Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Brønsted Acid-Catalysed Desilylative Heterocyclisation to form Substituted Furans

Emily G. Babcock, Md. Shafiqur Rahman, James E. Taylor*,‡

Department of Chemistry, University of Bath, Claverton Down, Bath, Somerset, BA2 7AY, U.K.

General Information

Reactions involving moisture sensitive reagents were carried out in flame-dried glassware under an inert atmosphere (N_2 or Ar) using standard vacuum line techniques. Anhydrous solvents (Et_2O, CH_2Cl_2, THF and PhMe) were obtained after passing through an alumina column (Mbraun SPS-800). Petrol is defined as petroleum ether 40–60 °C. All other solvents and commercial reagents were used as received without further purification unless otherwise stated.

Room temperature (rt) refers to 20–25 °C. Temperatures of 0 °C and –78 °C were obtained using ice/water and CO_2(s)/acetone baths, respectively. Reaction involving heating were performed using DrySyn blocks and a contact thermocouple.

Under reduced pressure refers to the use of either a Büchi Rotavapor R-200 with a Büchi V-491 heating bath and Büchi V-800 vacuum controller, a Büchi Rotavapor R-210 with a Büchi V-491 heating bath and Büchi V-850 vacuum controller, a Büchi Rotavapor R-114 with a Büchi B-480 heating bath and Büchi V-800 vacuum controller or Vacuubrand CVC3000 vacuum controller, an IKA RV3 eco Rotavapor with an IKA HB eco heating bath and Büchi V-800 vacuum controller or Vacuubrand CVC3000 vacuum controller. Rotary evaporator condensers are either fitted to Julabo FL601 Recirculating Coolers filled with ethylene glycol and set to –5 °C or a cold finger containing dry ice.

Analytical thin layer chromatography was performed on pre-coated aluminium plates (Kieselgel 60 F254 silica) and visualisation was achieved using ultraviolet light (254 nm) and/or staining with either aqueous $KMnO_4$ solution or ethanolic phosphomolybdic acid solution followed by heating. Manual column chromatography was performed in glass columns fitted with porosity 3 sintered discs over Kieselgel 60 silica using the solvent system stated. Automated chromatography was performed on a Teledyne ISCO Combi*Flash*® NextGen 300+ with a UV/Vis detector and an ELS detector using the method stated and Redi*Sep*® Rf Gold or Rf Silver columns.

Melting points were recorded on an Electrothermal 9100 melting point apparatus, (dec) refers to decomposition.

Infrared spectra were recorded on a Perkin-Elmer PerkinElmer Spectrum 100 ATR-FTIR spectrometer. Spectra were recorded of either thin films or solids, with characteristic absorption wavenumbers (νmax) reported in cm^{-1}.

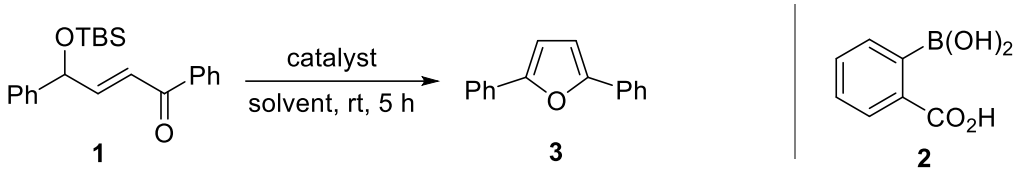
^{1}H, $^{13}C\{1H\}$, $^{19}F\{^{1}H\}$, and $^{31}P\{H\}$ NMR spectra were acquired on either a Bruker AV300 (^{1}H 300 MHz; $^{13}C\{^{1}H\}$ 75 MHz; $^{19}F\{^{1}H\}$ 282 MHz, $^{31}P\{H\}$ 162Hz), a Bruker AV400 (^{1}H 400 MHz; $^{13}C\{^{1}H\}$ 101 MHz; $^{19}F\{^{1}H\}$ 376 MHz, $^{31}P\{H\}$ 162Hz), or an Agilent ProPulse 500 (^{1}H 500 MHz, $^{13}C\{^{1}H\}$ 126 MHz, $^{19}F\{^{1}H\}$ 470 MHz) in the deuterated solvent stated. All chemical shifts are quoted in parts per million (ppm) relative to the residual solvent peak. All coupling constants, J, are quoted in Hz. Multiplicities are indicated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and multiples thereof. The abbreviation Ar denotes aromatic and app

denotes apparent. NMR peak assignments were confirmed using 2D ^{1}H correlated spectroscopy (COSY), 2D ^{1}H nuclear Overhauser effect spectroscopy (NOESY), 2D ^{1}H–^{13}C heteronuclear multiple-bond correlation spectroscopy (HMBC), and 2D ^{1}H–^{13}C heteronuclear single quantum coherence (HSQC) where necessary.

Mass spectrometry (m/z) data were acquired by either electrospray ionisation (ESI), chemical ionisation (CI), electron impact (EI), atmospheric solids analysis probe (ASAP), atmospheric pressure chemical ionization (APCI) or nanospray ionisation (NSI) at the University of Bath ([A]+ or [A]– quoted).

Reaction Optimization

Table S1. Additional Optimization[a]



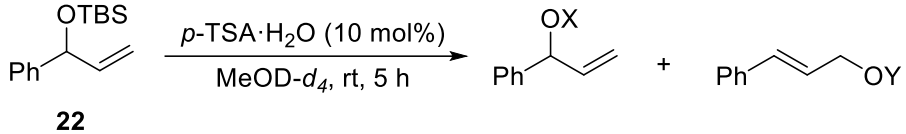
1 3 2

Entry	Catalyst (mol%)	Solvent (M)	Yield (%)[b]
1	**2** (5) + $(CO_2H)_2$ (10)	MeOH (1)	17
2	$(CO_2H)_2$ (5)	MeOH (1)	< 5
3	TFA (5)	MeOH (1)	< 5
4	AcOH (5)	MeOH (1)	< 5
5	HCl (5)	MeOH (1)	45
6	*p*-TSA·H_2O (5)	MeOH (1)	63
7	*p*-TSA·H_2O (5)	EtOH (1)	< 5
8	*p*-TSA·H_2O (5)	*i*-PrOH (1)	< 5
9	*p*-TSA·H_2O (5)	*s*-BuOH (1)	< 5
10	*p*-TSA·H_2O (5)	MeCN (1)	5
11	*p*-TSA·H_2O (5)	MeOH (0.1)	20
12	*p*-TSA·H_2O (5)	MeOH (0.2)	31
13	*p*-TSA·H_2O (5)	MeOH (0.5)	52
14[c]	*p*-TSA·H_2O (10)	MeOH (1)	99 (76)[d]

[a]Reactions performed on a 0.2 mmol scale. [b]Determined by ^{1}H NMR using 1,4-dinitrobenzene as an internal standard. [c]18 hours. [d]Isolated yield.

Control Experiments

Allylic Deprotection NMR Monitoring



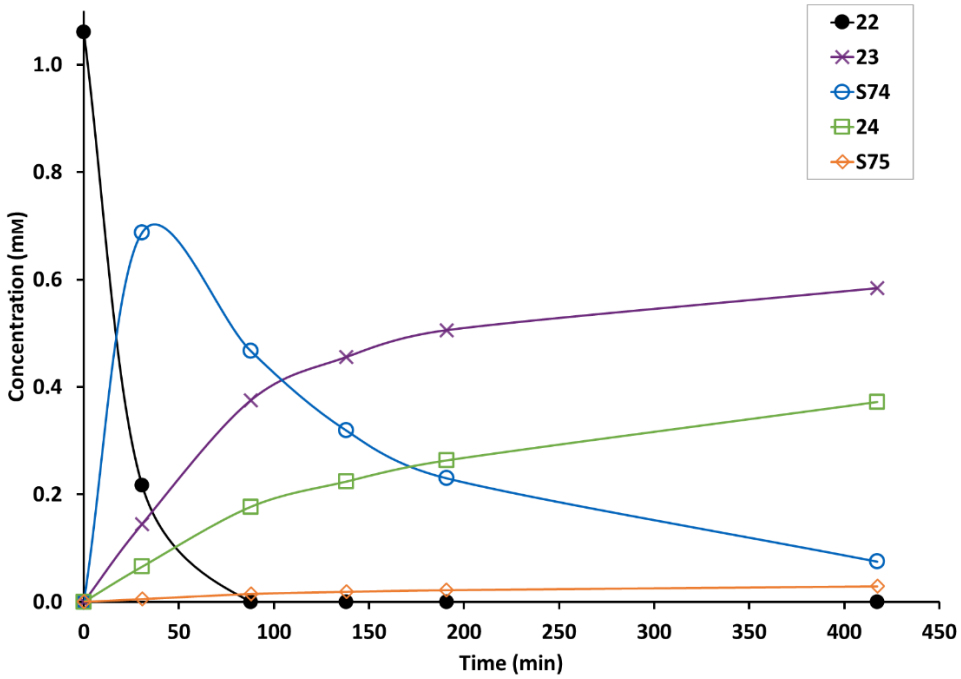
22

X	
CD_3	**23**
H	**S74**

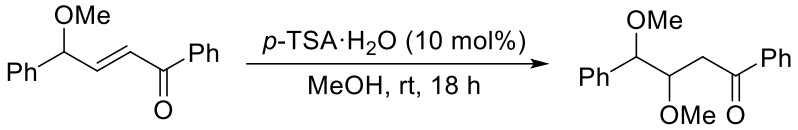
Y	
CD_3	**24**
H	**S75**

In an NMR tube, *tert*-butyldimethyl((1-phenylallyl)oxy)silane **22** (0.149 g, 0.600 mmol), 1,4-dinitrobenzene (5.0 mg, 0.030 mmol) were dissolved in MeOD-d_4 (0.6 mL). An initial ^{1}H NMR was taken, before *p*-TSA·H_2O (0.011 g, 0.060 mmol) was added. ^{1}H NMR spectra were acquired at the times indicated in the data table below. Concentrations were determined using processed NMR spectra relative to the internal standard.

Time (min)	[**22**] mM	[**23**] mM	[**S74**] mM	[**24**] mM	[**S75**] mM
0	1.060	0.000	0.000	0.000	0.000
31	0.217	0.145	0.687	0.066	0.005
88	0.000	0.375	0.467	0.177	0.015
138	0.000	0.456	0.319	0.224	0.019
191	0.000	0.506	0.230	0.264	0.022
417	0.000	0.584	0.075	0.372	0.029



Methyl Ether Substrate

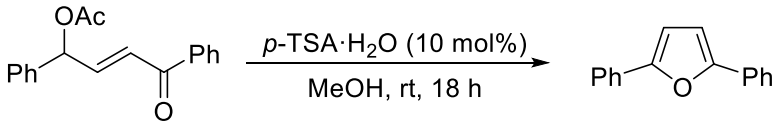


25

26, 34%
59:41 dr

(*E*)-4-Methoxy-1,4-diphenylbut-2-en-1-one **25** (0.051 g, 0.200 mmol) was dissolved in MeOH (0.2 mL) before *p*-TSA·H_2O (0.004 g, 0.020 mmol) was added. The reaction was stirred at rt for 18 h before being concentrated under reduced pressure. The crude material was analysed directly by ^{1}H NMR in $CDCl_3$.

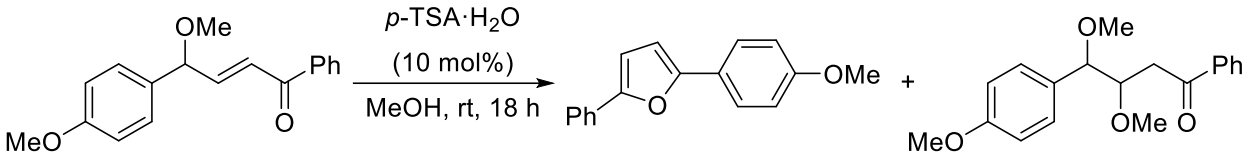
Acetate Substrate



S78 **3**, 50%

(*E*)-4-Oxo-1,4-diphenylbut-2-en-1-yl acetate **S78** (0.056 g, 0.200 mmol) was dissolved in MeOH (0.2 mL) and *p*-TSA monohydrate (0.004 g, 0.020 mmol) was added. The reaction mixture was stirred at rt for 18 h then concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography (100% to 97/3 cyclohexane/Et_2O) to give furan **3** (0.022 g, 50%) as a white solid.

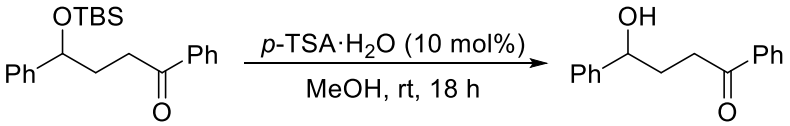
4-Methoxy Methyl Ether Substrate



S81 **9**, 28% **S83**, 72%
61:39 dr

(*E*)-4-Methoxy-1,4-diphenylbut-2-en-1-one **25** (0.051 g, 0.200 mmol) was dissolved in MeOH (0.2 mL) before *p*-TSA·H_2O (0.004 g, 0.020 mmol) was added. The reaction was stirred at rt for 18 h before being concentrated under reduced pressure. The crude material was analysed directly by ^1H NMR in $CDCl_3$.

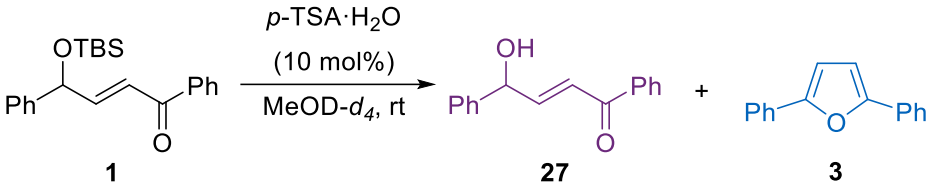
Saturated Substrate



S82 **S84**, 100% conversion

4-((*tert*-Butyldimethylsilyl)oxy)-1,4-diphenylbutan-1-one **S82** (0.036 g, 0.100 mmol) was dissolved in MeOH (0.1 mL) before *p*-TSA·H_2O (0.002 g, 0.010 mmol) was added. The reaction was stirred at rt for 18 h before being concentrated under reduced pressure. The crude material was analysed directly by ^1H NMR in $CDCl_3$.

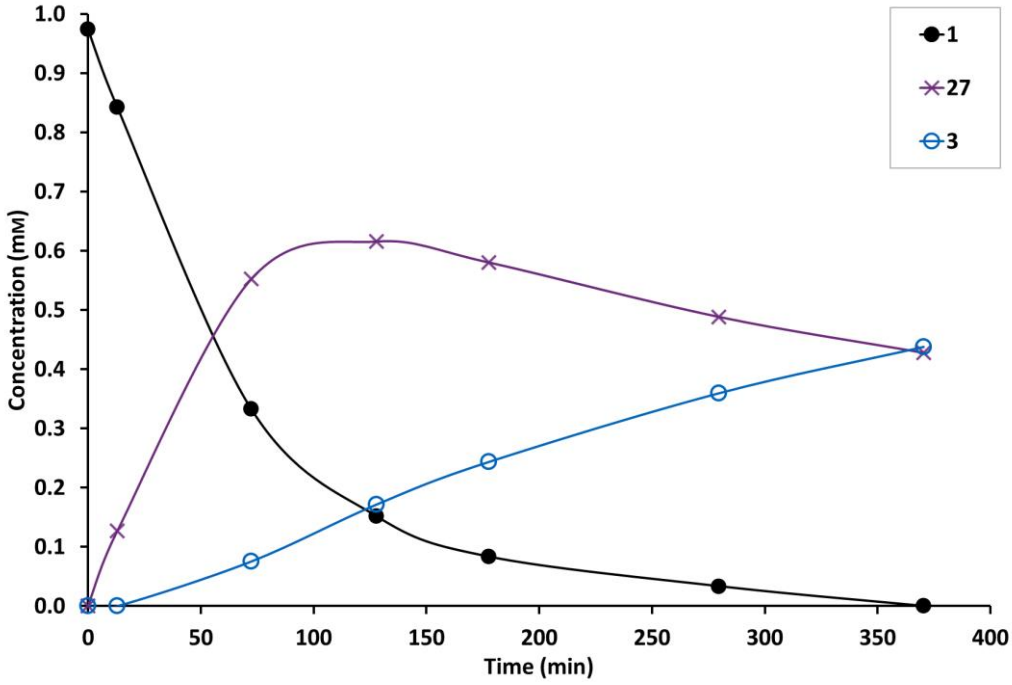
Heterocyclization NMR Monitoring



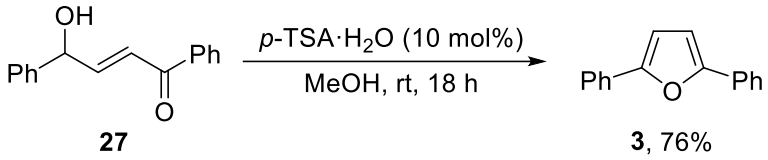
1 **27** **3**

In an NMR tube, (*E*)-4-((*tert*-butyldimethylsilyl)oxy)-1,4-diphenylbut-2-en-1-one **1** (0.212 g, 0.600 mmol), 1,4-dinitrobenzene (5.0 mg, 0.030 mmol) were dissolved in MeOD-d_4 (0.6 mL). An initial ^{1}H NMR was taken, before *p*-TSA·H_2O (0.011 g, 0.060 mmol) was added. ^{1}H NMR spectra were acquired at the times indicated in the data table below. Concentrations were determined using processed NMR spectra relative to the internal standard.

Time (min)	[**1**] mM	[**27**] mM	[**3**] mM
0	0.974	0.000	0.000
13	0.843	0.127	0.000
72	0.333	0.552	0.075
128	0.151	0.616	0.171
178	0.083	0.580	0.243
280	0.033	0.488	0.359
370	0.000	0.428	0.437



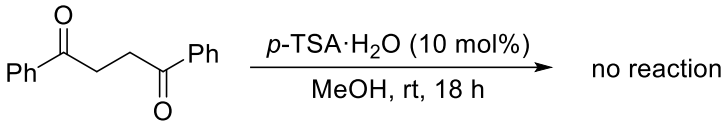
Allylic Alcohol Intermediate Heterocyclization



27 **3**, 76%

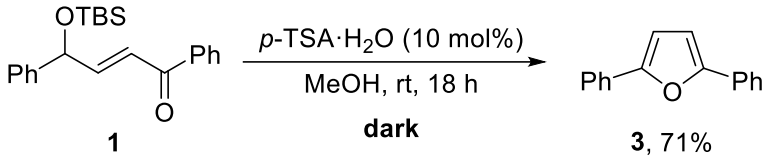
(*E*)-4-Hydroxy-1,4-diphenylbut-2-en-1-one **27** (0.048 g, 0.200 mmol) was dissolved in MeOH (0.2 mL) and *p*-TSA monohydrate (0.004 g, 0.020 mmol) was added. The reaction mixture was stirred at rt for 18 h then concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography (100% to 97/3 cyclohexane/Et_2O) to give furan **3** (0.034 g, 76%) as a white solid.

1,4-Diketone Substrate



1,4-Diphenylbutane-1,4-dione **S73** (0.048 g, 0.200 mmol) was dissolved in MeOH (0.2 mL) and *p*-TSA monohydrate (0.004 g, 0.020 mmol) was added. The reaction mixture was stirred at rt for 18 h then concentrated under reduced pressure. The ^1H NMR of the crude material showed no reaction.

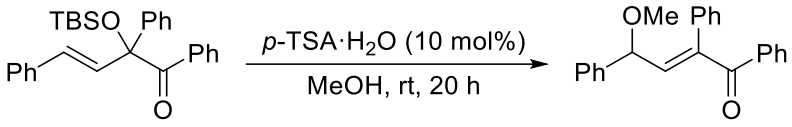
Reaction in the Dark



1 **3**, 71%

(*E*)-4-((*tert*-Butyldimethylsilyl)oxy)-1,4-diphenylbut-2-en-1-one **1** (0.071 g, 0.200 mmol) was dissolved in MeOH (0.2 mL) in a vial wrapped in tin foil before *p*-TSA monohydrate (0.004 g, 0.020 mmol) was added. The reaction mixture was stirred in the absence of light at rt for 18 h then concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography (100% to 97/3 cyclohexane/Et_2O) to give furan **3** (0.031 g, 71%) as a white solid.

Tertiary Substrate at RT



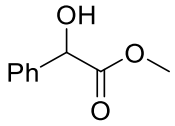
28 **S76**, 15%

(*E*)-2-((*tert*-Butyldimethylsilyl)oxy)-1,2,4-triphenylbut-3-en-1-one **28** (0.086 g, 0.20 mmol) was dissolved in MeOH (0.2 mL) and *p*-TSA monohydrate (0.004 g, 0.02 mmol) was added. The reaction mixture was stirred at rt for 20 h before being concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography (CombiFlash, 12 g, 1 CV 100% cyclohexane, to 5% Et_2O Et_2O 10 CV, to 100% Et_2O 3 CV) to give the title (*E*)-4-methoxy-1,2,4-triphenylbut-2-en-1-one **S76** (0.010 g, 15%) as a colourless oil. ν_{max} (liquid) 2930 (C-H aromatic), 2822 (C-H alkane), 1667 (C=O), 1595 (C=C aromatic); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.00 – 7.92 (m, 2H, C(1)-ArC(2,6)*H*), 7.58 – 7.52 (m, 1H, C(1)-ArC(4)*H*), 7.45 – 7.24 (m, 12H, ArC*H*), 6.30 (d, *J* = 8.9 Hz, 1H, C(3)*H*), 4.77 (d, *J* = 8.9 Hz, 1H, C(2)*H*), 3.20 (s, 3H, OCH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 197.7 (*C*(1)), 142.2 (*C*(2)), 140.4 (C(4)-Ar*C*(1)), 136.9 (C(1)-Ar*C*(1)), 136.5 (C(2)-ArC(1)), 133.8 (*C*(3)), 131.8 (Ar*C*), 129.9 (Ar*C*), 128.9 (Ar*C*), 128.8 (Ar*C*), 128.7 (Ar*C*), 128.5 (Ar*C*), 128.0 (Ar*C*), 126.9 (Ar*C*), 126.5 (Ar*C*), 80.9 (*C*(4)), 56.6 (O*C*H$_3$); HRMS (ESI$^+$) *m/z*: $[M+Na]^+$ calcd for $C_{23}H_{20}O_2Na$ 351.1361, found 351.1360.

Synthesis of Starting Materials

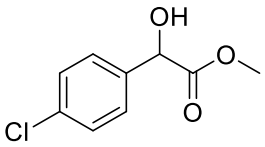
Mandelate Esters

Methyl 2-hydroxy-2-phenylacetate S1



Mandelic acid (5.00 g, 32.9 mmol) was dissolved in MeOH (65.8 mL) and a few drops of H_2SO_4 was added. The resultant solution was heated to 65 °C for 3 h then allowed to cool to rt. The reaction mixture was concentrated under reduced pressure, diluted with H_2O (50 mL), and pH neutralised with slow addition of $NaHCO_3$ (sat. aq.) solution, The aqueous solution was extracted with EtOAc (3 × 50 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give the title compound **S1** (4.69 g, 86%) as an off-white solid, with spectroscopic data in accordance with the literature.[1] mp 60–63 °C {Lit[1] 56–58 °C} ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.46 – 7.29 (m, 5H, ArC*H*), 5.18 (d, *J* = 5.5 Hz, 1H, O*H*), 3.77 (s, 3H, C*H*$_3$), 3.42 (d, *J* = 5.5 Hz, 1H, C(2)*H*)

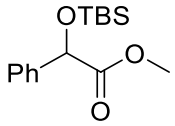
Methyl 2-(4-chlorophenyl)-2-hydroxyacetate S2



2-(4-chlorophenyl)-2-hydroxyacetic acid (2.00 g, 10.7 mmol) was dissolved in MeOH (21.4 mL) and a few drops of H_2SO_4 was added. The resultant solution was heated to 65 °C for 3 h then allowed to cool to rt. The reaction mixture was concentrated under reduced pressure, diluted with H_2O (20 mL), and pH neutralised with slow addition of $NaHCO_3$ (sat. aq.) solution, The aqueous solution was extracted with EtOAc (3 × 30 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give the title compound **S2** (1.98 g, 92%) as a white solid, with spectroscopic data in accordance with the literature.[2] mp 55–57 °C {Lit[2] 57–58 °C}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.41 – 7.30 (m, 4H, ArC*H*), 5.16 (d, *J* = 5.3 Hz, 1H, C(2)*H*), 3.77 (s, 3H, C*H*$_3$), 3.46 (d, *J* = 5.3 Hz, 1H, O*H*).

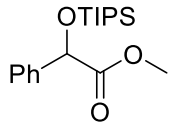
Silyl Protected α-Hydroxy Esters

Methyl 2-((*tert*-butyldimethylsilyl)oxy)-2-phenylacetate S3



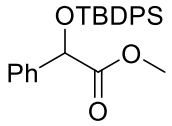
In flame-dried glassware under an Ar atmosphere, methyl mandelate (4.90 g, 29.5 mmol) was dissolved in anhydrous CH_2Cl_2 (29.5 mL) and 2,6-dimethylpyridine (6.88 mL, 59.0 mmol) was added. The resultant solution was cooled to 0 °C and TBSOTf (10.2 mL, 44.3 mmol) was added dropwise. Once addition was complete, the reaction mixture was warmed to rt and stirred for 1 h. The reaction mixture was quenched with 1 M HCl (30 mL) and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic extracts were washed with 1 M HCl (30 mL) then brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography (100% to 95/5 cyclohexane/Et_2O) to give the title compound **S3** (8.16 g, 99%) as a colourless liquid. ν_{max} (liquid) 2954 (C-H aromatic), 2930 (C-H alkane), 2858 (C-H alkane), 1759 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.48 (d, J = 7.4, 2H, ArC*H*), 7.23 – 7.39 (m, 3H, ArC*H*), 5.25 (s, 1H, C(2)*H*), 3.69 (s, 3H, CH_3), 0.93 (s, 9H, C(CH_3)$_3$), 0.11 (s, 3H, SiCH_3), 0.04 (s, 3H, SiCH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 172.8 (*C*(1)), 139.3 (Ar*C*(1)), 128.5 (ArC(2,6)), 128.2 (ArC(4)), 126.5 (ArC(3,5)), 74.6 (*C*(2)), 52.3 (O*C*H$_3$), 25.9 (C(*C*H$_3$)$_3$), 18.5 (*C*(CH$_3$)$_3$), -5.0 (Si*C*H$_3$), -5.0 (Si*C*H$_3$); HRMS (ESI$^+$) *m/z*: $[M+H]^+$ calcd for $C_{15}H_{25}O_3Si$ 281.1573, found 281.1571.

Methyl 2-phenyl-2-((triisopropylsilyl)oxy)acetate S4



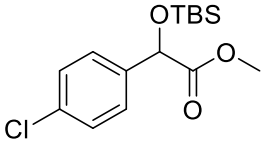
Methyl mandelate (0.332 g, 2.00 mmol) was dissolved in CH_2Cl_2 (5 mL) and imidazole (0.184 g, 2.70 mmol) then TIPS chloride (0.53 mL, 2.50 mmol) was added. The reaction mixture was stirred at rt for 18 h. The reaction mixture was diluted with H_2O (20 mL) and extracted with Et_2O (3 × 20 mL). The combined organic extracts were washed with H_2O (20 mL) then brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography (100% PhMe) to give the title compound **S4** (0.338 g, 52%) as a colourless oil. ν_{max} (liquid) 2945 (C-H aromatic), 2887 (C-H alkane), 1760 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.54 – 7.46 (m, 2H, ArC(2,6)*H*), 7.38 – 7.24 (m, 3H, ArC*H*), 5.32 (s, 1H, C(2)*H*), 3.67 (s, 3H, OC*H*$_3$), 1.19 – 1.08 (m, 3H, SiC*H*), 1.08 – 0.98 (m, 18H, SiCH(C*H*$_3$)$_2$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8 (*C*(1)), 139.6 (Ar*C*(1)), 128.4 (Ar*C*(2,6)), 128.2 (Ar*C*(4)), 126.5 (Ar*C*(3,5)), 74.7 (*C*(2)), 52.2 (O*C*H$_3$), 17.9 (SiCH(*C*H$_3$)$_2$), 17.9 (SiCH(*C*H$_3$)$_2$), 12.2 (Si*C*H(CH$_3$)$_2$); HRMS (ESI$^+$) *m/z*: $[M+Na]^+$ calcd for $C_{18}H_{30}O_3SiNa$ 345.1862, found 345.1873.

Methyl 2-((*tert*-butyldiphenylsilyl)oxy)-2-phenylacetate S5



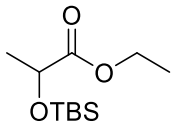
Methyl mandelate **S1** (0.332 g, 2.00 mmol) was dissolved in DMF (4 mL) and imidazole (0.340 g, 5.00 mmol) then TBDPS chloride (1.04 mL, 4.00 mmol) was added. The reaction mixture was stirred at rt for 3 h then diluted with Et_2O (20 mL). The organic solution was washed with 0.1 M HCl (20 mL), H_2O (2 × 20 mL) and brine. The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography (100% PhMe) to give the title compound **S5** (0.572 g, 71%) as a colourless oil. ν_{max} (liquid) 2952 (C-H aromatic), 2932 (C-H alkane), 2858 (C-H alkane), 1756 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.80 – 7.72 (m, 2H, Si-ArC(2,6)*H*), 7.58 – 7.52 (m, 2H, ArC*H*), 7.50 – 7.38 (m, 6H, ArC*H*), 7.37 – 7.28 (m, 5H, ArC*H*), 5.19 (s, 1H, C(2)*H*), 3.50 (s, 3H, OCH_3), 1.15 (s, 9H, C(CH_3)$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 172.3 (*C*(1)), 139.0 (C(2)-Ar*C*(1)), 136.0 (Si-Ar*C*(2,6)), 135.8 (Si-Ar*C*(2,6)), 133.1 (Si-Ar*C*(1)), 132.9 (Si-Ar*C*(1)), 130.0 (Si-Ar*C*(4)), 129.9 (Si-Ar*C*(4)), 128.5 (C(2)-Ar*C*(2,6)), 128.3 (C(2)-Ar*C*(4)), 127.8 (Si-Ar*C*(3,5)), 127.7 (Si-Ar*C*(3,5)), 126.7 (C(2)-Ar*C*(3,5)), 75.0 (*C*(2)), 52.0 (O*C*H$_3$), 27.1 (C(*C*H$_3$)$_3$), 19.5 (*C*(CH$_3$)$_3$); HRMS (ESI$^+$) *m/z*: $[M+Na]^+$ calcd for $C_{25}H_{28}O_3SiNa$ 427.1705, found 427.1729.

Methyl 2-((*tert*-butyldimethylsilyl)oxy)-2-(4-chlorophenyl)acetate S6



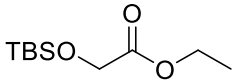
Methyl 2-(4-chlorophenyl)-2-hydroxyacetate **S2** (1.98 g, 9.85 mmol) was dissolved in CH_2Cl_2 (20 mL) and TBSCl (2.23 g, 14.8 mmol) and imidazole (1.34 g, 19.7 mmol) was added. The reaction mixture was stirred for 18 h at rt. The reaction mixture was diluted with CH_2Cl_2 (10 mL) and washed with H_2O (2 × 20 mL) and brine. The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography (100 to 95/5 cyclohexane/Et_2O) to give the title compound **S6** (2.91 g, 94%) as a colourless oil. ν_{max} (liquid) 2953 (C-H aromatic), 2930 (C-H alkane), 2858 (C-H alkane), 1759 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.1 Hz, 2H, ArC(3,5)*H*), 7.31 (d, *J* = 8.1 Hz, 2H, ArC(2,6)*H*), 5.20 (s, 1H, C(2)*H*), 3.69 (s, 3H, OCH_3), 0.91 (s, 9H, C(CH_3)$_3$), 0.11 (s, 3H, SiCH_3), 0.04 (s, 3H, SiCH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.3 (C(1)), 137.8 (Ar*C*(1)), 134.1 (Ar*C*(4)), 128.7 (Ar*C*(2,6)), 127.9 (Ar*C*(3,5)), 73.9 (C(*2*)), 52.5 (O*C*H$_3$), 25.8 (C(*C*H$_3$)$_3$), 18.5 (*C*(CH$_3$)$_3$), -5.0 (Si*C*H$_3$), -5.1 (Si*C*H$_3$); HRMS (ESI$^+$) *m/z*: $[M+H]^+$ calcd for $C_{15}H_{24}ClO_3Si$ 315.1183, found 315.1174.

Ethyl 2-((*tert*-butyldimethylsilyl)oxy)propanoate S7



Ethyl lactate (2.29 mL, 20 mmol) was dissolved in CH_2Cl_2 (40 mL) and TBSCl (2.72 g, 40 mmol) and imidazole (4.52 g, 30 mmol) was added. The resultant mixture was stirred for 18 h at rt. The reaction mixture was washed with H_2O (50 mL) and the aqueous layer was extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography (100 to 98/2 cyclohexane/Et_2O) to give the title compound **S7** (4.51 g, 97%) as a colourless liquid, with spectroscopic data in accordance with the literature.[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 4.30 (q, J = 6.8, 1H, C(2)H), 4.24 – 4.09 (m, 2H, C(5)H_2), 1.39 (d, J = 6.8 Hz, 3H, C(1)H_3), 1.27 (t, J = 7.1 Hz, 3H, C(6)H_3), 0.90 (s, 9H, C(CH_3)$_3$), 0.10 (s, 3H, SiCH_3), 0.07 (s, 3H, SiCH_3).

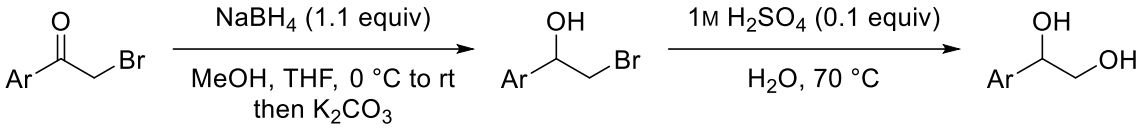
Ethyl 2-((*tert*-butyldimethylsilyl)oxy)acetate S8



Ethyl glycolate (0.95 mL, 10.0 mmol) was dissolved in CH_2Cl_2 (20 mL) and imidazole (1.36 g, 20.0 mmol) and TBSCl (2.26 g, 15.0 mmol) was added. The reaction mixture was stirred at rt for 1 h. The reaction mixture was washed with 1 M HCl (20 mL), and the aqueous layer was extracted with CH_2Cl_2 (2 × 20 mL). The combined organic extracts were was with H_2O (20 mL) then brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude oil was purified by silica gel column chromatography (CombiFlash, 40 g silver column, 100% cyclohexane 1 CV, to 10% Et_2O 10 CV, to 100% Et_2O 3 CV) to give the title compound **S8** (1.72 g, 79%) as a colourless oil, with spectroscopic data in accordance with the literature.[4] ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 4.23 – 4.16 (m, 4H, C(2)H_2 + OCH_2CH$_3$), 1.27 (t, J = 7.1 Hz, 3H, OCH$_2$CH_3), 0.92 (s, 9H, C(CH_3)$_3$), 0.10 (s, 6H, 2 × SiCH_3).

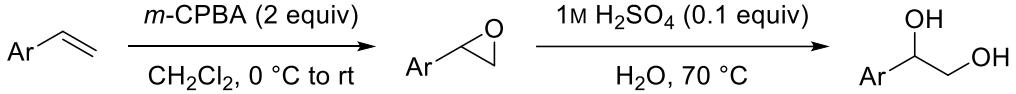
1,2-Diols

General Procedure A



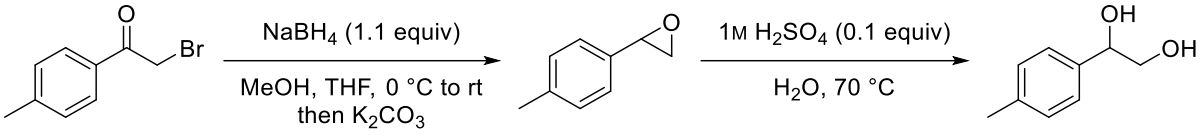
α-Bromoketones to Diols: $NaBH_4$ (1.1 equiv) was added portionwise to a stirred solution of the requisite α-bromoketone (1 equiv, 0.4 M in MeOH, with THF added as necessary to homogenise the mixture) at 0 ºC and the resultant mixture was stirred at this temperature until effervescence had ceased. The reaction mixture was then allowed to warm to rt over 2.5 h and K_2CO_3 (1 equiv) was added. The resultant mixture was stirred at rt for 18 h and was then concentrated under reduced pressure. The residue was partitioned between Et_2O and H_2O and the layers were separated. The aqueous layer was extracted twice with Et_2O and the combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude oil was used in the next step without further purification. The oil was dissolved in H_2O (0.5 M) and 1 M H_2SO_4 (10 mol%) was added and the resultant mixture was heated to 70 °C. The reaction mixture was stirred for 2 h or until the epoxide was no longer visible by TLC. The reaction mixture was allowed to cool to rt and extracted three times with EtOAc. The combined organic extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by silica-gel column chromatography (gradient 9:1 PE:EtOAc to 4:6 PE:EtOAc).

General Procedure B



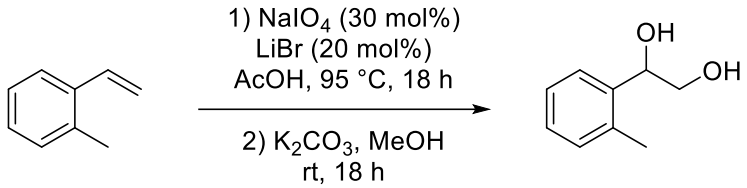
Dihydroxylation of styrenes: *m*-CPBA (2 equiv) was added in two portions to a stirred solution of the requisite alkene (1 equiv, 0.2 M in CH_2Cl_2) at 0 ºC over 2 h. The resultant mixture was allowed to slowly warm to rt and stirred at rt for 18 h or until the alkene was no longer visible by TLC. The reaction mixture was washed with sat. Na_2SO_3 solution then two times with sat. $NaHCO_3$ solution. The combined aqueous layers were extracted twice with CH_2Cl_2 and the combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude oil was used in the next step without further purification. The oil was dissolved in H_2O (0.5 M) and 1 M H_2SO_4 (10 mol%) was added and the resultant mixture was heated to 70 °C. The reaction mixture was stirred for 2 h or until the epoxide was no longer visible by TLC. The reaction mixture was allowed to cool to rt and extracted three times with EtOAc. The combined organic extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by silica-gel column chromatography (gradient 9:1 PE:EtOAc to 4:6 PE:EtOAc) to give the desired 1,2-diol.

1-(*p*-Tolyl)ethane-1,2-diol S9



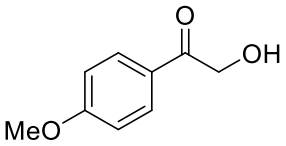
Following General Procedure A, 2-bromo-1-(*p*-tolyl)ethan-1-one (1.278 g, 6.00 mmol), $NaBH_4$ (0.250 g, 6.60 mmol), and K_2CO_3 (0.829 g, 6.00 mmol) were reacted in MeOH (15 mL) and THF (10 mL). Following aqueous extraction, the crude residue was reacted in H_2O (10 mL) with 1 M H_2SO_4 (0.60 mL, 0.60 mmol) to give the title compound **S9** (0.437 g, 49%) as a white solid, with spectroscopic data in accordance with the literature.[5] mp 76–78 °C {Lit[6] 76–77 °C}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.26 (d, *J* = 8.0 Hz, 2H, ArC(2,6)*H*), 7.18 (d, *J* = 8.0 Hz, 2H, ArC(3,5)*H*), 4.80 (ddd, *J* = 7.6, 3.5, 3.5 Hz, 1H, C(1)*H*), 3.75 (ddd, *J* = 11.3, 7.4, 3.7 Hz, 1H, C(2)*H*), 3.67 (ddd, *J* = 11.3, 8.1, 4.6 Hz, 1H, C(2)*H*), 2.45 – 2.42 (m, 1H, C(1)O*H*), 2.35 (s, 3H, ArC(4)CH_3), 2.08 – 1.97 (m, 1H, C(2)O*H*).

1-(*o*-Tolyl)ethane-1,2-diol S10



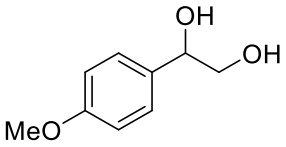
2-methylstyrene (0.65 mL, 5.00 mmol) was dissolved in glacial acetic acid (8.33 mL) and $NaIO_4$ (0.321 g, 1.50 mmol) and LiBr (0.0868 g, 1.00 mmol) were added. The reaction mixture was heated to 95 °C and stirred from 18 h. The reaction mixture changed from yellow to purple, indicating that the reaction was complete. The reaction mixture was cooled to rt, diluted with H_2O (50 mL) and extracted with EtOAc (3 × 50 mL). The combined organic extracts were washed with sat $Na_2S_2O_3$ solution, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was used without further purification. The residue was dissolved in MeOH (30 mL) and K_2CO_3 (1.04 g, 7.50 mmol) was added. The resultant mixture was stirred for 18 h at rt. The reaction mixture was concentrated under reduced pressure and dissolved in H_2O (50 mL). The aqueous solution was extracted with EtOAc (3 × 50 mL). The combined organic extracts were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was purified by silica-gel column chromatography (9:1 PE:EtOAc to 4:6 PE:EtOAc) to give the title compound **S10** (0.370 g, 49%) as a white solid, with spectroscopic data in accordance with the literature.[5] mp 108–110 °C {Lit[5] 104–105 °C}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.50 (dd, *J* = 7.4, 1.7 Hz, 1H, ArC(3)*H*), 7.25 – 7.13 (m, 3H, ArC*H*), 5.08 (ddd, *J* = 8.4, 3.3, 3.2 Hz, 1H, C(1)*H*), 3.74 (ddd, *J* = 11.0, 7.5, 3.3 Hz, 1H, C(2)*H*), 3.62 (ddd, *J* = 11.0, 8.4, 4.0 Hz, 1H, C(2)*H*), 2.40 (d, *J* = 3.2 Hz, 1H, C(1)O*H*), 2.35 (s, 3H, ArC(2)CH_3), 2.12 (dd, *J* = 7.5, 4.0 Hz, 1H, C(2)O*H*).

2-Hydroxy-1-(4-methoxyphenyl)ethan-1-one S11



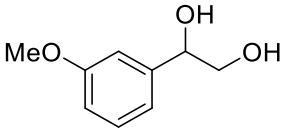
Potassium formate (1.26 g, 15.0 mmol) was dissolved in EtOH (50 mL) and stirred at rt for 15 min. 2-Bromo-1-(4-methoxyphenyl)ethan-1-one (1.15 g, 5.00 mmol) was added and the reaction mixture was heated to 70 °C for 16 h. The reaction mixture was cooled to rt and concentrated under reduced pressure. The residue was partitioned between EtOAc (30 mL) and H_2O (30 mL). The aqueous layer was extracted with EtOAc (2 × 30 mL), and the combined organics were washed with brine and dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography (9:1 to 7:3 PE:EtOAc) to give 0.340 g white solid. The solid was recrystalised from EtOH to give the title compound **S11** (0.283 g, 34%) as white crystals, with spectroscopic data in accordance with the literature.[7] mp 101–102 °C (EtOH) {Lit[7] 104–105 °C}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.90 (d, *J* = 8.9 Hz, 2H, ArC(2,6)*H*), 6.97 (d, *J* = 8.9 Hz, 2H, ArC(3,5)*H*), 4.82 (d, *J* = 4.5 Hz, 2H, C(2)*H*), 3.89 (s, 3H, OC*H*$_3$), 3.56 (t, *J* = 4.6 Hz, 1H, O*H*).

1-(4-Methoxyphenyl)ethane-1,2-diol S12



2-Hydroxy-1-(4-methoxyphenyl)ethan-1-one (0.283 g, 1.70 mmol) was dissolved in THF (6.8 mL) and H_2O (1.7 mL) and cooled to 0 °C. $NaBH_4$ (0.0774 g, 2.05 mmol) was added and stirred at 0 °C until effervescence ceased. The reaction mixture was warmed to rt and stirred for 3 h. Sat. NH_4Cl solution (20 mL) was added and the resultant mixture was extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give the title compound **S12** (0.253 g, 88%) as a white solid, with spectroscopic data in accordance with the literature.[5] mp 78–79 °C {Lit[5] 78–79 °C}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.29 (app d, *J* = 8.8 Hz, 2H, ArC(2,6)*H*), 6.89 (app d, *J* = 8.8 Hz, 2H, ArC(3,5)*H*), 4.78 (dd, *J* = 8.2, 3.7 Hz, 1H, C(1)*H*), 3.81 (s, 3H, OC*H*$_3$), 3.77 – 3.61 (m, 2H, C(2)*H*), 2.45 (br s, 1H, C(1)O*H*), 2.07 (br s, 1H, C(2)O*H*).

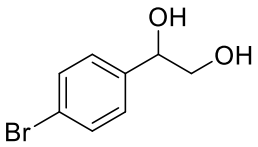
1-(3-Methoxyphenyl)ethane-1,2-diol S13



Following General Procedure A, 2-bromo-1-(3-methoxyphenyl)ethan-1-one (1.37 g, 6.00 mmol), $NaBH_4$ (0.250 g, 6.60 mmol), and K_2CO_3 (0.829 g, 6.00 mmol) were reacted in MeOH (15 mL) and THF (5 mL). Following aqueous extraction, the crude residue was reacted in H_2O (12 mL) with 1 M H_2SO_4 (0.60 mL, 0.60 mmol). The crude residue was recrystallised from

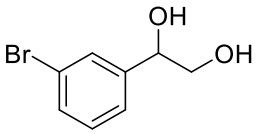
Et_2O to give the title compound **S13** (0.651 g, 65%) as a colourless solid, with spectroscopic data in accordance with the literature.[8] mp 67–69 °C (Et_2O) {Lit[8] 67.2–67.8 °C}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.26 (d, *J* = 8.2 Hz, 1H, ArC(5)*H*), 6.93 – 6.88 (m, 2H, ArC*H*), 6.81 (ddd, *J* = 8.2, 2.5, 1.0 Hz, 1H, ArC(4)*H*), 4.78 (dd, *J* = 8.1, 3.5 Hz, 1H, C(1)*H*), 3.78 (s, 3H, OC*H*$_3$), 3.77 – 3.70 (m, 1H, C(2)*H*), 3.68 – 3.60 (m, 1H, C(2)*H*), 2.50 (br s, 1H, C(1)O*H*), 2.03 (s, 1H, C(2)O*H*).

1-(4-Bromophenyl)ethane-1,2-diol S14



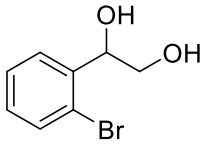
Following General Procedure B, 4-bromostyrene (0.52 mL, 4.00 mmol) was reacted with *m*-CPBA (1.38 g, 8.00 mmol) in CH_2Cl_2 (20 mL). Following aqueous extraction, the crude residue was reacted in H_2O (8 mL) with 1 M H_2SO_4 (0.40 mL, 0.40 mmol) to give the title compound **S14** (0.258 g, 30%) as a white solid, with spectroscopic data in accordance with the literature.[5] mp 96–98 °C {Lit[5] 100–101 °C}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.36 – 7.27 (m, 4H, ArC*H*), 4.81 (dd, *J* = 8.2, 3.5 Hz, 1H, C(1)*H*), 3.75 (dd, *J* = 11.3, 3.5 Hz, 1H, C(2)*H*), 3.62 (dd, *J* = 11.3, 8.2 Hz, 1H, C(2)*H*), 2.67 (br s, 1H, C(1)O*H*), 2.14 (br s, 1H, C(2)O*H*).

1-(3-Bromophenyl)ethane-1,2-diol S15



Following General Procedure B, 3-bromostyrene (0.78 mL, 6.00 mmol) was reacted with *m*-CPBA (2.07 g, 12.0 mmol) in CH_2Cl_2 (30 mL). Following aqueous extraction, the crude residue was reacted in H_2O (10 mL) with 1 M H_2SO_4 (0.60 mL, 0.60 mmol) to give the title compound **S15** (0.534 g, 41%) as an off-white solid. mp 58–60 °C; ν_{max} (solid) 3200 (O-H), 2916 (C-H aromatic), 2872 (C-H alkane), 1568 (C=C aromatic); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.52 (s, 1H, ArC(4)*H*), 7.41 (m, 1H, ArC(2)*H*), 7.30 – 7.17 (m, 2H, ArC*H*), 4.77 (m, 1H, C(1)*H*), 3.75 (m, 1H, C(2)*H*), 3.61 (m, 1H, C(2)*H*), 2.59 (d, *J* = 3.3 Hz, 1H, C(1)O*H*)), 2.07 – 1.99 (m, 1H, C(2)O*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 143.0 (Ar*C*(1)), 131.2 (Ar*C*(2)), 130.3 (Ar*C*(4)), 129.3 (Ar*C*(5)), 124.8 (Ar*C*(6)), 122.9 (Ar*C*(3)), 74.1 (*C*(1)), 68.1 (*C*(2)); HRMS (ESI+) m/z: [M+Na]+ calcd for $C_8H_9BrO_2Na$ 238.9684, found 238.9678.

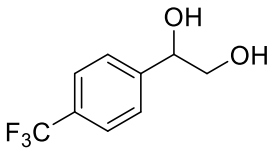
1-(2-Bromophenyl)ethane-1,2-diol S16



Following General Procedure B 2-bromostyrene (0.75 mL, 6.00 mmol) and *m*-CPBA (2.07 g, 12.0 mmol) were reacted in CH_2Cl_2 (12 mL). Following aqueous extraction, the crude residue was reacted in H_2O (10 mL) with 1 M H_2SO_4 (0.60 mL, 0.60 mmol) to give the title compound

S16 (0.998 g, 77%) as a white solid, with spectroscopic data in accordance with the literature.[8] mp 112–113 °C {Lit[8] 118.9–119.2 °C}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.59 (dd, *J* = 7.7, 1.5 Hz, 1H, ArC(3)*H*), 7.53 (dd, *J* = 8.0, 1.6 Hz, 1H, ArC(6)*H*), 7.35 (ddd, *J* = 8.0, 7.7, 1.5 Hz, 1H, ArC(5)*H*), 7.16 (ddd, *J* = 7.7, 7.7, 1.6 Hz, 1H, ArC(4)*H*), 5.20 (dd, *J* = 7.9, 3.0 Hz, 1H, C(1)*H*), 3.92 (dd, *J* = 11.5, 3.0 Hz, 1H, C(2)*H*), 3.57 (dd, *J* = 11.5, 7.9 Hz, 1H, C(2)*H*), 2.68 (br s, 1H, C(1)O*H*), 2.07 (br s, 1H, C(2)O*H*).

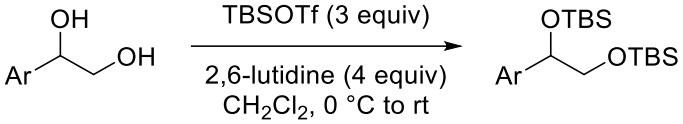
1-(4-(Trifluoromethyl)phenyl)ethane-1,2-diol S17



Following General Procedure A, 2-bromo-1-(4-(trifluoromethyl)phenyl)ethan-1-one (1.60 g, 6.00 mmol), $NaBH_4$ (0.250 g, 6.60 mmol), and K_2CO_3 (0.829 g, 6.00 mmol) were reacted in MeOH (15 mL). Following aqueous extraction, the crude residue was reacted in H_2O (12 mL) with 1 M H_2SO_4 (0.60 mL, 0.60 mmol). The crude residue was recrystallised with Et_2O to give the title compound **S17** (0.704 g, 57%) as a colourless solid, with spectroscopic data in accordance with the literature.[9] mp 113–115 °C (Et_2O) {Lit[9] 98–100 °C}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.63 (d, *J* = 7.9 Hz, 2H, ArC(3,5)*H*), 7.51 (d, *J* = 7.9 Hz, 2H, ArC(2,6)*H*), 4.91 (ddd, *J* = 8.0, 6.8, 3.4 Hz, 1H, C(1)*H*), 3.82 (ddd, *J* = 10.7, 6.8, 3.5 Hz, 1H, C(2)*H*), 3.65 (ddd, *J* = 11.2, 8.0, 4.8 Hz, 1H, C(2)*H*), 2.63 (d, *J* = 3.4 Hz, 1H, C(1)O*H*), 2.00 (dd, *J* = 6.8, 4.8 Hz, 1H, C(2)O*H*); ^{19}F NMR (376 MHz, $CDCl_3$) δ_F: -62.57.

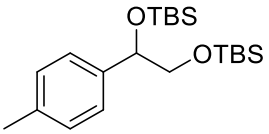
1,2-Disilyl Ethers

General Procedure C



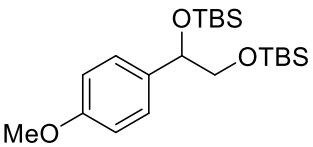
TBS triflate protection: Under an argon atmosphere in flame-dried glassware, the requisite 1,2-diol was dissolved in anhydrous CH_2Cl_2 (1 M) and 2,6-dimethylpyridine (4 equiv) was added. The resultant mixture was cooled to 0 °C and TBS triflate (3 equiv) was added dropwise. The reaction mixture was stirred for 1 h or until the 1,2-diol was no longer visible by TLC. 1 M HCl was added (0.1 M) and the reaction mixture was extracted with CH_2Cl_2 3 times. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude oil was purified by silica-gel column chromatography (100% to 96/4 cyclohexane/Et_2O) to give the desired 1,2-disilyl ether.

2,2,3,3,8,8,9,9-Octamethyl-5-(*p*-tolyl)-4,7-dioxa-3,8-disiladecane S18



Following General Procedure , 1-(*p*-Tolyl)ethane-1,2-diol **S9** (0.509 g, 3.34 mmol) was dissolved in anhydrous CH_2Cl_2 (3.34 mL) and reacted with 2,6-dimethylpyridine (2.30 mL, 10.0 mmol) and TBS triflate (1.56 mL, 13.4 mmol) to give the title compound **S18** (0.546 g, 43%) as a colourless oil. ν_{max} (liquid) 2954 (C-H aromatic), 2928 (C-H alkane), 2856 (C-H alkane); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.22 (d, J = 8.0 Hz, 2H, ArC(2,6)*H*), 7.11 (d, J = 8.0 Hz, 2H, ArC(3,5)*H*), 4.68 (dd, J = 7.3, 4.7 Hz, 1H, C(5)*H*), 3.63 (dd, J = 10.2, 7.3 Hz, 1H, C(6)*H*), 3.52 (dd, J = 10.2, 4.8 Hz, 1H, C(6)*H*), 2.33 (s, 3H, ArC(4)C*H*$_3$), 0.88 (s, 9H, C(C*H*$_3$)$_3$), 0.87 (s, 9H, C(C*H*$_3$)$_3$), 0.06 (s, 3H, SiC*H*$_3$), -0.02 (s, 3H, SiC*H*$_3$), -0.03 (s, 3H, SiC*H*$_3$), -0.05 (s, 3H, SiC*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 139.9 (Ar*C*(1)), 136.8 (Ar*C*(4)), 128.7 (Ar*C*(3,5)), 126.5 (Ar*C*(2,6)), 76.2 (*C*(5)), 70.3 (*C*(6)), 26.2 (C(*C*H$_3$)$_3$), 26.0 (C(*C*H$_3$)$_3$), 21.3 (ArC(4)-*C*H$_3$), 18.6 (*C*(CH$_3$)$_3$), 18.5 (*C*(CH$_3$)$_3$), -4.5 (Si*C*H$_3$), -4.6 (Si*C*H$_3$), -5.2 (Si*C*H$_3$), -5.3 (Si*C*H$_3$); HRMS (ESI$^+$) *m/z*: $[M+Na]^+$ calcd for $C_{21}H_{40}O_2Si_2Na$ 403.2465, found 403.2460.

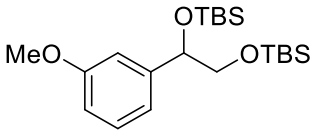
5-(4-Methoxyphenyl)-2,2,3,3,8,8,9,9-octamethyl-4,7-dioxa-3,8-disiladecane S19



Following General Procedure C, 1-(4-methoxyphenyl)ethane-1,2-diol **S12** (0.253 g, 1.50 mmol) was dissolved in anhydrous CH_2Cl_2 (1.50 mL) and reacted with 2,6-dimethylpyridine (0.71 mL, 6.01 mmol) and TBS triflate (1.04 mL, 4.51 mmol) to give the title compound **S19** (0.452 g, 76%) as a colourless oil. ν_{max} (liquid) 2954 (C-H aromatic), 2929 (C-H alkane), 2856 (C-H alkane); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.25 – 7.20 (app d, J = 8.7 Hz, 2H, ArC(2,6)*H*),

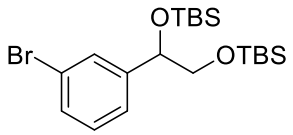
6.82 (app d, *J* = 8.7 Hz, 2H, ArC(3,5)*H*), 4.62 (dd, *J* = 7.2, 5.0 Hz, 1H, C(5)*H*), 3.77 (s, 3H, OCH_3), 3.61 (dd, *J* = 10.2, 7.2 Hz, 1H, C(6)*H*), 3.48 (dd, *J* = 10.2, 5.0 Hz, 1H, C(6)*H*), 0.85 (s, 9H, C(CH_3)$_3$), 0.84 (s, 9H, C(CH_3)$_3$), 0.03 (s, 3H, SiCH_3), -0.05 (s, 3H, SiCH_3), -0.07 (s, 3H, SiCH_3), -0.09 (s, 3H, SiCH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 158.9 (Ar*C*(4)), 135.1 (Ar*C*(1)), 127.7 (Ar*C*(2,6)), 113.4 (Ar*C*(3,5)), 75.8 (*C*(5)), 70.2 (*C*(6)), 55.4 (O*C*H$_3$), 26.1 (C(*C*H$_3$)$_3$), 26.0 (C(*C*H$_3$)$_3$), 18.6 (*C*(CH$_3$)$_3$), 18.5 (*C*(CH$_3$)$_3$), -4.5 (Si*C*H$_3$), -4.6 (Si*C*H$_3$), -5.2 (Si*C*H$_3$), -5.3 (Si*C*H$_3$); HRMS (ESI$^+$) *m/z*: $[M+Na]^+$ calcd for $C_{21}H_{40}O_3Si_2Na$ 419.2414, found 419.2411.

5-(3-Methoxyphenyl)-2,2,3,3,8,8,9,9-octamethyl-4,7-dioxa-3,8-disiladecane S20



Following General Procedure C, 1-(3-methoxyphenyl)ethane-1,2-diol **S13** (0.651 g, 3.87 mmol), TBS triflate (2.67 mL, 11.6 mmol), and 2,6-dimethylpyridine (1.80 mL, 15.5 mmol) were reacted in anhydrous CH_2Cl_2 (3.87 mL) to give the title compound **S20** (1.40 g, 91%) as a colourless oil. ν_{max} (liquid) 2954 (C-H aromatic), 2928 (C-H alkane), 2857 (C-H alkane); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.20 (dd, *J* = 8.2, 7.5 Hz, 1H, ArC(5)*H*), 6.95 – 6.87 (m, 2H, ArC(2)*H*, ArC(6)*H*), 6.78 (ddd, *J* = 8.2, 2.7, 1.0 Hz, 1H, ArC(4)*H*), 4.68 (dd, *J* = 7.1, 4.9 Hz, 1H, C(5)*H*), 3.80 (s, 3H, OCH_3), 3.64 (dd, *J* = 10.2, 7.1 Hz, 1H, C(6)*H*), 3.54 (dd, *J* = 10.2, 4.9 Hz, 1H, C(6)*H*), 0.89 (s, 9H, C(CH_3)$_3$), 0.86 (s, 9H, C(CH_3)$_3$), 0.06 (s, 3H, SiCH_3), -0.03 – -0.08 (m, 9H, 3 × SiCH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 159.5 (Ar*C*(3)), 144.6 (Ar*C*(1)), 129.0 (Ar*C*(5)), 119.0 (Ar*C*(6)), 113.0 (Ar*C*(4)), 111.9 (Ar*C*(2)), 76.3 (*C*(5)), 70.2 (*C*(6)), 55.3 (O*C*H$_3$), 26.1 (C(*C*H$_3$)$_3$), 25.9 (C(*C*H$_3$)$_3$), 18.6 (*C*(CH$_3$)$_3$), 18.5 (*C*(CH$_3$)$_3$), -4.5 (Si*C*H$_3$), -4.7 (Si*C*H$_3$), -5.1 (Si*C*H$_3$), -5.2 (Si*C*H$_3$); HRMS (ESI$^+$) *m/z*: $[M+Na]^+$ calcd for $C_{21}H_{40}O_3Si_2Na$ 419.2414, found 419.2411.

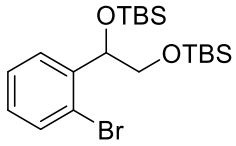
5-(3-Bromophenyl)-2,2,3,3,8,8,9,9-octamethyl-4,7-dioxa-3,8-disiladecane S21



Following General Procedure C, 1-(3-bromophenyl)ethane-1,2-diol **S15** (0.534 g, 2.46 mmol), TBS triflate (1.70 mL, 7.39 mmol), and 2,6-dimethylpyridine (1.15 mL, 9.85 mmol) were reacted in anhydrous CH_2Cl_2 to give the title compound **S21** (1.03 g, 94%) as a colourless oil. ν_{max} (liquid) 2954 (C-H aromatic), 2929 (C-H alkane), 2857 (C-H alkane); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.49 (t, *J* = 1.7 Hz, 1H, ArC(2)*H*), 7.37 (dt, *J* = 7.9, 1.7 Hz, 1H, ArC(4)*H*), 7.31 – 7.23 (m, 1H, ArC(6)*H*), 7.17 (dd, *J* = 7.9, 7.8 Hz, 1H, ArC(5)*H*), 4.64 (dd, *J* = 6.6, 5.7 Hz, 1H, C(5)*H*), 3.65 (dd, *J* = 10.1, 6.6 Hz, 1H, C(6)*H*), 3.48 (dd, *J* = 10.1, 5.7 Hz, 1H, C(6)*H*), 0.88 (s, 9H, C(CH_3)$_3$), 0.85 (s, 9H, C(CH_3)$_3$), 0.06 (s, 3H, SiCH$_3$), -0.02 – -0.10 (m, 9H, 3 × SiCH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 145.5 (Ar*C*(1)), 130.4 (Ar*C*(2)), 129.8 (Ar*C*(4)), 129.6 (Ar*C*(5)), 125.2 (Ar*C*(6)), 122.1 (Ar*C*(3)), 75.4 (*C*(5)), 69.7 (*C*(6)), 26.1 (C(*C*H$_3$)$_3$), 26.0

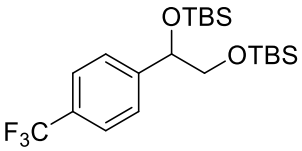
(C(*C*H$_3$)$_3$), 18.5 (*C*(CH$_3$)$_3$), 18.4 (*C*(CH$_3$)$_3$), -4.6 (Si*C*H$_3$), -4.7 (Si*C*H$_3$), -5.3 (Si*C*H$_3$), -5.4 (Si*C*H$_3$); HRMS (ESI+) m/z: [M+Na]+ calcd for $C_{20}H_{37}BrO_2Si_2Na$ 469.1393, found 469.1406.

5-(2-Bromophenyl)-2,2,3,3,8,8,9,9-octamethyl-4,7-dioxa-3,8-disiladecane S22



Following General Procedure C, 1-(2-bromophenyl)ethane-1,2-diol **S16** (0.998 g, 4.60 mmol) was dissolved in anhydrous CH_2Cl_2 (4.60 mL) and reacted with 2,6-dimethylpyridine (2.14 mL, 18.4 mmol) and TBS triflate (3.17 mL) to give the title compound **S22** (1.86 g, 91%) as a colourless liquid. ν_{max} (liquid) 2954 (C-H aromatic), 2929 (C-H alkane), 2857 (C-H alkane); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.56 (dd, *J* = 7.8, 1.8 Hz, 1H, ArC(3)*H*), 7.48 (dd, *J* = 8.0, 1.2 Hz, 1H, ArC(6)*H*), 7.30 (ddd, *J* = 7.8, 7.6, 1.2 Hz, 1H, ArC(4)*H*), 7.10 (ddd, *J* = 8.0, 7.6, 1.8 Hz, 1H, ArC(5)*H*), 5.12 (dd, *J* = 7.4, 3.4 Hz, 1H, C(5)*H*), 3.68 (dd, *J* = 10.4, 3.4 Hz, 1H, C(6)*H*), 3.53 (dd, *J* = 10.4, 7.4 Hz, 1H, C(6)*H*), 0.88 (s, 18H, 2 × C(C*H*$_3$)$_3$), 0.08 (s, 3H, SiC*H*$_3$), 0.02 (s, 3H, SiC*H*$_3$), 0.01 (s, 3H, SiC*H*$_3$), -0.03 (s, 3H, SiC*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 141.6 (Ar*C*(1)), 132.3 (Ar*C*(6)), 129.0 (Ar*C*(3)), 128.8 (Ar*C*(5)), 127.4 (Ar*C*(4)), 122.14 (Ar*C*(2)), 75.2 (*C*(5)), 68.6 (*C*(6)), 26.2 (C(*C*H$_3$)$_3$), 26.0 (C(*C*H$_3$)$_3$), 18.6 (*C*(CH$_3$)$_3$), 18.5 (*C*(CH$_3$)$_3$), -4.5 (Si*C*H$_3$), -4.8 (Si*C*H$_3$), -5.1 (Si*C*H$_3$), -5.2 (Si*C*H$_3$); HRMS (ESI$^+$) *m/z*: [M+Na]$^+$ calcd for $C_{20}H_{37}BrO_2Si_2Na$ 469.1393, found 469.1390.

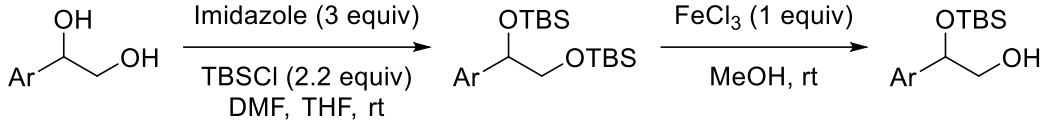
2,2,3,3,8,8,9,9-Octamethyl-5-(4-(trifluoromethyl)phenyl)-4,7-dioxa-3,8-disiladecane S23



Following General Procedure C, 1-(4-(trifluoromethyl)phenyl)ethane-1,2-diol **S17** (0.704 g, 3.41 mmol), TBS triflate (2.35 mL, 10.2 mmol), and 2,6-dimethylpyridine (1.59 mL, 13.6 mmol) were reacted in CH_2Cl_2 (3.41 mL) to give the title compound **S23** (1.32 g, 89%) as a colourless oil. ν_{max} (liquid) 2956 (C-H aromatic), 2930 (C-H alkane), 2859 (C-H alkane); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.57 (d, *J* = 8.3 Hz, 2H, ArC(3,5)*H*), 7.46 (d, *J* = 8.3 Hz, 2H, ArC(2,6)*H*), 4.74 (d, *J* = 6.6, 5.7 Hz, 1H, C(5)*H*), 3.68 (dd, *J* = 10.1, 6.6 Hz, 1H, C(6)*H*), 3.51 (dd, *J* = 10.1, 5.7 Hz, 1H, C(6)*H*), 0.89 (s, 9H, C(C*H*$_3$)$_3$), 0.84 (s, 9H, C(C*H*$_3$)$_3$), 0.07 (s, 3H, SiC*H*$_3$), -0.05 (m, 6H, 2 × SiC*H*$_3$), -0.07 (s, 3H, SiC*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 147.1 (q, *J* = 1.5 Hz, Ar*C*(2,6)), 129.6 (q, *J* = 32.2 Hz, Ar*C*(4)), 126.9 Ar*C*(1)), 125.0 (q, *J* = 3.8 Hz, Ar*C*(3,5)), 124.5 (q, *J* = 271.9 Hz, *C*F$_3$), 75.6 (*C*(5)), 69.7 (*C*(6)), 26.1 (C(*C*H$_3$)$_3$), 26.0 (C(*C*H$_3$)$_3$), 18.5 (*C*(CH$_3$)$_3$), 18.4 (*C*(CH$_3$)$_3$), -4.6 (Si*C*H$_3$), -4.7 (Si*C*H$_3$), -5.3 (Si*C*H$_3$), -5.4 (Si*C*H$_3$); ^{19}F NMR (376 MHz, $CDCl_3$) δ_F: -62.36; HRMS (ESI$^+$) *m/z*: [M+Na]$^+$ calcd for $C_{21}H_{37}F_3O_2Si_2Na$ 457.2182, found 457.2176.

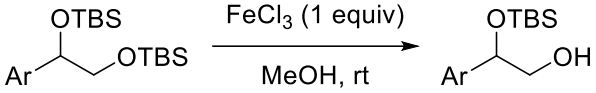
2-TBS Protected 1,2-Diols

General Procedure D



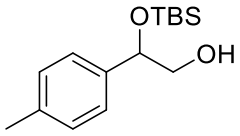
TBSCl protection and selective deprotection: Imidazole (3 equiv) and TBSCl (2.2 equiv) was added to a stirred solution of the requisite diol (1.0 equiv, in DMF/THF) at rt. The resultant mixture was stirred at rt for 18 h or until the diol was no longer visible by TLC. The reaction mixture was diluted with Et_2O and extracted with 0.1 M HCl, twice with H_2O, and brine. The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude oil was used without further purification. The oil was dissolved in MeOH (0.3 M) and cooled to 0 °C. $FeCl_3$ (1 equiv) was added slowly and the reaction mixture was allowed to warm to rt. The reaction mixture was stirred at rt for 2 h or until the 1,2-disilyl ether was no longer visible by TLC. Sat. $NaHCO_3$ solution (0.3 M) was added slowly and the reaction mixture stirred until effervescence had ceased. The reaction mixture was extracted with Et_2O three times. The combined organic extracts were washed with H_2O and brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude oil was purified by silica-gel column chromatography (100% PhMe) to give the desired alcohol.

General Procedure E



Selective deprotection: The requisite 1,2-disilyl ether was dissolved in MeOH (0.3 M) and cooled to 0 °C. $FeCl_3$ (1 equiv) was added slowly and the reaction mixture was allowed to warm to rt. The reaction mixture was stirred at rt for 2 h or until the 1,2-disilyl ether was no longer visible by TLC. Sat. $NaHCO_3$ solution (0.3 M) was added slowly and the reaction mixture stirred until effervescence had ceased. The reaction mixture was extracted with Et_2O three times. The combined organic extracts were washed with H_2O and brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude oil was purified by silica-gel column chromatography (100% PhMe or 100% to 96/4 cyclohexane/Et_2O) to give the desired alcohol.

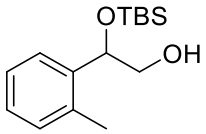
2-((*tert*-Butyldimethylsilyl)oxy)-2-(*p*-tolyl)ethan-1-ol S24



Following General Procedure E, 2,2,3,3,8,8,9,9-octamethyl-5-(p-tolyl)-4,7-dioxa-3,8-disiladecane **S18** (0.803 g, 2.11 mmol) was dissolved in MeOH (7.03 mL) and reacted with $FeCl_3$ (0.342 g, 2.11 mmol) then $NaHCO_3$ (sat. aq.) (7.03 mL) to give the title compound **S24** (0.171 g, 30%) as a colourless oil. ν_{max} (liquid) 3382 (O-H), 2954 (C-H aromatic), 2928 (C-H

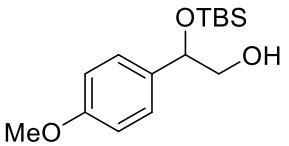
alkane);2857 (C-H alkane); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.20 (d, *J* = 8.1 Hz, 2H, ArC(2,6)*H*), 7.13 (d, *J* = 8.1 Hz, 2H, ArC(3,5)*H*), 4.73 (dd, *J* = 7.1, 4.9 Hz, 1H, C(2)*H*), 3.58 – 3.54 (m, 2H, C(1)H_2), 2.33 (s, 3H, ArC(4)CH_3), 2.12 – 2.03 (m, 1H, O*H*), 0.91 (s, 9H, C(CH_3)$_3$), 0.06 (s, 3H, SiCH_3), -0.10 (s, 3H, SiCH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 138.5 (Ar*C*(1)), 137.5 (Ar*C*(4)), 129.1 (Ar*C*(2,6)), 126.3 (Ar*C*(3,5)), 75.9 (*C*(2), 69.1 (*C*(1), 26.0 (C(*C*H$_3$)$_3$), 21.3 (ArC(4)*C*H$_3$), 18.4 (*C*(CH$_3$)$_3$), -4.4 (Si*C*H$_3$), -4.8 (Si*C*H$_3$). HRMS (ESI$^+$) *m/z*: [M+Na]$^+$ calcd for $C_{15}H_{26}O_2SiNa$ 289.1600, found 289.1596.

2-((*tert*-Butyldimethylsilyl)oxy)-2-(*o*-tolyl)ethan-1-ol S25



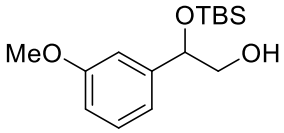
Following General Procedure D, 1-(*o*-tolyl)ethane-1,2-diol **S10** (0.370 g, 2.43 mmol) was reacted with TBSCl (0.807 g, 5.35 mmol) and imidazole (0.497 g, 7.30 mmol) in DMF (4.9 mL) and THF (1.6 mL). Following aqueous extraction, the crude residue was reacted with $FeCl_3$ (0.394 g, 2.43 mmol) in MeOH (8.1 mL) to give the title compound **S25** (0.467 g, 72%) as a pale yellow oil. ν_{max} (liquid) 3428 (O-H), 2954 (C-H aromatic), 2929 (C-H alkane), 2875 (C-H alkane); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.44 (dd, *J* = 7.4, 1.8 Hz, 1H, ArC(3)*H*), 7.23 – 7.13 (m, 2H, ArC(4)*H* + ArC(5)*H*), 7.10 (dd, *J* = 7.3, 1.8 Hz, 1H, ArC(6)*H*), 4.99 (dd, *J* = 8.1, 3.7 Hz, 1H, C(2)*H*), 3.63 – 3.45 (m, 2H, C(1)H_2), 2.33 (s, 3H, ArC(2)CH_3), 2.15 (dd, *J* = 9.6, 3.8 Hz, 1H, O*H*), 0.91 (s, 9H, C(CH_3)$_3$), 0.06 (s, 3H, SiCH_3), -0.12 (s, 3H, SiCH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 139.4 (Ar*C*(1)), 134.1 (Ar*C*(2)), 130.3 (Ar*C*(3)), 127.5 (Ar*C*(4)), 126.8 (Ar*C*(6)), 126.2 (Ar*C*(5)), 72.8 (*C*(2)), 67.9 (*C*(1)), 26.0 (*C*(CH$_3$)$_3$), 19.2 (ArC(2)*C*H$_3$), 18.4 (C(*C*H$_3$)$_3$), -4.4 (Si*C*H$_3$), -4.9 (Si*C*H$_3$); HRMS (ESI$^+$) *m/z*: [M+Na]$^+$ calcd for $C_{15}H_{26}O_2SiNa$ 289.1600, found 289.1594.

2-((*tert*-Butyldimethylsilyl)oxy)-2-(4-methoxyphenyl)ethan-1-ol S26



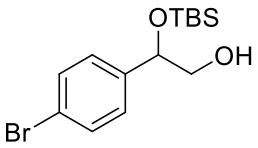
Following General Procedure E, 5-(4-methoxyphenyl)-2,2,3,3,8,8,9,9-octamethyl-4,7-dioxa-3,8-disiladecane **S19** (0.452 g, 1.14 mmol) was dissolved in MeOH (3.80 mL) and reacted with $FeCl_3$ (0.185 g, 1.14 mmol) then $NaHCO_3$ (sat. aq.) (3.80 mL) to give the title compound **S26** (0.104 g, 32%) as a colourless oil. ν_{max} (liquid) 3414 (O-H), 2953 (C-H aromatic), 2929 (C-H alkane), 2857 (C-H alkane); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.25 – 7.19 (m, 2H, ArC(2,6)*H*), 6.91 – 6.82 (m, 2H, ArC(3,5)*H*), 4.71 (t, *J* = 5.9 Hz, 1H, C(2)*H*), 3.80 (s, 3H, OCH_3), 3.55 (m, 2H, C(1)H_2), 2.06 (dd, *J* = 7.1, 6.1 Hz, 1H, O*H*), 0.90 (s, 9H, C(CH_3)$_3$), 0.05 (s, 3H, SiCH_3), -0.11 (s, 3H, SiCH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 159.3 (Ar*C*(4)), 133.6 (Ar*C*(1)), 127.6 (Ar*C*(2,6)), 113.8 (Ar*C*(3,5)), 75.6, 75.5 (*C*(2), 69.1 (*C*(1)), 55.5 (O*C*H$_3$), 26.0 (C(*C*H$_3$)$_3$), 18.4 (*C*(CH$_3$)$_3$), -4.5 (Si*C*H$_3$), -4.8 (Si*C*H$_3$); HRMS (ESI$^+$) *m/z*: [M+Na]$^+$ calcd for $C_{15}H_{26}O_3SiNa$ 305.1549, found 305.1538.

2-((*tert*-Butyldimethylsilyl)oxy)-2-(3-methoxyphenyl)ethan-1-ol S27



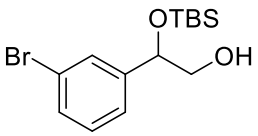
Following General Procedure E, 5-(3-methoxyphenyl)-2,2,3,3,8,8,9,9-octamethyl-4,7-dioxa-3,8-disiladecane **S20** (1.40 g, 3.53 mmol) was dissolved in MeOH (11.8 mL) and reacted with $FeCl_3$ (0.572 g, 3.53 mmol) then $NaHCO_3$ (sat. aq.) (11.8 mL) to give the title compound **S27** (0.482 g, 48%) as a colourless oil. ν_{max} (liquid) 3436 (O-H), 2954 (C-H aromatic), 2929 (C-H alkane), 2857 (C-H alkane); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.22 – 7.16 (m, 1H, ArC(5)*H*), 6.86 – 6.81 (m, 2H, ArC(6)*H* + ArC(2)*H*), 6.76 (ddd, *J* = 8.2, 2.4, 1.2 Hz, 1H, ArC(4)*H*), 4.69 (dd, *J* = 7.4, 4.3 Hz, 1H, C(2)*H*), 3.75 (s, 3H, OCH_3), 3.58 – 3.46 (m, 2H, C(1)H_2), 2.00 (br s, 1H, O*H*), 0.87 (s, 9H, C(CH_3)$_3$), 0.02 (s, 3H, SiCH_3), -0.12 (s, 3H, SiCH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 159.7 (Ar*C*(3)), 143.3 (Ar*C*(1)), 129.4 (Ar*C*(5)), 118.7 (Ar*C*(6)), 113.3 (Ar*C*(4)), 111.8 (Ar*C*(2)), 75.9 (*C*(2)), 69.1 (*C*(1)), 55.3 (O*C*H$_3$), 26.0 (C(*C*H$_3$)$_3$), 18.4 (*C*(CH$_3$)$_3$), -4.4 (Si*C*H$_3$), -4.8 (Si*C*H$_3$); HRMS (ESI$^+$) *m/z*: $[M+Na]^+$ calcd for $C_{15}H_{26}O_3SiNa$ 305.1549, found 305.1540.

2-(4-Bromophenyl)-2-((*tert*-butyldimethylsilyl)oxy)ethan-1-ol S28



Following General Procedure D, 1-(4-bromophenyl)ethane-1,2-diol **S14** (0.258 g, 1.19 mmol) was reacted with TBSCl (0.448 g, 2.97 mmol) and imidazole (0.243 g, 3.57 mmol) in DMF (2.4 mL) and THF (0.8 mL). Following aqueous extraction, the crude residue was reacted with $FeCl_3$ (0.193 g, 1.19 mmol) in MeOH (4.0 mL) to give the title compound **S28** (0.195 g, 50%) as a pale yellow oil. ν_{max} (liquid) 3448 (O-H), 2953 (C-H aromatic), 2928 (C-H alkane), 2856 (C-H alkane) ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.46 (d, *J* = 8.3 Hz, 2H, ArC(3,5)*H*), 7.20 (d, *J* = 8.3 Hz, 2H, ArC(2,6)*H*), 4.72 (dd, *J* = 7.3, 4.1 Hz, 1H, C(2)*H*), 3.62 – 3.48 (m, 2H, C(1)H_2), 2.02 (br s, 1H, O*H*), 0.91 (s, 9H, C(CH_3)$_3$), 0.07 (s, 3H, SiCH_3), -0.09 (s, 3H, SiCH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 140.7 (Ar*C*(1)), 131.6 (Ar*C*(3,5)), 128.1 (Ar*C*(2,6)), 121.7 (Ar*C*(4)), 75.4 (*C*(2)), 68.9 (*C*(1)), 26.0 (C(*C*H$_3$)$_3$), 18.3 (*C*(CH$_3$)$_3$), -4.4 (Si*C*H$_3$), -4.8 (Si*C*H$_3$); HRMS (ESI$^-$) *m/z*: $[M-H]^-$ calcd for $C_{14}H_{22}BrO_2Si$ 329.0572, found 329.0574.

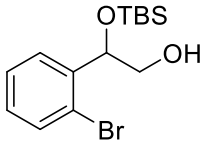
2-(3-Bromophenyl)-2-((*tert*-butyldimethylsilyl)oxy)ethan-1-ol S29



Following General Procedure E, 1-(3-bromophenyl)ethane-1,2-diol **S15** (0.402 g, 1.85 mmol) was reacted with TBSCl (0.614 g, 4.08 mmol) and imidazole (0.378 g, 5.56 mmol) in DMF (3.7 mL) and THF (1.2 mL). Following aqueous extraction, the crude residue was reacted with $FeCl_3$ (0.301 g, 1.85 mmol) in MeOH (6.2 mL) to give the title compound **S29** (0.284 g, 46%)

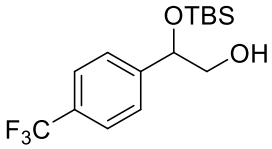
as a pale yellow oil. ν_{max} (liquid) 3424 (O-H), 2954 (C-H aromatic), 2929 (C-H alkane), 2857 (C-H alkane); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.56 (dd, *J* = 1.8, 1.7 Hz, 1H, ArC(2)*H*), 7.48 (ddd, *J* = 7.6, 1.8, 1.7 Hz, 1H, ArC(4)*H*), 7.37 – 7.26 (m, 2H, ArC(5)*H* + ArC(6)*H*), 4.80 (dd, *J* = 7.3, 4.1 Hz, 1H, C(2)*H*), 3.73 – 3.58 (m, 2H, C(1)H_2), 2.17 – 2.08 (m, 1H, O*H*), 1.00 (s, 9H, C(CH_3)$_3$), 0.16 (s, 3H, SiCH_3), 0.01 (s, 3H, SiCH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 144.0 (Ar*C*(1)), 130.9 (Ar*C*(4)), 130.0 (Ar*C*(6)), 129.5 (Ar*C*(2)), 125.0 (Ar*C*(5)), 122.6 (Ar*C*(3)), 75.3 (*C*(2)), 68.9 (*C*(1), 25.9 (C(*C*H_3)$_3$), 18.3 (*C*(CH_3)$_3$), -4.4 (Si*C*H_3), -4.8 (Si*C*H_3); HRMS (ESI+) m/z: [M+Na]+ calcd for $C_{14}H_{23}BrO_2SiNa$ 355.0528, found 355.0520.

2-(2-Bromophenyl)-2-((*tert*-butyldimethylsilyl)oxy)ethan-1-ol S30



Following General Procedure E, 5-(2-bromophenyl)-2,2,3,3,8,8,9,9-octamethyl-4,7-dioxa-3,8-disiladecane **S22** (1.86 g, 4.18 mmol) was dissolved in MeOH (13.9 mL) and reacted with $FeCl_3$ (0.678 g, 4.18 mmol) and $NaHCO_3$ (sat. aq.) (13.9 mL) to give the title compound **S30** (1.00 g, 76%) as a colourless liquid. ν_{max} (liquid) 3449 (O-H), 2953 (C-H aromatic), 2928 (C-H alkane), 2857 (C-H alkane); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 7.54 – 7.48 (m, 2H, ArC(3)*H* + ArC(6)*H*), 7.32 (ddd, *J* = 7.5, 7.5, 1.1 Hz, 1H, ArC(5)*H*), 7.13 (ddd, *J* = 7.5, 7.5, 1.7 Hz, 1H, ArC(4)*H*), 5.17 (dd, *J* = 7.3, 3.3 Hz, 1H, C(2)*H*), 3.73 (ddd, *J* = 11.7, 8.9, 3.3 Hz, 1H, C(1)*H*), 3.49 (ddd, *J* = 11.7, 7.3, 4.5 Hz, 1H, C(1)*H*), 2.09 (dd, *J* = 8.9, 4.5 Hz, 1H, O*H*), 0.92 (s, 9H, C(CH_3)$_3$), 0.09 (s, 3H, SiCH_3), -0.07 (s, 3H, SiCH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 140.4 (Ar*C*(1)), 132.6 (Ar*C*(3)), 129.2 (Ar*C*(4)), 128.8 (Ar*C*(6)), 127.5 (Ar*C*(5)), 121.7 (Ar*C*(2)), 74.7 (*C*(2)), 67.3 (*C*(1)), 26.0 (C(*C*H_3)$_3$), 18.3 (*C*(CH_3)$_3$), -4.5 (Si*C*H_3), -4.9 (Si*C*H_3); HRMS (ESI^+) *m/z*: $[M+Na]^+$ calcd for $C_{14}H_{23}BrO_2SiNa$ 353.0548, found 353.0539.

2-((*tert*-Butyldimethylsilyl)oxy)-2-(4-(trifluoromethyl)phenyl)ethan-1-ol S31

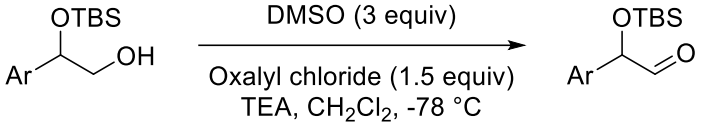


Following General Procedure E, 2,2,3,3,8,8,9,9-octamethyl-5-(4-(trifluoromethyl)phenyl)-4,7-dioxa-3,8-disiladecane **S23** (1.32 g, 3.05 mmol) was dissolved in MeOH (10.2 mL) and reacted with $FeCl_3$ (0.494 g, 3.05 mmol) then $NaHCO_3$ (sat. aq.) (10.2 mL) to give the title compound **S31** (0.723 g, 74%) as a colourless oil. ν_{max} (liquid) 3444 (O-H), 2955 (C-H aromatic), 2932 (C-H alkane), 2860 (C-H alkane); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.60 (d, *J* = 8.1 Hz, 2H, ArC(3,5)*H*), 7.45 (d, *J* = 8.1 Hz, 2H, ArC(2,6)*H*), 4.83 (dd, *J* = 7.2, 4.0 Hz, 1H, C(2)*H*), 3.68 – 3.52 (m, 2H, C(1)H_2), 2.04 (br s, 1H, O*H*), 0.92 (s, 9H, C(CH_3)$_3$), 0.09 (s, 3H, SiCH_3), -0.07 (s, 3H, SiCH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 145.7 (Ar*C*(1)), 130.1 (q, $^2J_{C\text{-}F}$ = 32.4 Hz, Ar*C*(4)), 126.6 (Ar*C*(2,6)), 125.4 (q, $^3J_{C\text{-}F}$ = 3.4 Hz, ArC(3,5)), 124.2 (q, $^1J_{C\text{-}F}$ = 272.0 Hz, *C*F_3), 75.4 (*C*(2)), 68.9 (*C*(1)), 25.9 (C(*C*H_3)$_3$), 18.3 (*C*(CH_3)$_3$), -4.5 (Si*C*H_3), -4.8 (Si*C*H_3); ^{19}F

NMR (376 MHz, $CDCl_3$) δ_F: -62.48; HRMS (ESI^-) *m/z*: $[M+HCOO]^-$ calcd for $C_{16}H_{24}F_3O_4Si$ 365.1396, found 365.1404.

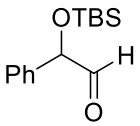
Aldehydes

General Procedure F



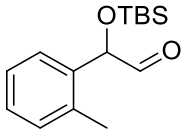
Swern Oxidation: Under an argon atmosphere in flame-dried glassware, oxalyl chloride (1.5 equiv) was dissolved in anhydrous CH_2Cl_2 (0.2 M) and cooled to -78 °C. DMSO (3 equiv) was dissolved in anhydrous CH_2Cl_2 (1.2 M) and added dropwise to the oxalyl chloride solution. The resultant mixture was stirred for 15 min. The requisite alcohol (1 equiv) was dissolved in anhydrous CH_2Cl_2 (0.5 M) and added dropwise to the reaction mixture. The resultant mixture was stirred for the requisite time (30-60 min). Triethylamine (4 equiv) was dissolved in CH_2Cl_2 (1 M) and added dropwise to the reaction mixture. The reaction mixture was warmed slowly to -20 °C, at which point 1 M HCl solution (0.2 M) was added. The layers were separated and the aqueous was washed twice with EtOAc. The combined organic layers were concentrated under reduced pressure to remove the CH_2Cl_2. The EtOAc solution was washed with 1 M HCl and brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give the desired aldehyde.

2-((*tert*-Butyldimethylsilyl)oxy)-2-phenylacetaldehyde S32



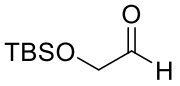
Methyl 2-((*tert*-butyldimethylsilyl)oxy)-2-phenylacetate **S3** (0.560 g, 2.00 mmol) was dissolved in anhydrous Et_2O (5 mL) under N_2 and cooled to –78 °C. DIBAL-H (1.2 M in PhMe, 2.00 mL, 2.40 mmol) was added dropwise and the solution was stirred at –78 °C for 1.5 h. The reaction mixture was diluted with Et_2O (10 mL) and quenched with MeOH (1 mL). The reaction mixture was stirred for 15 min then warmed to rt before saturated Rochelle salt solution (14 mL) was added. The biphasic reaction mixture was stirred vigorously for 16 h then the phases were separated. The aqueous layer was extracted with EtOAc (2 × 25 mL) and the combined organics were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give the title compound **S32** (0.526 g, 99%) as a colourless oil, with spectroscopic data in accordance with the literature.[10] ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 9.51 (s, 1H, C(1)*H*), 7.31 – 7.43 (m, 5H, ArC*H*), 5.01 (s, 1H, C(2)*H*), 0.95 (s, 9H, C(CH_3)$_3$), 0.12 (s, 3H, SiCH_3), 0.04 (s, 3H, SiCH_3).

2-((*tert*-Butyldimethylsilyl)oxy)-2-(*o*-tolyl)acetaldehyde S33



Following General Procedure F, 2-((*tert*-butyldimethylsilyl)oxy)-2-(*o*-tolyl)ethan-1-ol **S25** (0.467 g, 1.75 mmol) was reacted with DMSO (0.37 mL, 5.26 mmol), oxalyl chloride (0.23 mL, 2.63 mmol), and TEA (0.97 mL, 7.01 mmol) in CH_2Cl_2 (15.5 mL) to give the title compound **S33** (0.429 g, 93%) as a pale yellow oil. ν_{max} (liquid) 2955 (C-H aromatic), 2929 (C-H alkane), 2858 (C-H aldehyde), 1736 (C=O aldehyde); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 9.49 (d, *J* = 2.3 Hz, 1H, C(1)*H*), 7.52 – 7.42 (m, 1H, ArC(3)*H*), 7.29 – 7.08 (m, 3H, ArC*H*), 5.18 (d, 1H, *J* = 2.2 Hz, C(2)*H*), 2.35 (s, 3H, ArC(2)CH_3), 0.93 (s, 9H, C(CH_3)$_3$), 0.12 (s, 3H, SiCH_3), 0.01 (s, 3H, SiCH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 199.0 (*C*(1)), 135.9 (Ar*C*(1)), 135.3 (Ar*C*(2)), 130.9 (Ar*C*(3)), 128.5 (Ar*C*(4)), 127.6 (Ar*C*(6)), 126.4 (Ar*C*(5)), 78.0 (*C*(2)), 25.9 (C(*C*H$_3$)$_3$), 19.7 (ArC(2)*C*H$_3$), 18.4 (*C*(CH$_3$)$_3$), -4.7 (Si*C*H$_3$), -4.7 (Si*C*H$_3$); HRMS (ESI$^+$) *m/z*: $[M+H]^+$ calcd for $C_{15}H_{25}O_2Si$ 265.1624, found 265.1624.

