Photoinduced Nickel-Catalyzed Reductive Acyl Cross-Coupling: Facile Access to All Carbon Quaternary Aliphatic Ketones

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Electronic Supplementary Information

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1 General Information

Reactions were performed in flame-dried glassware or conventional Schlenk techniques under a static pressure of nitrogen unless otherwise stated. All the materials were purchased 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. All HRMS were recorded on high resolution Fourier transform mass spectrometer with Bruker Daltonics SolariX 7.0T with ESI mode, and the detector is FT-MS. 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 and ^{13}C NMR spectra ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm). *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: 1W purple LED, λ_{max} = 390 nm) (Figure S1). Unless otherwise photoredox reactions were set-up in 10 mL vial and stirred (1000 rpm) at a distance of 1.5 cm from the irradiating plate. In addition, fan (rear part) was used to maintain the temperature of 25 − 30 °C.

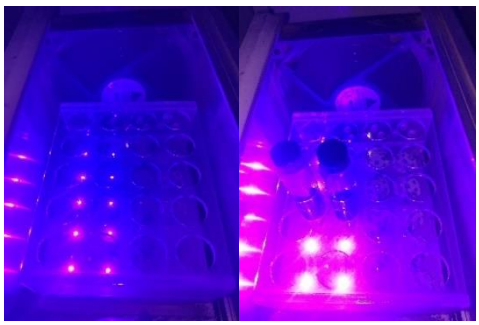
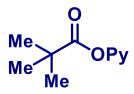


Figure S1. Set-up for photoredox reactions

2 Catalysts and Starting Materials

2.1 2-Pyridyl esters were synthesized according to the published procedure[1-3]



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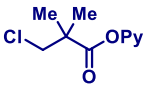

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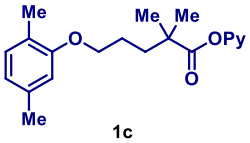

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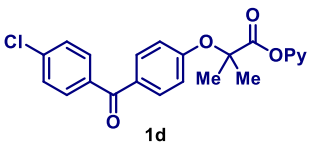

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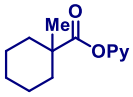

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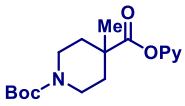

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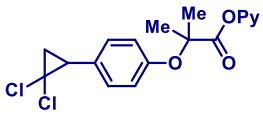

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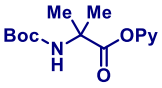

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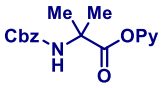

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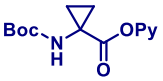

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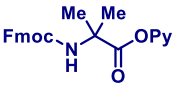
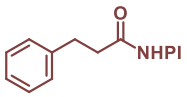


1k

2.2 The NHPI esters shown below were synthesized according to the published procedure[4-8]



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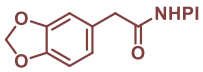

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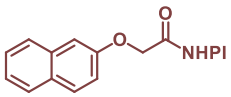

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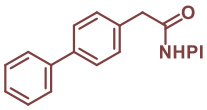

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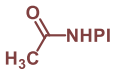

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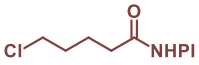

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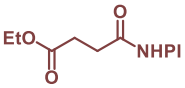

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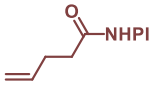

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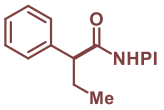

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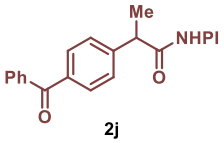

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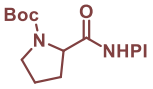

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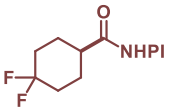

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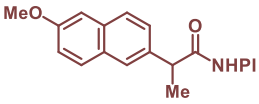

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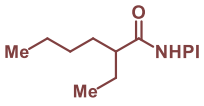

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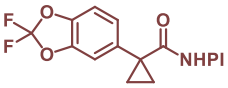

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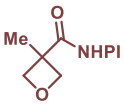

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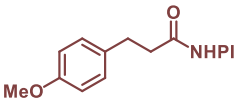

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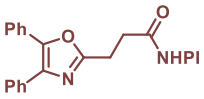

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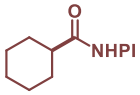

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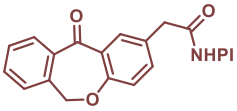

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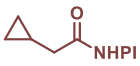
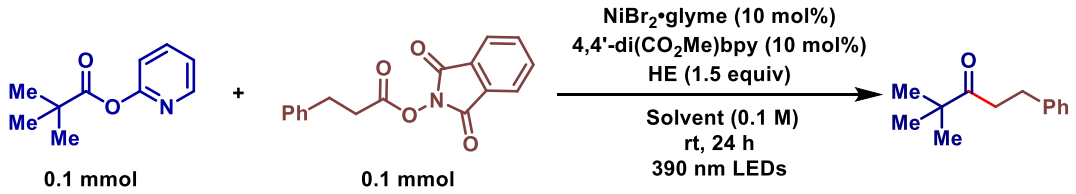


2v

3 Optimization of the Reaction Conditions

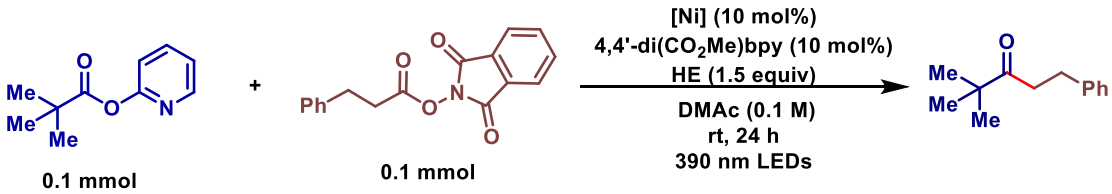
3.1 Table S1. The Effect of solvent



Entry	Solvent	Yield (%)[a]
1	DMAc	65
2	DMF	23
3	NMP	34
4	MeCN	trace
5	THF	trace
6	toluene	trace
7	EA	trace
8	1,4-dioxane	trace
9	DMSO	N.D.

[a] GC yield, with *n*-tridecane as internal standard. N.D. = not detected.

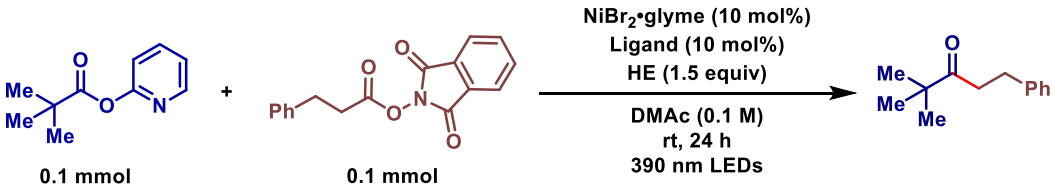
3.2 Table S2. The Effect of Ni-catalyst

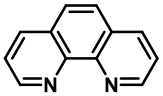
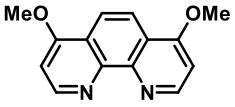
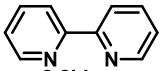
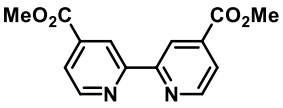
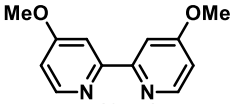
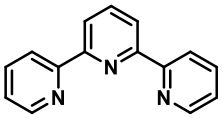
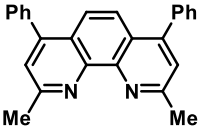
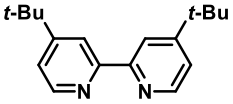
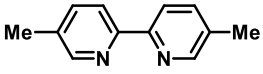


Entry	Ni-catalyst	Yield (%)[a]
1	$NiBr_2$•glyme	65
2	$Ni(OTf)_2$	N.D.
3	$Ni(OAc)_2$	trace
4	$NiCl_2$	37
5	$NiBr_2$	27
6	NiI_2	10
7	$NiCl_2$•glyme	12
8	$Ni(cod)_2$	trace
9	$NiCl_2(PPh_3)_2$	trace

[a] GC yield, with *n*-tridecane as internal standard. N.D. = not detected.

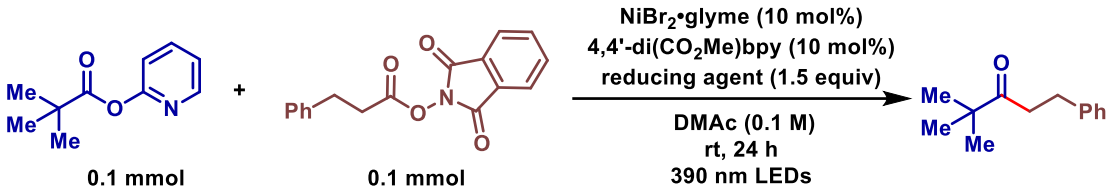
3.3 Table S3. The Effect of ligand



Entry	Ligand	Yield (%)[a]
1	 1,10-phen	35
2	 4,7-dimethoxy-1,10-phen	15
3	 2,2'-bpy	22
4	 4,4'-di(CO_2Me)bpy	65
5	 4,4'-di(OMe)bpy	20
6	 2,2':6',2''-terpyridine	27
7	 2,9-dimethyl-4,7-diphenyl-1,10-phen	trace
8	 4,4'-di(*t*-Bu)bpy	34
9	 5,5'-dimethylbpy	30

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

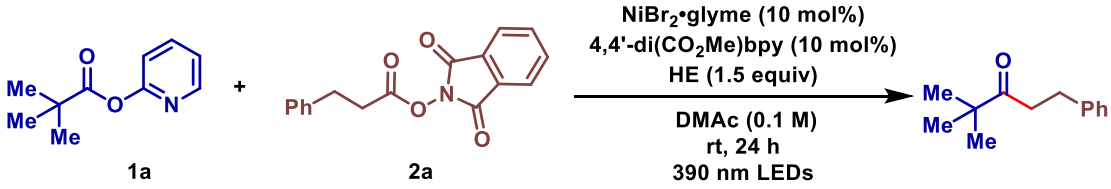
3.4 Table S4. The Effect of reducing agent



Entry	reducing agent	Yield (%)[a]
1	HE	65
2	B_2Cat_2	7
3	B_2Pin_2	trace
4	Et_3N	N.D.
5	Ph-HE	28
6	Me-HE	23
7	NaI	N.D.

[a] GC yield, with *n*-tridecane as internal standard. N.D. = not detected.

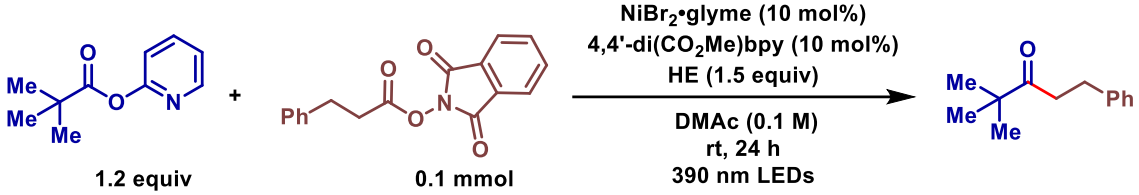
3.5 Table S5. The Effect of ratio of each substrate 1a and 2a



Entry	**1a**:**2a**	Yield (%)[a]
1	1:1	65
2	1:1.2	54
3	1:1.5	54
4	1.2:1	80(78)[b]
5	1.5:1	65

[a] GC yield, with *n*-tridecane as internal standard, [b] isolated yield.

3.6 Table S6. Control Experiments

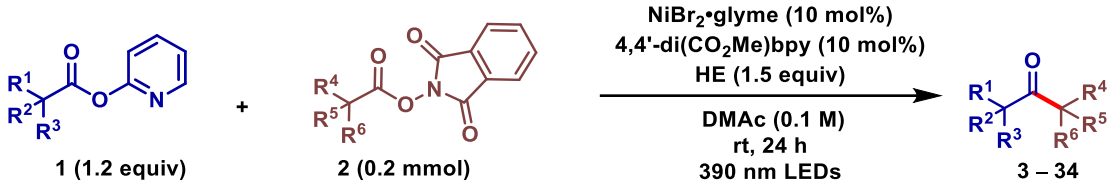


1.2 equiv　　0.1 mmol

Entry	Variation from "standard conditions"	Yield (%)[a]
1	none	80
2	w/o HE	N.D.
3	w/o [Ni]	N.D.
4	w/o Ligand	15
5	w/o Light	N.D.
6	450 nm LEDs instead of 390 nm LEDs	N.D.
7	Pivaloyl chloride instead of **1a**	90
8	Pivalic anhydride instead of **1a**	70

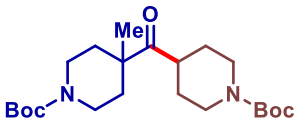
[a] GC yield, with *n*-tridecane as internal standard. N.D. = not detected.

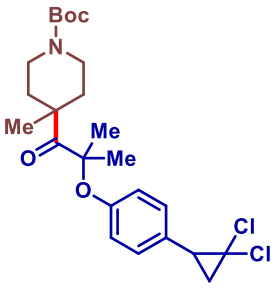
4 General Procedure for Ketone Synthesis

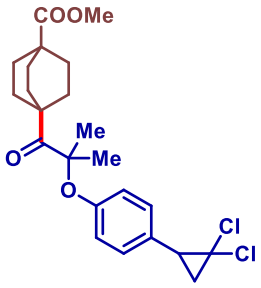


Reactions were carried out in a glove box filled with N_2. An oven-dried vial equipped with a PTFE-coated stir-bar was added $NiBr_2$•glyme (6.1 mg, 20 μmol, 0.10 equiv), 4,4'-di(CO_2Me)bpy (5.4 mg, 20 μmol, 0.10 equiv), 2-pyridyl ester **1** (0.24 mmol, 1.2 equiv), NHPI ester **2** (0.20 mmol, 1.0 equiv), HE (76 mg, 0.30 mmol, 1.5 equiv), and DMAc (0.10 M, 2.0 mL) was added via a syringe. The vial was capped with a screw capfitted with a PTFE-faced silicon septum, removed from the glovebox and irradiated with a 1 W purple LED lamp (at approximately 1.5 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. The combined organic layers were dried with Na_2SO_4, filtered, and concentrated in vacuo. The residue was isolated by flash chromatography to give the corresponding pure product.

5 Unsuccessful substrates

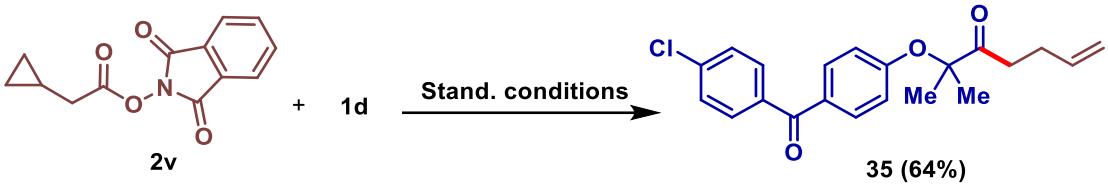






6 Mechanistic Studies

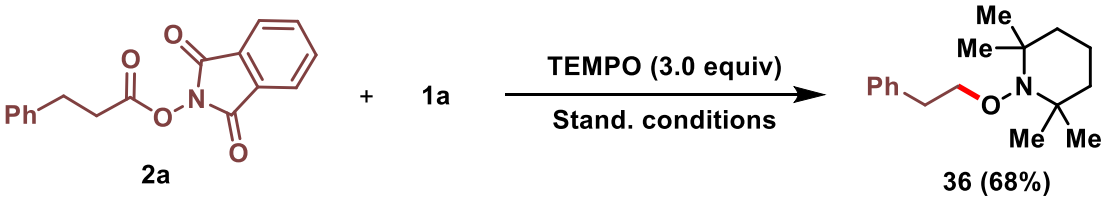
6.1 Radical clock experiment



Prepared according to the general procedure using **1d** (95 mg, 0.24 mmol, 1.2 equiv), **2v** (49 mg, 0.20 mmol, 1.0 equiv), $NiBr_2$•glyme (6.1 mg, 20 μmol, 0.10 equiv), 4,4'-di(CO_2Me)bpy (5.4 mg, 20 μmol, 0.10 equiv), HE (76 mg, 0.30 mmol, 1.5 equiv) and DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE/EA = 20/1) to give the product **35** (45 mg, 64% yield) as a yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) *δ*: 7.78 – 7.73 (m, 2H), 7.72 – 7.70 (m, 2H), 7.49 – ;7.45 (m, 2H), 6.83 – 6.80 (m, 2H), 5.79 – 5.72 (m, 1H), 5.02 (d, *J* = 17.2 Hz, 1H), 4.96 (dd, *J* = 10.8, 2.3 Hz, 1H), 2.75 – 2.71 (m, 2H), 2.34 (q, *J* = 7.1 Hz, 2H), 1.56 (s, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) *δ*: 212.2, 194.3, 159.6, 138.6, 137.0, 136.4, 132.3, 131.3, 130.8, 128.7, 117.5, 115.7, 84.9, 35.5, 27.7, 24.3 ppm. **IR:** 2924, 1716, 1654, 1596, 1504, 1381, 1302, 1283, 1245, 1169, 1146, 1089, 1014, 926, 853, 762, 741 cm^{-1}. **HRMS** (ESI) for $C_{21}H_{22}ClO_3^+$ [$(M+H)^+$]: calculated 357.1252, found 357.1242.

6.2 Radical trapping experiment



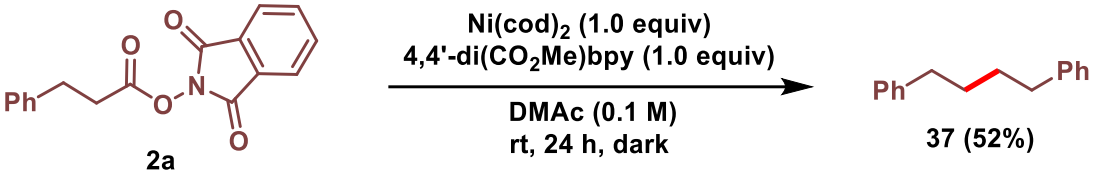
The reaction was set up in a glove box filled with N_2. An oven-dried vial equipped with a PTFE-coated stir-bar was added $NiBr_2$•glyme (6.1 mg, 20 μmol, 0.10 equiv), 4,4'-di(CO_2Me)bpy (5.4 mg, 20 μmol, 0.10 equiv), **1a** (43 mg, 0.24 mmol, 1.2 equiv), **2a** (59 mg, 0.20 mmol, 1.0 equiv), HE (76 mg, 0.30 mmol, 1.5 equiv), 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO, 94 mg, 0.60 mmol, 3.0 equiv) and DMAc (0.20 M, 2.0 mL) was added via a syringe. The reaction was quenched by H_2O, extracted with ethyl acetate. The organic layers were dried with Na_2SO_4, filtered, and concentrated in vacuo. The residue was

purified by flash column chromatography (PE/EA = 30/1) to give the TEMPO-trapped product **36** (35 mg, 68% yield) as a colorless oil.

No product **3** was observed and the TEMPO-trapped adduct **36** was detected by **^{1}H NMR** ,**^{13}C NMR** analysis. Spectroscopy data of **36** is agree with the literature values[9].

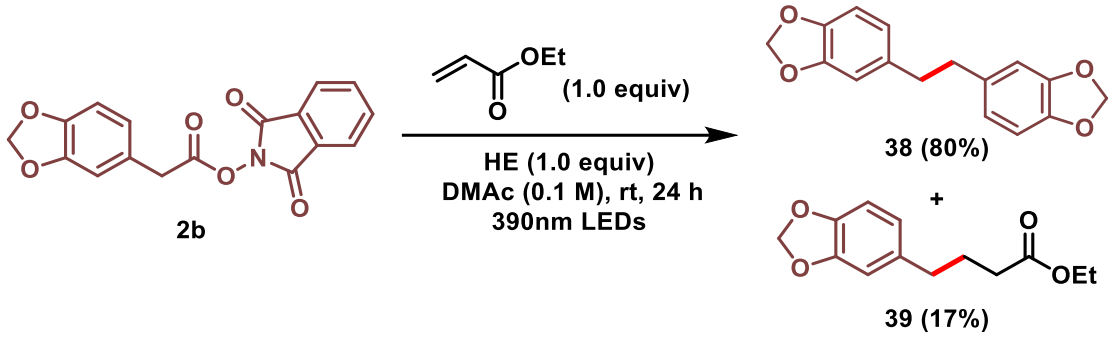
^{1}H NMR (600 MHz, $CDCl_3$) *δ*: 7.29 – 7.27 (m, 2H), 7.24 – 7.23 (m, 2H), 7.20 – 7.18 (m, 1H), 3.00 (t, *J* = 7.9 Hz, 2H), 2.68 (t, *J* = 7.9 Hz, 2H), 1.71 – 1.66 (m, 2H), 1.64 – 1.59 (m, 1H), 1.52 – 1.49 (m, 2H), 1.41 – 1.38 (m, 1H), 1.10 (s, 6H), 0.97 (s, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) *δ*: 140.6, 128.6, 128.5, 126.4, 60.0, 39.1, 32.0, 31.3, 20.6, 17.1 ppm.

6.3 Investigation of SET event



The reaction was set up in a glovebox filled with N_2. An oven-dried vial equipped with a PTFE-coated stir-bar was added **2a** (59 mg, 0.20 mmol, 1.0 equiv), $Ni(cod)_2$ (55 mg, 0.20 mmol, 1.0 equiv) and 4,4'-di(CO_2Me)bpy (54 mg, 0.20 mmol, 1.0 equiv) in DMAc (0.10 M, 2.0 mL). The mixture was stirred for 24 h in dark. The reaction was quenched by H_2O, extracted with ethyl acetate. The organic layers were dried with Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (PE) to give the homocoupling product **37** (22 mg, 52% yield) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) *δ*: 7.29 – 7.25 (m, 4H), 7.18 – 7.16 (m, 6H), 2.65 – 2.62 (m, 4H), 1.69 – 1.65 (m, 4H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) *δ*: 142.7, 128.6, 128.4, 125.8, 36.0, 31.2 ppm. **IR:** 3025, 2925, 2854, 1602, 1495, 1452, 1081, 1029, 741, 696, 596 cm^{-1}. **HRMS** (EI) for $C_{16}H_{18}$: calculated 210.1409, found 210.1403.



The reaction was set up in a glovebox filled with N_2. An oven-dried vial equipped with a PTFE-coated stir-bar was added **2b** (65 mg, 0.20 mmol, 1.0 equiv), ethyl acrylate (20 mg, 0.20 mmol, 1.0 equiv) and HE (76 mg, 0.30 mmol, 1.5 equiv) in DMAc (0.10 M, 2.0 mL). The mixture was irradiated with a 1 W purple LED lamp (at approximately 1.5 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. The combined organic layers were dried with Na_2SO_4, filtered, and concentrated in vacuo. The residue was isolated by flash chromatography (PE/EA = 30/1) to give the homocoupling product **38** (22 mg, 80% yield) as a colorless oil and Giese addition product **39** (8.1 mg, 17% yield) as a yellow oil.

Data of **38**:**^{1}H NMR** (600 MHz, $CDCl_3$) δ: 6.71 (d, J = 7.9 Hz, 2H), 6.66 (d, J = 1.7 Hz, 2H), 6.60 – 6.59 (m, 2H), 5.92 (s, 4H), 2.79 (s, 4H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ: 147.6, 145.8, 135.6, 121.3, 109.1, 108.2, 100.9, 38.0 ppm. **IR:** 2924, 2857, 1841, 1742, 1606, 1499, 1484, 1437, 1402, 1357, 1263, 1240, 1186, 1140, 1123, 1093, 1035, 935, 923, 870, 857, 812, 754, 726, 622 cm^{-1}. **HRMS** (EI) for $C_{16}H_{14}O_4$: calculated 270.0892, found 270.0887.

Data of **39**:**^{1}H NMR** (600 MHz, $CDCl_3$) δ: 6.72 (d, J = 7.9 Hz, 1H), 6.67 (s, 1H), 6.64 – 6.60 (m, 1H), 5.92 (s, 2H), 4.13 (q, J = 7.1 Hz, 2H), 2.57 (t, J = 7.6 Hz, 2H), 2.30 (t, J = 7.5 Hz, 2H), 1.90 (p, J = 7.5 Hz, 2H), 1.25 (t, J = 6 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ: 173.7, 147.7, 145.9, 135.4, 121.4, 109.1, 108.3, 100.9, 60.4, 35.0, 33.7, 26.9, 14.4 ppm. **IR:** 2953, 2922, 2852, 2361, 2158, 1732, 1503, 1489, 1443, 1375, 1245, 1188, 1146, 1038, 938, 856, 808, 735, 599 cm^{-1}. **HRMS** (EI) for $C_{13}H_{16}O_4$: calculated 236.1049, found 236.1043.

6.4 UV/vis Studies

6.4.1 UV/vis studies about the EDA complex

The UV-Vis absorption spectra were measured in a 1 cm quartz cuvette and recorded on SHIMADZU UV-3600 UV-visible spectrophotometer. A bathochromic shift was observed for a mixture of NHPI ester **2a** and Hantzsch-ester (HE) in DMAc (0.1 M) (Figure S2-B, blue band), which was visibly yellow in color (Figure S2-A). This indicates the formation of an electron donor-acceptor (EDA) complex. Notably, The UV absorption was affected by the concentration of EDA complex, a dilute reaction mixture (0.02 M) exhibits a blue-shifted absorption band, indicating the inhibition of EDA complex formation (Figure S2-C, red band), a significant bathochromic shift was observed when the concentration increased to 0.2 M (Figure S2-C, blue band).

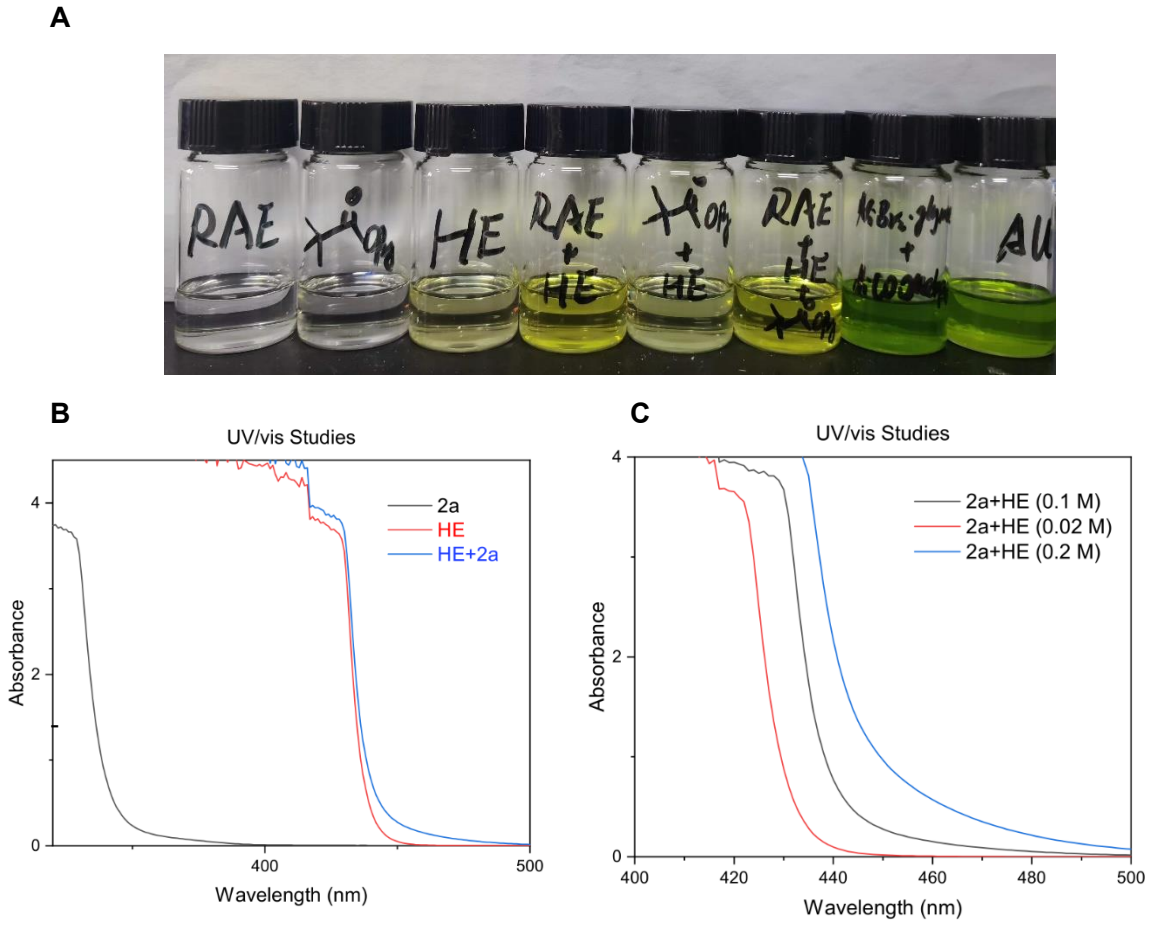


Figure S2. Spectra A shows the color of individual reaction component and a combination dissolved in DMAc. Spectra B was measured in DMAc with **2a** (0.1 M), HE (0.1 M) and a

mixture of them. Spectra C was measured in DMAc with different concentration of the EDA complex.

6.4.2 Determination of association constant (K_{EDA})

The association constant of the EDA complex formed between NHPI ester **2a** and Hantzsch ester (HE) was determined by UV-vis spectrum in DMAc employing the Benesi-Hildebrand method[10]. The absorbance of a constant concentration of **2a** (0.02 M) and an increasing concentration of HE (0.02-0.07 M) was recorded at 440 nm. All the absorption spectra were recorded in 1 cm path quartz cuvettes using a SHIMADZU UV-3600 UV-visible spectrophotometer. To determine the K_{EDA}, the reciprocal concentration of HE was plotted against the reciprocal absorbance of HE at 440 nm (Table S7 and Figure S4).

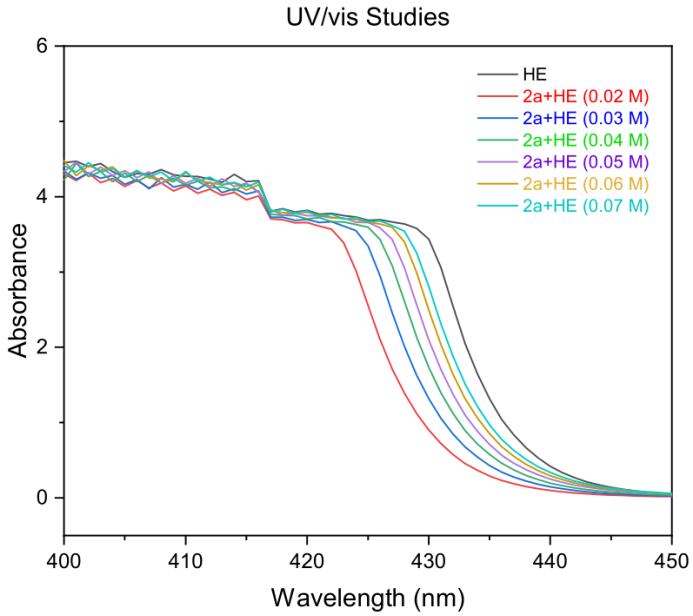


Figure S3. UV-vis absorption spectra of **2a** (0.02 M) in combination with increasing concentration of HE (0.02 M up to 0.07 M)

Table S7. Data obtained by UV/vis absorption spectra for EDA complex in DMAc

HE	ABS	1/HE	$1/(ABS_{EDA}-A_0)$
0.02	0.099	50	10.1
0.03	0.147	33.3	6.8
0.04	0.197	25	5.08
0.05	0.25	20	4
0.06	0.295	16.7	3.39
0.07	0.337	14.3	2.97

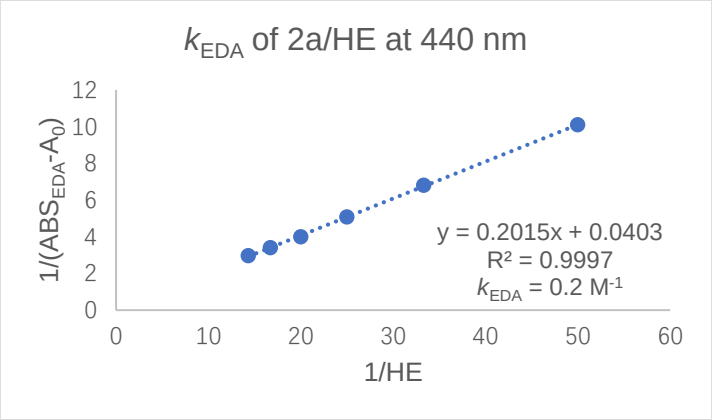


Figure S4. Benesi-Hildebrand[10] plot for the EDA complex generated in DMAc upon association of **2a** with HE

6.4.3 Job's method experiment

Job's method[11] was used to determine the stoichiometry of the EDA complex with varying ratios of NHPI ester **2a** and Hantzsch-ester (HE) in DMAc (0.10 M) at 450 nm. The absorbance was plotted against the molar fraction of HE. Maximum absorbance was detected at 50% molar fraction of HE, indicating a 1:1 stoichiometry of the EDA complex.

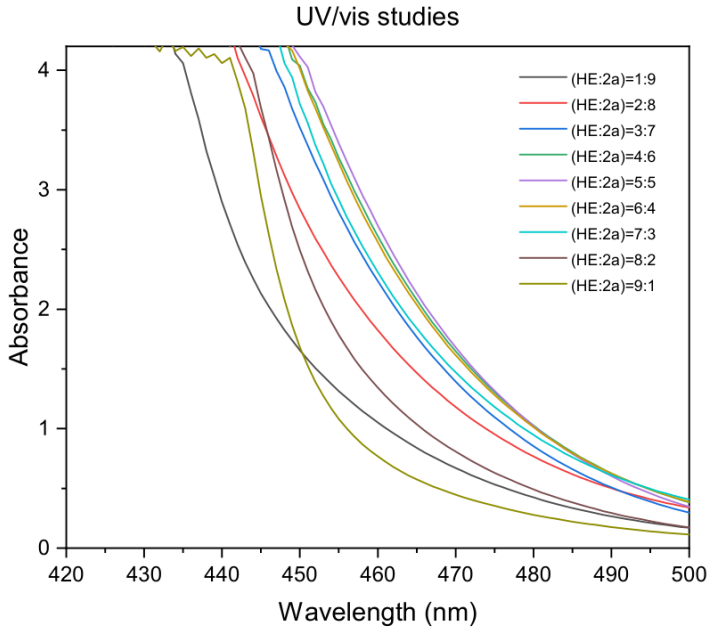


Figure S5. UV-vis absorption spectra of HE and **2a** with varying ratios

Table S8. Data obtained by UV/vis absorption spectra for EDA complex in DMAc

Molar fraction of HE	10	20	30	40	50	60	70	80	90
Absorbance	1.315	2.270	2.811	3.268	3.390	3.228	2.917	1.784	1.081

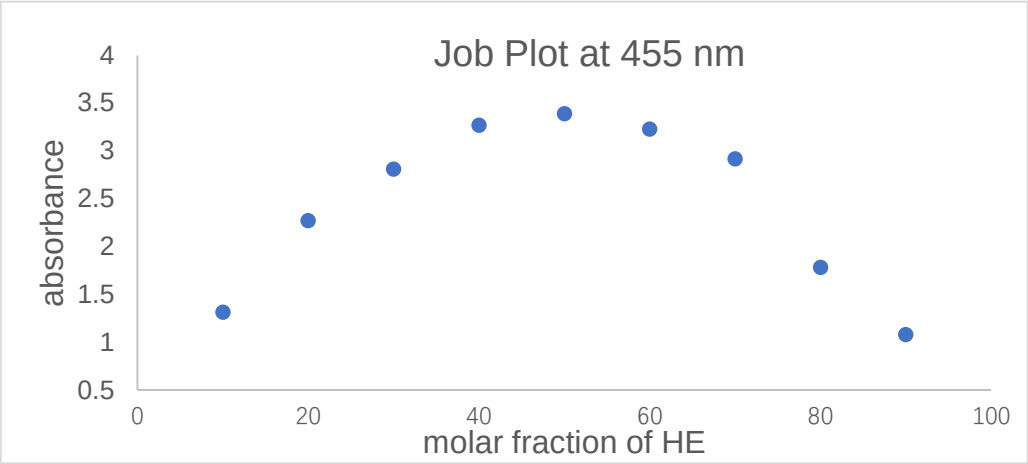


Figure S6. Job Plot at 450 nm

6.4.4 Fluorescence quenching (Stern-Volmer) studies

Emission intensities were recorded using Agilent Technologies of Cary Eclipse Fluorescence spectrophotometer. All Hantzsch-ester (HE) solutions were excited at 440 nm and the emission intensity was collected at 400-600 nm. In a typical experiment, to a 1.0 x 10^{-4} M solution of HE in DMAc was added the appropriate amount of quencher in a screw-top 1.0 cm quartz cuvette. the emission of the sample was collected. The linear slope suggests that nickel catalyst is the quencher of HE.

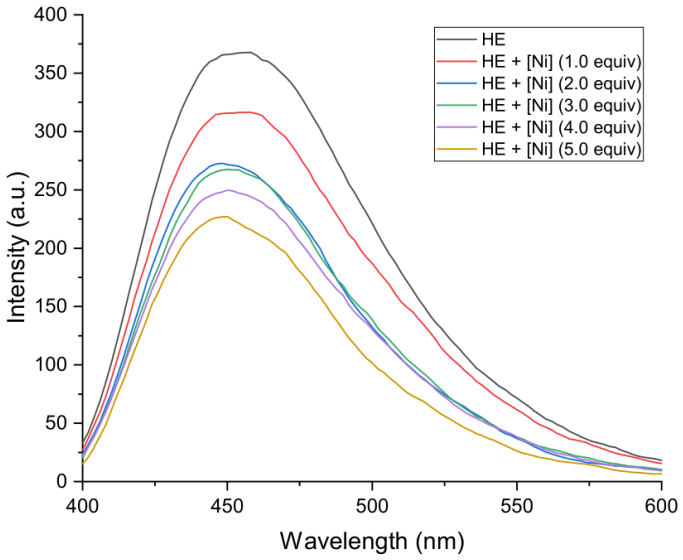


Figure S7. Quenching with variable amounts of $NiBr_2$•glyme

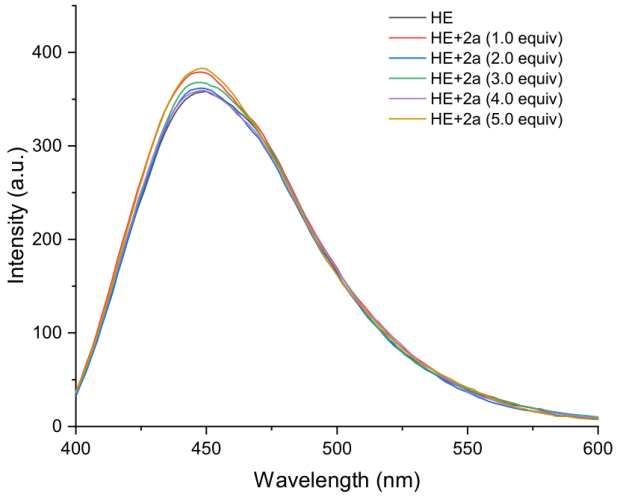


Figure S8. Quenching with variable amounts of NHPI ester **2a**

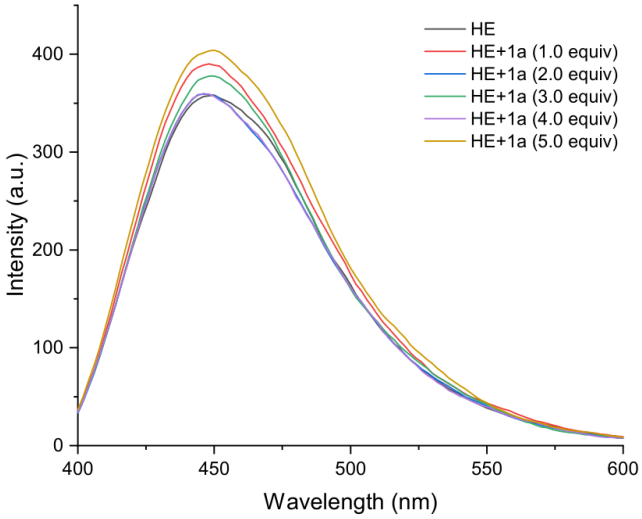


Figure S9. Quenching with variable amounts of 2-pyridyl ester **1a**

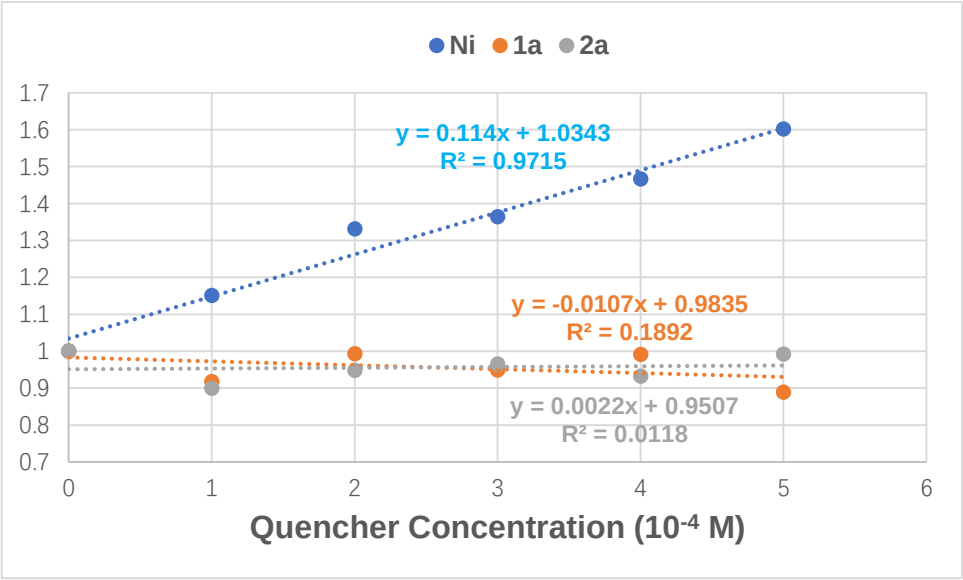
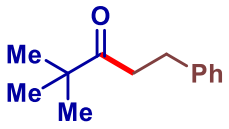


Figure S10. Stern-Volmer plot

7 Spectroscopic Data of the Products

4,4-Dimethyl-1-phenylpentan-3-one (3)

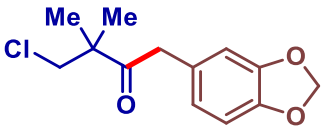


Chemical Formula: $C_{13}H_{18}O$
Molecular Weight: 190.2860

Prepared according to the general procedure using **1a** (43 mg, 0.24 mmol, 1.2 equiv), **2a** (59 mg, 0.20 mmol, 1.0 equiv), $NiBr_2$•glyme (6.1 mg, 20 μmol, 0.10 equiv), 4,4'-di(CO_2Me)bpy (5.4 mg, 20 μmol, 0.10 equiv), HE (76 mg, 0.30 mmol, 1.5 equiv) and DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE/EA = 30/1) to give the product **3** (30 mg, 78% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.29 – 7.26 (m, 2H), 7.22 – 7.13 (m, 3H), 2.89 – 2.85 (m, 2H), 2.83 – 2.75 (m, 2H), 1.10 (s, 9H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) *δ*: 215.0, 141.7, 128.6, 128.5, 126.1, 44.2, 38.6, 30.2, 26.4 ppm. **IR:** 2974, 1718, 1632, 1607, 1512, 1460, 1387, 1359, 1173, 987, 836, 749, 620 cm^{-1}. **HRMS** (ESI) for $C_{13}H_{19}O^+$ [$(M+H)^+$]: calculated 191.1430, found 191.1435.

