Supporting information

H-Bonded Duplexes based on a Phenylacetylene Backbone

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NMR binding studies

A•D, AA•DD, and DMSO•D complexes

Binding constants were measured by ^{31}P NMR titrations in a Bruker 500 MHz AVIII HD Smart Probe spectrometer. The host (phosphine oxide derivatives **A** or **AA**, or phenol derivative **D**) was dissolved in toluene-d_8 at a known concentration. The guest (phenol derivatives **D** or **DD,** or DMSO) was dissolved in the host solution and made to a known concentration. A known volume of host was added to an NMR tube and the spectrum was recorded. Known volumes of guest in host solution were added to the NMR tube, and the spectra were recorded after each addition. The chemical shifts of the host spectra were monitored as a function of guest concentration and analysed using a purpose written software in Microsoft Excel. Errors were calculated as two times the standard deviation from the average value (95% confidence limit).

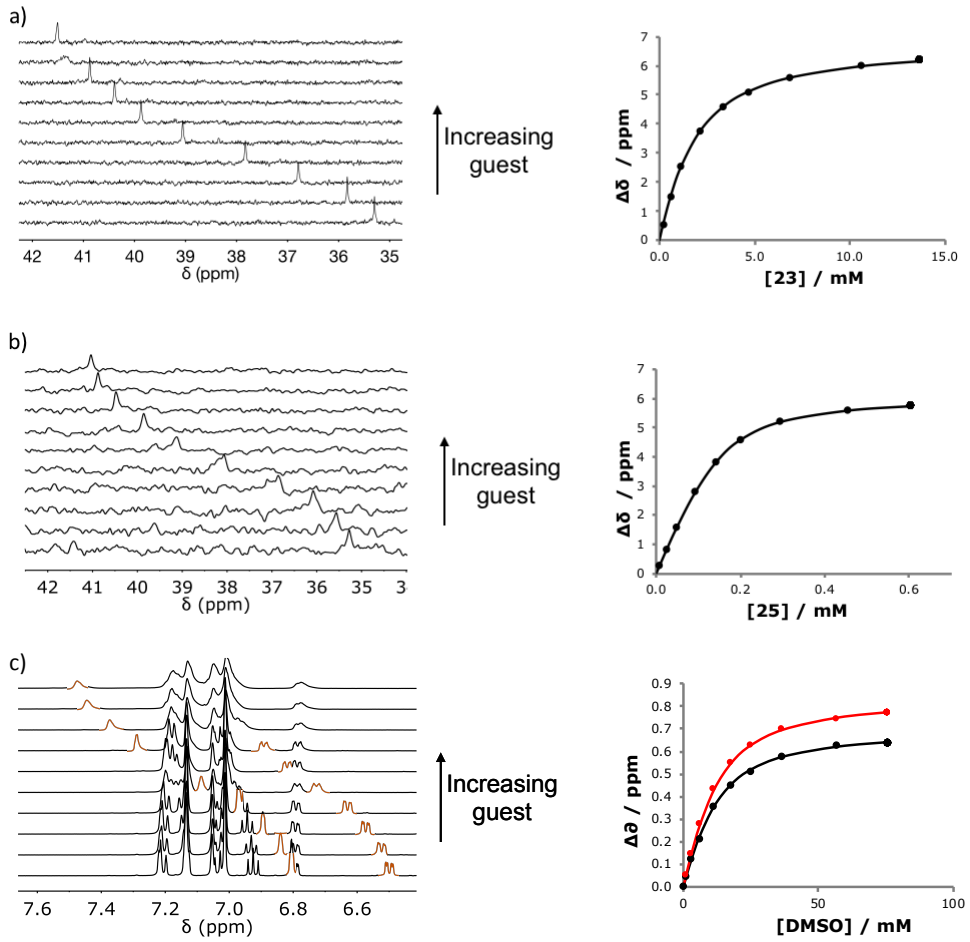


Figure S1. 202 MHz ^{31}P NMR data (202 MHz) for titration of a) **D** into **A** (1.02 mM), b) **DD** into **AA** (0.15 mM), and c) ^{1}H NMR data (500 MHz) for titration of DMSO into **23** (D) (9.6 mM) at 298 K in toluene-d_8. Representative titration spectra and plots of complexation-

induced change in chemical shift versus guest concentration (the line represents the best fit to a 1:1 binding isotherm).

AA•DD, AAA•DDD and AAAA•DDDD complexes

Binding constants were measured by ^{31}P NMR denaturation experiments in a Bruker 500 MHz AVIII HD Smart Probe spectrometer. An equimolar solution of complementary homo-oligomers (phosphine oxide derivatives **AA**, **18** or **19**, and phenol derivatives **DD**, **14** or **15**) was produced at a concentration of 1 mM in toluene-d_8. A known volume of solution was added to an NMR and the spectrum recorded. Known volumes of DMSO-d_6 in toluene-d_8 and neat DMSO-d_6 were added and the spectrum recorded after each addition. The chemical shifts of the acceptor homo-oligomer spectra were monitored as a function of DMSO-d_6 concentration. Free ^{31}P NMR shifts were monitored for a 1 mM solution of **A** in toluene-d_8 with the same concentrations of DMSO-d_6 to account for solvent effects. These were subtracted from the raw data and the corrected data analysed using a purpose written software in Microsoft Excel.

The denaturation data did not fit to a simple two-state isotherm for any of the duplexes (Figure S2a). Therefore all of the denaturation data were analysed taking into account partially denatured species as described in the main text, and excellent agreement with the experimental data was obtained (Figure S2b).

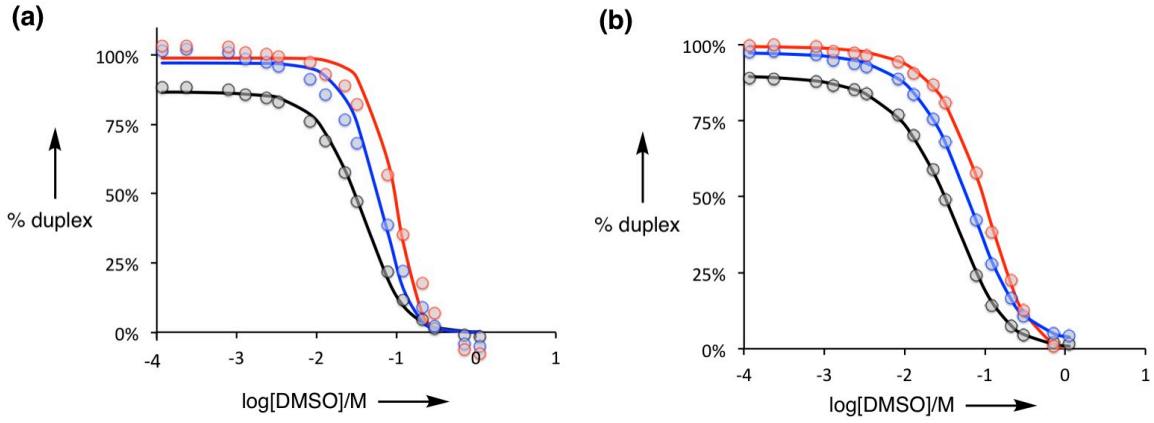


Figure S2. Duplex denaturation data plotted as a function of DMSO-d_6 concentration in toluene-d_8 at 298 K for AA•DD (black), AAA•DDD (blue) and AAAA•DDDD (red). The dots represent the experimental values, and the lines are (a) calculated two-state denaturation isotherms, and (b) calculated denaturation isotherms considering all possible species.

In order to fit the denaturation data using the minimum number of variables, the association constants for certain species were fixed using experimentally determined values as explained in the main text (see Figs 10-12). In addition the chemical shifts of the partially denatured species were fixed using the chemical shifts of the fully bound duplex and fully denatured species.

For the AA•DD fitting, the ^{31}P NMR shift of the phosphine oxide in the AA•DD•DMSO complex was fixed by equation 2 due to the formation of only one H-bond.

$$\delta_{\mathrm{AA{\bullet}DD{\bullet}DMSO}} = \frac{(\delta_{\mathrm{bound}} - \delta_{\mathrm{free}})}{2} \qquad 2$$

For the AAA•DDD fitting, the ^{31}P NMR shifts of the phosphine oxides in the AAA•DDD•DMSO and AAA•DDD•$(DMSO)_2$ were fixed by equations 3 and 4.

$$\delta_{\mathrm{AAA{\bullet}DDD{\bullet}DMSO}} = \frac{2(\delta_{\mathrm{bound}} - \delta_{\mathrm{free}})}{3} \qquad 3$$

$$\delta_{\mathrm{AAA{\bullet}DDD{\bullet}(DMSO)_2}} = \frac{(\delta_{\mathrm{bound}} - \delta_{\mathrm{free}})}{3} \qquad 4$$

For the AAAA•DDDD fitting the ^{31}P NMR shifts of the phosphine oxides in the AAAA•DDDD•DMSO, AAAA•DDDD•$(DMSO)_2$, and AAAA•DDDD•$(DMSO)_3$ complexes were fixed by equations 5, 6 and 7.

$$\delta_{\mathrm{AAAA{\bullet}DDDD{\bullet}DMSO}} = \frac{3(\delta_{\mathrm{bound}} - \delta_{\mathrm{free}})}{4} \qquad 5$$

$$\delta_{\mathrm{AAAA{\bullet}DDDD{\bullet}(DMSO)_2}} = \frac{2(\delta_{\mathrm{bound}} - \delta_{\mathrm{free}})}{4} \qquad 6$$

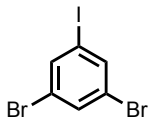
$$\delta_{\mathrm{AAAA{\bullet}DDDD{\bullet}(DMSO)_3}} = \frac{(\delta_{\mathrm{bound}} - \delta_{\mathrm{free}})}{4} \qquad 7$$

Synthesis and characterisation of compounds

General experimental details

All the reagents were obtained from commercial sources (Sigma-Aldrich, Alfa Aesar, Fisher Scientific and Fluorochem) and were used without further purification. Thin layer chromatography was carried out using with silica gel 60F (Merck) on aluminium. Flash chromatography was carried out on an automated system (Combiflash Rf+ or Combiflash Rf Lumen) using prepacked cartridges of silica (25µ or 50µ PuriFlash® Columns). ^{1}H and ^{13}C NMR spectra were recorded on either a Bruker AV3400 or AV3500 spectrometer at 298 K unless specifically stated otherwise. Residual solvent was used as an internal standard. All chemical shifts are quoted in ppm on the δ scale and the coupling constants expressed in Hz. Signal splitting patterns are described as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). ES+ mass spectra were obtained on a Waters LCT premier mass spectrometer. FTIR spectra were recorded on a PerkinElmer Spectrum One FT-IR spectrometer. Melting points were recorded on a Mettler Toledo MP90 melting point apparatus and are reported as an uncorrected range of three repeats. ES+ was carried out on a Waters LCT-TOF spectrometer or a Waters Xevo G2-S bench top QTOF machine. Compounds **2, D, A, DD** and **AA** have been previously described.[1]

3,5-dibromoiodobenzene (**4**)



1,3,5-tribomobenzene (2.00 g, 6.35 mmol) was dissolved in dry Et_2O (60 mL) in a dried flask. The reaction was cooled to -78 °C. ^{n}BuLi (1.6 M in hexanes, 4.37 mL, 6.99 mmol) was added slowly over 1 h, and the reaction was stirred for 1 h at -78 °C. A solution of I_2 (3.20 g, 12.7 mmol) in dry Et_2O (10 mL) was added and reaction stirred at -78 °C for 1 h before being allowed to warm to room temperature over 1 h. Saturated $Na_2S_2O_3$ (50 mL) solution was added and reaction stirred until colourless. The organic phase was separated and washed with water (2 × 50 mL) and brine (50 mL). The solution was dried ($MgSO_4$) and the solvent was removed by rotary evaporation under reduced pressure yielding crude product (2.40 g). This solid was washed through a plug of silica by 40-60 pet. ether (300 mL), and the solvent was removed to yield the desired compound **4** as white needles (2.20 g, 6.08 mmol, 96% yield). The spectroscopic data matches previously reported literature.[2]

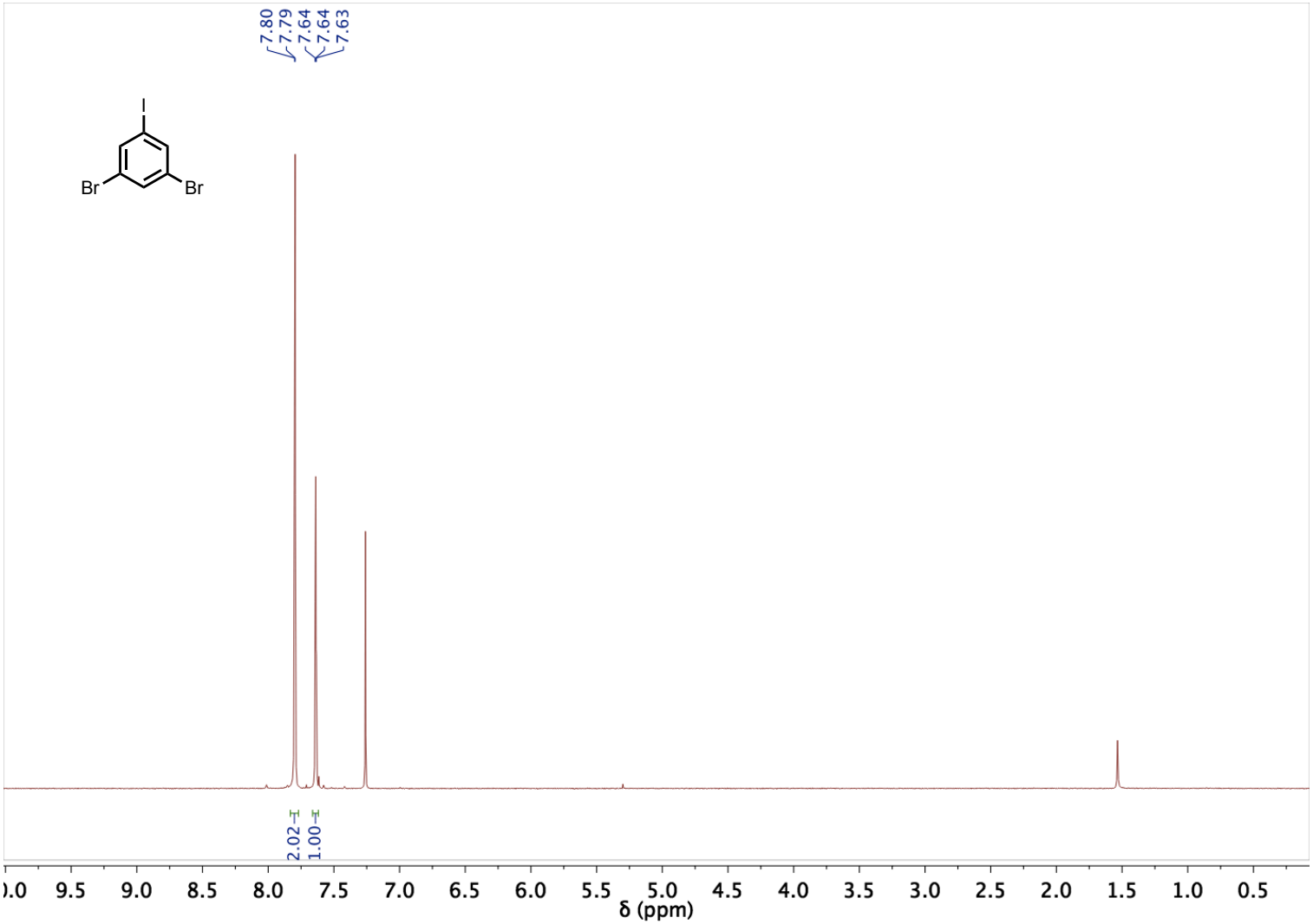
Melting Point: 120.0-122.0 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 1.5 Hz, 2H), 7.64 (t, *J* = 1.5 Hz, 1H).

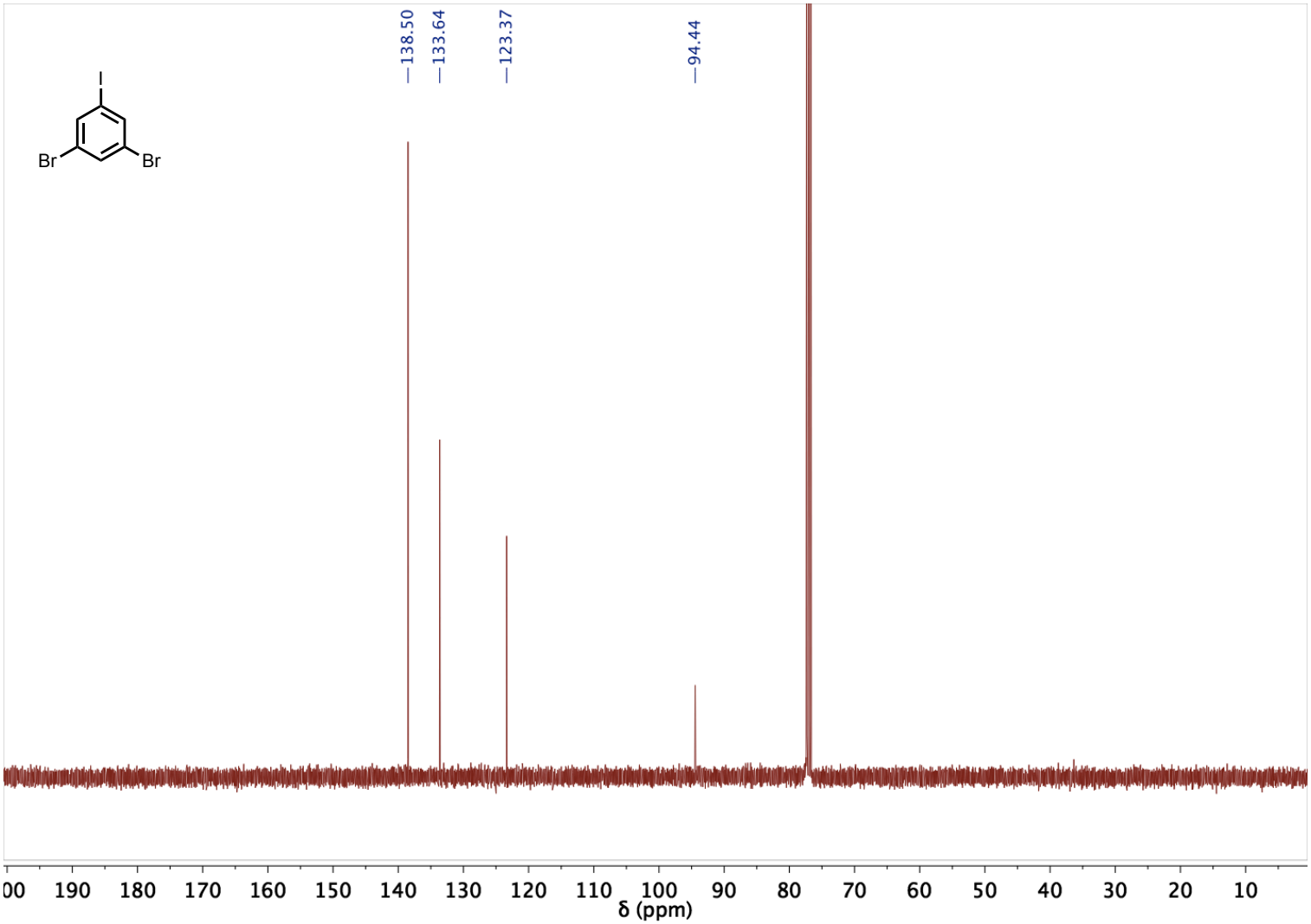
^{13}C NMR (101 MHz, $CDCl_3$): δ 138.5, 133.6, 123.4, 94.4.

FT-IR (ATR): 3062, 1546, 1397, 1096 ν_{max}/cm^{-1}.

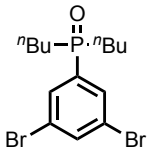
^{1}H NMR (400 MHz, $CDCl_3$) compound 4



^{13}C NMR (101 MHz, $CDCl_3$) compound 4



Dibutyl(3,5-dibromophenyl)phosphine oxide (**5**)



^{n}Butylphosphine oxide (693 mg, 4.27 mmol) was added to a dried flask and the flask evacuated and back-filled with nitrogen (×3). Compound **4** (1.70 g, 4.70 mmol) was added and 1,4-dioxane (deoxygenated by freeze-pump-thaw, 5 mL) was added. In a separate flask, $Pd_2(dba)_3$ (108 mg, 0.118 mmol) and Xantphos (68.0 mg, 0.118 mmol) were placed in a flask and evacuated and back-filled with nitrogen (×3). These were dissolved in 1,4-dioxane (5 mL) and the solution transferred to the initial flask. Et_3N (600 µL, 4.27 mmol) was added and the reaction stirred at room temperature for 2 h. CH_2Cl_2 (20 mL) was added and the reaction washed with saturated $NaHCO_3$ solution (25 mL). The aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL) combined organics dried ($MgSO_4$), and solvent removed by rotary evaporation under reduced pressure yielding a brown solid (2.16 g). This solid was separated by flash chromatography (MeOH:CH_2Cl_2, 1:20) to yield the desired compound **5** as an orange crystalline solid (1.00 g, 2.52 mmol, 59% yield).

Melting Point: 90.3-92.2 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (td, *J* = 2.0, 0.5 Hz, 1H), 7.76 (dd, *J* = 10.5, 2.0 Hz, 2H), 2.02-1.78 (m, 4H), 1.70-1.54 (m, 2H), 1.49-1.35 (m, 6H), 0.91 (t, *J* = 7.0 Hz, 6H).

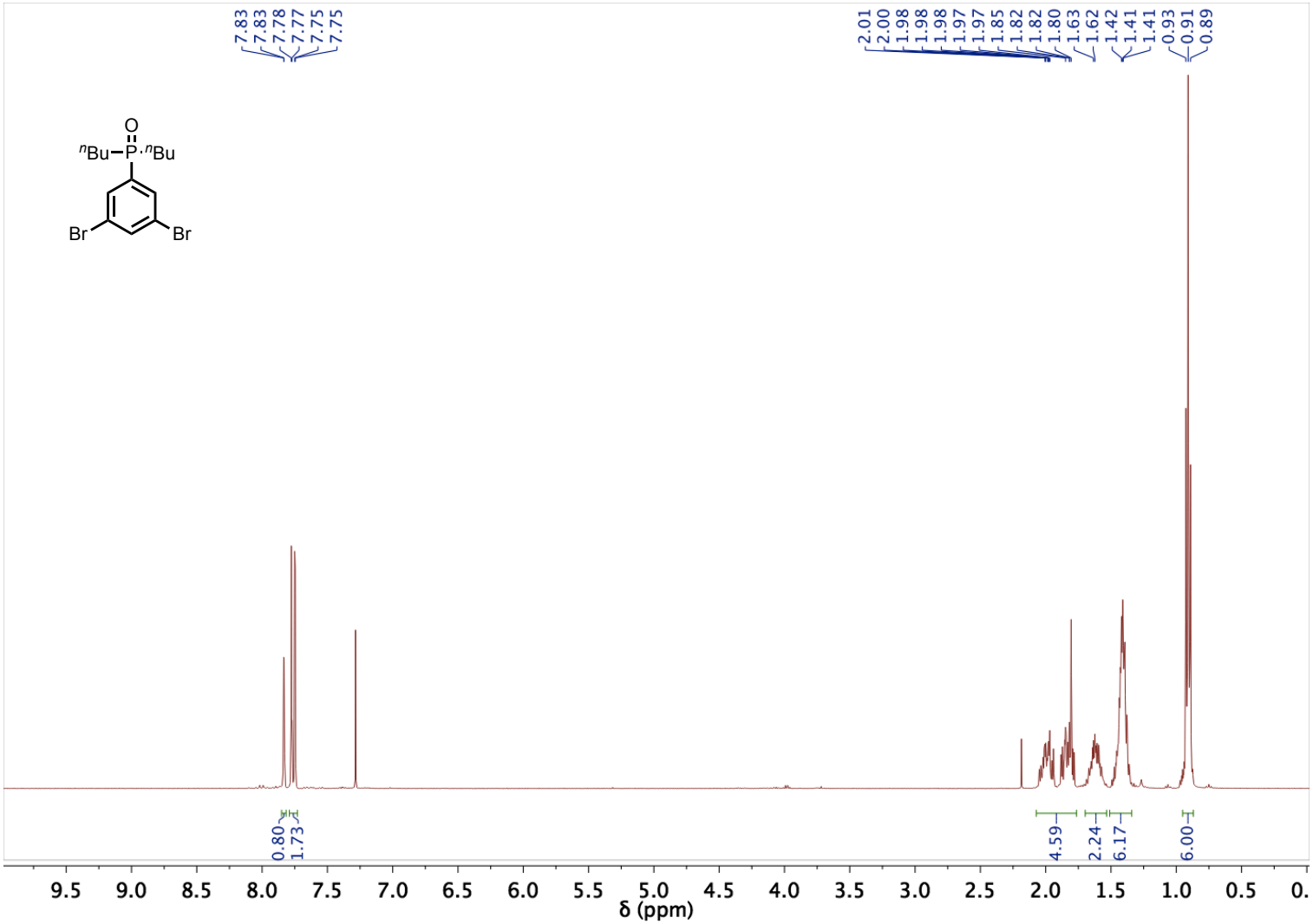
^{13}C NMR (101 MHz, $CDCl_3$): δ 137.2, 137.0 (d, *J* = 2 Hz), 131.8 (d, *J* = 9 Hz), 123.8 (d, *J* = 14 Hz), 29.7 (d, *J* = 69 Hz), 24.0 (d, *J* = 15 Hz), 23.4 (d, *J* = 4 Hz), 13.6.

^{31}P NMR (162 MHz, $CDCl_3$): δ 39.5.

