Supporting information

H-BOND SELF-ASSEMBLY: FOLDING VERSUS DUPLEX FORMATION

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NMR binding studies.

C8-PO, C8-N, C8-NO, N8-PO, N7-PO and C9-PO A•D and AA•DD complexes.

Binding constants for C8-PO,[S1] C8-N,[S2] C8-NO,[S2] N8-PO,[S3] N7-PO[S3] and C9-PO[S4] A•D and AA•DD complexes have been previously reported.

C7-PO A•D and AA•DD 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 **S11** or **41**) was dissolved in toluene-d_8 at a known concentration. The guest (phenol derivatives **S10** or **40**) 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).

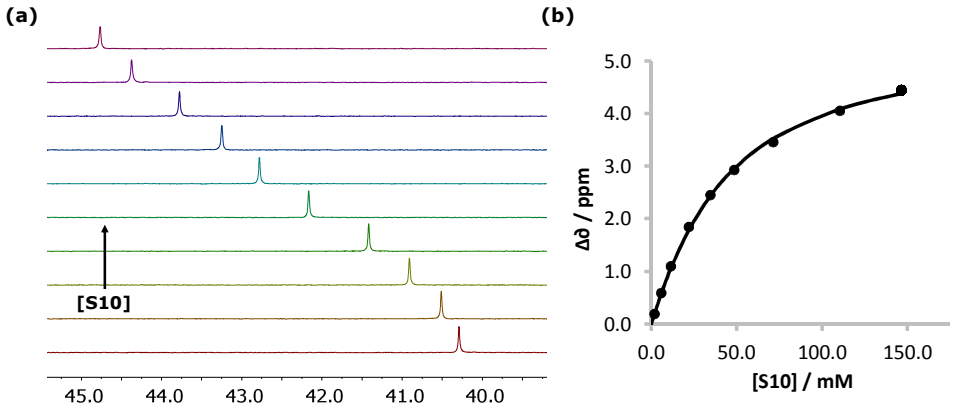


Figure S1. C7-PO A•D 1-mer complex (a) 202 MHz ^{31}P NMR data for titration of **S10** into **S11** (18.4 mM) at 298 K in toluene-d_8. (b) Plot of the change in chemical shift of the ^{31}P signal as a function of guest concentration (the line represents the best fit to a 1:1 binding isotherm).

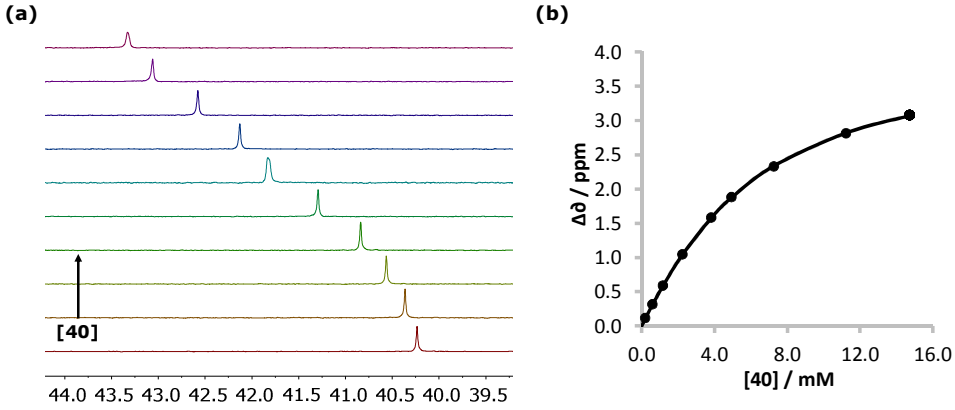


Figure S2. C7-PO AA•DD 2-mer complex (a) 202 MHz ^{31}P NMR data for titration of **40** into **41** (3.68 mM) at 298 K in toluene-d_8. (b) Plot of the change in chemical shift of the ^{31}P signal as a function of guest concentration (the line represents the best fit to a 1:1 binding isotherm).

NMR dilutions of AD 2-mers.

^{31}P NMR dilution experiments for C8-PO (**16**), N8-PO (**26**), N7-PO (**29**), C9-PO (**33**) and C7-PO (**44**) AD 2-mers were performed in a Bruker 400 MHz AVIII or Bruker 500 MHz AVIII HD Smart Probe spectrometer.

^{1}H NMR dilution experiments for C8-N (**21**) and C8-NO (**13**) were performed in a Bruker 400 MHz AVIII or Bruker 500 MHz Avance TCI Cryoprobe spectrometer.

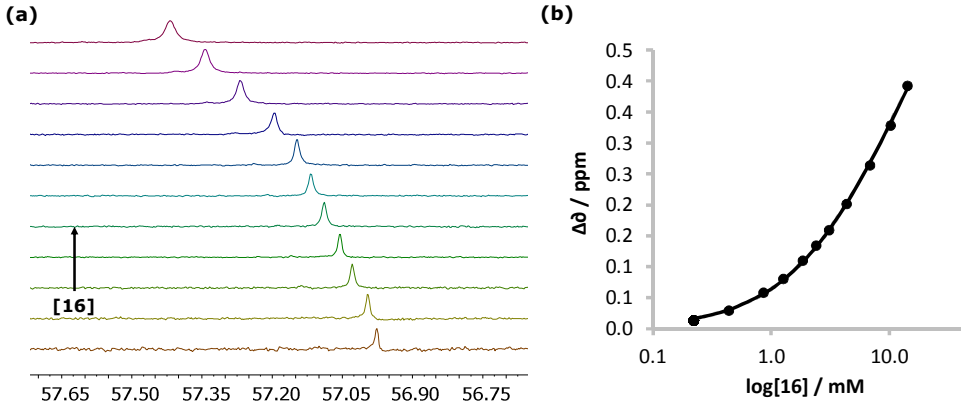


Figure S3. a) 162 MHz ^{31}P NMR data for dilution of C8-PO AD-2 mer (**16**) at 298 K in toluene-d_8. (b) Plot of the change in chemical shift as a function of concentration (the line represents the best fit to a dimerisation isotherm).

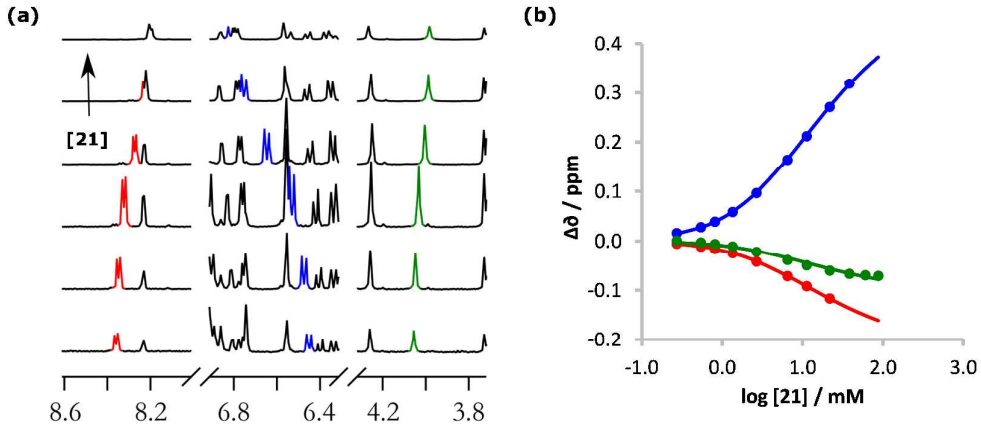


Figure S4. a) 400 MHz ^{1}H NMR data for dilution of C8-N AD-2 mer (**21**) at 298 K in toluene-d_8. (b) Plot of the change in chemical shift as a function of concentration (the line represents the best fit to a dimerisation isotherm). The red signal corresponds to the protons *ortho* to the pyridine nitrogen; the blue signal corresponds to the protons *ortho* to the phenol oxygen; the green signal corresponds to the benzylic methylene protons of the pyridine recognition unit.

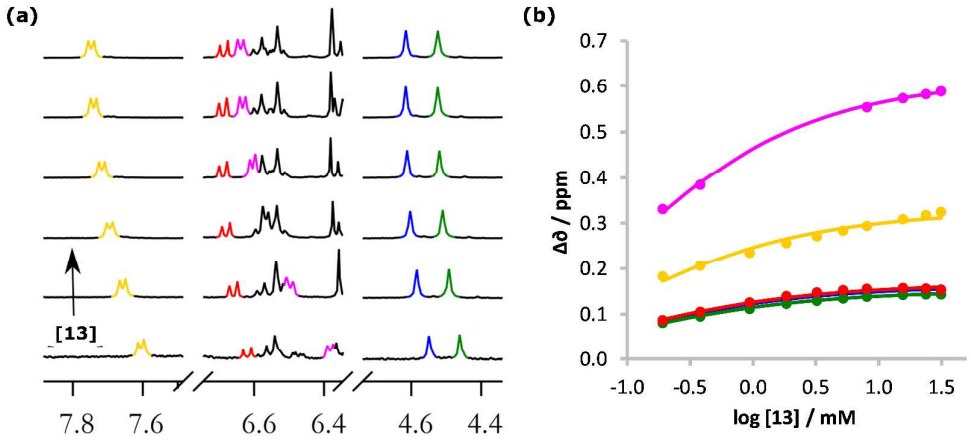


Figure S5. a) 400 MHz ^{1}H NMR data for dilution of C8-NO AD-2 mer (**13**) at 298 K in toluene-d_8. (b) Plot of the change in chemical shift as a function of concentration (the line represents the best fit to a dimerisation isotherm). The yellow signal corresponds to the protons *ortho* to the N-oxide nitrogen; the red signal corresponds to the protons *meta* to the phenol oxygen; the pink signal corresponds to the protons *ortho* to the phenol oxygen; the blue and green signals correspond to the benzylic methylene protons of the backbone.

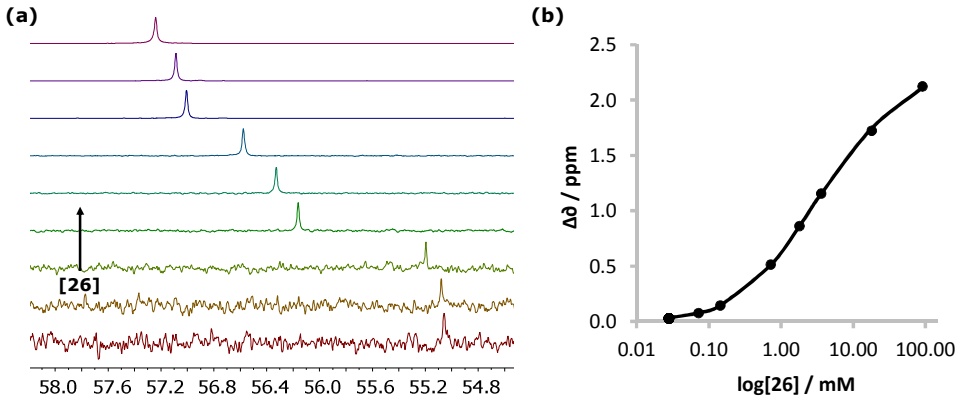


Figure S6. a) 162 MHz ^{31}P NMR data for dilution of N8-PO AD-2 mer (**26**) at 298 K in toluene-d_8. (b) Plot of the change in chemical shift as a function of concentration (the line represents the best fit to a dimerisation isotherm).

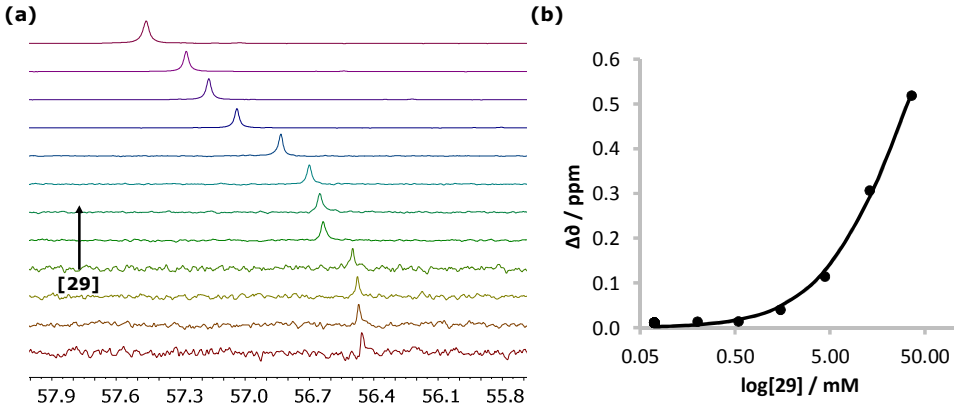


Figure S7. a) 162 MHz ^{31}P NMR data for dilution of N7-PO AD-2 mer (**29**) at 298 K in toluene-d_8. (b) Plot of the change in chemical shift as a function of concentration (the line represents the best fit to a dimerisation isotherm).

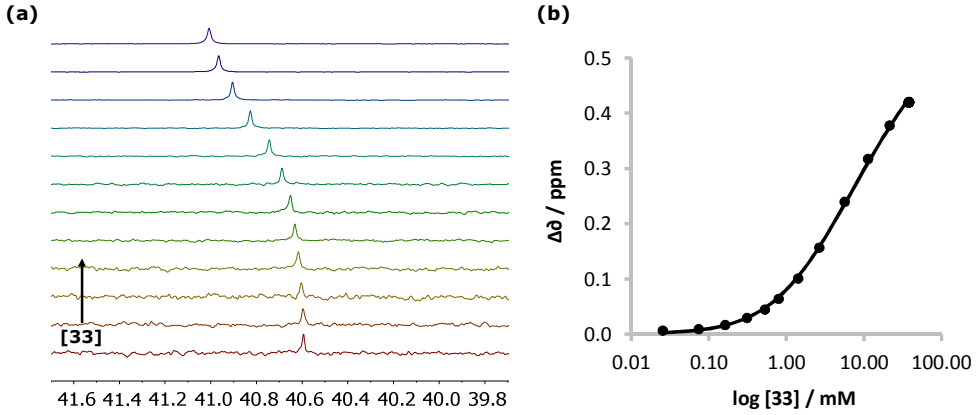


Figure S8. a) 202 MHz ^{31}P NMR data for dilution of C9-PO AD-2 mer (**33**) at 298 K in toluene-d_8. (b) Plot of the change in chemical shift as a function of concentration (the line represents the best fit to a dimerisation isotherm).

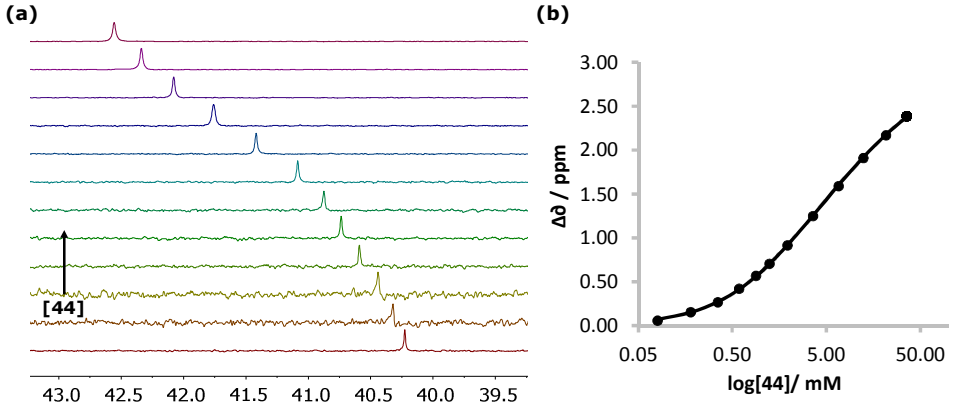


Figure S9. a) 202 MHz ^{31}P NMR data for dilution of C7-PO AD-2 mer (**44**) at 298 K in $CDCl_3$. (b) Plot of the change in chemical shift as a function of concentration (the line represents the best fit to a dimerisation isotherm).

Molecular mechanics calculations.

Molecular mechanics calculations were performed using MacroModel version 9.8 (Schrödinger Inc.) on simplified AD 2-mers in which the solubilising groups were changed to methyl groups in order to reduce the computational cost. All structures were minimized first and the minimized structures were then used as the starting molecular structures for all MacroModel conformational searches. The force field used was MMFFs as implemented in this software. The charges were defined by the force field library and no cut off were used for non-covalent interaction. A Polak-Ribiere Conjugate Gradient (PRCG) was used and each structure was subjected to 10000 iterations. The minima converged on a gradient with a threshold of 0.01. Conformational search was performed from previously minimized structures using 10000 steps. Only the structures in a 5 $kJ \cdot mol^{-1}$ window from the global minimum were analysed. Images shown in Fig. 6 were created using PyMOL.[S5]

X-ray crystallography.

X-ray structure of compound 12.

Pure compound **12** (4 mg) was dissolved in $CHCl_3$ (1 mL), and the mixture was filtered to a vial and sealed with a plastic cap, resulting in crystallization after 14 days at room temperature. Crystals suitable for X-ray crystallography were selected using an optical microscope and examined at 100 K on a Bruker SMART APEX-II CCD diffractometer operating with a Cu Kα sealed tube X-ray source. The structures were solved using SHELXL-97 and refined using WinGX V1.64.05.23.24. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealised position.

Formula	$C_{39}H_{40}N_4O_9$		
Temperature / K	100		
Space Group	P-1		
Cell Lengths/ Å	**a** 8.2839 (0.0005)	**b** 12.3644 (0.0008)	**c** 17.9163 (0.0012)
Cell Angles/ °	**α** 102.994 (0.0042)	**β** 103.082 (0.0045)	**γ** 91.085 (0.0047)
Cell Volume/ Å^3	1736.97		
Z	2		
R factor	0.1135		

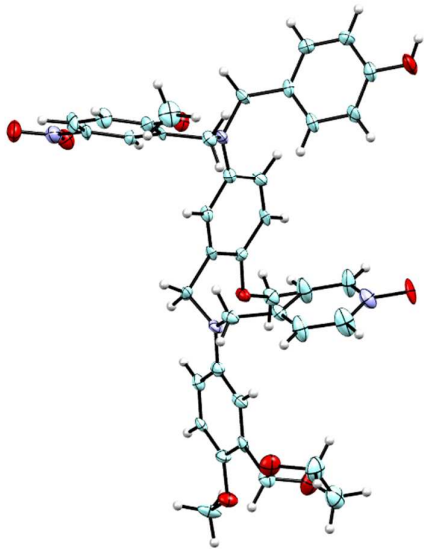


Figure S10. X-ray structure of derivative **12 i**n ORTEP view (ellipsoids are drawn at 50% probability level).

X-ray structure of compound 47.

Pure compound **47** (4 mg) was dissolved in toluene (0.5 mL), and the mixture was filtered to a vial and sealed with a plastic cap, resulting in crystallization after 10 days at room temperature. Crystals suitable for X-ray crystallography were selected using an optical microscope and examined at 180 K on a Nonius KappaCCD diffractometer using Mo Kα radiation (λ = 0.7107 Å). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealized position.

Formula	$C_{30}H_{31}O_2P$		
Temperature / K	180		
Space Group	P 2_1/n		
Cell Lengths/ Å	**a** 9.0540 (0.0004)	**b** 25.6599 (0.0011)	**c** 11.7725 (0.0005)
Cell Angles/ °	**α** 90	**β** 111.578 (0.002)	**γ** 90
Cell Volume/ Å^3	2543.37		
Z	4		
R factor	0.0686		

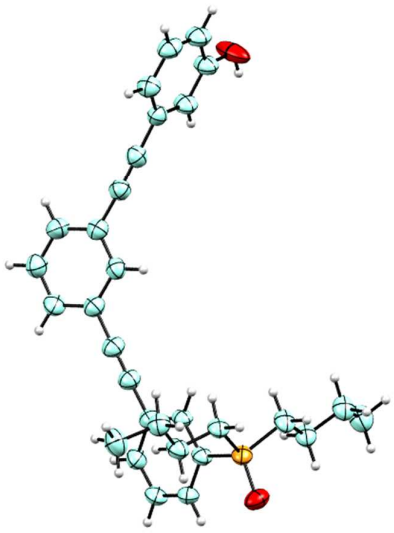


Figure S11. X-ray structure of derivative **47 i**n ORTEP view (ellipsoids are drawn at 50% probability level).

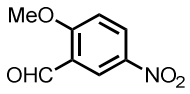
Synthesis and characterization of described compounds

General experimental details

All the reagents and materials used in the synthesis of the compounds described below were bought from commercial sources, without prior purification. UV irradiations were performed using an UVP lamp model UVL-28 (2x365 nm tubes, 8 watt). Thin layer chromatography was carried out using with silica gel 60F (Merck) on aluminium. Flash chromatography was carried out on an automated system (Combiflash Companion, Combiflash Rf+ or Combiflash Rf Lumen) using prepacked cartridges of silica (25µ or 50µ PuriFlash® Columns). All NMR spectroscopy was carried out on a Bruker AVI250, AVI400, DPX400, AVIII400 spectrometer using the residual solvent as the internal standard. All chemical shifts (δ) are quoted in ppm and coupling constants given in Hz. Splitting patterns are given as follows: s (singlet), bs (broad singlet), d (doublet), t (triplet), q (quadruplet), m (multiplet). FT-IR spectra were measured on a PerkinElmer Spectrum 100 or One spectrometer equipped with an ATR cell. Melting points were measured in a Mettler Toledo MP50 Melting Point System. Optical activity was measured in an AA-10 or an Anton Paar (MCP 100) at 589 nm. ES+ was carried out on a Waters LCT-TOF spectrometer or a Waters Xevo G2-S bench top QTOF machine.

Compounds **6**,[S4] **8**,[S1] **9**,[S2] **14**,[S1] **17**,[S1] **18**,[S1] **20**,[S2] **23**,[S3] **24**,[S3] **27**,[S3], **30**,[S4] **32**[S4] and **34**[S4] have been previously described.

Synthesis of 2-methoxy-5-nitrobenzaldehyde (S1).

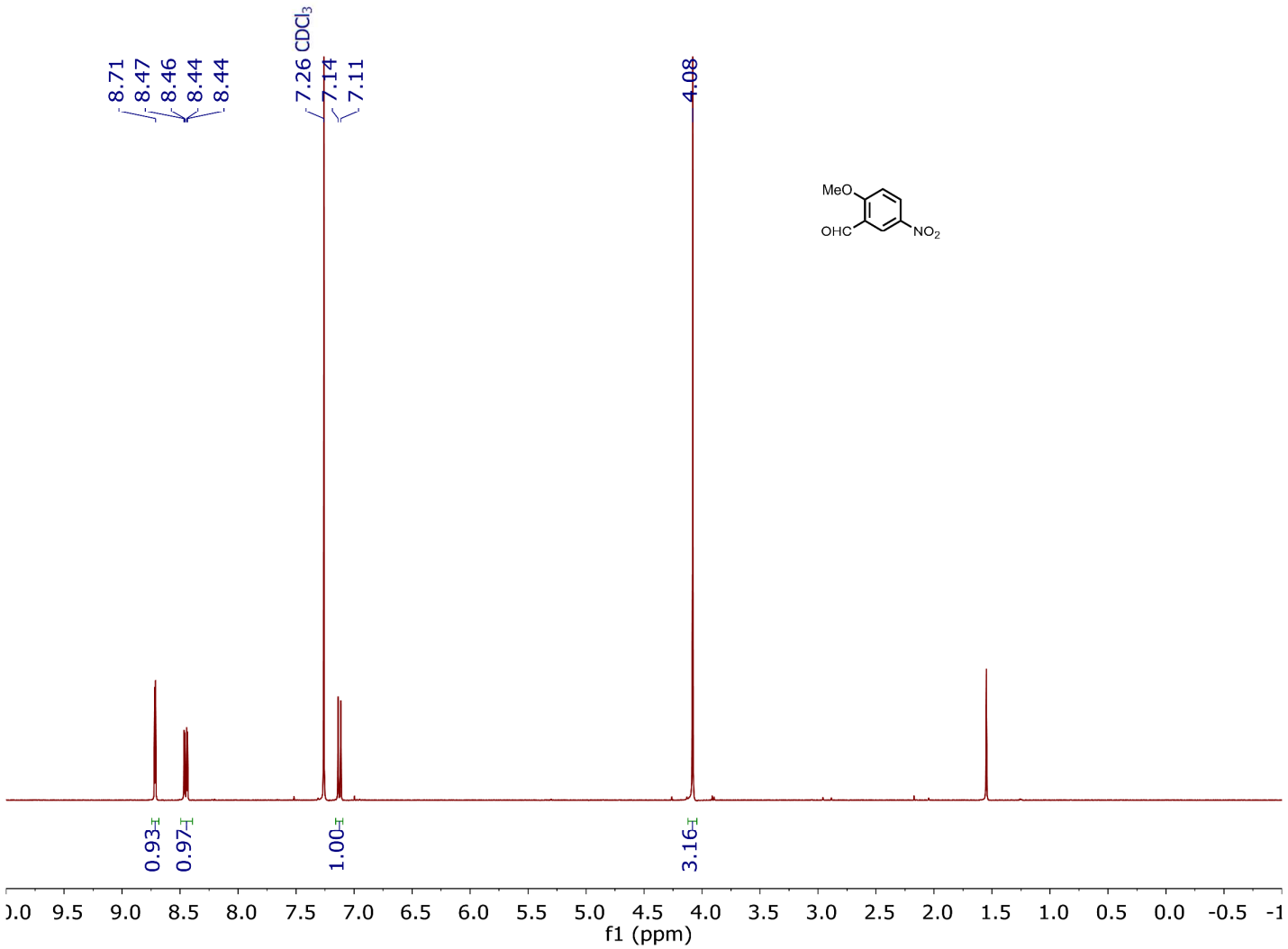


5-Hydroxy-2-nitrobenzaldehyde (10.0 g, 59.8 mmol), K_2CO_3 (18.6 g, 135 mmol), methyl iodide (3.2 mL, 134.8 mmol) and DMF (100 mL) were stirred at room temperature for 16 h. The suspension was then poured into water (100 mL) and washed with EtOAc (3 x 200 mL). The combined organic extracts were subsequently washed with water (5 x 100 mL) then brine (100 mL), dried with $MgSO_4$, filtered and the solvent was removed on a rotary evaporator to yield the product as a yellow solid, which required no further purification (10.1 g, 92 %). The spectroscopic data matches previously reported literature.[S6]

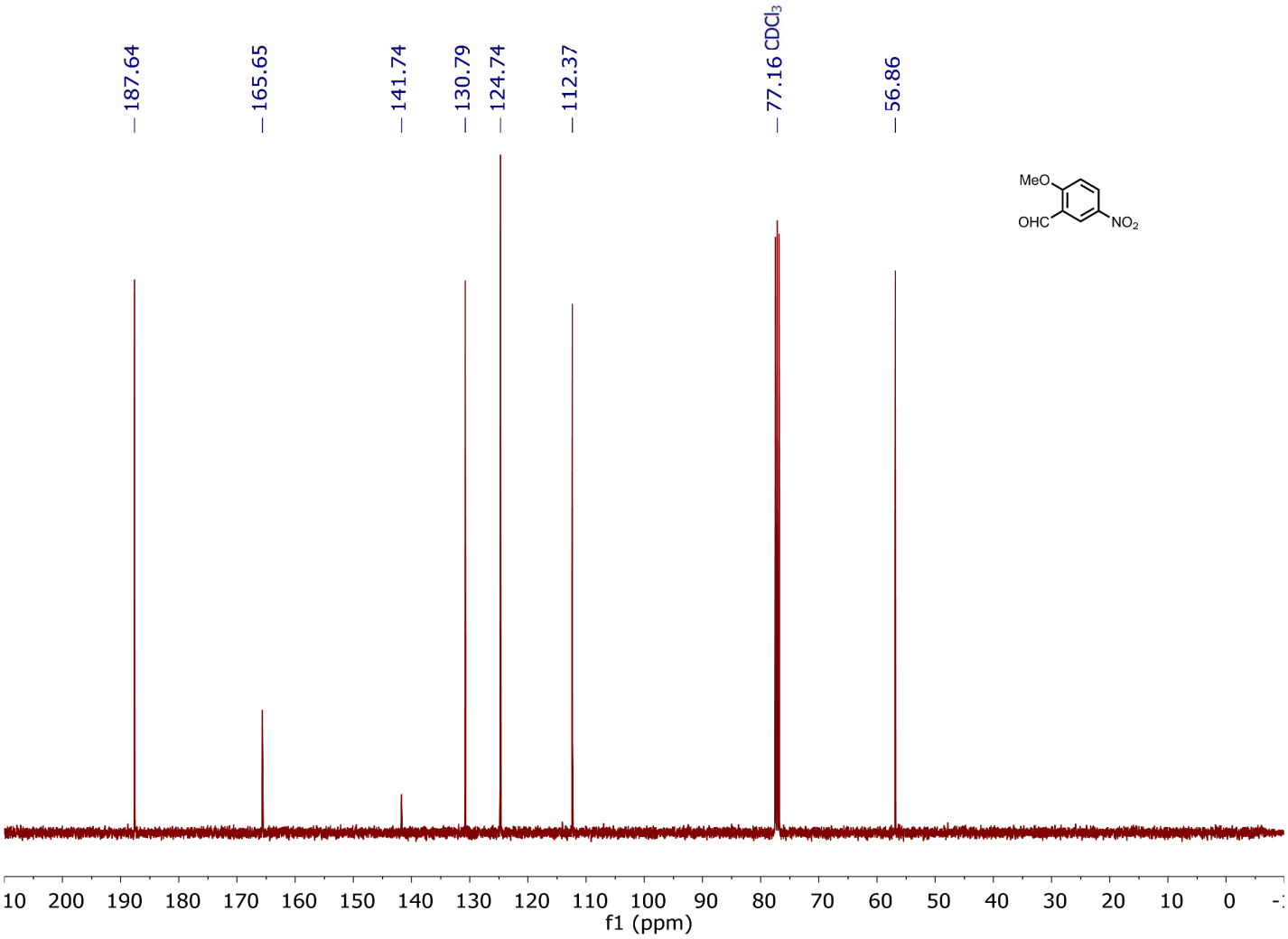
^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 10.45 (s, 1H), 8.69 (d, 1H, *J* = 2.0), 8.45 (dd, 1H, *J* = 9.5, 2.0), 7.15 (d, 1H, *J* = 9.5), 4.09 (s, 3H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C = 187.5, 141.6, 130.7, 124.6, 114.0, 112.3, 56.8.

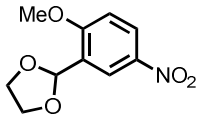
^{1}H NMR (400 MHz, $CDCl_3$) 2-methoxy-5-nitrobenzaldehyde (S1)



^{13}C NMR (100.6 MHz, $CDCl_3$) 2-methoxy-5-nitrobenzaldehyde (S1)



Synthesis of 2-(2-methoxy-5-nitrophenyl)-1,3-dioxolane (2).



2-Methoxy-5-nitrobenzaldehyde (**S1**, 8.72 g, 48.2 mmol), *p*-toluenesulfonic acid monohydrate (4.58 g, 24.1 mmol), ethylene glycol (13.4 mL, 241 mmol), toluene (50 mL) and 1,4-dioxane (200 mL) were stirred at reflux for 3 days. The solvent was removed on a rotary evaporator, and the residue was dissolved in ethyl acetate (200 mL). The solution was filtered, washed with water (3 x 100 mL) then brine (100 mL), dried with $MgSO_4$, filtered and the solvent was removed on a rotary evaporator, to yield the product as a yellow solid, which required no further purification (10.8 g, 99 %).

Mpt: 77-79 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 8.46 (d, 1H, *J* = 3.0), 8.29 (dd, 1H, *J* = 9.0, 3.0), 7.00 (d, 1H, *J* = 9.0), 6.05 (s, 1H); 4.23-4.05 (m, 4H), 4.01 (s, 3H).

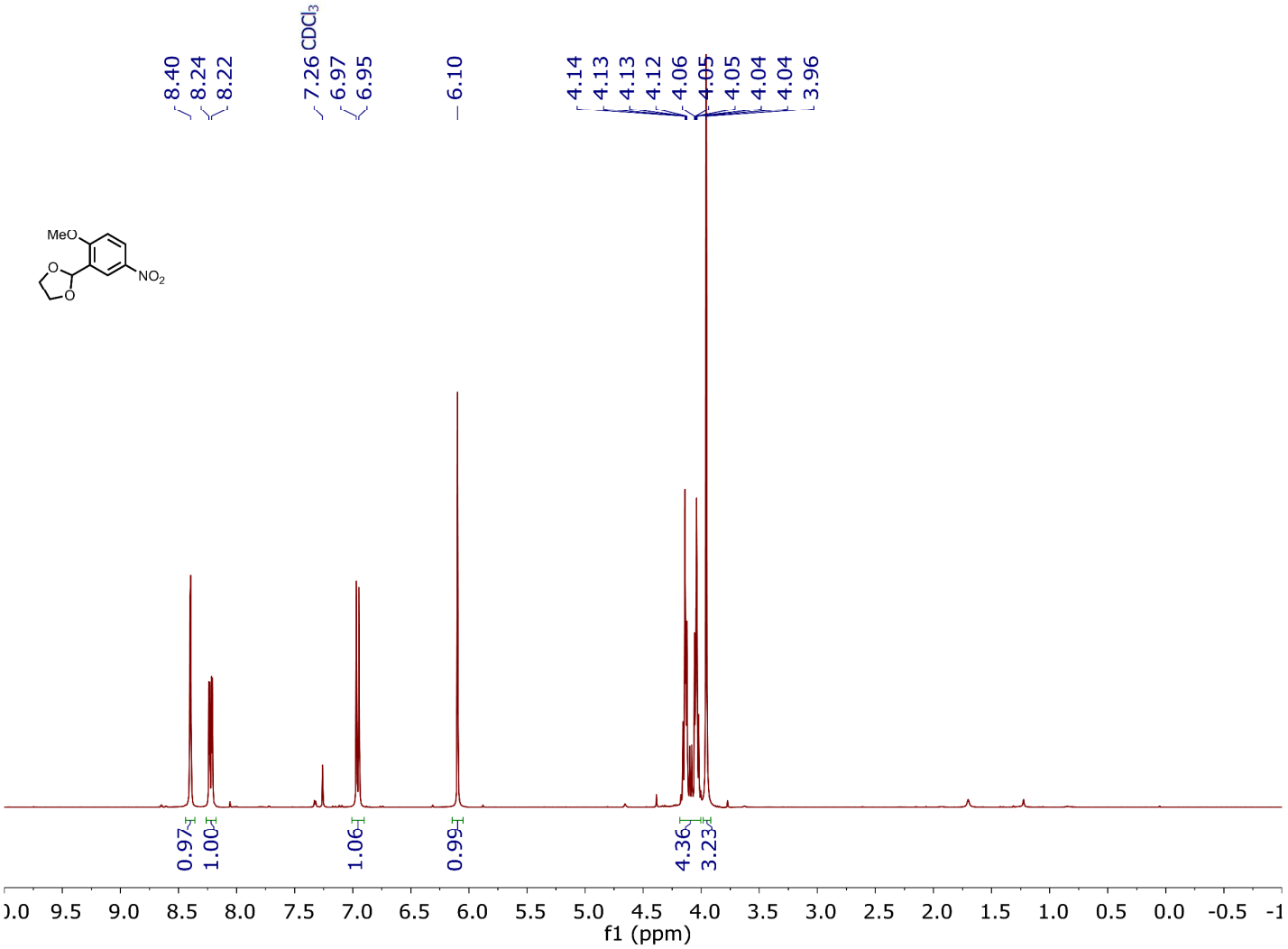
^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C = 162.5, 141.3, 127.4, 126.5, 123.2, 110.6, 98.2, 65.5, 56.5.

MS (ES+): m/z (%) = 226.1 $[M+H]^+$.

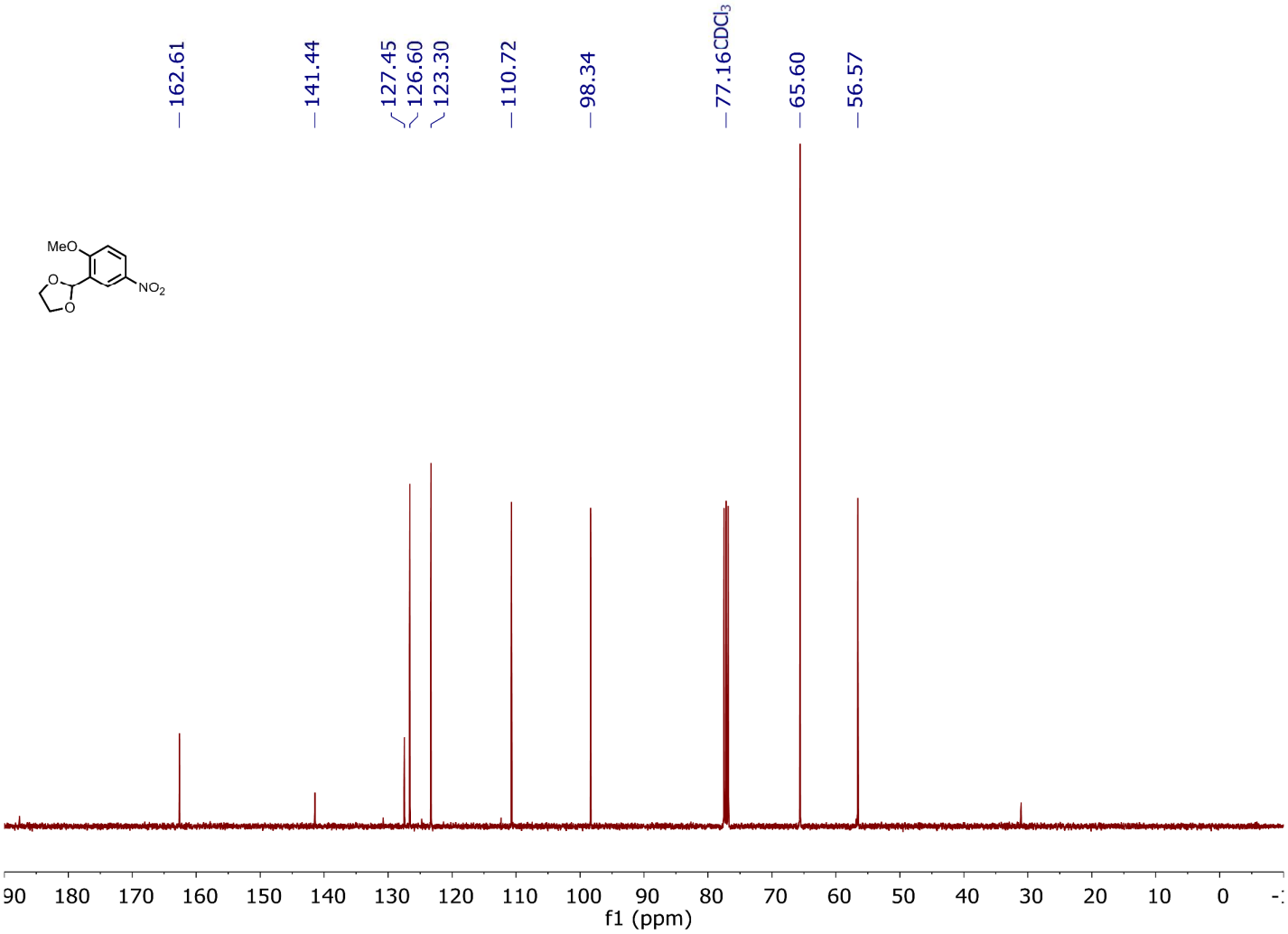
HRMS (ES+): calcd for $C_{10}H_{12}NO_5$ 226.0715, found 226.0715.

FT-IR (ATR): ν_{max} 2945, 2907, 2884, 1733, 1616, 1506, 1496, 1334, 1265 cm^{-1}.

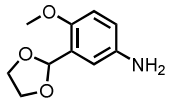
^{1}H NMR (400 MHz, $CDCl_3$) 2-(2-methoxy-5-nitrophenyl)-1,3-dioxolane (2)



^{13}C NMR (100.6 MHz, $CDCl_3$) 2-(2-methoxy-5-nitrophenyl)-1,3-dioxolane (2)



Synthesis of 3-(1,3-dioxolan-2-yl)-4-methoxyaniline (3).



Compound **2** (9.84 g, 38.5 mmol), 10% Pd/C (0.750 g, 7.00 mmol) and degassed EtOAc (195 mL) was stirred under a H_2 atmosphere at room temperature for 2 days. Filtration through a celite plug and removal of the solvent on a rotary evaporator yielded the product as an orange oil, which required no further purification (7.51 g, quant.).

^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 6.94 (d, 1H, *J* = 3.0), 6.76 (d, 1H, *J* = 8.5), 6.68 (dd, 1H, *J* = 8.5, 3.0), 6.12 (s, 1H), 4.16-4.10 (m, 2H), 4.08-4.02 (m, 2H), 3.81 (s, 3H), 3.50-3.30 (bs, 2H).

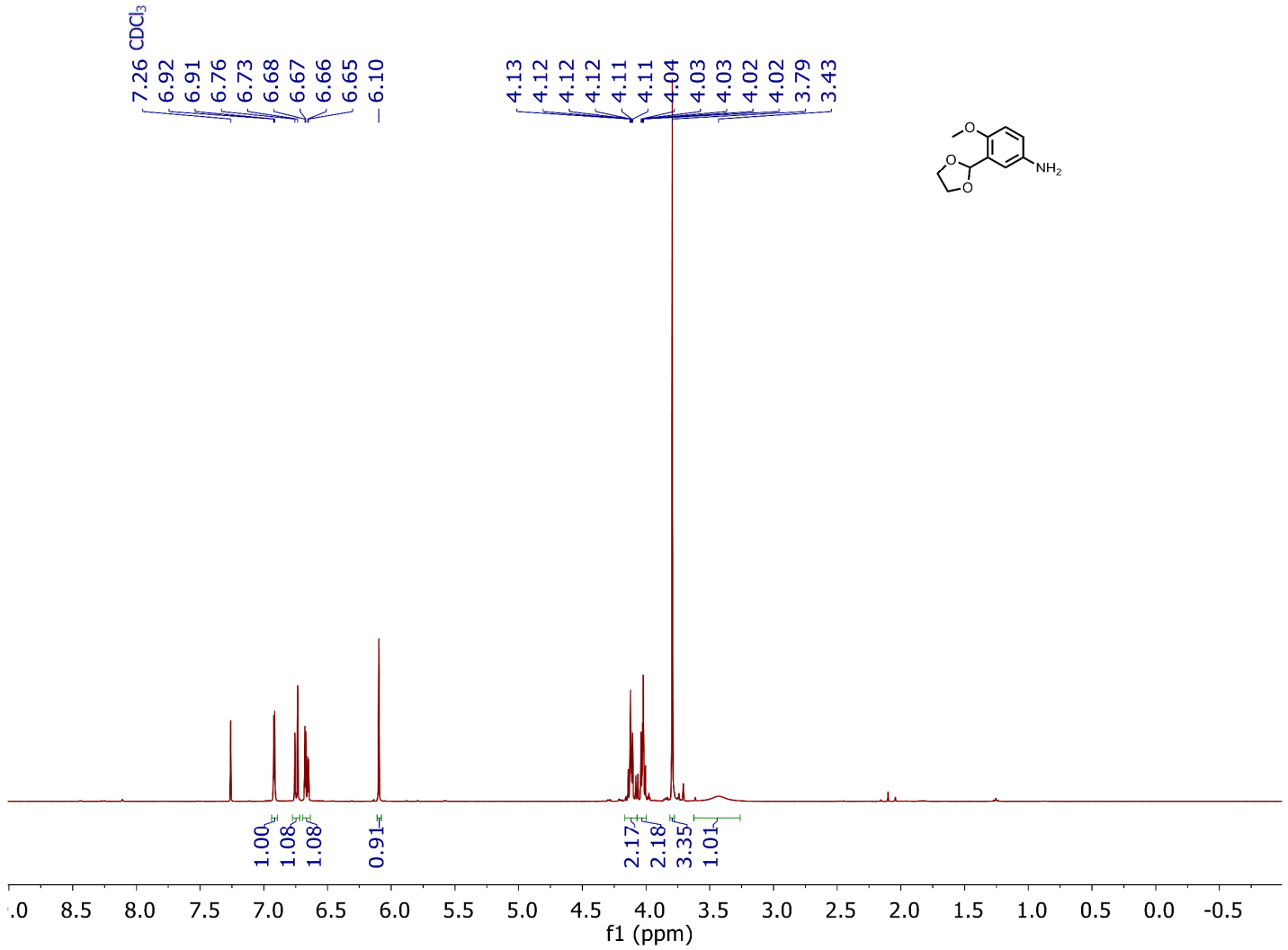
^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C = 151.0, 139.9, 126.6, 116.7, 114.1, 112.4, 99.3, 65.3, 56.4.

MS (ES+): m/z (%) = 237.1 $[M+MeCN+H]^+$, 196.1 $[M+H]^+$.

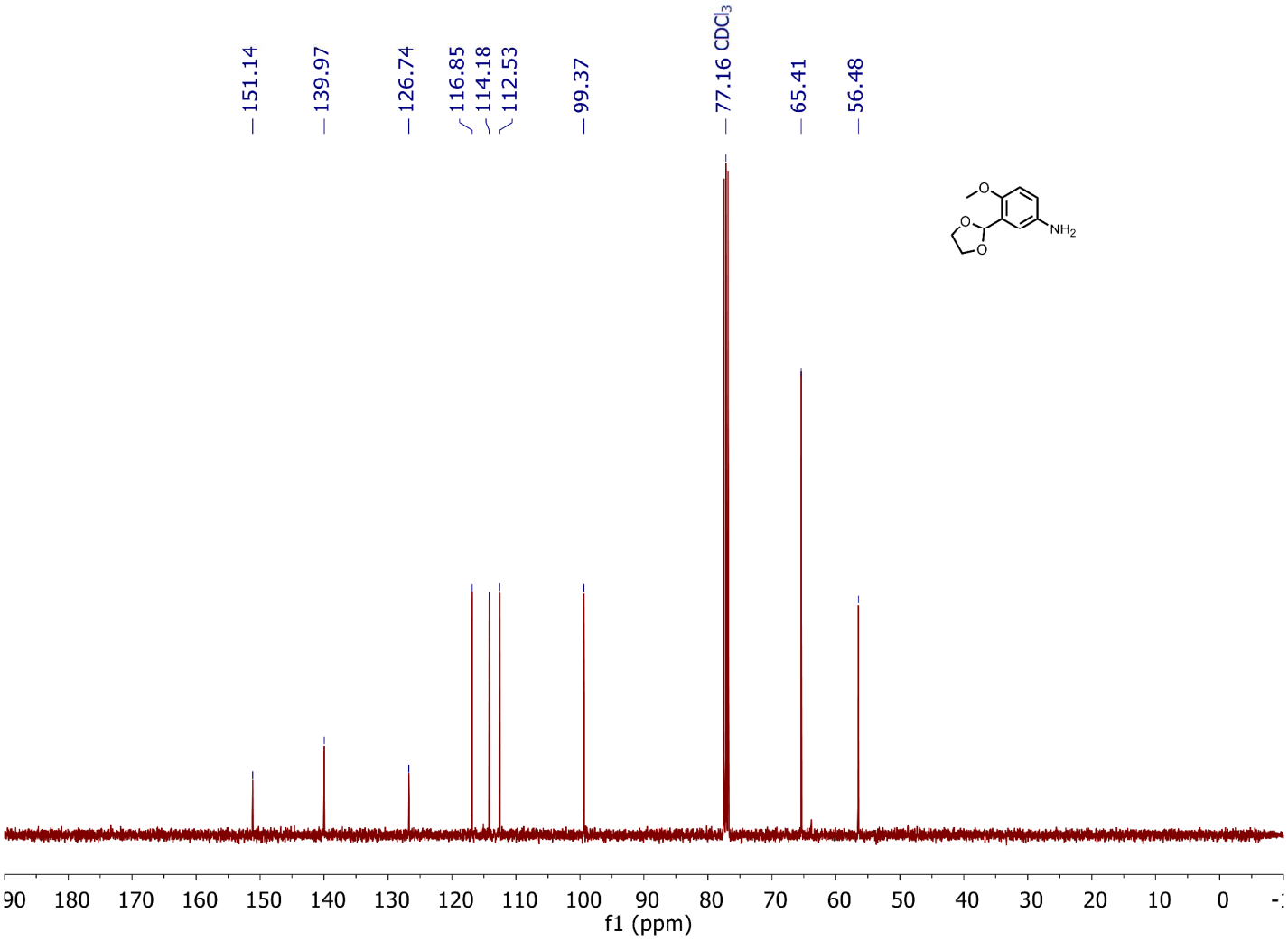
HRMS (ES+): calcd for $C_{10}H_{14}NO_3$ 196.0974, found 196.0966.

FT-IR (ATR): ν_{max} 3354, 2949, 2887, 2834, 1626, 1500, 1464, 1225, 1063 cm^{-1}.

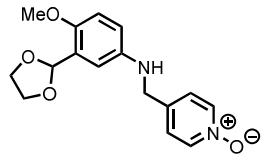
^{1}H NMR (400 MHz, $CDCl_3$) 3-(1,3-dioxolan-2-yl)-4-methoxyaniline (3)



^{13}C NMR (100.6 MHz, $CDCl_3$) 3-(1,3-dioxolan-2-yl)-4-methoxyaniline (3)



Synthesis of 4.



4-Pyridinecarboxaldehyde N-oxide (1.01 g, 8.20 mmol), compound **3** (1.69 g, 8.67 mmol) and $CHCl_3$ (50 mL), over 4 Å molecular sieves, were allowed to stand at room temperature for 16 h. The solution was filtered and had the solvent removed on a rotary evaporator to yield the crude imine (2.69 g), which was used without further purification. The crude imine was dissolved in MeOH (60 mL). $NaBH_4$ (0.93 g, 36.0 mmol) was added at 0 ^{o}C, protected by a N_2 atmosphere, and the solution stirred at room temperature for 30 minutes. Acetone (60 mL) was added and the solvent was removed on a rotary evaporator. The solid residue was dissolved in CH_2Cl_2 (100 mL), which was washed with water (3 x 40 mL) and brine (40 mL). The organic extracts were dried with Na_2SO_4, filtered and the solvent removed on a rotary evaporator. The residue was purified by flash chromatography on silica (gradient from 0 to 10% of MeOH in CH_2Cl_2) to yield compound **4** as an off white solid (2.07 g, 84 %).

Mpt: 181-184 °C.

^{1}H NMR (400 MHz, 9:1 CD_3OD-$CDCl_3$): δ_H = 8.22 (d, 2H, *J* = 7.0), 7.50 (d, 2H, *J* = 7.0), 6.83-6.77 (m, 2H), 6.55 (dd, 1H, J = 8.5, 3.0), 6.01 (s, 1H), 4.36 (s, 2H), 4.08-4.01 (m, 2H), 4.01-3.94 (m, 2H), 3.75 (s, 3H).

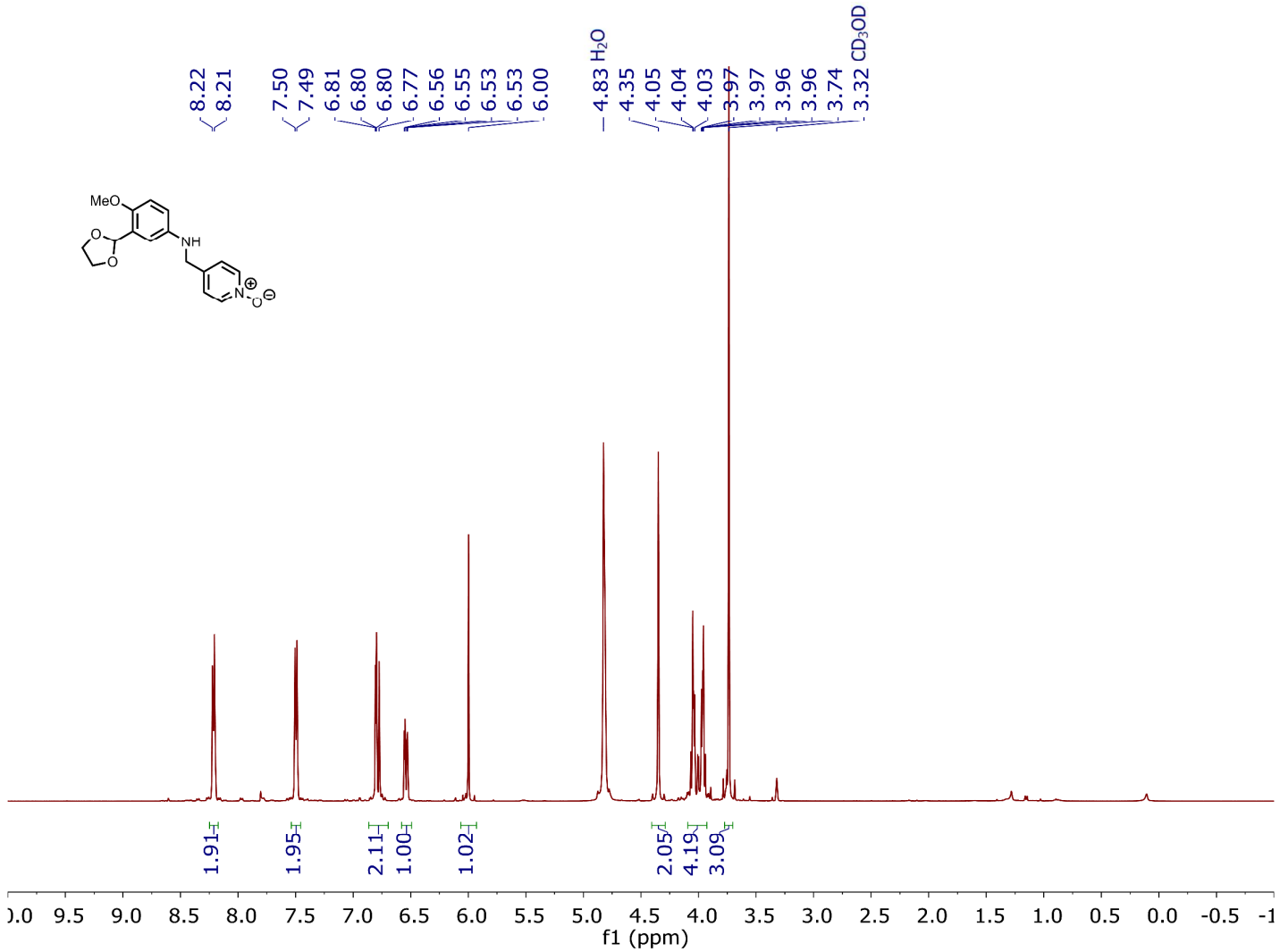
^{13}C NMR (100.6 MHz, 9:1 CD_3OD-$CDCl_3$): δ_C = 150.5, 145.1, 141.6, 138.64, 126.5, 125.2, 114.1, 112.6, 112.0, 99.1, 64.9, 55.7, 46.2.

MS (ES+): m/z (%) = 303.1 $[M+H]^+$;

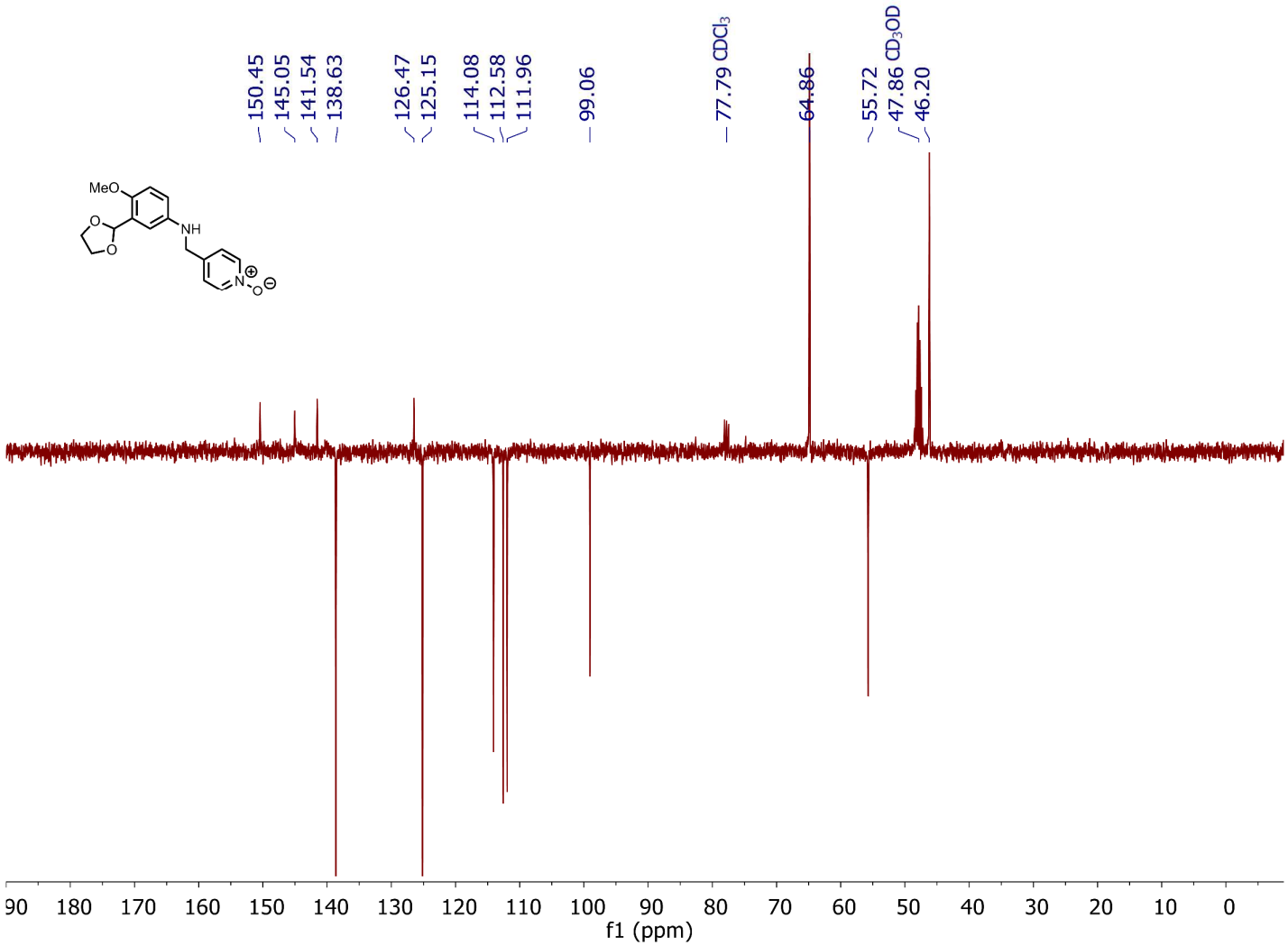
HRMS (ES+): calcd for $C_{16}H_{19}N_2O_4$ 303.1345, found 303.1354.

FT-IR (ATR): ν_{max} 3293, 2923, 1535, 1507, 1484, 1439, 1391, 1289, 1228, 1604, 960 cm^{-1}.

