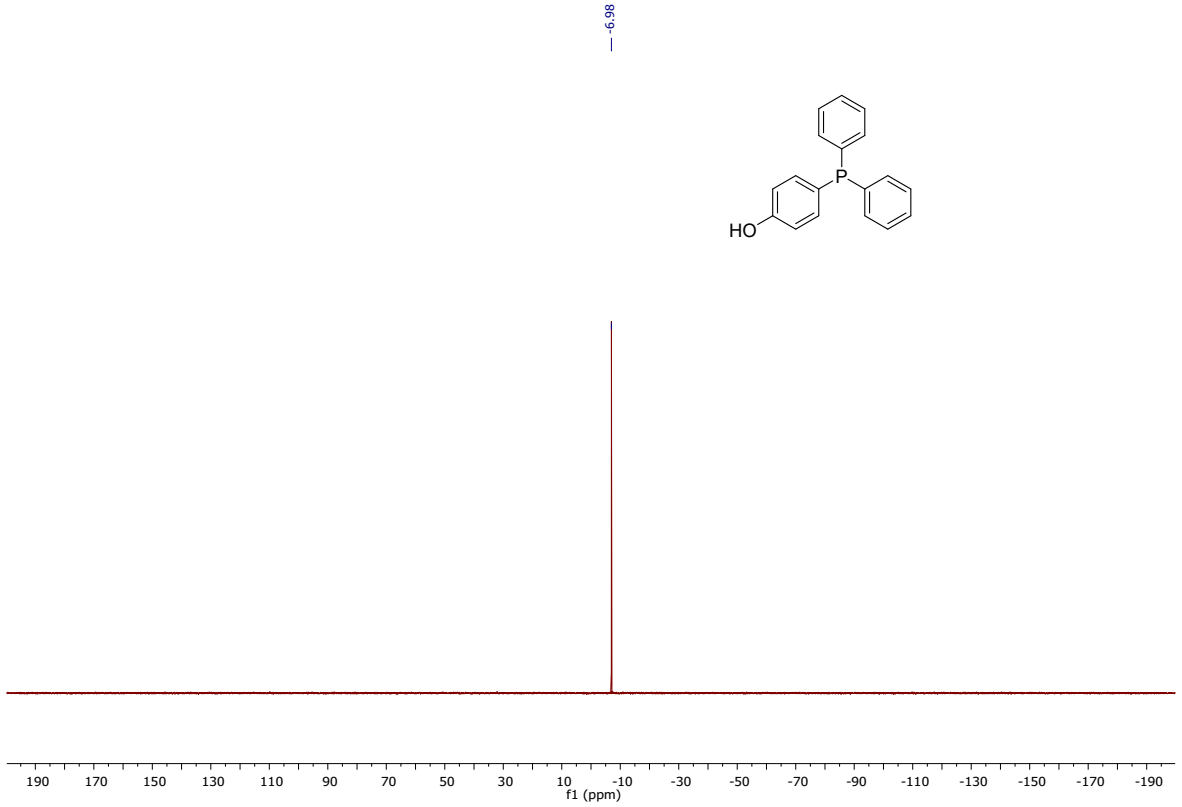


Figure S72. $^{31}P\{^{1}H\}$ NMR spectrum of 4-(diphenylphosphoryl)phenol **15** in $CDCl_3$ recorded at room temperature (162 MHz).

3.17. Synthesis of 16-[G_1][G_1]-PEG

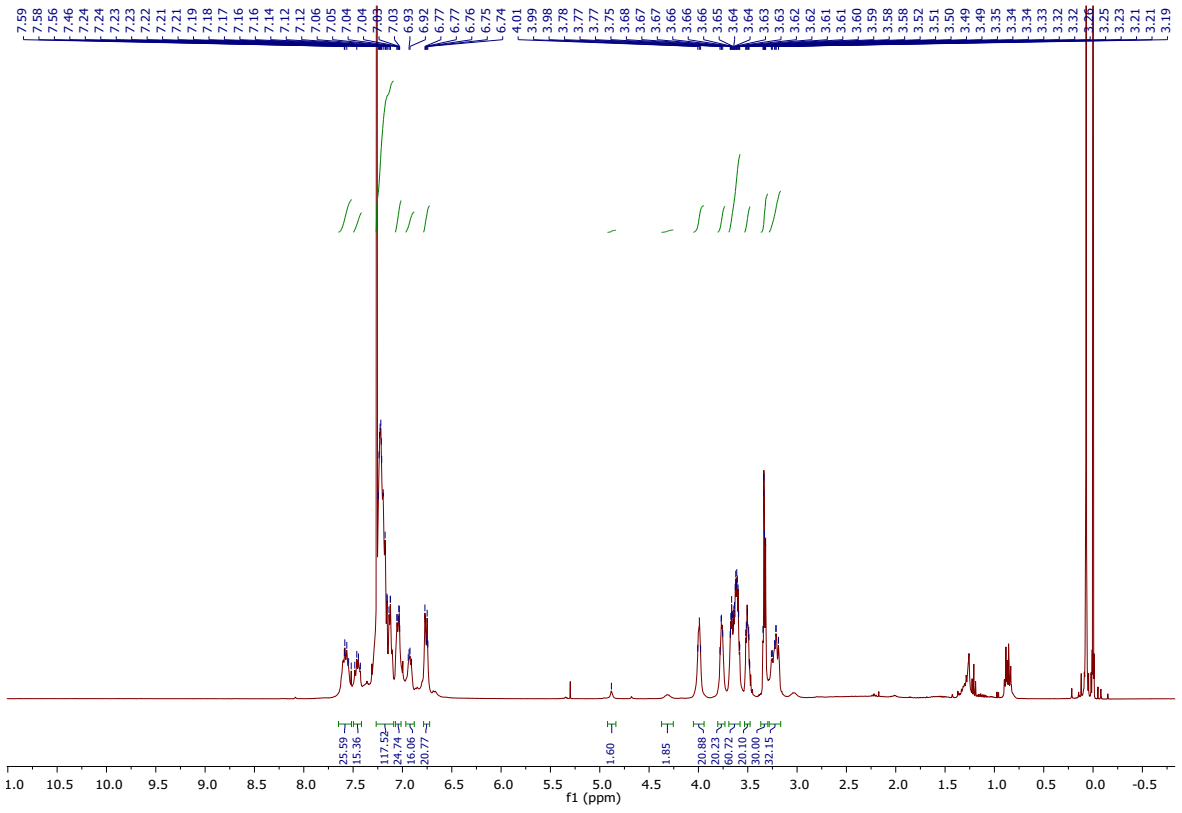


Figure S73. ^{1}H NMR spectrum of **16-[G_1][G_1]-PEG** in $CDCl_3$ recorded at room temperature (400 MHz).

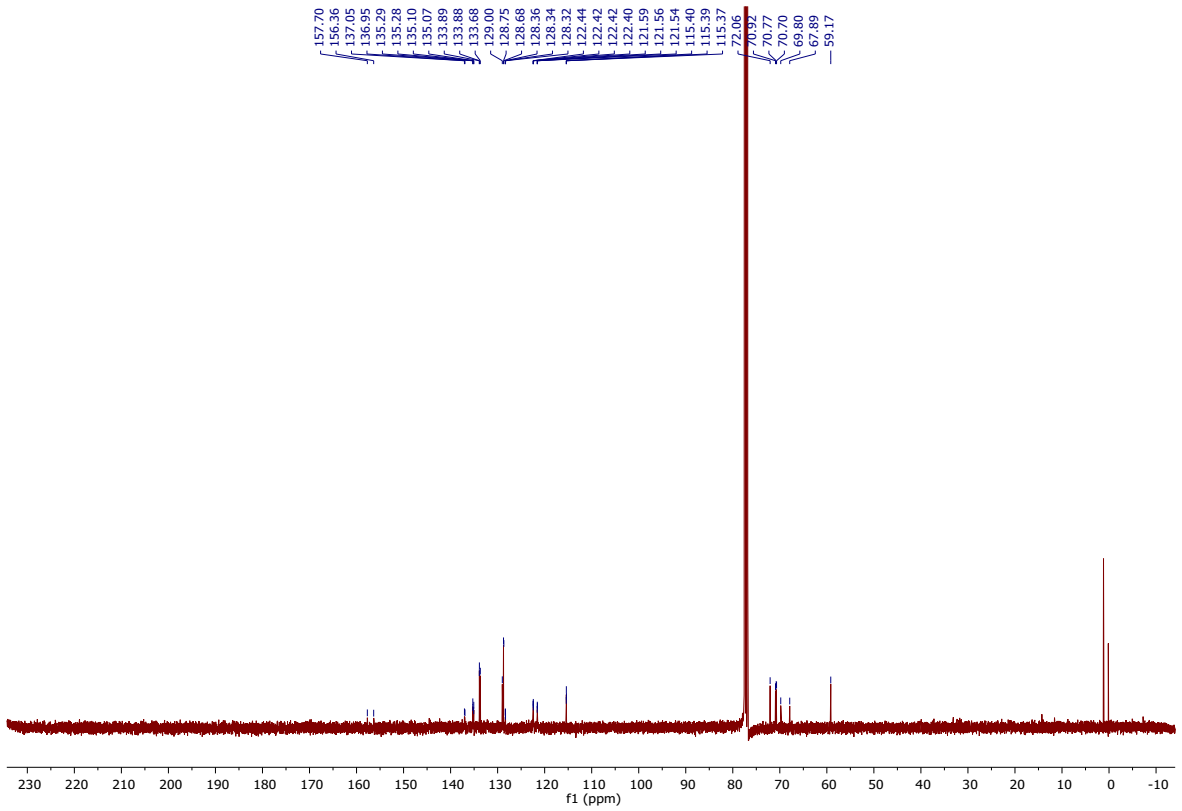


Figure S74. $^{13}C\{^{1}H\}$ NMR spectrum of **16-[G_1][G_1]-PEG** in $CDCl_3$ recorded at room temperature (101 MHz).

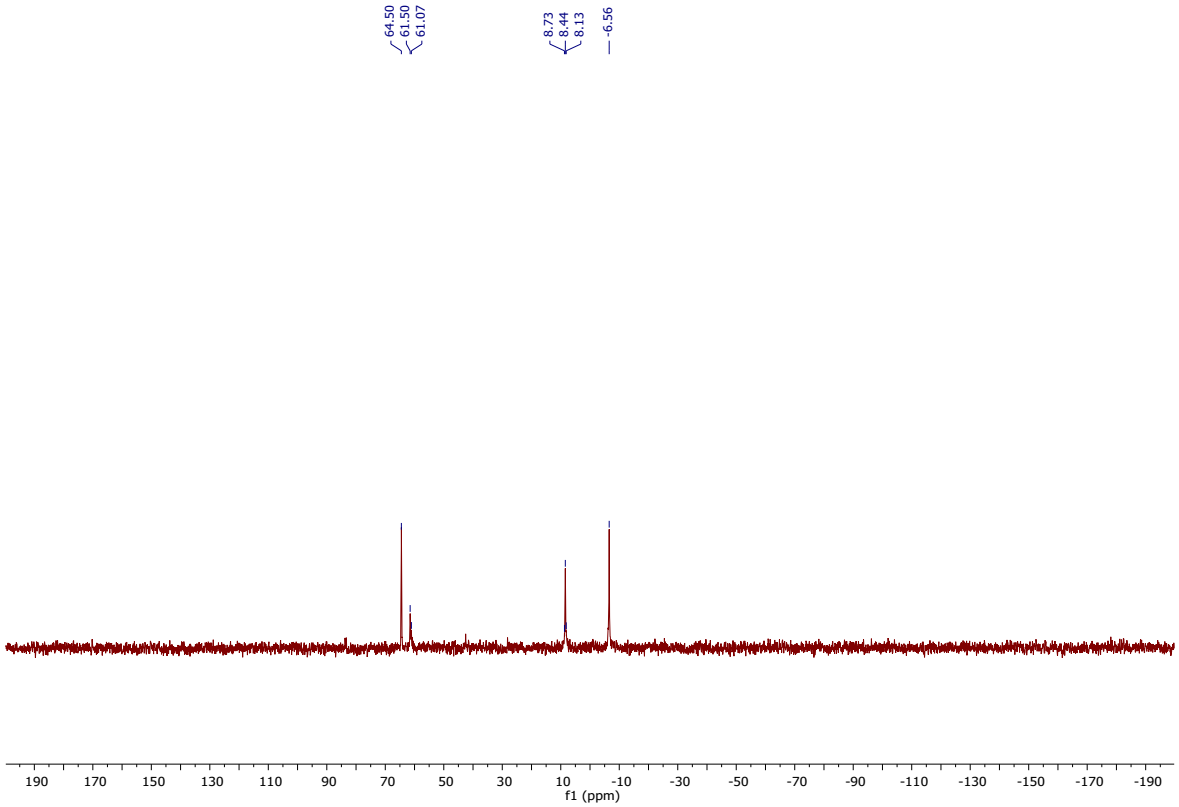


Figure S75. $^{31}P\{^{1}H\}$ NMR spectrum of **16-[G_1][G_1]-PEG** in $CDCl_3$ recorded at room temperature (162 MHz).

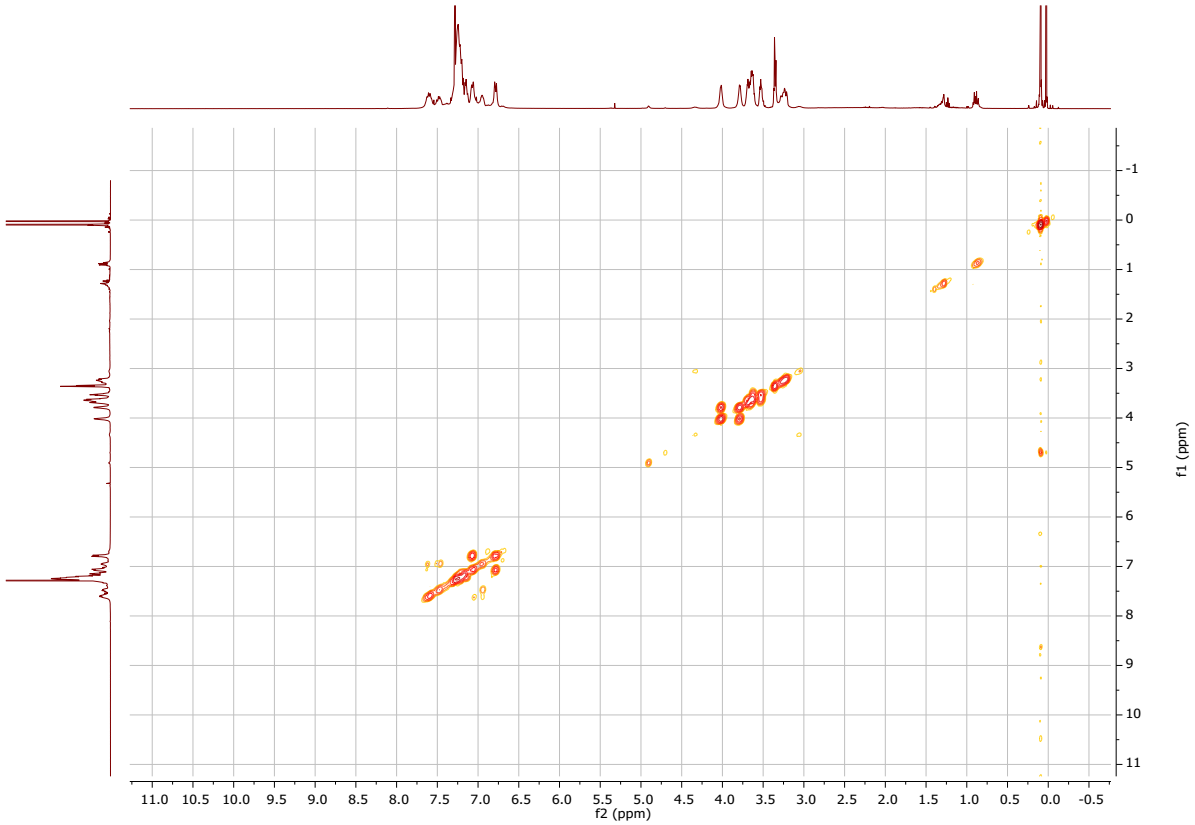


Figure S76. ^{1}H-^{1}H COSY spectrum of **16-[G_1][G_1]-PEG** in $CDCl_3$ recorded at room temperature (400 MHz).