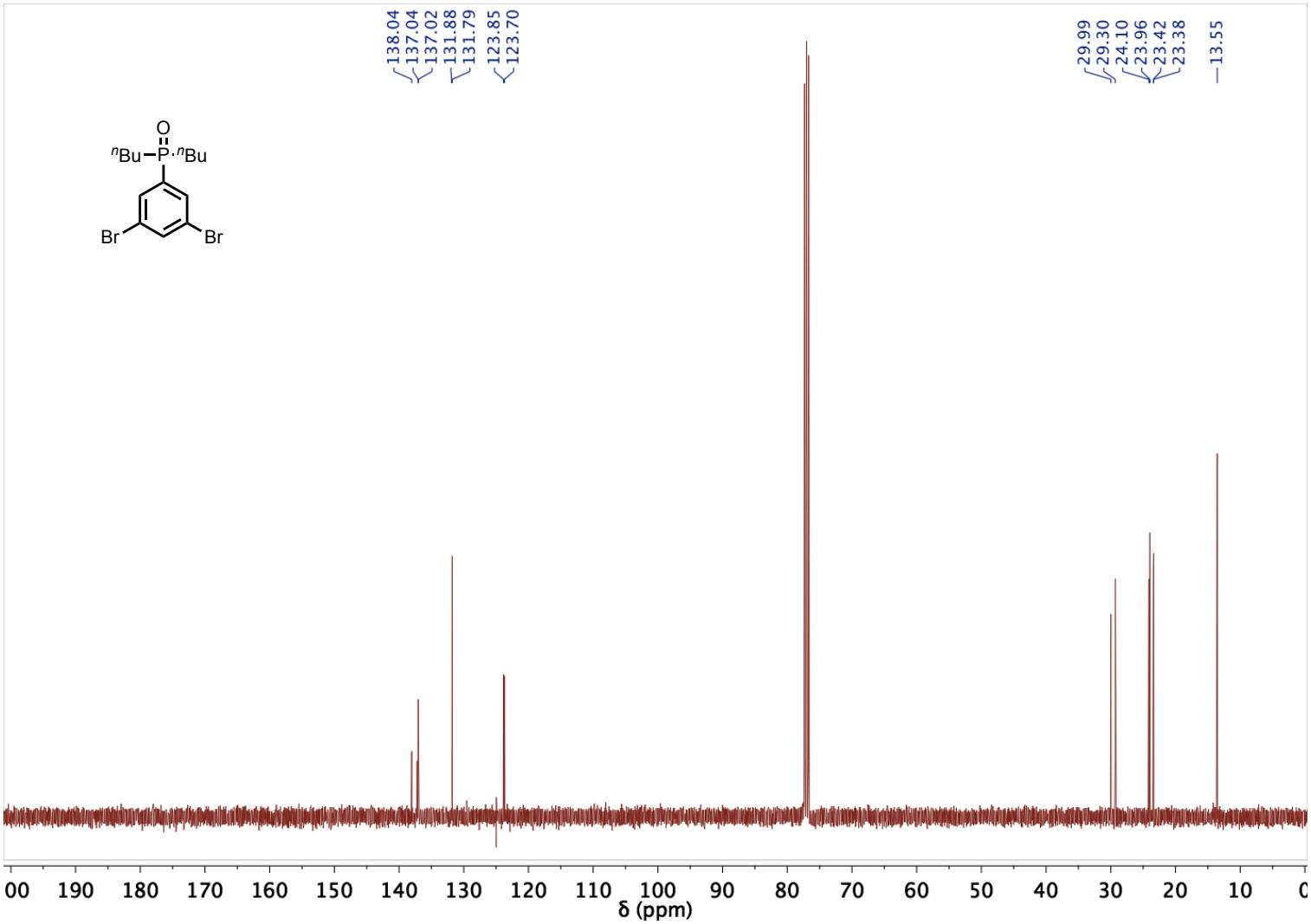
FT-IR (ATR): 2956, 2928, 2869, 1546, 1397, 1169, 1130, 736 ν_{max}/cm^{-1}.

HRMS (ES+): $C_{13}H_{22}Br_2OP$ calcd. 394.9775 found 394.9769, Δ = -1.5 ppm.

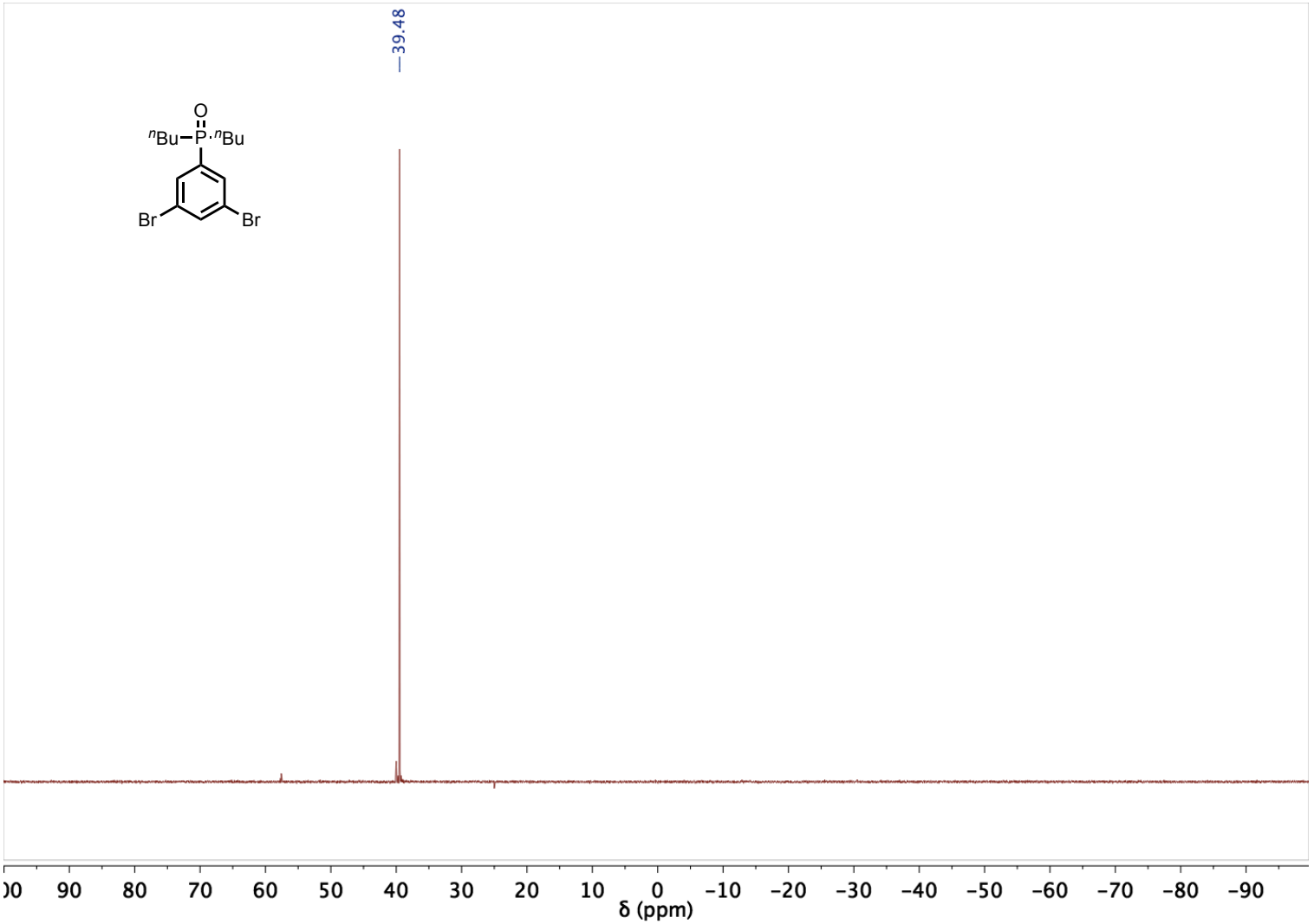
^{1}H NMR (400 MHz, $CDCl_3$) compound 5



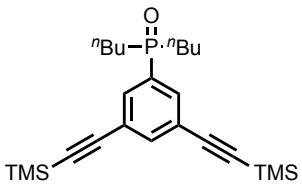
^{13}C NMR (101 MHz, $CDCl_3$) compound 5



^{31}P NMR (162 MHz, $CDCl_3$) compound 5



(3,5-bis((trimethylsilyl)ethynyl)phenyl)dibutylphosphine oxide (**6**)



Compound **5** (300 mg, 0.757 mmol), $Pd_2(dba)_3$ (14 mg, 1.51×10^{-2} mmol), CuI (3 mg, 1.51×10^{-2} mmol) and PPh_3 (20 mg, 0.0757 mmol) were added to a flask of Et_3N (5 mL) and N_2 bubbled through the reaction for 15 min. TMSA (0.26 mL, 1.82 mmol) was added and the reaction stirred at 50 °C overnight under N_2. The reaction was filtered through celite and washed through with EtOAc (10 mL). The solution was washed with 1 M HCl (3 × 10 mL). The solvent was removed by rotary evaporation under reduced pressure yielding a brown oil (420 mg). This solid was separated by flash chromatography (methanol:dichloromethane, 1:19) to yield the desired compound **6** as a brown oil (315 mg, 0.731 mmol, 97% yield).

Melting Point: 103.3-106.0 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71-7.68 (m, 3H), 2.01-1.70 (m, 4H), 1.64-1.51 (m, 2H), 1.45-1.30 (m, 6H), 0.87 (t, *J* = 7.0 Hz, 6H), 0.24 (s, 18H).

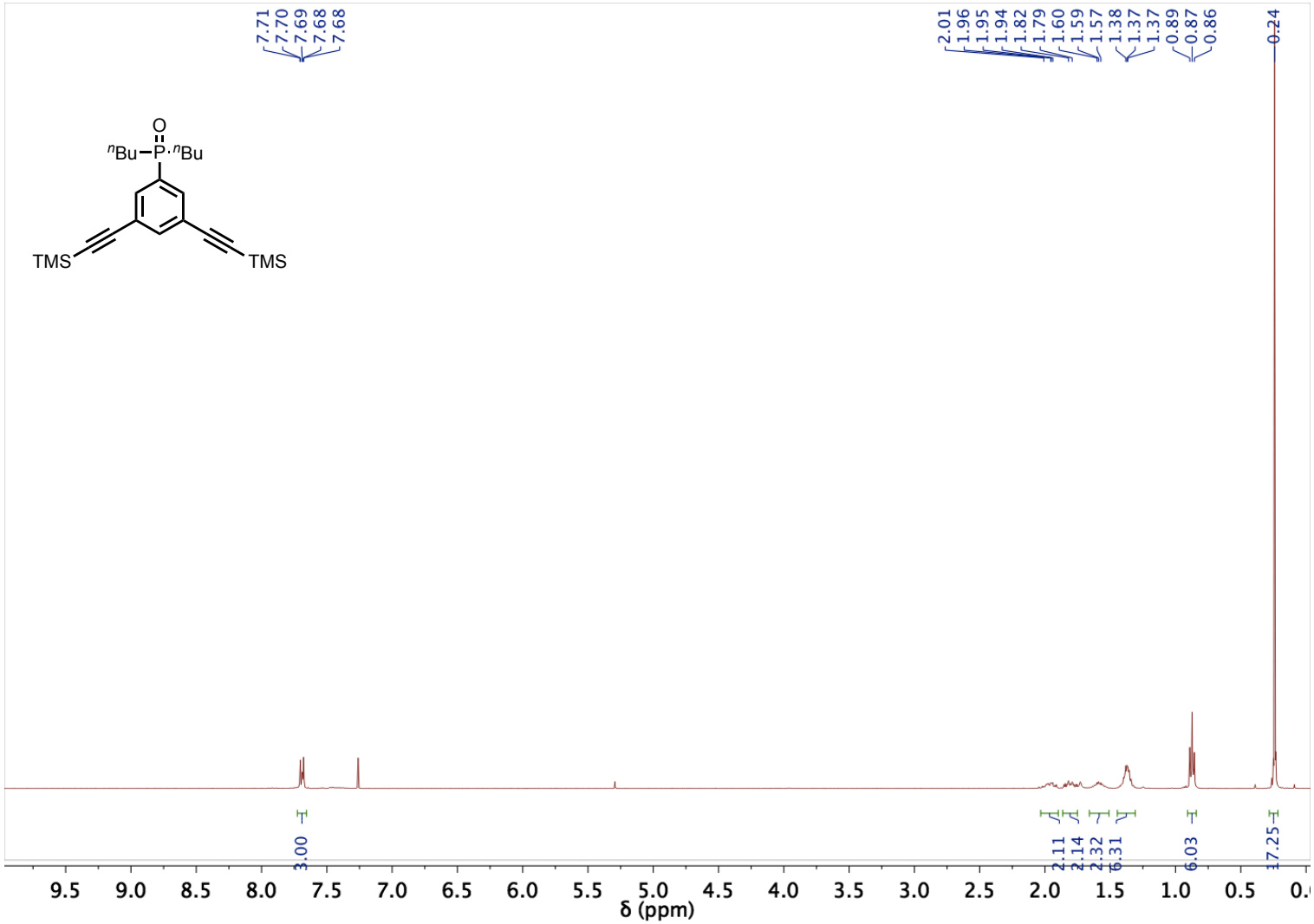
^{13}C NMR (101 MHz, $CDCl_3$): δ 137.7 (d, *J* = 3 Hz), 133.7 (d, *J* = 89 Hz), 131.8 (d, *J* = 9 Hz), 124.1 (d, *J* = 13 Hz), 103.0, 96.6, 29.6 (d, *J* = 69 Hz), 24.1 (d, *J* = 14 Hz), 23.4 (d, *J* = 4 Hz), 13.6, -0.2.

31P NMR (162 MHz, $CDCl_3$): δ 40.0.

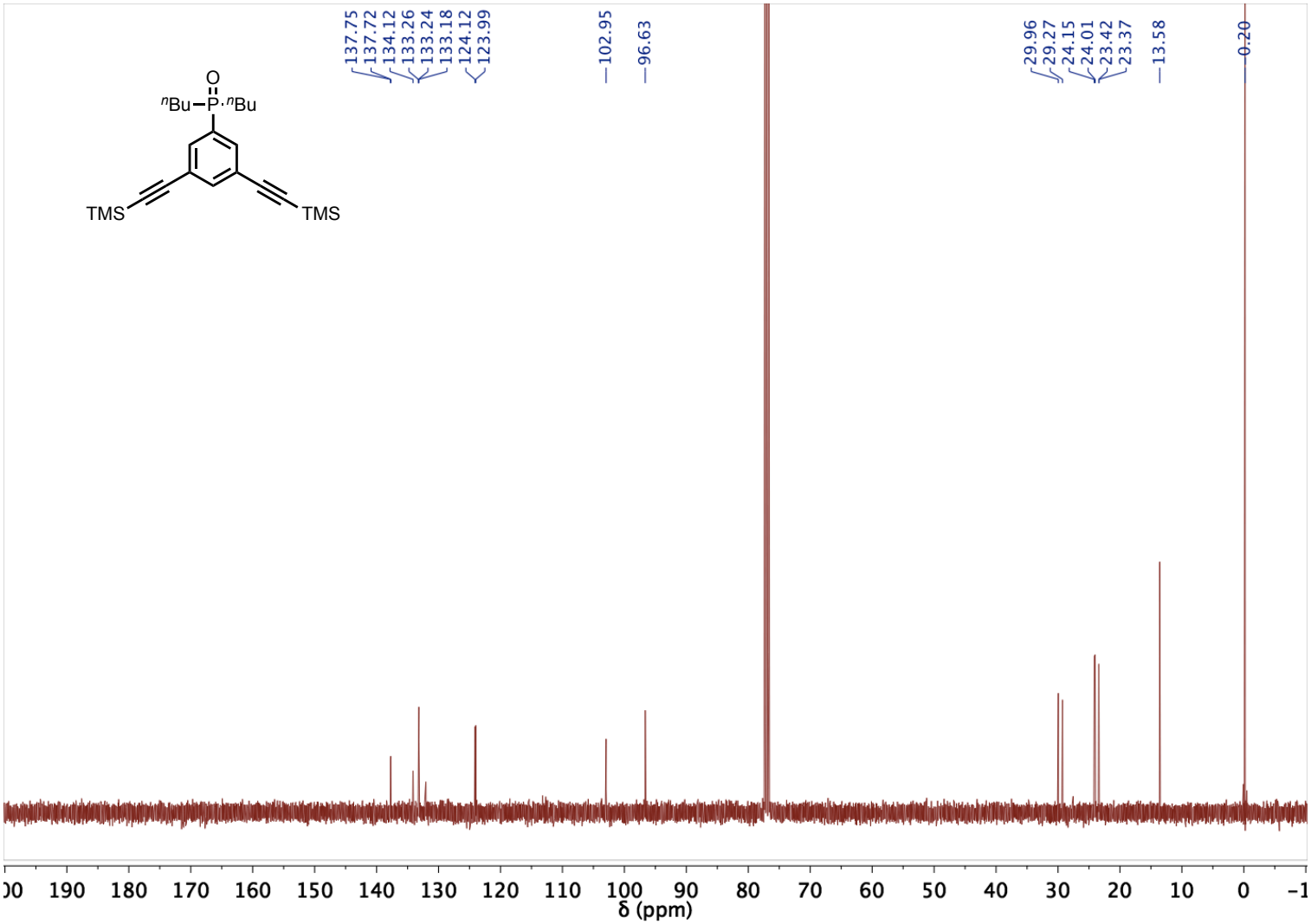
FT-IR (ATR): 2956, 2928, 2869, 1546, 1397, 1169, 1130, 736 ν_{max}/cm^{-1}.

HRMS (ES+): $C_{24}H_{40}OPSi_2$ (M+H) calcd. 431.2355 found 431.2355, Δ = 0 ppm.

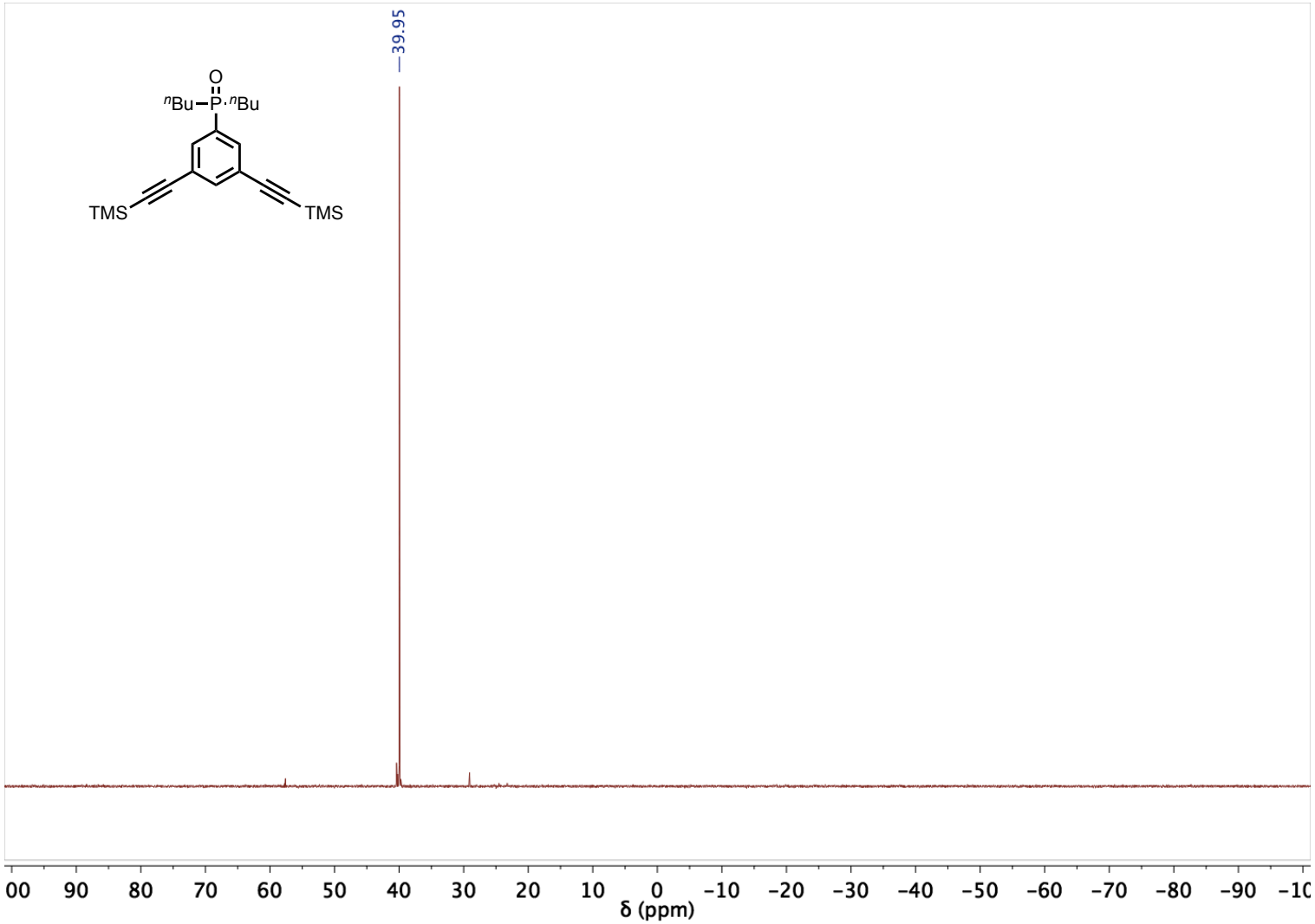
^{1}H NMR (400 MHz, $CDCl_3$) compound 6



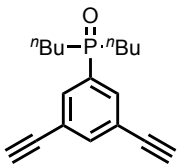
^{13}C NMR (101 MHz, $CDCl_3$) compound 6



^{31}P NMR (162 MHz, $CDCl_3$) compound 6



Dibutyl(3,5-diethylphenyl)phosphine oxide (**7**)



Compound **6** (100 mg, 0.232 mmol) was dissolved in dry THF (8 mL) and reaction purged with nitrogen. Reaction was cooled to 0 °C and TBAF (1M in THF, 0.510 mL, 0.510 mmol) added. Reaction was stirred for 10 min, diluted with EtOAc (25 mL) washed with 1M HCl (3 × 25 mL). The solution was dried ($MgSO_4$) and solvent was removed by rotary evaporation under reduced pressure yielding compound **7** as a brown oil (66.0 mg, 0.232 mmol, 100% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 – 7.71 (m, 3H), 3.19 (s, 2H), 2.11-1.80 (m, 4H), 1.67-1.53 (m, 2H), 1.45-1.30 (m, 6H), 0.88 (t, *J* = 7.0 Hz, 6H).

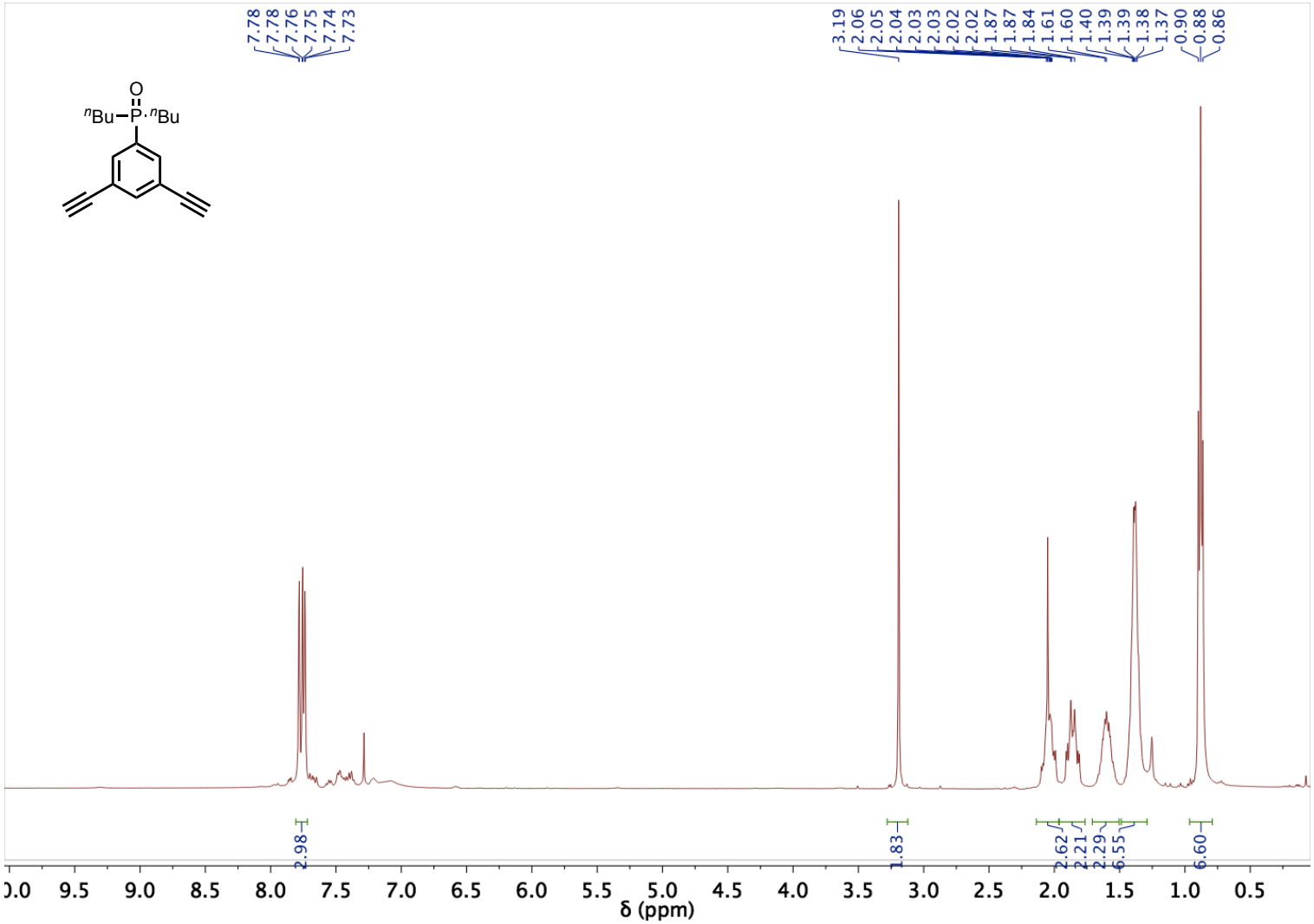
^{13}C NMR (101 MHz, $CDCl_3$): δ 138.2 (d, *J* = 3 Hz), 133.8 (d, *J* = 9 Hz), 132.5 (d, *J* = 89 Hz), 123.3 (d, *J* = 13 Hz), 81.5, 79.5, 29.2 (d, *J* = 69 Hz), 24.0 (d, *J* = 14 Hz), 23.3 (d, *J* = 4 Hz), 13.5.

^{31}P NMR (162 MHz, $CDCl_3$): 40.3.