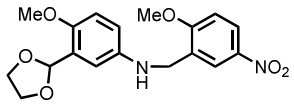
^{1}H NMR (400 MHz, 9:1 CD_3OD-$CDCl_3$) compound 4



^{13}C NMR (100.6 MHz, 9:1 CD_3OD-$CDCl_3$) compound 4



Synthesis of 5.



2-Methoxy-5-nitrobenzaldehyde (0.735 g, 4.60 mmol), compound **3** (0.959 g, 4.87 mmol) and $CHCl_3$ (50 mL), over 4 Å molecular sieves, were allowed to stand at room temperature for 16 h. The solution was filtered and had the solvent removed on a rotary evaporator to yield the crude imine (2.71 g), which was used without further purification. The crude imine was dissolved in MeOH (60 mL). $NaBH_4$ (0.70 g, 20.3 mmol) was added at 0 ^{o}C, protected by a N_2 atmosphere, and the solution stirred at room temperature for 30 minutes. Acetone (60 mL) was added and the solvent was removed on a rotary evaporator. The solid residue was dissolved in CH_2Cl_2 (100 mL), which was washed with water (3 x 40 mL) and brine (40 mL). The organic extracts were dried with Na_2SO_4, filtered and the solvent removed on a rotary evaporator. The residue was purified by flash chromatography on silica (gradient from 0 to 100% EtOAc in hexane) to yield compound **5** as a yellow solid (0.900 g, 62 %.).

Mpt: 118-119 °C.

^{1}H NMR (400 MHz, CD_3CN): δ_H = 8.19-8.15 (m, 2H), 7.12 (dt, 1H, *J* = 9.0, 1.5), 6.83-6.89 (m, 2H), 6.59 (dd, 1H, *J* = 9.0, 3.0), 5.97 (s, 1H), 4.83-4.35 (bs, 1H), 4.33 (d, 2H, *J* = 5.0), 4.05-4.01 (m, 2H), 4.01 (s, 3H), 3.96-3.92 (m, 2H), 3.72 (s, 3H).

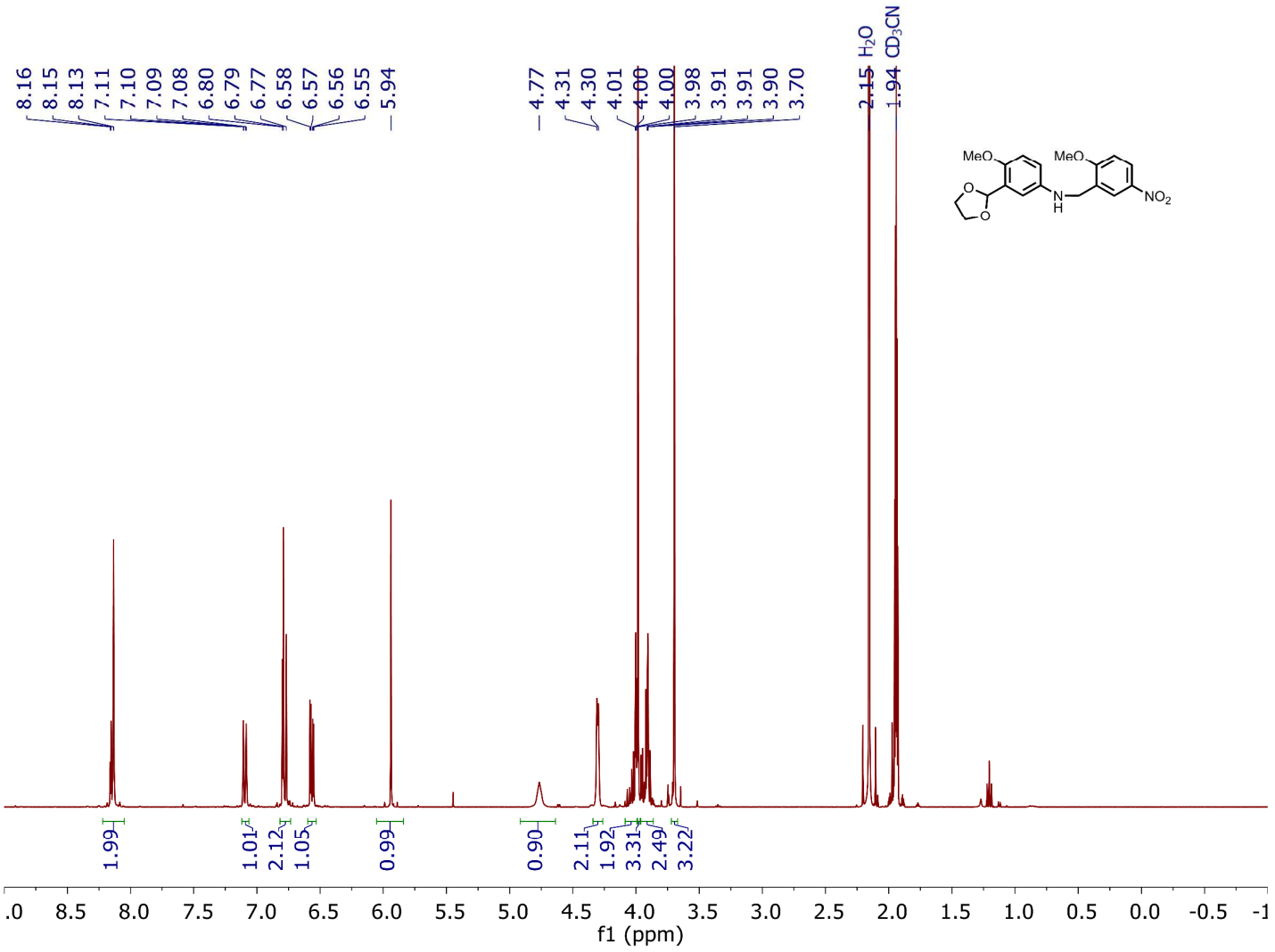
^{13}C NMR (100.6 MHz, CD_3CN): δ_C = 163.6, 151.1, 143.1, 142.3, 130.7, 128.1, 125.4, 124.4, 114.9, 113.8, 112.7, 111.6, 99.7, 65.9, 57.2, 56.9, 43.2.

MS (ES+): m/z (%) = 361.1 $[M+H]^+$.

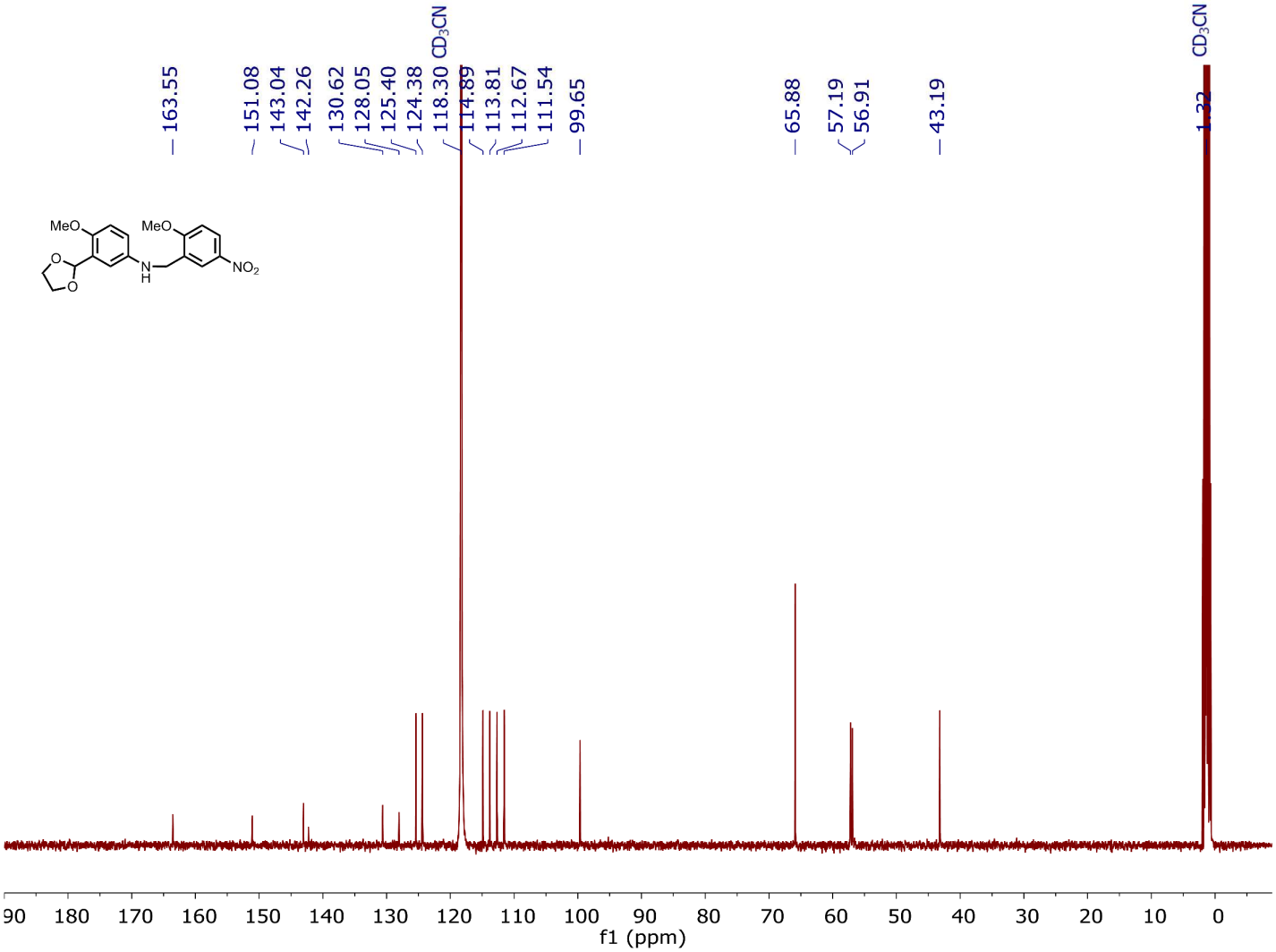
HRMS (ES+): calcd for $C_{18}H_{21}N_2O_6$ 361.1400, found 361.1399.

FT-IR (ATR): ν_{max} 3363, 3064, 3029, 2921, 2844, 1590, 1511, 1494, 1335, 1295, 1054 cm^{-1}.

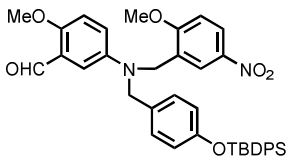
^{1}H NMR (400 MHz, CD_3CN) compound 5



^{13}C NMR (100.6 MHz, CD_3CN) compound 5



Synthesis of 7.



Benzaldehyde derivative **6** (2.14 g, 3.40 mmol), aniline **5** (0.820 g, 1.52 mmol), $NaBH(AcO)_3$ (0.902 g, 4.26 mmol) and degassed $CHCl_3$ (15 mL) were stirred at room temperature for 24 h. Na_2CO_3 (10 mL of a 1M solution) was added and the aqueous layer was extracted with $CHCl_3$ (3 x 30 mL). The organic extract was dried with $MgSO_4$, filtered and the solvent removed on a rotary evaporator to yield the yellow solid, which was partially purified by flash chromatography (a gradient from 0 to 100% EtOAc in hexane) to yield a mixture of the acetal and the aldehyde (1.51 g), which was immediately dissolved in $CHCl_3$ (10 mL) and HCl (3 mL of a 10 M solution), which was vigorously stirred at room temperature for 16 h. The reaction mixture was neutralized with $NaHCO_3$ (20 mL of a 1 M solution), and the aqueous layer was extracted with $CHCl_3$ (3 x 50 mL). The combined organic extracts were washed with brine (50 mL), dried with $MgSO_4$ and filtered. The solvent was removed on a rotary evaporator and the residue was purified by flash chromatography on silica (gradient from 0 to 100% EtOAc in hexane) to yield compound **7** as a yellow foam (0.950 g, 95 %).

Mpt: 57-59 ^{o}C.

^{1}H NMR (400 MHz, CD_3CN): δ_H = 10.32 (s, 1H), 8.16 (dd, 1H, *J* = 9.0, 3.0), 7.88 (d, 1H, *J* = 3.0), 7.72 (dt, 4H, *J* = 6.5, 1.5), 7.48-7.39 (m, 6H), 7.10 (d, 1H, *J* = 9.0), 7.02 (d, 2H, *J* = 9.0), 7.00-6.95 (m, 3H), 6.73 (d, 2H, *J* = 8.5), 4.56 (s, 2H), 4.54 (s, 2H), 3.95 (s, 3H), 3.83 (s, 3H), 1.08 (s, 9H).

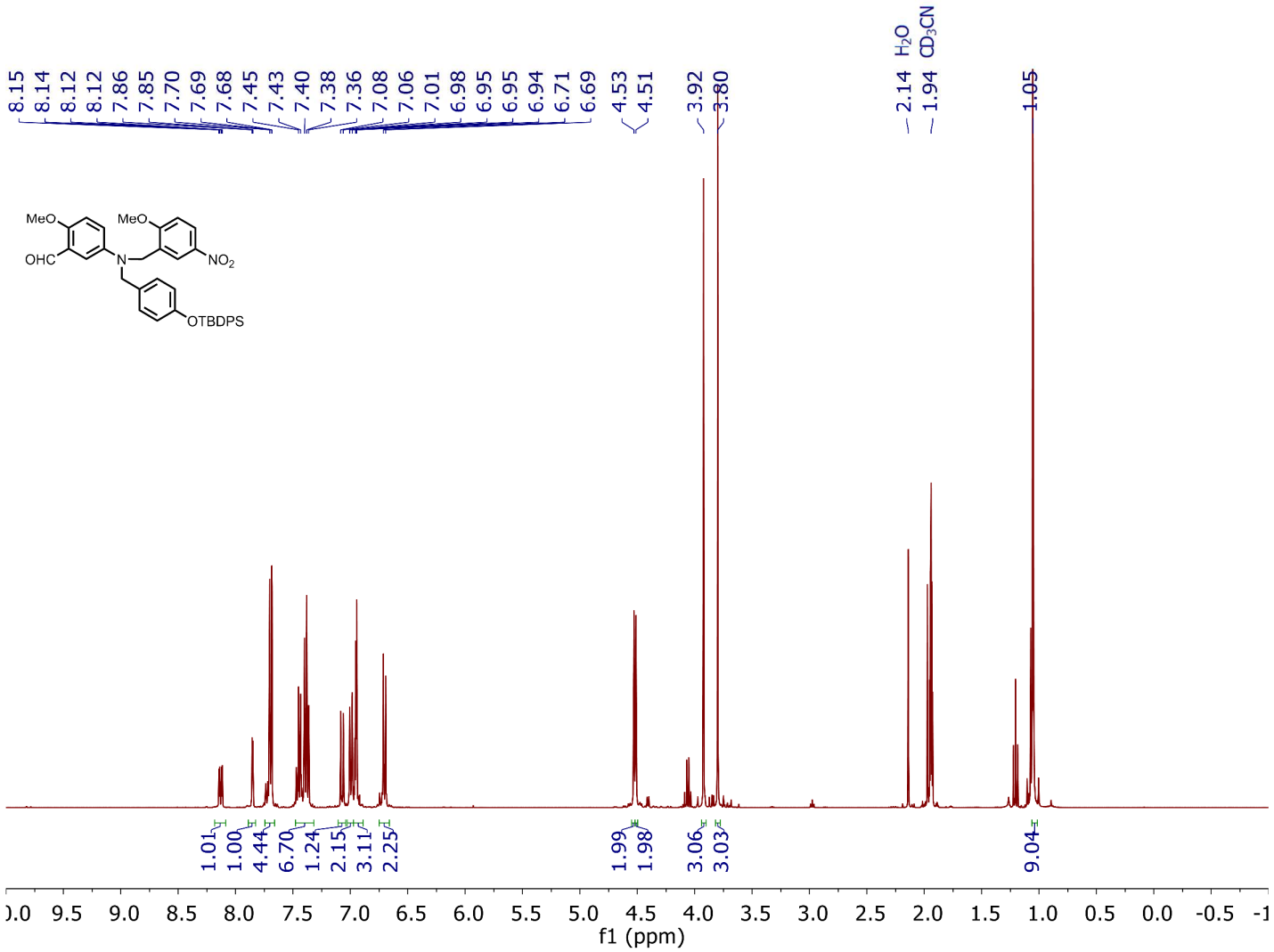
^{13}C NMR (100.6 MHz, CD_3CN): δ_C = 190.0, 163.4, 155.5, 143.4, 142.2, 136.3, 133.6, 132.1, 131.1, 128.9, 128.8, 128.7, 125.7, 125.5, 123.6, 122.1, 120.6, 118.2, 114.7, 111.6, 111.4, 57.1, 56.8, 55.3, 50.7, 26.2, 19.9.

MS (ES+): m/z (%) = 661.3 $[M+H]^+$.

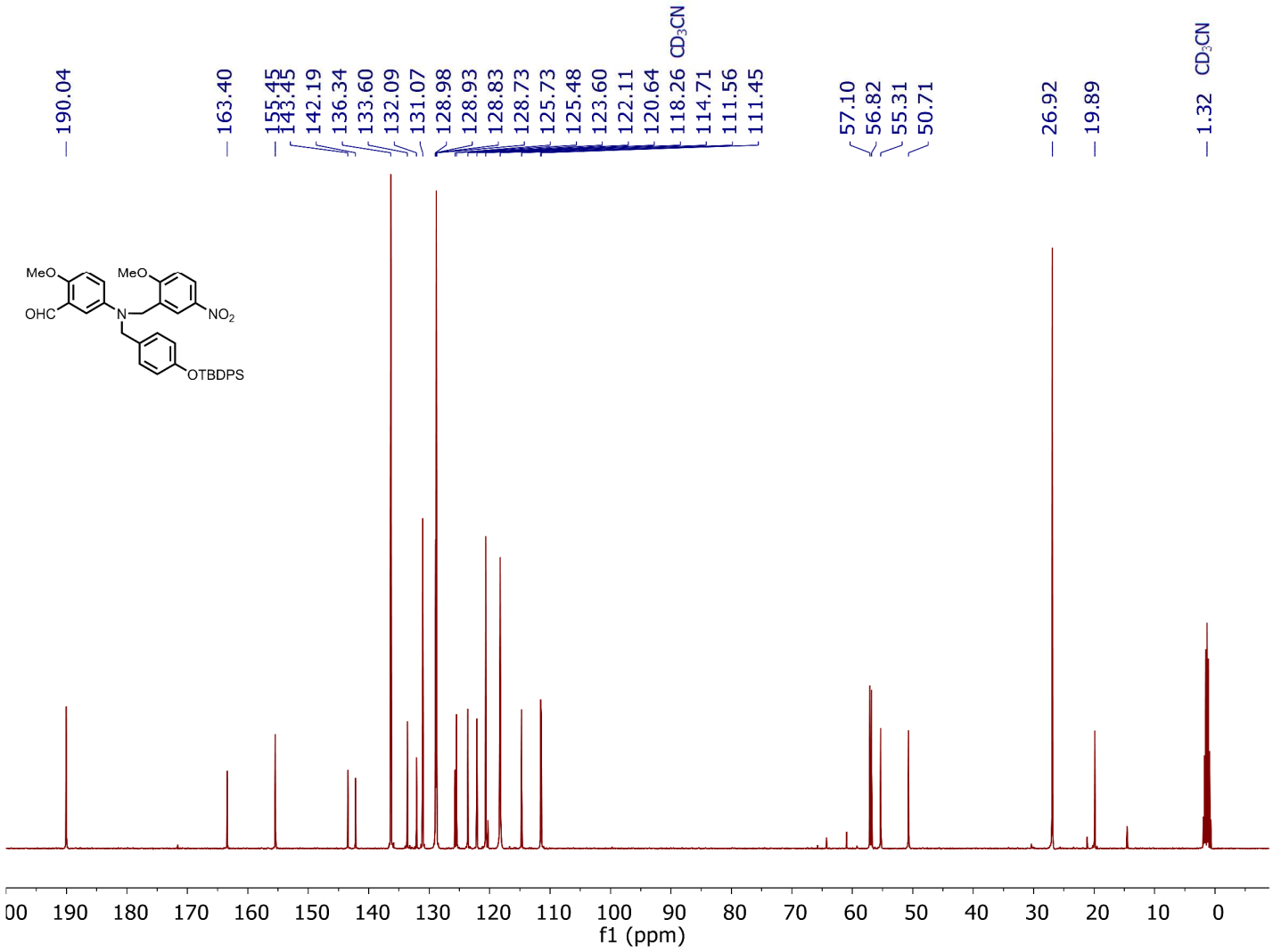
HRMS (ES+): calcd for $C_{39}H_{41}N_2O_6Si$ 661.2743, found 661.2725.

FT-IR (ATR): ν_{max} 2931, 2857, 1677, 1608, 1591, 1500, 1337, 1251, 913 cm^{-1}.

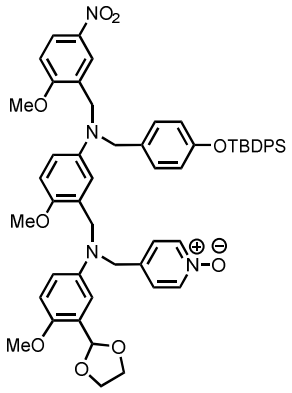
^{1}H NMR (400 MHz, CD_3CN) compound 7



^{13}C NMR (100.6 MHz, CD_3CN) compound 7



Synthesis of 10.



Aldehyde **7** (0.423 g, 0.640 mmol), aniline derivative **4** (0.093 g, 0.307 mmol), $NaBH(AcO)_3$ (0.182 g, 0.860 mmol) and degassed $CHCl_3$ (2 mL) were stirred at room temperature for 24 h. Na_2CO_3 (2 mL of a 1M solution) was added, and the aqueous layer was extracted with $CHCl_3$ (5 x 10 mL) The organic extract was dried with $MgSO_4$, filtered and the solvent removed on a rotary. The obtained residue was purified by flash chromatography on silica (gradient from 0:1:0 to 1:9:0 to 0:9:1 MeOH:EtOAc:CH_2Cl_2)to yield compound **10** as a yellow foam (0.219 g, 75 %).

Mpt: 85-88 ^{o}C.

^{1}H NMR (400 MHz, CD_3CN): δ_H = 8.06 (dd, 1H, *J* = 9.0, 3.0), 7.97 (dt, 2H, *J* = 7.0, 1.5), 7.76-7.70 (m, 5H), 7.50-7.45 (m, 2H), 7.40 (m, 4H), 7.07 (d, 2H, *J* = 7.0), 6.97 (d, 1H, *J* = 9.5), 6.94, (d, 2H, *J* = 9.5), 6.78 (d, 1H,*J* = 9.0), 6.72 (dt, 2H, *J* = 8.5, 2.0), 6.68 (d, 1H, *J* = 3.0), 6.63 (d, 1H, *J* = 9.0), 6.55 (dd, 1H, *J* = 9.0, 3.0), 6.35 (dd, 1H, *J* = 9.0, 3.0), 6.31 (d, 1H, *J* = 3.0), 5.90 (s, 1H), 4.45 (s, 2H), 4.42 (s, 2H), 4.40 (s, 2H), 4.19 (s, 2H), 3.89 (s, 3H), 3.88-3.85 (m, 4H), 3.73 (s, 3H), 3.71 (s, 3H), 1.09 (s, 9H).

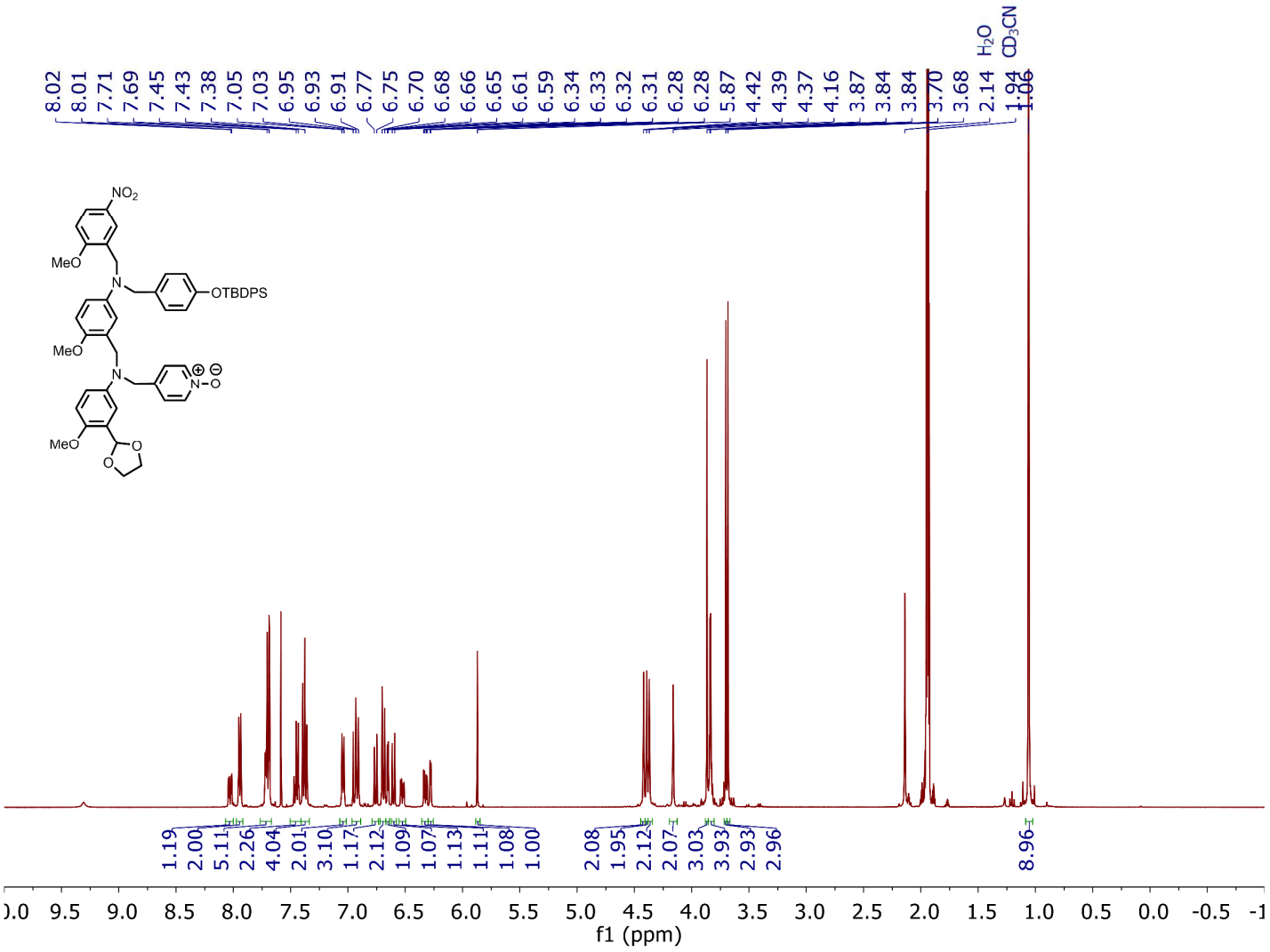
^{13}C NMR (100.6 MHz, CD_3CN): δ_C = 163.1, 155.4, 155.4, 150.9, 150.4, 143.2, 143.1, 139.5, 139.3, 136.4, 133.7, 133.7, 133.0, 131.1, 129.1, 128.9, 127.4, 125.5, 125.2, 123.4, 120.6, 115.2, 114.1, 113.1, 112.8, 112.7, 112.6, 111.6, 99.7, 65.8, 57.1, 56.6, 56.4, 55.8, 54.5, 51.2, 51.1, 26.9, 19.9.

MS (ES+): m/z (%) = 474.2 $[M+2H]^+$, 947.4 $[M+H]^+$.

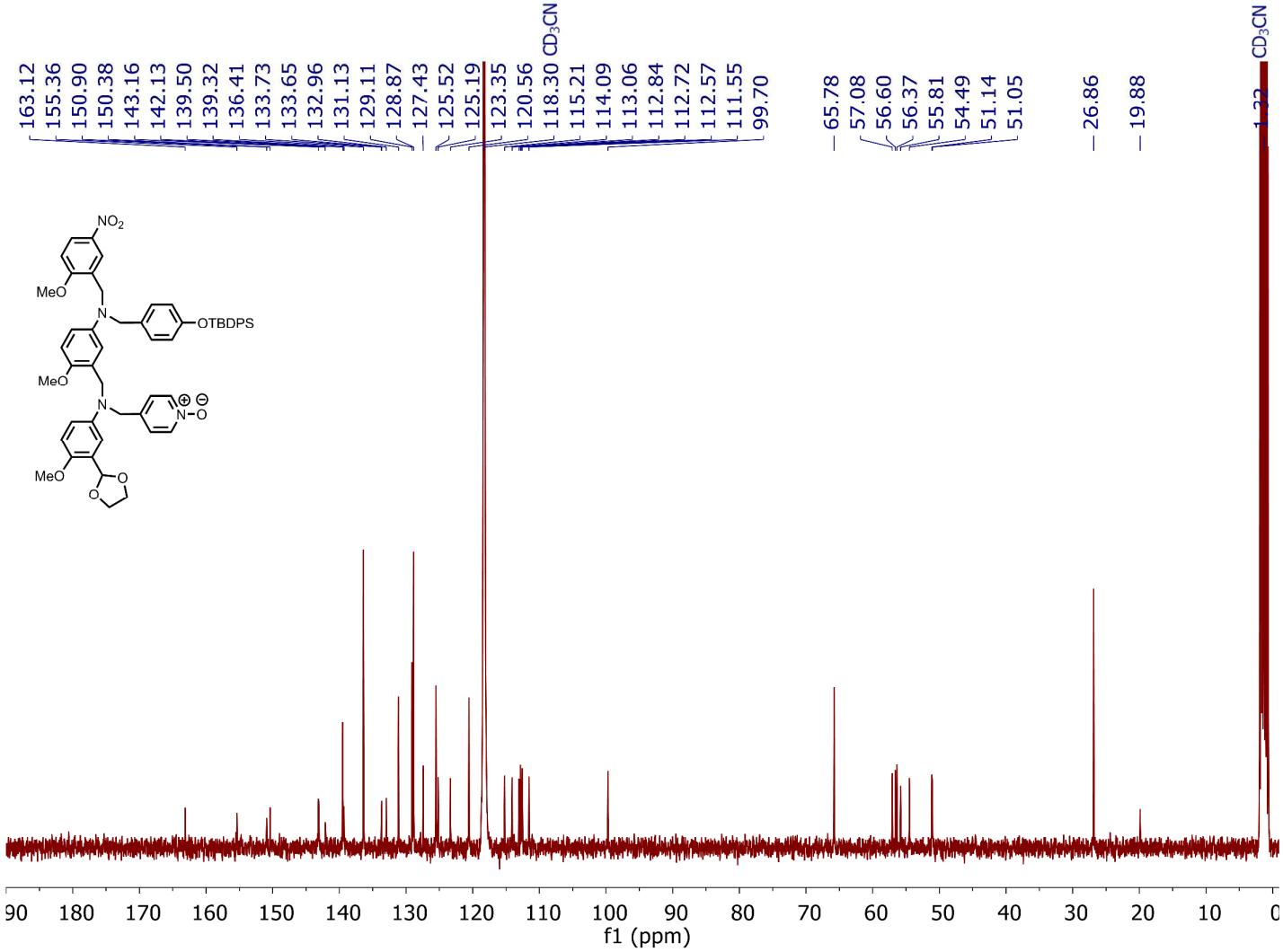
HRMS (ES+): calcd for $C_{55}H_{59}N_4O_9Si$ 947.4051, found 947.4033.

FT-IR (ATR): ν_{max} 2931, 2898, 2858, 1609, 1591, 1504, 1464, 1428, 1337, 1260, 1227, 1021 cm^{-1}.

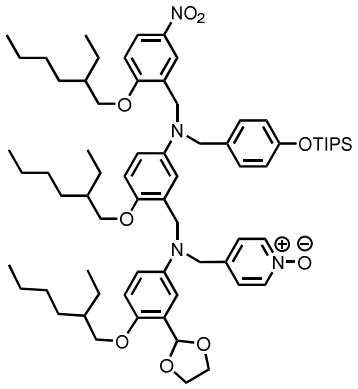
^{1}H NMR (400 MHz, CD_3CN) compound 10



^{13}C NMR (100.6 MHz, CD_3CN) compound 10



Synthesis of 11.



Aldehyde **8** (2.02 g, 2.60 mmol) and aniline derivative **9** (2.09 g, 5.21 mmol) were dissolved in $CHCl_3$ (9 mL) and $NaBH(OAc)_3$ (1.55 g, 7.29 mmol, 2.8 equiv.) was added with stirring. After 2 days of stirring more $NaBH(OAc)_3$ was added (1.0 g) and then after 2 more days the reaction was quenched with saturated aqueous $NaHCO_3$ solution and extracted into $CHCl_3$ (4 × 10 mL). All the organic fractions were washed with water (1 × 10 mL), brine (1 × 10 mL) and dried ($MgSO_4$) before the solvent removed with a rotary evaporator. The crude product was purified using flash chromatography on silica (gradient from 5 to 10% of EtOAc in hexane and then 10 to 100% MeOH in a 1:1 mixture of CH_3CN and $CHCl_3$) to yield compound **11** as a pale yellow oil (2.24 g, 74%).

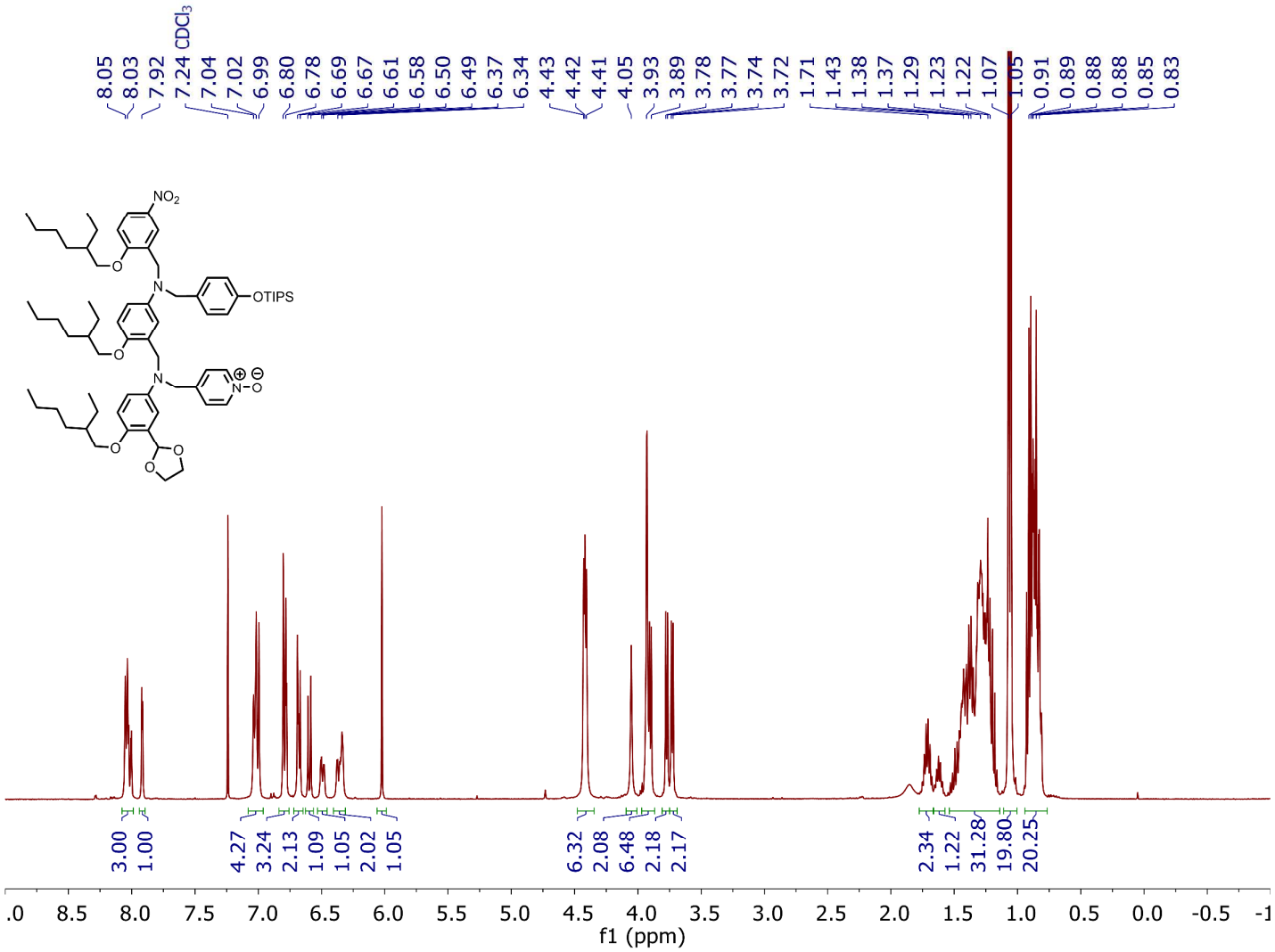
^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 8.06-7.99 (m, 3H), 7.92 (d, 1H, *J* = 3.0), 7.08-6.96 (m, 4H), 6.82-6.76 (m, 3H), 6.70-6.65 (m, 2H), 6.60 (d, 1H, *J* = 9.0), 6.49 (dd, 1H, *J* = 9.0, 3.0), 6.36 (dd, 1H, *J* = 9.0, 3.0), 6.34 (d, 1H, *J* = 3.0), 6.02 (s, 1H), 4.46-4.37 (m, 6H), 4.05 (s, 2H), 3.99-3.87 (m, 6H), 3.77 (d, 2H, *J* = 5.5), 3.73 (d, 2H, *J* = 5.5), 1.77-1.57 (m, 3H), 1.55-1.15 (m, 27H), 1.06 (d, 18H, *J* = 7.0), 0.94-0.79 (m, 18H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C = 161.7, 155.1, 150.2, 149.4, 142.6, 142.5, 141.5, 140.0, 139.1, 131.3, 128.6, 128.2, 126.8, 126.3, 124.5, 124.4, 123.2, 120.2, 114.7, 113.7, 113.4, 112.6, 112.0, 111.7, 110.6, 99.5, 71.9, 71.6, 70.9, 65.3, 55.7, 53.0, 50.6, 50.4, 39.7, 39.7, 39.4, 30.8, 30.7, 30.7, 29.3, 29.3, 29.3, 24.2, 24.1, 24.1, 23.3, 23.2, 23.2, 18.1, 14.3, 14.3, 12.8, 11.4.

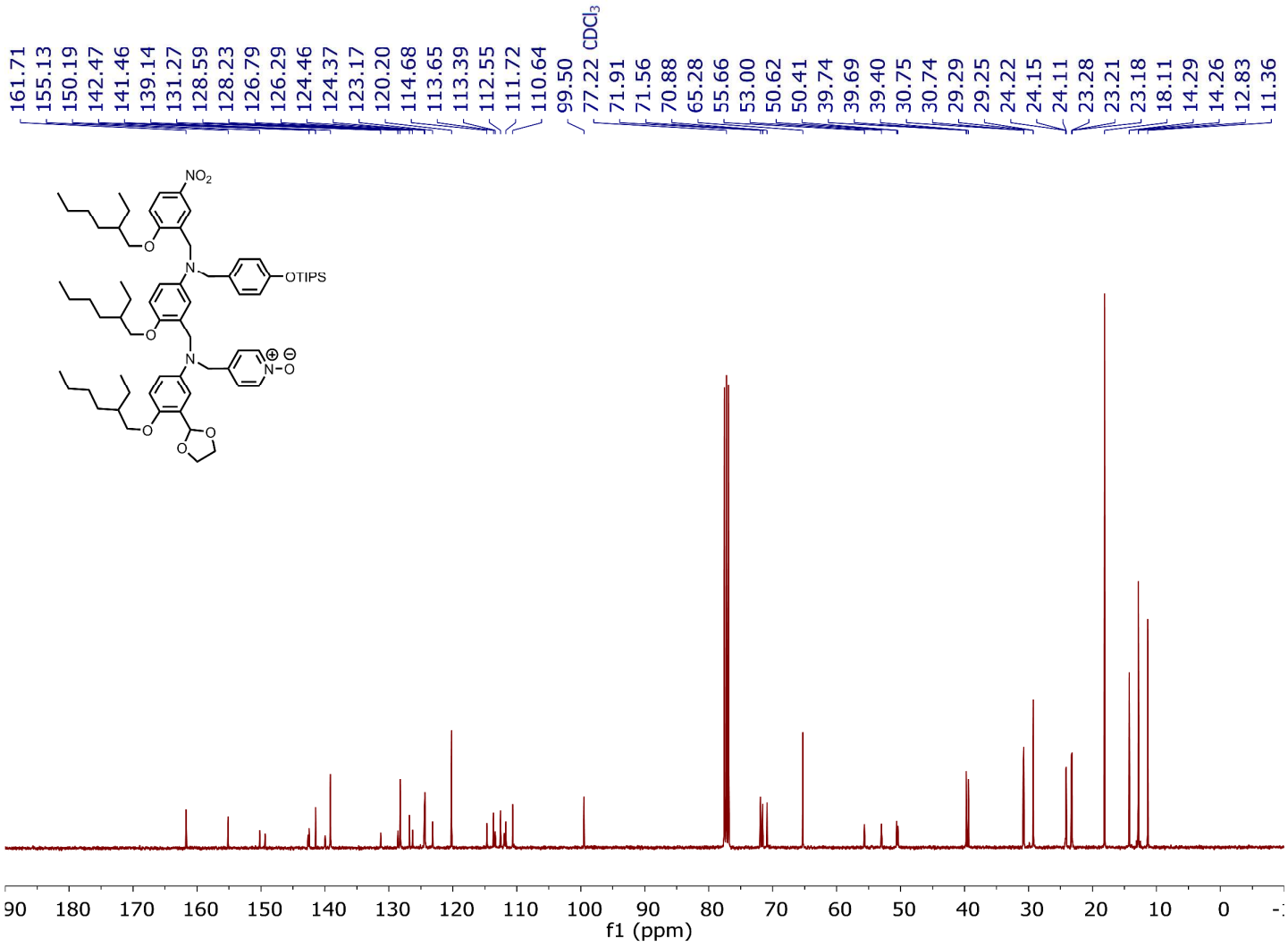
HRMS (ES+): calculated for $C_{69}H_{103}N_4O_9Si$ 1159.7494, found 1159.7439.

FT-IR (thin film): ν_{max} 2958, 2926, 2863, 1681, 1609, 1592, 1504, 1463, 1338, 1262, 1227, 1166 cm^{-1}.

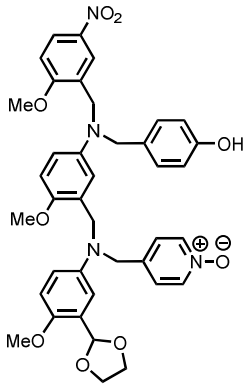
^{1}H NMR (400 MHz, $CDCl_3$) compound 11



^{13}C NMR (100.6 MHz, $CDCl_3$) compound 11



Synthesis of 12.



Compound **10** (0.082 g, 0.086 mmol) was dissolved in THF (1 mL) and a solution of TBAF in THF (1M, 0.300 mL, 0.300 mmol) was added dropwise at 0 °C. The reaction was stirred at 0 °C for 30 minutes and the solvent was removed on a rotary evaporator. The residue was purified by flash chromatography on silica (gradient from 10 to 100% of MeOH in CH_2Cl_2) to yield compound **12** as a yellow solid, which was recrystallized from chloroform (0.056 g, 91 %).

Mpt: 181 °C ($CHCl_3$).

^{1}H NMR (400 MHz, DMSO-d_6): δ_H = 9.26 (s, 1H), 8.11-8.04 (m, 3H), 7.73 (d, 1H, *J* = 2.5), 7.12-7.07 (m, 3H), 6.98 (d, 2H, *J* = 8.5), 6.81 (d, 1H, *J* = 9.0), 6.69-6.64 (m, 3H), 6.61 (d, 1H, *J* = 3.0), 6.55 (dd, 1H, J = 9.0, 3.0), 6.34 (d, 1H, *J* = 3.5), 6.33-6.29, (m, 1H), 5.85 (s, 1H), 4.46 (s, 2H), 4.39 (s, 4H), 4.21 (s, 2H), 3.90 (s, 3H), 3.86-3.82 (m, 4H), 3.68 (s, 3H), 3.67 (s, 3H).

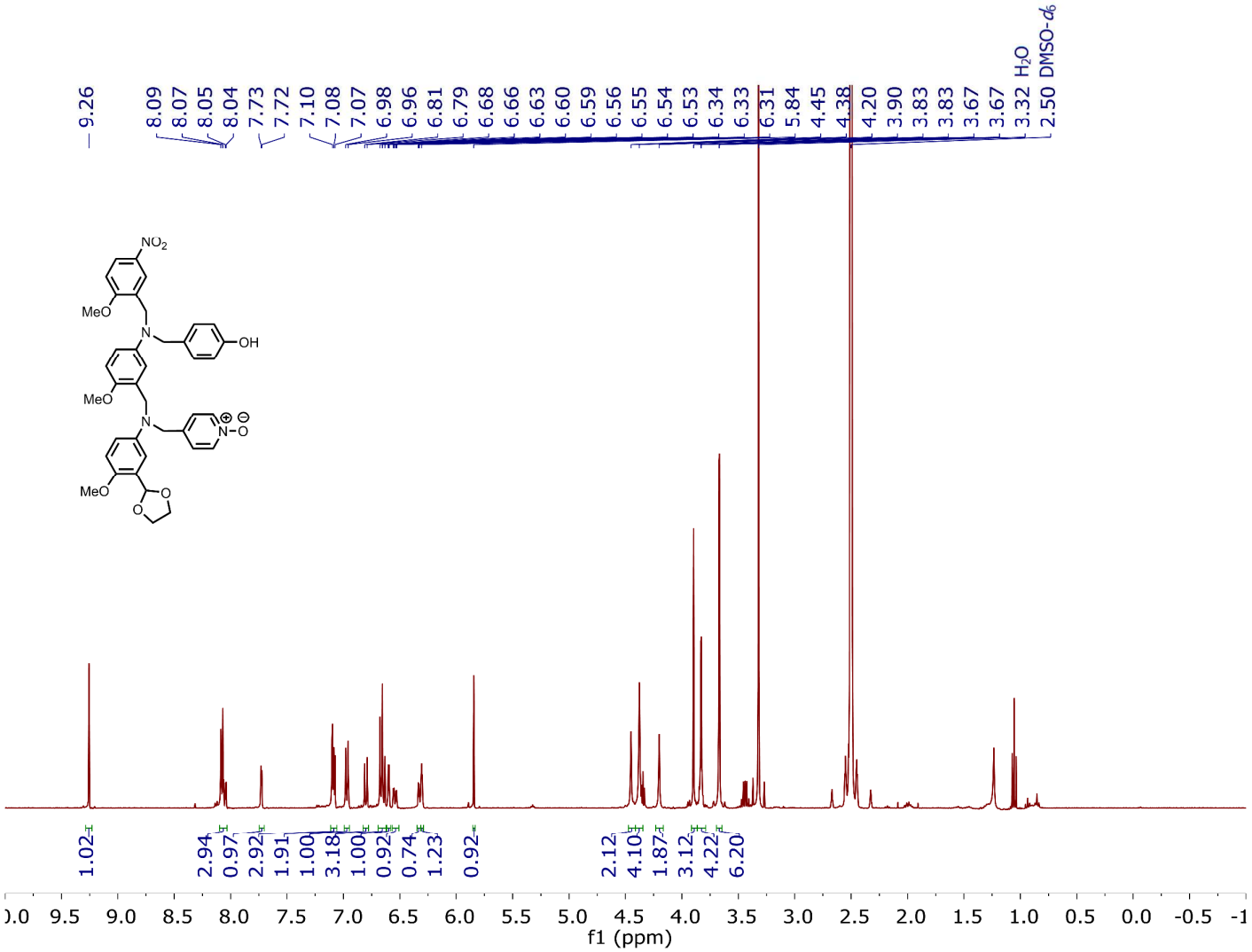
^{13}C NMR (100.6 MHz, DMSO-d_6): δ_C = 161.8, 156.2, 149.3, 148.7, 142.0, 141.6, 140.6, 138.4, 137.7, 128.9, 128.2, 127.9, 126.0, 125.9, 124.5, 124.2, 121.9, 115.2, 113.9, 112.7, 112.1, 111.9, 111.5, 111.2, 111.0, 98.3, 64.4, 56.4, 56.0, 55.7, 55.5, 54.5, 52.8, 50.3, 49.6.

MS (ES+): m/z (%) = 709.3 $[M+H]^+$, 375.7 $[M+CH_3CN+2H]^{2+}$, 355.1 $[M+2H]^{2+}$.

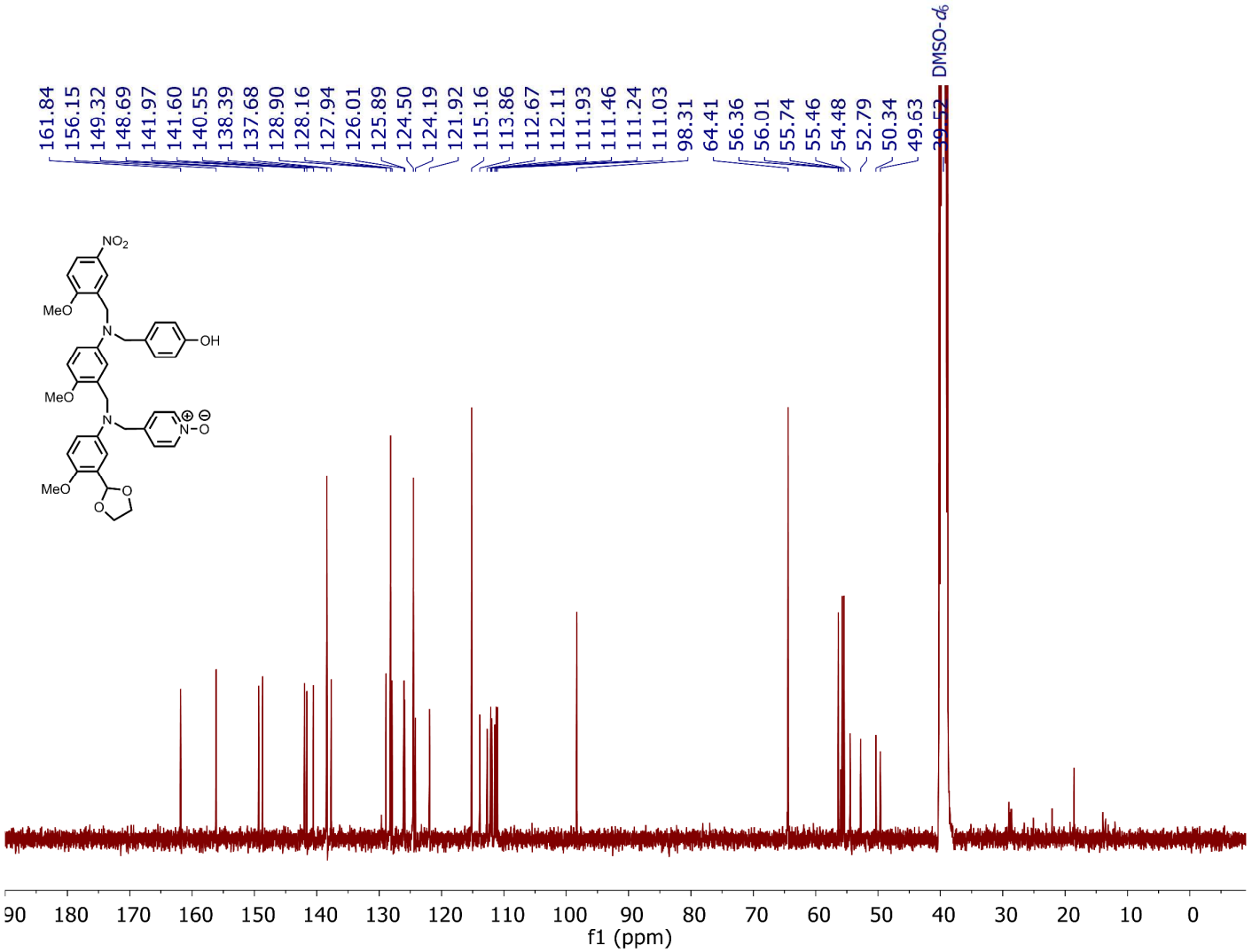
HRMS (ES+): calcd for $C_{39}H_{41}N_4O_9$ 709.2874, found 947.4033.

FTIR (ATR): ν_{max} 3115, 2936, 2832, 1591, 1502, 1336, 1261, 1224, 1020 cm^{-1}.

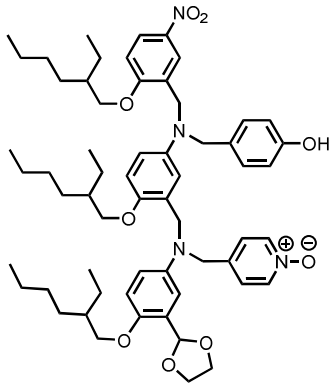
^{1}H NMR (400 MHz, DMSO-d_6) compound 12



^{13}C NMR (100.6 MHz, DMSO-d_6) compound 12



Synthesis of 13.



Compound **11** (0.082 g, 0.070 mmol) was dissolved in THF (2 mL) and a solution of TBAF in THF (1M, 0.140 mL, 0.140 mmol) was added dropwise at 0 °C. After 1 h of stirring at room temperature, water (5 mL) was added and the aqueous mixture washed with Et_2O (4 × 10 mL). All organic fractions were combined and washed with brine (1 × 10 mL) dried ($MgSO_4$) and the solvent removed on a rotary evaporator. The crude mixture was then purified by flash chromatography on silica (gradient from 0 to 5% of MeOH in CH_2Cl_2) to yield compound **13** as a yellow oil (0.048 g, 66%).

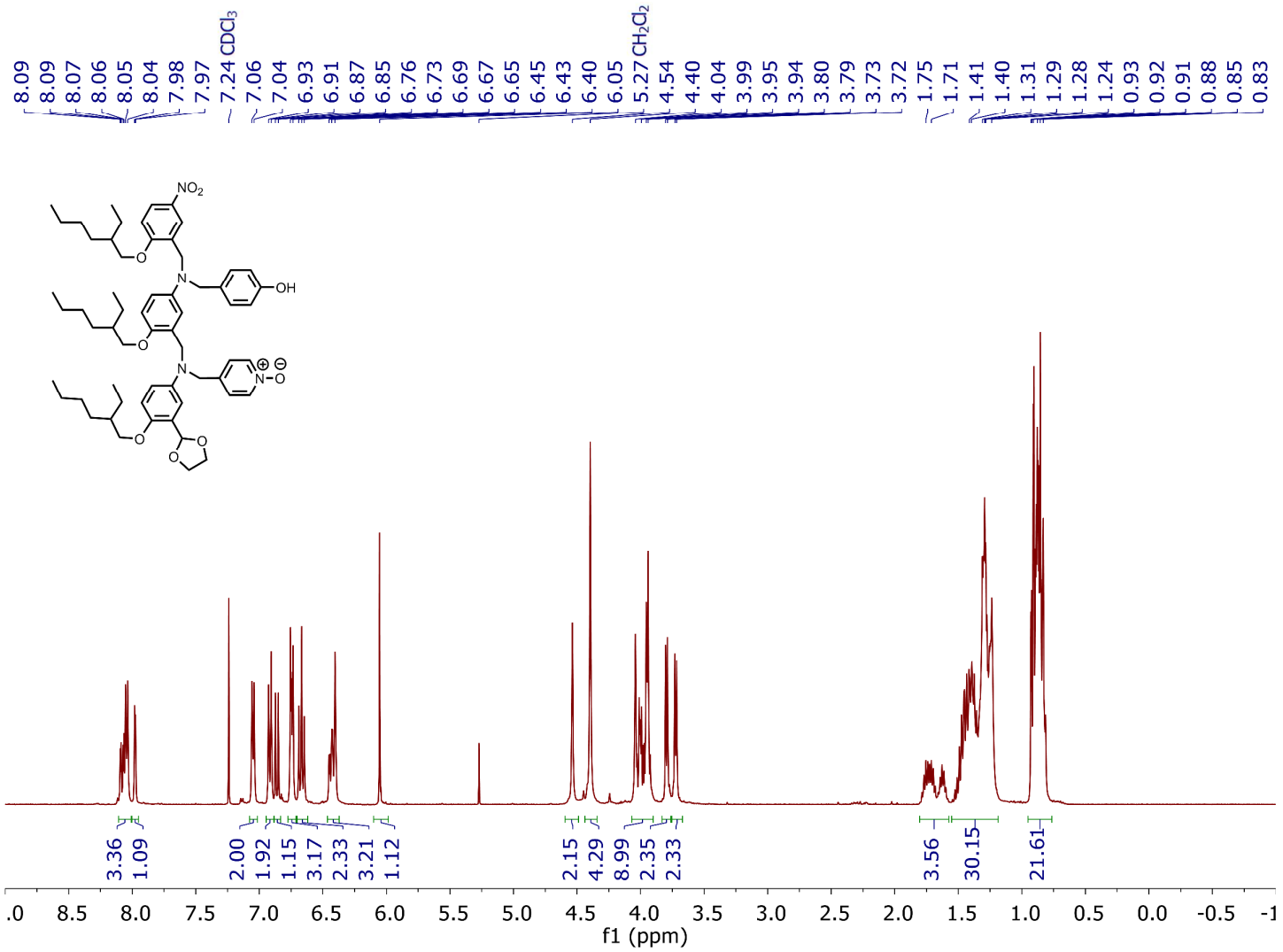
^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 8.08 (dd, 1H, *J* = 9.0, 3.0), 8.04 (d, 2H, *J* = 6.5), 7.98 (d, 1H, *J* = 9.0, 3.0), 7.05 (d, 2H, *J* = 6.5), 6.92 (d, 2H, *J* = 8.5), 6.86 (d, 1H, *J* = 9.0), 6.77-6.72 (m, 3H), 6.68 (d, 1H, *J* = 9.0), 6.66 (d, 1H, *J* = 9.0), 6.46-6.38 (m, 3H), 6.05 (s, 1H), 4.54 (s, 2H), 4.40 (s, 4H), 4.04 (s, 2H), 4.03-3.92 (m, 6H) 3.80 (d, 2H, *J* = 5.5), 3.72 (d, 2H, *J* = 5.5), 1.81-1.57 (m, 3H,), 1.55-1.18 (m, 24H), 0.94-0.79 (m, 18H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C = δ 161.9, 156.0, 150.5, 149.2, 142.5, 142.4, 141.6, 139.0, 129.7, 128.8, 127.9, 126.6, 126.3, 124.6, 124. 5, 123.3, 116.2, 115.4, 113.9, 113.7, 112.6, 112.5, 111.9, 110.6, 99.7, 71.9, 71.6, 70.8, 65.3, 55.9, 53.5, 51.4, 51.1, 39.7, 39.4, 30.8, 30.7, 29.3, 29.2, 24.3, 24.2, 24.1, 23.4, 23.2, 23.1, 14.3, 11.3.