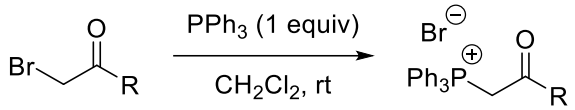
2-((*tert*-Butyldimethylsilyl)oxy)acetaldehyde S34



In flame-dried glassware under an Ar atmosphere, ethyl 2-((*tert*-butyldimethylsilyl)oxy)acetate **S8** (1.00 g, 4.58 mmol) was dissolved in anhydrous Et_2O (22.9 mL) and cooled to -78 °C. DIBAL-H (1 M in PhMe, 5.50 mL, 5.50 mmol) was added dropwise. Once addition was complete, the reaction mixture was stirred at -78 °C for 1.5 h. The reaction was quenched with dropwise addition of MeOH (2 mL) and warmed to rt. Rochelle salt solution (sat. aq., 20 mL) was added and the biphasic mixture was stirred vigorously until both phases were clear (approx. 4 h). The layers were separated and the aqueous layer was extracted with Et_2O (2 × 20 mL). The combined organic extracts were washed with water (20 mL) then brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give the title compound **S34** (0.674 g, 69%) as a colourless oil, with spectroscopic data in accordance with the literature.[11] ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 9.71 – 9.69 (t, *J* = 0.8 Hz, 1H, C(1)*H*), 4.21 (d, *J* = 0.8 Hz, 2H, C(2)H_2), 0.93 (s, 9H, C(CH_3)$_3$), 0.10 (s, 6H, 2 × SiCH_3).

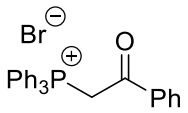
Phosphonium Salts

General Procedure G



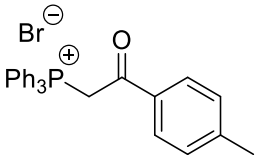
Phosphonium salt formation: The requisite α-bromoketone was dissolved in CH_2Cl_2 (0.2 M) and triphenylphosphine (1 equiv) was added. The reaction mixture was stirred at rt for 16 h then concentrated under reduced pressure. The resultant residue was washed with hexane two times to give the desired phosphonium salt.

(2-Oxo-2-phenylethyl)triphenylphosphonium bromide S35



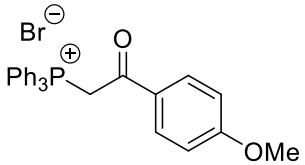
Following General Procedure G, bromoacetophenone (1.98 g, 10.0 mmol) was reacted with triphenylphosphine (2.62 g, 10.0 mmol) in CH_2Cl_2 (50 mL) to give the title compound **S35** (4.01 g, 87%) as a white solid, with spectroscopic data in accordance with the literature.[12] mp 270–274 °C {Lit[13] 270–273 °C}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.38 (dd, J = 7.3, 1.5 Hz, 2H, C(2)-ArC(2,6)*H*), 8.03 – 7.87 (m, 7H, C(1)-ArC(4)*H* + P-ArC(2,6)*H*), 7.80 – 7.71 (m, 3H, P-ArC(4)*H*), 7.69 – 7.61 (m, 6H, P-ArC(3,5)*H*), 7.55 – 7.45 (m, 2H, C(2)-ArC(3,5)*H*), 6.39 (d, J = 12.2 Hz, 2H, C(1)H_2); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ_P: 22.0.

(2-Oxo-2-(*p*-tolyl)ethyl)triphenylphosphonium bromide S36



Following General Procedure G, 2-bromo-1-(*p*-tolyl)ethan-1-one (1.06 g, 5.00 mmol) was reacted with triphenylphosphine (1.31 g, 5.00 mmol) in CH_2Cl_2 (25 mL) to give the title compound **S36** (2.08 g, 88%) as a white solid, with spectroscopic data in accordance with the literature. [14] mp 265–268 °C {Lit[15] 277–278 °C}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.25 (d, J = 8.0 Hz, 2H, C(2)-ArC(2,6)*H*), 7.98 – 7.88 (m, 6H, P-ArC(2,6)*H*), 7.78 – 7.71 (m, 3H, P-ArC(4)*H*), 7.67 – 7.61 (m, 6H, P-ArC(3,5)*H*), 7.29 (d, J = 7.9 Hz, 2H, C(2)-ArC(3,5)*H*), 6.31 (d, J = 12.1 Hz, 2H, C(1)H_2), 2.38 (s, 3H, ArCH_3); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ_P: 22.1.

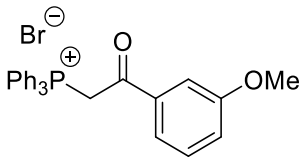
(2-(4-Methoxyphenyl)-2-oxoethyl)triphenylphosphonium bromide S37



Following General Procedure G, 2-Bromo-1-(4-methoxyphenyl)ethan-1-one (1.15 g, 5.00 mmol) was reacted with triphenylphosphine (1.31 g, 5.00 mmol) in CH_2Cl_2 (25 mL) to give

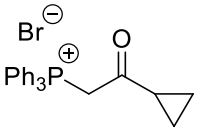
the title compound **S37** (2.02 g, 82%) as a white solid, with spectroscopic data in accordance with the literature.[14] mp 226–228 °C {Lit[16] 228–229 °C}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.40 (d, *J* = 8.4 Hz, 2H, C(2)-ArC(2,6)*H*), 7.96 – 7.88 (m, 6H, P-ArC(2,6)*H*), 7.77 – 7.70 (m, 3H, P-ArC(4)*H*), 7.66 – 7.60 (m, 6H, P-ArC(3,5)*H*), 6.96 (d, *J* = 8.4 Hz, 2H, C(2)-ArC(3,5)*H*), 6.20 (d, *J* = 12.2 Hz, 2H, C(1)H_2), 3.84 (s, 3H, OCH_3); ^{31}P{^{1}H} NMR (162 Hz, $CDCl_3$) δ_P: 22.1.

(2-(3-Methoxyphenyl)-2-oxoethyl)triphenylphosphonium bromide S38



Following General Procedure G, 2-bromo-1-(3-methoxyphenyl)ethan-1-one (1.15 g, 5.00 mmol) was reacted with triphenylphosphine (1.31 g, 5.00 mmol) in CH_2Cl_2 (25 mL) to give the title compound **S38** (2.03 g, 83%) as a white solid. mp 178–180 °C {Lit[15] 178 °C}; ν_{max} (film) 2772 (C-H aromatic), 1670 (C=O), 1584 (C=C); ^{1}H NMR (400 MHz, $CDCl_3$) δ_h: 8.01 – 7.89 (m, 7H, P-ArC(2,6)*H* + C(2)-ArC(6)*H*), 7.87 – 7.81 (m, 1H, C(2)-ArC(5)*H*), 7.80 – 7.72 (m, 3H, P-ArC(4)*H*), 7.68 – 7.62 (m, 6H, P-ArC(3,5)*H*), 7.44 – 7.36 (m, 1H, C(2)-ArC(2)*H*), 7.20 – 7.12 (m, 1H, C(2)-ArC(4)*H*), 6.43 (d, *J* = 12.1 Hz, 2H, C(1)*H*), 3.95 (s, 3H, OCH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 192.2 (*C*(2)), 160.1 (C(2)-Ar*C*(3)), 136.7 (C(2)-Ar*C*(1)), 134.8 (P-Ar*C*(4)), 134.1 (d, *J* = 10.7 Hz, P-Ar*C*(3,5)), 130.2 (d, *J* = 13.1 Hz, P-Ar*C*(2,6)), 130.1 (C(2)-Ar*C*(2)), 122.8 (C(2)-Ar*C*(5)), 122.7 (C(2)-Ar*C*(6)), 119.03 (d, *J* = 88.5 Hz, P-Ar*C*(1)), 112.9 (C(2)-Ar*C*(4)), 56.5 (O*C*H$_3$), 39.05 (d, *J* = 63.9 Hz, *C*(1)); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ_P: 21.9; HRMS (ESI$^+$) *m/z*: $[M+H]^+$ calcd for $C_{27}H_{25}O_2P$ 412.1592, found 412.1547.

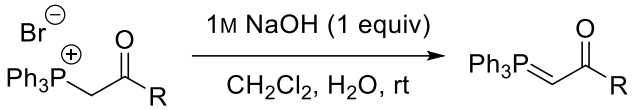
(2-Cyclopropyl-2-oxoethyl)triphenylphosphonium bromide S39



In flame-dried glassware under an N_2 atmosphere, 2-bromo-1-cyclopropylethan-1-one (0.29 mL, 3.00 mmol) was dissolved in anhydrous THF (3 mL) and triphenylphosphine (0.472 g, 1.80 mmol) was added. The reaction mixture was heated to 80 °C for 2 h then allowed to cool to rt. The white precipitate was filtered and washed with EtOAc (3 × 10 mL) to give the title compound **S39** (0.705 g, 92%) as a white solid. mp 163–168 °C; ν_{max} (film) 2779 (C-H aromatic), 2709 (C-H alkane), 1685 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.88 – 7.80 (m, 6H, ArC(2,6)*H*), 7.78 – 7.72 (m, 3H, ArC(4)*H*), 7.68 – 7.61 (m, 6H, ArC(3,5)*H*), 5.96 (d, *J* = 12.1 Hz, 2H C(1)H_2), 2.86 (ttd, *J* = 7.6, 4.6, 1.7 Hz, 1H, C(3)*H*), 1.11 – 0.96 (m, 4H, C(4)H_2); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 203.0 (*C*(2)), 134.9 (d, *J* = 3.2 Hz, Ar*C*(4)), 134.0 (d, *J* = 10.7 Hz, Ar*C*(3,5)), 130.2 (d, *J* = 13.1 Hz, Ar*C*(2,6)), 118.8 (d, *J* = 88.9 Hz, Ar*C*(1)), 40.4 (d, *J* = 57.0 Hz, *C*(1)), 23.5 (C(2)-*C*H), 13.8 (CH(*C*H$_2$-*C*H$_2$)); ^{31}P NMR (162 MHz, $CDCl_3$) δ_P: 20.1; HRMS (ESI$^+$) *m/z*: $[M+H]^+$ calcd for $C_{23}H_{23}OP$ 346.1487, found 346.1443.

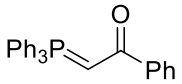
Phosphonium Ylides

General Procedure H



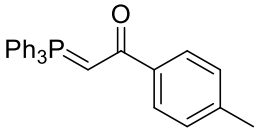
Deprotonation: The requisite phosphonium salt was dissolved in CH_2Cl_2 (0.75 M) and H_2O (0.5 M). 2 M NaOH (1 equiv) was added and the reaction mixture was stirred vigorously overnight. The layers were separated and the aqueous layer was extracted with CH_2Cl_2 three times. The combined organic extracts were washed with brine and dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give the title compound which was either used without further purification or purified through silica gel column chromatography or recrystallisation.

1-Phenyl-2-(triphenyl-λ^5-phosphaneylidene)ethan-1-one S40



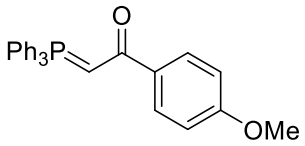
Following General Procedure H, (2-Oxo-2-phenylethyl)triphenylphosphonium bromide **S35** (9.84 g, 21.3 mmol) was dissolved in CH_2Cl_2 (28.4 mL) and H_2O (42.7 mL) and reacted with 2 M NaOH (12.8 mL) to give the title compound **S40** (7.78 g, 96%) as a pale yellow solid, with spectroscopic data in accordance with the literature.[17] mp 179–183 °C {Lit[18] 174–176 °C}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.93 (m, 2H, C(1)-ArC(2,6)*H*), 7.77 – 7.69 (m, 6H, P-ArC(2,6)*H*), 7.60 – 7.53 (m, 3H, P-ArC(4)*H*), 7.51 – 7.42 (m, 6H, P-ArC(3,5)*H*), 7.40 – 7.32 (m, 3H, C(1)-ArC*H*), 4.43 (br s, 1H, C(2)*H*); ^{31}P NMR (162 MHz, $CDCl_3$) δ 16.6.

1-(*p*-Tolyl)-2-(triphenyl- λ^5-phosphaneylidene)ethan-1-one S41



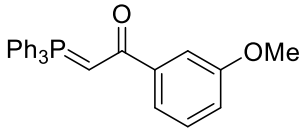
Following General Procedure H, (2-oxo-2-(*p*-tolyl)ethyl)triphenylphosphonium bromide **S36** (1.53 g, 3.22 mmol) was reacted with 2 M NaOH (1.90 mL) in CH_2Cl_2 (4.3 mL) and H_2O (6.4 mL) to give the title compound **S41** (1.14 g, 89%) as a white solid, with spectroscopic data in accordance with the literature.[17] mp 180–182 °C {Lit[18] 174–176 °C}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.87 (d, *J* = 8.2 Hz, 2H, C(1)-ArC(2,6)*H*), 7.78 – 7.64 (m, 6H, P-ArC(2,6)*H*), 7.60 – 7.51 (m, 3H, P-ArC(4)*H*), 7.51 – 7.41 (m, 6H, P-ArC(3,5)*H*), 7.16 (d, *J* = 7.9 Hz, 2H, C(1)-ArC(3,5)*H*), 4.40 (d, *J* = 24.5 Hz, 1H, C(2)*H*), 2.36 (s, 3H, C(1)-ArC*H*$_3$); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ_P: 16.6.

1-(4-Methoxyphenyl)-2-(triphenyl- λ^5-phosphaneylidene)ethan-1-one S42



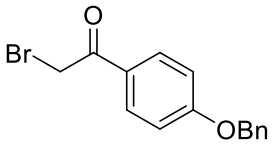
Following General Procedure H, (2-(4-methoxyphenyl)-2-oxoethyl)triphenylphosphonium bromide **S37** (2.00 g, 4.08 mmol) was reacted with 2 M NaOH (2.50 mL) in CH_2Cl_2 (5.5 mL) and H_2O (8.2 mL) to give the title compound **S42** (1.24 g, 74%) as a white solid, with spectroscopic data in accordance with the literature.[17] mp 154–156 °C {Lit[18] 156–158 °C}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.93 (d, *J* = 8.7 Hz, 2H, ArC(2,6)*H*), 7.76 – 7.68 (m, 6H, P-ArC(2,6)*H*), 7.58 – 7.52 (m, 3H, P-ArC(4)*H*), 7.50 – 7.43 (m, 6H, P-ArC(3,5)*H*), 6.87 (d, *J* = 8.7 Hz, 2H, ArC(3,5)*H*), 4.35 (d, *J* = 22.0 Hz, 1H, C(2)*H*), 3.82 (s, 3H, OC*H*$_3$); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ_P: 16.6.

1-(3-Methoxyphenyl)-2-(triphenyl- λ^5-phosphaneylidene)ethan-1-one S43



Following General Procedure H, (2-(3-methoxyphenyl)-2-oxoethyl)triphenylphosphonium bromide **S38** (1.58 g, 3.22 mmol) was reacted with 2 M NaOH (1.90 mL) in CH_2Cl_2 (4.3 mL) and H_2O (6.4 mL) to give the title compound **S43** (1.13 g, 85%). mp 169–171 °C {Lit[15] 164 °C}; ν_{max} (film) 3048 (C-H aromatic), 2998 (C-H aromatic), 2933 (C-H alkane); 1515 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.78 – 7.64 (m, 6H, P-ArC(2,6)*H*), 7.61 – 7.52 (m, 5H, ArC*H*), 7.51 – 7.41 (m, 6H, P-ArC(3,5)*H*), 7.29 – 7.20 (m, 1H, ArC(2)*H*), 6.96 – 6.88 (m, 1H, ArC(4)*H*), 4.42 (d, *J* = 24.6 Hz, 1H, C(1)*H*), 3.83 (s, 3H, OC*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 184.6 (d, *J* = 3.5 Hz, *C*(1)), 159.5 (C(1)-Ar*C*(3)), 143.0 (d, *J* = 14.7 Hz, C(1)-Ar*C*(1)), 133.2 (d, *J* = 10.2 Hz, P-Ar*C*(3,5)), 132.2 (d, *J* = 2.9 Hz, P-Ar*C*(4)), 129.0 (d, *J* = 12.3 Hz, P-Ar*C*(2,6)), 128.7 (C(1)-Ar*C*(5)), 127.13 (d, *J* = 91.2 Hz, P-Ar*C*(1)), 119.6 (C(1)-Ar*C*(6)), 116.2 (C(1)-Ar*C*(4)), 111.4 (C(1)-Ar*C*(2)), 55.5 (O*C*H$_3$), 50.9 (d, *J* = 112.2 Hz, *C*(2)); ^{31}P NMR (162 MHz, $CDCl_3$) δ_P: 16.6; HRMS (ESI$^+$) *m/z*: $[M+H]^+$ calcd for $C_{27}H_{24}O_2P$ 411.1514, found 411.1514.

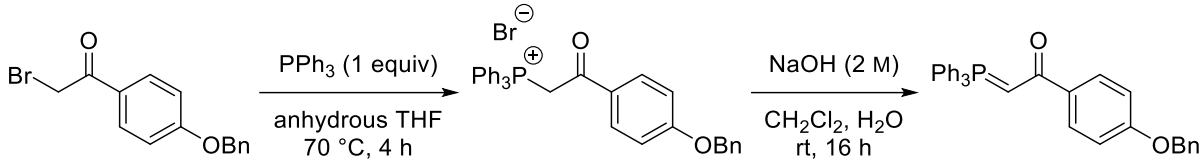
1-(4-(Benzyloxy)phenyl)-2-bromoethan-1-one S44



In flame-dried glassware under an Ar atmosphere, 2-bromo-1-(4-hydroxyphenyl)ethan-1-one (1.72 g, 8.00 mmol) was dissolved in anhydrous THF (40 mL). Silver carbonate (4.12 g, 16.0 mmol) was added and the solution was cooled to 0 °C. Benzyl bromide (1.14 mL, 9.60 mmol) was added dropwise and the reaction mixture was warmed to rt and stirred for 16 h. The reaction mixture was filtered through a pad of celite and diluted with H_2O (50 mL). The

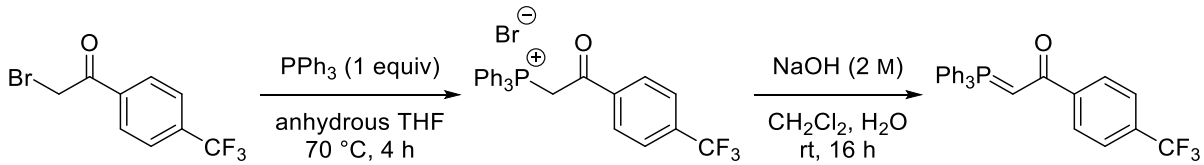
aqueous solution was extracted with EtOAc (2 × 100 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography (92/8 PE/EtOAc) to give the title compound **S44** (1.19 g, 49%) as a white solid, with spectroscopic data in accordance with the literature.[19] mp 88–90 °C {Lit[19] 91–91.4 °C}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.99-7.95 (2H, m, C(1)-ArC(3,5)*H*)), 7.45-7.33 (5H, m, OCH_2Ar*H*)), 7.06-7.02 (2H, m, C(1)-ArC(2,6)*H*)), 5.15 (2H, s, O*C*H_2Ph), 4.40 (2H, s, C(2)*H*).

1-(4-(Benzyloxy)phenyl)-2-(triphenyl- λ^5-phosphaneylidene)ethan-1-one S45



Following General Procedure G, 1-(4-(benzyloxy)phenyl)-2-bromoethan-1-one **S44** (0.650 g, 2.13 mmol) was reacted with triphenylphosphine (0.560 g, 2.13 mmol) in CH_2Cl_2 (10 mL) to give crude (2-(4-(benzyloxy)phenyl)-2-oxoethyl)triphenylphosphonium bromide which was used without further purification. Following General Procedure H, crude (2-(4-(benzyloxy)phenyl)-2-oxoethyl)triphenylphosphonium bromide was reacted with 2 M NaOH (1.1 mL) in CH_2Cl_2 (2.4 mL) and H_2O (3.6 mL). The crude residue was purified by recrystallization from $CHCl_3$ to give the title compound **S45** (0.76 g, 73%) as white solid. mp 176–178 °C ($CHCl_3$); ν_{max} (film) 3058 (C-H aromatic), 2889 (C-H alkane), 1599 (C=O), 1583 (C=C); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.93 (d, *J* = 8.7 Hz, 2H, C(1)-ArC(2,6)*H*), 7.77 – 7.66 (m, 6H, P-ArC(2,6)*H*), 7.60 – 7.50 (m, 3H, P-ArC(4)*H*), 7.51 – 7.40 (m, 8H, P-ArC(2,6)*H* + OCH_2ArC(2,6)*H*), 7.42 – 7.33 (m, 2H, OCH_2ArC(3,5)*H*), 7.36 – 7.27 (m, 1H, OCH_2ArC(4)*H*), 6.94 (d, *J* = 8.7 Hz, 2H, C(1)-ArC(3,5)*H*), 5.09 (s, 2H, O*C*H_2), 4.35 (d, *J* = 24.6 Hz, 1H, C(2)*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.5 (d, *J* = 3.3 Hz, *C*(1)), 160.1 (C(1)-Ar*C*(4)), 137.1 (OCH_2-Ar*C*(1)), 134.5 (C(1)-Ar*C*(2,6)), 133.3 (d, *J* = 10.2 Hz, P-Ar*C*(3,5)), 132.1 (d, *J* = 2.9 Hz, P-Ar*C*(4)), 129.0 (d, *J* = 12.2 Hz, P-Ar*C*(2,6)), 128.7 (OCH_2-Ar*C*(3,5)), 128.0 (OCH_2-Ar*C*(4)), 127.6 (OCH_2-Ar*C*(2,6)), 127.4 (d, *J* = 91.2 Hz, P-Ar*C*(1)), 114.0 (C(1)-Ar*C*(3,5)), 70.1 (O*C*H_2), 49.9 (d, *J* = 112.9 Hz, *C*(2)); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ_P: 16.6; HRMS (ESI$^+$) *m/z*: $[M+H]^+$ calcd for $C_{33}H_{28}O_2P$ 487.1827, found 487.1830.

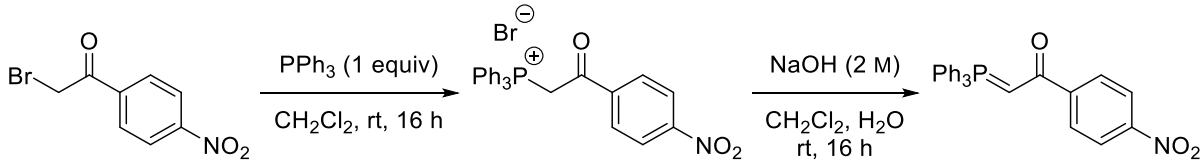
1-(4-(Trifluoromethyl)phenyl)-2-(triphenyl- λ^5-phosphaneylidene)ethan-1-one S46



In flame-dried glassware under an Ar atmosphere, 2-bromo-1-(4-(trifluoromethyl)phenyl)ethan-1-one (0.800 g, 3.00 mmol) was dissolved in anhydrous THF (11 mL) and triphenylphosphine (0.790 g, 3.00 mmol) was added. The reaction mixture was heated to 70 °C for 4 h then cooled to rt and concentrated under reduced pressure. The solid was washed with hexane (2 × 20 mL) and dried under reduced pressure to give crude (2-oxo-2-(4-(trifluoromethyl)phenyl)ethyl)triphenylphosphonium bromide which was used without

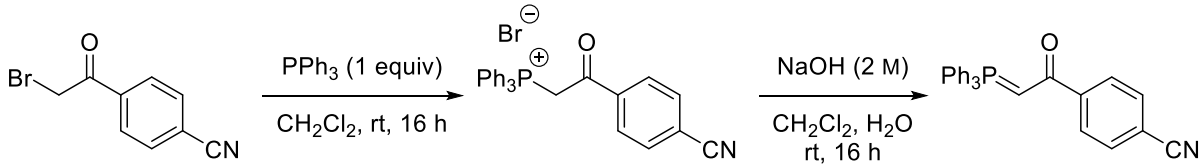
further purification. Following General Procedure H, crude 2-(4-(trifluoromethyl)phenyl)ethyl)triphenylphosphonium bromide was reacted with 2 M NaOH (1.7 mL) in dissolved in CH_2Cl_2 (3.8 mL) and H_2O (5.6 mL). The crude residue was purified by silica gel column chromatography (PE:EtOAc 3:7) to give the title compound **S46** (0.550 g, 43%) as a white solid, with spectroscopic data in accordance with the literature.[20] mp 199–201 °C {Lit[20] 199–201 °C}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.05 (d, J = 8.0 Hz, 2H, ArC(3,5)*H*), 7.80 – 7.66 (m, 6H, P-ArC(2,6)*H*), 7.64 – 7.54 (m, 5H, ArC(2,6)*H* + P-ArC(4)*H*), 7.55 – 7.42 (m, 6H, P-ArC(3,5)*H*), 4.45 (d, J = 23.6 Hz, 1H, C(2)*H*); ^{19}F NMR (376 MHz, $CDCl_3$) δ_F: -62.42; ^{31}P NMR (162 MHz, $CDCl_3$) δ_P: 16.7.

1-(4-Nitrophenyl)-2-(triphenyl- λ^5-phosphaneylidene)ethan-1-one S47



Following General Procedure G, 2-bromo-1-(4-nitrophenyl)ethan-1-one (1.22 g, 5.00 mmol) was reacted with triphenylphosphine (1.31 g, 5.00 mmol) in CH_2Cl_2 (25 mL) to give crude (2-(4-nitrophenyl)-2-oxoethyl)triphenylphosphonium bromide (2.27 g, 90%) which was used without further purification. Following General Procedure H, (2-(4-nitrophenyl)-2-oxoethyl)triphenylphosphonium bromide (1.63 g, 3.22 mmol) was reacted with 2 M NaOH (1.90 mL) in CH_2Cl_2 (4.3 mL) and H_2O (6.4 mL) to give the title compound **S47** (0.970 g, 71%) as a yellow solid, with spectroscopic data in accordance with the literature.[21] mp 179–181 °C {Lit[21] 182–184 °C}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.19 (d, J = 8.8 Hz, 2H, C(1)-ArC(3,5)*H*), 8.08 (d, J = 8.8 Hz, 2H, C(1)-ArC(2,6)*H*), 7.77 – 7.66 (m, 6H, P-ArC(2,6)*H*), 7.63 – 7.57 (m, 3H, P-ArC(4)*H*), 7.54 – 7.46 (m, 6H, P-ArC(3,5)*H*), 4.49 (d, J = 23.0 Hz, 1H, C(2)*H*); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ_P: 16.7.

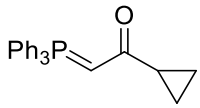
4-(2-(Triphenyl-λ^5-phosphaneylidene)acetyl)benzonitrile S48



Following General Procedure G, 4-(2-bromoacetyl)benzonitrile (1.12 g, 5.00 mmol) was reacted with triphenylphosphine (1.31 g, 5.00 mmol) in CH_2Cl_2 (25 mL) to give crude (2-(4-cyanophenyl)-2-oxoethyl)triphenylphosphonium bromide which was used without further purification. Following General Procedure H, crude (2-(4-cyanophenyl)-2-oxoethyl)triphenylphosphonium bromide was reacted with 2 M NaOH (1.9 mL) in CH_2Cl_2 (4.3 mL) and H_2O (6.4 mL). The crude residue was purified by silica gel column chromatography (PE:EtOAc 3:7) to give the title compound **S48** (1.11 g, 85%) as an off-white solid, with spectroscopic data in accordance with the literature.[18] mp 208–210 °C {Lit[18] 199–201 °C}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.03 (d, J = 8.3 Hz, 2H, C(1)-ArC(3,5)*H*), 7.76 – 7.66 (m, 6H, P-

ArC(2,6)*H*), 7.66 – 7.55 (m, 5H, C(1)-ArC(2,6)*H* + P-ArC(4)*H*), 7.53 – 7.46 (m, 6H, P-ArC(3,5)*H*), 4.45 (d, J = 23.1 Hz, 1H, C(2)*H*); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ_P: 16.8.

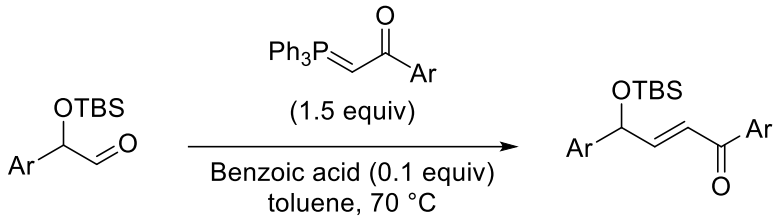
1-Cyclopropyl-2-(triphenyl-λ^5-phosphaneylidene)ethan-1-one S49



Following General Procedure H, (2-cyclopropyl-2-oxoethyl)triphenylphosphonium bromide **S39** (0.705 g, 1.66 mmol) was reacted with 2 M NaOH (1.00 mL) in CH_2Cl_2 (4.3 mL) and H_2O (6.4 mL) to give the title compound **S49** (0.554 g, 97%) as an off-white solid, with spectroscopic data in accordance with the literature.[22] mp 181–184 °C {Lit[22] 181–182 °C}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.70 – 7.58 (m, 6H, P-ArC(2,6)*H*), 7.57 – 7.49 (m, 3H, P-ArC(4)*H*), 7.49 – 7.39 (m, 6H, P-ArC(3,5)*H*), 3.79 (d, J = 25.5 Hz, 1H, C(2)*H*), 1.85 – 1.73 (m, 1H, C(1)C*H*$(CH_2)_2$), 0.95 – 0.84 (m, 2H, C(1)CH(C*H*$_2)_2$), 0.66 – 0.55 (m, 2H, C(1)CH(C*H*$_2)_2$); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ_P: 13.9.

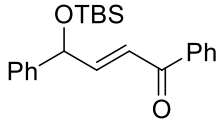
TBS-Hydroxy Enones

General Procedure I



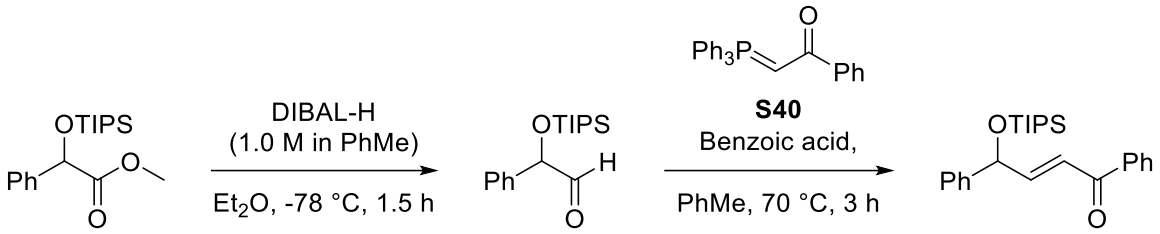
Wittig olefination: Under an argon atmosphere in flame-dried glassware, the requisite ylide (1.4 equiv) and benzoic acid (0.1 equiv) were dissolved in anhydrous PhMe (0.25 M). The requisite aldehyde was dissolved in anhydrous PhMe (0.35 M) and added to the ylide solution. The resultant mixture was heated to 100 °C for the 5 h or until on aldehyde was visible by NMR. The reaction mixture was allowed to cool to rt and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography (100% PhMe) to give the desired γ-TBS hydroxy enone.

(*E*)-4-((*tert*-Butyldimethylsilyl)oxy)-1,4-diphenylbut-2-en-1-one 1



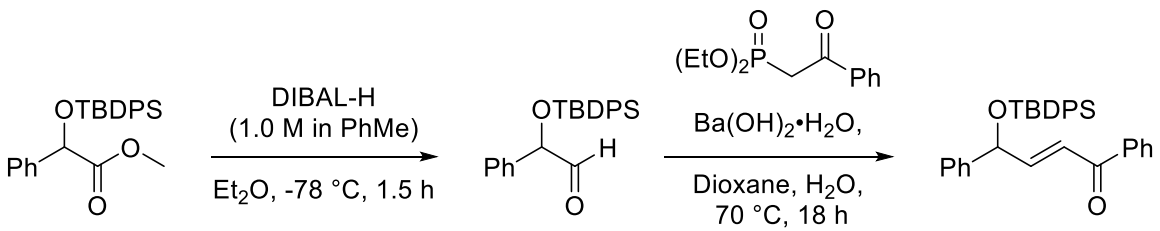
Following General Procedure I, 2-((*tert*-butyldimethylsilyl)oxy)-2-phenylacetaldehyde **S32** (3.51 g, 14.0 mmol) was reacted with 1-phenyl-2-(triphenylphosphoranylidene)ethenone **S40** (7.99 g, 21.0 mmol) and benzoic acid (0.171 g, 1.40 mmol) in anhydrous PhMe (93 mL) to give the title compound **1** (3.25 g, 66%) as a yellow oil. ν_{max} (liquid) 2955 (C-H aromatic), 2929 (C-H alkane), 2857 (C-H alkane), 1672 (C=O), 1642 (C=C aromatic); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.96 – 7.88 (m, 2H, C(1)-ArC(2,6)*H*), 7.61 – 7.51 (m, 1H, C(1)-ArC(4)*H*), 7.52 – 7.42 (m, 3H, ArC*H*), 7.39 – 7.26 (m, 4H, ArC*H*), 7.21 (dd, *J* = 15.2, 1.7 Hz, 1H, C(2)*H*), 7.07 (dd, *J* = 15.2, 4.1 Hz, 1H, C(3)*H*), 5.43 (dd, *J* = 4.2, 1.7 Hz, 1H, C(4)*H*), 0.96 (s, 9H, C(C*H*$_3$)$_3$), 0.11 (s, 3H, SiC*H*$_3$), -0.01 (s, 3H, SiC*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 191.1 (*C*(1)), 150.6 (*C*(3)), 141.8 (C(1)-Ar*C*(1)), 138.1 (C(4)-Ar*C*(1)), 132.9 (C(1)-Ar*C*(4)), 128.7 (Ar*C*), 128.7 (Ar*C*), 127.9 (C(4)-Ar*C*(4)), 126.4 (C(4)-Ar*C*(2,6)), 122.7 (*C*(2)), 74.7 (*C*(4)), 26.0 (C(*C*H$_3$)$_3$), 18.5 (*C*(CH$_3$)$_3$), -4.7 (Si*C*H$_3$), -4.7 (Si*C*H$_3$); HRMS (ESI$^+$) *m/z*: $[M+H]^+$ calcd for $C_{22}H_{29}O_2Si$ 353.1937, found 353.1926.

(*E*)-1,4-diphenyl-4-((triisopropylsilyl)oxy)but-2-en-1-one 5



In flame-dried glassware under an Ar atmosphere, methyl 2-phenyl-2-((triisopropylsilyl)oxy)acetate **S4** (0.674 g, 2.40 mmol) was dissolved in anhydrous Et_2O (12 mL) and cooled to –78 °C. DIBAL-H (1 M in PhMe, 2.88 mL, 2.88 mmol) was added dropwise and the solution was stirred at –78 °C for 1.5 h. The reaction mixture was quenched with MeOH (1.2 mL). The reaction mixture was stirred for 15 min then warmed to rt and saturated Rochelle salt solution (15 mL) was added. The biphasic reaction mixture was stirred vigorously for 16 h. The reaction mixture was diluted with Et_2O (20 mL) and the layers separated. The aqueous layer was extracted with Et_2O (2 × 20 mL) and the combined organic extracts were washed with H_2O then brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give crude 2-phenyl-2-((triisopropylsilyl)oxy)acetaldehyde which was used without further purification. Following General Procedure I, 2-phenyl-2-((triisopropylsilyl)oxy)acetaldehyde (0.356 g, 1.22 mmol) was reacted with 1-phenyl-2-(triphenylphosphoranylidene)ethenone **S40** (0.694 g, 1.82 mmol) and benzoic acid (0.015 g, 0.120 mmol) in anhydrous PhMe (8.11 mL) to give the title compound **5** (3.25 g, 66%) as a yellow oil. ν_{max} (liquid) 2943 (C-H aromatic), 2866 (C-H alkane), 1672 (C=O), 1624 (C=C); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.91 – 7.83 (m, 2H, C(1)-ArC(2,6)*H*), 7.55 – 7.46 (m, 1H, C(1)-ArC(4)*H*), 7.45 – 7.38 (m, 2H, C(1)-ArC(3,5)*H*), 7.36 – 7.25 (m, 4H, C(4)-ArC*H*), 7.24 – 7.17 (m, 2H, C(4)-ArC*H* + C(2)*H*), 7.02 (dd, *J* = 15.2, 4.4 Hz, 1H, C(3)*H*), 5.48 (dd, *J* = 4.4, 1.6 Hz, 1H, C(4)*H*), 1.14 – 1.05 (m, 3H, SiC*H*(CH_3)$_2$), 1.00 (dd, *J* = 16.6, 7.1 Hz, 18H, SiCH(C*H*$_3$)$_2$); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 191.0 (*C*(1)), 151.0 (*C*(3)), 142.1 (C(1)-Ar*C*(1)), 138.1 (C(4)-Ar*C*(1)), 132.9 (C(1)-Ar*C*(4)), 128.7 (Ar*C*), 128.7 (Ar*C*), 127.9 (C(4)-Ar*C*(4)), 126.4 (C(4)-Ar*C*(2,6)), 122.3 (*C*(2)), 75.0 (*C*(4)), 18.2 (SiCH(*C*H$_3$)$_2$), 18.1 (SiCH(*C*H$_3$)$_2$), 12.4 (Si*C*H(CH$_3$)$_2$); HRMS (ESI$^+$) *m/z*: [M+Na]$^+$ calcd for $C_{25}H_{34}O_2SiNa$ 417.2226, found 417.2220.

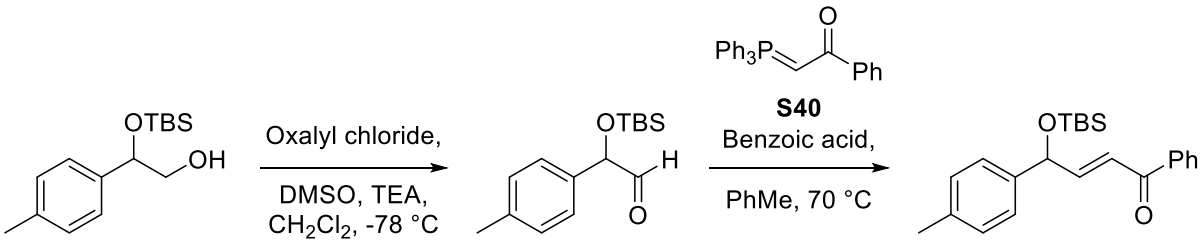
(*E*)-4-((*tert*-butyldiphenylsilyl)oxy)-1,4-diphenylbut-2-en-1-one 6



In flame-dried glassware under an Ar atmosphere, methyl 2-((*tert*-butyldiphenylsilyl)oxy)-2-phenylacetate **S5** (0.572 g, 1.41 mmol) was dissolved in anhydrous Et_2O (7.06 mL) and cooled to –78 °C. DIBAL-H (1 M in PhMe, 1.70 mL, 1.70 mmol) was added dropwise and the solution was stirred at –78 °C for 1.5 h. The reaction mixture was quenched with MeOH (1.00 mL).

The reaction mixture was stirred for 15 min then warmed to rt and saturated Rochelle salt solution (15 mL) was added. The biphasic reaction mixture was stirred vigorously for 16 h. The reaction mixture was diluted with Et_2O (20 mL) and the layers separated. The aqueous layer was extracted with Et_2O (2 × 20 mL) and the combined organic extracts were washed with H_2O then brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give crude 2-((*tert*-butyldiphenylsilyl)oxy)-2-phenylacetaldehyde which was used without further purification. Diethyl (2-oxo-2-phenylethyl)phosphonate (0.483 g, 1.88 mmol) and $Ba(OH)_2$ monohydrate (0.178 g, 0.942 mmol) were dissolved in 1,4-dioxane (2.2 mL) and heated to 70 °C. After 15 min a solution of 2-((*tert*-butyldiphenylsilyl)oxy)-2-phenylacetaldehyde (0.471 g, 1.26 mmol) in 1,4-dioxane (2 mL) and H_2O (0.03 mL) was added and the reaction mixture was stirred at 70 °C for 18 h. The reaction mixture was cooled to rt and filtered. The filtrate was diluted with Et_2O (20 mL) and washed with H_2O (20 mL) then brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography (50:50 hexane:PhMe to 20:80 hexane:PhMe) to give the title compound **6** (0.204 g, 34%) as a yellow oil. ν_{max} (liquid) 2928 (C-H aromatic), 2852 (C-H alkane), 1673 (C=O), 1625 (C=C); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.76 – 7.69 (m, 2H, C(1)-ArC(2,6)*H*), 7.69 – 7.61 (m, 2H, Si-ArC(2,6)*H*), 7.49 – 7.40 (m, 3H, C(1)-ArC(4)*H* + Si-ArC(2,6)*H*), 7.40 – 7.25 (m, 6H, ArC*H*), 7.25 – 7.10 (m, 7H, ArC*H*), 7.02 (dd, *J* = 15.3, 1.4 Hz, 1H, C(2)*H*), 6.91 (dd, *J* = 15.3, 4.7 Hz, 1H, C(3)*H*), 5.33 (dd, *J* = 4.7, 1.4 Hz, 1H, C(4)*H*), 1.05 (s, 9H, C(C*H*$_3$)$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 190.8 (*C*(1)), 149.8 (*C*(3)), 141.2 (C(4)-Ar*C*(1)), 137.9 (C(1)-Ar*C*(1)), 136.0 (Si-Ar*C*(2,6)), 135.9 (Si-Ar*C*(2,6)), 133.6 (Si-Ar*C*(1)), 133.0 (Si-Ar*C*(1)), 132.8 (C(1)-Ar*C*(4)), 130.0 (Ar*C*), 129.9 (Ar*C*), 128.7 (Ar*C*), 128.6 (Ar*C*), 128.6 (Ar*C*), 127.9 (Ar*C*), 127.8 (Ar*C*), 127.6 (Ar*C*), 126.7 (Ar*C*), 123.1 (*C*(2)), 75.7 (*C*(4)), 27.1 (C(*C*H$_3$)$_3$), 19.6 (*C*(CH$_3$)$_3$); HRMS (ESI$^+$) *m/z*: $[M+H]^+$ calcd for $C_{32}H_{33}O_2Si$ 477.2250, found 477.2248.

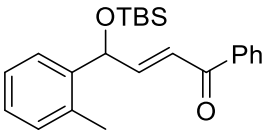
(*E*)-4-((*tert*-Butyldimethylsilyl)oxy)-1-phenyl-4-(*p*-tolyl)but-2-en-1-one S50



Following General Procedure F, 2-((*tert*-butyldimethylsilyl)oxy)-2-(*p*-tolyl)ethan-1-ol **S24** (0.141 g, 0.530 mmol) was reacted with DMSO (0.34 mL, 4.77 mmol, 9 equiv), oxalyl chloride (0.20 mL, 2.39 mmol, 4.5 equiv), and TEA (0.78 mL, 6.36 mmol, 12 equiv) in CH_2Cl_2 (12.5 mL) to give crude 2-((*tert*-butyldimethylsilyl)oxy)-2-(*p*-tolyl)acetaldehyde (0.140 g) as a yellow oil, which was used without further purification. Following General Procedure I, 2-((*tert*-butyldimethylsilyl)oxy)-2-(*p*-tolyl)acetaldehyde (0.140 g, 0.530 mmol), 1-phenyl-2-(triphenylphosphoranylidene)ethan-1-one **S40** (0.303 g, 0.795 mmol), and benzoic acid (0.007 g, 0.053 mmol) were reacted in anhydrous PhMe (3.54 mL) to give the title compound **S50** (0.034 g, 17%) as a yellow oil. ν_{max} (liquid) 2954 (C-H aromatic), 2928 (C-H alkane), 2856 (C-

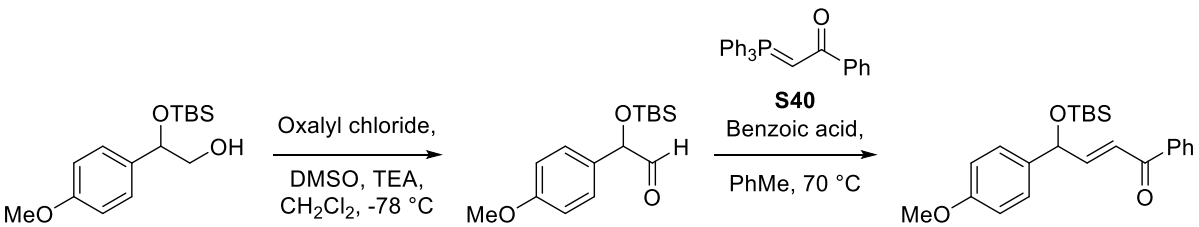
H alkane), 1671 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.93–7.90 (m, 2H, C(1)-ArC(2,6)*H*), 7.58–7.53 (m, 1H, C(1)-ArC(4)*H*), 7.49–7.44 (m, 2H, C(1)-ArC(3,5)*H*), 7.23 (d, 2H, *J* = 8.1 Hz, C(4)-ArC(2,6)*H*), 7.19 (dd, *J* = 15.2, 1.7 Hz, 1H, C(2)*H*), 7.14 (d, *J* = 8.1 Hz, 2H, C(4)-ArC(3,5)*H*), 7.05 (dd, *J* = 15.2, 4.3 Hz, 1H, C(3)*H*), 5.40 (dd, *J* = 4.3, 1.7 Hz, 1H, C(4)*H*), 2.34 (s, 3H, ArC*H*$_3$), 0.95 (s, 9H, C(C*H*$_3$)$_3$), 0.11 (s, 3H, SiC*H*$_3$), -0.02 (s, 3H, SiC*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 191.1 (*C*(1)), 150.9 (*C*(3)), 138.8 (C(4)-Ar*C*(1)), 138.1 (C(1)-Ar*C*(1)), 137.6 (C(4)-Ar*C*(4)), 132.9 (C(1)-Ar*C*(4)), 129.4 (C(4)-Ar*C*(3,5)), 129.0 (C(1)-Ar*C*(3,5)), 128.6 (C(1)-Ar*C*(2,6)), 126.4 (C(4)-Ar*C*(2,6)), 122.6 (*C*(2)), 74.6 (*C*(4)), 26.0 (C(*C*H$_3$)$_3$), 21.3 (Ar*C*H$_3$), 18.5 (*C*(CH$_3$)$_3$), -4.5 (Si*C*H$_3$), -4.7 (Si*C*H$_3$); HRMS (ESI$^+$) *m/z*: $[M+Na]^+$ calcd for $C_{23}H_{30}O_2SiNa$ 389.1913, found 389.1905.

(*E*)-4-((*tert*-Butyldimethylsilyl)oxy)-1-phenyl-4-(*o*-tolyl)but-2-en-1-one S51



Following General Procedure I, 2-((*tert*-butyldimethylsilyl)oxy)-2-(*o*-tolyl)acetaldehyde **S33** (0.217 g, 0.821 mmol), 1-phenyl-2-(triphenylphosphoranylidene)ethan-1-one **S40** (0.468 g, 1.23 mmol), and benzoic acid (0.010 g, 0.082 mmol) were reacted in anhydrous PhMe (5.47 mL) to give the title compound **S51** (0.184 g, 60%) as a yellow oil. ν_{max} (liquid) 2953 (C-H aromatic), 2928 (C-H alkane), 2856 (C-H alkane), 1672 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.95 – 7.87 (m, 2H, C(1)-ArC(2,6)*H*), 7.56 (m, 2H, C(1)-ArC(4)*H*), 7.51 – 7.39 (m, 3H, C(1)-ArC(3,5)*H* + C(4)-ArC(3)*H*), 7.23 – 7.09 (m, 4H, C(4)-ArC*H* + C(2)*H*), 7.05 (dd, 1H, *J* = 15.1, 4.0 Hz, C(3)*H*), 5.60 (dd, 1H, *J* = 4.0, 1.7 Hz, C(4)*H*), 2.38 (s, 3H, C(4)-ArC(2)C*H*$_3$), 0.95 (s, 9H, C(C*H*$_3$)$_3$), 0.10 (s, 3H, SiC*H*$_3$), -0.04 (s, 3H, SiC*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 191.0 (*C*(1)), 149.6 (*C*(3)), 139.6 (C(4)-Ar*C*(1)), 138.1 (C(1)-Ar*C*(1)), 134.5 (C(4)-Ar*C*(2)), 132.9 (C(1)-Ar*C*(4)), 130.7 (C(4)-Ar*C*(3)), 128.7 (C(1)-Ar*C*(2,6)), 128.7 (C(1)-Ar*C*(3,5)), 127.7 (C(4)-Ar*C*(4)), 127.1 (C(4)-Ar*C*(6)), 126.5 (C(4)-Ar*C*(5)), 122.8 (*C*(2)), 72.3 (*C*(4)), 26.0 (C(*C*H$_3$)$_3$), 19.4 (C(4)-ArC(2)*C*H$_3$), 18.5 (*C*(CH$_3$)$_3$), -4.7 (Si*C*H$_3$), -4.8 (Si*C*H$_3$); HRMS (ESI$^+$) *m/z*: $[M+H]^+$ calcd for $C_{23}H_{31}O_2Si$ 367.2093, found 367.2091.

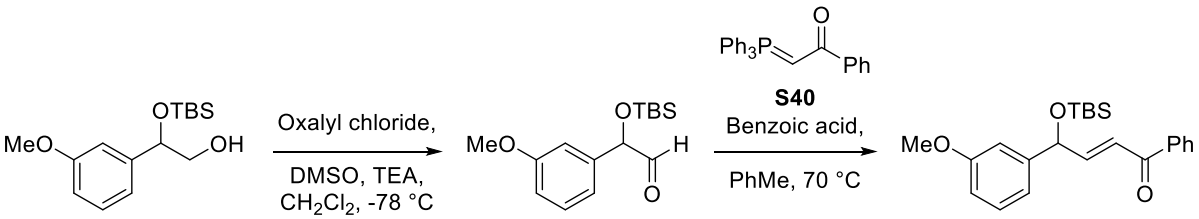
(*E*)-4-((*tert*-Butyldimethylsilyl)oxy)-4-(4-methoxyphenyl)-1-phenylbut-2-en-1-one S52



Following General Procedure F, 2-((*tert*-butyldimethylsilyl)oxy)-2-(4-methoxyphenyl)ethan-1-ol **S26** (0.104 g, 0.370 mmol) was reacted with DMSO (0.08 mL, 1.10 mmol, 3 equiv), oxalyl chloride (0.05 mL, 0.552 mmol, 1.5 equiv), and TEA (0.18 mL, 1.47 mmol, 4 equiv) in CH_2Cl_2 (8.65 mL) to give crude 2-((*tert*-butyldimethylsilyl)oxy)-2-(4-methoxyphenyl)acetaldehyde (0.087 g) as a yellow oil, which was used without further purification. Following General

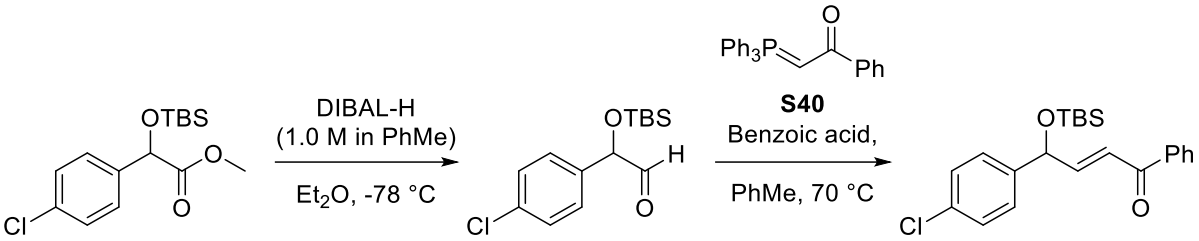
Procedure I, 2-((*tert*-butyldimethylsilyl)oxy)-2-(4-methoxyphenyl)acetaldehyde (0.087 g, 0.312 mmol), 1-phenyl-2-(triphenylphosphoranylidene)ethan-1-one (0.178 g, 0.467 mmol), and benzoic acid (0.004 g, 0.031 mmol) were reacted in anhydrous PhMe (2.08 mL) to give the title compound **S52** (0.080 g, 67%) as a pale yellow oil. ν_{max} (liquid) 2954 (C-H aromatic), 2929 (C-H alkane), 2856 (C-H alkane), 1671 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.92 (m, 2H, C(1)-ArC(2,6)*H*), 7.60–7.51 (m, 1H, C(1)-ArC(4)*H*), 7.49–7.42 (m, 2H, C(1)-ArC(3,5)*H*), 7.29–7.23 (m, 2H, C(4)-Ar(2,6)*H*), 7.18 (dd, *J* = 15.2, 4.9 Hz, 1H, C(3)*H*), 7.04 (m, 1H, C(2)*H*), 6.91–6.82 (m, 2H, C(4)-ArC(3,5)*H*), 5.38 (d, *J* = 4.9 Hz, 1H, C(4)*H*), 3.79 (s, 3H, OC*H*$_3$), 0.94 (s, 9H, C(C*H*$_3$)$_3$), 0.10 (s, 3H, SiC*H*$_3$), -0.03 (s, 3H, SiC*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 191.1 (*C*(1)), 159.3 (C(4)-Ar*C*(4)), 150.9 (*C*(3)), 138.1 (C(1)-Ar*C*(1)), 133.9 (C(4)-Ar*C*(1)), 132.9 (C(1)-Ar*C*(4)), 128.7 (Ar*C*), 128.7 (Ar*C*), 127.7 (C(1)-Ar*C*(2,6)), 122.5 (*C*(2)), 114.1 (C(4)-Ar*C*(3,5)), 74.3 (*C*(4)), 55.4 (O*C*H$_3$), 26.0 (C(*C*H$_3$)$_3$), 18.5 (*C*(CH$_3$)$_3$), -4.6 (Si*C*H$_3$), -4.7 (Si*C*H$_3$); HRMS (ESI+) m/z: [M+Na]+ calcd for $C_{23}H_{30}O_3SiNa$ 405.1862, found 405.1861.

(*E*)-4-((*tert*-Butyldimethylsilyl)oxy)-4-(3-methoxyphenyl)-1-phenylbut-2-en-1-one S53



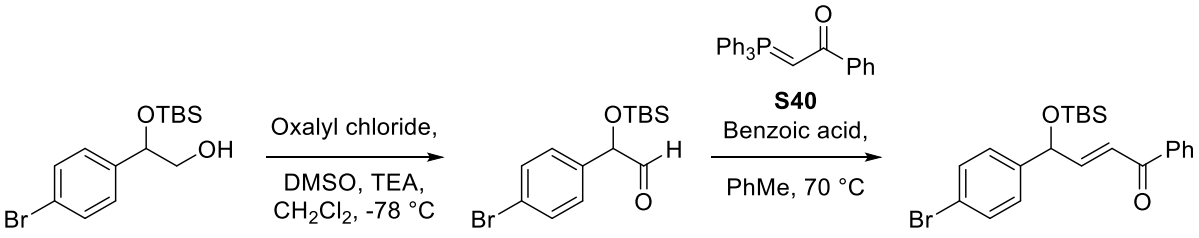
Following General Procedure F, 2-((*tert*-butyldimethylsilyl)oxy)-2-(3-methoxyphenyl)ethan-1-ol **S27** (0.428 g, 1.52 mmol) was reacted with DMSO (0.65 mL, 9.09 mmol, 6 equiv), oxalyl chloride (0.39 mL, 4.55 mmol, 3 equiv), and TEA (1.30 mL, 10.6 mmol, 7 equiv) in CH_2Cl_2 (35.6 mL) to give crude 2-((*tert*-butyldimethylsilyl)oxy)-2-(3-methoxyphenyl)acetaldehyde (0.253 g) as a yellow oil, which was used without further purification. Following General Procedure I, 2-((*tert*-butyldimethylsilyl)oxy)-2-(3-methoxyphenyl)acetaldehyde (0.253 g, 0.904 mmol), 1-phenyl-2-(triphenylphosphoranylidene)ethan-1-one **S40** (0.516 g, 1.36 mmol), and benzoic acid (0.011 g, 0.090 mmol) were reacted in anhydrous PhMe (6.02 mL) to give the title compound **S53** (0.131 g, 38%) as a pale yellow oil. ν_{max} (liquid) 2953 (C-H aromatic), 2929 (C-H alkane), 2857 (C-H alkane), 1671 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.94–7.90 (m, 2H, C(1)-ArC(2,6)*H*), 7.59–7.53 (m, 1H, C(1)-ArC(4)*H*), 7.47 (m, 2H, C(1)-ArC(3,5)*H*), 7.28–7.25 (m, 1H, C(4)-ArC(5)*H*), 7.20 (dd, *J* = 15.2, 1.7 Hz, 1H, C(2)*H*), 7.06 (dd, *J* = 15.2, 4.3 Hz, 1H, C(3)*H*), 6.95–6.90 (m, 2H, C(4)-ArC(2)*H* + C(4)-ArC(6)*H*), 6.84–6.79 (m, 1H, C(4)-ArC(4)*H*), 5.41 (dd, *J* = 4.3, 1.7 Hz, 1H C(4)*H*), 3.81 (s, 3H, OC*H*$_3$), 0.97 (s, 9H, C(C*H*$_3$)$_3$), 0.12 (s, 3H, SiC*H*$_3$), 0.01 (s, 3H, SiC*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 191.0 (*C*(1)), 160.0 (C(4)-Ar*C*(3)), 150.5 (*C*(3)), 143.4 (C(4)-Ar*C*(1)), 138.1 (C(1)-Ar*C*(1)), 132.9 (C(1)-Ar*C*(4)), 129.7 (C(4)-Ar*C*(5)), 128.7 (Ar*C*), 128.7 (Ar*C*), 122.8 (*C*(2)), 118.7 (C(4)-Ar*C*(6)), 113.3 (C(4)-Ar*C*(4)), 111.8 (C(4)-Ar*C*(2)), 74.6 (*C*(4)), 55.4 (O*C*H$_3$), 26.0 (C(*C*H$_3$)$_3$), 18.5 (*C*(CH$_3$)$_3$), -4.7 (Si*C*H$_3$), -4.7 (Si*C*H$_3$); HRMS (ESI+) m/z: [M+Na]+ calcd for $C_{23}H_{30}O_3SiNa$ 405.1862, found 405.1852.

(*E*)-4-((*tert*-Butyldimethylsilyl)oxy)-4-(4-chlorophenyl)-1-phenylbut-2-en-1-one S54



In flame-dried glassware under an Ar atmosphere, methyl 2-((*tert*-butyldimethylsilyl)oxy)-2-(4-chlorophenyl)acetate **S6** (0.500 g, 1.59 mmol) was dissolved in anhydrous hexane (7.94 mL) then cooled to -78 °C. DIBAL-H (1 M in PhMe, 2.06 mL, 2.06 mmol) was added dropwise and the solution was stirred at –78 °C for 1.5 h. The reaction mixture was quenched with MeOH (0.79 mL). The reaction mixture was stirred for 15 min then warmed to rt and saturated Rochelle salt solution (10 mL) was added. The biphasic reaction mixture was stirred vigorously for 16 h. The reaction mixture was diluted with Et_2O (20 mL) and the layers separated. The aqueous layer was extracted with Et_2O (2 × 20 mL) and the combined organic extracts were washed with H_2O then brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give crude 2-((*tert*-butyldimethylsilyl)oxy)-2-(4-chlorophenyl)-acetaldehyde (0.284 g) as a cloudy yellow oil, which was used without further purification. Following General Procedure I, 2-((*tert*-butyldimethylsilyl)oxy)-2-(4-chlorophenyl)-acetaldehyde (0.284 g, 0.996 mmol), 1-phenyl-2-(triphenylphosphoranylidene)ethan-1-one **S40** (0.568 g, 1.49 mmol), and benzoic acid (0.012 g, 0.080 mmol) in anhydrous PhMe (6.64 mL) to give the title compound **S54** (0.194 g, 50%) as a yellow oil. ν_{max} (liquid) 2954 (C-H aromatic), 2929 (C-H alkane), 2857 (C-H alkane), 1672 (C=O), 1624 (C=C aromatic); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.94 – 7.89 (m, 2H, C(1)-ArC(2,6)*H*), 7.60 – 7.54 (m, 1H, C(1)-ArC(4)*H*), 7.47 (m, 2H, C(1)-ArC(3,5)*H*), 7.33 – 7.27 (m, 4H, C(4)-ArC*H*), 7.19 (dd, 1H, *J* = 15.1, 1.7 Hz, C(2)*H*), 7.01 (dd, 1H, *J* = 15.2, 4.2 Hz, C(3)*H*), 5.40 (dd, 1H, *J* = 4.3, 1.7 Hz, C(4)*H*), 0.95 (s, 9H, C(C*H*$_3$)$_3$), 0.11 (s, 3H, SiC*H*$_3$), -0.01 (s, 3H, SiC*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 190.8 (*C*(1)), 149.9 (*C*(3)), 140.4 (C(4)-Ar*C*(1)), 137.9 (C(1)-Ar*C*(1)), 133.6 (C(1)-Ar*C*(4)), 132.8 (C(4)-Ar*C*(4)), 129.0 (C(4)-Ar*C*(3,5)), 128.9 (C(1)-Ar*C*(3,5)), 128.6 (C(1)-Ar*C*(2,6)), 127.8 (C(4)-Ar*C*(2,6)), 123.0 (*C*(2)), 74.1 (*C*(4)), 25.9 (C(*C*H$_3$)$_3$), 18.5 (*C*(CH$_3$)$_3$), -4.6 (Si*C*H$_3$), -4.8 (Si*C*H$_3$); HRMS (ESI$^-$) *m/z*: [M-H]$^-$ calcd for $C_{22}H_{26}ClO_2Si$ 385.1391, found 385.1393.

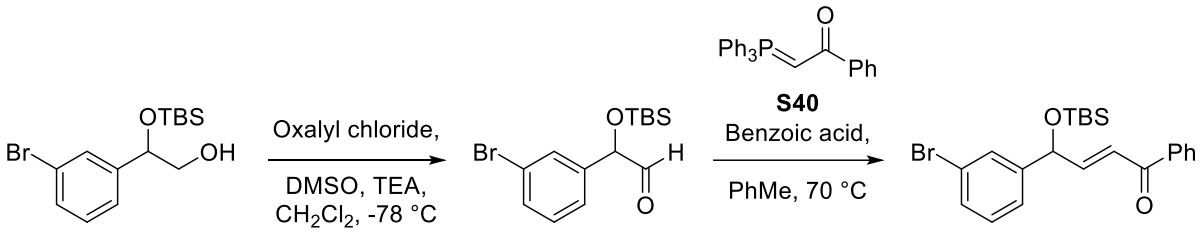
(*E*)-4-(4-Bromophenyl)-4-((*tert*-butyldimethylsilyl)oxy)-1-phenylbut-2-en-1-one S55



Following General Procedure F, 2-(4-bromophenyl)-2-((*tert*-butyldimethylsilyl)oxy)ethan-1-ol **S28** (0.195 g, 0.590 mmol) was reacted with DMSO (0.38 mL, 5.31 mmol, 9 equiv), oxalyl chloride (0.23 mL, 2.65 mmol, 4.5 equiv), and TEA (0.87 mL, 7.08 mmol, 12 equiv) in CH_2Cl_2

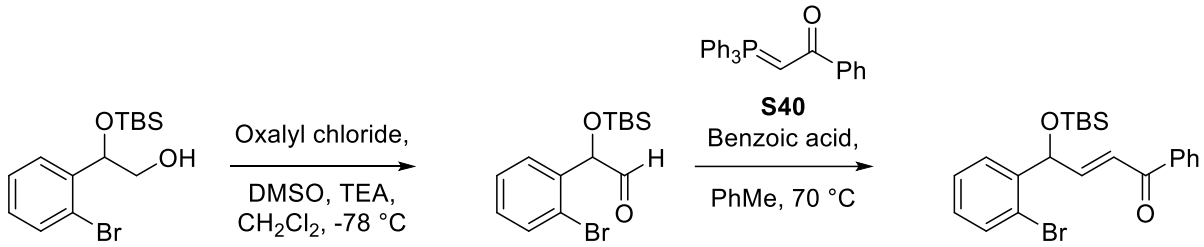
(13.9 mL) to give crude 2-(4-bromophenyl)-2-((tert-butyldimethylsilyl)oxy)-acetaldehyde (0.188 g). Following General Procedure I, 2-(4-bromophenyl)-2-((tert-butyldimethylsilyl)oxy)-acetaldehyde (0.188 g, 0.571 mmol), 1-phenyl-2-(triphenylphosphoranylidene)ethan-1-one **S40** (0.326 g, 0.856 mmol), and benzoic acid (0.007 g, 0.057 mmol) in anhydrous PhMe (3.81 mL) to give the title compound **S55** (0.095 g, 38%) as a yellow oil. ν_{max} (liquid) 2953 (C-H aromatic), 2928 (C-H alkane), 2856 (C-H alkane), 1672 (C=O), 1624 (C=C aromatic); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.95 – 7.89 (m, 2H, C(1)-ArC(2,6)*H*), 7.60 – 7.54 (m, 1H, C(1)-ArC(4)*H*), 7.51 – 7.44 (m, 4H, C(1)-ArC(3,5)*H* + C(4)-ArC(3,5)*H*), 7.25 – 7.21 (m, 2H, C(4)-ArC(2,6)*H*), 7.19 (dd, 1H, *J* = 15.2, 1.7 Hz, C(2)*H*), 7.01 (dd, 1H, *J* = 15.2, 4.3 Hz, C(3)*H*), 5.38 (dd, 1H, *J* = 4.3, 1.7 Hz, C(4)*H*), 0.95 (s, 9H, C(C*H*$_3$)$_3$), 0.11 (s, 3H, SiC*H*$_3$), -0.00 (s, 3H, SiC*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 190.8 (*C*(1), 149.8 (*C*(3)), 140.9 (C(4)-Ar*C*(1)), 137.9 (C(1)-Ar*C*(1)), 133.0 (C(1)-Ar*C*(4)), 131.9 (C(4)-Ar*C*(3,5)), 128.8 (C(1)-Ar*C*(3,5)), 128.7 (C(1)-Ar*C*(2,6)), 128.1 (C(4)-Ar*C*(2,6)), 123.0 (*C*(2)), 121.8 (C(4)-Ar*C*(4)), 74.1 (*C*(4)), 25.9 (C(*C*H$_3$)$_3$), 18.5 (*C*(CH$_3$)$_3$), -4.7 (Si*C*H$_3$), -4.7 (Si*C*H$_3$); HRMS (ESI$^+$) *m/z*: $[M+Na]^+$ calcd for $C_{22}H_{27}BrO_2SiNa$ 455.0841, found 455.0836.

(*E*)-4-(3-Bromophenyl)-4-((*tert*-butyldimethylsilyl)oxy)-1-phenylbut-2-en-1-one S56



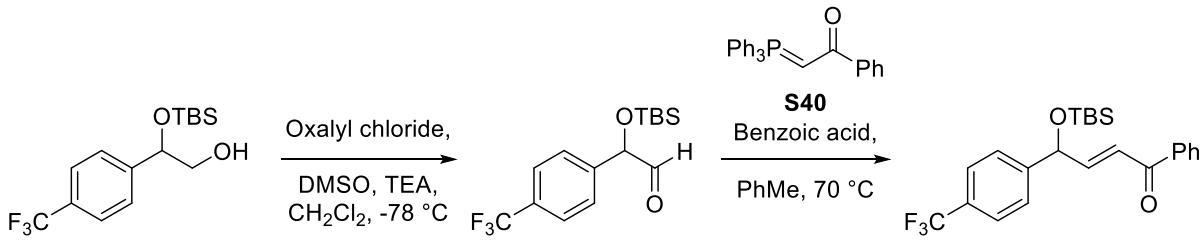
Following General Procedure F, 2-(3-bromophenyl)-2-((*tert*-butyldimethylsilyl)oxy)ethan-1-ol **S29** (0.505 g, 1.52 mmol) was reacted with DMSO (0.97 mL, 13.7 mmol, 9 equiv), oxalyl chloride (0.59 mL, 6.85 mmol, 4.5 equiv), and TEA (2.25 mL, 18.3 mmol, 12 equiv) in CH_2Cl_2 (35.8 mL) to give crude 2-(3-bromophenyl)-2-((*tert*-butyldimethylsilyl)oxy)acetaldehyde (0.497 g) which was used without further purification. Following General Procedure I, 2-(3-bromophenyl)-2-((tert-butyldimethylsilyl)oxy)-acetaldehyde (0.497 g, 1.51 mmol), 1-phenyl-2-(triphenylphosphoranylidene)ethan-1-one **S40** (0.861 g, 2.26 mmol), and benzoic acid (0.018 g, 0.015 mmol) in anhydrous PhMe (10.1 mL) to give the title compound **S56** (0.096 g, 38%) as a yellow oil. ν_{max} (liquid) 2954 (C-H aromatic), 2929 (C-H alkane), 2857 (C-H alkane), 1671 (C=O), 1625 (C=C aromatic); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.95 – 7.89 (m, 2H, C(1)-ArC(2,6)*H*), 7.60 – 7.54 (m, 1H, C(1)-ArC(4)*H*), 7.52 – 7.45 (m, 3H, C(1)-ArC(3,5)*H* + C(4)-ArC(2)*H*), 7.40 (ddd, *J* = 7.7, 2.0, 1.2 Hz, 1H, C(4)-ArC(4)*H*), 7.32 – 7.26 (m, 1H, C(4)-ArC(6)*H*), 7.24 – 7.17 (m, 2H, C(2)*H* + C(4)-ArC(5)*H*), 7.02 (dd, *J* = 15.2, 4.3 Hz, 1H, C(3)*H*), 5.39 (dd, *J* = 4.3, 1.7 Hz, 1H, C(4)*H*), 0.96 (s, 9H, C(C*H*$_3$)$_3$), 0.12 (s, 3H, SiC*H*$_3$), 0.01 (s, 3H, SiC*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 190.7 (*C*(1)), 149.6 (*C*(3)), 144.2 (C(4)-Ar*C*(1)), 137.9 (C(1)-Ar*C*(1)), 133.1 (C(1)-Ar*C*(4)), 131.1 (C(4)-Ar*C*(2)), 130.3 (C(4)-Ar*C*(4)), 129.5 (C(4)-Ar*C*(5)), 128.8 (C(1)-Ar*C*(3,5)), 128.8 (C(1)-Ar*C*(2,6)), 125.0 (C(1)-Ar*C*(6)), 123.1 (C(1)-Ar*C*(3)), 122.8 (*C*(2)), 77.5 (*C*(4)), 25.9 (C(*C*H$_3$)$_3$), 18.5 (*C*(CH$_3$)$_3$), -4.6 (Si*C*H$_3$), -4.7 (Si*C*H$_3$); HRMS (ESI$^+$) *m/z*: $[M+H]^+$ calcd for $C_{22}H_{28}BrO_2Si$ 433.1022, found 433.1022.

(*E*)-4-(2-Bromophenyl)-4-((*tert*-butyldimethylsilyl)oxy)-1-phenylbut-2-en-1-one S57



Following General Procedure F, 2-(2-bromophenyl)-2-((*tert*-butyldimethylsilyl)oxy)ethan-1-ol **S30** (0.500 g, 1.51 mmol) was reacted with DMSO (0. 96 mL, 13.6 mmol, 9 equiv), oxalyl chloride (0.58 mL, 6.79 mmol, 4.5 equiv), and TEA (2.23 mL, 18.1 mmol, 12 equiv) in CH_2Cl_2 (20.4 mL) to give crude 2-(2-bromophenyl)-2-((*tert*-butyldimethylsilyl)oxy)-acetaldehyde (0.550 g) as a pale yellow oil, which was used without further purification. Following General Procedure I, 2-(2-bromophenyl)-2-((*tert*-butyldimethylsilyl)oxy)-acetaldehyde (0.550 g, 1.67 mmol) was reacted with 1-phenyl-2-(triphenylphosphoranylidene)ethenone **S40** (0.953 g, 2.50 mmol) and benzoic acid (0.020 g, 0.167 mmol) in anhydrous PhMe (11.1 mL) to give the title compound **S57** (0.381 g, 53%) as an off white solid. mp 55–56 °C; ν_{max} (liquid) 2952 (C-H aromatic), 2927 (C-H alkane), 2856 (C-H alkane), 1672 (C=O), 1621 (C=C aromatic); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.96 – 7.88 (m, 2H, C(1)-ArC(2,6)*H*), 7.59 – 7.43 (m, 5H, ArC*H*), 7.35 – 7.29 (m, 1H, ArC(6)*H*), 7.26 (dd, *J* = 15.2, 1.7 Hz, 1H, C(2)*H*), 7.13 (m, 1H, ArC(4)*H*), 7.07 (dd, *J* = 15.2, 4.1 Hz, 1H, C(3)*H*), 5.86 (dd, *J* = 4.1, 1.7 Hz, 1H, C(4)*H*), 0.95 (s, 9H, C(C*H*$_3$)$_3$), 0.13 (s, 3H, SiC*H*$_3$), 0.00 (s, 3H, SiC*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 191.0 (*C*(1)), 148.5 (*C*(3)), 140.9 (C(4)-Ar*C*(1)), 138.0 (C(1)-Ar*C*(1)), 133.0 (C(1)-Ar*C*(4)), 132.7 (C(4)-Ar*C*(3)), 129.4 (C(4)-Ar*C*(4)), 128.7 (C(1)-Ar*C*(3,5)), 128.7 (C(1)-Ar*C*(2,6)), 128.7 (C(4)-Ar*C*(5)), 128.1 (C(4)-Ar*C*(6)), 123.1 (*C*(2)), 121.6 (C(4)-Ar*C*(2)),73.2 (*C*(4)), 26.0 (C(*C*H$_3$)$_3$), 18.5 (*C*(CH$_3$)$_3$), -4.8 (Si*C*H$_3$), -4.8 (Si*C*H$_3$); HRMS (ESI$^+$) *m/z*: $[M+Na]^+$ calcd for $C_{22}H_{27}BrO_2SiNa$ 455.0841, found 455.0836.

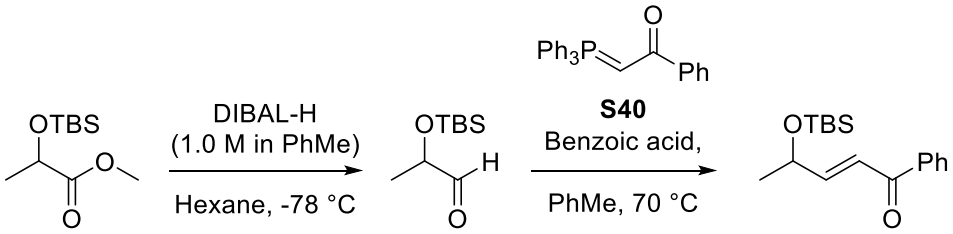
(*E*)-4-((*tert*-Butyldimethylsilyl)oxy)-1-phenyl-4-(4-(trifluoromethyl)phenyl)but-2-en-1-one S58



Following General Procedure F, 2-((*tert*-butyldimethylsilyl)oxy)-2-(4-(trifluoromethyl)phenyl)ethan-1-ol **S31** (0.723 g, 2.26 mmol) was reacted with DMSO (0.96 mL, 13.5 mmol, 6 equiv), oxalyl chloride (0.58 mL, 6.77 mmol, 3 equiv), and TEA (1094 mL, 15.8 mmol, 7 equiv) in CH_2Cl_2 (30.5 mL) to give crude 2-((tert-butyldimethylsilyl)oxy)-2-(4-(trifluoromethyl)phenyl)acetaldehyde (0.482 g) as a yellow oil, which was used without further purification. Following General Procedure I, 2-((tert-butyldimethylsilyl)oxy)-2-(4-(trifluoromethyl)phenyl)acetaldehyde (0.482 g, 1.51 mmol), 1-phenyl-2-(triphenylphosphoranylidene)ethan-1-one **S40** (0.864 g, 2.27 mmol), and benzoic acid (0.019

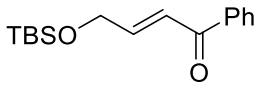
g, 0.151 mmol) were reacted in anhydrous PhMe (10.1 mL) to give the title compound **S58** (0.107 g, 20%) as an orange oil. ν_{max} (liquid) 2956 (C-H aromatic), 2931 (C-H alkane), 2858 (C-H alkane), 1672 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.96–7.89 (m, 2H, C(1)-ArC(2,6)*H*), 7.63–7.55 (m, 3H, C(4)-ArC(3,5)*H* + C(1)-ArC(4)*H*), 7.52–7.45 (m, 4H, C(4)-ArC(2,6)*H* + C(1)-ArC(3,5)*H*), 7.23 (dd, *J* = 15.1, 1.7 Hz, 1H, C(2)*H*), 7.03 (dd, *J* = 15.1, 4.4 Hz, 1H, C(3)*H*), 5.49 (dd, *J* = 4.5, 1.6 Hz, 1H, C(4)*H*), 0.97 (s, 9H, C(C*H*$_3$)$_3$), 0.14 (s, 3H, SiC*H*$_3$), 0.02 (s, 3H, SiC*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 190.6 (*C*(1)), 149.3 (C(4)-Ar*C*(1)), 145.8 (*C*(3)), 137.8 (C(1)-Ar*C*(1)), 133.11 (C(1)-Ar*C*(4)), 130.1 (q, $^2J_{C\text{-}F}$ = 32.4 Hz, C(4)-Ar*C*(4)), 128.8 (C(1)-Ar*C*(3,5)), 128.7 (C(1)-Ar*C*(2,6)), 126.9 (q, $^1J_{C\text{-}F}$ = 272.7 Hz, *C*F$_3$), 126.6 (*C*(2)), 125.6 (q, $^3J_{C\text{-}F}$ 3.8 Hz, C(4)-ArC(3,5)), 123.3 (C(4)-Ar*C*(2,6)), 74.2 (*C*(4)), 25.9 (C(*C*H$_3$)$_3$), 18.6 (*C*(CH$_3$)$_3$), -4.7 (Si*C*H$_3$); ^{19}F NMR (376 MHz, $CDCl_3$) δ_F: -62.48; HRMS (ESI+) m/z: [M+Na]+ calcd for $C_{23}H_{27}F_3O_2SiNa$ 443.1630, found 443.1626.

(*E*)-4-((*tert*-Butyldimethylsilyl)oxy)-1-phenylpent-2-en-1-one S59



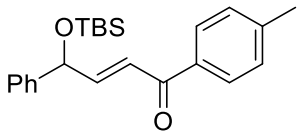
In flame-dried glassware under an Ar atmosphere, ethyl 2-((*tert*-butyldimethylsilyl)oxy)propanoate **S7** (0.697 g, 3.00 mmol) was dissolved in anhydrous hexane (15 mL) then cooled to -78 °C. DIBAL-H (1 M in PhMe, 3.90 mL, 3.90 mmol) was added dropwise and the solution was stirred at –78 °C for 1.5 h. The reaction mixture was quenched with MeOH (1.50 mL). The reaction mixture was stirred for 15 min then warmed to rt and saturated Rochelle salt solution (15 mL) was added. The biphasic reaction mixture was stirred vigorously for 16 h. The reaction mixture was diluted with hexane (10 mL) and the layers separated. The aqueous layer was extracted with hexane (3 × 30 mL) and the combined organic extracts were washed with H_2O then brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give crude 2-((*tert*-butyldimethylsilyl)oxy)propanal (0.565 g) as a colourless oil, which was used without further purification. Following General Procedure I, 2-((tert-butyldimethylsilyl)oxy)propanal (0.565 g, 3.00 mmol), 1-phenyl-2-(triphenylphosphoranylidene)ethan-1-one **S40** (1.71 g, 4.50 mmol), and benzoic acid (0.037 g, 0.30 mmol) were reacted in anhydrous PhMe (20 mL) to give the title compound **S59** (0.618 g, 71%) as a yellow oil. ν_{max} (liquid) 2955 (C-H aromatic), 2929 (C-H alkane), 2857 (C-H alkane), 1672 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.97–7.90 (m, 2H, ArC(2,6)*H*), 7.60–7.53 (m, 1H, ArC(4)*H*), 7.50–7.44 (m, 2H, ArC(3,5)*H*), 7.12 (dd, *J* = 15.2, 1.5 Hz, 1H, C(2)*H*), 7.04 (dd, *J* = 15.2, 3.5 Hz, 1H, C(3)*H*), 4.58 (qdd, *J* = 6.6, 3.5, 1.5 Hz, 1H, C(4)*H*), 1.32 (d, *J* = 6.6 Hz, 3H, C(5)*H*$_3$), 0.95 (s, 9H, C(C*H*$_3$)$_3$), 0.11 (s, 6H, 2 × SiC*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 191.0 (*C*(1)), 152.3 (*C*(3)), 138.1 (Ar*C*(1)), 132.9 (Ar*C*(4)), 128.7 (Ar*C*), 128.7 (Ar*C*), 122.9 (*C*(2)), 68.3 (*C*(4)), 26.0 (C(*C*H$_3$)$_3$), 23.7 (*C*(5)), 18.4 (*C*(CH$_3$)$_3$), -4.6 (Si*C*H$_3$), -4.7 (Si*C*H$_3$); HRMS (ESI+) m/z: [M+Na]+ calcd for $C_{17}H_{26}O_2SiNa$ 313.1600, found 313.1597.

(*E*)-4-((*tert*-Butyldimethylsilyl)oxy)-1-phenylbut-2-en-1-one S60



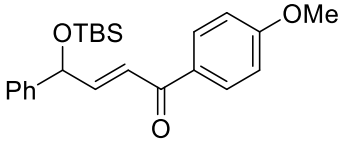
Following General Procedure I, 2-((*tert*-butyldimethylsilyl)oxy)acetaldehyde **S34** (0.250 g, 1.43 mmol) was reacted with 1-phenyl-2-(triphenylphosphoranylidene)ethan-1-one **S40** (0.818 g, 2.15 mmol), and benzoic acid (0.018 g, 0.143 mmol) were reacted in anhydrous PhMe (10 mL) to give the title compound **S60** (0.299 g, 75%) as a yellow oil. ν_{max} (liquid) 2954 (C-H aromatic), 2929 (C-H alkane), 2857 (C-H alkane), 1674 (C=O), 1628 (C=C); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.00 – 7.92 (m, 2H, ArC(2,6)*H*), 7.62 – 7.52 (m, 1H, ArC(4)*H*), 7.52 – 7.43 (m, 2H, ArC(3,5)*H*), 7.22 (dt, *J* = 15.2, 2.1 Hz, 1H, C(2)*H*), 7.11 (dt, *J* = 15.2, 3.2 Hz, 1H, C(3)*H*), 4.46 (dd, *J* = 3.2, 2.1 Hz, 2H, C(4)H_2), 0.97 (s, 9H, C(CH_3)$_3$), 0.13 (s, 6H, 2 × SiCH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 190.7 (*C*(1)), 147.9 (*C*(3)), 138.1 (Ar*C*(1)), 132.9 (Ar*C*), 128.7 (Ar*C*(4)), 128.7 (Ar*C*), 123.6 (*C*(2)), 62.8 (*C*(4)), 26.0 (C(*C*H$_3$)$_3$), 18.5 (*C*(CH$_3$)$_3$), -5.2 (Si*C*H$_3$); HRMS (ESI+) m/z: [M+H]+ calcd for $C_{16}H_{25}O_2Si$ 277.1619, found 276.1547.

(*E*)-4-((*tert*-Butyldimethylsilyl)oxy)-4-phenyl-1-(*p*-tolyl)but-2-en-1-one S61



Following General Procedure I, 1-(*p*-tolyl)-2-(triphenyl-λ^5-phosphaneylidene)ethan-1-one **S41** (0.237 g, 0.60 mmol), benzoic acid (0.005 g, 0.040 mmol), and 2-((*tert*-butyldimethylsilyl)oxy)-2-phenylacetaldehyde **S32** (0.100 g, 0.40 mmol) were reacted in anhydrous PhMe (2.8 mL). The crude product was purified by silica gel chromatography (cyclohexane:Et_2O 97:3) to give the title compound **S61** (0.105 g, 72%) as colourless oil. ν_{max} (liquid) 2929 (C-H aromatic), 2857 (C-H alkane), 1665 (C=O), 1624 (C=C); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.84 (d, *J* = 8.2 Hz, 2H, C(1)-ArC(2,6)*H*), 7.39 – 7.30 (m, 4H, ArC*H*), 7.30 – 7.25 (m, 3H, ArC*H*), 7.20 (dd, *J* = 15.1, 1.7 Hz, 1H, C(2)*H*), 7.05 (dd, *J* = 15.1, 4.2 Hz, 1H, C(3)*H*), 5.43 (dd, *J* = 4.2, 1.7 Hz, 1H, C(4)*H*), 2.42 (s, 3H, C(1)-ArC(4)H_3), 0.95 (s, 9H, C(CH_3)$_3$), 0.11 (s, 3H, SiCH_3), -0.01 (s, 3H, SiCH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 190.5 (*C*(1)), 150.1 (*C*(3)), 143.7 (C(1)-Ar*C*(4)), 141.8 (C(1)-Ar*C*(1)), 135.5 (C(1)-Ar*C*(1)), 129.4 (C(1)-Ar*C*(2,6)), 128.8 (C(1)-Ar*C*(3,5)), 128.7 (C(4)-Ar*C*(3,5)), 127.8 (C(4)-Ar*C*(4)), 126.4 (C(4)-Ar*C*(2,6)), 122.7 (*C*(2)), 74.7 (*C*(4)), 26.0 (C(*C*H$_3$)$_3$), 21.8 (C(1)-ArC(4)*C*H$_3$), 18.5 (*C*(CH$_3$)$_3$), -4.7 (Si*C*H$_3$), -4.7 (Si*C*H$_3$); HRMS (ESI$^+$) *m*/*z*: [M+H]$^+$ cald for $C_{23}H_{31}O_2Si$ 367.2093, found 367.2091.

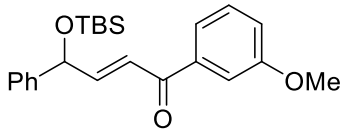
(*E*)-4-((*tert*-Butyldimethylsilyl)oxy)-1-(4-methoxyphenyl)-4-phenylbut-2-en-1-one S62



Following General Procedure I, 1-(4-methoxyphenyl)-2-(triphenyl-λ^5-phosphaneylidene)ethan-1-one **S42** (0.246 g, 0.60 mmol), benzoic acid (0.005 g, 0.040 mmol),

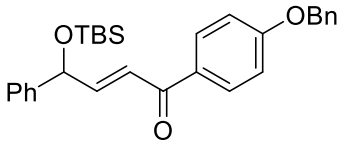
and 2-((tert-butyldimethylsilyl)oxy)-2-phenylacetaldehyde **S32** (0.100 mg, 0.40 mmol) were reacted in anhydrous PhMe (2.8 mL). The crude product was purified by silica gel chromatography (cyclohexane: Et_2O 97:3) to give the title compound **S62** (0.110 g, 72%) as an off-white solid. mp 65-67 °C; ν_{max} (film) 2929 (C-H aromatic), 2853 (C-H alkane), 1665 (C=O), 1624 (C=C); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.96-7.92 (2H, app d, J 8.9 Hz, C(1)-ArC(2,6)*H*), 7.36-7.31 (4H, m, C(4)-ArC*H*), 7.28-7.24 (1H, m, C(4)-Ar(4)*H*), 7.23 (1H, dd, J 15.1, 1.7 Hz, C(3)*H*), 7.07 (1H, dd, J 15.1, 4.2 Hz, C(2)*H*), 6.97-6.93 (2H, app d, J 8.9 Hz, C(1)-ArC(3,5)*H*), 5.42 (1H, dd, J 4.2, 1.7 Hz, C(4)*H*), 3.87 (3H, s, OCH_3), 0.96 (9H, s, C(CH_3)$_3$), 0.11 (3H, s, SiCH_3), -0.02 (3H, s, SiCH_3); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C: 189.2 (*C*(1)), 163.5 (C(1)-Ar*C*(4)), 149.6 (*C*((3)), 141.9 (C(4)-Ar*C*(1)), 131.0 (C(1)-Ar*C*(1)), 128.6 (C(1)-Ar*C*(2,6)), 127.7 (C(4)-Ar*C*(3,5)), 126.3 (C(4)-Ar*C*(2,6)), 126.1 (C(4)-Ar*C*(4)), 122.4 (*C*(2)), 113.8 (C(1)-Ar*C*(3,5)), 74.6 (*C*(4)), 55.5 (O*C*H$_3$), 25.9 (C(*C*H$_3$)$_3$), 18.4 (*C*(CH$_3$)$_3$), -4.8 (Si*C*H$_3$), -4.8 (Si*C*H$_3$); HRMS (ESI$^+$) *m*/*z*: [M+H]$^+$ cald for $C_{23}H_{31}O_3Si$ 383.2042, found 383.2039.

(*E*)-4-((*tert*-Butyldimethylsilyl)oxy)-1-(3-methoxyphenyl)-4-phenylbut-2-en-1-one S63



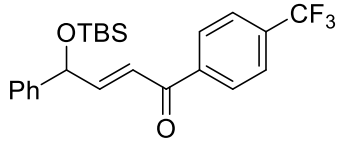
Following General Procedure I, 1-(3-methoxyphenyl)-2-(triphenyl-λ^5-phosphaneylidene)ethan-1-one **S43** (0.246 g, 0.56 mmol), benzoic acid (0.005 g, 0.040 mmol), and 2-((*tert*-butyldimethylsilyl)oxy)-2-phenylacetaldehyde **S32** (0.100 g, 0.40 mmol) were reacted in anhydrous PhMe (2.8 mL). The crude product was purified by silica gel chromatography (cyclohexane:Et_2O 97:3) to give the title compound **S63** (0.097 g, 63%) as a colourless oil. ν_{max} (liquid) 2957 (C-H aromatic), 2929 (C-H alkane), 2857 (C-H alkane), 1671 (C=O), 1597 (C=C); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.50 (dd, *J* = 7.6, 0.8 Hz, 1H, C(1)-ArC(6)*H*), 7.46 – 7.45 (m, 1H, C(1)-ArC(2)*H*), 7.42 – 7.31 (m, 5H, ArC*H*), 7.33 – 7.24 (m, 1H, ArC*H*), 7.20 (dd, *J* = 15.2, 1.6 Hz, 1H, C(2)*H*), 7.15 – 7.01 (m, 2H, C(3)H + C(1)-ArC(4)*H*), 5.43 (dd, *J* = 4.1, 1.6 Hz, 1H), 3.84 (s, 3H, OC*H*$_3$), 0.96 (s, 9H, C(C*H*$_3$)$_3$), 0.11 (s, 3H, SiC*H*$_3$), -0.02 (s, 3H, SiC*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 190.7 (*C*(1)), 159.9 (C(1)-Ar*C*(3)), 150.6 (*C*(3)), 141.7 (C(4)-Ar*C*(1)), 139.4 (C(1)-Ar*C*(1)), 129.7 (C(1)-Ar*C*(6)), 128.7 (C(4)-Ar*C*(3,5)), 127.9 (C(4)-Ar*C*(4)), 126.4 (C(4)-Ar*C*(2,6)), 122.7 (*C*(2)), 121.3 (C(1)-Ar*C*(4)), 119.7 (C(1)-Ar*C*(5)), 112.8 (C(1)-Ar*C*(2)), 74.7 (*C*(4)), 55.5 (O*C*H$_3$), 26.0 (C(*C*H$_3$)$_3$), 18.5 (*C*(CH$_3$)$_3$), -4.7 (Si*C*H$_3$), -4.8 (Si*C*H$_3$); HRMS (ESI$^+$) *m*/*z*: [M]$^+$ cald for $C_{23}H_{30}O_3Si$ 382.1964 found 382.1968.

