Electronic Supplementary Material (ESI) for ChemComm.
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Supporting Information

Exceptionally Large Two- and Three-Photon Absorption Cross-Sections by OPV Organometalation

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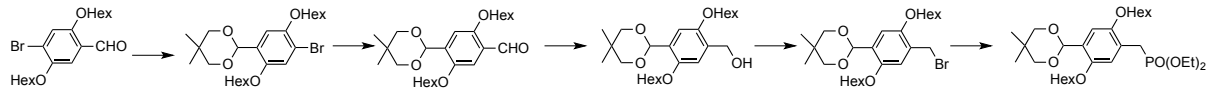
Materials and instrumentation

Materials. All reactions were performed under a nitrogen atmosphere with the use of standard Schlenk techniques unless otherwise stated. Tetrahydrofuran and toluene were dried by distilling over sodium/benzophenone, dichloromethane and chloroform were dried and distilled over calcium hydride. NEt_3 was deoxygenated prior to use; other solvents were used as received. Triethylphosphite (Aldrich) was distilled before use. Petrol refers to a fraction of petroleum spirits with a boiling range 60-90°C. The following compounds were synthesized by literature procedures: 4-bromo-2,5-bis(hexyloxy)benzaldehyde,[1] 2,5-bis(hexyloxy)-1,4-phenylenebis(methylphosphonate diethyl ester),[2] diethyl(4-(5,5-dimethyl-1,3-dioxan-2-yl)benzyl)phosphonate,[3] 4-[(trimethylsilyl)ethynyl]benzaldehyde,[4] diethyl(4-[(trimethylsilyl)ethynyl]benzyl)phosphonate,[5] and $[RuCl(dppe)_2]PF_6$[6]. All other reagents were obtained from commercial sources and used as received. Chromatography was on silica gel (200-300 mesh) or basic alumina. All commercially available materials were used as received.

Instrumentation. NMR spectra were recorded using a Bruker AVANCE III-400 FT-NMR spectrometer, and are referenced to residual chloroform (^{1}H, 7.26 ppm), $CDCl_3$ (^{13}C, 77.0 ppm) or external 85% H_3PO_4 (^{31}P, 0.0 ppm). UV-vis-NIR spectra were recorded as CH_2Cl_2 solutions in 1 cm quartz cells using a Lambda TU1901 spectrophotometers, and are reported as λ_{max} nm (ε 10^4 M^{-1} cm^{-1}). Vibrational spectra were recorded using a Thermo Fisher Nicolet 6700 ATR FT-IR spectrometer. Electrospray ionization mass spectra (low resolution and high resolution) were recorded using a Micromass/Waters LC-ZMD single quadrupole liquid chromatography MS, and electron impact mass spectra (low resolution and high resolution) were recorded using a Fisons 3-Sector VG AutoSpec MS at the Australian National University. All mass spectrometry peaks are reported as *m/z* (assignment, relative intensity). Microanalyses were carried out at the Science Centre, London Metropolitan University. Electrochemical measurements were recorded using a Zahner IM6 potentiostat. Electrochemical solutions contained 0.1 M $[Bu_4N][PF_6]$ and *ca*. 10^{-3} M analyte in CH_2Cl_2, and were purged and maintained under N_2. Analytes were internally referenced to the ferrocene/ferrocenium redox couple, which was located at 0.56 V (ΔE = 0.9 - 1.0 V). Scan rates were typically 100 mV s^{-1}.
UV-vis spectroelectrochemical measurements were carried out using a Lambda 9 spectrophotometer and a bespoke low-temperature optically transparent thin-layer electrochemical (OTTLE) cell. The cell utilized platinum working- and auxilliary- eletrodes, and a silver wire reference electrode; solutions were typically 10^{-4} M analyte in CH_2Cl_2.

Syntheses.

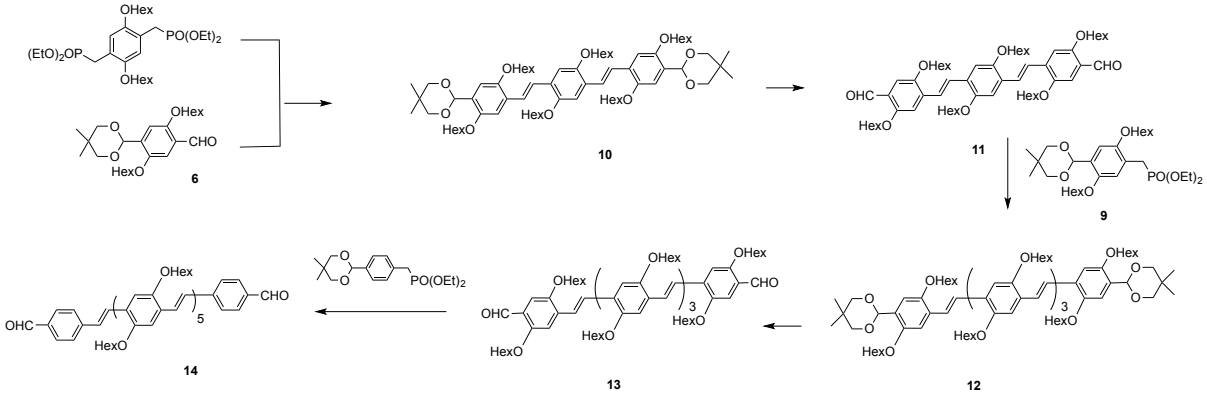


*Synthesis of 2-(4-bromo-2,5-bis(hexyloxy)phenyl)-5,5-dimethyl-1,3-dioxane (**5**).*
A solution of 4-bromo-2,5-bis(hexyloxy)benzaldehyde (5.00 g 13.02 mmol), 2,2-dimethylpropane-1,3-diol (5.40 g, 52.08 mmol), and *p*-TsOH (50 mg, 0.26 mmol) in toluene (80 ml) was heated at reflux for 48 h using a Dean-Stark trap. After cooling to room temperature, the solution was evaporated to dryness. The crude residue was taken up in CH_2Cl_2, washed with water, stirred over anhydrous $MgSO_4$, filtered and the filtrate taken to dryness. Column chromatography (SiO_2, petrol) afforded a main yellow band that was collected and the solvent removed to give **5** as a light yellow oil (4.9 g,10.4 mmol, 80%). R_f = 0.5 (CH_2Cl_2:petrol 1:1); ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.20 (s, 1H), 7.07 (s, 1H), 5.68 (s, 1H), 4.01 (t, J_{HH} = 6.5 Hz, 2H), 3.91 (t, J_{HH} = 6.5 Hz, 2H), 3.74 (d, J_{HH} = 11 Hz, 2H), 3.64 (d, J_{HH} = 10 Hz, 2H), 1.78 (m, 4H), 1.41 (m, 15H), 0.91 (m, 6H), 0.79 (s, 3H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 150.49, 149.92, 127.16, 117.81, 113.11, 112.56, 96.77, 77.85, 70.10, 69.63, 31.53, 31.51, 30.26, 29.23, 29.21, 25.70, 25.67, 23.20, 22.63, 22.59, 21.85, 14.01 ppm; IR: 1206 ν(C-O), 1096 ν(C-O-C) cm^{-1}; HRMS: $C_{24}H_{39}O_4{}^{79/81}$Br expected 470.2032/ 472.2003, Found 470.2032 / 472.2003.

*Synthesis of 4-(5,5-dimethyl-1,3-dioxan-2-yl)-2,5-bis(hexyloxy)benzaldehyde (**6**).*
n-BuLi (9 mL of 1.6 M solution in hexane, 14 mmol) was added dropwise to a solution of **5** (4.50 g, 9.57 mmol) in THF (60 mL) at -78 °C under argon. The solution was stirred at -78 °C for 2 h, then dried DMF (2 mL) was added quickly and the mixture was stirred at room temperature for 2 h before being poured into water. The product was extracted with diethylether and the organic layer washed with water and brine and stirred over anhydrous $MgSO_4$. The solvent was removed and the residue subjected to column chromatography (SiO_2, petrol/CH_2Cl_2 4:1). The main yellow band was collected and the solvent removed to give **6** as a yellow oil (3.2 g, 7.63 mmol, 80%). R_f = 0.3 (CH_2Cl_2:petrol 1:1); ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 10.46 (s, 1H, CHO), 7.30 (s, 2H), 5.73 (s, 1H), 4.09 (t, J_{HH} = 6 Hz, 2H), 3.98 (t, J_{HH} = 6 Hz, 2H), 3.76 (d, J_{HH} = 11 Hz, 2H), 3.66 (d, J_{HH} = 11 Hz, 2H) 1.80 (m, 4H), 1.39 (m, 15H), 0.91 (m, 6H), 0.81 (s, 3H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$) : δ = 189.58, 156.31, 150.14, 134.64, 125.29, 112.13, 110.27, 96.53, 77.88, 69.16, 69.13, 31.50, 30.34, 29.16, 29.12, 25.73, 25.69, 23.21, 22.62, 22.55, 21.84, 14.00, 13.98 ppm; IR: 2857 ν(=C-H), 1681 ν(-C=O), 1205 ν(C-O), 1094 ν(C-O-C) cm^{-1}; HRMS: Calc. for $C_{25}H_{40}O_5$ 420.2876, Found 420.2873.

*Synthesis of Synthesis of 2-(4-(bromomethyl)-2,5-bis(hexyloxy)phenyl)-5,5-dimethyl-1,3-dioxane (**8**).*
Compound **6** (3.00 g, 7.14 mmol) was dissolved in THF (60 mL) and stirred at 0 °C for 10 min. $LiAlH_4$ (0.42 g, 11.07 mmol) was added and the mixture was stirred for 4 h. Methanol was added to quench the $LiAlH_4$ and CH_2Cl_2 (100 mL) was added. The mixture was extracted with water (2 x 50 mL) and brine (50 mL). The organic layer was stirred over anhydrous $MgSO_4$, and the mixture filtered through a silica pad. The solvent volume was reduced and the residue subjected to column chromatography (SiO_2, CH_2Cl_2/petrol 3:2). The main pale yellow band was collected and the solvent removed to give (4-(5,5-dimethyl-1,3-dioxan-2-yl)-2,5-bis(hexyloxy)phenyl)methanol (**7**) as a yellow oil (2.45 g, 5.80 mmol, 81%). R_f = 0.5 (EtOAc); ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.15 (s, 1H), 6.84 (s, 1H), 5.74 (s, 1H), 4.65 (s, 2H), 4.03 (t, J_{HH} = 6 Hz, 2H), 3.94 (t, J_{HH} = 6 Hz, 2H), 3.75 (d, J_{HH} = 11 Hz, 2H), 3.65 (d, J_{HH} = 11 Hz, 2H), 1.77 (m, 4H), 1.39 (m, 15H), 0.90 (s, 6H), 0.79 (s, 3H) ppm; IR: 3476 ν(-OH), 1197 ν(C-O), 1092 ν(C-O-C) cm^{-1}. Compound **7** was then used in the synthesis of compound **8**. CBr_4 (2.45 g, 7.4 mmol) and PPh_3 (1.94 g, 7.4 mmol) were added to a solution of compound **7** (2.35 g, 5.56 mmol) in THF (60 mL) at 0° C. The mixture was stirred for 4 h. CH_2Cl_2 (100 mL) was added and the mixture was extracted with water (2 x 50 mL) and brine (50 mL). The organic layer was stirred over anhydrous $MgSO_4$ and the volume of the solvent reduced. The residue was purified by silica gel chromatography (CH_2Cl_2/petrol 1:4). The main pale yellow band was collected and the solvent removed to give **8** as a yellow oil (1.23 g, 2.5 mmol, 51%). R_f = 0.7 (CH_2Cl_2:petrol 1:1); ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.15 (s, 1H), 6.86 (s, 1H), 5.71 (s, 1H), 4.53 (s, 2H), 4.03 (t, J_{HH} = 6 Hz, 2H), 3.94 (t, J_{HH} = 6 Hz, 2H), 3.75 (d, J_{HH} = 11 Hz, 2H), 3.65 (d, J_{HH} = 11 Hz, 2H), 1.79 (m, 4H), 1.39 (m, 15H), 0.89 (m, 6H), 0.79 (s, 3H) ppm; HRMS *m/z (%)*: Calc. for $C_{24}H_{39}O_4{}^{79/81}$Br 470.2032/472.2011, found 470.2032/472.2003. This compound proved to be unstable to thin layer chromatography, forming the aldehyde, and was used without further purification in the next step.

*Synthesis of diethyl(4-(5,5-dimethyl-1,3-dioxan-2-yl)-2,5-bis(hexyloxy)benzyl)phosphonate (**9**).*
A mixture of **8** (0.32 g, 0.59 mmol) and triethylphosphite (0.12 g, 0.71 mmol) was heated at 150 °C for 4 h. After allowing to cool to room temperature, the excess triethylphosphite was removed by vacuum distillation. The residue was subjected to column chromatography (SiO_2, CH_2Cl_2), and the main band collected and the solvent removed to give **9** as a yellow oil (0.28 g, 0.52 mmol, 89%). R_f = 0.3 (EtOAc); ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.13 (s, 1H), 6.94 (d, *J* = 3 Hz, 1H), 5.72 (s, 1H), 3.99 (m, 8H), 3.75 (d, *J* = 11 Hz, 2H), 3.65 (d, *J* = 11 Hz, 2H), 3.23 (d, *J* = 22 Hz, 2H), 1.76 (m, 4H), 1.33 (m, 15H), 1.23 (t, *J* = 8 Hz, 6H), 0.91 (m, 6H), 0.79 (s, 3H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 150.93, 150.85, 149.76, 149.72, 126.38, 126.34, 121.70, 121.61, 115.90, 115.85, 110.37, 110.34, 97.07, 77.84, 69.40, 68.85, 61.99, 61.81, 61.75, 53.37, 31.56, 31.52, 29.42, 29.29, 25.78, 25.71, 23.18, 22.60, 22.55, 16.35, 16.29, 13.96 ppm;^{31}P NMR (162 MHz, $CDCl_3$): δ 26.94 ppm; HRMS *m/z (%)*: Calc. for $C_{29}H_{51}O_7P$ 542.3372, Found 542.3373.



*Synthesis of compound **11**.*
t-BuOK (0.35 g, 3.16 mmol) was added to a solution of 2,5-bis(hexyloxy)-1,4-phenylenebis(methylphosphonate diethyl ester) (0.46 g, 0.79 mmol) and compound **6** (0.70 g, 1.67 mmol) in THF at 0 °C. The mixture was stirred for 1 h, and then the solvent was evaporated to dryness and the residue taken up in CH_2Cl_2. The organic layer was washed with H_2O, stirred over anhydrous MgSO4, filtered and the filtrate evaporated to dryness. The residue was subjected to column chromatography (SiO_2, CH_2Cl_2:petrol 1:1), and the major band was collected and taken to dryness to give **10** as a mixture of *E:Z* isomers. The *E:Z* mixture was dissolved in toluene (15 mL) and I_2 (0.010 g, 0.039 mmol) was added. The reaction was heated at reflux for 12 h and then allowed to cool to room temperature. The solution was washed with aqueous 0.3 M $Na_2S_2O_3$ and water, stirred over anhydrous $MgSO_4$, filtered and the filtrate evaporated to dryness. The residue was subjected to column chromatography (SiO_2, CH_2Cl_2:petrol 1:2) to give **10** as a yellow solid (0.73 g, 0.067 mmol, 83%). R_f = 0.4 (CH_2Cl_2:petrol 2:1); ^{1}H-NMR (400 MHz,$CDCl_3$): δ = 7.45 (d, *J* = 2 Hz, 4H), 7.15 (m, 6H), 5.75 (s, 2H), 4.03 (m, 12H), 3.77 (d, *J* = 11 Hz, 4H), 3.67 (d, *J* = 11 Hz, 4H), 1.82 (m, 12H), 1.43 (m, 42H), 0.91 (m, 18H), 0.80 (s, 6H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 151.07, 150.35, 128.60, 127.36, 127.06, 123.70, 123.39, 111.51, 110.58, 97.14, 77.91, 77.34, 77.23, 77.02, 76.71, 69.54, 69.51, 69.39, 31.67, 31.66, 31.61, 30.31, 29.51, 29.46, 29.44, 25.96, 25.92, 25.84, 23.25, 22.68, 22.66, 21.92, 14.06 ppm; IR: 1610 ν(-C=C), 1199 ν(C-O), 1097 ν(C-O-C) cm^{-1}. Compound **10** was then used in the synthesis of compound **11**. A mixture of compound **10** (0.73 g, 0.066 mmol) and CF_3CO_2H (10 mL) in a mixture of CH_2Cl_2 and water (1:1, 40 mL) was stirred at room temperature for 4 h. The organic layer was then washed with water, stirred over anhydrous $MgSO_4$, filtered and the filtrate evaporated to dryness. The residue was subjected to column chromatography (SiO_2, CH_2Cl_2:petrol 1:2), and the main band was collected and reduced in volume to give compound **11** as an orange solid (0.56 g, 0.059 mmol, 90%). R_f = 0.7 (CH_2Cl_2:petrol = 2:1); ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 10.45 (s, 2H, CHO), 7.60 (d, *J* = 16 Hz, 2H), 7.51 (d, *J* = 16 Hz, 2 H), 7.33 (s, 2H), 7.21 (s, 2 H), 7.16 (s, 2 H), 4.08 (m, 12 H), 1.87 (m, 12H), 1.45 (m, 36H), 0.91 (q, *J* = 7 Hz, 18H) ppm; ^{13}C-NMR (101MHz, $CDCl_3$): δ = 189.14, 156.30, 151.41, 150.78, 135.02, 127.54, 126.94, 124.25, 123.23, 110.85, 110.51, 110.21, 77.34, 77.02, 76.71, 69.48, 69.25, 69.20, 69.15, 31.66, 31.61, 31.57, 29.47, 29.28, 29.26, 25.96, 25.87, 25.82, 22.67, 22.62, 22.60, 14.07, 14.04, 14.01 ppm; IR: 1676, 2854 ν(-CHO),1595 ν(-C=C) cm^{-1}; HRMS: Calc. for $C_{60}H_{90}O_8$ 938.6636, Found 938.6641.

*Synthesis of compound **12**.*
t-BuOK (0.14 g, 1.28 mmol) was added to a solution of compound **11** (0.30 g, 0.32 mmol) and compound **9** (0.38 g, 0.70 mmol) in THF (50 mL) at 0 °C. The mixture was stirred for 4 h, the solvent was evaporated to dryness and the residue was taken up in CH_2Cl_2. The organic layer was washed with water, stirred over anhydrous $MgSO_4$, filtered and the filtrate evaporated to dryness. The residue was subjected to column chromatography (SiO_2, CH_2Cl_2:petrol = 1:1), and the major band was collected and taken to dryness to give compound **12** as a mixture of *E:Z* isomers. The *E:Z* mixture was dissolved in toluene (15 mL) and I_2 (4.10 mg, 0.016 mmol) was added and the solution was heated at reflux for 12 h. The reaction was allowed to cool to room temperature, then washed with an aqueous 0.3 M $Na_2S_2O_3$ solution and water, and stirred over anhydrous $MgSO_4$. The mixture was filtered and the solvent evaporated. The residue was subjected to

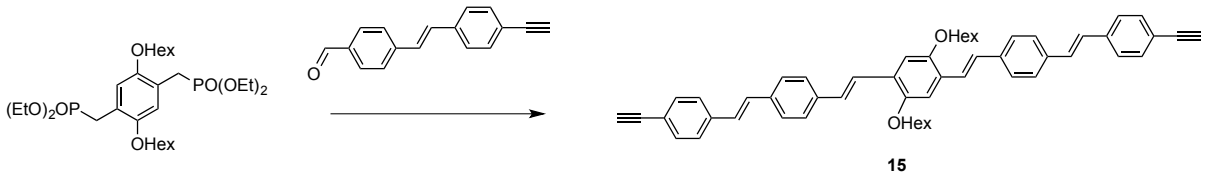
column chromatography (SiO_2, CH_2Cl_2:petrol 1:1), and the main band was collected and reduced in volume to give compound **12** as an orange solid (0.34 g, 0.020 mmol, 61%). R_f = 0.4 (CH_2Cl_2:petrol 2:1); ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.48 (d, J = 12 Hz, 8H), 7.17 (t, J = 10 Hz, 10H), 5.76 (s, 2H), 4.02 (m, 20H), 3.77 (d, *J* = 10 Hz, 4H), 3.67 (d, *J* = 10 Hz, 4H), 1.83 (m, 20H), 1.42 (m, 66H), 0.91 (d, *J* = 2 Hz, 30H), 0.81 (s, 6H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$): = 151.12, 150.38, 128.61, 127.53, 127.38, 127.10, 123.70, 123.41, 123.30, 111.55, 110.59, 97.15, 77.92, 77.35, 77.03, 76.71, 69.54, 69.40, 31.70, 31.67, 31.62, 30.31, 29.54, 29.48, 29.45, 25.98, 25.93, 25.85, 23.26, 22.69, 21.92, 14.07 ppm; IR: 1611 ν(-C=C), 1201 ν(C-O), 1099 ν(C-O-C) cm^{-1}; HRMS: Calc for $C_{110}H_{170}O_{14}$ 1715.2591, Found 1715.2582.

*Synthesis of compound **13**.*

A mixture of compound **12 (**0.34 g, 0.20 mmol**)** and CF_3CO_2H (10 ml) in a mixture of CH_2Cl_2 and water (1:1, 40 mL) was stirred at room temperature for 4 h. The organic layer was then washed with water, stirred over anhydrous $MgSO_4$, filtered and evaporated to dryness. The residue was subjected to column chromatography (CH_2Cl_2: petrol = 1:2), and the main band was collected and reduced in volume to give **13** as a red solid (0.27 g, 0.017 mmol, 88%). R_f = 0.3 (CH_2Cl_2:petrol 2:1); ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 10.45 (s, 2H, CHO), 7.64 (d, *J* = 16 Hz, 2H), 7.53 (d, *J* = 16 Hz, 6H); 7.33 (s, 2H), 7.18 (m, 8H), 4.08 (m, 20H), 1.87 (m, 20H), 1.47 (m, 60H), 0.91 (s, 30H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 189.11, 156.31, 151.48, 151.19, 151.07, 150.71, 135.22, 128.53, 127.52, 127.10, 126.54, 124.08, 123.87, 123.24, 122.61, 110.93, 110.59, 110.43, 110.37, 110.13, 77.34, 77.02, 76.70, 69.56, 69.53, 69.43, 69.20, 69.12, 31.69, 31.61, 31.57, 29.53, 29.51, 29.49, 29.27, 29.26, 25.97, 25.87, 25.82, 22.68, 22.66, 22.60, 14.06, 14.04, 14.01 ppm; IR: 1591 ν(-C=C), 1678, 2854 ν(-CHO) cm^{-1}; HRMS: Calc. for $C_{100}H_{150}O_{12}$ 1543.1127, Found 1543.1100.