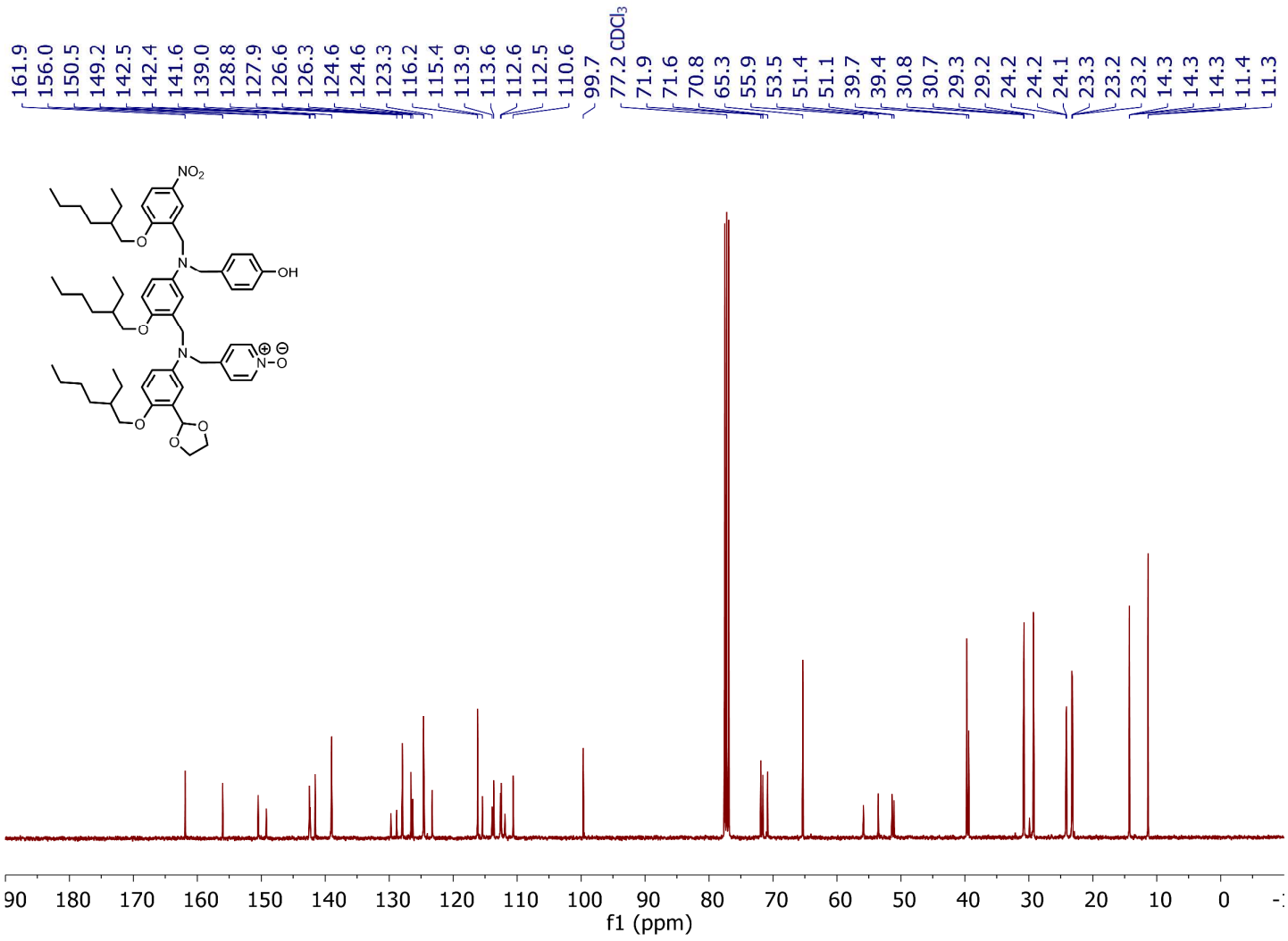
HRMS (ES+): calculated for $C_{60}H_{82}N_4O_9{}^{23}Na$ 1025.5974, found 1025.5943.

FT-IR (thin film): ν_{max} 2956, 2925, 2857, 1681, 1613, 1592, 1500, 1463, 1338, 1263, 1221, 1167 cm^{-1}.

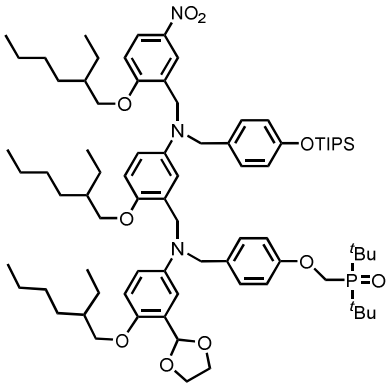
^{1}H NMR (400 MHz, $CDCl_3$) compound 13



^{13}C NMR (100.6 MHz, $CDCl_3$) compound 13



Synthesis of 15.



Aldehyde **8** (0.158 g, 0.20 mmol) and aniline **14** (0.175 g, 0.31 mmol) were dissolved in DCE (0.700 mL) and $NaBH(OAc)_3$ (0.121 g, 0.57 mmol) was added. After 2 days od stirring at room temperature the reaction was quenched with saturated aqueous $NaHCO_3$ solution, and extracted into $CHCl_3$ (4 × 10 mL). All the organic fractions were washed with water (1 × 10 mL), brine (1 × 10 mL) and dried ($MgSO_4$) before the solvent removed on a rotary evaporator. The crude product was purified using flash chromatography on silica (gradient from 0 to 10% of MeOH in Et_2O) to yield compound **15** a pale yellow oil (0.217 g, 80%).

^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 8.00 (dd, 1H, *J* = 9.0, 3.0), 7.94 (d, 1H, *J* = 3.0), 7.11 (d, 2H, *J* = 8.5), 7.07 (d, 2H, *J* = 8.5), 6.79-6.85 (m, 4H), 6.76 (d, 1H, *J* = 9.0), 6.74 (d, 1H, *J* = 3.0) 6.72 (dd, 1H, *J* = 9.0, 3.0), 6.51-6.58 (m, 2H), 6.41 (d, 1H, *J* = 3.0), 6.34 (dd, 1H, *J* = 9.0, 3.0), 6.08 (s, 1H), 4.49 (s, 2H), 4.41-4.45 (m, 4H), 4.36 (d, 2H, *J* = 7.5), 4.21 (s, 2H), 3.90-3.93 (m, 6H), 3.79 (d, 2H, *J* = 5.5), 3.76 (d, 2H, *J* = 5.5), 1.60-1.79 (m, 3H), 1.18-1.58 (m, 45H), 1.09 (d, 18H, *J* = 7.5), 0.81-0.98 (m, 17H).

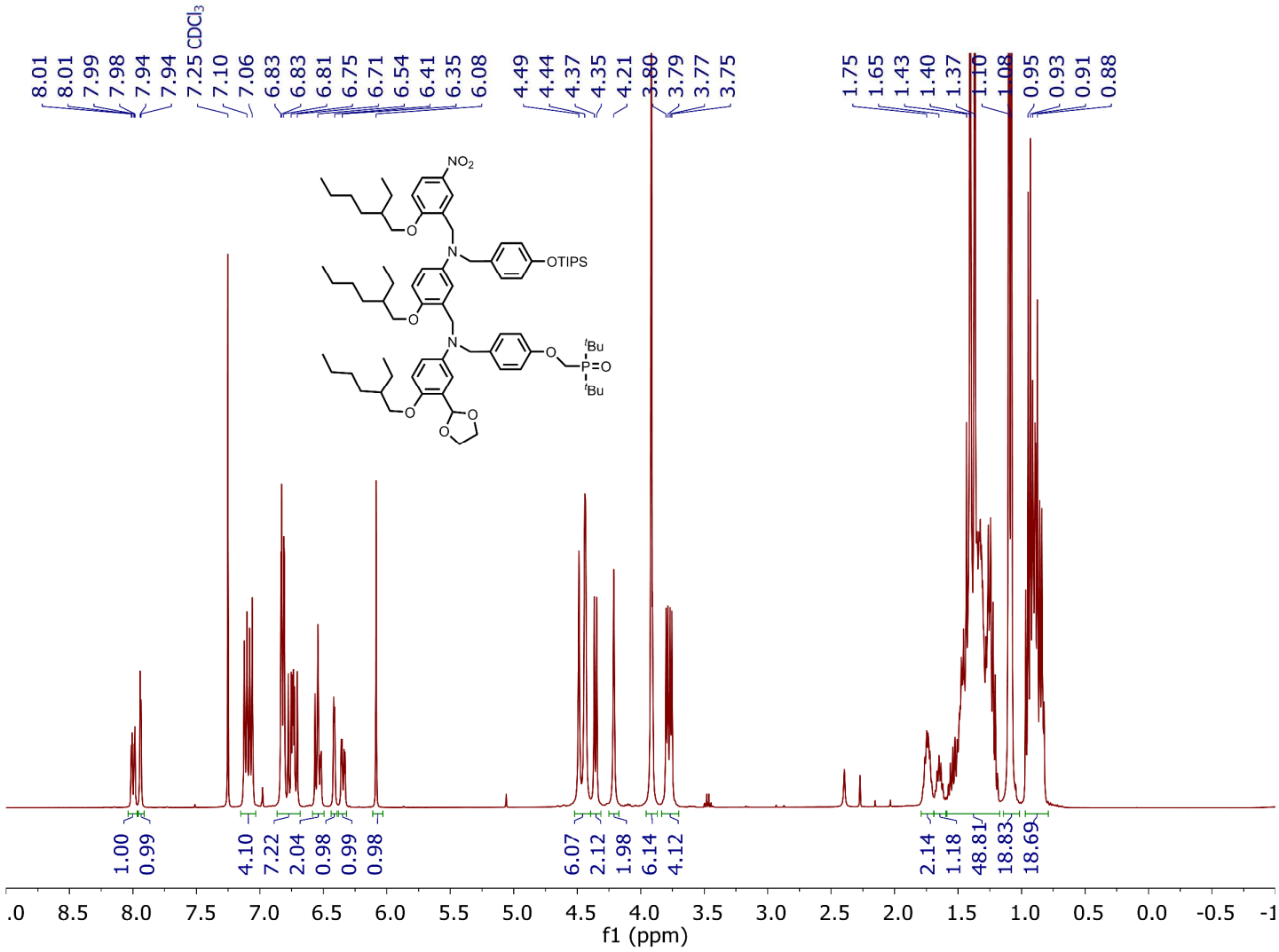
^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C = 161.6, 157.4 (d, *J* = 11.0), 155.1, 149.3, 149.3, 143.3, 142.8, 141.5, 132.9, 131.4, 128.6, 128.4, 128.3, 127.3, 126.6, 124.4, 123.2, 120.1, 114.2, 113.9, 113.5, 113.2, 112.5, 111.6, 111.2, 110.6, 99.9, 71.9, 71.5, 71.0, 65.2, 62.8 (d, *J* = 70.5), 55.8, 54.0, 50.4, 49.8, 39.9, 39.7, 39.5, 35.7 (d, *J* = 57.5), 30.9, 30.8, 30.8, 29.3, 29.3, 29.3, 26.7, 24.3, 24.2, 24.2, 23.3, 23.2, 18.2, 14.3, 14.3, 12.9, 11.4.

MS (MALDI+): m/z (%) = 1332.2 $[M+H]^+$.

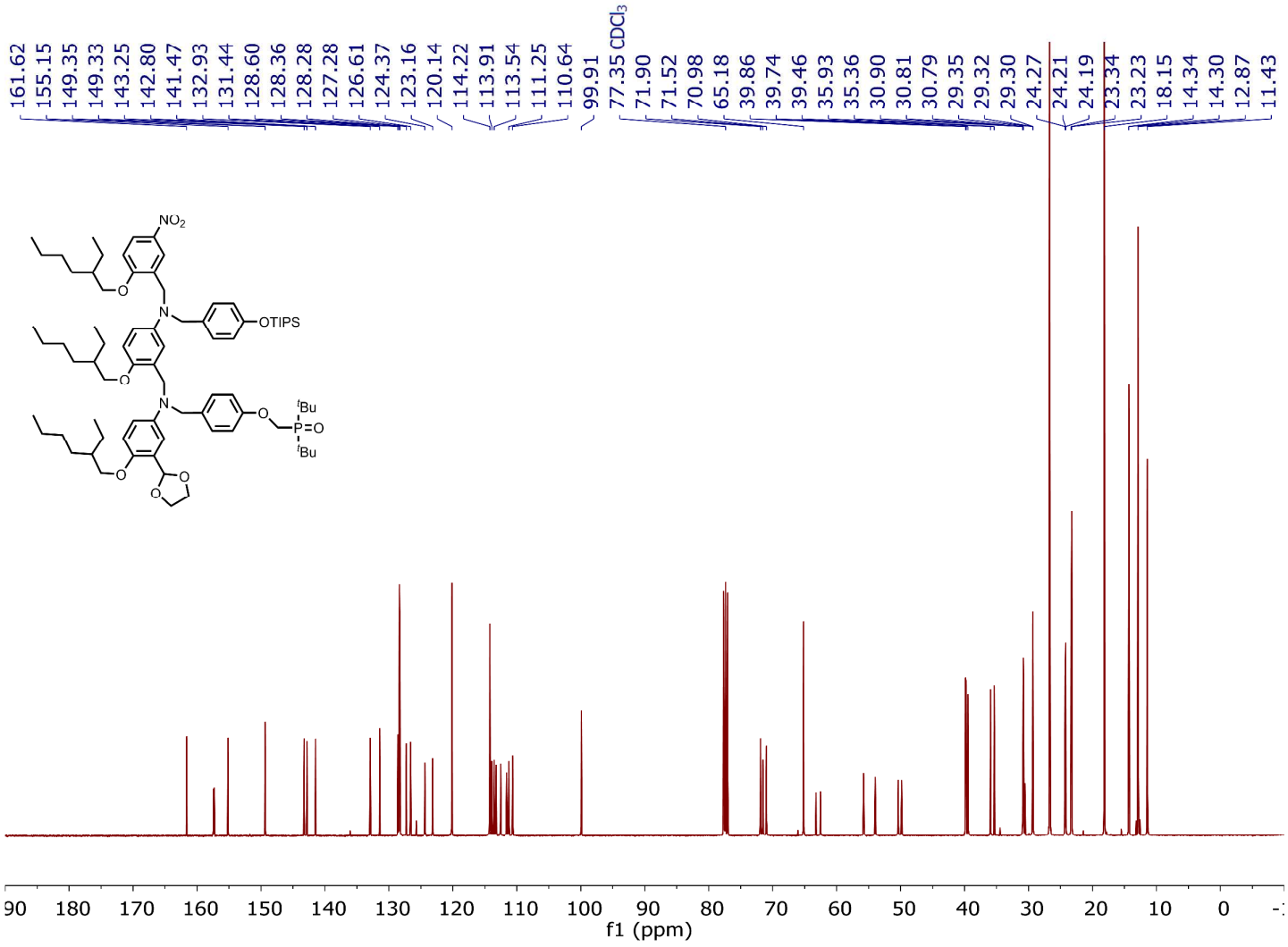
HRMS (ES+): calculated for $C_{79}H_{123}N_3O_{10}P_{28}Si$ 1332.8710, found 1332.8678.

FT-IR (thin film): ν_{max} 2953, 2929, 2867, 1609, 1507, 1464, 1339, 1263, 1226 cm^{-1}.

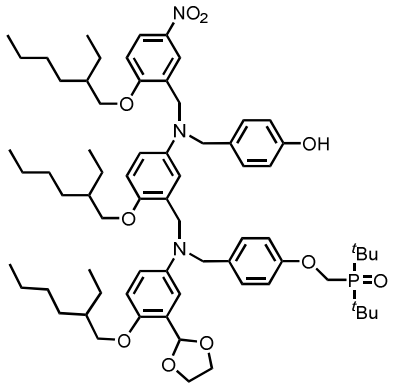
^{1}H NMR (400 MHz, $CDCl_3$) compound 15



^{13}C NMR (100.6 MHz, $CDCl_3$) compound 15



Synthesis of 16.



Compound **15** (0.101 g, 0.08 mmol) was dissolved in THF (2 mL) and a solution of TBAF in THF (1M, (0.080 mL, 0.08 mmol) was added at 0 ^{o}C. After 1 h of stirring at room temperature, water (5 mL) was added and the aqueous mixture washed with Et_2O (3 × 10 mL). All organic fractions were combined and washed with brine (3 × 10 mL) dried ($MgSO_4$) and the solvent removed on a rotary evaporator. The crude mixture was then purified by flash chromatography on silica (gradient from 50 to 100% of EtOAc in hexane) to yield compound **16** as a light yellow oil (0.030 g, 34%).

^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 8.03 (dd, 1H, *J* = 9.0, 3.0), 7.97 (d, 1H, *J* = 3.0), 7.09 (d, 2H, *J* = 8.5), 6.93 (d, 2H, *J* = 7.0), 6.82 (d, 1H, *J* = 3.0), 6.80 (d, 1H, *J* = 9.0), 6.72 (d, 2H, *J* = 7.0), 6.70 (d, 2H, *J* = 7.0), 6.63 (d, 1H, *J* = 9.0), 6.61-6.56 (m, 2H), 6.44-6.35 (m, 2H), 6.07 (s, 1H), 4.44 (s, 4H), 4.37 (s, 2H), 4.33 (d, 2H, *J* = 6.5), 4.28 (s, 2H), 4.01-3.89 (m, 4H), 3.91 (d, 2H, *J* = 6.0), 3.78 (d, 2H, *J* = 5.5), 3.72 (d, 2H, *J* = 5.5), 1.79-1.57 (m, 3H), 1.56-1.15 (m, 42H), 0.97 0.77 (18H, m).

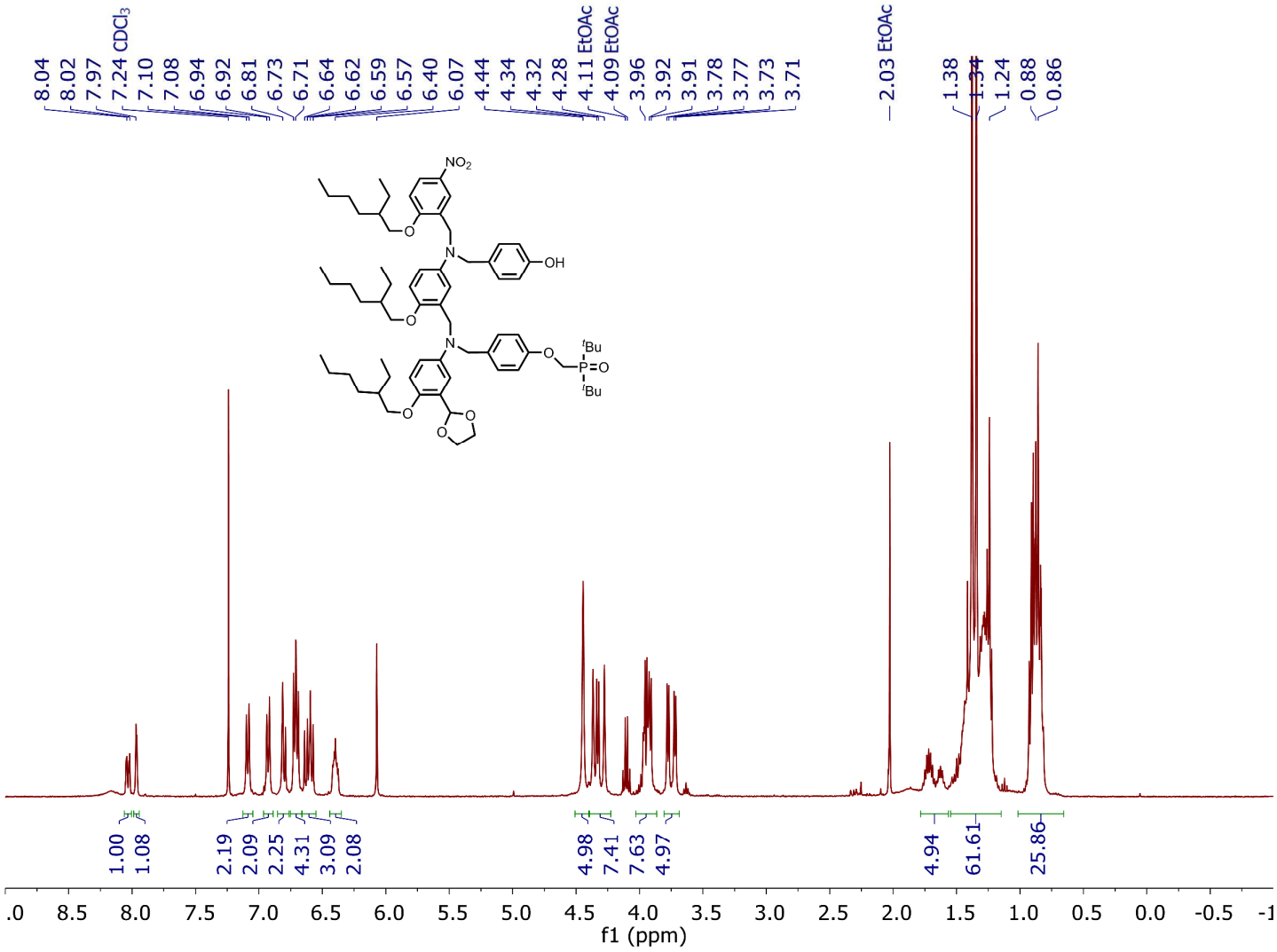
^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C = 161. 8, 157.3 (d, *J* = 10.5), 155.9, 149.6, 148.9, 143.7, 142.7, 141.5, 133.2, 129.7, 128.8, 128.5, 127.9, 127.8, 126.1, 124.4, 123.2, 116.1, 114.9, 114.2, 113.9, 113.5, 112.2, 111.5, 110.5, 100.1, 71.8, 71.5, 70.8, 65.2, 62.6 (d, *J* = 70.0), 55.7, 55.5, 50.9, 50.3, 39.7, 39.3, 35.5 (d, *J* = 57.5), 30.8, 30.7, 29.2, 26.6, 24.2, 24.1, 23.2 23.1, 14.2, 11.3.

^{31}P NMR (161.3 MHz, $CDCl_3$): δ_P = 58.4.

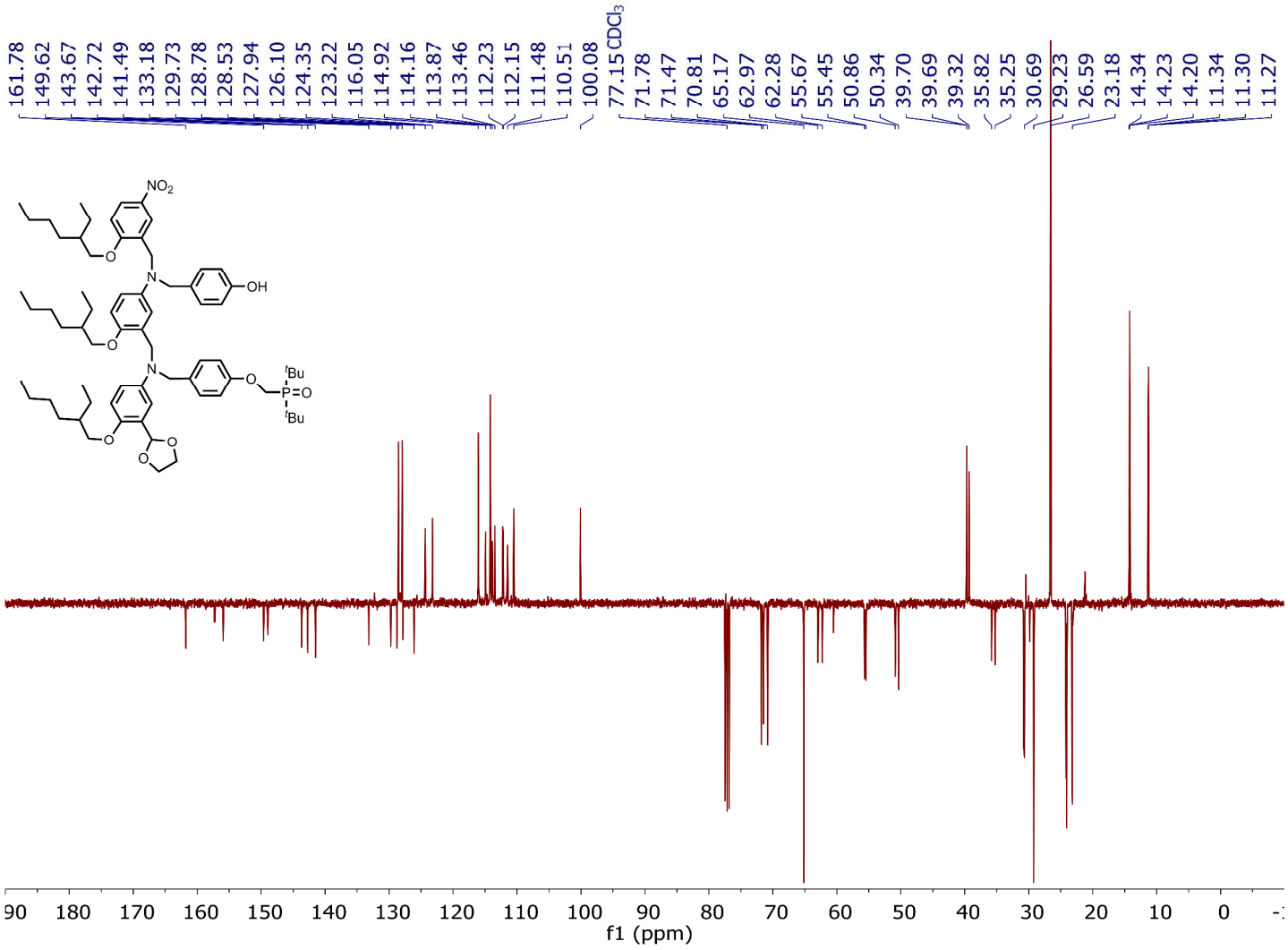
HRMS (ES+): calculated for $C_{70}H_{103}N_3O_{10}P$ 1176.7381, found 1176.7355.

FT-IR (thin film): ν_{max} 2956, 2921, 2853, 1679, 1609, 1592, 1502, 1467, 1336, 1263, 1225, 1175, 1124 cm^{-1}.

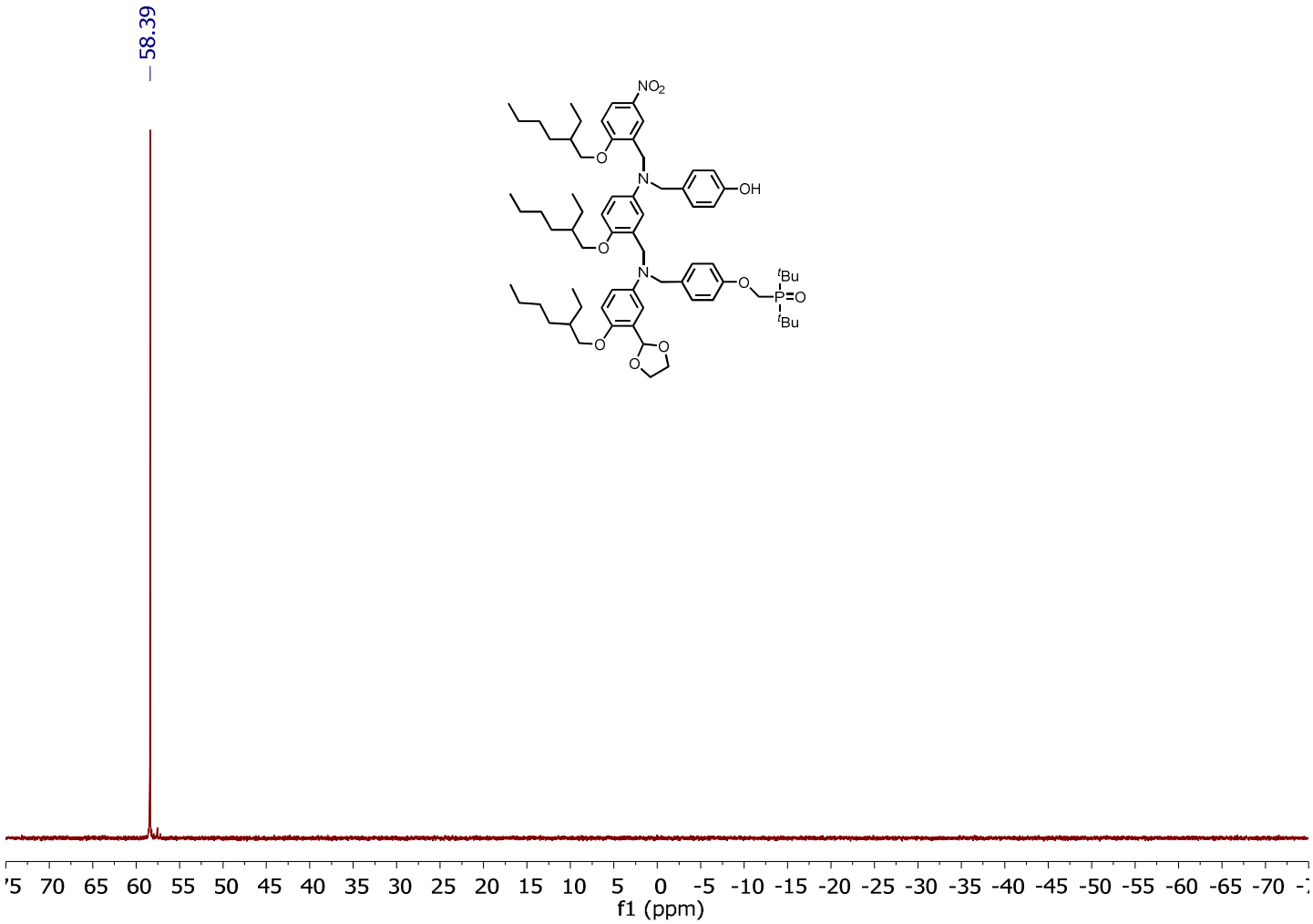
^{1}H NMR (400 MHz, $CDCl_3$) compound 16



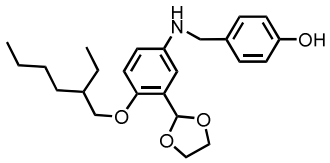
^{13}C NMR (100.6 MHz, $CDCl_3$) compound 16



^{31}P NMR (161.3 MHz, $CDCl_3$) compound 16



Synthesis of S2.



Derivative **17** (3.66 g, 6.58 mmol) was dissolved in THF (20 mL) and a solution of TBAF in THF (1M, (13.2 mL, 13.2 mmol) was added at 0 ^{o}C. After 1 h of stirring at room temperature, water (5 mL) was added and the aqueous mixture washed with Et_2O (4 × 10 mL). All organic fractions were combined and washed with brine (1 × 10 mL) dried ($MgSO_4$) and the solvent removed on a rotary evaporator. The crude mixture was then purified by recrystallization from hot CH_2Cl_2 and hexane to yield compound **S2** as a yellow solid (1.80 g, 69%).

Mpt: 110-114 °C.

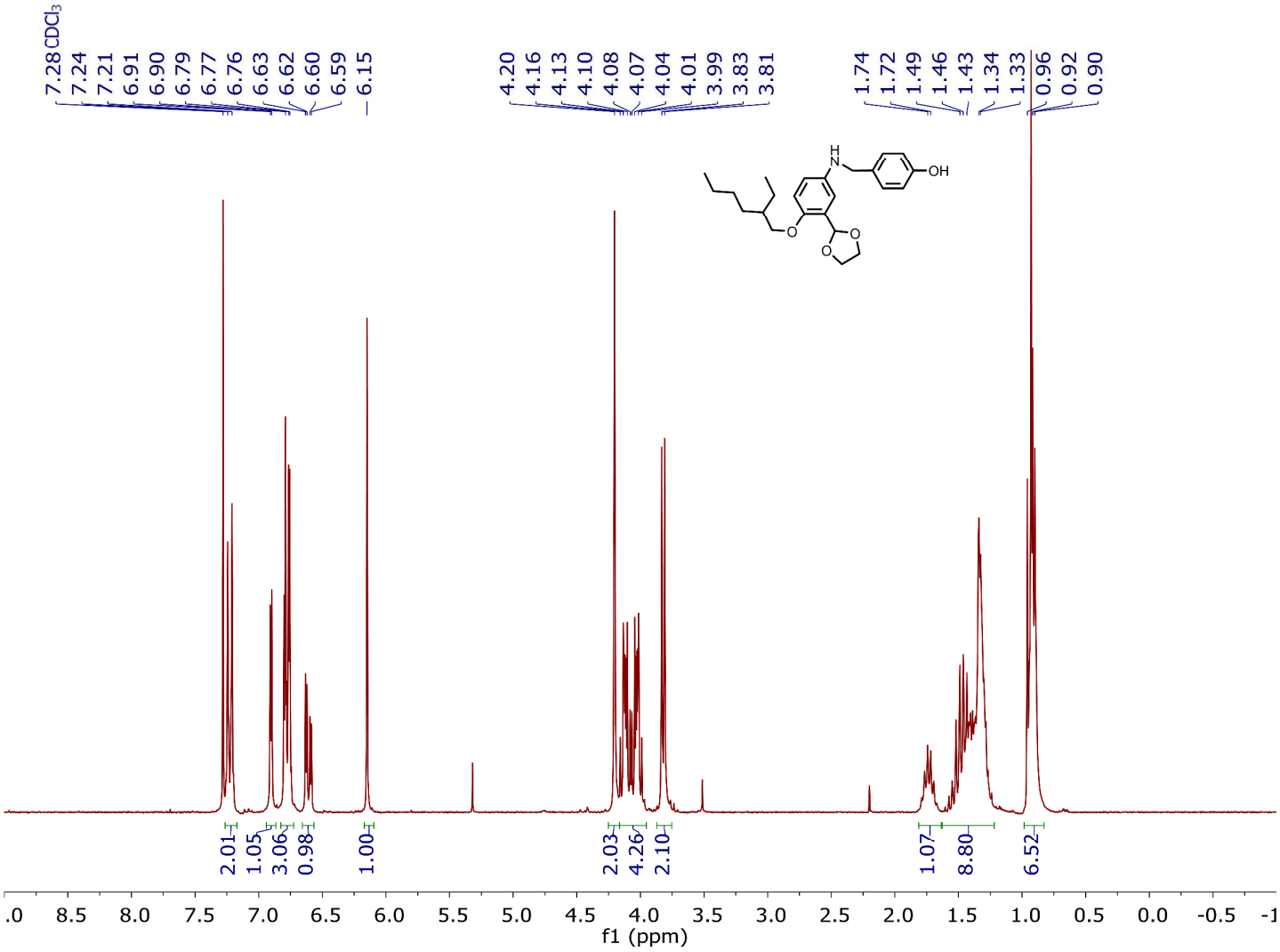
^{1}H NMR (250 MHz, $CDCl_3$): δ_H = 7.23 (d, 2H, *J* = 8.5), 6.90 (d, 1H, *J* = 3.0), 6.81-6.73 (m, 3H), 6.61 (dd, 1H, *J* = 9.0, 3.0), 6.15 (s, 1H), 4.20 (s, 2H), 4.17-3.98 (m, 4H), 3.82 (d, 2H), 1.80-1.66 (m, 1H), 1.62-1.22 (m, 8H), 0.99-0.86 (m, 6H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C = 154.8, 150.2, 142.1, 131.6, 129.1, 126.9, 115.4, 114.5, 113.9, 112.2, 99.4, 72.0, 65.2, 48.8, 39.5, 30.5, 29.1, 23.9, 23.1, 14.1, 11.1.

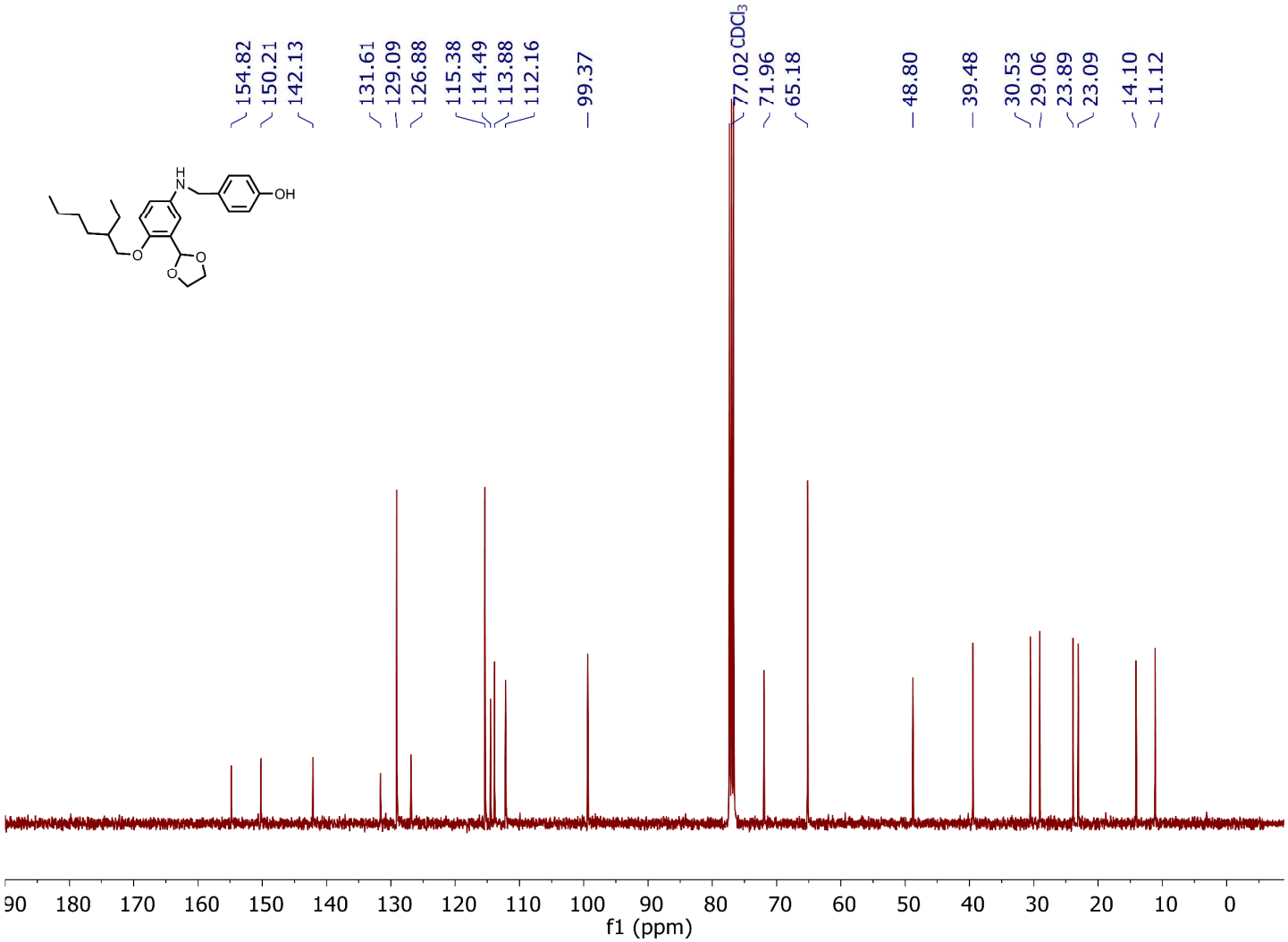
HRMS (ES+): calculated for $C_{24}H_{34}NO_4$ 400.2488, found 400.2495.

FT-IR (thin film): ν_{max} 3290, 2952, 2921, 2873, 2853, 1611, 1598, 1493, 1469, 1243, 1074 cm^{-1}.

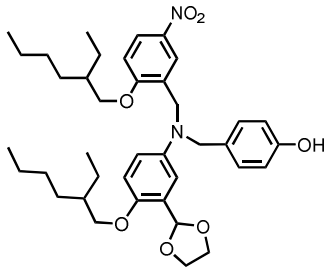
^{1}H NMR (250 MHz, $CDCl_3$) compound S2



^{13}C NMR (100.6 MHz, $CDCl_3$) compound S2



Synthesis of 19.



Compounds **S2** (1.30 g, 3.25 mmol) and **18** (1.82 g, 6.51 mmol) were dissolved in DCE (12 mL) and $NaBH(OAc)_3$ (1.93 g, 9.11 mmol) was added at room temperature with stirring. After 18 h of stirring at room temperature, the reaction was quenched with saturated aqueous $NaHCO_3$ solution and extracted into $CHCl_3$ (4 × 10 mL). All the organic fractions were washed with water (1 × 10 mL), brine (1 × 10 mL) and dried ($MgSO_4$) before the solvent removed on a rotary evaporator. The crude product was purified using flash chromatography on silica (20% EtOAc in hexane) to yield compound **19** a waxy yellow solid (2.05 g, 95%).

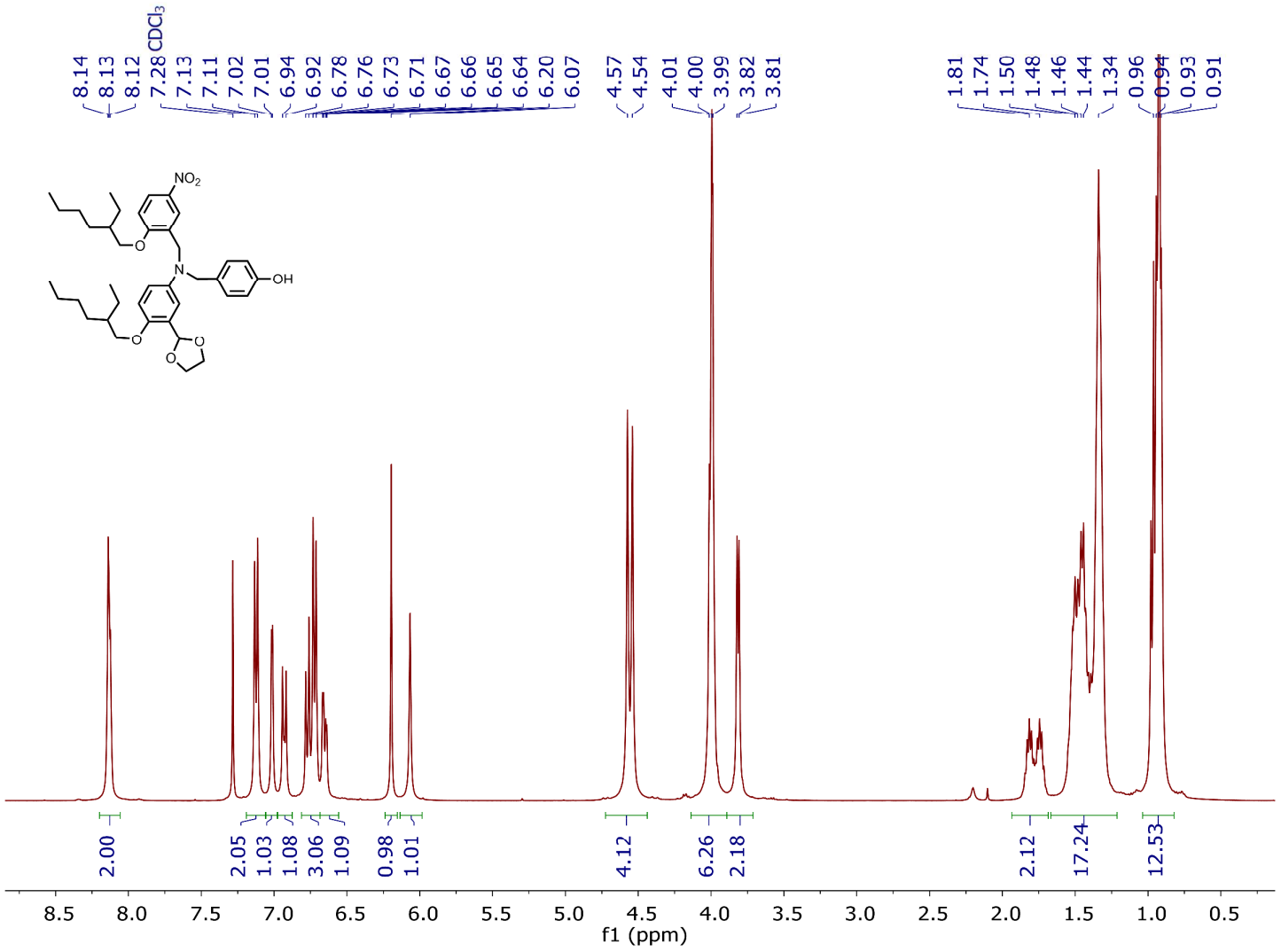
^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 8.17-8.10 (m, 2H), 7.12 (d, 2H, *J* = 8.0) 7.01 (d, 1H, *J* = 3.0), 6.93 (d, 1H, *J* = 10.0), 6.77 (d, 1H, *J* = 9.0), 6.72 (d, 2H, *J* = 8.0), 6.55 (dd, 1H, *J* = 9.0, 3.0), 6.20 (s, 1H), 4.57 (s, 2H), 4.54 (s, 2H), 4.06-3.94 (m, 6H), 3.81 (d, 2H, *J* = 6.0), 1.86-1.68 (m, 2H), 1.58-1.25 (m, 16H), 1.02-0.86 (m, 12H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C = 161.9, 154.9, 150.0, 143.0, 141.3, 130.2, 128.8, 128.4, 126.6, 124.4, 123.5, 115.4, 115.2, 113.6, 112.5, 110.4, 99.7, 71.7, 71.4, 65.0, 55.2, 50.0, 39.5, 39.2, 30.5, 29.1, 29.0, 24.0, 23.9, 23.1, 23.0, 14.1, 14.1, 11.1.

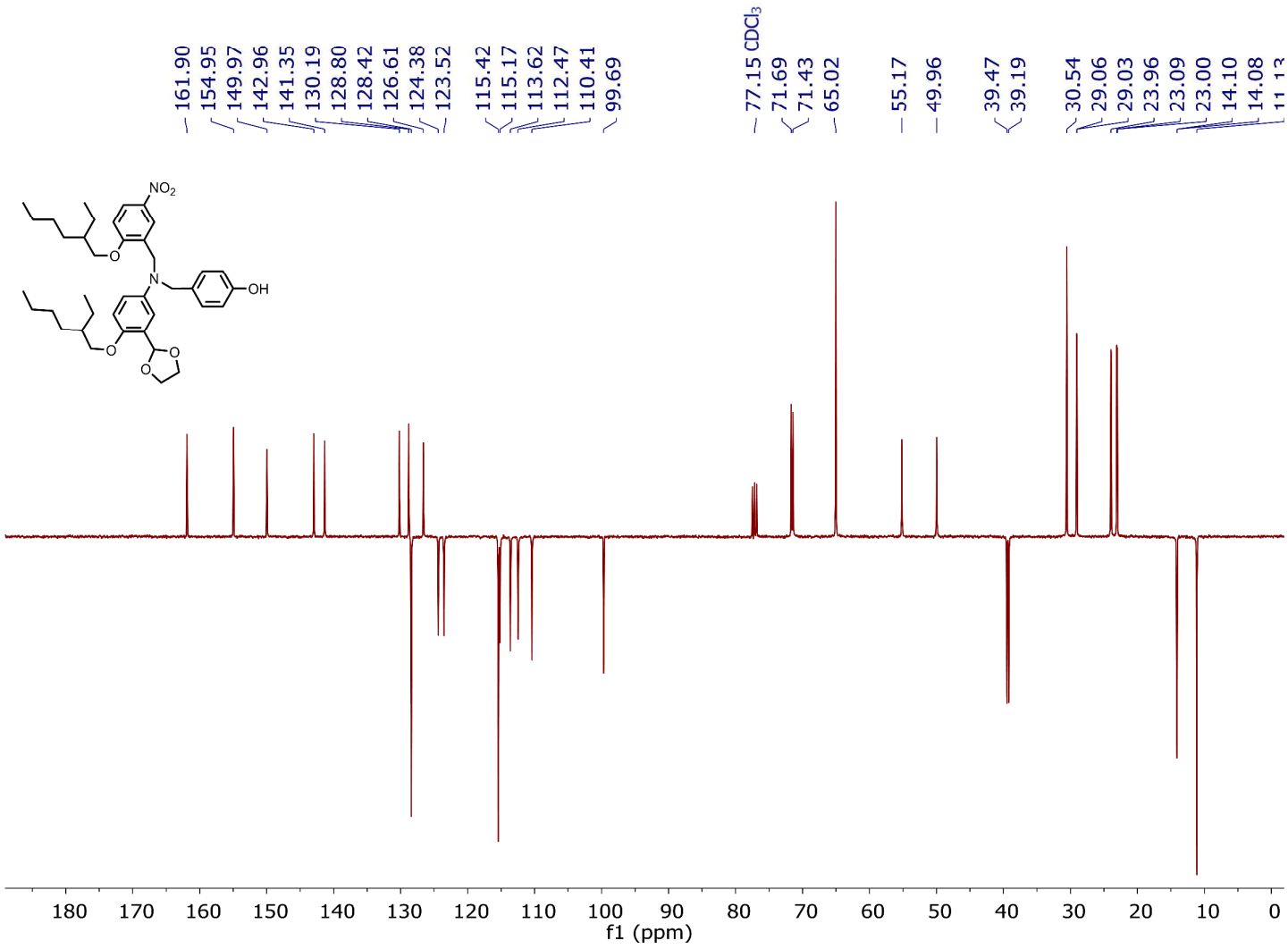
HRMS (ES+): calculated for $C_{39}H_{55}N_2O_7$ 663.4009, found 663.4008.

FT-IR (thin film): ν_{max} 3421, 2956, 2929, 2869, 1677, 1609, 1592, 1510, 1494, 1336, 1267, 1177 cm^{-1}.

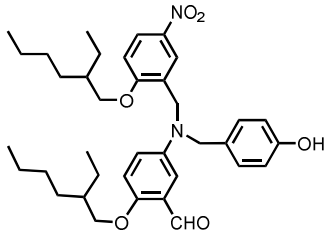
^{1}H NMR (400 MHz, $CDCl_3$) compound 19



^{13}C NMR (100.6 MHz, $CDCl_3$) compound 19



Synthesis of S3.



Compound **19** (1.23 g, 1.85 mmol) was dissolved in $CHCl_3$ (10 mL) and concentrated aqueous HCl (10 mL) was added with stirring. After 2 days the mixture was neutralised using aqueous $NaHCO_3$ and the organic portion separated from the aqueous part. The aqueous layer was washed with $CHCl_3$ (3 × 10 mL) before all organic fractions were washed with brine (1 × 10 mL) dried ($MgSO_4$) and the solvent removed on a rotary evaporator to yield a yellow solid which was recrystallized from CH_2Cl_2 and hexane (1.15 g, 95%).

Mpt: 105-107 °C.

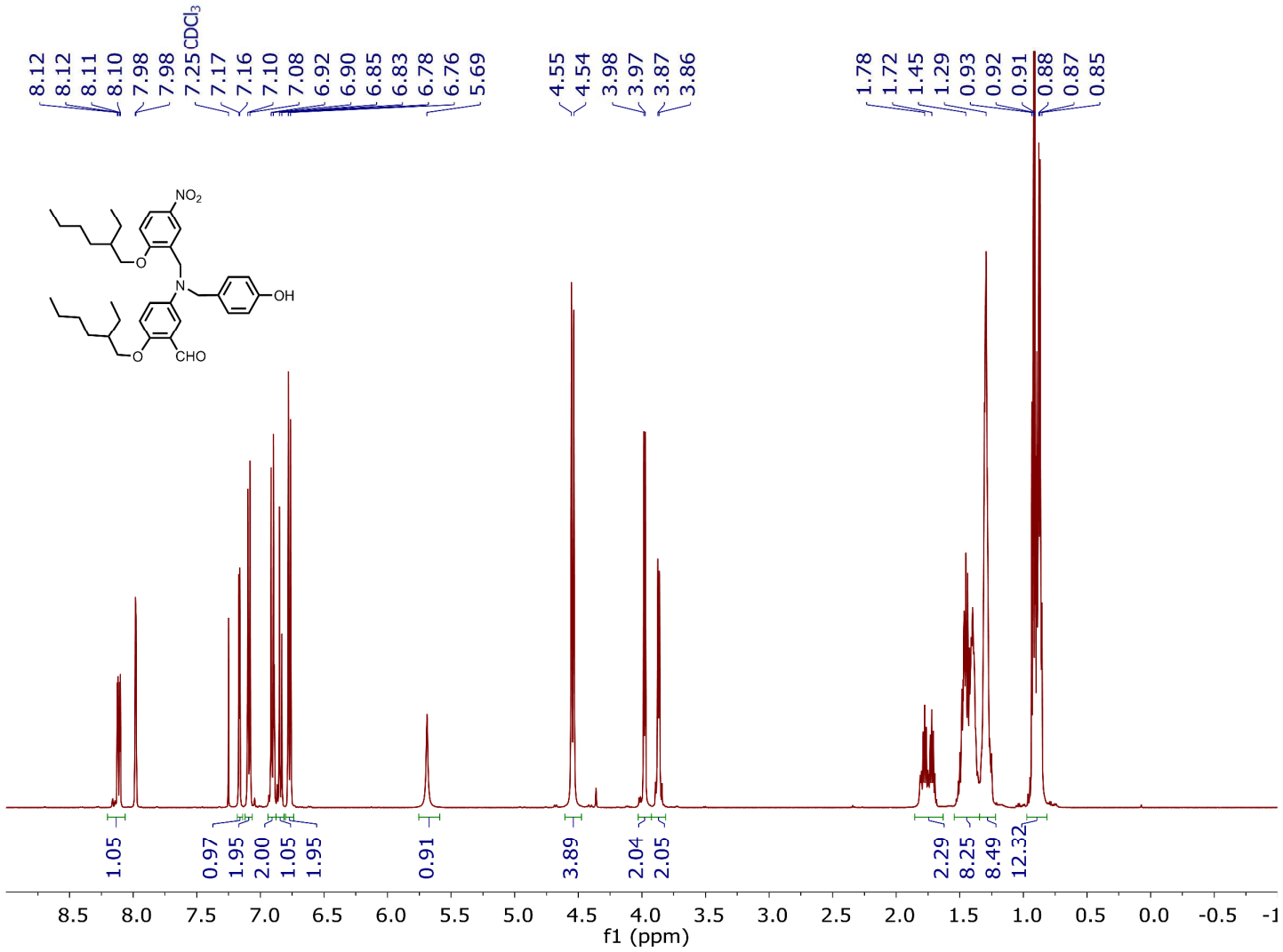
^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 10.42 (s, 1H), 8.11 (dd, 1H, *J* = 9.0, 3.0), 7.98 (d, 1H, *J* = 3.0), 7.17 (d, 1H, *J* = 3.0), 7.09 (d, 2H, *J* = 8.5), 6.93-6.88 (m, 2H), 6.84 (d, 1H, *J* = 9.0), 6.77 (d, 2H, *J* = 8.5), 4.55 (s, 2H), 4.54 (s, 2H), 3.98 (d, 2H, *J* = 5.5), 3.87 (dd, 2H, *J* = 5.5, 1.5), 1.83-1.68 (m, 2H), 1.52-1.23 (m, 16H), 0.96-0.82 (m, 12H).

^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C = 190.4, 161.9, 155.0, 154.7, 142.7, 141.3, 129.7, 128.2, 127.8, 125.1, 124.5, 123.0, 121.4, 115.5, 114.2, 110.9, 110.5, 71.5, 71.2, 54.6, 49.6, 39.5, 39.1, 30.6, 30.5, 29.0, 28.9, 23.9, 23.9, 22.9, 22.9, 14.0, 14.0, 11.1, 11.1.

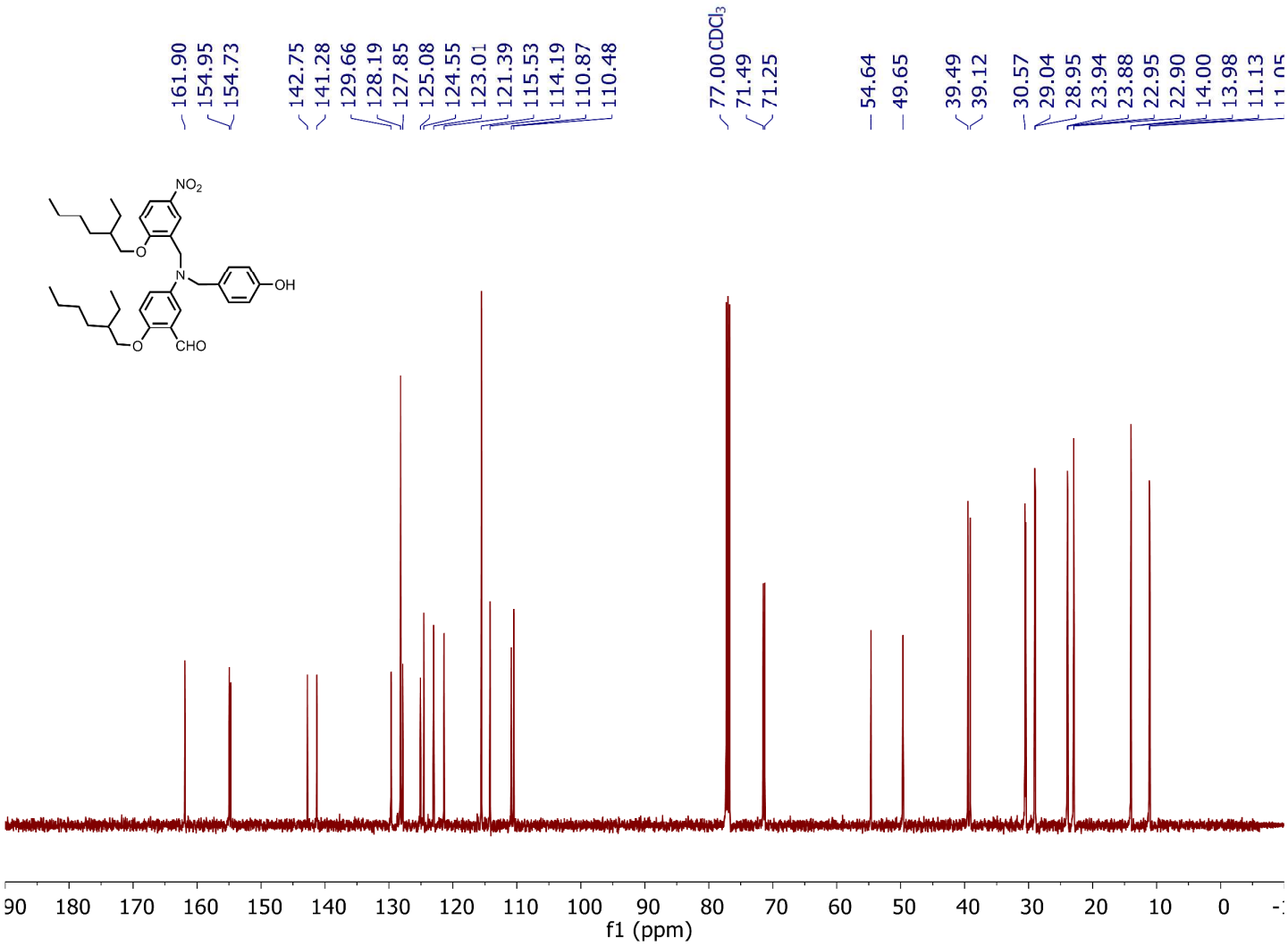
HRMS (ES+): calculated for $C_{37}H_{51}N_2O_6$ 619.3747, found 619.3738.

