Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Silver oxide(I) promoted Conia-ene/radical cyclization for a straightforward access to furan derivatives

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Abstract: A novel access to fused furan cores using silver oxide(I) has been developed. Mechanistic investigations would indicate the involvement of a Conia-ene reaction/radical cyclization for an expedient path to complex furan derivatives. The reaction is broad in scope with interesting atom economy and can also be conducted in a one-pot fashion from readily accessible α-ß-unsaturated ketones.

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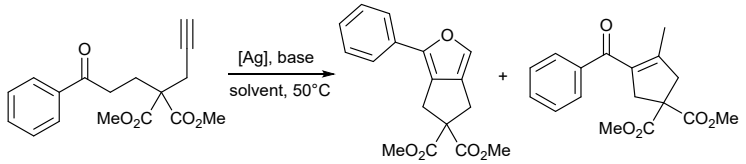
1. General Informations

All reactions sensitive to moisture and/or air were carried out under argon atmosphere in dry, freshly distilled solvents under anhydrous conditions using oven-dried glassware, unless otherwise noted. THF and toluene were distilled over sodium/benzophenone system, DCM, DMSO and DMF were distilled over calcium hydride, MeOH and EtOH were distilled over magnesium turnings. Reactions were monitored by TLC (silica gel 60 F254plates) and visualization was accomplished with UV light (254 nm & 366 nm) and subsequent use of phosphomolybdic acid solution in EtOH (5%), $KMnO_4$ solution or vanillin/sulphuric acid solution in EtOH, followed by heating at 100-110 °C. Flash chromatography was performed with silica gel 60 (particle size 0.040-0.063 μm). Yield refers to chromatographically and spectroscopically pure compounds, unless otherwise noted. Optical rotations were recorded on a Jasco P-1010 digital polarimeter at 579 nm and reported as follows: $[\alpha]_D^{20}$, concentration (c in g/100 mL) in $CHCl_3$. ^1H NMR spectra were recorded at 300 and 400 MHz. Chemical shifts are expressed in ppm, relative to the residual ^1H solvent signal ($CDCl_3$: δ = 7.26 ppm) as the internal reference. Coupling constants (*J*) are reported in hertz (Hz). The following abbreviations are used to designate the multiplicities: s = singlet; d = doublet; t = triplet; q = quartet; quint. = quintet, sext. = sextet, sept. = septet, m = multiplet; br = broad. ^1H NMR assignments were confirmed by 2D COSY spectra. The given multiplicities reflect apparent signal patterns. Diastereomer ratio (*dr*) was estimated by ^1H NMR spectroscopic analysis (300, 400 and 600 MHz), unless otherwise noted. ^{13}C NMR spectra were recorded at 75 MHz and 100 MHz MHz. Chemical shifts are given in ppm relative to the residual ^{13}C solvent signal ($CDCl_3$: δ = 77.16 ppm, CD_3OD: δ = 49.00 ppm). ^{13}C NMR assignments were confirmed by 2D HSQC and HMBC spectra. Coupling constants (*J*) are given in Hz for all NMR spectroscopic data. IR spectra were recorded with a FT-IR spectrometer. High-resolution mass spectra (HRMS) were measured on a mass spectrometer equipped with a TOF system and an electrospray ionization (ESI) ion source. Deuterated solvents were used as supplied.

2. Reaction Optimization

The optimization of the reaction conditions were performed on compound 1.

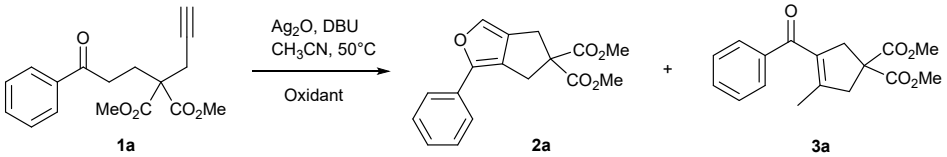


1a **2a** **3a**

Entry	[Ag]	Base	Solvent	Time[a]	^{1}H NMR yield[b] **2a** / **3a**
1	$AgNO_3$ 1 eq	DBU	CH_3CN	24h[b]	24% / 4%
2	Ag_2CO_3 0.5 eq	DBU	CH_3CN	2h	53% / 5 %
3	AgOTf 1 eq	DBU	CH_3CN	2h	44% / 4%
4	$AgNTf_2$ 1 eq	DBU	CH_3CN	2h	70% / 7%
5	$AgSbF_6$ 1 eq	DBU	CH_3CN	4h	54% / 3%
6	Ag_3PO_4 0.33 eq	DBU	CH_3CN	4h	47% / 12%
7	Ag_2O 0.5 eq	DBU	CH_3CN	2h	75% / -
8	Ag_2O 0.5 eq	K_2CO_3	CH_3CN	24h[c]	40% / 8%
9	Ag_2O 0.5 eq	NEt_3	CH_3CN	24h[b]	66% / 3%
10	Ag_2O 0.5 eq	Pyrrolidine	CH_3CN	4h	73% / 4%
11	Ag_2O 0.5 eq	*i*Pr_2NEt	CH_3CN	24h[c]	45% 5%
12	Ag_2O 0.5 eq	DBU	DMF	2h	62% / 3%
13	Ag_2O 0.5 eq	DBU	CH_2Cl_2	24h[c]	14% / 2%
14	Ag_2O 0.5 eq	DBU	THF	3h	66% / 3%
15	Ag_2O 0.5 eq	DBU	MeOH	3h	20% / 2%
16	Ag_2O 0.5 eq	DBU	Toluene	3h	54% / 5%
17	Ag_2O 0.5 eq	-	CH_3CN	24h[c]	19% / 2%
18	-	DBU	CH_3CN	24h	n.r

[a] The reaction was monitored by TLC. [b] ^{1}H NMR yield was determined from 1,3,5-trimethoxybenzene as internal standard. [c] Not complete after 24h.

Catalytic Attempts



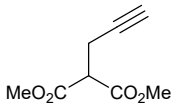
1a **2a** **3a**

Entry	Ag_2O	Oxidant	DBU	Time	^{1}H NMR yield[b] **2a** / **3a**
1	0.5 eq	-	1 eq	2h	75%[c]/-
2	0.5 eq	-	0.5 eq	2h	68% / -
3	0.5 eq	-	0.2 eq	2h	70% / 3 %
4	0.25 eq	-	0.2 eq	24h[a]	49% / 3%
5	0.25 eq	O_2	0.2 eq	18h	67% / 3%
6	0.25 eq	O_2	1 eq	3h	56% / 6%
7	0.25 eq	CeO_2 1 eq	1 eq	8h	45% / 13%
8	0.25 eq	$K_2S_2O_8$ 1 eq	1 eq	4h	16% / 25%
9	0.25 eq	$PhI(OAc)_2$ 1 eq	1 eq	24h[a]	44% / 3%

[a] Not complete after 24h. [b] ^{1}H NMR yield was determined from internal standard 1,3,5-trimethoxybenzen. [c]The reaction has been performed twice more with a respectively 75% (at the 0.2 mmol scale) and 74% (at the 1 mmol scale) isolated yield.

3. Preparation of the cyclization precursors

dimethyl 2-(prop-2-yn-1-yl)malonate **14**

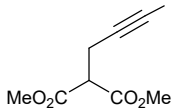


14

A flask containing powdered potassium carbonate (20.05 g, 145 mmol) was charged with dry acetone (125 mL) and dimethyl malonate (17.5 mL, 140 mmol). The suspension was warmed to reflux and propargyl bromide (80% in toluene, 6.25 mL, 56 mmol) was slowly added over 30 minutes. The mixture was stirred overnight at reflux. The reaction was cooled to room temperature and filtered over sand. The solution was concentrated under reduced pressure then purified by flash chromatography on silica gel (EtOAc/Cyclohexane : 5/95 to 10/90) to afford dimethyl 2-(prop-2-yn-1-yl)malonate as a colorless oil (m= 7.6 g, 80% yield).

All the spectroscopic data are in accordance with those described in the literature[1].

dimethyl 2-(but-2-yn-1-yl)malonate **15**

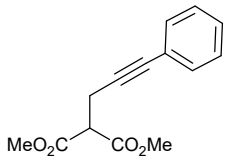


15

To a dry flask containing dimethyl malonate (9.0 mL, 78.9 mmol) and THF (245 mL) was slowly added NaH (60% w/w in mineral oil, 28.93 mmol) at 0 °C. 1-Bromo-2-butyne (2.3 mL, 26.3 mmol) was then slowly added then the solution was stirred for 30 min at 0 °C at which time a white precipitated formed. The mixture was then warmed to room temperature and stirred for 5h. The reaction was quenched by a saturated solution of NH_4Cl and the aqueous layer was extracted twice by EtOAc. The combined organics extracts were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by flash chromatography on silica gel (EtOAc/Cyclohexane : 5/95) affording the expected compound as a colorless oil (m= 3.5 g, 73% yield).

All the spectroscopic data are in accordance with those described in the literature[2].

dimethyl 2-(3-phenylprop-2-yn-1-yl)malonate **16**



16

A flask containing powdered potassium carbonate (4 g, 29.3 mmol) was charged with dry acetone (25 mL) and dimethyl malonate (3.2 mL, 28.4 mmol). The suspension was warmed to reflux and (3-iodoprop-1-yn-1-yl)benzene (11.3 mmol) was slowly added over 30 minutes. The mixture was stirred overnight at reflux. The reaction was cooled to room temperature and filtered over sand. The solution was concentrated under vacuum then purified by flash chromatography on silica gel (EtOAc/Cyclohexane : 5/95) affording the expected product as yellow oil (m= 1.7 g, 62% yield).

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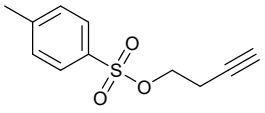
[1] R. G. Iafe, J. L. Kuo, D. G. Hochstatter, T. Saga, J. W. Turner, C. A. Merlic. *Org. Lett.* 2013, **15**, 582-585.
[2] B. M. Trost, M. T. Rudd, *J. Am. Chem. Soc.*, 2005, **127**, 4763-4776.

All the spectroscopic data are in accordance with those described in the literature[3].

but-3-yn-1-yl 4-methylbenzenesulfonate **17**

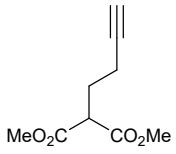


17

To a solution of but-3-yn-1-ol (701 mg, 10 mmol) in CH_2Cl_2 (15 mL) were added NEt_3 (2.7 mL, 20 mmol) and TsCl (1.9 g, 10 mmol) at 0 °C. The solution was stirred for 18 h at r.t. and then quenched with sat. NH_4Cl. The mixture was extracted with CH_2Cl_2 (3x), the combined organic layers were neutralized with sat. $NaHCO_3$, washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by flash chromatography on silica gel (EtOAc/Cyclohexane : 2/98 to 10/90) affording the expected compound as a colorless oil (m= 2.1 g, 90% yield).

All the spectroscopic data are in accordance with those described in the literature[4].

dimethyl 2-(but-3-yn-1-yl)malonate **18**

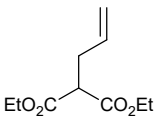


18

To a dry flask containing NaH (60% in mineral oil, 396 mg, 9.90 mmol) and anhydrous DMF (16 ml) was slowly added dimethylmalonate (3.56 g, 26.9 mmol) at 0 °C. The solution was stirred for 15 min at r.t. After this, but-3-yn-1-yl 4-methylbenzenesulfonate (2.01 g, 8.97 mmol) was added and the resulting mixture was stirred at 90 °C for 21 h. The reaction was quenched by water and the aqueous layer was extracted twice by Et_2O. The combined organics extracts were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by flash chromatography on silica gel (EtOAc/Cyclohexane : 5/95 to 10/90) affording the expected compound as a colorless oil (m= 1 g, 61% yield).

All the spectroscopic data are in accordance with those described in the literature[5].

diethyl 2-allylmalonate **19**



19

A flask containing powdered potassium carbonate (10.4 g, 75 mol) was charged with dry acetone (1.24 L) and diethyl malonate (5.7 mL, 37.5 mol). The suspension was warmed to reflux and allyl bromide (2.16 mL, 25 mol) was slowly added over 30 minutes. The mixture was stirred overnight at reflux. The reaction was cooled to room temperature and filtered over sand. The solution was concentrated under vacuum then purified by flash chromatography on silica gel (EtOAc/Cyclohexane : 5/95) affording the expected product as colorless oil (m= 4.1 g, 82% yield).

All the spectroscopic data are in accordance with those described in the literature.[6]

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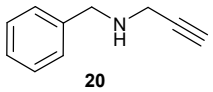
[3] R. Schiller, M. Pour, H. Fáková, J. Kuneš, I. Císařová, *J. Org. Chem.* 2004, **69**, 6761-6765.
[4] X.-J. Dai, O.D. Engl, T. León, S.L. Buchwald, *Angew. Chem.* 2019, **131**, 3445-3449.
[5] D. Gasperini, L. Maggi, S. Dupuy, R. M. Veenboer, D. B. Cordes, A. M. Slawin, S. P. Nolan, *Adv. Synth. Catal.* 2016, **358**, 3857-3862.
[6] J.-C. Su, Y.-T. Huang, C.-S. Chen, H.-C. Chiu, C.-W. Shiau, *Molecules*, 2018, **23**, 27.

N-benzylprop-2-yn-1-amine **20**



20

Propargyl bromide (4.3 mL, 38 mmol) was added to benzyl amine (25 mL, 228 mmol) over 30 min *via* addition funnel and allowed to stir overnight. The resulting mixture was diluted in Et_2O and extracted with saturated aq. $NaHCO_3$ and dried over $MgSO_4$. The reaction mixture was concentrated under reduced pressure then purified by flash chromatography on silica gel (EtOAc/Cyclohexane : 10/90 to 15/85) affording the expected product as pale yellow oil (m= 4.7 g, 85% yield).

All the spectroscopic data are in accordance with those described in the literature[1].

4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide **21**

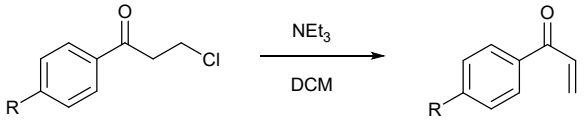
21

p-toluenesulfonyl chloride (4.8 g, 25 mmol) was added dropwise to a solution of propargylamine (1.9 mL, 30 mmol) and Et_3N (4.7 mL, 35 mmol) in DCM (25 mL) at 0 °C under argon. Then the resulting mixture was warmed up to room temperature and stirred overnight. The reaction was quenched by H_2O, extracted twice with DCM, dried over $MgSO_4$ and concentrated under reduced pressutre . The residue was purified by flash chromatography on silica gel (EtOAc/Cyclohexane : 10/90) to afford the expected product as white solid (m= 5.1 g, 97% yield).

All the spectroscopic data are in accordance with those described in the literature[7].

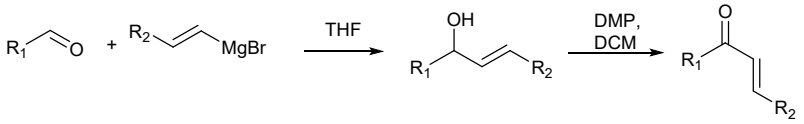
General procedure for the synthesis of vinyl ketones (GPI and GPII) :

GPI



To a pre-stirred solution of 3-chloropropionyl aryl ketone (5.0 mmol, 1.0 eq.) in CH_2Cl_2 (10 mL), triethylamine (10.0 mmol, 2 eq.) was added dropwise over 5 min under argon atmosphere. The reaction mixture was stirred for 18 h at room temperature followed by washing with 0.1 N HCl aq., distilled water, saturated $NaHCO_3$ aq., and brine. The organic layer was dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel yielding the α,β-unsaturated ketone.

GPII



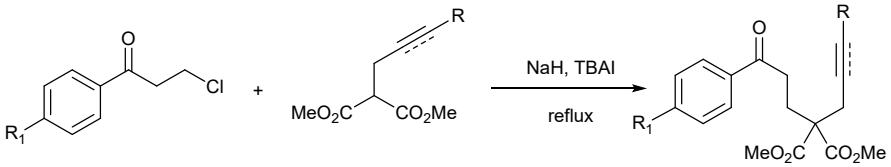
A solution of aldehyde (3 mmol, 1 eq.) in dry THF (5 mL) was cooled to 0 °C in an ice –water bath and Grignard reagent (3.6 mmol, 1.2 eq.) was added dropwise. The mixture was warmed to room temperature and stirred for overnight. Saturated NH_4Cl solution (20 mL) was added to quench the reaction and the aqueous layer was extracted with EtOAc (3 × 15 mL). The combined organic layers were washed with brine (20 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The residue was dissolved in

[7] Y. Kavanagh, C. M. Chaney, J. Muldoon, P. Evans, *J. Org. Chem.* 2008, **73**, 8601-8604.

CH_2Cl_2 (10 mL) and Dess-Martin periodinane (4.0 mmol, 1.3 eq.) was added. The mixture was stirred at room temperature until TLC showed complete disappearance of the starting alcohol. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel affording the expected compound in a pure form.

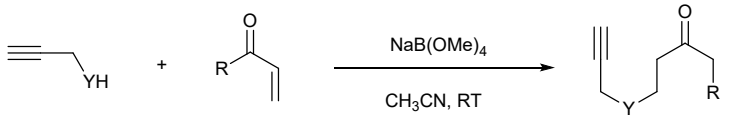
General procedure for the synthesis of cyclization precursors (GPIII, GPIV, GPV and GPVI) :

GPIII



The alkyne or alkene (2.0 mmol, 1 eq.) was dissolved in THF (5 mL) and cooled to 0 °C. NaH (60% w/w in mineral oil, 2.6 mmol, 1.3 eq.) was added in one portion. The reaction mixture was stirred for 30 min at 0 °C. The 3-chloropropiophenone or derivatives (4.0 mmol, 2 eq.) was dissolved in THF (8 mL) and transferred slowly to the reaction mixture. Tetrabutylammonium iodide (0.2 mmol, 0.1 eq.) was added in one portion. The reaction was warmed to room temperature and then stirred at reflux overnight. The suspension was cooled to room temperature, quenched by a saturated solution of NH_4Cl and the aqueous layer was extracted twice by EtOAc. The combined organics extracts were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by flash chromatography on silica gel affording the expected compound in a pure form.

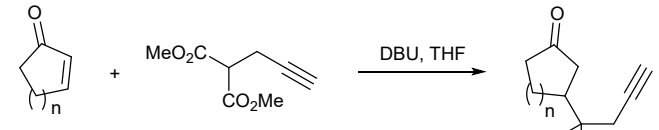
GPIV



Y=C(CO_2Me)$_2$, NBn or NTs

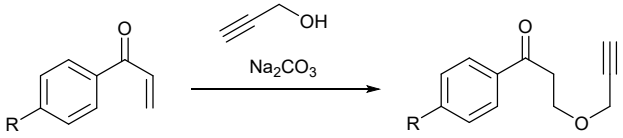
To a solution of Michael donor (1.2 mmol, 1.2 eq.) and $NaB(OMe)_4$ (0.2 mmol, 0.2 eq.) in CH_3CN (3 mL) was added α-β-unsaturated ketone (1.0 mmol, 1 eq.) at room temperature. The resulting solution was stirred at room temperature under air atmosphere and monitored by TLC. Upon completion, solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel to give the desired product in a pure form.

GPV



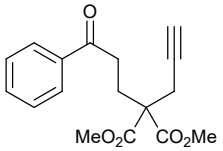
A solution of cyclic vinyl ketone (10 mmol, 1 eq.), dimethylpropargyl-malonate (13 mmol, 1.3 eq.) and DBU (13 mmol, 1.3 eq.) in THF (15 mL) was stirred for 24 h under argon at 50 °C. The solvent was removed under reduced pressure and the crude residue was purified by flash column chromatography on silica gel to give the desired product in a pure form.

GPVI



To a solution of activated alkene (0.5 mmol, 1 eq.) in propargyl alcohol (2.0 mmol, 4 eq.) was added Na_2CO_3 (0.2 mL, 0.05M aq.), and the solution was stirred until alkene was completely consumed (monitored by TLC). The reaction mixture was extracted with ethyl acetate (3 × 5 mL) and the combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel to give the expected product in a pure form.

dimethyl 2-(3-oxo-3-phenylpropyl)-2-(prop-2-yn-1-yl)malonate **1a**

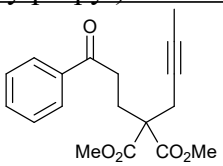


1a

The compound **1a** was obtained from 3-chloropropiophenone and compound **14** following the **GPIII** on 47 mmol scale (8 g). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 10/90) afforded **1a** as a pale yellow solid (m= 10.9 g, 77% yield).

All the spectroscopic data are in accordance with those described in the literature[8].

dimethyl 2-(but-2-yn-1-yl)-2-(3-oxo-3-phenylpropyl)malonate **1p**

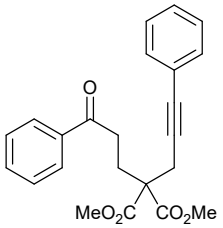


1p

The compound **1p** was obtained from 3-chloropropiophenone and compound **15** following the **GPIII** on 8.1 mmol scale (1.5 g). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 5/95 to 8/92) afforded **1p** as a white solid (m= 1.0 g, 41% yield).

All the spectroscopic data are in accordance with those described in the literature[9].

dimethyl 2-(3-oxo-3-phenylpropyl)-2-(3-phenylprop-2-yn-1-yl)malonate **1q**



1q

The compound **1q** was obtained from 3-chloropropiophenone and compound **16** following the **GPIII** on 4.9 mmol scale (1.2 g). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 5/95 to 8/92) afforded **1q** as a yellow solid (m= 1.3 g, 70% yield).

^{1}H NMR (400 MHz, $CDCl_3$) ***δ*** 7.98 – 7.95 (m, 2H), 7.55 – 7.51 (m, 1H), 7.44 - 7.39 (m, 2H), 7.36 – 7.34 (m, 2H), 7.28 -7.23 (m, 3H), 3.76 (s, 6H), 3.13 (s, 2H), 3.12 – 3.09 (m, 2H), 2.60 – 2.56 (m, 2H)
^{13}C NMR (100 MHz, $CDCl_3$) ***δ*** 198.8, 170.7 (2C), 136.7, 133.2, 131.8 (2C), 128.7 (2C), 128.3 (2C), 128.2 (4C), 123.1, 84.1, 56.8, 53.0 (2C), 34.0, 27.6, 25.0

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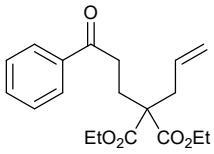
[8] L. Huang, L. Ye, X. H., Li, Z. L. Li, J. S. Lin, X. Y. Liu, *Org. Lett.*, 2016, **18**, 5284-5287.
[9] J.-F. Brazeau, S. Zhang, I. Colomer, B. K. Corkey, F. D. Toste, *J. Am. Chem.Soc*. 2012, **134**, 2742−2749.

FTIR (neat): ν = 2954, 2255, 1732, 1204, 906, 725, 690 cm^{-1}
HRMS (ESI): *m/z* calcd for $C_{23}H_{22}O_5Na^+$: $[M+Na]^+$: 401.1365; found: 401.1367

diethyl 2-allyl-2-(3-oxo-3-phenylpropyl)malonate **1r**

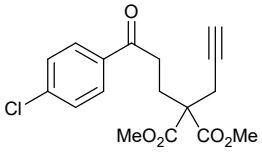


1r

The compound **1r** was obtained from 3-chloropropiophenone and compound **19** following the **GPIII** on 7.5 mmol scale (1.5 g). Purification by flash chromatography (EtOAc/Cyclohexane: 3/97 to 4/96) afforded **1r** as a pale yellow solid (m= 1.1 g, 45% yield).

All the spectroscopic data are in accordance with those described in the literature[10].

dimethyl 2-(3-(4-chlorophenyl)-3-oxopropyl)-2-(prop-2-yn-1-yl)malonate **1b**

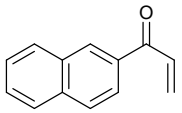


1b

The compound **1b** was obtained from 3,4'-dichloropropiophenone and compound **14** following the **GPIII** on 2.9 mmol scale (500 mg). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 5/95 to 10/90) afforded **1b** as a white solid (m= 781 mg, 80% yield).

All the spectroscopic data are in accordance with those described in the literature[5].

1-(naphthalen-2-yl)prop-2-en-1-one **22**

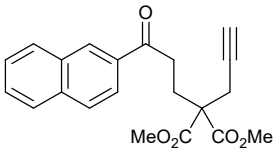


22

The compound **22** was obtained from 2-naphthaldehyde and vinylmagnesium bromide following the **GPII** on 20 mmol scale (3.2 g). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 6/94) afforded **22** as a colorless oil (m= 3 g, 84% yield over 2 steps).

All the spectroscopic data are in accordance with those described in the literature[11].

dimethyl 2-(3-(naphthalen-2-yl)-3-oxopropyl)-2-(prop-2-yn-1-yl)malonate **1d**



1d

The compound **1d** was obtained from compound **22** and **14** following the **GPIV** on 10 mmol scale (1.8 g). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 5/95) afforded **1d** as a pale yellow solid (m= 1.4 g, 41% yield).