1-(Benzo[*d*][1,3]dioxol-5-yl)-4-chloro-3,3-dimethylbutan-2-one (4)



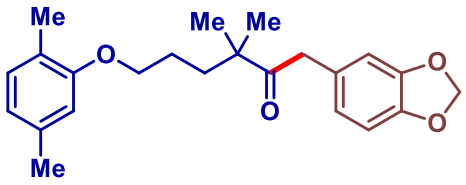
Chemical Formula: $C_{13}H_{15}ClO_3$
Molecular Weight: 254.7100

Prepared according to the general procedure using **1b** (51 mg, 0.24 mmol, 1.2 equiv), **2b** (65 mg, 0.20 mmol, 1.0 equiv), $NiBr_2$•glyme (6.1 mg, 20 μmol, 0.10 equiv), 4,4'-di(CO_2Me)bpy (5.4 mg, 20 μmol, 0.10 equiv), HE (76 mg, 0.30 mmol, 1.5 equiv) and DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE/EA = 30/1 to PE/DCM = 1/1) to give the product **4** (18 mg, 35% yield) as a yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) *δ*: 6.75 (d, *J* = 7.9 Hz, 1H), 6.66 (d, *J* = 1.7 Hz, 1H), 6.61 – 6.59 (m, 1H), 5.94 (s, 2H), 3.76 (s, 2H), 3.65 (s, 2H), 1.30 (s, 6H) ppm. **^{13}C NMR** (101 MHz,

$CDCl_3$) δ: 210.0, 147.9, 146.7, 127.7, 122.8, 110.2, 108.40, 101.1, 52.0, 49.6, 44.1, 23.1 ppm. **IR:** 2923, 1712, 1503, 1490, 1444, 1246, 1038, 927, 811, 785, 734 cm^{-1}. **HRMS** (ESI) for $C_{13}H_{16}ClO_3^+$ [$(M+H)^+$]: calculated 255.0782, found 255.0777.

1-(Benzo[*d*][1,3]dioxol-5-yl)-6-(2,5-dimethylphenoxy)-3,3-dimethylhexan-2-one (5)

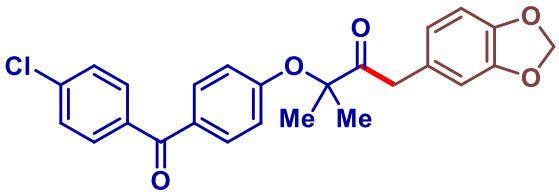


Chemical Formula: $C_{23}H_{28}O_4$
Molecular Weight: 368.4730

Prepared according to the general procedure using **1c** (65 mg, 0.24 mmol, 1.2 equiv), **2b** (65 mg, 0.20 mmol, 1.0 equiv), $NiBr_2$•glyme (6.1 mg, 20 μmol, 0.10 equiv), 4,4'-di(CO_2Me)bpy (5.4 mg, 20 μmol, 0.10 equiv), HE (76 mg, 0.30 mmol, 1.5 equiv) and DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE/EA = 10/1) to give the product **5** (40 mg, 55% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.00 (d, J = 7.5 Hz, 1H), 6.73 (d, J = 7.9 Hz, 1H), 6.67 – 6.65 (m, 2H), 6.60 – 6.57 (m, 2H), 5.92 (s, 2H), 3.91 (t, J = 5.9 Hz, 2H), 3.71 (s, 2H), 2.31 (s, 3H), 2.18 (s, 3H), 1.82 – 1.77 (m, 2H), 1.69 – 1.62 (m, 2H), 1.21 (s, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 212.7, 156.9, 147.7, 146.5, 136.6, 130.4, 128.4, 123.6, 122.7, 120.9, 112.0, 110.2, 108.3, 101.0, 67.8, 47.9, 43.1, 36.5, 25.1, 24.5, 21.5, 15.9 ppm. **IR:** 2953, 2922, 1707, 1503, 1489, 1443, 1245, 1156, 1129, 1036, 928, 805, 785 cm^{-1}. **HRMS** (ESI) for $C_{23}H_{29}O_4^+$ [$(M+H)^+$]: calculated 369.2060, found 369.2055.

1-(Benzo[*d*][1,3]dioxol-5-yl)-3-(4-(4-chlorobenzoyl)phenoxy)-3-methylbutan-2-one (6)



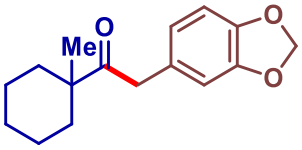
Chemical Formula: $C_{25}H_{21}ClO_5$
Molecular Weight: 436.8880

Prepared according to the general procedure using **1d** (95 mg, 0.24 mmol, 1.2 equiv), **2b**

(65 mg, 0.20 mmol, 1.0 equiv), $NiBr_2$•glyme (6.1 mg, 20 μmol, 0.10 equiv), 4,4'-di(CO_2Me)bpy (5.4 mg, 20 μmol, 0.10 equiv), HE (76 mg, 0.30 mmol, 1.5 equiv) and DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE/EA = 10/1) to give the product **6** (52 mg, 60% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.75 – 7.70 (m, 4H), 7.47 – 7.44 (m, 2H), 6.86 – 6.82 (m, 2H), 6.71 (d, *J* = 7.9 Hz, 1H), 6.60 (d, *J* = 1.8 Hz, 1H), 6.52 (dd, *J* = 7.9, 1.7 Hz, 1H), 5.92 (s, 2H), 3.83 (s, 2H), 1.59 (s, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) *δ*: 210.6, 194.2, 159.5, 147.8, 146.7, 138.6, 136.3, 132.3, 131.3, 130.9, 128.7, 127.4, 122.9, 117.5, 110.2, 108.3, 101.1, 85.1, 42.4, 24.4 ppm. **IR:** 2924, 1720, 1652, 1596, 1502, 1488, 1443, 1241, 1165, 1144, 1088, 1037, 925, 852, 762, 735 cm^{-1}. **HRMS** (ESI) for $C_{25}H_{22}ClO_5^+$ [$(M+H)^+$]: calculated 437.1150, found 437.1146. **Melting point:** 96.5 – 97.6 °C.

2-(Benzo[*d*][1,3]dioxol-5-yl)-1-(1-methylcyclohexyl)ethan-1-one (7)

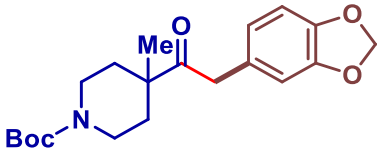


Chemical Formula: $C_{16}H_{20}O_3$
Molecular Weight: 260.3330

Prepared according to the general procedure using **1e** (53 mg, 0.24 mmol, 1.2 equiv), **2b** (65 mg, 0.20 mmol, 1.0 equiv), $NiBr_2$•glyme (6.1 mg, 20 μmol, 0.10 equiv), 4,4'-di(CO_2Me)bpy (5.4 mg, 20 μmol, 0.10 equiv), HE (76 mg, 0.30 mmol, 1.5 equiv) and DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE/EA = 30/1) to give the product **7** (28 mg, 53% yield) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) *δ*: 6.74 (d, *J* = 7.9 Hz, 1H), 6.68 (d, *J* = 1.9 Hz, 1H), 6.60 (dd, *J* = 7.9, 1.8 Hz, 1H), 5.93 (s, 2H), 3.69 (s, 2H), 2.00 – 1.97 (m, 2H), 1.56 – 1.54 (m, 2H), 1.45 – 1.42 (m, 1H), 1.37 – 1.31 (m, 5H), 1.14 (s, 3H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) *δ*: 213.1, 147.8, 146.5, 128.8, 122.8, 110.3, 108.3, 101.1, 48.7, 42.9, 34.8, 26.0, 24.8, 23.0 ppm. **IR:** 2927, 2854, 1705, 1503, 1489, 1443, 1254, 1187, 1038, 1015, 926, 782, 745 cm^{-1}. **HRMS** (ESI) for $C_{16}H_{21}O_3^+$ [$(M+H)^+$]: calculated 261.1485, found 261.1480.

tert-Butyl 4-(2-(benzo[*d*][1,3]dioxol-5-yl)acetyl)-4-methylpiperidine-1-carboxylate (8)

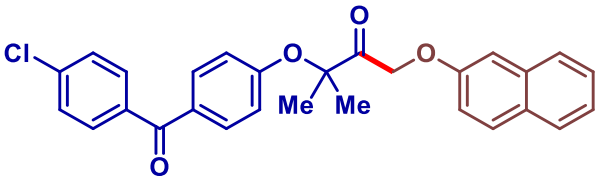


Chemical Formula: $C_{20}H_{27}NO_5$
Molecular Weight: 361.4380

Prepared according to the general procedure using **1f** (77 mg, 0.24 mmol, 1.2 equiv), **2b** (65 mg, 0.20 mmol, 1.0 equiv), $NiBr_2$•glyme (6.1 mg, 20 μmol, 0.10 equiv), 4,4'-di(CO_2Me)bpy (5.4 mg, 20 μmol, 0.10 equiv), HE (76 mg, 0.30 mmol, 1.5 equiv) and DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE/EA = 20/1) to give the product **8** (28 mg, 38% yield) as a yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) *δ*: 6.75 (d, *J* = 7.9 Hz, 1H), 6.67 (s, 1H), 6.60 (d, *J* = 7.9 Hz, 1H), 5.94 (s, 2H), 3.68 (s, 2H), 3.57 (s, 2H), 3.12 (s, 2H), 2.07 – 1.99 (m, 2H), 1.50 – 1.42 (m, 2H), 1.44 (s, 9H), 1.21 (s, 3H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) *δ*: 211.6, 154.9, 147.9, 146.7, 128.0, 122.7, 110.1, 108.4, 101.2, 79.7, 47.2, 43.2, 33.8, 28.6, 24.0 ppm. **IR:** 2927, 1686, 1503, 1490, 1443, 1423, 1365, 1246, 1158, 1039, 969, 928, 864, 784, 735 cm^{-1}. **HRMS** (ESI) for $C_{20}H_{27}NO_5Na^+$ [$(M+Na)^+$]: calculated 384.1781, found 384.1767.

3-(4-(4-Chlorobenzoyl)phenoxy)-3-methyl-1-(naphthalen-2-yloxy)butan-2-one (9)



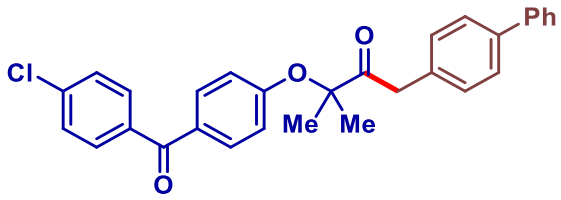
Chemical Formula: $C_{28}H_{23}ClO_4$
Molecular Weight: 458.9380

Prepared according to the general procedure using **1d** (95 mg, 0.24 mmol, 1.2 equiv), **2c** (69 mg, 0.20 mmol, 1.0 equiv), $NiBr_2$•glyme (6.1 mg, 20 μmol, 0.10 equiv), 4,4'-di(CO_2Me)bpy (5.4 mg, 20 μmol, 0.10 equiv), HE (76 mg, 0.30 mmol, 1.5 equiv) and DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE/EA = 10/1) to give the product **9** (56 mg, 61% yield) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.70 – 7.76 (m, 4H), 7.73 – 7.70 (m, 2H), 7.65 (d, *J* = 7.7 Hz, 1H), 7.46 – 7.40 (m, 3H), 7.37 – 7.33 (m, 1H), 7.25 – 7.23 (m, 1H), 7.02 (d, *J* = 2.6 Hz, 1H),

7.00 – 6.97 (m, 2H), 5.21 (s, 2H), 1.68 (s, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 206.5, 194.2, 158.7, 156.0, 138.8, 136.1, 134.3, 132.4, 131.8, 131.3, 129.9, 129.5, 128.8, 127.8, 126.9, 126.7, 124.3, 118.9, 118.8, 107.4, 85.2, 69.2, 24.6 ppm. **IR:** 2926, 1739, 1654, 1629, 1597, 1505, 1468, 1273, 1247, 1217, 1170, 1148, 1089, 1032, 926, 852, 835, 762, 748 cm^{-1}. **HRMS** (ESI) for $C_{28}H_{24}ClO_4^+$ [$(M+H)^+$]: calculated 459.1358, found 459.1351.

1-([1,1'-Biphenyl]-4-yl)-3-(4-(4-chlorobenzoyl)phenoxy)-3-methylbutan-2-one (10)

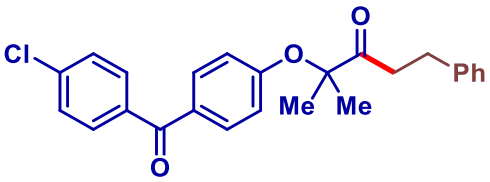


Chemical Formula: $C_{30}H_{25}ClO_3$
Molecular Weight: 468.9770

Prepared according to the general procedure using **1d** (95 mg, 0.24 mmol, 1.2 equiv), **2d** (72 mg, 0.20 mmol, 1.0 equiv), $NiBr_2$•glyme (6.1 mg, 20 μmol, 0.10 equiv), 4,4'-di(CO_2Me)bpy (5.4 mg, 20 μmol, 0.10 equiv), HE (76 mg, 0.30 mmol, 1.5 equiv) and DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE/EA = 10/1) to give the product **10** (60 mg, 64% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.76 – 7.72 (m, 2H), 7.71 – 7.68 (m, 2H), 7.57 – 7.55 (m, 2H), 7.52 – 7.49 (m, 2H), 7.45 – 7.40 (m, 4H), 7.36 – 7.32 (m, 1H), 7.19 – 7.16 (m, 2H), 6.88 – 6.84 (m, 2H), 3.97 (s, 2H), 1.62 (s, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 210.5, 194.2, 159.5, 140.8, 140.0, 138.6, 136.3, 132.9, 132.4, 131.3, 130.9, 130.3, 128.9, 128.7, 127.4, 127.3, 127.1, 117.6, 85.2, 42.4, 24.4 ppm. **IR:** 2924, 1719, 1652, 1596, 1504, 1486, 1396, 1381, 1301, 1283, 1242, 1166, 1144, 1088, 1049, 955, 926, 852, 754, 739, 697 cm^{-1}. **HRMS** (ESI) for $C_{30}H_{26}ClO_3^+$ [$(M+H)^+$]: calculated 469.1565, found 469.1556. **Melting point:** 135.2 – 133.5 °C.

4-(4-(4-Chlorobenzoyl)phenoxy)-4-methyl-1-phenylpentan-3-one (11)

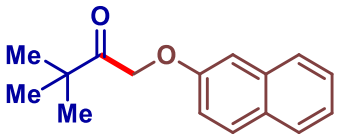


Chemical Formula: $C_{25}H_{23}ClO_3$
Molecular Weight: 406.9060

Prepared according to the general procedure using **1d** (95 mg, 0.24 mmol, 1.2 equiv), **2a** (59 mg, 0.20 mmol, 1.0 equiv), $NiBr_2$•glyme (6.1 mg, 20 μmol, 0.10 equiv), 4,4'-di(CO_2Me)bpy (5.4 mg, 20 μmol, 0.10 equiv), HE (76 mg, 0.30 mmol, 1.5 equiv) and DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE/EA = 10/1) to give the product **11** (55 mg, 68% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.72 – 7.66 (m, 4H), 7.47 – 7.44 (m, 2H), 7.26 – 7.22 (m, 2H), 7.18 – 7.15 (m, 1H), 7.14 – 7.11 (m, 2H), 6.75 – 6.71 (m, 2H), 2.97 – 2.88 (m, 4H), 1.50 (s, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) *δ*: 212.1, 194.2, 159.5, 140.9, 138.6, 136.4, 132.3, 131.3, 130.7, 128.7, 128.6 (2C), 126.3, 117.4, 84.9, 38.1, 29.8, 24.2 ppm. **IR:** 2988, 2929, 1715, 1653, 1596, 1503, 1301, 1283, 1273, 1243, 1163, 1144, 1088, 1014, 952, 925, 852, 837, 762, 698, 678 cm^{-1}. **HRMS** (ESI) for $C_{25}H_{24}ClO_3^+$ [$(M+H)^+$]: calculated 407.1408, found 407.1401.

3,3-Dimethyl-1-(naphthalen-2-yloxy)butan-2-one (12)



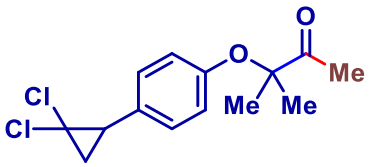
Chemical Formula: $C_{16}H_{18}O_2$
Molecular Weight: 242.3180

Prepared according to the general procedure using **1a** (43 mg, 0.24 mmol, 1.2 equiv), **2c** (69 mg, 0.20 mmol, 1.0 equiv), $NiBr_2$•glyme (6.1 mg, 20 μmol, 0.10 equiv), 4,4'-di(CO_2Me)bpy (5.4 mg, 20 μmol, 0.10 equiv), HE (76 mg, 0.30 mmol, 1.5 equiv) and DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE/EA = 30/1 to 10/1) to give the product **12** (30 mg, 61% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.78 – 7.75 (m, 2H), 7.70 (d, *J* = 8.3 Hz, 1H), 7.45 – 7.41 (m,

1H), 7.37 – 7.32 (m, 1H), 7.24 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.03 (d, *J* = 2.6 Hz, 1H), 4.97 (s, 2H), 1.29 (s, 9H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) *δ*: 209.3, 156.1, 134.3, 129.8, 129.4, 127.8, 126.8, 126.5, 124.1, 118.9, 107.2, 69.0, 43.4, 26.5 ppm. **IR:** 2965, 1721, 1629, 1600, 1509, 1468, 1389, 1366, 1253, 1215, 1179, 1045, 990, 832, 744, 623 cm^{-1}. **HRMS** (ESI) for $C_{16}H_{18}O_2Na^+$ [(M+Na)$^+$]: calculated 265.1199, found 265.1191. **Melting point:** 97.8 – 98.7 °C.

3-(4-(2,2-Dichlorocyclopropyl)phenoxy)-3-methylbutan-2-one (13)

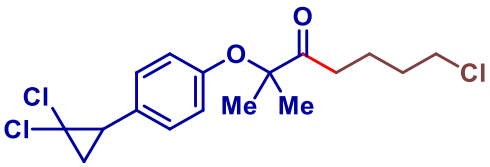


Chemical Formula: $C_{14}H_{16}Cl_2O_2$
Molecular Weight: 287.1800

Prepared according to the general procedure using **1g** (88 mg, 0.24 mmol, 1.2 equiv), **2e** (41 mg, 0.20 mmol, 1.0 equiv), $NiBr_2$•glyme (6.1 mg, 20 μmol, 0.10 equiv), 4,4'-di(CO_2Me)bpy (5.4 mg, 20 μmol, 0.10 equiv), HE (76 mg, 0.30 mmol, 1.5 equiv) and DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE/EA = 30/1) to give the product **13** (33 mg, 57% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.13 – 7.10 (m, 2H), 6.77 – 6.73 (m, 2H), 2.85 – 2.81 (m, 1H), 2.26 (s, 3H), 1.97 – 1.92 (m, 1H), 1.81 – 1.76 (m, 1H), 1.48 (s, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) *δ*: 212.2, 154.9, 130.0, 128.3, 118.3, 84.3, 60.9, 34.9, 25.6, 24.5, 24.0 ppm. **IR:** 2988, 1716, 1509, 1240, 1160, 1125, 954, 833, 761 cm^{-1}. **HRMS** (ESI) for $C_{14}H_{17}Cl_2O_2^+$ [(M+H)$^+$]: calculated 287.0600, found 287.0602.

7-Chloro-2-(4-(2,2-dichlorocyclopropyl)phenoxy)-2-methylheptan-3-one (14)

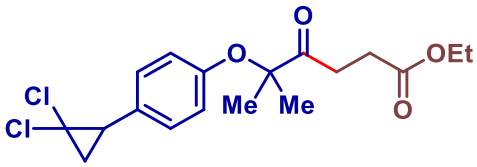


Chemical Formula: $C_{17}H_{21}Cl_3O_2$
Molecular Weight: 363.7030

Prepared according to the general procedure using **1g** (88 mg, 0.24 mmol, 1.2 equiv), **2f** (56 mg, 0.20 mmol, 1.0 equiv), $NiBr_2$•glyme (6.1 mg, 20 μmol, 0.10 equiv), 4,4'-di(CO_2Me)bpy (5.4 mg, 20 μmol, 0.10 equiv), HE (76 mg, 0.30 mmol, 1.5 equiv) and DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE/EA = 30/1) to give the product **14** (48 mg, 66% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.14 – 7.10 (m, 2H), 6.75 – 6.72 (m, 2H), 3.50 – 3.47 (m, 2H), 2.83 (dd, *J* = 10.7, 8.3 Hz, 1H), 2.72 – 2.68 (m, 2H), 1.95 (dd, *J* = 10.7, 7.4 Hz, 1H), 1.81 – 1.76 (m, 1H), 1.75 – 1.70 (m, 4H), 1.48 (s, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) *δ*: 213.4, 154.7, 130.0, 128.5, 118.6, 84.4, 60.9, 44.7, 35.2, 34.9, 32.0, 26.0, 24.3, 21.0 ppm. **IR:** 2936, 1714, 1610, 1509, 1380, 1294, 1239, 1154, 1114, 1049, 956, 833, 759, 730, 650, 577 cm^{-1}. **HRMS** (ESI) for $C_{17}H_{22}Cl_3O_2^+$ [$(M+H)^+$]: calculated 363.0680, found 363.0676.

Ethyl 5-(4-(2,2-dichlorocyclopropyl)phenoxy)-5-methyl-4-oxohexanoate (15)

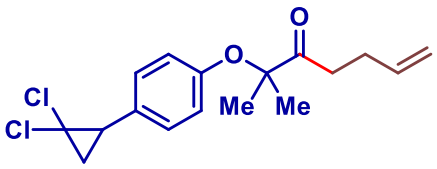


Chemical Formula: $C_{18}H_{22}Cl_2O_4$
Molecular Weight: 373.2700

Prepared according to the general procedure using **1g** (88 mg, 0.24 mmol, 1.2 equiv), **2g** (58 mg, 0.20 mmol, 1.0 equiv), $NiBr_2$•glyme (6.1 mg, 20 μmol, 0.10 equiv), 4,4'-di(CO_2Me)bpy (5.4 mg, 20 μmol, 0.10 equiv), HE (76 mg, 0.30 mmol, 1.5 equiv) and DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE/EA = 10/1) to give the product **15** (39 mg, 53% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.15 – 7.11 (m, 2H), 6.79 – 6.76 (m, 2H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.02 (t, *J* = 6.5 Hz, 2H), 2.83 (dd, *J* = 10.7, 8.3 Hz, 1H), 2.57 (t, *J* = 6.5 Hz, 2H), 1.97 – 1.93 (m, 1H), 1.80 – 1.76 (m, 1H), 1.50 (s, 6H), 1.26 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) *δ*: 212.2, 172.9, 154.6, 130.0, 128.6, 119.0, 84.5, 60.8, 34.9, 31.7, 28.0, 26.0, 24.4 (2C), 14.3 ppm. **IR:** 2983, 2930, 1716, 1610, 1509, 1376, 1227, 1148, 1114, 1079, 1016, 956, 865, 834, 761, 575 cm^{-1}. **HRMS** (ESI) for $C_{18}H_{23}Cl_2O_4^+$ [$(M+H)^+$]: calculated 373.0968, found 373.0966.

2-(4-(2,2-Dichlorocyclopropyl)phenoxy)-2-methylhept-6-en-3-one (16)

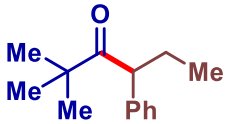


Chemical Formula: $C_{17}H_{20}Cl_2O_2$
Molecular Weight: 327.2450

Prepared according to the general procedure using **1g** (88 mg, 0.24 mmol, 1.2 equiv), **2h** (49 mg, 0.20 mmol, 1.0 equiv), $NiBr_2$•glyme (6.1 mg, 20 μmol, 0.10 equiv), 4,4'-di(CO_2Me)bpy (5.4 mg, 20 μmol, 0.10 equiv), HE (76 mg, 0.30 mmol, 1.5 equiv) and DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE/EA = 30/1) to give the product **16** (38 mg, 59% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.16 – 7.10 (m, 2H), 6.76 – 6.72 (m, 2H), 5.81 – 5.71 (m, 1H), 5.04 – 4.93 (m, 2H), 2.86 – 2.81 (m, 1H), 2.77 (t, *J* = 7.4 Hz, 2H), 2.35 – 2.29 (m, 2H), 1.97 – 1.92 (m, 1H), 1.80 – 1.76 (m, 1H), 1.48 (s, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) *δ*: 213.1, 154.8, 137.3, 129.9, 128.4, 118.7, 115.5, 84.4, 60.9, 35.5, 34.9, 27.7, 26.0, 24.3 (2C) ppm. **IR:** 2981, 2930, 1715, 1610, 1509, 1240, 1153, 1114, 1054, 956, 915, 833, 760 cm^{-1}. **HRMS** (ESI) for $C_{17}H_{21}Cl_2O_2^+$ [$(M+H)^+$]: calculated 327.0913, found 327.0905.

2,2-Dimethyl-4-phenylhexan-3-one (17)



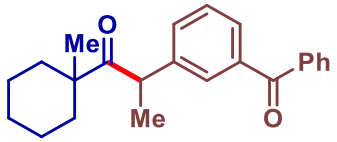
Chemical Formula: $C_{14}H_{20}O$
Molecular Weight: 204.3130

Prepared according to the general procedure using **1a** (43 mg, 0.24 mmol, 1.2 equiv), **2i** (62 mg, 0.20 mmol, 1.0 equiv), $NiBr_2$•glyme (6.1 mg, 20 μmol, 0.10 equiv), 4,4'-di(CO_2Me)bpy (5.4 mg, 20 μmol, 0.10 equiv), HE (76 mg, 0.30 mmol, 1.5 equiv) and DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE/EA = 30/1) to give the product **17** (25 mg, 61% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.30 – 7.24 (m, 4H), 7.22 – 7.18 (m, 1H), 3.98 (t, *J* = 7.4 Hz, 1H), 2.02 – 1.91 (m, 1H), 1.75 – 1.64 (m, 1H), 1.08 (s, 9H), 0.80 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) *δ*: 215.7, 140.0, 128.7, 128.4, 126.9, 54.6, 45.3, 28.8, 26.6, 12.6 ppm. **IR:** 2954, 2922, 2852, 1740, 1659, 1632, 1459, 1377, 1189, 1082, 970, 848, 766, 668 cm^{-1}. **HRMS** (ESI) for $C_{14}H_{21}O^+$ [$(M+H)^+$]: calculated 205.1587, found 205.1585.

2-(3-Benzoylphenyl)-1-(1-methylcyclohexyl)propan-1-one (18)

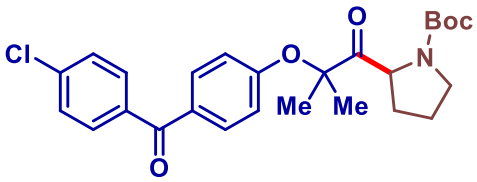


Chemical Formula: $C_{23}H_{26}O_2$
Molecular Weight: 334.4590

Prepared according to the general procedure using **1e** (53 mg, 0.24 mmol, 1.2 equiv), **2j** (80 mg, 0.20 mmol, 1.0 equiv), $NiBr_2$•glyme (6.1 mg, 20 μmol, 0.10 equiv), 4,4'-di(CO_2Me)bpy (5.4 mg, 20 μmol, 0.10 equiv), HE (76 mg, 0.30 mmol, 1.5 equiv) and DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE/EA = 10/1) to give the product **18** (24 mg, 36% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.80 – 7.77 (m, 2H), 7.75 – 7.74 (m, 1H), 7.66 – 7.63 (m, 1H), 7.63 – 7.57 (m, 2H), 7.51 – 7.47 (m, 2H), 7.42 (t, *J* = 7.7 Hz, 1H), 4.35 (q, *J* = 6.9 Hz, 1H), 2.02 – 1.82 (m, 2H), 1.56 – 1.49 (m, 2H), 1.41 (d, *J* = 6.9 Hz, 3H), 1.38 – 1.25 (m, 6H), 1.08 (s, 3H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) *δ*: 215.8, 196.8, 142.0, 138.0, 137.7, 132.7, 131.9, 130.2, 129.8, 128.7, 128.4, 49.4, 45.9, 34.6, 34.5, 26.0, 22.9, 22.8, 21.6 ppm. **IR:** 2926, 2853, 1700, 1659, 1596, 1579, 1447, 1373, 1317, 1280, 1178, 1075, 998, 950, 820, 785, 718, 702, 644, 603 cm^{-1}. **HRMS** (ESI) for $C_{23}H_{27}O_2^+$ [$(M+H)^+$]: calculated 335.2006, found 335.2002.

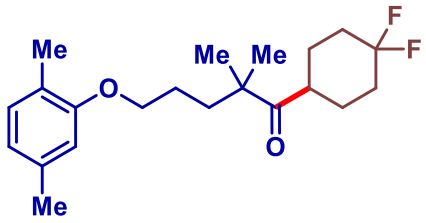
***tert*-Butyl-2-(2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoyl)pyrrolidine-1-carboxylate (19)**



Chemical Formula: $C_{26}H_{30}ClNO_5$
Molecular Weight: 471.9780

Prepared according to the general procedure using **1d** (95 mg, 0.24 mmol, 1.2 equiv), **2k** (72 mg, 0.20 mmol, 1.0 equiv), $NiBr_2$•glyme (6.1 mg, 20 μmol, 0.10 equiv), 4,4'-di(CO_2Me)bpy (5.4 mg, 20 μmol, 0.10 equiv), HE (76 mg, 0.30 mmol, 1.5 equiv) and DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE/EA = 10/1) to give the product **19** (43 mg, 46% yield, the ratio of two rotamers is 1.5:1) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) for rotamers (* minor rotamer) *δ*: 7.80 – 7.70 (m, 4H), 7.48 – 7.44 (m, 2H), 7.08 – 7.05 (m, 2H), (5.11*) 5.06 (dd, *J* = 12.0, 6.0 Hz, 1H), 3.61 – 3.42 (m, 2H), 2.43 – 1.91 (m, 2H), 1.92 – 1.77 (m, 2H), 1.64 (1.58*) (d, *J* = 6.0 Hz, 6H), 1.47 (1.45*) (s, 9H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) for rotamers (* minor rotamer) *δ*: 210.4 (209.7*), 194.5 (194.4*), 159.1 (158.5*), 154.38 (154.0*), (138.9*) 138.7, 136.4 (136.2*), 132.9 (132.4*), (132.0*) 131.9, (131.6*) 131.4, (128.8*) 128.7, (121.7*) 120.8, (86.6*) 86.2, (80.2*) 79.7, (61.7*) 60.7, 47.1 (46.9*), (30.6*) 30.1, (28.7*) 28.6, 25.2 (25.1*), (24.4*) 24.4 ppm.**IR:** 2926, 2853, 2369, 2164, 2032, 1978, 1718, 1597, 1508, 1457, 1395, 1246, 1162, 927, 764, 645 cm^{-1}. **HRMS** (ESI) for $C_{26}H_{30}ClNO_5Na^+$ [$(M+Na)^+$]: calculated 494.1705, found 494.1692.

1-(4,4-Difluorocyclohexyl)-5-(2,5-dimethylphenoxy)-2,2-dimethylpentan-1-one (20)



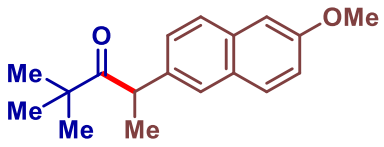
Chemical Formula: $C_{21}H_{30}F_2O_2$
Molecular Weight: 352.4658

Prepared according to the general procedure using **1c** (66 mg, 0.24 mmol, 1.2 equiv), **2l** (62 mg, 0.20 mmol, 1.0 equiv), $NiBr_2$•glyme (6.1 mg, 20 μmol, 0.10 equiv), 4,4'-di(CO_2Me)bpy (5.4 mg, 20 μmol, 0.10 equiv), HE (76 mg, 0.30 mmol, 1.5 equiv) and DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE/EA = 30/1) to give the product **20** (25 mg, 35% yield) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) *δ*: 7.00 (d, *J* = 7.4 Hz, 1H), 6.66 (d, *J* = 7.5 Hz, 1H), 6.60 (s, 1H), 3.92 (t, *J* = 5.9 Hz, 2H), 2.93 – 2.87 (m, 1H), 2.30 (s, 3H), 2.16 (s, 3H), 1.82 – 1.76

(m, 2H), 1.75 – 1.72 (m, 4H), 1.72 – 1.65 (m, 4H), 1.64 – 1.62 (m, 2H), 1.18 (s, 6H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) *δ*: 217.1, 156.9, 136.7, 130.5, 123.5, 122.6 (t, *J* = 249.2 Hz), 121.0, 112.0, 67.9, 48.3, 42.4, 36.0, 33.1 (t, *J* = 24.2 Hz), 26.6, 26.5, 25.2, 24.0, 21.5, 16.0 ppm. **^{19}F NMR** (565 MHz, $CDCl_3$) δ: -91.65 (d, *J* = 231.7 Hz, 1F), -101.64 (d, *J* = 237.3 Hz, 1F) ppm. **IR:** 2922, 2852, 2953, 1735, 1654, 1507, 1458, 1376, 1188, 1129, 969, 856, 720, 668 cm^{-1}. **HRMS** (ESI) for $C_{21}H_{31}F_2O_2^+$ [(M+H)$^+$]: calculated 353.2287, found 353.2279.

4-(6-Methoxynaphthalen-2-yl)-2,2-dimethylpentan-3-one (21)

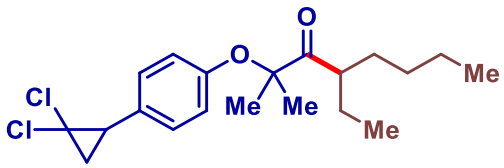


Chemical Formula: $C_{18}H_{22}O_2$
Molecular Weight: 270.3720

Prepared according to the general procedure using **1a** (43 mg, 0.24 mmol, 1.2 equiv), **2m** (69 mg, 0.20 mmol, 1.0 equiv), $NiBr_2$•glyme (6.1 mg, 20 μmol, 0.10 equiv), 4,4'-di(CO_2Me)bpy (5.4 mg, 20 μmol, 0.10 equiv), HE (76 mg, 0.30 mmol, 1.5 equiv) and DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE/EA = 30/1) to give the product **21** (36 mg, 66% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.68 (dd, *J* = 3.4, 8.8 Hz, 2H), 7.63 (d, *J* = 1.8 Hz, 1H), 7.40 (dd, *J* = 1.9, 8.4 Hz, 1H), 7.13 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.09 (d, *J* = 2.6 Hz, 1H), 4.38 (q, *J* = 6.9 Hz, 1H), 3.90 (s, 3H), 1.43 (d, *J* = 6.9 Hz, 3H), 1.12 (s, 9H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) *δ*: 216.4, 157.7, 136.7, 133.6, 129.4, 129.1, 127.3, 126.8, 126.3, 119.0, 105.6, 55.4, 46.4, 45.3, 26.8, 21.3 ppm. **IR:** 2954, 2924, 2868, 1702, 1633, 1605, 1505, 1478, 1463, 1392, 1366, 1264, 1227, 1213, 1172, 1034, 976, 922, 852, 811, 751 cm^{-1}. **HRMS** (ESI) for $C_{18}H_{23}O_2^+$ [(M+H)$^+$]: calculated 271.1693, found 271.1690. **Melting point:** 66.9 – 68.7 °C.

2-(4-(2,2-Dichlorocyclopropyl)phenoxy)-4-ethyl-2-methyloctan-3-one (22)

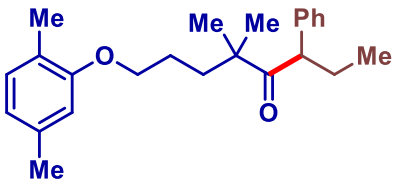


Chemical Formula: $C_{20}H_{28}Cl_2O_2$
Molecular Weight: 371.3420

Prepared according to the general procedure using **1g** (88 mg, 0.24 mmol, 1.2 equiv), **2n** (58 mg, 0.20 mmol, 1.0 equiv), $NiBr_2$•glyme (6.1 mg, 20 μmol, 0.10 equiv), 4,4'-di(CO_2Me)bpy (5.4 mg, 20 μmol, 0.10 equiv), HE (76 mg, 0.30 mmol, 1.5 equiv) and DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE/EA = 30/1) to give the product **22** (31 mg, 41% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.21 – 7.07 (m, 2H), 7.01 – 6.83 (m, 2H), 3.35 – 3.20 (m, 1H), 2.86 (dd, *J* = 10.7, 8.3 Hz, 1H), 1.96 (dd, *J* = 10.7, 7.4 Hz, 1H), 1.81 (dd, *J* = 8.4, 7.4 Hz, 1H), 1.75 – 1.61 (m, 2H), 1.59 – 1.44 (m, 2H), 1.42 (s, 6H), 1.29 – 1.21 (m, 4H), 0.90 – 0.84 (m, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) *δ*: 216.3, 154.4, 134.5, 129.7, 122.0, 85.6, 60.9, 46.8, 35.0, 31.2, 29.8, 26.0, 24.8, 24.4, 24.3, 23.0, 14.1, 12.0 ppm. **IR:** 2959, 2930, 2872, 2359, 1711, 1609, 1509, 1459, 1378, 1228, 1159, 1114, 1044, 954, 836, 763, 578 cm^{-1}. **HRMS** (ESI) for $C_{20}H_{29}Cl_2O_2^+$ [$(M+H)^+$]: calculated 371.1539, found 371.1529.

8-(2,5-Dimethylphenoxy)-5,5-dimethyl-3-phenyloctan-4-one (23)

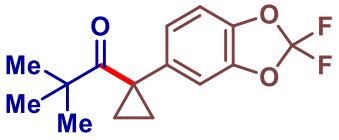


Chemical Formula: $C_{24}H_{32}O_2$
Molecular Weight: 352.5180

Prepared according to the general procedure using **1c** (66 mg, 0.24 mmol, 1.2 equiv), **2i** (62 mg, 0.20 mmol, 1.0 equiv), $NiBr_2$•glyme (6.1 mg, 20 μmol, 0.10 equiv), 4,4'-di(CO_2Me)bpy (5.4 mg, 20 μmol, 0.10 equiv), HE (76 mg, 0.30 mmol, 1.5 equiv) and DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE/EA = 40/1 to PE/DCM = 1/1) to give the product **23** (41 mg, 58% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.27 – 7.25 (m, 4H), 7.23 – 7.19 (m, 1H), 6.99 (d, *J* = 7.4 Hz, 1H), 6.65 (d, *J* = 7.5 Hz, 1H), 6.54 (s, 1H), 3.98 (t, *J* = 7.4 Hz, 1H), 3.79 – 3.69 (m, 2H), 2.30 (s, 3H), 2.15 (s, 3H), 1.99 – 1.89 (m, 1H), 1.77 – 1.75 (m, 1H), 1.72 – 1.57 (m, 2H), 1.54 – 1.23 (m, 2H), 1.09 (d, *J* = 8.4 Hz, 6H), 0.79 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) *δ*: 215.3, 157.1, 139.6, 136.6, 130.4, 128.7, 128.5, 127.0, 123.7, 120.8, 112.1, 68.1, 54.8, 48.5, 36.2, 28.7, 25.0, 24.7, 24.6, 21.5, 15.9, 12.5 ppm. **IR:** 2959, 2923, 2870, 1699, 1614, 1584, 1508, 1453, 1378, 1284, 1263, 1156, 1129, 1032, 842, 802, 766, 740, 699, 586 cm^{-1}. **HRMS** (ESI) for $C_{24}H_{33}O_2^+$ [$(M+H)^+$]: calculated 353.2475, found 353.2468.

1-(1-(2,2-Difluorobenzo[*d*][1,3]dioxol-5-yl)cyclopropyl)-2,2-dimethylpropan-1-one(24)

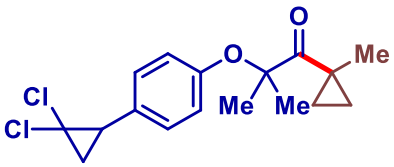


Chemical Formula: $C_{15}H_{16}F_2O_3$
Molecular Weight: 282.2868

Prepared according to the general procedure using **1a** (43 mg, 0.24 mmol, 1.2 equiv), **2o** (77 mg, 0.20 mmol, 1.0 equiv), $NiBr_2$•glyme (6.1 mg, 20 μmol, 0.10 equiv), 4,4'-di(CO_2Me)bpy (5.4 mg, 20 μmol, 0.10 equiv), HE (76 mg, 0.30 mmol, 1.5 equiv) and DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE/EA = 30/1) to give the product **24** (32 mg, 57% yield) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) *δ*: 7.06 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.04 (d, *J* = 1.7 Hz, 1H), 6.99 (d, *J* = 8.2 Hz, 1H), 1.45 – 1.42 (m, 2H), 1.03 (s, 9H), 1.03 – 1.00 (m, 2H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) *δ*: 212.4, 143.8, 142.8, 137.3, 131.8 (t, *J* = 255.2 Hz), 125.4, 111.2, 109.3, 46.0, 36.0, 28.5, 15.6 ppm. **^{19}F NMR** (565 MHz, $CDCl_3$) δ: -49.97 ppm. **IR:** 2954, 2924, 2854, 2359, 1686, 1495, 1458, 1364, 1238, 1160, 1032, 957, 815, 705, 639 cm^{-1}. **HRMS** (ESI) for $C_{15}H_{17}F_2O_3^+$ [$(M+H)^+$]: calculated 283.1140, found 283.1137.