FT-IR (thin film): ν_{max} 3433, 2956 2925, 2861, 1677, 1610, 1592, 1510, 1493, 1465, 1439, 1338, 1269, 1245, 1207, 1177 cm^{-1}.

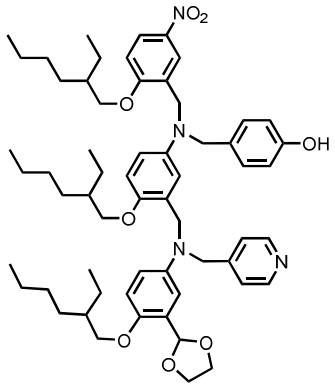
^{1}H NMR (500 MHz, $CDCl_3$) compound S3



^{13}C NMR (125.7 MHz, $CDCl_3$) compound S3



Synthesis of 21.



Compounds **S3** (0.100 g, 0.26 mmol) and **20** (0.242 g, 0.39 mmol) were dissolved in DCE (1 mL) and $NaBH(OAc)_3$ (0.155 g, 0.73 mmol) was added at room temperature with stirring. After 18 h of stirring at room temperature, the reaction was quenched with saturated aqueous $NaHCO_3$ solution, and extracted into $CHCl_3$ (4 × 10 mL). All the organic fractions were washed with water (1 × 10 mL), brine (1 × 10 mL) and dried ($MgSO_4$) before the solvent removed on a rotary evaporator. The crude product was purified using flash chromatography on silica (gradient from 40 to 70% of EtOAc in hexane) to yield compound **21** as an orange oil (0.134 g, 52%).

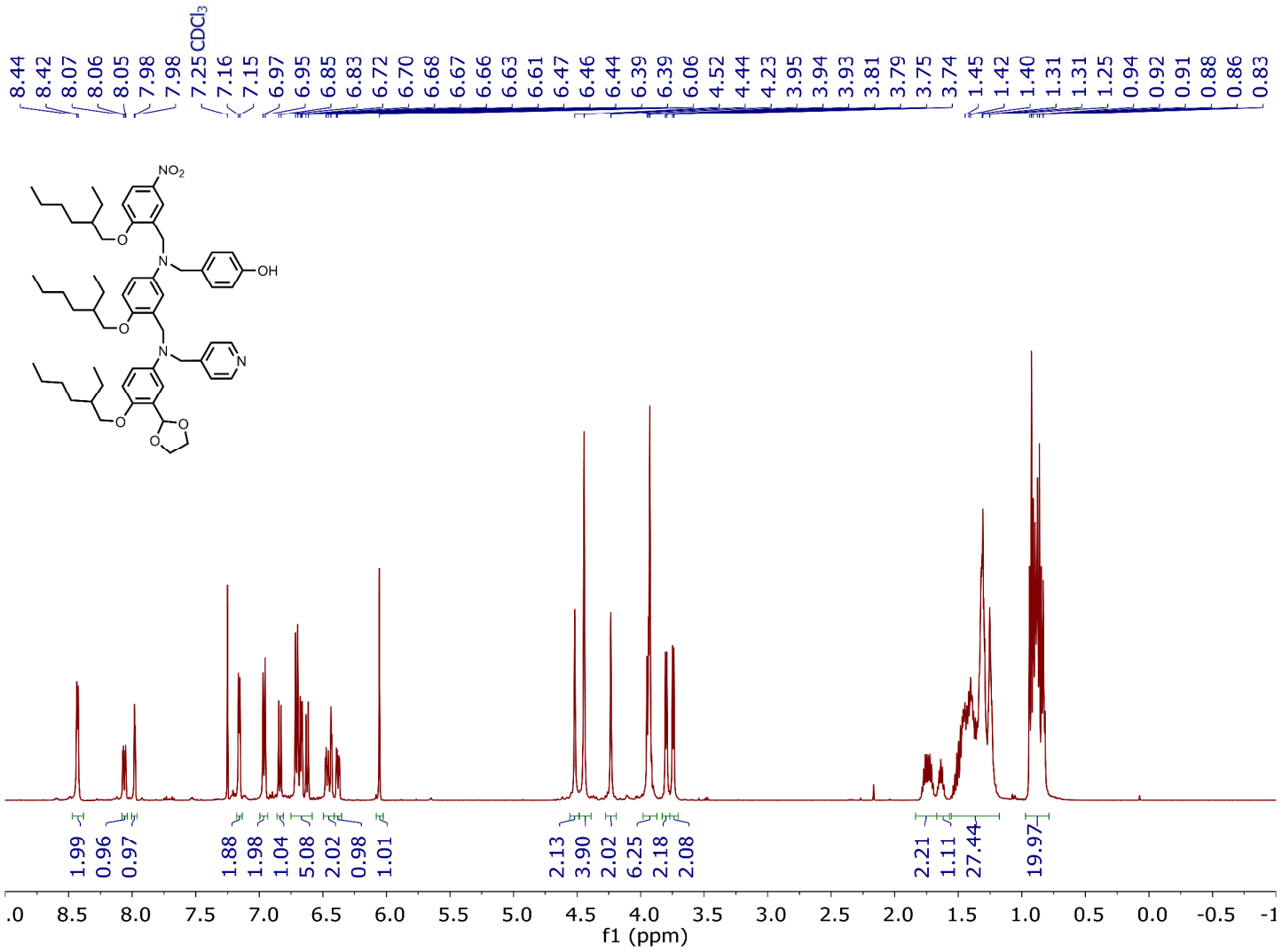
^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 8.43 (d, 2H, *J* = 5.5), 8.06 (dd, 1H, *J* = 9.0, 3.0), 7.98 (d, 1H, *J* = 3.0), 7.16 (d, 2H, *J* = 5.5), 6.96 (d, 2H, *J* = 8.5), 6.84 (d, 1H, *J* = 9.0), 6.71 (d, 2H, *J* = 8.5), 6.69 (d, 1H, *J* = 9.0), 6.67 (d, 1H, *J* = 3.0), 6.62 (d, 1H, *J* = 9.0), 6.47 (dd, 1H, *J* = 9.0, 3.0), 6.43 (d, 1H, *J* = 3.0), 6.38 (dd, 1H, *J* = 9.0, 3.0), 6.06 (s, 1H), 4.52 (s, 1H), 4.44 (m, 4H), 4.23 (s, 1H), 3.96-3.90 (m, 6H), 3.80 (d, 2H, *J* = 6.0), 3.74 (d, 2H, *J* = 6.0), 1.80-1.69 (m, 2H), 1.67-1.60 (m, 1H), 1.56-1.19 (m, 24H), 0.97-0.80 (m, 18H).

^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C = 161.6, 155.5, 151.1, 149.7, 149.0, 148.2, 142.4, 141.3, 129.8, 128.5, 127.7, 126.4, 126.1, 124.3, 123.0, 122.3, 115.8, 114.3, 113.4, 113.3, 112.3, 111.6, 111.5, 110.4, 99.6, 71.6, 71.3, 70.6, 65.0, 55.7, 53.9, 50.8, 50.4, 39.5, 39.4, 39.2, 30.6, 30.5, 29.0, 29.0, 24.0, 23.9, 23.9, 23.0, 23.0, 22.9, 14.0, 14.0, 11.1.

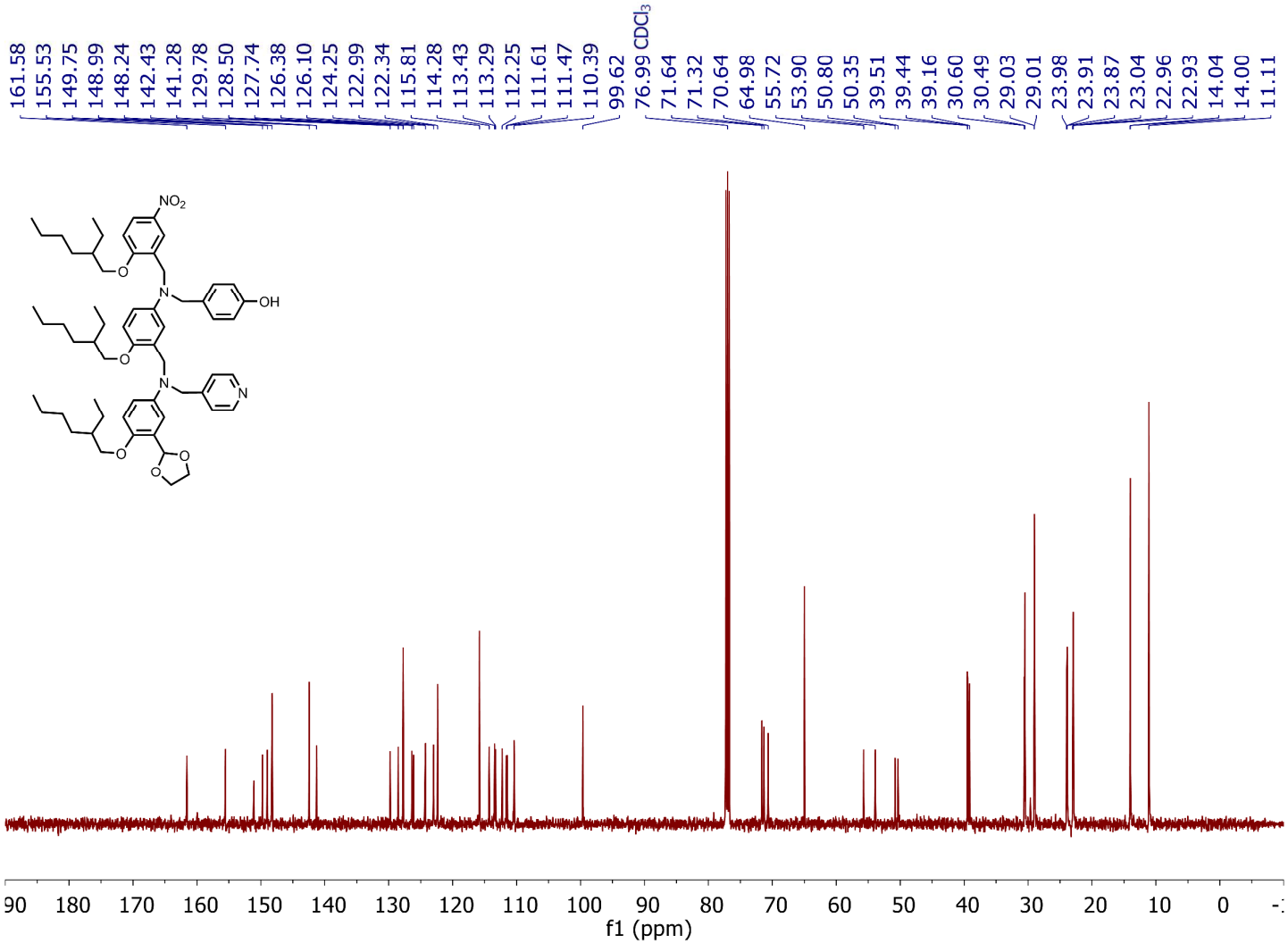
HRMS (ES+): calculated for $C_{60}H_{83}N_4O_8$ 987.6205, found 987.6201.

FT-IR (thin film): ν_{max} 3671, 2988, 2901, 1502, 1405, 1336, 1225 cm^{-1}.

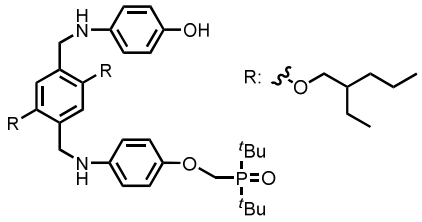
^{1}H NMR (500 MHz, $CDCl_3$) compound 21



^{13}C NMR (125.7 MHz, $CDCl_3$) compound 21



Synthesis of 25.



A mixture of *p*-aminophenol (0.092 g, 0.85 mmol), terephthalaldehyde derivative **23** (0.333 g, 0.85 mmol) and compound **24** (0.240 g, 0.85 mmol) in $CHCl_3$ (10 mL) was stirred under N_2 atmosphere at room temperature for 48 h. The solvent was then removed under reduced pressure and the crude dissolved in MeOH. $NaBH_4$ (0.380 g, 9.50 mmol) was added at 0°C and the solution left stirring for 10 min. The solution was neutralized with 2M HCl (4 mL) and extracted with CH_2Cl_2 (3 x 10 mL). The organic layers were combined and washed with brine (1 x 10 mL). The solution was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude material was then purified by column chromatography on silica (EtOAc/MeOH 90:10). Compound **25** was isolated as a pink oil (0.130 g, 20%).

^{1}H NMR (400 MHz, CD_3CN): δ_H = 6.94 (bs, 1H), 6.88 (d, 2H, *J* = 6.0), 6.76-6.74 (m, 2H), 6.56-6.52 (m, 4H), 6.46-6.44 (m, 2H), 4.46 (bs, 2H), 4.25 (d, 2H, *J* = 6.0), 4.17 (s, 2H), 4.13 (s, 2H), 3.77-3.75 (m, 4H), 1.64-1.62 (m, 2H), 1.44-1.34 (m, 8H), 1.34-1.23 (m, 26H), 0.89-0.83 (m, 12H).

^{13}C NMR (100.6 MHz, CD_3CN): δ_c = 151.0, 150.9, 150.9, 149.1, 144.0, 142.2, 127.9, 127.4, 115.9, 115.5, 114.5, 114.2, 113.2, 113.1, 71.1, 71.1, 63.4 (d, *J* = 70), 43.6, 43.1, 39.6, 39.5, 35.1 (d, *J* = 58), 30.7, 30.7, 29.1, 29.0, 26.0, 24.0, 23.0, 23.0, 13.7, 10.8.

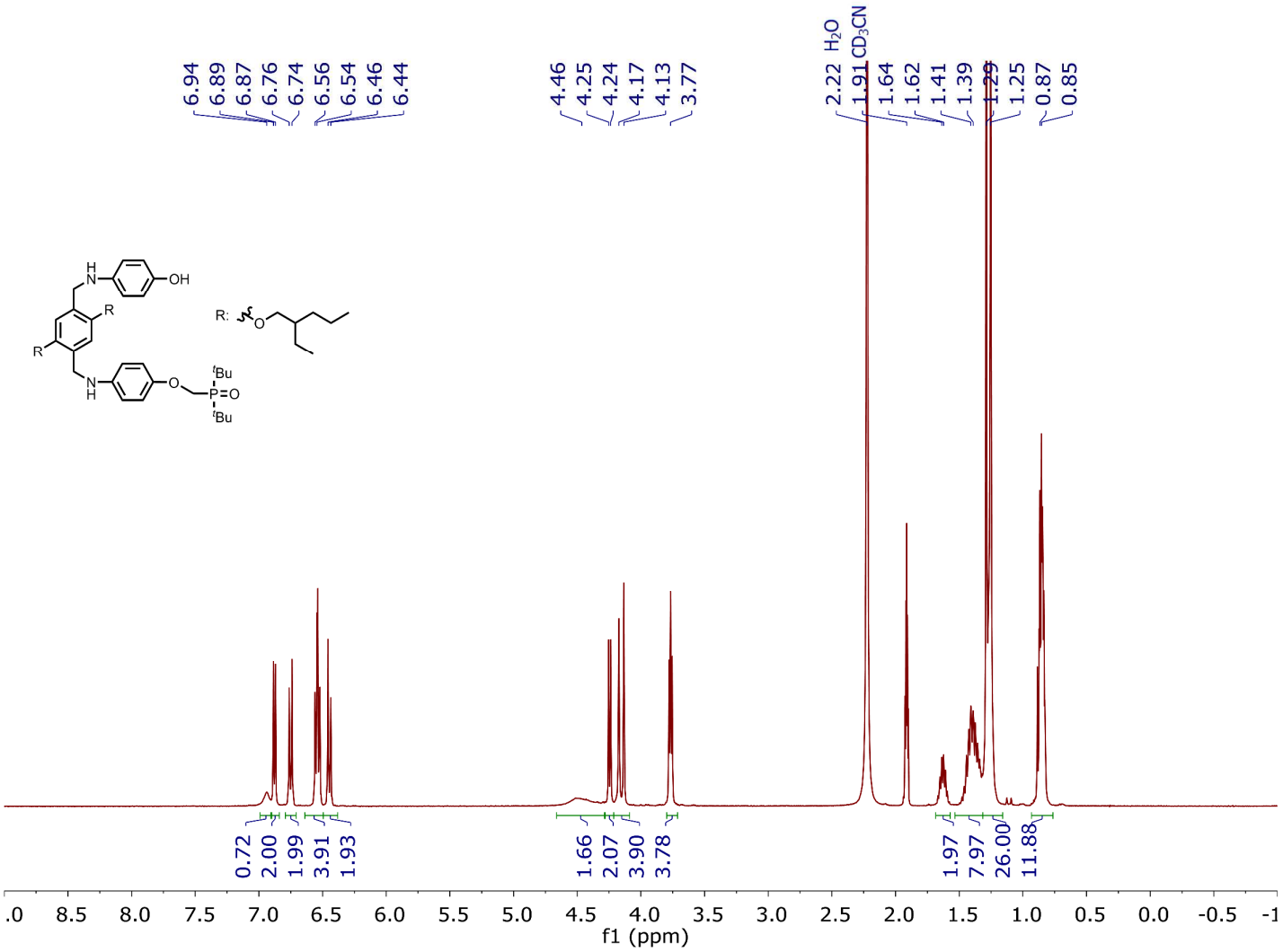
^{31}P NMR (161.3.0 MHz, CD_3CN): δ_p = 56.7.

MS (ES+): m/z (%) =751.5 $[M+H]^+$.

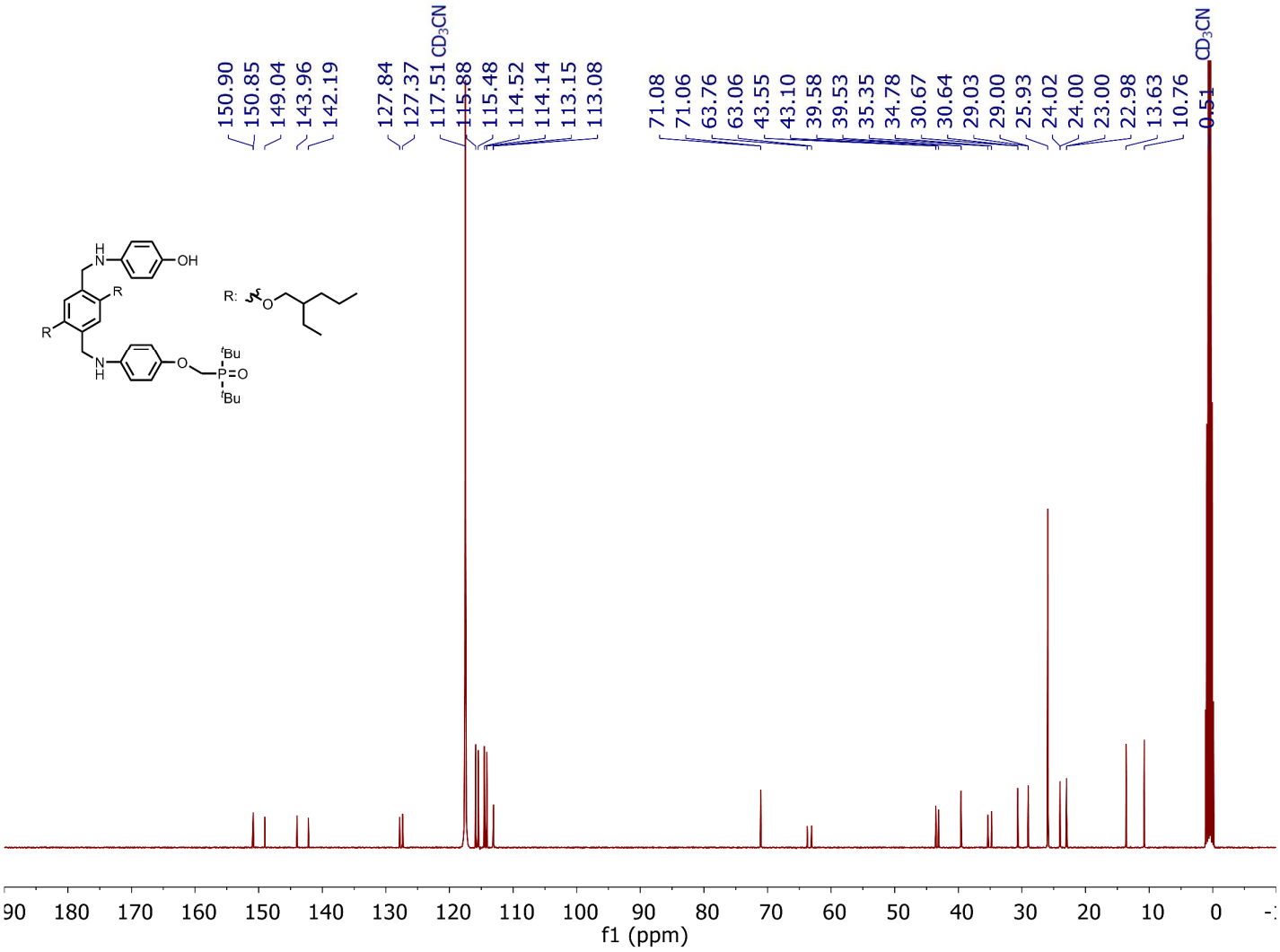
HRMS (ES+): calcd for $C_{45}H_{72}N_2O_5P$ 751.5179, found 751.5172.

FT-IR (thin film): ν_{max} 3050, 2961, 2929, 2873, 1509 cm^{-1}.

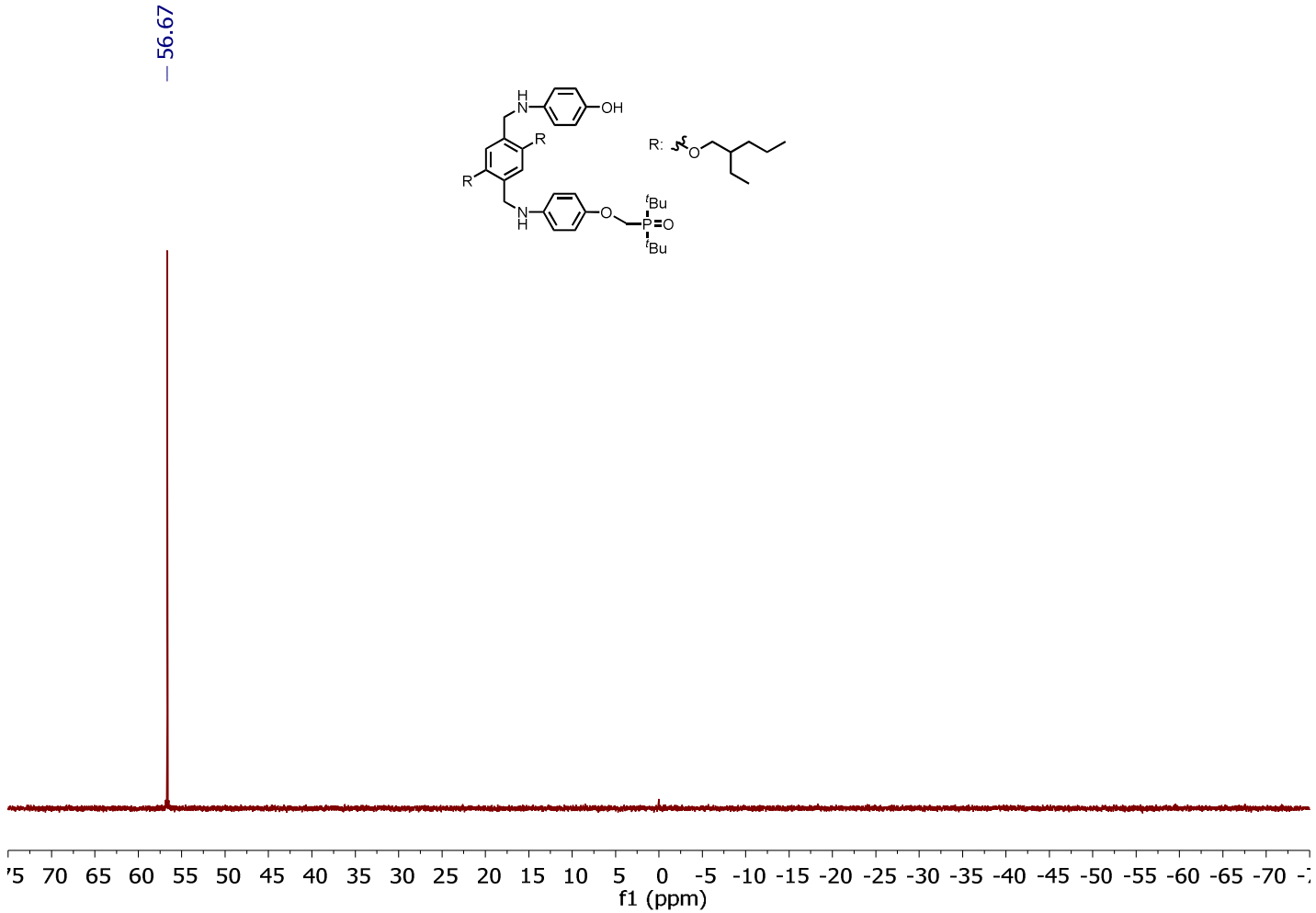
^{1}H NMR (400 MHz, CD_3CN) compound 25



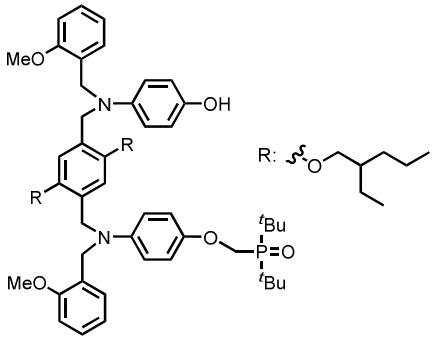
^{13}C NMR (100.6 MHz, CD_3CN) compound 25



^{31}P NMR (161.3.0 MHz, CD_3CN) compound 25



Synthesis of 26.



A mixture of compound **25** (0.100 g, 0.14 mmol), 2-methoxybenzaldehyde (0.064 mL, 0.42 mmol) and $NaBH(AcO)_3$ (0.150 g, 0.71 mmol) in DCE (0.6 mL) was stirred under N_2 atmosphere at room temperature for 2 h. The solution was diluted with DCE and then washed with saturated aqueous $NaHCO_3$ (1 x 10 mL), water (1 x 10 mL) and brine (1 x 10 mL). The organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was then purified by column chromatograph on silica (CH_2Cl_2/EtOAc 90:10). The product was isolated as a pink oil (0.100 g, 76%).

^{1}H NMR (400 MHz, CD_3CN): δ_H = 7.19-7.07 (m, 4H), 6.91-6.88 (m, 2H), 6.82-6.78 (m, 2H), 6.76-6.73 (m, 3H), 6.68 (s, 1H), 6.57-6.55 (m, 4H), 6.49-6.47 (m, 2H), 4.53 (s, 2H), 4.49 (s, 2H), 4.46 (s, 2H), 4.44 (s, 2H), 4.23 (d, 2H, *J* = 6.0), 3.76 (d, 6H, *J* = 3.0), 3.62-3.59 (m, 4H), 1.58-1.49 (m, 2H), 1.36-1.16 (m, 34H), 0.83-0.76 (m, 12H).

^{13}C NMR (100.6 MHz, CD_3CN): δ_c = 157.6, 157.6, 150.6 (d, *J* = 8), 150.4 (d, *J* = 11), 148.7, 144.3, 142.9, 128.1, 127.9, 127.7, 127.2, 126.9, 126.2, 120.3, 120.3, 115.8, 115.3, 114.4, 113.8, 112.2, 112.1, 110.6, 110.6, 71.1, 71.0, 63.4 (d, *J* = 70), 55.2, 55.2, 50.6, 50.6, 50.5, 50.4, 39.4, 39.3, 35.1 (d, *J* = 58), 30.6, 30.6, 29.0, 28.9, 26.0, 23.9, 23.9, 23.0, 23.0, 13.7, 10.8.

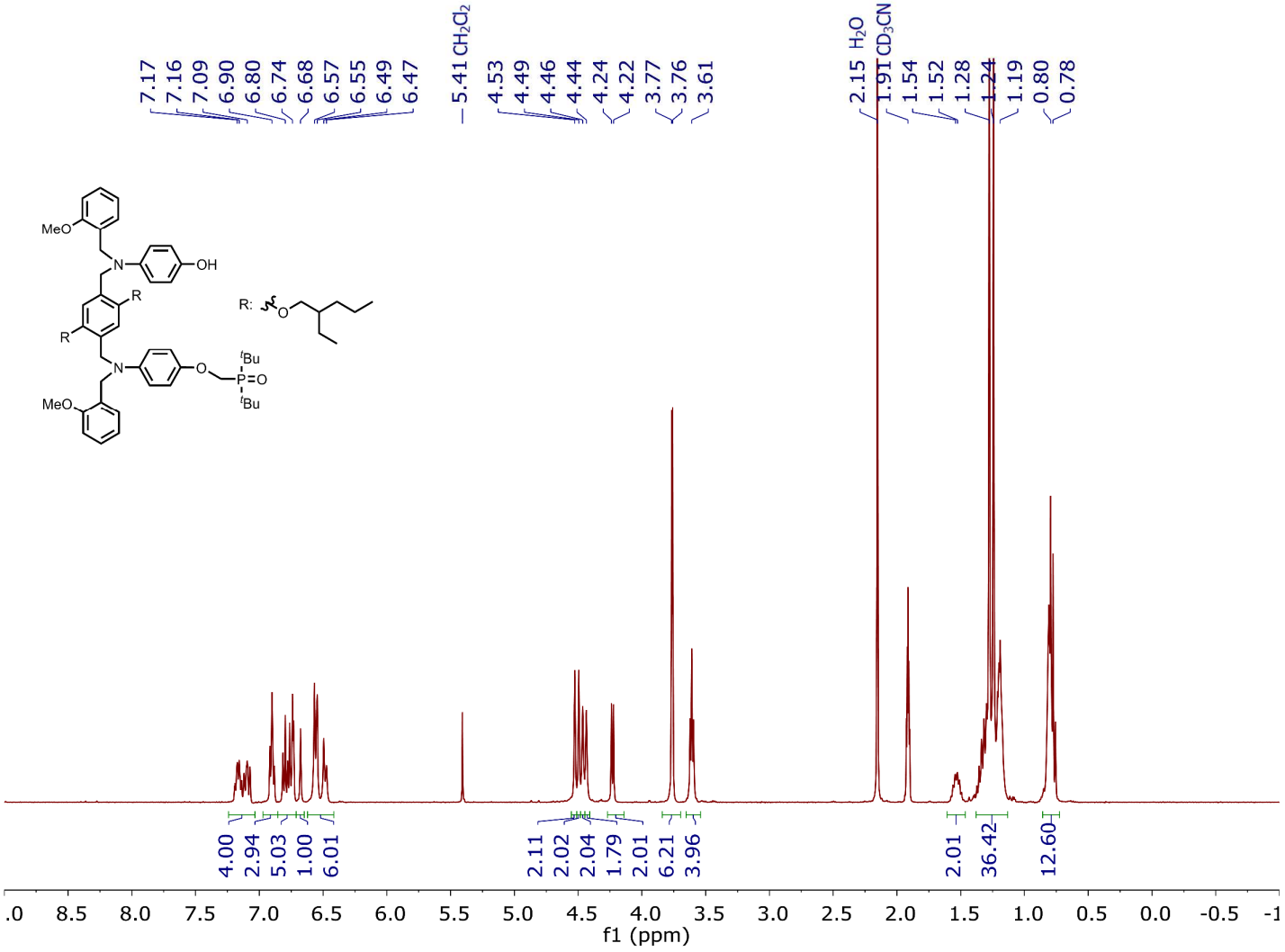
^{31}P NMR (161.3.0 MHz, CD_3CN): δ_p =56.3.

MS (ES+): m/z (%) =991.6 $[M+H]^+$.

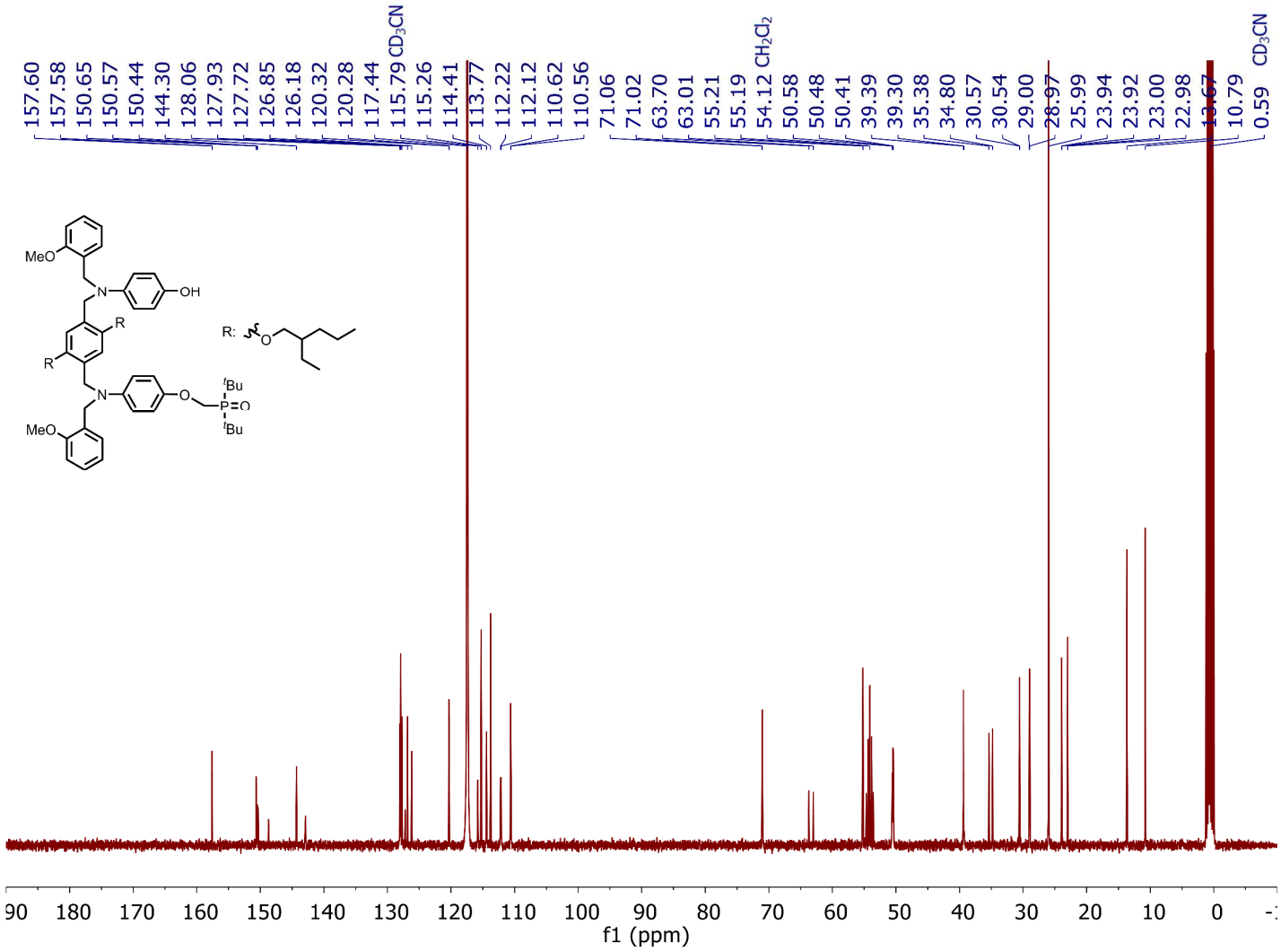
HRMS (ES+): calcd for $C_{61}H_{88}N_2O_7P$ 991.6329, found 991.6309.

FT-IR (thin film): ν_{max} 2956, 2927, 2871, 1510 cm^{-1}.

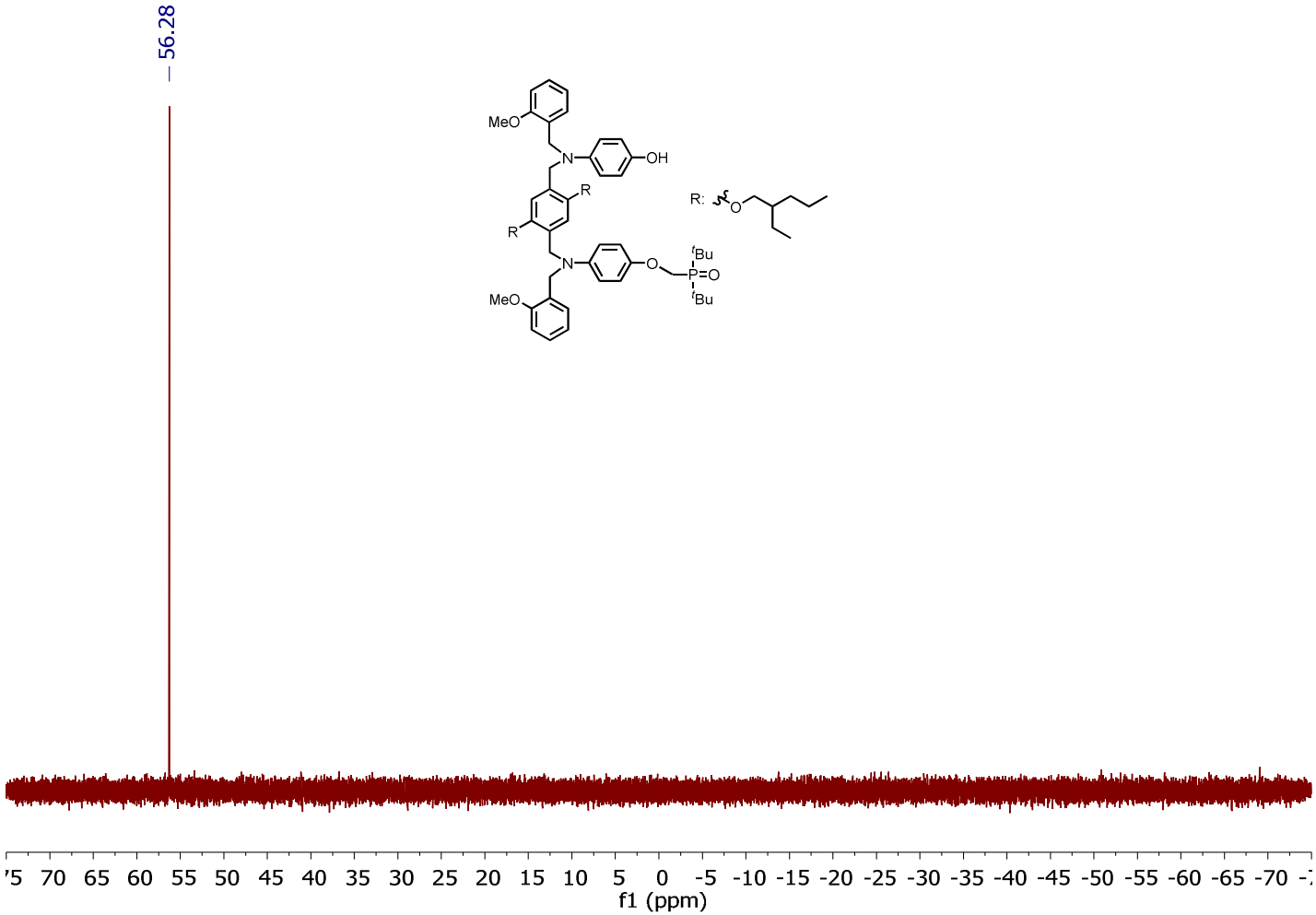
^{1}H NMR (400 MHz, CD_3CN) compound 26



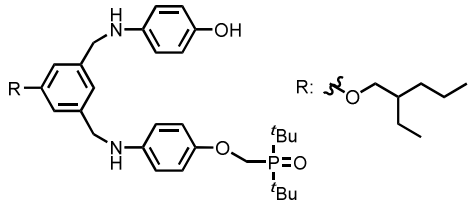
^{13}C NMR (100.6 MHz, CD_3CN) compound 26



^{31}P NMR (161.3.0 MHz, CD_3CN) compound 26



Synthesis of 28.

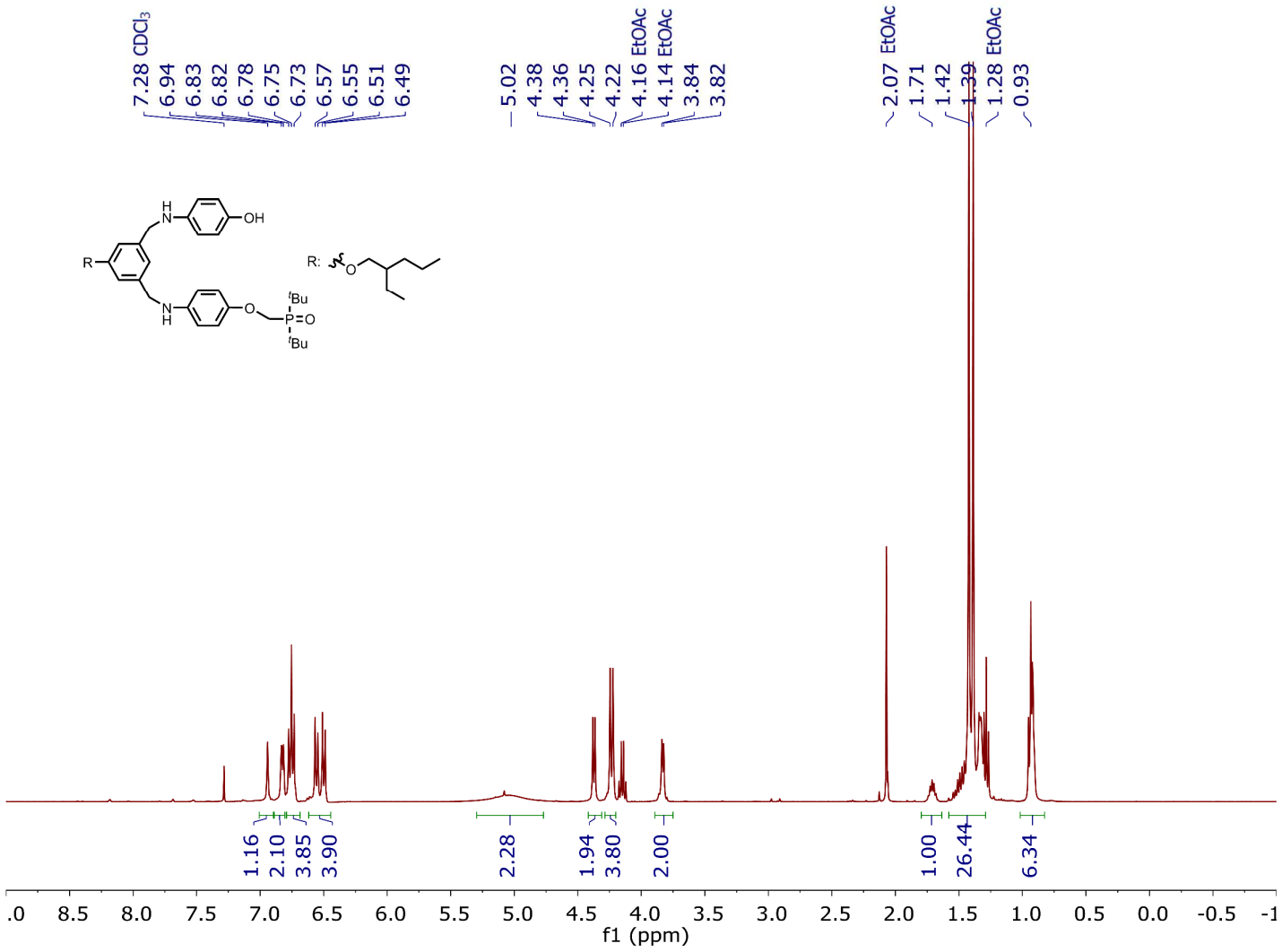


A mixture of *p*-aminophenol (0.225 g, 2.06 mmol), compound **24** (0.584 g, 2.06 mmol) and aldehyde derivative **27** (0.540 g, 2.06 mmol) in $CHCl_3$ (1 mL) was stirred under N_2 atmosphere at room temperature for 48 h. The solvent was then removed under reduced pressure and the crude dissolved in MeOH. $NaBH_4$ (1.000 g, 26.43 mmol) was added at 0°C and the solution left stirring for 10 min. The solution was neutralized with 2M HCl (4 mL) and extracted with CH_2Cl_2 (3x10 mL). The organic layers were combined and washed with brine (1 x 10 mL). The solution was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude material was then purified by column chromatography on silica (EtOAc/MeOH 95:5). Compound **28** was isolated as a pink oil (0.200 g, 16%).

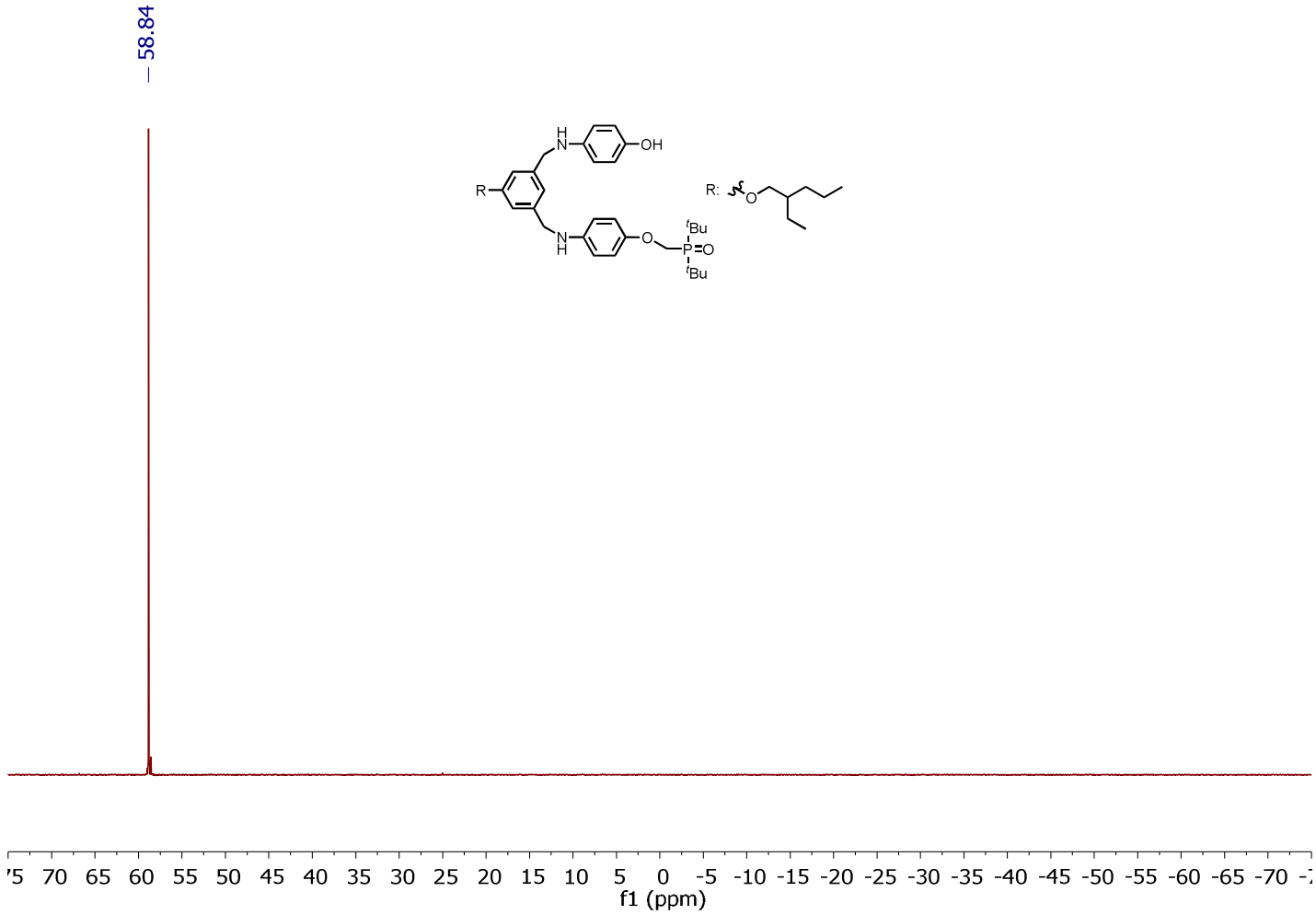
^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 6.94 (s, 1H), 6.83-6.82 (m, 2H), 6.78-6.73 (m, 4H), 6.58-6.49 (m, 4H), 5.02 (bs, 2H), 4.37 (d, 2H, *J* = 7.0), 4.23 (d, 4H, *J* = 9.0), 3.83 (dd, 2H, J = 6.0, 1.0), 1.75-1.66 (m,1H), 1.54-1.26 (m, 26H), 0.95-0.90 (m, 6H).

^{31}P NMR (161.3.0 MHz, $CDCl_3$): δ_P =58.8.

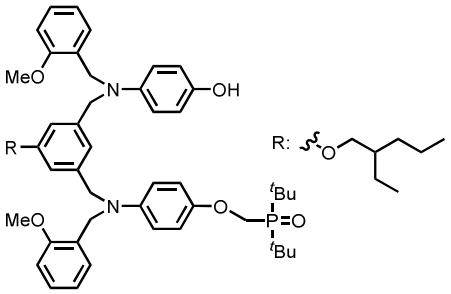
^{1}H NMR (400 MHz, $CDCl_3$) compound 28



^{31}P NMR (161.3.0 MHz, $CDCl_3$) compound 28



Synthesis of 29.



A mixture of **28** (0.200 g, 0.32 mmol), 2-methoxybenzaldehyde (0.130 mL, 0.80 mmol) and $NaBH(AcO)_3$ (0.330 g, 1.56 mmol) in DCE (1 mL) was stirred under N_2 atmosphere at room temperature for 2 h. The solution was then diluted with DCE and washed with saturated aqueous $NaHCO_3$ (1 x 10 mL), water (1 x 10 mL) and brine (1 x 10 mL). The organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was then purified by column chromatograph on silica (CH_2Cl_2/EtOAc 90:10). Compound **29** was isolated as a pink oil (0.190 g, 69%).

^{1}H NMR (500 MHz, CD_3CN): δ_H = 7.86 (s, 1H), 7.21-7.16 (m, 2H), 7.10 (d, 2H, *J* = 7.0), 6.93 (t, 2H, *J* = 8), 6.84-6.81 (m, 2H), 6.73 (s, 2H), 6.71 (s, 1H) 6.61 (s, 2H), 6.53-6.49 (m, 4H), 6.39 (d, 2H, *J* = 8.0), 4.51 (s, 2H), 4.47 (s, 2H), 4.43 (s, 2H), 4.37 (s, 2H), 4.31 (d, 2H, *J* = 5.0), 3.80 (s, 3H), 3.79 (s, 3H), 3.72 (d, 2H, *J* = 6.0), 1.62-1.59 (m, 1H), 1.43-1.27 (m, 26H), 0.88-0.85 (m, 6H).

^{13}C NMR (125.7 MHz, CD_3CN): δ_c = 160.7, 158.3, 151.4 (d, *J* = 10), 150.0, 144.7, 143.1, 142.8, 142.1, 128.8, 128.8, 128.7, 128.5, 127.9, 127.6, 121.1, 121.1, 118.8, 116.5, 116.1, 115.6, 114.9, 112.2, 112.2, 111.4, 111.3, 71.1, 64.2 (d, *J* = 69), 56.6, 56.1, 55.9, 55.9, 51.9, 51.7, 40.1, 35.9 (d, *J* = 58), 31.2, 29.7, 26.8, 24.5, 23.7, 14.4, 11.4.

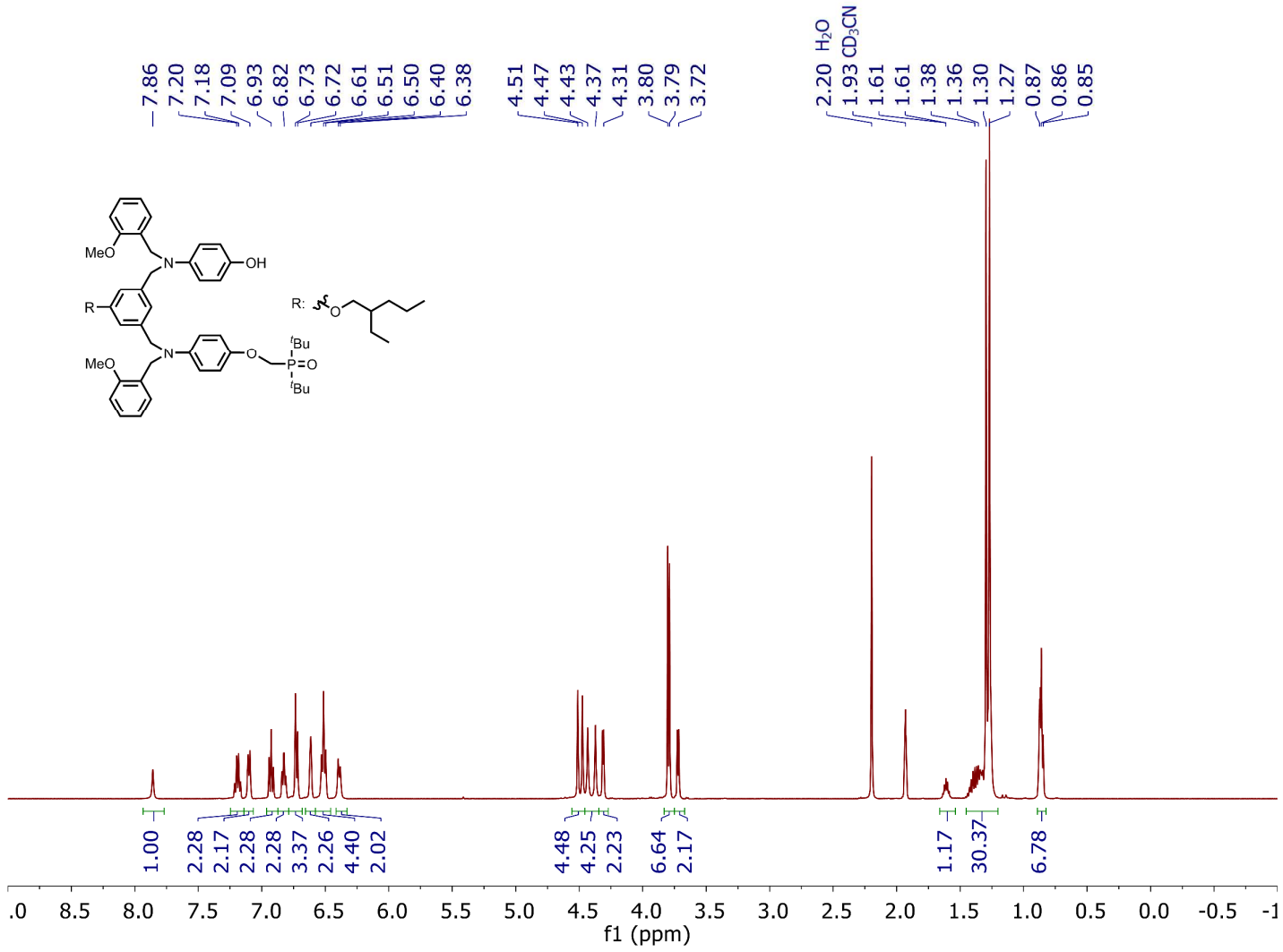
^{31}P NMR (202.4 MHz, CD_3CN): δ_p = 57.3.

MS (ES+): m/z (%) =863.5 $[M+H]^+$.

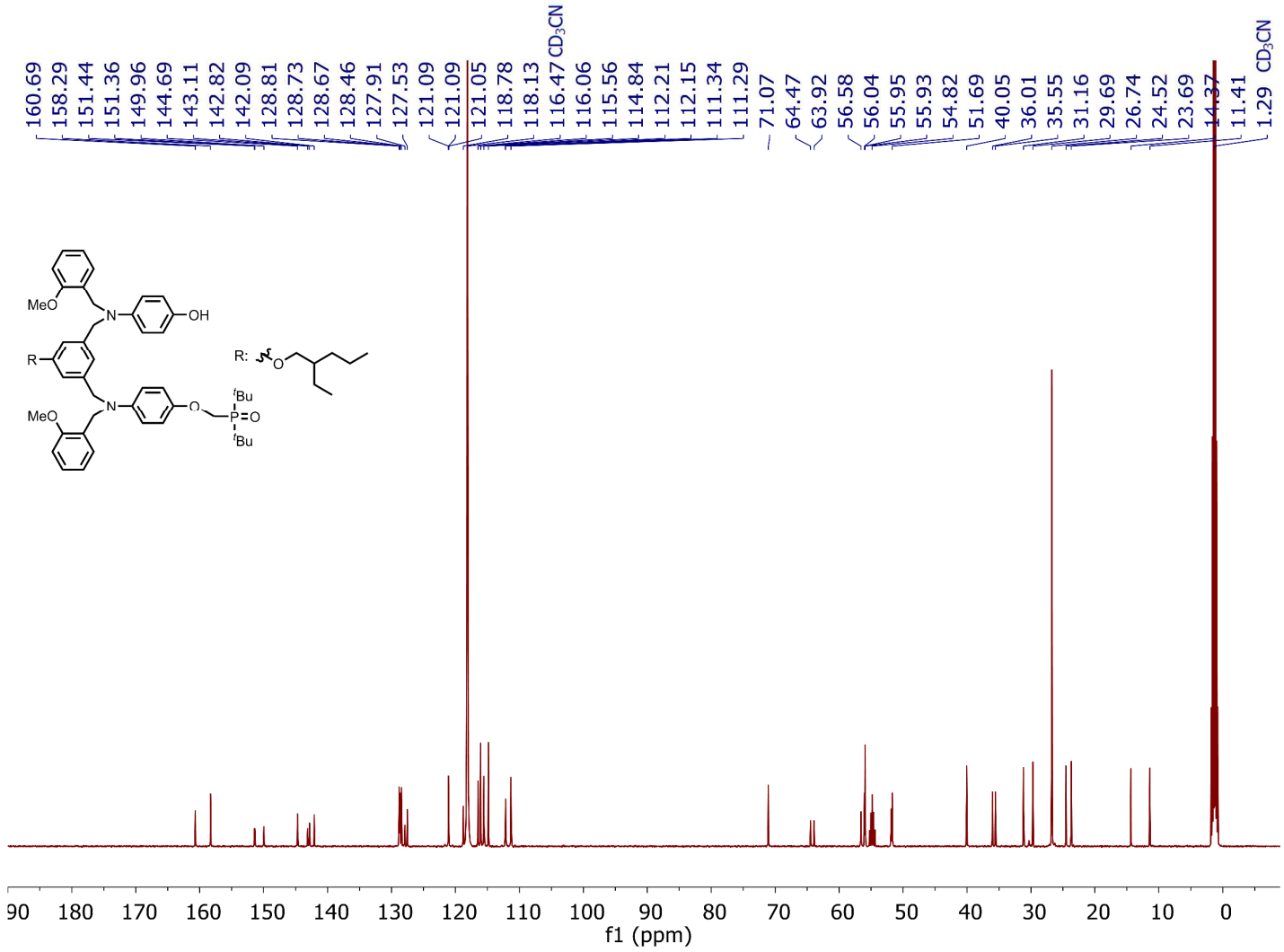
HRMS (ES+): calcd for $C_{53}H_{72}N_2O_6P$ 863.5128, found 863.5163.