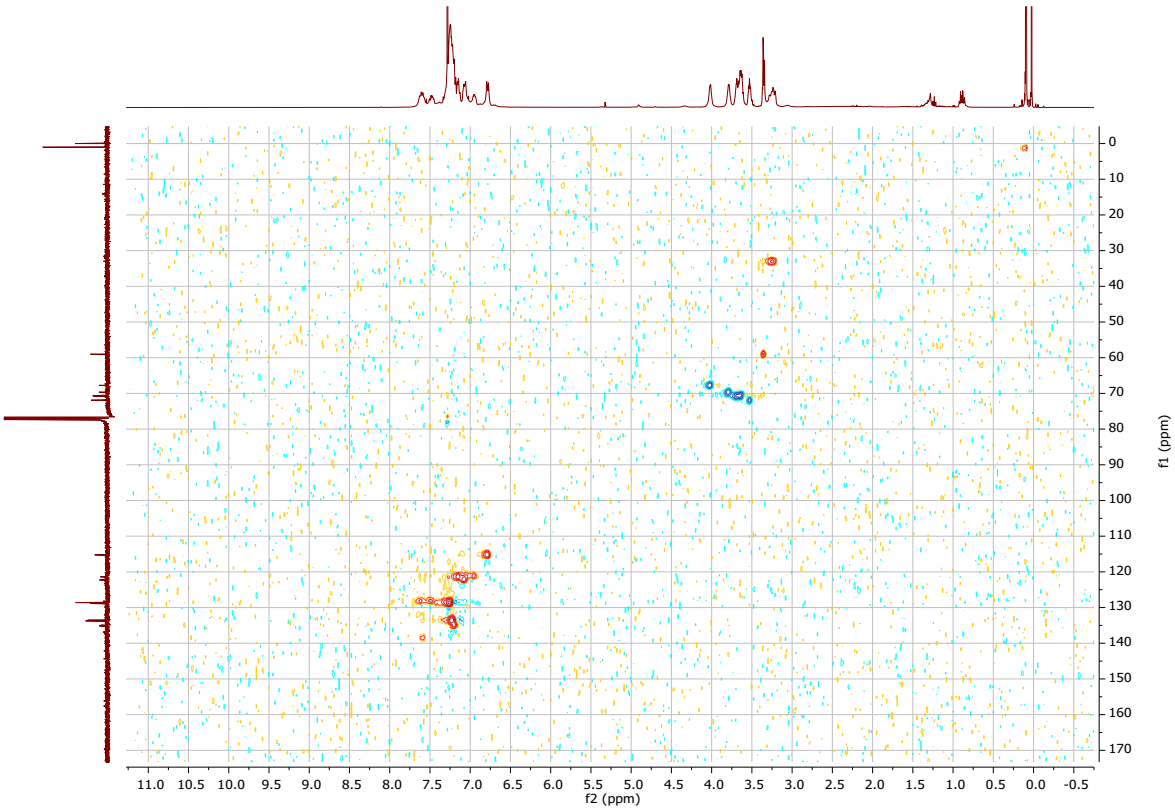


Figure S77. ^{1}H-$^{13}C\{^{1}H\}$ HSQC spectrum of **16-[G_1][G_1]-PEG** in $CDCl_3$ recorded at room temperature (400 MHz, 101 MHz).

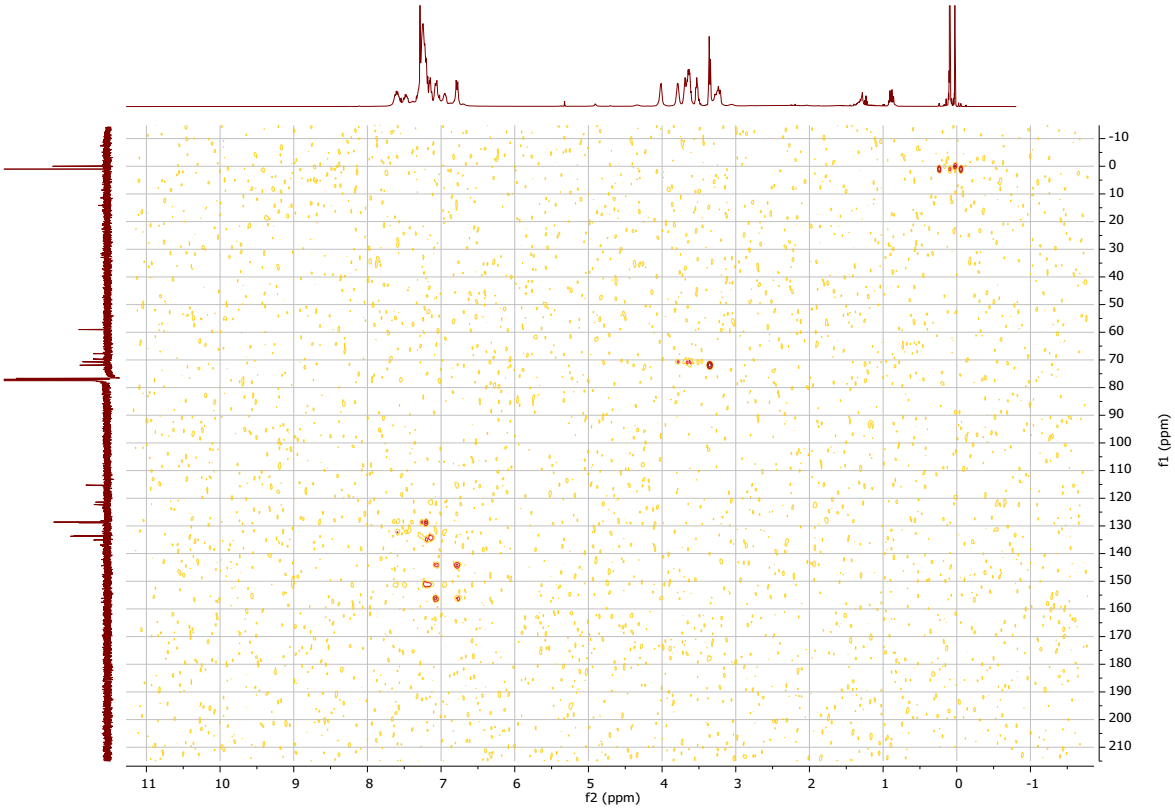


Figure S78. ^{1}H-$^{13}C\{^{1}H\}$ HMBC spectrum of **16-[G_1][G_1]-PEG** in $CDCl_3$ recorded at room temperature (400 MHz, 101 MHz).

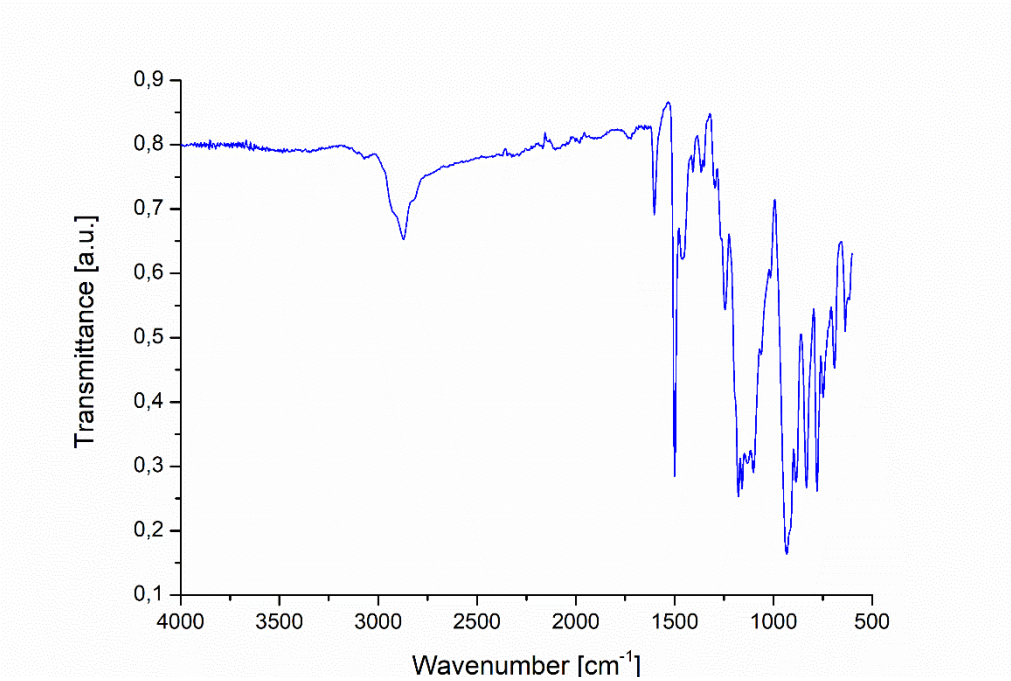


Figure S79. FT-IR spectrum of **16-[G_1][G_1]-PEG**.

3.18. Synthesis of 17-Ru@[G_1][G_1]-PEG

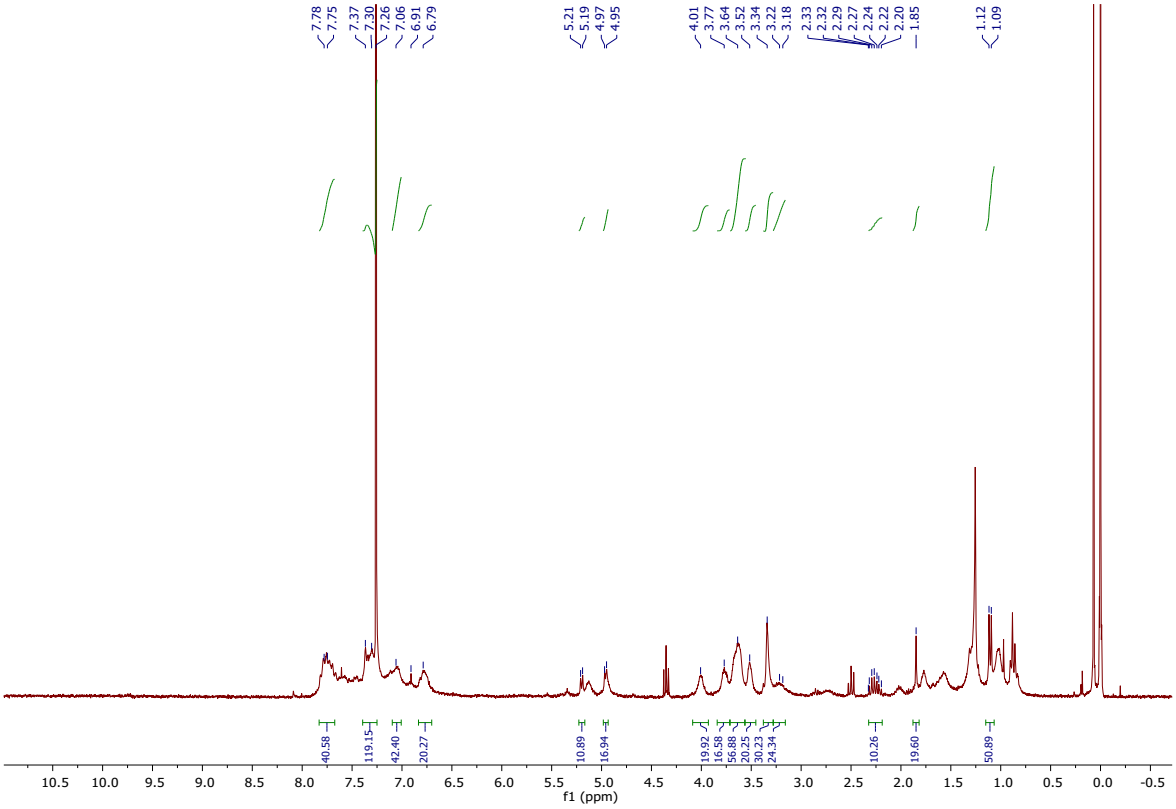


Figure S80. ^{1}H NMR spectrum of **17-Ru@[G_1][G_1]-PEG** in $CDCl_3$ recorded at room temperature (400 MHz).

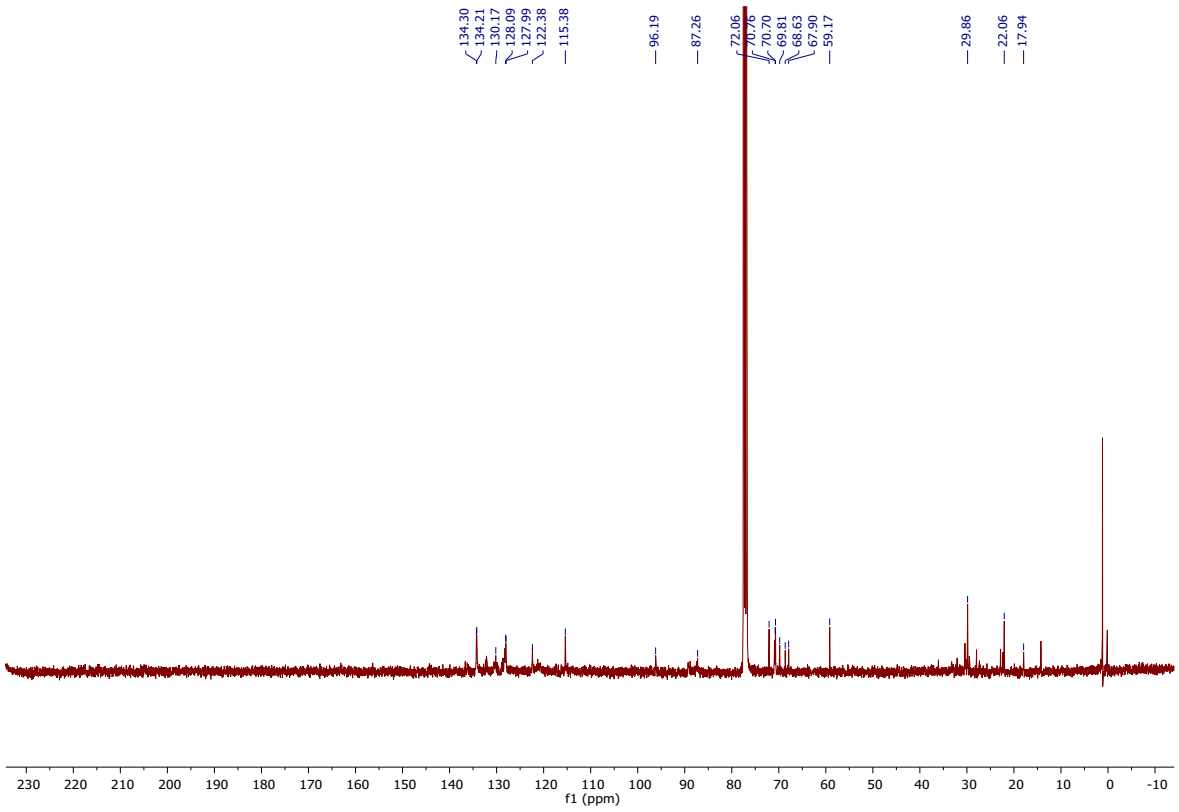


Figure S81. $^{13}C\{^{1}H\}$ NMR spectrum of **17-Ru@[G_1][G_1]-PEG** in $CDCl_3$ recorded at room temperature (101 MHz).

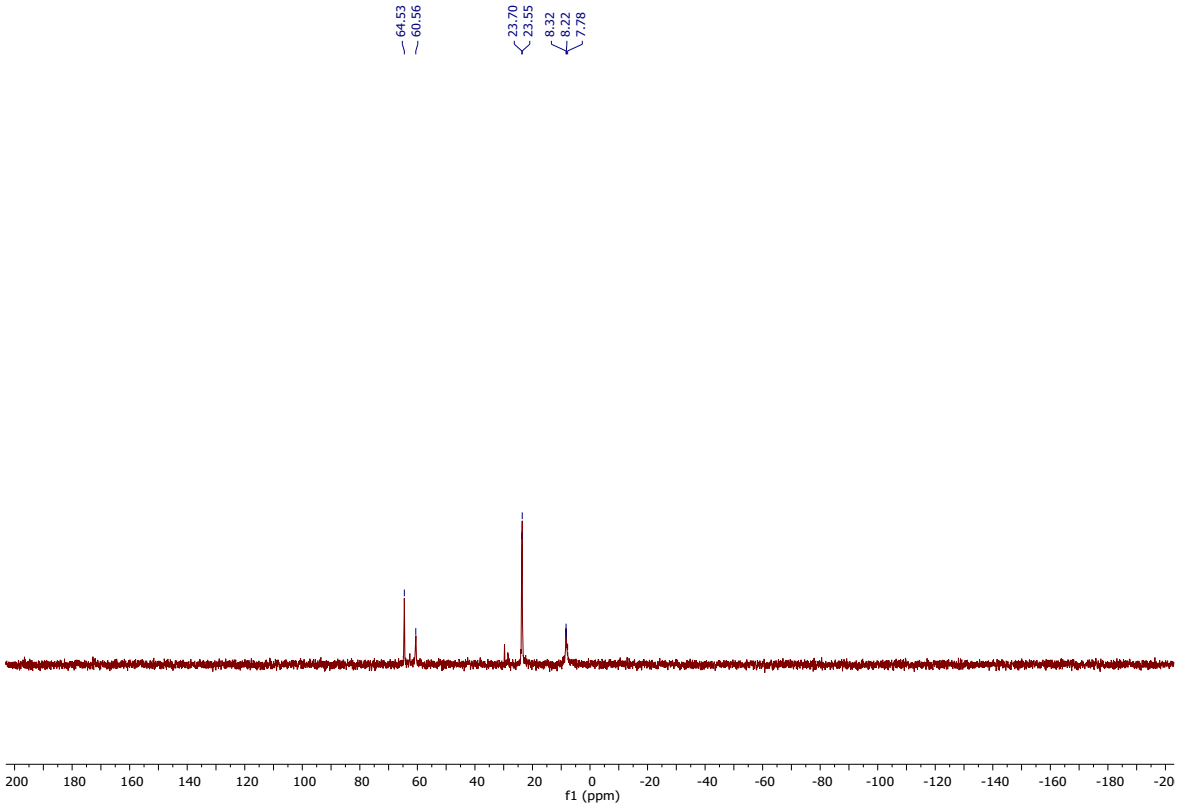


Figure S82. $^{31}P\{^{1}H\}$ NMR spectrum of **17-Ru@[G_1][G_1]-PEG** in $CDCl_3$ recorded at room temperature (162 MHz).

