Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Nickel/photoredox dual-catalyzed reductive cross-coupling of aryl halides and aldehydes

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Electronic Supplementary Information

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1 General Information

Reactions were performed in flame-dried glassware under a static pressure of nitrogen unless otherwise stated. All the materials were purchased from Bidepharm, Energy Chemical, Adamas-beta® *etc*. and used as received unless otherwise noted. Anhydrous DMSO, DMF, DMAc, Dioxane, CH_3CN (99.8%, extra dry) were purchased from Energy Chemical and stored in a glovebox. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gels using the indicated solvents. The High Resolution MS analyses were performed on BRUKER FT-ICR-MS SolariX 7T with ESI mode. GC analyses were performed on Shimadzu GC 2010 Pro instrument. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a *Bruker* AV600 and *Bruker* AV400 instrument, respectively. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent signals were used as references for ^{1}H (TMS: δ_H = 0.00 ppm) and ^{13}C NMR spectra ($CDCl_3$: δ_C = 77.16 ppm, middle line). *n*-Tridecane was used as an internal standard to calculate GC yields. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br s = broad singlet), coupling constants (Hz), and integration.

The photoreactor is homemade and each vial was illuminated by one lamp bead (parameters: 1.5 W blue LED, λ_{max} = 455 nm, Cree xpe2 royal blue). Unless otherwise photoredox reactions were set-up in 10 mL vial and stirred (800 rpm) at a distance of 1.0 cm from the irradiating plate. In addition, fan (rear part) was used to maintain a temperature of 25−35 °C.

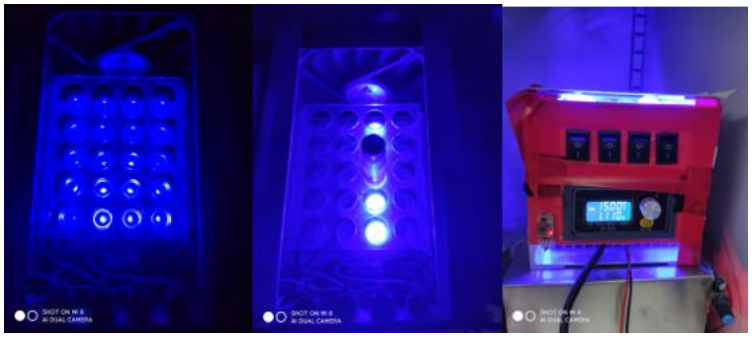
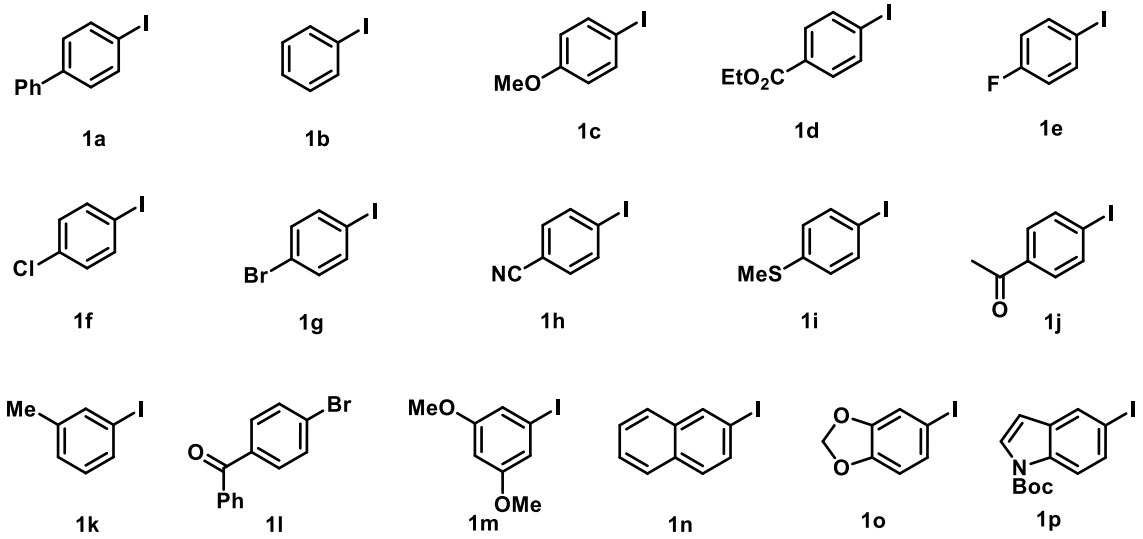


Figure S1. Set-up for photoredox reactions

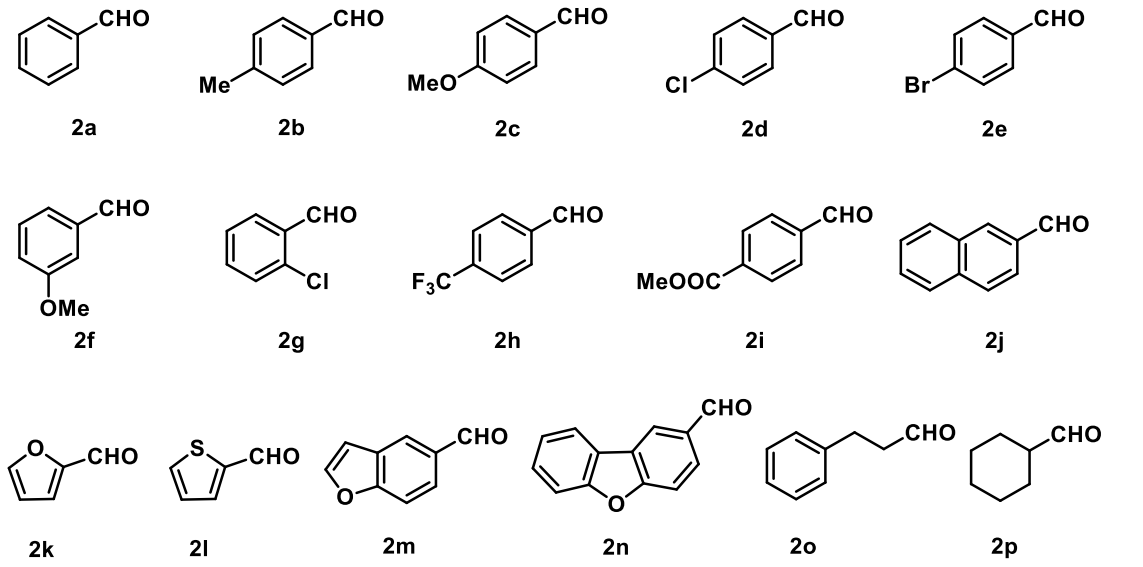
2 Catalysts and Starting Materials

The photocatalysts 4-CzIPN, $Ir[dFppy]_2(dtbbpy)PF_6$, $Ir(ppy)_2(dtbbpy)PF_6$, $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$, $Ir(ppy)_2bpyPF_6$ and $Ir[dF(CF_3)ppy]_2(bpy)PF_6$ were prepared according to the reported procedures[S1]-[S2]. The photocatalysts $Ru(bpy)_3Cl_2$, $Ru(bpy)_3PF_6$, and $Ir(ppy)_3$ were purchased from Energy Chemical.

2.1 The following aryl halides were used in this study

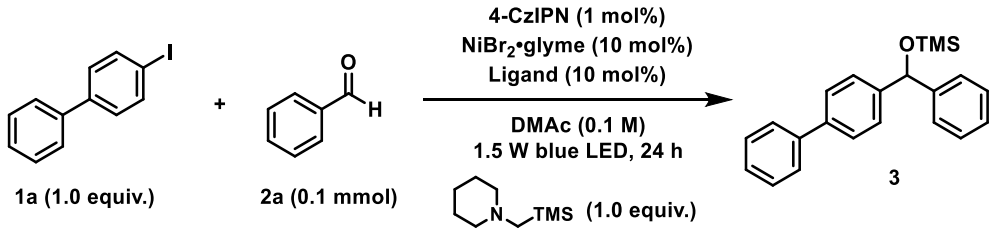


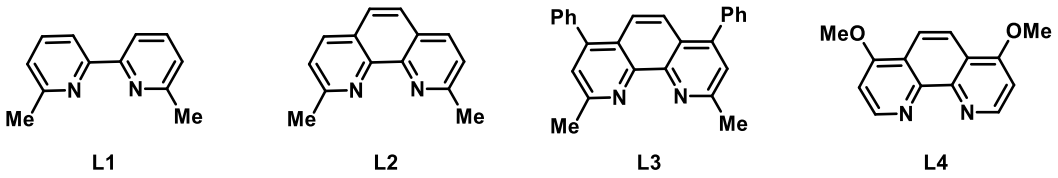
2.2 The following aldehydes were used in this study

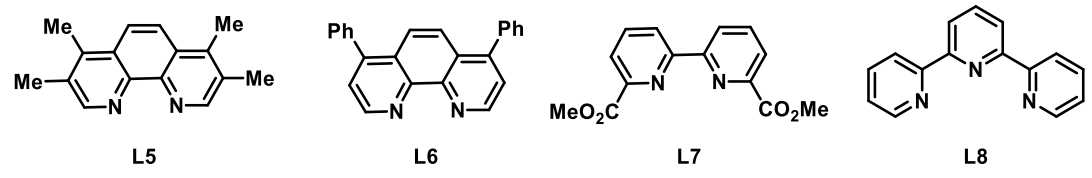


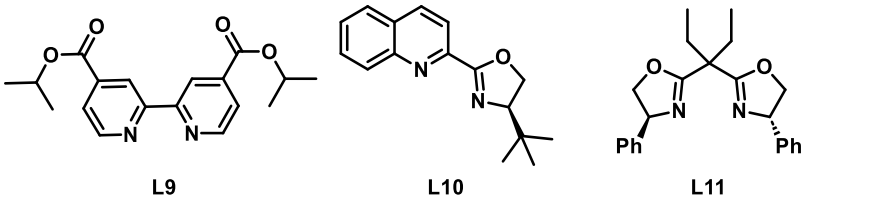
3 Optimization of the Reaction Conditions

3.1 Table S1. The effect of ligands





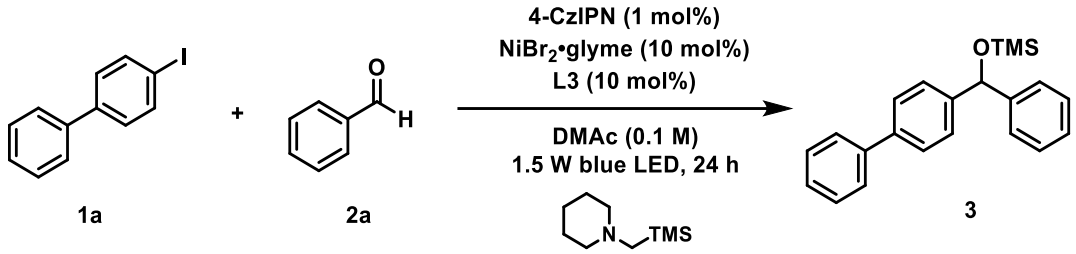




Entry	Ligand	Yield of **3** (%)[a]
1	L1	60
2	L2	63
3	L3	65
4	L4	11
5	L5	8
6	L6	7
7	L7	6
8	L8	trace
9	L9	10
10	L10	28
11	L11	28

[a] GC yield, with tridecane as internal standard.

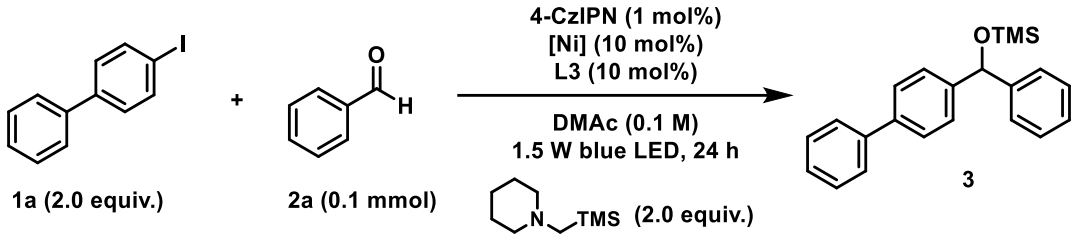
3.2 Table S2. The effect of molar ratio of the reaction components



Entry	Ratio of **1a** : **2a** : silylamine	Yield of **3** (%)[a]
1	1.0 : 1.0 : 1.0	65
2	2.0 : 1.0 : 2.0	89
3	1.0 : 2.0 : 2.0	77
4	2.0 : 2.0 : 1.0	78
5	1.5 : 1.0 : 1.5	80

[a] GC yield, with tridecane as internal standard.

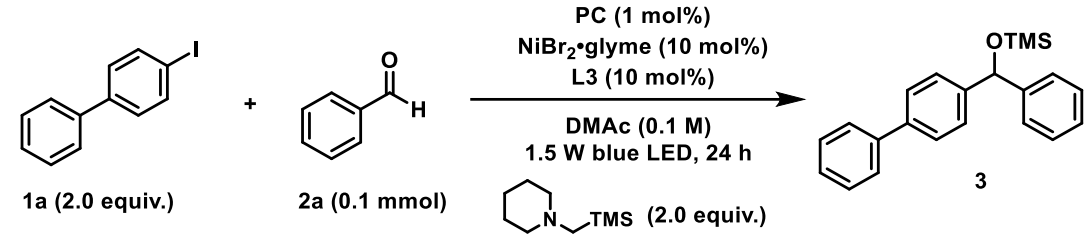
3.3 Table S3. The effect of Ni-catalyst

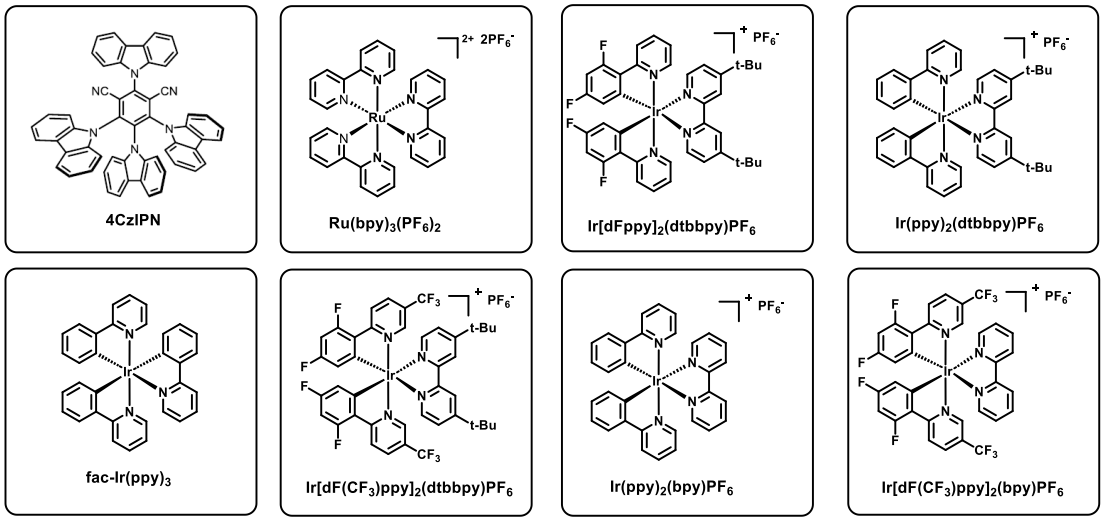


Entry	Ni-catalyst	Yield of **3** (%)[a]
1	$NiBr_2$•glyme	89
2	$NiCl_2$•glyme	27
3	$Ni(cod)_2$	70
4	$Ni(PPh_3)_2Br_2$	77
5	$Ni(acac)_2$	16
6	$NiCl_2$	61
7	$NiBr_2$	85

[a] GC yield, with tridecane as internal standard.

3.4 Table S4. The effect of photocatalysts

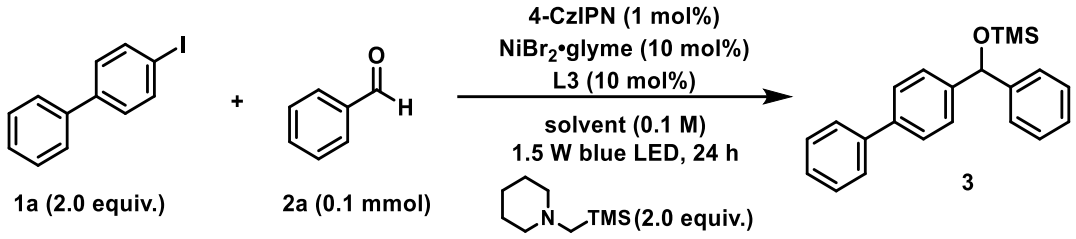




Entry	Photocatalyst	Yield of **3** (%)[a]
1	4-CzIPN	89
2	$Ru(bpy)_3Cl_2$	85
3	$Ru(bpy)_3(PF6)_2$	81
4	$Ir(dF(CF_3)ppy)_2dtbbpyPF_6$	75
5	$Ir(ppy)_2dtbbpyPF_6$	70
6	*fac*-$Ir(ppy)_3$	71
7	$Ir(ppy)_2bpyPF_6$	73
8	$Ir(dF(CF_3)ppy)_2bpyPF_6$	62
9	$Ir(dFppy)_2dtbbpyPF_6$	54

[a] GC yield, with tridecane as internal standard.

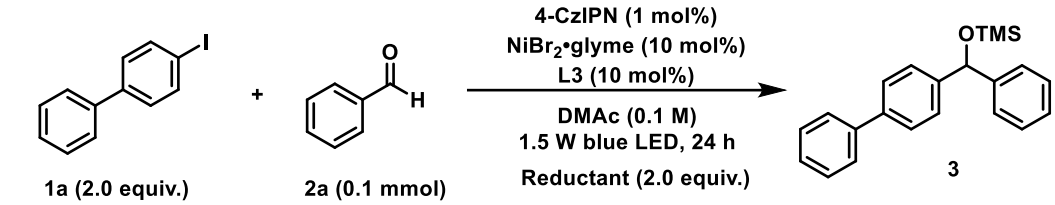
3.5 Table S5. The effect of solvents

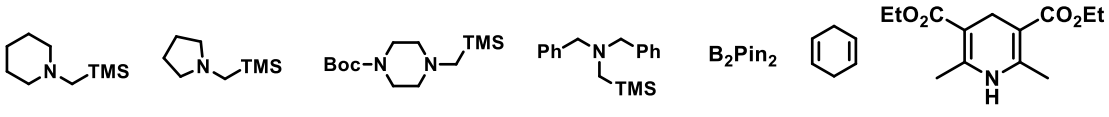


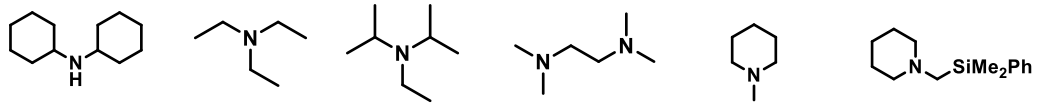
Entry	Solvent	Yield of **3** (%)[a]
1	DMAc	89
2	NMP	78
3	MeCN	8
4	PhMe	trace
5	DMF	41
6	DMSO	0
7	THF	trace

[a] GC yield, with tridecane as internal standard.

3.6 Table S6. The effect of reductants



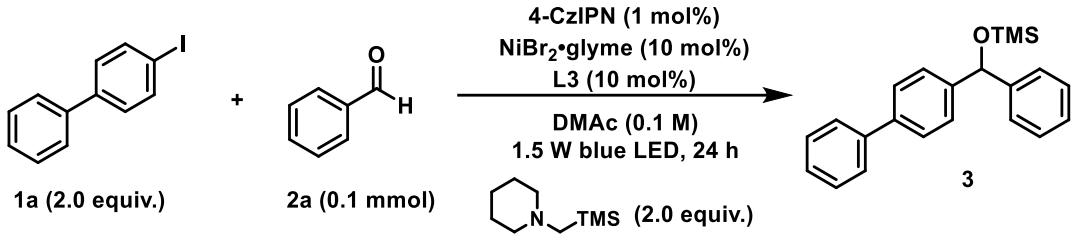




Entry	Reductant	Yield of **3** (%)[a]
1	R1	89
2	R2	74
3	R3	64
4	R4	trace
5	R5	0
6	R6	0
7	R7	0
8	R8	0
9	R9	0
10	R10	0
11	R11	0
12	R12	0
13	R12 + TMSOTf	0
14	R12 + TMSCl	0
15	R13	46[b]

[a] GC yield, with tridecane as internal standard. [b] The corresponding $SiMe_2Ph$-protected secondary alcohol was obtained.

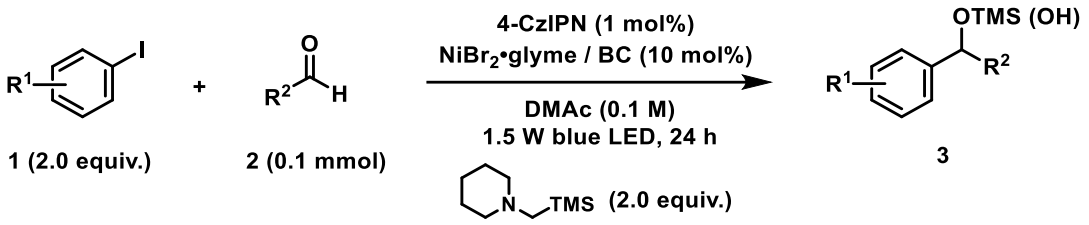
3.7 Table S7. Control experiments



Entry	Deviation	Yield of **3** (%)[a]
1	none	89
2	no Ni	0
3	no Ligand	32
4	no PC	0
5	no Light	0

[a] GC yield, with tridecane as internal standard.

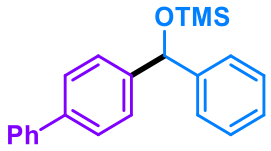
4 General procedure for reductive carbonyl-aryl coupling



The reactions were set up in an N_2 filled glovebox. An oven-dried vial equipped with a stir-bar was added 4-CzIPN (1.6 mg, 2.0 μmol, 0.010 equiv.), **BC** (7.2 mg, 20 μmol, 0.10 equiv.), $NiBr_2$•glyme (6.4 mg, 20 μmol, 0.10 equiv.), aryl iodide **1** (0.40 mmol, 2.0 equiv.), aldehyde **2** (0.20 mmol, 1.0 equiv.). Then, DMAc (0.10 M, 2.0 mL), reductant **R3** (69 mg, 0.40 mmol, 2.0 equiv.) were added. The vial was sealed and removed from the glovebox, then irradiated with a 1.5 W blue LED lamp (at approximately 1.0 cm away from the light source) with cooling from a fan for 24 h. The reaction was quenched by H_2O, extracted with ethyl acetate (60 mL). The combined organic layers were washed with brine, dried with Na_2SO_4, filtered, and concentrated in vacuo. Then the residue was purified by flash chromatography to give the corresponding product.

5 Spectroscopic data of the products

([1,1'-Biphenyl]-4-yl(phenyl)methoxy)trimethylsilane (3)

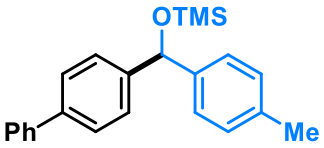


Chemical Formula: $C_{22}H_{24}OSi$
Exact Mass: 332.1596

Prepared according to the general procedure using **1a** (112.0 mg, 0.4 mmol, 2.0 equiv.), **2a** (21.2 mg, 0.2 mmol, 1.0 equiv.), **R3** (69 mg, 0.40 mmol, 2.0 equiv.), 4-CzIPN (1.6 mg, 2.0 μmol, 0.010 equiv.), BC (7.2 mg, 20 μmol, 0.10 equiv.), $NiBr_2$•glyme (6.4 mg, 20 μmol, 0.10 equiv.) in DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE / EA = 200:1 to 100:1, visualized by UV) to give the corresponding product (62.4 mg, 93% yield) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 – 7.61 (m, 2H), 7.60 – 7.57 (m, 2H), 7.49 – 7.43 (m, 6H), 7.40 – 7.35 (m, 3H), 7.31 – 7.29 (m, 1H), 5.87 (s, 1H), 0.16 (s, 9H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.9, 144.1, 141.1, 140.0, 128.8, 128.4, 127.5, 127.3, 127.2, 127.1, 127.0, 126.7, 76.4, 0.3 ppm. **HRMS** (ESI) for $C_{22}H_{25}OSi^+$ [$(M+H)^+$]: calculated 333.1669, found 333.1645.

([1,1'-Biphenyl]-4-yl(p-tolyl)methoxy)trimethylsilane (4)



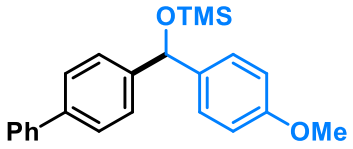
Chemical Formula: $C_{23}H_{26}OSi$
Exact Mass: 346.1753

Prepared according to the general procedure using **1a** (112.0 mg, 0.4 mmol, 2.0 equiv.), **2b** (24.0 mg, 0.2 mmol, 1.0 equiv.), **R3** (69 mg, 0.40 mmol, 2.0 equiv.), 4-CzIPN (1.6 mg, 2.0 μmol, 0.010 equiv.), BC (7.2 mg, 20 μmol, 0.10 equiv.), $NiBr_2$•glyme (6.4 mg, 20 μmol, 0.10 equiv.) in DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE / EA = 200:1 to 100:1, visualized by UV) to give the corresponding product (31.1 mg, 45% yield) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (m, 4H), 7.47 – 7.41 (m, 4H), 7.35 (t, *J* = 7.4 Hz,

1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 7.6 Hz, 2H), 5.82 (s, 1H), 2.36 (s, 3H), 0.14 (s, 9H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.3, 142.0, 141.2, 140.0, 136.9, 129.1, 128.8, 127.24, 127.20, 127.1, 127.0, 126.7, 76.3, 21.3, 0.2 ppm. **HRMS** (ESI) for $C_{23}H_{26}OSiNa^+$ [$(M+Na)^+$]: calculated 369.1645, found 369.1654.

([1,1'-Biphenyl]-4-yl(4-methoxyphenyl)methoxy)trimethylsilane (5)

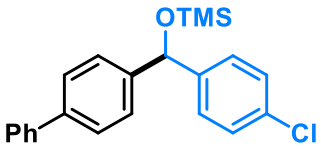


Chemical Formula: $C_{23}H_{26}O_2Si$
Exact Mass: 362.1702

Prepared according to the general procedure using **1a** (112.0 mg, 0.4 mmol, 2.0 equiv.), **2c** (27.2 mg, 0.2 mmol, 1.0 equiv.), **R3** (69 mg, 0.40 mmol, 2.0 equiv.), 4-CzIPN (1.6 mg, 2.0 μmol, 0.010 equiv.), BC (7.2 mg, 20 μmol, 0.10 equiv.), $NiBr_2$•glyme (6.4 mg, 20 μmol, 0.10 equiv.) in DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE / EA = 200:1 to 100:1, visualized by UV) to give the corresponding product (47.0 mg, 65% yield) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 – 7.56 (m, 2H), 7.53 – 7.51 (m, 2H), 7.42 – 7.38 (m, 4H), 7.32 – 7.30 (m, 1H), 7.28 – 7.27 (m, 2H), 6.86 – 6.84 (m, 2H), 5.77 (s, 1H), 3.78 (s, 3H), 0.09 (s, 9H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 158.8, 144.3, 141.1, 139.9, 137.2, 128.8, 127.9, 127.3, 127.2, 127.1, 126.9, 113.8, 75.9, 55.4, 0.3 ppm. **HRMS** (ESI) for $C_{23}H_{27}O_2Si^+$ [$(M+H)^+$]: calculated 363.1775, found 363.1781.

([1,1'-Biphenyl]-4-yl(4-chlorophenyl)methoxy)trimethylsilane (6)



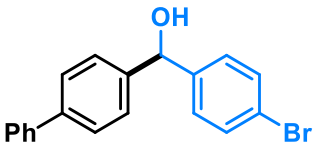
Chemical Formula: $C_{22}H_{23}ClOSi$
Exact Mass: 366.1207

Prepared according to the general procedure using **1a** (112.0 mg, 0.4 mmol, 2.0 equiv.), **2d** (28.1 mg, 0.2 mmol, 1.0 equiv.), **R3** (69 mg, 0.40 mmol, 2.0 equiv.), 4-CzIPN (1.6 mg, 2.0 μmol, 0.010 equiv.), BC (7.2 mg, 20 μmol, 0.10 equiv.), $NiBr_2$•glyme (6.4 mg,

20 μmol, 0.10 equiv.) in DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE / EA = 200:1 to 100:1, visualized by UV) to give the corresponding product (51.2 mg, 70% yield) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 – 7.58 (m, 2H), 7.57 – 7.55 (m, 2H), 7.45 – 7.43 (m, 2H), 7.41 – 7.39 (m, 2H), 7.37 – 7.33 (m, 3H), 7.32 – 7.29 (m, 2H), 5.80 (s, 1H), 0.13 (s, 9H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.6, 143.5, 140.9, 140.3, 132.9, 128.8, 128.6, 127.9, 127.4, 127.2, 127.2, 126.9, 75.8, 0.3 ppm. **HRMS** (ESI) for $C_{22}H_{23}ClOSiNa^+$ [$(M+Na)^+$]: calculated 389.1099, found 389.1107.

[1,1'-Biphenyl]-4-yl(4-bromophenyl)methanol (7)

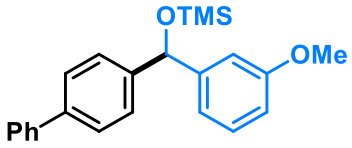


Chemical Formula: $C_{19}H_{15}BrO$
Exact Mass: 338.0306

Prepared according to the general procedure using **1a** (112.0 mg, 0.4 mmol, 2.0 equiv.), **2e** (37.0 mg, 0.2 mmol, 1.0 equiv.), **R3** (69 mg, 0.40 mmol, 2.0 equiv.), 4-CzIPN (1.6 mg, 2.0 μmol, 0.010 equiv.), BC (7.2 mg, 20 μmol, 0.10 equiv.), $NiBr_2$•glyme (6.4 mg, 20 μmol, 0.10 equiv.) in DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE / EA = 20:1 to 10:1, visualized by UV) to give the corresponding product (31.7 mg, 47% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.3 Hz, 4H), 7.54 – 7.41 (m, 6H), 7.38 (t, *J* = 7.3 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 2H), 5.86 (s, 1H), 2.47 (s, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.7, 142.4, 140.8, 140.6, 131.6, 128.8, 128.3, 127.44, 127.42, 127.1, 127.0, 121.5, 75.5 ppm. **HRMS** (ESI) for $C_{19}H_{16}BrO^+$ [$(M+H)^+$]: calculated 339.0379, found 339.0385.

([1,1'-Biphenyl]-4-yl(3-methoxyphenyl)methoxy)trimethylsilane (8)

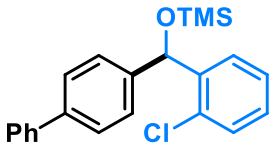


Chemical Formula: $C_{23}H_{26}O_2Si$
Exact Mass: 362.1702

Prepared according to the general procedure using **1a** (112.0 mg, 0.4 mmol, 2.0 equiv.), **2f** (27.2 mg, 0.2 mmol, 1.0 equiv.), **R3** (69 mg, 0.40 mmol, 2.0 equiv.), 4-CzIPN (1.6 mg, 2.0 μmol, 0.010 equiv.), BC (7.2 mg, 20 μmol, 0.10 equiv.), $NiBr_2$•glyme (6.4 mg, 20 μmol, 0.10 equiv.) in DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE / EA = 200:1 to 100:1, visualized by UV) to give the corresponding product (45.6 mg, 63% yield) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 (m, 4H), 7.48 (m, 4H), 7.38 (m, 1H), 7.32 – 7.27 (m, 1H), 7.08 – 7.01 (m, 2H), 6.84 (m, 1H), 5.85 (s, 1H), 3.85 (s, 3H), 0.19 (s, 9H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.7, 146.5, 143.9, 141.0, 140.1, 129.3, 128.8, 127.2, 127.13, 127.06, 127.0, 119.1, 112.4, 112.3, 76.3, 55.2, 0.3 ppm. **HRMS** (ESI) for $C_{23}H_{27}OSi^+$ [$(M+H)^+$]: calculated 363.1775, found 363.1780.

([1,1'-Biphenyl]-4-yl(2-chlorophenyl)methoxy)trimethylsilane (9)



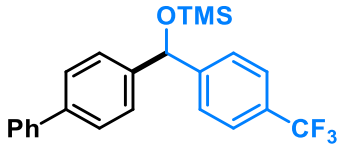
Chemical Formula: $C_{22}H_{23}ClOSi$
Exact Mass: 366.1207

Prepared according to the general procedure using **1a** (112.0 mg, 0.4 mmol, 2.0 equiv.), **2g** (28.1 mg, 0.2 mmol, 1.0 equiv.), **R3** (69 mg, 0.40 mmol, 2.0 equiv.), 4-CzIPN (1.6 mg, 2.0 μmol, 0.010 equiv.), BC (7.2 mg, 20 μmol, 0.10 equiv.), $NiBr_2$•glyme (6.4 mg, 20 μmol, 0.10 equiv.) in DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE / EA = 200:1 to 100:1, visualized by UV) to give the corresponding product (35.1 mg, 48% yield) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.84 – 7.82 (m, 2H), 7.80 – 7.78 (m, 2H), 7.71 – 7.69 (m, 2H), 7.68 – 7.66 (m, 2H), 7.61 – 7.58 (m, 2H), 7.55 –

7.53 (m, 1H), 7.47 – 7.44 (m, 1H), 6.53 (s, 1H), 0.38 (s, 9H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.7, 142.4, 141.1, 140.2, 131.9, 131.1, 129.3, 128.8, 128.5, 128.3, 127.3, 127.2, 127.1, 126.2, 72.3, 0.2 ppm. **HRMS** (ESI) for $C_{22}H_{23}ClOSiNa^+$ [$(M+Na)^+$]: calculated 389.1099, found 389.1107.

([1,1'-Biphenyl]-4-yl(4-(trifluoromethyl)phenyl)methoxy)trimethylsilane (10)

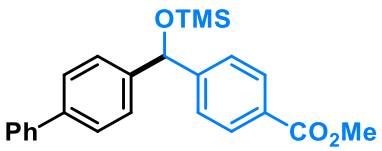


Chemical Formula: $C_{23}H_{23}F_3OSi$
Exact Mass: 400.1470

Prepared according to the general procedure using **1a** (112.0 mg, 0.4 mmol, 2.0 equiv.), **2h** (34.8 mg, 0.2 mmol, 1.0 equiv.), **R3** (69 mg, 0.40 mmol, 2.0 equiv.), 4-CzIPN (1.6 mg, 2.0 μmol, 0.010 equiv.), BC (7.2 mg, 20 μmol, 0.10 equiv.), $NiBr_2$•glyme (6.4 mg, 20 μmol, 0.10 equiv.) in DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE / EA = 200:1 to 100:1, visualized by UV) to give the corresponding product (51.2 mg, 64% yield) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 – 7.59 (m, 4H), 7.59 – 7.57 (m, 2H), 7.55 (d, *J* = 8.1 Hz, 2H), 7.47 – 7.44 (m, 2H), 7.43 (d, *J* = 8.2 Hz, 2H), 7.38 – 7.34 (m, 1H), 5.88 (s, 1H), 0.15 (s, 9H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 148.9, 143.2, 140.9, 140.6, 129.3 (q, $J_{C\text{-}F}$ = 31.7 Hz), 128.9, 127.4, 127.3, 127.2, 127.1, 126.8, 125.4 (q, $J_{C\text{-}F}$ = 3.1 Hz), 125.3 (q, $J_{C\text{-}F}$ = 271.8 Hz), 76.0, 0.3 ppm. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.32 ppm. **HRMS** (ESI) for $C_{23}H_{23}F_3OSiNa^+$ [$(M+Na)^+$]: calculated 423.1362, found 423.13. **Melting point:** 38.9~40.2 °C.

Methyl 4-([1,1'-biphenyl]-4-yl((trimethylsilyl)oxy)methyl)benzoate (11)



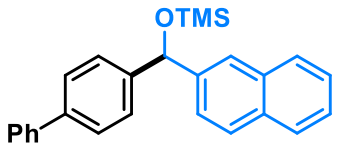
Chemical Formula: $C_{24}H_{26}O_3Si$
Exact Mass: 390.1651

Prepared according to the general procedure using **1a** (112.0 mg, 0.4 mmol, 2.0 equiv.),

2i (32.8 mg, 0.2 mmol, 1.0 equiv.), **R3** (69 mg, 0.40 mmol, 2.0 equiv.), 4-CzIPN (1.6 mg, 2.0 μmol, 0.010 equiv.), BC (7.2 mg, 20 μmol, 0.10 equiv.), $NiBr_2$•glyme (6.4 mg, 20 μmol, 0.10 equiv.) in DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE / EA = 100:1 to 50:1, visualized by UV) to give the corresponding product (41.3 mg, 53% yield) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.4 Hz, 2H), 7.58 (m, 4H), 7.50 (m, 2H), 7.47 – 7.40 (m, 4H), 7.36 (m, 1H), 5.87 (s, 1H), 3.93 (s, 3H), 0.14 (s, 9H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.0, 149.9, 143.2, 140.8, 140.3, 129.7, 129.0, 128.8, 127.3, 127.2, 127.1, 127.0, 126.4, 76.0, 52.1, 0.1 ppm. **HRMS** (ESI) for $C_{24}H_{26}O_3SiNa^+$ [$(M+Na)^+$]: calculated 413.1543, found 413.1552.

([1,1'-Biphenyl]-4-yl(naphthalen-2-yl)methoxy)trimethylsilane (12)

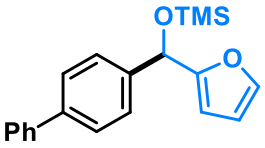


Chemical Formula: $C_{26}H_{26}OSi$
Exact Mass: 382.1753

Prepared according to the general procedure using **1a** (112.0 mg, 0.4 mmol, 2.0 equiv.), **2j** (31.2 mg, 0.2 mmol, 1.0 equiv.), **R3** (69 mg, 0.40 mmol, 2.0 equiv.), 4-CzIPN (1.6 mg, 2.0 μmol, 0.010 equiv.), BC (7.2 mg, 20 μmol, 0.10 equiv.), $NiBr_2$•glyme (6.4 mg, 20 μmol, 0.10 equiv.) in DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE / EA = 200:1 to 100:1, visualized by UV) to give the corresponding product (59.5 mg, 78% yield) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.91 – 7.89 (m, 1H), 7.86 – 7.83 (m, 2H), 7.63 – 7.61 (m, 2H), 7.60 – 7.58 (m, 2H), 7.55 – 7.50 (m, 5H), 7.48 – 7.45 (m, 2H), 7.38 – 7.36 (m, 1H), 6.03 (s, 1H), 0.19 (s, 9H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.9, 142.3, 141.1, 140.1, 133.4, 132.9, 128.8, 128.3, 128.2, 127.8, 127.5, 127.3, 127.2, 127.1, 126.2, 125.9, 125.2, 125.0, 76.6, 0.3 ppm. **HRMS** (ESI) for $C_{26}H_{27}OSi^+$ [$(M+H)^+$]: calculated 383.1826, found 383.18.

([1,1'-Biphenyl]-4-yl(furan-2-yl)methoxy)trimethylsilane (13)

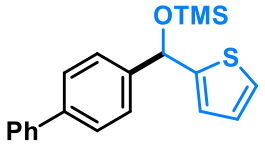


Chemical Formula: $C_{20}H_{22}O_2Si$
Exact Mass: 322.1389

Prepared according to the general procedure using **1a** (112.0 mg, 0.4 mmol, 2.0 equiv.), **2k** (19.2 mg, 0.2 mmol, 1.0 equiv.), **R3** (69 mg, 0.40 mmol, 2.0 equiv.), 4-CzIPN (1.6 mg, 2.0 μmol, 0.010 equiv.), BC (7.2 mg, 20 μmol, 0.10 equiv.), $NiBr_2$•glyme (6.4 mg, 20 μmol, 0.10 equiv.) in DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE / EA = 200:1 to 100:1, visualized by UV) to give the corresponding product (27.7 mg, 43% yield) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 – 7.56 (m, 4H), 7.56-7.55 (m, 1H), 7.48 (m, 1H), 7.43 (m, 2H), 7.37 – 7.32 (m, 2H), 6.31 – 6.30 (m, 1H), 6.13 (d, *J* = 3.0 Hz, 1H), 5.83 (s, 1H), 0.13 (s, 9H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 156.6, 142.4, 141.1, 140.9, 140.5, 128.8, 127.3, 127.2, 127.1, 126.9, 110.3, 107.3, 70.1, 0.1 ppm. **HRMS** (ESI) for $C_{20}H_{23}O_2Si^+$ [$(M+H)^+$]: calculated 323.1462, found 345.1468.

([1,1'-Biphenyl]-4-yl(thiophen-2-yl)methoxy)trimethylsilane (14)



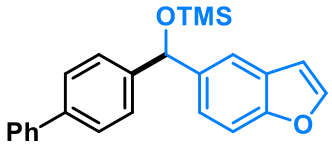
Chemical Formula: $C_{20}H_{22}OSSi$
Exact Mass: 338.1161

Prepared according to the general procedure using **1a** (112.0 mg, 0.4 mmol, 2.0 equiv.), **2l** (22.4 mg, 0.2 mmol, 1.0 equiv.), **R3** (69 mg, 0.40 mmol, 2.0 equiv.), 4-CzIPN (1.6 mg, 2.0 μmol, 0.010 equiv.), BC (7.2 mg, 20 μmol, 0.10 equiv.), $NiBr_2$•glyme (6.4 mg, 20 μmol, 0.10 equiv.) in DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE / EA = 200:1 to 100:1, visualized by UV) to give the corresponding product (41.9 mg, 62% yield) as a light yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 – 7.51 (m, 2H), 7.50 – 7.48 (m, 2H), 7.41 – 7.39 (m, 2H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.27 – 7.24 (m, 1H), 7.15 – 7.14 (m, 1H), 6.84 – 6.83 (m,

1H), 6.75 (d, *J* = 1.2 Hz, 1H), 5.96 (s, 1H), 0.06 (s, 9H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 149.8, 143.3, 140.9, 140.5, 128.9, 127.4, 127.2, 127.1, 126.8, 126.6, 125.0, 124.2, 72.6, 0.2 ppm. **HRMS** (ESI) for $C_{20}H_{22}OSSiNa^+$ [$(M+Na)^+$]: calculated 361.1053, found 361.1061. **Melting point:** 47.6 - 48.7 °C.

([1,1'-Biphenyl]-4-yl(benzofuran-5-yl)methoxy)trimethylsilane (15)

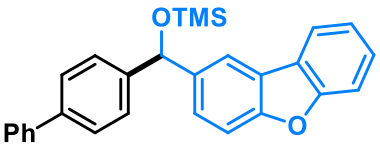


Chemical Formula: $C_{24}H_{24}O_2Si$
Exact Mass: 372.1546

Prepared according to the general procedure using **1a** (112.0 mg, 0.4 mmol, 2.0 equiv.), **2m** (29.2 mg, 0.2 mmol, 1.0 equiv.), **R3** (69 mg, 0.40 mmol, 2.0 equiv.), 4-CzIPN (1.6 mg, 2.0 μmol, 0.010 equiv.), BC (7.2 mg, 20 μmol, 0.10 equiv.), $NiBr_2$•glyme (6.4 mg, 20 μmol, 0.10 equiv.) in DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE / EA = 200:1 to 100:1, visualized by UV) to give the corresponding product (37.9 mg, 51% yield) as a light yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (m, 1H), 7.63 (m, 1H), 7.61 – 7.53 (m, 4H), 7.49 – 7.41 (m, 5H), 7.38 – 7.30 (m, 2H), 6.77 (m, 1H), 5.95 (s, 1H), 0.14 (s, 9H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.3, 145.3, 144.3, 141.0, 139.9, 139.6, 128.7, 127.3, 127.13, 127.07, 127.0, 126.9, 123.3, 119.1, 111.1, 106.8, 76.4, 0.2 ppm. **HRMS** (ESI) for $C_{24}H_{24}O_2SiNa^+$ [$(M+Na)^+$]: calculated 395.1438, found 395.1443.