FT-IR (thin film): ν_{max} 3151, 2956, 2932, 2870, 1593, 1512 cm^{-1}.

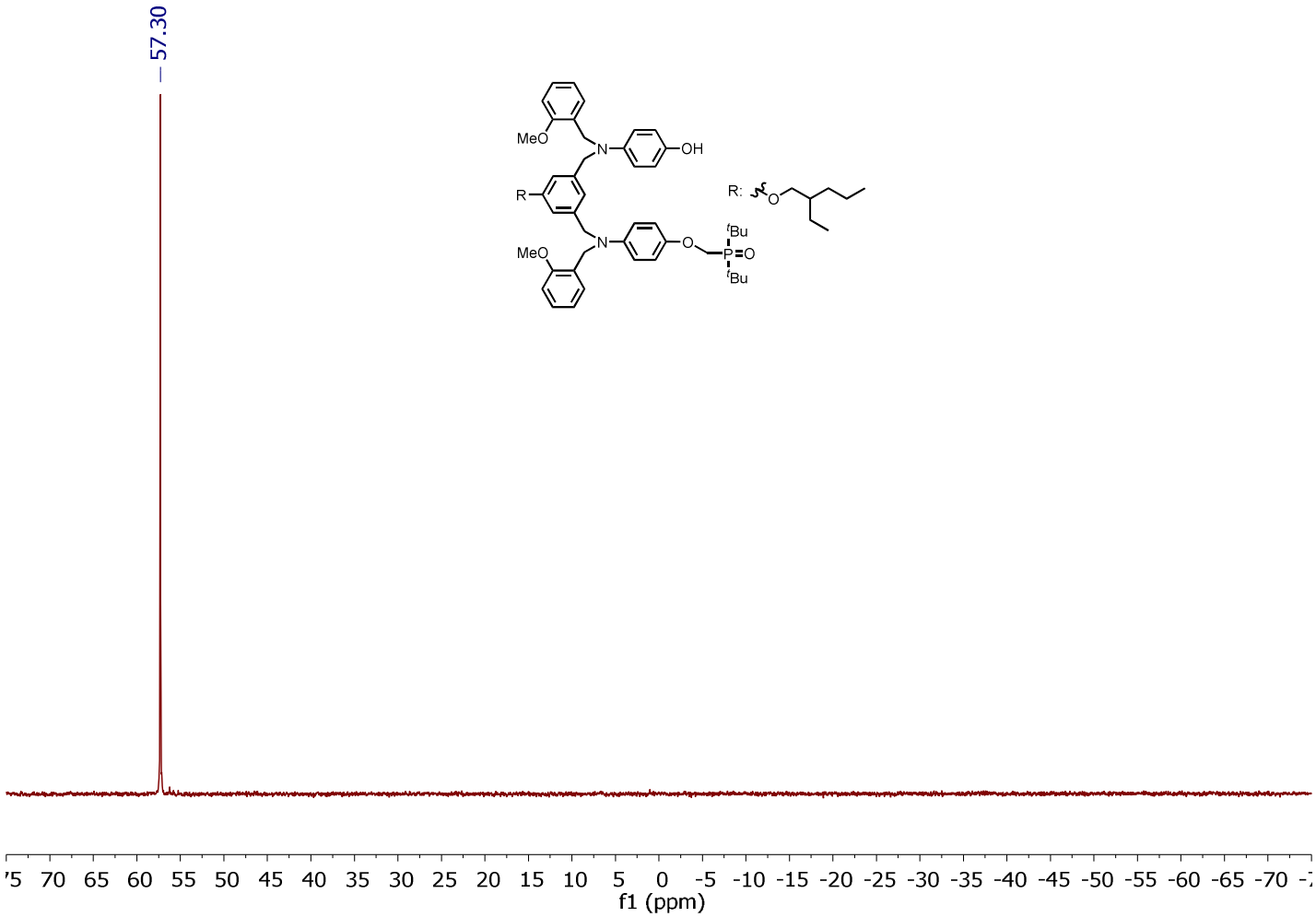
^{1}H NMR (500 MHz, CD_3CN) compound 29



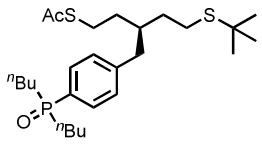
^{13}C NMR (125.7 MHz, CD_3CN) compound 29



^{31}P NMR (202.4 MHz, CD_3CN) compound 29



Synthesis of 31.



To a solution of compound **30** (0.051 g, 0.13 mmol) in dry and degassed MeOH (0.5 mL) under N_2 atmosphere was added DMPA (0.003 g, 0.01 mmol) and *tert*-butyl mercaptan (0.044 mL, 0.39 mmol). The reaction was stirred at room temperature under UV irradiation (365 nm) for 45 min. Then, the solvent was removed under vacuum and the crude purified by flash chromatography on silica (CH_2Cl_2/MeOH 30:1) to yield compound **31** (0.056 g, 90%) as a syrup.

$[\alpha]_D^{20}$= + 4.0 (*c* 0.24, CHCl*3*).

^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 7.58 (dd, 2H, *J* = 10.5, 8.1), 7.27 (m, 2H), 2.85 (m, 2H), 2.63 (m, 2H), 2.50 (m, 2H), 2.29 (s, 3H), 1.92 (m, 3H), 1.81 (m, 2H), 1.55 (m, 6H), 1.36 (m, 6H), 1.26 (s, 9H), 0.85 (t, 3H, *J* = 7.0).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C = 195.6, 144.2 (d, *J* = 3), 130.5 (d, *J* = 9), 130.1 (d, *J* = 94), 129.4 (d, *J* = 11), 42.0, 40.0, 38.6, 33.2, 33.1, 31.0, 30.6, 29.7 (d, *J* = 69), 26.5, 25.7, 24.1 (d, *J* = 15), 23.5 (d, *J* = 4), 13.6.

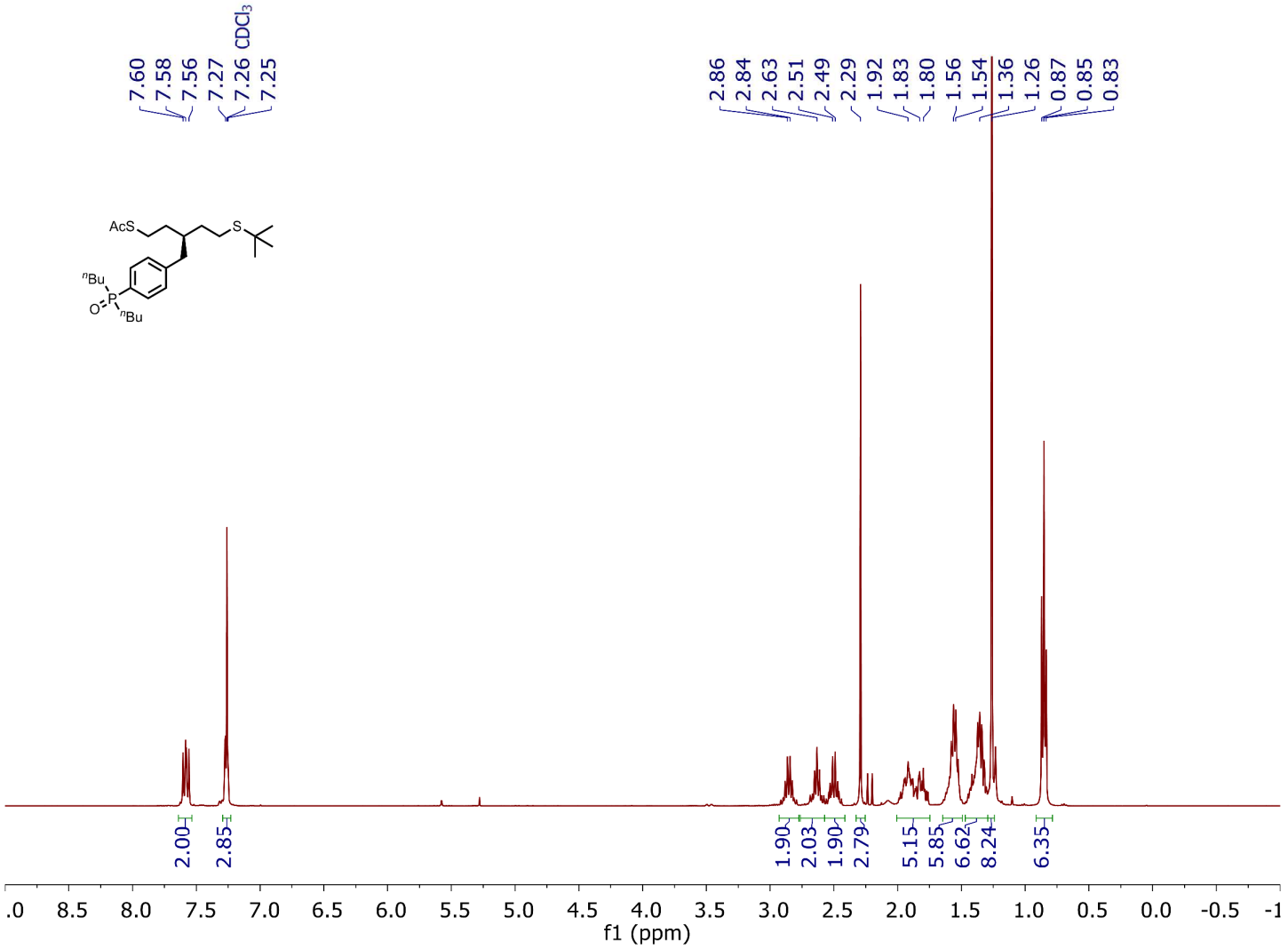
^{31}P NMR (161.3 MHz, $CDCl_3$): δ_P = 40.5.

MS (ES+): m/z (%) = 485.3 $[M+H]^+$.

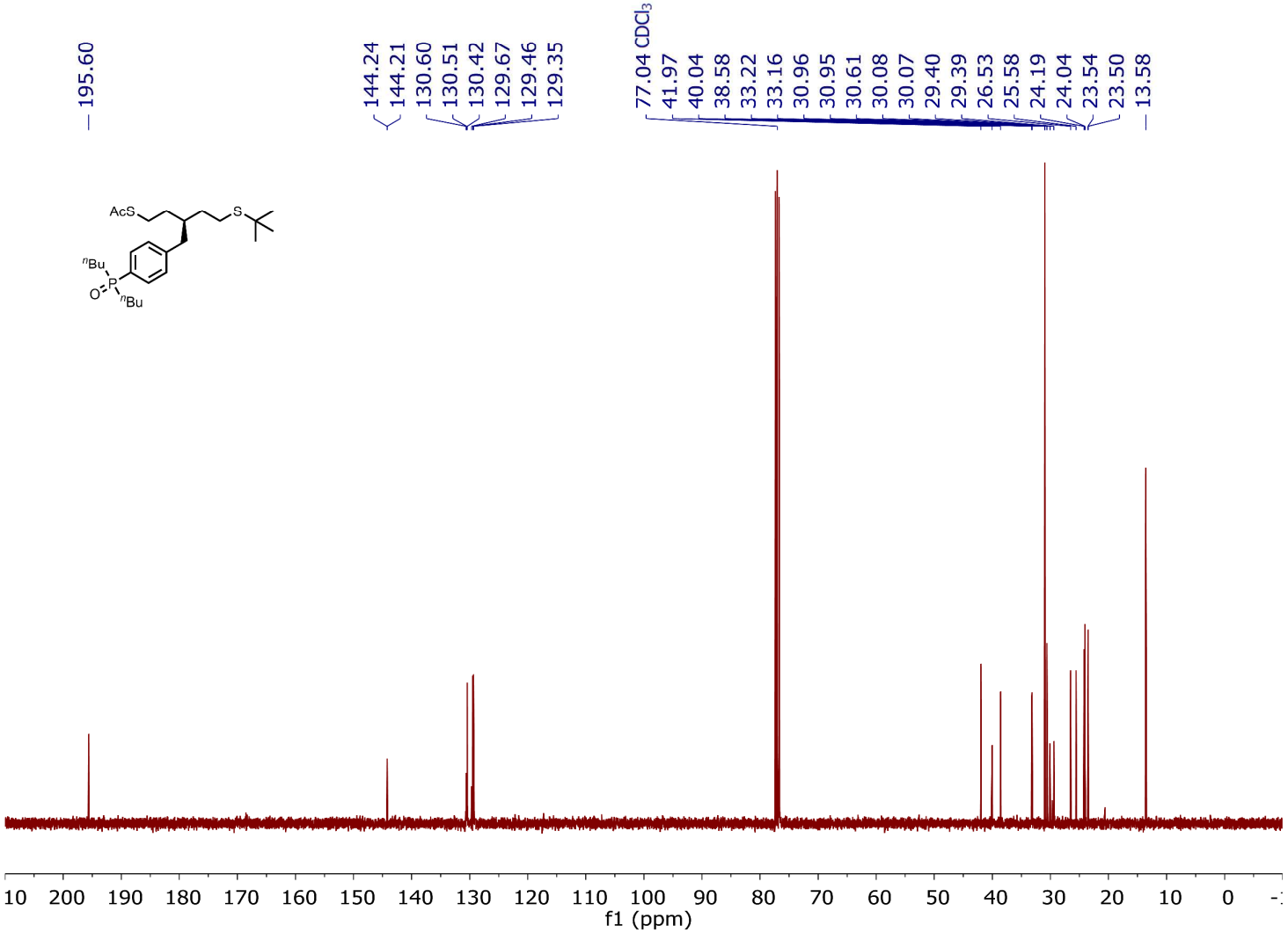
HRMS (ES+): calcd for $C_{26}H_{46}O_2PS_2$ 485.2677, found 485.2676.

FT-IR (ATR): ν_{max} 2957, 2930, 2866, 1689, 1458, 1363, 1164, 1135, 1111, 796 cm^{-1}.

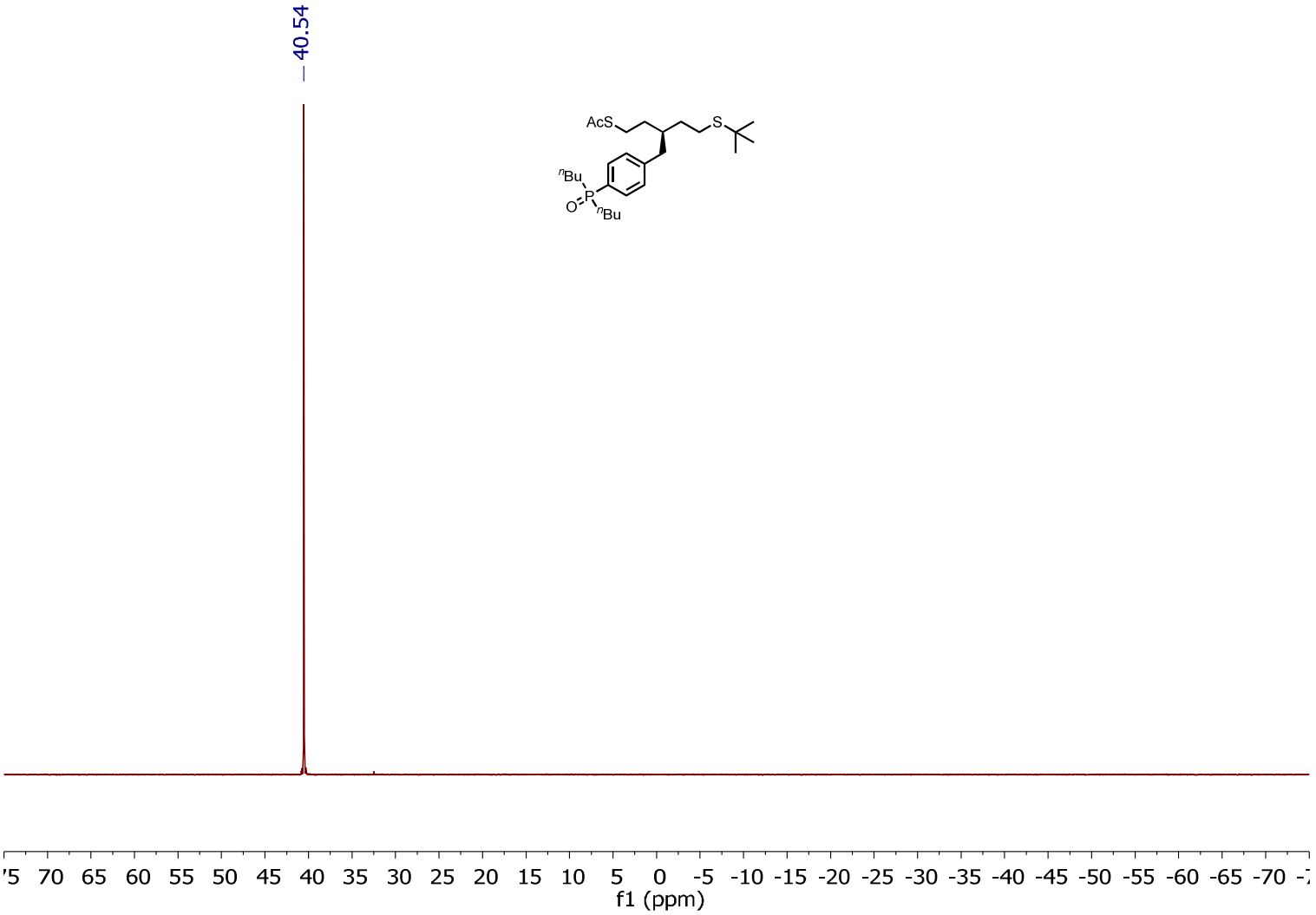
^{1}H NMR (400 MHz, $CDCl_3$) compound 31



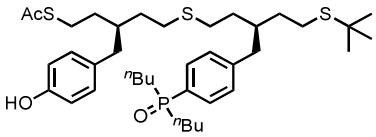
^{13}C NMR (100.6 MHz, $CDCl_3$) compound 31



^{31}P NMR (161.3 MHz, $CDCl_3$) compound 31



Synthesis of 33.



A solution of **31** (0.116 g, 0.24 mmol) in MeOH (4.5 mL) was treated with 2N NaOH solution (0.359 mL, 0.72 mmol). After stirring at room temperature for 30 min, the reaction was quenched with diluted HCl solution (2 mL) and extracted with EtOAc (3 x 10 mL). The organic phase was dried over $MgSO_4$, evaporated and dried in a high vacuum pump for 30 min. The obtained residue was dissolved in dry and degassed MeOH (1 mL) under N_2 atmosphere. DMPA (0.006 g, 0.02 mmol) and **32** (0.060 g, 0.24 mmol) were added and the reaction was stirred at room temperature under UV irradiation (365 nm) for 1.5 h. Then, the solvent was removed under vacuum and the crude purified by flash chromatography on silica (CH_2Cl_2:MeOH 25:1) to yield compound **33** (0.116 g, 70%) as a syrup.

$[\alpha]_D^{20}$= +15.0 (*c* 0.16, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 7.64 (bs, 1H), 7.58 (dd, 2H, *J* = 10.5, 8.0), 7.25 (m, 2H), 6.93 (d, 2H, *J* = 8.5 Hz), 6.76 (d, 2H, *J* = 8.5), 2.90 (t, 2H. *J* = 7.5 Hz), 2.66 (m, 2H), 2.54 (m, 1H), 2.50 (m, 2H), 2.37 (m, 5H), 2.32 (s, 3H), 1.90 (m, 6H), 1.44 (m, 16H), 1.31 (s, 9H), 0.88 (td, 6H, *J* = 7.2, 2.1 Hz).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C = 196.0, 155.5, 144.9 (d, *J* = 3), 130.9, 130.6, 130.5, 129.9, 129.7, 129.6, 129.0, 130.0, 115.7, 42.1, 40.1, 39.2, 38.7, 38.6, 33.6, 33.4, 33.2, 32.8, 31.1, 30.8, 29.7 (d, *J* = 37), 29.3, 29.2, 26.9, 25.9, 24.2 (d, *J* = 15), 23.6 (d, *J* = 4), 13.7.

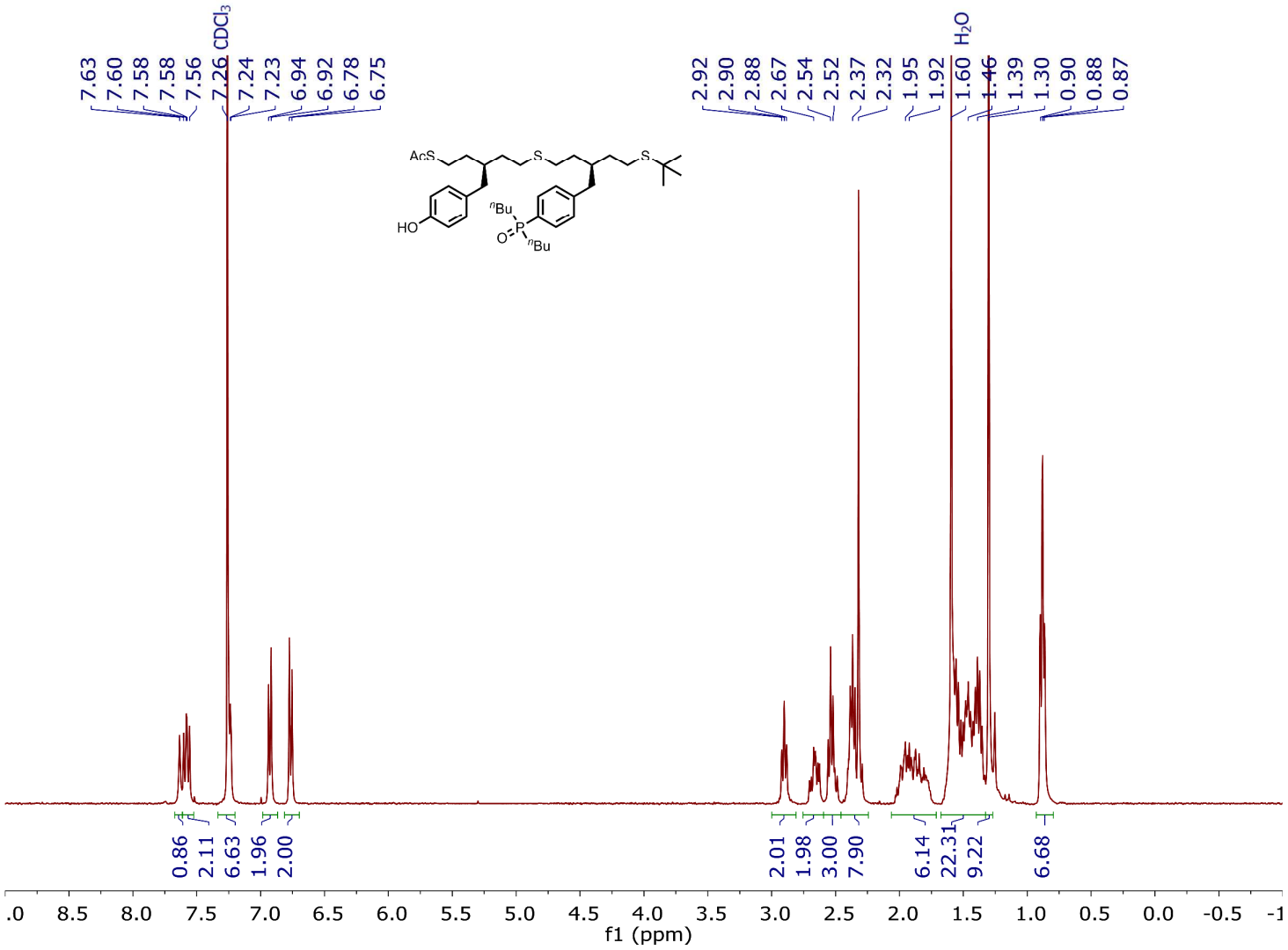
^{31}P NMR (161.3 MHz, $CDCl_3$): δ_P = 42.4.

MS (ES+): m/z (%) = 693.4$[M+H]^+$.

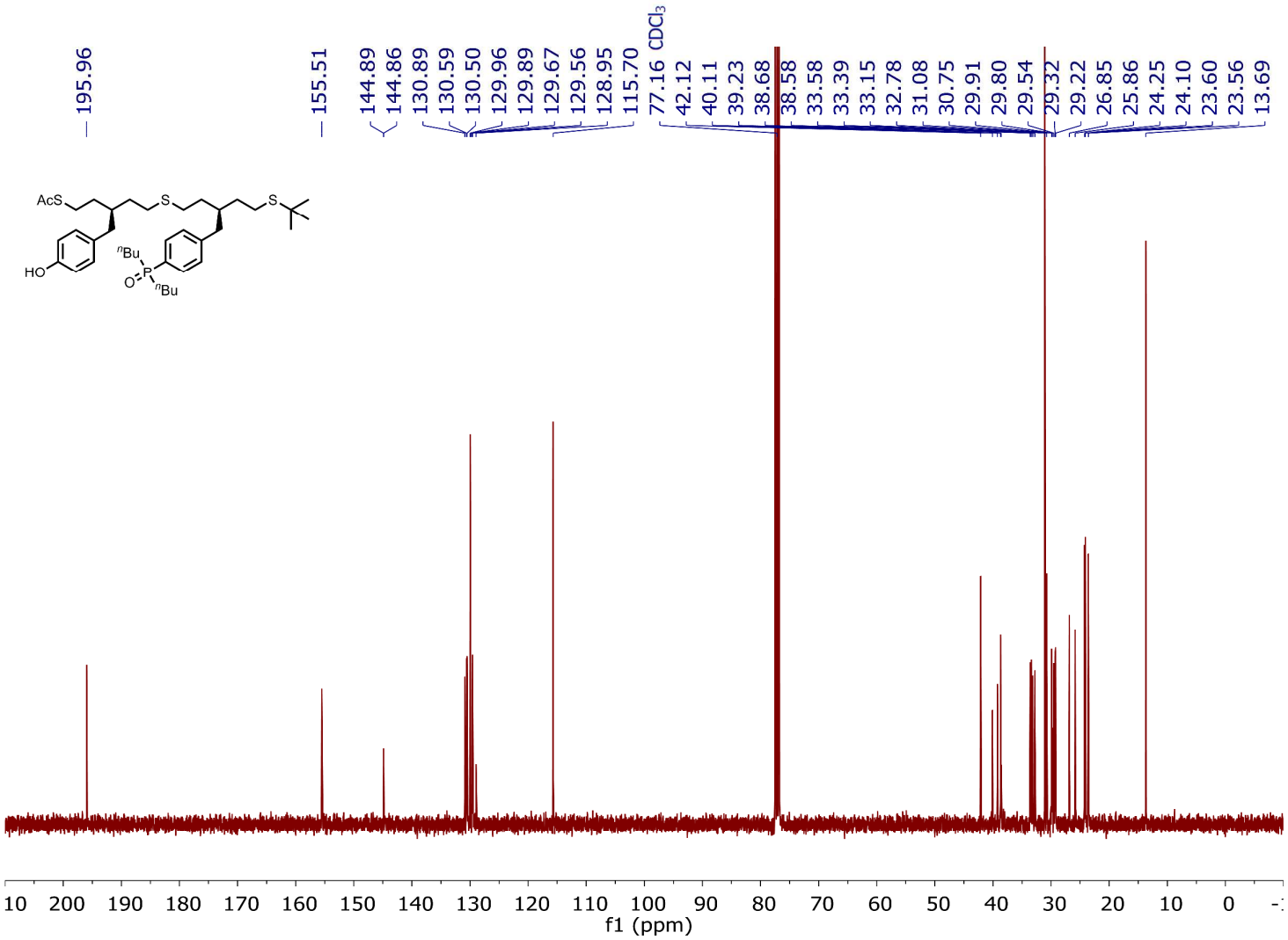
HRMS (ES+): calcd for $C_{38}H_{62}O_3PS_3$ 693.3599, found 693.3602.

FT-IR (ATR): ν_{max} 2955, 2927, 2869, 1688, 1515, 1455, 1153, 1107, 797 cm^{-1}.

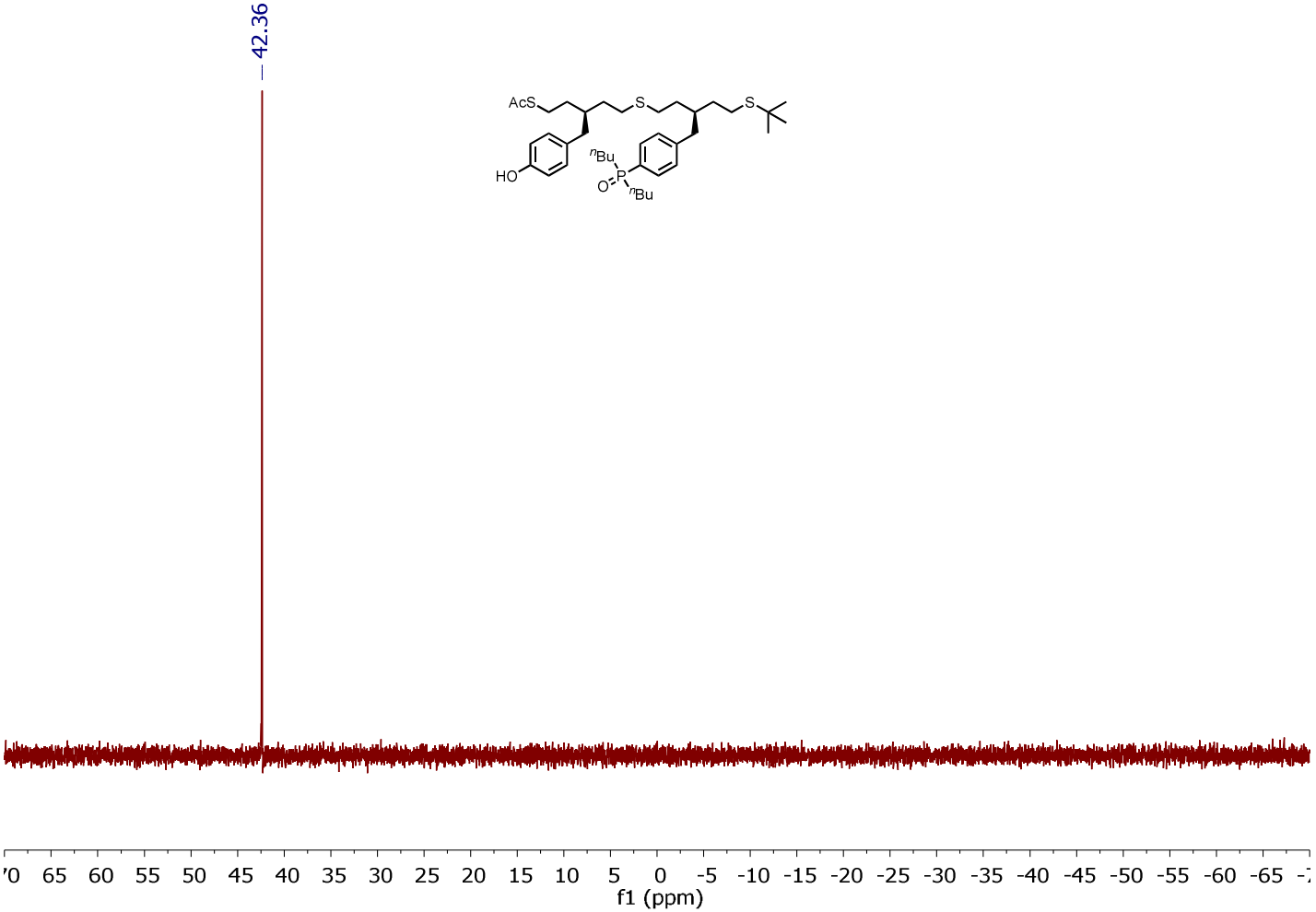
^{1}H NMR (400 MHz, $CDCl_3$) compound 33



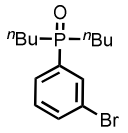
^{13}C NMR (100.6 MHz, $CDCl_3$) compound 33



^{31}P NMR (161.3 MHz, $CDCl_3$) compound 33



Synthesis of 35.



34 (0.250 g, 1.55 mmol) was added to a dried flask and the flask evacuated and back-filled with N_2 (3x). 3-Bromoiodobenzene (0.217 mL, 1.71 mmol) and 1,4-dioxane (deoxygenated by freeze-pump-thaw, 4 mL) were added. In a separate flask, $Pd_2(dba)_3$ (0.031 g, 0.03 mmol) and Xantphos (0.020 g, 0.03 mmol) were placed in a flask and evacuated and back-filled with N_2 (3x). These were dissolved in 1,4-dioxane (3 mL) and the solution transferred to the initial flask. Et_3N (0.230 mL, 1.55 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 $NaHCO_3$ (25 mL). The aqueous layer was extracted with CH_2Cl_2 (3x 10 mL) and combined organics dried ($MgSO_4$) and solvent removed. The obtained brown solid was purified by flash chromatography on silica (CH_2Cl_2/MeOH 20:1) to yield the compound **35** as a yellow oil (0.459 g, 93%).

^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 7.83 (d, 1H, *J* = 10.4), 7.67-7.63 (m, 1H), 7.63-7.57 (m, 1H), 7.36 (td, 1H, *J* = 8.0, 2.8), 2.04-1.75 (m, 4H), 1.69-1.30 (m, 8H), 0.87 (t, 6H, *J* = 8.0).

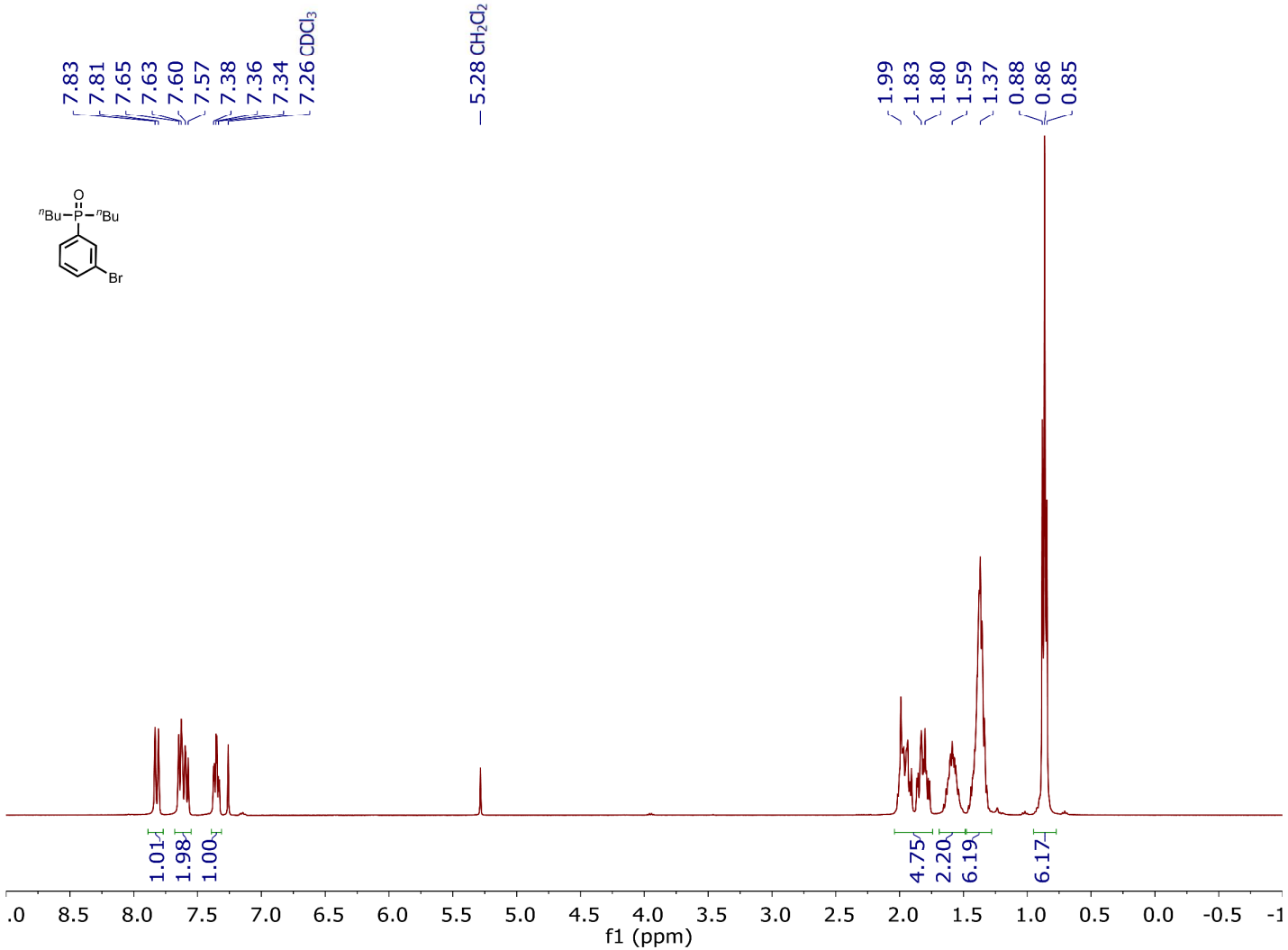
^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C = 135.6 (d, *J* = 89 Hz), 134.5 (d, *J* = 3), 133.2 (d, *J* = 9 Hz), 130.3 (d, *J* = 12), 128.9 (d, *J* = 9), 123.3 (d, *J* = 14), 29.7 (d, *J* = 65), 24.1 (d, *J* = 14), 23.5 (d, *J* = 4), 13.6.

^{31}P NMR (161.3 MHz, $CDCl_3$): δ_P = 39.8.

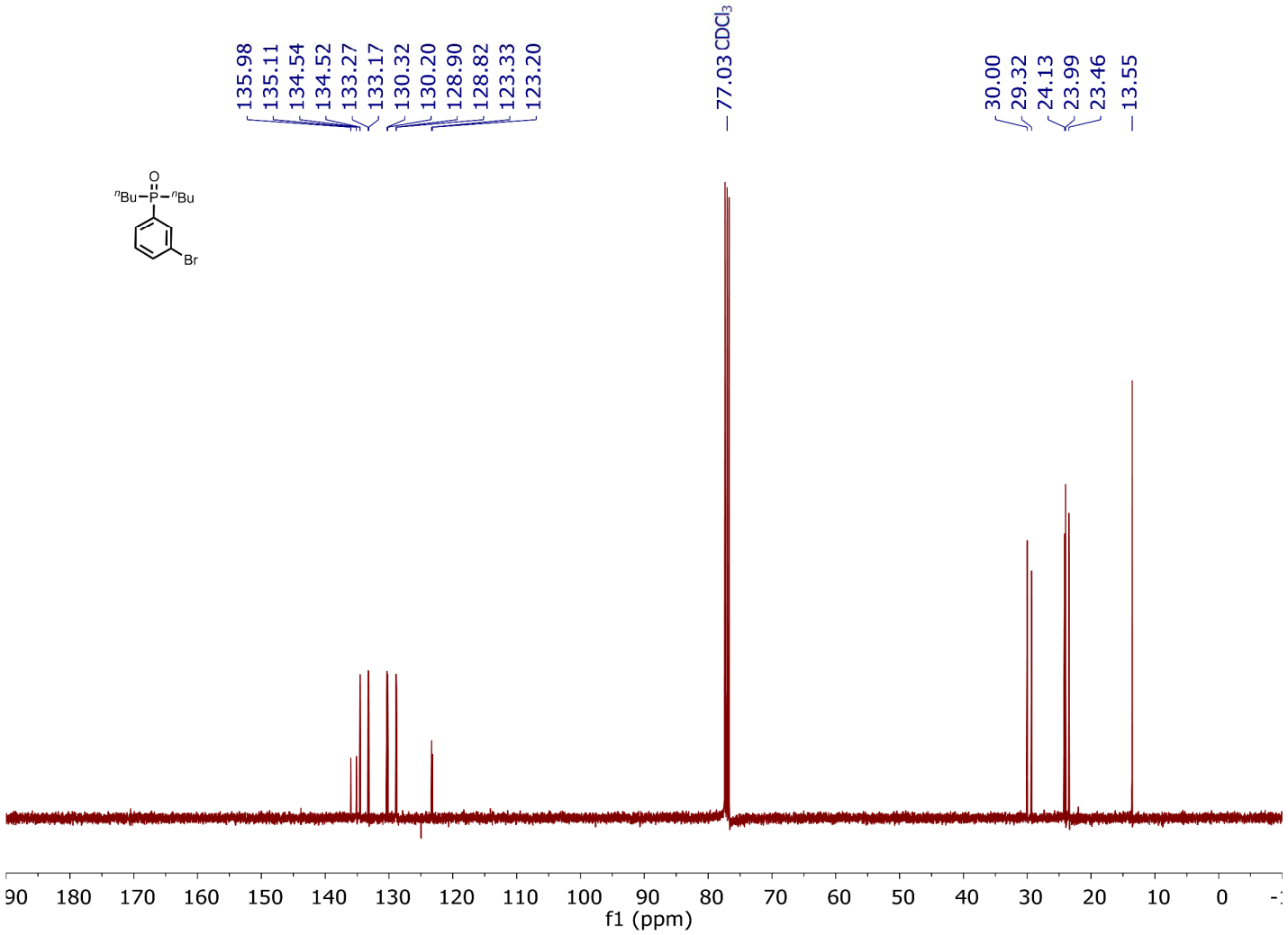
HRMS (ES+): calcd for $C_{14}H_{23}{}^{79}BrOP$ 317.0670, found 317.0668.

FT-IR (ATR): ν_{max} 2956, 2932, 2871, 1465, 1398, 1169 cm^{-1}.

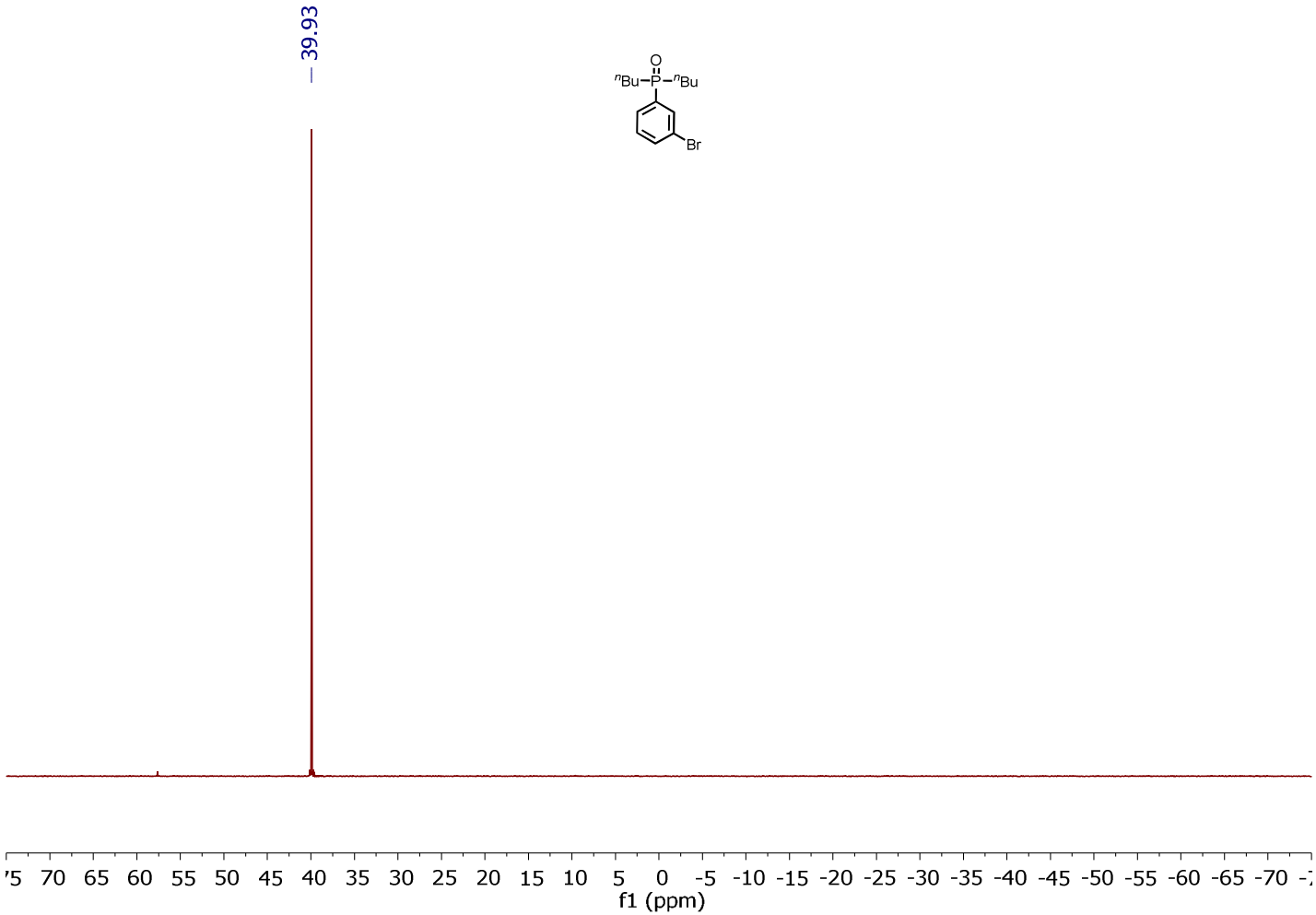
^{1}H NMR (400 MHz, $CDCl_3$) compound 35



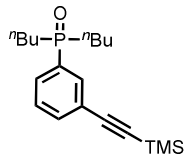
^{13}C NMR (100.6 MHz, $CDCl_3$) compound 35



^{31}P NMR (161.3 MHz, $CDCl_3$) compound 35



Synthesis of S4.



35 (0.317 g, 1.00 mmol), $Pd_2(dba)_3$ (0.018 g, 0.02), CuI (0.004 g, 0.02 mmol) and PPh_3 (0.026 g, 0.10 mmol) were added to a flask with Et_3N (5 mL) and DMF (5 mL). N_2 was bubbled through the reaction for 15 minutes. TMSA (0.170 mL, 1.20 mmol) was added and the reaction stirred at 50 °C for 4 hin the dark under N_2 atmosphere. The reaction was filtered through celite and washed through with EtOAc (30 mL). The solution was washed with 1M HCl (3x 30 mL) and 5% LiCl solution (2x 30mL), and then dried ($MgSO_4$). The solvent was removed by rotary evaporation under reduced pressure. The residue was purified by flash chromatography on silica (CH_2Cl_2/MeOH 19:1) to yield the desired compound **S4** as a brown oil (0.268 g, 90%).

^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 7.74 (dt, 1H, *J* = 11.0, 1.5), 7.63 (ddt, 1H, *J* = 10.5, 7.5, 1.5), 7.57 (dd, 1H, *J* = 8.0, 1.5), 7.40 (td, 1H, *J* = 8.0, 2.5), 2.06-1.88 (m, 2H), 1.87-1.75 (m, 2H), 1.70-1.44 (m, 2H), 1.45-1.27 (m, 6H), 0.84 (t, , 6H, *J* = 7.0), 0.23 (s, 9H).

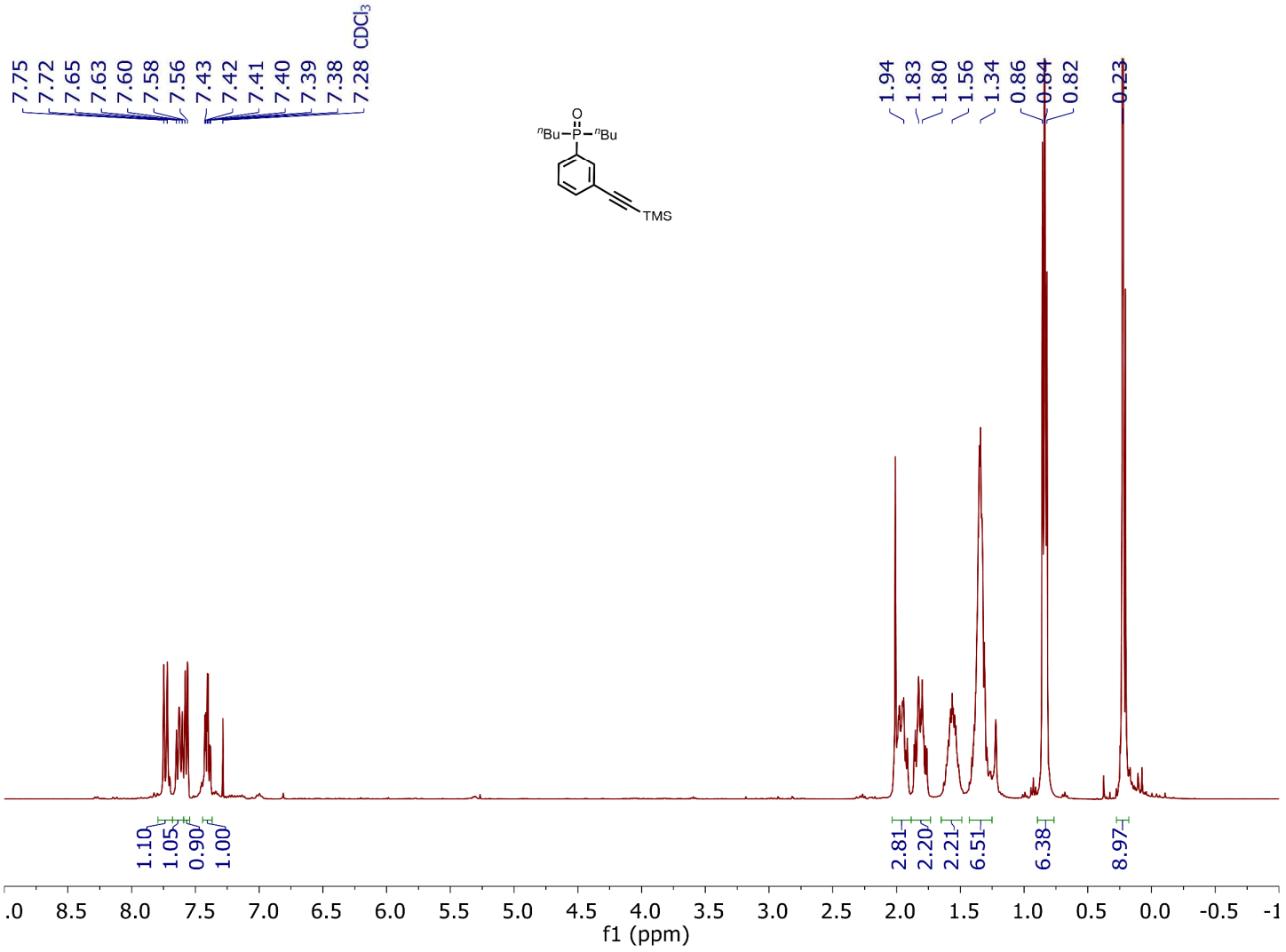
^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C = 134.7 (d, *J* = 3), 133.6 (d, *J* = 10), 132.8 (d, *J* = 91), 130.2 (d, *J* = 8), 128.5 (d, *J* = 12), 123.8 (d, *J* = 12), 103.8, 95.9, 29.5 (d, *J* = 69), 24.0 (d, *J* = 14), 23.4 (d, *J* = 4), 13.52, -0.17.

^{31}P NMR (161.3 MHz, $CDCl_3$): δ_P = 41.3.

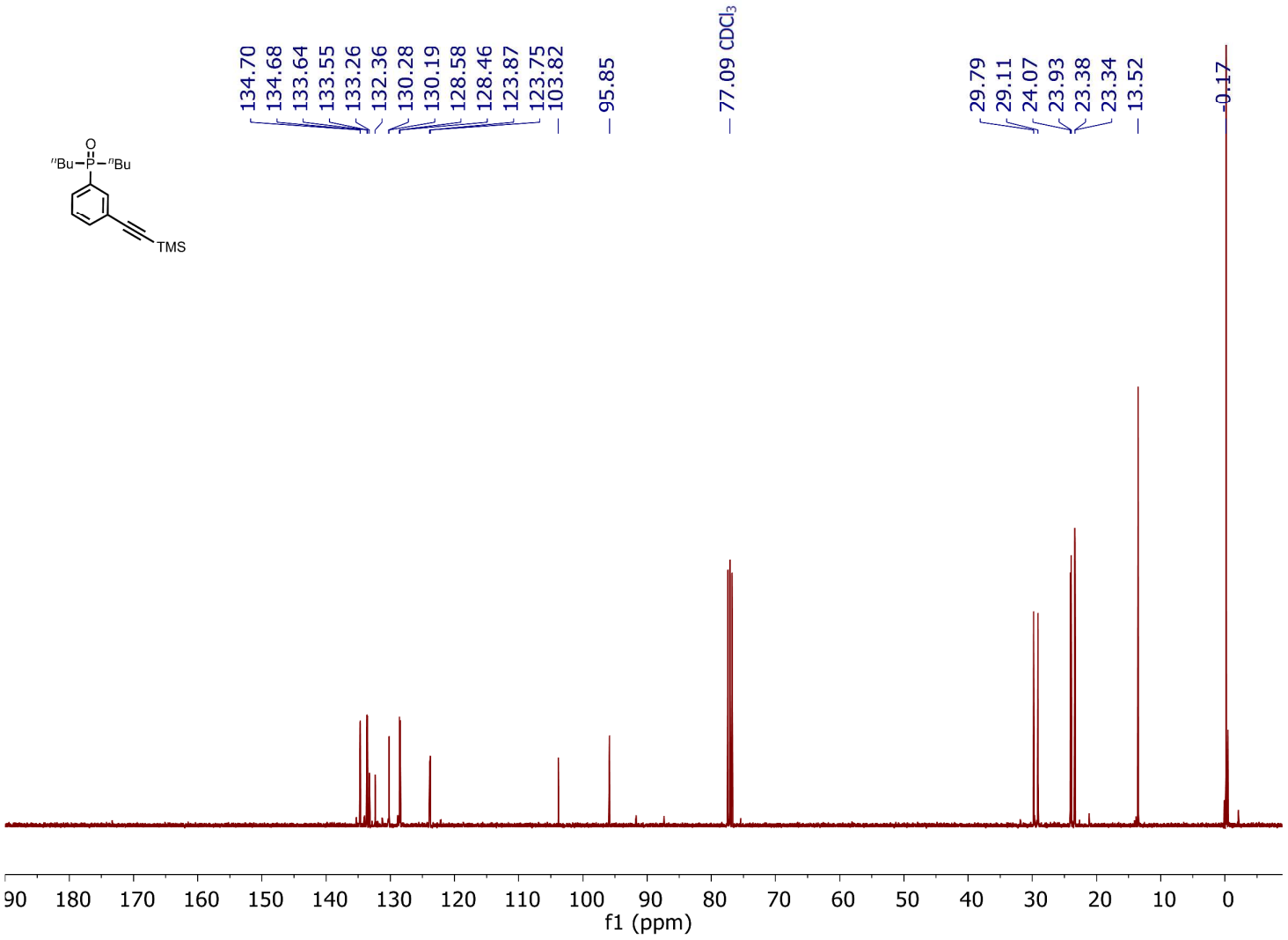
HRMS (ES+): calcd for $C_{19}H_{32}OPSi$ 335.1960, found 335.1956.

FT-IR (ATR): ν_{max} 2958, 2930, 2163, 1467, 1400, 1164, 842, 759, 693 cm^{-1}.

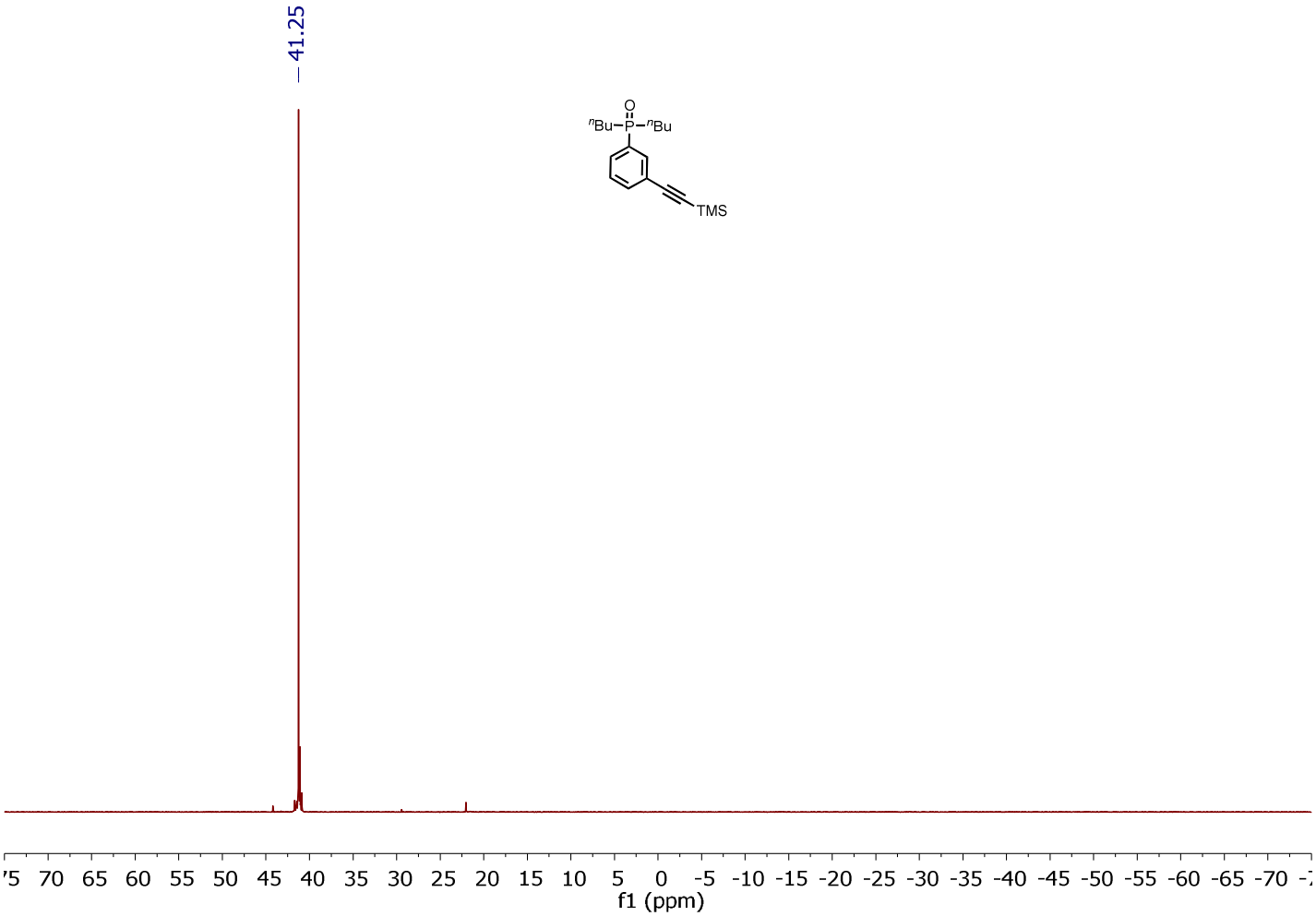
^{1}H NMR (400 MHz, $CDCl_3$) compound S4



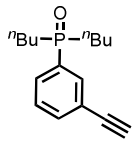
^{13}C NMR (100.6 MHz, $CDCl_3$) compound S4



^{31}P NMR (161.3 MHz, $CDCl_3$) compound S4



Synthesis of 36.