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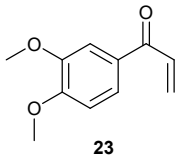
[10] L. Huang, S-C. Zheng, B. Tan, X-Y. Liu, *Org. Lett*. 2015, **17**, 1589−1592.
[11] S. H. Guo, S. Z., Xing, S. Mao, Y. R. Gao, W. L. Chen, Y. Q. Wang, *Tetrahedron Lett.*, 2014, **55**, 6718-6720.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 8.04 – 8.01 (m, 1H), 7.98 – 7.96 (m, 1H), 7.90 – 7.86 (m, 2H), 7.62 – 7.53 (m, 2H), 3.76 (s, 6H), 3.19 (t, J = 7.8 Hz, 2H), 2.95 (d, J = 2.8 Hz, 2H), 2.58 (t, J = 7.8 Hz, 2H), 2.07 (t, J = 2.8 Hz, 1H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 198.7, 170.6 (2C), 135.8, 134.1, 132.6, 129.9, 129.7, 128.7, 128.6, 127.9, 126.9, 124.0, 78.7, 72.1, 56.4, 53.1 (2C), 33.9, 27.4, 24.2
FTIR (neat): ν = 3291, 2954, 1731, 1679, 1436, 1203, 1125, 909, 732 cm^{-1}
HRMS (ESI): *m/z* calcd for $C_{21}H_{20}O_5Na^+$: $[M+Na]^+$: 375.1208; found: 375.1208

1-(3,4-dimethoxyphenyl)prop-2-en-1-one **23**

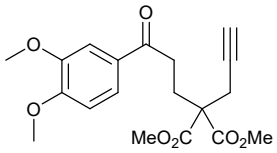


23

The compound **23** was obtained from 3,4-dimethoxybenzaldehyde and vinylmagnesium bromide following the **GPII** on 20 mmol scale (3.4 g). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 10/90) afforded **23** as a pale yellow solid (m= 3.4 g, 90% yield over 2 steps).

All the spectroscopic data are in accordance with those described in the literature[12].

dimethyl 2-(3-(3,4-dimethoxyphenyl)-3-oxopropyl)-2-(prop-2-yn-1-yl)malonate **1e**

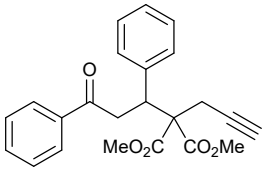


1e

The compound **1e** was obtained from compound **23** and **14** following the **GPIV** on 10 mmol scale (1.9 g). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 10/90 to 20/80) afforded **1e** as a yellow solid (m= 2.3 g, 64% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 8.4 Hz, 1H), 7.41 (s, 1H), 6.78 (d, J = 8.4 Hz, 1H), 3.82 (d, J = 4.8 Hz, 6H), 3.64 (s, 6H), 2.89 (t, J = 7.8 Hz, 2H), 2.78 (d, J = 2.6 Hz, 2H), 2.38 (t, J = 7.8 Hz, 2H), 1.99 (t, J = 2.6 Hz, 1H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 197.0, 170.2 (2C), 153.2, 148.9, 129.6, 122.6, 110.0, 109.9, 78.4, 71.8, 56.1, 55.9, 55.8, 52.7 (2C), 33.1, 27.4, 23.8
FTIR (neat): ν = 2256, 1733, 1515, 1265, 1023, 905, 724 cm^{-1}
HRMS (ESI): *m/z* calcd for $C_{19}H_{22}O_7Na^+$: $[M+Na]^+$: 385.1263; found: 385.1260

dimethyl 2-(3-oxo-1,3-diphenylpropyl)-2-(prop-2-yn-1-yl)malonate **1g**



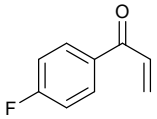
1g

The compound **1g** was obtained from chalcone and compound **14** following the **GPIV** on 10 mmol scale (2.1 g). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 10/90 to 20/80) afforded **1g** as a white solid (m= 710 mg, 18% yield).

[12] S. F. Musolino, O. S. Ojo, N. J. Westwood, J. E. Taylor, A. D. Smith, *Chem. Eur. J.*, 2016, **22**, 18916-18922.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.91 (m, 2H), 7.53 – 7.49 (m, 1H), 7.43 – 7.39 (m, 2H), 7.26 – 7.19 (m, 5H), 4.43 (dd, *J* = 10.6, 2.8 Hz, 1H), 3.84 (d, *J* = 2.8 Hz, 1H), 3.82 (s, 3H), 3.79 (d, *J* = 10.6 Hz, 1H), 3.75 (s, 3H), 2.77 (dd, *J* = 17.2, 2.8 Hz, 1H), 2.52 (dd, *J* = 17.2, 2.8 Hz, 1H), 2.18 (t, *J* = 2.8 Hz, 1H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 170.1, 170.0, 138.6, 137.1, 133.0, 129.0 (2C), 128.5 (2C), 128.4 (2C), 128.1 (2C), 127.7, 79.3, 72.5, 61.0, 52.9, 52.7, 43.6, 41.5, 24.3
FTIR (neat): ν = 3308, 2251, 1734, 1214, 905, 725 cm^{-1}
HRMS (ESI): *m/z* calcd for $C_{23}H_{23}O_5$: $[M+H]^+$: 379.1545; found: 379.1542

1-(4-fluorophenyl)prop-2-en-1-one **24**

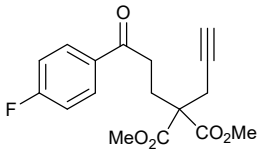


24

The compound **24** was obtained from 3-chloro-4'-fluoropropiophenone following the **GPI** on 16 mmol scale (3 g). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 10/90) afforded **24** as a colorless oil (m= 2.3 g, 96% yield).

All the spectroscopic data are in accordance with those described in the literature[13].

dimethyl 2-(3-(4-fluorophenyl)-3-oxopropyl)-2-(prop-2-yn-1-yl)malonate **1c**

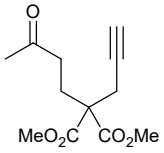


1c

The compound **1c** was obtained from compound **24** and **14** following the **GPIV** on 10 mmol scale (1.5 g). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 10/90) afforded **1c** as a white solid (m= 2.6 g, 81% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 – 7.94 (m, 2H), 7.14 – 7.08 (m, 2H), 3.73 (s, 6H), 3.02 (t, *J* = 7.7 Hz, 2H), 2.88 (d, *J* = 2.7 Hz, 2H), 2.48 (t, *J* = 7.7 Hz, 2H), 2.04 (t, *J* = 2.7 Hz, 1H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 170.5 (2C), 165.8 (d, *J* = 253 Hz), 133.1 (d, *J* = 3 Hz), 130.8 (d, *J* = 9 Hz, 2C), 115.7 (d, *J* = 21 Hz, 2C), 78.6, 72.0, 56.3, 52.9 (2C), 33.7, 27.3, 24.1
^{19}F NMR (280 MHz, $CDCl_3$) δ -105.15
FTIR (neat): ν = 3308, 2257, 1733, 1686, 1599, 1206, 1157, 906, 726 cm^{-1}
HRMS (ESI): *m/z* calcd for $C_{17}H_{18}O_5F$: $[M+H]^+$: 321.1138; found: 321.1137

dimethyl 2-(3-oxobutyl)-2-(prop-2-yn-1-yl)malonate **4c**



4c

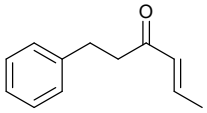
The compound **4c** was obtained from methyl vinyl ketone and compound **14** following the **GPIV** on 10 mmol scale (0.7 g). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 10/90 to 15/85) afforded **4c** as a white solid (m= 1.8 g, 75% yield).

All the spectroscopic data are in accordance with those described in the literature[14].

---

[13] G. Zhang, F. Jia, L. J. Gooßen, *Chem. Eur. J.*, 2018, **24**, 4537-4541.
[14] J. Muñoz-Bascón, C. Hernández-Cervantes, N. M. Padial, M. Álvarez-Corral, A, Rosales, I. Rodríguez-García, J. E. Oltra,

(*E*)-1-phenylhex-4-en-3-one **25**

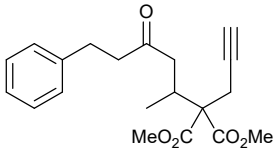


25

The compound **25** was obtained from 3-phenylpropionaldehyde and (*E*)-1-propenylmagnesium bromide following the **GPII** on 6 mmol scale (0.8 g). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 10/90 to 15/85) afforded **25** as a colorless oil (m= 966 mg, 92% yield over 2 steps).

All the spectroscopic data are in accordance with those described in the literature[15].

dimethyl 2-(4-oxo-6-phenylhexan-2-yl)-2-(prop-2-yn-1-yl)malonate **4a**

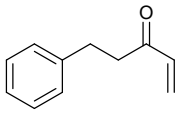


4a

The compound **4a** was obtained from compound **25** and **14** following the **GPIV** on 2.3 mmol scale (401 mg). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 10/90 to 15/85) afforded **4a** as a yellow solid (m= 142 mg, 18% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 - 7.25 (m, 2H), 7.20 – 7.16 (m, 3H), 3.73 (s, 6H), 3.04 – 2.96 (m, 1H), 2.94 – 2.83 (m, 4H), 2.82 – 2.66 (m, 3H), 2.23 (dd, J = 16.8, 10.4 Hz, 1H), 2.03 (t, J = 2.8 Hz, 1H), 0.89 (d, J = 6.8 Hz, 3H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 208.4, 170.3, 170.0, 141.1, 128.6 (2C), 128.4 (2C), 126.2, 79.1, 71.8, 60.3, 52.8, 52.6, 46.7, 44.5, 31.9, 29.9, 23.04, 15.7
FTIR (neat): ν = 2954, 1730, 1435, 1202, 1049, 908, 728, 700 cm^{-1}
HRMS (ESI): *m/z* calcd for $C_{20}H_{25}O_5$: $[M+H]^+$: 345.1702; found: 345.1699

5-phenylpent-1-en-3-one **26**

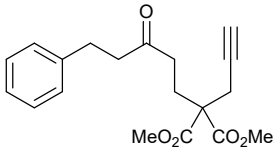


26

The compound **26** was obtained from 3-phenylpropionaldehyde and vinylmagnesium bromide following the **GPII** on 14.9 mmol scale (2 g). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 20/80) afforded **26** as a yellow oil (m= 2.2 g, 94% yield over 2 steps).

All the spectroscopic data are in accordance with those described in the literature[16].

dimethyl 2-(3-oxo-5-phenylpentyl)-2-(prop-2-yn-1-yl)malonate **4b**



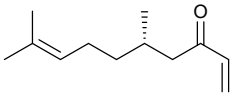
4b

Chem. Eur. J. 2014, **20**, 801-810.
[15] Y. Sugawara, W. Yamada, S. Yoshida, T. Ikeno, T. Yamada, *J. Am. Chem. Soc.* 2007, **129**, 12902-12903.
[16] G. A., Molander, L. Jean-Gérard, *J. Org. Chem.*, 2009, **74**, 1297-1303.

The compound **4b** was obtained from compound **26** and **14** following the **GPIV** on 2.2 mmol scale (350 mg). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 5/95) afforded **4b** as a white solid (m= 405 mg, 56% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 2H), 7.20-7.16 (m, 3H), 3.71 (s, 6H), 2.89 (t, *J* = 7.6 Hz, 2H), 2.79 (d, *J* = 2.7 Hz, 2H), 2.73 (t, *J* = 7.6 Hz, 2H), 2.44 (t, *J* = 8.0 Hz, 2H), 2.32 (t, *J* = 8.0 Hz, 2H), 2.02 (t, *J* = 2.7 Hz, 1H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 208.3, 170.5 (2C), 141.0, 128.6 (2C), 128.4 (2C), 126.2, 78.5, 71.9, 56.1, 52.9 (2C), 44.3, 37.9, 29.8, 26.5, 23.9
FTIR (neat): ν = 3308, 2254, 1733, 1204, 905, 725 cm^{-1}
HRMS (ESI): *m/z* calcd for $C_{19}H_{23}O_5$: $[M+H]^+$: 331.1545; found: 331.1540

(*S*)-5,9-dimethyldeca-1,8-dien-3-one **27**

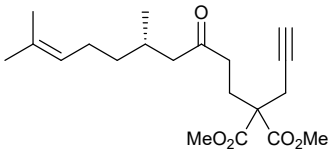


27

The compound **27** was obtained from (*S*)-(−)-citronellal and vinylmagnesium bromide following the **GPII** on 13.3 mmol scale (2.1 g). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 5/95) afforded **27** as a pale yellow oil (m= 2.2 g, 90% yield for 2 steps).

All the spectroscopic data are in accordance with those described in the literature[17].

dimethyl (S)-2-(5,9-dimethyl-3-oxodec-8-en-1-yl)-2-(prop-2-yn-1-yl)malonate **4e**

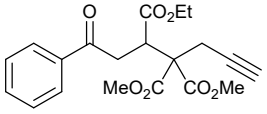


4e

The compound **4e** was obtained from compound **27** and **14** following the **GPIV** on 1.7 mmol scale (300 mg). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 10/90) afforded **4e** as a colorless oil (m= 367 mg, 63% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.09 – 5.06 (m, 1H), 3.74 (s, 6H), 2.81 (d, *J* = 2.8 Hz, 2H), 2.46 – 2.41 (m, 2H), 2.38 – 2.30 (m, 3H), 2.21 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.02 (t, *J* = 2.6 Hz, 1H), 2.00 – 1.90 (m, 3H), 1.68 (s, 3H), 1.59 (s, 3H), 1.34 – 1.25 (m, 1H), 1.22 – 1.13 (m, 1H), 0.89 (d, *J* = 6.8 Hz, 3H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 209.2, 170.5 (2C), 131.6, 124.4, 78.6, 71.9, 56.2, 53.0 (2C), 50.3, 38.2, 37.1, 29.1, 26.5, 25.8, 25.6, 23.9, 19.8, 17.8
FTIR (neat): ν = 3310, 2956, 2256, 1734, 1437, 1205, 906, 727 cm^{-1}
HRMS (ESI): *m/z* calcd for $C_{20}H_{30}O_5Na^+$: $[M+Na]^+$: 373.1991; found: 373.1990
$[\alpha]_D^{25}$ = -1.8 (c = 0.5, $CHCl_3$)

(+/-)-3-ethyl 4,4-dimethyl 1-oxo-1-phenylhept-6-yne-3,4,4-tricarboxylate **1h**



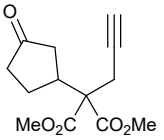
1h

[17] H., Hagiwara, T., Okabe, H., Ono, V. P., Kamat, T., Hoshi, T., Suzuki, M. Ando, *J. Chem. Soc., Perkin Trans. 1*, 2002, 895-900.

The compound **1h** was obtained from ethyl 3-benzoylacrylate and compound **14** following the **GPIV** on 2.45 mmol scale (500 mg). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 20/80) afforded **1h** as a yellow solid (m= 830 mg, 91% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 – 7.95 (m, 2H), 7.54 – 7.59 (m, 1H), 7.48 – 7.43 (m, 2H), 4.12 (q, *J* = 7.2 Hz, 2H), 4.06 (dd, *J* = 10.6, 3.0 Hz, 1H), 3.79 (s, 3H), 3.78 (s, 3H), 3.77 (dd, *J* = 18.0, 10.6 Hz, 1H), 3.53 (dd, *J* = 18.0, 3.0 Hz, 1H), 3.04 (dd, *J* = 17.4, 2.7 Hz, 1H), 2.91 (dd, *J* = 17.4, 2.7 Hz, 1H), 2.12 (t, *J* = 2.7 Hz, 1H), 1.21 (t, *J* = 7.2 Hz, 3H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 171.9, 169.5, 169.2, 136.6, 133.3, 128.7 (2C), 128.2 (2C), 79.5, 72.1, 61.5, 58.5, 53.2, 53.1, 44.5, 37.9, 23.2, 14.1
FTIR (neat): ν = 2955, 1734, 1689, 1436, 1207, 1027, 908, 730, 690 cm^{-1}
HRMS (ESI): *m/z* calcd for $C_{20}H_{23}O_7$: $[M+H]^+$: 375.1444; found: 375.1441

dimethyl 2-(3-oxocyclopentyl)-2-(prop-2-yn-1-yl)malonate **6a**

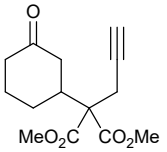


6a

The compound **6a** was obtained from 2-cyclopentenone following the **GPV** on 5.9 mmol scale (482 mg). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 30/70 to 50/50) afforded **6a** as a white solid (m= 900 mg, 61% yield).

All the spectroscopic data are in accordance with those described in the literature[18].

dimethyl 2-(3-oxocyclohexyl)-2-(prop-2-yn-1-yl)malonate **6b**

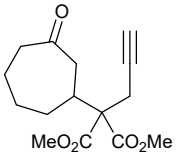


6b

The compound **6b** was obtained from 2-cyclohexen-1-one following the **GPV** on 5.9 mmol scale (564 mg). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 30/70 to 50/50) afforded **6b** as a colorless oil (m= 1.35 g, 86% yield).

All the spectroscopic data are in accordance with those described in the literature[14].

dimethyl 2-(3-oxocycloheptyl)-2-(prop-2-yn-1-yl)malonate **6c**



6c

The compound **6c** was obtained from cyclohept-2-en-1-one following the **GPV** on 3.8 mmol scale (419 mg). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 20/80 to 30/70) afforded **6c** as a yellow oil (m= 959 mg, 90% yield).

All the spectroscopic data are in accordance with those described in the literature[19].

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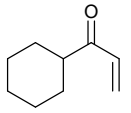
[18] F., Beaufils, F., Dénès, P. Renaud, *Angew. Chem. Int. Ed.*, 2005, **44**, 5273-5275.
[19] F., Beaufils, F., Dénès, B., Becattini, P., Renaud, K. Schenk, *Adv. Synth. Cat.*, 2005, **347**, 1587-1594.

1-cyclohexylprop-2-en-1-one **28**

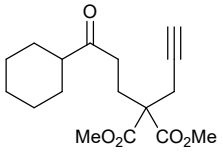


28

The compound **28** was obtained from cyclohexanecarboxaldehyde and vinylmagnesium bromide following the **GPII** on 20 mmol scale (2.2 g). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 5/95) afforded **28** as a yellow oil (m= 2.4 g, 88% yield for 2 steps).

All the spectroscopic data are in accordance with those described in the literature[20].

dimethyl 2-(3-cyclohexyl-3-oxopropyl)-2-(prop-2-yn-1-yl)malonate **4d**

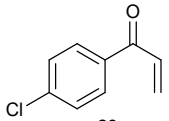


4d

The compound **4d** was obtained from compound **28** and **14** following the **GPIV** on 10 mmol scale (1.38 g). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 10/90) afforded **4d** as a white solid (m= 2.3 g, 75% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.71 (s, 6H), 2.78 (d, J = 2.6 Hz, 2H), 2.50 – 2.45 (m, 2H), 2.33 – 2.26 (m, 3H), 2.01 (t, J = 2.6 Hz, 1H), 1.82 – 1.72 (m, 4H), 1.66 – 1.61 (m, 1H), 1.34 – 1.14 (m, 5H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 212.3, 170.5 (2C), 78.5, 71.8, 56.2, 52.9 (2C), 50.8, 35.4, 28.6 (2C), 26.5, 25.9, 25.7 (2C), 23.9
FTIR (neat): ν = 2931, 1732, 1437, 1200, 910, 729 cm^{-1}
HRMS (ESI): *m/z* calcd for $C_{17}H_{25}O_5$: $[M+H]^+$: 309.1702; found: 309.1702

1-(4-chlorophenyl)prop-2-en-1-one **29**

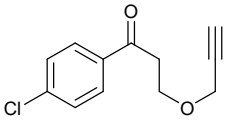


29

The compound **29** was obtained from 3,4'-dichloropropiophenone following the **GPI** on 14.8 mmol scale (3 g). Purification by flash chromatography (EtOAc/Cyclohexane: 10/90) afforded **29** as a colorless oil (m= 2.4 g, 96% yield).

All the spectroscopic data are in accordance with those described in the literature[8].

1-(4-chlorophenyl)-3-(prop-2-yn-1-yloxy)propan-1-one **1o**



1o

The compound **1o** was obtained from compound **29** following the **GPVI** on 7.4 mmol scale (1.2 g). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 5/95) afforded **1o** as a white solid (m= 1.2 g, 74% yield).

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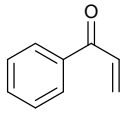
[20] S., Feuillastre, B., Pelotier, O. Piva, *Eur. J. Org. Chem.*, 2014, 1753-1759.

All the spectroscopic data are in accordance with those described in the literature[5].

1-phenylprop-2-en-1-one **30**

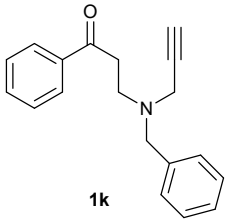


30

The compound **30** was obtained from 3-chloropropiophenone following the **GPI** on 20 mmol scale (3.4 g). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 5/95 to 10/90) afforded **30** as a yellow oil (m= 2.5 g, 95% yield).

All the spectroscopic data are in accordance with those described in the literature[17].

3-(benzyl(prop-2-yn-1-yl)amino)-1-phenylpropan-1-one **1k**

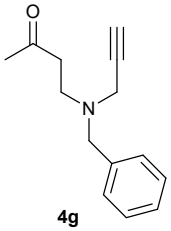


1k

The compound **1k** was obtained from compound **30** and **20** following the **GPIV** on 17.8 mmol scale (2.3 g). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 5/95) afforded **1k** as a colorless oil (m= 3.4 g, 84% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.97 (m, 2H), 7.60 – 5.55 (m, 1H), 7.49 – 7.45 (m, 2H), 7.37 – 7.25 (m, 5H), 3.74 (s, 2H), 3.41 (d, J = 2.4 Hz, 2H), 3.21 (t, J = 7.2 Hz, 2H), 3.10 (t, J = 7.2 Hz, 2H), 2.32 (t, J = 2.4 Hz, 1H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 199.0, 138.4, 136.9, 132.9, 128.9 (2C), 128.5 (2C), 128.2 (2C), 128.0 (2C), 127.1, 78.3, 73.5, 58.0, 48.8, 41.6, 37.2
FTIR (neat): ν = 3295, 1682, 1448, 1212, 1120, 909, 735, 689 cm^{-1}
HRMS (ESI): *m/z* calcd for $C_{19}H_{20}NO$: $[M+H]^+$: 278.1545; found: 278.1544

4-(benzyl(prop-2-yn-1-yl)amino)butan-2-one **4g**

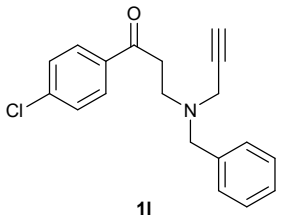


4g

The compound **4g** was obtained from methyl vinyl ketone and compound **20** following the **GPIV** on 2.1 mmol scale (145 mg). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 7/93 to 10/90) afforded **4g** as a colorless oil (m= 365 mg, 82% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.21 (m, 5H), 3.62 (s, 2H), 3.29 (d, J = 2.4 Hz, 2H), 2.88 (t, J = 7.2 Hz, 2H), 2.60 (t, J = 7.2 Hz, 2H), 2.24 (t, J = 2.4 Hz, 1H), 2.12 (s, 3H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 207.8, 138.3, 129.0 (2C), 128.3 (2C), 127.2, 78.1, 73.5, 57.8, 48.2, 42.1, 41.3, 29.8
FTIR (neat): ν = 3287, 2834, 1710, 1454, 1358, 1123, 1028, 738, 699 cm^{-1}
HRMS (ESI): *m/z* calcd for $C_{14}H_{18}NO$: $[M+H]^+$: 216.1388; found: 216.1386

3-(benzyl(prop-2-yn-1-yl)amino)-1-(4-chlorophenyl)propan-1-one **1l**

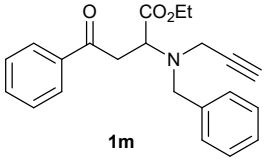


1l

The compound **1l** was obtained from compound **29** and **20** following the **GPIV** on 2.7 mmol scale (458 mg). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 5/95) afforded **1l** as a colorless oil (m= 729 mg, 85% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.8 Hz, 2H), 7.39 (d, *J* = 8.8 Hz, 2H), 7.30 – 7.24 (m, 5H), 3.69 (s, 2H), 3.38 (d, *J* = 2.4 Hz, 2H), 3.13 (t, *J* = 7.2 Hz, 2H), 3.04 (t, *J* = 7.2 Hz, 2H), 2.29 (t, *J* = 2.4 Hz, 1H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 139.3, 138.3, 135.2, 129.4 (2C), 129.0 (2C), 128.8 (2C), 128.3 (2C), 127.2, 78.3, 73.6, 58.0, 48.6, 41.7, 37.2
FTIR (neat): ν = 3302, 1683, 1588, 1400, 1092, 906, 729, 698 cm^{-1}
HRMS (ESI): *m/z* calcd for $C_{19}H_{19}NOCl$: $[M+H]^+$: 312.1155; found: 312.1154

(+/-)-ethyl 2-(benzyl(prop-2-yn-1-yl)amino)-4-oxo-4-phenylbutanoate **1m**

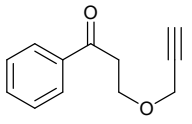


1m

The compound **1m** was obtained from ethyl 3-benzoylacrylate and compound **20** following the **GPIV** on 2.4 mmol scale (500 mg). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 3/97) afforded **1m** as a pale yellow solid (m= 663 mg, 79% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.94 (m, 2H), 7.58 – 7.54 (m, 1H), 7.48 – 7.43 (m, 2H), 7.36 – 7.22 (m, 5H), 4.30 (dd, *J* = 9.4, 4.8 Hz, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 4.02 (d, *J* = 13.6 Hz, 1H), 3.80 (d, *J* = 13.6 Hz, 1H), 3.70 (dd, *J* = 17.2, 9.4 Hz, 1H), 3.47 (d, *J* = 2.4 Hz, 2H), 3.33 (dd, *J* = 17.2, 4.8 Hz, 1H), 2.22 (t, *J* = 2.4 Hz, 1H), 1.33 (t, *J* = 7.2 Hz, 3H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 171.7, 138.5, 136.8, 133.3, 128.9 (2C), 128.7 (2C), 128.5 (2C), 128.2 (2C), 127.4, 80.2, 73.0, 60.9, 60.2, 54.8, 40.4, 39.1, 14.4
FTIR (neat): ν = 1724, 1683, 1449, 1207, 1174, 907, 735, 689 cm^{-1}
HRMS (ESI): *m/z* calcd for $C_{22}H_{24}NO_3$: $[M+H]^+$: 350.1756; found: 350.1755

1-phenyl-3-(prop-2-yn-1-yloxy)propan-1-one **1n**

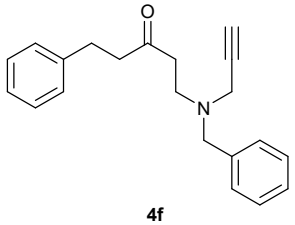


1n

The compound **1n** was obtained from compound **30** following the **GPVI** on 17.8 mmol scale (2.4 g). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 4/96) afforded **1n** as a colorless oil (m= 2.8 g, 83% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.94 (m, 2H), 7.58 – 7.53 (m, 1H), 7.48 – 7.43 (m, 2H), 4.18 (d, *J* = 2.4 Hz, 2H), 3.97 (t, *J* = 6.4 Hz, 2H), 3.27 (t, *J* = 6.4 Hz, 2H), 2.44 (t, *J* = 2.4 Hz, 1H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 198.0, 137.0, 133.3, 128.7 (2C), 128.2 (2C), 79.7, 74.6, 65.4, 58.5, 38.7
FTIR (neat): ν = 3298, 1680, 1449, 1216, 1099, 908, 728, 688 cm^{-1}
HRMS (ESI): *m/z* calcd for $C_{12}H_{12}O_2Na^+$: $[M+Na]^+$: 211.0735; found: 211.0734

1-(benzyl(prop-2-yn-1-yl)amino)-5-phenylpentan-3-one **4f**

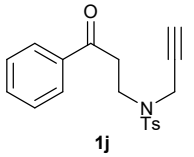


4f

The compound **4f** was obtained from compound **26** and **20** following the **GPIV** on 1.6 mmol scale (256 mg). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 5/95) afforded **4f** as a yellow oil (m= 460 mg, 94% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.21 (m, 10H), 3.67 (s, 2H), 3.34 (d, *J* = 2.4 Hz, 2H), 2.94 (t, *J* = 7,4 Hz, 2H), 2.93 (t, *J* = 7,0 Hz, 2H), 2.77 (t, *J* = 7.4 Hz, 2H), 2.62 (t, *J* = 7.0 Hz, 2H), 2.29 (t, *J* = 2.4 Hz, 1H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 208.8, 141.1, 138.4, 129.1 (2C), 128.5 (2C), 128.4 (2C), 128.3 (2C), 127.3, 126.1, 78.2, 73.5, 57.9, 48.3, 44.1, 41.5, 41.4, 29.6
FTIR (neat): ν = 1710, 1454, 906, 729, 698 cm^{-1}
HRMS (ESI): *m/z* calcd for $C_{21}H_{24}NO$: $[M+H]^+$: 306.1858; found: 306.1852

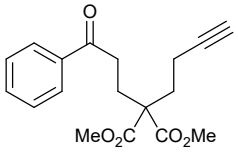
4-methyl-*N*-(3-oxo-3-phenylpropyl)-*N*-(prop-2-yn-1-yl)benzenesulfonamide **1j**



1j

The compound **1j** was obtained from compound **30** and **21** following the **GPIV** on 12 mmol scale (1.6 g). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 5/95 to 15/85) provided **1j** as a white solid (m=1.2 g, 30% yield).
All the spectroscopic data are in accordance with those described in the literature[21].

dimethyl 2-(but-3-yn-1-yl)-2-(3-oxo-3-phenylpropyl)malonate **1f**



1f

The compound **1f** was obtained from compound **30** and **18** following the **GPIV** on 4 mmol scale (528.6 mg). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 5/95 to 7/93) provided **1f** as a white solid (m=822.5 mg, 65% yield).