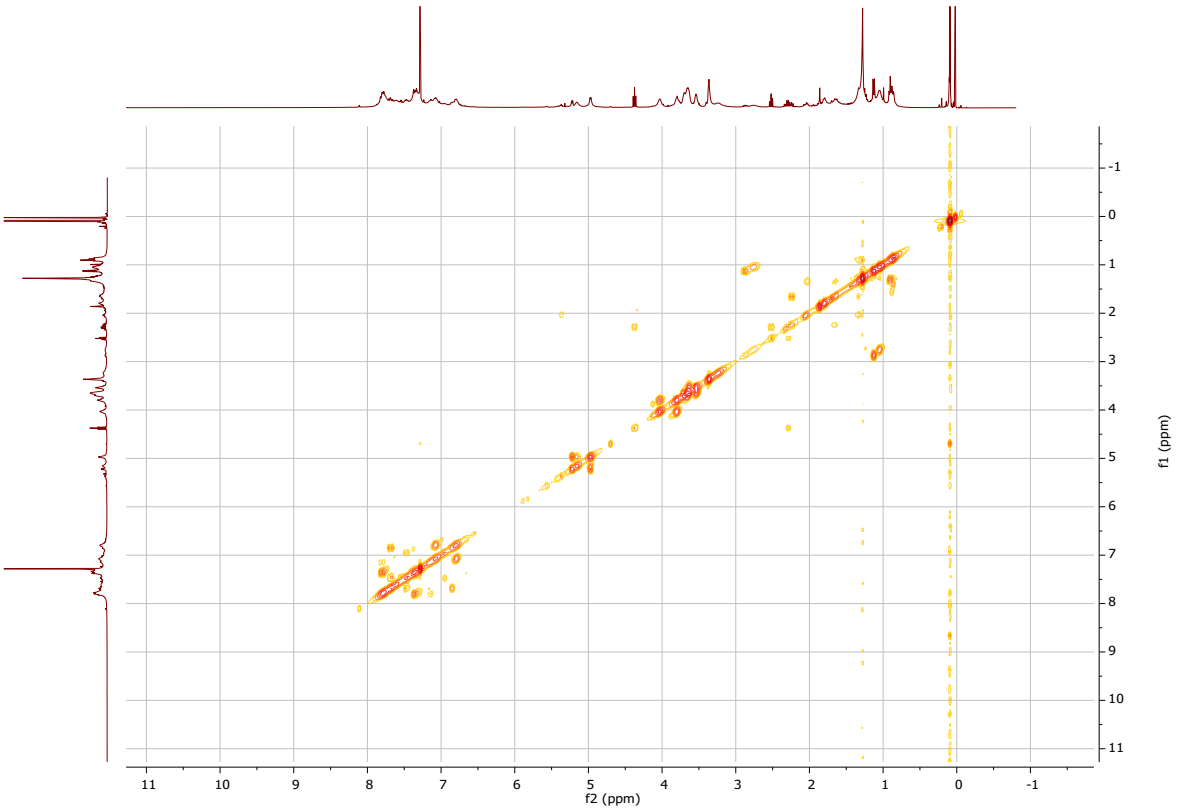


Figure S83. ^{1}H-^{1}H COSY spectrum of **17-Ru@[G_1][G_1]-PEG** in $CDCl_3$ recorded at room temperature (400 MHz).

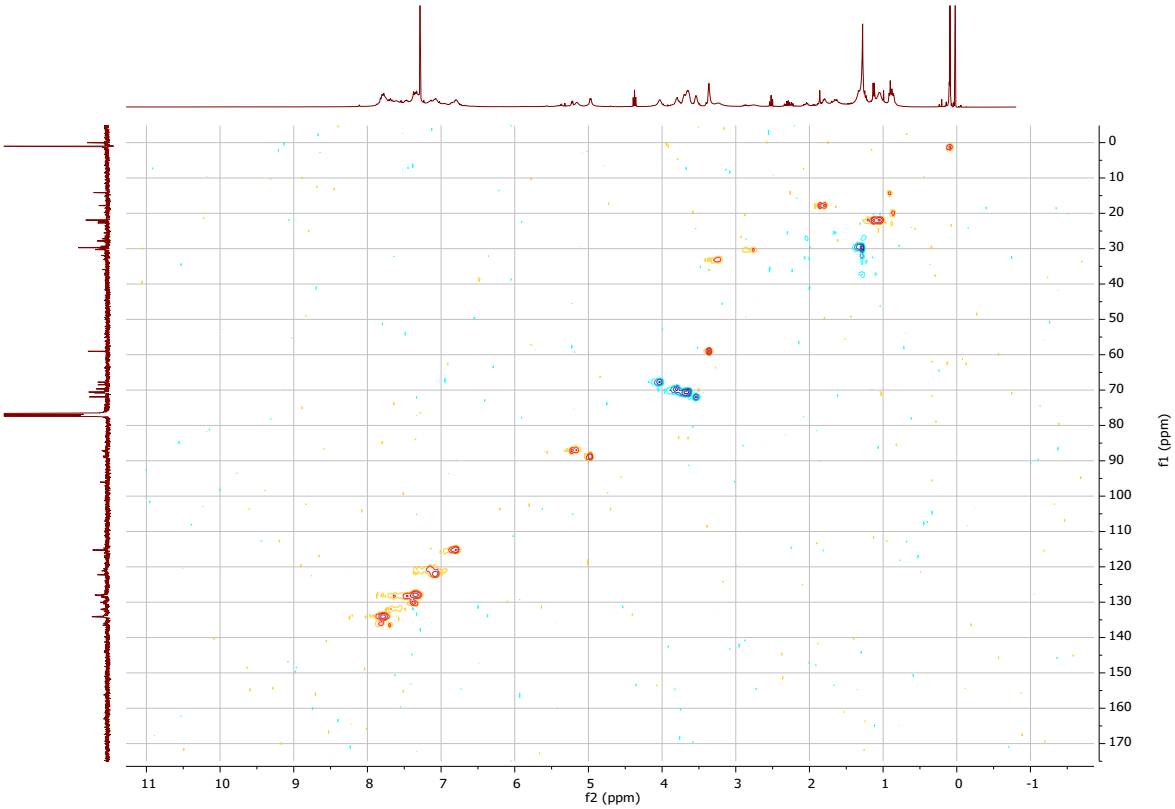


Figure S84. ^{1}H-^{13}C{^{1}H} HSQC spectrum of **17-Ru@[G_1][G_1]-PEG** in $CDCl_3$ recorded at room temperature (400 MHz, 101 MHz).

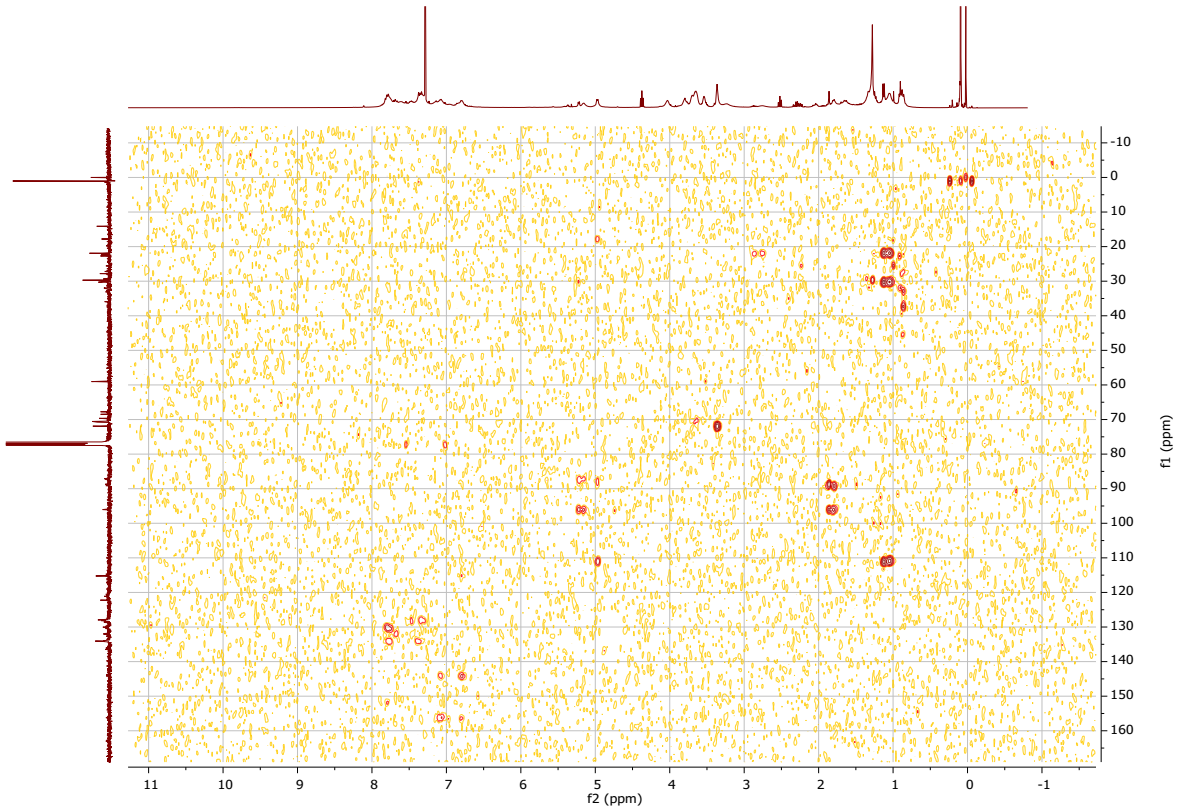


Figure S85. ^{1}H-$^{13}C\{^{1}H\}$ HMBC spectrum of **17-Ru@[G_1][G_1]-PEG** in $CDCl_3$ recorded at room temperature (400 MHz, 101 MHz).

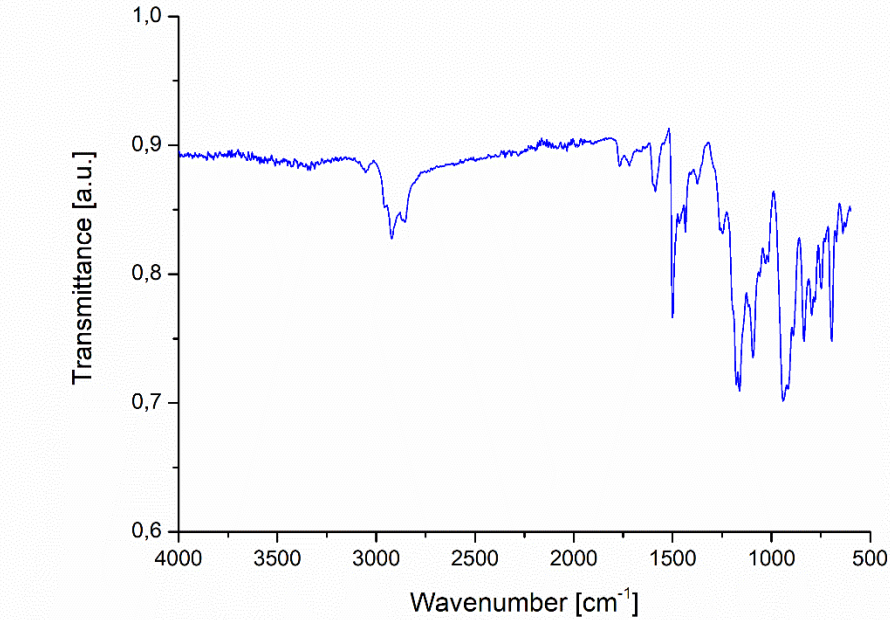


Figure S86. FT-IR spectrum of **17-Ru@[G_1][G_1]-PEG**.

Codi SAQ	Ref. mostra	%C	%H	%N	%S
23AE038/024	JCS-201	54,37	5,50	2,69	2,24

Figure S87. Elemental analysis of **17-Ru@[G_1][G_1]-PEG**.

Mostra	Codi SAQ	Ru (% (p/p))	%rsd
JCS-201	23EAt095/001	9,1	--

Figure S88. ICP analysis of **17-Ru@[G_1][G_1]-PEG**.

3.19. Synthesis of diphenyl(4-methoxyphenyl)phosphine 19

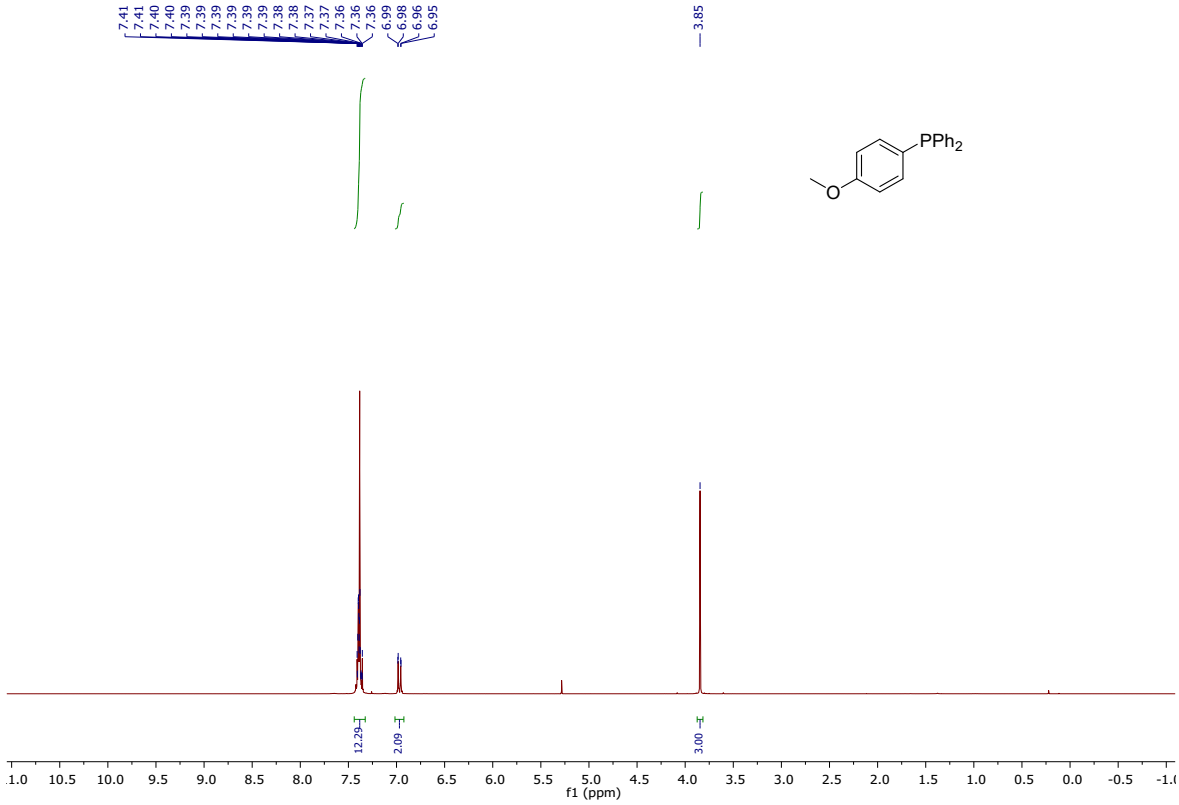


Figure S89. ^{1}H NMR spectrum of (4-((*tert*-butyldimethylsilyl)oxy)phenyl)diphenylphosphane **19** in $CDCl_3$ recorded at room temperature (400 MHz).