*Synthesis of compound **14**.*

t-BuOK (0.10 g, 0.92 mmol) was added to a solution of diethyl(4-(5,5-dimethyl-1,3-dioxan-2-yl)benzyl)phosphonate (0.22 g, 0.64 mmol) and compound **13** (0.35 g, 0.23 mmol) in THF (50 mL) at 0 °C. The mixture was stirred overnight at 45 °C, and then allowed to cool to room temperature. The solvent was evaporated to dryness and the residue taken up with CH_2Cl_2.The organic layer was washed with water, stirred over anhydrous $MgSO_4$, filtered and the solvent evaporated to dryness. The residue was subjected to column chromatography (CH_2Cl_2: petrol = 2:1), The main band was collected and taken to dryness to give **14** as a *E:Z* isomer mixture. The mixture was dissolved in toluene (15 mL) and I_2 was added. The reaction was heated at reflux for 12 h and then cooled to room temperature. The solution was then washed with aqueous 0.3 M $Na_2S_2O_3$ and water, stirred over anhydrous $MgSO_4$, filtered and the solvent evaporated to dryness. The residue **(**0.25 g, 0.13 mmol**)** was stirred with CF_3CO_2H (10 mL) in a mixture of CH_2Cl_2 and water (1:1, 40 mL) at room temperature for 4 h. The organic layer was then washed with water, stirred over anhydrous $MgSO_4$, filtered and the solvent evaporated to dryness. The residue was subjected to column chromatography (CH_2Cl_2: petrol 1:1). The main band was collected and reduced in volume to give **14** as a dark red solid (0.20 g, 0.11 mmol, 49%). R_f = 0.2 (CH_2Cl_2:petrol 2:1); ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 9.99 (s, 2H), 7.87 (d, *J* = 8 Hz, 4H), 7.66 (m, 6H), 7.51 (s, 8H), 7.17 (t, *J* = 14 Hz, 12H), 4.07 (t, *J* = 6 Hz, 20H), 1.89 (s, 20H), 1.51 (m, 60H), 0.93 (d, *J* = 6 Hz, 30H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 191.64, 151.57, 151.20, 151.14, 151.10, 151.00, 144.29, 135.05, 130.26, 128.86, 127.76, 127.49, 127.21,127.10, 126.81, 125.62, 124.11, 123.44, 123.25, 123.01, 110.89, 110.59, 110.52, 110.46, 110.35, 77.35, 77.03, 76.71, 69.62, 69.52, 69.47, 69.42, 31.70, 31.65, 29.53, 29.49, 29.46, 25.99, 22.70, 14.09, 14.05 ppm; IR: 2855, 1697 ν(-CHO), 1594 ν(-C=C) cm^{-1}; HRMS: Calc. for $C_{106}H_{162}O_{12}$ 1747.2066, Found 1747.2094.



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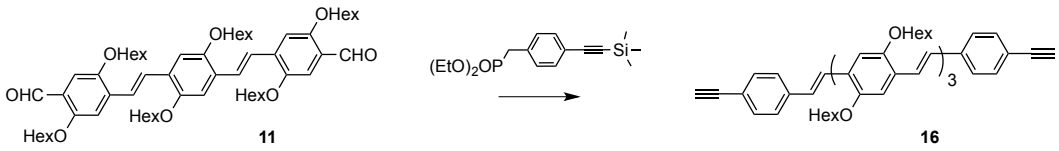
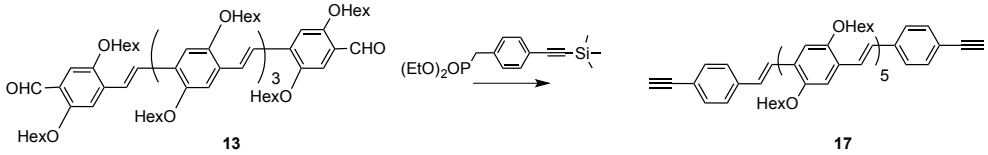
*Synthesis of compound **15**.*

NaOMe (excess) was added to a solution of 2,5-bis(hexyloxy)-1,4-phenylenebis(methylphosphonate diethyl ester) (320 mg, 0.54 mmol) in THF (30 mL) and the mixture was stirred at 0°C for 30 min. 4-[(Trimethylsilyl)ethynyl]benzaldehyde (240 mg, 1.19 mmol) was added and the mixture was stirred at 0°C for 30 min, and then at room temperature for a further 30 min. Water (30 mL) and MeOH (12 mL) were added to the mixture to afford a yellow precipitate. This was collected, washed (H_2O/MeOH mixture) and dried in vacuo to afford **15** as a yellow powder (215 mg, 0.41 mmol, 75%). ^{1}H NMR: (400 MHz, $CDCl_3$): δ = 7.49 (m, 10H), 7.11 (m, 4H), 4.05 (t, J_{HH} = 6 Hz, 4H), 3.13 (s, 2H, ≡CH), 1.88 (m, 4H), 1.54 (m, 4H), 1.39 (m, 8H) ppm, 0.92 (t, J_{HH} = 6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 151.24, 138.49, 132.45, 128.08, 126.88, 126.35, 124.71, 120.80, 110.70, 83.88, 77.85, 76.71, 69.59, 31.65, 29.46, 25.97, 22.67, 14.04 ppm; IR: 3260 ν(≡C-H), 2097ν(-C≡C), 1597ν(-C=C) cm^{-1}; UV-Vis: 409 (3.4); HRMS: Calc. for $C_{38}H_{42}O_2$ 530.3185, Found 530.3188; elemental analysis (%) calcd for $C_{38}H_{42}O_2$: C 85.99, H 7.98, found C 85.83, H 7.96.



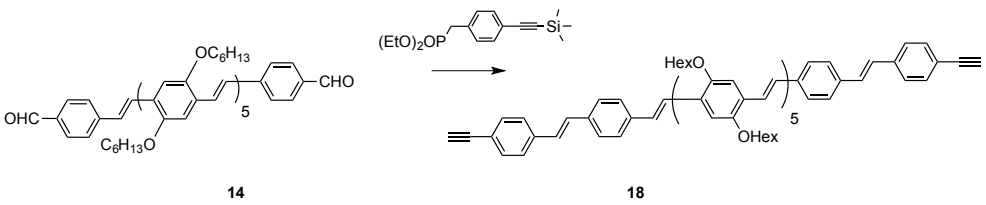
*Synthesis of compound **16**.*

t-BuOK (0.14 g, 1.28 mmol) was added to a solution of diethyl(4-[(trimethylsilyl)ethynyl]benzyl)phosphonate (0.21 g, 0.64 mmol) and compound **11** (0.30 g, 0.32 mmol) in THF (50 mL) at 0 °C. The mixture was stirred overnight, the solvent evaporated to dryness and the residue taken up with CH_2Cl_2.The organic layer was washed with water, stirred over anhydrous $MgSO_4$, filtered and the solvent evaporated to dryness. The residue was subjected to column chromatography (CH_2Cl_2:petrol 1:2). The main band was collected and reduced in volume to give **16** as an orange solid (0.17 g, 0.15 mmol, 47%). R_f = 0.7 (CH_2Cl_2:petrol 2:1); ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.50 (m, 14H), 7.13 (m, 8H), 4.06 (t, J_{HH} = 6 Hz, 12H), 3.14 (s, 2H, ≡CH), 1.87 (m, 12H), 1.43 (m, 34H), 0.92 (m, 20H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 151.32, 151.15, 151.04, 138.60, 132.43, 128.17, 127.68, 127.49, 126.30, 126.24, 124.84, 123.70, 123.22, 120.66, 110.77, 110.57, 110.48, 83.91, 77.77, 69.63, 69.50, 31.68, 31.66, 29.53, 29.51, 26.00, 25.98, 25.96, 22.69, 22.67, 14.07, 14.04 ppm; IR: 2110 ν(-C≡C), 3321 ν(≡C-H), 1592 ν(-C=C) cm^{-1}; UV-Vis: 458 (10.3); elemental analysis (%) calcd for $C_{78}H_{102}O_6$: C 82.49, H 9.05, found C 82.40, H 8.92.



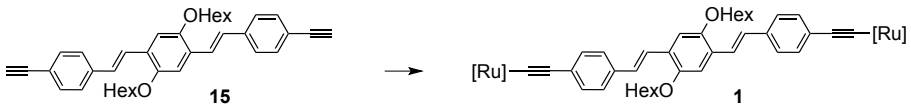
*Synthesis of compound **17**.*

t-BuOK (0.12 g, 1.04 mmol) was added to a solution of diethyl(4-[(trimethylsilyl)ethynyl)benzyl]phosphonate (0.18 g, 0.54 mmol) and compound **13** (0.40g, 0.26 mmol) in THF (50 mL) at 0 °C. The mixture was stirred overnight, the solvent evaporated to dryness and the residue taken up with CH_2Cl_2. The organic layer was washed with water, stirred over anhydrous $MgSO_4$, filtered and the solvent evaporated to dryness. The residue was subjected to column chromatography (CH_2Cl_2: petrol 3:2). The main band was collected and reduced in volume to give **17** as a red solid (0.23 g, 0.13 mmol, 50%). R_f = 0.7 (CH_2Cl_2:petrol 2:1); ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.51 (m, 18H), 7.13 (m, 12H), 4.06 (t, J_{HH} = 6 Hz, 20H), 3.14 (s, 2H, ≡CH), 1.88 (m, 20H), 1.45 (m, 60H), 0.93 (m, 30H) ppm; ^{13}C-NMR (101MHz, $CDCl_3$)**: δ =** 151.32, 151.15, 138.61, 132.43, 127.65, 126.30, 124.83, 123.36, 120.66, 110.52, 83.91, 77.77, 69.64, 69.54, 69.51, 31.70, 31.66, 29.54, 29.51, 29.50, 25.99, 25.97, 22.69, 22.67, 14.08, 14.04 ppm; IR: 2106 ν(-C≡C), 3318 ν(≡C-H), 1588 ν(-C=C) cm^{-1}; UV-Vis: 476 (14.4); elemental analysis (%) calcd for $C_{118}H_{162}O_{10}$: C 81.43, H 9.38, found C 81.38 H 9.40.



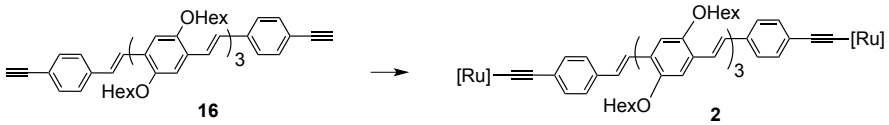
*Synthesis of compound **18**.*

t-BuOK (80 mg, 0.69 mmol) was added to a solution of diethyl(4-[(trimethylsilyl)ethynyl)benzyl]phosphonate (120 mg, 0.36 mmol) and compound **14** (0.30 g, 0.17 mmol) in THF (50 mL) at 0 °C. The mixture was stirred overnight and then water (30 mL) and MeOH (12 mL) were added to afford a yellow precipitate. This was collected, washed (H_2O/MeOH mixture) and dried in vacuo to afford compound **18** as a red powder (268 mg, 0.14 mmol, 81%). ^{1}H-NMR (400 MHz, $CDCl_3$**)**: δ = 7.52 (m, 26H), 7.14 (m, 16H), 4.07 (t, J_{HH} = 6 Hz, 20H), 3.14 (s, 2H, ≡CH), 1.87 (m, 20H), 1.55 (m, 60H), 0.93 (m, 30H) ppm; IR: 2105 (-C≡C), 3310 ν(≡C-H), 1589 ν(-C=C) cm^{-1}; UV-Vis: 478 (14.3). This compound was found to be too insoluble to obtain a ^{13}C NMR spectrum.



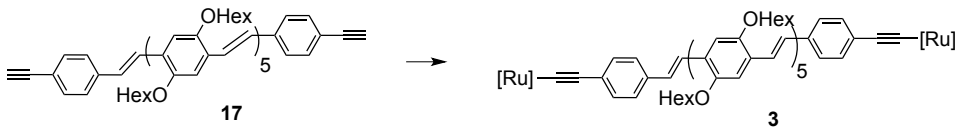
*Synthesis of complex **1**.*

A mixture of **15** (30 mg, 0.057 mmol) and $[RuCl(dppe)_2]PF_6$ (244 mg, 0.21 mmol) in distilled CH_2Cl_2 (50 mL) was stirred and heated at reflux for 2 days. The reaction mixture was reduced in volume on a rotary evaporator, and added dropwise to pentane (50 mL). The resulting solid was collected, washed with pentane and dried. The solid was dissolved in CH_2Cl_2 and NEt_3 (1 mL) was added, resulting in a colour change to light red, and the solution was stirred for 2 min. The solution was filtered through a pad of Celite directly into rapidly stirring MeOH. The resulting precipitate was collected, washed with MeOH and pentane, and dried to afford **1** as an orange powder (60 mg, 0.025 mmol, 44%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (m, 16H), 7.40 (d, J_{HH} = 16 Hz, 2H), 7.30 (m, 20H), 7.19 (m, 16H), 7.14 (s, 2H), 7.10 (d, J_{HH} = 16 Hz, 2H), 6.99 (m, 32H), 6.65 (d, J = 8 Hz, 4H), 4.08 (t, J = 6.5 Hz, 4H), 2.70 (m, 16H), 1.96 – 1.86 (m, 4H), 1.65 – 1.53 (m, 4H), 1.45 (m, 8H), 0.98 (t, J_{HH} = 6.9 Hz, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 151.09, 136.68, 136.58, 136.48, 135.75, 135.66, 135.56, 134.43, 134.32, 132.45, 130.26, 129.69, 128.94, 128.84, 128.79, 127.24, 126.95, 125.83, 121.19, 114.81, 110.63, 69.77, 31.76, 30.85, 30.73, 30.61, 29.71, 29.61, 26.06, 22.74, 14.13 ppm; ^{31}P-NMR (162 MHz, $CDCl_3$): δ = 49.43 ppm; IR: 2049 ν(-C≡C), 1589ν(C=C) cm^{-1}; UV-Vis: 463 [7.7]; HRMS Calc. for $C_{144}H_{139}P_8N^{35}ClO_2Ru_2$: 2400.6482, Found 2400.6548 ($[M\text{-}Cl+CH_3CN]^+$); elemental analysis (%) calcd for $C_{142}H_{136}Cl_2O_2P_8Ru_2$: C 71.20 H 5.72, found C 71.02, H 5.80.



*Synthesis of complex **2**.*

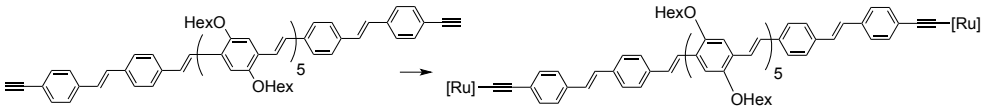
A mixture of compound **16** (50 mg, 0.044 mmol) and $[RuCl(dppe)_2]PF_6$ (190 mg, 0.176 mmol) in CH_2Cl_2 (50 mL) was heated at reflux for 2 days. The reaction mixture was reduced on a rotary evaporator, and added dropwise to pentane (50 mL). The resulting solid was collected, washed with pentane and dried in vacuo. The solid was dissolved in CH_2Cl_2 (15 mL) and NEt_3 (1 mL) was added, resulting in a colour change to light red. The mixture was stirred for 2 min, then filtered through a pad of Celite directly into rapidly stirring MeOH (60 mL). The resulting precipitate was collected, washed with MeOH and pentane, and dried to afford complex **2** as a dark red powder (67 mg, 0.022 mmol, 50%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = δ 7.58 – 7.48 (m, 20H), 7.40 (d, J = 16 Hz, 2H), 7.30 (m, 20H), 7.19 (m, 20H), 7.14 (s, 2H), 7.10 (d, J_{HH} = 16 Hz, 2H), 6.99 (m, 32H), 6.65 (d, J_{HH} = 8 Hz, 4H), 4.08 (t, J_{HH} = 6 Hz, 12H), 2.70 (s, 16H), 1.90 (m, 12H), 1.57 (m, 10H), 1.42 (m, 26H), 1.02 – 0.87 (m, 18H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 151.11, 151.01, 136.61, 136.51, 136.41, 135.68, 135.58, 135.48, 134.40, 134.28, 132.35, 130.24, 129.70, 129.03, 128.82, 128.78, 127.49, 127.44, 127.22, 127.12, 126.94, 125.83, 123.25, 123.11, 121.09, 114.76, 110.60, 110.50, 110.40, 77.22, 69.61, 69.53, 31.74, 31.70, 30.81, 30.69, 30.57, 30.45, 29.58, 29.53, 26.06, 25.98, 22.73, 22.70, 14.12, 14.10 ppm; ^{31}P-NMR (162 MHz, $CDCl_3$): δ = 49.4 ppm; IR: 2050 ν(-C≡C), 1587 ν(-C=C) cm^{-1}; UV-Vis: 476 (11.8); MS: 3010 ($[M - 2Cl + 2MeCN]^+$), 1505 ($[M - 2Cl + 2MeCN]^{2+}$); HRMS Calc. for $C_{186}H_{202}N_2O_6P_8Ru_2$: 1507.0895, Found 1507.1837 ($[M - 2Cl + 2CH_3CN]^{2+}$); elemental analysis (%) calcd for $C_{182}H_{196}Cl_2O_6P_8Ru_2$: C 72.86, H 6.58, found C 72.42, H 6.50.



*Synthesis of complex **3**.*

A mixture of compound **17** (60 mg, 0.034 mmol) and $[RuCl(dppe)_2]PF_6$ (148 mg, 0.14 mmol) in CH_2Cl_2 (50 mL) was stirred and heated at reflux for 2 days. The reaction mixture was reduced in volume on a rotary evaporator, and added dropwise to stirring pentane (50 mL). The resulting solid was collected, washed with pentane and dried in vacuo. The solid was dissolved in CH_2Cl_2 (15 mL) and NEt_3 (1 mL) added, resulting in a colour change to light red. The mixture was stirred for 2 min, and then filtered through a pad of Celite directly into rapidly stirring MeOH (60 mL). The resulting precipitate was collected, washed with MeOH and pentane, and dried to afford complex **3** a dark red powder (61 mg, 0.017 mmol, 50%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 – 7.46 (m, 23H), 7.40 (m, 3H), 7.29 (m, 20H), 7.20 (m, 23H), 7.14 (m, 2H), 7.10 (m, 3H), 6.99 (m, 32H), 6.65 (d, J_{HH} = 8 Hz, 4H), 4.07 (t, J_{HH} = 6 Hz, 20H), 2.70 (m, 16H), 1.90 (m, 20H), 1.57 (m, 20H), 1.42 (m, 40H), 0.96 (m, 30H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$)**:** δ = 151.13, 151.02, 136.62, 136.52, 136.42, 135.69, 135.59, 135.49, 134.40, 134.28, 132.35, 130.24, 129.70, 129.04, 128.82, 128.79, 127.54, 127.50, 127.46, 127.22, 127.12, 126.94, 125.84, 123.28, 123.11, 121.10, 114.76, 110.62, 110.52, 110.42, 77.23, 69.62, 69.53, 31.74, 31.70, 30.81, 30.70, 30.58, 30.46, 29.70, 29.58, 29.54, 26.06, 25.99, 22.73, 22.70, 14.12, 14.09 ppm; ^{31}P-NMR (162 MHz, $CDCl_3$): δ 49.4 ppm; IR: 2050 ν(-C≡C), 1587 ν(-C=C) cm^{-1}; UV-Vis: 487 (17.5); MS: 3616 ([M - 2Cl + 2MeCN]$^+$), 1808 ([M - 2Cl + 2MeCN]$^{2+}$); HRMS Calc for $C_{226}H_{262}N_2O_{10}P_8Ru_2$: 1809.3146, Found 1809.4150 ([M - 2Cl + 2CH_3CN]$^{2+}$); elemental analysis (%) calcd for $C_{222}H_{256}Cl_2O_{10}P_8Ru_2$: C 73.96, H 7.16, found C 73.96, H 6.94.