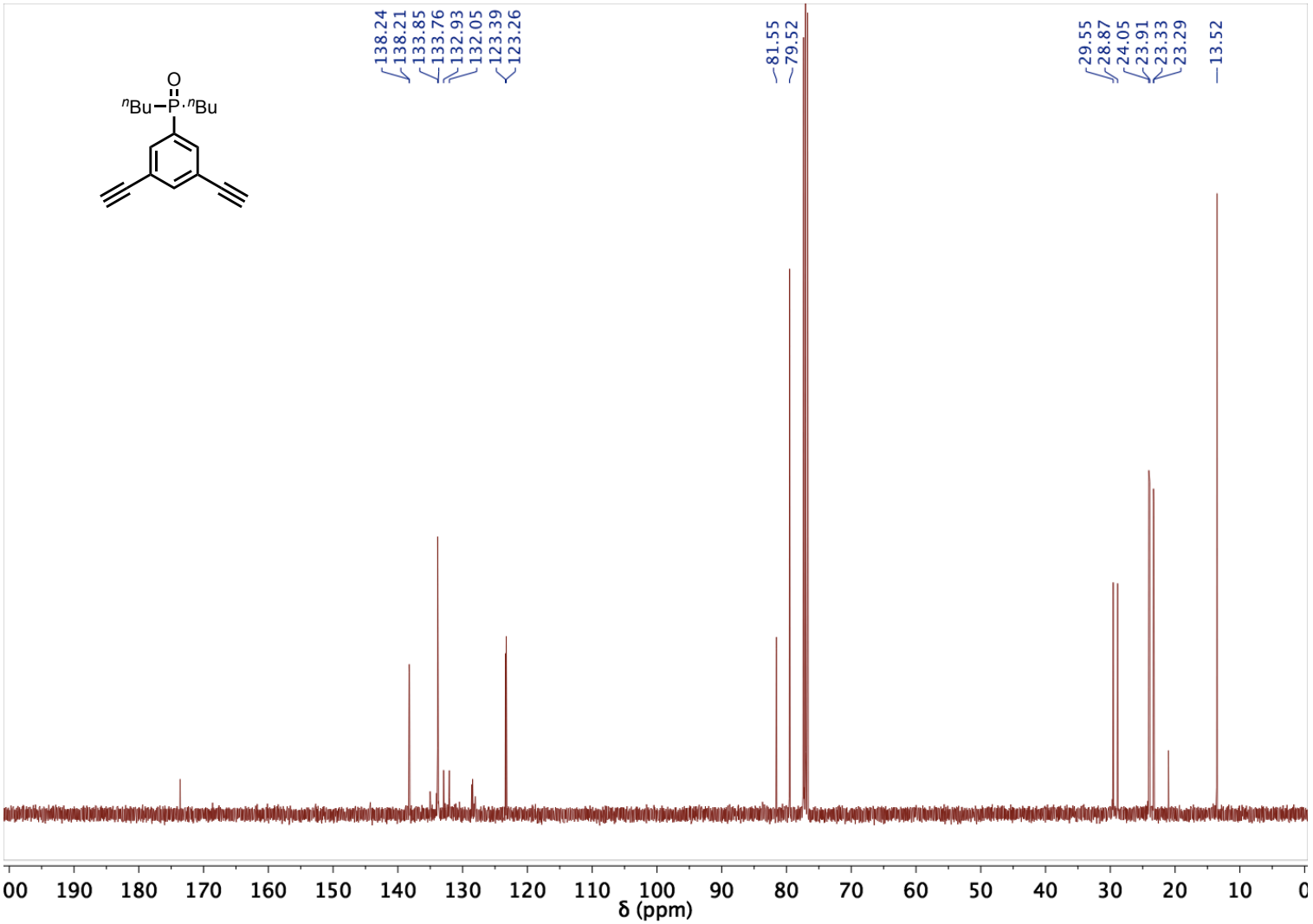
FT-IR (ATR): 2956, 2928, 2869, 1546, 1397, 1169, 1130, 736 ν_{max}/cm^{-1}.

HRMS (ES+): $C_{18}H_{24}OP$ calcd. 287.1559 found 287.1152, Δ = -2.58 ppm.

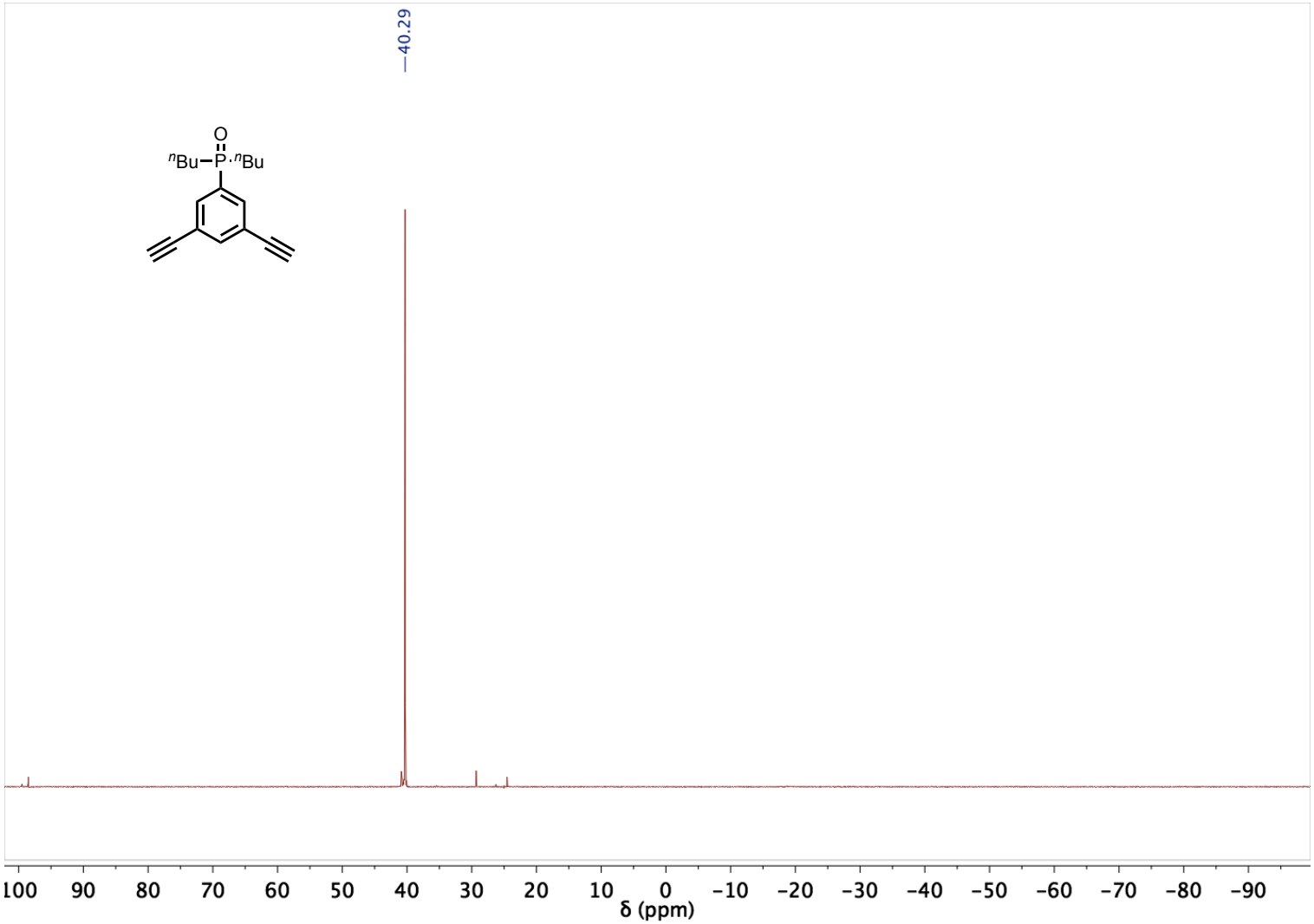
^{1}H NMR (400 MHz, $CDCl_3$) compound 7



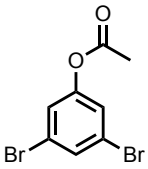
^{13}C NMR (101 MHz, $CDCl_3$) compound 7



^{31}P NMR (162 MHz, $CDCl_3$) compound 7



3,5-dibromophenyl acetate (**9**)



3,5-dibromophenol (2.50 g, 10.0 mmol) and DMAP (122 mg, 1.00 mmol) were added to a flask under N_2. Toluene (20 mL) and acetic anhydride (1.00 mL, 11.0 mmol) were added and the reaction stirred at room temperature overnight. The solvent was removed by rotary evaporation under reduced pressure to yield a brown oil. This oil was separated by flash chromatography (EtOAc:40-60 pet. ether, 1:9) to yield the desired compound **9** as a slightly yellow solid (2.73 g, 9.3 mmol, 93% yield). The spectroscopic data matches previously reported literature.[3]

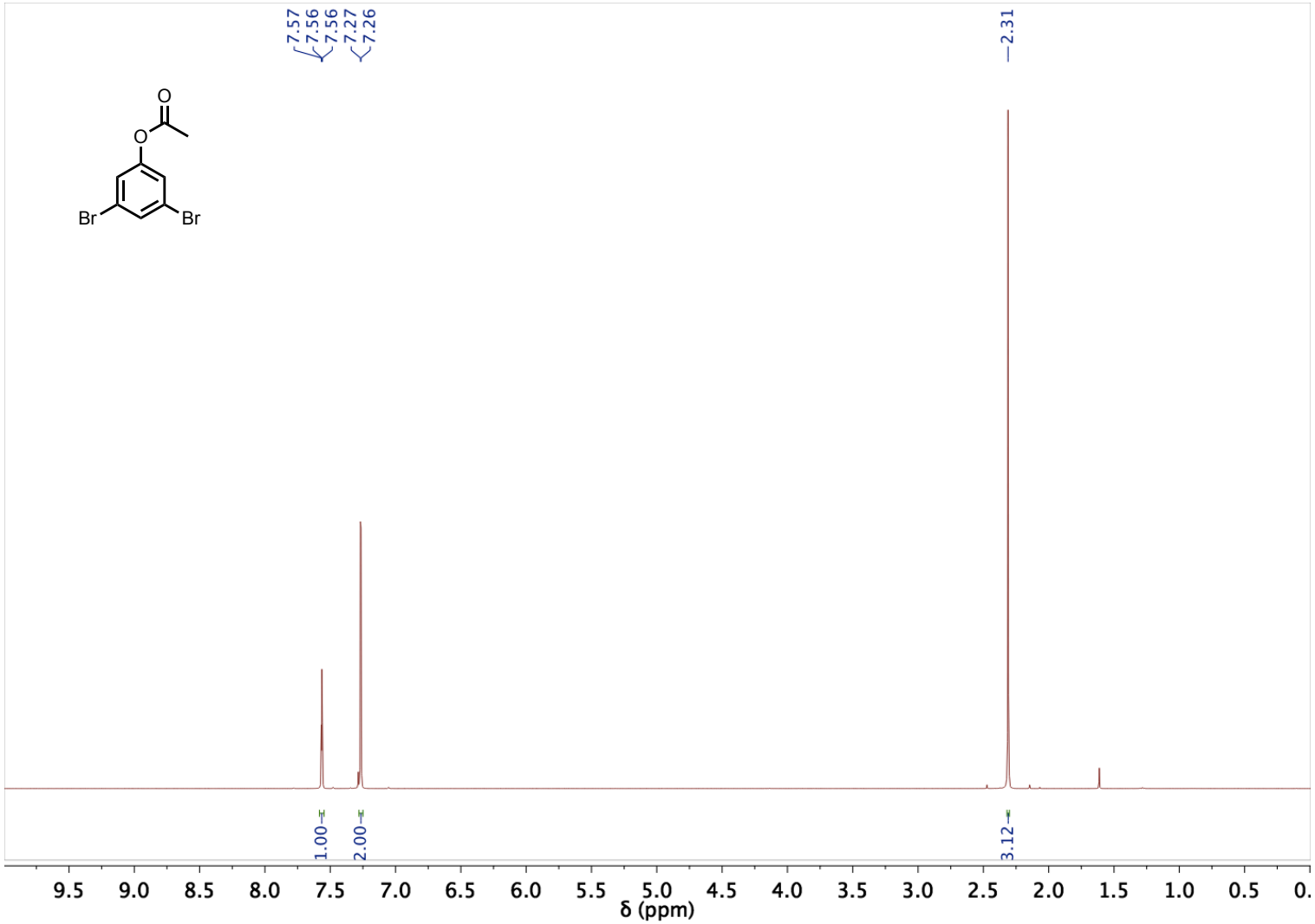
Melting Point: 57.2-59.1 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (t, *J* = 1.5 Hz, 1H), 7.27 (d, *J* = 1.5 Hz, 2H), 2.31 (s, 3H).

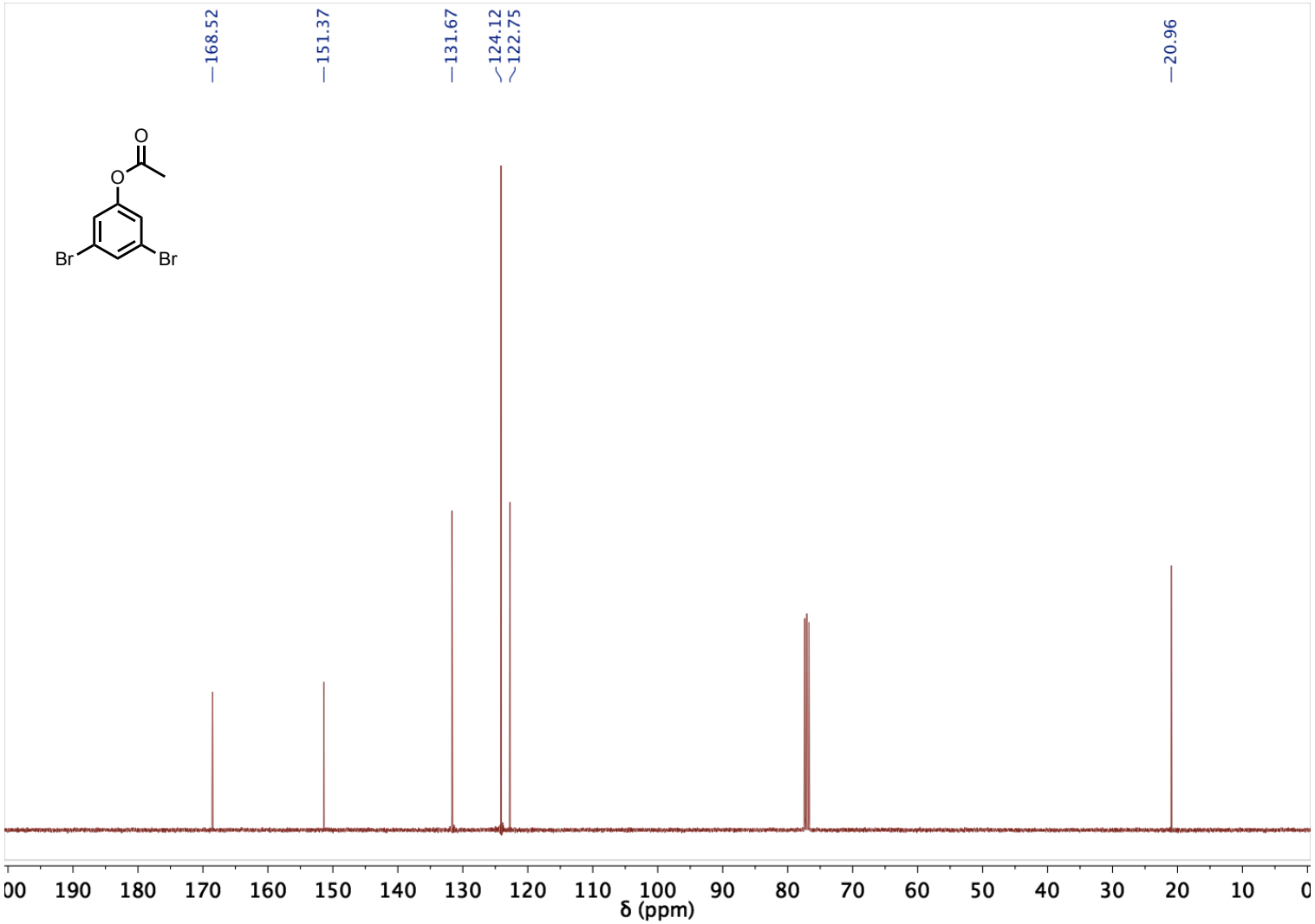
^{13}C NMR (101 MHz, CDCl3): δ 168.5, 151.4, 131.7, 124.1, 122.8, 21.0;

FT-IR (ATR): 3081, 1771, 1566, 1418, 1223, 933, 747 ν_{max}/cm^{-1}.

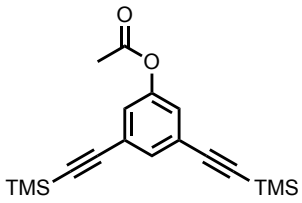
^{1}H NMR (400 MHz, $CDCl_3$) compound 9



^{13}C NMR (101 MHz, $CDCl_3$) compound 9



3,5-bis((trimethylsilyl)ethynyl)phenyl acetate (**10**)



Compound **9** (600 mg, 2.04 mmol), $Pd(PPh_3)_4$ (236 mg, 0.204 mmol) and CuI (39.0 mg, 0.204 mmol) were dissolved in toluene (6 mL) and Et_3N (6 mL). Nitrogen was bubbled through the solution for 20 min and TMSA (707 µL, 5.10 mmol) was added. The reaction was heated to 110 °C by microwave irradiation for 30 min. The reaction was filtered through celite and washed through with EtOAc (30 mL). The solution was washed with 1M HCl (3 × 30mL), dried ($MgSO_4$) and the solvent was removed by rotary evaporation under reduced pressure to yield a brown slid (900 mg). This oil was separated by flash chromatography (EtOAc:40-60 pet. ether, 1:19) to yield the desired compound **10** as a white powder (576 mg, 1.75 mmol, 86% yield). The spectroscopic data matches previously reported literature.[3]

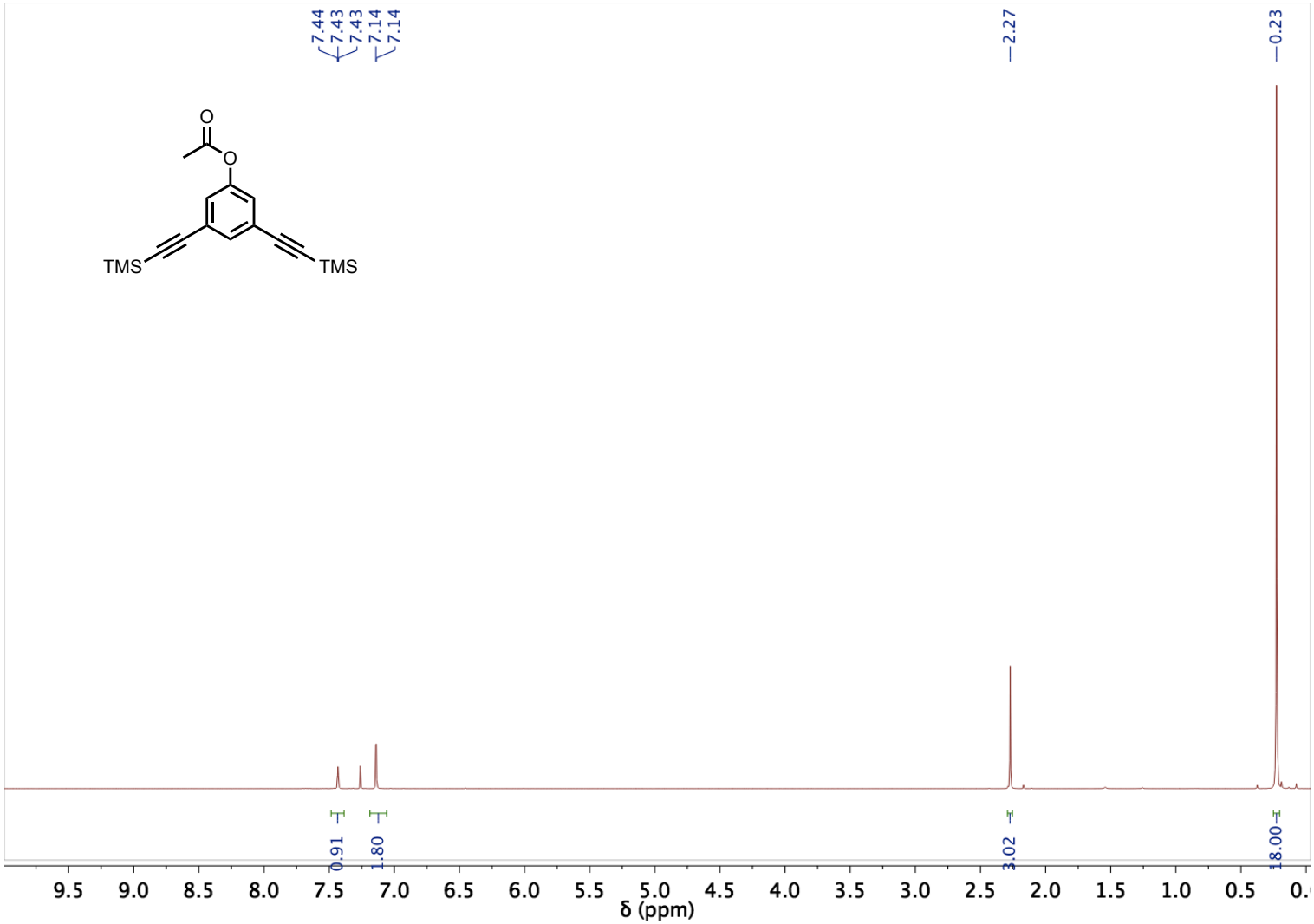
Melting Point: 95.0-96.6 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (t, *J* = 1.5 Hz, 1H), 7.14 (d, *J* = 1.5 Hz, 2H), 2.27 (s, 3H), 0.23 (s, 18H).

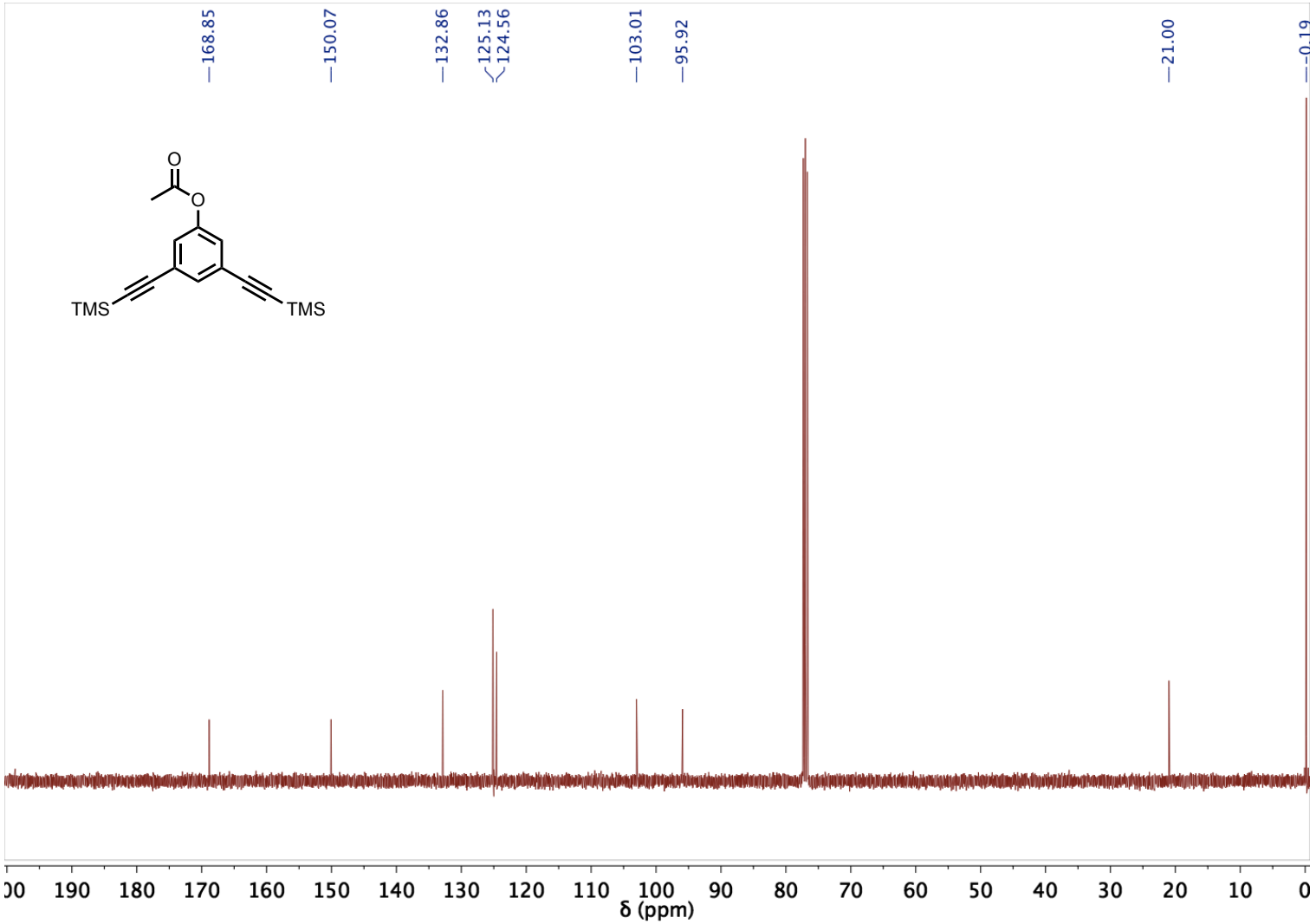
^{13}C NMR (101 MHz, $CDCl_3$): δ 168.9, 150.1, 132.9, 125.1, 124.6, 103.0, 95.9, 21.0, -0.2.

FT-IR (ATR): 2960, 2159, 1773, 1195, 840 ν_{max}/cm^{-1}.