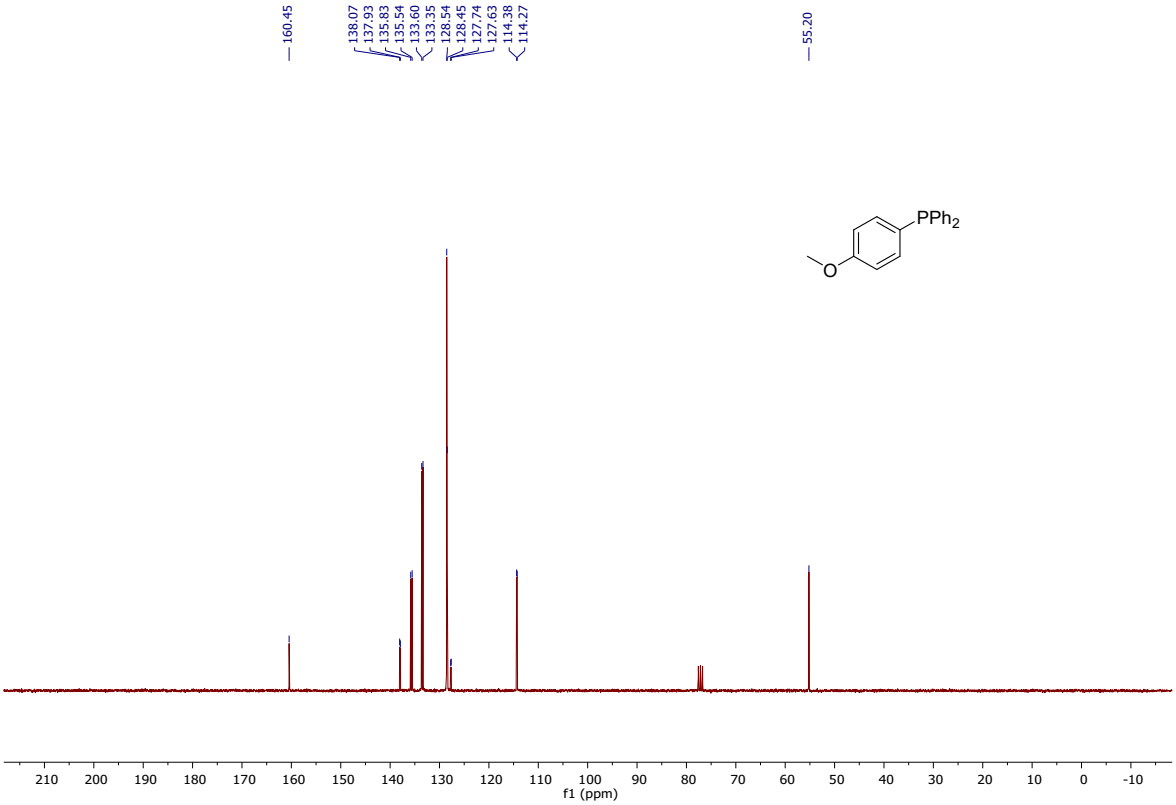


Figure S90. $^{13}C\{^{1}H\}$ NMR spectrum of (4-((*tert*-butyldimethylsilyl)oxy)phenyl)diphenylphosphane **19** in $CDCl_3$ recorded at room temperature (101 MHz).

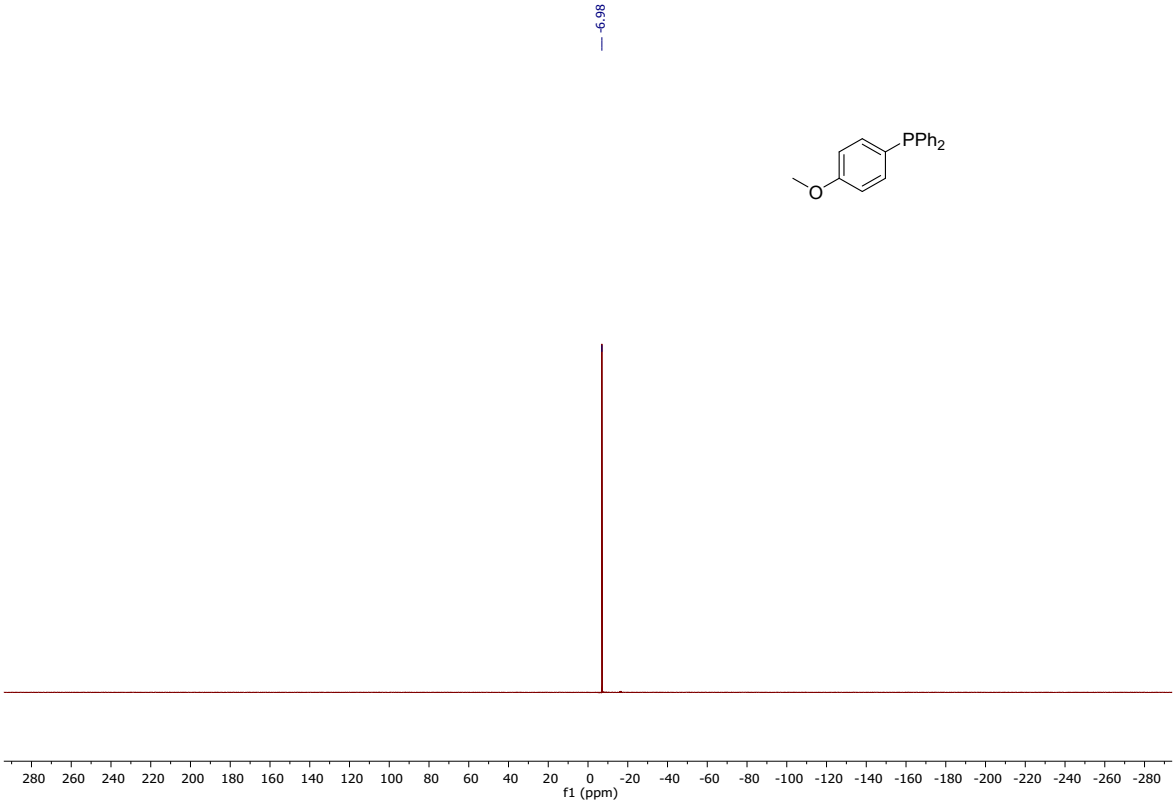


Figure S91. $^{31}P\{^{1}H\}$ NMR spectrum of (4-((*tert*-butyldimethylsilyl)oxy)phenyl)diphenylphosphane **19** in $CDCl_3$ recorded at room temperature (161 MHz).

3.20. Synthesis of monometallic complex 20

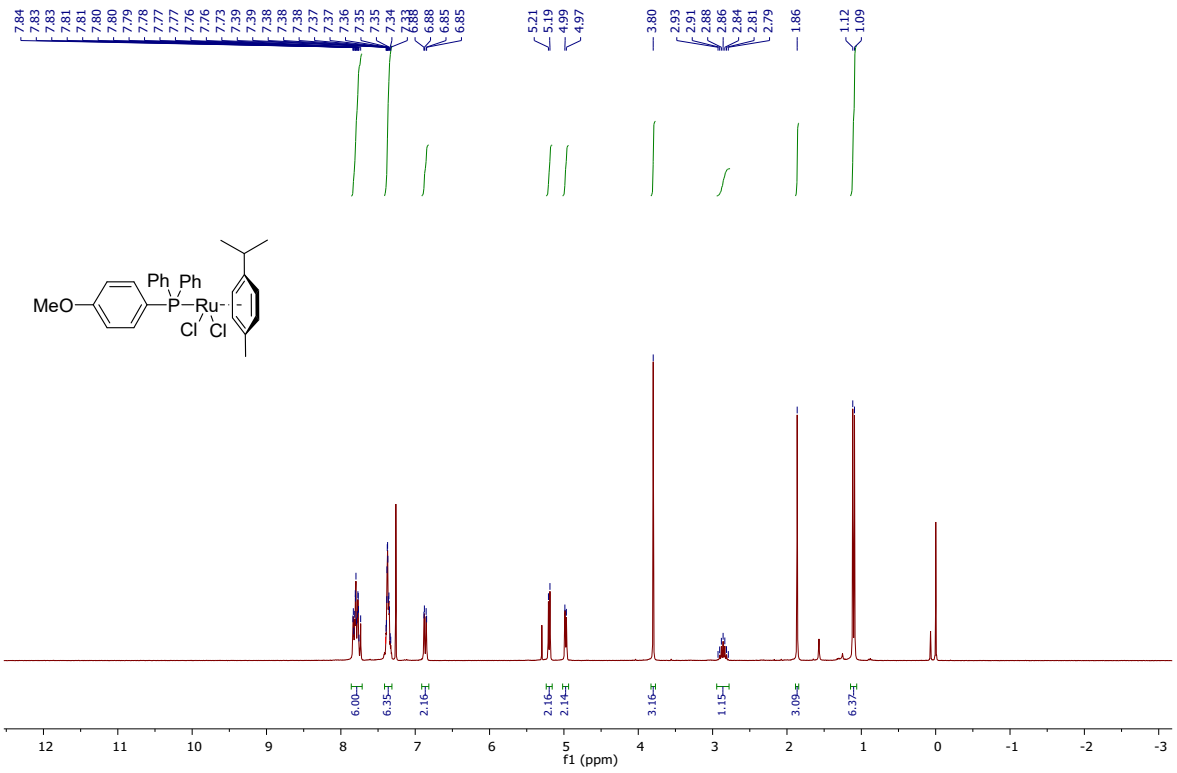


Figure S92. ^{1}H NMR spectrum of **20** in $CDCl_3$ recorded at room temperature (400 MHz).

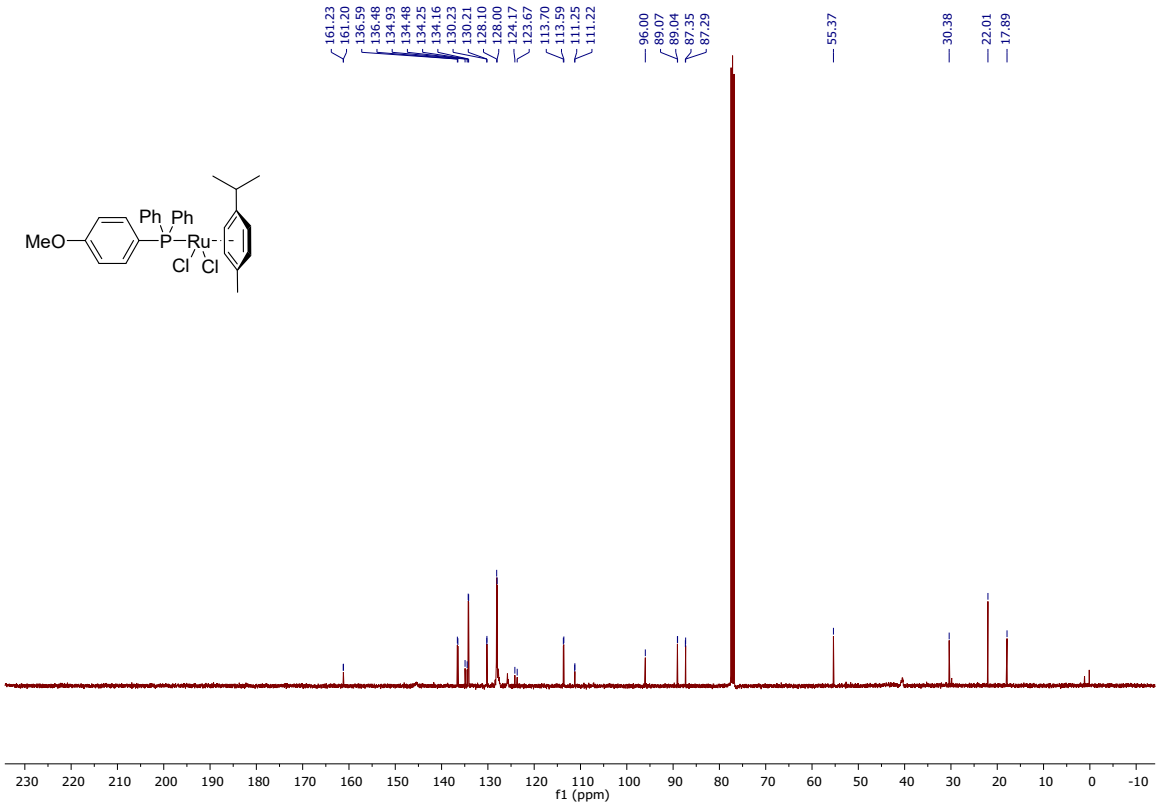


Figure S93. $^{13}C\{^{1}H\}$ NMR spectrum of **20** in $CDCl_3$ recorded at room temperature (101 MHz).

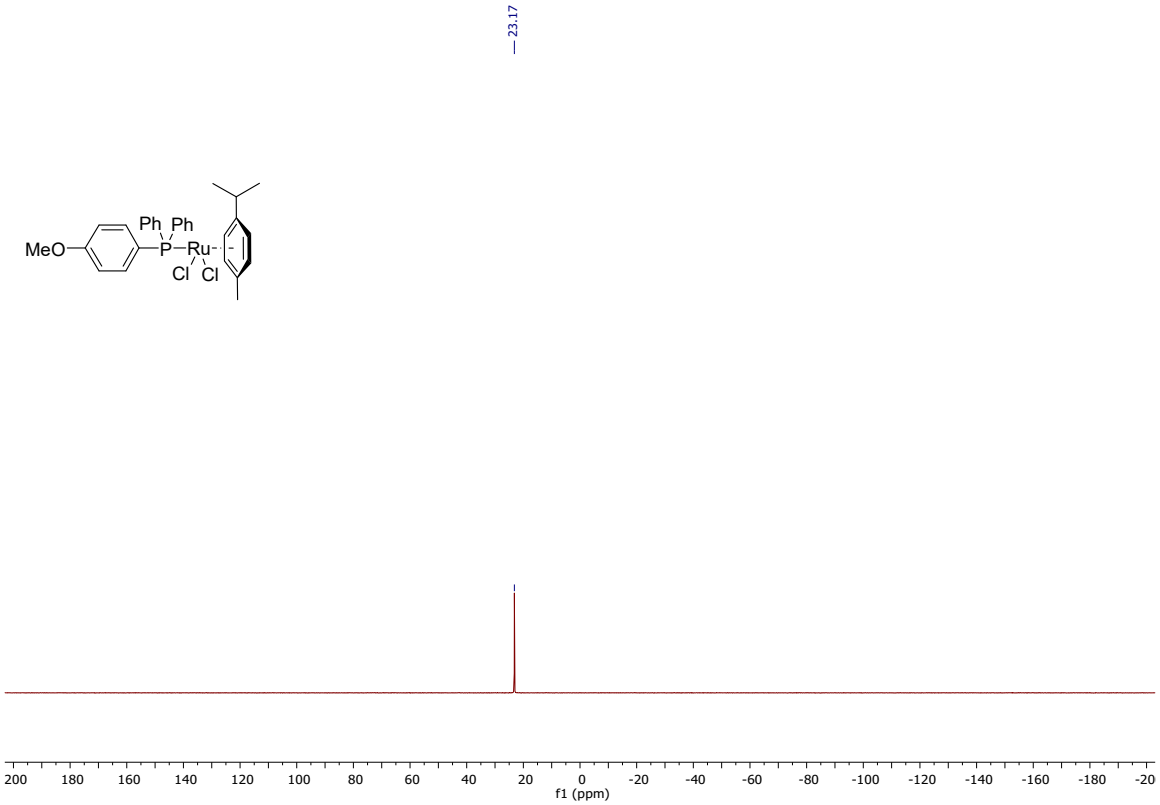


Figure S94. $^{31}P\{^{1}H\}$ NMR spectrum of **20** in $CDCl_3$ recorded at room temperature (162 MHz).

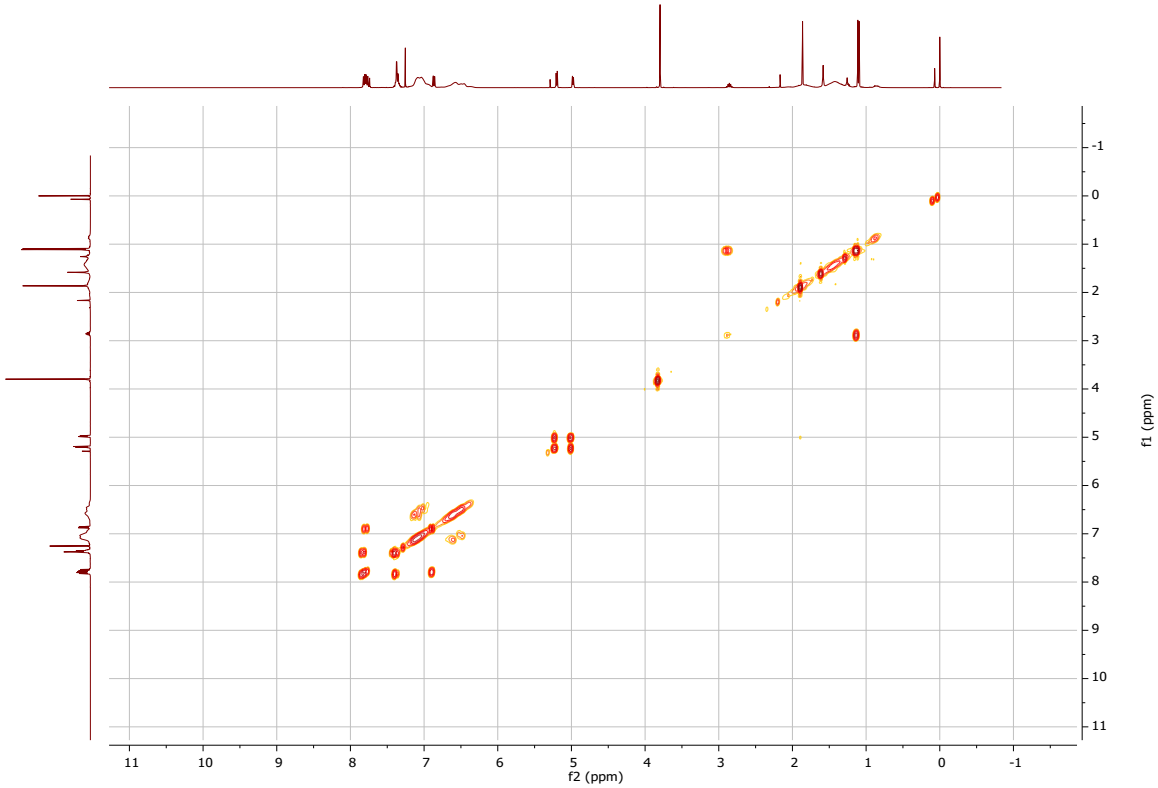


Figure S95. ^{1}H-^{1}H COSY spectrum of **20** recorded in $CDCl_3$ at room temperature (400 MHz).