2-(4-(2,2-Dichlorocyclopropyl)phenoxy)-2-methyl-1-(1-methylcyclopropyl)propan-1-one (25)

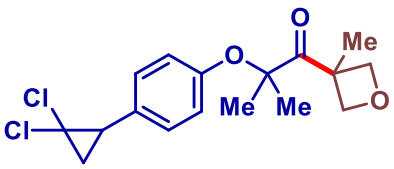


Chemical Formula: $C_{17}H_{20}Cl_2O_2$
Molecular Weight: 327.2450

Prepared according to the general procedure using **1g** (88 mg, 0.24 mmol, 1.2 equiv), **2p** (49 mg, 0.20 mmol, 1.0 equiv), $NiBr_2$•glyme (6.1 mg, 20 μmol, 0.10 equiv), 4,4'-di(CO_2Me)bpy (5.4 mg, 20 μmol, 0.10 equiv), HE (76 mg, 0.30 mmol, 1.5 equiv) and DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE/EA = 30/1) to give the product **25** (40 mg, 61% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.14 – 7.08 (m, 2H), 6.79 – 6.73 (m, 2H), 2.83 (dd, *J* = 10.7, 8.3 Hz, 1H), 1.94 (dd, *J* = 10.7, 7.3 Hz, 1H), 1.86 – 1.73 (m, 1H), 1.55 (s, 6H), 1.44 (s, 3H), 1.35 – 1.33 (m, 2H), 0.66 – 0.63 (m, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) *δ*: 213.8, 155.4, 129.9, 127.9, 117.8, 85.3, 61.0, 35.0, 26.0, 25.4, 25.1, 25.0, 22.5, 22.4, 21.0 ppm. **IR:** 2925, 2359, 1681, 1610, 1510, 1464, 1380, 1264, 1241, 1154, 1054, 960, 878, 832, 735, 703, 557 cm^{-1}. **HRMS** (ESI) for $C_{17}H_{21}Cl_2O_2^+$ [$(M+H)^+$]: calculated 327.0913, found 327.0909.

2-(4-(2,2-Dichlorocyclopropyl)phenoxy)-2-methyl-1-(3-methyloxetan-3-yl)propan-1-one (26)



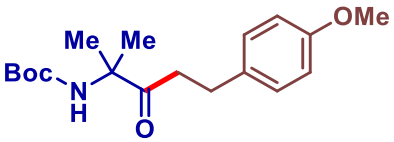
Chemical Formula: $C_{17}H_{20}Cl_2O_3$
Molecular Weight: 343.2440

Prepared according to the general procedure using **1g** (88 mg, 0.24 mmol, 1.2 equiv), **2q** (52 mg, 0.20 mmol, 1.0 equiv), $NiBr_2$•glyme (6.1 mg, 20 μmol, 0.10 equiv), 4,4'-di(CO_2Me)bpy (5.4 mg, 20 μmol, 0.10 equiv), HE (76 mg, 0.30 mmol, 1.5 equiv) and DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE/EA = 10/1)

to give the product **26** (34 mg, 50% yield) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.18 (d, J = 8.1 Hz, 2H), 6.95 (d, J = 7.1 Hz, 2H), 5.13 (d, J = 6.4 Hz, 2H), 4.42 (d, J = 6.4 Hz, 2H), 2.90 – 2.84 (m, 1H), 1.98 (m, 1H), 1.84 (s, 3H), 1.83 – 1.79 (m, 1H), 1.47 (s, 6H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ: 214.2, 153.1, 130.6, 129.9, 123.0, 87.1, 79.8, 60.8, 50.9, 34.9, 26.0, 25.6 (2C), 23.3 ppm. **IR:** 2960, 2877, 1710, 1608, 1509, 1463, 1375, 1225, 1171, 1152, 1041, 971, 937, 838, 763, 562 cm^{-1}. **HRMS** (ESI) for $C_{17}H_{21}Cl_2O_3^+$ [$(M+H)^+$]: calculated 343.0862, found 343.0860.

***tert*-Butyl (5-(4-methoxyphenyl)-2-methyl-3-oxopentan-2-yl)carbamate (27)**

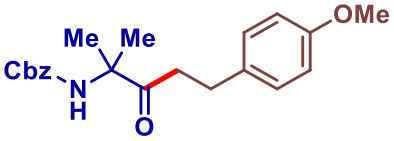


Chemical Formula: $C_{18}H_{27}NO_4$
Molecular Weight: 321.4170

Prepared according to the general procedure using **1h** (67 mg, 0.24 mmol, 1.2 equiv), **2r** (65 mg, 0.20 mmol, 1.0 equiv), $NiBr_2$•glyme (6.1 mg, 20 μmol, 0.10 equiv), 4,4'-di(CO_2Me)bpy (5.4 mg, 20 μmol, 0.10 equiv), HE (76 mg, 0.30 mmol, 1.5 equiv) and DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE/EA = 30/1) to give the product **27** (43 mg, 67% yield) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.18 – 7.04 (m, 2H), 6.85 – 6.74 (m, 2H), 3.78 (s, 3H), 2.89 – 2.77 (m, 4H), 1.43 (s, 9H), 1.32 (s, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 210.4, 158.1, 154.7, 133.6, 129.5, 114.0, 79.9, 55.4, 37.8, 30.5, 29.8, 29.4, 28.5, 24.1 ppm. **IR:** 3365, 2926, 1711, 1611, 1511, 1454, 1365, 1299, 1244, 1176, 1082, 1035, 824, 737 cm^{-1}. **HRMS** (ESI) for $C_{18}H_{27}NO_4Na^+$ [$(M+Na)^+$]: calculated 344.1832, found 344.1825.

Benzyl (5-(4-methoxyphenyl)-2-methyl-3-oxopentan-2-yl)carbamate (28)

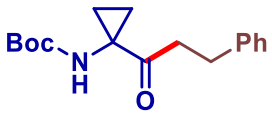


Chemical Formula: $C_{21}H_{25}NO_4$
Molecular Weight: 355.4340

Prepared according to the general procedure using **1i** (75 mg, 0.24 mmol, 1.2 equiv), **2r** (65 mg, 0.20 mmol, 1.0 equiv), $NiBr_2$•glyme (6.1 mg, 20 μmol, 0.10 equiv), 4,4'-di(CO_2Me)bpy (5.4 mg, 20 μmol, 0.10 equiv), HE (76 mg, 0.30 mmol, 1.5 equiv) and DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE/EA = 10/1) to give the product **28** (35 mg, 50% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.37 – 7.33 (m, 5H), 7.07 (d, *J* = 8.1 Hz, 2H), 6.81 (d, *J* = 8.5 Hz, 2H), 5.07 (s, 2H), 3.78 (s, 3H), 2.91 – 2.74 (m, 4H), 1.39 (s, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) *δ*: 209.9, 158.1, 155.3, 133.3, 129.5, 128.7, 128.7, 128.3, 128.2, 114.0, 66.7, 61.1, 55.4, 37.9, 29.3, 23.9 ppm. **IR:** 3340, 2929, 1704, 1611, 1511, 1454, 1384, 1244, 1177, 1069, 1029, 953, 824, 739, 697 cm^{-1}. **HRMS** (ESI) for $C_{21}H_{26}NO_4^+$ [$(M+H)^+$]: calculated 356.1856, found 356.1849.

***tert*-Butyl (1-(3-phenylpropanoyl)cyclopropyl)carbamate (29)**

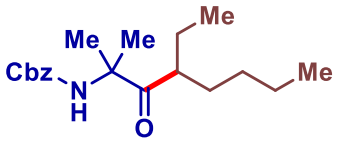


Chemical Formula: $C_{17}H_{23}NO_3$
Molecular Weight: 289.3750

Prepared according to the general procedure using **1j** (67 mg, 0.24 mmol, 1.2 equiv), **2a** (59 mg, 0.20 mmol, 1.0 equiv), $NiBr_2$•glyme (6.1 mg, 20 μmol, 0.10 equiv), 4,4'-di(CO_2Me)bpy (5.4 mg, 20 μmol, 0.10 equiv), HE (76 mg, 0.30 mmol, 1.5 equiv) and DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE/EA = 10/1) to give the product **29** (31 mg, 53% yield) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.30 – 7.28 (m, 2H), 7.22 – 7.14 (m, 3H), 5.12 (s, 1H), 3.05 – 2.91 (m, 2H), 2.91 – 2.85 (m, 2H), 1.58 – 1.50 (m, 2H), 1.44 (s, 9H), 1.16 – 1.02 (m, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) *δ*: 209.4, 155.9, 141.5, 128.6, 128.5, 126.2, 80.4, 41.6, 40.2, 30.0, 28.4, 20.6 ppm. **IR:** 3347, 2976, 2927, 1688, 1496, 1454, 1365, 1248, 1163, 1070, 1013, 749, 698 cm^{-1}. **HRMS** (ESI) for $C_{17}H_{23}NO_3Na^+$ [$(M+Na)^+$]: calculated 312.1570, found 312.1559.

Benzyl -(4-ethyl-2-methyl-3-oxooctan-2-yl)carbamate (30)

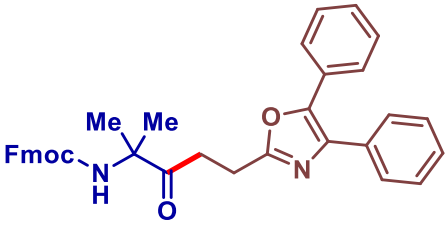


Chemical Formula: $C_{19}H_{29}NO_3$
Molecular Weight: 319.4450

Prepared according to the general procedure using **1i** (75 mg, 0.24 mmol, 1.2 equiv), **2n** (58 mg, 0.20 mmol, 1.0 equiv), $NiBr_2$•glyme (6.1 mg, 20 μmol, 0.10 equiv), 4,4'-di(CO_2Me)bpy (5.4 mg, 20 μmol, 0.10 equiv), HE (76 mg, 0.30 mmol, 1.5 equiv) and DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE/EA = 10/1) to give the product **30** (24 mg, 37% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.40 – 7.28 (m, 5H), 6.08 (s, 1H), 5.07 (s, 2H), 2.77 (p, *J* = 6.4 Hz, 1H), 1.57 (s, 6H), 1.54 – 1.38 (m, 3H), 1.35 – 1.09 (m, 5H), 0.90 – 0.81 (m, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) *δ*: 213.5, 154.8, 136.8, 128.6, 128.2, 128.1, 66.3, 61.5, 46.5, 32.1, 29.9, 25.6, 23.3, 23.0, 14.1, 12.2 ppm. **IR:** 3396, 2930, 2872, 1699, 1497, 1454, 1383, 1262, 1087, 1029, 824, 735, 697 cm^{-1}. **HRMS** (ESI) for $C_{19}H_{30}NO_3^+$ [$(M+H)^+$]: calculated 320.2220, found 320.2211.

(9*H*-Fluoren-9-yl)methyl (5-(4,5-diphenyloxazol-2-yl)-2-methyl-3-oxopentan-2-yl)carbamate (31)

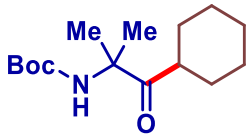


Chemical Formula: $C_{36}H_{32}N_2O_4$
Molecular Weight: 556.6620

Prepared according to the general procedure using **1k** (96 mg, 0.24 mmol, 1.2 equiv), **2s** (88 mg, 0.20 mmol, 1.0 equiv), $NiBr_2$•glyme (6.1 mg, 20 μmol, 0.10 equiv), 4,4'-di(CO_2Me)bpy (5.4 mg, 20 μmol, 0.10 equiv), HE (76 mg, 0.30 mmol, 1.5 equiv) and DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE/EA = 30/1 to 10/1) to give the product **31** (34 mg, 31% yield) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) *δ*: 7.76 – 7.73 (m, 2H), 7.62 – 7.54 (m, 6H), 7.43 – 7.36 (m, 2H), 7.36 – 7.31 (m, 5H), 7.31 – 7.27 (m, 3H), 5.55 (s, 1H), 4.43 (d, *J* = 6.3 Hz, 2H), 4.19 (t, *J* = 6.5 Hz, 1H), 3.16 – 3.07 (m, 4H), 1.50 (s, 6H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) *δ*: 209.0, 162.5, 155.1, 145.5, 143.9, 141.5, 135.1, 129.6, 129.1, 128.8, 128.7, 128.6, 128.1, 128.0, 127.8, 127.2, 126.6, 125.1, 120.1, 66.4, 61.1, 47.5, 32.6, 24.3, 22.6 ppm. **IR:** 2923, 1715, 1569, 1501, 1448, 1383, 1363, 1260, 1177, 1105, 1079, 1024, 963, 912, 761, 734, 693, 674, 620, 586 cm^{-1}. **HRMS** (ESI) for $C_{36}H_{33}N_2O_4^+$ [$(M+H)^+$]: calculated 557.2435, found 557.2433. **Melting point:** 68.5 – 69.5 °C.

***tert*-Butyl (1-cyclohexyl-2-methyl-1-oxopropan-2-yl)carbamate (32)**

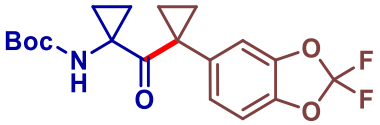


Chemical Formula: $C_{15}H_{27}NO_3$
Molecular Weight: 269.3850

Prepared according to the general procedure using **1h** (67 mg, 0.24 mmol, 1.2 equiv), **2t** (55 mg, 0.20 mmol, 1.0 equiv), $NiBr_2$•glyme (6.1 mg, 20 μmol, 0.10 equiv), 4,4'-di(CO_2Me)bpy (5.4 mg, 20 μmol, 0.10 equiv), HE (76 mg, 0.30 mmol, 1.5 equiv) and DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE/EA = 30/1 to 10/1) to give the product **32** (23 mg, 43% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 2.94 – 2.76 (m, 1H), 1.83 – 1.73 (m, 2H), 1.72 – 1.68 (m, 2H), 1.67 – 1.54 (m, 2H), 1.48 (s, 6H), 1.43 (s, 9H), 1.40 – 1.14 (m, 4H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) *δ*: 214.2, 154.6, 79.4, 61.1, 44.3, 30.3, 29.8, 28.5, 25.9, 23.6 ppm. **IR:** 3415, 2930, 2853, 1734, 1598, 1436, 1376, 1248, 1195, 1154, 995, 859, 782 cm^{-1}. **HRMS** (ESI) for $C_{15}H_{28}NO_3^+$ [$(M+H)^+$]: calculated 270.2064, found 270.2054. **Melting point:** 78.5 – 79.8 °C.

***tert*-Butyl (1-(1-(2,2-difluorobenzo[*d*][1,3]dioxol-5-yl)cyclopropane-1-carbonyl)cyclopropyl)carbamate (33)**

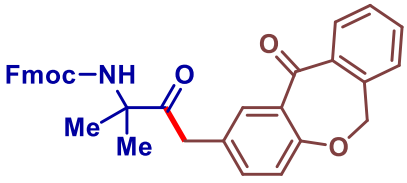


Chemical Formula: $C_{19}H_{21}F_2NO_5$
Molecular Weight: 381.3758

Prepared according to the general procedure using **1j** (67 mg, 0.24 mmol, 1.2 equiv), **2o** (77 mg, 0.20 mmol, 1.0 equiv), $NiBr_2$•glyme (6.1 mg, 20 μmol, 0.10 equiv), 4,4'-di(CO_2Me)bpy (5.4 mg, 20 μmol, 0.10 equiv), HE (76 mg, 0.30 mmol, 1.5 equiv) and DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE/EA = 30/1 to 10/1) to give the product **33** (32 mg, 42% yield) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) *δ*: 7.07 – 6.96 (m, 3H), 1.57 – 1.52 (m, 4H), 1.46 (s, 9H), 1.11 – 0.90 (m, 4H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) *δ*: 206.7, 155.0, 144.1, 142.7, 136.9, 131.8 (t, *J* = 255.2 Hz), 123.7, 109.7, 109.5, 80.1, 41.2, 35.3, 28.5, 20.5, 15.6 ppm. **^{19}F NMR** (565 MHz, $CDCl_3$) δ: -49.83 ppm. **IR:** 3378, 2927, 1704, 1495, 1441, 1391, 1366, 1234, 1154, 1085, 1055, 1031, 1018, 959, 911, 814, 738, 704, 638, 607 cm^{-1}. **HRMS** (ESI) for $C_{19}H_{22}F_2NO_5^+$ [$(M+H)^+$]: calculated 382.1461, found 382.1463. **Melting point:** 98.6 – 99.8 °C.

(9*H*-Fluoren-9-yl)methyl (2-methyl-3-oxo-4-(11-oxo-6,11-dihydrodibenzo[*b,e*]oxepin-2-yl)butan-2-yl)carbamate (34)



Chemical Formula: $C_{34}H_{29}NO_5$
Molecular Weight: 531.6080

Prepared according to the general procedure using **1k** (96 mg, 0.24 mmol, 1.2 equiv), **2u** (83 mg, 0.20 mmol, 1.0 equiv), $NiBr_2$•glyme (6.1 mg, 20 μmol, 0.10 equiv), 4,4'-di(CO_2Me)bpy (5.4 mg, 20 μmol, 0.10 equiv), HE (76 mg, 0.30 mmol, 1.5 equiv) and DMAc (0.10 M, 2.0 mL). The residue was purified by flash column chromatography (PE/EA = 30/1

to 10/1) to give the product **34** (40 mg, 38% yield) as a yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) *δ*: 7.99 (s, 1H), 7.88 (d, *J* = 6.5 Hz, 1H), 7.76 (d, *J* = 7.5 Hz, 2H), 7.61 (d, *J* = 7.5 Hz, 2H), 7.56 – 7.54 (m, 1H), 7.49 – 7.44 (m, 1H), 7.41 – 7.34 (m, 4H), 7.33 – 7.29 (m, 2H), 7.02 (d, *J* = 8.4 Hz, 1H), 5.45 (s, 1H), 5.18 (s, 2H), 4.49 – 4.45 (m, 2H), 4.22 – 4.21 (m, 1H), 3.80 (s, 2H), 1.49 (s, 6H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) *δ*: 208.1, 191.0, 160.5, 155.1, 143.9, 141.5, 140.6, 137.2, 135.8, 132.9, 132.7, 129.6, 129.4, 128.4, 127.9 (2C), 127.2, 125.2, 121.0, 120.2, 73.8, 66.4, 61.3, 47.5, 41.2, 29.8, 24.3 ppm. **IR:** 3341, 2923, 2853, 1715, 1644, 1610, 1490, 1450, 1413, 1379, 1299, 1256, 1138, 1121, 1089, 1051, 1016, 906, 802, 759, 728, 643, 621, 540 cm^{-1}. **HRMS** (ESI) for $C_{34}H_{29}NO_5Na^+$ [$(M+Na)^+$]: calculated 554.1938, found 554.1919.

8 References

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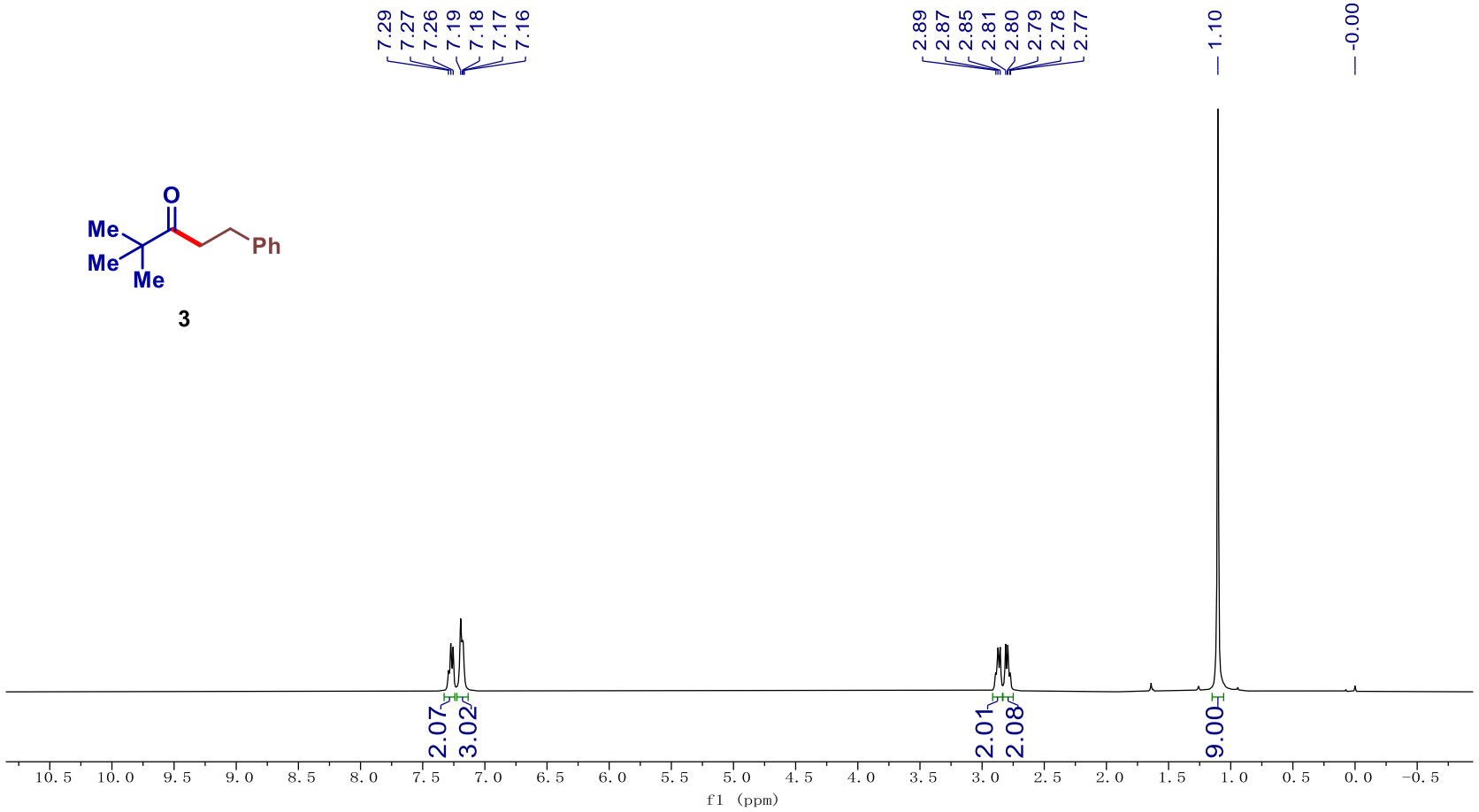
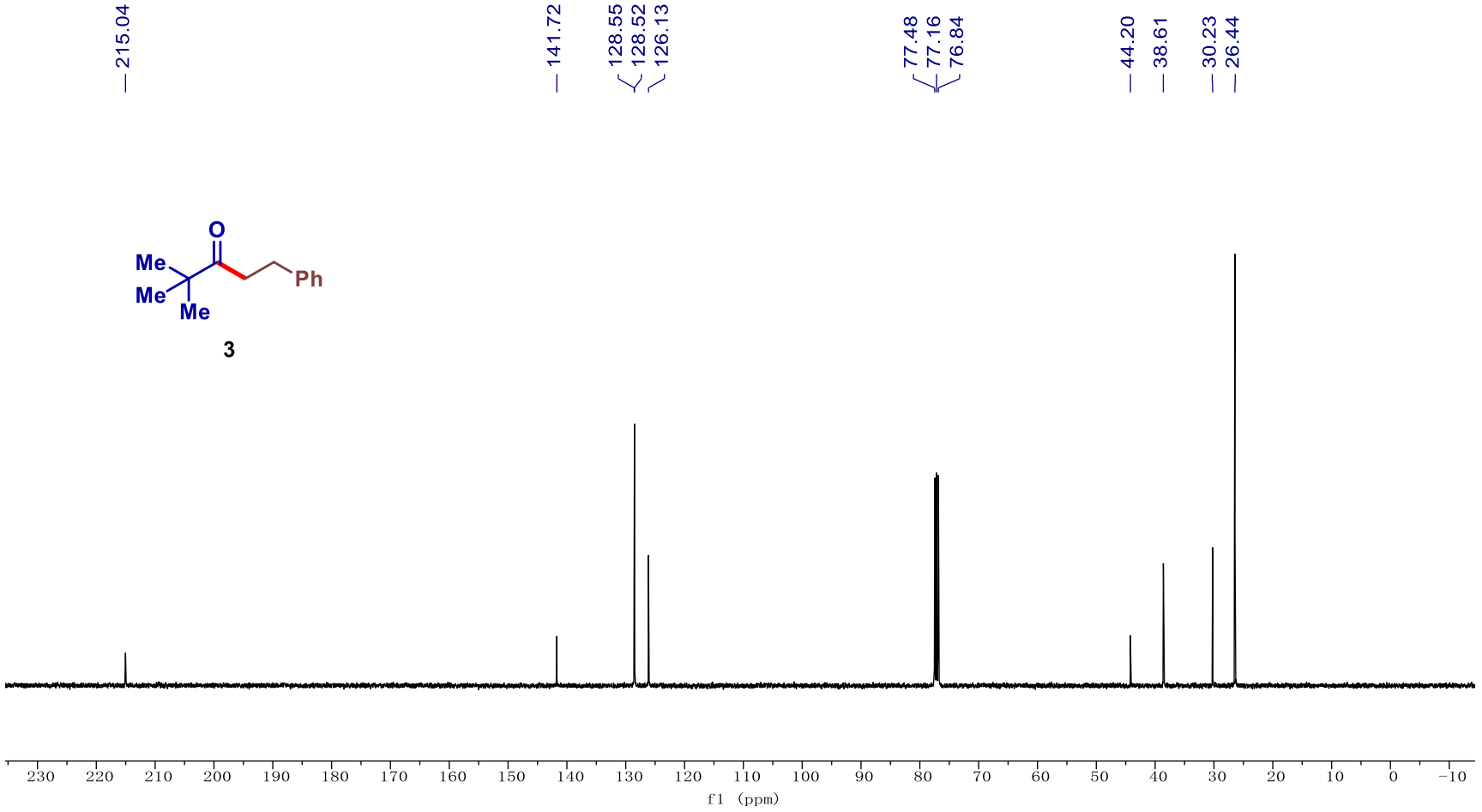
9 NMR Spectra

^{1}H NMR of 3 (400 MHz, $CDCl_3$)

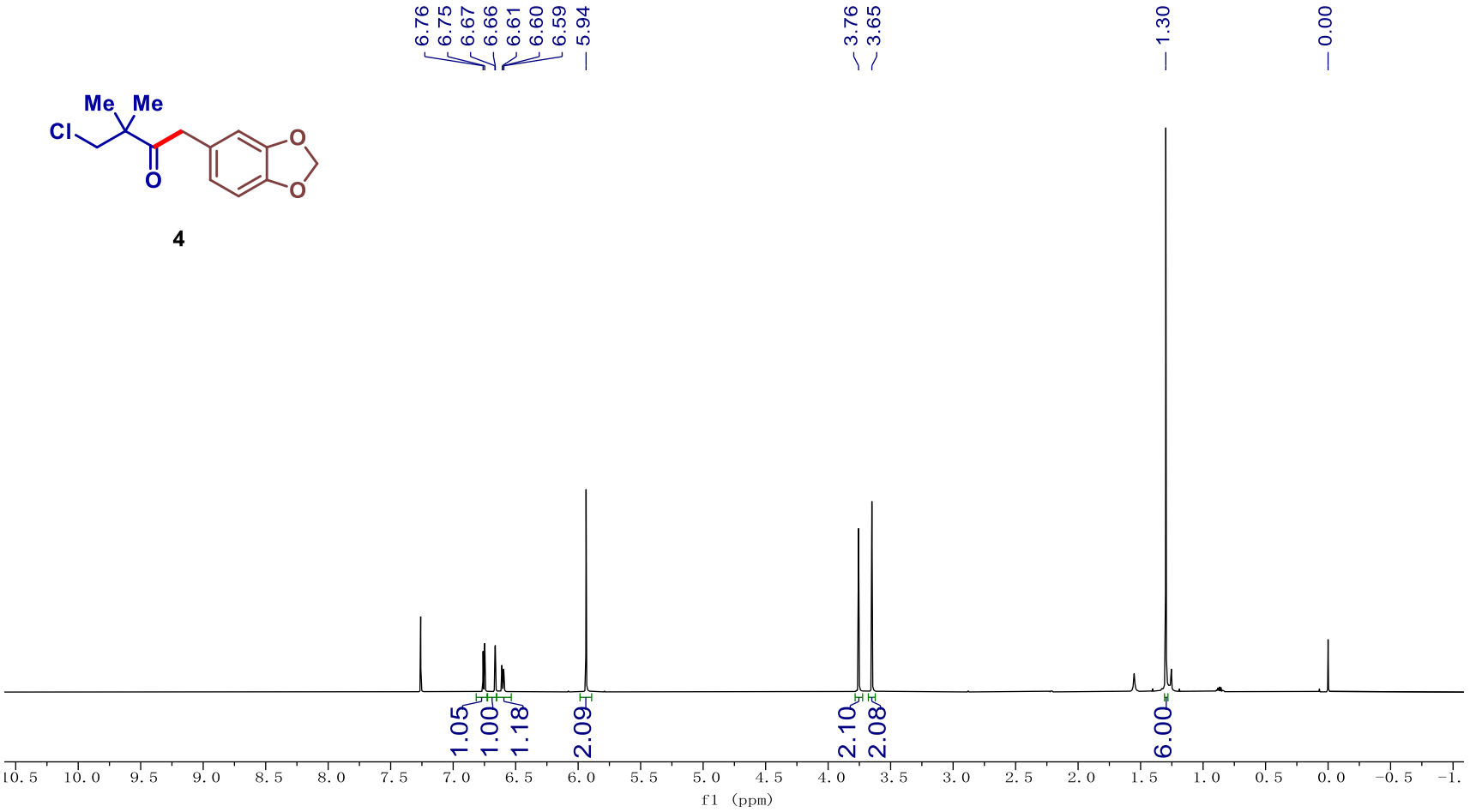


^{13}C NMR of 3 (101 MHz, $CDCl_3$)



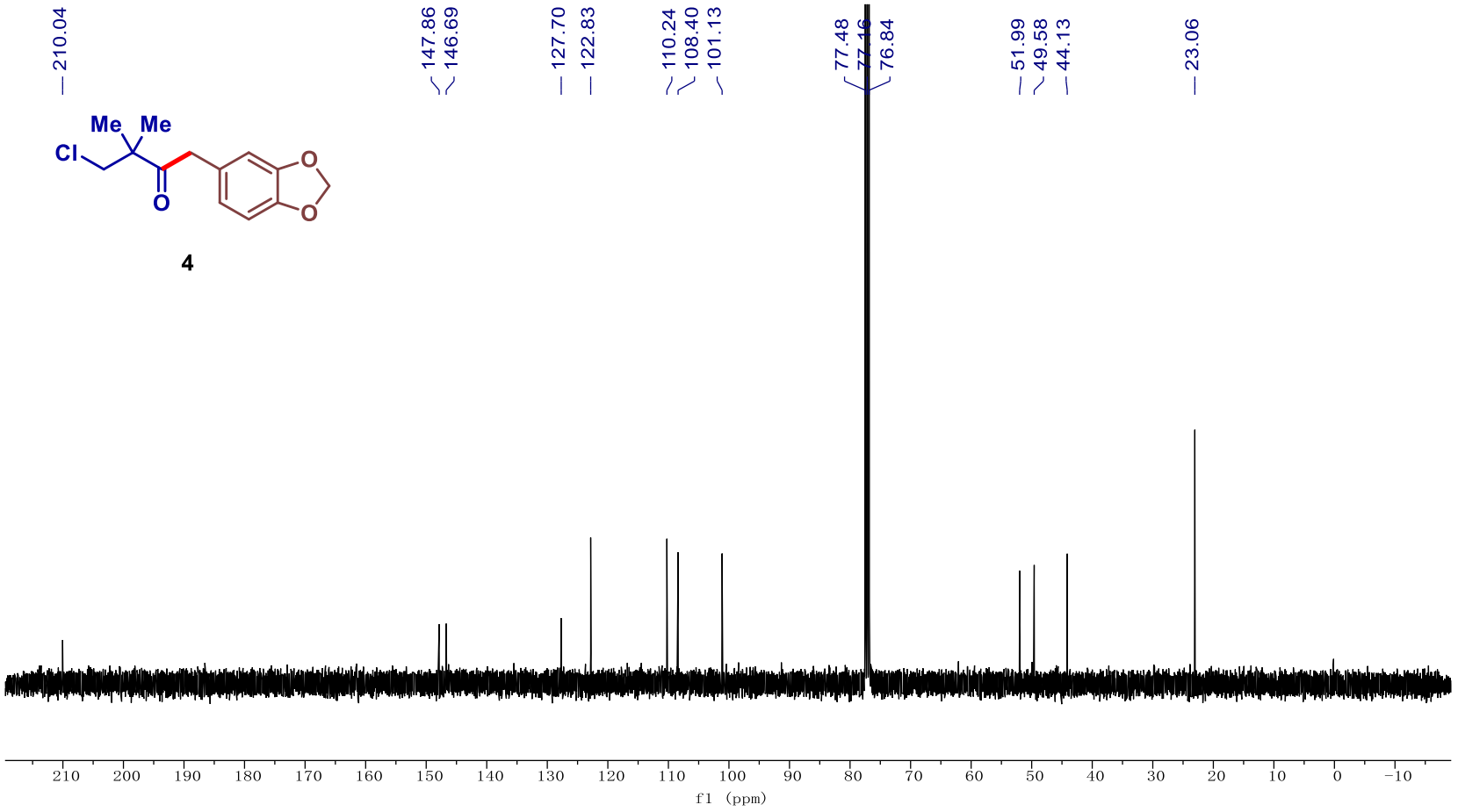
3

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

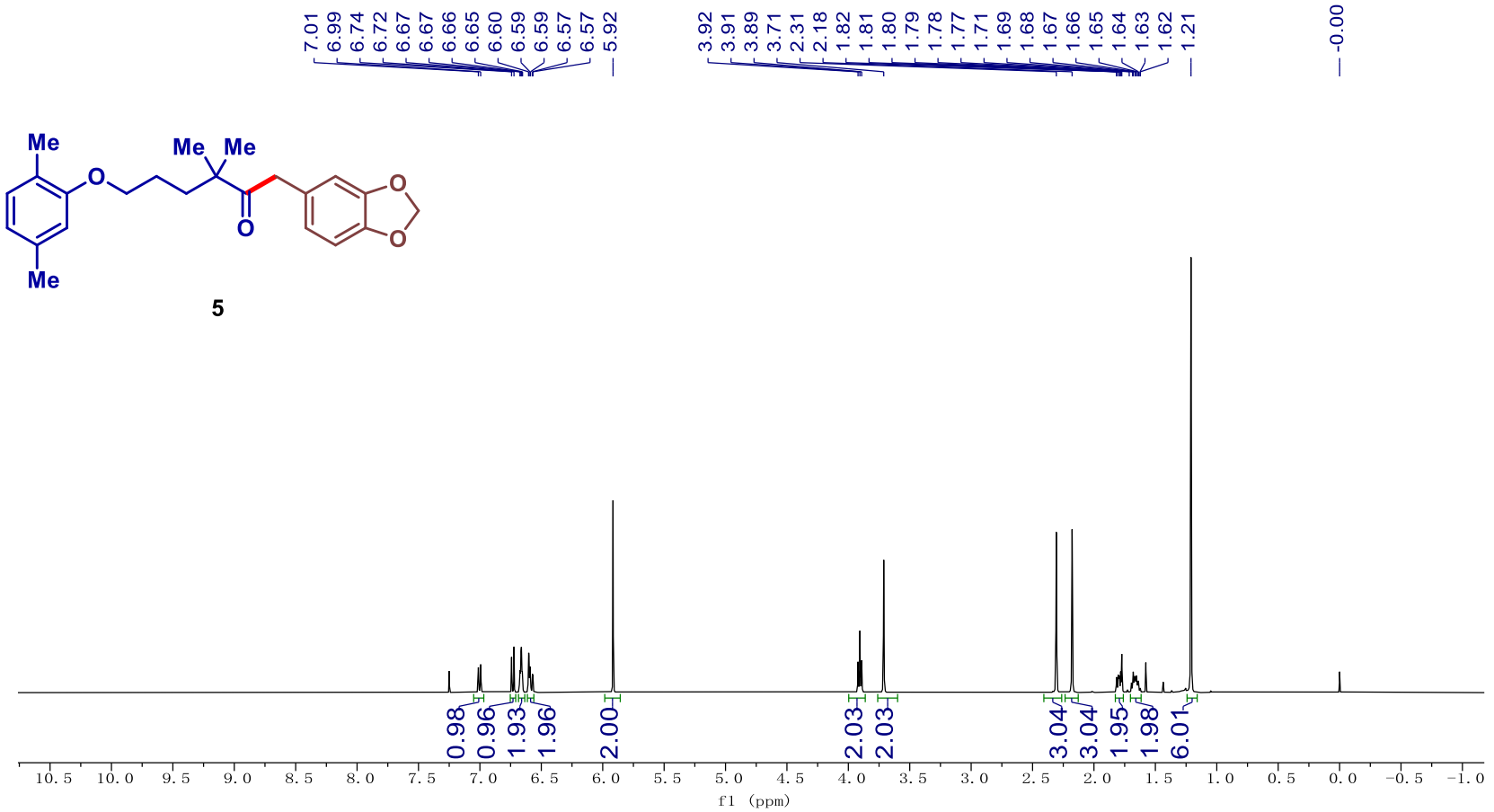


4

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

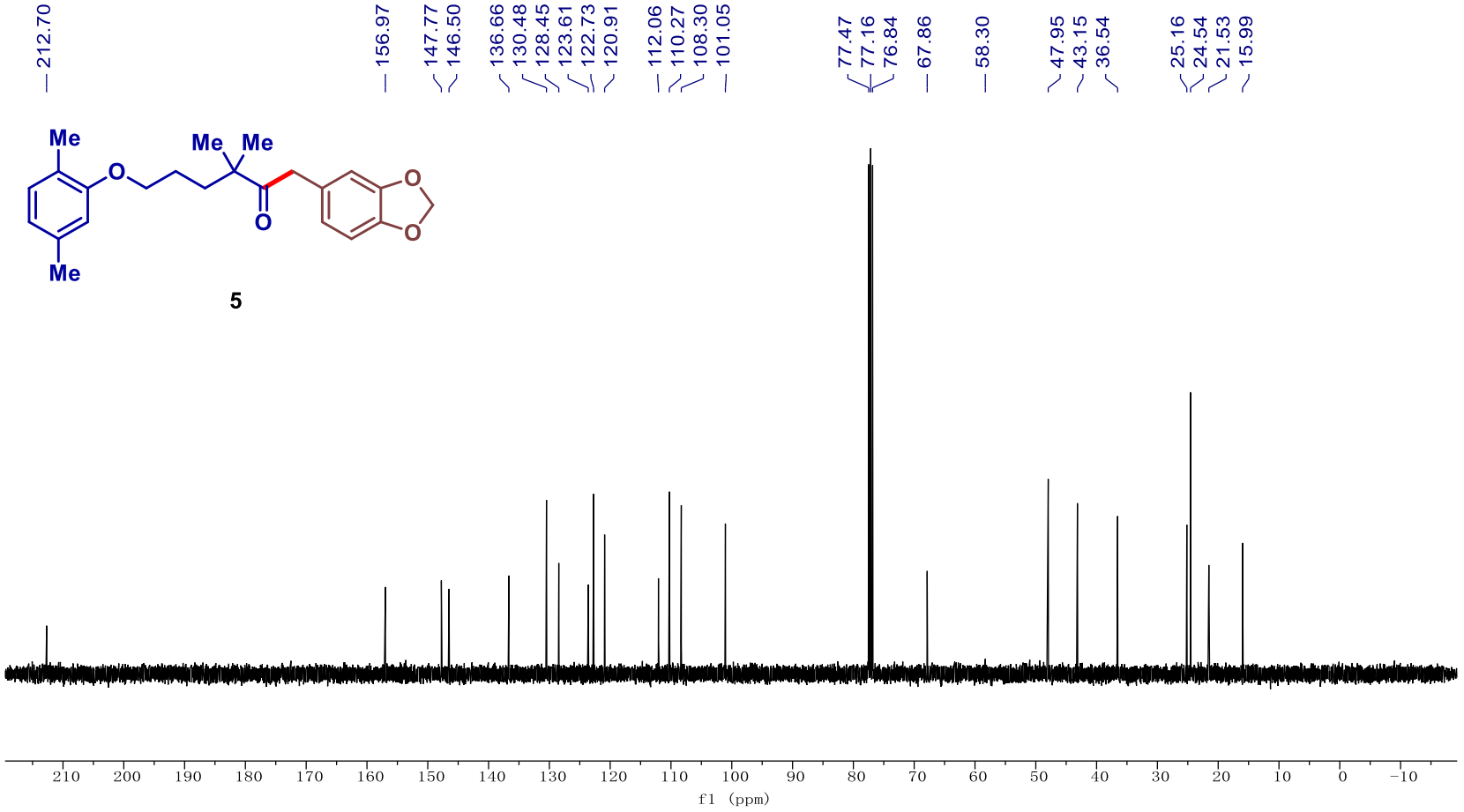


^{1}H NMR of 5 (400 MHz, $CDCl_3$)