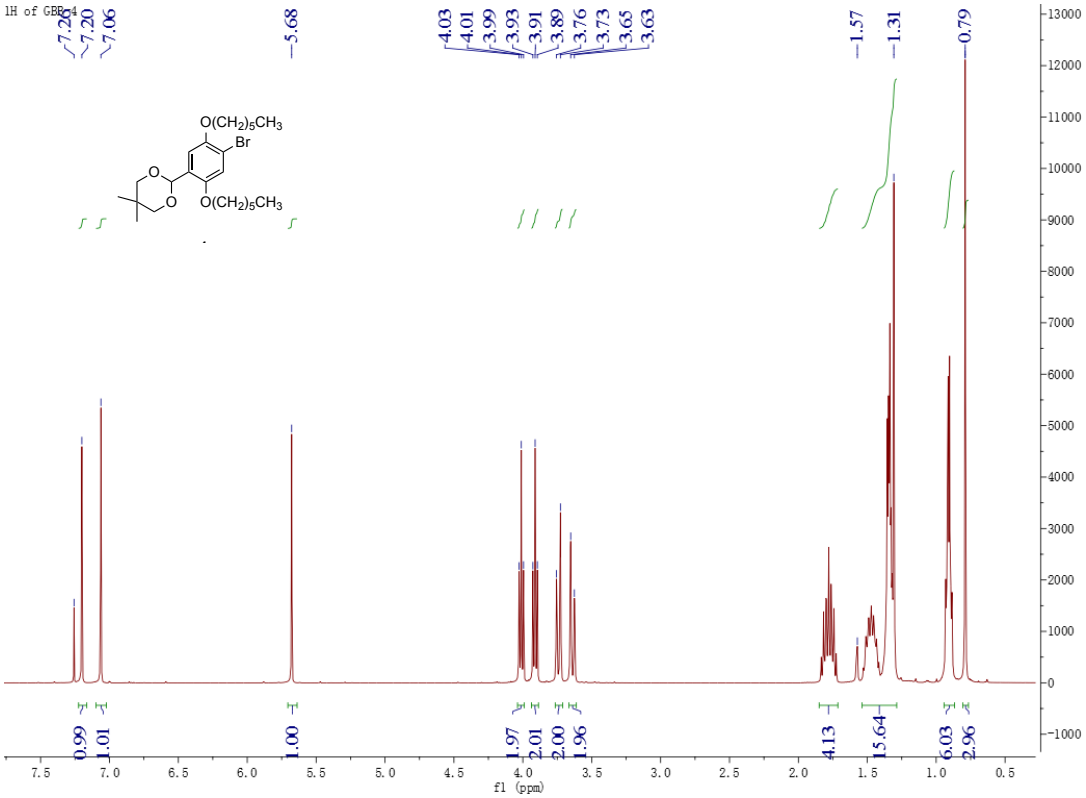
18 **4**

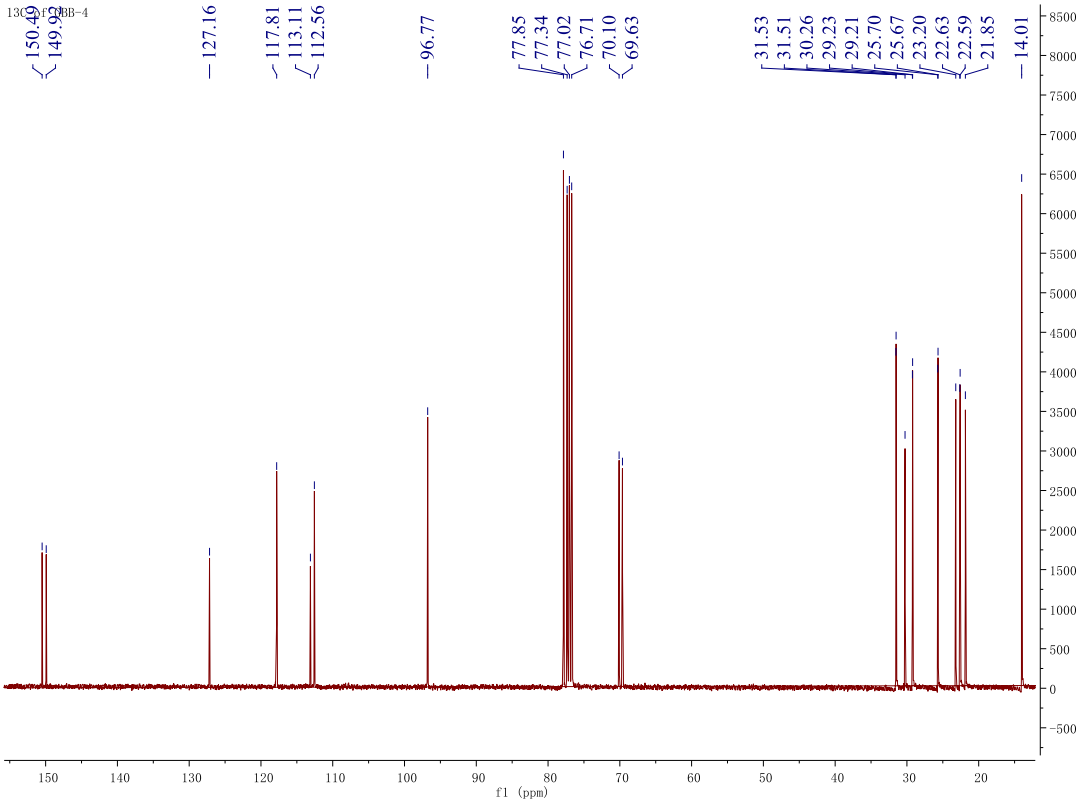
*Synthesis of complex **4**.*

A mixture of compound **18** (60 mg, 0.031 mmol) and $[RuCl(dppe)_2]PF_6$ (133 mg, 0.12 mmol) in CH_2Cl_2 (50 mL) was heated at reflux for 2 days. The reaction mixture was reduced on a rotary evaporator, and added dropwise to stirring pentane (50 mL). The resulting solid was collected, washed with pentane and dried in vacuo. The solid was dissolved in CH_2Cl_2 (15 mL) and NEt_3 (1 mL) was added, resulting in a colour change to light red. The mixture was stirred for 2 min, and then filtered through a pad of Celite directly into rapidly stirring MeOH (60 mL). The resulting precipitate was collected, washed with MeOH and pentane, and dried to afford **4** as a dark red powder (55 mg, 0.014 mmol, 47%). ^{1}H NMR (400 MHz, $CDCl_3$)**:** δ = 7.52 (m, 32H), 7.28 (m, 22H), 7.23 – 7.12 (m, 28H), 7.07 (m, 5H), 7.00 (m, 31H), 6.65 (d, J_{HH} = 7 Hz, 4H), 4.08 (s, 20H), 2.70 (s, 16H), 1.89 (m, 20H), 1.57 (m, 20H), 1.40 (m, 40H), 1.01 – 0.88 (m, 30H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$)**:** δ = 151.20, 151.13, 151.10, 137.11, 136.91, 136.60, 136.50, 136.40, 135.69, 135.59, 135.49, 134.40, 134.27, 131.70, 130.28, 129.93, 128.84, 128.79, 128.30, 127.73, 127.56, 127.51, 127.45, 1223, 126.95, 126.83, 126.53, 125.98, 125.82, 123.44, 123.30, 123.22, 123.14, 114.72, 110.53, 77.23, 69.63, 69.52, 31.70, 30.81, 30.69, 30.57, 29.70, 29.54, 26.01, 25.98, 22.69, 14.08 ppm; ^{31}P-NMR (162 MHz, $CDCl_3$): δ 49.4 ppm; IR: 2050 δ(-C≡C), 1586 ν(-C=C) cm^{-1}; UV-Vis: 484 (18.0); MS: 1910 ([M - 2Cl + 2MeCN]$^{2+}$); HRMS Calc for $C_{242}H_{274}N_2O_{10}P_8Ru_2$: 1911.3617, Found 1911.0660 ([M - 2Cl + 2CH_3CN]$^{2+}$); elemental analysis (%) calcd for $C_{238}H_{268}Cl_2O_{10}P_8Ru_2$: C 75.04, H 7.09, found C 74.90, H 6.97.

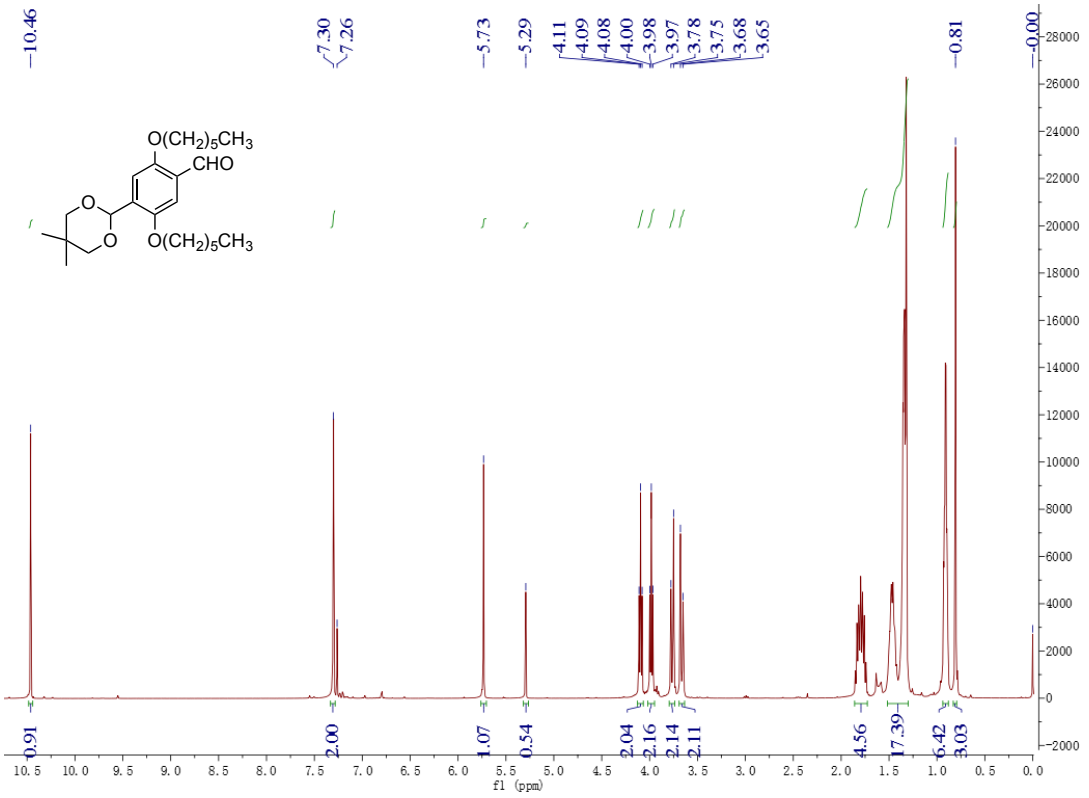
NMR spectra

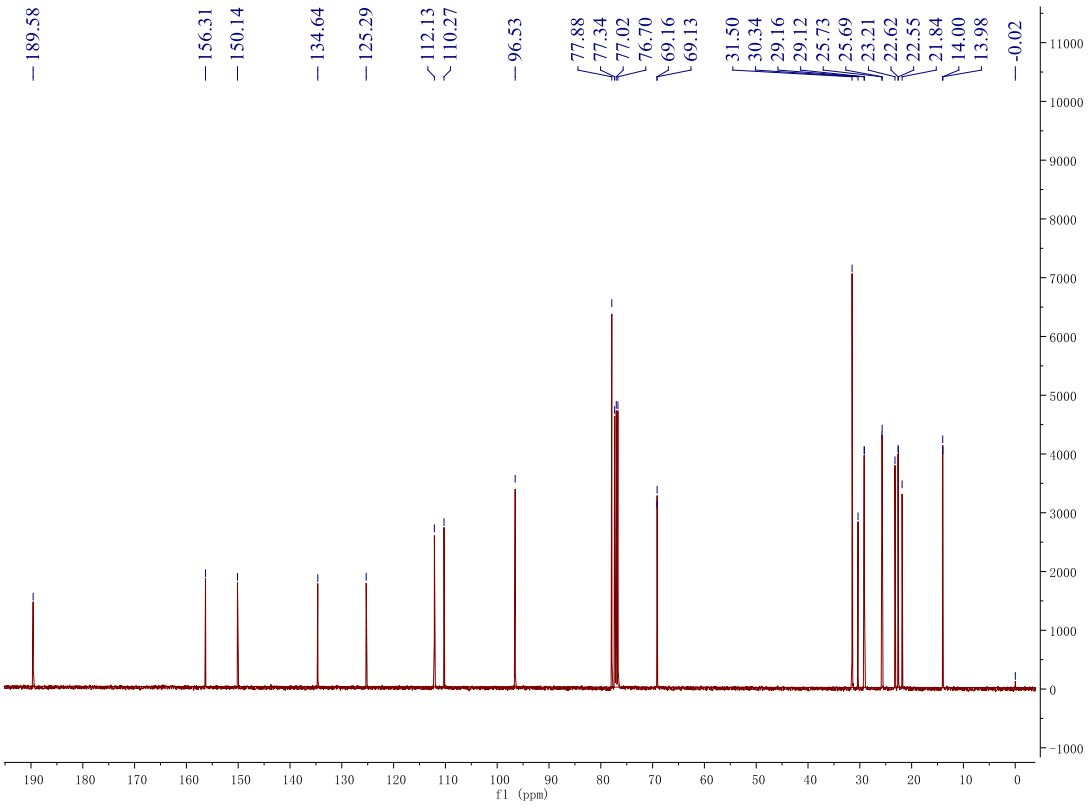
*2-(4-bromo-2,5-bis(hexyloxy)phenyl)-5,5-dimethyl-1,3-dioxane (**5**)*



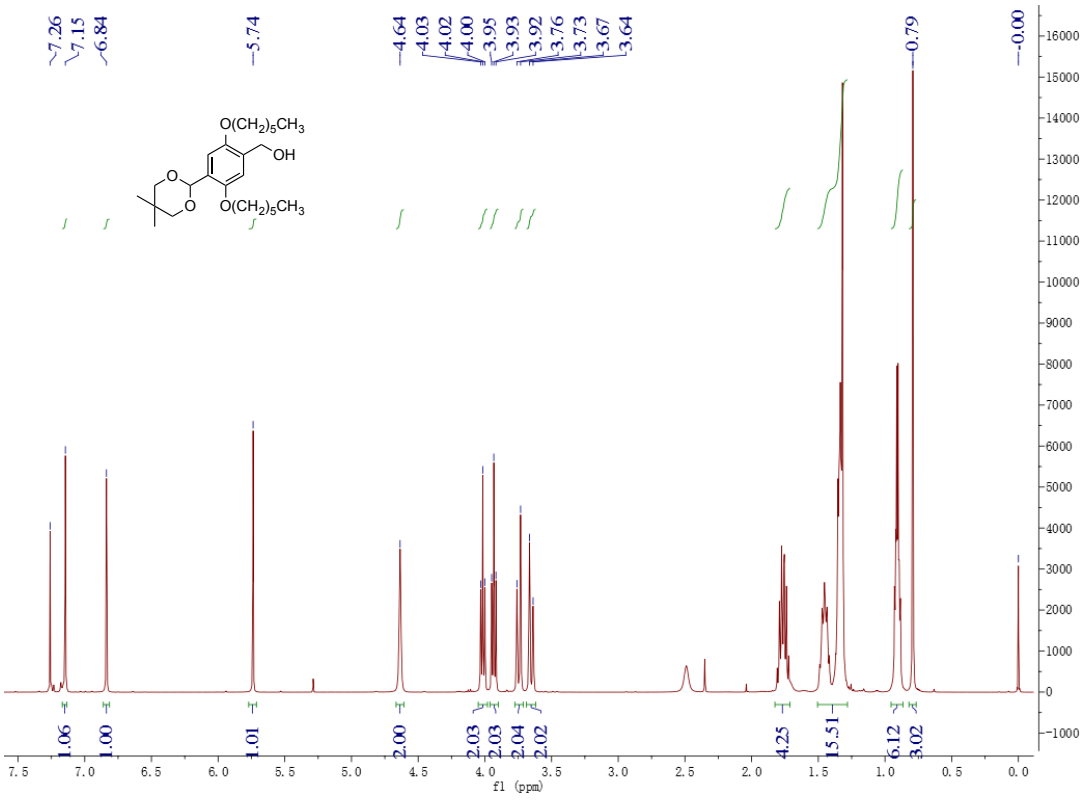


*4-(5,5-dimethyl-1,3-dioxan-2-yl)-2,5-bis(hexyloxy)benzaldehyde (**6**)*

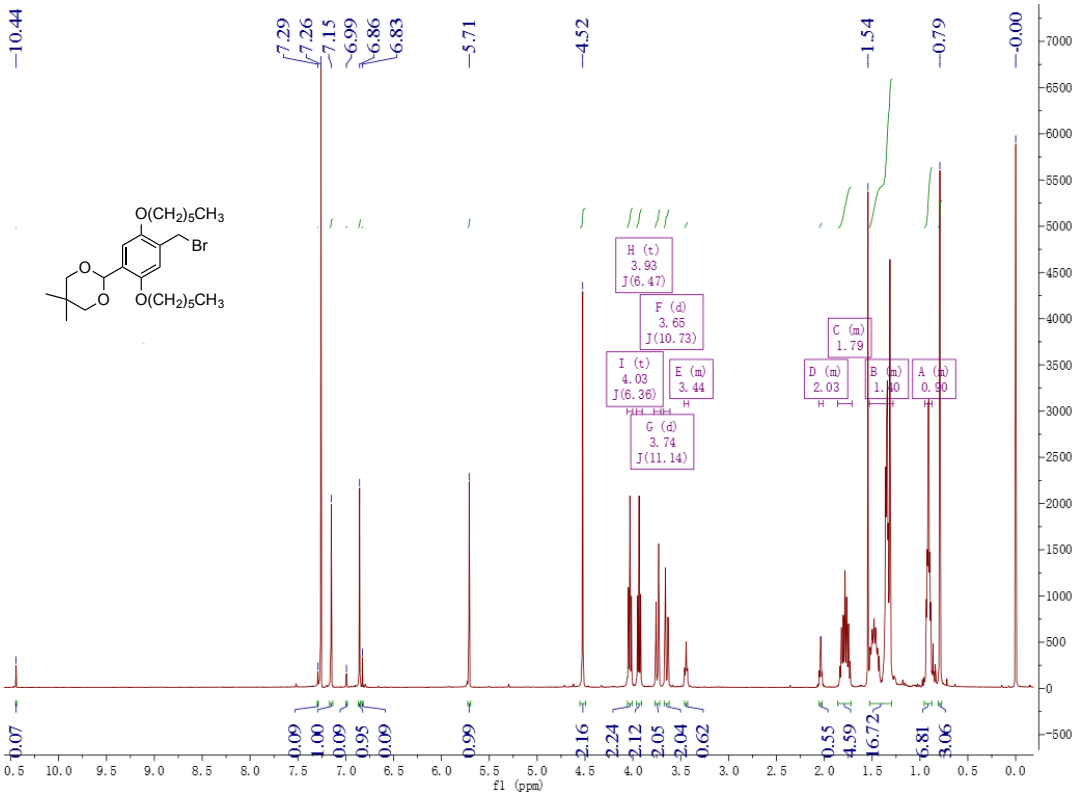




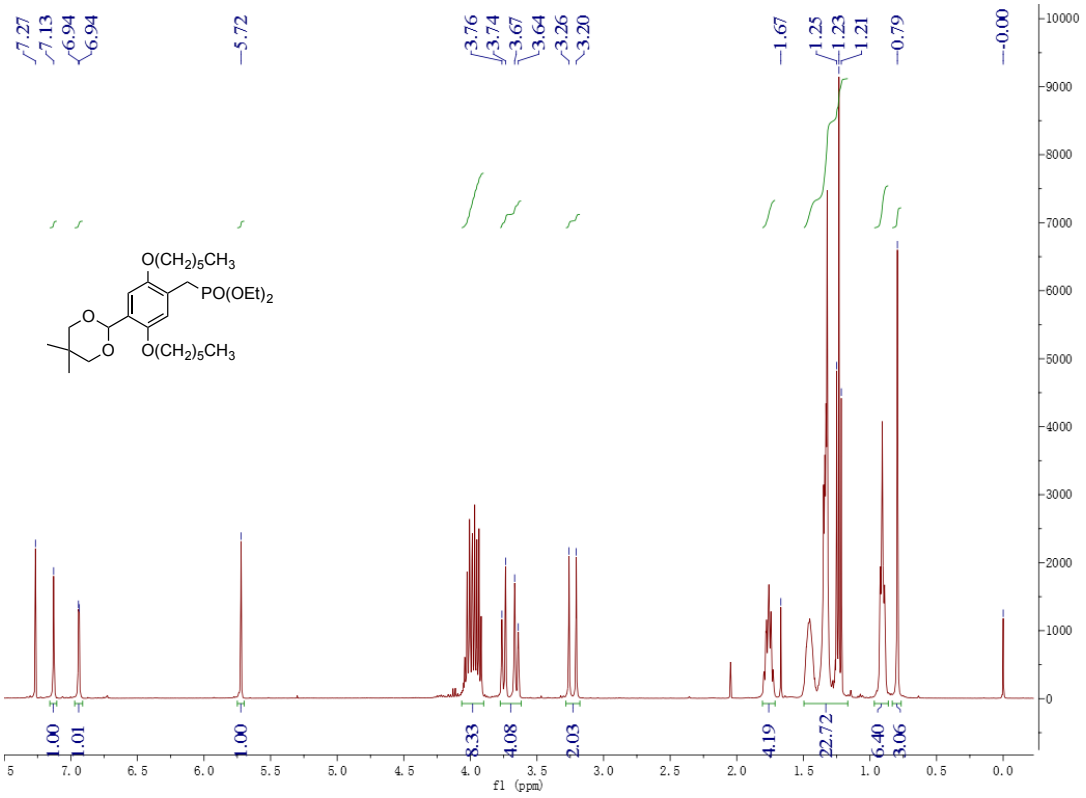
*(4-(5,5-dimethyl-1,3-dioxan-2-yl)-2,5-bis(hexyloxy)phenyl)methanol (**7**)*

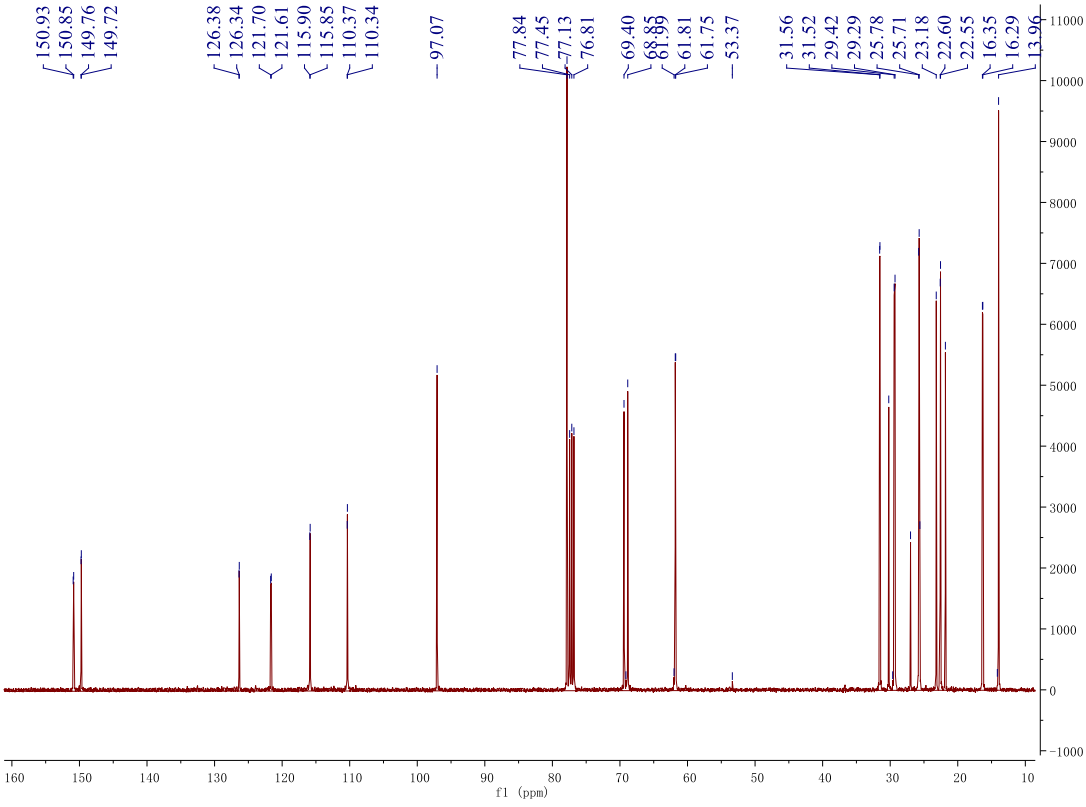


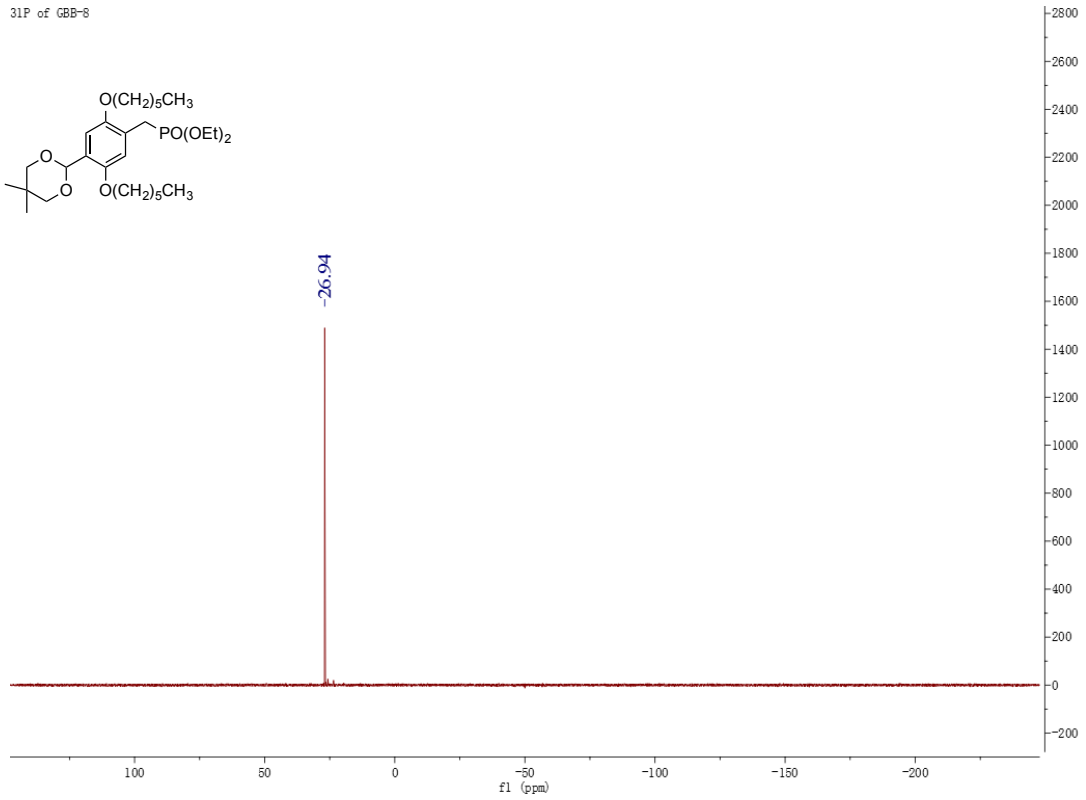
*2-(4-(bromomethyl)-2,5-bis(hexyloxy)phenyl)-5,5-dimethyl-1,3-dioxane (**8**)*