(*E*)-1-(4-(Benzyloxy)phenyl)-4-((*tert*-butyldimethylsilyl)oxy)-4-phenylbut-2-en-1-one S64



Following General Procedure I, 1-(4-(benzyloxy)phenyl)-2-(triphenyl-λ^5-phosphaneylidene)ethan-1-one **S45** (0.379 g, 0.790 mmol), benzoic acid (0.006 g, 0.052 mmol), and 2-((*tert*-butyldimethylsilyl)oxy)-2-phenylacetaldehyde **S32** (0.140 g, 0.520 mmol) were reacted in anhydrous PhMe (3.0 mL). The crude product was purified by silica gel chromatography (cyclohexane:Et_2O 85:15) to give the title compound **S64** (0.210 g, 82%) as a colourless oil. ν_{max} (liquid) 2953 (C-H aromatic), 2929 (C-H alkane), 2856 (C-H alkane), 1667 (C=O), 1598 (C=C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.9 Hz, 2H, C(1)-ArC(2,6)*H*), 7.47 – 7.27 (m, 10H, ArC*H*), 7.20 (dd, *J* = 15.1, 1.7 Hz, 1H, C(2)*H*), 7.08 – 6.99 (m, 3H, C(3)H + C(1)-ArC(3,5)*H*), 5.42 (dd, *J* = 4.3, 1.6 Hz, 1H, C(4)*H*), 5.14 (s, 2H, OCH_2), 0.95 (s, 9H, C(CH_3)$_3$), 0.11 (s, 3H, SiCH_3), -0.02 (s, 3H, SiCH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.2 (*C*(1)), 162.7 (C(1)-Ar*C*(4)), 149.7 (*C*(3)), 141.9 (C(4)-Ar*C*(1)), 136.4 (OCH_2-Ar*C*(1)), 131.2 (C(1)-Ar*C*(1)), 131.0 (C(1)-Ar*C*(2,6)), 128.8 (C(4)-Ar*C*(3,5)), 128.7 (C(4)-Ar*C*(2,6)), 128.4 (C(4)-Ar*C*(4)), 127.8 (OCH_2-Ar*C*(4)), 127.6 (OCH_2-Ar*C*(3,5)), 126.4 (OCH_2-Ar*C*(2,6)), 122.5 (*C*(2)), 114.8 (C(1)-Ar*C*(3,5)), 74.7 (*C*(4)), 70.3 (O*C*H_2), 26.0 (C(*C*H_3)$_3$), 18.5 (*C*(CH$_3$)$_3$), -4.7 (Si*C*H_3), -4.7 (Si*C*H_3); HRMS (ESI$^+$) *m*/*z*: $[M+H]^+$ cald for $C_{29}H_{35}O_3Si$ 459.2355, found 459.2349.

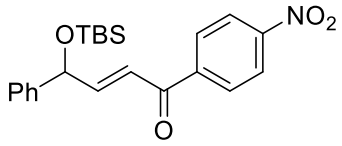
(*E*)-4-((*tert*-Butyldimethylsilyl)oxy)-4-phenyl-1-(4-(trifluoromethyl)phenyl)but-2-en-1-one S65



Following General Procedure I, 1-(4-(trifluoromethyl)phenyl)-2-(triphenyl-λ^5-phosphaneylidene)ethan-1-one **S46** (0.471 g, 1.05 mmol), benzoic acid (0.009 g, 0.070 mmol), and 2-((*tert*-butyldimethylsilyl)oxy)-2-phenylacetaldehyde **S32** (0.175 g, 0.70 mmol) were reacted in anhydrous PhMe (5.0 mL). The crude product was purified by silica gel chromatography (cyclohexane:Et_2O 97:3) to give the title compound **S65** (0.165 g, 56%) as colourless oil. ν_{max} (liquid) 2957 (C-H aromatic), 2929 (C-H alkane), 2857 (C-H alkane), 1671 (C=O), 1597 (C=C); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.00 (d, *J* = 8.0 Hz, 2H, C(1)-ArC(2,6)*H*), 7.74 (d, *J* = 8.0 Hz, 2H, C(1)-ArC(3,5)*H*), 7.40 – 7.33 (m, 4H, C(1)-ArC*H*), 7.31 – 7.27 (m, 1H, C(1)-ArC(4)*H*), 7.19 (dd, *J* = 15.2, 1.6 Hz, 1H, C(2)*H*), 7.10 (dd, *J* = 15.2, 3.9 Hz, 1H, C(3)*H*), 5.44 (dd, *J* = 3.9, 1.6 Hz, 1H, C(4)*H*), 0.96 (s, 9H, C(CH_3)$_3$), 0.11 (s, 3H, SiCH_3), -0.02 (s, 3H, SiCH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.2 (*C*(1)), 152.1 (*C*(3)), 141.4 (C(4)-Ar*C*(1)), 140.9 (C(1)-Ar*C*(1)), 134.2 (q, *J* = 32.8 Hz, C(1)-Ar*C*(4)), 129.0 (C(1)-Ar*C*(2,6)), 128.8 (C(4)-Ar*C*(3,5)), 128.0 (C(4)-Ar*C*(4)), 126.6 (q, *J* = 272.9 Hz, *C*F$_3$), 126.4 (C(4)-Ar*C*(2,6)), 125.8 (q, *J* = 3.7 Hz, C(1)-Ar*C*(3,5)), 122.3 (*C*(2)), 74.7 (*C*(4)), 26.0 (C(*C*H$_3$)$_3$),

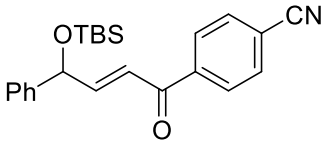
18.5 ($C(CH_3)_3$), -4.6 (SiCH_3), -4.8 (SiCH_3); ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.07; HRMS (ESI^+) *m*/*z*: $[M+Na]^+$ cald for $C_{23}H_{27}F_3O_2SiNa$ 443.1630, found 443.1621.

(*E*)-4-((*tert*-Butyldimethylsilyl)oxy)-1-(4-nitrophenyl)-4-phenylbut-2-en-1-one S66



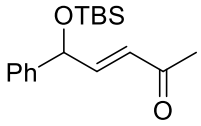
Following General Procedure I, 1-(4-nitrophenyl)-2-(triphenyl-λ^5-phosphaneylidene)ethan-1-one **S47** (0.225 g, 0.600 mmol), benzoic acid (0.005 g, 0.040 mmol), and 2-((*tert*-butyldimethylsilyl)oxy)-2-phenylacetaldehyde **S32** (0.100 g, 0.400 mmol) were reacted in anhydrous PhMe (2.8 mL). The crude product was purified by silica gel chromatography (cyclohexane:Et_2O 97/3) to give the title compound **S66** (0.079 g, 50%) as a yellow oil. ν_{max} (liquid) 2953 (C-H aromatic), 2932 (C-H alkane), 2859 (C-H alkane), 1670 (C=O), 1621 (C=C); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.32 (d, *J* = 8.2 Hz, 2H, C(1)-ArC(2,6)*H*), 8.03 (d, *J* = 8.2 Hz, 2H, C(1)-ArC(3,5)*H*), 7.38 – 7.25 (m, 5H, C(4)-ArC*H*), 7.19 (dd, *J* = 15.1, 1.4 Hz, 1H, C(2)*H*), 7.12 (dd, *J* = 15.1, 3.4 Hz, 1H, C(3)*H*), 5.45 (dd, *J* = 3.4, 1.4 Hz, 1H, C(4)*H*), 0.96 (s, 9H, C(C*H*$_3$)$_3$), 0.11 (s, 3H, SiC*H*$_3$), -0.02 (s, 3H, SiC*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 189.5 (*C*(1)), 152.9 (C(1)-Ar*C*(4)), 150.2 (*C*(3)), 142.8 (C(1)-Ar*C*(1)), 141.2 (C(4)-Ar*C*(1)), 129.6 (C(1)-Ar*C*(2,6)), 128.8 (C(4)-Ar*C*(3,5)), 128.1 (C(4)-Ar*C*(4)), 126.4 (C(4)-Ar*C*(2,6)), 124.0 (C(1)-Ar*C*(3,5)), 122.0 (*C*(2)), 74.6 (*C*(4)), 26.0 (C(*C*H$_3$)$_3$), 18.5 (*C*(CH$_3$)$_3$), -4.6 (Si*C*H$_3$), -4.8 (Si*C*H$_3$); HRMS (ESI^-) *m*/*z*: $[M-H]^-$ cald for $C_{22}H_{26}NO_4Si$ 396.1631, found 396.1638.

(*E*)-4-(4-((*tert*-Butyldimethylsilyl)oxy)-4-phenylbut-2-enoyl)benzonitrile S67



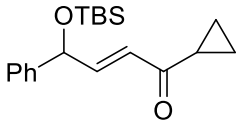
Following General Procedure I, 4-(2-(triphenyl-λ^5-phosphaneylidene)acetyl)benzonitrile **S48** (0.243 g, 0.600 mmol), benzoic acid (0.005 g, 0.040 mmol), and 2-((*tert*-butyldimethylsilyl)oxy)-2-phenylacetaldehyde **S32** (0.100 g, 0.400 mmol) were reacted in anhydrous PhMe (2.8 mL). The crude product was purified by silica gel chromatography (cyclohexane:Et_2O 97:3) to give the title compound **S67** (0.079 g, 52%) as colourless oil. ν_{max} (liquid) 2953 (C-H aromatic), 2929 (C-H alkane), 2857 (C-H alkane), 1668 (C=O), 1618 (C=C); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.97 (d, *J* = 8.5 Hz, 2H, C(1)-ArC(2,6)*H*), 7.77 (d, *J* = 8.5 Hz, 2H, C(1)-ArC(3,5)*H*), 7.40 – 7.26 (m, 5H, C(4)-ArC*H*), 7.17 (dd, *J* = 15.2, 1.3 Hz, 1H, C(2)*H*), 7.10 (dd, *J* = 15.2, 3.6 Hz, 1H, C(3)*H*), 5.44 (dd, *J* = 3.6, 1.3 Hz, 1H, C(4)*H*), 0.95 (s, 9H, C(C*H*$_3$)$_3$), 0.11 (s, 3H, SiC*H*$_3$), -0.02 (s, 3H, SiC*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 189.7 (*C*(1)), 152.6 (*C*(3)), 141.3 (C(4)-Ar*C*(1)), 132.6 (C(1)-Ar*C*(2,6)), 129.0 (C(1)-Ar*C*(3,5)), 128.8 (C(4)-Ar*C*(3,5)), 128.1 (C(4)-Ar*C*(4)), 126.4 (C(4)-Ar*C*(2,6)), 121.9 (*C*(2)), 118.1 (C(1)-Ar*C*(4)), 116.1 (*C*≡N), 74.6 (*C*(4)), 25.9 (C(*C*H$_3$)$_3$), 18.5 (*C*(CH$_3$)$_3$), -4.6 (Si*C*H$_3$), -4.8 (Si*C*H$_3$); HRMS (ESI^-) *m*/*z*: $[M-H]^-$ cald for $C_{23}H_{26}NO_2Si$ 376.1733 found 376.1737.

(*E*)-5-((*tert*-Butyldimethylsilyl)oxy)-5-phenylpent-3-en-2-one S68



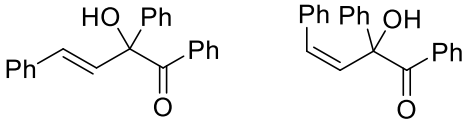
$Ba(OH)_2 \cdot H_2O$ (0.095 g, 0.50 mmol) and dimethyl (2-oxopropyl)phosphonate (0.17 mL, 1.20 mmol) were dissolved in 1,4-dioxane (2.0 mL). The reaction mixture was stirred at 80 °C for 15 min. 2-((*tert*-butyldimethylsilyl)oxy)-2-phenylacetaldehyde **S32** (0.250 g, 1.00 mmol) dissolved in 1,4-dioxane (1.33 mL) and water (0.02 mL) was added to the reaction mixture at 80 °C and stirred for 1 h then cooled to rt. The reaction mixture was diluted with H_2O (20 mL) and extracted with EtOAc (3 × 20 mL). The combined organic extract were washed with H_2O (20 mL) then brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by silica gel chromatography (cyclohexane:Et_2O 97:3) to give the title compound **S68** (0.187 g, 64%) as colourless oil. ν_{max} (liquid) 2956 (C-H aromatic), 2929 (C-H alkane), 2857 (C-H alkane), 1675 (C=O), 1629 (C=C); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.42 – 7.26 (m, 5H, ArC*H*), 6.76 (dd, *J* = 15.8, 4.7 Hz, 1H, C(4)*H*), 6.33 (dd, *J* = 15.8, 1.6 Hz, 1H, C(3)*H*), 5.33 (dd, *J* = 4.8, 1.6 Hz, 1H, C(5)*H*), 2.24 (s, 3H, C(1)*H*$_3$), 0.91 (s, 9H, C(C*H*$_3$)$_3$), 0.07 (s, 3H, SiC*H*$_3$), -0.05 (s, 3H, SiC*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 198.8 (*C*(2)), 149.3 (C(4)), 141.8 (C(5)-Ar*C*(1)), 128.7 (C(5)-Ar*C*(2,6)), 128.1 (*C*(3)), 127.9 (C(5)-Ar*C*(4)), 126.28 (C(5)-Ar*C*(3,5)), 74.4 (*C*(5)), 27.2 (*C*(1)), 25.9 (C(*C*H$_3$)$_3$), 18.4 (*C*(CH$_3$)$_3$), -4.8 (Si*C*H$_3$), -4.8 (Si*C*H$_3$); HRMS (ESI$^+$) *m*/*z*: $[M+H]^+$ cald for $C_{17}H_{27}O_2Si$ 291.1780, found 291.1775.

(*E*)-4-((*tert*-Butyldimethylsilyl)oxy)-1-cyclopropyl-4-phenylbut-2-en-1-one S69



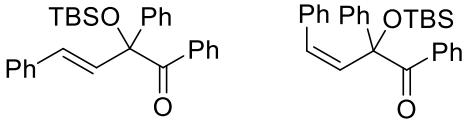
Following General Procedure I, 1-cyclopropyl-2-(triphenyl-λ^5-phosphaneylidene)ethan-1-one **S49** (0.554 g, 1.61 mmol), benzoic acid (0.013 g, 0.107 mmol), and 2-((*tert*-butyldimethylsilyl)oxy)-2-phenylacetaldehyde **S32** (0.268 g, 1.07 mmol) were reacted in anhydrous PhMe (7.14 mL). The crude product was purified by silica gel chromatography (CombiFlash, 12 g column, 100% cyclohexane 1 CV, to 10% Et_2O 10 CV, to 100% Et_2O 3 CV)) to give the title compound **S69** (0.211 g, 62%) as a colourless oil. ν_{max} (liquid) 2955 (C-H aromatic), 2929 (C-H alkane), 2857 (C-H alkane), 1665 (C=O), 1629 (C=C); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.39 – 7.26 (m, 5H, ArC*H*), 6.88 (dd, *J* = 15.6, 4.7 Hz, 1H, C(3)*H*), 6.47 (dd, *J* = 15.6, 1.7 Hz, 1H, C(2)*H*), 5.35 (dd, *J* = 4.7, 1.7 Hz, 1H, C(4)*H*), 2.13 (tt, *J* = 7.8, 4.5 Hz, 1H, C(1)-C*H*(CH$_2$)$_2$), 1.13 – 0.99 (m, 2H, C(1)-CH(C*H*$_2$)$_2$), 0.94 – 0.86 (m, 11H, C(1)-CH(C*H*$_2$)$_2$ + C(C*H*$_3$)$_3$), 0.08 (s, 3H, SiC*H*$_3$), -0.04 (s, 3H, SiC*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.6 (*C*(1)), 147.9 (*C*(3)), 142.0 (Ar*C*(1)), 128.7 (Ar*C*(2,6)), 127.9 (Ar*C*(4)), 127.4 (*C*(2)), 126.4 (Ar*C*(3,5)), 74.6 (*C*(4)), 26.0 (C(*C*H$_3$)$_3$), 19.2 (C(1)-*C*H(CH$_2$)$_2$), 18.5 (*C*(CH$_3$)$_3$), 11.5 (C(1)-CH(*C*H$_2$)$_2$), 11.4 (C(1)-CH(*C*H$_2$)$_2$), -4.7 (Si*C*H$_3$), -4.7 (Si*C*H$_3$); HRMS (ESI$^+$) *m*/*z*: $[M+Na]^+$ cald for $C_{19}H_{28}O_2SiNa$ 339.1756, found 339.1756.

(*E*)-2-Hydroxy-1,2,4-triphenylbut-3-en-1-one S70



In flame-dried glassware under an Ar atmosphere, Mg (0.146 g, 6.00 mmol) and a crystal of iodine was suspended in anhydrous THF (10 mL). (*E*)-(2-bromovinyl)benzene (0.915 g, 5.00 mmol) was added and the reaction mixture was stirred for 2 h. Benzil (1.05 g, 5.00 mmol) was dissolved in anhydrous THF (15 mL) and the freshly Grignard reagent solution was added dropwise at 0 °C. The resulting mixture was warmed to rt and stirred for 2 h. The reaction was quenched with NH_4Cl (sat. aq., 5 mL) and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 × 20 mL). The combined organic extracts were washed with brine (3 × 10 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by silica-gel column chromatography (Petrol/EtOAc 100 to 95/5) to yield the combined E and Z isomers (78:22) of the title compound **S70** (1.01 g, 64%) as a sticky yellow oil, with spectroscopic data in accordance with the literature.[23] Data for major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.82 – 7.72 (m, 2H, C(1)-ArC(2,6)*H*), 7.55 – 7.49 (m, 1H, C(1)-ArC(4)*H*), 7.48 – 7.20 (m, 12H, ArC*H*), 7.17 (d, *J* = 15.6 Hz, 1H, C(3)*H*), 6.89 (d, *J* = 15.6 Hz, 1H, C(4)*H*), 5.28 (s, 1H, O*H*).

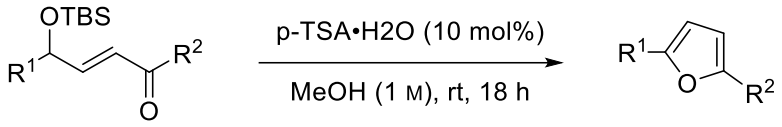
(*E*)-2-((*tert*-Butyldimethylsilyl)oxy)-1,2,4-triphenylbut-3-en-1-one 28



In flame-dried glassware under an Ar atmosphere, (*E*)-2-Hydroxy-1,2,4-triphenylbut-3-en-1-one **S70** (0.157 g, 0.50 mmol) was dissolved in anhydrous CH_2Cl_2 (5 mL) and 2,6-dimethyl pyridine (0.17 mL, 1.50 mmol) was added. The reaction mixture was cooled to 0 °C and TBSOTf (0.23 mL, 1.00 mmol) was added dropwise. The reaction mixture was warmed to rt and stirred for 6 h. The reaction mixture was diluted with CH_2Cl_2 (20 mL) and washed with H_2O (20 mL) , 1 M HCl (20 mL), and brine. The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography (CombiFlash, 12 g column, cyclohexane/Et_2O 100/0 to 90/10 over 15 CV) to give the title compound **28** (0.095 g, 44%) as a colourless oil. Data for major isomer: ν_{max} (liquid) 2955 (C-H aromatic), 2929 (C-H alkane), 2856 (C-H alkane), 1662 (C=O), 1597 (C=C); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.83 (dd, *J* = 8.5, 1.3 Hz, 2H, C(1)-ArC(2,6)*H*), 7.56 – 7.48 (m, 2H, ArC*H*), 7.50 – 7.15 (m, 11H, ArC*H*), 7.16 – 6.95 (m, 1H, C(3)*H*), 6.09 (d, *J* = 16.1 Hz, 1H, C(4)*H*), 0.81 (s, 9H, C(C*H*$_3$)$_3$), 0.07 (s, 3H, SiC*H*$_3$), -0.10 (s, 3H, SiC*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.2 (*C*(1)), 141.9 (Ar*C*), 136.6 (Ar*C*), 135.5 (Ar*C*), 134.3 (Ar*C*), 133.0 (Ar*C*), 132.4 (Ar*C*), 130.9 (Ar*C*), 130.7 (Ar*C*), 129.6 (Ar*C*), 128.7 (Ar*C*), 128.6 (Ar*C*), 128.1 (Ar*C*), 127.9 (Ar*C*), 126.9 (Ar*C*), 126.5 (Ar*C*), 85.2 (*C*(2)), 26.1 (C(*C*H$_3$)$_3$), 18.8 (*C*(CH$_3$)$_3$), -1.7 (Si*C*H$_3$), -2.5 (Si*C*H$_3$); HRMS (ESI$^+$) *m*/*z*: [M+H]$^+$ cald for $C_{28}H_{33}O_2Si$ 429.2250, found 429.2234.

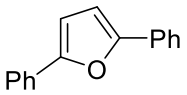
Heterocyclization Compound Data

General Procedure J



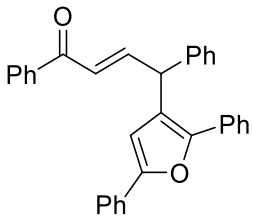
Cyclisation: The requisite TBS-protected γ-hydroxy-α,β-unsaturated ketone was dissolved in MeOH (1 M) and *p*-TSA monohydrate (0.1 equiv) was added. The reaction mixture was stirred at rt for 18 h then concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography (100% to 97/3 cyclohexane/Et_2O) to give the desired 2,5-disubstituted furan.

2,5-Diphenylfuran 3



Oxalic acid (0.332 mg, 20.0 μmol) and 2-carboxyphenylboronic acid **2** (0.090 mg, 10.0 μmol) were dissolved in MeCN (0.5 mL) and stirred at rt for 10 min. (*E*)-4-((*tert*-Butyldimethylsilyl)oxy)-1,4-diphenylbut-2-en-1-one **1** (0.0710 g, 0.200 mmol) was dissolved in MeCN (0.5 mL) and the resulting solution was added to the oxalic acid solution. The reaction was stirred at rt for 30 min and concentrated under reduced pressure. The crude residue was purified by silica-gel column chromatography (98:2 Petrol:EtOAc) to give the title compound **3** (26 mg, 59%) as a white solid, with spectroscopic data in accordance with the literature.[24] mp 86–88 °C {Lit[24] 87–88 °C}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.79 - 7.72 (m, 4H, ArC(2,6)*H*), 7.46 - 7.36 (m, 4H, ArC(3,5)*H*), 7.32 - 7.23 (m, 2H, ArC(4)*H*), 6.74 (s, 2H, HetArC(3,4)*H*).

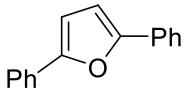
(*E*)-4-(2,5-Diphenylfuran-3-yl)-1,4-diphenylbut-2-en-1-one 4



The title compound **4** was obtained as a side-product from the previous reaction as a yellow residue (17.4 mg, 19%). ν_{max} (film) 3057 (C-H Ar), 2925 (C-H), 1669 (C=O), 1617 (C=C Ar); ^{1}H NMR (500 MHz, DMSO-d_6) δ_H: 7.90 – 7.83 (m, 2H, C(1)-ArC(2,6)*H*); 7.76 – 7.68 (m, 2H, ArC*H*), 7.68 – 7.61 (m, 2H, ArC*H*), 7.57 – 7.23 (m, 15H, ArC*H*), 6.91 (dd, *J* = 15.4, 1.6 Hz, 1H, C(2)*H*), 6.62 (s, 1H, HetArC(4)*H*), 5.21 (d, *J* = 6.5, 1H, C(4)*H*); ^{13}C NMR (126 MHz, DMSO-d_6) δ_C: 189.6 (*C*(1)), 152.1 (HetAr*C*(5)), 148.5 (*C*(3)), 148.0 (HetAr*C*(2)), 141.3 (C(4)-Ar*C*(1)), 137.1 (C(1)-Ar*C*(1)), 133.2 (C(1)-Ar*C*(4)), 130.1 (Ar*C*), 129.8 (Ar*C*), 128.9 (Ar*C*), 128.9 (Ar*C*), 128.9 (Ar*C*), 128.8 (Ar*C*), 128.3 (Ar*C*), 127.9 (Ar*C*), 127.8 (Ar*C*), 127.8 (Ar*C*),

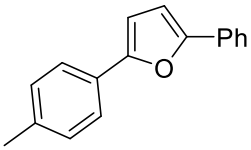
127.0 (Ar*C*), 126.1 (Ar*C*), 125.8 (Ar*C*), 123.6 (HetAr*C*(3)), 123.4 (*C*(2)), 108.7 (HetAr*C*(4)), 44.2 (*C*(4)); HRMS (ESI$^-$) $C_{32}H_{24}O_2$ [M+Na]$^+$ found 463.1677, requires 463.1669 (+1.8 ppm).

2,5-Diphenylfuran 3



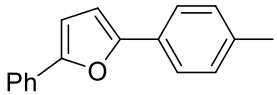
Following General Procedure , (*E*)-4-((*tert*-butyldimethylsilyl)oxy)-1,4-diphenylbut-2-en-1-one **1** (0.070 g, 0.20 mmol) and and *p*-TSA monohydrate (0.004 g, 0.02 mmol) were reacted in MeOH (0.2 mL) to give the title compound **3** (0.034 g, 76%) as a white solid, with spectroscopic data in accordance with the literature.[24] mp 86–88 °C {Lit[24] 87–88 °C}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.79 - 7.72 (m, 4H, ArC(2,6)*H*), 7.46 - 7.36 (m, 4H, ArC(3,5)*H*), 7.32 - 7.23 (m, 2H, ArC(4)*H*), 6.74 (s, 2H, HetArC(3,4)*H*).

2-Phenyl-5-(*p*-tolyl)furan 7



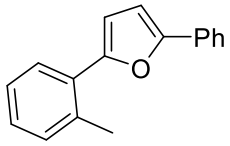
Following General Procedure , (*E*)-4-((*tert*-butyldimethylsilyl)oxy)-1-phenyl-4-(*p*-tolyl)but-2-en-1-one **S50** (0.073 g, 0.20 mmol) and *p*-TSA monohydrate (0.004 g, 0.02 mmol) were reacted in MeOH (0.2 mL) to give the title compound **7** (0.026 g, 56%) as a white solid, with spectroscopic data in accordance with the literature.[25] mp 96–98 °C {Lit[25] 97–99 °C}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.66 (d, *J* = 8.0 Hz, 2H, C(2)-ArC(2,6)*H*), 7.57 (d, *J* = 8.1 Hz, 2H, C(5)-ArC(2,6)*H*), 7.32 (dd, *J* = 8.0, 7.8 Hz, 2H, C(2)-ArC(3,5)*H*), 7.21–7.12 (m, 3H, C(5)-ArC(3,5)*H* + C(2)-ArC(4)*H*), 6.65 (d, *J* = 3.5 Hz, 1H, HetArC(4)*H*), 6.63–6.58 (d, *J* = 3.5 Hz, 1H, HetArC(3)*H*), 2.30 (s, 3H, C*H*$_3$).

2-Phenyl-5-(*p*-tolyl)furan 7



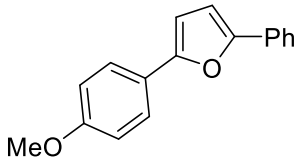
Following General Procedure , (*E*)-4-((*tert*-butyldimethylsilyl)oxy)-4-phenyl-1-(*p*-tolyl)but-2-en-1-one **S61** (0.073 g, 0.20 mmol) and *p*-TSA monohydrate (0.004 g, 0.02 mmol) were reacted in MeOH (0.2 mL) to give the title compound **7** (0.038 g, 80%) as a white solid, with spectroscopic data in accordance with the literature.[25] mp 96–98 °C {Lit[25] 97–99 °C}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.66 (d, *J* = 8.0 Hz, 2H, C(2)-ArC(2,6)*H*), 7.57 (d, *J* = 8.1 Hz, 2H, C(5)-ArC(2,6)*H*), 7.32 (dd, *J* = 8.0, 7.8 Hz, 2H, C(2)-ArC(3,5)*H*), 7.21–7.12 (m, 3H, C(5)-ArC(3,5)*H* + C(2)-ArC(4)*H*), 6.65 (d, *J* = 3.5 Hz, 1H, HetArC(4)*H*), 6.63–6.58 (d, *J* = 3.5 Hz, 1H, HetArC(3)*H*), 2.30 (s, 3H, C*H*$_3$).

2-Phenyl-5-(*o*-tolyl)furan 8



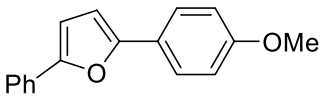
Following General Procedure , (*E*)-4-((*tert*-butyldimethylsilyl)oxy)-1-phenyl-4-(*o*-tolyl)but-2-en-1-one **S51** (0.073 g, 0.20 mmol) and *p*-TSA monohydrate (0.004 g, 0.02 mmol) were reacted in MeOH (0.2 mL) to give the title compound **8** (0.038 g, 80%) as a white solid, with spectroscopic data in accordance with the literature.[26] mp 49–50 °C {Lit[26] 49–51 °C} ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.77 (d, *J* = 7.7 Hz, 1H, C(5)-ArC(6)*H*), 7.75–7.70 (m, 2H, C(2)-ArC(2,6)*H*), 7.39 (dd, *J* = 8.4, 7.1 Hz, 2H, C(2)-ArC(3,5)*H*), 7.30–7.17 (m, 4H, ArC*H*), 6.75 (d, *J* = 3.5 Hz, 1H, HetArC(3)*H*), 6.63 (d, *J* = 3.5 Hz, 1H, HetArC(4)*H*), 2.56 (s, 3H, C*H*$_3$).

2-(4-Methoxyphenyl)-5-phenylfuran 9



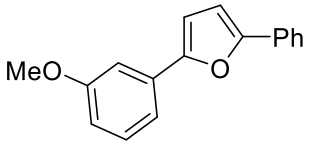
Following General Procedure , (*E*)-4-((*tert*-butyldimethylsilyl)oxy)-4-(4-methoxyphenyl)-1-phenylbut-2-en-1-one **S52** (0.077 g, 0.20 mmol) and *p*-TSA monohydrate (0.004 g, 0.02 mmol) were reacted in MeOH (0.2 mL) to give the title compound **9** (0.009 g, 18%) as a white solid, with spectroscopic data in accordance with the literature.[27] mp 116–119 °C {Lit[27] 115–118°C}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.77–7.71 (m, 2H, C(5)-ArC(2,6)*H*), 7.71–7.66 (m, 2H, C(2)-ArC(2,6)*H*), 7.44–7.36 (m, 2H, C(5)-ArC(3,5)*H*), 7.25 (tt, *J* = 6.9, 1.3 Hz, 1H, C(5)-ArC(4)*H*), 6.98–6.91 (m, 2H, C(2)-ArC(3,5)*H*), 6.72 (d, *J* = 3.5 Hz, 1H, HetArC(4)*H*), 6.61 (d, *J* = 3.5 Hz, 1H, HetArC(3)*H*), 3.85 (s, 3H, OC*H*$_3$).

2-(4-Methoxyphenyl)-5-phenylfuran 9



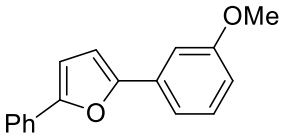
Following General Procedure , (*E*)-4-((*tert*-butyldimethylsilyl)oxy)-1-(4-methoxyphenyl)-4-phenylbut-2-en-1-one **S62** (0.077 g, 0.20 mmol) and *p*-TSA monohydrate (0.004 g, 0.02 mmol) were reacted in MeOH (0.2 mL) to give the title compound **9** (0.048 g, 97%) as a white solid, with spectroscopic data in accordance with the literature.[27] mp 116–119 °C {Lit[27] 115–118°C}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.77–7.71 (m, 2H, C(5)-ArC(2,6)*H*), 7.71–7.66 (m, 2H, C(2)-ArC(2,6)*H*), 7.44–7.36 (m, 2H, C(5)-ArC(3,5)*H*), 7.25 (tt, *J* = 6.9, 1.3 Hz, 1H, C(5)-ArC(4)*H*), 6.98–6.91 (m, 2H, C(2)-ArC(3,5)*H*), 6.72 (d, *J* = 3.5 Hz, 1H, HetArC(4)*H*), 6.61 (d, *J* = 3.5 Hz, 1H, HetArC(3)*H*), 3.85 (s, 3H, OC*H*$_3$).

2-(3-Methoxyphenyl)-5-phenylfuran 10



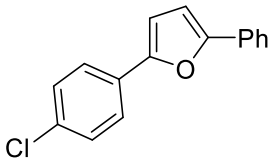
Following General Procedure , (*E*)-4-((*tert*-butyldimethylsilyl)oxy)-4-(3-methoxyphenyl)-1-phenylbut-2-en-1-one **S53** (0.077 g, 0.20 mmol) and *p*-TSA monohydrate (0.004 g, 0.02 mmol) were reacted in MeOH (0.2 mL) to give the title compound **10** (0.044 g, 89%) as a white solid, with spectroscopic data in accordance with the literature.[26] mp 81–82 °C {Lit[26] 83–84 °C}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.77–7.72 (m, 2H, C(5)-ArC(2,6)*H*), 7.41 (dd, *J* = 8.5, 7.0 Hz, 2H, C(5)-ArC(3,5)*H*), 7.36 – 7.27 (m, 4H, ArC*H*), 6.83 (dt, *J* = 7.1, 2.3 Hz, 1H, C(2)-ArC(4)*H*), 6.74 (s, 2H, HetArC*H*), 3.89 (s, 3H, OCH_3).

2-(3-Methoxyphenyl)-5-phenylfuran 10



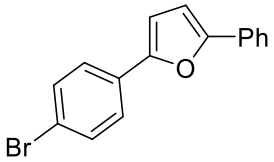
Following General Procedure , (*E*)-4-((*tert*-butyldimethylsilyl)oxy)-1-(3-methoxyphenyl)-4-phenylbut-2-en-1-one **S63** (0.077 g, 0.20 mmol) and *p*-TSA monohydrate (0.004 g, 0.02 mmol) were reacted in MeOH (0.2 mL) to give the title compound **10** (0.049 g, 98%) as a white solid, with spectroscopic data in accordance with the literature.[26] mp 81–82 °C {Lit[26] 83–84 °C}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.77–7.72 (m, 2H, C(5)-ArC(2,6)*H*), 7.41 (dd, *J* = 8.5, 7.0 Hz, 2H, C(5)-ArC(3,5)*H*), 7.36 – 7.27 (m, 4H, ArC*H*), 6.83 (dt, *J* = 7.1, 2.3 Hz, 1H, C(2)-ArC(4)*H*), 6.74 (s, 2H, HetArC*H*), 3.89 (s, 3H, OCH_3).

2-(4-Chlorophenyl)-5-phenylfuran 11



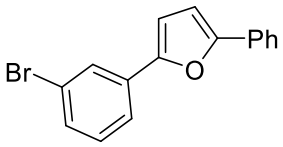
Following General Procedure , (*E*)-4-((*tert*-butyldimethylsilyl)oxy)-4-(4-chlorophenyl)-1-phenylbut-2-en-1-one **S54** (0.077 g, 0.20 mmol) and *p*-TSA monohydrate (0.004 g, 0.02 mmol) were reacted in MeOH (0.2 mL) to give the title compound **11** (0.038 g, 73%) as a white solid, with spectroscopic data in accordance with the literature.[26] mp 122–124 °C {Lit[26] 126–128 °C}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.77–7.72 (m, 2H, C(5)-ArC(2,6)*H*), 7.69–7.65 (m, 2H, C(2)-ArC(2,6)*H*), 7.44–7.35 (m, 4H, C(5)-ArC(3,5)H + C(2)-ArC(3,5)H), 7.31–7.26 (m, 1H, C(5)-ArC(4)*H*), 6.76–6.71 (m, 2H, HetArC*H*).

2-(4-Bromophenyl)-5-phenylfuran 12



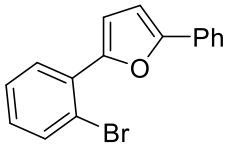
Following General Procedure , (*E*)-4-(4-bromophenyl)-4-((*tert*-butyldimethylsilyl)oxy)-1-phenylbut-2-en-1-one **S55** (0.086 g, 0.20 mmol) and *p*-TSA monohydrate (0.004 g, 0.02 mmol) were reacted in MeOH (0.2 mL) to give the title compound **12** (0.035 g, 58%) as a white solid, with spectroscopic data in accordance with the literature.[28] mp 127–129 °C {Lit[28] 125–127 °C}; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 7.74 (d, *J* = 8.3 Hz, 2H, C(5)-ArC(2,6)*H*), 7.65–7.57 (m, 2H, C(2)-ArC(2,6)*H*), 7.56–7.49 (m, 2H, C(2)-ArC(3,5)*H*), 7.41 (dd, *J* = 8.3, 7.7 Hz, 2H, C(2)-ArC(3,5)*H*), 7.33–7.26 (t, *J* = 7.7 Hz, 1H, C(5)-ArC(4)*H*), 6.74 (m, 2H, HetArC*H*).

2-(3-Bromophenyl)-5-phenylfuran 13



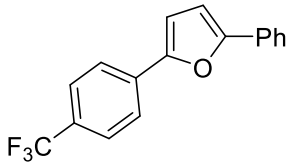
Following General Procedure , (*E*)-4-(3-bromophenyl)-4-((*tert*-butyldimethylsilyl)oxy)-1-phenylbut-2-en-1-one **S56** (0.086 g, 0.20 mmol) and *p*-TSA monohydrate (0.004 g, 0.02 mmol) were reacted in MeOH (0.2 mL) to give the title compound **13** (0.043 g, 72%) as a white solid. mp 104–106 °C; ν_{max} (film) 2922 (C-H Aromatic), 1575 (C=C Aromatic); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.91 (dd, *J* = 1.6, 1.6 Hz, 1H, C(2)-ArC(2)*H*), 7.80–7.75 (m, 2H, C(5)-ArC(2,6)*H*), 7.68 (dt, *J* = 7.8, 1.6 Hz, 1H, C(2)-ArC(6)*H*), 7.47–7.39 (m, 3H, ArC*H*), 7.35–7.29 (m, 2H, ArC*H*), 6.81–6.75 (m, 2H, HetArC*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 154.1 (HetAr*C*(2)), 151.8 (HetAr*C*(5)), 132.8 (C(2)-Ar*C*(1)), 130.6 (C(5)-Ar*C*(1)), 130.4 (C(2)-Ar*C*(2)), 130.2 (C(2)-Ar*C*(5)), 128.9 (C(5)-Ar*C*(3,5)), 127.8 (C(5)-Ar*C*(4)), 126.6 (C(2)-Ar*C*(4)), 124.0 (C(5)-Ar*C*(2,6)), 123.1 (C(2)-Ar*C*(3)), 122.3 (C(2)-Ar*C*(6)), 108.5 (HetAr*C*(4)), 107.4 (HetAr*C*(3)); HRMS (ESI+) m/z: [M]+ calcd for $C_{16}H_{11}OBr$ 297.9993, found 297.9983.

2-(2-Bromophenyl)-5-phenylfuran 14



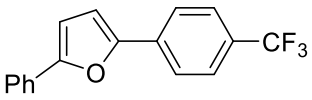
Following General Procedure , (E)-4-(2-bromophenyl)-4-((tert-butyldimethylsilyl)oxy)-1-phenylbut-2-en-1-one **S57** (0.086 g, 0.20 mmol) and *p*-TSA monohydrate (0.004 g, 0.02 mmol) were reacted in MeOH (0.2 mL) to give the title compound **14** (30.3 mg, 51%) as a white solid, with spectroscopic data in accordance with the literature.[29] mp 68–70 °C {Lit[29] 65–67 °C}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.91 (dd, *J* = 7.9, 1.7 Hz, 1H, C(2)-ArC(3)*H*), 7.79–7.73 (m, 2H, C(5)-ArC(2,6)*H*), 7.67 (dd, *J* = 8.1, 1.3 Hz, 1H, C(2)-ArC(6)*H*), 7.45–7.36 (m, 3H, C(2)-ArC(4)*H* + C(5)-ArC(3,5)*H*), 7.33–7.24 (m, 2H, C(5)-ArC(4)H + HetArC(3)*H*), 7.13 (ddd, *J* = 8.0, 7.3, 1.7 Hz, 1H, C(2)-ArC(5)*H*), 6.79 (d, *J* = 3.5 Hz, 1H, HetArC(4)*H*).

2-Phenyl-5-(4-(trifluoromethyl)phenyl)furan 15



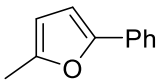
Following General Procedure , (*E*)-4-((*tert*-butyldimethylsilyl)oxy)-1-phenyl-4-(4-(trifluoromethyl)phenyl)but-2-en-1-one **S58** (0.084 g, 0.20 mmol) and *p*-TSA monohydrate (0.004 g, 0.02 mmol) were reacted in MeOH (0.2 mL) to give the title compound **15** (0.031 g, 53%) as a white solid, with spectroscopic data in accordance with the literature.[26] mp 131–132 °C {Lit[26] 133–135 °C}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.83 (d, *J* = 8.1 Hz, 2H, C(5)-ArC(3,5)*H*), 7.80 – 7.73 (m, 2H, C(2)-ArC(2,6)*H*), 7.65 (d, *J* = 8.1 Hz, 2H, C(5)-ArC(2,6)*H*), 7.47 – 7.39 (m, 2H, C(2)-ArC(3,5)*H*), 7.36 – 7.27 (m, 1H, C(2)-ArC(4)*H*), 6.86 (d, *J* = 3.5 Hz, 1H, HetArC(4)*H*), 6.81 – 6.75 (d, *J* = 3.5 Hz, 1H, HetArC(3)*H*). ^{19}F NMR (376 MHz, $CDCl_3$) δ_F: -62.49.

2-Phenyl-5-(4-(trifluoromethyl)phenyl)furan 15



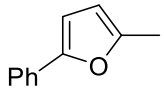
Following General Procedure , (*E*)-4-((*tert*-butyldimethylsilyl)oxy)-4-phenyl-1-(4-(trifluoromethyl)phenyl)but-2-en-1-one **S65** (0.084 g, 0.20 mmol) and *p*-TSA monohydrate (0.004 g, 0.02 mmol) were reacted in MeOH (0.2 mL) to give the title compound **15** (0.038 g, 65%) as a white solid, with spectroscopic data in accordance with the literature.[26] mp 131–132 °C {Lit[26] 133–135 °C}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.83 (d, *J* = 8.1 Hz, 2H, C(5)-ArC(3,5)*H*), 7.80 – 7.73 (m, 2H, C(2)-ArC(2,6)*H*), 7.65 (d, *J* = 8.1 Hz, 2H, C(5)-ArC(2,6)*H*), 7.47 – 7.39 (m, 2H, C(2)-ArC(3,5)*H*), 7.36 – 7.27 (m, 1H, C(2)-ArC(4)*H*), 6.86 (d, *J* = 3.5 Hz, 1H, HetArC(4)*H*), 6.81 – 6.75 (d, *J* = 3.5 Hz, 1H, HetArC(3)*H*). ^{19}F NMR (376 MHz, $CDCl_3$) δ_F: -62.49.

2-Methyl-5-phenylfuran 16



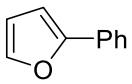
Following General Procedure , (*E*)-4-((*tert*-butyldimethylsilyl)oxy)-1-phenylpent-2-en-1-one **S59** (0.058 g, 0.20 mmol) and *p*-TSA monohydrate (0.004 g, 0.02 mmol) were reacted in MeOH (0.2 mL) to give the title compound **16** (0.020 g, 63%) as a white solid, with spectroscopic data in accordance with the literature.[28,30] mp 38–39 °C {Lit[30] 38–39 °C}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.63 (2H, m, ArC(2,6)*H*), 7.39–7.32 (m, 2H, ArC(3,5)*H*), 7.24–7.18 (tt, *J* = 7.0, 1.2 Hz, 1H, ArC(4)*H*), 6.54 (d, *J* = 3.2 Hz, 1H, HetArC(4)*H*), 6.05 (dq, *J* = 3.2, 1.0 Hz, 1H, HetArC(3)*H*), 2.37 (d, *J* = 1.0 Hz, 3H, C*H*$_3$).

2-Methyl-5-phenylfuran 16



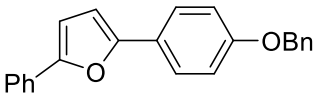
Following General Procedure , (*E*)-5-((*tert*-butyldimethylsilyl)oxy)-5-phenylpent-3-en-2-one **S68** (0.058 g, 0.20 mmol) and *p*-TSA monohydrate (0.004 g, 0.02 mmol) were reacted in MeOH (0.2 mL) to give the title compound **16** (0.023 g, 71%) as a white solid, with spectroscopic data in accordance with the literature.[28,30] mp 38–39 °C {Lit[30] 38–39 °C}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.63 (m, 2H, ArC(2,6)*H*), 7.39–7.32 (m, 2H, ArC(3,5)*H*), 7.24–7.18 (tt, *J* = 7.0, 1.2 Hz, 1H, ArC(4)*H*), 6.54 (d, *J* = 3.2 Hz, 1H, HetArC(4)*H*), 6.05 (dq, *J* = 3.2, 1.0 Hz, 1H, HetArC(3)*H*), 2.37 (d, *J* = 1.0 Hz, 3H, C*H*$_3$).

2-Phenylfuran 17



(*E*)-4-((*tert*-butyldimethylsilyl)oxy)-1-phenylbut-2-en-1-one **S60** (0.111 g, 0.40 mmol) was dissolved in MeOH (4 mL) and *p*-TSA monohydrate (0.008 g, 0.04 mmol) was added. The reaction mixture was stirred at rt for 18 h then concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography (CombiFlash, 12 g, 1 CV 100% cyclohexane, to 5% Et_2O Et_2O 10 CV, to 100% Et_2O 3 CV) to give the title compound **17** (0.035 g, 61%) as a colourless oil, with spectroscopic data in accordance with the literature.[31] ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.72 – 7.63 (m, 2H, ArC(2,6)*H*), 7.47 (dd, *J* = 1.9, 0.7 Hz, 1H, HetArC(5)*H*), 7.43 – 7.33 (m, 2H, ArC(3,5)*H*), 7.30 – 7.21 (m, 1H, ArC(4)*H*), 6.65 (dd, *J* = 3.4, 0.8 Hz, 1H, HetArC(3)*H*), 6.47 (dd, *J* = 3.4, 1.8 Hz, 1H, HetArC(4)*H*).

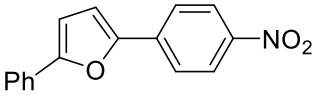
2-(4-(Benzyloxy)phenyl)-5-phenylfuran 18



Following General Procedure , (*E*)-1-(4-(benzyloxy)phenyl)-4-((*tert*-butyldimethylsilyl)oxy)-4-phenylbut-2-en-1-one **S64** (0.091 g, 0.20 mmol) and *p*-TSA monohydrate (0.004 g, 0.02 mmol) were reacted in MeOH (0.2 mL) to give the title compound **18** (0.047 g, 72%) as a white solid. mp 134–135 °C; ν_{max} (film) 3058 (C-H aromatic), 2880 (C-H alkane); 1602 (C=C aromatic); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 7.75–7.71 (m, 2H, C(5)-ArC(2,6)*H*), 7.68 (d, *J* = 8.9 Hz, 2H, C(2)-ArC(2,6)*H*), 7.48–7.44 (m, 2H, OCH_2ArC(2,6)*H*), 7.42 – 7.37 (m, 4H, ArC*H*), 7.36–7.32 (m, 1H, C(5)-ArC(4)*H*), 7.28–7.23 (m, 1H, OCH2ArC(4)*H*), 7.02 (d, *J* = 8.9 Hz, 2H, C(2)-ArC(3,5)*H*), 6.72 (d, *J* = 3.4 Hz, 1H, HetArC(4)*H*), 6.61 (d, *J* = 3.4 Hz, 1H, HetArC(3)*H*), 5.11 (s, 2H, C*H*$_2$); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 158.4 (HetArC(2)-Ar*C*(4)), 153.5 (HetAr*C*(2)), 152.9 (HetAr*C*(5)), 137.0 (OCH_2Ar*C*(1)), 131.0 (HetArC(5)-Ar*C*(1)), 128.8 (HetArC(5)-Ar*C*(3,5)), 128.8 (OCH_2-Ar*C*(3,5)), 128.2 (HetArC(5)-Ar*C*(4)), 127.6 (OCH_2-Ar*C*(2,6)), 127.2 (OCH_2-Ar*C*(4)), 125.3 (HetArC(2)-Ar*C*(2,6)), 124.3 (HetArC(2)-Ar*C*(1)), 123.7 (HetArC(5)-Ar*C*(2,6)), 115.3 (HetArC(2)-Ar*C*(3,5)), 107.3 (HetAr*C*(4)), 105.9

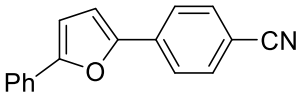
(HetAr*C*(3)), 70.2 (O*C*H$_2$); HRMS (ESI$^-$) *m/z*: [M-H]$^-$ calcd for $C_{23}H_{17}O_2$ 325.1229, found 325.1217.

2-(4-Nitrophenyl)-5-phenylfuran 19



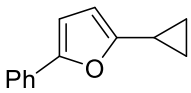
Following General Procedure , (*E*)-4-((*tert*-butyldimethylsilyl)oxy)-1-(4-nitrophenyl)-4-phenylbut-2-en-1-one **S66** (0.080 g, 0.20 mmol) and *p*-TSA monohydrate (0.004 g, 0.02 mmol) were reacted in MeOH (0.2 mL) to give the title compound **S19** (0.033, 62%) as a bright yellow solid, with spectroscopic data in accordance with the literature.[32] mp 136–137 °C {Lit[32] 134–135 °C}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.27 (d, *J* = 9.0 Hz, 2H, C(2)-ArC(3,5)*H*), 7.86 (d, *J* = 9.0 Hz, 2H, C(2)-ArC(2,6)*H*), 7.81–7.74 (m, 2H, C(5)-ArC(2,6)*H*), 7.49–7.40 (m, 2H, C(5)-ArC(3,5)*H*), 7.38–7.29 (m, 1H, C(5)-ArC(4)*H*), 6.98 (d, *J* = 3.6 Hz, 1H, HetArC(3)*H*), 6.81 (d, *J* = 3.6 Hz, 1H, HetArC(4)*H*).

4-(5-Phenylfuran-2-yl)benzonitrile 20



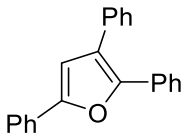
Following General Procedure , (*E*)-4-(4-((*tert*-butyldimethylsilyl)oxy)-4-phenylbut-2-enoyl)benzonitrile **S67** (0.076 g, 0.20 mmol) and *p*-TSA monohydrate (0.004 g, 0.02 mmol) were reacted in MeOH (0.2 mL) to give the title compound **20** (0.022 g, 44%) as a white solid, with spectroscopic data in accordance with the literature.[29] mp 125–127 °C {Lit[29] 118–120 °C}; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 7.81 (d, *J* = 8.7 Hz, 2H, ArC(3,5)*H*), 7.78 – 7.72 (m, 2H, HetArC(5)-ArC(2,6)*H*), 7.68 (d, *J* = 8.7 Hz, 2H, ArC(2,6)*H*), 7.47 – 7.39 (m, 2H, HetArC(5)-ArC(3,5)*H*), 7.36 – 7.29 (m, 1H, HetArC(5)-ArC(4)*H*), 6.90 (d, *J* = 3.6 Hz, 1H, HetArC(3)*H*), 6.79 (d, *J* = 3.6 Hz, 1H, HetArC(4)*H*).

2-Cyclopropyl-5-phenylfuran 21



Following General Procedure , (*E*)-4-((*tert*-butyldimethylsilyl)oxy)-1-cyclopropyl-4-phenylbut-2-en-1-one **S69** (0.063 g, 0.20 mmol) and *p*-TSA monohydrate (0.004 g, 0.02 mmol) were reacted in MeOH (0.2 mL) to give the title compound **21** (0.029 g, 80%) as a colourless oil, with spectroscopic data in accordance with the literature.[25] ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.63 – 7.57 (m, 2H, ArC(2,6)*H*), 7.39 – 7.31 (m, 2H, Ar(3,5)*H*), 7.24 – 7.17 (m, 1H, ArC(4)*H*), 6.53 (d, *J* = 3.2 Hz, 1H, HetArC(4)*H*), 6.03 (d, *J* = 3.3 Hz, 1H HetArC(3)*H*), 1.95 (tt, *J* = 8.3, 5.1 Hz, 1H, HetArC(2)-C(1)*H*), 0.95 – 0.81 (m, 4H, HetArC(2)-C(2,3)H_2).

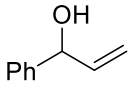
2,3,5-Triphenylfuran 29



(*E*)-2-((*tert*-Butyldimethylsilyl)oxy)-1,2,4-triphenylbut-3-en-1-one **28** (0.086 g, 0.20 mmol) was dissolved in MeOH (0.2 mL) and *p*-TSA monohydrate (0.004 g, 0.02 mmol) was added. The reaction mixture was heated to 70 °C stirred for 20 h. The reaction mixture was cooled to rt and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography (CombiFlash, 12 g, 1 CV 100% cyclohexane, to 5% Et_2O Et_2O 10 CV, to 100% Et_2O 3 CV) to give the title compound **17** (0.050 g, 76%) as a colourless oil, with spectroscopic data in accordance with the literature.[17] ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.81 – 7.73 (m, 2H, ArC*H*), 7.66 – 7.58 (m, 2H, ArC*H*), 7.50 – 7.21 (m, 11H, ArC*H*), 6.83 (s, 1H, HetArC(4)*H*).

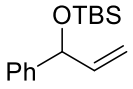
Mechanistic Studies Compound Data

1-Phenylprop-2-en-1-ol S71



In flame-dried glassware under an Ar atmosphere, benzaldehyde (0.31 mL, 3.00 mmol) was dissolved in anhydrous THF (15 mL) and cooled to 0 °C. Vinylmagnesium bromide (1 M in THF, 3.00 mL, 3.00 mmol) was added dropwise and the resultant mixture was stirred at 0 °C for 10 min then warmed to rt. The reaction mixture was stirred at rt for 4 h then quenched by slow addition of NH_4Cl (sat. aq.) (12 mL). The reaction mixture was extracted with Et_2O (3 × 30 mL). The combined organic layers were washed with brine and dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography (100% to 8/2 PE/Et_2O) to give the title compound **S71** (0.179 g, 45%) as a colourless oil, with spectroscopic data in accordance with the literature.[33] ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.41–7.31 (m, 4H, ArC*H*), 7.33–7.23 (m, 1H, ArC*H*), 6.05 (dddd, *J* = 17.1, 10.1, 6.3, 0.9 Hz, 1H, C(2)*H*), 5.39–5.31 (m, 1H, C(3)*H*), 5.24–5.15 (m, 2H, C(1)*H* + C(3)*H*), 2.00 (br s, 1H, O*H*).

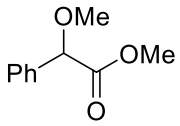
tert-Butyldimethyl((1-phenylallyl)oxy)silane 22



In flame-dried glassware under an Ar atmosphere, 1-phenylprop-2-en-1-ol **S71** (0.179 g, 1.34 mmol) was dissolved in anhydrous CH_2Cl_2 (1.34 mL) and 2,6-dimethylpyridine (0.31 mL, 2.67 mmol). The reaction mixture was cooled to 0 °C and TBS triflate (0.46 mL, 2.00 mmol) was added dropwise. The reaction mixture was warmed to rt and stirred for 1 h then quenched by addition of 1 M HCl (5 mL). The resultant mixture was extracted with CH_2Cl_2 (3 × 15 mL) and the combined organics were washed with 1 M HCl (15 mL) then brine. The organic layer was

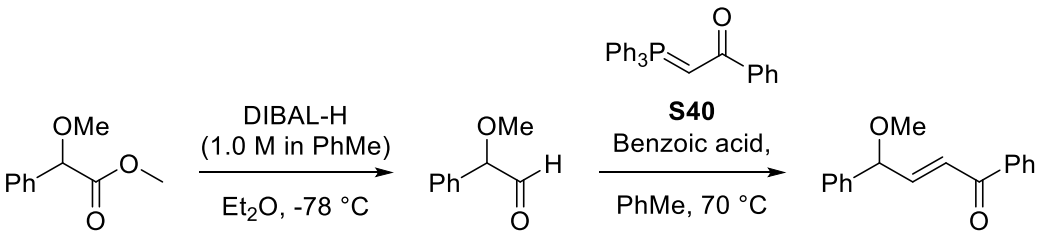
dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography (100% to 98/2 cyclohexane/Et_2O) to give the title compound **22** (0.166 g, 50%) as a colourless oil, with spectroscopic data in accordance with the literature.[34] ^1H NMR (400 MHz, $CDCl_3$) δ_H: 7.40–7.29 (m, 4H, ArC*H*), 7.27–7.22 (m, 1H, ArC*H*), 5.94 (ddd, *J* = 16.8, 10.2, 5.8 Hz, 1H, C(2)*H*), 5.30 (d, *J* = 16.8 Hz, 1H, C(3)*H*), 5.19 (d, *J* = 5.8 Hz, 1H, C(1)*H*), 5.09 (d, *J* = 10.2 Hz, 1H, C(3)*H*), 0.94 (s, 9H, C(C*H*$_3$)$_3$), 0.10 (s, 3H, SiC*H*$_3$), 0.02 (s, 3H, SiC*H*$_3$).

Methyl 2-methoxy-2-phenylacetate S72



In flame-dried glassware under a N_2 atmosphere, Sodium hydride (60% dispersion in mineral oil, 0.336 g, 8.40 mmol) was dissolved in anhydrous THF (12 mL) and cooled to 0 °C. Methyl mandelate **S1** (0.997 g, 6.00 mmol) was dissolved in anhydrous THF (3 mL) and added dropwise to the sodium hydride solution. The reaction mixture was warmed to rt and stirred for 15 min. Methyl iodide (0.52 mL) was added dropwise and the reaction mixture was stirred for 18 h. The reaction mixture was quenched by addition of NH_4Cl (sat. aq.) (12 mL) and extracted with Et_2O (2 × 50 mL). The combined organic extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give the title compound **S72** (0.858 g, 79%) as a yellow oil, with spectroscopic data in accordance with the literature.[35] ^1H NMR (400 MHz, $CDCl_3$) δ_H: 7.48–7.41 (m, 2H, ArC*H*), 7.40–7.33 (m, 3H, ArC*H*), 4.78 (s, 1H, C(2)*H*), 3.72 (s, 3H, CO_2CH_3), 3.41 (s, 3H, C(2)(OC*H*$_3$)).

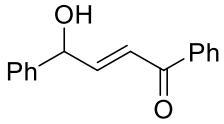
(*E*)-4-Methoxy-1,4-diphenylbut-2-en-1-one 25



In flame-dried glassware under an Ar atmosphere, methyl 2-methoxy-2-phenylacetate **S72** (0.678 g, 3.76 mmol) was dissolved in anhydrous Et_2O (19 mL) and cooled to -78 °C. DIBAL-H (1 M in PhMe, 4.51 mL, 4.51 mmol) was added dropwise and the resultant mixture was stirred for 1.5 h. The reaction mixture was quenched by dropwise addition of MeOH (2 mL) and warmed to 0 °C. Rochelle salt solution (sat. aq.) (20 mL) was added and the biphasic solution was stirred vigorously overnight. The layers were separated and the aqueous layer was extracted with Et_2O (3 × 30 mL). The combined organics were washed with Rochelle salt solution (sat. aq.) and dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give 2-methoxy-2-phenylacetaldehyde (0.576 g) as a yellow oil. The crude aldehyde was used without further purification. In flame-dried glassware under an Ar atmosphere, 2-methoxy-2-phenylacetaldehyde (0.576 g, 3.84 mmol), 1-phenyl-2-(triphenyl-λ^5-phosphaneylidene)ethan-

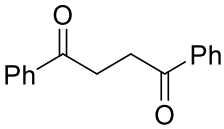
1-one **S40** (2.19 g, 5.75 mmol), and benzoic acid (0.047 g, 0.384 mmol) were dissolved in anhydrous PhMe (28 mL) and heated to 70 °C for 3 h. The reaction mixture was cooled to rt and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (99/1 to 92/8 cyclohexane/Et_2O) to give the title compound **25** (0.622 g, 64%) as a yellow solid, with spectroscopic data in accordance with the literature.[36] mp 97–99 °C {Lit[37] 98–98.5 °C}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.98–7.92 (m, 2H, C(1)-ArC(2,6)*H*), 7.56 (ddd, *J* = 6.6, 1.3, 1.2 Hz, 1H, C(1)-ArC(4)*H*), 7.50–7.44 (m, 2H, C(1)-ArC(3,5)*H*), 7.40–7.30 (m, 5H, C(4)-ArC*H*), 7.18 (dd, *J* = 15.4, 1.5 Hz, 1H, C(2)*H*), 7.04 (dd, *J* = 15.4, 5.0 Hz, 1H, C(3)*H*), 4.91 (dd, *J* = 5.0, 1.5 Hz, 1H, C(4)*H*), 3.38 (s, 3H, OCH_3).

(*E*)-4-Hydroxy-1,4-diphenylbut-2-en-1-one 27



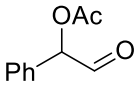
(*E*)-4-((*tert*-butyldimethylsilyl)oxy)-1,4-diphenylbut-2-en-1-one **1** (0.156 g, 0.44 mmol) was dissolved in MeOH (0.44 mL) and *p*-TSA monohydrate (0.008 g, 0.044 mmol) was added. The reaction mixture was left to stand for 3 h then immediately loaded onto a silica column (CombiFlash, 12 g silver column, 100% cyclohexane 0.5 CV, to 10% Et_2O 15 CV, to 100% Et_2O 4 CV, 100% Et_2O 4 CV) to give the title compound **27** (0.051 g, 48%) as a colourless oil, with spectroscopic data in accordance with the literature.[38] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.86 (m, 2H, C(1)-ArC(2,6)*H*), 7.53 – 7.47 (m, 1H, C(1)-ArC(2,6)*H*), 7.43 – 7.38 (m, 2H, C(1)-ArC(3,5)*H*), 7.35 – 7.24 (m, 5H, C(4)-ArC*H*), 7.22 (dd, *J* = 15.3, 1.7 Hz, 1H, C(2)*H*), 7.07 (dd, *J* = 15.3, 4.5 Hz, 1H, C(3)*H*), 5.43 (dd, *J* = 4.5, 1.7 Hz, 1H, C(4)*H*), 2.16 (br s, 1H, O*H*).

1,4-Diphenylbutane-1,4-dione S73



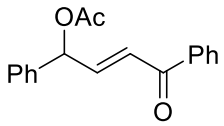
In flame-dried glassware under an N_2 atmosphere, (*E*)-4-((*tert*-butyldimethylsilyl)oxy)-1,4-diphenylbut-2-en-1-one **1** (0.352 g, 1.00 mmol) was dissolved in anhydrous THF (10 mL) and cooled to 0 °C. TBAF (1 M in THF, 2.00 mL, 2.00 mmol) was added dropwise and the reaction mixture was stirred at 0 °C for 1 h. The reaction was quenched with H_2O (10 mL) and extracted with EtOAc (2 × 20 mL). The combined organic extracts were washed with H_2O (20 mL) then brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography (CombiFlash, 12 g silver column, 100% cyclohexane 0.5 CV, to 10% Et_2O 10 CV, to 100% Et_2O 3.5 CV) to give the title compound **S73** (0.095 g, 40%) as a white solid, with spectroscopic data in accordance with the literature.[39] mp 144–146 °C {Lit[39] 144–145 °C}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.09 – 8.01 (m, 4H, ArC(2,6)*H*), 7.63 – 7.54 (m, 2H, ArC(4)*H*), 7.53 – 7.44 (m, 4H, Ar(3,5)*H*), 3.47 (s, 4H, C(2,3)H_2).

2-Oxo-1-phenylethyl acetate S77



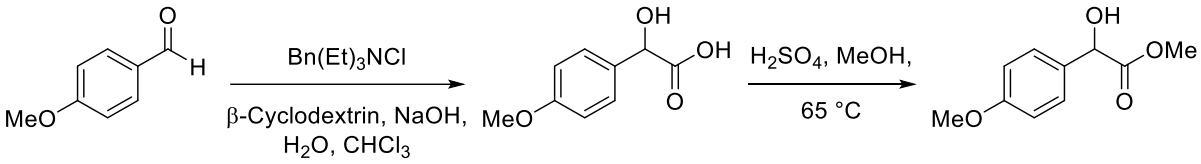
(*E*)-4-Phenylbut-3-en-2-one (1.78 g, 11.0 mmol) was added to a vigorously stirred solution of *m*-CPBA (2.96 g, 13.2 mmol) in PhMe (38.5 mL) and the reaction mixture was stirred for 24 h at rt. The reaction mixture was filtered and the white precipitate was washed with $NaHCO_3$ (sat. aq., 4 × 30 mL). The filtrate was extracted with EtOAc (3 × 50 mL) and the combined organics were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (CombiFlash, 24 g silver column, 0.5 CV 100% PE, to 30% EtOAc over 20 CV) to give the title compound **S77** (0.362 g, 15%) as a colourless oil, with spectroscopic data in accordance with the literature.[40] ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.56 (s, 1H, C(O)*H*), 7.46 – 7.38 (m, 5H, ArC*H*), 6.05 (s, 1H, C(1)*H*), 2.24 (s, 3H, C*H*$_3$).

(*E*)-4-Oxo-1,4-diphenylbut-2-en-1-yl acetate S78



Following General Procedure I, 2-oxo-1-phenylethyl acetate **S77** (0.267 g, 1.50 mmol) was reacted with 1-phenyl-2-(triphenylphosphoranylidene)ethenone **S40** (0.856 g, 2.25 mmol) and benzoic acid (0.018 g, 0.15 mmol) in anhydrous PhMe (10 mL) to give the title compound **S78** (0.316 g, 75%) as a yellow solid, with spectroscopic data in accordance with the literature.[41] mp 72-74 °C {Lit[41] 76 °C}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.94 – 7.89 (m, 2H, C(4)-ArC(2,6)*H*), 7.60 – 7.55 (m, 1H, C(4)-ArC(4)*H*), 7.50 – 7.45 (m, 2H, C(4)-ArC(3,5)*H*), 7.42 – 7.31 (m, 5H, C(1)-ArC*H*), 7.09 – 7.05 (m, 2H, C(2)*H* + C(3)*H*), 6.51 (dd, *J* = 2.2, 1.5 Hz, 1H, C(1)*H*), 2.17 (s, 3H, C*H*$_3$).

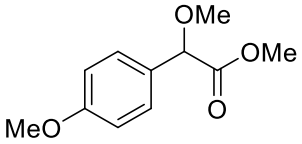
Methyl 2-hydroxy-2-(4-methoxyphenyl)acetate S79



4-Methoxybenzaldehyde (3.00 mL, 25.0 mmol), $Bn(Et)_3NCl$ (0.570 g, 2.50 mmol) and β-cyclodextrin (0.560 g, 0.500 mmol) was dissolved in $CHCl_3$ (3 mL) and heated to 50 °C. NaOH (50% w/w, 10 mL) was added dropwise *via* an addition funnel. After the addition was complete, the reaction mixture was stirred for 30 min at 50 °C then cooled to rt. The reaction mixture was diluted with 1 M NaOH (50 mL) and washed with EtOAc (2 × 50 mL). The combined organic washings were extracted with 1 M NaOH (2 × 50 mL). The combined aqueous layers were acidified to pH = 1 with conc HCl and extracted with EtOAc (3 × 50 mL). The combined organic extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resultant oil was dissolved in MeOH (15 mL) and a few drops of H_2SO_4

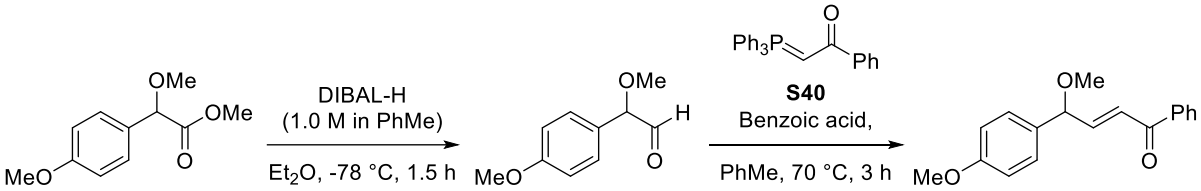
was added. The reaction mixture was heated to 70 °C for 2 h then cooled to rt. The pH was neutralised with $NaHCO_3$ (sat. aq.) and diluted with H_2O (30 mL). The aqueous solution was extracted with EtOAc (3 × 50 mL) and the combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (CombiFlash, 24 g silver column, 100% PE to 30% EtOAc over 20 CV) to give the title compound **S79** (2.10 g, 36%) as a pale yellow oil, with spectroscopic data in accordance with the literature.[42] ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.33 (d, *J* = 8.7 Hz, 2H, ArC(2,6)*H*), 6.89 (d, *J* = 8.7 Hz, 2H, ArC(3,5)*H*), 5.13 (d, *J* = 5.5 Hz, 1H, C(2)*H*), 3.80 (s, 3H, ArC(4)OC*H*$_3$), 3.75 (s, 3H, OC*H*$_3$), 3.39 (d, *J* = 5.5 Hz, 1H, O*H*).

Methyl 2-methoxy-2-(4-methoxyphenyl)acetate S80



In flame-dried glassware under an N_2 atmosphere, NaH (60% dispersion on mineral oil) (0.600 g, 15.0 mmol) was dissolved in anhydrous THF (15 mL) and cooled to 0 °C. Methyl 2-hydroxy-2-(4-methoxyphenyl)acetate **S79** (2.10 g, 10.7 mmol) was dissolved in anhydrous THF (3 mL) and added dropwise to the NaH solution. The reaction mixture was stirred for 5 min then warmed to rt. Methyl iodide (0.93 mL, 15.0 mmol) was dissolved in anhydrous THF (2 mL) and added to the reaction mixture. The reaction was stirred at rt for 3 h then quenched with NH_4Cl (sat. aq., 10 mL) and diluted with H_2O (10 mL). The solution was extracted with EtOAc (3 × 30 mL) and the combined organics were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (CombiFlash, 24 g silver column, 100% PE to 20% EtOAc over 20 CV) to give the title compound **S80** (1.04 g, 46%) as a pale yellow oil, with spectroscopic data in accordance with the literature.[43] ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.35 (d, *J* = 8.7 Hz, 2H, ArC(2,6)*H*), 6.89 (d, *J* = 8.7 Hz, 2H, ArC(3,5)*H*), 4.72 (s, 1H, C(2)*H*), 3.80 (s, 3H, ArC(4)OC*H*$_3$), 3.72 (s, 3H, CO_2C*H*$_3$), 3.38 (s, 3H, CHOC*H*$_3$).

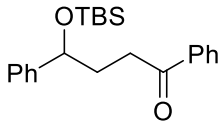
(*E*)-4-Methoxy-4-(4-methoxyphenyl)-1-phenylbut-2-en-1-one S81



In flame-dried glassware under an Ar atmosphere, methyl 2-methoxy-2-(4-methoxyphenyl)acetate **S80** (0.500 g, 2.38 mmol) was dissolved in anhydrous Et_2O (12 mL) and cooled to –78 °C. DIBAL-H (1 M in PhMe, 2.88 mL, 2.88 mmol) was added dropwise and the solution was stirred at –78 °C for 1.5 h. The reaction mixture was quenched with MeOH (1.2 mL). The reaction mixture was stirred for 15 min then warmed to rt and saturated Rochelle salt solution (15 mL) was added. The biphasic reaction mixture was stirred vigorously for 16 h. The reaction mixture was diluted with Et_2O (20 mL) and the layers separated. The aqueous

layer was extracted with Et_2O (2 × 20 mL) and the combined organic extracts were washed with H_2O then brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give crude 2-methoxy-2-(4-methoxyphenyl)acetaldehyde which was used without further purification. Following General Procedure I, 2-methoxy-2-(4-methoxyphenyl)acetaldehyde (0.401 g, 2.26 mmol) was reacted with 1-phenyl-2-(triphenylphosphoranylidene)ethenone **S40** (1.29 g, 3.39 mmol) and benzoic acid (0.027 g, 0.226 mmol) in anhydrous PhMe (15.1 mL) to give the title compound **S81** (0.374 g, 59%) as a yellow oil. ν_{max} (liquid) 2934 (C-H aromatic), 2823 (C-H alkane), 1735 (C=O), 1669 (C=C aromatic); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.99 – 7.91 (m, 2H, C(1)-ArC(2,6)*H*), 7.62 – 7.51 (m, 1H, C(1)-ArC(4)*H*), 7.51 – 7.42 (m, 2H, C(1)-ArC(3,5)*H*), 7.29 – 7.22 (m, 2H, C(4)-ArC(2,6)*H*), 7.16 (dd, *J* = 15.4, 1.5 Hz, 1H, C(2)*H*), 7.03 (dd, *J* = 15.4, 4.9 Hz, 1H, C(3)*H*), 6.91 (d, *J* = 8.7 Hz, 2H, C(1)-ArC(3,5)*H*), 4.86 (dd, *J* = 4.9, 1.5 Hz, 1H, C(4)*H*), 3.81 (s, 3H, ArCOC*H*$_3$), 3.35 (s, 3H, C(4)OC*H*$_3$); HRMS (ESI$^+$) *m/z*: $[M+Na]^+$ calcd for $C_{18}H_{18}O_3Na$ 305.1154, found 305.1155.

4-((*tert*-Butyldimethylsilyl)oxy)-1,4-diphenylbutan-1-one S82



1,4-diphenylbutane-1,4-dione (0.215 g, 0.900 mmol) was dissolved in MeOH (18 mL) and cooled to 0 °C. $NaBH_4$ (0.038 g, 1.00 mmol) was added. The reaction mixture was warmed to rt and stirred for 5 h. The reaction mixture was quenched with NH_4Cl (sat. aq., 5 mL) and diluted with H_2O (15 mL). The aqueous solution was extracted with EtOAc (3 × 20 mL) and the combined organic extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 (3 mL) and TBSCl (0.203 g, 1.35 mmol) and imidazole (0.123 g, 1.80 mmol) was added. The reaction mixture was stirred for 16 h at rt then diluted with 0.1 M HCl (20 mL). The aqueous solution was extracted with CH_2Cl_2 (3 × 20 mL) and the combined organic extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (CombiFlash, 12 g silver column, 0.5 CV 100% PE, to 20% Et_2O over 15 CV) to give the title compound **S82** (0.075 g, 24%) as a colourless oil. ν_{max} (liquid) 2927 (C-H aromatic), 2855 (C-H alkane), 1685 (C=O), 1598 (C=C aromatic); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.88 – 7.80 (m, 2H, C(1)-ArC(2,6)*H*), 7.51 – 7.42 (m, 1H, C(1)-ArC(4)*H*), 7.41 – 7.31 (m, 2H, C(1)-ArC(3,5)*H*), 7.31 – 7.20 (m, 4H, C(4)-ArC*H*), 7.19 – 7.13 (m, 1H, C(4)-ArC*H*), 4.78 (dd, *J* = 6.9, 4.8 Hz, 1H, C(4)*H*), 3.00 (ddd, *J* = 17.2, 8.9, 6.4 Hz, 1H, C(3)*H*H), 2.88 (ddd, *J* = 17.1, 8.7, 5.7 Hz, 1H, C(3)H*H*), 2.14 – 1.94 (m, 2H, C(2)*H*$_2$), 0.83 (s, 9H, C(C*H*$_3$)$_3$), -0.05 (s, 3H, SiC*H*$_3$), -0.20 (s, 3H, SiC*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 200.3 (*C*=O), 145.0 (C(4)-Ar*C*(1)), 137.1 (C(1)-Ar*C*(1)), 133.0 (C(1)-Ar*C*(4)), 128.7 (Ar*C*), 128.3 (Ar*C*), 128.1 (Ar*C*), 127.2 (C(4)-Ar*C*(4)), 126.0 (Ar*C*), 73.9 (*C*(4)), 35.0, (*C*(3)), 34.3 (*C*(2)), 26.0 (C(*C*H$_3$)$_3$), 18.4 (*C*(CH$_3$)$_3$), -4.6 (Si*C*H$_3$), -4.8 (Si*C*H$_3$); HRMS (ESI$^+$) *m/z*: $[M+Na]^+$ calcd for $C_{22}H_{30}O_2SiNa$ 377.1912, found 377.1915.

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NMR Spectra

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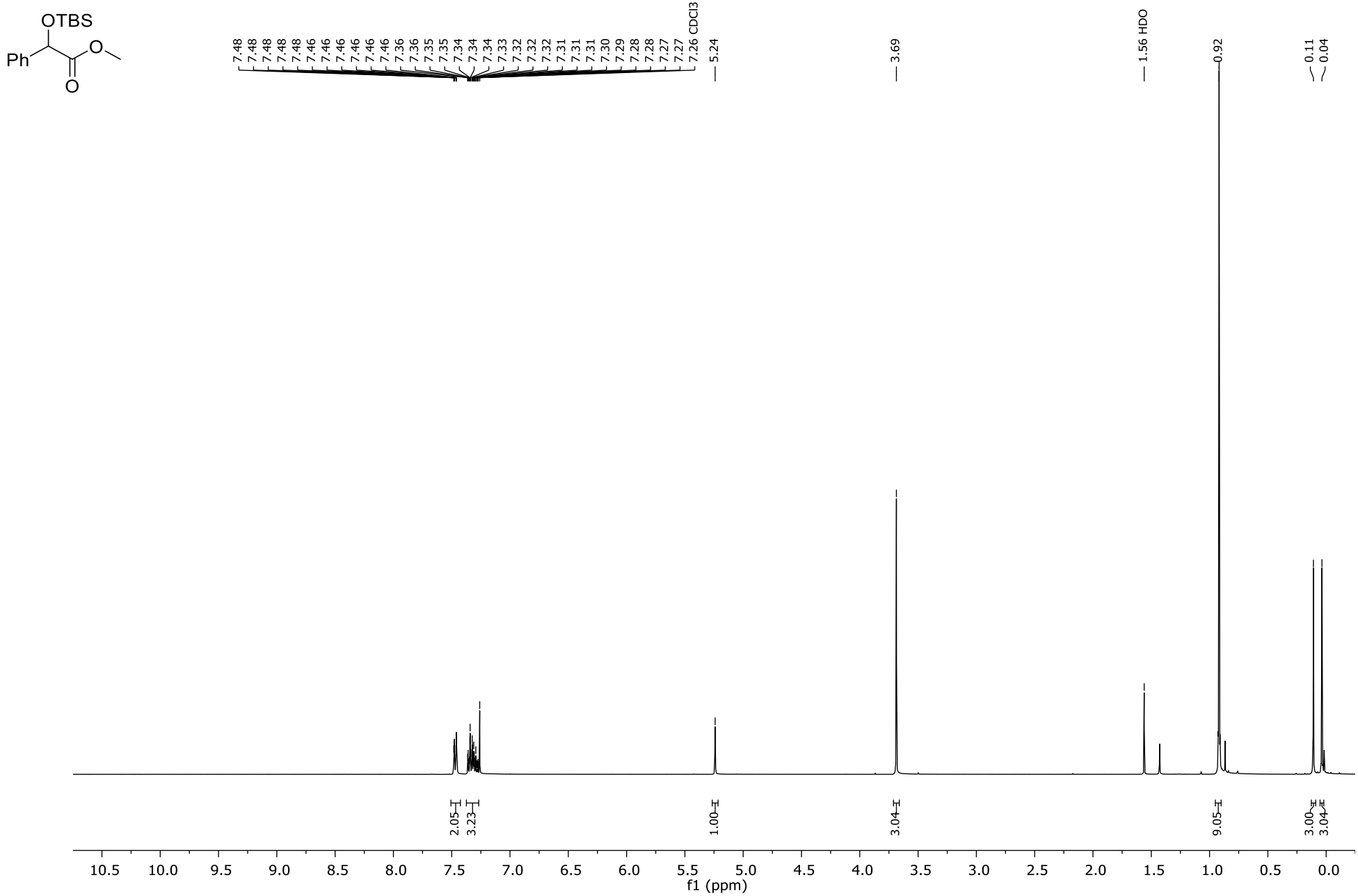

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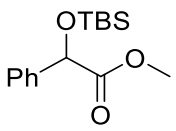

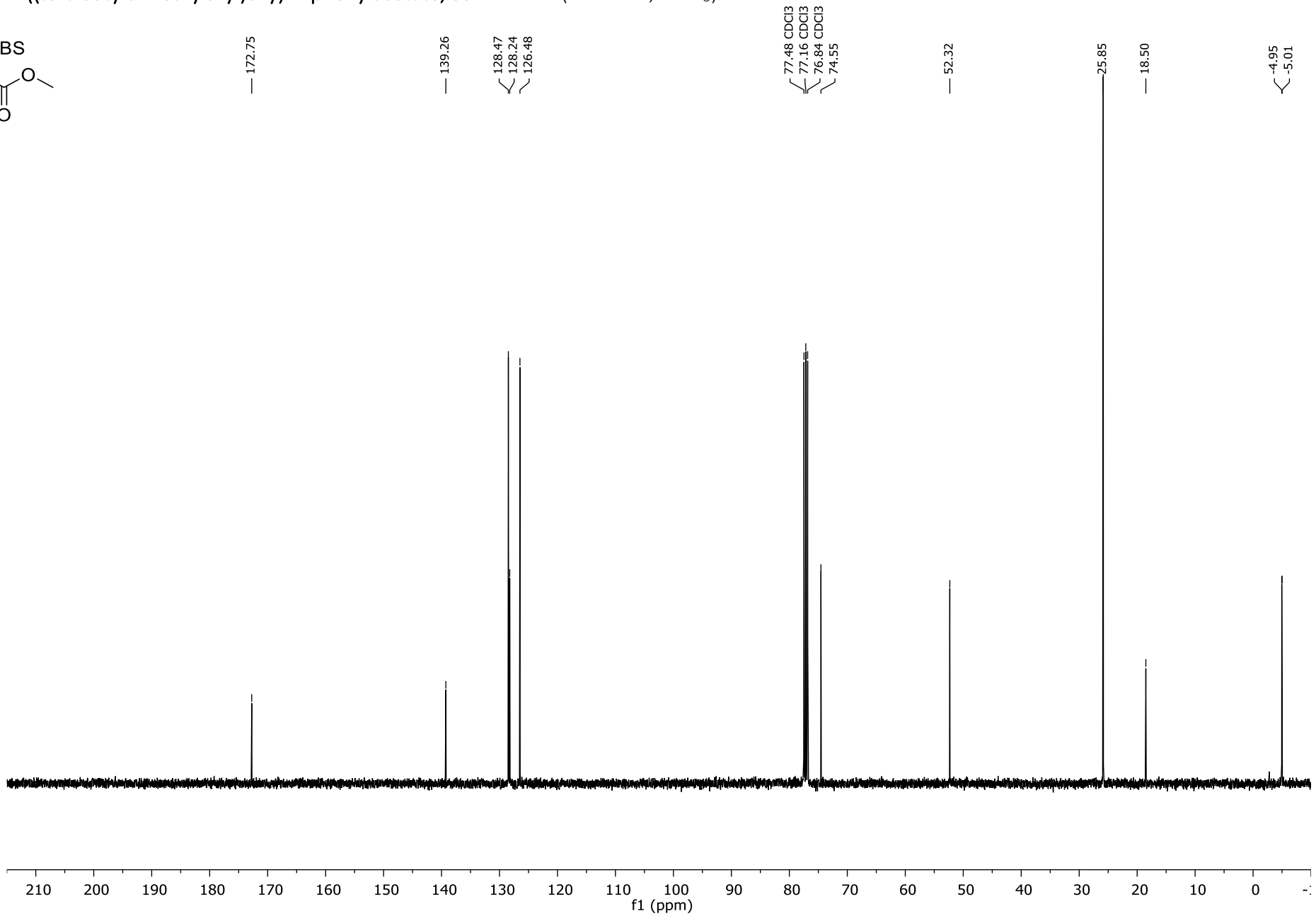

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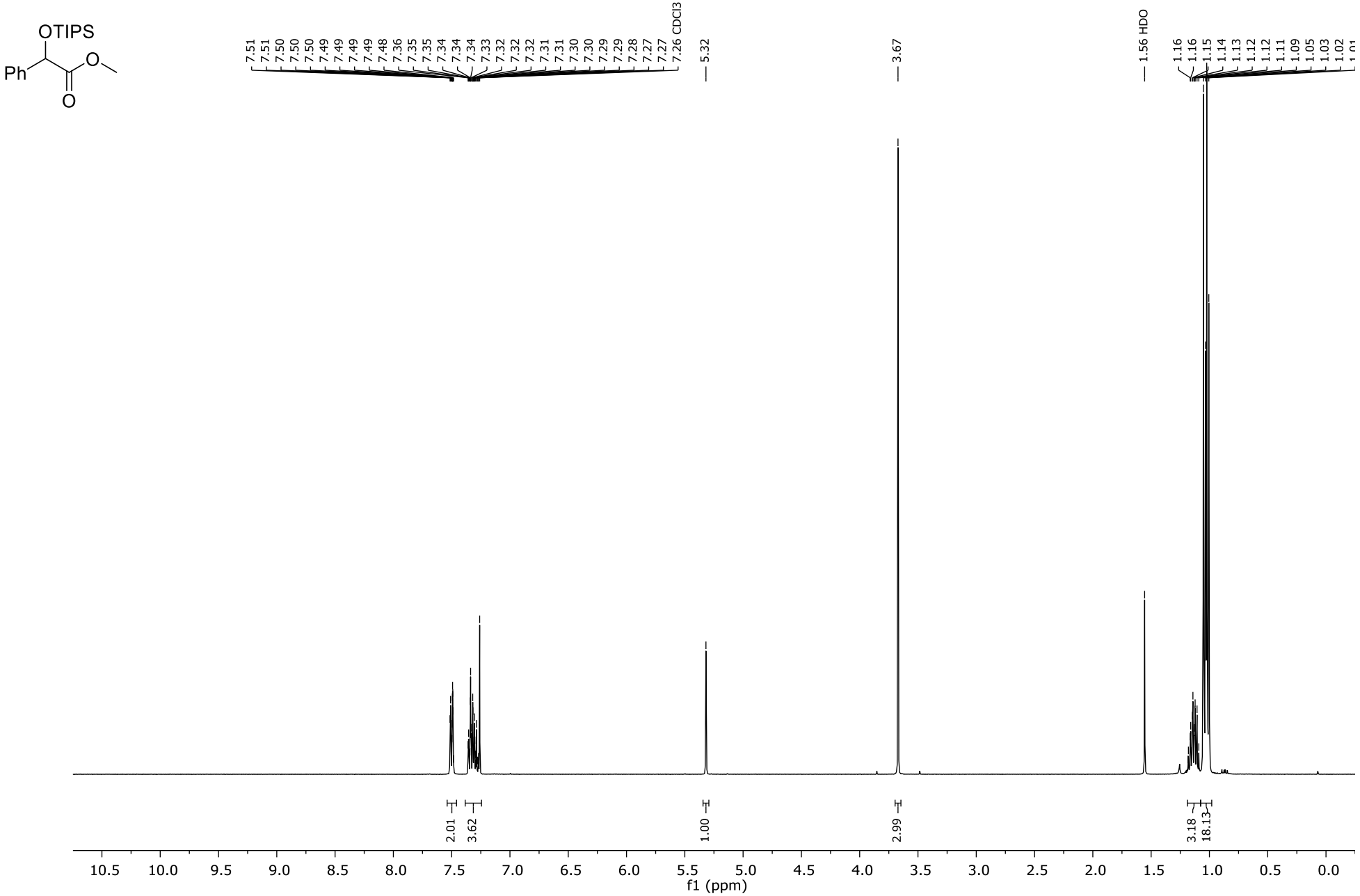

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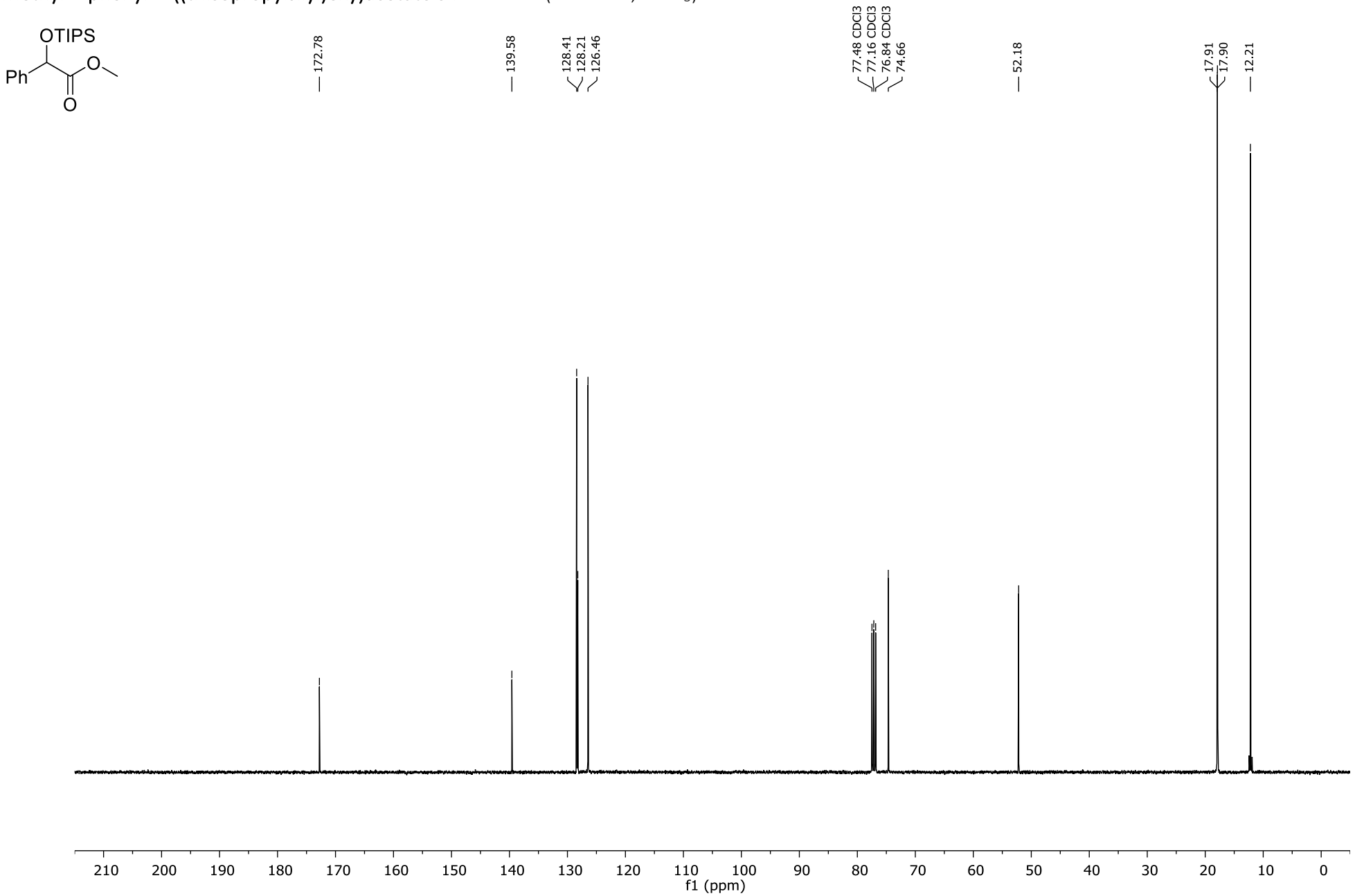