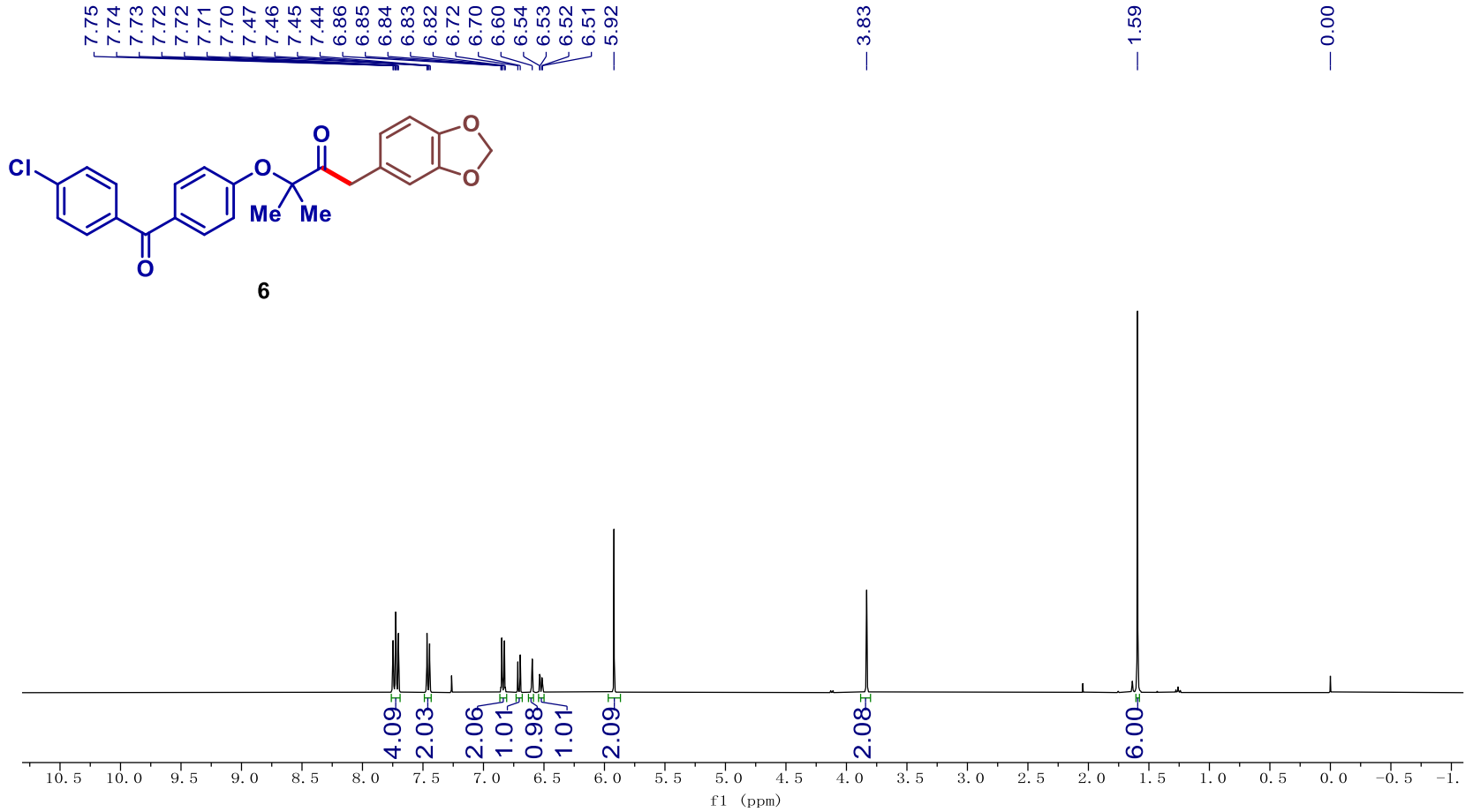


5

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

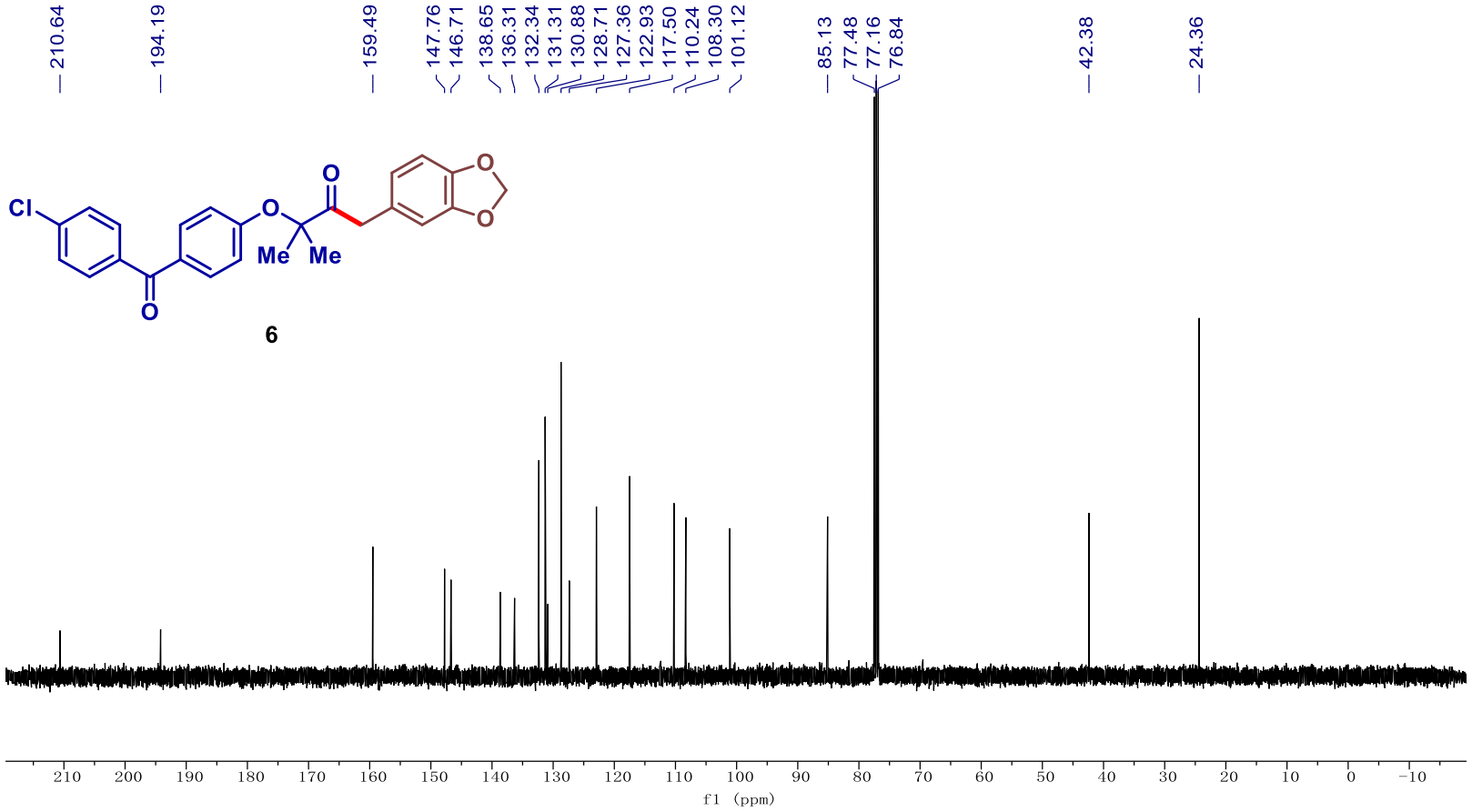


^{1}H NMR of 6 (400 MHz, $CDCl_3$)

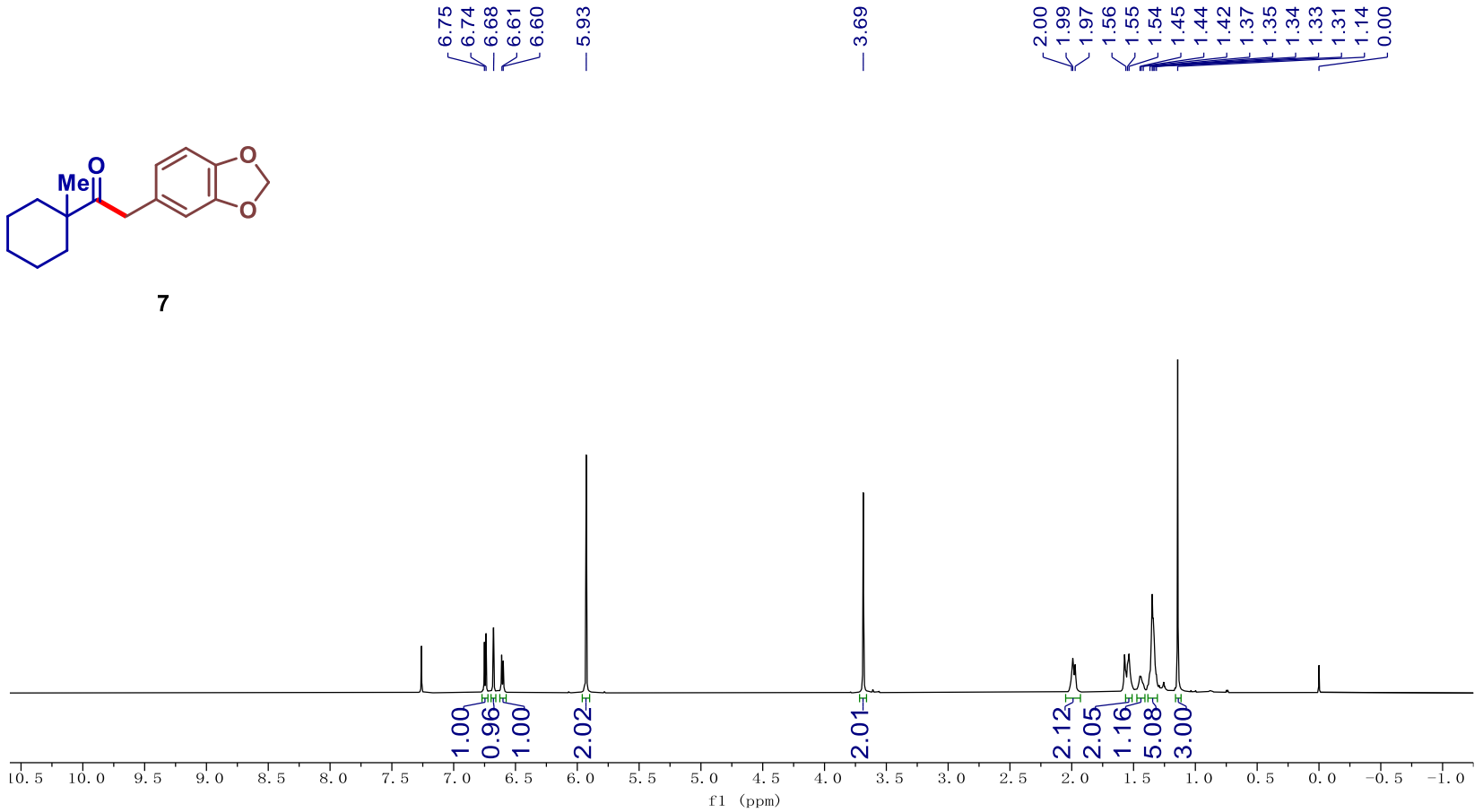


6

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

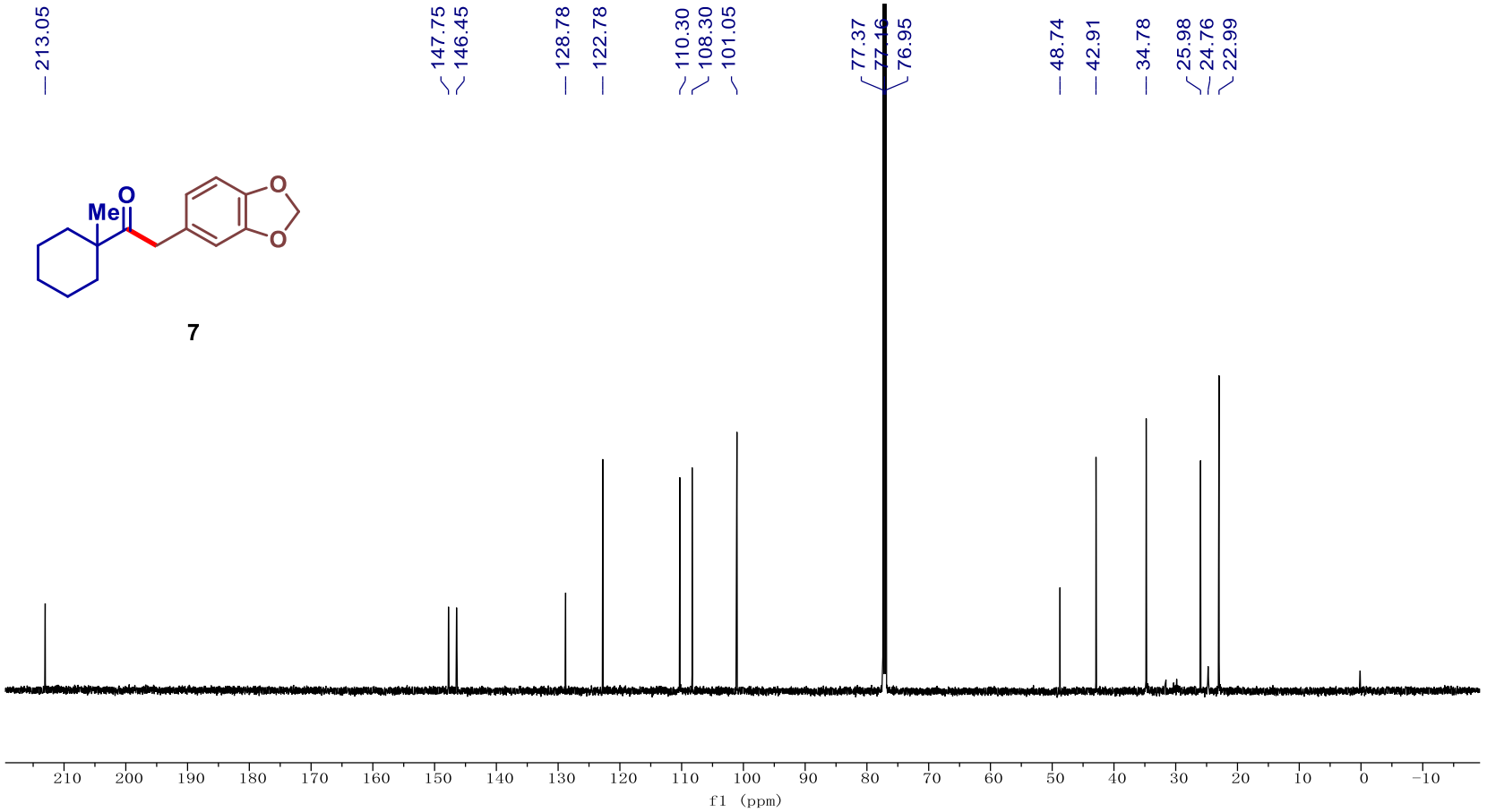


^{1}H NMR of 7 (600 MHz, $CDCl_3$)



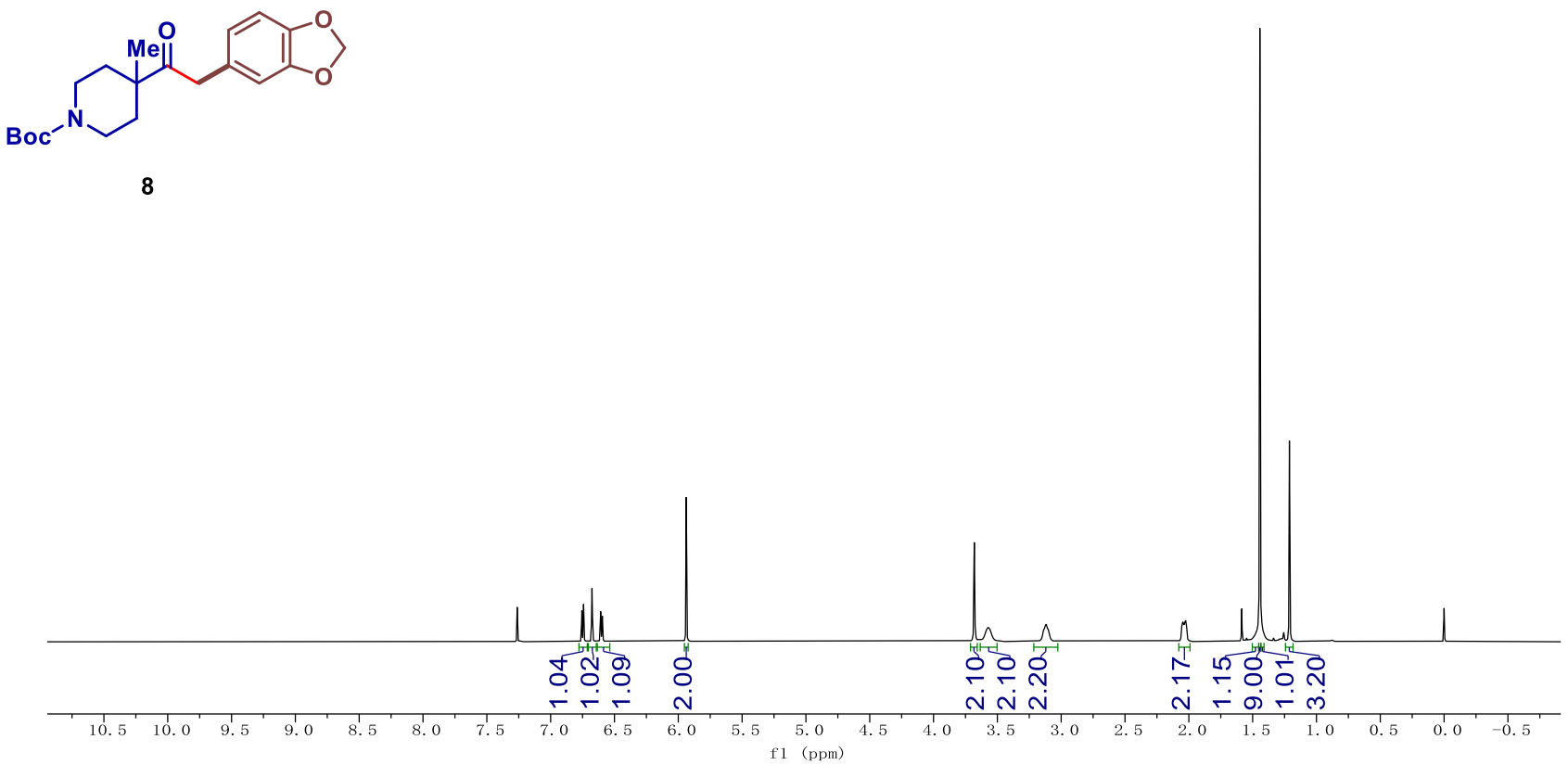
7

^{13}C NMR of 7 (151 MHz, $CDCl_3$)



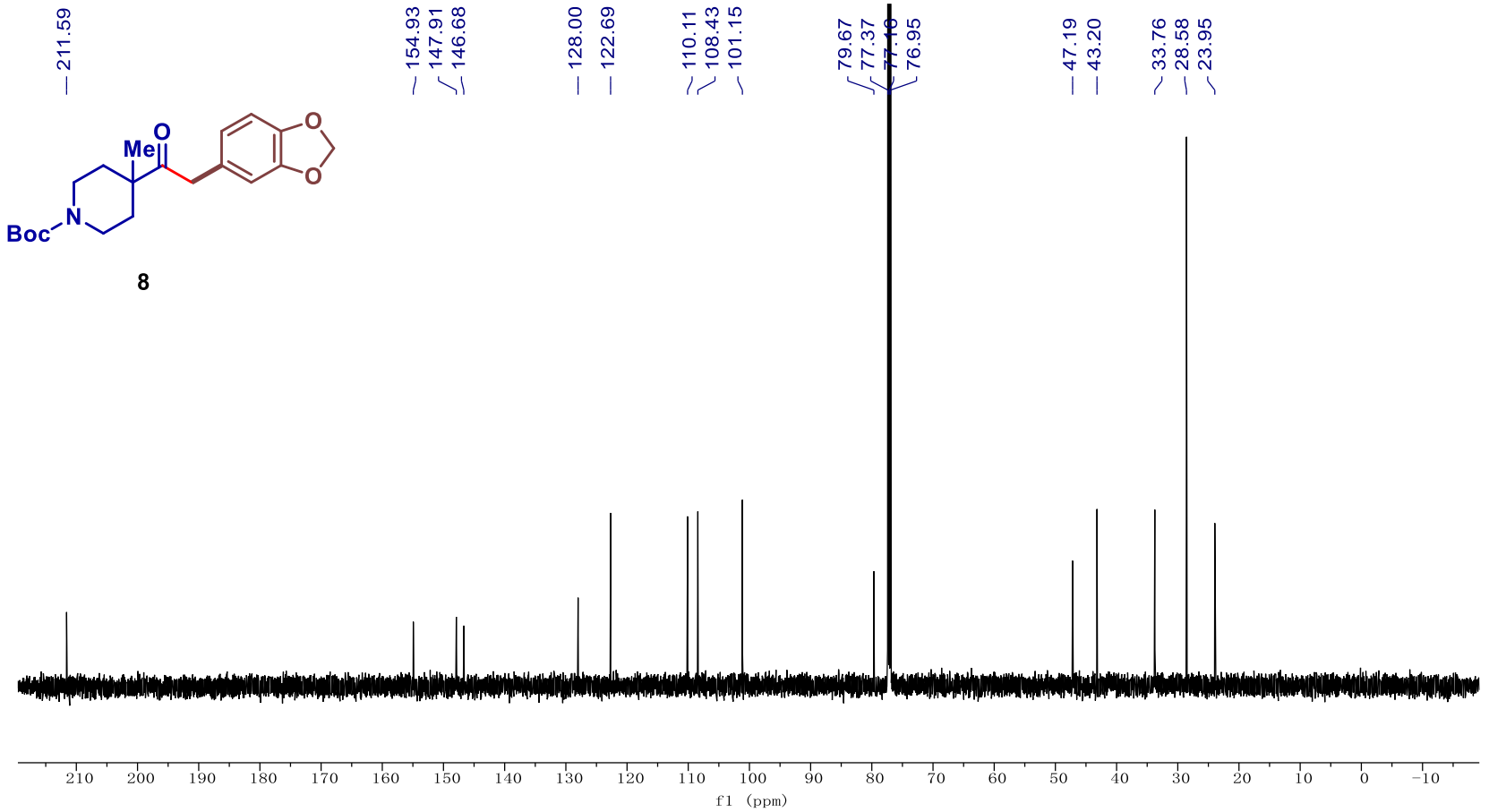
7

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



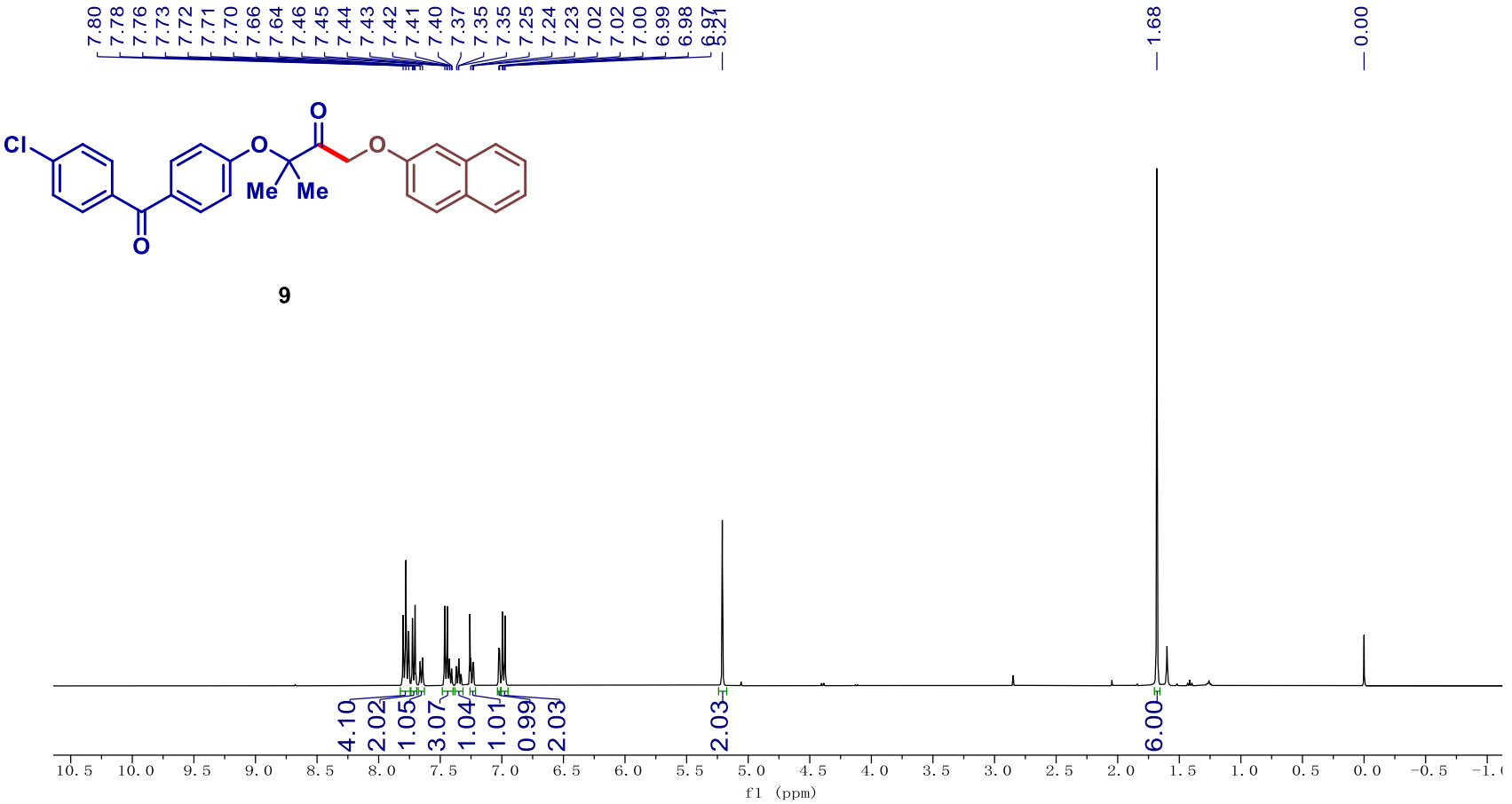
8

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



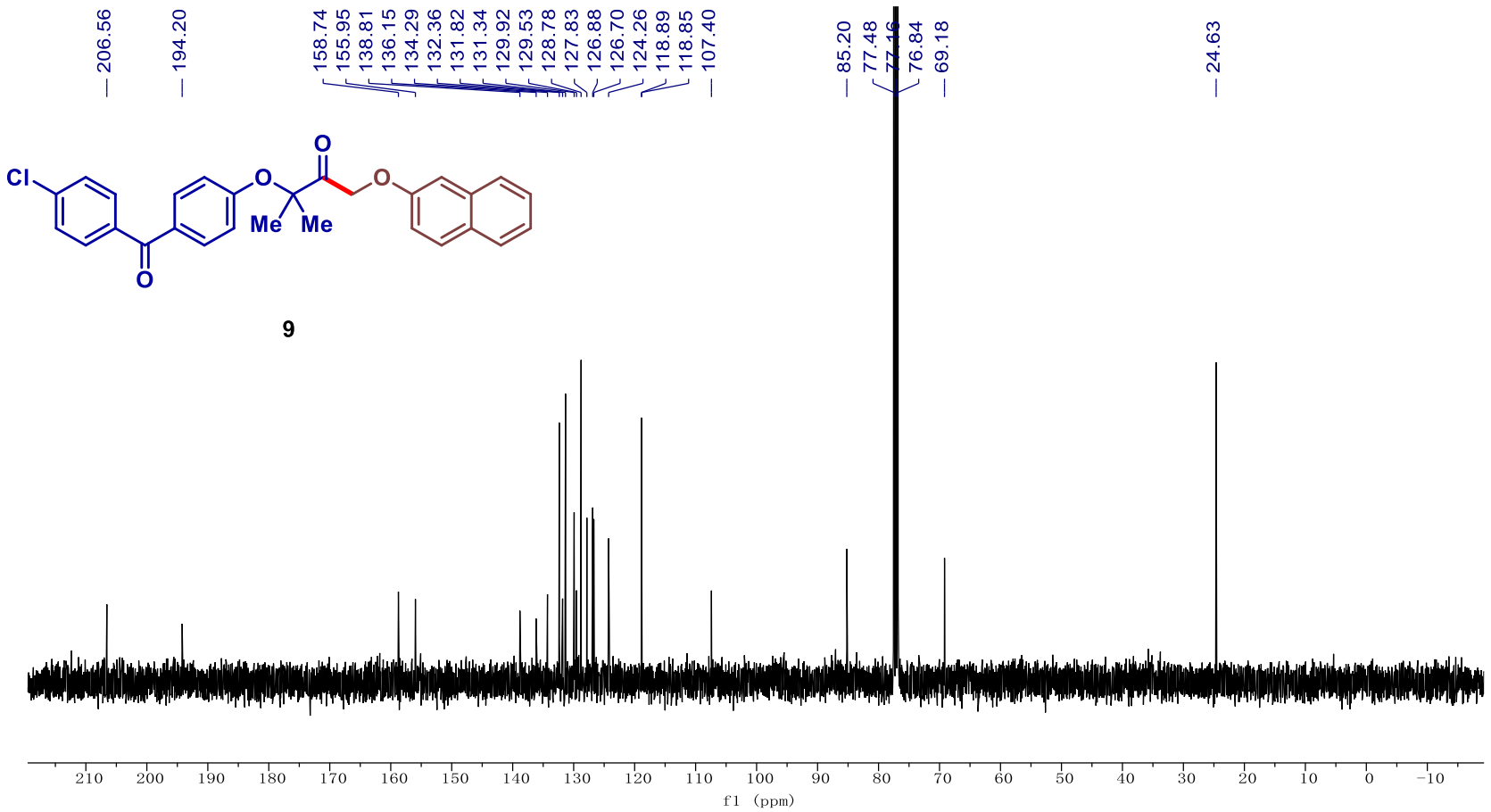
8

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

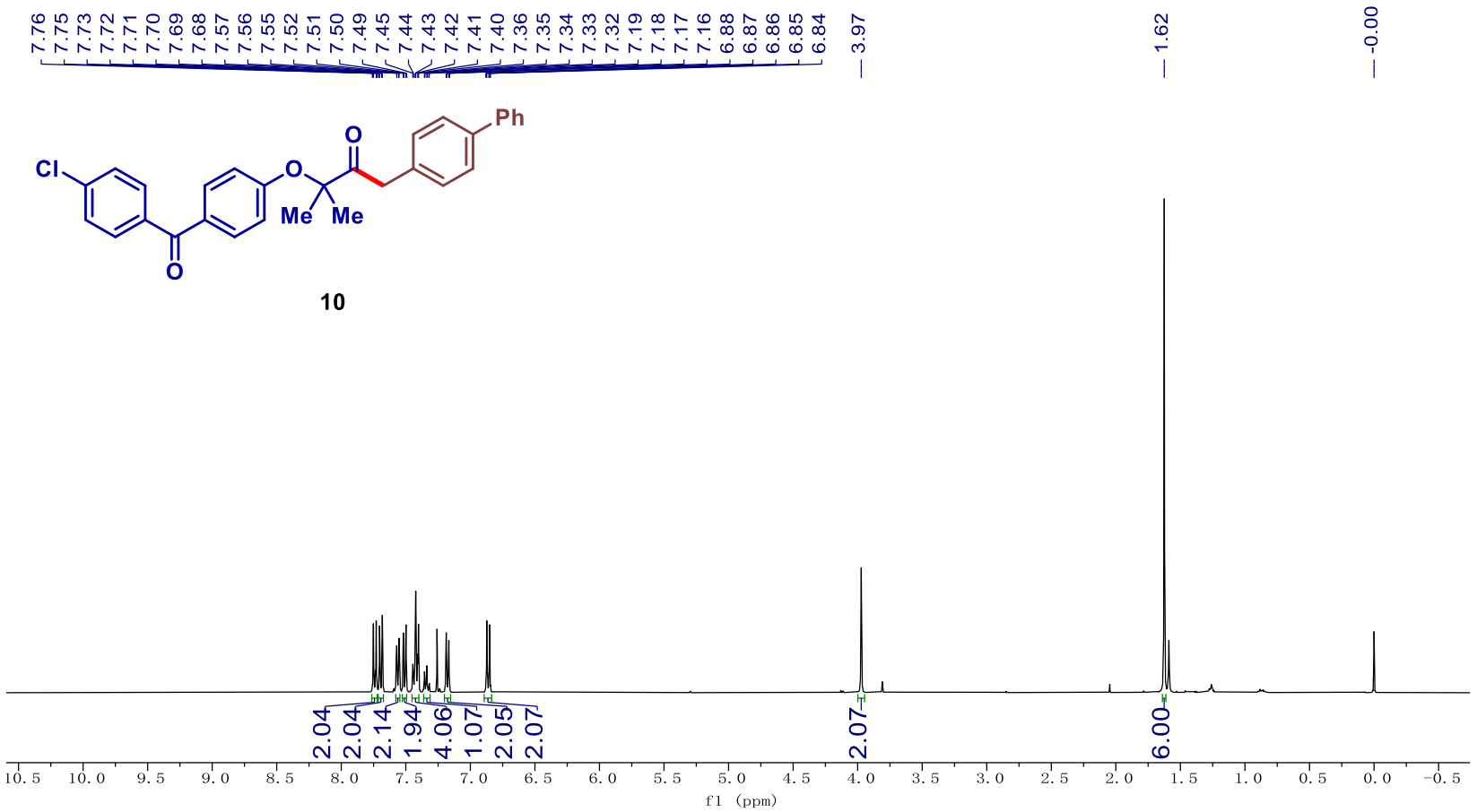


9

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

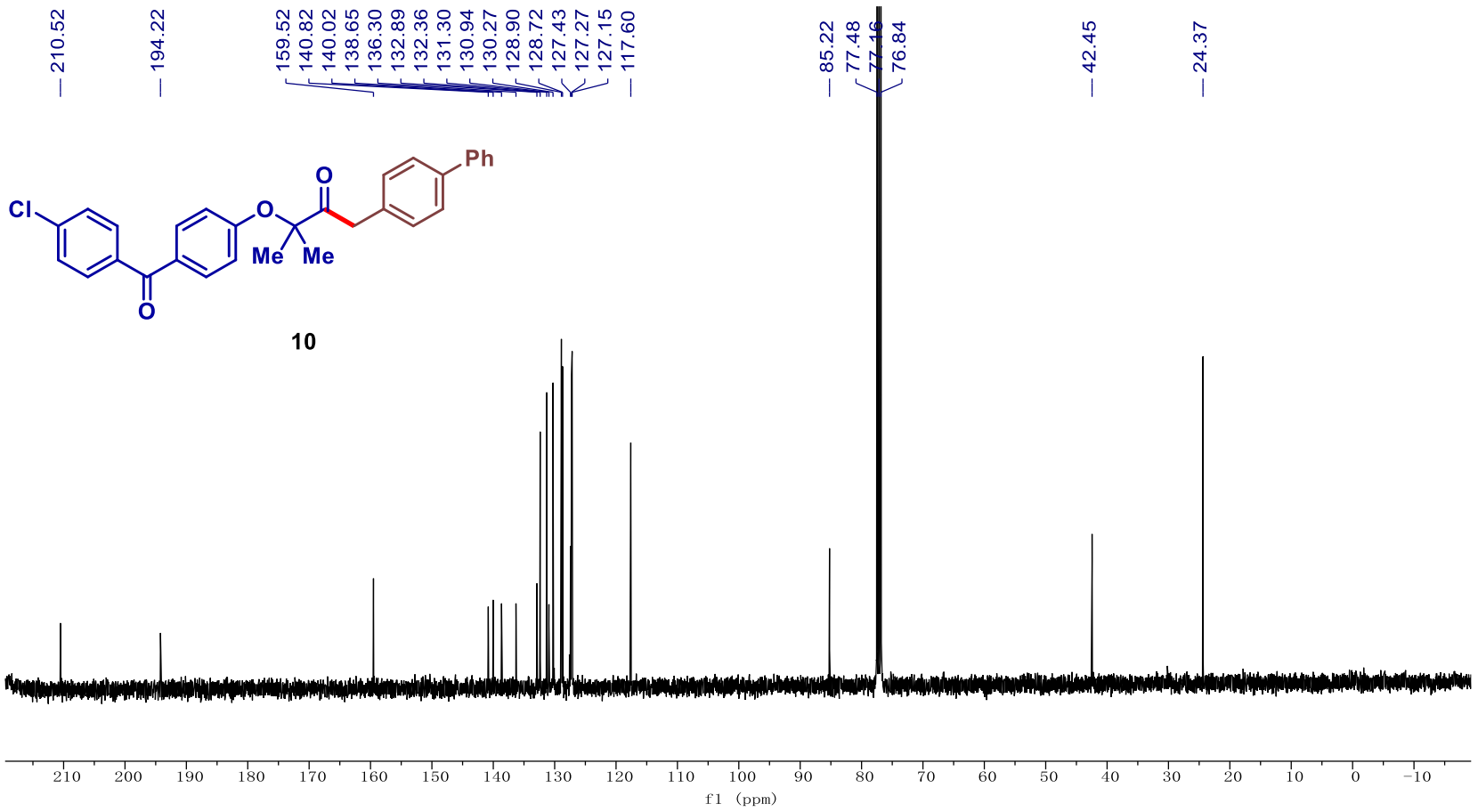


^{1}H NMR of 10 (400 MHz, $CDCl_3$)

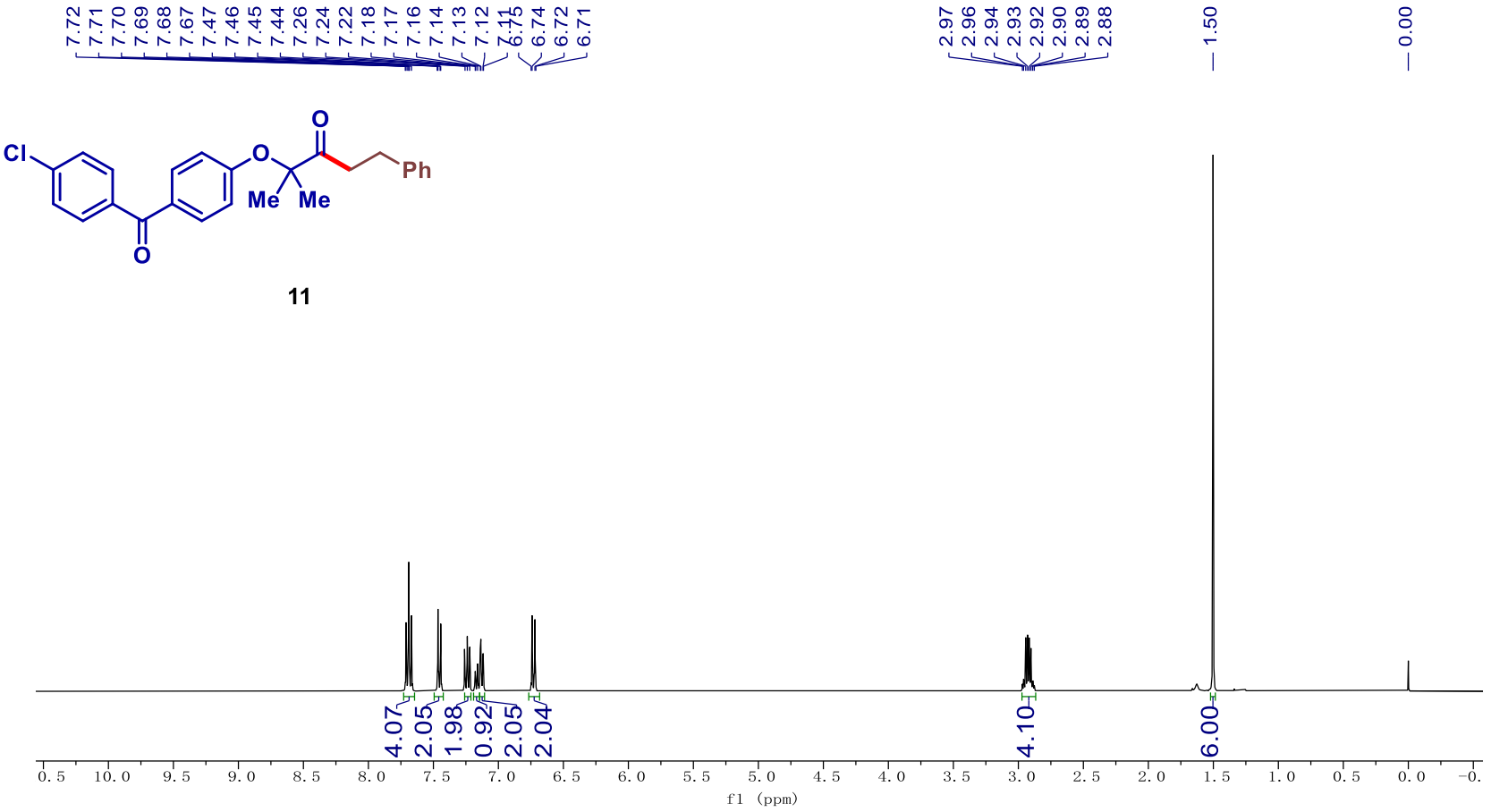


10

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

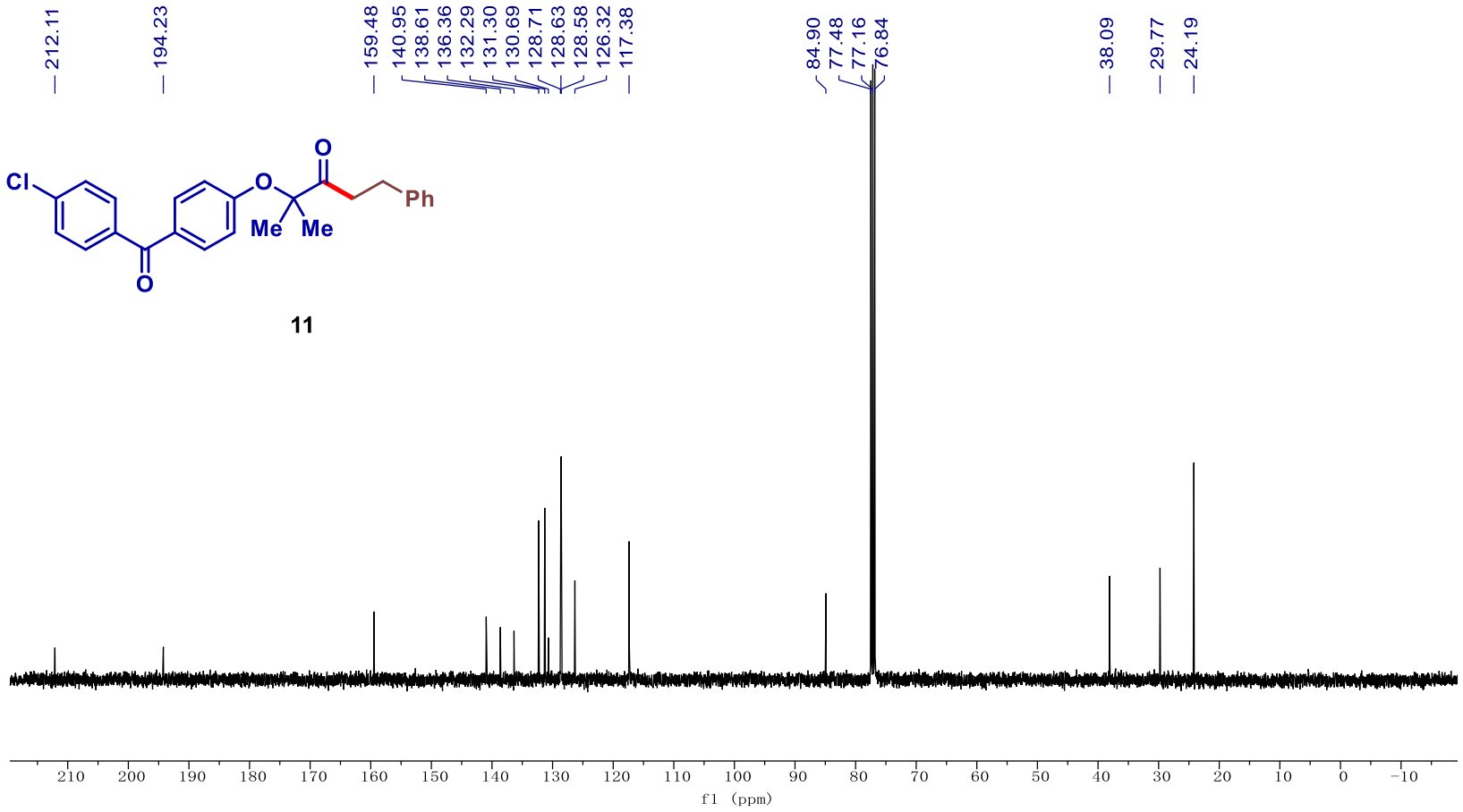


^{1}H NMR of 11 (400 MHz, $CDCl_3$)