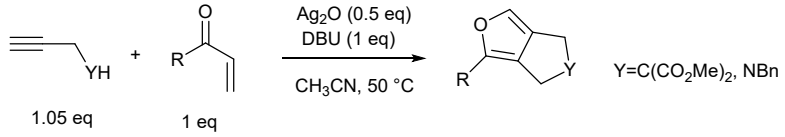
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 – 7.91 (m, 2H), 7.57 – 7.52 (m, 1H), 7.47 - 7.42 (m, 2H), 3.72 (s, 6H), 2.98 (t, *J* = 7.8 Hz, 2H), 2.33 (t, *J* = 7.8 Hz, 2H), 2.21 (s, 4H), 1.95 (t, *J* = 2.4 Hz, 1H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 198.6, 171.3 (2C), 136.7, 133.3, 128.7 (2C), 128.1 (2C), 83.1, 69.1, 56.6, 52.7 (2C), 33.8, 32.9, 27.5, 14.2
FTIR (neat): ν = 3292, 2954, 1728, 1686, 1449, 1202, 906, 732 cm^{-1}
HRMS (ESI): *m/z* calcd for $C_{18}H_{21}O_5$: $[M+H]^+$: 317.1389; found: 317.1386

[21] S., Watanuki, N., Ochifuji, M., Mori, *Organometallics*, 1995, **14**, 5062-5067.

4. Cyclized Products

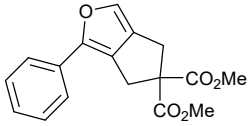
General procedure for the cyclization reaction GPVII:
In a vial protected from the light was placed a suspension of Ag_2O (0.1 mmol, 0.5 eq.) in CH_3CN (0.5 mL). DBU (0.2 mmol, 1 eq.) was added, then a solution of corresponding precursors (0.2 mmol, 1 eq.) in CH_3CN (0.5 mL) was added dropwise. The mixture was heated to 50 °C under air atmosphere and stirred until TLC showed complete disappearance of the starting material. The reaction mixture was quenched by water and extracted twice with Et_2O. The combined organic layers were dried over $MgSO_4$ and evaporated under reduced pressure. The crude mixture was purified by flash chromatography on silica gel affording the expected compound in a pure form.

General procedure for the one-pot reaction GPVIII:



A vial protected from the light was charged with the alkyne (0.21 mmol, 1. 05 eq.) and the α-β unsaturated ketone (0.2 mmol, 1 eq.). The mixture was solubilized in CH_3CN (1 mL) then Ag_2O (0.1 mmol, 0.5 eq.) and DBU (0.2 mmol, 1 eq.) was successively introduced. The reaction was heated to 50 °C under air atmosphere and stirred until TLC showed complete disappearance of the starting materials. The reaction was quenched by water and extracted twice with Et_2O. The combined organic layers were dried over $MgSO_4$ and evaporated under reduced pressure. The crude mixture was purified by flash chromatography on silica gel affording the expected compound in a pure form.

dimethyl 1-phenyl-4*H*-cyclopenta[*c*]furan-5,5(6*H*)-dicarboxylate **2a**

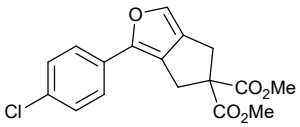


2a

The compound **2a** was obtained from compound **1a** following the **GPVII** on 0.2 mmol scale (60.5 mg). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 5/95 to 10/90) afforded **2a** as a pale yellow solid (m= 45 mg, 75% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.55 (m, 2H), 7.40 – 7.36 (m, 2H), 7.24 -7.21 (m, 1H), 7.12 (s, 1H), 3.77 (s, 6H), 3.56 (s, 2H), 3.35 (d, J = 1.2 Hz, 2H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6 (2C), 144.3, 132.5, 131.1, 130.9, 128.8 (2C), 126.8, 125.1, 123.9 (2C), 67.5, 53.2 (2C), 33.5, 31.8
FTIR (neat): ν = 2954, 1732, 1435, 1248, 1199, 963, 906, 728, 692 cm^{-1}
HRMS (ESI): *m/z* calcd for $C_{17}H_{16}O_5Na^+$: $[M+Na]^+$: 323.0895; found: 323.0892

dimethyl 1-(4-chlorophenyl)-4*H*-cyclopenta[*c*]furan-5,5(6*H*)-dicarboxylate **2b**



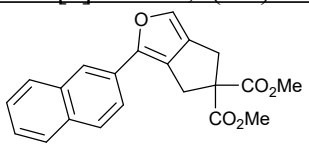
2b

The compound **2b** was obtained from compound **2a** following the **GPVII** on 0.2 mmol scale (67.4 mg). Purification by flash chromatography (EtOAc/Cyclohexane: 5/95) afforded **2b** as white solid (m= 45.5 mg, 68% yield).

The compound **2b** was obtained from compound **29** and **14** following the **GPVIII** on 0.2 mmol scale (33.3 mg). Purification by flash chromatography (EtOAc/Cyclohexane: 5/95) afforded **2b** as a white solid (m= 43.5 mg, 65% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.45 (m, 2H), 7.35 – 7.31 (m, 2H), 7.10 (s, 1H), 3.77 (s, 6H), 3.52 (s, 2H), 3.34 (d, J = 1.6 Hz, 2H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5 (2C), 143.4, 132.8, 132.4, 131.1, 129.6, 129.0 (2C), 125.6, 125.1 (2C), 67.5, 53.3 (2C), 33.4, 31.8
FTIR (neat): ν = 2955, 1733, 1489, 1435, 1250, 1092, 908, 830, 730 cm^{-1}
HRMS (ESI): *m/z* calcd for $C_{17}H_{16}ClO_5$: $[M+H]^+$: 335.0686; found: 335.0684

dimethyl 1-(naphthalen-2-yl)-4*H*-cyclopenta[*c*]furan-5,5(6*H*)-dicarboxylate **2d**

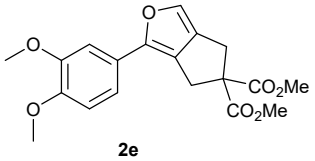


2d

The compound **2d** was obtained from compound **1d** following the **GPVII** on 0.2 mmol scale (70.5 mg). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 10/90 to 15/85) afforded **2d** as a white solid (m= 56.3 mg, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.86- 7.80 (m, 3H), 7.72 - 7.69 (m, 1H), 7.50 – 7.42 (m, 2H), 7.18 (s, 1H), 3.80 (s, 6H), 3.66 (s, 2H), 3.39 (d, J = 1.6 Hz, 2H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6 (2C), 144.5, 133.6, 132.7, 132.3, 131.1, 128.5, 128.4, 128.1, 127.8, 126.5, 125.9, 125.6, 122.4, 122.2, 67.5, 53.2 (2C), 33.6, 31.8
FTIR (neat): ν = 2954, 1732, 1435, 1250, 1199, 1066, 905, 816, 725 cm^{-1}
HRMS (ESI): *m/z* calcd for $C_{21}H_{19}O_5$: $[M+H]^+$: 351.1232; found: 351.1237

dimethyl 1-(3,4-dimethoxyphenyl)-4*H*-cyclopenta[*c*]furan-5,5(6*H*)-dicarboxylate **2e**

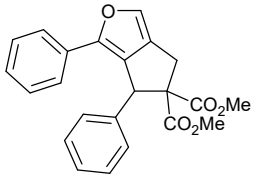


2e

The compound **2e** was obtained from compound **1e** following the **GPVII** on 0.2 mmol scale (72.5 mg). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 20/80 to 30/70) afforded **2e** as a yellow solid (m= 52.6 mg, 73% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 – 7.10 (m, 1H), 7.08 - 7.05 (m, 2H), 6.88 – 6.86 (m, 1H), 3.92 (s, 3H), 3.88 (s, 3H), 3.76 (s, 6H), 3.51 (s, 2H), 3.32 (d, J = 1.6 Hz, 2H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6 (2C), 149.3, 148.2, 144.3, 131.8, 130.9, 124.5, 123.5, 116.7, 111.5, 107.2, 67.5, 56.0, 55.9, 53.2 (2C), 33.3, 31.8
FTIR (neat): ν = 2256, 1733, 1512, 1247, 1025, 906, 730 cm^{-1}
HRMS (ESI): *m/z* calcd for $C_{19}H_{21}O_7$: $[M+H]^+$: 361.1287; found: 361.1289

dimethyl 1,6-diphenyl-4*H*-cyclopenta[*c*]furan-5,5(6*H*)-dicarboxylate **2g**



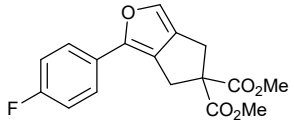
2g

The compound **2g** was obtained from compound **1g** following the **GPVII** on 0.2 mmol scale (75.7 mg). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 5/95) afforded **2g** as a white solid (m= 31.6 mg, 42% yield).

The compound **2g** was obtained from chalcone and compound **14** following the **GPVIII** on 0.2 mmol scale (41.6 mg). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 5/95) afforded **2g** as a white solid (m= 35.4 mg, 47% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.35 (m, 2H), 7.27 – 7.18 (m, 8H), 7.14 – 7.10 (m, 1H), 5.30 (s, 1H), 3.79 (d, J = 16.4 Hz, 1H), 3.77 (s, 3H), 3.31 (s, 3H), 3.24 (d, J = 16.4 Hz, 1H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 168.8, 145.1, 138.1, 132.6, 130.7, 130.6, 129.0 (2C), 128.8, 128.5 (2C), 128.4 (2C), 127.7, 126.9, 124.3 (2C), 73.8, 53.3, 52.3, 50.0, 30.6
FTIR (neat): ν = 2952, 1733, 1435, 1259, 1160, 907, 729 cm^{-1}
HRMS (ESI): *m/z* calcd for $C_{23}H_{21}O_5$: $[M+H]^+$: 377.1389; found: 377.1388

dimethyl 1-(4-fluorophenyl)-4*H*-cyclopenta[*c*]furan-5,5(6*H*)-dicarboxylate **2c**



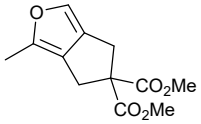
2c

The compound **2c** was obtained from compound **1c** following the **GPVII** on 0.2 mmol scale (64.1 mg). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 5/95) afforded **2c** a as white solid (m= 50.9 mg, 80% yield).

The compound **2c** was obtained from compound **24** and **14** following the **GPVIII** on 0.2 mmol scale (30 mg). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 5/95) afforded **2c** as a white solid (m= 48.4 mg, 76% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.49 (m, 2H), 7.09 – 7.04 (m, 3H), 3.77 (s, 6H), 3.51 (s, 2H), 3.34 (d, J = 1.6 Hz, 2H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5 (2C), 161.7 (d, J = 245.0 Hz), 143.6, 132.4, 131.0, 127.5 (d, J = 3.0 Hz), 125.6 (d, J = 8.0 Hz, 2C), 124.6, 115.8 (d, J = 21.0 Hz, 2C), 67.5, 53.2 (2C), 33.3, 31.9
^{19}F NMR (280 MHz, $CDCl_3$) δ -114.8
FTIR (neat): ν = 2955, 1732, 1506, 1435, 1232, 1157, 1064, 907, 835, 731 cm^{-1}
HRMS (ESI): *m/z* calcd for $C_{17}H_{16}O_5F$: $[M+H]^+$: 319.0982; found: 319.0980

dimethyl 1-methyl-4*H*-cyclopenta[*c*]furan-5,5(6*H*)-dicarboxylate **5c**



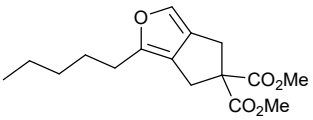
5c

The compound **5c** was obtained from compound **4c** following the **GPVII** on 0.2 mmol scale (48.1 mg). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 5/95) afforded **5c** as a yellow solid (m= 34.7 mg, 73% yield).

The compound **5c** was obtained from methyl vinyl ketone and compound **14** following the **GPVIII** on 0.2 mmol scale (14 mg). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 5/95) afforded **5c** as a yellow solid (m= 33.4 mg, 70% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (s, 1H), 3.74 (s, 6H), 3.26 (s, 2H), 3.19 (s, 2H), 2.18 (s, 3H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8 (2C), 142.5, 131.3, 129.2, 123.8, 67.3, 53.1 (2C), 32.2, 31.6, 12.7
FTIR (neat): ν = 2955, 2258, 1732, 1435, 1257, 1199, 1066, 908, 727 cm^{-1}
HRMS (ESI): *m/z* calcd for $C_{12}H_{14}O_5Na^+$: $[M+Na]^+$: 261.0739; found: 261.0737

dimethyl 1-pentyl-4*H*-cyclopenta[*c*]furan-5,5(6*H*)-dicarboxylate **13a**

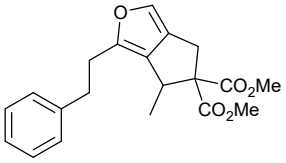


13a

The compound **13a** was obtained from oct-1-en-3-one and compound **14** following the **GPVIII** on 0.2 mmol scale (25.2 mg). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 5/95) afforded **13a** as a yellow solid (m= 37.7 mg, 64% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.93 (s, 1H), 3.75 (s, 6H), 3.26 – 3.22 (m, 4H), 2.53 (t, J = 7.6 Hz, 2H), 1.65 - 1.56 (m, 2H), 1.34 - 1.25 (m, 4H), 0.89 (t, J = 6.8 Hz, 3H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8 (2C), 146.8, 131.2, 129.1, 123.3, 67.3, 53.1 (2C), 32.0, 31.9, 31.5, 27.4, 27.3, 22.5, 14.1
FTIR (neat): ν = 2955, 1735, 1435, 1254, 1198, 1159, 1066, 731 cm^{-1}
HRMS (ESI): *m/z* calcd for $C_{16}H_{23}O_5$: $[M+H]^+$: 295.1545; found: 295.1544

dimethyl 6-methyl-1-phenethyl-4*H*-cyclopenta[*c*]furan-5,5(6*H*)-dicarboxylate **5a**

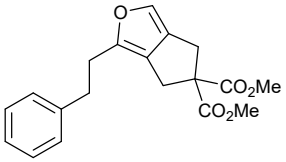


5a

The compound **5a** was obtained from compound **4a** following the **GPVII** on 0.2 mmol scale (68.8 mg). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 3/97 to 7/93) afforded **5a** as a yellow solid (m= 45.8 mg, 67% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 2H), 7.20 – 7.16 (m, 1H), 7.14 – 7.12 (m, 2H), 6.95 (s, 1H), 3.75-3.69 (m, 7H), 3.43 (dd, J = 16, 1.6 Hz, 1H), 3.03 (dd, J = 16, 1.6 Hz, 1H), 2.97 – 2.91 (m, 2H), 2.90 – 2.78 (m, 2H), 0.96 (d, J = 7.2 Hz, 3H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 170.2, 145.4, 141.4, 131.4, 129.4, 128.5 (2C), 128.4 (2C), 127.7, 126.1, 71.2, 52.9, 52.4, 37.6, 34.7, 30.6, 29.5, 16.2
FTIR (neat): ν = 2953, 1733, 1434, 1252, 1159, 1084, 1042, 738, 700 cm^{-1}
HRMS (ESI): *m/z* calcd for $C_{20}H_{23}O_5$: $[M+H]^+$: 343.1545; found: 343.1545

dimethyl 1-phenethyl-4*H*-cyclopenta[*c*]furan-5,5(6*H*)-dicarboxylate **5b**

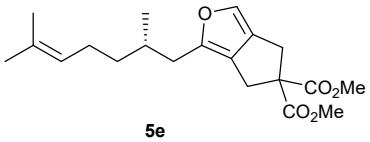


5b

The compound **5b** was obtained from compound **4b** following the **GPVII** on 0.2 mmol scale (66.1 mg). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 8/92) afforded **5b** as a white solid (m= 45.3 mg, 69% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 2H), 7.21 – 7.12 (m, 3H), 6.96 (s, 1H), 3.73 (s, 6H), 3.24 (d, J = 1.6 Hz, 2H), 3.07 (s, 2H), 2.95 – 2.90 (m, 2H), 2.87 – 2.82 (m, 2H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7 (2C), 145.4, 141.2, 131.4, 129.2, 128.4 (2C), 128.3 (2C), 126.0, 124.0, 67.2, 53.0 (2C), 34.0, 31.9, 31.7, 29.3
FTIR (neat): ν = 2953, 1733, 1434, 1253, 1198, 1065, 909, 729, 699 cm^{-1}
HRMS (ESI): *m/z* calcd for $C_{19}H_{21}O_5$: $[M+H]^+$: 329.1389; found: 329.1386

dimethyl (*S*)-1-(2,6-dimethylhept-5-en-1-yl)-4*H*-cyclopenta[*c*]furan-5,5(6*H*)-dicarboxylate **5e**

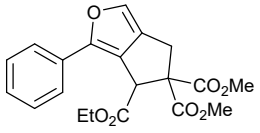


5e

The compound **5e** was obtained from compound **4e** following the **GPVII** on 0.2 mmol scale (70.1 mg). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 5/95) afforded **5e** as a pale yellow oil (m= 41.8 mg, 60% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.94 (s, 1H), 5.11 – 5.05 (m, 1H), 3.74 (s, 6H), 3.26 (d, *J* = 1.2 Hz, 2H), 3.19 (s, 2H), 2.53 (dd, *J* = 15.0, 6.0 Hz, 1H), 2.35 (dd, *J* = 15.0, 6.0 Hz, 1H), 2.07 – 1.89 (m , 2H), 1.85-1.73 (m, 1H), 1.67 (s, 3H), 1.60 (s, 3H), 1.40 – 1.10 (m, 3H), 0.88 (d, *J* = 6.6 Hz, 3H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7 (2C), 145.9, 131.4, 131.3, 128.9, 124.8, 124.1, 67.3, 53.0 (2C), 36.8, 34.8, 32.4, 32.1, 32.0, 25.8, 25.7, 19.7, 17.7
FTIR (neat): ν = 2955, 1734, 1435, 1255, 1199, 1066, 908, 729 cm^{-1}
HRMS (ESI): *m/z* calcd for $C_{20}H_{29}O_5$: $[M+H]^+$: 349.2015; found: 349.2013
$[\alpha]_D^{25}$ = -1.6 (c = 0.5, $CHCl_3$)

4-ethyl 5,5-dimethyl 3-phenyl-4*H*-cyclopenta[*c*]furan-4,5,5(6*H*)-tricarboxylate **2h**

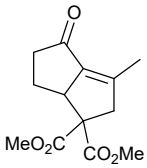


2h

The compound **2h** was obtained from compound **1h** following the **GPVII** on 0.2 mmol scale (74.9 mg). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 8/92 to 13/87) afforded **2h** as a white solid (m= 52.1 mg, 70% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.77 (m, 2H), 7.41 - 7.37 (m, 2H), 7.28 – 7.23 (m, 1H), 7.15 (s, 1H), 4.84 (s, 1H), 4.17 – 4.03 (m, 2H), 3.78 (s, 3H), 3.71 (s, 3H), 3.70 (dd, *J* = 16.0, 2.0 Hz, 1H), 3.36 (d, *J* = 16.0 Hz, 1H), 1.16 (t, *J* = 7.0 Hz, 3H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 170.2, 169.1, 146.0, 133.1, 130.3, 130.2, 128.6 (2C), 127.5, 124.6 (2C), 123.6, 71.2, 61.6, 53.7, 53.0, 49.9, 30.9, 14.0
FTIR (neat): ν = 2955, 2259, 1735, 1239, 1163, 1025, 905, 725, 691 cm^{-1}
HRMS (ESI): *m/z* calcd for $C_{20}H_{21}O_7$: $[M+H]^+$: 373.1287; found: 373.1283

dimethyl 3-methyl-4-oxo-4,5,6,6a-tetrahydropentalene-1,1(2*H*)-dicarboxylate **7a**



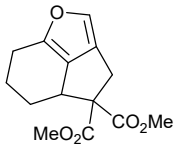
7a

The compound **7a** was obtained from compound **6a** following the **GPVII** on 0.2 mmol scale (50.5 mg). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 15/85 to 20/80) afforded **7a** as a colorless oil (m= 24.2 mg, 48% yield).

All the spectroscopic datas are in accordance with those described in the literature[22]

dimethyl 3,4,5,5a-tetrahydroindeno[7,1-*bc*]furan-6,6(7*H*)-dicarboxylate **8b**

[22] T., Yang, A., Ferrali, L., Campbell, D. J. Dixon, *Chem. Commun.*, 2008, 2923-2925.

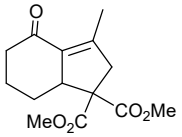


8b

The compound **8b** was obtained from compound **6b** following the **GPVII** on 0.4 mmol scale (106.5 mg). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 5/95) afforded **8b** as a yellow solid (m= 50 mg, 47% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.04 (s,1H), 3.78 (s, 3H), 3.70 – 3.64 (m, 1H), 3.63 (s, 3H), 3.36 (d, *J* = 15.3 Hz, 1H), 3.11 (dd, *J* = 15.3, 1.8 Hz, 1H), 2.65 – 2.58 (m, 1H), 2.44 – 2.32 (m, 1H), 2.15 – 2.06 (m, 2H), 1.95 – 1.79 (m, 1H), 0.72 – 0.59 (m, 1H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 170.4, 147.8, 134.8, 133.4, 126.5, 73.1, 52.8, 52.1, 40.6, 35.6, 27.6, 25.2, 23.8
FTIR (neat): ν = 2951, 1731, 1435, 1269, 1242, 1081, 1037, 933 cm^{-1}
HRMS (ESI): *m/z* calcd for $C_{14}H_{17}O_5$: $[M+H]^+$: 265.1076; found: 265.1075

dimethyl 3-methyl-4-oxo-2,4,5,6,7,7a-hexahydro-1*H*-indene-1,1-dicarboxylate **7b**

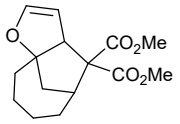


7b

The compound **7b** was obtained from compound **6b** following the **GPVII** on 0.4 mmol scale (106.5 mg). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 5/95) afforded **7b** as a white solid (m= 32 mg, 30% yield).

