Three-Component Reductive Conjugate Addition/Aldol Tandem Reaction Enabled by Nickel/Photoredox Dual Catalysis

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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. GCMS analyses were performed on Thermo Scientific TRACE 1310 ISQ LT instrument. ^1H 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 ^1H (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.

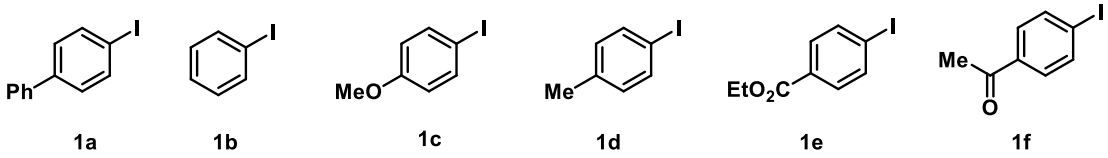
The photoreactor is homemade and each vial was illuminated by one lamp bead (parameters: 1.5 W blue LED, λ_{max} = 455 nm, Cree xpe2 royal blue). Unless otherwise photoredox reactions were set-up in 10 mL vial and stirred (800 rpm) at a distance of 1.0 cm from the irradiating plate. In addition, fan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

Figure S1. Set-up for photoredox reactions

2 Catalysts and Starting Materials

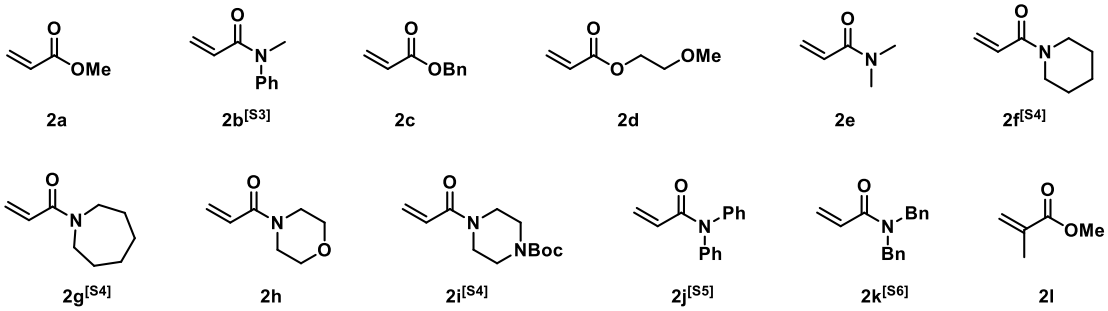
The photocatalysts 4-CzIPN[S1], Ir[dFppy]$_2$(dtbbpy)PF$_6$[S2], Ir(ppy)$_2$(dtbbpy)PF$_6$[S2], Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$[S2], Ir(ppy)$_2$bpyPF$_6$[S2] and Ir[dF(CF$_3$)ppy]$_2$(bpy)PF$_6$[S2] were prepared according to the reported procedures.

2.1 The following electrophiles were used in this study

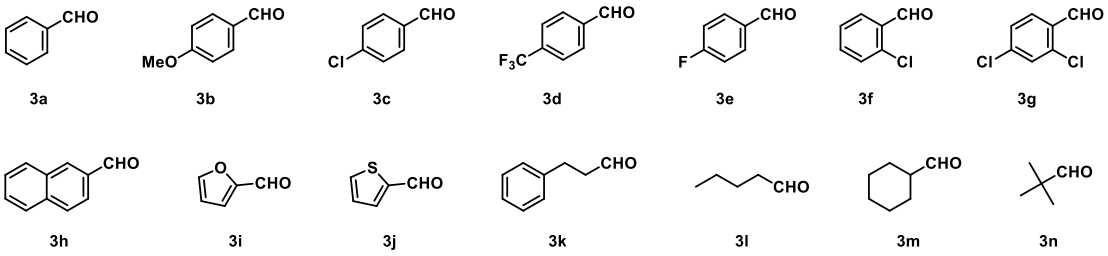


2.2 The following alkenes were used in this study

2b, **2f**, **2g**, **2i**, **2j** and **2k** were synthesized according to the reported procedures.

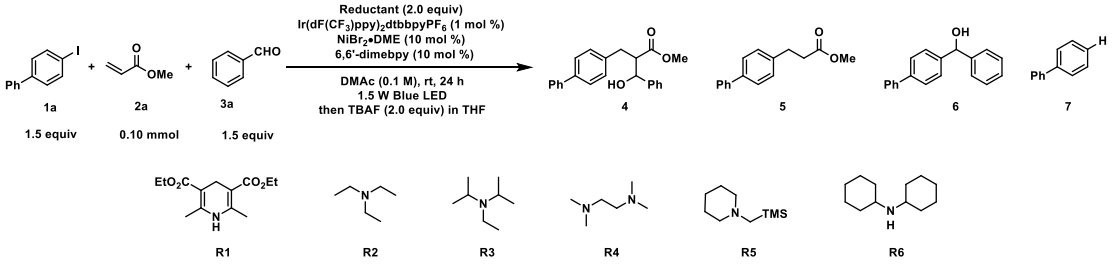


2.3 The following aldehydes were used in this study



3 Optimization of the Reaction Conditions

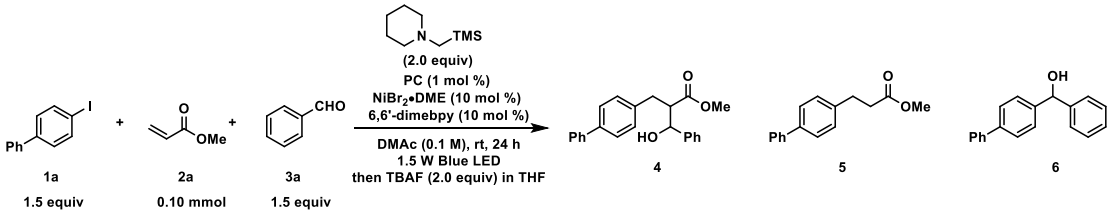
3.1 Table S1. The Effect of Reductant

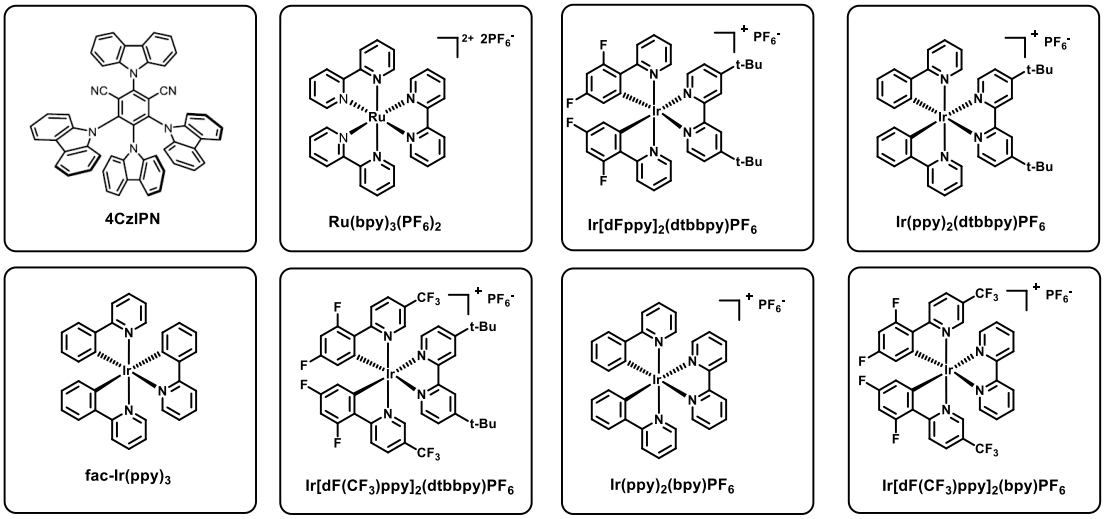


Entry	Reductant	Yield of **4** (%)[a]	Yield of **5** (%)[a]	Yield of **6** (%)[a]	Yield of **7** (%)[a]
1	R1	0	24	0	84
2	R2	0	11	0	23
3	R3	0	0	0	28
4	R4	0	0	0	34
5	R5	23	21	12	trace
6	R1+R6	0	35	0	46

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

3.2 Table S2. The Effect of Photocatalyst

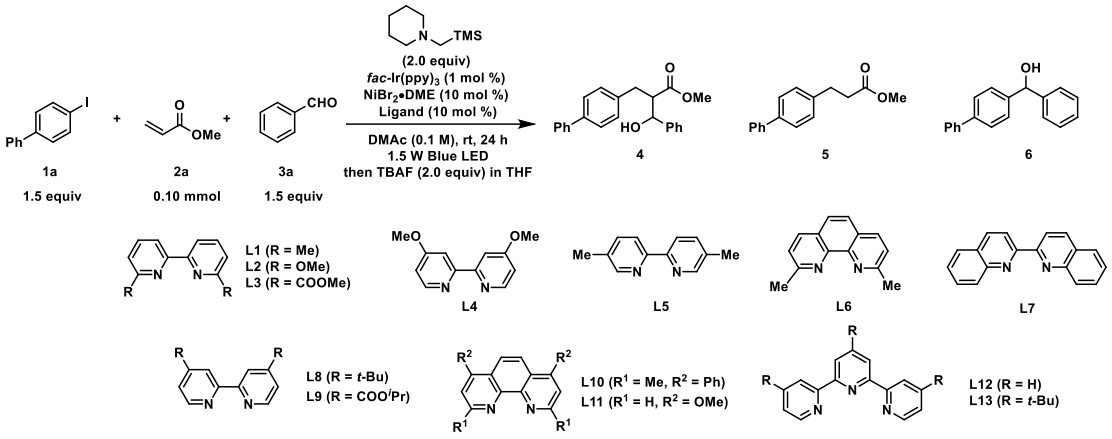




Entry	Photocatalyst	Yield of **4** (%)[a]	Yield of **5** (%)[a]	Yield of **6** (%)[a]
1	4-CzIPN	15	0	62
2	$Ru(bpy)_3(PF_6)_2$	32	16	5
3	$Ir(dFppy)_2dtbbpyPF_6$	28	16	32
4	$Ir(ppy)_2dtbbpyPF_6$	32	22	20
5	*fac*-$Ir(ppy)_3$	34	23	21
6	$Ir(dF(CF_3)ppy)_2dtbbpyPF_6$	23	21	12
7	$Ir(ppy)_2bpyPF_6$	21	11	43
8	$Ir(dF(CF_3)ppy)_2bpyPF_6$	30	16	25

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

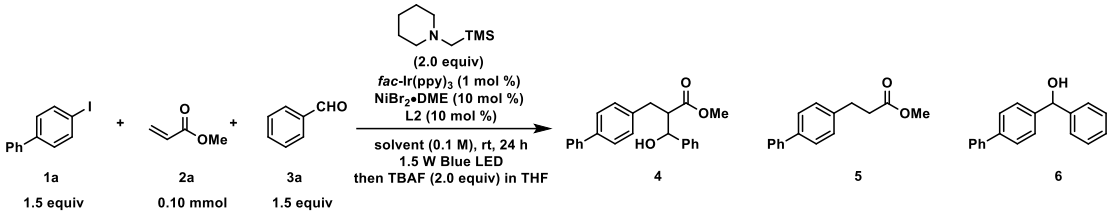
3.3 Table S3. The Effect of Ligand



Entry	Ligand	Yield of **4** (%)[a]	Yield of **5** (%)[a]	Yield of **6** (%)[a]
1	**L1**	34	23	21
2	**L2**	62	20	5
3	**L3**	44	22	1
4	**L4**	19	9	3
5	**L5**	21	8	4
6	**L6**	24	16	51
7	**L7**	31	14	0
8	**L8**	31	5	10
9	**L9**	22	12	4
10	**L10**	22	13	57
11	**L11**	25	9	2
12	**L12**	25	11	2
13	**L13**	41	21	2

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

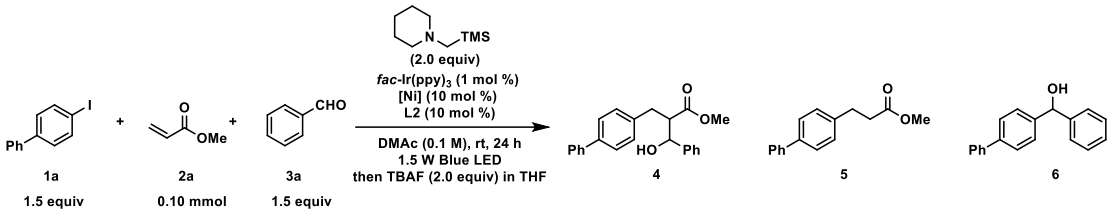
3.4 Table S4. The Effect of Solvent



Entry	Solvent	Yield of **4** (%)[a]	Yield of **5** (%)[a]	Yield of **6** (%)[a]
1	DMAc	62	20	5
2	DMF	3	0	4
3	DMSO	0	0	0
4	NMP	39	12	2
5	MeCN	24	43	2
6	THF	0	3	0
7	Dioxane	0	8	0
8	DME	0	4	0
9	Toluene	0	8	0
10	*t*-BuOH	0	16	0

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

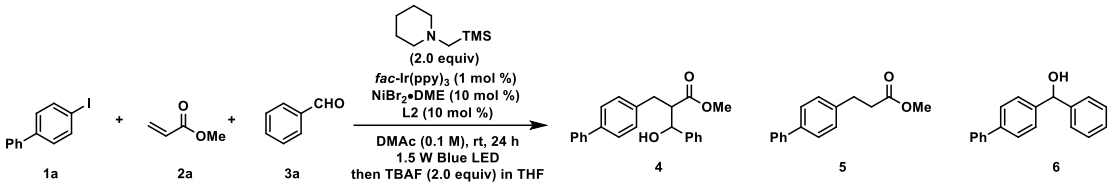
3.5 Table S5. The Effect of Ni-catalyst



Entry	Ni-catalyst	Yield of **4** (%)[a]	Yield of **5** (%)[a]	Yield of **6** (%)[a]
1	$NiBr_2$•DME	62	20	5
2	$NiCl_2$•DME	22	17	0
3	$NiBr_2$	45	13	2
4	NiI_2	47	5	10
5	$Ni(acac)_2$	25	14	0
6	$Ni(OTf)_2$	0	3	2
7	$Ni(COD)_2$	55	4	10
8	$Ni(PPh_3)_2Br_2$	29	21	4
9	$Ni(PPh_3)_2Cl_2$	22	9	1

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

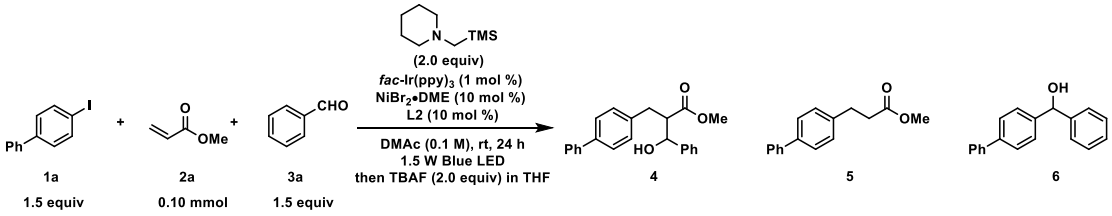
3.6 Table S6. The Effect of Molar Ratio of the Reaction component



Entry	**1a: 2a: 3a**	Yield of **4** (%)[a]	Yield of **5** (%)[a]	Yield of **6** (%)[a]
1	1.5: 1.0: 1.5	62	20	5
2	1.0: 1.5: 1.5	55	21	0
3	1.5: 1.5: 1.0	62	35	0
4	1.0: 1.0: 1.0	38	20	2
5	2.0: 1.0: 2.0	61	16	4
6	1.0: 2.0: 2.0	43	8	0
7	2.0: 2.0: 1.0	78	43	0

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

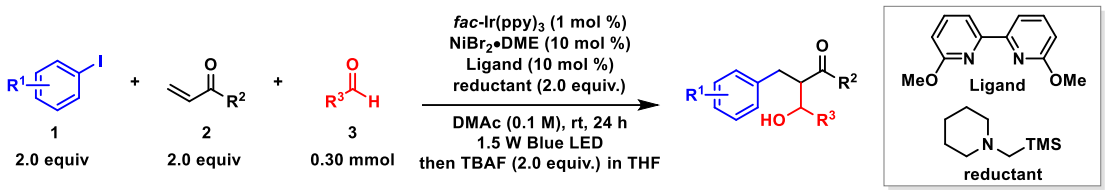
3.7 Table S7. Control Experiments



Entry	Deviation	Yield of **4** (%)[a]	Yield of **5** (%)[a]	Yield of **6** (%)[a]
1	5 mol% Ni and Ligand	61	45	0
2	DMAc (0.2 M)	53	23	2
3	DMAc (0.05 M)	56	20	3
4	no light	0	0	0
5	no PC	0	0	0
6	no Ni	0	0	0
7	no Ligand	40	22	0
8[b]	no Ligand	44	13	0
9	no Ligand and no Ni	0	0	0
10[b]	**1k** instead of **1a**	22	4	50
11[b]	**1l** instead of **1a**	15	6	8

[a] GC yields, tridecane as the internal standard; [b] **1a**:**2a**:**3a** = 2:2:1.

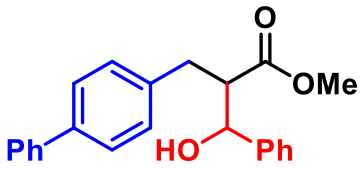
4 General Procedure for Three-Component Reductive Conjugate Addition/Aldol Tandem Reaction



The reactions were set up in an N_2 filled glovebox. An oven-dried vial equipped with a stir-bar was added *fac*-Ir(ppy)$_3$ (2.0 mg, 3.0 μmol, 0.010 equiv), Ligand (6.5 mg, 30 μmol, 0.10 equiv), NiBr$_2$•DME (9.3 mg, 30 μmol, 0.10 equiv), Aryl iodide **1** (0.60 mmol, 2.0 equiv), alkene **2** (0.60 mmol, 2.0 equiv), Aldehyde **3** (0.30 mmol, 1.0 equiv). Then, DMAc (0.10 M, 3.0 mL), reductant (103 mg, 0.60 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 (90 mL). The combined organic layers were washed with brine, dried with Na_2SO_4, filtered, and concentrated in vacuo. Then the crude product was dissolved in THF (0.10 M, 3.0 mL), tetrabutylammonium fluoride (157 mg, 0.6 mmol, 2.0 equiv) was added. The reaction stirred vigorously at room temperature for 1 h. After completion, the solvent was removed under reduced pressure and the residue was purified by flash chromatography to give the corresponding product.

5 Spectroscopic Data of the Products

Methyl 2-([1,1'-biphenyl]-4-ylmethyl)-3-hydroxy-3-phenylpropanoate (4)



Chemical Formula: $C_{23}H_{22}O_3$
Exact Mass: 346.1569

Prepared according to the general procedure using **1a** (168 mg, 0.60 mmol, 2.0 equiv), **2a** (52 mg, 0.60 mmol, 2.0 equiv), **3a** (32 mg, 0.30 mmol, 1.0 equiv), *fac*-Ir(ppy)$_3$ (2.0 mg, 3.0 μmol, 0.010 equiv), Ligand (6.5 mg, 30 μmol, 0.10 equiv), $NiBr_2$•DME (9.3 mg, 30 μmol, 0.10 equiv), DMAc (0.10 M, 3.0 mL), reductant (103 mg, 0.60 mmol, 2.0 equiv), tetrabutylammonium fluoride (157 mg, 0.6 mmol, 2.0 equiv), THF (0.10 M, 3.0 mL). The residue was purified by flash column chromatography (PE/EA = 50:1 to PE/EA = 6:1) to give the product **4** (77 mg, 74% yield, *dr* = 1:1.4) as a white solid.

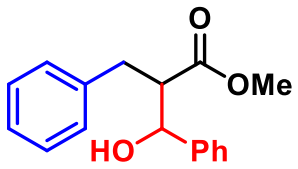
One isomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.5 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.42 – 7.27 (m, 8H), 7.14 (d, *J* = 8.2 Hz, 2H), 5.04 (d, *J* = 4.5 Hz, 1H), 3.43 (s, 3H), 3.08 – 2.99 (m, 3H), 2.93 (s, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.6, 141.4, 141.0, 139.3, 138.4, 129.3, 128.8, 128.6, 128.0, 127.2 (2C), 127.1, 126.3, 74.3, 55.4, 51.7, 33.0 ppm. **HRMS** (ESI) for $C_{23}H_{23}O_3^+$ [(M+H)$^+$]: calculated 347.1642, found 347.1668. **Melting point:** 94.0 – 95.0 °C.

Another isomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.0 Hz, 2H), 7.48 (d, *J* = 7.8 Hz, 2H), 7.43 – 7.39 (m, 2H), 7.37 – 7.30 (m, 6H), 7.17 (d, *J* = 7.9 Hz, 2H), 4.84 (t, *J* = 6.5 Hz, 1H), 3.54 (s, 3H), 3.14 – 3.06 (m, 2H), 2.94 (dd, *J* = 13.6, 9.6 Hz, 1H), 2.76 (dd, *J* = 13.6, 5.8 Hz, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.1, 142.0, 140.9, 139.5, 137.6, 129.3, 128.9, 128.8, 128.2, 127.3 (2C), 127.1, 126.4, 74.9, 55.0, 51.9, 35.5 ppm. **HRMS** (ESI) for $C_{23}H_{22}NaO_3^+$ [(M+Na)$^+$]: calculated 369.1461, found 369.1444. **Melting point:** 132.5 – 133.5 °C.

Methyl 2-benzyl-3-hydroxy-3-phenylpropanoate (8)



Chemical Formula: $C_{17}H_{18}O_3$
Exact Mass: 270.1256

Prepared according to the general procedure using **1b** (122 mg, 0.60 mmol, 2.0 equiv), **2a** (52 mg, 0.60 mmol, 2.0 equiv), **3a** (32 mg, 0.30 mmol, 1.0 equiv), *fac*-Ir(ppy)$_3$ (2.0 mg, 3.0 μmol, 0.010 equiv), Ligand (6.5 mg, 30 μmol, 0.10 equiv), $NiBr_2$•DME (9.3 mg, 30 μmol, 0.10 equiv), DMAc (0.10 M, 3.0 mL), reductant (103 mg, 0.60 mmol, 2.0 equiv), tetrabutylammonium fluoride (157 mg, 0.6 mmol, 2.0 equiv), THF (0.10 M, 3.0 mL). The residue was purified by flash column chromatography (PE/EA = 50:1 to PE/EA = 6:1) to give the product **8** (58 mg, 71% yield, *dr* = 1:1.4) as a white solid.

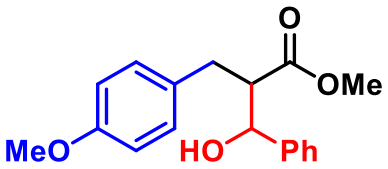
One isomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 4H), 7.30 – 7.27 (m, 1H), 7.25 – 7.20 (m, 2H), 7.17 – 7.14 (m, 1H), 7.07 (d, *J* = 6.7 Hz, 2H), 5.02 (s, 1H), 3.41 (s, 3H), 3.03 – 2.92 (m, 4H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.7, 141.4, 139.3, 128.9, 128.6, 128.5, 128.0, 126.4, 126.3, 74.2, 55.4, 51.7, 33.4 ppm. **HRMS** (ESI) for $C_{17}H_{18}NaO_3^+$ [$(M+Na)^+$]: calculated 293.1148, found 293.1130. **Melting point:** 68.6 – 68.0 °C.

Another isomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.30 (m, 5H), 7.27 – 7.23 (m, 2H), 7.20 – 7.17 (m, 1H), 7.10 (d, *J* = 6.9 Hz, 2H), 4.82 (t, *J* = 6.4 Hz, 1H), 3.56 (s, 3H), 3.10 – 3.04 (m, 2H), 2.90 (dd, *J* = 13.6, 9.7 Hz, 1H), 2.72 (dd, *J* = 13.5, 5.9 Hz, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.1, 142.0, 138.5, 128.9, 128.8, 128.6, 128.2, 126.7, 126.4, 74.8, 55.1, 51.8, 35.9 ppm. **HRMS** (ESI) for $C_{17}H_{18}NaO_3^+$ [$(M+Na)^+$]: calculated 293.1148, found 293.1132. **Melting point:** 95.9 – 97.0 °C.

Methyl 3-hydroxy-2-(4-methoxybenzyl)-3-phenylpropanoate (9)



Chemical Formula: $C_{18}H_{20}O_4$
Exact Mass: 300.1362

Prepared according to the general procedure using **1c** (140 mg, 0.60 mmol, 2.0 equiv), **2a** (52 mg, 0.60 mmol, 2.0 equiv), **3a** (32 mg, 0.30 mmol, 1.0 equiv), *fac*-Ir(ppy)$_3$ (2.0 mg, 3.0 μmol, 0.010 equiv), Ligand (6.5 mg, 30 μmol, 0.10 equiv), $NiBr_2$•DME (9.3 mg, 30 μmol, 0.10 equiv), DMAc (0.10 M, 3.0 mL), reductant (103 mg, 0.60 mmol, 2.0 equiv), tetrabutylammonium fluoride (157 mg, 0.6 mmol, 2.0 equiv), THF (0.10 M, 3.0 mL). The residue was purified by flash column chromatography (PE/EA = 50:1 to PE/EA = 6:1) to give the product **9** (40 mg, 44% yield, *dr* = 1:1.3) as a colorless oil.

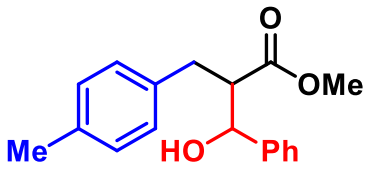
One isomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.29 (m, 5H), 6.99 (d, *J* = 8.7 Hz, 2H), 6.77 (d, *J* = 8.7 Hz, 2H), 5.02 (d, *J* = 3.7 Hz, 1H), 3.76 (s, 3H), 3.43 (s, 3H), 3.03 – 2.87 (m, 4H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.8, 158.2, 141.5, 131.2, 129.9, 128.6, 128.0, 126.3, 113.9, 74.2, 55.6, 55.3, 51.7, 32.5 ppm. **HRMS** (ESI) for $C_{18}H_{20}NaO_4^+$ [$(M+Na)^+$]: calculated 323.1254, found 323.1234.

Another isomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 5H), 7.04 – 7.00 (m, 2H), 6.81 – 6.77 (m, 2H), 4.80 (t, *J* = 6.2 Hz, 1H), 3.77 (s, 3H), 3.53 (s, 3H), 3.05 – 3.00 (m, 2H), 2.84 (dd, *J* = 13.7, 9.6 Hz, 1H), 2.67 (dd, *J* = 13.6, 5.9 Hz, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.2, 158.4, 142.1, 130.5, 129.9, 128.7, 128.2, 126.4, 114.0, 74.7, 55.3 (2C), 51.8, 35.0 ppm. **HRMS** (ESI) for $C_{18}H_{20}NaO_4^+$ [$(M+Na)^+$]: calculated 323.1254, found 323.1238.

Methyl 3-hydroxy-2-(4-methylbenzyl)-3-phenylpropanoate (10)



Chemical Formula: $C_{18}H_{20}O_3$
Exact Mass: 284.1412

Prepared according to the general procedure using **1d** (131 mg, 0.60 mmol, 2.0 equiv), **2a** (52 mg, 0.60 mmol, 2.0 equiv), **3a** (32 mg, 0.30 mmol, 1.0 equiv), *fac*-Ir(ppy)$_3$ (2.0 mg, 3.0 μmol, 0.010 equiv), Ligand (6.5 mg, 30 μmol, 0.10 equiv), $NiBr_2$•DME (9.3 mg, 30 μmol, 0.10 equiv), DMAc (0.10 M, 3.0 mL), reductant (103 mg, 0.60 mmol, 2.0 equiv), tetrabutylammonium fluoride (157 mg, 0.6 mmol, 2.0 equiv), THF (0.10 M, 3.0 mL). The residue was purified by flash column chromatography (PE/EA = 50:1 to PE/EA = 6:1) to give the product **10** (38 mg, 45% yield, *dr* = 1:1.4) as a white solid.

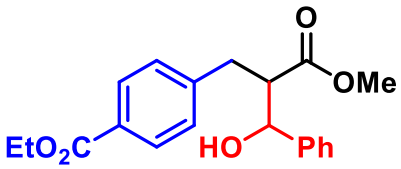
One isomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 4H), 7.30 – 7.26 (m, 1H), 7.03 (d, *J* = 7.7 Hz, 2H), 6.96 (d, *J* = 8.2 Hz, 2H), 5.02 – 5.00 (m, 1H), 3.42 (s, 3H), 3.04 – 2.89 (m, 4H), 2.28 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.8, 141.5, 136.1, 135.9, 129.2, 128.8, 128.5, 128.0, 126.3, 74.3, 55.5, 51.7, 32.9, 21.1 ppm. **HRMS** (ESI) for $C_{18}H_{20}NaO_3^+$ [(M+Na)$^+$]: calculated 307.1305, found 307.1294. **Melting point:** 64.2 – 65.2 °C.

Another isomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 5H), 7.05 (d, *J* = 7.8 Hz, 2H), 6.99 (d, *J* = 8.1 Hz, 2H), 4.80 (t, *J* = 6.6 Hz, 1H), 3.53 (s, 3H), 3.07 – 3.01 (m, 2H), 2.86 (dd, *J* = 13.6, 9.6 Hz, 1H), 2.68 (dd, *J* = 13.5, 5.9 Hz, 1H), 2.29 (s, 3H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 175.2, 142.1, 136.1, 135.4, 129.3, 128.8, 128.7, 128.1, 126.4, 74.8, 55.1, 51.8, 35.4, 21.2 ppm. **HRMS** (ESI) for $C_{18}H_{20}NaO_3^+$ [(M+Na)$^+$]: calculated 307.1305, found 307.1287. **Melting point:** 89.8 – 91.0 °C.

Ethyl 4-(3-hydroxy-2-(methoxycarbonyl)-3-phenylpropyl)benzoate (11)



Chemical Formula: $C_{20}H_{22}O_5$
Exact Mass: 342.1467

Prepared according to the general procedure using **1e** (166 mg, 0.60 mmol, 2.0 equiv), **2a** (52 mg, 0.60 mmol, 2.0 equiv), **3a** (32 mg, 0.30 mmol, 1.0 equiv), *fac*-Ir(ppy)$_3$ (2.0 mg, 3.0 μmol, 0.010 equiv), Ligand (6.5 mg, 30 μmol, 0.10 equiv), $NiBr_2$•DME (9.3 mg, 30 μmol, 0.10 equiv), DMAc (0.10 M, 3.0 mL), reductant (103 mg, 0.60 mmol, 2.0 equiv), tetrabutylammonium fluoride (157 mg, 0.6 mmol, 2.0 equiv), THF (0.10 M, 3.0 mL). The residue was purified by flash column chromatography (PE/EA = 50:1 to PE/EA = 6:1) to give the product **11** (55 mg, 54% yield, *dr* = 1:1.1) as a colorless oil.

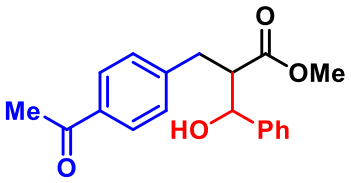
One isomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.40 – 7.30 (m, 5H), 7.14 (d, *J* = 8.2 Hz, 2H), 5.05 (d, *J* = 4.4 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 3.41 (s, 3H), 3.11 – 3.00 (m, 3H), 2.92 (s, 1H), 1.37 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.3, 166.7, 144.8, 141.3, 129.8, 128.9, 128.8, 128.6, 128.1, 126.2, 74.2, 61.0, 55.1, 51.8, 33.3, 14.5 ppm. **HRMS** (ESI) for $C_{20}H_{22}NaO_5^+$ [(M+Na)$^+$]: calculated 365.1359, found 365.1345.

Another isomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.2 Hz, 2H), 7.40 – 7.30 (m, 5H), 7.16 (d, *J* = 8.2 Hz, 2H), 4.83 (d, *J* = 9.4 Hz, 1H), 4.35 (q, *J* = 7.0 Hz, 2H), 3.52 (s, 3H), 3.11 – 3.05 (m, 1H), 2.99 – 2.91 (m, 2H), 2.73 (dd, *J* = 13.4, 5.5 Hz, 1H), 1.38 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.7, 166.6, 143.9, 141.7, 129.9, 129.0, 128.9, 128.8, 128.4, 126.4, 75.1, 61.0, 54.9, 51.9, 35.8, 14.5 ppm. **HRMS** (ESI) for $C_{20}H_{22}NaO_5^+$ [(M+Na)$^+$]: calculated 365.1359, found 365.1353.

Methyl 2-(4-acetylbenzyl)-3-hydroxy-3-phenylpropanoate (12)



Chemical Formula: $C_{19}H_{20}O_4$
Exact Mass: 312.1362

Prepared according to the general procedure using **1f** (148 mg, 0.60 mmol, 2.0 equiv), **2a** (52 mg, 0.60 mmol, 2.0 equiv), **3a** (32 mg, 0.30 mmol, 1.0 equiv), *fac*-Ir(ppy)$_3$ (2.0 mg, 3.0 μmol, 0.010 equiv), Ligand (6.5 mg, 30 μmol, 0.10 equiv), $NiBr_2$•DME (9.3 mg, 30 μmol, 0.10 equiv), DMAc (0.10 M, 3.0 mL), reductant (103 mg, 0.60 mmol, 2.0 equiv), tetrabutylammonium fluoride (157 mg, 0.6 mmol, 2.0 equiv), THF (0.10 M, 3.0 mL). The residue was purified by flash column chromatography (PE/EA = 50:1 to PE/EA = 6:1) to give the product **12** (58 mg, 62% yield, *dr* = 1:1.4) as a colorless oil.

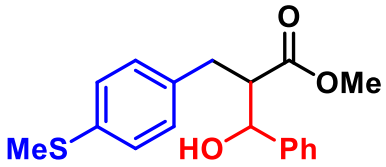
One isomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.41 – 7.28 (m, 5H), 7.17 (d, *J* = 8.3 Hz, 2H), 5.05 (d, *J* = 4.5 Hz, 1H), 3.42 (s, 3H), 3.09 – 3.01 (m, 3H), 2.55 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.0, 174.2, 145.2, 141.3, 135.5, 129.2, 128.6 (2C), 128.1, 126.2, 74.2, 55.1, 51.8, 33.3, 26.7 ppm. **HRMS** (ESI) for $C_{19}H_{21}O_4^+$ [$(M+H)^+$]: calculated 313.1434, found 313.1425.

Another isomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.4 Hz, 2H), 7.40 – 7.30 (m, 5H), 7.19 (d, *J* = 8.4 Hz, 2H), 4.83 (d, *J* = 7.3 Hz, 1H), 3.53 (s, 3H), 3.11 – 2.91 (m, 3H), 2.73 (dd, *J* = 13.6, 5.4 Hz, 1H), 2.57 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.9, 174.7, 144.3, 141.7, 135.7, 129.1, 128.8, 128.7, 128.4, 126.4, 75.0, 54.8, 51.9, 35.7, 26.7 ppm. **HRMS** (ESI) for $C_{19}H_{20}NaO_4^+$ [$(M+Na)^+$]: calculated 335.1254, found 335.1233.

Methyl 3-hydroxy-2-(4-(methylthio)benzyl)-3-phenylpropanoate (13)



Chemical Formula: $C_{18}H_{20}O_3S$
Exact Mass: 316.1133

Prepared according to the general procedure using **1g** (150 mg, 0.60 mmol, 2.0 equiv), **2a** (52 mg, 0.60 mmol, 2.0 equiv), **3a** (32 mg, 0.30 mmol, 1.0 equiv), *fac*-Ir(ppy)$_3$ (2.0 mg, 3.0 μmol, 0.010 equiv), Ligand (6.5 mg, 30 μmol, 0.10 equiv), $NiBr_2$•DME (9.3 mg, 30 μmol, 0.10 equiv), DMAc (0.10 M, 3.0 mL), reductant (103 mg, 0.60 mmol, 2.0 equiv), tetrabutylammonium fluoride (157 mg, 0.6 mmol, 2.0 equiv), THF (0.10 M, 3.0 mL). The residue was purified by flash column chromatography (PE/EA = 50:1 to PE/EA = 6:1) to give the product **13** (47 mg, 50% yield, *dr* = 1:1.6) as a colorless oil.

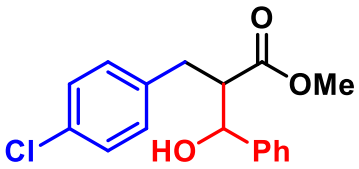
One isomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.26 (m, 5H), 7.14 – 7.10 (m, 2H), 6.99 (d, *J* = 8.3 Hz, 2H), 5.01 – 4.99 (m, 1H), 3.42 (s, 3H), 3.02 – 2.91 (m, 4H), 2.43 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.5, 141.4, 136.2, 136.1, 129.4, 128.6, 128.0, 127.0, 126.2, 74.2, 55.4, 51.7, 32.8, 16.2 ppm. **HRMS** (ESI) for $C_{18}H_{20}NaO_3S^+$ [(M+Na)$^+$]: calculated 339.1025, found 339.1007.

Another isomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 5H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.02 (d, *J* = 8.3 Hz, 2H), 4.79 (t, *J* = 6.5 Hz, 1H), 3.53 (s, 3H), 3.06 – 3.00 (m, 2H), 2.85 (dd, *J* = 13.7, 9.8 Hz, 1H), 2.66 (dd, *J* = 13.6, 5.8 Hz, 1H), 2.44 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.0, 141.9, 136.5, 135.4, 129.4, 128.8, 128.2, 127.0, 126.4, 74.8, 55.0, 51.9, 35.3, 16.1 ppm. **HRMS** (ESI) for $C_{18}H_{20}NaO_3S^+$ [(M+Na)$^+$]: calculated 339.1025, found 339.1002.

Methyl 2-(4-chlorobenzyl)-3-hydroxy-3-phenylpropanoate (14)



Chemical Formula: $C_{17}H_{17}ClO_3$
Exact Mass: 304.0866

Prepared according to the general procedure using **1h** (143 mg, 0.60 mmol, 2.0 equiv), **2a** (52 mg, 0.60 mmol, 2.0 equiv), **3a** (32 mg, 0.30 mmol, 1.0 equiv), *fac*-Ir(ppy)$_3$ (2.0 mg, 3.0 μmol, 0.010 equiv), Ligand (6.5 mg, 30 μmol, 0.10 equiv), $NiBr_2$•DME (9.3 mg, 30 μmol, 0.10 equiv), DMAc (0.10 M, 3.0 mL), reductant (103 mg, 0.60 mmol, 2.0 equiv), tetrabutylammonium fluoride (157 mg, 0.6 mmol, 2.0 equiv), THF (0.10 M, 3.0 mL). The residue was purified by flash column chromatography (PE/EA = 50:1 to PE/EA = 6:1) to give the product **14** (39 mg, 43% yield, *dr* = 1:1.4) as a colorless oil.

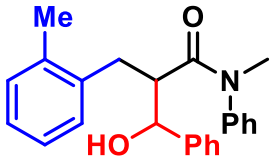
One isomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 5H), 7.20 – 7.17 (m, 2H), 7.02 – 6.98 (m, 2H), 5.03 – 5.01 (m, 1H), 3.42 (s, 3H), 3.00 – 2.92 (m, 3H), 2.85 (d, *J* = 2.9 Hz, 1H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 174.4, 141.3, 137.8, 132.2, 130.3, 128.6 (2C), 128.1, 126.2, 74.1, 55.3, 51.8, 32.7 ppm. **HRMS** (ESI) for $C_{17}H_{17}ClNaO_3^+$ [(M+Na)$^+$]: calculated 327.0758, found 327.0751.

Another isomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 5H), 7.23 – 7.19 (m, 2H), 7.04 – 7.01 (m, 2H), 4.82 – 4.78 (m, 1H), 3.53 (s, 3H), 3.05 – 3.00 (m, 1H), 2.96 (d, *J* = 6.0 Hz, 1H), 2.85 (dd, *J* = 13.6, 9.9 Hz, 1H), 2.65 (dd, *J* = 13.6, 5.7 Hz, 1H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 174.8, 141.8, 137.0, 132.5, 130.3, 128.8, 128.7, 128.4, 126.4, 74.9, 55.0, 51.9, 35.1 ppm. **HRMS** (ESI) for $C_{17}H_{17}ClNaO_3^+$ [(M+Na)$^+$]: calculated 327.0758, found 327.0738.

3-Hydroxy-*N*-methyl-2-(2-methylbenzyl)-*N*,3-diphenylpropanamide (15)



Chemical Formula: $C_{24}H_{25}NO_2$
Exact Mass: 359.1885

Prepared according to the general procedure using **1i** (131 mg, 0.60 mmol, 2.0 equiv), **2b** (97 mg, 0.60 mmol, 2.0 equiv), **3a** (32 mg, 0.30 mmol, 1.0 equiv), *fac*-Ir(ppy)$_3$ (2.0 mg, 3.0 μmol, 0.010 equiv), Ligand (6.5 mg, 30 μmol, 0.10 equiv), $NiBr_2$•DME (9.3 mg, 30 μmol, 0.10 equiv), DMAc (0.10 M, 3.0 mL), reductant (103 mg, 0.60 mmol, 2.0 equiv), tetrabutylammonium fluoride (157 mg, 0.6 mmol, 2.0 equiv), THF (0.10 M, 3.0 mL). The residue was purified by flash column chromatography (PE/EA = 50:1 to PE/EA = 4:1) to give the product **15** (70 mg, 65% yield, *dr* = 1:1) as a white solid.

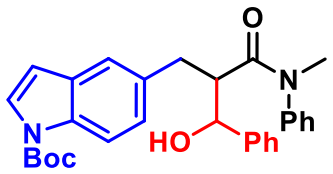
One isomer

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 – 7.20 (m, 7H), 7.14 – 7.07 (m, 3H), 7.02 (d, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 7.3 Hz, 1H), 5.05 (d, *J* = 3.6 Hz, 1H), 4.37 (s, 1H), 3.09 (s, 3H), 3.00 (t, *J* = 12.7 Hz, 1H), 2.74 (dt, *J* = 11.9, 3.1 Hz, 1H), 2.61 (dd, *J* = 13.3, 2.9 Hz, 1H), 1.47 (s, 3H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 175.2, 142.9, 141.7, 137.6, 137.0, 130.4, 130.3, 129.4, 128.2, 128.0, 127.4, 127.3, 126.6, 125.9, 125.8, 73.7, 48.8, 37.0, 30.0, 18.2 ppm. **HRMS** (ESI) for $C_{24}H_{26}NO_2^+$ [(M+H)$^+$]: calculated 360.1958, found 360.1960. **Melting point:** 129.3 – 130.3 °C.

Another isomer

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 3H), 7.17 – 7.09 (m, 6H), 7.06 (d, *J* = 7.3 Hz, 1H), 7.00 – 6.98 (m, 2H), 5.63 (s, 2H), 5.26 (d, *J* = 8.2 Hz, 1H), 4.71 (dd, *J* = 7.8, 3.9 Hz, 1H), 3.19 (dd, *J* = 13.4, 10.4 Hz, 1H), 2.99 (s, 3H), 2.89 (dd, *J* = 13.5, 5.0 Hz, 1H), 2.76 – 2.73 (m, 1H), 1.85 (s, 3H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 174.29, 143.85, 142.45, 137.12, 136.83, 130.44, 130.36, 129.08, 128.44, 127.76, 127.60, 127.36, 126.85, 126.09, 126.03, 75.94, 48.50, 36.94, 35.34, 18.85 ppm. **HRMS** (ESI) for $C_{24}H_{26}NO_2^+$ [(M+H)$^+$]: calculated 360.1958, found 360.1960. **Melting point:** 133.8 – 134.8 °C.

***Tert*-butyl 5-(3-hydroxy-2-(methyl(phenyl)carbamoyl)-3-phenylpropyl)-1*H*-indole-1-carboxylate (16)**



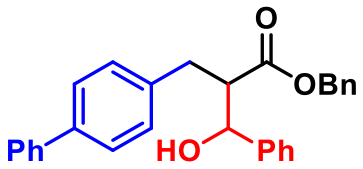
Chemical Formula: $C_{30}H_{32}N_2O_4$
Exact Mass: 484.2362

Prepared according to the general procedure using **1j** (206 mg, 0.60 mmol, 2.0 equiv), **2b** (97 mg, 0.60 mmol, 2.0 equiv), **3a** (32 mg, 0.30 mmol, 1.0 equiv), *fac*-Ir(ppy)$_3$ (2.0 mg, 3.0 μmol, 0.010 equiv), Ligand (6.5 mg, 30 μmol, 0.10 equiv), $NiBr_2$•DME (9.3 mg, 30 μmol, 0.10 equiv), DMAc (0.10 M, 3.0 mL), reductant (103 mg, 0.60 mmol, 2.0 equiv), tetrabutylammonium fluoride (157 mg, 0.6 mmol, 2.0 equiv), THF (0.10 M, 3.0 mL). The residue was purified by flash column chromatography (PE/EA = 50:1 to PE/EA = 4:1) to give the product **16** (55 mg, 38% yield, *dr* = 1:1.1) as a white solid.

Note: these two diastereoisomers cannot be separated by column chromatography

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.98 (m, 2H), 7.58 – 7.57 (m, 2H), 7.33 – 7.20 (m, 11H), 7.18 – 7.06 (m, 6H), 6.98 – 6.88 (m, 5H), 6.49 (d, *J* = 3.8 Hz, 1H), 6.46 (d, *J* = 3.8 Hz, 1H), 5.66 (d, *J* = 8.2 Hz, 2H), 5.46 (d, *J* = 8.9 Hz, 1H), 5.04 (d, *J* = 4.2 Hz, 1H), 4.68 (dd, *J* = 8.5, 3.6 Hz, 1H), 4.25 (s, 1H), 3.30 (dd, *J* = 13.3, 9.3 Hz, 1H), 3.19 – 3.13 (m, 1H), 3.03 (s, 3H), 3.00 (d, *J* = 7.2 Hz, 1H), 2.98 (s, 3H), 2.87 – 2.82 (m, 1H), 2.78 – 2.74 (m, 1H), 2.70 (dd, *J* = 13.1, 3.4 Hz, 1H), 1.68 (s, 9H), 1.67 (s, 9H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.7, 174.4, 149.8 (2C), 143.9, 142.8, 142.4, 142.0, 134.2, 134.0, 133.8, 133.3, 130.9 130.8, 129.2, 129.0, 128.3 (2C), 127.9, 127.8, 127.4, 127.3 (2C), 126.3, 126.1, 126.0, 125.9 (2C), 125.7, 121.6 (2C), 115.0, 114.8, 107.2, 83.7 (2C), 75.0, 73.9, 51.9, 51.0, 37.5, 37.1, 36.9, 32.8, 28.3 (2C) ppm. **HRMS** (ESI) for $C_{30}H_{33}N_2O_4^+$ [$(M+H)^+$]: calculated 485.2435, found 485.2413. **Melting point:** 152.2 – 158.3 °C.

Benzyl 2-([1,1'-biphenyl]-4-ylmethyl)-3-hydroxy-3-phenylpropanoate (17)



Chemical Formula: $C_{29}H_{26}O_3$
Exact Mass: 422.1882

Prepared according to the general procedure using **1a** (168 mg, 0.60 mmol, 2.0 equiv), **2c** (97 mg, 0.60 mmol, 2.0 equiv), **3a** (32 mg, 0.30 mmol, 1.0 equiv), *fac*-Ir(ppy)$_3$ (2.0 mg, 3.0 μmol, 0.010 equiv), Ligand (6.5 mg, 30 μmol, 0.10 equiv), $NiBr_2$•DME (9.3 mg, 30 μmol, 0.10 equiv), DMAc (0.10 M, 3.0 mL), reductant (103 mg, 0.60 mmol, 2.0 equiv), tetrabutylammonium fluoride (157 mg, 0.6 mmol, 2.0 equiv), THF (0.10 M, 3.0 mL). The residue was purified by flash column chromatography (PE/EA = 50:1 to PE/EA = 6:1) to give the product **17** (85 mg, 67% yield, *dr* = 1:1.4) as a white solid.

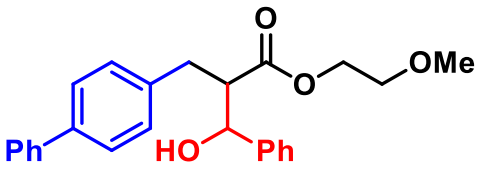
One isomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.9 Hz, 2H), 7.44 – 7.29 (m, 10H), 7.23 – 7.13 (m, 5H), 6.90 (d, *J* = 7.0 Hz, 2H), 5.06 (dd, *J* = 5.6, 2.8 Hz, 1H), 4.89 – 4.79 (m, 2H), 3.16 – 3.05 (m, 3H), 2.89 (d, *J* = 2.9 Hz, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.1, 141.4, 141.0, 139.3, 138.2, 135.3, 129.5, 128.9, 128.6, 128.5, 128.2, 128.1, 127.2 (2C), 127.1, 126.4, 74.3, 66.5, 55.4, 33.3 ppm. **HRMS** (ESI) for $C_{29}H_{26}NaO_3^+$ [$(M+Na)^+$]: calculated 445.1774, found 445.1761. **Melting point:** 69.7 – 71.0 °C.

Another isomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.6 Hz, 2H), 7.46 – 7.41 (m, 4H), 7.36 – 7.30 (m, 6H), 7.24 – 7.15 (m, 5H), 6.98 (d, *J* = 6.9 Hz, 2H), 5.01 – 4.91 (m, 2H), 4.88 (t, *J* = 6.1 Hz, 1H), 3.20 – 3.14 (m, 1H), 3.07 (d, *J* = 6.5 Hz, 1H), 2.96 (dd, *J* = 13.6, 10.0 Hz, 1H), 2.78 (dd, *J* = 13.5, 5.7 Hz, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.5, 141.9, 140.9, 139.5, 137.5, 135.4, 129.4, 128.9, 128.8, 128.5, 128.2 (2C), 127.3 (2C), 127.1, 126.4, 74.9, 66.6, 55.1, 35.6 ppm. **HRMS** (ESI) for $C_{29}H_{26}NaO_3^+$ [$(M+Na)^+$]: calculated 445.1774, found 445.1763. **Melting point:** 124.3 – 125.3 °C.

2-Methoxyethyl 2-([1,1'-biphenyl]-4-ylmethyl)-3-hydroxy-3-phenylpropanoate (18)



Chemical Formula: $C_{25}H_{26}O_4$
Exact Mass: 390.1831

Prepared according to the general procedure using **1a** (168 mg, 0.60 mmol, 2.0 equiv), **2d** (78 mg, 0.60 mmol, 2.0 equiv), **3a** (32 mg, 0.30 mmol, 1.0 equiv), *fac*-Ir(ppy)$_3$ (2.0 mg, 3.0 μmol, 0.010 equiv), Ligand (6.5 mg, 30 μmol, 0.10 equiv), $NiBr_2$•DME (9.3 mg, 30 μmol, 0.10 equiv), DMAc (0.10 M, 3.0 mL), reductant (103 mg, 0.60 mmol, 2.0 equiv), tetrabutylammonium fluoride (157 mg, 0.6 mmol, 2.0 equiv), THF (0.10 M, 3.0 mL). The residue was purified by flash column chromatography (PE/EA = 50:1 to PE/EA = 6:1) to give the product **18** (75 mg, 64% yield, *dr* = 1:1.3) as a colorless oil.

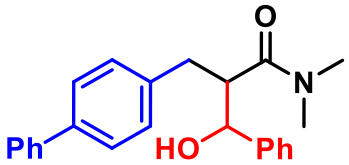
One isomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.53 (m, 2H), 7.46 – 7.26 (m, 10H), 7.16 (d, *J* = 8.2 Hz, 2H), 5.08 (d, *J* = 5.2 Hz, 1H), 4.03 – 4.01 (m, 2H), 3.30 – 3.20 (m, 2H), 3.17 (s, 3H), 3.16 – 3.10 (m, 2H), 3.05 (d, *J* = 10.7 Hz, 1H), 2.98 (dd, *J* = 13.2, 3.7 Hz, 1H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 174.0, 141.4, 141.0, 139.3, 138.4, 129.4, 128.8, 128.5, 128.0, 127.2, 127.1, 127.0, 126.3, 74.2, 70.2, 63.4, 58.9, 55.2, 32.7 ppm. **HRMS** (ESI) for $C_{25}H_{26}NaO_4^+$ [$(M+Na)^+$]: calculated 413.1723, found 413.1694.

Another isomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.5 Hz, 2H), 7.48 (d, *J* = 8.2 Hz, 2H), 7.43 – 7.30 (m, 8H), 7.20 (d, *J* = 8.2 Hz, 2H), 4.84 (t, *J* = 6.6 Hz, 1H), 4.15 (t, *J* = 4.8 Hz, 2H), 3.37 – 3.34 (m, 2H), 3.26 (d, *J* = 6.3 Hz, 1H), 3.22 (s, 3H), 3.18 – 3.14 (m, 1H), 2.95 (dd, *J* = 13.7, 9.8 Hz, 1H), 2.76 (dd, *J* = 13.6, 5.9 Hz, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.3, 141.9, 141.0, 139.5, 137.6, 129.4, 128.9, 128.7, 128.2, 127.3, 127.2, 127.1, 126.5, 74.9, 70.3, 63.4, 58.9, 55.2, 35.3 ppm. **HRMS** (ESI) for $C_{25}H_{26}NaO_4^+$ [$(M+Na)^+$]: calculated 413.1723, found 413.1696.

2-([1,1'-Biphenyl]-4-ylmethyl)-3-hydroxy-*N,N*-dimethyl-3-phenylpropanamide (19)



Chemical Formula: $C_{24}H_{25}NO_2$
Exact Mass: 359.1885

Prepared according to the general procedure using **1a** (168 mg, 0.60 mmol, 2.0 equiv), **2e** (60 mg, 0.60 mmol, 2.0 equiv), **3a** (32 mg, 0.30 mmol, 1.0 equiv), *fac*-Ir(ppy)$_3$ (2.0 mg, 3.0 μmol, 0.010 equiv), Ligand (6.5 mg, 30 μmol, 0.10 equiv), $NiBr_2$•DME (9.3 mg, 30 μmol, 0.10 equiv), DMAc (0.10 M, 3.0 mL), reductant (103 mg, 0.60 mmol, 2.0 equiv), tetrabutylammonium fluoride (157 mg, 0.6 mmol, 2.0 equiv), THF (0.10 M, 3.0 mL). The residue was purified by flash column chromatography (PE/EA = 50:1 to PE/EA = 6:1) to give the product **19** (43 mg, 40% yield, *dr* = 1:1.6) as a white solid.

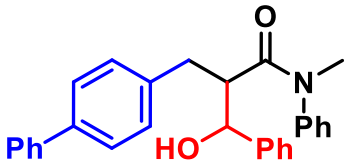
One isomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.57 (m, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.45 – 7.41 (m, 2H), 7.36 – 7.22 (m, 8H), 5.26 (d, *J* = 8.6 Hz, 1H), 4.90 (dd, *J* = 8.4, 3.5 Hz, 1H), 3.29 – 3.20 (m, 2H), 3.10 – 3.04 (m, 1H), 2.71 (s, 3H), 2.29 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.7, 143.7, 140.8, 139.5, 138.4, 129.5, 128.9, 128.4, 127.5, 127.4, 127.2, 127.0, 125.6, 75.0, 50.0, 37.2, 37.0, 35.3 ppm. **HRMS** (ESI) for $C_{24}H_{26}NO_2^+$ [$(M+H)^+$]: calculated 360.1958, found 360.1950. **Melting point:** 110.2 – 111.2 °C.

Another isomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.54 (m, 2H), 7.48 – 7.39 (m, 8H), 7.35 – 7.29 (m, 2H), 7.07 (d, *J* = 8.2 Hz, 2H), 5.08 (d, *J* = 3.0 Hz, 1H), 5.04 (d, *J* = 1.0 Hz, 1H), 3.20 – 3.09 (m, 2H), 2.82 – 2.78 (m, 4H), 2.35 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.7, 141.9, 140.8, 139.3, 138.8, 129.5, 128.9, 128.5, 127.5, 127.4, 127.0, 127.0, 126.1, 73.8, 50.0, 37.3, 35.5, 32.2 ppm. **HRMS** (ESI) for $C_{24}H_{25}NNaO_2^+$ [$(M+Na)^+$]: calculated 382.1778, found 382.1755. **Melting point:** 162.8 – 163.8 °C.

2-([1,1'-Biphenyl]-4-ylmethyl)-3-hydroxy-*N*-methyl-*N*,3-diphenylpropanamide (20)



Chemical Formula: $C_{29}H_{27}NO_2$
Exact Mass: 421.2042

Prepared according to the general procedure using **1a** (168 mg, 0.60 mmol, 2.0 equiv), **2b** (97 mg, 0.60 mmol, 2.0 equiv), **3a** (32 mg, 0.30 mmol, 1.0 equiv), *fac*-Ir(ppy)$_3$ (2.0 mg, 3.0 μmol, 0.010 equiv), Ligand (6.5 mg, 30 μmol, 0.10 equiv), $NiBr_2$•DME (9.3 mg, 30 μmol, 0.10 equiv), DMAc (0.10 M, 3.0 mL), reductant (103 mg, 0.60 mmol, 2.0 equiv), tetrabutylammonium fluoride (157 mg, 0.6 mmol, 2.0 equiv), THF (0.10 M, 3.0 mL). The residue was purified by flash column chromatography (PE/EA = 50:1 to PE/EA = 4:1) to give the product **20** (102 mg, 81% yield, *dr* = 1:1) as a white solid.

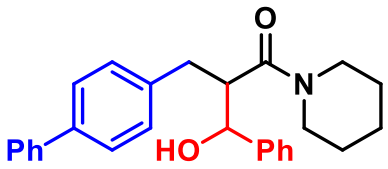
One isomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.60 (m, 2H), 7.47 – 7.44 (m, 4H), 7.37 – 7.13 (m, 9H), 6.98 (d, *J* = 8.3 Hz, 2H), 5.05 (d, *J* = 4.2 Hz, 1H), 4.16 (s, 1H), 3.12 (dd, *J* = 12.9, 11.8 Hz, 1H), 3.08 (s, 3H), 2.81 (dt, *J* = 11.7, 3.3 Hz, 1H), 2.64 (dd, *J* = 13.0, 3.3 Hz, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.7, 142.9, 141.9, 141.1, 139.3, 138.9, 129.9, 129.4, 129.0, 128.4, 128.0, 127.5, 127.4, 127.3, 127.1, 126.0, 73.9, 51.7, 37.2, 32.6 ppm. **HRMS** (ESI) for $C_{29}H_{28}NO_2^+$ [$(M+H)^+$]: calculated 422.2115, found 422.2104. **Melting point:** 187.5 – 188.5 °C.

Another isomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.1 Hz, 2H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.36 – 7.29 (m, 4H), 7.18 – 7.11 (m, 5H), 7.01 (t, *J* = 7.4 Hz, 2H), 5.74 (s, 2H), 5.41 (dd, *J* = 8.8, 3.5 Hz, 1H), 4.72 (dd, *J* = 8.9, 3.3 Hz, 1H), 3.29 (dd, *J* = 13.1, 9.6 Hz, 1H), 3.01 (s, 3H), 2.94 (dd, *J* = 13.1, 5.8 Hz, 1H), 2.77 – 2.74 (m, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.3, 143.9, 142.5, 141.0, 139.6, 138.3, 129.9, 129.2, 129.0, 128.4, 127.9, 127.5, 127.4, 127.3, 127.2, 127.1, 126.0, 75.3, 50.8, 37.4, 37.0 ppm. **HRMS** (ESI) for $C_{29}H_{27}NNaO_2^+$ [$(M+Na)^+$]: calculated 444.1934, found 444.1906. **Melting point:** 146.5 – 147.5 °C.

2-([1,1'-Biphenyl]-4-ylmethyl)-3-hydroxy-3-phenyl-1-(piperidin-1-yl)propan-1-one (21)



Chemical Formula: $C_{27}H_{29}NO_2$
Exact Mass: 399.2198

Prepared according to the general procedure using **1a** (168 mg, 0.60 mmol, 2.0 equiv), **2f** (83 mg, 0.60 mmol, 2.0 equiv), **3a** (32 mg, 0.30 mmol, 1.0 equiv), *fac*-Ir(ppy)$_3$ (2.0 mg, 3.0 μmol, 0.010 equiv), Ligand (6.5 mg, 30 μmol, 0.10 equiv), $NiBr_2$•DME (9.3 mg, 30 μmol, 0.10 equiv), DMAc (0.10 M, 3.0 mL), reductant (103 mg, 0.60 mmol, 2.0 equiv), tetrabutylammonium fluoride (157 mg, 0.6 mmol, 2.0 equiv), THF (0.10 M, 3.0 mL). The residue was purified by flash column chromatography (PE/EA = 50:1 to PE/EA = 4:1) to give the product **21** (71 mg, 59% yield, *dr* = 1:1.6) as a white solid.

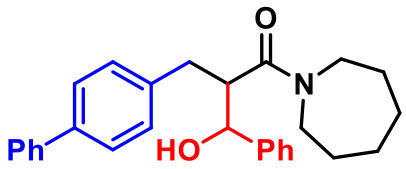
One isomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.50 (m, 2H), 7.47 – 7.36 (m, 8H), 7.34 – 7.27 (m, 2H), 7.10 (d, *J* = 8.2 Hz, 2H), 5.04 (d, *J* = 3.7 Hz, 1H), 4.94 (s, 1H), 3.63 – 3.59 (m, 1H), 3.23 – 3.10 (m, 3H), 2.94 – 2.79 (m, 3H), 1.38 – 1.22 (m, 4H), 1.07 – 1.01 (m, 1H), 0.55 – 0.46 (m, 1H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 173.4, 142.1, 141.1, 139.3, 138.9, 129.7, 128.9, 128.4, 127.5, 127.3, 127.1, 127.0, 126.2, 74.2, 49.6, 46.9, 42.8, 32.5, 25.7, 25.5, 24.2 ppm. **HRMS** (ESI) for $C_{27}H_{30}NO_2^+$ [$(M+H)^+$]: calculated 400.2271, found 400.2253. **Melting point:** 144.3 – 145.5 °C.

Another isomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.50 (m, 4H), 7.45 – 7.41 (m, 2H), 7.35 – 7.28 (m, 7H), 7.25 – 7.19 (m, 1H), 5.61 (d, *J* = 8.8 Hz, 1H), 4.91 (dd, *J* = 8.7, 3.1 Hz, 1H), 3.48 – 3.42 (m, 1H), 3.32 – 3.08 (m, 4H), 2.81 – 2.75 (m, 1H), 2.70 – 2.64 (m, 1H), 1.31 – 1.10 (m, 4H), 0.79 – 0.70 (m, 1H), 0.63 – 0.54 (m, 1H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 172.5, 143.9, 141.0, 139.5, 138.5, 129.6, 128.9, 128.4, 127.3 (3C), 127.1, 125.6, 75.1, 49.2, 46.8, 42.6, 37.3, 25.7, 25.4, 24.2 ppm. **HRMS** (ESI) for $C_{27}H_{30}NO_2^+$ [$(M+H)^+$]: calculated 400.2271, found 400.2252. **Melting point:** 146.9 – 147.9 °C.

2-([1,1'-Biphenyl]-4-ylmethyl)-1-(azepan-1-yl)-3-hydroxy-3-phenylpropan-1-one (22)



Chemical Formula: $C_{28}H_{31}NO_2$
Exact Mass: 413.2355

Prepared according to the general procedure using **1a** (168 mg, 0.60 mmol, 2.0 equiv), **2g** (92 mg, 0.60 mmol, 2.0 equiv), **3a** (32 mg, 0.30 mmol, 1.0 equiv), *fac*-Ir(ppy)$_3$ (2.0 mg, 3.0 μmol, 0.010 equiv), Ligand (6.5 mg, 30 μmol, 0.10 equiv), $NiBr_2$•DME (9.3 mg, 30 μmol, 0.10 equiv), DMAc (0.10 M, 3.0 mL), reductant (103 mg, 0.60 mmol, 2.0 equiv), tetrabutylammonium fluoride (157 mg, 0.6 mmol, 2.0 equiv), THF (0.10 M, 3.0 mL). The residue was purified by flash column chromatography (PE/EA = 50:1 to PE/EA = 4:1) to give the product **22** (56 mg, 45% yield, *dr* = 1:1.5) as a white solid.

One isomer

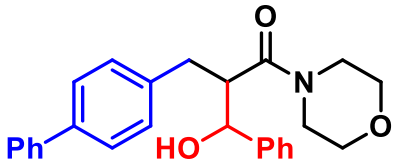
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.8 Hz, 2H), 7.46 (d, *J* = 7.6 Hz, 2H), 7.42 – 7.37 (m, 6H), 7.33 – 7.28 (m, 2H), 7.10 (d, *J* = 8.1 Hz, 2H), 5.05 (s, 1H), 4.77 (s, 1H), 3.48 – 3.32 (m, 2H), 3.20 – 3.09 (m, 2H), 3.01 – 2.93 (m, 1H), 2.82 – 2.75 (m, 2H), 1.55 – 1.45 (m, 1H), 1.30 – 1.26 (m, 5H), 1.03 – 0.83 (m, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.9, 142.0, 141.1, 139.4, 138.9, 129.8, 128.9, 128.4, 127.5, 127.3, 127.1, 127.0, 126.2, 74.2, 50.5, 47.8, 45.7, 32.3, 28.8, 27.7, 26.6, 26.5 ppm. **HRMS** (ESI) for $C_{28}H_{32}NO_2^+$ [(M+H)$^+$]: calculated 414.2428, found 414.2407. **Melting point:** 123.3 – 124.5 °C.

Another isomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.8 Hz, 2H), 7.51 (d, *J* = 8.1 Hz, 2H), 7.45 – 7.41 (m, 2H), 7.35 – 7.19 (m, 8H), 5.76 (d, *J* = 8.9 Hz, 1H), 4.88 (d, *J* = 8.8 Hz, 1H), 3.49 – 3.42 (m, 1H), 3.35 – 3.28 (m, 1H), 3.18 – 3.10 (m, 3H), 2.78 – 2.72 (m, 1H), 2.64 – 2.57 (m, 1H), 1.49 – 1.43 (m, 2H), 1.26 – 0.83 (m, 6H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 174.3, 144.0, 141.0, 139.7, 138.4, 129.8, 128.9, 128.4, 127.4 (2C), 127.3, 127.1, 125.8, 75.2, 50.1, 47.5, 45.4, 37.5, 28.4, 27.6, 26.3, 26.1 ppm. **HRMS** (ESI) for

$C_{28}H_{32}NO_2^+$ [(M+H)$^+$]: calculated 414.2428, found 414.2417. **Melting point:** 146.9 – 147.9 °C.

2-([1,1'-Biphenyl]-4-ylmethyl)-3-hydroxy-1-morpholino-3-phenylpropan-1-one (23)



Chemical Formula: $C_{26}H_{27}NO_3$
Exact Mass: 401.1991

Prepared according to the general procedure using **1a** (168 mg, 0.60 mmol, 2.0 equiv), **2h** (85 mg, 0.60 mmol, 2.0 equiv), **3a** (32 mg, 0.30 mmol, 1.0 equiv), *fac*-Ir(ppy)$_3$ (2.0 mg, 3.0 μmol, 0.010 equiv), Ligand (6.5 mg, 30 μmol, 0.10 equiv), $NiBr_2$•DME (9.3 mg, 30 μmol, 0.10 equiv), DMAc (0.10 M, 3.0 mL), reductant (103 mg, 0.60 mmol, 2.0 equiv), tetrabutylammonium fluoride (157 mg, 0.6 mmol, 2.0 equiv), THF (0.10 M, 3.0 mL). The residue was purified by flash column chromatography (PE/EA = 50:1 to PE/EA = 4:1) to give the product **23** (61 mg, 51% yield, *dr* = 1:1.2) as a white solid.

One isomer

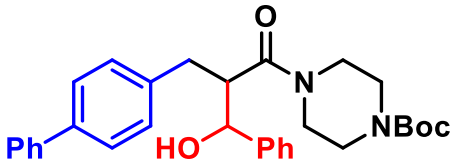
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.50 (m, 4H), 7.45 – 7.41 (m, 2H), 7.36 – 7.26 (m, 8H), 5.07 (d, *J* = 8.6 Hz, 1H), 4.96 (dd, *J* = 8.6, 3.5 Hz, 1H), 3.45 – 3.20 (m, 6H), 3.05 (dd, *J* = 11.8, 3.8 Hz, 1H), 2.81 – 2.71 (m, 4H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.9, 143.5, 140.8, 139.8, 138.2, 129.6, 129.0, 128.5, 127.7, 127.5, 127.4, 127.1, 125.6, 75.2, 66.5, 66.0, 49.6, 46.2, 41.9, 37.1 ppm. **HRMS** (ESI) for $C_{26}H_{28}NO_3^+$ [(M+H)$^+$]: calculated 402.2064, found 402.2055. **Melting point:** 144.3 – 145.5 °C.

Another isomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.52 (m, 2H), 7.47 – 7.44 (m, 3H), 7.43 – 7.29 (m, 7H), 7.14 (d, *J* = 8.3 Hz, 2H), 5.05 (d, *J* = 4.2 Hz, 1H), 4.48 (d, *J* = 1.6 Hz, 1H), 3.69 – 3.63 (m, 1H), 3.45 – 3.40 (m, 1H), 3.27 – 2.92 (m, 7H), 2.79 – 2.73 (m, 1H), 2.54 – 2.49 (m, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.4, 142.0, 140.8, 139.6, 138.6, 129.7, 128.9, 128.5, 127.8, 127.4, 127.3, 127.0, 126.2, 74.4, 66.6, 65.9, 50.1, 46.1,

41.9, 33.1 ppm. **HRMS** (ESI) for $C_{26}H_{27}NNaO_3^+$ [(M+Na)$^+$]: calculated 424.1883, found 424.1865. **Melting point:** 163.0 – 164.0 °C.

***Tert*-butyl 4-(2-([1,1'-biphenyl]-4-ylmethyl)-3-hydroxy-3-phenylpropanoyl) piperazine-1-carboxylate (24)**



Chemical Formula: $C_{31}H_{36}N_2O_4$
Exact Mass: 500.2675

Prepared according to the general procedure using **1a** (168 mg, 0.60 mmol, 2.0 equiv), **2i** (144 mg, 0.60 mmol, 2.0 equiv), **3a** (32 mg, 0.30 mmol, 1.0 equiv), *fac*-Ir(ppy)$_3$ (2.0 mg, 3.0 μmol, 0.010 equiv), Ligand (6.5 mg, 30 μmol, 0.10 equiv), $NiBr_2$•DME (9.3 mg, 30 μmol, 0.10 equiv), DMAc (0.10 M, 3.0 mL), reductant (103 mg, 0.60 mmol, 2.0 equiv), tetrabutylammonium fluoride (157 mg, 0.6 mmol, 2.0 equiv), THF (0.10 M, 3.0 mL). The residue was purified by flash column chromatography (PE/EA = 50:1 to PE/EA = 4:1) to give the product **24** (96 mg, 64% yield, *dr* = 1:1.3) as a white solid.

One isomer

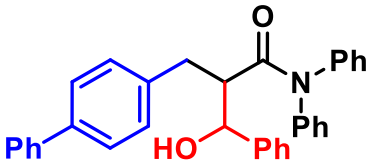
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.50 (m, 2H), 7.45 – 7.27 (m, 10H), 7.14 (d, *J* = 8.2 Hz, 2H), 5.03 (d, *J* = 4.2 Hz, 1H), 4.35 (s, 1H), 3.57 (s, 1H), 3.22 – 3.10 (m, 4H), 3.03 – 2.85 (m, 4H), 2.79 – 2.72 (m, 1H), 2.25 (s, 1H), 1.35 (s, 9H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.3, 154.3, 142.1, 140.8, 139.6, 138.6, 129.7, 128.9, 128.5, 127.8, 127.4, 127.3, 127.0, 126.2, 80.3, 74.4, 50.6, 45.4, 41.4, 33.4, 28.4 ppm. **HRMS** (ESI) for $C_{31}H_{37}N_2O_4^+$ [(M+H)$^+$]: calculated 501.2748, found 501.2733. **Melting point:** 79.2 – 80.5 °C.

Another isomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.49 (m, 4H), 7.44 – 7.41 (m, 2H), 7.36 – 7.30 (m, 5H), 7.27 – 7.22 (m, 3H), 5.09 (d, *J* = 8.6 Hz, 1H), 4.95 (dd, *J* = 8.5, 3.5 Hz, 1H), 3.48 – 3.42 (m, 1H), 3.31 – 3.22 (m, 3H), 3.16 – 3.03 (m, 2H), 2.94 (s, 1H), 2.77 – 2.66 (m, 3H), 2.45 – 2.39 (m, 1H), 1.36 (s, 9H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.0, 154.3,

143.5, 140.8, 139.8, 138.1, 129.5, 128.9, 128.6, 127.7, 127.4 (2C), 127.1, 125.6, 80.3, 75.3, 49.8, 45.5, 41.4, 37.2, 28.4 ppm. **HRMS** (ESI) for $C_{31}H_{37}N_2O_4^+$ [(M+H)$^+$]: calculated 501.2748, found 501.2733. **Melting point:** 136.7 – 137.7 °C.

2-([1,1'-Biphenyl]-4-ylmethyl)-3-hydroxy-*N,N*,3-triphenylpropanamide (25)



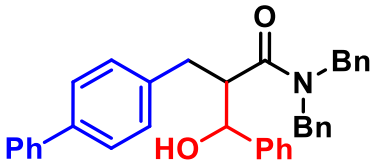
Chemical Formula: $C_{34}H_{29}NO_2$
Exact Mass: 483.2198

Prepared according to the general procedure using **1a** (168 mg, 0.60 mmol, 2.0 equiv), **2j** (134 mg, 0.60 mmol, 2.0 equiv), **3a** (32 mg, 0.30 mmol, 1.0 equiv), *fac*-Ir(ppy)$_3$ (2.0 mg, 3.0 μmol, 0.010 equiv), Ligand (6.5 mg, 30 μmol, 0.10 equiv), $NiBr_2$•DME (9.3 mg, 30 μmol, 0.10 equiv), DMAc (0.10 M, 3.0 mL), reductant (103 mg, 0.60 mmol, 2.0 equiv), tetrabutylammonium fluoride (157 mg, 0.6 mmol, 2.0 equiv), THF (0.10 M, 3.0 mL). The residue was purified by flash column chromatography (PE/EA = 50:1 to PE/EA = 4:1) to give the product **25** (70 mg, 48% yield, *dr* = 1:1.3) as a white solid.

Note: these two diastereoisomers cannot be separated by column chromatography

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.7 Hz, 4H), 7.58 – 7.53 (m, 4H), 7.48 – 7.41 (m, 6H), 7.39 – 7.34 (m, 6H), 7.32 – 7.31 (m, 2H), 7.29 – 7.23 (m, 8H), 7.22 – 7.12 (m, 8H), 7.04 – 7.00 (m, 2H), 6.98 – 6.94 (m, 4H), 6.19 (s, 2H), 5.88 (d, *J* = 7.9 Hz, 2H), 5.26 (d, *J* = 8.9 Hz, 1H), 5.16 (d, *J* = 5.0 Hz, 1H), 4.81 (dd, *J* = 9.0, 3.5 Hz, 1H), 3.86 (d, *J* = 1.6 Hz, 1H), 3.42 (dd, *J* = 13.0, 9.6 Hz, 1H), 3.25 – 3.19 (m, 1H), 3.05 – 3.02 (m, 1H), 3.02 – 2.99 (m, 1H), 2.98 – 2.93 (m, 1H), 2.83 (dd, *J* = 12.8, 3.3 Hz, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.8 (2C), 143.7 (2C), 142.2, 142.0, 141.9, 141.5, 141.1, 141.0, 139.9, 139.6, 138.8, 138.2, 130.3, 130.1, 129.4, 129.2, 129.1, 129.0, 128.8, 128.7, 128.5 (2C), 128.1 (2C), 127.8, 127.7, 127.4 (2C), 127.3, 127.2, 127.1 (3C), 126.8, 126.6 (2C), 126.3, 126.2, 75.5, 74.2, 52.3, 51.1, 37.6, 33.4 ppm. **HRMS** (ESI) for $C_{34}H_{30}NO_2^+$ [(M+H)$^+$]: calculated 484.2271, found 484.2248. **Melting point:** 143.4 – 145.5 °C.

2-([1,1'-Biphenyl]-4-ylmethyl)-*N,N*-dibenzyl-3-hydroxy-3-phenylpropanamide (26)



Chemical Formula: $C_{36}H_{33}NO_2$
Exact Mass: 511.2511

Prepared according to the general procedure using **1a** (168 mg, 0.60 mmol, 2.0 equiv), **2k** (151 mg, 0.60 mmol, 2.0 equiv), **3a** (32 mg, 0.30 mmol, 1.0 equiv), *fac*-Ir(ppy)$_3$ (2.0 mg, 3.0 μmol, 0.010 equiv), Ligand (6.5 mg, 30 μmol, 0.10 equiv), $NiBr_2$•DME (9.3 mg, 30 μmol, 0.10 equiv), DMAc (0.10 M, 3.0 mL), reductant (103 mg, 0.60 mmol, 2.0 equiv), tetrabutylammonium fluoride (157 mg, 0.6 mmol, 2.0 equiv), THF (0.10 M, 3.0 mL). The residue was purified by flash column chromatography (PE/EA = 50:1 to PE/EA = 4:1) to give the product **26** (78 mg, 51% yield, *dr* = 1:1.4) as a white solid.

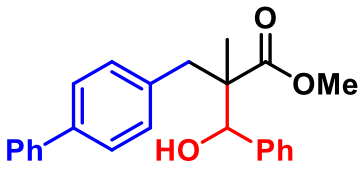
One isomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.52 (m, 2H), 7.46 – 7.42 (m, 2H), 7.38 – 7.21 (m, 12H), 7.05 (d, *J* = 8.2 Hz, 2H), 7.02 – 6.98 (m, 4H), 6.93 – 6.91 (m, 2H), 5.16 (d, *J* = 14.6 Hz, 1H), 4.94 (d, *J* = 2.8 Hz, 1H), 4.90 (s, 1H), 4.05 (d, *J* = 14.6 Hz, 1H), 3.86 (s, 2H), 3.22 – 3.07 (m, 2H), 2.71 (dd, *J* = 12.8, 3.0 Hz, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.9, 141.5, 140.8, 139.4, 138.6, 136.9, 136.5, 129.8, 129.3, 128.9, 128.7, 128.6, 128.4, 127.9, 127.6, 127.4, 127.2, 127.0, 126.3, 125.9, 73.8, 50.5, 50.0, 49.6, 31.9 ppm. **HRMS** (ESI) for $C_{36}H_{34}NO_2^+$ [$(M+H)^+$]: calculated 512.2584, found 512.2574. **Melting point:** 114.3 – 115.5 °C.

Another isomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.54 (m, 2H), 7.46 – 7.39 (m, 4H), 7.37 – 7.33 (m, 1H), 7.29 – 7.10 (m, 13H), 6.98 – 6.95 (m, 2H), 6.58 – 6.56 (m, 2H), 5.35 (d, *J* = 8.7 Hz, 1H), 4.88 (dd, *J* = 8.6, 3.6 Hz, 1H), 4.45 – 4.37 (m, 2H), 3.90 – 3.77 (m, 2H), 3.27 – 3.11 (m, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.5, 143.6, 140.9, 139.6, 137.9, 136.4, 136.0, 129.9, 129.0, 128.9, 128.7 (2C), 128.6, 127.7, 127.6, 127.4, 127.1, 126.7, 126.0, 74.7, 50.2, 49.7, 48.3, 37.1 ppm. **HRMS** (ESI) for $C_{36}H_{34}NO_2^+$ [$(M+H)^+$]: calculated 512.2584, found 512.2560. **Melting point:** 140.8 – 141.8 °C.

Methyl 2-([1,1'-biphenyl]-4-ylmethyl)-3-hydroxy-2-methyl-3-phenylpropanoate (27)



Chemical Formula: $C_{24}H_{24}O_3$
Exact Mass: 360.1725

Prepared according to the general procedure using **1a** (168 mg, 0.60 mmol, 2.0 equiv), **2l** (60 mg, 0.60 mmol, 2.0 equiv), **3a** (32 mg, 0.30 mmol, 1.0 equiv), *fac*-Ir(ppy)$_3$ (2.0 mg, 3.0 μmol, 0.010 equiv), Ligand (6.5 mg, 30 μmol, 0.10 equiv), $NiBr_2$•DME (9.3 mg, 30 μmol, 0.10 equiv), DMAc (0.10 M, 3.0 mL), reductant (103 mg, 0.60 mmol, 2.0 equiv), tetrabutylammonium fluoride (157 mg, 0.6 mmol, 2.0 equiv), THF (0.10 M, 3.0 mL). The residue was purified by flash column chromatography (PE/EA = 50:1 to PE/EA = 6:1) to give the product **27** (40 mg, 37% yield, *dr* = 1:1.1) as a white solid.

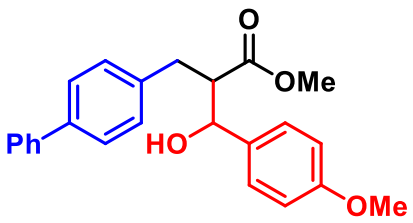
One isomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.56 (m, 2H), 7.49 – 7.40 (m, 4H), 7.40 – 7.30 (m, 6H), 7.16 (d, *J* = 8.3 Hz, 2H), 5.06 (d, *J* = 2.6 Hz, 1H), 3.56 (s, 3H), 3.47 (d, *J* = 13.2 Hz, 1H), 3.10 (d, *J* = 2.8 Hz, 1H), 2.84 (d, *J* = 13.1 Hz, 1H), 1.07 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.3, 141.0, 140.2, 139.5, 136.8, 130.8, 128.9, 128.1 (2C), 127.8, 127.3, 127.1, 126.9, 78.5, 53.6, 51.8, 40.8, 16.2 ppm. **HRMS** (ESI) for $C_{24}H_{24}NaO_3^+$ [$(M+Na)^+$]: calculated 383.1618, found 383.1603. **Melting point:** 98.7 – 99.7 °C.

Another isomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.56 (m, 2H), 7.50 – 7.41 (m, 4H), 7.38 – 7.29 (m, 6H), 7.17 (d, *J* = 8.3 Hz, 2H), 4.88 (d, *J* = 6.5 Hz, 1H), 3.66 (s, 3H), 3.33 (d, *J* = 6.5 Hz, 1H), 3.30 (d, *J* = 13.1 Hz, 1H), 2.64 (d, *J* = 13.0 Hz, 1H), 1.03 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.9, 141.0, 140.5, 139.7, 136.0, 130.7, 128.9, 128.2 (2C), 127.8, 127.3, 127.1, 126.9, 79.5, 53.2, 52.1, 43.0, 16.5 ppm. **HRMS** (ESI) for $C_{24}H_{24}NaO_3^+$ [$(M+Na)^+$]: calculated 383.1618, found 383.1606. **Melting point:** 94.8 – 95.8 °C.

Methyl 2-([1,1'-biphenyl]-4-ylmethyl)-3-hydroxy-3-(4-methoxyphenyl)propanoate (28)



Chemical Formula: $C_{24}H_{24}O_4$
Exact Mass: 376.1675

Prepared according to the general procedure using **1a** (168 mg, 0.60 mmol, 2.0 equiv), **2a** (52 mg, 0.60 mmol, 2.0 equiv), **3b** (41 mg, 0.30 mmol, 1.0 equiv), *fac*-Ir(ppy)$_3$ (2.0 mg, 3.0 μmol, 0.010 equiv), Ligand (6.5 mg, 30 μmol, 0.10 equiv), $NiBr_2$•DME (9.3 mg, 30 μmol, 0.10 equiv), DMAc (0.10 M, 3.0 mL), reductant (103 mg, 0.60 mmol, 2.0 equiv), tetrabutylammonium fluoride (157 mg, 0.6 mmol, 2.0 equiv), THF (0.10 M, 3.0 mL). The residue was purified by flash column chromatography (PE/EA = 50:1 to PE/EA = 6:1) to give the product **28** (51 mg, 45% yield, *dr* = 1:1.5) as a white solid.

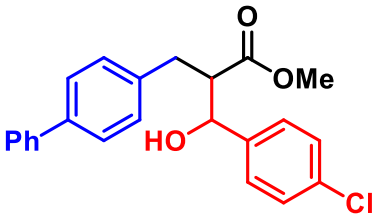
One isomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.55 (m, 2H), 7.48 – 7.46 (m, 2H), 7.43 – 7.39 (m, 2H), 7.34 – 7.30 (m, 3H), 7.18 – 7.15 (m, 2H), 6.91 – 6.88 (m, 2H), 4.99 (q, *J* = 3.1 Hz, 1H), 3.81 (s, 3H), 3.43 (s, 3H), 3.05 (q, *J* = 2.0 Hz, 3H), 2.74 (d, *J* = 2.9 Hz, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.6, 159.4, 141.0, 139.3, 138.4, 133.6, 129.3, 128.9, 127.5, 127.2 (2C), 127.1, 114.0, 74.0, 55.5, 55.4, 51.7, 33.3 ppm. **HRMS** (ESI) for $C_{24}H_{24}NaO_4^+$ [(M+Na)$^+$]: calculated 399.1567, found 399.1539. **Melting point:** 105.0 – 106.0 °C.

Another isomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.55 (m, 2H), 7.49 – 7.46 (m, 2H), 7.43 – 7.39 (m, 2H), 7.34 – 7.27 (m, 3H), 7.17 – 7.14 (m, 2H), 6.92 – 6.88 (m, 2H), 4.80 (dd, *J* = 7.4, 4.2 Hz, 1H), 3.80 (s, 3H), 3.56 (s, 3H), 3.10 – 3.05 (m, 1H), 2.92 – 2.87 (m, 2H), 2.70 (dd, *J* = 13.6, 5.4 Hz, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.2, 159.5, 140.9, 139.5, 137.7, 134.1, 129.3, 128.9, 127.7, 127.3, 127.2, 127.1, 114.1, 74.7, 55.4, 55.2, 51.9, 35.5 ppm. **HRMS** (ESI) for $C_{24}H_{24}NaO_4^+$ [(M+Na)$^+$]: calculated 399.1567, found 399.1545. **Melting point:** 126.6 – 127.6 °C.

Methyl 2-([1,1'-biphenyl]-4-ylmethyl)-3-(4-chlorophenyl)-3-hydroxypropanoate (29)



Chemical Formula: $C_{23}H_{21}ClO_3$
Exact Mass: 380.1179

Prepared according to the general procedure using **1a** (168 mg, 0.60 mmol, 2.0 equiv), **2a** (52 mg, 0.60 mmol, 2.0 equiv), **3c** (42 mg, 0.30 mmol, 1.0 equiv), *fac*-Ir(ppy)$_3$ (2.0 mg, 3.0 μmol, 0.010 equiv), Ligand (6.5 mg, 30 μmol, 0.10 equiv), $NiBr_2$•DME (9.3 mg, 30 μmol, 0.10 equiv), DMAc (0.10 M, 3.0 mL), reductant (103 mg, 0.60 mmol, 2.0 equiv), tetrabutylammonium fluoride (157 mg, 0.6 mmol, 2.0 equiv), THF (0.10 M, 3.0 mL). The residue was purified by flash column chromatography (PE/EA = 50:1 to PE/EA = 6:1) to give the product **29** (66 mg, 58% yield, *dr* = 1:1.3) as a white solid.

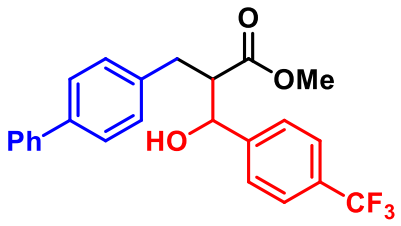
One isomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.54 (m, 2H), 7.48 – 7.40 (m, 4H), 7.34 – 7.30 (m, 5H), 7.14 – 7.12 (m, 2H), 5.07 – 5.00 (m, 1H), 3.47 (s, 3H), 3.08 – 2.94 (m, 4H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 174.6, 141.0, 139.9, 139.4, 138.0, 133.8, 129.3, 128.9, 128.8, 127.7, 127.3, 127.2, 127.1, 73.5, 55.1, 51.9, 32.9 ppm. **HRMS** (ESI) for $C_{23}H_{21}ClNaO_3^+$ [(M+Na)$^+$]: calculated 403.1071, found 403.1060. **Melting point:** 84.2 – 85.2 °C.

Another isomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.55 (m, 2H), 7.52 – 7.49 (m, 2H), 7.45 – 7.41 (m, 2H), 7.35 – 7.27 (m, 5H), 7.21 – 7.18 (m, 2H), 4.81 (t, *J* = 6.5 Hz, 1H), 3.55 (s, 3H), 3.21 (d, *J* = 6.9 Hz, 1H), 3.09 – 2.94 (m, 2H), 2.82 (dd, *J* = 13.3, 6.3 Hz, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.0, 140.9, 140.6, 139.7, 137.3, 133.9, 129.4, 128.9 (2C), 127.7, 127.4, 127.1, 73.8, 54.7, 52.0, 35.4 ppm. **HRMS** (ESI) for $C_{23}H_{21}ClNaO_3^+$ [(M+Na)$^+$]: calculated 403.1071, found 403.1084. **Melting point:** 126.6 – 127.6 °C.

Methyl 2-([1,1'-biphenyl]-4-ylmethyl)-3-hydroxy-3-(4-(trifluoromethyl)phenyl) propanoate (30)



Chemical Formula: $C_{24}H_{21}F_3O_3$
Exact Mass: 414.1443

Prepared according to the general procedure using **1a** (168 mg, 0.60 mmol, 2.0 equiv), **2a** (52 mg, 0.60 mmol, 2.0 equiv), **3d** (52 mg, 0.30 mmol, 1.0 equiv), *fac*-Ir(ppy)$_3$ (2.0 mg, 3.0 μmol, 0.010 equiv), Ligand (6.5 mg, 30 μmol, 0.10 equiv), $NiBr_2$•DME (9.3 mg, 30 μmol, 0.10 equiv), DMAc (0.10 M, 3.0 mL), reductant (103 mg, 0.60 mmol, 2.0 equiv), tetrabutylammonium fluoride (157 mg, 0.6 mmol, 2.0 equiv), THF (0.10 M, 3.0 mL). The residue was purified by flash column chromatography (PE/EA = 50:1 to PE/EA = 6:1) to give the product **30** (65 mg, 52% yield, *dr* = 1:1.1) as a white solid.