([1,1'-Biphenyl]-4-yl(dibenzo[b,d]furan-2-yl)methoxy)trimethylsilane (16)



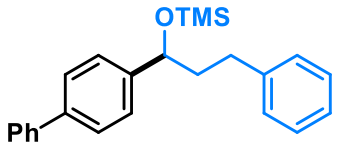
Chemical Formula: $C_{28}H_{26}O_2Si$
Exact Mass: 422.1702

Prepared according to the general procedure using **1a** (112.0 mg, 0.4 mmol, 2.0 equiv.), **2n** (39.2 mg, 0.2 mmol, 1.0 equiv.), **R3** (69 mg, 0.40 mmol, 2.0 equiv.), 4-CzIPN (1.6 mg, 2.0 μmol, 0.010 equiv.), BC (7.2 mg, 20 μmol, 0.10 equiv.), $NiBr_2$•glyme (6.4 mg,

20 μmol, 0.10 equiv.) in DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE / EA = 200:1 to 100:1, visualized by UV) to give the corresponding product (60.8 mg, 72% yield) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (m, 2H), 7.65 – 7.54 (m, 6H), 7.54 – 7.42 (m, 6H), 7.37-7.35 (m, 2H), 6.04 (s, 1H), 0.19 (s, 9H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.6, 155.5, 144.2, 141.0, 140.0, 139.7, 128.7, 127.2, 127.13, 127.10, 127.07, 126.9, 126.1, 124.3, 124.2, 122.7, 120.8, 118.7, 111.7, 111.4, 76.4, 0.3 ppm. **HRMS** (ESI) for $C_{28}H_{26}O_2SiNa^+$ [$(M+Na)^+$]: calculated 445.1594, found 445.1599.

(1-([1,1'-Biphenyl]-4-yl)-3-phenylpropoxy)trimethylsilane (17)

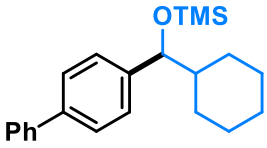


Chemical Formula: $C_{24}H_{28}OSi$
Exact Mass: 360.1909

Prepared according to the general procedure using **1a** (112.0 mg, 0.4 mmol, 2.0 equiv.), **2o** (26.8 mg, 0.2 mmol, 1.0 equiv.), **R3** (69 mg, 0.40 mmol, 2.0 equiv.), 4-CzIPN (1.6 mg, 2.0 μmol, 0.010 equiv.), BC (7.2 mg, 20 μmol, 0.10 equiv.), $NiBr_2$•glyme (6.4 mg, 20 μmol, 0.10 equiv.) in DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE / EA = 200:1 to 100:1, visualized by UV) to give the corresponding product (21.5 mg, 31% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.4 Hz, 2H), 7.56 – 7.54 (m, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.38 (d, *J* = 7.9 Hz, 2H), 7.35 – 7.30 (m, 1H), 7.28 – 7.24 (m, 2H), 7.22 – 7.14 (m, 3H), 4.72-4.70 (m, 1H), 2.80 – 2.57 (m, 2H), 2.14 – 1.93 (m, 2H), 0.07 (s, 9H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.4, 142.3, 141.1, 140.0, 128.8, 128.5, 128.4, 127.3, 127.2, 127.0, 126.5, 125.8, 74.3, 42.2, 32.2, 0.4 ppm. **HRMS** (ESI) for $C_{24}H_{29}OSi^+$ [$(M+H)^+$]: calculated 361.1982, found 361.19.

([1,1'-Biphenyl]-4-yl(cyclohexyl)methoxy)trimethylsilane (18)

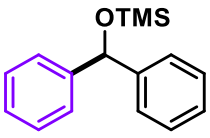


Chemical Formula: $C_{22}H_{30}OSi$
Exact Mass: 338.2066

Prepared according to the general procedure using **1a** (112.0 mg, 0.4 mmol, 2.0 equiv.), **2p** (22.4 mg, 0.2 mmol, 1.0 equiv.), **R3** (69 mg, 0.40 mmol, 2.0 equiv.), 4-CzIPN (1.6 mg, 2.0 μmol, 0.010 equiv.), BC (7.2 mg, 20 μmol, 0.10 equiv.), $NiBr_2$•glyme (6.4 mg, 20 μmol, 0.10 equiv.) in DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE / EA = 200:1 to 100:1, visualized by UV) to give the corresponding product (20.3 mg, 30% yield) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.2 Hz, 2H), 7.53 (d, *J* = 7.9 Hz, 2H), 7.44 – 7.41 (m, 2H), 7.34 – 7.30 (m, 3H), 4.31 (d, *J* = 6.9 Hz, 1H), 1.93 (d, *J* = 13.1 Hz, 1H), 1.75 – 1.72 (m, 1H), 1.68 – 1.61 (m, 2H), 1.23 – 1.08 (m, 4H), 1.04 – 0.84 (m, 3H), 0.01 (s, 9H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.6, 141.2, 139.6, 128.8, 127.3, 127.2, 127.1, 126.6, 79.7, 46.0, 29.7, 29.0, 26.7, 0.3 ppm. **HRMS** (ESI) for $C_{22}H_{31}OSi^+$ [$(M+H)^+$]: calculated 339.2139, found 339.2143.

(Benzhydryloxy)trimethylsilane (19)



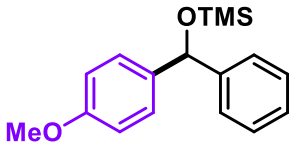
Chemical Formula: $C_{16}H_{20}OSi$
Exact Mass: 256.1283

Prepared according to the general procedure using **1b** (81.6 mg, 0.4 mmol, 2.0 equiv.), **2a** (21.2 mg, 0.2 mmol, 1.0 equiv.), **R3** (69 mg, 0.40 mmol, 2.0 equiv.), 4-CzIPN (1.6 mg, 2.0 μmol, 0.010 equiv.), BC (7.2 mg, 20 μmol, 0.10 equiv.), $NiBr_2$•glyme (6.4 mg, 20 μmol, 0.10 equiv.) in DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE / EA = 200:1 to 100:1, visualized by UV) to give the corresponding product (27.1 mg, 53% yield) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 4H), 7.31 – 7.26 (m, 4H), 7.23 – 7.19 (m,

2H), 5.76 (s, 1H), 0.07 (s, 9H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.9, 128.3, 127.2, 126.7, 76.6, 0.3 ppm. **HRMS** (ESI) for $C_{16}H_{21}OSi^+$ [$(M+H)^+$]: calculated 257.1356, found 257.1363.

((4-Methoxyphenyl)(phenyl)methoxy)trimethylsilane (20)

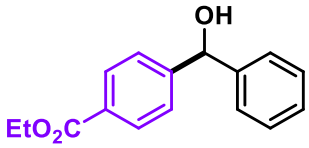


Chemical Formula: $C_{17}H_{22}O_2Si$
Exact Mass: 286.1389

Prepared according to the general procedure using **1c** (93.6 mg, 0.4 mmol, 2.0 equiv.), **2a** (21.2 mg, 0.2 mmol, 1.0 equiv.), **R3** (69 mg, 0.40 mmol, 2.0 equiv.), 4-CzIPN (1.6 mg, 2.0 μmol, 0.010 equiv.), BC (7.2 mg, 20 μmol, 0.10 equiv.), $NiBr_2$•glyme (6.4 mg, 20 μmol, 0.10 equiv.) in DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE / EA = 200:1 to 100:1, visualized by UV) to give the corresponding product (38.3 mg, 67% yield) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 – 7.47 (m, 1H), 7.33 – 7.26 (m, 3H), 7.24 – 7.19 (m, 2H), 6.97 – 6.95 (m, 1H), 6.84 – 6.82 (m, 2H), 5.75 (s, 1H), 3.81 (s, 3H), 0.09 (s, 9H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 158.7,137.3, 128.3, 127.9 (2 C), 126.5, 114.3, 113.7, 76.2, 55.4, 0.3 ppm. **HRMS** (ESI) for $C_{17}H_{23}O_2Si^+$ [$(M+H)^+$]: calculated 287.1462, found 287.1467.

Ethyl 4-(hydroxy(phenyl)methyl)benzoate (21)



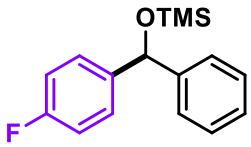
Chemical Formula: $C_{16}H_{16}O_3$
Exact Mass: 256.1099

Prepared according to the general procedure using **1d** (110.4 mg, 0.4 mmol, 2.0 equiv.), **2a** (21.2 mg, 0.2 mmol, 1.0 equiv.), **R3** (69 mg, 0.40 mmol, 2.0 equiv.), 4-CzIPN (1.6 mg, 2.0 μmol, 0.010 equiv.), BC (7.2 mg, 20 μmol, 0.10 equiv.), $NiBr_2$•glyme (6.4 mg, 20 μmol, 0.10 equiv.) in DMAc (0.10 M, 2.0 mL). The residue was purified by flash

column chromatography (PE / EA = 20:1 to 10:1, visualized by UV) to give the corresponding product (36.3 mg, 71% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.36 – 7.24 (m, 5H), 5.86 (s, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 2.57 (s, 1H), 1.37 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.6, 148.7, 143.4, 129.8, 129.7, 128.8, 128.1, 126.8, 126.4, 76.0, 61.1, 14.4 ppm. **HRMS** (ESI) for $C_{16}H_{17}O_3^+$ [(M+H)$^+$]: calculated 257.1172, found 257.1170.

((4-Fluorophenyl)(phenyl)methoxy)trimethylsilane (22)

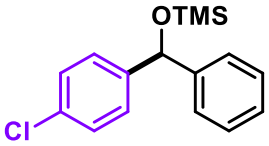


Chemical Formula: $C_{16}H_{19}FOSi$
Exact Mass: 274.1189

Prepared according to the general procedure using **1e** (88.8 mg, 0.4 mmol, 2.0 equiv.), **2a** (21.2 mg, 0.2 mmol, 1.0 equiv.), **R3** (69 mg, 0.40 mmol, 2.0 equiv.), 4-CzIPN (1.6 mg, 2.0 μmol, 0.010 equiv.), BC (7.2 mg, 20 μmol, 0.10 equiv.), $NiBr_2$•glyme (6.4 mg, 20 μmol, 0.10 equiv.) in DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE / EA = 200:1 to 100:1, visualized by UV) to give the corresponding product (30.6 mg, 56% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.28 (m, 5H), 7.28 – 7.19 (m, 2H), 7.00 –6.95 (m, 2H), 5.74 (s, 1H), 0.07 (s, 9H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 162.8 (d, $J_{C\text{-}F}$ = 244.6 Hz), 144.8, 140.8 (d, $J_{C\text{-}F}$ = 3.0 Hz), 128.4, 128.3 (d, $J_{C\text{-}F}$ = 7.6 Hz), 127.3, 126.6, 115.2 (d, $J_{C\text{-}F}$ = 22.7 Hz), 76.0, 0.2 ppm. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -115.95 ppm. **HRMS** (ESI) for $C_{16}H_{20}FOSi^+$ [(M+H)$^+$]: calculated 297.1262, found 275.1260.

((4-Chlorophenyl)(phenyl)methoxy)trimethylsilane (23)

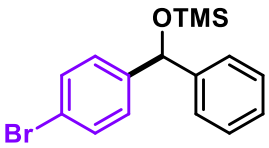


Chemical Formula: $C_{16}H_{19}ClOSi$
Exact Mass: 290.0894

Prepared according to the general procedure using **1f** (95.2 mg, 0.4 mmol, 2.0 equiv.), **2a** (21.2 mg, 0.2 mmol, 1.0 equiv.), **R3** (69 mg, 0.40 mmol, 2.0 equiv.), 4-CzIPN (1.6 mg, 2.0 μmol, 0.010 equiv.), BC (7.2 mg, 20 μmol, 0.10 equiv.), $NiBr_2$•glyme (6.4 mg, 20 μmol, 0.10 equiv.) in DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE / EA = 200:1 to 100:1, visualized by UV) to give the corresponding product (29.5 mg, 51% yield) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 – 7.29 (m, 4H), 7.27 – 7.21 (m, 5H), 5.72 (s, 1H), 0.07 (s, 9H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.5, 143.6, 132.9, 128.5, 128.5, 127.9, 127.4, 126.6, 75.9, 0.2 ppm. **HRMS** (ESI) for $C_{16}H_{20}ClOSi^+$ [$(M+H)^+$]: calculated 291.0966, found 291.0953.

((4-Bromophenyl)(phenyl)methoxy)trimethylsilane (24)

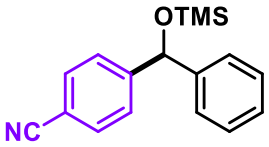


Chemical Formula: $C_{16}H_{19}BrOSi$
Exact Mass: 334.0389

Prepared according to the general procedure using **1g** (113.1 mg, 0.4 mmol, 2.0 equiv.), **2a** (21.2 mg, 0.2 mmol, 1.0 equiv.), **R3** (69 mg, 0.40 mmol, 2.0 equiv.), 4-CzIPN (1.6 mg, 2.0 μmol, 0.010 equiv.), BC (7.2 mg, 20 μmol, 0.10 equiv.), $NiBr_2$•glyme (6.4 mg, 20 μmol, 0.10 equiv.) in DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE / EA = 200:1 to 100:1, visualized by UV) to give the corresponding product (35.4 mg, 53% yield) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 – 7.39 (m, 2H), 7.35 – 7.30 (m, 4H), 7.29 – 7.22 (m, 3H), 5.74 (s, 1H), 0.11 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.3, 144.0, 131.3, 128.3, 128.2, 127.3, 126.5, 120.9, 75.9, 0.1. **HRMS** (ESI) for $C_{16}H_{20}BrOSi^+$ [$(M+H)^+$]: calculated 335.0461, found 335.0470.

4-(Phenyl((trimethylsilyl)oxy)methyl)benzonitrile (25)

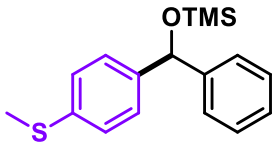


Chemical Formula: $C_{17}H_{19}NOSi$
Exact Mass: 281.1236

Prepared according to the general procedure using **1h** (91.6 mg, 0.4 mmol, 2.0 equiv.), **2a** (21.2 mg, 0.2 mmol, 1.0 equiv.), **R3** (69 mg, 0.40 mmol, 2.0 equiv.), 4-CzIPN (1.6 mg, 2.0 μmol, 0.010 equiv.), BC (7.2 mg, 20 μmol, 0.10 equiv.), $NiBr_2$•glyme (6.4 mg, 20 μmol, 0.10 equiv.) in DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE / EA = 200:1 to 100:1, visualized by UV) to give the corresponding product (39.9 mg, 70% yield) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.34 – 7.28 (m, 4H), 7.26 – 7.23 (m, 1H), 5.76 (s, 1H), 0.07 (s, 9H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 150.4, 143.6, 132.3, 128.7, 127.8, 127.1, 126.7, 119.1, 110.9, 76.1, 0.2 ppm. **HRMS** (ESI) for $C_{17}H_{20}NOSi^+$ [$(M+H)^+$]: calculated 282.1309, found 282.1315.

Trimethyl((4-(methylthio)phenyl)(phenyl)methoxy)silane (26)



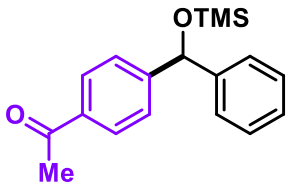
Chemical Formula: $C_{17}H_{22}OSSi$
Exact Mass: 302.1161

Prepared according to the general procedure using **1i** (100.0 mg, 0.4 mmol, 2.0 equiv.), **2a** (21.2 mg, 0.2 mmol, 1.0 equiv.), **R3** (69 mg, 0.40 mmol, 2.0 equiv.), 4-CzIPN (1.6 mg, 2.0 μmol, 0.010 equiv.), BC (7.2 mg, 20 μmol, 0.10 equiv.), $NiBr_2$•glyme (6.4 mg, 20 μmol, 0.10 equiv.) in DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE / EA = 200:1 to 100:1, visualized by UV) to give the corresponding product (27.2 mg, 45% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.30 (m, 2H), 7.30 – 7.22 (m, 4H), 7.22 – 7.14 (m, 3H), 5.72 (s, 1H), 2.44 (s, 3H), 0.07 (s, 9H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.8,

142.1, 137.1, 128.3, 127.2, 127.2, 126.7, 126.6, 76.2, 16.1, 0.3 ppm. **HRMS** (ESI) for $C_{17}H_{22}ClOSSiNa^+$ [(M+Na)$^+$]: calculated 325.1053, found 325.1057.

1-(4-(Phenyl((trimethylsilyl)oxy)methyl)phenyl)ethan-1-one (27)

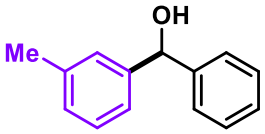


Chemical Formula: $C_{18}H_{22}O_2Si$
Exact Mass: 298.1389

Prepared according to the general procedure using **1j** (98.4 mg, 0.4 mmol, 2.0 equiv.), **2a** (21.2 mg, 0.2 mmol, 1.0 equiv.), **R3** (69 mg, 0.40 mmol, 2.0 equiv.), 4-CzIPN (1.6 mg, 2.0 μmol, 0.010 equiv.), BC (7.2 mg, 20 μmol, 0.10 equiv.), $NiBr_2$•glyme (6.4 mg, 20 μmol, 0.10 equiv.) in DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE / EA = 100:1 to 50:1, visualized by UV) to give the corresponding product (31.0 mg, 52% yield) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.36 – 7.32 (m, 4H), 7.30 – 7.22 (m, 1H), 5.82 (s, 1H), 2.60 (s, 3H), 0.11 (s, 9H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 197.9, 150.3, 144.1, 136.0, 128.5, 128.4, 127.5, 126.6, 126.5, 76.2, 26.6, 0.1 ppm. **HRMS** (ESI) for $C_{18}H_{22}O_2SiNa^+$ [(M+Na)$^+$]: calculated 321.1281 found 321.1290.

Phenyl(*m*-tolyl)methanol (28)



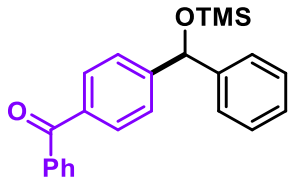
Chemical Formula: $C_{14}H_{14}O$
Exact Mass: 198.1045

Prepared according to the general procedure using **1k** (87.2 mg, 0.4 mmol, 2.0 equiv.), **2a** (21.2 mg, 0.2 mmol, 1.0 equiv.), **R3** (69 mg, 0.40 mmol, 2.0 equiv.), 4-CzIPN (1.6 mg, 2.0 μmol, 0.010 equiv.), BC (7.2 mg, 20 μmol, 0.10 equiv.), $NiBr_2$•glyme (6.4 mg, 20 μmol, 0.10 equiv.) in DMAc (0.10 M, 2.0 mL). The residue was purified by flash

column chromatography (PE / EA = 20:1 to 10:1, visualized by UV) to give the corresponding product (19.4 mg, 49% yield) as a colorless oil.

1H NMR (600 MHz, $CDCl_3$) δ 7.46 – 7.37 (m, 4H), 7.34 - 7.31 (m, 1H), 7.30 – 7.27 (m, 1H), 7.25 (s, 1H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.14 (d, *J* = 7.6 Hz, 1H), 5.82 (s, 1H), 2.54 (s, 1H), 2.40 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.0, 143.9, 138.2, 128.5, 128.44, 128.38, 127.5, 127.3, 126.6, 123.7, 76.3, 21.5 ppm. **HRMS** (ESI) for $C_{14}H_{15}O^+$ [$(M+H)^+$]: calculated 199.1117, found 199.1125.

Phenyl(4-(phenyl((trimethylsilyl)oxy)methyl)phenyl)methanone (29)

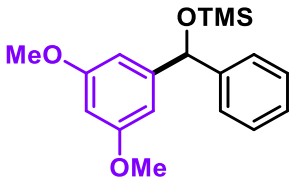


Chemical Formula: $C_{23}H_{24}O_2Si$
Exact Mass: 360.1546

Prepared according to the general procedure using **1l** (104.4 mg, 0.4 mmol, 2.0 equiv.), **2a** (21.2 mg, 0.2 mmol, 1.0 equiv.), **R3** (69 mg, 0.40 mmol, 2.0 equiv.), 4-CzIPN (1.6 mg, 2.0 μmol, 0.010 equiv.), BC (7.2 mg, 20 μmol, 0.10 equiv.), $NiBr_2$•glyme (6.4 mg, 20 μmol, 0.10 equiv.) in DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE / EA = 100:1 to 50:1, visualized by UV) to give the corresponding product (33.1 mg, 46% yield) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 – 7.76 (m, 4H), 7.62 – 7.58 (m, 1H), 7.53 – 7.48 (m, 4H), 7.41 – 7.33 (m, 4H), 7.31 – 7.27 (m, 1H), 5.86 (s, 1H), 0.13 (s, 9H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.4, 149.6, 144.1, 137.8, 136.3, 132.3, 130.2, 130.0, 128.4, 128.2, 127.5, 126.6, 126.2, 76.3, 0.1 ppm. **HRMS** (ESI) for $C_{23}H_{25}O_2Si^+$ [$(M+H)^+$]: calculated 361.1618, found 361.1626.

((3,5-Dimethoxyphenyl)(phenyl)methoxy)trimethylsilane (30)

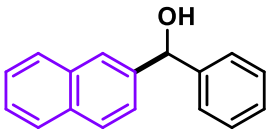


Chemical Formula: $C_{18}H_{24}O_3Si$
Exact Mass: 316.1495

Prepared according to the general procedure using **1m** (87.2 mg, 0.4 mmol, 2.0 equiv.), **2a** (21.2 mg, 0.2 mmol, 1.0 equiv.), **R3** (69 mg, 0.40 mmol, 2.0 equiv.), 4-CzIPN (1.6 mg, 2.0 μmol, 0.010 equiv.), BC (7.2 mg, 20 μmol, 0.10 equiv.), $NiBr_2$•glyme (6.4 mg, 20 μmol, 0.10 equiv.) in DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE / EA = 100:1 to 50:1, visualized by UV) to give the corresponding product (50.5 mg, 80% yield) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.37 (m, 2H), 7.34 – 7.32 (m, 2H), 7.28 – 7.22 (m, 1H), 6.57 (s, 2H), 6.37 (s, 1H), 5.72 (s, 1H), 3.79 (s, 6H), 0.13 (s, 9H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 160.7, 147.3, 144.6, 128.2, 127.2, 126.5, 104.7, 98.8, 76.5, 55.3, 0.2 ppm. **HRMS** (ESI) for $C_{18}H_{25}O_3Si^+$ [(M+H)$^+$]: calculated 317.1567, found 317.1574.

Naphthalen-2-yl(phenyl)methanol (31)



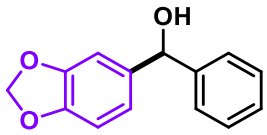
Chemical Formula: $C_{17}H_{14}O$
Exact Mass: 234.1045

Prepared according to the general procedure using **1n** (101.6 mg, 0.4 mmol, 2.0 equiv.), **2a** (21.2 mg, 0.2 mmol, 1.0 equiv.), **R3** (69 mg, 0.40 mmol, 2.0 equiv.), 4-CzIPN (1.6 mg, 2.0 μmol, 0.010 equiv.), BC (7.2 mg, 20 μmol, 0.10 equiv.), $NiBr_2$•glyme (6.4 mg, 20 μmol, 0.10 equiv.) in DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE / EA = 20:1 to 10:1, visualized by UV) to give the corresponding product (36.0 mg, 77% yield) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.84 – 7.76 (m, 3H), 7.49 – 7.43 (m, 2H), 7.42 – 7.39 (m, 3H), 7.34 – 7.32 (m, 2H), 7.28 – 7.25 (m, 1H), 5.98 (s, 1H), 2.39 (s, 1H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.7, 141.2, 133.4, 132.9, 128.7, 128.5, 128.2,

127.8 (2 C), 126.8, 126.3, 126.1, 125.1, 124.9, 76.5 ppm. **HRMS** (ESI) for $C_{17}H_{15}ONa^+$ [(M+H)$^+$]: calculated 235.1117, found 235.1114. **Melting point**: 81.5 - 82.1 °C.

Benzo[*d*][1,3]dioxol-5-yl(phenyl)methanol (32)



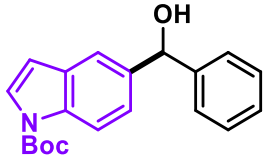
Chemical Formula: $C_{14}H_{12}O_3$
Exact Mass: 228.0786

Prepared according to the general procedure using **1o** (99.2 mg, 0.4 mmol, 2.0 equiv.), **2a** (21.2 mg, 0.2 mmol, 1.0 equiv.), **R3** (69 mg, 0.40 mmol, 2.0 equiv.), 4-CzIPN (1.6 mg, 2.0 μmol, 0.010 equiv.), BC (7.2 mg, 20 μmol, 0.10 equiv.), $NiBr_2$•glyme (6.4 mg, 20 μmol, 0.10 equiv.) in DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE / EA = 20:1 to 10:1, visualized by UV) to give the corresponding product (32.3 mg, 71% yield) as a colorless oil.

This compound was prepared according to General procedure from the reaction of **1a** (99.2 mg, 0.4 mmol) and **2a** (21.2 mg, 0.2 mmol). 32.3 mg, 71% yield, colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 – 7.34 (m, 4H), 7.32 – 7.27 (m, 1H), 6.91 – 6.83 (m, 2H), 6.79 (d, *J* = 8.2 Hz, 1H), 5.95 (s, 2H), 5.78 (s, 1H), 2.32 (s, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.8, 147.0, 143.8, 138.0, 128.5, 127.6, 126.3, 120.0, 108.1, 107.2, 101.0, 76.0 ppm. **HRMS** (ESI) for $C_{14}H_{13}O_3^+$ [(M+H)$^+$]: calculated 229.0859, found 229.0863.

***tert*-Butyl 5-(hydroxy(phenyl)methyl)-*1*H-indole-1-carboxylate (33)**



Chemical Formula: $C_{20}H_{21}NO_3$
Exact Mass: 323.1521

Prepared according to the general procedure using **1p** (137.2 mg, 0.4 mmol, 2.0 equiv.), **2a** (21.2 mg, 0.2 mmol, 1.0 equiv.), **R3** (69 mg, 0.40 mmol, 2.0 equiv.), 4-CzIPN (1.6 mg, 2.0 μmol, 0.010 equiv.), BC (7.2 mg, 20 μmol, 0.10 equiv.), $NiBr_2$•glyme (6.4 mg, 20 μmol, 0.10 equiv.) in DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE / EA = 20:1 to 10:1, visualized by UV) to give the corresponding product (48.4 mg, 75% yield) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.58 – 7.57 (m, 2H), 7.39 (d, *J* = 7.4 Hz, 2H), 7.34 – 7.31 (m, 2H), 7.30 – 7.29 (m, 1H), 7.27 – 7.24 (m, 1H), 6.53 (d, *J* = 3.7 Hz, 1H), 5.94 (s, 1H), 2.35 (s, 1H), 1.65 (s, 9H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 149.8, 144.3, 138.6, 134.7, 130.8, 128.6, 127.5, 126.6, 123.2, 119.0, 115.3, 113.1, 107.5, 83.9, 76.5, 28.3 ppm. **HRMS** (ESI) for $C_{20}H_{21}NO_3Na^+$ [$(M+Na)^+$]: calculated 346.1414, found 346.1419.

6 Mechanistic Studies

6.1 Fluorescence quenching (Stern-Volmer) studies

Emission intensities were recorded using Agilent Technologies of Cary Eclipse Fluorescence spectrophotometer. All 4-CzIPN solutions were excited at 450 nm and the emission intensity was collected at 400-740 nm. In a typical experiment, to a 1 x 10^{-4} M solution of 4-CzIPN in DMAc was added the appropriate amount of quencher in a screw-top 1.0 cm quartz cuvette (we used the relative concentrations of this reaction under standard conditions to compare different components as quenchers). The emission of the sample was collected. The linear slope suggests that the reductant is the most efficient quencher of photocatalyst.

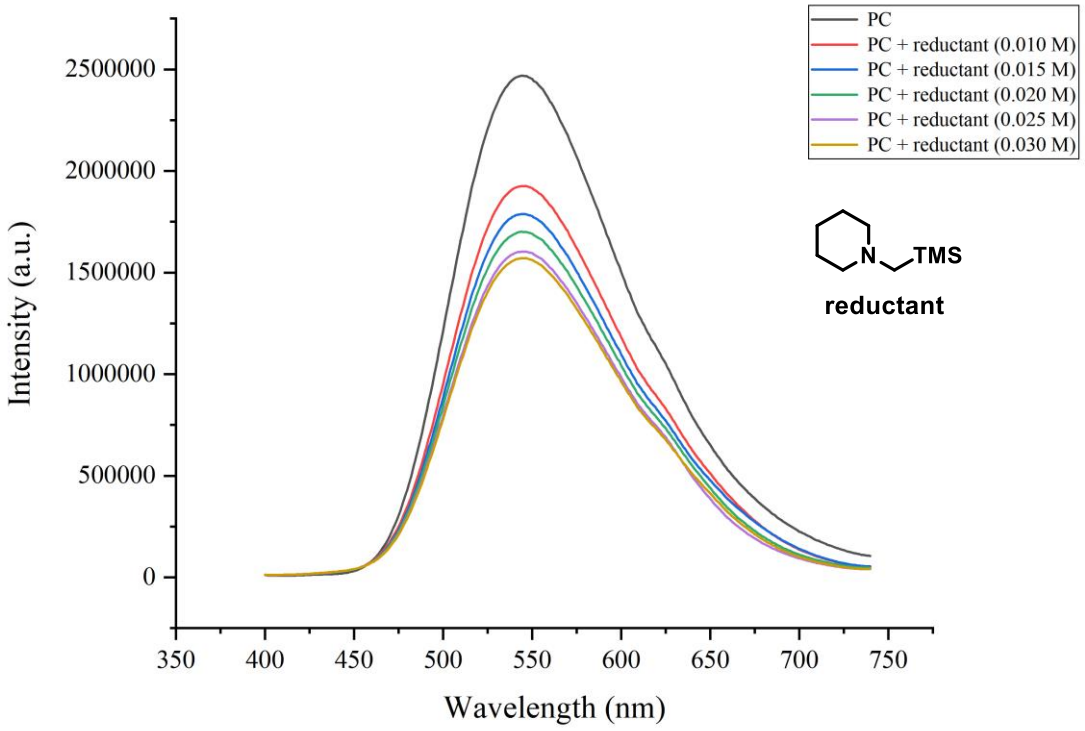


Figure S2 Quenching with variable amounts of reductant

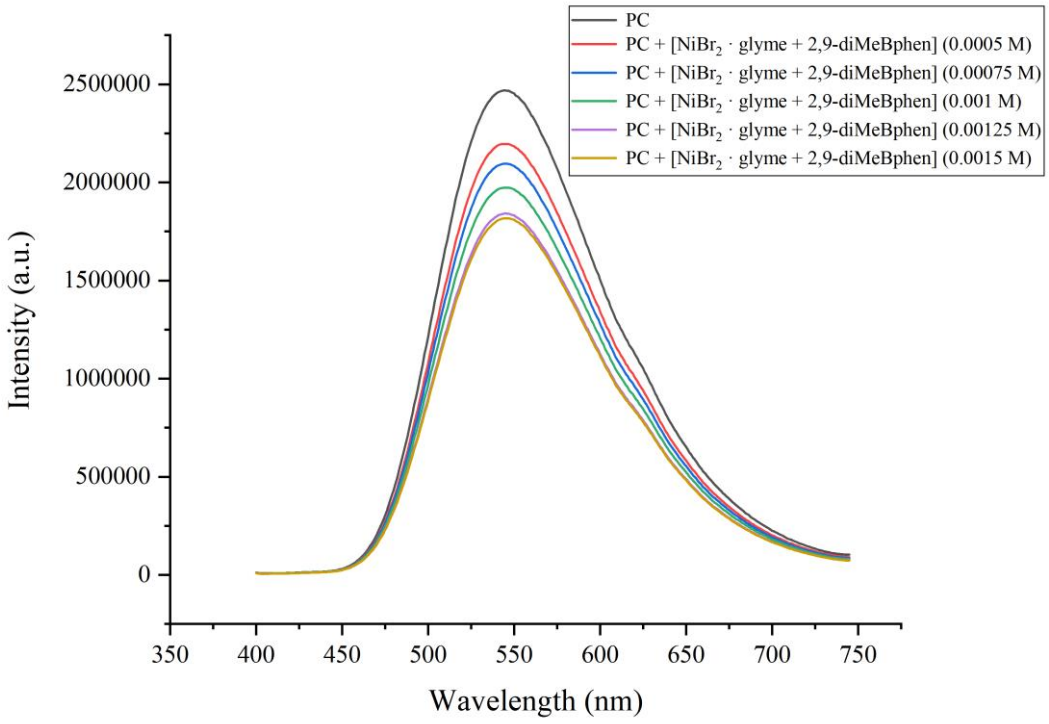


Figure S3 Quenching with variable amounts of **[$NiBr_2$•glyme and 2,9-diMeBphen]**

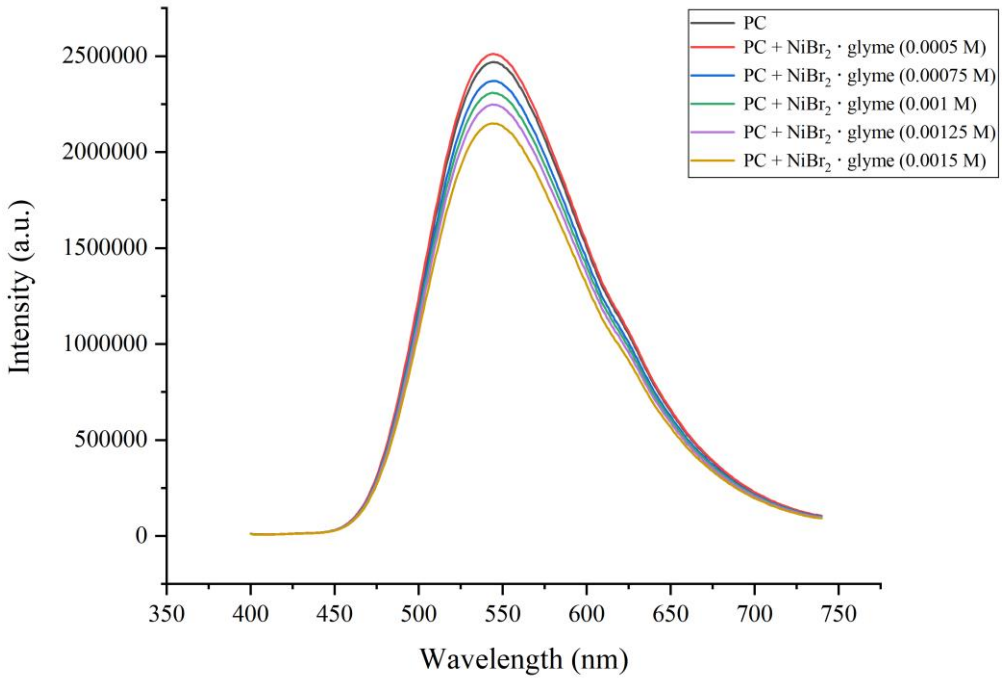


Figure S4 Quenching with variable amounts of **$NiBr_2$•glyme**

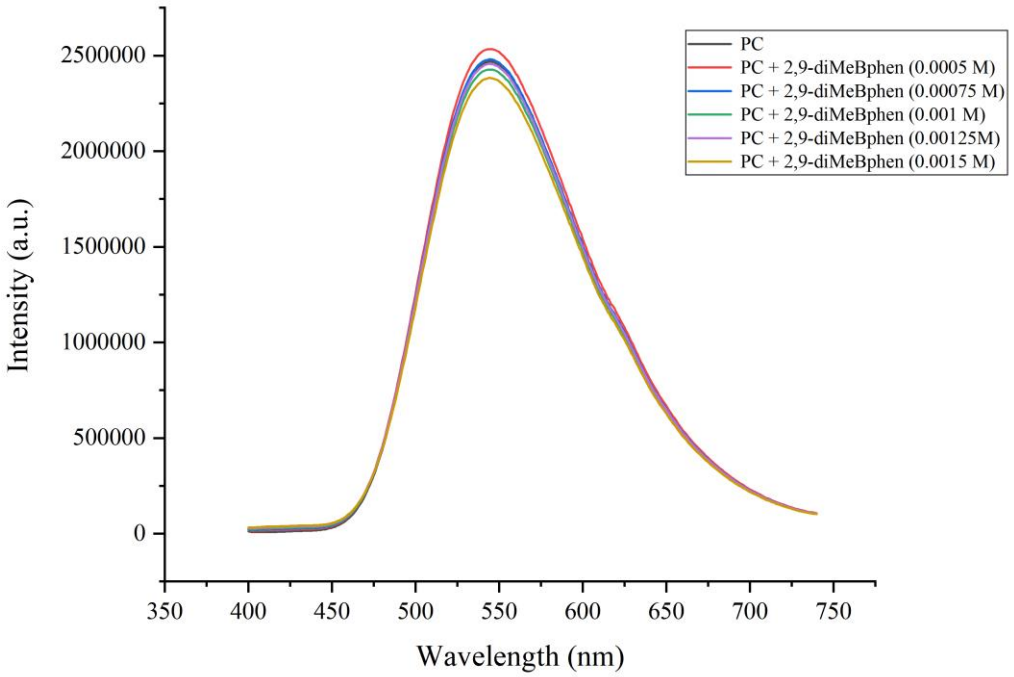


Figure S5 Quenching with variable amounts of **2,9-diMeBphen**

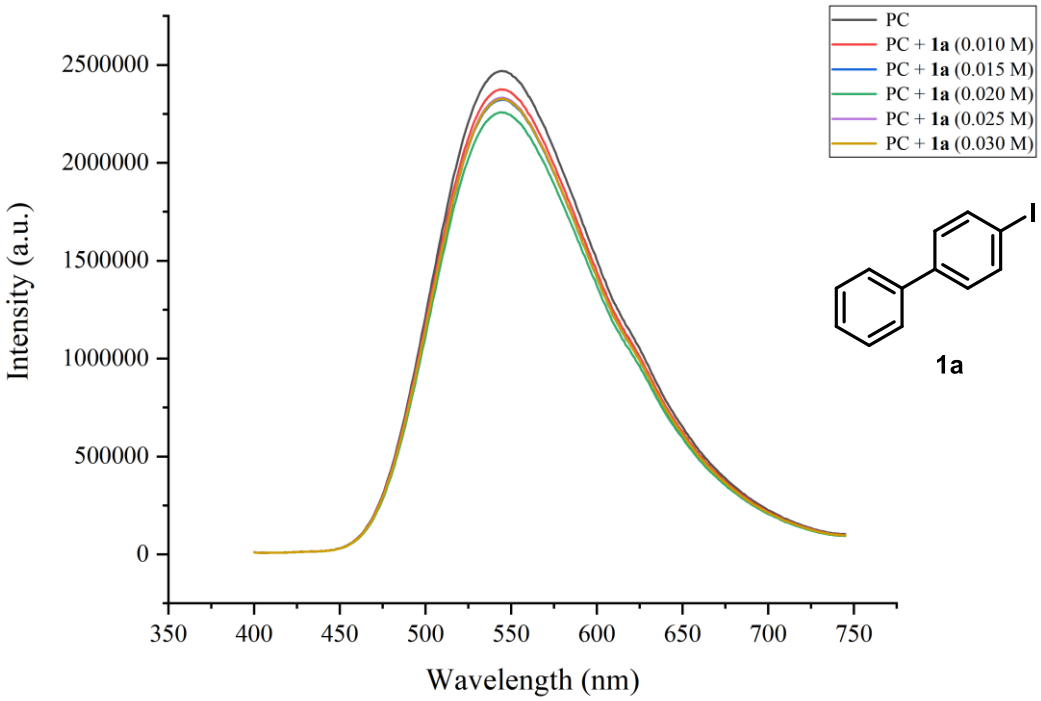


Figure S6 Quenching with variable amounts of **1a**

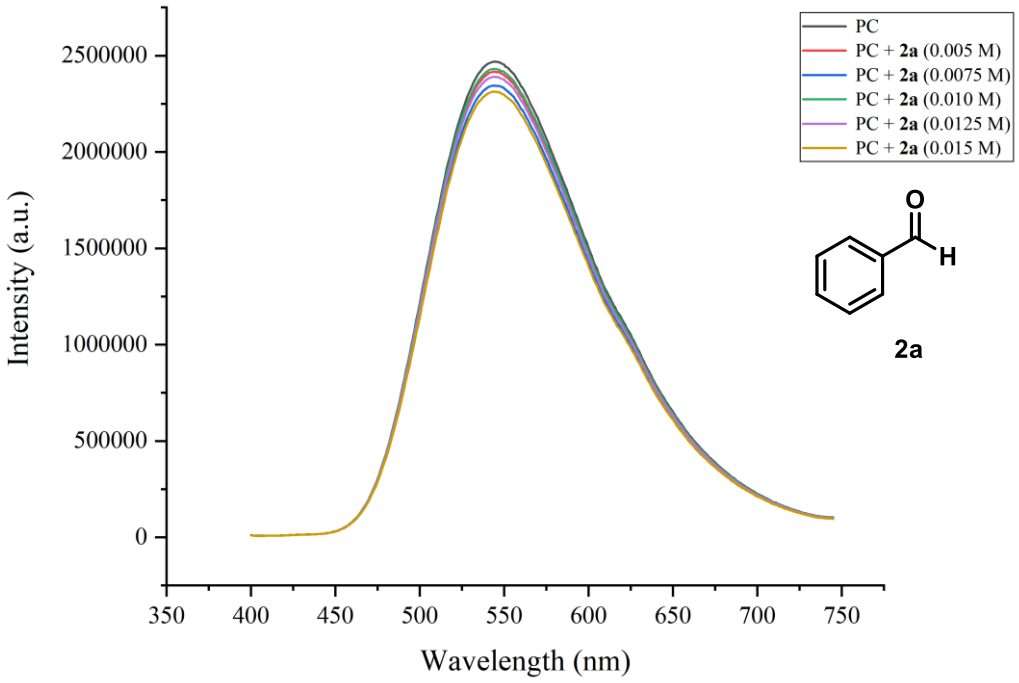


Figure S7 Quenching with variable amounts of **2a**

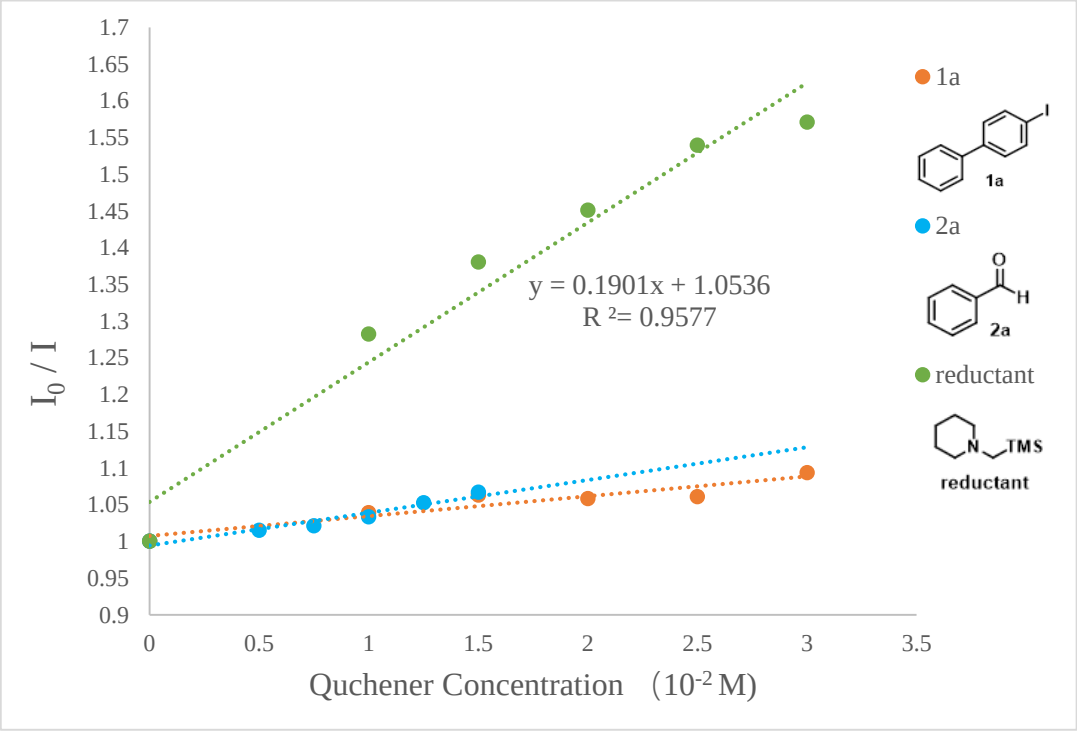
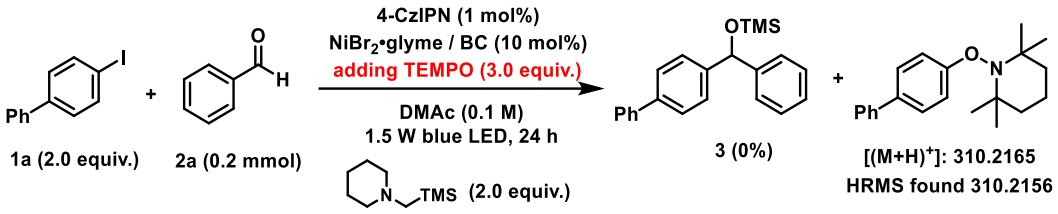


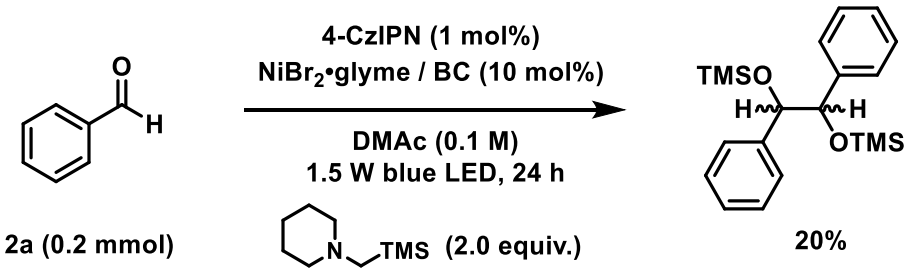
Figure S8 Fluorescence quenching (Stern-Volmer) curve of **1a, 2a and reductant**

6.2 Radical trapping experiment



An oven-dried vial equipped with a stir-bar was added **1a** (112 mg, 0.40 mmol, 2.0 equiv.), **2a** (21 mg, 0.20 mmol, 1.0 equiv.), 4-CzIPN (1.6 mg, 2.0 μmol, 0.010 equiv.), **BC** (7.2 mg, 20 μmol, 0.10 equiv.), $NiBr_2$•glyme (6.4 mg, 20 μmol, 0.10 equiv.), 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO, 94 mg, 0.60 mmol, 3.0 equiv.). Then, DMAc (0.10 M, 2.0 mL), reductant **R3** (69 mg, 0.40 mmol, 2.0 equiv.) were added. The vial was sealed and removed from the glovebox then irradiated with a 1.5 W blue LED lamp (at approximately 1.0 cm away from the light source) with cooling from a fan for 24 h. The desired product **3** was not detected in this experiment. We detected 1,1'-biphenyl radical-trapped adduct by HRMS.