*Diethyl(4-(5,5-dimethyl-1,3-dioxan-2-yl)-2,5-bis(hexyloxy)benzyl)phosphonate (**9**)*






31P of GBB-8
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PO(OEt)2
O
O
O(CH2)5CH3
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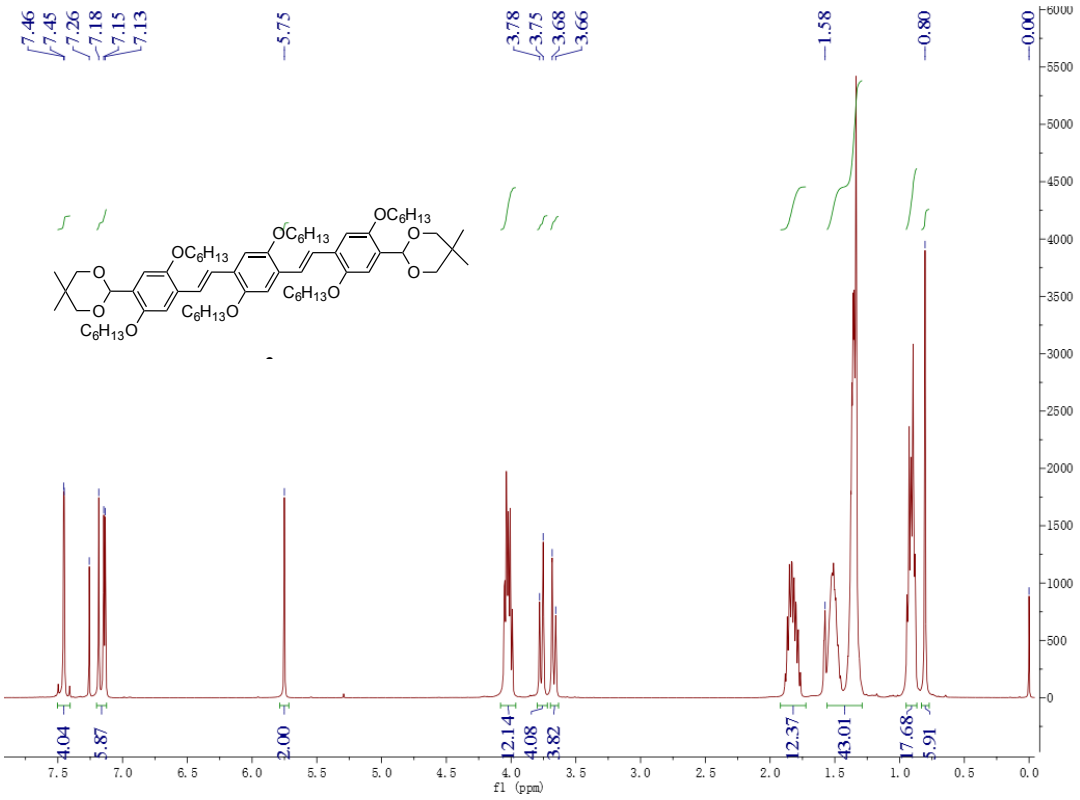
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
100
50
0
-50
-100
-150
-200
f1 (ppm)

*Compound **10***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7.18
7.15
7.13
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3.68
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0.80
0.00
OC6H13
C6H13O
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2.00
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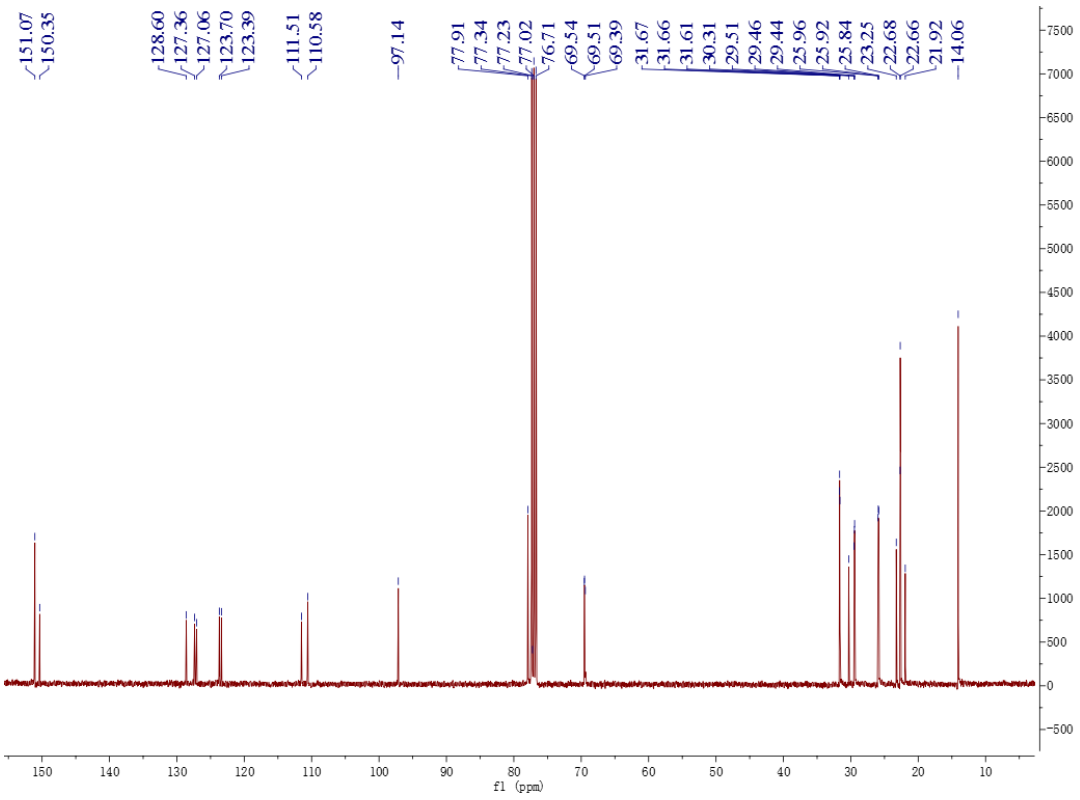
4.08
3.82
12.37
43.01
17.68
5.91
f1 (ppm)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69.51
69.39
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31.66
31.61
30.31
29.51
29.46
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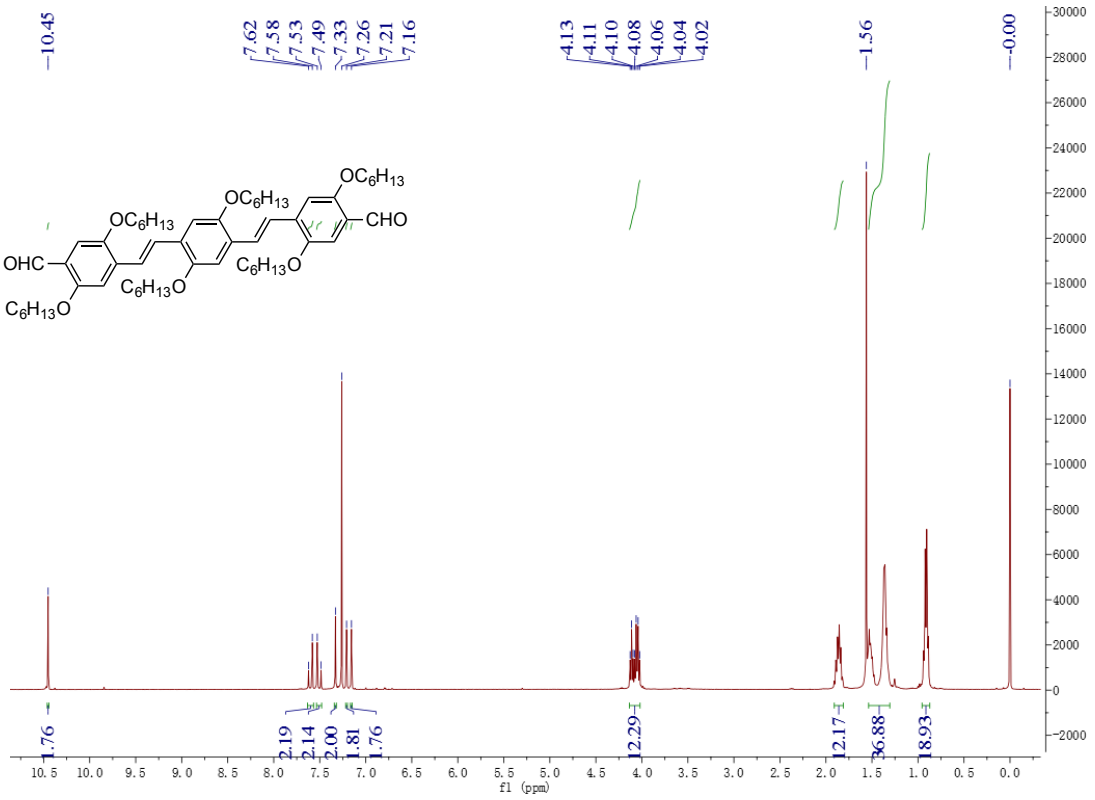
23.25
22.68
22.66
21.92
14.06
f1 (ppm)

*Compound **11***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4.11
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4.08
4.06
4.04
4.02
1.56
0.00
OC6H13
OC6H13
OC6H13
CHO
OHC
C6H13O
C6H13O
C6H13O
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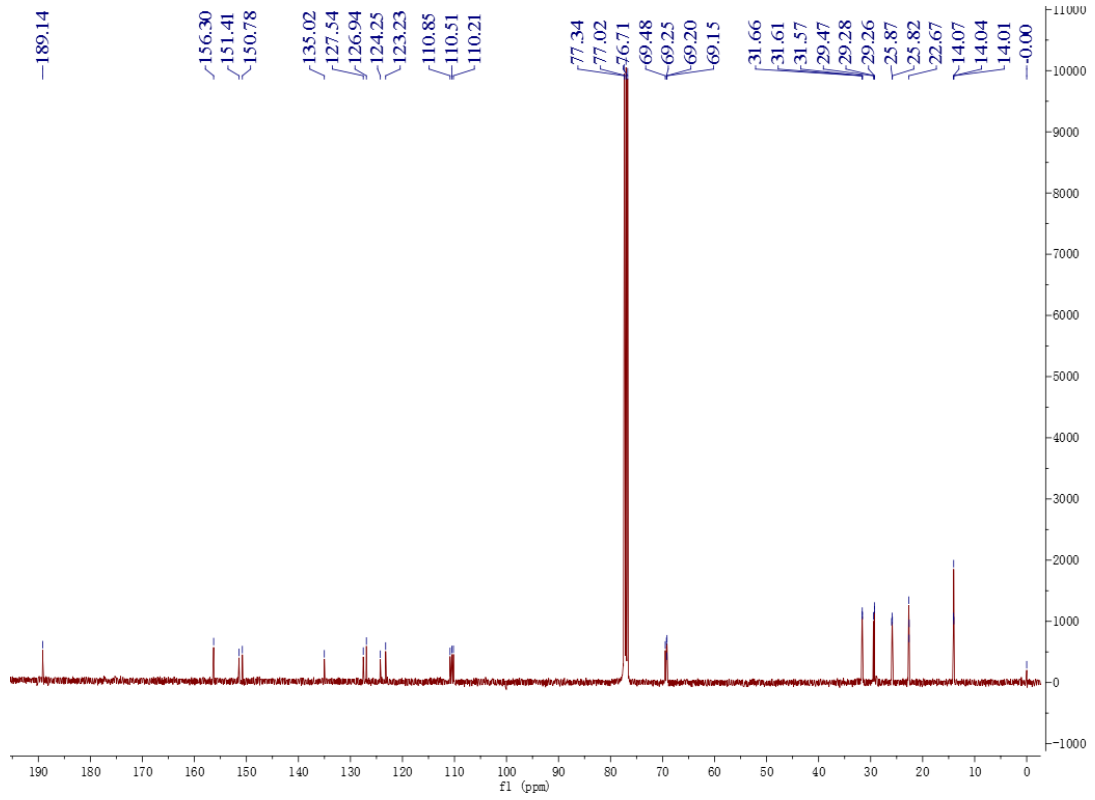
12.17
36.88
18.93
f1 (ppm)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77.02
76.71
69.48
69.25
69.20
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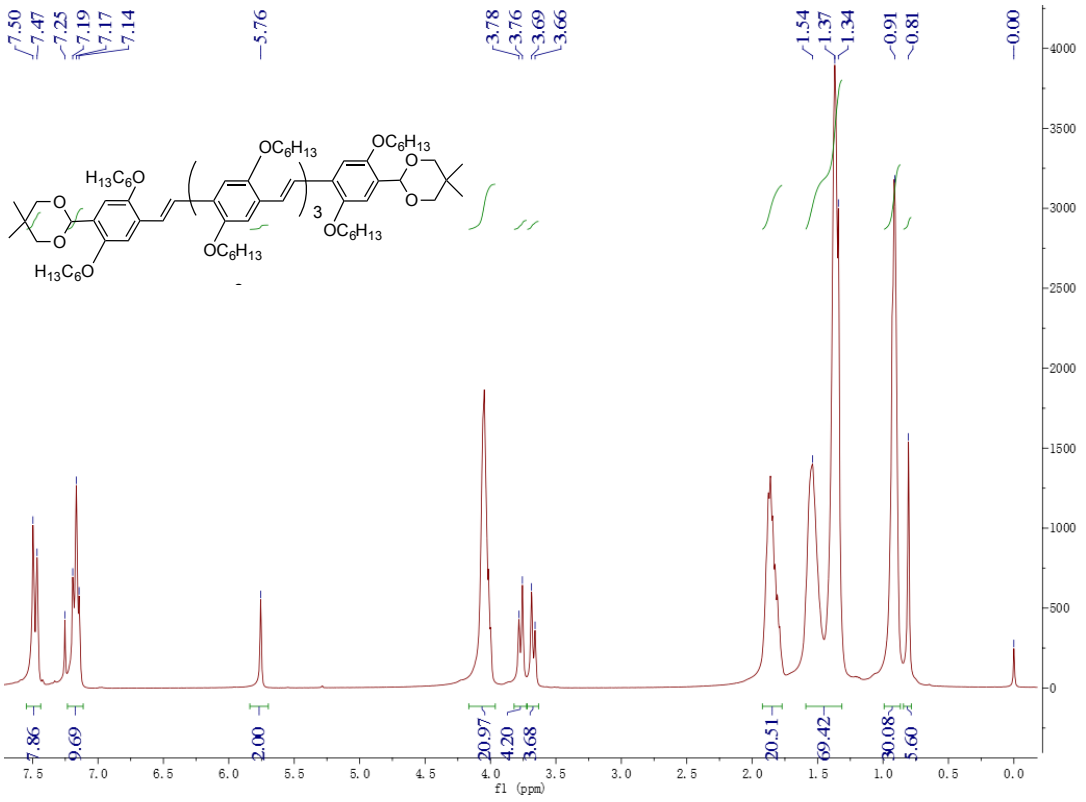
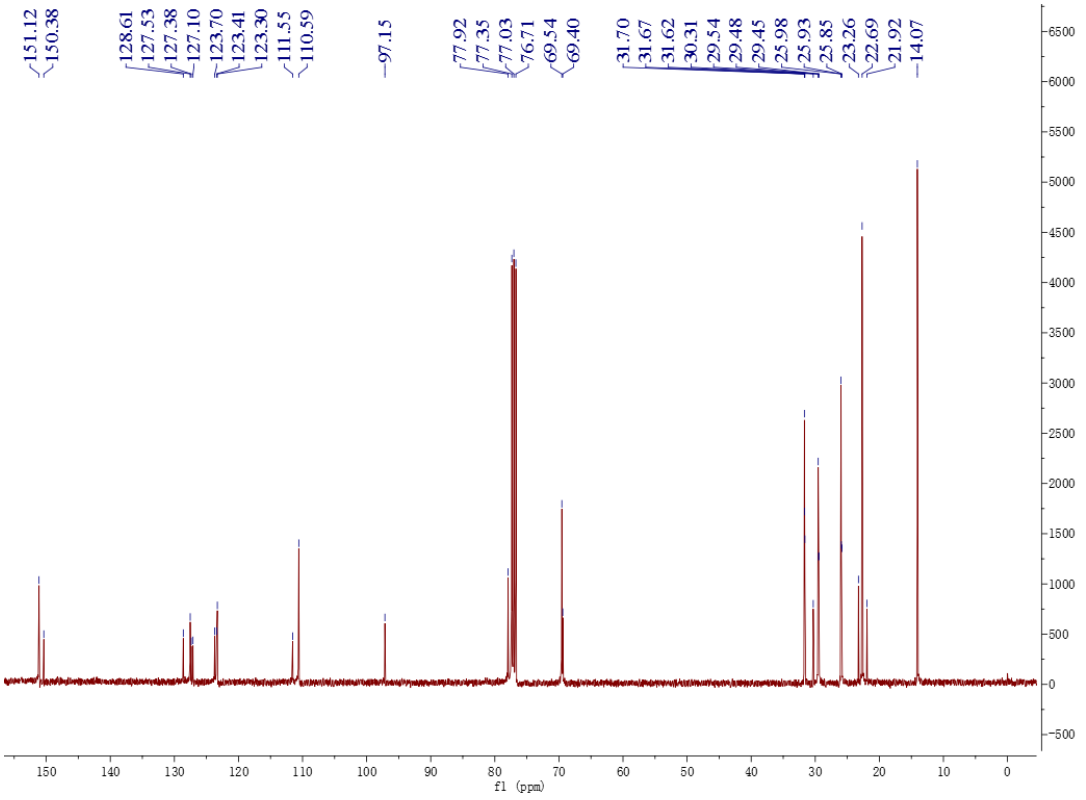
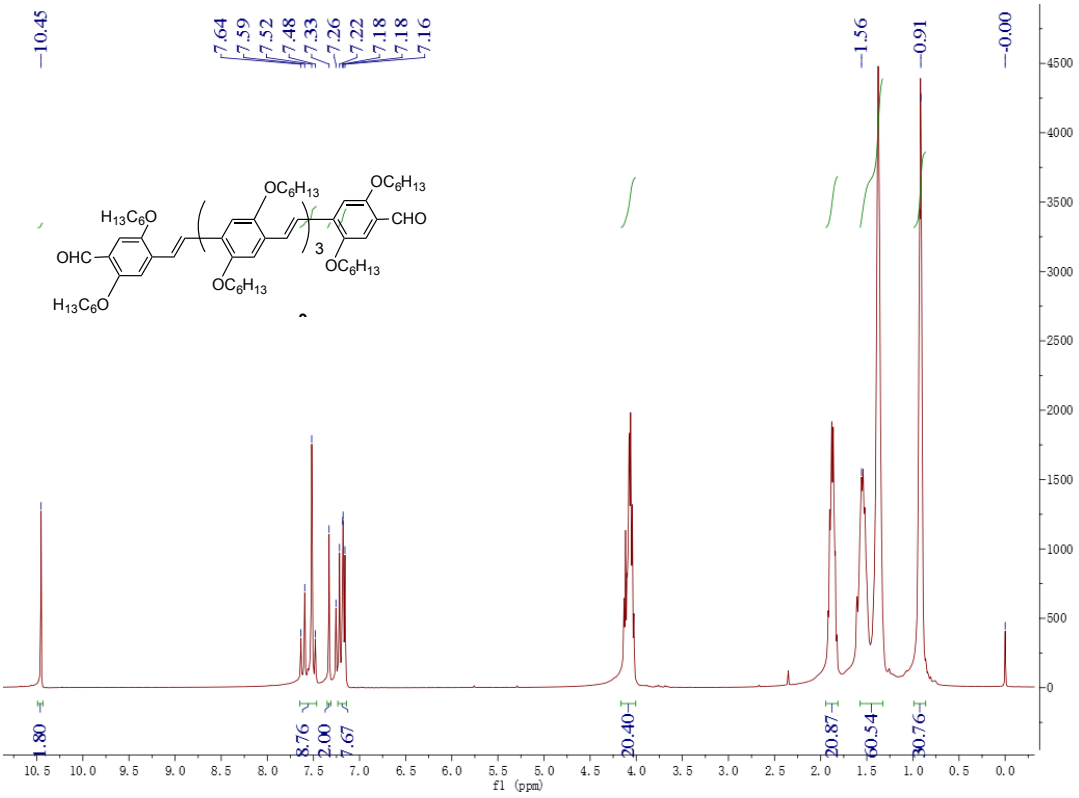
31.66
31.61
31.57
29.47
29.28
29.26
25.87
25.82
22.67
14.07
14.04
14.01
0.00
f1 (ppm)