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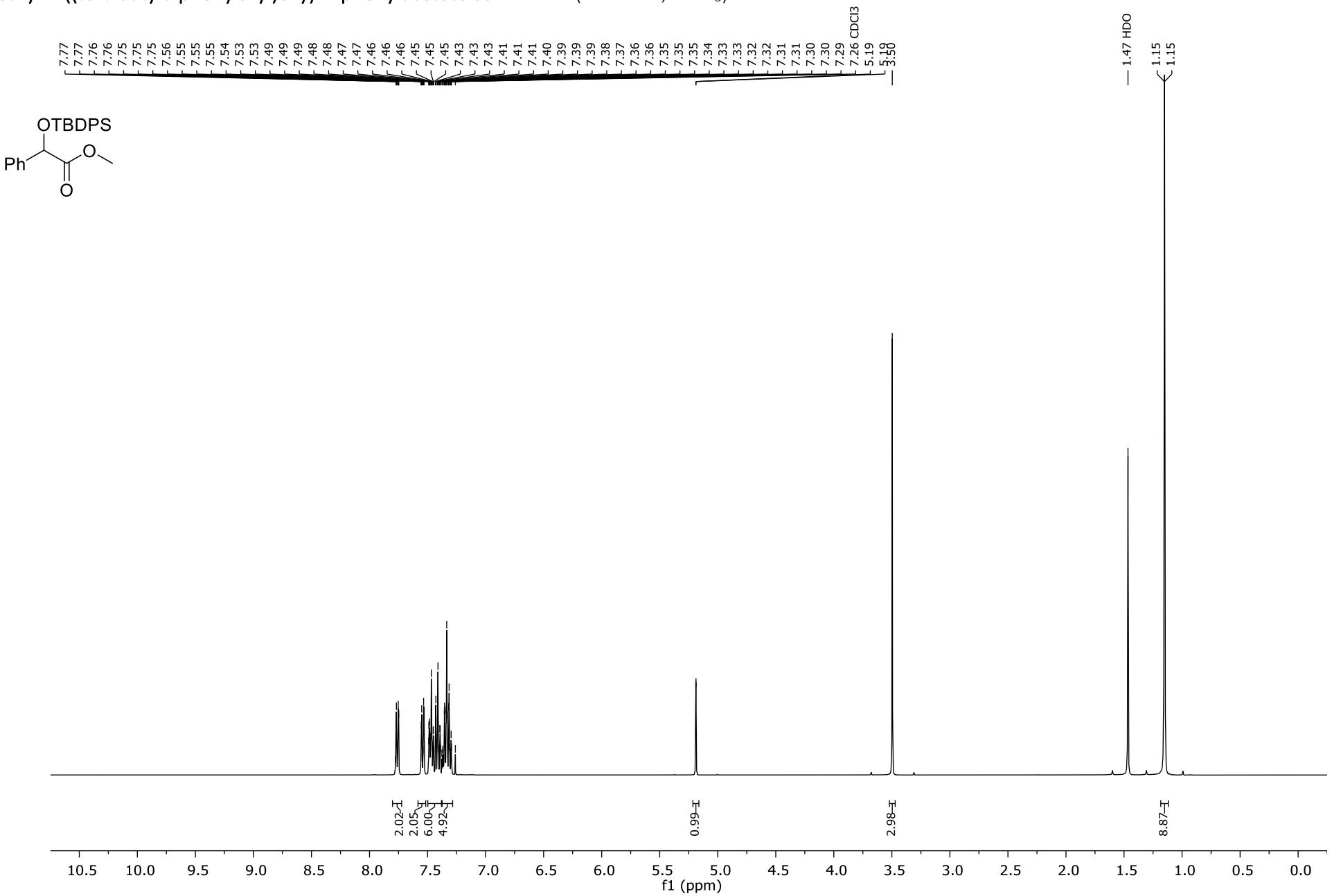

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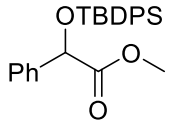

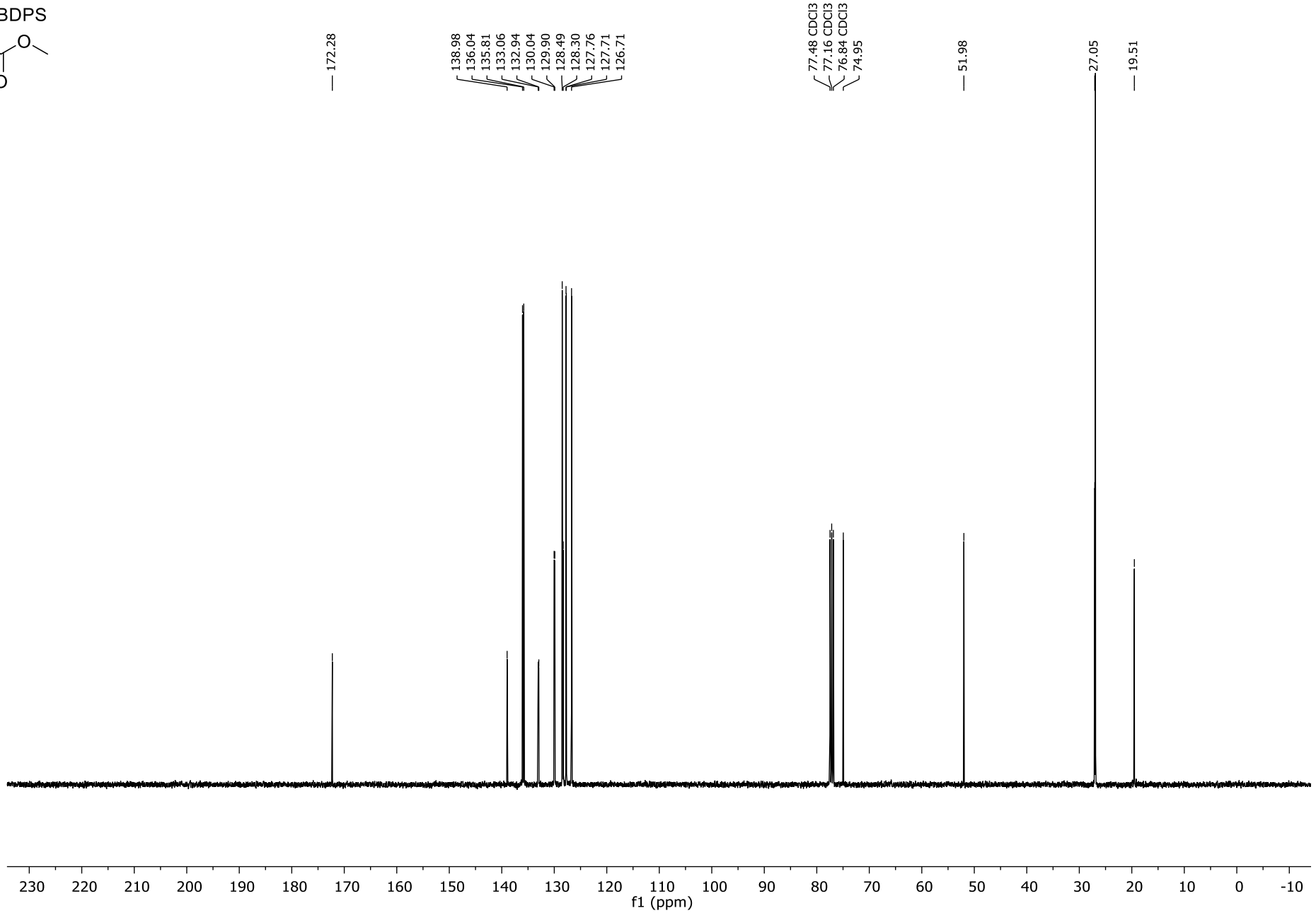

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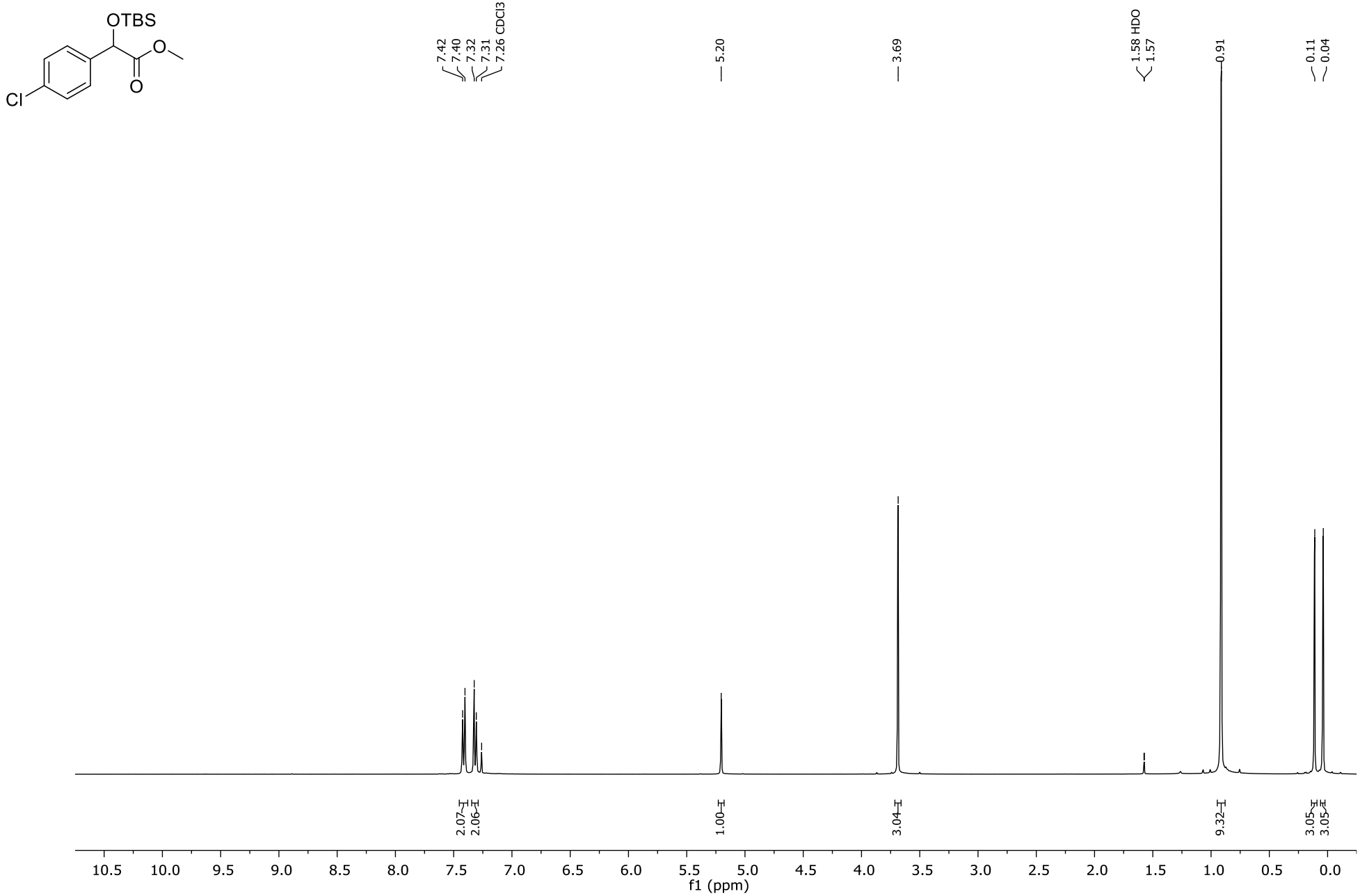

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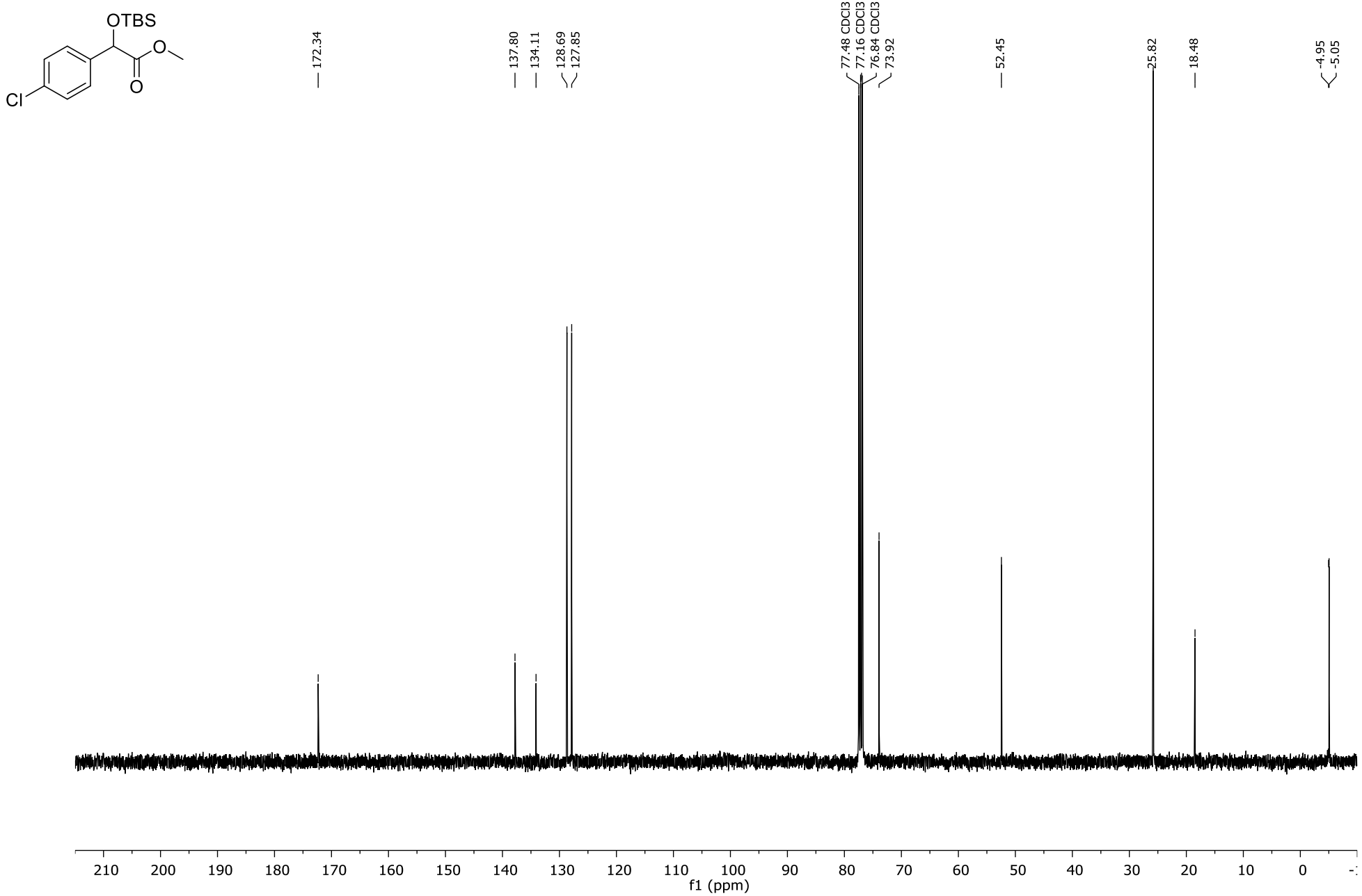

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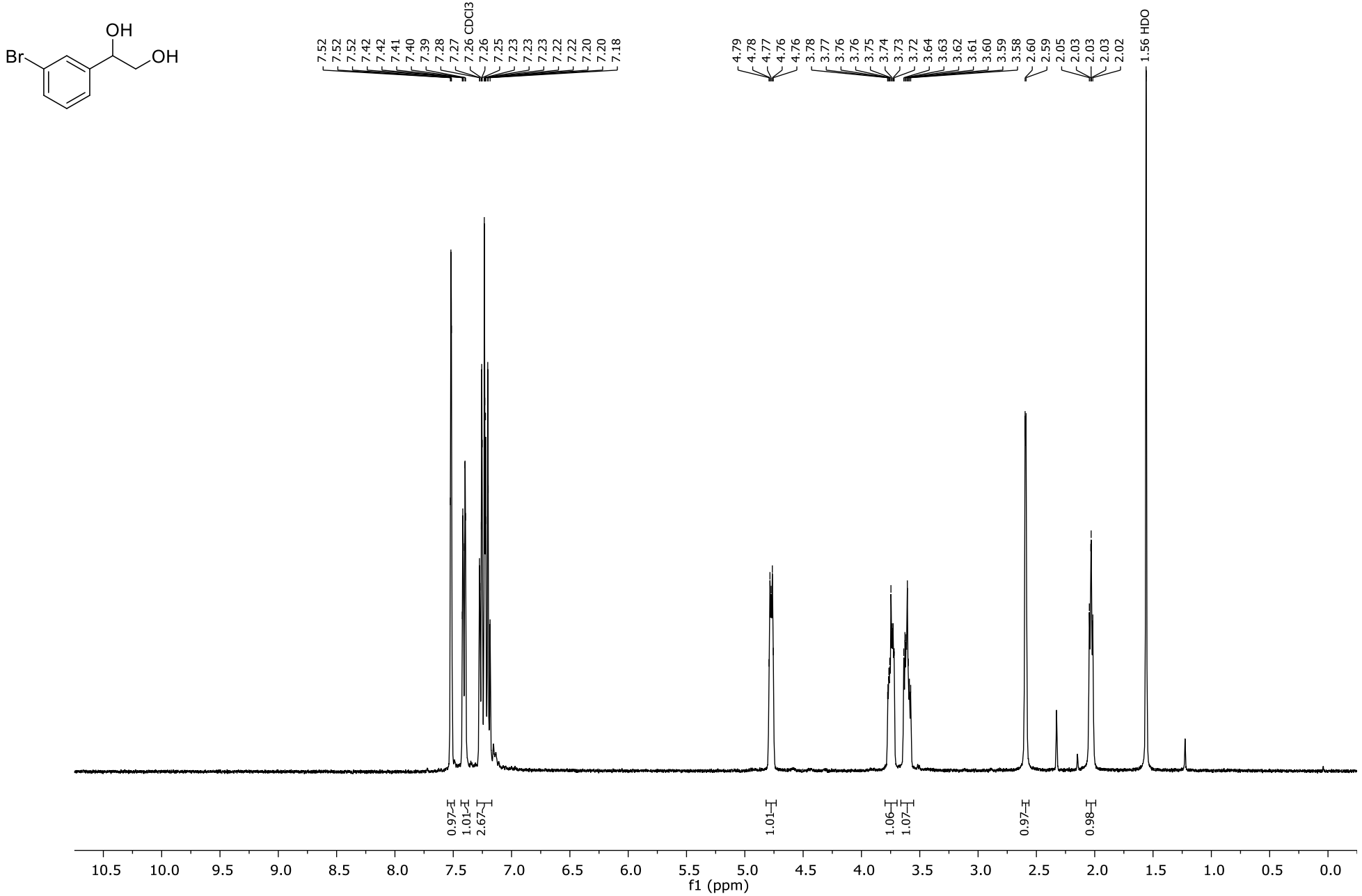

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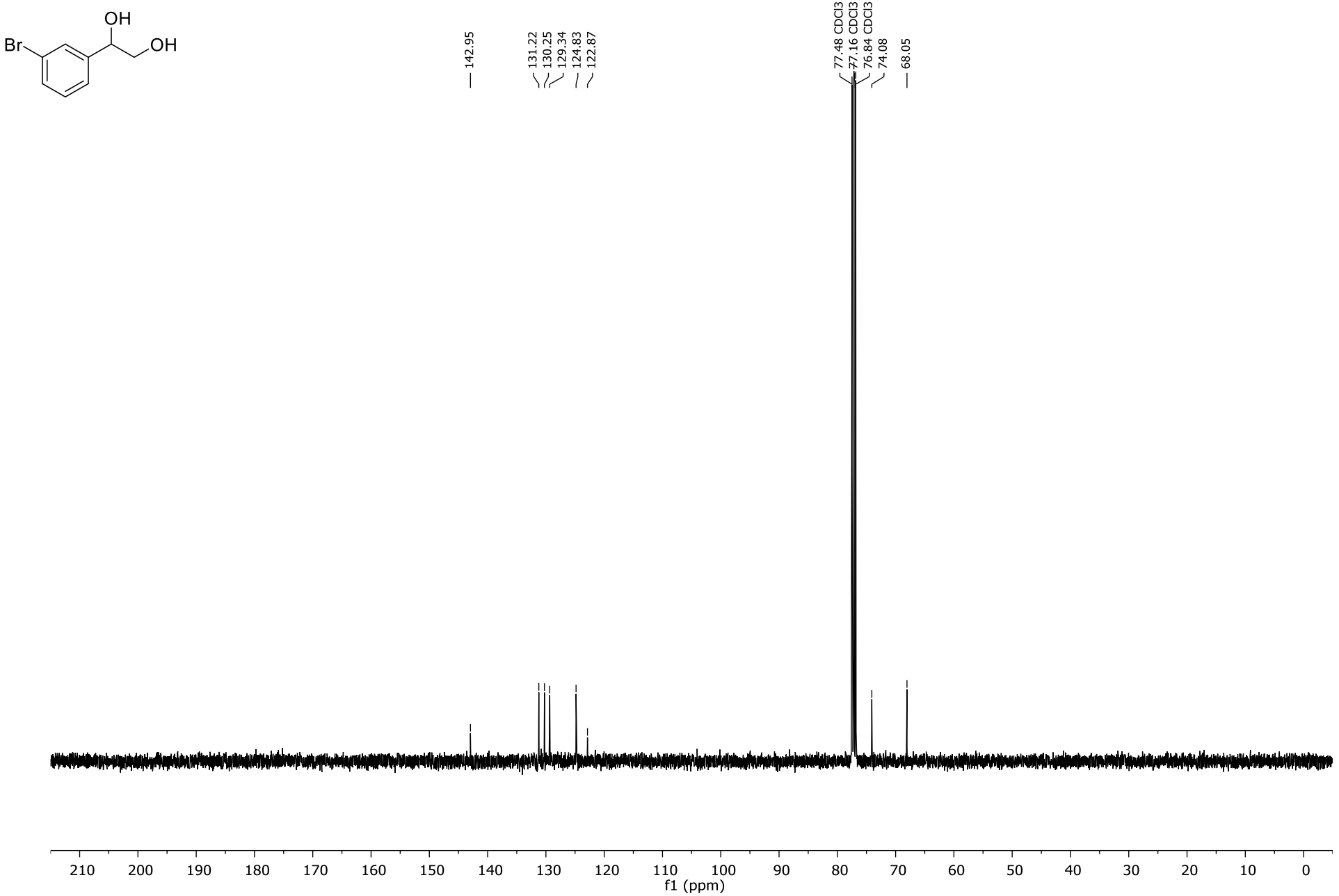

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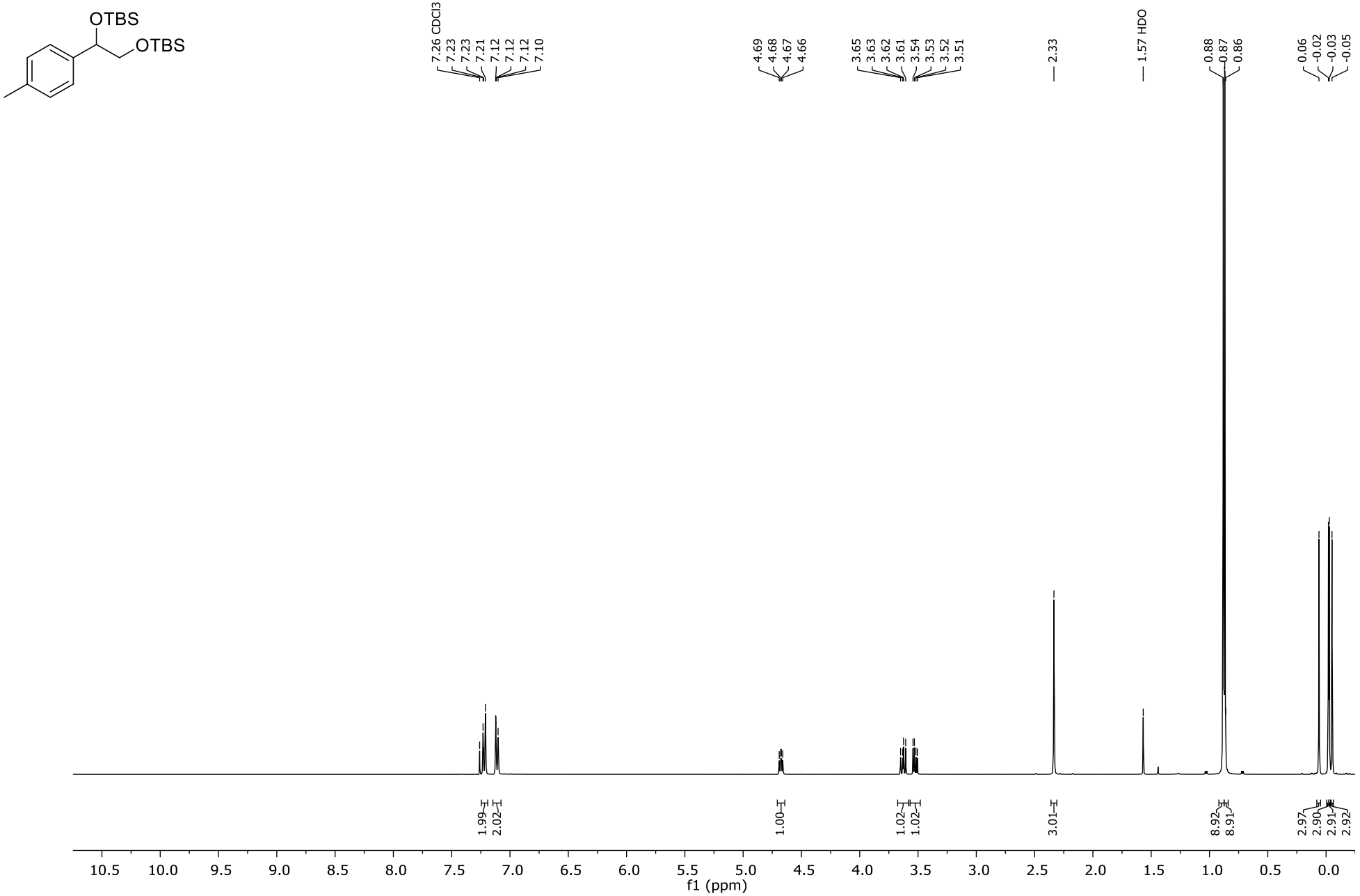
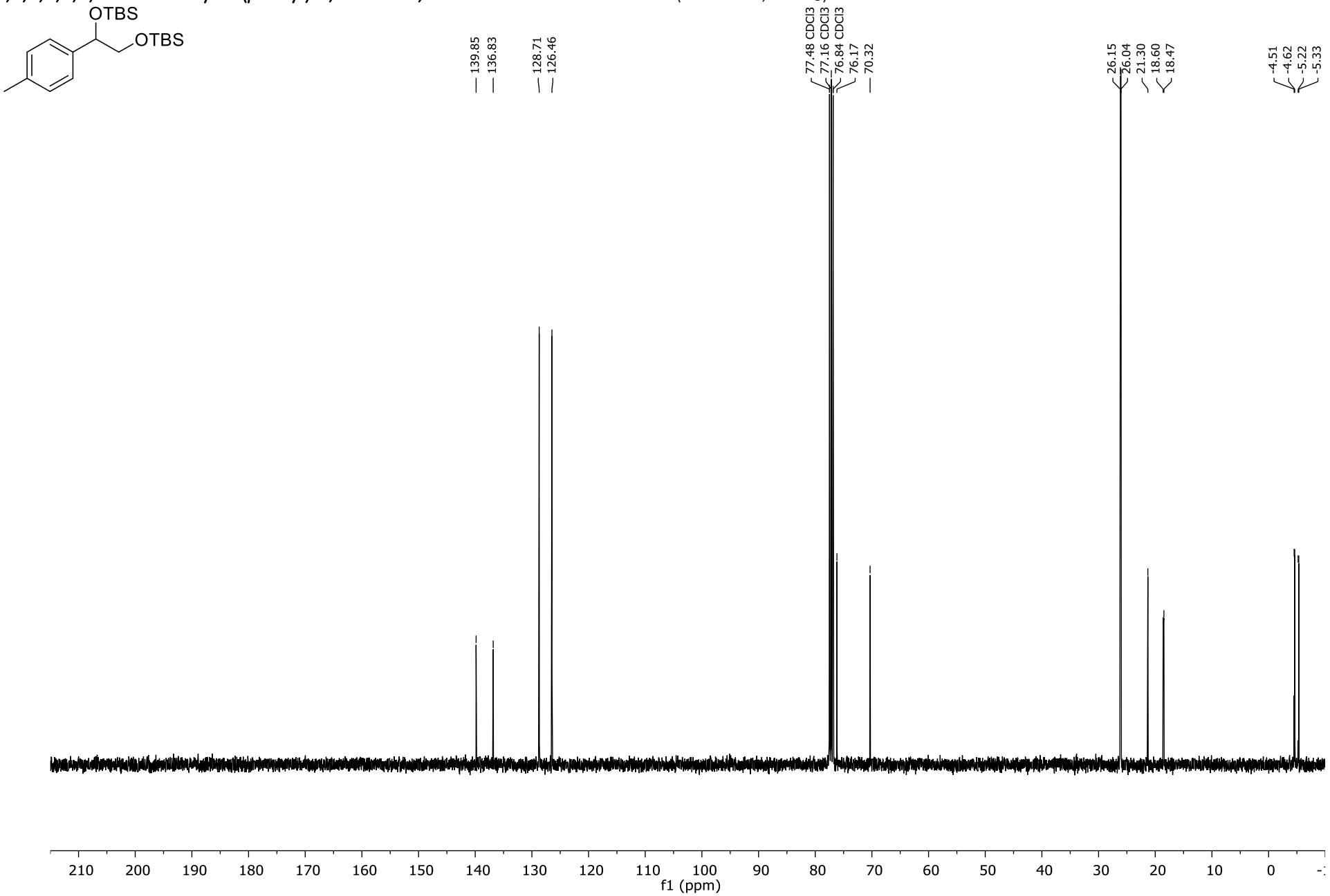
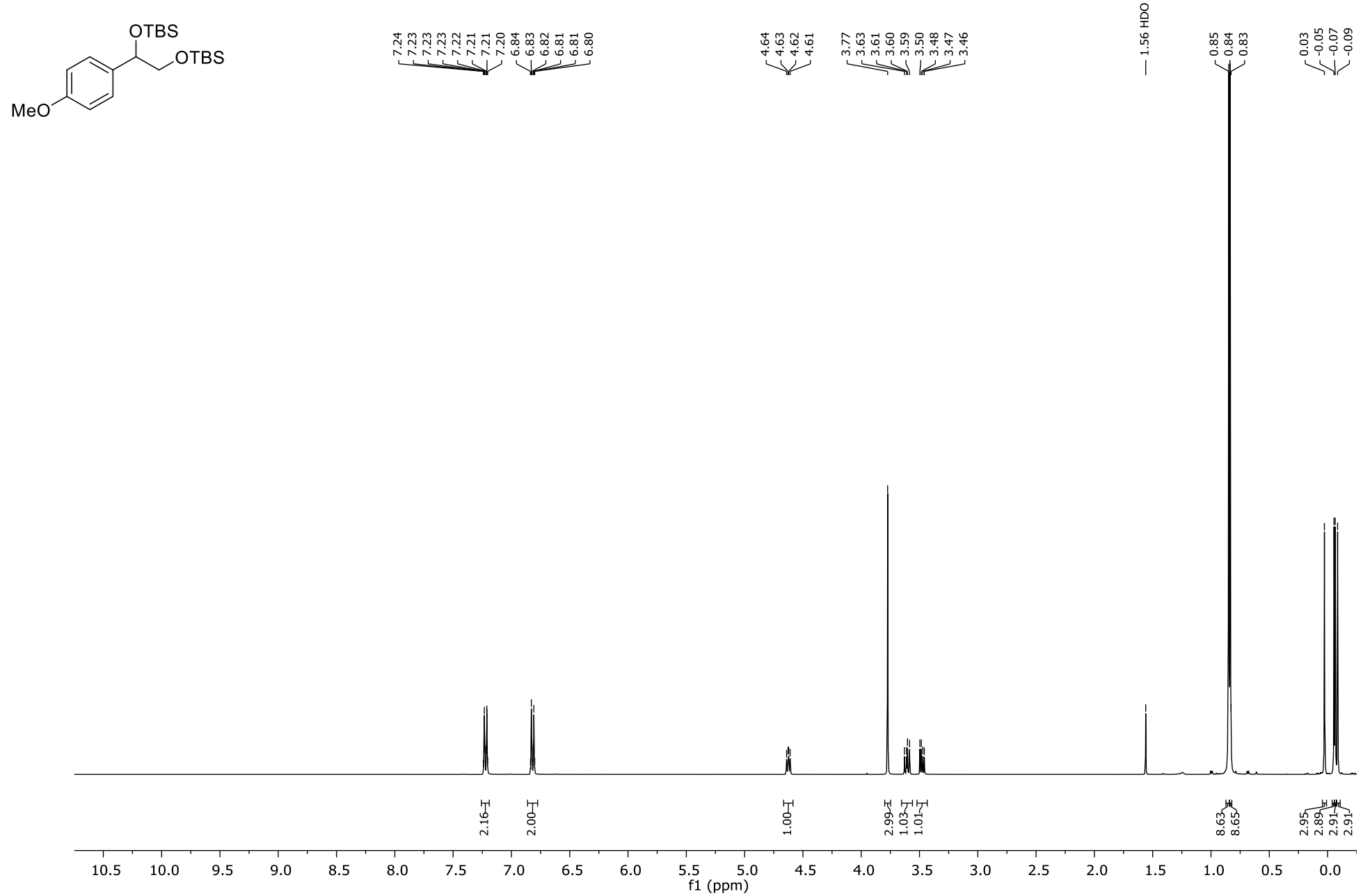


2,2,3,3,8,8,9,9-Octamethyl-5-(*p*-tolyl)-4,7-dioxa-3,8-disiladecane S18 ^{13}C NMR (101 MHz, $CDCl_3$)



5-(4-methoxyphenyl)-2,2,3,3,8,8,9,9-octamethyl-4,7-dioxa-3,8-disiladecane **S19** ^{1}H NMR (400 MHz, $CDCl_3$)



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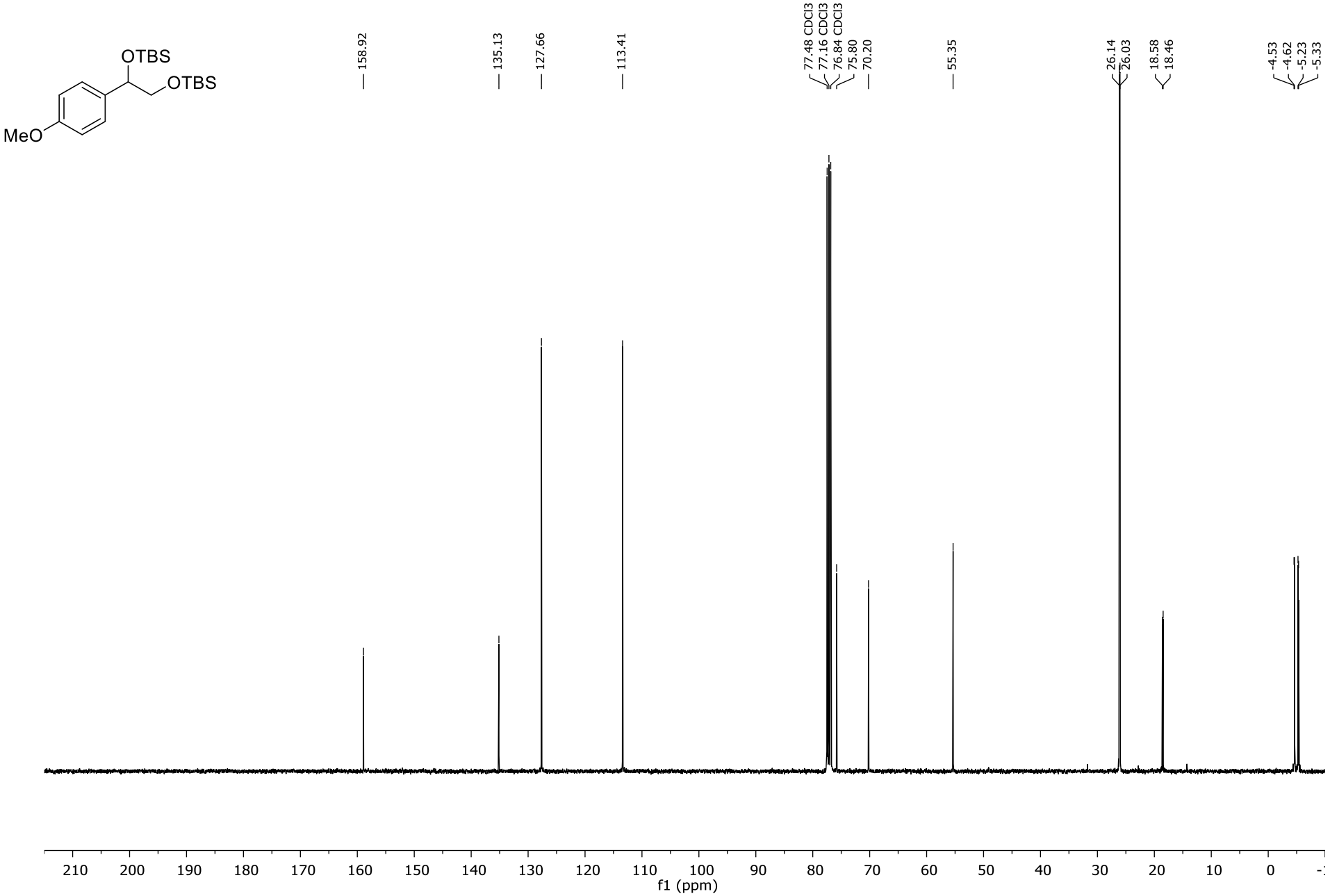

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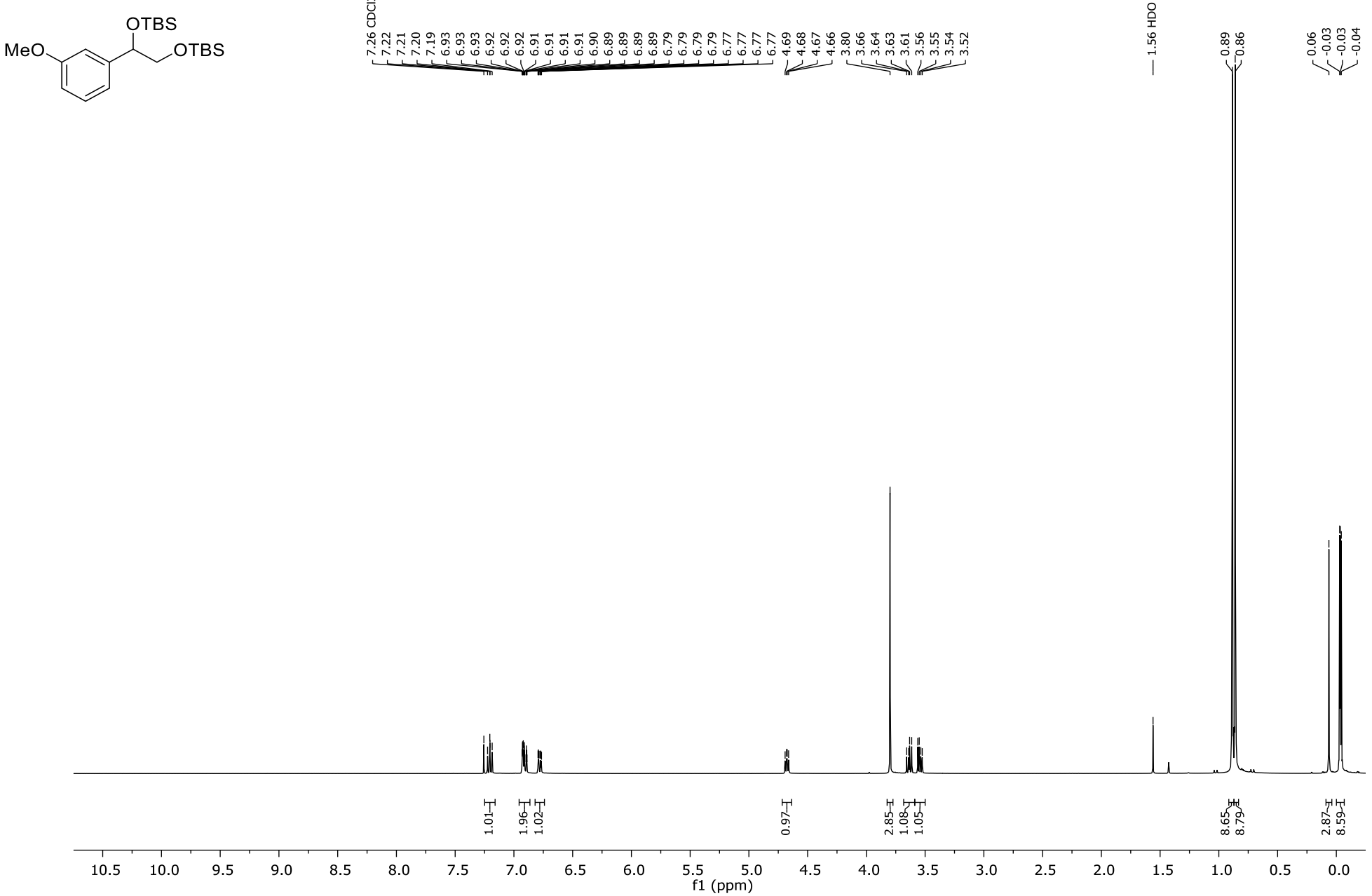

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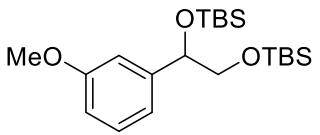

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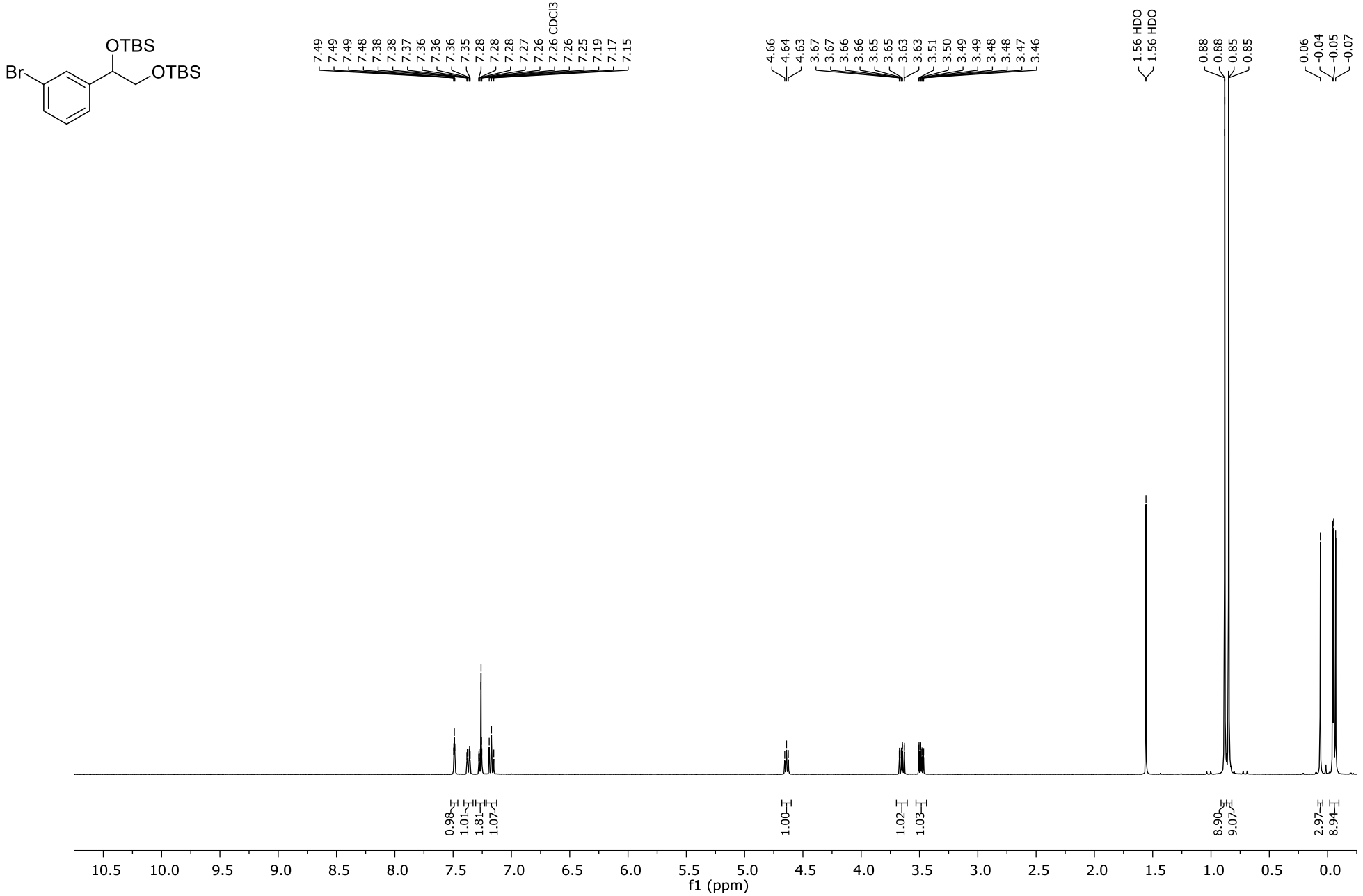

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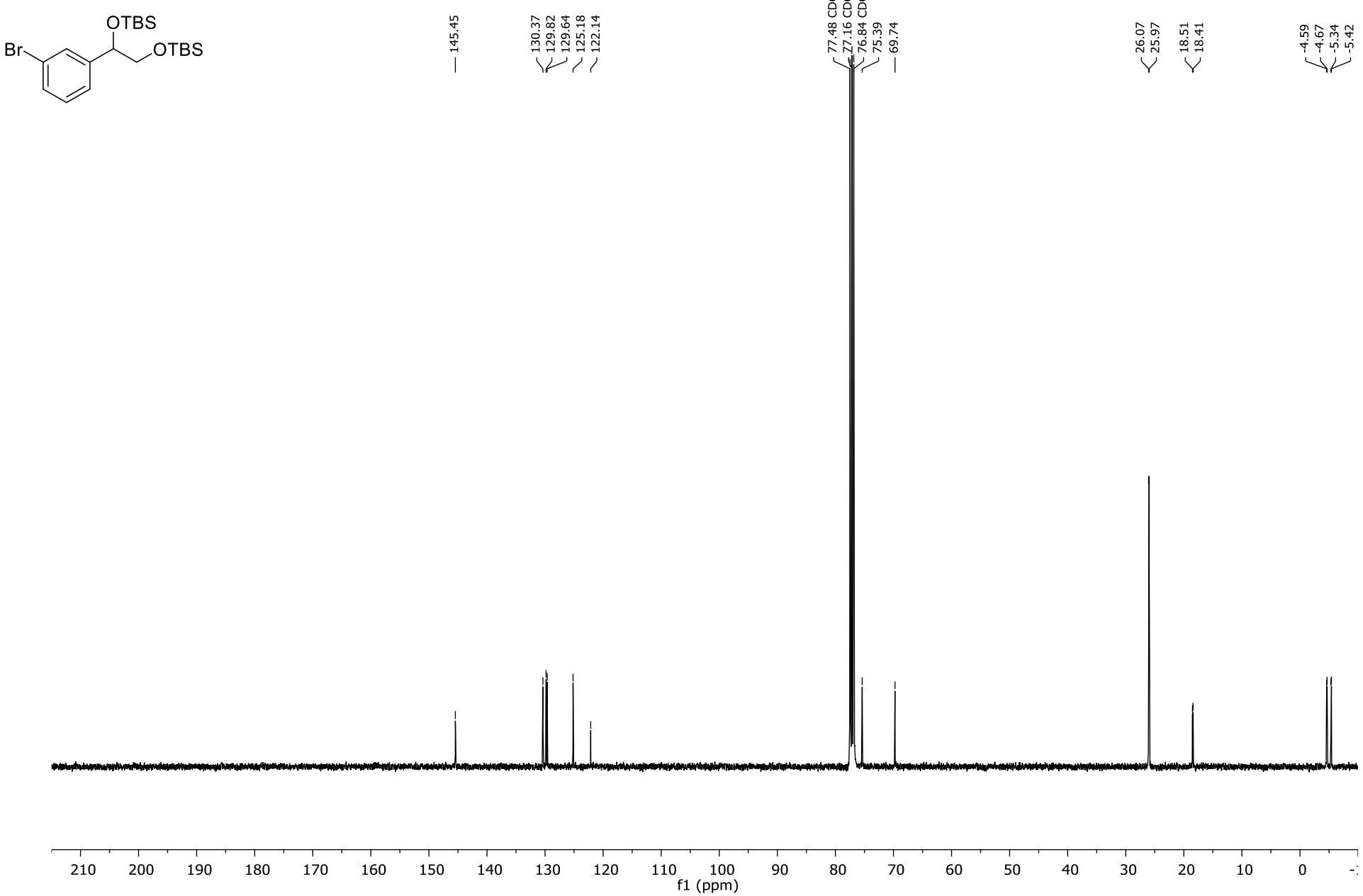

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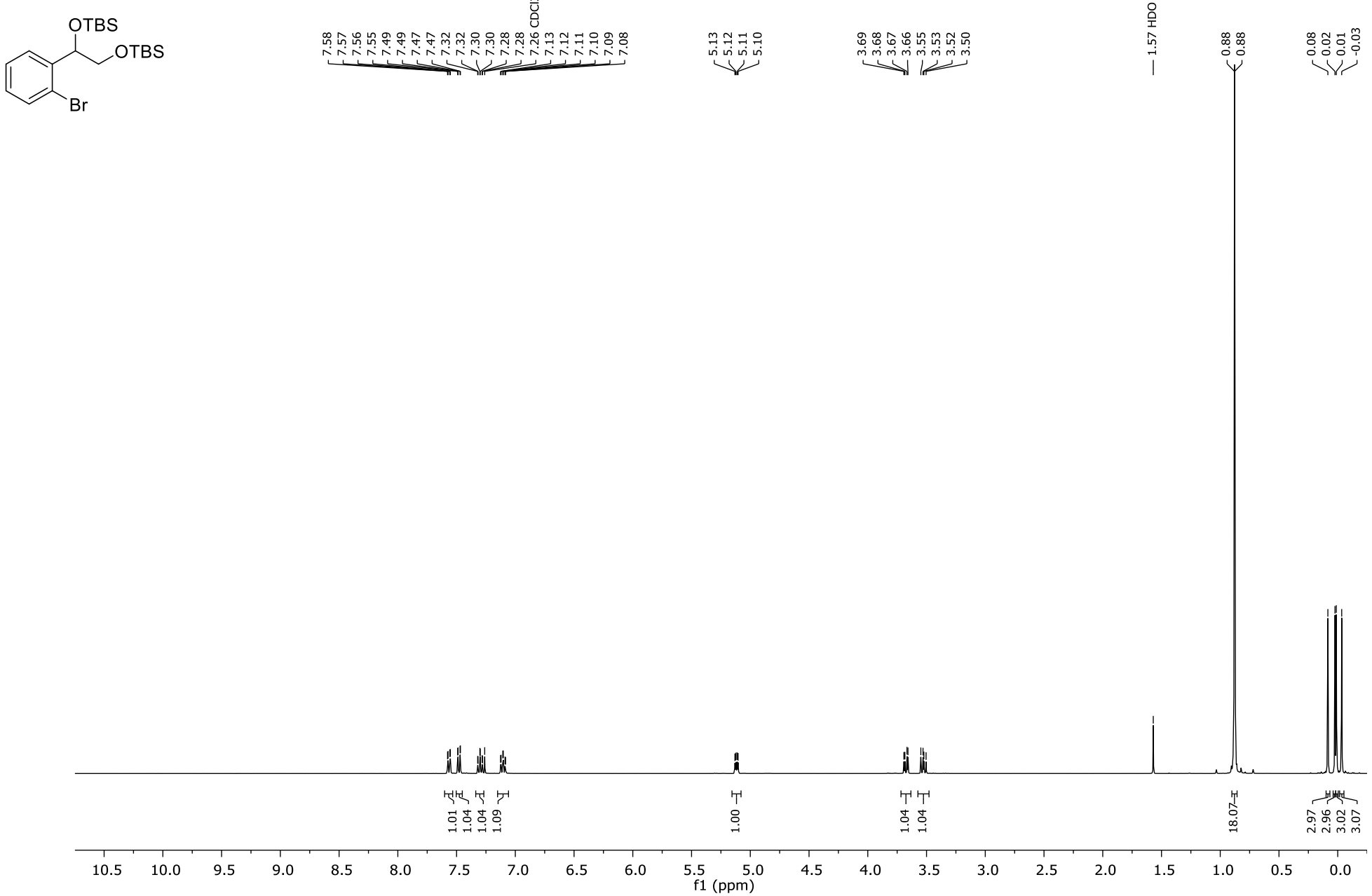

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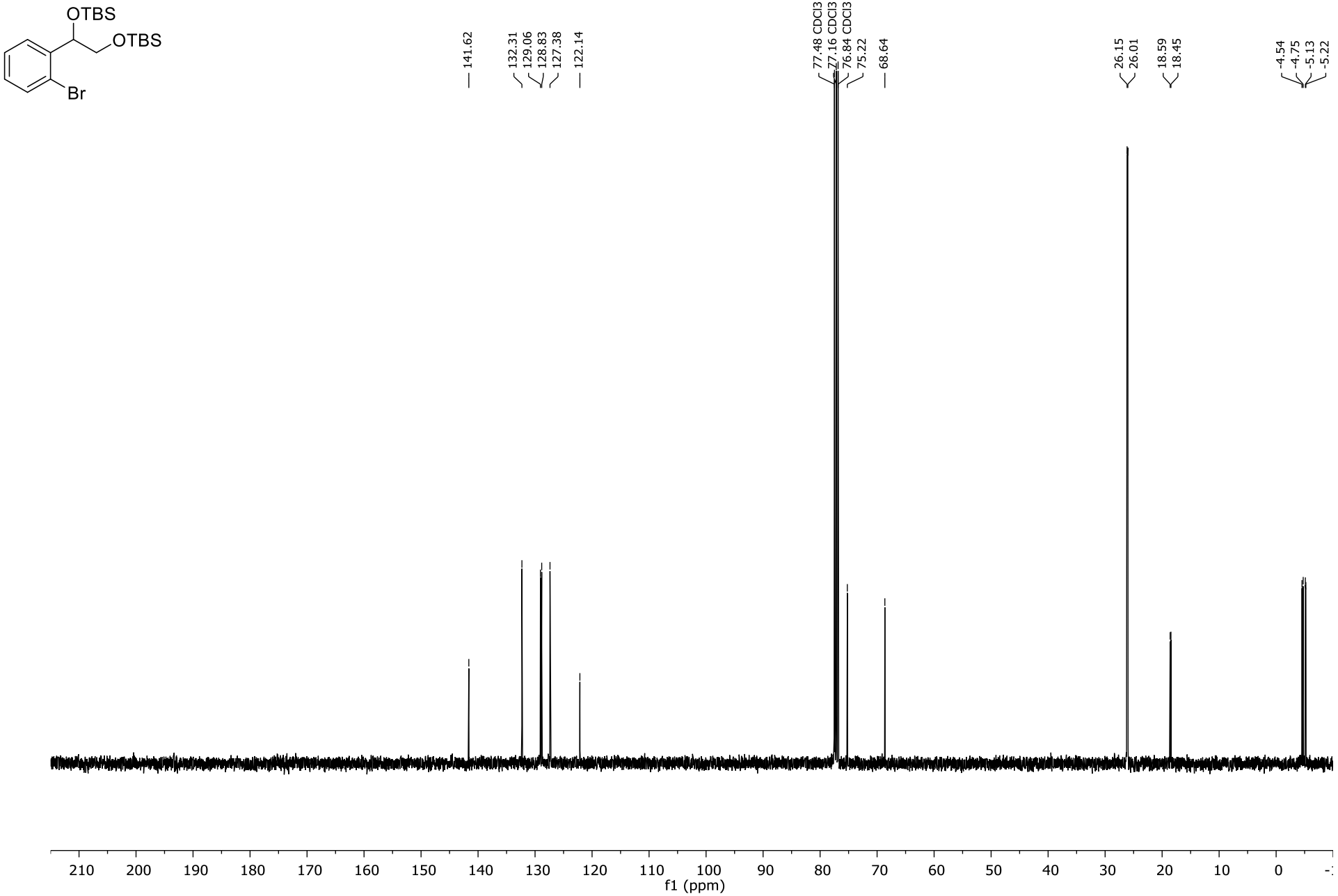

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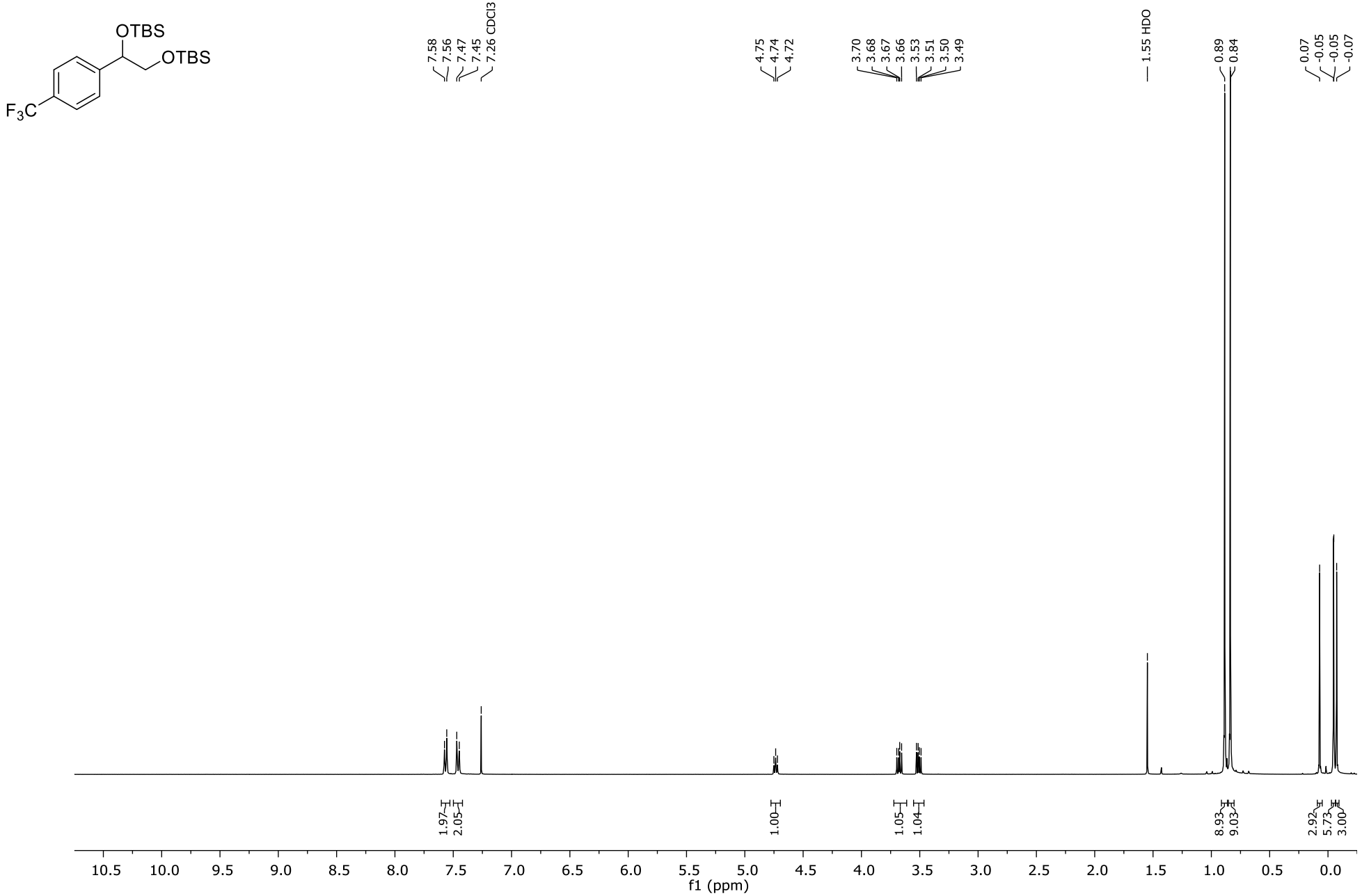
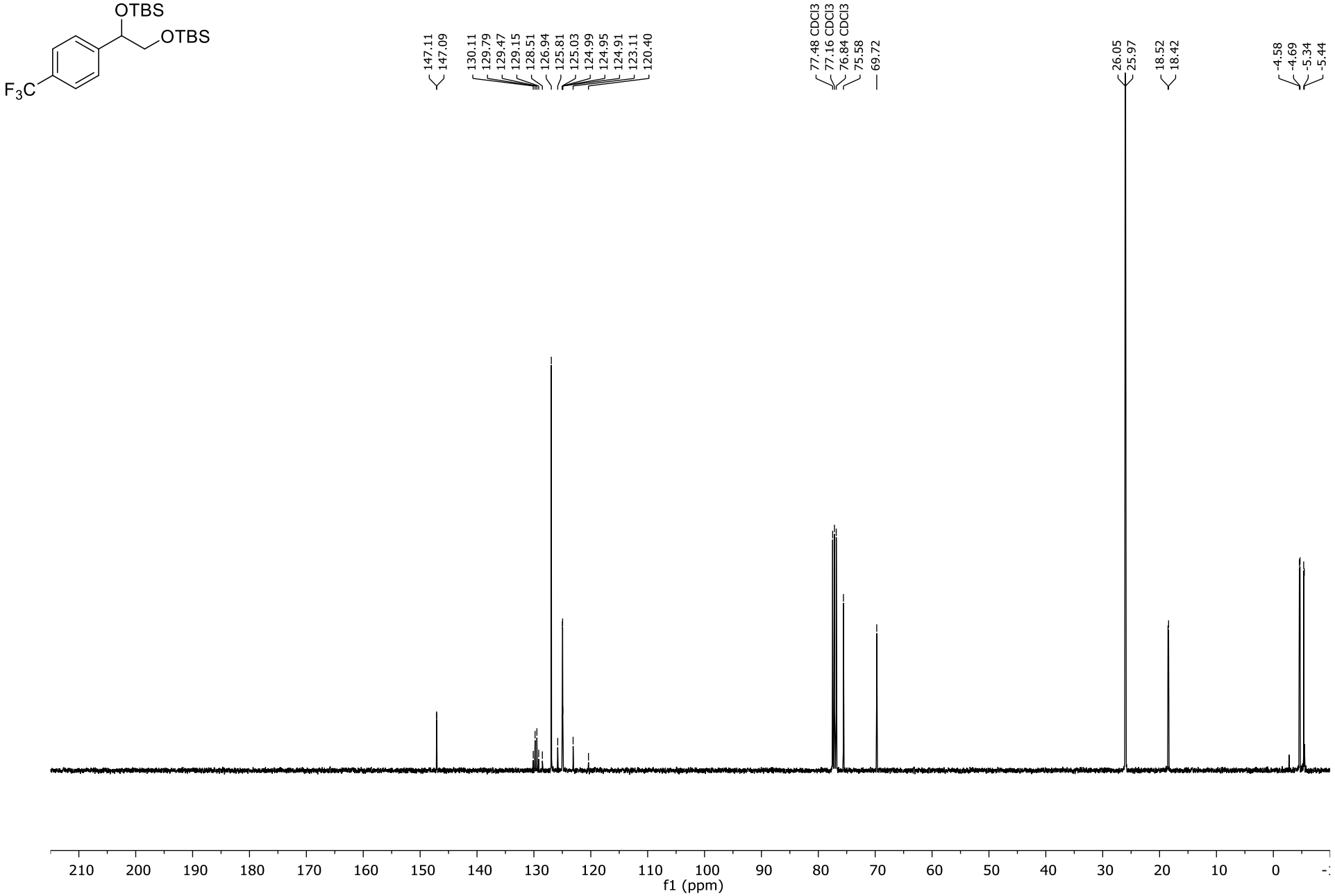
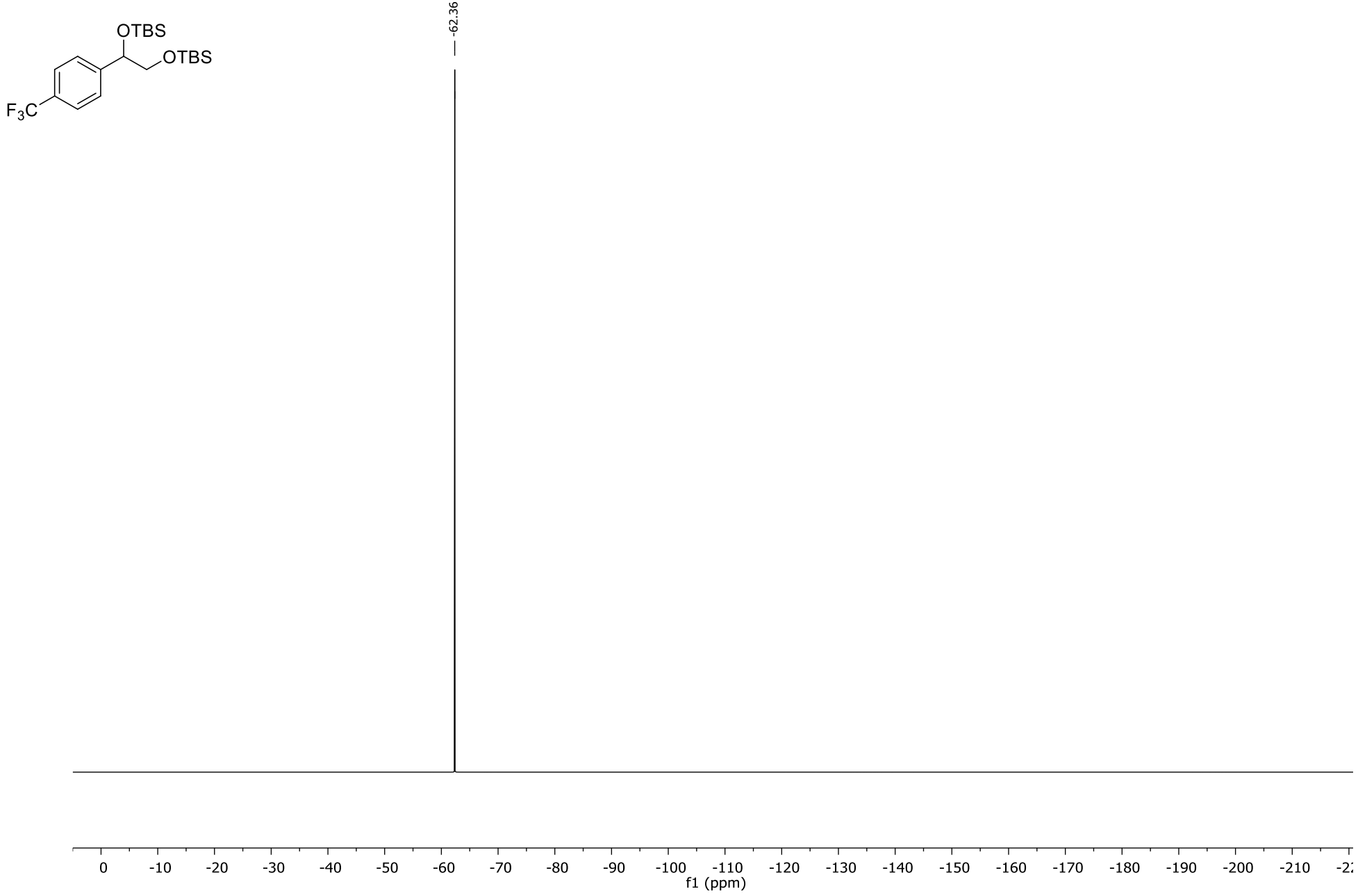


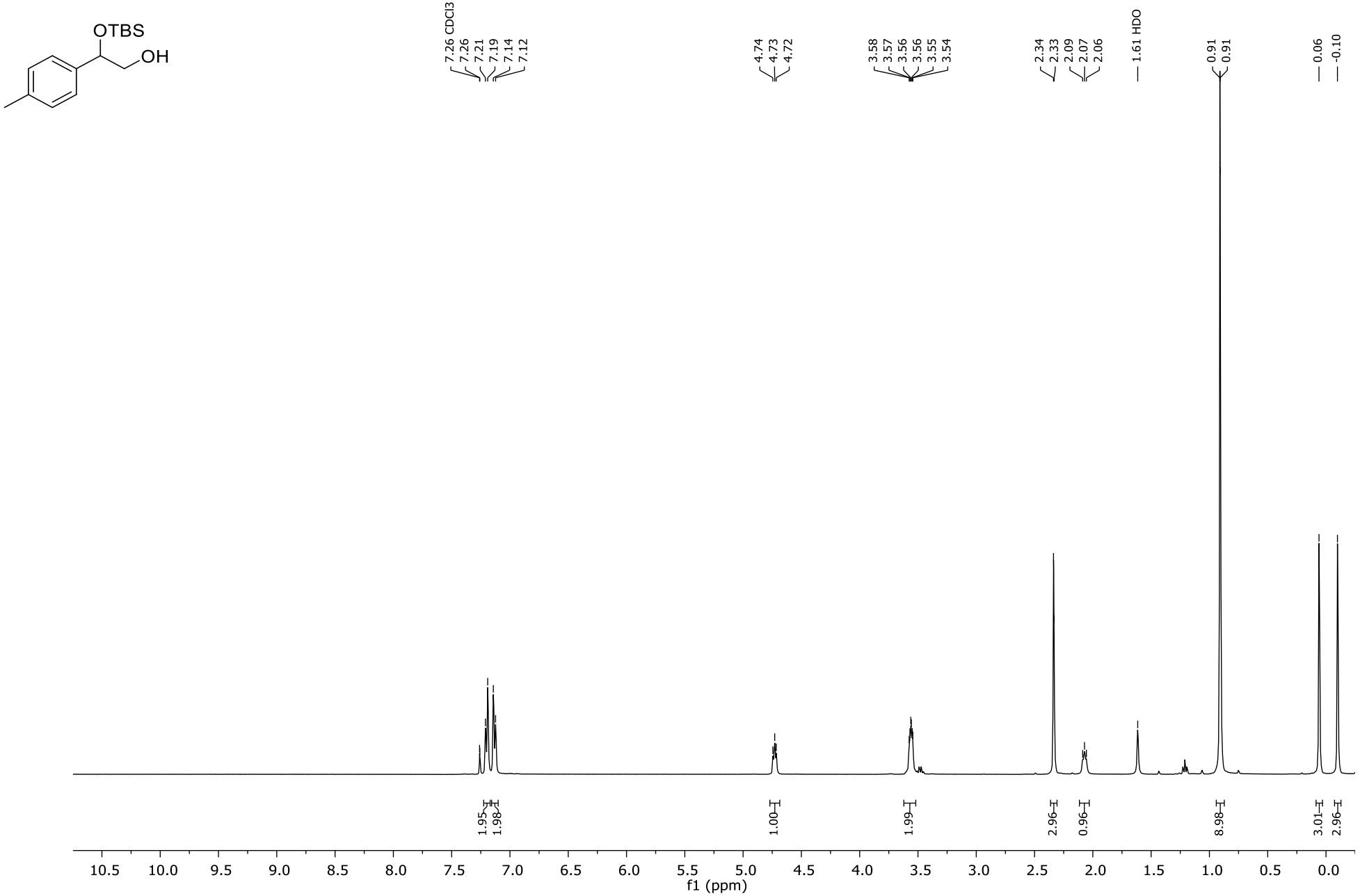
2,2,3,3,8,8,9,9-Octamethyl-5-(4-(trifluoromethyl)phenyl)-4,7-dioxa-3,8-disiladecane S23 ^{13}C NMR (101 MHz, $CDCl_3$)



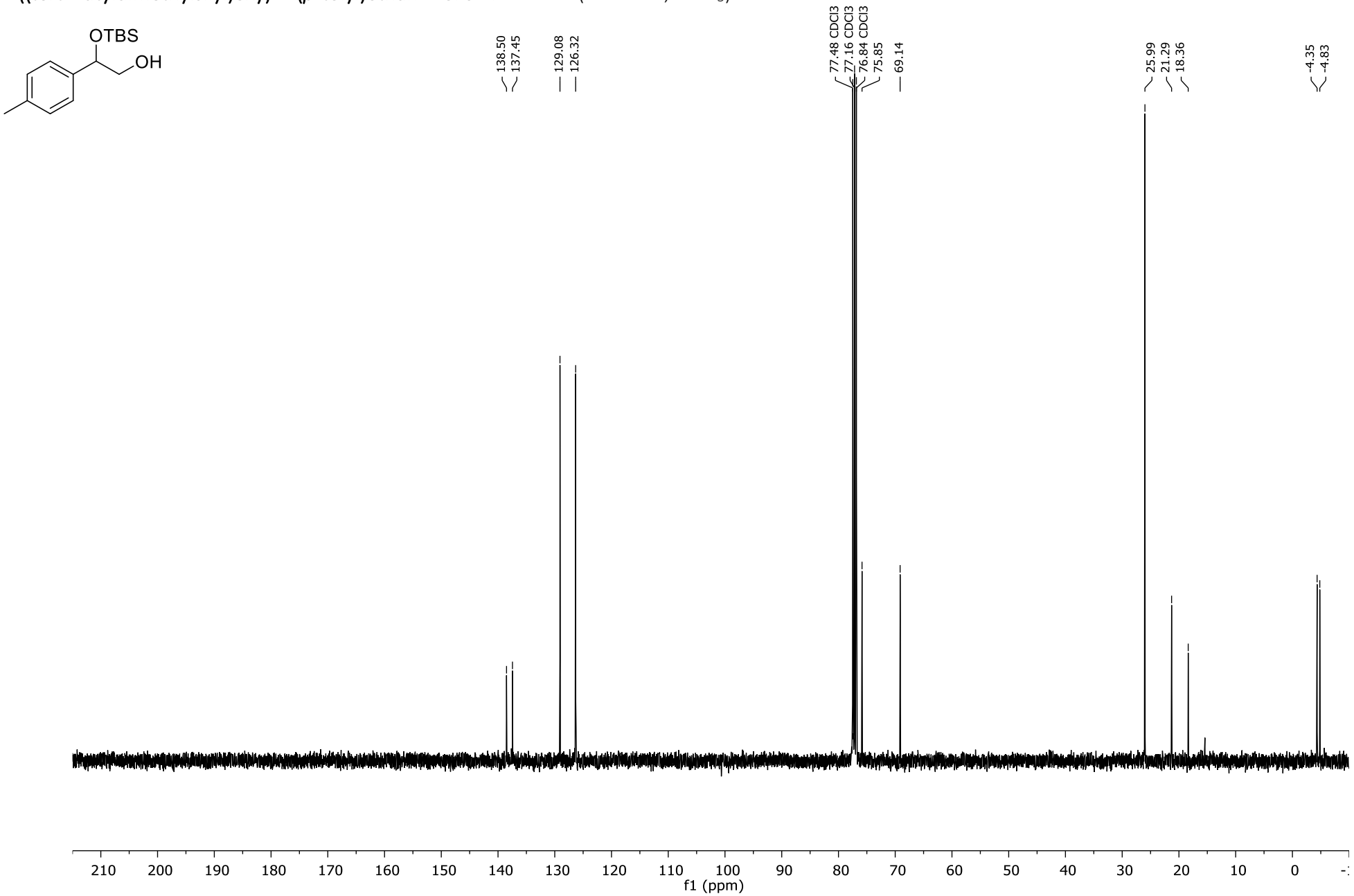
2,2,3,3,8,8,9,9-Octamethyl-5-(4-(trifluoromethyl)phenyl)-4,7-dioxa-3,8-disiladecane S23 ^{19}F NMR (376 MHz, $CDCl_3$)



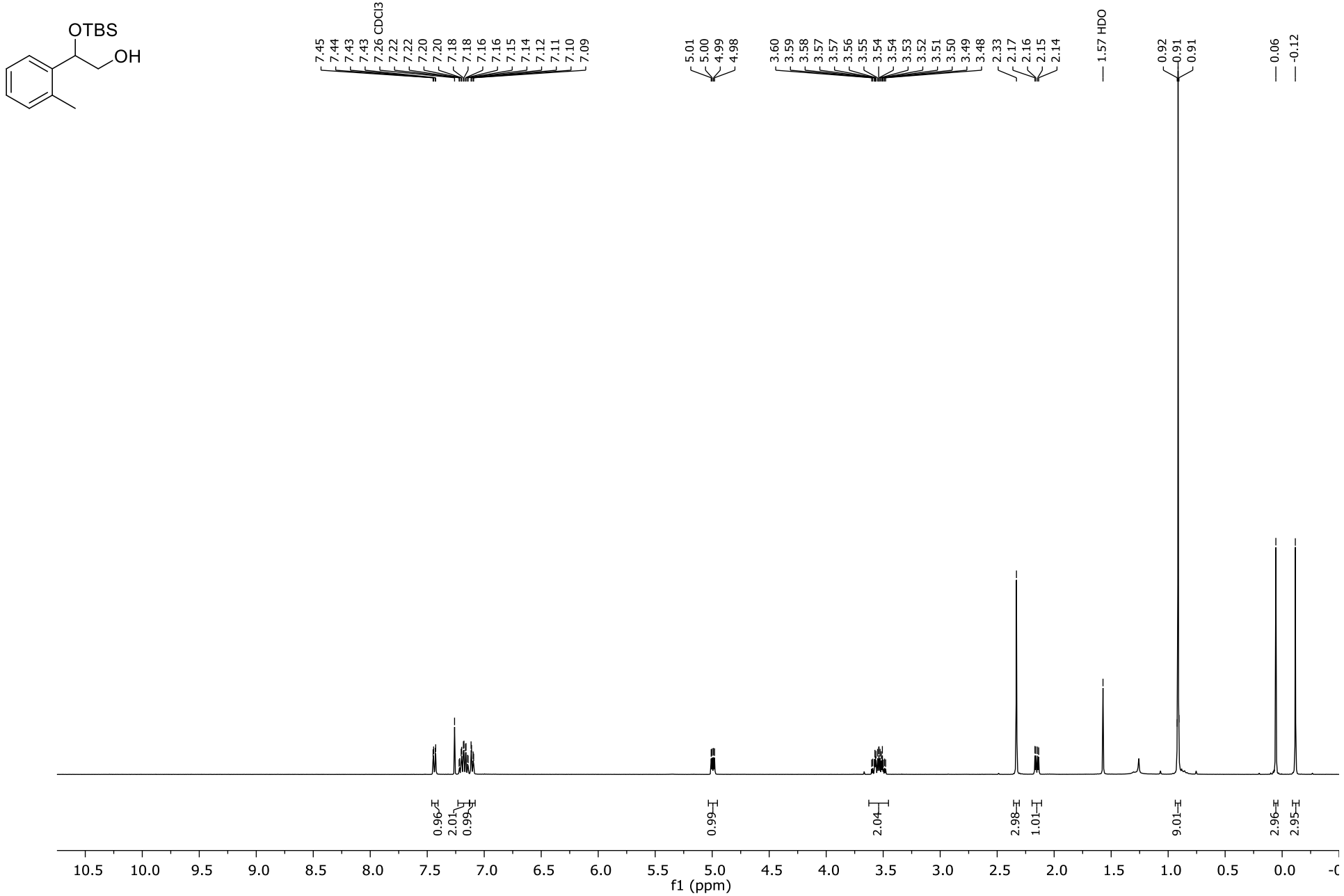
2-((*tert*-Butyldimethylsilyl)oxy)-2-(*p*-tolyl)ethan-1-ol S24 ^{1}H NMR (400 MHz, $CDCl_3$)



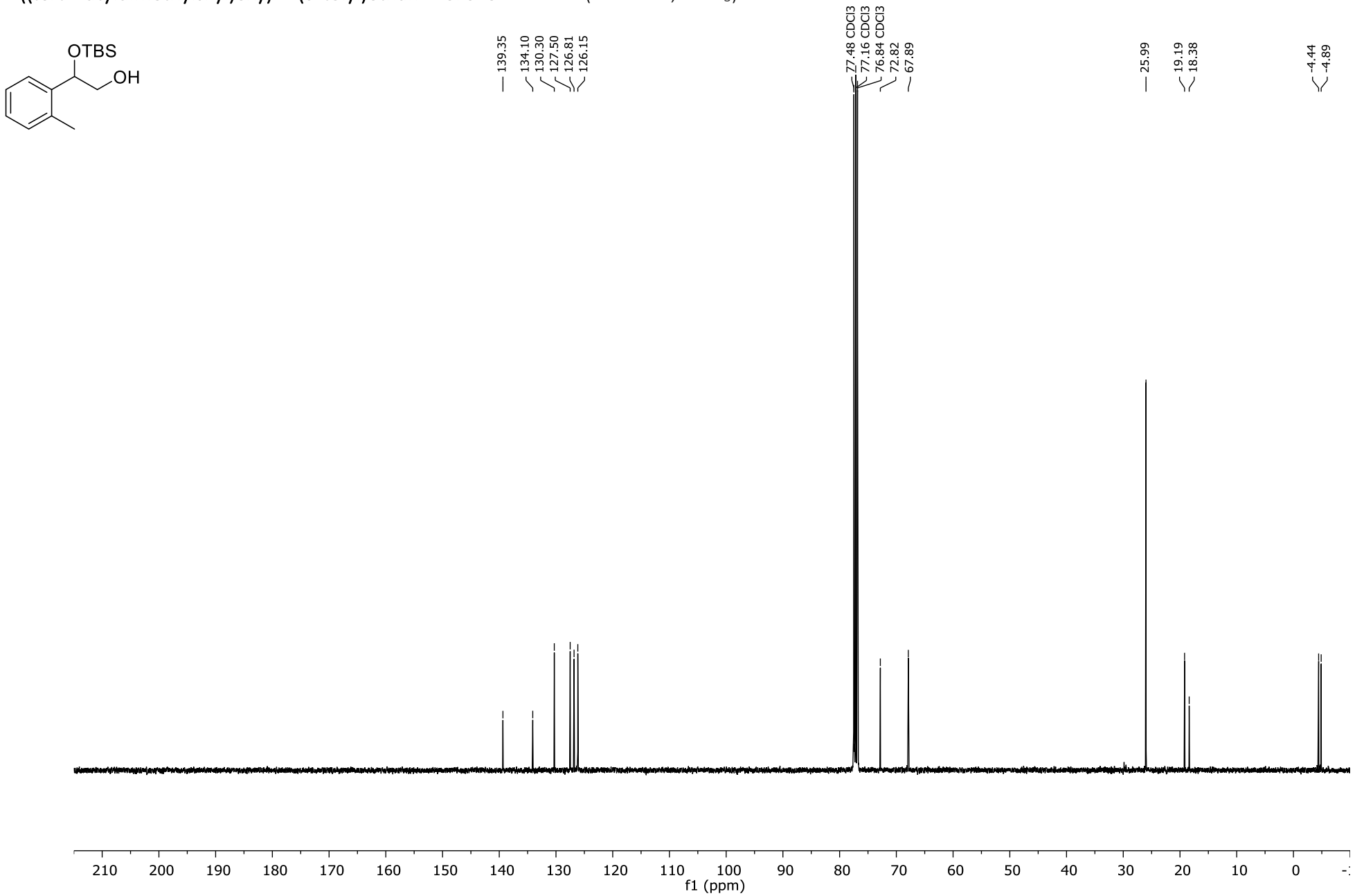
2-((*tert*-Butyldimethylsilyl)oxy)-2-(*p*-tolyl)ethan-1-ol S24 ^{1}H NMR (400 MHz, $CDCl_3$)



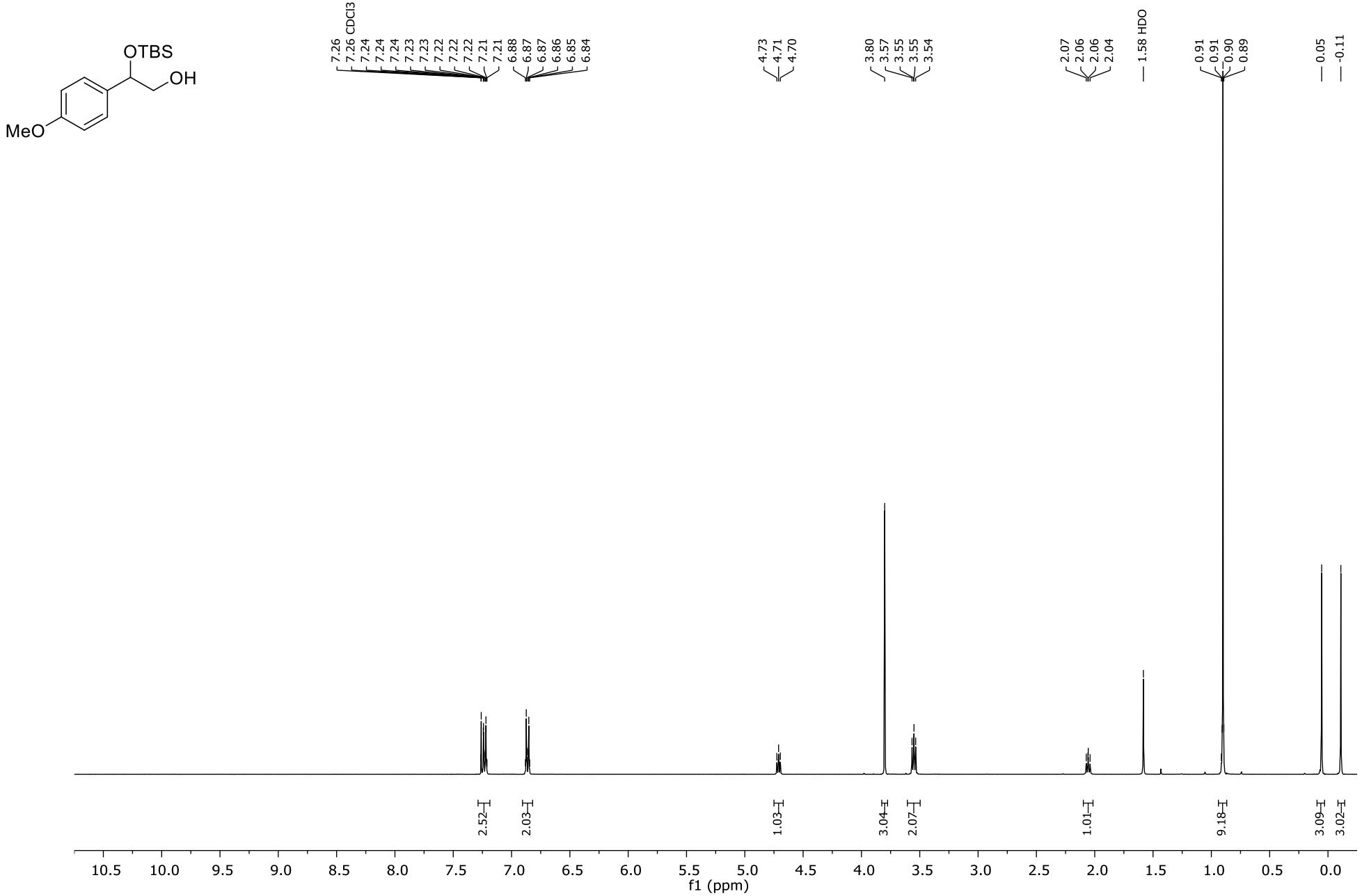
2-((*tert*-Butyldimethylsilyl)oxy)-2-(*o*-tolyl)ethan-1-ol S25 ^{1}H NMR (400 MHz, $CDCl_3$)



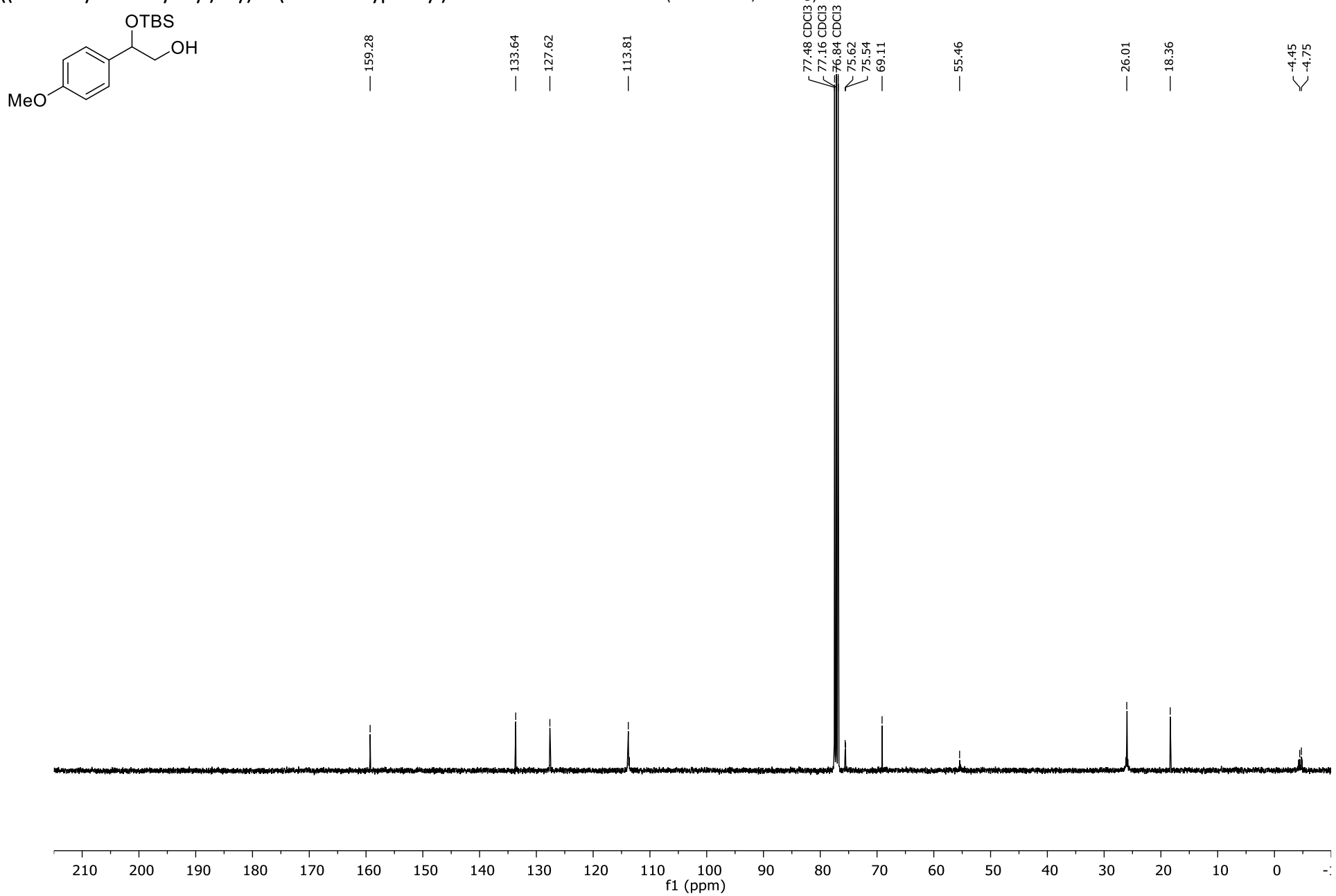
2-((*tert*-Butyldimethylsilyl)oxy)-2-(*o*-tolyl)ethan-1-ol S25 ^{13}C NMR (101 MHz, $CDCl_3$)