6.3 Control experiment without aryl iodide

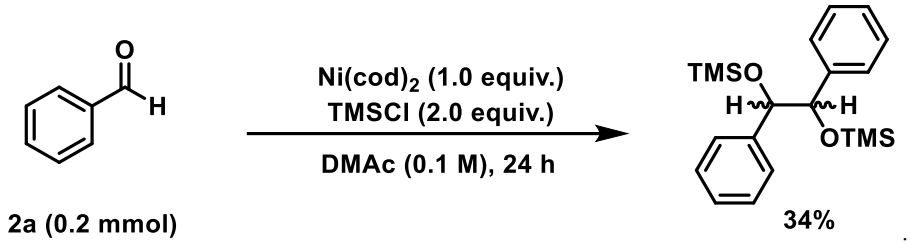


An oven-dried vial equipped with a stir-bar was added aldehyde **2a** (21 mg, 0.20 mmol, 1.0 equiv.), 4-CzIPN (1.6 mg, 2.0 μmol, 0.010 equiv.), **BC** (7.2 mg, 20 μmol, 0.10 equiv.), $NiBr_2$•glyme (6.4 mg, 20 μmol, 0.10 equiv.). Then, DMAc (0.10 M, 2.0 mL), reductant **R3** (69 mg, 0.40 mmol, 2.0 equiv.) were added. The vial was sealed and removed from the glovebox, then irradiated with a 1.5 W blue LED lamp (at approximately 1.0 cm away from the light source) with cooling from a fan for 24 h. The reaction was quenched by H_2O, extracted with ethyl acetate (60 mL). The combined organic layers were washed with brine, dried with Na_2SO_4, filtered, and concentrated

in vacuo. Then the residue was purified by flash chromatography to give the silyl-protected 1,2-diols (7.3 mg, 20% yield, d.r. = 1:1) as a white solid.

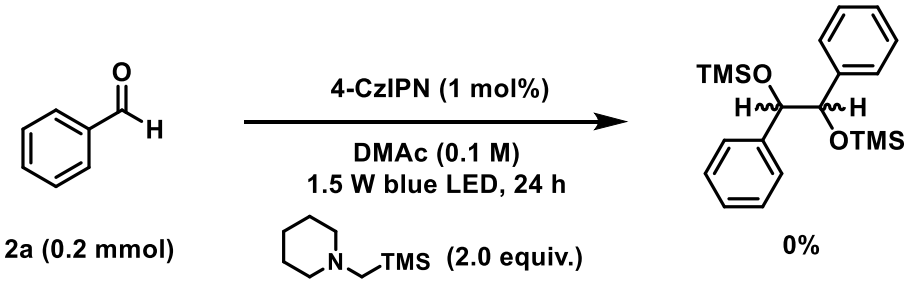
^{1}H NMR (600 MHz, $CDCl_3$) δ ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 – 7.38 (m, 2H), 7.33 – 7.31 (m, 2H), 7.29 – 7.26 (m, 1H), 7.22 – 7.18 (m, 3H), 7.13 – 7.12 (m, 2H), 4.70 (s, 1H), 4.50 (s, 1H), -0.02 (s, 9H), -0.22 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.1, 142.0, 127.6 (2 C), 127.5, 127.3, 127.2, 127.0, 79.9, 79.6, 0.1, - 0.3.

6.4 Reaction of aldehyde 2a with stoichiometric $Ni(cod)_2$ and TMSCl



An oven-dried vial equipped with a stir-bar was added aldehyde **2a** (21 mg, 0.20 mmol, 1.0 equiv.), $Ni(cod)_2$ (55.3 mg, 0.20 mol, 1.0 equiv.). Then, DMAc (0.10 M, 2.0 mL), TMSCl (43.5 mg, 0.40 mmol, 2.0 equiv.) were added. The vial was sealed and removed from the glovebox, then stirred at room temperature for 24 h. The reaction was quenched by H_2O, extracted with ethyl acetate (60 mL). The combined organic layers were washed with brine, dried with Na_2SO_4, filtered, and concentrated in vacuo. Then the residue was purified by flash chromatography to give the silyl-protected 1,2-diols (12.2 mg, 34% yield, d.r. = 1:1) as a white solid.

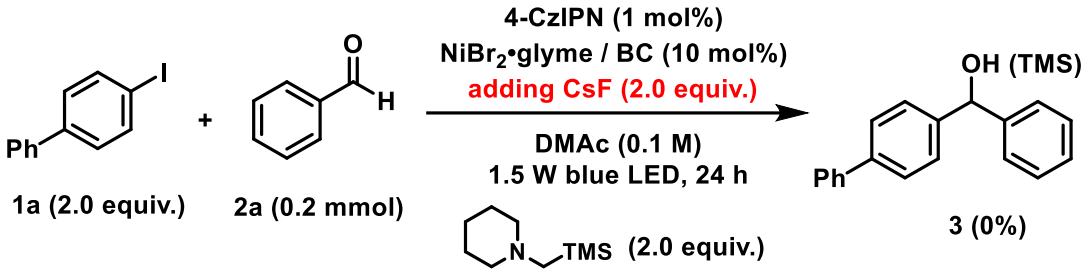
6.5 Control experiment without aryl iodide, Ni and ligand



An oven-dried vial equipped with a stir-bar was added aldehyde **2a** (21 mg, 0.20 mmol, 1.0 equiv.), 4-CzIPN (1.6 mg, 2.0 μmol, 0.010 equiv.). Then, DMAc (0.10 M, 2.0 mL),

reductant **R3** (69 mg, 0.40 mmol, 2.0 equiv.) were added. The vial was sealed and removed from the glovebox, then irradiated with a 1.5 W blue LED lamp (at approximately 1.0 cm away from the light source) with cooling from a fan for 24 h. The silyl-protected 1,2-diols was not detected in this experiment.

6.6 Control experiment with adding CsF



1a (2.0 equiv.) **2a (0.2 mmol)** **3 (0%)**

An oven-dried vial equipped with a stir-bar was added **1a** (112 mg, 0.40 mmol, 2.0 equiv.), **2a** (21 mg, 0.20 mmol, 1.0 equiv.), 4-CzIPN (1.6 mg, 2.0 μmol, 0.010 equiv.), **BC** (7.2 mg, 20 μmol, 0.10 equiv.), $NiBr_2$•glyme (6.4 mg, 20 μmol, 0.10 equiv.), cesium fluoride (60.8 mg, 0.40 mmol, 2.0 equiv.). Then, DMAc (0.10 M, 2.0 mL), reductant **R3** (69 mg, 0.40 mmol, 2.0 equiv.) were added. The vial was sealed and removed from the glovebox then irradiated with a 1.5 W blue LED lamp (at approximately 1.0 cm away from the light source) with cooling from a fan for 24 h. The desired product **3** was not detected in this experiment.

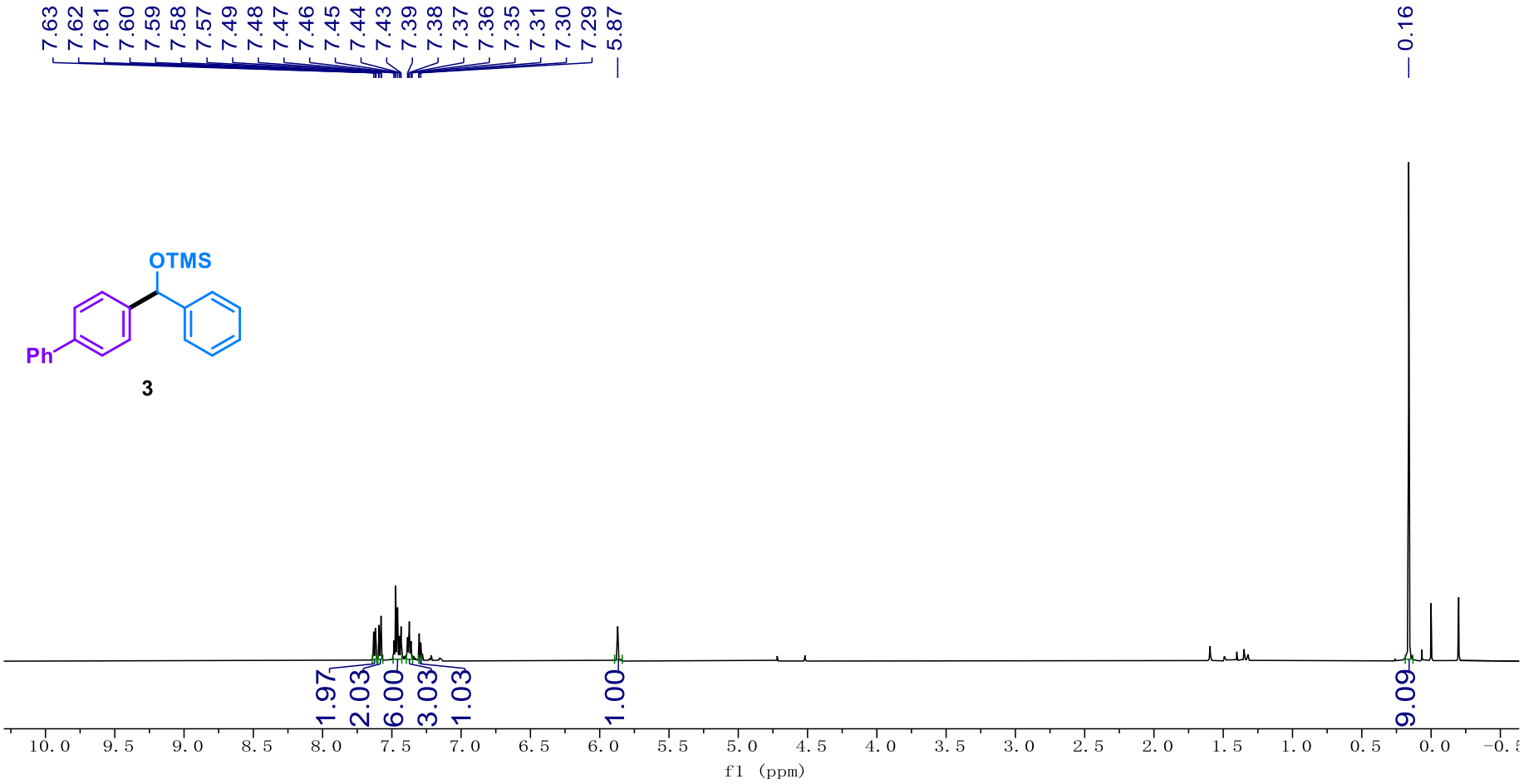
7 References

[S1] Luo, J.; Zhang, J. *ACS Catal.* **2016**, *6*, 873−877.

[S2] Singh, A.; Teegardin, K.; Kelly, M.; Prasad, K. S.; Krishnan, S.; Weaver, J. D. *J. Organomet. Chem.* **2015**, *776*, 51–59.

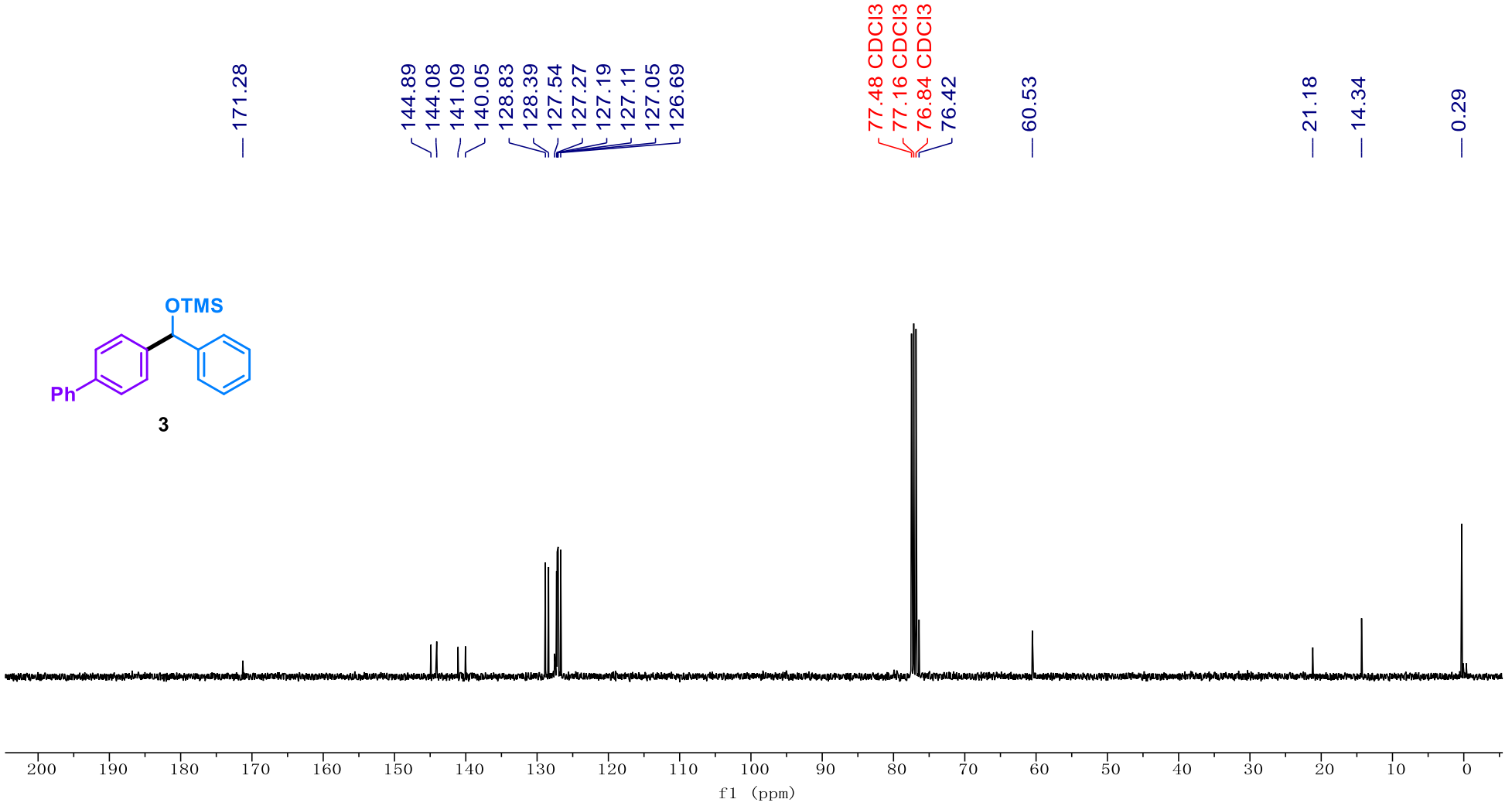
8 NMR Spectra

^{1}H NMR of 3 (600 MHz, $CDCl_3$)

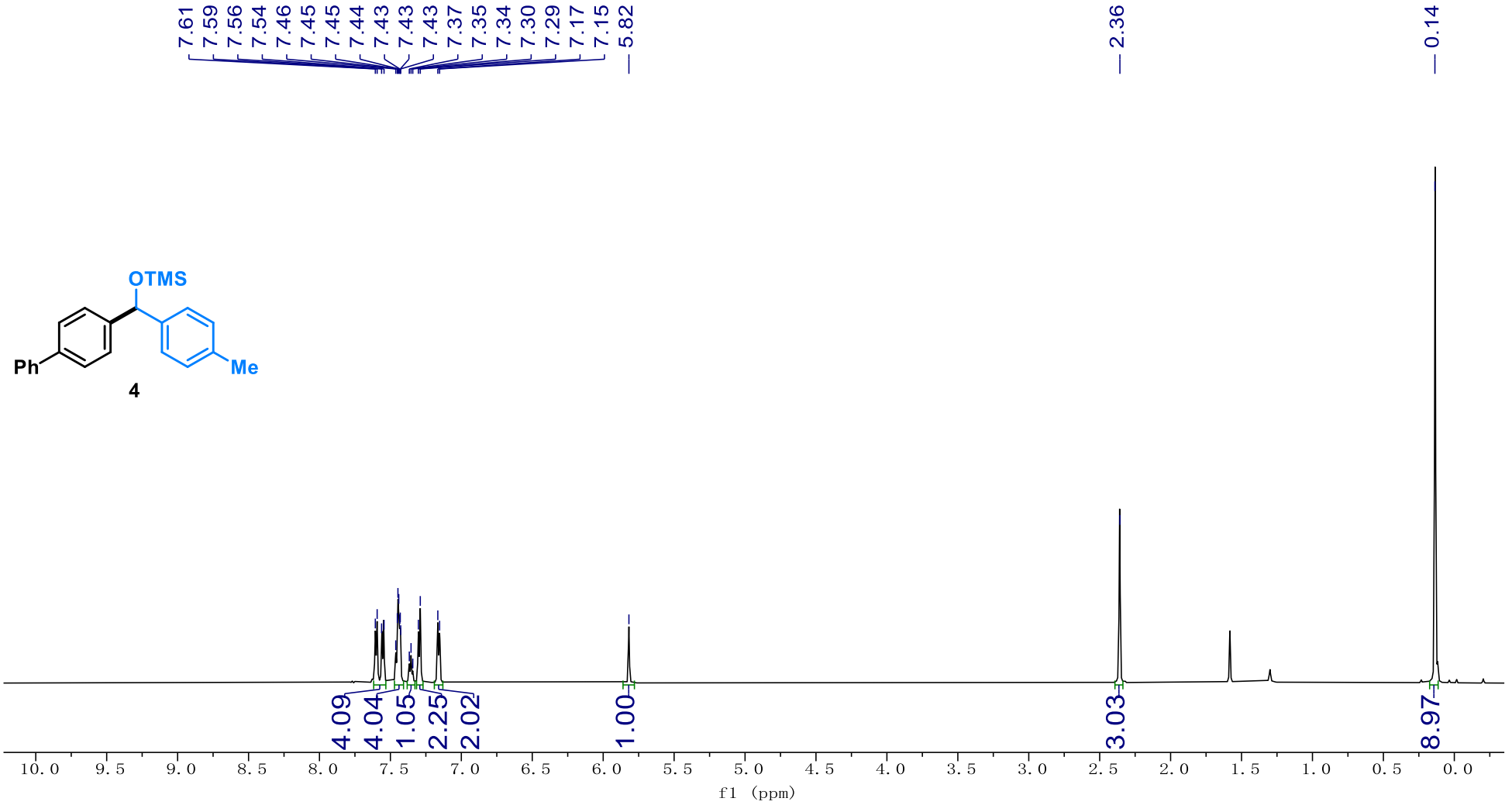


3

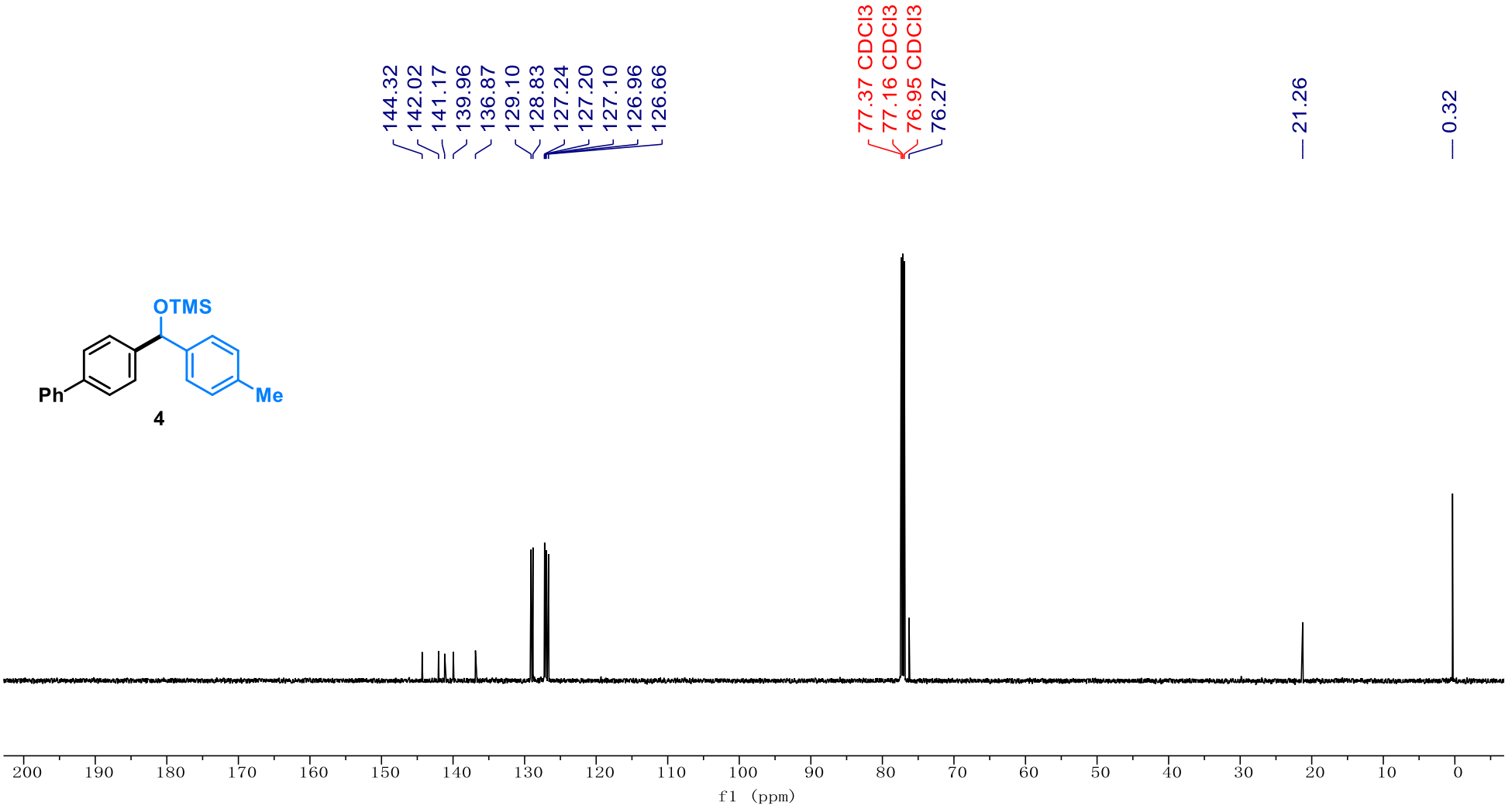
^{13}C NMR of 3 (101 MHz, $CDCl_3$)



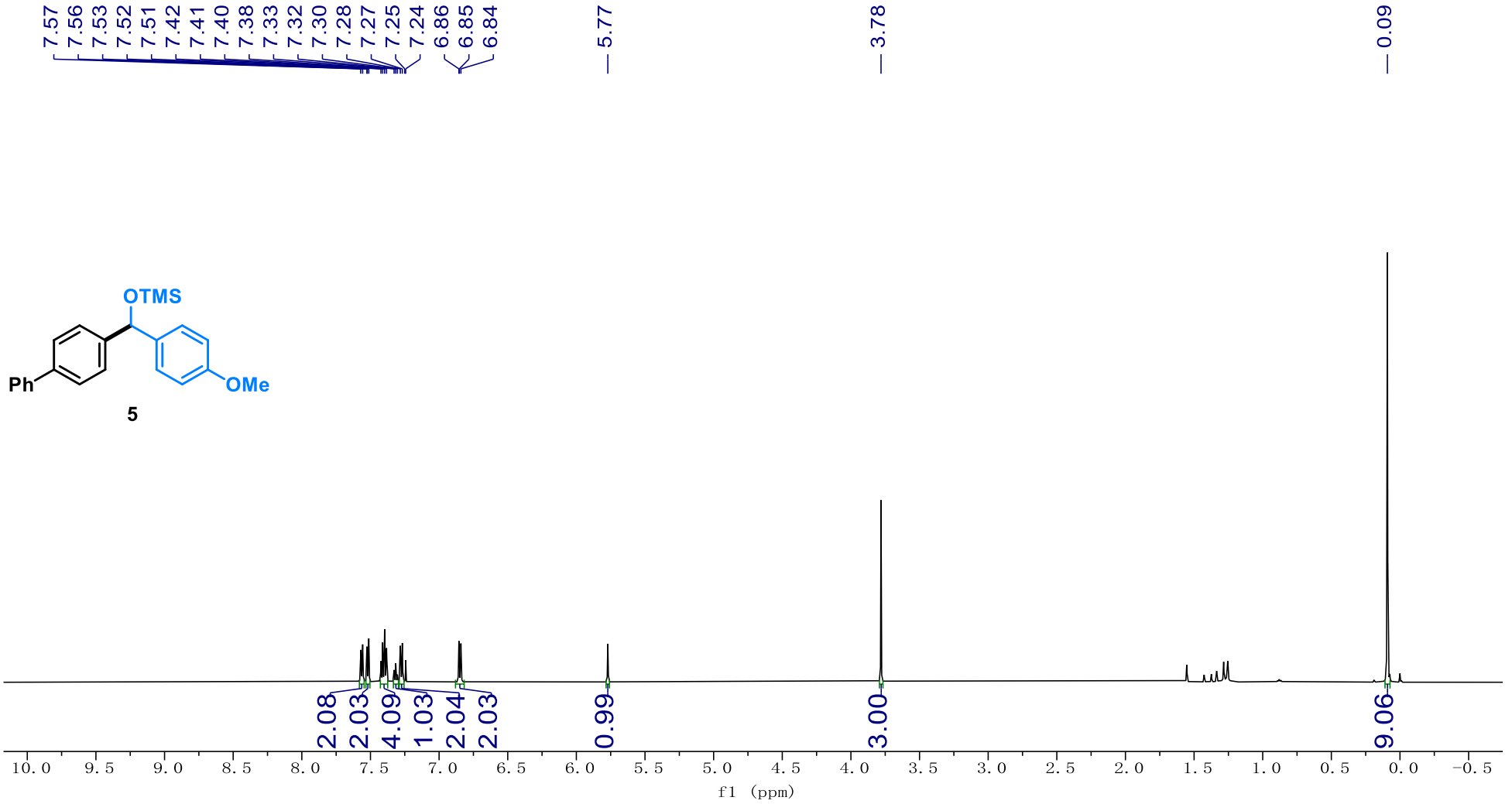
^{1}H NMR of 4 (600 MHz, $CDCl_3$)



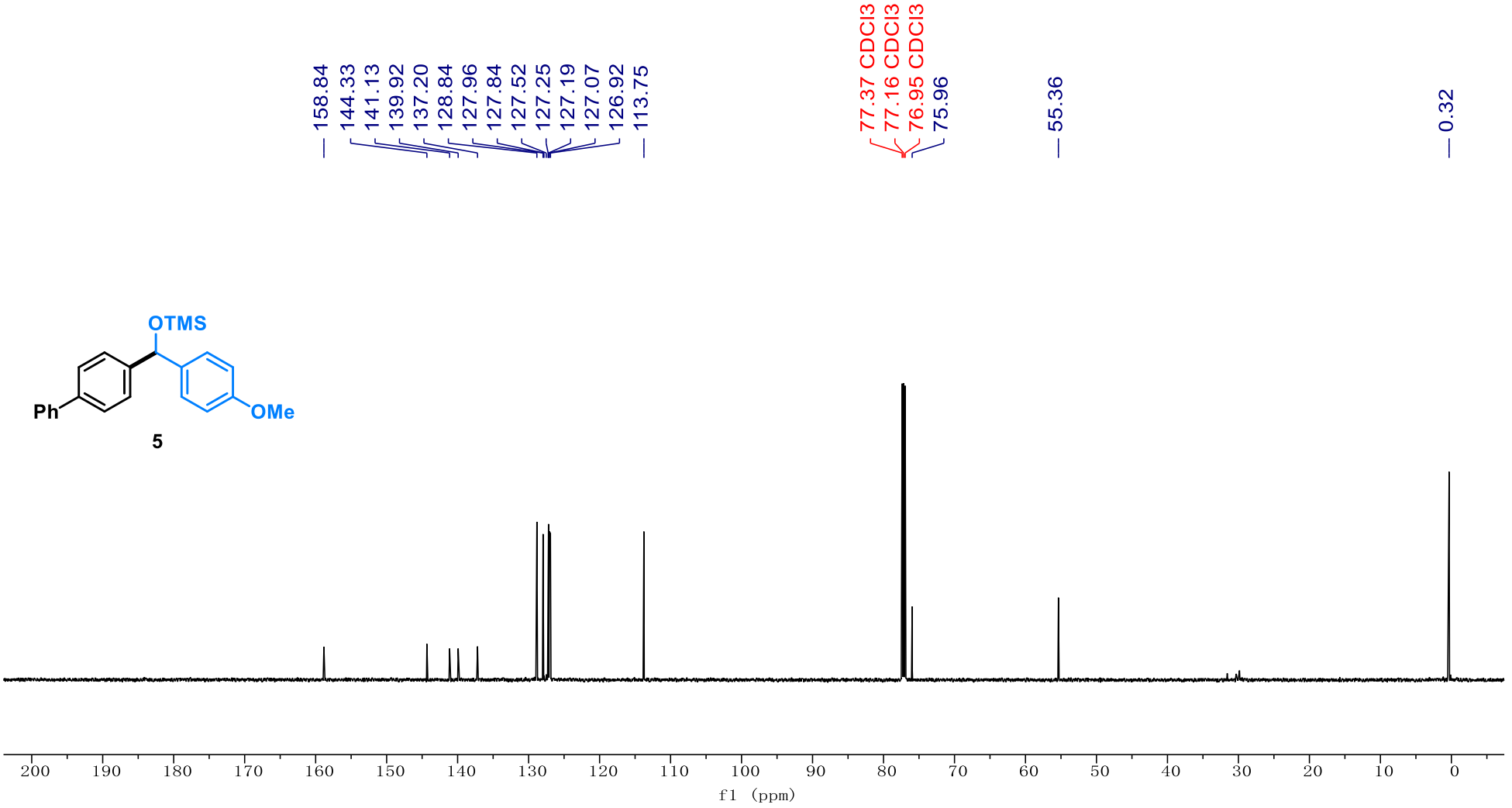
^{13}C NMR of 4 (151 MHz, $CDCl_3$)



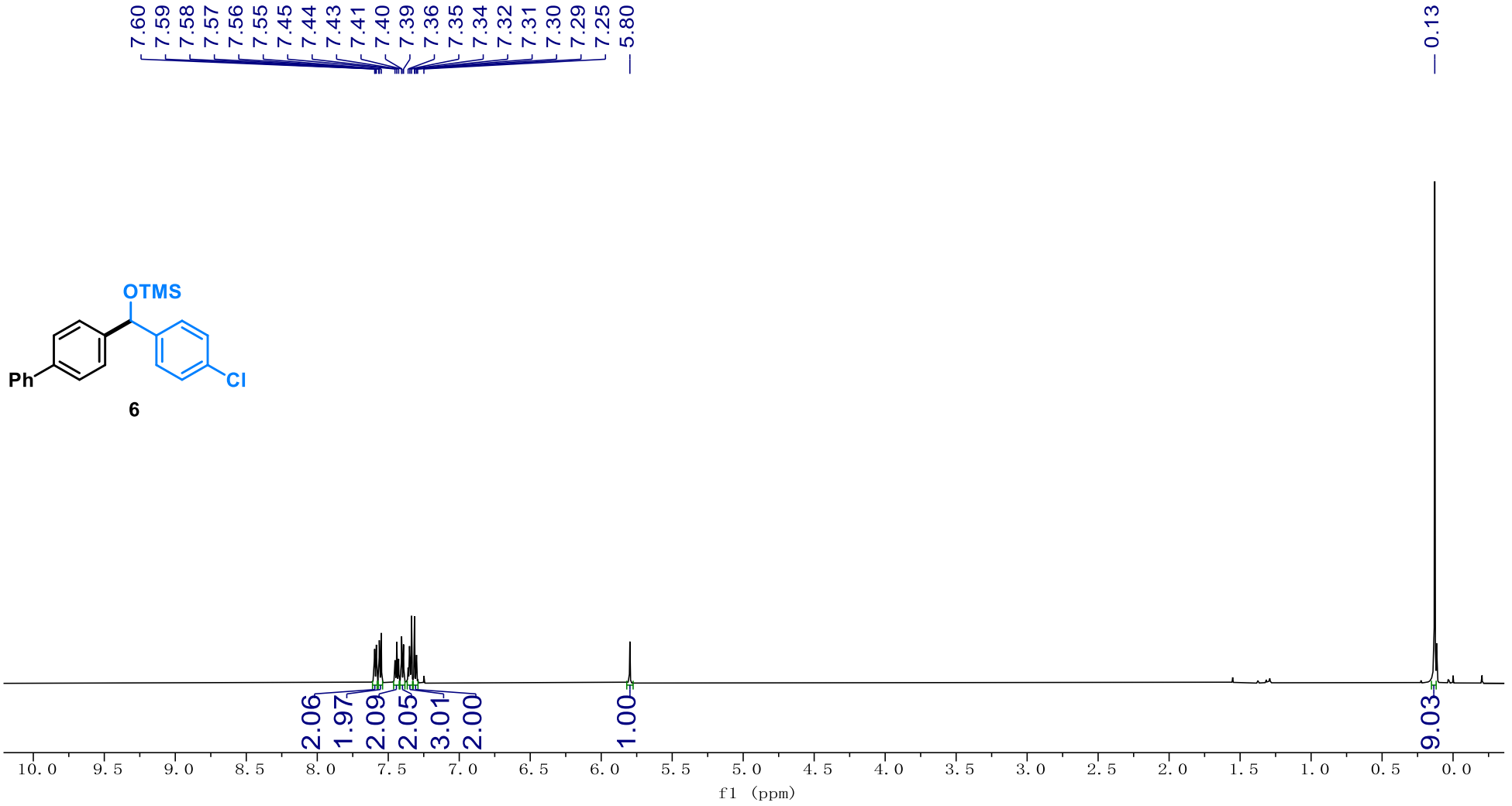
^{1}H NMR of 5 (600 MHz, $CDCl_3$)



^{13}C NMR of 5 (151 MHz, $CDCl_3$)

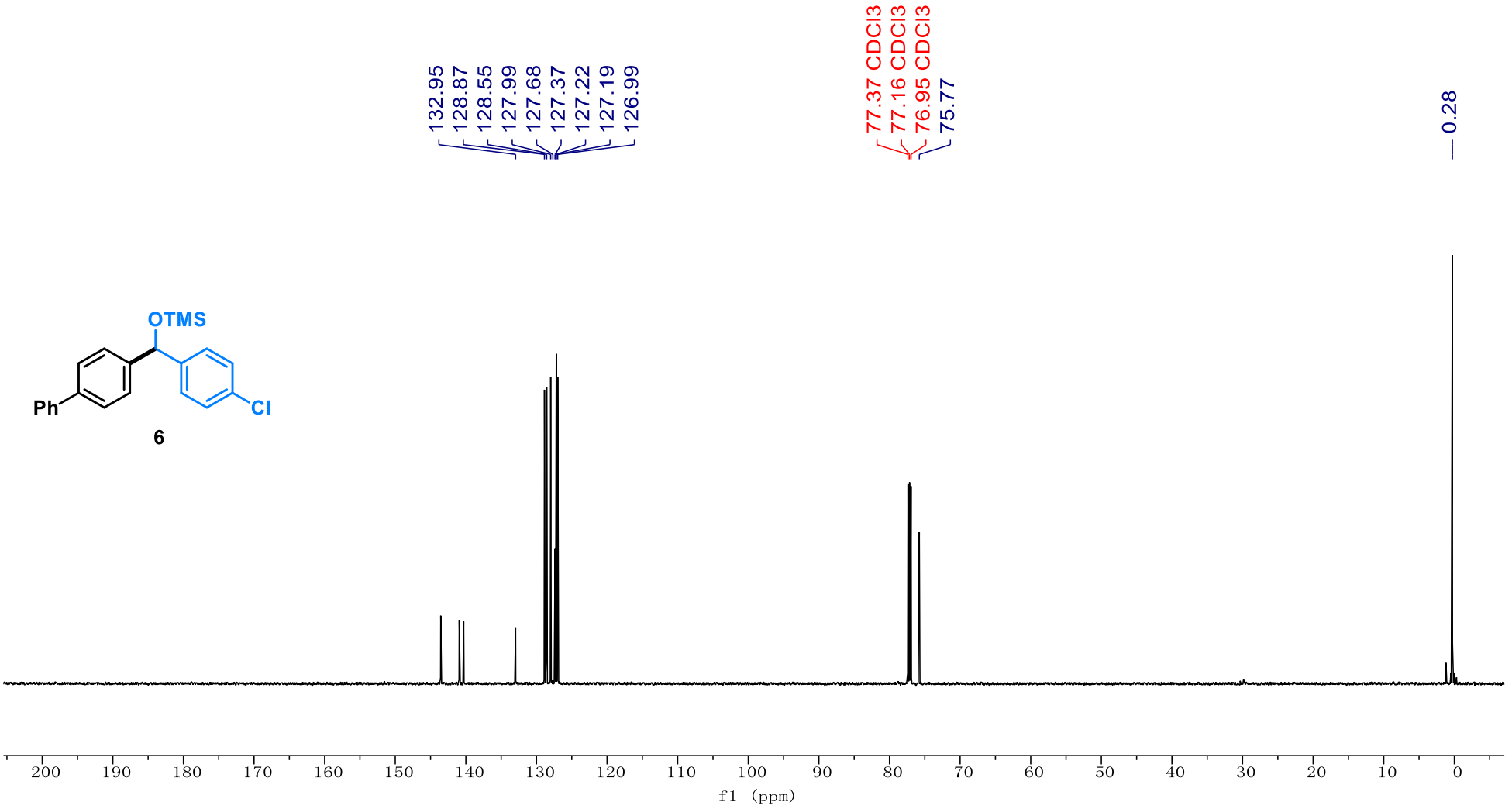


^{1}H NMR of 6 (600 MHz, $CDCl_3$)