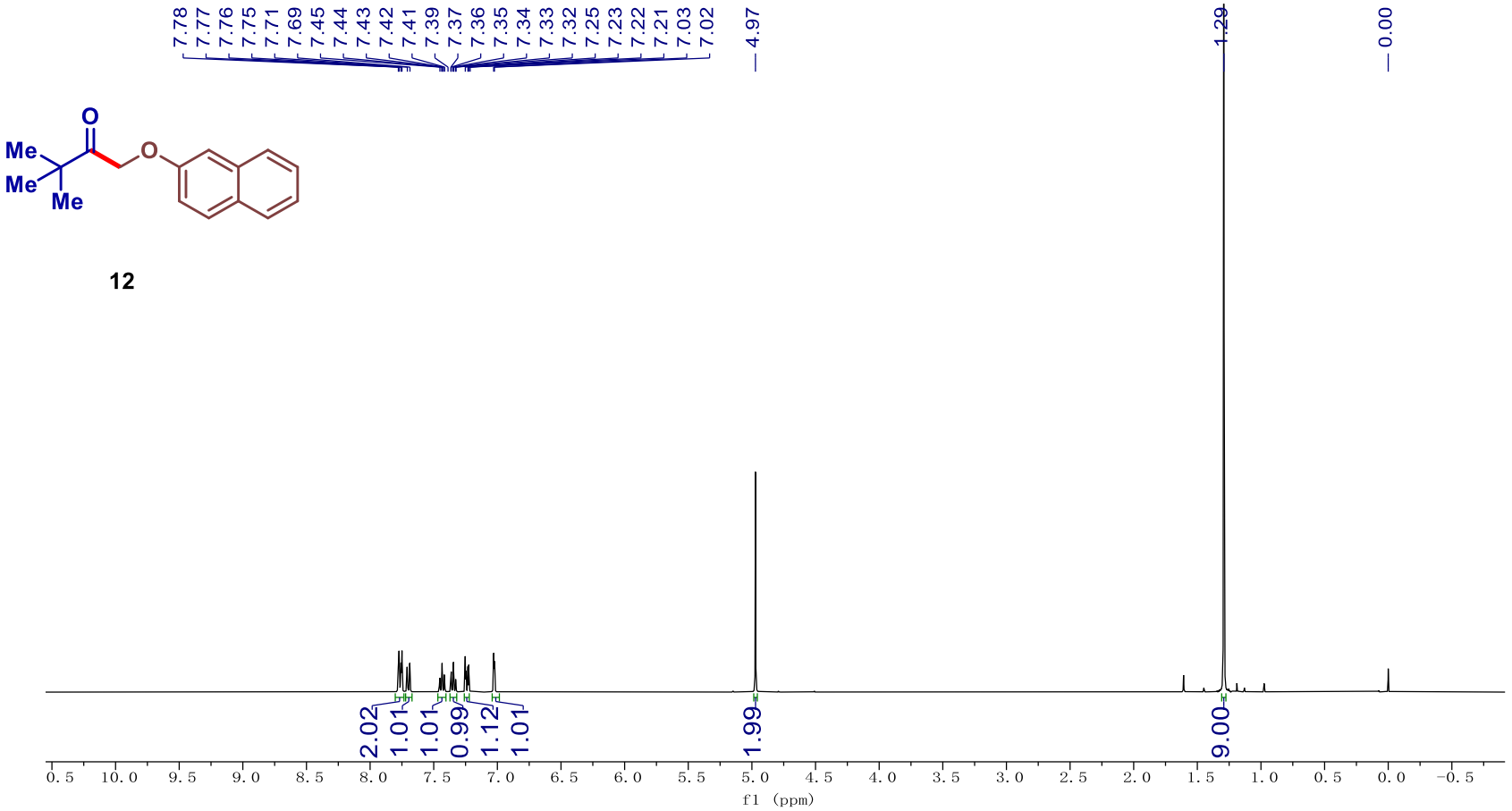


11

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

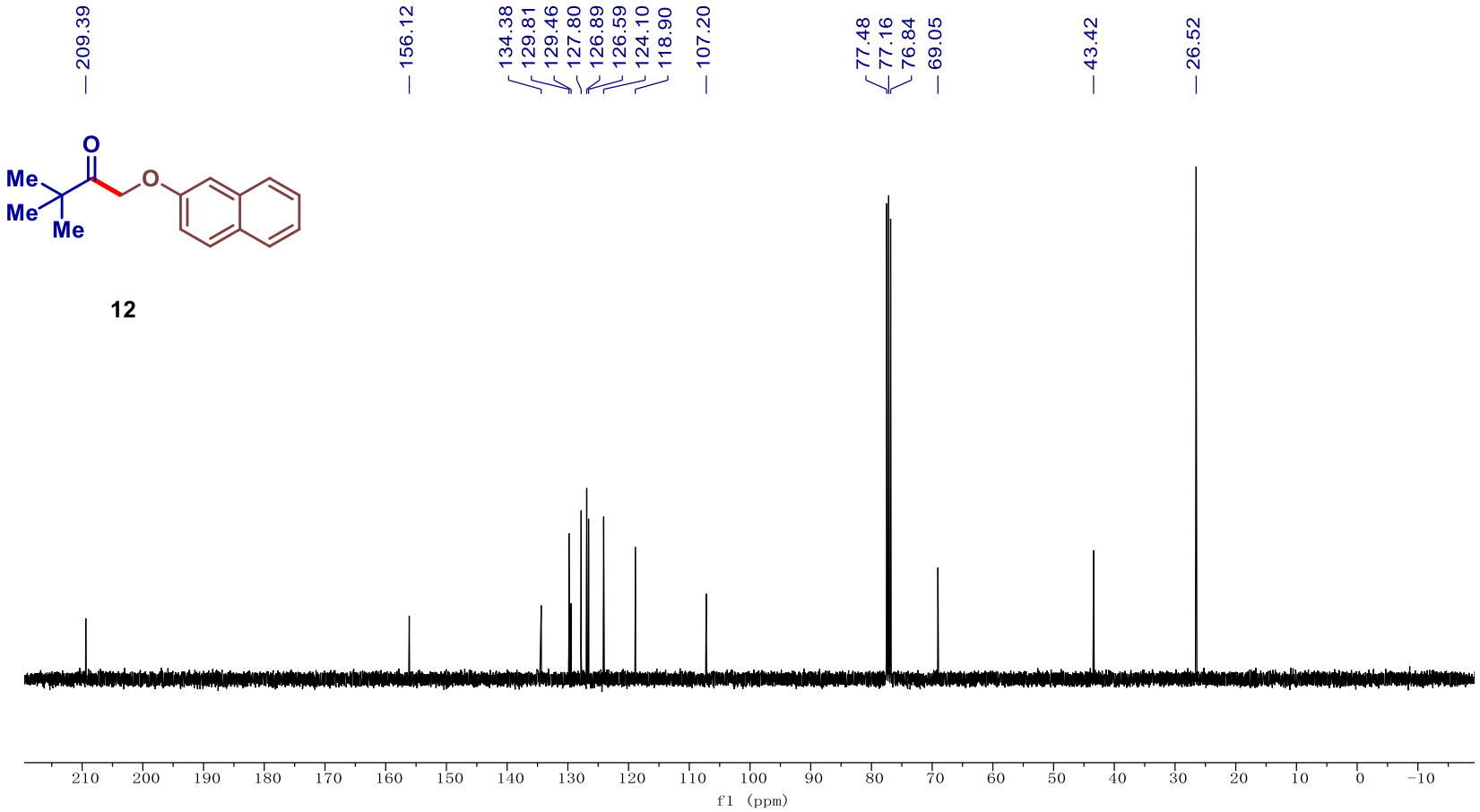


^{1}H NMR of 12 (400 MHz, $CDCl_3$)



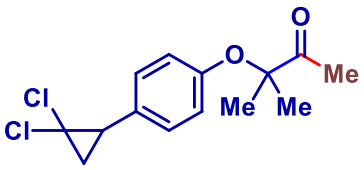
12

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



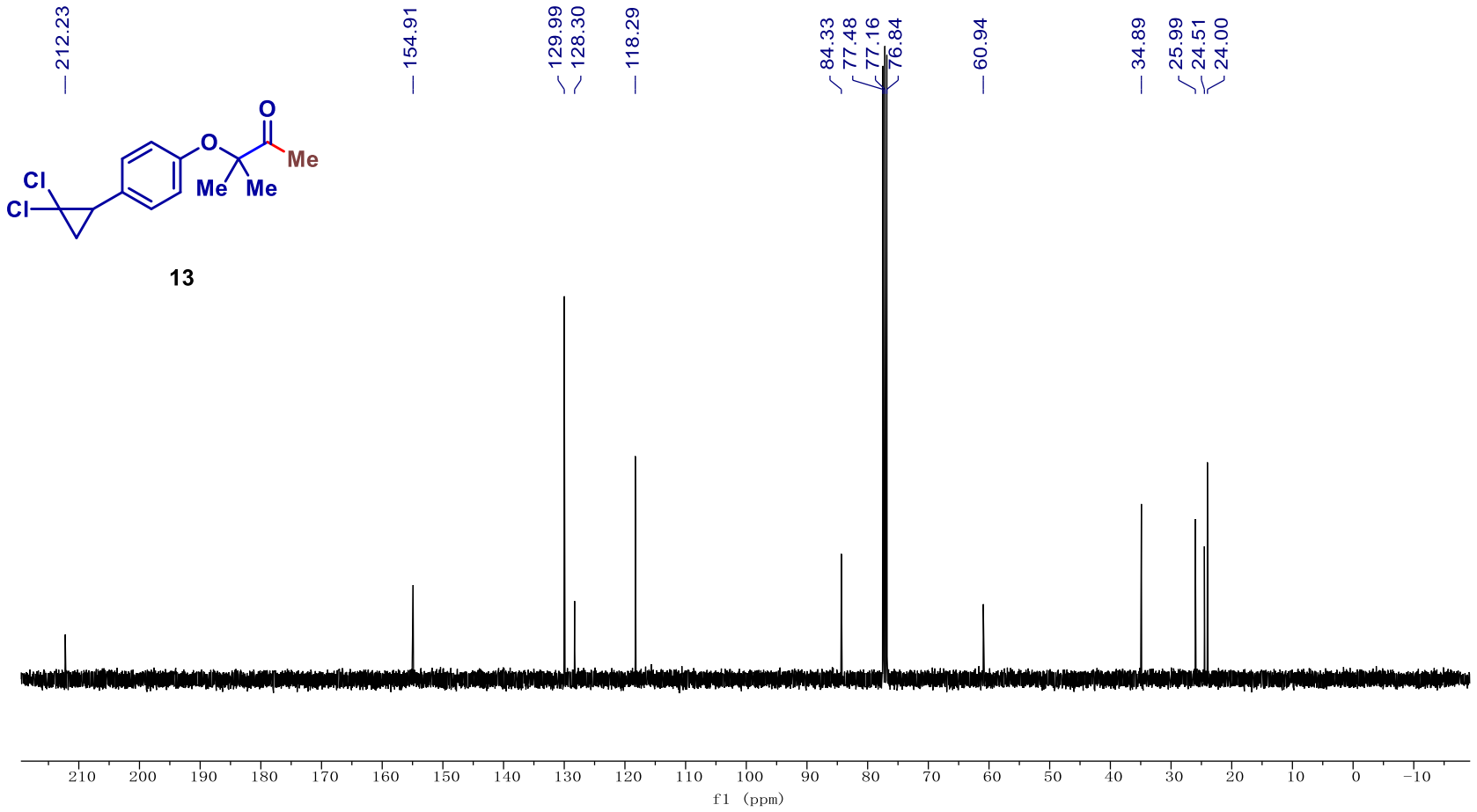
12

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



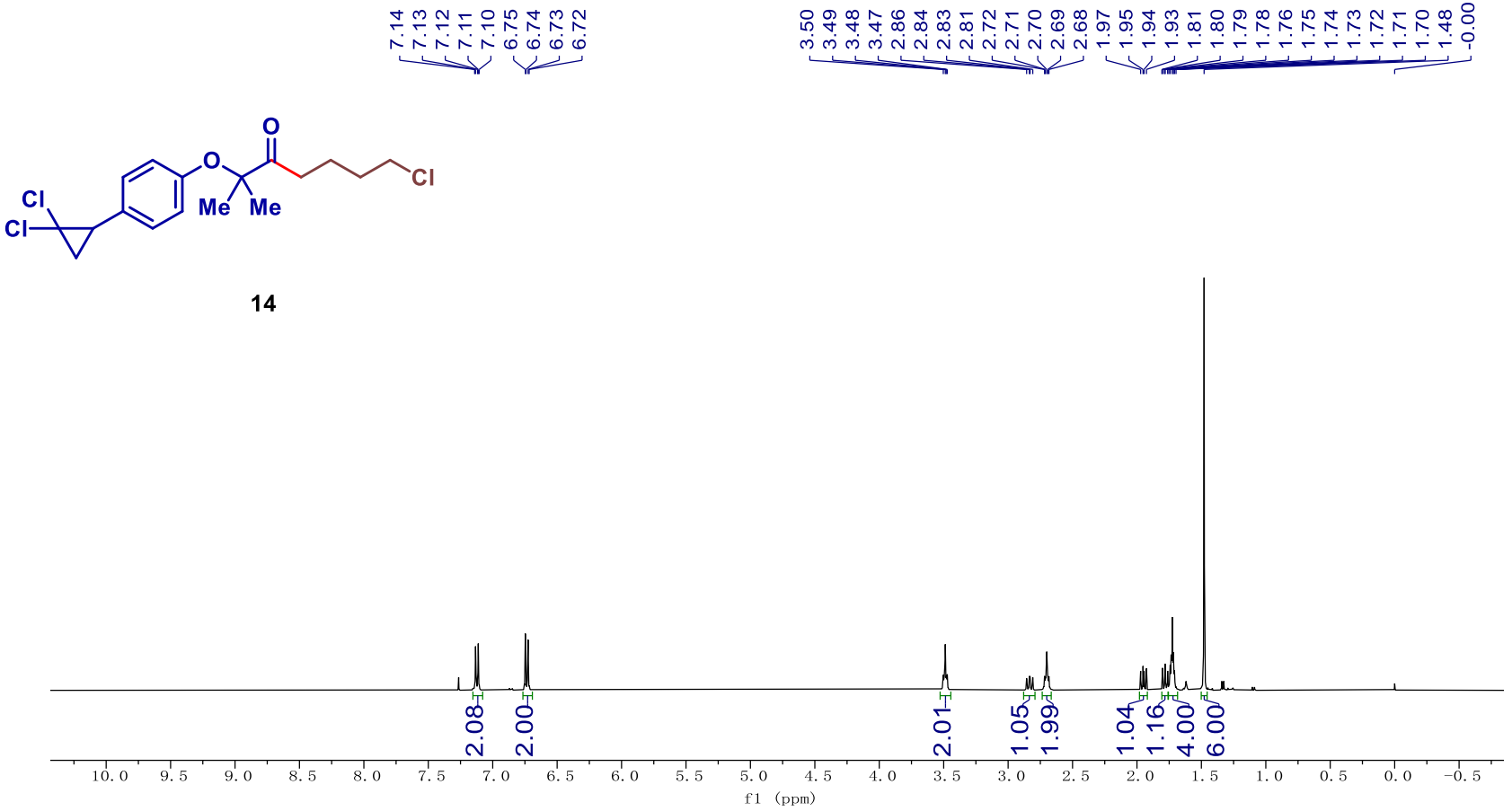
13

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



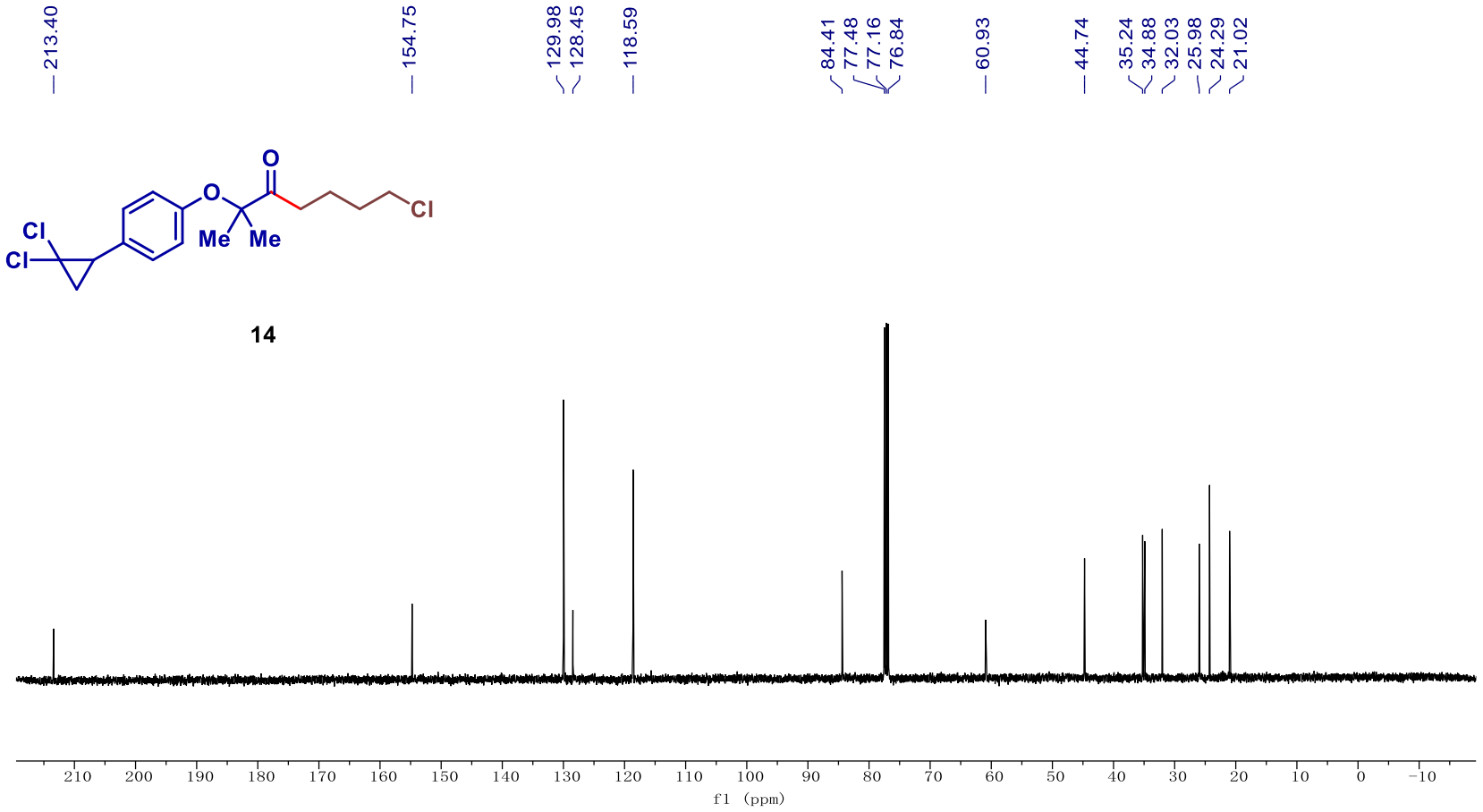
13

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

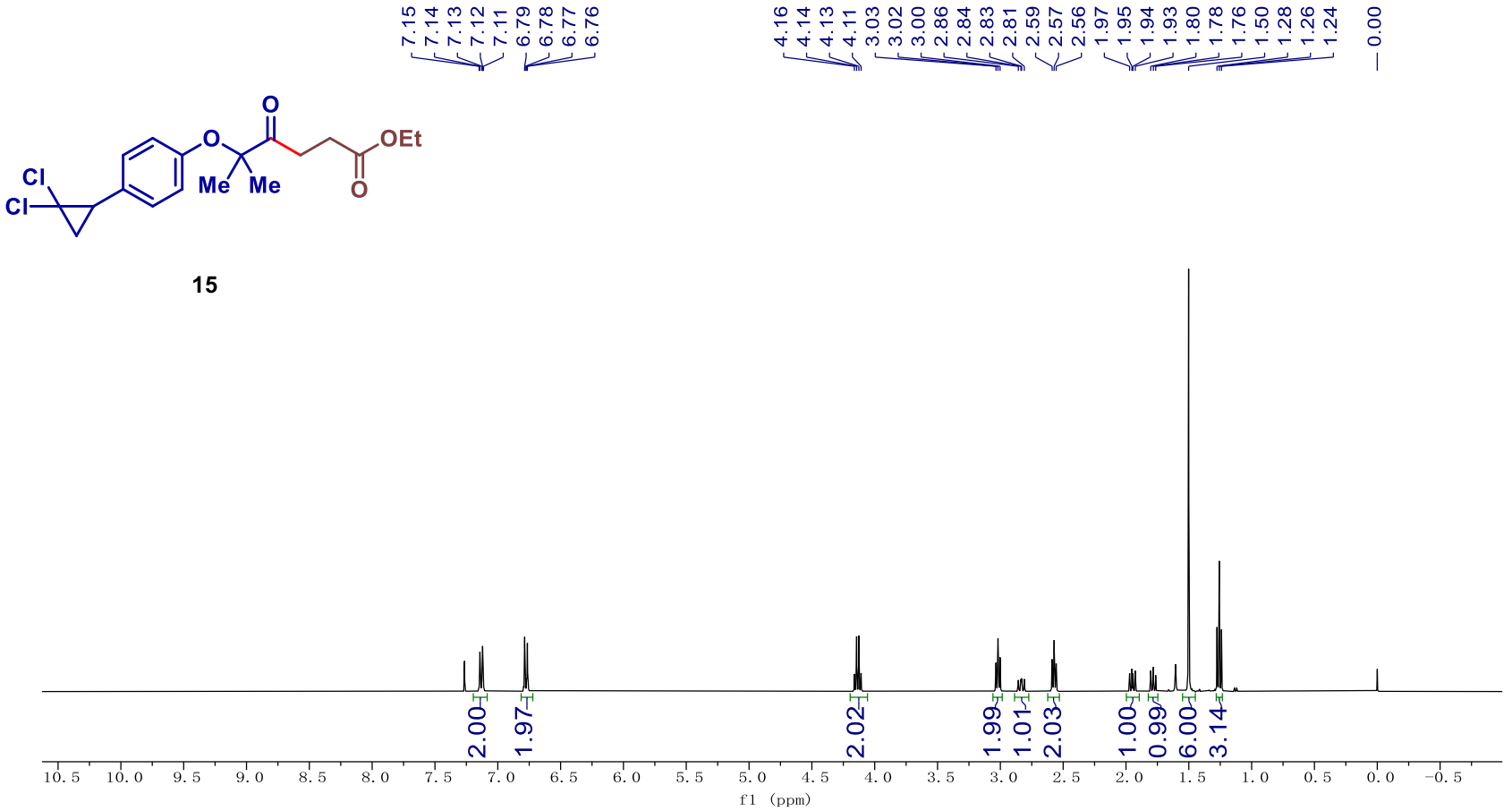


14

^{13}C NMR of 14 (101 MHz, $CDCl_3$)

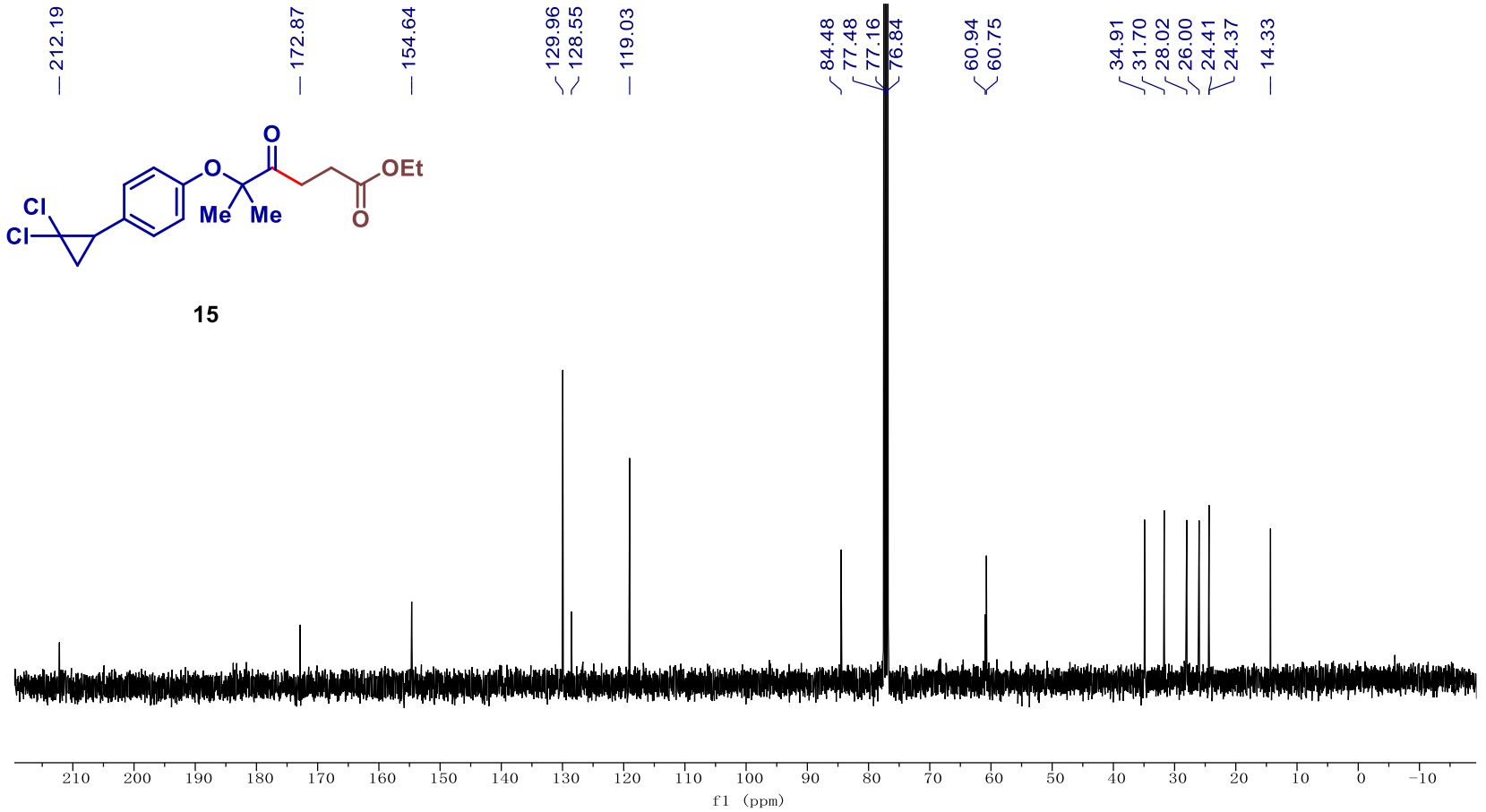


^{1}H NMR of 15 (400 MHz, $CDCl_3$)



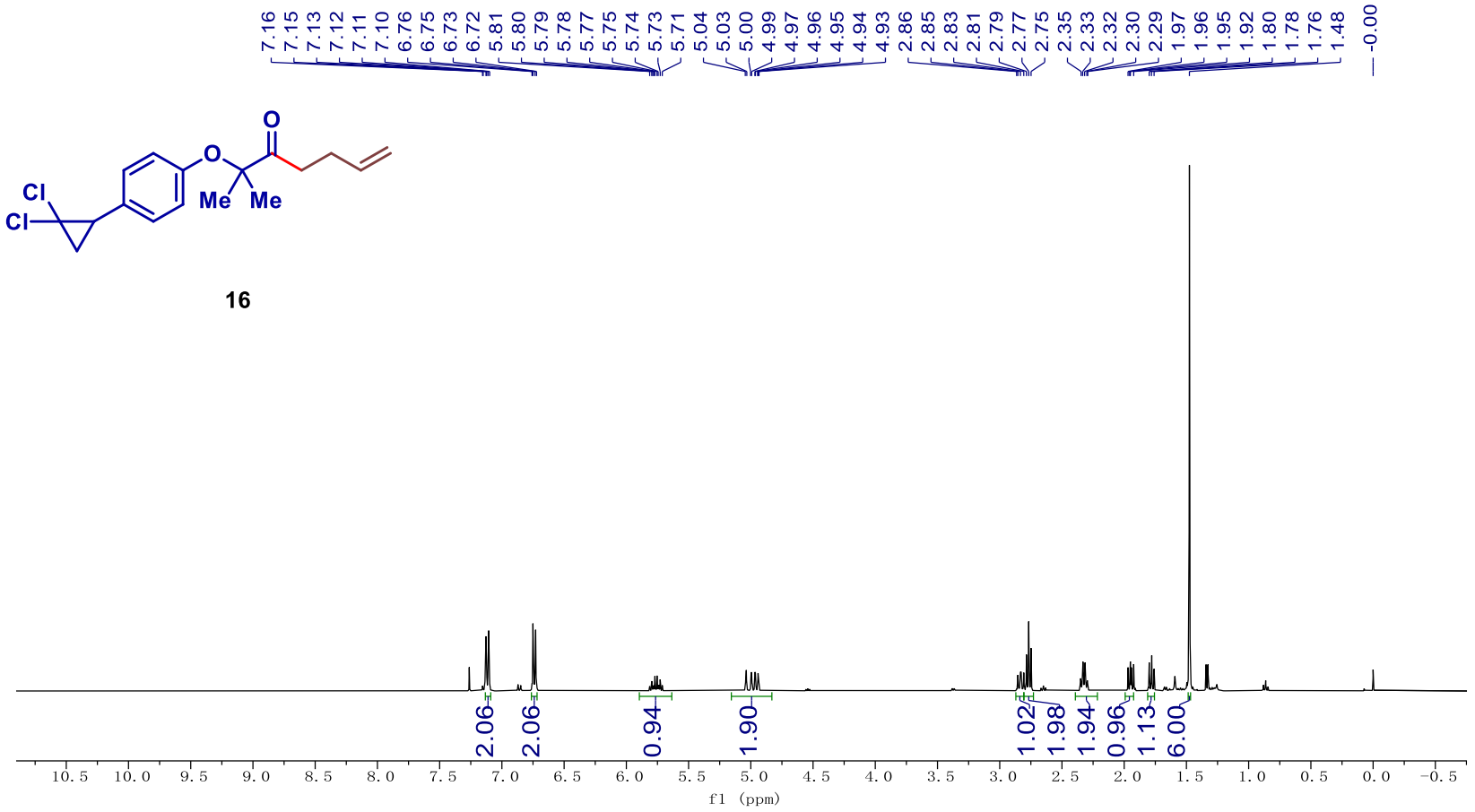
15

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

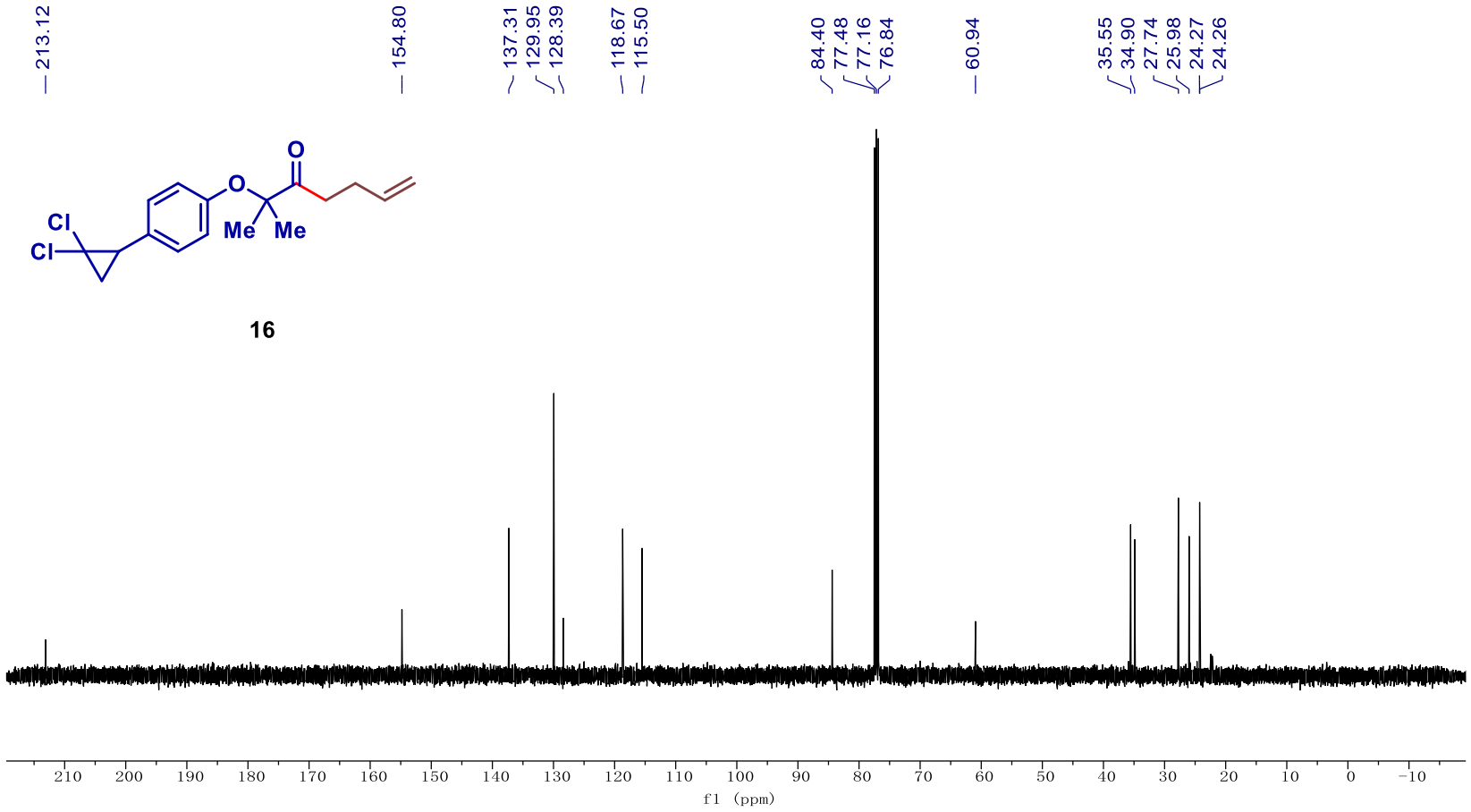


15

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

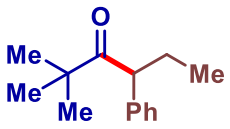


^{13}C NMR of 16 (101 MHz, $CDCl_3$)