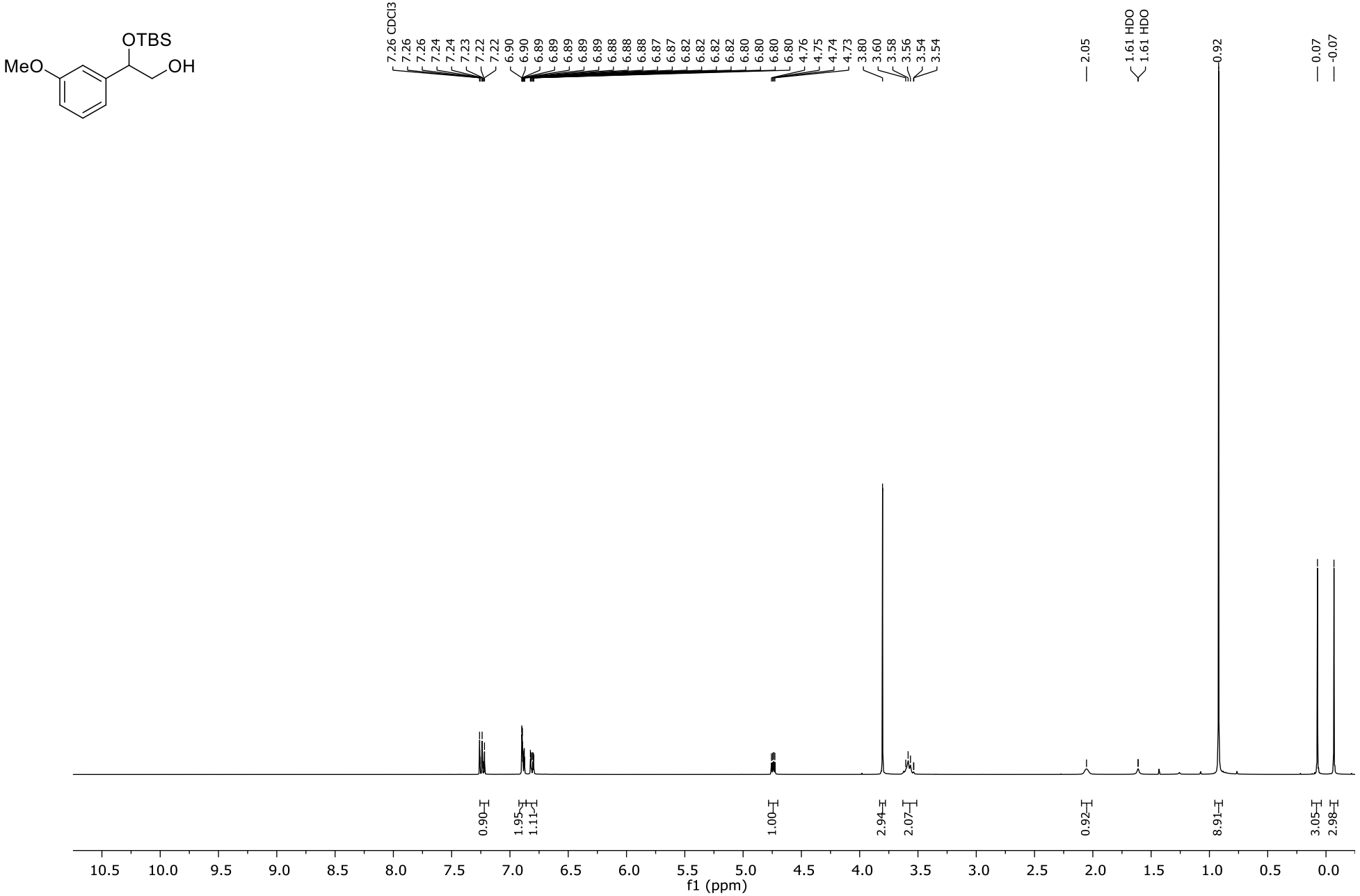
2-((*tert*-Butyldimethylsilyl)oxy)-2-(4-methoxyphenyl)ethan-1-ol S26 ^{1}H NMR (400 MHz, $CDCl_3$)



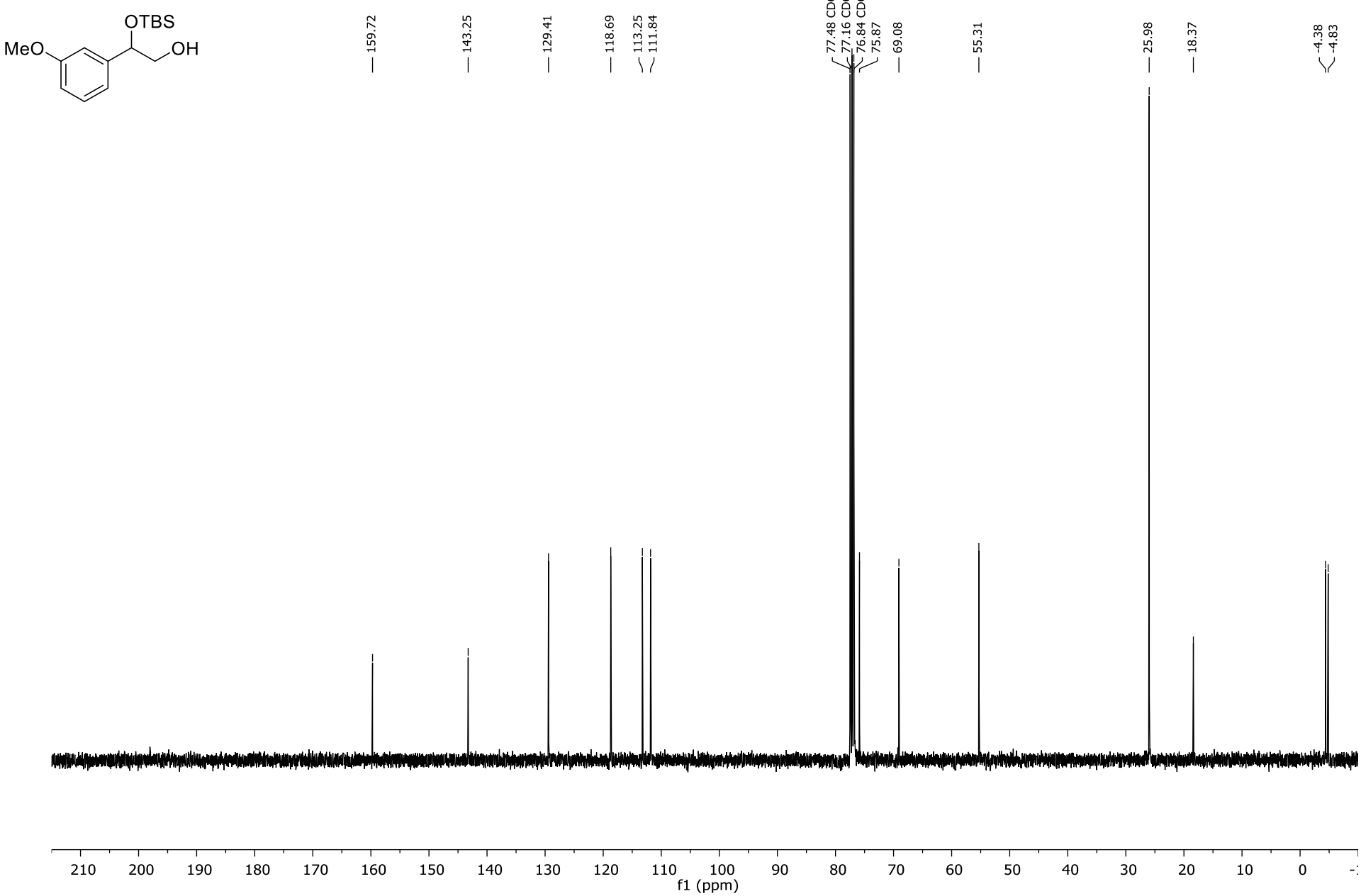
2-((*tert*-Butyldimethylsilyl)oxy)-2-(4-methoxyphenyl)ethan-1-ol S26 ^{13}C NMR (101 MHz, $CDCl_3$)



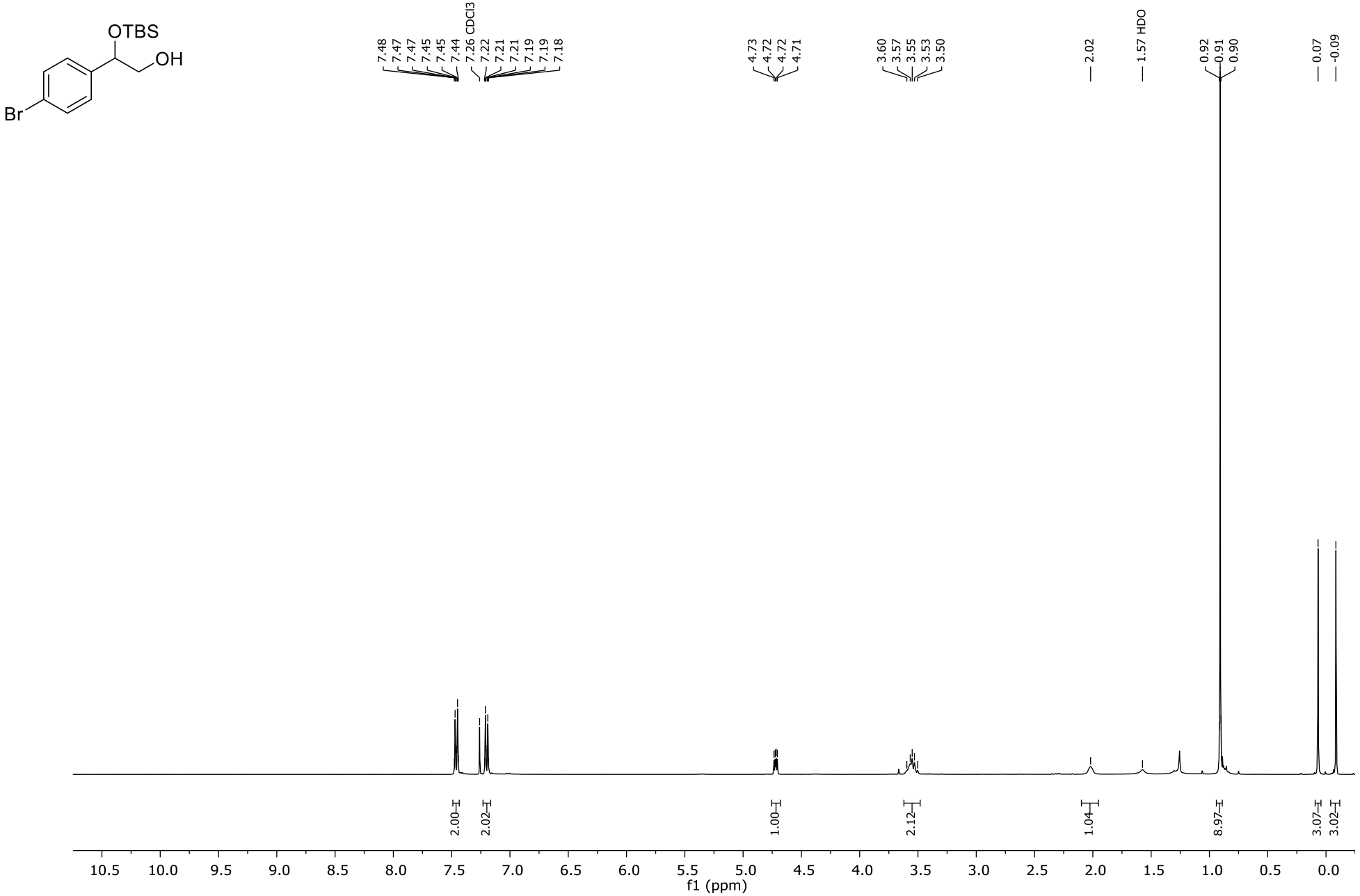
2-((*tert*-Butyldimethylsilyl)oxy)-2-(3-methoxyphenyl)ethan-1-ol S27 ^{1}H NMR (400 MHz, $CDCl_3$)



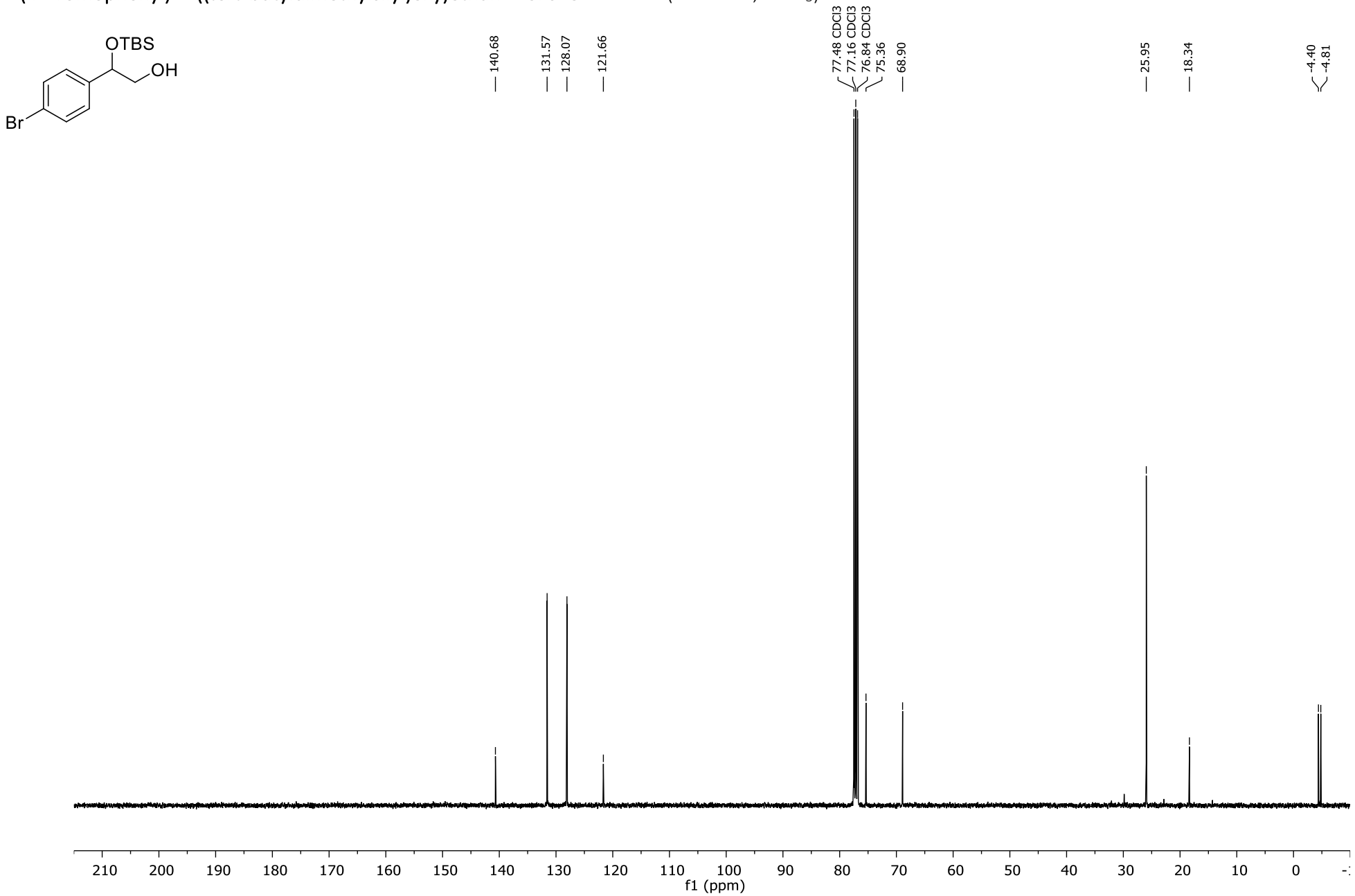
2-((*tert*-Butyldimethylsilyl)oxy)-2-(3-methoxyphenyl)ethan-1-ol S27 ^{13}C NMR (101 MHz, $CDCl_3$)



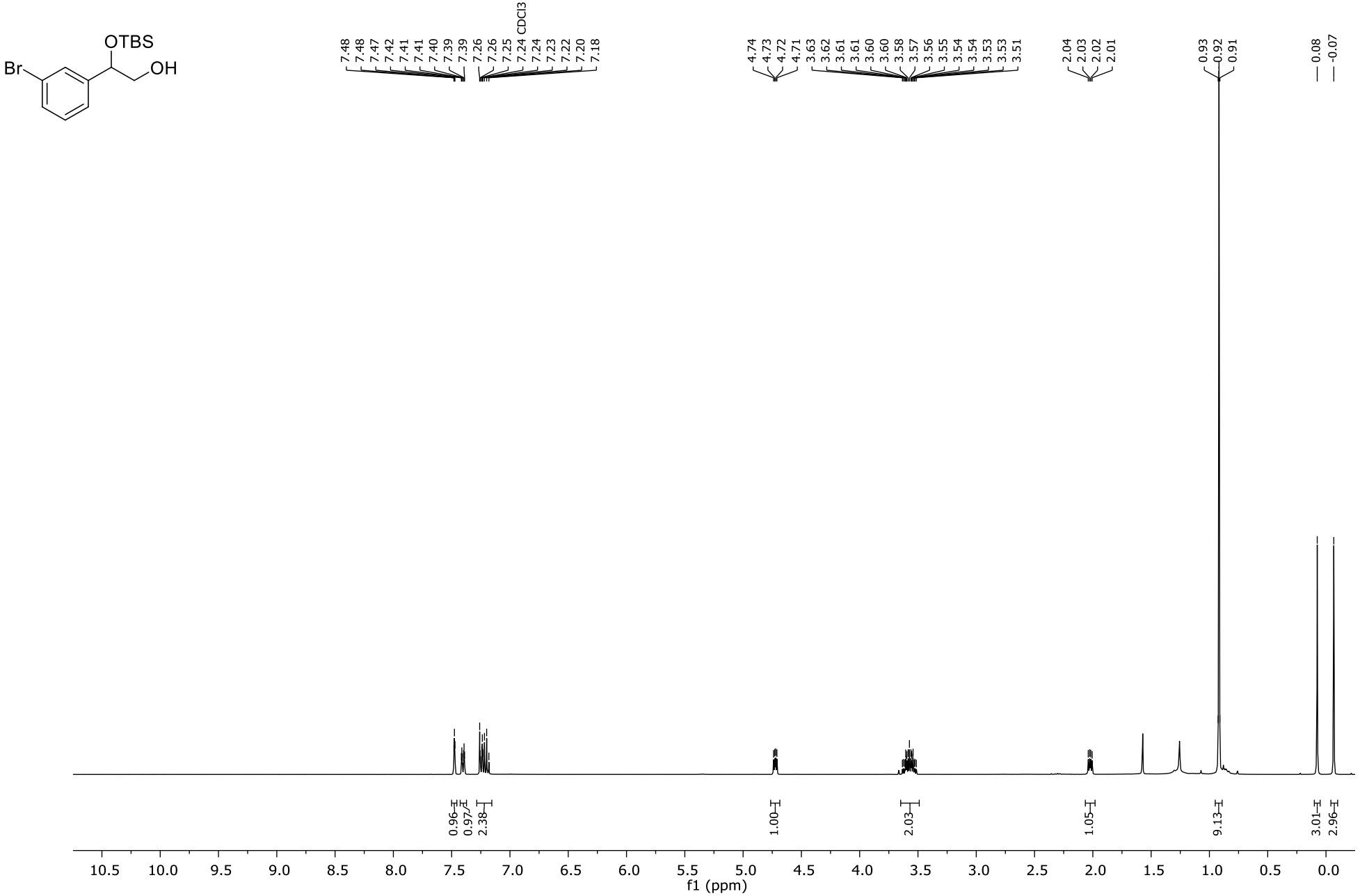
2-(4-Bromophenyl)-2-((*tert*-butyldimethylsilyl)oxy)ethan-1-ol S28 ^{1}H NMR (400 MHz, $CDCl_3$)



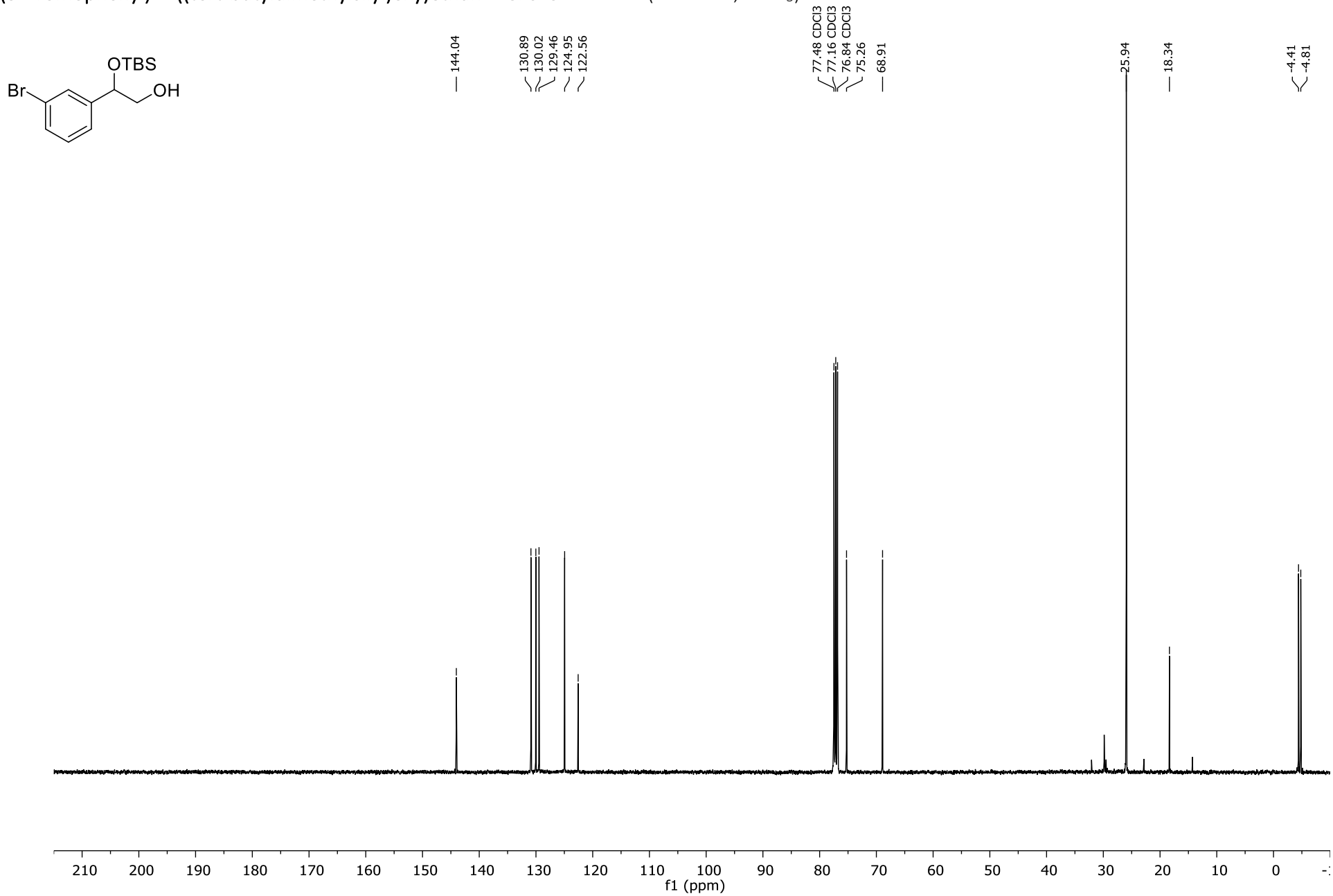
2-(4-Bromophenyl)-2-((*tert*-butyldimethylsilyl)oxy)ethan-1-ol S28 ^{13}C NMR (101 MHz, $CDCl_3$)



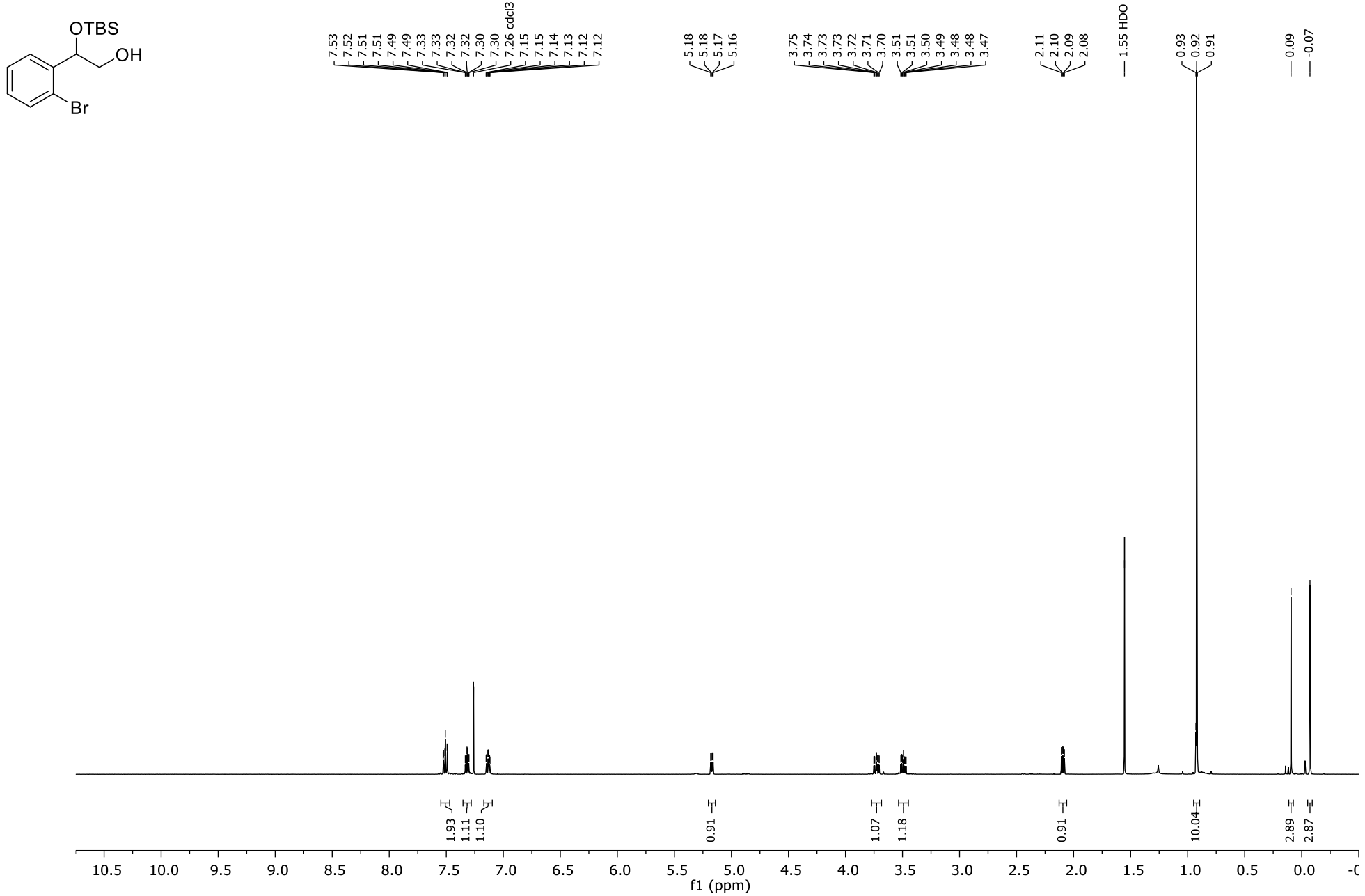
2-(3-Bromophenyl)-2-((*tert*-butyldimethylsilyl)oxy)ethan-1-ol S29 ^{1}H NMR (400 MHz, $CDCl_3$)



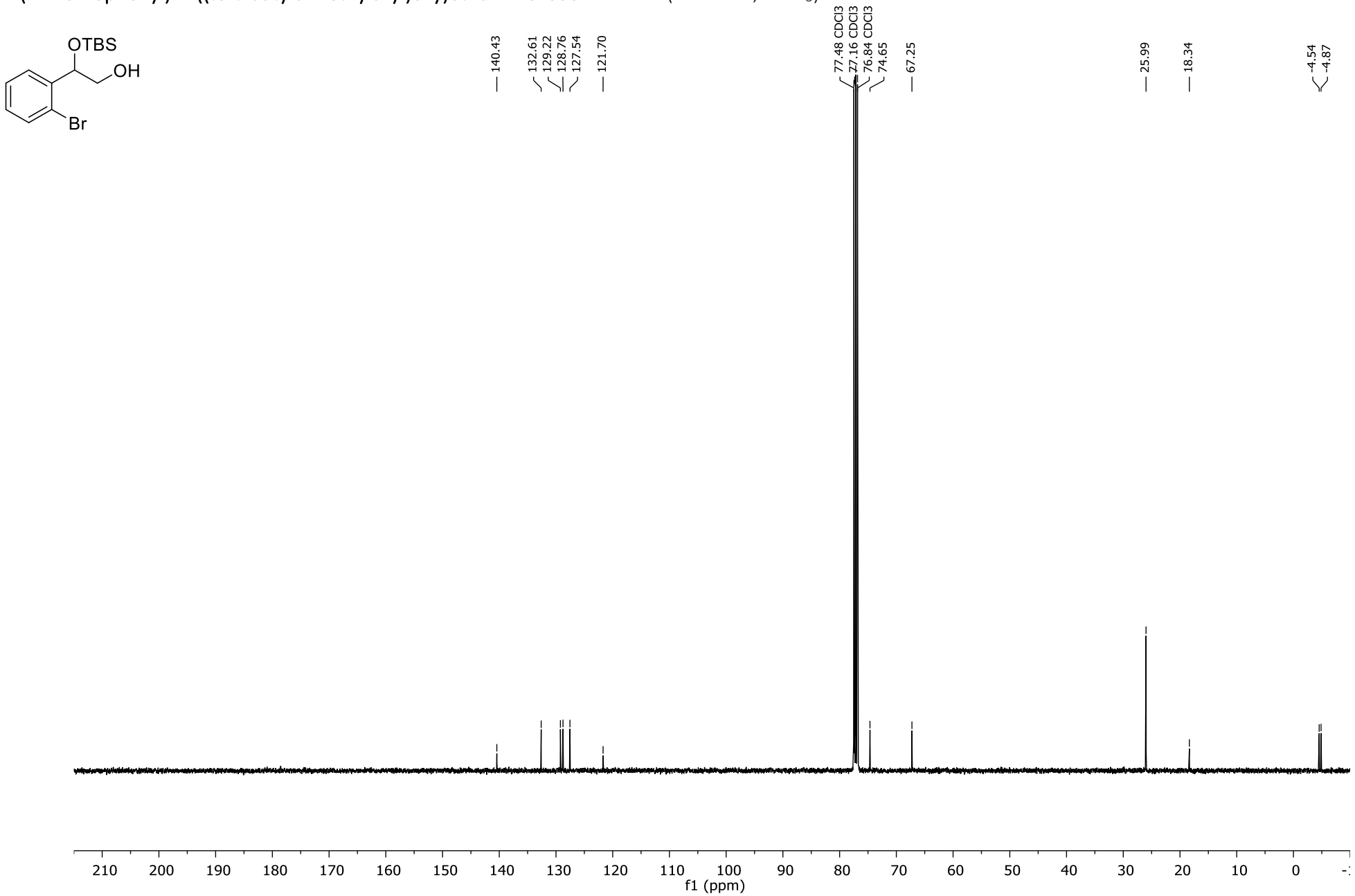
2-(3-Bromophenyl)-2-((tert-butyldimethylsilyl)oxy)ethan-1-ol S29 ^{13}C NMR (101 MHz, $CDCl_3$)



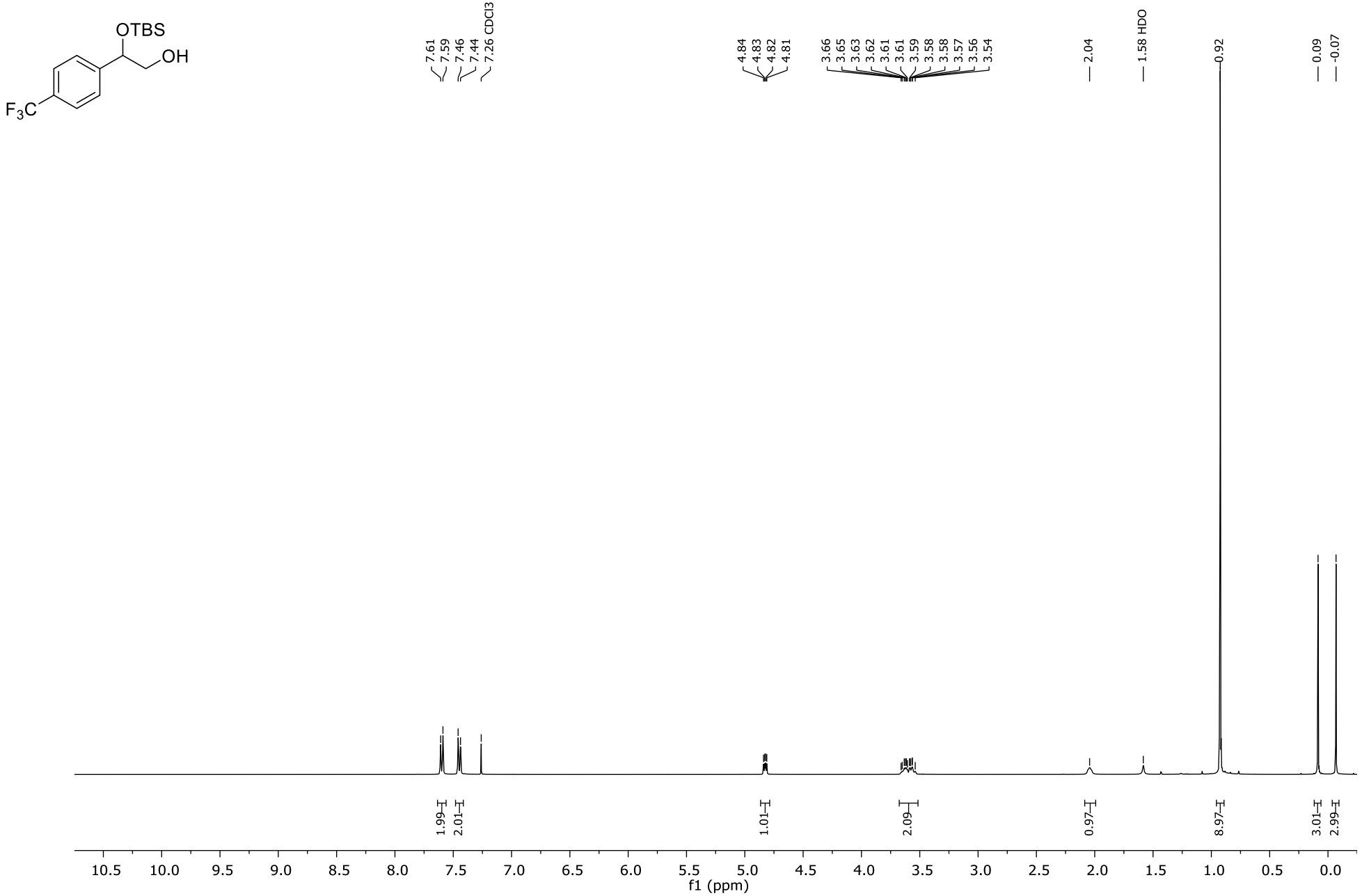
2-(2-Bromophenyl)-2-((*tert*-butyldimethylsilyl)oxy)ethan-1-ol S30 ^{1}H NMR (500 MHz, $CDCl_3$)



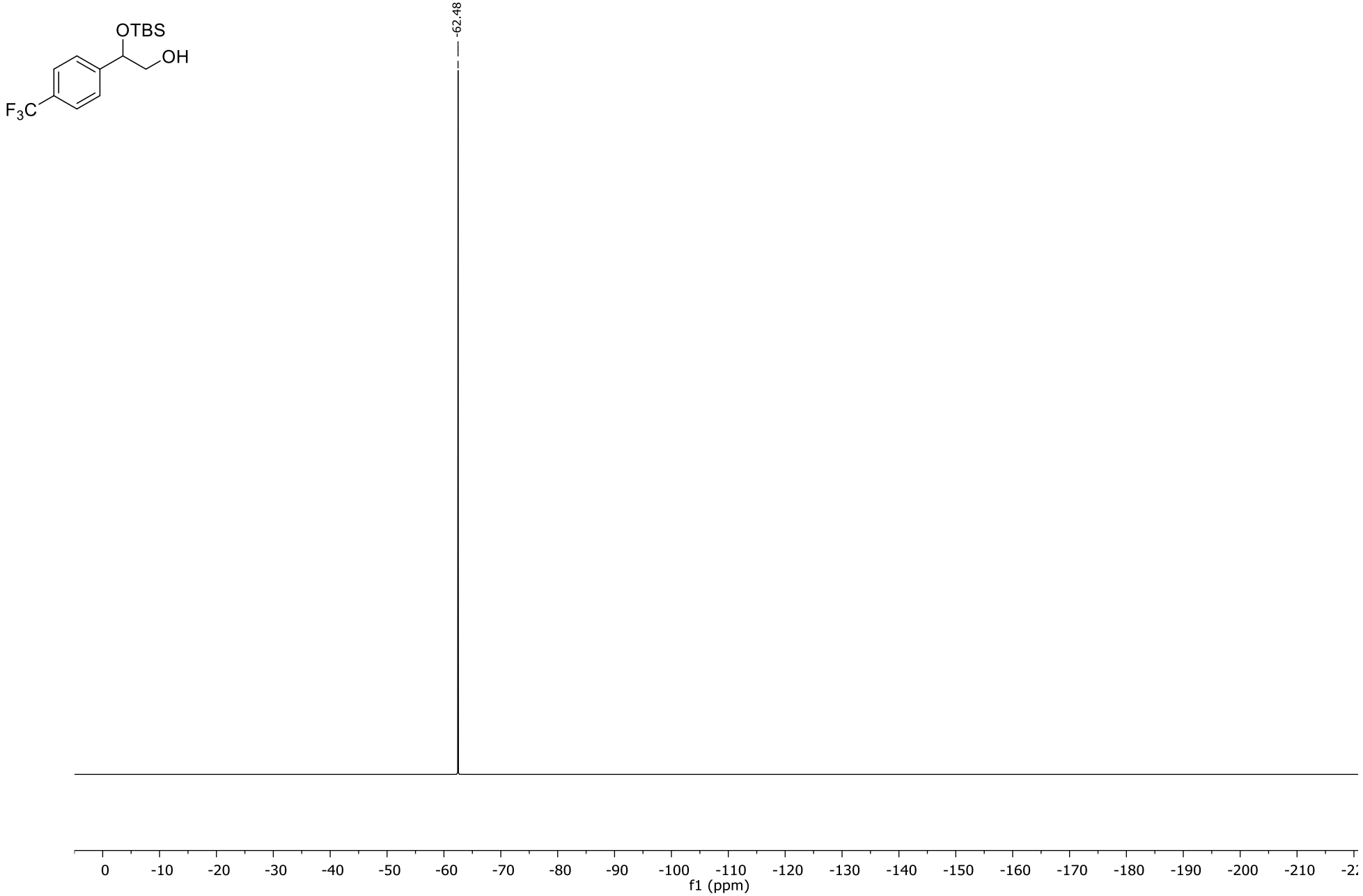
2-(2-Bromophenyl)-2-((*tert*-butyldimethylsilyl)oxy)ethan-1-ol S30 ^{13}C NMR (101 MHz, $CDCl_3$)



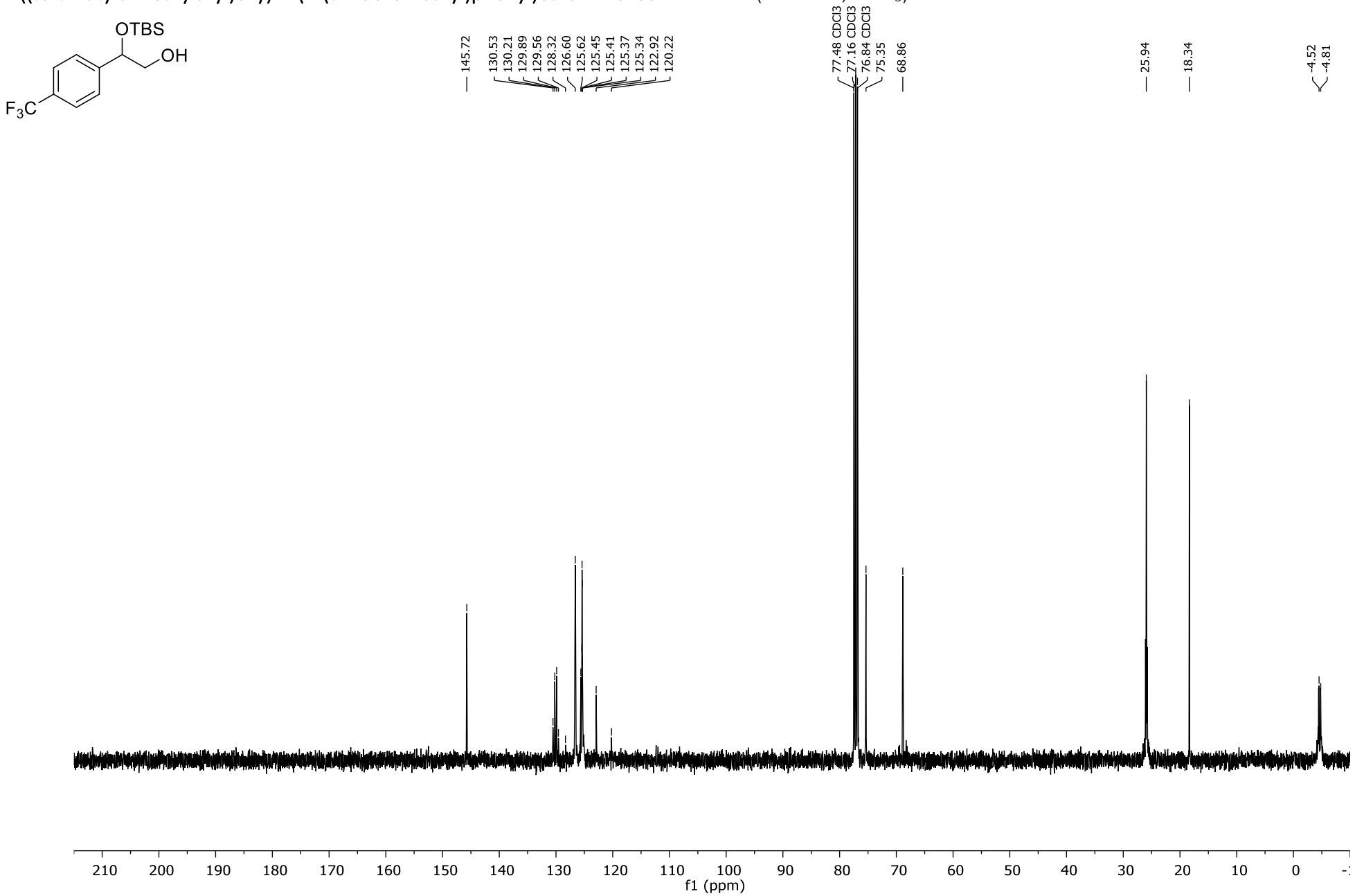
2-((*tert*-Butyldimethylsilyl)oxy)-2-(4-(trifluoromethyl)phenyl)ethan-1-ol S31 ^{1}H NMR (400 MHz, $CDCl_3$)



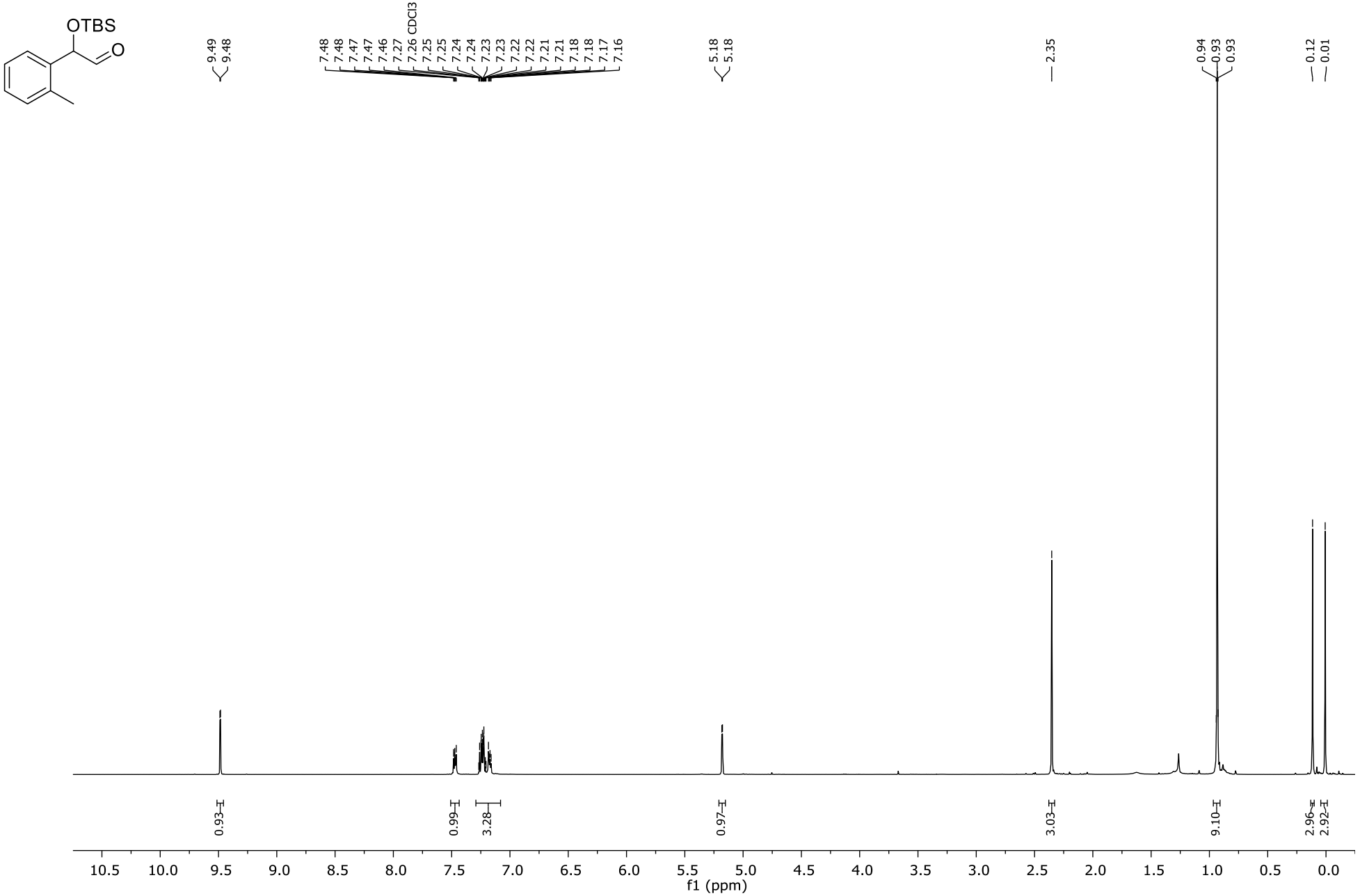
2-((*tert*-Butyldimethylsilyl)oxy)-2-(4-(trifluoromethyl)phenyl)ethan-1-ol S31 ^{19}F NMR (376 MHz, $CDCl_3$)



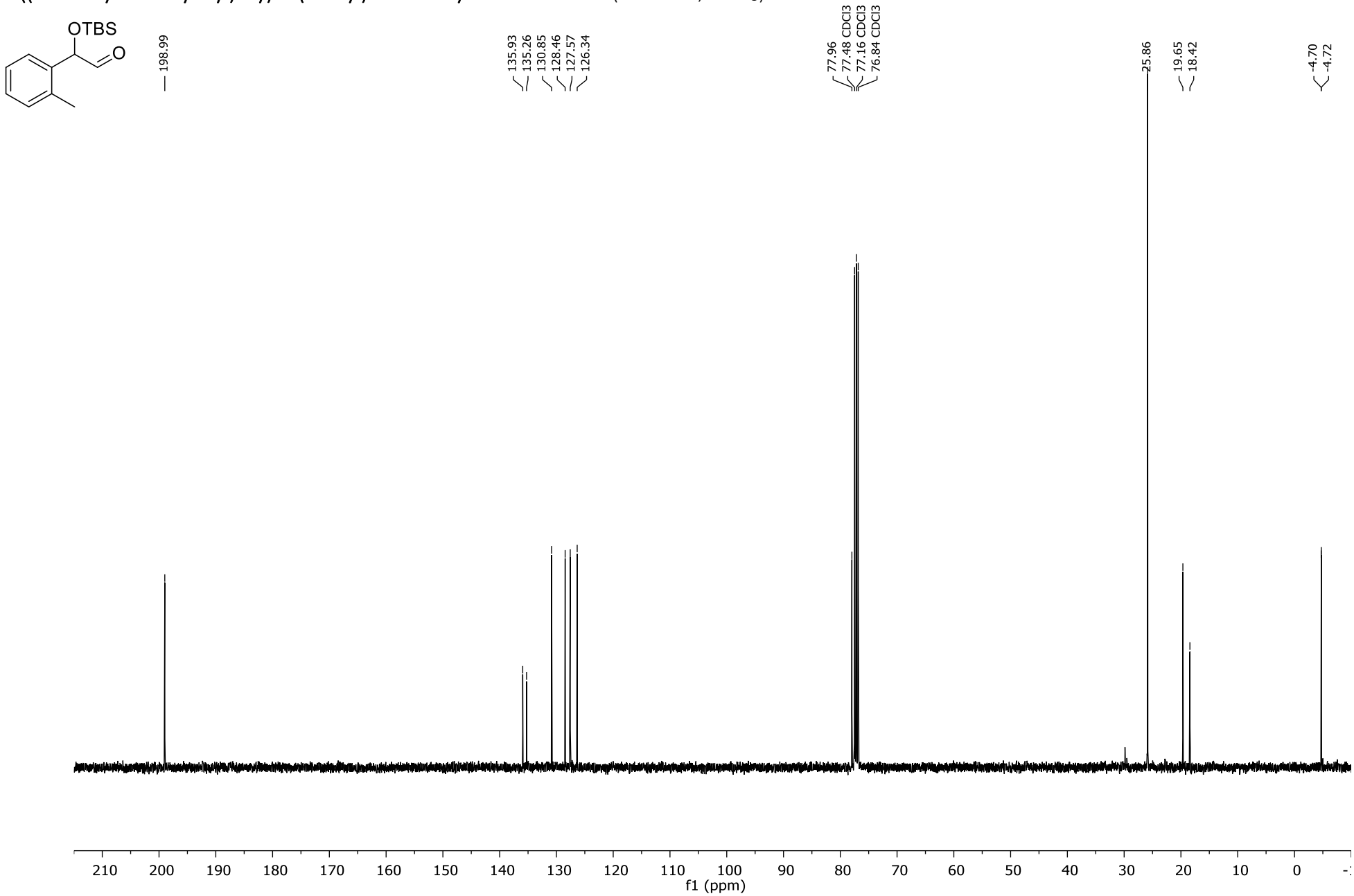
2-((*tert*-Butyldimethylsilyl)oxy)-2-(4-(trifluoromethyl)phenyl)ethan-1-ol **S31** ^{13}C NMR (101 MHz, $CDCl_3$)



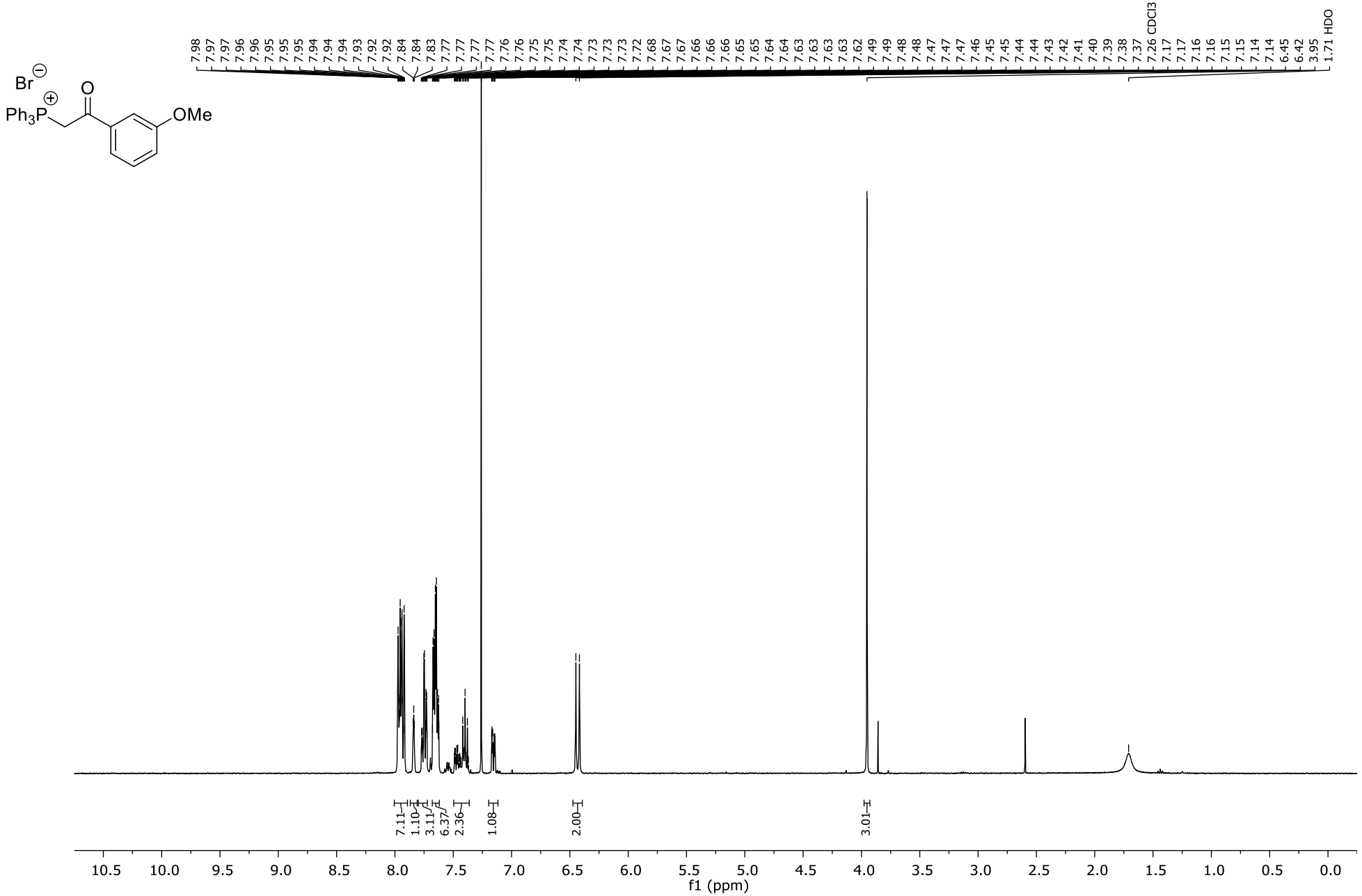
2-((*tert*-Butyldimethylsilyl)oxy)-2-(*o*-tolyl)acetaldehyde S33 ^{1}H NMR (400 MHz, $CDCl_3$)



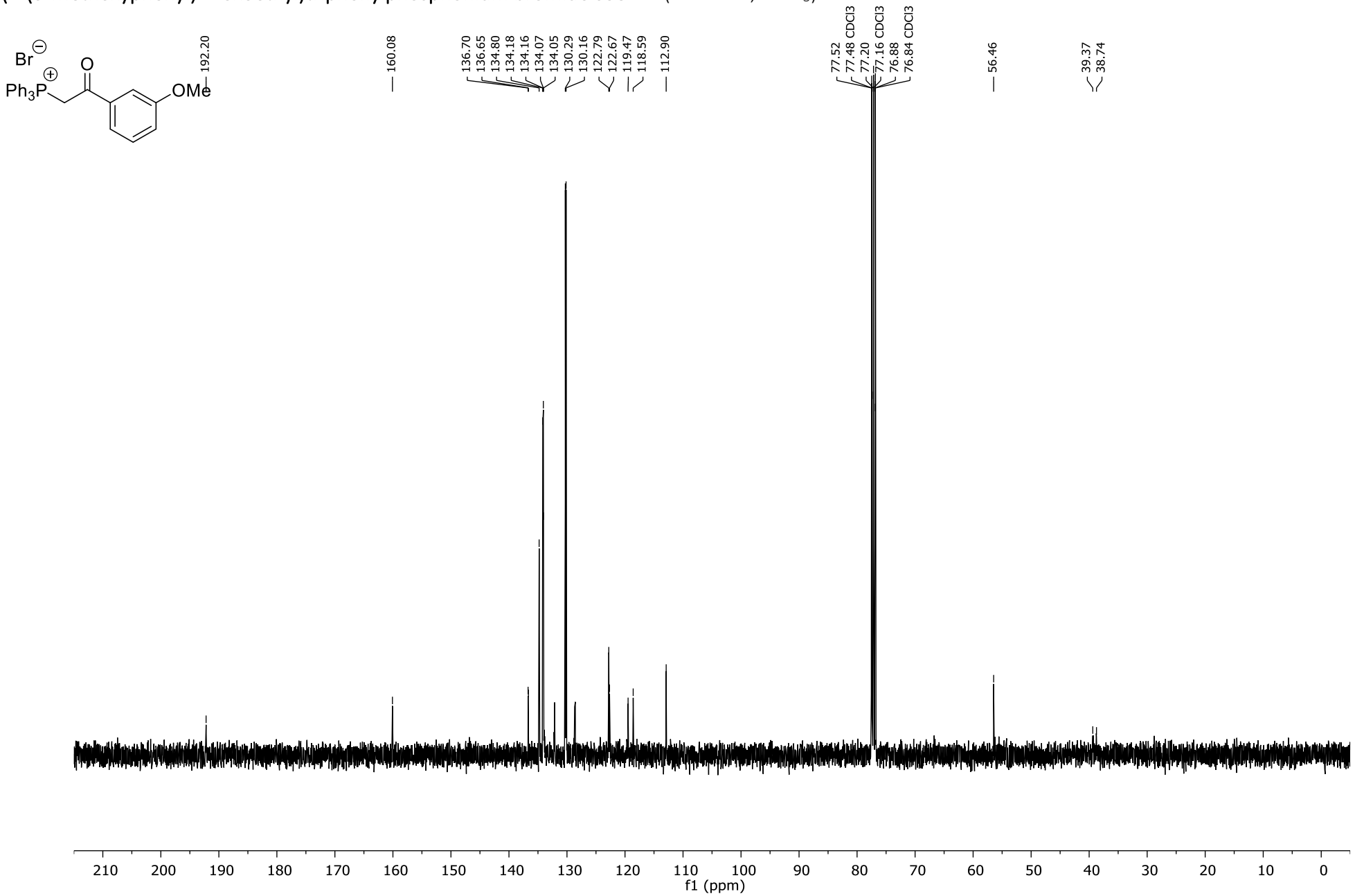
2-((*tert*-Butyldimethylsilyl)oxy)-2-(*o*-tolyl)acetaldehyde S33 ^{13}C NMR (101 MHz, $CDCl_3$)



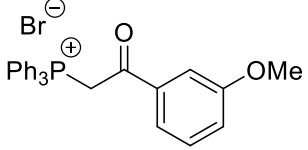
(2-(3-Methoxyphenyl)-2-oxoethyl)triphenylphosphonium bromide S38 ^{1}H NMR (400 MHz, $CDCl_3$)



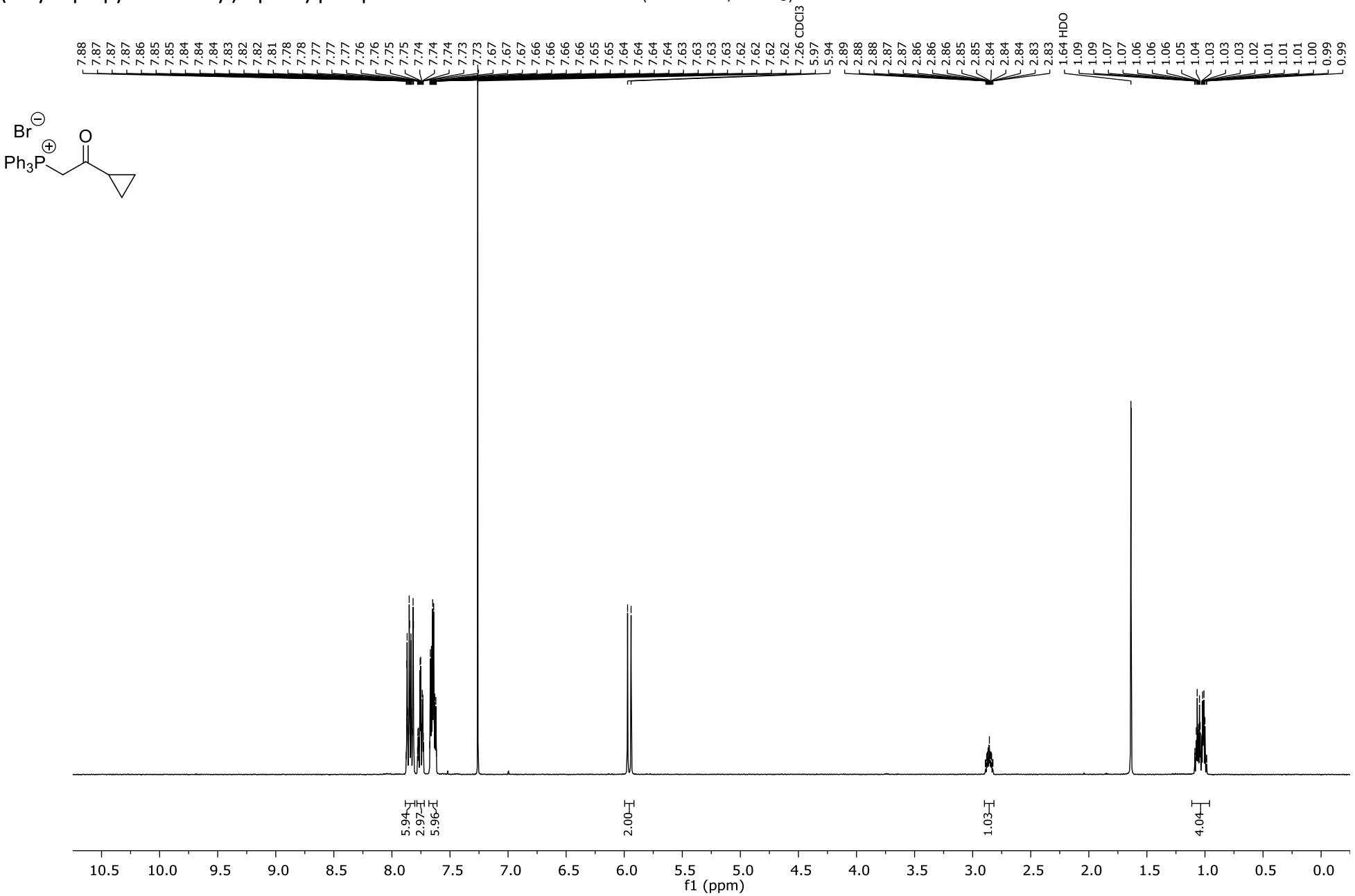
(2-(3-Methoxyphenyl)-2-oxoethyl)triphenylphosphonium bromide S38 ^{13}C (101 MHz, $CDCl_3$)



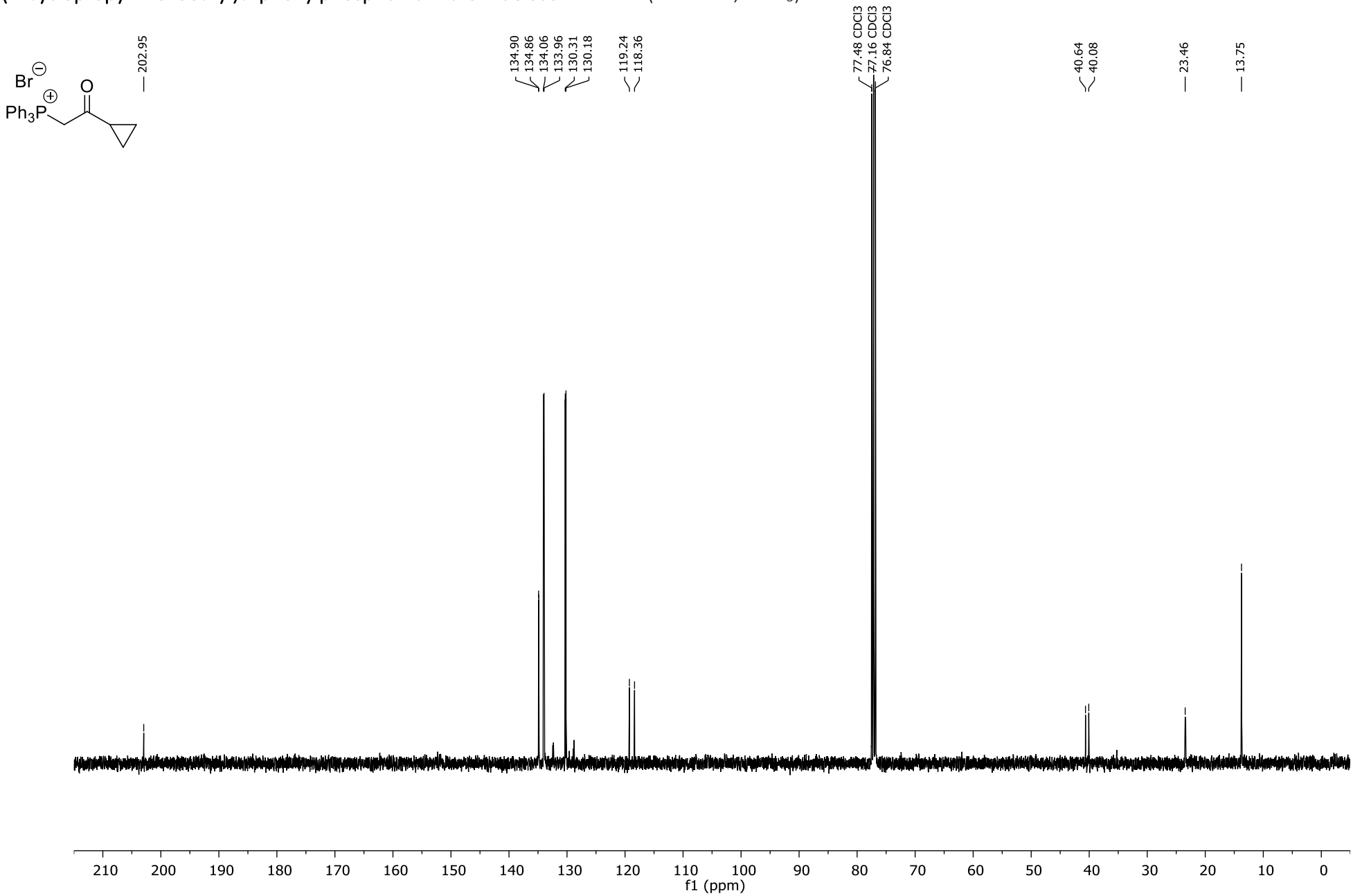
(2-(3-Methoxyphenyl)-2-oxoethyl)triphenylphosphonium bromide S38 $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$)



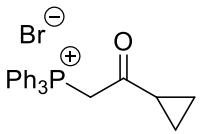
(2-Cyclopropyl-2-oxoethyl)triphenylphosphonium bromide S39 ^{1}H NMR (400 MHz, $CDCl_3$)



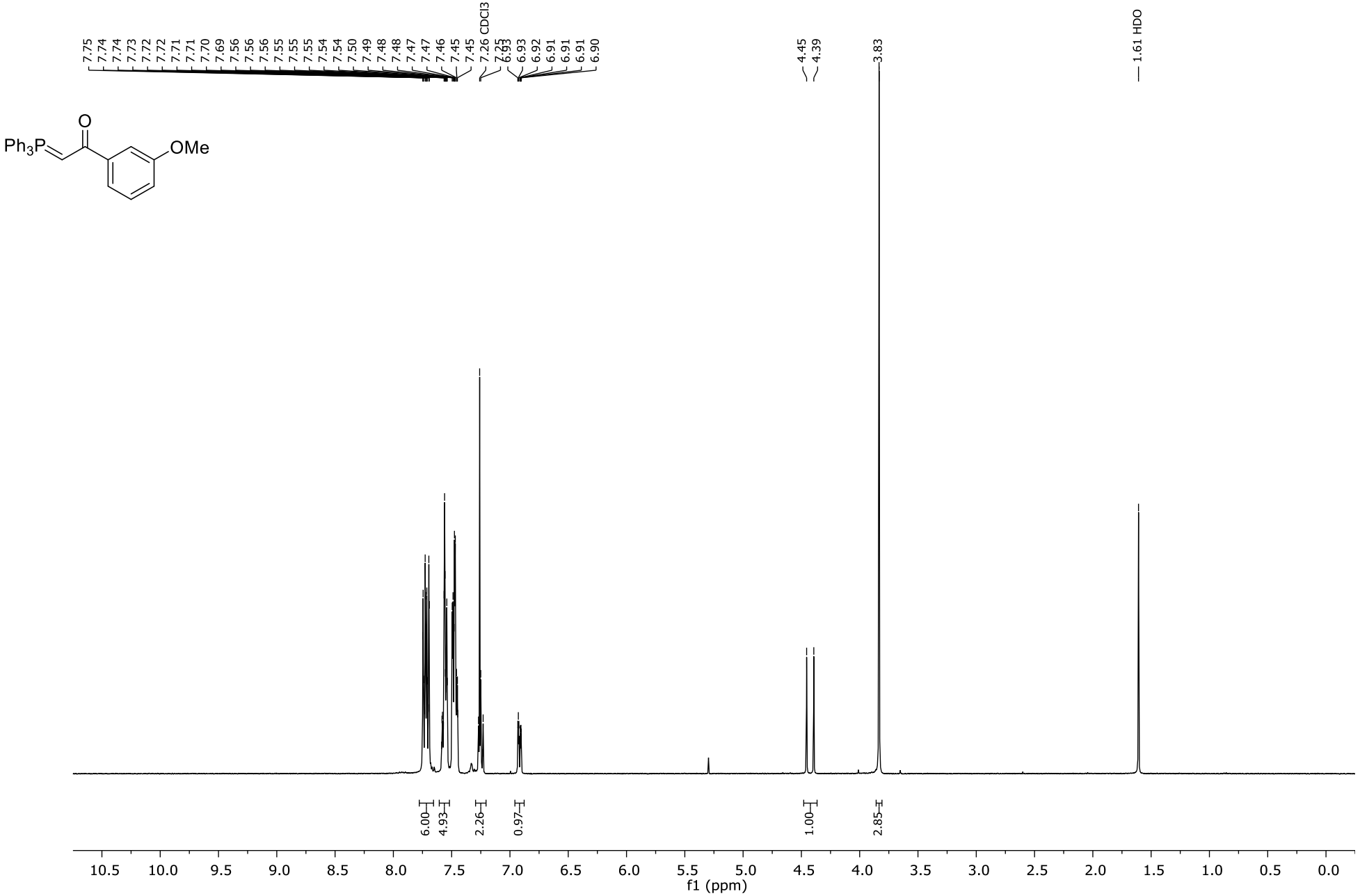
(2-Cyclopropyl-2-oxoethyl)triphenylphosphonium bromide S39 ^{13}C NMR (101 MHz, $CDCl_3$)



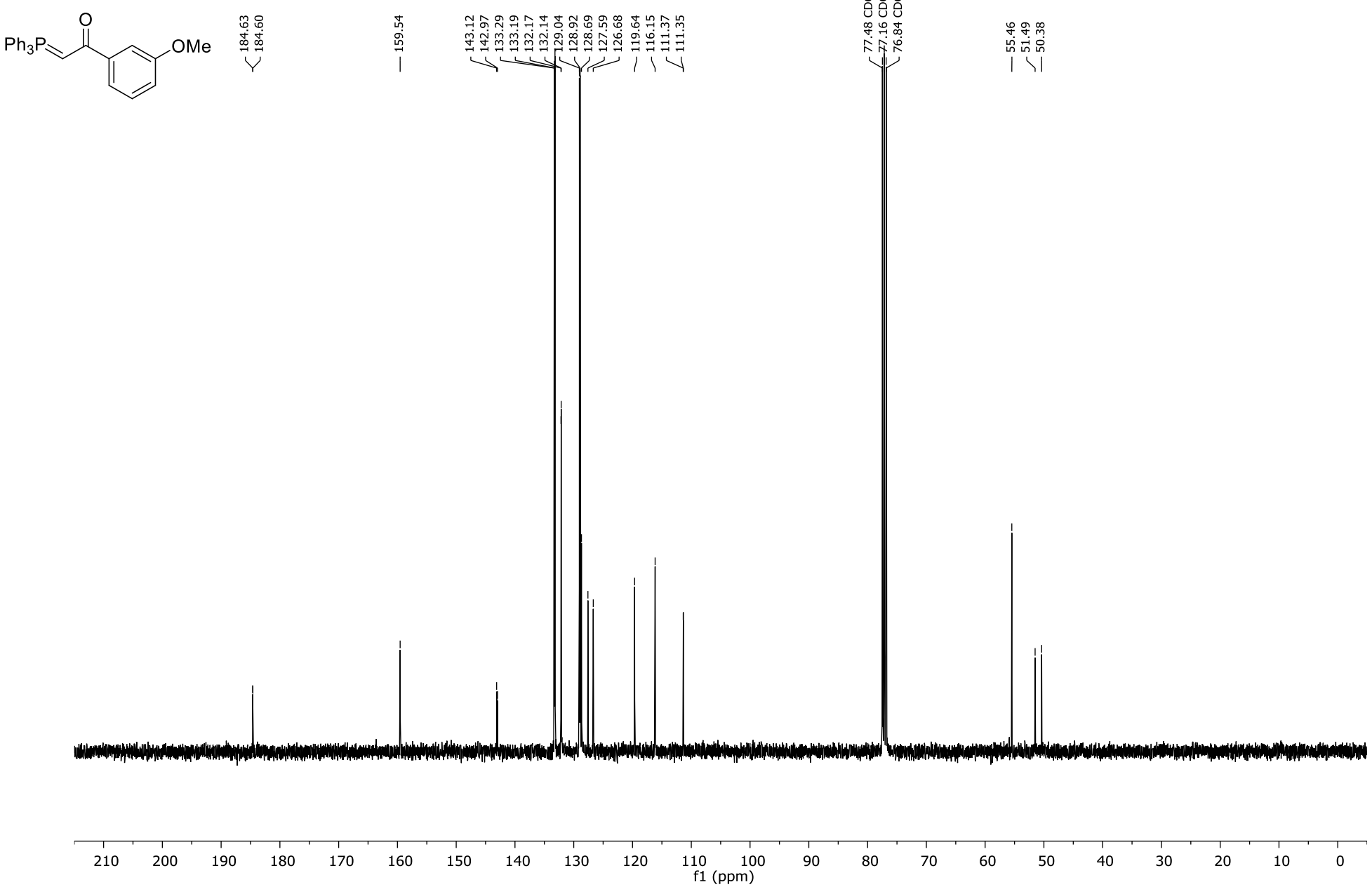
(2-Cyclopropyl-2-oxoethyl)triphenylphosphonium bromide S39 $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$)



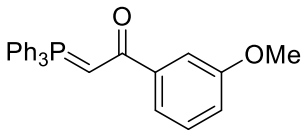
1-(3-Methoxyphenyl)-2-(triphenyl- λ^5-phosphaneylidene)ethan-1-one S43 ^{1}H NMR (400 MHz, $CDCl_3$)



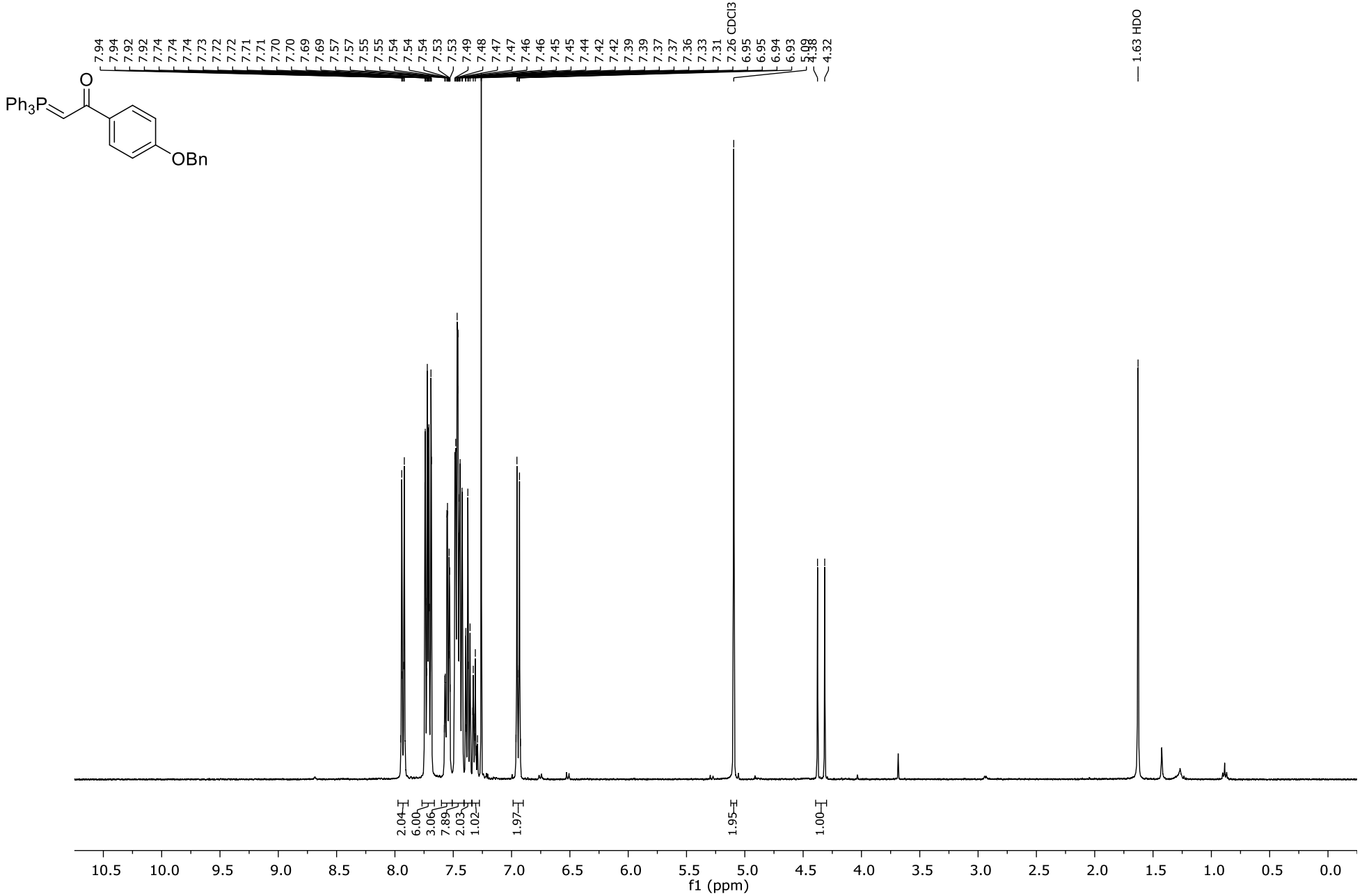
1-(3-Methoxyphenyl)-2-(triphenyl- λ^5-phosphaneylidene)ethan-1-one S43 ^{13}C NMR (101 MHz, $CDCl_3$)



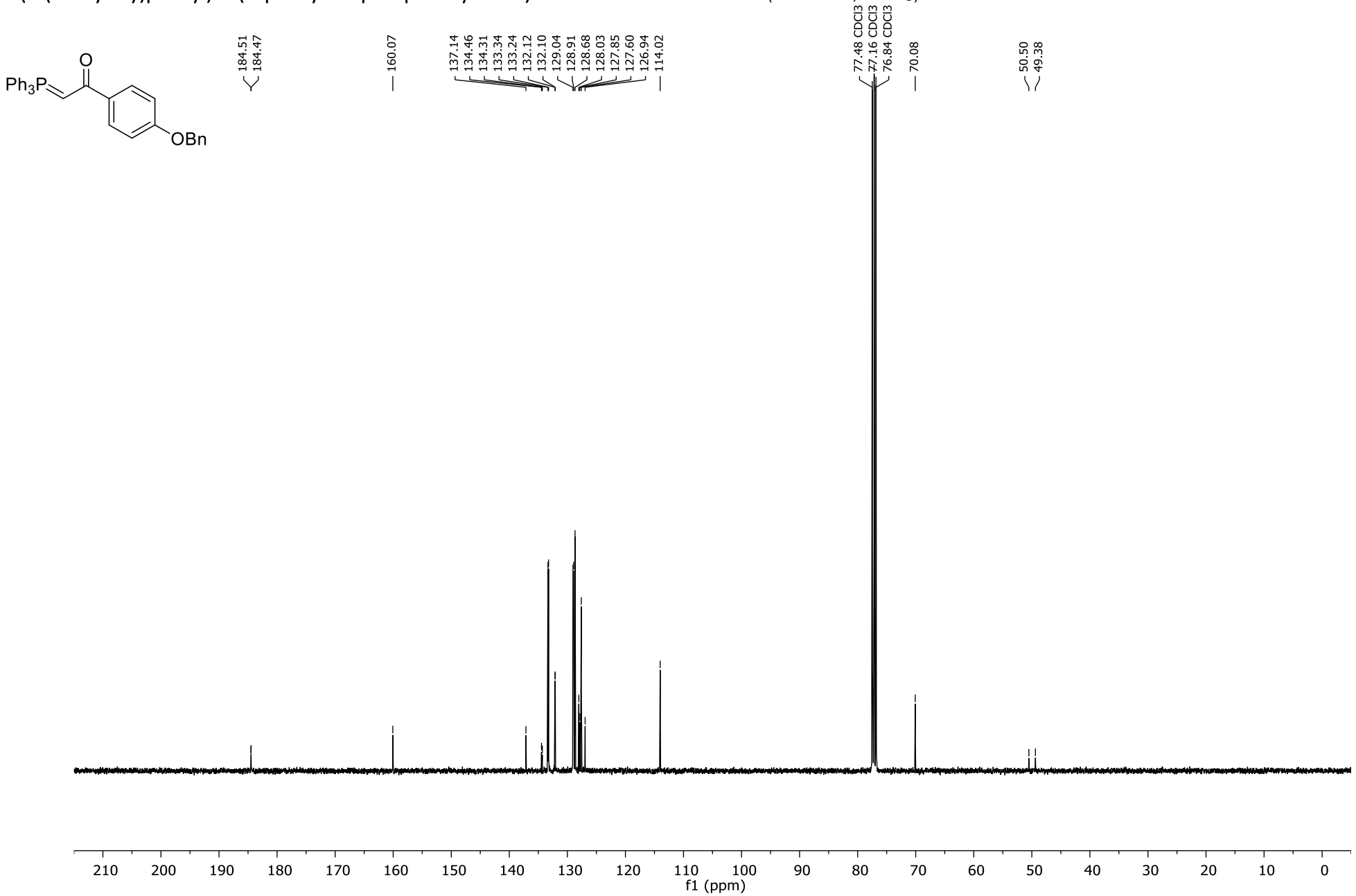
1-(3-Methoxyphenyl)-2-(triphenyl- λ^5-phosphaneylidene)ethan-1-one S43 $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$)



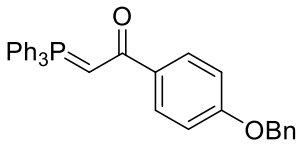
1-(4-(Benzyloxy)phenyl)-2-(triphenyl- λ^5-phosphaneylidene)ethan-1-one S45 ^{1}H NMR (400 MHz, $CDCl_3$)



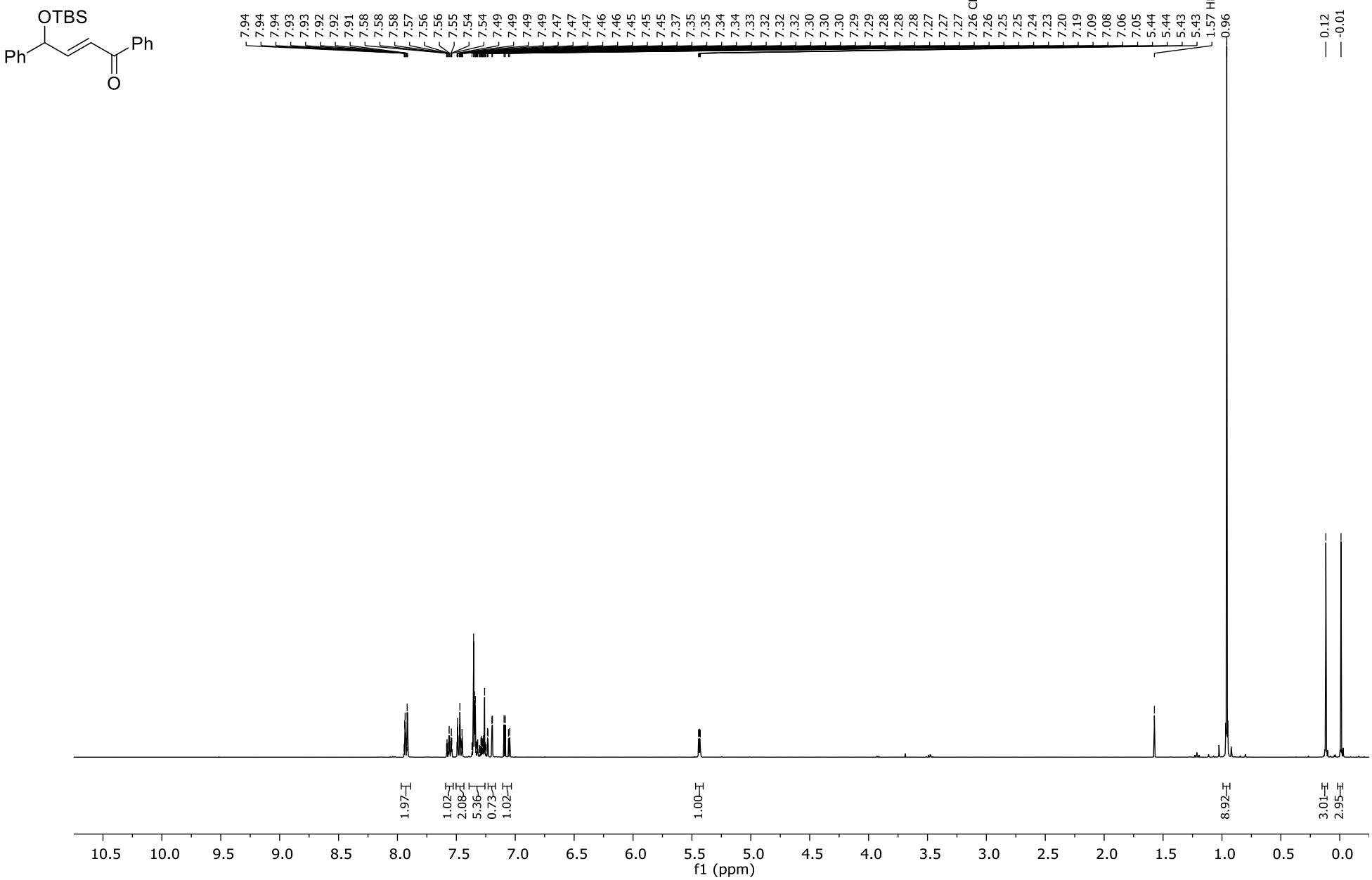
1-(4-(Benzyloxy)phenyl)-2-(triphenyl- λ^5-phosphaneylidene)ethan-1-one S45 ^{13}C NMR (101 MHz, $CDCl_3$)



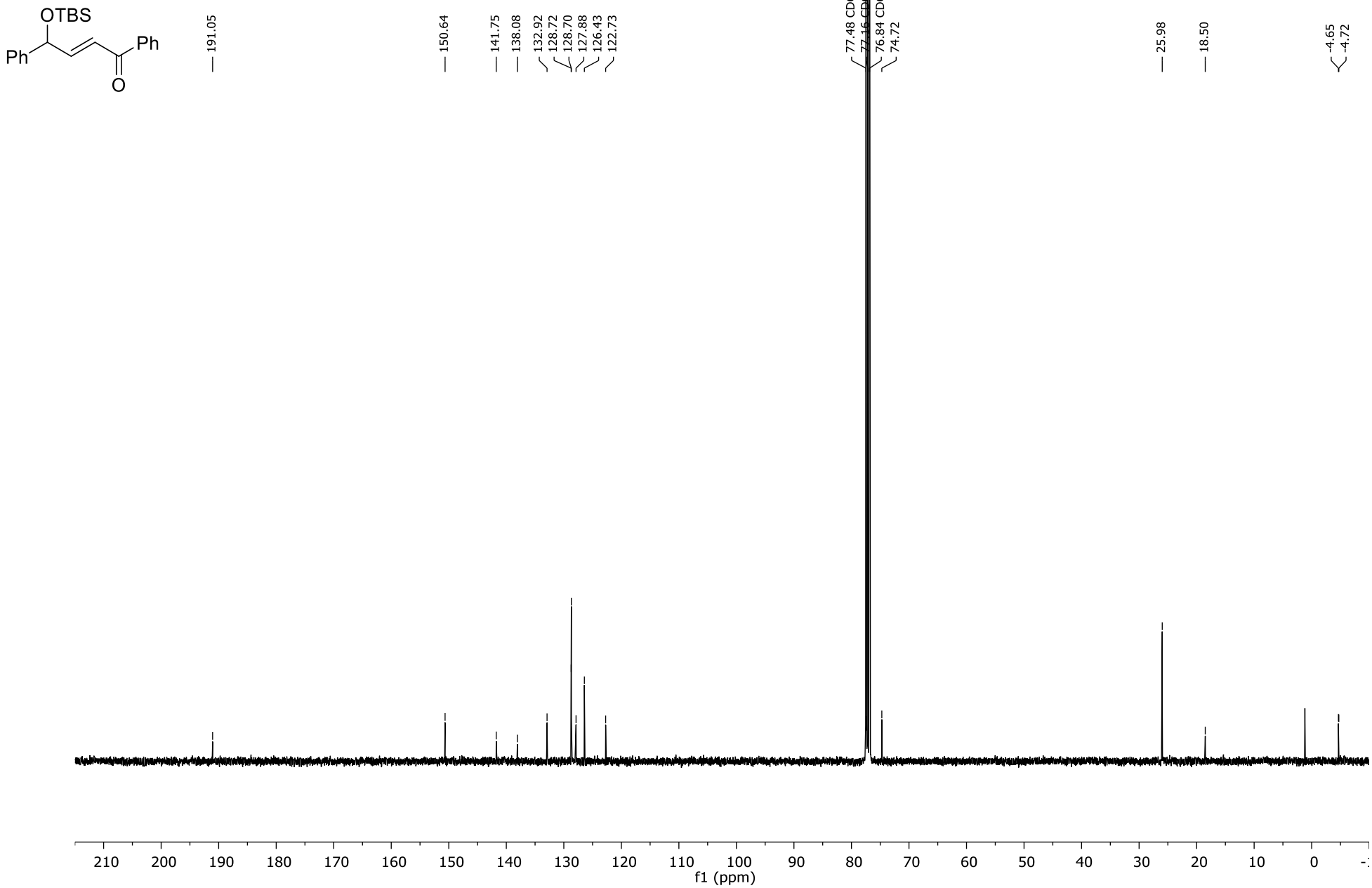
1-(4-(Benzyloxy)phenyl)-2-(triphenyl- λ^5-phosphaneylidene)ethan-1-one S45 $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$)