One isomer

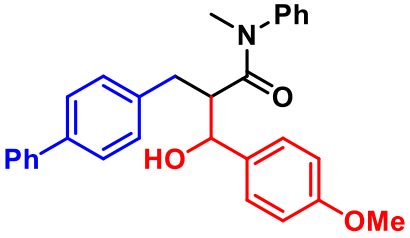
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.57 – 7.53 (m, 4H), 7.48 – 7.40 (m, 4H), 7.35 – 7.30 (m, 1H), 7.12 (d, *J* = 8.3 Hz, 2H), 5.15 (t, *J* = 3.3 Hz, 1H), 3.49 (s, 3H), 3.14 (d, *J* = 2.8 Hz, 1H), 3.11 – 3.04 (m, 2H), 2.94 – 2.87 (m, 1H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 174.7, 145.3, 140.9, 139.5, 137.8, 130.5 (q, J_{C-F} = 33.2 Hz), 129.3, 128.9, 127.3, 127.2, 127.1, 126.9 (q, J_{C-F} = 271.8 Hz), 126.7, 125.6 (q, J_{C-F} = 3.0 Hz), 73.4, 54.8, 51.9, 32.6 ppm. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.49 ppm. **HRMS** (ESI) for $C_{24}H_{22}F_3O_3^+$ [(M+H)$^+$]: calculated 415.1516, found 415.1505. **Melting point:** 79.8 – 80.8 °C.

Another isomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.56 (m, 4H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.47 – 7.41 (m, 4H), 7.36 – 7.32 (m, 1H), 7.23 (d, *J* = 8.3 Hz, 2H), 4.88 (t, *J* = 6.5 Hz, 1H), 3.55 (s, 3H), 3.44 (d, *J* = 7.3 Hz, 1H), 3.14 – 3.00 (m, 2H), 2.89 (dd, *J* = 13.3, 6.7 Hz, 1H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 174.9, 146.2, 140.8, 139.8, 137.1, 130.6 (q, J_{C-F} = 31.7 Hz), 129.4, 128.9, 127.4, 127.1, 126.9 (q, J_{C-F} = 271.8 Hz), 126.6, 125.7 (q, J_{C-F} = 3.0 Hz), 73.6, 54.4, 52.0, 35.4 ppm. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.51 ppm. **HRMS** (ESI)

for $C_{24}H_{21}F_3NaO_3^+$ [(M+Na)$^+$]: calculated 437.1335, found 437.1309. **Melting point:** 102.7 – 103.7 °C.

2-([1,1'-Biphenyl]-4-ylmethyl)-3-hydroxy-3-(4-methoxyphenyl)-*N*-methyl-*N*-phenylpropanamide (31)



Chemical Formula: $C_{30}H_{29}NO_3$
Exact Mass: 451.2147

Prepared according to the general procedure using **1a** (168 mg, 0.60 mmol, 2.0 equiv), **2b** (97 mg, 0.60 mmol, 2.0 equiv), **3b** (41 mg, 0.30 mmol, 1.0 equiv), *fac*-Ir(ppy)$_3$ (2.0 mg, 3.0 μmol, 0.010 equiv), Ligand (6.5 mg, 30 μmol, 0.10 equiv), $NiBr_2$•DME (9.3 mg, 30 μmol, 0.10 equiv), DMAc (0.10 M, 3.0 mL), reductant (103 mg, 0.60 mmol, 2.0 equiv), tetrabutylammonium fluoride (157 mg, 0.6 mmol, 2.0 equiv), THF (0.10 M, 3.0 mL). The residue was purified by flash column chromatography (PE/EA = 50:1 to PE/EA = 4:1) to give the product **31** (79 mg, 58% yield, *dr* = 1:1.2) as a white solid.

One isomer

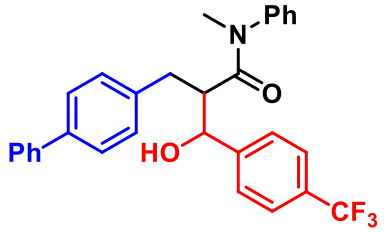
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.60 (m, 2H), 7.47 – 7.43 (m, 4H), 7.37 – 7.33 (m, 1H), 7.22 – 7.12 (m, 5H), 6.99 (d, *J* = 8.3 Hz, 2H), 6.87 – 6.83 (m, 2H), 5.00 (d, *J* = 4.4 Hz, 1H), 4.10 (s, 1H), 3.80 (s, 3H), 3.12 (d, *J* = 12.8 Hz, 1H), 3.07 (s, 3H), 2.79 – 2.75 (m, 1H), 2.67 (dd, *J* = 12.8, 3.3 Hz, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.7, 158.9, 142.9, 141.1, 139.3, 139.0, 134.0, 129.9, 129.4, 128.9, 127.9, 127.4, 127.3, 127.1, 127.0 (2C), 113.7, 73.6, 55.4, 51.9, 37.2, 32.7 ppm. **HRMS** (ESI) for $C_{30}H_{29}NNaO_3^+$ [(M+Na)$^+$]: calculated 474.2040, found 474.2014. **Melting point:** 166.5 – 167.8 °C.

Another isomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.59 (m, 2H), 7.50 – 7.43 (m, 4H), 7.37 – 7.33 (m, 1H), 7.19 – 7.15 (m, 1H), 7.12 – 7.03 (m, 6H), 6.89 – 6.87 (m, 2H), 5.88 – 5.85 (m, 2H),

5.15 (d, *J* = 8.4 Hz, 1H), 4.69 (dd, *J* = 8.4, 3.9 Hz, 1H), 3.83 (s, 3H), 3.23 (dd, *J* = 13.0, 9.7 Hz, 1H), 3.03 (s, 3H), 2.87 (dd, *J* = 13.2, 5.6 Hz, 1H), 2.77 – 2.72 (m, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.4, 159.1, 142.6, 141.0, 139.6, 138.4, 136.0, 129.8, 129.2, 128.9, 127.8, 127.4 (2C), 127.2 (2C), 127.1, 113.8, 75.0, 55.5, 51.0, 37.3, 37.0 ppm. **HRMS** (ESI) for $C_{30}H_{29}NNaO_3^+$ [(M+Na)$^+$]: calculated 474.2040, found 474.2012. **Melting point:** 164.2 – 165.2 °C.

2-([1,1'-Biphenyl]-4-ylmethyl)-3-hydroxy-*N*-methyl-*N*-phenyl-3-(4-(trifluoromethyl) phenyl)propenamide (32)



Chemical Formula: $C_{30}H_{26}F_3NO_2$
Exact Mass: 489.1916

Prepared according to the general procedure using **1a** (168 mg, 0.60 mmol, 2.0 equiv), **2b** (97 mg, 0.60 mmol, 2.0 equiv), **3d** (52 mg, 0.30 mmol, 1.0 equiv), *fac*-Ir(ppy)$_3$ (2.0 mg, 3.0 μmol, 0.010 equiv), Ligand (6.5 mg, 30 μmol, 0.10 equiv), $NiBr_2$•DME (9.3 mg, 30 μmol, 0.10 equiv), DMAc (0.10 M, 3.0 mL), reductant (103 mg, 0.60 mmol, 2.0 equiv), tetrabutylammonium fluoride (157 mg, 0.6 mmol, 2.0 equiv), THF (0.10 M, 3.0 mL). The residue was purified by flash column chromatography (PE/EA = 50:1 to PE/EA = 4:1) to give the product **32** (109 mg, 74% yield, *dr* = 1:1) as a white solid.

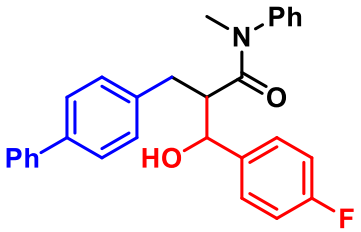
One isomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.56 (m, 4H), 7.48 – 7.44 (m, 4H), 7.38 – 7.31 (m, 3H), 7.27 – 7.16 (m, 3H), 6.95 (d, *J* = 8.3 Hz, 2H), 5.09 (d, *J* = 3.9 Hz, 1H), 4.48 (s, 1H), 3.16 – 3.09 (m, 4H), 2.84 – 2.79 (m, 1H), 2.51 (dd, *J* = 13.0, 3.3 Hz, 1H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 174.4, 146.0, 142.7, 141.0, 139.5, 138.4, 130.0 (q, J_{C-F} = 31.7 Hz), 129.9, 129.6, 129.0, 128.2, 127.4, 127.2, 127.1, 127.0, 126.9 (q, J_{C-F} = 271.8 Hz), 126.3, 125.3 (q, J_{C-F} = 3.0 Hz), 73.4, 51.3, 37.2, 32.5 ppm. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.39 ppm. **HRMS** (ESI) for $C_{30}H_{27}F_3NO_2^+$ [(M+H)$^+$]: calculated 490.1988, found 490.1977. **Melting point:** 149.8 – 150.8 °C.

Another isomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.58 (m, 4H), 7.53 (d, *J* = 8.3 Hz, 2H), 7.47 – 7.43 (m, 2H), 7.37 – 7.34 (m, 1H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.21 – 7.17 (m, 1H), 7.14 (d, *J* = 8.3 Hz, 2H), 7.07 – 7.03 (m, 2H), 5.77 (s, 2H), 5.66 (d, *J* = 8.9 Hz, 1H), 4.75 (dd, *J* = 9.0, 3.2 Hz, 1H), 3.30 (dd, *J* = 13.2, 8.9 Hz, 1H), 3.03 – 2.99 (m, 4H), 2.77 – 2.73 (m, 1H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 174.0, 148.1, 142.2, 140.9, 139.9, 137.8, 130.1 (q, $J_{C\text{-}F}$ = 31.7 Hz), 129.8, 129.4, 129.0, 128.1, 127.4, 127.3, 127.1, 127.0, 126.3, 125.4 (q, $J_{C\text{-}F}$ = 3.0 Hz), 125.2 (q, $J_{C\text{-}F}$ = 271.8 Hz), 74.5, 50.4, 37.3, 37.0 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.29 ppm. **HRMS** (ESI) for $C_{30}H_{27}F_3NO_2^+$ [(M+H)$^+$]: calculated 490.1988, found 490.1973. **Melting point:** 126.6 – 127.6 °C.

2-([1,1'-Biphenyl]-4-ylmethyl)-3-(4-fluorophenyl)-3-hydroxy-*N*-methyl-*N*-phenyl-propanamide (33)



Chemical Formula: $C_{29}H_{26}FNO_2$
Exact Mass: 439.1948

Prepared according to the general procedure using **1a** (168 mg, 0.60 mmol, 2.0 equiv), **2b** (97 mg, 0.60 mmol, 2.0 equiv), **3e** (37 mg, 0.30 mmol, 1.0 equiv), *fac*-Ir(ppy)$_3$ (2.0 mg, 3.0 μmol, 0.010 equiv), Ligand (6.5 mg, 30 μmol, 0.10 equiv), $NiBr_2$•DME (9.3 mg, 30 μmol, 0.10 equiv), DMAc (0.10 M, 3.0 mL), reductant (103 mg, 0.60 mmol, 2.0 equiv), tetrabutylammonium fluoride (157 mg, 0.6 mmol, 2.0 equiv), THF (0.10 M, 3.0 mL). The residue was purified by flash column chromatography (PE/EA = 50:1 to PE/EA = 4:1) to give the product **33** (74 mg, 56% yield, *dr* = 1:1.8) as a white solid.

One isomer

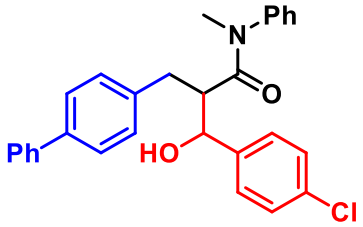
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.2 Hz, 2H), 7.48 – 7.45 (m, 4H), 7.37 – 7.35 (m, 1H), 7.24 – 7.18 (m, 5H), 7.03 – 6.97 (m, 4H), 5.03 (d, *J* = 4.1 Hz, 1H), 4.21 (s, 1H), 3.13 – 3.10 (m, 4H), 2.79 – 2.76 (m, 1H), 2.61 (dd, *J* = 13.1, 3.3 Hz, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.6, 163.4 (d, $J_{C\text{-}F}$ = 246.4 Hz), 142.8, 141.1, 139.4, 138.7,

137.6 (d, $J_{C\text{-}F}$ = 3.0 Hz), 129.9, 129.5, 129.0, 128.1, 127.6 (d, $J_{C\text{-}F}$ = 8.1 Hz), 127.4, 127.3, 127.1 (2C), 115.3 (d, $J_{C\text{-}F}$ = 21.2 Hz), 73.4, 51.7, 37.2, 32.6 ppm. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -115.28 ppm. **HRMS** (ESI) for $C_{29}H_{27}FNO_2^+$ [$(M+H)^+$]: calculated 440.2020, found 440.2009. **Melting point:** 182.4 – 183.4 °C.

Another isomer

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.1 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.46 – 7.43 (m, 2H), 7.36 – 7.33 (m, 1H), 7.20 – 7.17 (m, 1H), 7.15 – 7.12 (m, 2H), 7.11 – 7.01 (m, 6H), 5.87 (d, *J* = 7.2 Hz, 2H), 5.41 (d, *J* = 8.7 Hz, 1H), 4.69 (dd, *J* = 8.7, 3.6 Hz, 1H), 3.25 (dd, *J* = 13.2, 9.3 Hz, 1H), 3.03 (s, 3H), 2.93 (dd, *J* = 13.2, 6.1 Hz, 1H), 2.75 – 2.72 (m, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.2, 163.5 (d, $J_{C\text{-}F}$ = 246.4 Hz), 142.4, 140.9, 139.7, 139.6 (d, $J_{C\text{-}F}$ = 3.0 Hz), 138.1, 129.8, 129.3, 129.0, 128.0, 127.6 (d, $J_{C\text{-}F}$ = 8.1 Hz), 127.4, 127.3, 127.2, 127.1, 115.3 (d, $J_{C\text{-}F}$ = 22.2 Hz), 74.5, 50.7, 37.2, 37.0 ppm. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -115.30 ppm. **HRMS** (ESI) for $C_{29}H_{27}FNO_2^+$ [$(M+H)^+$]: calculated 440.2020, found 440.2008. **Melting point:** 156.3 – 157.4 °C.

2-([1,1'-Biphenyl]-4-ylmethyl)-3-(4-chlorophenyl)-3-hydroxy-*N*-methyl-*N*-phenylpropanamide (34)



Chemical Formula: $C_{29}H_{26}ClNO_2$
Exact Mass: 455.1652

Prepared according to the general procedure using **1a** (168 mg, 0.60 mmol, 2.0 equiv), **2b** (97 mg, 0.60 mmol, 2.0 equiv), **3c** (42 mg, 0.30 mmol, 1.0 equiv), *fac*-Ir(ppy)$_3$ (2.0 mg, 3.0 μmol, 0.010 equiv), Ligand (6.5 mg, 30 μmol, 0.10 equiv), $NiBr_2$•DME (9.3 mg, 30 μmol, 0.10 equiv), DMAc (0.10 M, 3.0 mL), reductant (103 mg, 0.60 mmol, 2.0 equiv), tetrabutylammonium fluoride (157 mg, 0.6 mmol, 2.0 equiv), THF (0.10 M, 3.0 mL). The residue was purified by flash column chromatography (PE/EA = 50:1 to PE/EA = 4:1) to give the product **34** (105 mg, 77% yield, *dr* = 1:1.5) as a white solid.

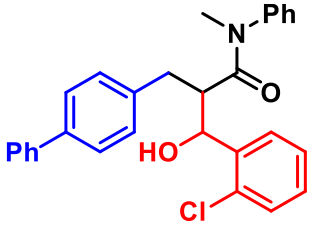
One isomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.59 (m, 2H), 7.47 – 7.44 (m, 4H), 7.37 – 7.34 (m, 1H), 7.30 – 7.28 (m, 2H), 7.25 – 7.13 (m, 5H), 6.97 – 6.95 (m, 2H), 5.01 (d, *J* = 3.9 Hz, 1H), 4.33 (d, *J* = 1.3 Hz, 1H), 3.13 – 3.07 (m, 4H), 2.78 – 2.74 (m, 1H), 2.56 (dd, *J* = 13.0, 3.3 Hz, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.6, 142.8, 141.0, 140.4, 139.5, 138.6, 133.1, 129.9, 129.5, 129.0, 128.5, 128.1, 127.4, 127.1 (2C), 73.3, 51.4, 37.2, 32.4 ppm. **HRMS** (ESI) for $C_{29}H_{27}ClNO_2^+$ [(M+H)$^+$]: calculated 456.1725, found 456.1711. **Melting point:** 181.6 – 182.6 °C.

Another isomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.59 (m, 2H), 7.52 – 7.43 (m, 4H), 7.37 – 7.29 (m, 3H), 7.22 – 7.17 (m, 1H), 7.11 – 7.06 (m, 6H), 5.87 (d, *J* = 7.9 Hz, 2H), 5.48 (d, *J* = 8.8 Hz, 1H), 4.67 (dd, *J* = 8.8, 3.4 Hz, 1H), 3.25 (dd, *J* = 13.2, 9.1 Hz, 1H), 3.03 (s, 3H), 2.95 (dd, *J* = 13.2, 6.2 Hz, 1H), 2.75 – 2.70 (m, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.1, 142.4 (2C), 140.9, 139.8, 138.0, 133.2, 129.8, 129.3, 129.0, 128.5, 128.1, 127.4, 127.3, 127.2, 127.1, 74.4, 50.5, 37.2, 37.0 ppm. **HRMS** (ESI) for $C_{29}H_{26}ClNNaO_2^+$ [(M+Na)$^+$]: calculated 478.1544, found 478.1524. **Melting point:** 168.9 – 169.9 °C.

2-([1,1'-Biphenyl]-4-ylmethyl)-3-(2-chlorophenyl)-3-hydroxy-*N*-methyl-*N*-phenylpropanamide (35)



Chemical Formula: $C_{29}H_{26}ClNO_2$
Exact Mass: 455.1652

Prepared according to the general procedure using **1a** (168 mg, 0.60 mmol, 2.0 equiv), **2b** (97 mg, 0.60 mmol, 2.0 equiv), **3f** (42 mg, 0.30 mmol, 1.0 equiv), *fac*-Ir(ppy)$_3$ (2.0 mg, 3.0 μmol, 0.010 equiv), Ligand (6.5 mg, 30 μmol, 0.10 equiv), $NiBr_2$•DME (9.3 mg, 30 μmol, 0.10 equiv), DMAc (0.10 M, 3.0 mL), reductant (103 mg, 0.60 mmol, 2.0 equiv), tetrabutylammonium fluoride (157 mg, 0.6 mmol, 2.0 equiv), THF (0.10 M, 3.0 mL).

The residue was purified by flash column chromatography (PE/EA = 50:1 to PE/EA = 4:1) to give the product **35** (75 mg, 55% yield, *dr* = 1:1.4) as a white solid.

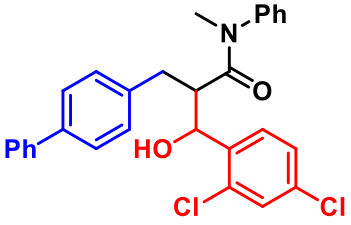
One isomer

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.8 Hz, 1H), 7.59 (d, *J* = 7.2 Hz, 2H), 7.46 – 7.43 (m, 4H), 7.36 – 7.33 (m, 1H), 7.29 – 7.16 (m, 6H), 6.90 (d, *J* = 8.2 Hz, 2H), 5.47 (s, 1H), 5.31 (s, 1H), 3.18 (s, 3H), 3.16 – 3.10 (m, 2H), 2.38 (dd, *J* = 12.4, 2.9 Hz, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.9, 142.3, 141.0, 139.4, 138.5, 138.2, 131.2, 130.0, 129.4 (2C), 129.3, 129.0, 128.6, 128.0, 127.7, 127.4, 127.1, 127.0, 126.8, 70.7, 46.4, 37.7, 31.8 ppm. **HRMS** (ESI) for $C_{29}H_{26}ClNNaO_2^+$ [$(M+Na)^+$]: calculated 478.1544, found 478.1516. **Melting point:** 166.1 – 167.1 °C.

Another isomer

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.9 Hz, 2H), 7.56 (d, *J* = 7.5 Hz, 1H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.46 – 7.44 (m, 2H), 7.37 – 7.34 (m, 2H), 7.28 – 7.24 (m, 2H), 7.19 – 7.15 (m, 3H), 7.02 – 6.99 (m, 2H), 5.90 (d, *J* = 9.3 Hz, 1H), 5.02 (dd, *J* = 9.3, 2.6 Hz, 1H), 3.38 (dd, *J* = 13.1, 9.5 Hz, 1H), 3.06 – 2.97 (m, 5H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.4, 142.1, 141.1, 141.0, 139.7, 138.1, 132.1, 129.9, 129.4, 129.3, 129.0, 128.6, 128.0, 127.4 (2C), 127.2, 127.1, 127.0, 126.8, 72.1, 46.7, 37.6, 36.8 ppm. **HRMS** (ESI) for $C_{29}H_{27}ClNO_2^+$ [$(M+H)^+$]: calculated 456.1725, found 456.1698. **Melting point:** 138.6 – 139.6 °C.

2-([1,1'-Biphenyl]-4-ylmethyl)-3-(2,4-dichlorophenyl)-3-hydroxy-*N*-methyl-*N*-phenylpropanamide (36)



Chemical Formula: $C_{29}H_{25}Cl_2NO_2$
Exact Mass: 489.1262

Prepared according to the general procedure using **1a** (168 mg, 0.60 mmol, 2.0 equiv), **2b** (97 mg, 0.60 mmol, 2.0 equiv), **3g** (52 mg, 0.30 mmol, 1.0 equiv), *fac*-$Ir(ppy)_3$ (2.0 mg, 3.0 μmol, 0.010 equiv), Ligand (6.5 mg, 30 μmol, 0.10 equiv), $NiBr_2$•DME (9.3 mg,

30 μmol, 0.10 equiv), DMAc (0.10 M, 3.0 mL), reductant (103 mg, 0.60 mmol, 2.0 equiv), tetrabutylammonium fluoride (157 mg, 0.6 mmol, 2.0 equiv), THF (0.10 M, 3.0 mL). The residue was purified by flash column chromatography (PE/EA = 50:1 to PE/EA = 4:1) to give the product **36** (87 mg, 59% yield, *dr* = 1:1.4) as a white solid.

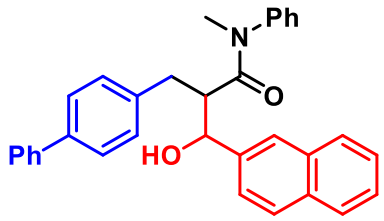
One isomer

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.4 Hz, 1H), 7.60 (d, *J* = 7.1 Hz, 2H), 7.47 – 7.44 (m, 4H), 7.37 – 7.34 (m, 1H), 7.27 – 7.22 (m, 5H), 6.90 (d, *J* = 8.3 Hz, 2H), 5.52 (s, 1H), 5.25 (s, 1H), 3.19 (s, 3H), 3.15 – 3.06 (m, 2H), 2.32 (dd, *J* = 12.7, 3.3 Hz, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.7, 142.3, 141.0, 139.6, 138.2, 136.9, 133.7, 131.8, 130.3, 129.9, 129.5, 129.1, 129.0, 128.2, 127.7, 127.4, 127.1 (2C), 70.4, 46.1, 37.7, 31.7 ppm. **HRMS** (ESI) for $C_{29}H_{26}Cl_2NO_2^+$ [(M+H)$^+$]: calculated 490.1335, found 490.1329. **Melting point:** 112.5 – 113.5 °C.

Another isomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.60 (m, 2H), 7.57 – 7.51 (m,3H), 7.47 – 7.43 (m, 2H), 7.38 – 7.33 (m, 2H), 7.29 – 7.24 (m, 2H), 7.19 – 7.15 (m, 3H), 7.03 – 6.99 (m, 2H), 5.92 (d, *J* = 9.3 Hz, 1H), 5.02 (dd, *J* = 9.3, 2.4 Hz, 1H), 3.38 (dd, *J* = 12.8, 9.4 Hz, 1H), 3.07 – 2.98 (m, 2H), 2.97 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.3, 142.1, 141.0, 139.9, 139.8, 137.8, 133.7, 132.7, 129.9, 129.5, 129.1, 129.0, 128.6, 128.2, 127.4, 127.3, 127.1, 126.8, 71.6, 46.5, 37.5, 36.9 ppm. **HRMS** (ESI) for $C_{29}H_{25}Cl_2NNaO_2^+$ [(M+Na)$^+$]: calculated 512.1155, found 512.1127. **Melting point:** 129.7 – 130.7 °C.

2-([1,1'-Biphenyl]-4-ylmethyl)-3-hydroxy-*N*-methyl-3-(naphthalen-2-yl)-*N*-phenylpropanamide (37)



Chemical Formula: $C_{33}H_{29}NO_2$
Exact Mass: 471.2198

Prepared according to the general procedure using **1a** (168 mg, 0.60 mmol, 2.0 equiv),

2b (97 mg, 0.60 mmol, 2.0 equiv), **3h** (47 mg, 0.30 mmol, 1.0 equiv), *fac*-Ir(ppy)$_3$ (2.0 mg, 3.0 μmol, 0.010 equiv), Ligand (6.5 mg, 30 μmol, 0.10 equiv), $NiBr_2$•DME (9.3 mg, 30 μmol, 0.10 equiv), DMAc (0.10 M, 3.0 mL), reductant (103 mg, 0.60 mmol, 2.0 equiv), tetrabutylammonium fluoride (157 mg, 0.6 mmol, 2.0 equiv), THF (0.10 M, 3.0 mL). The residue was purified by flash column chromatography (PE/EA = 50:1 to PE/EA = 4:1) to give the product **37** (85 mg, 60% yield, *dr* = 1:1.2) as a white solid.

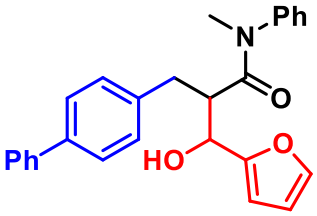
One isomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.75 (m, 4H), 7.60 – 7.58 (m, 2H), 7.49 – 7.42 (m, 6H), 7.36 – 7.32 (m, 1H), 7.24 – 6.94 (m, 6H), 5.20 (d, *J* = 4.0 Hz, 1H), 4.40 (s, 1H), 3.20 – 3.14 (m, 1H), 3.09 (s, 3H), 2.94 – 2.90 (m, 1H), 2.64 (dd, *J* = 13.0, 4.2 Hz, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.8, 142.9, 141.1, 139.3, 139.2, 138.9, 133.4, 132.9, 129.9, 129.4, 128.9, 128.2, 128.0, 127.7, 127.4, 127.3, 127.0, 126.2, 125.9, 125.0, 124.0, 74.0, 51.5, 37.2, 32.6 ppm. **HRMS** (ESI) for $C_{33}H_{29}NNaO_2^+$ [(M+Na)$^+$]: calculated 494.2091, found 494.2068. **Melting point:** 140.2 – 141.2 °C.

Another isomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.79 (m, 3H), 7.65 – 7.59 (m, 3H), 7.51 – 7.41 (m, 6H), 7.35 – 7.25 (m, 2H), 7.14 – 7.08 (m, 3H), 6.88 (s, 2H), 5.66 (s, 2H), 5.52 (d, *J* = 8.6 Hz, 1H), 4.89 (dd, *J* = 8.6, 3.7 Hz, 1H), 3.31 (dd, *J* = 13.0, 9.3 Hz, 1H), 3.00 – 2.95 (m, 4H), 2.91 – 2.86 (m, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.3, 142.3, 141.2, 140.9, 139.6, 138.2, 133.4, 132.9, 129.8, 129.0, 128.9, 128.1, 128.0, 127.8, 127.7, 127.3, 127.2, 127.0, 126.2, 125.9, 124.8, 124.1, 75.2, 50.7, 37.3, 36.9 ppm. **HRMS** (ESI) for $C_{33}H_{29}NNaO_2^+$ [(M+Na)$^+$]: calculated 494.2091, found 494.2072. **Melting point:** 119.4 – 120.4 °C.

2-([1,1'-Biphenyl]-4-ylmethyl)-3-(furan-2-yl)-3-hydroxy-*N*-methyl-*N*-phenylpropanamide (38)



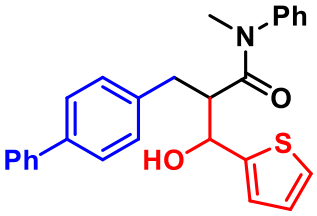
Chemical Formula: $C_{27}H_{25}NO_3$
Exact Mass: 411.1834

Prepared according to the general procedure using **1a** (168 mg, 0.60 mmol, 2.0 equiv), **2b** (97 mg, 0.60 mmol, 2.0 equiv), **3i** (29 mg, 0.30 mmol, 1.0 equiv), *fac*-Ir(ppy)$_3$ (2.0 mg, 3.0 μmol, 0.010 equiv), Ligand (6.5 mg, 30 μmol, 0.10 equiv), $NiBr_2$•DME (9.3 mg, 30 μmol, 0.10 equiv), DMAc (0.10 M, 3.0 mL), reductant (103 mg, 0.60 mmol, 2.0 equiv), tetrabutylammonium fluoride (157 mg, 0.6 mmol, 2.0 equiv), THF (0.10 M, 3.0 mL). The residue was purified by flash column chromatography (PE/EA = 50:1 to PE/EA = 4:1) to give the product **38** (89 mg, 72% yield, *dr* = 1:1) as a white solid.

Note: these two diastereoisomers cannot be separated by column chromatography

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.58 (m, 4H), 7.49 – 7.41 (m, 8H), 7.36 – 7.31 (m, 4H), 7.25 – 7.21 (m, 2H), 7.19 – 7.14 (m, 3H), 7.10 – 7.05 (m, 5H), 6.37 (dd, *J* = 3.3, 1.9 Hz, 1H), 6.35 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.32 (d, *J* = 3.3 Hz, 1H), 6.28 (d, *J* = 3.3 Hz, 1H), 6.22 (s, 2H), 5.06 (d, *J* = 5.3 Hz, 1H), 4.72 (d, *J* = 4.0 Hz, 1H), 3.20 – 3.13 (m, 2H), 3.10 (s, 3H), 3.06 (s, 3H), 3.04 – 2.96 (m, 2H), 2.93 – 2.83 (m, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.4, 173.9, 156.3, 154.3, 142.7, 141.5, 141.3, 141.0, 140.9, 139.5, 139.3, 138.7, 137.8, 129.9, 129.7, 129.3, 129.2, 128.9, 128.8, 127.9, 127.7, 127.3, 127.2 (2C), 127.1, 127.0, 126.9, 110.6, 110.4, 106.8, 106.3, 69.4, 69.3, 49.6, 48.1, 37.2, 37.1, 36.5, 34.0 ppm. **HRMS** (ESI) for $C_{27}H_{26}NO_3^+$ [(M+H)$^+$]: calculated 412.1907, found 412.1893. **Melting point:** 92.7 – 94.4 °C.

2-([1,1'-Biphenyl]-4-ylmethyl)-3-hydroxy-*N*-methyl-*N*-phenyl-3-(thiophen-2-yl)propenamide (39)



Chemical Formula: $C_{27}H_{25}NO_2S$
Exact Mass: 427.1606

Prepared according to the general procedure using **1a** (168 mg, 0.60 mmol, 2.0 equiv), **2b** (97 mg, 0.60 mmol, 2.0 equiv), **3j** (34 mg, 0.30 mmol, 1.0 equiv), *fac*-Ir(ppy)$_3$ (2.0 mg, 3.0 μmol, 0.010 equiv), Ligand (6.5 mg, 30 μmol, 0.10 equiv), $NiBr_2$•DME (9.3 mg, 30 μmol, 0.10 equiv), DMAc (0.10 M, 3.0 mL), reductant (103 mg, 0.60 mmol, 2.0 equiv), tetrabutylammonium fluoride (157 mg, 0.6 mmol, 2.0 equiv), THF (0.10 M, 3.0 mL). The residue was purified by flash column chromatography (PE/EA = 50:1 to PE/EA = 4:1) to give the product **39** (67 mg, 52% yield, *dr* = 1:1) as a white solid.

One isomer

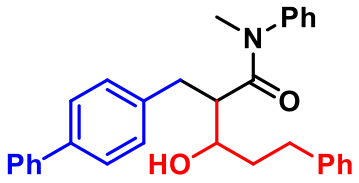
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.60 (m, 2H), 7.50 – 7.44 (m, 4H), 7.38 – 7.34 (m, 1H), 7.25 – 7.11 (m, 4H), 7.04 – 7.02 (m, 2H), 6.98 (dd, *J* = 5.0, 3.5 Hz, 1H), 6.83 – 6.82 (m, 1H), 5.31 (d, *J* = 6.9 Hz, 1H), 4.25 (d, *J* = 1.5 Hz, 1H), 3.17 – 3.14 (m, 1H), 3.10 (s, 3H), 2.92 – 2.80 (m, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.3, 146.1, 142.8, 141.1, 139.4, 138.7, 130.0, 129.5, 129.0, 127.9, 127.4, 127.3, 127.1 (2C), 126.9, 124.1, 123.2, 71.5, 52.3, 37.2, 33.2 ppm. **HRMS** (ESI) for $C_{27}H_{25}NNaO_2S^+$ [(M+Na)$^+$]: calculated 450.1498, found 450.1472. **Melting point:** 155.2 – 156.2 °C.

Another isomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.3 Hz, 2H), 7.50 – 7.43 (m, 4H), 7.37 – 7.33 (m, 1H), 7.25 – 7.20 (m, 2H), 7.15 – 7.07 (m, 4H), 7.00 – 6.98 (m, 1H), 6.84 (d, *J* = 3.7 Hz, 1H), 6.12 (d, *J* = 7.6 Hz, 2H), 5.37 (d, *J* = 8.5 Hz, 1H), 4.96 (dd, *J* = 8.5, 3.8 Hz, 1H), 3.20 (dd, *J* = 12.8, 8.8 Hz, 1H), 3.11 (s, 3H), 2.94 – 2.81 (m, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.4, 148.1, 142.7, 141.0, 139.7, 138.0, 129.8, 129.4, 129.0, 128.0, 127.4 (2C), 127.3, 127.1, 126.8, 124.3, 123.8, 71.6, 51.1, 37.2, 37.0 ppm. **HRMS** (ESI) for $C_{27}H_{25}NNaO_2S^+$ [(M+Na)$^+$]: calculated 450.1498, found 450.1480.

Melting point: 143.8 – 144.8 °C.

2-([1,1'-Biphenyl]-4-ylmethyl)-3-hydroxy-*N*-methyl-*N*,5-diphenylpentanamide (40)



Chemical Formula: $C_{31}H_{31}NO_2$
Exact Mass: 449.2355

Prepared according to the general procedure using **1a** (168 mg, 0.60 mmol, 2.0 equiv), **2b** (97 mg, 0.60 mmol, 2.0 equiv), **3k** (40 mg, 0.30 mmol, 1.0 equiv), *fac*-Ir(ppy)$_3$ (2.0 mg, 3.0 μmol, 0.010 equiv), Ligand (6.5 mg, 30 μmol, 0.10 equiv), $NiBr_2$•DME (9.3 mg, 30 μmol, 0.10 equiv), DMAc (0.10 M, 3.0 mL), reductant (103 mg, 0.60 mmol, 2.0 equiv), tetrabutylammonium fluoride (157 mg, 0.6 mmol, 2.0 equiv), THF (0.10 M, 3.0 mL). The residue was purified by flash column chromatography (PE/EA = 50:1 to PE/EA = 4:1) to give the product **40** (61 mg, 45% yield, *dr* = 1:1) as a white solid.

One isomer

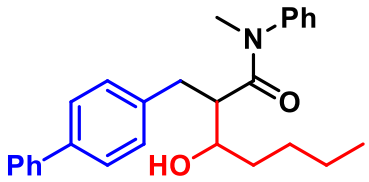
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.57 (m, 2H), 7.49 – 7.43 (m, 4H), 7.37 – 7.33 (m, 1H), 7.30 – 7.25 (m, 5H), 7.19 – 7.15 (m, 3H), 7.04 (d, *J* = 8.3 Hz, 2H), 6.63 (s, 2H), 4.33 (d, *J* = 9.6 Hz, 1H), 3.55 – 3.48 (m, 1H), 3.20 (s, 3H), 3.13 (dd, *J* = 13.2, 8.3 Hz, 1H), 2.95 – 2.83 (m, 2H), 2.63 – 2.55 (m, 2H), 1.85 – 1.75 (m, 1H), 1.62 – 1.54 (m, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.4, 143.2, 142.3, 141.0, 139.6, 138.4, 129.9, 129.8, 128.9, 128.7, 128.5, 128.2, 127.6, 127.4, 127.2, 127.1, 125.9, 71.9, 48.5, 38.6, 37.3, 36.8, 32.6 ppm. **HRMS** (ESI) for $C_{31}H_{31}NNaO_2^+$ [(M+Na)$^+$]: calculated 472.2247, found 472.2224. **Melting point:** 101.9 – 102.9 °C.

Another isomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.61 (m, 2H), 7.51 – 7.44 (m, 4H), 7.39 – 7.34 (m, 1H), 7.30 – 7.12 (m, 8H), 7.02 (d, *J* = 8.3 Hz, 2H), 4.06 (s, 1H), 3.89 – 3.85 (m, 1H), 3.13 – 3.07 (m, 4H), 2.80 – 2.72 (m, 2H), 2.63 – 2.48 (m, 2H), 2.00 – 1.90 (m, 1H), 1.66 – 1.57 (m, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.5, 143.1, 141.9, 141.1, 139.4, 139.0, 129.9, 129.6, 129.0, 128.6, 128.5, 127.9, 127.4 (2C), 127.1 (2C), 126.0,

71.5, 48.6, 37.3, 35.9, 32.3, 32.2 ppm. **HRMS** (ESI) for $C_{31}H_{32}NO_2^+$ [(M+H)$^+$]: calculated 450.2428, found 450.2431. **Melting point:** 138.9 – 139.9 °C.

2-([1,1'-Biphenyl]-4-ylmethyl)-3-hydroxy-*N*-methyl-*N*-phenylheptanamide (41)



Chemical Formula: $C_{27}H_{31}NO_2$
Exact Mass: 401.2355

Prepared according to the general procedure using **1a** (168 mg, 0.60 mmol, 2.0 equiv), **2b** (97 mg, 0.60 mmol, 2.0 equiv), **3l** (26 mg, 0.30 mmol, 1.0 equiv), *fac*-Ir(ppy)$_3$ (2.0 mg, 3.0 μmol, 0.010 equiv), Ligand (6.5 mg, 30 μmol, 0.10 equiv), $NiBr_2$•DME (9.3 mg, 30 μmol, 0.10 equiv), DMAc (0.10 M, 3.0 mL), reductant (103 mg, 0.60 mmol, 2.0 equiv), tetrabutylammonium fluoride (157 mg, 0.6 mmol, 2.0 equiv), THF (0.10 M, 3.0 mL). The residue was purified by flash column chromatography (PE/EA = 50:1 to PE/EA = 4:1) to give the product **41** (36 mg, 30% yield, *dr* = 1:1.6) as a white solid.

One isomer

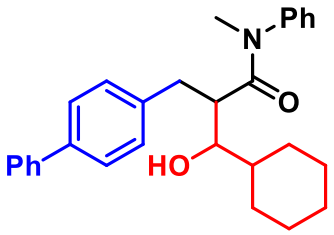
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.62 (m, 2H), 7.52 – 7.45 (m, 4H), 7.39 – 7.35 (m, 1H), 7.24 – 7.07 (m, 5H), 3.96 (s, 1H), 3.86 – 3.81 (m, 1H), 3.13 – 3.05 (m, 4H), 2.78 (dd, *J* = 13.1, 3.5 Hz, 1H), 2.62 (dt, *J* = 11.5, 3.5 Hz, 1H), 1.62 – 1.54 (m, 1H), 1.41 – 1.24 (m, 4H), 1.19 – 1.10 (m, 1H), 0.87 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.7, 143.1, 141.1, 139.4, 139.2, 129.9, 129.5, 129.0, 127.9, 127.5, 127.4, 127.2, 127.1, 72.1, 48.3, 37.2, 33.8, 32.1, 28.1, 22.7, 14.1 ppm. **HRMS** (ESI) for $C_{27}H_{31}NNaO_2^+$ [(M+Na)$^+$]: calculated 424.2247, found 424.2222. **Melting point:** 93.6 – 94.6 °C.

Another isomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.58 (m, 2H), 7.50 – 7.43 (m, 4H), 7.37 – 7.28 (m, 4H), 7.08 – 7.06 (m, 2H), 6.66 (s, 2H), 4.16 (d, *J* = 9.6 Hz, 1H), 3.50 – 3.43 (m, 1H), 3.22 (s, 3H), 3.13 (dd, *J* = 13.1, 8.3 Hz, 1H), 2.93 (dd, *J* = 13.2, 6.8 Hz, 1H), 2.59 – 2.54 (m, 1H), 1.52 – 1.41 (m, 2H), 1.36 – 1.24 (m, 3H), 1.23 – 1.17 (m, 1H), 0.87 (t, *J*

= 7.2 Hz, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.5, 143.3, 141.1, 139.5, 138.6, 129.9, 129.7, 128.9, 128.2, 127.6, 127.3, 127.2, 127.1, 72.7, 48.6, 37.3, 36.8, 36.6, 28.5, 22.8, 14.2 ppm. **HRMS** (ESI) for $C_{27}H_{31}NNaO_2^+$ [$(M+Na)^+$]: calculated 424.2247, found 424.2227. **Melting point:** 97.0 – 98.0 °C.

2-([1,1'-Biphenyl]-4-ylmethyl)-3-cyclohexyl-3-hydroxy-*N*-methyl-*N*-phenylpropanamide (42)



Chemical Formula: $C_{29}H_{33}NO_2$
Exact Mass: 427.2511

Prepared according to the general procedure using **1a** (168 mg, 0.60 mmol, 2.0 equiv), **2b** (97 mg, 0.60 mmol, 2.0 equiv), **3m** (34 mg, 0.30 mmol, 1.0 equiv), *fac*-Ir(ppy)$_3$ (2.0 mg, 3.0 μmol, 0.010 equiv), Ligand (6.5 mg, 30 μmol, 0.10 equiv), $NiBr_2$•DME (9.3 mg, 30 μmol, 0.10 equiv), DMAc (0.10 M, 3.0 mL), reductant (103 mg, 0.60 mmol, 2.0 equiv), tetrabutylammonium fluoride (157 mg, 0.6 mmol, 2.0 equiv), THF (0.10 M, 3.0 mL). The residue was purified by flash column chromatography (PE/EA = 50:1 to PE/EA = 4:1) to give the product **42** (62 mg, 48% yield, *dr* = 1:1.2) as a white solid.

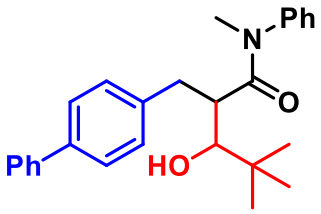
One isomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.62 (m, 2H), 7.52 – 7.45 (m, 4H), 7.39 – 7.35 (m, 1H), 7.26 – 7.18 (m, 3H), 7.07 (d, *J* = 8.2 Hz, 2H), 4.38 (s, 1H), 3.45 (d, *J* = 10.1 Hz, 1H), 3.14 – 3.07 (m, 4H), 2.85 – 2.80 (m, 1H), 2.68 (dd, *J* = 13.1, 3.4 Hz, 1H), 2.13 (d, *J* = 16.7 Hz, 1H), 1.75 (d, *J* = 16.4 Hz, 1H), 1.63 (d, *J* = 12.0 Hz, 2H), 1.53 – 1.43 (m, 1H), 1.25 – 1.09 (m, 4H), 0.97 – 0.87 (m, 1H), 0.66 – 0.57 (m, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.1, 143.0, 141.1, 139.4, 139.3, 129.9 (2C), 129.5, 129.0, 128.0, 127.3, 127.1 (2C), 76.1, 45.1, 40.0, 37.2, 31.6, 30.0, 28.4, 26.5, 26.0, 25.8 ppm. **HRMS** (ESI) for $C_{29}H_{33}NNaO_2^+$ [$(M+Na)^+$]: calculated 450.2404, found 450.2382. **Melting point:** 128.7 – 129.7 °C.

Another isomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.58 (m, 2H), 7.49 – 7.42 (m, 4H), 7.36 – 7.30 (m, 4H), 7.05 (d, *J* = 8.2 Hz, 2H), 6.72 (s, 2H), 4.32 (d, *J* = 9.3 Hz, 1H), 3.23 (s, 3H), 3.18 – 3.10 (m, 2H), 2.98 – 2.92 (m, 1H), 2.77 – 2.72 (m, 1H), 1.92 (d, *J* = 13.2 Hz, 1H), 1.74 (d, *J* = 12.7 Hz, 1H), 1.62 (s, 1H), 1.30 – 1.07 (m, 6H), 0.98 – 0.87 (m, 1H), 0.80 – 0.71 (m, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.8, 143.1, 141.0, 139.5, 138.5, 129.8, 129.6, 128.9, 128.2, 127.5, 127.3, 127.2, 127.1, 76.9, 45.4, 42.5, 37.5, 37.0, 30.4, 28.4, 26.5, 26.2 (2C) ppm. **HRMS** (ESI) for $C_{29}H_{33}NNaO_2^+$ [$(M+Na)^+$]: calculated 450.2404, found 450.2377. **Melting point:** 140.0 – 141.0 °C.

2-([1,1'-Biphenyl]-4-ylmethyl)-3-hydroxy-*N*,4,4-trimethyl-*N*-phenylpentanamide (43)



Chemical Formula: $C_{27}H_{31}NO_2$
Exact Mass: 401.2355

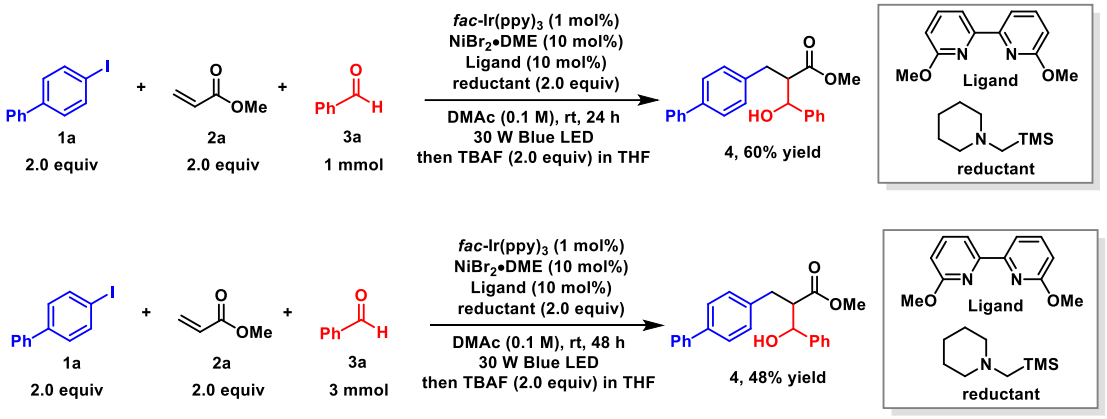
Prepared according to the general procedure using **1a** (168 mg, 0.60 mmol, 2.0 equiv), **2b** (97 mg, 0.60 mmol, 2.0 equiv), **3n** (26 mg, 0.30 mmol, 1.0 equiv), *fac*-Ir(ppy)$_3$ (2.0 mg, 3.0 μmol, 0.010 equiv), Ligand (6.5 mg, 30 μmol, 0.10 equiv), $NiBr_2$•DME (9.3 mg, 30 μmol, 0.10 equiv), DMAc (0.10 M, 3.0 mL), reductant (103 mg, 0.60 mmol, 2.0 equiv), tetrabutylammonium fluoride (157 mg, 0.6 mmol, 2.0 equiv), THF (0.10 M, 3.0 mL). The residue was purified by flash column chromatography (PE/EA = 50:1 to PE/EA = 4:1) to give the product **43** (40 mg, 33% yield, *dr* = 1:1.2) as a colorless oil.

Note: these two diastereoisomers cannot be separated by column chromatography

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.64 (m, 2H), 7.59 – 7.57 (m, 2H), 7.54 – 7.31 (m, 14H), 7.23 – 7.20 (m, 2H), 7.12 – 6.99 (m,8H), 5.57 (d, *J* = 8.8 Hz, 1H), 3.94 (s, 1H), 3.50 (s, 1H), 3.26 (s, 3H), 3.18 – 3.11 (m, 6H), 3.04 (dd, *J* = 8.8, 1.8 Hz, 1H), 2.96 – 2.89 (m, 2H), 2.73 – 2.69 (m, 1H), 0.90 (s, 9H), 0.75 (s, 9H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.8, 176.6, 143.1, 143.0, 141.1, 140.9, 139.5 (2C), 139.3, 138.2, 130.0,

129.9, 129.6, 129.4, 129.0, 128.8, 128.6, 127.9, 127.5, 127.4, 127.3 (2C), 127.2, 127.1 (2C), 127.0, 80.0, 78.9, 45.5, 41.7, 37.9, 37.6, 37.2, 35.9, 35.8, 32.9, 27.4, 26.3 ppm. **HRMS** (ESI) for $C_{27}H_{32}NO_2^+$ [(M+H)$^+$]: calculated 402.2428, found 402.2418.

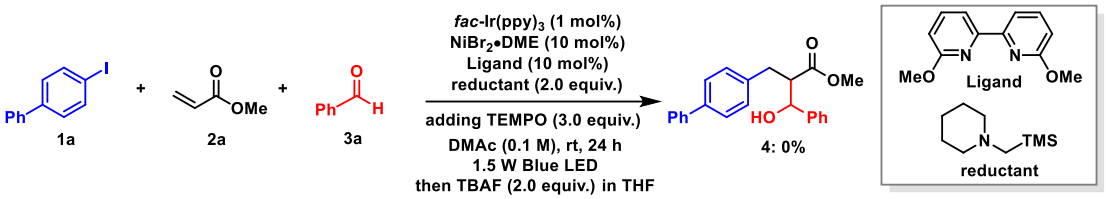
6 Scale-up Reactions on a 1 mmol and 3 mmol



The reactions were set up in an N_2 filled glovebox. An oven-dried vial equipped with a stir-bar was added *fac*-Ir(ppy)$_3$ (0.010 equiv), Ligand (0.10 equiv), $NiBr_2$•DME (0.10 equiv), Aryl iodide **1a** (2.0 equiv), alkene **2a** (2.0 equiv), Aldehyde **3a** (1.0 equiv). Then, DMAc (0.10 M), reductant (2.0 equiv) were added. The vial was sealed and removed from the glovebox, then irradiated with a 30 W blue LED lamp with cooling from a fan for 24 h or 48 h. The reaction was quenched by H_2O, extracted with ethyl acetate. The combined organic layers were washed with brine, dried with Na_2SO_4, filtered, and concentrated in vacuo. Then the crude product was dissolved in THF (0.10 M), tetrabutylammonium fluoride (2.0 equiv) was added. The reaction stirred vigorously at room temperature for 1 h. After completion, the solvent was removed under reduced pressure and the residue was purified by flash chromatography to give the corresponding product **4**.

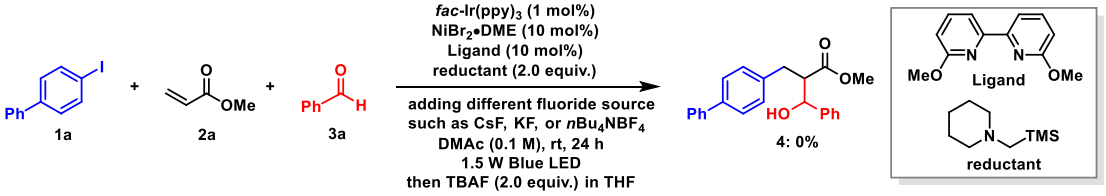
7 Mechanistic Studies

7.1 Radical trapping experiment



The reactions were set up in an N_2 filled glovebox. An oven-dried vial equipped with a stir-bar was added **1a** (168 mg, 0.60 mmol, 2.0 equiv), **2a** (52 mg, 0.60 mmol, 2.0 equiv), **3a** (32 mg, 0.30 mmol, 1.0 equiv), *fac*-Ir(ppy)$_3$ (2.0 mg, 3.0 μmol, 0.010 equiv), Ligand (6.5 mg, 30 μmol, 0.10 equiv), NiBr$_2$•DME (9.3 mg, 30 μmol, 0.10 equiv), 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO, 141 mg, 0.90 mmol, 3.0 equiv). Then, DMAc (0.10 M, 3.0 mL), reductant (103 mg, 0.60 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. Then the reaction was quenched by H_2O, extracted with ethyl acetate (90 mL). The combined organic layers were washed with brine, dried with Na_2SO_4, filtered, and concentrated in vacuo. Then the crude product was dissolved in THF (0.10 M, 3.0 mL), tetrabutylammonium fluoride (157 mg, 0.6 mmol, 2.0 equiv) was added. The reaction stirred vigorously at room temperature for 1 h. The desired product **4** was not detected in this experiment.

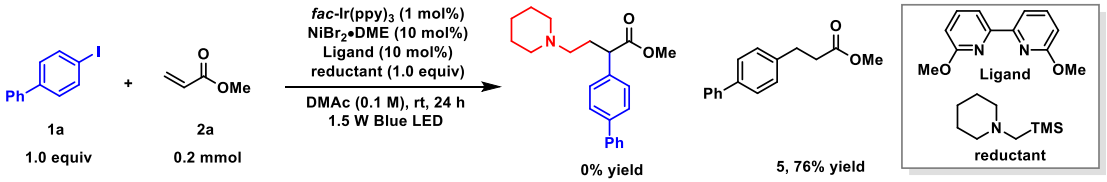
7.2 Control experiments with adding different fluoride sources



The reactions were set up in an N_2 filled glovebox. An oven-dried vial equipped with a stir-bar was added **1a** (168 mg, 0.60 mmol, 2.0 equiv), **2a** (52 mg, 0.60 mmol, 2.0 equiv), **3a** (32 mg, 0.30 mmol, 1.0 equiv), *fac*-Ir(ppy)$_3$ (2.0 mg, 3.0 μmol, 0.010 equiv), Ligand (6.5 mg, 30 μmol, 0.10 equiv), NiBr$_2$•DME (9.3 mg, 30 μmol, 0.10 equiv). Then, different fluoride source (0.60 mmol, 2.0 equiv), DMAc (0.10 M, 3.0 mL), reductant (103

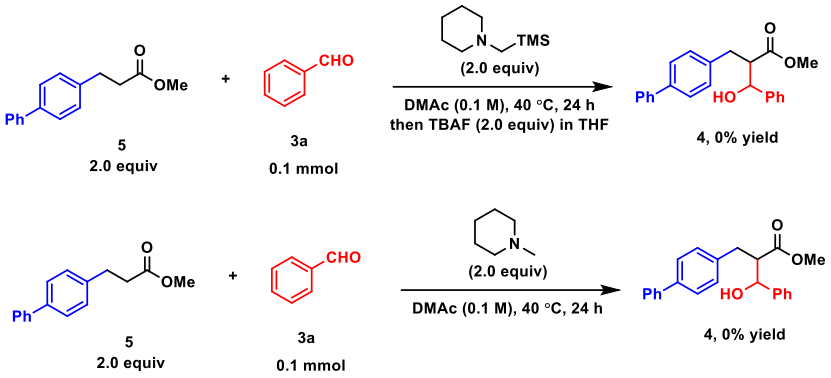
mg, 0.60 mmol, 2.0 equiv) were added. The vial was sealed and removed from the glovebox then irradiated with a 1.5 W blue LED lamp (at approximately 1.0 cm away from the light source) with cooling from a fan for 24 h. Then the reaction was quenched by H_2O, extracted with ethyl acetate (90 mL). The combined organic layers were washed with brine, dried with Na_2SO_4, filtered, and concentrated in vacuo. Then the crude product was dissolved in THF (0.10 M, 3.0 mL), tetrabutylammonium fluoride (157 mg, 0.6 mmol, 2.0 equiv) was added. The reaction stirred vigorously at room temperature for 1 h. The desired product **4** was not detected in each experiment.

7.3 Control experiment without aldehyde



The reaction was set up in an N_2 filled glovebox. An oven-dried vial equipped with a stir-bar was added **1a** (56 mg, 0.20 mmol, 1.0 equiv), **2a** (17 mg, 0.20 mmol, 1.0 equiv), *fac*-Ir(ppy)$_3$ (1.3 mg, 2.0 μmol, 0.010 equiv), Ligand (4.3 mg, 20 μmol, 0.10 equiv), $NiBr_2$•DME (6.2 mg, 20 μmol, 0.10 equiv). Then, DMAc (0.10 M, 2.0 mL), reductant (34 mg, 0.20 mmol, 1.0 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 alpha amino radical attaches to the olefin product could not be obtained, the reaction mainly afforded the reductive Heck product **5** in 76% yield.

7.4 Control experiments with reductive Heck product 5 react with benzaldehyde under thermal reactions



The reactions were set up in an N_2 filled glovebox. An oven-dried vial equipped with a stir-bar was added **5** (48 mg, 0.20 mmol, 2.0 equiv), **3a** (11 mg, 0.10 mmol, 1.0 equiv). Then, DMAc (0.10 M, 1.0 mL), 1-((trimethylsilyl)methyl)piperidine (34 mg, 0.20 mmol, 2.0 equiv) or 1-methylpiperidine (20 mg, 0.20 mmol, 2.0 equiv) were added. The vial was sealed and removed from the glovebox then stirred vigorously at 40 ℃ for 24 h. After reaction, the desired product **4** could not be detected in each case. Indicating that **5** is not the intermediate for producing the desired product.

7.5 Fluorescence quenching (Stern-Volmer) studies

Emission intensities were recorded using Agilent Technologies of Cary Eclipse Fluorescence spectrophotometer. All *fac*-Ir(ppy)$_3$ solutions were excited at 400 nm and the emission intensity was collected at 410-700 nm. In a typical experiment, to a 1 x 10^{-4} M solution of *fac*-Ir(ppy)$_3$ 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 $NiBr_2$•DME complex is the quencher of photocatalyst.

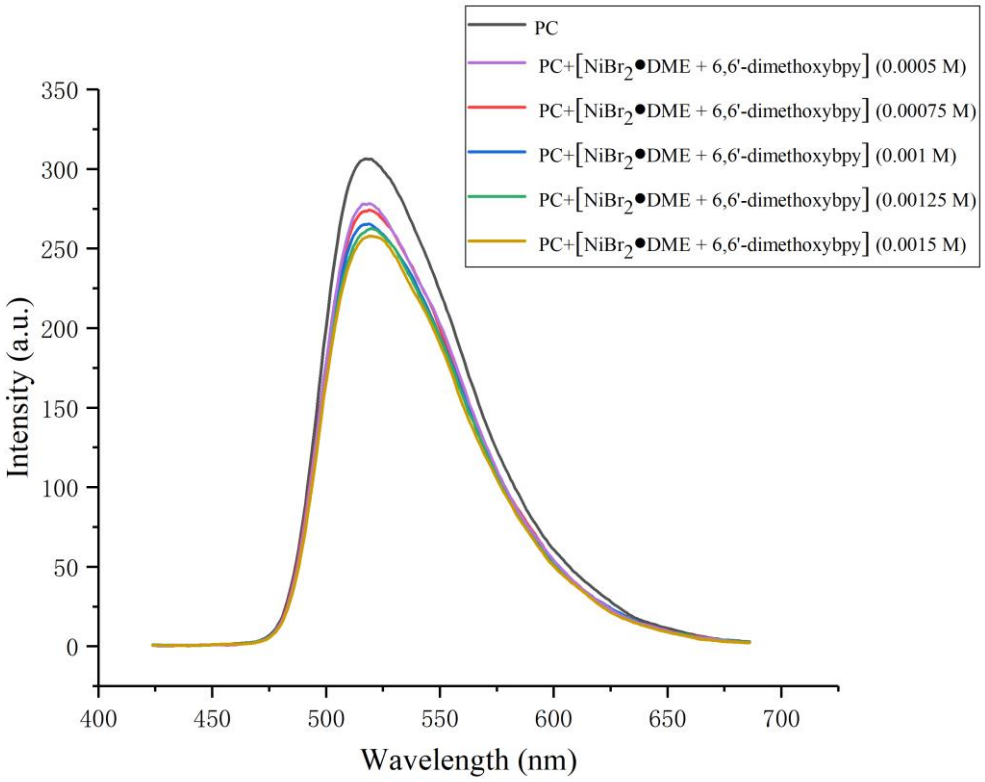


Figure S2 Quenching with variable amounts of [$NiBr_2$•DME and 6,6'-dimethoxybpy]

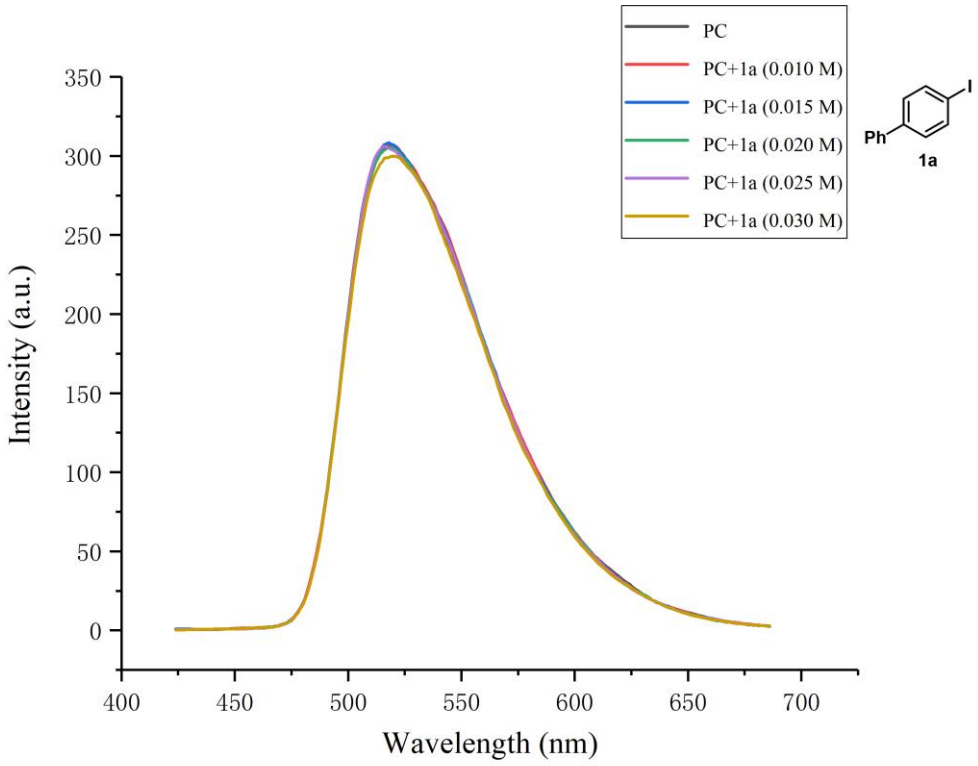


Figure S3 Quenching with variable amounts of **1a**

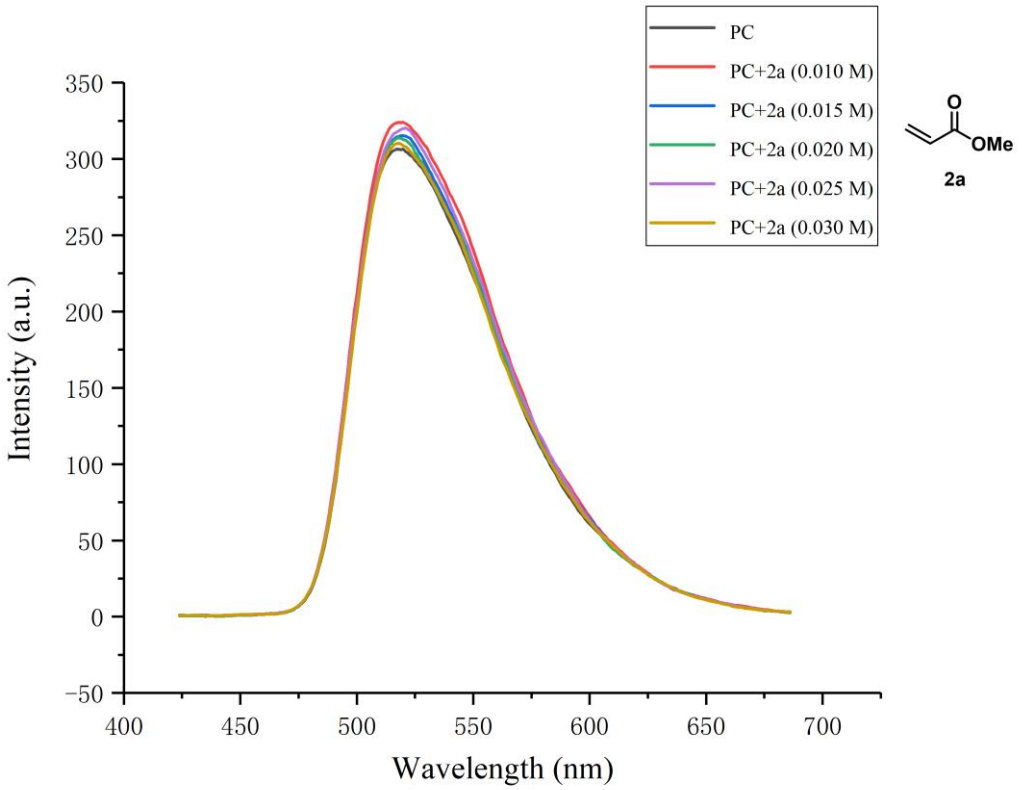


Figure S4 Quenching with variable amounts of **2a**

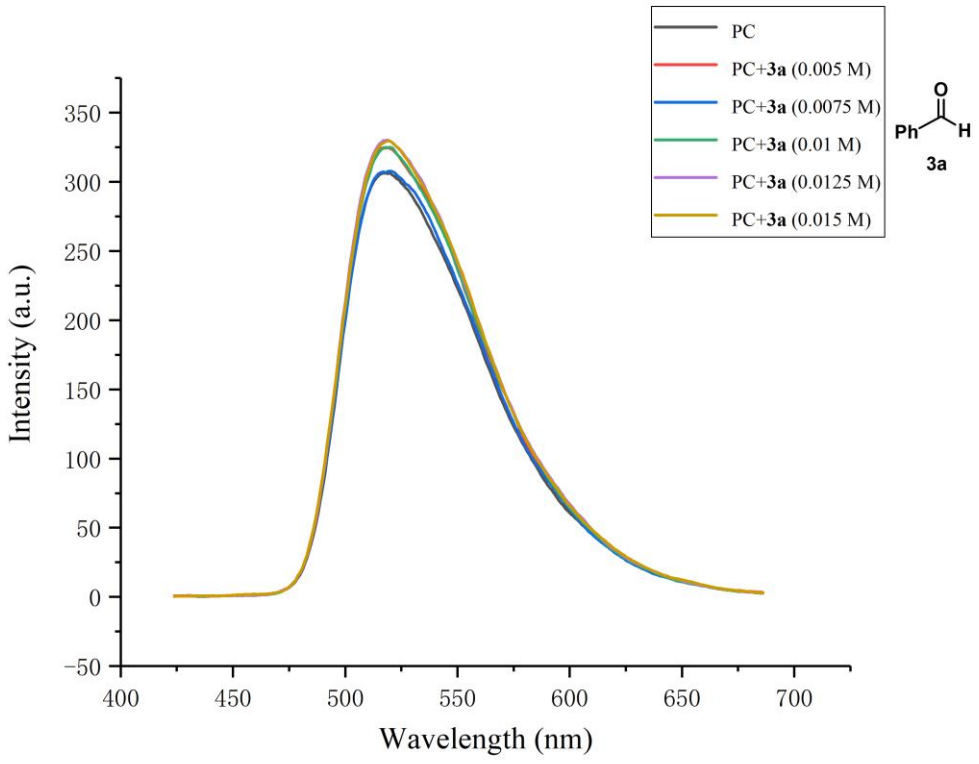


Figure S5 Quenching with variable amounts of **3a**

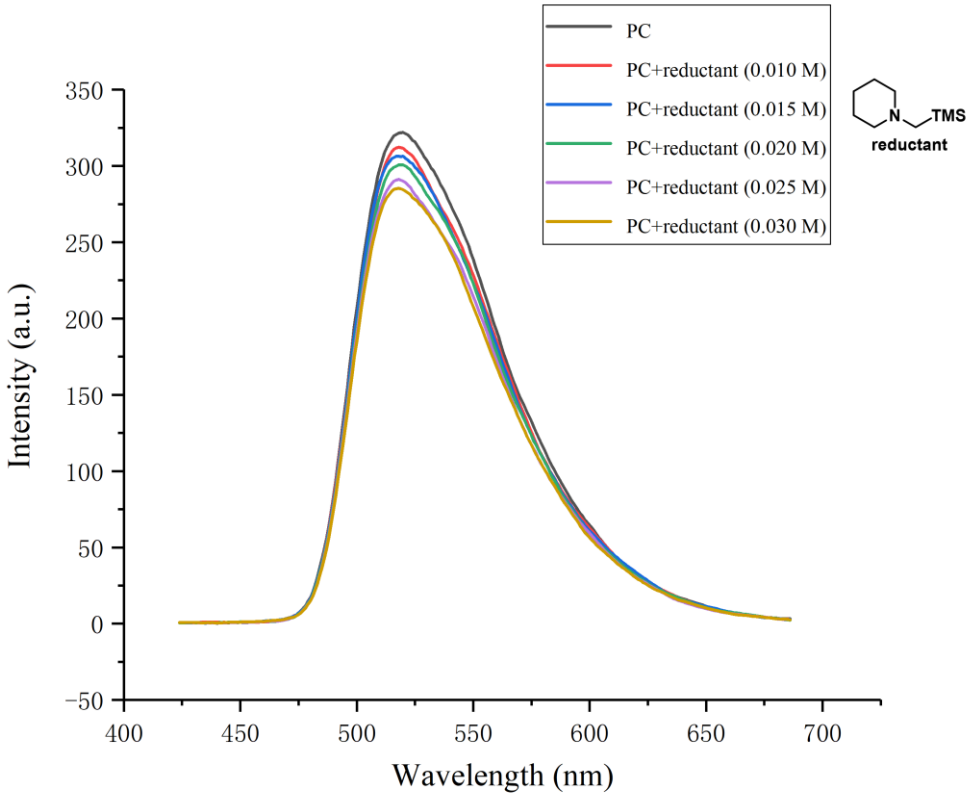


Figure S6 Quenching with variable amounts of reductant

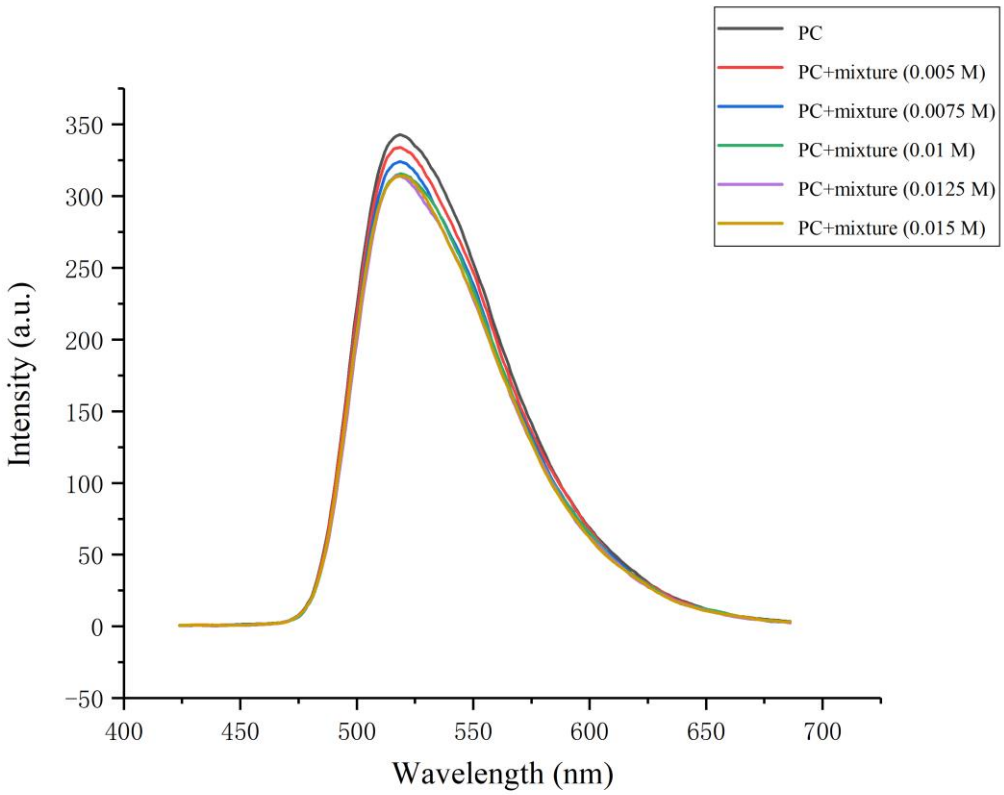


Figure S7 Quenching with variable amounts of the mix of all the components

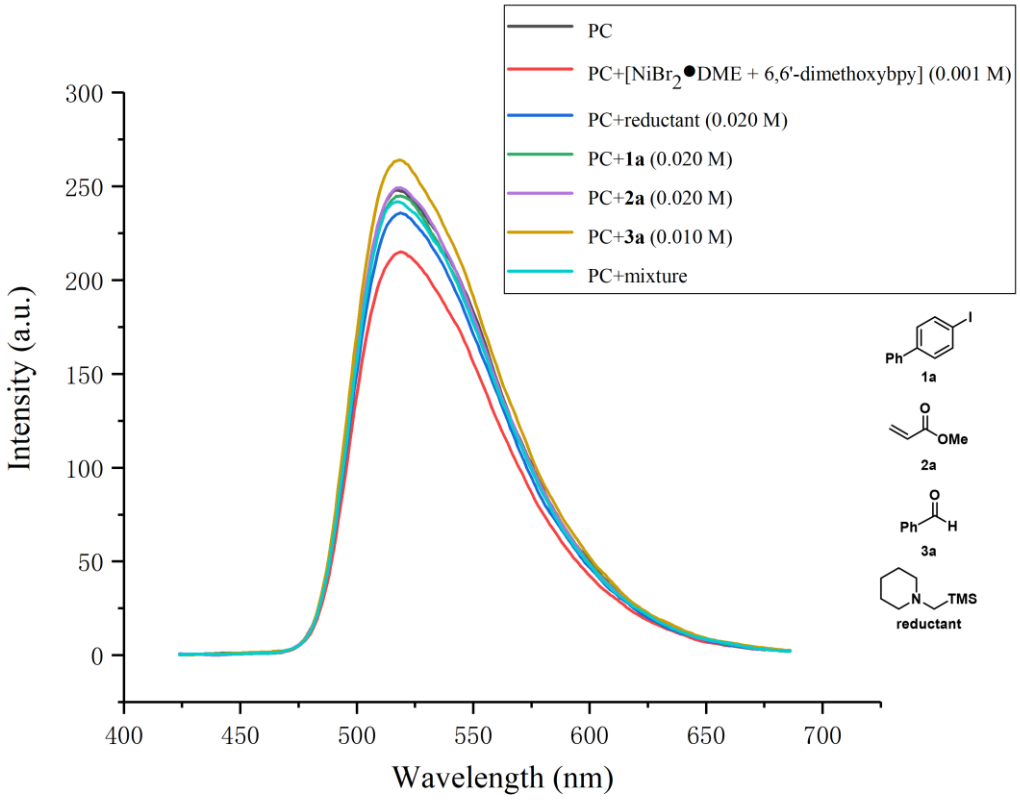


Figure S8 Quenching with [$NiBr_2$•DME+6,6'-dimethoxybpy], reductant**, 1a**, **2a**, **3a** and the mix of all the components

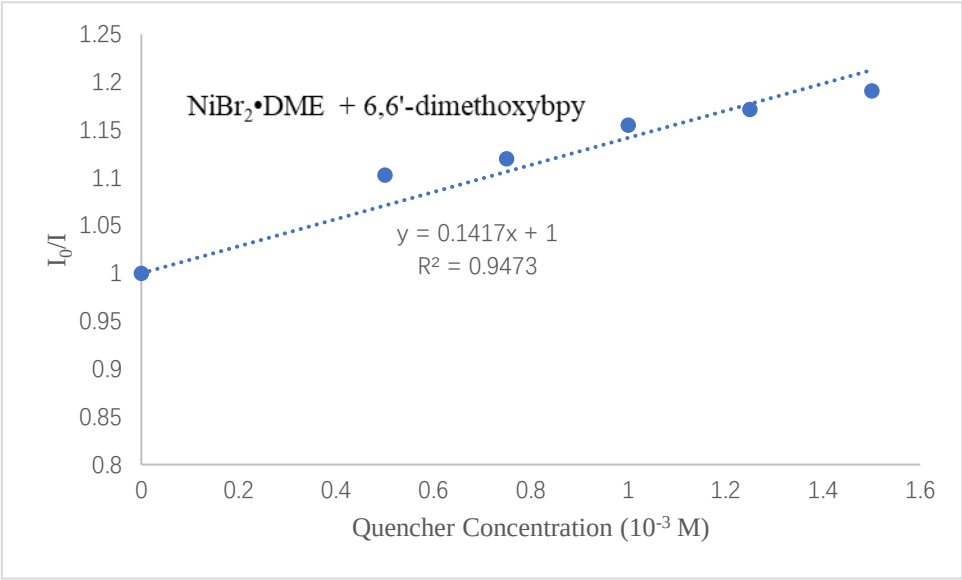


Figure S9 Fluorescence quenching (Stern-Volmer) curve of [$NiBr_2$ • DME+6,6'-dimethoxybpy]

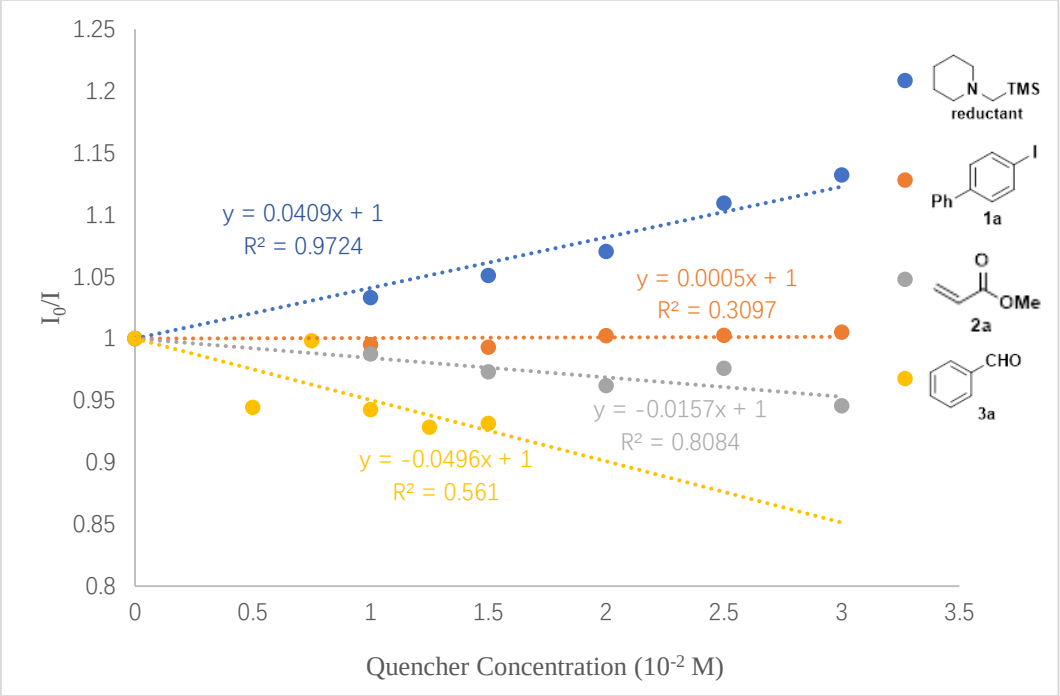


Figure S10 Fluorescence quenching (Stern-Volmer) curve of reductant**, 1a**, **2a** and **3a**

7.6 The studies of the effect of each component on the emission intensity of photocatalyst

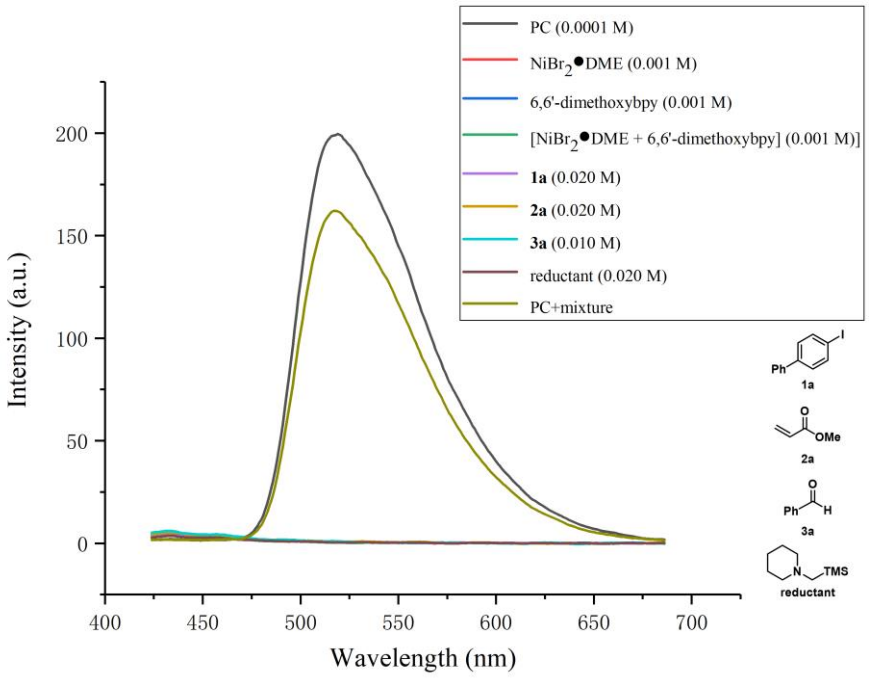


Figure S11 The effect of each component on the emission intensity of photocatalyst

8 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.

[S3] Yi, X.; Lei, S.; Liu, W.; Che, F.; Yu, C.; Liu, X.; Wang, Z.; Zhou, X.; Zhang, Y. *Org. Lett.* **2020**, *22*, 4583–4587.

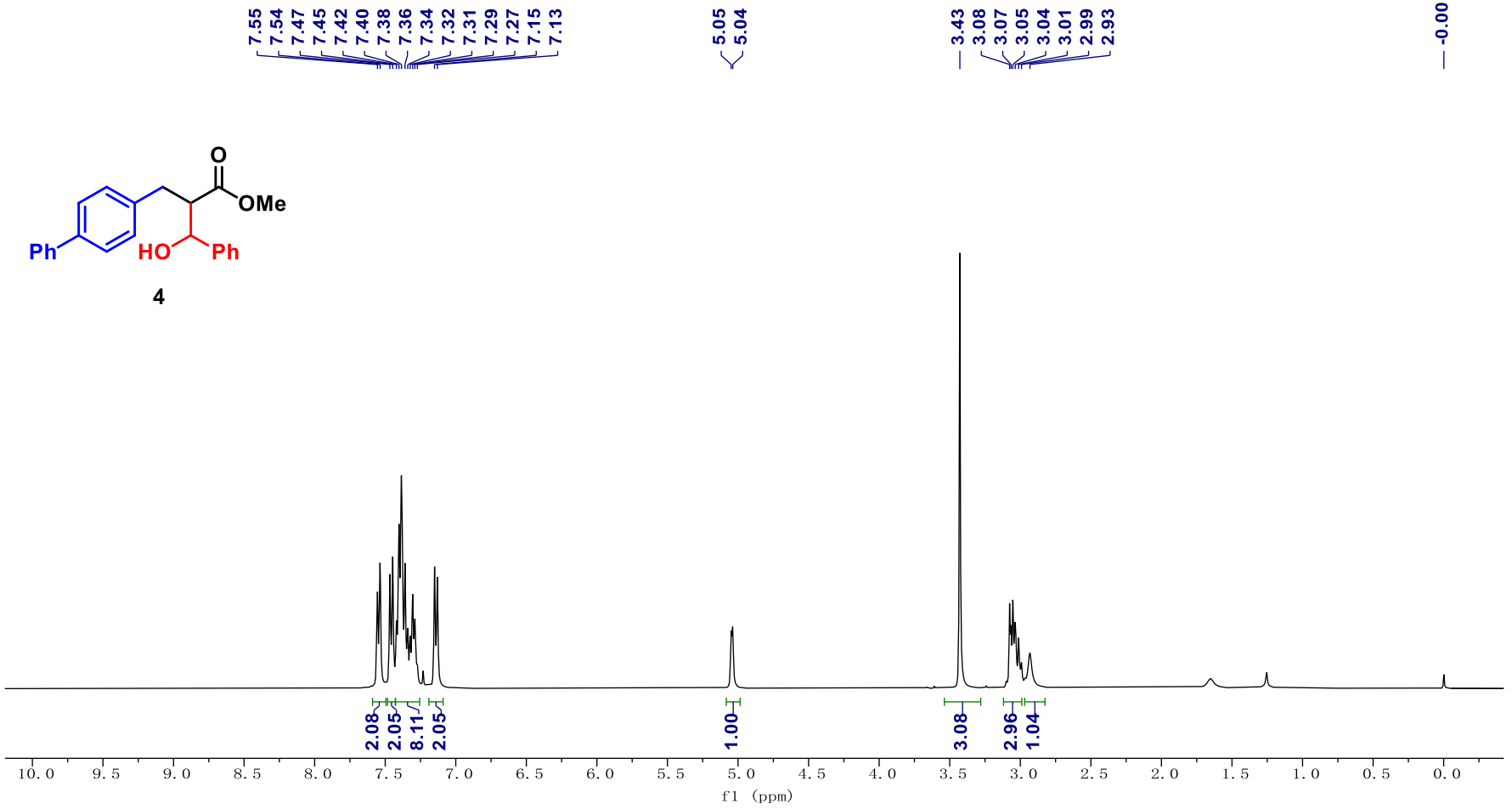
[S4] Liu, Q.; Zhu, F.-P.; Jin, X.- L.; Wang, X.-J.; Chen, H.; Wu, L.-Z. *Chem. Eur. J.* **2015**, *21*, 10326–10329.

[S5] Cai, L.; Fu, L.; Zhou, C.; Gao, Y.; Li, S.; Li, G. *Green Chem.*, **2020**, *22*, 7328–7332.

[S6] Sai, M.; Kurouchi, H. *Adv. Synth. Catal.* **2021**, *363*, 3585–3591.