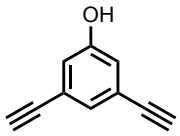
^{1}H NMR (400 MHz, $CDCl_3$) compound 10



^{13}C NMR (101 MHz, $CDCl_3$) compound 10



3,5-diethynylphenol (**11**)



Compound **10** (116 mg, 0.350 mmol) and $NaHCO_3$ (148 mg, 1.77 mmol) were dissolved in MeOH (1 mL), THF (1 mL) and water (2 mL). The reaction was stirred overnight at 55 °C. The reaction was cooled to room temperature and water (10 mL) was added. The aqueous solution was extracted with Et_2O (6 × 10 mL). The combined organic extracted were dried ($MgSO_4$) and solvent removed by rotary evaporation under reduced pressure yielding an orange oil (99.5 mg). This oil was separated by flash chromatography (EtOAc:40-60 pet. ether, 1:4) to yield the desired compound **11** as an off-white powder (48.5 mg, 0.34 mmol, 97% yield). The spectroscopic data matches previously reported literature.[3]

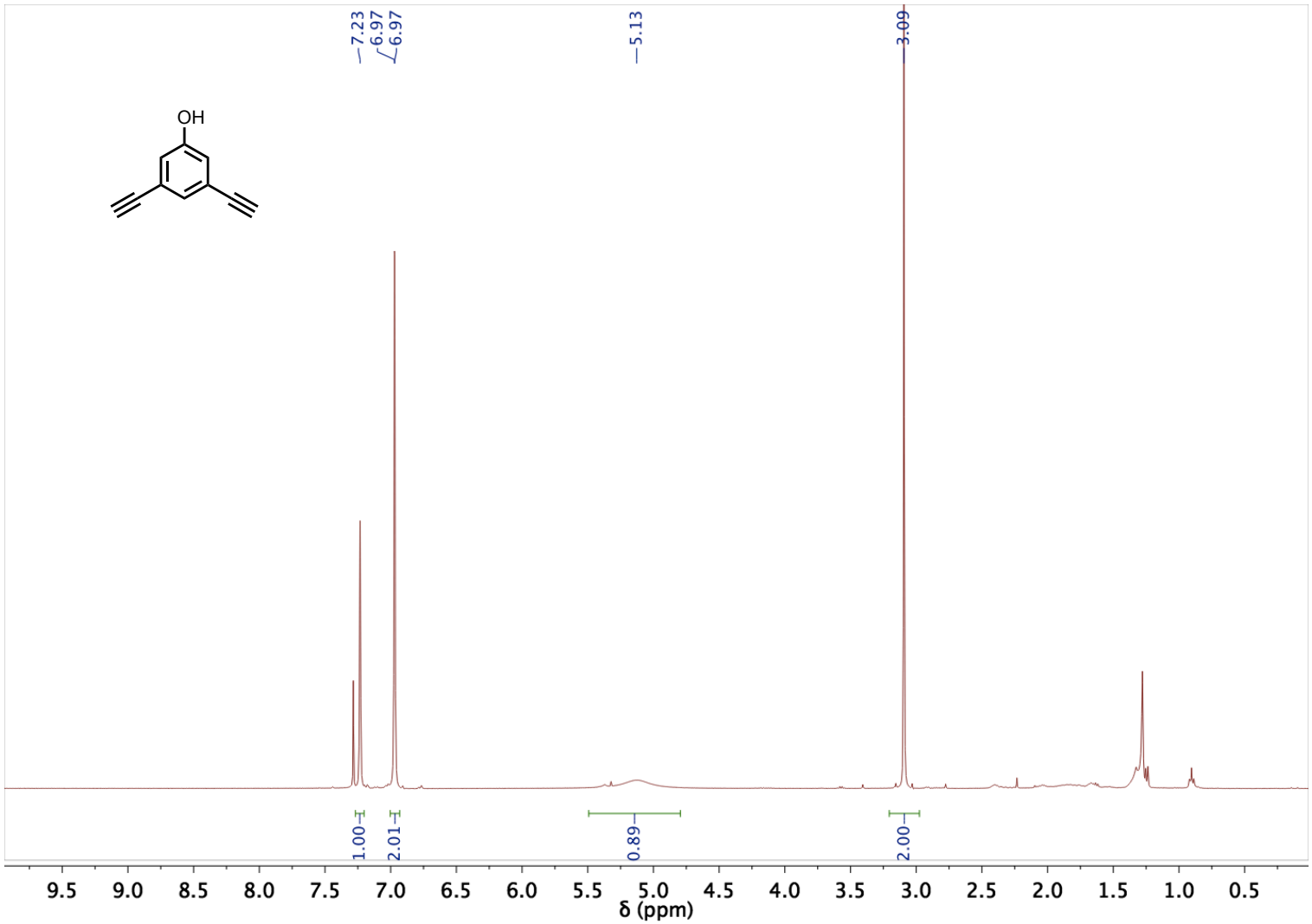
Melting Point: 83.7-84.7.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (s, 1H), 6.97 (s, 2H), 5.13 (bs, 1H), 3.09 (s, 2H).

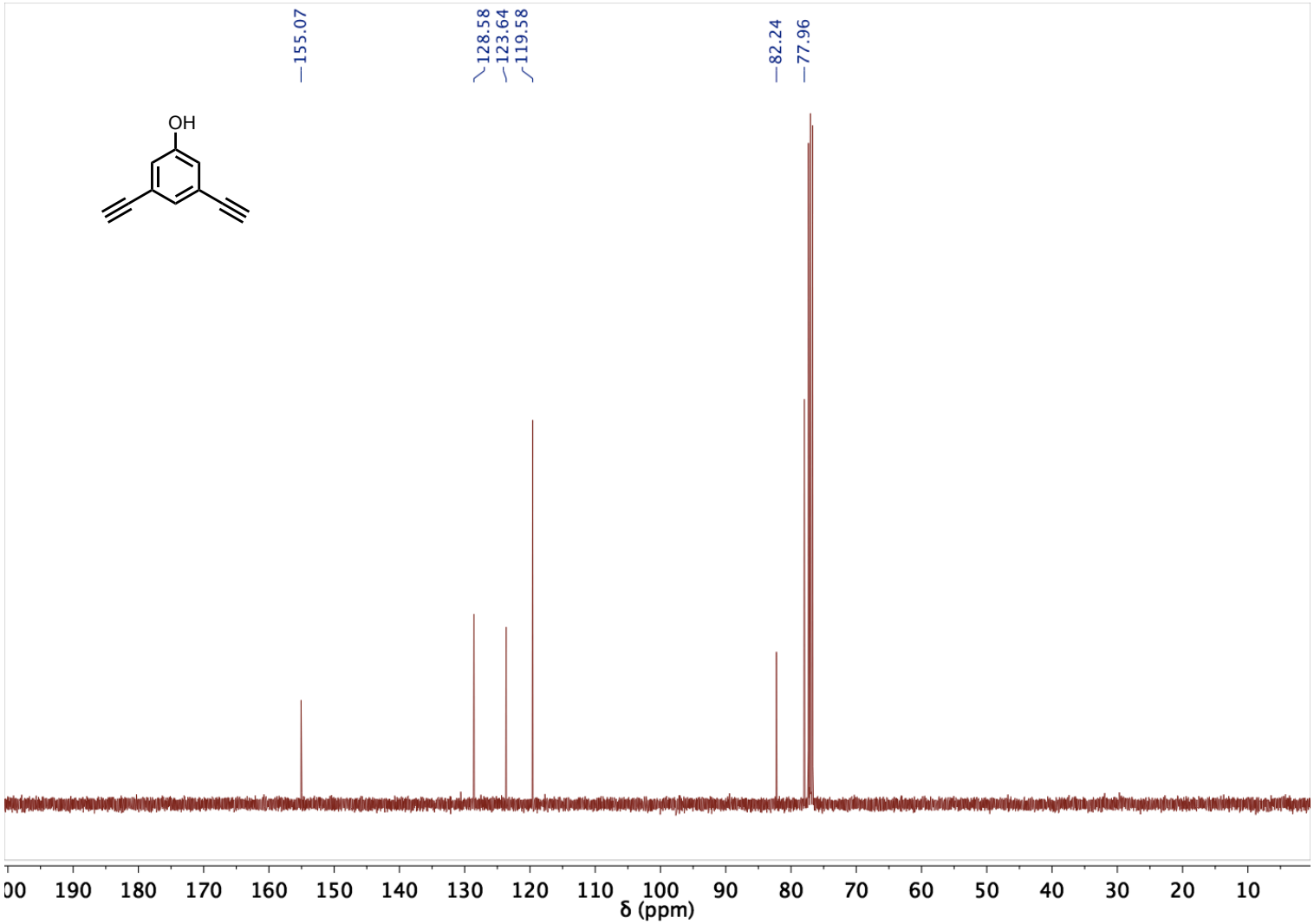
^{13}C NMR (101 MHz, $CDCl_3$): δ 155.1, 128.6, 123.6, 119.6, 82.2, 78.0.

FT-IR (ATR): 3081, 1771, 1566, 933 ν_{max}/cm^{-1};

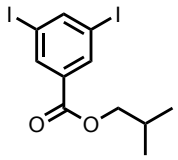
^{1}H NMR (400 MHz, $CDCl_3$) compound 11



^{13}C NMR (101 MHz, $CDCl_3$) compound 11



Isobutyl 3,5-diiodobenzoate (**13**)



3,5-diiodobenzoic acid (200 mg, 0.530 mmol), EDC•HCl (113 mg, 0.588 mmol) and DMAP (6.50 mg, 53.5 µmol) were dissolved in dry CH_2Cl_2 (5.3 mL) under N_2. ^{i}BuOH (0.101 µL, 1.07 mmol) was added and reaction stirred for 2 h. The reaction was washed with 1M HCl (20 mL), water (20 mL) and brine (20 mL). The organic solution was dried ($MgSO_4$) and solvent was removed by rotary evaporation under reduced pressure yielding a pink solid (199 mg). This solid was separated by flash chromatography (EtOAc:40-60 pet. ether, 1:19) to yield the desired compound **13** as a white crystal plates (130 mg, 0.313 mmol, 58% yield).

Melting Point: 56.5-57.8 °C.

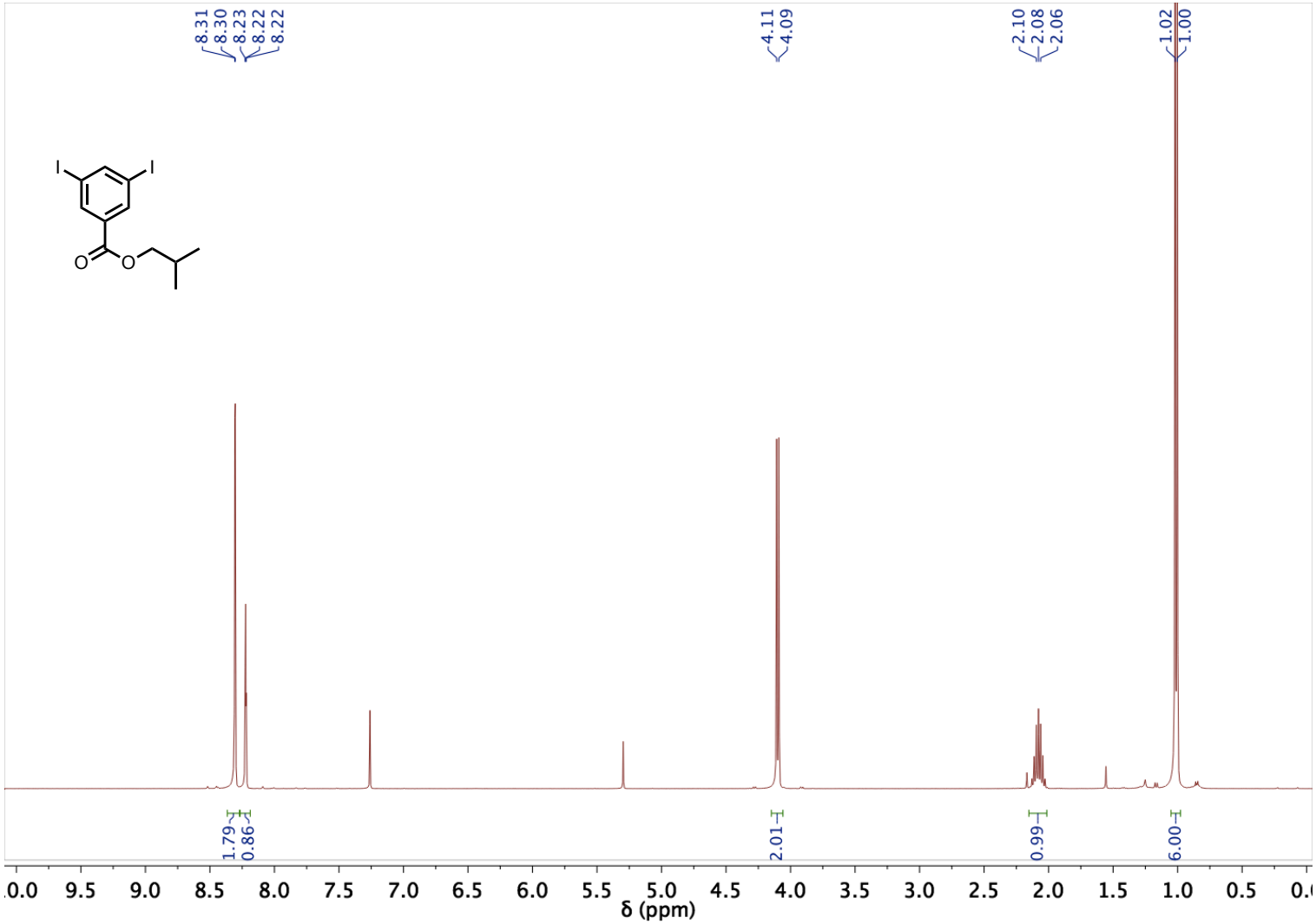
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (d, *J* = 1.5 Hz, 2H), 8.22 (t, *J* = 1.5 Hz, 1H), 4.10 (d, J = 6.5 Hz, 2H), 2.16 – 1.85 (m, 1H), 1.01 (d, J = 6.5 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 163.7, 149.1, 137.7, 133.7, 94.4 , 71.8, 27.8, 19.2.

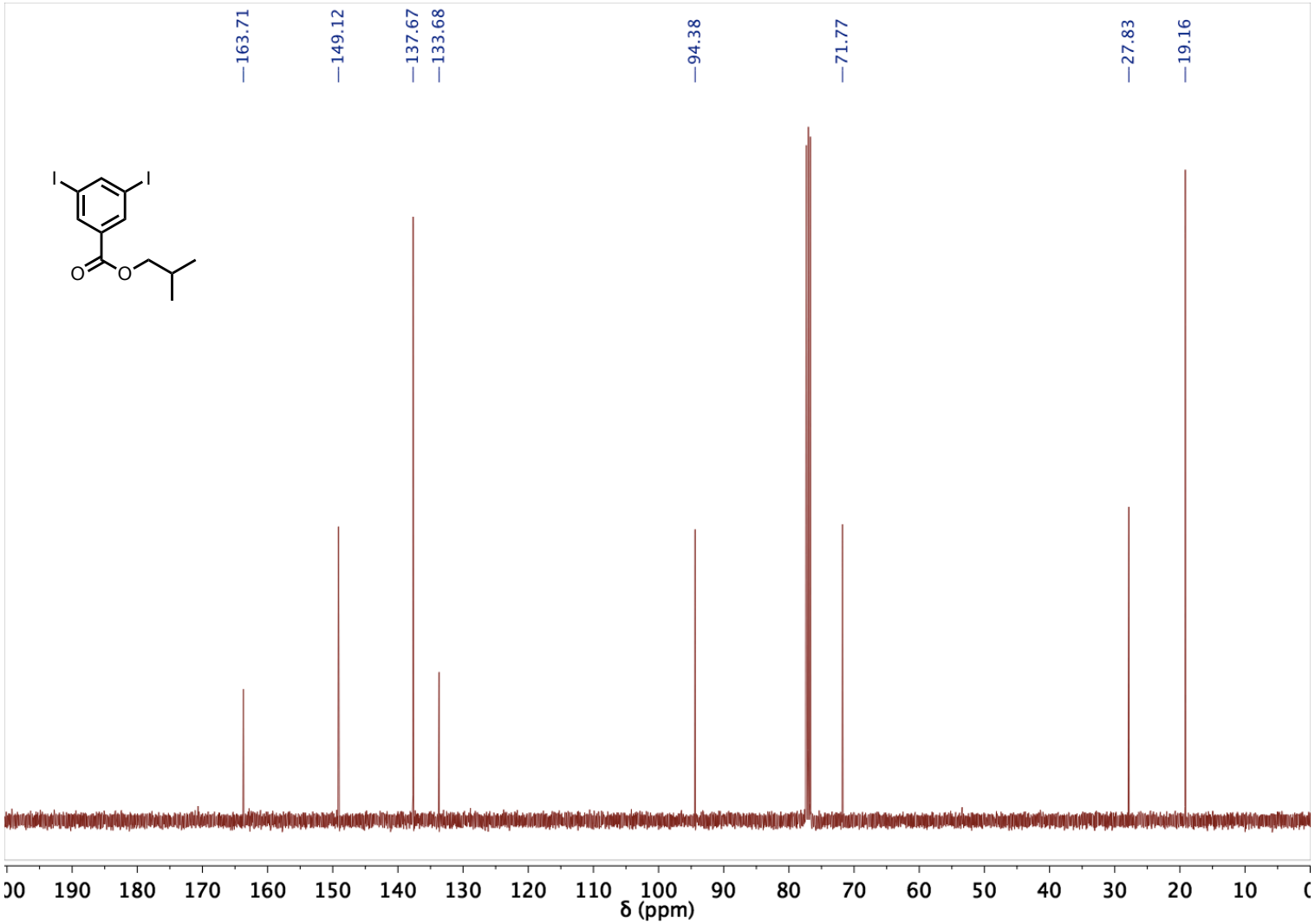
FT-IR (ATR): 2961, 2363, 1723, 1546, 1416, 1254, 1120, 982 ν_{max}/cm^{-1}.

HRMS (ES+): $C_{18}H_{24}OP$ calcd. 429.8927 found 429.8911, Δ = -3.72 ppm.

^{1}H NMR (400 MHz, $CDCl_3$) compound 13



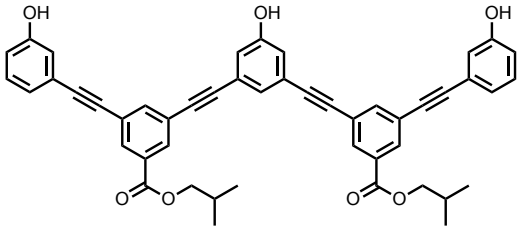
^{13}C NMR (101 MHz, $CDCl_3$) compound 13



Donor oligomerization (**14** - **17**)

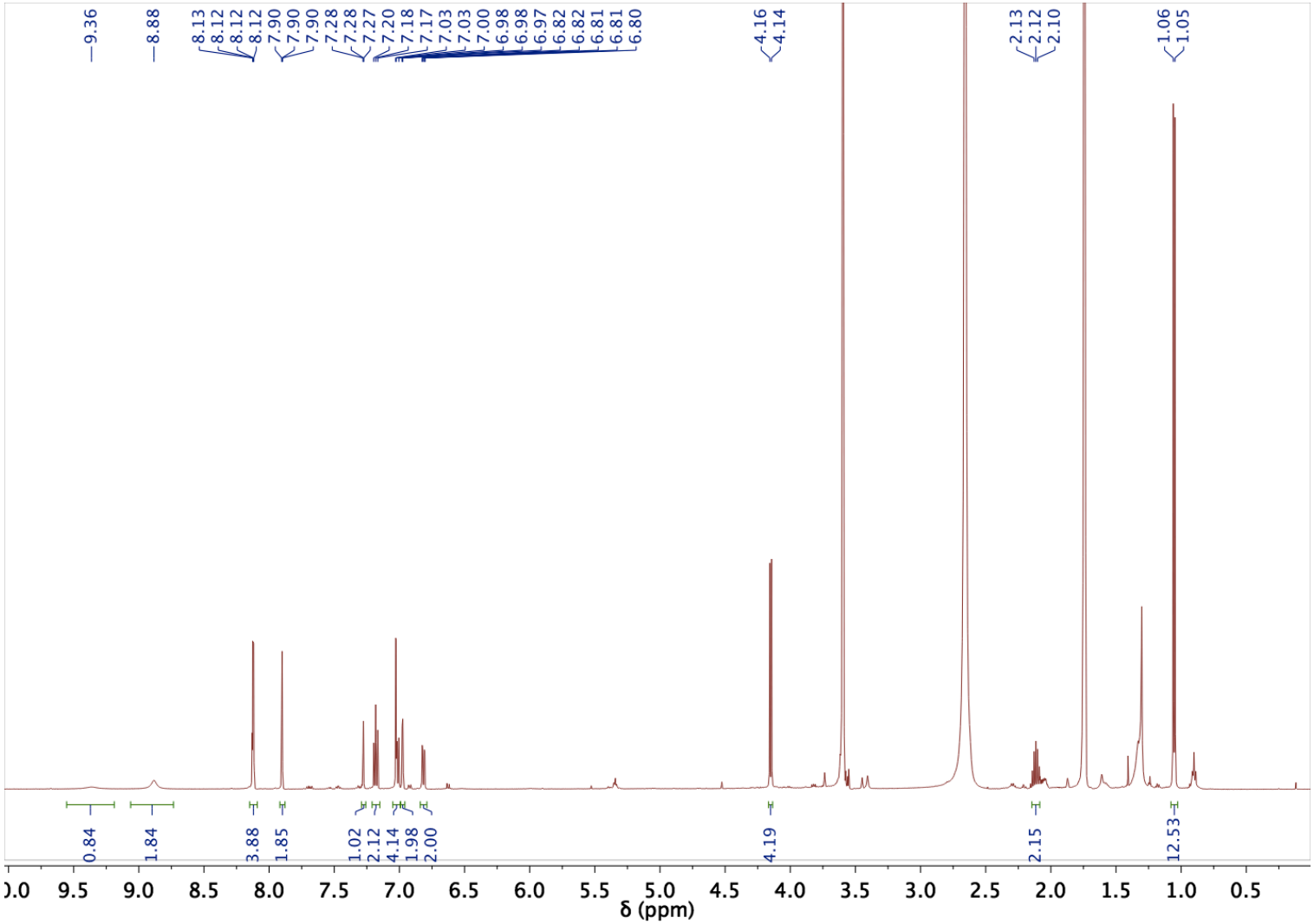
Compounds **1** (47.3 mg, 0.400 mmol), **11** (28.4 mg, 0.200 mmol) and **13** (172 mg, 0.400 mmol) were placed in a flask and degassed with N_2 for 30 min. $Pd_2(dba)_3$ (7.30 mg, 8.00 µmol) and CuI (1.50 mg, 8.00 µmol) and PPh_3 (10.5 mg, 40.0 µmol) were placed in a separate flask and degassed with N_2. Degassed Et_3N (167 µL, 1.20 mmol) was added and the contents of this flask transferred to the first using degassed toluene (8 mL). The reaction was stirred overnight at room temperature, in the dark under N_2. The solvent was removed by rotary evaporation under reduced pressure yielding a brown solid (186 mg). The sample was dissolved in DMSO and sonicated, before filtering. Preparative HPLC separation of the oligomerisation mixture was completed using a HIRBP-6988 prep column (250 × 25 mm, 5 µm particle size) with a water/THF solvent system (THF: 58% for 21 min, 65% for 31 min) at 15 mL min^{-1}.

Donor 3-mer (**14**)

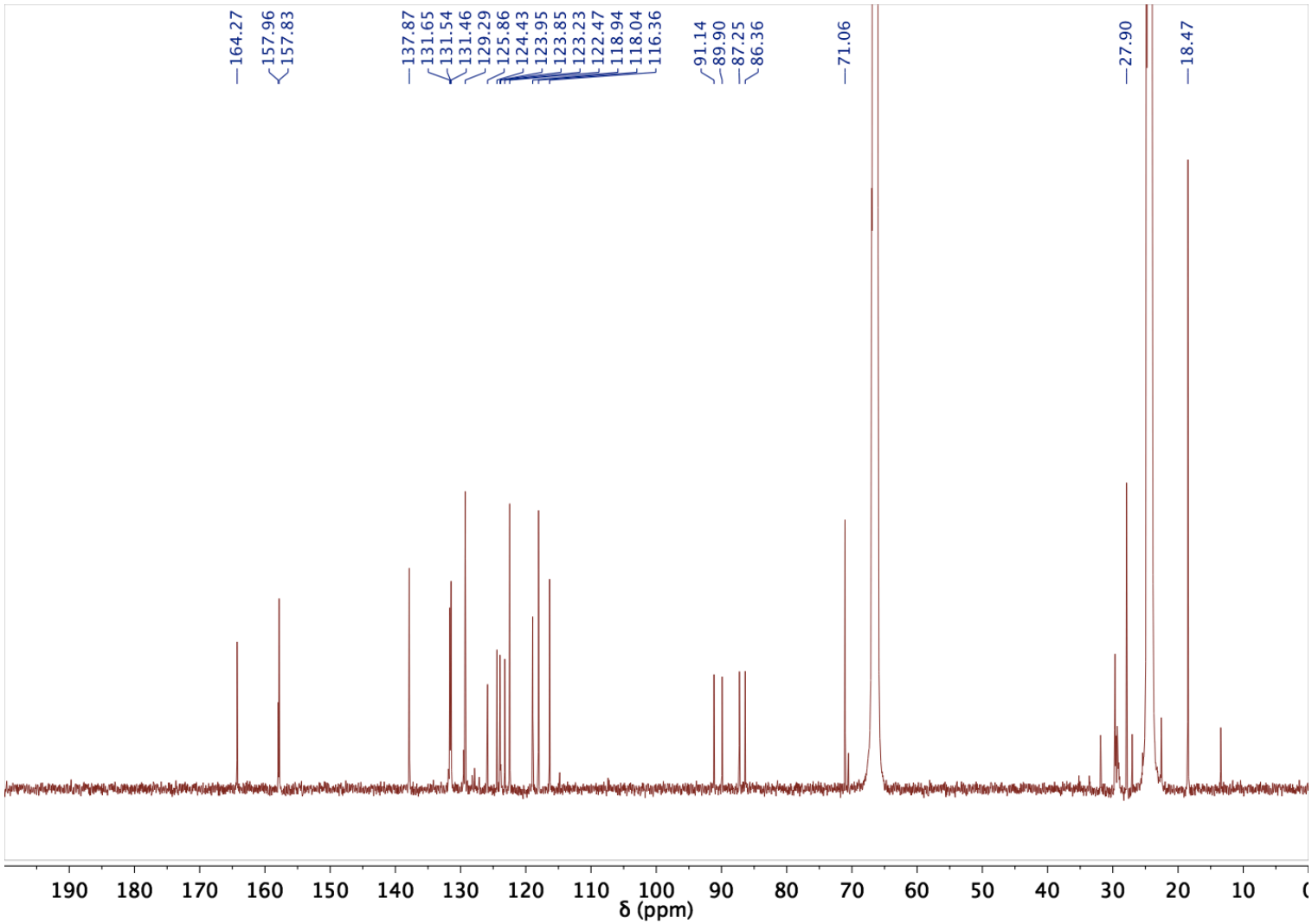


^{1}H NMR (500 MHz, THF-d$_8$): δ 9.36 (bs, 1H), 8.88 (bs, 2H), 8.14 – 8.11 (m, 4H), 7.90 (t, *J* = 1.5 Hz, 2H), 7.28 (t, *J* = 1.5 Hz, 1H), 7.18 (t, *J* = 8.0 Hz, 2H), 7.06 – 6.99 (m, 4H), 6.99 – 6.96 (m, 2H), 6.89 – 6.77 (m, 2H), 4.15 (d, J = 6.5 Hz, 4H), 2.14 – 2.10 (m, 2H), 1.05 (d, J = 6.5 Hz, 12H).
^{13}C NMR (126 MHz, THF-d$_8$): δ 165.1, 158.7, 158.6, 138.6, 132.4, 132.3, 132.2, 130.1, 126.6, 125.2, 124.7, 124.6, 124.0, 123.2, 119.7, 118.8, 117.1, 92.0, 90.7, 88.0, 87.1, 71.8, 28.7, 19.2.
FT-IR (ATR): 3412 (br), 2221, 1700, 1591, 1579, 1283, 1242 ν_{max}/cm^{-1}.
HRMS (ES+): $C_{48}H_{38}O_7$ calcd. 727.2690 found 727.2658, Δ = -4.46 ppm.