Compound **S4** (0.365 g, 0.86 mmol) was dissolved in dry THF (29 mL) and reaction purged with N_2. Reaction was cooled to 0 °C and TBAF (1M in THF, 1.89 mL, 1.89 mmol) added. The reaction was stirred for 10 min and then diluted with EtOAc (50 mL). This solution was washed with 1M HCl (3 x 50 mL) and then dried ($MgSO_4$). The solvent was removed by rotary evaporation under reduced pressure yielding **36** as a brown oil (0.230 g, 95%).

^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 7.80 (dt, 1H, *J* = 11.0, 1.5), 7.73 (ddt, 1H, *J* = 10.5, 7.5, 1.5), 7.65 (dd, 1H, *J* = 8.0, 1.5), 7.48 (td, 1H, *J* = 8.0, 2.5), 3.17 (s, 1H), 2.06-1.93 (m, 2H), 1.91-1.78 (m, 2H), 1.61-1.55 (m, 2H), 1.48-1.33 (m, 6H), 0.89 (t, 6H, *J* = 7.0).

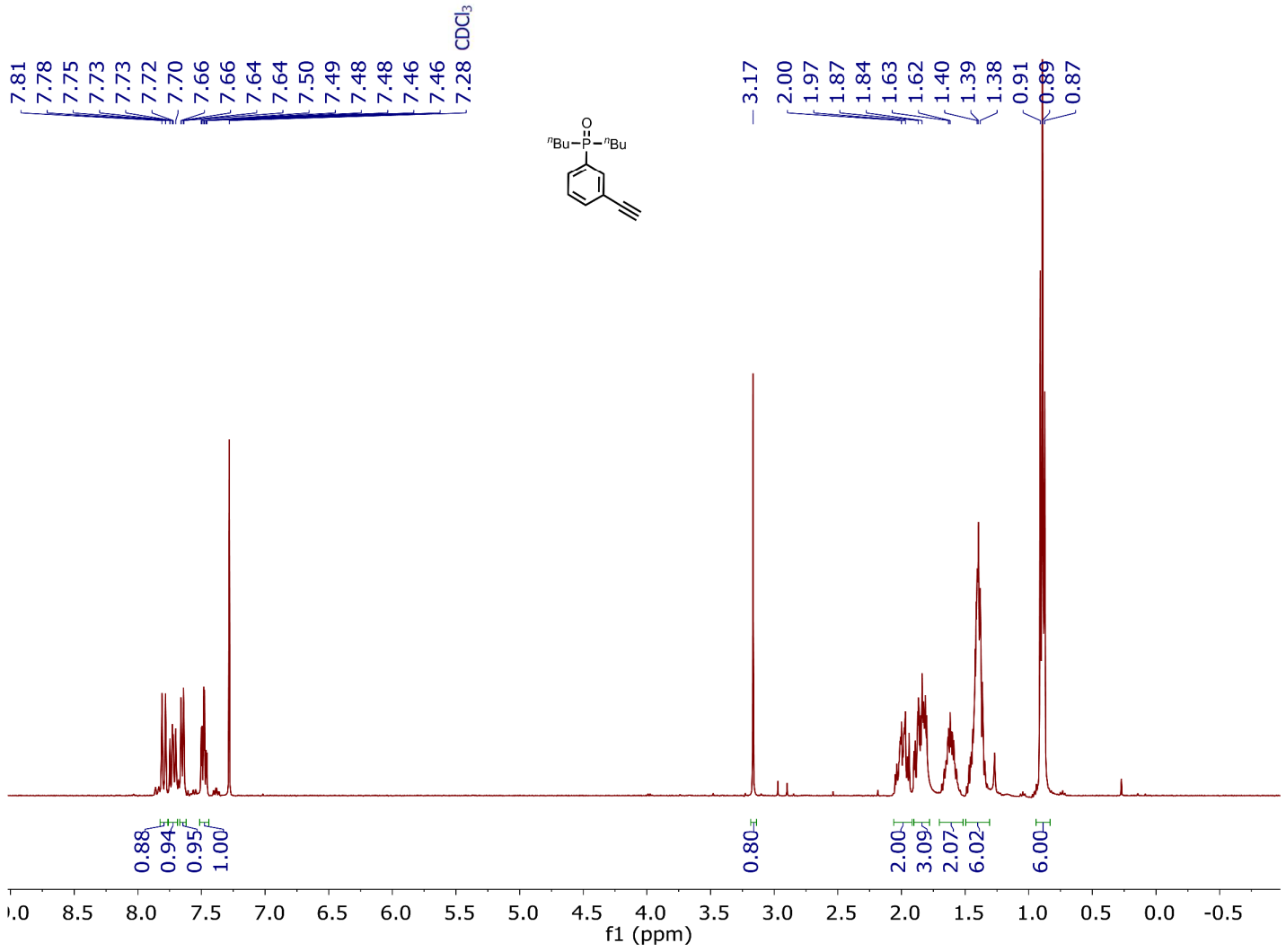
^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C = 134.9 (d, *J* = 3), 133.7 (d, *J* = 10), 133.3 (d, *J* = 91), 133.7 (d, *J* = 8), 128.7 (d, *J* = 12), 125.0 (d, *J* = 12), 122.9, 78.5, 29.6 (d, *J* = 69), 24.1 (d, *J* = 14), 23.5 (d, *J* = 4), 13.6.

^{31}P NMR (161.3 MHz, $CDCl_3$): δ_P = 40.2.

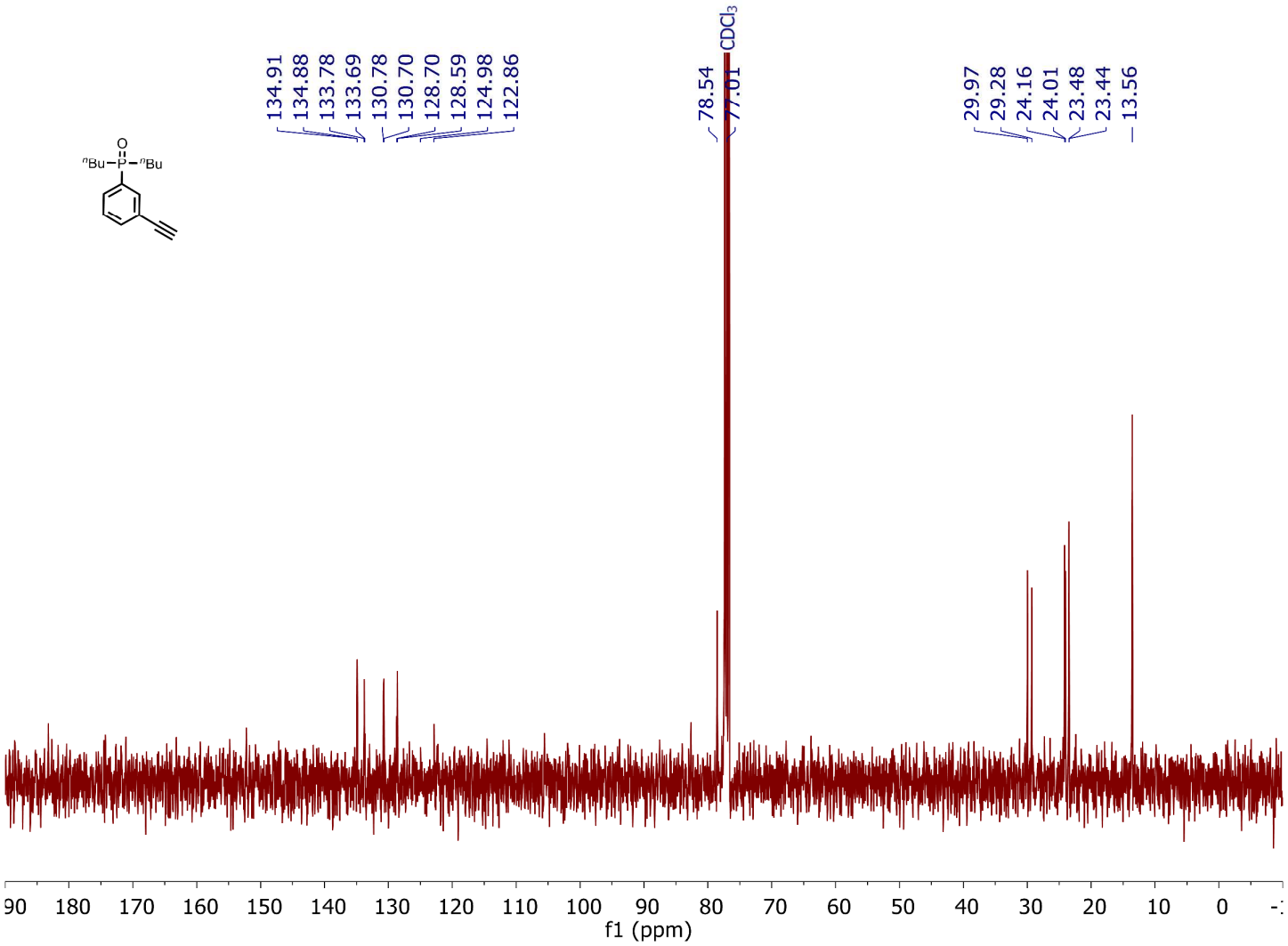
HRMS (ES+): calcd for $C_{19}H_{32}OPSi$ 335.1960, found 335.1956.

FT-IR (ATR): ν_{max} 2958, 2930, 2163, 1467, 1400, 1164, 842, 759, 693 cm^{-1}.

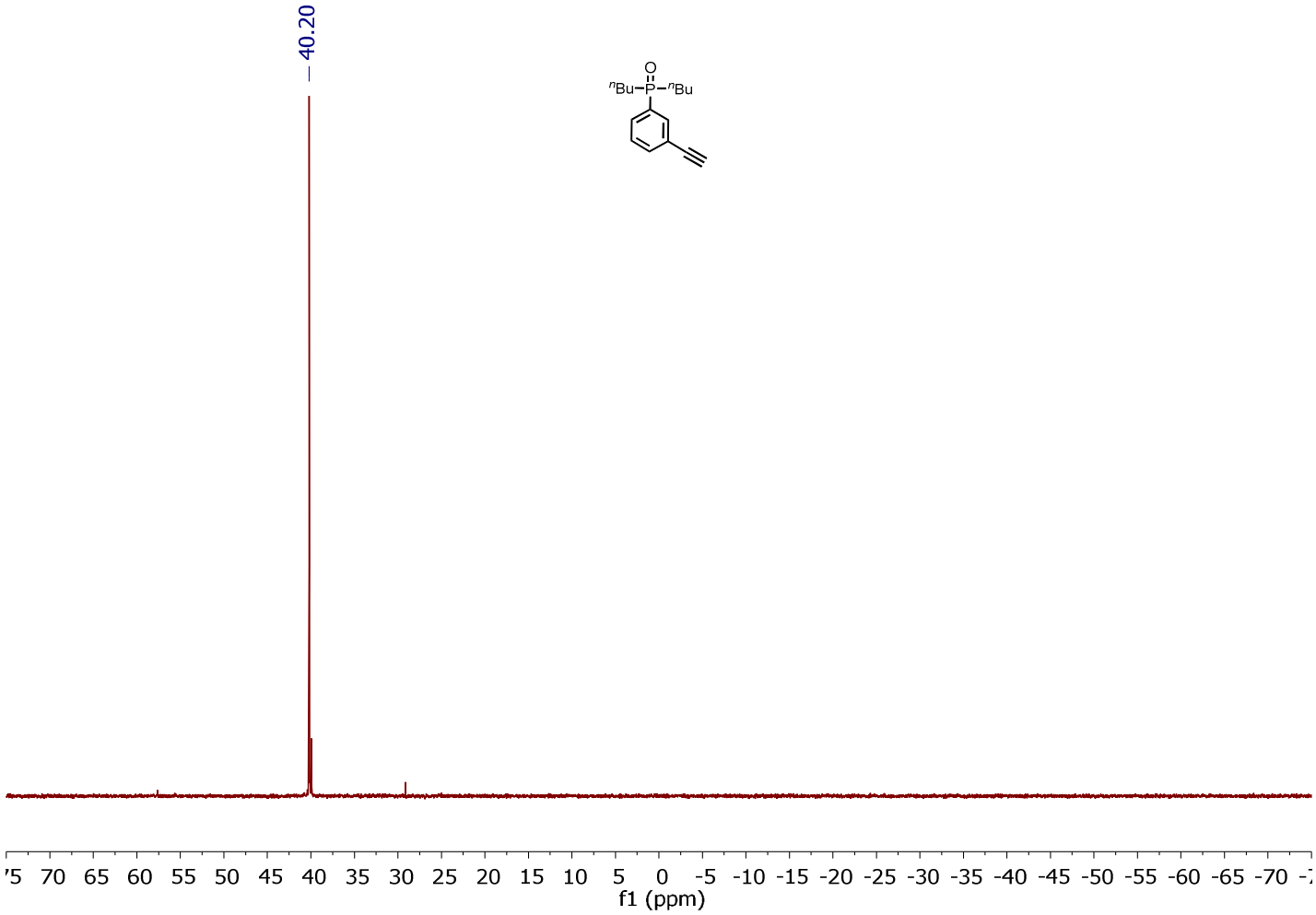
^{1}H NMR (400 MHz, $CDCl_3$) compound 36



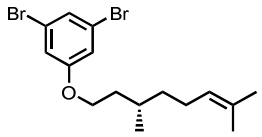
^{13}C NMR (100.6 MHz, $CDCl_3$) compound 36



^{31}P NMR (161.3 MHz, $CDCl_3$) compound 36



Synthesis of 38.



3,5-Dibromophenol (3.00 g, 11.90 mmol), *S-(-)*-β-citronellol (4.34 mL, 23.80 mmol) and PPh_3 (4.14 g, 15.8 mmol) were dissolved in dry THF (90 mL) under N_2. Diisopropyl azodicarboxylate (3.11 mL, 15.80 mmol) was added slowly at 0 °C. The reaction was allowed to warm to room temperature and was stirred overnight under N_2. The solvent was removed by rotary evaporation under reduced pressure yielding a brown solid, which was purified by flash chromatography on silica (40-60 pet. ether) to yield the desired compound **38** as a yellow oil (4.55 g, 98%).

$[\alpha]_D^{20}$ = -4.11 (*c* 1.31, $CHCl_3$).

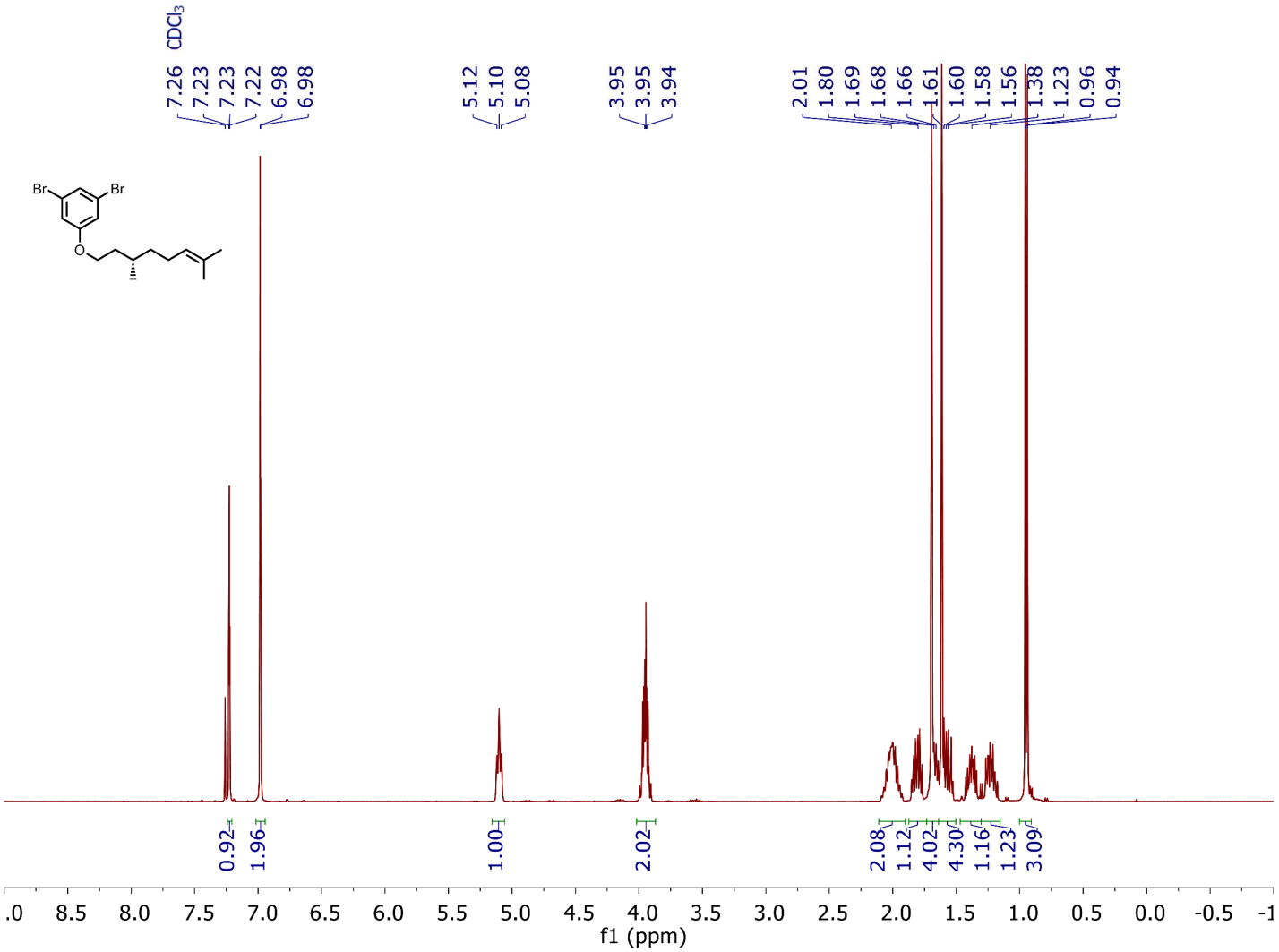
^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 7.23 (t, 1H, *J* = 1.5), 6.98 (d, 2H, *J* = 1.5), 5.14-5.06 (m, 1H), 4.00-3.89 (m, 2H), 2.08-1.92 (m, 2H), 1.85-1.76 (m, 1H), 1.69 (s, 3H), 1.68-1.63 (m, 1H), 1.61 (s, 3H), 1.60-1.55 (m, 1H), 1.42-1.33 (m, 1H), 1.28-1.18 (m, 1H), 0.95 (d, 3H, *J* = 6.5).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C = 160.3, 131.4, 126.2, 124.5, 123.1, 116.9, 66.9, 37.0, 35.9, 29.4, 25.7, 25.4, 19.5, 17.7.

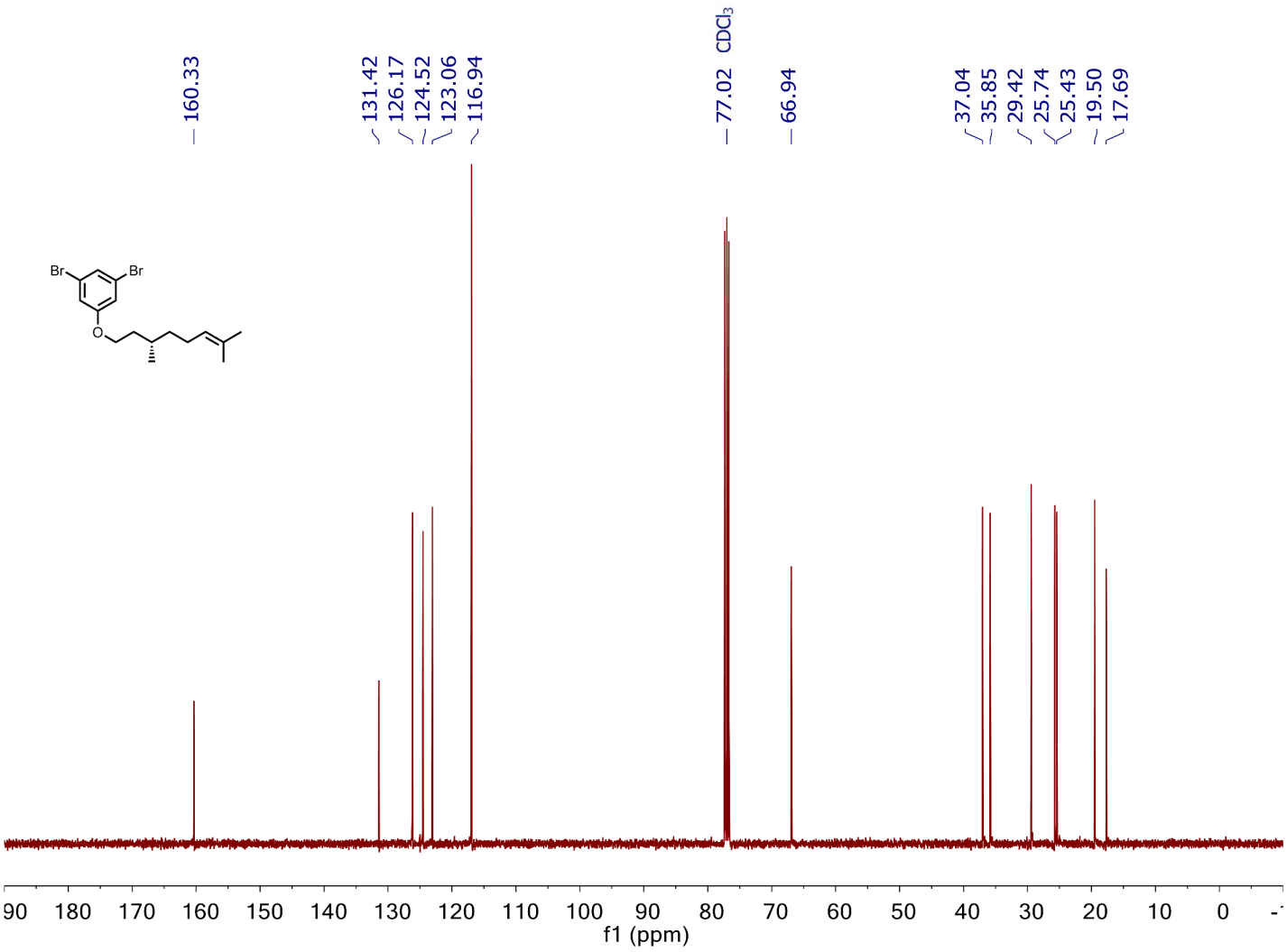
HRMS (ES+): calcd for $C_{16}H_{22}{}^{79}Br_2O$ 386.9954, found 386.9960.

FT-IR (ATR): ν_{max} 2955, 2913, 1583, 1557, 1437, 1254, 828 cm^{-1}.

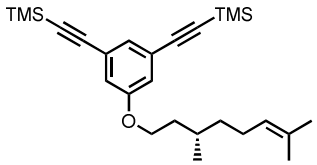
^{1}H NMR (400 MHz, $CDCl_3$) compound 38



^{13}C NMR (100.6 MHz, $CDCl_3$) compound 38



Synthesis of S5.



38 (1.00 g, 2.56 mmol), $Pd_2(dba)_3$ (0.094 g, 0.10 mmol), CuI (0.020 g, 0.10 mmol) and PPh_3 (0.134 g, 0.51 mmol) were added to a flask with Et_3N (8.5 mL) and DMF (8.5 mL), and N_2 bubbled through the reaction for 15 minutes. TMSA (0.87 mL, 6.15 mmol) was added and the reaction heated by microwave irradiation at 95 °C for 15 min. The reaction was filtered through celite and washed through with EtOAc (80 mL). The solution was washed with 1 M HCl (3 x 50 mL), 5% LiCl solution (2 x 50 mL) and then dried ($MgSO_4$). The solvent was removed by rotary evaporation under reduced pressure yielding and the residue was purified by flash chromatography on silica (40-60 pet. ether) to yield the desired compound **S5** as a light yellow oil (1.07 g, 98%).

$[\alpha]_D$ = -3.51 (*c* 1.03, $CHCl_3$).

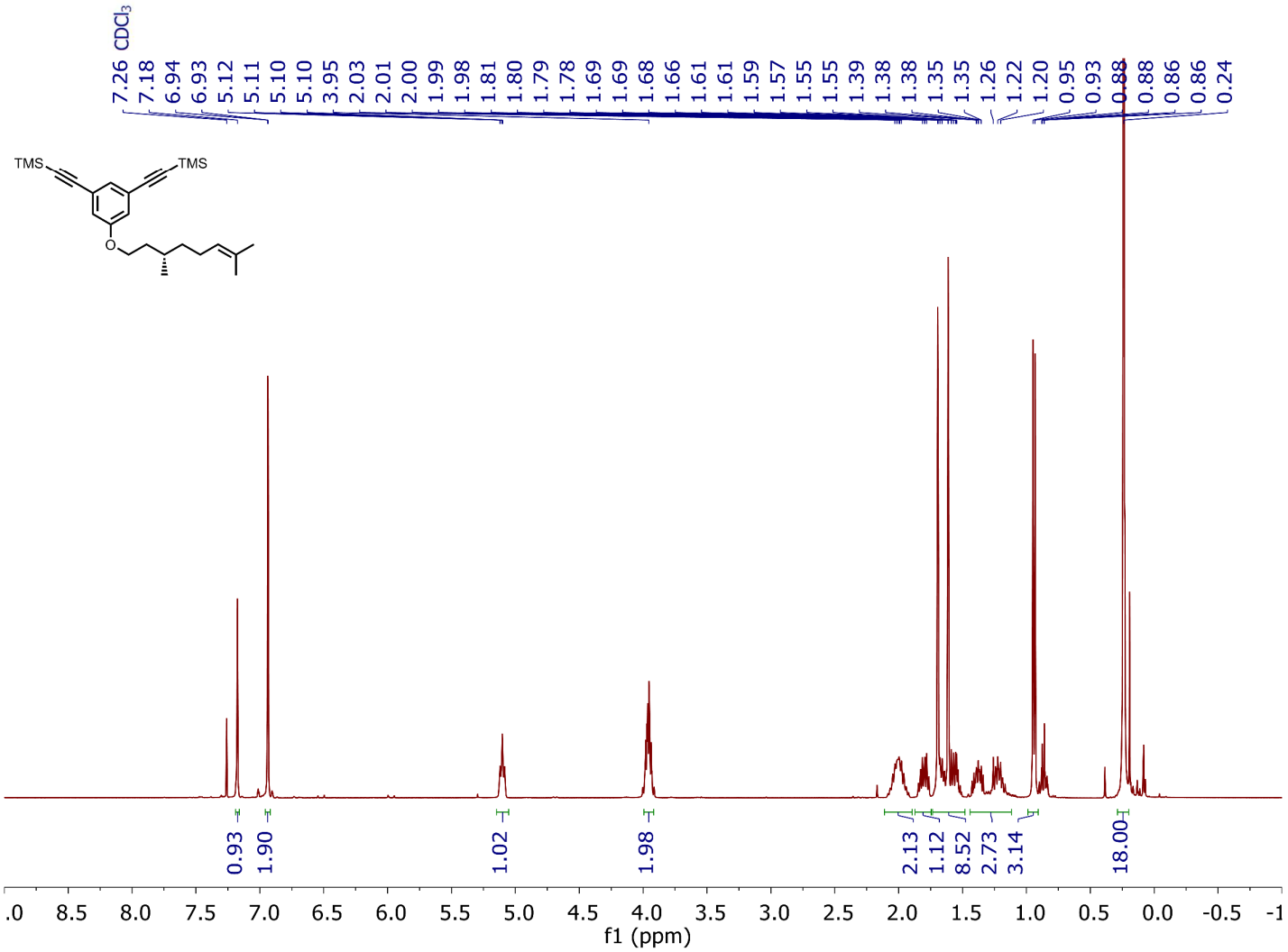
^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 7.18 (t, 1H, *J* = 1.5), 6.93 (d, 2H, *J* = 1.5), 5.13-5.07 (m, 1H), 3.99-3.92 (m, 2H), 2.09-1.92 (m, 2H), 1.85-1.76 (m, 1H), 1.69 (s, 3H), 1.68-1.63 (m, 1H), 1.61 (s, 3H), 1.60-1.55 (m, 1H), 1.42-1.33 (m, 1H), 1.28-1.18 (m, 1H), 0.95 (d, 3H, *J* = 6.5), 0.24 (s, 18H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C = 158.6, 131.3, 128.0, 124.6, 124.2, 118.3, 104.1, 94.5, 66.7, 37.0 (, 35.9, 29.7, 25.7, 25.4, 19.5, 17.7, -0.09.

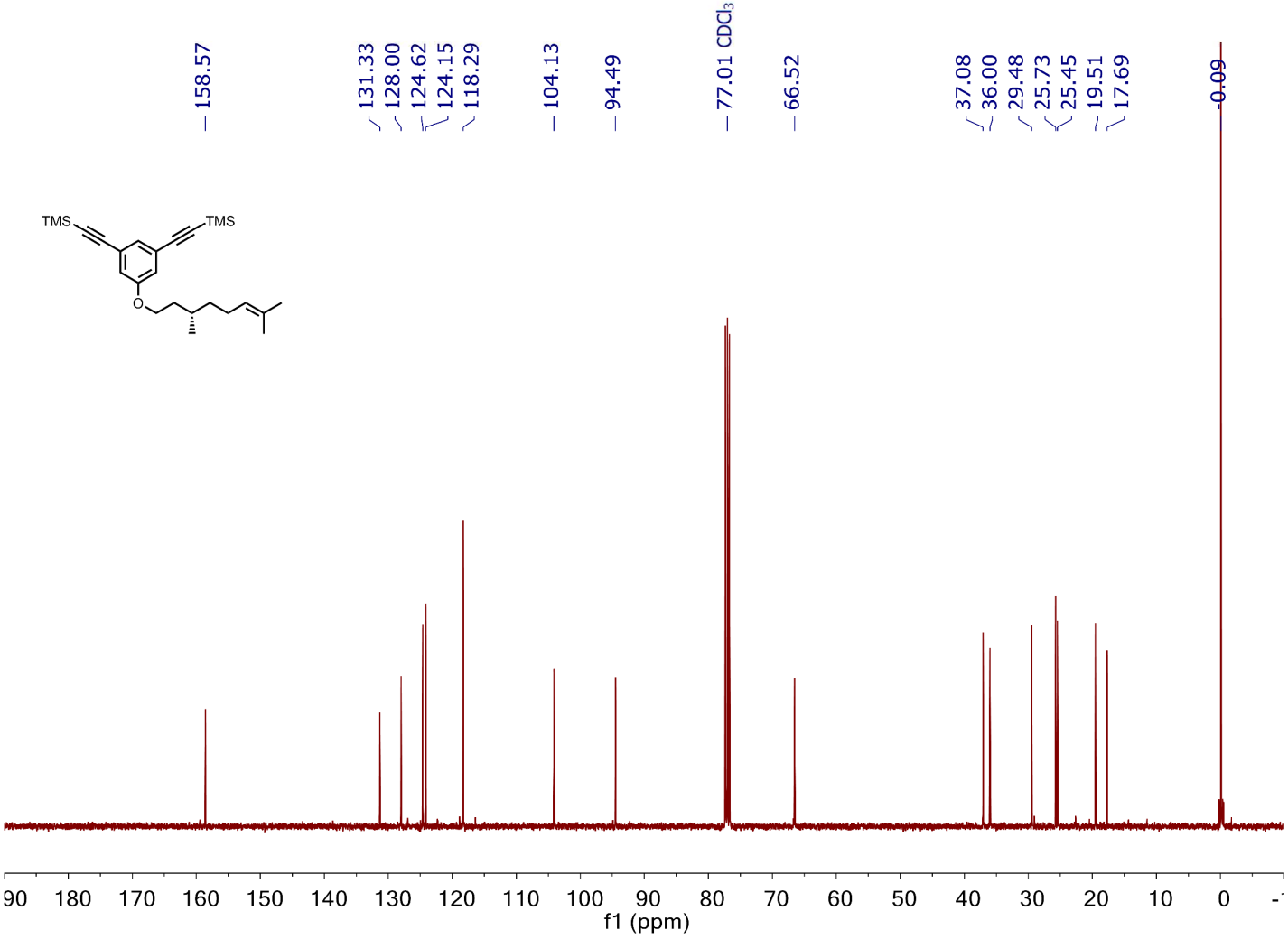
HRMS (ES+): calcd for $C_{26}H_{41}OSi_2$ 425.2696, found 425.2698.

FT-IR (ATR): ν_{max} 2961, 2929, 1578, 1249, 1156, 837, 758 cm^{-1}.

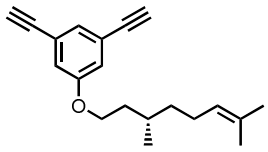
^{1}H NMR (400 MHz, $CDCl_3$) compound S5



^{13}C NMR (100.6 MHz, $CDCl_3$) compound S5



Synthesis of 39.



S5 (0.365 g, 0.86 mmol) was dissolved in dry THF (29 mL) and reaction purged with N_2. Reaction was cooled to 0 °C and TBAF (1M in THF, 1.89 mL, 1.89 mmol) added. Reaction was stirred for 10 min and filtered through a plug of silica, washing through with 40-60 pet. ether. The solvent was removed by rotary evaporation under reduced pressure yielding **39** as a brown oil (0.230 g, 95%).

$[\alpha]_D$ = -4.44 (*c* 0.70, $CHCl_3$).

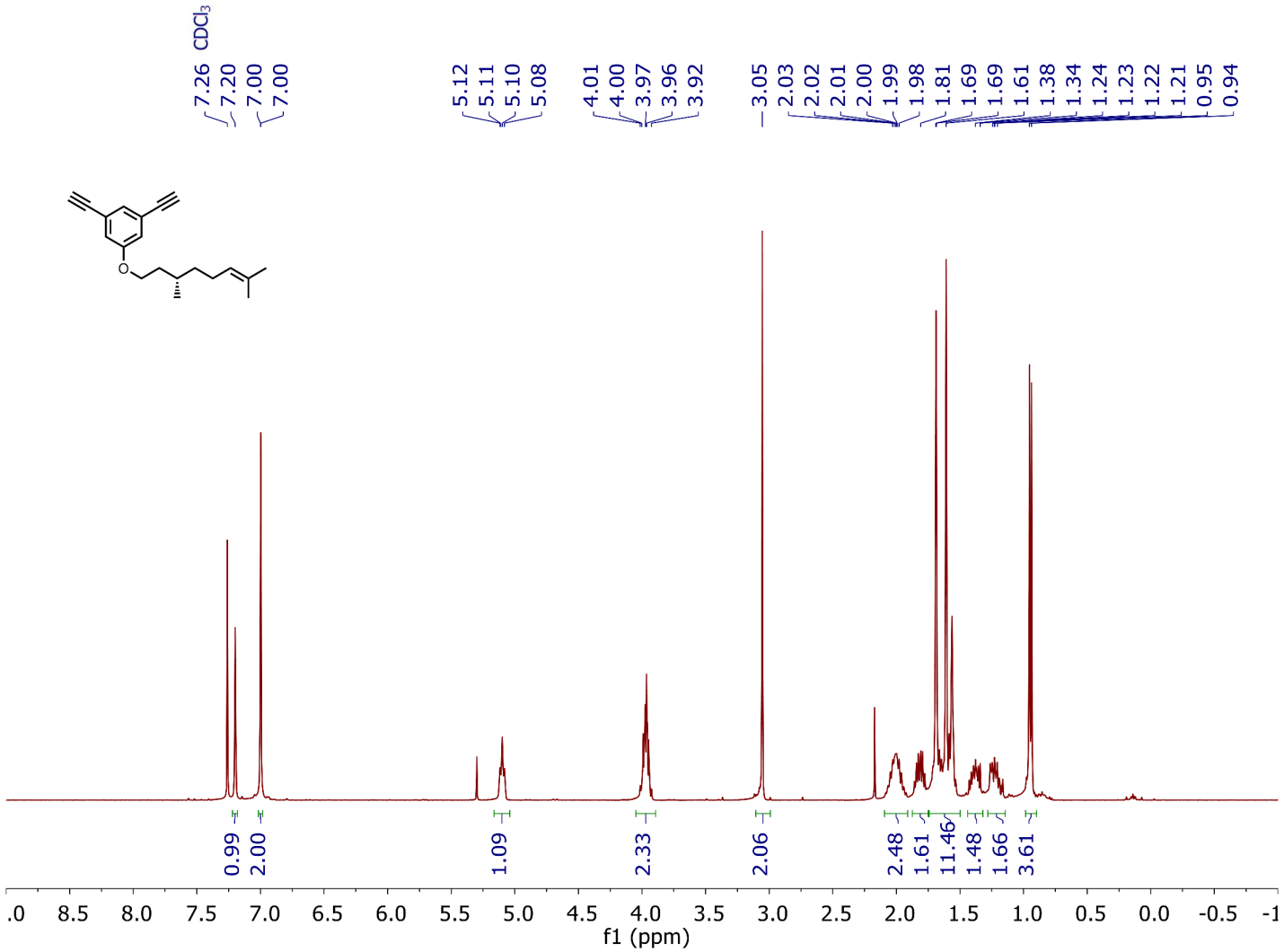
^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 7.20 (t, 1H, *J* = 1.5), 7.00 (d, 2H, *J* = 1.5), 5.13-5.07 (m, 1H), 3.99-3.92 (m, 2H) 3.05 (s, 1H), 2.09-1.92 (m, 2H), 1.85-1.76 (m, 1H), 1.69 (s, 3H), 1.68-1.63 (m, 1H), 1.61 (s, 3H), 1.60-1.55 (m, 1H), 1.42-1.33 (m, 1H), 1.28-1.18 (m, 1H), 0.95 (d, 3H, *J* = 6.5).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C = 158.7, 131.4, 128.1, 124.6, 123.3, 118.9, 82.64, 77.52, 66.6, 37.1, 35.9, 29.5, 25.7, 25.4, 19.5, 17.7.

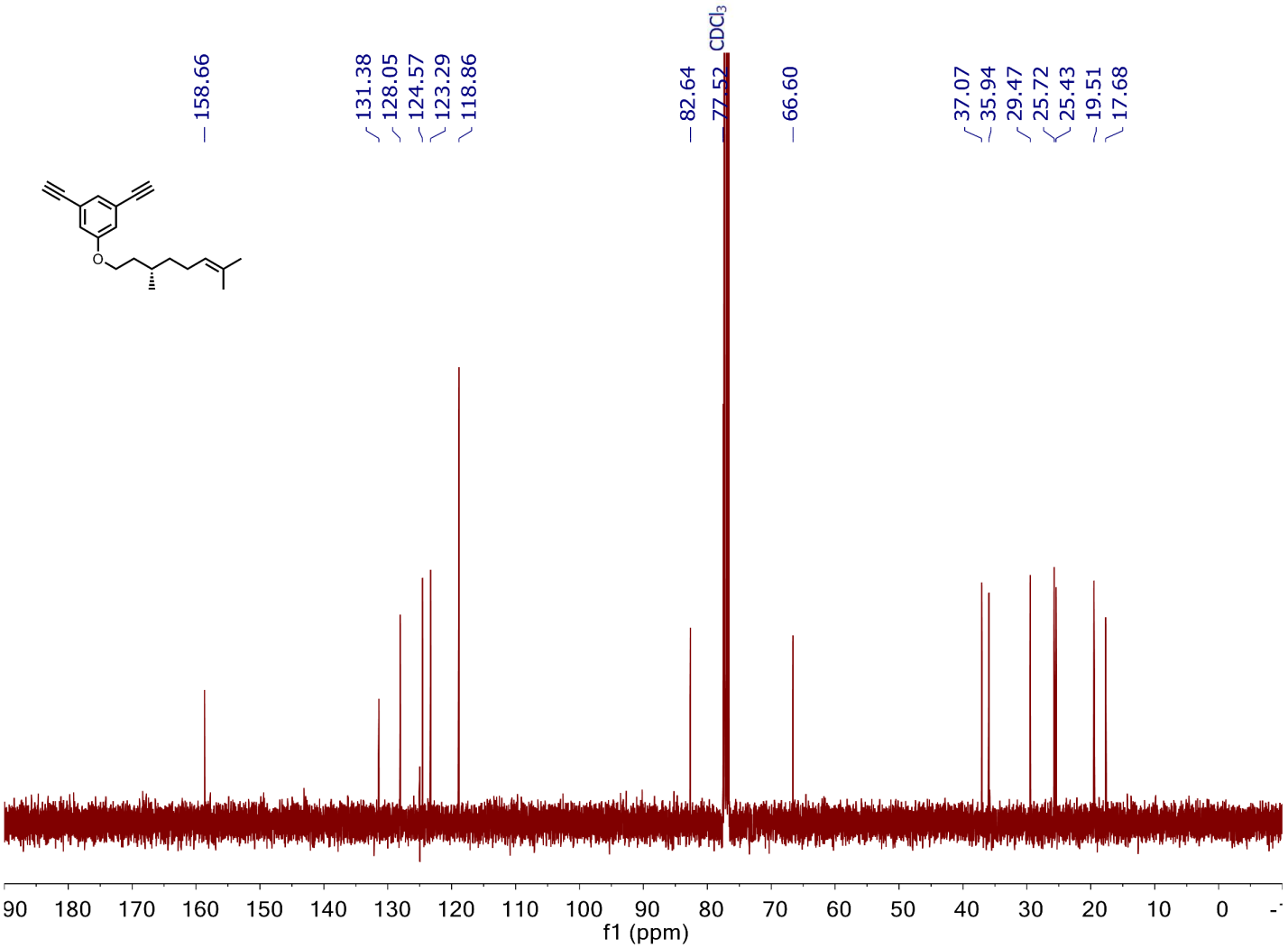
HRMS (ES+): calcd for $C_{20}H_{25}O$ 281.1905, found 281.1905.

FT-IR (ATR): ν_{max} 3297, 2960, 2925, 1579, 1420, 1321, 1294, 1158 cm^{-1}.

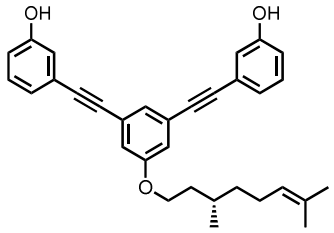
^{1}H NMR (400 MHz, $CDCl_3$) compound 39



^{13}C NMR (100.6 MHz, $CDCl_3$) compound 39



Synthesis of 40.



Compound **39** (0.075 g, 0.27 mmol), 3-iodophenol (0.118 g, 0.54 mmol), $Pd_2(dba)_3$ (5 mg, 0.55 x 10^{-2} mmol), CuI (1 mg, 0.55 x 10^{-2} mmol) and PPh_3 (7 mg, 0.027) were added to a flask with Et_3N (1.5 mL) and DMF (1.5 mL), and N_2 bubbled through the reaction for 15 min. The reaction was stirred at room temperature for 4 h in the dark 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 x 10 mL), 5% LiCl solution (2 x 10 mL) and then dried ($MgSO_4$). The solvent was removed by rotary evaporation under reduced pressure and the residue was purified by flash chromatography on silica (40-60 pet. ether/EtOAc 4:1) to yield the desired compound **40** as a brown solid (0.110 g, 88%).

Mpt: 65-68 ^{o}C.

$[\alpha]_D$ = -2.519 (*c* 0.68, $CHCl_3$).

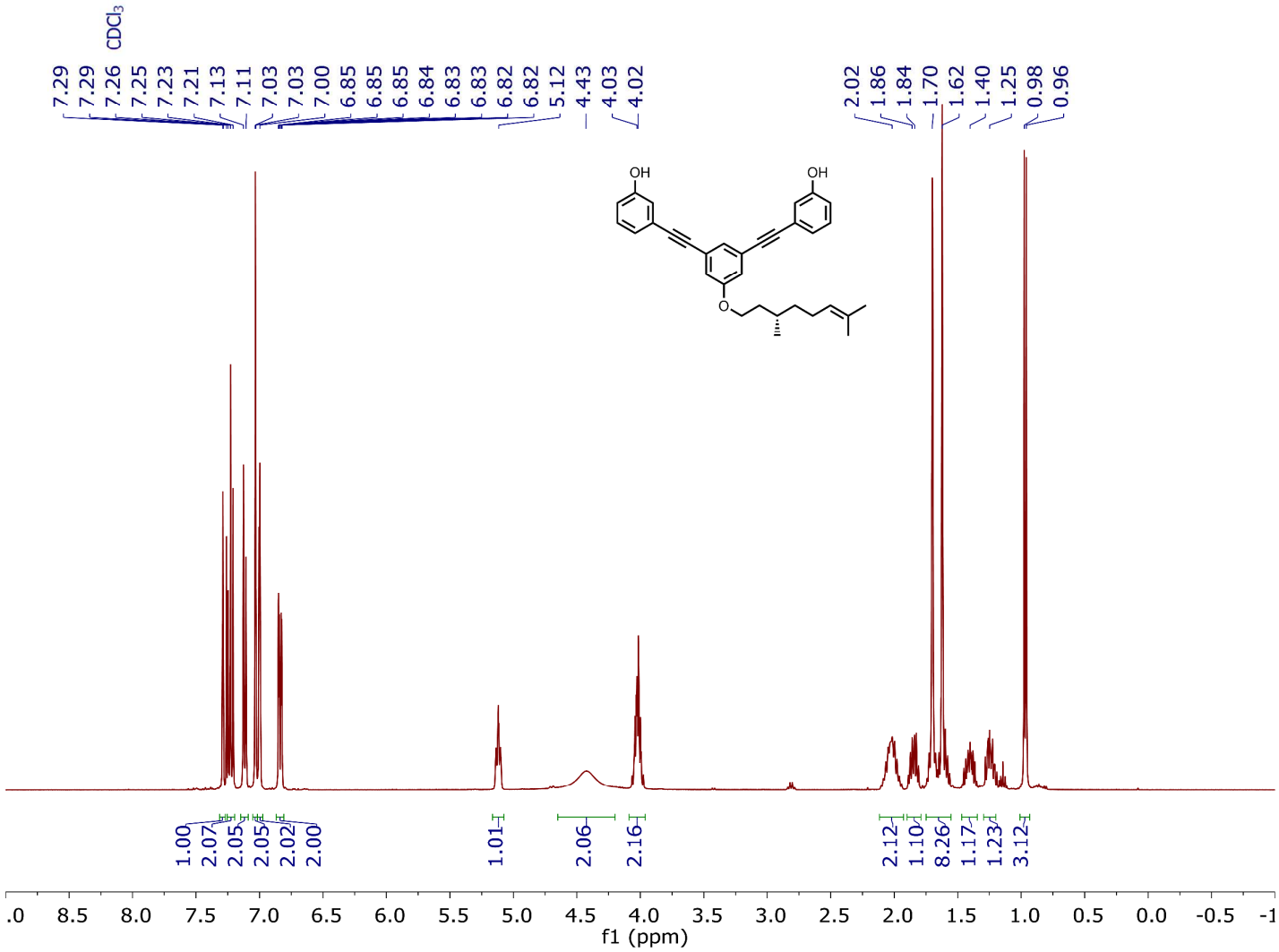
^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 7.28 (t, 1H, *J* = 1.5), 7.22 (t, 2H, *J* = 8.0), 7.07 (m, 2H), 7.05-6.96 (m, 4H), 6.84 (ddd, 2H, *J* = 8.0, 2.5, 1.0), 5.17-5.09 (m, 1H), 5.06 (bs, 2H), 4.07-3.96 (m, 2H), 2.09-1.92 (m, 2H), 1.85-1.76 (m, 1H), 1.70 (s, 3H), 1.60-1.63 (m, 1H), 1.62 (s, 3H), 1.60-1.55 (m, 1H), 1.42-1.33 (m, 1H), 1.28-1.18 (m, 1H), 0.96 (d, 3H, *J* = 6.5).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C = 158.8, 155.3, 131.4, 129.7, 127.3, 124.6, 124.4, 124.3, 124.2, 118.3, 117.9, 116.0, 89.2, 88.6, 66.6, 37.1, 36.0, 29.5, 25.8, 25.5, 19.6.

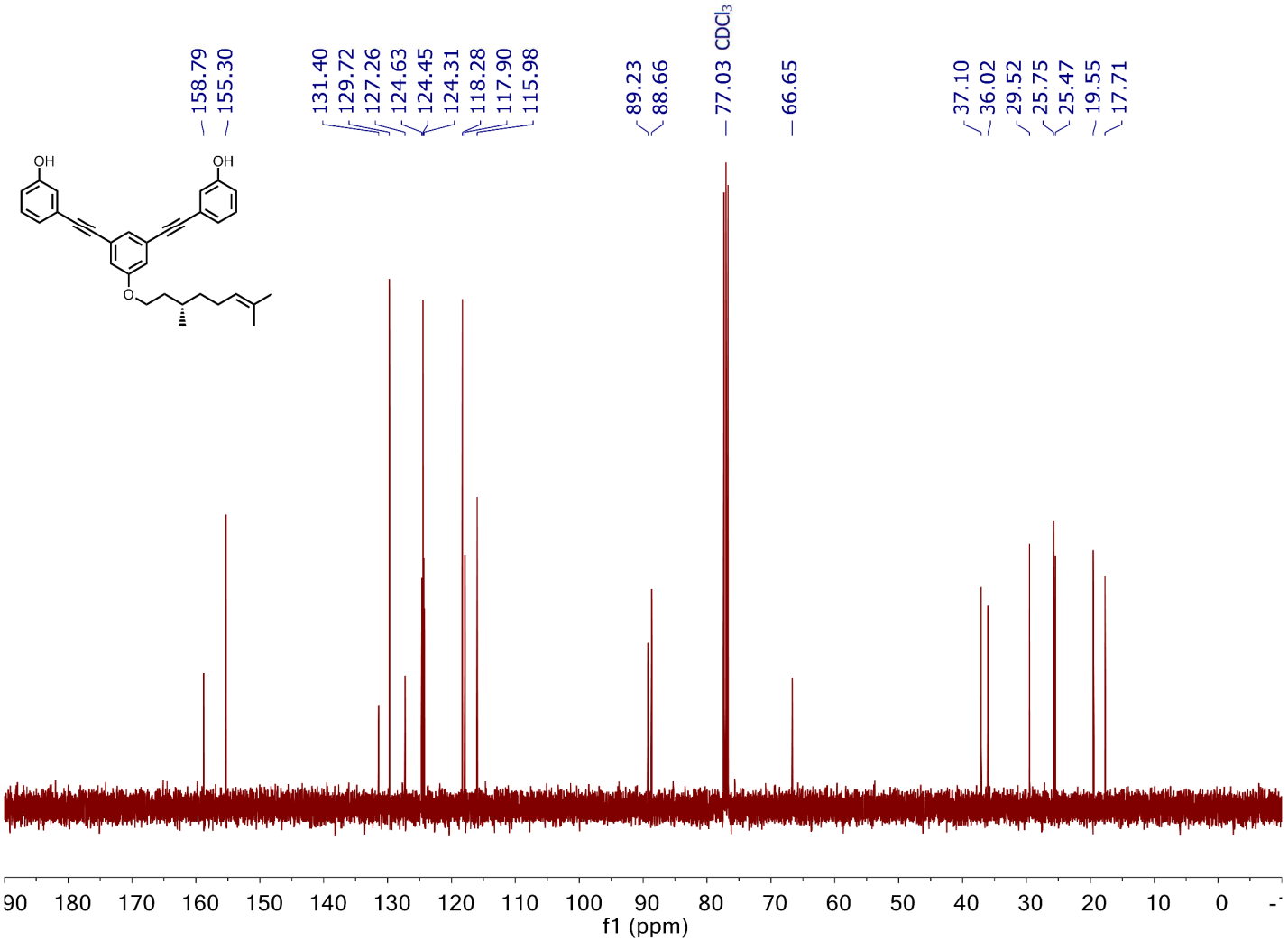
HRMS (ES+): calcd for $C_{32}H_{32}O_3$ 465.2417, found 465.2424.

FT-IR (ATR): ν_{max} 3390 (br), 1577, 1184, 864, 781, 735 cm^{-1}.

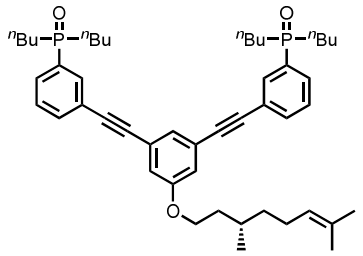
^{1}H NMR (400 MHz, $CDCl_3$) compound 40



^{13}C NMR (100.6 MHz, $CDCl_3$) compound 40



Synthesis of 41.



Compounds **39** (0.080 g, 0.29 mmol), **8** (0.217 g, 0.69 mmol), $Pd_2(dba)_3$ (13 mg, 1.37 x 10^{-2} mmol), CuI (3 mg, 1.37 x 10^{-2} mmol) and PPh_3 (0.018 g, 0.07 mmol) were added to a flask with Et_3N (2 mL) and DMF (2 mL), and N_2 bubbled through the reaction for 15 min. The reaction was heated by microwave irradiation at 95 °C for 10 min. The reaction was filtered through celite and washed through with EtOAc (10 mL). The solution was washed with 1M HCl (3x 10 mL), 5% LiCl solution (2x 10 mL) and then dried ($MgSO_4$). The solvent was removed by rotary evaporation under reduced pressure and the obtained residue was purified by flash chromatography in silica (CH_2Cl_2/MeOH 19:1) to yield the desired compound **41** as a brown oil (0.107 g, 50%).

Mpt: 40-43 °C.

$[\alpha]_D$ = -1.16 (*c* 1.3, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 7.83 (d, 1H, *J* = 11.0), 7.70-7.62 (m, 2H), 7.44 (td, 1H, *J* = 8, 2.5), 7.29 (t, 1H, *J* = 1.5), 7.04 (d, 2H, *J* = 2.5 Hz), 5.11-5.04 (m, 1H), 4.01-3.91 (m, 2H), 2.04-1.73 (m, 7H), 1.71-1.49 (m, 12H), 1.46-1.27 (m, 5H), 0.92 (d, 3H, *J* = 6.5), 0.84 (t, 6H, *J* = 7 Hz).

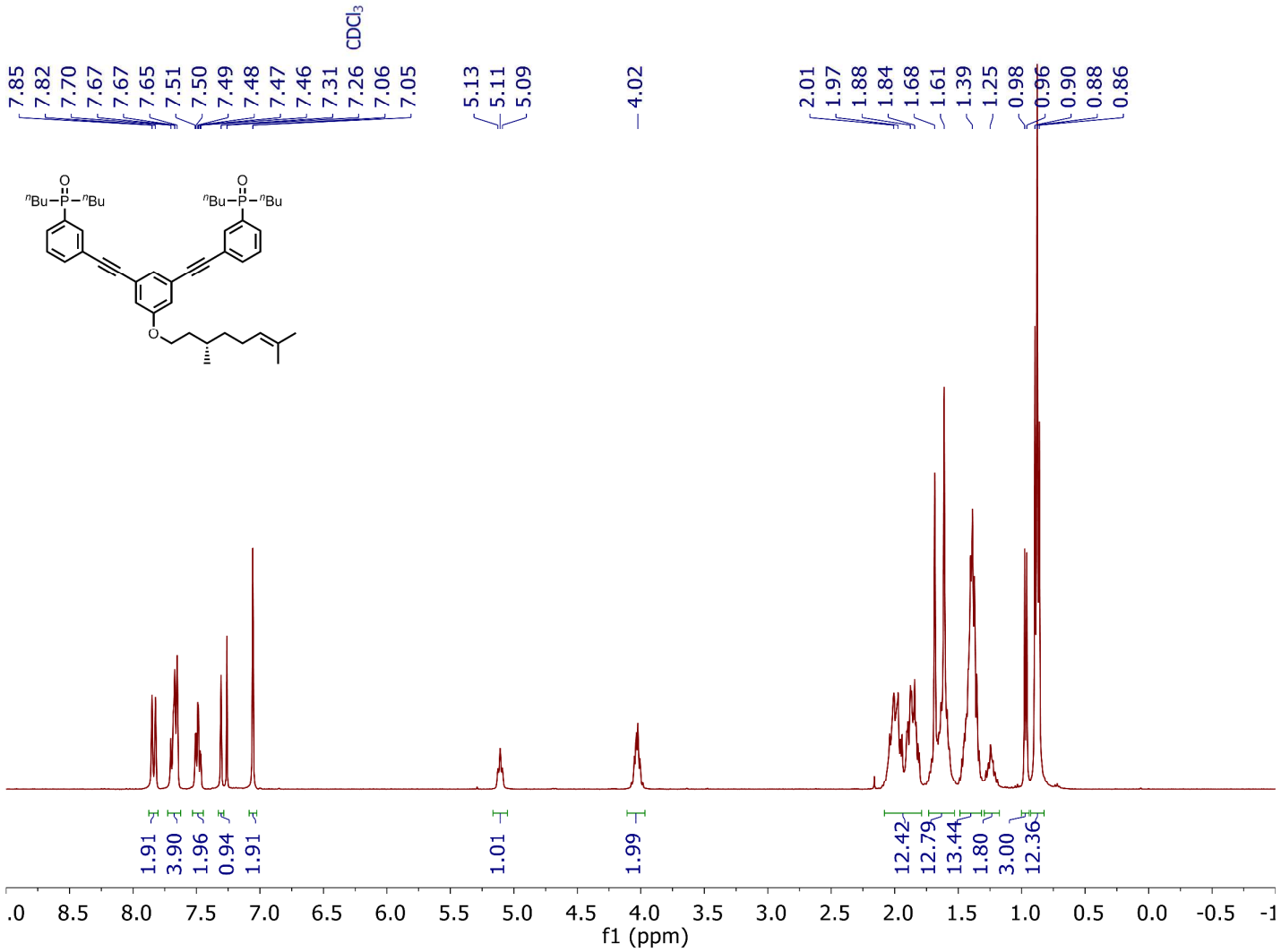
^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C = 158.9, 134.3 (d, *J* = 2.5), 133.8 (d, *J* = 86), 133.5 (d, *J* = 10), 131.3, 130.2 (d, *J* = 6), 128.7 (d, *J* = 10), 127.2, 124.6, 124.1, 118.1, 89.8, 88.7, 66.4, 37.1, 36.1, 29.6 (d, *J* = 69), 29.5, 25.7, 25.4, 24.1 (d, *J* = 15), 23.4 (d, *J* = 2), 19.6, 17.7, 13.5 (d, *J* = 1).