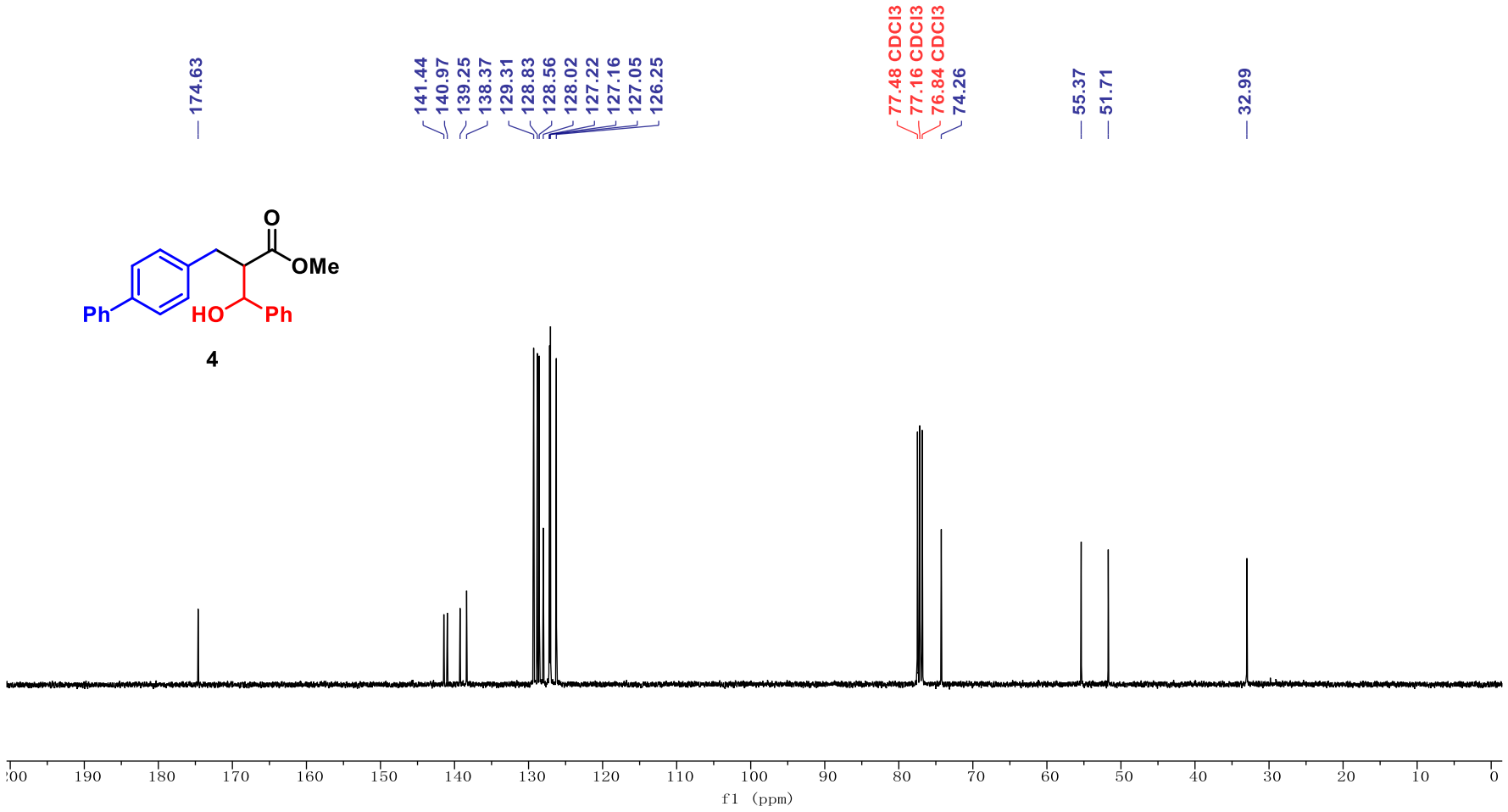
9 NMR Spectra

^{1}H NMR of 4 (One isomer) (400 MHz, $CDCl_3$)

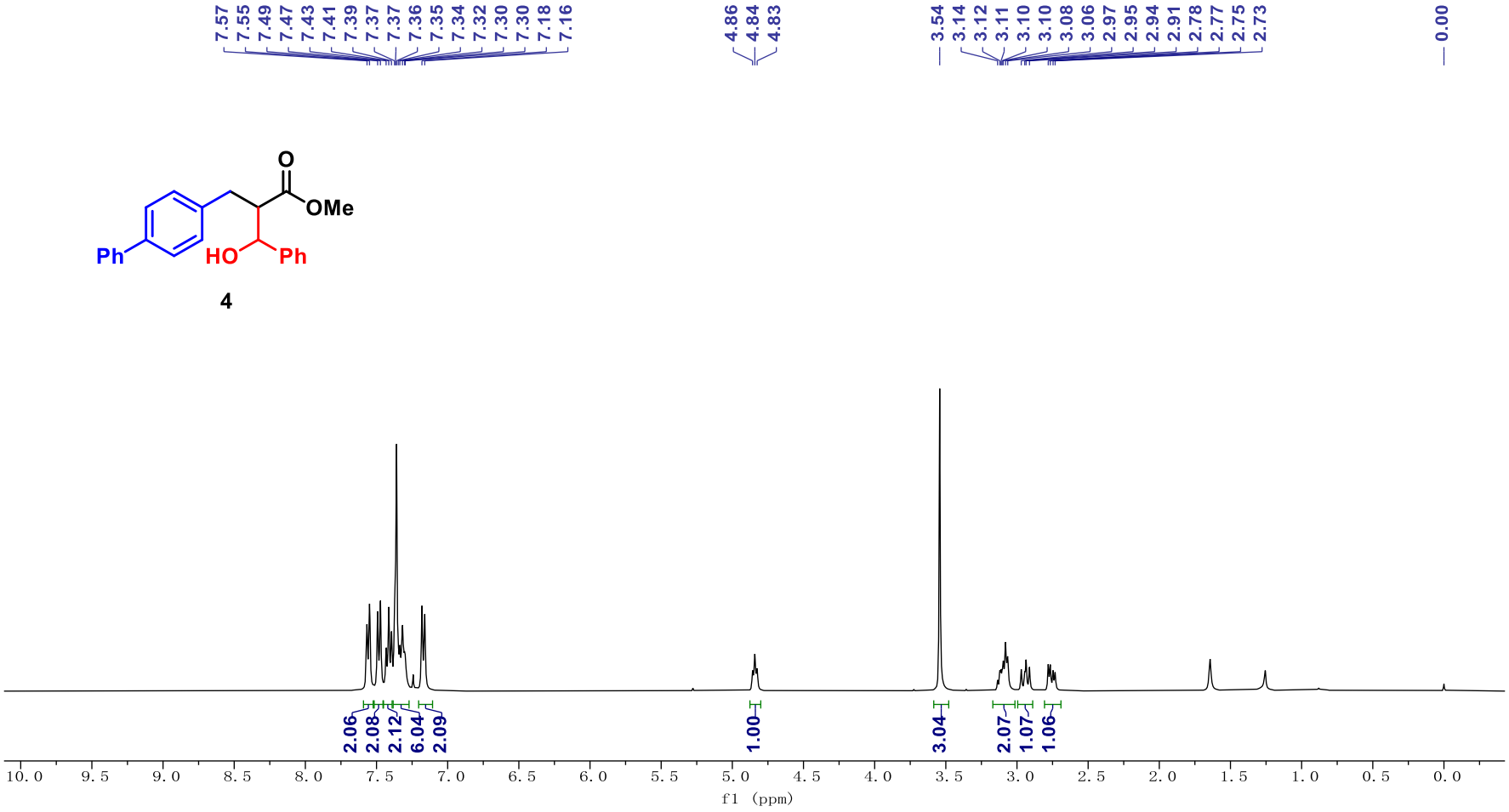


4

^{13}C NMR of 4 (One isomer) (101 MHz, $CDCl_3$)



^{1}H NMR of 4 (Another isomer) (400 MHz, $CDCl_3$)



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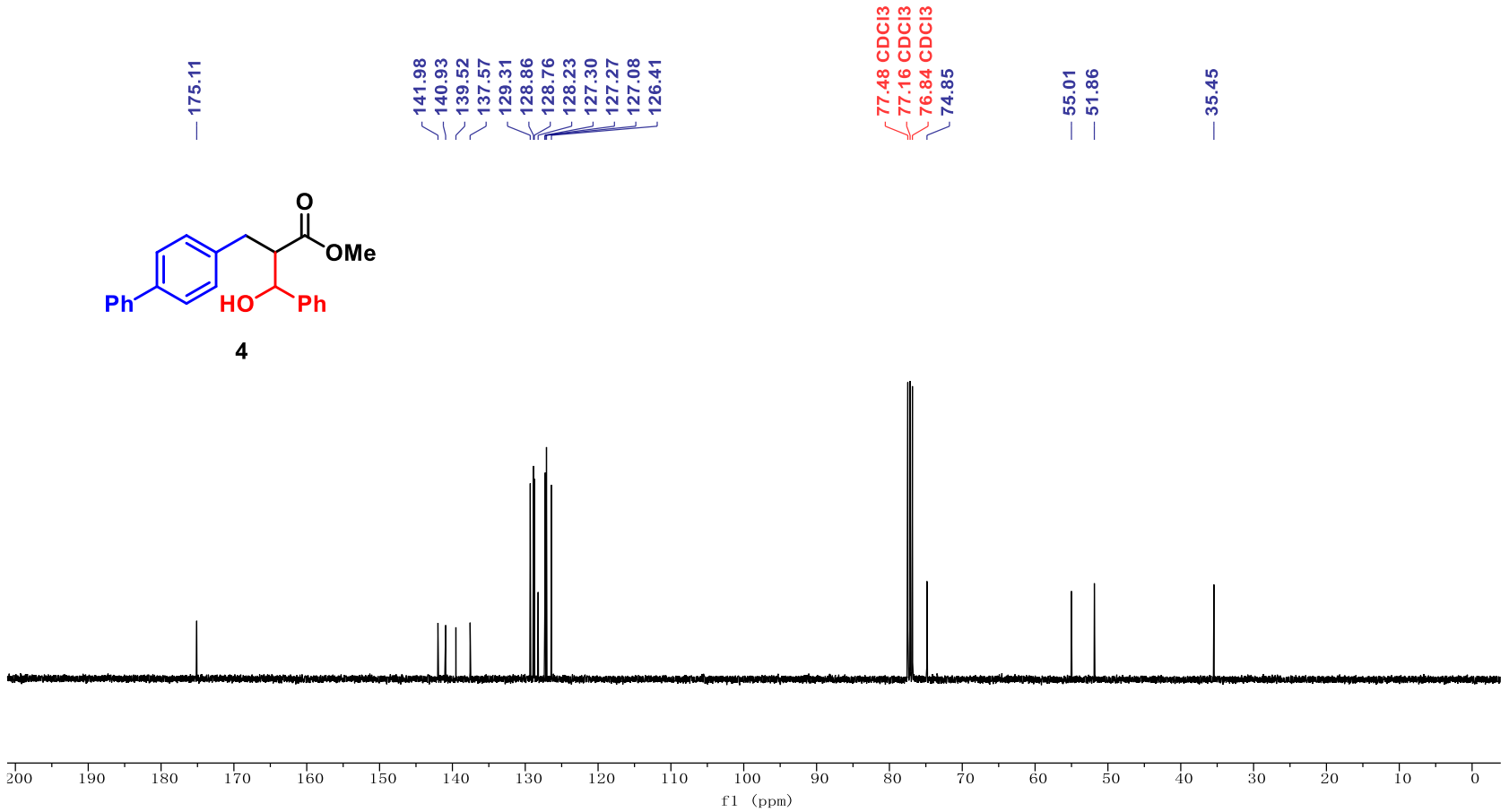
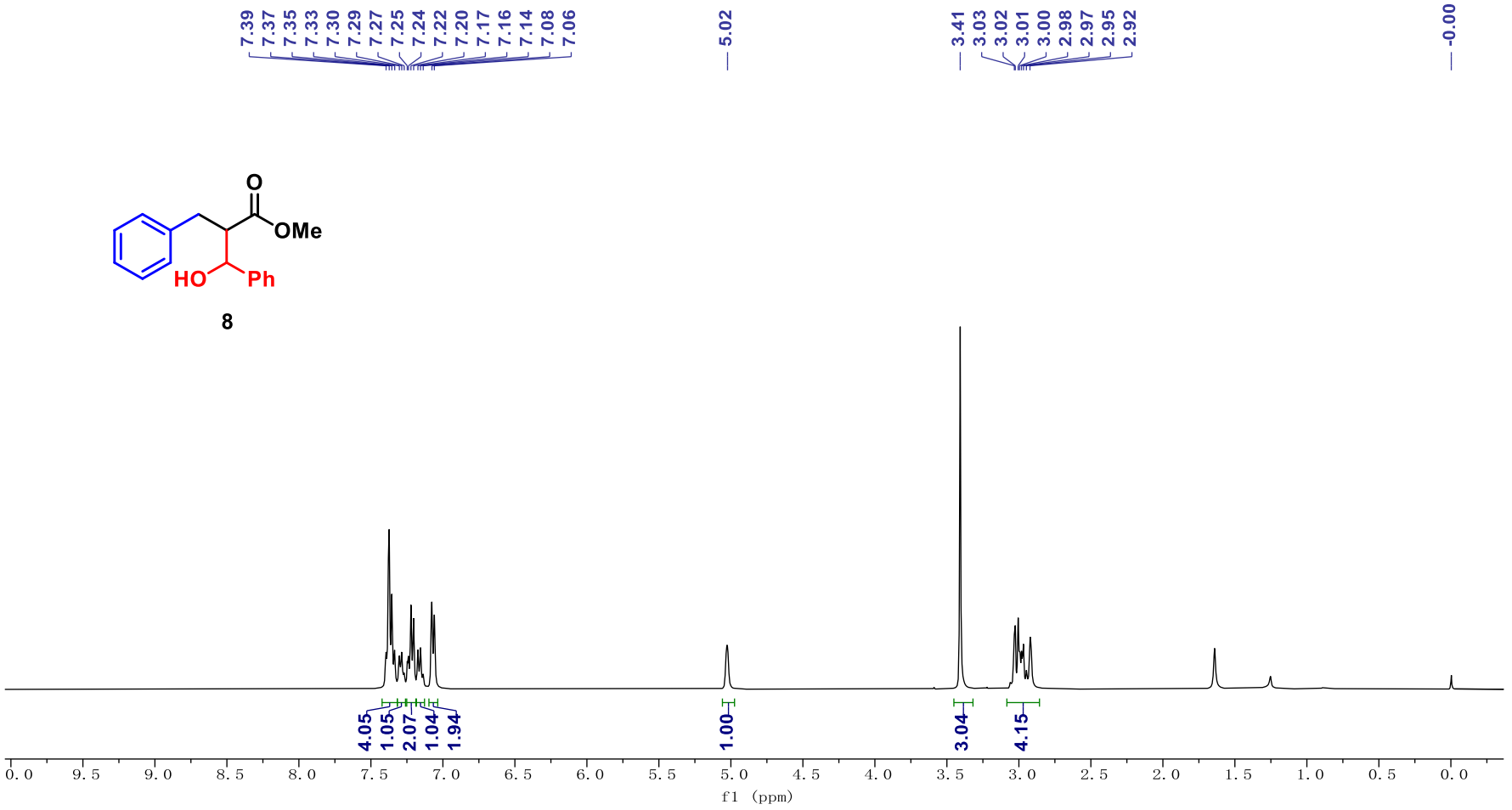
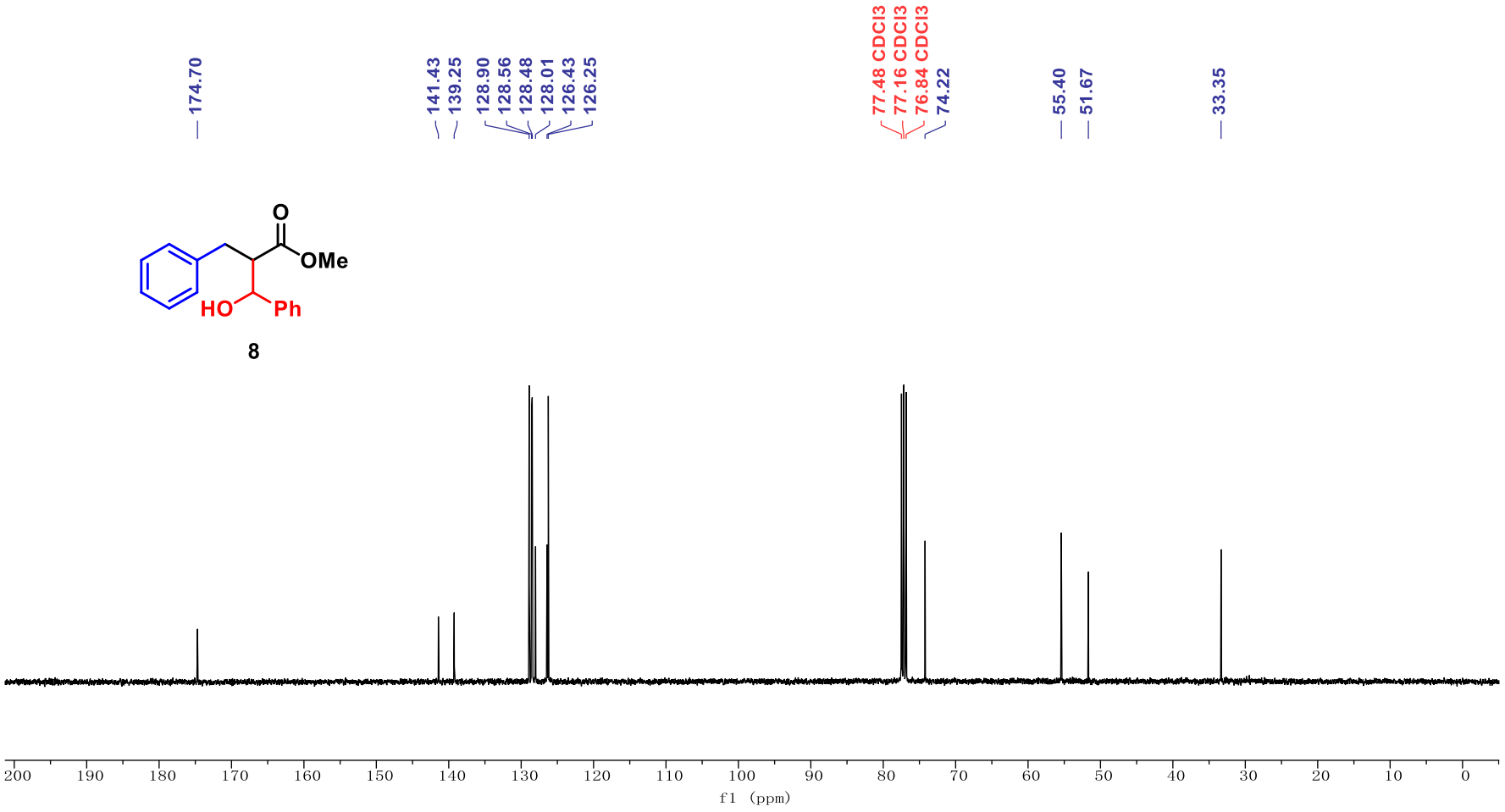
^{13}C NMR of 4 (Another isomer) (101 MHz, $CDCl_3$)



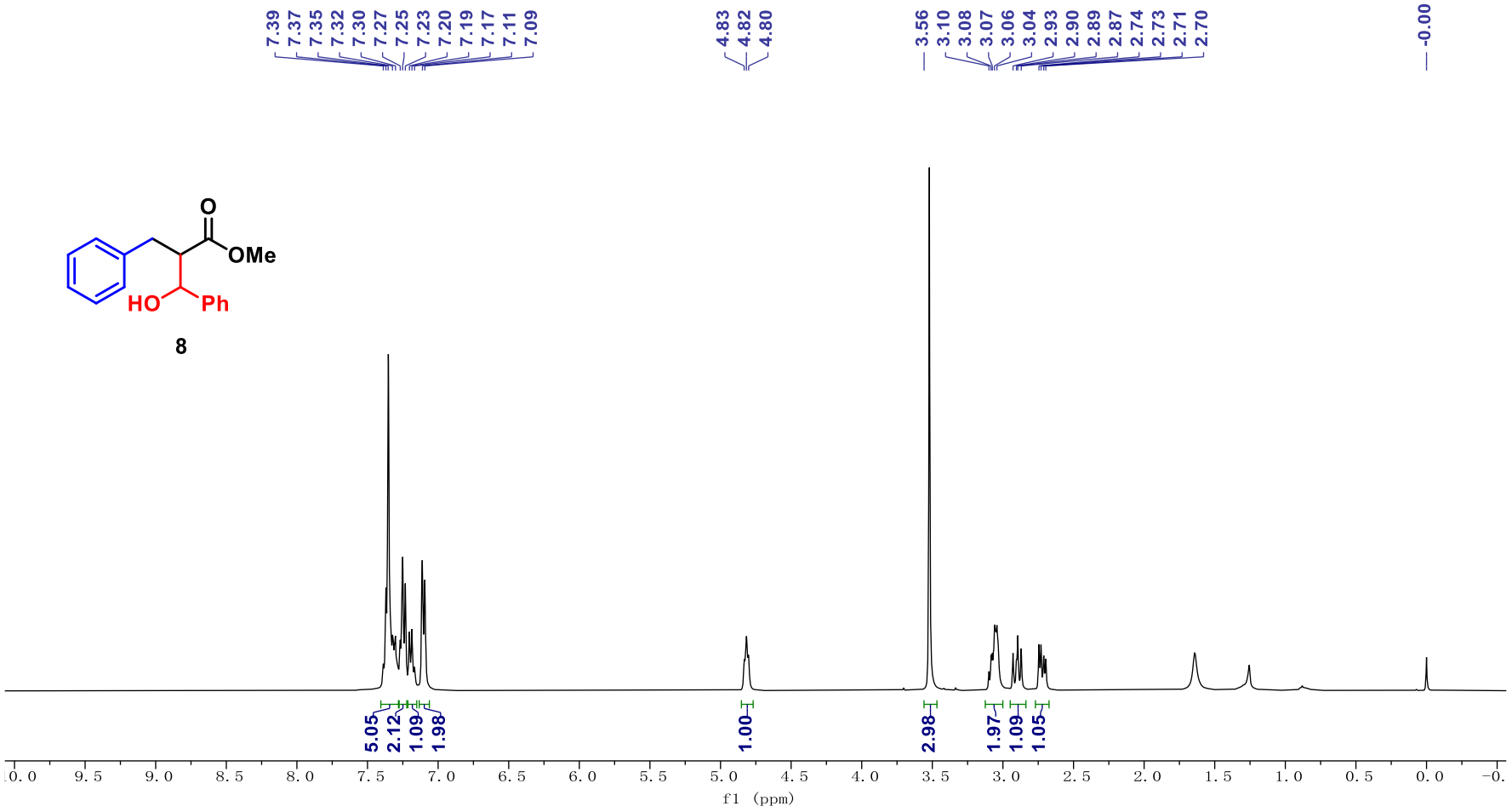
^{1}H NMR of 8 (One isomer) (400 MHz, $CDCl_3$)



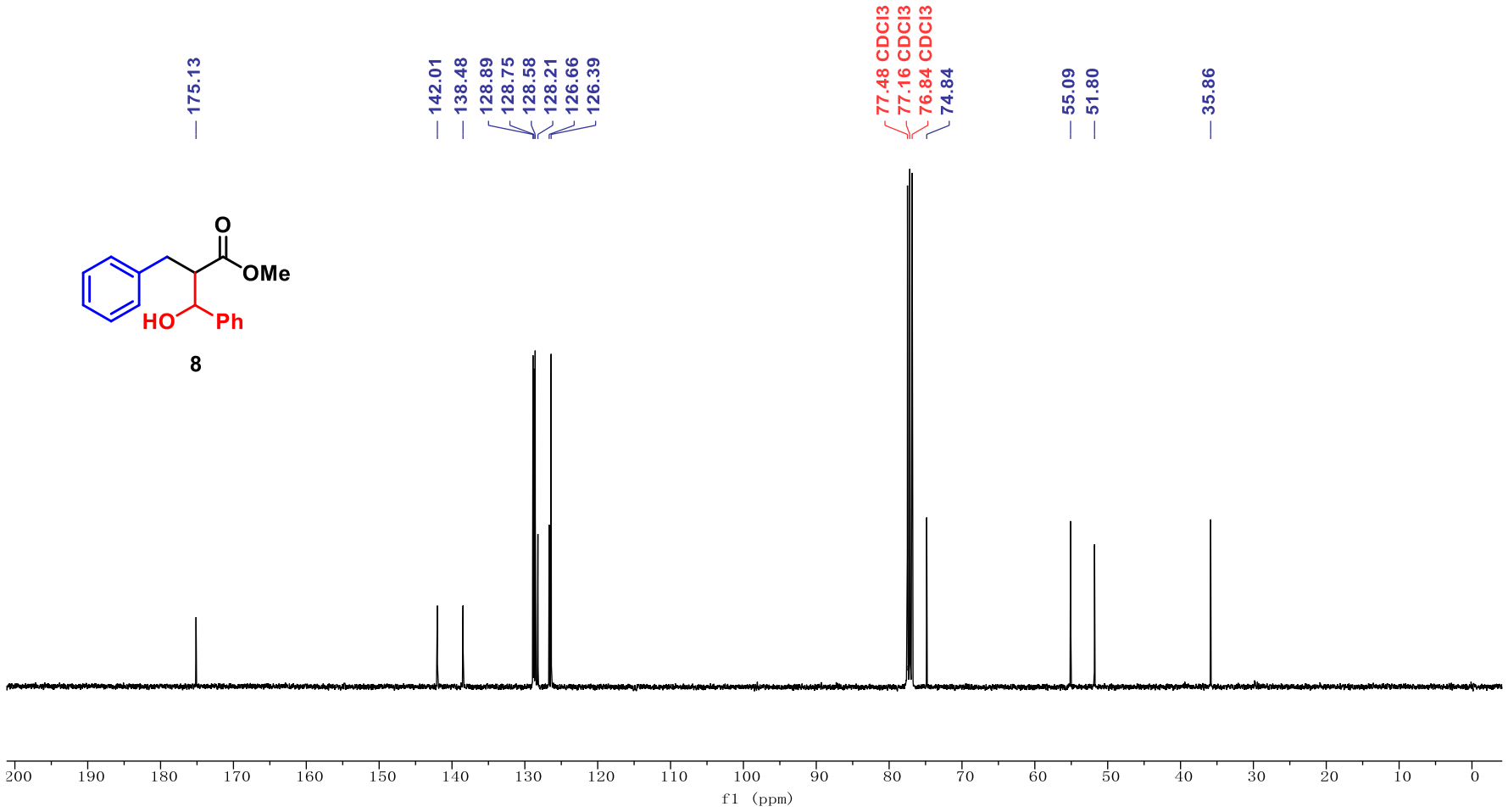
^{13}C NMR of 8 (One isomer) (101 MHz, $CDCl_3$)



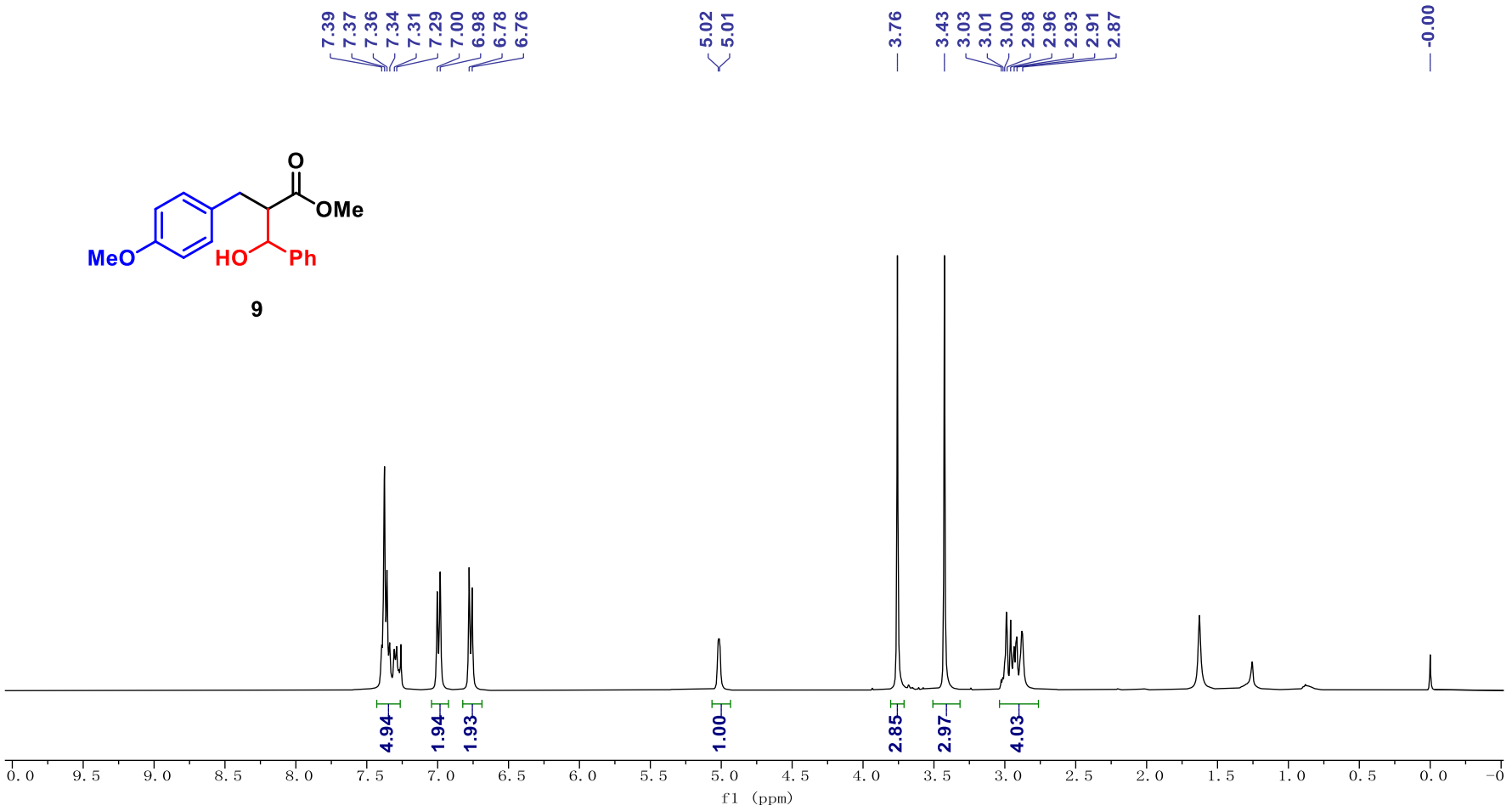
^{1}H NMR of 8 (Another isomer) (400 MHz, $CDCl_3$)



^{13}C NMR of 8 (Another isomer) ($CDCl_3$, 101 MHz)



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



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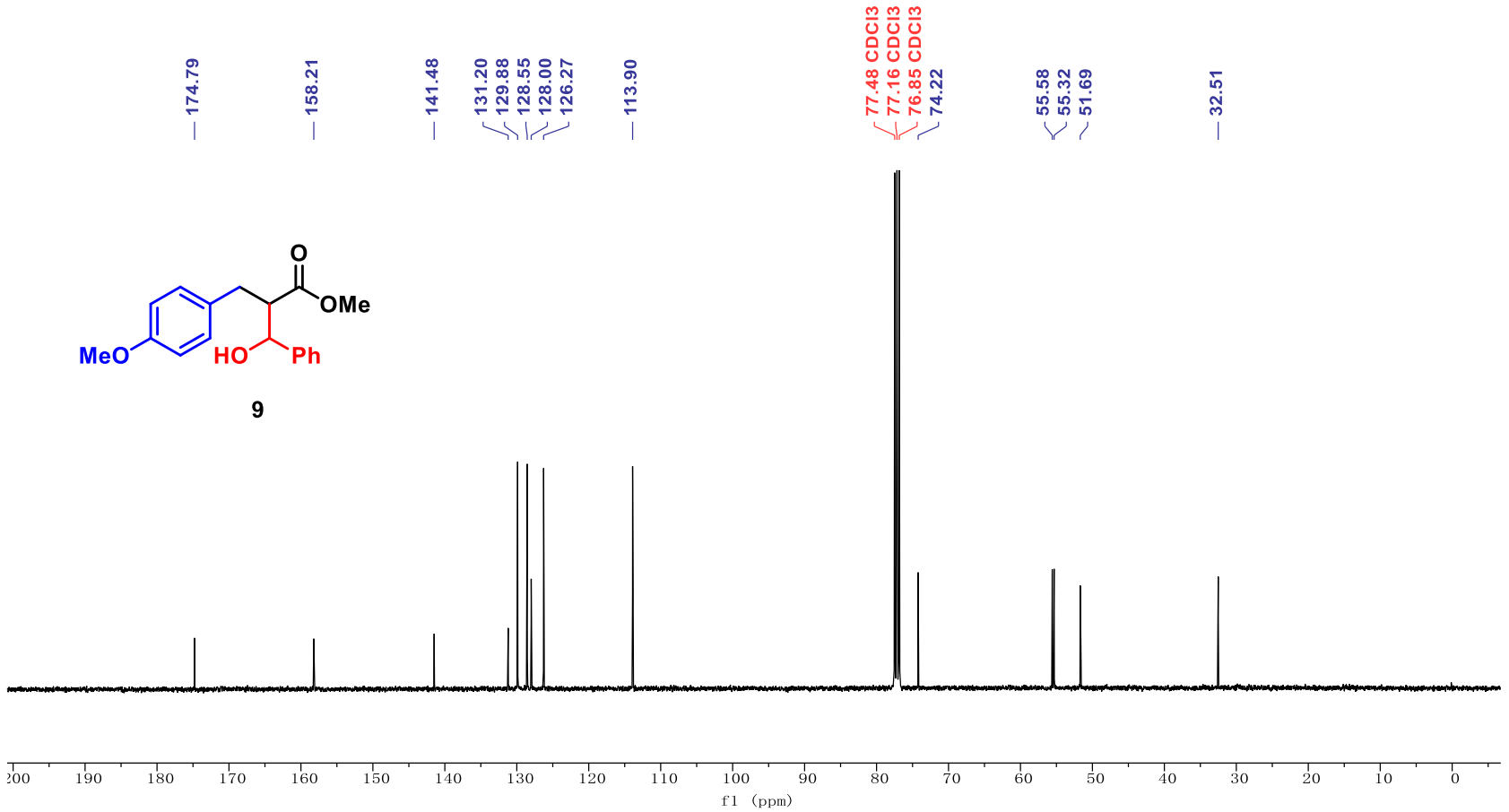
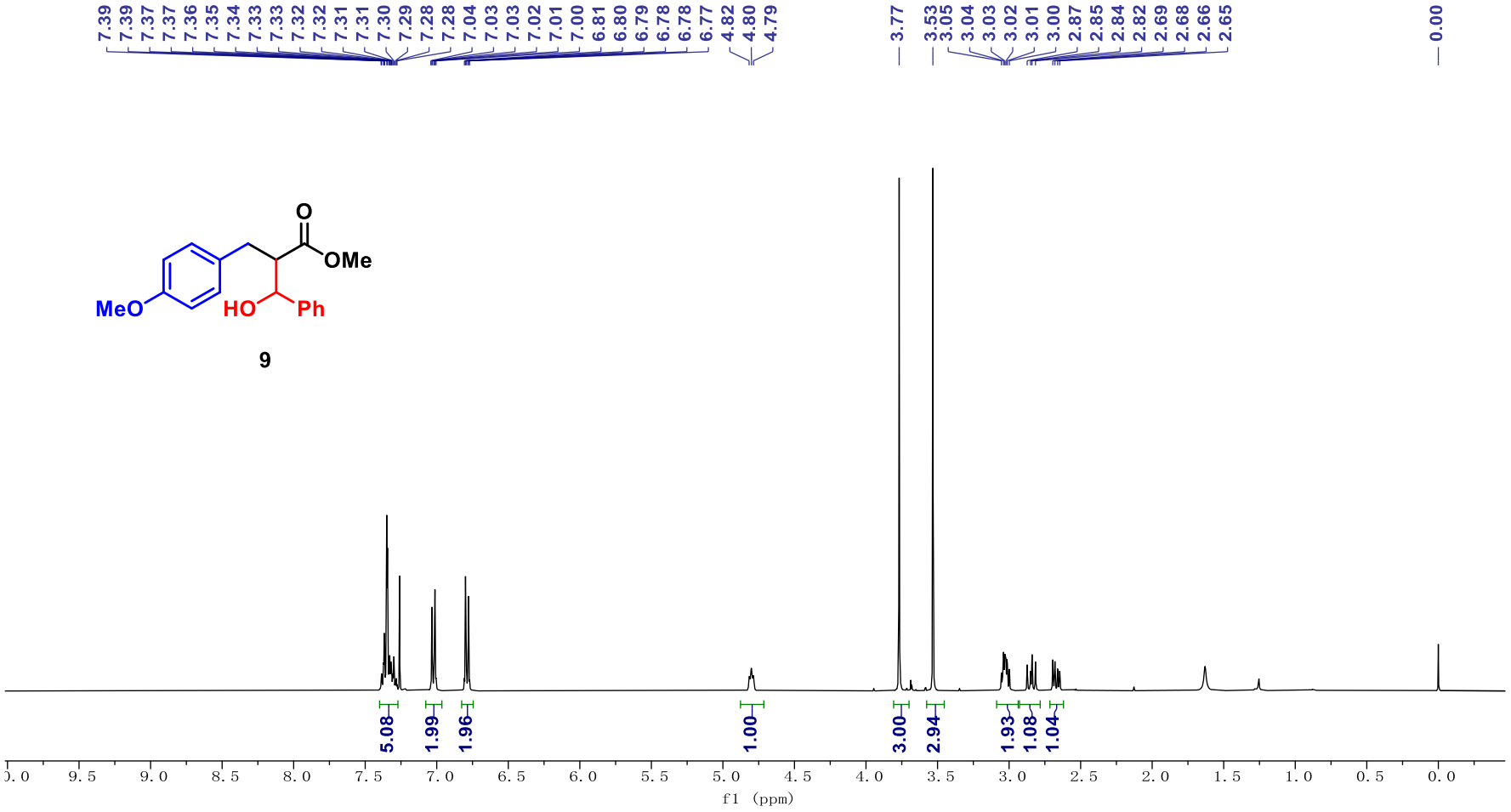
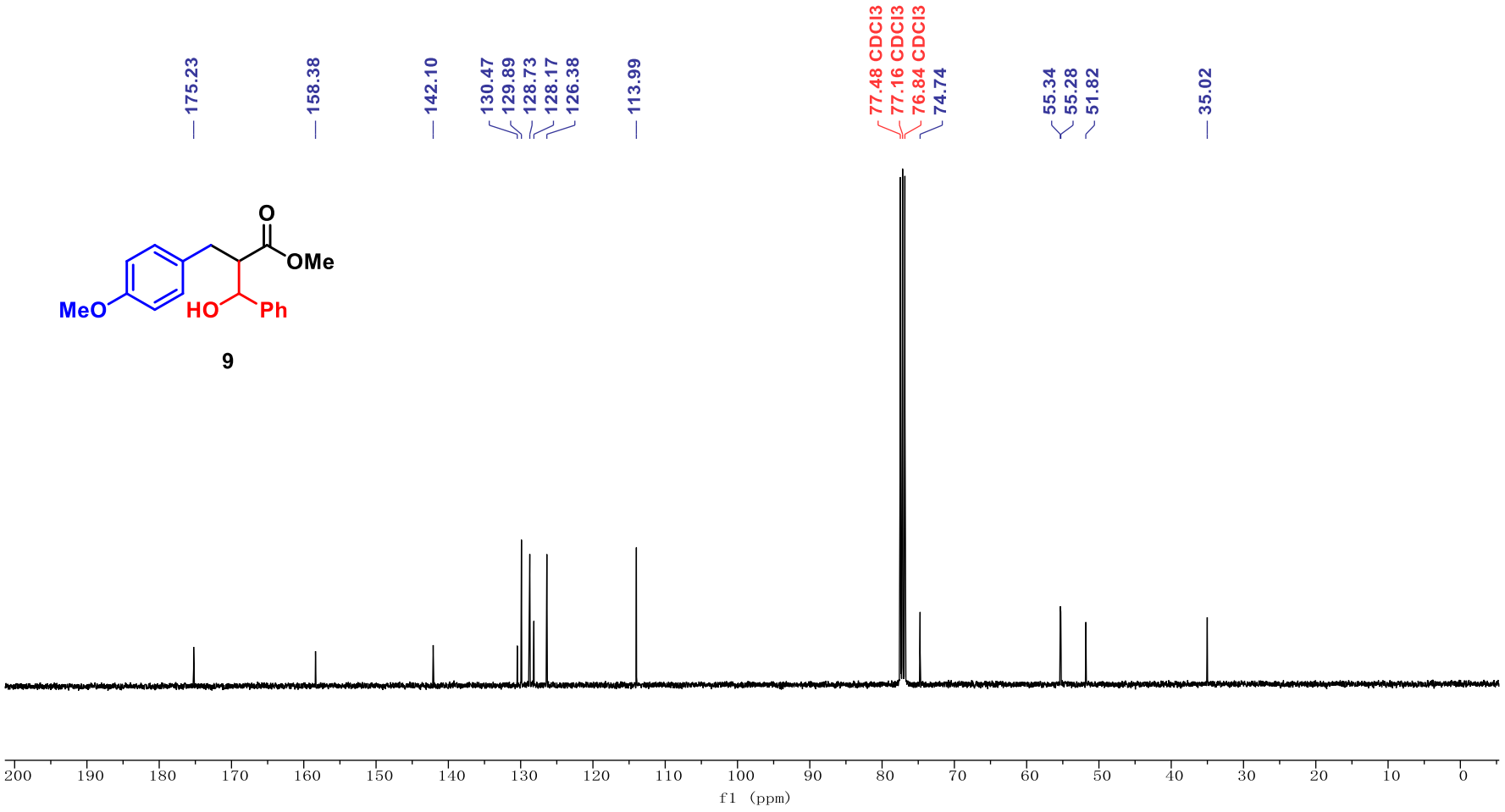
^{13}C NMR of 9 (One isomer) (101 MHz, $CDCl_3$)



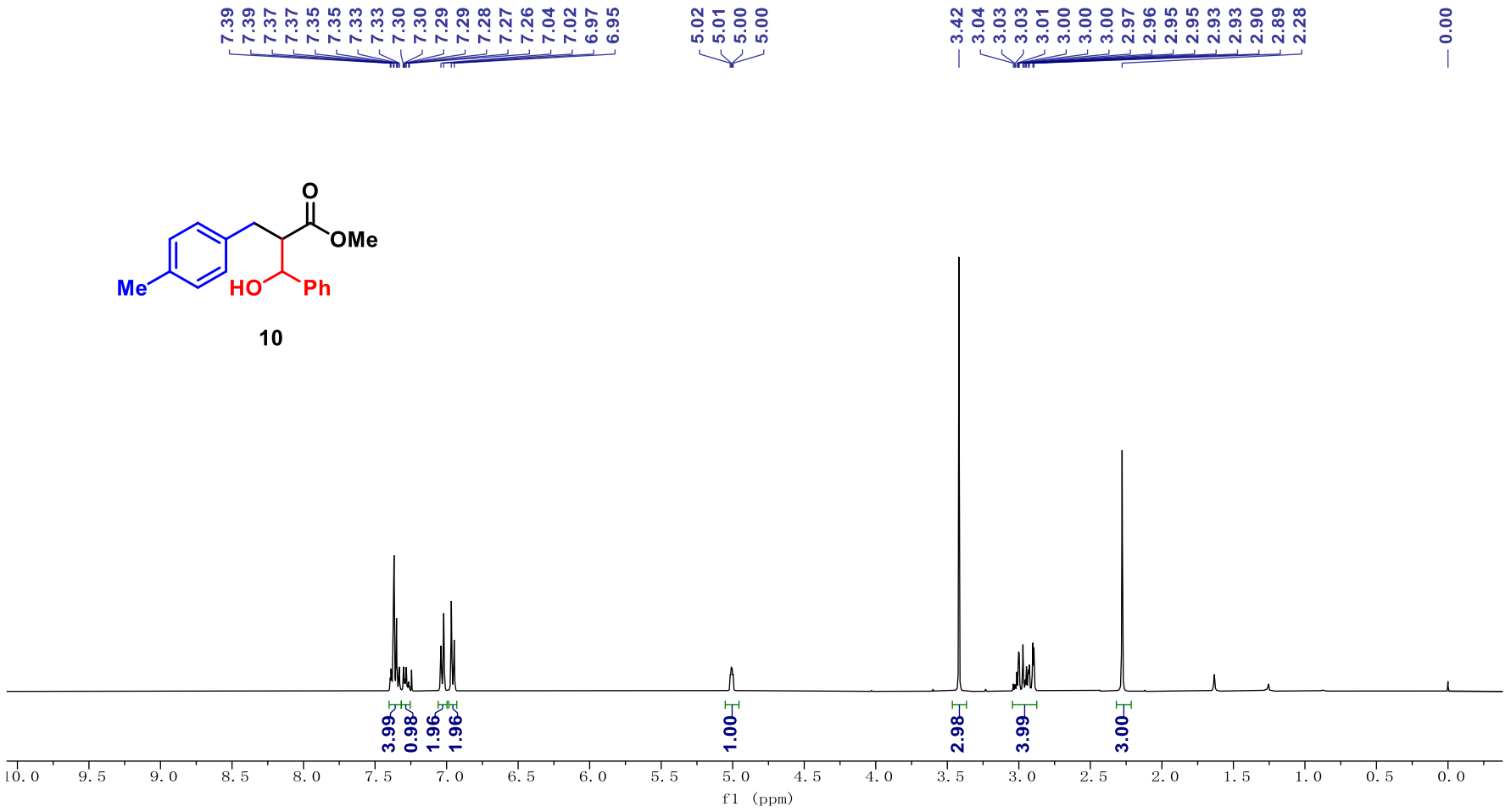
^{1}H NMR of 9 (Another isomer) (400 MHz, $CDCl_3$)



^{13}C NMR of 9 (Another isomer) (101 MHz, $CDCl_3$)



^{1}H NMR of 10 (One isomer) (400 MHz, $CDCl_3$)



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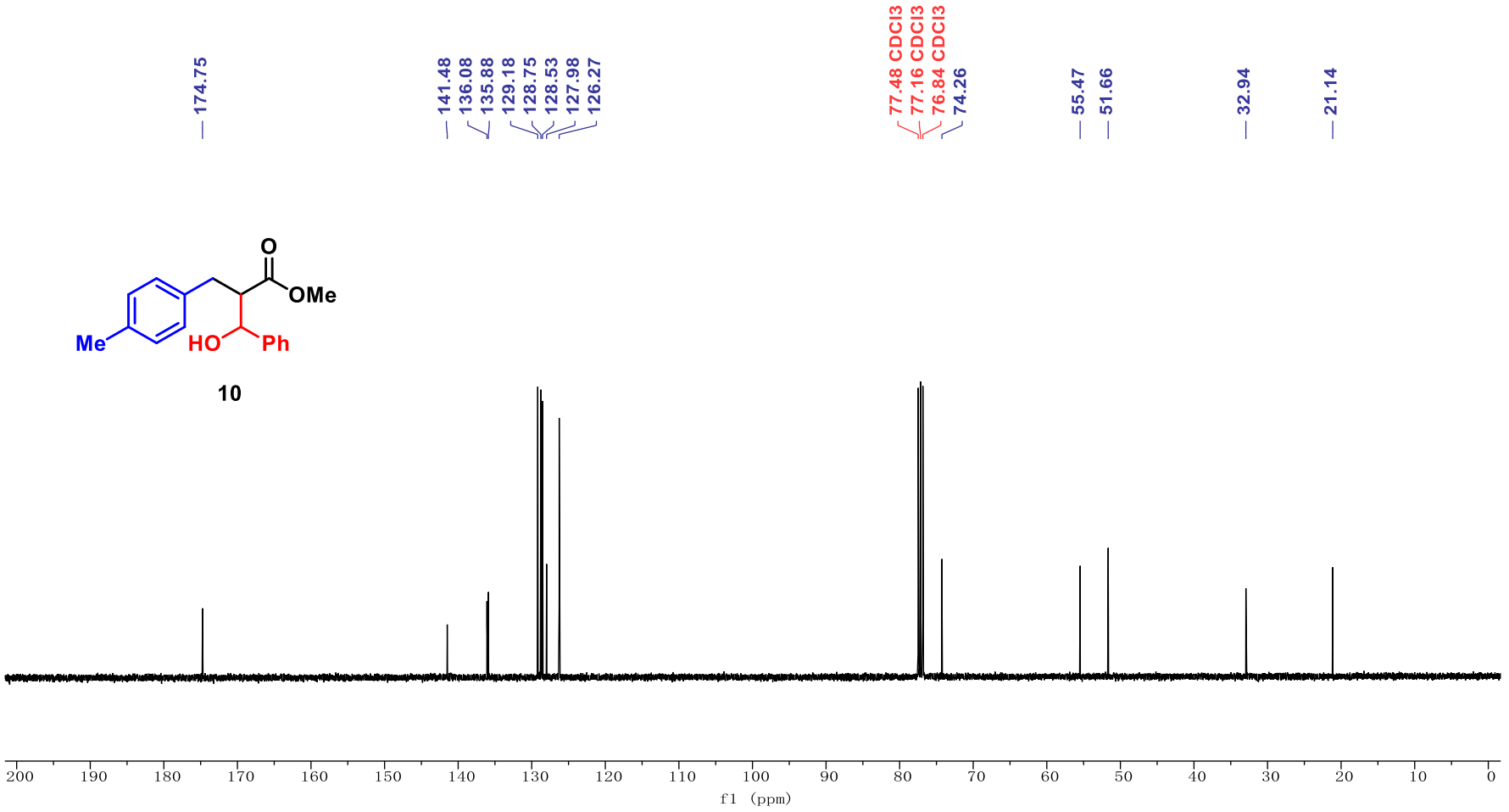
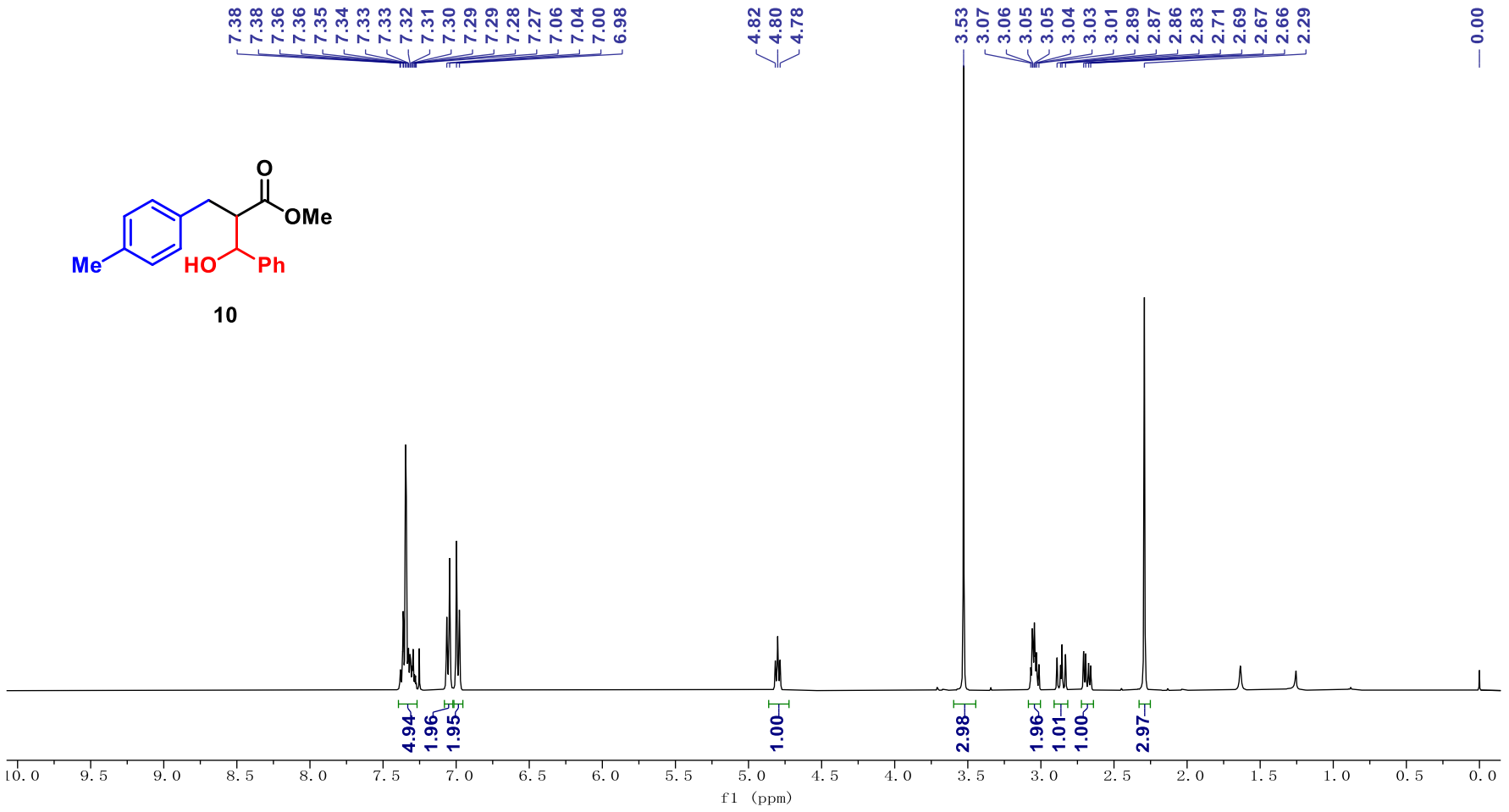
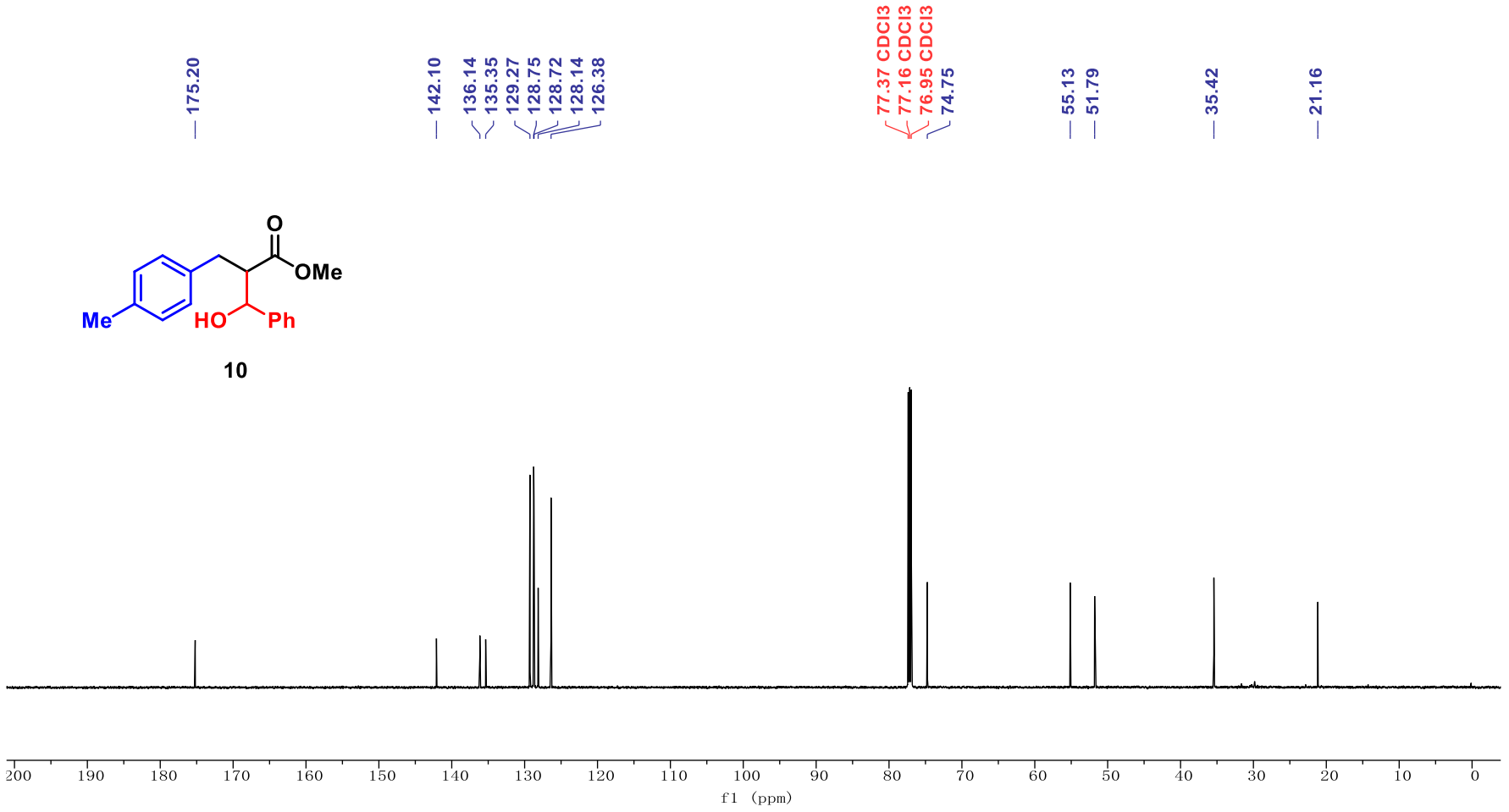


^{1}H NMR of 10 (Another isomer) (400 MHz, $CDCl_3$)

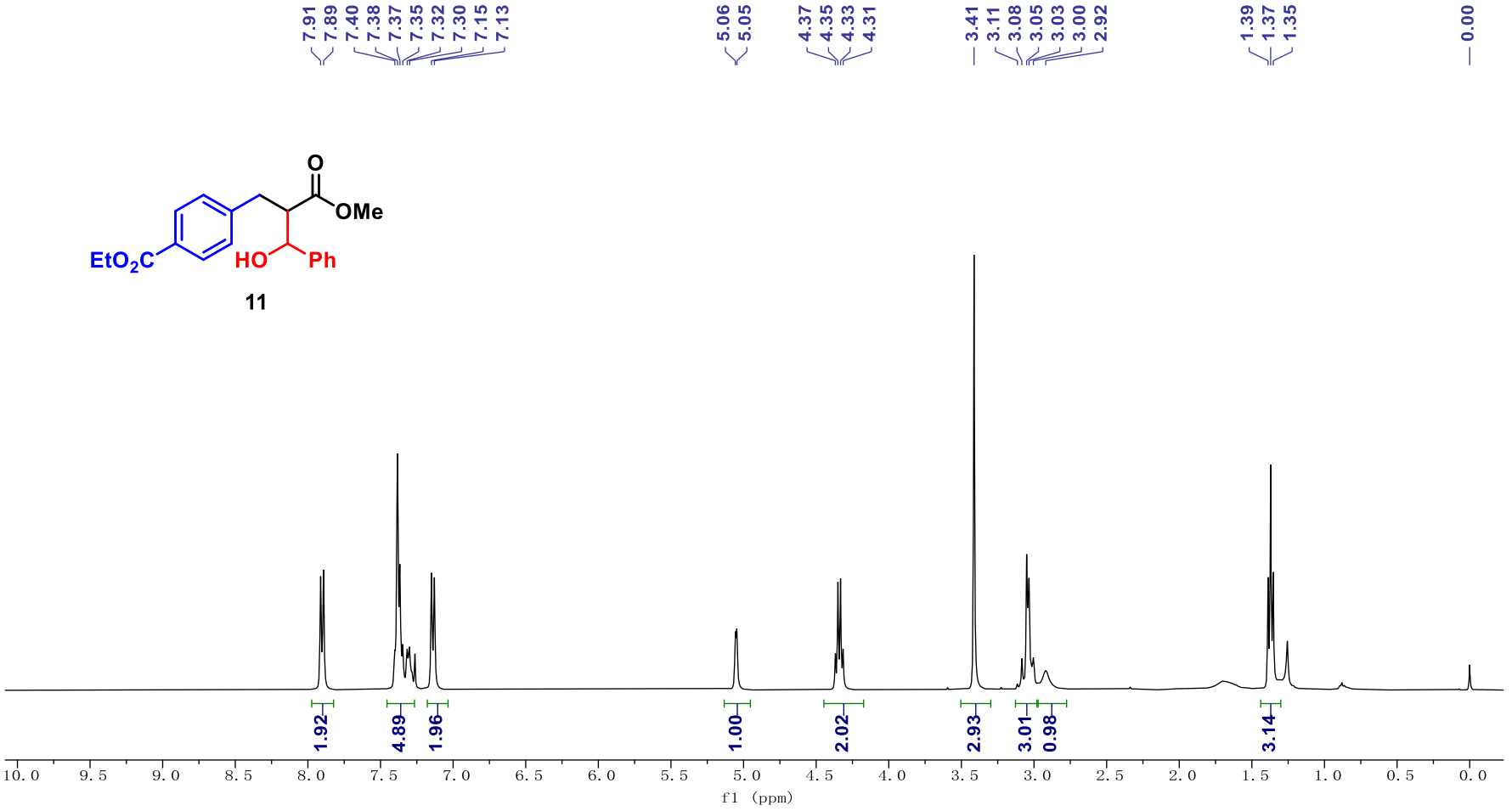


10

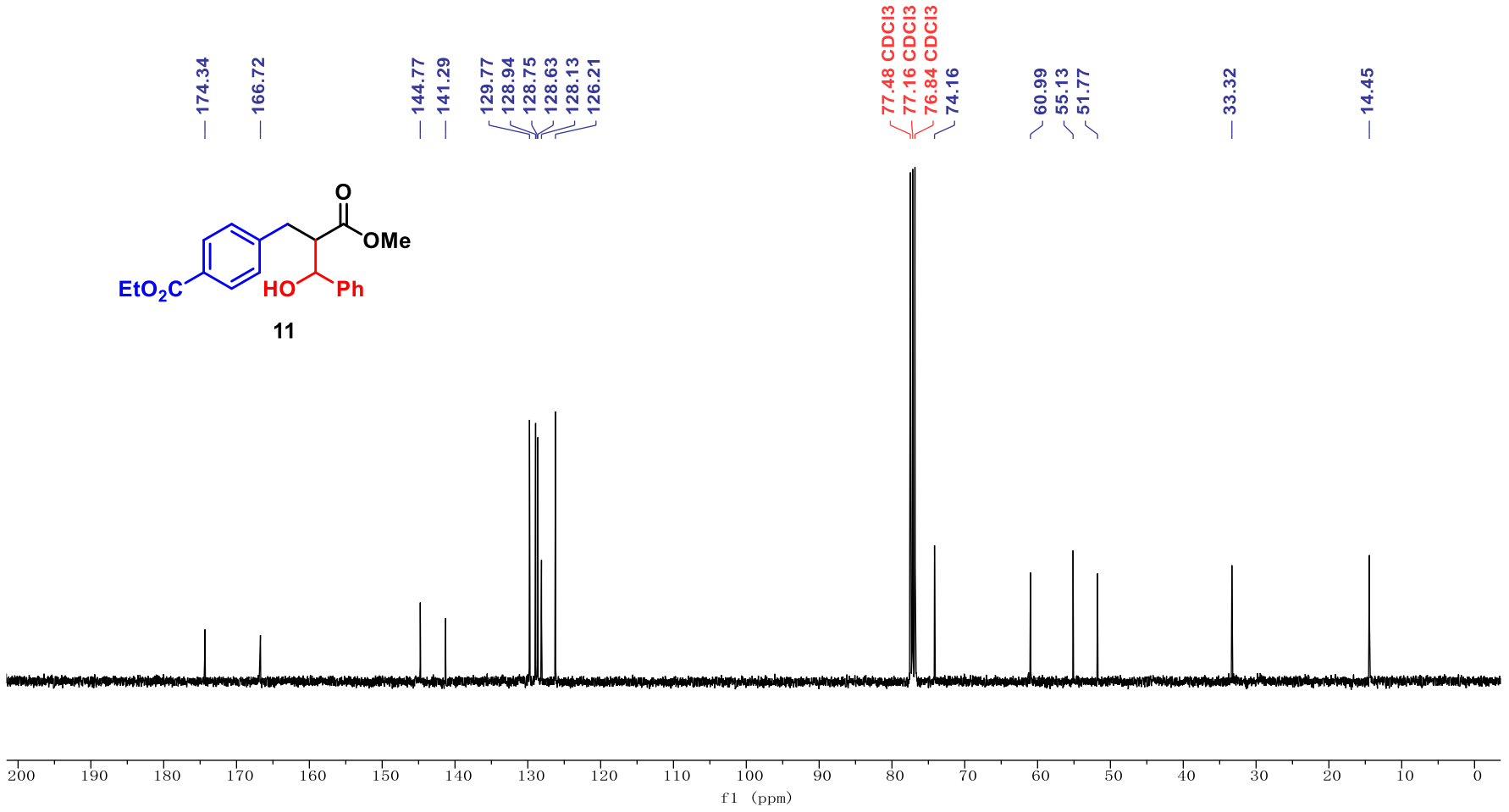
^{13}C NMR of 10 (Another isomer) (151 MHz, $CDCl_3$)



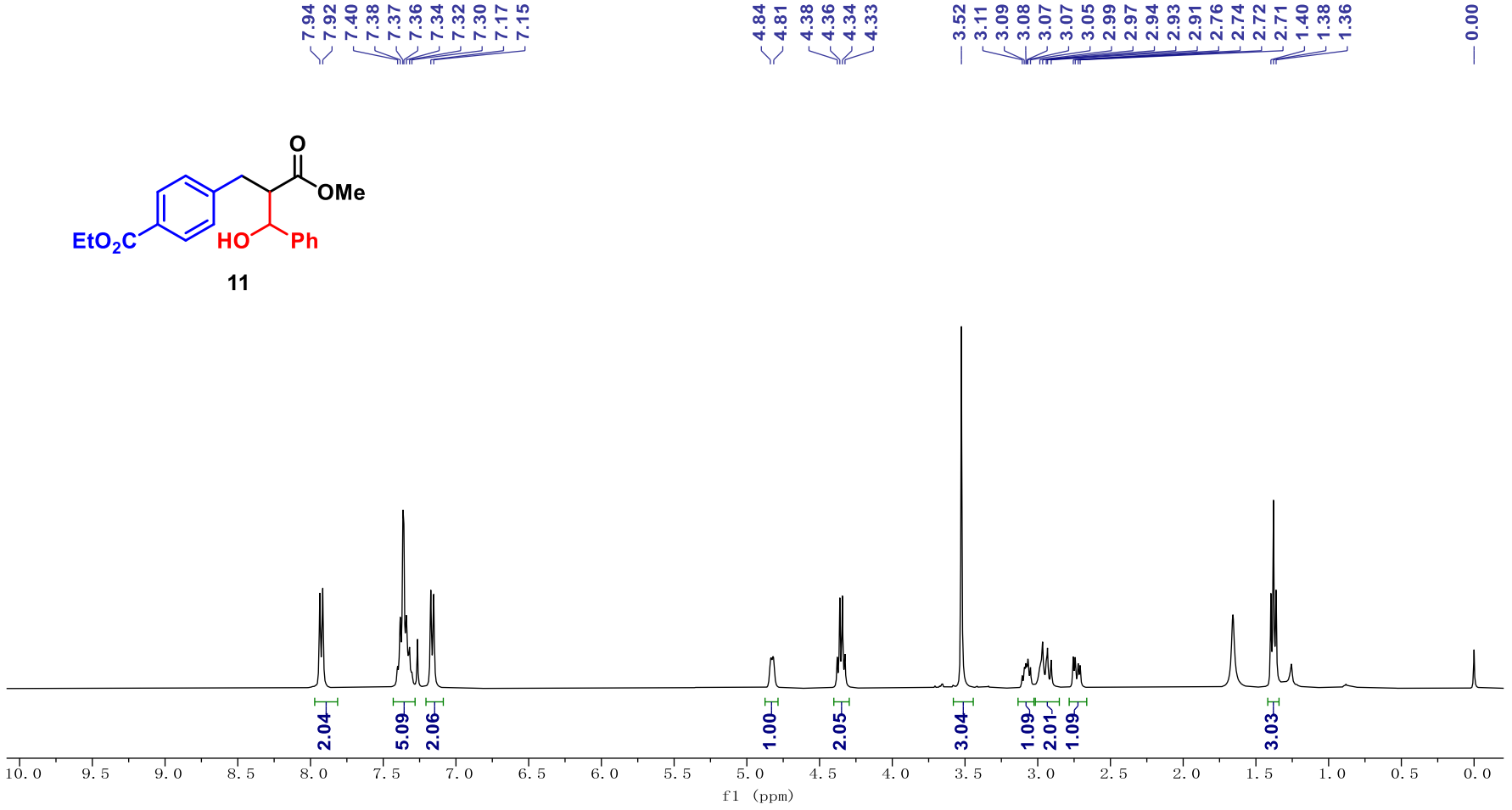
^{1}H NMR of 11 (One isomer) (400 MHz, $CDCl_3$)



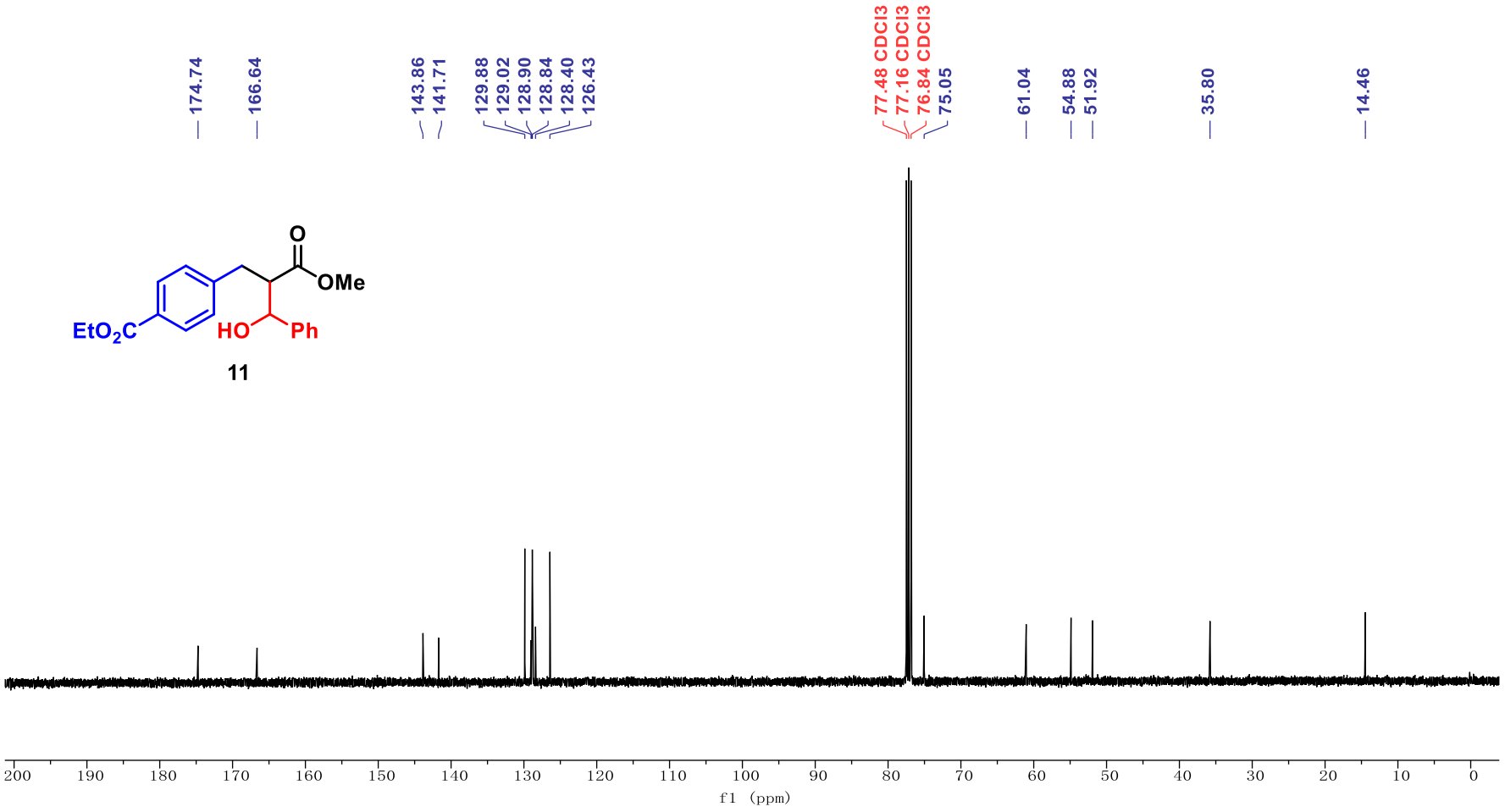
^{13}C NMR of 11 (One isomer) (101 MHz, $CDCl_3$)



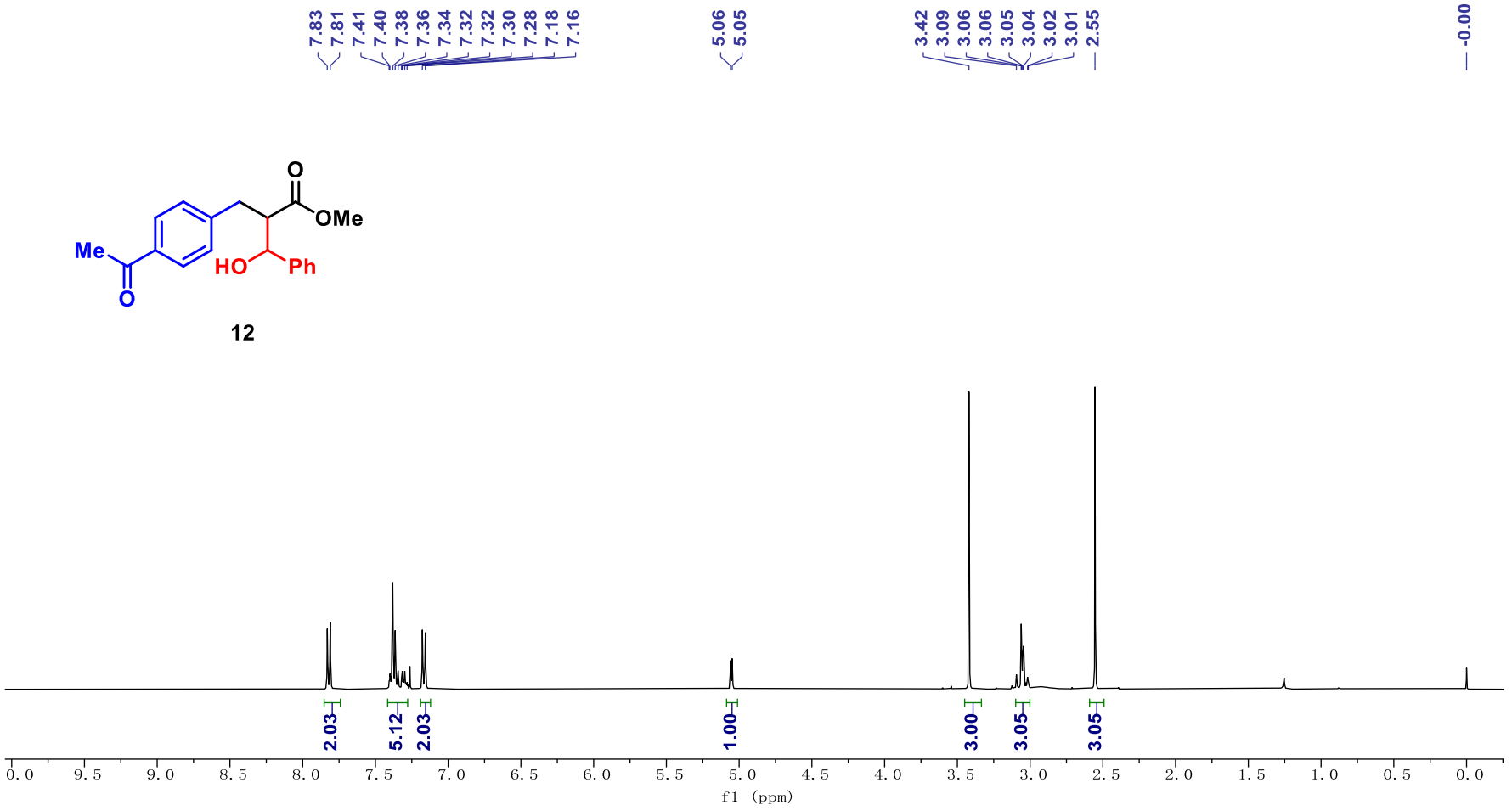
^{1}H NMR of 11 (Another isomer) (400 MHz, $CDCl_3$)



^{13}C NMR of 11 (Another isomer) (101 MHz, $CDCl_3$)

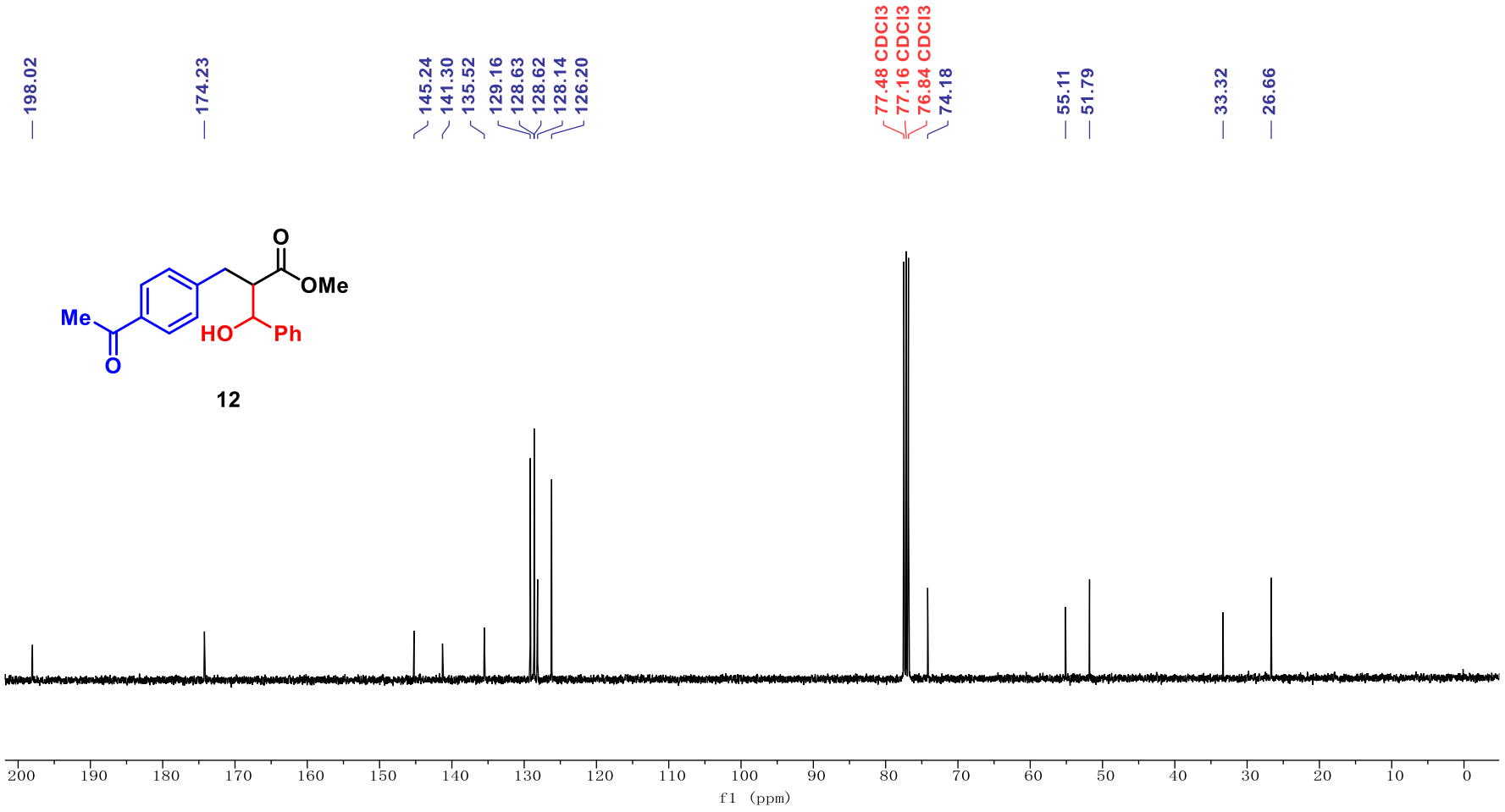


^{1}H NMR of 12 (One isomer) (400 MHz, $CDCl_3$)

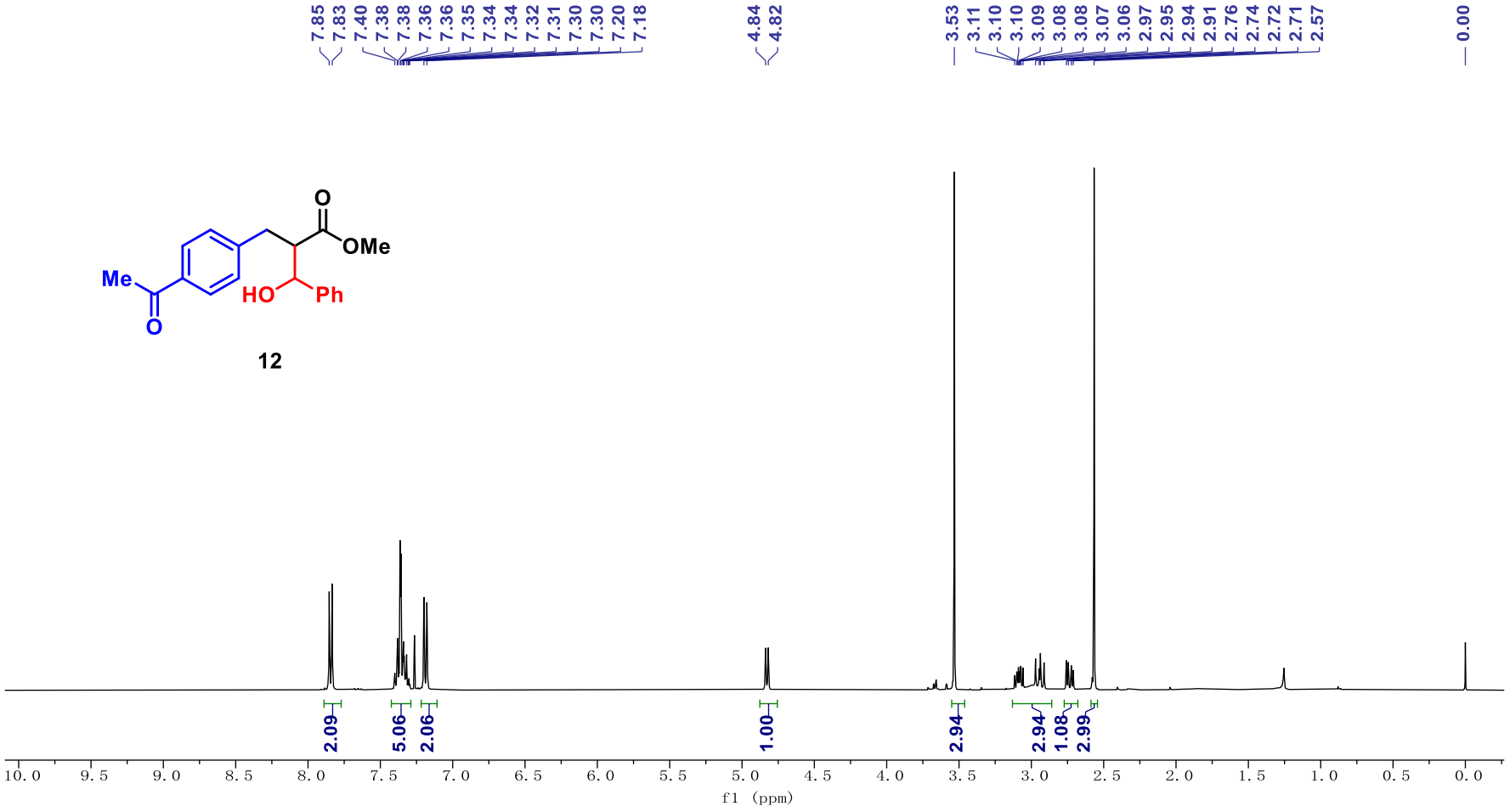


12

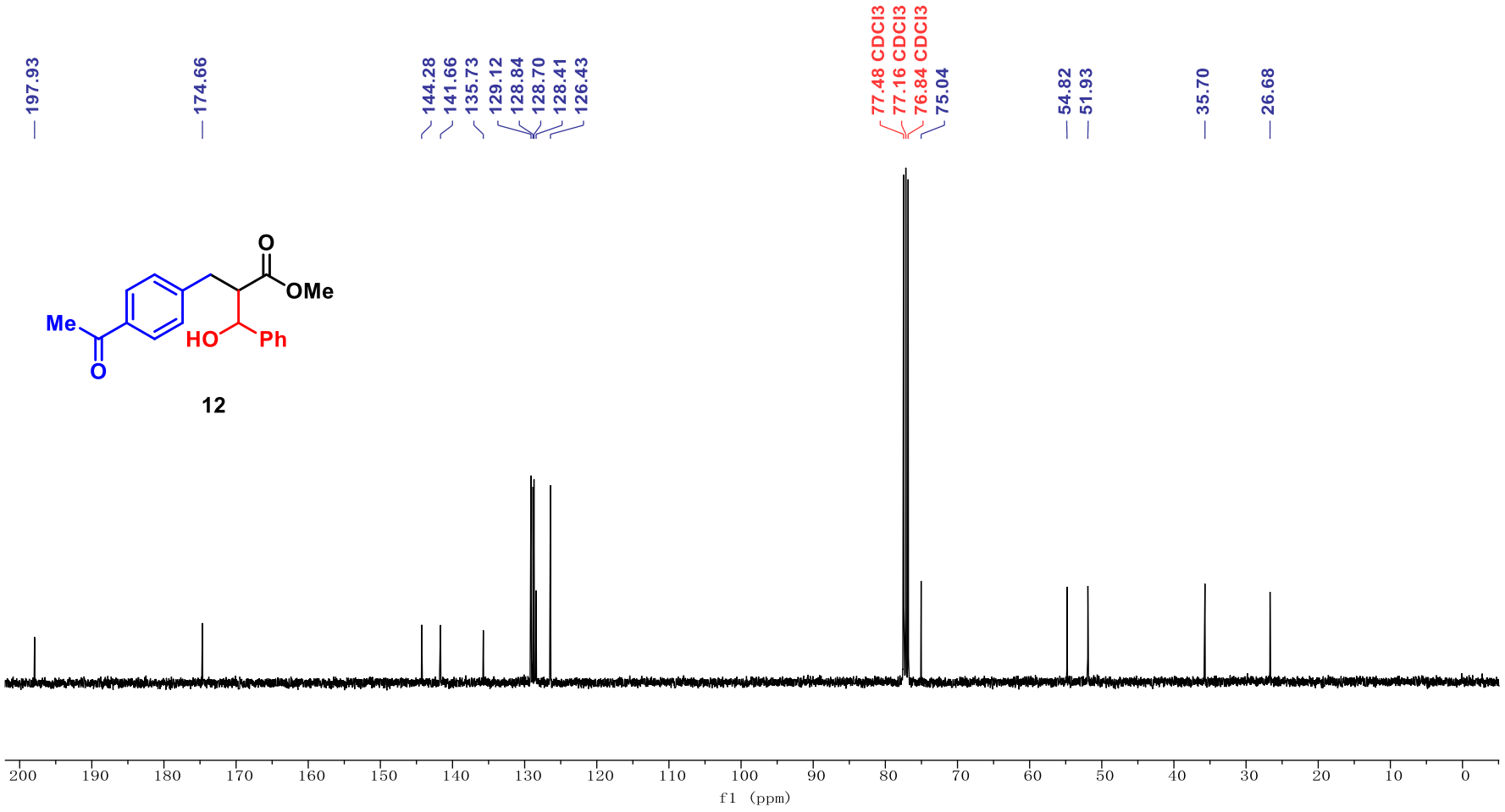
^{13}C NMR of 12 (One isomer) (101 MHz, $CDCl_3$)



^{1}H NMR of 12 (Another isomer) (400 MHz, $CDCl_3$)



^{13}C NMR of 12 (Another isomer) (101 MHz, $CDCl_3$)



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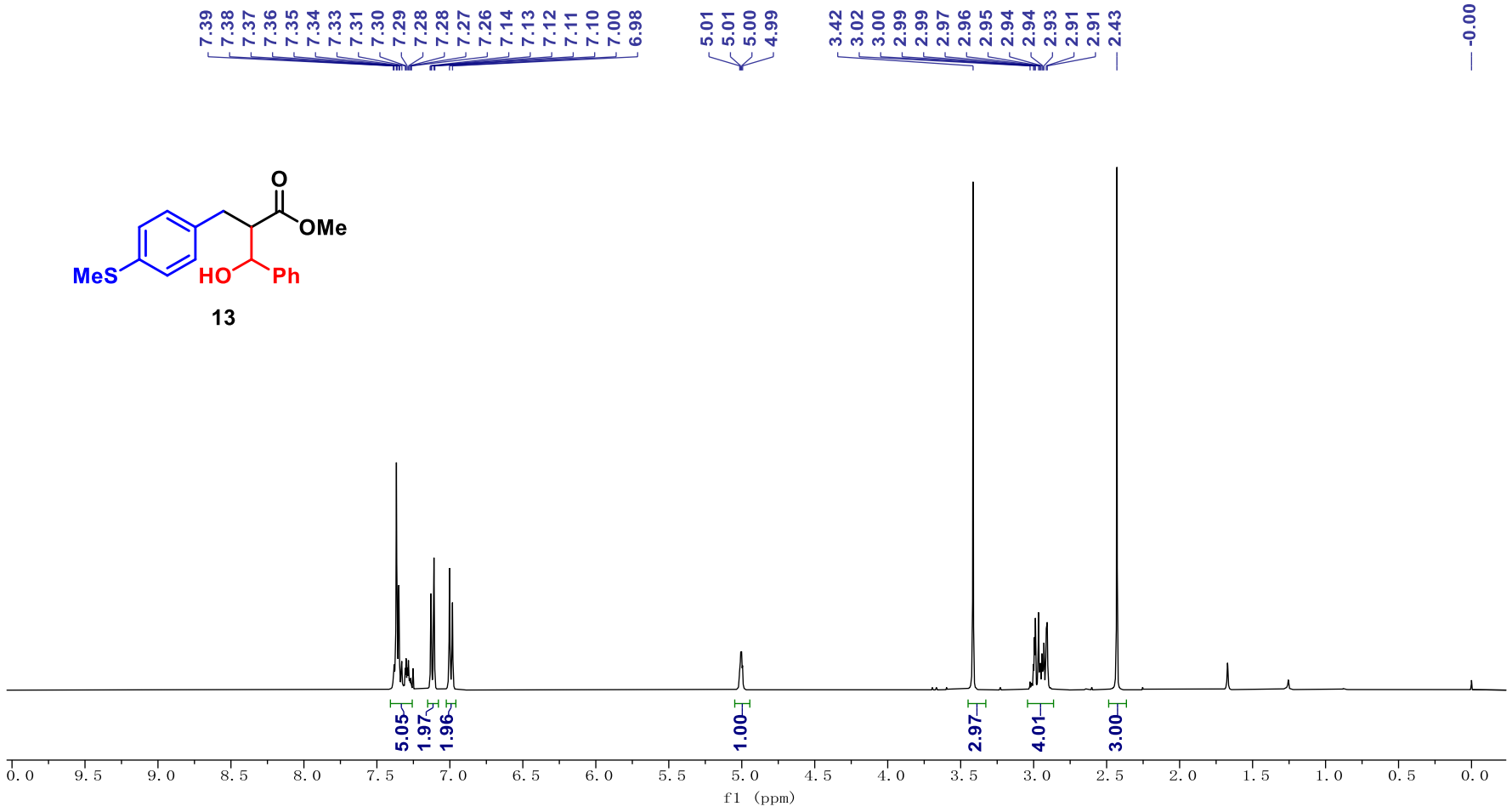
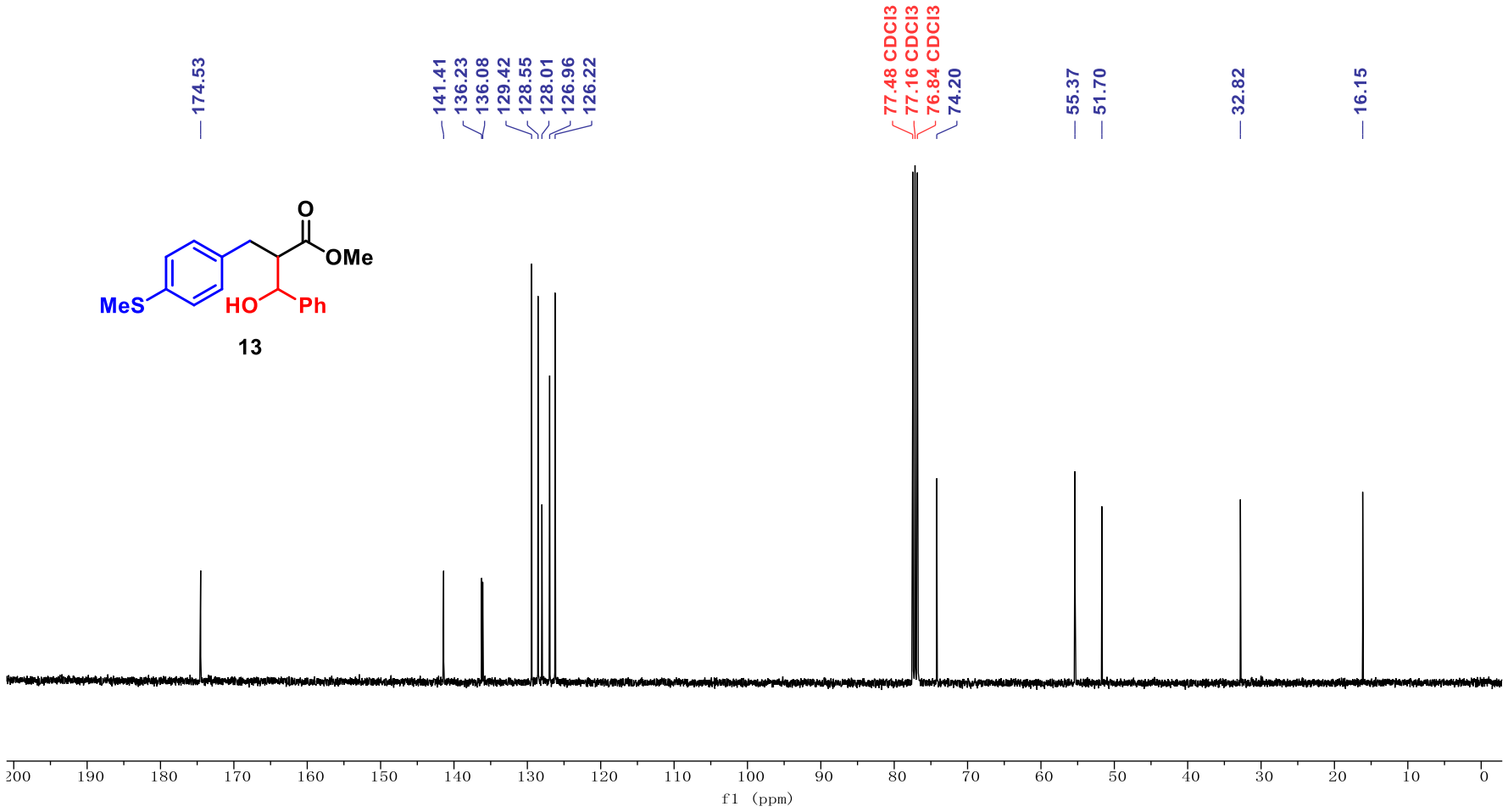
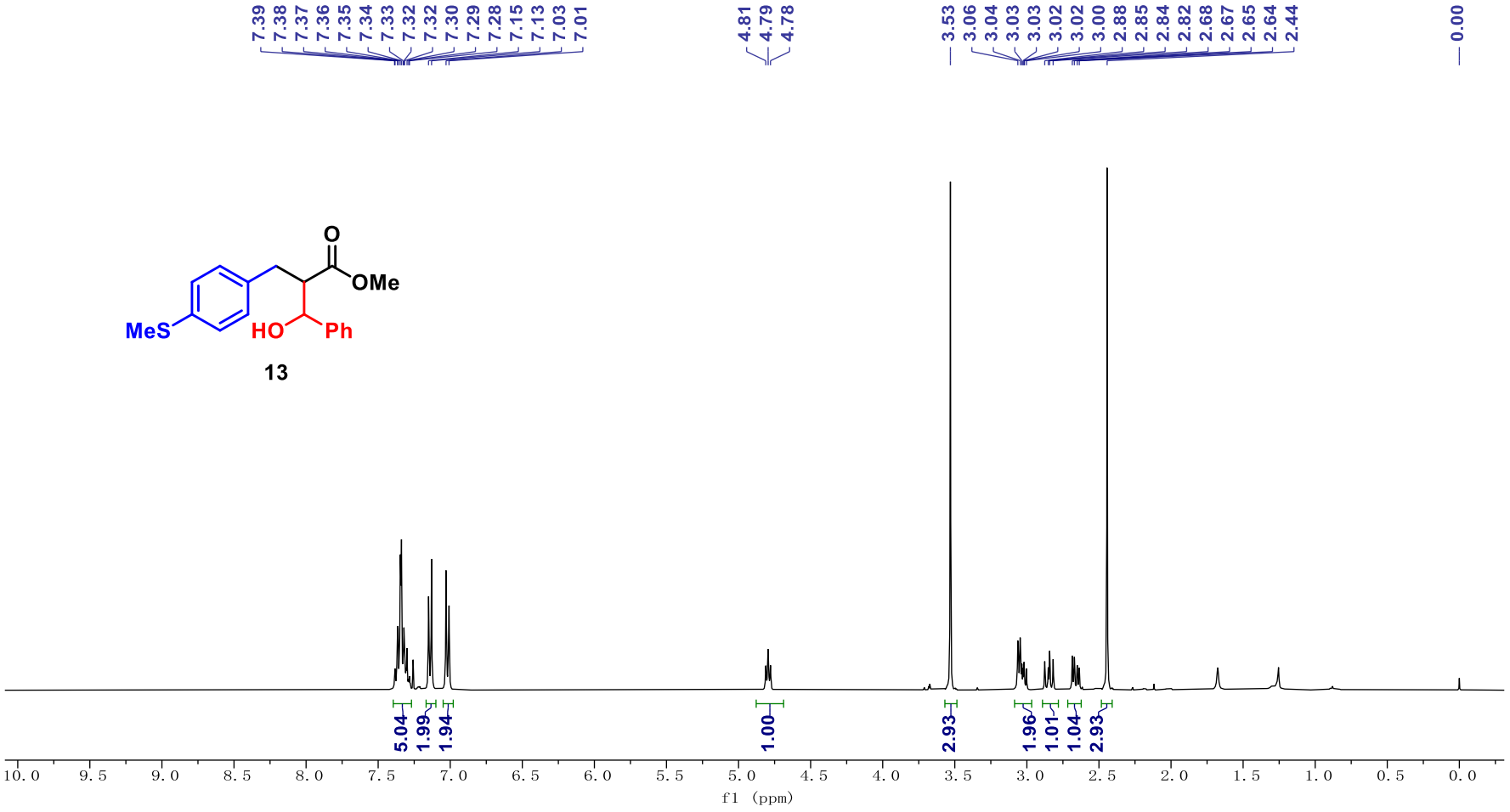