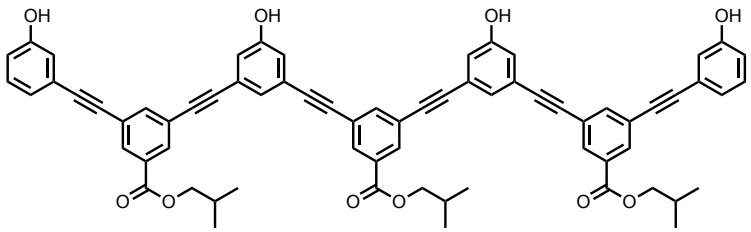
^{1}H NMR (500 MHz, THF-d$_{8}$) compound 14



^{13}C NMR (126 MHz, THF-d_8) compound 14



Donor 4-mer (**15**)



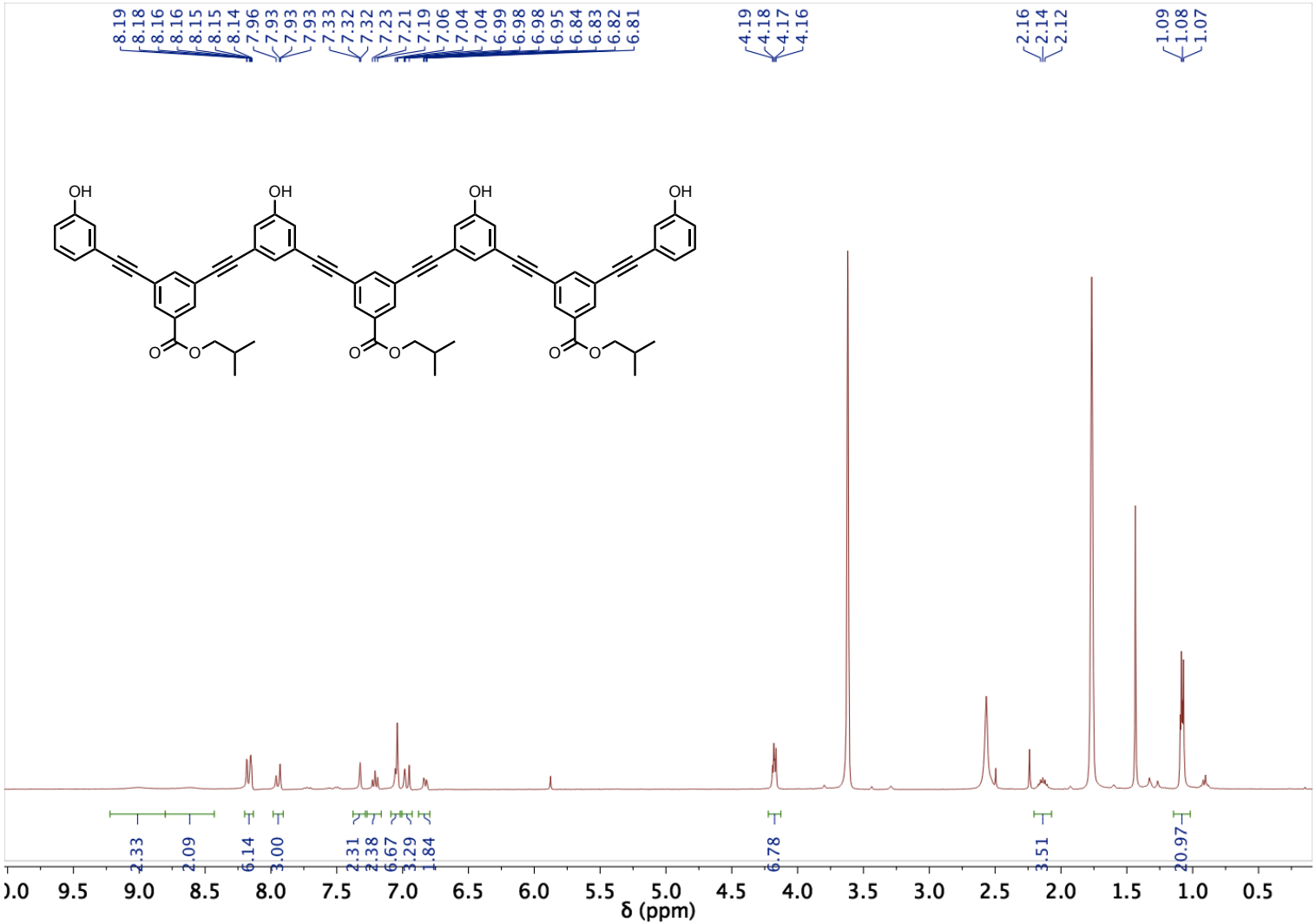
^{1}H NMR (500 MHz, THF-d$_8$): δ 9.80 (bs, 2H), 9.30 (bs, 2H), 8.15 (d, *J* = 1.5 Hz, 2H) 8.13 – 8.10 (m, 4H), 7.94 (t, *J* = 1.5 Hz, 1H), 7.90 (t, *J* = 1.5 Hz, 2H), 7.28 (t, *J* = 1.5 Hz, 2H), 7.18 (t, *J* = 8.0 Hz, 2H), 7.06 – 6.99 (m, 6H), 6.99 – 6.96 (m, 2H), 6.89 – 6.77 (m, 2H), 4.15 (d, J = 6.5 Hz, 6H), 2.14 – 2.10 (m, 3H), 1.05 (d, J = 6.5 Hz, 18H).

^{13}C NMR (126 MHz, THF-d$_8$): δ 165.1, 165.0, 159.0, 158.8, 138.7, 138.6, 132.5, 132.4, 132.4, 132.3, 132.2, 130.0, 126.4, 125.3, 124.8, 124.7, 124.5, 124.5, 124.0, 123.0, 119.9, 118.9, 117.2, 92.1, 90.9, 90.8, 87.9, 87.9, 87.0, 71.8, 28.7, 19.2.

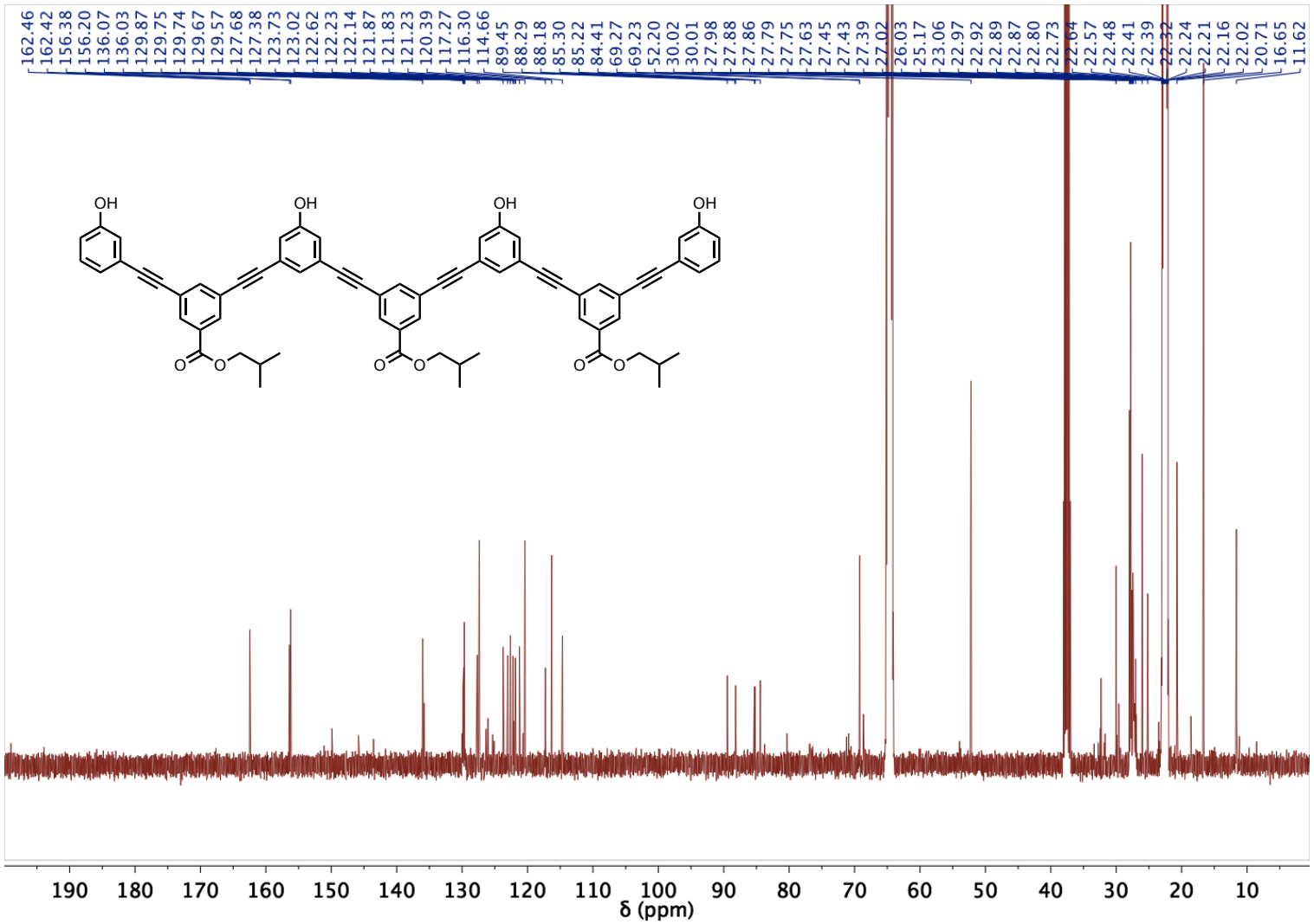
FT-IR (ATR): 3392 (br), 2925, 2226, 1721, 1591, 1560, 1282, 1239 ν_{max}/cm^{-1}.

HRMS (ES+): $C_{69}H_{58}O_{10}$ calcd. 1046.4030 found 1046.4003, Δ = -2.58 ppm.

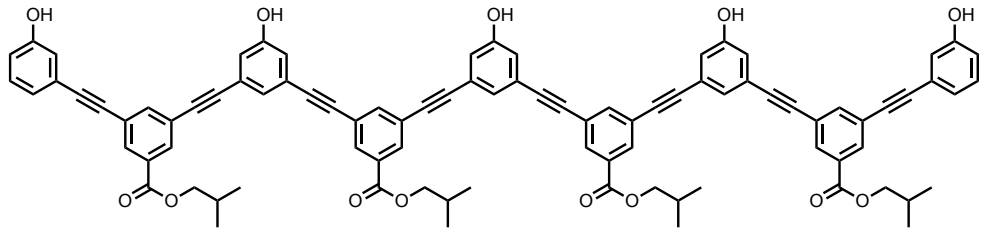
^{1}H NMR (500 MHz, THF-d$_8$) compound 15



^{13}C NMR (126 MHz, THF-d_8) compound 15



Donor 5-mer (**16**)



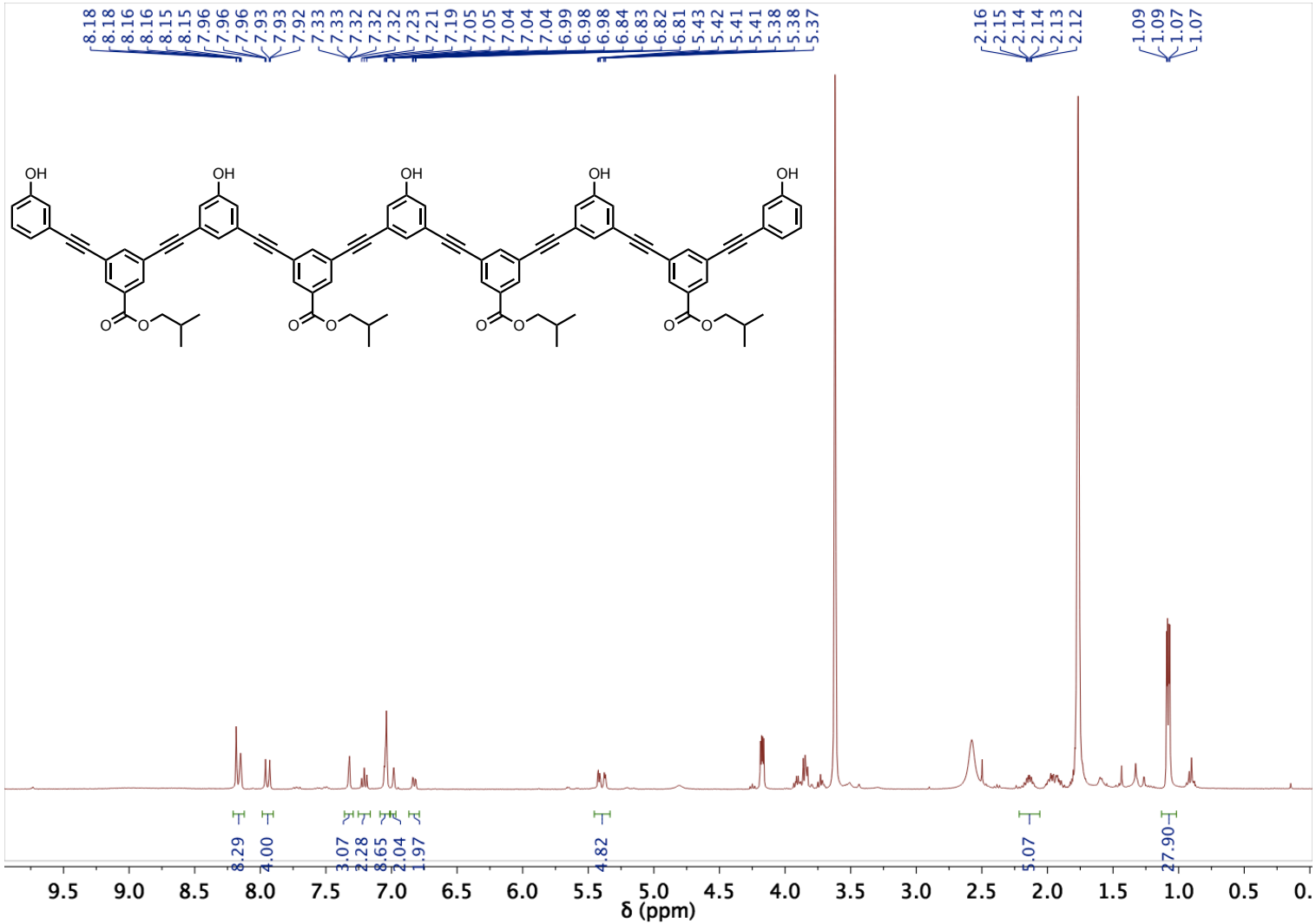
^{1}H NMR (500 MHz, THF-d$_8$): δ 9.03 (bs, 3H), 8.65 (bs, 2H), 8.16 (d, *J* = 1.5 Hz, 4H) 8.13 – 8.10 (m, 4H), 7.94 (t, *J* = 1.5 Hz, 2H), 7.90 (t, *J* = 1.5 Hz, 2H), 7.32-7.29 (m, 3H), 7.18 (t, *J* = 8.0 Hz, 2H), 7.06 – 6.99 (m, 8H), 6.99 – 6.96 (m, 2H), 6.89 – 6.77 (m, 2H), 4.15 (d, J = 6.5 Hz, 8H), 2.14 – 2.10 (m, 4H), 1.05 (d, J = 6.5 Hz, 24H).

^{13}C NMR (126 MHz, THF-d$_8$): δ 165.0, 165.0, 158.6, 158.5, 138.7, 138.6, 132.6, 132.5, 132.4, 132.3, 132.3, 130.1, 126.8, 125.2, 124.8, 124.7, 124.7, 124.7, 124.1, 123.4, 119.7, 118.9, 117.1, 91.9, 90.7, 90.7, 88.2, 88.1, 87.2, 71.8, 28.7, 19.2.

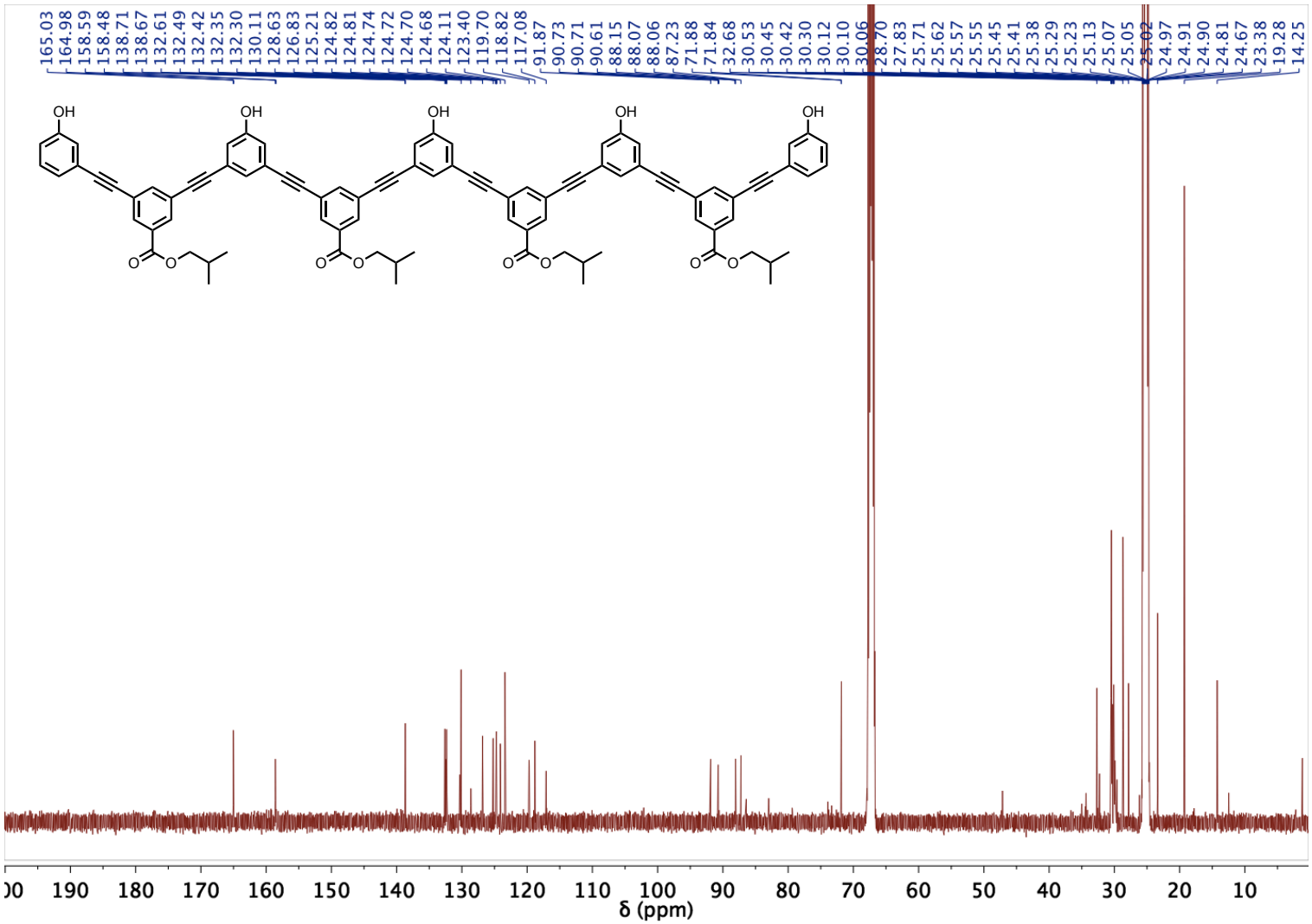
FT-IR (ATR): 3453 (br), 2958, 2269, 1720, 1703 1591, 1580, 1237 ν_{max}/cm^{-1}.

MS (ES+): m/z (%) = 678.0 (100) [M-2H$^+$], 1358.5 (50) [M-H$^+$].

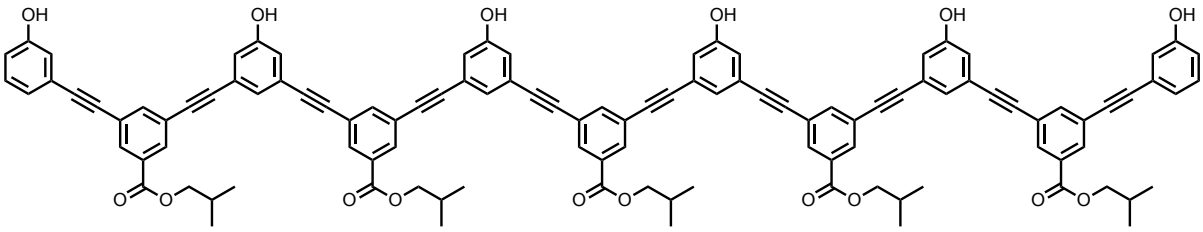
^{1}H NMR (500 MHz, THF-d$_{8}$) compound 16



^{13}C NMR (126 MHz, THF-d_8) compound 16



Donor 6-mer (**17**)



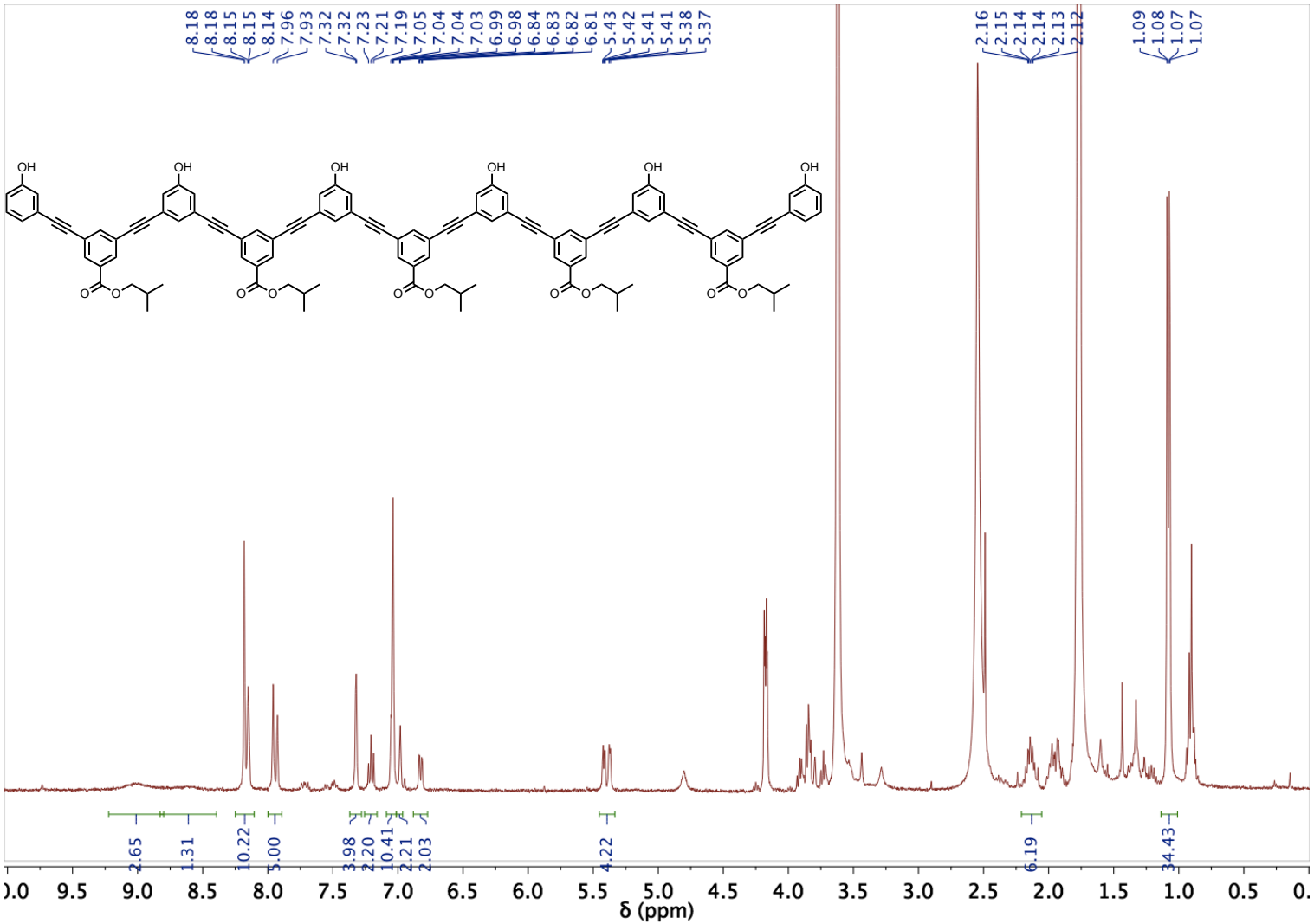
^{1}H NMR (500 MHz, THF-d$_8$): δ 9.03 (bs, 4H), 8.61 (bs, 2H), 8.16 (d, *J* = 1.5 Hz, 6H), 8.13 – 8.10 (m, 4H), 7.94 (t, *J* = 1.5 Hz, 3H), 7.90 (t, *J* = 1.5 Hz, 2H), 7.32-7.29 (m, 4H), 7.18 (t, *J* = 8.0 Hz, 2H), 7.06 – 6.99 (m, 10H), 6.99 – 6.96 (m, 2H), 6.89 – 6.77 (m, 2H), 4.15 (d, J = 6.5 Hz, 10H), 2.14 – 2.10 (m, 5H), 1.05 (d, J = 6.5 Hz, 30H).