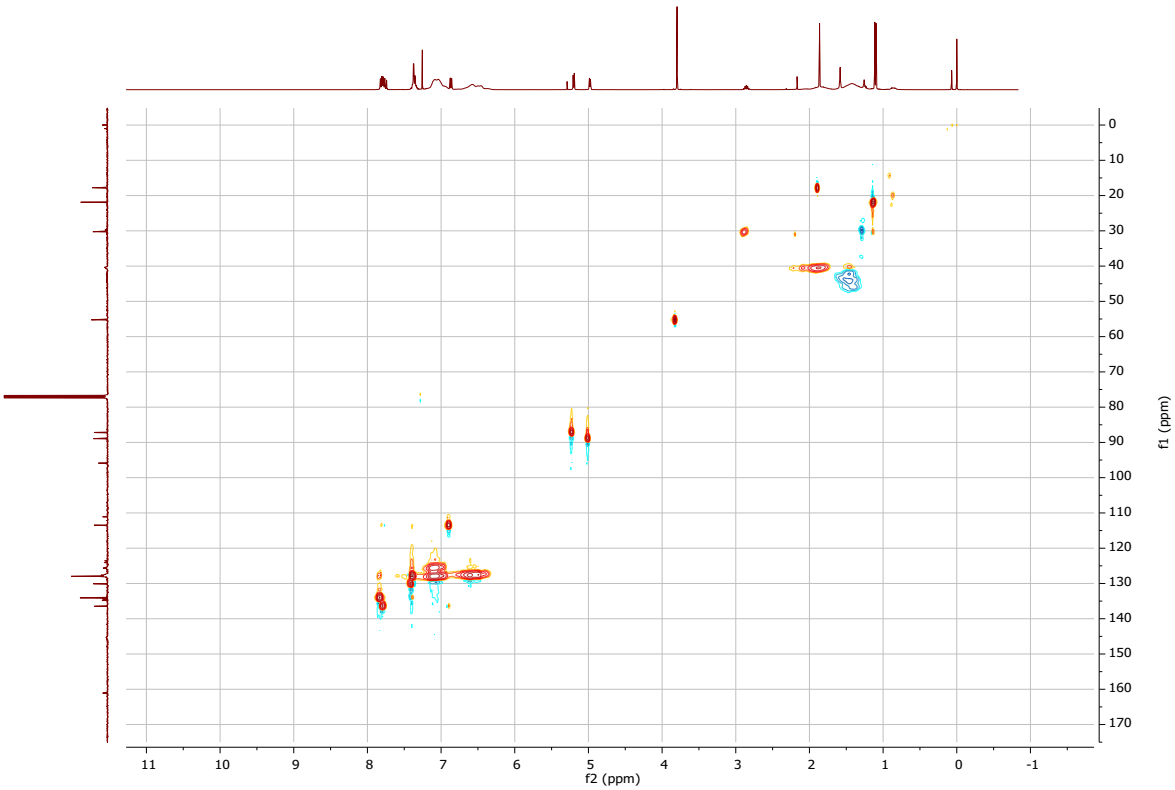


Figure S96. ^{1}H-$^{13}C\{^{1}H\}$ HSQC spectrum of **20** recorded in $CDCl_3$ at room temperature (400 MHz, 101 MHz).

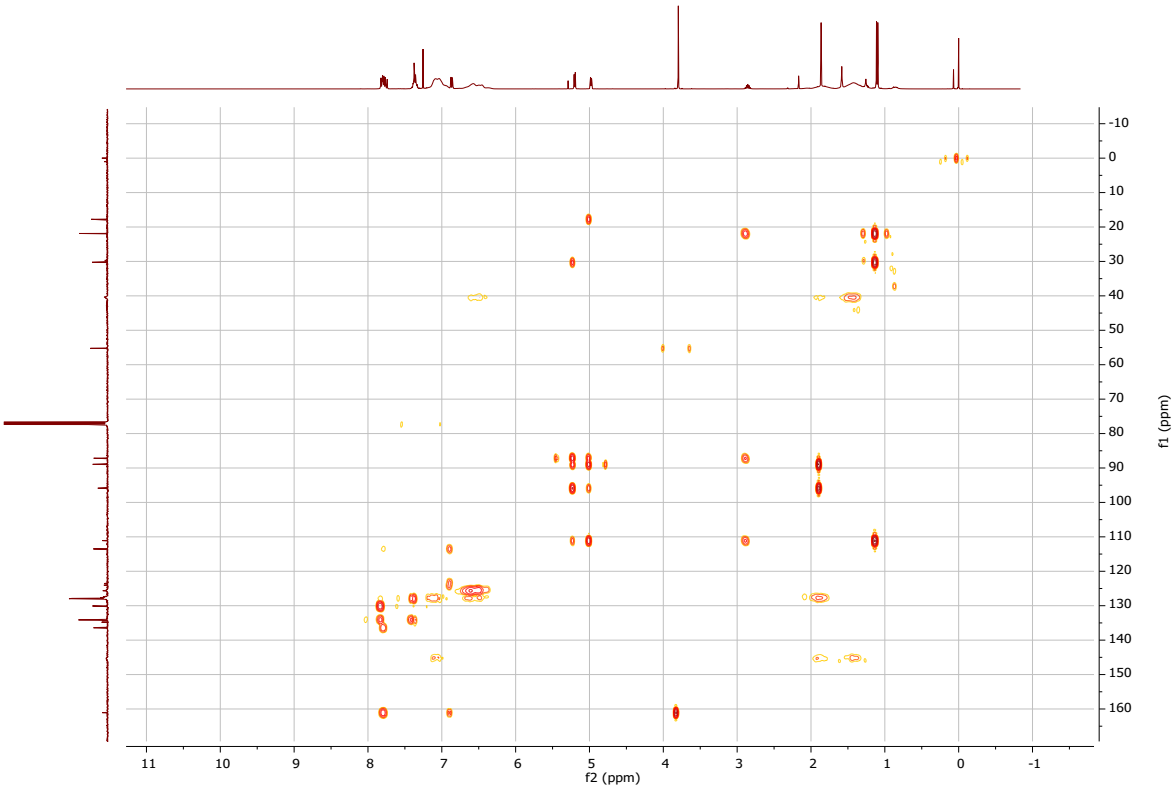


Figure S97. ^{1}H-$^{13}C\{^{1}H\}$ HMBC spectrum of **20** recorded in $CDCl_3$ at room temperature (400 MHz, 101 MHz).

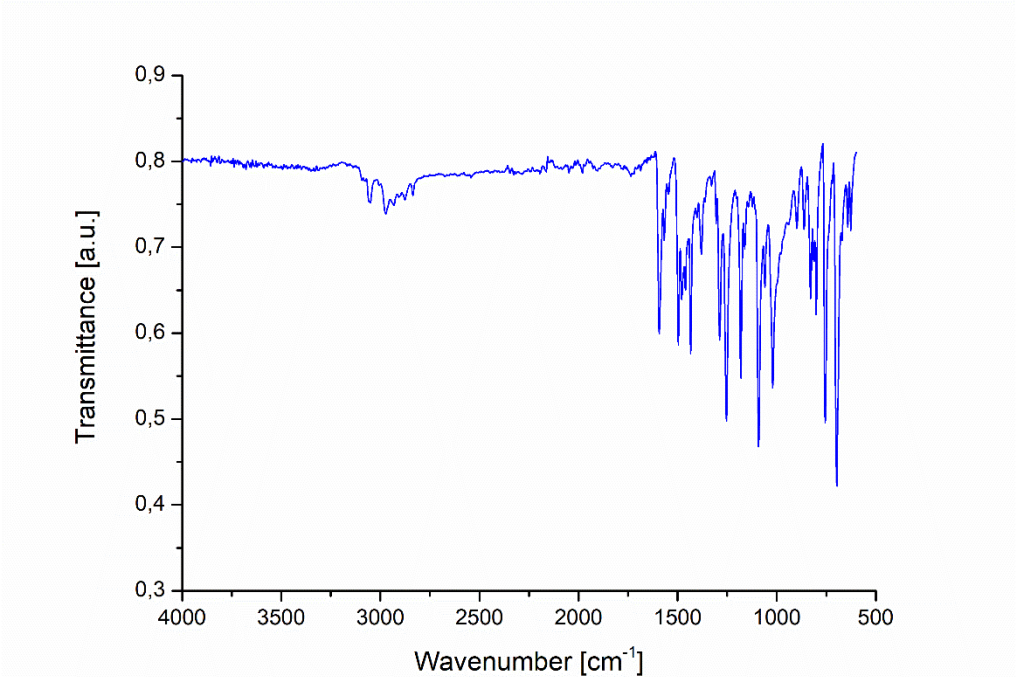


Figure S98. FT-IR spectrum of **20**.

Meas. m/z	#	Ion Formula	err [mDa]	err [ppm]	mSigma
563.084629	1	C29H31ClOPRu	-0.2	-0.4	8.1

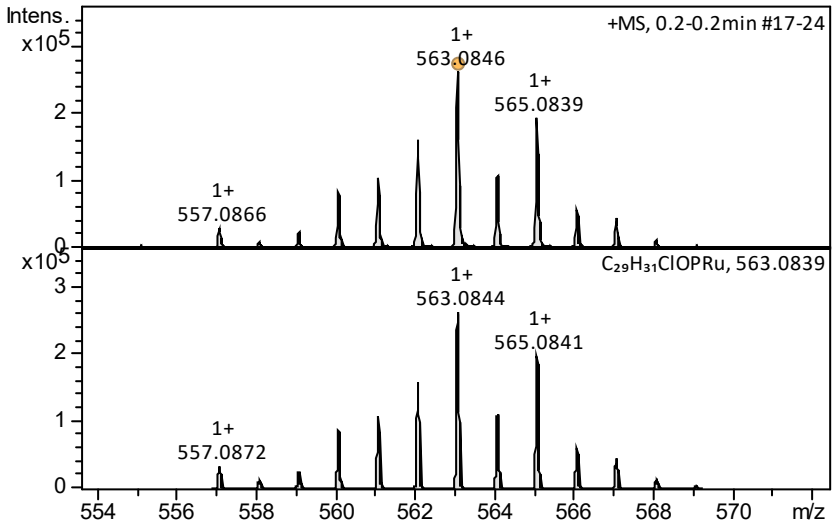


Figure S99. HRMS of **20**.

Codi SAQ	Ref. mostra	%C	%H	%N	%S
23AE038/022	JCS-210	55,65	5,05	<0.1	<0.1

Figure S100. Elemental Analysis of **20**.

3.21. Synthesis of (2-benzylidene-1-methylhydrazineyl)phosphonothioic dichloride 21

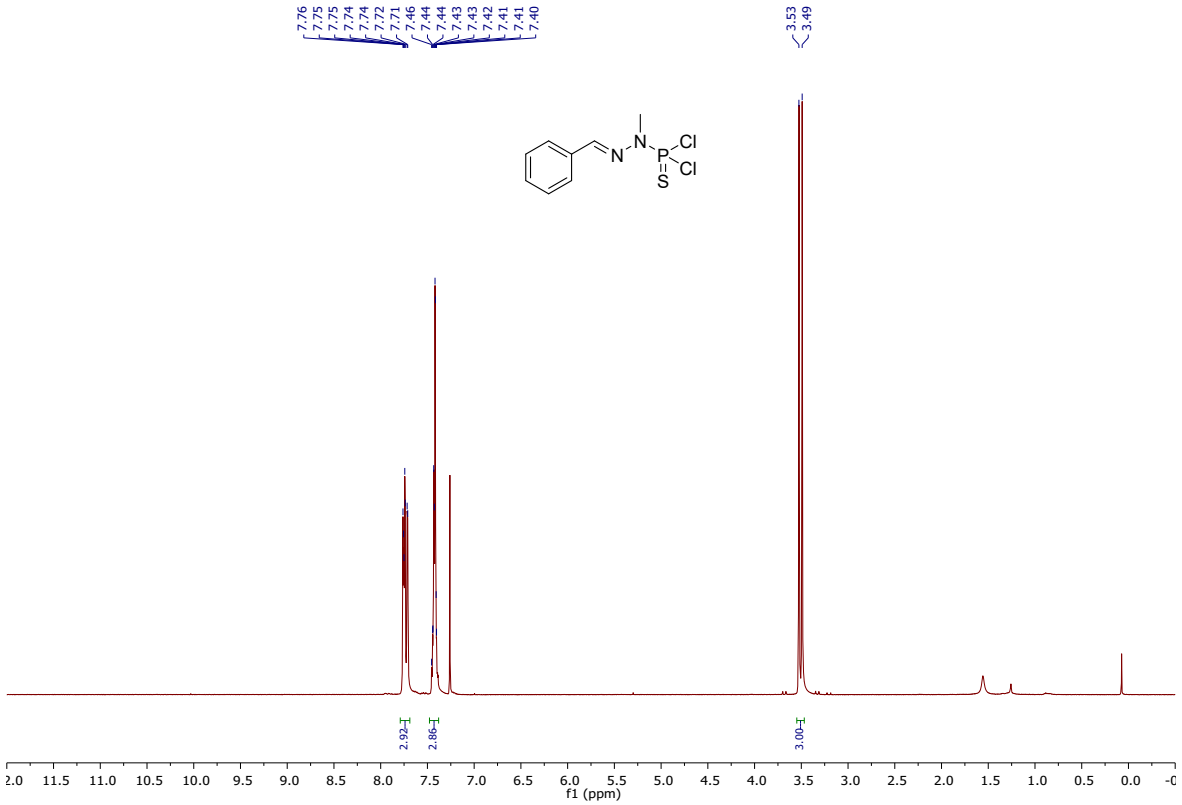


Figure S101. ^{1}H NMR spectrum of (2-benzylidene-1-methylhydrazineyl)phosphonothioic dichloride **21** in $CDCl_3$ recorded at room temperature (400 MHz).

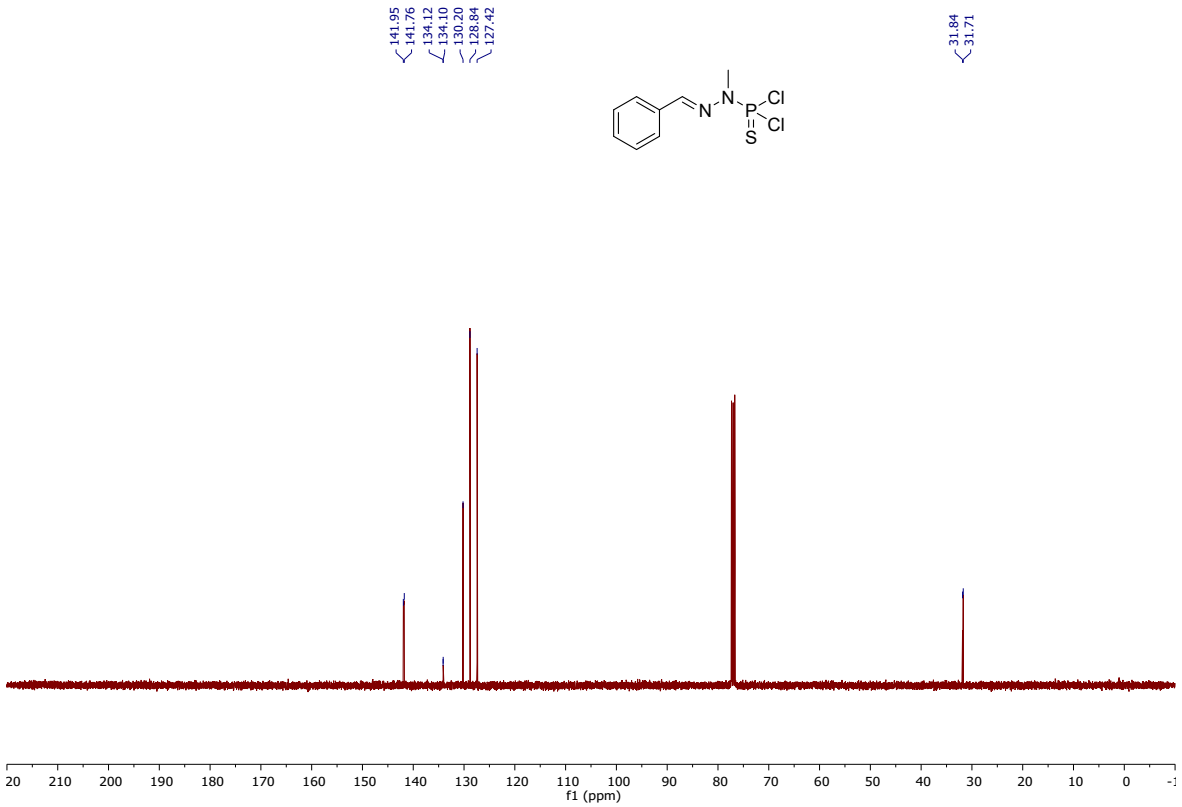


Figure S102. $^{13}C\{^{1}H\}$ NMR spectrum of (2-benzylidene-1-methylhydrazineyl)phosphonothioic dichloride **21** in $CDCl_3$ recorded at room temperature (101 MHz).