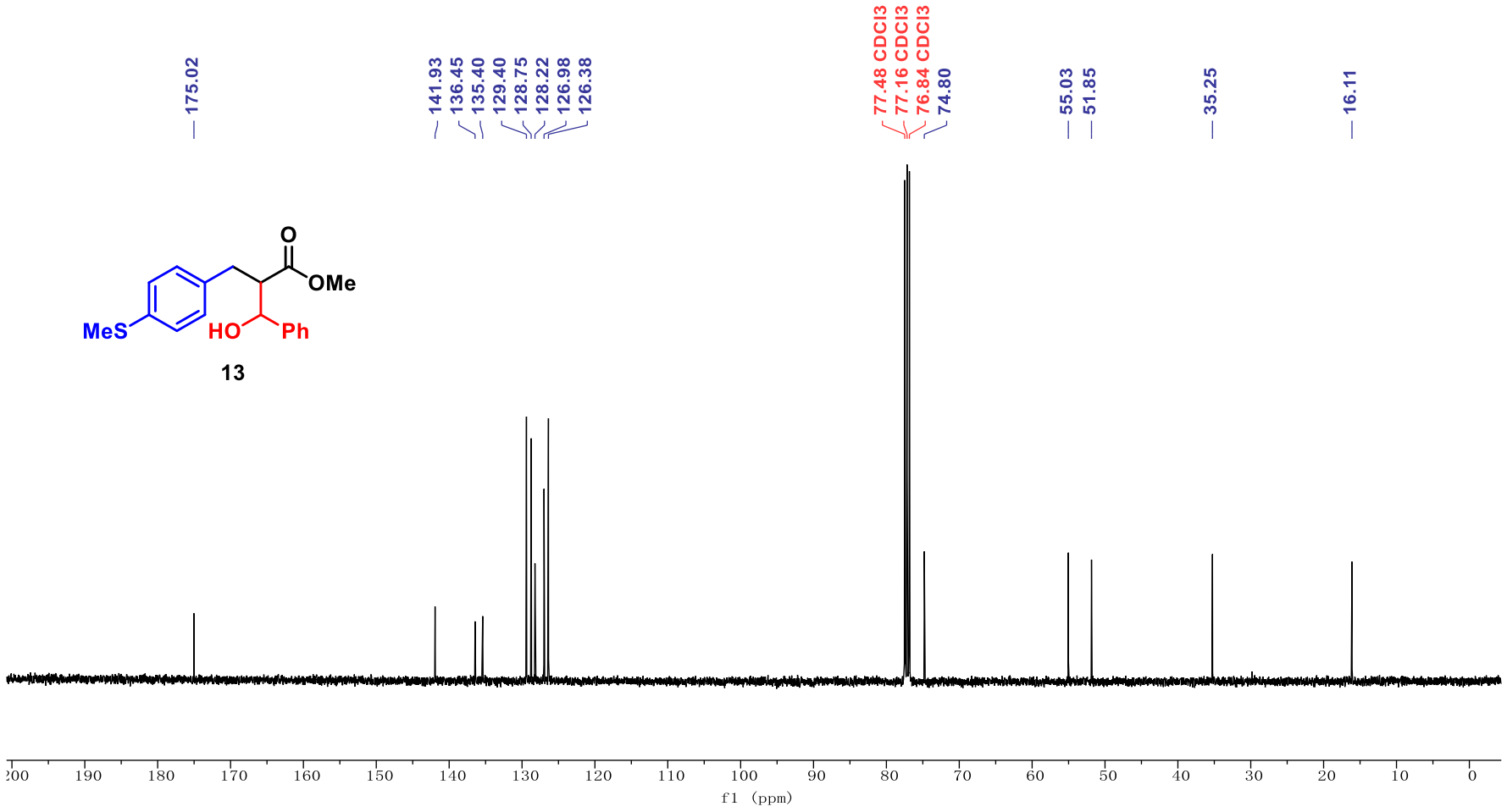
^{13}C NMR of 13 (One isomer) (101 MHz, $CDCl_3$)



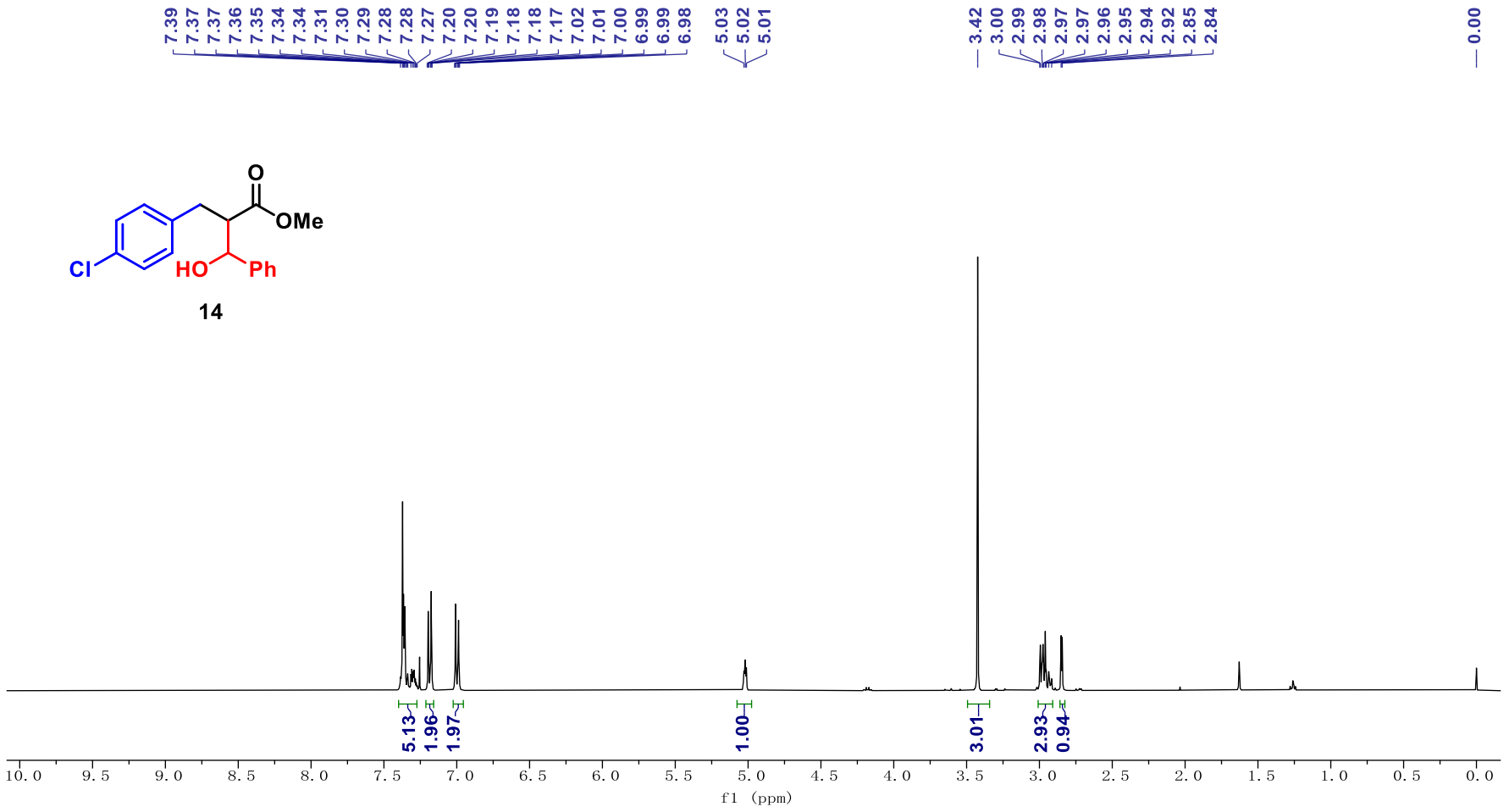
^{1}H NMR of 13 (Another isomer) (400 MHz, $CDCl_3$)



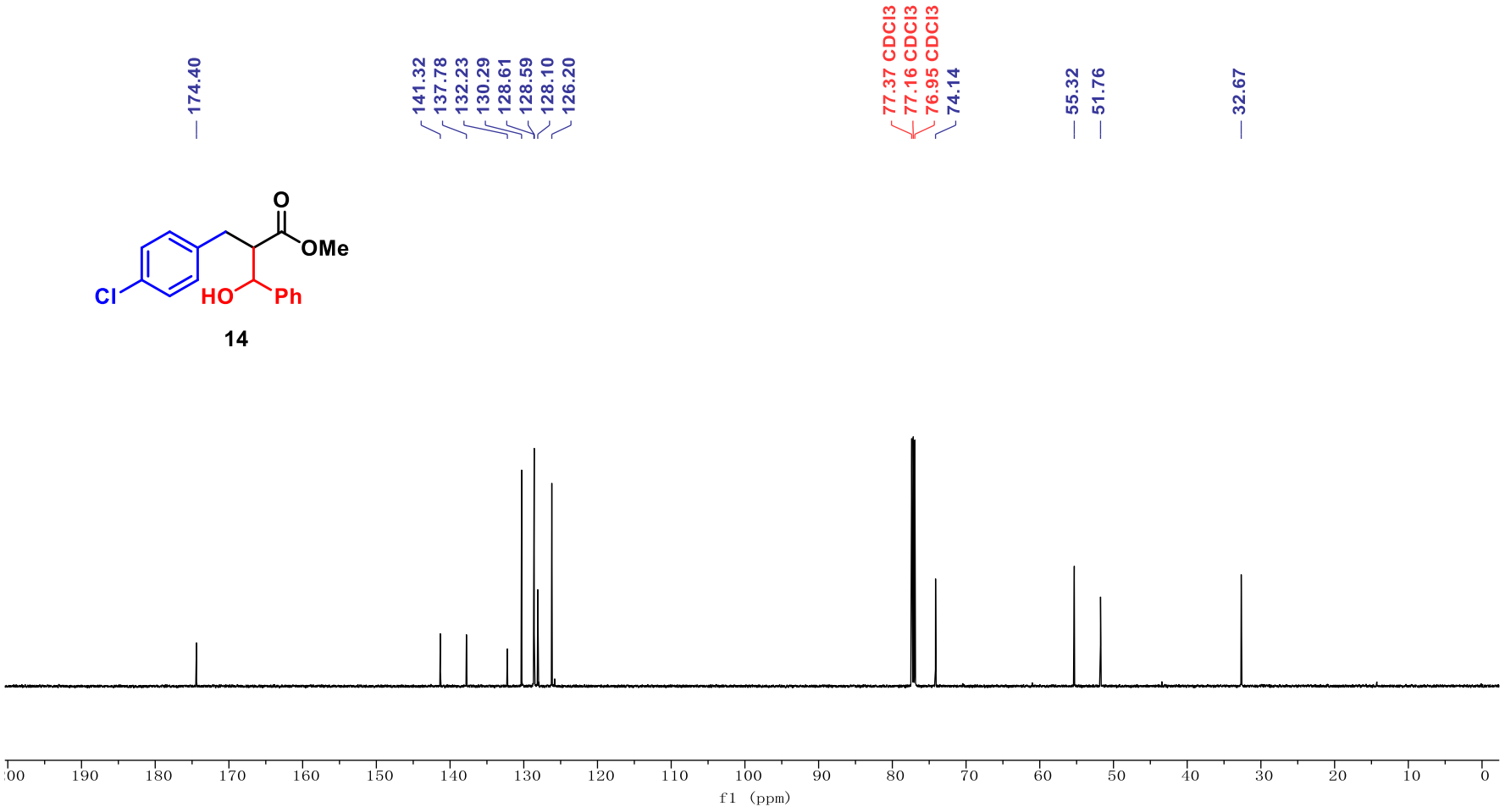
^{13}C NMR of 13 (Another isomer) (101 MHz, $CDCl_3$)



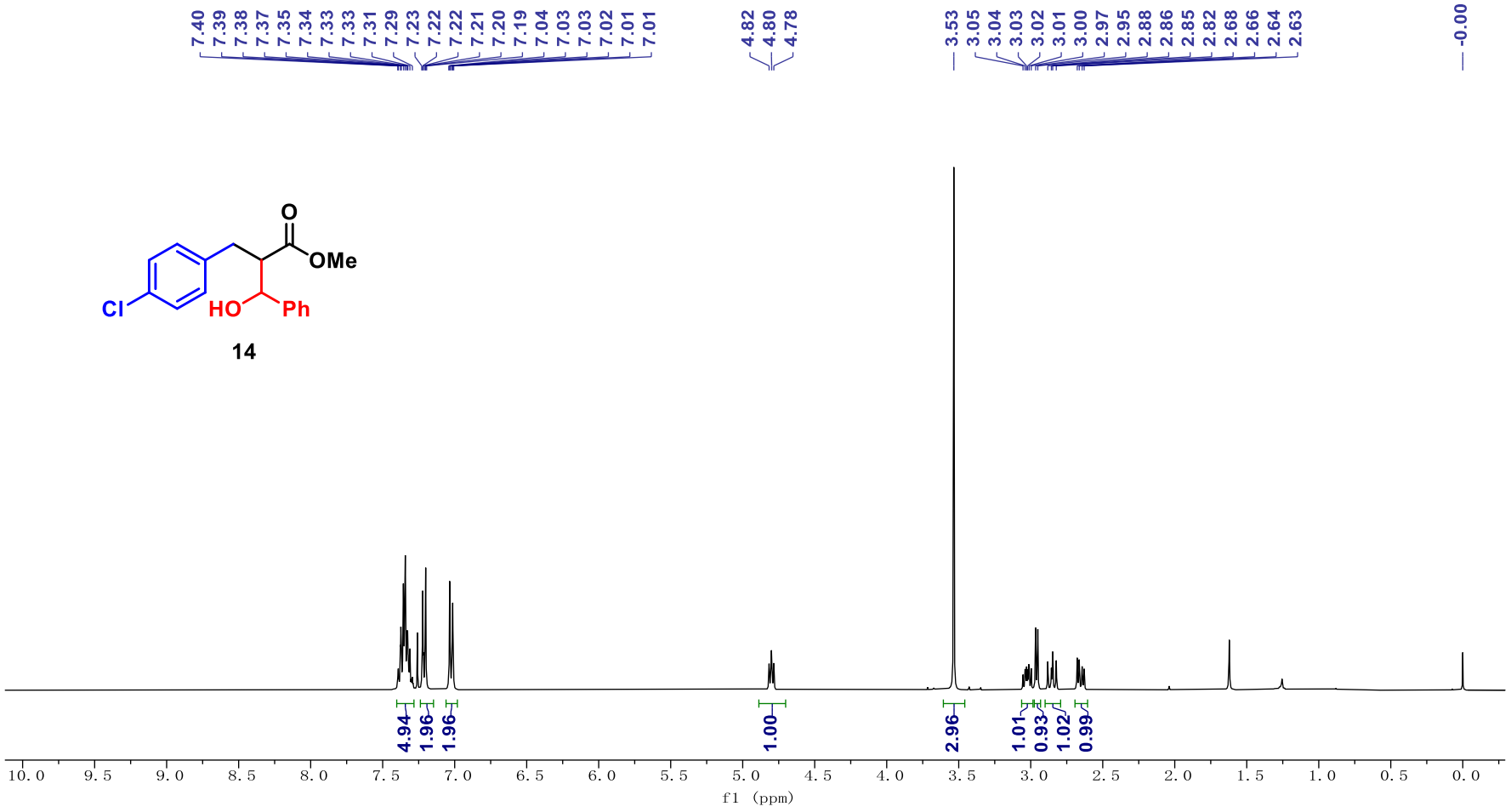
^{1}H NMR of 14 (One isomer) (400 MHz, $CDCl_3$)



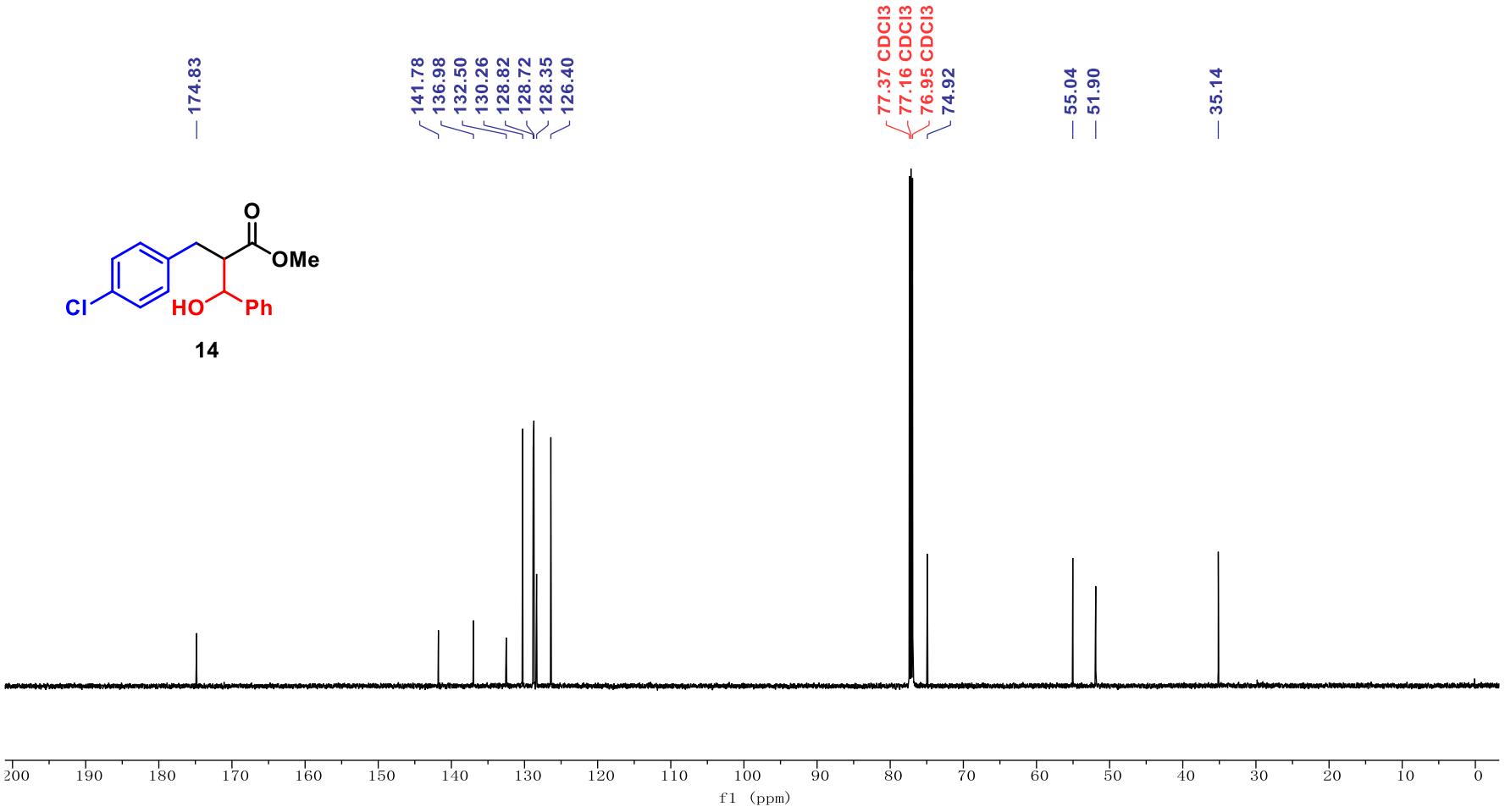
^{13}C NMR of 14 (One isomer) (151 MHz, $CDCl_3$)



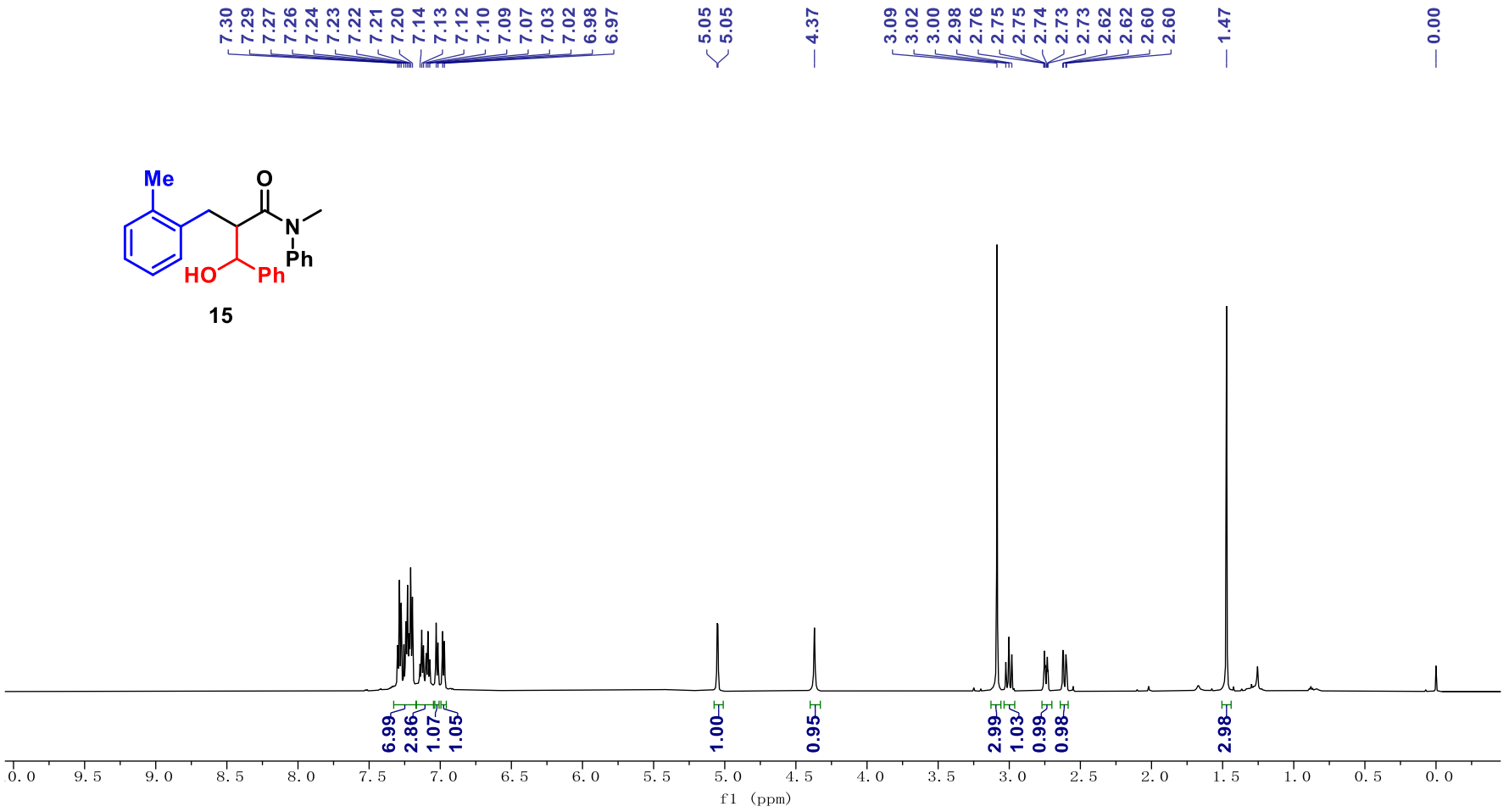
^{1}H NMR of 14 (Another isomer) (400 MHz, $CDCl_3$)



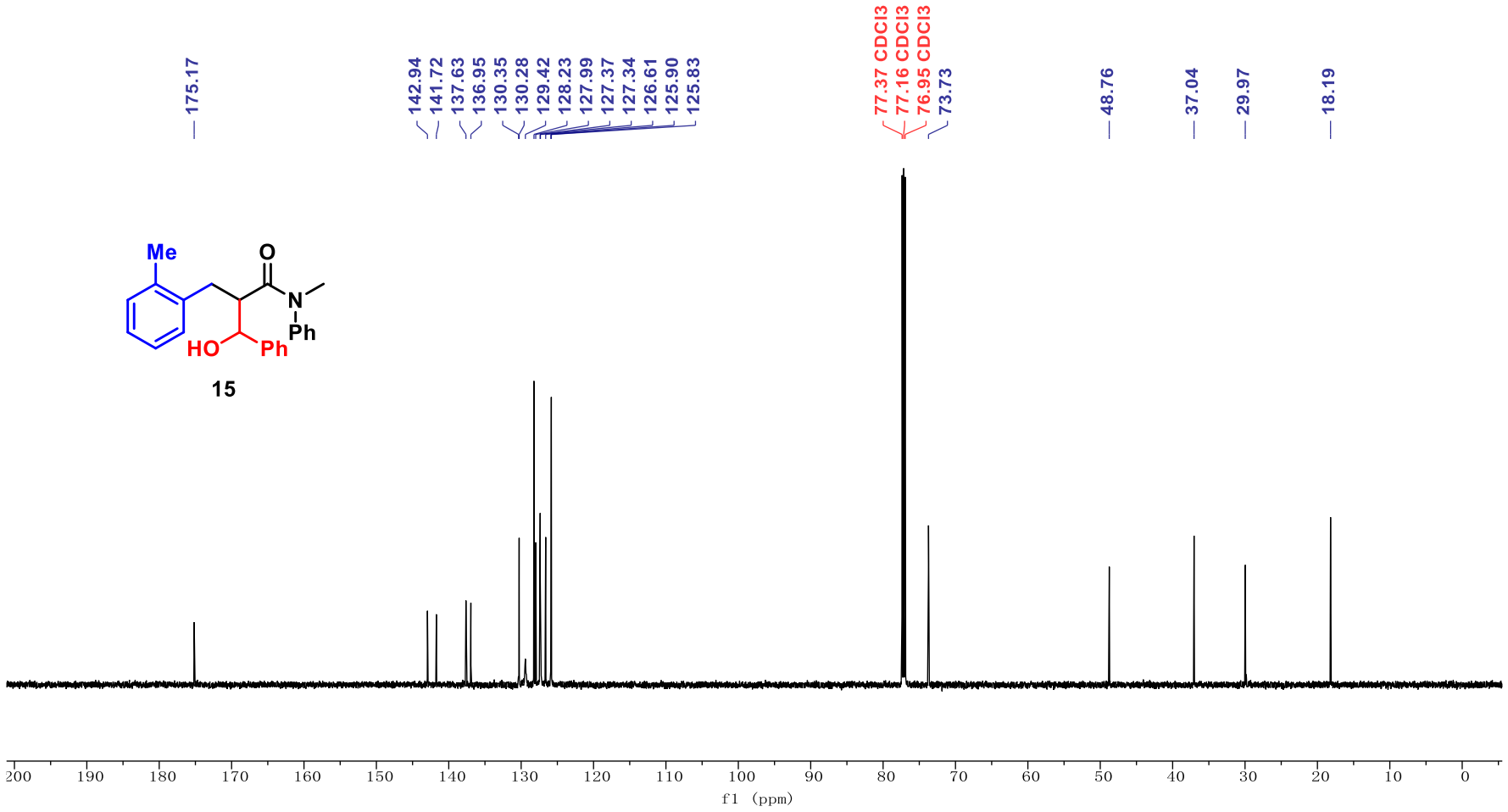
^{13}C NMR of 14 (Another isomer) (151 MHz, $CDCl_3$)



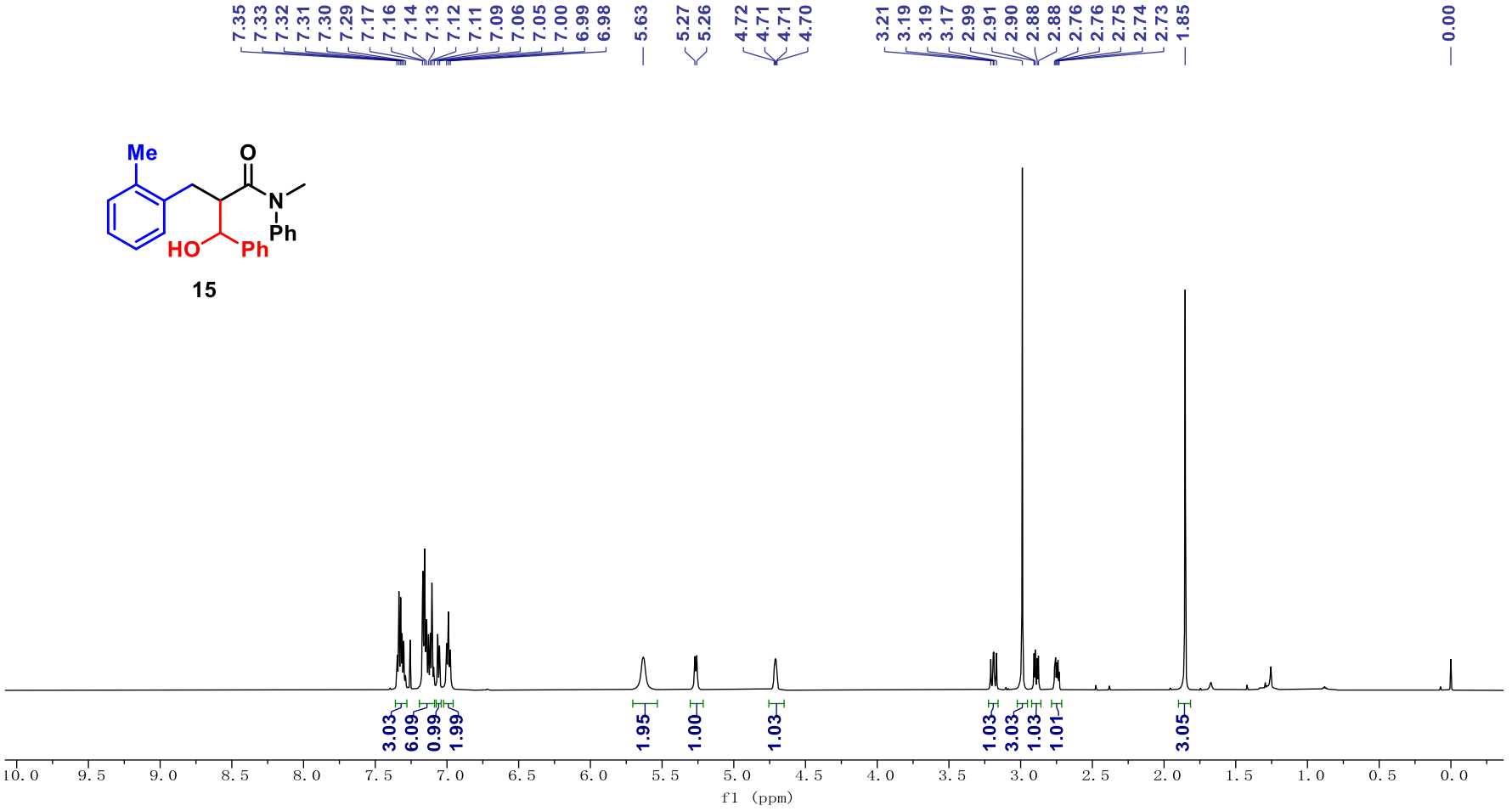
^{1}H NMR of 15 (One isomer) (600 MHz, $CDCl_3$)



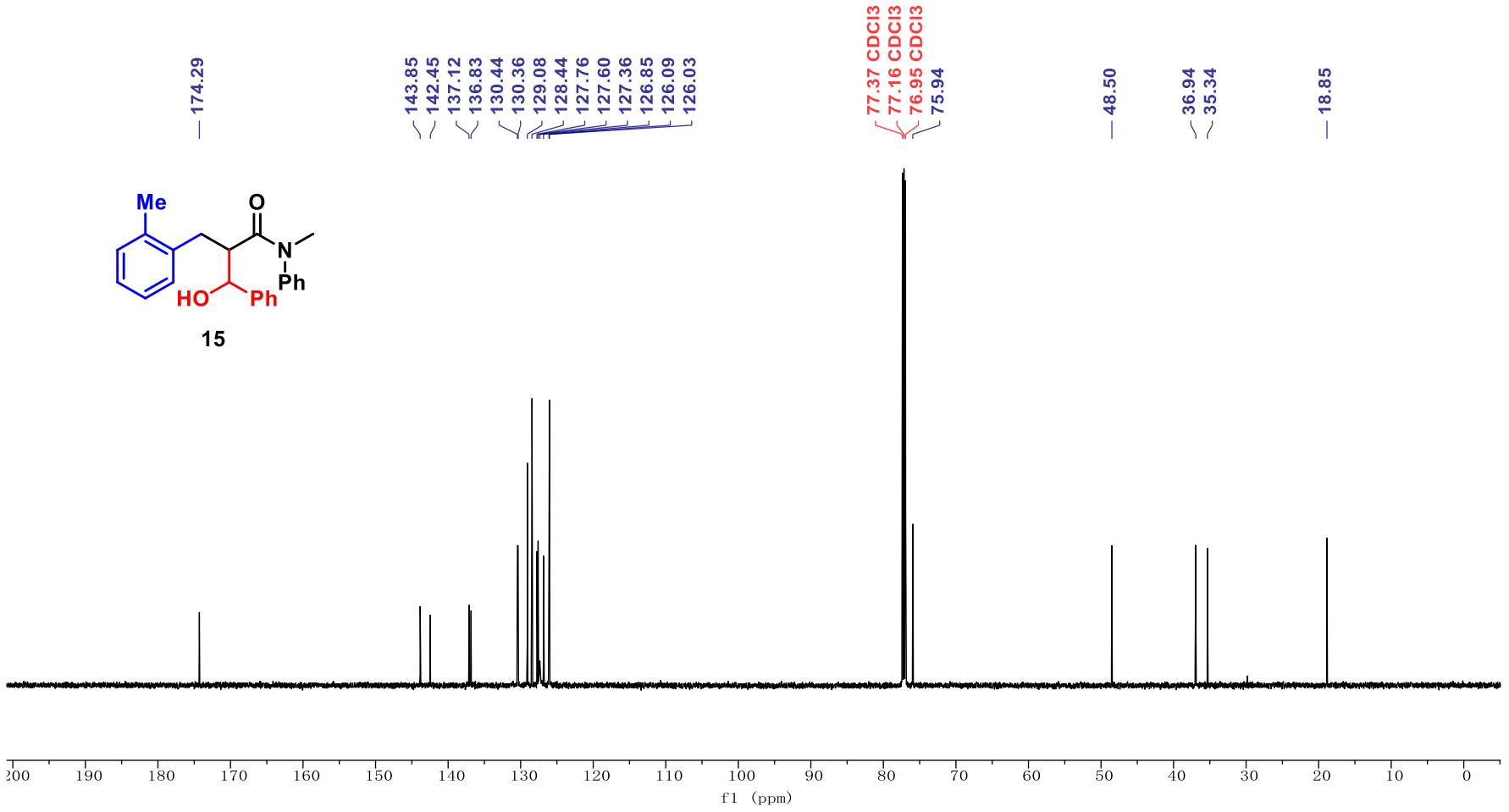
^{13}C NMR of 15 (One isomer) (151 MHz, $CDCl_3$)



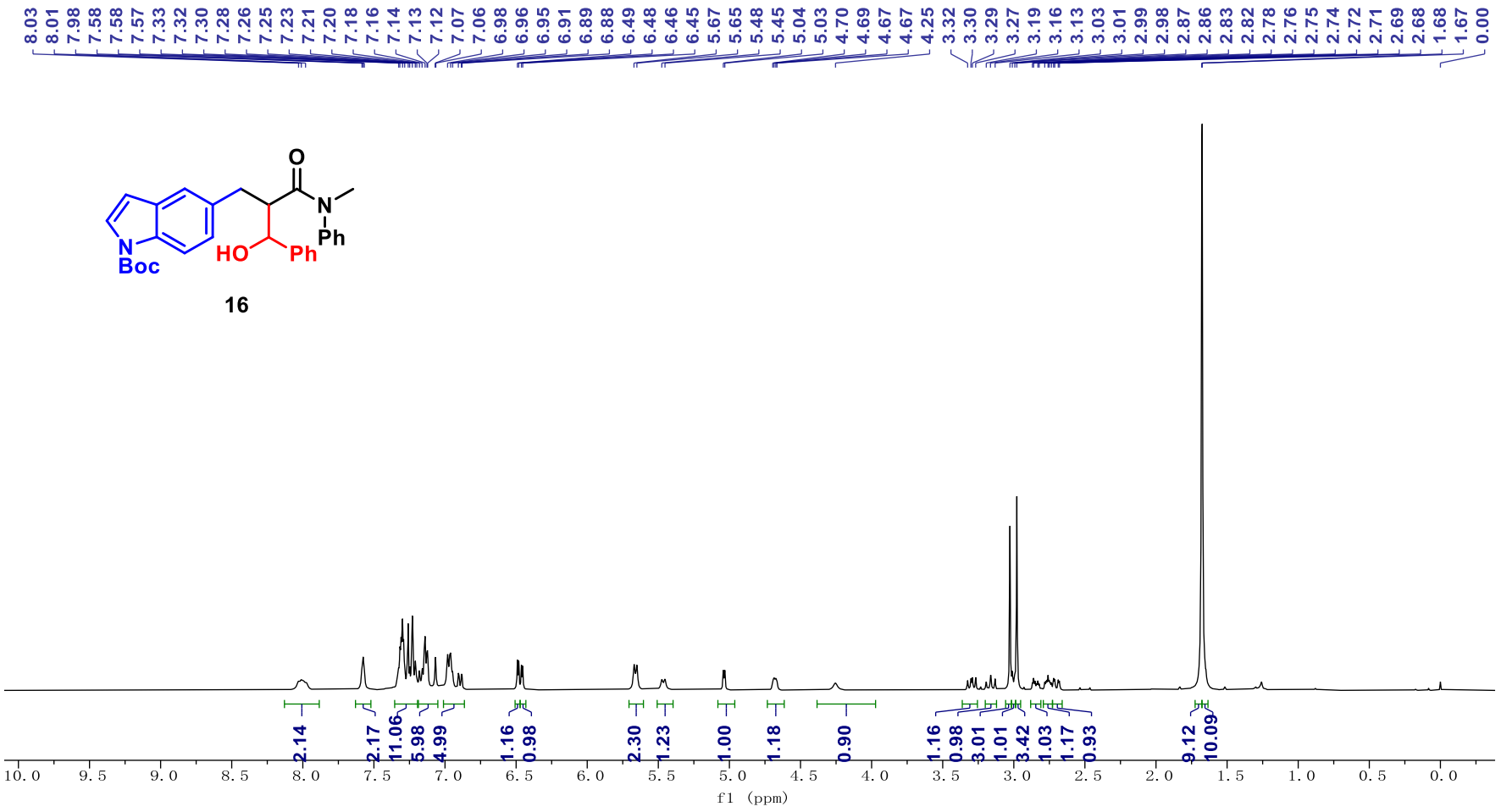
^{1}H NMR of 15 (Another isomer) (600 MHz, $CDCl_3$)



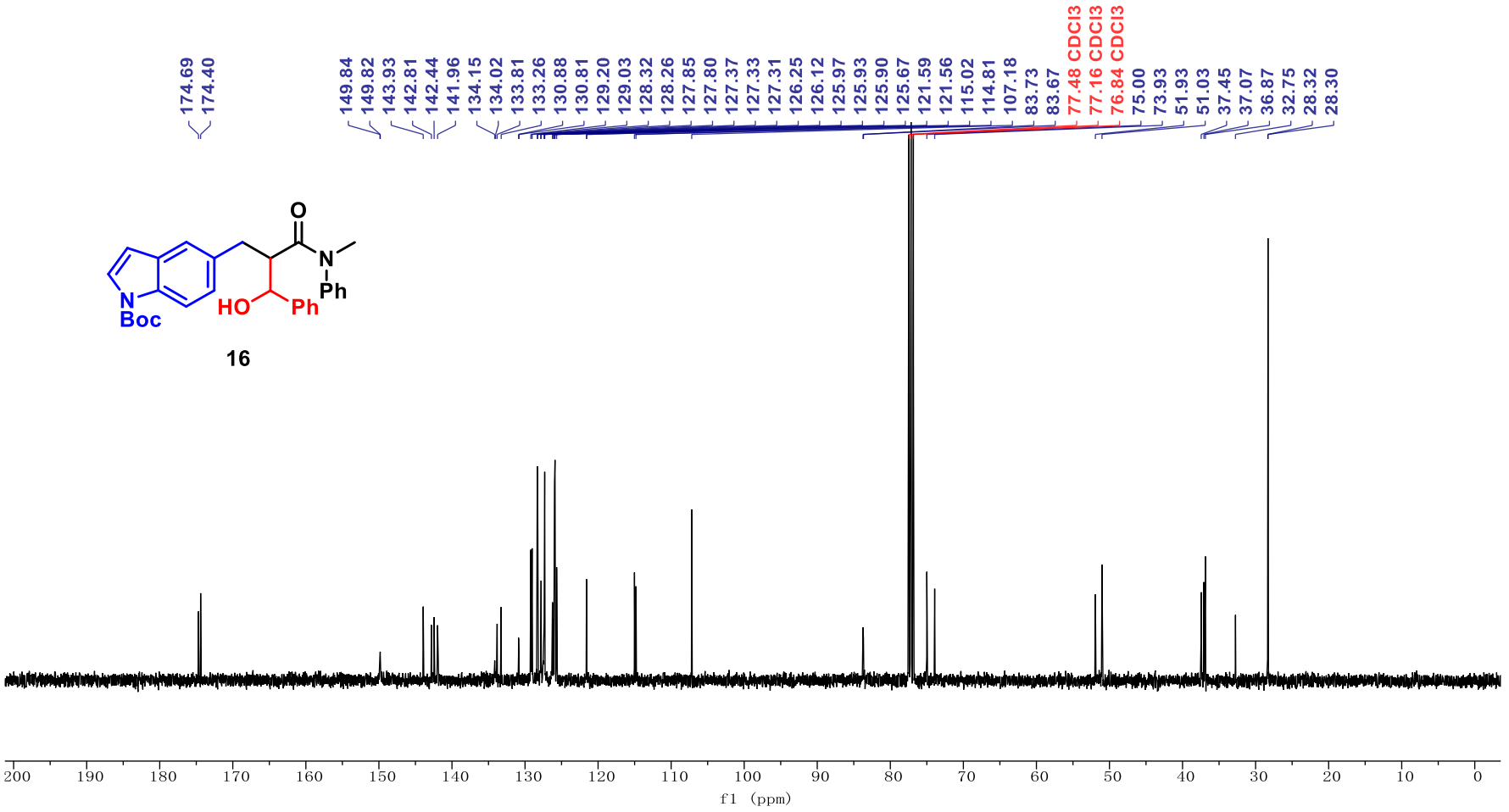
^{13}C NMR of 15 (Another isomer) (151 MHz, $CDCl_3$)



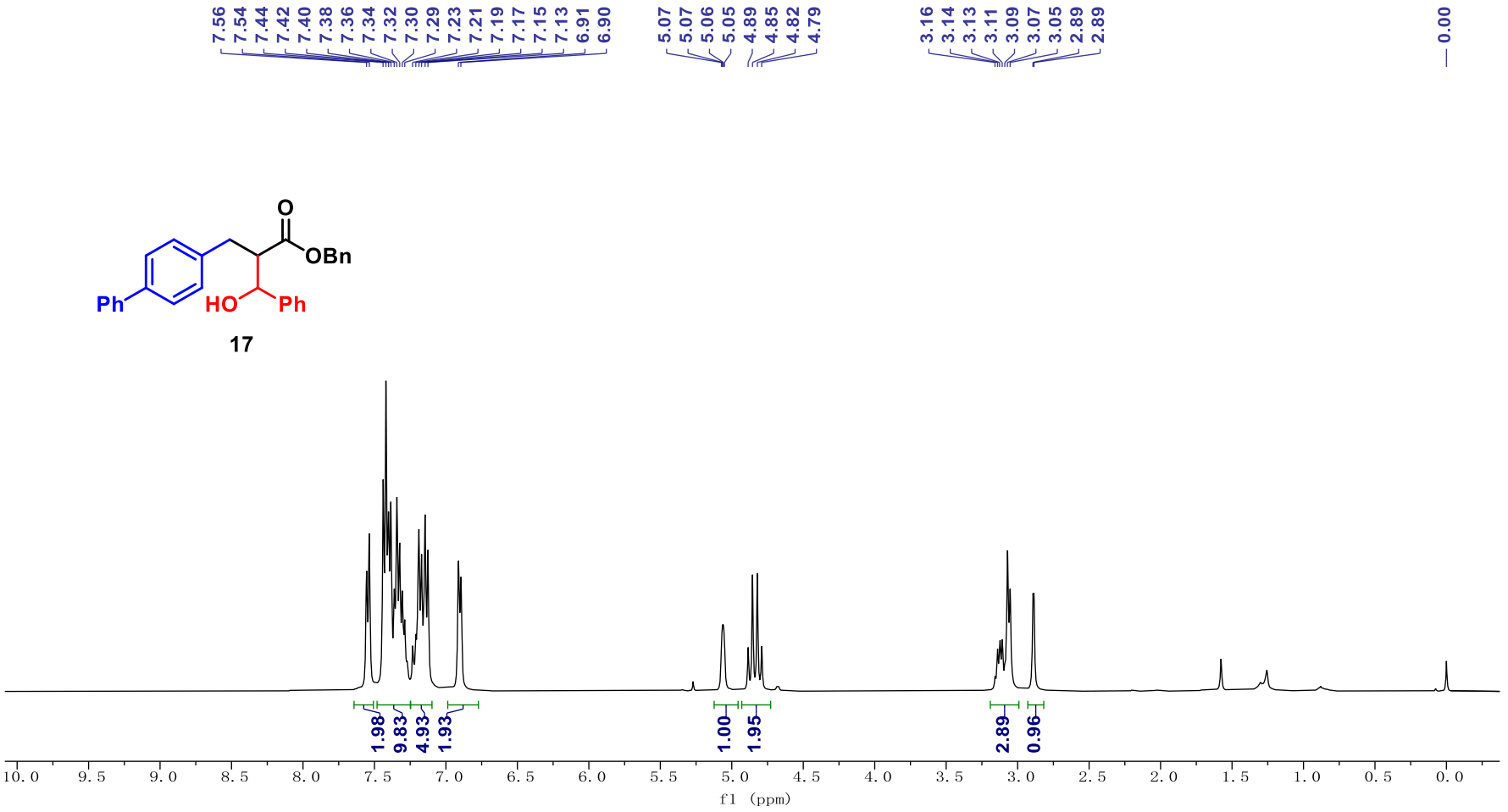
^{1}H NMR of 16 (400 MHz, $CDCl_3$)



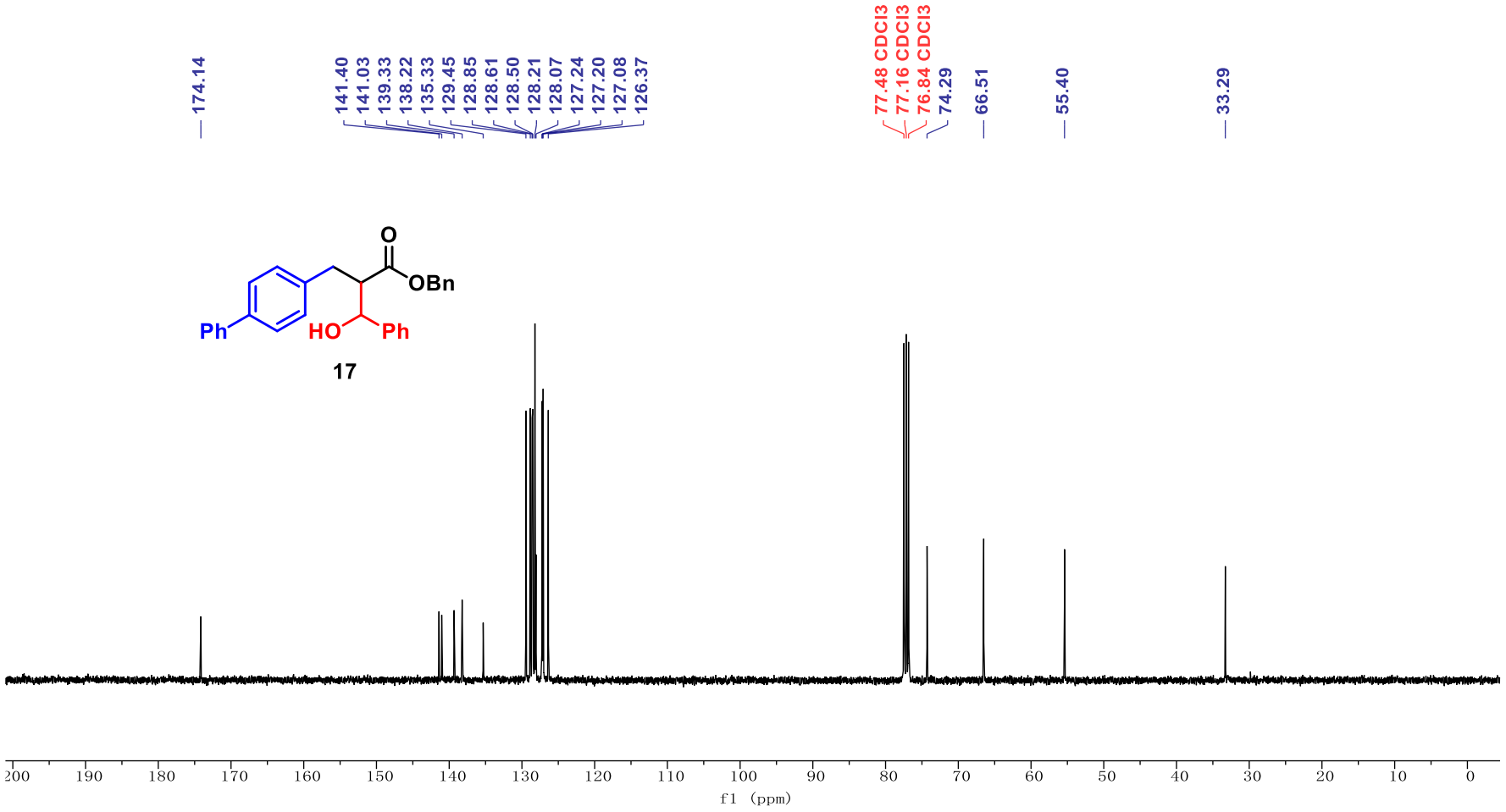
^{13}C NMR of 16 (101 MHz, $CDCl_3$)



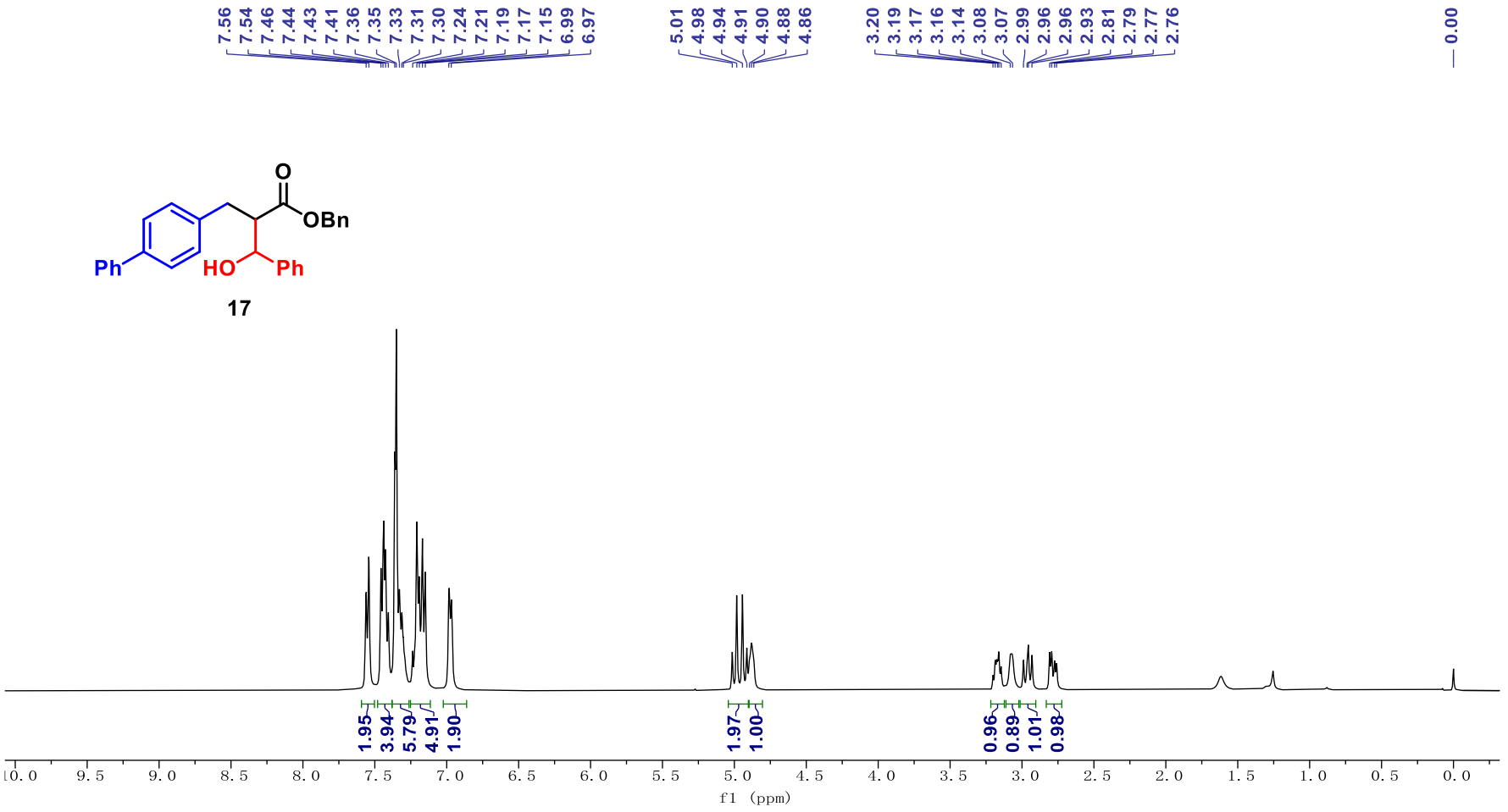
^{1}H NMR of 17 (One isomer) (400 MHz, $CDCl_3$)



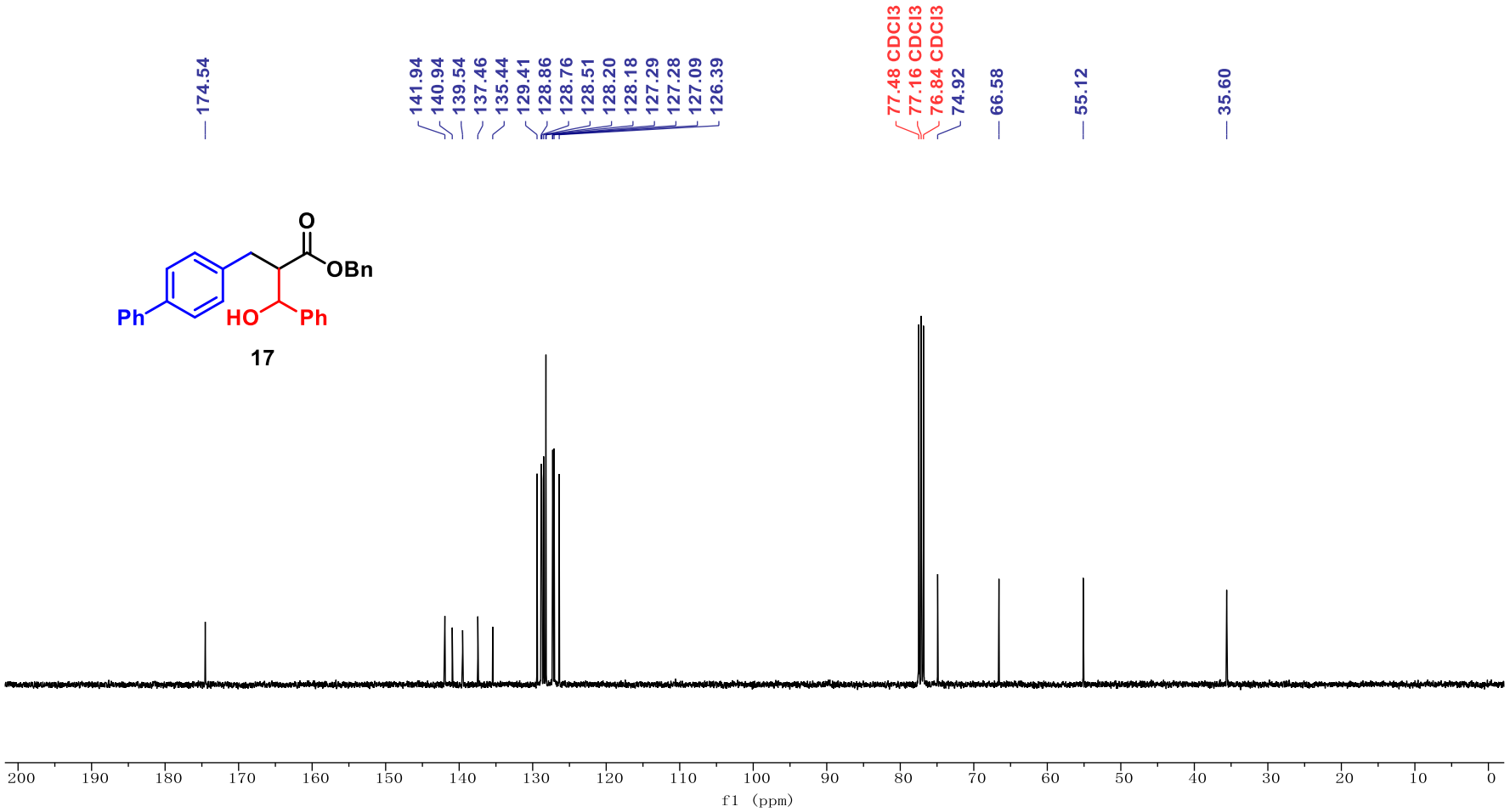
^{13}C NMR of 17 (One isomer) (101 MHz, $CDCl_3$)



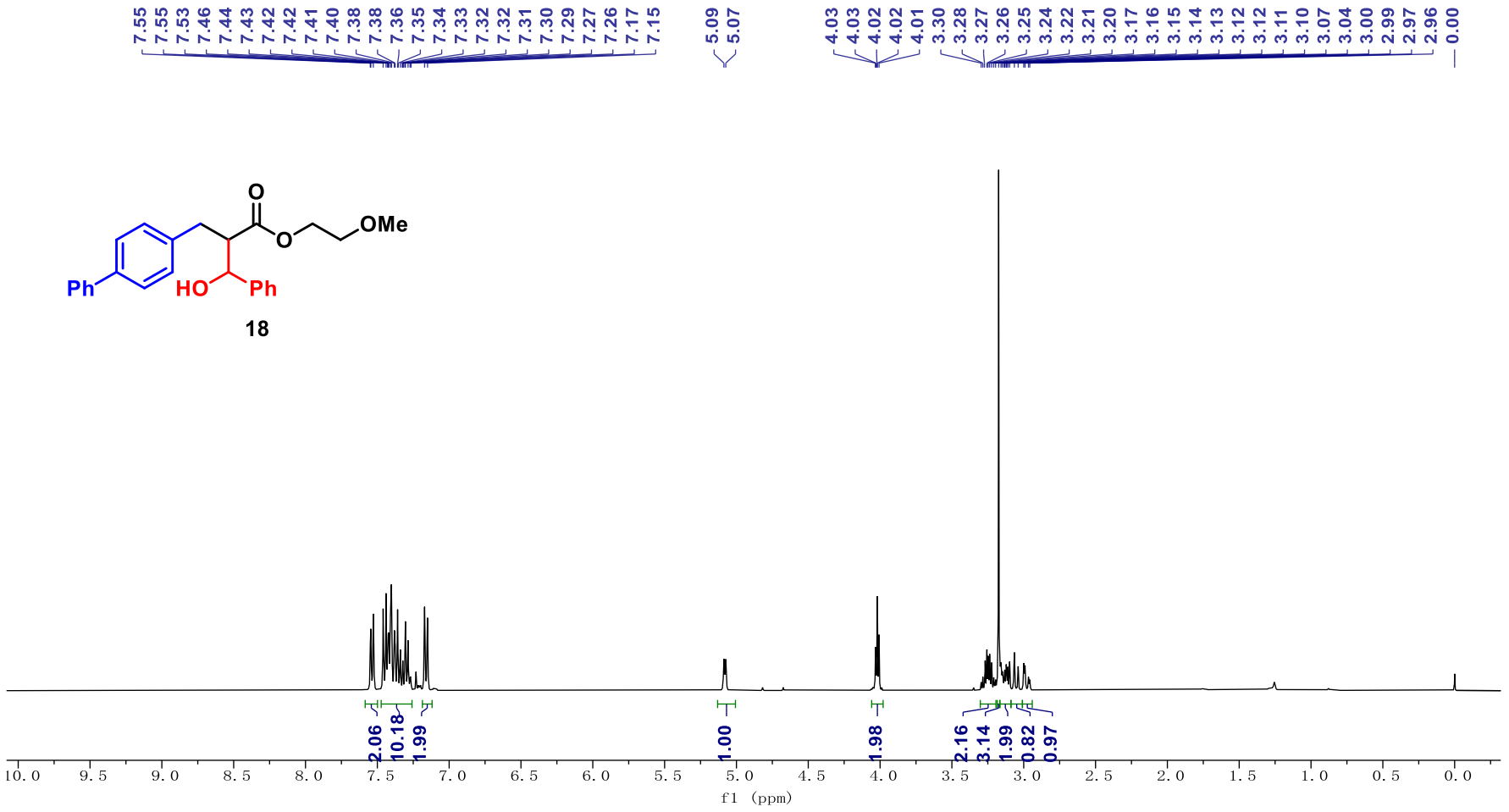
^{1}H NMR of 17 (Another isomer) (400 MHz, $CDCl_3$)



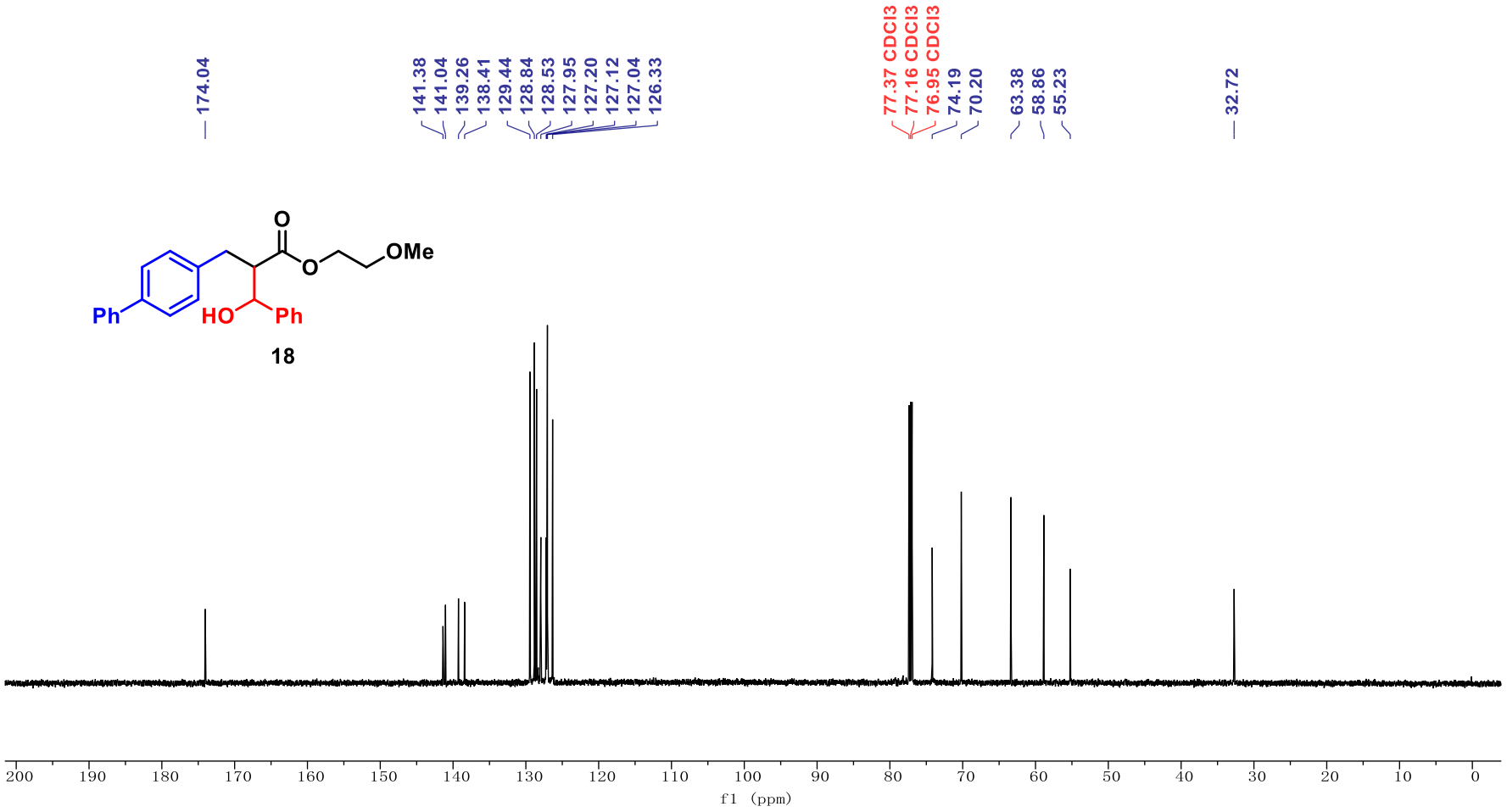
^{13}C NMR of 17 (Another isomer) (101 MHz, $CDCl_3$)



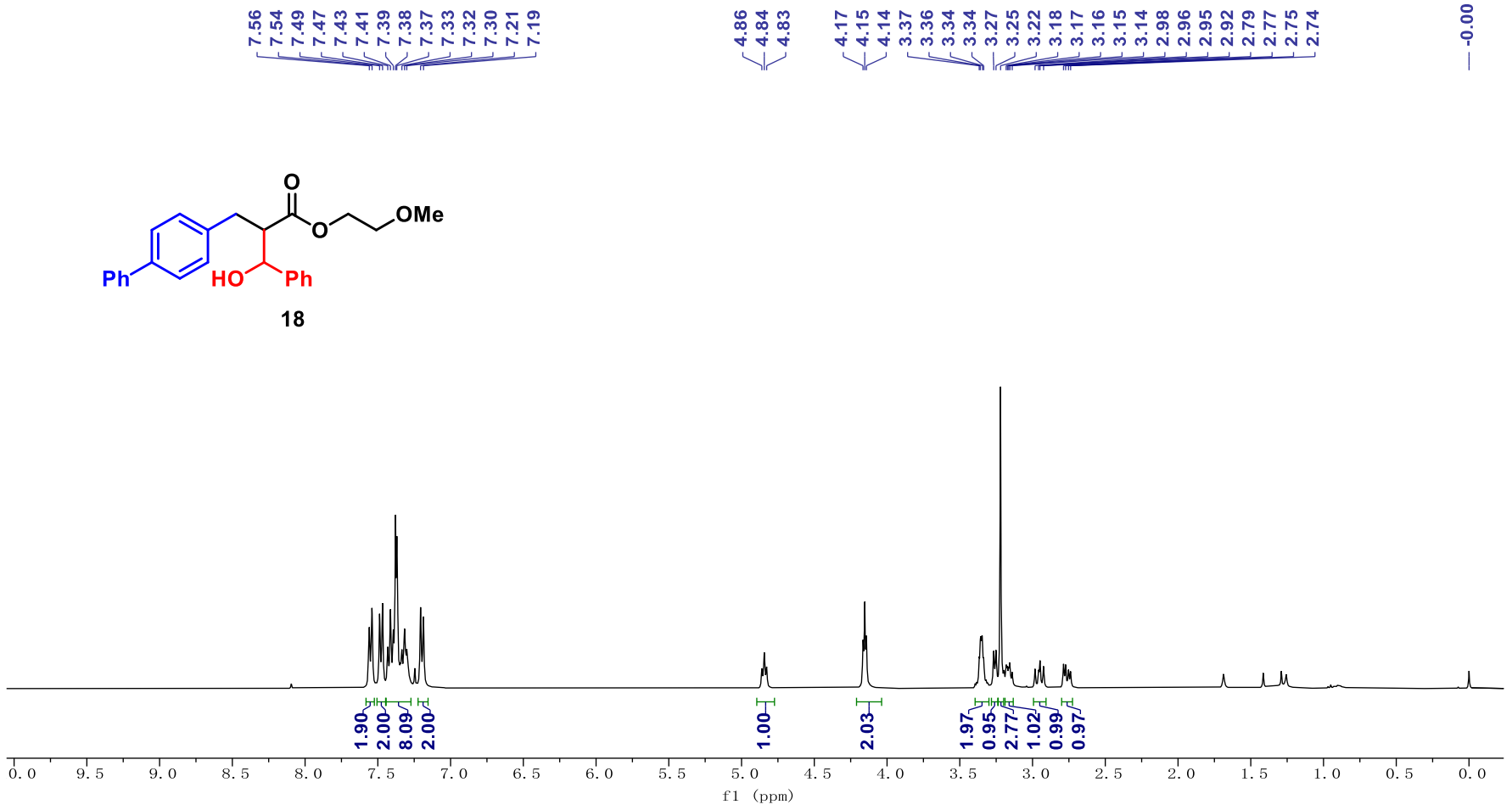
^{1}H NMR of 18 (One isomer) (400 MHz, $CDCl_3$)



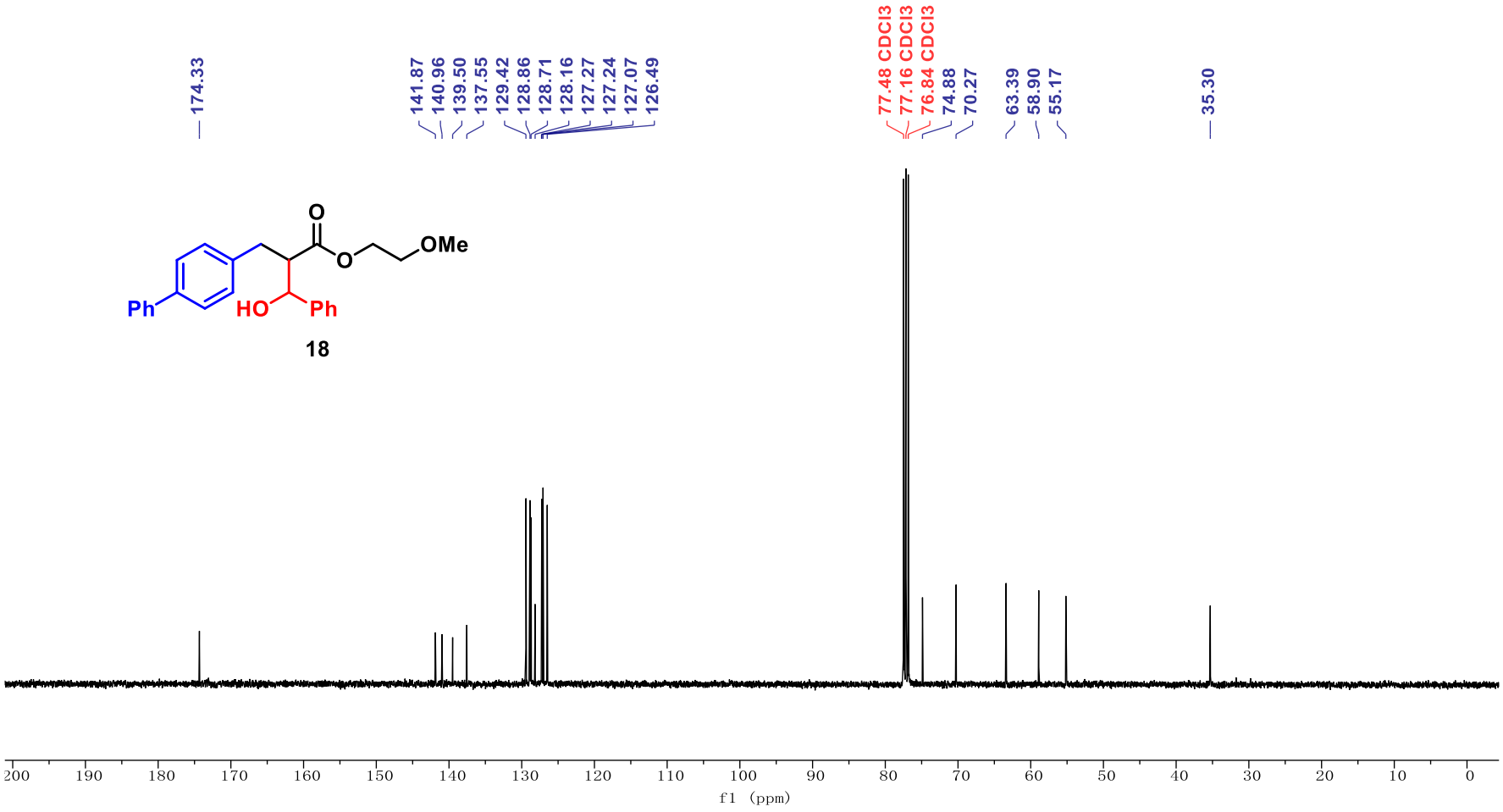
^{13}C NMR of 18 (One isomer) (151 MHz, $CDCl_3$)



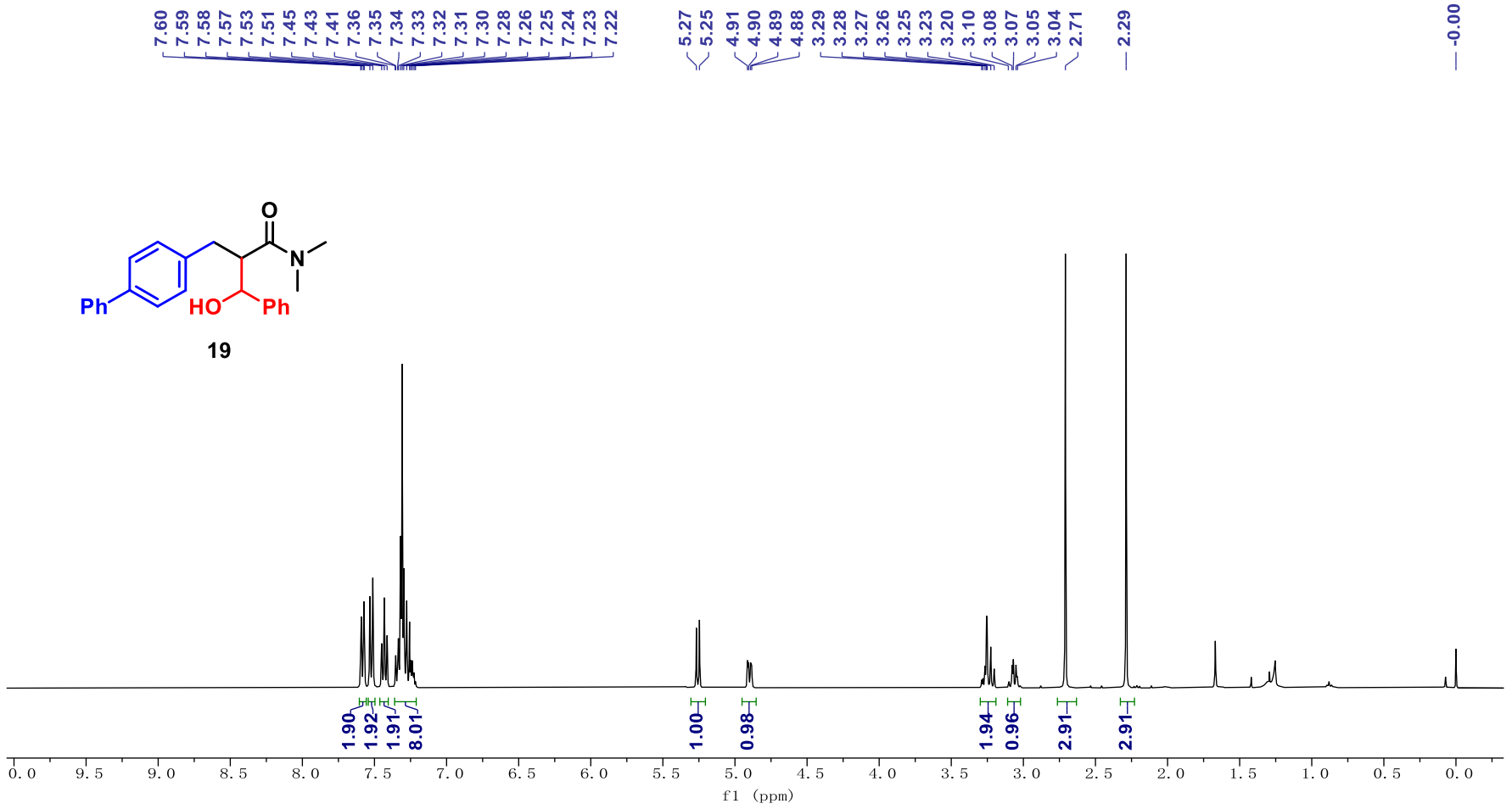
^{1}H NMR of 18 (Another isomer) (400 MHz, $CDCl_3$)



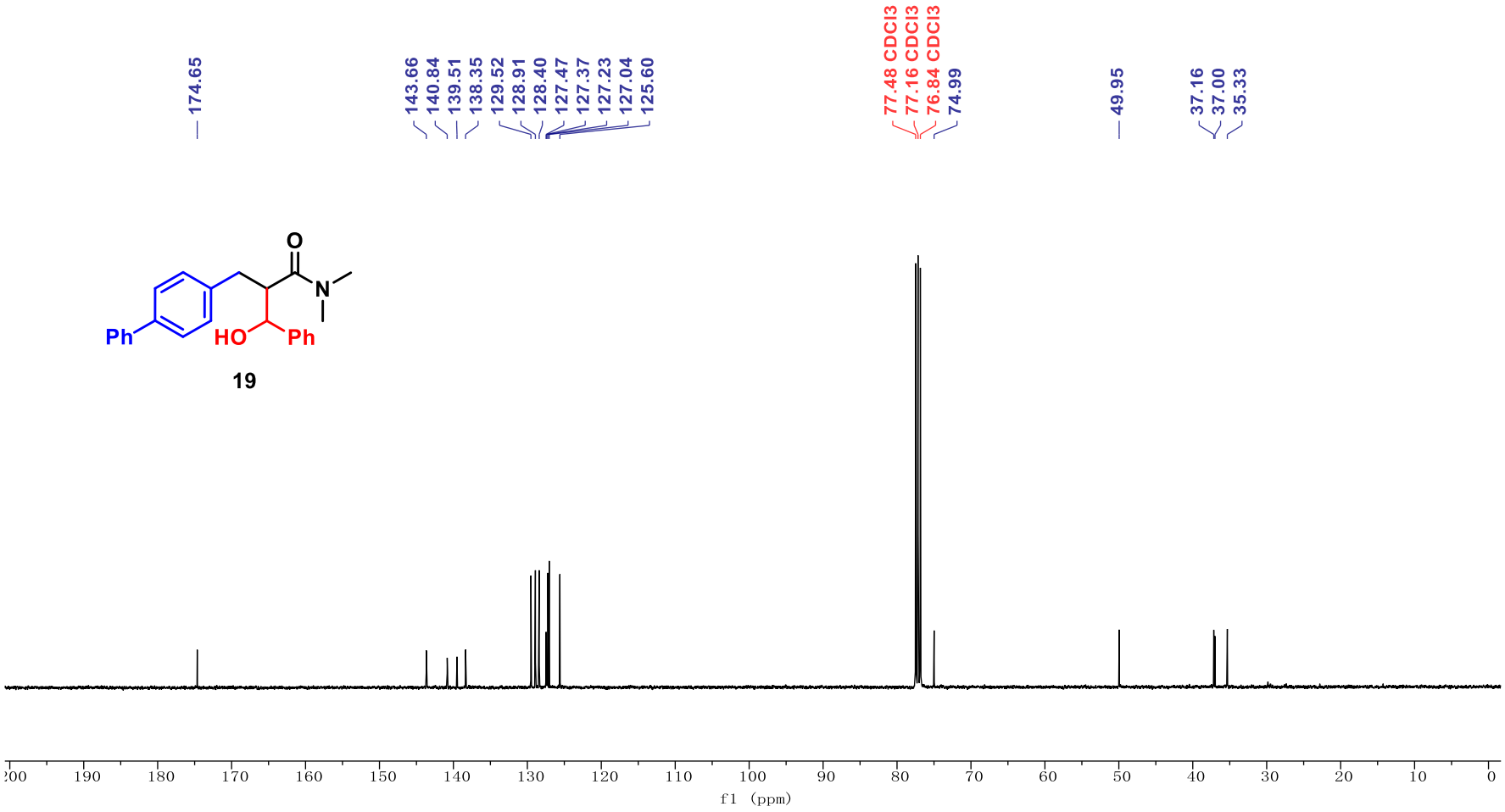
^{13}C NMR of 18 (Another isomer) (101 MHz, $CDCl_3$)



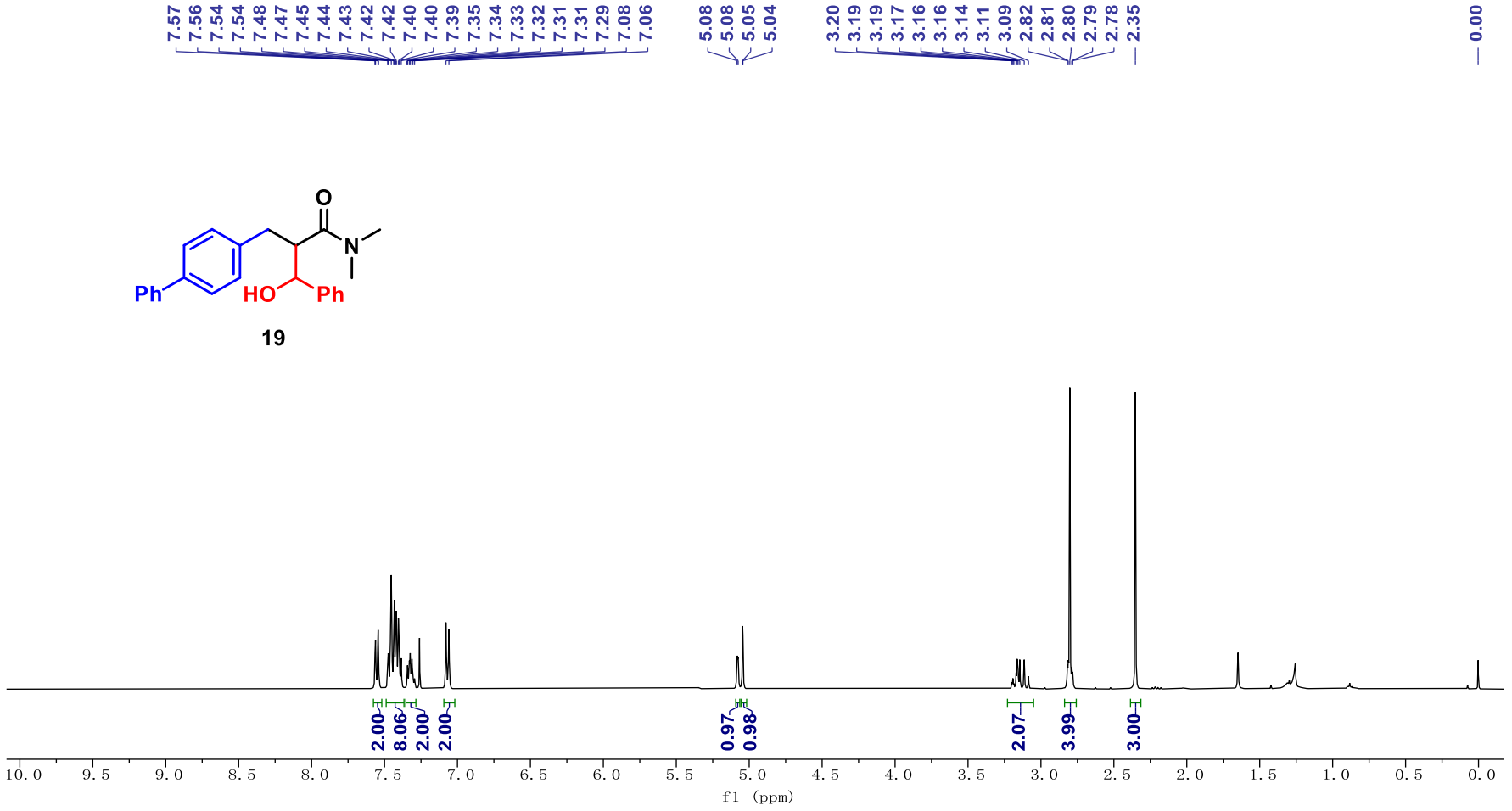
^{1}H NMR of 19 (One isomer) (400 MHz, $CDCl_3$)



^{13}C NMR of 19 (One isomer) (101 MHz, $CDCl_3$)

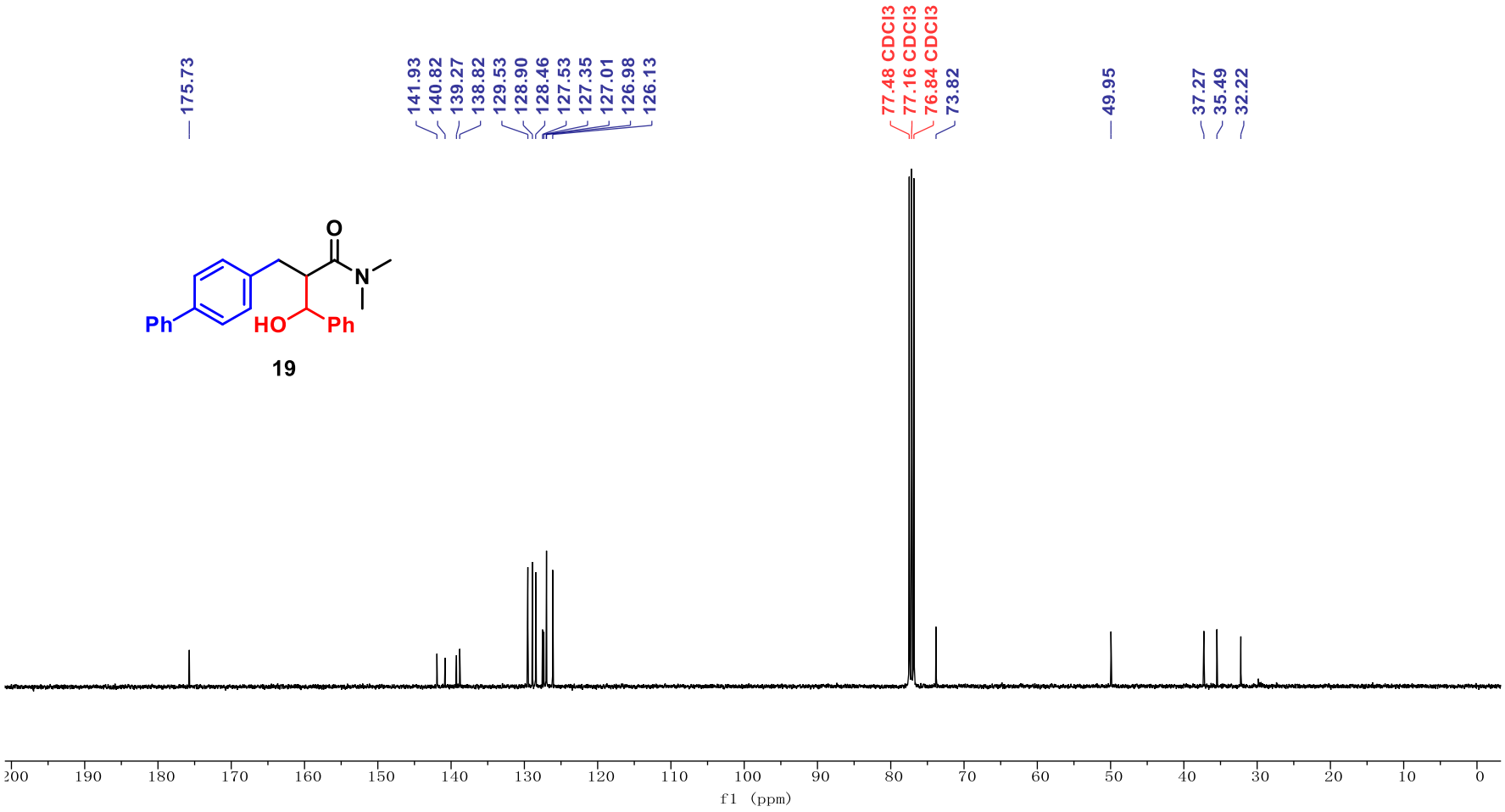


^{1}H NMR of 19 (Another isomer) (400 MHz, $CDCl_3$)