^{13}C NMR (126 MHz, THF-d$_8$): δ 165.0, 165.0, 158.6, 158.5, 138.7, 138.6, 132.6, 132.5, 132.4, 132.3, 132.3, 130.1, 126.8, 125.2, 124.8, 124.7, 124.7, 124.7, 124.1, 123.4, 119.7, 118.9, 117.1, 91.9, 90.7, 90.7, 88.2, 88.1, 87.2, 71.8, 28.7, 19.2.

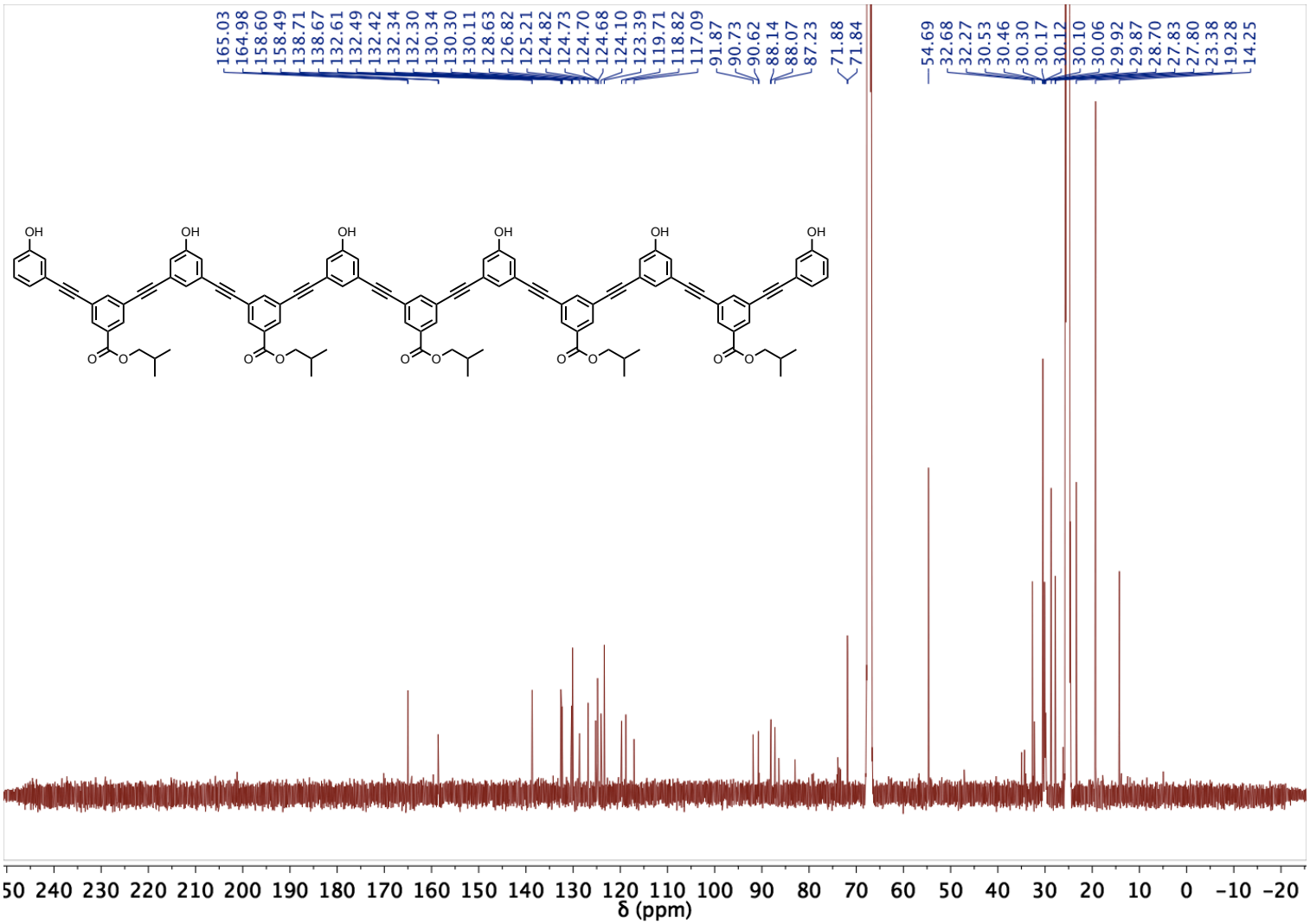
FT-IR (ATR): 3411 (br), 2925, 2110, 1699, 1581, 1288 ν_{max}/cm^{-1}.

MS (ES+): m/z (%) = 836.3 (100) [M-2H$^+$], 1673.6 (20) [M-H$^+$].

^{1}H NMR (500 MHz, THF-d$_{8}$) compound 17



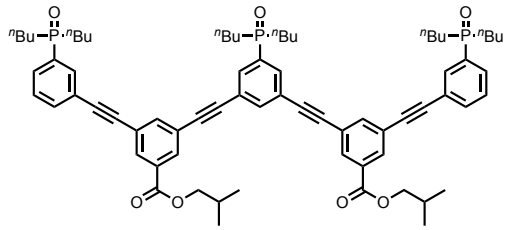
^{13}C NMR (126 MHz, THF-d_8) compound 17



Acceptor oligomerization (**18** - **22**)

Compounds **2** (105 mg, 0.400 mmol), **7** (57.3 mg, 0.200 mmol) and **13** (172 mg, 0.400 mmol) were placed in a flask and degassed with N_2 for 30 min. $Pd_2(dba)_3$ (7.30 mg, 8.00 µmol) and CuI (1.50 mg, 8.00 µmol) and PPh_3 (10.5 mg, 40.0 µmol) were placed in a separate flask and degassed with N_2. Degassed Et_3N (167 µL, 1.20 mmol) was added and the contents of this flask transferred to the first using degassed toluene (8 mL). The reaction was stirred overnight at room temperature, in the dark under N_2. The solvent was removed by rotary evaporation under reduced pressure yielding a brown solid (260 mg). The sample was dissolved in EtOH and sonicated, before filtering. Preparative HPLC separation of the oligomerisation mixture was completed using a HIRBP-6988 prep column (250 × 25 mm, 5 µm particle size) with a water/THF solvent system (THF: 60% for 42 mins, 65% for 33 mins) at 15 mL min^{-1}.

Acceptor 3-mer (**18**)



^{1}H NMR (500 MHz, $CDCl_3$): δ 8.19-8.15 (m, 4H), 7.90 – 7.84 (m, 7H), 7.74-7.69 (m, 4H), 7.51 (td, *J* = 7.5, 2.5 Hz, 2H), 4.16 (d, J = 6.5 Hz, 4H), 2.14 – 2.10 (m, 2H), 2.07-1.81 (m, 12H), 1.71-1.55 (m, 6H), 1.49-1.35 (m, 18H), 1.06 (d, J = 6.5 Hz, 12H), 0.91-0.87 (m, 18H).

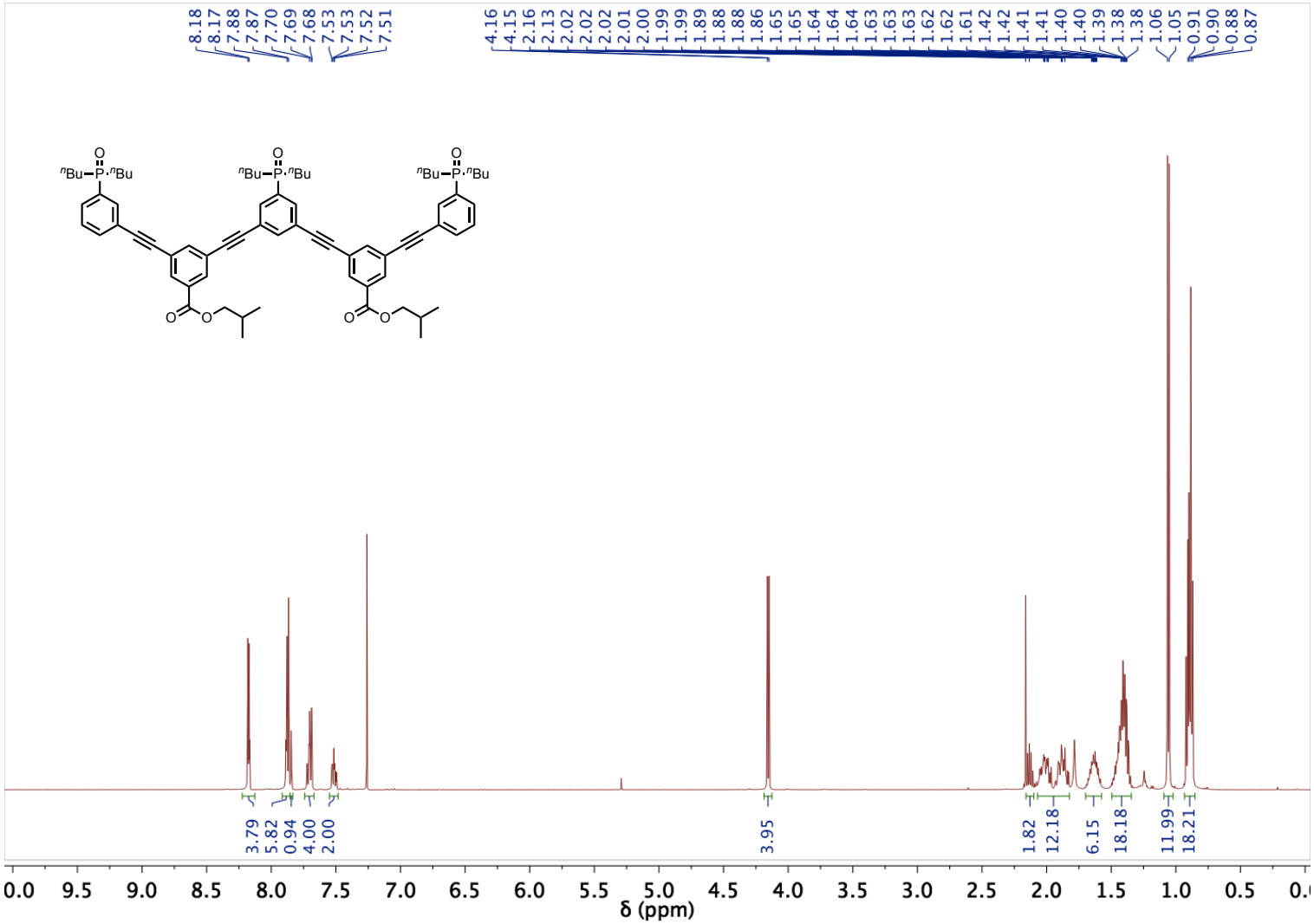
^{13}C NMR (126 MHz, $CDCl_3$): δ 165.1, 138.2, 137.0 (d, *J* = 3 Hz), 134.4, 134,4 (d, *J* = 88 Hz), 133.6 (d, *J* = 10 Hz), 133.6 (d, *J* = 89.5 Hz), 133.3 (d, *J* = 8 Hz), 132.7, 132.5, 131.5, 130.5 (d, *J* = 8 Hz), 128.8 (d, *J* = 11 Hz), 123.9, 123.8 (d, *J* = 13 Hz), 123.5, 123.3 (d, *J* = 12 Hz), 90.0, 89.6, 89.0, 88.8, 71.7, 29.7 (d, *J* = 69 Hz), 27.9, 24.1 (d, *J* = 14 Hz), 23.5 (d, *J* = 4 Hz), 19.3, 13.6.

^{31}P NMR (162 MHz, $CDCl_3$): δ 40.3, 40.1.

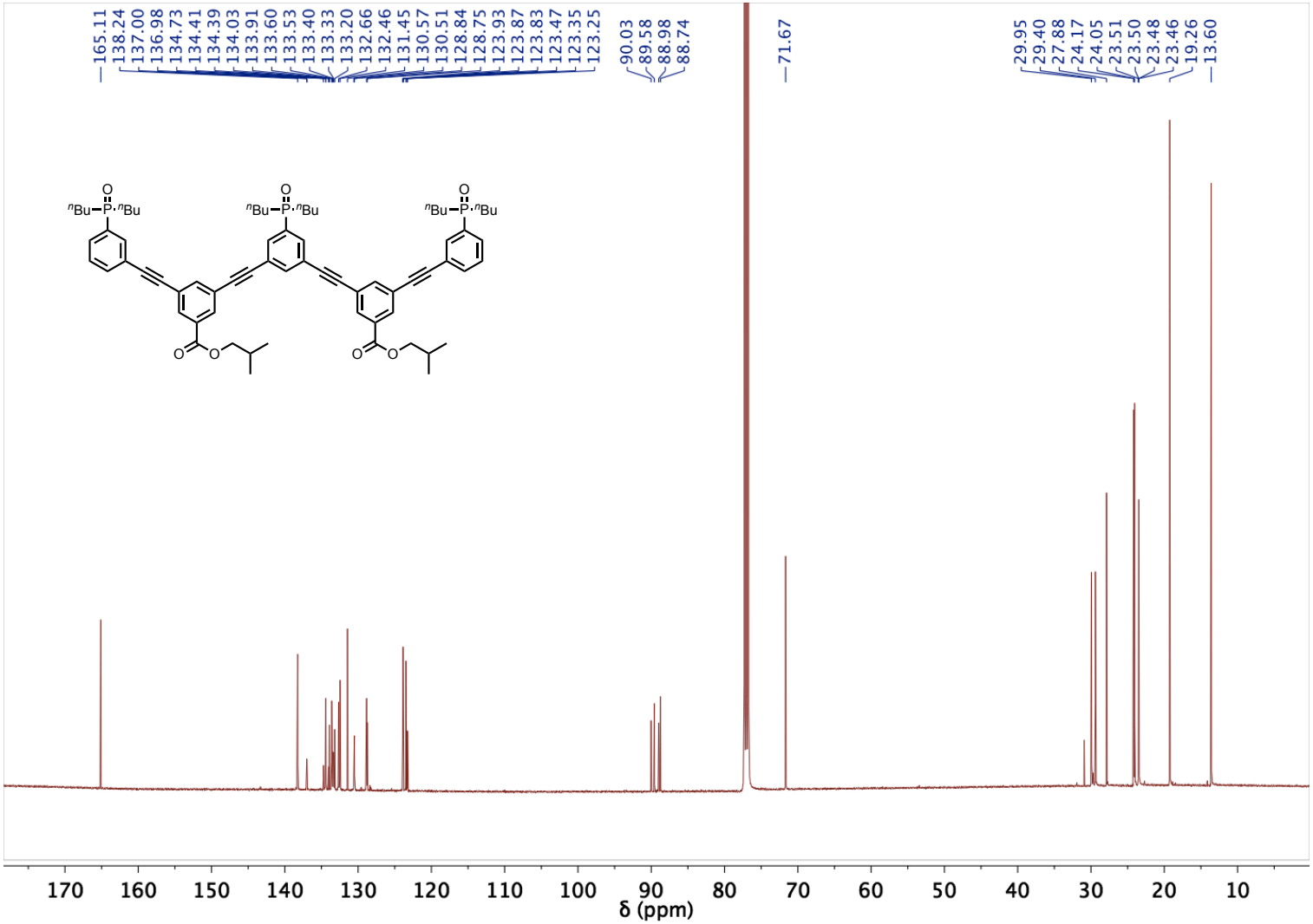
FT-IR (ATR): 2957, 2220, 1718, 1594, 1440, 1221, 1169 ν_{max}/cm^{-1}.

HRMS (ES+): $C_{72}H_{90}O_7P_3$ calcd. 1159.5894 found 1159.5886, Δ = -0.67 ppm.

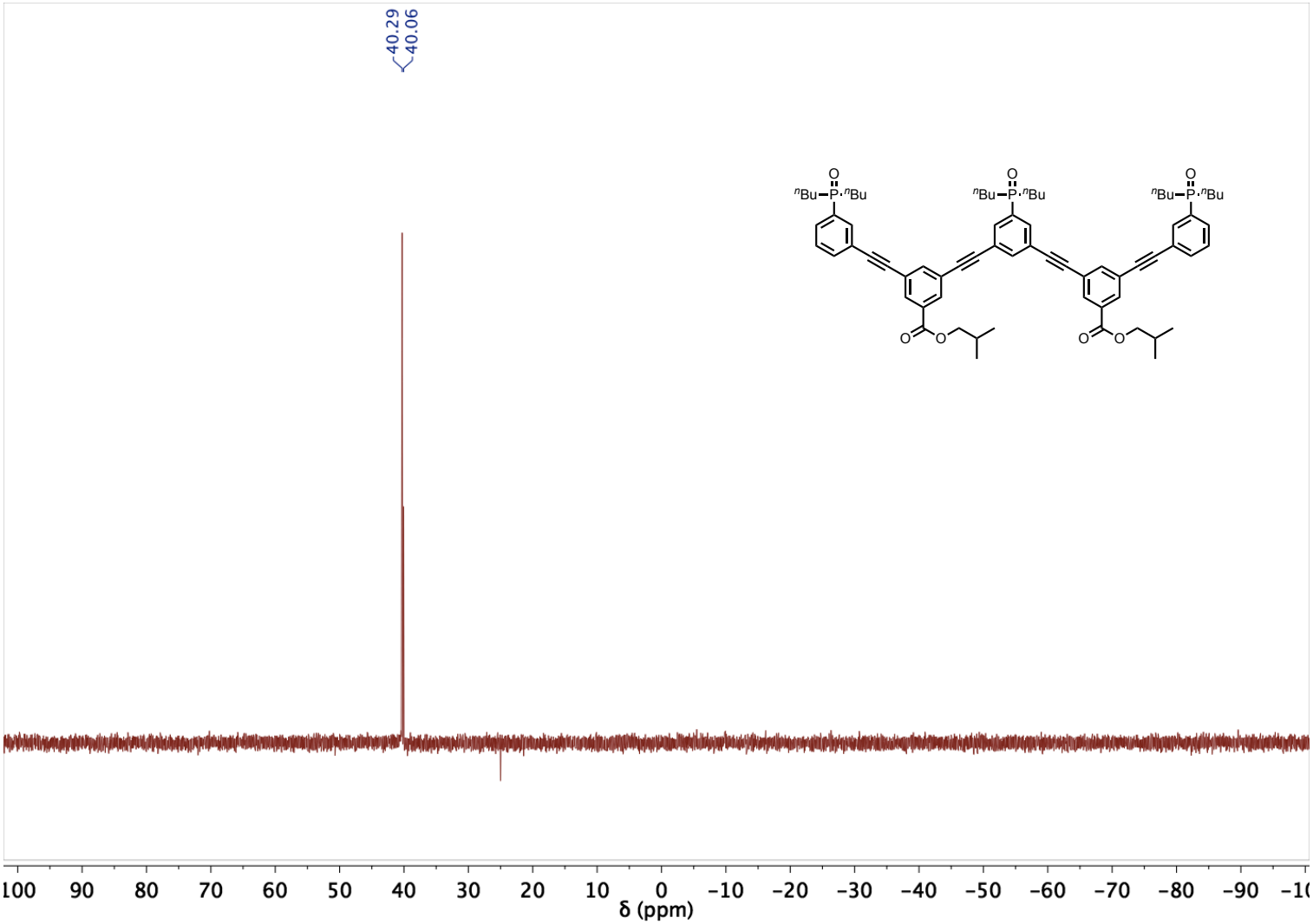
^{1}H NMR (500 MHz, $CDCl_3$) compound 18



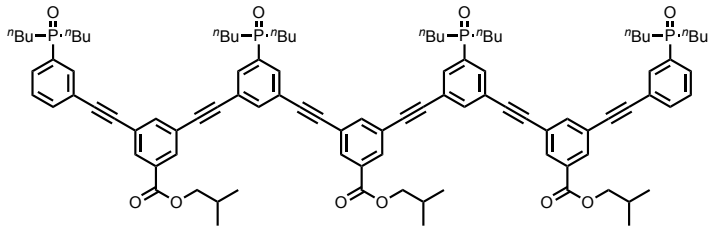
^{13}C NMR (126 MHz, $CDCl_3$) compound 18



^{31}P NMR (162 MHz, $CDCl_3$) compound 18



Acceptor 4-mer (**19**)



^{1}H NMR (500 MHz, $CDCl_3$): δ 8.20 (d, *J* = 1.5 Hz, 2H), 8.19-8.15 (m, 4H), 7.91 – 7.84 (m, 11H), 7.74-7.69 (m, 4H), 7.51 (td, *J* = 7.5, 2.5 Hz, 2H), 4.16 (d, J = 6.5 Hz, 6H), 2.14 – 2.10 (m, 3H), 2.07-1.81 (m, 16H), 1.71-1.55 (m, 8H), 1.49-1.35 (m, 24H), 1.06 (d, J = 6.5 Hz, 18H), 0.91-0.87 (m, 24H).

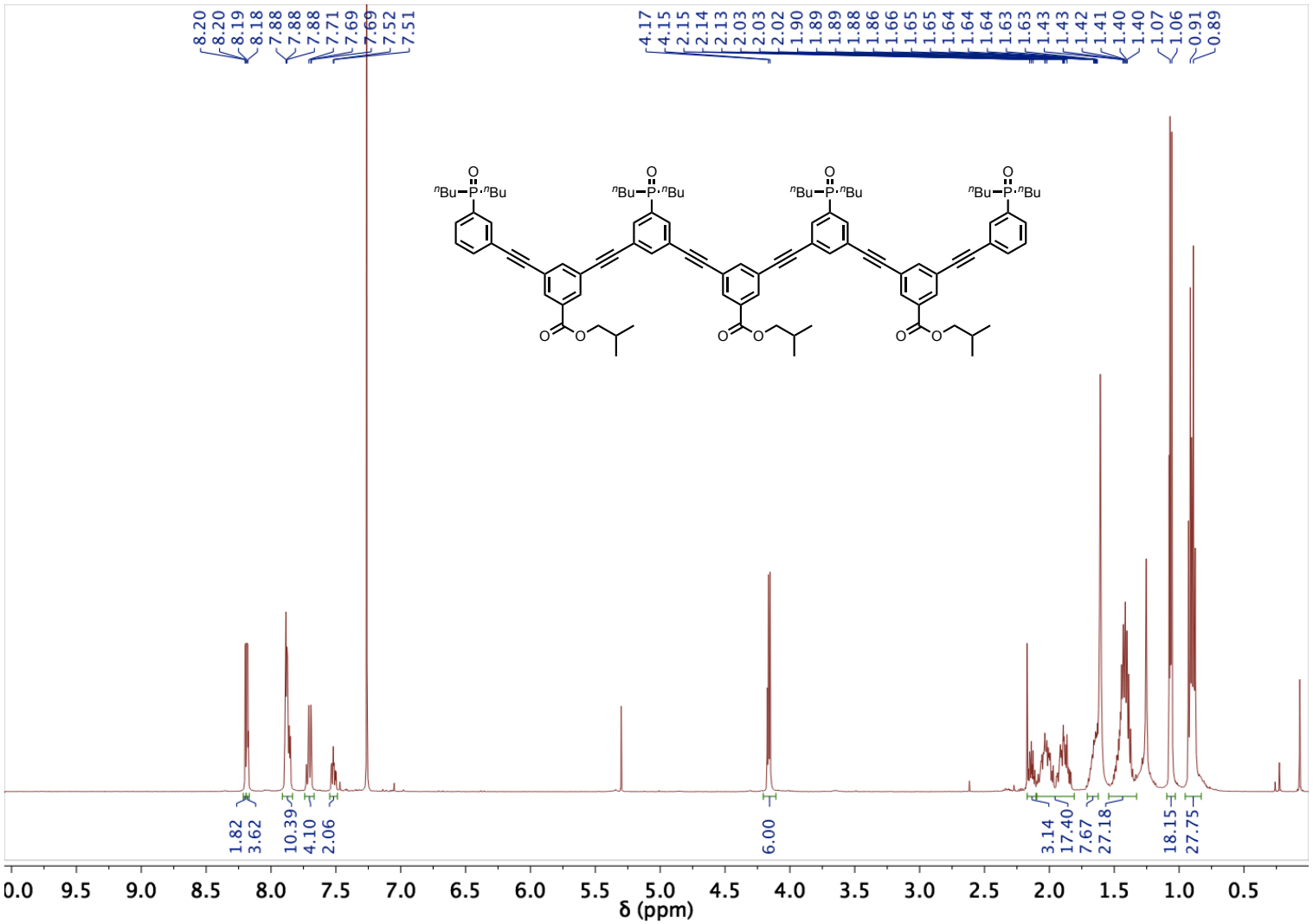
^{13}C NMR (126 MHz, $CDCl_3$): δ 165.1, 165.1, 138.3, 137.0 (d, *J* = 2 Hz), 134.4, 134,4 (d, *J* = 88 Hz), 133.6 (d, *J* = 9 Hz), 133.6 (d, *J* = 89 Hz), 133.3 (d, *J* = 8 Hz), 132.7, 132.7, 132.5, 131.5, 131.5, 130.5 (d, *J* = 8 Hz), 128.8 (d, *J* = 11 Hz), 123.9, 123.8 (d, *J* = 12 Hz), 123.6, 123.5, 123.3 (d, *J* = 12 Hz), 90.0, 89.6, 89.5, 89.1, 89.0, 88.8, 71.7, 29.7 (d, *J* = 68 Hz), 27.9, 24.1 (d, *J* = 15 Hz), 23.5 (d, *J* = 4 Hz), 19.3, 13.6.

^{31}P NMR (162 MHz, $CDCl_3$): δ 40.5, 40.2.