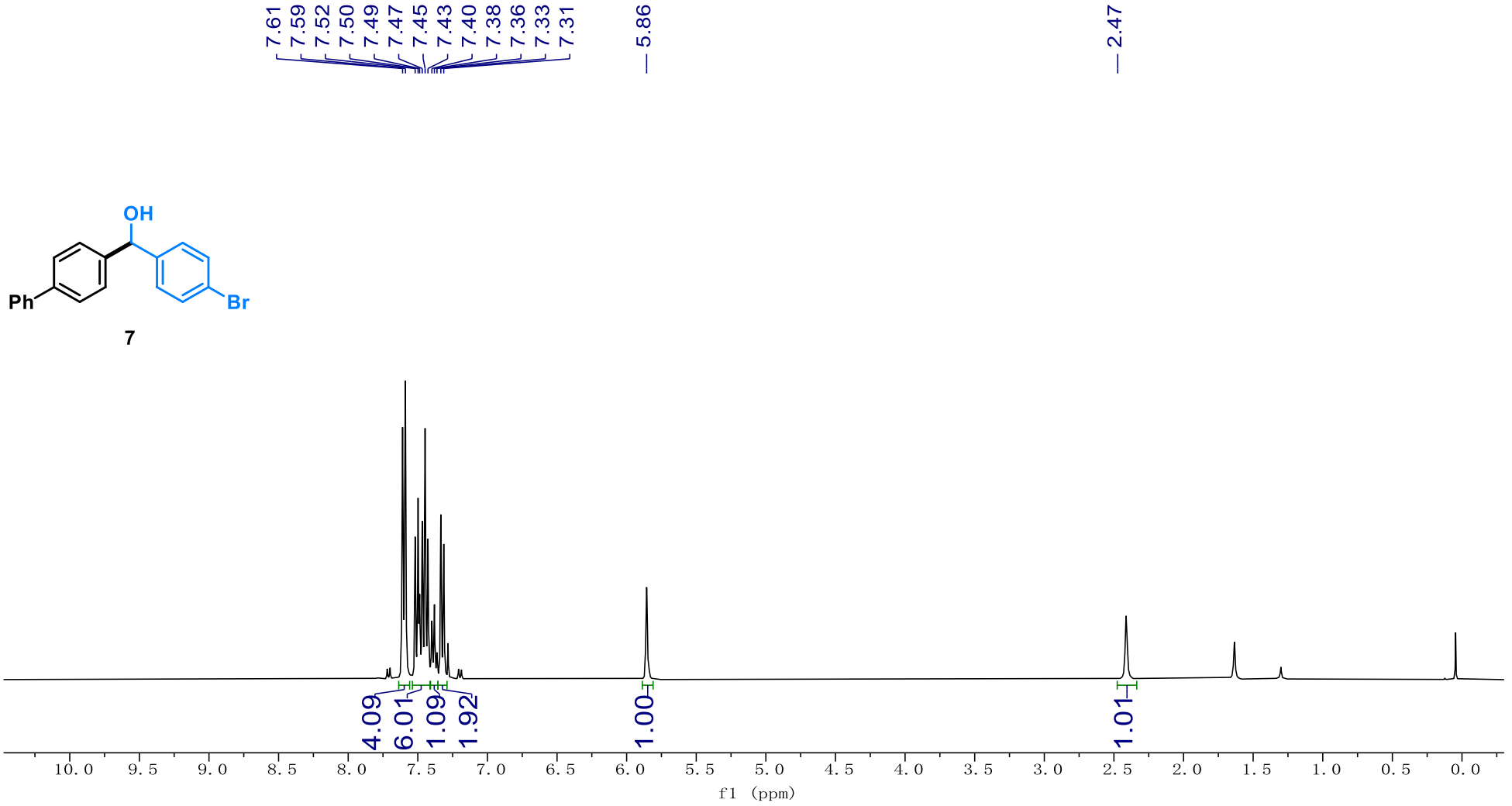


6

^{13}C NMR of 6 (151 MHz, $CDCl_3$)



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



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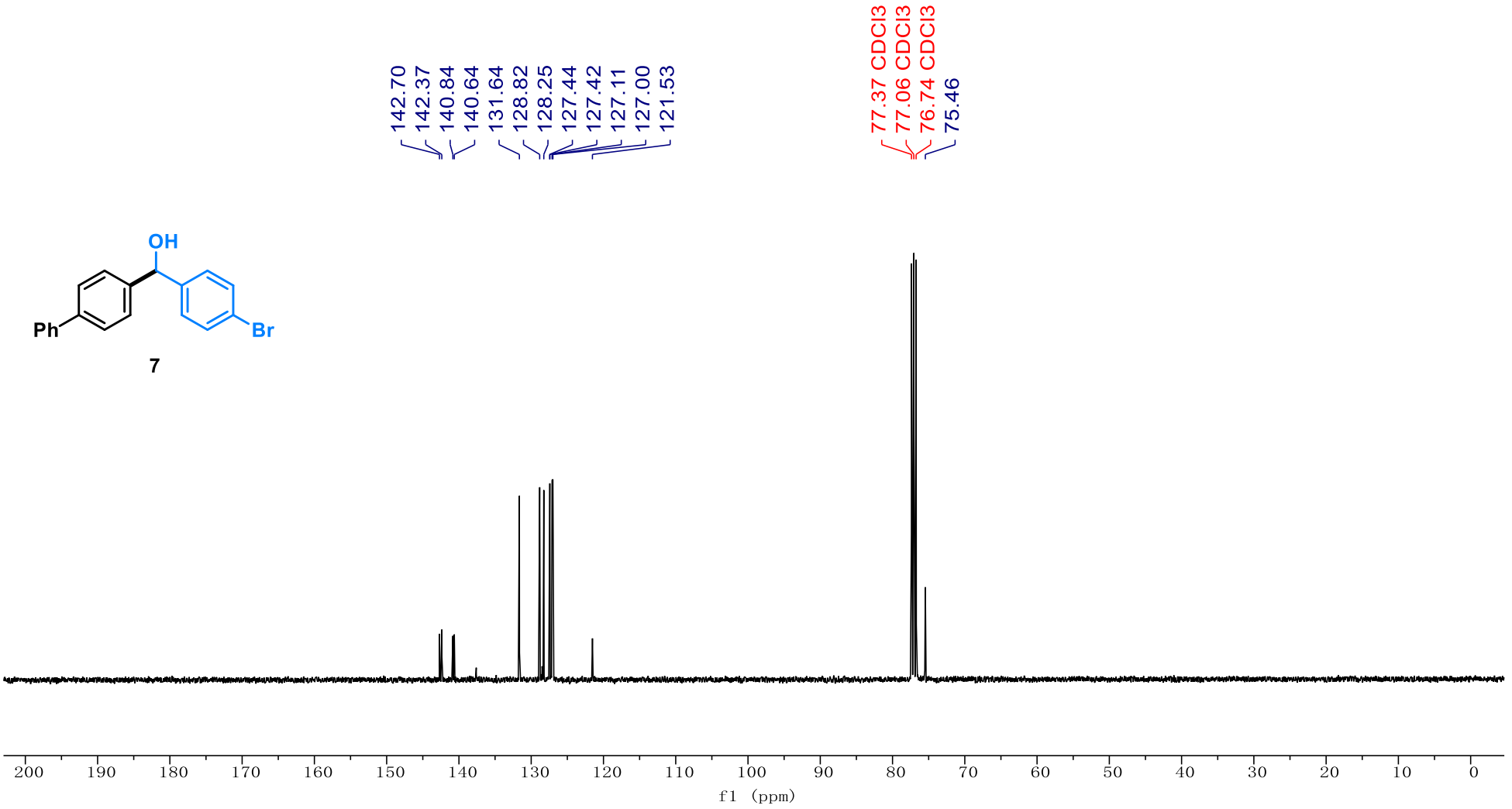
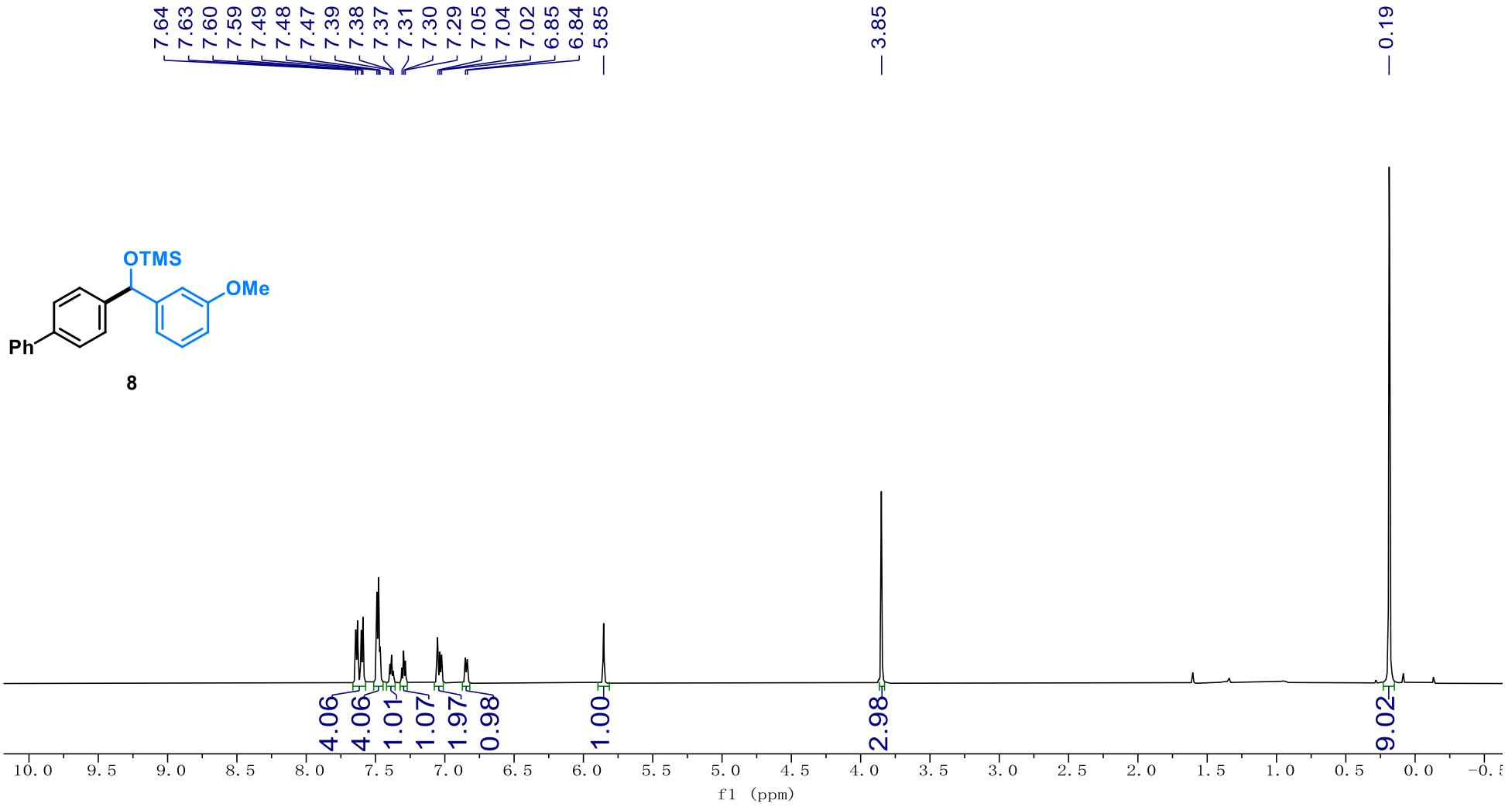
^{13}C NMR of 7 (101 MHz, $CDCl_3$)



^{1}H NMR of 8 (600 MHz, $CDCl_3$)



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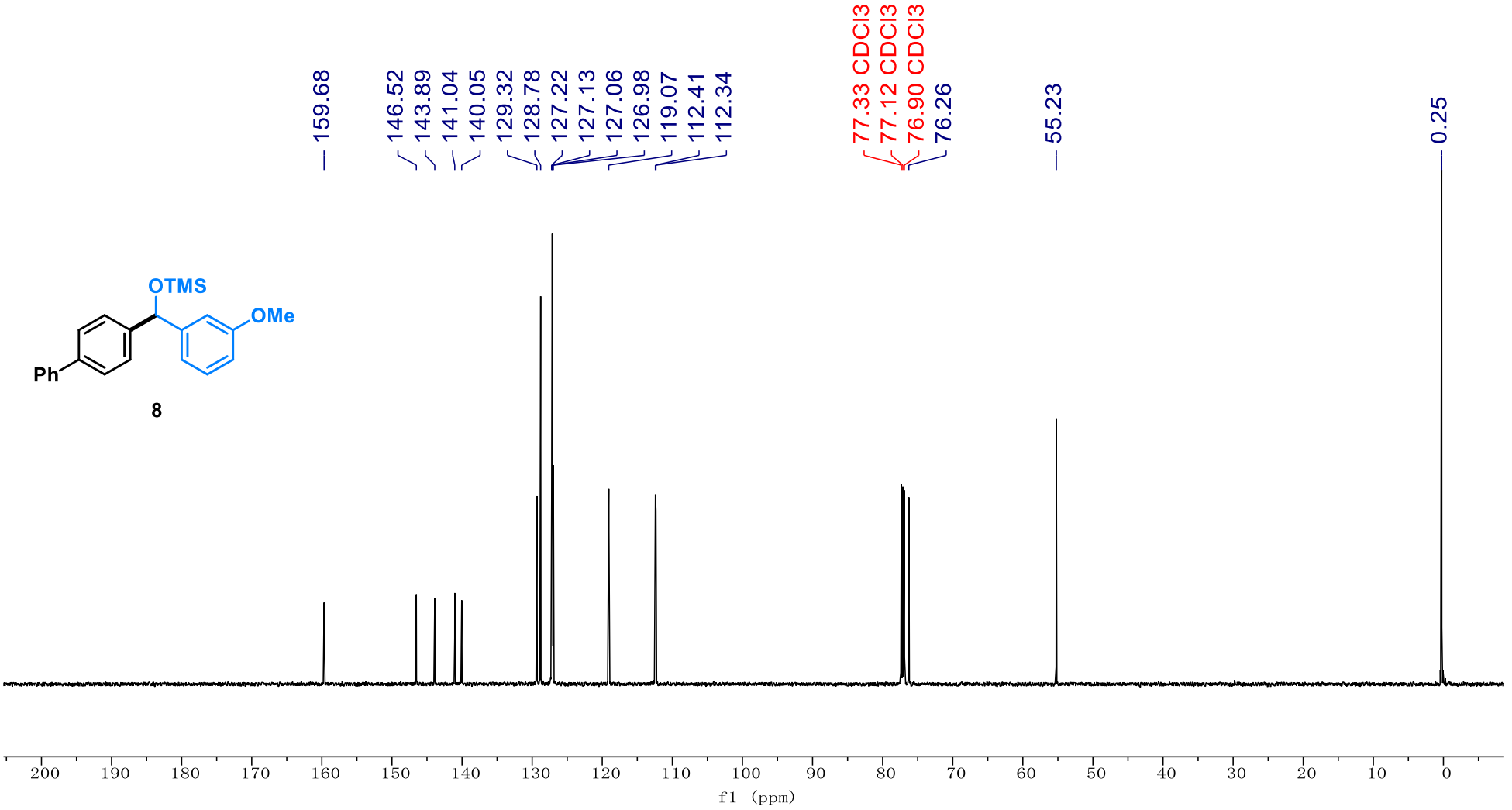
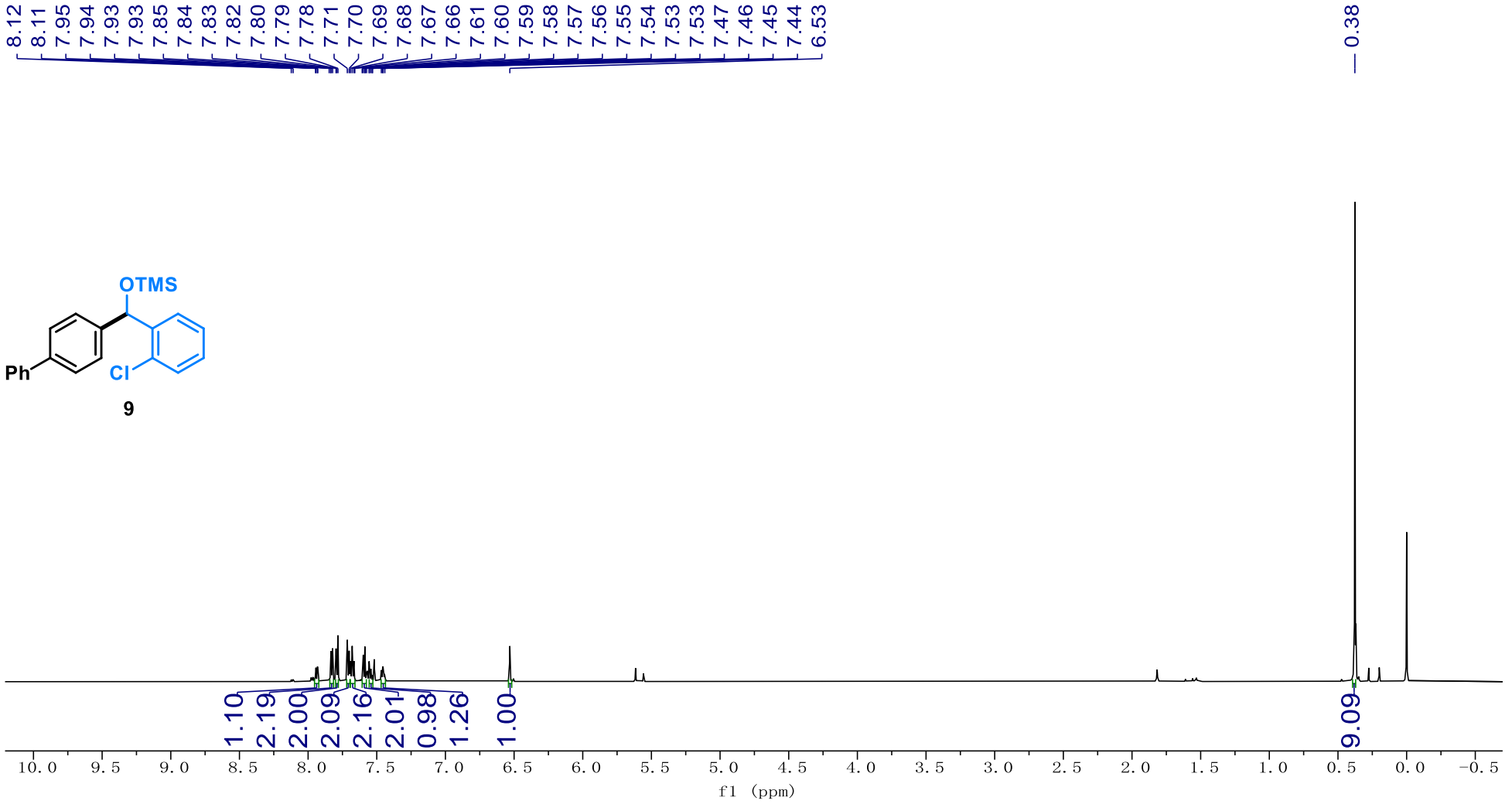
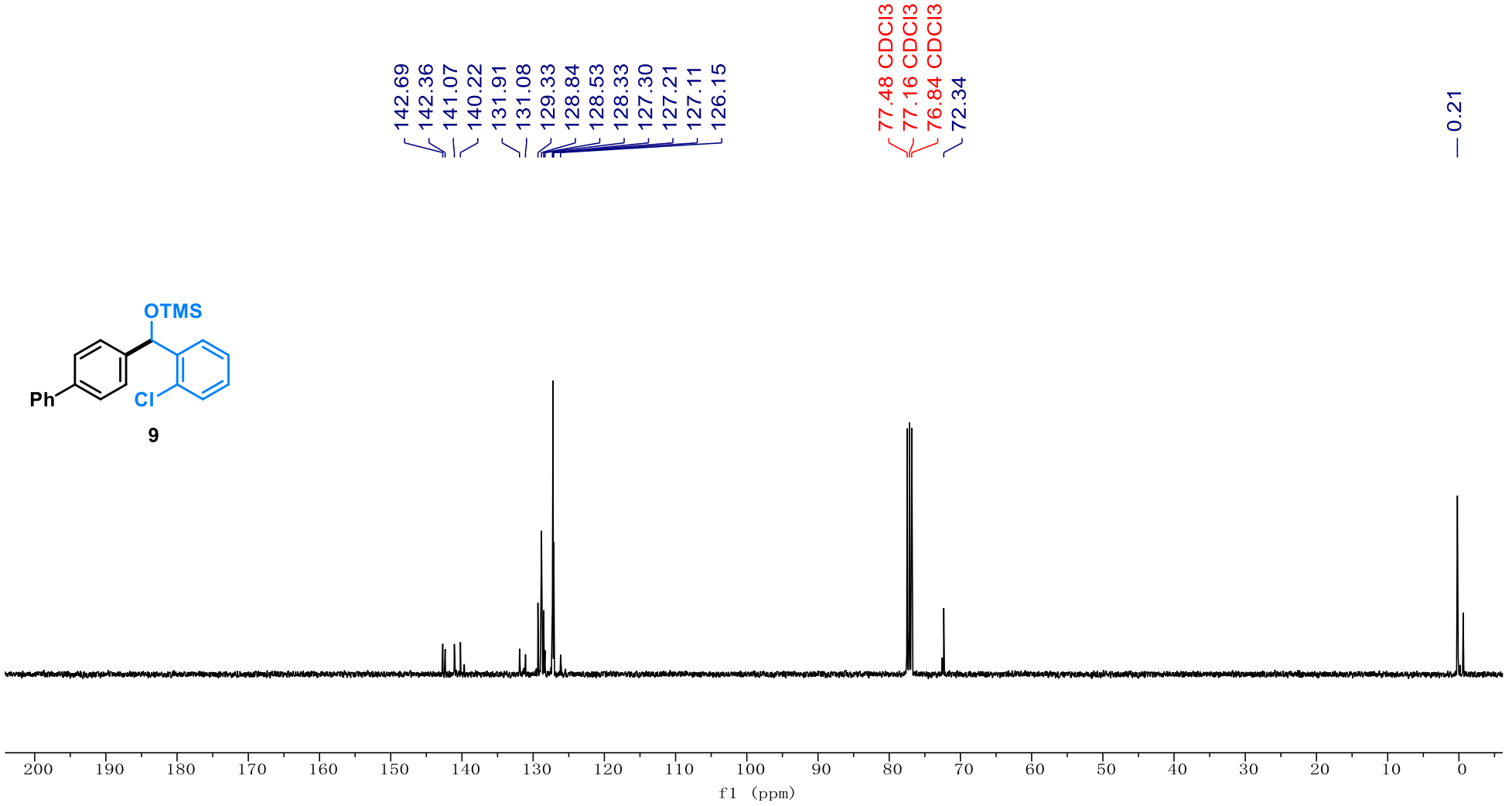
^{13}C NMR of 8 (151 MHz, $CDCl_3$)



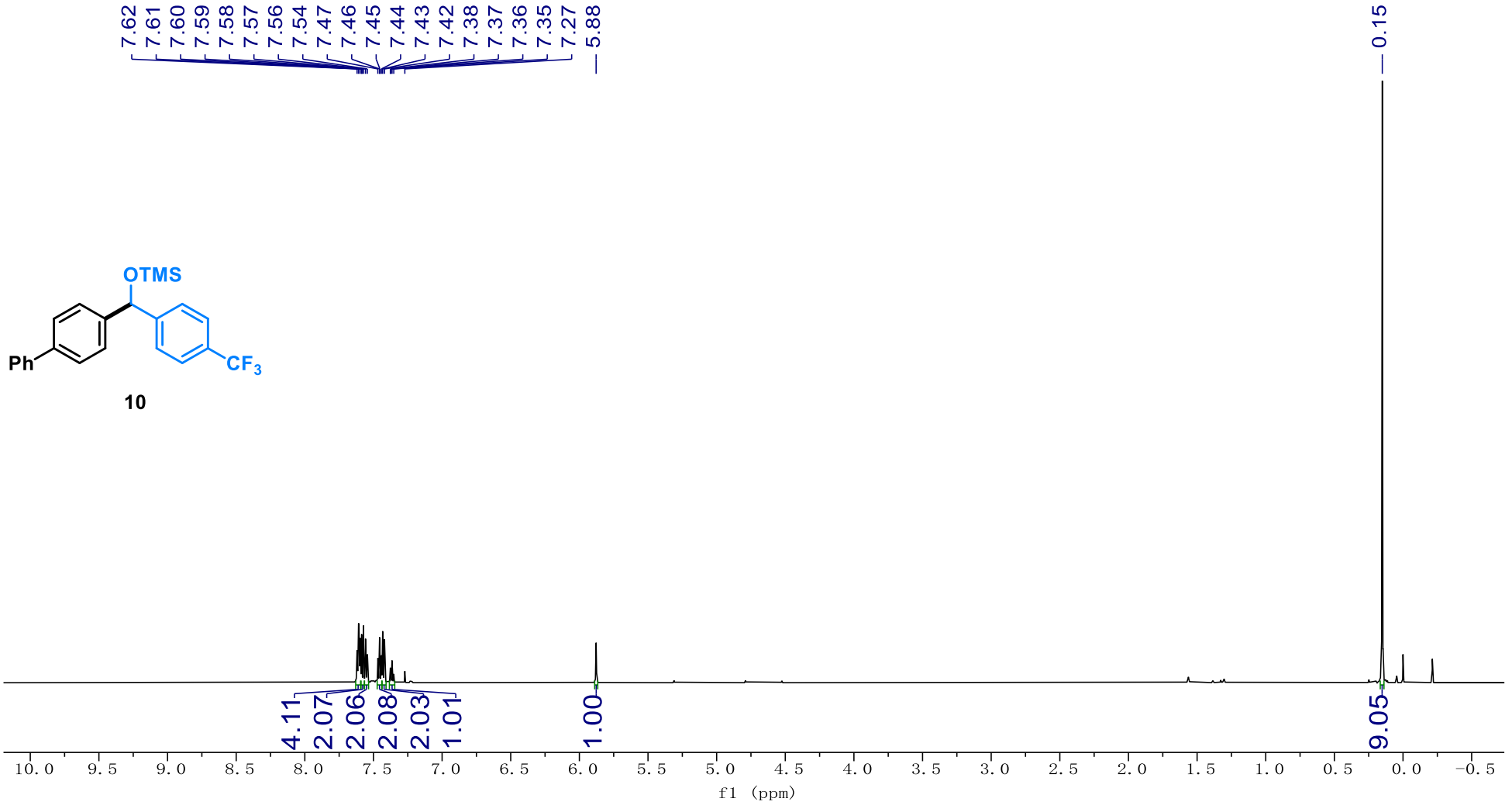
^{1}H NMR of 9 (400 MHz, $CDCl_3$)



^{13}C NMR of 9 (151 MHz, $CDCl_3$)

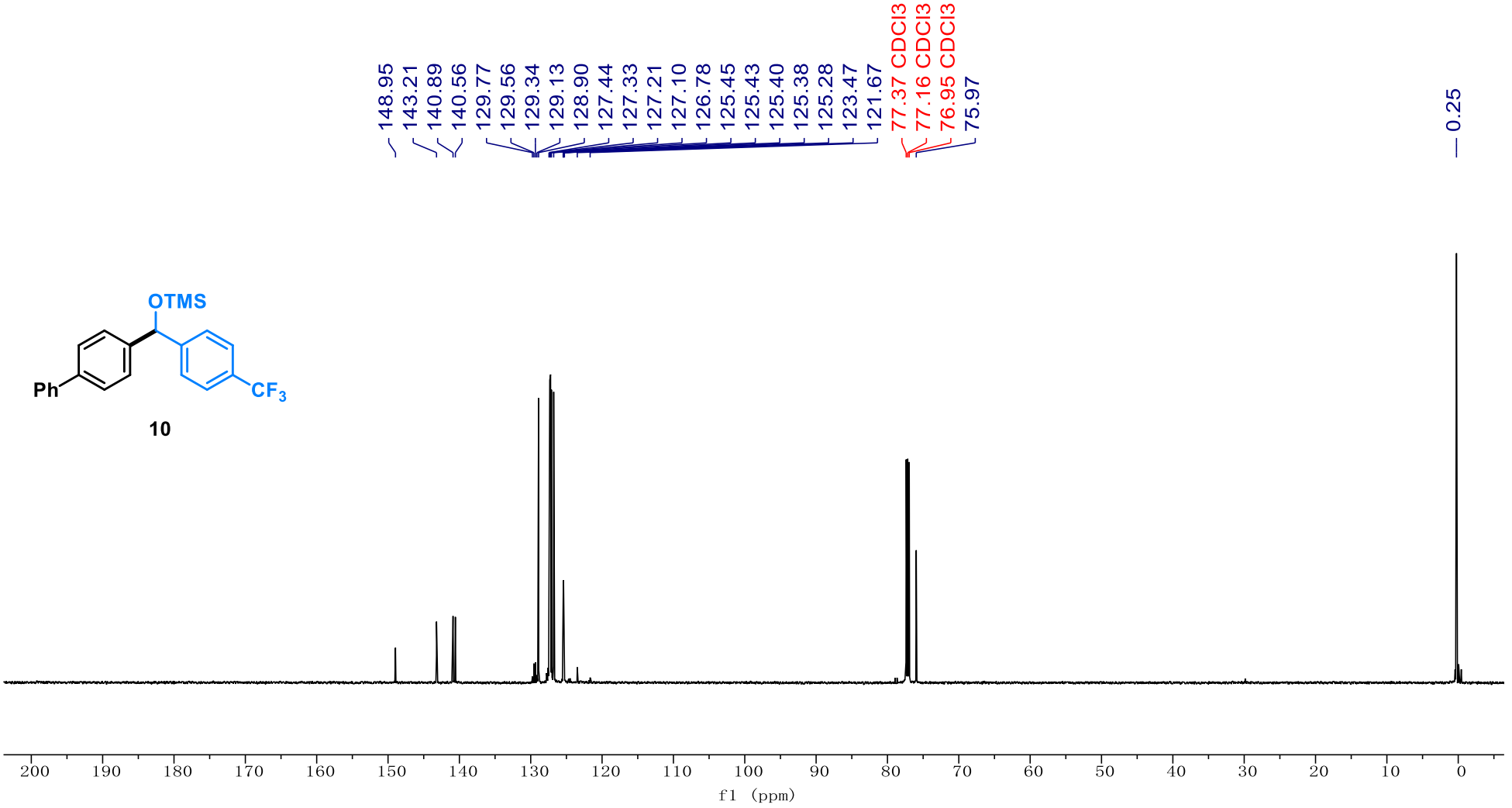


^{1}H NMR of 10 (600 MHz, $CDCl_3$)

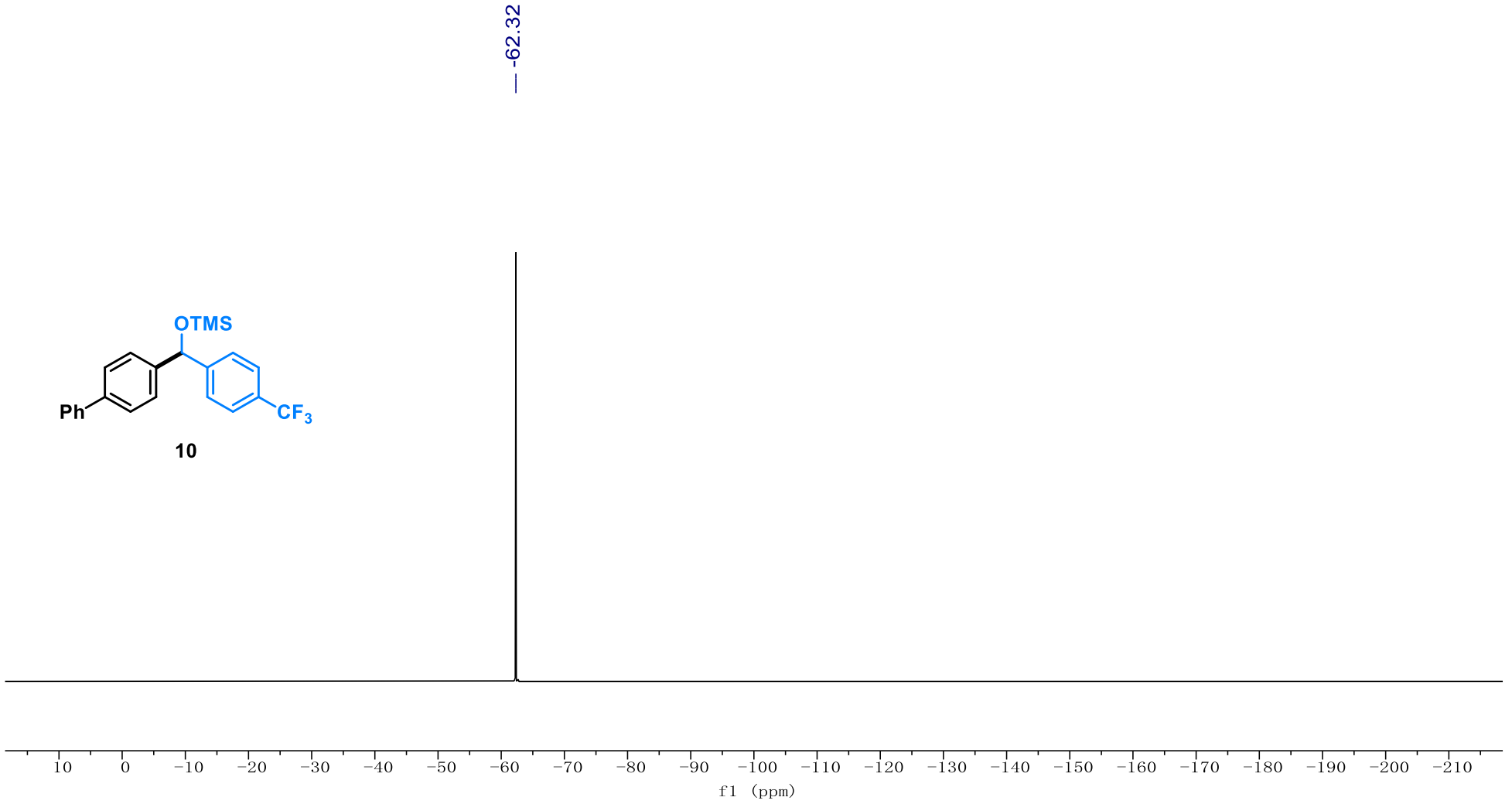


10

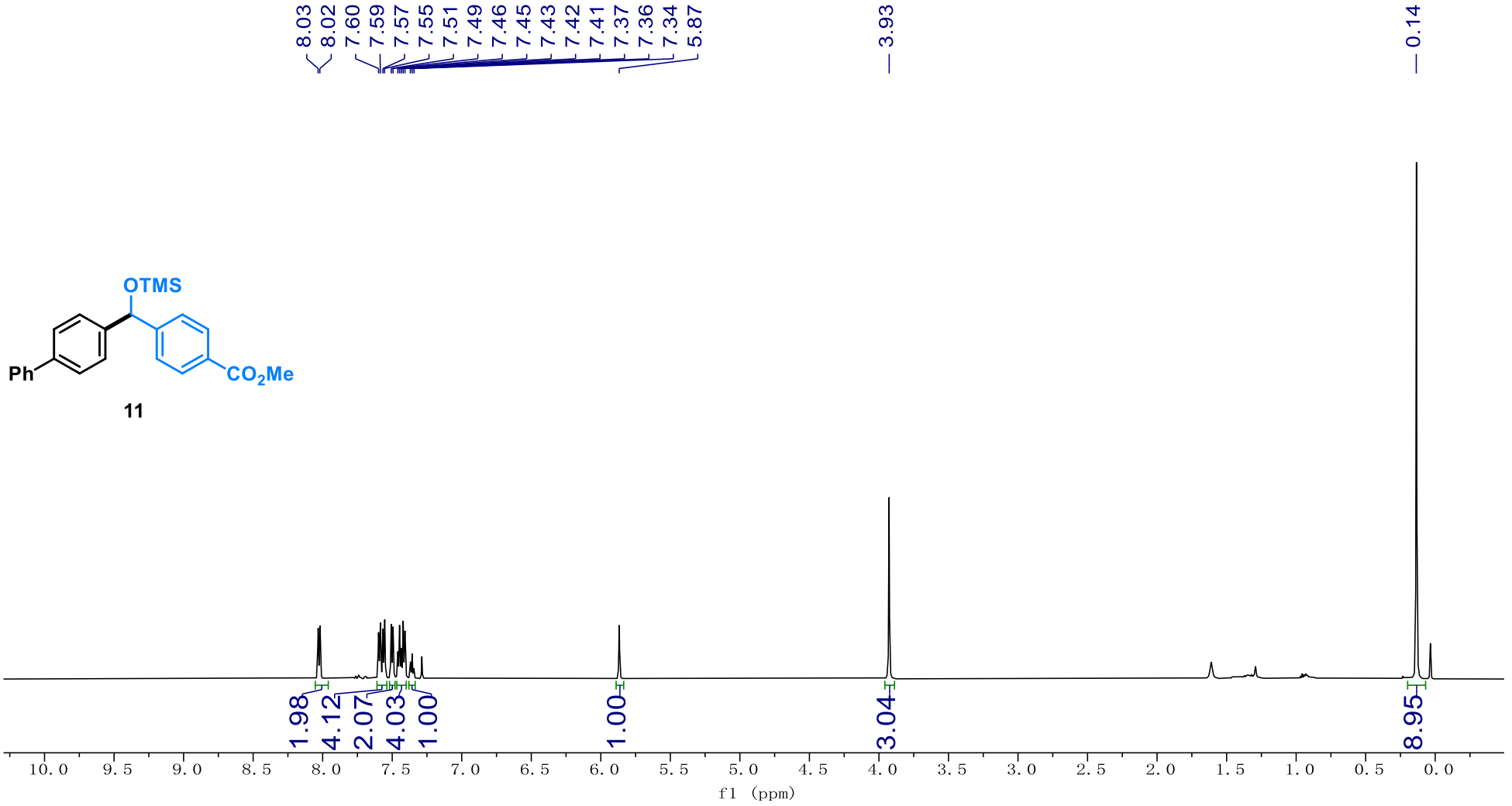
^{13}C NMR of 10 (151 MHz, $CDCl_3$)



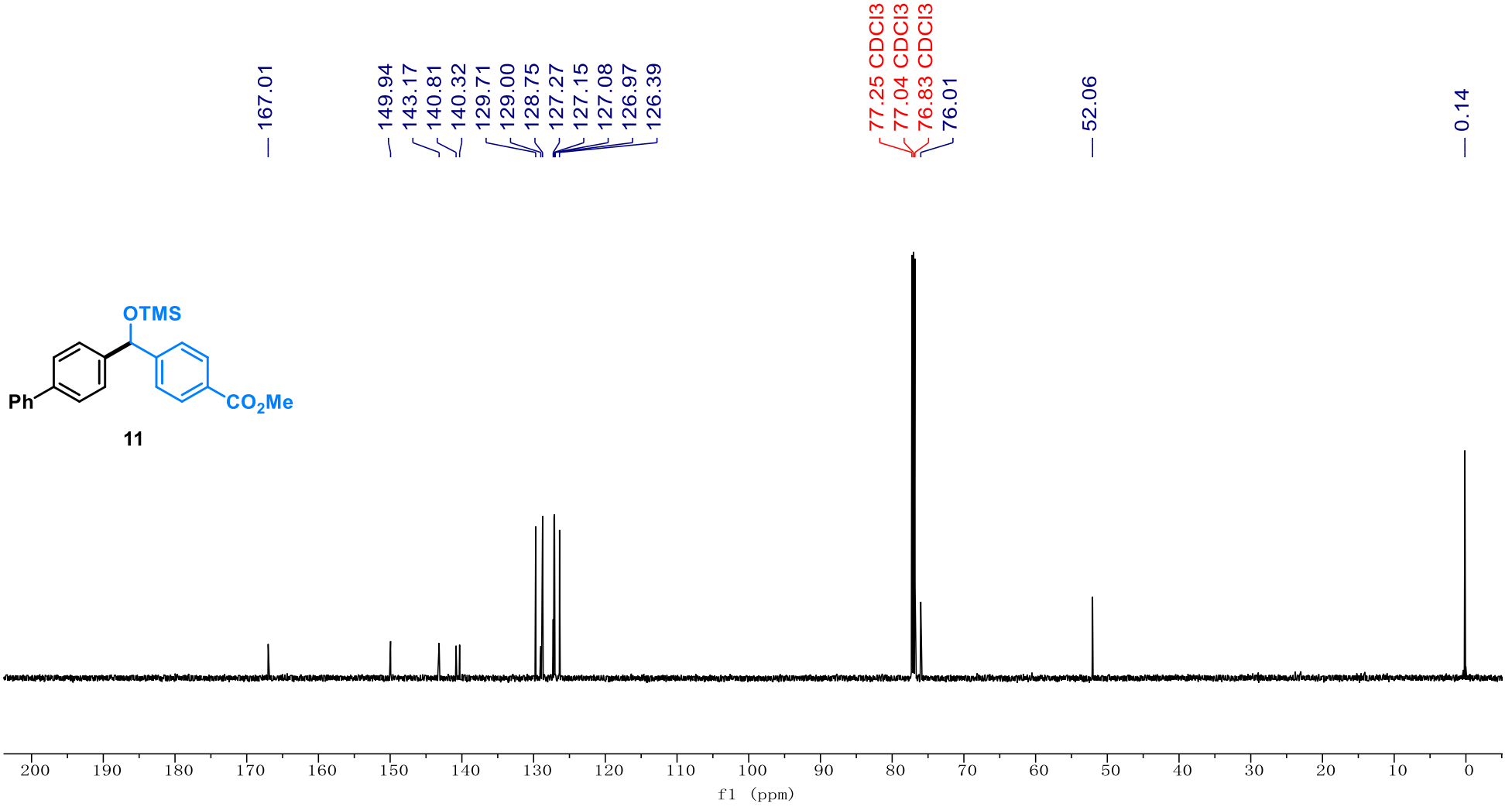
^{19}F NMR of 10 (565 MHz, $CDCl_3$)



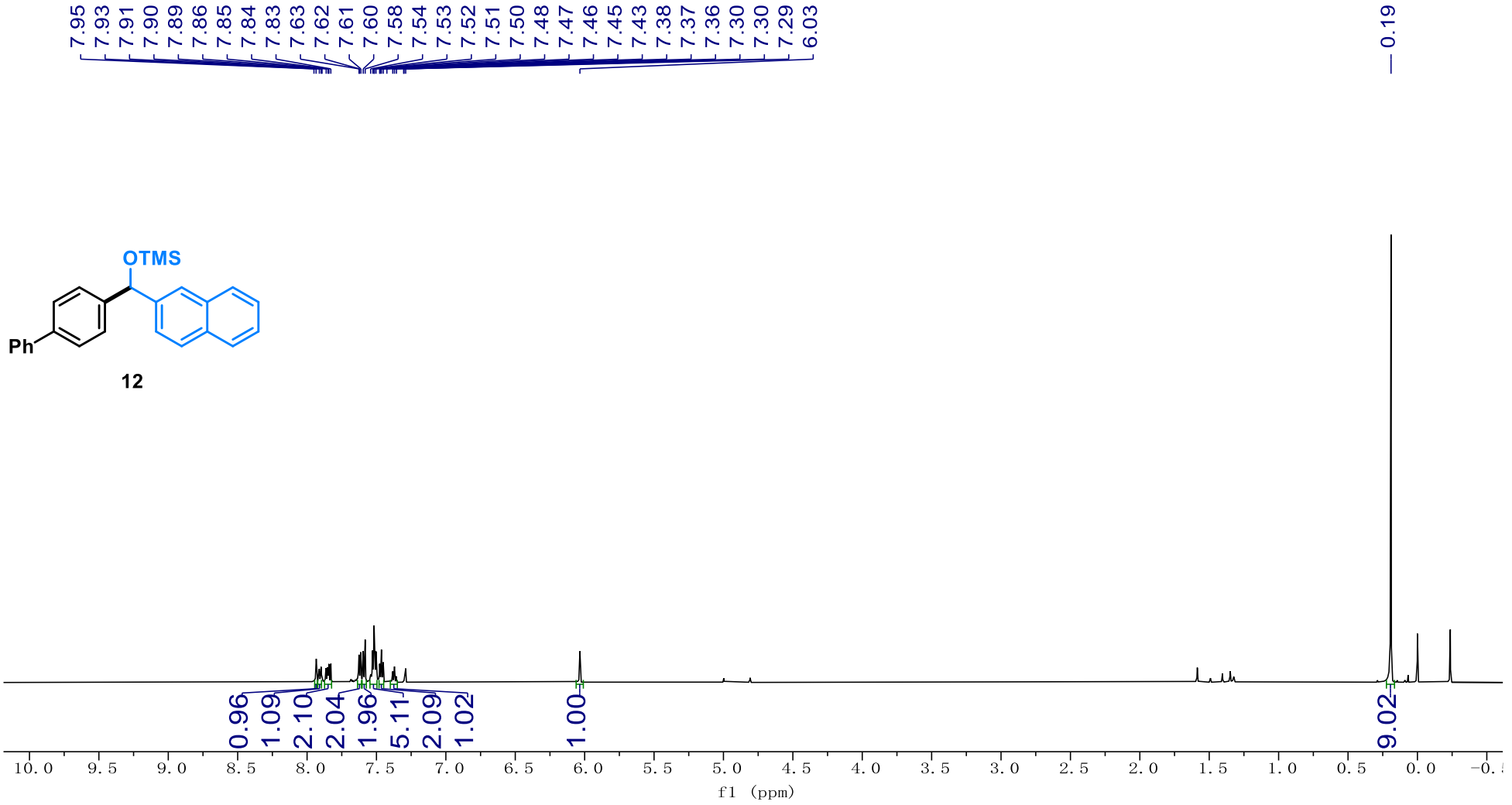
^{1}H NMR of 11 (600 MHz, $CDCl_3$)