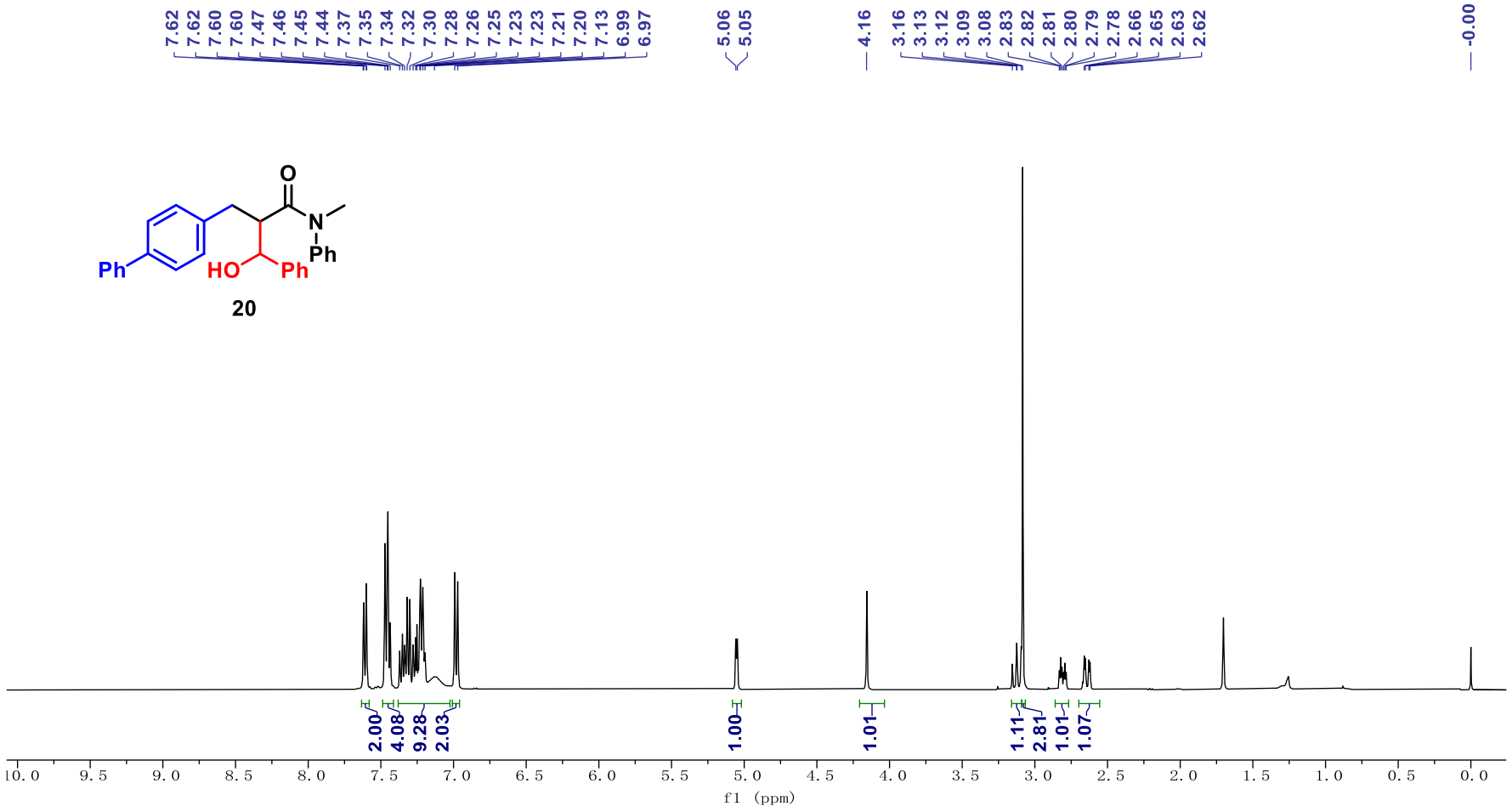


19

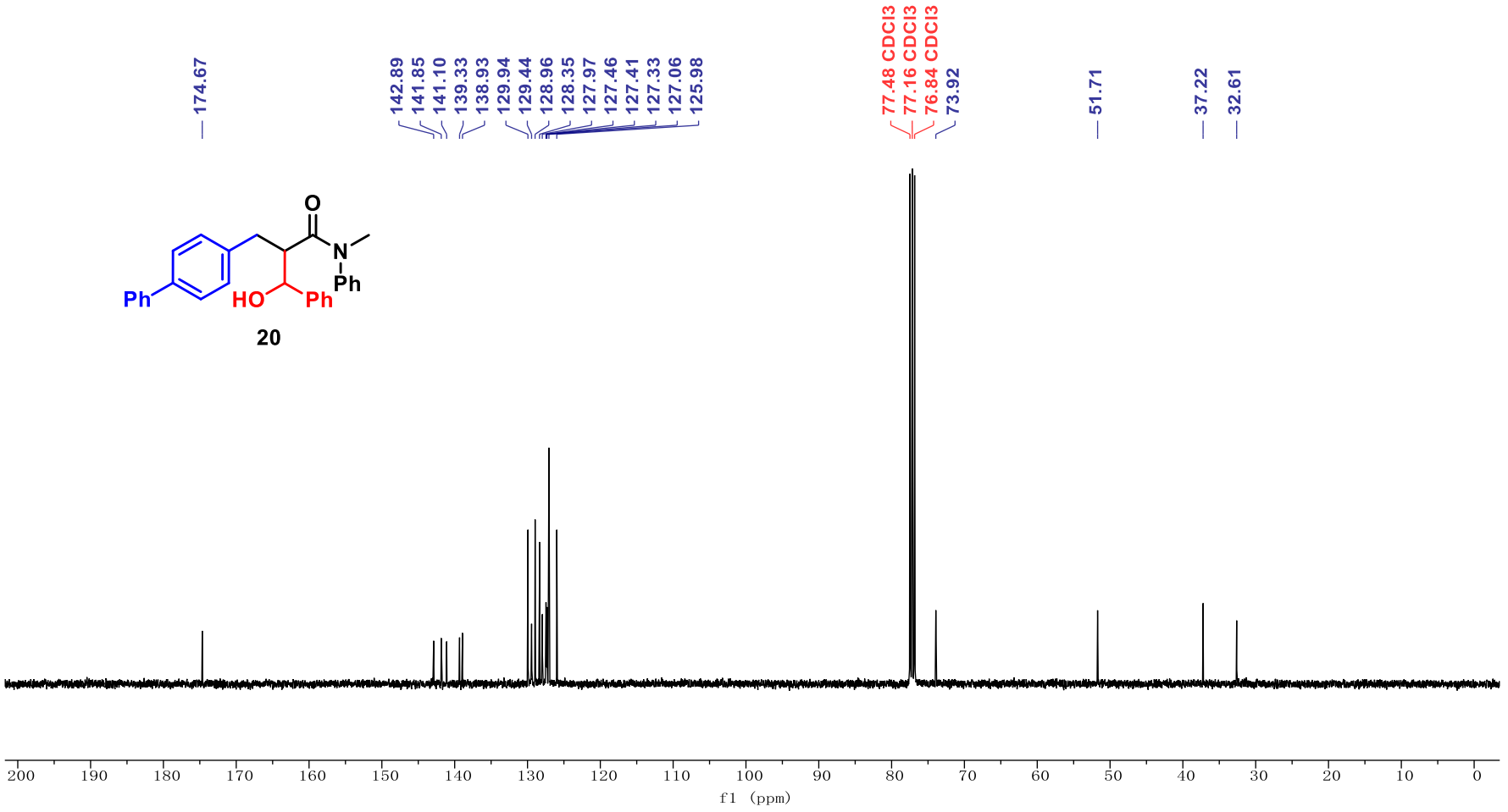
^{13}C NMR of 19 (Another isomer) (101 MHz, $CDCl_3$)



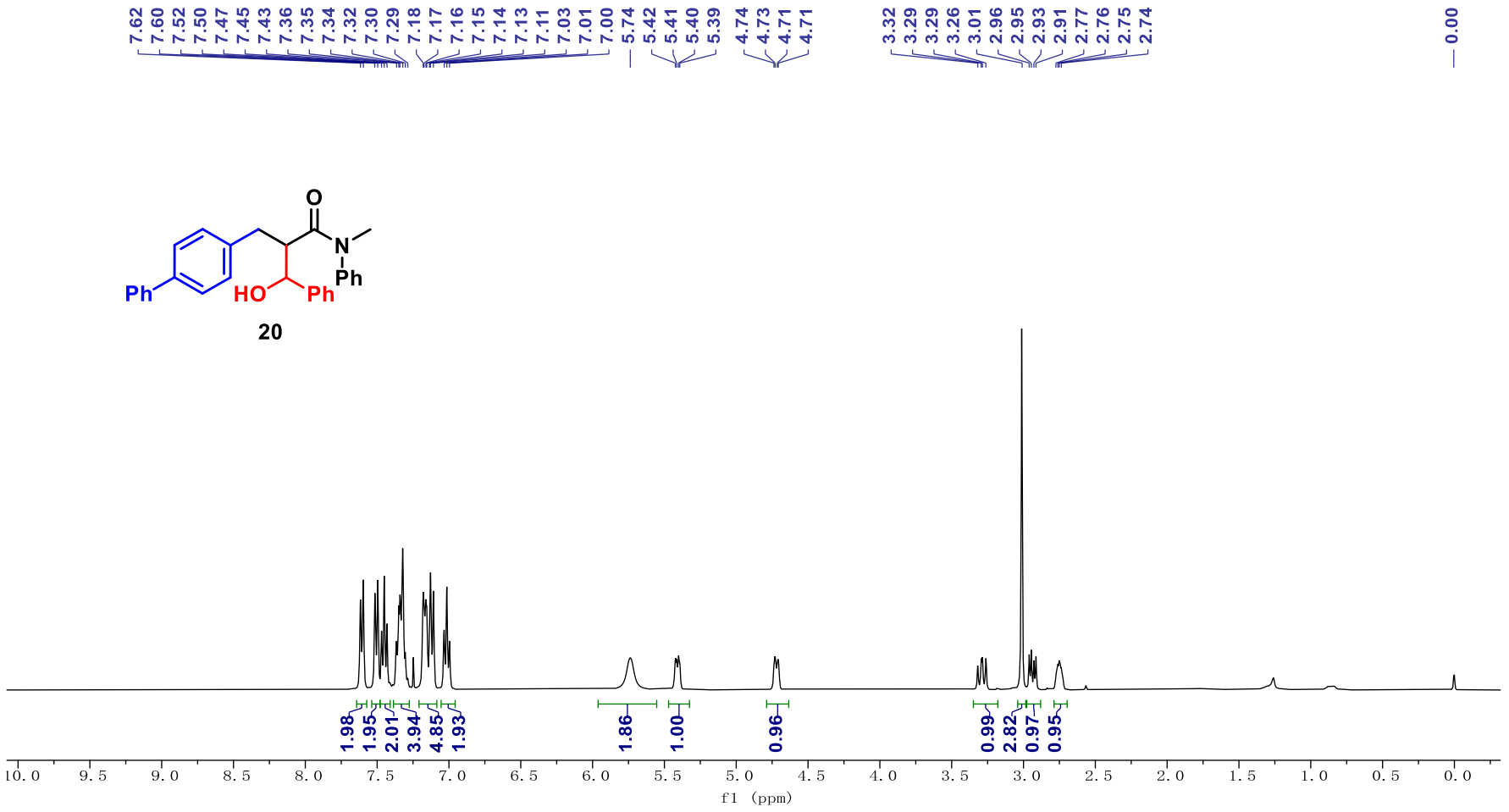
^{1}H NMR of 20 (One isomer) (400 MHz, $CDCl_3$)



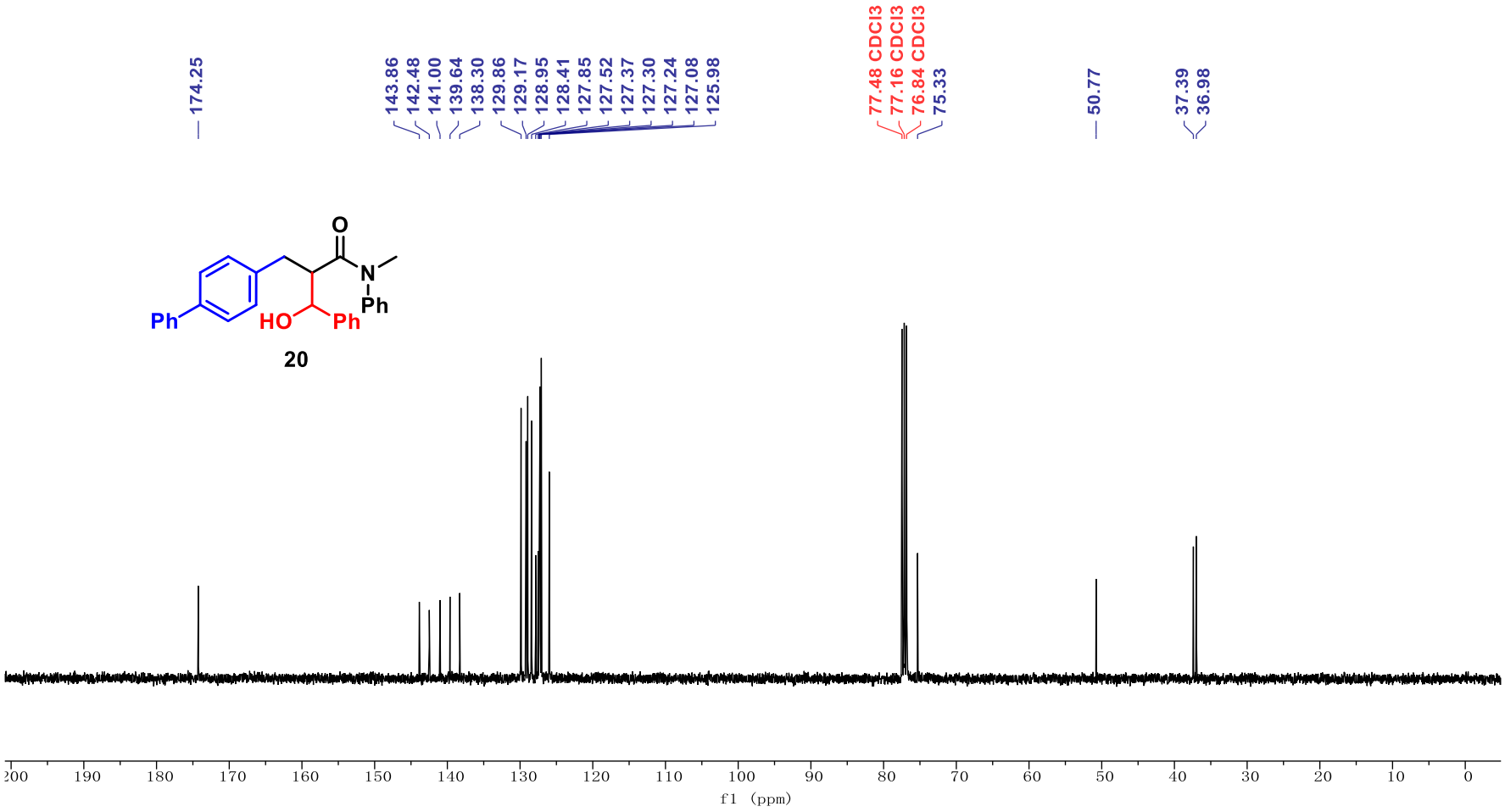
^{13}C NMR of 20 (One isomer) (101 MHz, $CDCl_3$)



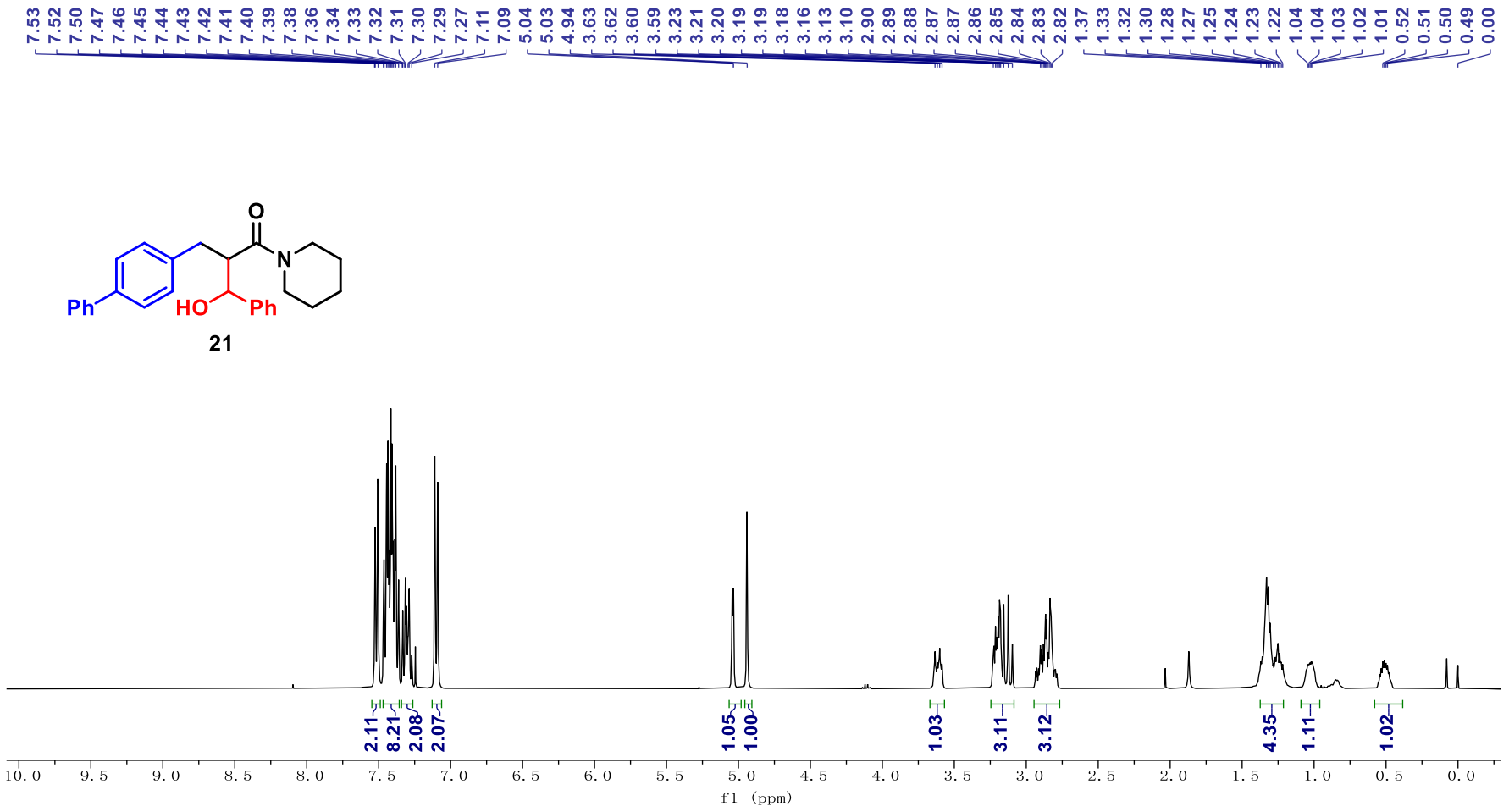
^{1}H NMR of 20 (Another isomer) (400 MHz, $CDCl_3$)



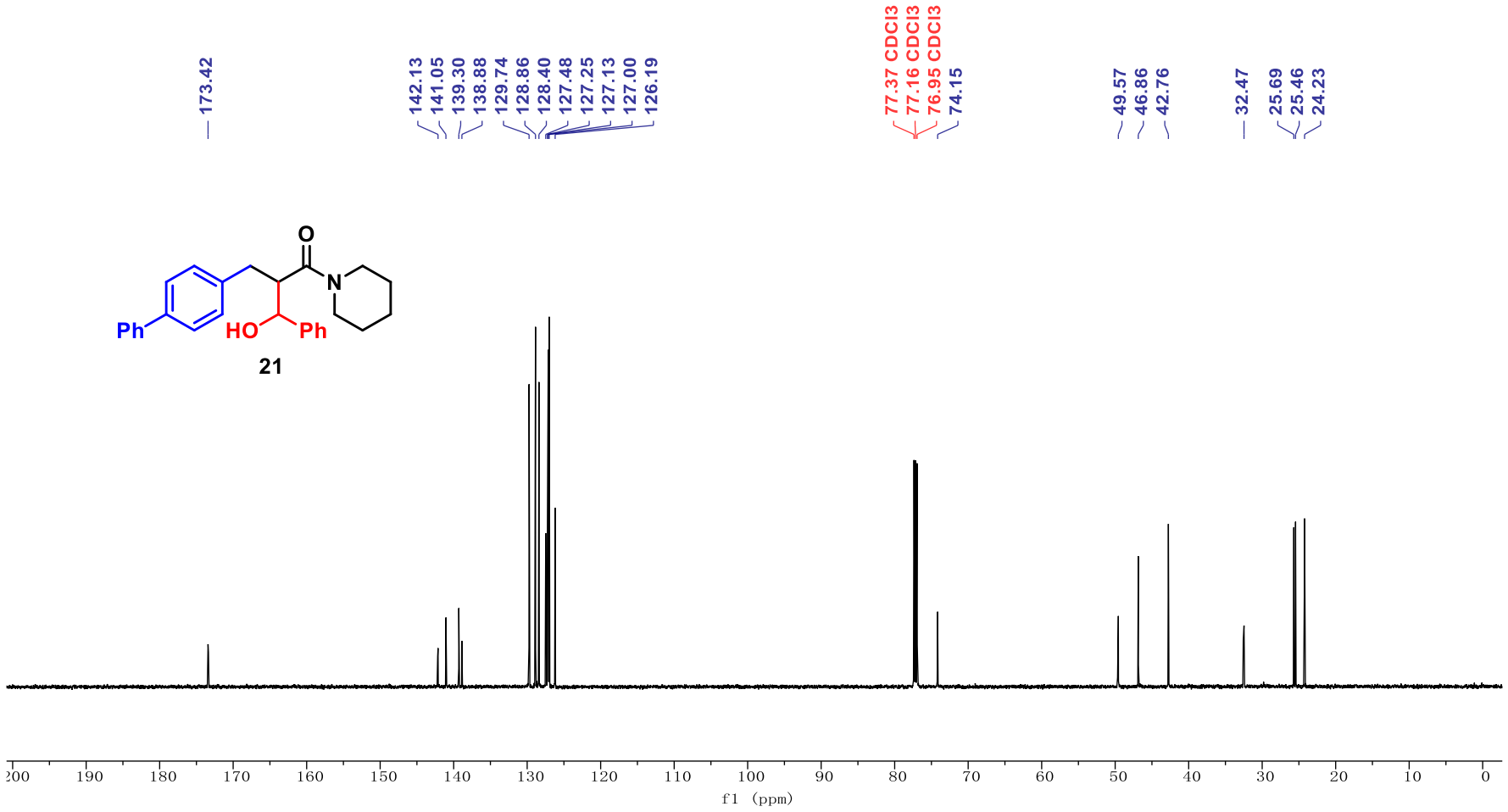
^{13}C NMR of 20 (Another isomer) (101 MHz, $CDCl_3$)



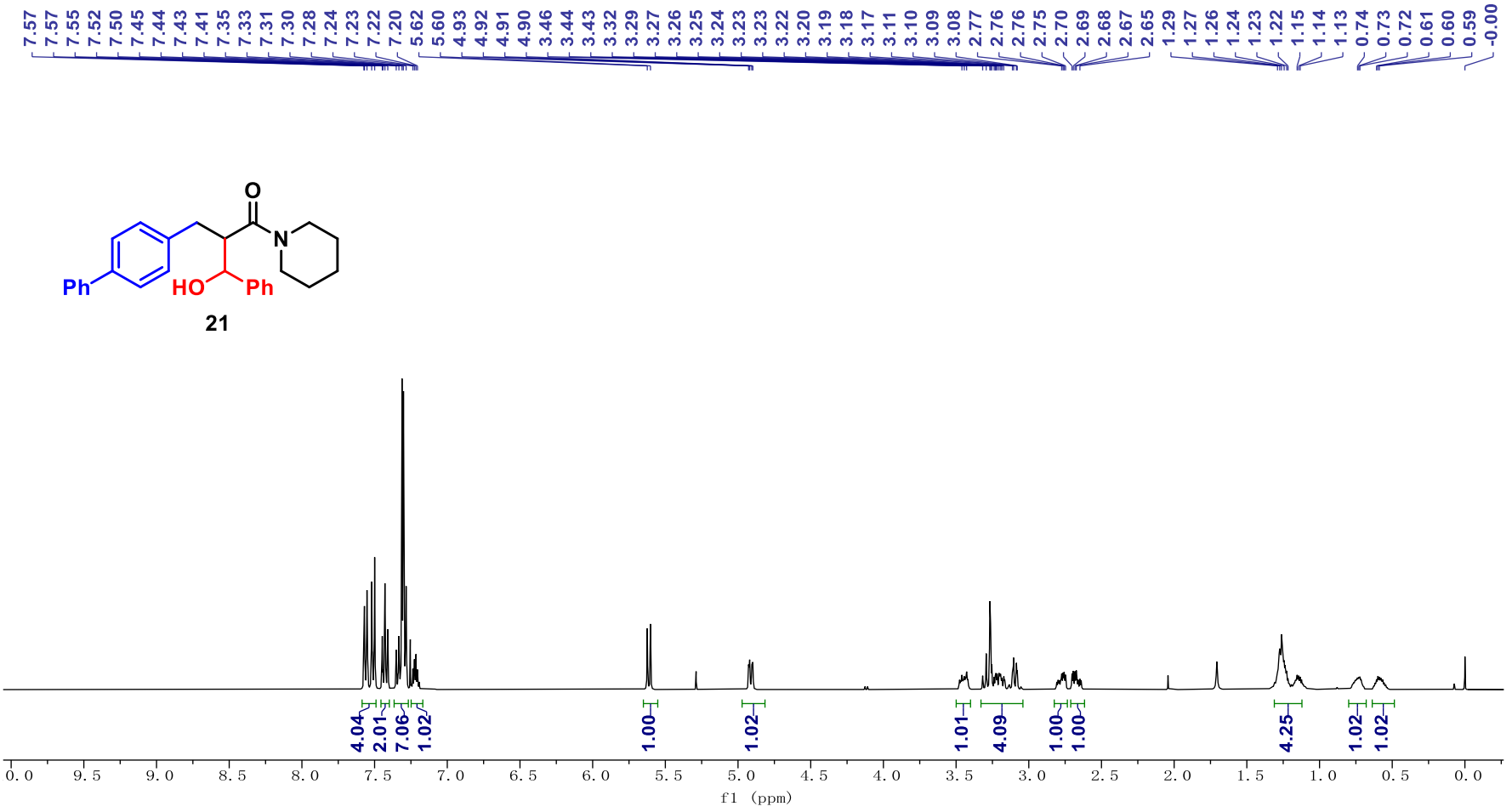
^{1}H NMR of 21 (One isomer) (400 MHz, $CDCl_3$)



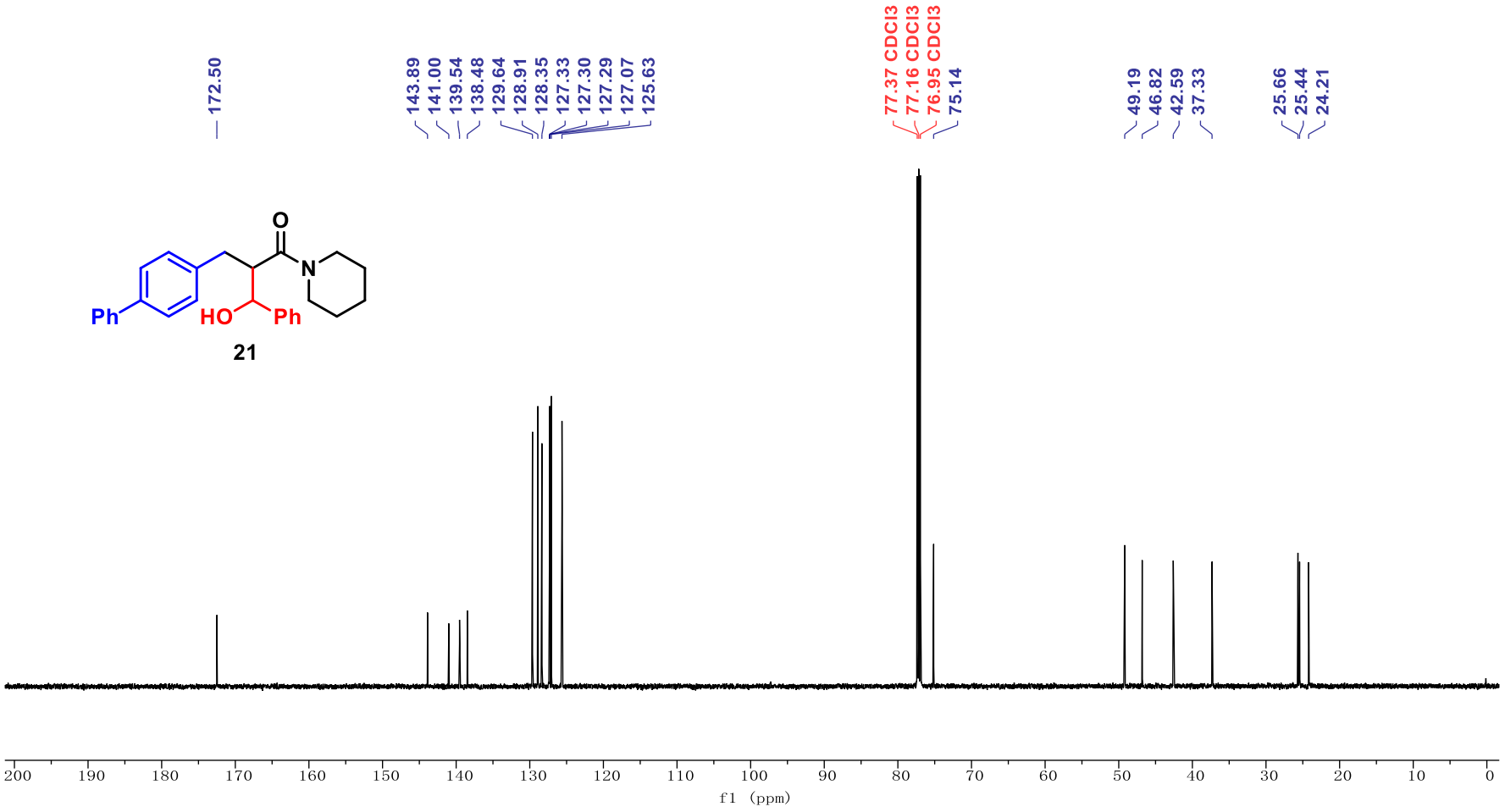
^{13}C NMR of 21 (One isomer) (151 MHz, $CDCl_3$)



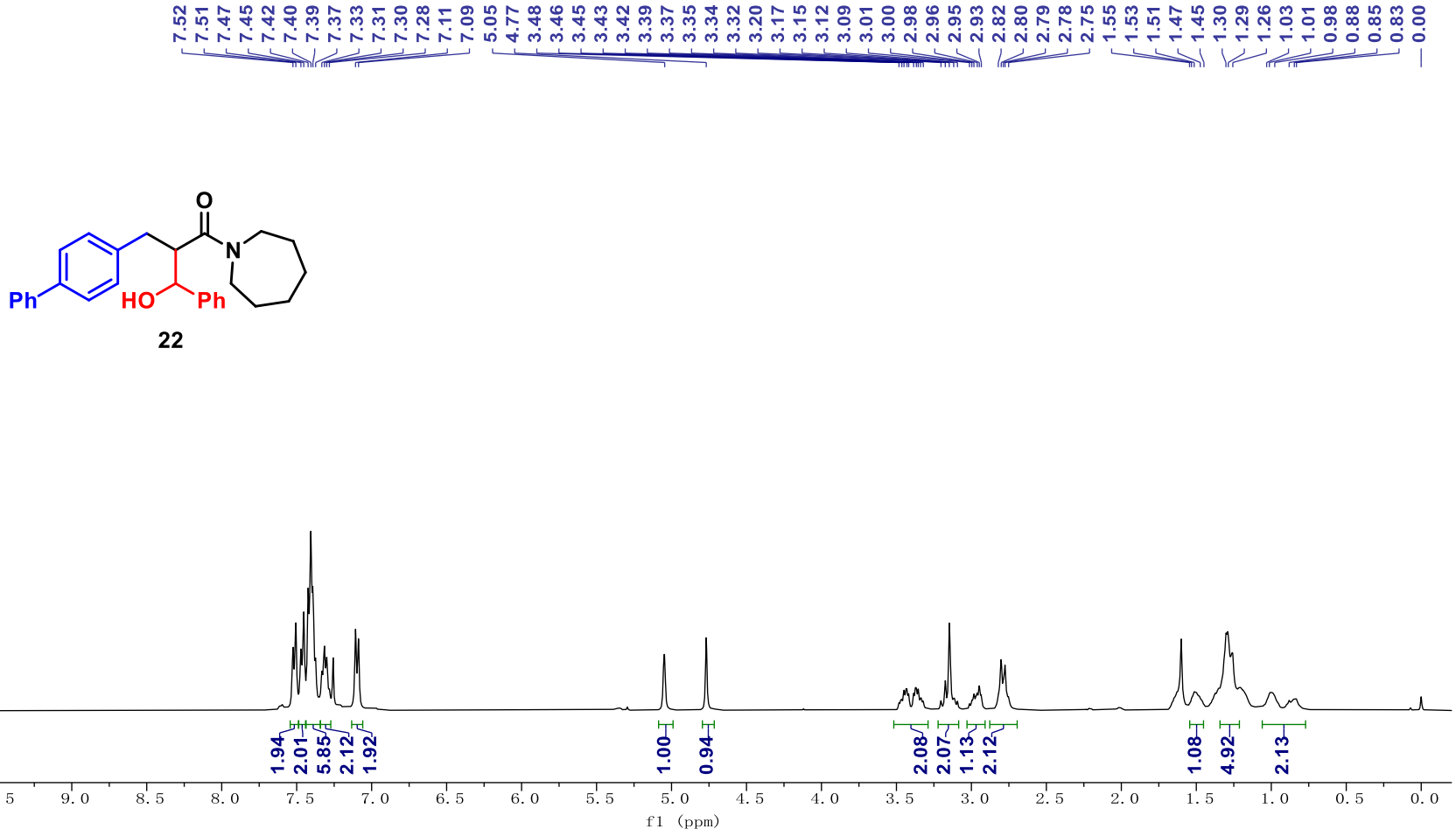
^{1}H NMR of 21 (Another isomer) (400 MHz, $CDCl_3$)



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

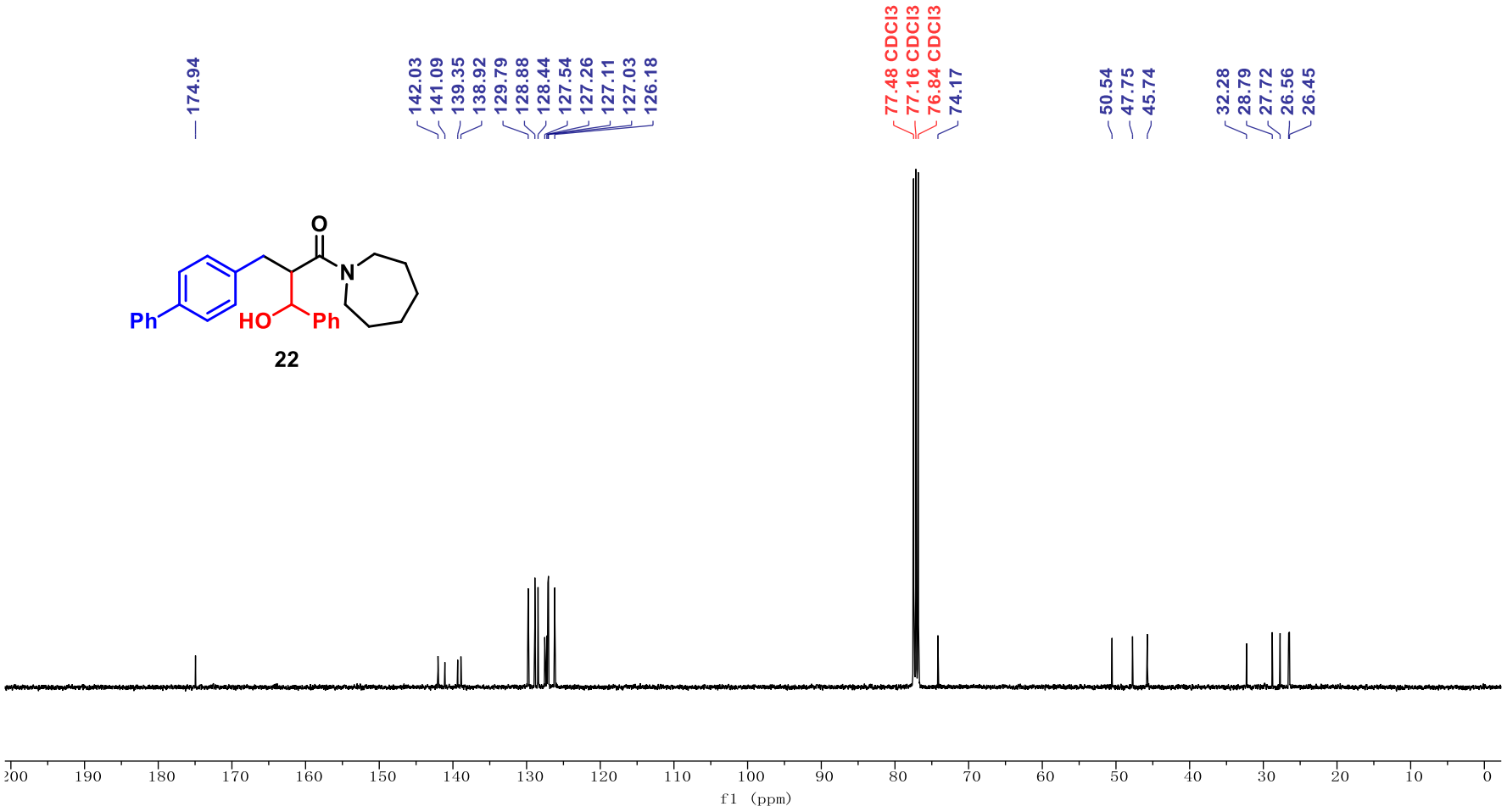


^{1}H NMR of 22 (One isomer) (400 MHz, $CDCl_3$)

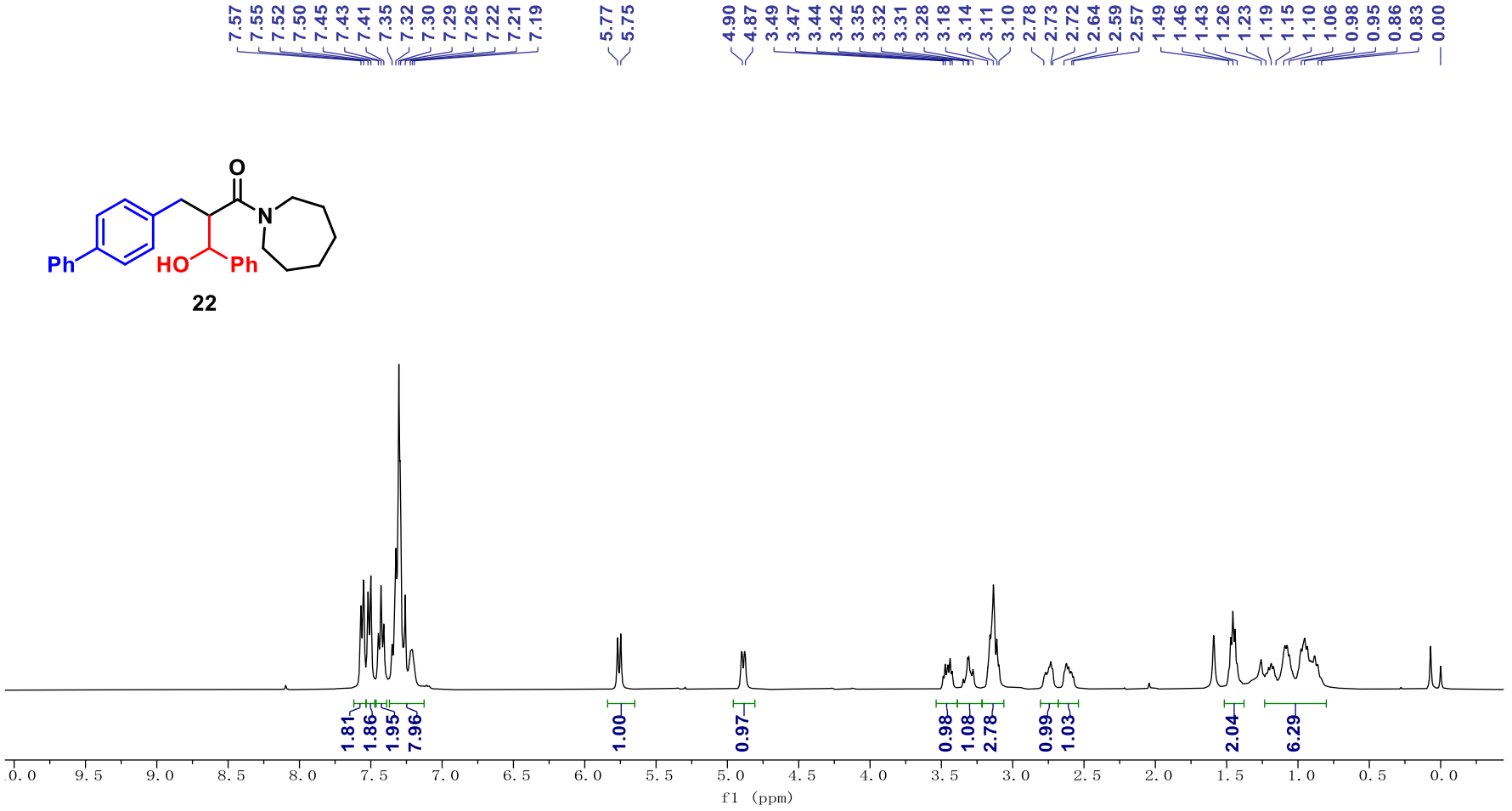


22

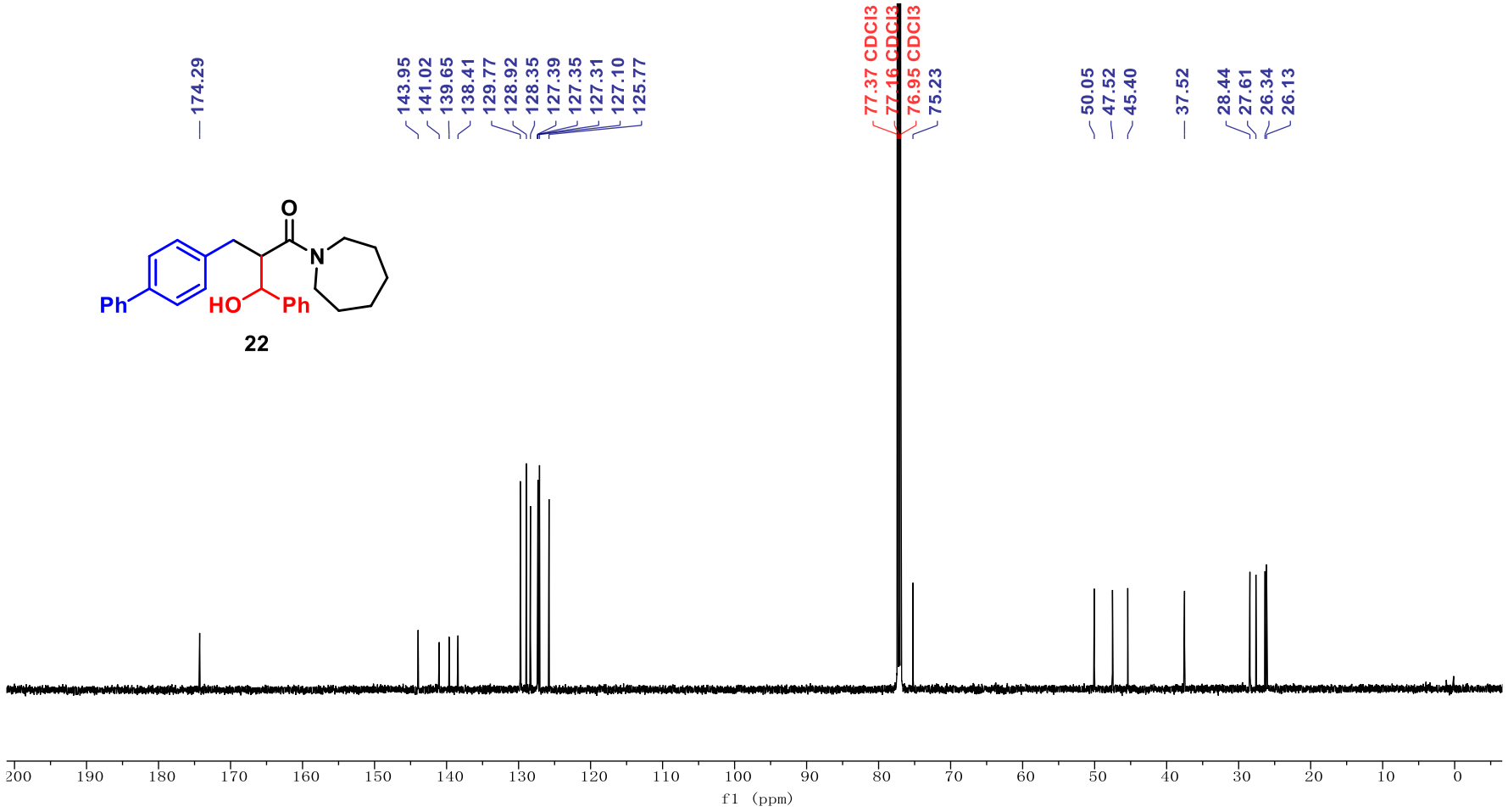
^{13}C NMR of 22 (One isomer) (101 MHz, $CDCl_3$)



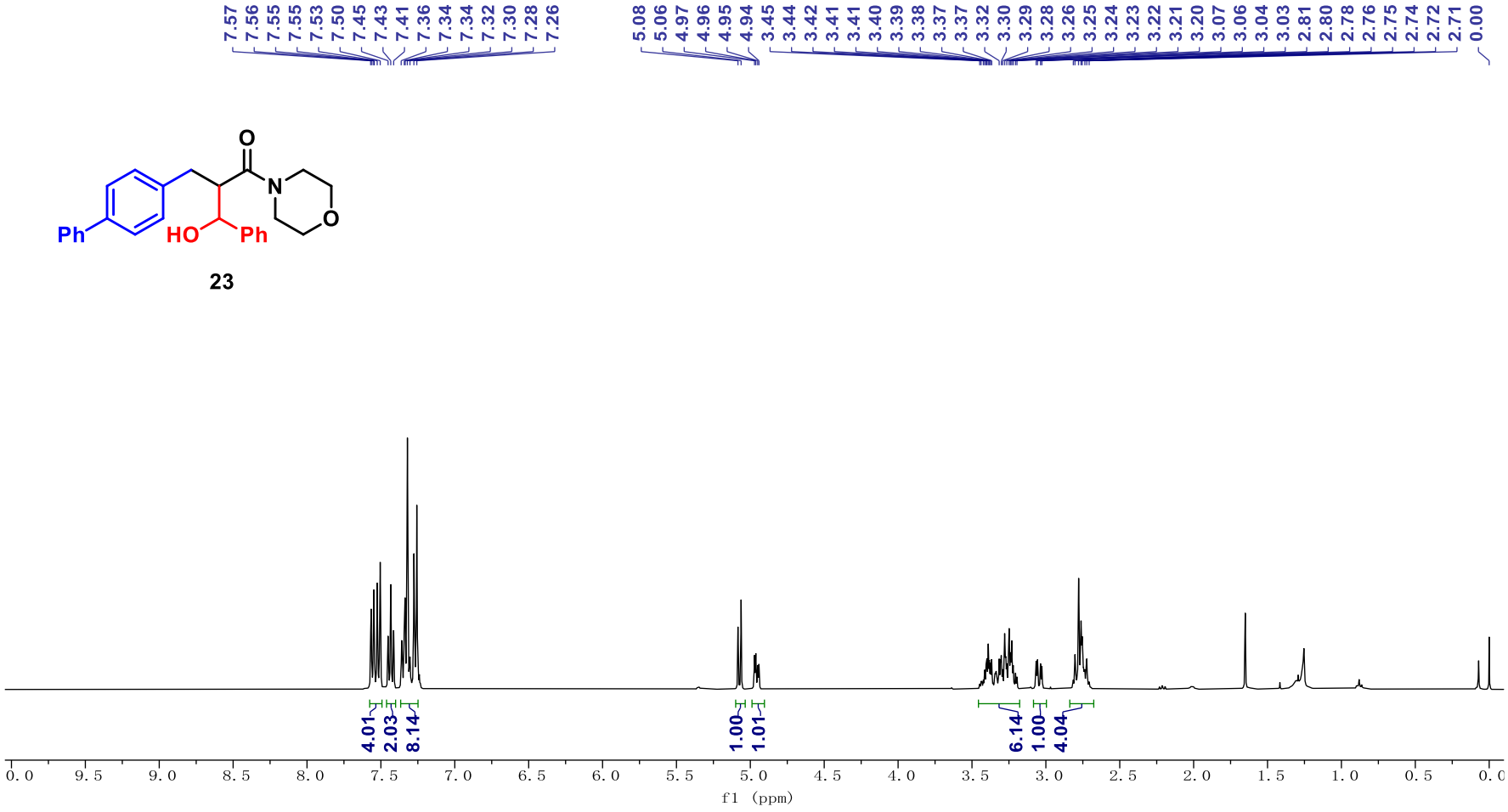
^{1}H NMR of 22 (Another isomer) (400 MHz, $CDCl_3$)



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

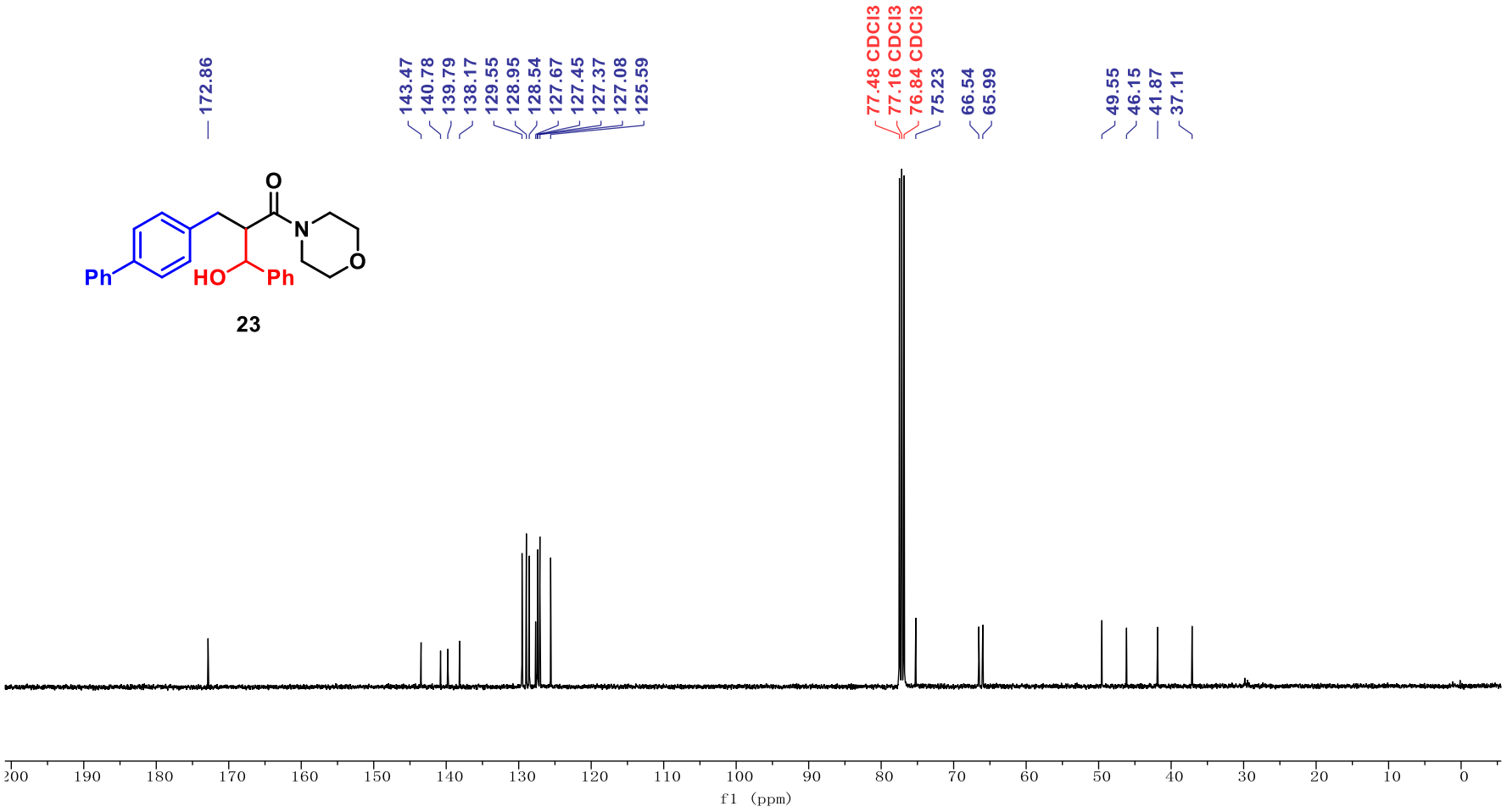


^{1}H NMR of 23 (One isomer) (400 MHz, $CDCl_3$)

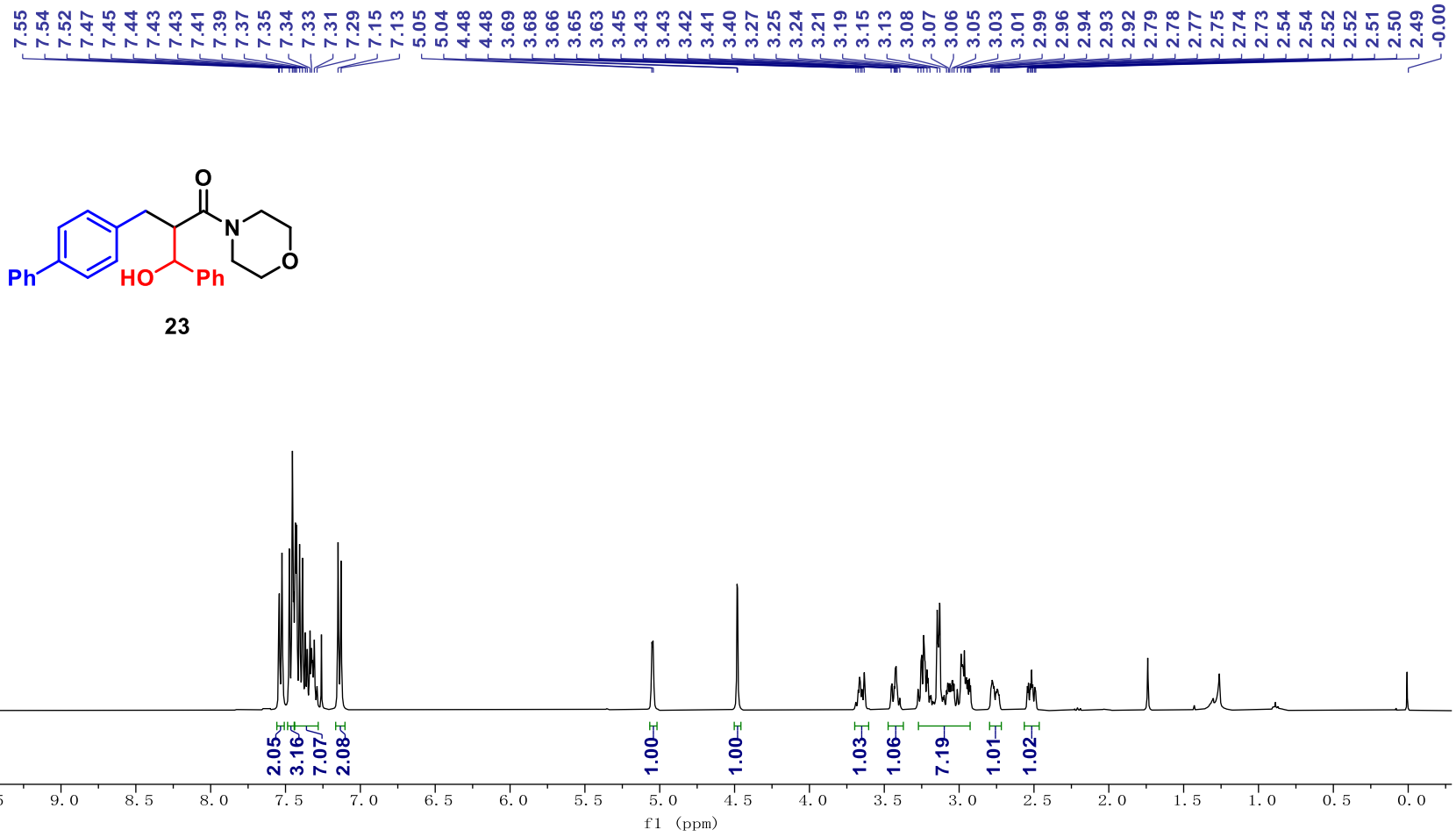


23

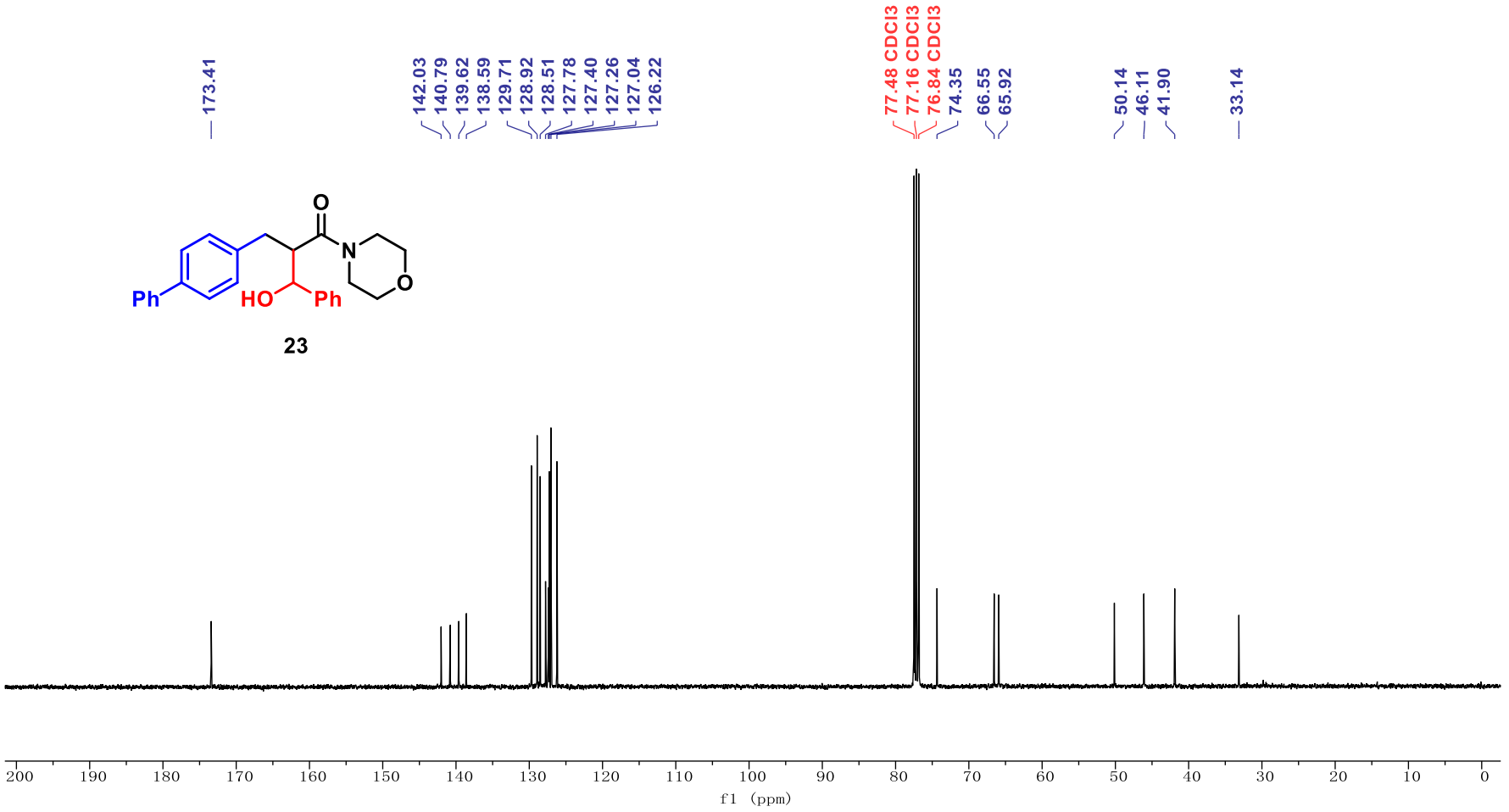
^{13}C NMR of 23 (One isomer) (101 MHz, $CDCl_3$)



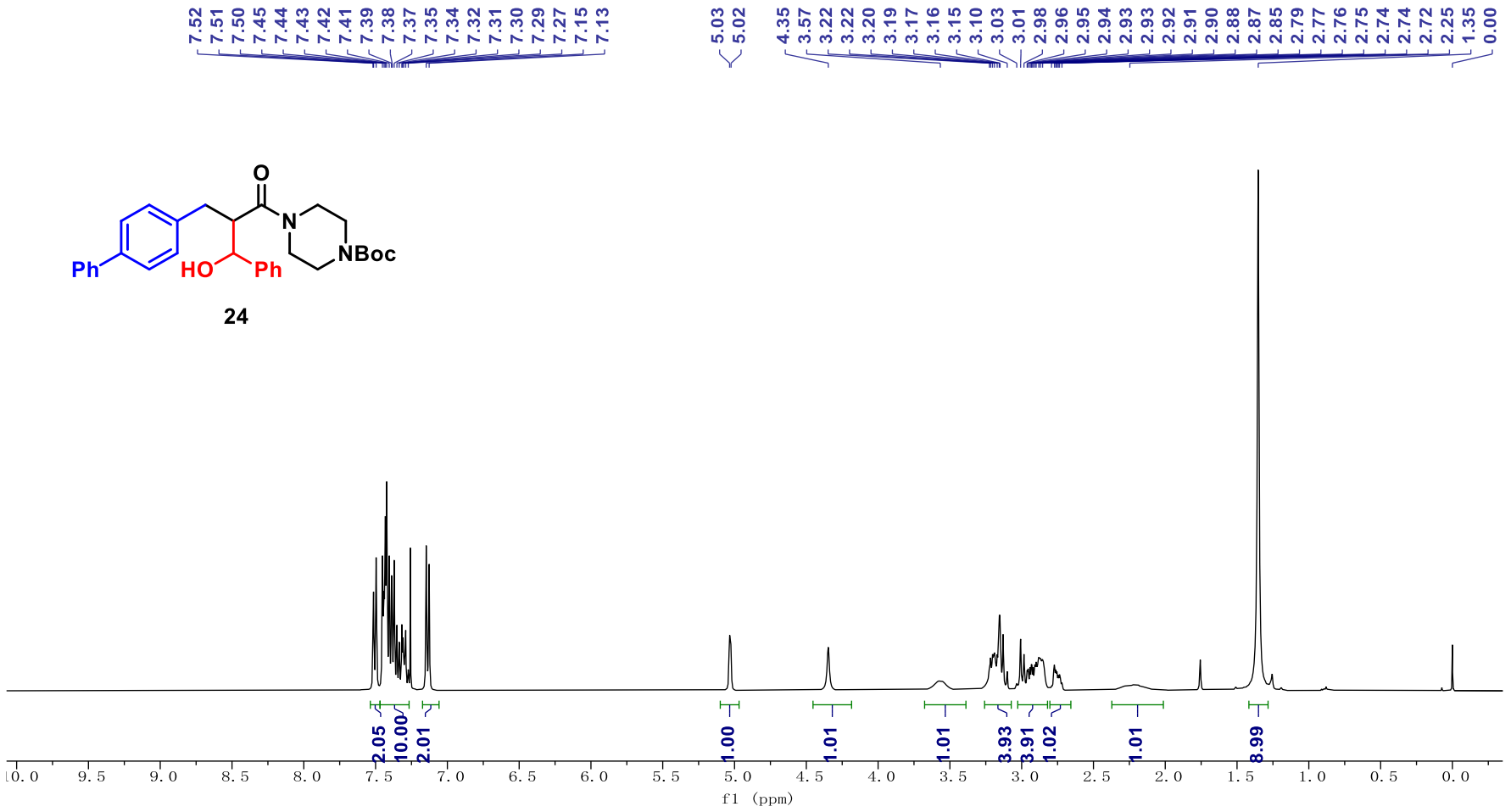
^{1}H NMR of 23 (Another isomer) (400 MHz, $CDCl_3$)



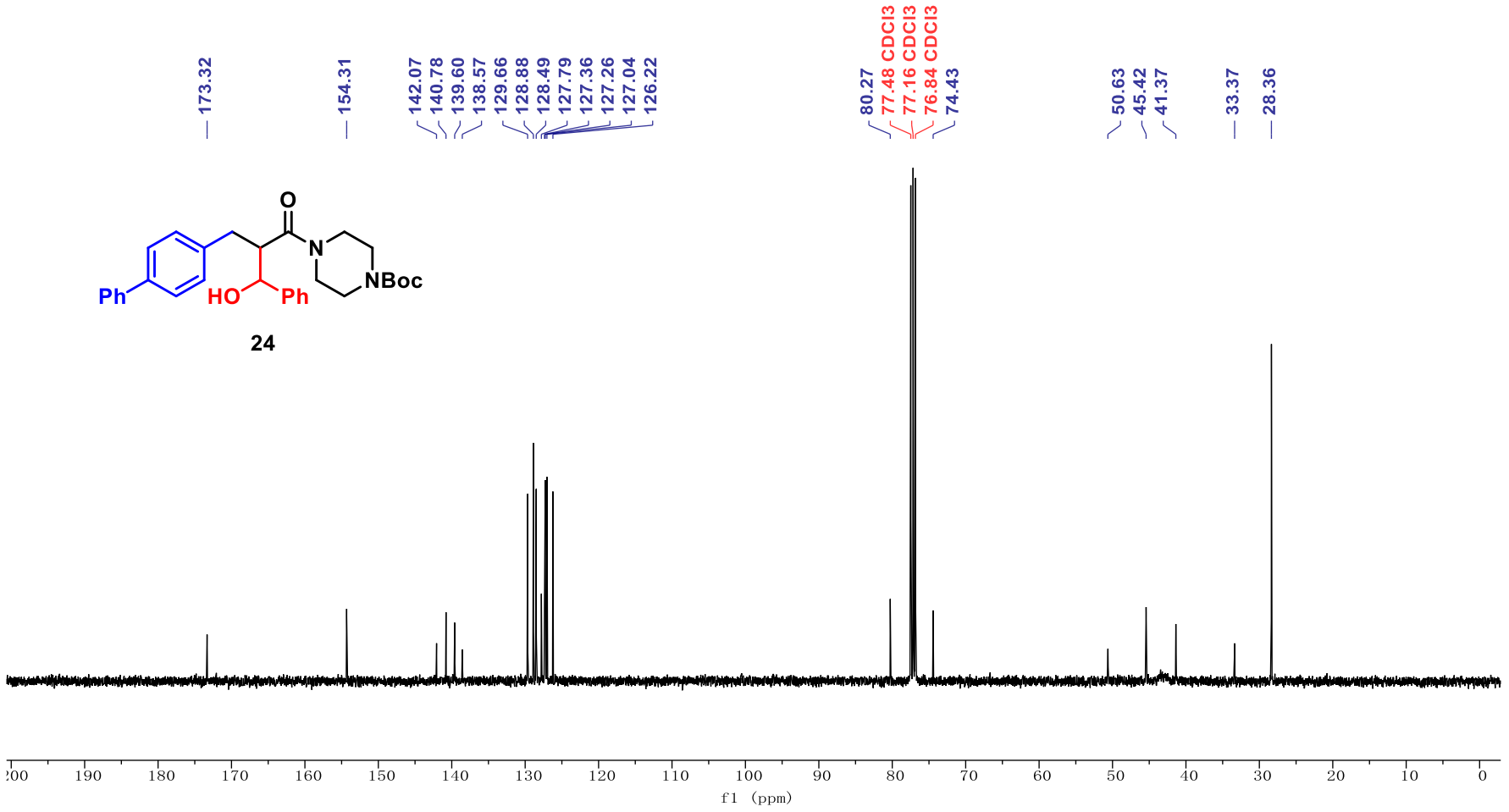
^{13}C NMR of 23 (Another isomer) (101 MHz, $CDCl_3$)



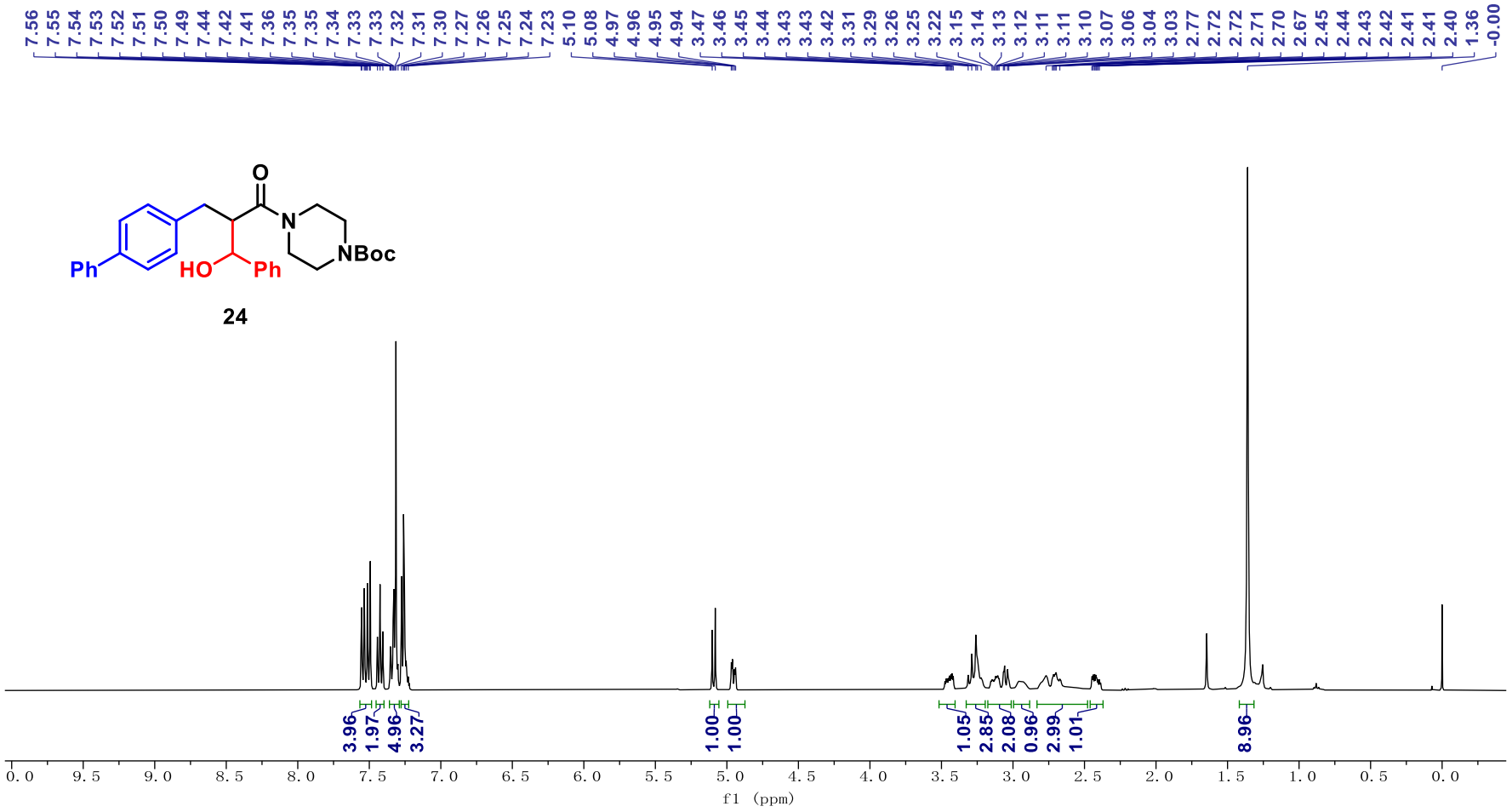
^{1}H NMR of 24 (One isomer) (400 MHz, $CDCl_3$)



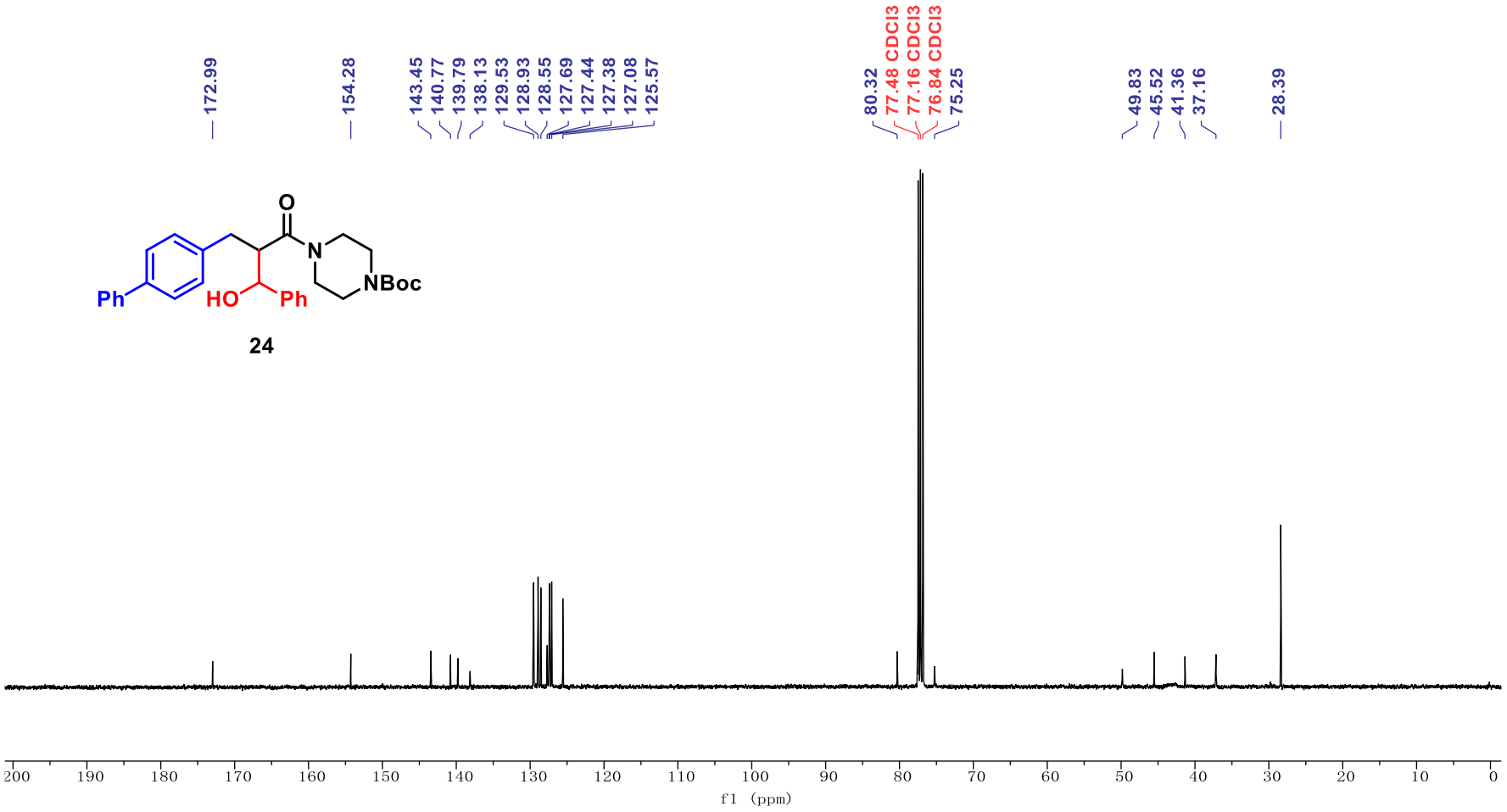
^{13}C NMR of 24 (One isomer) (101 MHz, $CDCl_3$)



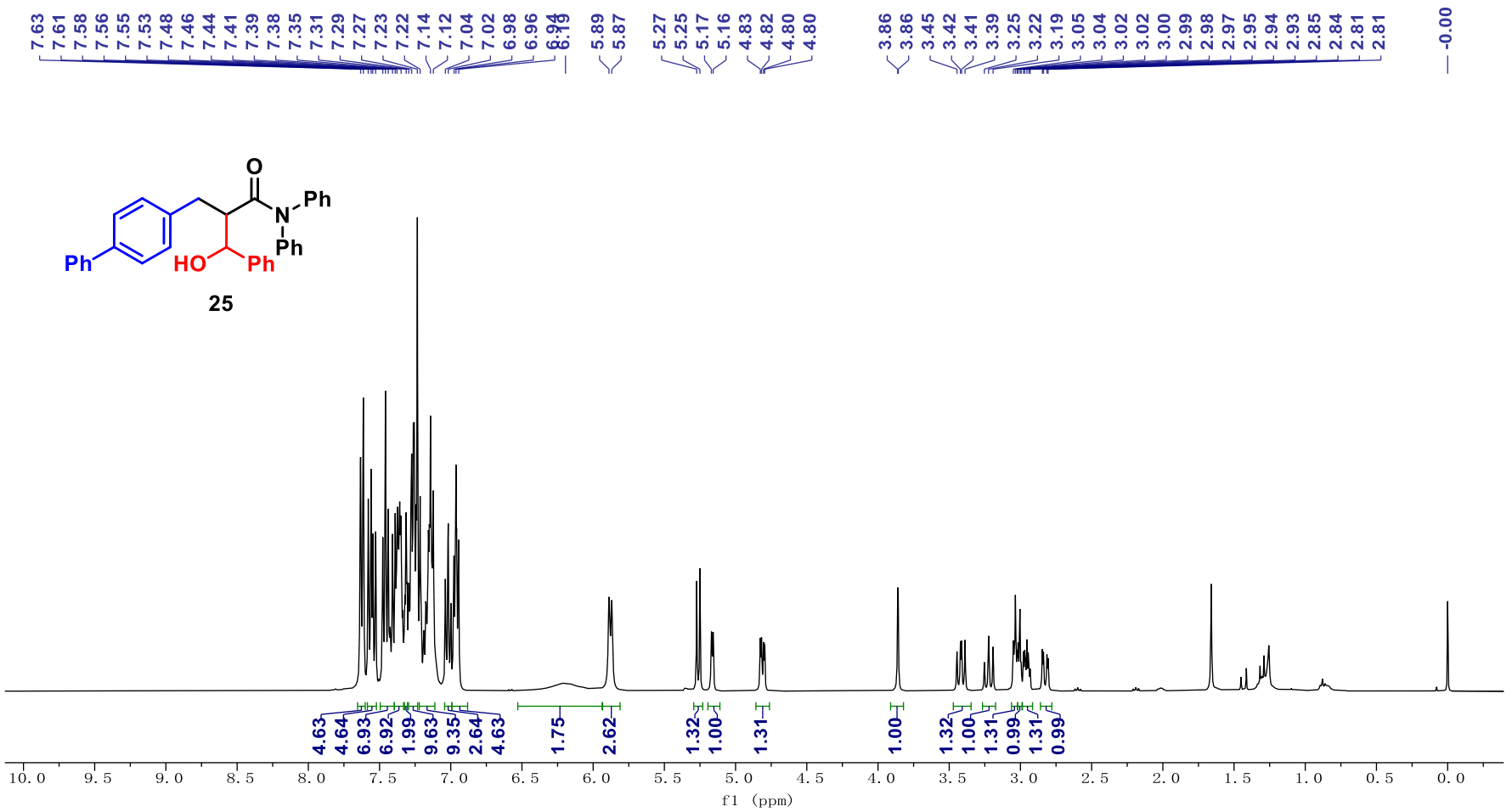
^{1}H NMR of 24 (Another isomer) (400 MHz, $CDCl_3$)



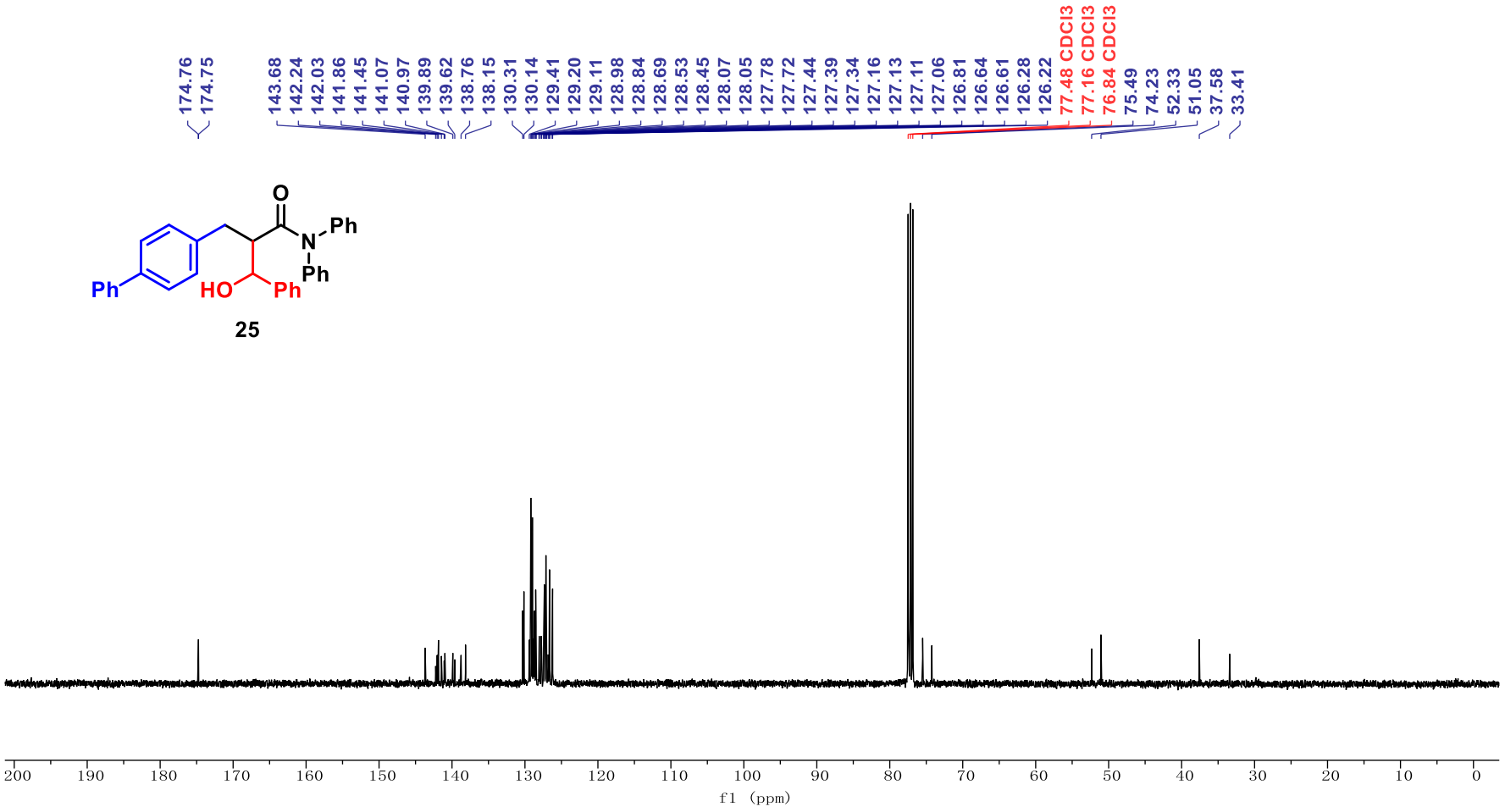
^{13}C NMR of 24 (Another isomer) (101 MHz, $CDCl_3$)



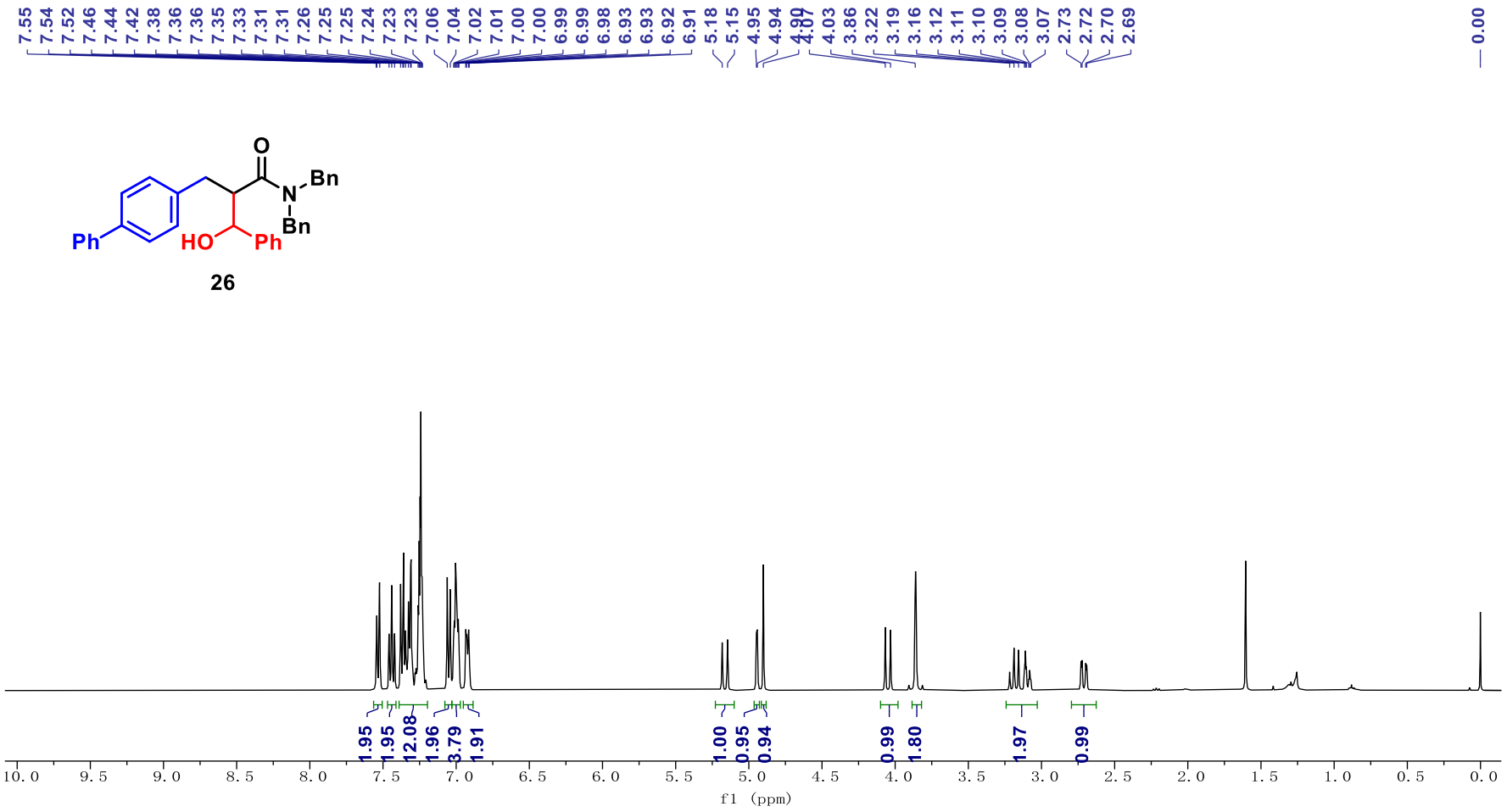
^{1}H NMR of 25 (400 MHz, $CDCl_3$)