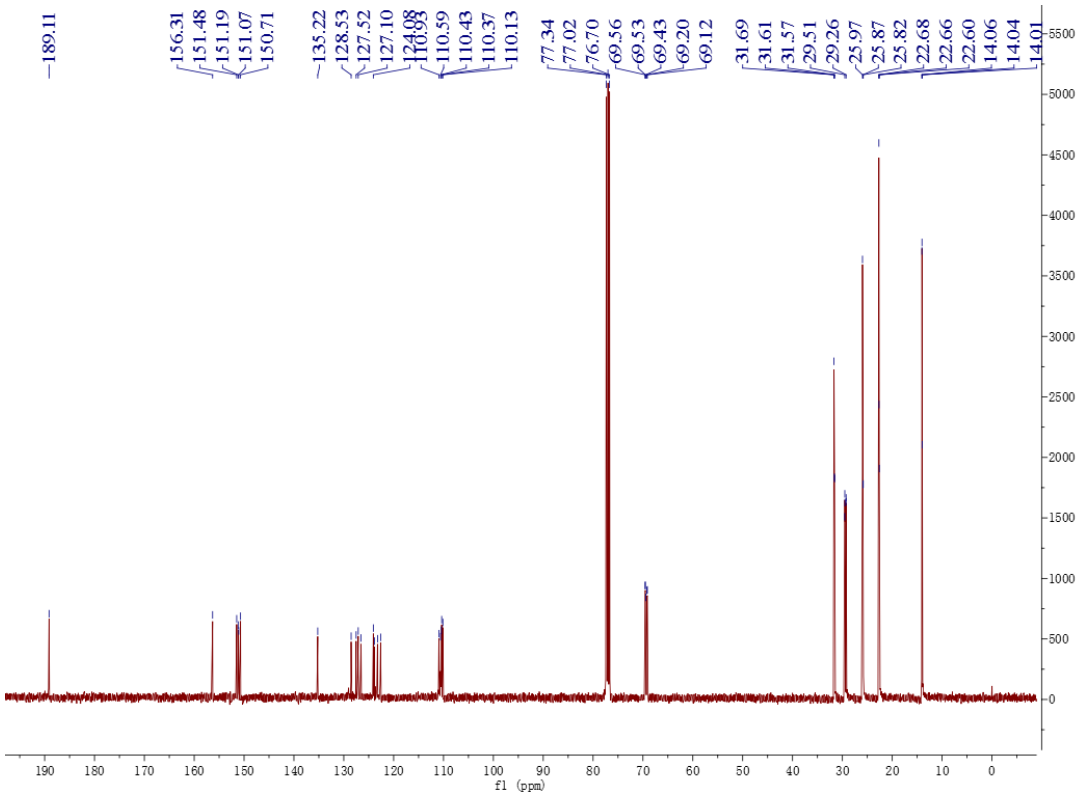
*Compound **12***


7.50
7.47
7.25
7.19
7.17
7.14
5.76
3.78
3.76
3.69
3.66
1.54
1.37
1.34
0.91
0.81
0.00
7.86
9.69
2.00
20.97
4.20
3.68
20.51
69.42
30.08
5.60
f1 (ppm)

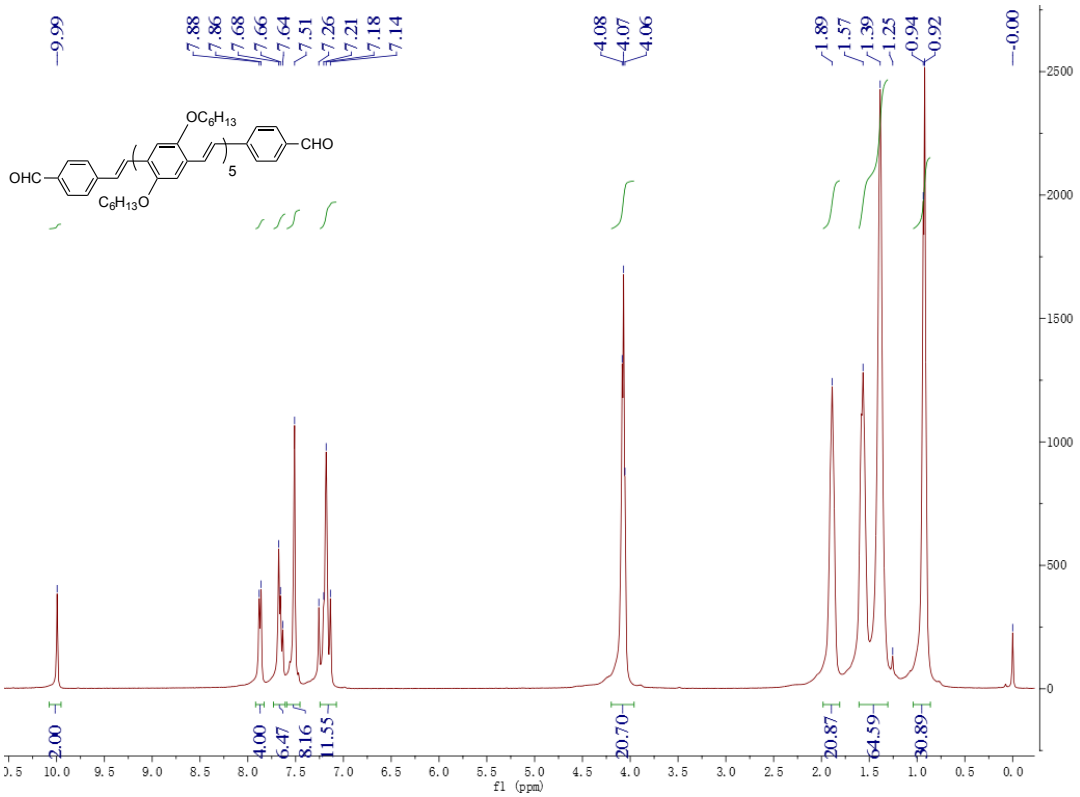

151.12
150.38
128.61
127.53
127.38
127.10
123.70
123.41
123.30
111.55
110.59
97.15
77.92
77.35
77.03
76.71
69.54
69.40
31.70
31.67
31.62
30.31
29.54
29.48
29.45
25.98
25.93
25.85
23.26
22.69
21.92
14.07
f1 (ppm)

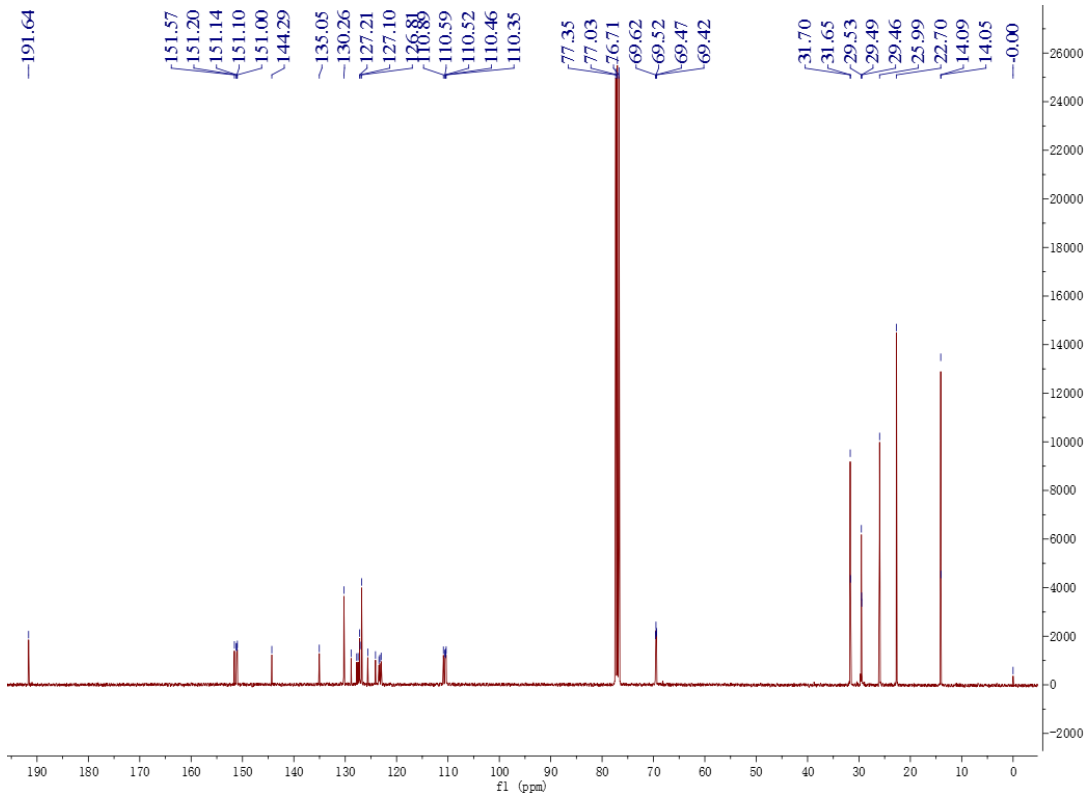
*Compound **13***


10.45
7.64
7.59
7.52
7.48
7.33
7.26
7.22
7.18
7.18
7.16
1.56
0.91
0.00
OC6H13
OC6H13
H13C6O
CHO
OHC
3
OC6H13
OC6H13
H13C6O
1.80
8.76
2.00
7.67
20.40
20.87
60.54
30.76
f1 (ppm)

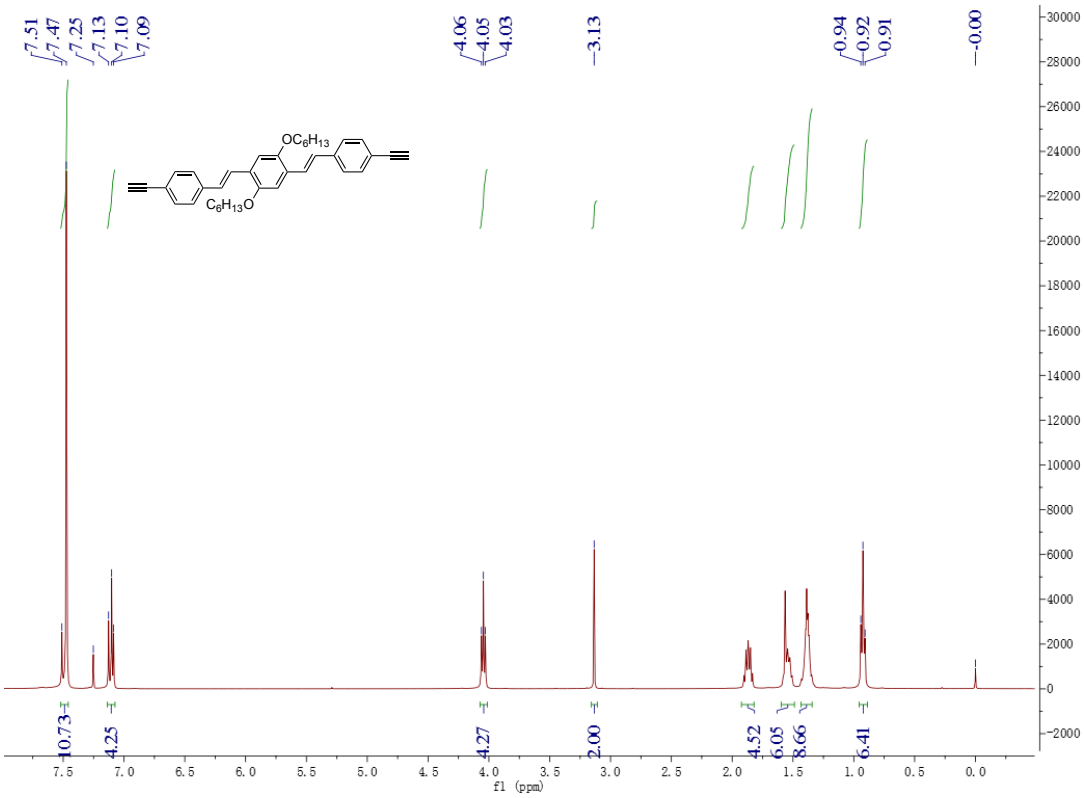

189.11
156.31
151.48
151.19
151.07
150.71
135.22
128.53
127.52
127.10
124.08
110.93
110.59
110.43
110.37
110.13
77.34
77.02
76.70
69.56
69.53
69.43
69.20
69.12
31.69
31.61
31.57
29.51
29.26
25.97
25.87
25.82
22.68
22.66
22.60
14.06
14.04
14.01
f1 (ppm)

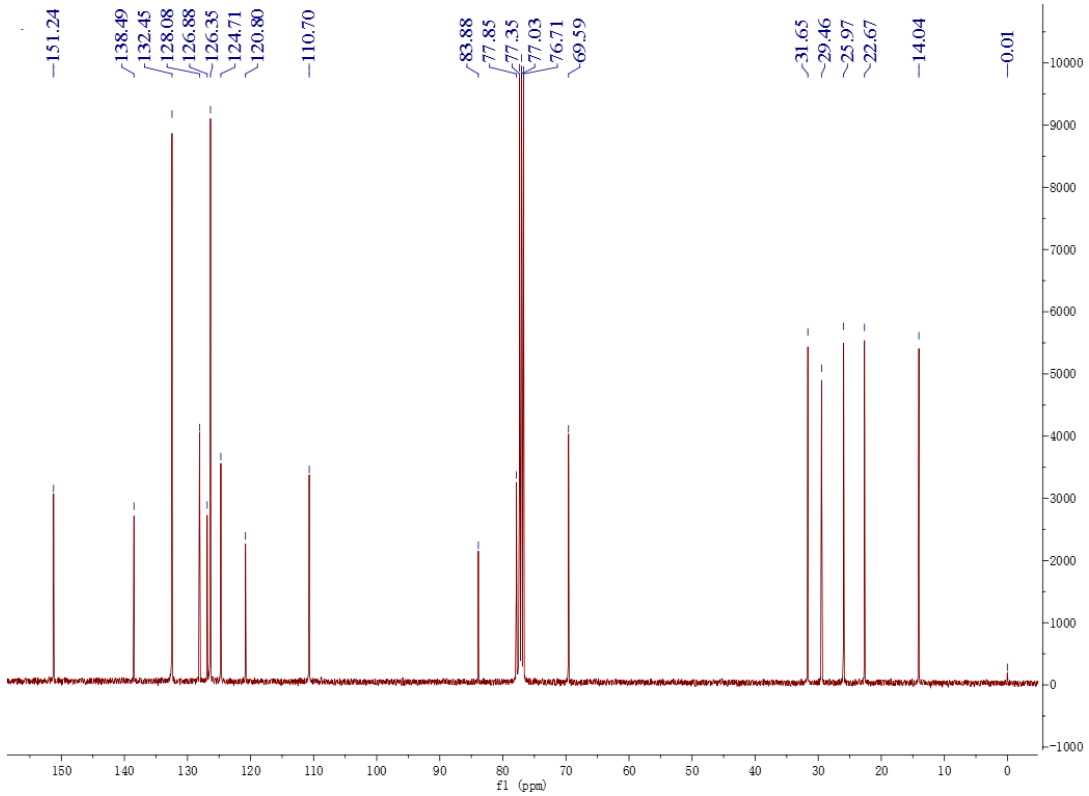
*Compound **14***


9.99
7.88
7.86
7.68
7.66
7.64
7.51
7.26
7.21
7.18
7.14
4.08
4.07
4.06
1.89
1.57
1.39
1.25
0.94
0.92
0.00
OC6H13
CHO
OHC
C6H13O
5
2.00
4.00
6.47
8.16
11.55
20.70
20.87
64.59
30.89
f1 (ppm)

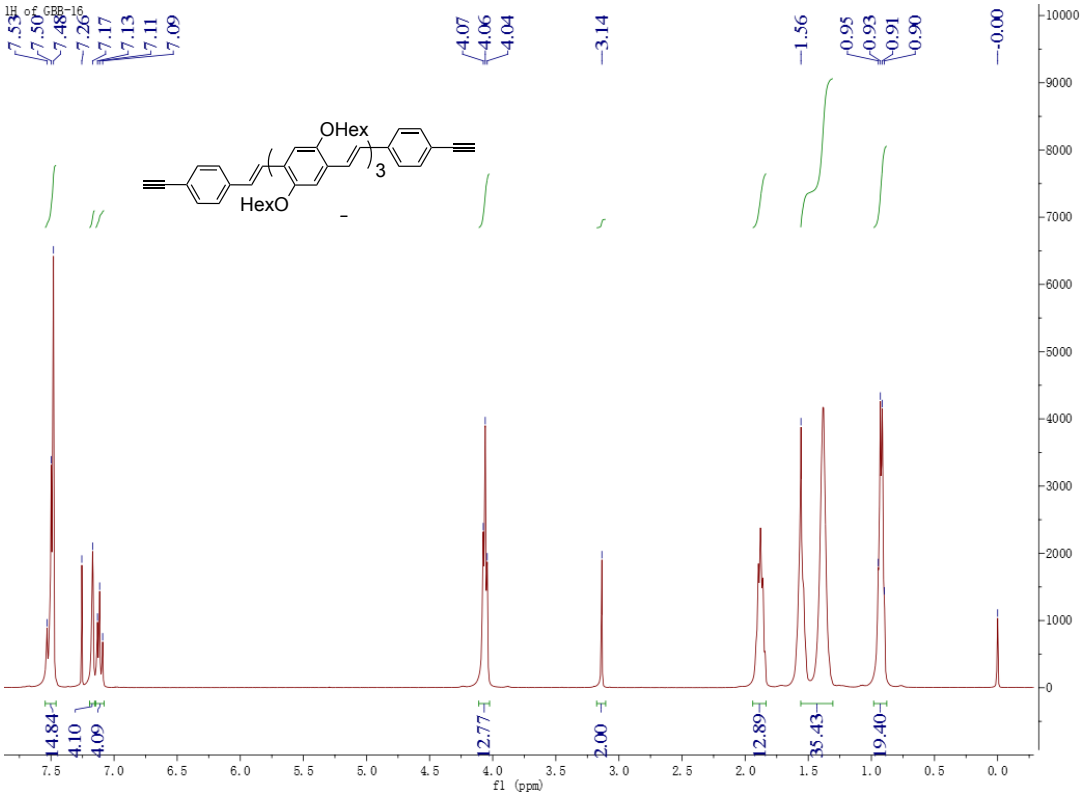

191.64
151.57
151.20
151.14
151.10
151.00
144.29
135.05
130.26
127.21
127.10
110.59
110.52
110.46
110.35
77.35
77.03
76.71
69.62
69.52
69.47
69.42
31.70
31.65
29.53
29.49
29.46
25.99
22.70
14.09
14.05
0.00
f1 (ppm)

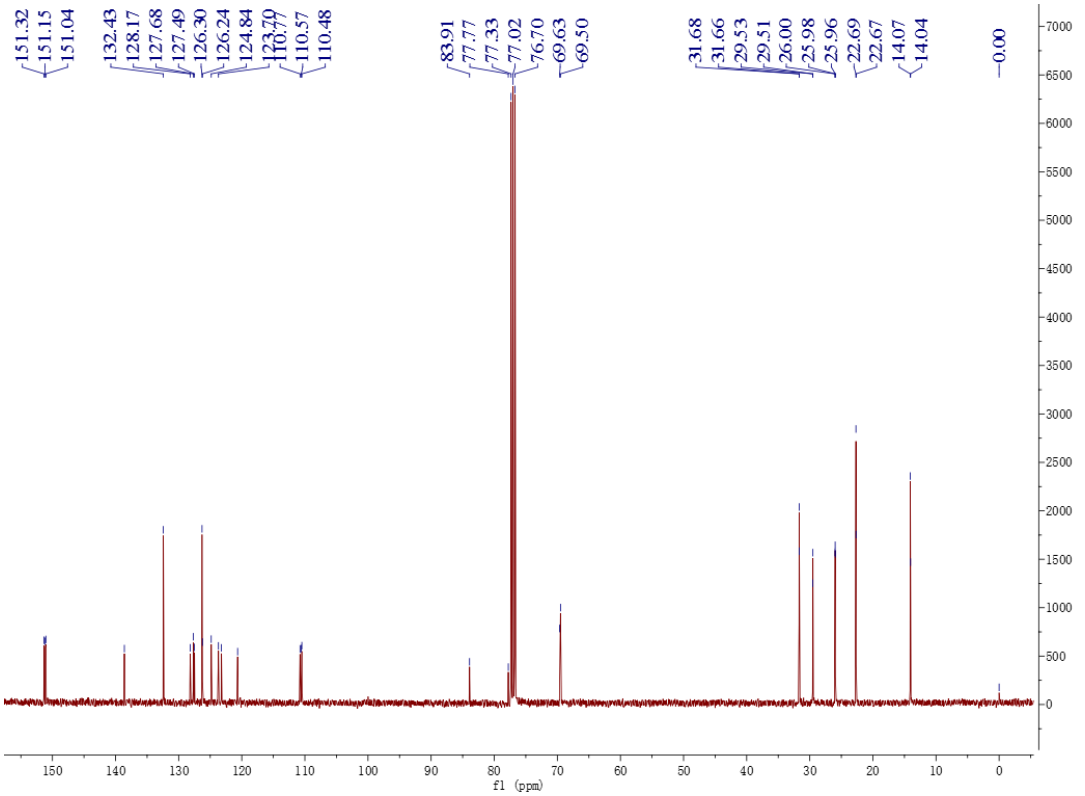
*Compound **15***


7.51
7.47
7.25
7.13
7.10
7.09
4.06
4.05
4.03
3.13
0.94
0.92
0.91
-0.00
OC6H13
C6H13O
10.73
4.25
4.27
2.00
4.52
6.05
8.66
6.41
f1 (ppm)

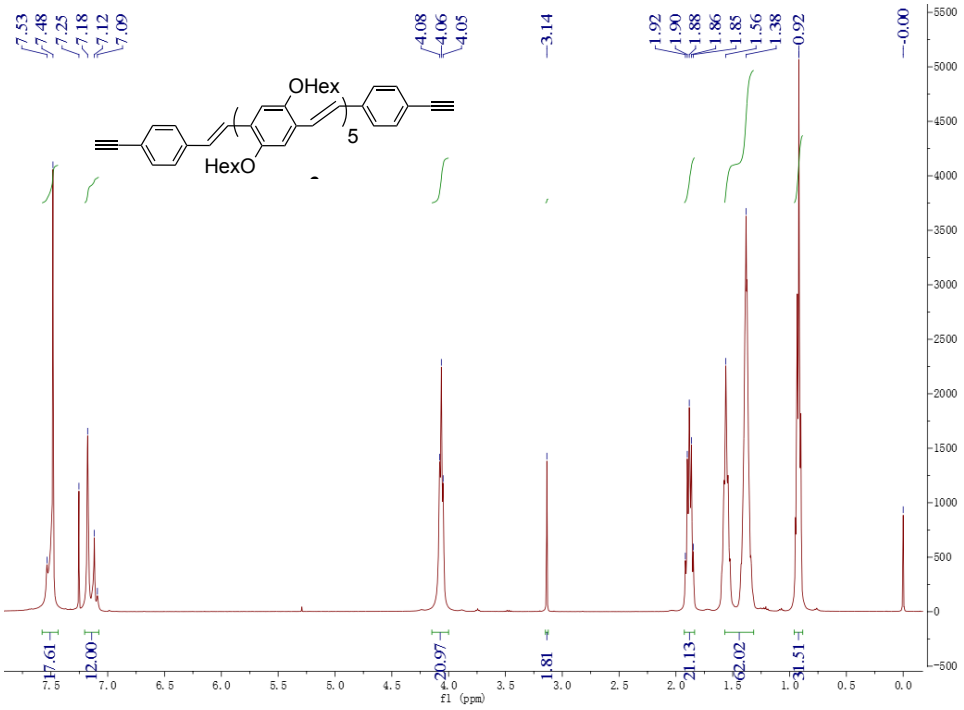

151.24
138.49
132.45
128.08
126.88
126.35
124.71
120.80
110.70
83.88
77.85
77.35
77.03
76.71
69.59
31.65
29.46
25.97
22.67
14.04
-0.01
f1 (ppm)