All the spectroscopic datas are in accordance with those described in the literature[20].

dimethyl 6,7,8,9-tetrahydro-5*H*-5,9a-methanocycloocta[*b*]furan-4,4(3a*H*)-dicarboxylate **9c**

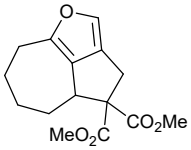


9c

The compound **9c** was obtained from compound **6c** following the **GPVII** on 0.2 mmol scale (56.1 mg). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 2/98 to 5/95) afforded **9c** as a yellow solid (m= 28.2 mg, 51% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.15 (t, *J* = 2.4 Hz, 1H), 4.72 (t, *J* = 2.4 Hz, 1H), 3.95 (s, 1H), 3.72 (s, 3H), 3.65 (s, 3H), 2.85 – 2.81 (m, 1H), 2.35 (dd, *J* = 12.8, 7.2 Hz, 1H), 2.21 (d, *J* = 12.8 Hz, 1H), 1.98 – 1.92 (m, 1H), 1.85 – 1.78 (m, 1H), 1.75 – 1.68 (m, 1H), 1.59 - 1.48 (m, 2H), 1.46 – 1.31 (m, 3H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 170.9, 144.6, 99.2, 96.4, 69.5, 59.3, 52.4, 51.9, 42.3, 42.2, 37.5, 31.3, 24.0, 23.7
FTIR (neat): ν = 2950, 1729, 1615, 1434, 1262, 1195, 1155, 1073, 909, 727 cm^{-1}
HRMS (ESI): *m/z* calcd for $C_{15}H_{21}O_5$: $[M+H]^+$: 281.1389; found: 281.1385

dimethyl 5,6,7,8-tetrahydro-3*H*-azuleno[8,1-bc]furan-4,4(4a*H*)-dicarboxylate **8c**

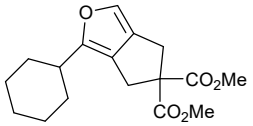


8c

The compound **8c** was obtained from compound **6c** following the **GPVII** on 0.2 mmol scale (56.1 mg). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 2/98 to 5/95) afforded **8c** as a yellow solid (m= 22.3 mg, 40% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.89 (s, 1H), 3.78 (s, 3H), 3.68 (s, 3H), 3.66 – 3.59 (m, 1H), 3.37 (dd, *J* = 15.9, 0.9 Hz, 1H), 2.96 (dd, *J* = 15.9, 1.8 Hz, 1H), 2.75 – 2.67 (m, 1H), 2.64 - 2.52 (m, 1H), 2.27 – 2.17 (m, 1H), 2.17-2.09 (m, 1H), 2.06-1.96 (m, 1H), 1.51 – 1.37 (m, 2H), 1.06 – 0.94 (m, 1H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 171.1, 148.0, 130.8, 129.5, 128.1, 70.4, 52.8, 52.2, 44.5, 33.5, 31.6, 28.1, 27.7, 27.6
FTIR (neat): ν = 2925, 1730, 1435, 1264, 1219, 1173, 1071, 910, 728 cm^{-1}
HRMS (ESI): *m/z* calcd for $C_{15}H_{19}O_5$: $[M+H]^+$: 279.1232; found: 279.1230

dimethyl 1-cyclohexyl-4*H*-cyclopenta[*c*]furan-5,5(6*H*)-dicarboxylate **5d**

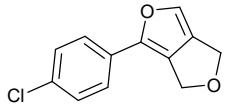


5d

The compound **5d** was obtained from compound **4d** following the **GPVII** on 0.2 mmol scale (61.7 mg). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 10/90 to 20/80) afforded **5d** as a colorless oil (m= 38.3 mg, 63% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (s, 1H), 3.74 (s, 6H), 3.26 (dd, *J* = 14.0, 1.2 Hz, 4H), 2.60 – 2.55 (m, 1H), 2.00 – 1.97 (m, 2H), 1.77 – 1.76 (m, 3H), 1.43 – 1.21 (m, 5H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8 (2C), 150.5, 130.8, 129.2, 121.9, 67.3, 53.1 (2C), 37.3, 32.6, 31.7, 31.2 (2C), 26.2, 26.0 (2C)
FTIR (neat): ν = 2928, 2854, 1734, 1435, 1256, 1199, 1066, 909, 730 cm^{-1}
HRMS (ESI): *m/z* calcd for $C_{17}H_{23}O_5$: $[M+H]^+$: 307.1545; found: 307.1541

4-(4-chlorophenyl)-1*H*,3*H*-furo[3,4-*c*]furan **2o**

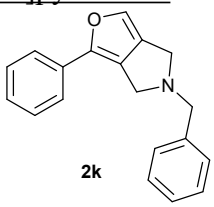


2o

The compound **2o** was obtained from compound **1o** following the **GPVII** on 0.2 mmol scale (44.5 mg). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 5/95) afforded **2o** as a yellow solid (m= 15.4 mg, 35% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (s, 4H), 7.15 (s, 1H), 4.99 (s, 2H), 4.86 (s, 2H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8, 132.9, 132.7, 130.5, 129.2 (2C), 129.1, 127.1, 125.2 (2C), 66.4, 65.6
FTIR (neat): ν = 2925, 1490, 1092, 1015, 908, 732 cm^{-1}
HRMS (ESI): *m/z* calcd for $C_{12}H_{10}ClO_2$: $[M+H]^+$: 221.0369; found: 221.0368

5-benzyl-1-phenyl-5,6-dihydro-4*H*-furo[3,4-*c*]pyrrole **2k**

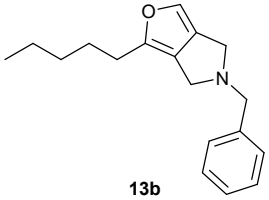


2k

The compound **2k** was obtained from compound **1k** following the **GPVII** on 0.4 mmol scale (110.9 mg). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 5/95 to 10/90) afforded **2k** as a white solid (m= 78.2 mg, 71% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.50 (m, 2H), 7.48 – 7.44 (m, 2H), 7.42 – 7.30 (m, 5H), 7.26 – 7.21 (m, 1H), 7.14 (s, 1H), 3.98 (s, 2H), 3.93 (s, 2H), 3.78 (s, 2H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 139.1, 131.2, 131.1, 131.0, 128.8 (2C), 128.7 (2C), 128.6 (2C), 127.3, 126.8, 125.5, 123.9 (2C), 60.4, 52.2, 51.1
FTIR (neat): ν = 2789, 1494, 1044, 966, 906, 841, 762, 731, 689 cm^{-1}
HRMS (ESI): *m/z* calcd for $C_{19}H_{18}NO$: $[M+H]^+$: 276.1388; found: 276.1387

5-benzyl-1-pentyl-5,6-dihydro-4*H*-furo[3,4-*c*]pyrrole **13b**

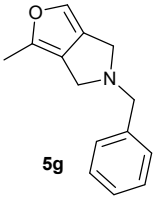


13b

The compound **13b** was obtained from oct-1-en-3-one and compound **20** following the **GPVIII** on 0.4 mmol scale (50.5 mg). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 5/95 to 7/93) afforded **13b** as a colorless oil (m= 71.1 mg, 66% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 - 7.41 (m, 2H), 7.39 – 7.26 (m, 3H), 6.97 (s, 1H), 3.91 (s, 2H), 3.67 (s, 2H), 3.63 (s, 2H), 2.55 (t, J = 7.6 Hz, 2H), 1.66 – 1.56 (m, 2H), 1.35-1.31 (m, 4H), 0.93 – 0.88 (m, 3H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6, 139.1, 129.8, 129.4, 128.8 (2C), 128.5 (2C), 127.2, 123.6, 60.5, 51.2, 51.1, 31.6, 27.5, 27.3, 22.5, 14.1
FTIR (neat): ν = 2929, 2788, 1592, 1454, 1139, 908, 784, 732, 698 cm^{-1}
HRMS (ESI): *m/z* calcd for $C_{18}H_{24}NO$: $[M+H]^+$: 270.1858; found: 270.1855

5-benzyl-1-methyl-5,6-dihydro-4*H*-furo[3,4-*c*]pyrrole **5g**

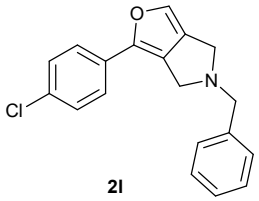


5g

The compound **5g** was obtained from compound **4g** following the **GPVII** on 0.2 mmol scale (43.1 mg). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 7/93) afforded **5g** as a colorless oil (m= 29.4 mg, 69% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.42 (m, 2H), 7.38 – 7.35 (m, 2H), 7.31 – 7.28 (m, 1H), 6.97 (s, 1H), 3.91 (s, 2H), 3.68 (s, 2H), 3.59 (s, 2H), 2.22 (s, 3H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1, 139.1, 130.0, 129.6, 128.8 (2C), 128.4 (2C), 127.2, 124.1, 60.4, 51.4, 50.8, 12.7
FTIR (neat): ν = 2787, 1594, 1453, 1367, 1254, 1087, 926, 841, 732, 697 cm^{-1}
HRMS (ESI): *m/z* calcd for $C_{14}H_{16}NO$: $[M+H]^+$: 214.1232; found: 214.1230

5-benzyl-1-(4-chlorophenyl)-5,6-dihydro-4*H*-furo[3,4-*c*]pyrrole **2l**

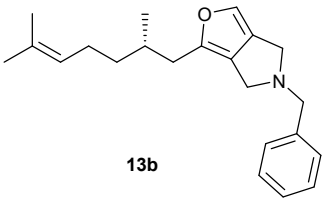


2l

The compound **2l** was obtained from compound **1l** following the **GPVII** on 0.4 mmol scale (124.7 mg). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 5/95 to 10/90) afforded **2l** as a yellow solid (m= 97.8 mg, 79% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.44 (m, 2H), 7.42 – 7.37 (m, 4H), 7.34 – 7.30 (m, 3H), 7.13 (s 1H), 3.97 (s, 2H), 3.88 (s, 2H), 3.76 (s, 2H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 138.9, 132.3, 131.4, 131.3, 129.5, 128.9 (2C), 128.8 (2C), 128.6 (2C), 127.3, 126.0, 125.1 (2C), 60.3, 52.1, 51.0
FTIR (neat): ν = 2792, 1489, 1091, 968, 905, 828, 733, 698 cm^{-1}
HRMS (ESI): *m/z* calcd for $C_{19}H_{17}NOCl$: $[M+H]^+$: 310.0999; found: 310.0998

(*S*)-5-benzyl-1-(2,6-dimethylhept-5-en-1-yl)-5,6-dihydro-4*H*-furo[3,4-*c*]pyrrole **13b**

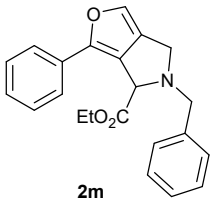


13b

The compound **13b** was obtained from compound **27** and **20** following the **GPVIII** on 0.4 mmol scale (72.1 mg). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 5/95) afforded **13b** as a colorless oil (m= 80.2 mg, 62% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.43 (m, 2H), 7.39 – 7.36 (m, 2H), 7.33 – 7.28 (m, 1H), 7.00 (s, 1H), 5.15 – 5.12 (m, 1H), 3.93 (s, 2H), 3.71 (s, 2H), 3.64 (s, 2H), 2.58 (dd, *J* = 14.8, 7.6 Hz, 1H), 2.41 (dd, *J* = 14.8, 7.6 Hz, 1H), 2.10 – 1.98 (m, 2H), 1.88 – 1.80 (m, 1H), 1.73 (s, 3H), 1.64 (s, 3H), 1.46 – 1.37 (m, 1H), 1.27 - 1.19 (m, 1H), 0.94 (d, *J* = 6.8 Hz, 3H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 139.0, 131.2, 129.9, 129.3, 128.8 (2C), 128.4 (2C), 127.1, 124.7, 124.4, 60.4, 51.3, 51.1, 36.7, 34.8, 32.3, 25.8, 25.6, 19.8, 17.7
FTIR (neat): ν = 2913, 1454, 1376, 906, 728, 698 cm^{-1}
HRMS (ESI): *m/z* calcd for $C_{22}H_{30}NO$: $[M+H]^+$: 324.2327; found: 324.2326
$[\alpha]_D^{25}$ = -0.83 (c = 0.48, $CHCl_3$)

ethyl 5-benzyl-3-phenyl-5,6-dihydro-4*H*-furo[3,4-*c*]pyrrole-4-carboxylate **2m**



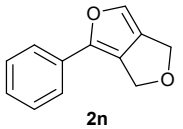
2m

The compound **2m** was obtained from compound **1m** following the **GPVII** on 0.4 mmol scale (139.8 mg). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 5/95 to 7/93) afforded **2m** as a yellow solid (m= 87.5 mg, 63% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.65 (m, 2H), 7.44 – 7.41 (m, 2H),7.40 – 7.35 (m, 4H), 7.33 – 7.29 (m, 1H), 7.27 – 7.23 (m, 1H), 7.17 (s, 1H), 4.85 (s, 1H), 4.21 - 4.07 (m, 5H), 3.88 (d, *J* = 11.6 Hz, 1H), 1.18 (t, *J* = 7.0 Hz, 3H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 144.8, 138.5, 131.4, 131.1, 130.3, 128.8 (2C), 128.6 (2C), 128.5 (2C), 127.4, 127.3, 124.6 (2C), 124.5, 63.6, 61.0, 56.3, 49.5, 14.3

FTIR (neat): ν = 1728, 1495, 1179, 1027, 906, 727, 692 cm^{-1}
HRMS (ESI): *m/z* calcd for $C_{22}H_{22}NO_3$: $[M+H]^+$: 348.1600; found: 348.1598

4-phenyl-1*H*,3*H*-furo[3,4-*c*]furan **2n**

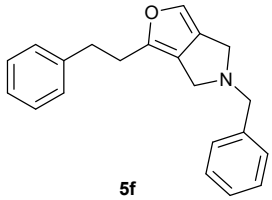


2n

The compound **2n** was obtained from compound **1n** following the **GPVII** on 0.4 mmol scale (75.3 mg). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 5/95 to 7/93) afforded **2n** as a yellow solid (m= 38.4 mg, 52% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.37 (m, 4H), 7.27 – 7.23 (m, 1H), 7.15 (s, 1H), 5.02 (s, 2H), 4.86 (s, 2H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 132.5, 130.6, 130.2, 128.9 (2C), 127.1, 126.6, 123.9 (2C), 66.5, 65.5
FTIR (neat): ν = 2863, 2251, 1495, 1049, 905, 725, 690 cm^{-1}
HRMS (ESI): *m/z* calcd for $C_{12}H_{10}O_2Na^+$: $[M+Na]^+$: 209.0578; found: 209.0575

5-benzyl-1-phenethyl-5,6-dihydro-4*H*-furo[3,4-*c*]pyrrole **5f**

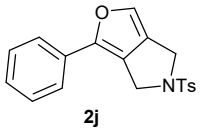


5f

The compound **5f** was obtained from compound **4f** following the **GPVII** on 0.4 mmol scale (122.2 mg). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 5/95) afforded **5f** as a yellow solid (m= 88.6 mg, 73% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.34 (m, 4H), 7.31 – 7.27 (m, 3H), 7.23 – 7.16 (m, 3H), 7.00 (s, 1H), 3.87 (s, 2H), 3.66 (s, 2H), 3.48 (s, 2H), 2.95 – 2.85 (m, 4H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 141.3, 139.1, 130.1, 129.5, 128.9 (2C), 128.6 (2C), 128.5 (2C), 128.4 (2C), 127.2, 126.2, 124.3, 60.4, 51.2, 50.9, 34.1, 29.4
FTIR (neat): ν = 2925, 2792, 1454, 908, 731, 699 cm^{-1}
HRMS (ESI): *m/z* calcd for $C_{21}H_{22}NO$: $[M+H]^+$: 304.1701; found: 304.1697

1-phenyl-5-tosyl-5,6-dihydro-4*H*-furo[3,4-*c*]pyrrole **2j**

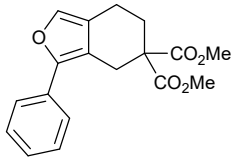


2j

The compound **2j** was obtained from compound **1j** following the **GPVII** on 0.2 mmol scale (68.3 mg). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 5/95 to 15/85) afforded **2j** as a white solid (m= 35.9 mg, 53% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 – 7.76 (m, 2H), 7.45 – 7.32 (m, 6H), 7.28 – 7.23 (m, 1H), 7.14 (s, 1H), 4.58 (s, 2H), 4.41 (s, 2H), 2.41 (s, 3H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 144.0, 134.2, 131.9, 130.1, 130.0 (2C), 129.0 (2C), 127.7, 127.6 (2C), 127.5, 124.0 (2C), 121.6, 47.6, 46.3, 21.7
FTIR (neat): ν = 1343, 1160, 907, 814, 728, 659 cm^{-1}
HRMS (ESI): *m/z* calcd for $C_{19}H_{18}NO_3S$: $[M+H]^+$: 340.1007; found: 340.1005

dimethyl 3-phenyl-6,7-dihydroisobenzofuran-5,5(4H)-dicarboxylate **2f**

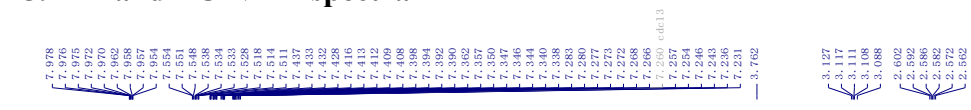


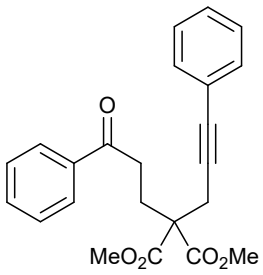
2f

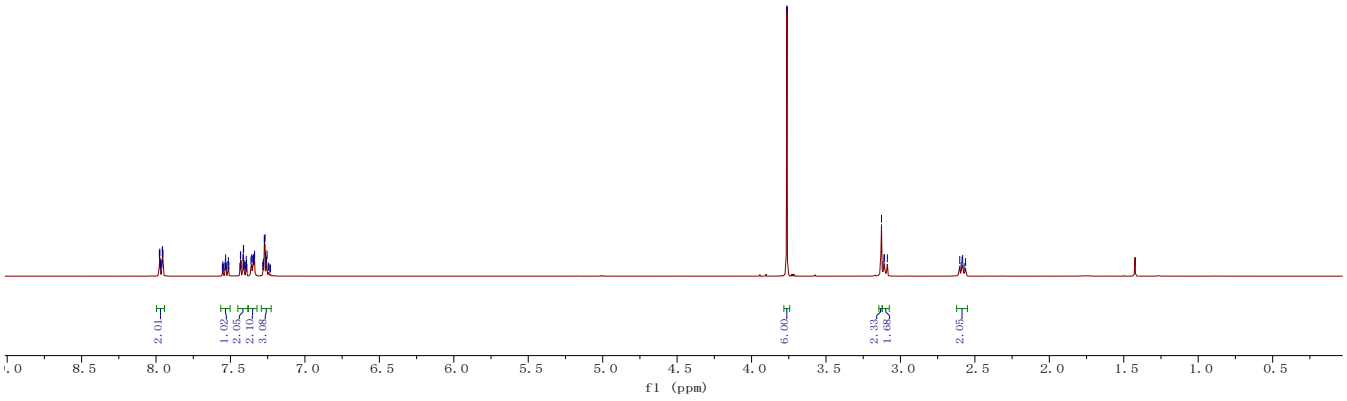
The compound **2f** was obtained from compound **1f** following the **GPVII** on 0.4 mmol scale (126.5 mg). Purification by flash chromatography on silica gel (EtOAc/Cyclohexane: 2/98 to 4/96) afforded **2f** as a white solid (m= 93.0 mg, 74% yield).

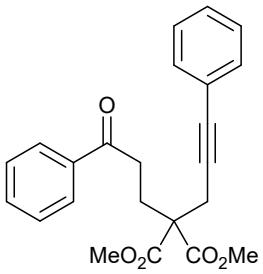
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.61 (m, 2H), 7.42 – 7.38 (m, 2H), 7.27 – 7.22 (m, 1H), 7.20 (s, 1H), 3.75 (s, 6H), 3.35 (s, 2H), 2.66 (t, J = 6.6 Hz, 2H), 2.31 (t, J = 6.6 Hz, 2H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8 (2C), 147.5, 136.5, 131.8, 128.7 (2C), 126.8, 124.7 (2C), 121.4, 115.2, 54.2, 53.0 (2C), 28.6, 28.5, 17.0
FTIR (neat): ν = 2954, 1733, 1248, 905, 728, 692 cm^{-1}
HRMS (ESI): *m/z* calcd for $C_{18}H_{19}O_5$: $[M+H]^+$: 315.1232; found: 315.1228

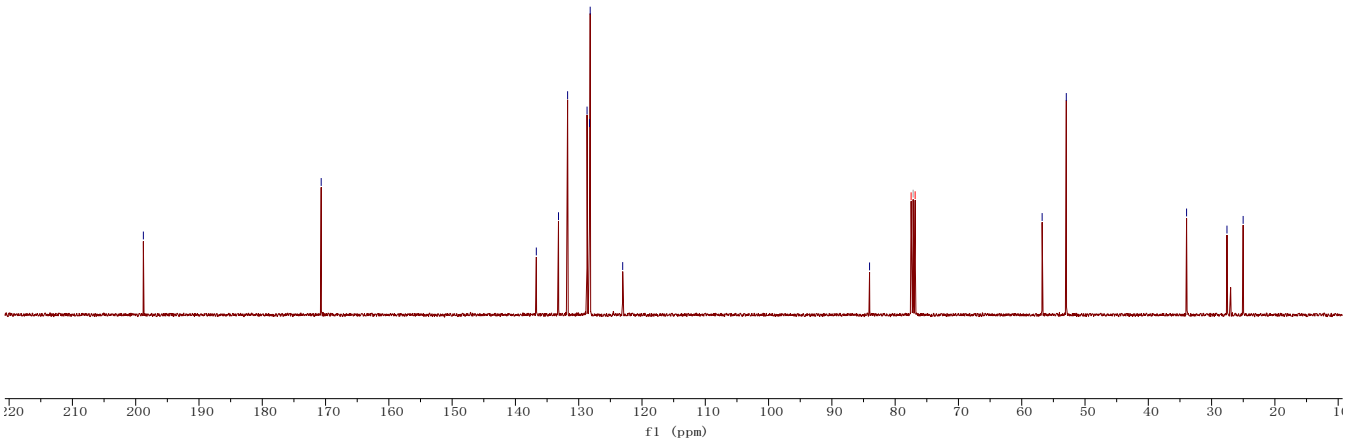
5. ^{1}H and ^{13}C NMR spectra

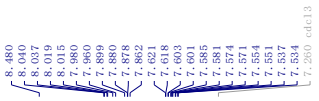








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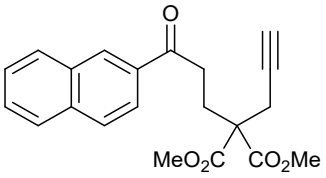
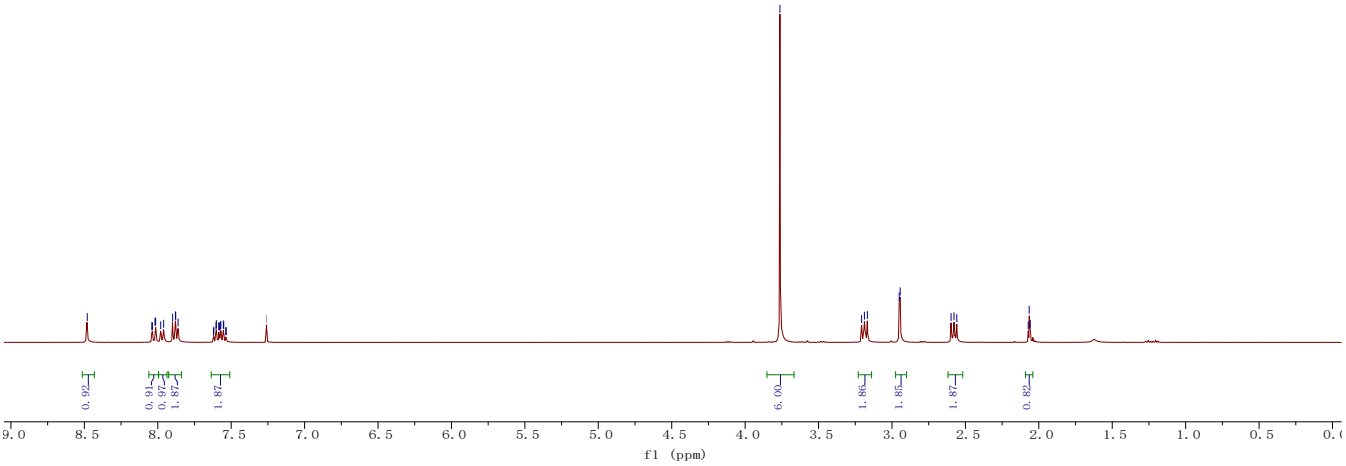
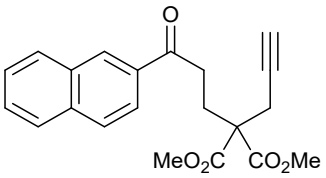
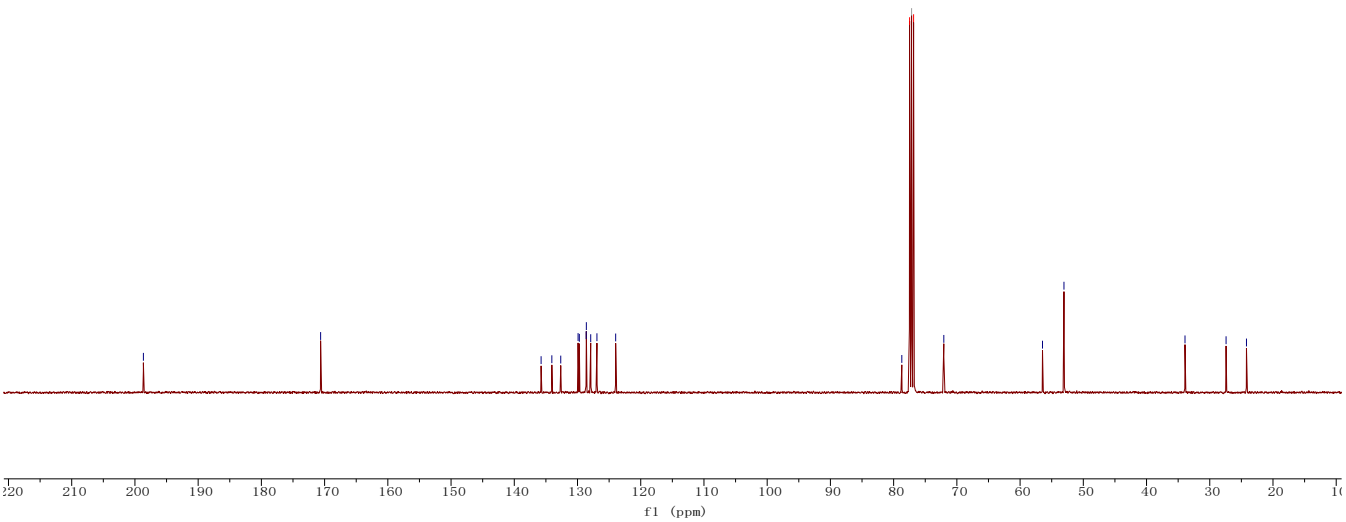
2.059