^{13}C NMR of 11 (151 MHz, $CDCl_3$)



^{1}H NMR of 12 (600 MHz, $CDCl_3$)



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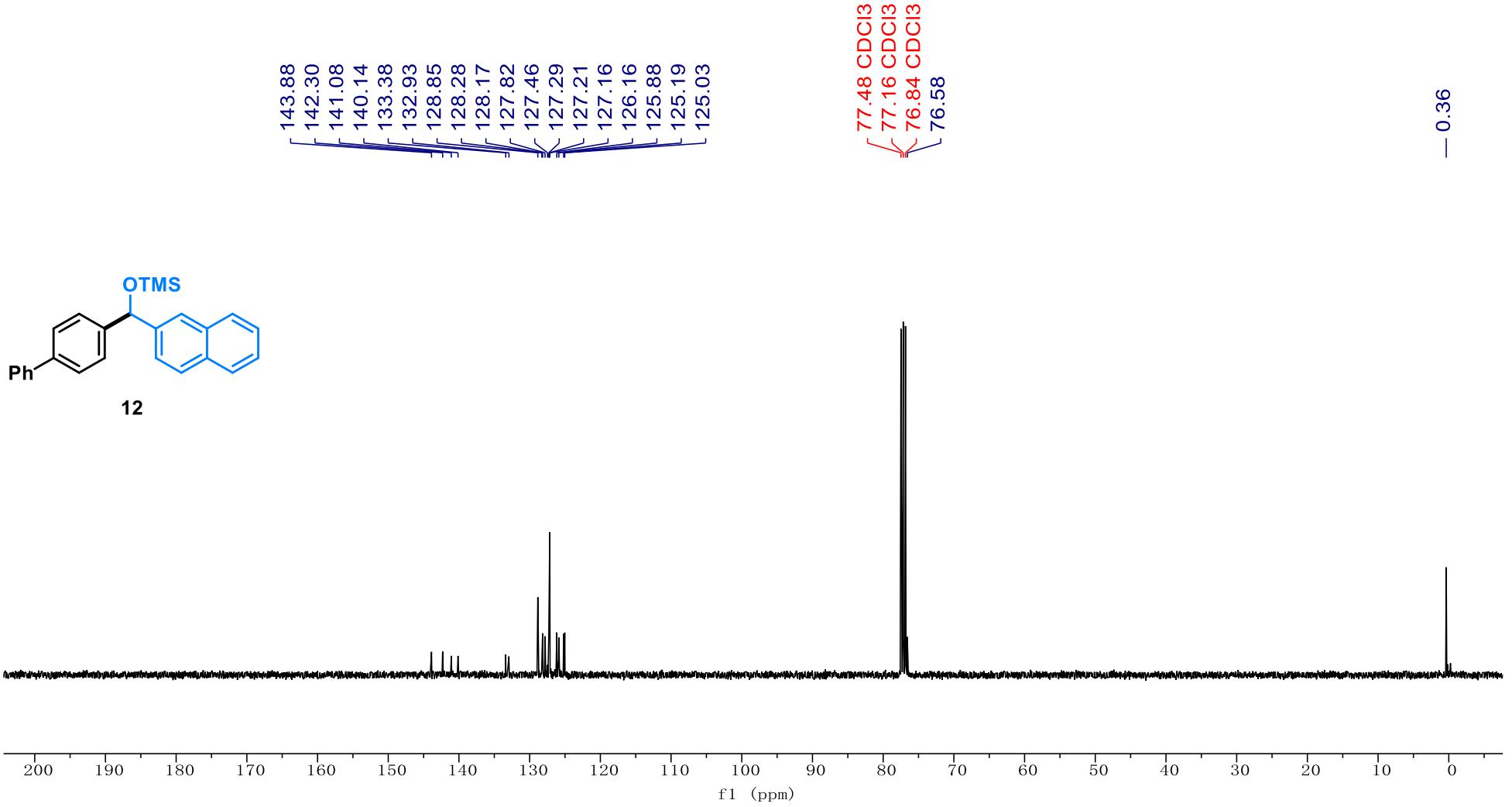

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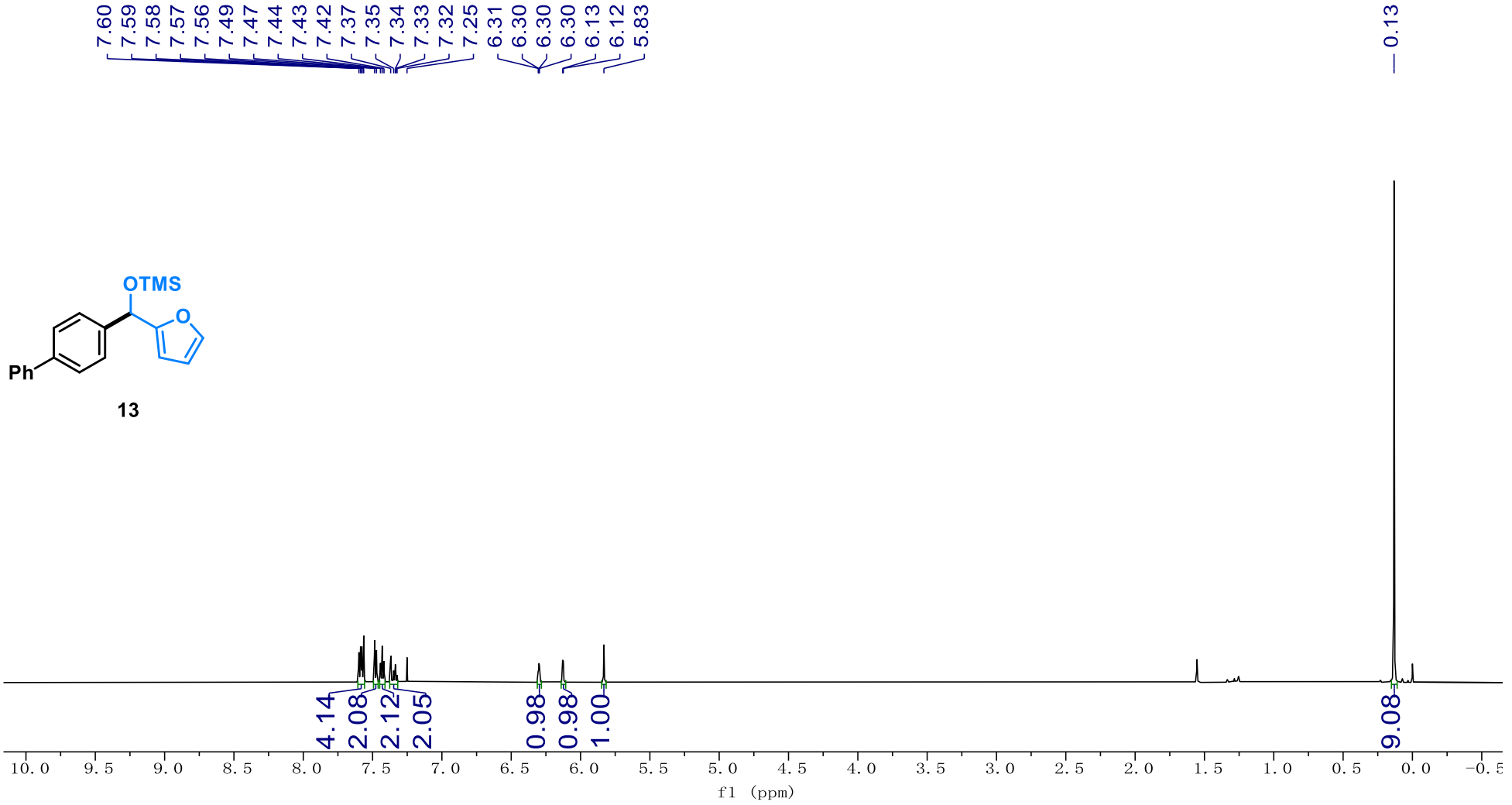
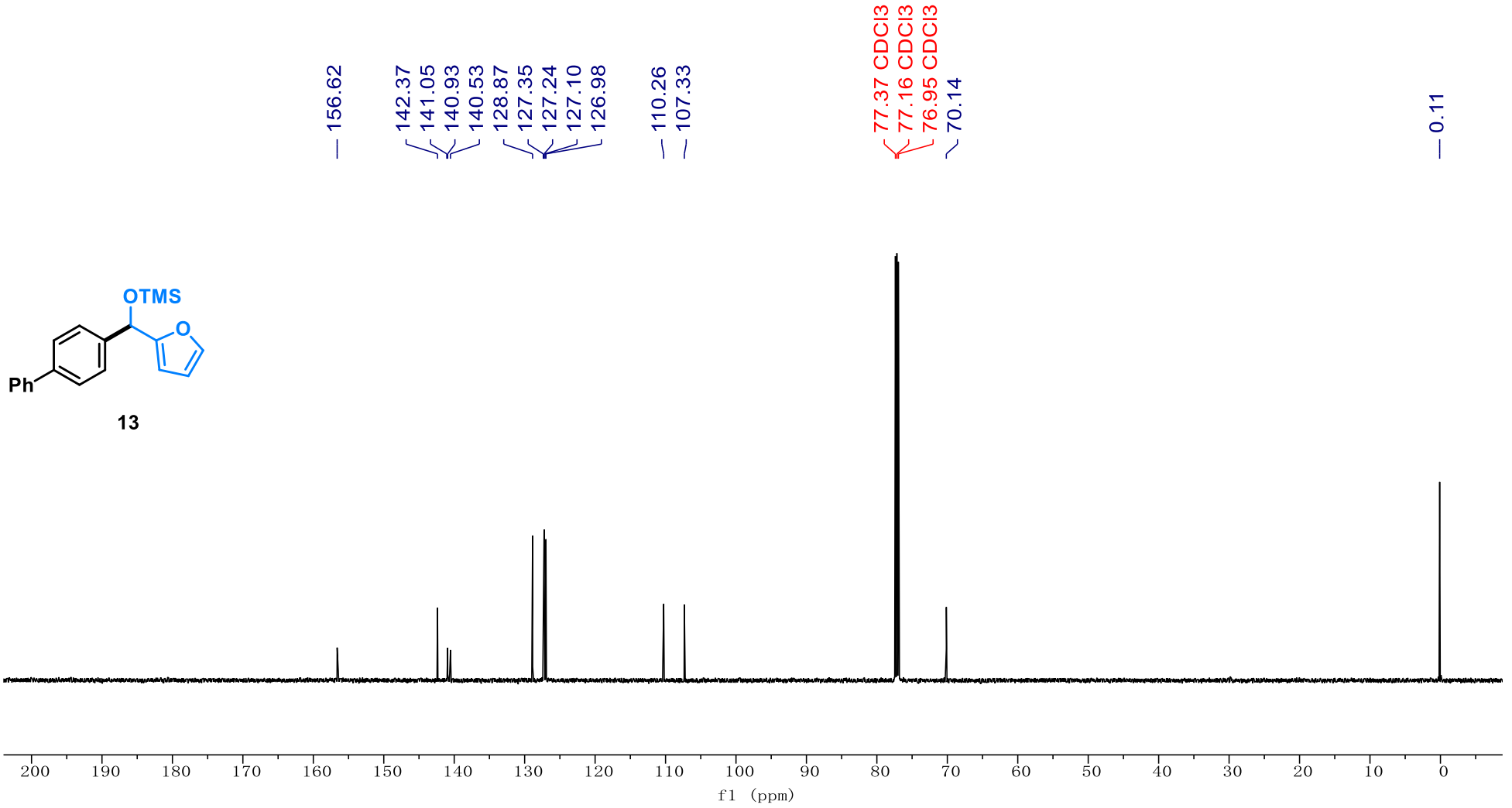


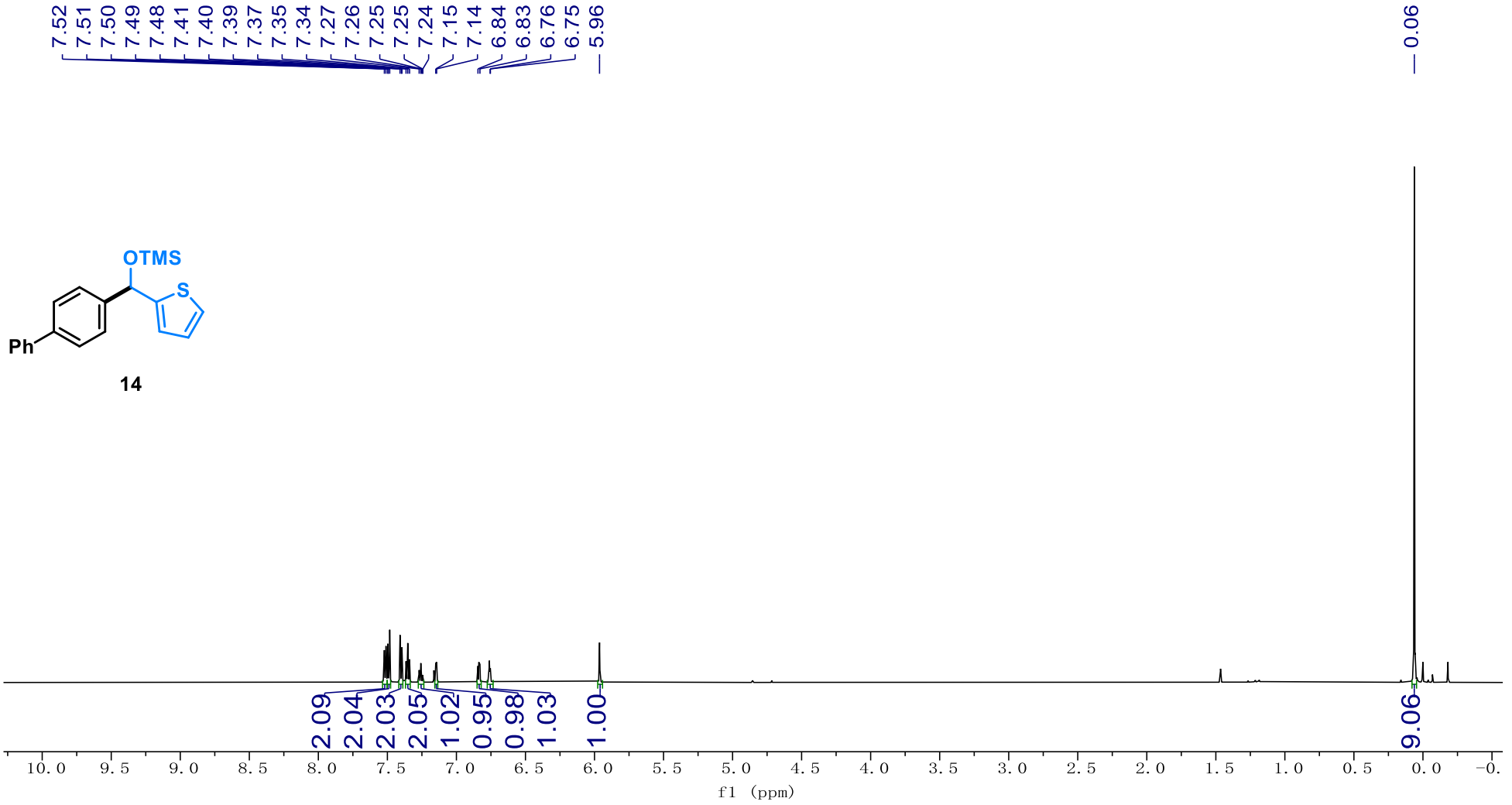
13

^{13}C NMR of 13 (151 MHz, $CDCl_3$)

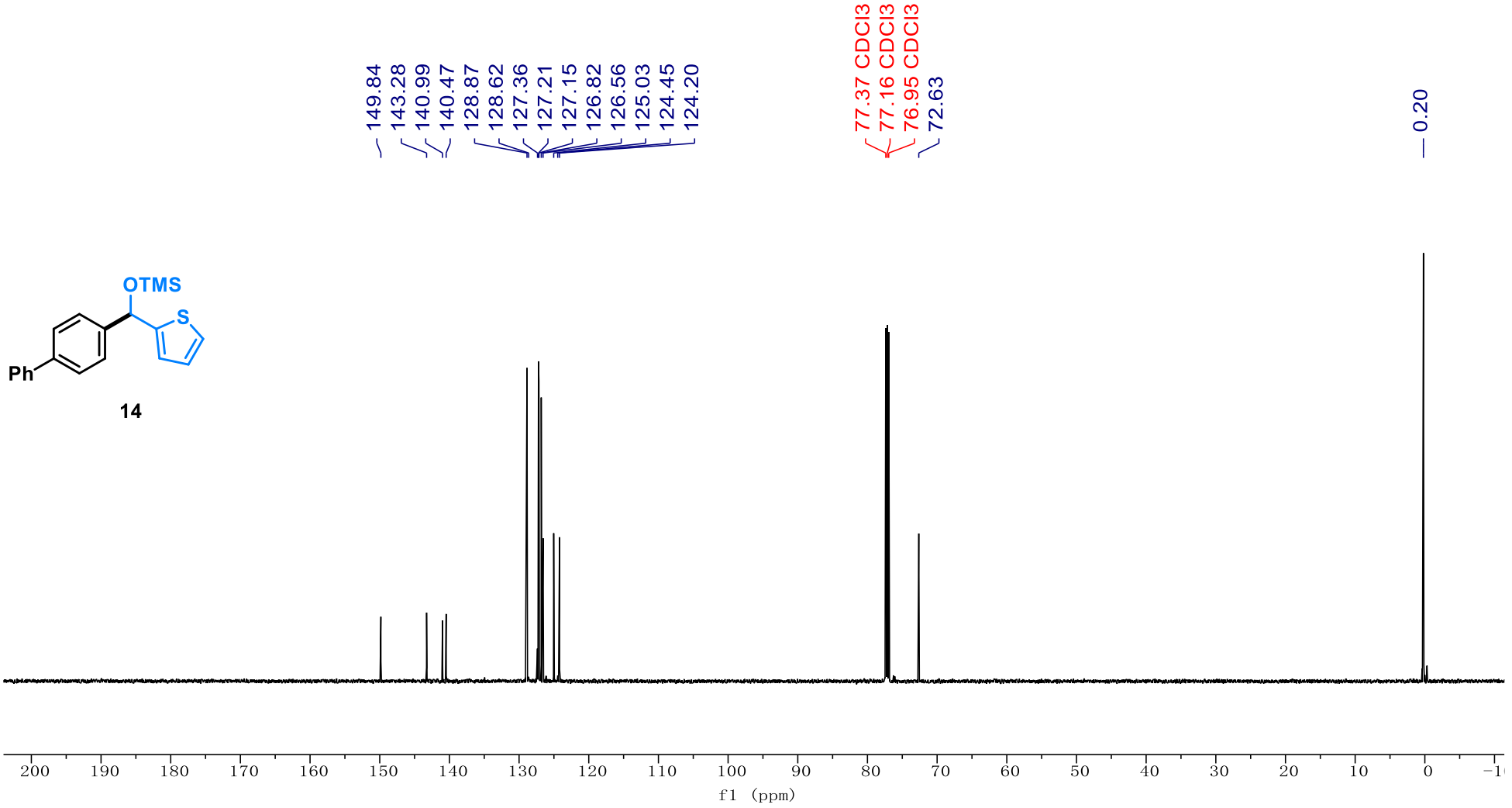


13

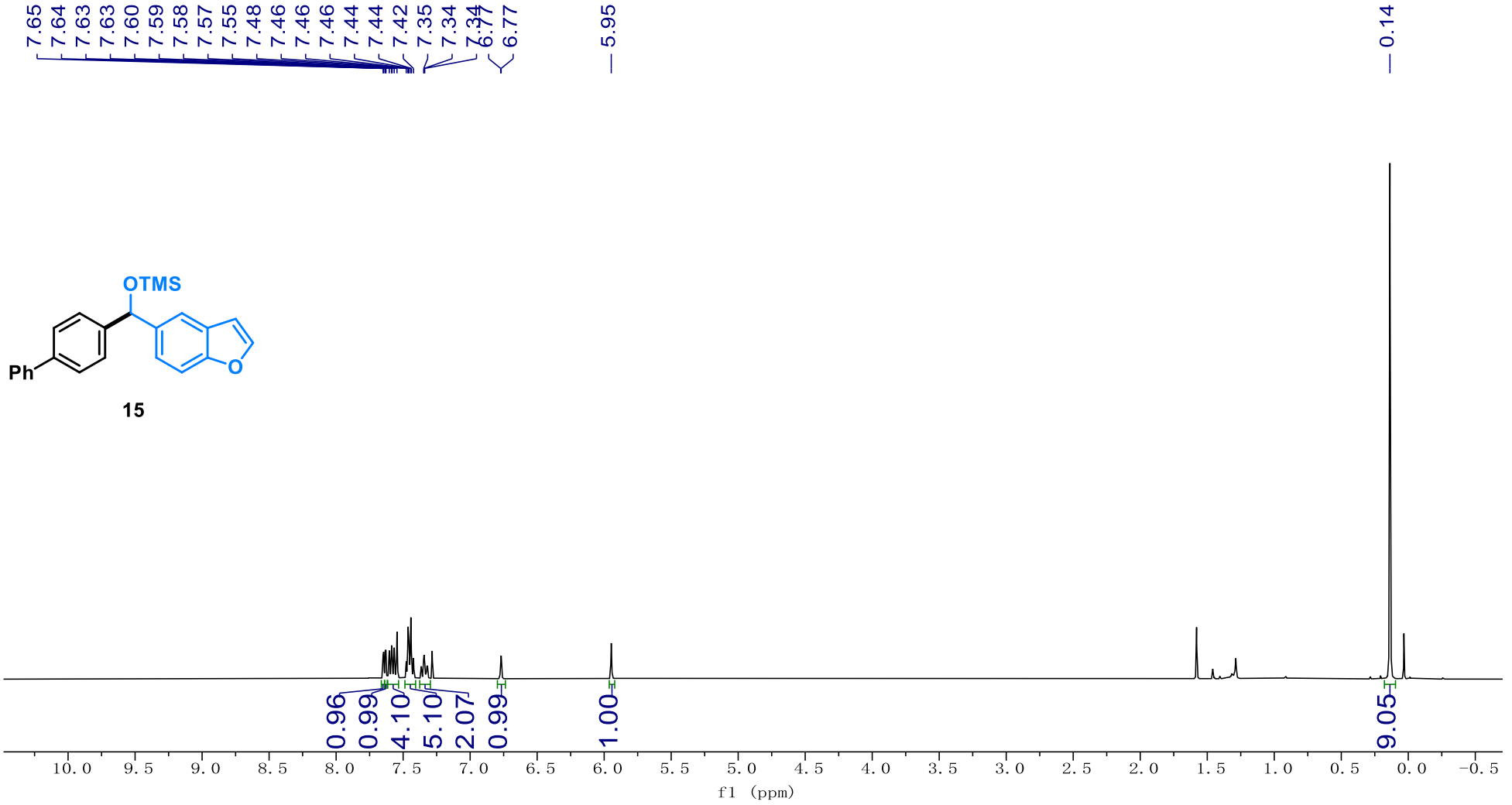
^{1}H NMR of 14 (600 MHz, $CDCl_3$



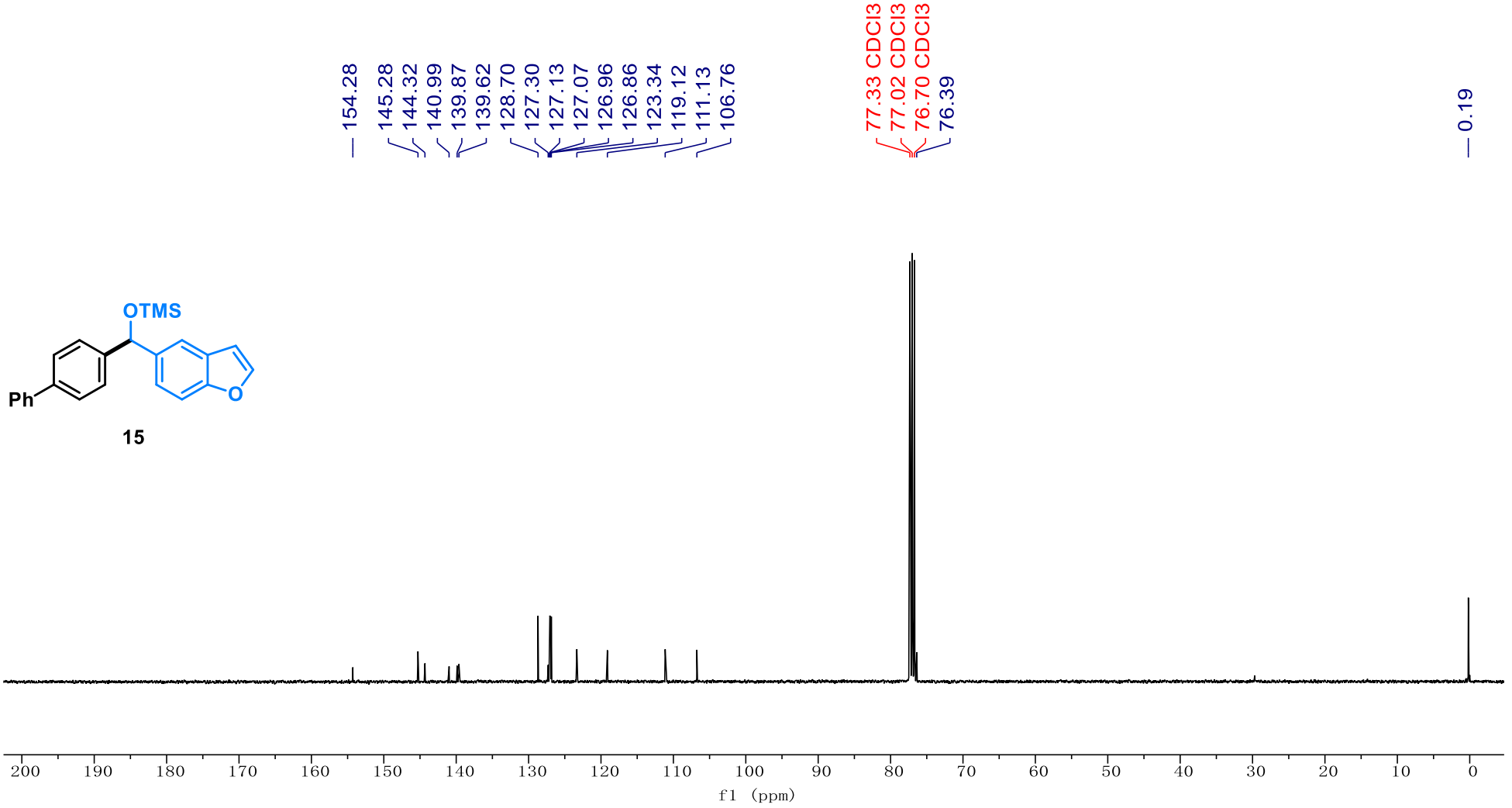
^{13}C NMR of 14 (151 MHz, $CDCl_3$)



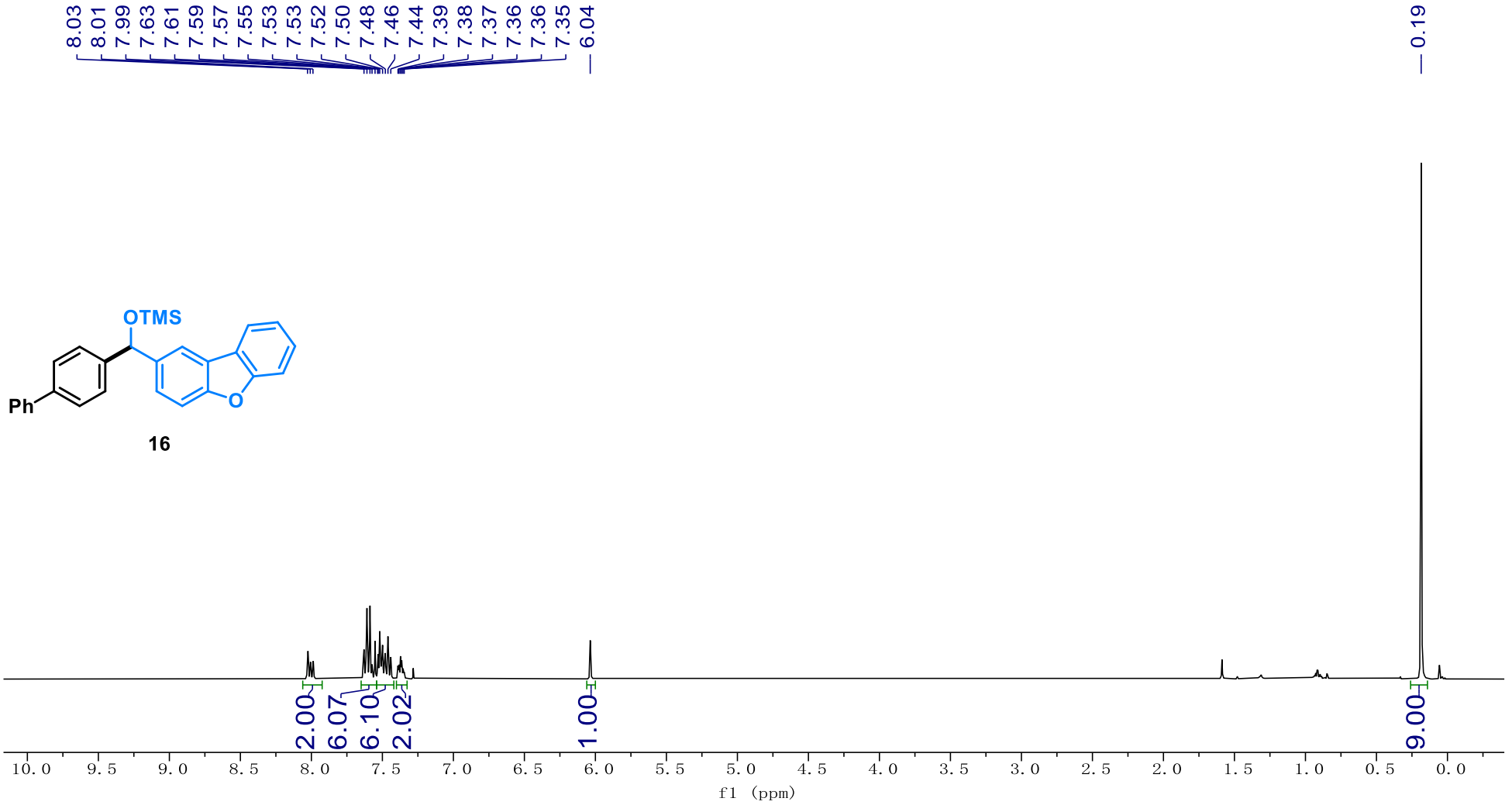
^{1}H NMR of 15 (400 MHz, $CDCl_3$)



^{13}C NMR of 15 (101 MHz, $CDCl_3$)

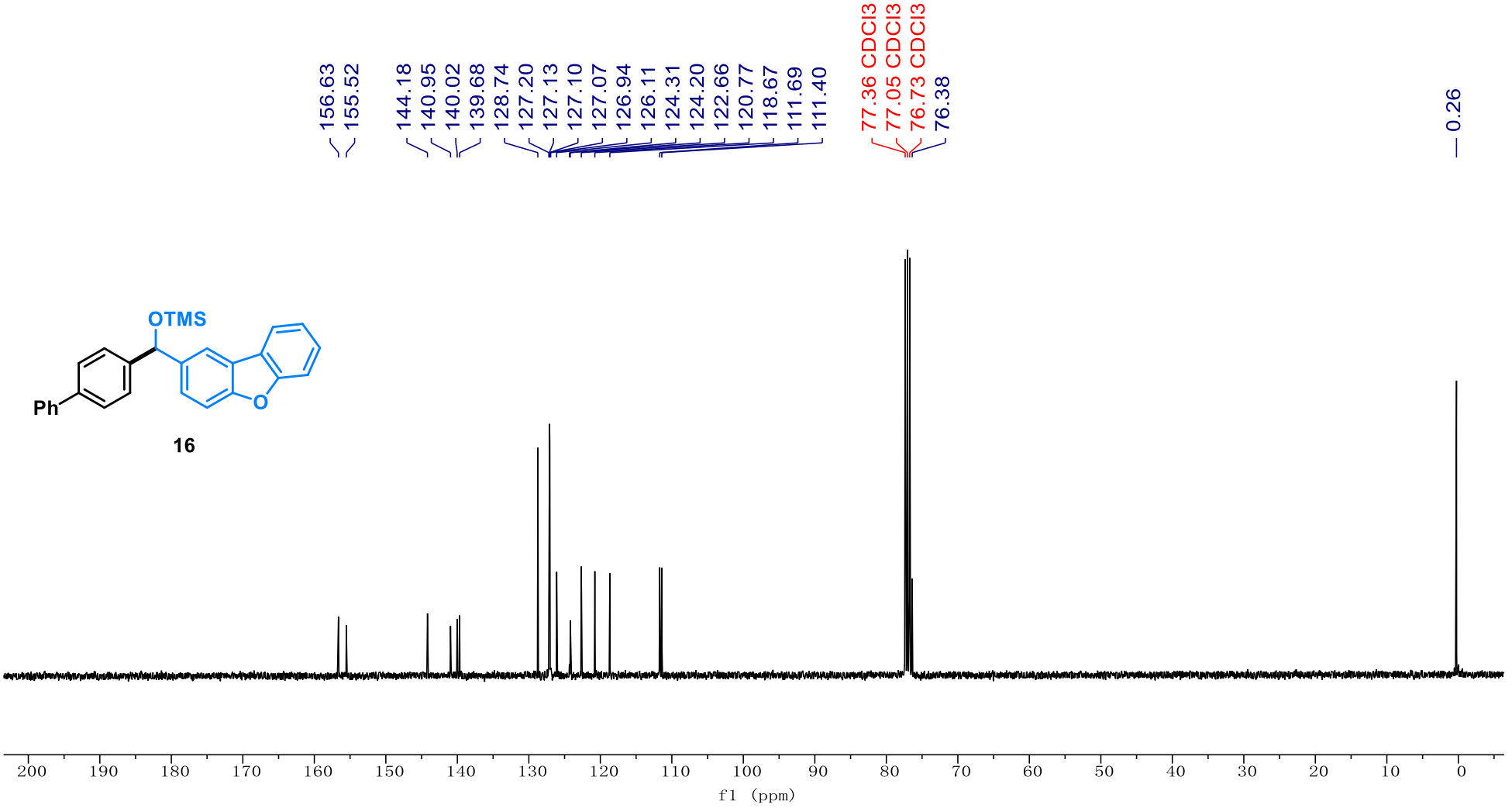


^{1}H NMR of 16 (400 MHz, $CDCl_3$)

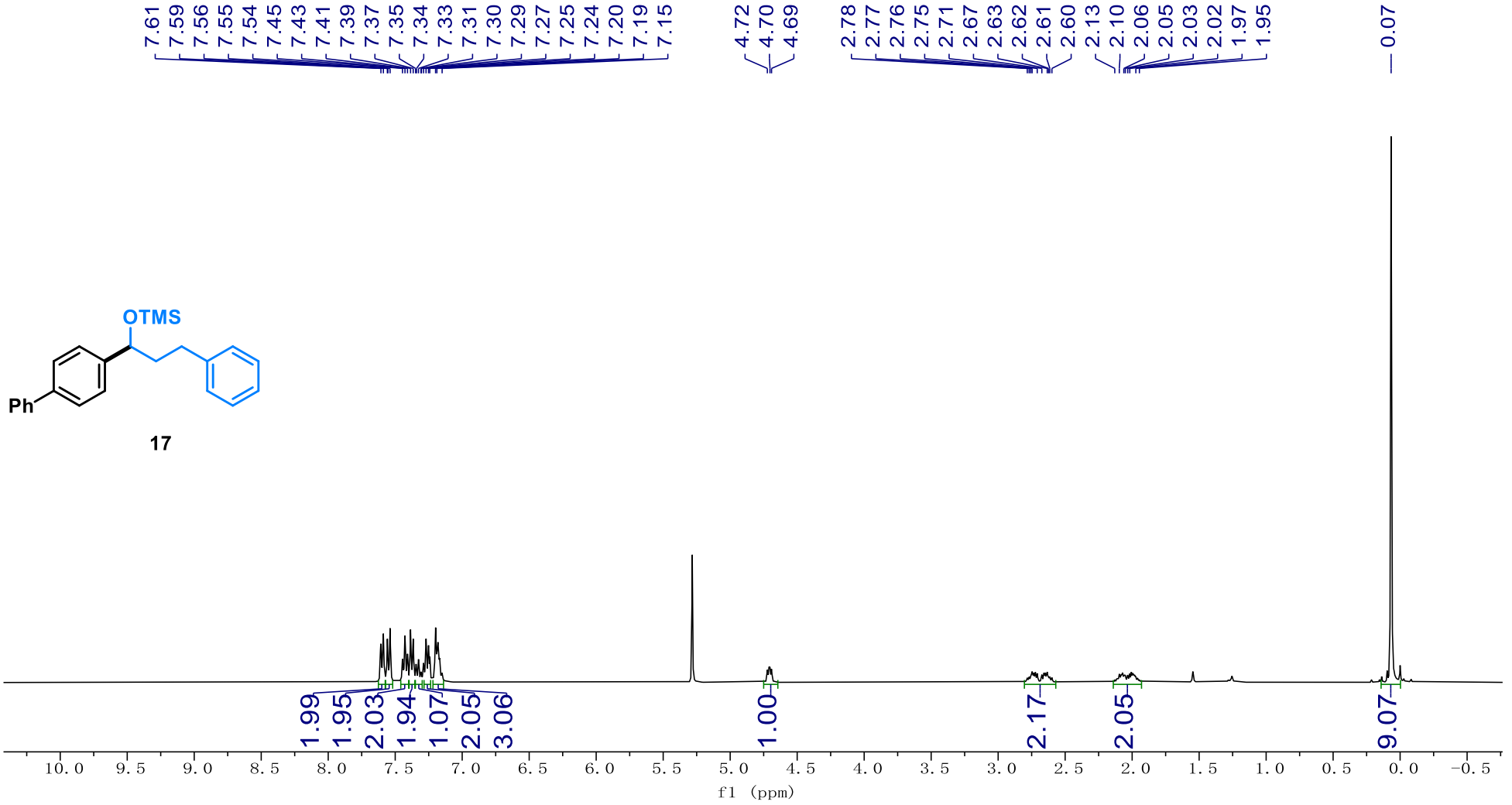


16

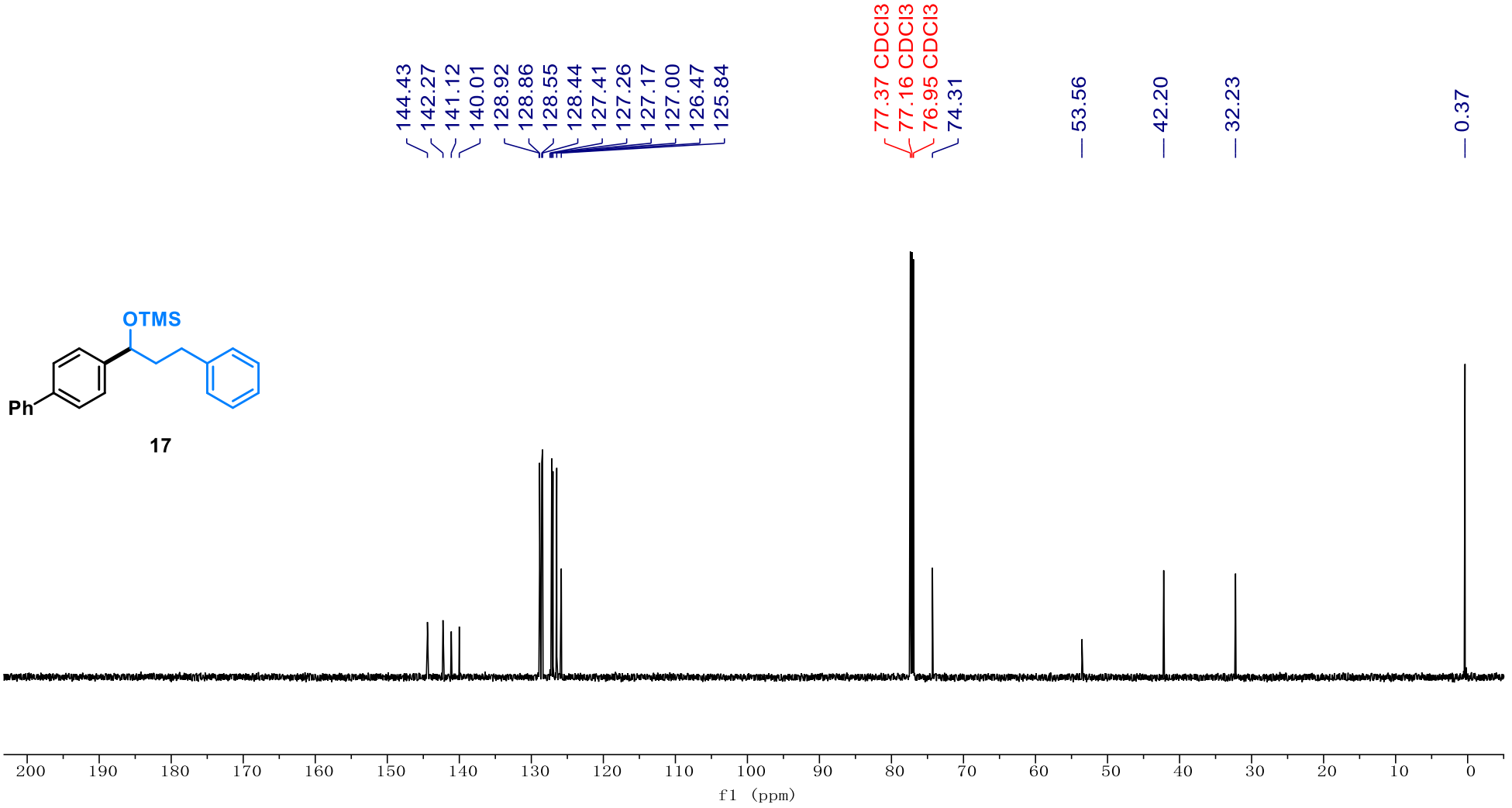
^{13}C NMR of 16 (101 MHz, $CDCl_3$)