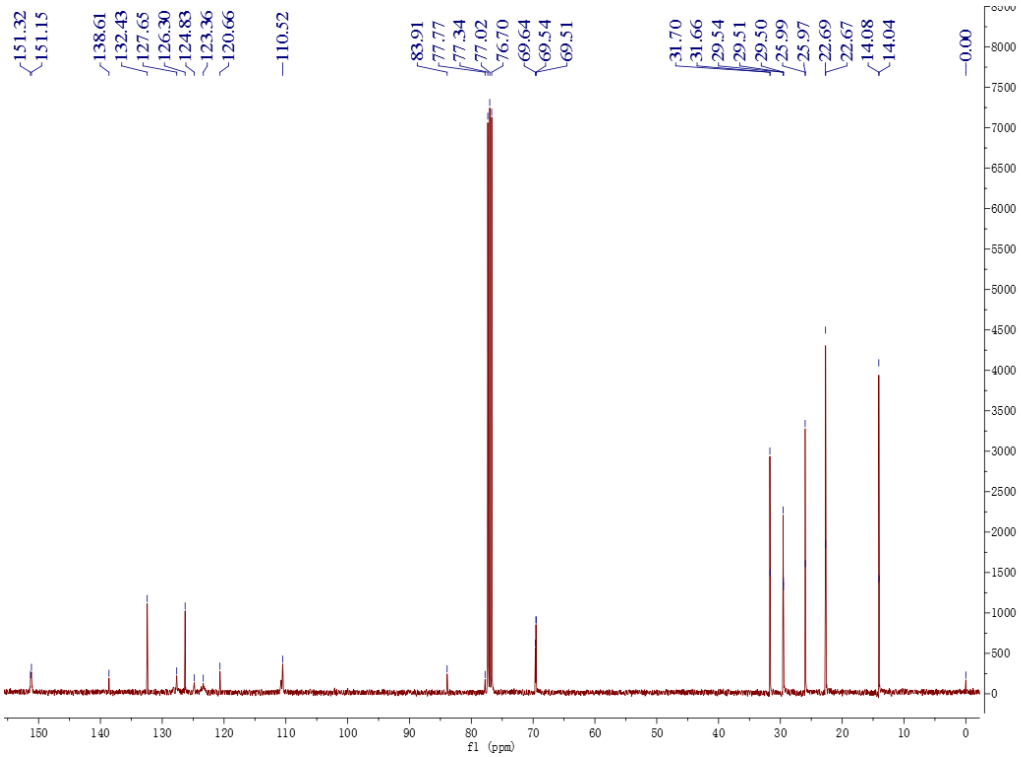
*Compound **16***


1H of GBB-16
7.53
7.50
7.48
7.26
7.17
7.13
7.11
7.09
4.07
4.06
4.04
3.14
1.56
0.95
0.93
0.91
0.90
0.00
OHex
3
HexO
14.84
4.10
4.09
12.77
2.00
12.89
35.43
19.40
f1 (ppm)

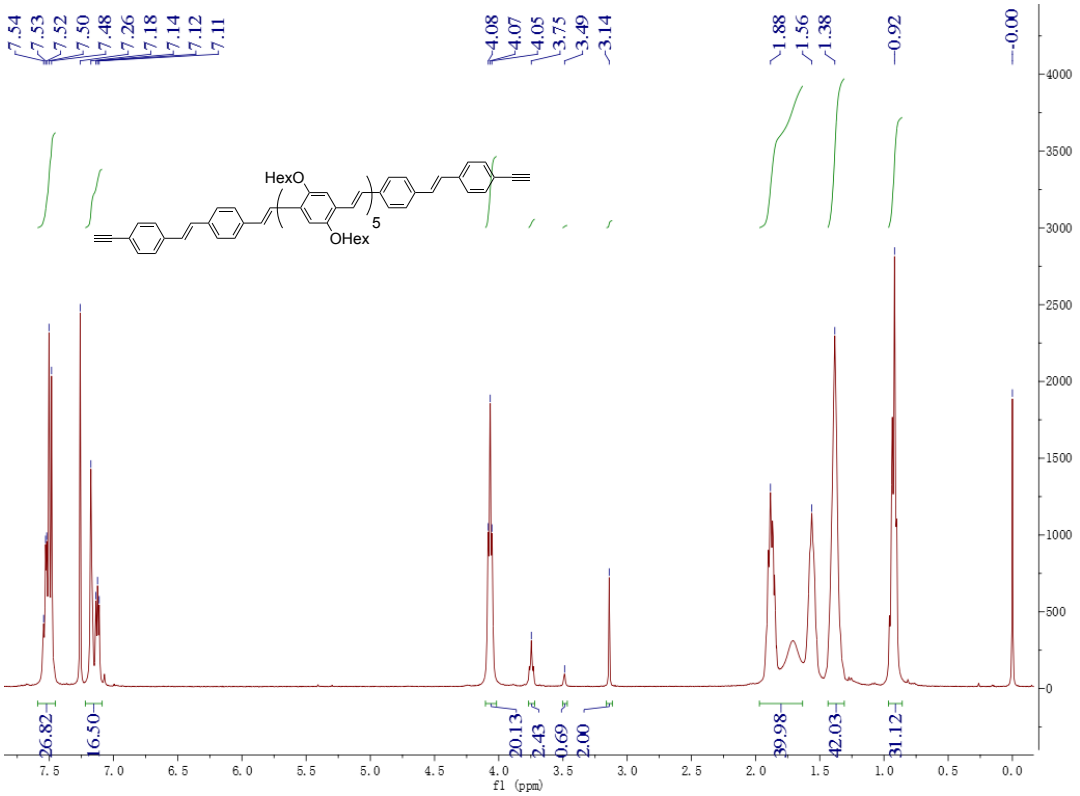

151.32
151.15
151.04
132.43
128.17
127.68
127.49
126.30
126.24
124.84
123.70
110.77
110.57
110.48
83.91
77.77
77.33
77.02
76.70
69.63
69.50
31.68
31.66
29.53
29.51
26.00
25.98
25.96
22.69
22.67
14.07
14.04
0.00
f1 (ppm)

*Compound **17***

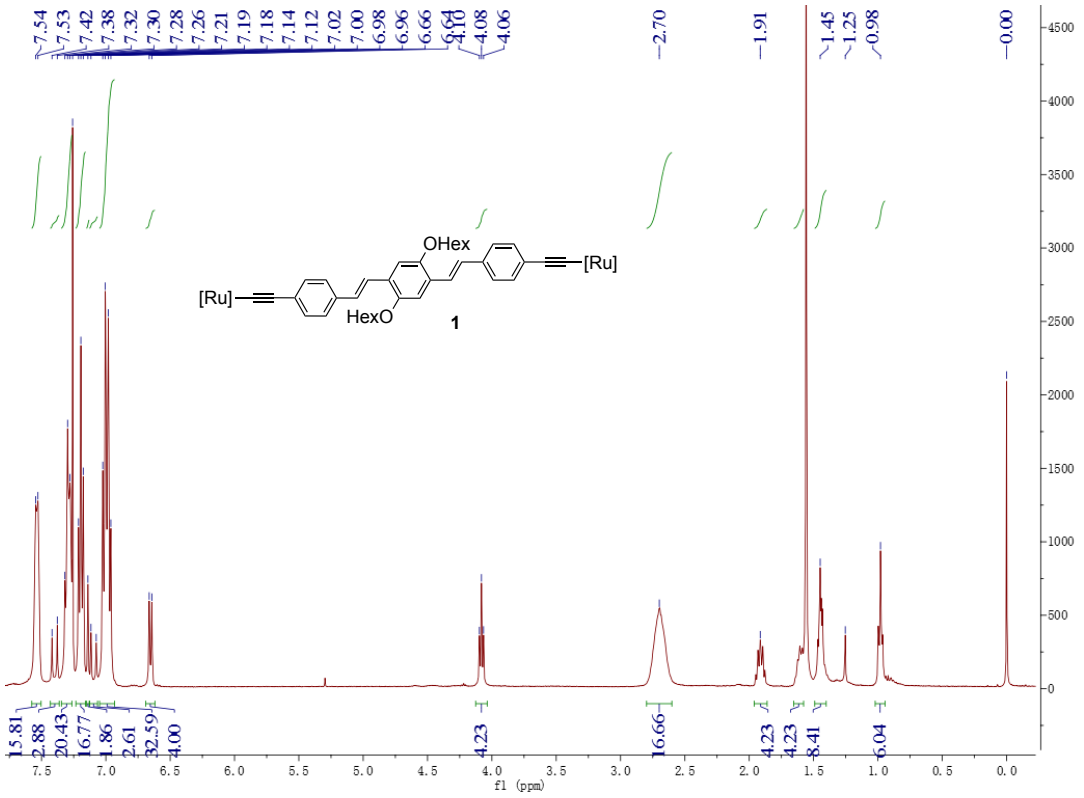

7.53
7.48
7.25
7.18
7.12
7.09
4.08
4.06
4.05
3.14
1.92
1.90
1.88
1.86
1.85
1.56
1.38
0.92
0.00
OHex
HexO
5
17.61
12.00
20.97
1.81
21.13
62.02
31.51
f1 (ppm)

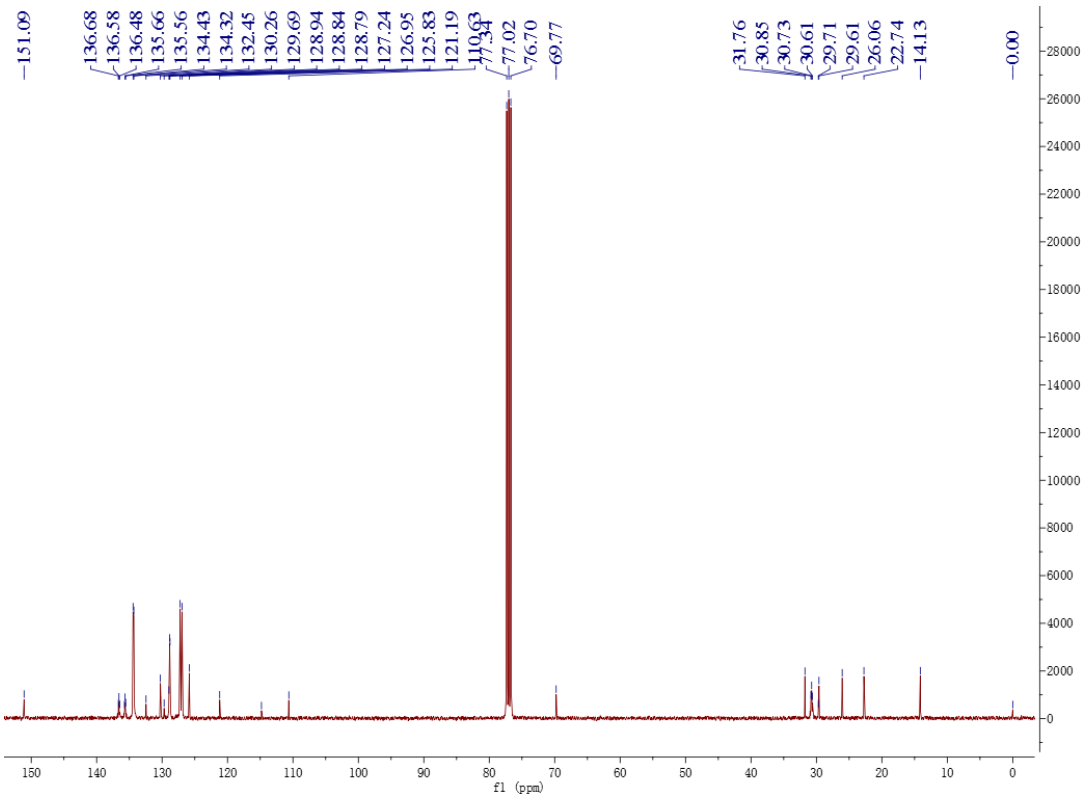

151.32
151.15
138.61
132.43
127.65
126.30
124.83
123.36
120.66
110.52
83.91
77.77
77.34
77.02
76.70
69.64
69.54
69.51
31.70
31.66
29.54
29.51
29.50
25.99
25.97
22.69
22.67
14.08
14.04
0.00
f1 (ppm)

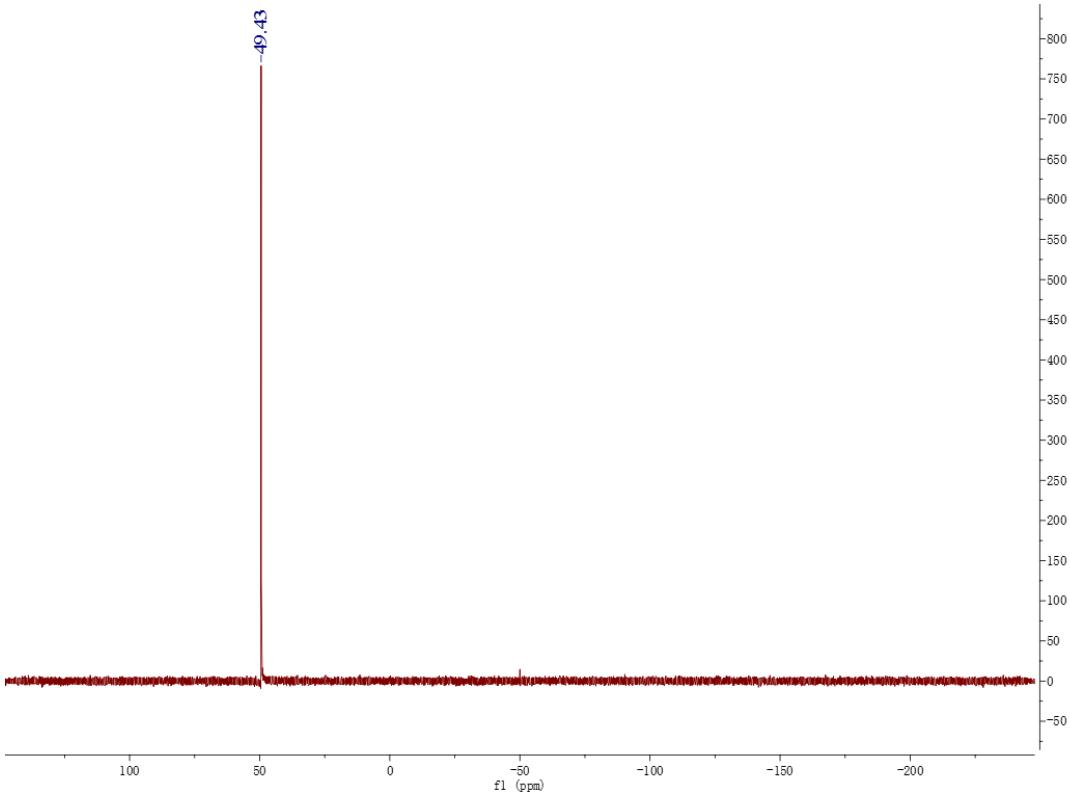
*Compound **18***


7.54
7.53
7.52
7.50
7.48
7.26
7.18
7.14
7.12
7.11
4.08
4.07
4.05
3.75
3.49
3.14
1.88
1.56
1.38
0.92
0.00
HexO
OHex
5
26.82
16.50
20.13
2.43
0.69
2.00
39.98
42.03
31.12
f1 (ppm)

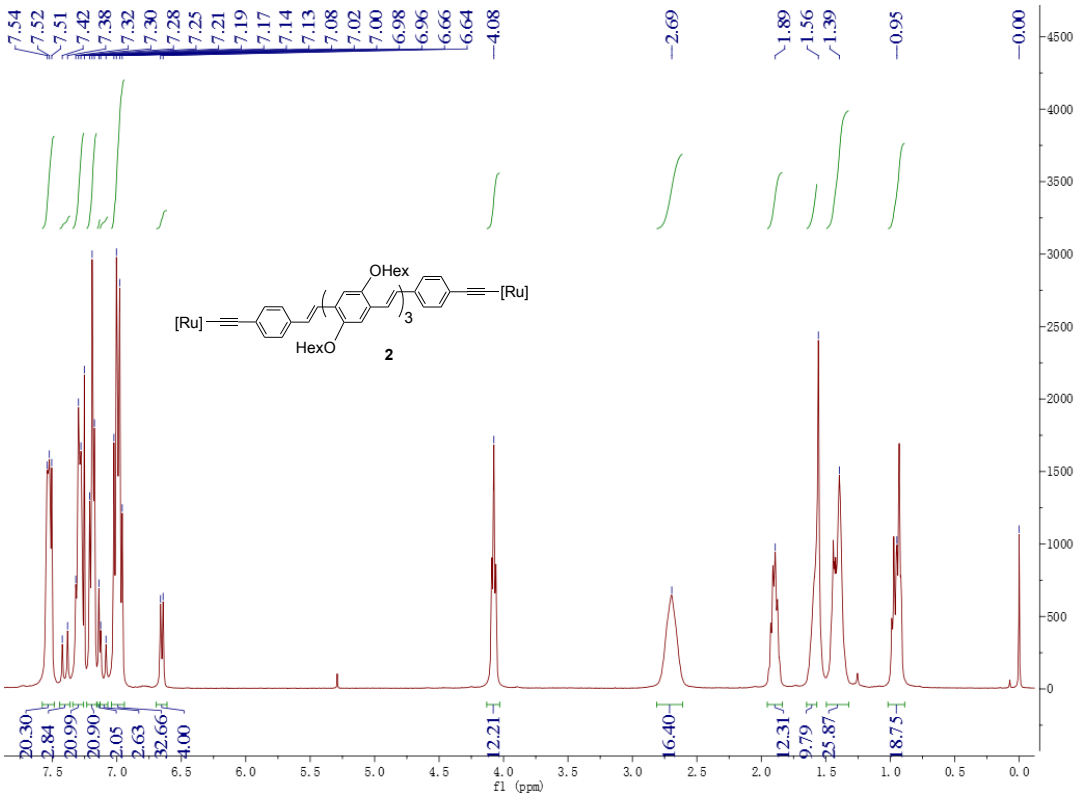
*Complex **1***

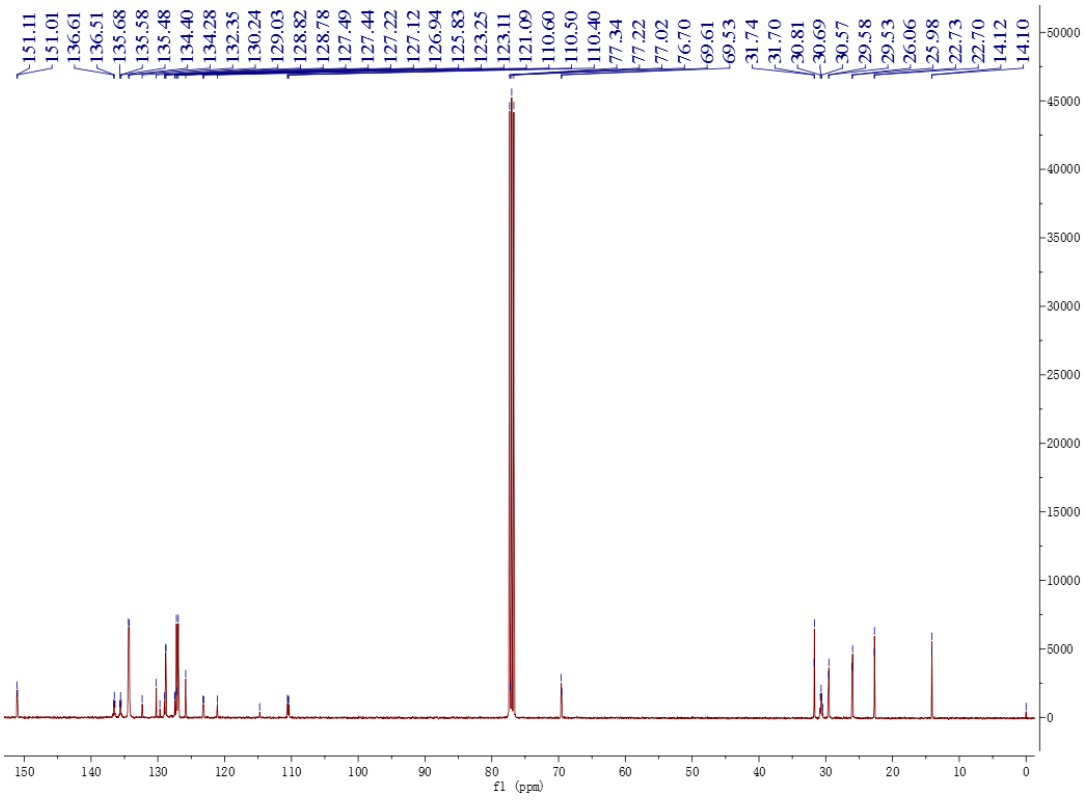

7.54
7.53
7.42
7.38
7.32
7.30
7.28
7.26
7.21
7.19
7.18
7.14
7.12
7.02
7.00
6.98
6.96
6.66
6.64
4.10
4.08
4.06
2.70
1.91
1.45
1.25
0.98
0.00
OHex
[Ru]
[Ru]
HexO
1
15.81
2.88
20.43
16.77
1.86
2.61
32.59
4.00
4.23
16.66
4.23
4.23
8.41
6.04
f1 (ppm)