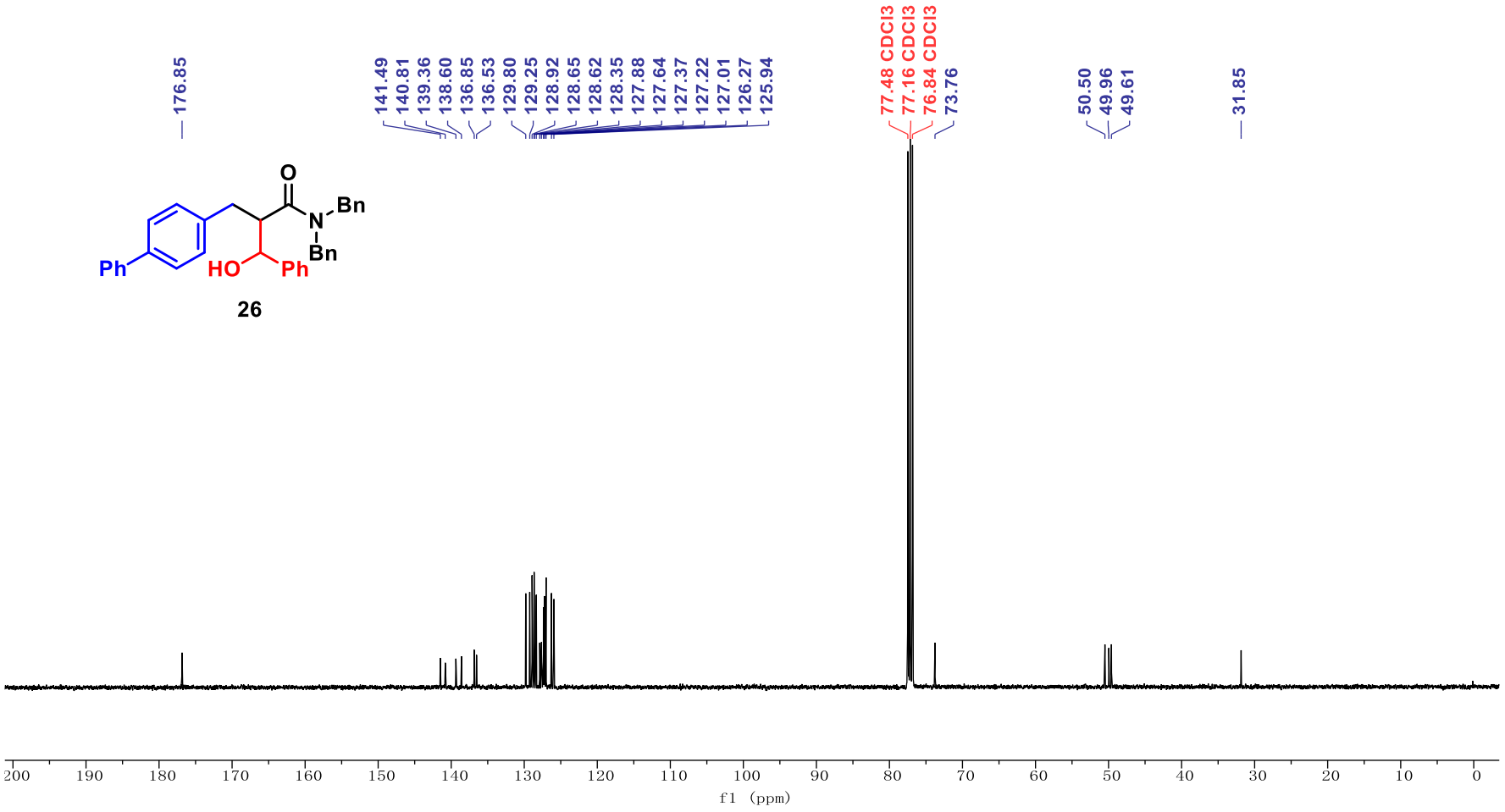
^{13}C NMR of 25 (101 MHz, $CDCl_3$)



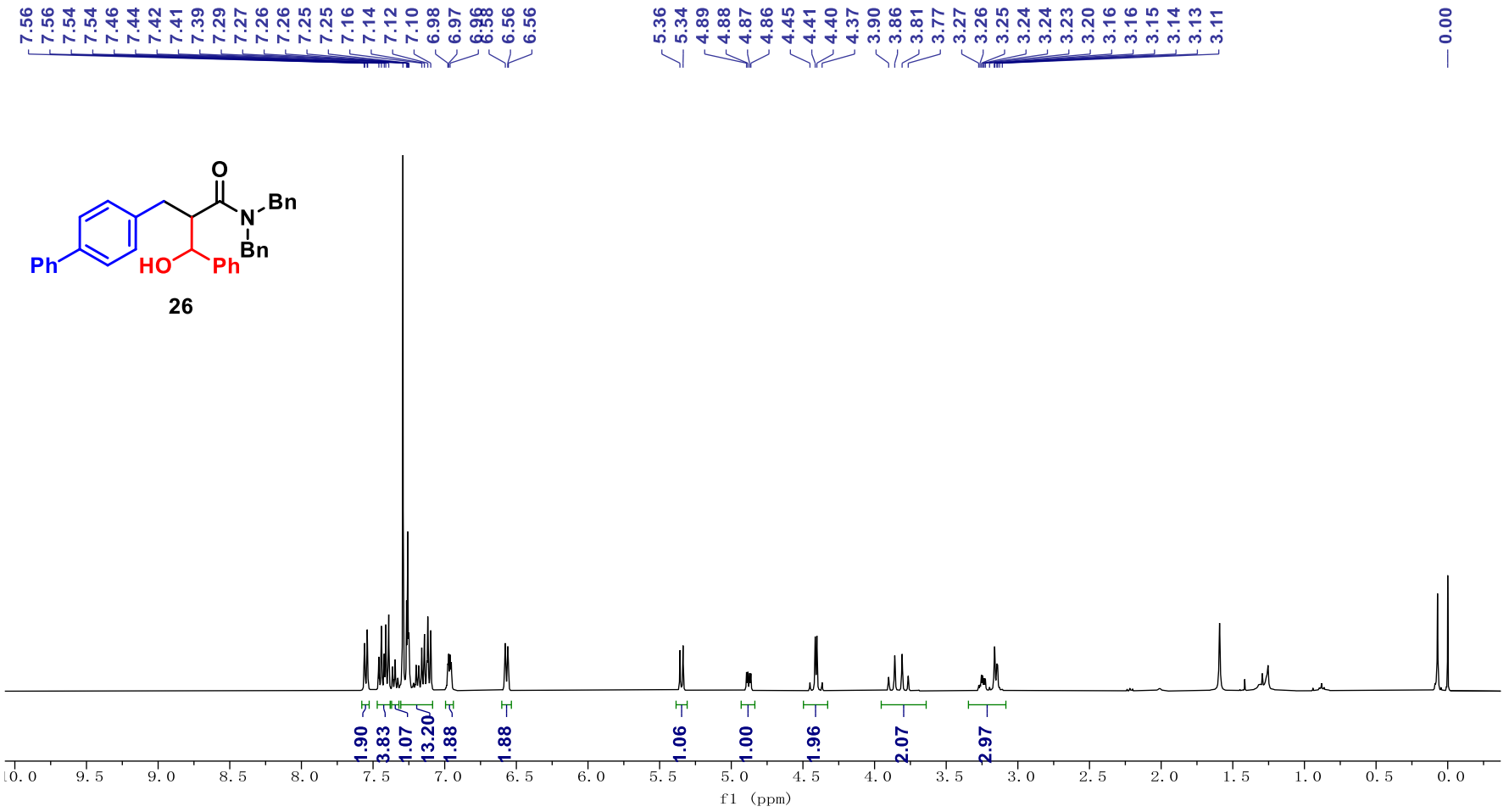
^{1}H NMR of 26 (One isomer) (400 MHz, $CDCl_3$)



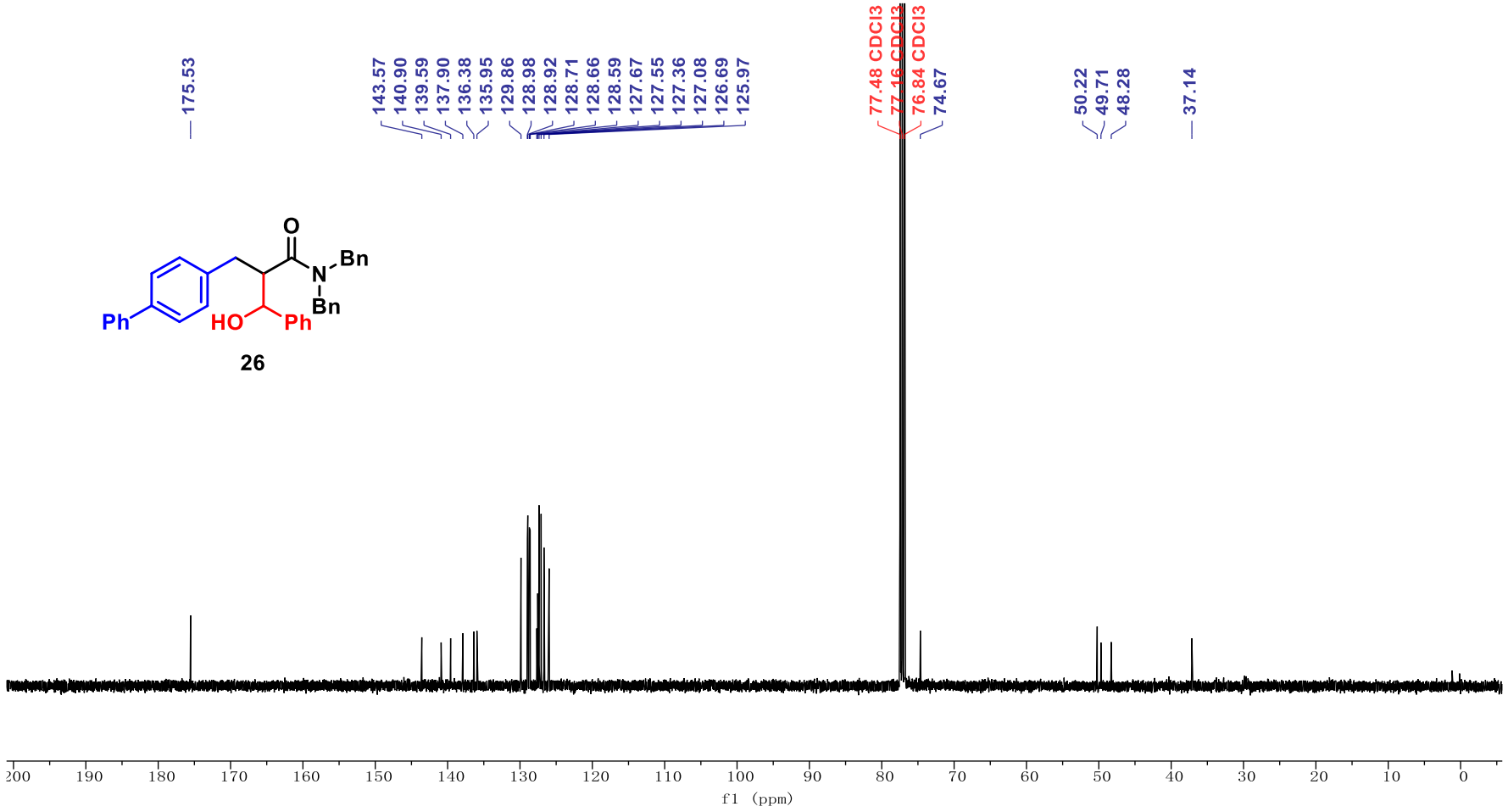
^{13}C NMR of 26 (One isomer) (101 MHz, $CDCl_3$)



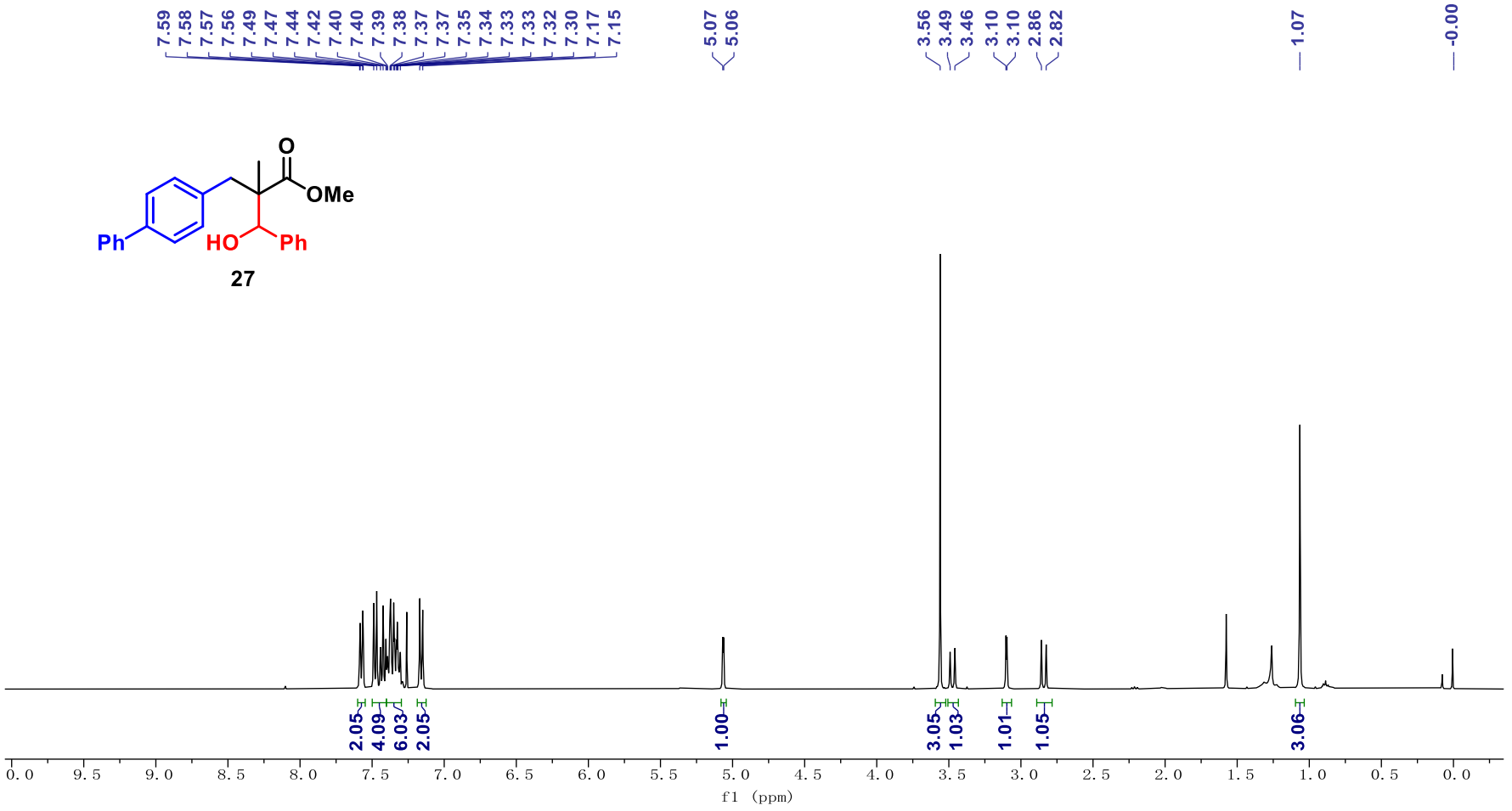
^{1}H NMR of 26 (Another isomer) (400 MHz, $CDCl_3$)



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

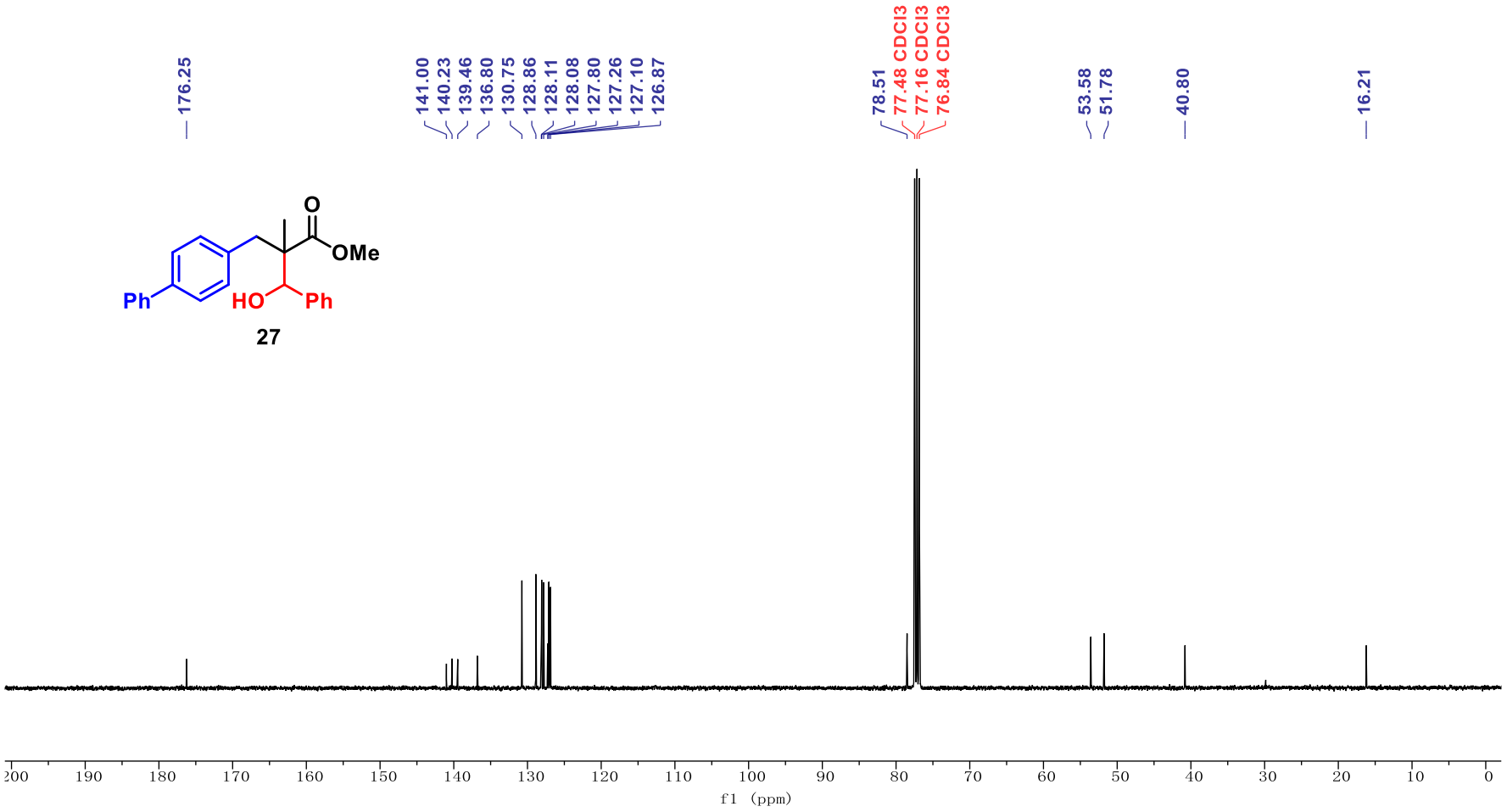


^{1}H NMR of 27 (One isomer) (400 MHz, $CDCl_3$)

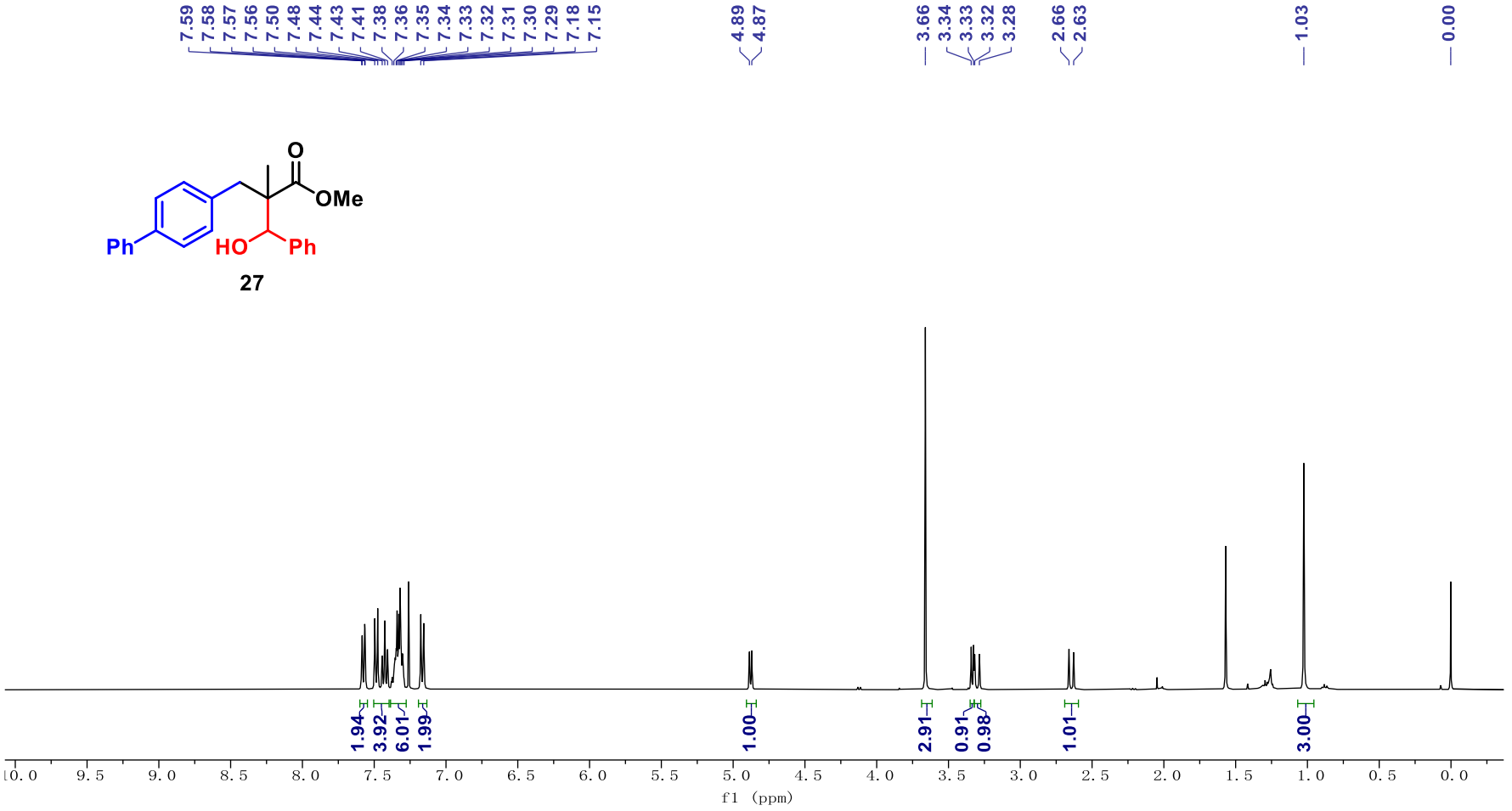


27

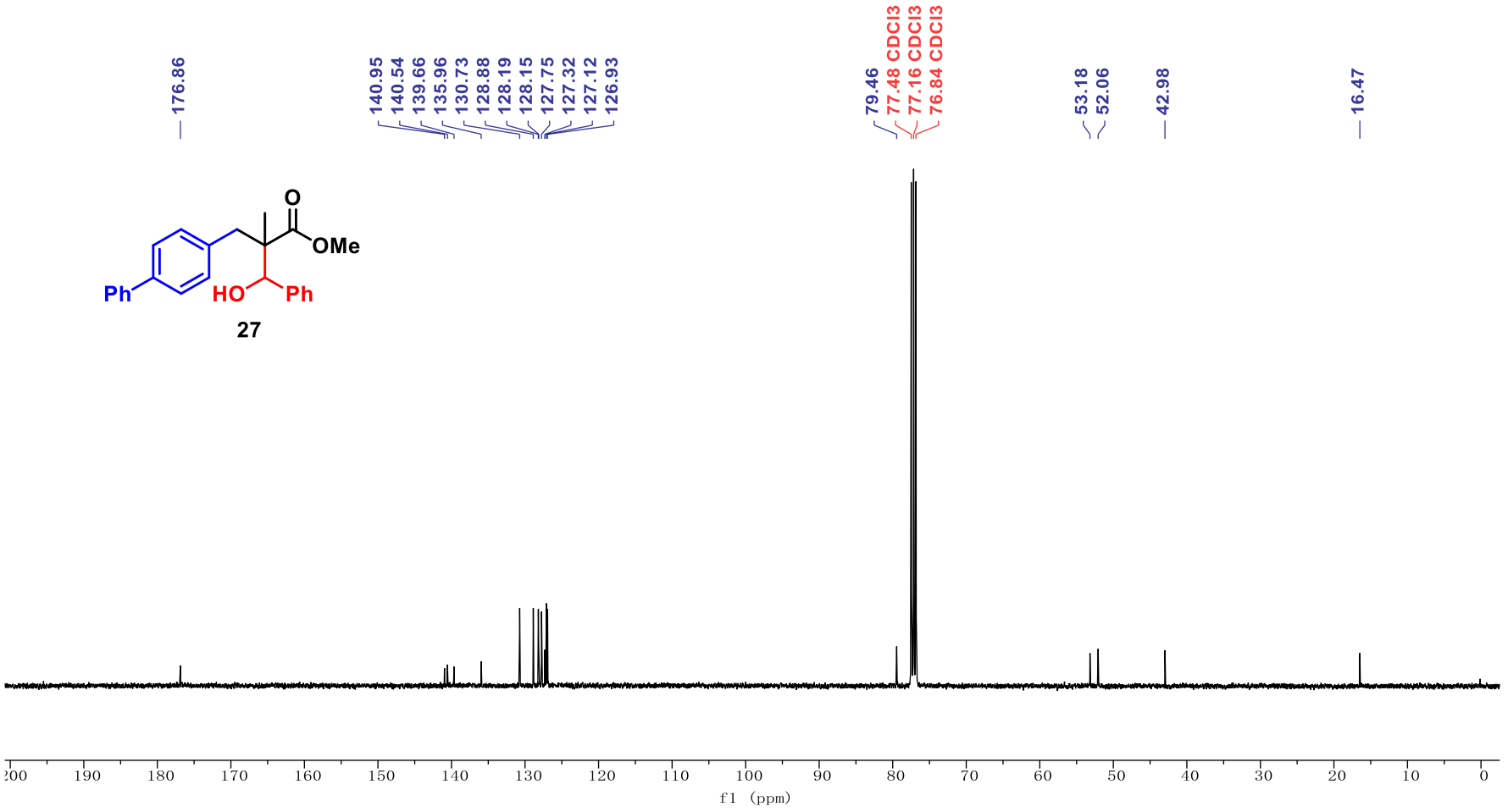
^{13}C NMR of 27 (One isomer) (101 MHz, $CDCl_3$)



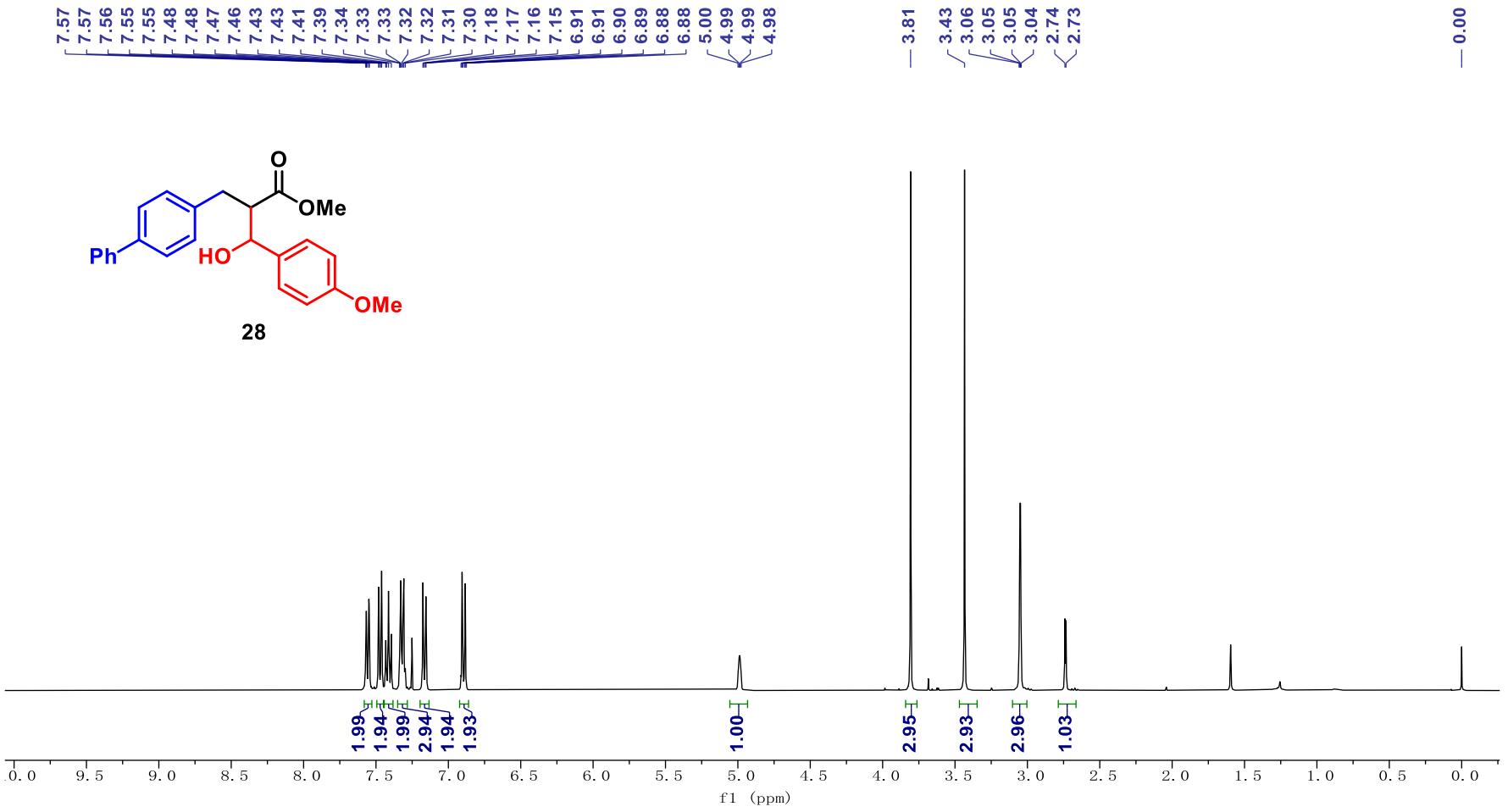
^{1}H NMR of 27 (Another isomer) (400 MHz, $CDCl_3$)



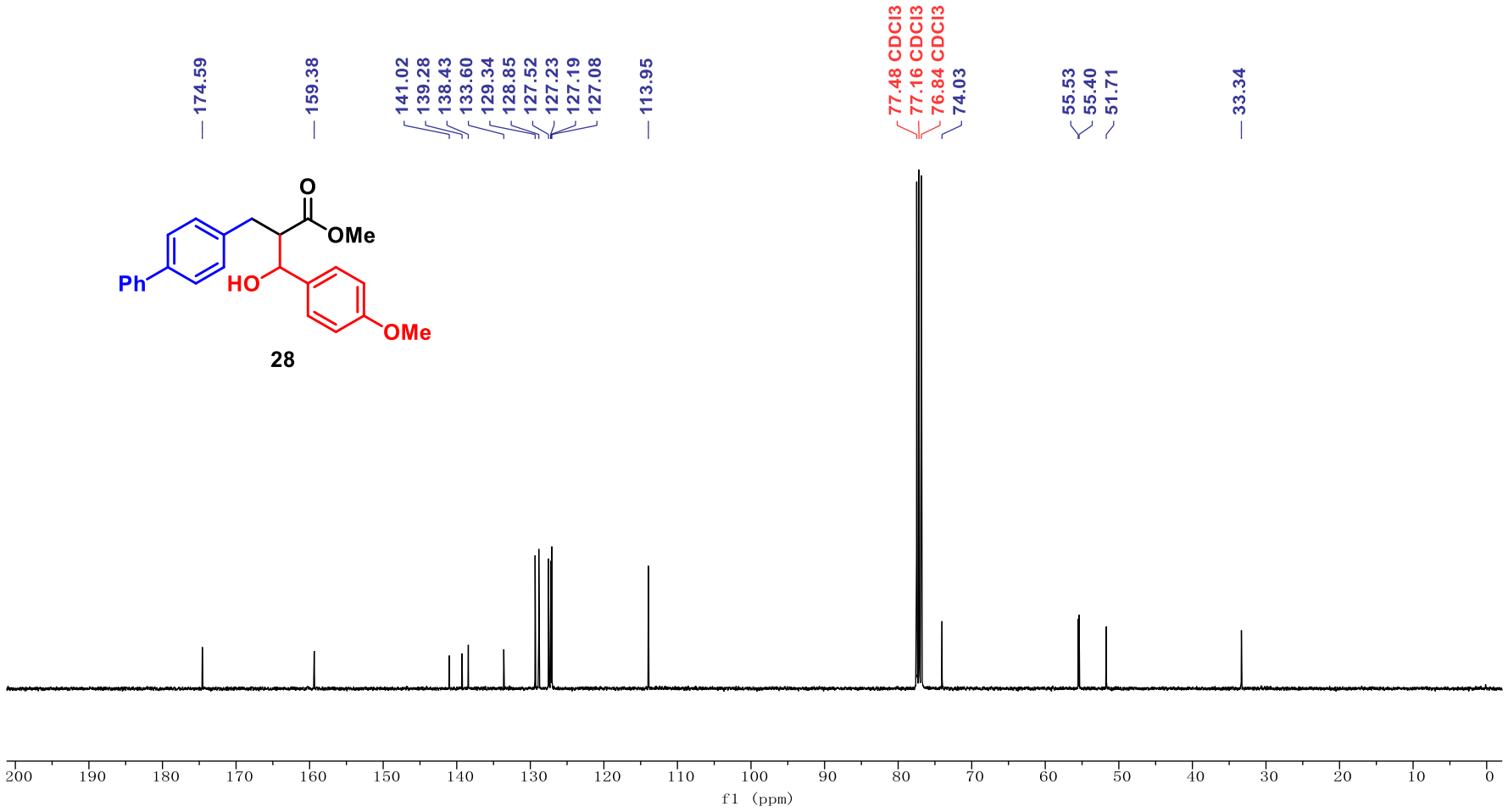
^{13}C NMR of 27 (Another isomer) (101 MHz, $CDCl_3$)



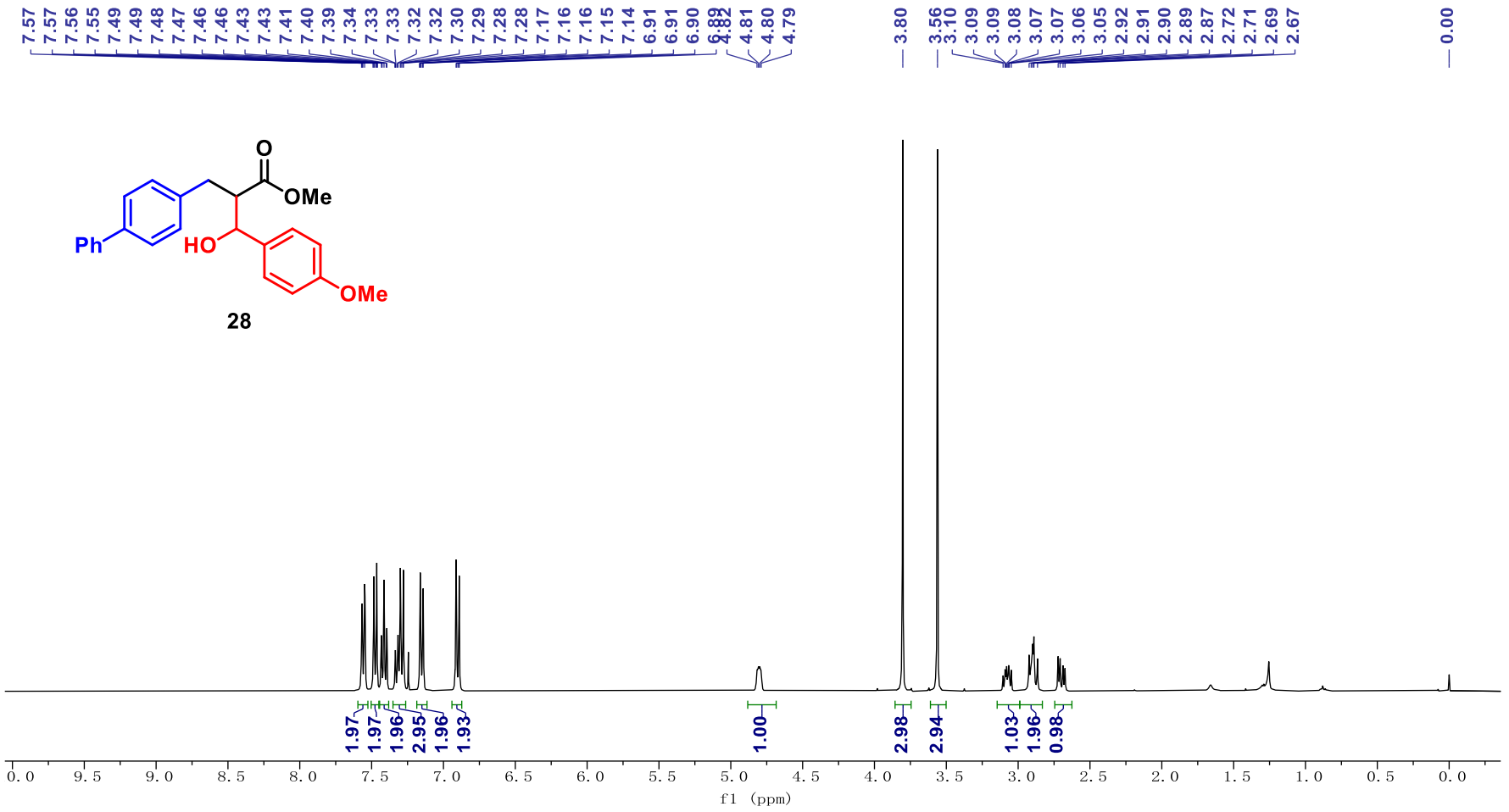
^{1}H NMR of 28 (One isomer) (400 MHz, $CDCl_3$)



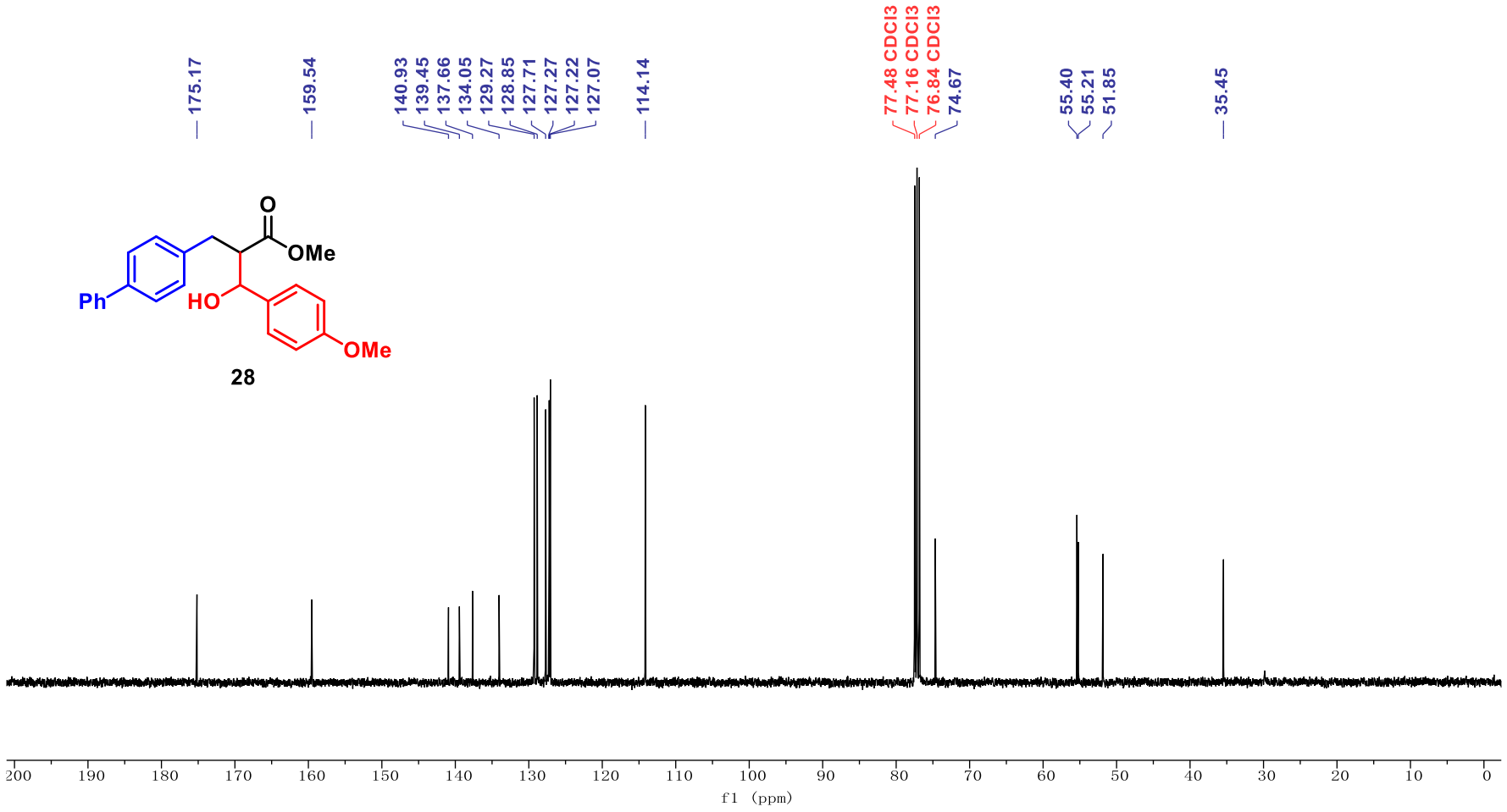
^{13}C NMR of 28 (One isomer) (101 MHz, $CDCl_3$)



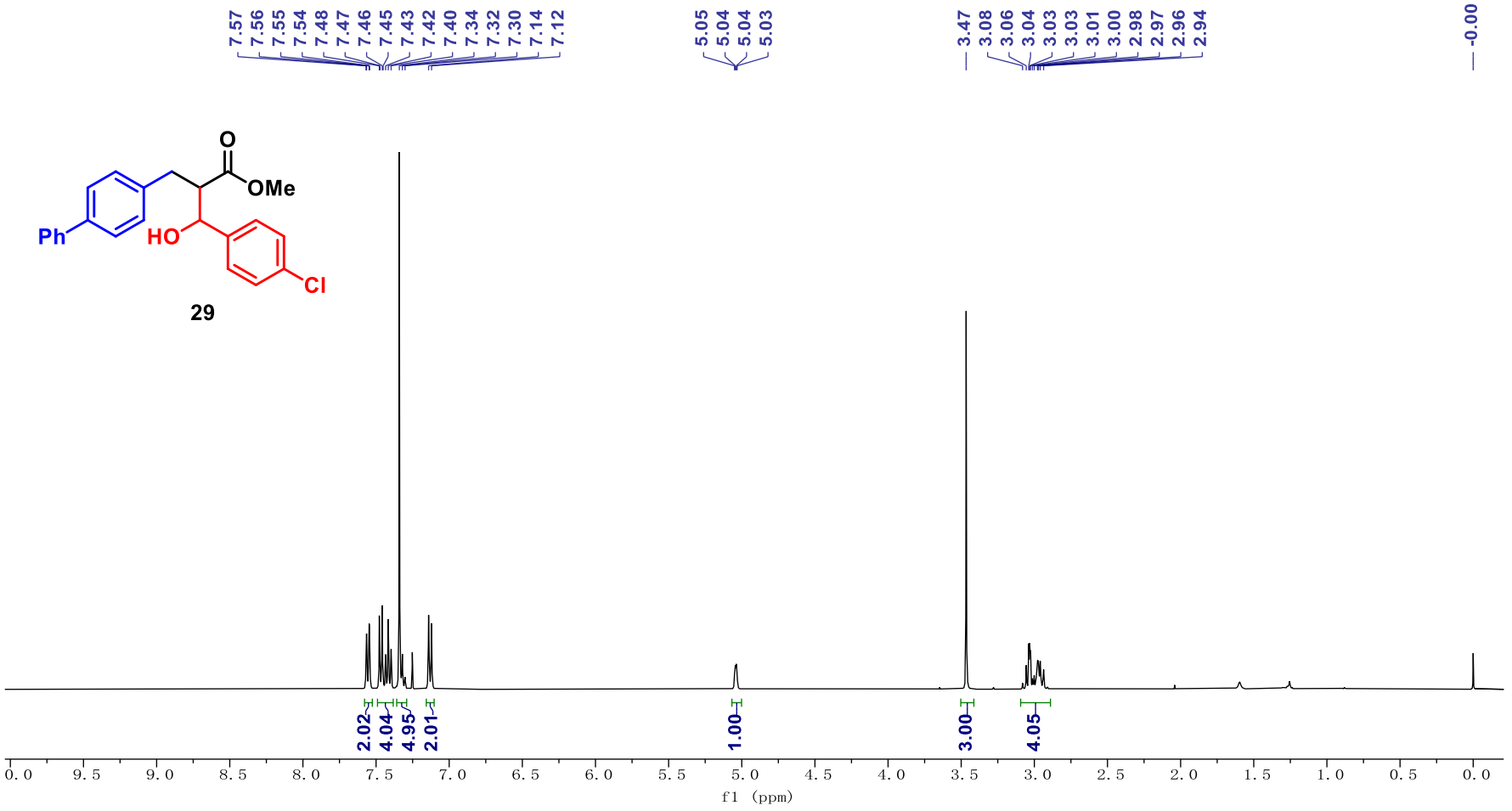
^{1}H NMR of 28 (Another isomer) (400 MHz, $CDCl_3$)



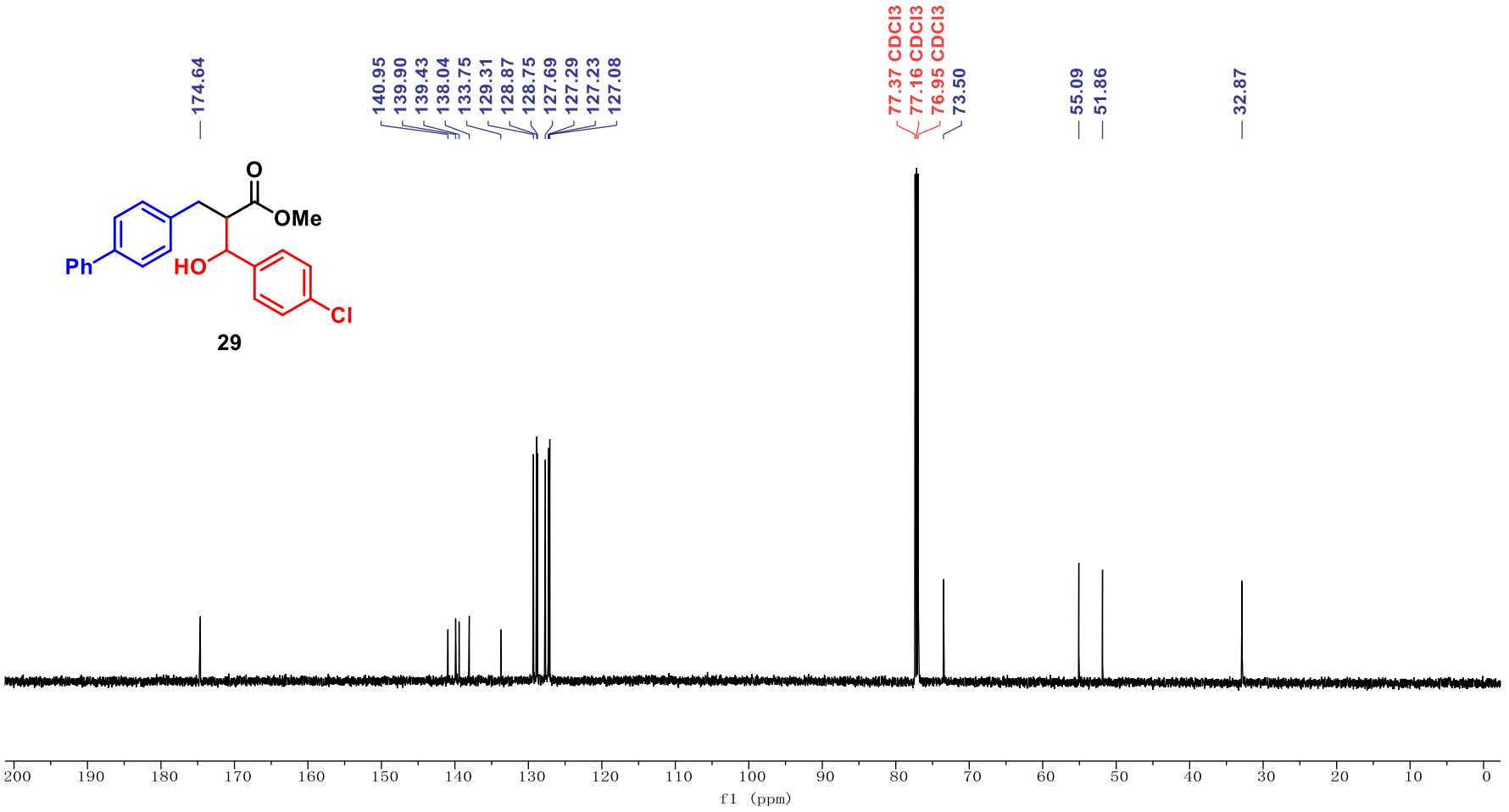
^{13}C NMR of 28 (Another isomer) (101 MHz, $CDCl_3$)



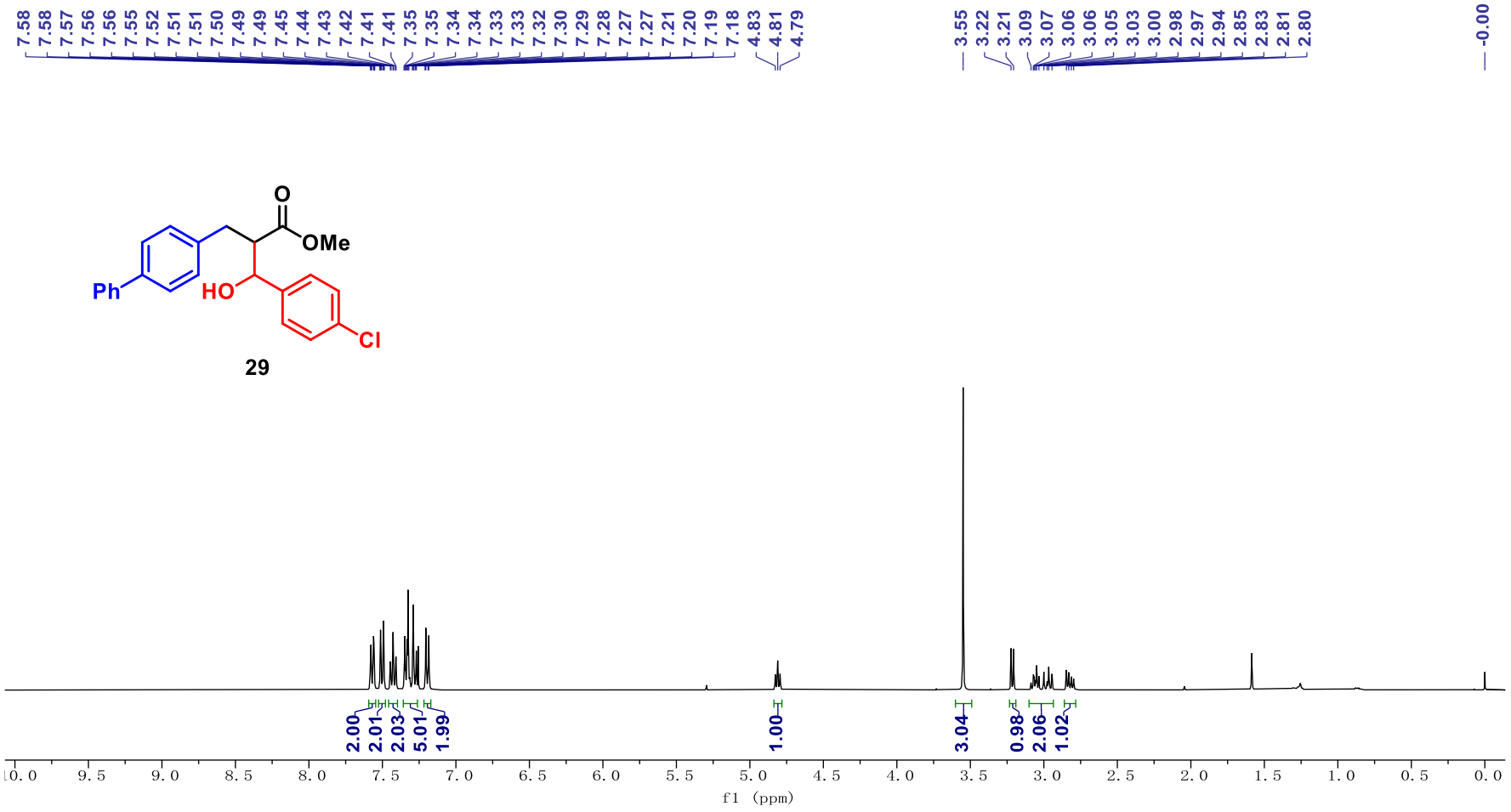
^{1}H NMR of 29 (One isomer) (400 MHz, $CDCl_3$)



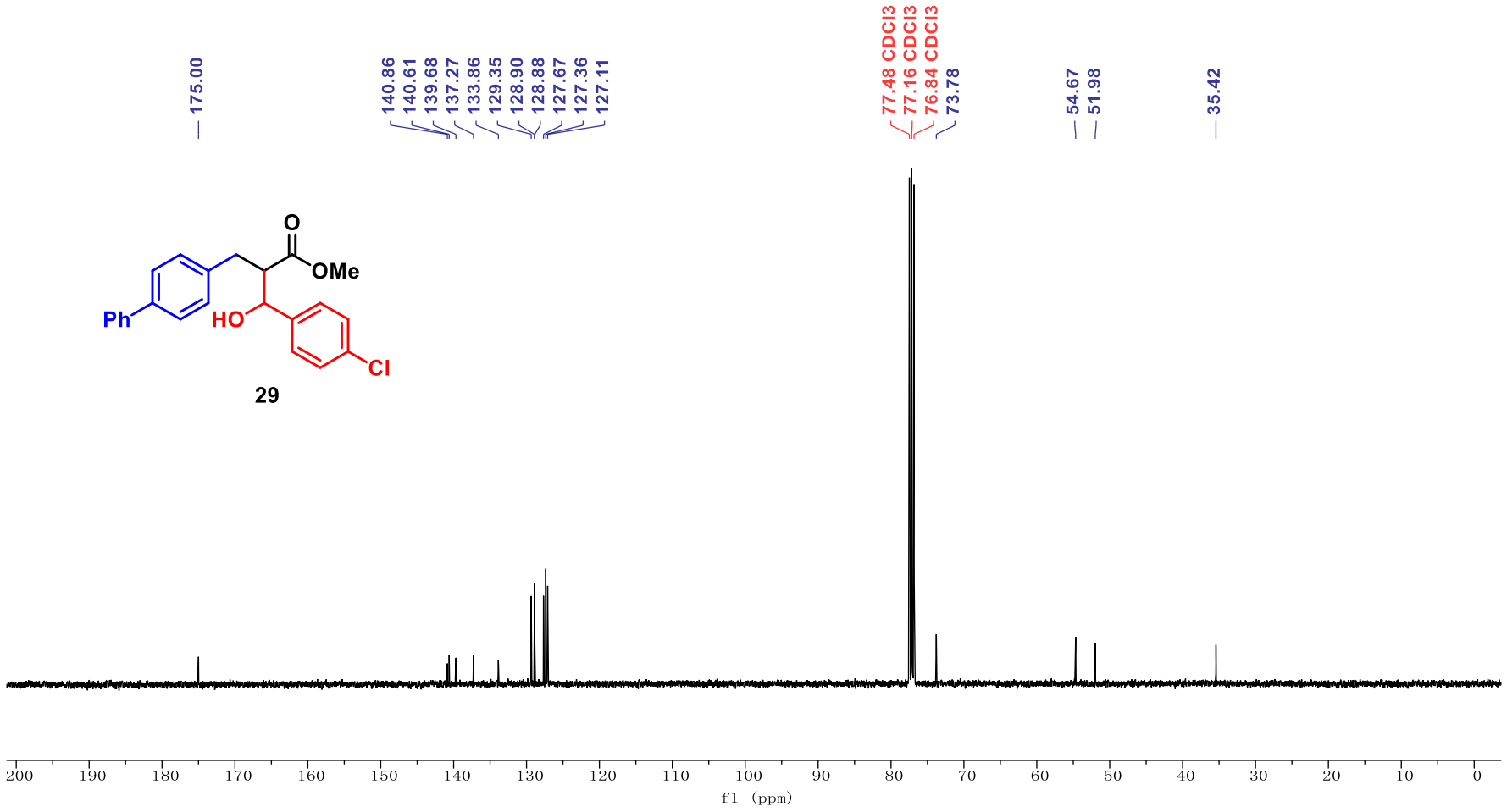
^{13}C NMR of 29 (One isomer) (151 MHz, $CDCl_3$)



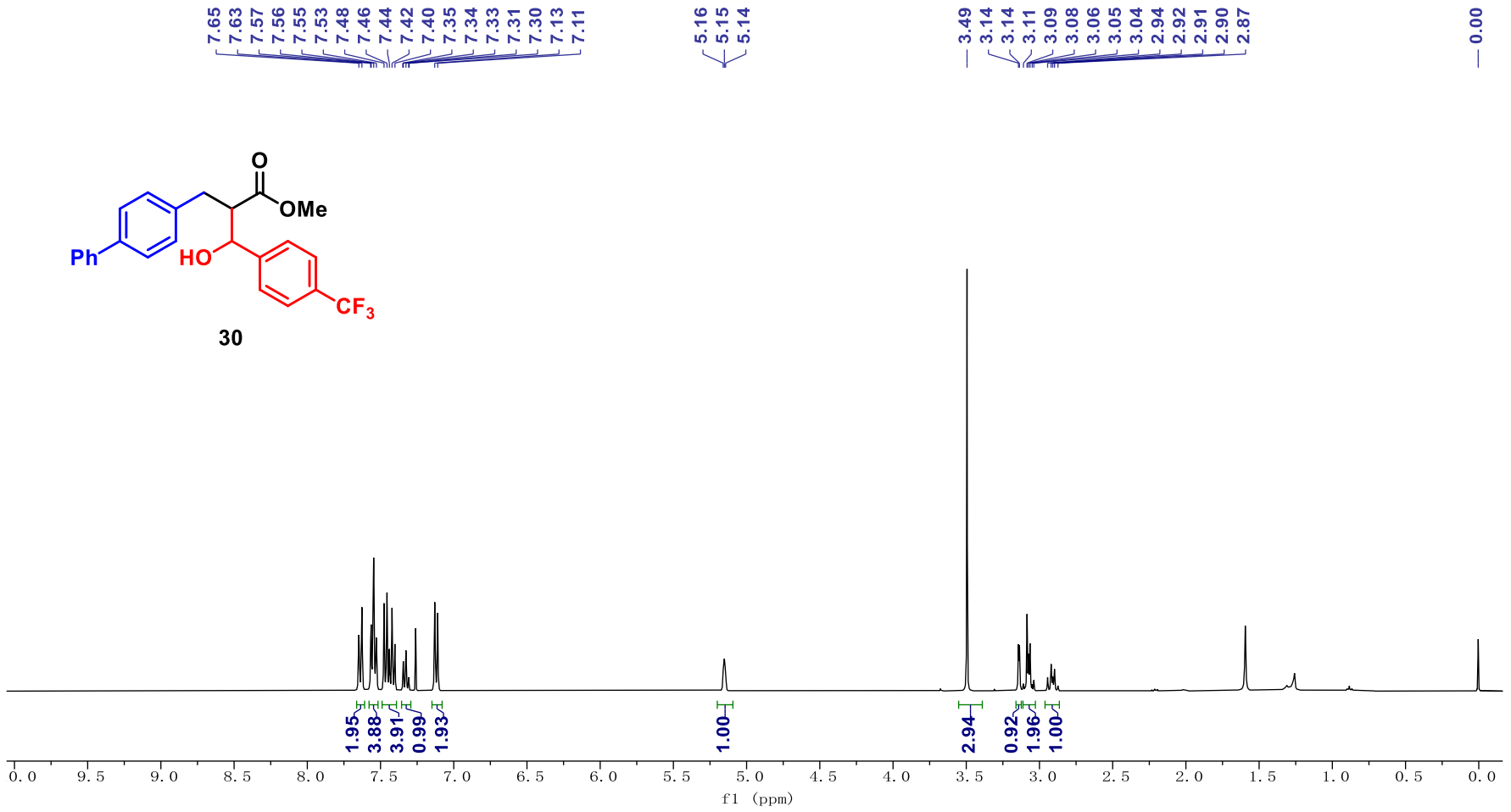
^{1}H NMR of 29 (Another isomer) (400 MHz, $CDCl_3$)



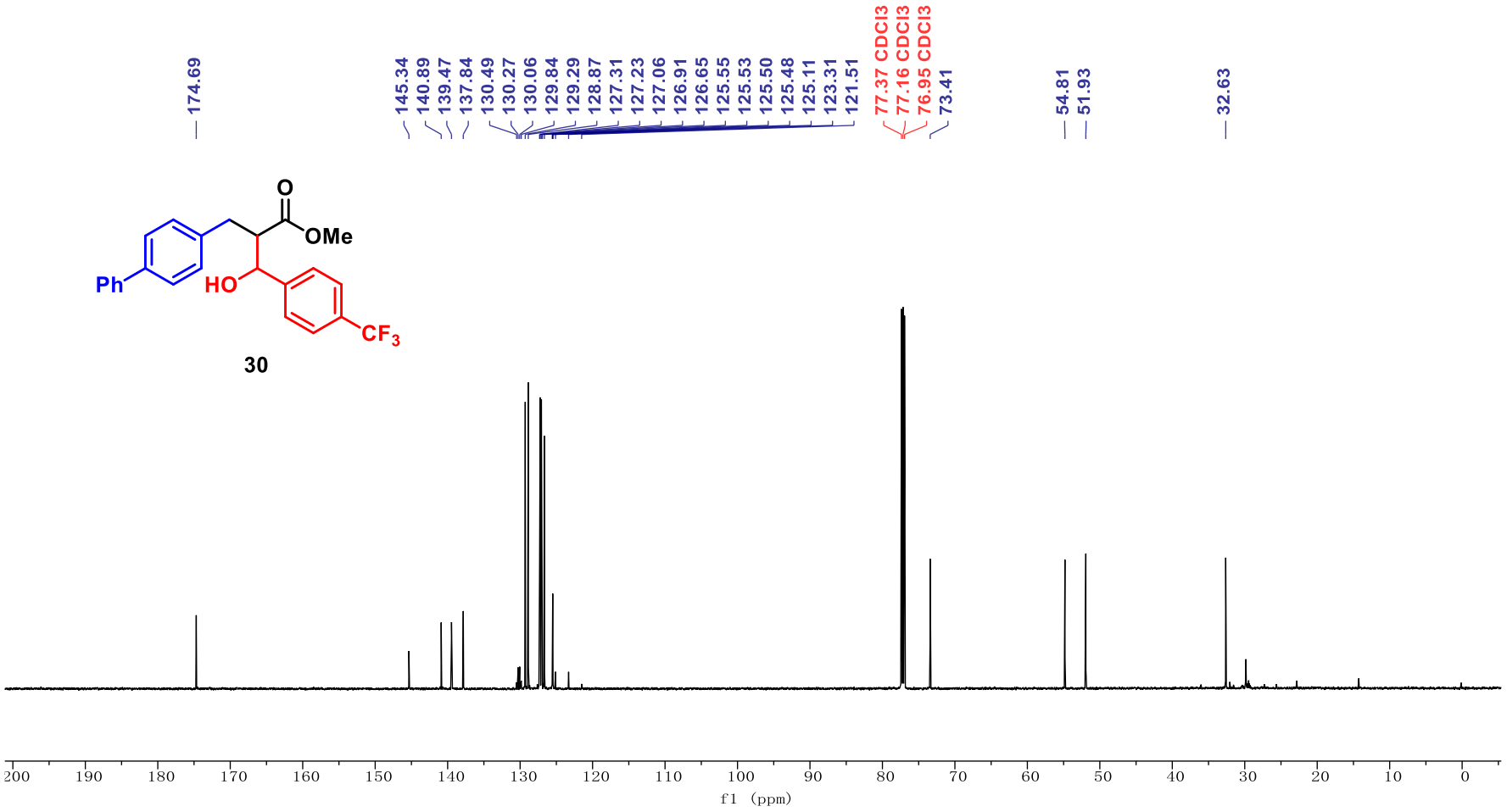
^{13}C NMR of 29 (Another isomer) (101 MHz, $CDCl_3$)



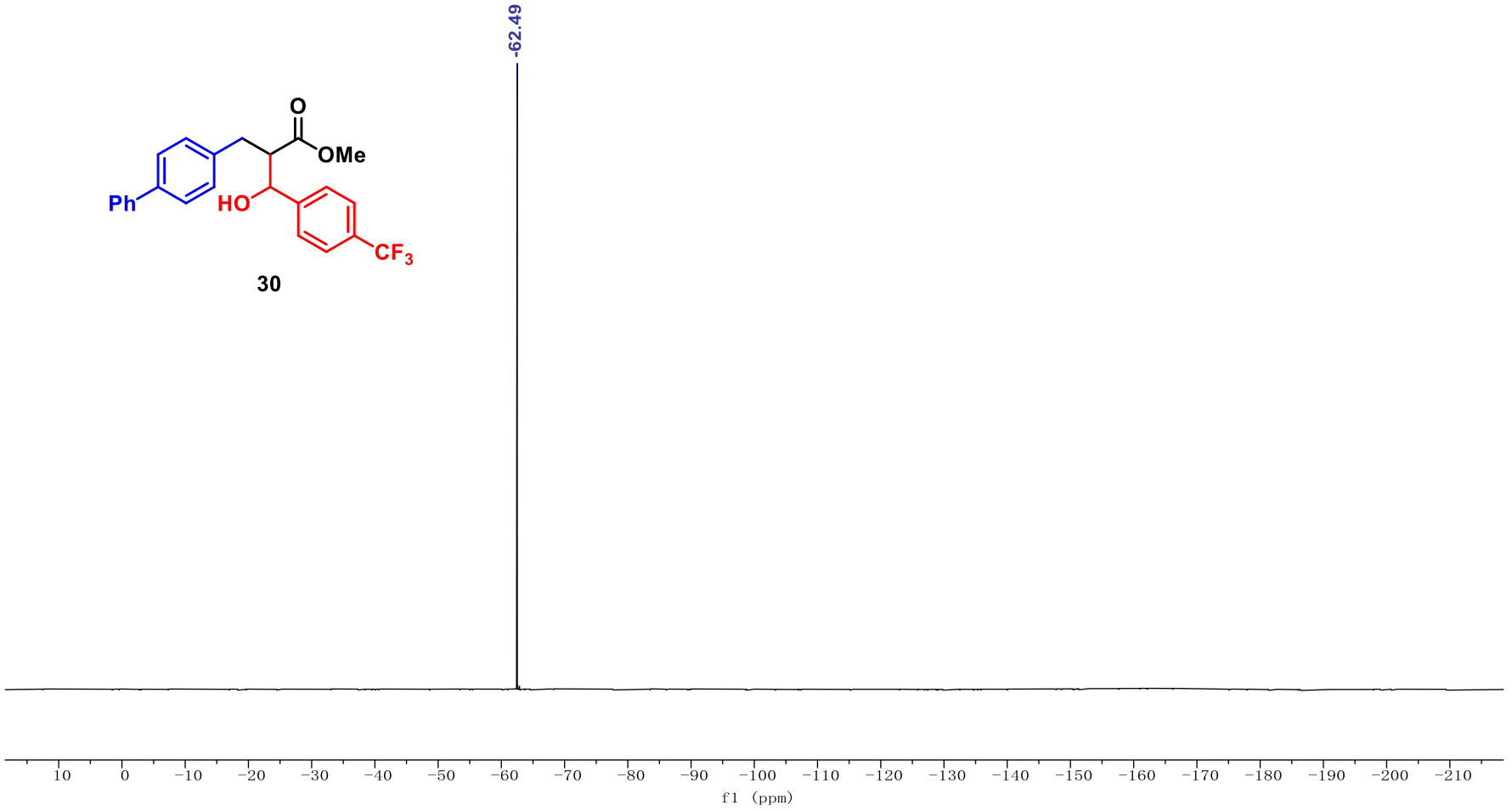
^{1}H NMR of 30 (One isomer) (400 MHz, $CDCl_3$)



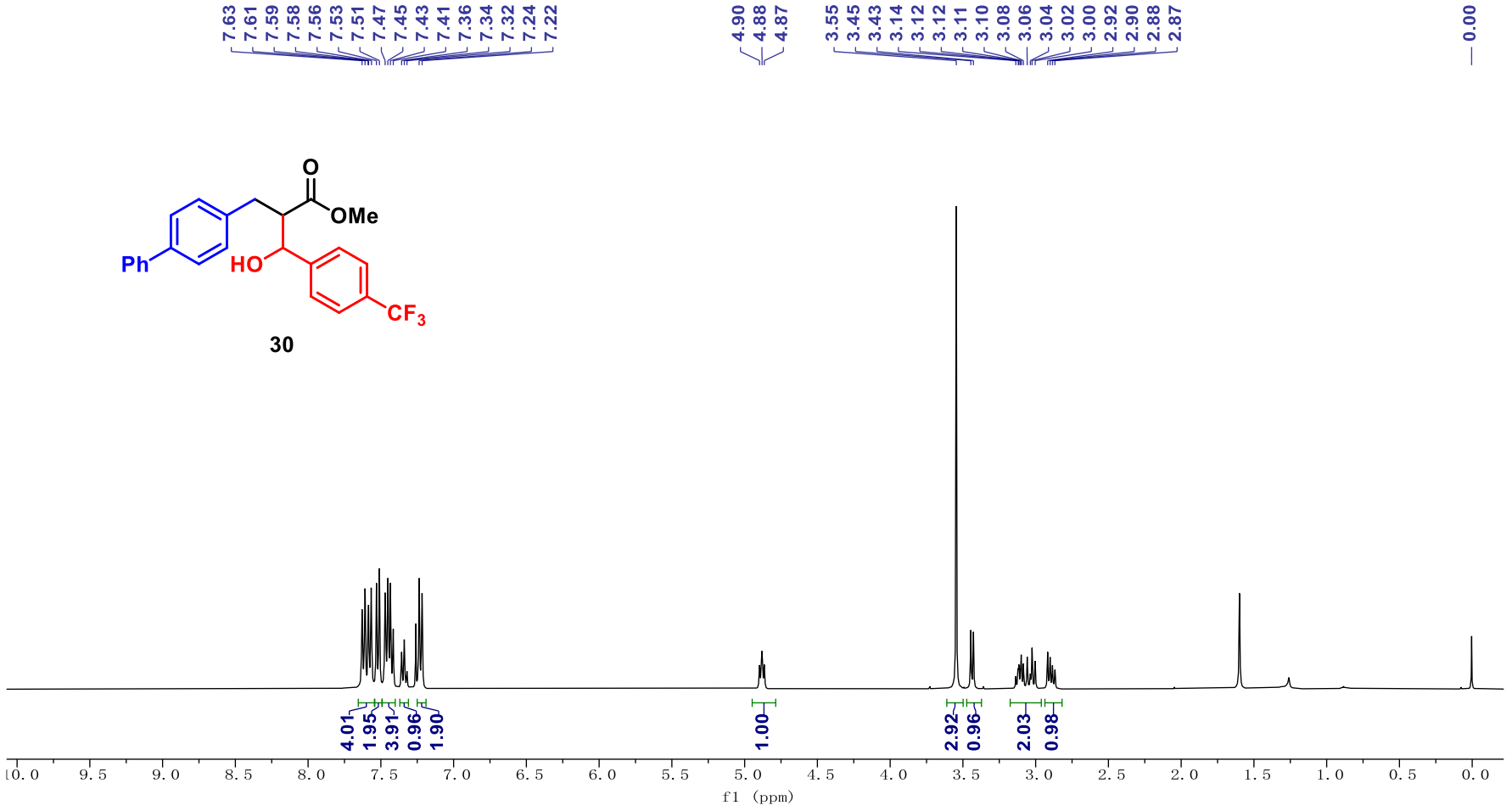
^{13}C NMR of 30 (One isomer) (151 MHz, $CDCl_3$)



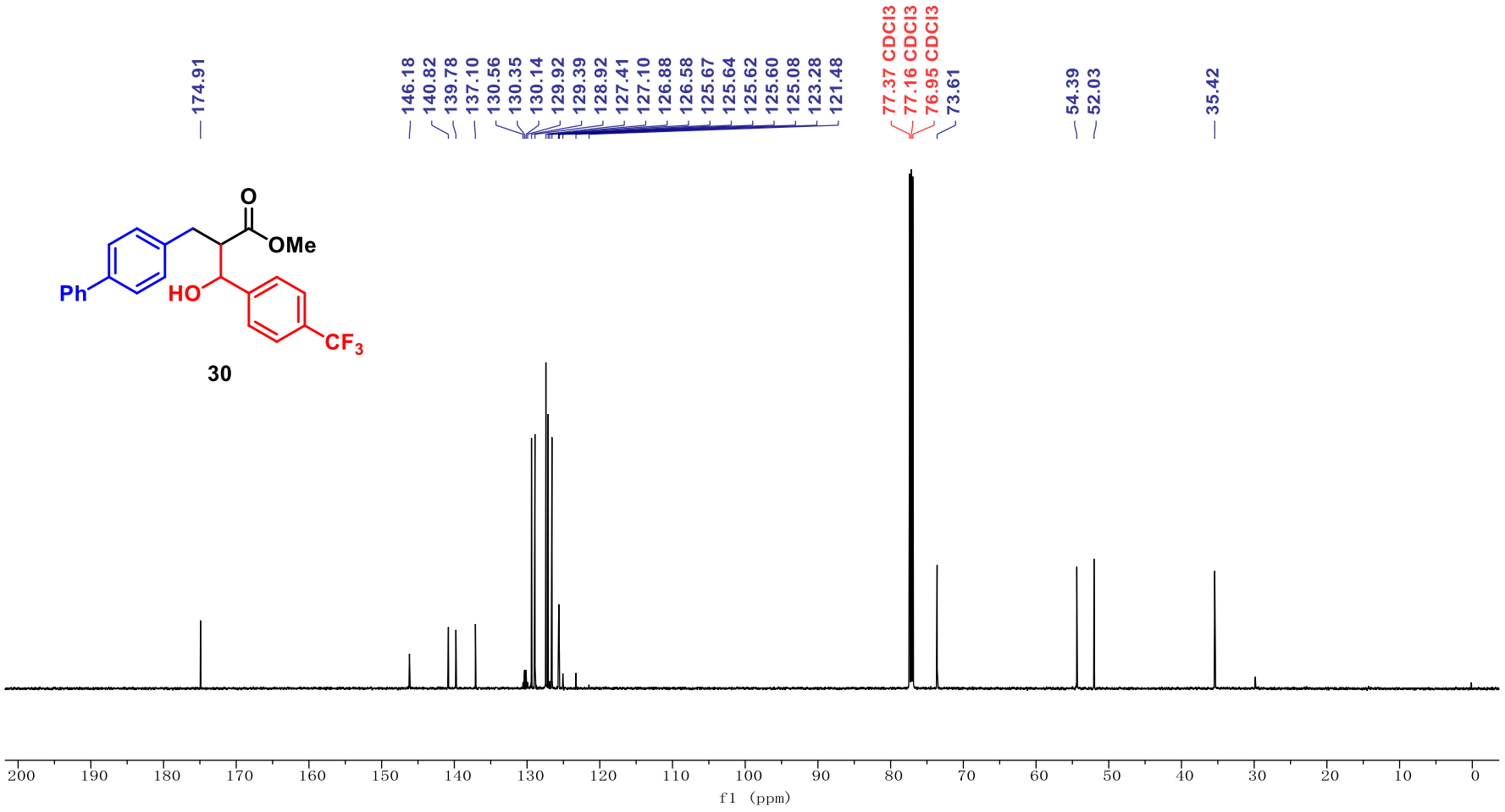
^{19}F NMR of 30 (One isomer) (565 MHz, $CDCl_3$)



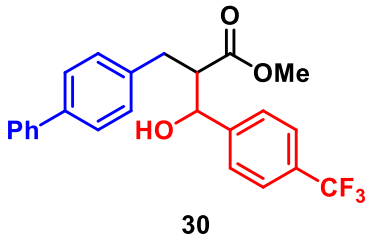
^{1}H NMR of 30 (Another isomer) (400 MHz, $CDCl_3$)



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

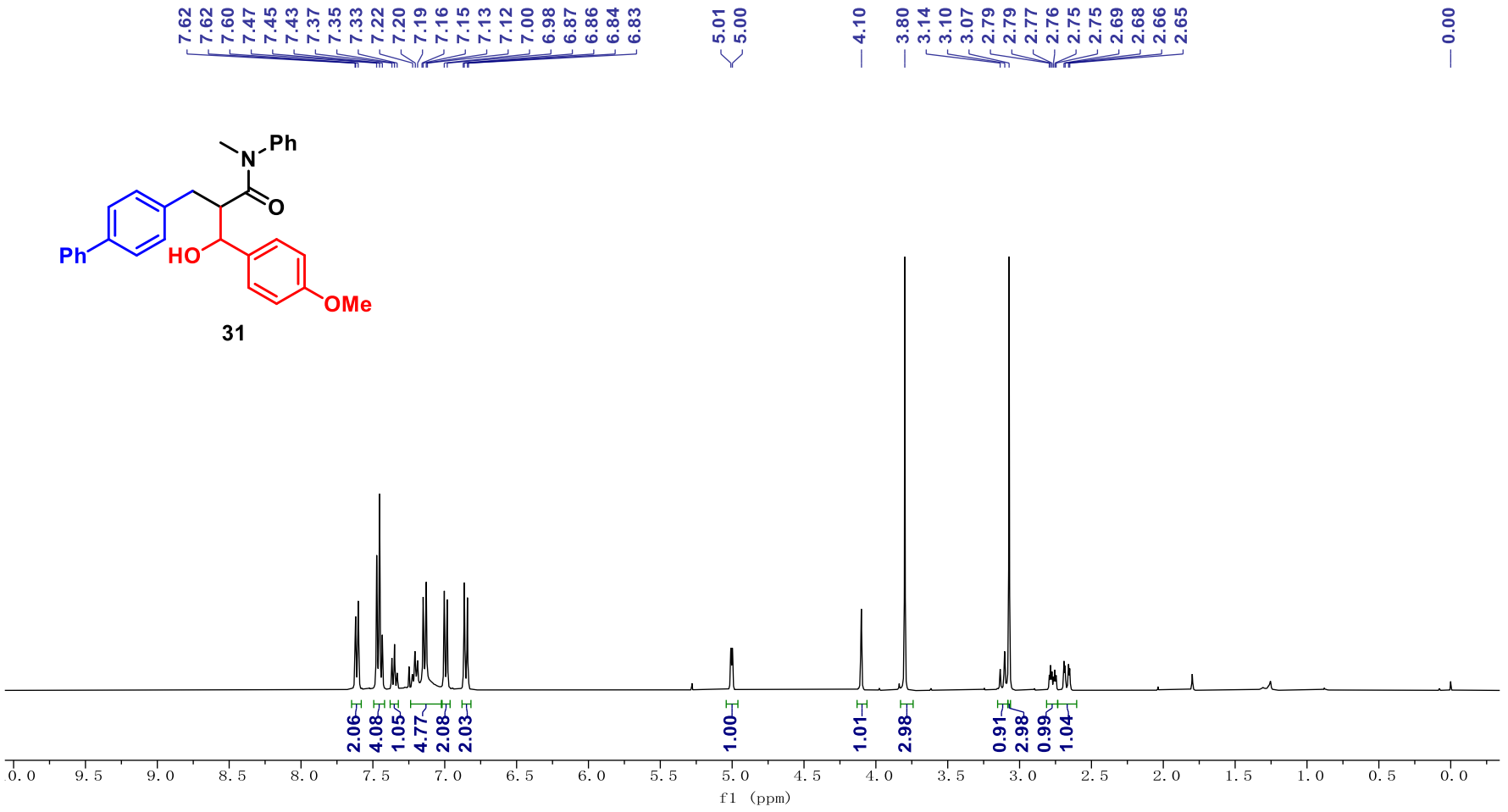


^{19}F NMR of 30 (Another isomer) (565 MHz, $CDCl_3$)

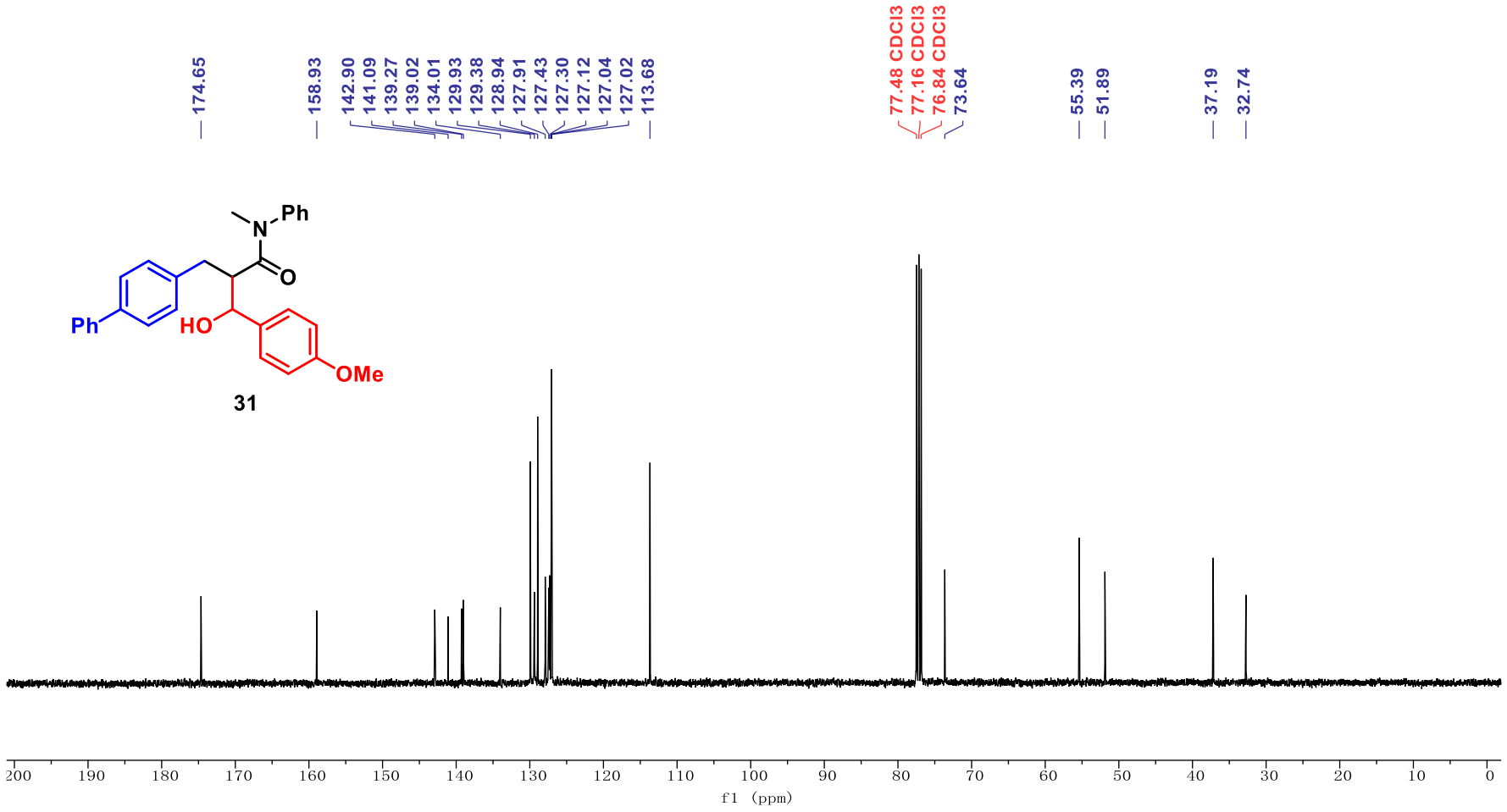


30

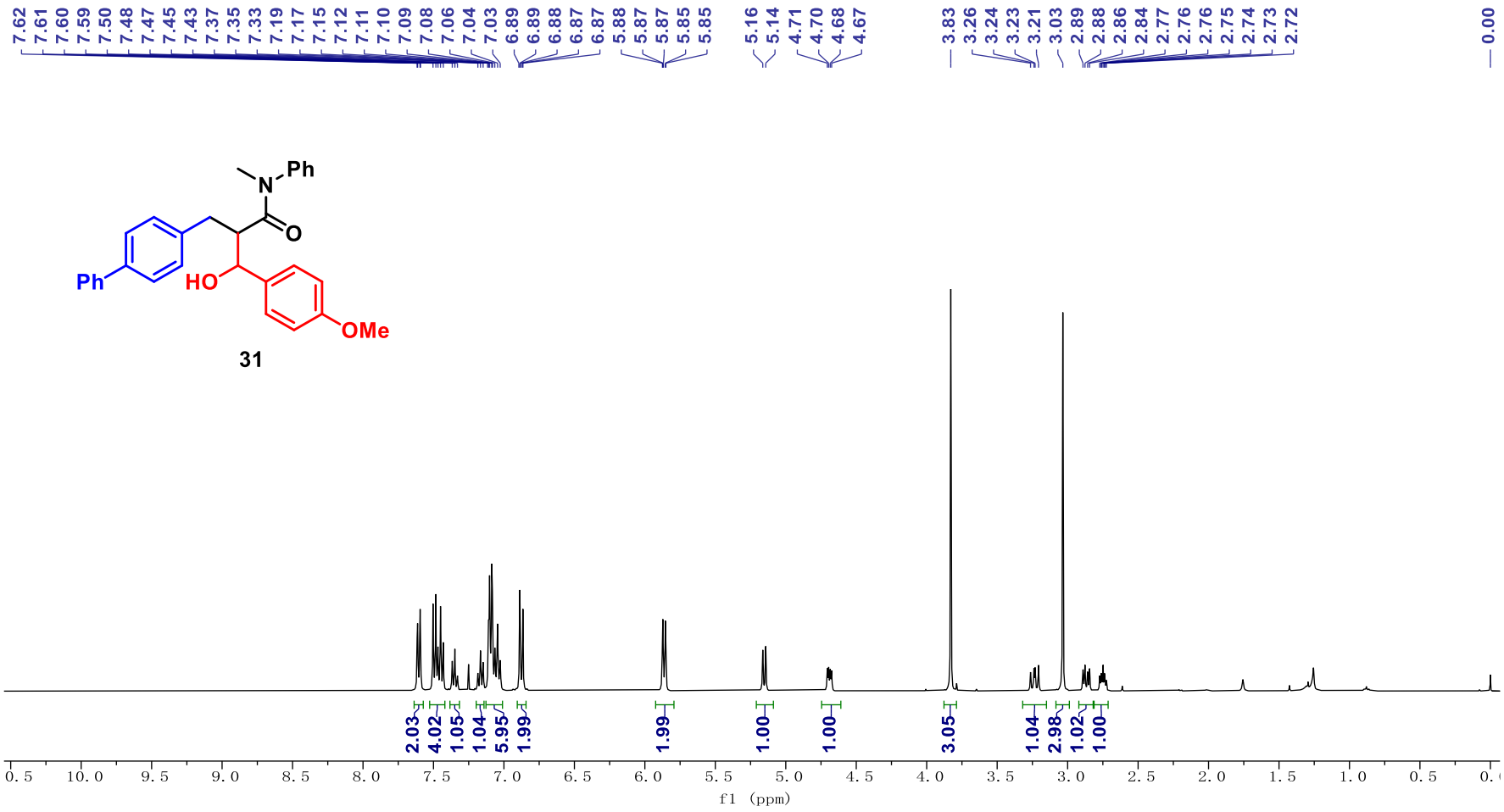
^{1}H NMR of 31 (One isomer) (400 MHz, $CDCl_3$)



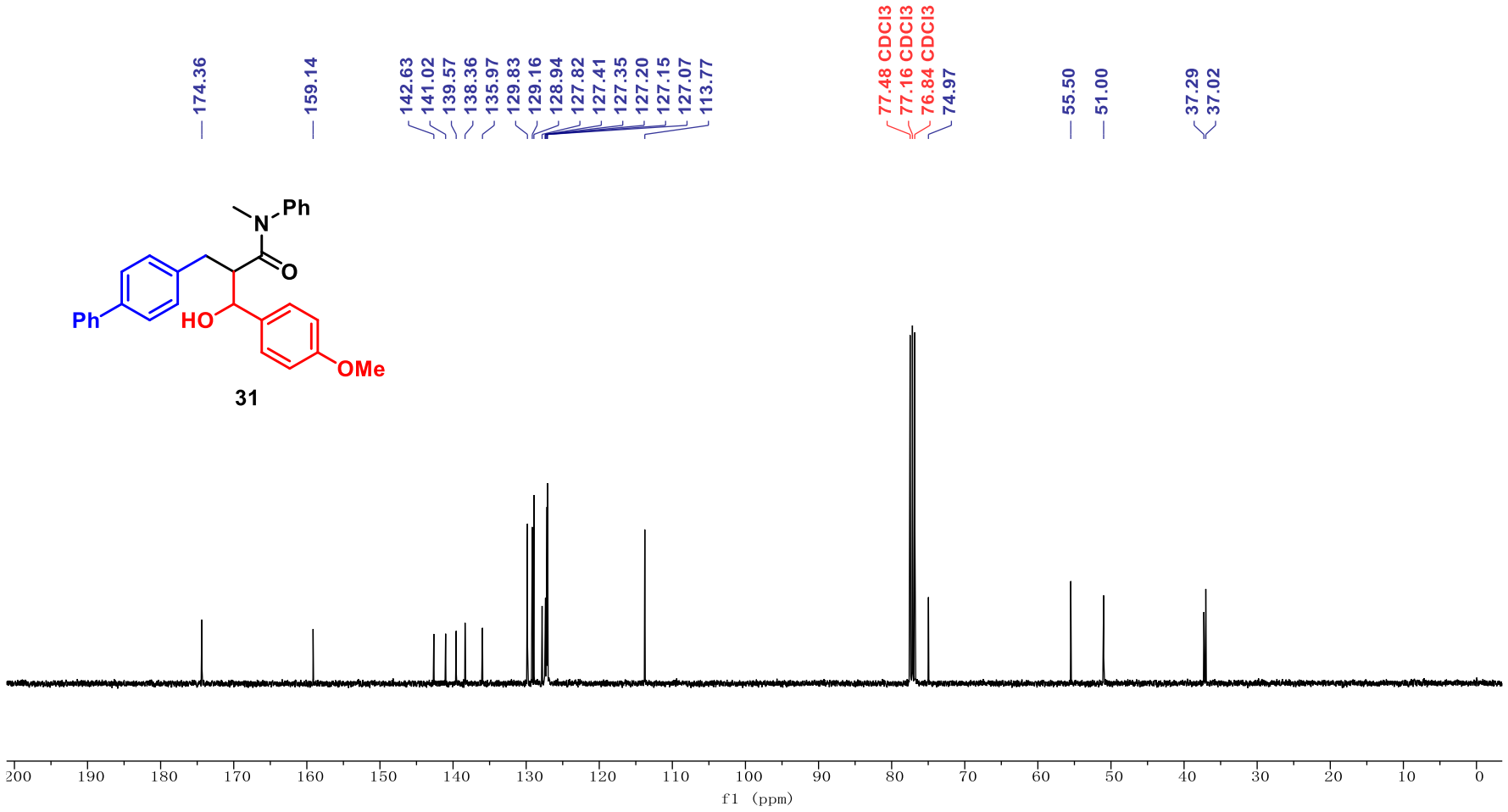
^{13}C NMR of 31 (One isomer) (101 MHz, $CDCl_3$)