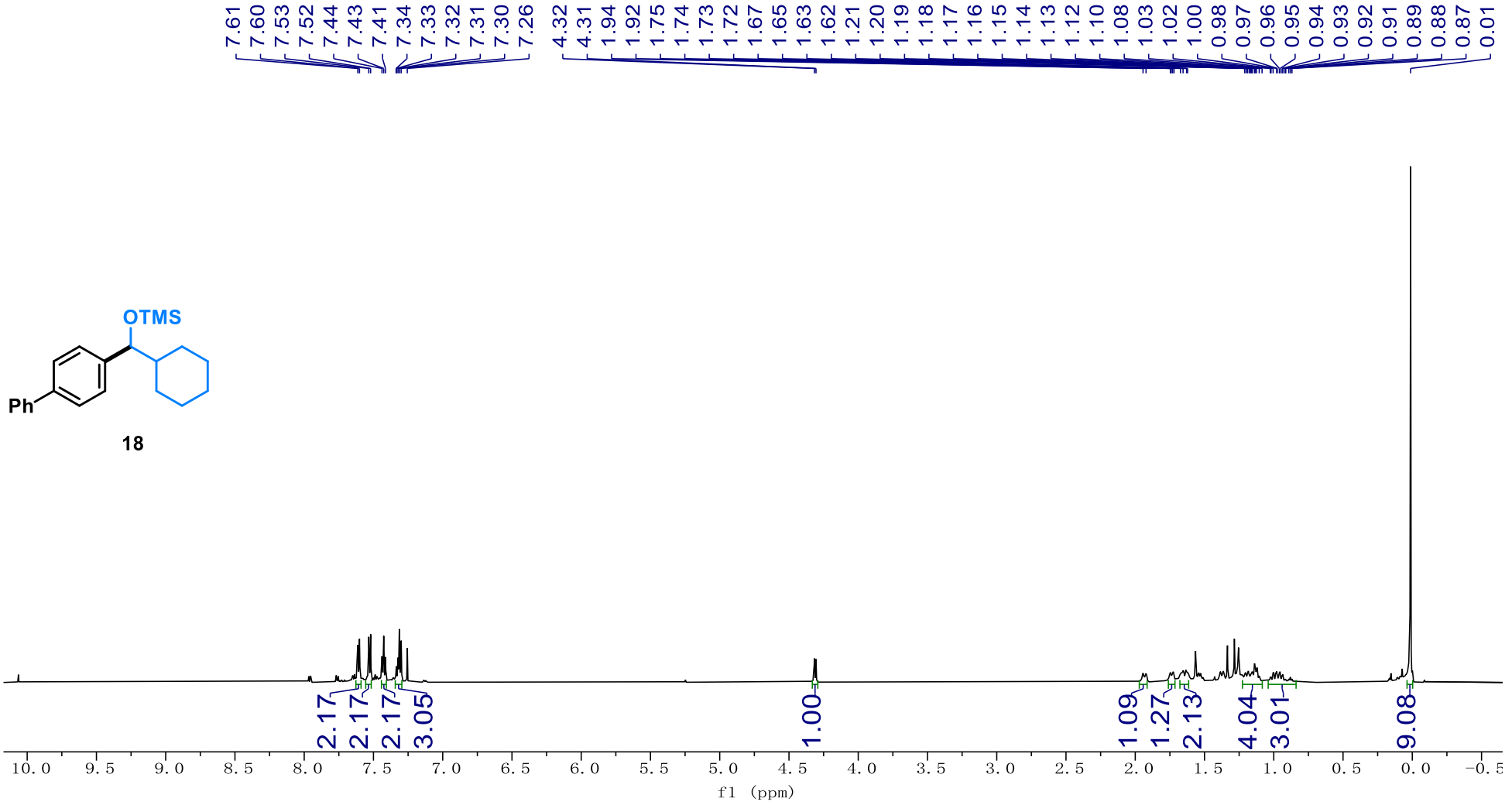
^{1}H NMR of 17 (400 MHz, $CDCl_3$)



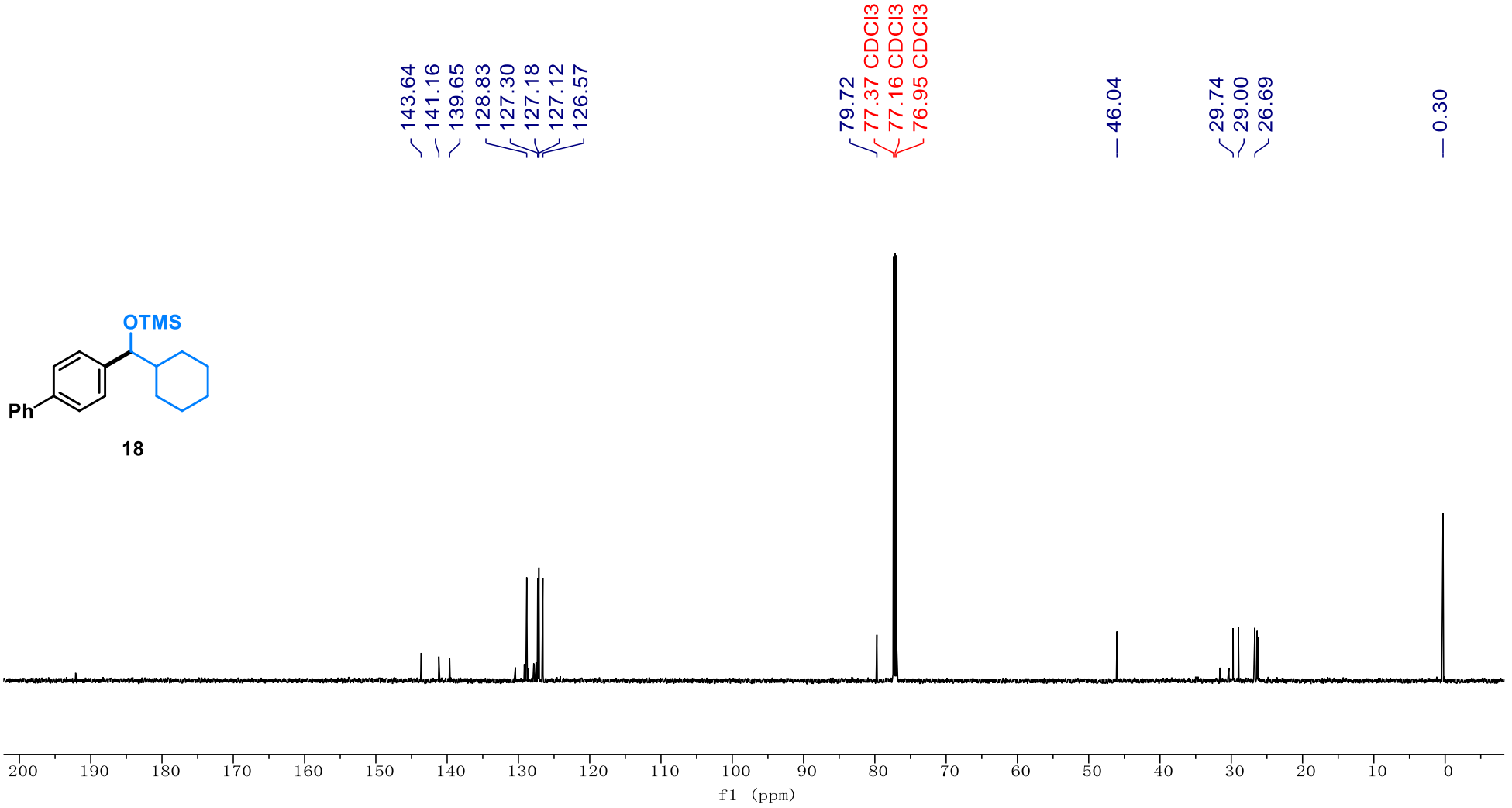
^{13}C NMR of 17 (101 MHz, $CDCl_3$)



^{1}H NMR of 18 (600 MHz, $CDCl_3$)

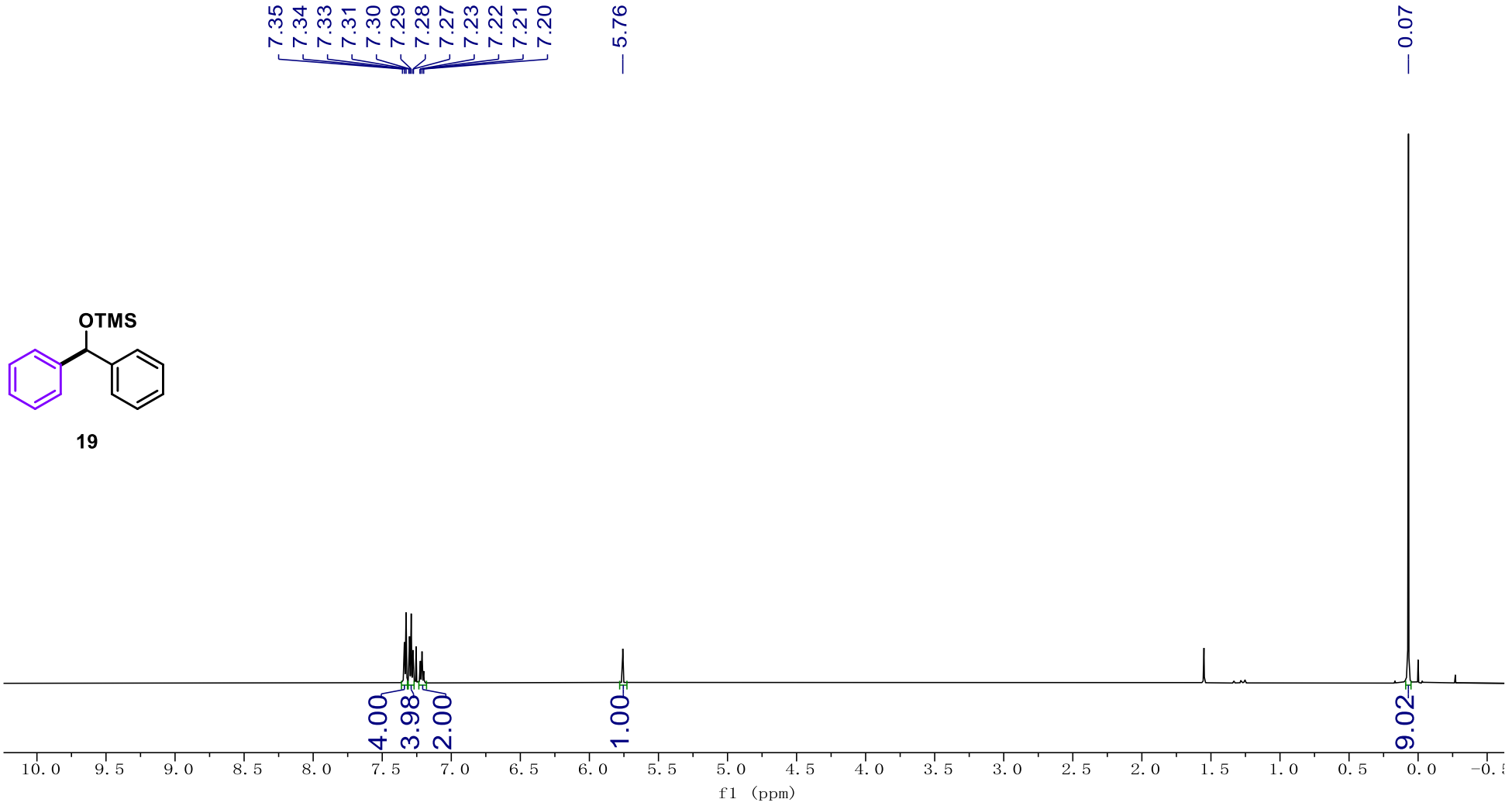


^{13}C NMR of 18 (151 MHz, $CDCl_3$)

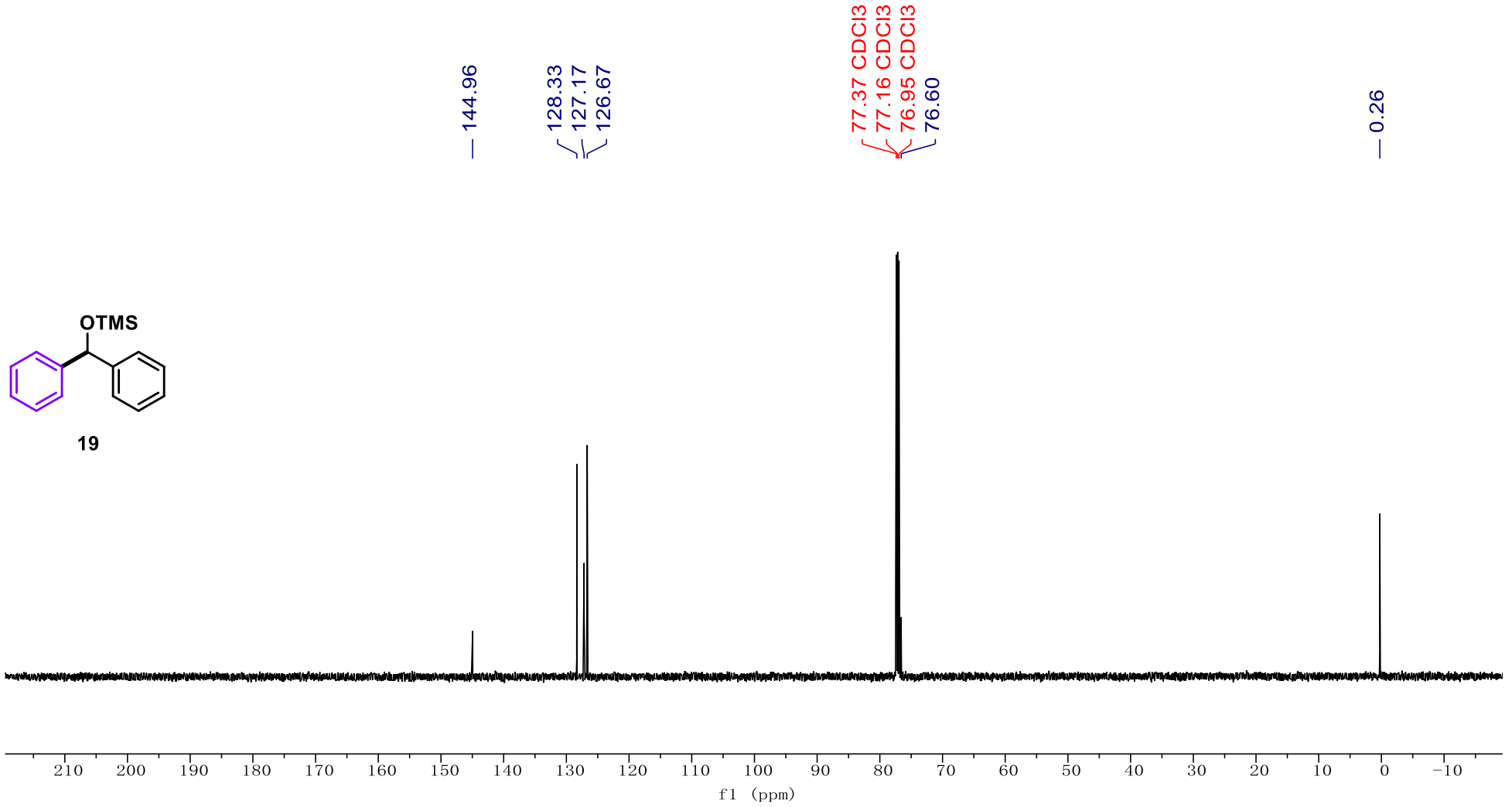


18

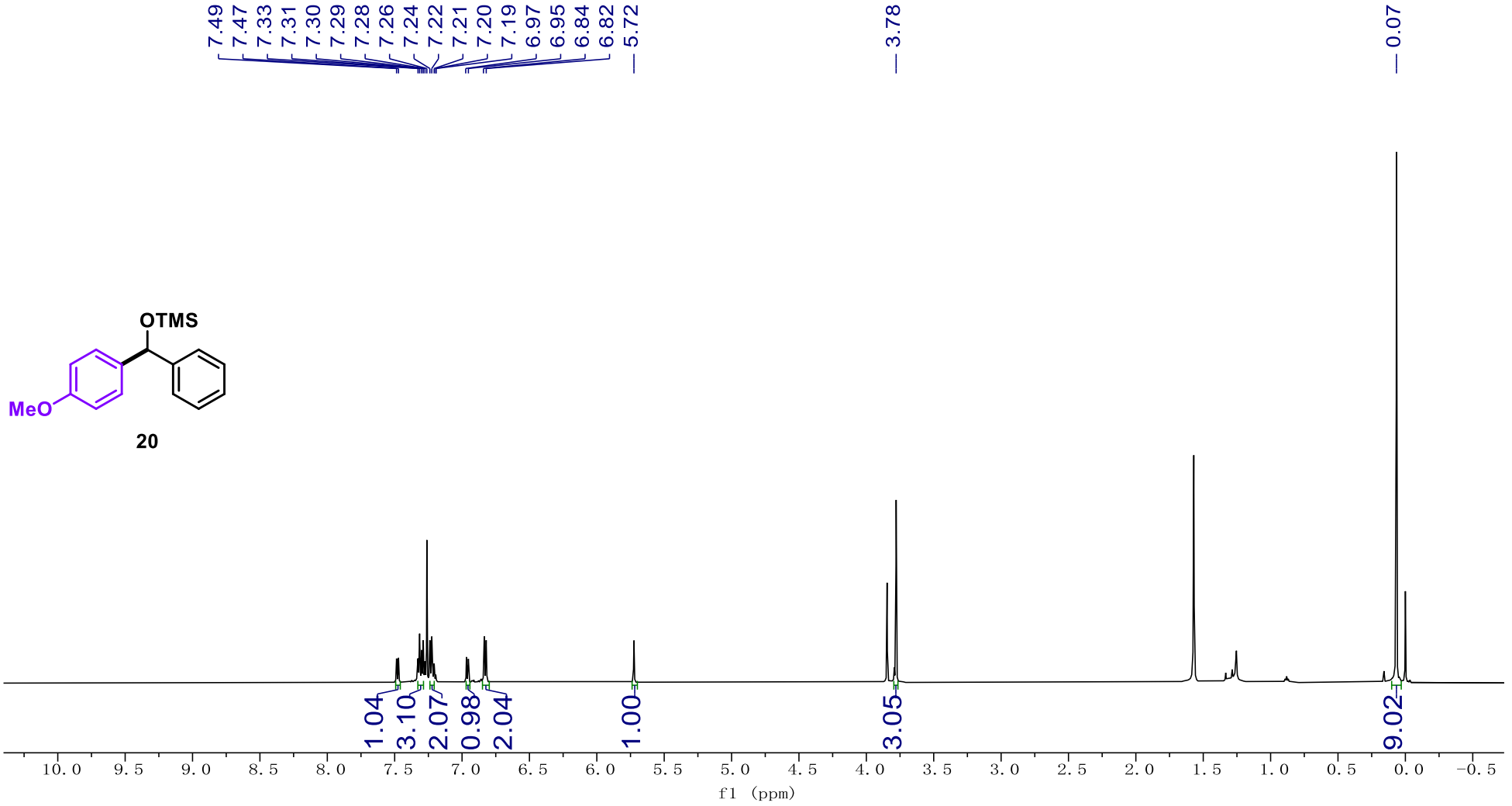
^{1}H NMR of 19 (600 MHz, $CDCl_3$)



^{13}C NMR of 19 (151 MHz, $CDCl_3$)

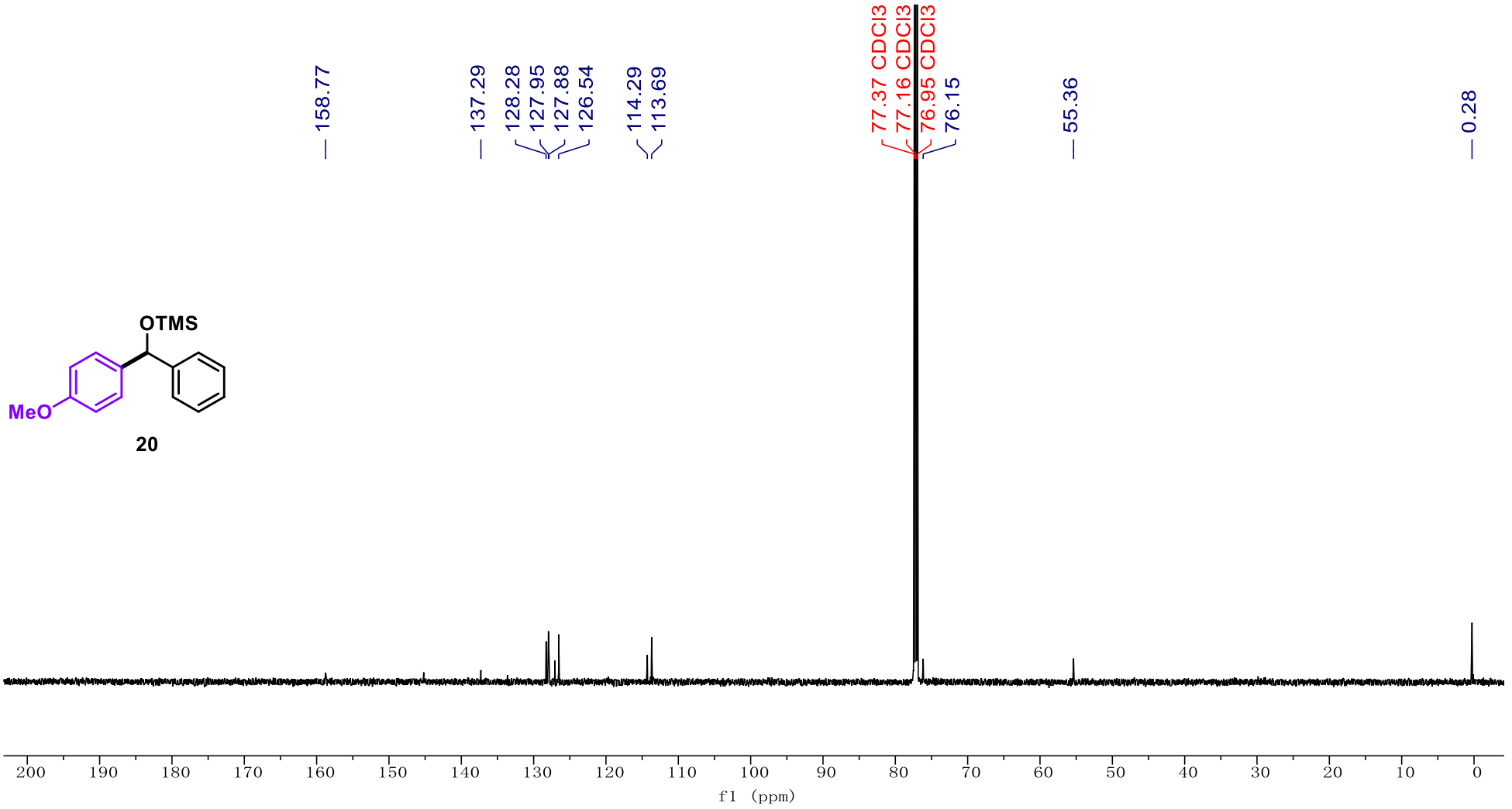


^{1}H NMR of 20 (600 MHz, $CDCl_3$)



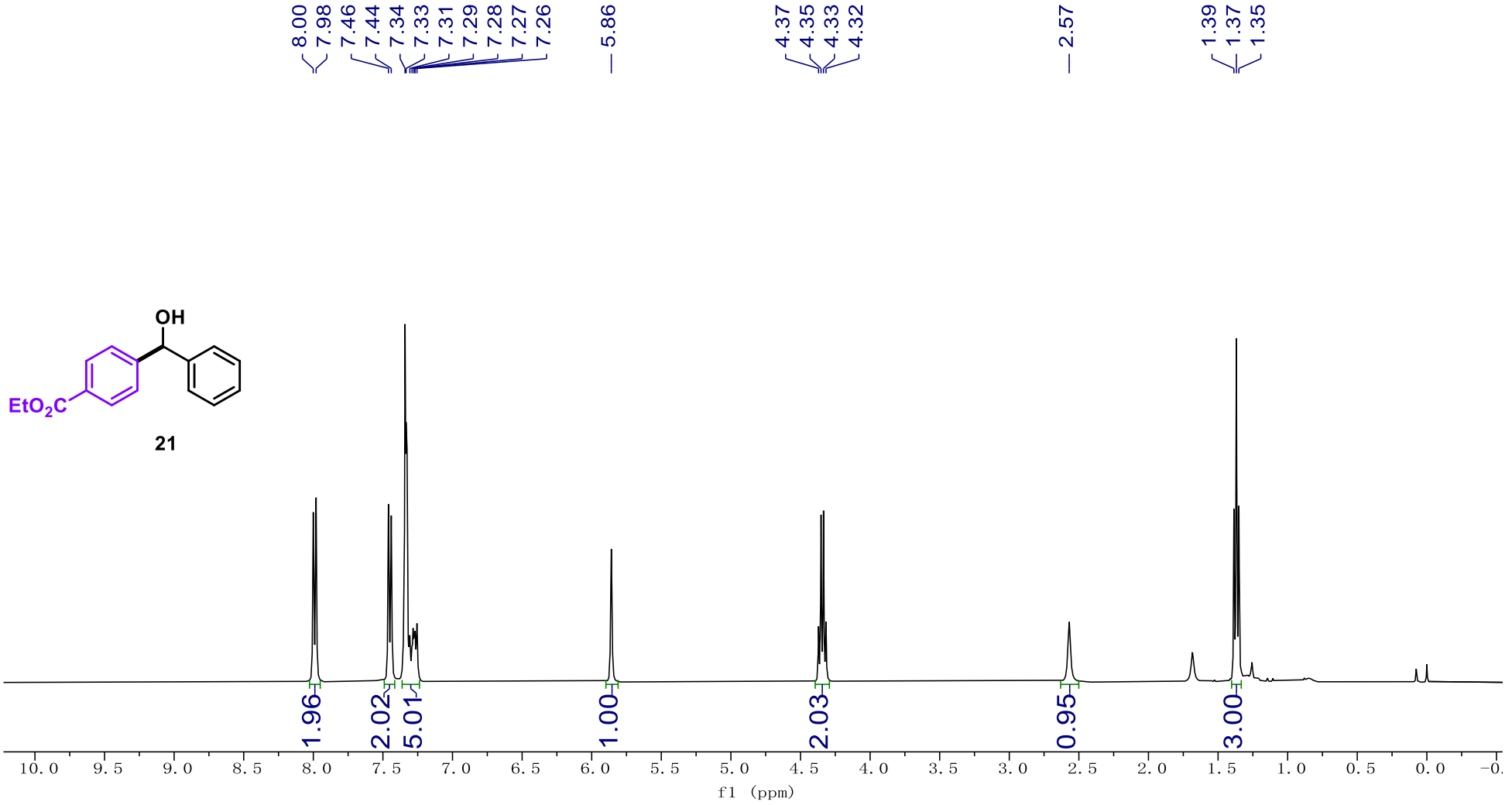
20

^{13}C NMR of 20 (101 MHz, $CDCl_3$)

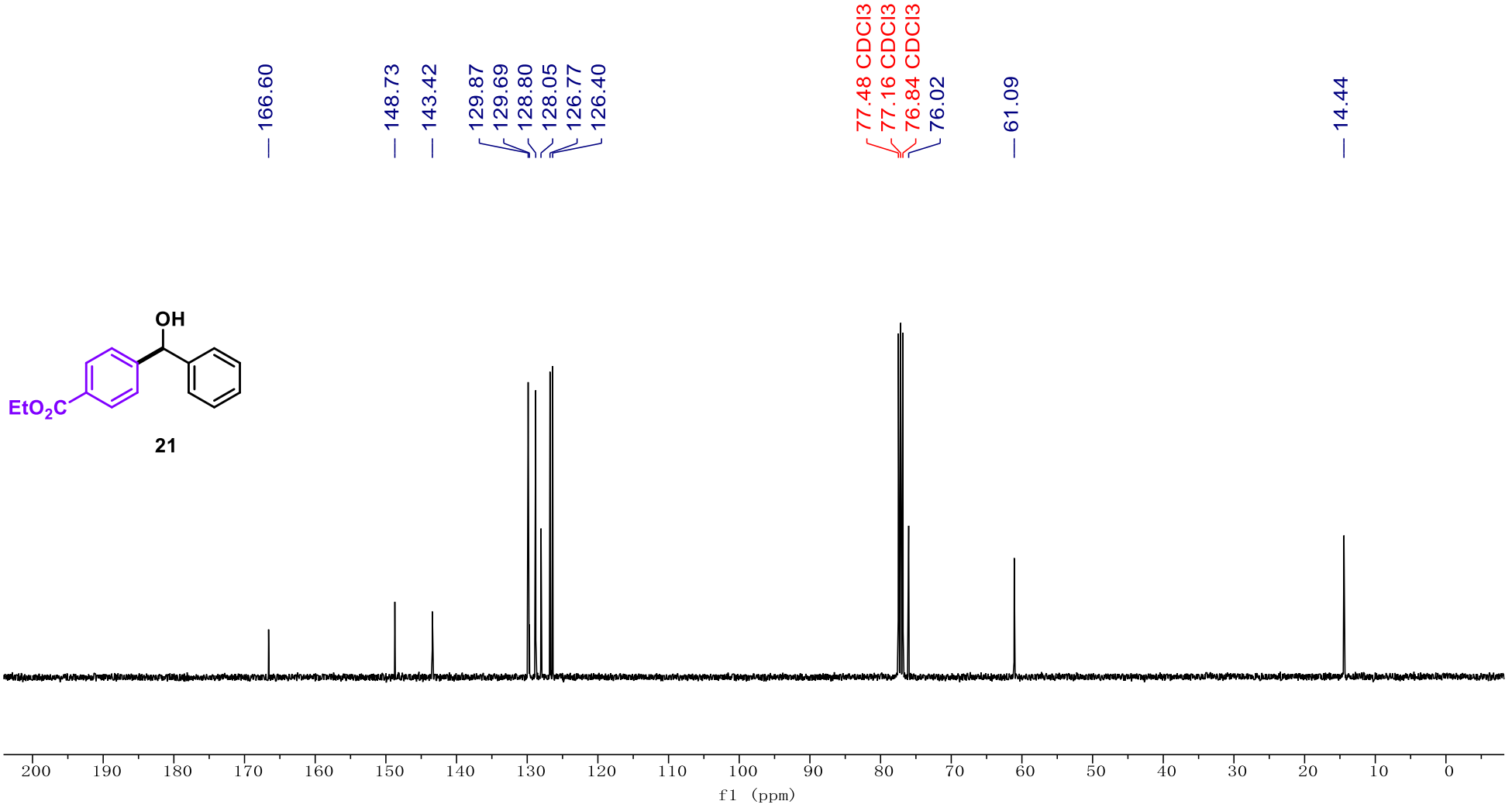


20

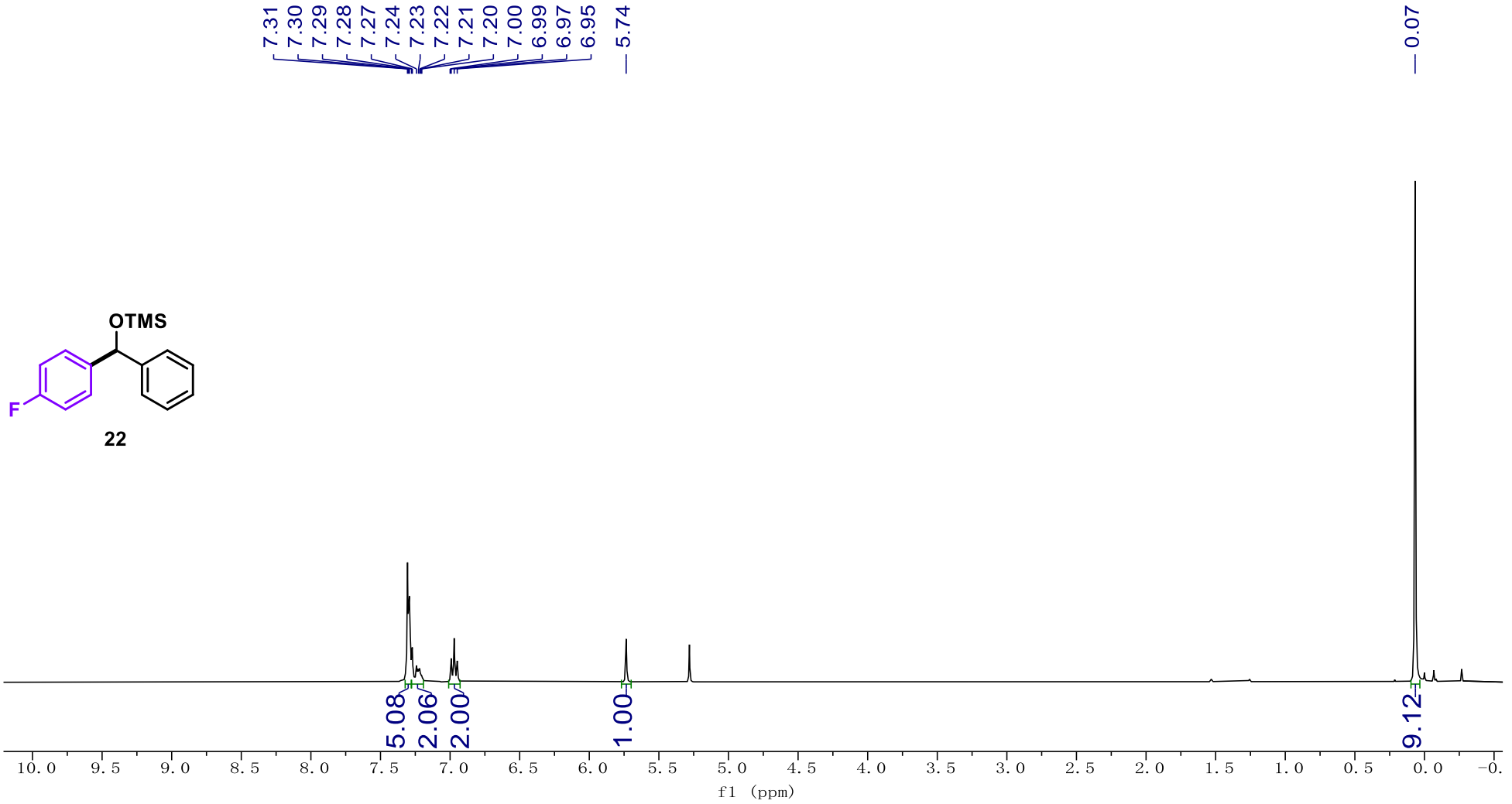
^{1}H NMR of 21 (600 MHz, $CDCl_3$)



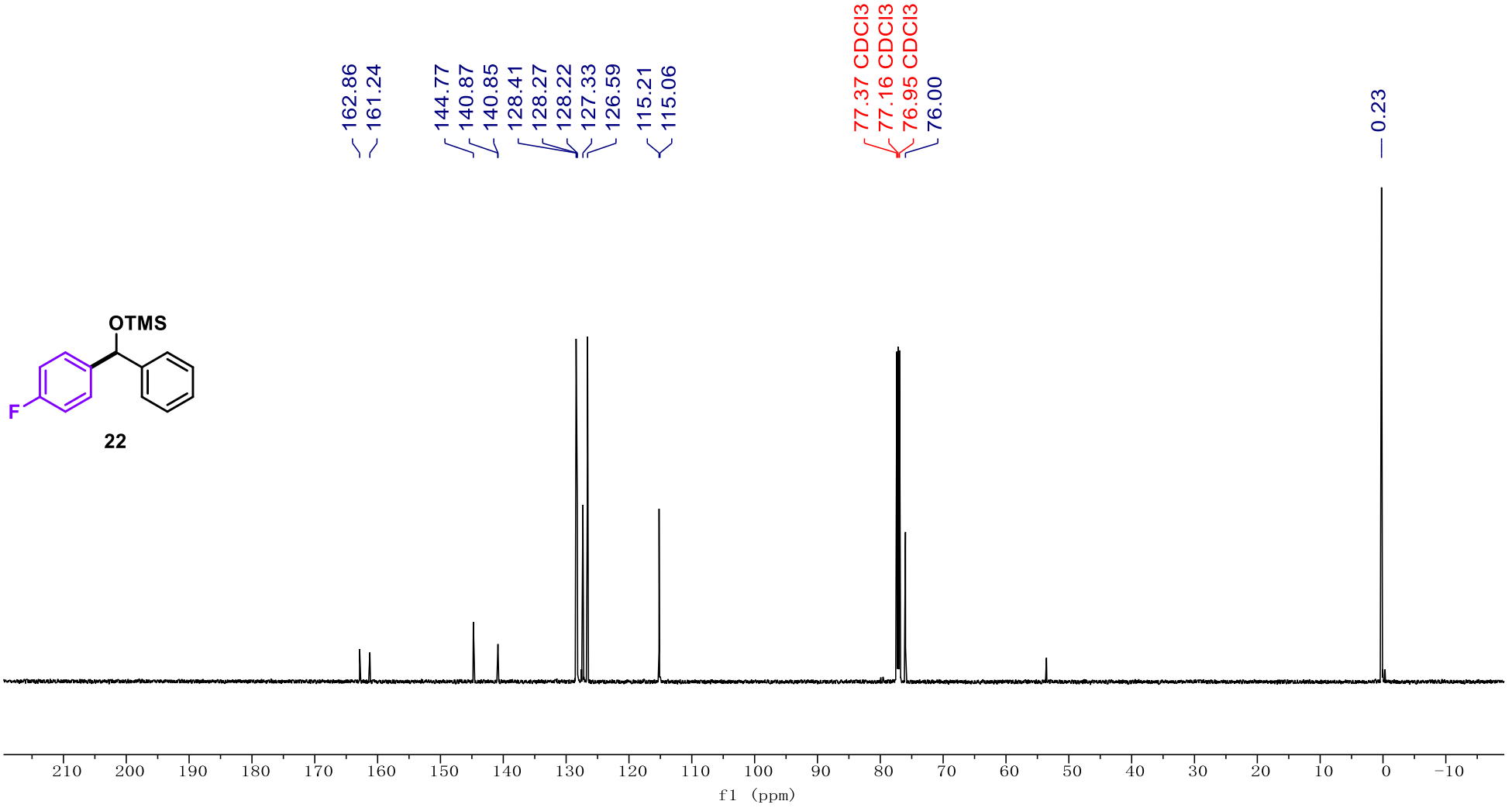
^{13}C NMR of 21 (151 MHz, $CDCl_3$)



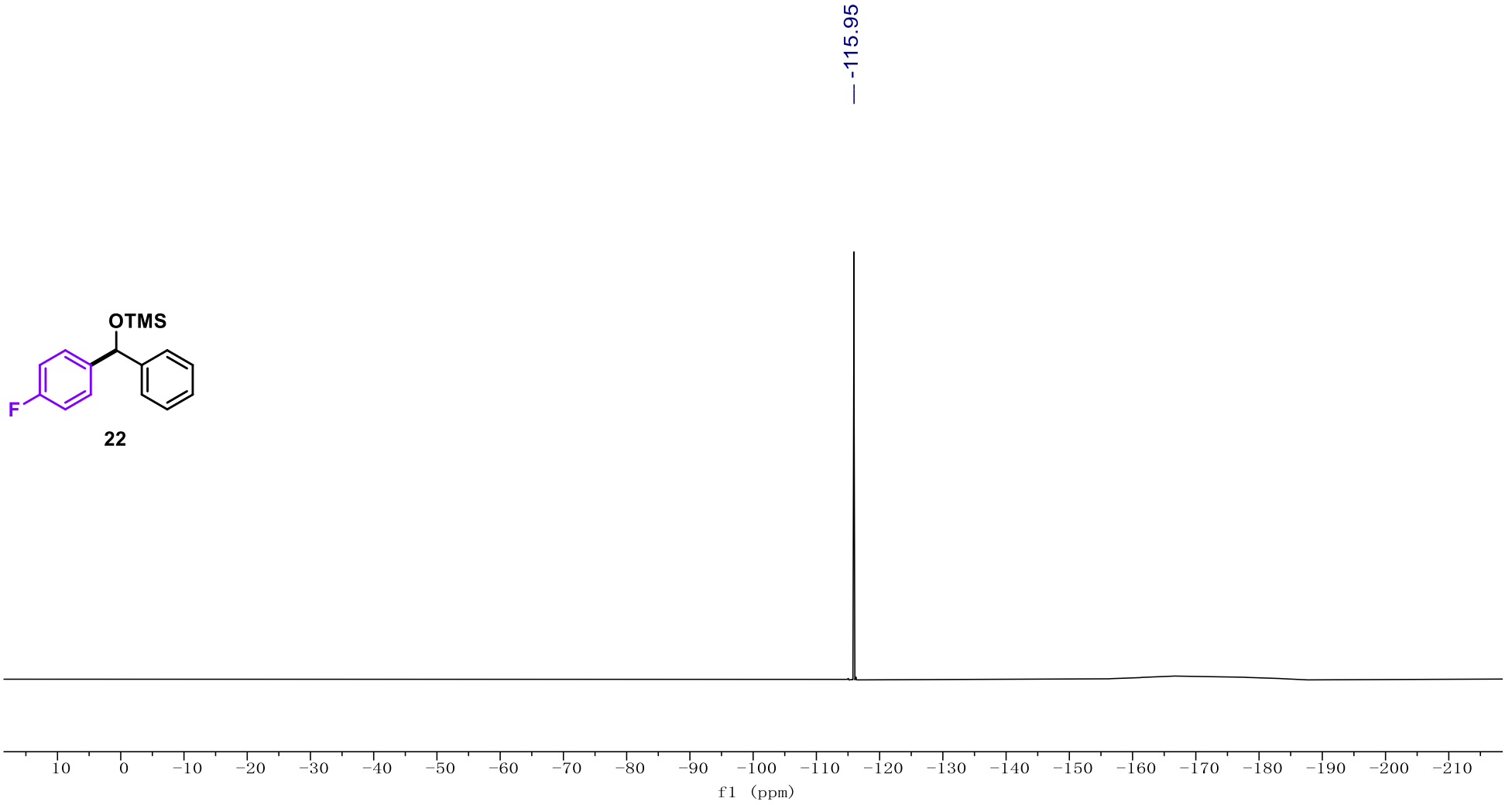
^{1}H NMR of 22 (400 MHz, $CDCl_3$)