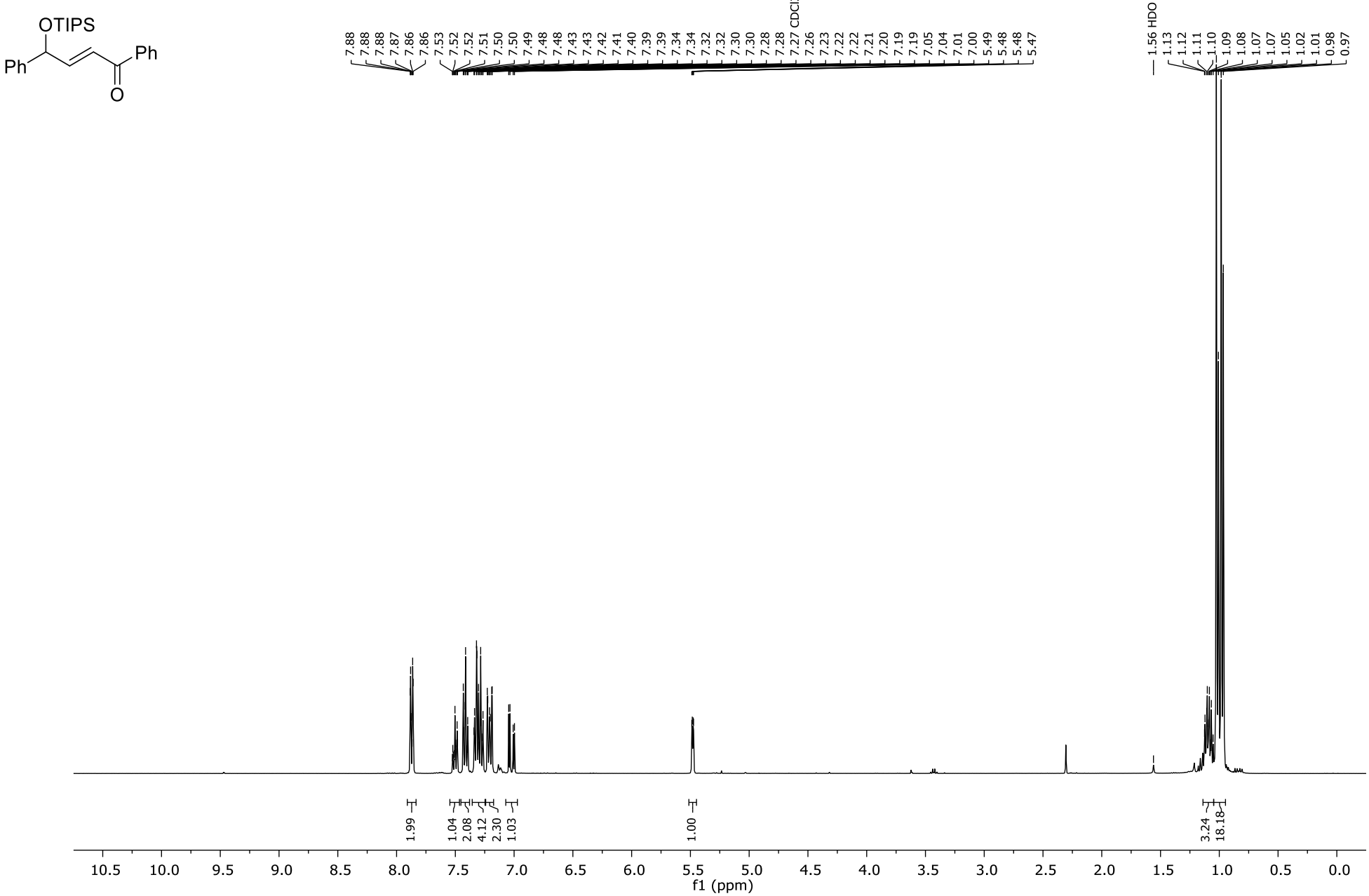
(*E*)-4-((*tert*-Butyldimethylsilyl)oxy)-1,4-diphenylbut-2-en-1-one **1** ^{1}H NMR (400 MHz, $CDCl_3$)



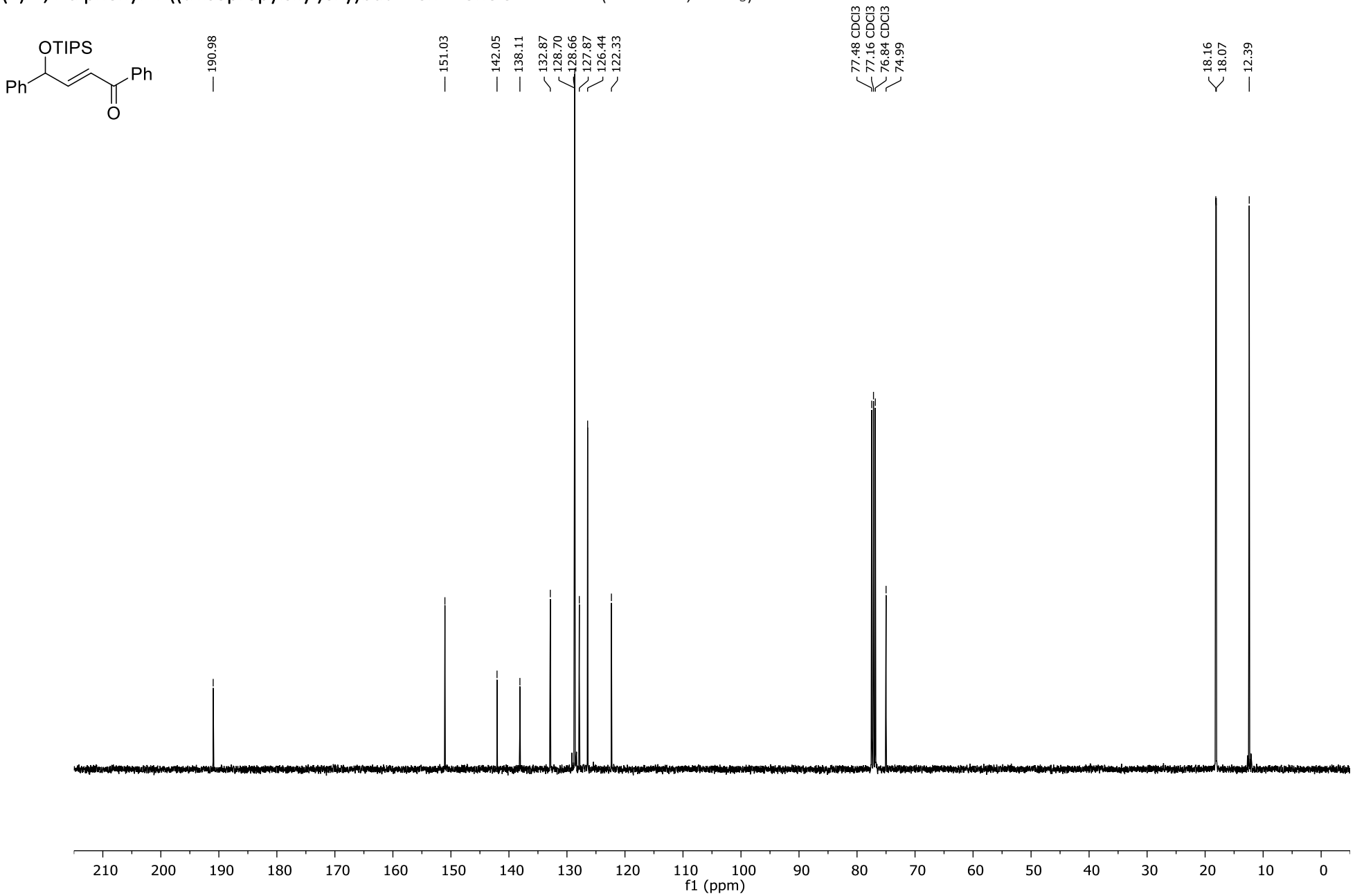
(*E*)-4-((*tert*-Butyldimethylsilyl)oxy)-1,4-diphenylbut-2-en-1-one 1 ^{13}C NMR (101 MHz, $CDCl_3$)



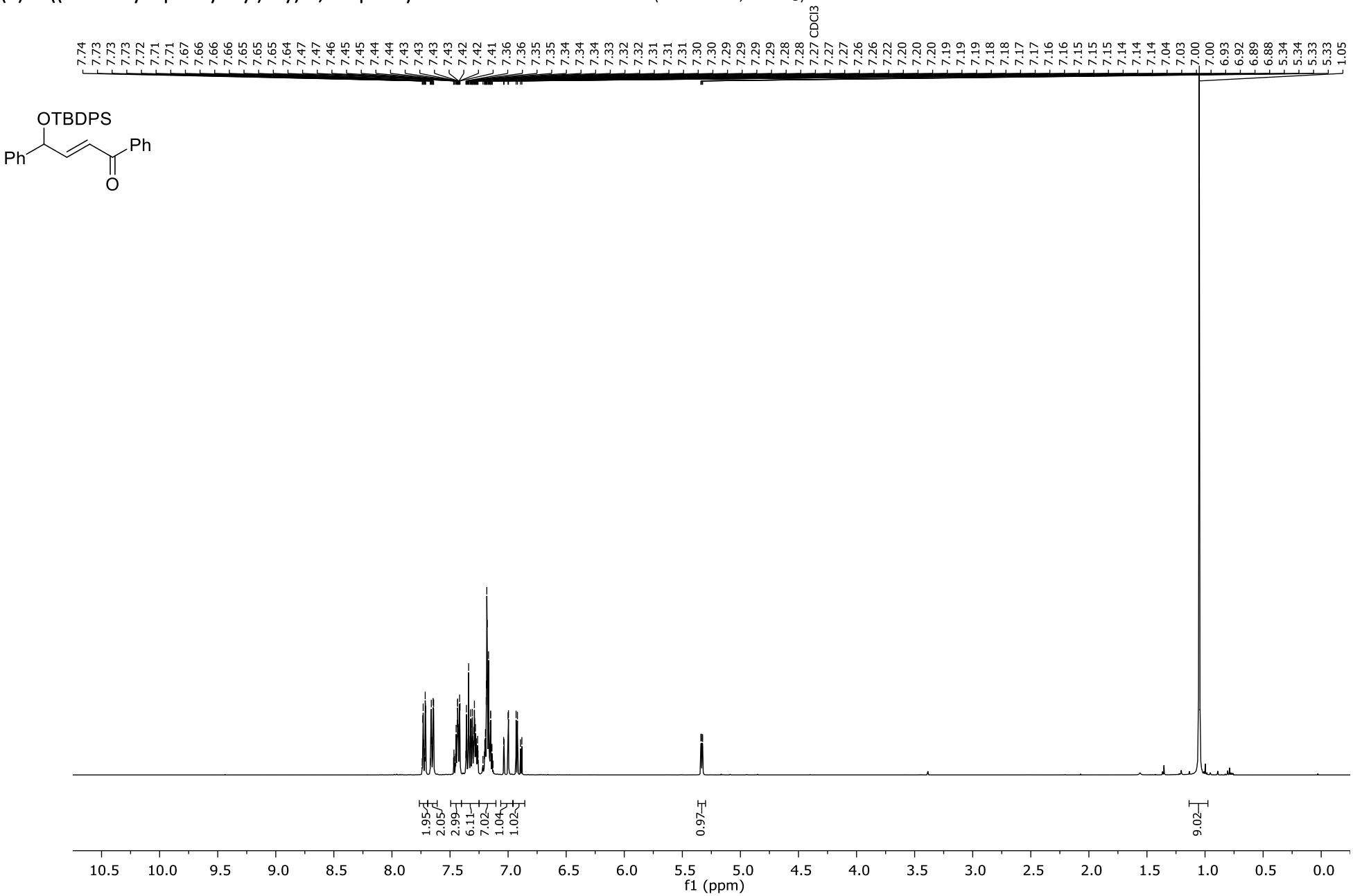
(*E*)-1,4-diphenyl-4-((triisopropylsilyl)oxy)but-2-en-1-one **5** ^{1}H NMR (400 MHz, $CDCl_3$)



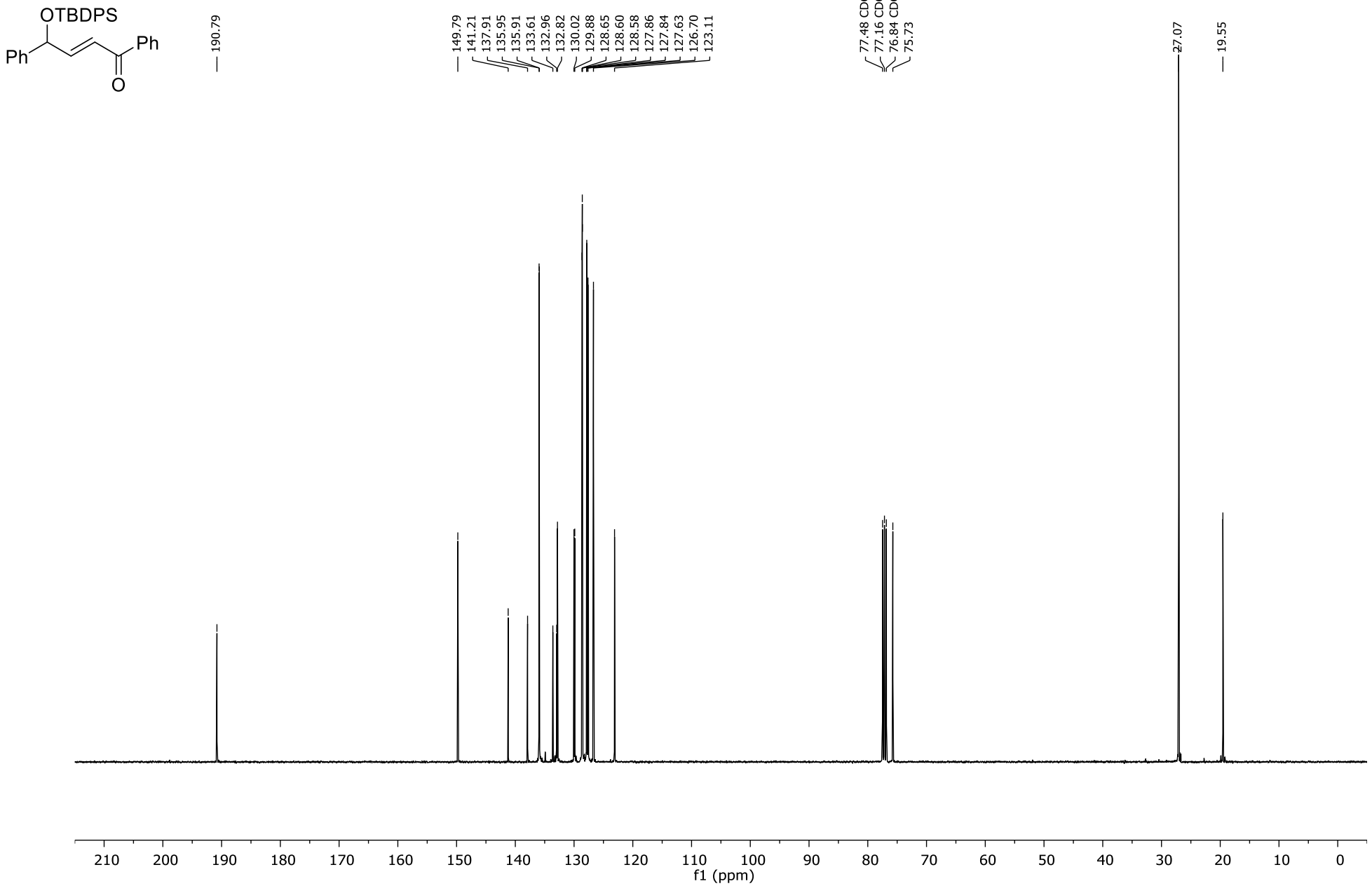
(*E*)-1,4-diphenyl-4-((triisopropylsilyl)oxy)but-2-en-1-one 5 ^{13}C NMR (101 MHz, $CDCl_3$)



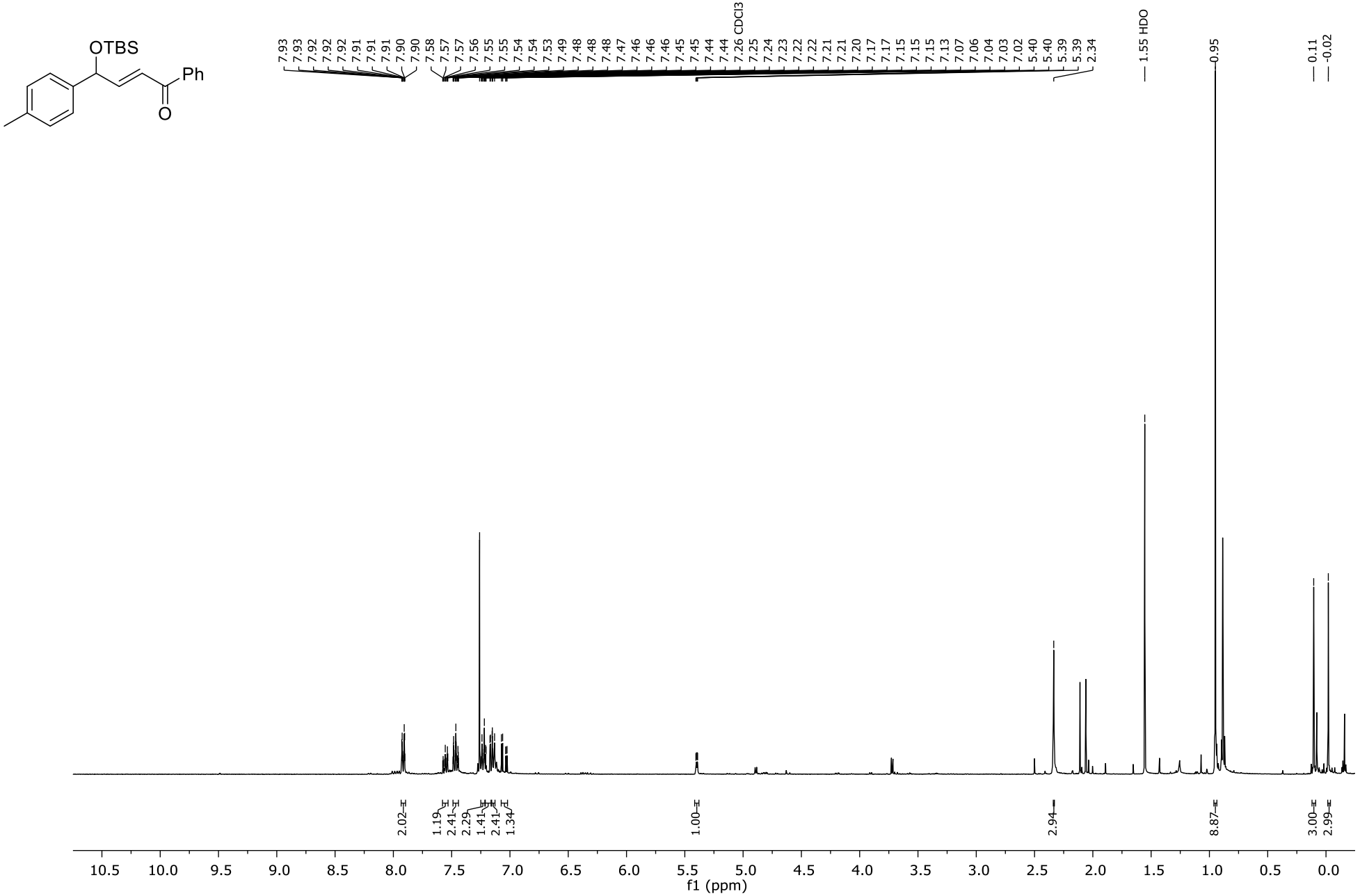
(*E*)-4-((*tert*-butyldiphenylsilyl)oxy)-1,4-diphenylbut-2-en-1-one **6** ^{1}H NMR (400 MHz, $CDCl_3$)



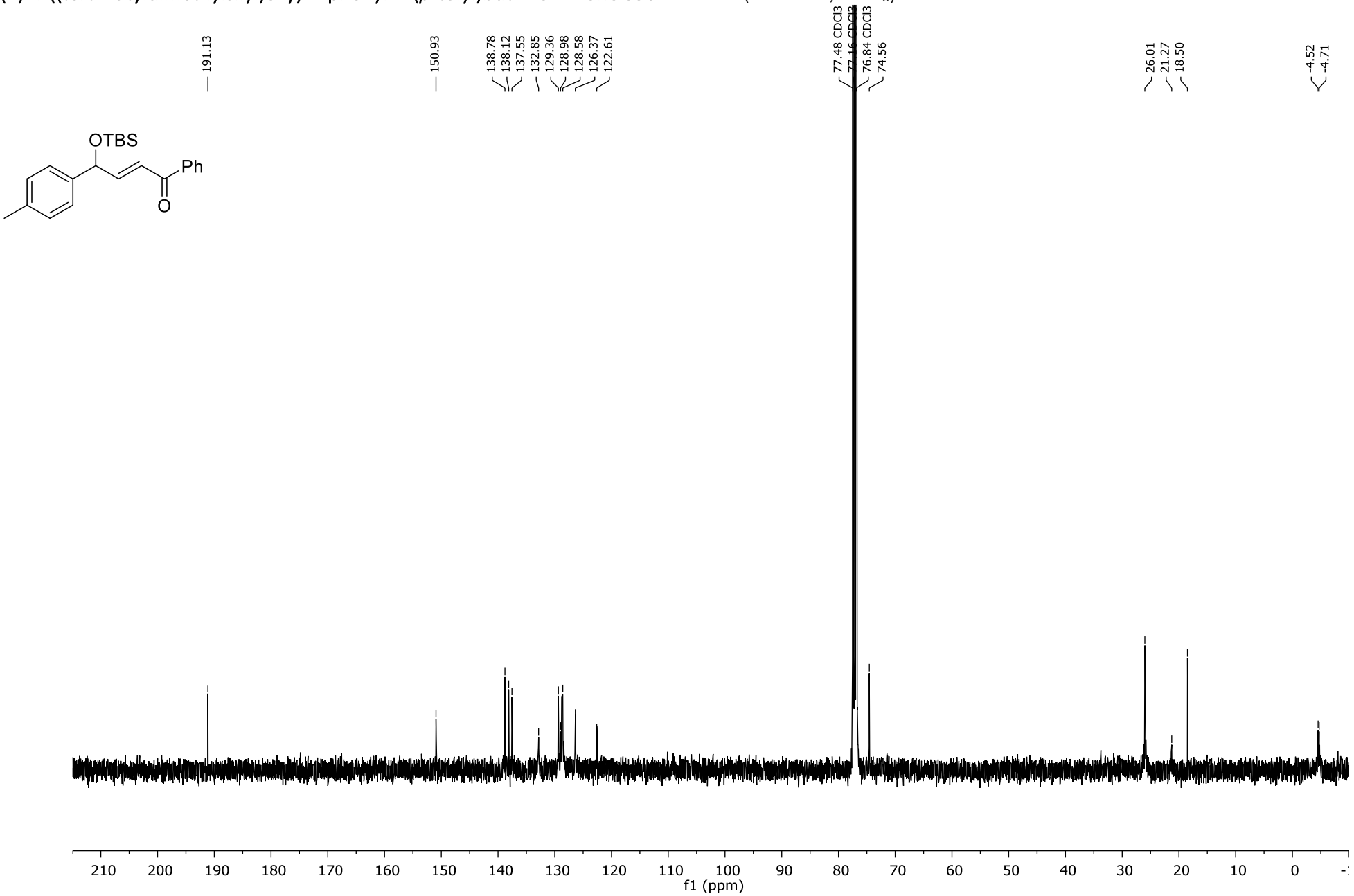
(*E*)-4-((*tert*-butyldiphenylsilyl)oxy)-1,4-diphenylbut-2-en-1-one 6 ^{13}C NMR (101 MHz, $CDCl_3$)



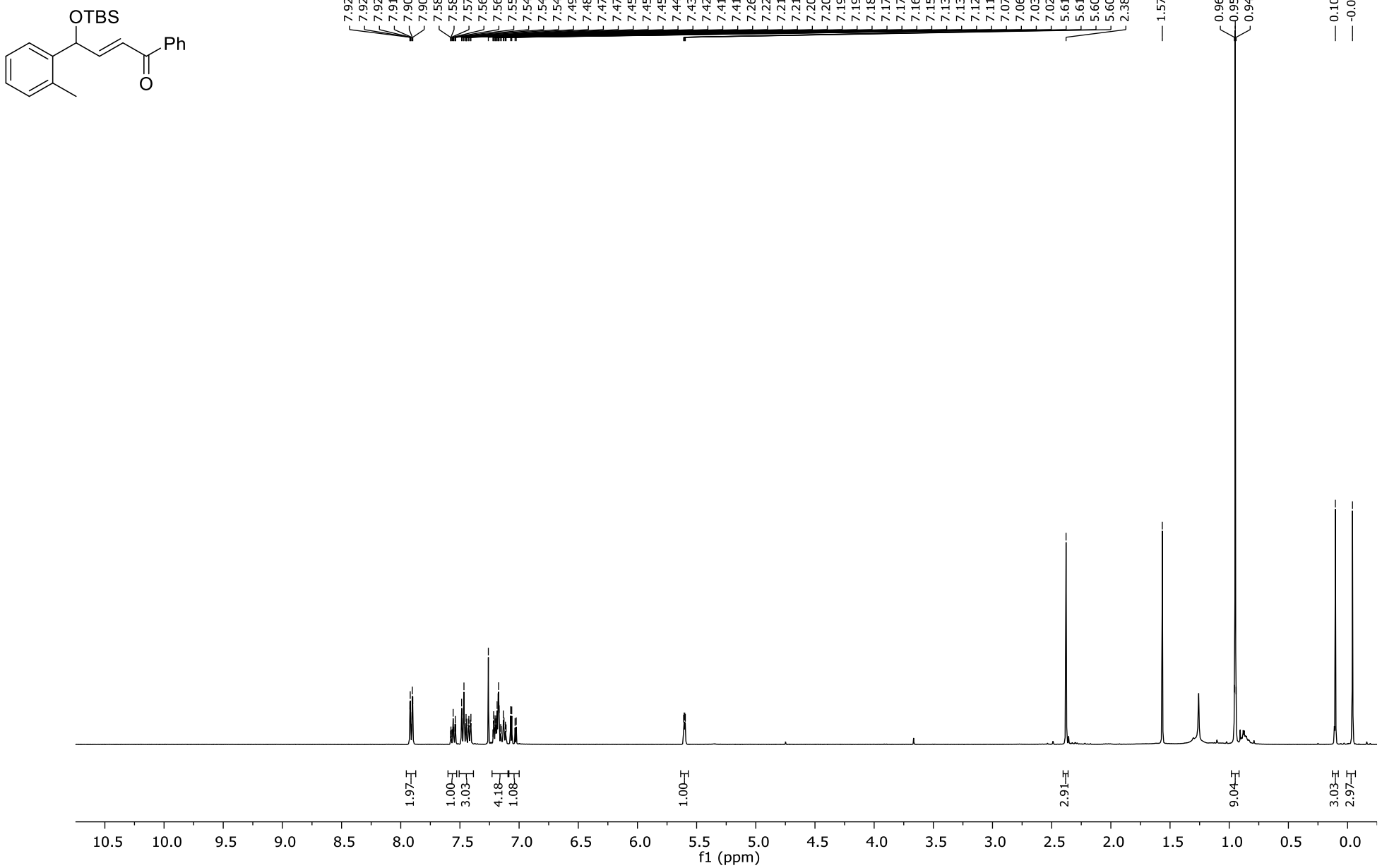
(*E*)-4-((*tert*-Butyldimethylsilyl)oxy)-1-phenyl-4-(*p*-tolyl)but-2-en-1-one S50 ^{1}H NMR (400 MHz, $CDCl_3$)



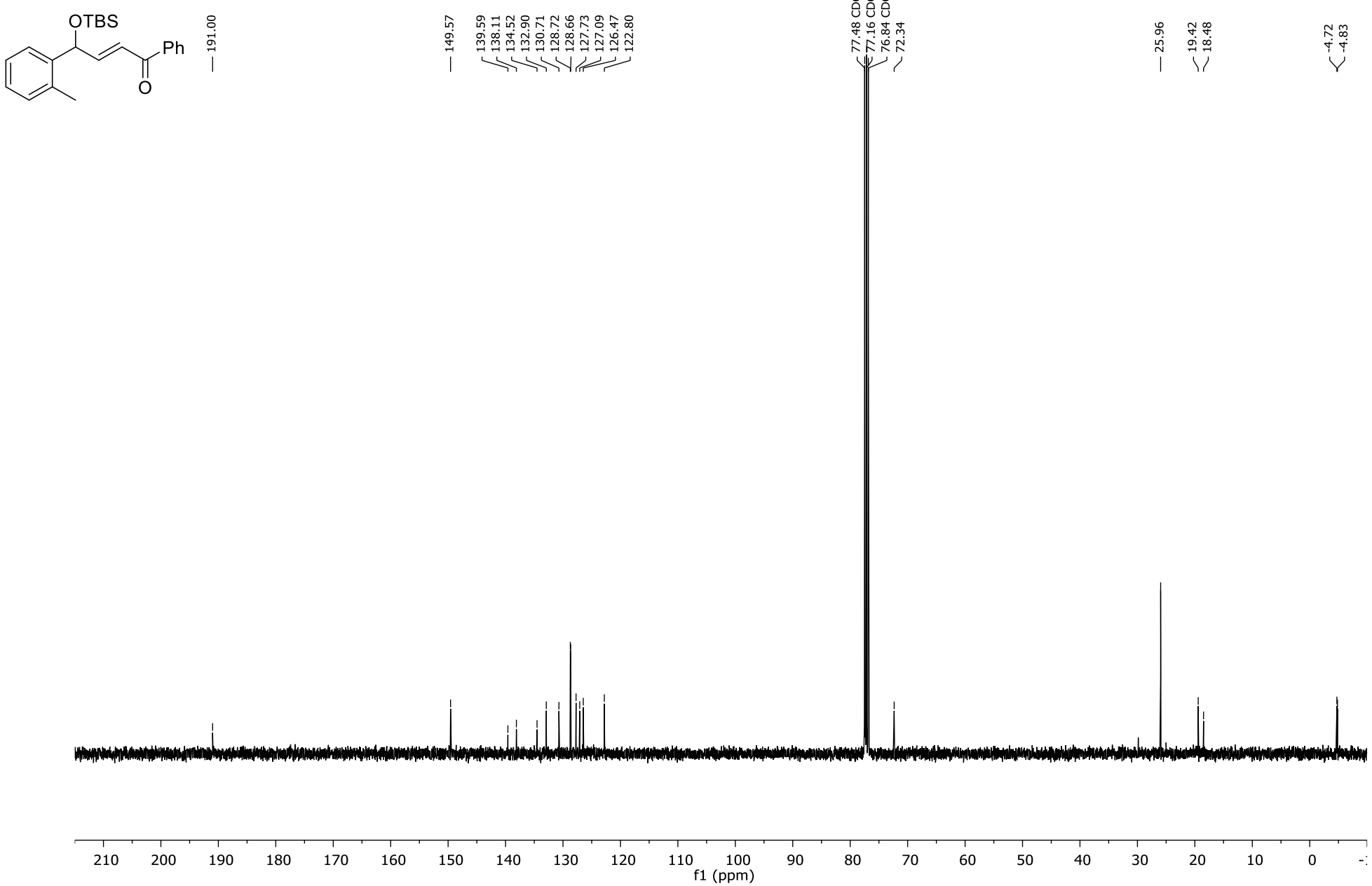
(*E*)-4-((*tert*-Butyldimethylsilyl)oxy)-1-phenyl-4-(*p*-tolyl)but-2-en-1-one S50 ^{13}C NMR (101 MHz, $CDCl_3$)



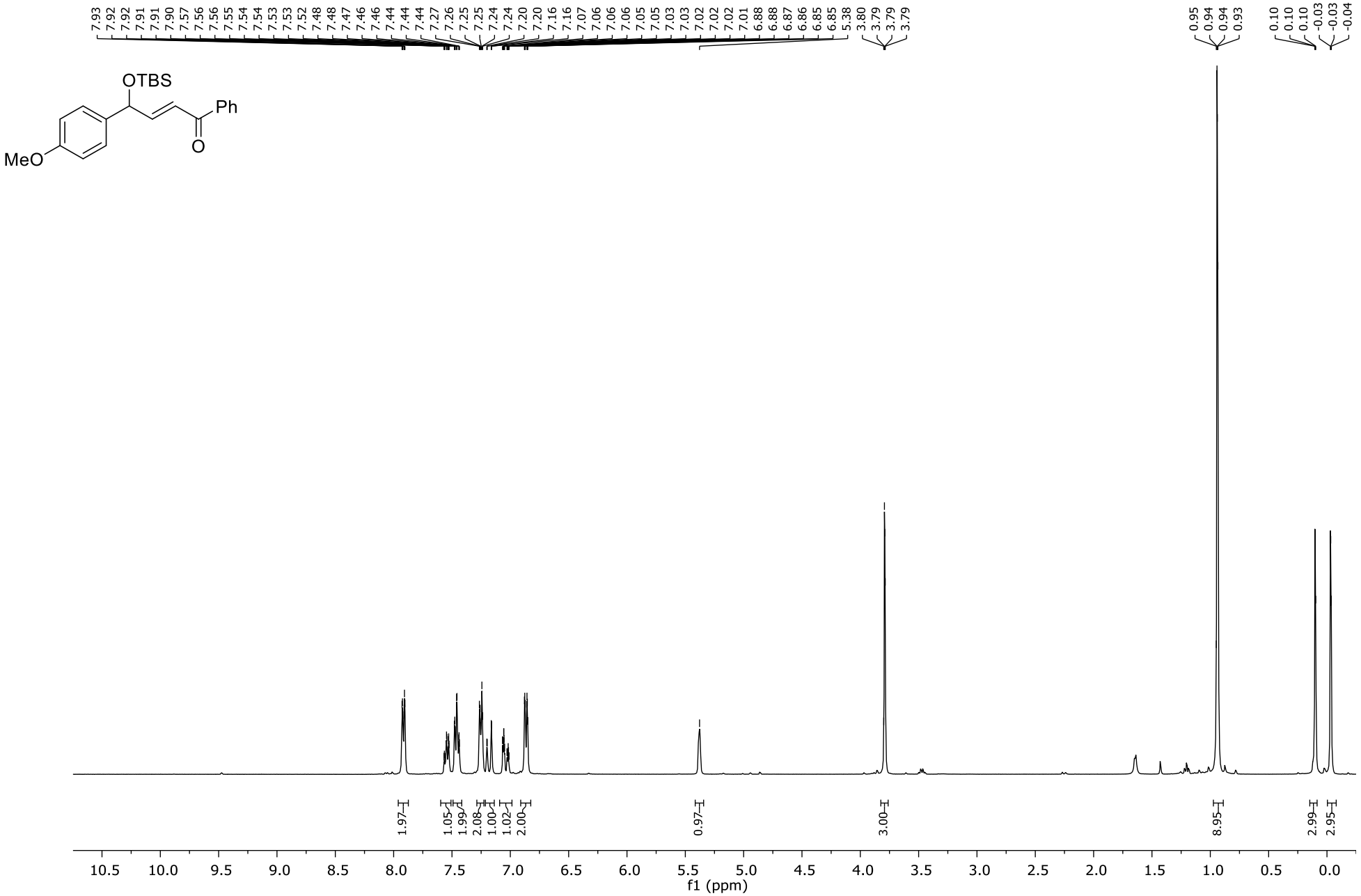
(*E*)-4-((*tert*-Butyldimethylsilyl)oxy)-1-phenyl-4-(*o*-tolyl)but-2-en-1-one S51 ^{1}H NMR (400 MHz, $CDCl_3$)



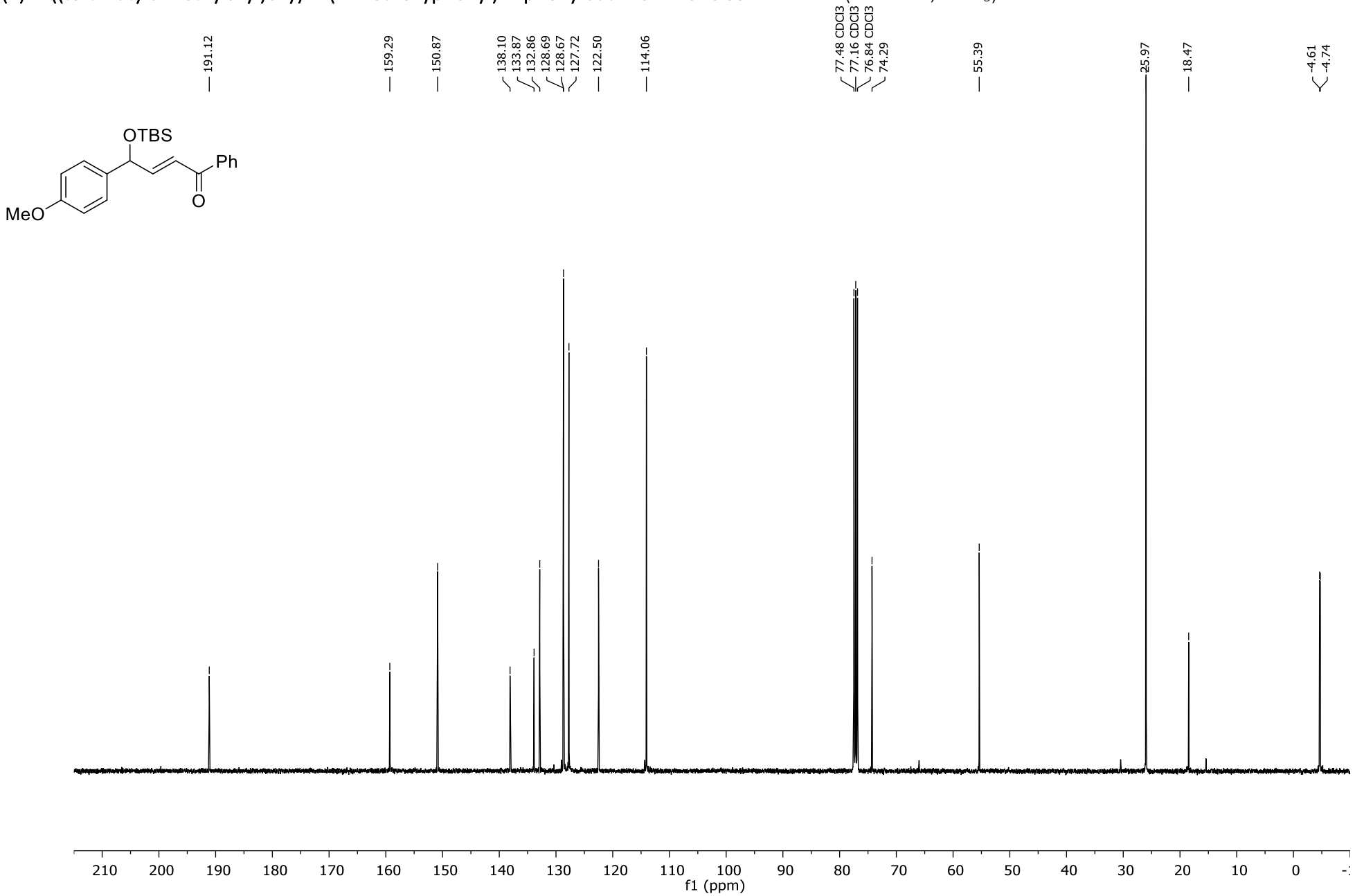
(*E*)-4-((*tert*-Butyldimethylsilyl)oxy)-1-phenyl-4-(*o*-tolyl)but-2-en-1-one **S51** ^{13}C NMR (101 MHz, $CDCl_3$)



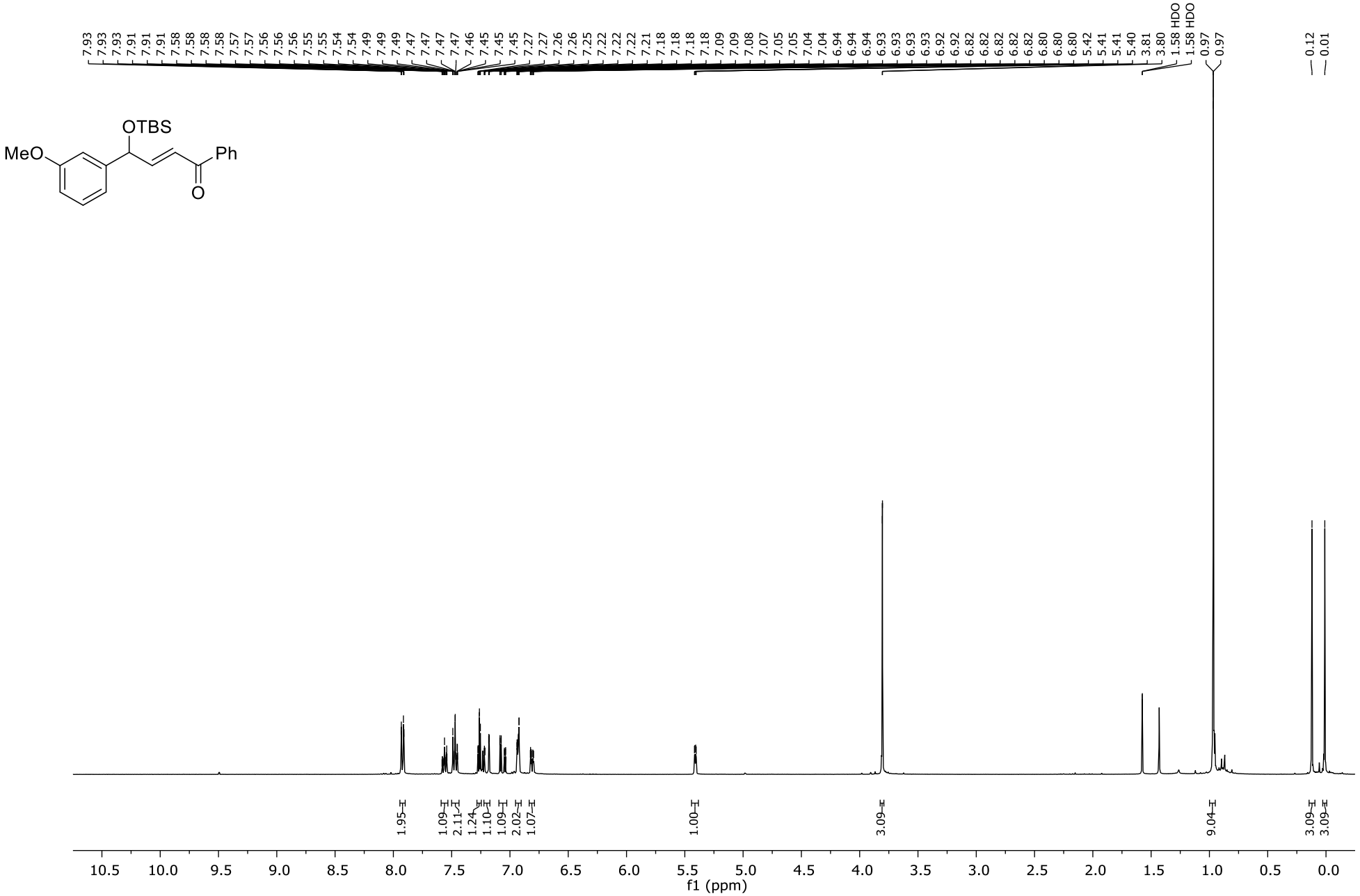
(*E*)-4-((*tert*-Butyldimethylsilyl)oxy)-4-(4-methoxyphenyl)-1-phenylbut-2-en-1-one S52 ^{1}H NMR (400 MHz, $CDCl_3$)



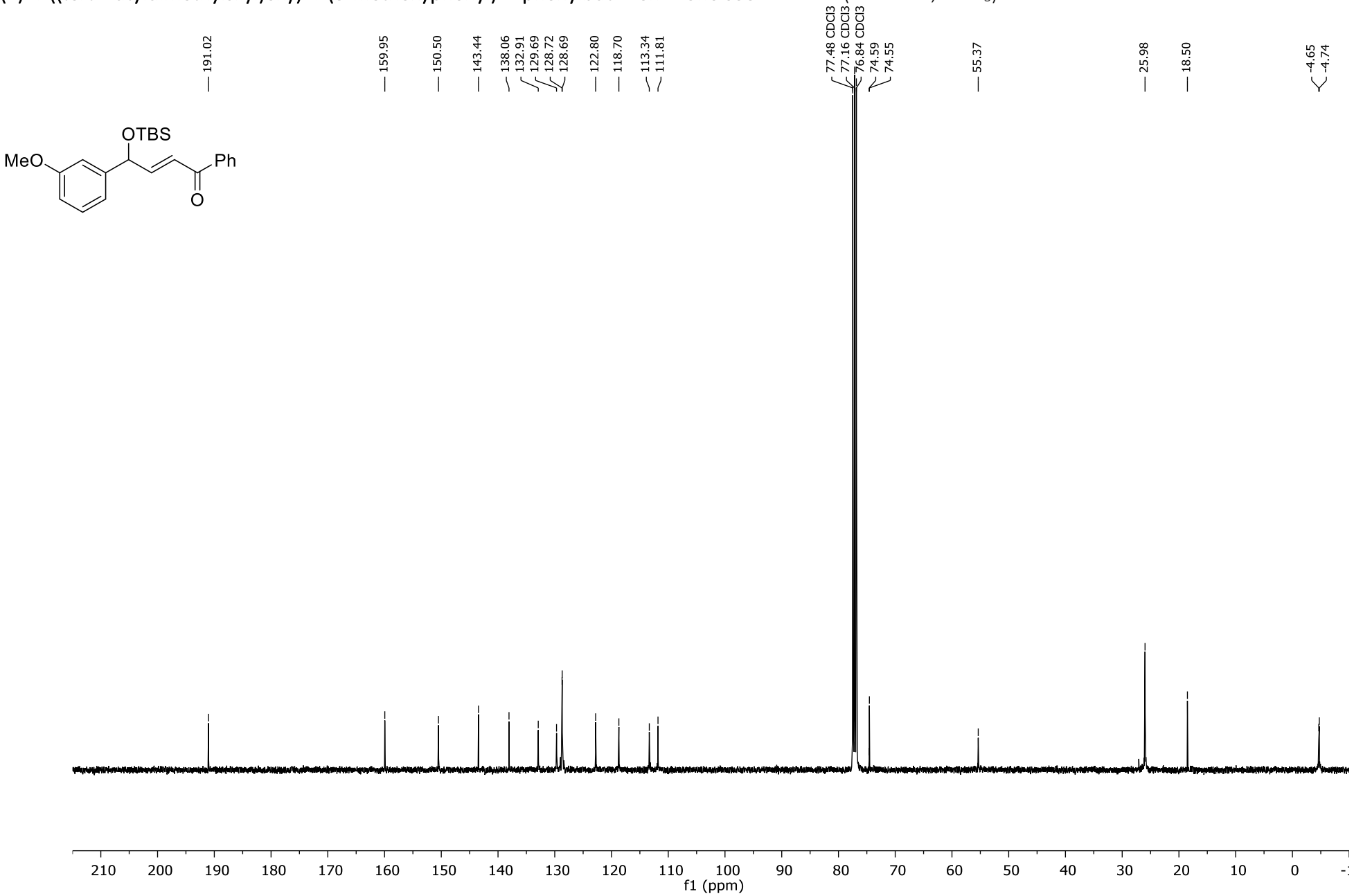
(*E*)-4-((*tert*-Butyldimethylsilyl)oxy)-4-(4-methoxyphenyl)-1-phenylbut-2-en-1-one S52 ^{13}C NMR (101 MHz, $CDCl_3$)



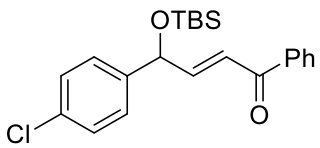
(*E*)-4-((*tert*-Butyldimethylsilyl)oxy)-4-(3-methoxyphenyl)-1-phenylbut-2-en-1-one S53 ^{1}H NMR (400 MHZ, $CDCl_3$)



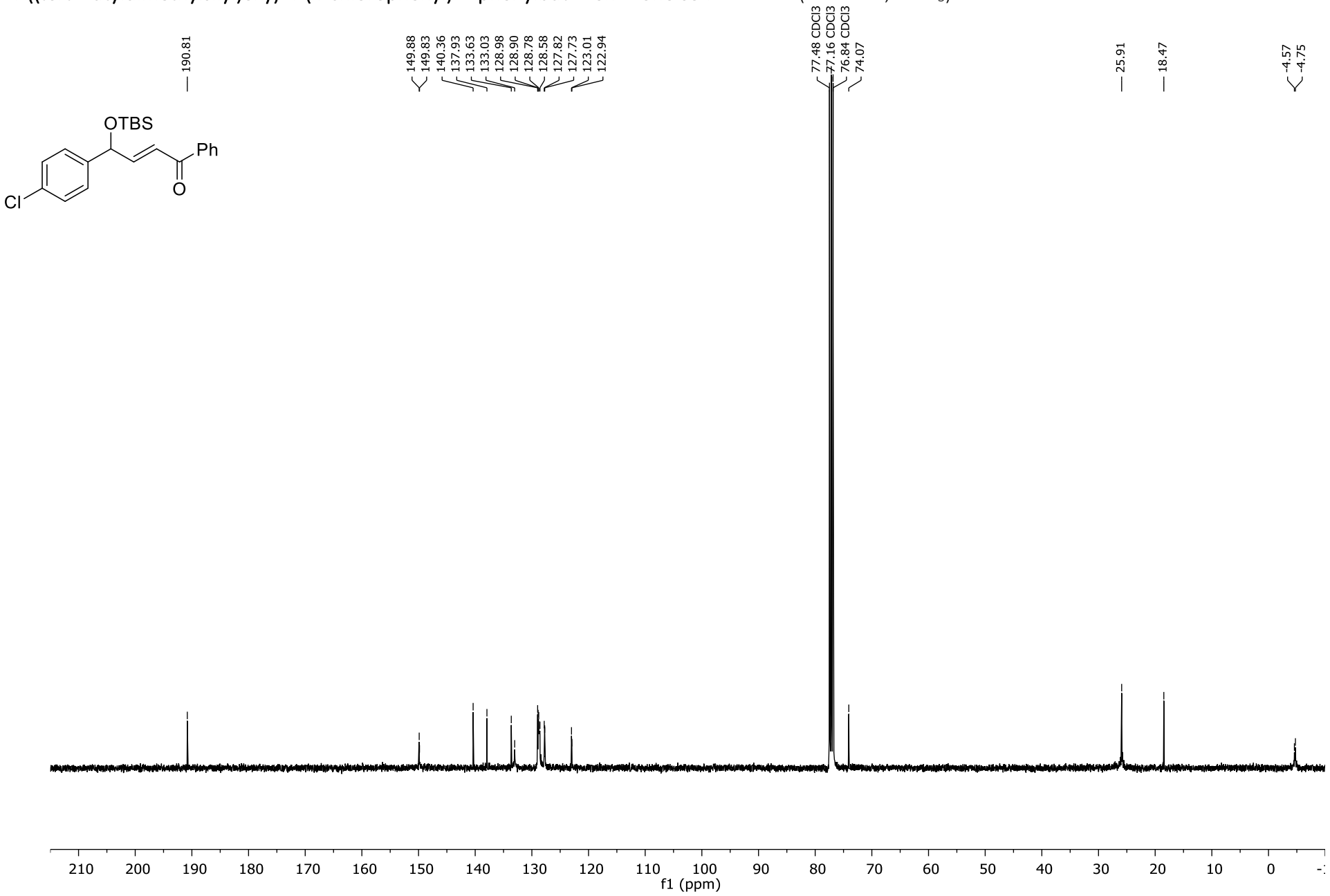
(*E*)-4-((*tert*-Butyldimethylsilyl)oxy)-4-(3-methoxyphenyl)-1-phenylbut-2-en-1-one S53 ^{13}C NMR (101 MHZ, $CDCl_3$)



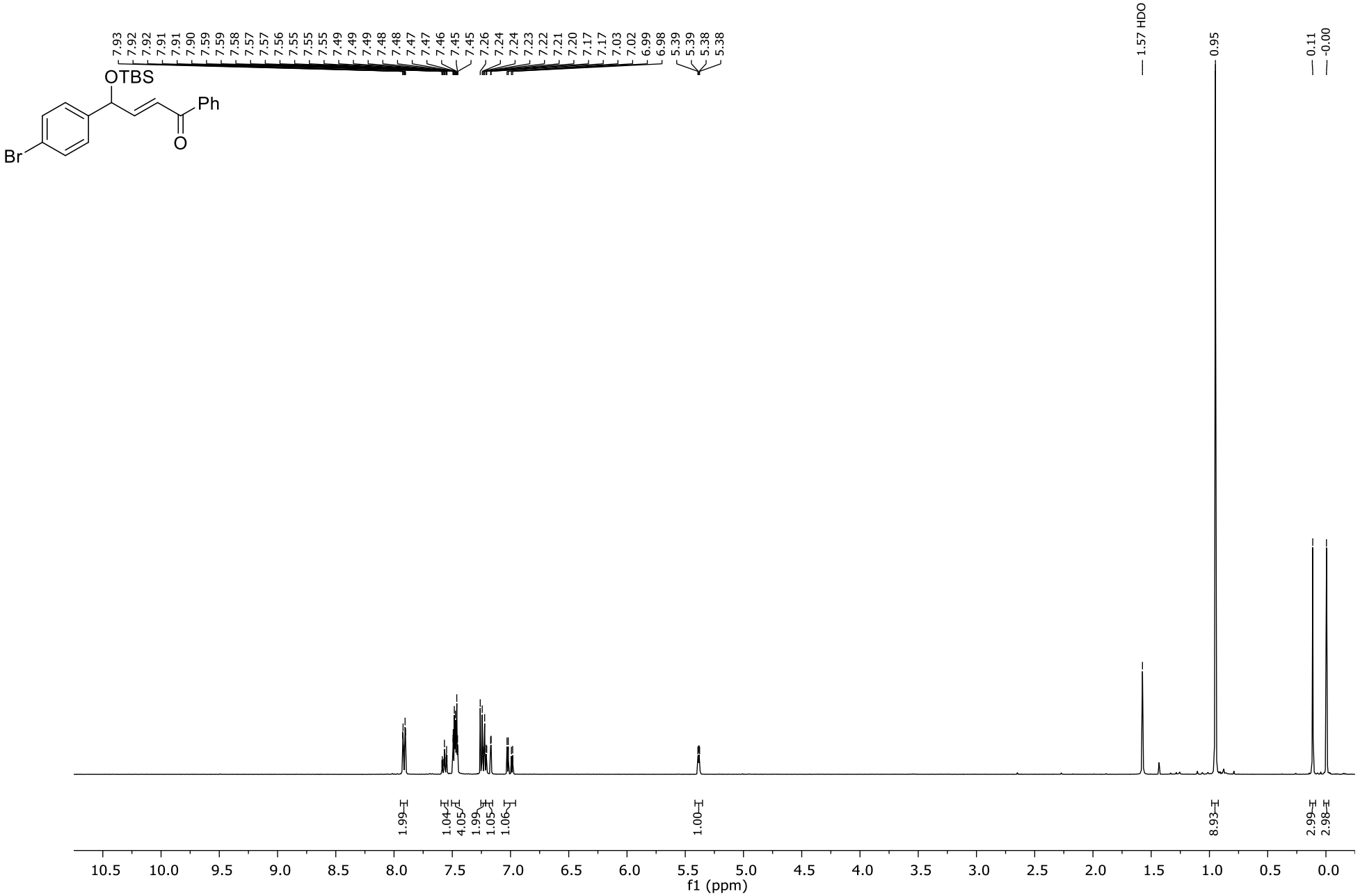
(*E*)-4-((*tert*-Butyldimethylsilyl)oxy)-4-(4-chlorophenyl)-1-phenylbut-2-en-1-one **S54** ^{1}H NMR (400 MHz, $CDCl_3$)



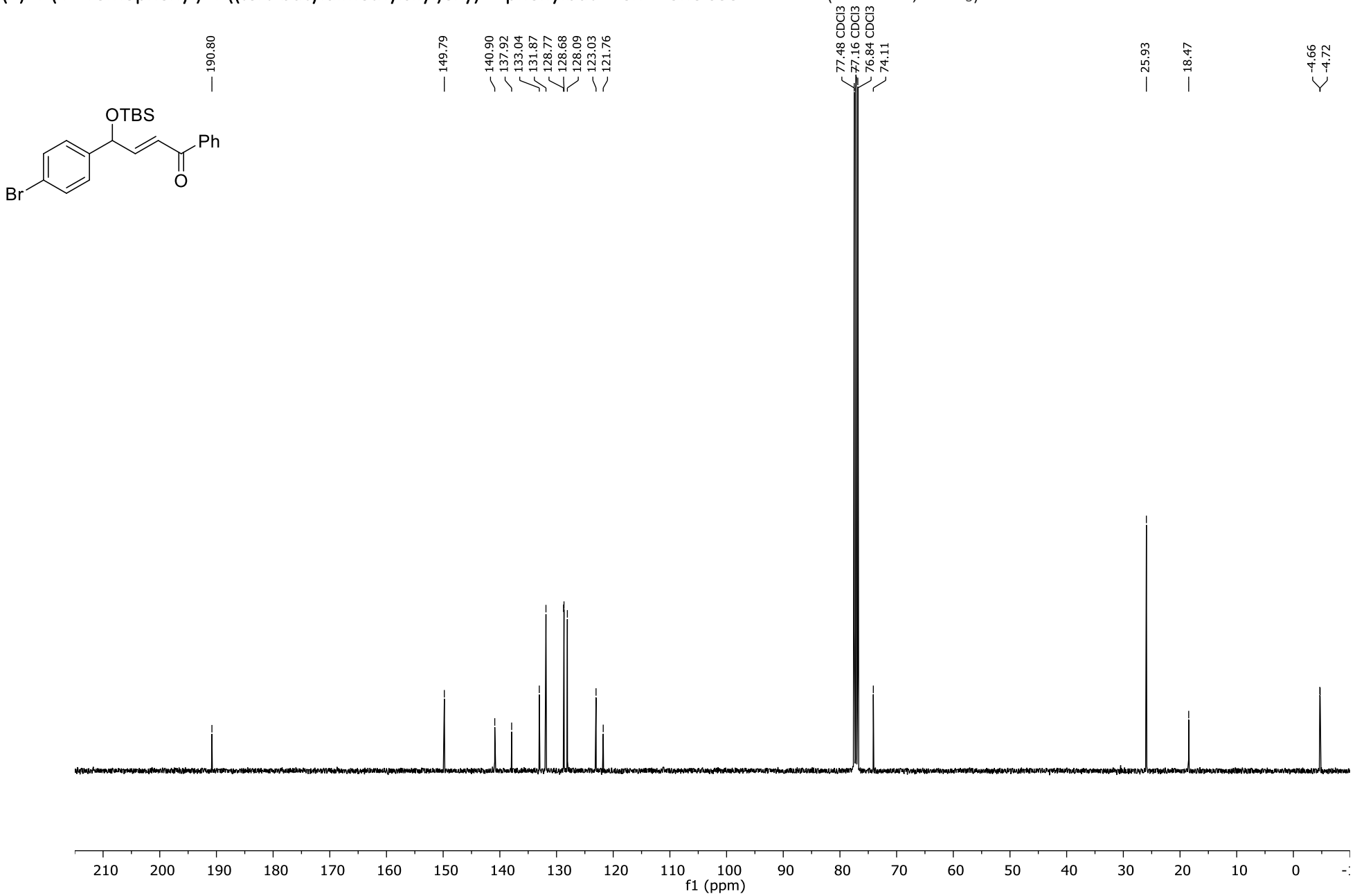
(*E*)-4-((*tert*-Butyldimethylsilyl)oxy)-4-(4-chlorophenyl)-1-phenylbut-2-en-1-one S54 ^{13}C NMR (101 MHz, $CDCl_3$)



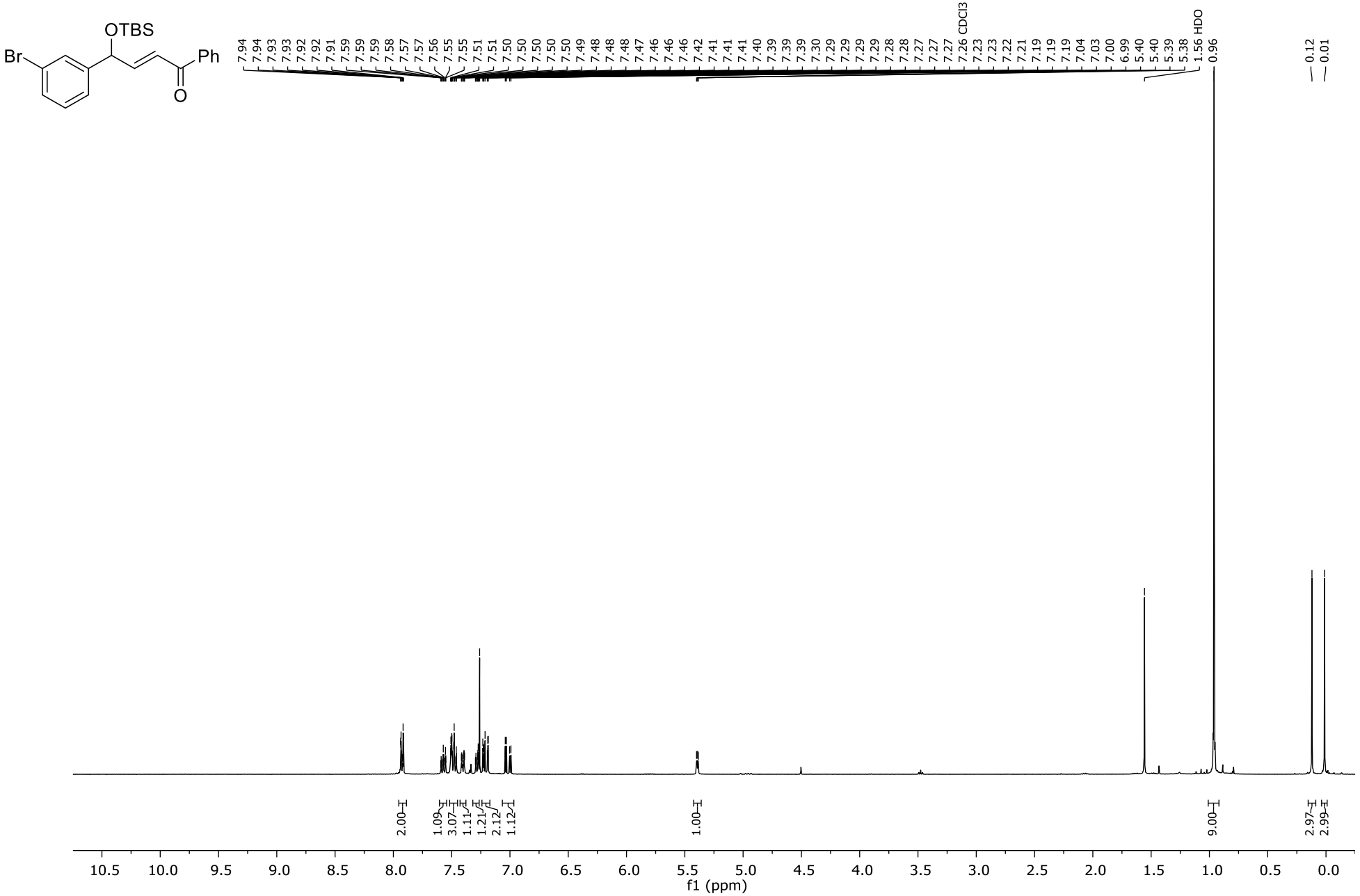
(*E*)-4-(4-Bromophenyl)-4-((*tert*-butyldimethylsilyl)oxy)-1-phenylbut-2-en-1-one S55 ^{1}H NMR (400 MHz, $CDCl_3$)



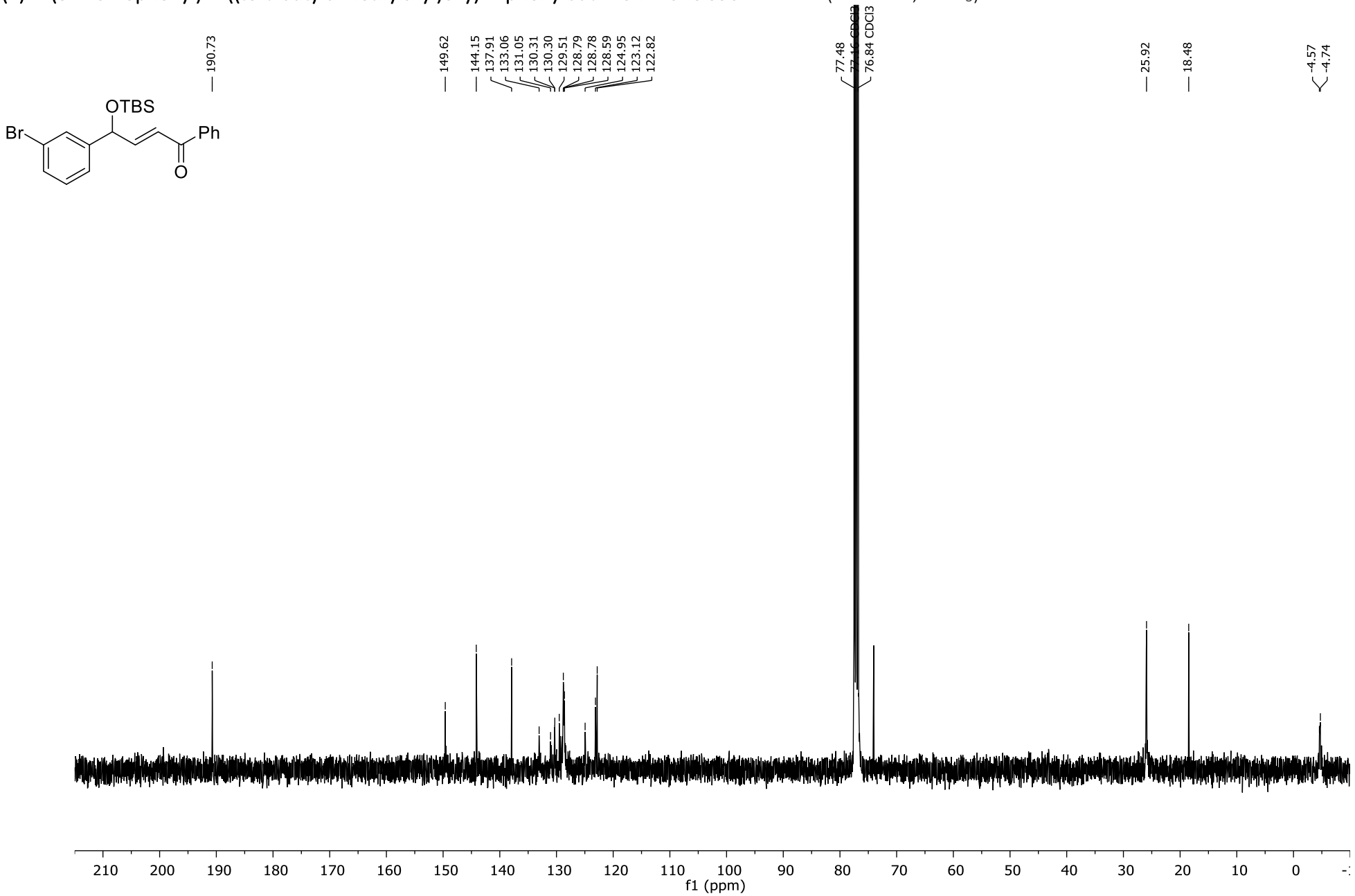
(*E*)-4-(4-Bromophenyl)-4-((*tert*-butyldimethylsilyl)oxy)-1-phenylbut-2-en-1-one S55 ^{13}C NMR (101 MHz, $CDCl_3$)



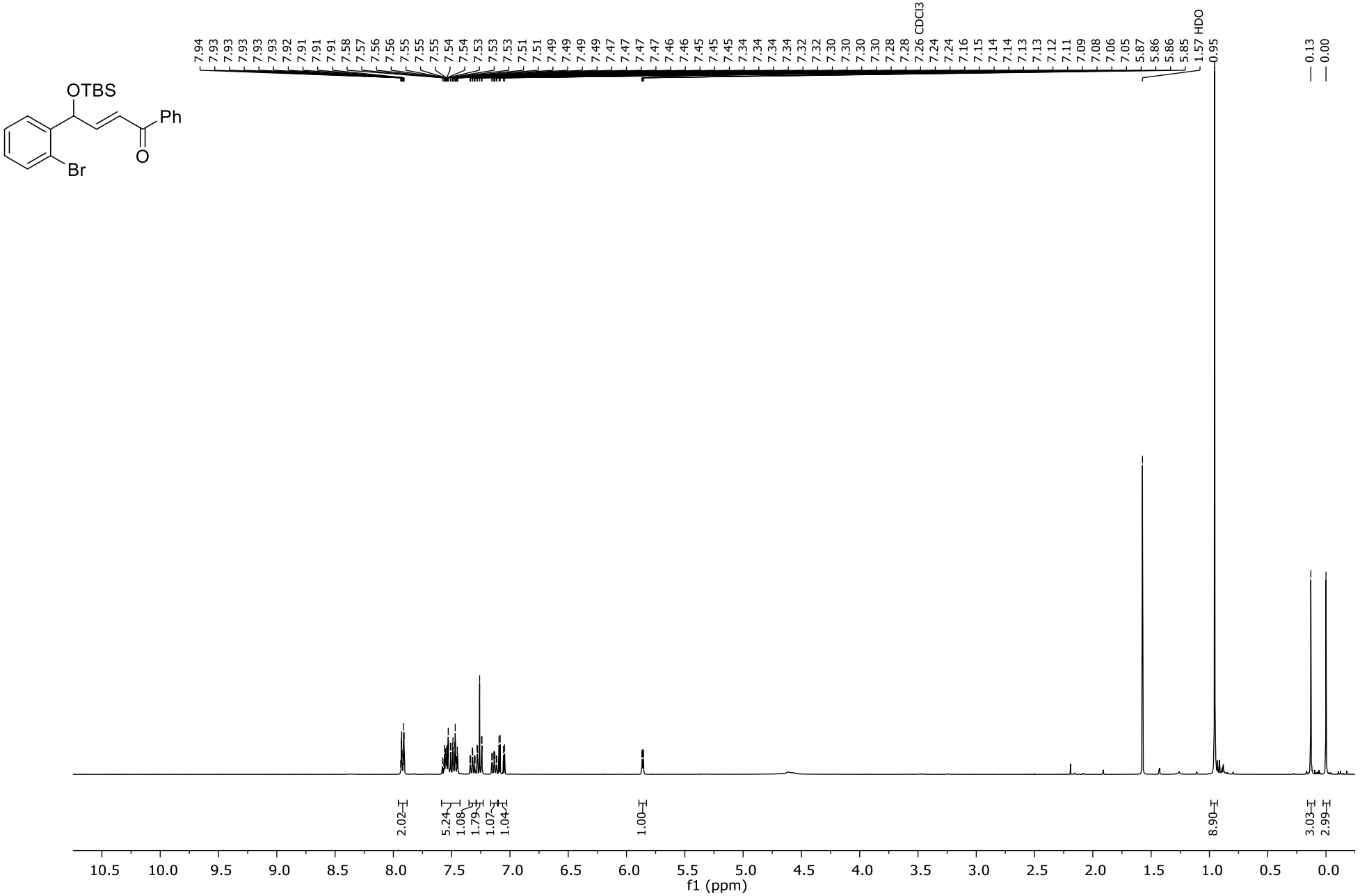
(*E*)-4-(3-Bromophenyl)-4-((*tert*-butyldimethylsilyl)oxy)-1-phenylbut-2-en-1-one S56 ^{1}H NMR (400 MHz, $CDCl_3$)



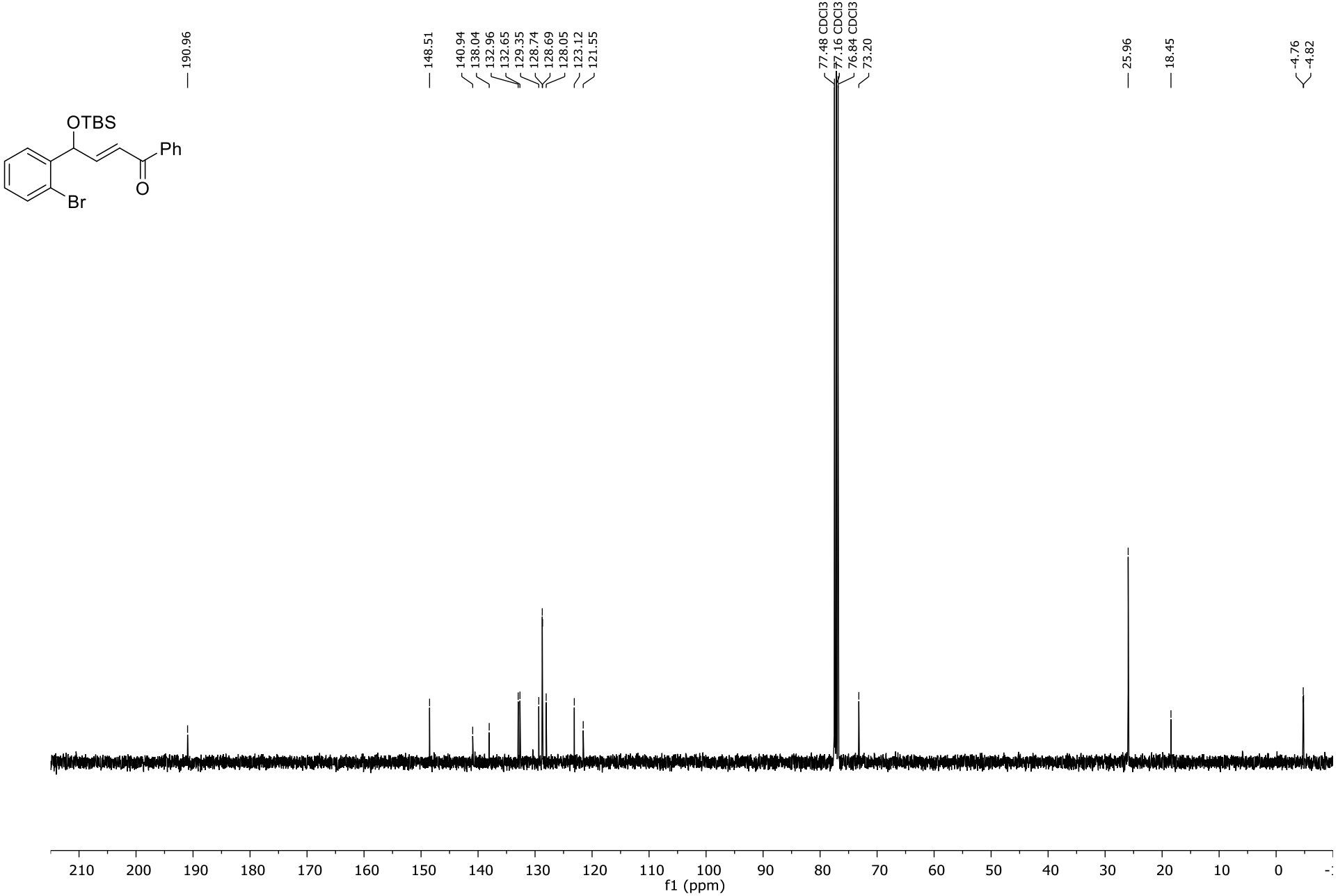
(*E*)-4-(3-Bromophenyl)-4-((*tert*-butyldimethylsilyl)oxy)-1-phenylbut-2-en-1-one S56 ^{13}C NMR (101 MHz, $CDCl_3$)



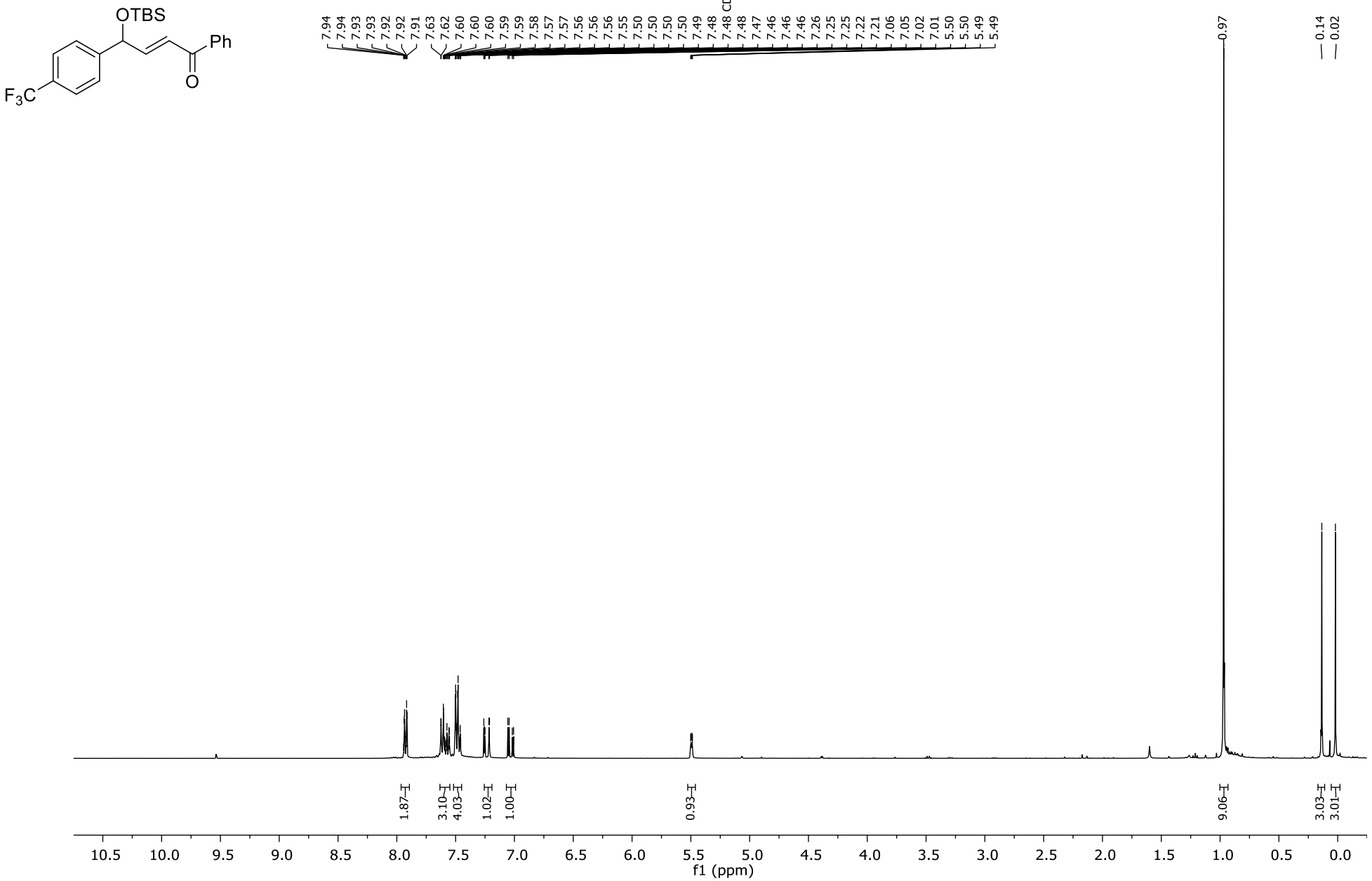
(*E*)-4-(2-Bromophenyl)-4-((*tert*-butyldimethylsilyl)oxy)-1-phenylbut-2-en-1-one S57 ^{1}H NMR (400 MHz, $CDCl_3$)



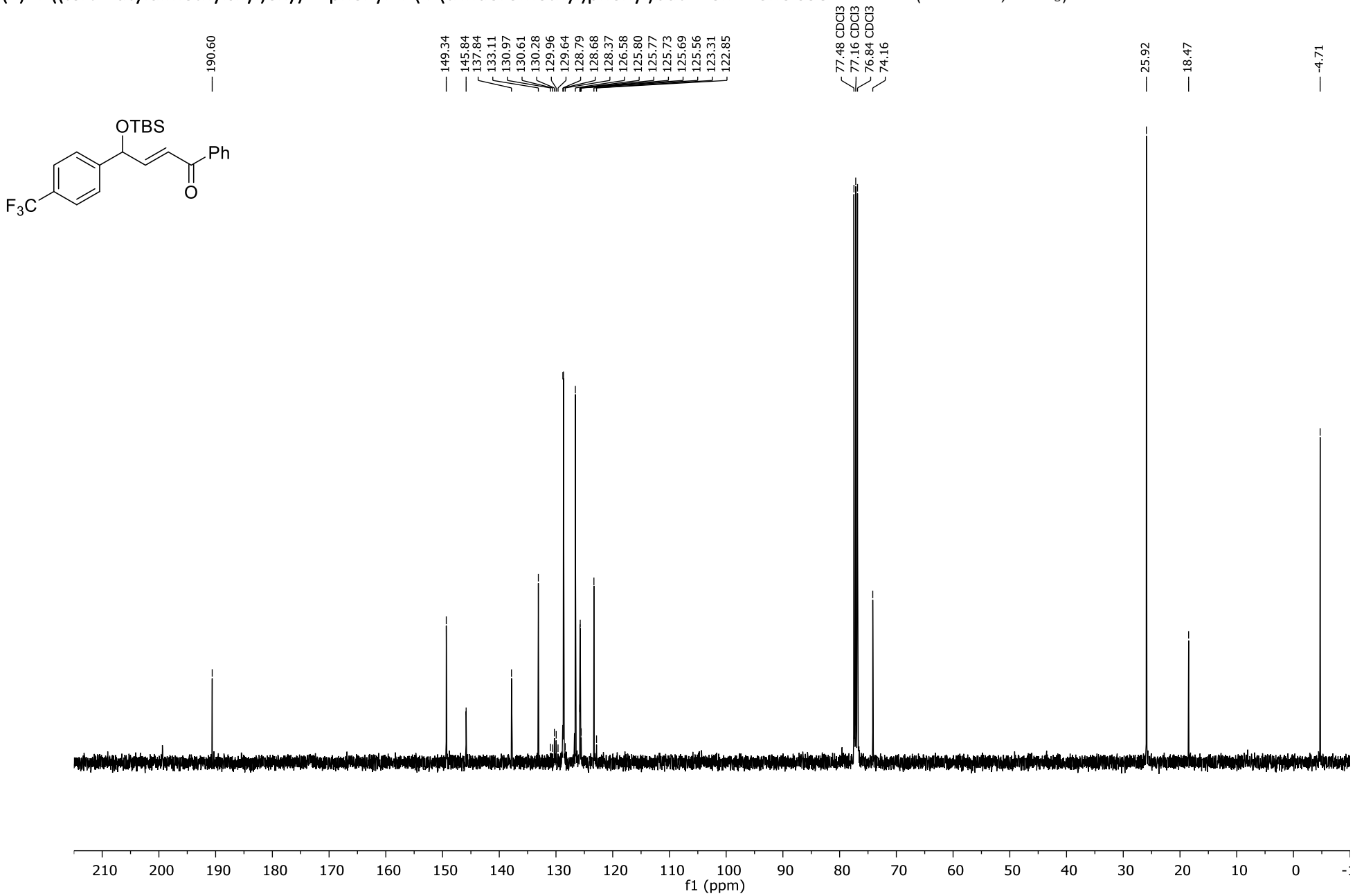
(*E*)-4-(2-Bromophenyl)-4-((*tert*-butyldimethylsilyl)oxy)-1-phenylbut-2-en-1-one S57 ^{13}C NMR (101 MHz, $CDCl_3$)



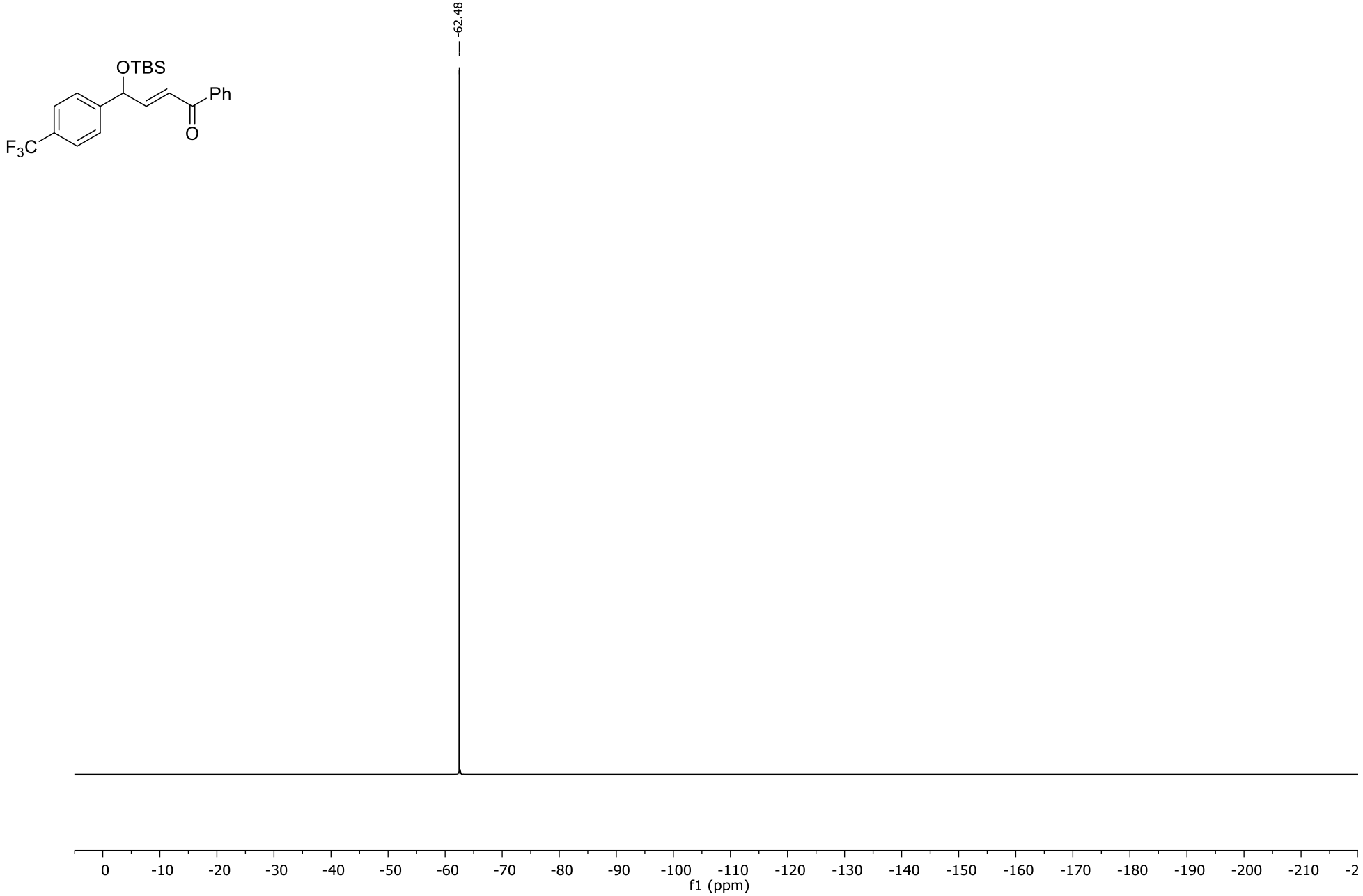
(*E*)-4-((*tert*-Butyldimethylsilyl)oxy)-1-phenyl-4-(4-(trifluoromethyl)phenyl)but-2-en-1-one S58 ^{1}H NMR (400 MHz, $CDCl_3$)



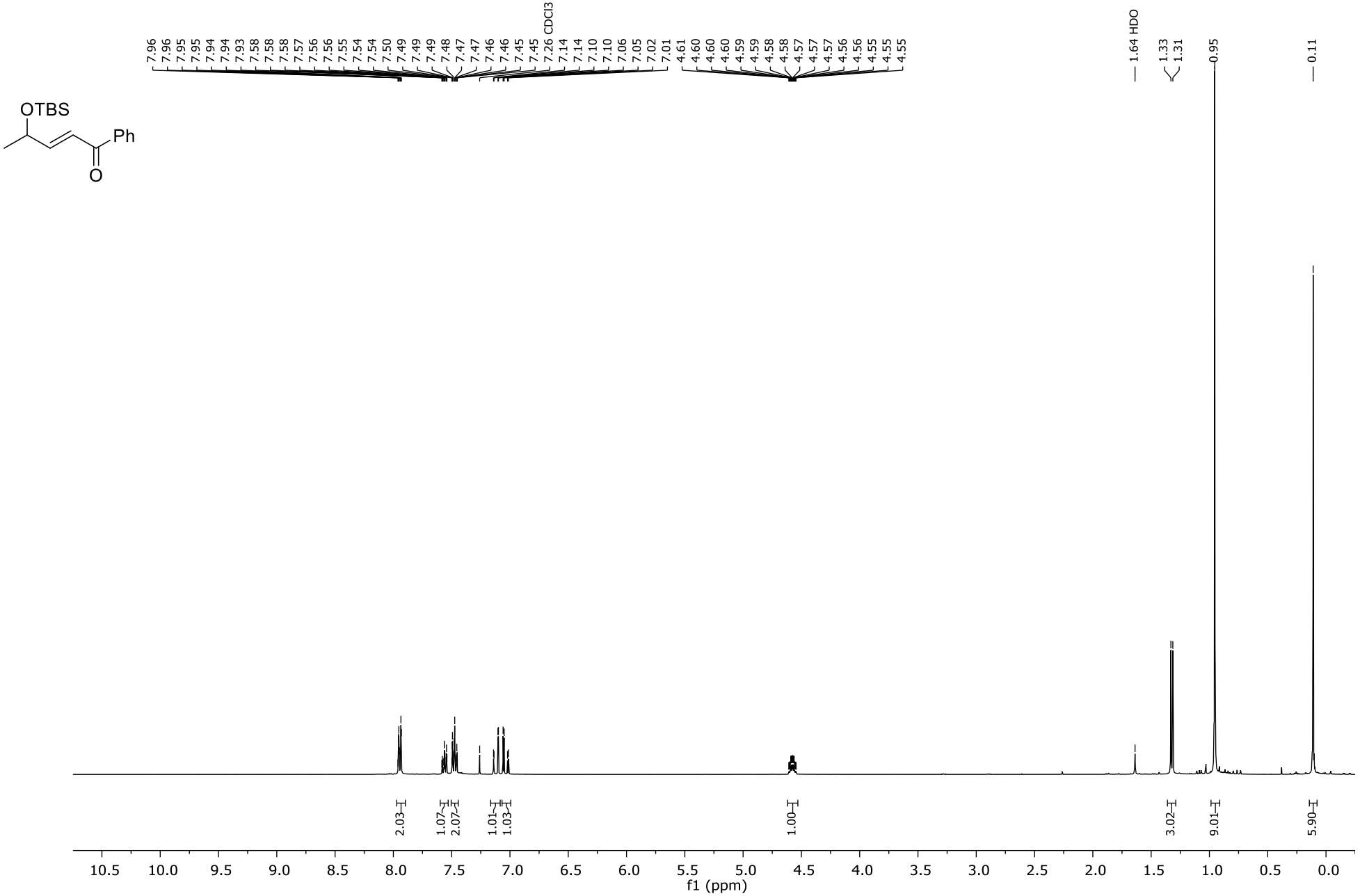
(*E*)-4-((*tert*-Butyldimethylsilyl)oxy)-1-phenyl-4-(4-(trifluoromethyl)phenyl)but-2-en-1-one S58 ^{13}C NMR (101 MHz, $CDCl_3$)