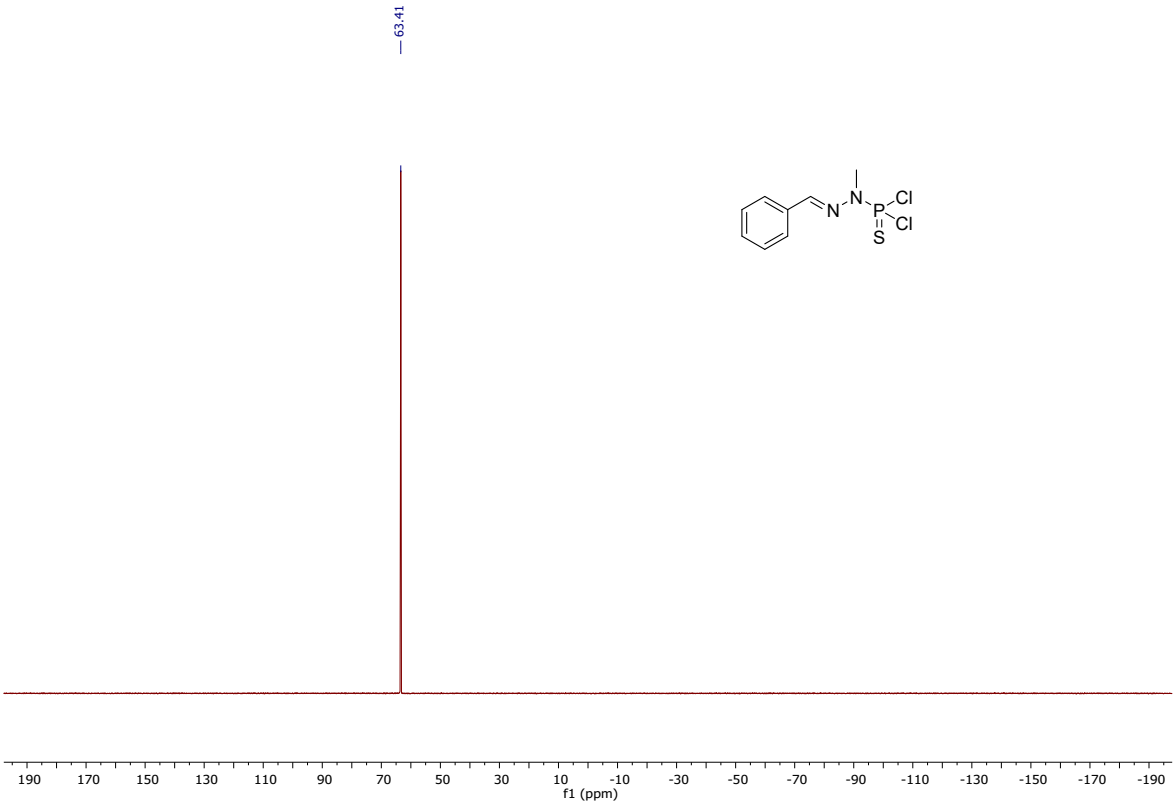


Figure S103. $^{31}P\{^{1}H\}$ NMR spectrum of (2-benzylidene-1-methylhydrazineyl)phosphonothioic dichloride **21** in $CDCl_3$ recorded at room temperature (162 MHz).

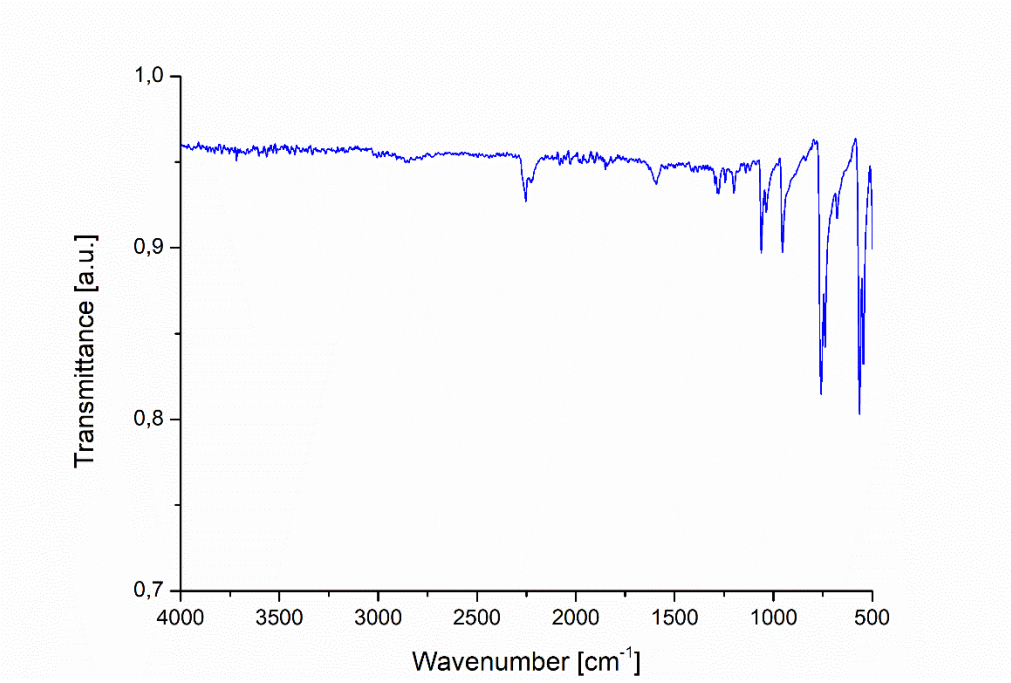


Figure S104. FT-IR spectrum of (2-benzylidene-1-methylhydrazineyl)phosphonothioic dichloride **21**.

3.22. Synthesis of *O,O*-bis(4-(diphenylphosphanyl)phenyl)(2-benzylidene-1-methylhydrazineyl)-phosphonothioate 22

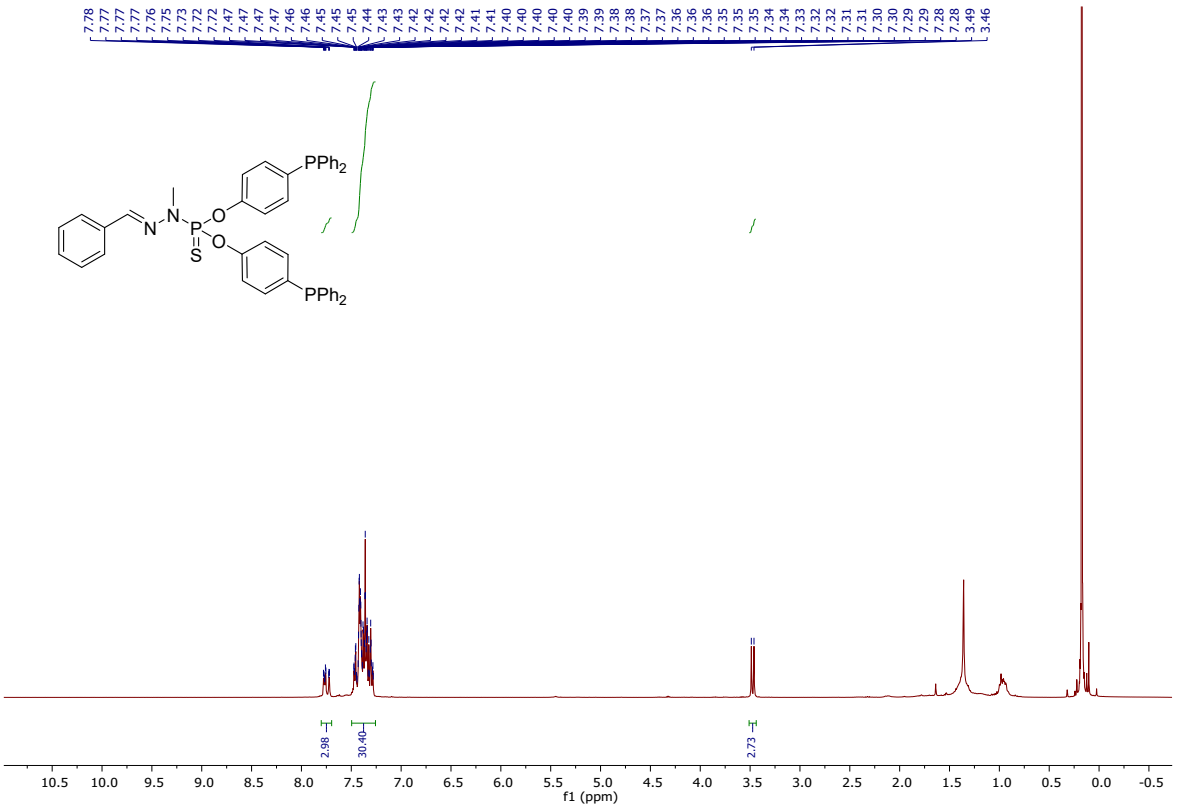


Figure S105. ^{1}H NMR spectrum of compound *O,O*-bis(4-(diphenylphosphanyl)phenyl)(2-benzylidene-1-methylhydrazineyl)phosphonothioate **22** in $CDCl_3$ recorded at room temperature (400 MHz).

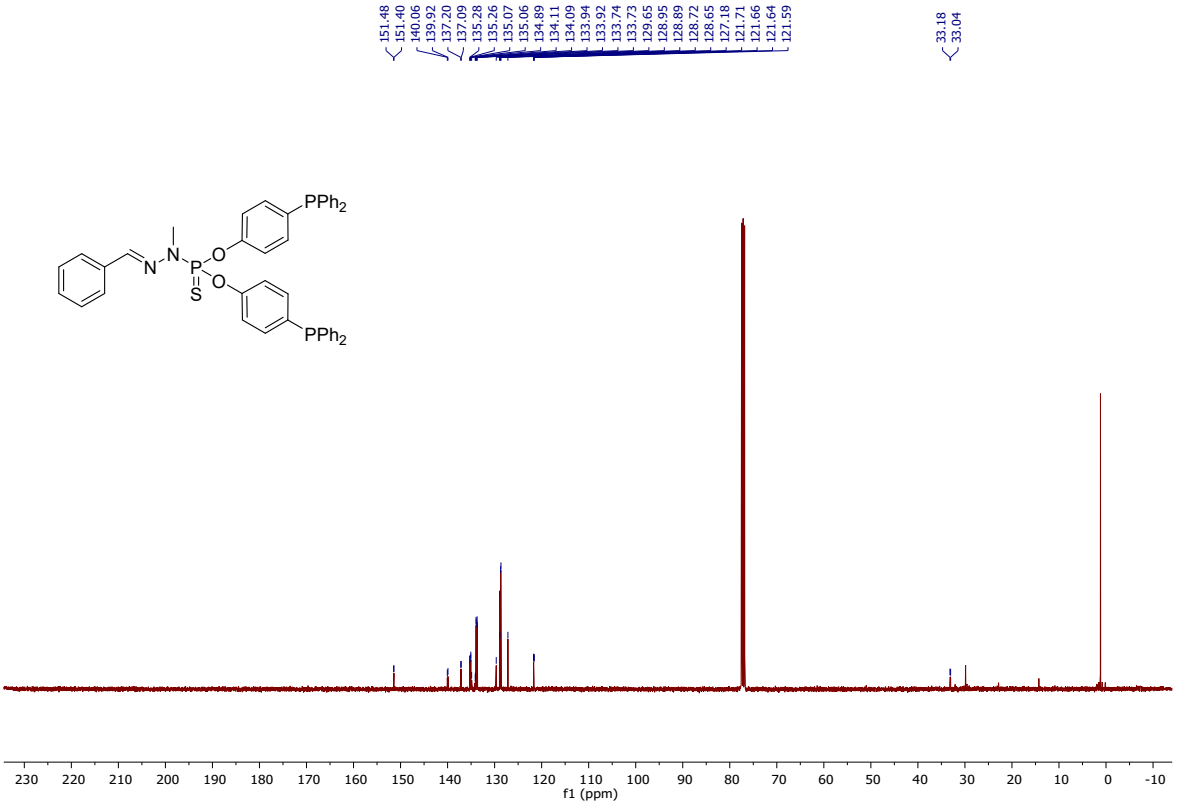


Figure S106. $^{13}C\{^{1}H\}$ NMR spectrum of *O,O*-bis(4-(diphenylphosphanyl)phenyl)(2-benzylidene-1-methylhydrazineyl)phosphonothioate **22** in $CDCl_3$ recorded at room temperature (101 MHz).

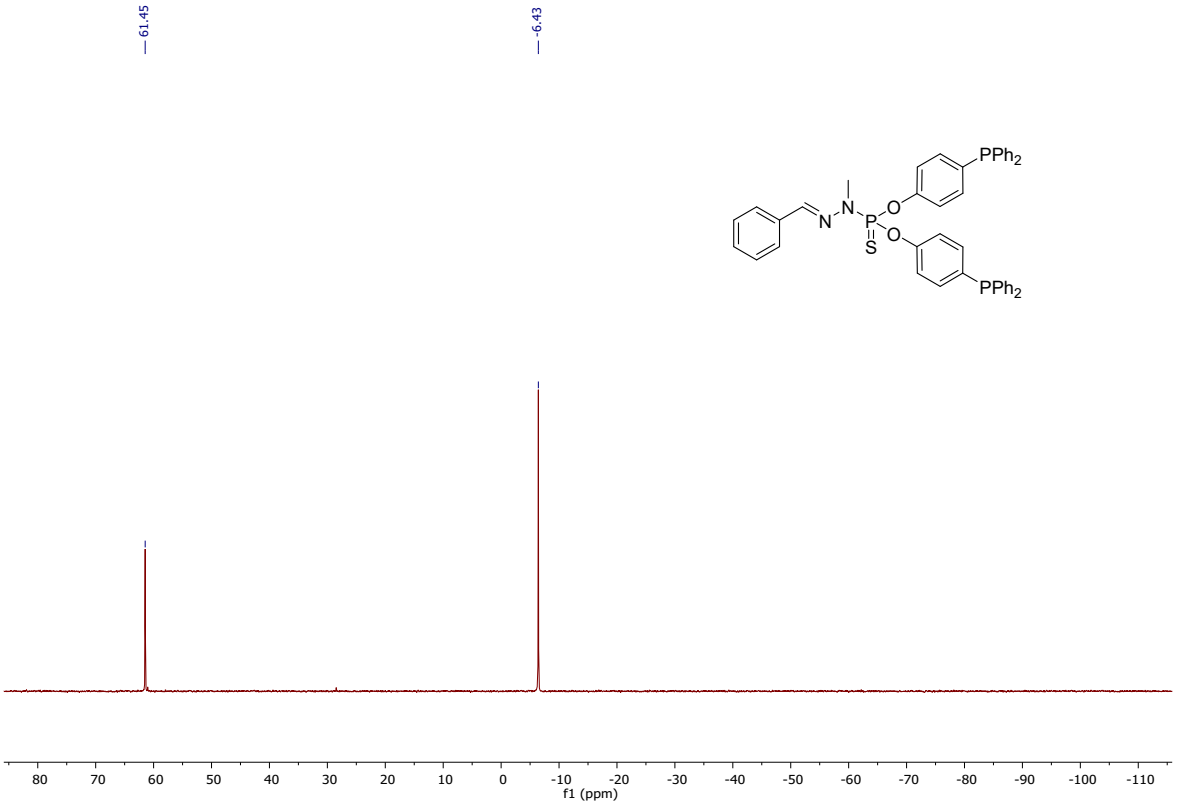


Figure S107. $^{31}P\{^{1}H\}$ NMR spectrum of *O,O*-bis(4-(diphenylphosphanyl)phenyl)(2-benzylidene-1-methylhydrazineyl)phosphonothioate **22** in $CDCl_3$ recorded at room temperature (162 MHz).