^{31}P NMR (161.3 MHz, $CDCl_3$): δ_P = 35.3.

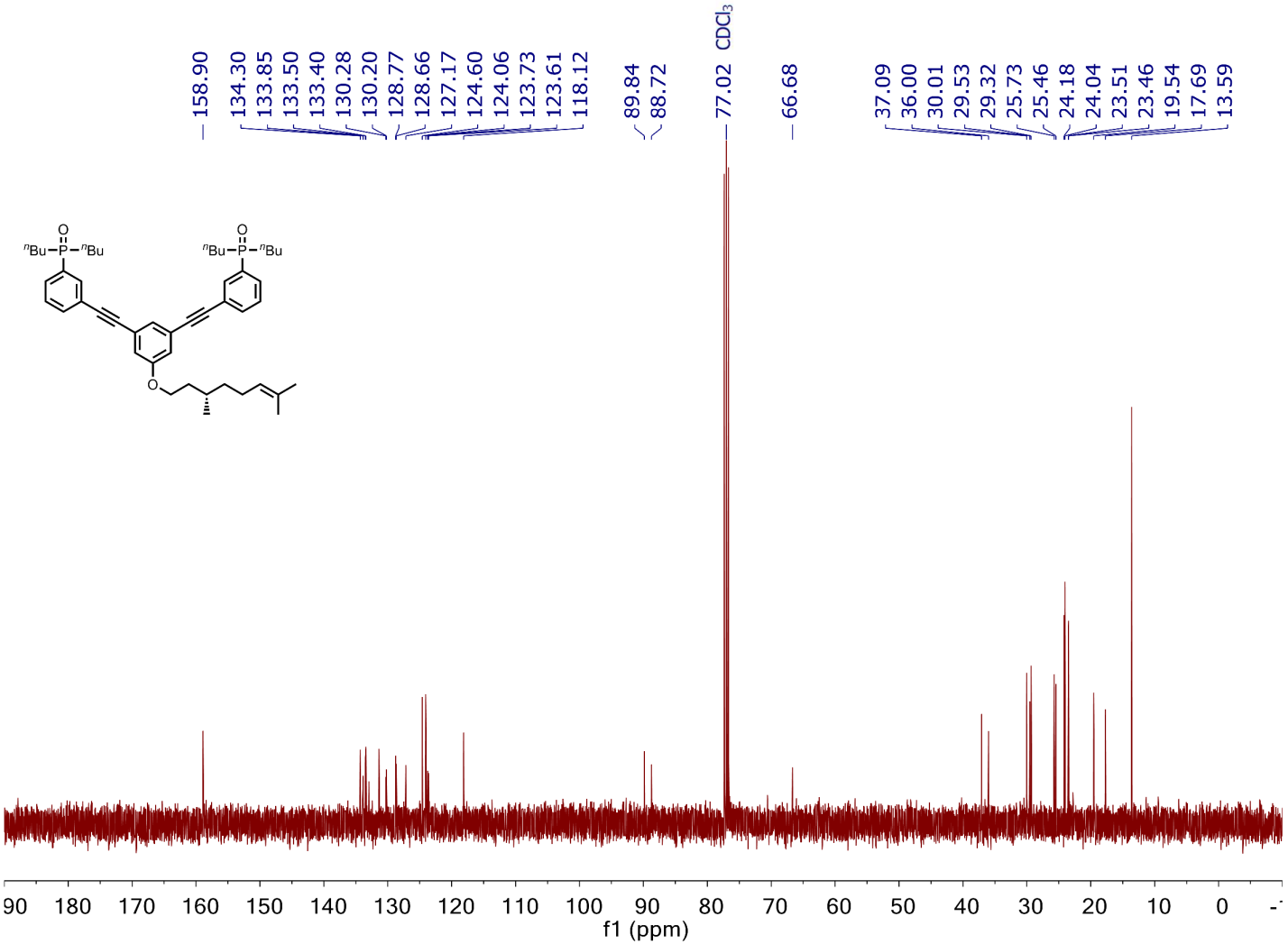
HRMS (ES+): calcd for $C_{24}H_{28}O_2$ 349.2155, found 349.2162.

FT-IR (ATR): ν_{max} 2958, 2929, 1578, 1221, 1170, 1046, 793, 692 cm^{-1}.

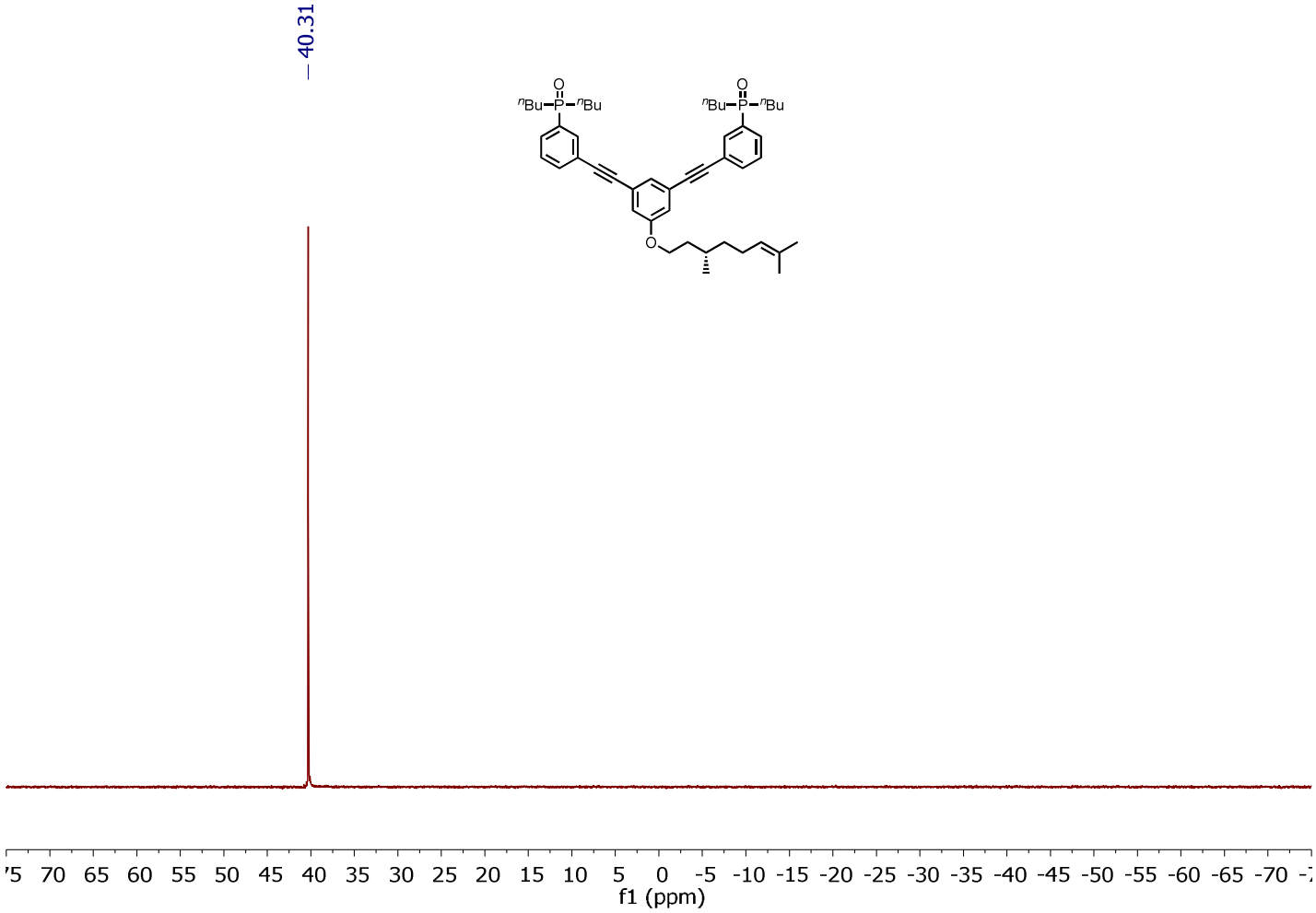
^{1}H NMR (400 MHz, $CDCl_3$) compound 41



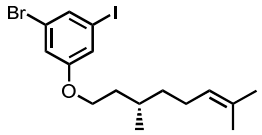
^{13}C NMR (100.6 MHz, $CDCl_3$) compound 41



^{31}P NMR (161.3 MHz, $CDCl_3$) compound 41



Synthesis of 42.



Compound **38** (1.00 g, 2.56 mmol) was dissolved in dry Et_2O (30 mL) in a dried flask. The reaction was cooled to -78 °C. ^{n}BuLi (1.6M in hexanes, 1.76 mL, 2.82 mmol) was added slowly over 1 h, and the reaction was stirred for 1 h at -78 °C. A solution of I_2 (1.30 g, 5.13 mmol) in dry Et_2O (5 mL) was added and reaction stirred at -78 °C for 1 hr before being allowed to warm to room temperature over 1 h. Saturated aqueous $Na_2S_2O_3$ solution (30 mL) was added and reaction stirred until colourless. The organic phase was separated and washed with water (2 x 30 mL), brine (30 mL) and then dried ($MgSO_4$). The solvent was removed by rotary evaporation under reduced pressure and the obtained oil was purified by flash chromatography on silica (40-60 pet. ether) to yield the desired compound **42** as a light yellow oil (0.972 g, 87%).

$[\alpha]_D^{20}$ = -3.72 (*c* 1.26, $CHCl_3$).

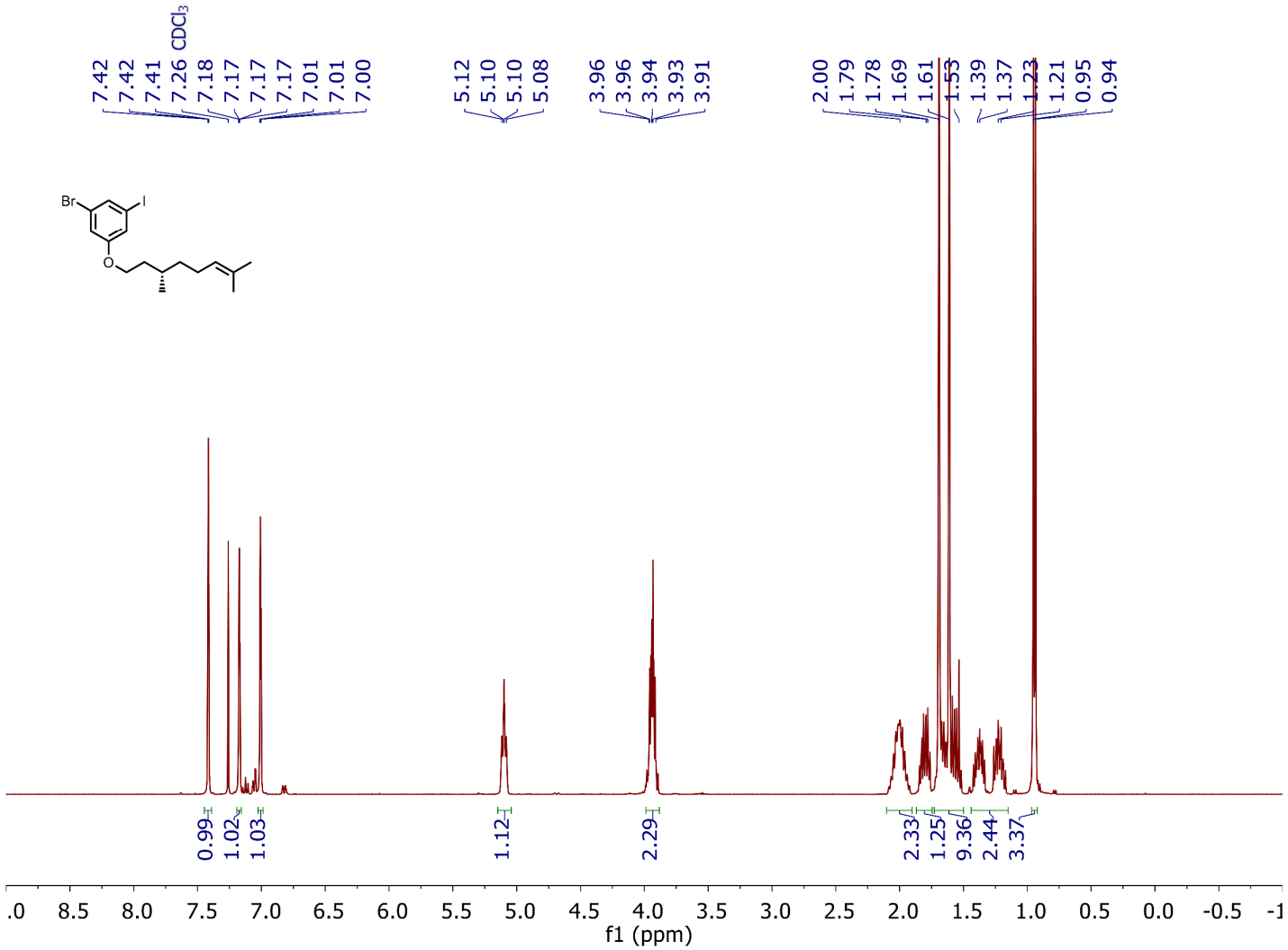
^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 7.42 (dd, 1H, *J* = 1.5, 1.5), 7.17 (dd, 1H, *J* = 2.0, 1.5), 7.01 (dd, 1H, *J* = 2.0, 1.5), 5.15-5.04 (m, 1H), 3.99-3.88 (m, 2H), 2.10-1.90 (m, 2H), 1.87-1.75 (m, 1H), 1.69 (s, 3H), 1.68-1.63 (m, 1H), 1.61 (s, 3H), 1.60-1.55 (m, 1H), 1.42-1.33 (m, 1H), 1.28-1.18 (m, 1H), 0.95 (d, 3H, *J* = 6.5), 0.24 (s, 9H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C = 160.1, 131.8, 131.4, 124.5, 123.1, 122.8, 117.6, 94.2, 66.9, 37.0, 35.9, 29.4, 25.8, 25.4, 19.5, 17.7.

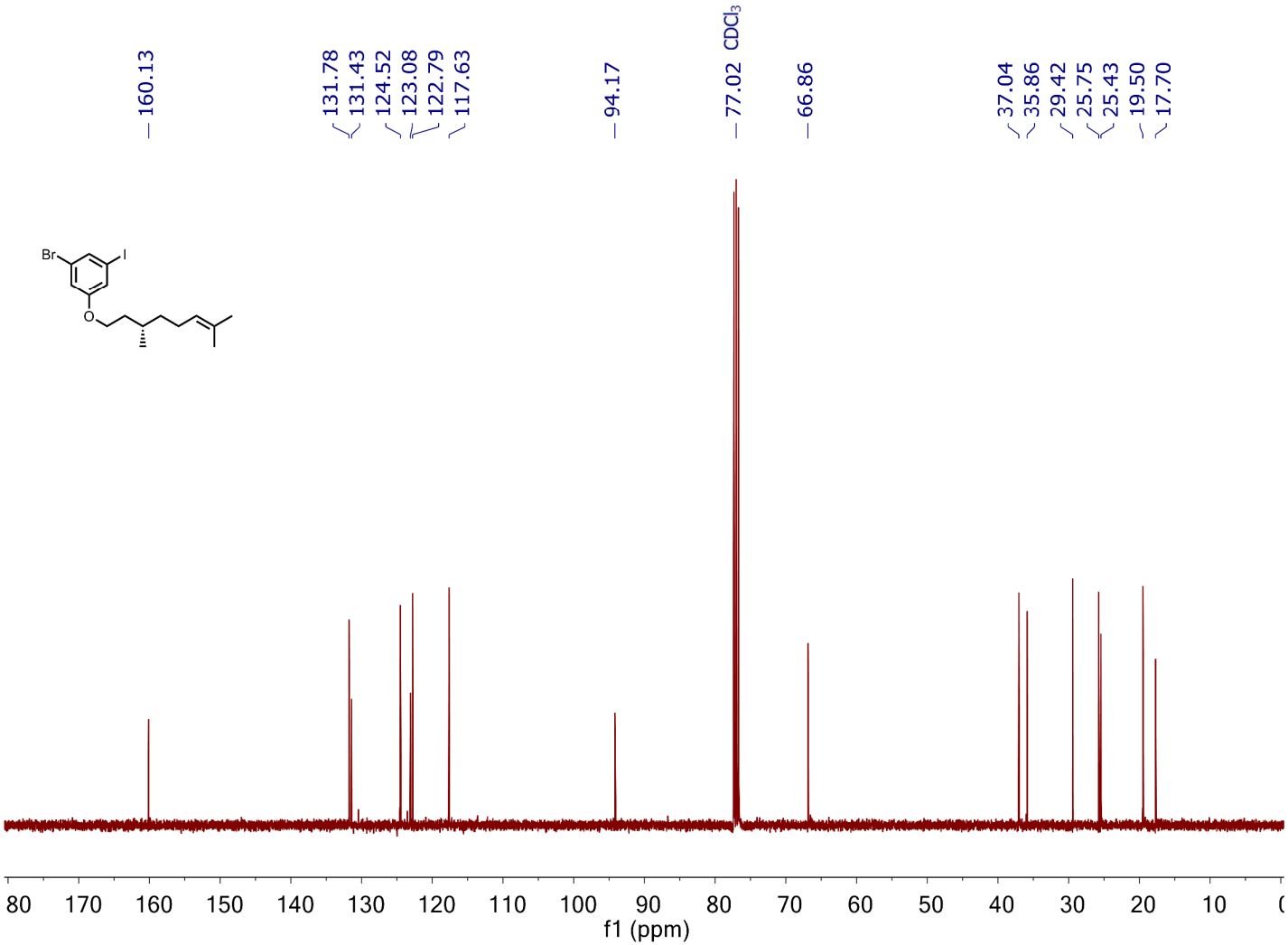
HRMS (ES+): calcd for $C_{16}H_{22}{}^{79}BrIO$ 436.9977, found 436.9971.

FT-IR (ATR): ν_{max} 2962, 2914, 1577, 1550, 1433, 1228, 829 cm^{-1}.

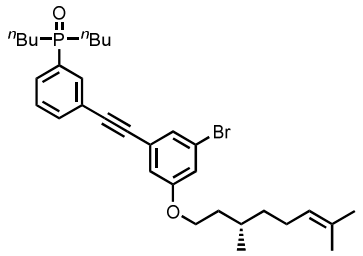
^{1}H NMR (400 MHz, $CDCl_3$) compound 42



^{13}C NMR (100.6 MHz, $CDCl_3$) compound 42



Synthesis of 43.



Compounds **36** (0.226 g, 0.86 mmol), **42** (0.343 g, 0.78 mmol), $Pd_2(dba)_3$ (15 mg, 1.6 x10^{-2} mmol), CuI (3 mg, 1.6 x10^{-2} mmol) and PPh_3 (21 mg, 0.079 mmol) were added to a flask under N_2. Et_3N (5 mL) and DMF (5 mL) were added and the reaction purged with N_2 for 20 minutes, then stirred at room temperature overnight in the dark. The reaction was washed through celite with EtOAc (30 mL), and washed with 1M HCl (3 x 30 mL), 5% LiCl solution (2x 30 mL) and then dried ($MgSO_4$). The solvent was removed by rotary evaporation under reduced pressure and the obtained oil was purifed by flash chromatography in silica (CH_2Cl_2/MeOH 19:1) to yield the desired compound **43** as a light brown oil (0.420 mg, 94%).

$[\alpha]_D^{20}$ = -3.31 (*c* 0.90, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 7.82 (dt, 1H, *J* = 11.0, 1.5), 7.68 (ddt, 1H, *J* = 10.5, 7.5, 1.5), 7.65 (dd, 1H, *J* = 8.0, 1.5), 7.49 (td, 1H, *J* = 8.0, 2.5), 7.26 (t, 1H, *J* = 1.5), 7.05 (t, 1H, *J* = 1.5 Hz), 6.98 (d, 1H, *J* = 1.5), 5.13-5.06 (m, 1H), 4.03-3.95 (m, 2H), 2.08-1.89 (m, 4H), 1.91-1.77 (m, 3H), 1.70-1.44 (m, 10H), 1.47-1.34 (m, 7H), 1.32-1.20 (m, 1H), 0.95 (d, 3H, *J* = 6.5), 0.88 (t, 6H, *J* = 7.0).

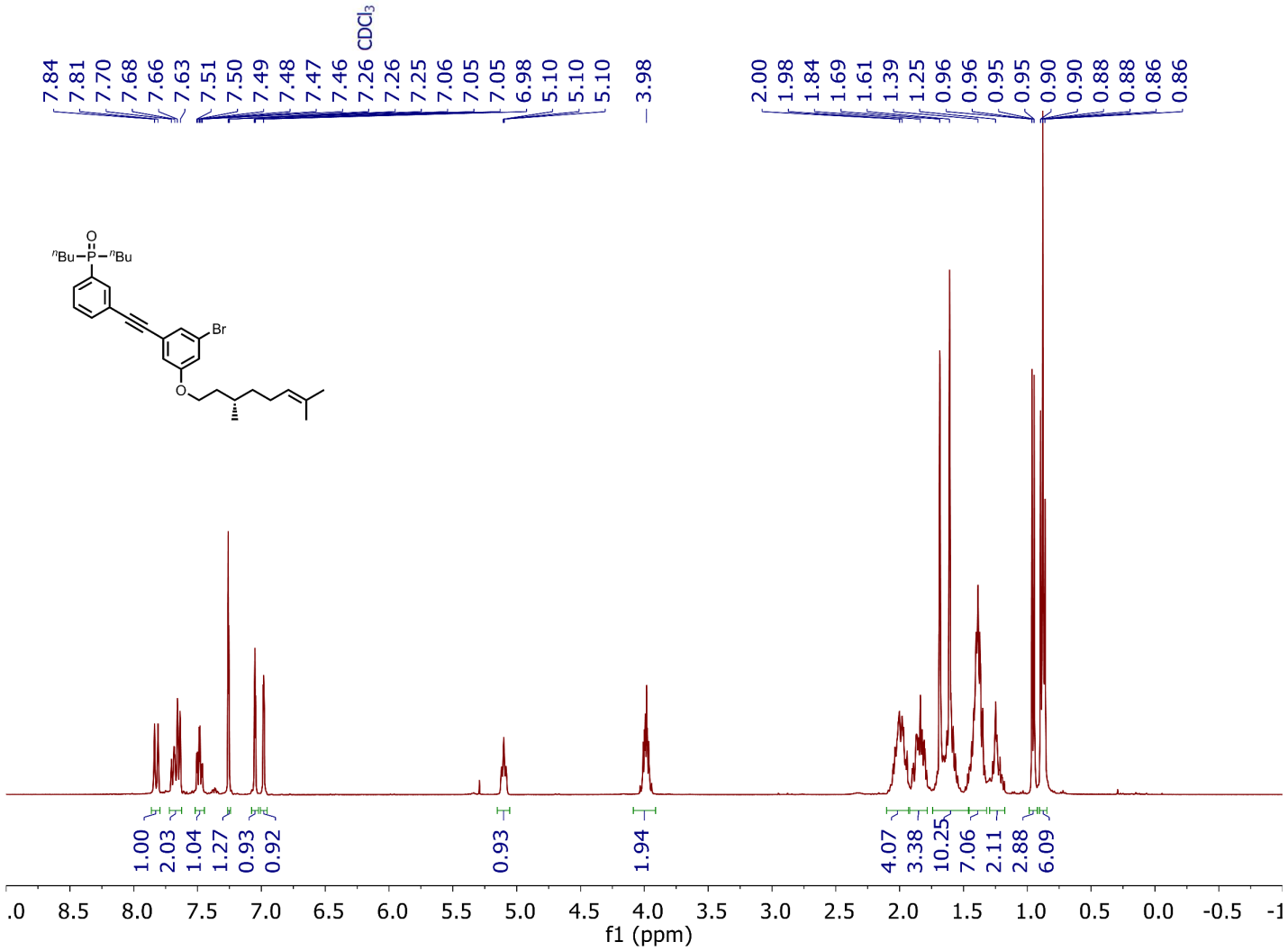
^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C = 159.6, 134.3 (d, *J* = 3), 133.5 (d, *J* = 9), 133.4 (d, 91), 131.4, 130.4 (d, *J* = 8), 128.7 (d, *J* = 11), 126.6, 125.1, 124.6, 123.5 (d, *J* = 12), 122.6, 118.9, 116.2, 89.2, 89.2, 66.8, 37.1, 35.9, 29.6 (d, *J* = 69), 29.5, 25.7, 25.4, 24.1 (d, *J* = 14), 23.5 (d, *J* = 4), 19.5, 17.7, 13.6.

^{31}P NMR (161.3 MHz, $CDCl_3$): δ_P = 40.4.

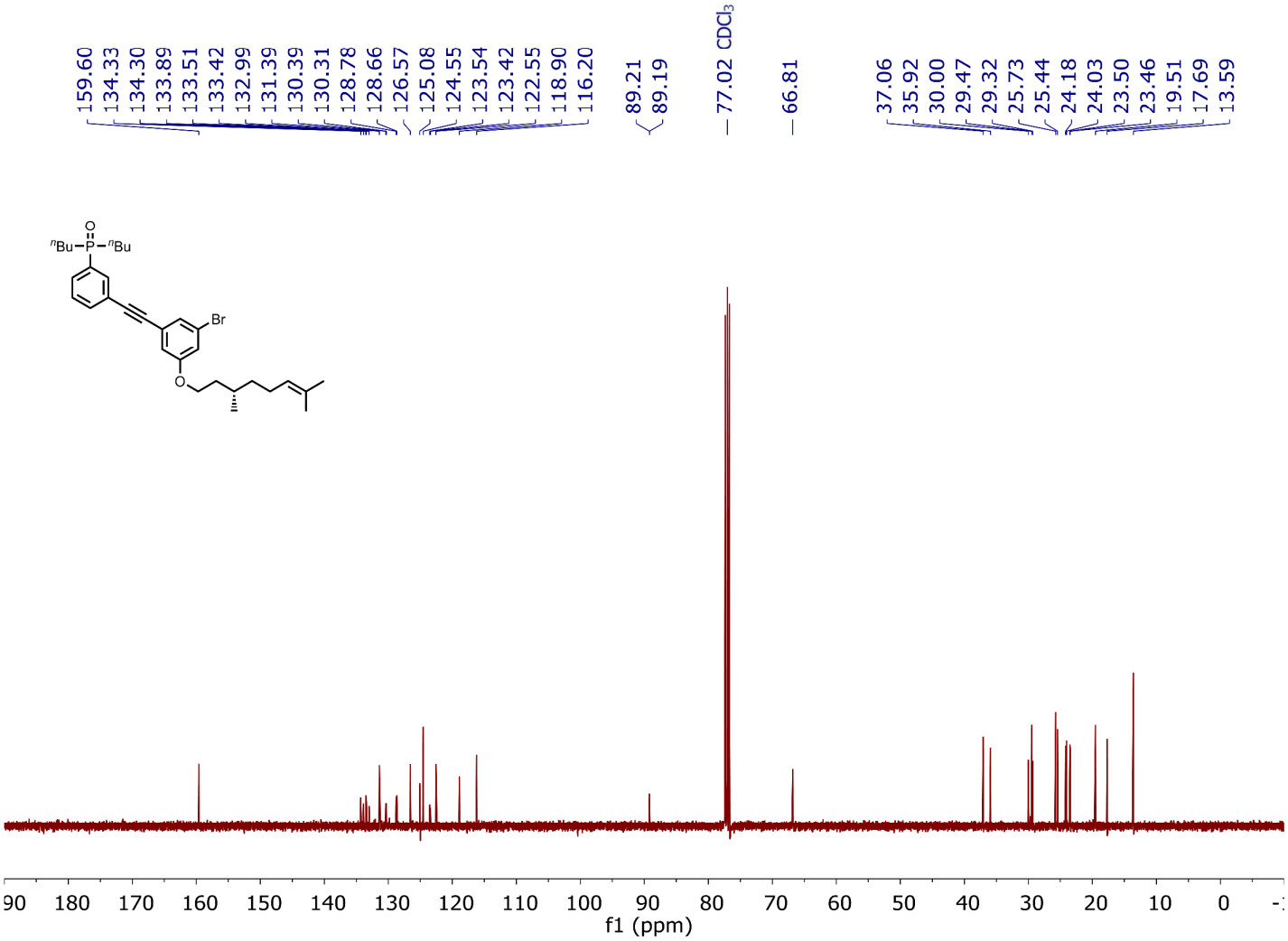
HRMS (ES+): calcd for $C_{32}H_{45}O_2{}^{79}BrP$ 571.2341, found 571.2331.

FT-IR (ATR): ν_{max} 2957, 2929, 2110, 1593, 1558, 1424, 1173, 796 cm^{-1}.

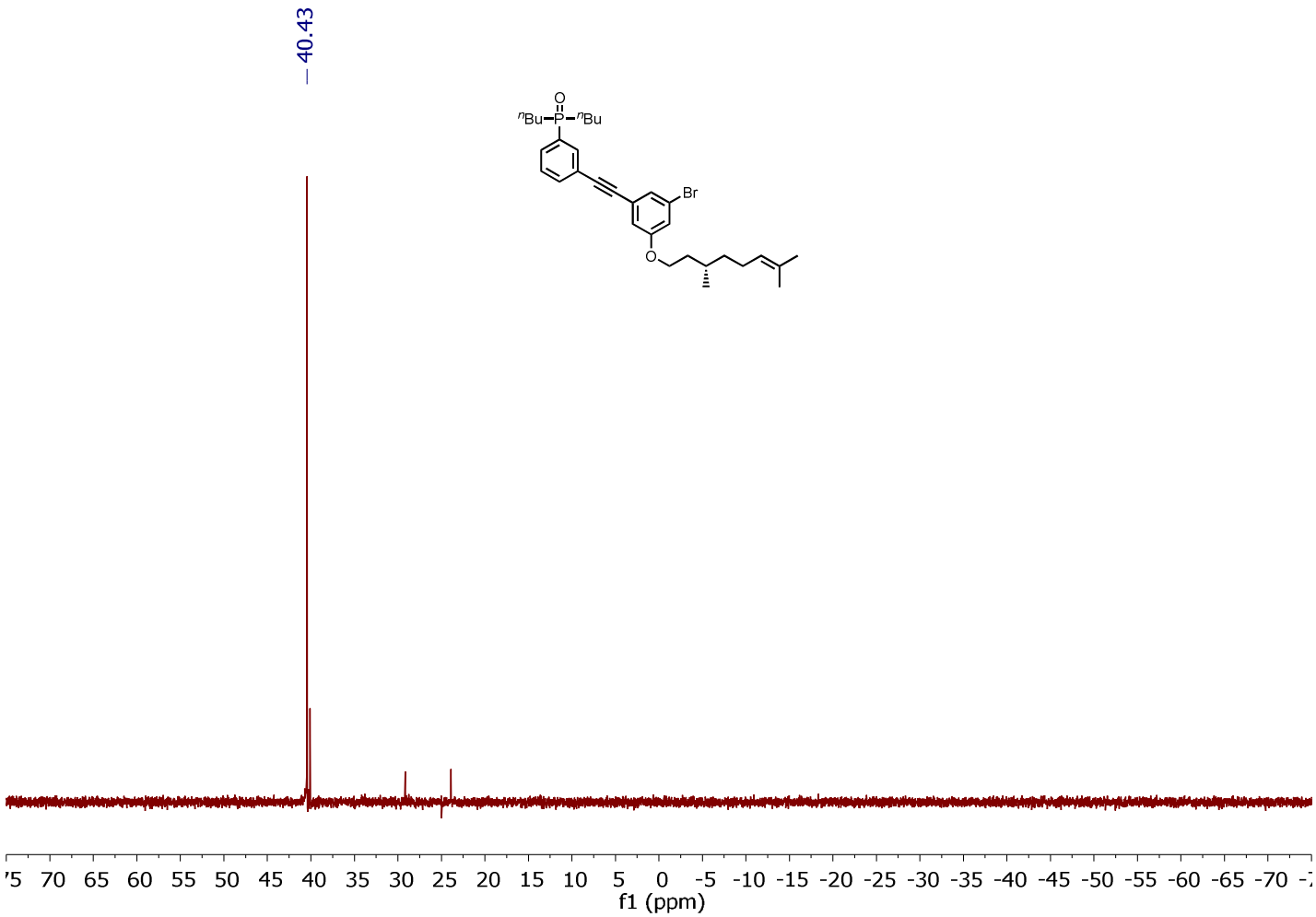
^{1}H NMR (400 MHz, $CDCl_3$) compound 43



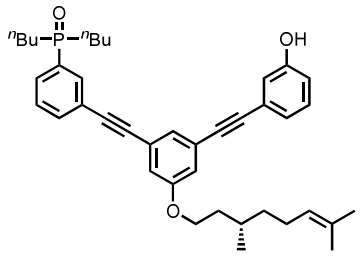
^{13}C NMR (100.6 MHz, $CDCl_3$) compound 43



^{31}P NMR (161.3 MHz, $CDCl_3$) compound 43



Synthesis of 44.



43 (0.390 g, 0.68 mmol), 3-hydroxyphenylacetylene (0.373 mL, 3.41 mmol), $Pd_2(dba)_3$ (13 mg, 1.4 x10^{-2} mmol), CuI (2.7 mg, 1.4 x10^{-2} mmol), and PPh_3 (19 mg, 7.1 x10^{-2} mmol) were placed in a flask under N_2. Degassed DMF (5 mL) and Et_3N (5 mL) were added and reaction stirred overnight at 50 °C in the dark. The reaction was washed through celite with EtOAc (30 mL), washed with 1M HCl (3x 30 mL) and then dried ($MgSO_4$). The solvent was removed by rotary evaporation under reduced pressure and the obtained residue was purified by flash chromatography (CH_2Cl_2/MeOH 19:1) to yield the desired compound **44** as a brown oil (0.149 g, 36%).

$[\alpha]_D^{20}$ = -3.94 (*c* 1.10, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 8.72 (bs, 1H), 7.83 (dt, 1H, *J* = 11.5, 1.5), 7.75-7.63 (m, 2H), 7.50 (td, 1H *J* = 7.5, 2.5), 7.25 (t, 1H, *J* = 1.5), 7.19 (t, 1H, *J* = 8.0), 7.13 (dd, 1H, *J* = 2.5, 1.5), 7.04 (dt,1H, *J* = 7.5, 1.0), 7.01 (qd,2H, *J* = 2.5, 1.5), 6.93 (ddd,1H, *J* = 8.0, 2.5, 1.0), 5.14-5.07 (m, 1H), 4.05-3.95 (m, 2H), 2.10-1.77 (m, 7H), 1.73-1.54 (m, 8H), 1.50-1.33 (m, 6H), 1.28-1.16 (m, 1H), 0.96 (d, 3H, *J* = 6.5), 0.87 (t, 6H, *J* = 7.0 z).

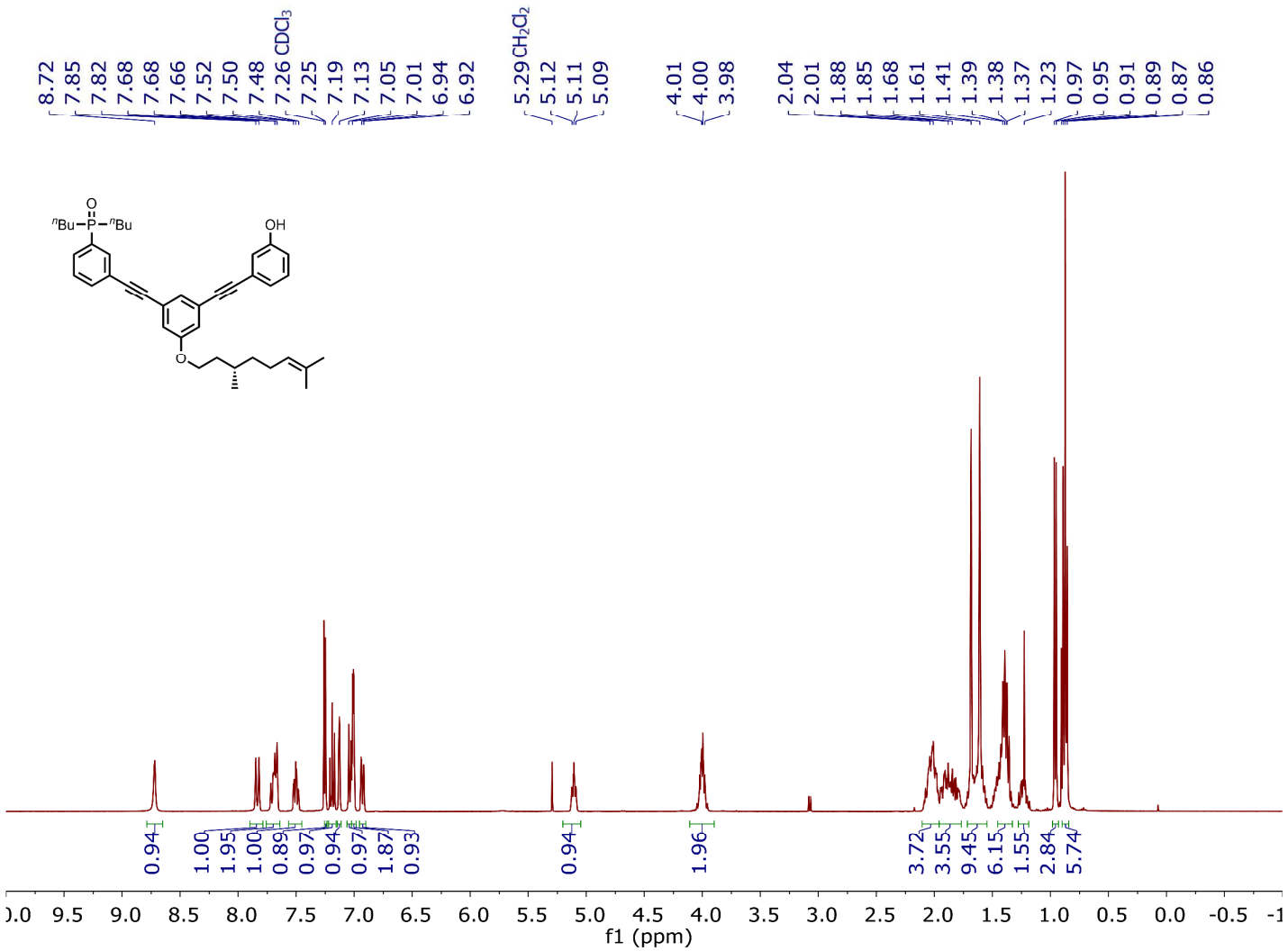
^{13}C NMR (101 MHz, $CDCl_3$): δ_C = 158.8, 157.1, 134.6 (d, *J* = 2), 133.3 (d, *J* = 10), 133.0 (d, *J* = 2), 131.4, 130.1 (d, *J* = 8), 129.5, 128.9 (d, *J* = 11), 127.3, 124.7, 124.6, 124.1, 124.0, 123.7 (d, *J* = 3), 123.1, 118.7, 118.1, 117.6, 116.5, 90.3, 90.1, 88.3, 87.9, 66.6, 37.1, 36.0, 29.5, 27.5 (d, *J* = 51), 25.7, 25.5, 24.1 (d, *J* = 15), 23.4 (d, *J* = 4), 19.5, 17.7, 13.6.

^{31}P NMR (161.3 MHz, $CDCl_3$): δ_P = 43.3.

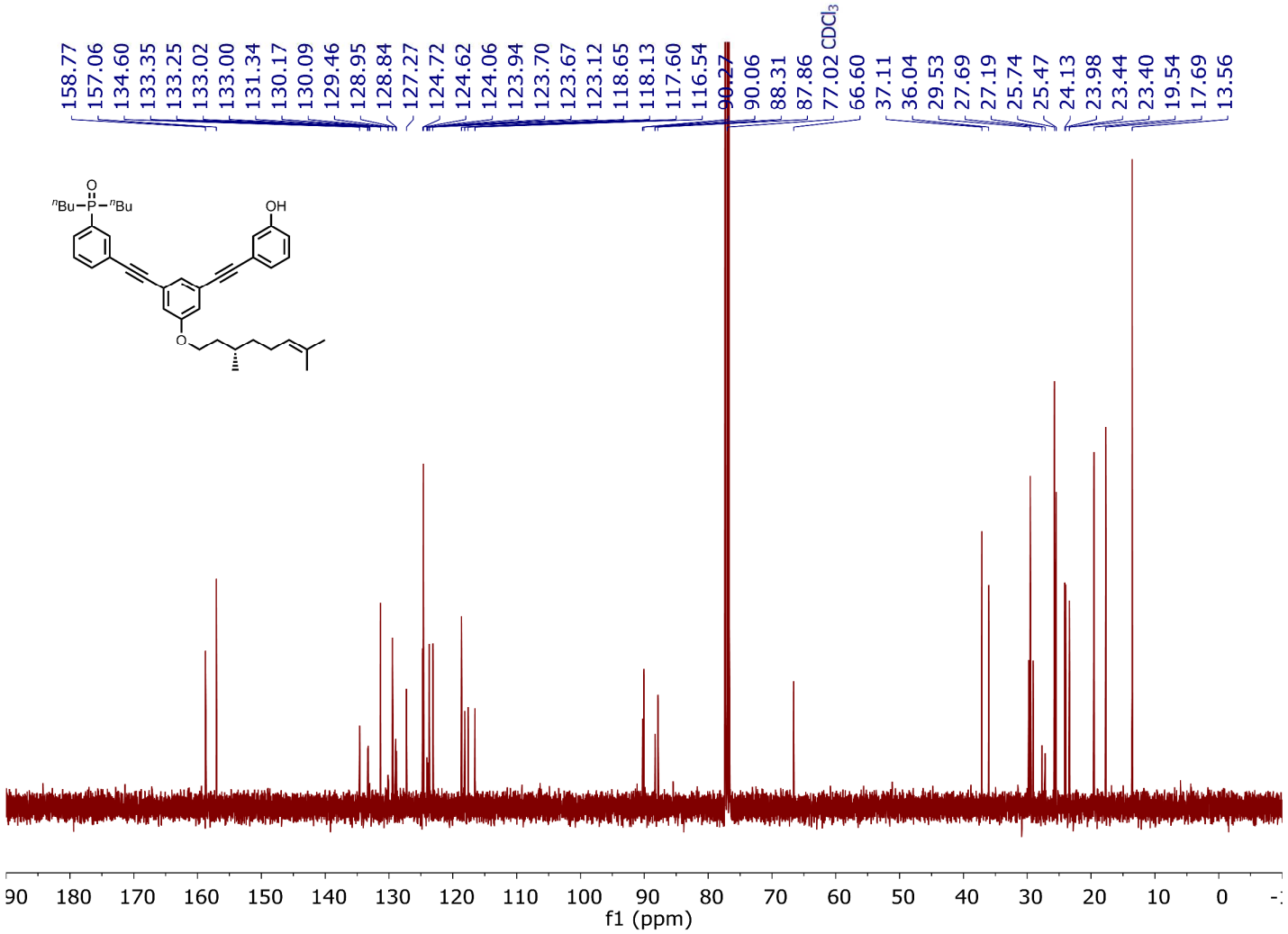
FT-IR (ATR): ν_{max} 2958, 2929, 2215, 1577, 1449, 1195, 1156 cm^{-1}.

HRMS (ES+): calcd for $C_{40}H_{50}O_3P$ 609.3498, found 609.3492.

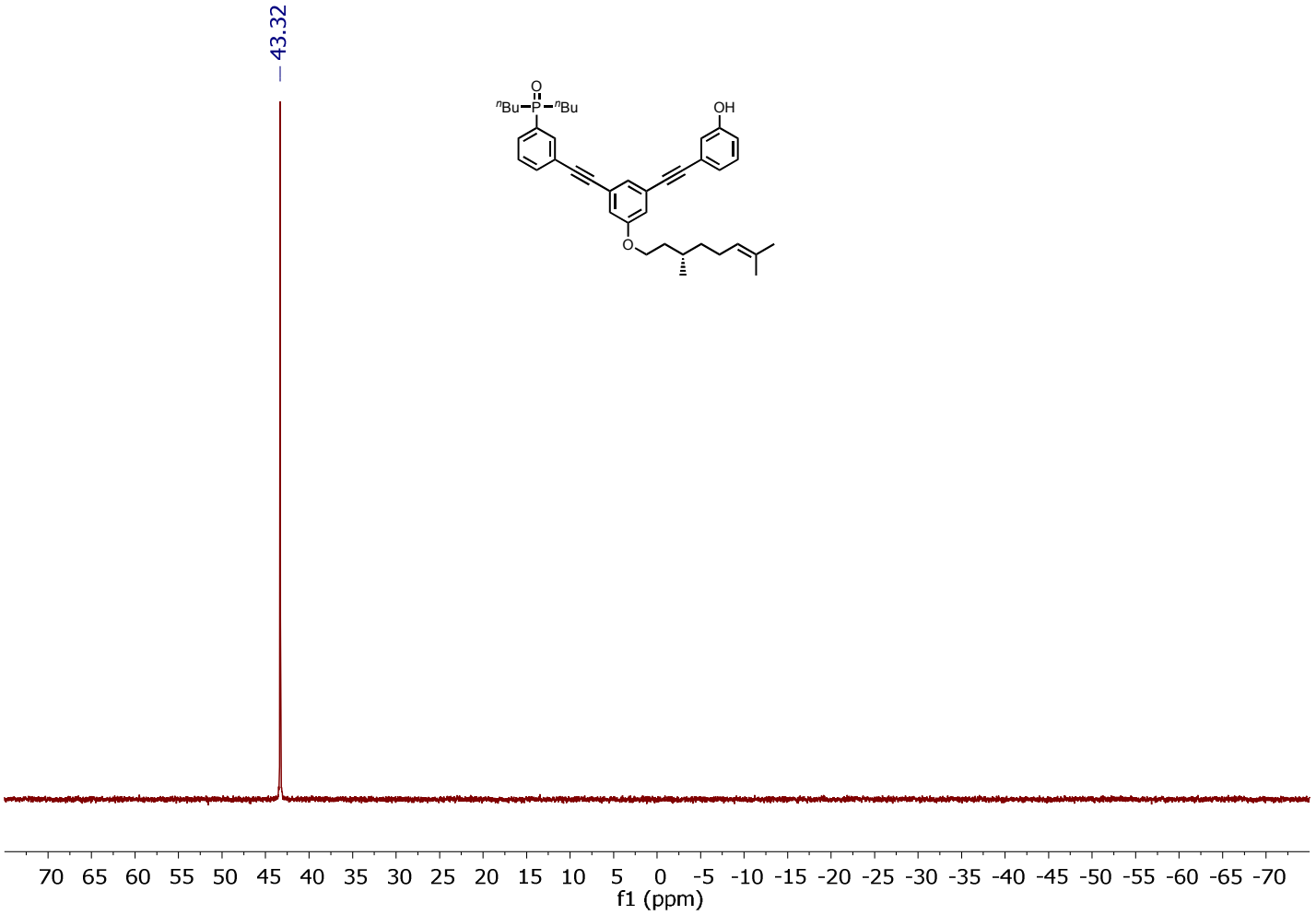
^{1}H NMR (400 MHz, $CDCl_3$) compound 44



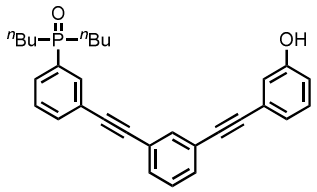
^{13}C NMR (100.6 MHz, $CDCl_3$) compound 44



^{31}P NMR (161.3 MHz, $CDCl_3$) compound 44



Synthesis of 47.



3-Hydroxyphenylacetylene (0.052 g, 0.44 mmol), 1,3-diiodobenzene (0.145 g, 0.44 mmol), compound **36** (0.115 g, 0.44 mmol), $Pd_2(dba)_3$ (8 mg, 8.8 x 10^{-3} mmol), CuI (2 mg, 8.8 x 10^{-3} mmol) and PPh_3 (12 mg, 4.4 x10^{-2} mmol) were added to a flask under N_2. Degassed Et_3N (2.2 mL) and DMF (2.2 mL) were added and the reaction stirred at room temperature overnight in the dark. The reaction was washed through celite with EtOAc (20 mL), washed with 1M HCl (3 x 20 mL), 5% LiCl solution (2 x 30 mL) and then dried ($MgSO_4$). The solvent was removed under reduced pressure and the obtained solid was purified by flash chromatography (CH_2Cl_2/MeOH 19:1) to yield the desired compound **47** as a yellow crystalline solid (0.069 g, 35%).

Mpt: 146-149 ^oC ($CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 8.40 (bs, 1H), 7.85 (d, 1H, *J* = 11.0), 7.74-7.60 (m, 3H), 7.57-7.40 (m, 3H), 7.31 (t, 1H, *J* = 8.0), 7.19 (t, , 1H *J* = 8.0 Hz), 7.12 (d, 1H, *J* = 1.0), 7.05 (d, 1H, *J* = 7.6), 6.92 (dd, 1H, *J* = 8.0, 1.5), 2.10-1.97 (m, 2H), 1.96-1.85 (m, 2H), 1.70-1.56 (m, 2H), 1.50-1.34 (m, 6H), 0.87 (t, 6H, *J* = 7.0 Hz).

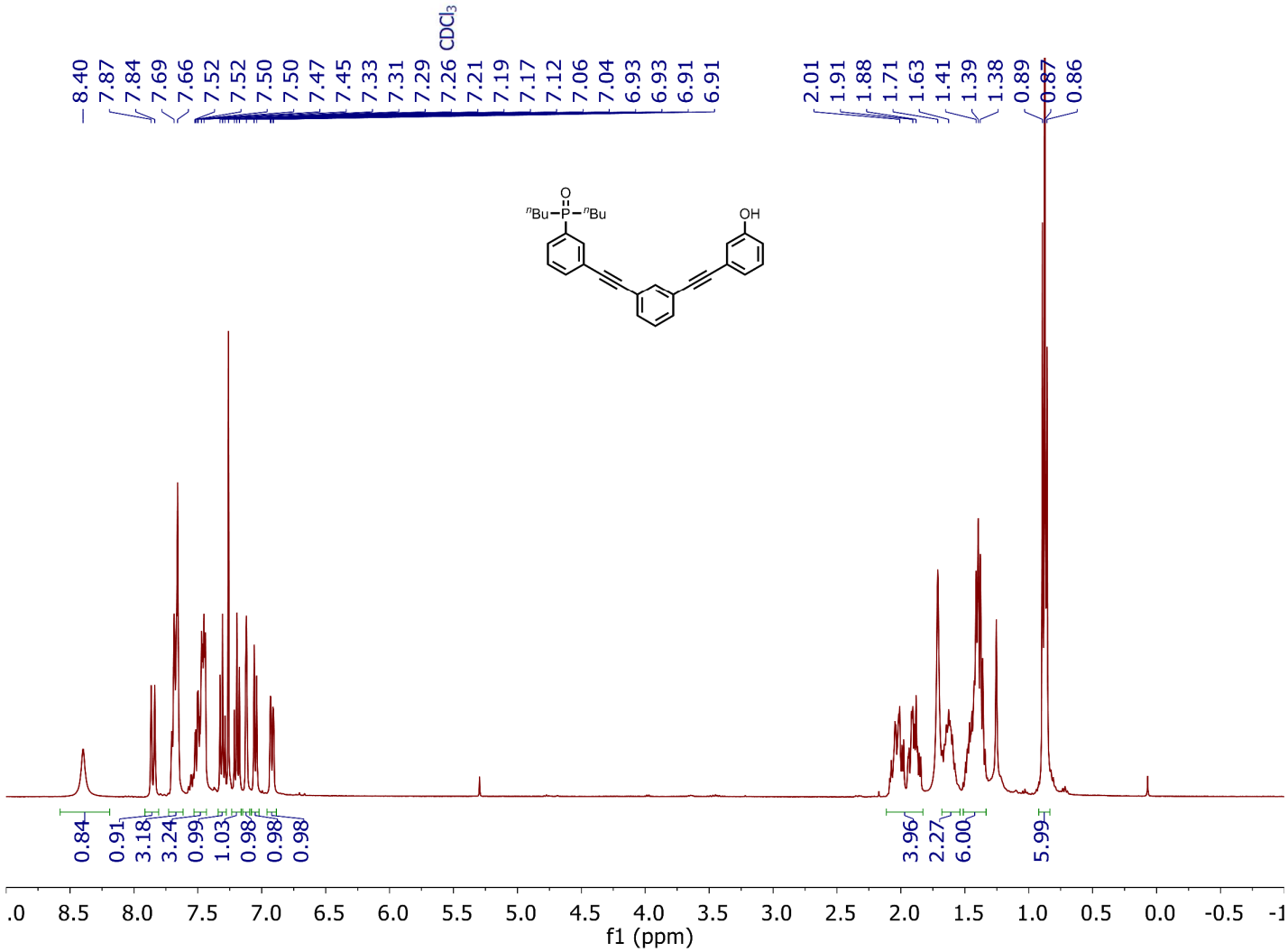
^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C = 156.9, 134.7, 134.6 (d, *J* = 3), 133.4 (d, *J* = 10), 133.1, 132.2 (d, *J* = 4), 132.1, 132.1, 132.1, 131.4 (d, *J* = 52), 130.1, 130.0, 129.5, 128.9 (d, *J* = 12), 128.6 (d, *J* = 17), 123.2, 122.9, 118.6, 116.5, 90.4, 90.1, 88.7, 87.8, 29.4 (d, *J* = 70), 24.1 (d, *J* = 15), 23.4 (d, *J* = 4), 13.6.

^{31}P NMR (161.3 MHz, $CDCl_3$): δ_P = 43.3.

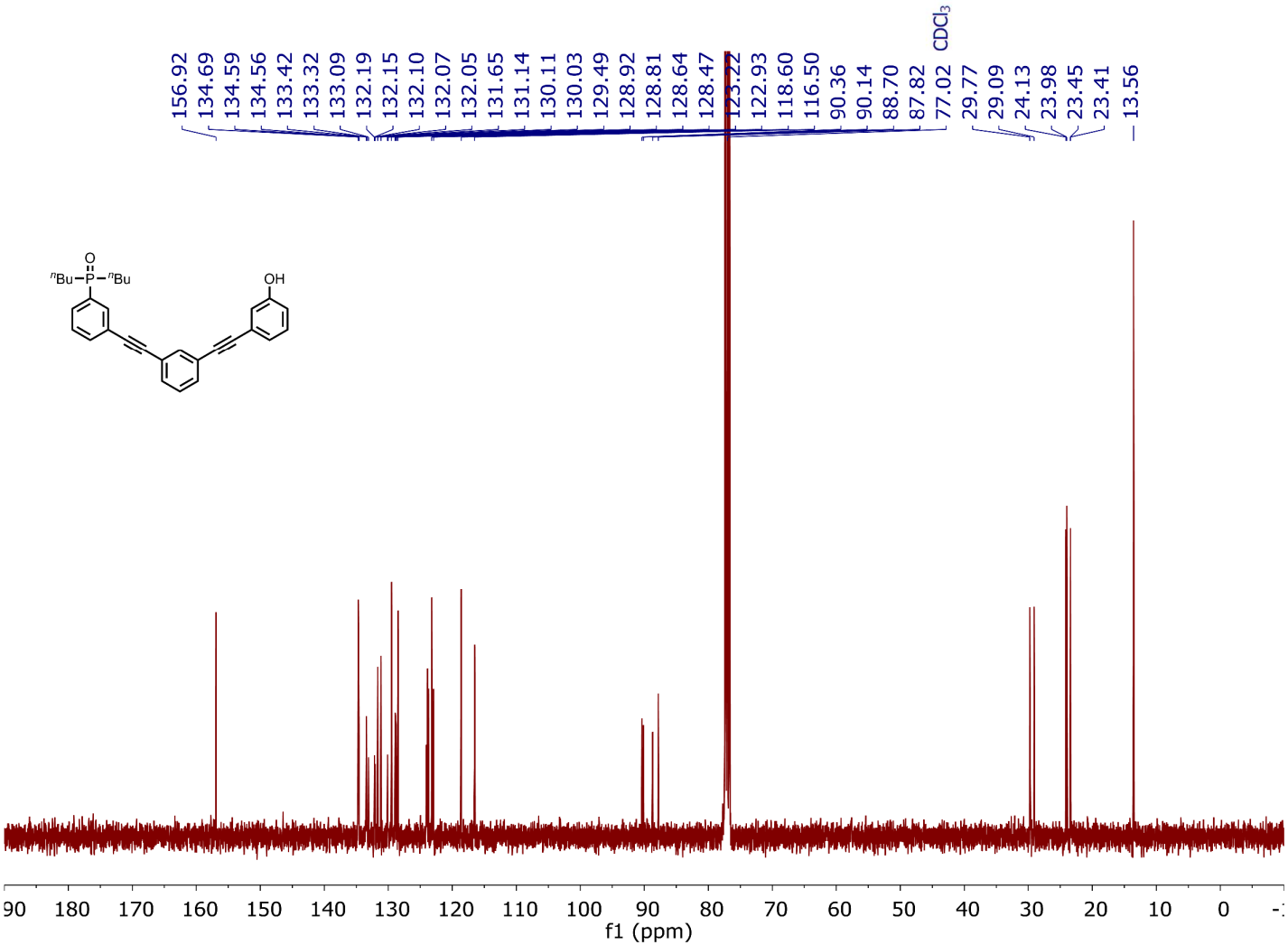
HRMS (ES+): calcd for $C_{30}H_{32}O_2P$ 455.2140, found 455.2144.

FT-IR (ATR): ν_{max} 3073 (br), 2957, 2930, 2217, 1593, 1144, 791, 731, 687 cm^{-1}.