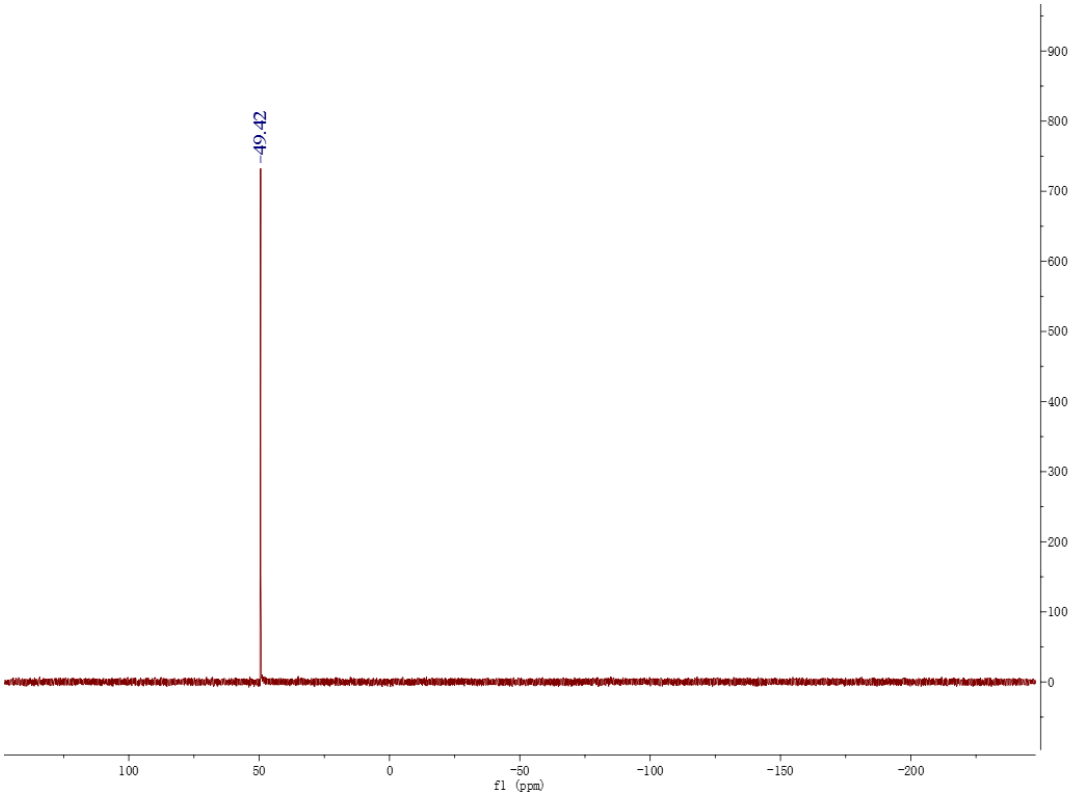

151.09
136.68
136.58
136.48
135.66
135.56
134.43
134.32
132.45
130.26
129.69
128.94
128.84
128.79
127.24
126.95
125.83
121.19
110.63
77.34
77.02
76.70
69.77
31.76
30.85
30.73
30.61
29.71
29.61
26.06
22.74
14.13
0.00
f1 (ppm)


49.43
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
100
50
0
-50
-100
-150
-200
f1 (ppm)

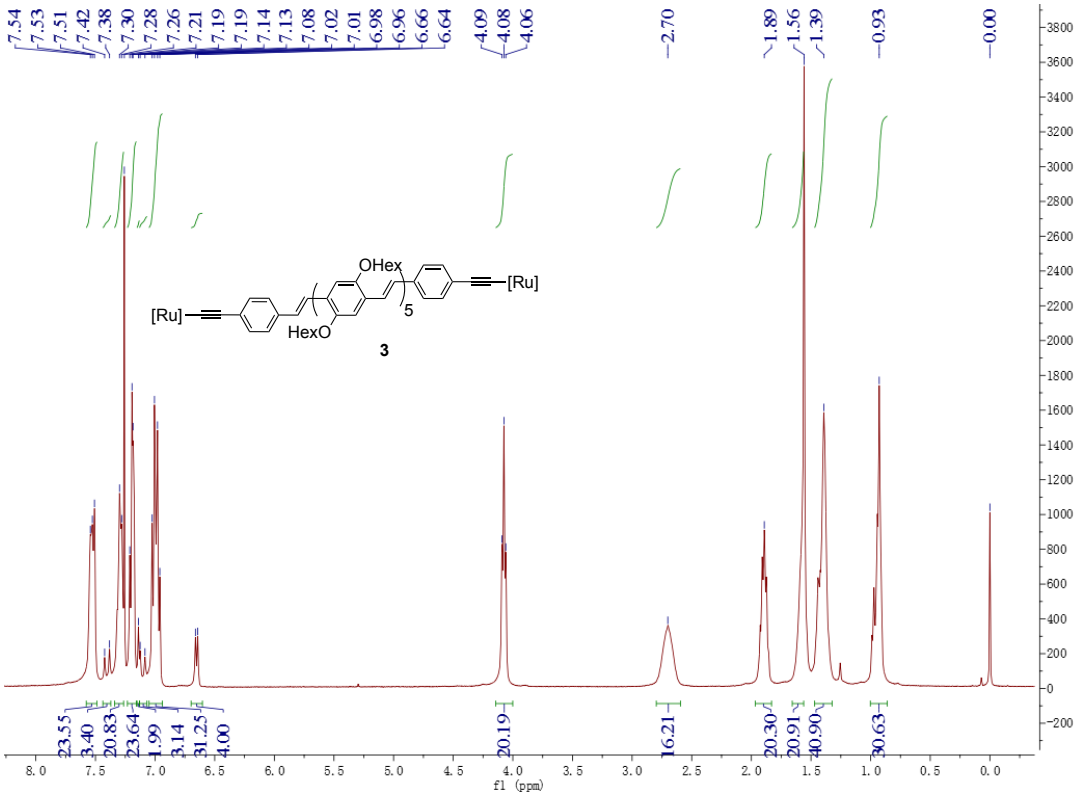
Complex ***2***

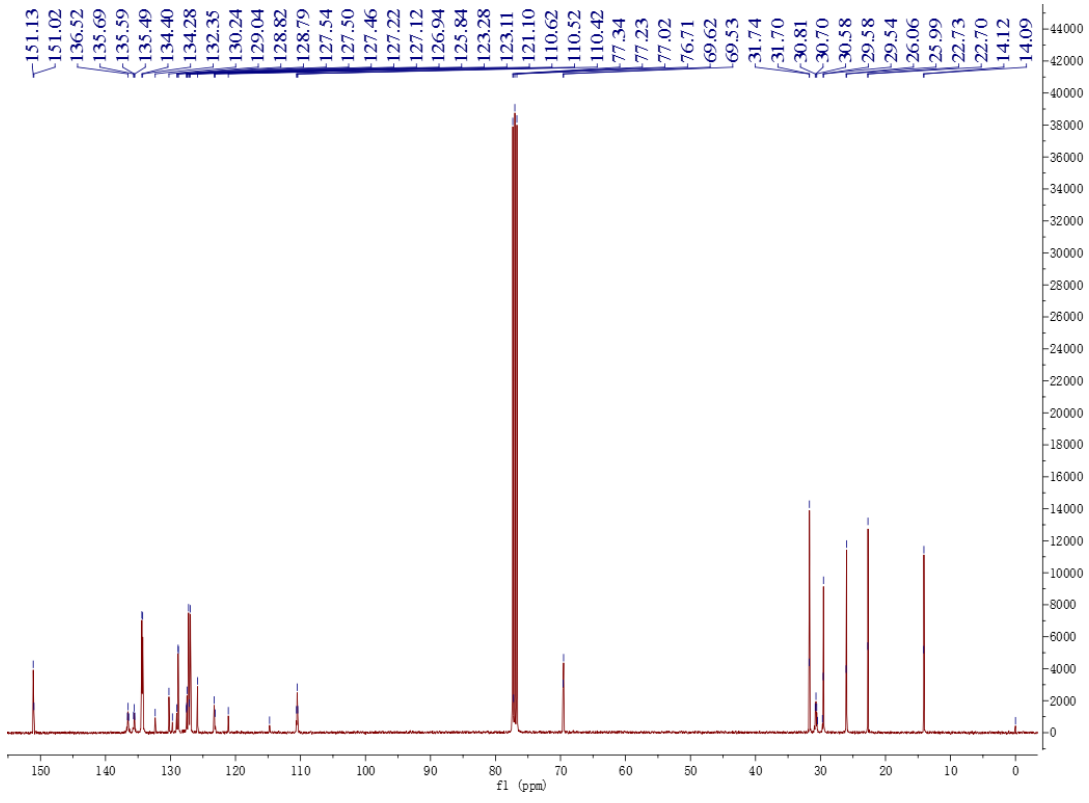

7.54
7.52
7.51
7.42
7.38
7.32
7.30
7.28
7.25
7.21
7.19
7.17
7.14
7.13
7.08
7.02
7.00
6.98
6.96
6.66
6.64
4.08
2.69
1.89
1.56
1.39
0.95
0.00
OHex
[Ru]
[Ru]
3
HexO
2
20.30
2.84
20.99
20.90
2.05
2.63
32.66
4.00
12.21
16.40
12.31
9.79
25.87
18.75
f1 (ppm)

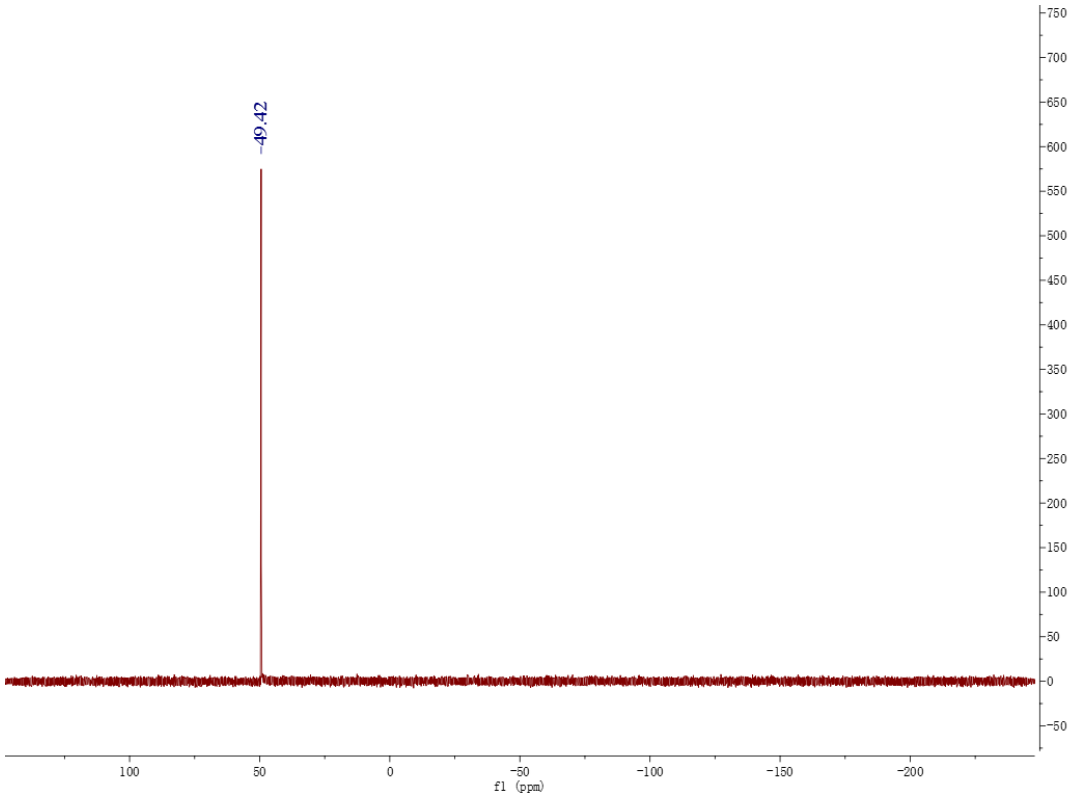

151.11
151.01
136.61
136.51
135.68
135.58
135.48
134.40
134.28
132.35
130.24
129.03
128.82
128.78
127.49
127.44
127.22
127.12
126.94
125.83
123.25
123.11
121.09
110.60
110.50
110.40
77.34
77.22
77.02
76.70
69.61
69.53
31.74
31.70
30.81
30.69
30.57
29.58
29.53
26.06
25.98
22.73
22.70
14.12
14.10
f1 (ppm)


-49.42
900
800
700
600
500
400
300
200
100
0
100
50
0
-50
-100
-150
-200
f1 (ppm)

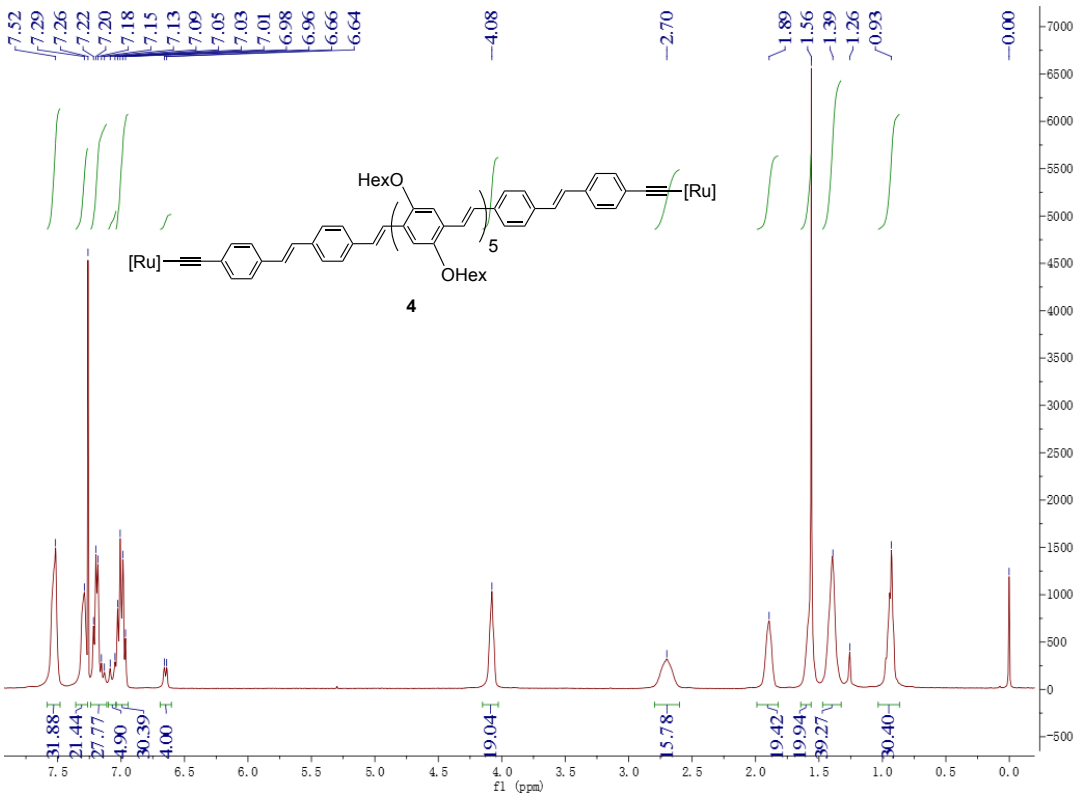
*Complex **3***

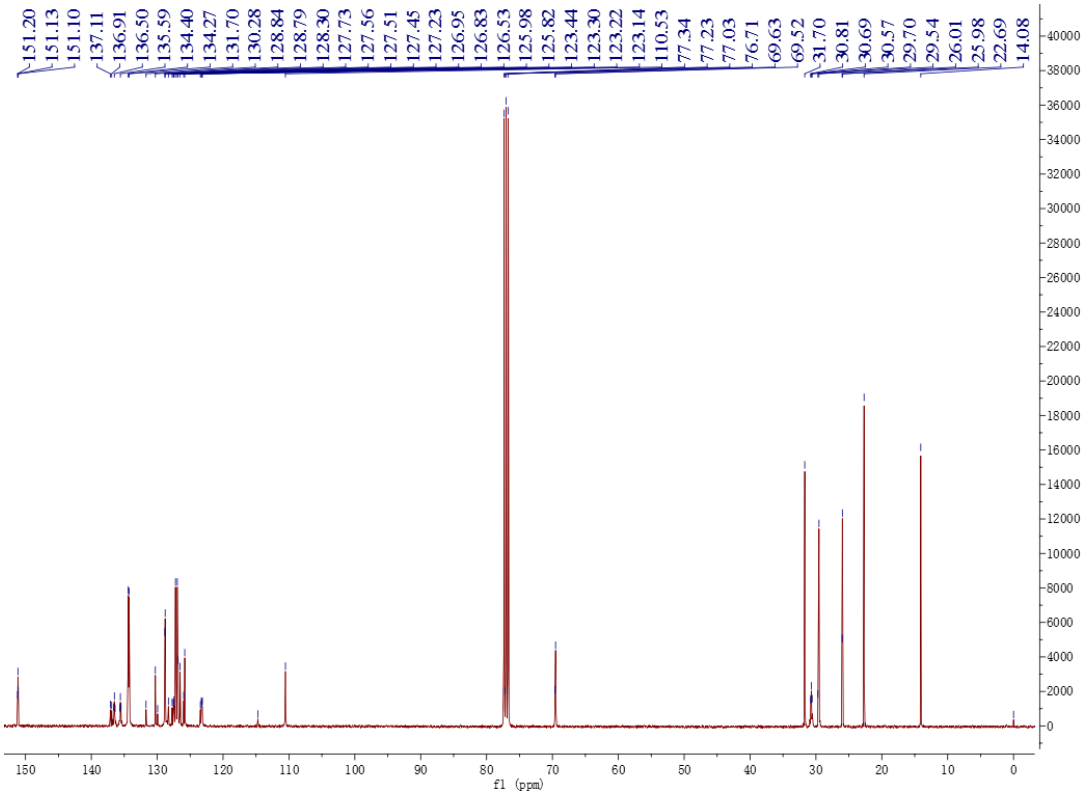

7.54
7.53
7.51
7.42
7.38
7.30
7.28
7.26
7.21
7.19
7.19
7.14
7.13
7.08
7.02
7.01
6.98
6.96
6.66
6.64
4.09
4.08
4.06
2.70
1.89
1.56
1.39
0.93
0.00
OHex
[Ru]
5
[Ru]
HexO
3
23.55
3.40
20.83
23.64
1.99
3.14
31.25
4.00
20.19
16.21
20.30
20.91
40.90
30.63
f1 (ppm)

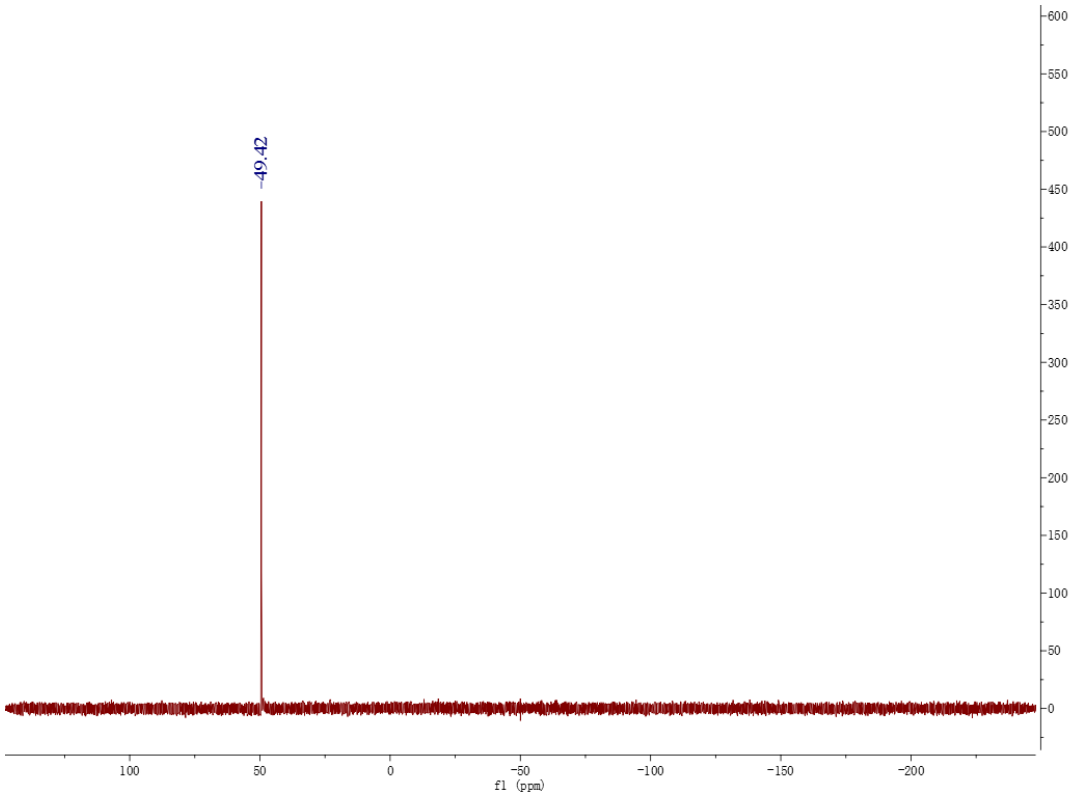

151.13
151.02
136.52
135.69
135.59
135.49
134.40
134.28
132.35
130.24
129.04
128.82
128.79
127.54
127.50
127.46
127.22
127.12
126.94
125.84
123.28
123.11
121.10
110.62
110.52
110.42
77.34
77.23
77.02
76.71
69.62
69.53
31.74
31.70
30.81
30.70
30.58
29.58
29.54
26.06
25.99
22.73
22.70
14.12
14.09
f1 (ppm)


49.42
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
100
50
0
-50
-100
-150
-200
f1 (ppm)

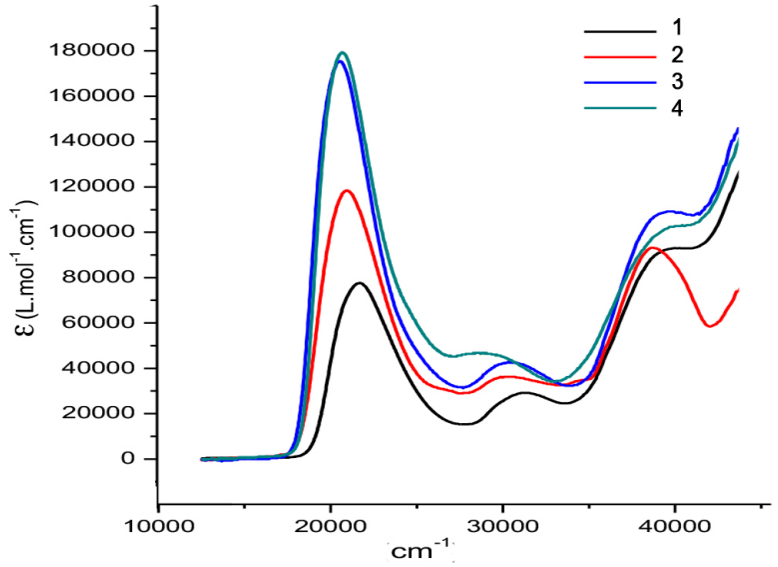
*Complex **4***

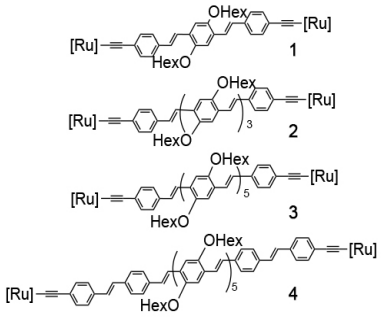

7.52
7.29
7.26
7.22
7.20
7.18
7.15
7.13
7.09
7.05
7.03
7.01
6.98
6.96
6.66
6.64
4.08
2.70
1.89
1.56
1.39
1.26
0.93
0.00
HexO
[Ru]
5
[Ru]
OHex
4
31.88
21.44
27.77
4.90
30.39
4.00
19.04
15.78
19.42
19.94
39.27
30.40
f1 (ppm)

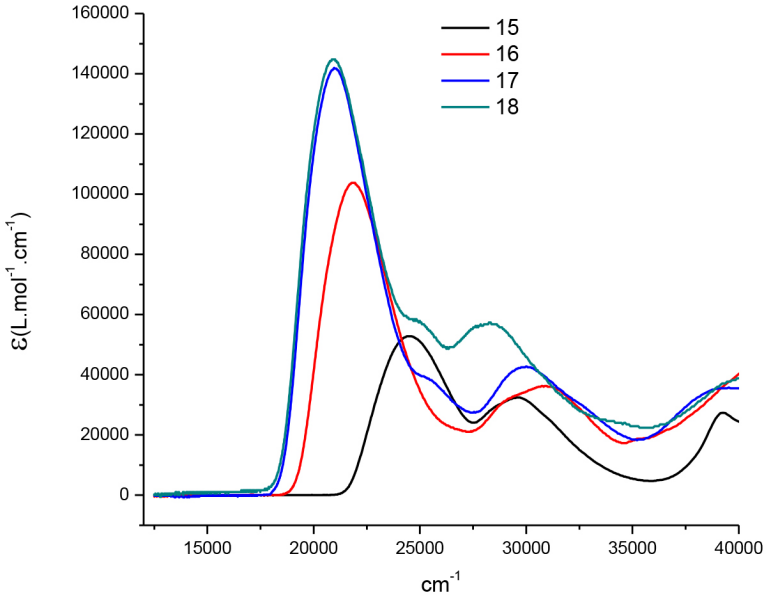

151.20
151.13
151.10
137.11
136.91
136.50
135.59
134.40
134.27
131.70
130.28
128.84
128.79
128.30
127.73
127.56
127.51
127.45
127.23
126.95
126.83
126.53
125.98
125.82
123.44
123.30
123.22
123.14
110.53
77.34
77.23
77.03
76.71
69.63
69.52
31.70
30.81
30.69
30.57
29.70
29.54
26.01
25.98
22.69
14.08
f1 (ppm)

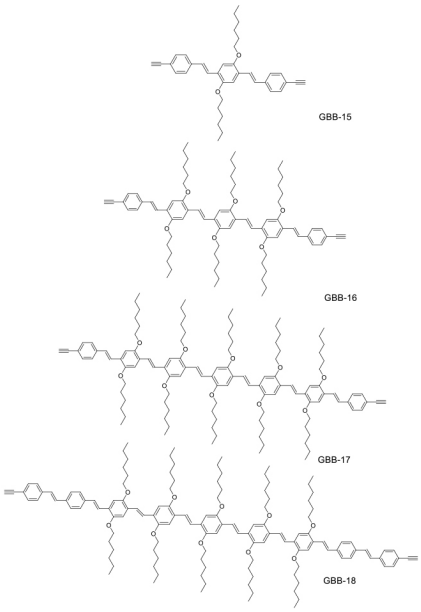

-49.42
600
550
500
450
400
350
300
250
200
150
100
50
0
100
50
0
-50
-100
-150
-200
f1 (ppm)

UV-vis spectra.