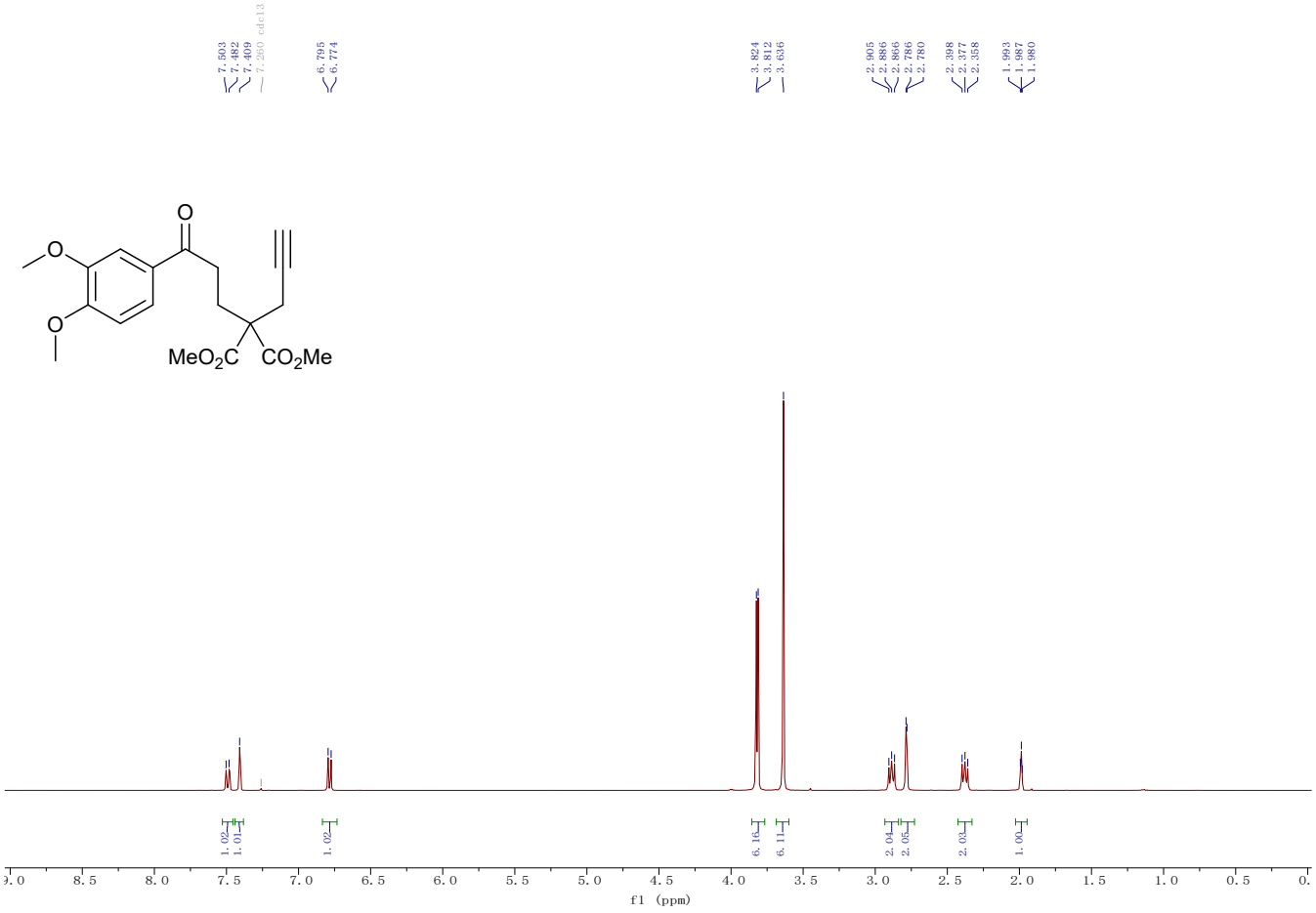

O
MeO2C
CO2Me

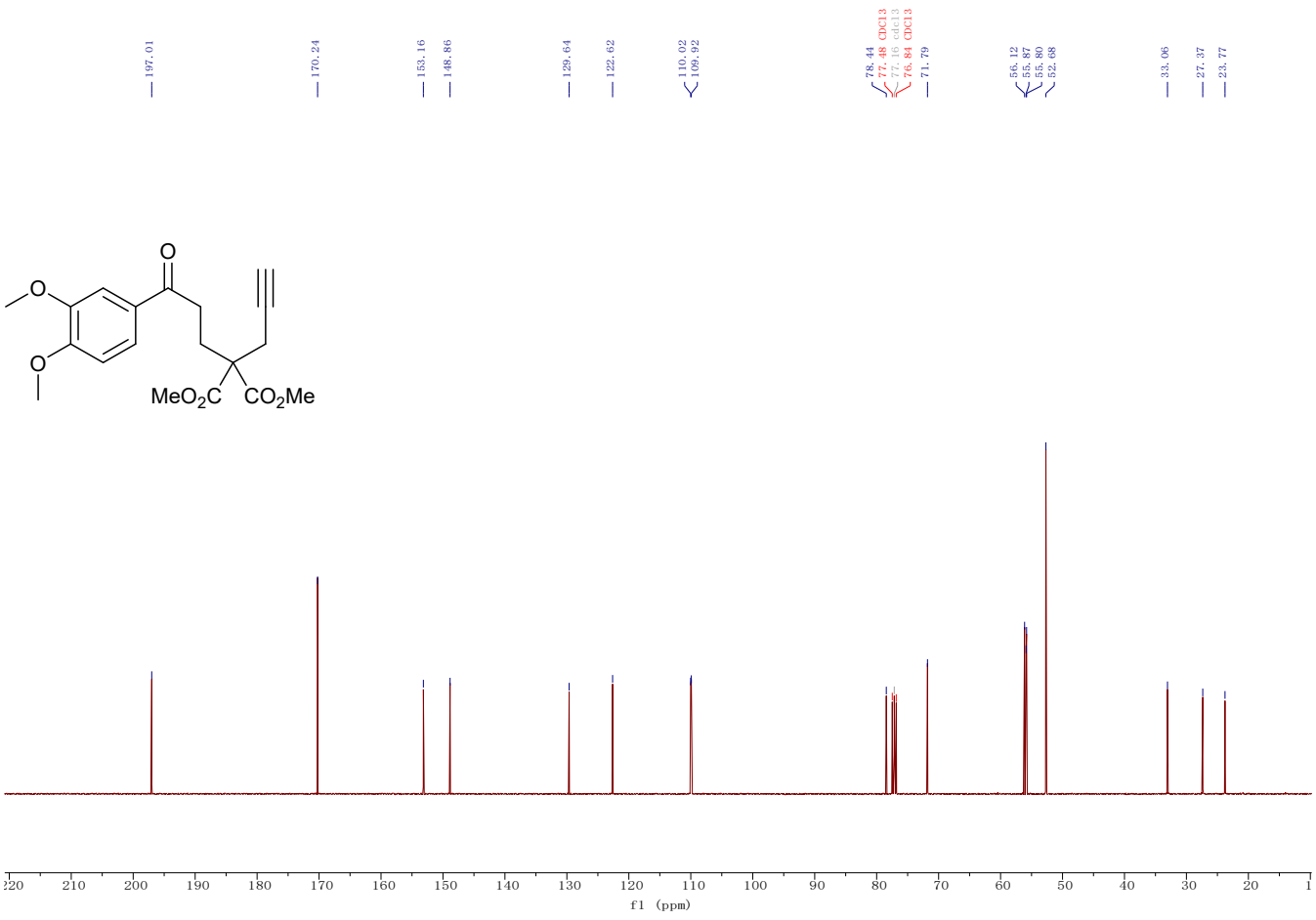

0.92
0.91
0.97
1.87
1.87
6.00
1.86
1.85
1.87
0.82
f1 (ppm)

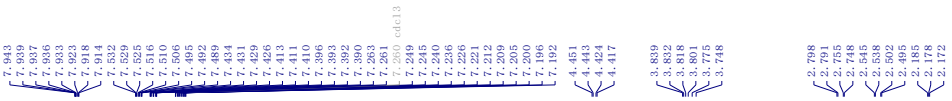

198.66
170.63
135.76
134.06
132.65
129.91
129.71
128.63
128.60
127.91
126.93
126.86
78.71
77.48 CDCl3
77.16 cdcl3
76.84 CDCl3
72.06
56.45
53.06
33.92
27.42
24.19

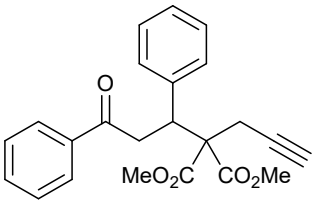

O
MeO2C
CO2Me

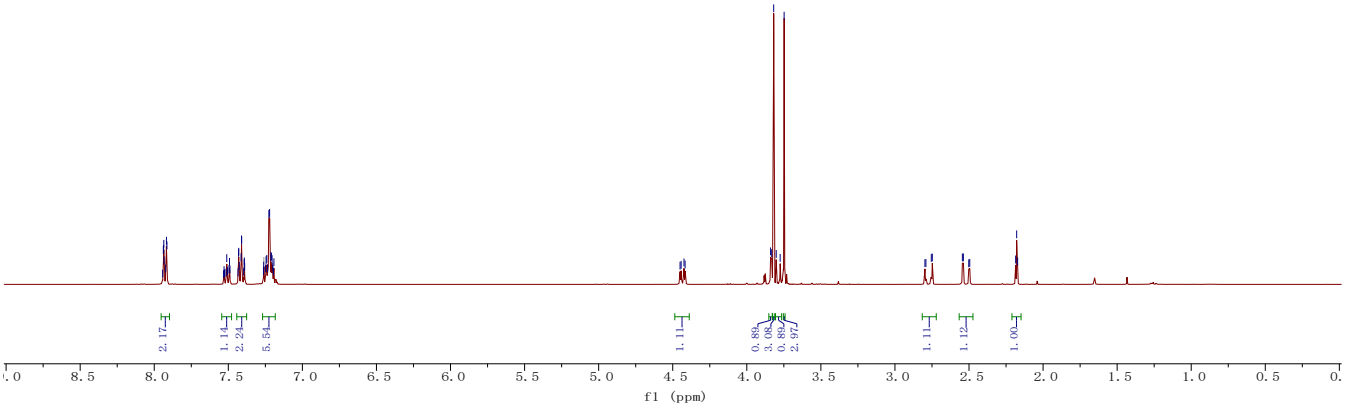

f1 (ppm)


7.503
7.482
7.409
7.260 cdcl3
6.795
6.774
3.824
3.812
3.636
2.905
2.886
2.866
2.846
2.780
2.398
2.377
2.358
1.993
1.987
1.980
O
O
O
MeO2C
CO2Me
1.02
1.01
1.02
6.16
6.11
2.04
2.05
2.03
1.00
f1 (ppm)

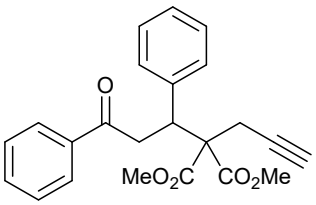

197.01
170.24
153.16
148.86
129.64
122.62
110.02
109.92
78.44
77.48 CDCl3
77.13 CDCl3
76.84 CDCl3
71.79
56.12
55.87
55.80
52.68
33.06
27.37
23.77
O
O
O
MeO2C
CO2Me
f1 (ppm)

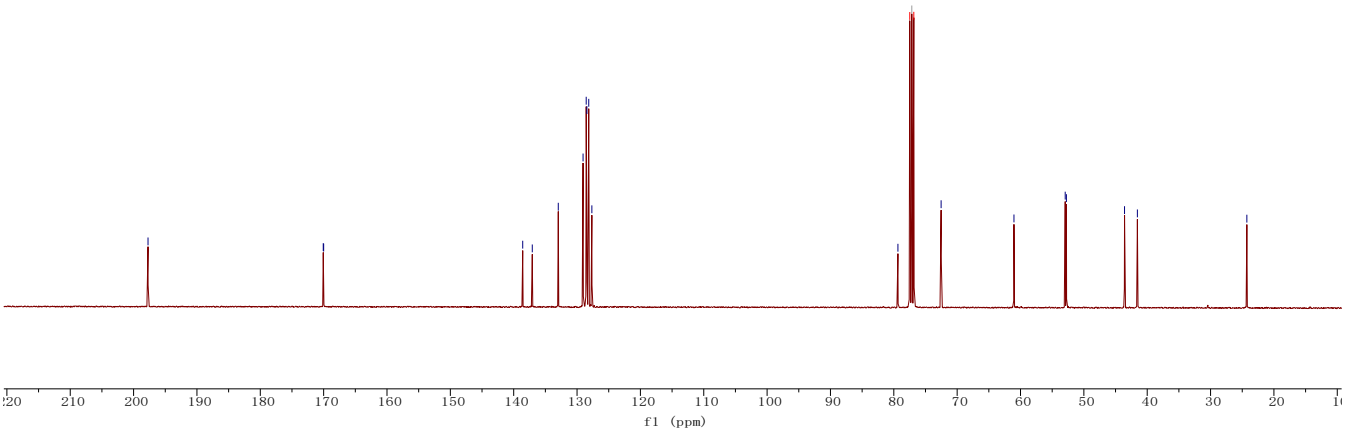

7.943
7.939
7.937
7.936
7.923
7.918
7.914
7.532
7.529
7.525
7.516
7.510
7.506
7.495
7.492
7.489
7.434
7.431
7.429
7.426
7.413
7.411
7.410
7.396
7.393
7.392
7.390
7.263
7.261
7.260 cdcl3
7.249
7.245
7.240
7.226
7.221
7.212
7.209
7.205
7.200
7.196
7.192
4.451
4.443
4.424
4.417
3.839
3.832
3.818
3.801
3.775
3.748
2.798
2.791
2.755
2.748
2.545
2.538
2.502
2.495
2.185
2.178
2.172

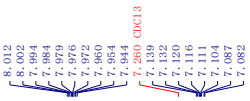

O
MeO2C
CO2Me


2.17
1.14
2.24
5.54
1.11
0.89
3.08
0.89
2.97
1.11
1.12
1.00
f1 (ppm)

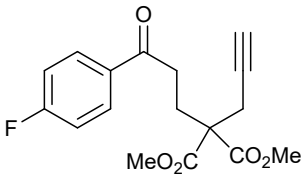

197.72
170.06
170.00
138.58
137.07
132.96
129.05
128.55
128.45
128.15
127.66
79.35
77.48 CDCl3
77.16 cdcl3
76.84 CDCl3
72.53
61.03
52.94
52.75
43.58
41.55
24.27

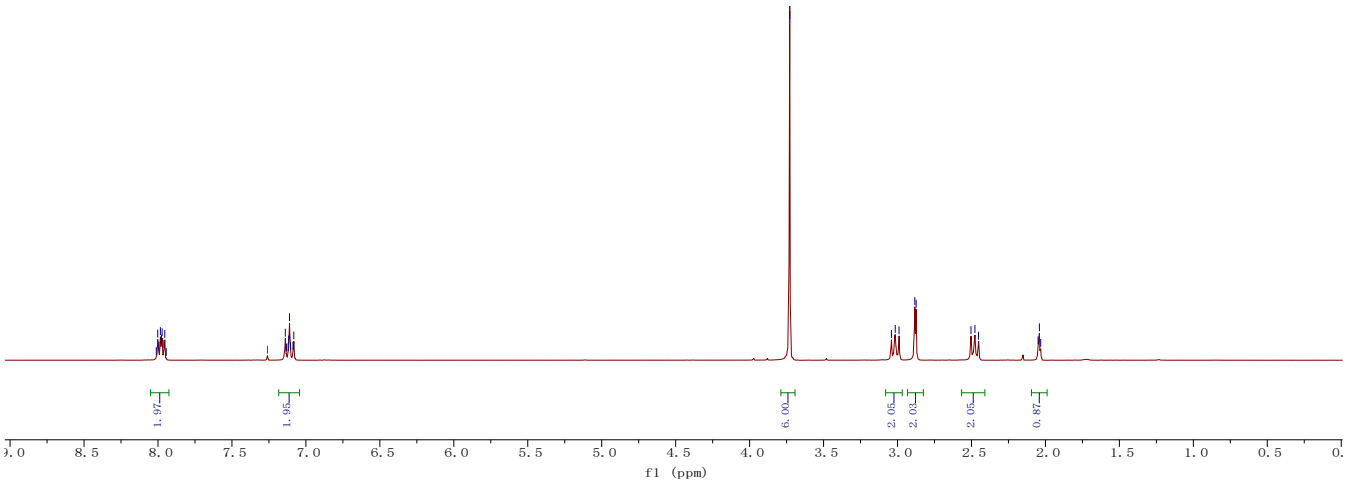

O
MeO2C
CO2Me


f1 (ppm)

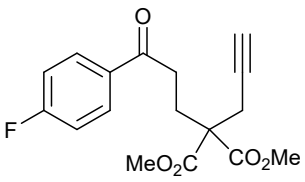

8.012
8.002
7.994
7.984
7.979
7.976
7.972
7.965
7.954
7.944
7.260 CDCl3
7.139
7.132
7.120
7.116
7.111
7.104
7.087
7.082

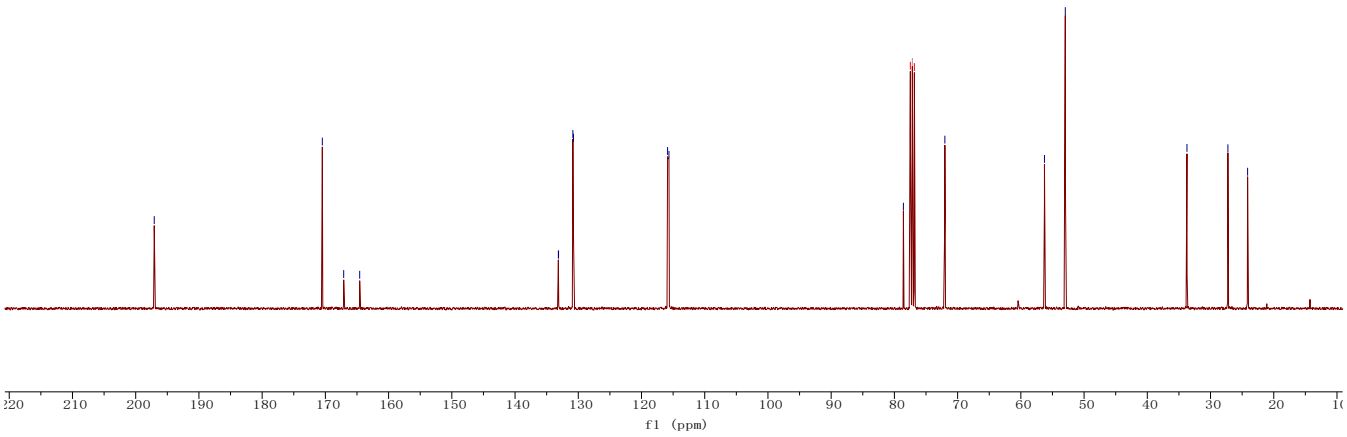

3.729
3.041
3.015
2.990
2.883
2.874
2.503
2.477
2.452
2.050
2.041
2.032

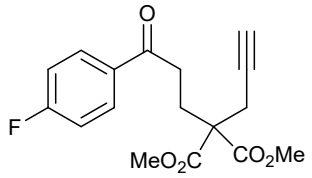

O
F
MeO2C
CO2Me


1.97
1.95
6.00
2.05
2.03
2.05
0.87
f1 (ppm)

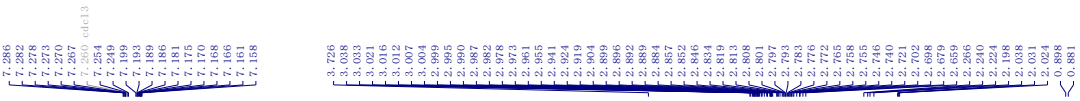

197.07
170.48
167.10
164.57
133.15
133.12
130.85
130.76
115.87
115.66
78.58
77.48 CDCl3
77.16 cdcl3
76.84 CDCl3
72.02
56.27
52.97
33.73
27.25
24.14

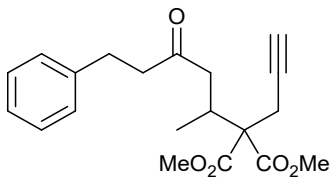

O
F
MeO2C
CO2Me

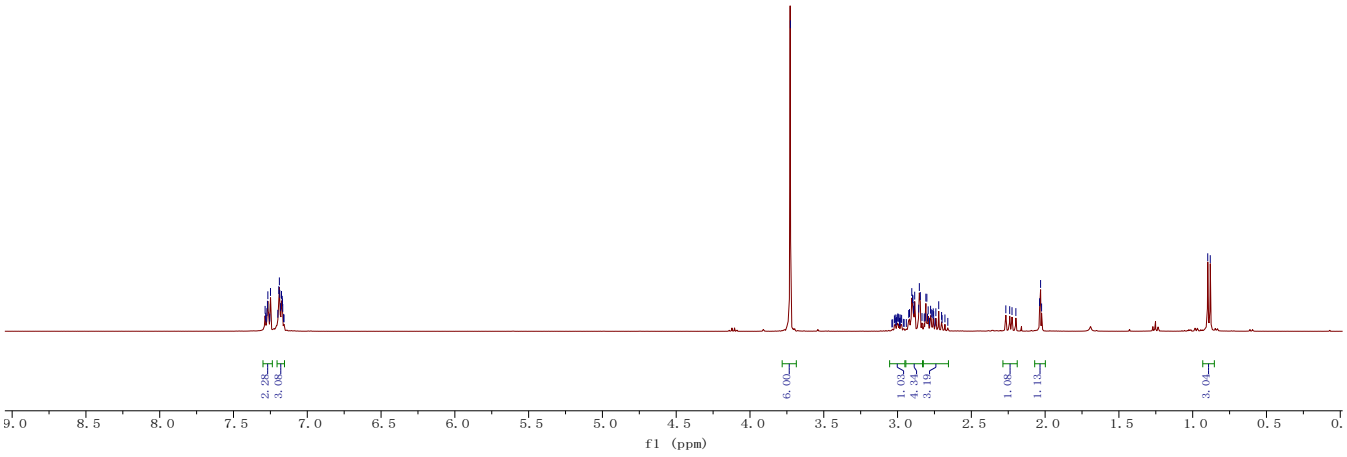

f1 (ppm)


O
F
MeO2C
CO2Me

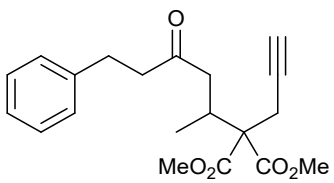
-105.147
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
f1 (ppm)