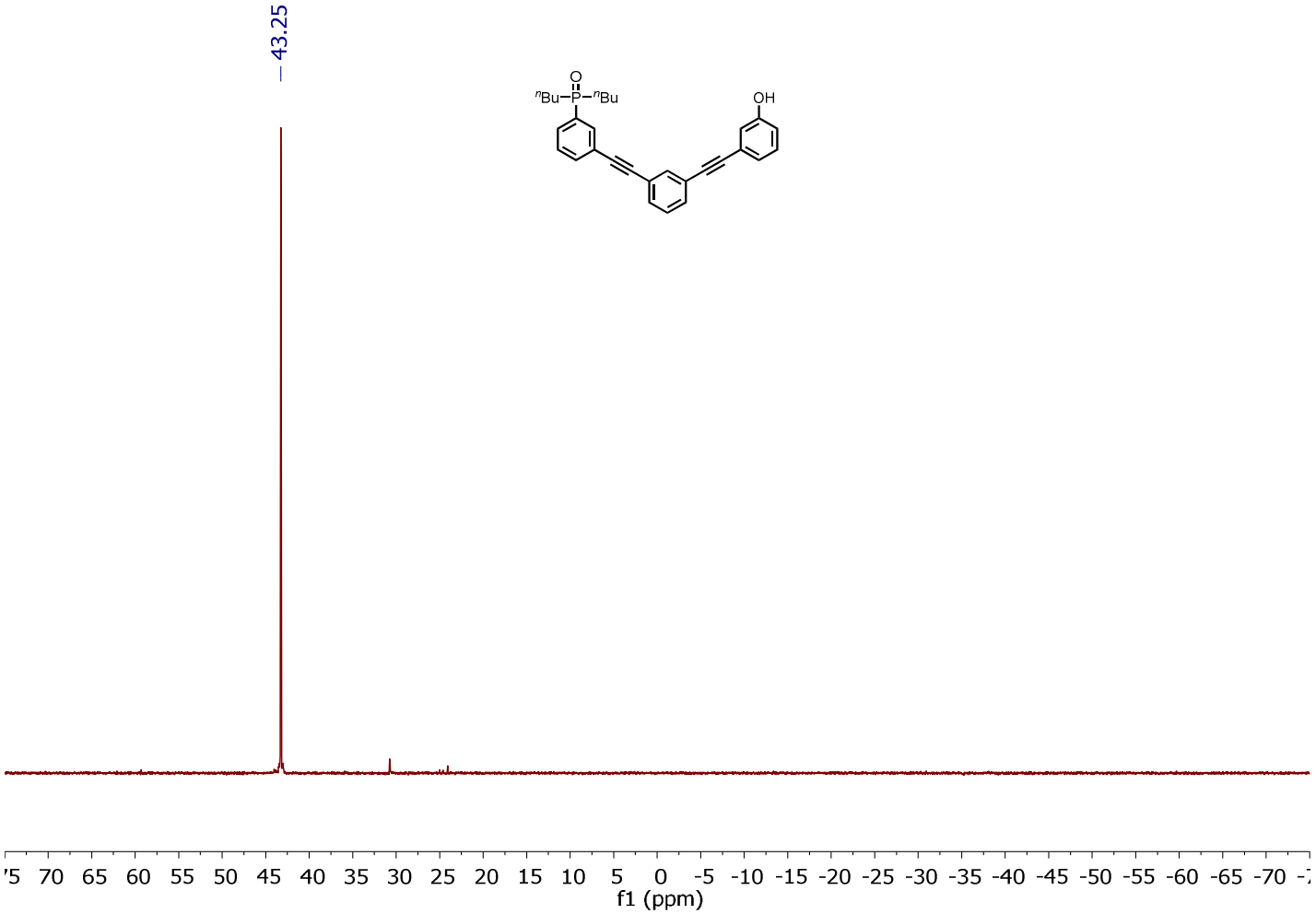
^{1}H NMR (400 MHz, $CDCl_3$) compound 47



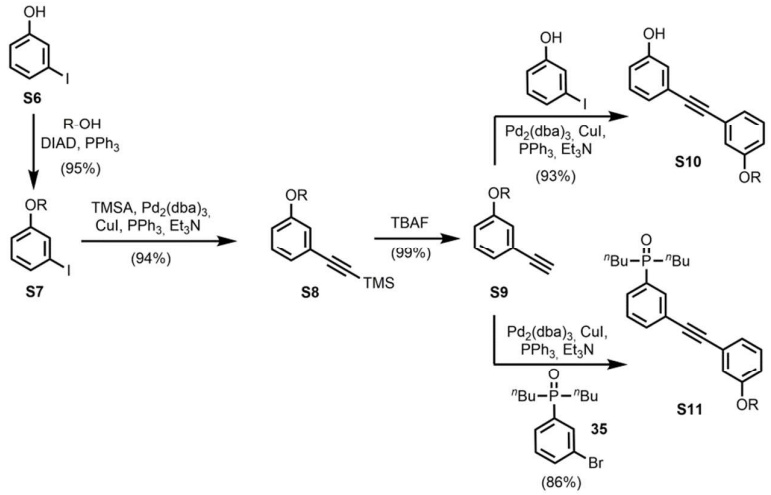
^{13}C NMR (100.6 MHz, $CDCl_3$) compound 47



^{31}P NMR (161.3 MHz, $CDCl_3$) compound 47

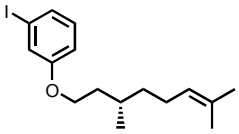


Synthesis of C7-PO A and D 1-mers.



Scheme S1: Synthesis of C7-PO A and D 1-mers.

Synthesis of S7.



3-Iodophenol (1.00 g, 4.55 mmol), *S-(-)-β*-citronellol (1.66 mL, 9.09 mmol) and PPh_3 (1.55 g, 5.91 mmol) were dissolved in dry THF (30 mL) under N_2. Diisopropyl azodicarboxylate (1.17 mL, 5.91 mmol) was added slowly at 0 °C. The reaction was allowed to warm to room temperature and was stirred overnight under N_2. The solvent was removed by rotary evaporation under reduced pressure and the obtained brown solid was purified by flash chromatography on silica (40-60 pet. ether) to yield the **S7** as a light yellow oil (1.55 g, 95%).

$[\alpha]_D^{20}$ = -4.27 (*c* 1.02, $CHCl_3$.

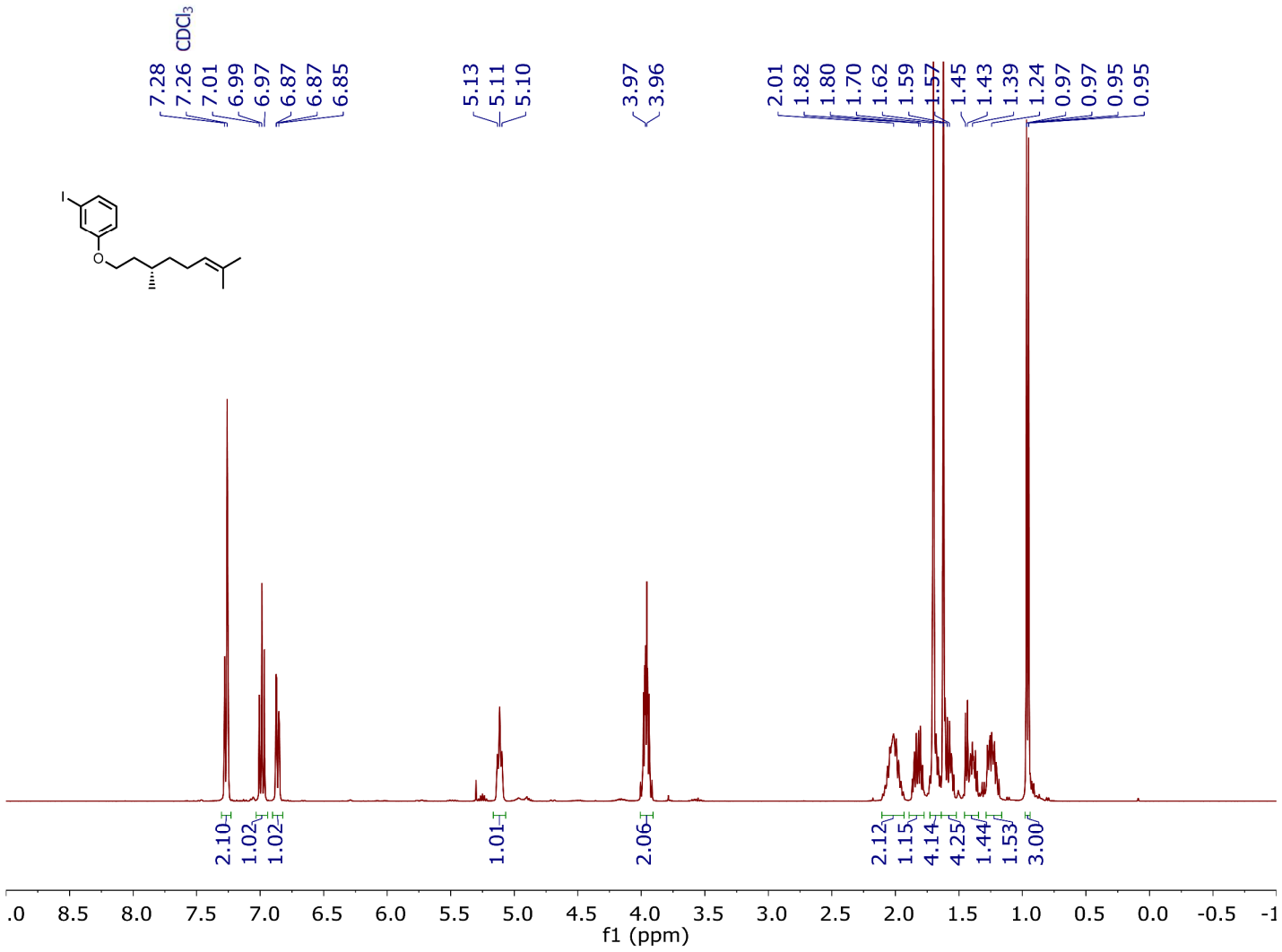
^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 7.27 (d, , 1H *J* = 8.0), 7.26 (s, 1H), 6.99 (t, , 1H *J* = 8.0), 6.86 (m. 1H), 5.14-5.06 (m, 1H), 4.00-3.89 (m, 2H), 2.08-1.92 (m, 2H), 1.85-1.76 (m, 1H), 1.69 (s, 3H), 1.68-1.63 (m, 1H), 1.61 (s, 3H), 1.60-1.55 (m, 1H), 1.42-1.33 (m, 1H), 1.28-1.18 (m, 1H), 0.95 (d, 3H, *J* = 6.5 Hz).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C = 159.7, 131.4, 130.7, 129.6, 124.6, 123.6, 114.2, 94.4, 66.5, 37.1, 36.0, 29.5, 25.8, 25.5, 19.6, 17.7.

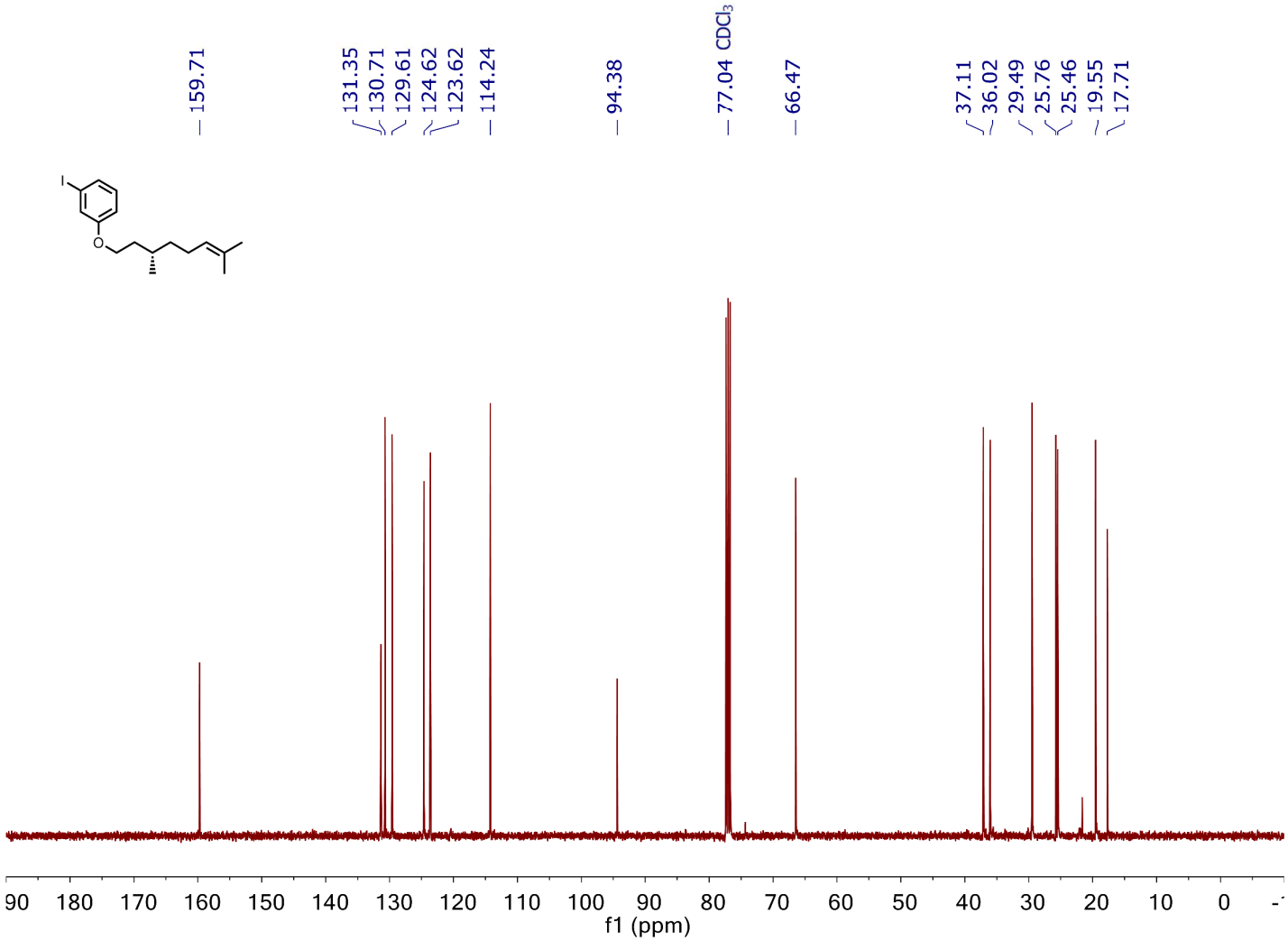
HRMS (ES+): calcd for $C_{16}H_{24}IO$ 359.0872, found 359.0861.

FT-IR (ATR): ν_{max} 2958, 2923, 2873, 1584, 1567, 1467, 1241, 1224 cm^{-1}.

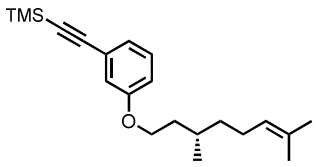
^{1}H NMR (400 MHz, $CDCl_3$) compound S7



^{13}C NMR (100.6 MHz, $CDCl_3$) compound S7



Synthesis of S8.



S7 (1.00 g, 2.79 mmol), $Pd_2(dba)_3$ (51 mg, 5.58 x 10^{-2} mmol), CuI (10 mg, 5.58 x 10^{-2} mmol) and PPh_3 (73 mg, 0.279 mmol) were added to a flask with Et_3N (9 mL) and DMF (9 mL), and N_2 bubbled through the reaction for 15 min. TMSA (0.44 mL, 3.07 mmol) was added and the reaction stirred at room temperature for 4 h in the dark under N_2 atmosphere. The reaction was filtered through celite and washed through with EtOAc (50 mL). The solution was washed with 1M HCl (2 x 50 mL), 5% LiCl solution (2 x 50 mL) and then dried ($MgSO_4$). The solvent was removed by rotary evaporation under reduced pressure and the obtained brown solid was purified by flash chromatography on silica (40-60 pet. ether) to yield the desired compound **S8** as a light yellow oil (0.860 g, 94%).

$[\alpha]_D^{20}$ = -5.48 (*c* 0.91, $CHCl_3$).

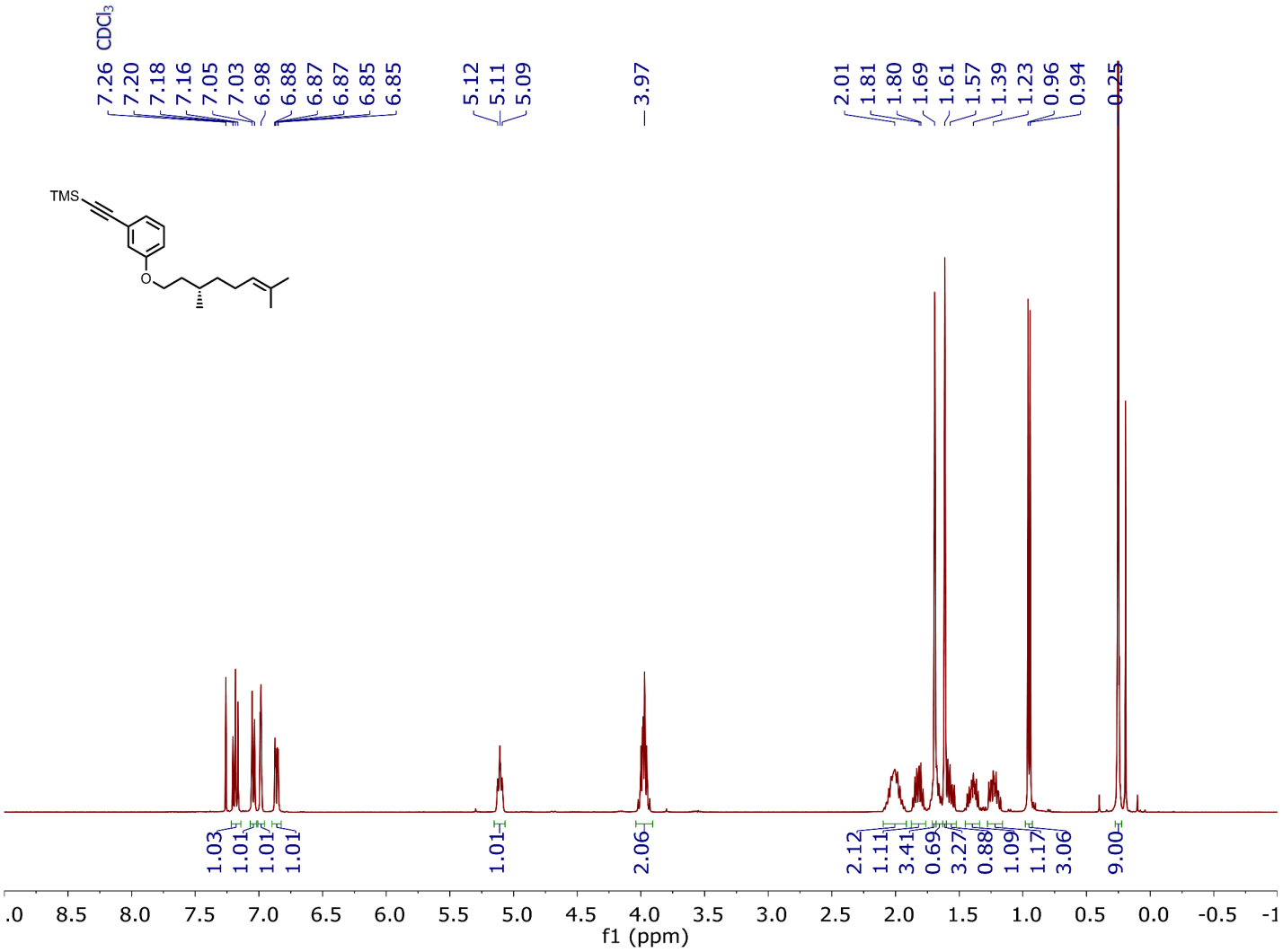
^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 7.18 (t, 1H, *J* = 8.0), 7.04 (dt, 1H, *J* = 8.0, 1.0), 6.99 (dd, 1H, *J* = 2.5, 1.0), 6.86 (ddd, 1H, *J* = 8.0, 2.5, 1.0), 5.15-5.07 (m, 1H), 4.01-3.93 (m, 2H), 2.10-1.92 (m, 2H), 1.88-1.76 (m, 1H), 1.69 (s, 3H), 1.68-1.63 (m, 1H), 1.61 (s, 3H), 1.60-1.55 (m, 1H), 1.42-1.33 (m, 1H), 1.28-1.18 (m, 1H), 0.95 (d, 3H, *J* = 6.5), 0.25 (s, 9H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C = 158.8, 131.3, 129.2, 124.6, 124.3, 124.0, 117.2, 115.9, 105.1, 93.8, 66.3, 37.1, 36.1, 29.5, 25.7, 25.5, 19.6, 17.7, -0.01.

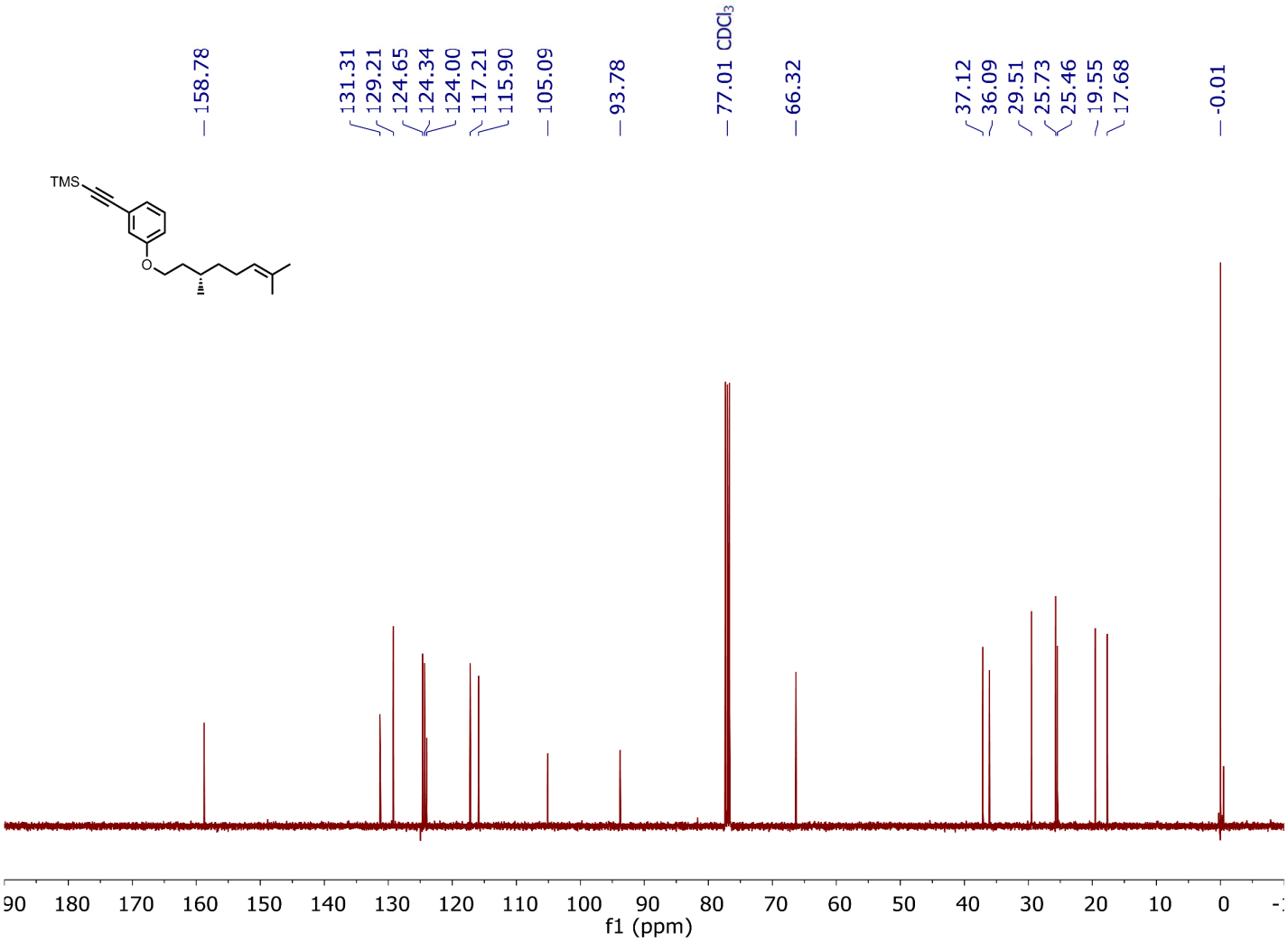
HRMS (ES+): calcd for $C_{21}H_{33}OSi$ 329.2301, found 329.2301.

FT-IR (ATR): ν_{max} 2959, 2925, 1596, 1574, 1249, 1156, 934 cm^{-1}.

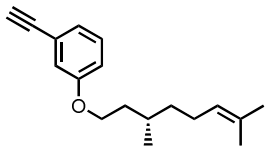
^{1}H NMR (400 MHz, $CDCl_3$) compound S8



^{13}C NMR (100.6 MHz, $CDCl_3$) compound S8



Synthesis of S9.



S8 (0.350 g, 1.07 mmol) was dissolved in dry THF (30 mL) and the reaction purged with N_2. The reaction was cooled to 0 °C and TBAF (1M in THF, 2.13 mL, 2.13 mmol) was added. The reaction was stirred for 10 min and filtered through a plug of silica, washing through 40-60 pet. ether:EtOAc (49:1). The solvent was removed by rotary evaporation under reduced pressure yielding **S9** as a yellow oil (0.270 g, 99%).

$[\alpha]_D^{20}$ = -5.98 (*c* 0.93, $CHCl_3$).

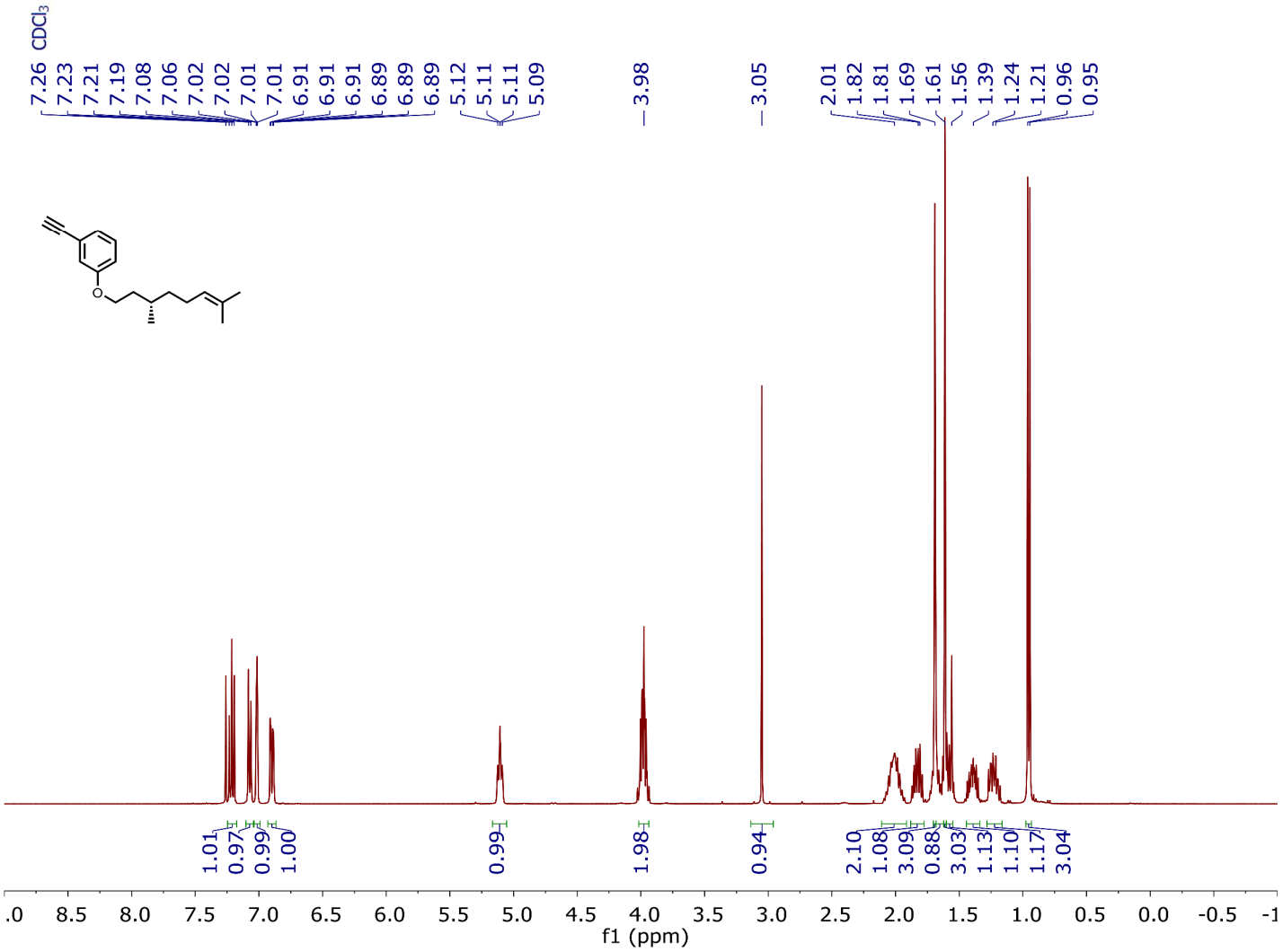
^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 7.21 (t, 1H, *J* = 8.0 Hz), 7.07 (dt, 1H, *J* = 8.0, 1.0), 7.01 (dd, 1H, *J* = 2.5, 1.0), 6.90 (ddd, 1H, *J* = 8.0, 2.5, 1.0), 5.14-5.07 (m, 1H), 4.03-3.93 (m, 2H) 3.05 (s, 1H), 2.10-1.92 (m, 2H), 1.88-1.76 (m, 1H), 1.69 (s, 3H), 1.68-1.63 (m, 1H), 1.61 (s, 3H), 1.60-1.55 (m, 1H), 1.42-1.33 (m, 1H), 1.28-1.18 (m, 1H), 0.95 (d, 3H, *J* = 6.5).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C = 158.8, 131.3, 129.3, 124.6, 124.4, 123.0, 117.6, 116.0, 83.7, 76.8, 66.5, 37.1, 36.1, 29.5, 25.7, 25.5, 19.5, 17.7.

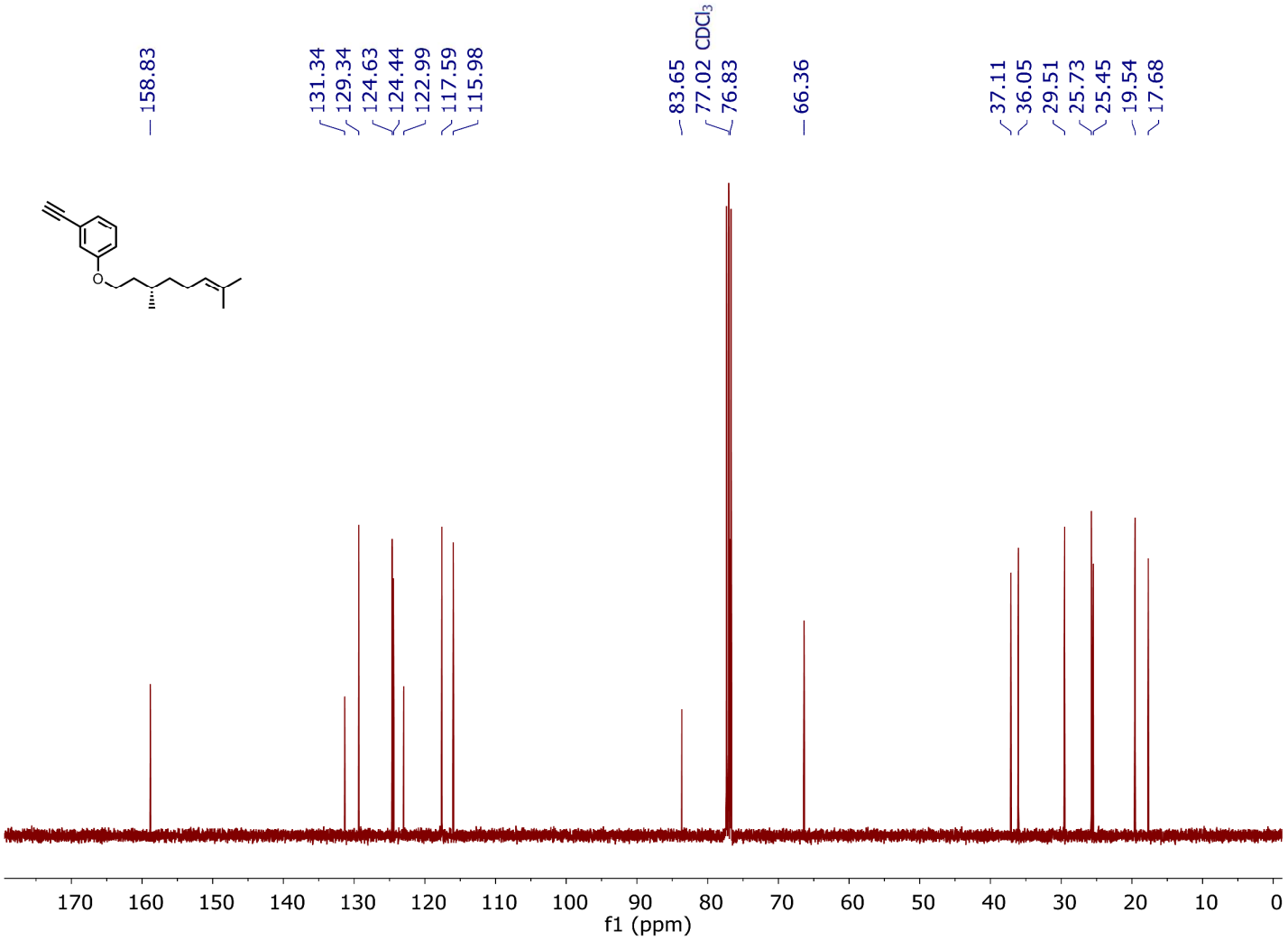
HRMS (ES+): calcd for $C_{18}H_{24}OH$ 257.1905, found 257.1905.

FT-IR (ATR): ν_{max} 3299, 2961, 2915, 1975, 1575, 1474, 1257, 1145 cm^{-1}.

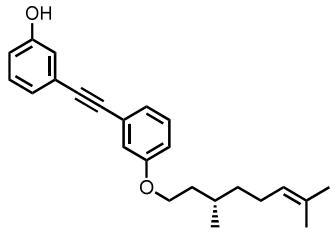
^{1}H NMR (400 MHz, $CDCl_3$) compound S9



^{13}C NMR (100.6 MHz, $CDCl_3$) compound S9



Synthesis of S10.



S9 (0.350 g, 1.37 mmol), 3-iodophenol (0.301 g, 1.37 mmol), $Pd_2(dba)_3$ (25 mg, 2.70 x 10^{-2} mmol), CuI (5 mg, 2.70 x 10^{-2} mmol) and PPh_3 (36 mg, 0.14 mmol) were added to a flask with Et_3N (5 mL) and DMF (5 mL), and N_2 bubbled through the reaction for 15 min. The reaction was stirred at room temperature for 4 h in the dark under N_2 atmosphere. The reaction was filtered through celite and washed through with EtOAc (30 mL). The solution was washed with 1M HCl (2 x 30 mL), 5% LiCl solution (2 x 50 mL) and then dried ($MgSO_4$). The solvent was removed by rotary evaporation under reduced pressure yielding a brown solid which was purified by flash chromatography on silica (40-60 pet. ether/EtOAc 4:1) to yield the desired compound **S10** as a brown solid (0.442 g, 93%).

Mpt: 40-43 ^{o}C.

$[\alpha]_D$ = -4.54 (*c* 0.48, $CHCl_3$).

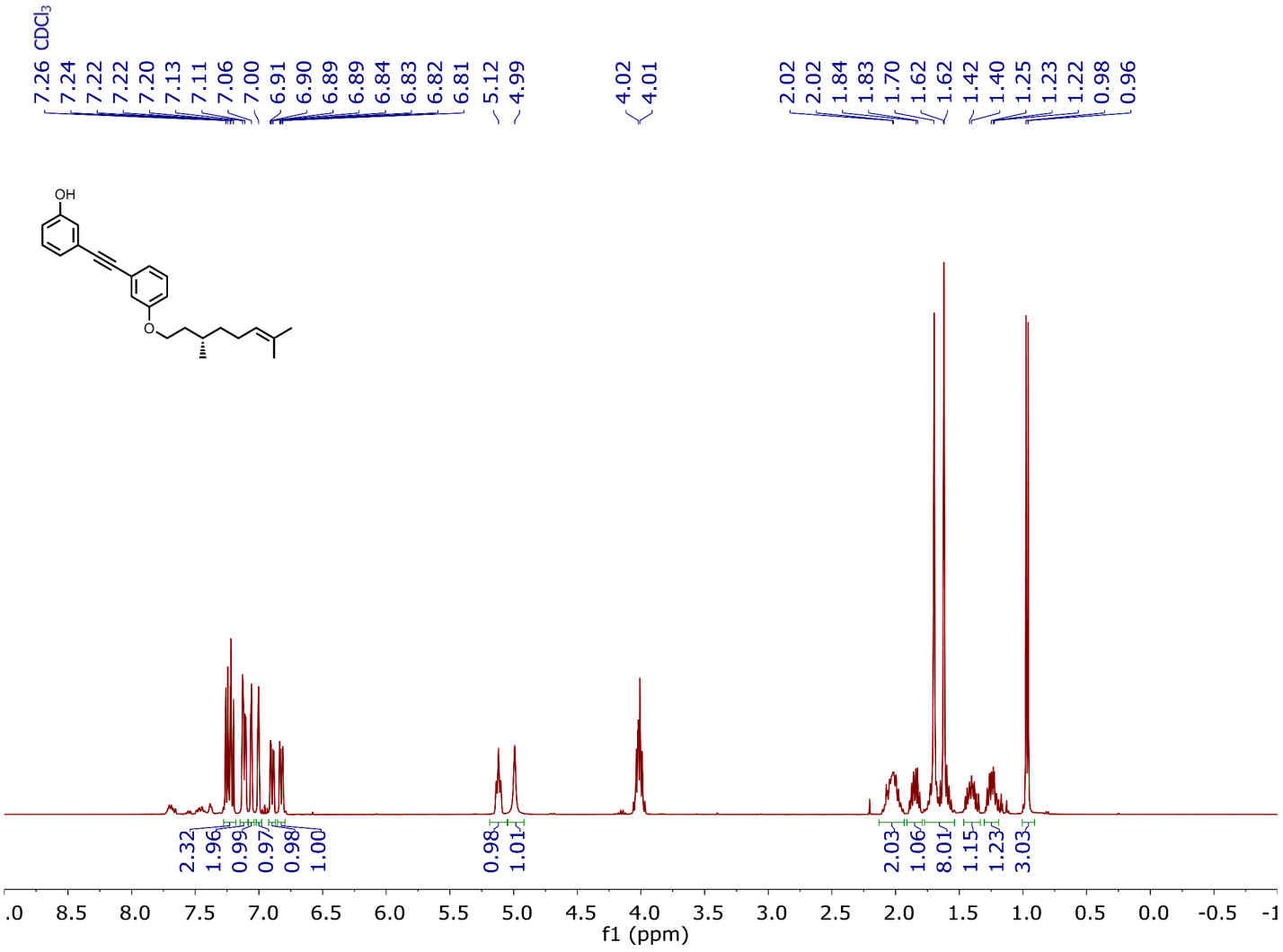
^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 7.27-7.17 (m, 2H), 7.14-7.09 (m, 2H), 7.06 (dd, 1H, *J* = 2.5, 1.5), 7.00 (dd, 1H, *J* = 2.5, 1.5), 6.90 (ddd, 1H, *J* = 8.5, 2.5), 6.82 (ddd, 1H, *J* = 8.0, 2.5, 1.0), 5.13-5.07 (m, 1H), 4.99 (bs, 1H), 4.01-3.91 (m, 2H), 2.09-1.92 (m, 2H), 1.85-1.76 (m, 1H), 1.70 (s, 3H), 1.60-1.63 (m, 1H), 1.62 (s, 3H), 1.60-1.55 (m, 1H), 1.42-1.33 (m, 1H), 1.28-1.18 (m, 1H), 0.96 (d, 3H, *J* = 6.5).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C = 158.9, 155.3, 131.4, 129.7, 129.4, 124.7, 124.5, 124.4, 124.1, 124.0, 118.2, 117.0, 115.8, 115.6, 89.5, 88.7, 66.4, 37.1, 36.1, 29.5, 25.8, 25.5, 19.6, 17.7.

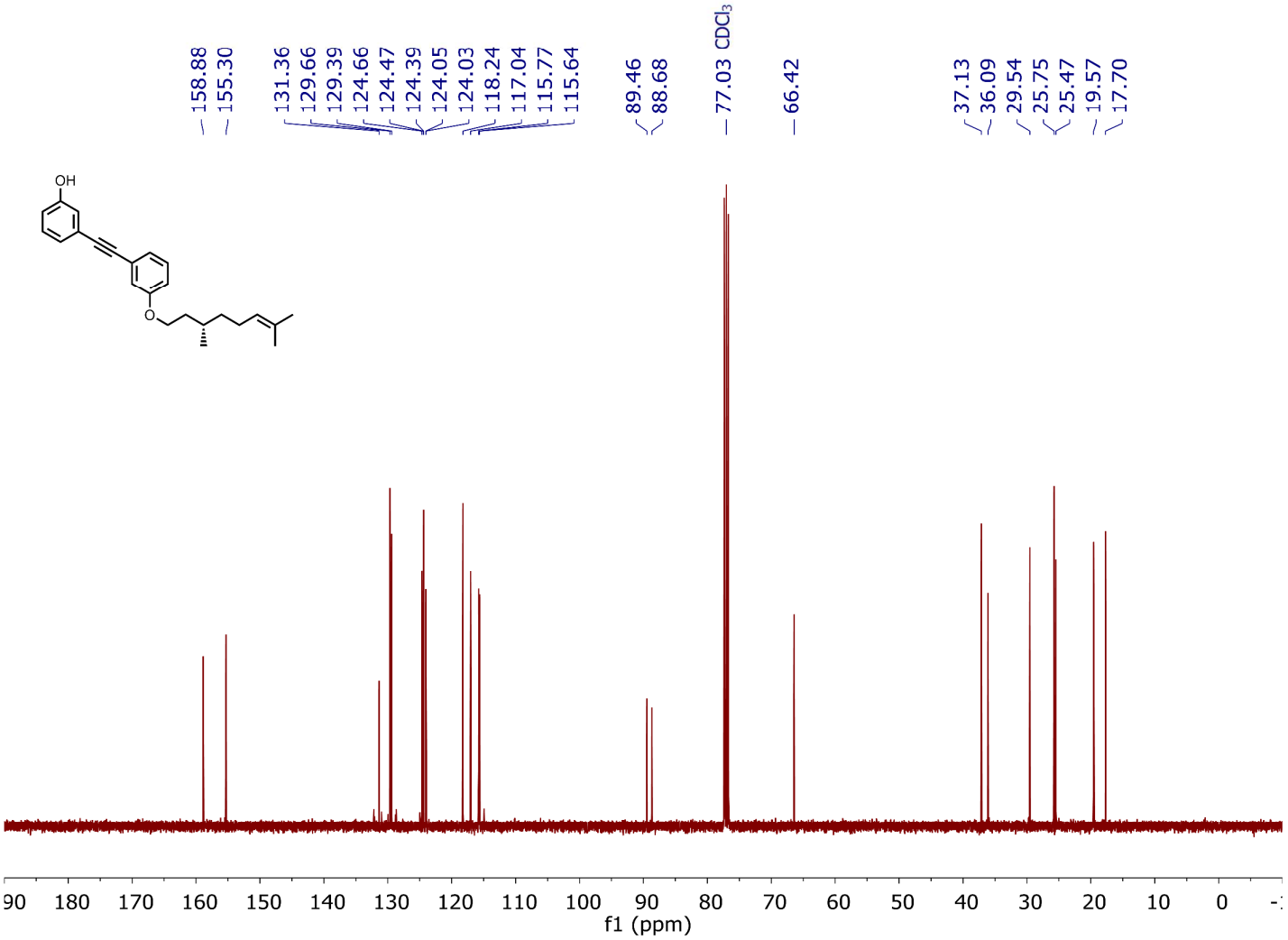
HRMS (ES+): calcd for $C_{24}H_{28}O_2$ 349.2155, found 349.2162.

FT-IR (ATR): ν_{max} 3365 (br), 2911, 1612, 1574, 1496, 1324, 1189 cm^{-1}.

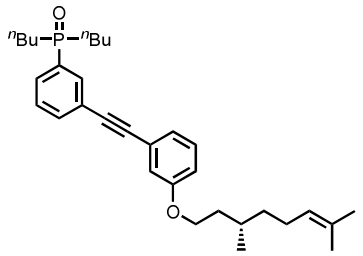
^{1}H NMR (400 MHz, $CDCl_3$) compound S10



^{13}C NMR (100.6 MHz, $CDCl_3$) compound S10



Synthesis of S11.



Compounds **S9** (103 mg, 0.40 mmol), **35** (152 mg, 0.48 mmol), $Pd_2(dba)_3$ (7.3 mg, 8.0 x 10^{-3} mmol), CuI (1.5 mg, 8.0 x 10^{-3} mmol) and PPh_3 (10.5 mg, 0.04 mmol) were added to a flask with Et_3N (2 mL) and DMF (2 mL). N_2 was bubbled through the reaction for 15 min. The reaction was heated by microwave irradiation at 95 °C for 10 min. The reaction was filtered through celite and washed through with EtOAc (10 mL). The solution was washed with 1M HCl (3 x 10 mL), 5% LiCl solution (2 x 10 mL) and the dried ($MgSO_4$). The solvent was removed by rotary evaporation under reduced pressure yielding a brown solid which was purified by flash chromatography on silica (CH_2Cl_2/MeOH 20:1) to yield the desired compound **S11** as a brown waxy solid (0.169 g, 86%).

$[\alpha]_D$ = -4.48 (*c* 0.96, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 7.81 (d, 1H, *J* = 10.0), 7.67-7.59 (m, 2H), 7.44 (t, 1H, *J* = 8.0), 7.21 (t, 1H, *J* = 8.0), 7.08 (d, 1H, *J* = 8.0), 7.03 (t, 1H, *J* = 2.0), 6.87 (dd, 1H, *J* = 8.0, 2.0), 5.11-5.04 (m, 1H), 4.01-3.91 (m, 2H), 2.04-1.73 (m, 7H), 1.71-1.49 (m, 12H), 1.46-1.27 (m, 5H), 0.92 (d, 3H, *J* = 6.5), 0.84 (t, 6H, *J* = 7.0).

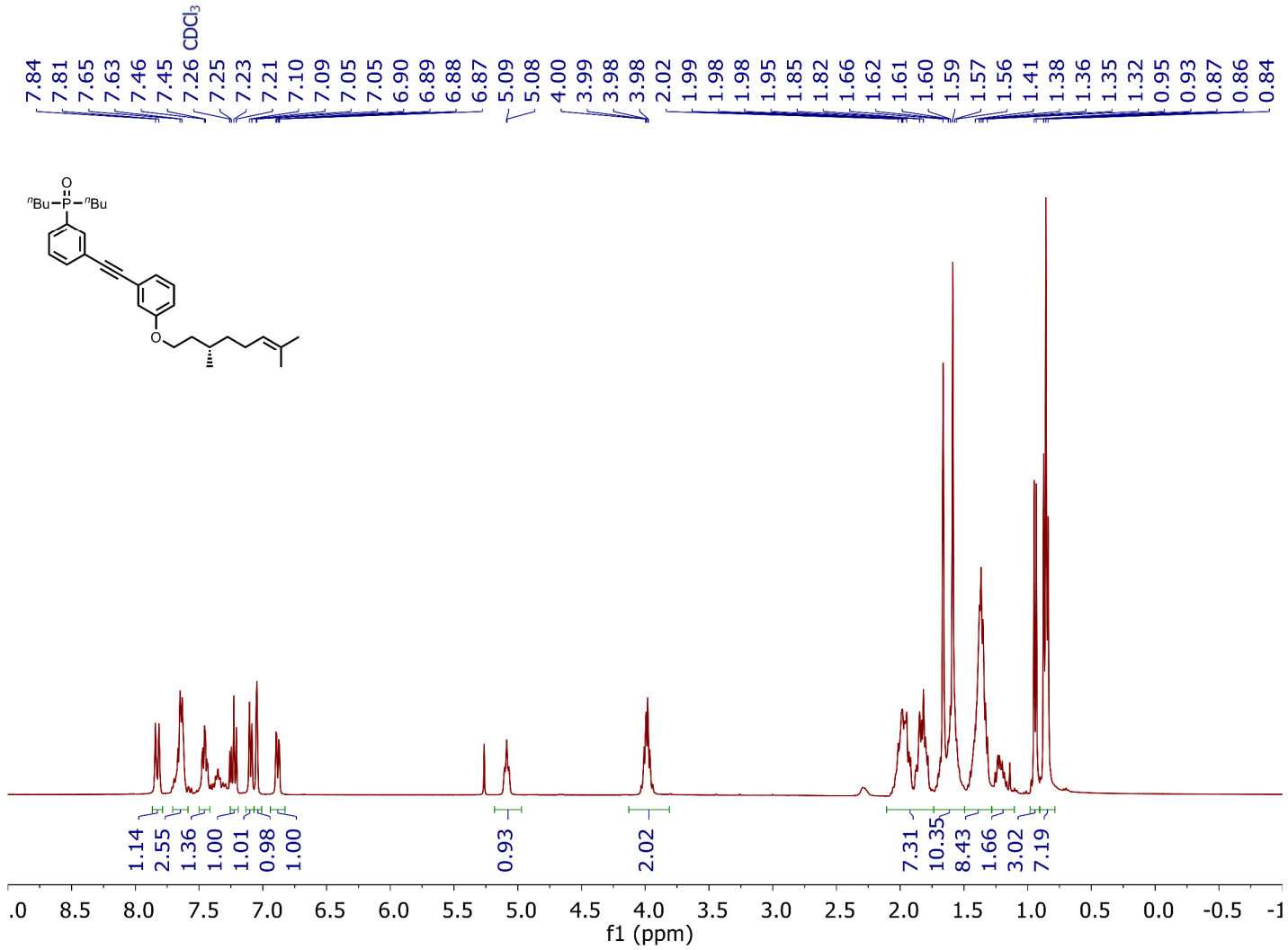
^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C = 158.9, 134.3, 133.4 (d, *J* = 9), 132.0 (d, *J* = 10), 131.2, 130.0 (d, *J* = 6), 129.4, 128.7 (d, *J* = 10), 124.6, 124.0, 123.9 (d, *J* = 10), 123.6, 117.0, 115.9, 90.8, 88.1, 66.4, 37.1, 36.1, 29.6 (d, *J* = 69), 29.5, 25.7, 25.4, 24.1 (d, *J* = 15), 23.4 (d, *J* = 2), 19.6, 17.7, 13.5 (d, *J* = 1).

^{31}P NMR (161.3 MHz, $CDCl_3$): δ_P = 40.3.

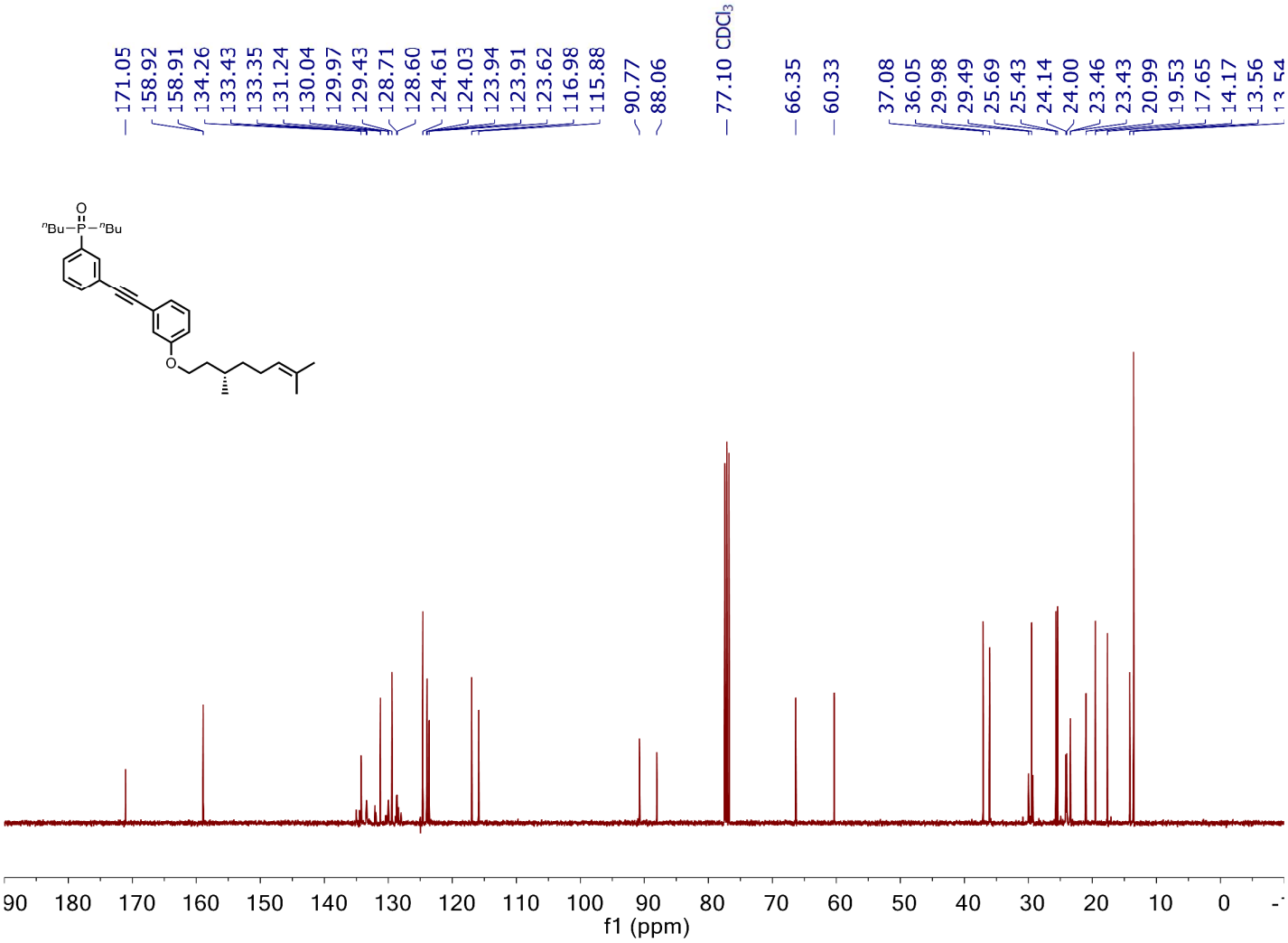
HRMS (ES+): calcd for $C_{24}H_{28}O_2$ 349.2155, found 349.2162.

FT-IR (ATR): ν_{max} 2957, 2929, 1596, 1574, 1466, 1222, 1170, 686 cm^{-1}.

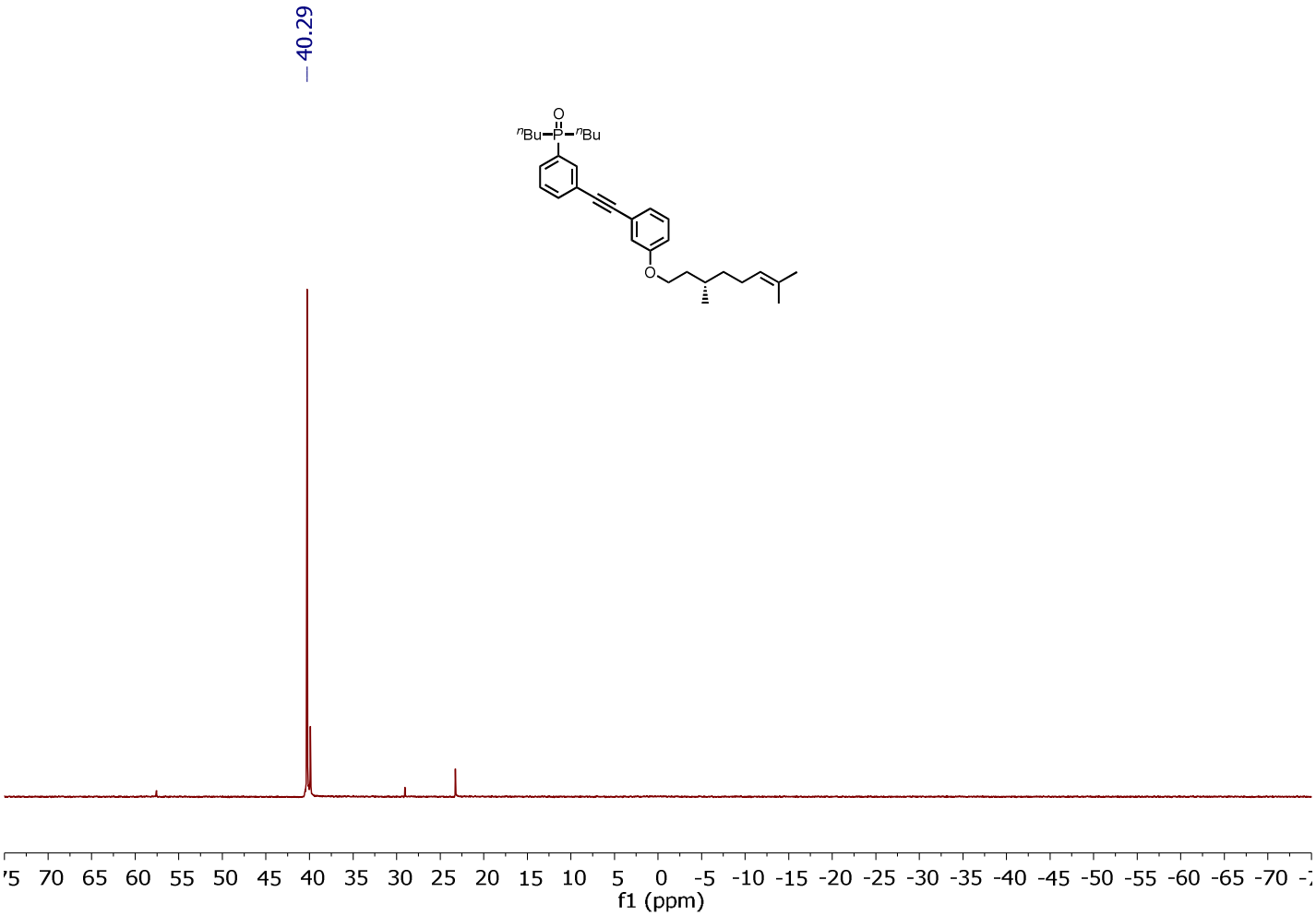
^{1}H NMR (400 MHz, $CDCl_3$) compound S11



^{13}C NMR (100.6 MHz, $CDCl_3$) compound S11



^{31}P NMR (161.3 MHz, $CDCl_3$) compound S11



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