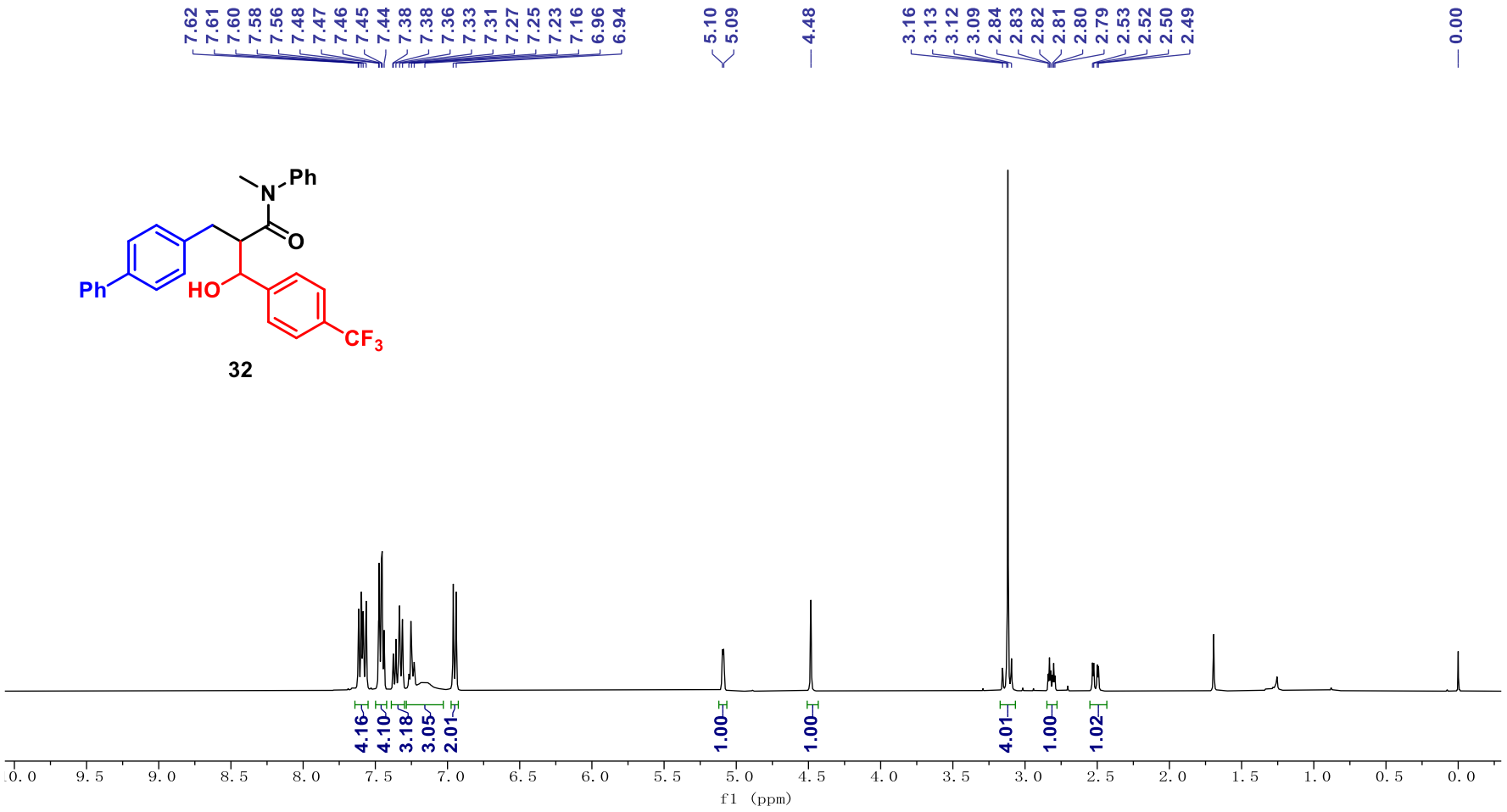
^{1}H NMR of 31 (Another isomer) (400 MHz, $CDCl_3$)



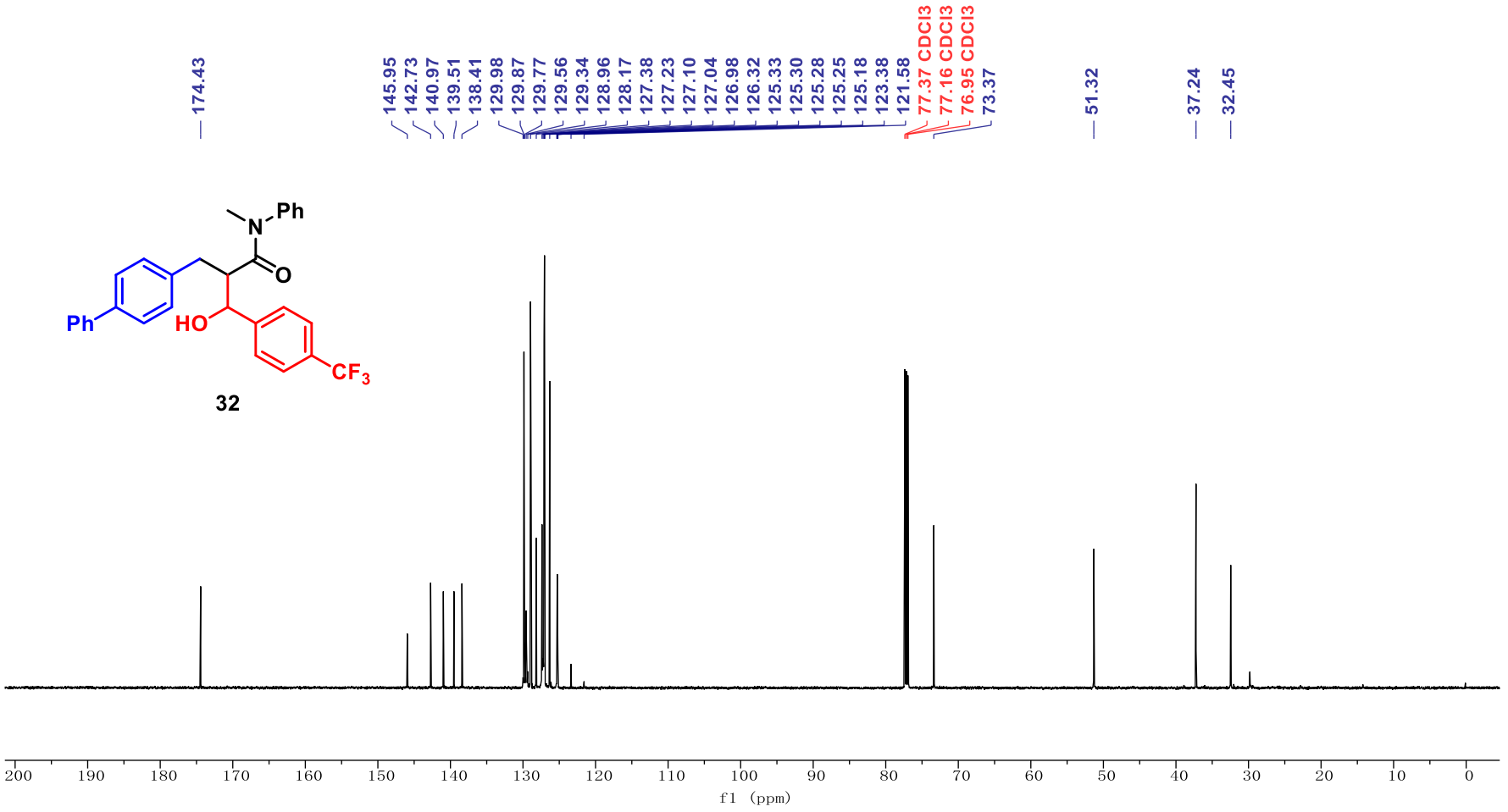
^{13}C NMR of 31 (Another isomer) (101 MHz, $CDCl_3$)



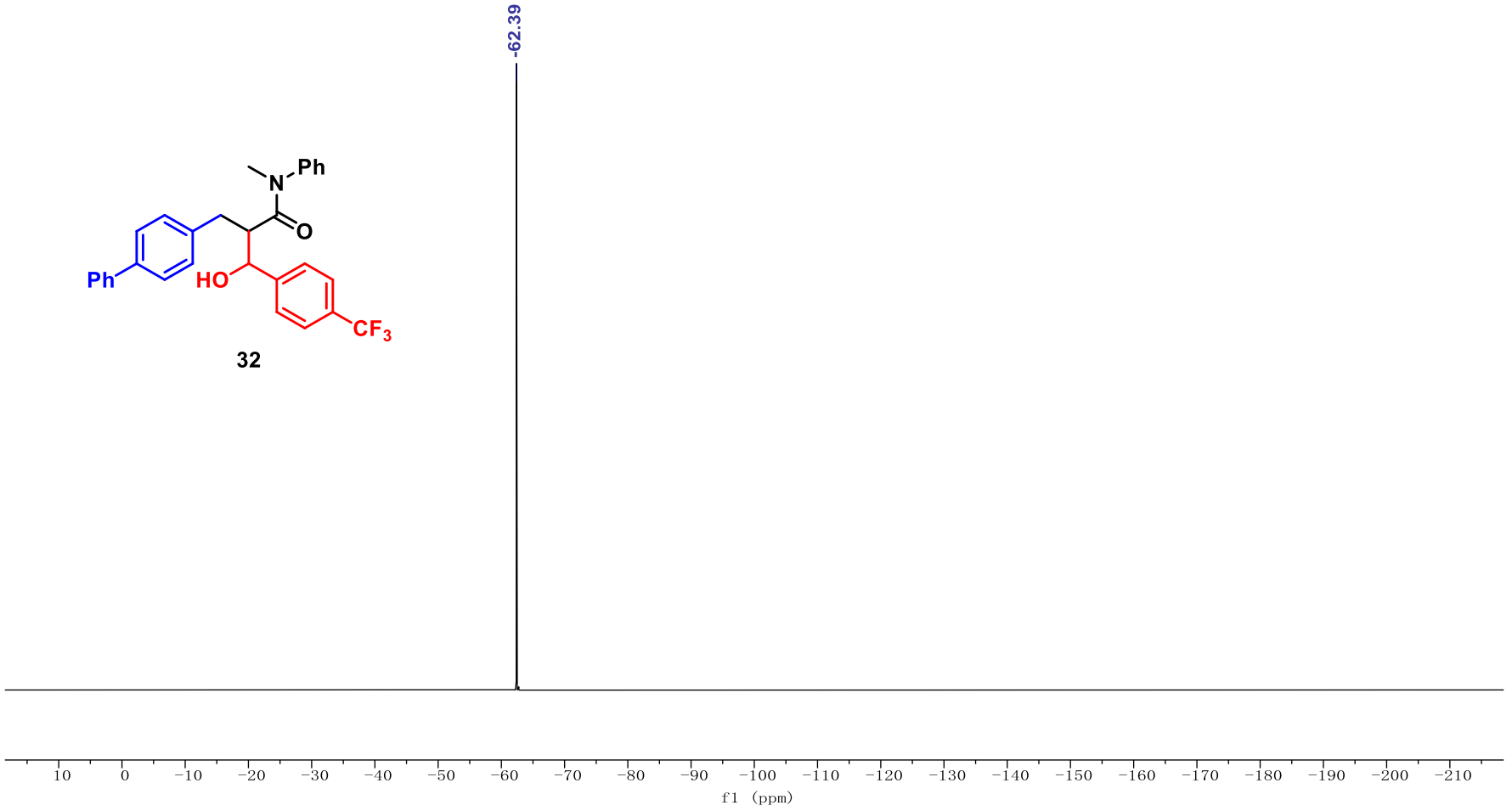
^{1}H NMR of 32 (One isomer) (400 MHz, $CDCl_3$)



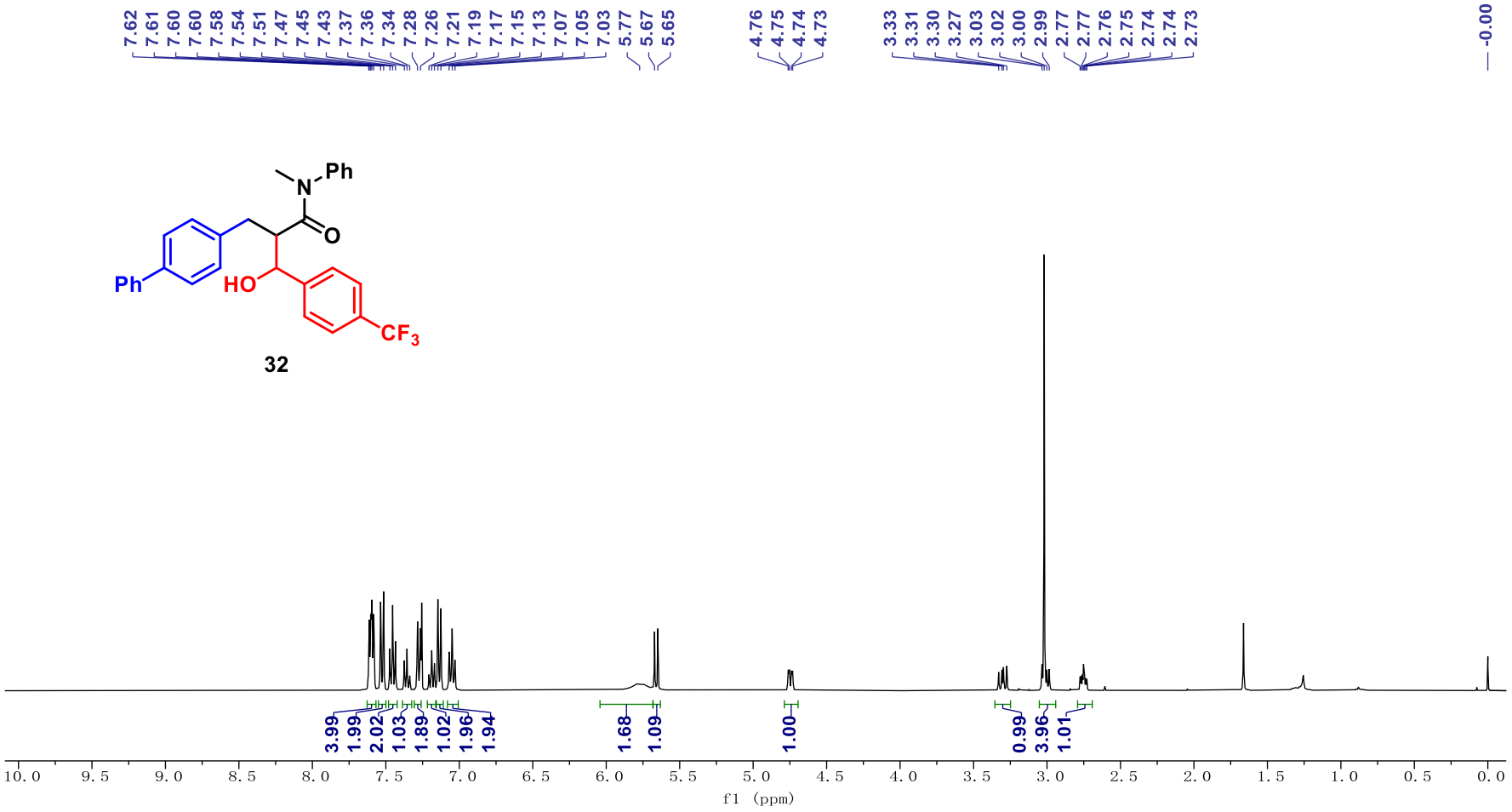
^{13}C NMR of 32 (One isomer) (151 MHz, $CDCl_3$)



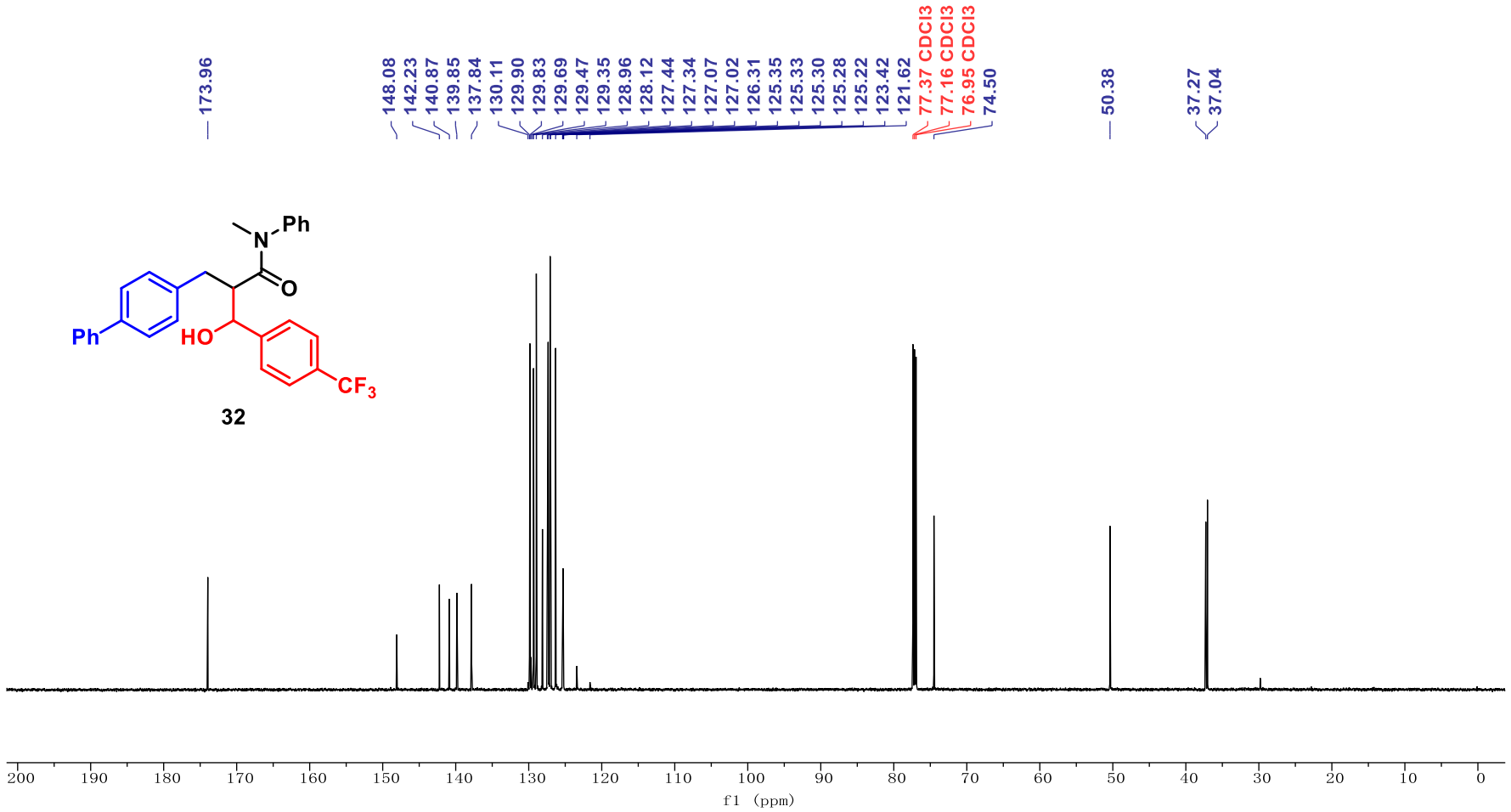
^{19}F NMR of 32 (One isomer) (565 MHz, $CDCl_3$)



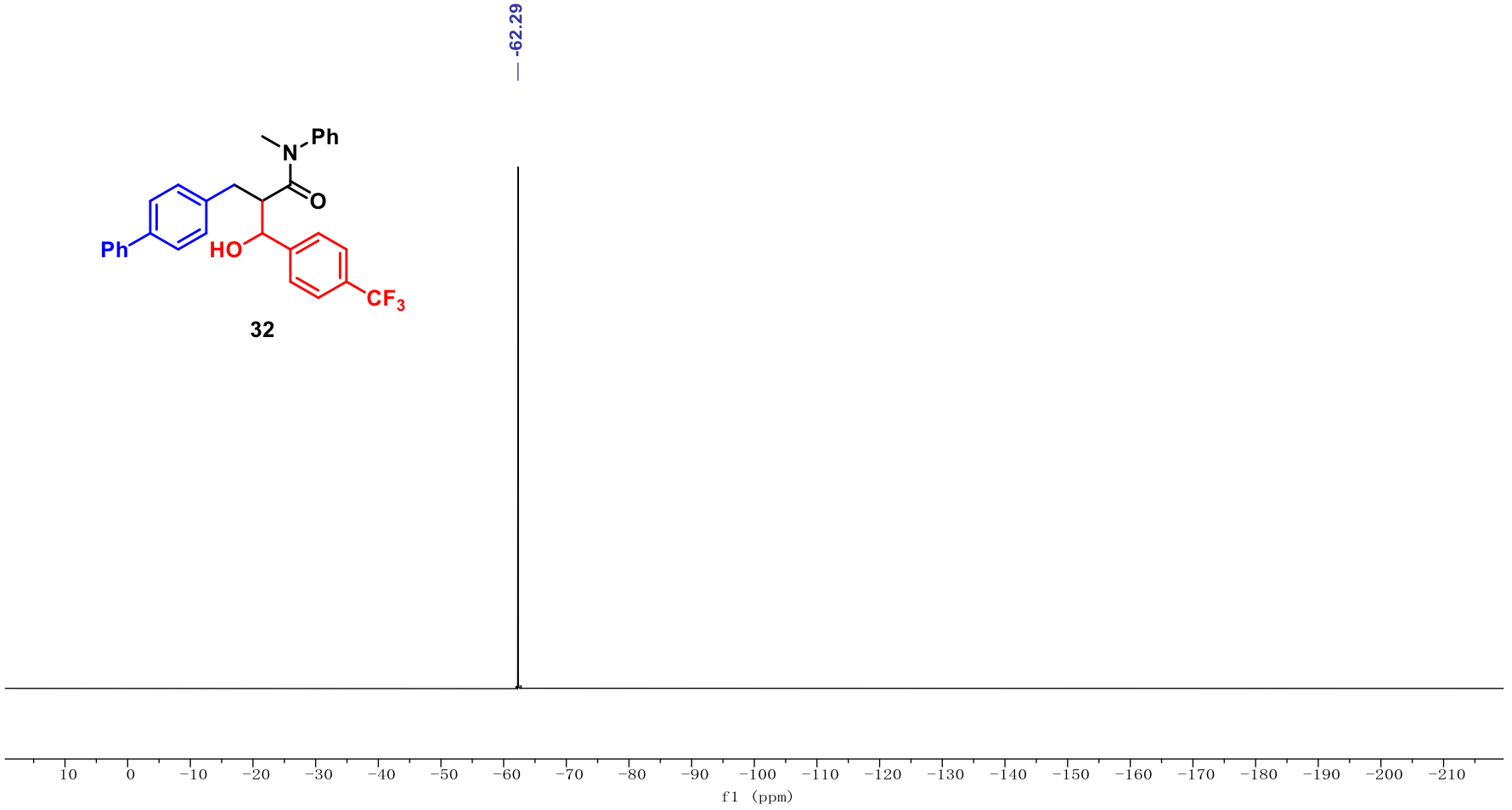
^{1}H NMR of 32 (Another isomer) (400 MHz, $CDCl_3$)



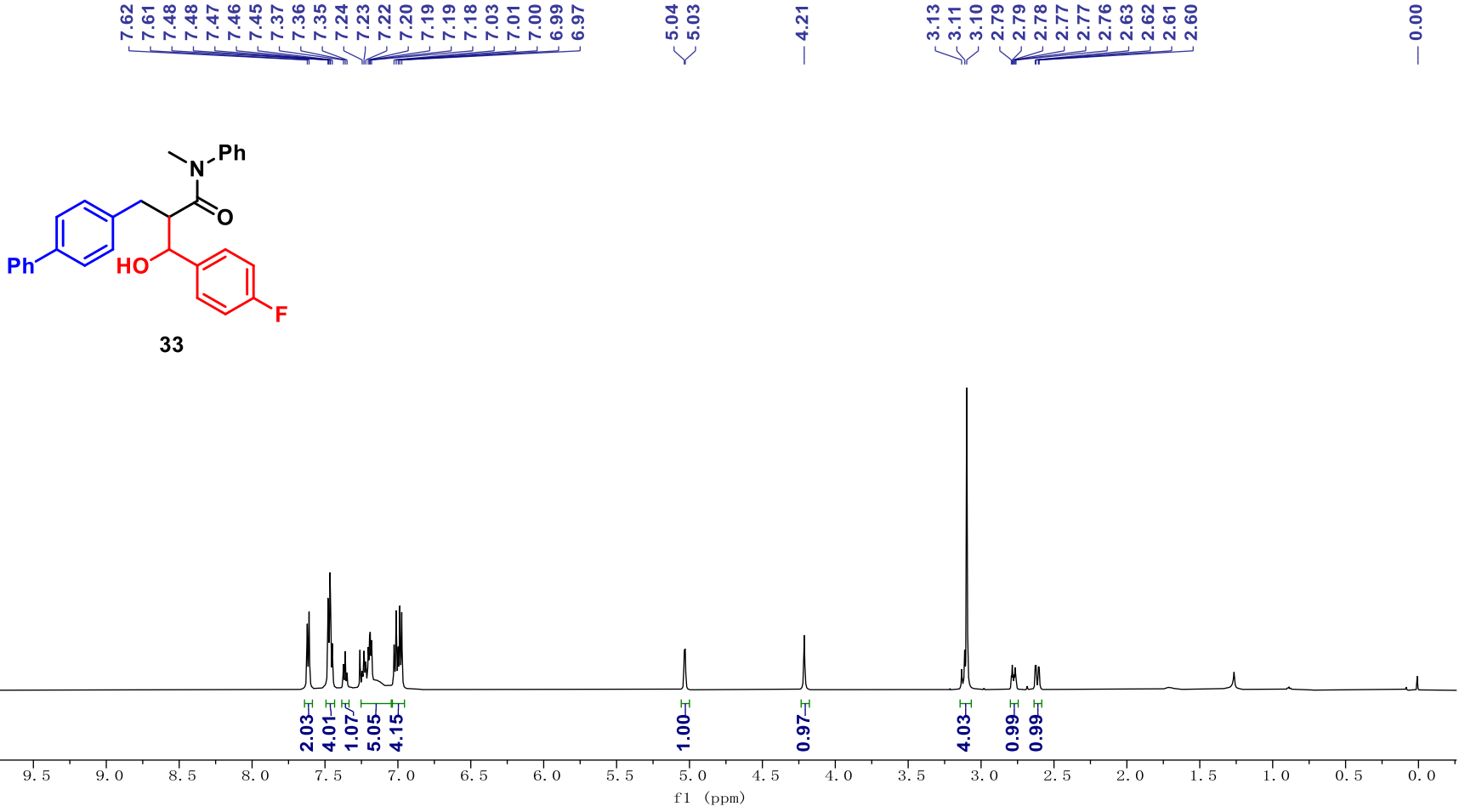
^{13}C NMR of 32 (Another isomer) (151 MHz, $CDCl_3$)



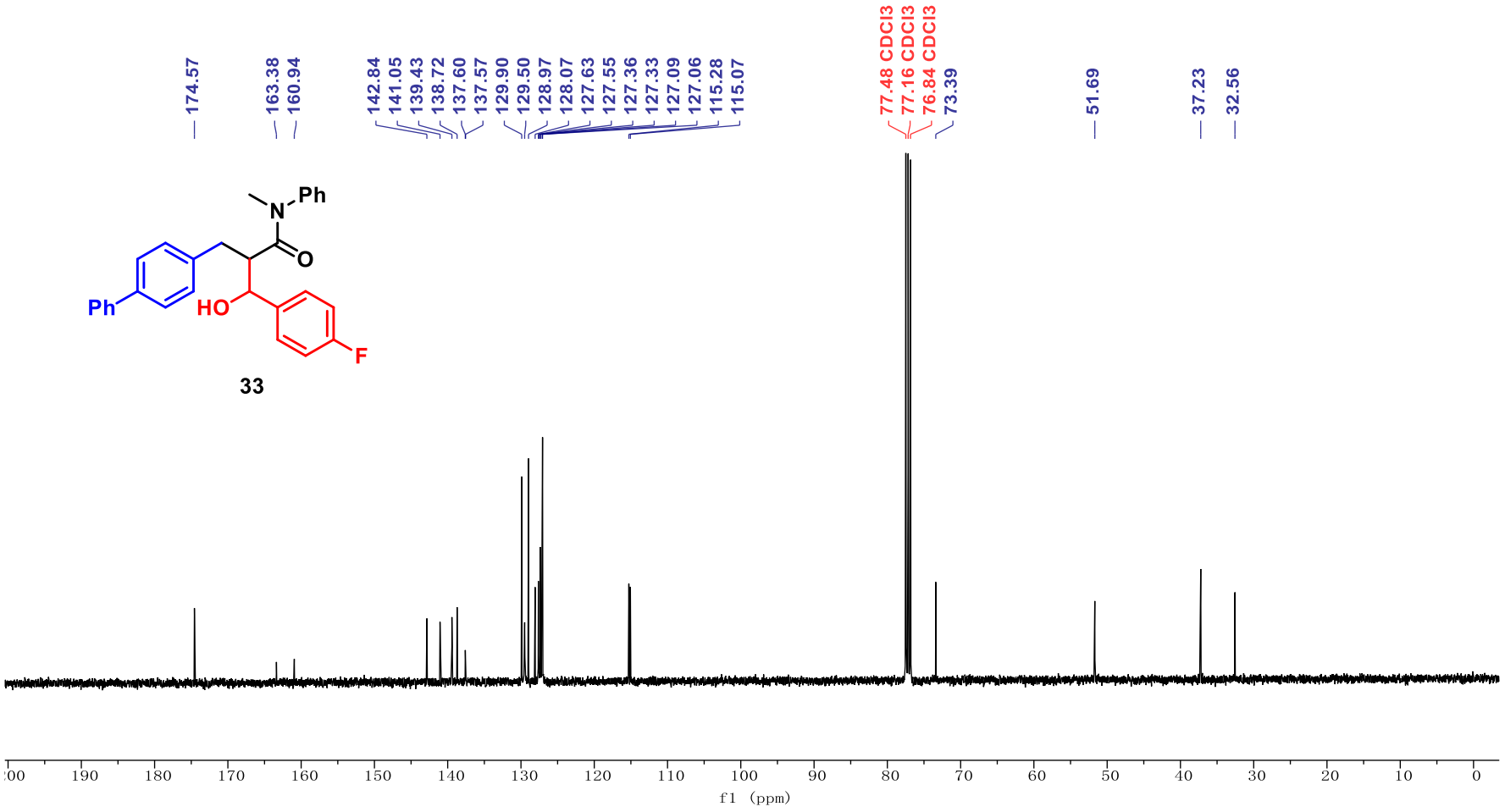
^{19}F NMR of 32 (Another isomer) (376 MHz, $CDCl_3$)



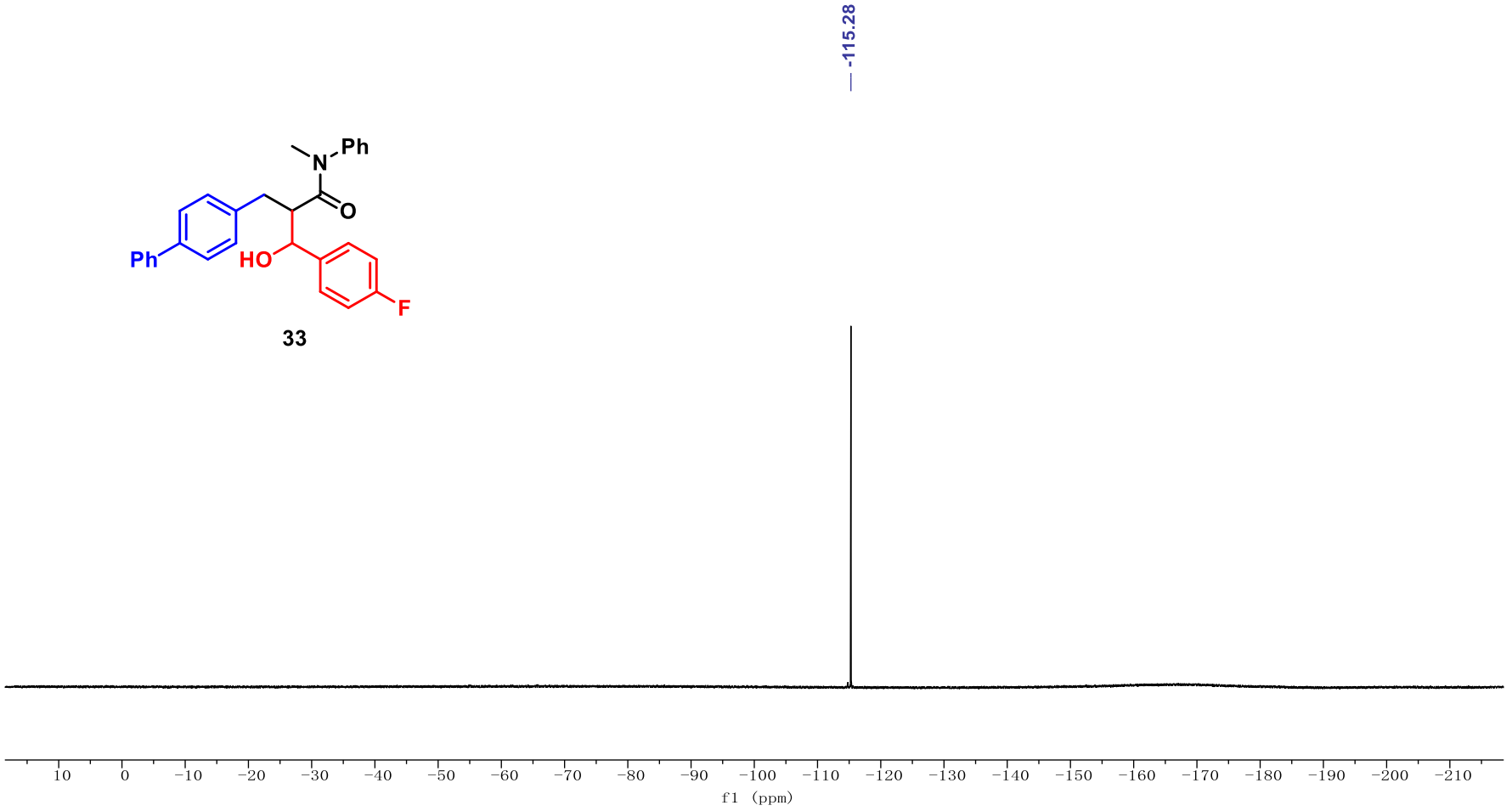
^{1}H NMR of 33 (One isomer) (600 MHz, $CDCl_3$)



^{13}C NMR of 33 (One isomer) (101 MHz, $CDCl_3$)

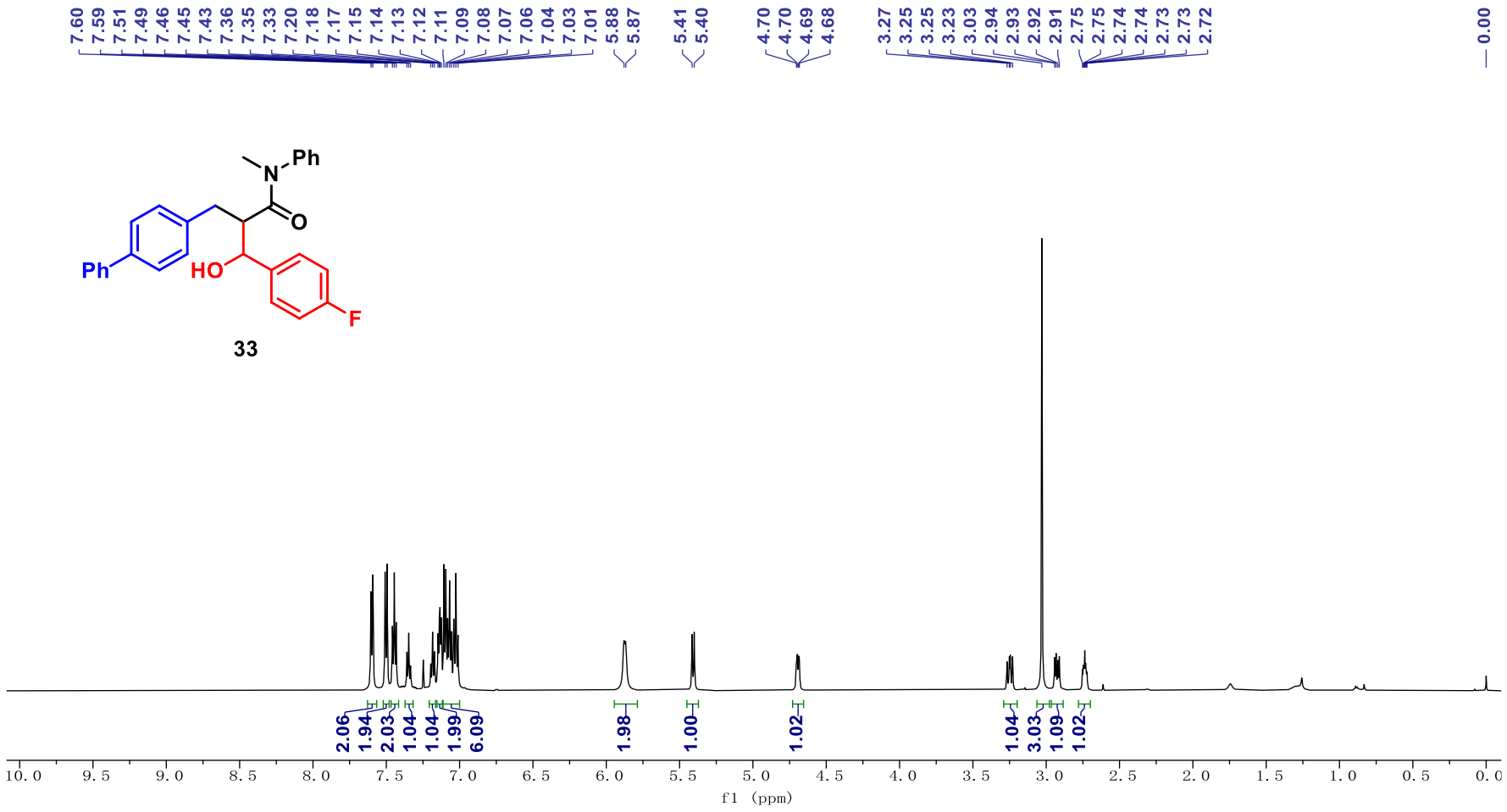


^{19}F NMR of 33 (One isomer) (565 MHz, $CDCl_3$)

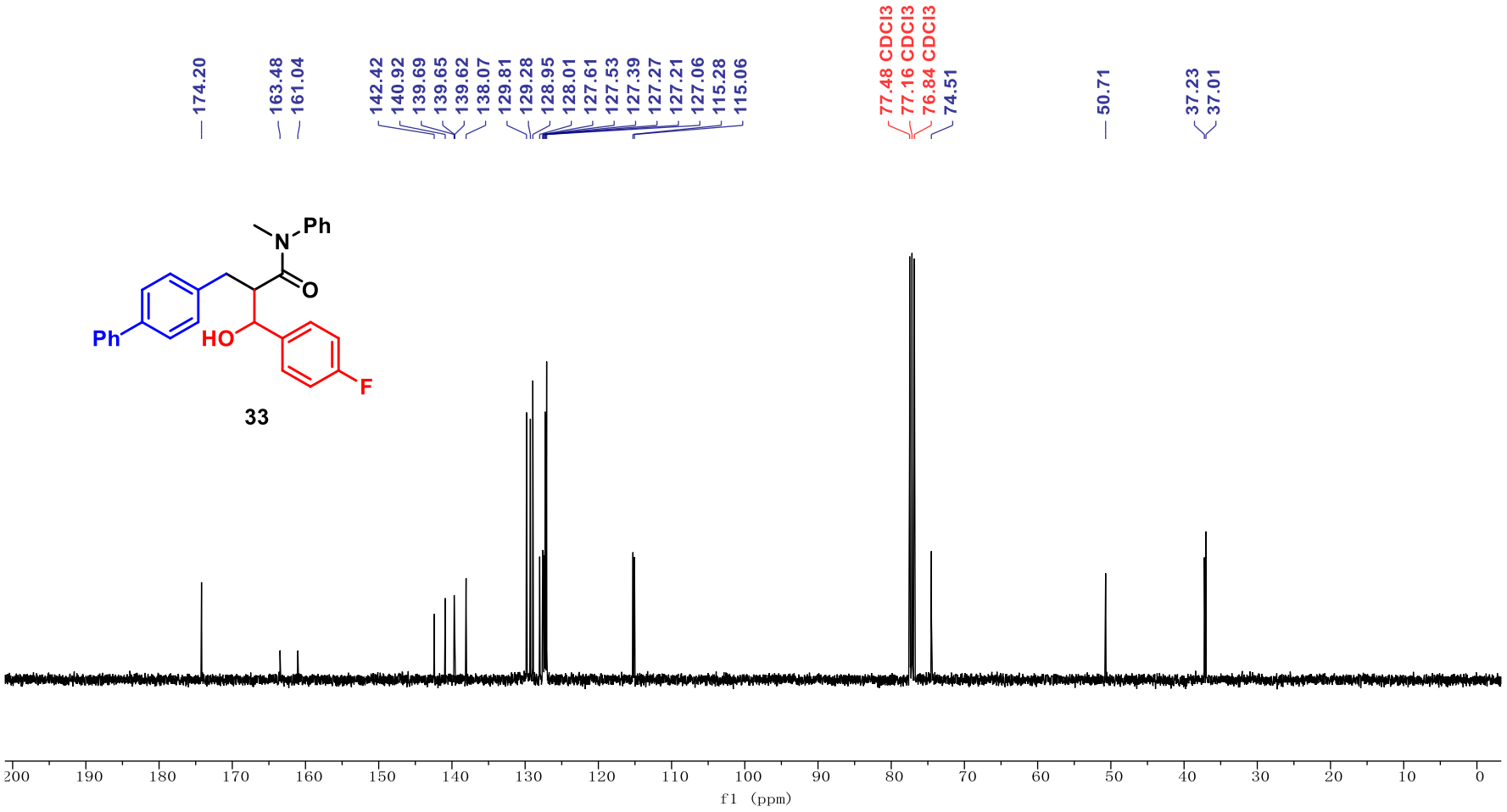


33

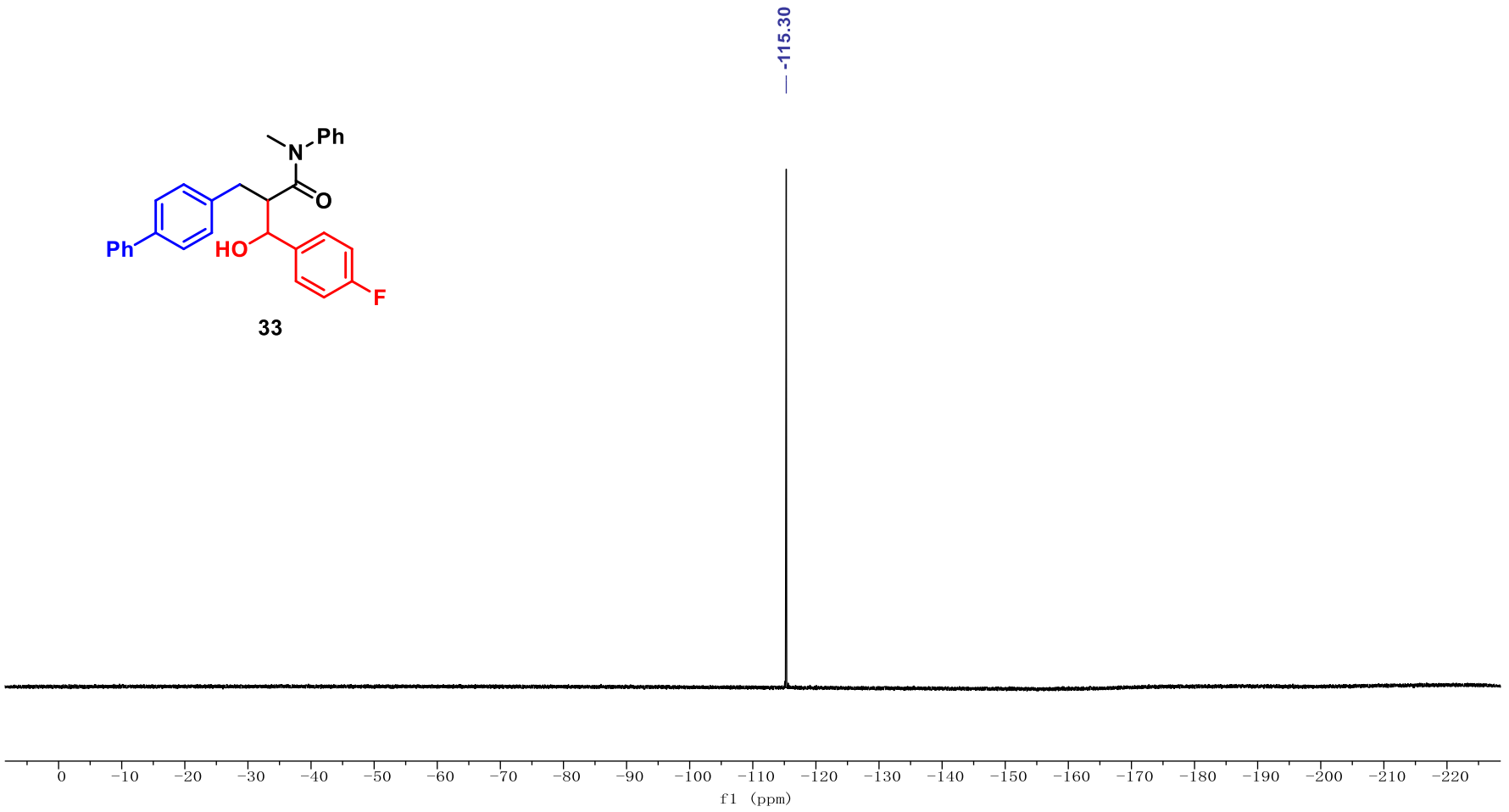
^{1}H NMR of 33 (Another isomer) (600 MHz, $CDCl_3$)



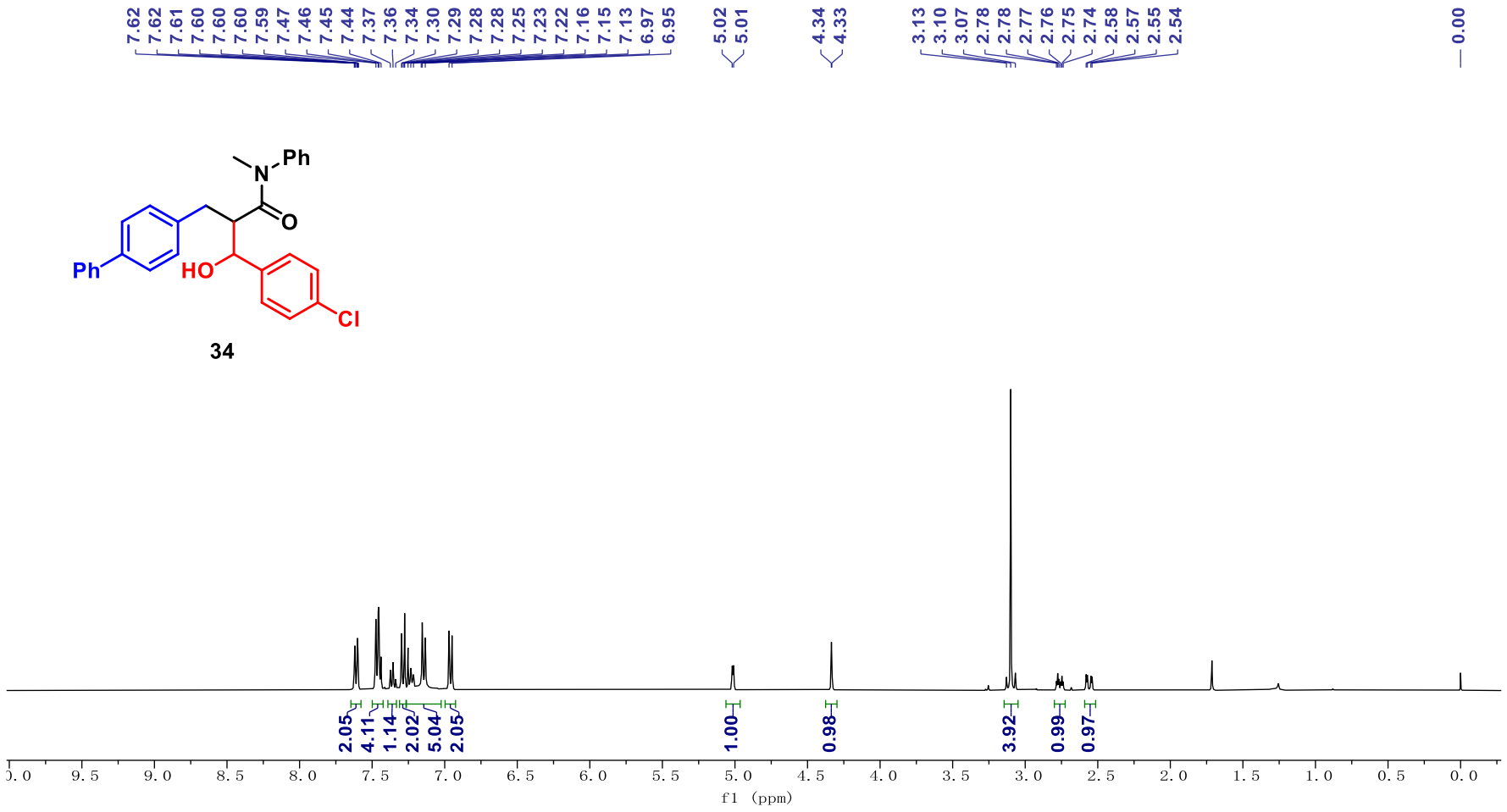
^{13}C NMR of 33 (Another isomer) (101 MHz, $CDCl_3$)



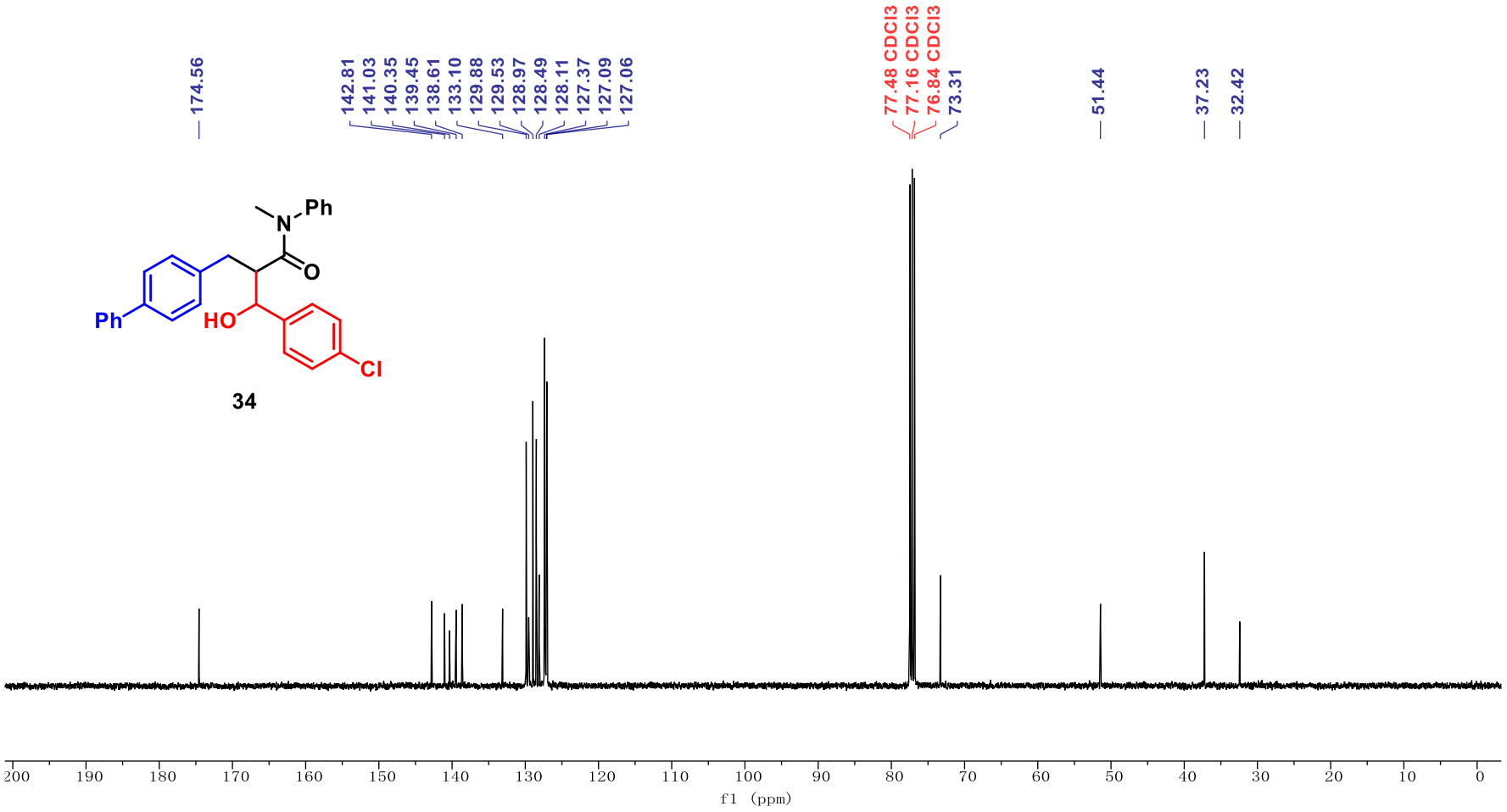
^{19}F NMR of 33 (Another isomer) (565 MHz, $CDCl_3$)



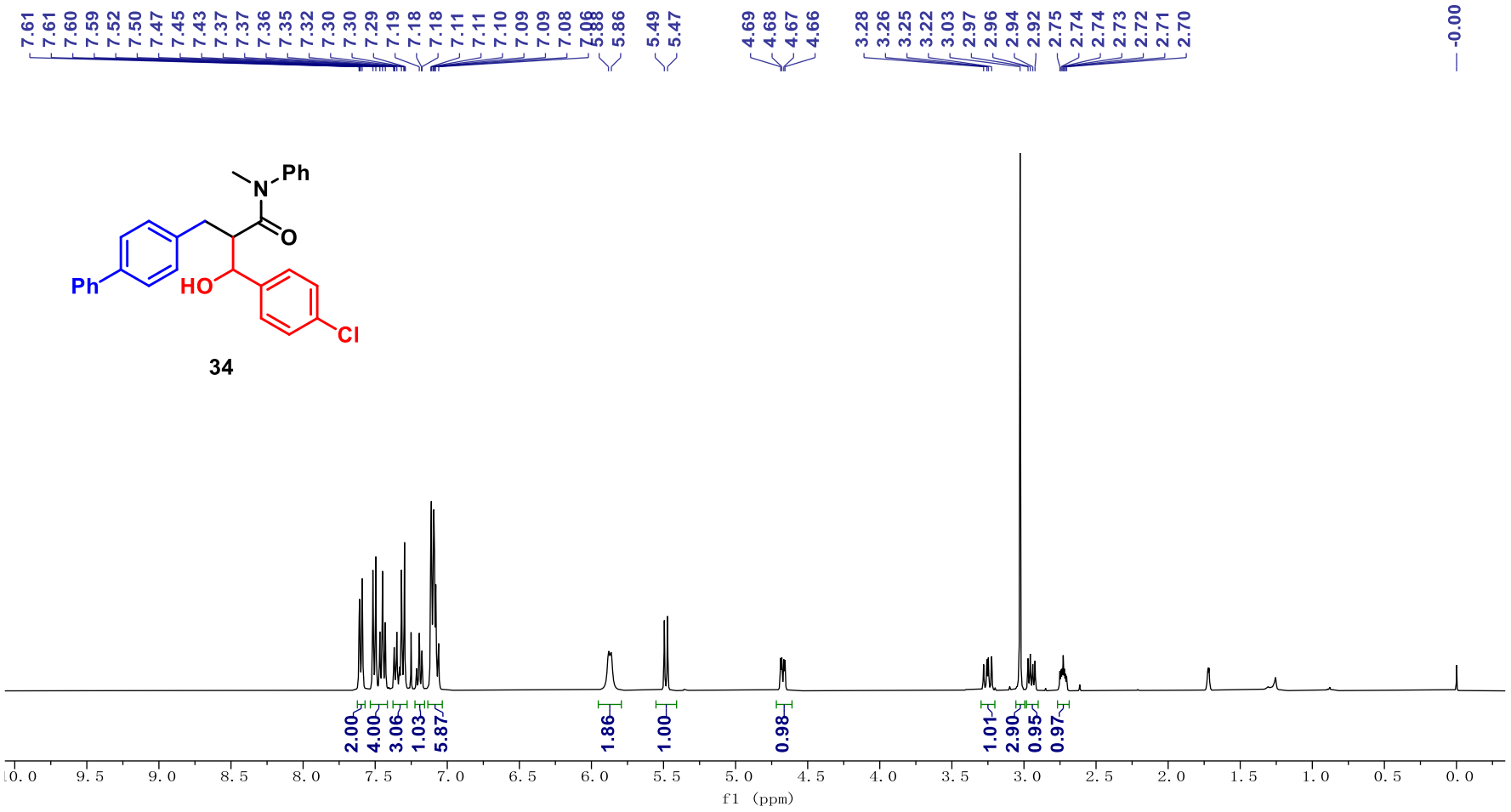
^{1}H NMR of 34 (One isomer) (400 MHz, $CDCl_3$)



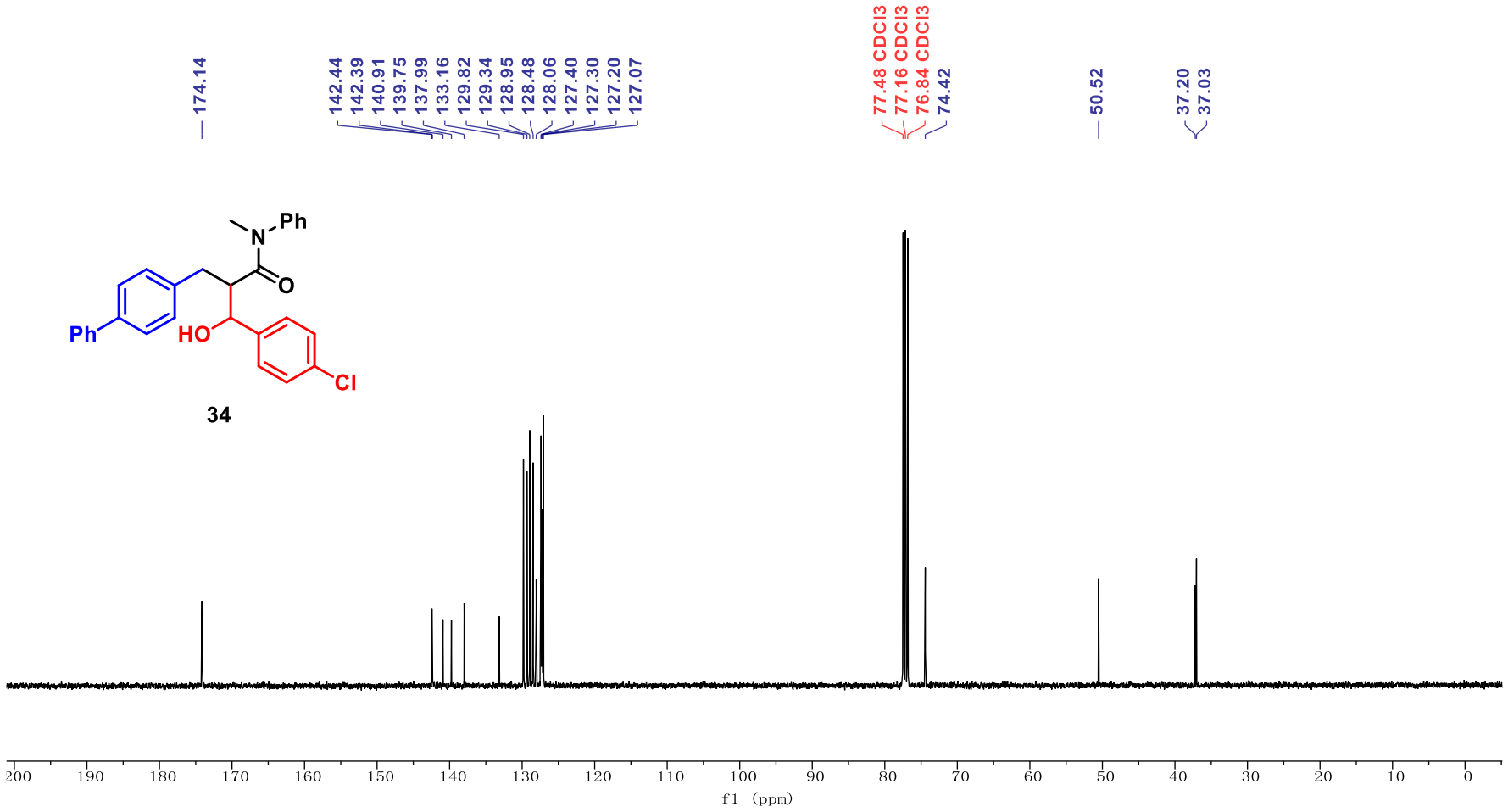
^{13}C NMR of 34 (One isomer) (101 MHz, $CDCl_3$)



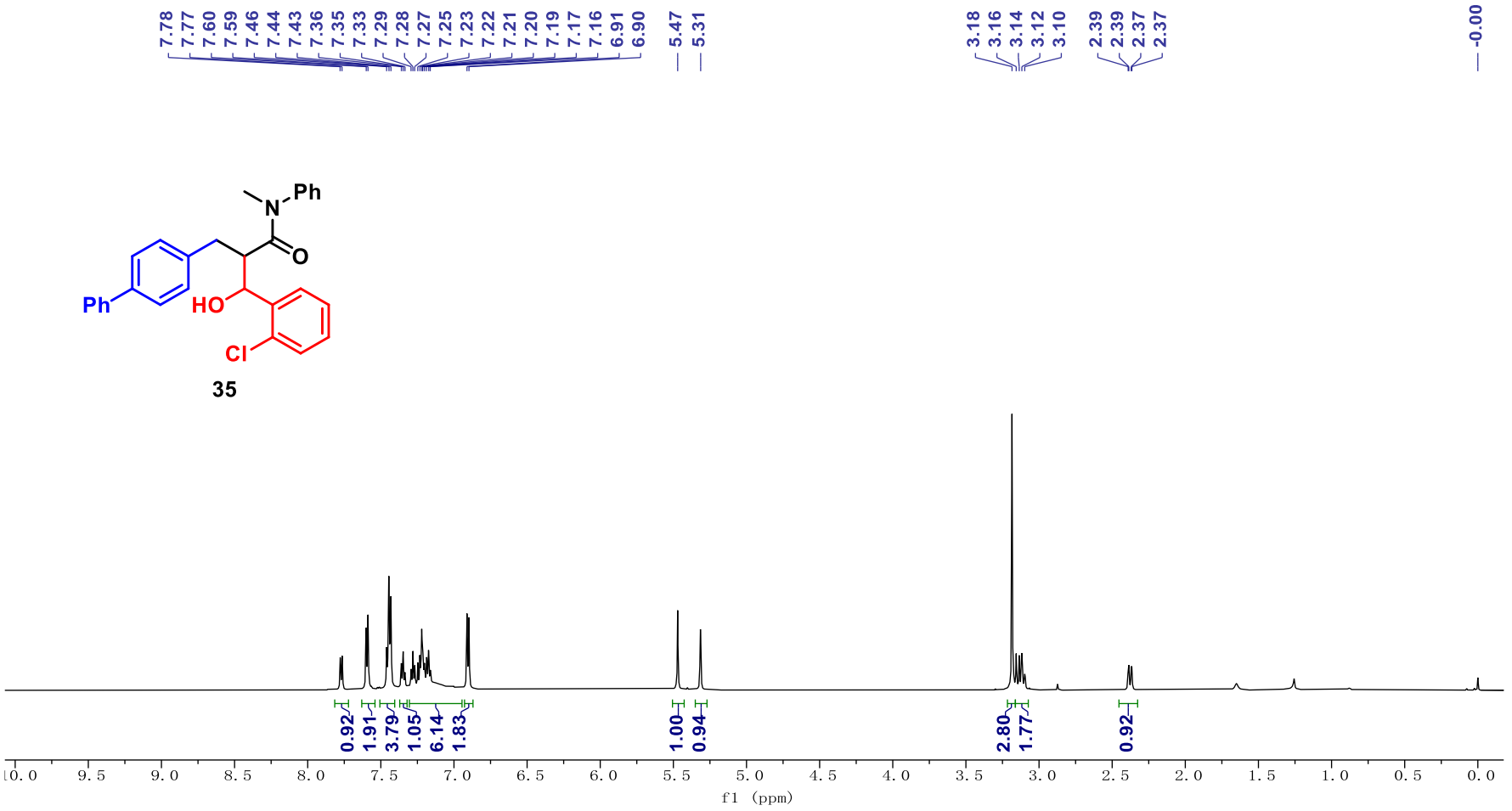
^{1}H NMR of 34 (Another isomer) (400 MHz, $CDCl_3$)



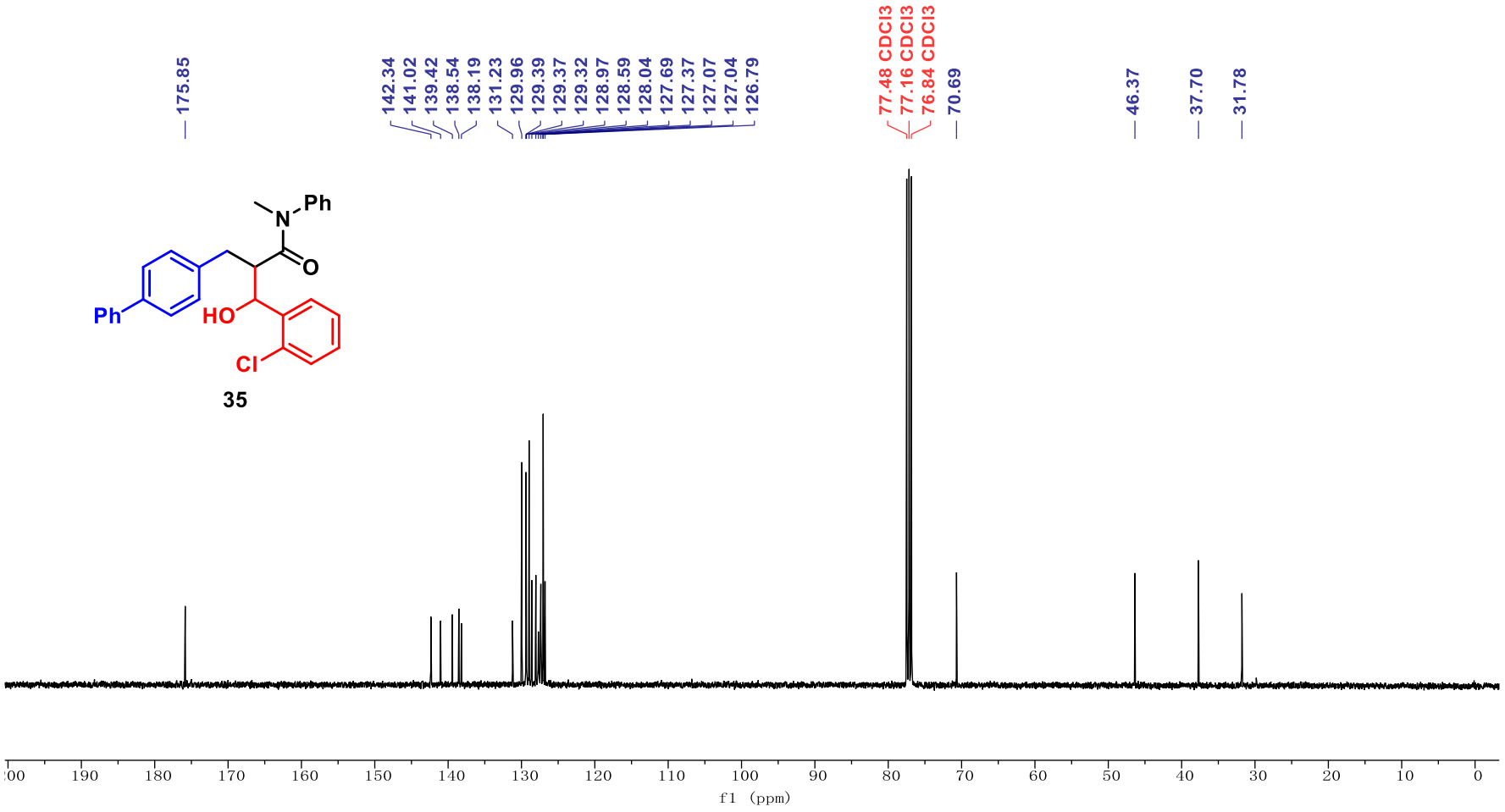
^{13}C NMR of 34 (Another isomer) (101 MHz, $CDCl_3$)



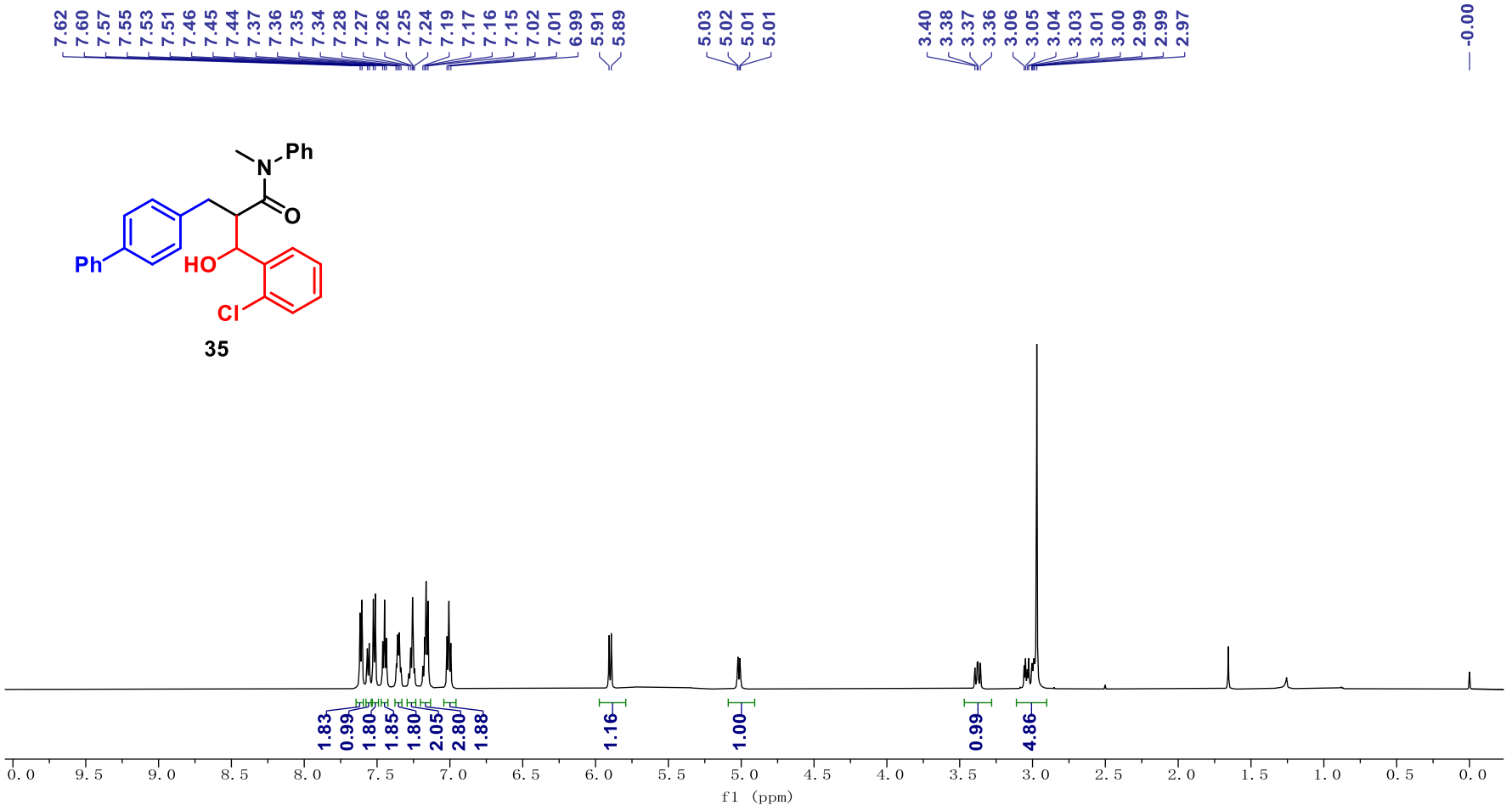
^{1}H NMR of 35 (One isomer) (600 MHz, $CDCl_3$)



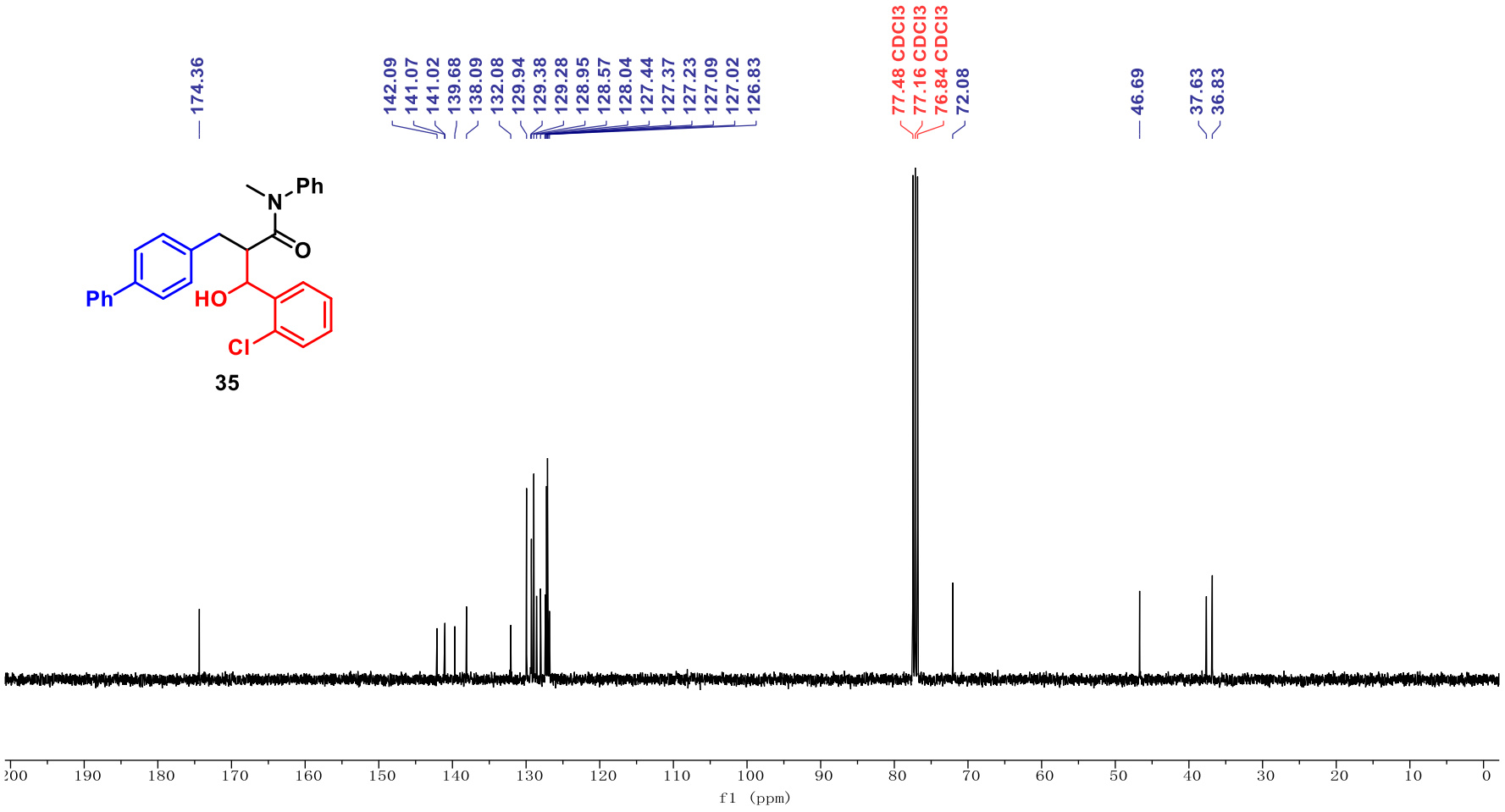
^{13}C NMR of 35 (One isomer) (101 MHz, $CDCl_3$)



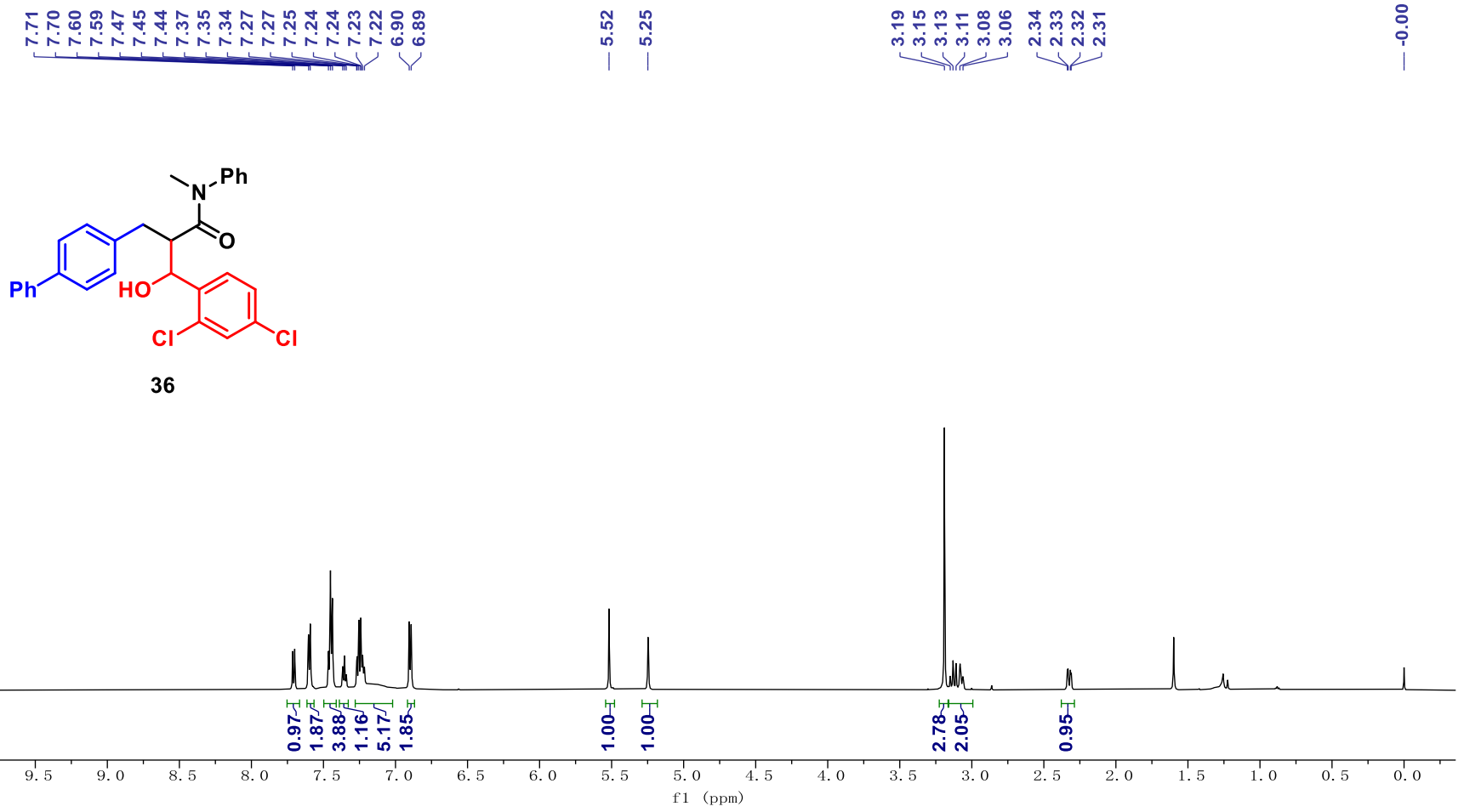
^{1}H NMR of 35 (Another isomer) (600 MHz, $CDCl_3$)



^{13}C NMR of 35 (Another isomer) (101 MHz, $CDCl_3$)

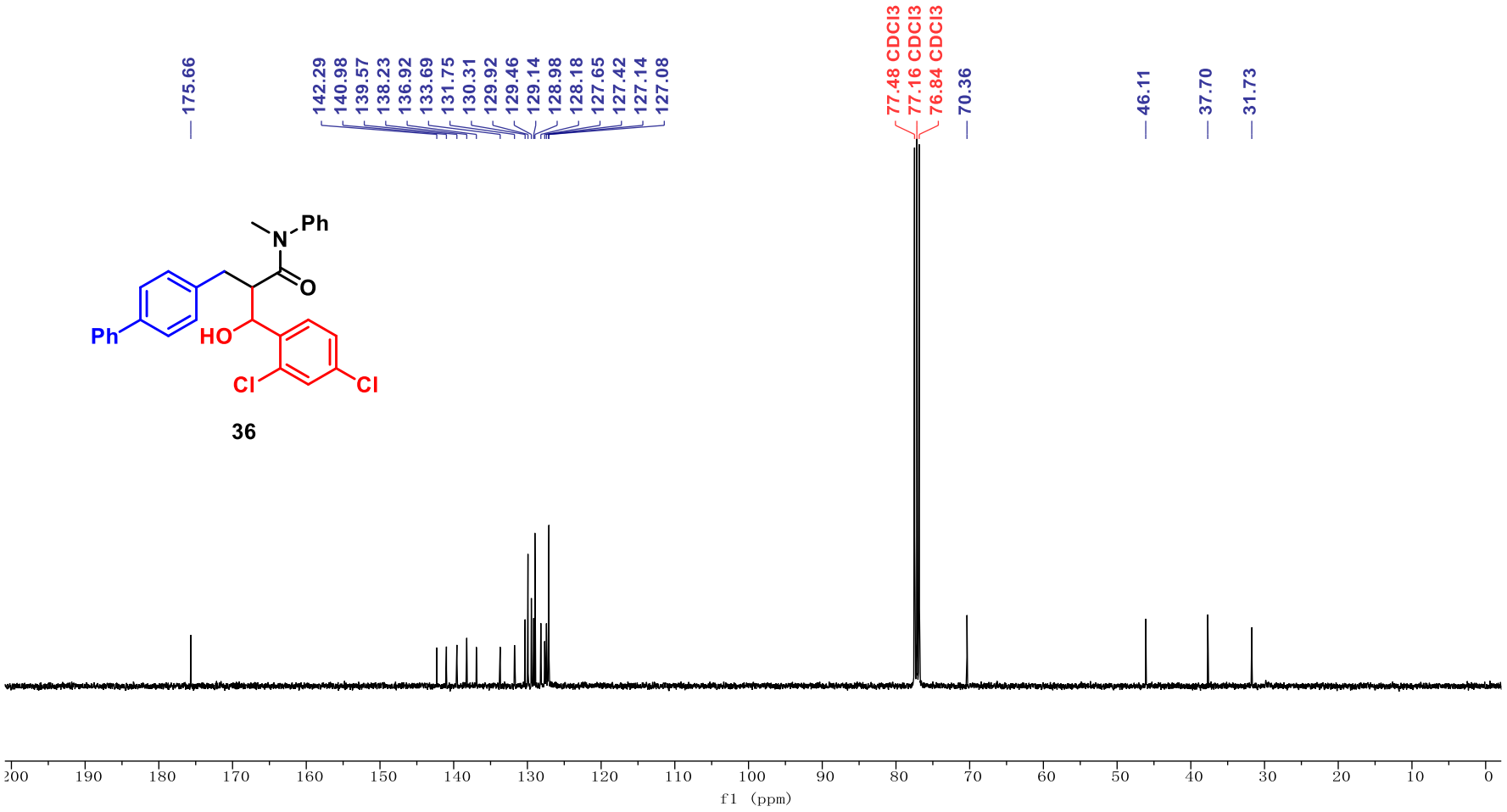


^{1}H NMR of 36 (One isomer) (600 MHz, $CDCl_3$)

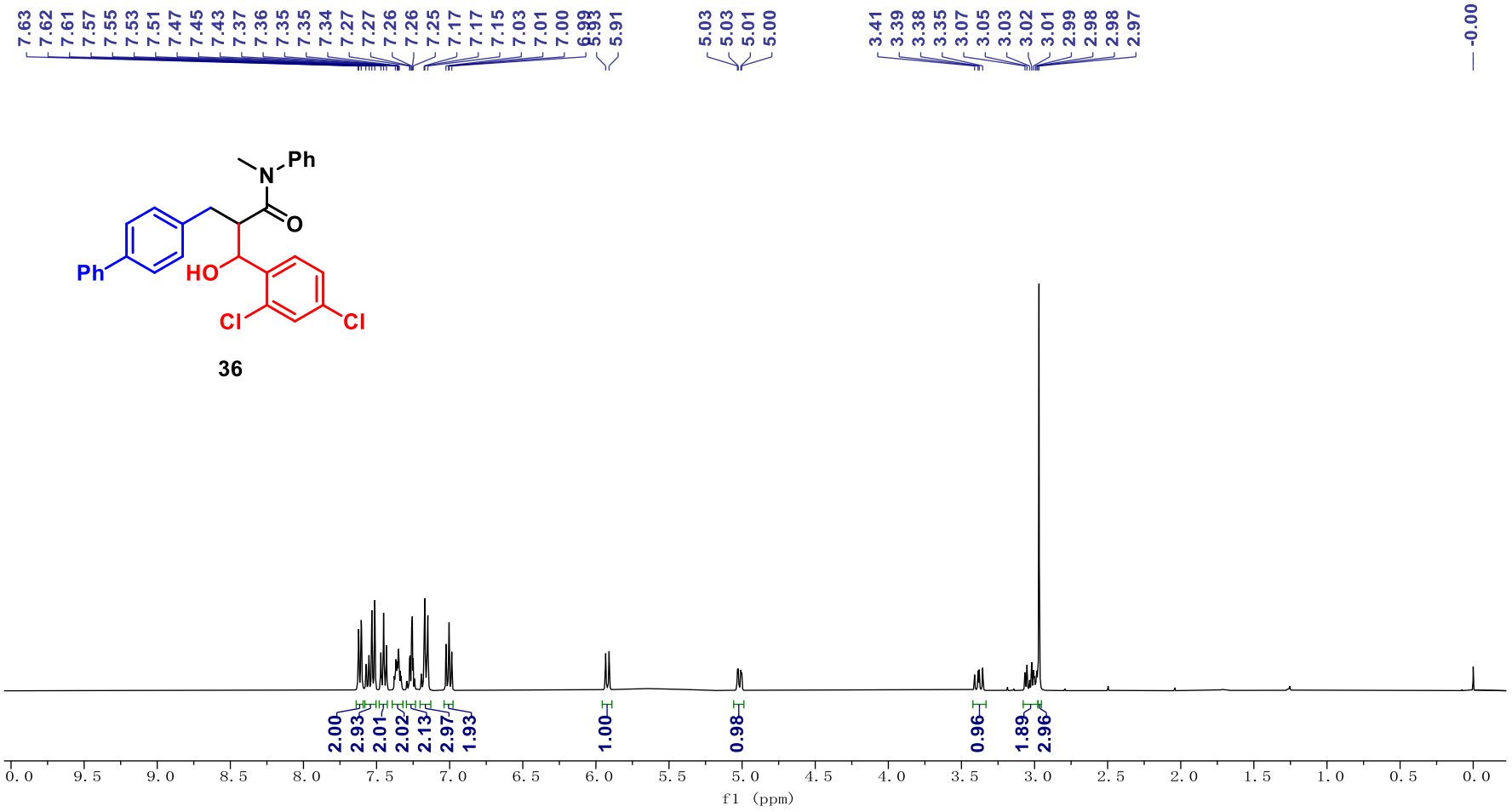


36

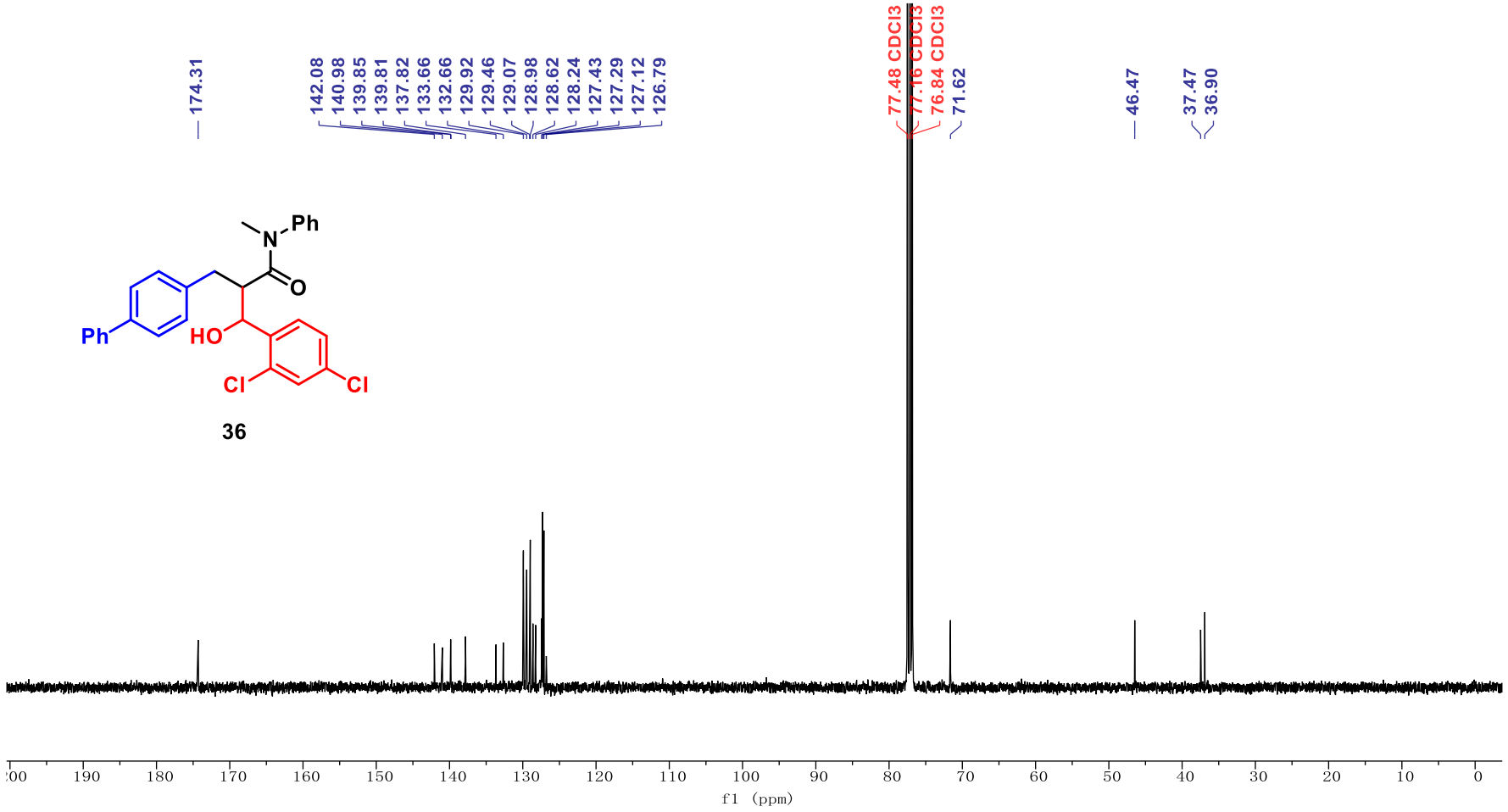
^{13}C NMR of 36 (One isomer) (101 MHz, $CDCl_3$)