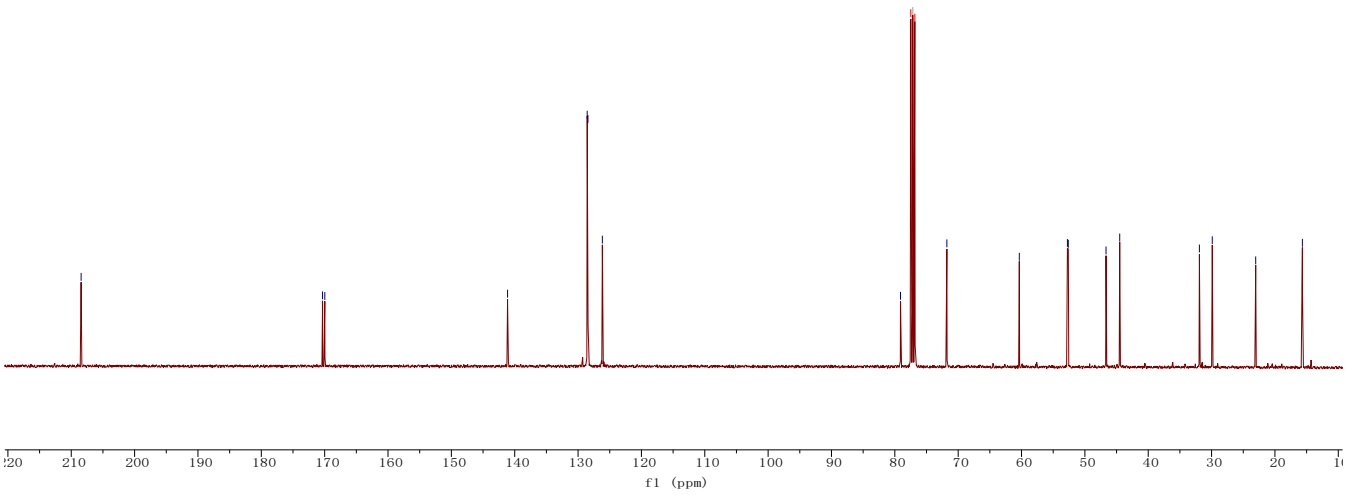


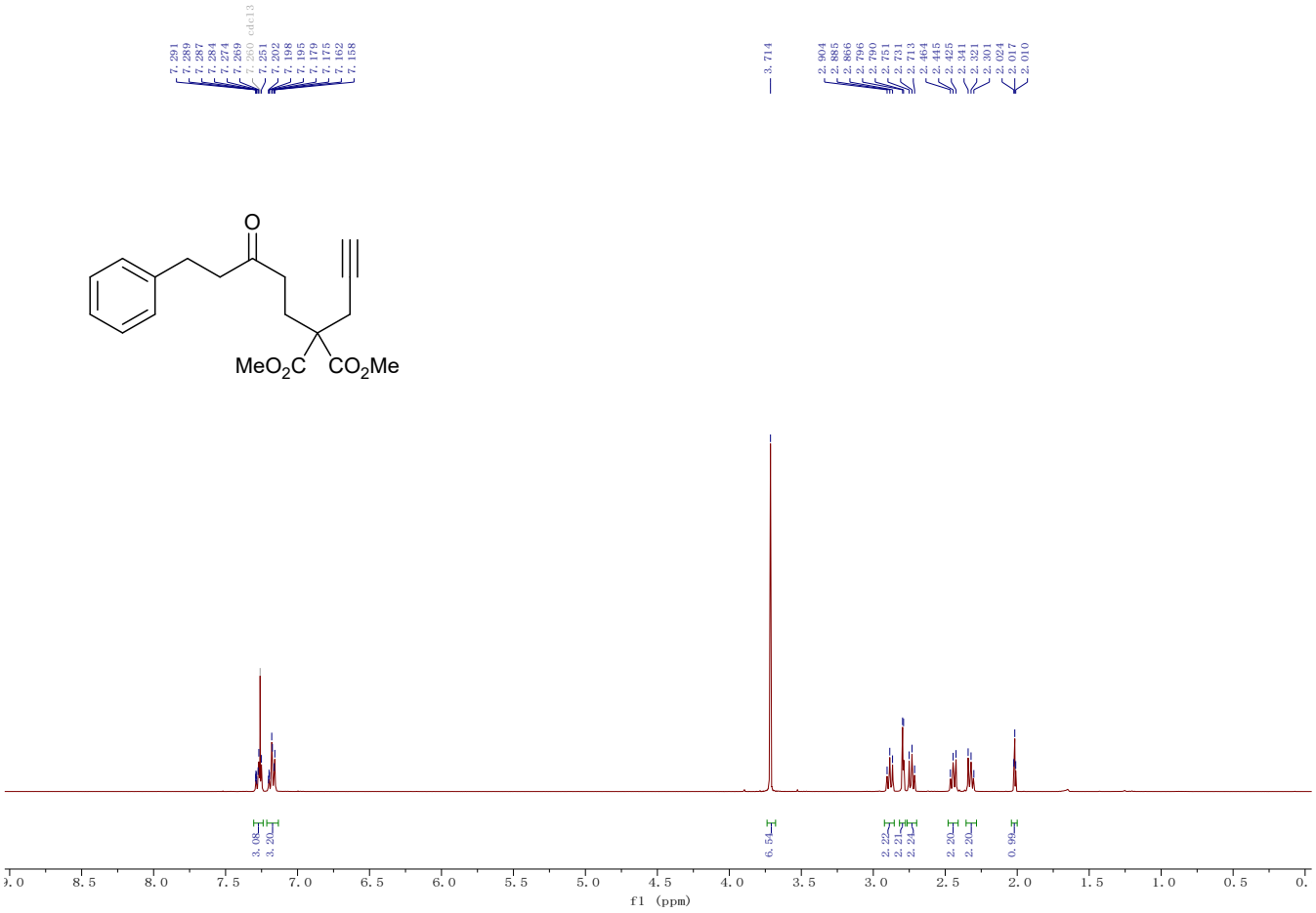

O
MeO2C
CO2Me

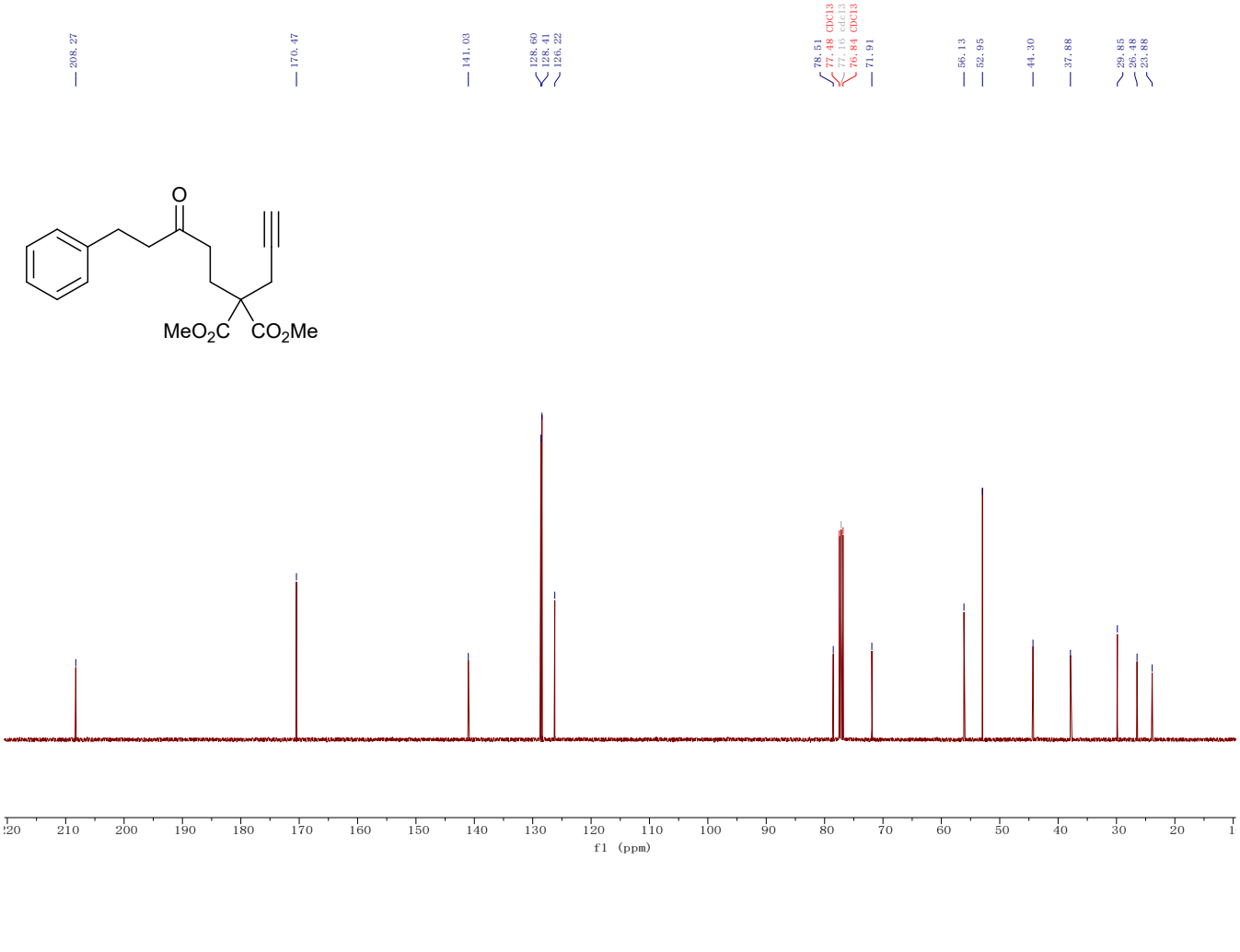

2.28
3.08
6.00
1.03
4.34
3.19
1.08
1.13
3.04
f1 (ppm)

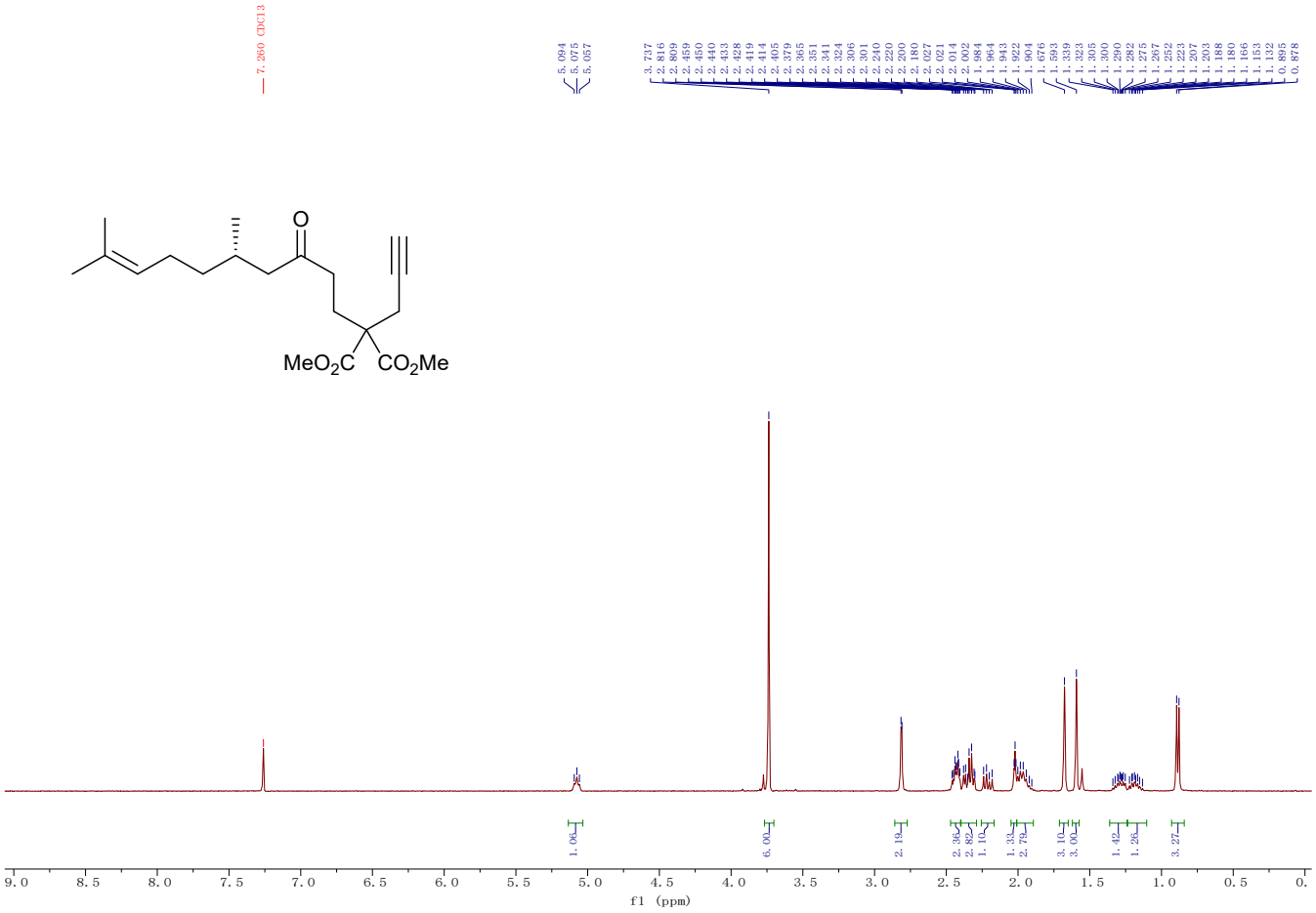

208.44
170.35
169.98
141.13
128.56
128.44
126.17
79.10
77.48 CDCl3
77.16 cdcl3
76.84 CDCl3
71.78
60.35
52.76
52.62
46.66
44.50
31.92
29.89
23.04
15.67

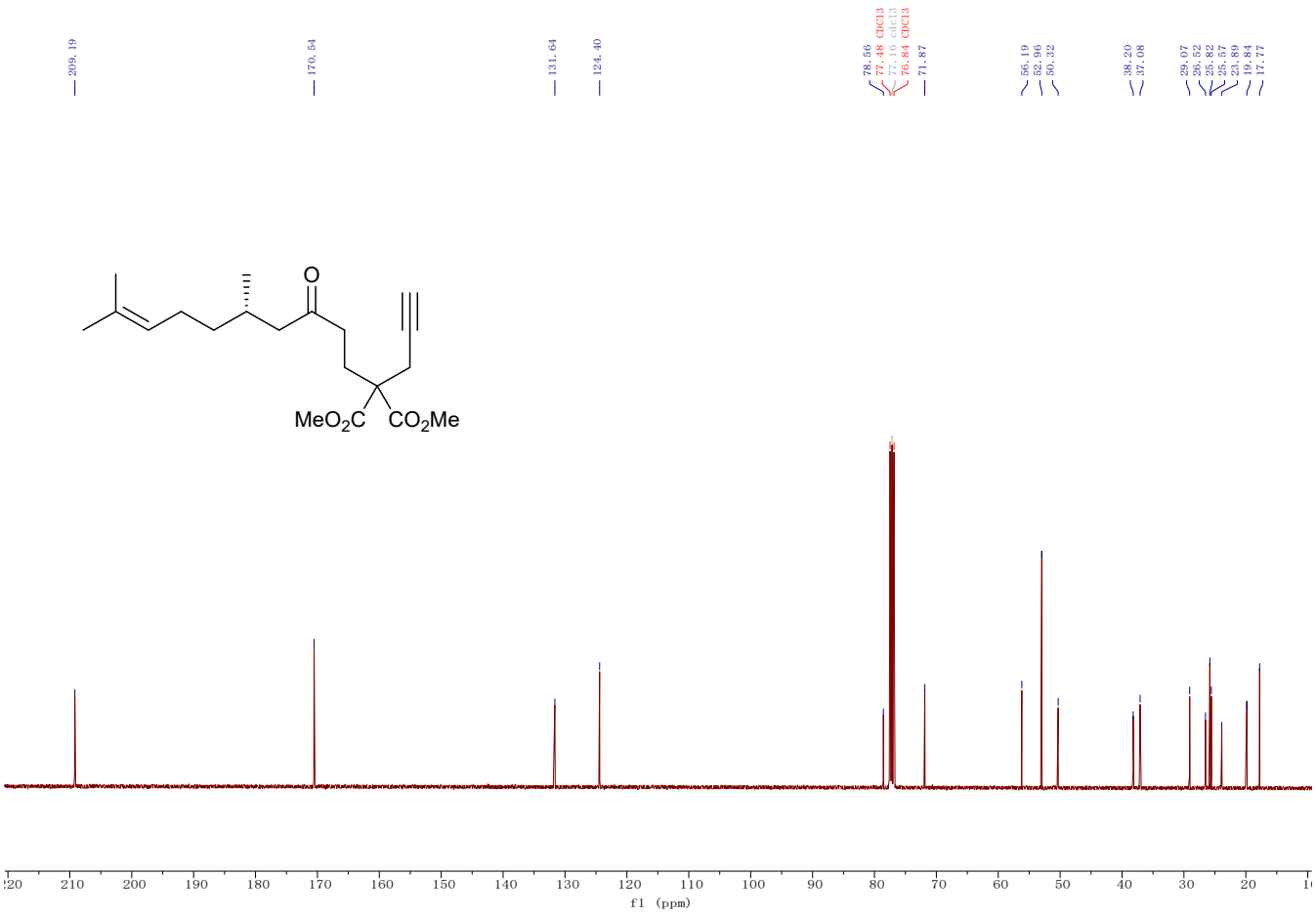

O
MeO2C
CO2Me

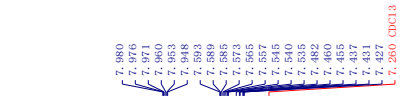

f1 (ppm)


7.291
7.289
7.287
7.284
7.274
7.269
7.260 cdcl3
7.251
7.202
7.198
7.195
7.179
7.175
7.162
7.158
3.714
2.904
2.885
2.866
2.796
2.790
2.751
2.731
2.713
2.464
2.445
2.425
2.341
2.321
2.301
2.024
2.017
2.010
O
MeO2C
CO2Me
3.08
3.20
6.54
2.22
2.21
2.24
2.20
2.20
0.98
f1 (ppm)


208.27
170.47
141.03
128.60
128.41
126.22
78.51
77.48 CDCl3
77.16 cdcl3
76.84 CDCl3
71.91
56.13
52.95
44.30
37.88
29.85
26.48
23.88
O
MeO2C
CO2Me
f1 (ppm)


7.260 CDCl3
5.094
5.075
5.057
3.737
2.816
2.809
2.459
2.450
2.440
2.433
2.428
2.419
2.414
2.405
2.379
2.365
2.351
2.341
2.324
2.306
2.301
2.240
2.220
2.200
2.180
2.027
2.021
2.014
2.002
1.984
1.964
1.943
1.922
1.904
1.676
1.593
1.339
1.323
1.305
1.300
1.290
1.282
1.275
1.267
1.252
1.223
1.207
1.203
1.188
1.180
1.166
1.153
1.132
0.895
0.878
O
MeO2C
CO2Me
1.06
6.00
2.18
2.36
2.82
1.10
1.33
2.79
3.10
3.00
1.42
1.26
3.27
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


209.19
170.54
131.64
124.40
78.56
77.48 CDCl3
77.16
76.84 CDCl3
71.87
56.19
52.96
50.32
38.20
37.08
29.07
26.62
25.82
25.57
23.89
19.84
17.77
O
MeO2C
CO2Me
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


7.980
7.976
7.971
7.966
7.953
7.948
7.593
7.589
7.585
7.573
7.565
7.557
7.545
7.540
7.535
7.482
7.466
7.455
7.437
7.431
7.427
7.260 CDCl3
4.158
4.135
4.111
4.085
4.081
4.072
4.047
4.037
3.822
3.796
3.782
3.762
3.727
3.566
3.556
3.506
3.497
3.071
3.062
3.013
3.004
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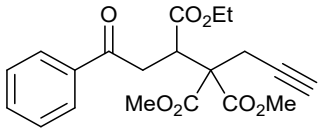
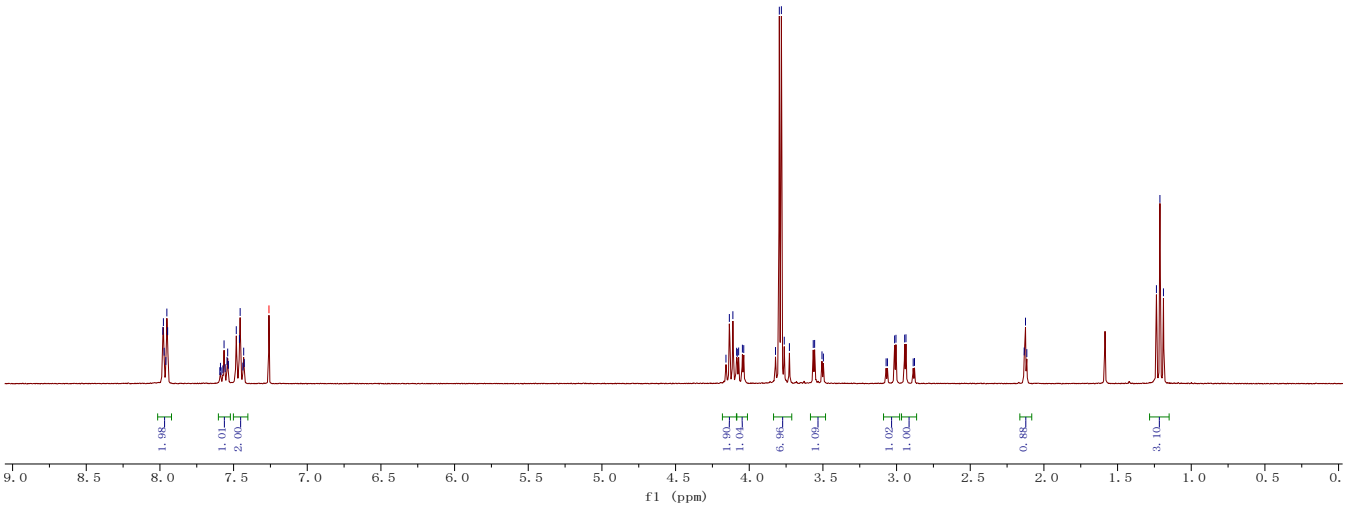
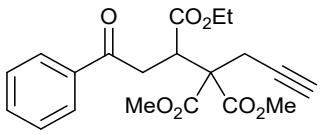
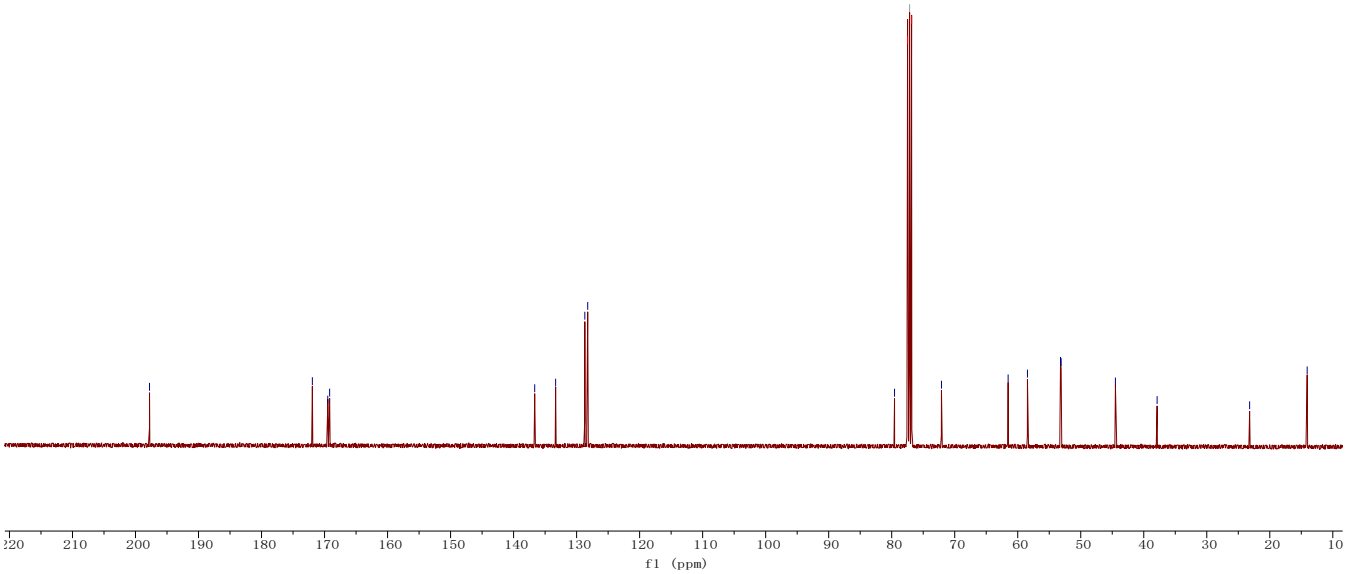
2.936
2.887
2.878
2.134
2.125
2.116
1.236
1.213
1.189