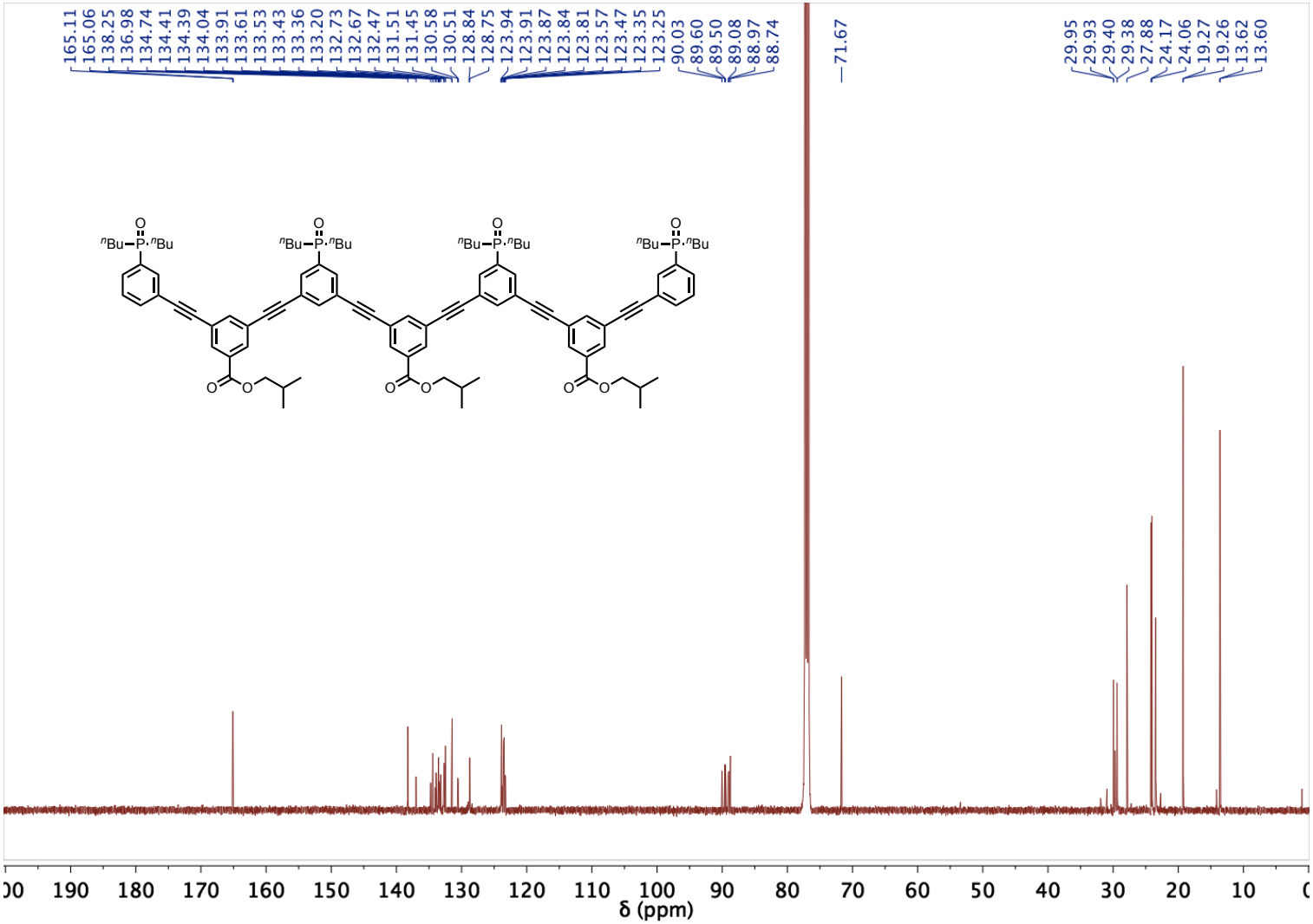
FT-IR (ATR): 2957, 2215, 1722, 1594, 1443, 1220, 1172 ν_{max}/cm^{-1};

HRMS (ES+): $C_{101}H_{123}O_{10}P_4$ calcd. 1642.7959 found 1642.7893, Δ = -4.00 ppm.

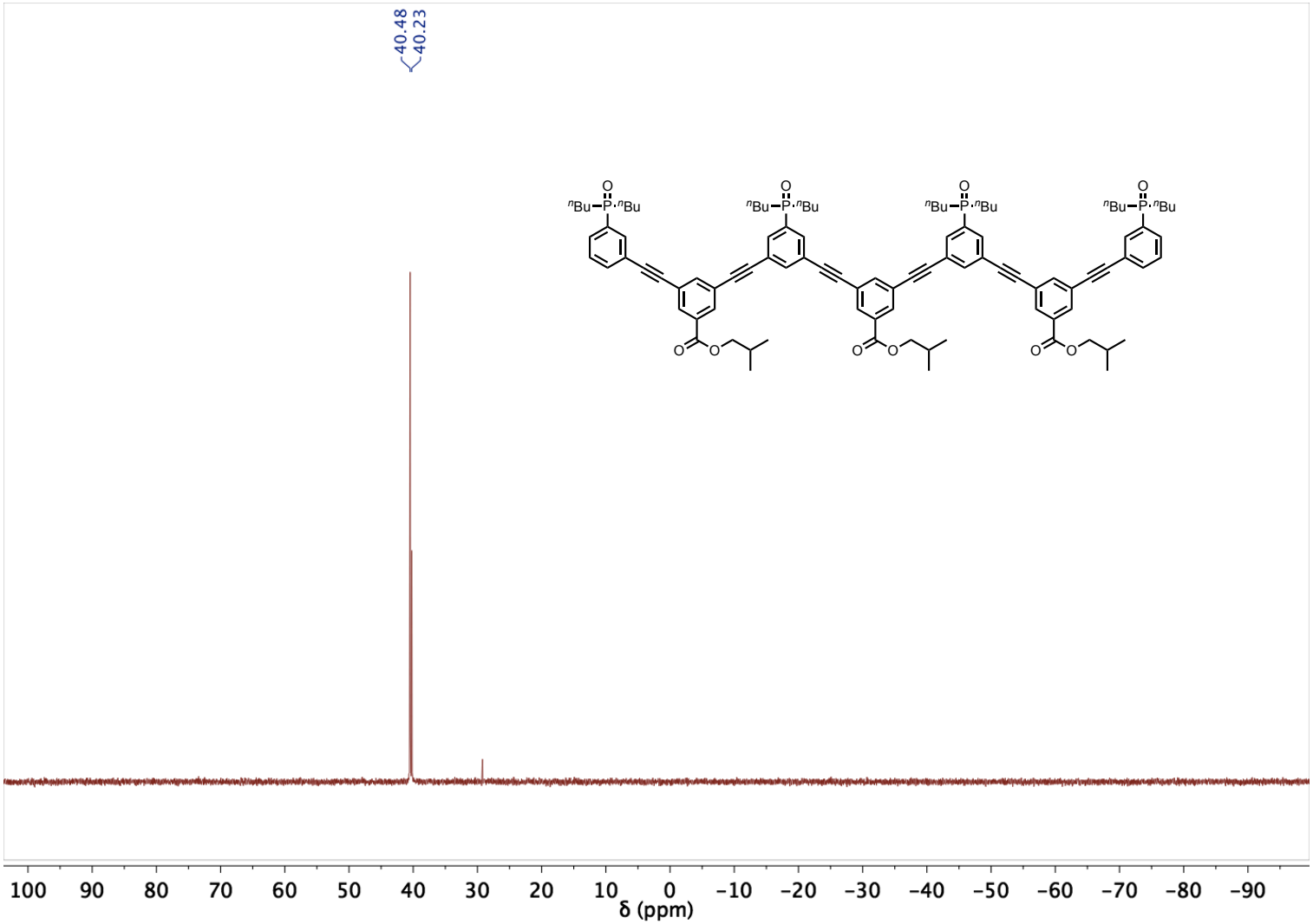
^{1}H NMR (500 MHz, $CDCl_3$) compound 19



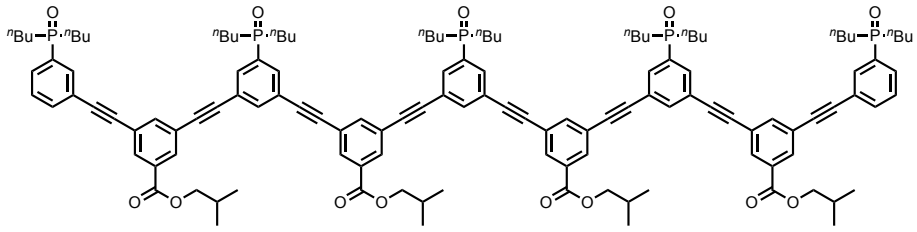
^{13}C NMR (126 MHz, $CDCl_3$) compound 19



^{31}P NMR (162 MHz, $CDCl_3$) compound 19



Acceptor 5-mer (**20**)



^{1}H NMR (500 MHz, $CDCl_3$): δ 8.20 (d, *J* = 1.5 Hz, 4H), 8.19-8.15 (m, 4H), 7.91 – 7.84 (m, 15H), 7.74-7.69 (m, 4H), 7.51 (td, *J* = 7.5, 2.5 Hz, 2H), 4.16 (d, J = 6.5 Hz, 8H), 2.14 – 2.10 (m, 4H), 2.07-1.81 (m, 20H), 1.71-1.55 (m, 10H), 1.49-1.35 (m, 30H), 1.06 (d, J = 6.5 Hz, 24H), 0.91-0.87 (m, 30H).

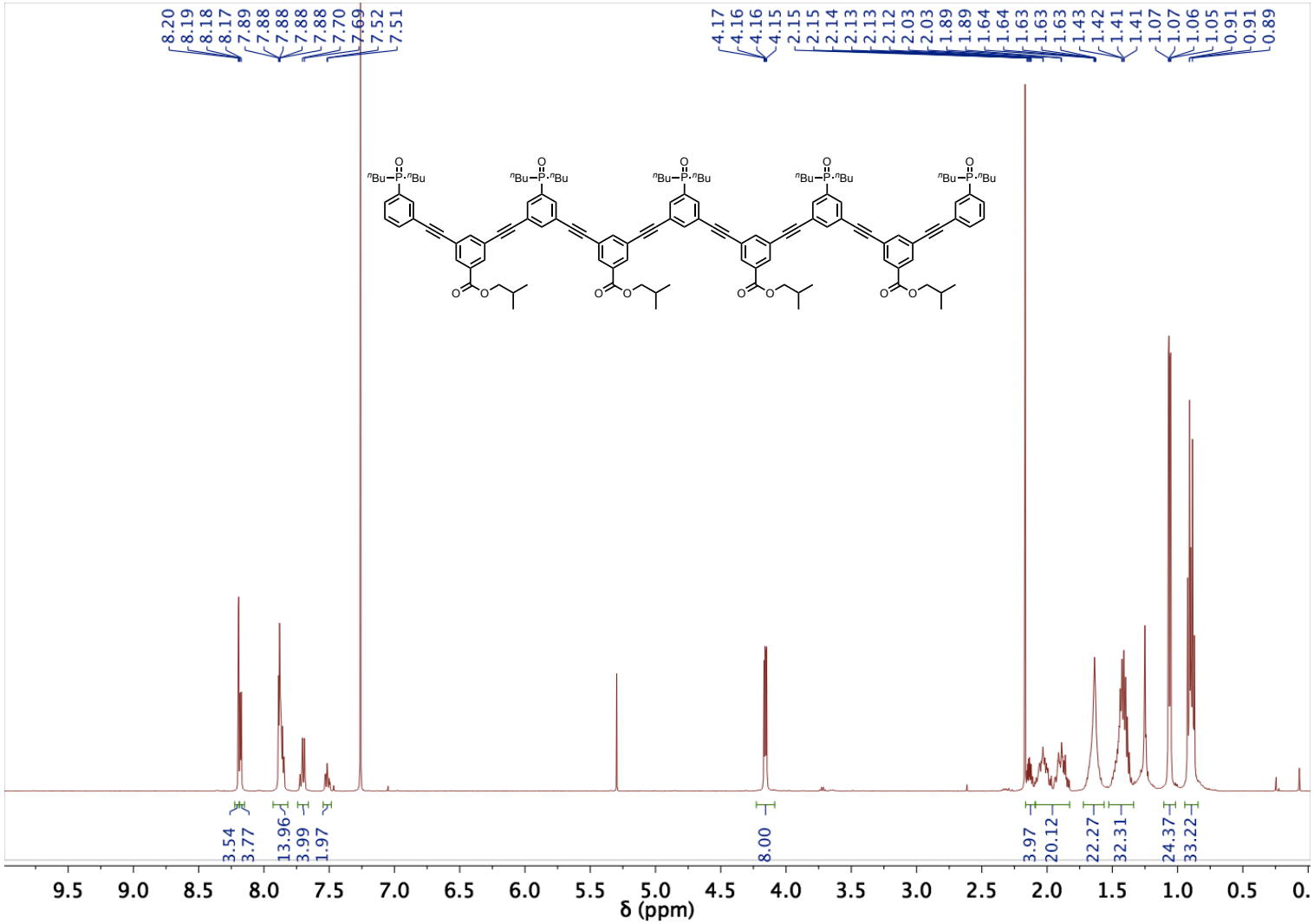
^{13}C NMR (126 MHz, $CDCl_3$): δ 165.1, 165.1, 138.3, 137.0 (d, *J* = 3 Hz), 134.4, 134,4 (d, *J* = 88 Hz), 133.6 (d, *J* = 9 Hz), 133.6 (d, *J* = 89 Hz), 133.3 (d, *J* = 8 Hz), 132.7, 132.7, 132.5, 131.5, 131.5, 130.5 (d, *J* = 8 Hz), 128.8 (d, *J* = 11 Hz), 123.9, 123.8 (d, *J* = 12.5 Hz), 123.6, 123.5, 123.3 (d, *J* = 13 Hz), 90.0, 89.6, 89.5, 89.1, 89.0, 88.8, 71.7, 29.7 (d, *J* = 68 H), 27.9, 24.1 (d, *J* = 14 Hz), 23.5 (d, *J* = 4 Hz) 19.3, 13.6.

^{31}P NMR (162 MHz, $CDCl_3$): δ 40.7, 40.4.

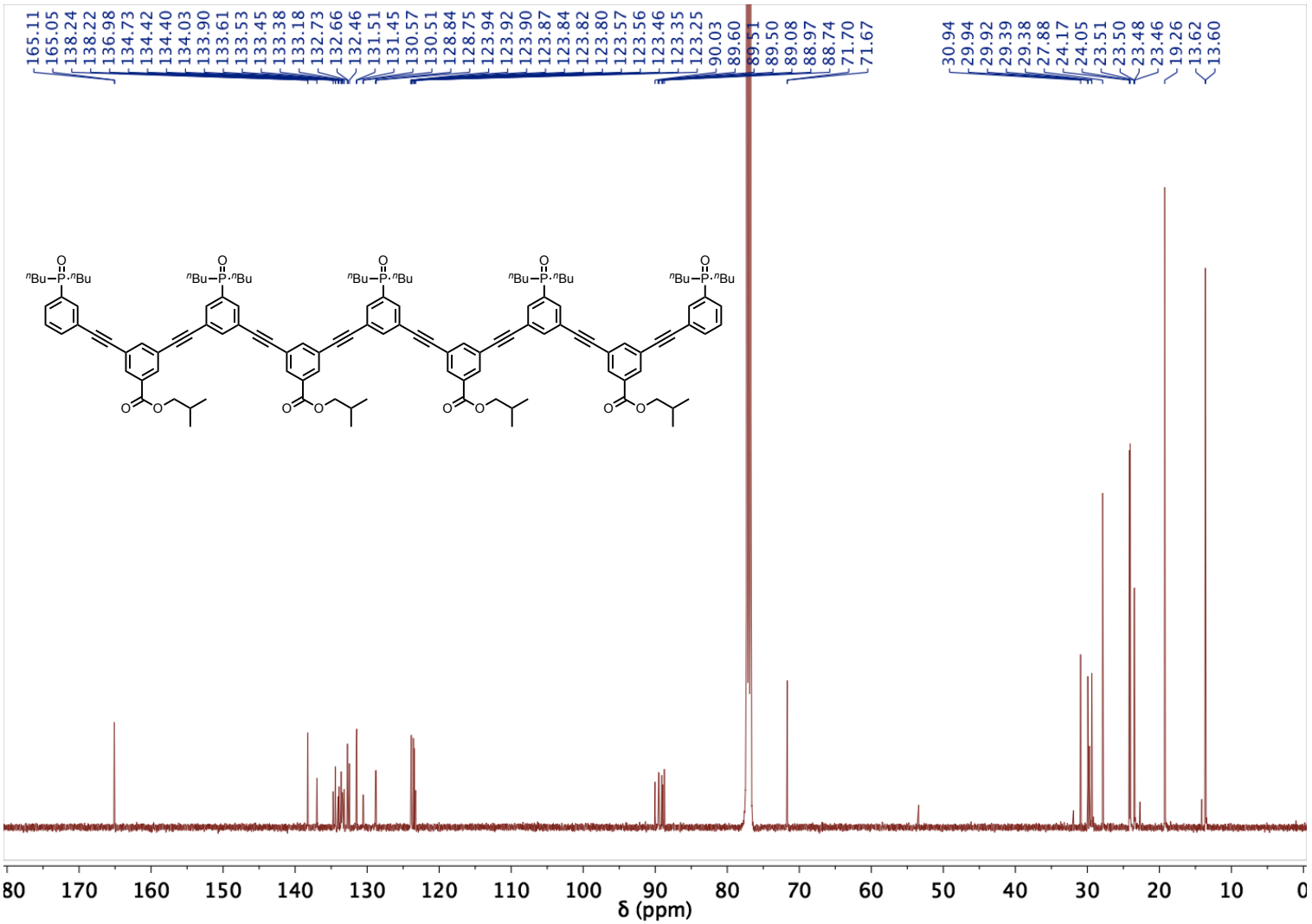
FT-IR (ATR): 2958, 2216, 1721, 1594, 1235, 1168, 726 ν_{max}/cm^{-1}.

HRMS (ES+): $C_{130}H_{155}O_{13}P_5$ calcd. 2102.0048 found 2101.9944, Δ = -4.97 ppm.

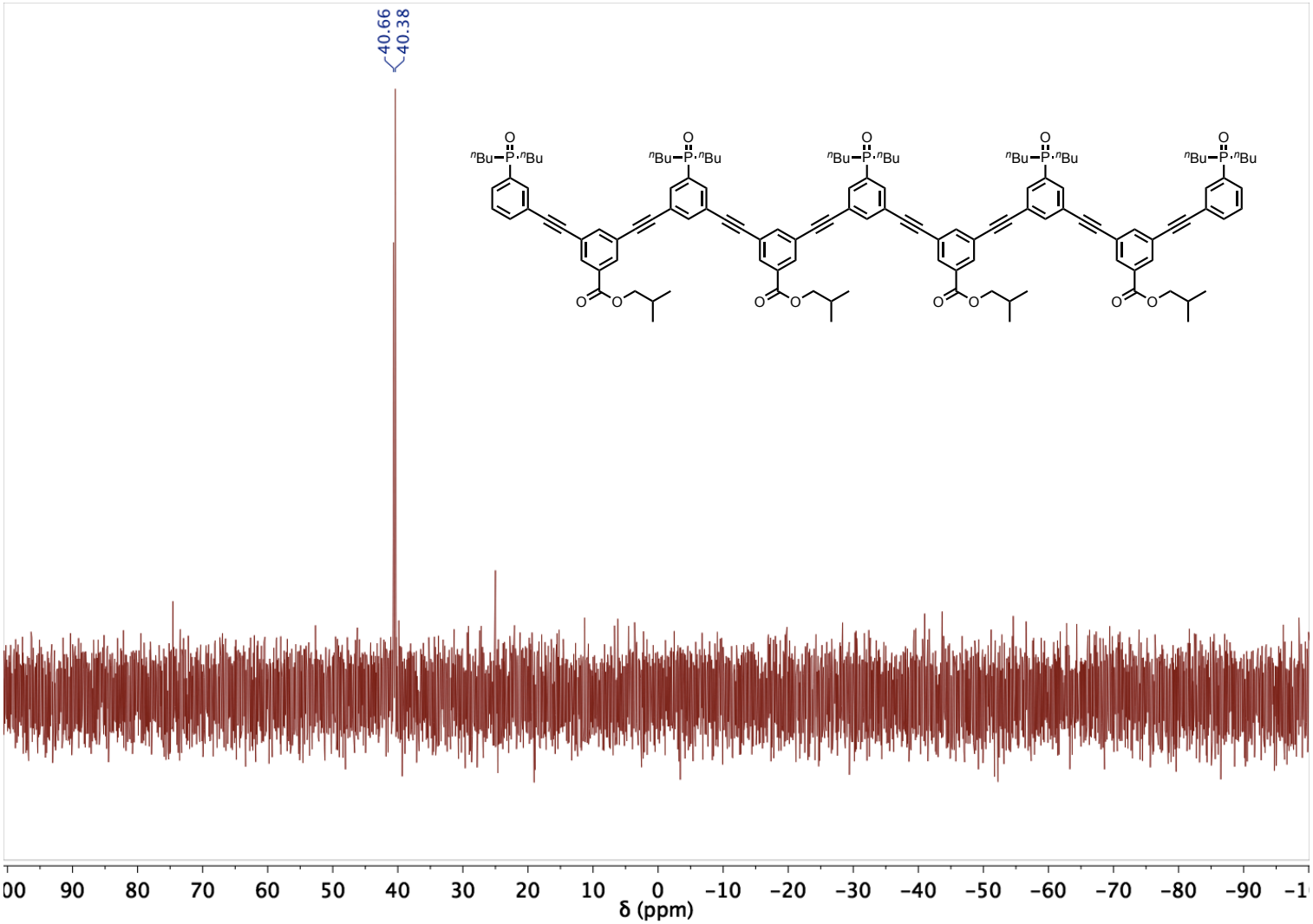
^{1}H NMR (500 MHz, $CDCl_3$) compound 20



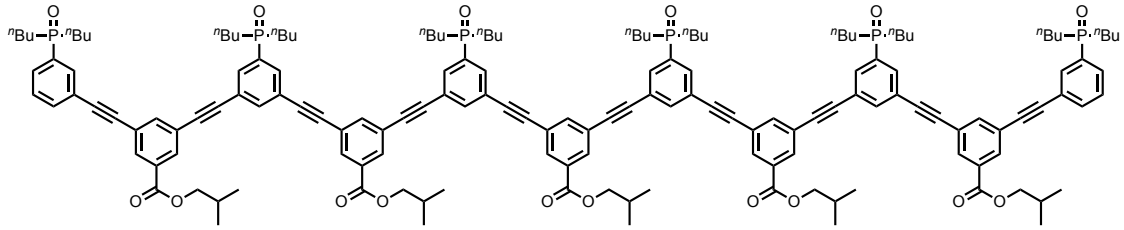
^{13}C NMR (126 MHz, $CDCl_3$) compound 20



^{31}P NMR (162 MHz, $CDCl_3$) compound 20



Acceptor 6-mer (**21**)



^{1}H NMR (500 MHz, $CDCl_3$): δ 8.20 (d, *J* = 1.5 Hz, 6H), 8.19-8.15 (m, 4H), 7.91 – 7.84 (m, 19H), 7.74-7.69 (m, 4H), 7.51 (td, *J* = 7.5, 2.5 Hz, 2H), 4.16 (d, J = 6.5 Hz, 10H), 2.14 – 2.10 (m, 5H), 2.07-1.81 (m, 24H), 1.71-1.55 (m, 12H), 1.49-1.35 (m, 36H), 1.06 (d, J = 6.5 Hz, 30H), 0.91-0.87 (m, 36H);

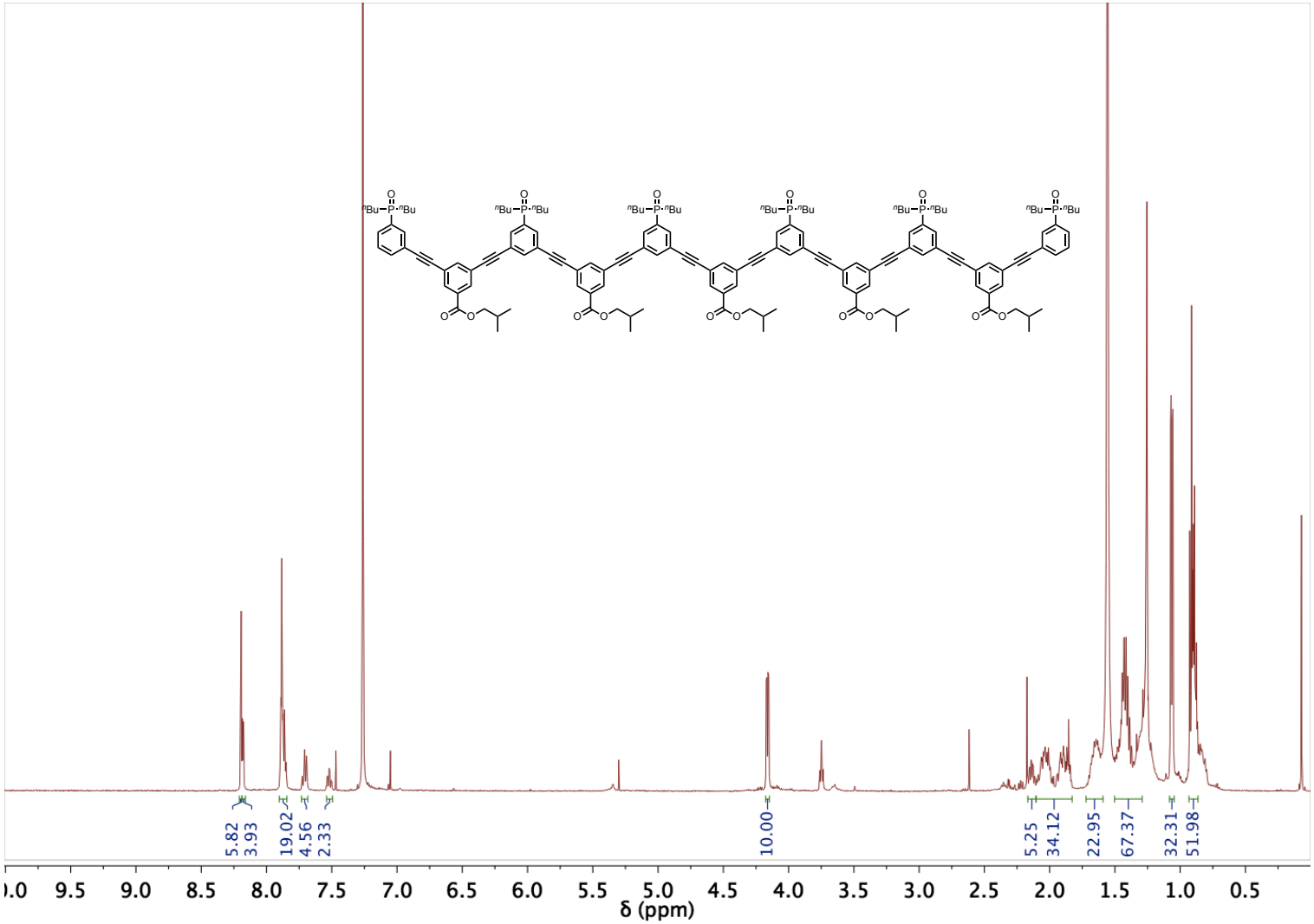
^{13}C NMR (126 MHz, $CDCl_3$): δ 165.1, 165.1, 138.3, 137.0 (d, *J* = 2 Hz), 134.4, 134,4 (d, *J* = 88 Hz), 133.6 (d, *J* = 9 Hz), 133.6 (d, *J* = 89 Hz), 133.3 (d, *J* = 8 Hz), 132.7, 132.7, 132.5, 131.5, 131.5, 130.5 (d, *J* = 8 Hz), 128.8 (d, *J* = 11 Hz), 123.9, 123.8 (d, *J* = 12 Hz), 123.6, 123.5, 123.3 (d, *J* = 12 Hz), 90.0, 89.6, 89.5, 89.1, 89.0, 88.8, 71.7, 29.7 (d, *J* = 68 Hz), 27.9, 24.1 (d, *J* = 14 Hz), 23.5 (d, *J* = 4 Hz) 19.3, 13.6.