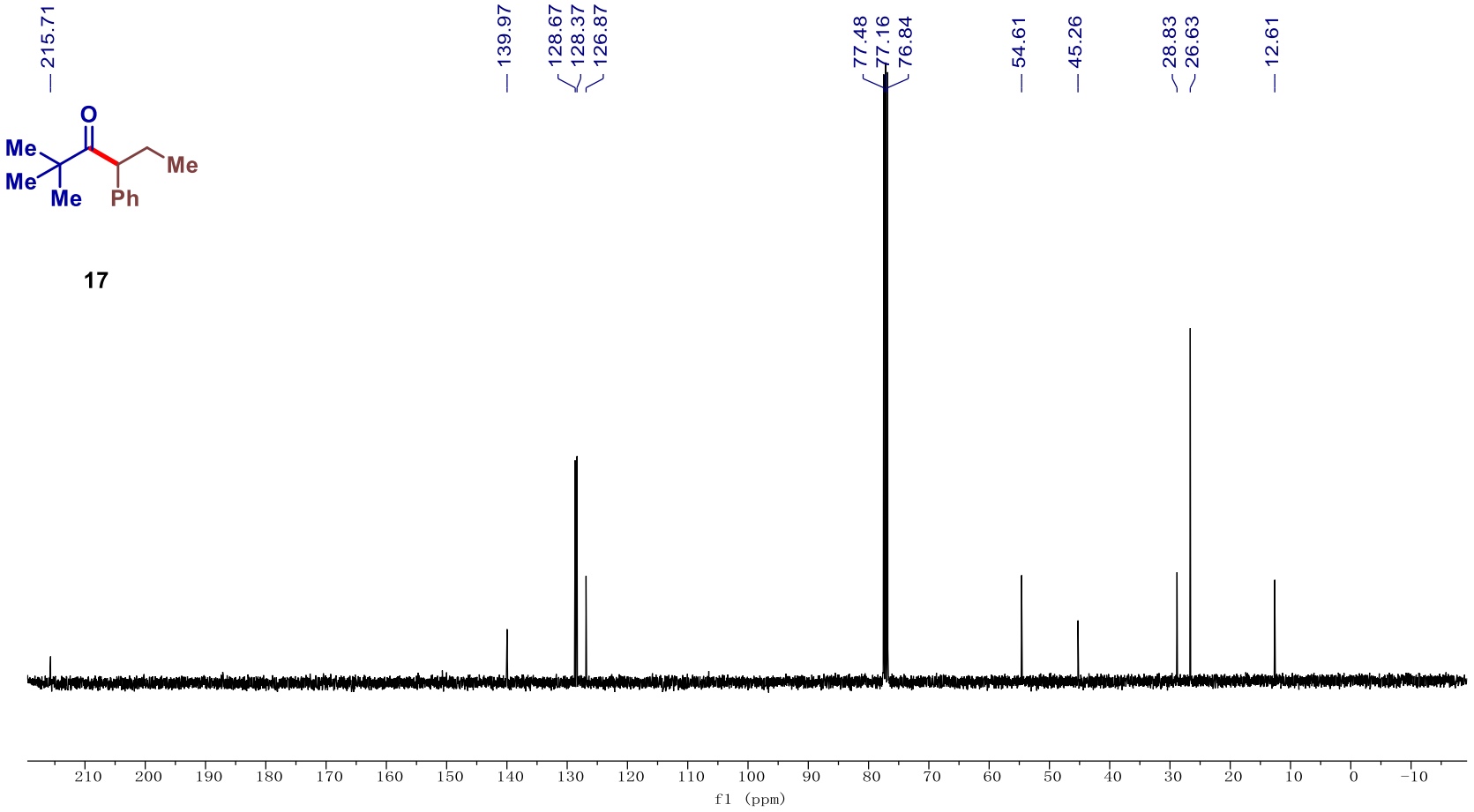
16

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



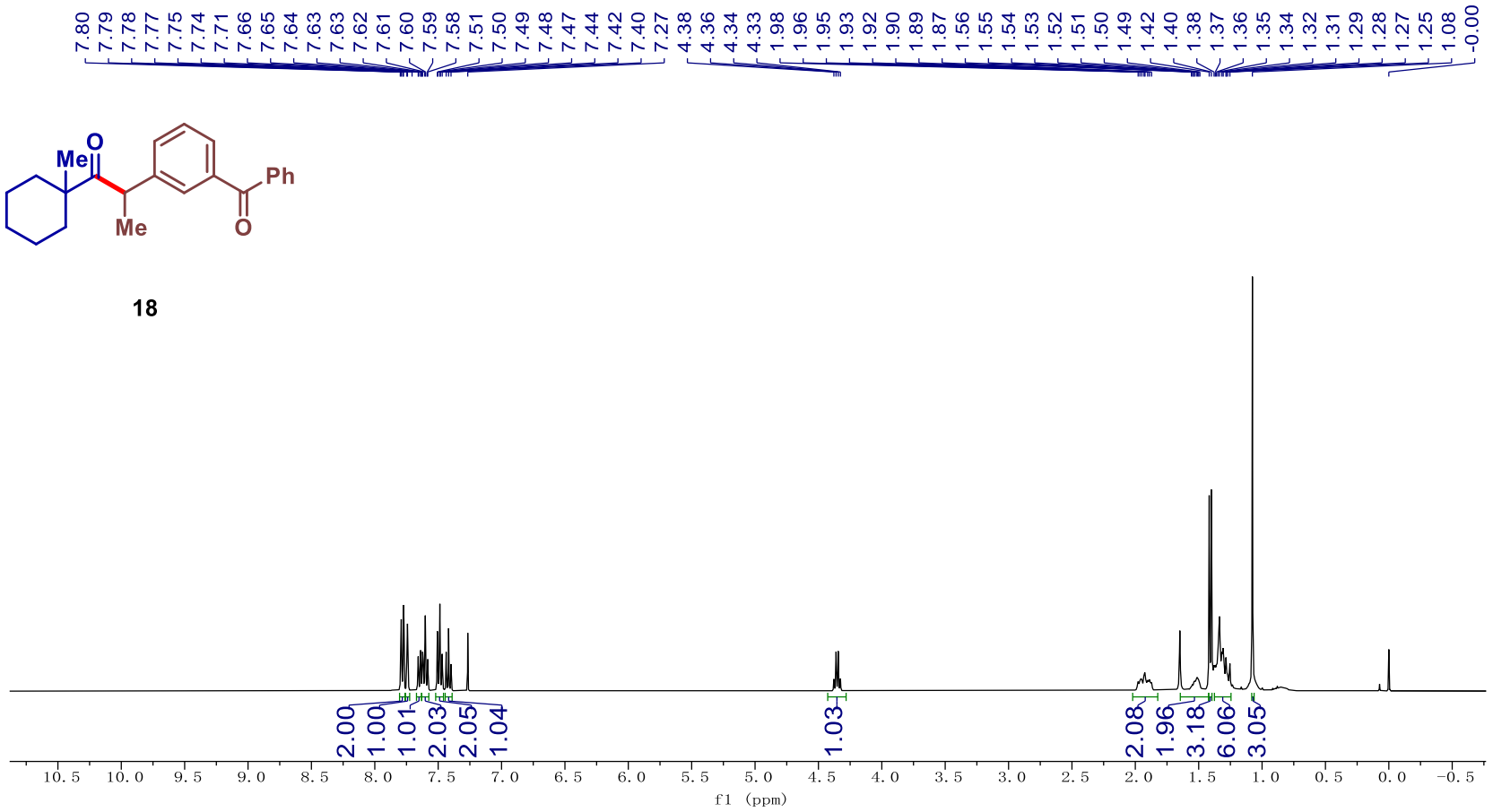
17

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



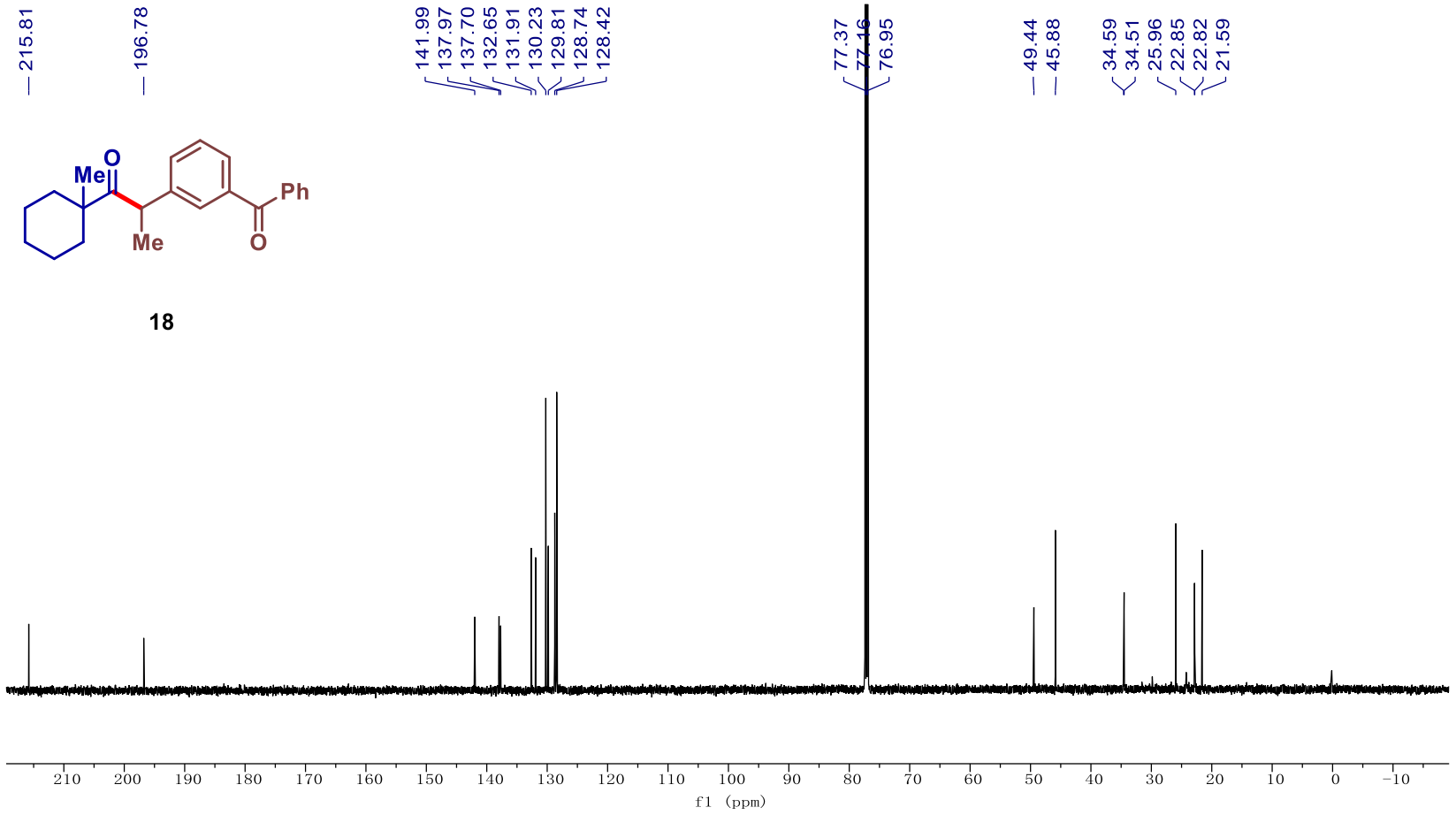
17

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



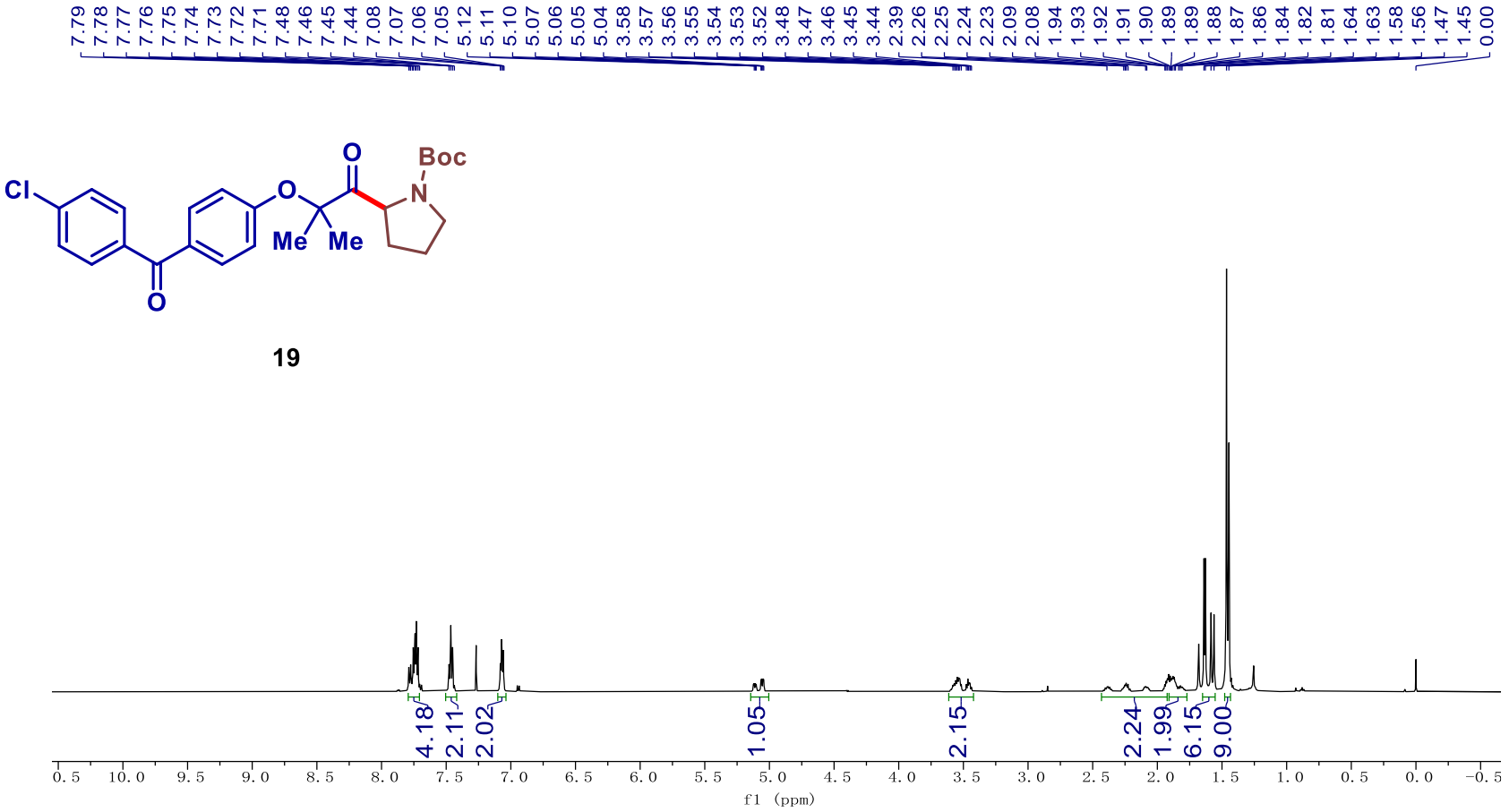
18

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



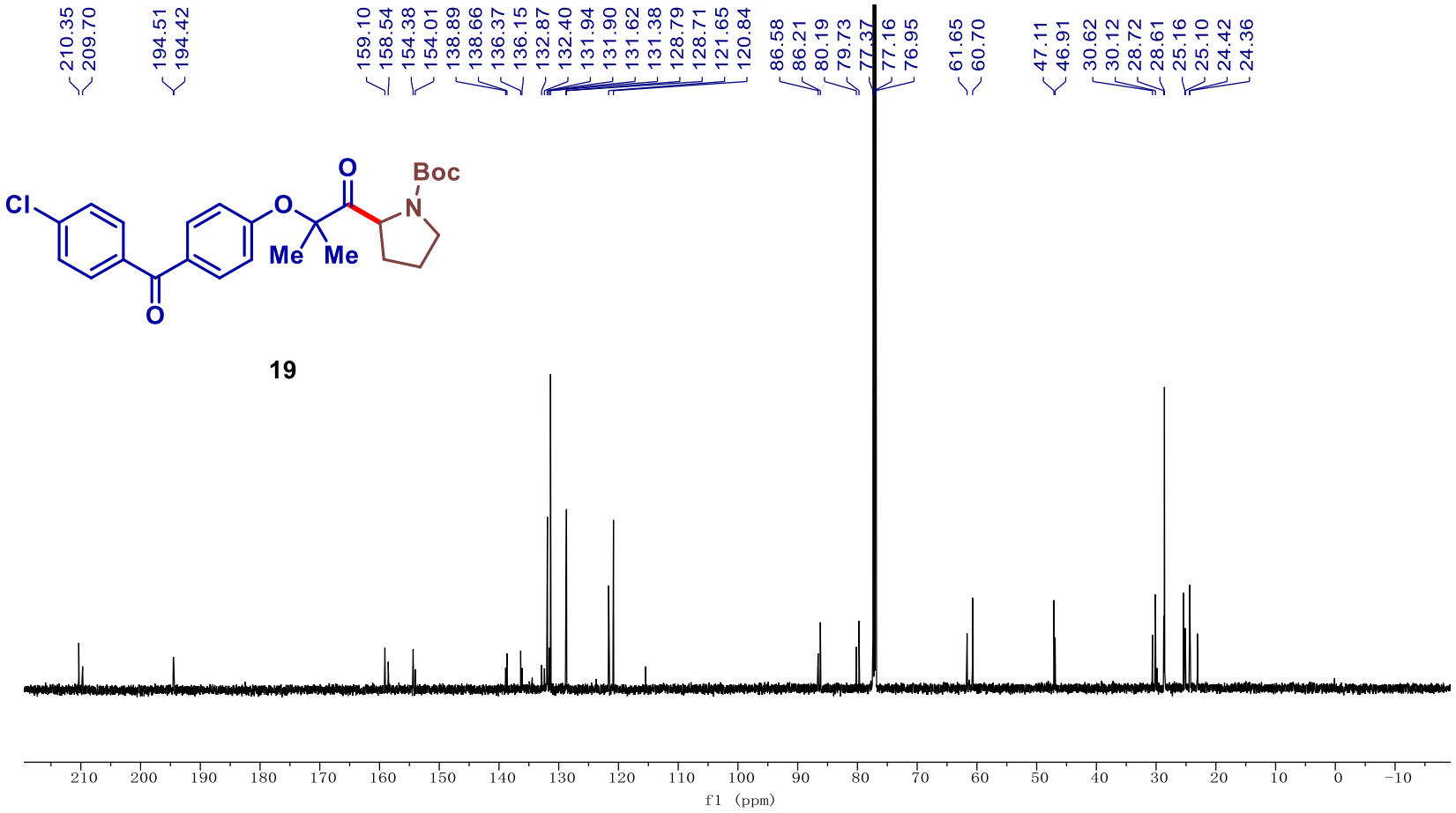
18

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

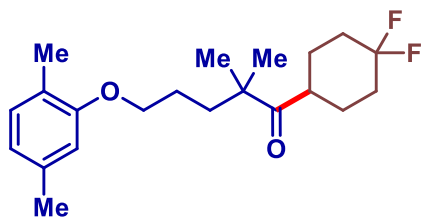


19

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

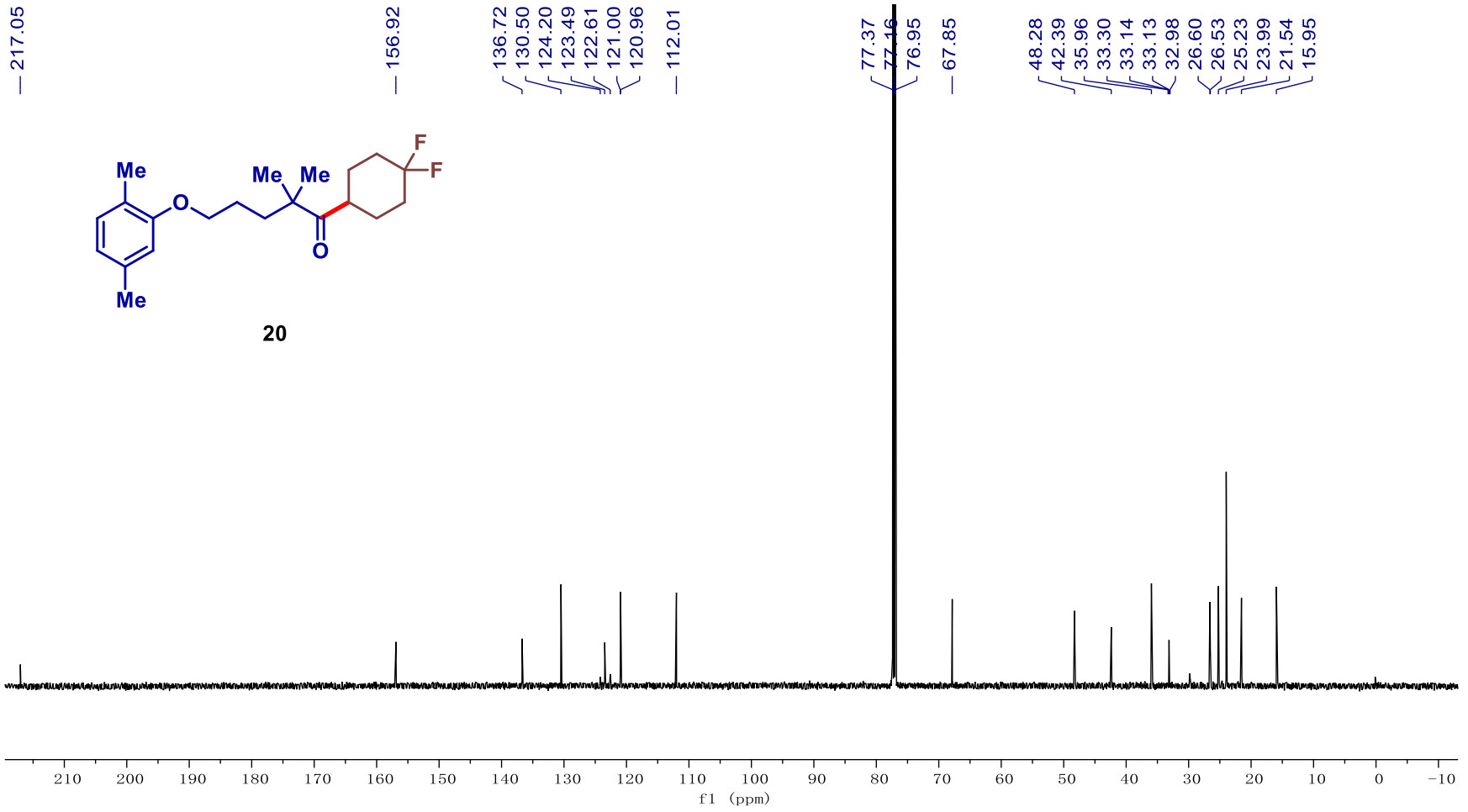


^{1}H NMR of 20 (600 MHz, $CDCl_3$)



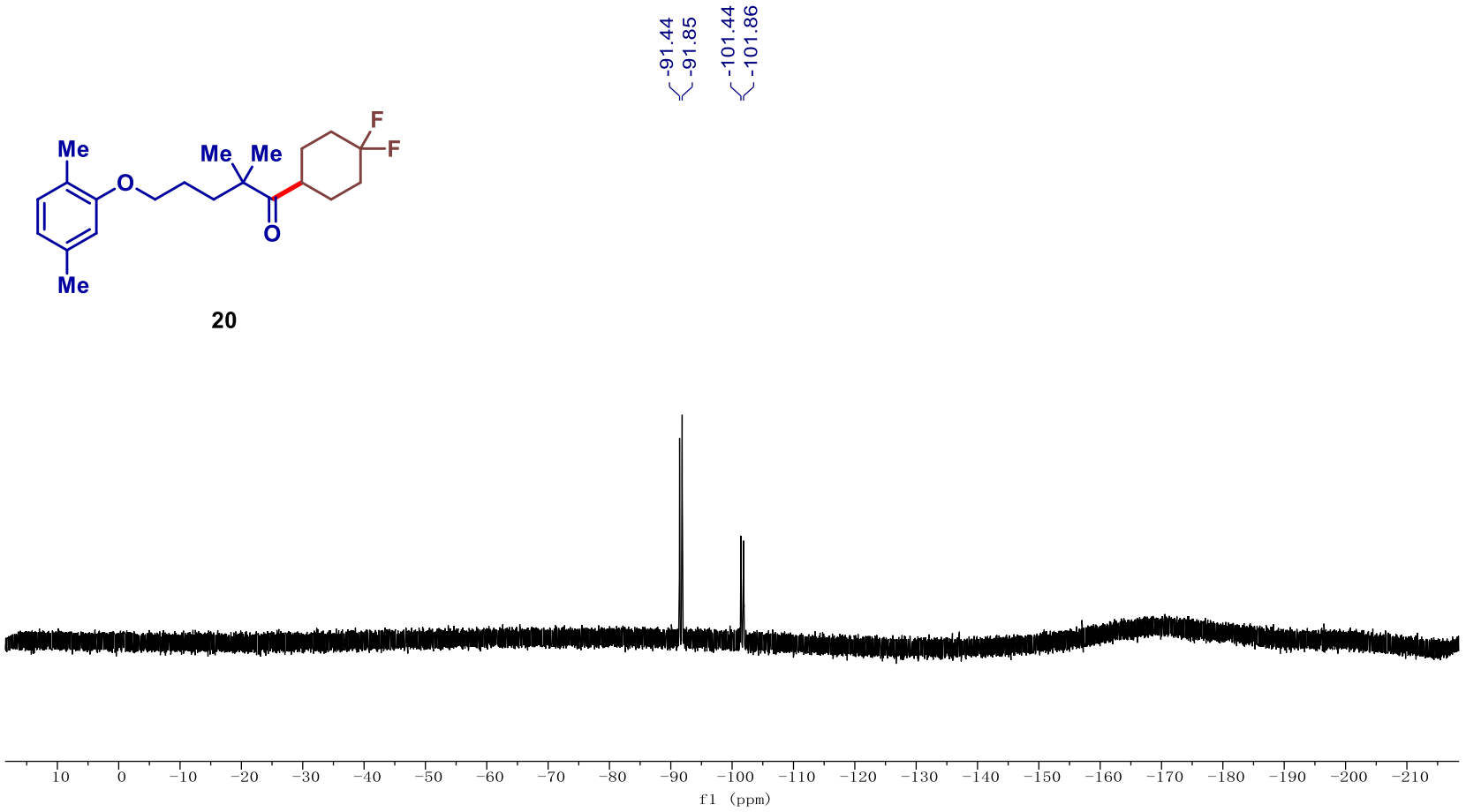
20

^{13}C NMR of 20 (151 MHz, $CDCl_3$)



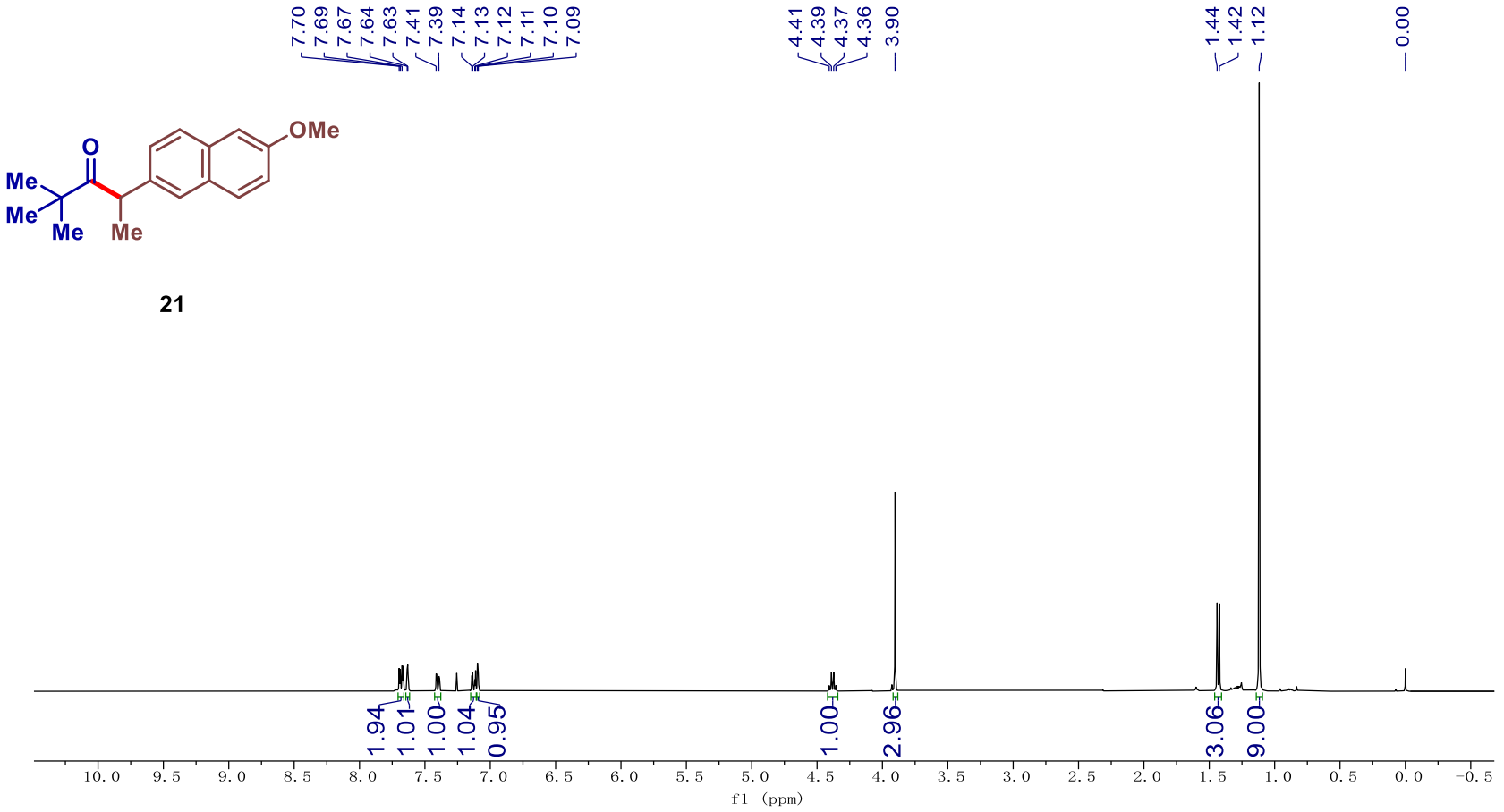
20

^{19}F NMR of 20 (565 MHz, $CDCl_3$)



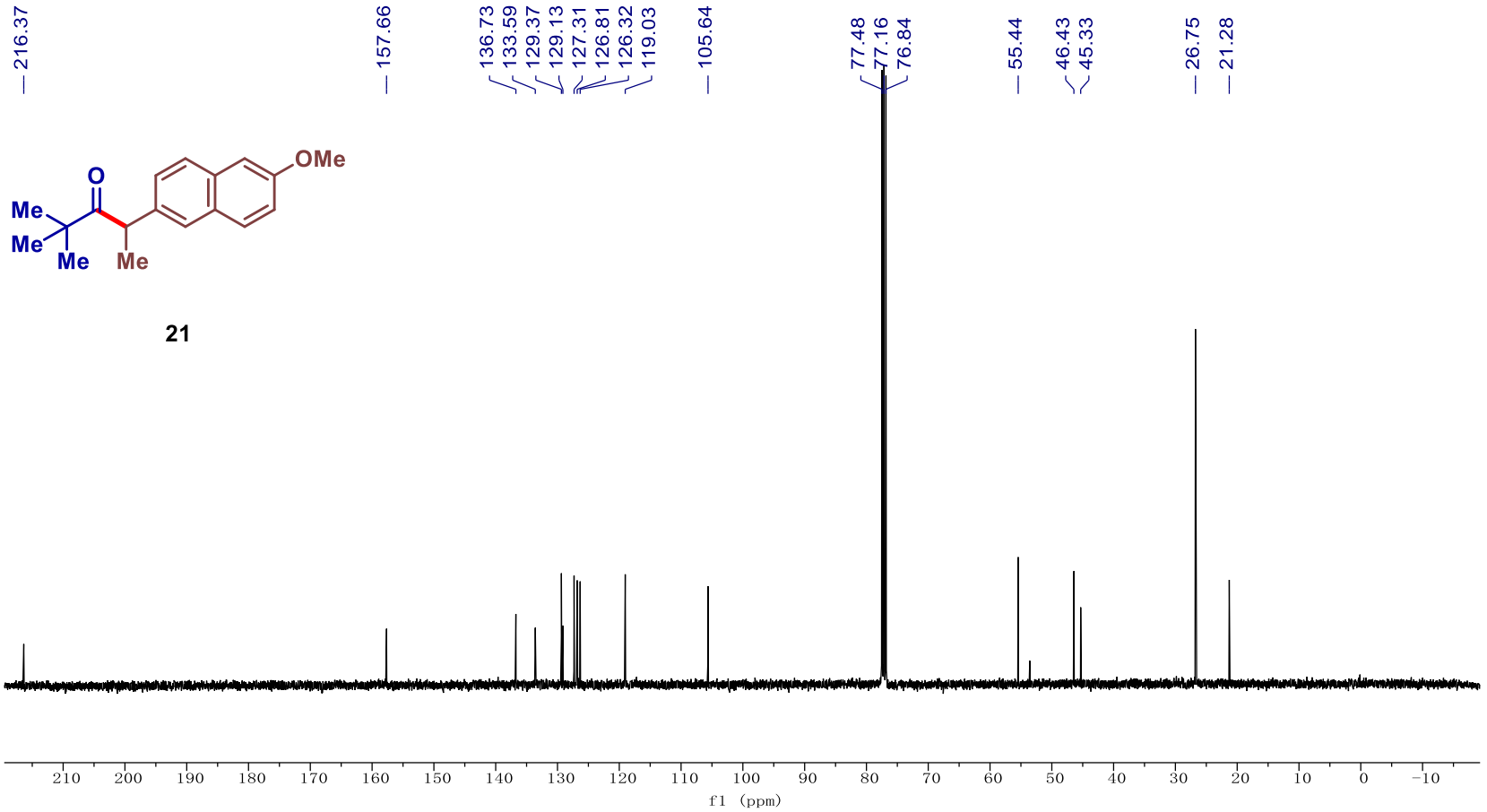
20

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



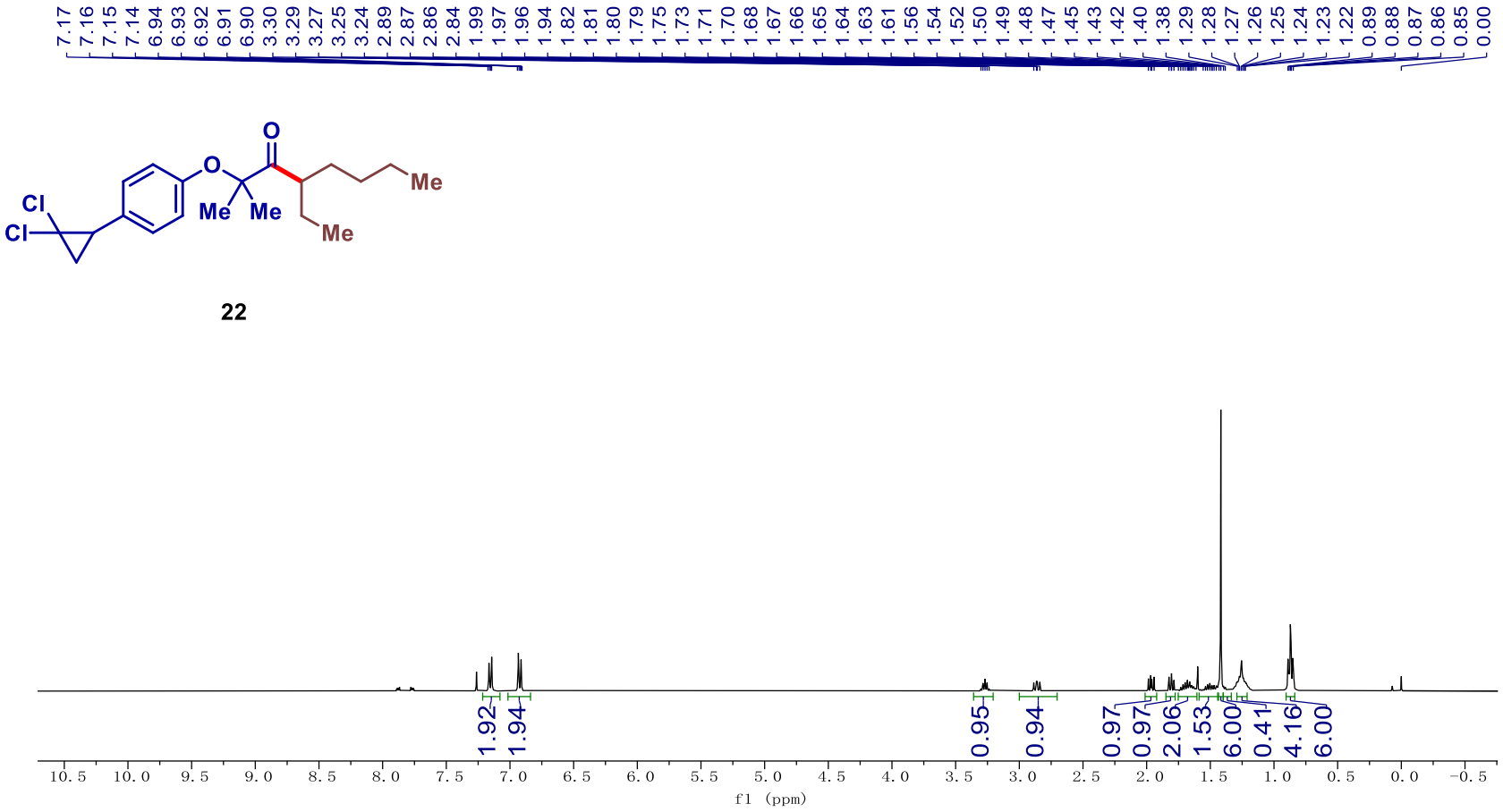
21

^{13}C NMR of 21 (101 MHz, $CDCl_3$)