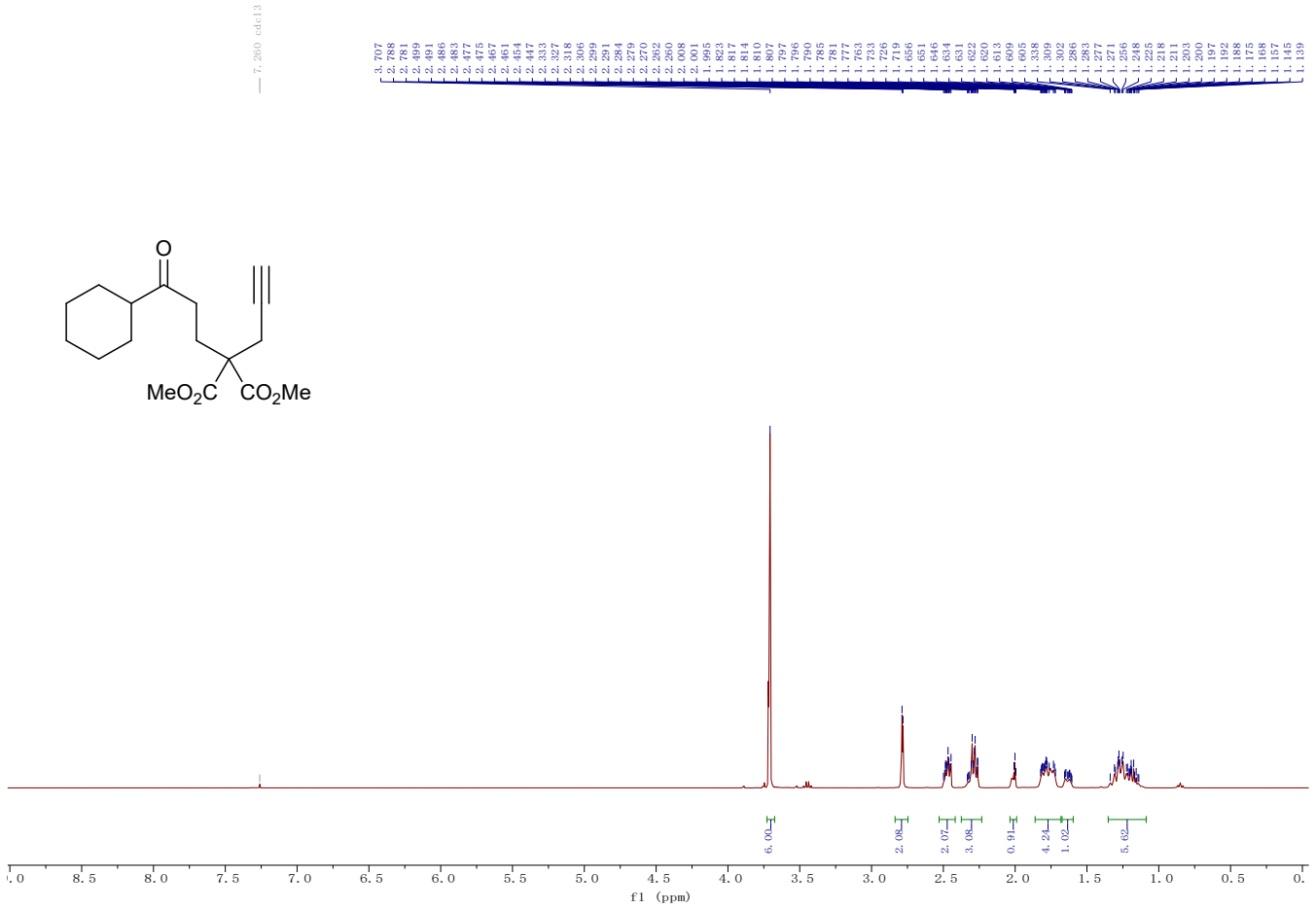

O
CO2Et
MeO2C
CO2Me

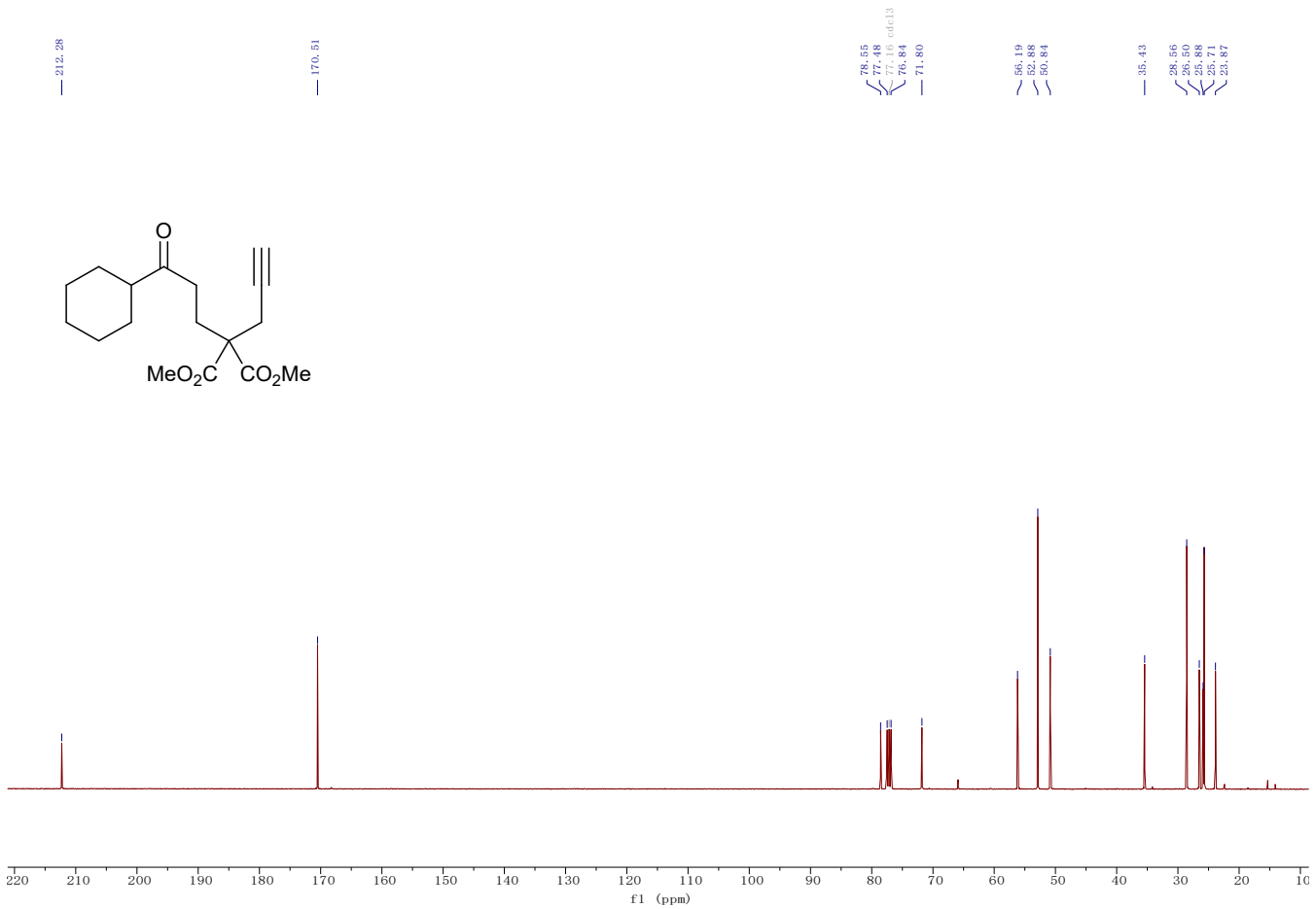

1.98
1.01
2.00
1.90
1.04
6.96
1.08
1.02
1.00
0.88
3.10
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

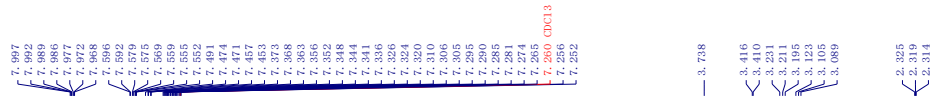

197.77
171.93
169.49
169.19
136.65
133.33
128.70
128.24
79.55
77.48 CDCl3
77.16 cdcl3
76.84 CDCl3
72.10
61.52
58.46
53.21
53.11
44.50
37.88
23.20
14.07


O
CO2Et
MeO2C
CO2Me


220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.260 cdcl3
3.707
2.788
2.781
2.499
2.491
2.486
2.483
2.477
2.475
2.467
2.461
2.454
2.447
2.333
2.327
2.318
2.306
2.299
2.291
2.284
2.279
2.270
2.262
2.260
2.008
2.001
1.995
1.823
1.817
1.814
1.810
1.807
1.797
1.796
1.790
1.785
1.781
1.777
1.763
1.733
1.726
1.719
1.656
1.651
1.646
1.634
1.631
1.622
1.620
1.613
1.609
1.605
1.338
1.309
1.302
1.286
1.283
1.277
1.271
1.256
1.248
1.225
1.218
1.211
1.203
1.200
1.197
1.192
1.188
1.175
1.168
1.157
1.145
1.139
O
MeO2C
CO2Me
6.00
2.08
2.07
3.08
0.91
4.24
1.02
5.62
f1 (ppm)


212.28
170.51
78.55
77.48
77.16 cdcl3
76.84
71.80
56.19
52.88
50.84
35.43
28.56
26.50
25.88
25.71
23.87
O
MeO2C
CO2Me
f1 (ppm)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7.989
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7.977
7.972
7.968
7.596
7.592
7.578
7.575
7.569
7.559
7.555
7.552
7.491
7.474
7.471
7.457
7.453
7.373
7.368
7.363
7.355
7.352
7.348
7.344
7.341
7.336
7.326
7.324
7.320
7.310
7.306
7.305
7.295
7.290
7.285
7.281
7.274
7.265
7.260 CDCl3
7.256
7.252
3.738
3.416
3.410
3.231
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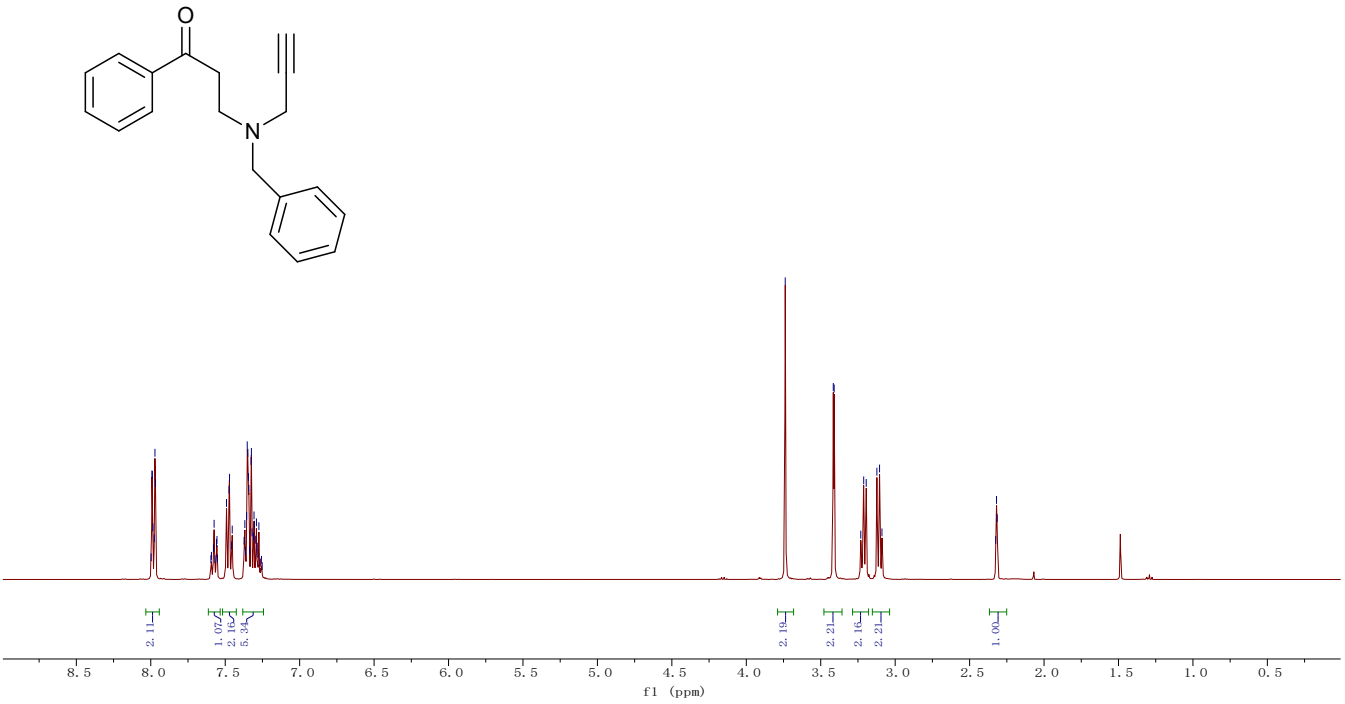
3.123
3.105
3.089
2.325
2.319
2.314


O
N
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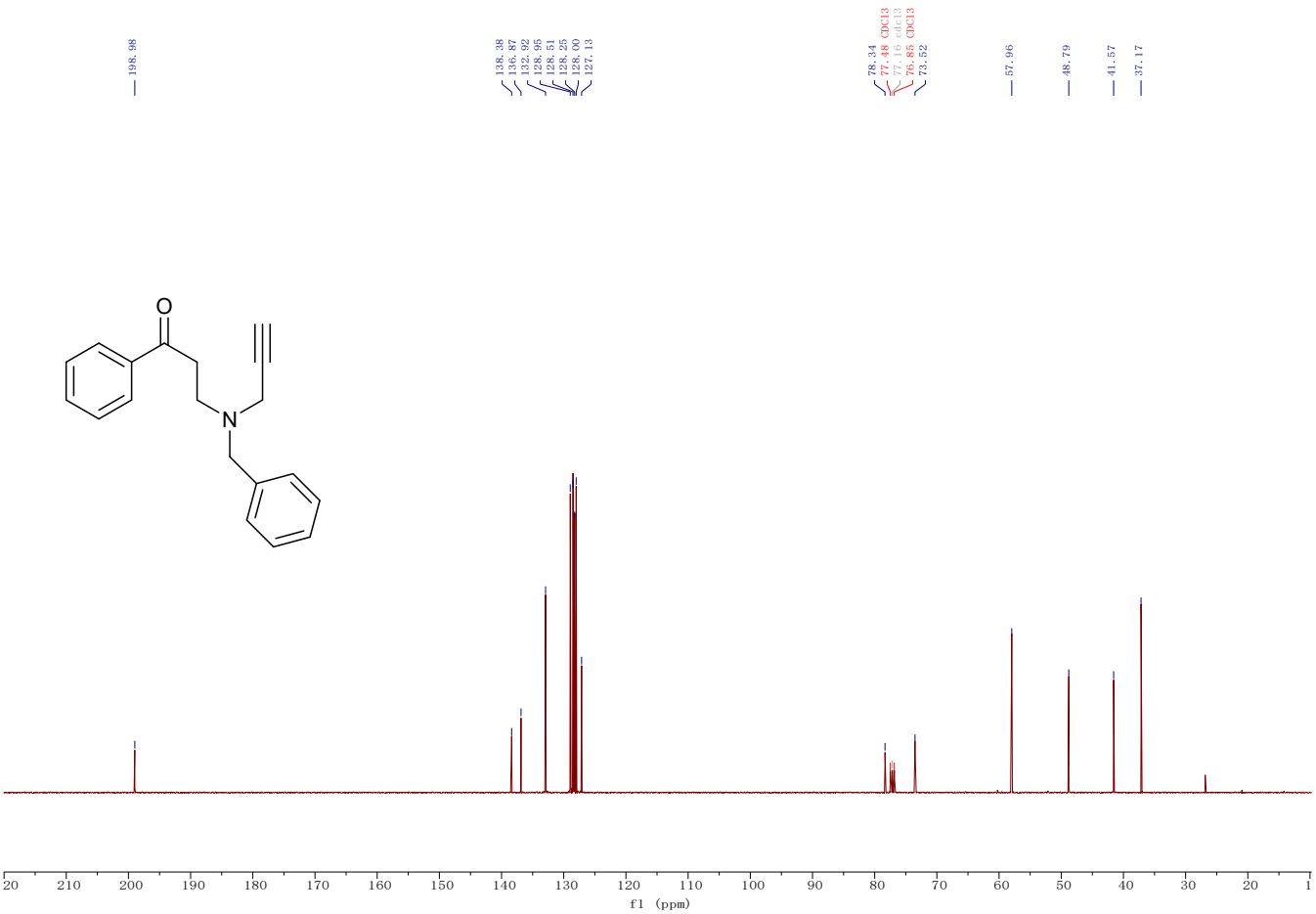
1.07
2.16
5.38
2.19
2.21
2.16
2.21
1.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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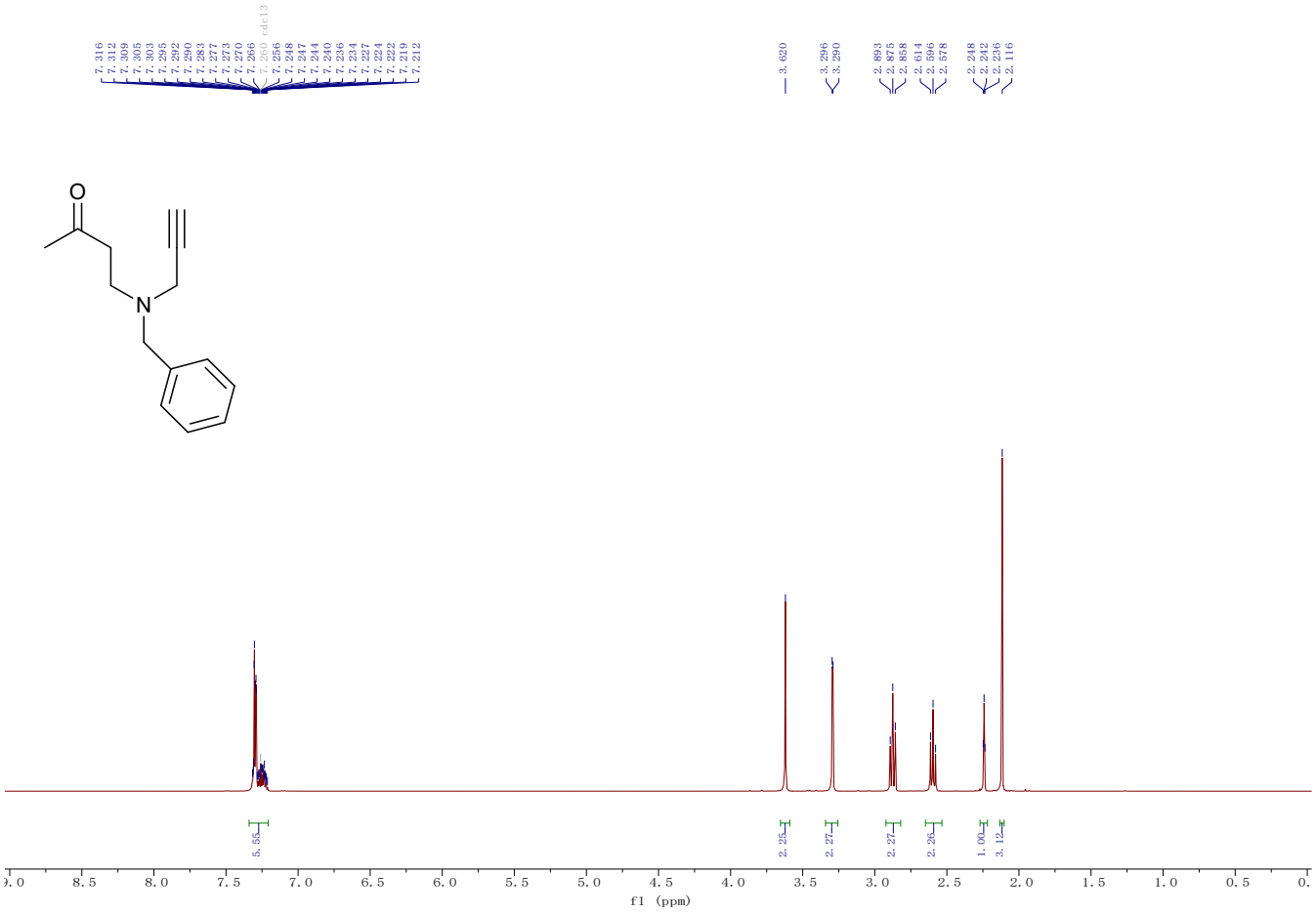
138.38
136.87
132.92
128.95
128.51
128.25
128.00
127.13
78.34
77.48 CDCl3
77.16
76.85 CDCl3
73.52
57.96
48.79
41.57
37.17
O
N
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
1
f1 (ppm)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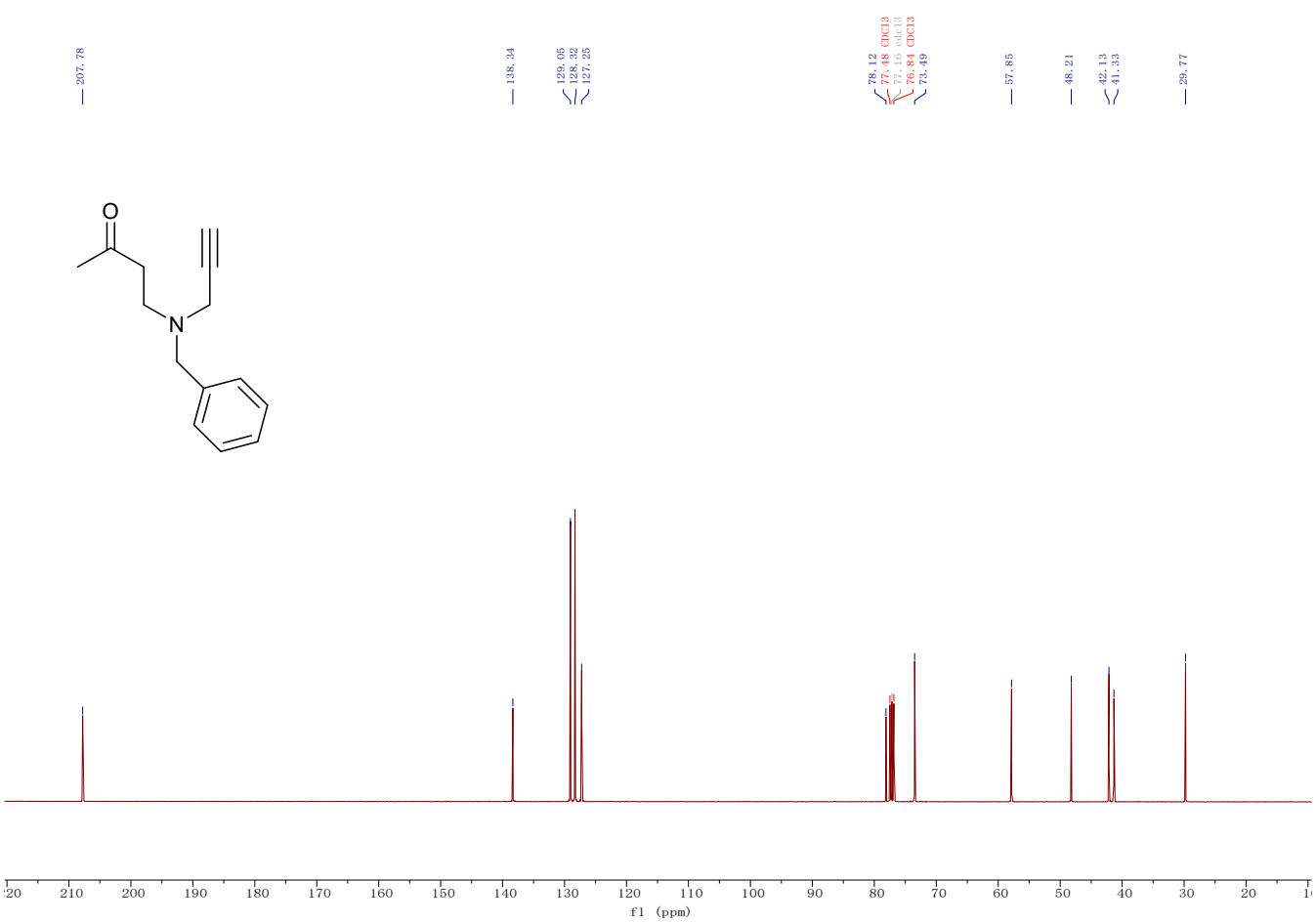
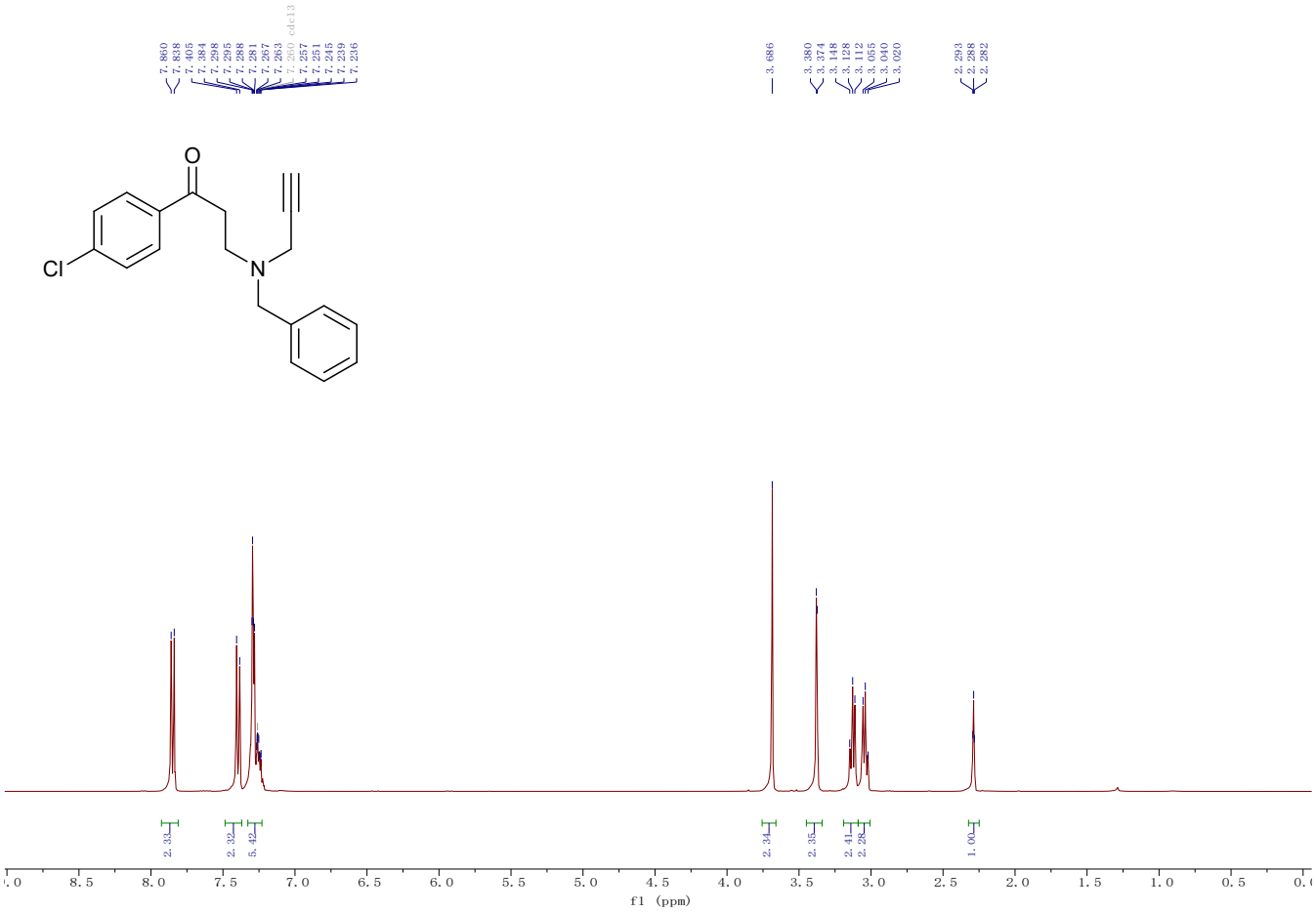
7.309
7.305
7.303
7.295
7.292
7.290
7.283
7.277
7.273
7.270
7.265
7.260 cdcl3
7.256
7.248
7.247
7.244
7.240
7.236
7.234
7.227
7.224
7.222
7.219
7.212
3.620
3.296
3.290
2.893
2.875
2.858
2.614
2.596
2.578
2.248
2.242
2.236
2.116
O
N
5.55
2.25
2.27
2.27
2.26
1.00
3.12
f1 (ppm)