3.23. Synthesis of bimetallic complex 23

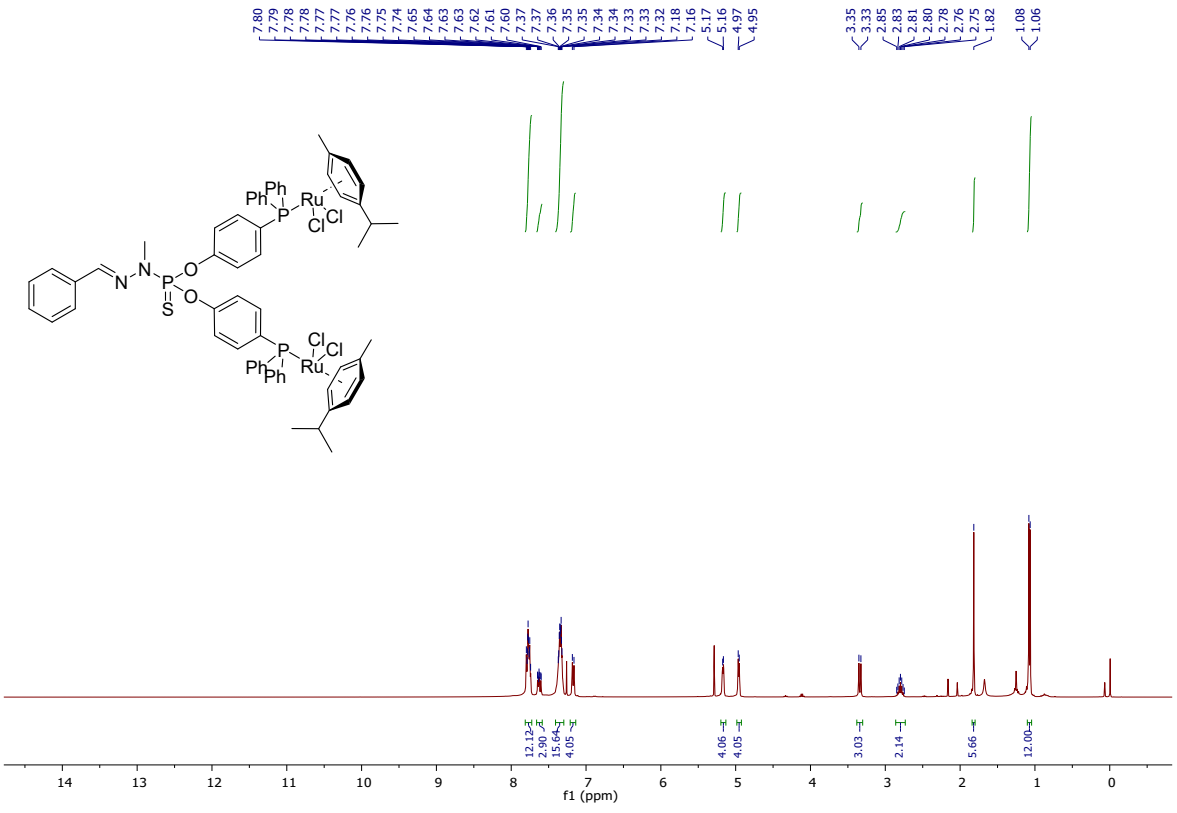


Figure S108. ^{1}H NMR spectrum of **23** in $CDCl_3$ recorded at room temperature (400 MHz).

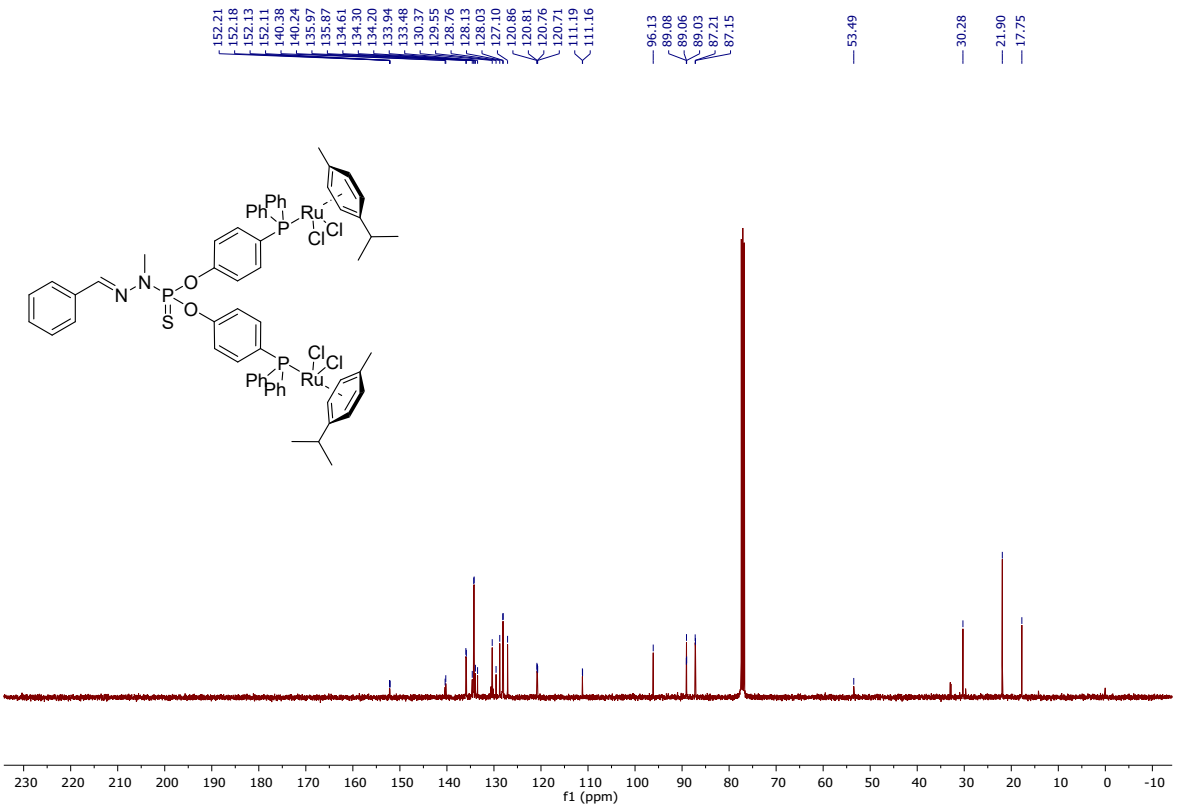


Figure S109. $^{13}C\{^{1}H\}$ NMR spectrum of **23** in $CDCl_3$ recorded at room temperature (101 MHz).

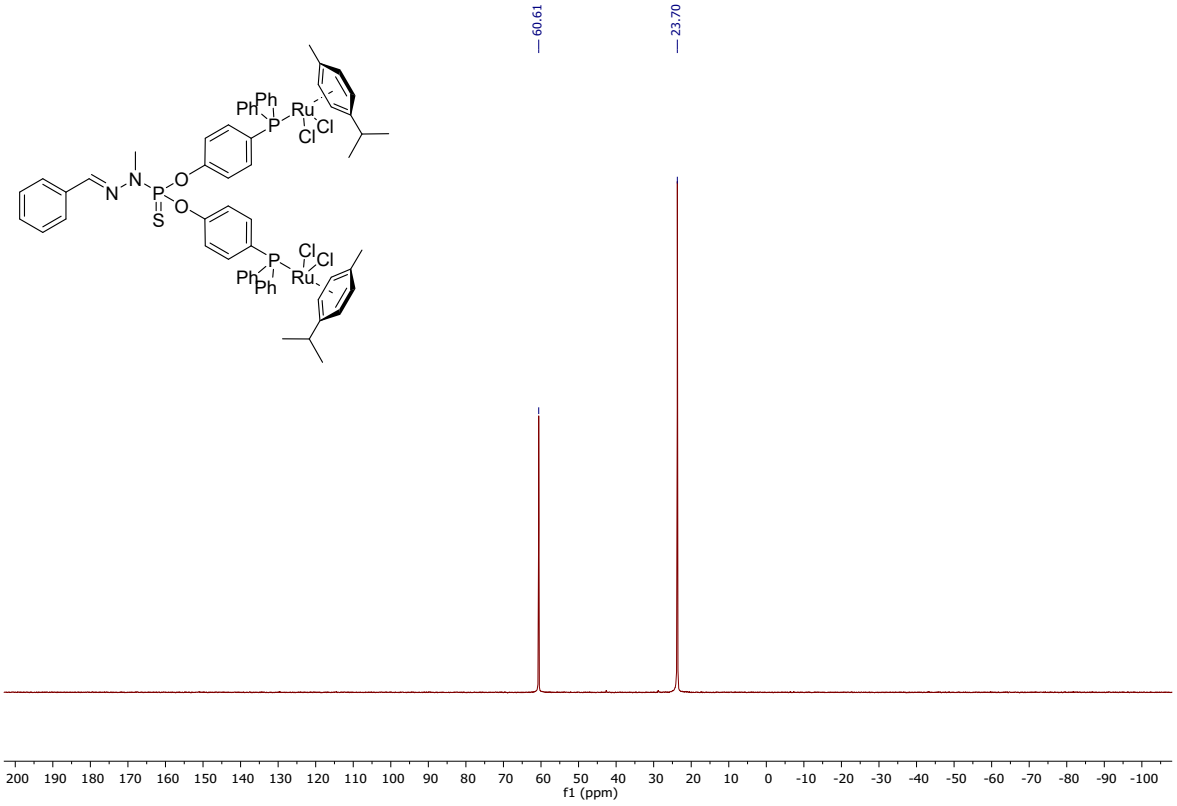


Figure S110. $^{31}P\{^{1}H\}$ NMR spectrum of **23** in $CDCl_3$ recorded at room temperature (162 MHz).

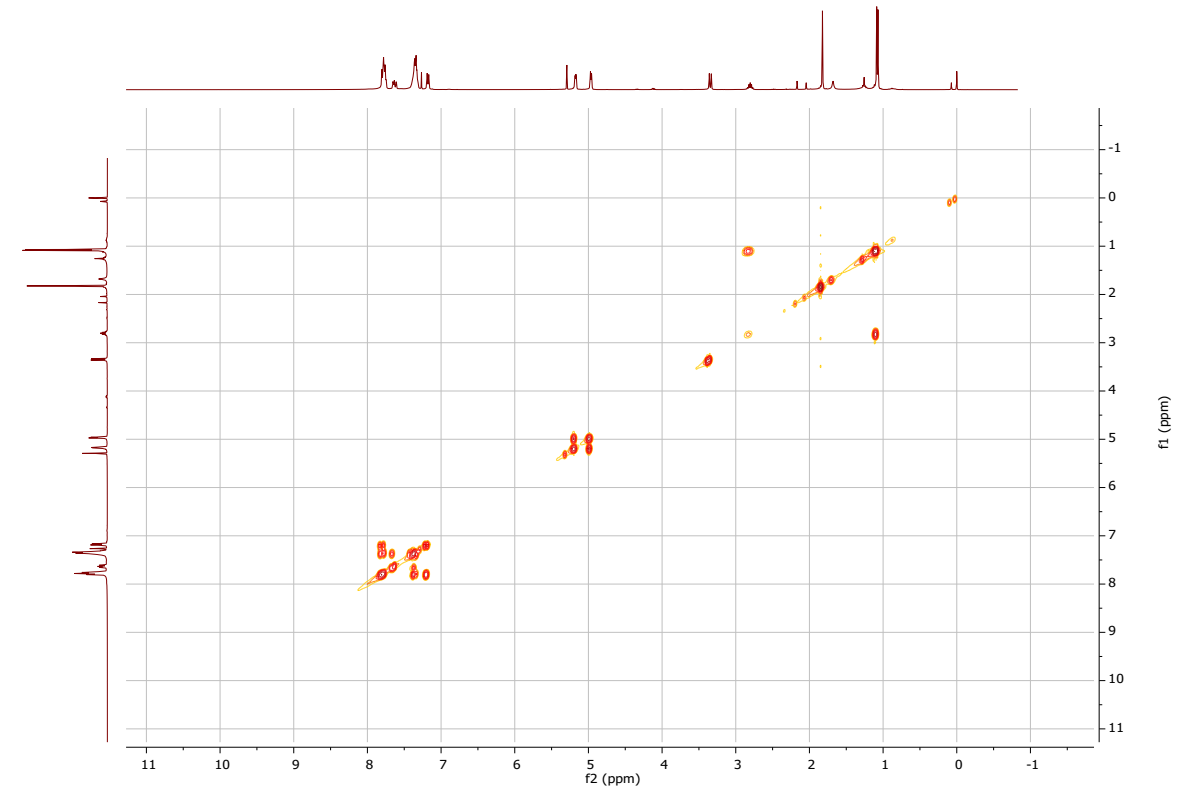


Figure S111. ^{1}H-^{1}H COSY spectrum of **23** in $CDCl_3$ recorded at room temperature (400 MHz).

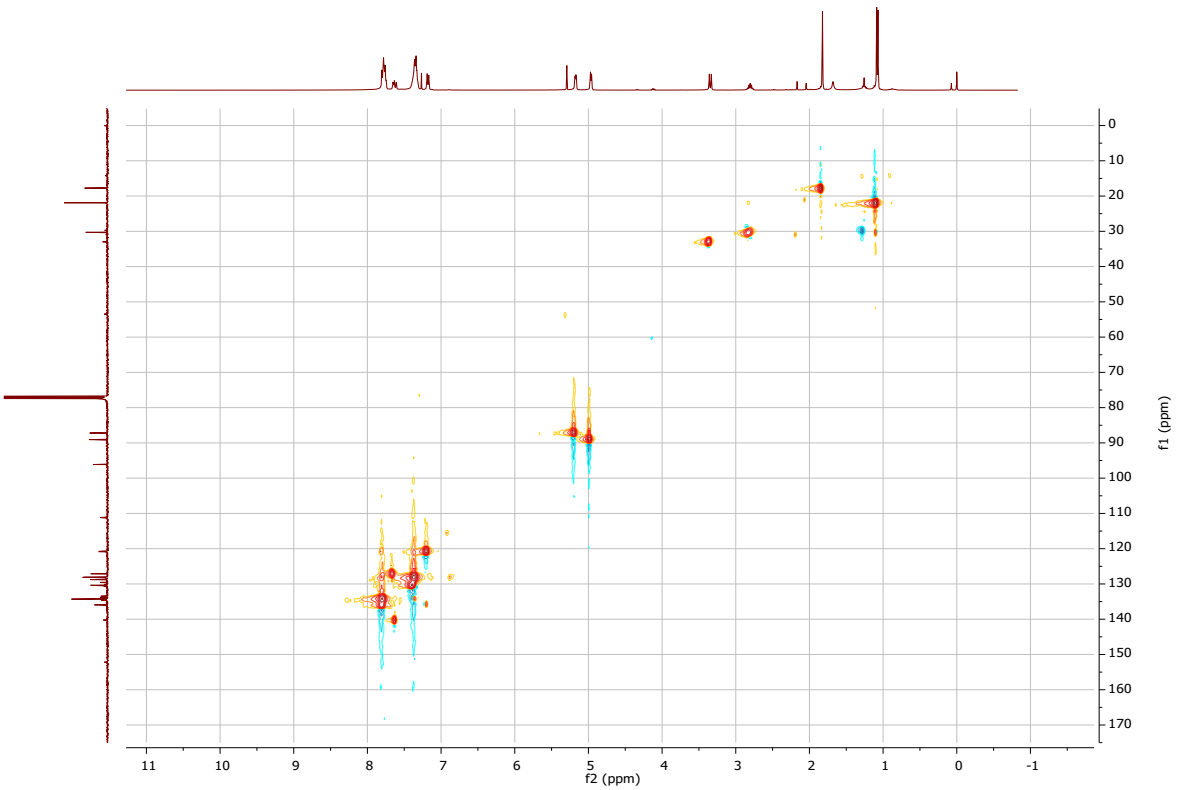


Figure S112. ^{1}H-^{13}C{^{1}H} HSQC spectrum of **23** in $CDCl_3$ recorded at room temperature (400 MHz, 101 MHz).

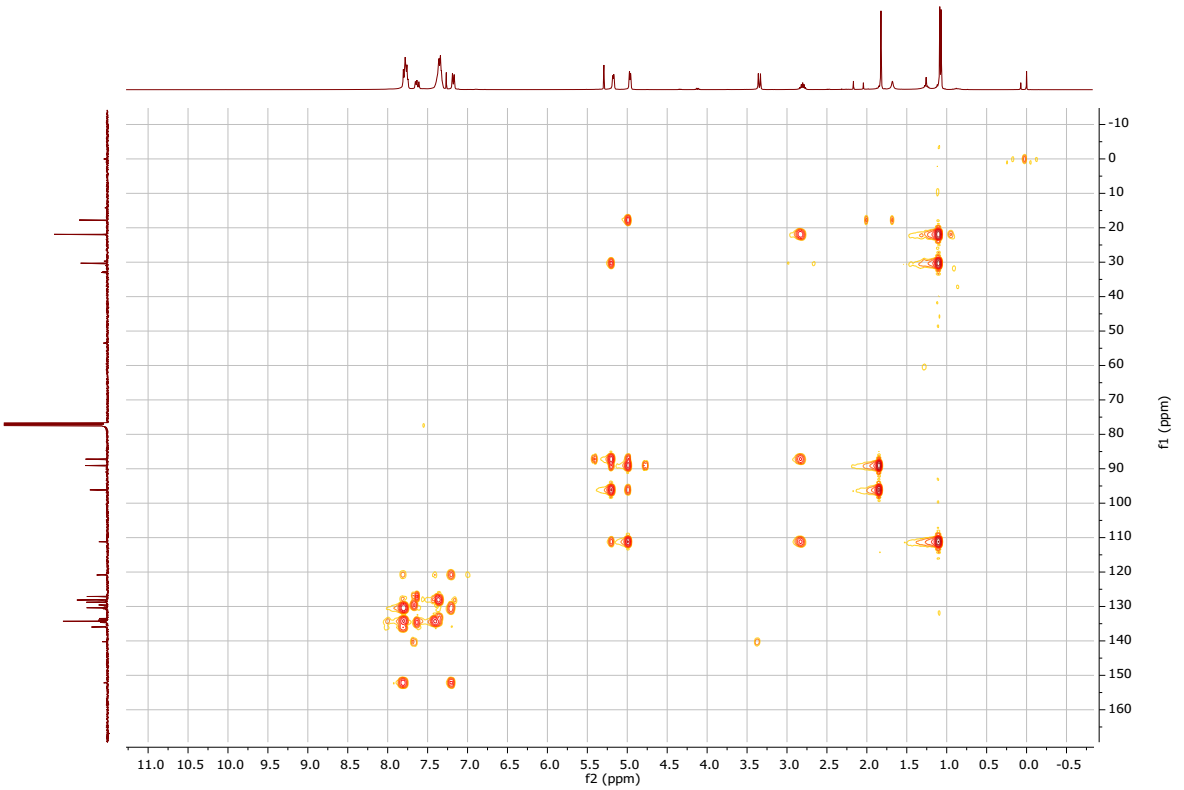


Figure S113. ^{1}H-$^{13}C\{^{1}H\}$ HMBC spectrum of **23** in $CDCl_3$ recorded at room temperature (400 MHz, 101 MHz).