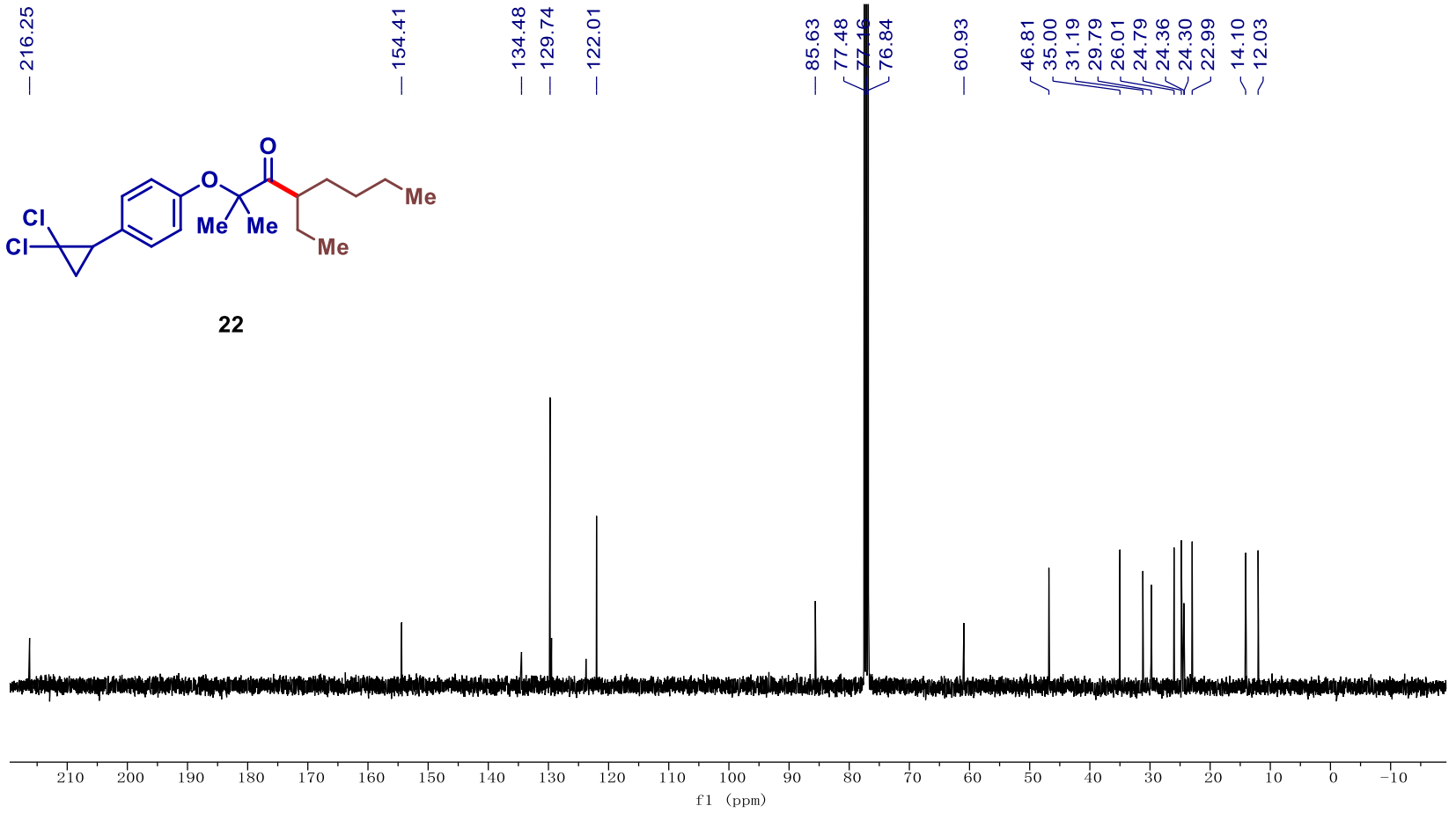
21

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



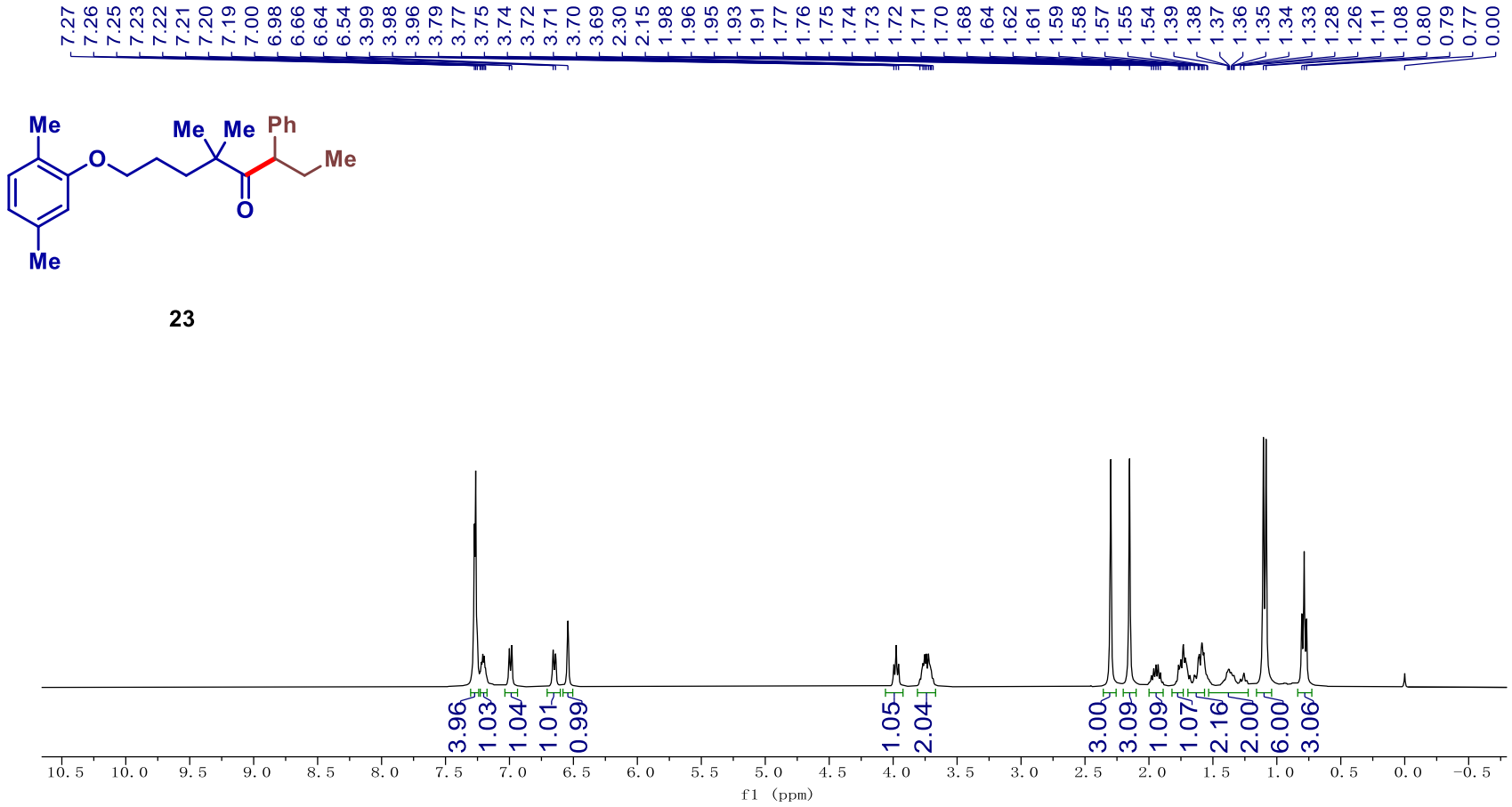
22

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



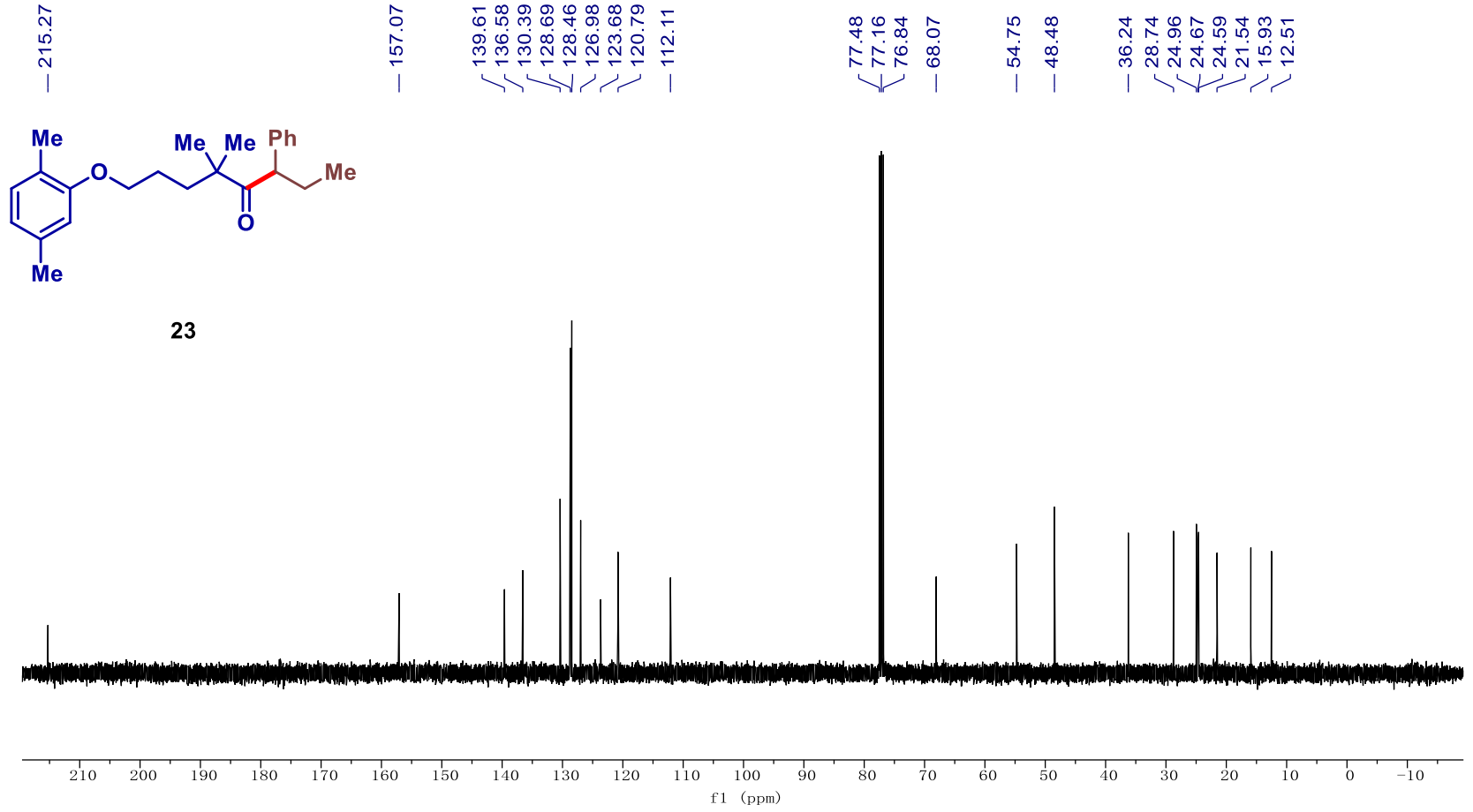
22

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

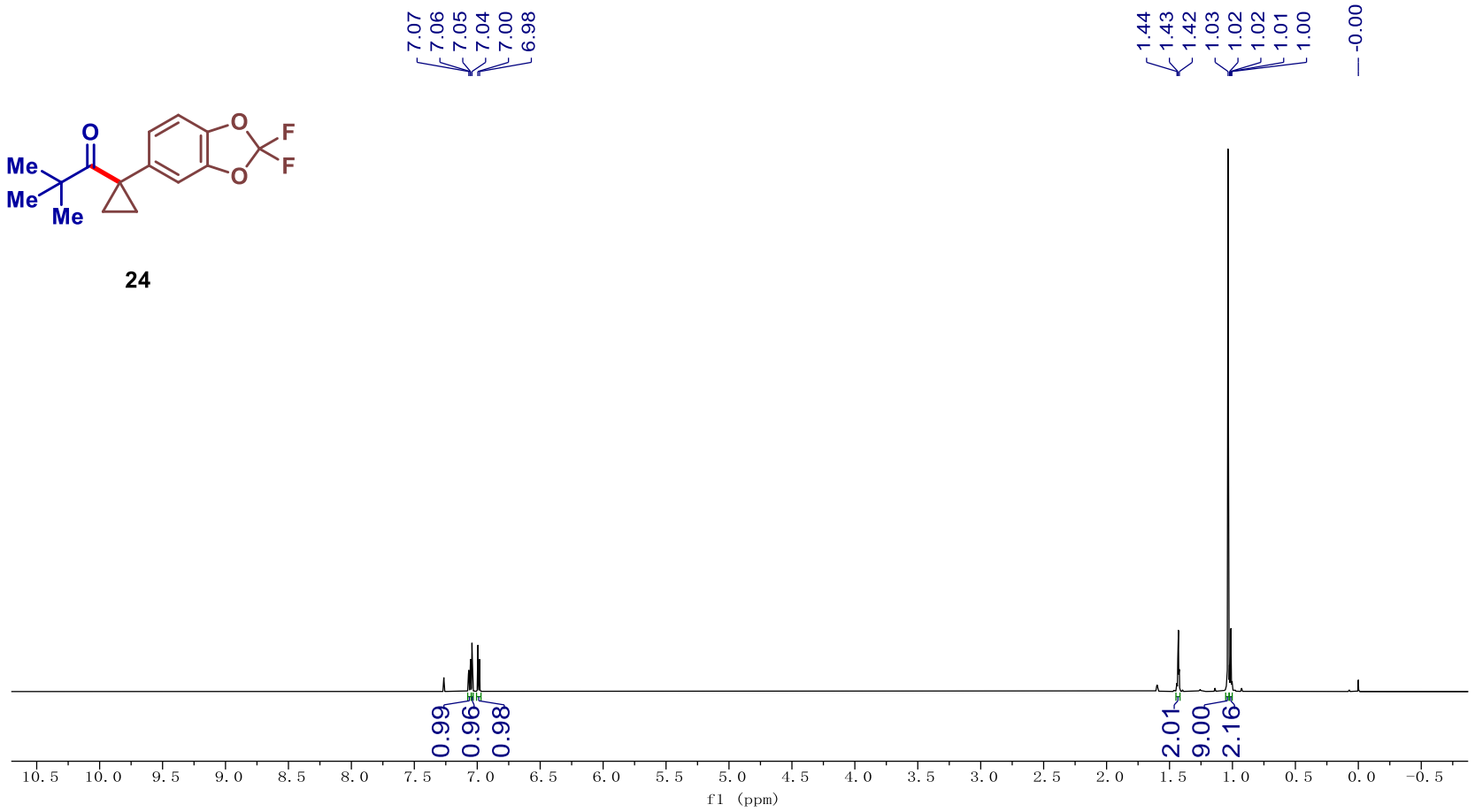


23

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

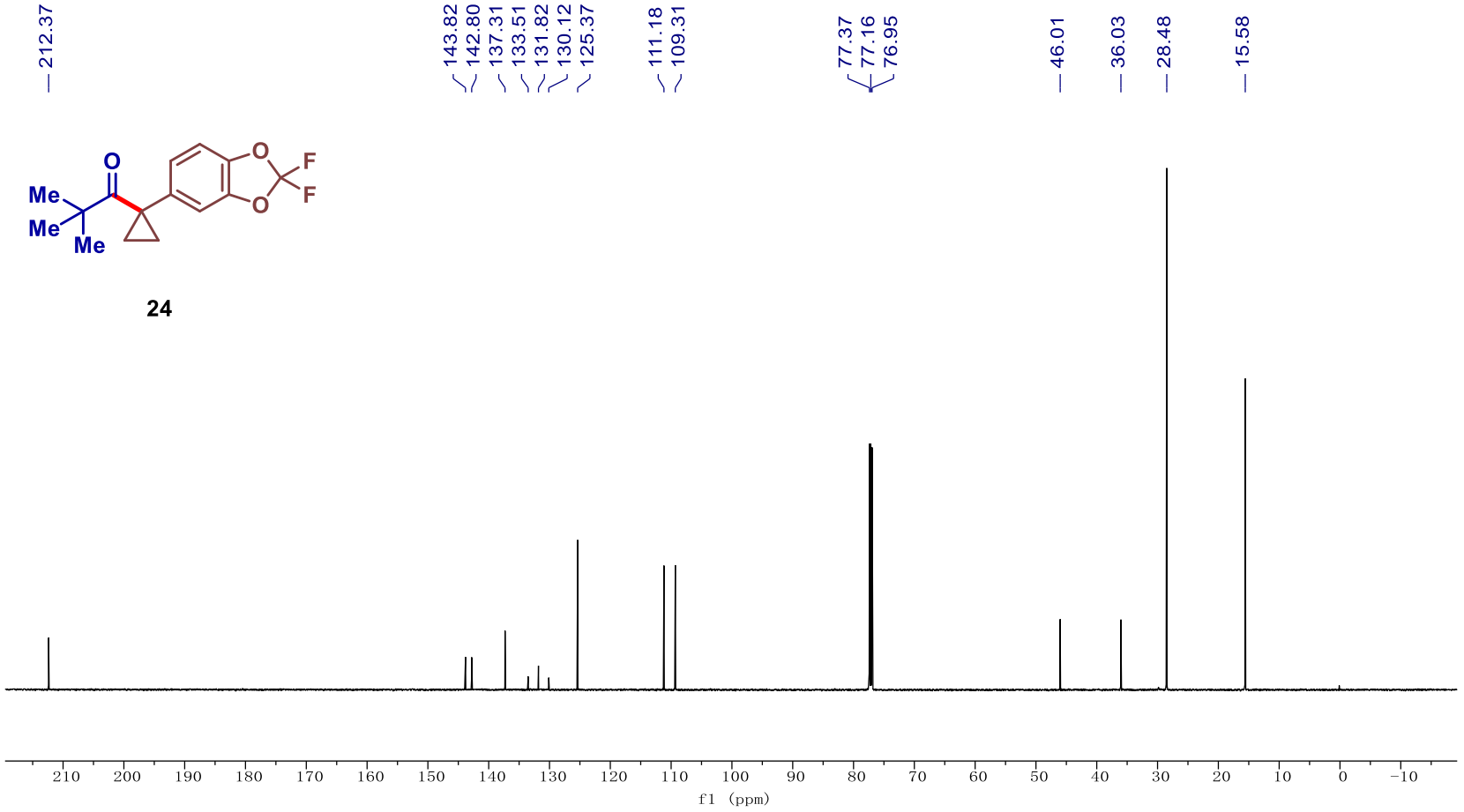


^{1}H NMR of 24 (600 MHz, $CDCl_3$)



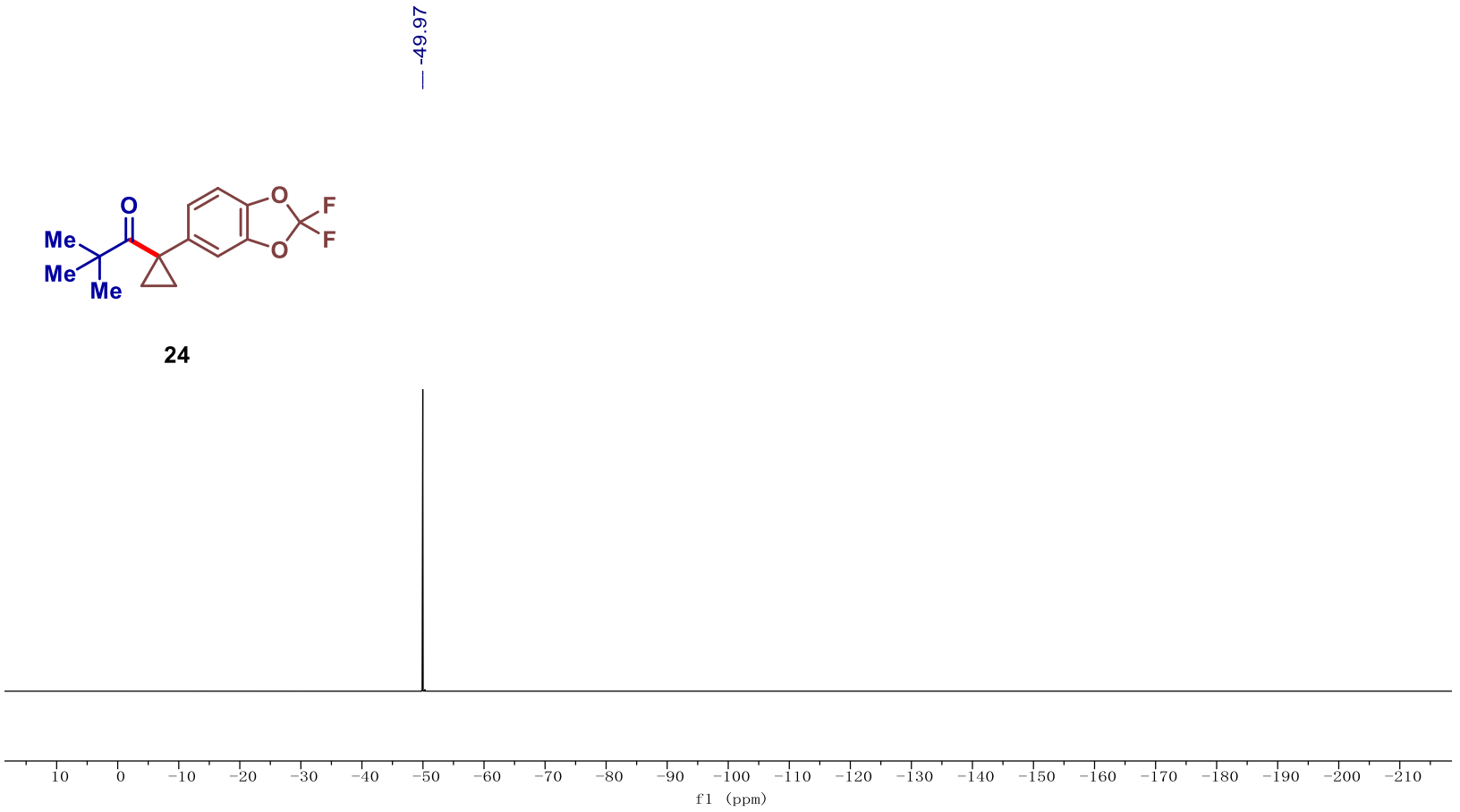
24

^{13}C NMR of 24 (151 MHz, $CDCl_3$)



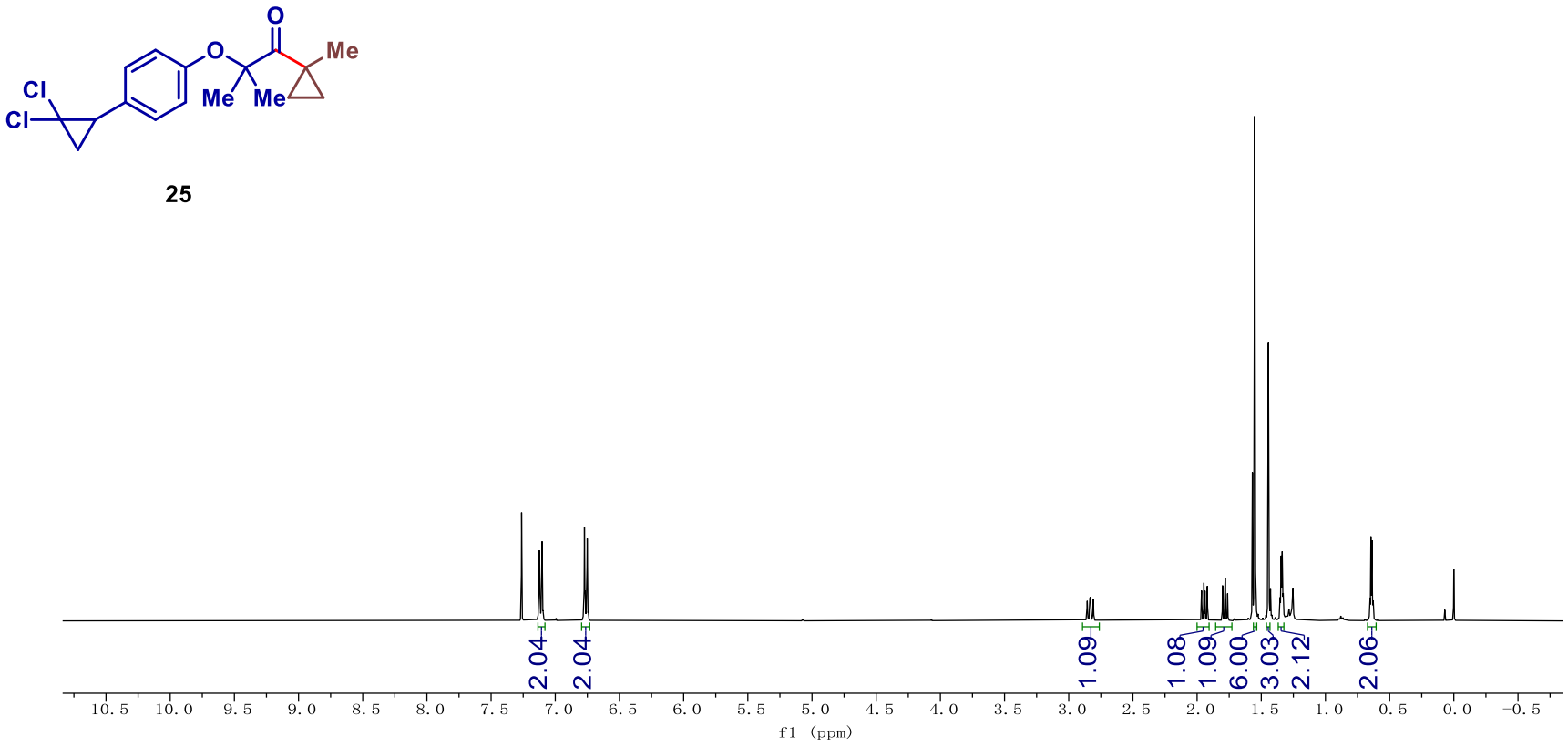
24

^{19}F NMR of 24 (565 MHz, $CDCl_3$)



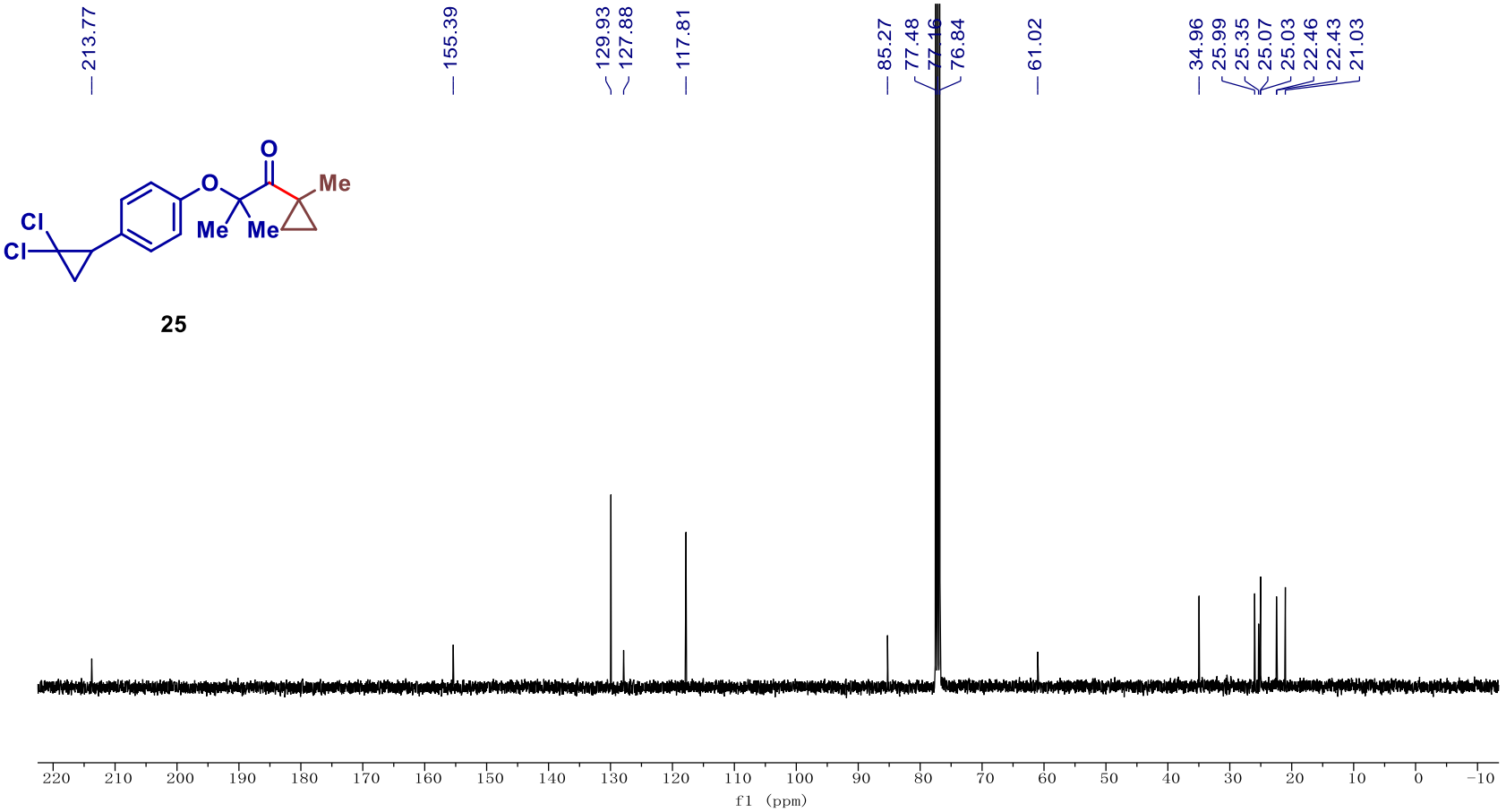
24

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



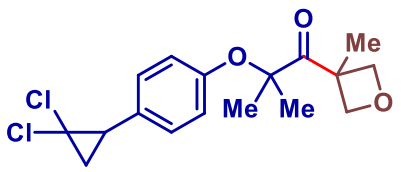
25

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



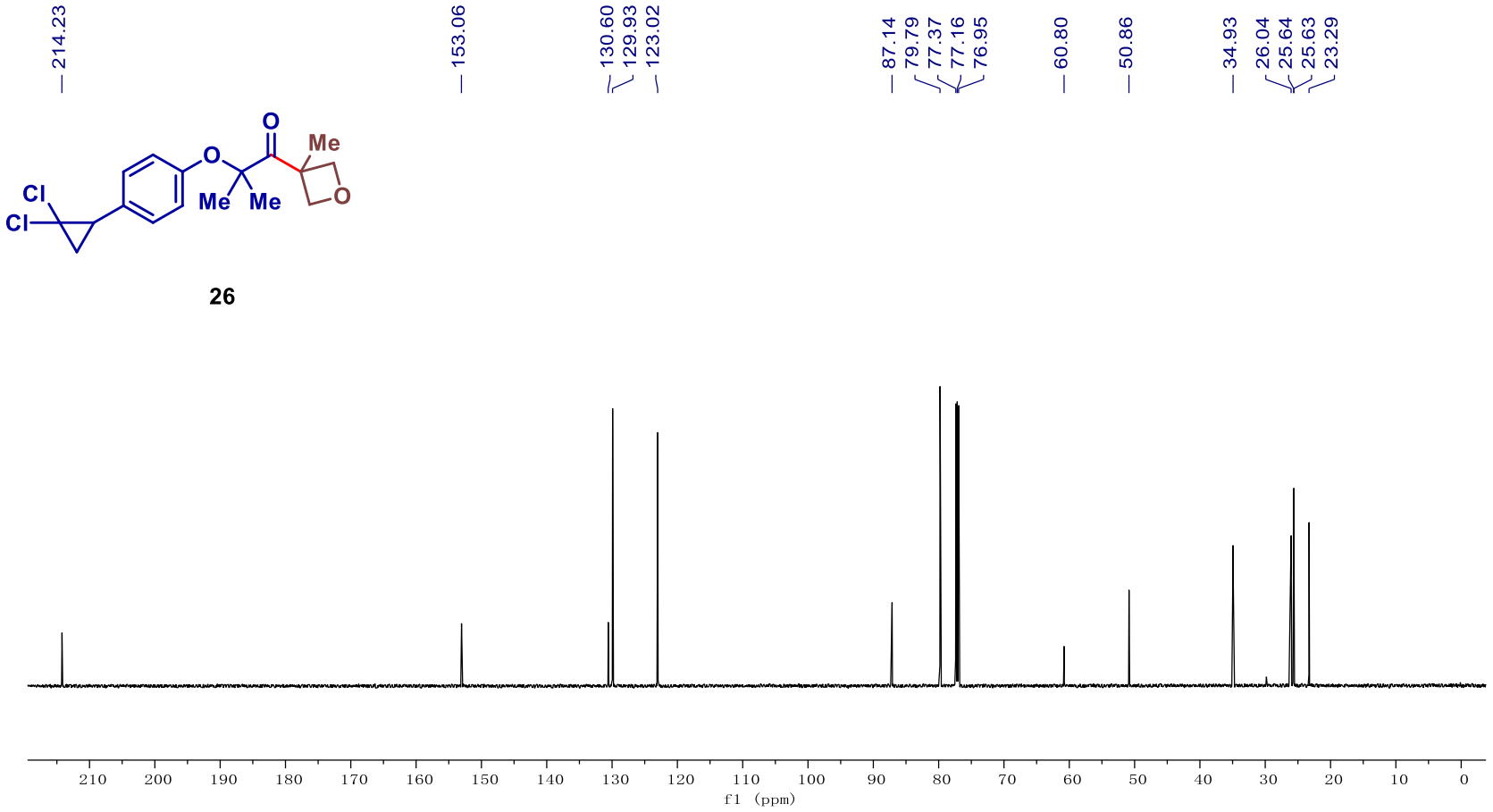
25

^{1}H NMR of 26 (600 MHz, $CDCl_3$)



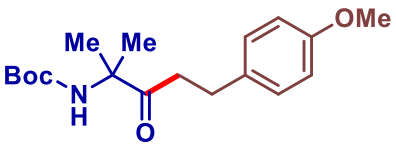
26

^{13}C NMR of 26 (151 MHz, $CDCl_3$)



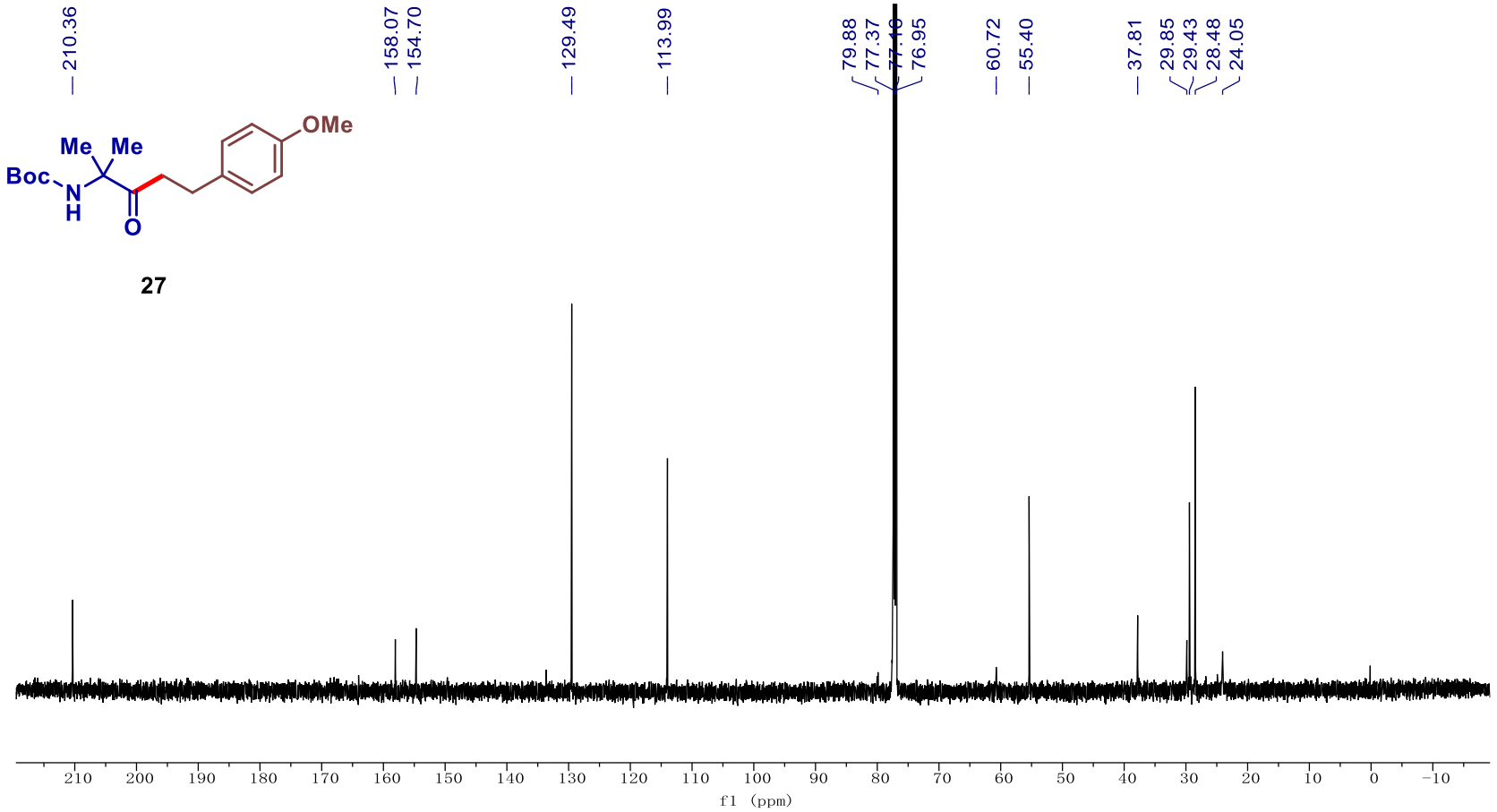
26

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



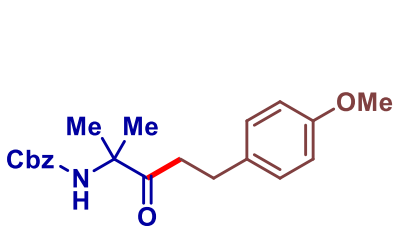
27

^{13}C NMR of 27 (151 MHz, $CDCl_3$)



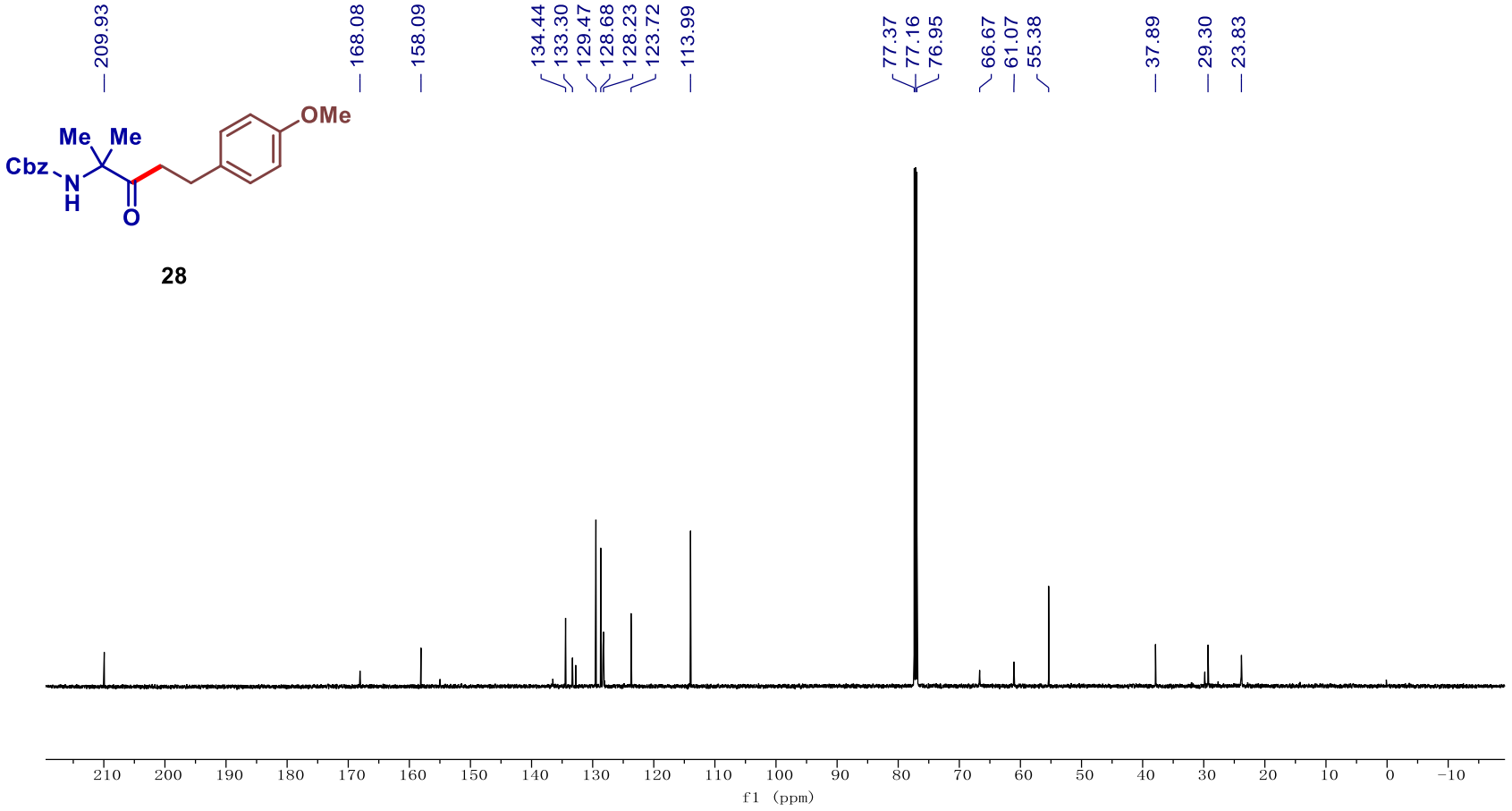
27

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



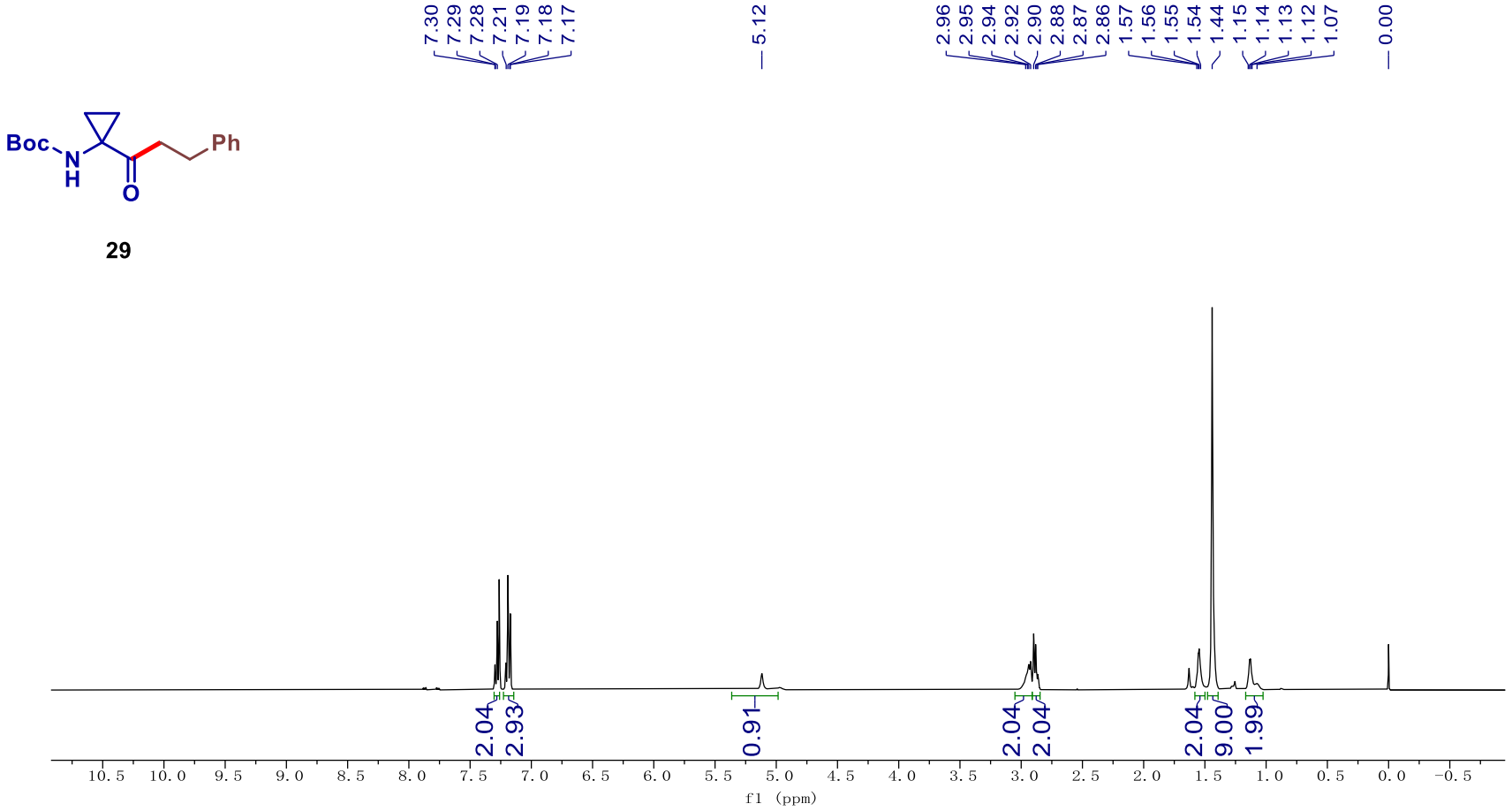
28

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



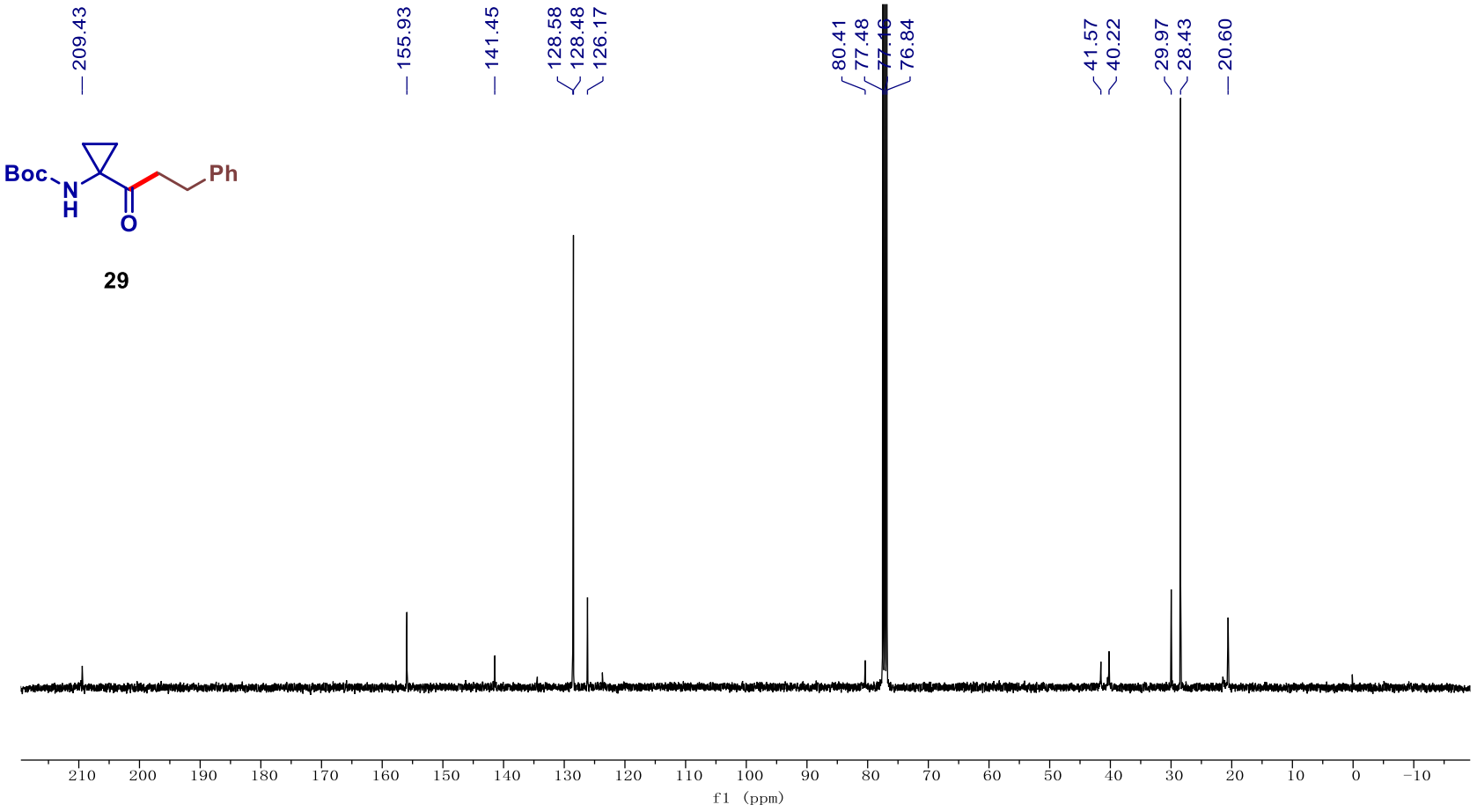
28

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

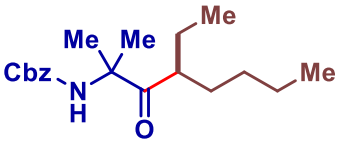


29

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

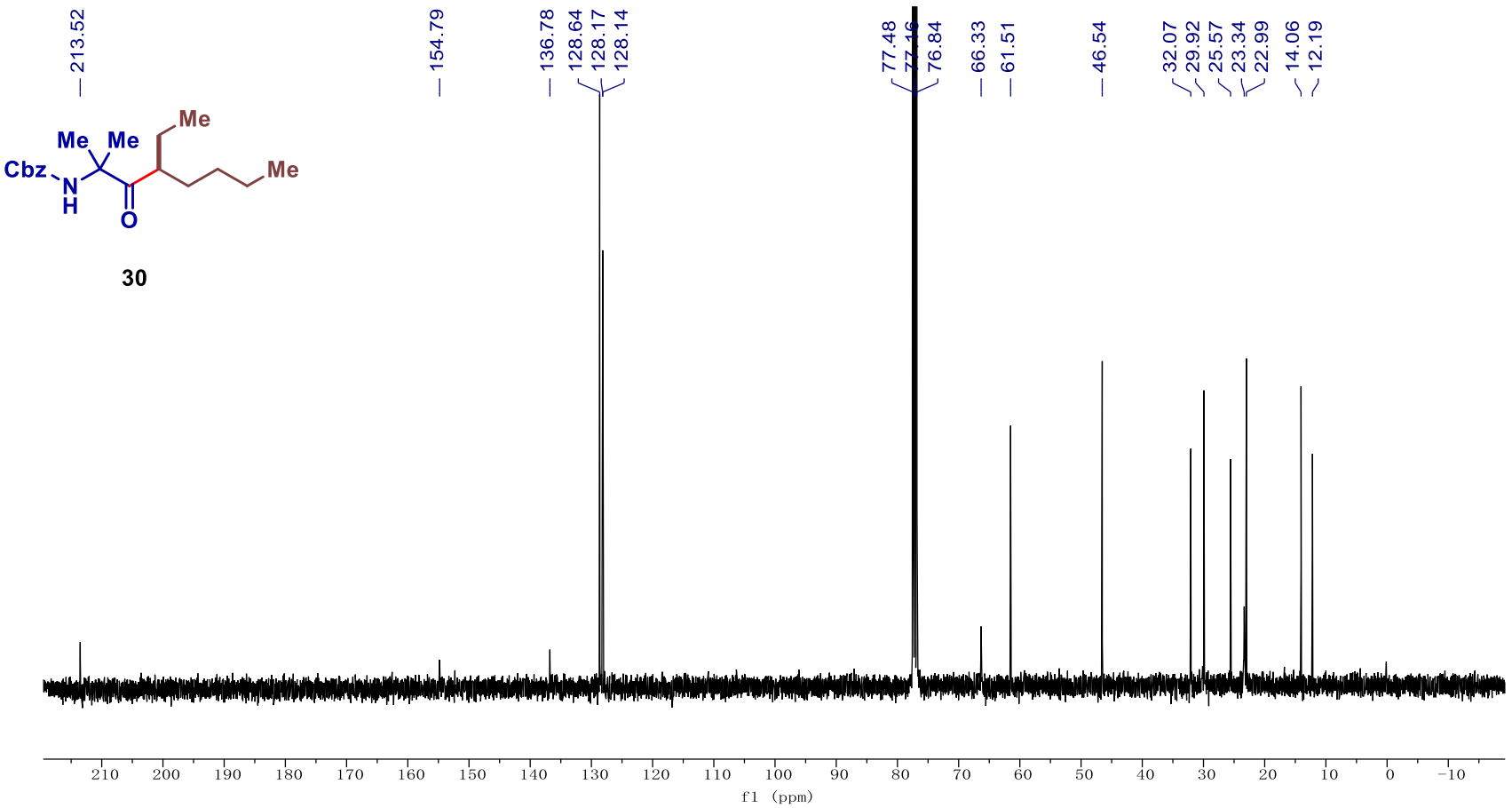


^{1}H NMR of 30 (400 MHz, $CDCl_3$)