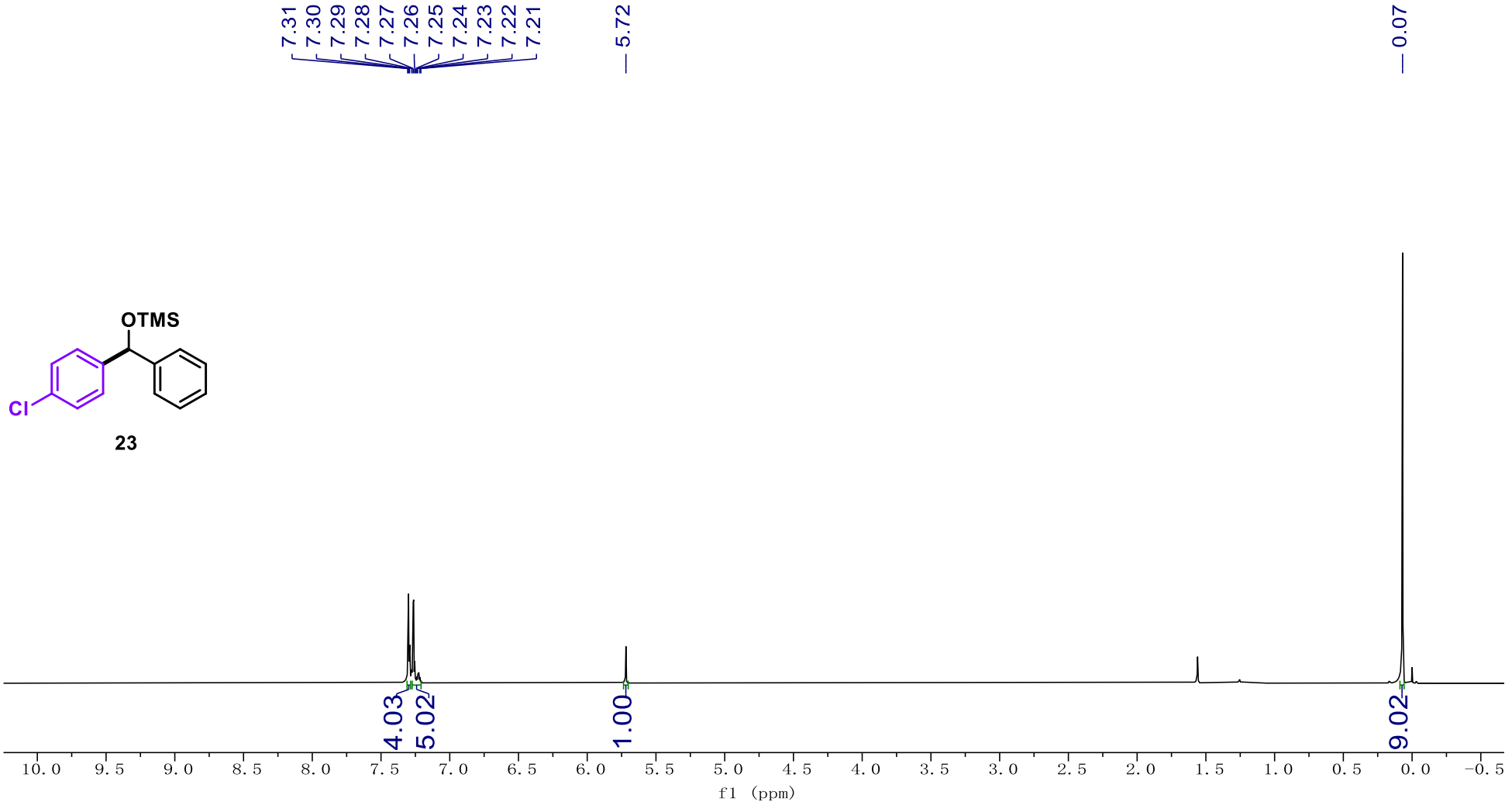
^{13}C NMR of 22 (151 MHz, $CDCl_3$)



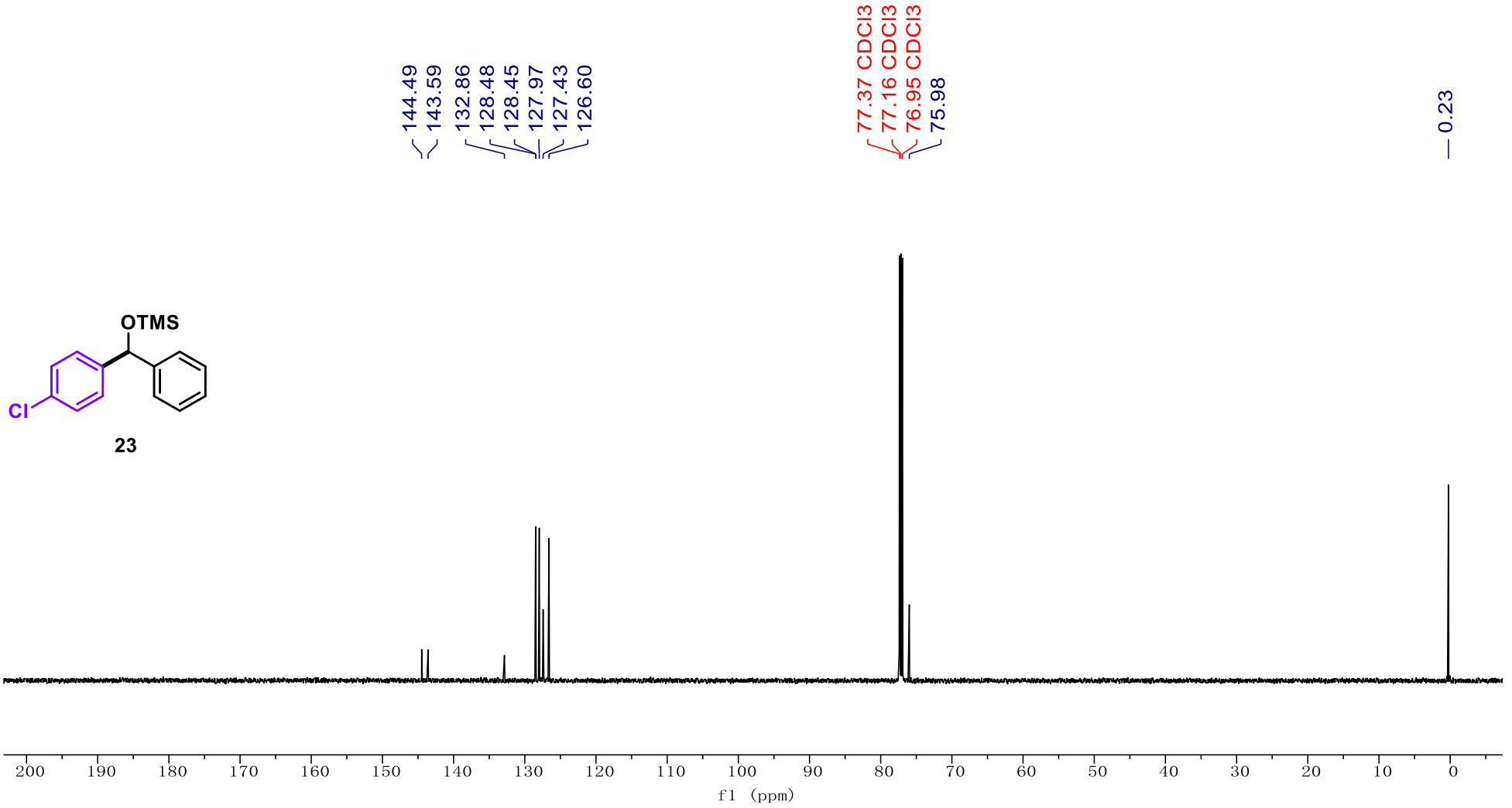
^{19}F NMR of 22 (565 MHz, $CDCl_3$)



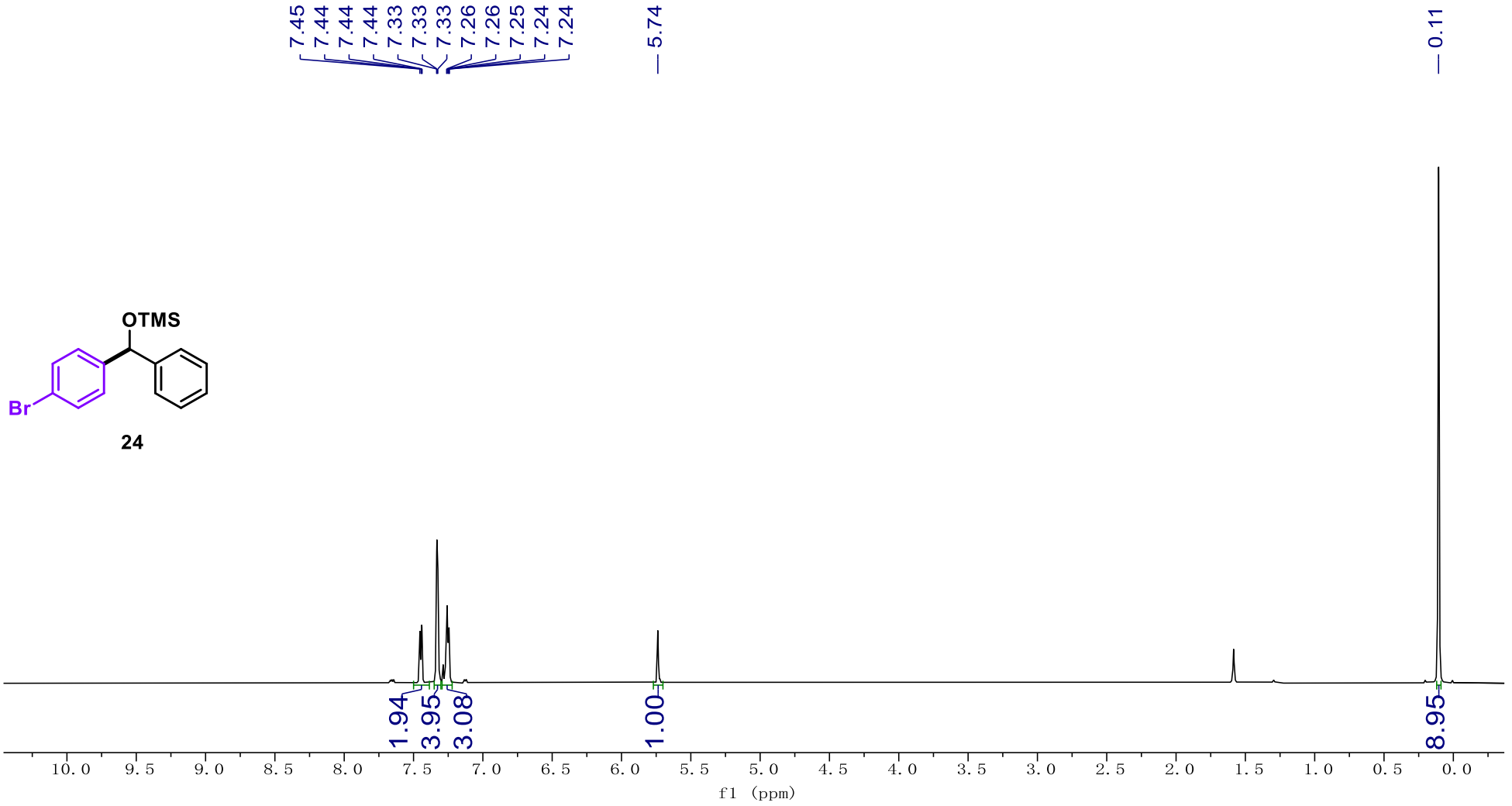
^{1}H NMR of 23 (600 MHz, $CDCl_3$)



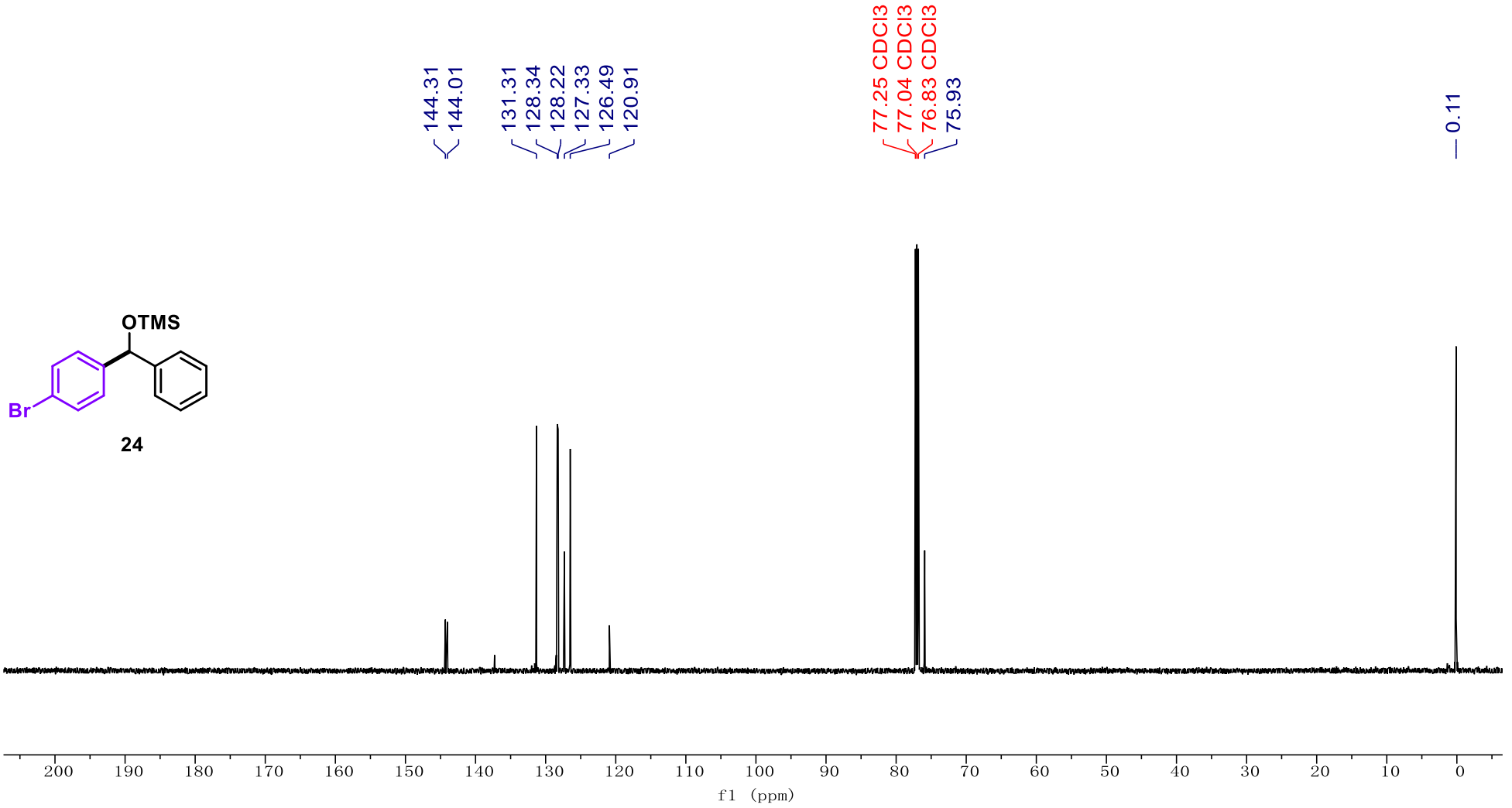
^{13}C NMR of 23 (151 MHz, $CDCl_3$)



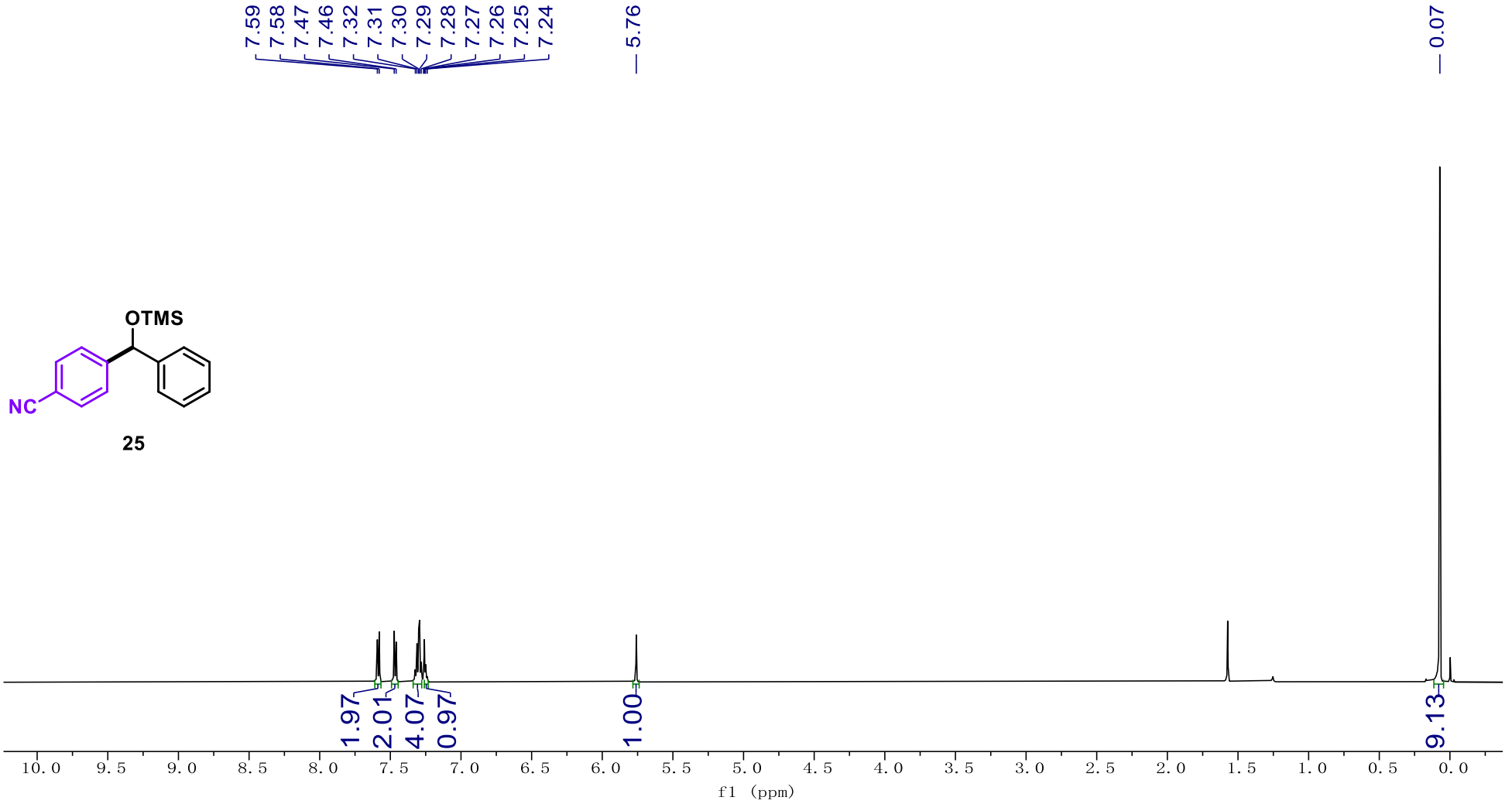
^{1}H NMR of 24 (400 MHz, $CDCl_3$)



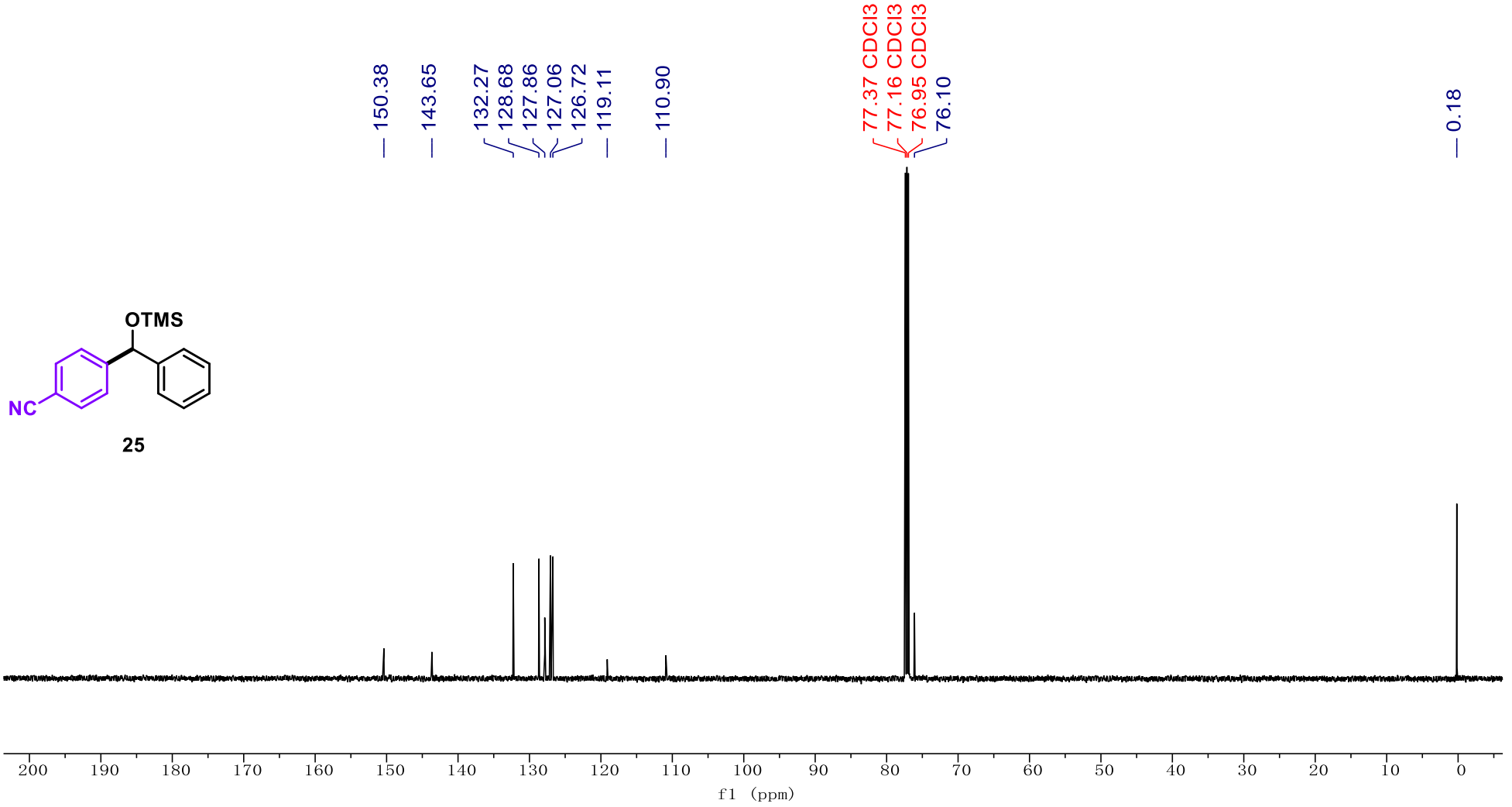
^{13}C NMR of 24 (101 MHz, $CDCl_3$)



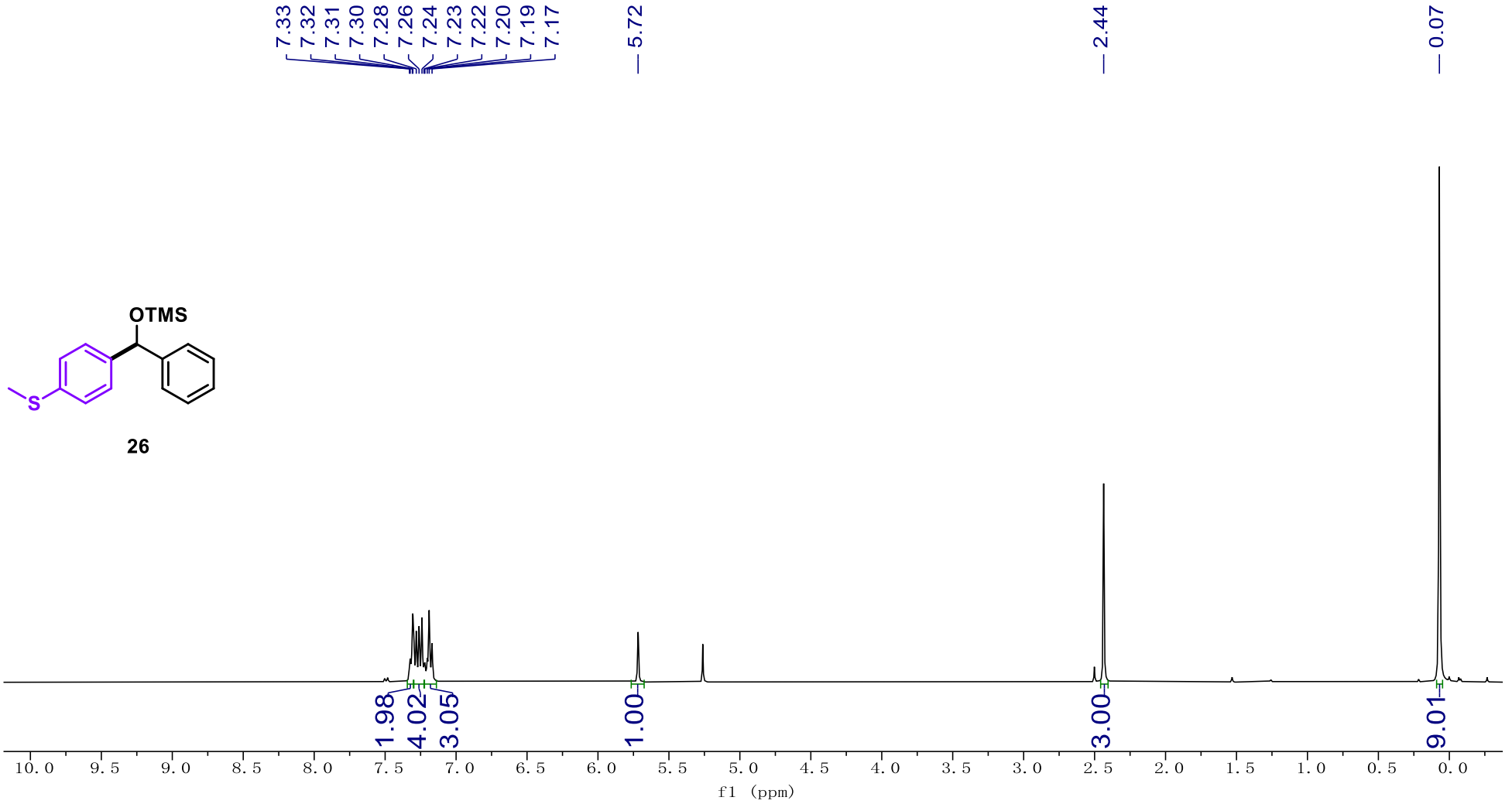
^{1}H NMR of 25 (600 MHz, $CDCl_3$)



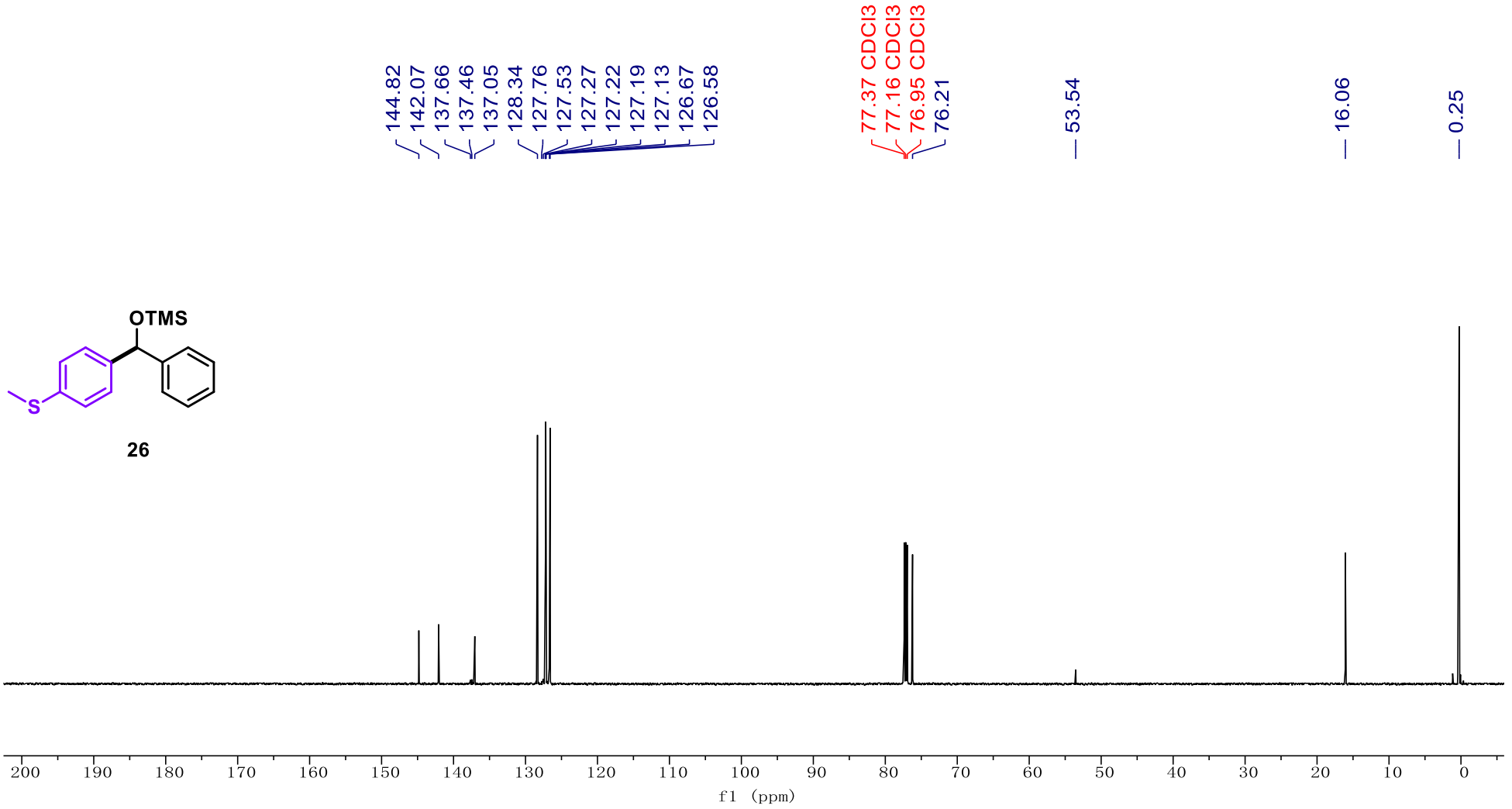
^{13}C NMR of 25 (151 MHz, $CDCl_3$)



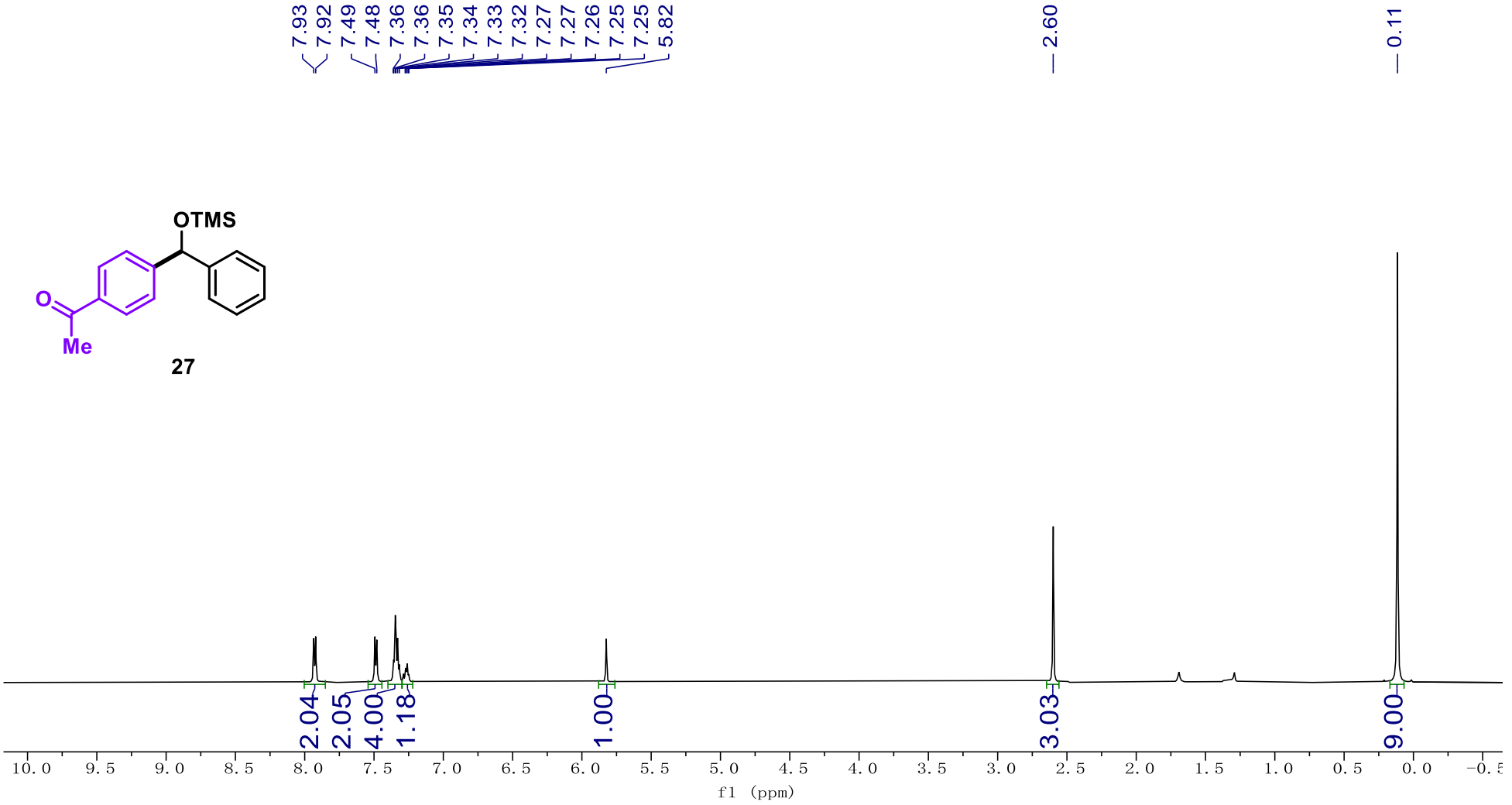
^{1}H NMR of 26 (400 MHz, $CDCl_3$)



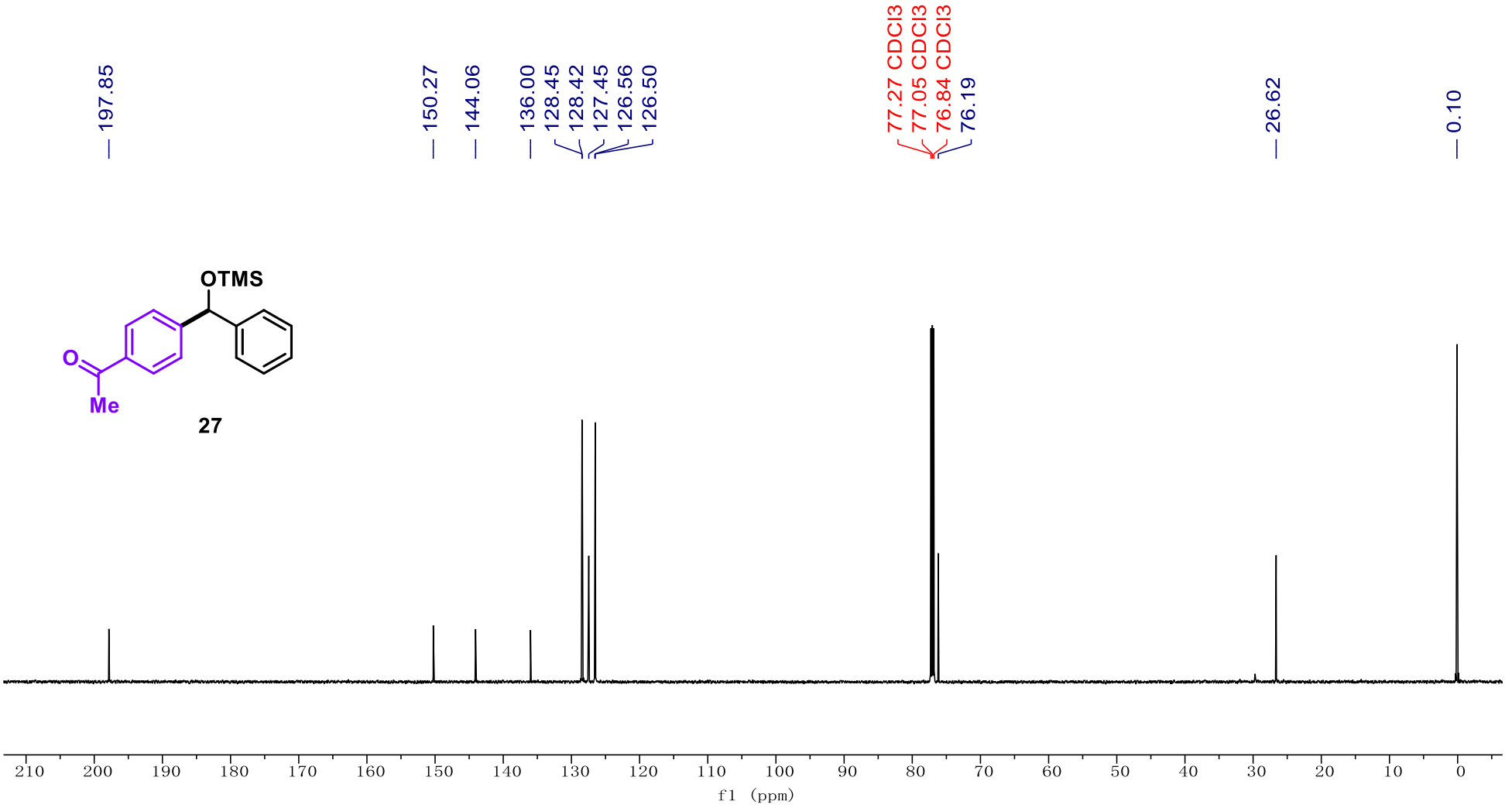
^{13}C NMR of 26 (101 MHz, $CDCl_3$)



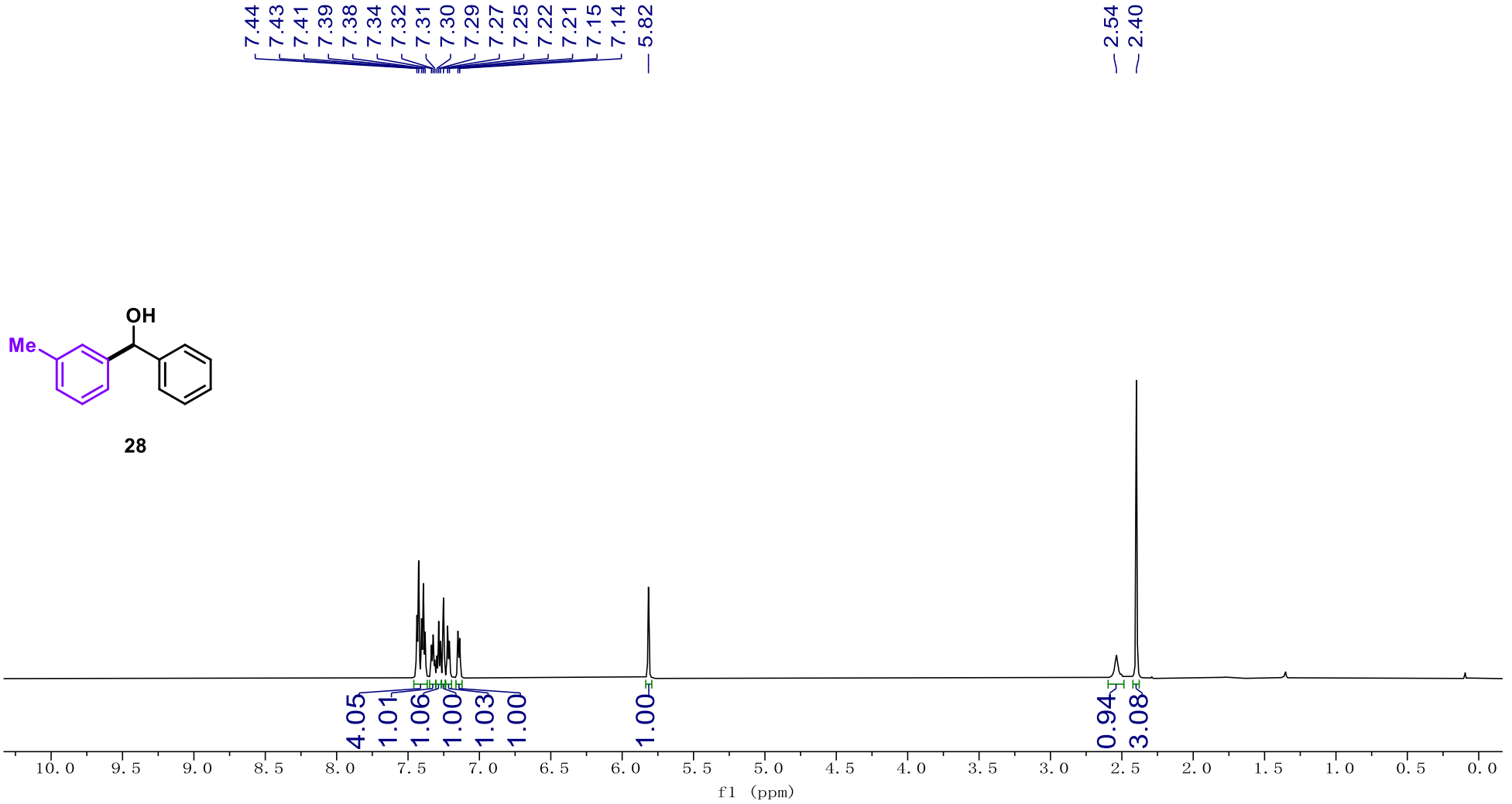
^{1}H NMR of 27 (400 MHz, $CDCl_3$)



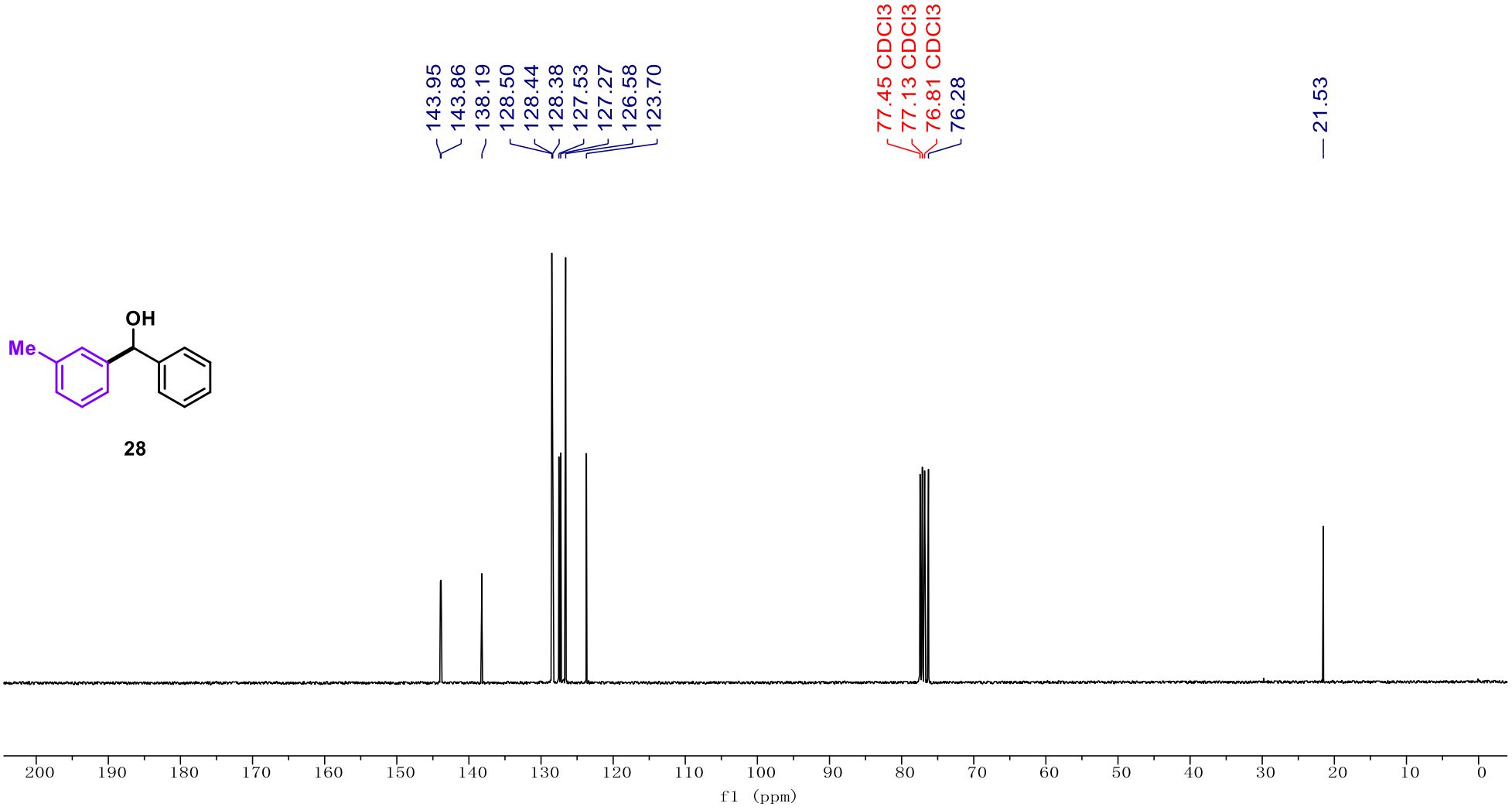
^{13}C NMR of 27 (101 MHz, $CDCl_3$)