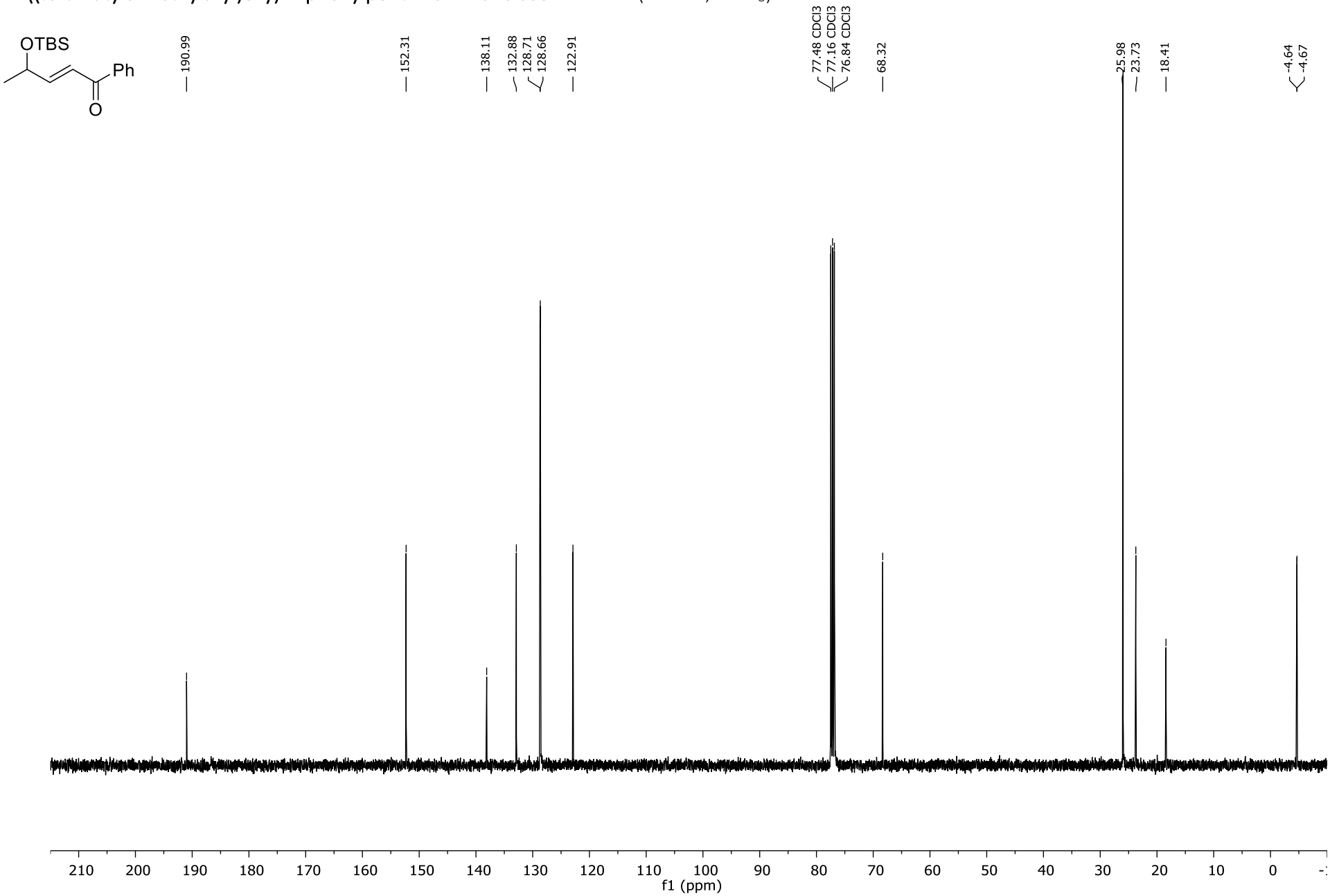
(*E*)-4-((*tert*-Butyldimethylsilyl)oxy)-1-phenyl-4-(4-(trifluoromethyl)phenyl)but-2-en-1-one **S58** ^{19}F NMR (376 MHz, $CDCl_3$)



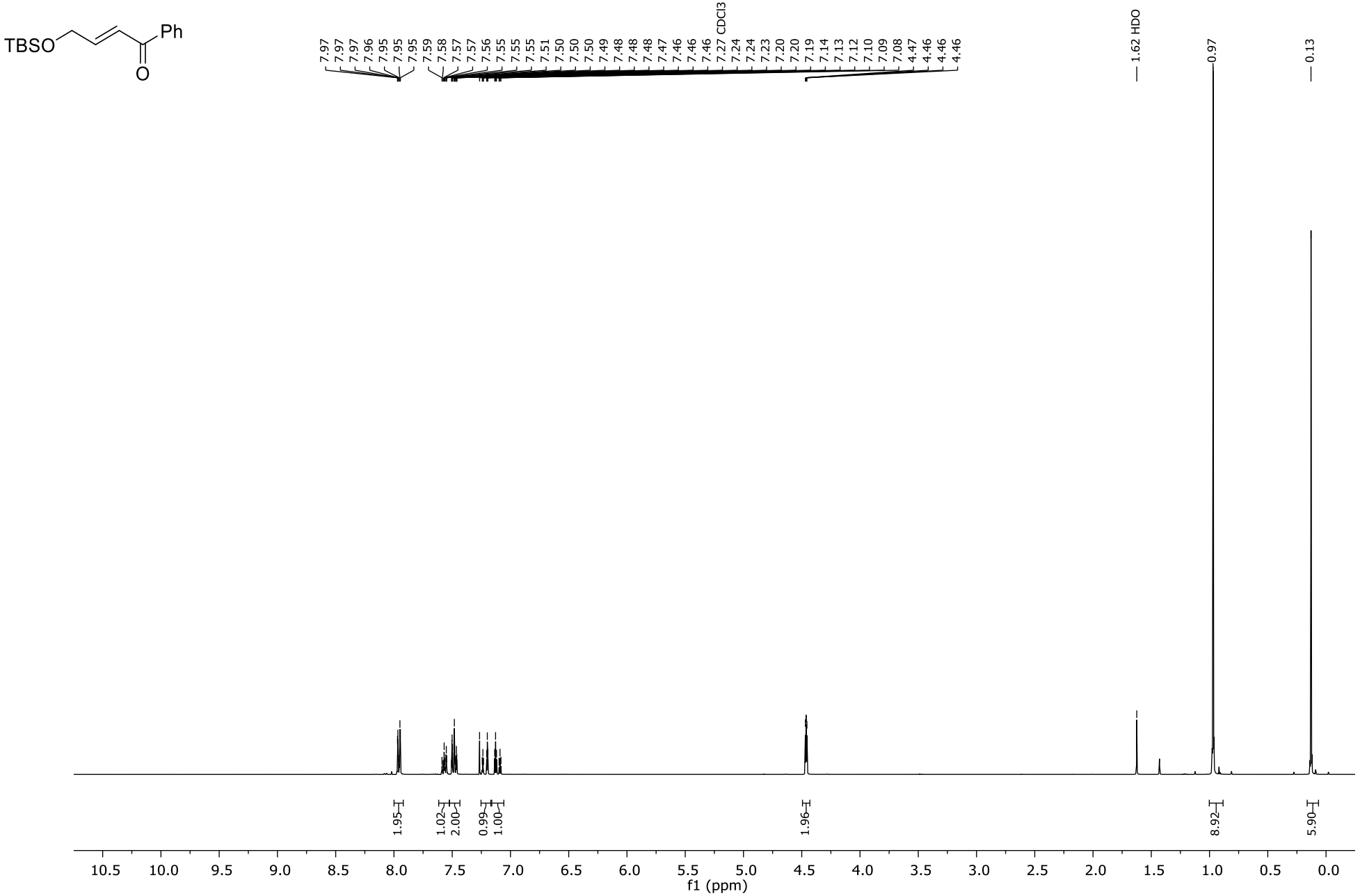
(*E*)-4-((*tert*-Butyldimethylsilyl)oxy)-1-phenylpent-2-en-1-one S59 ^{1}H NMR (400 Hz, $CDCl_3$)



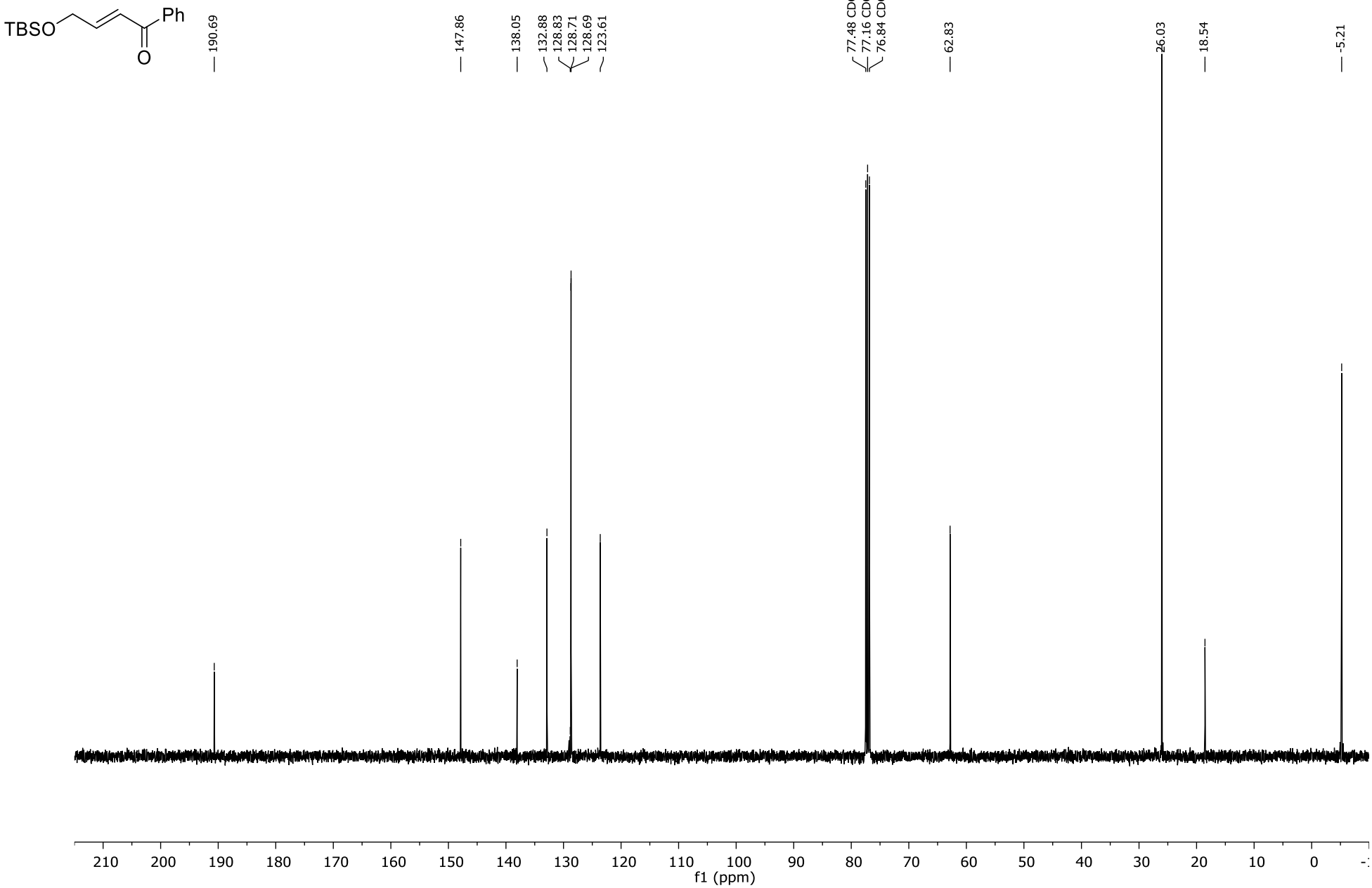
(*E*)-4-((*tert*-Butyldimethylsilyl)oxy)-1-phenylpent-2-en-1-one S59 ^{13}C NMR (101 Hz, $CDCl_3$)



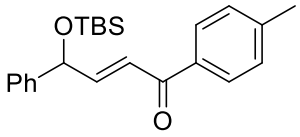
(*E*)-4-((*tert*-Butyldimethylsilyl)oxy)-1-phenylbut-2-en-1-one S60 ^{1}H NMR (400 MHz, $CDCl_3$)



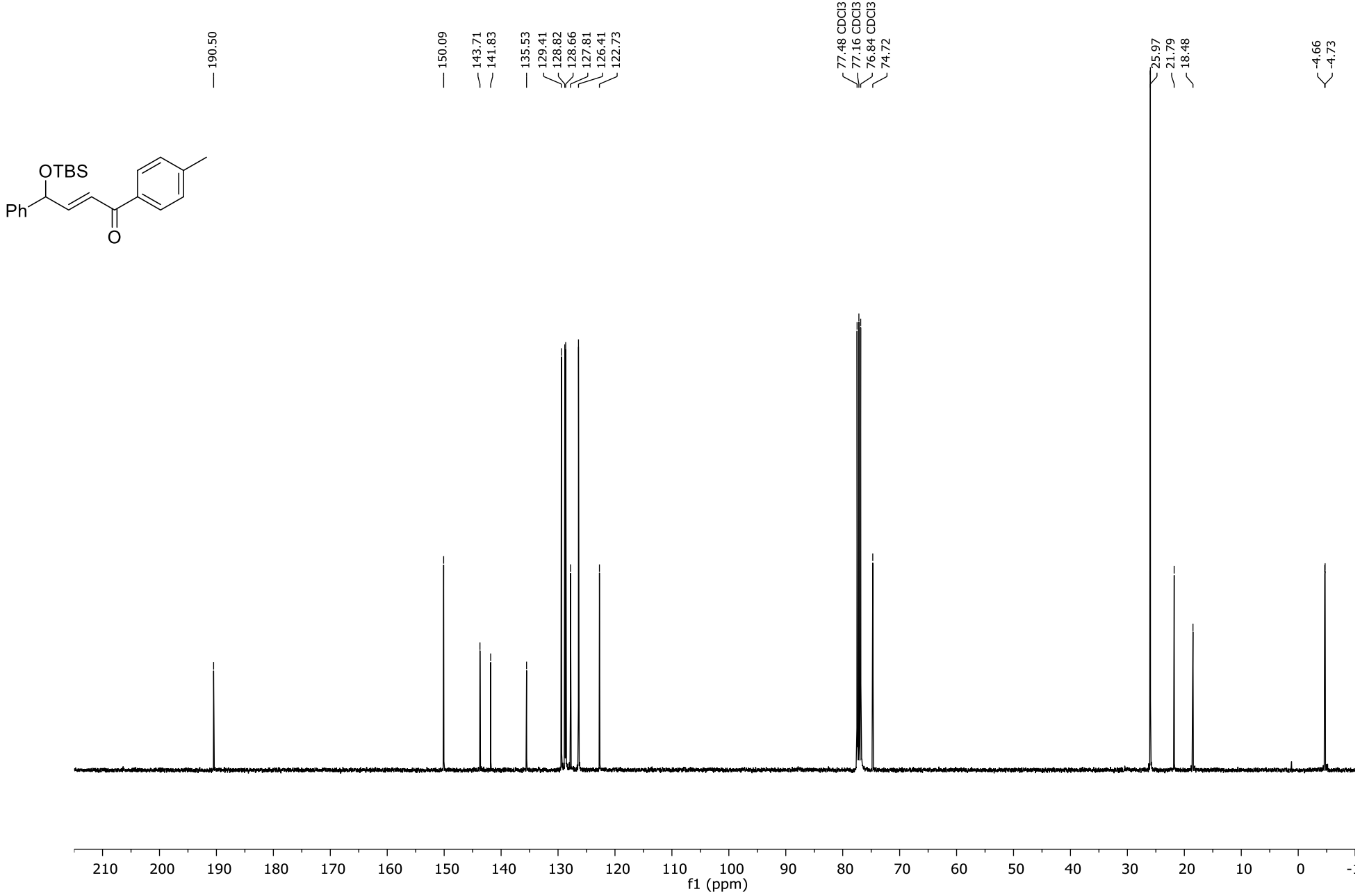
(*E*)-4-((*tert*-Butyldimethylsilyl)oxy)-1-phenylbut-2-en-1-one S60 ^{13}C NMR (101 MHz, $CDCl_3$)



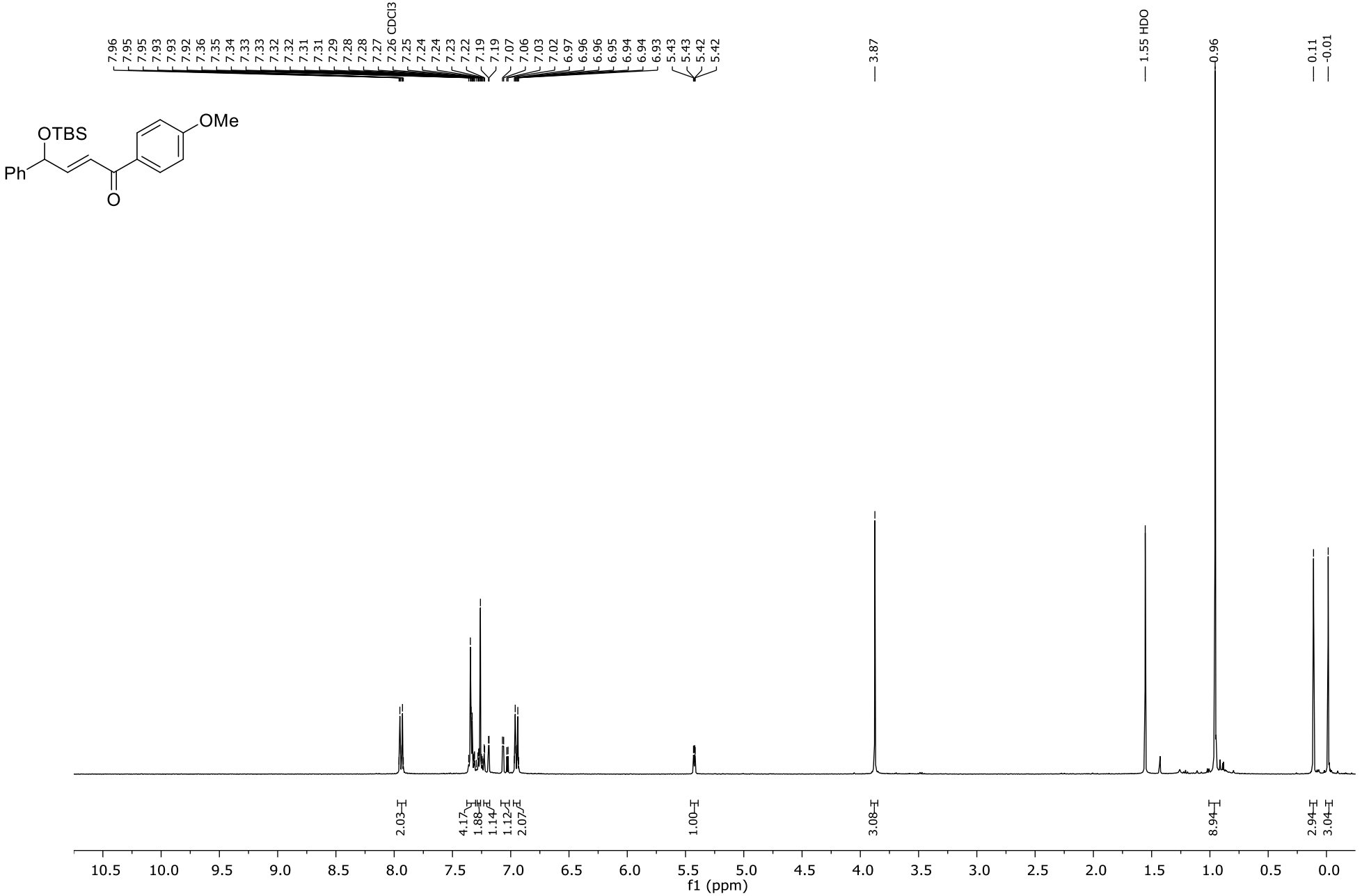
(*E*)-4-((*tert*-Butyldimethylsilyl)oxy)-4-phenyl-1-(*p*-tolyl)but-2-en-1-one S61 ^{1}H NMR (400 MHz, $CDCl_3$)



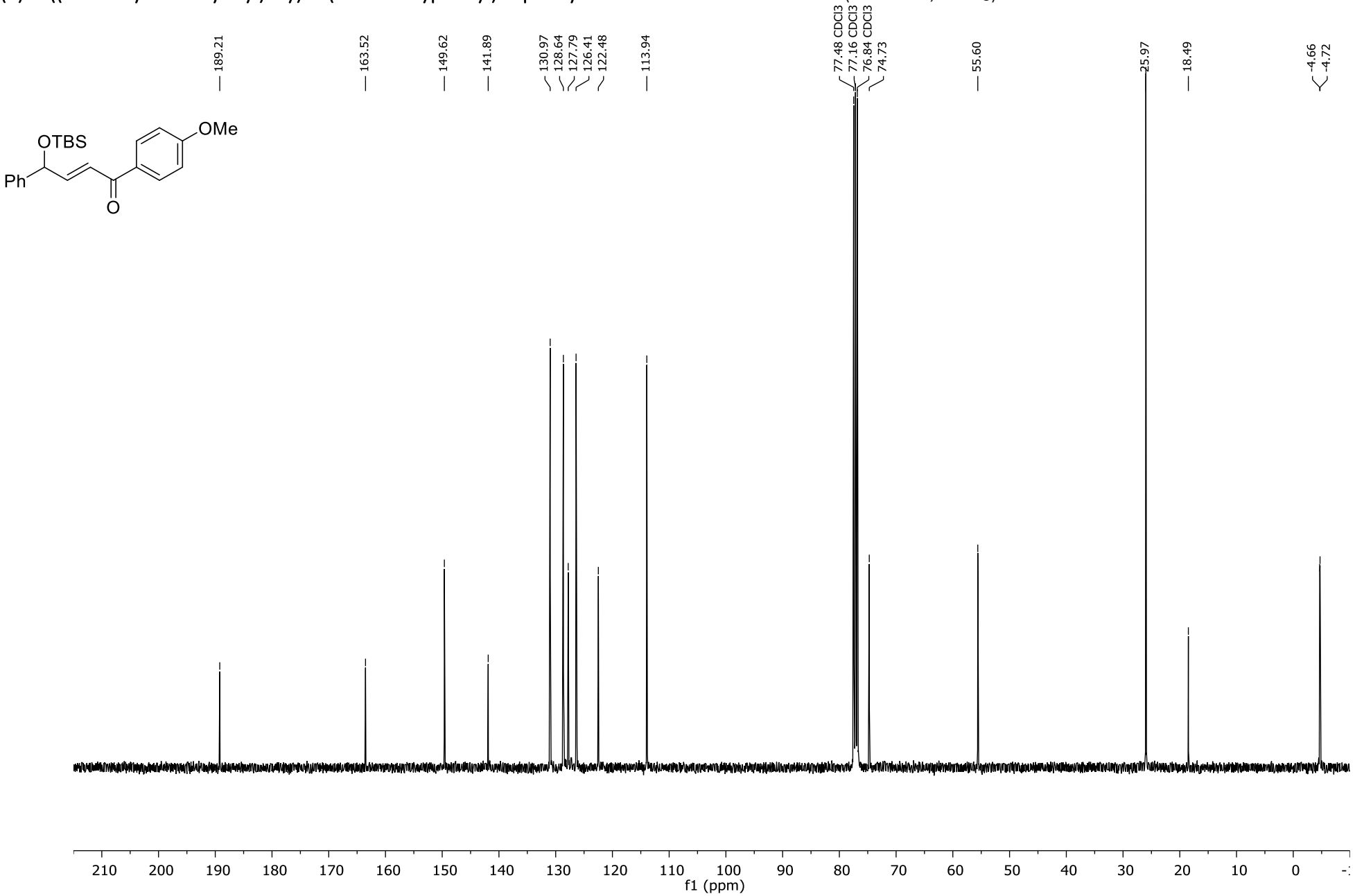
(*E*)-4-((*tert*-Butyldimethylsilyl)oxy)-4-phenyl-1-(*p*-tolyl)but-2-en-1-one S61 ^{13}C NMR (101 MHz, $CDCl_3$)



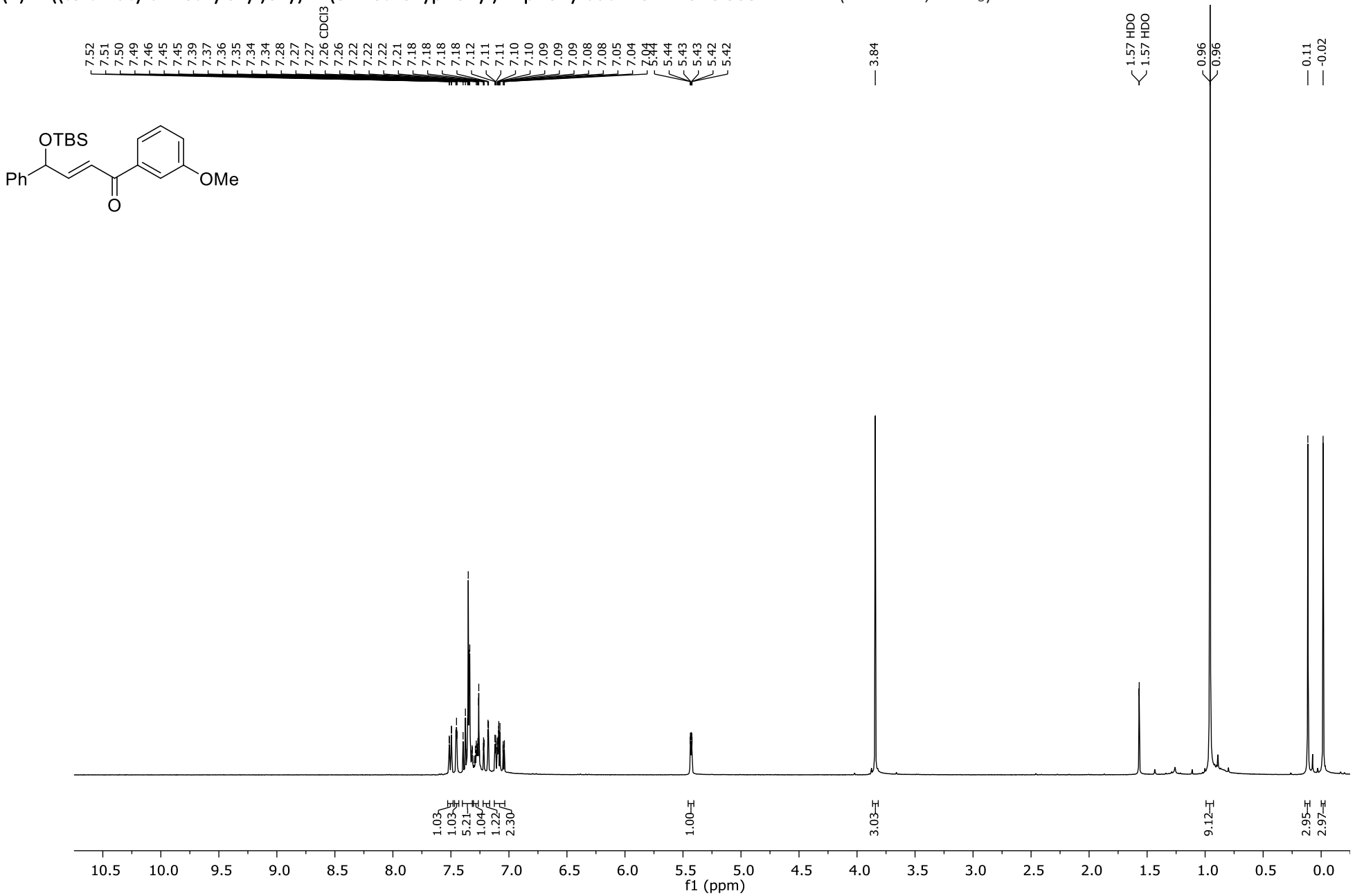
(*E*)-4-((*tert*-Butyldimethylsilyl)oxy)-1-(4-methoxyphenyl)-4-phenylbut-2-en-1-one S62 ^{1}H NMR (400 MHz, $CDCl_3$)



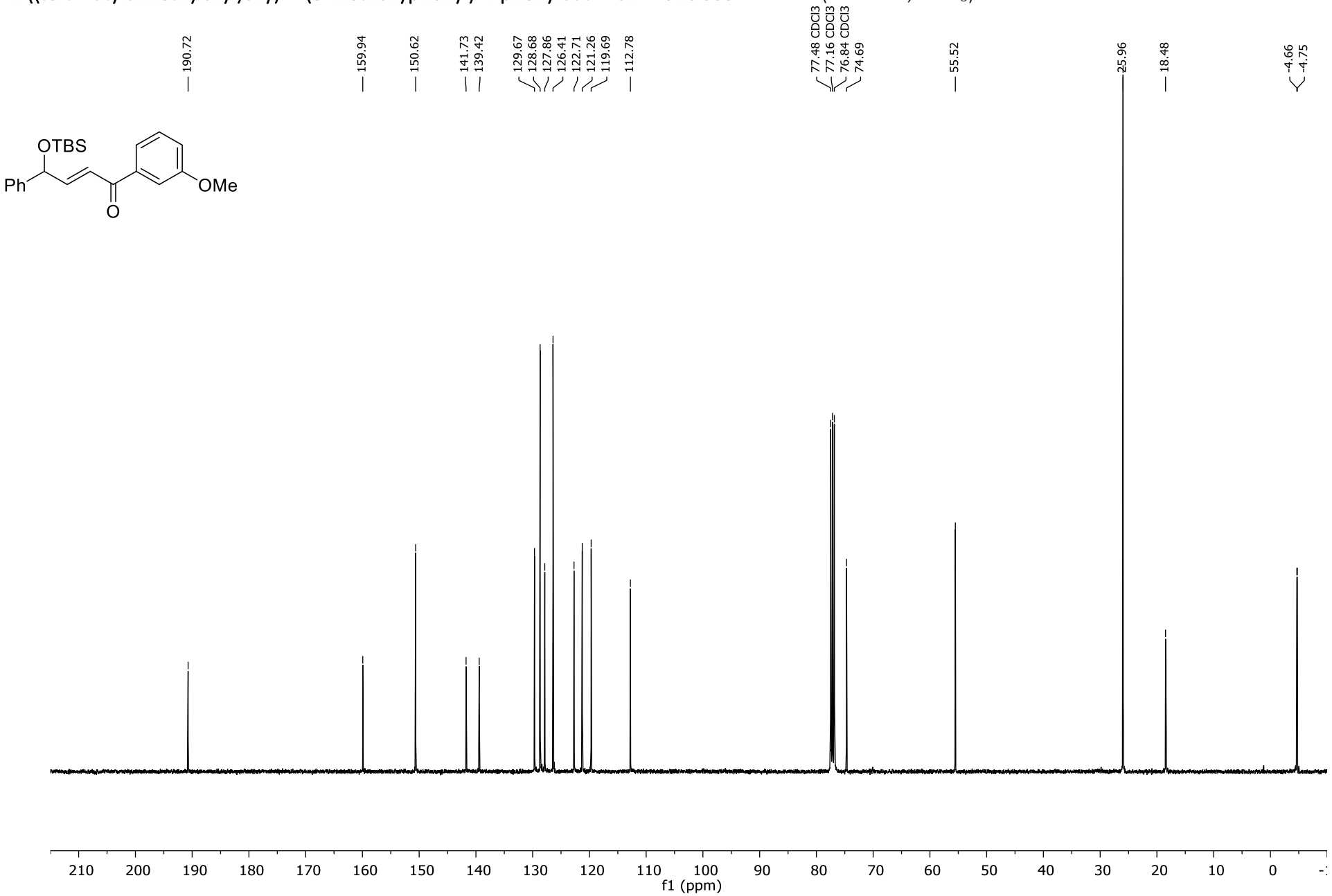
(*E*)-4-((*tert*-Butyldimethylsilyl)oxy)-1-(4-methoxyphenyl)-4-phenylbut-2-en-1-one S62 ^{13}C NMR (101 MHz, $CDCl_3$)



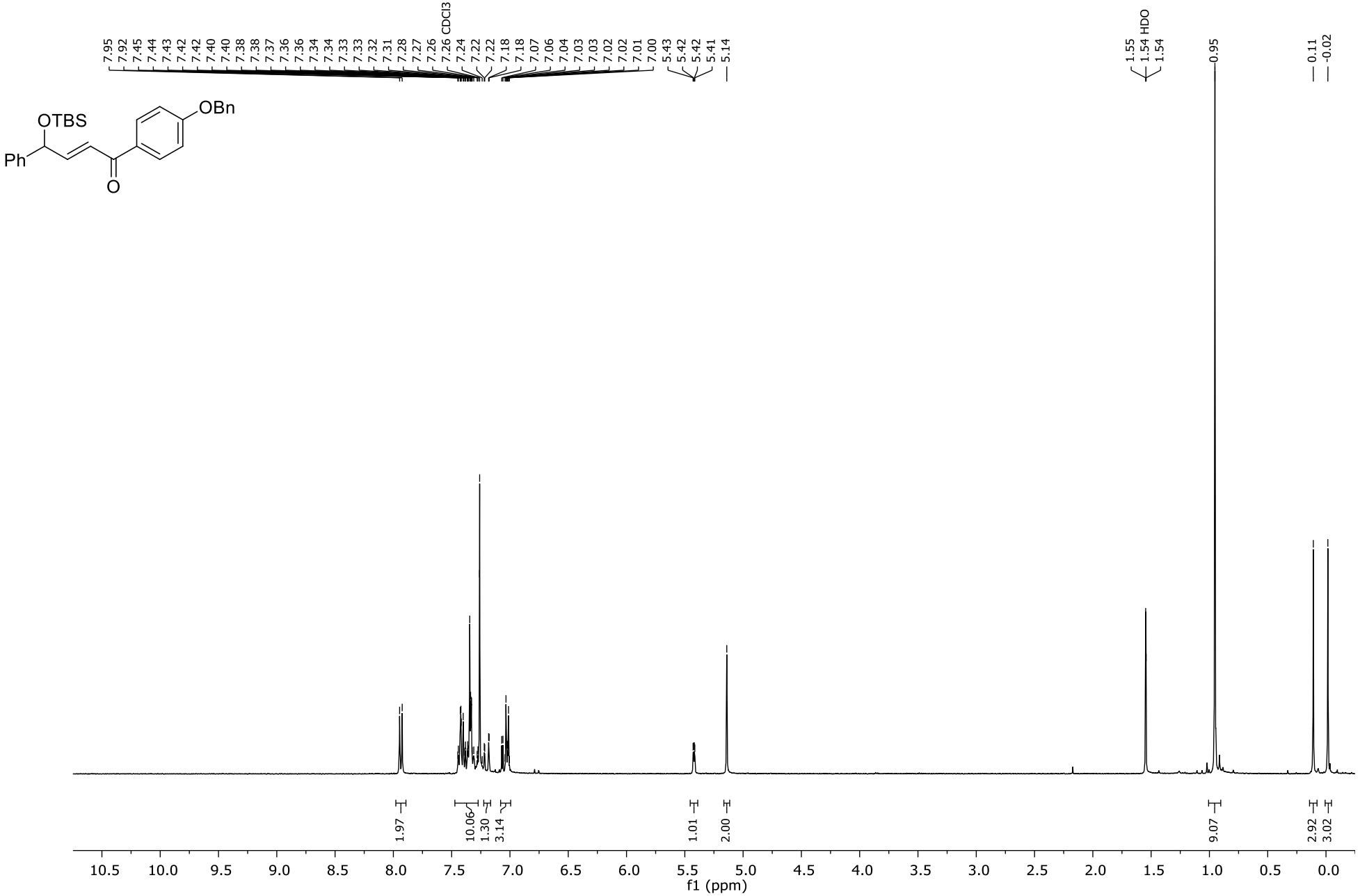
(*E*)-4-((*tert*-Butyldimethylsilyl)oxy)-1-(3-methoxyphenyl)-4-phenylbut-2-en-1-one **S63** ^{1}H NMR (400 MHz, $CDCl_3$)



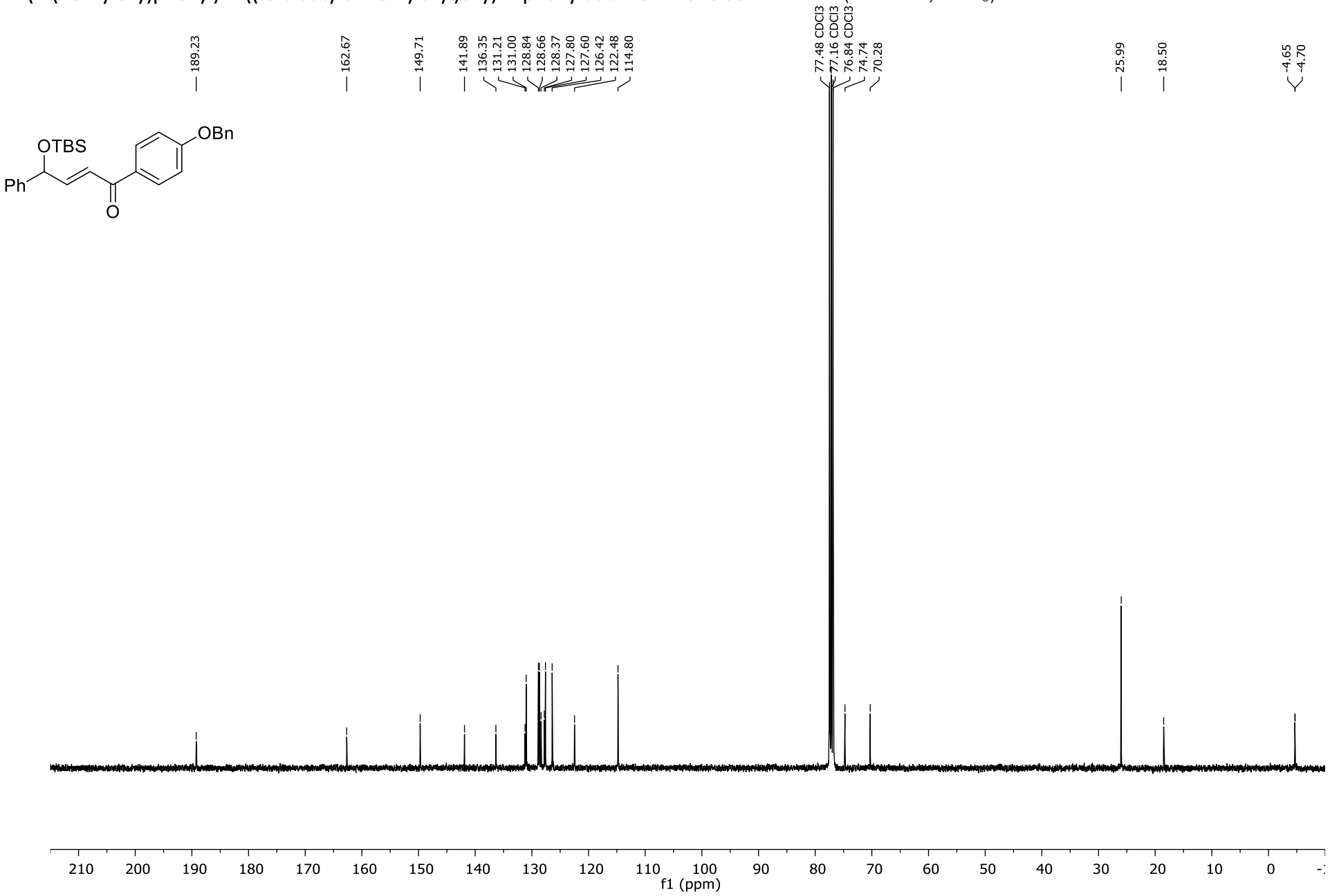
(*E*)-4-((*tert*-Butyldimethylsilyl)oxy)-1-(3-methoxyphenyl)-4-phenylbut-2-en-1-one S63 ^{13}C NMR (101 MHz, $CDCl_3$)



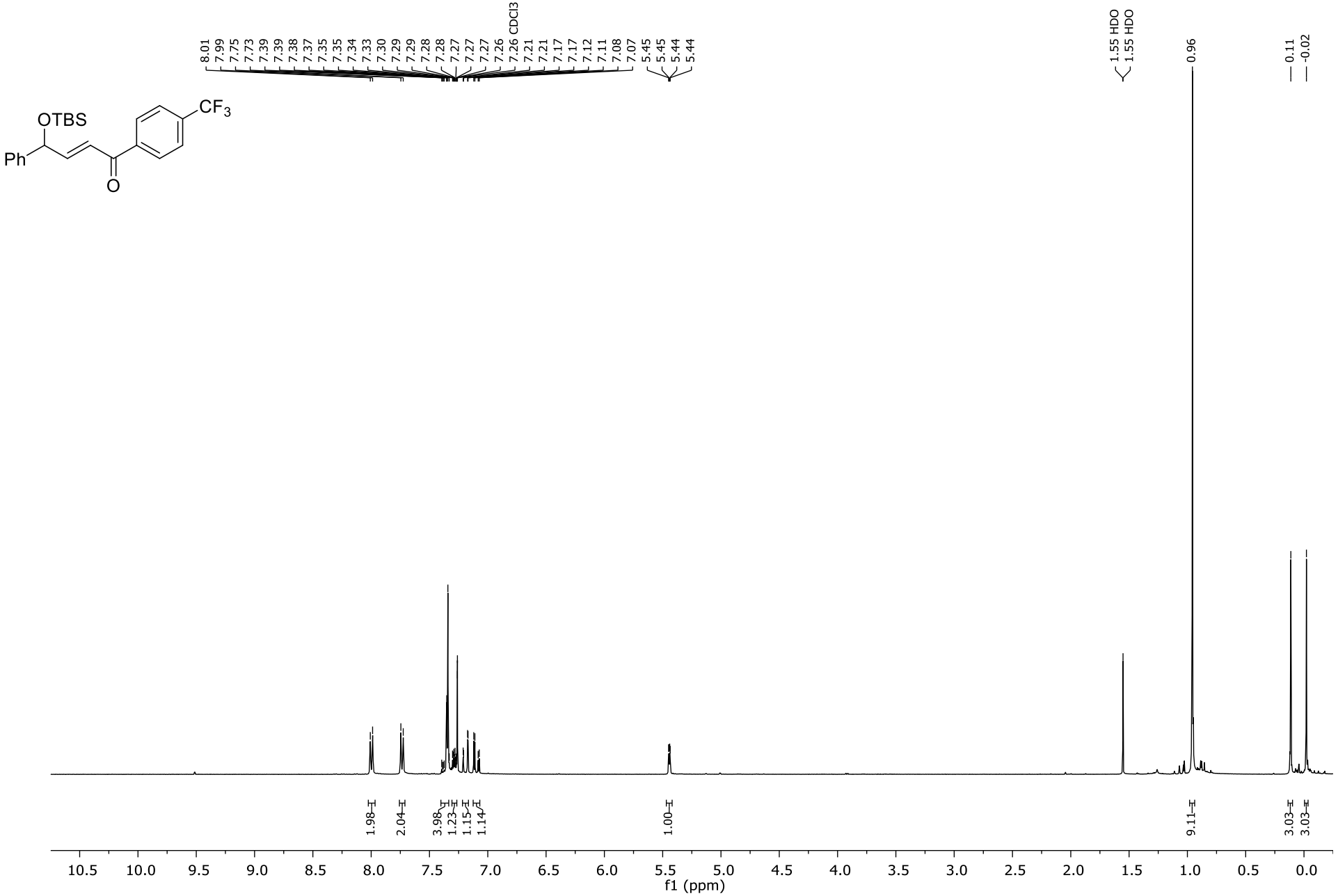
(*E*)-1-(4-(Benzyloxy)phenyl)-4-((*tert*-butyldimethylsilyl)oxy)-4-phenylbut-2-en-1-one S64 ^{1}H NMR (400 MHz, $CDCl_3$)



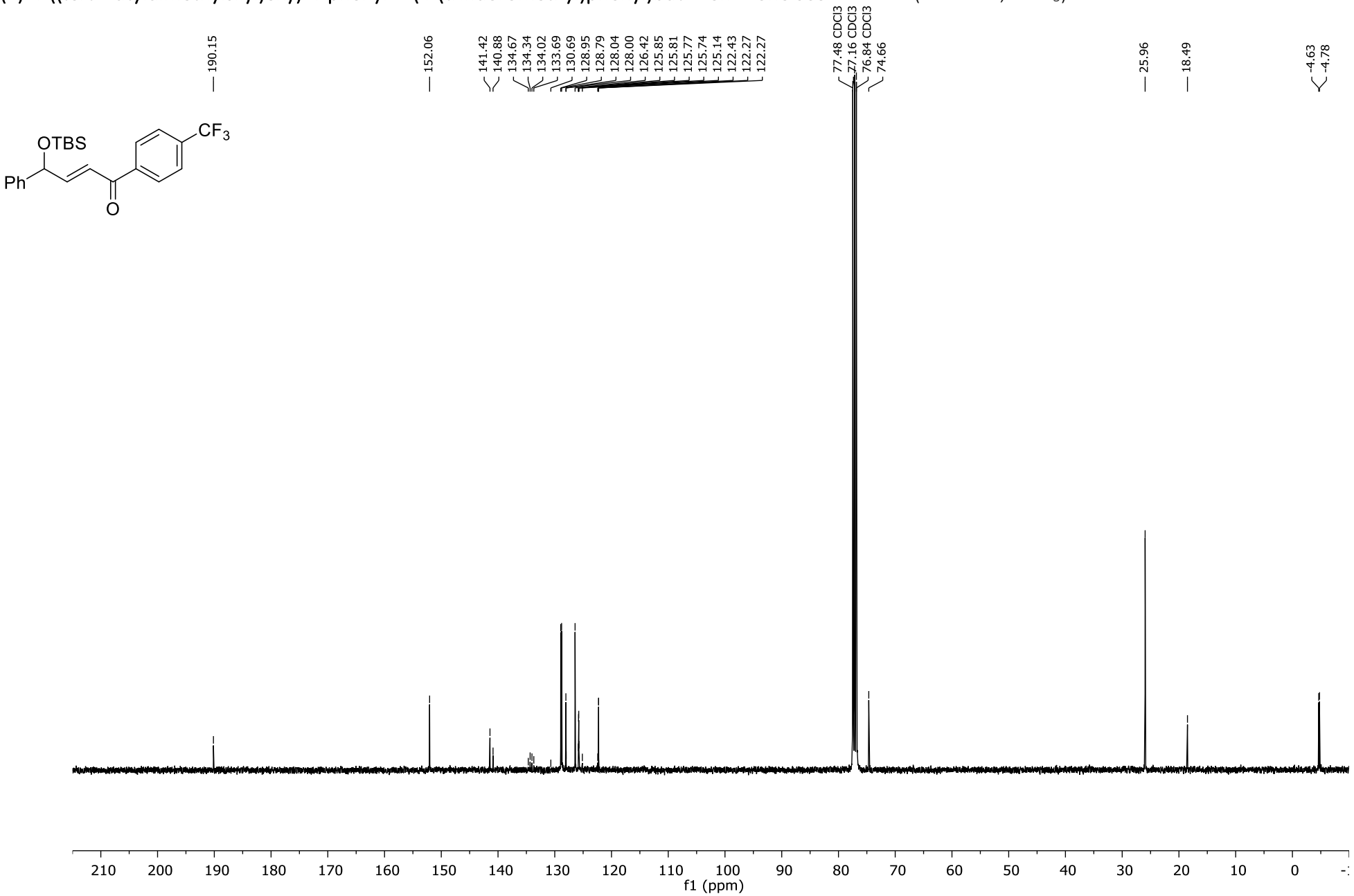
(*E*)-1-(4-(Benzyloxy)phenyl)-4-((*tert*-butyldimethylsilyl)oxy)-4-phenylbut-2-en-1-one S64 ^{13}C NMR (101 MHz, $CDCl_3$)



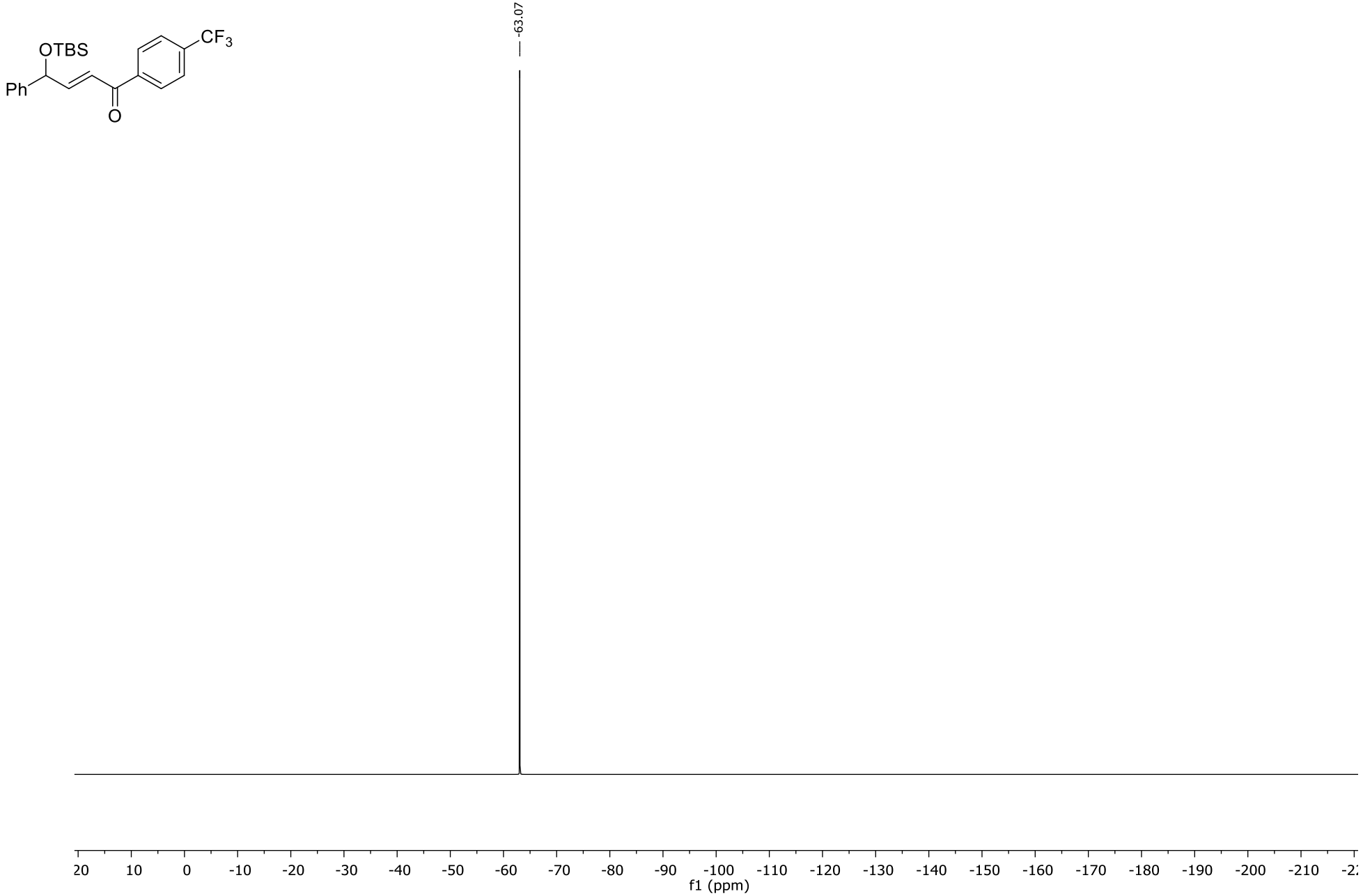
(*E*)-4-((*tert*-Butyldimethylsilyl)oxy)-4-phenyl-1-(4-(trifluoromethyl)phenyl)but-2-en-1-one **S65** ^{1}H NMR (400 MHz, $CDCl_3$)



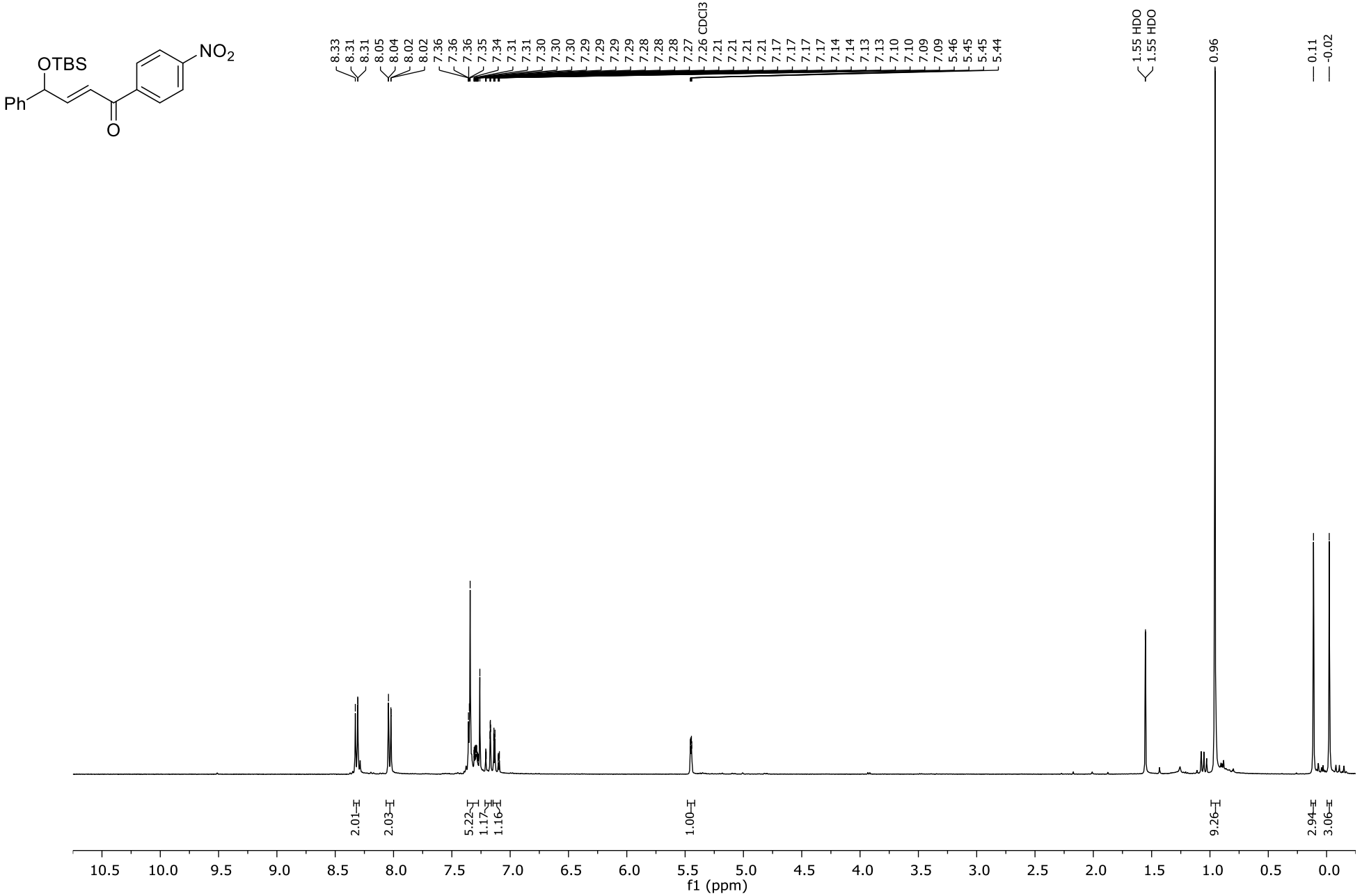
(*E*)-4-((*tert*-Butyldimethylsilyl)oxy)-4-phenyl-1-(4-(trifluoromethyl)phenyl)but-2-en-1-one **S65** ^{13}C NMR (101 MHz, $CDCl_3$)



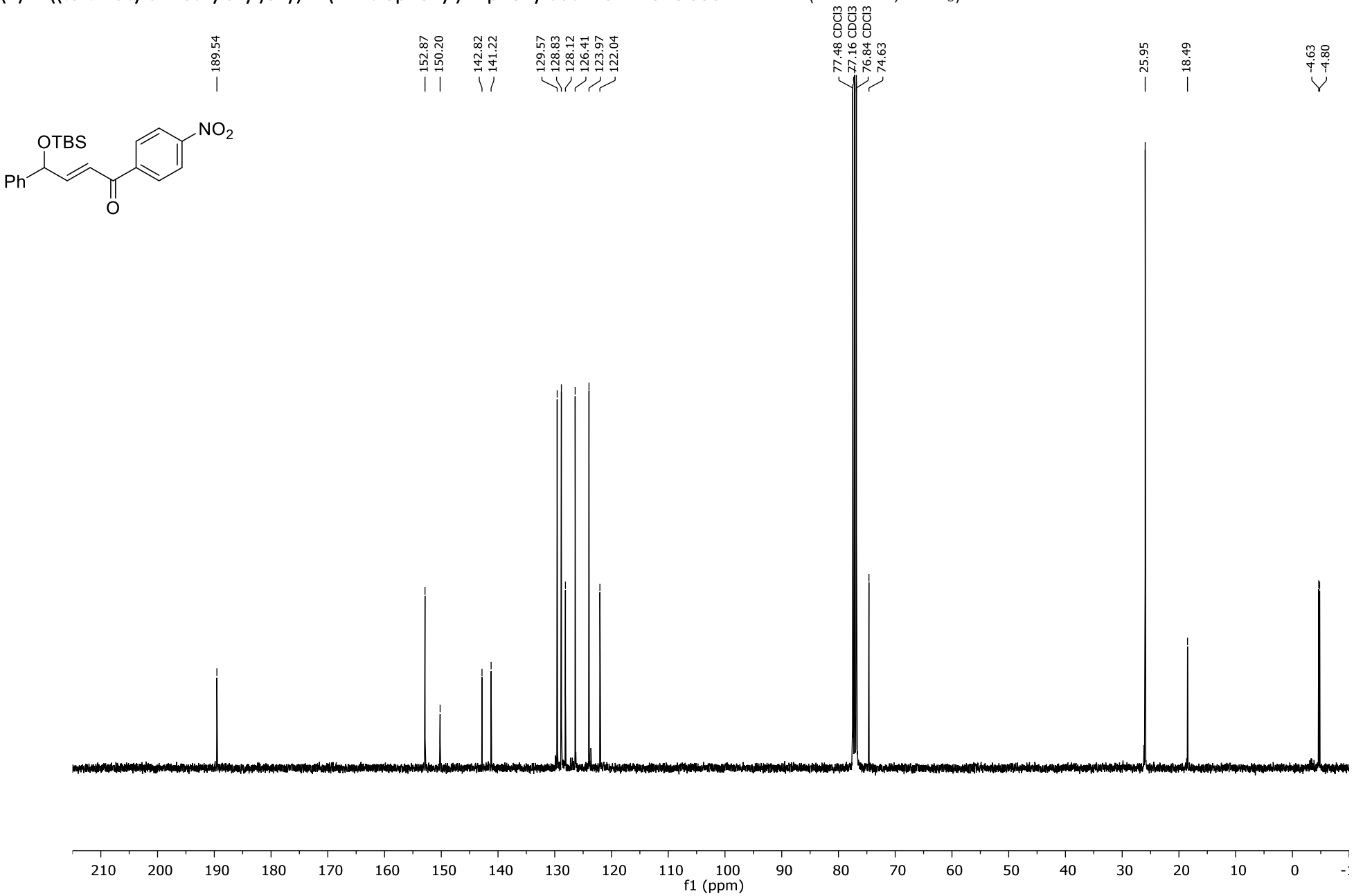
(*E*)-4-((*tert*-Butyldimethylsilyl)oxy)-4-phenyl-1-(4-(trifluoromethyl)phenyl)but-2-en-1-one **S65** ^{19}F NMR (376 MHz, $CDCl_3$)



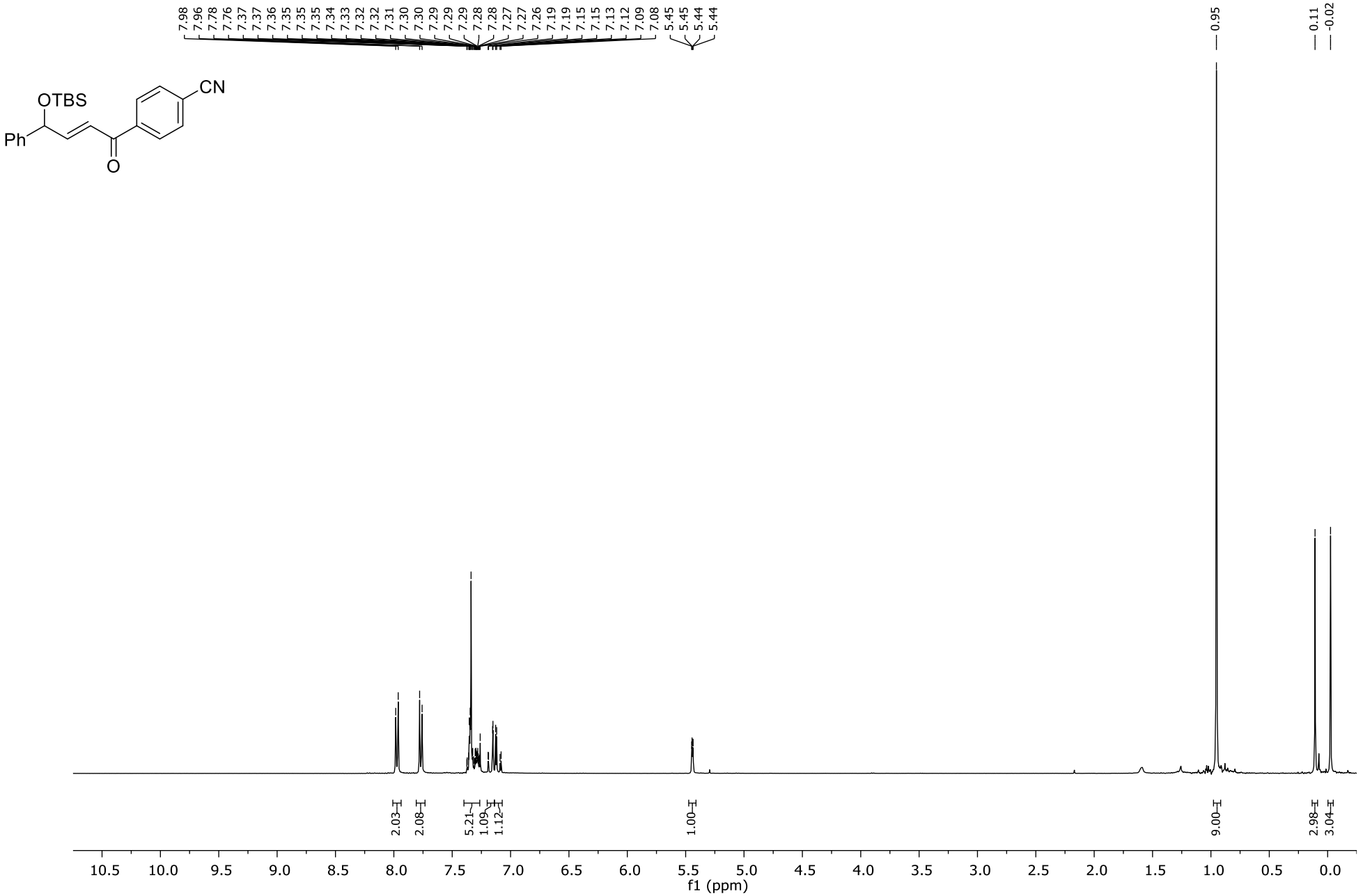
(*E*)-4-((*tert*-Butyldimethylsilyl)oxy)-1-(4-nitrophenyl)-4-phenylbut-2-en-1-one **S66** ^{1}H NMR (400 MHz, $CDCl_3$)



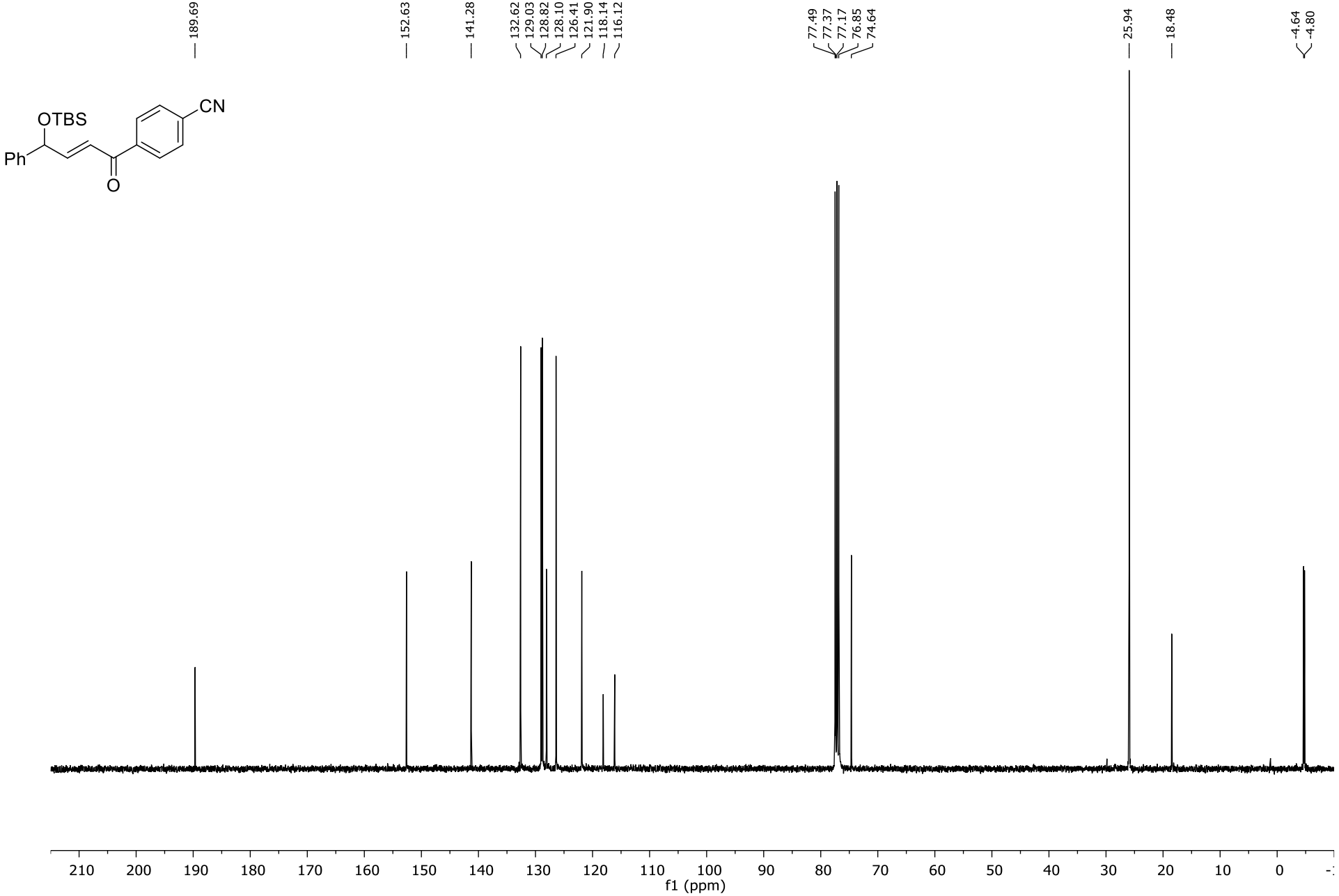
(*E*)-4-((*tert*-Butyldimethylsilyl)oxy)-1-(4-nitrophenyl)-4-phenylbut-2-en-1-one **S66** ^{13}C NMR (400 MHz, $CDCl_3$)



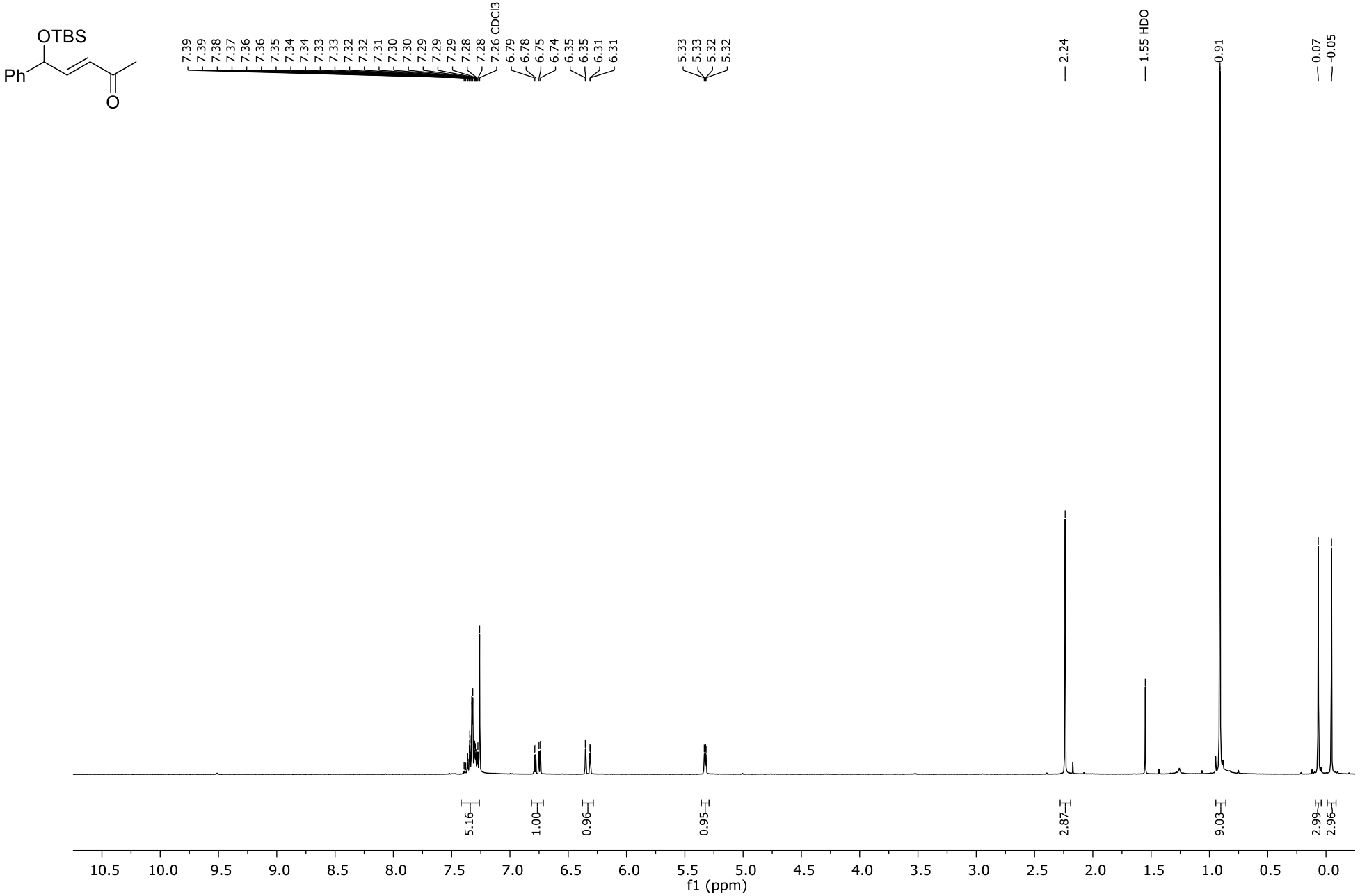
(*E*)-4-(4-((*tert*-Butyldimethylsilyl)oxy)-4-phenylbut-2-enoyl)benzonitrile S67 ^{1}H NMR (400 MHz, $CDCl_3$)



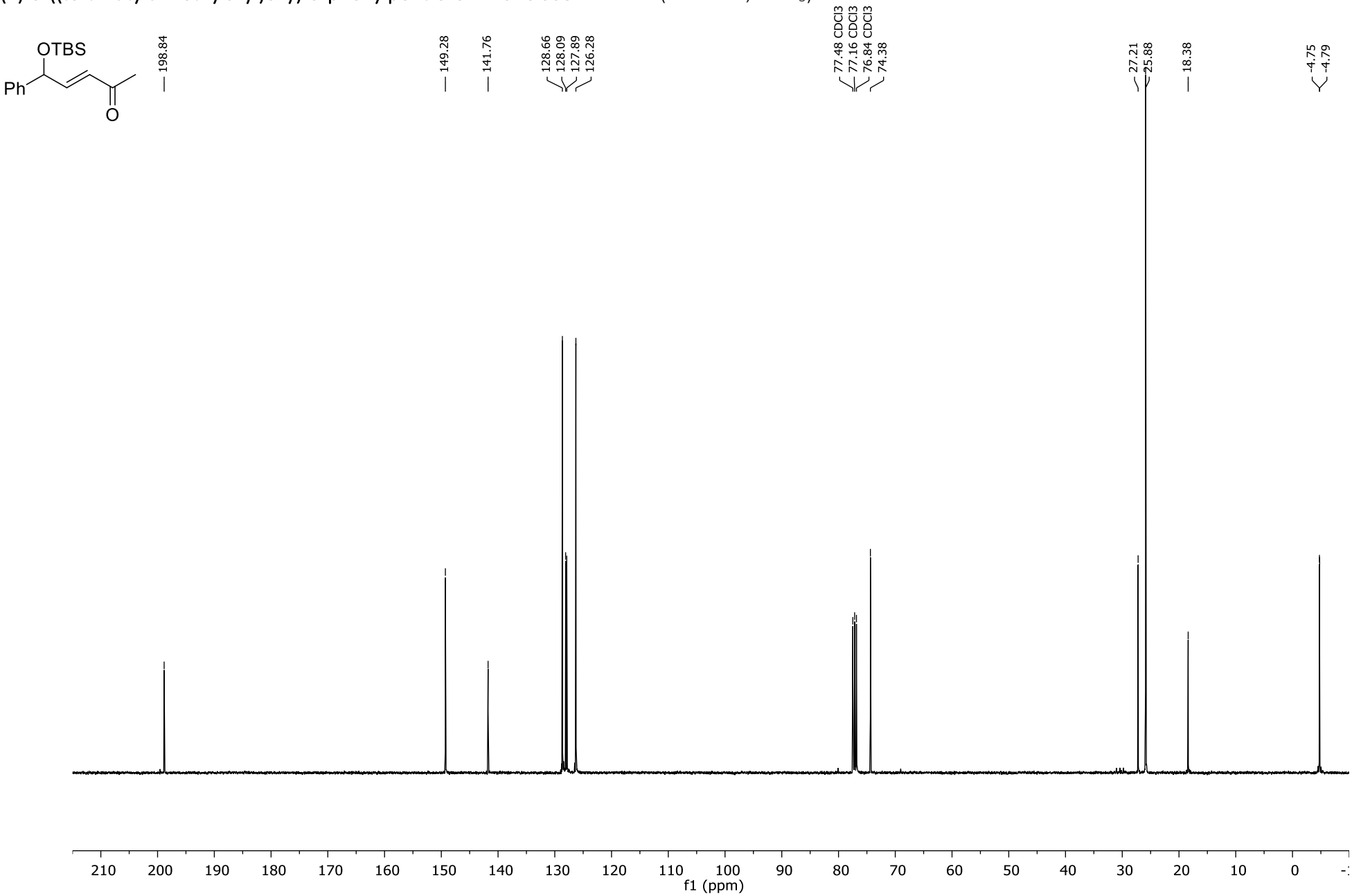
(*E*)-4-(4-((*tert*-Butyldimethylsilyl)oxy)-4-phenylbut-2-enoyl)benzonitrile S67 ^{13}C NMR (101 MHz, $CDCl_3$)



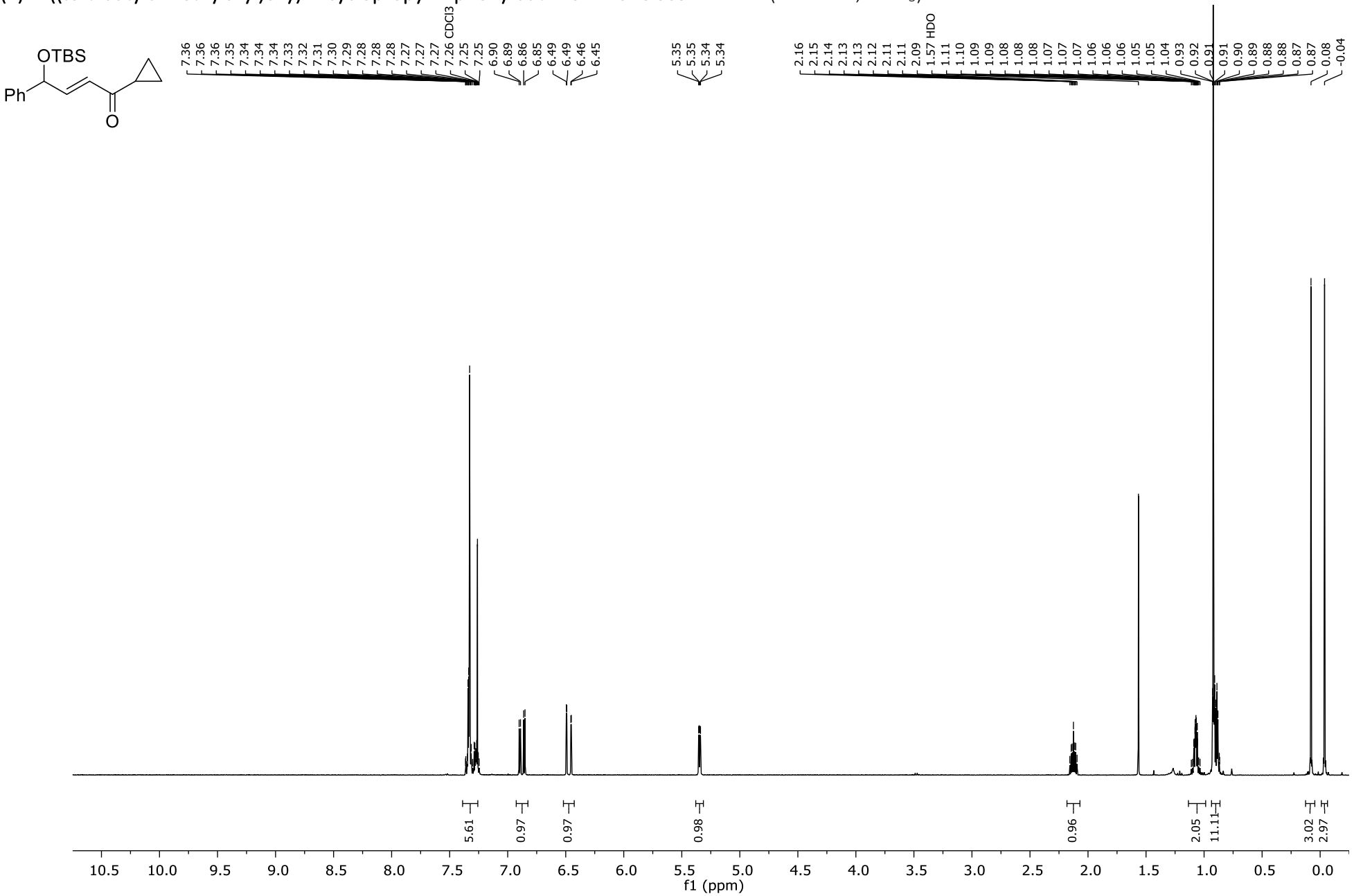
(*E*)-5-((*tert*-Butyldimethylsilyl)oxy)-5-phenylpent-3-en-2-one S68 ^{1}H NMR (400 MHz, $CDCl_3$)



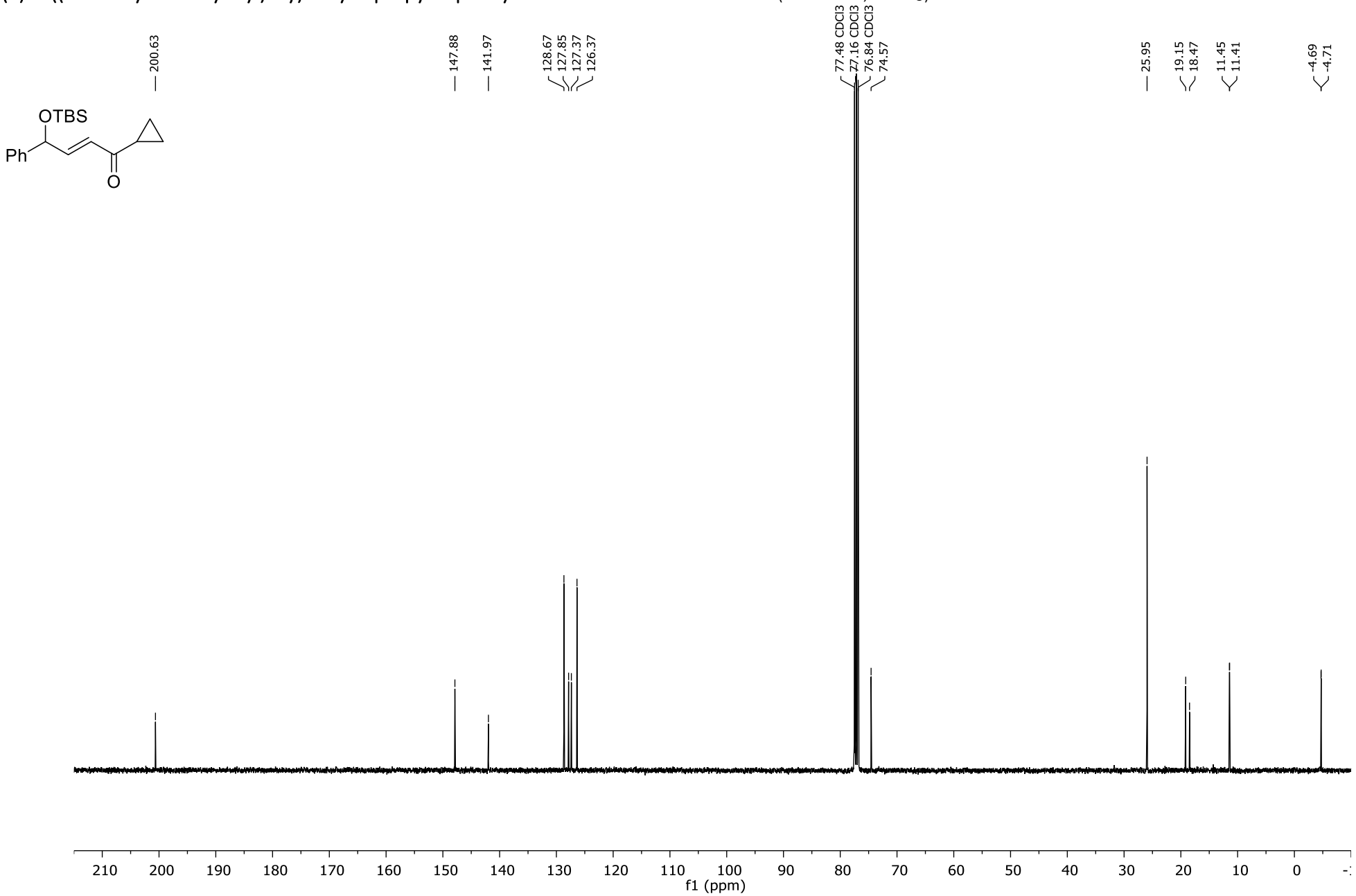
(*E*)-5-((*tert*-Butyldimethylsilyl)oxy)-5-phenylpent-3-en-2-one **S68** ^{13}C NMR (101 MHz, $CDCl_3$)



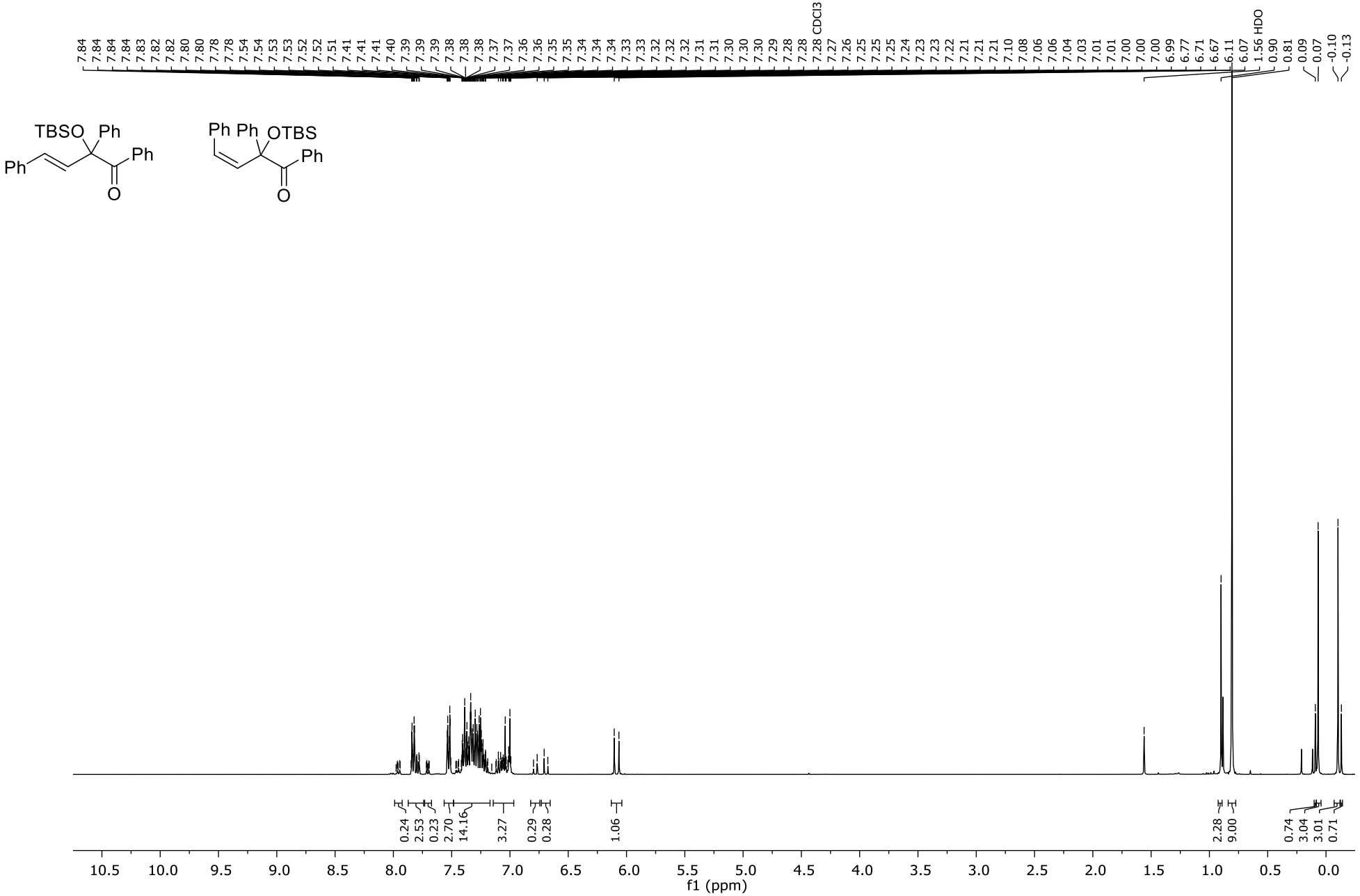
(*E*)-4-((*tert*-butyldimethylsilyl)oxy)-1-cyclopropyl-4-phenylbut-2-en-1-one S69 ^{1}H NMR (400 MHz, $CDCl_3$)



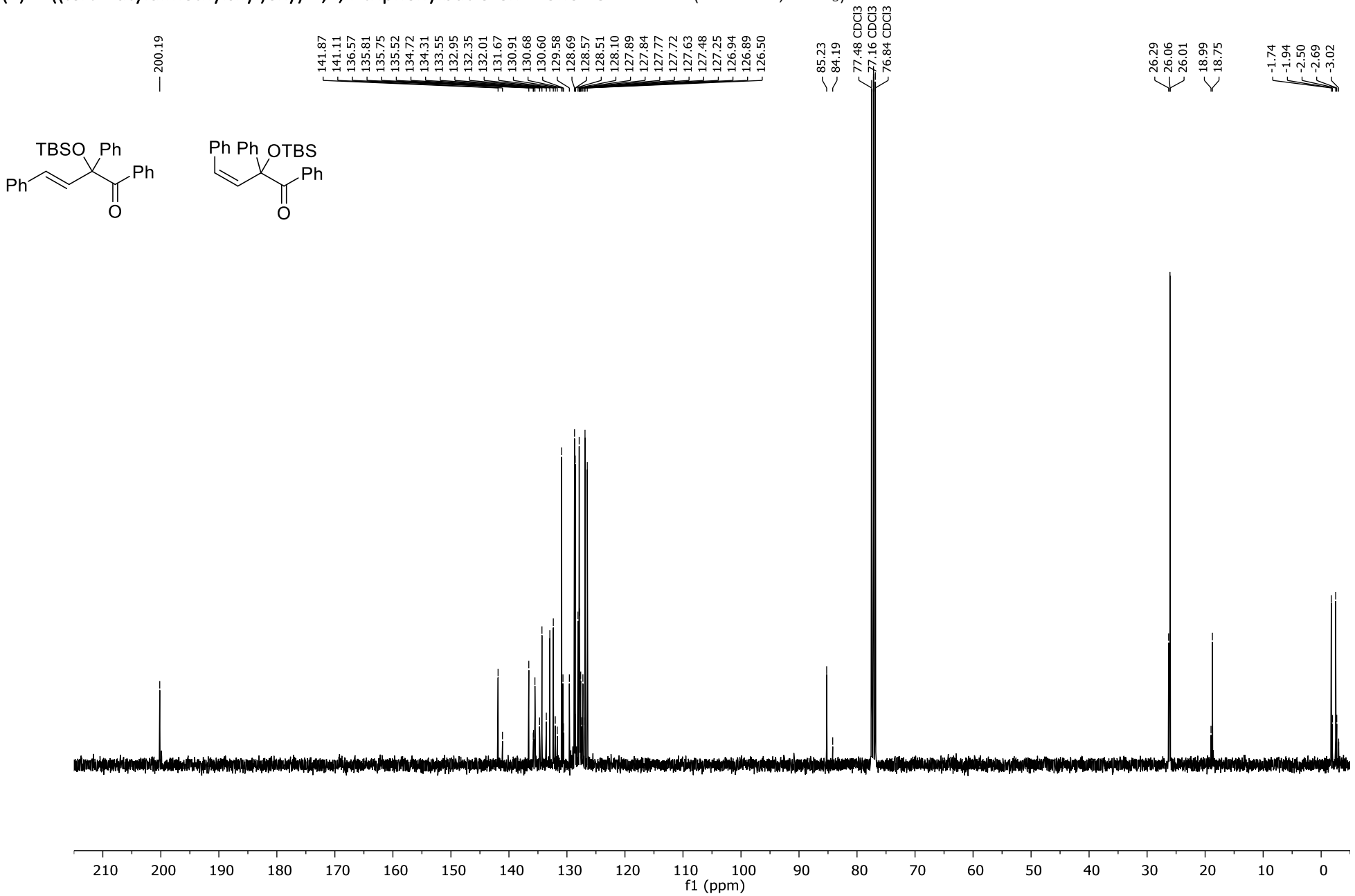
(*E*)-4-((*tert*-butyldimethylsilyl)oxy)-1-cyclopropyl-4-phenylbut-2-en-1-one S69 ^{13}C NMR (101 MHz, $CDCl_3$)



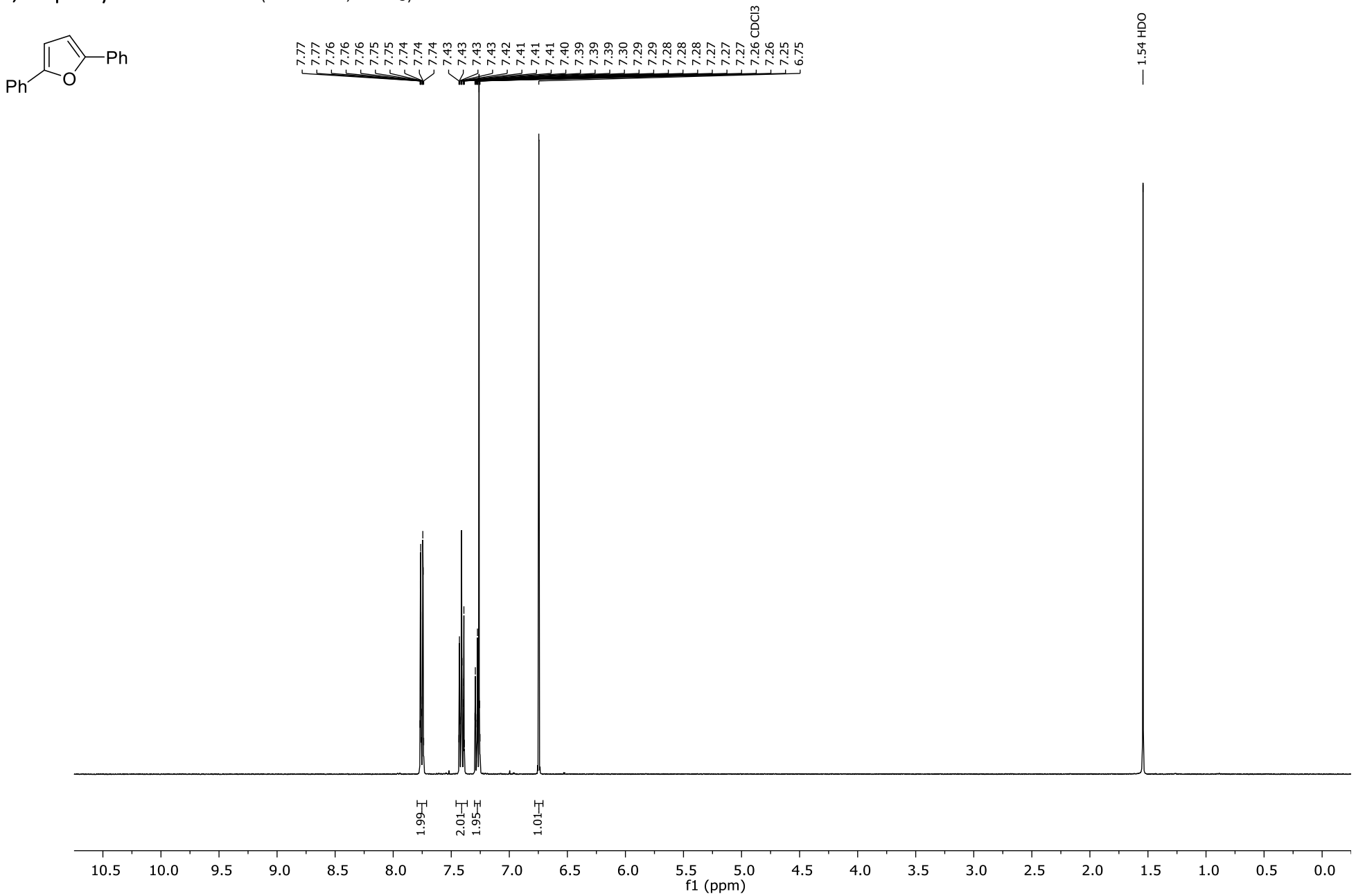
(*E*)-2-((*tert*-Butyldimethylsilyl)oxy)-1,2,4-triphenylbut-3-en-1-one 28 ^{1}H NMR (400 MHz, $CDCl_3$)