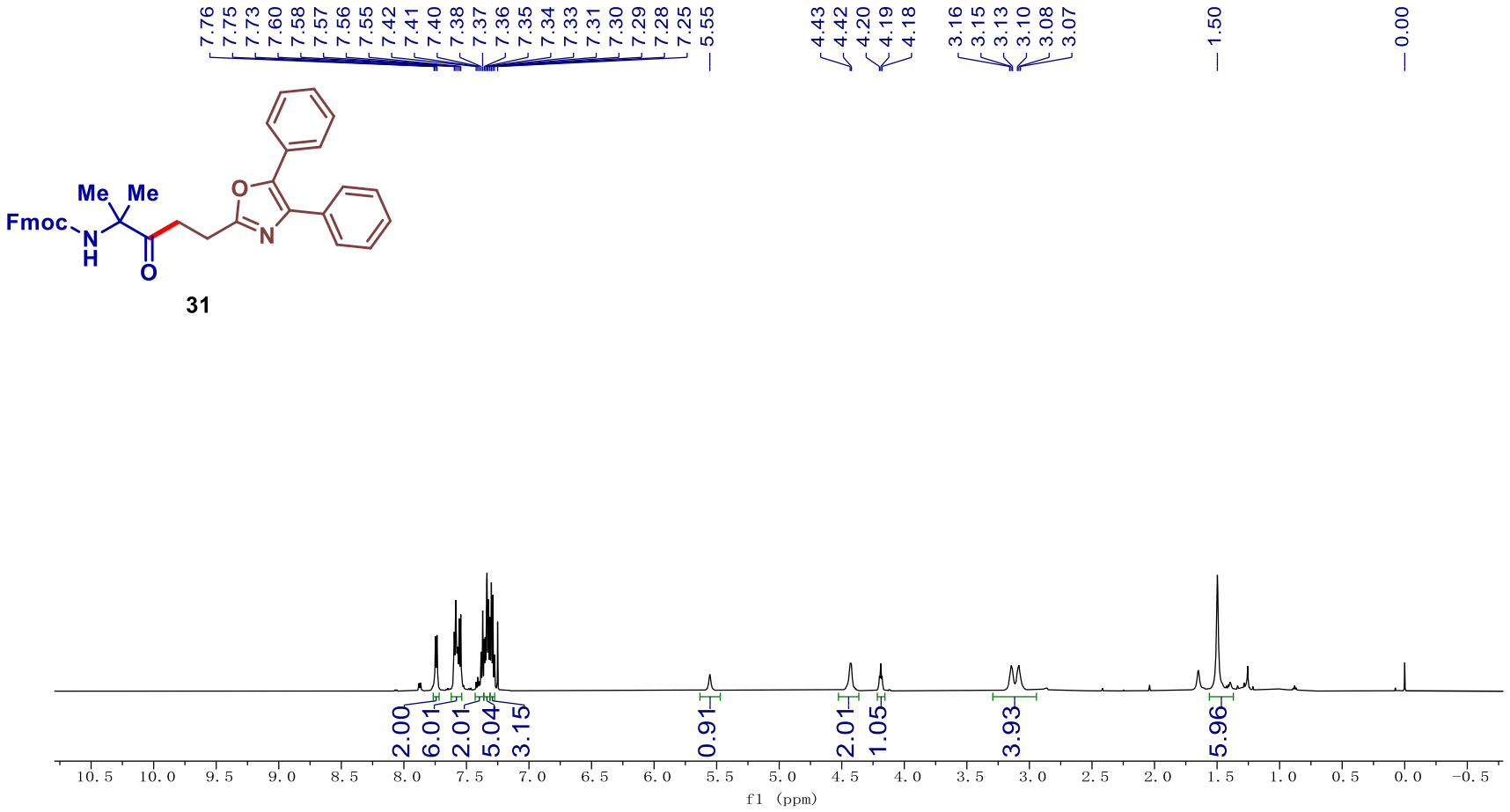
30

^{13}C NMR of 30 (101 MHz, $CDCl_3$)



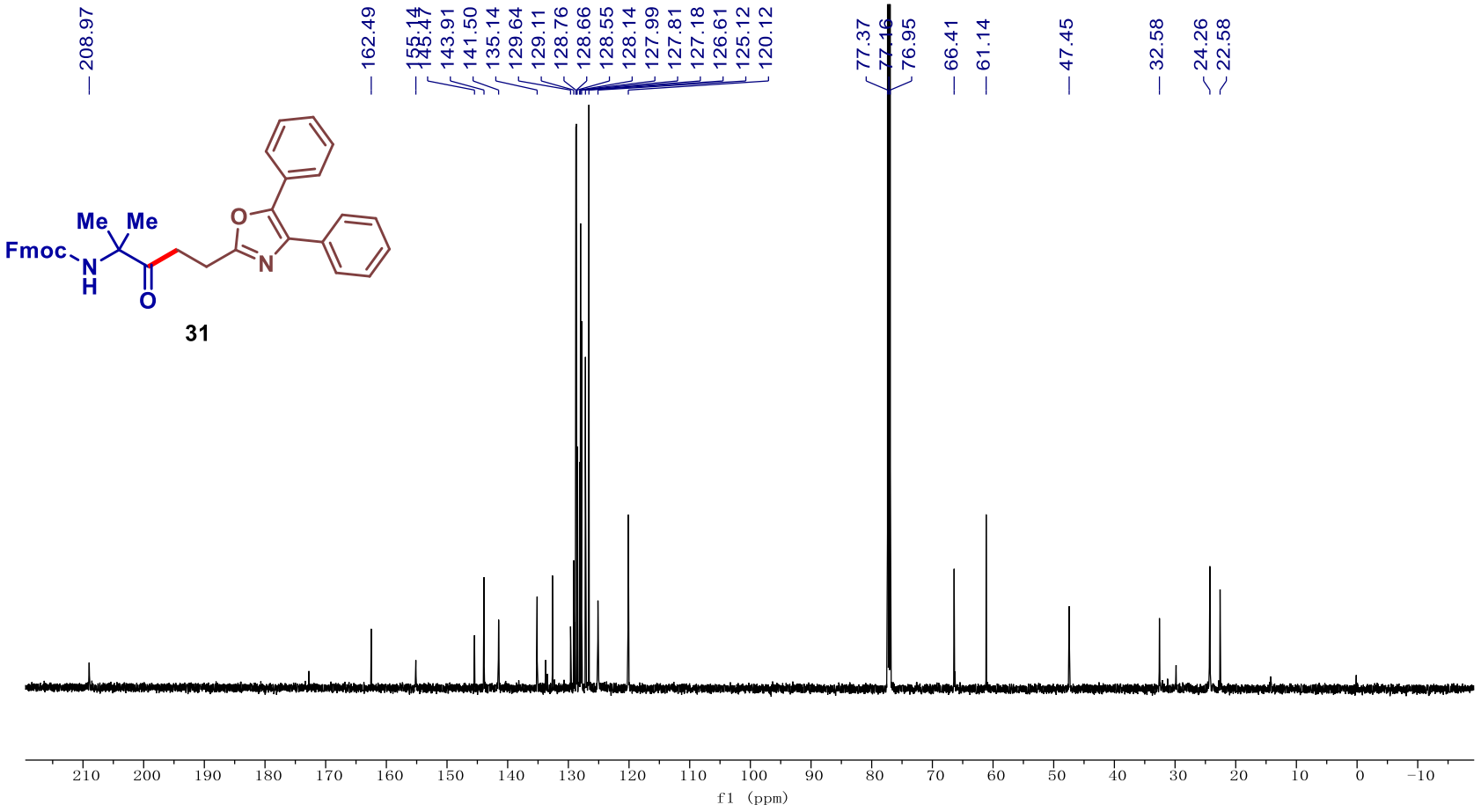
30

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

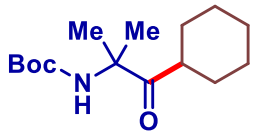


31

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

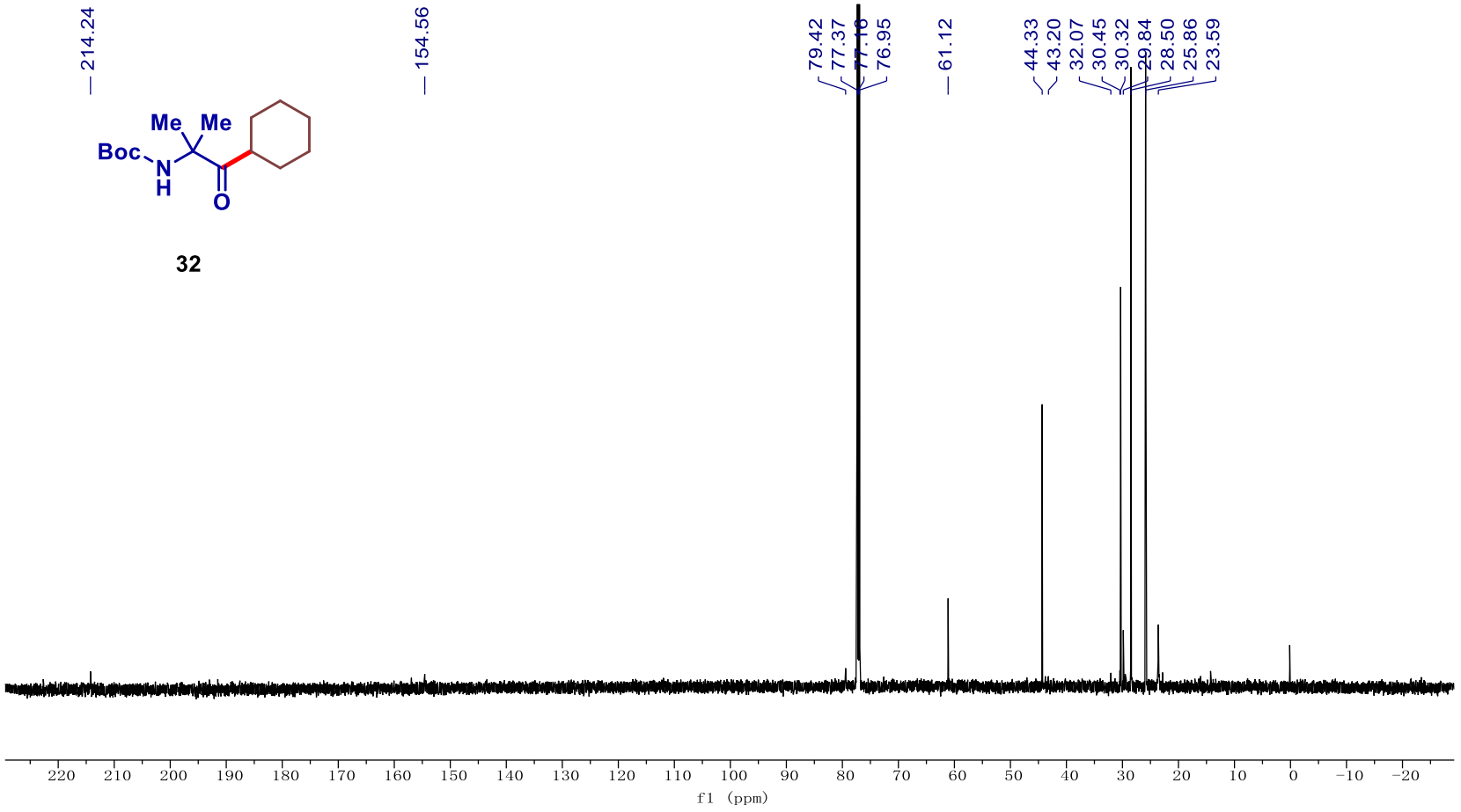


^{1}H NMR of 32 (400 MHz, $CDCl_3$)



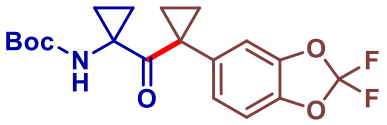
32

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



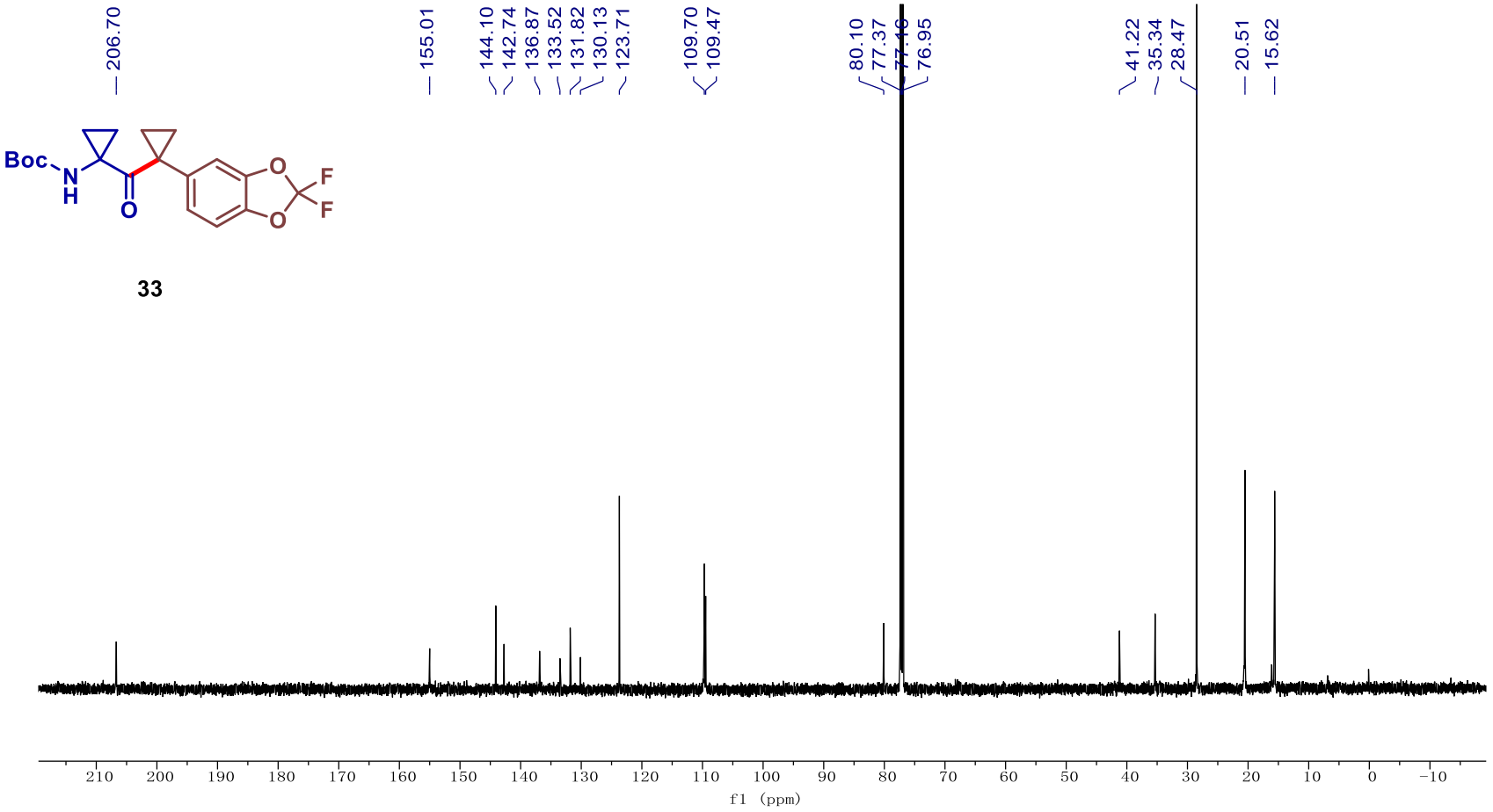
32

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



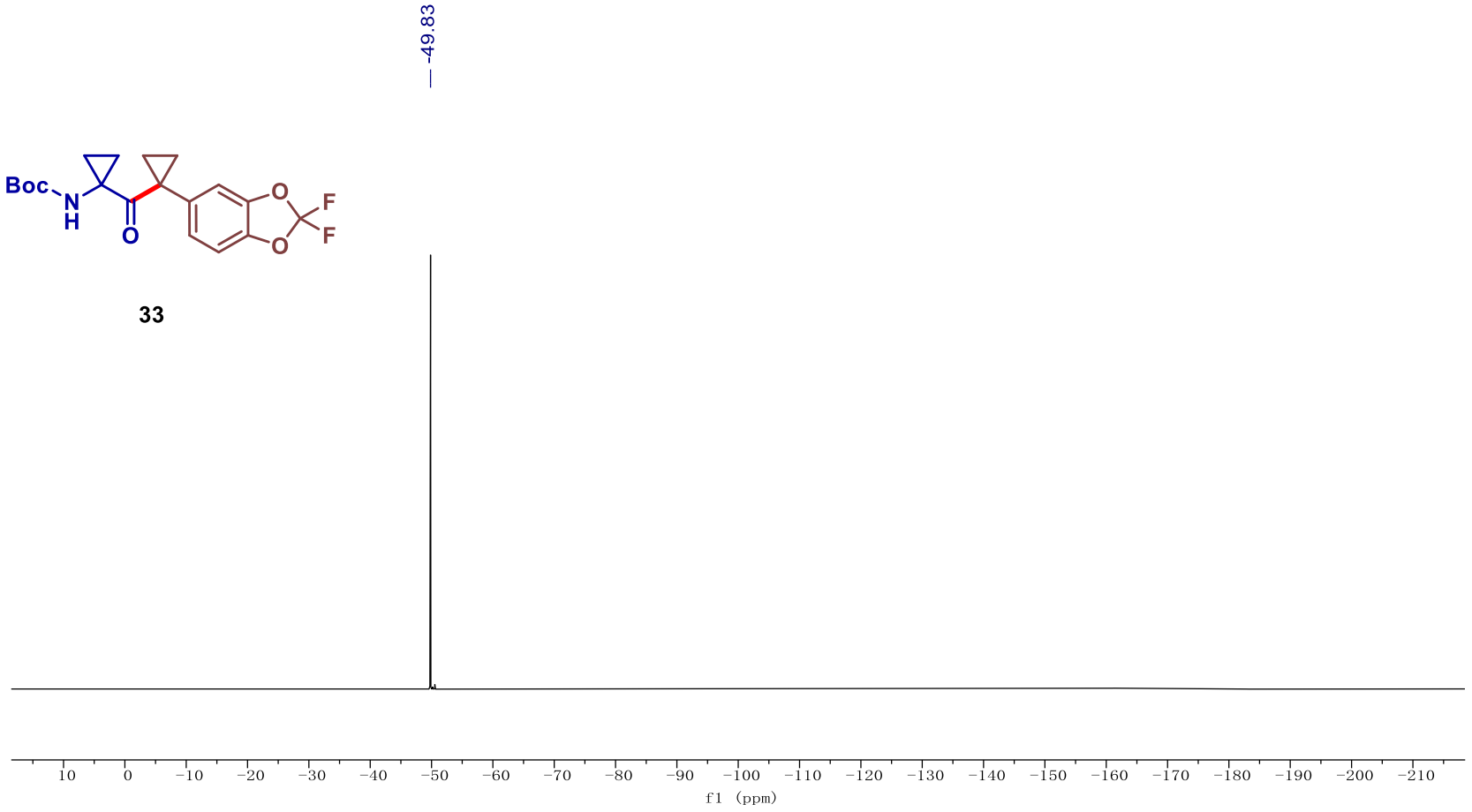
33

^{13}C NMR of 33 (151 MHz, $CDCl_3$)



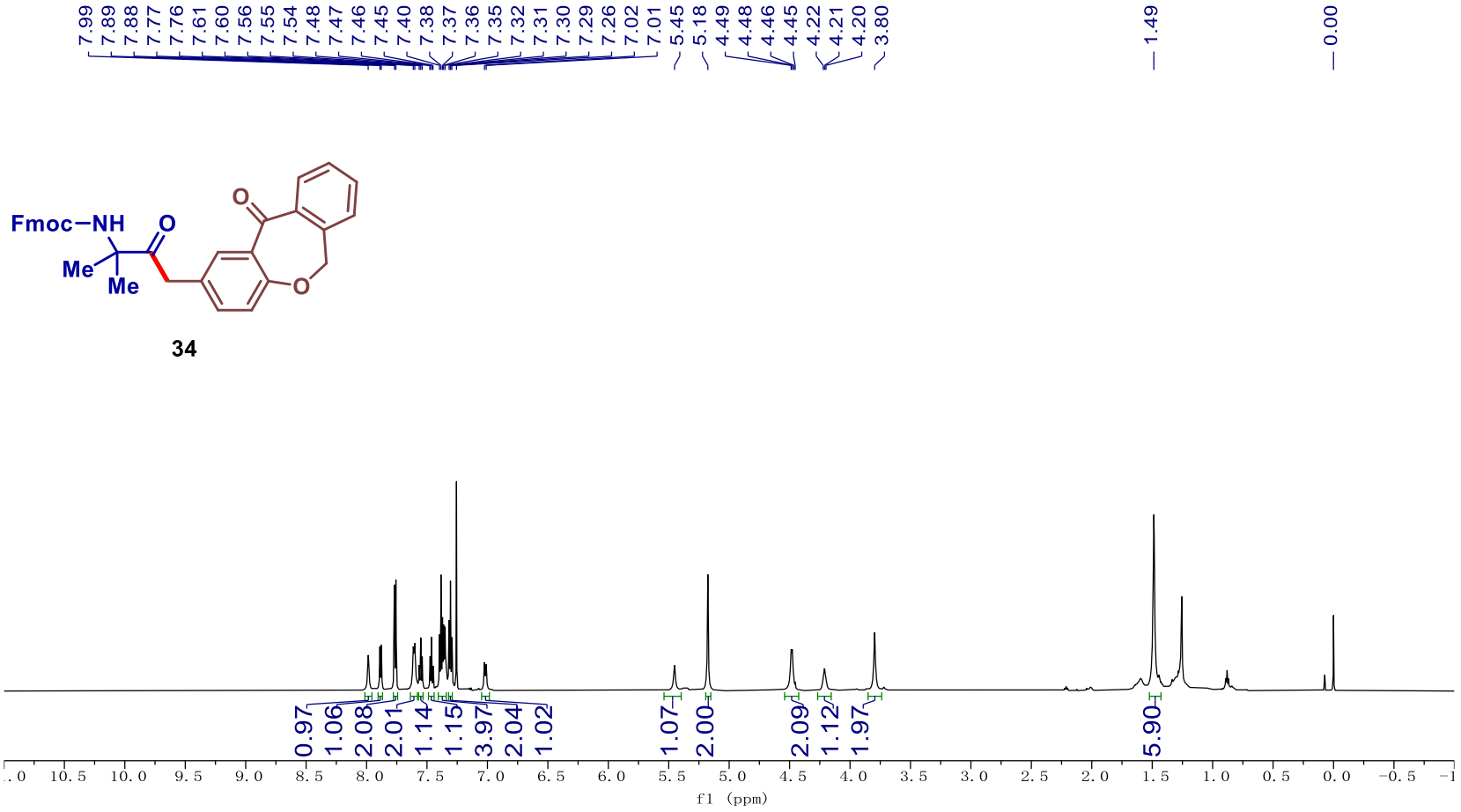
33

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



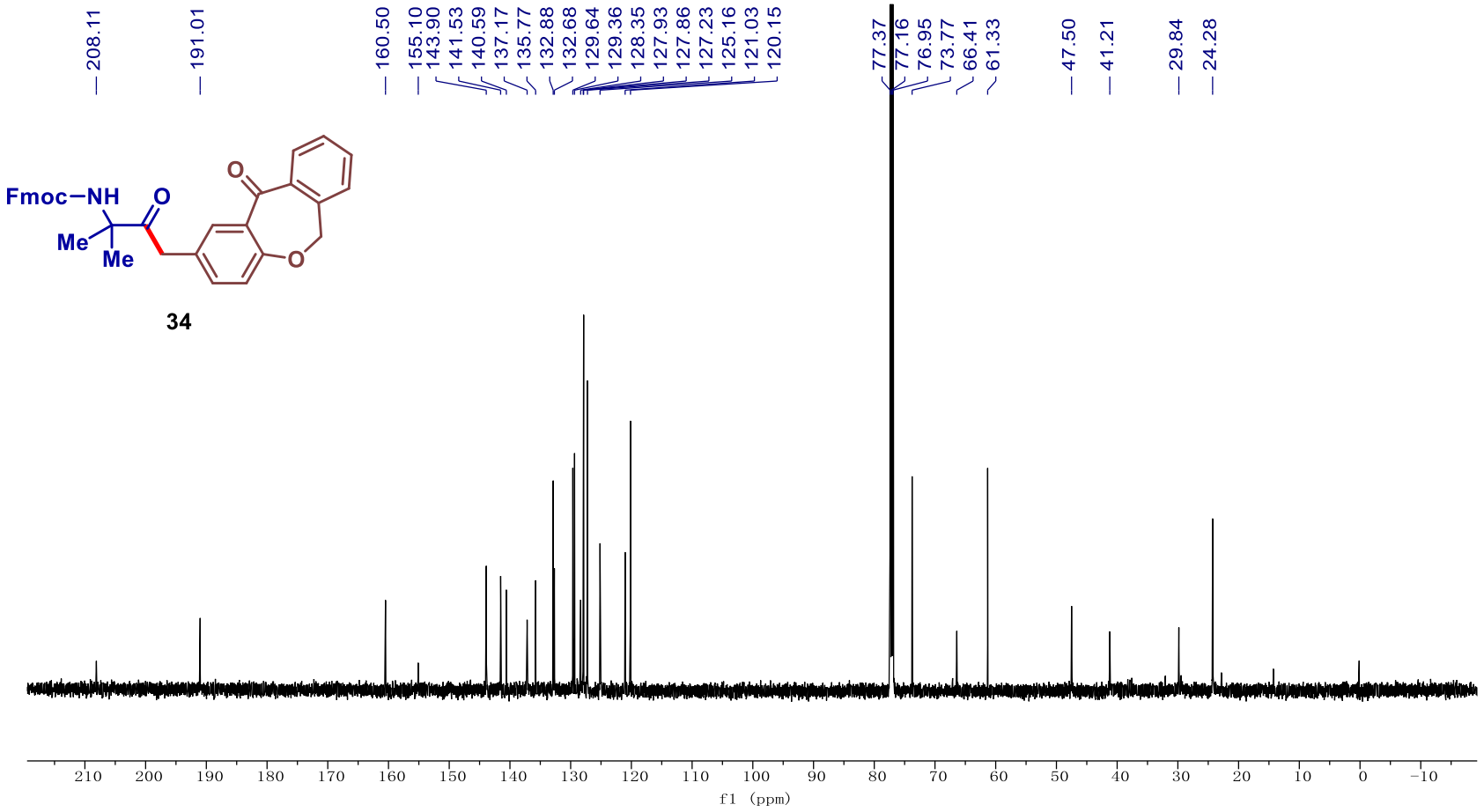
33

^{1}H NMR of 34 (600 MHz, $CDCl_3$)

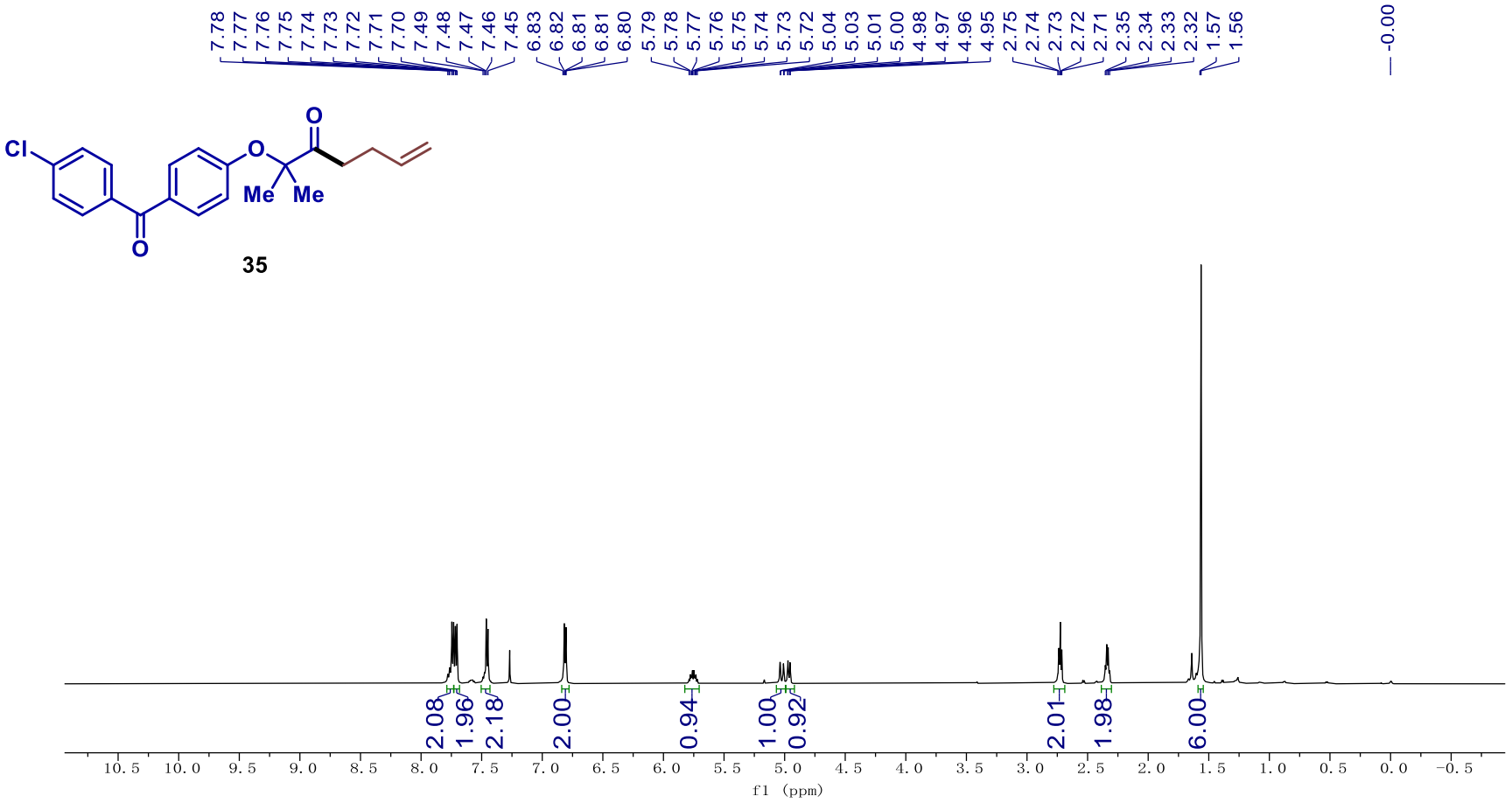


34

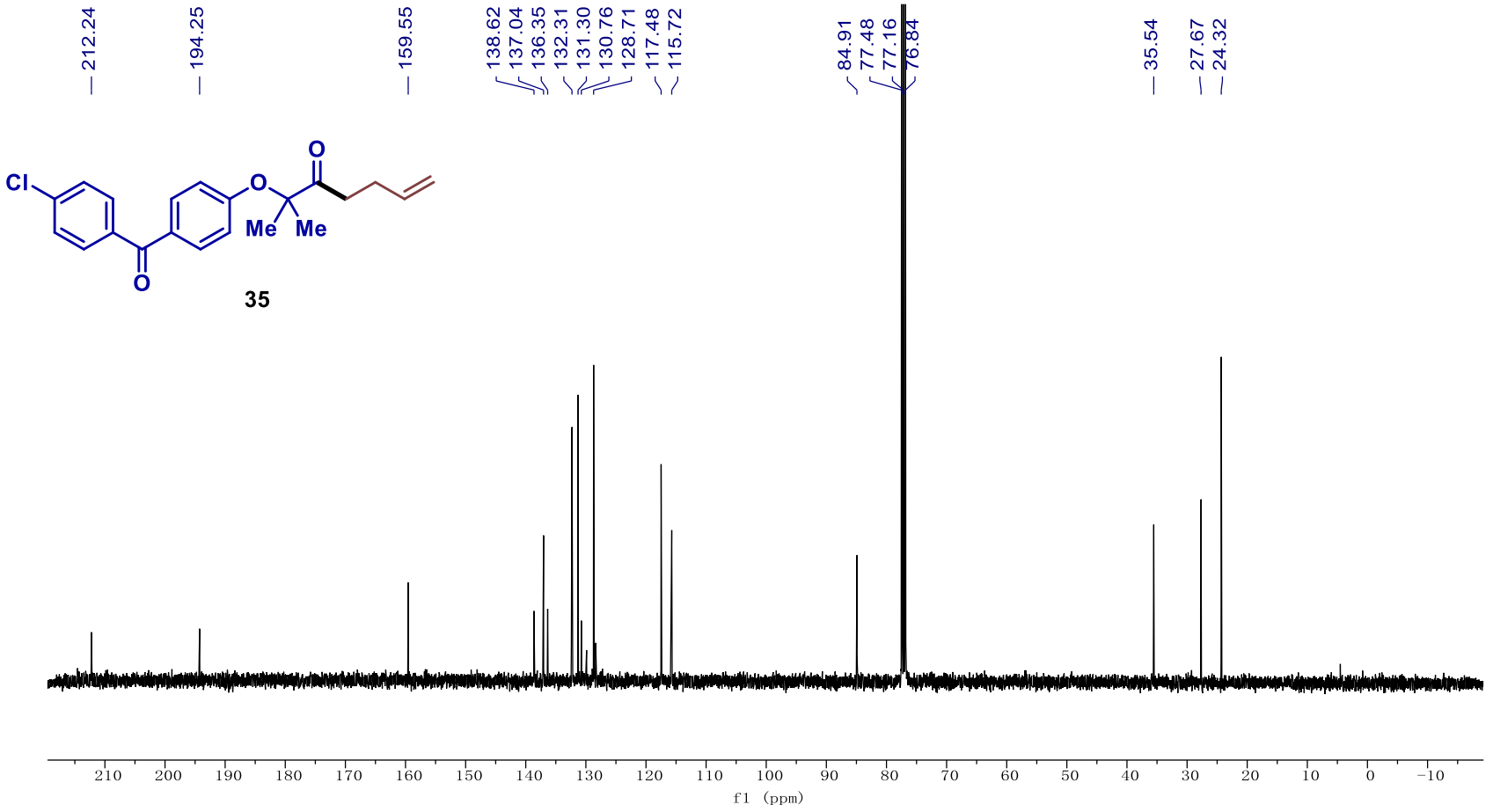
^{13}C NMR of 34 (151 MHz, $CDCl_3$)



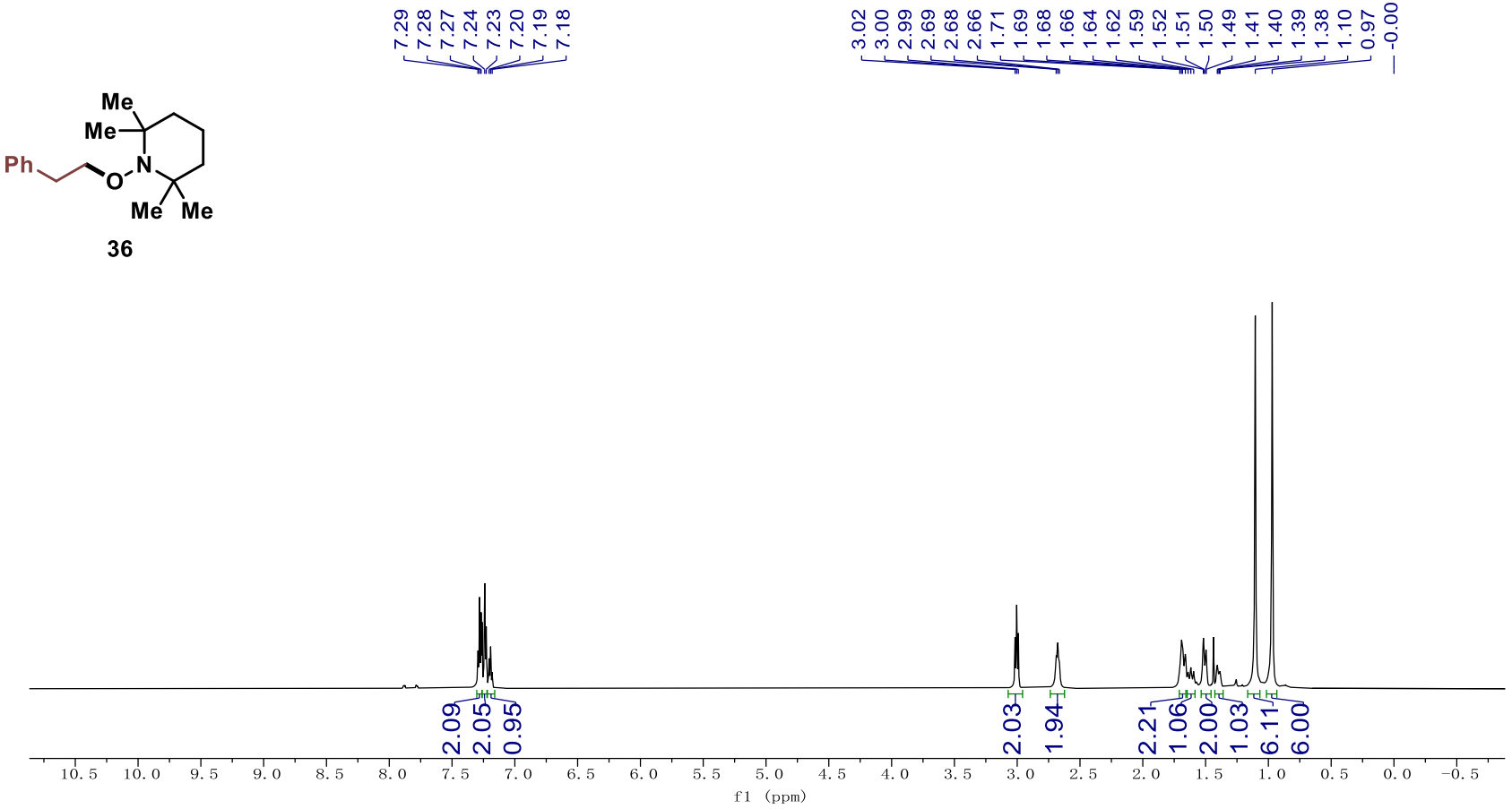
^{1}H NMR of 35 (600 MHz, $CDCl_3$)



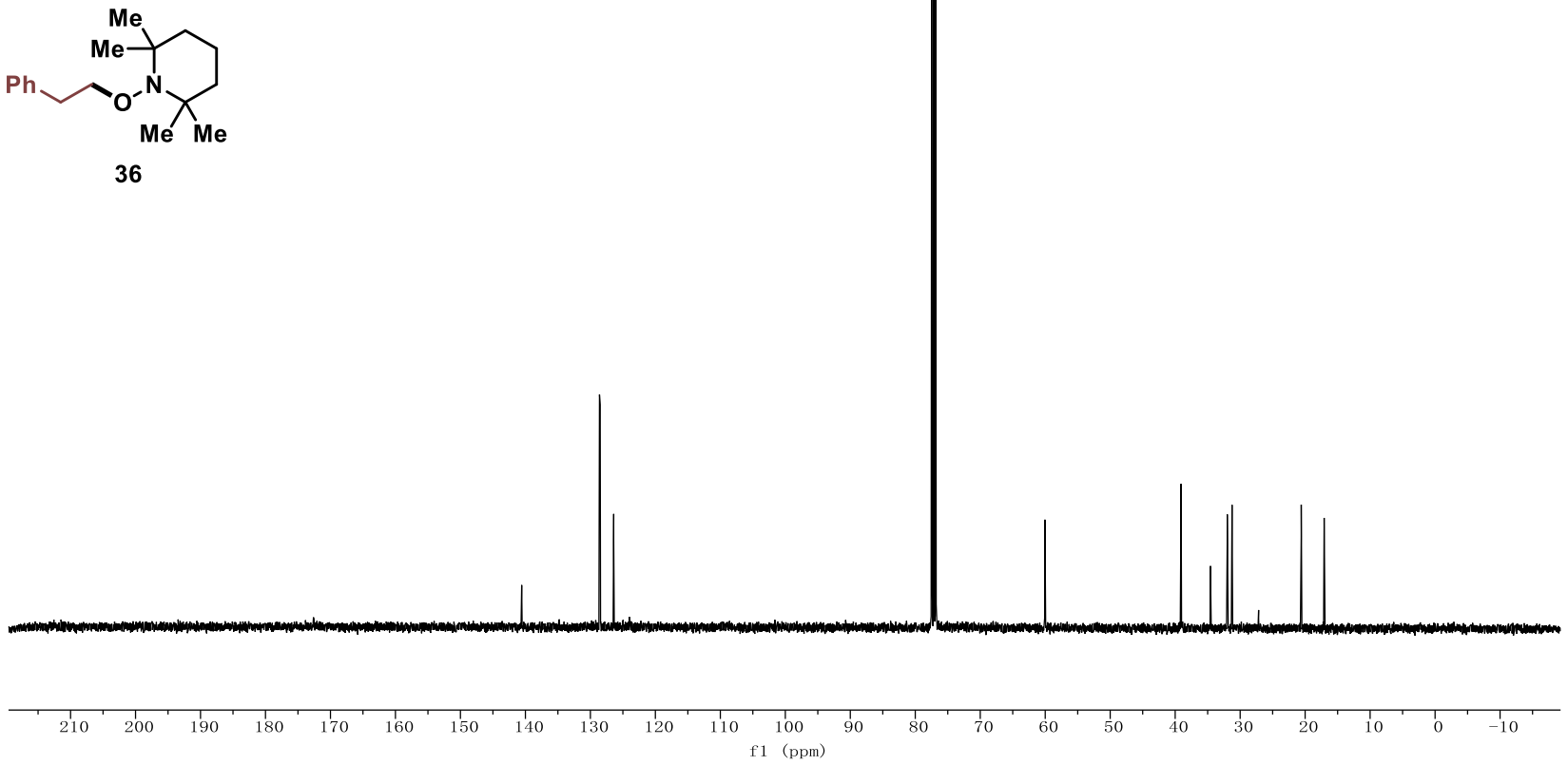
^{13}C NMR of 35 (101 MHz, $CDCl_3$)



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

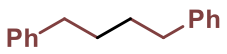


^{13}C NMR of 36 (101 MHz, $CDCl_3$)



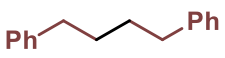
36

^{1}H NMR of 37 (600 MHz, $CDCl_3$)



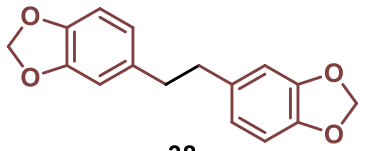
37

^{13}C NMR of 37 (151 MHz, $CDCl_3$)



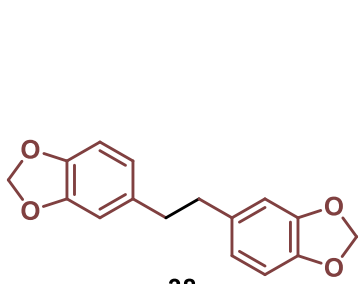
37

^{1}H NMR of 38 (600 MHz, $CDCl_3$)



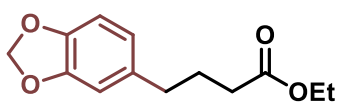
38

^{13}C NMR of 38 (151 MHz, $CDCl_3$)



38

^{1}H NMR of 39 (600 MHz, $CDCl_3$)



39

^{13}C NMR of 39 (151 MHz, $CDCl_3$)