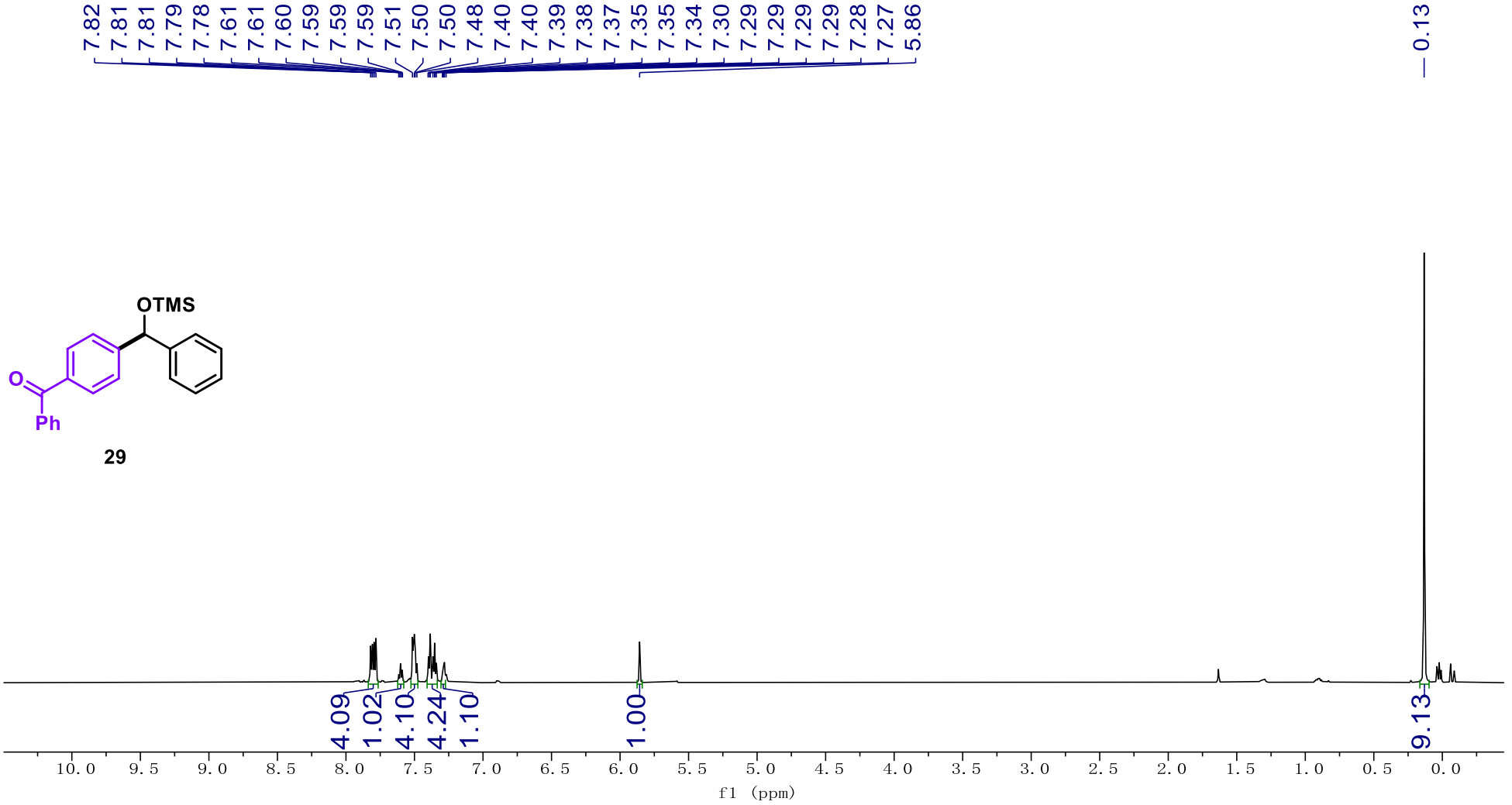
^{1}H NMR of 28 (600 MHz, $CDCl_3$)



^{13}C NMR of 28 (151 MHz, $CDCl_3$)

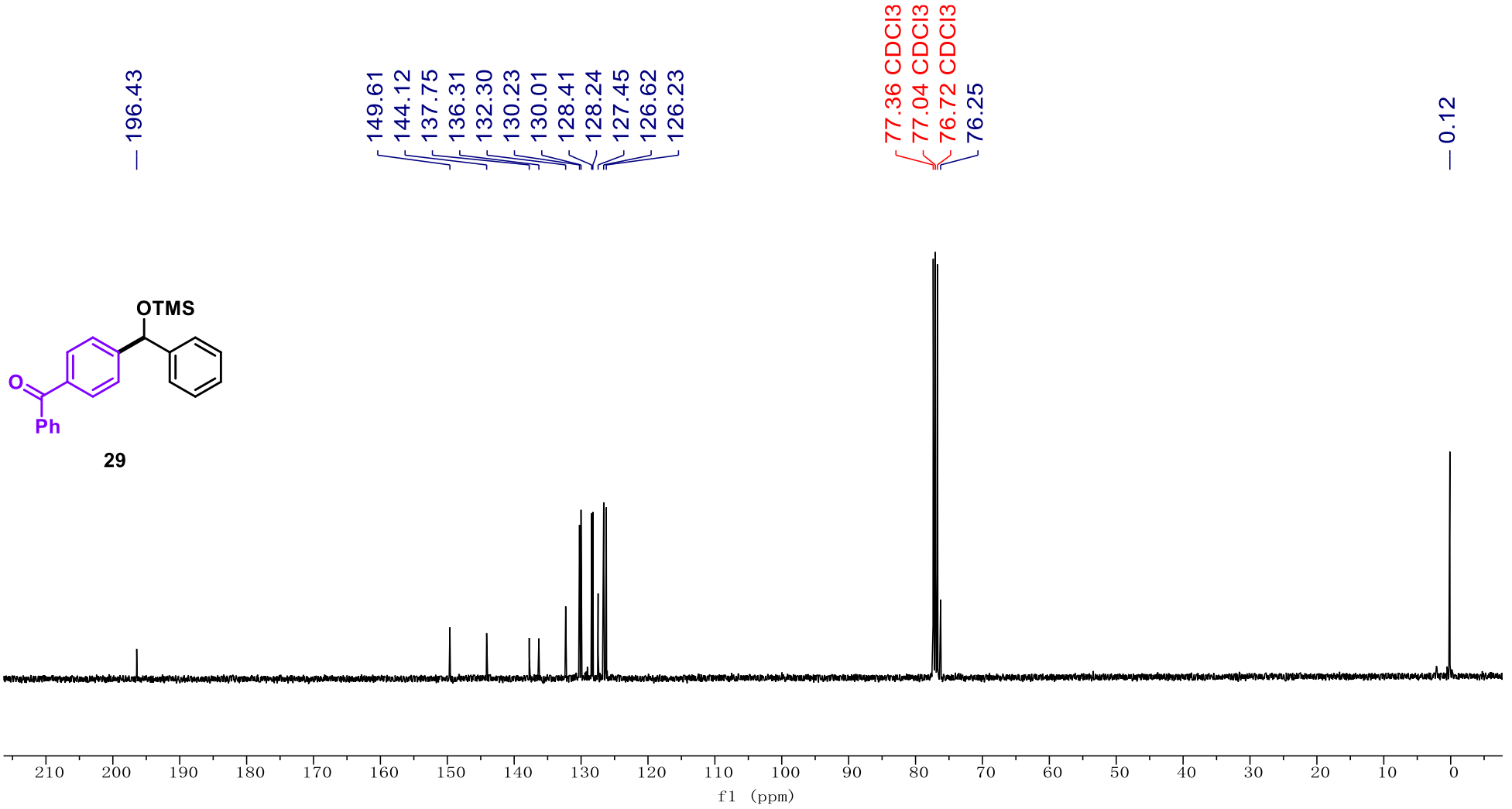


^{1}H NMR of 29 (600 MHz, $CDCl_3$)

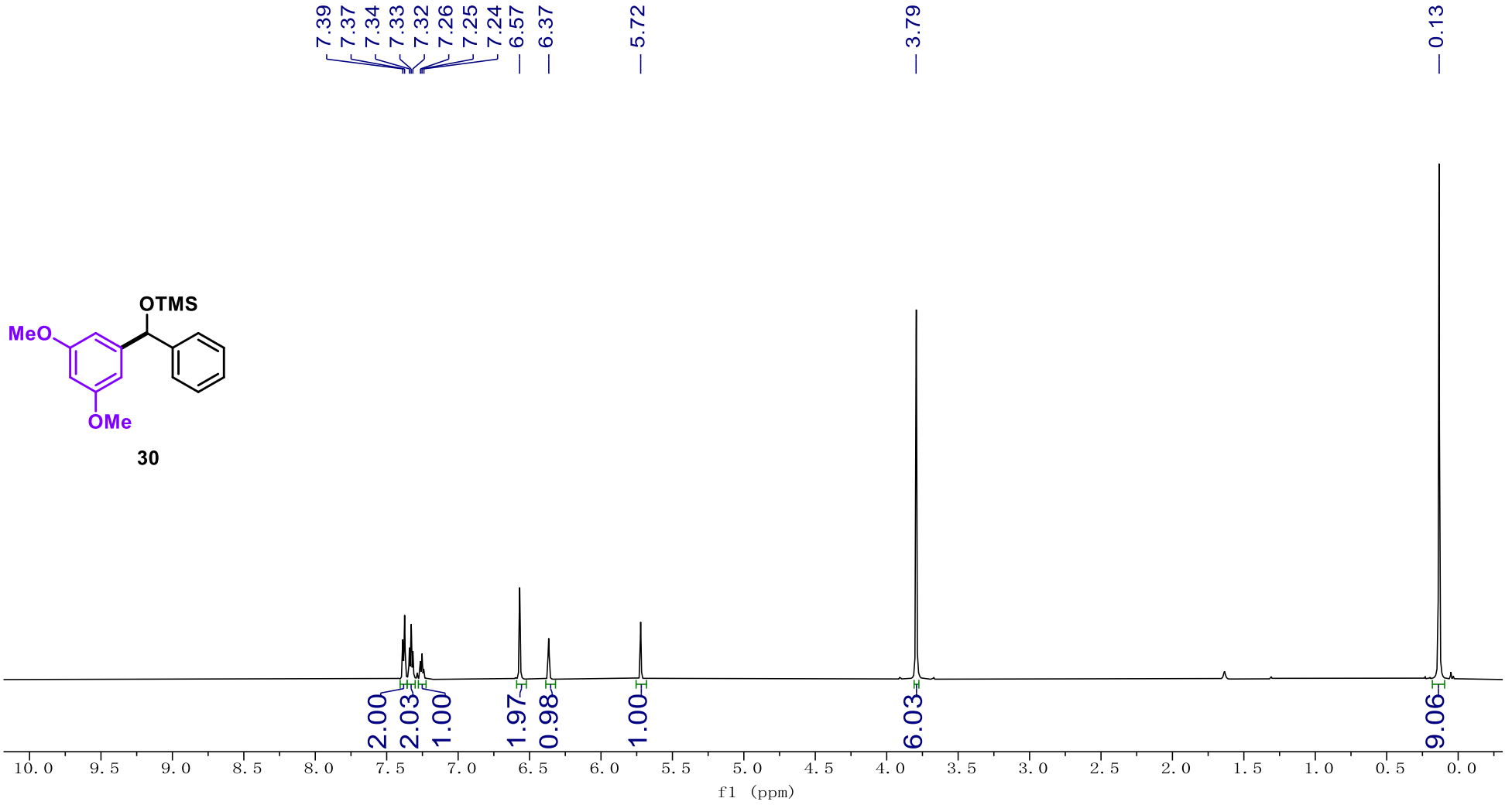


29

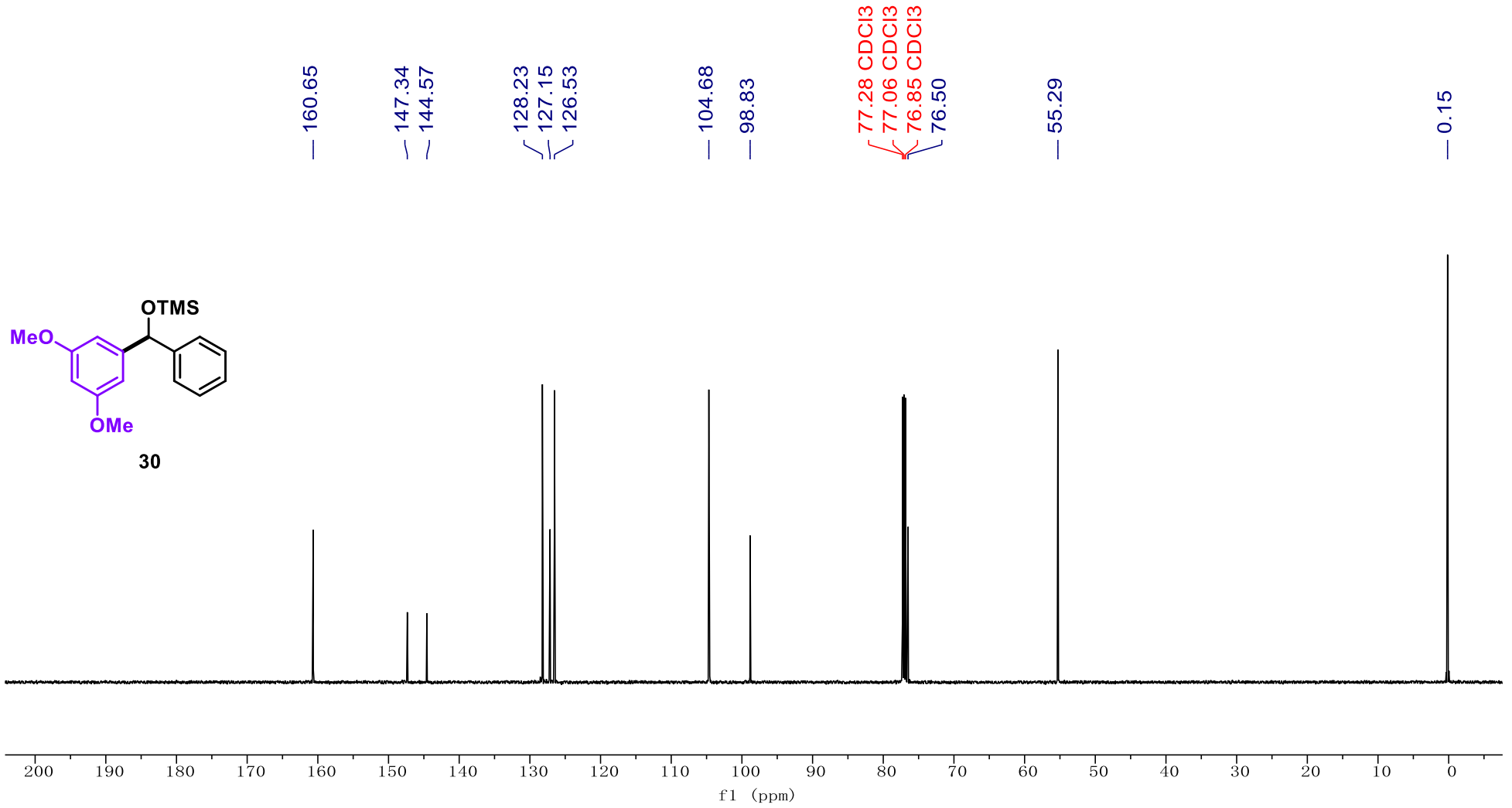
^{13}C NMR of 29 (151 MHz, $CDCl_3$)



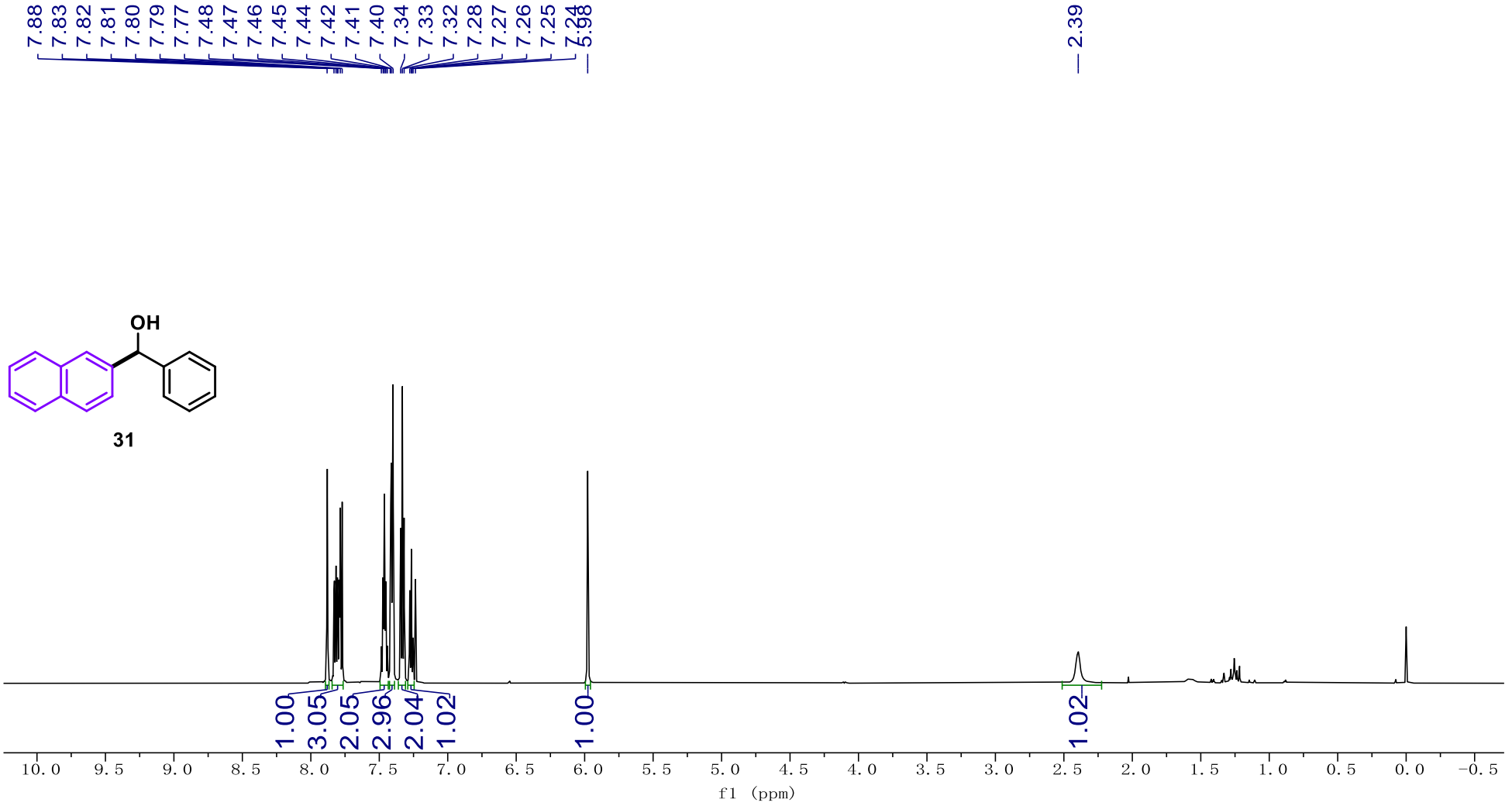
^{1}H NMR of 30 (600 MHz, $CDCl_3$)



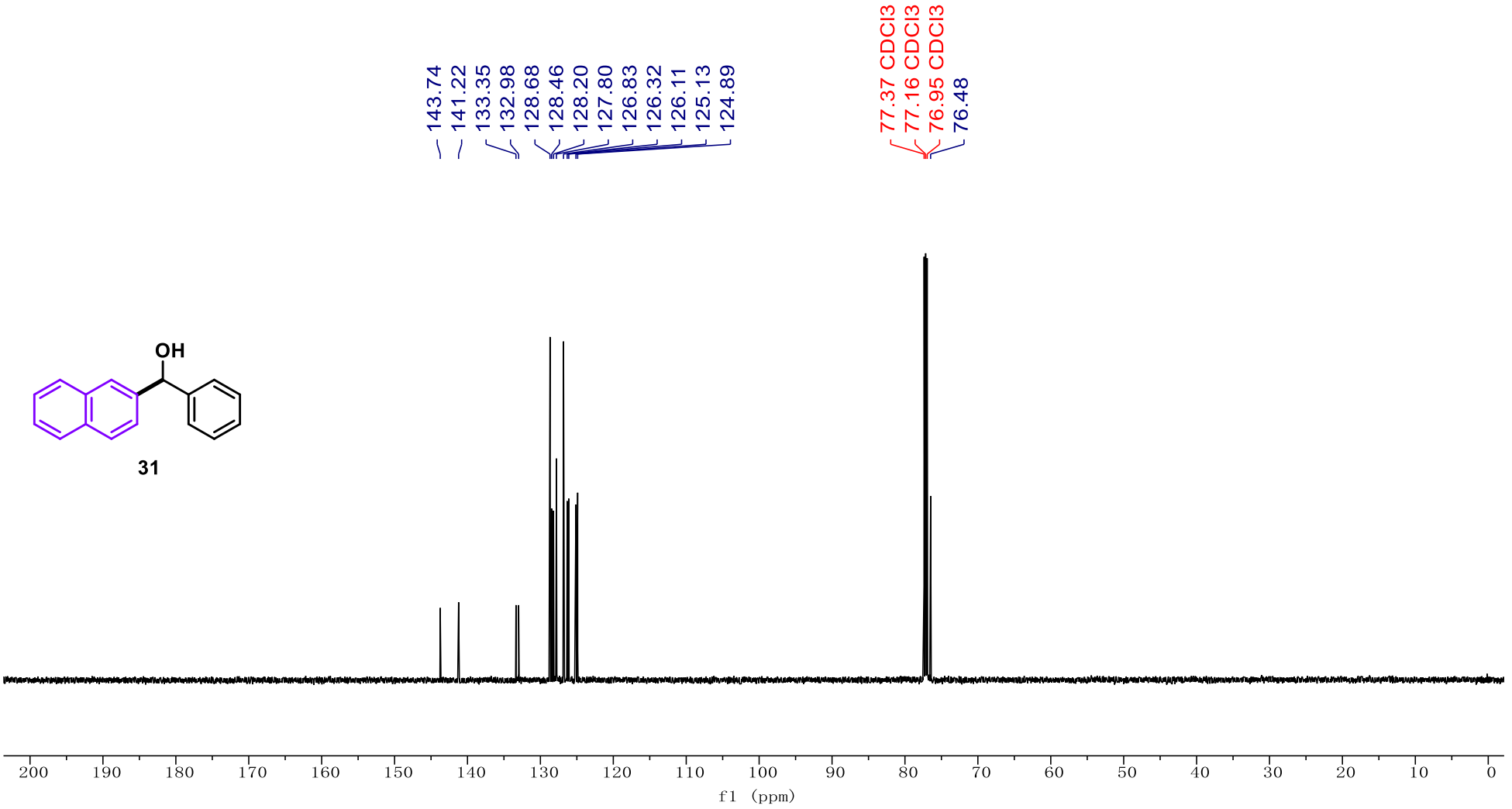
^{13}C NMR of 30 (151 MHz, $CDCl_3$)



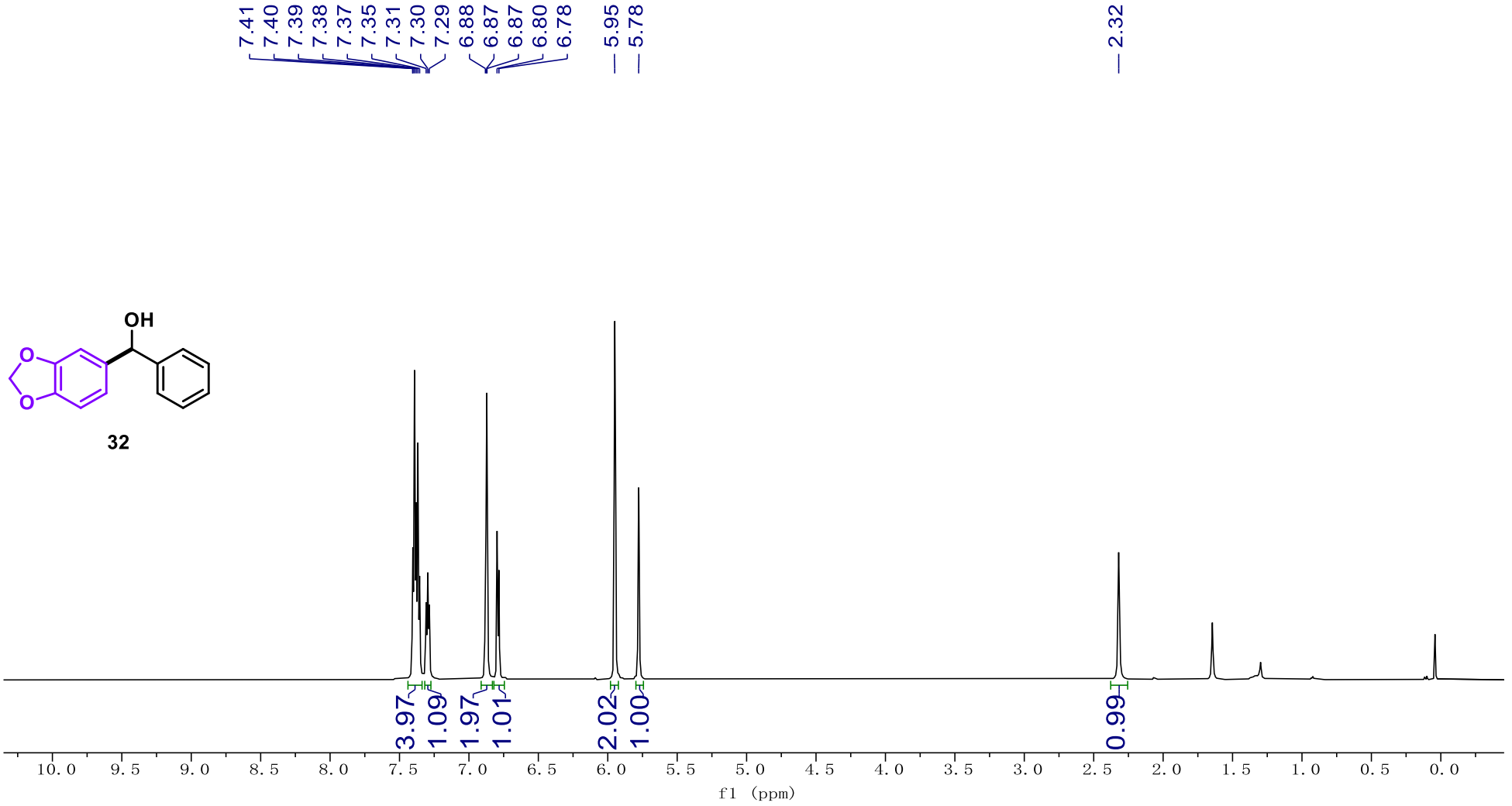
^{1}H NMR of 31 (600 MHz, $CDCl_3$)



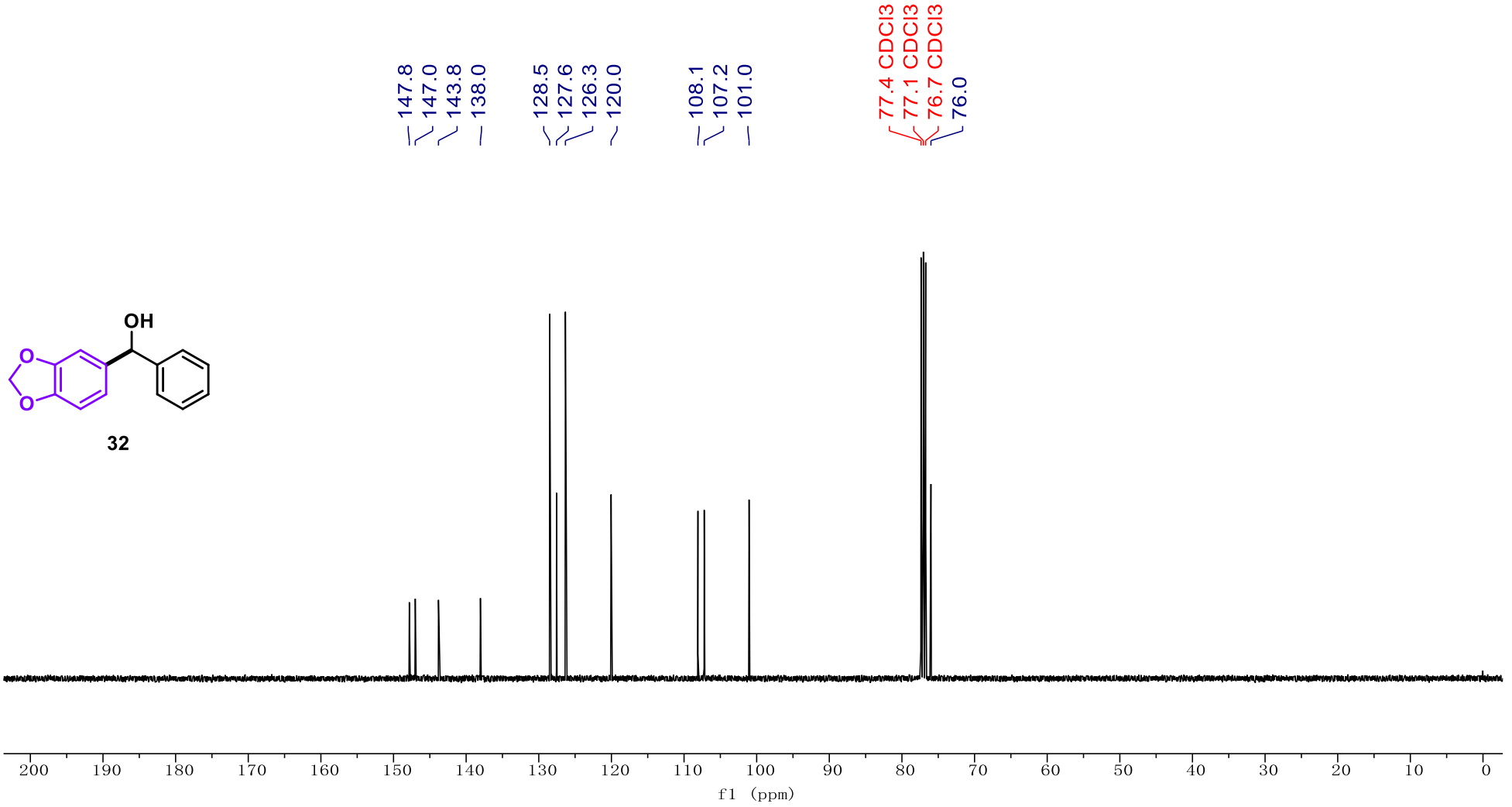
^{13}C NMR of 31 (151 MHz, $CDCl_3$)



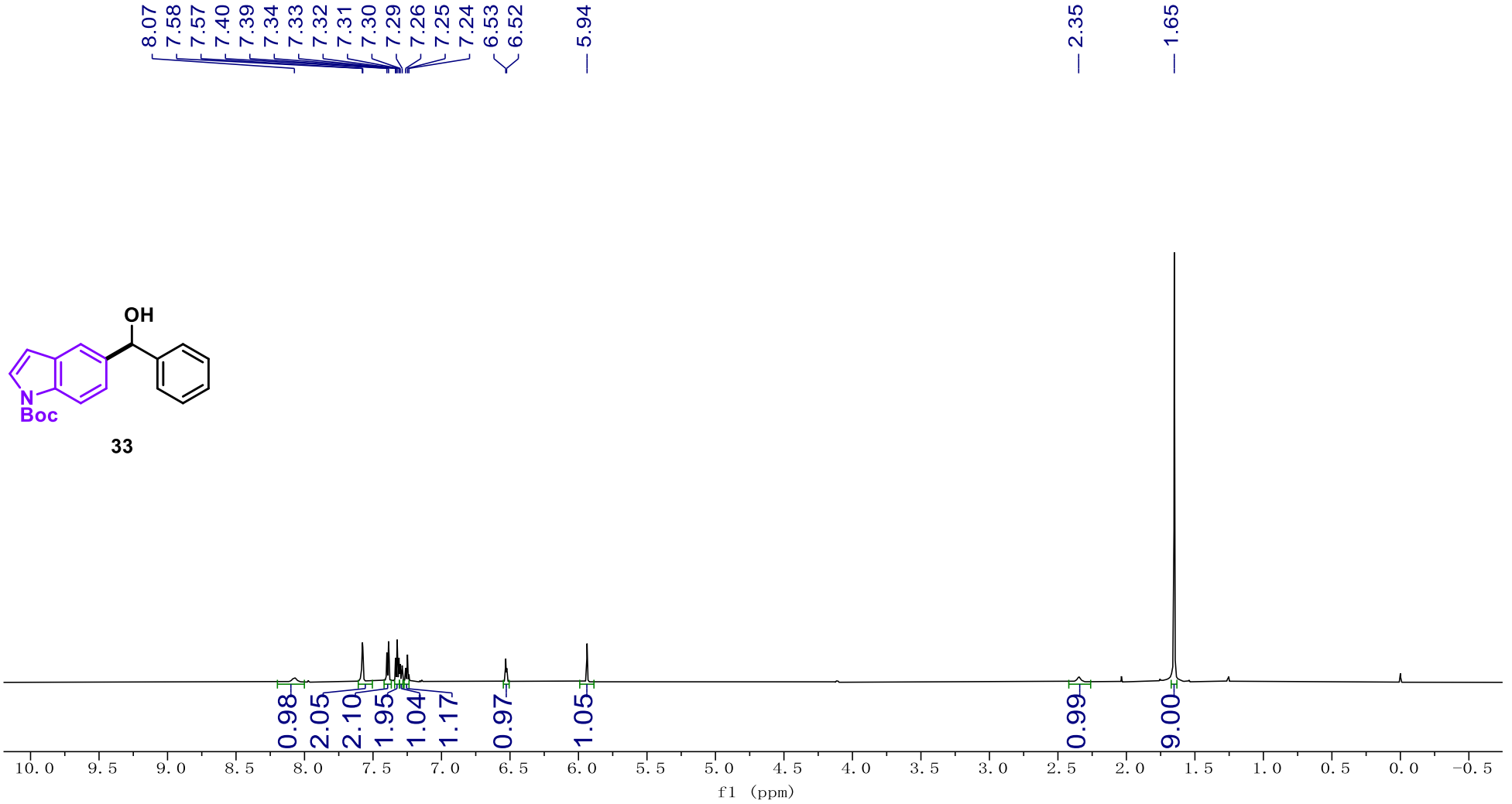
^{1}H NMR of 32 (600 MHz, $CDCl_3$)



^{13}C NMR of 32 (151 MHz, $CDCl_3$)

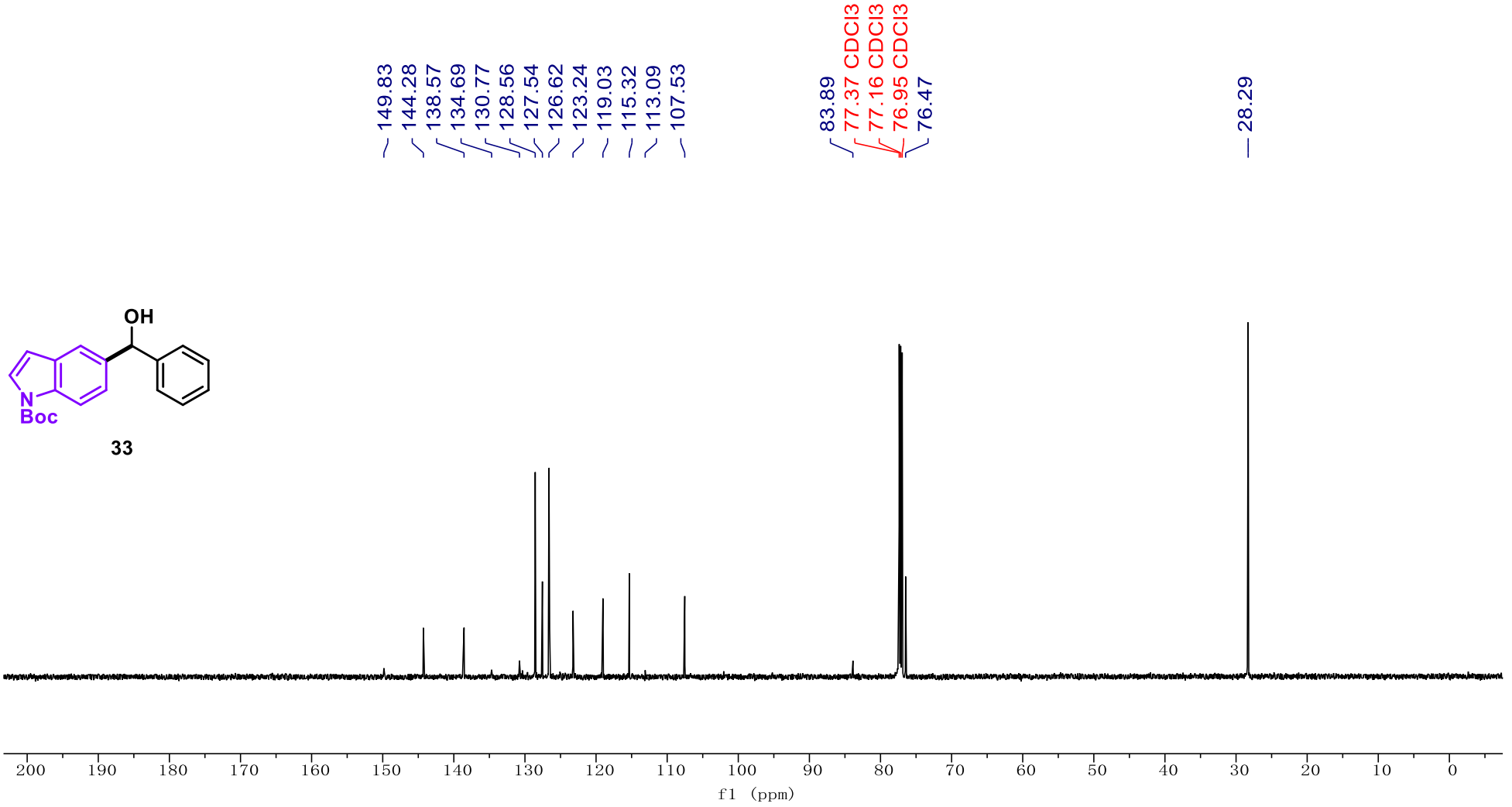


^{1}H NMR of 33 (600 MHz, $CDCl_3$)

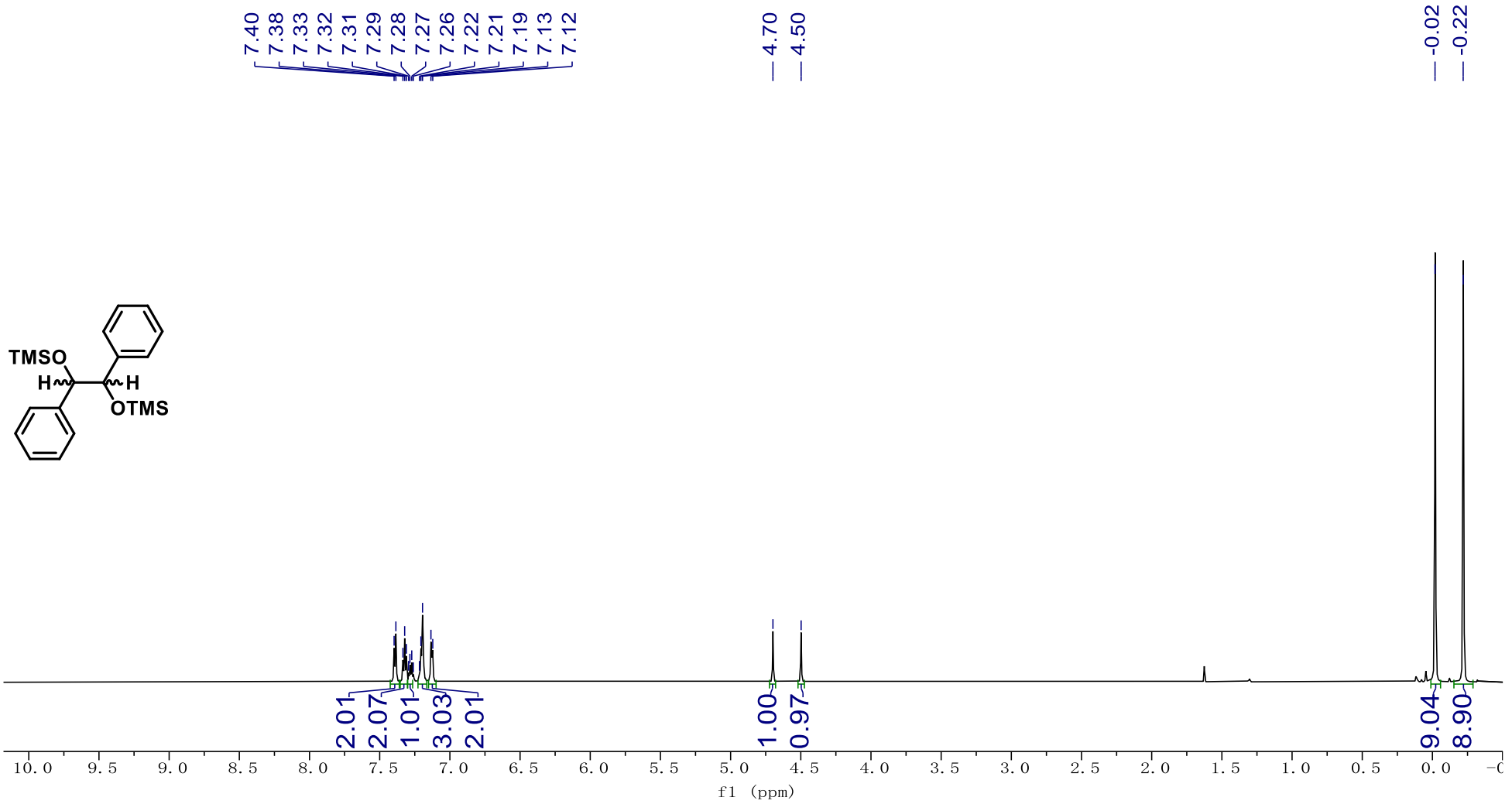


33

^{13}C NMR of 33 (600 MHz, $CDCl_3$)



^{1}H NMR of silyl-protected 1,2-diols (600 MHz, $CDCl_3$)



^{13}C NMR of silyl-protected 1,2-diols (151 MHz, $CDCl_3$)