^{31}P NMR (162 MHz, $CDCl_3$): δ 40.3, 40.1.

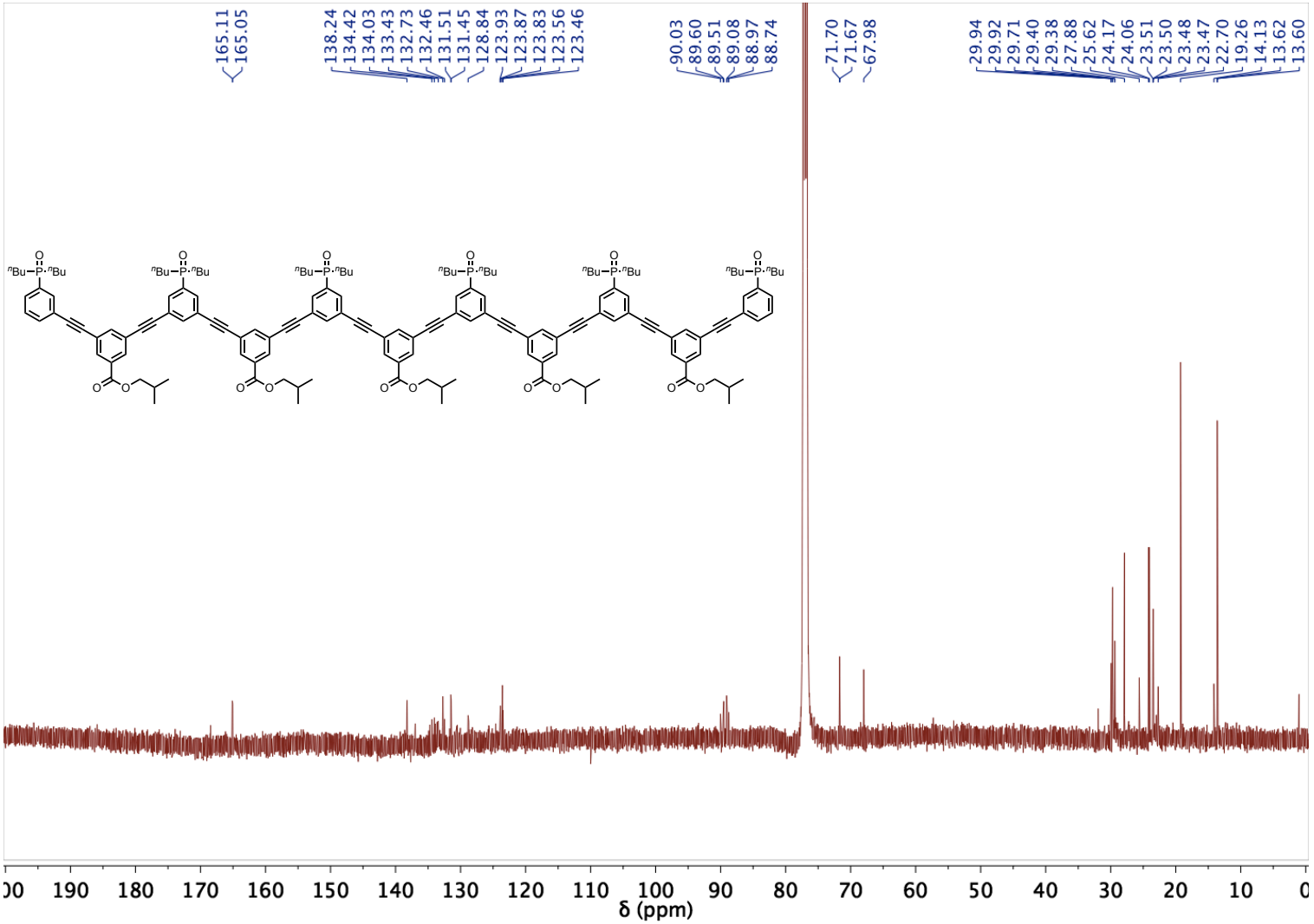
FT-IR (ATR): 2958, 2246, 1723, 1594, 1444, 1236, 1172 ν_{max}/cm^{-1}.

MS (ES+): m/z (%) = 1271.0 (100) [$M+2H^+$], 2540.2 (20) [$M+H^+$].

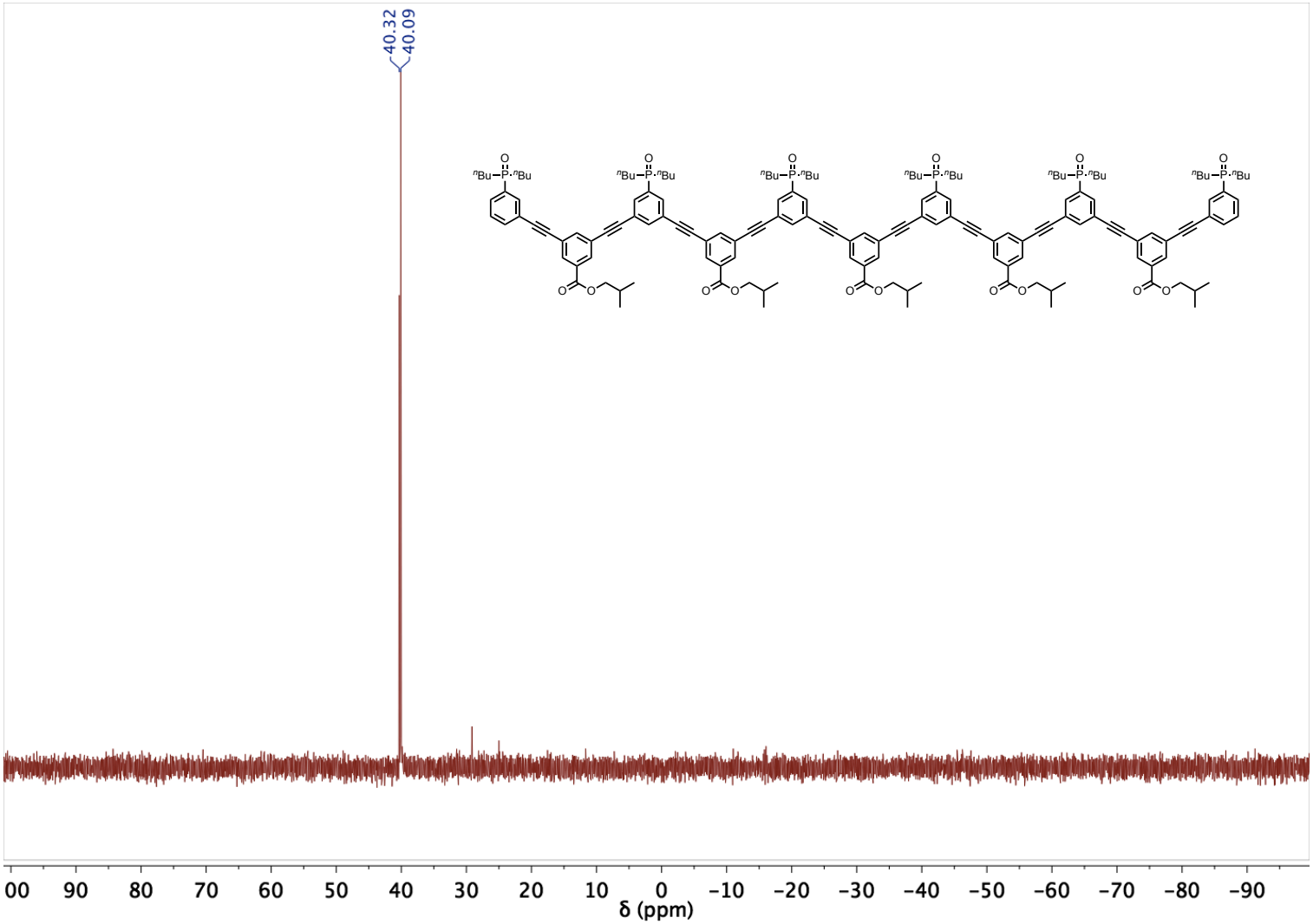
^{1}H NMR (500 MHz, $CDCl_3$) compound 21



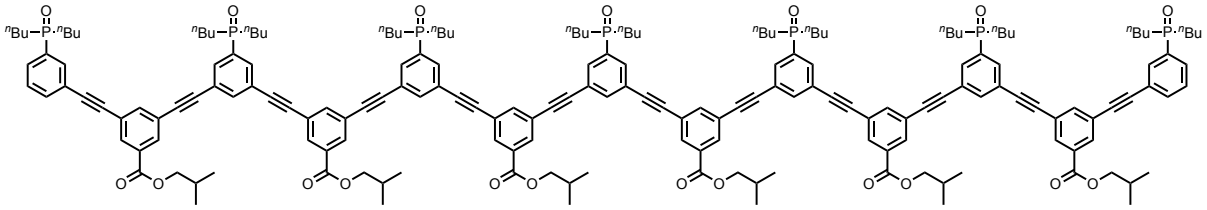
^{13}C NMR (126 MHz, $CDCl_3$) compound 21



^{31}P NMR (162 MHz, $CDCl_3$) compound 21



Acceptor 7-mer (**22**)



^{1}H NMR (500 MHz, $CDCl_3$): δ 8.20 (d, *J* = 1.5 Hz, 8H), 8.19-8.15 (m, 4H), 7.91 – 7.84 (m, 23H), 7.74-7.69 (m, 4H), 7.51 (td, *J* = 7.5, 2.5 Hz, 2H), 4.16 (d, J = 6.5 Hz, 12H), 2.14 – 2.10 (m, 6H), 2.07-1.81 (m, 28H), 1.71-1.55 (m, 14H), 1.49-1.35 (m, 42H), 1.06 (d, J = 6.5 Hz, 36H), 0.91-0.87 (m, 42H).

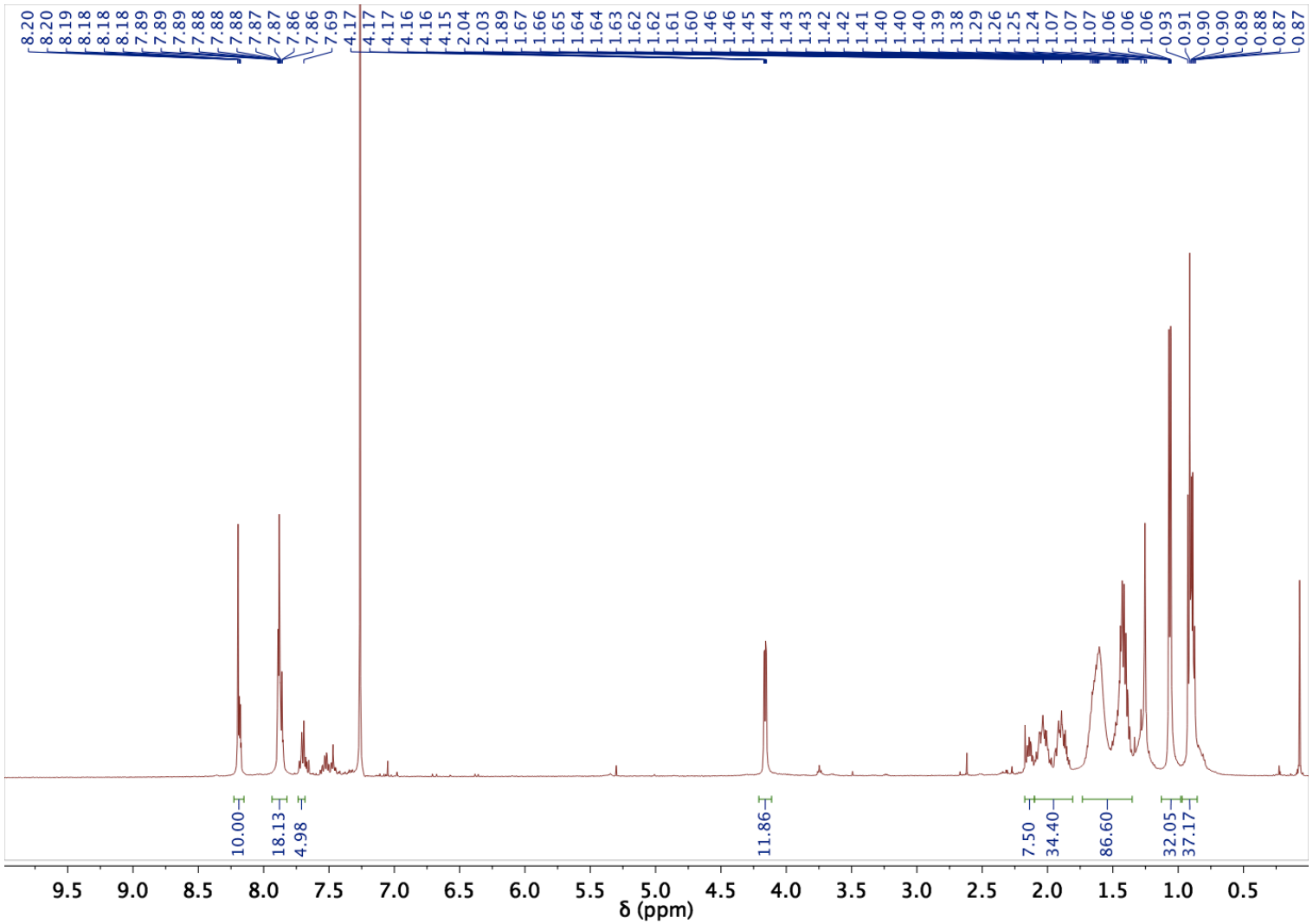
^{13}C NMR (126 MHz, $CDCl_3$): δ 165.1, 165.1, 138.3, 137.0 (d, *J* = 2 Hz), 134.4, 134,4 (d, *J* = 88 Hz), 133.6 (d, *J* = 9 Hz), 133.6 (d, *J* = 89 Hz), 133.3 (d, *J* = 8 Hz), 132.7, 132.7, 132.5, 131.5, 131.5, 130.5 (d, *J* = 8 Hz), 128.8 (d, *J* = 11 Hz), 123.9, 123.8 (d, *J* = 12 Hz), 123.6, 123.5, 123.3 (d, *J* = 12 Hz), 90.0, 89.6, 89.5, 89.1, 89.0, 88.8, 71.7, 29.7 (d, *J* = 68 Hz), 27.9, 24.1 (d, *J* = 14 Hz), 23.5 (d, *J* = 4 Hz) 19.3, 13.6.

^{31}P NMR (162 MHz, $CDCl_3$): δ 40.3, 40.1.

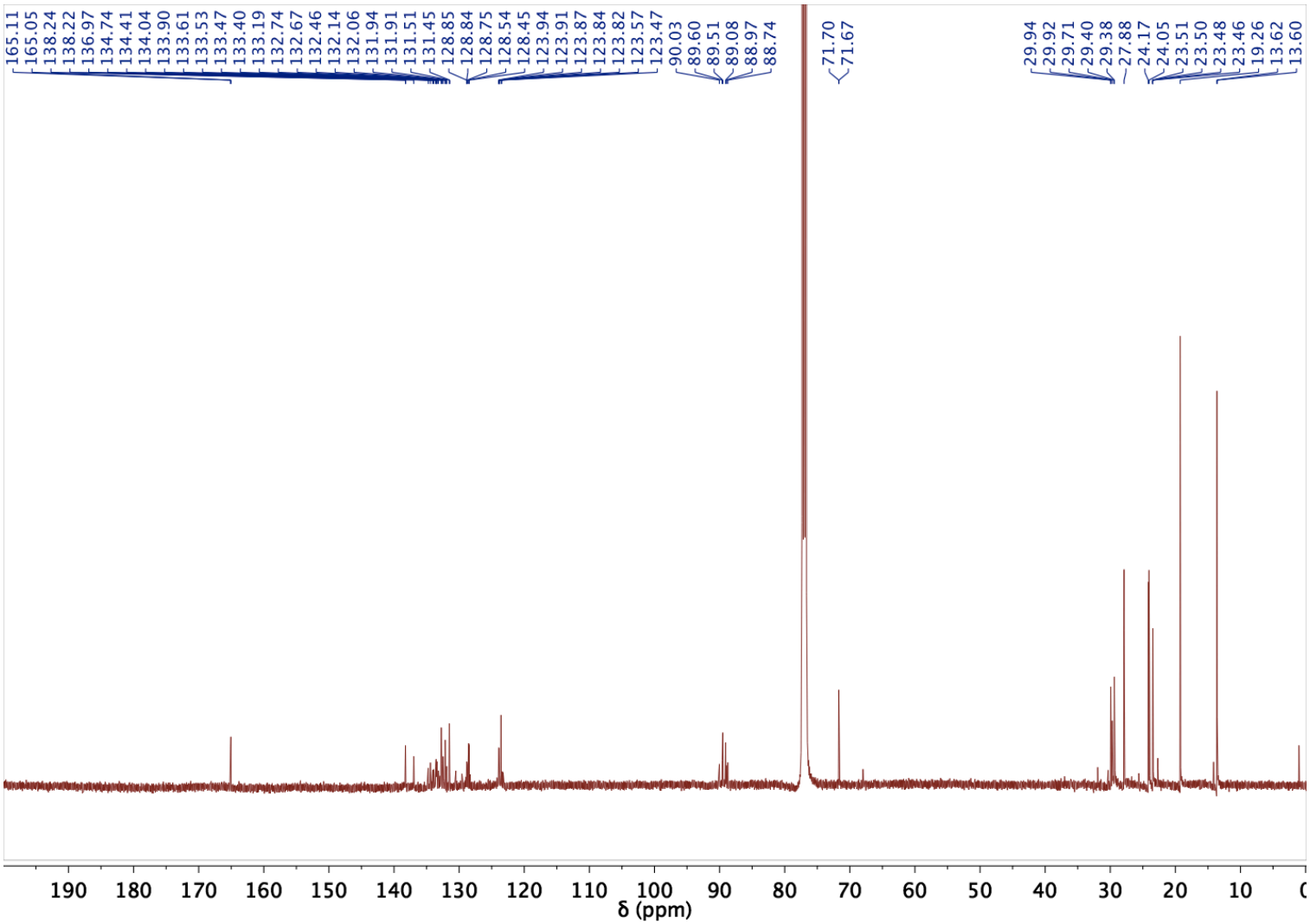
FT-IR (ATR): 2932, 2184, 1723, 1595, 1444, 1236, 1129 ν_{max}/cm^{-1}.

MS (ES+): m/z (%) = 1501.1 (100) [M+2H$^+$], 3000.6.1 (5) [M+H$^+$].

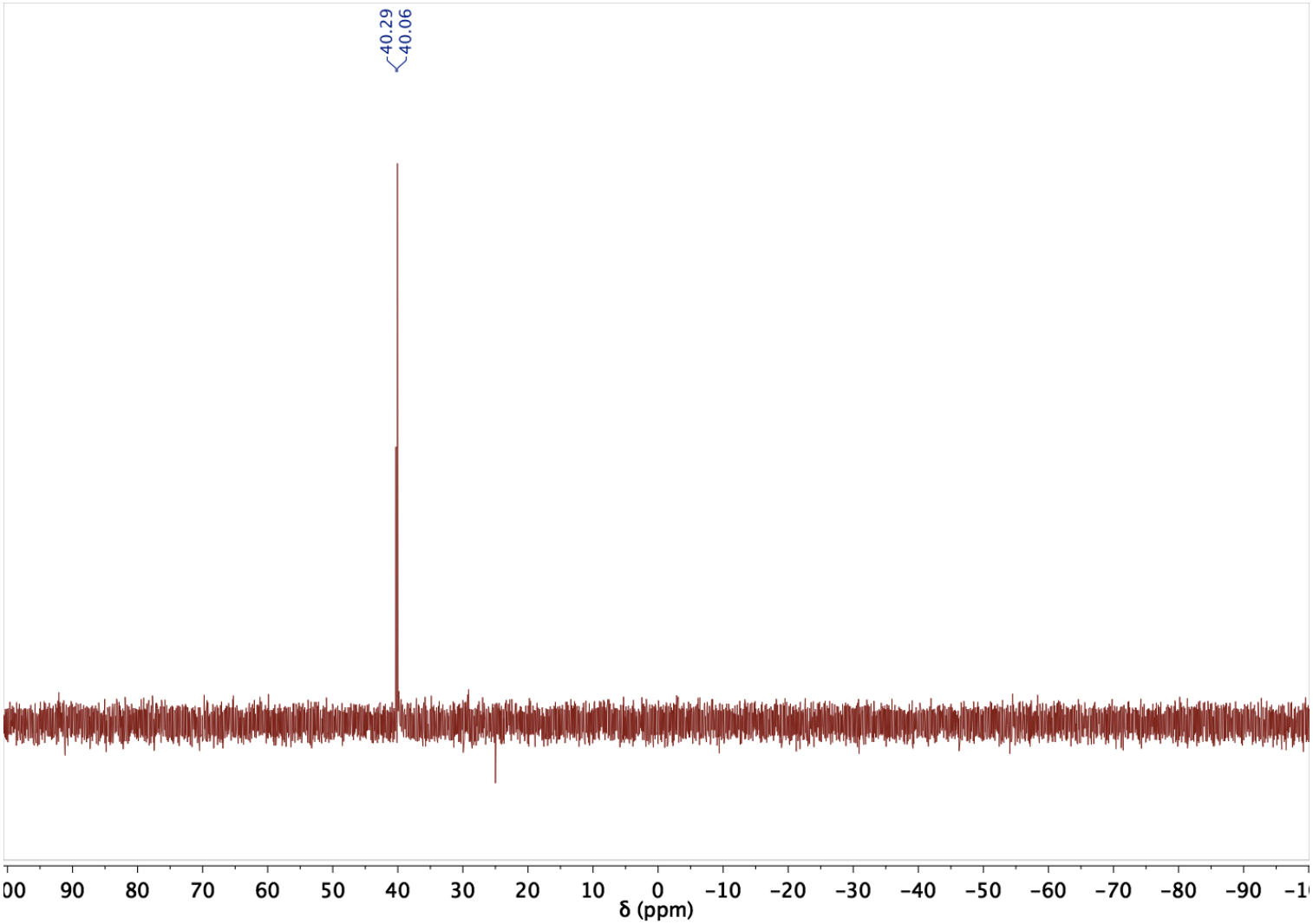
^{1}H NMR (500 MHz, $CDCl_3$) compound 22



^{13}C NMR (126 MHz, $CDCl_3$) compound 22



^{31}P NMR (162 MHz, $CDCl_3$) compound 22



HPLC Separation of Oligomers

The samples were analyzed by reverse phase HPLC using an Agilent LC-MSD ionTrap model XCT LCMS equipment in Electrospray mode. This system is composed of a modular Agilent 1200 Series HPLC system connected to an Agilent/Bruker ionTrap model XCT with MSMS capabilities. The modular Agilent 1200 Series HPLC system is composed of a HPLC high pressure binary pump, autosampler with injector programming capabilities, column oven with 6 µL heat exchanger and a Diode Array Detector with a semimicro flow cell (6 mm path length, 1.7 µl volume) to reduce peak dispersion when using short columns as in this case. The flow-path was connected using 0.12 mm ID stainless steel tubing to minimize peak dispersion. The outlet of the Diode Array Detector flowcell is connected via a switching valve to the IonTrap, the switching valve allowing directing the first segment of the chromatography corresponding to solvent front to waste. After removing the contamination ions associated with the solvent front, the switching valve directs the solvent to the electronspray ion source. While the solvent rate of the method is 1mL/min, the ion source has a dead volume passive splitting union installed which splits the flow rate entering the ion source to <100 µL/min, the rest of the flow rate is directed to waste. This reduction in flow rate enhances the electrospray signal and reduces the contamination in the ion source.

The Electrospray was set to +ve mode. The capillary needle has an orthogonal-flow sprayer design with respect to the ion transmission. The capillary needle voltage was set to +3500 V and the end plate offset was set to -500 V. The solvent eluting from the HPLC column entering the ESI capillary needle in the Ion Source Interface was nebulised with the assistance of N_2 at 15 psi. Drying N_2 gas heated to 325 °C and flowing at 5 L/min was used for the ESI desolvation stage. The ion transport and focusing region of the LC/MSD Trap is enclosed in the vacuum manifold, formed by a rough pump and two turbopumps. The ions formed on the Ion Source Interface enter and are guided through the glass capillary, where the capillary exit is set to -178 V. The bulk of the drying gas is removed by the rough pump before the skimmer which is set to -178 V. The ions then pass into an octopole ion guide (Octopole 1 set to -12 V DC followed by Octopole 2 set to -3 V DC set to a radio frequency of 200 Vpp) that focuses and transports the ions from a relatively high pressure position directly behind the skimmer to the focusing/exit lenses (Lens 1 set to +5 V followed by Lens

2 set to +60 V) coupling the ion transport to the ion trap. The selected ions entered the ion trap which had been set to a value of 109.9. For efficient trapping and cooling of the ions generated by the electrospray interface, helium gas is introduced into the ion trap.

The fractions were isolated using an Agilent HP-1100 preparative HPLC system. This is composed by a high pressure mixing binary pump capable of flow rates up to 50 mL/min at 400 bar back-pressure, with dual injector autosamplers lops (500 uL and a 5 mL loop), a variable detector (190 nm to 600 nm) and a fraction collector. UV/vis absorption was measured at 290 nm (8 nm bandwidth) with reference 550 nm (100 nm bandwidth). The software for the fraction collector can be set to automatically collect on peak recognition.

References

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(2) Zhao, W.; Huang, L.; Guan, Y.; Wulff, W. D. *Angew. Chem. Int. Ed.* **2014**, *53* (13), 3436–3441.

(3) Ghosh, K.; Yang, H. B.; Northrop, B. H.; Lyndon, M. M.; Zheng, Y. R.; Muddiman, D. C.; Stang, P. J. *J. Am. Chem. Soc.* **2008**, *130* (15), 5320–5334.