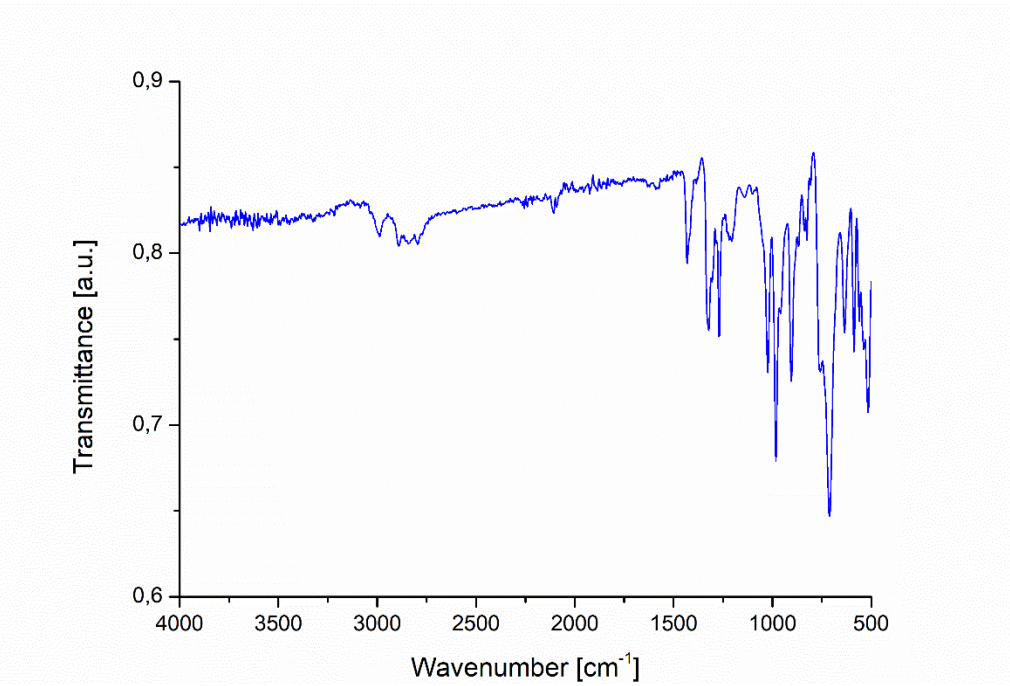


Figure S114. FT-IR spectrum of **23**.

Meas. m/z	#	Ion Formula	err [mDa]	err [ppm]	mSigma
1385.071718	1	C64H65Cl4N2NaO2P3Ru2S	0.6	0.4	342.4

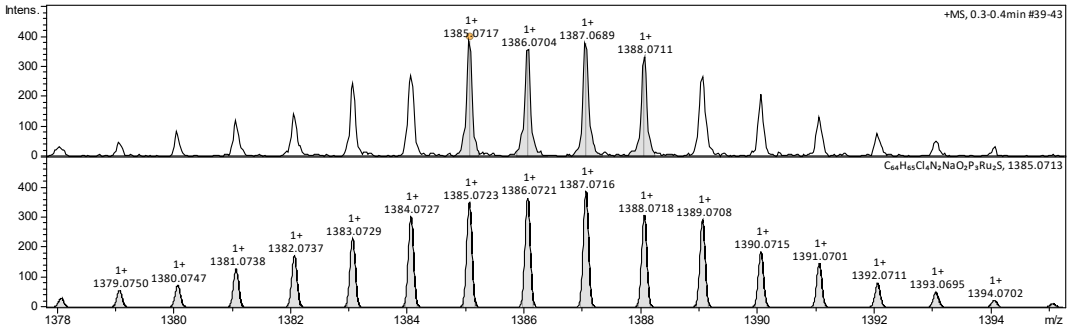


Figure S115. HRMS of **23**.

Codi SAQ	Ref. mostra	%C	%H	%N	%S
23AE038/023	JCS-207	52,04	4,61	1,59	1,89

Figure S116. Elemental analysis of **23**.

3.24. Synthesis of 3-octanone 24

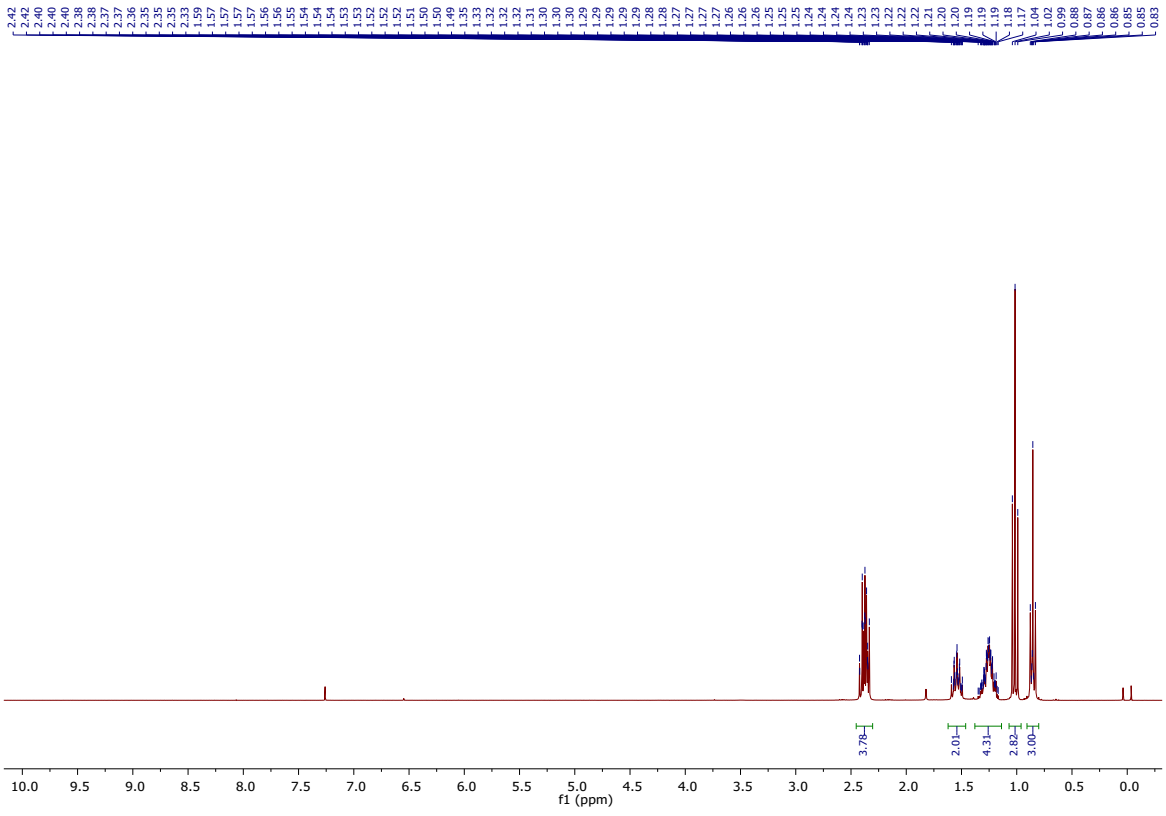


Figure S117. ^{1}H NMR spectrum of **24** in $CDCl_3$ recorded at room temperature (400 MHz).

3.25. Synthesis of 3-pentanone 26

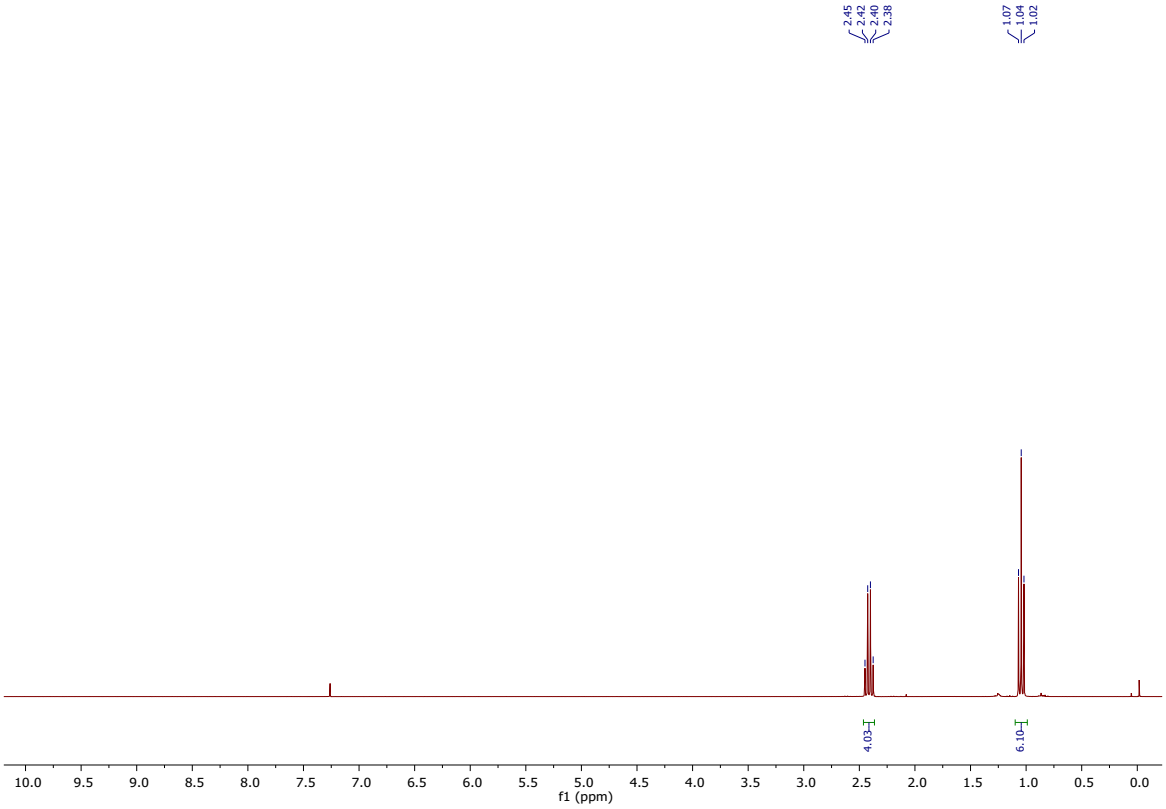


Figure S118. ^{1}H NMR spectrum of **26** in $CDCl_3$ recorded at room temperature (400 MHz).

3.26. Synthesis of 3-phenylpropanal 27

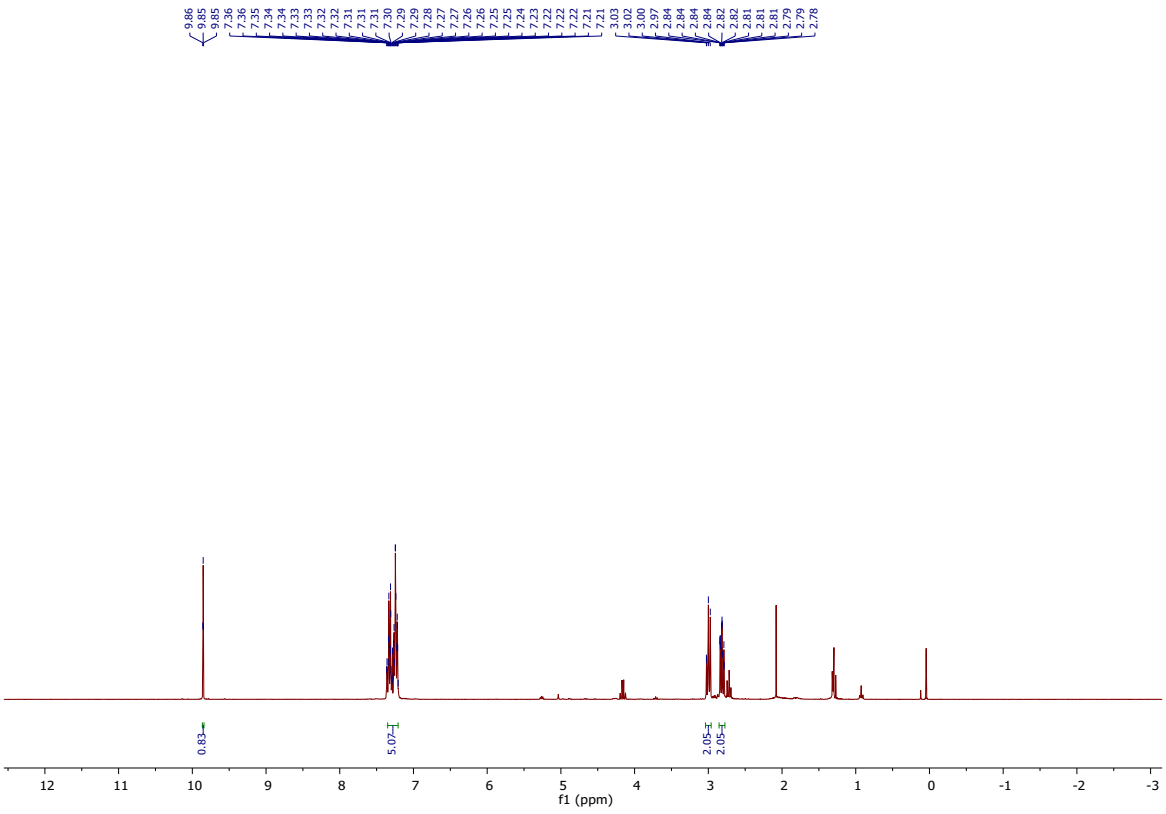


Figure S119. ^{1}H NMR spectrum of **27** in $CDCl_3$ recorded at room temperature (400 MHz).

3.27. Synthesis of 1,3-diphenylpropan-1-one 29

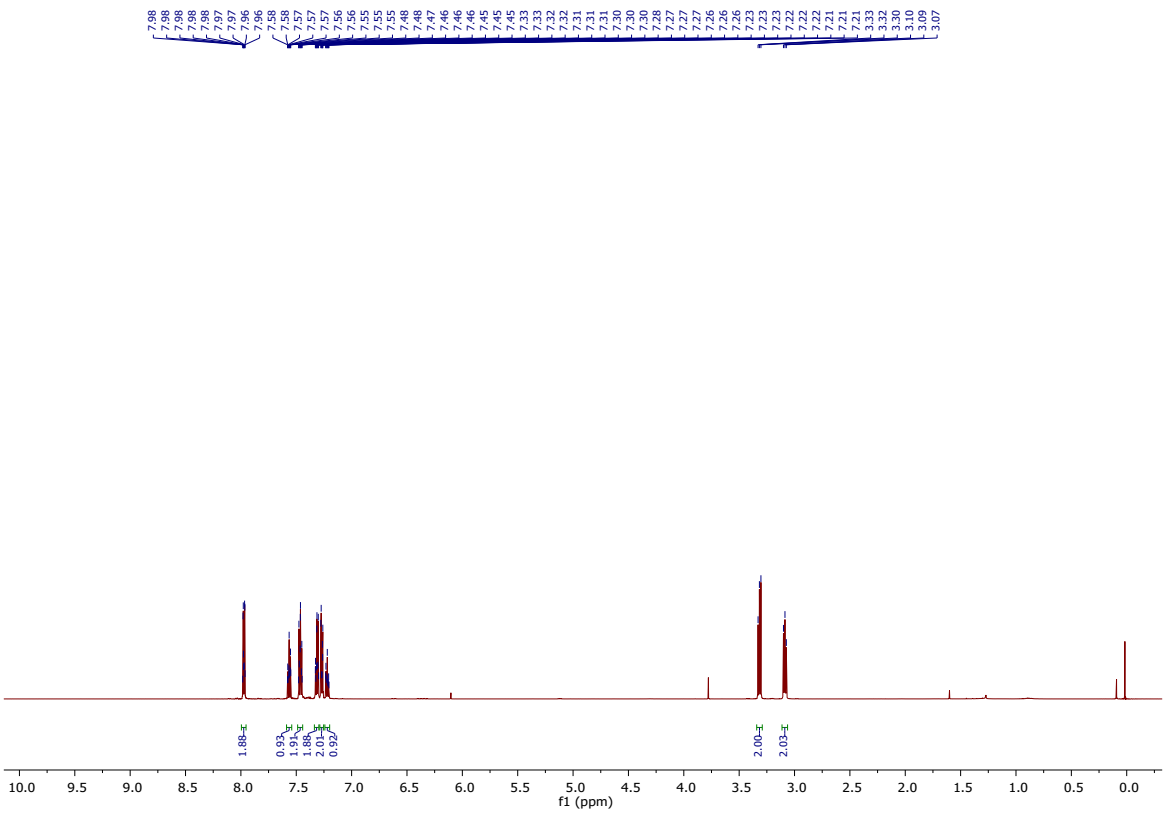


Figure S120. ^{1}H NMR spectrum of **29** in $CDCl_3$ recorded at room temperature (600 MHz).

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