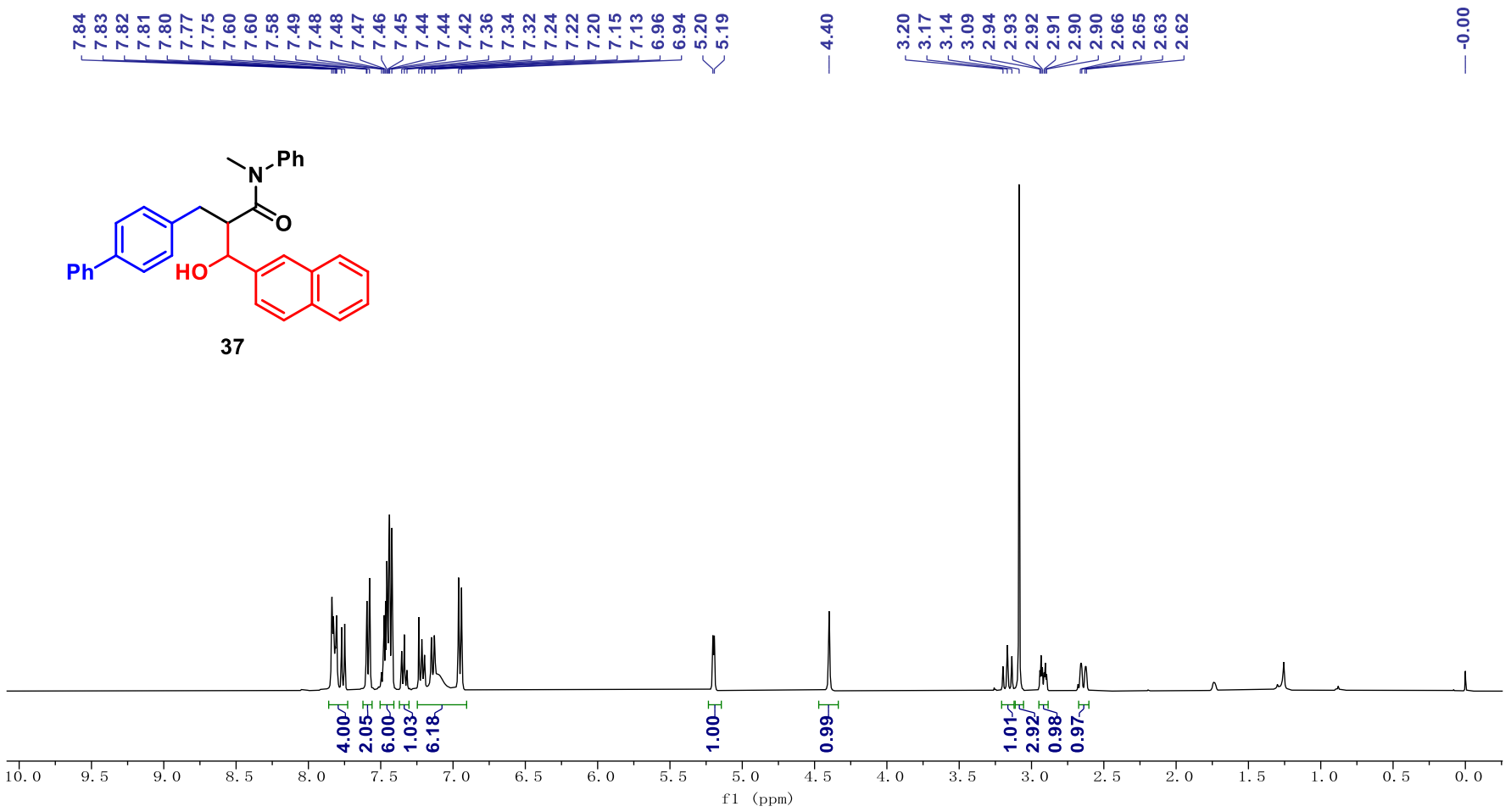
^{1}H NMR of 36 (Another isomer) (400 MHz, $CDCl_3$)



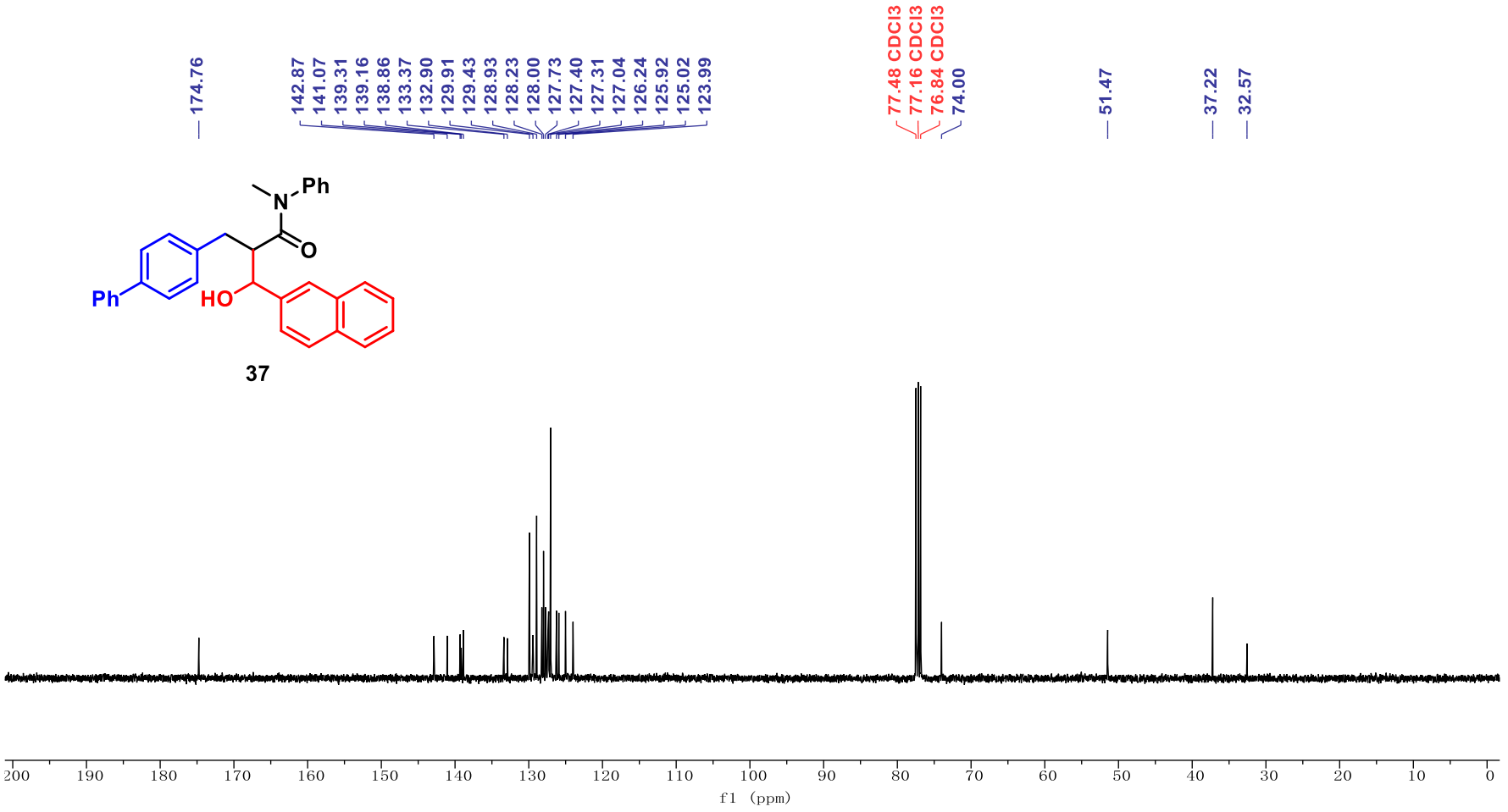
^{13}C NMR of 36 (Another isomer) (101 MHz, $CDCl_3$)



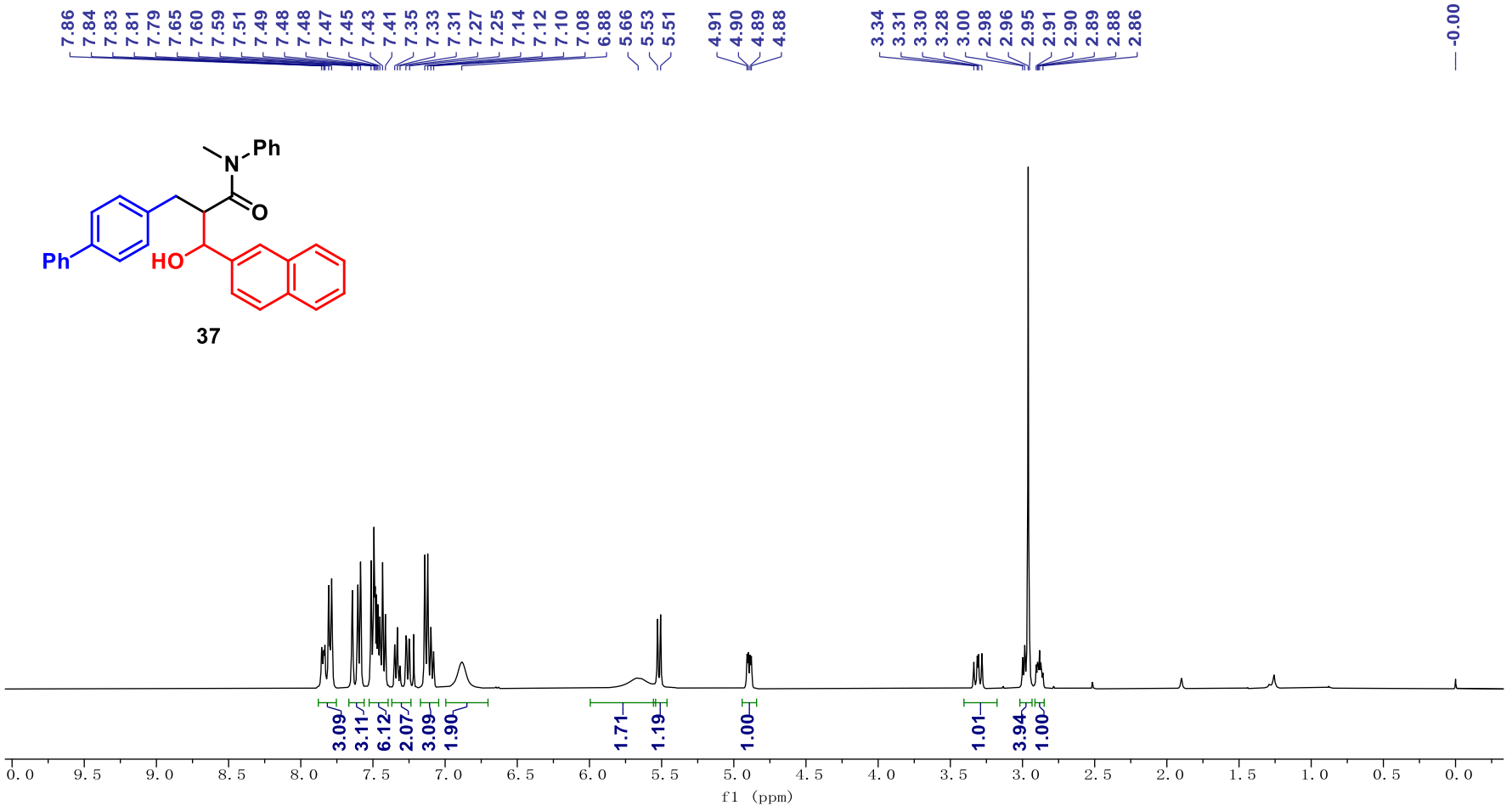
^{1}H NMR of 37 (One isomer) (400 MHz, $CDCl_3$)



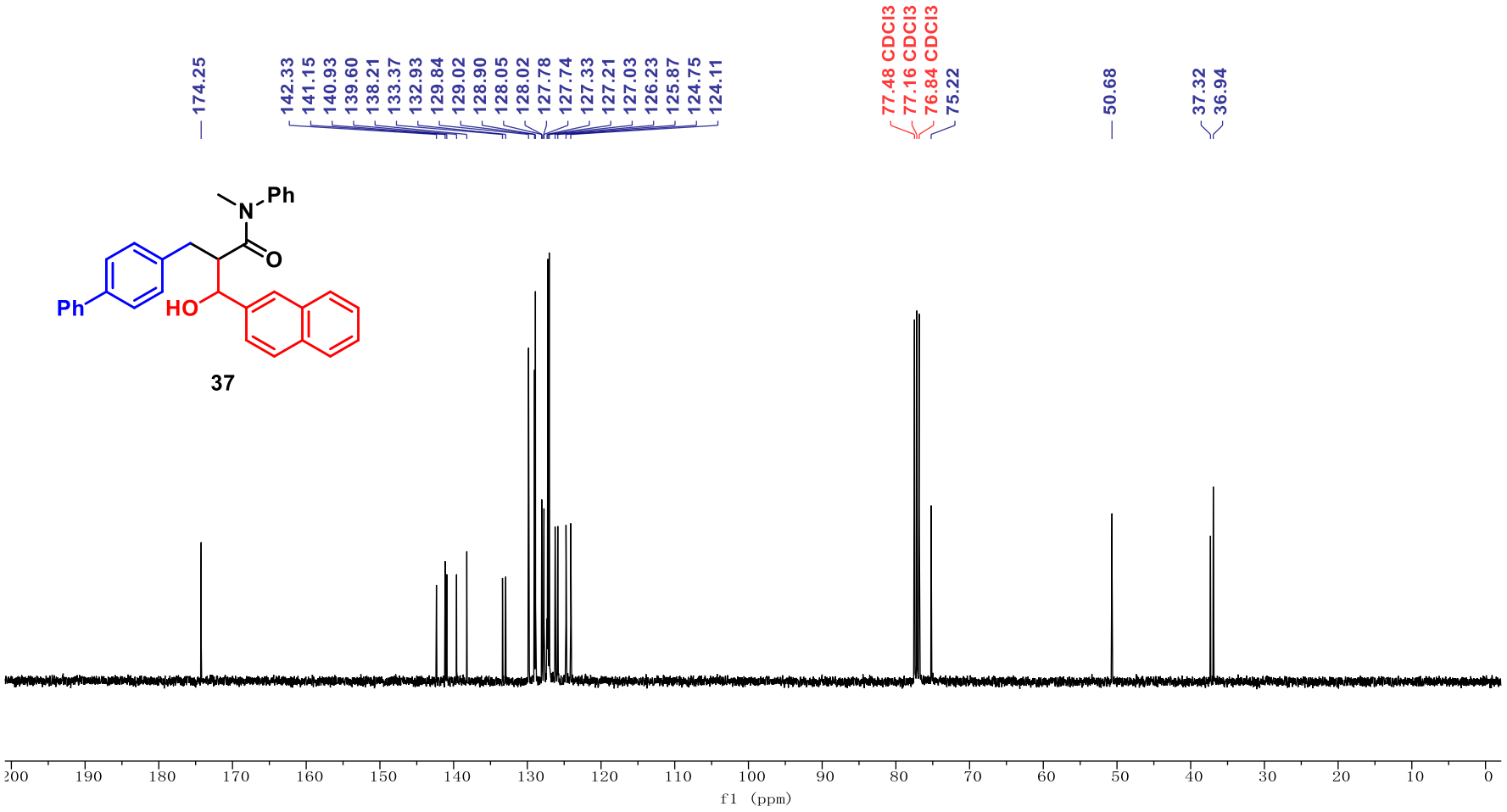
^{13}C NMR of 37 (One isomer) (101 MHz, $CDCl_3$)



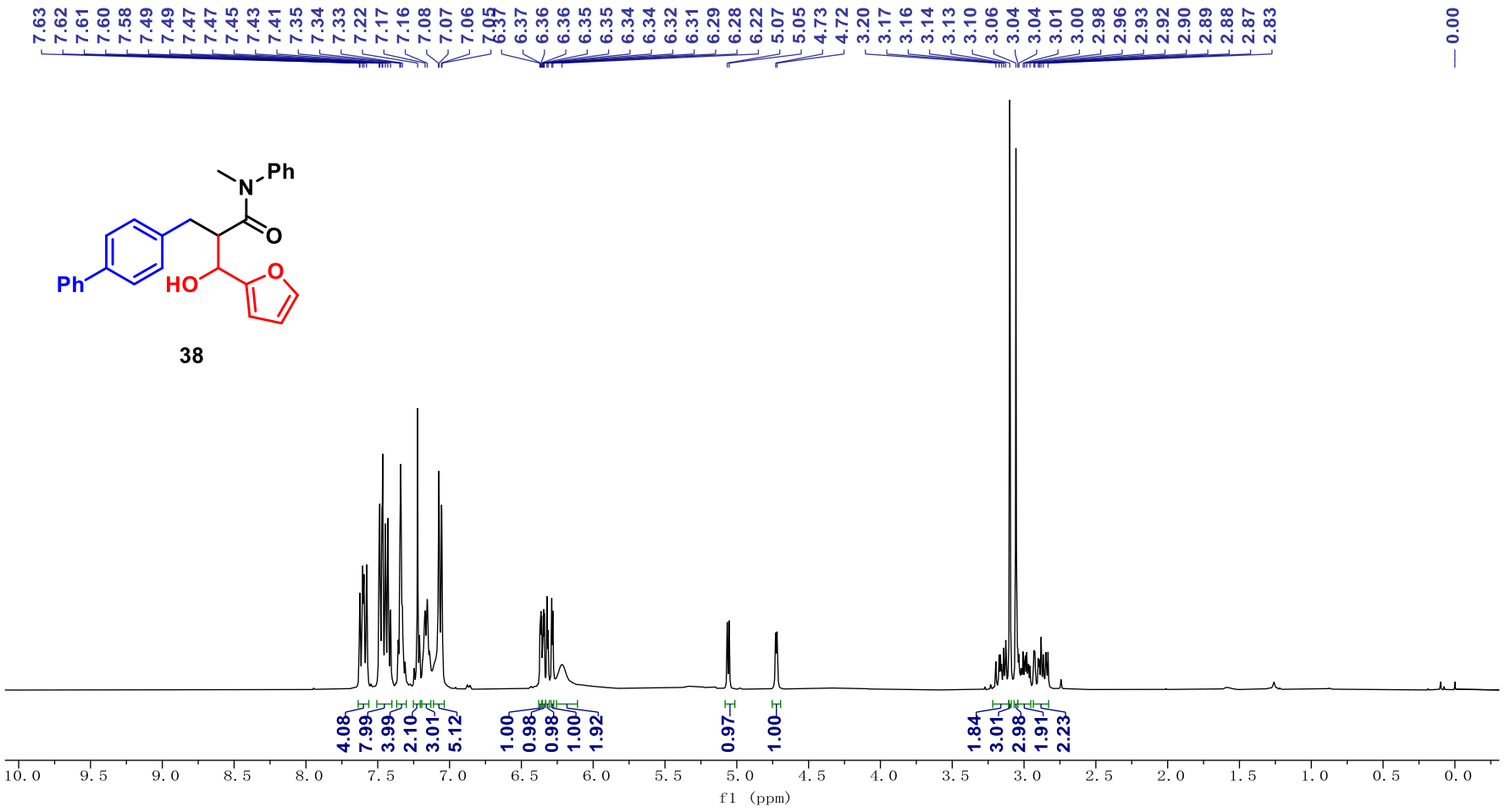
^{1}H NMR of 37 (Another isomer) (400 MHz, $CDCl_3$)



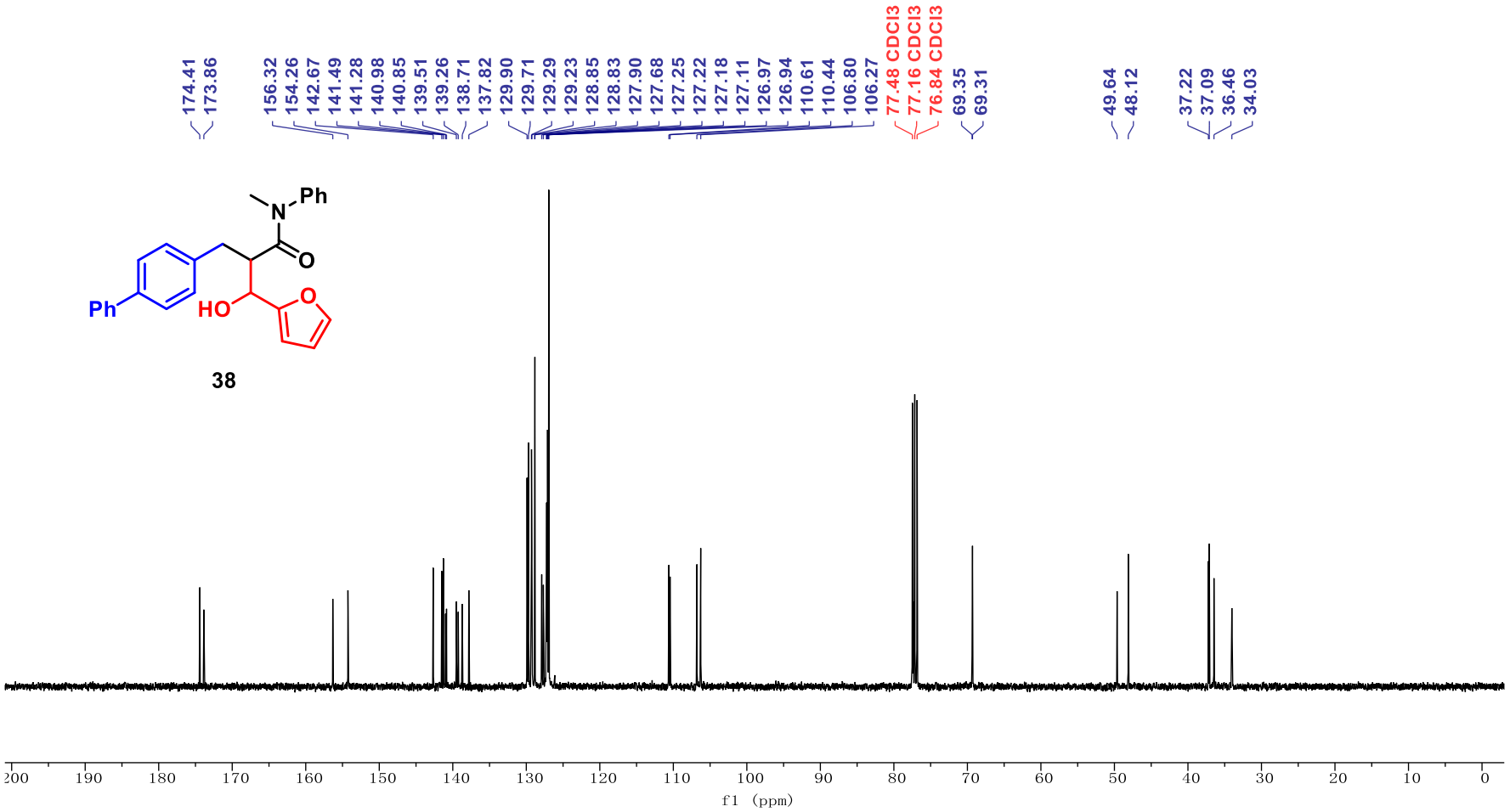
^{13}C NMR of 37 (Another isomer) (101 MHz, $CDCl_3$)



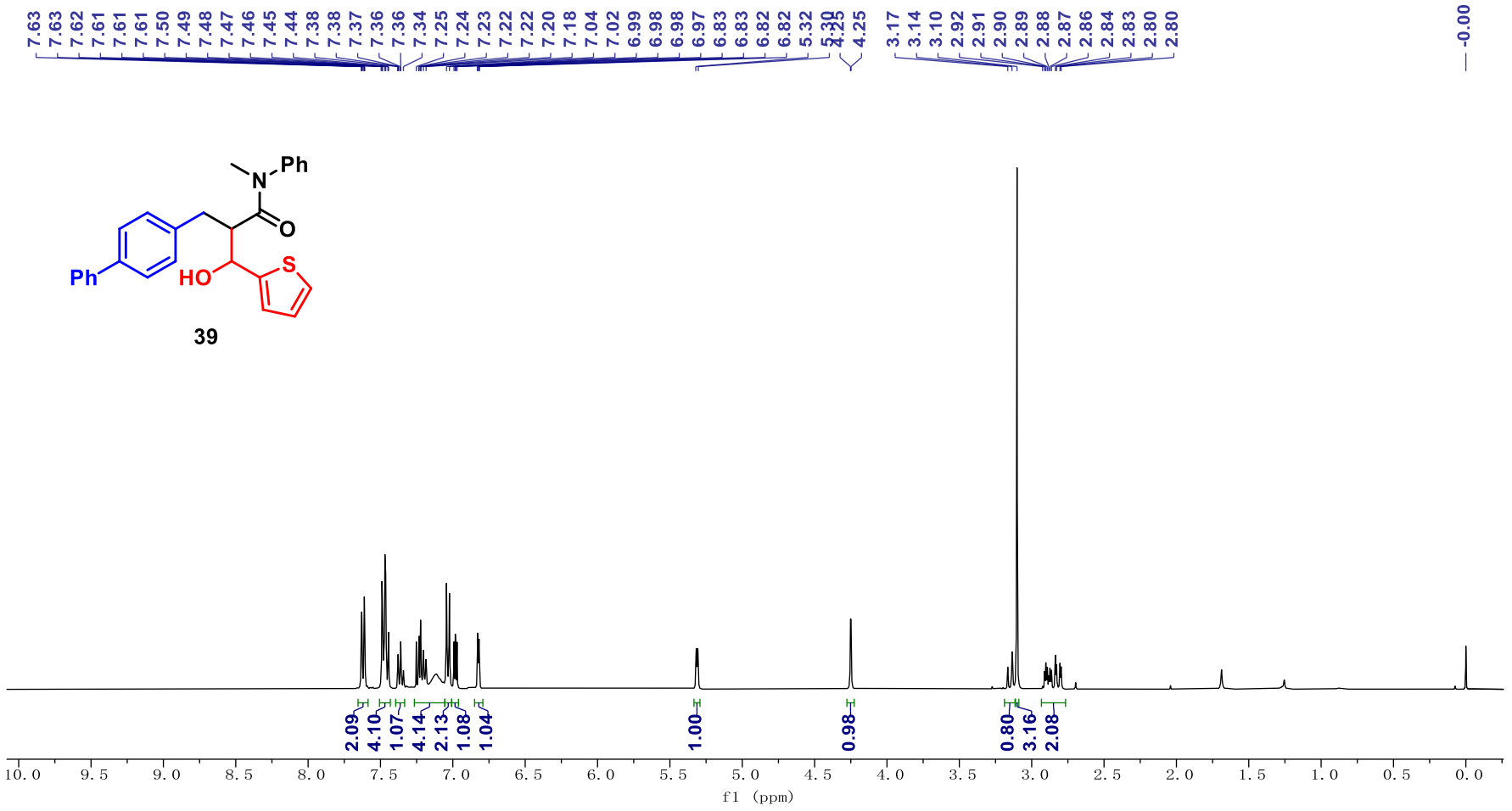
^{1}H NMR of 38 (400 MHz, $CDCl_3$)



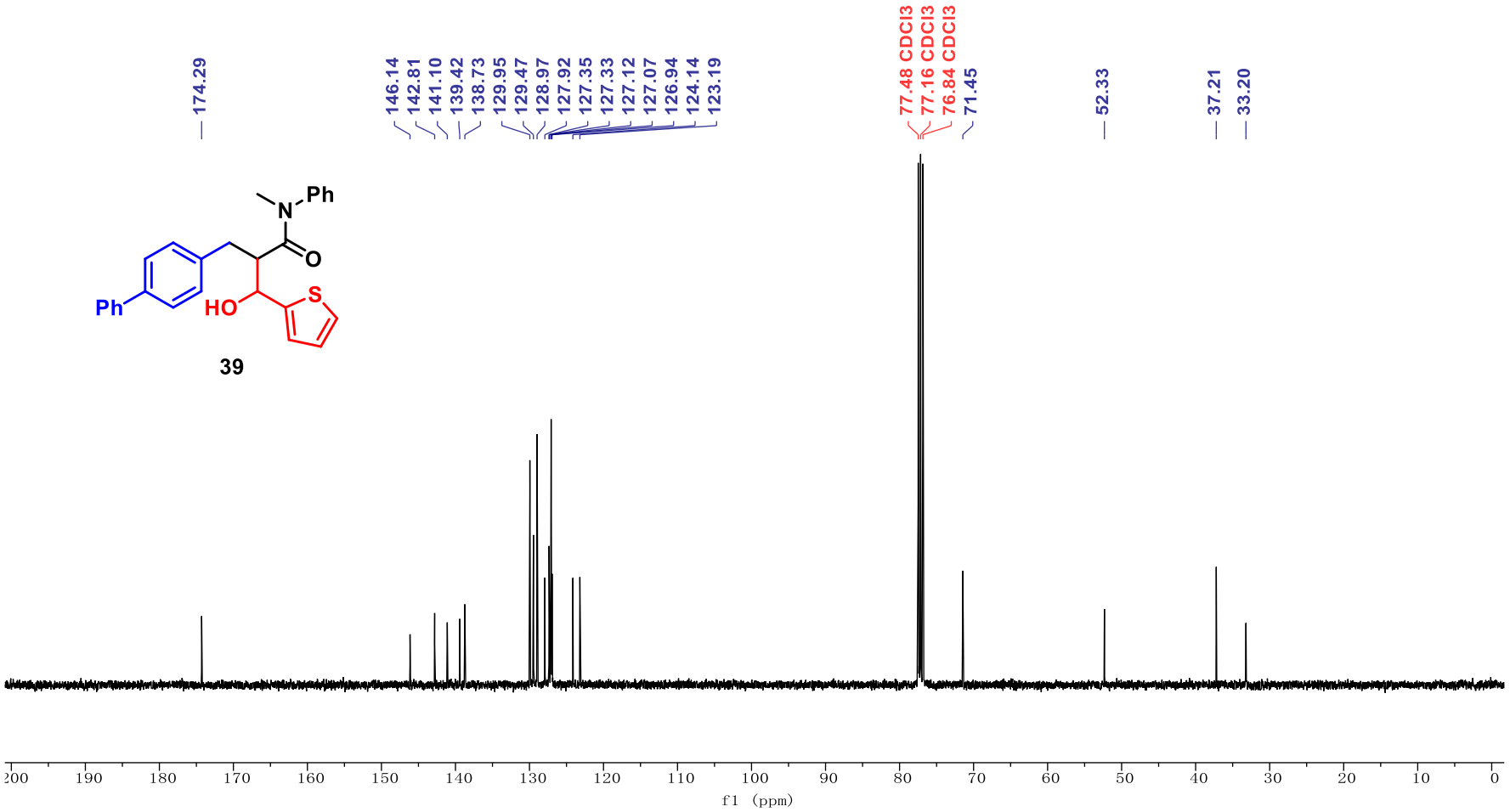
^{13}C NMR of 38 (101 MHz, $CDCl_3$)



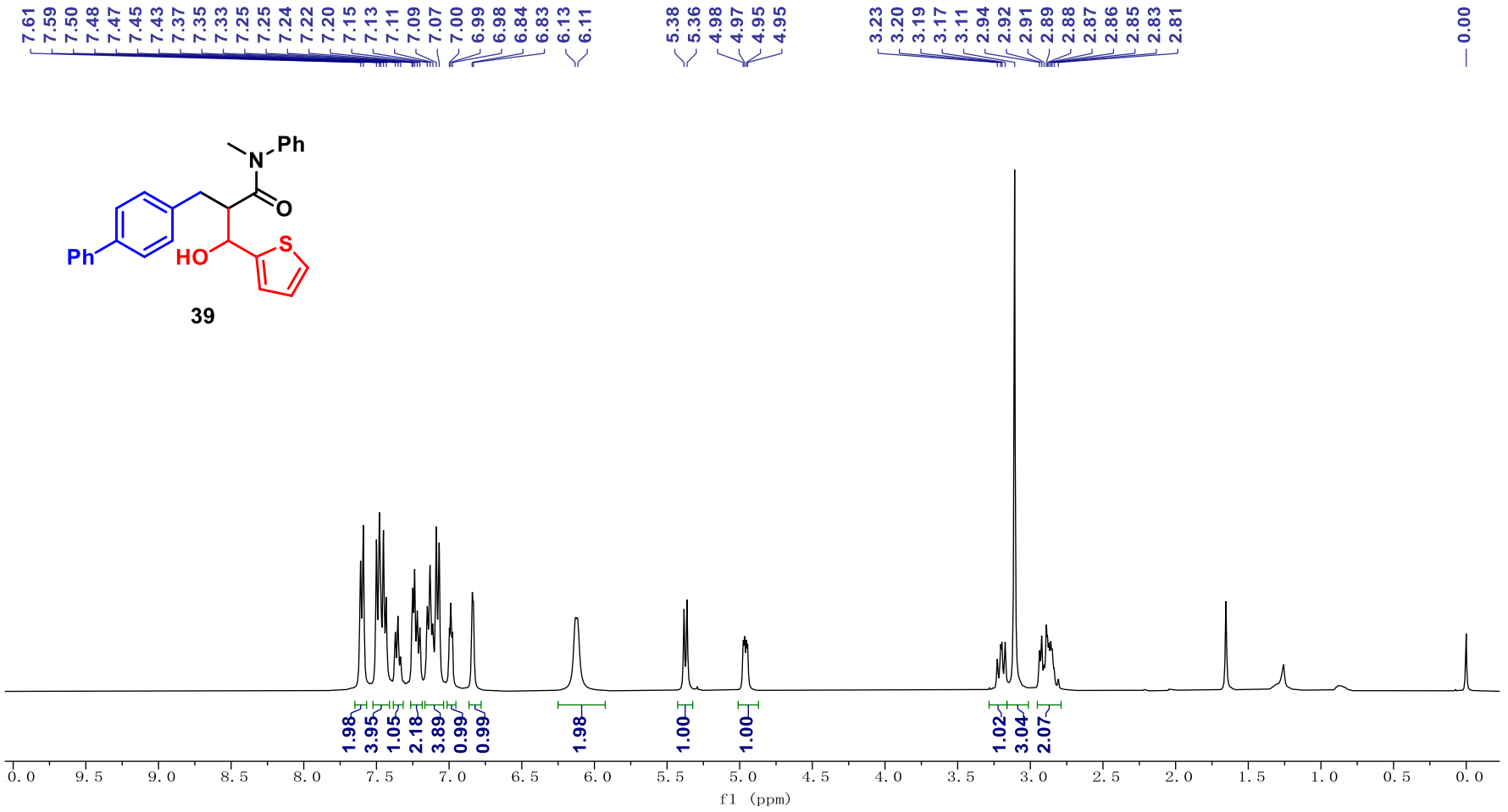
^{1}H NMR of 39 (One isomer) (400 MHz, $CDCl_3$)



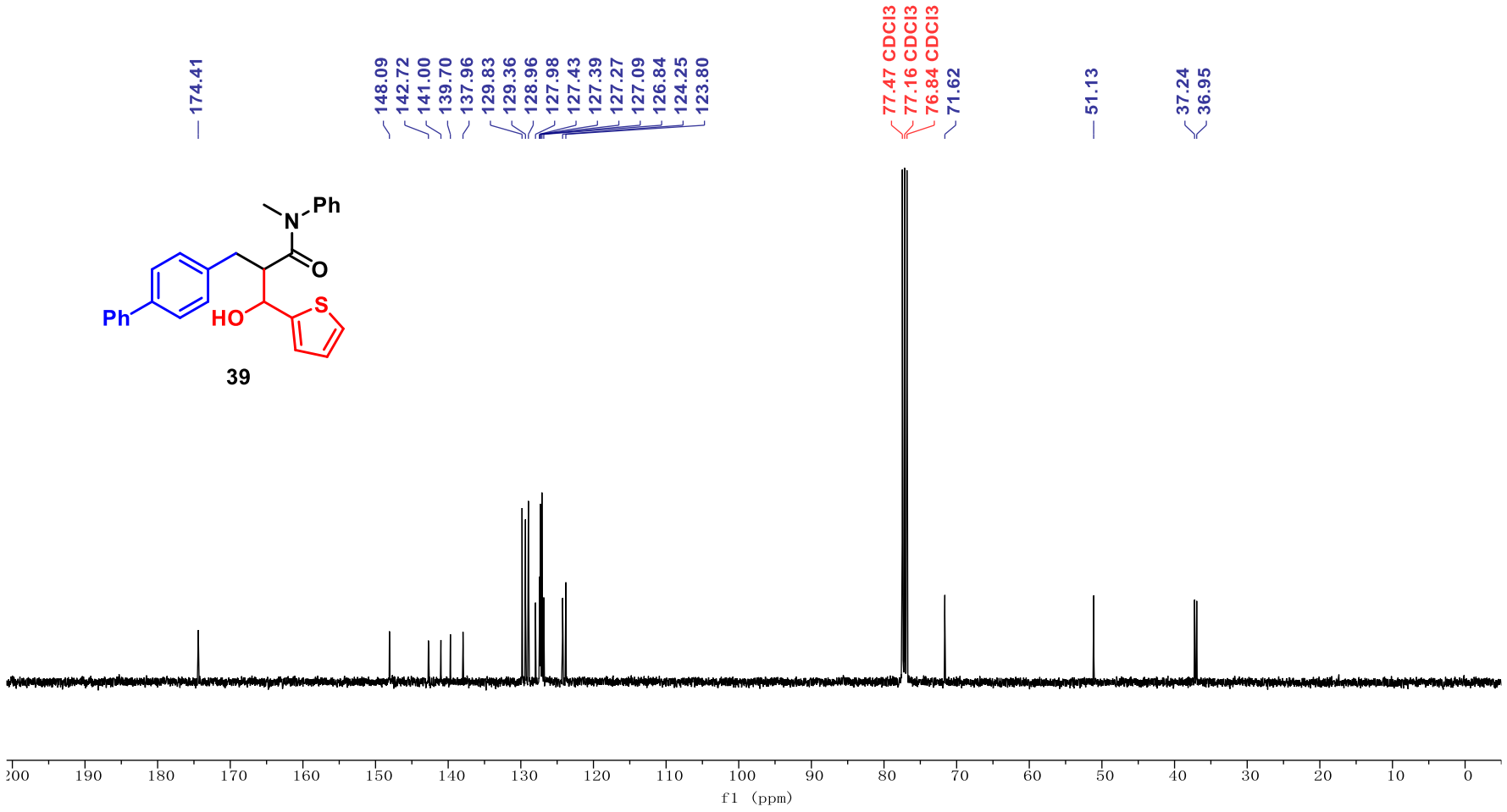
^{13}C NMR of 39 (One isomer) (101 MHz, $CDCl_3$)



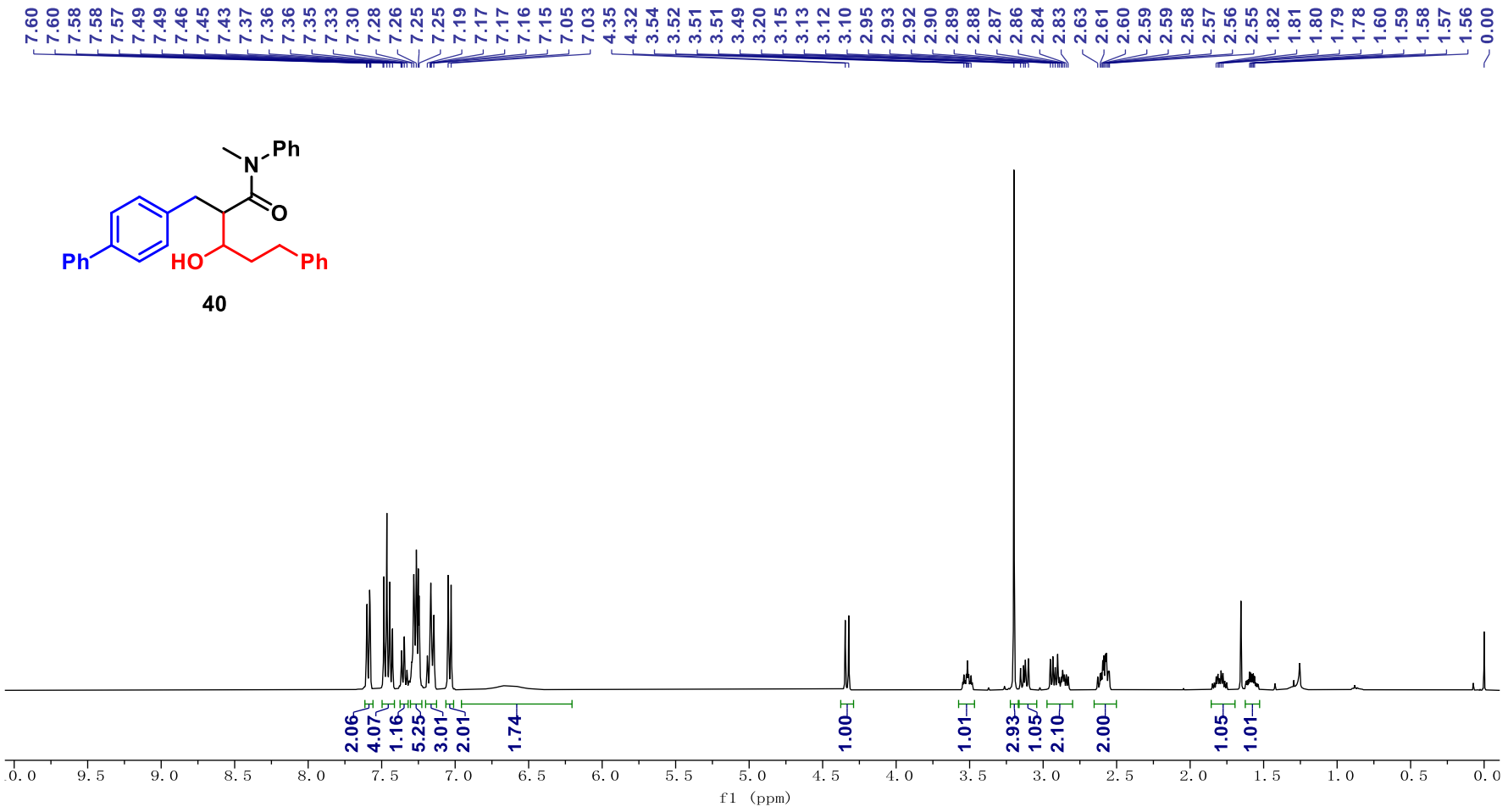
^{1}H NMR of 39 (Another isomer) (400 MHz, $CDCl_3$)



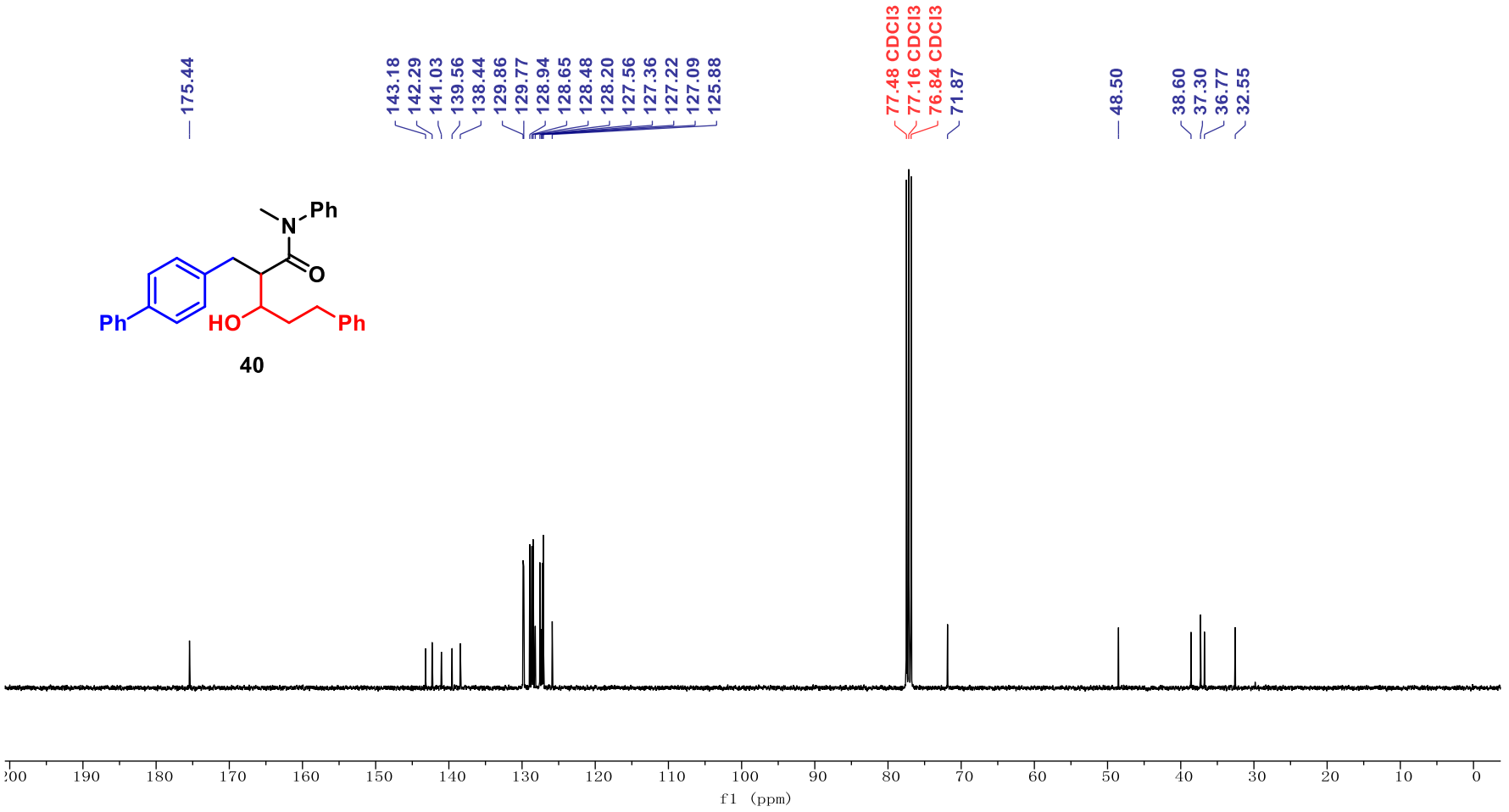
^{13}C NMR of 39 (Another isomer) (101 MHz, $CDCl_3$)



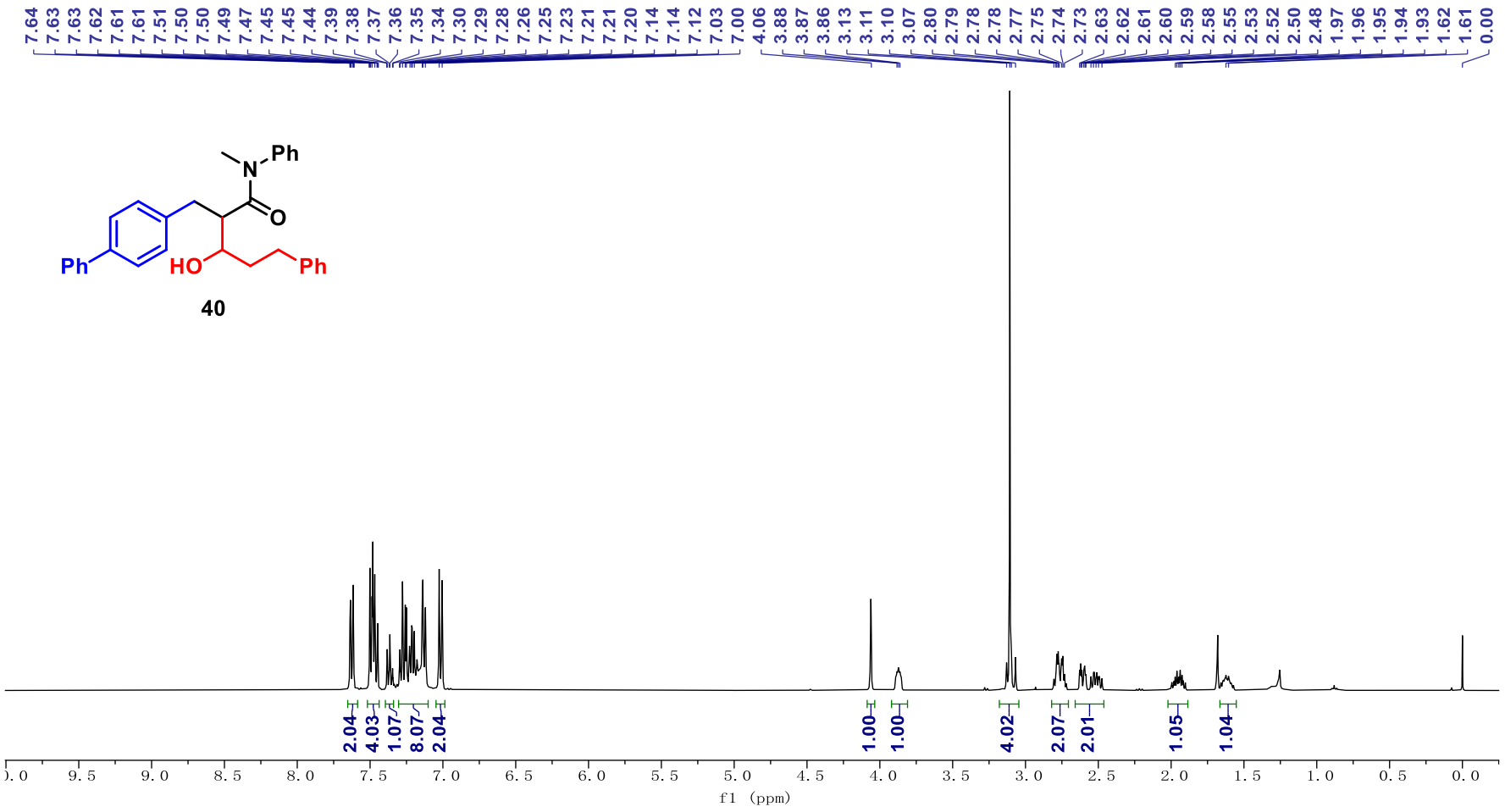
^{1}H NMR of 40 (One isomer) (400 MHz, $CDCl_3$)



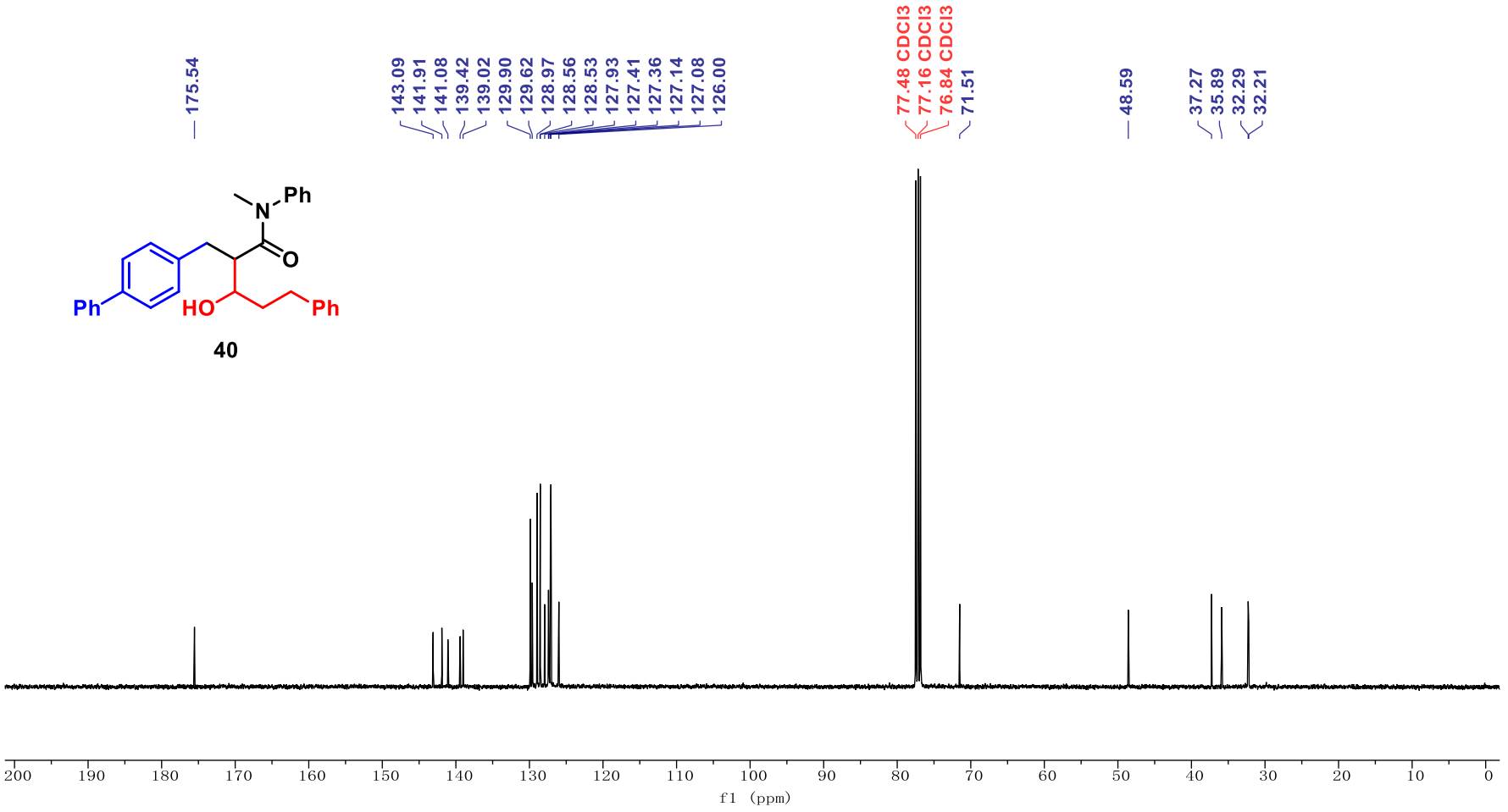
^{13}C NMR of 40 (One isomer) (101 MHz, $CDCl_3$)



^{1}H NMR of 40 (Another isomer) (400 MHz, $CDCl_3$)

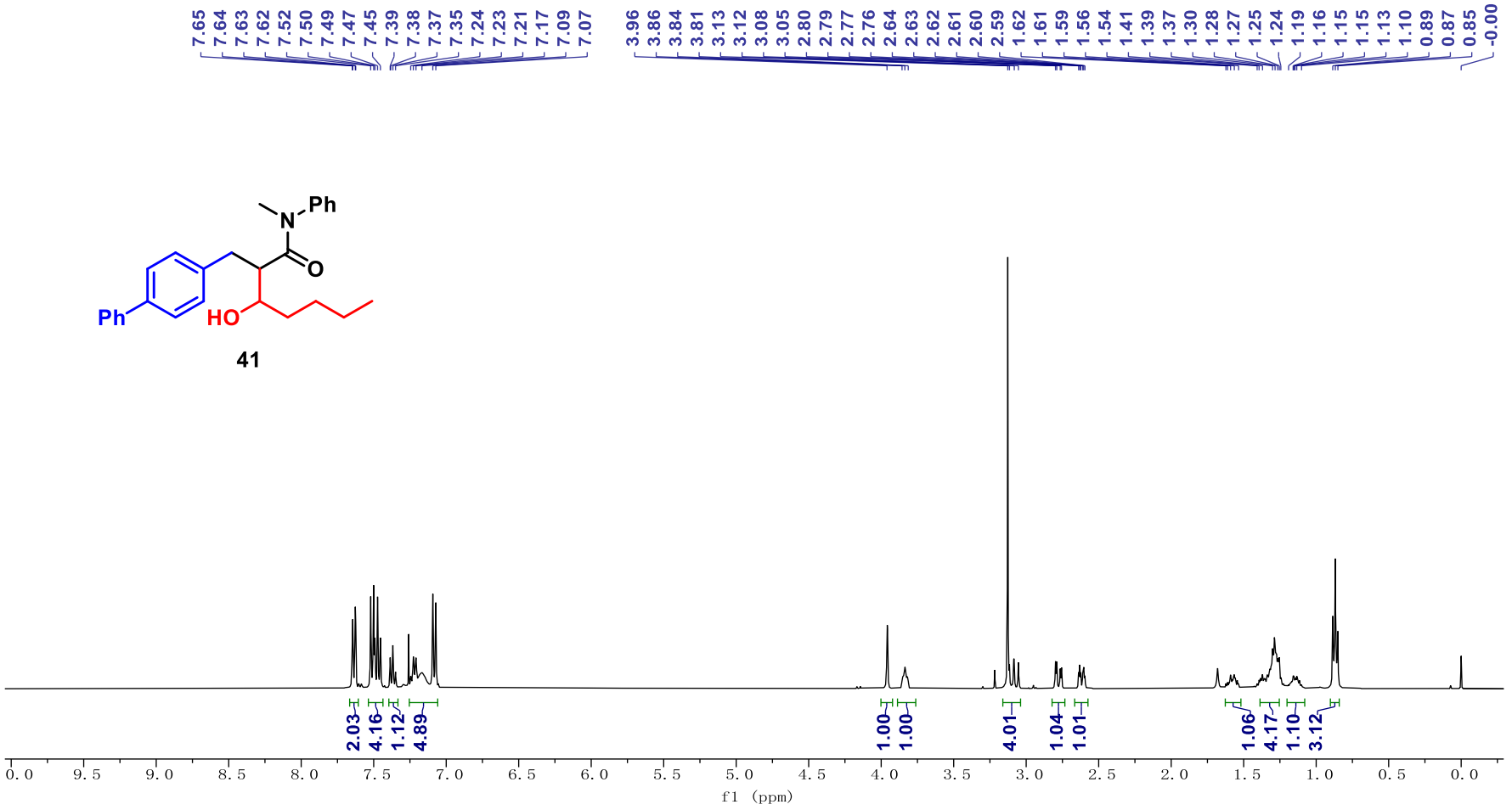


^{13}C NMR of 40 (Another isomer) (101 MHz, $CDCl_3$)

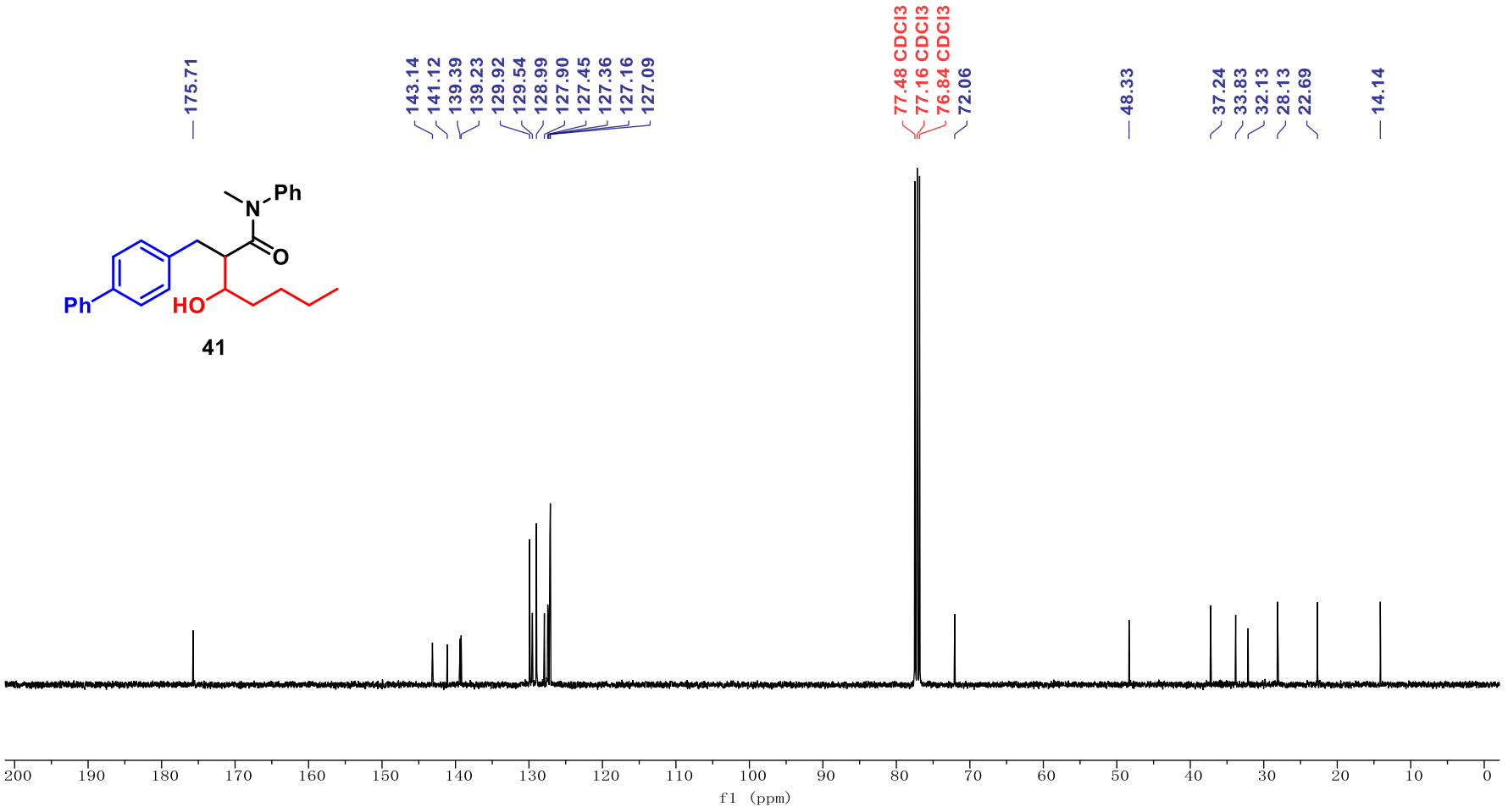


40

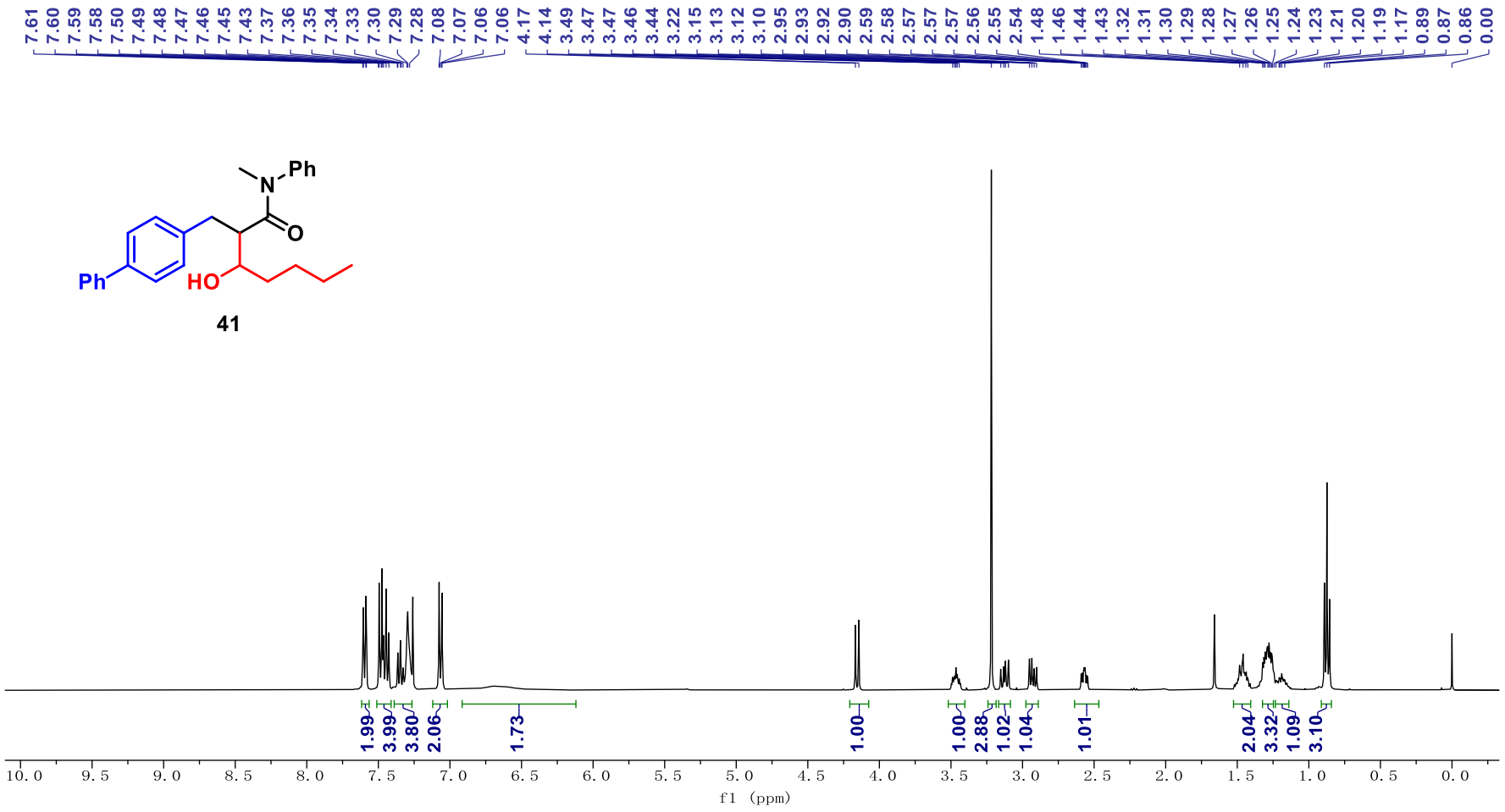
^{1}H NMR of 41 (One isomer) (400 MHz, $CDCl_3$)



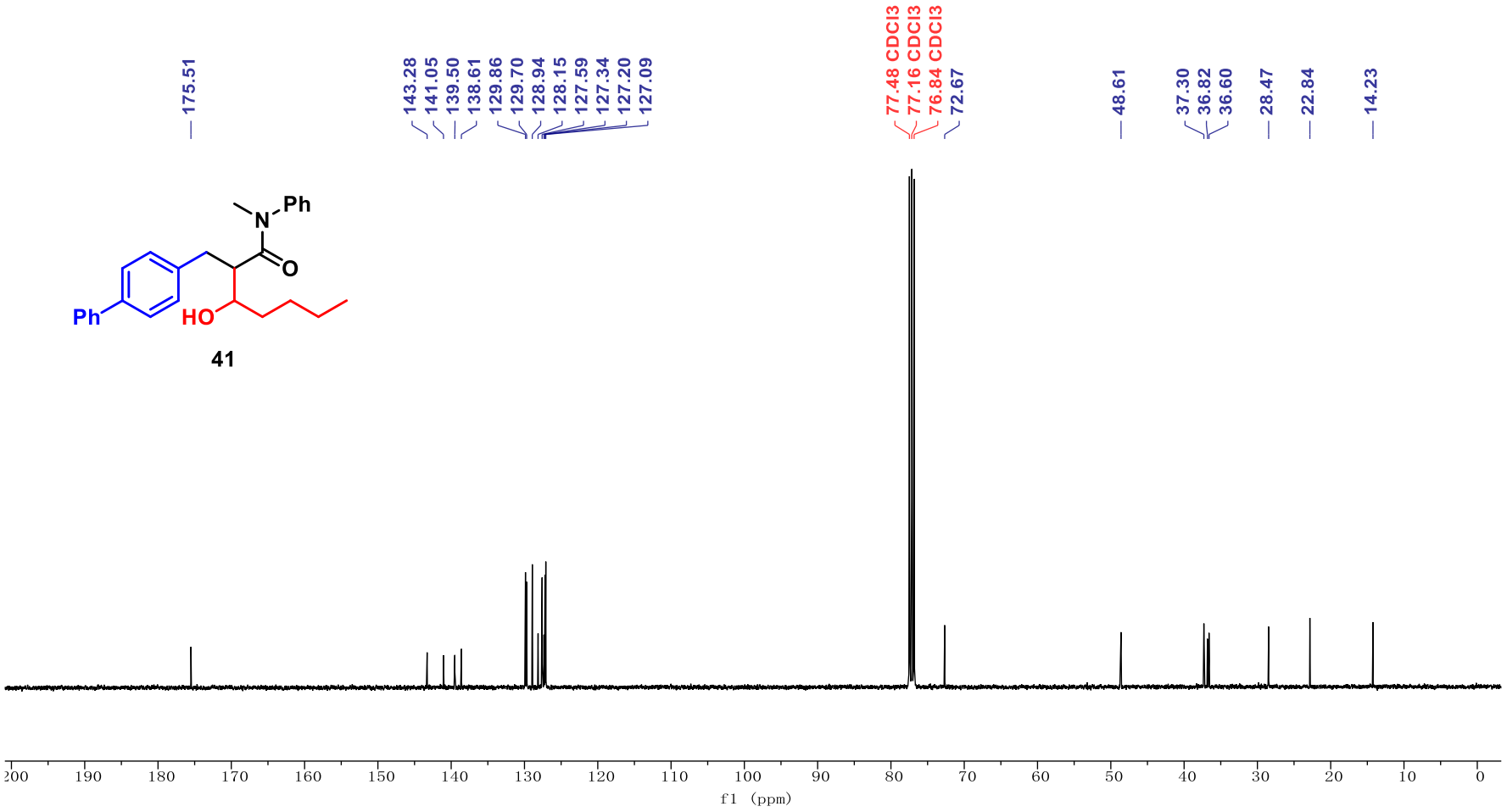
^{13}C NMR of 41 (One isomer) (101 MHz, $CDCl_3$)



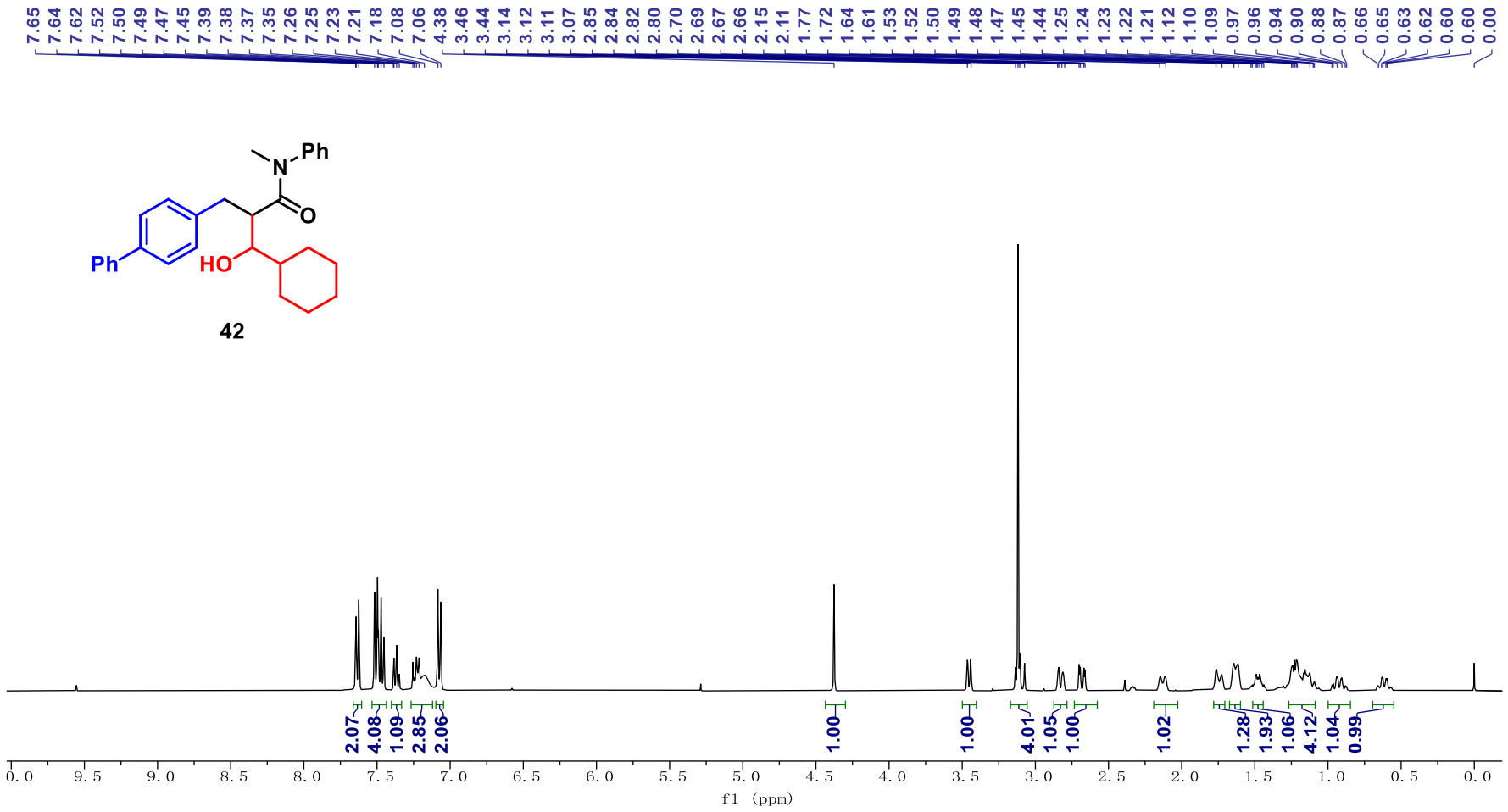
^{1}H NMR of 41 (Another isomer) (400 MHz, $CDCl_3$)



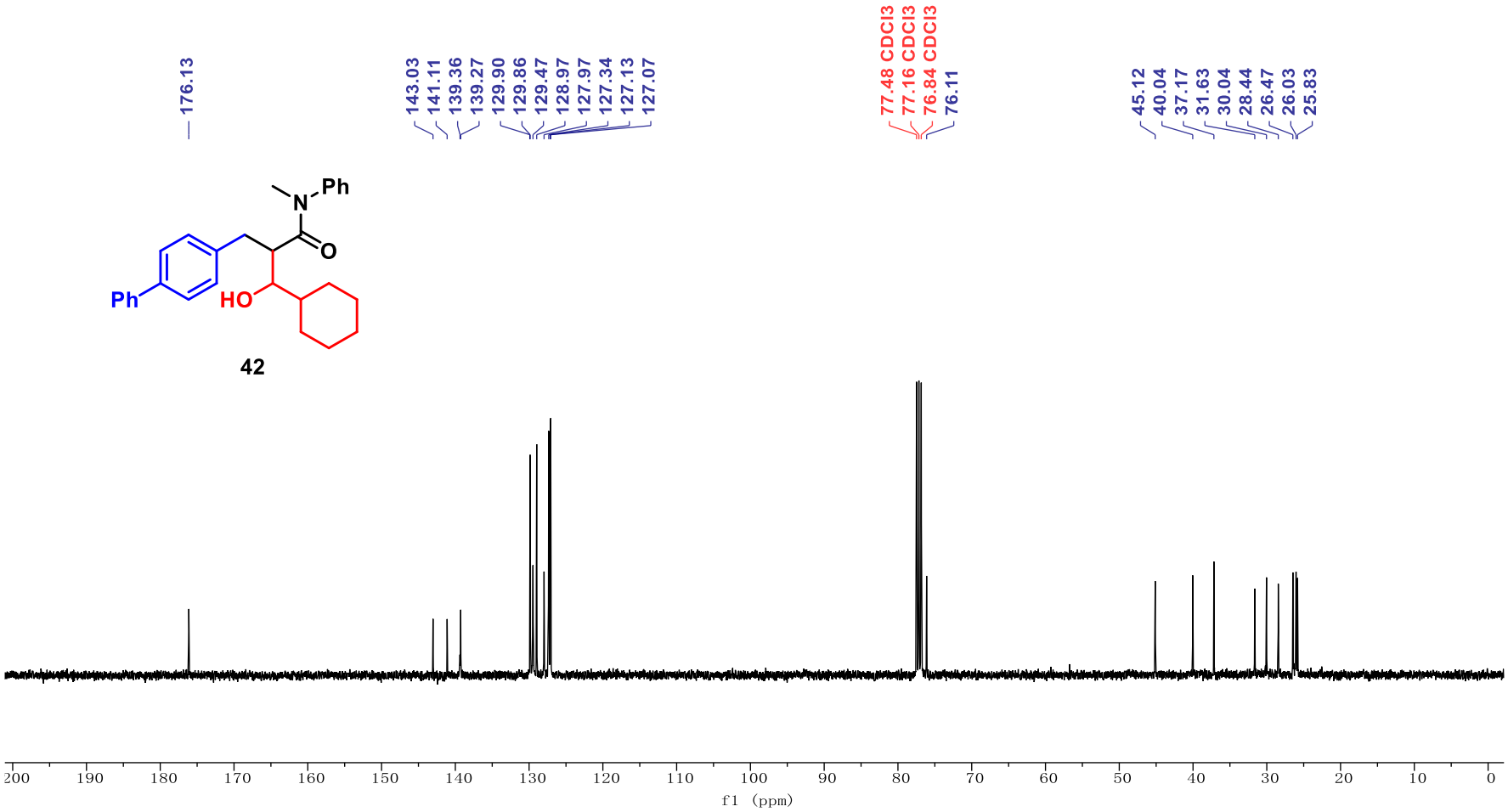
^{13}C NMR of 41 (Another isomer) (101 MHz, $CDCl_3$)



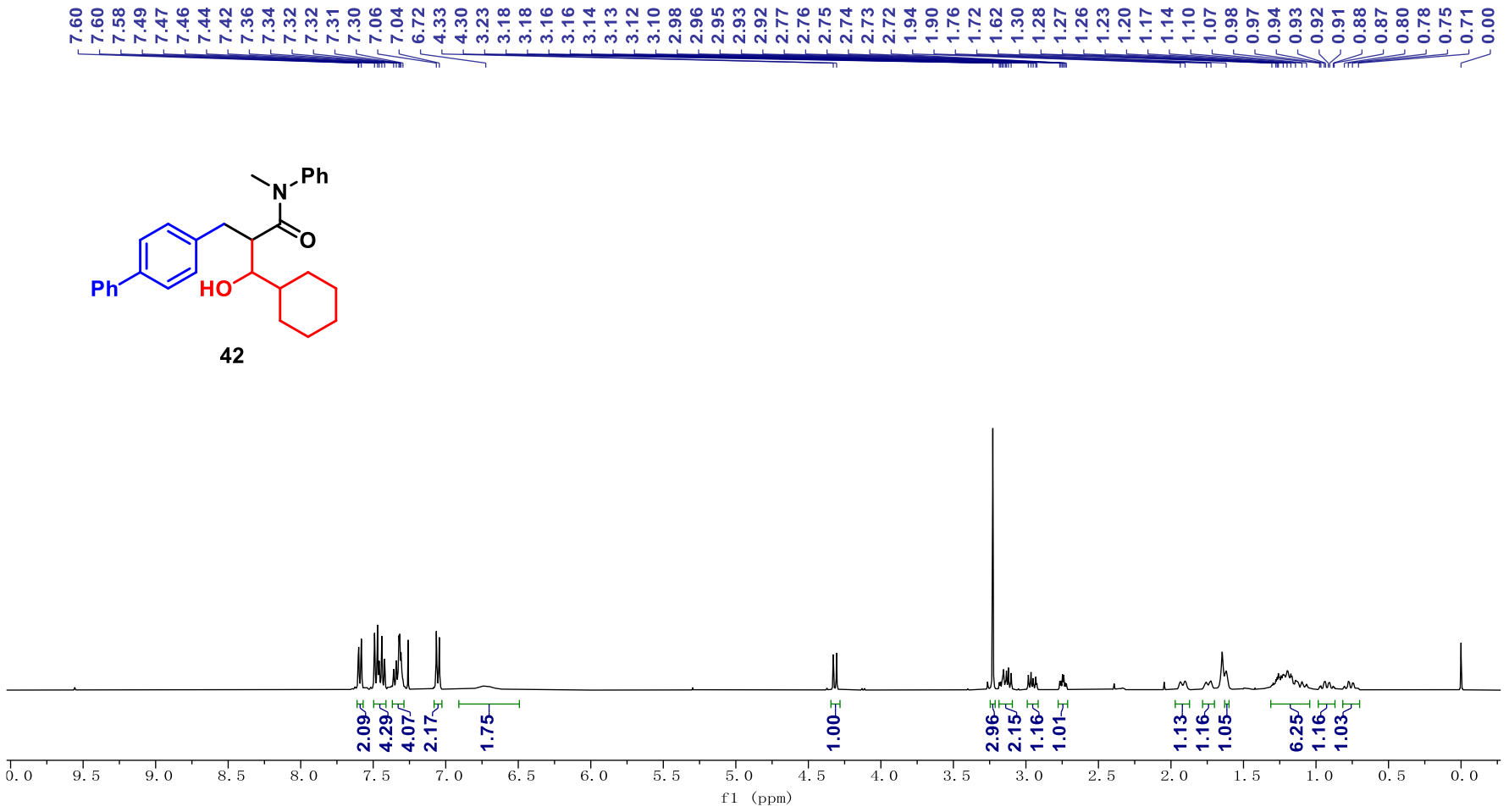
^{1}H NMR of 42 (One isomer) (400 MHz, $CDCl_3$)



^{13}C NMR of 42 (One isomer) (101 MHz, $CDCl_3$)

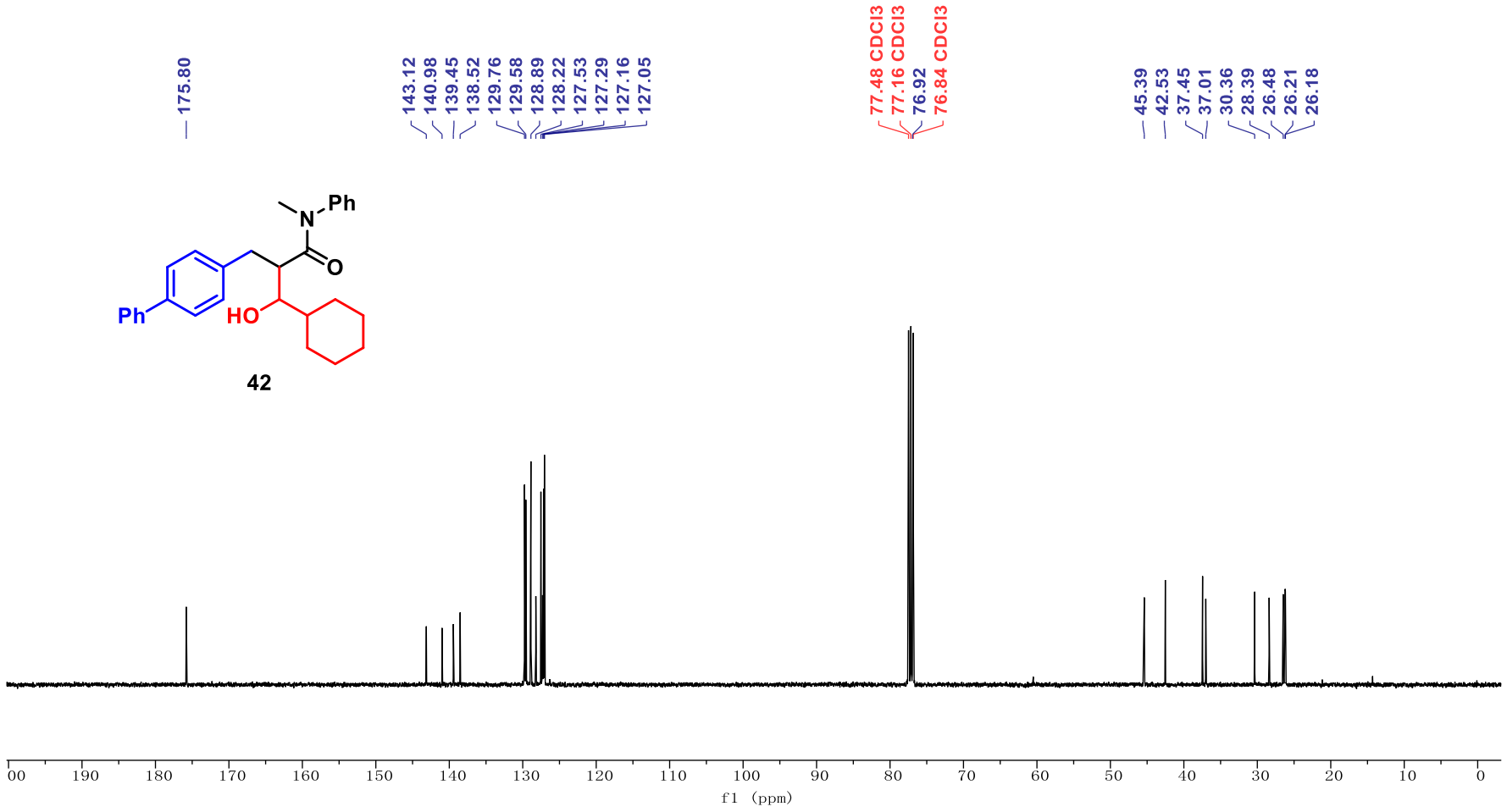


^{1}H NMR of 42 (Another isomer) (400 MHz, $CDCl_3$)

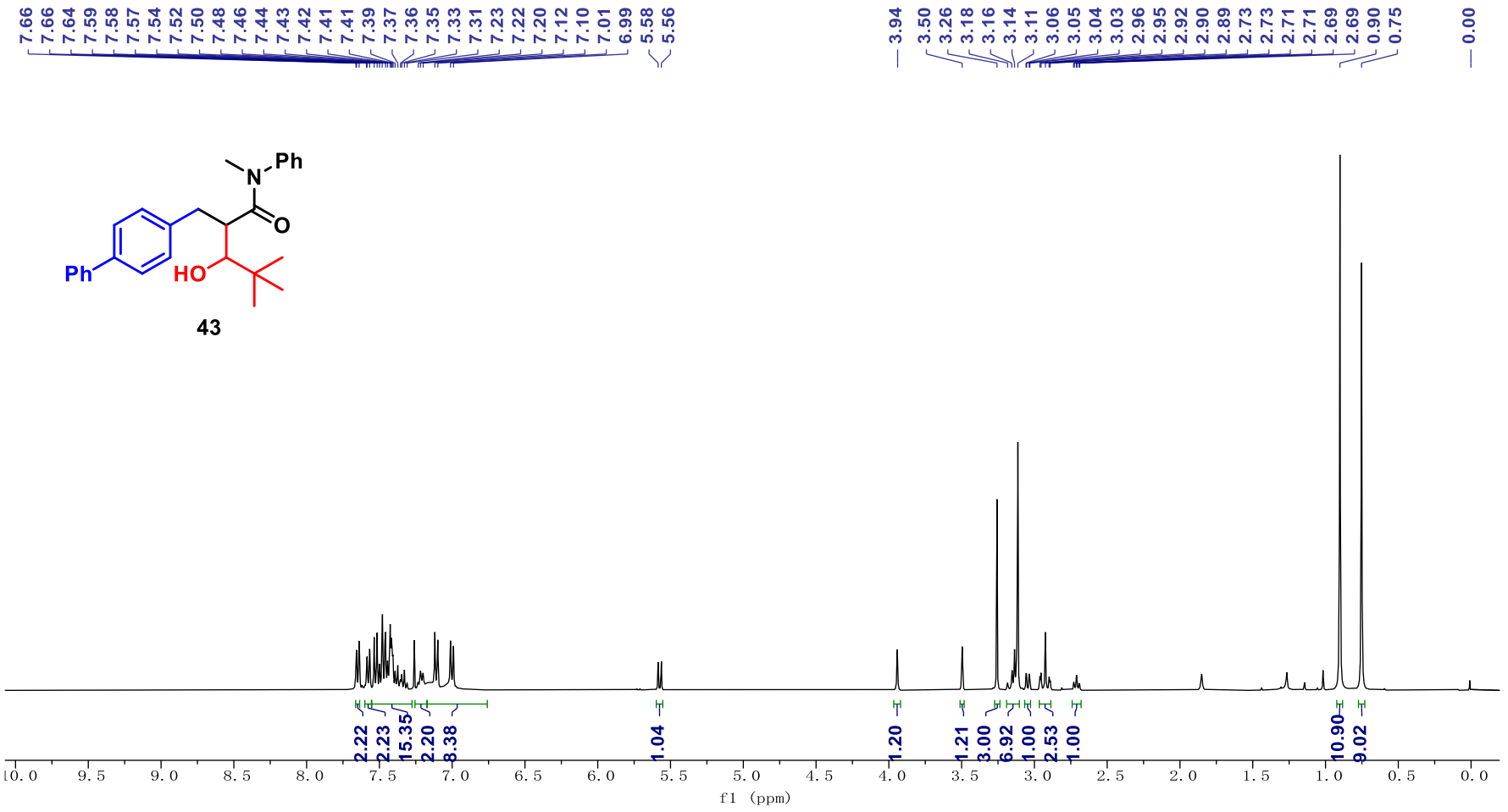


42

^{13}C NMR of 42 (Another isomer) (101 MHz, $CDCl_3$)



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



43

^{13}C NMR of 43 (101 MHz, $CDCl_3$)