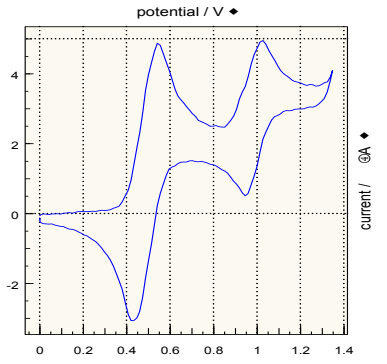
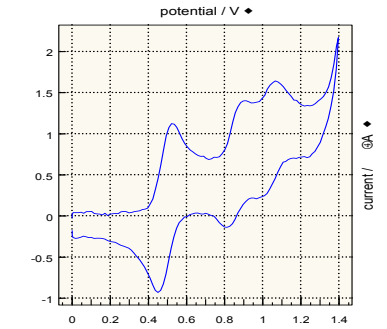
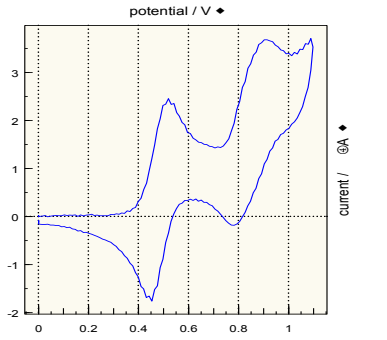
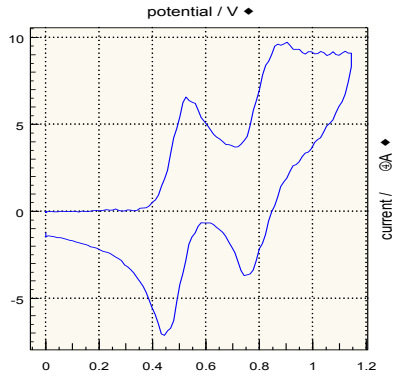
Linear optical data.[a]

Complex	λ_{max} (nm) ε (10^4 M^{-1} cm^{-1})
1	463 [7.7]
2	476 [11.8]
3	487 [17.5]
4	484 [18.0]
15	406 [5.3]
16	458 [10.3]
17	476 [14.2]
18	478 [14.5]

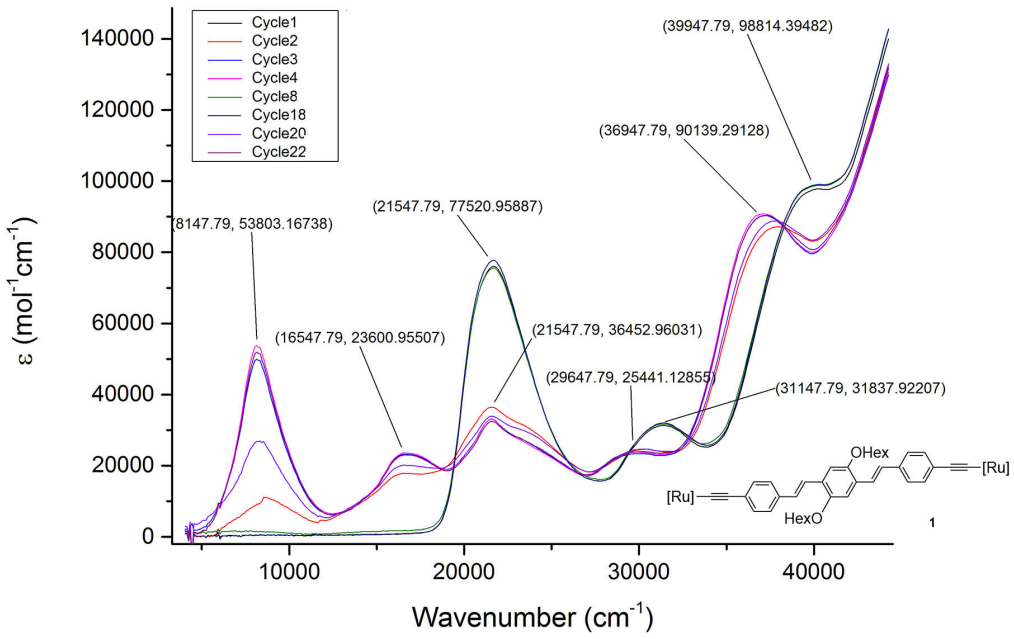
[a] Solutions in CH_2Cl_2. [Ru] = *trans*-RuCl(dppe)$_2$

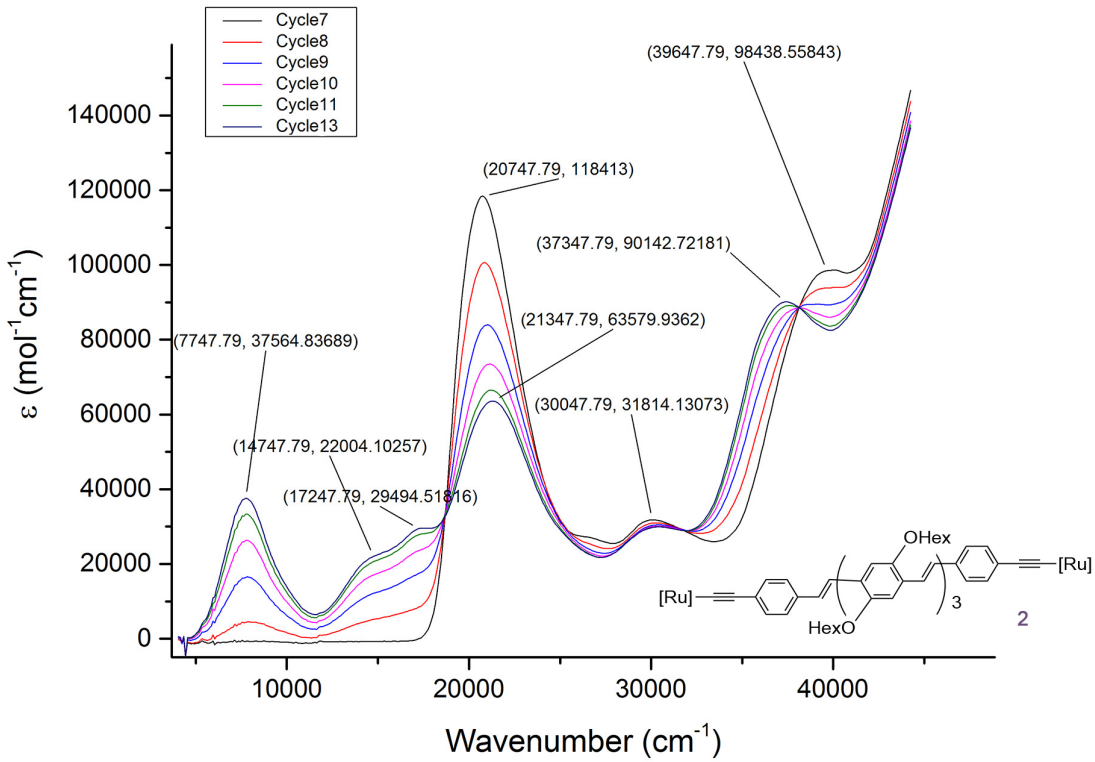
Cyclic voltammetry.

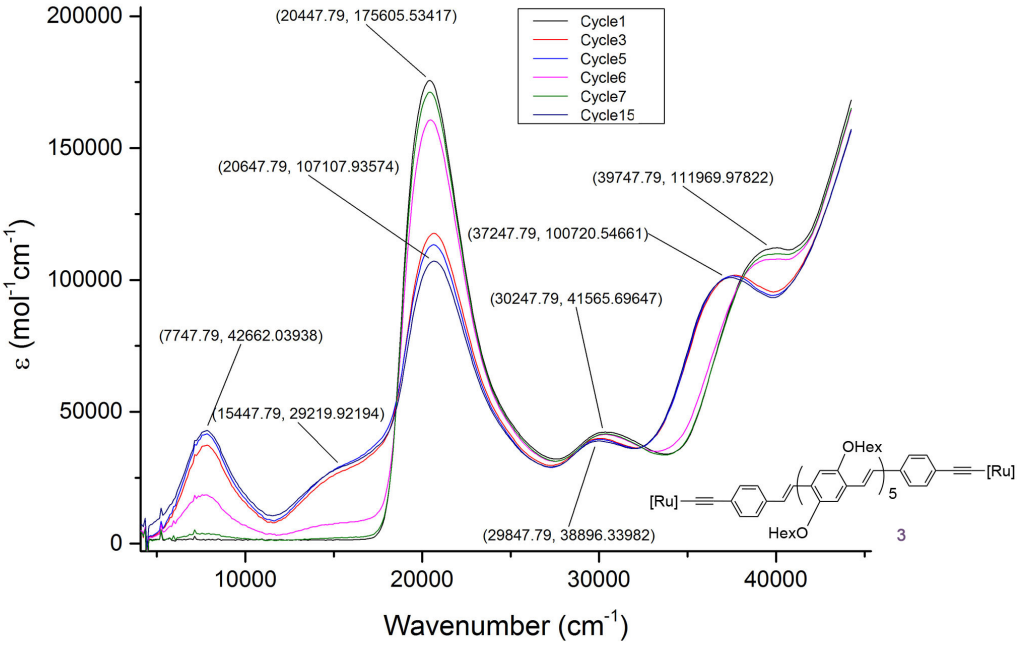
Measurements were carried out in CH_2Cl_2 at room temperature using Pt disc working-, Pt wire auxiliary-, and Ag/AgCl reference electrodes, such that the ferrocene/ferrocenium redox couple was located at 0.56 V (i_{pa}/i_{pc} = 1,ΔE_p ~ 0.09 V).

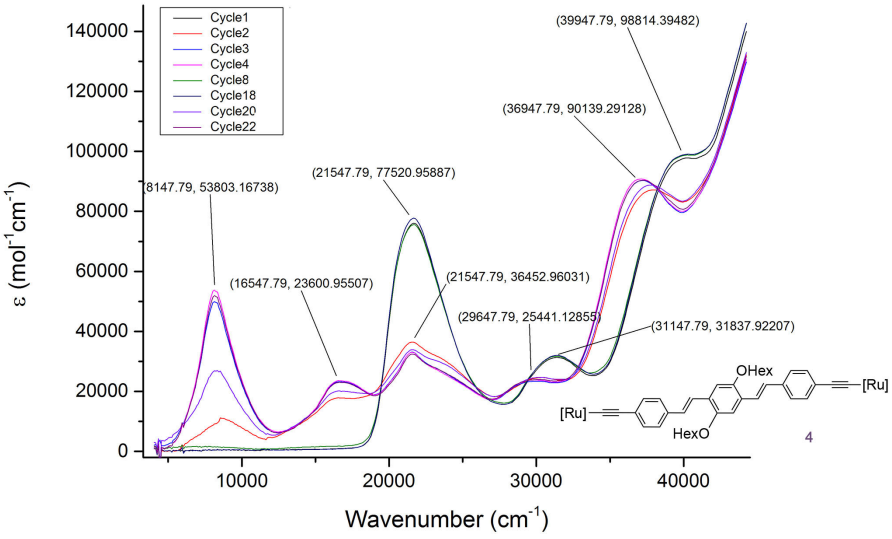
	Compound **1**. $E_1^{1/2}$ = 0.56 V ΔE_1 = 0.09 V i_{pc}/i_{pa}= 1 $E_2^{1/2}$ = 1.01 V ΔE_2 = 0.09 V i_{pc}/i_{pa}= 1
	Compound **2.** $E_1^{1/2}$ = 0.55 V ΔE_1 = 0.09 V i_{pc}/i_{pa}= 1 $E_2^{1/2}$ = 0.92 V ΔE_2 = 0.10 V i_{pc}/i_{pa}= 0.9 $E_3^{1/2}$ = 1.09 V ΔE_2 = 0.09 V i_{pc}/i_{pa}= 0.9
	Compound **3.** $E_1^{1/2}$ = 0.54V ΔE_1 = 0.07 V i_{pc}/i_{pa} = 1 $E_2^{1/2}$ = 0.90V ΔE_2 = 0.13 V i_{pc}/i_{pa} = 1
	Compound **4.** $E_1^{1/2}$ = 0.54 V ΔE_1 = 0.07 V i_{pc}/i_{pa}= 1 $E_2^{1/2}$ = 0.90 V ΔE_2 = 0.13 V i_{pc}/i_{pa}= 1

Spectroelectrochemistry studies.



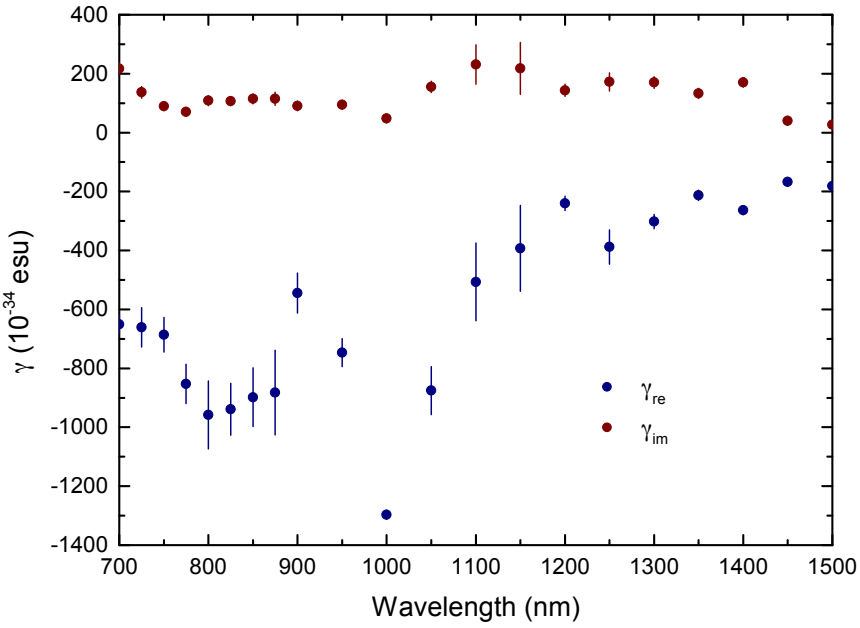



(20447.79, 175605.53417)
Cycle1
Cycle3
Cycle5
Cycle6
Cycle7
Cycle15
(20647.79, 107107.93574)
(39747.79, 111969.97822)
(37247.79, 100720.54661)
(30247.79, 41565.69647)
(7747.79, 42662.03938)
(15447.79, 29219.92194)
(29847.79, 38896.33982)
ε (mol-1cm-1)
Wavenumber (cm-1)
OHex
[Ru]
5
HexO
3

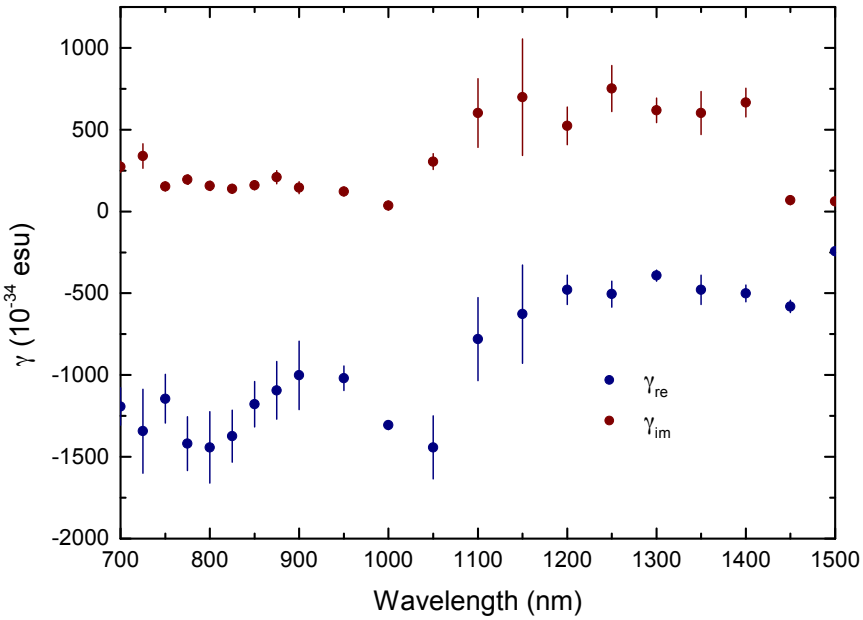

Cycle1
Cycle2
Cycle3
Cycle4
Cycle8
Cycle18
Cycle20
Cycle22
(39947.79, 98814.39482)
(36947.79, 90139.29128)
(21547.79, 77520.95887)
(8147.79, 53803.16738)
(16547.79, 23600.95507)
(21547.79, 36452.96031)
(29647.79, 25441.12855)
(31147.79, 31837.92207)
ε (mol-1cm-1)
Wavenumber (cm-1)
OHex
[Ru]
HexO
4

Z-scan studies.

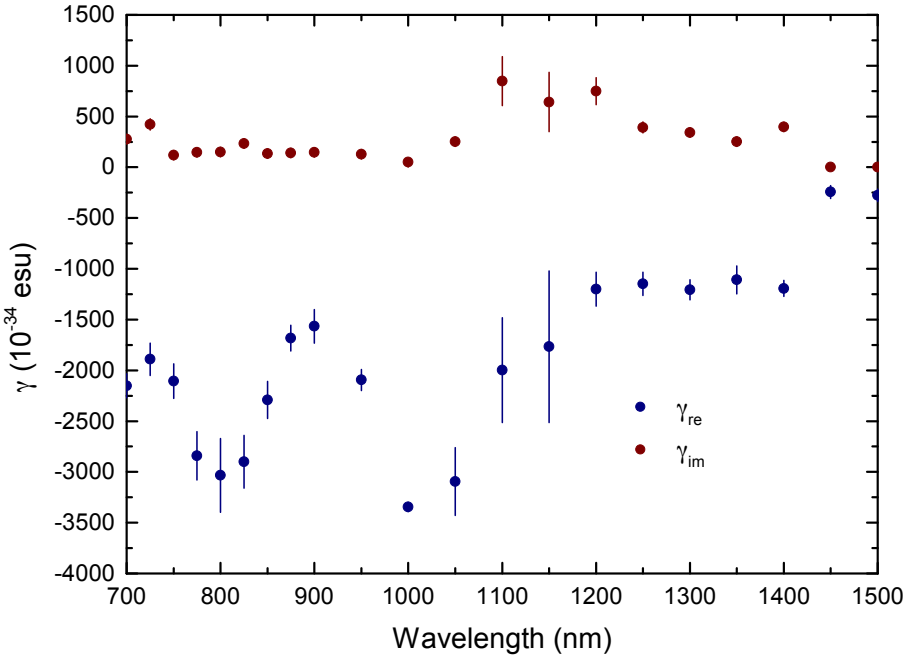
Complexes **1** and **2** were dissolved in dichloromethane at concentrations equal to 0.2% (w/w), whereas **3** and **4** were dissolved in the same solvent at concentrations equal to 0.1% (w/w). The solutions were placed in 1 mm path length optical glass cells. The measurements were carried out in a relative manner, calibrating all the data against Z-scans carried out on a fused silica plate and taking into account the nonlinear signals obtained on a cell containing pure solvent, as described in reference [7]. The tunable excitation was achieved by directing the beam from a Quantronix Integra Ti:sapphire regenerative amplifier (output wavelength 800 nm, pulse duration 130 fs, repetition rate 1 kHz) to an optical parametric amplifier (OPA, a Quantronix Palitra). The open-aperture (OA) scans were fitted with theoretical traces, corresponding to two-photon absorption (2PA) in the range 700-1000 nm and to three-photon absorption (3PA) in the range 1050-1500 nm.



The real (blue) and imaginary (red) parts of the third-order hyperpolarizability of complex 1



The real (blue) and imaginary (red) parts of the third-order hyperpolarizability of complex 2



The real (blue) and imaginary (red) parts of the third-order hyperpolarizability of complex 4

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