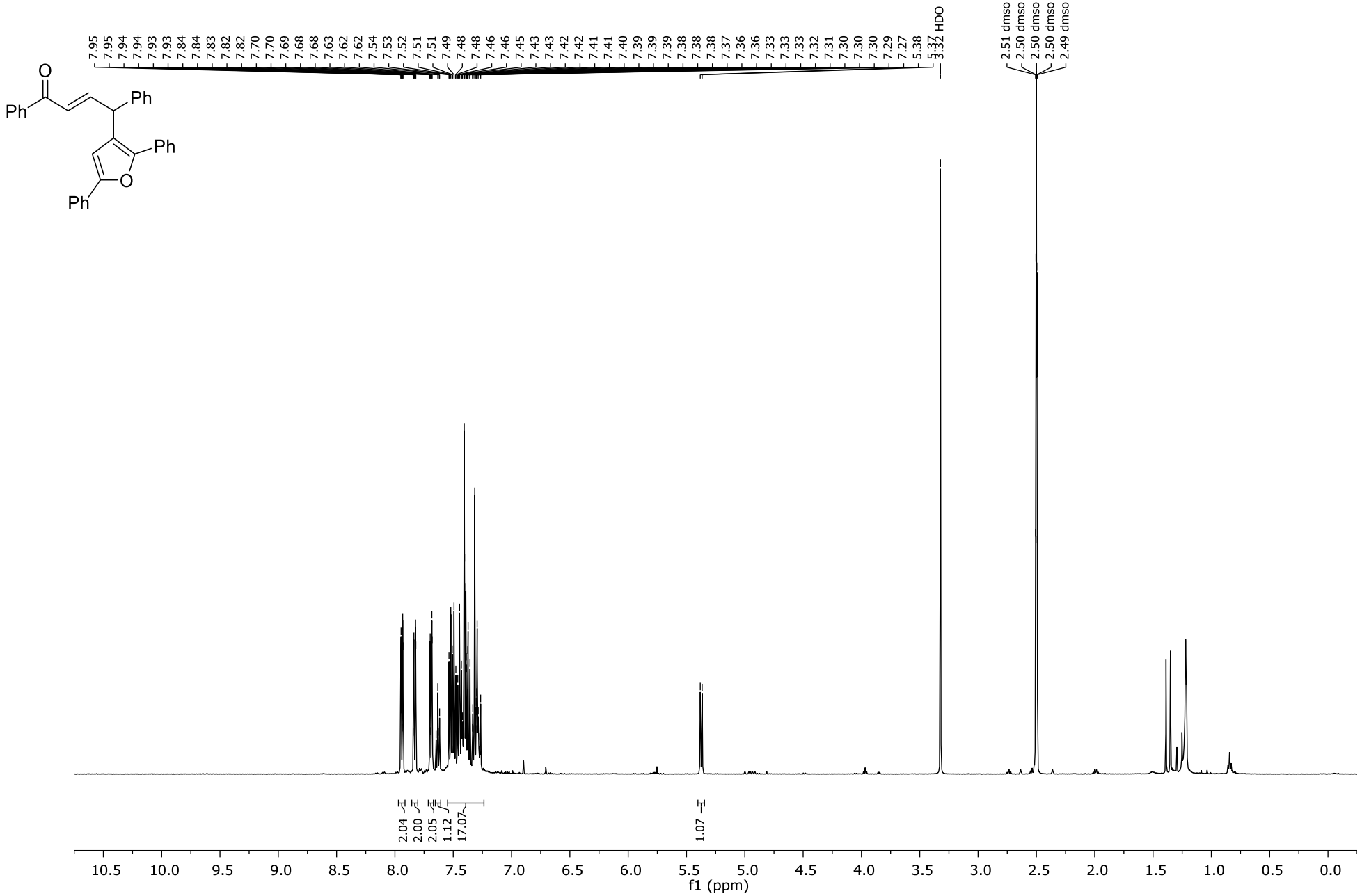
(*E*)-2-((*tert*-Butyldimethylsilyl)oxy)-1,2,4-triphenylbut-3-en-1-one 28 ^{13}C NMR (101 MHz, $CDCl_3$)



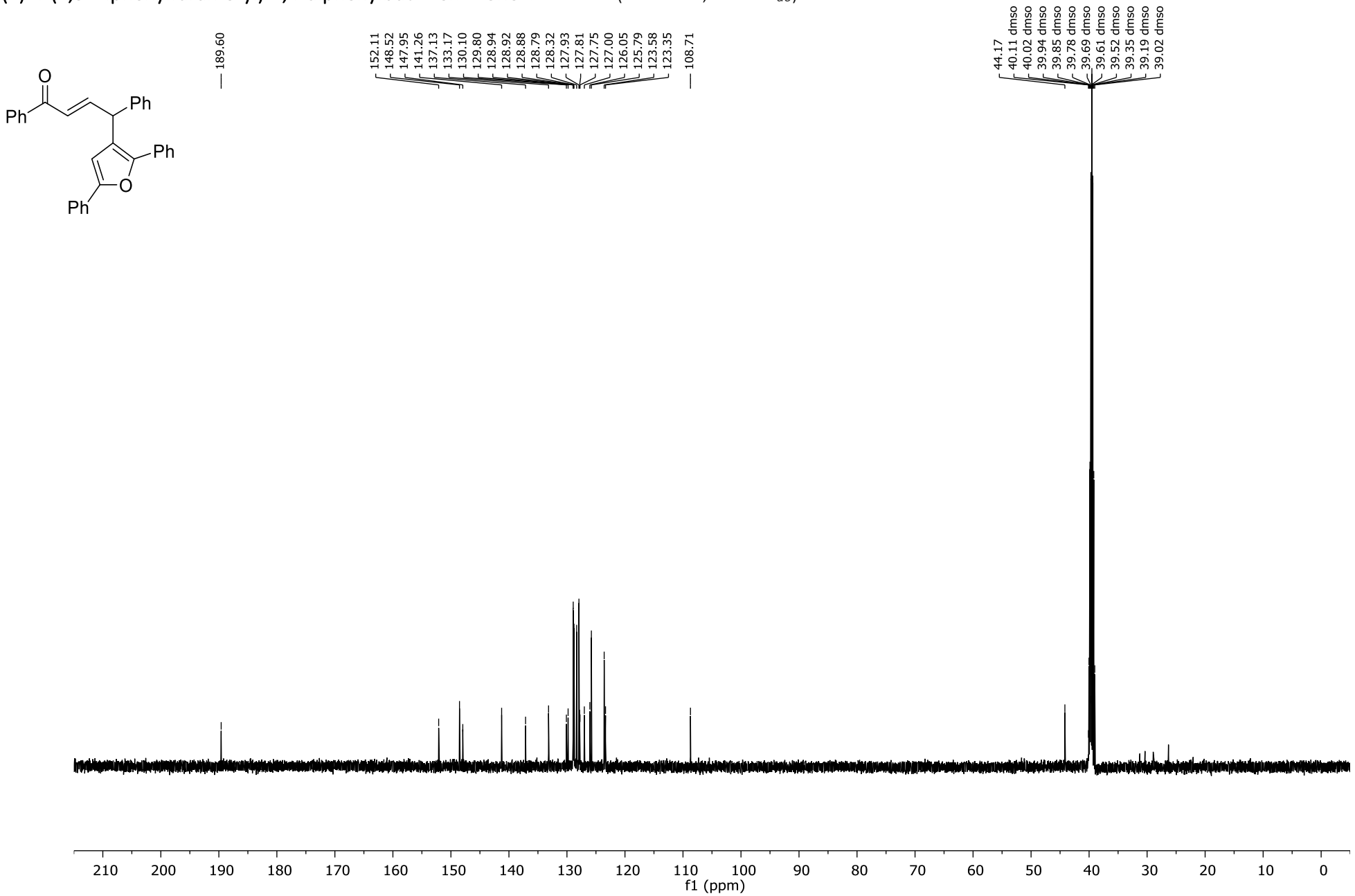
2,5-Diphenylfuran 3 ^{1}H NMR (400 MHz, $CDCl_3$)



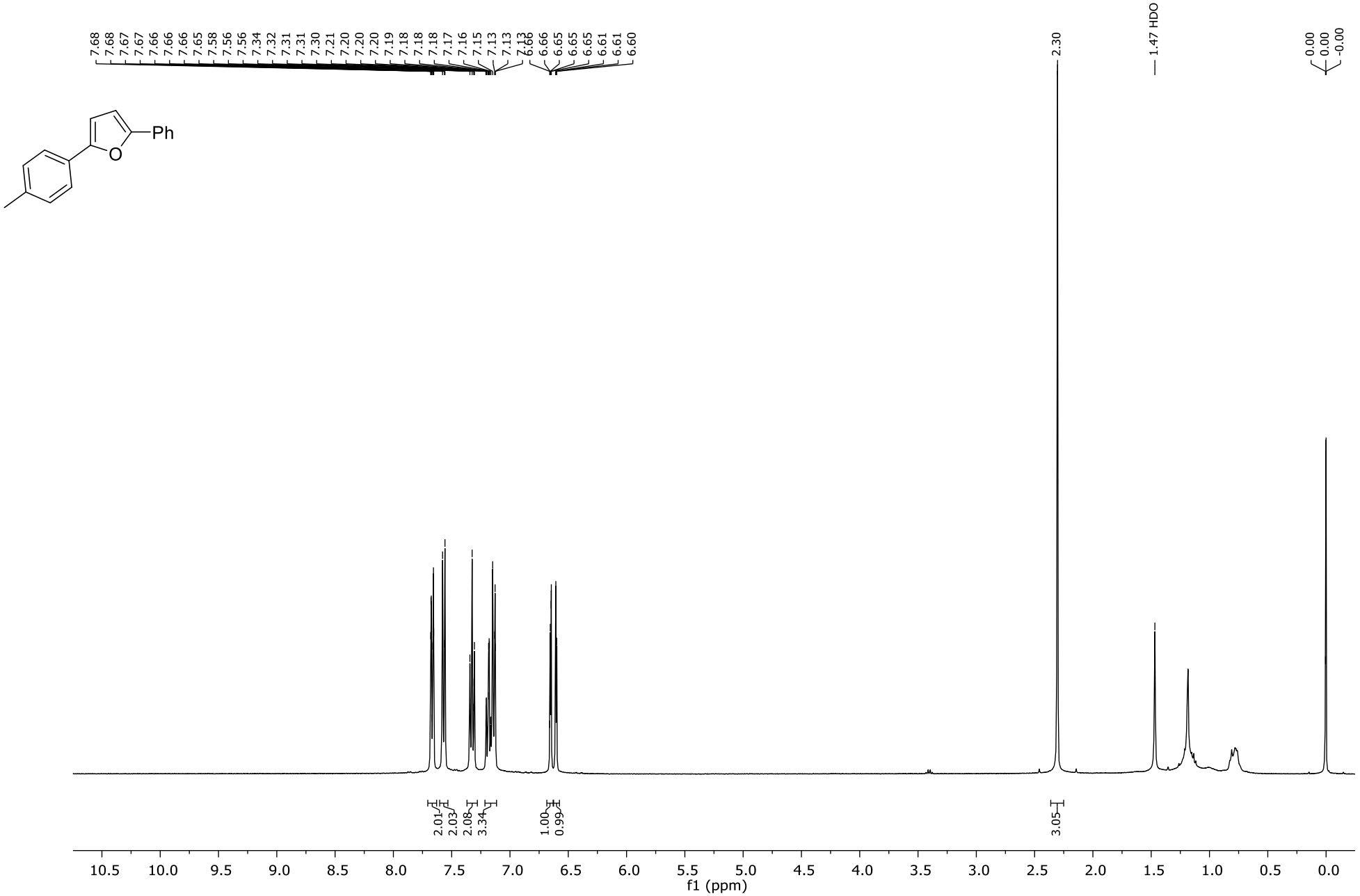
(*E*)-4-(2,5-Diphenylfuran-3-yl)-1,4-diphenylbut-2-en-1-one **4** ^{1}H NMR (500 MHz, DMSO-$_{d6}$)



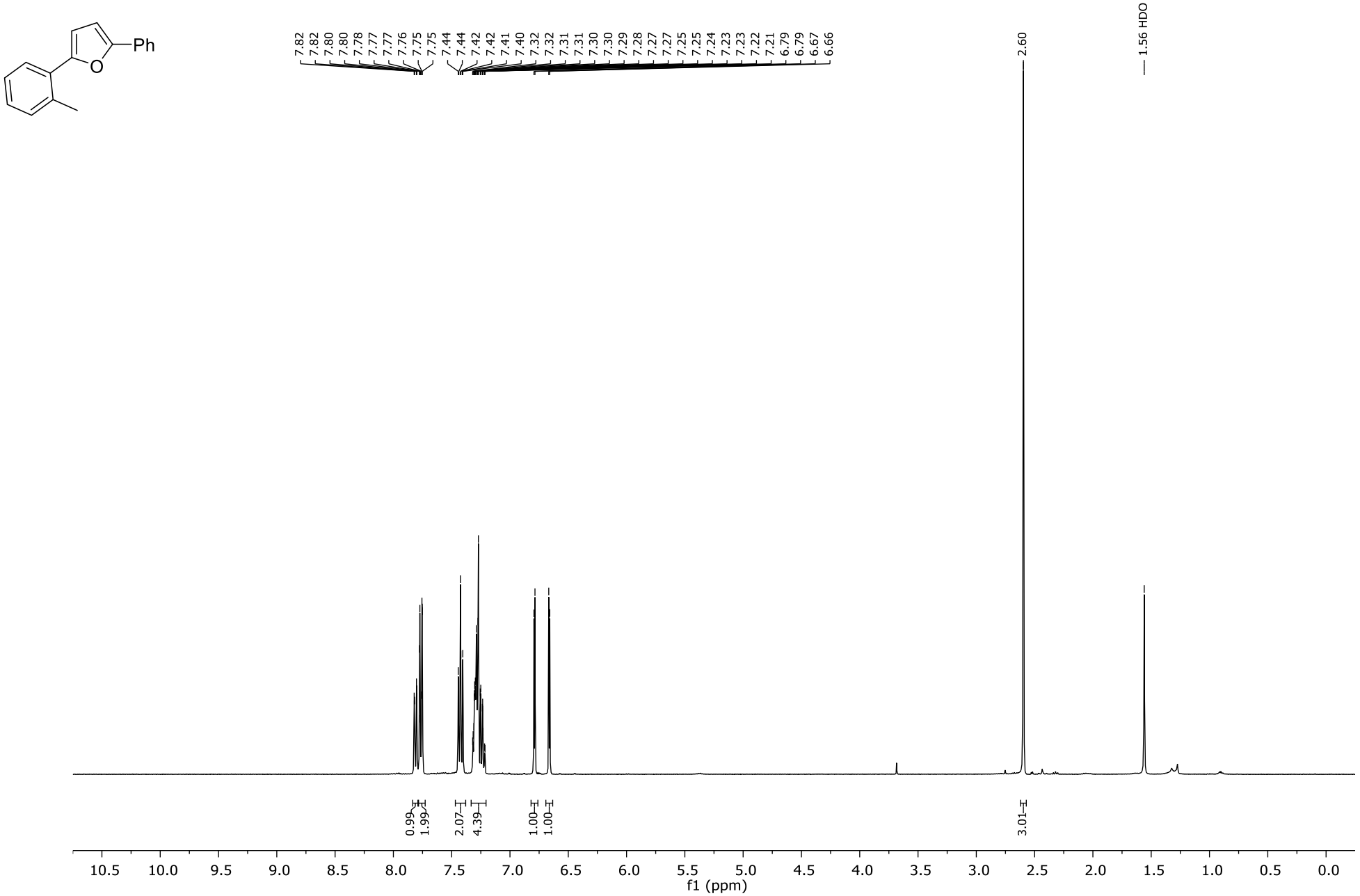
(*E*)-4-(2,5-Diphenylfuran-3-yl)-1,4-diphenylbut-2-en-1-one **4** ^{1}H NMR (126 MHz, DMSO-$_{d6}$)



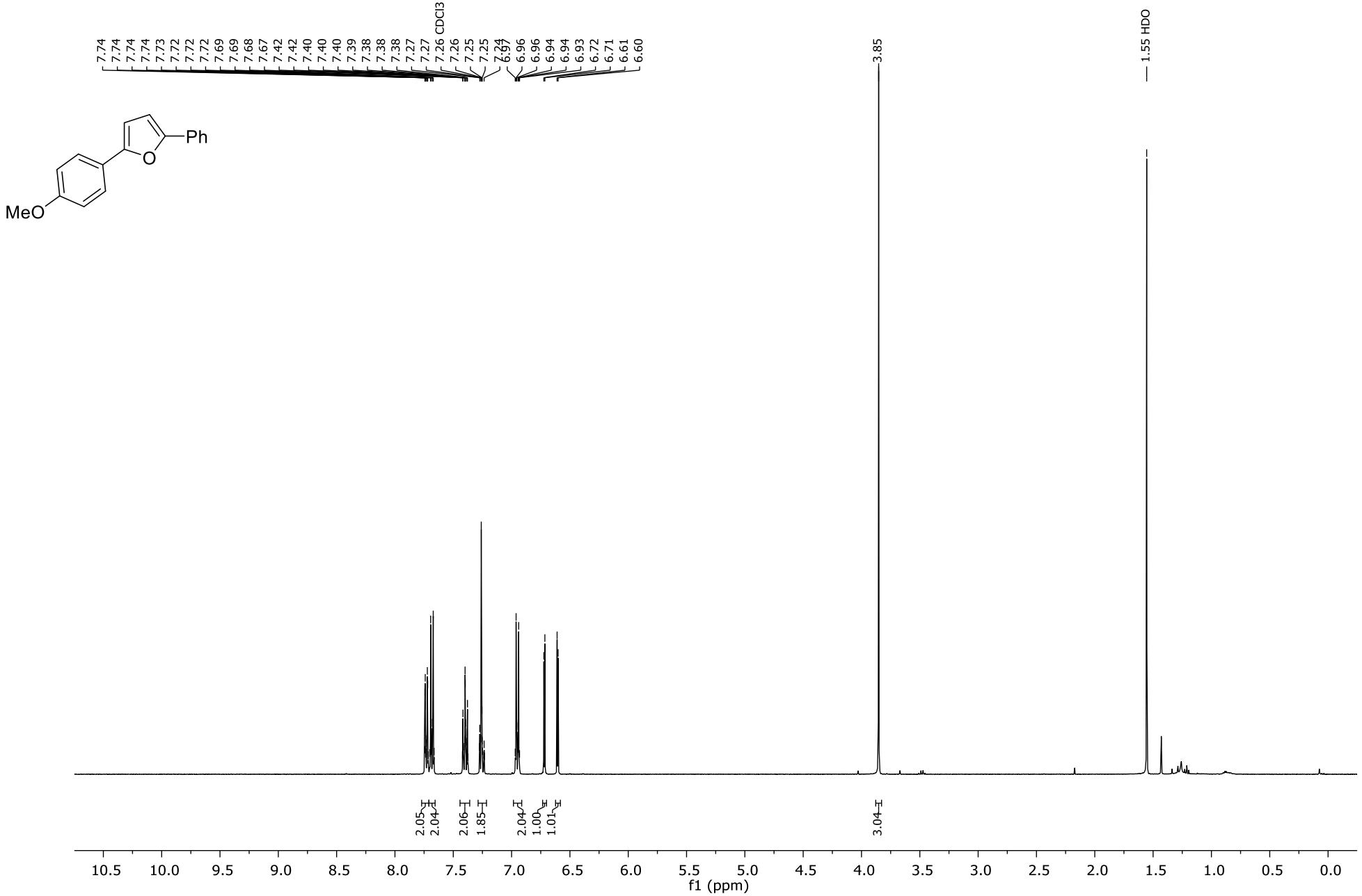
2-Phenyl-5-(*p*-tolyl)furan **7** ^{1}H NMR (400 MHz, $CDCl_3$)



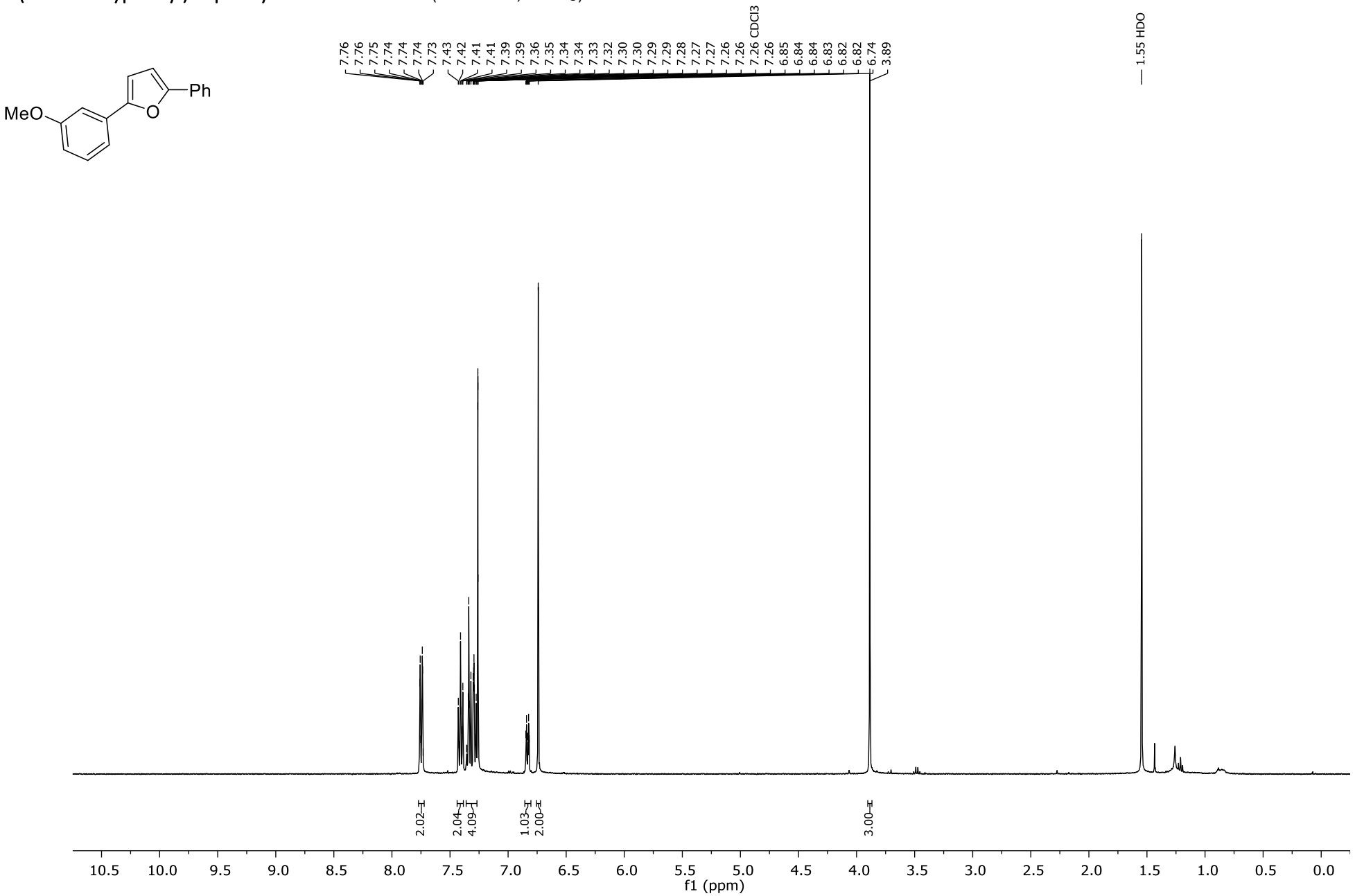
2-Phenyl-5-(*o*-tolyl)furan 8 ^{1}H NMR (400 MHz, $CDCl_3$)



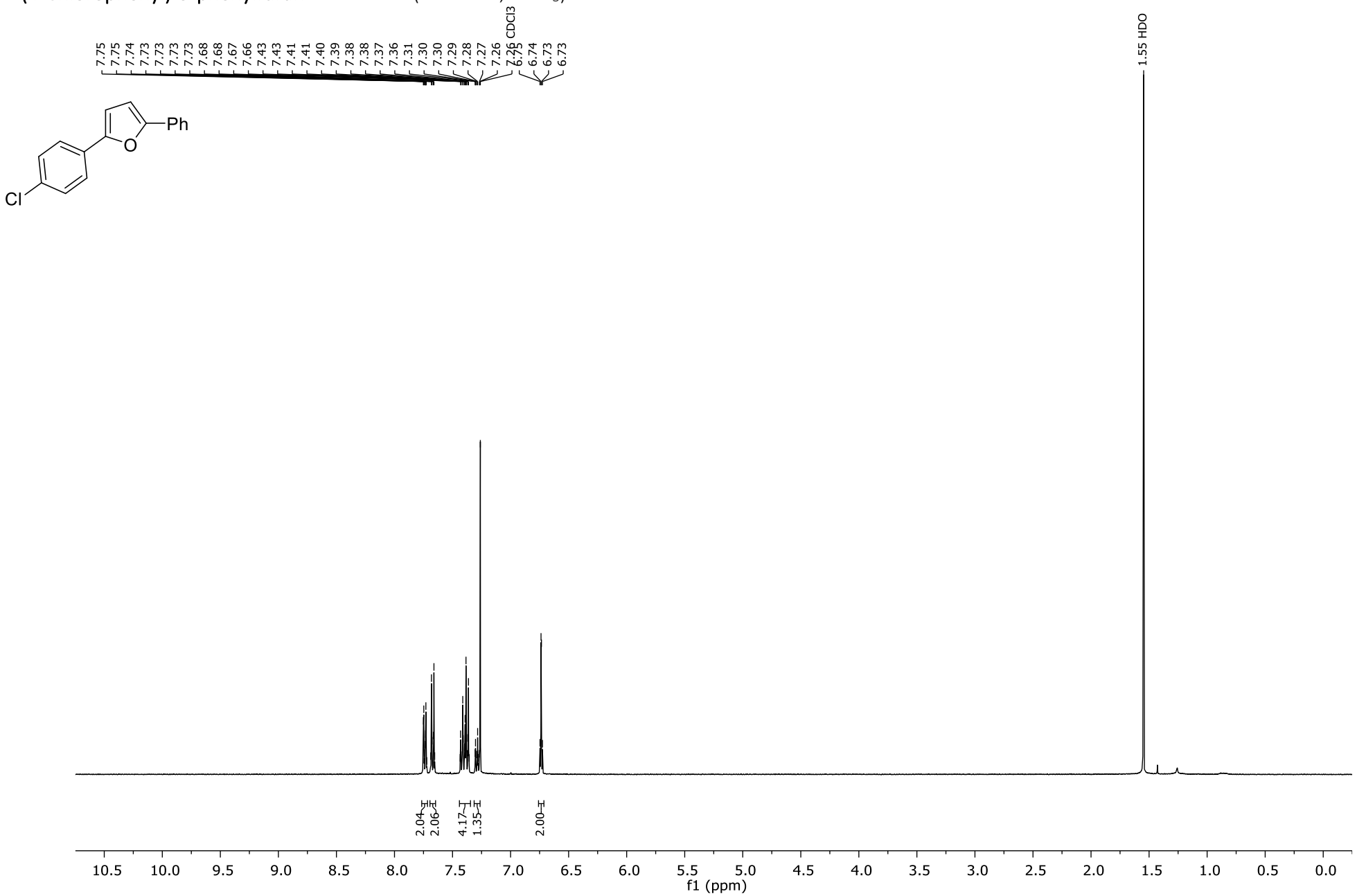
2-(4-Methoxyphenyl)-5-phenylfuran 9 ^{1}H NMR (400 MHz, $CDCl_3$)



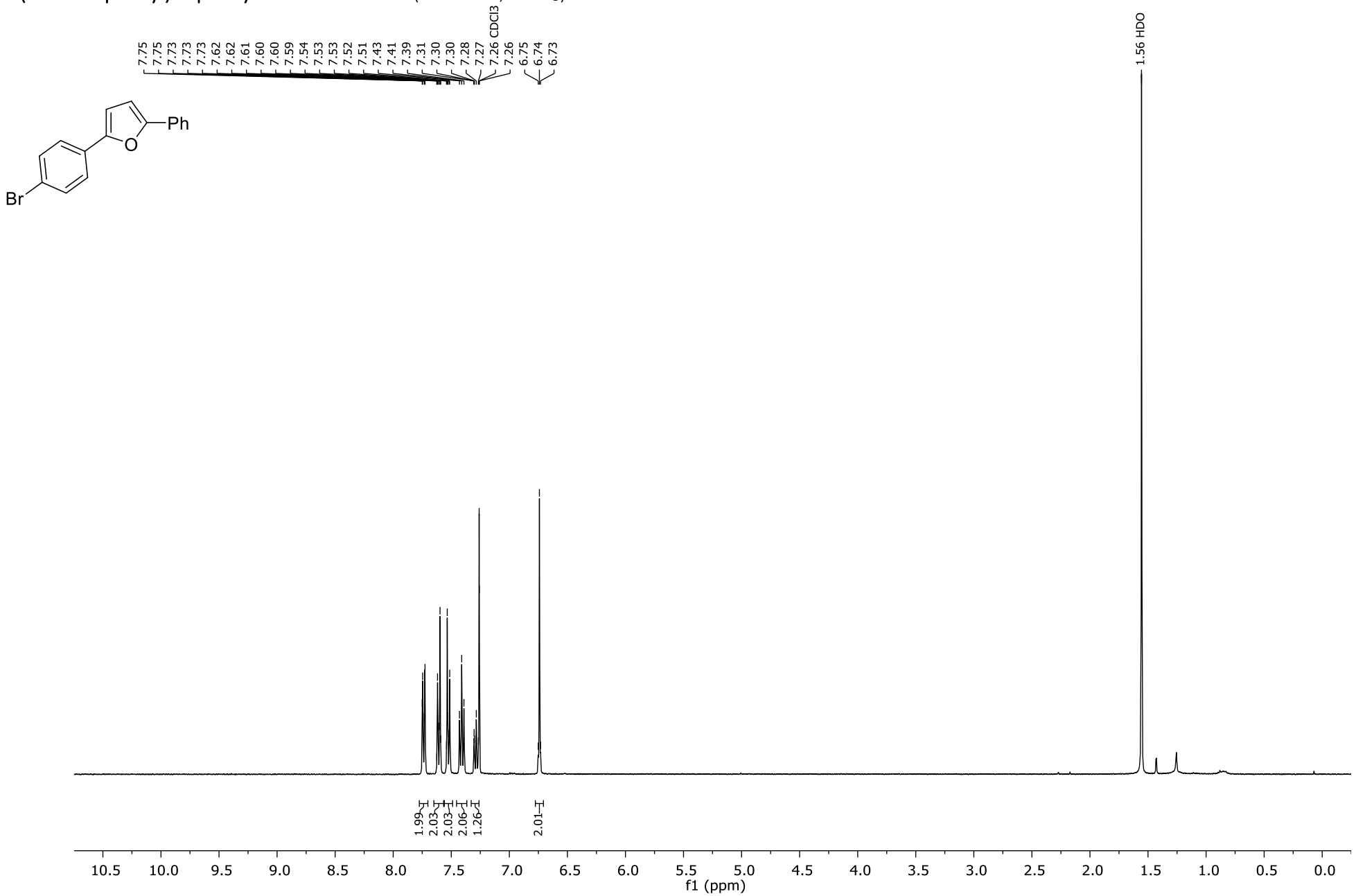
2-(3-Methoxyphenyl)-5-phenylfuran 10 ^{1}H NMR (400 MHz, $CDCl_3$)



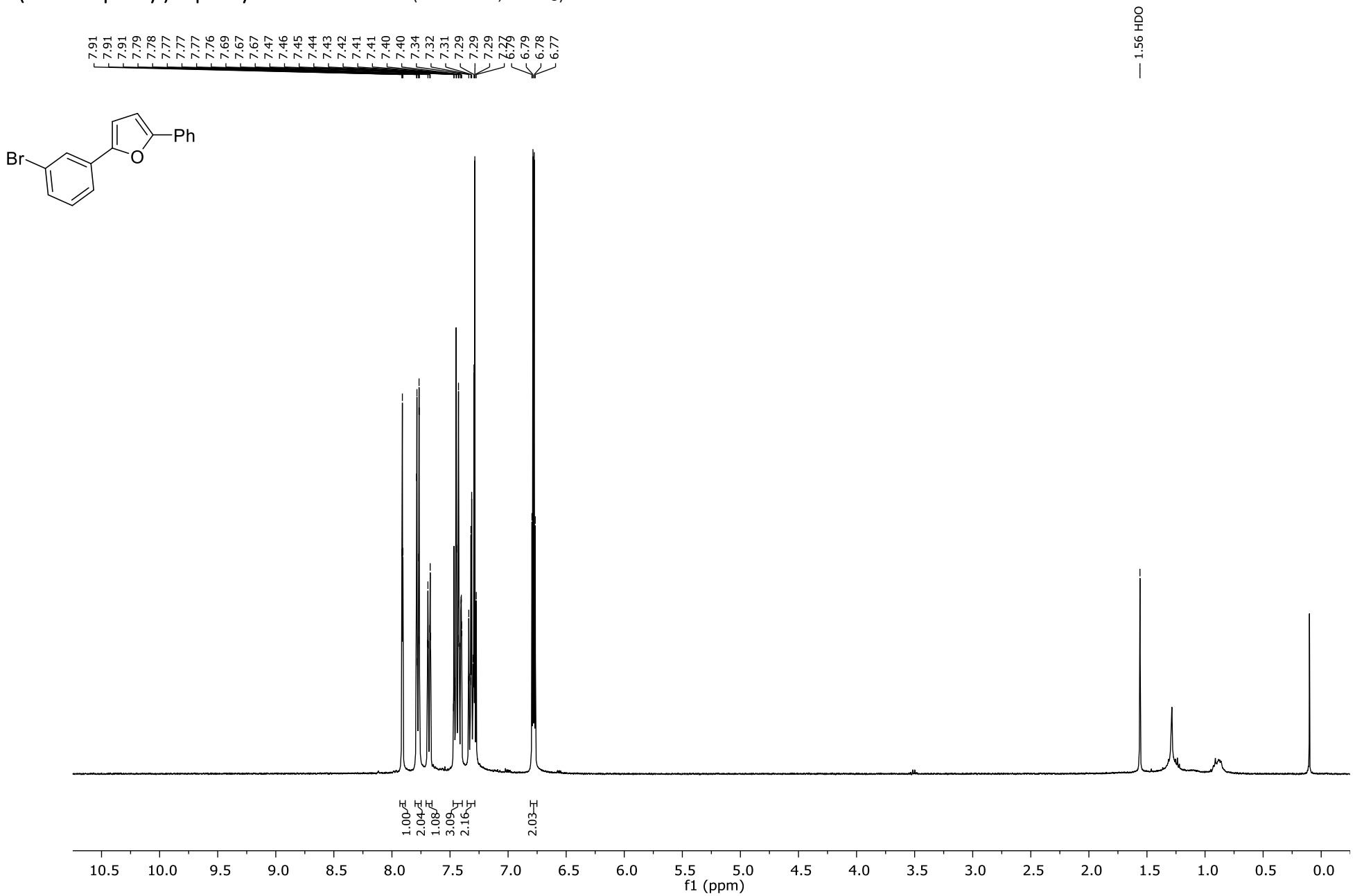
2-(4-Chlorophenyl)-5-phenylfuran 11 ^{1}H NMR (400 MHz, $CDCl_3$)



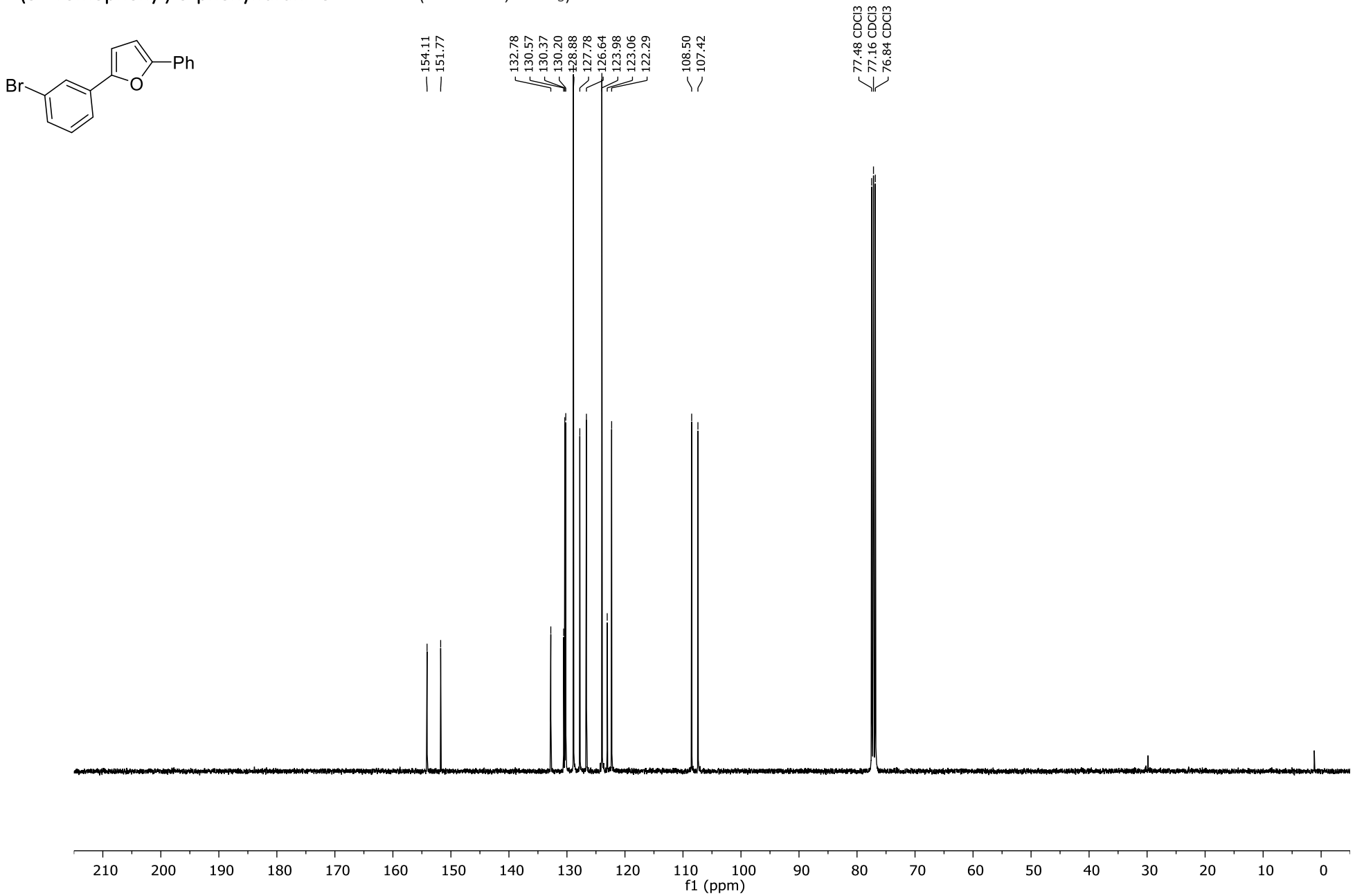
2-(4-Bromophenyl)-5-phenylfuran 12 ^{1}H NMR (400 MHz, $CDCl_3$)



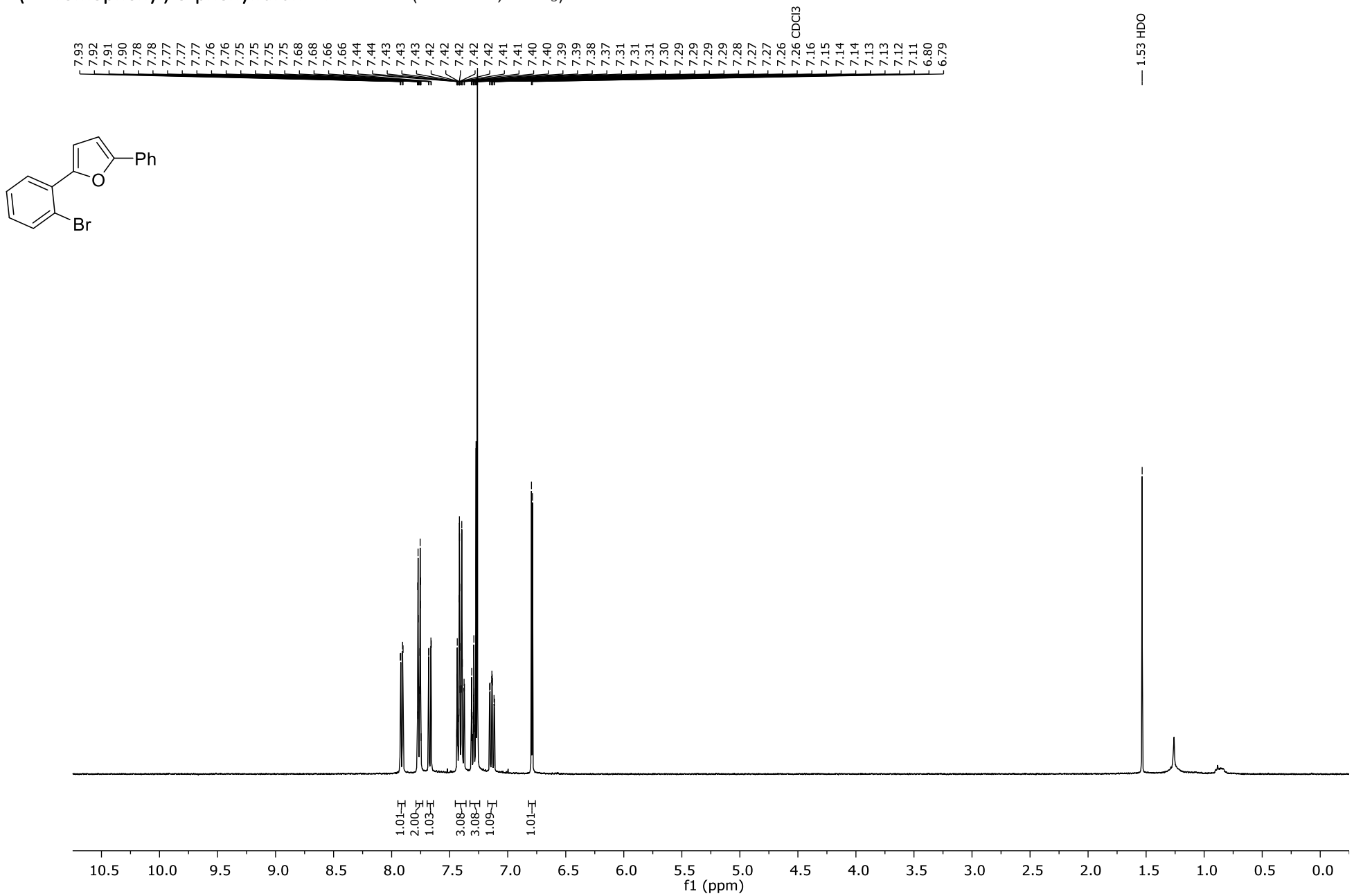
2-(3-Bromophenyl)-5-phenylfuran 13 ^{1}H NMR (400 MHz, $CDCl_3$)



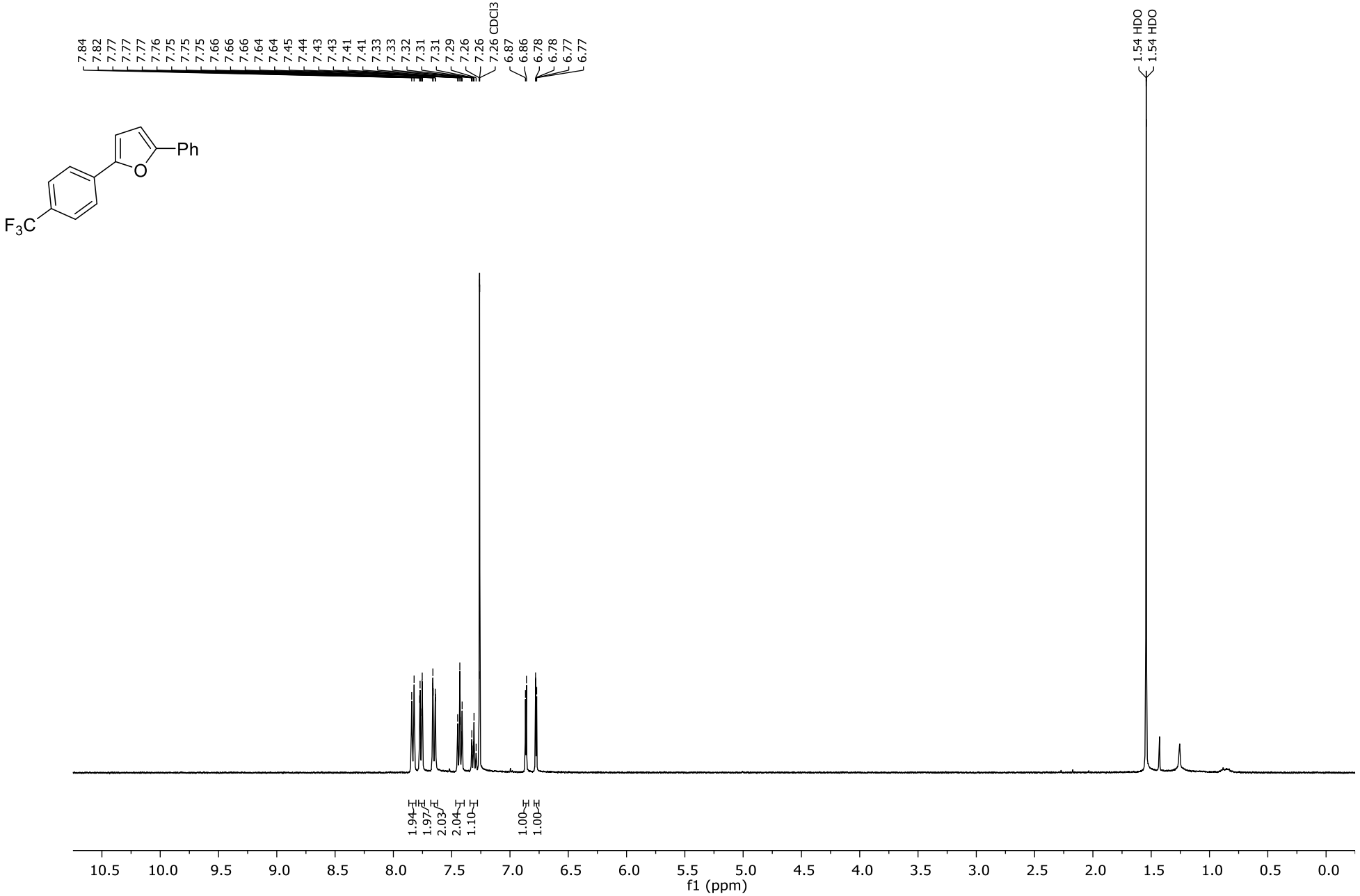
2-(3-Bromophenyl)-5-phenylfuran 13 ^{13}C NMR (101 MHz, $CDCl_3$)



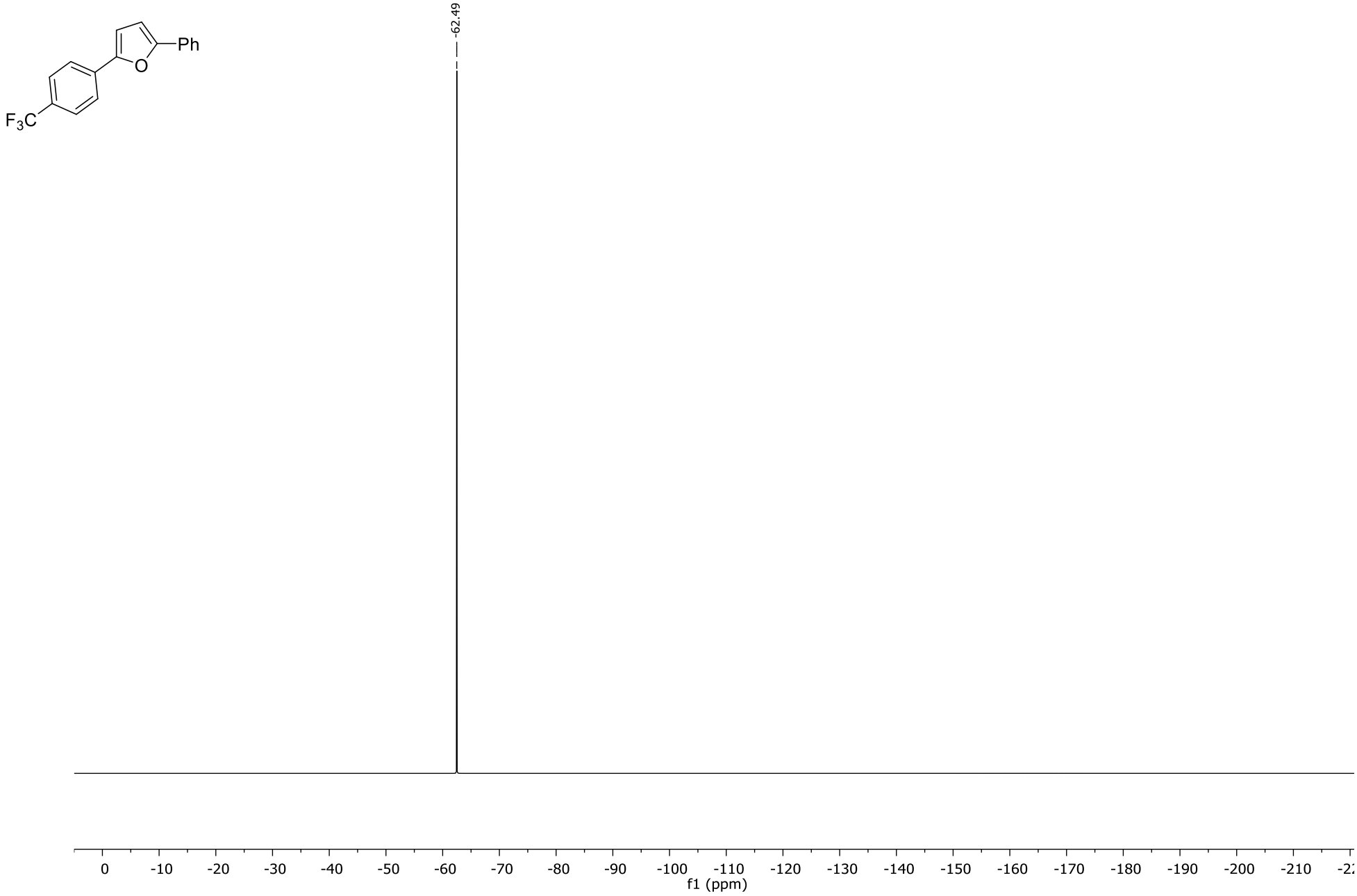
2-(2-Bromophenyl)-5-phenylfuran 14 ^{1}H NMR (400 MHz, $CDCl_3$)



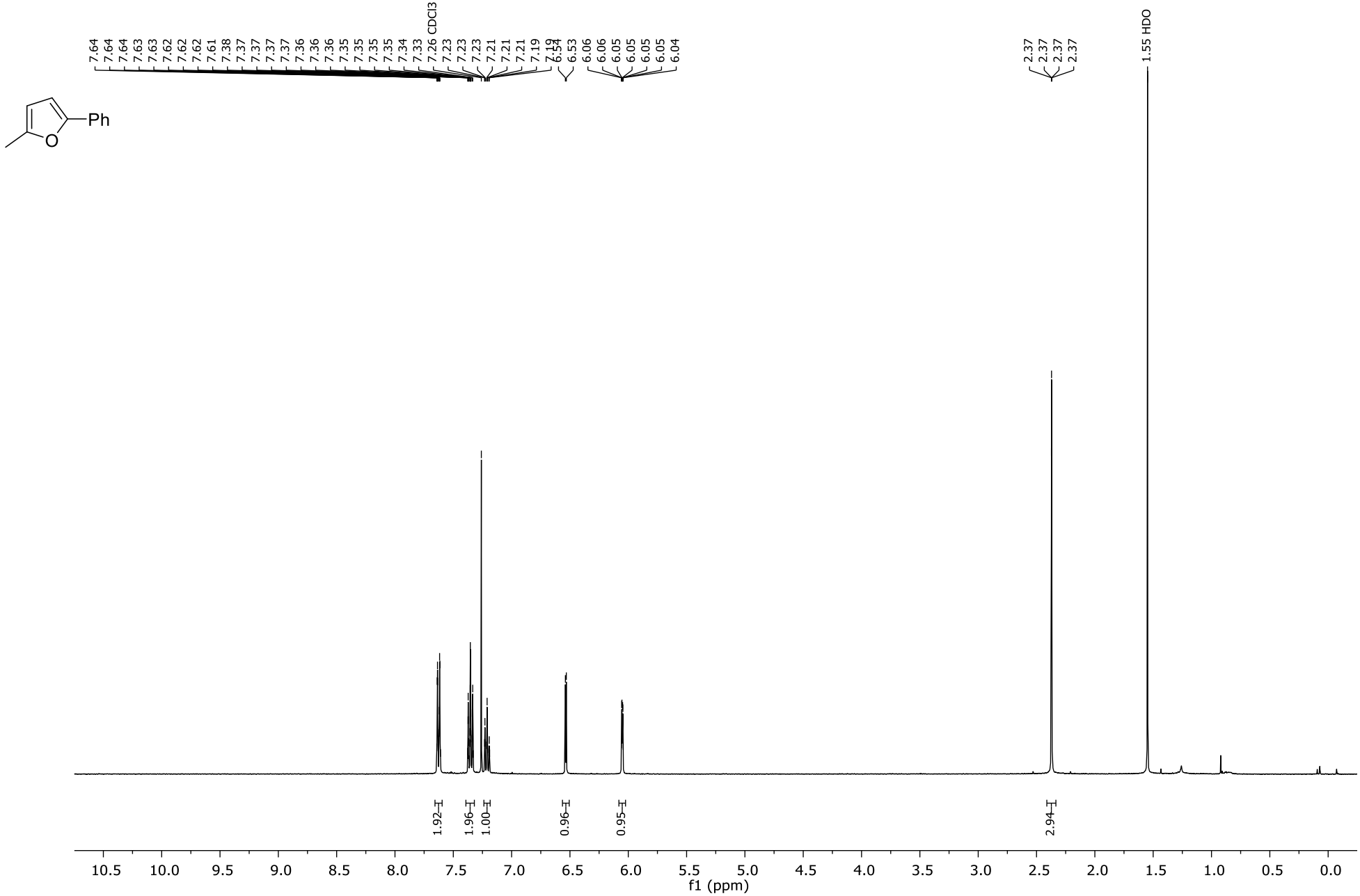
2-Phenyl-5-(4-(trifluoromethyl)phenyl)furan **15** ^{1}H NMR (400 MHz, $CDCl_3$)



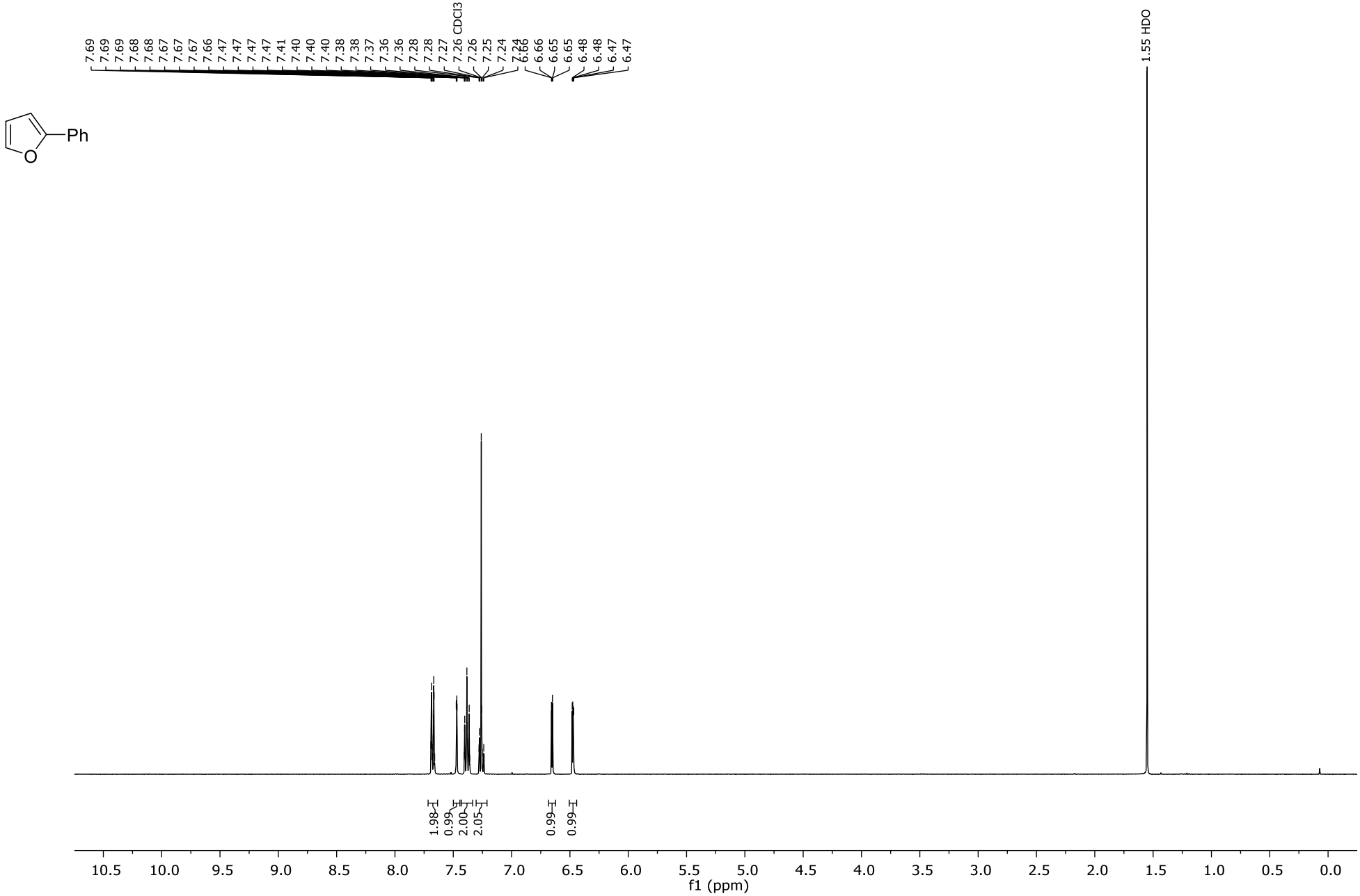
2-Phenyl-5-(4-(trifluoromethyl)phenyl)furan 15 ^{19}F NMR (376 MHz, $CDCl_3$)



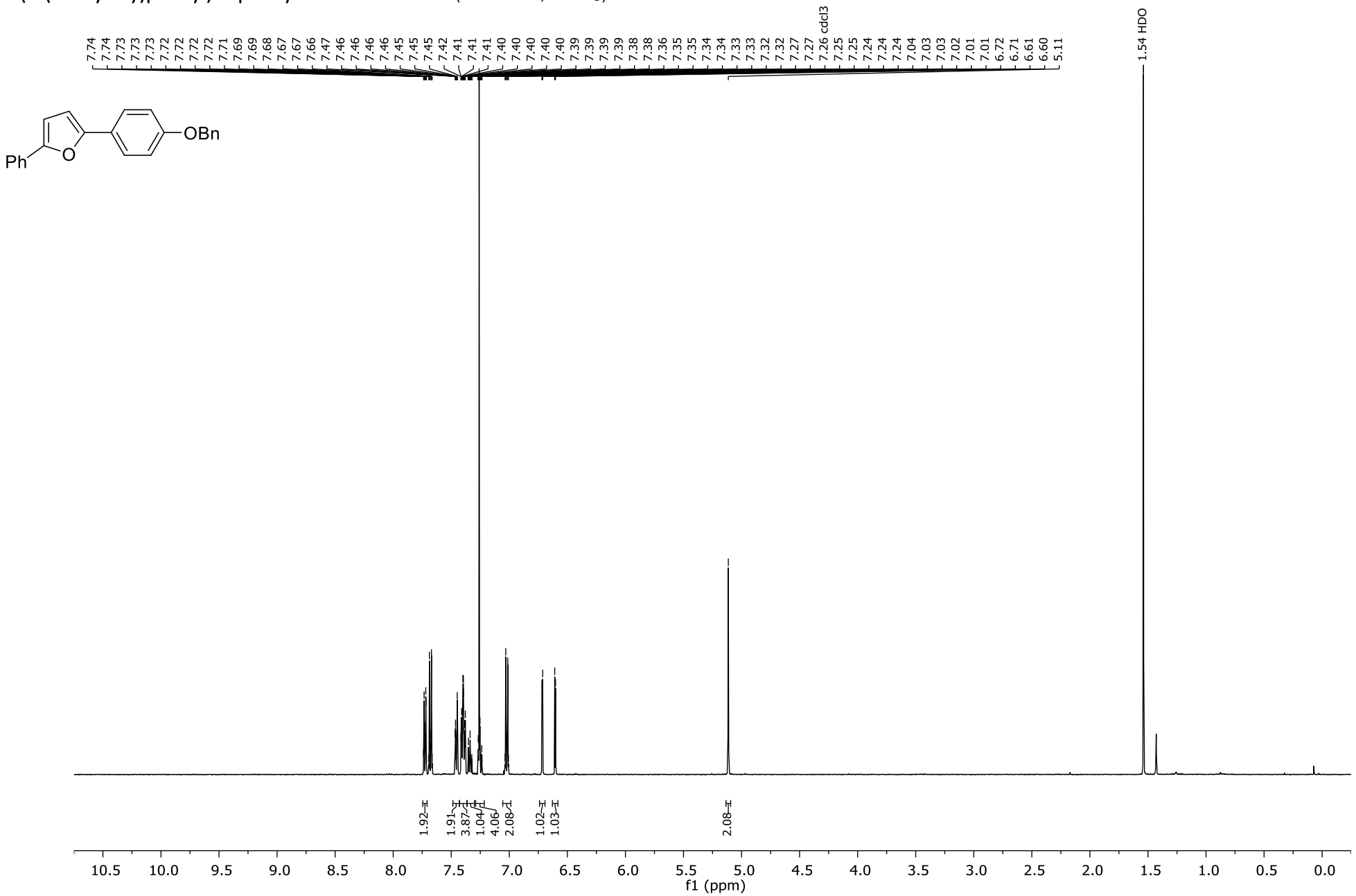
2-Methyl-5-phenylfuran 16 ^{1}H NMR (400 MHz, $CDCl_3$)



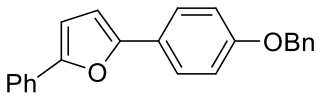
2-Phenylfuran 17 ^{1}H NMR (400 MHz, $CDCl_3$)



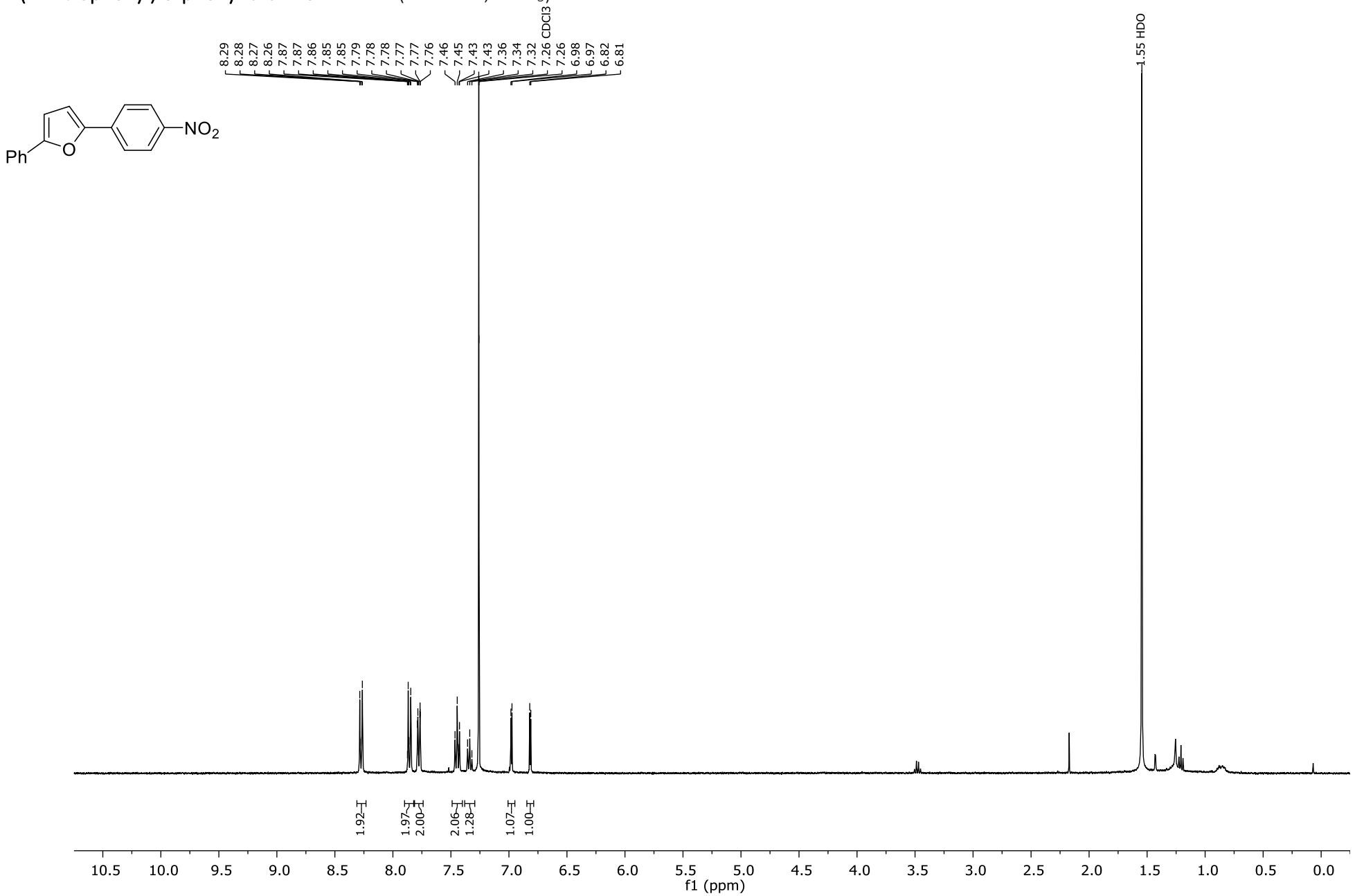
2-(4-(Benzyloxy)phenyl)-5-phenylfuran 18 ^{1}H NMR (400 MHz, $CDCl_3$)



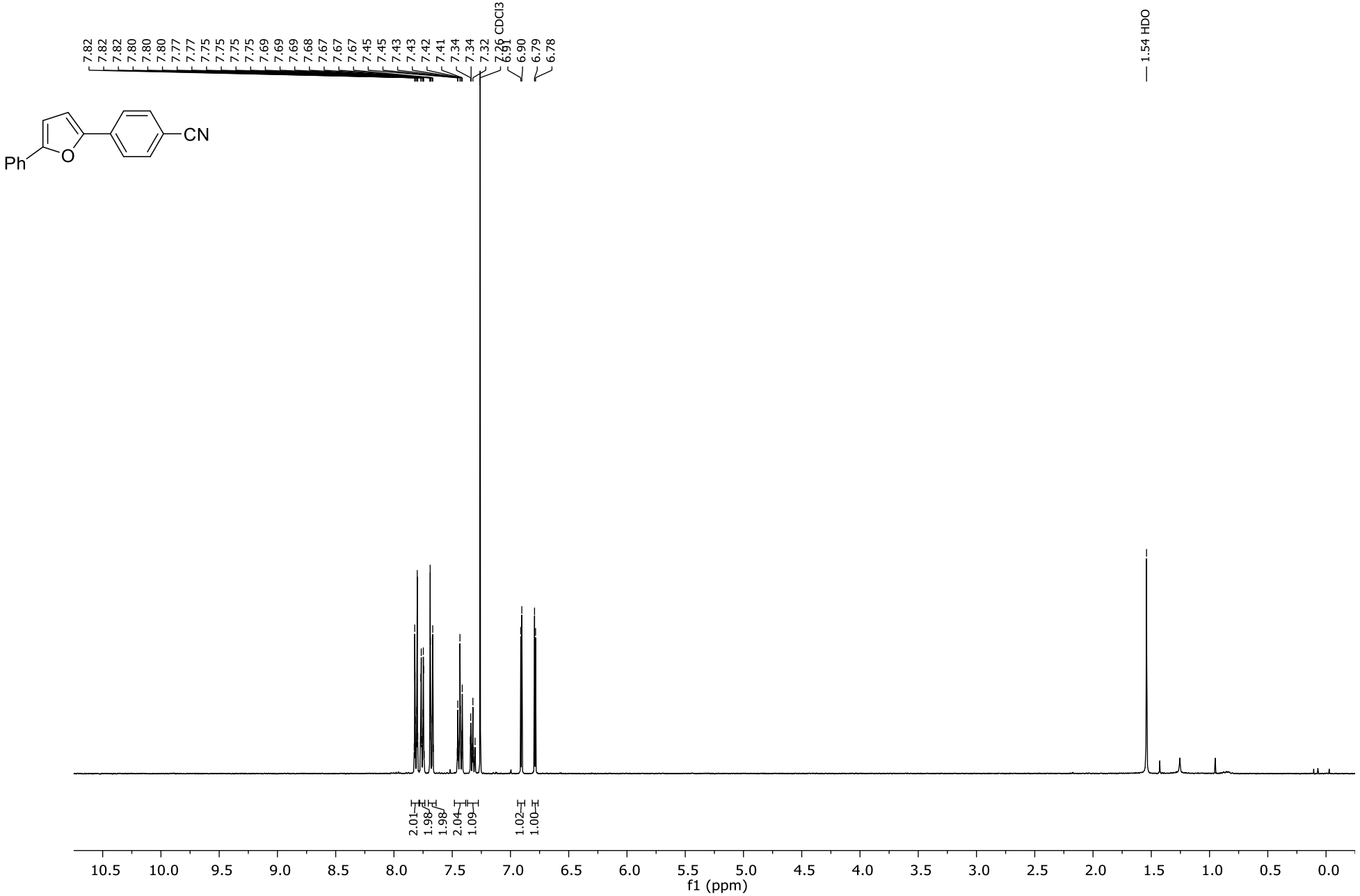
2-(4-(Benzyloxy)phenyl)-5-phenylfuran 18 ^{13}C NMR (101 MHz, $CDCl_3$)



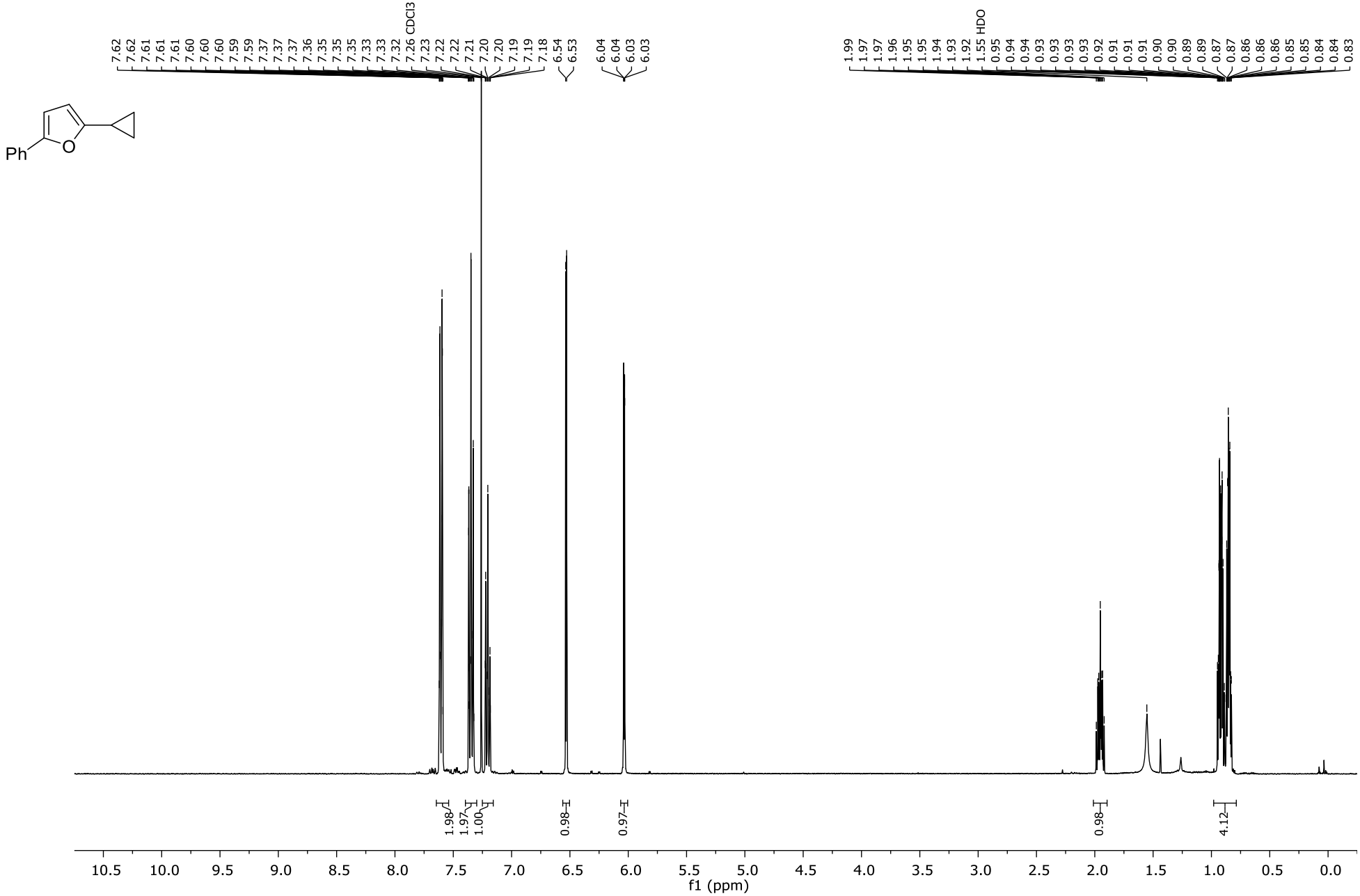
2-(4-Nitrophenyl)-5-phenylfuran 19 ^{1}H NMR (400 MHz, $CDCl_3$)



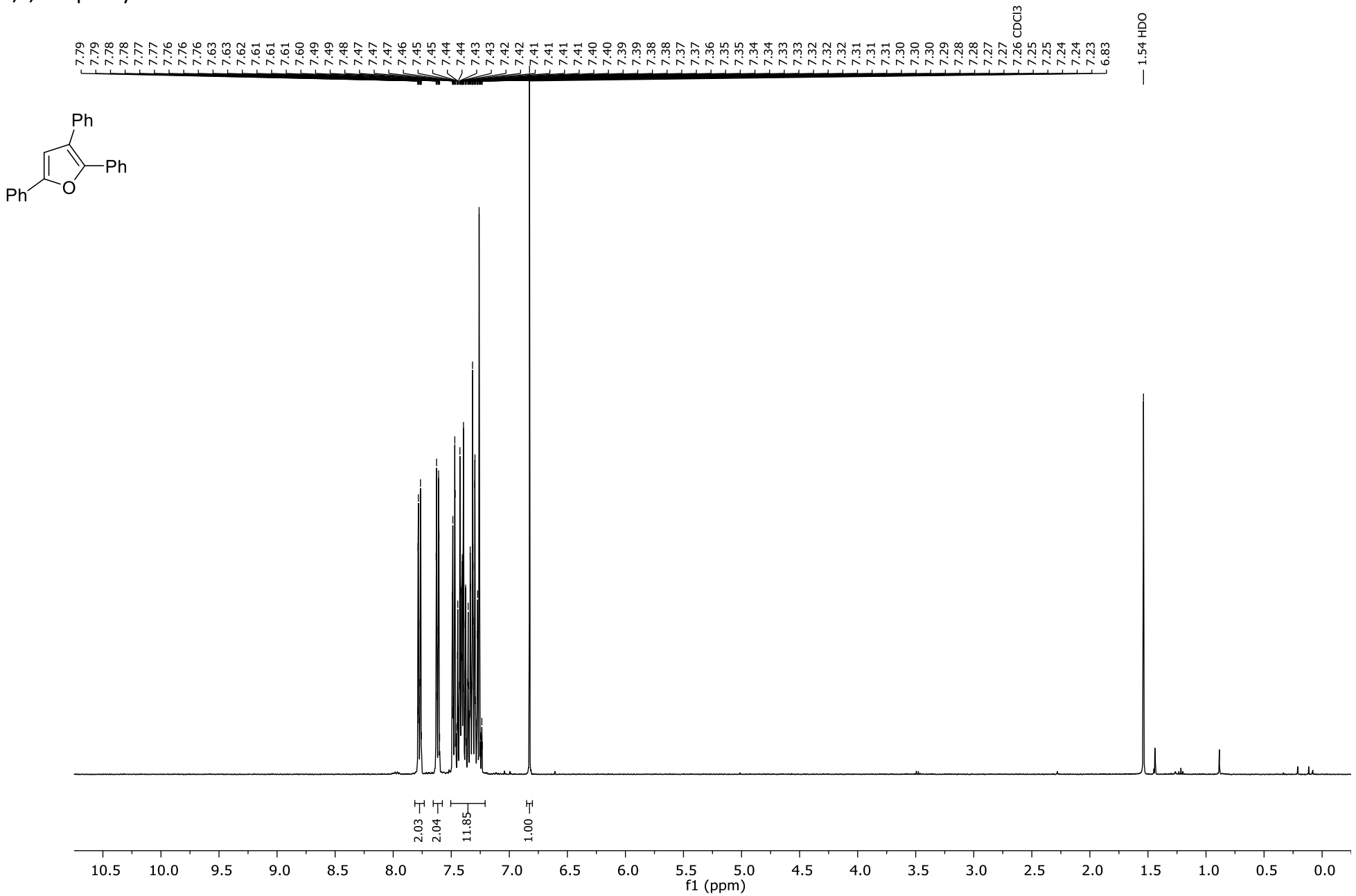
4-(5-Phenylfuran-2-yl)benzonitrile 20 ^{1}H NMR (400 MHz, $CDCl_3$)



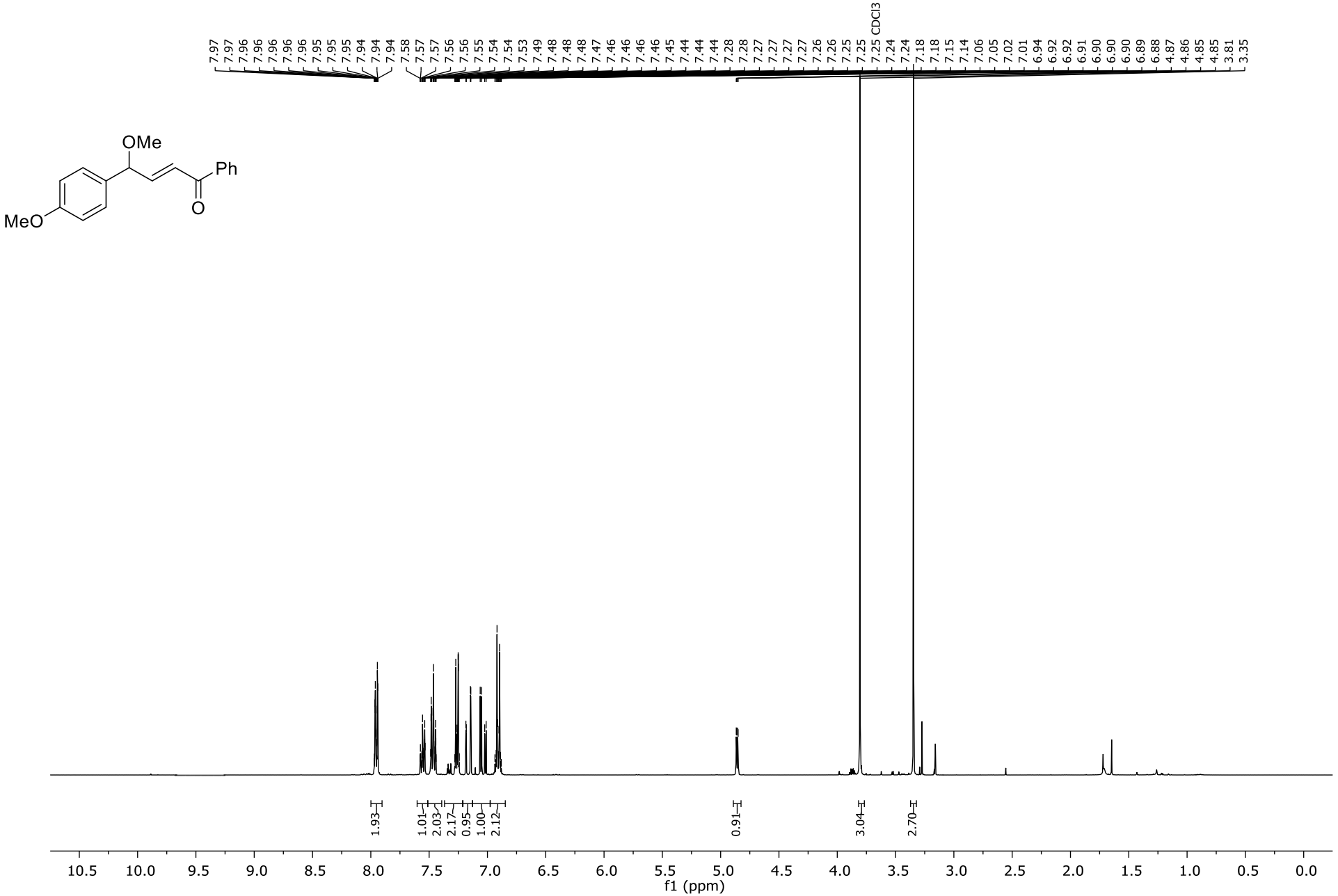
2-cyclopropyl-5-phenylfuran 21 ^{1}H NMR (400 MHz, $CDCl_3$)



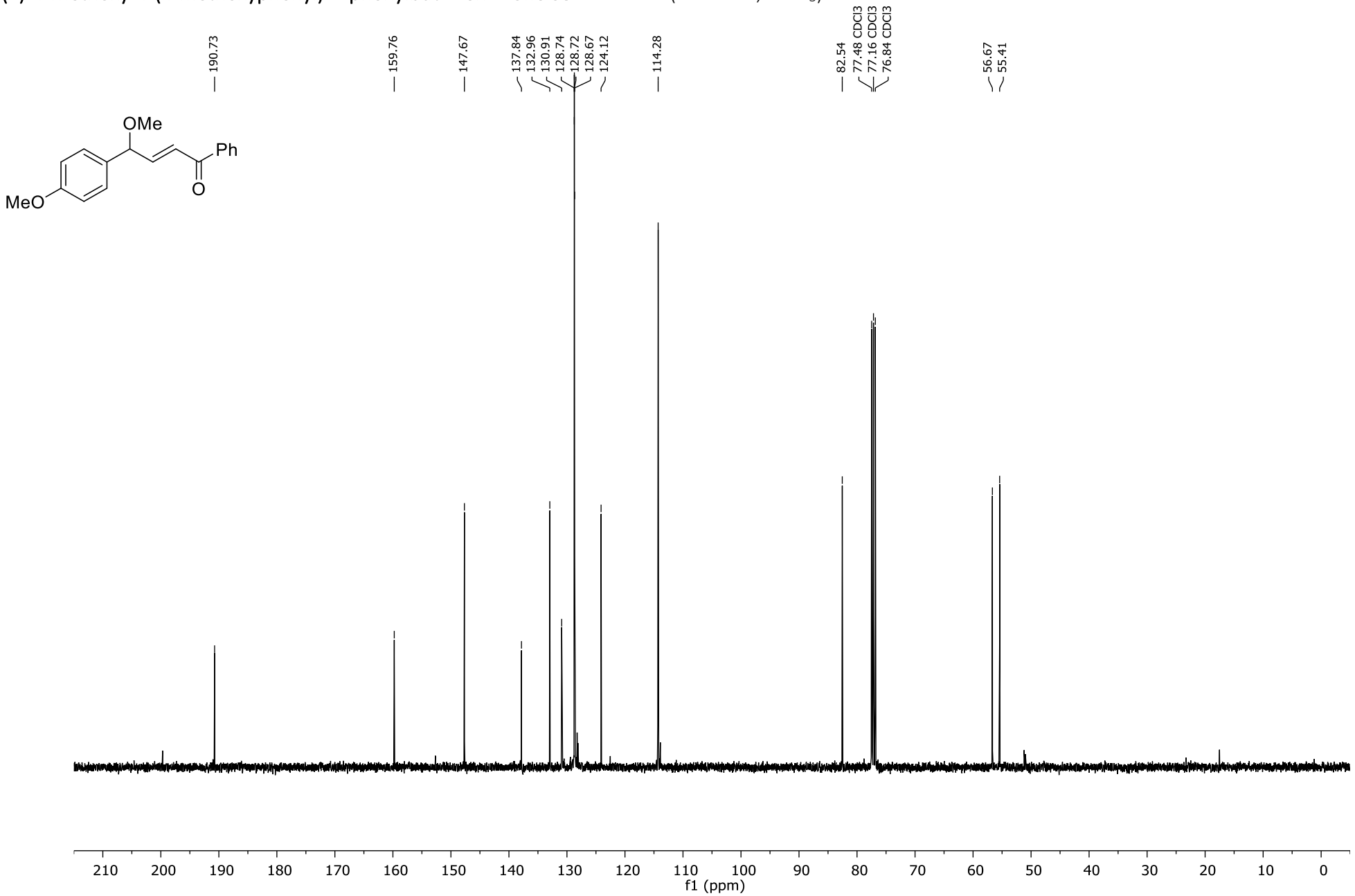
2,3,5-Triphenylfuran 29



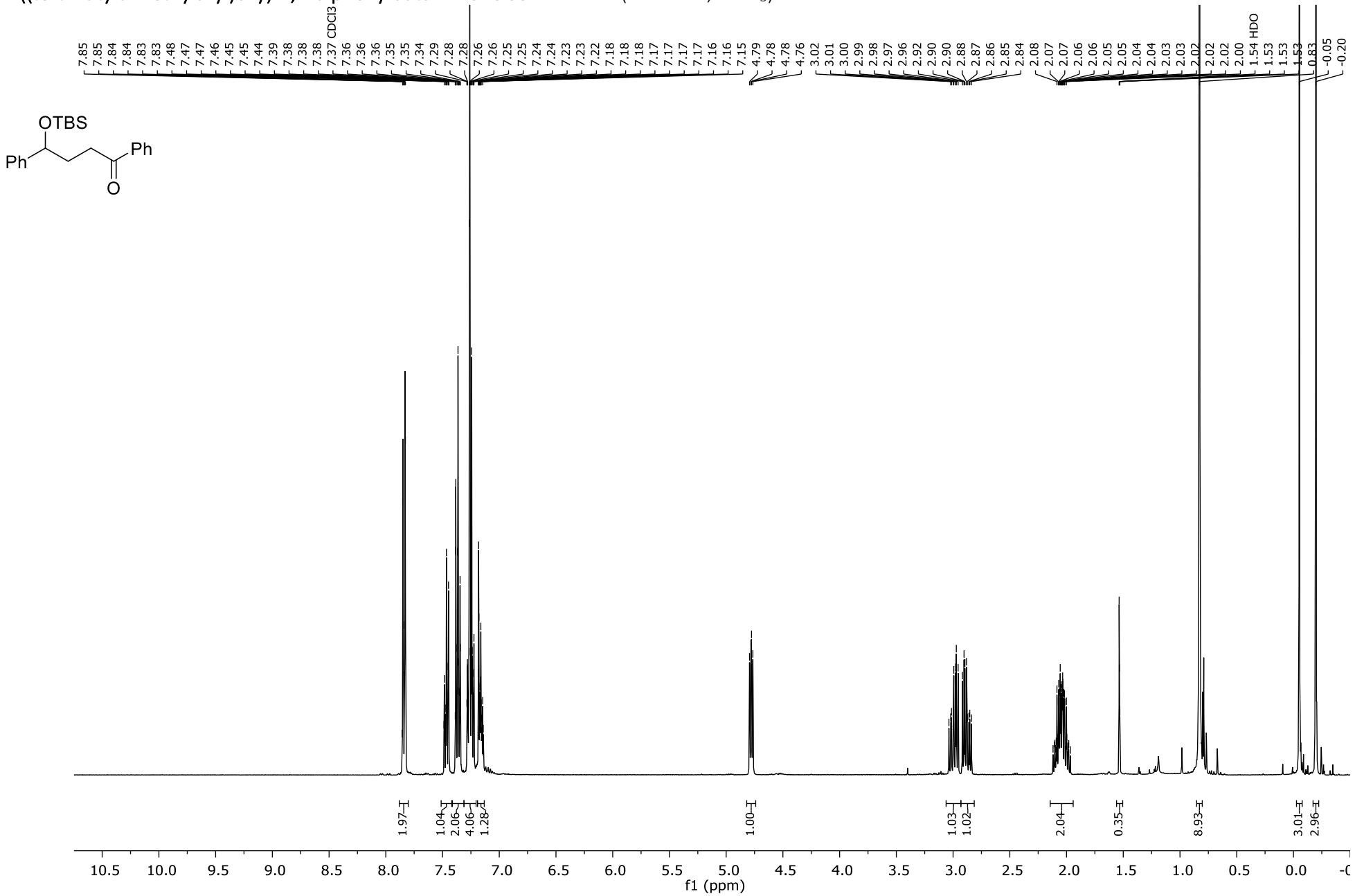
(*E*)-4-Methoxy-4-(4-methoxyphenyl)-1-phenylbut-2-en-1-one S81 ^{1}H NMR (400 MHz, $CDCl_3$)



(*E*)-4-Methoxy-4-(4-methoxyphenyl)-1-phenylbut-2-en-1-one S81 ^{13}C NMR (101 MHz, $CDCl_3$)



4-((*tert*-Butyldimethylsilyl)oxy)-1,4-diphenylbutan-1-one S82 ^{1}H NMR (400 MHz, $CDCl_3$)



4-((*tert*-Butyldimethylsilyl)oxy)-1,4-diphenylbutan-1-one S82 ^{13}C NMR (101 MHz, $CDCl_3$)