207.78
138.34
129.05
128.32
127.25
78.12
77.48 CDCl3
77.16 cdcl3
76.84 CDCl3
73.49
57.85
48.21
42.13
41.33
29.77
O
N
f1 (ppm)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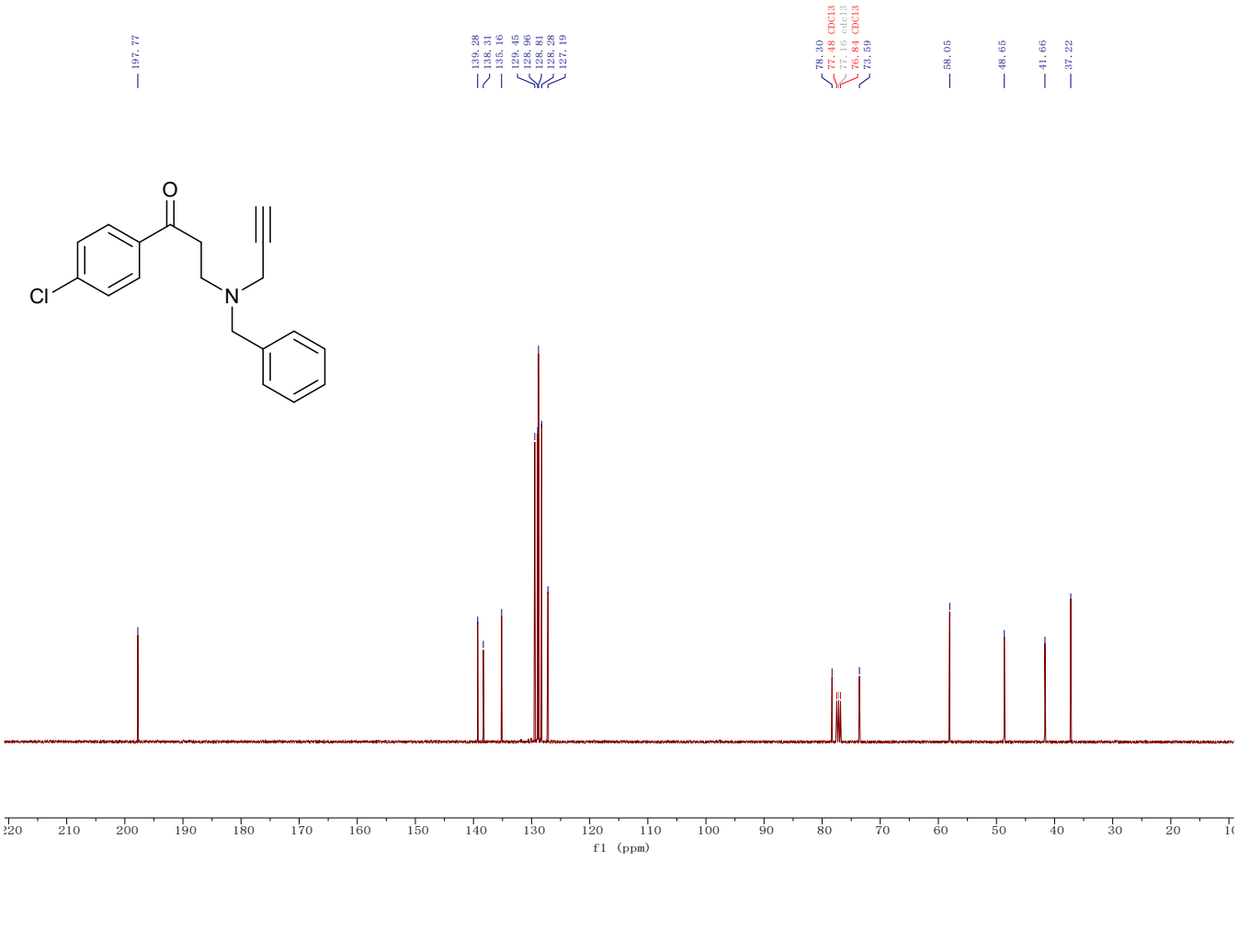
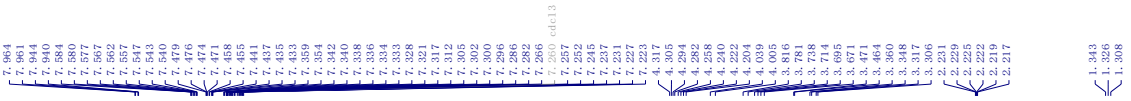
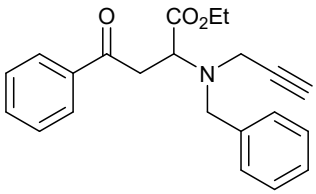
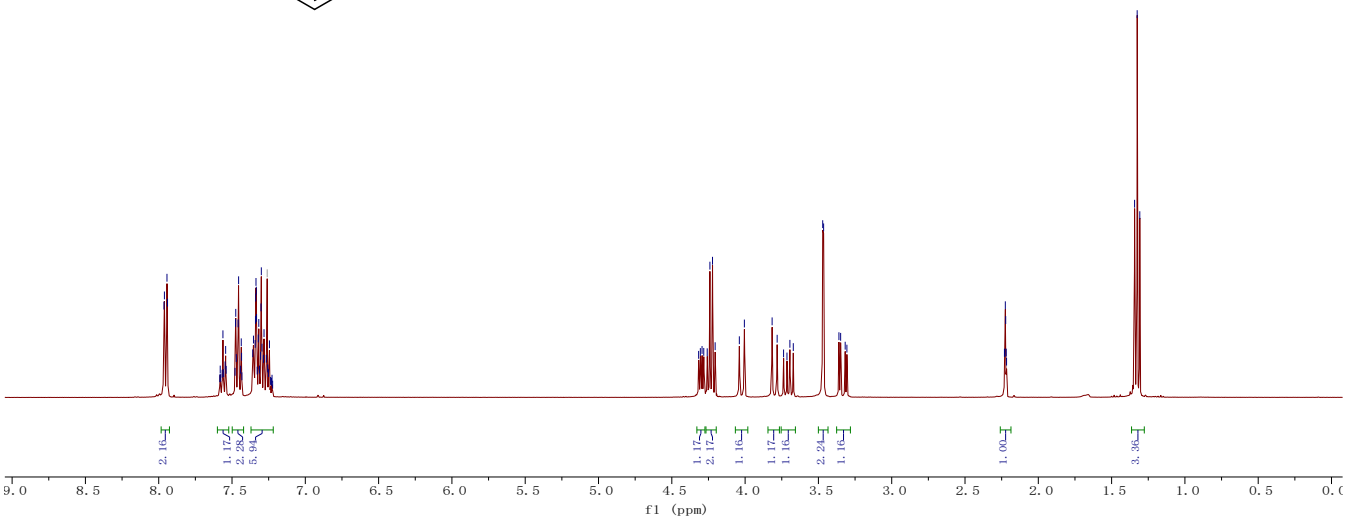
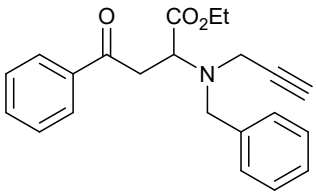
7.838
7.405
7.384
7.298
7.295
7.288
7.281
7.263
7.260 cdcl3
7.257
7.251
7.245
7.239
7.236
3.686
3.380
3.374
3.148
3.128
3.112
3.055
3.040
3.020
2.293
2.288
2.282
O
Cl
N
2.33
2.32
5.42
2.34
2.35
2.41
2.28
1.00
f1 (ppm)

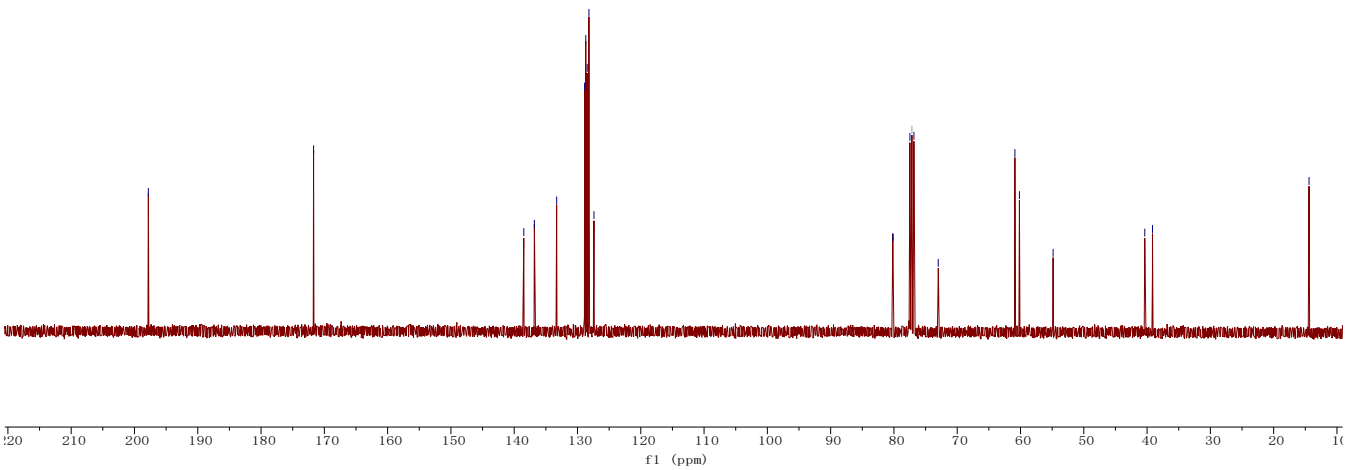

197.77
139.28
138.31
135.16
129.45
128.96
128.81
128.28
127.19
78.30
77.48 CDCl3
77.15 cdcl3
76.84 CDCl3
73.59
58.05
48.65
41.66
37.22
O
Cl
N
f1 (ppm)

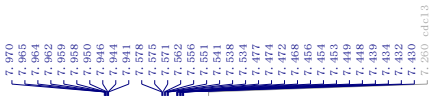



O
CO2Et
N


f1 (ppm)


O
CO2Et
N


f1 (ppm)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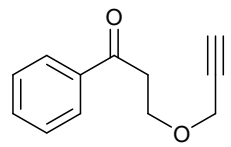
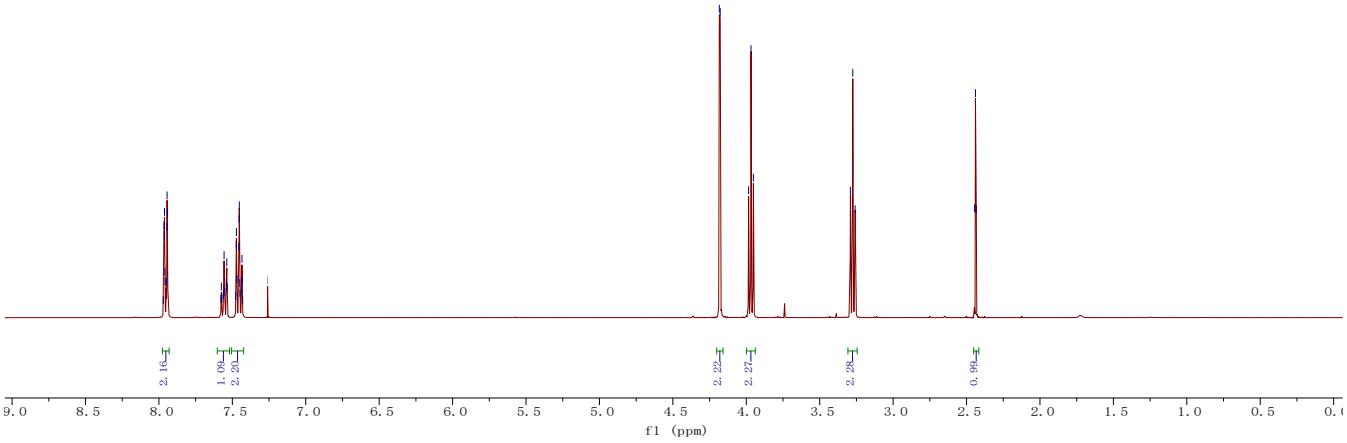
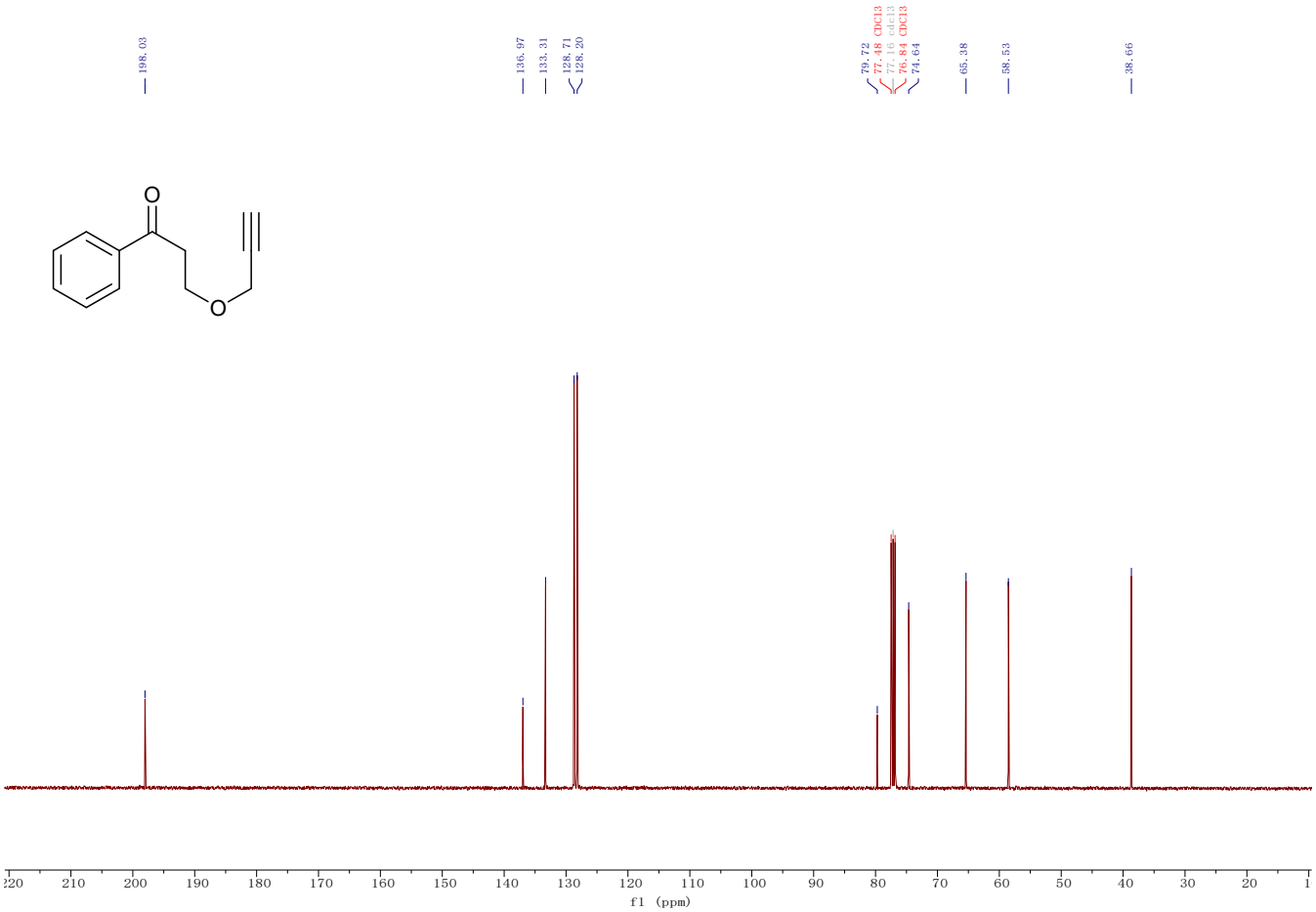
7.965
7.964
7.962
7.959
7.958
7.950
7.946
7.944
7.941
7.578
7.575
7.571
7.562
7.556
7.551
7.541
7.538
7.534
7.477
7.474
7.472
7.468
7.456
7.454
7.453
7.449
7.448
7.439
7.434
7.432
7.430
7.260 cdcl3
4.184
4.178
3.984
3.968
3.952
3.291
3.275
3.259
2.445
2.439
2.433

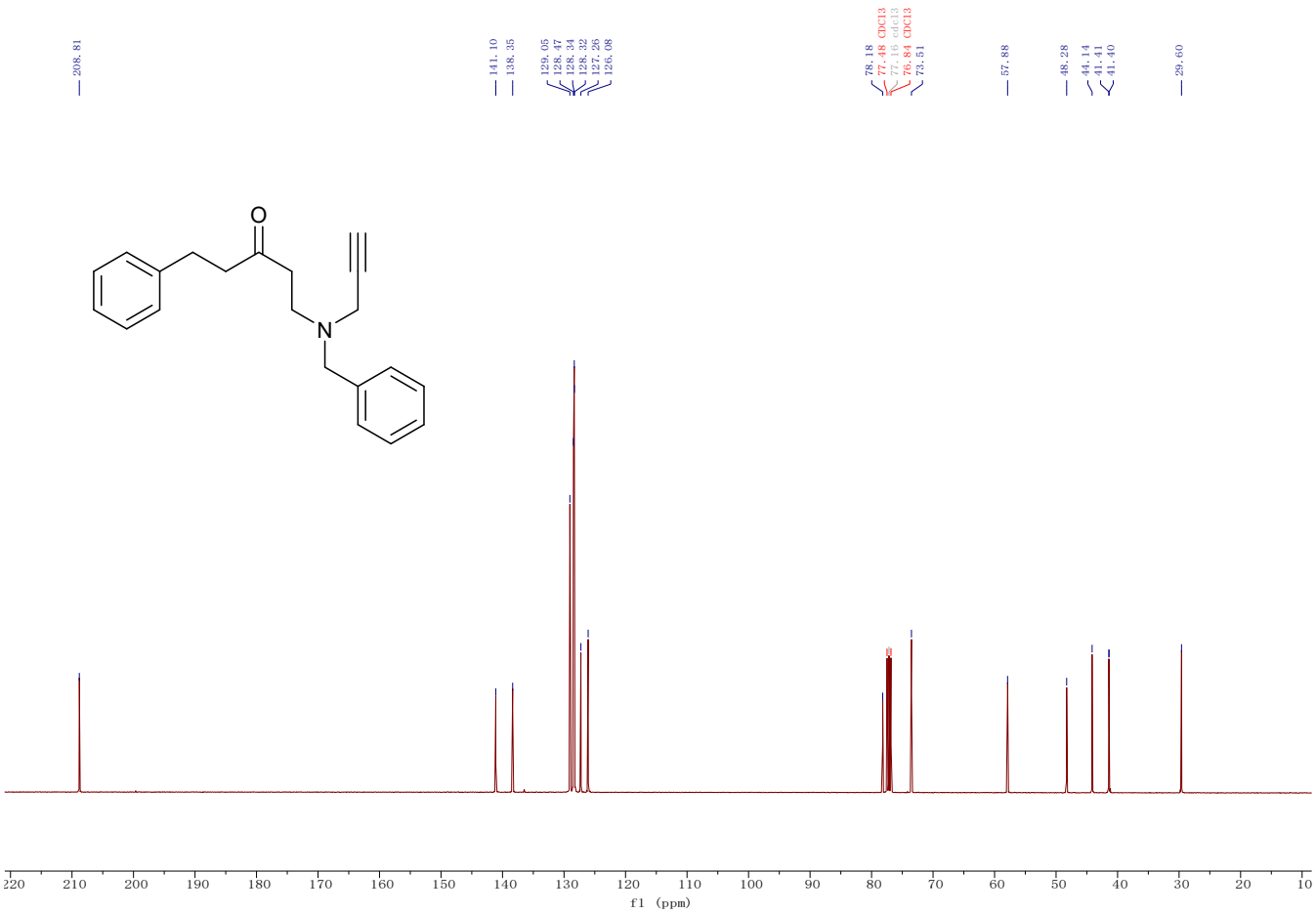

O
O

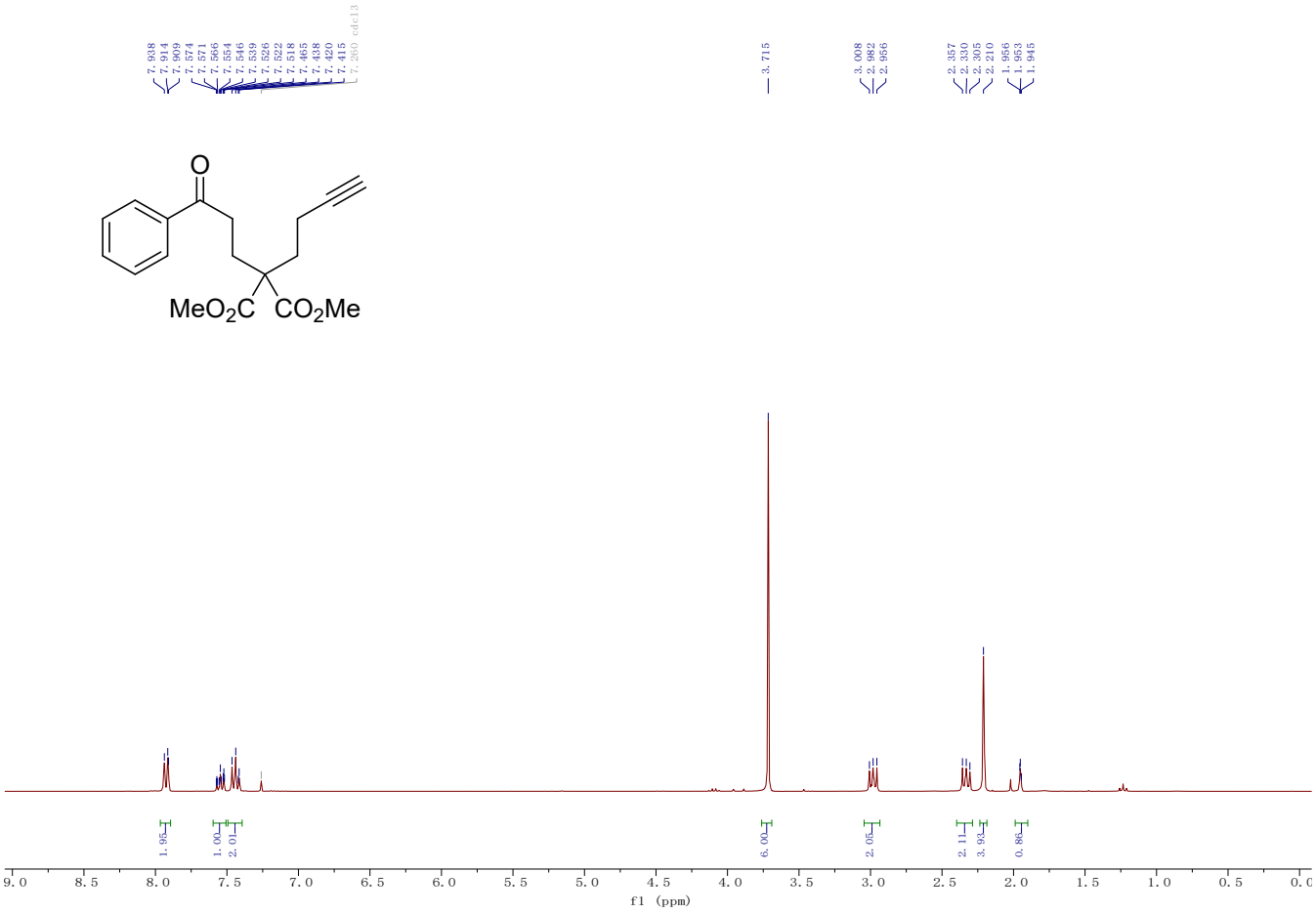

2.16
1.08
2.20
2.22
2.27
2.28
0.98
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


198.03
136.97
133.31
128.71
128.20
79.72
77.48 CDCl3
77.16 cdcl3
76.84 CDCl3
74.64
65.38
58.53
38.66
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
1
f1 (ppm)

O
O


7.352
7.341
7.328
7.322
7.311
7.308
7.304
7.302
7.299
7.291
7.260 cdcl3
7.253
7.250
7.234
7.229
7.212
3.668
3.339
3.333
2.966
2.949
2.932
2.915
2.791
2.771
2.753
2.633
2.616
2.598
2.292
2.286
2.280
O
N
10.64
2.19
2.19
4.42
2.23
2.22
1.00
f1 (ppm)


208.81
141.10
138.35
129.05
128.47
128.34
128.32
127.25
126.08
78.18
77.48 CDCl3
77.16 cdcl3
76.84 CDCl3
73.51
57.88
48.28
44.14
41.41
41.40
29.60
O
N
f1 (ppm)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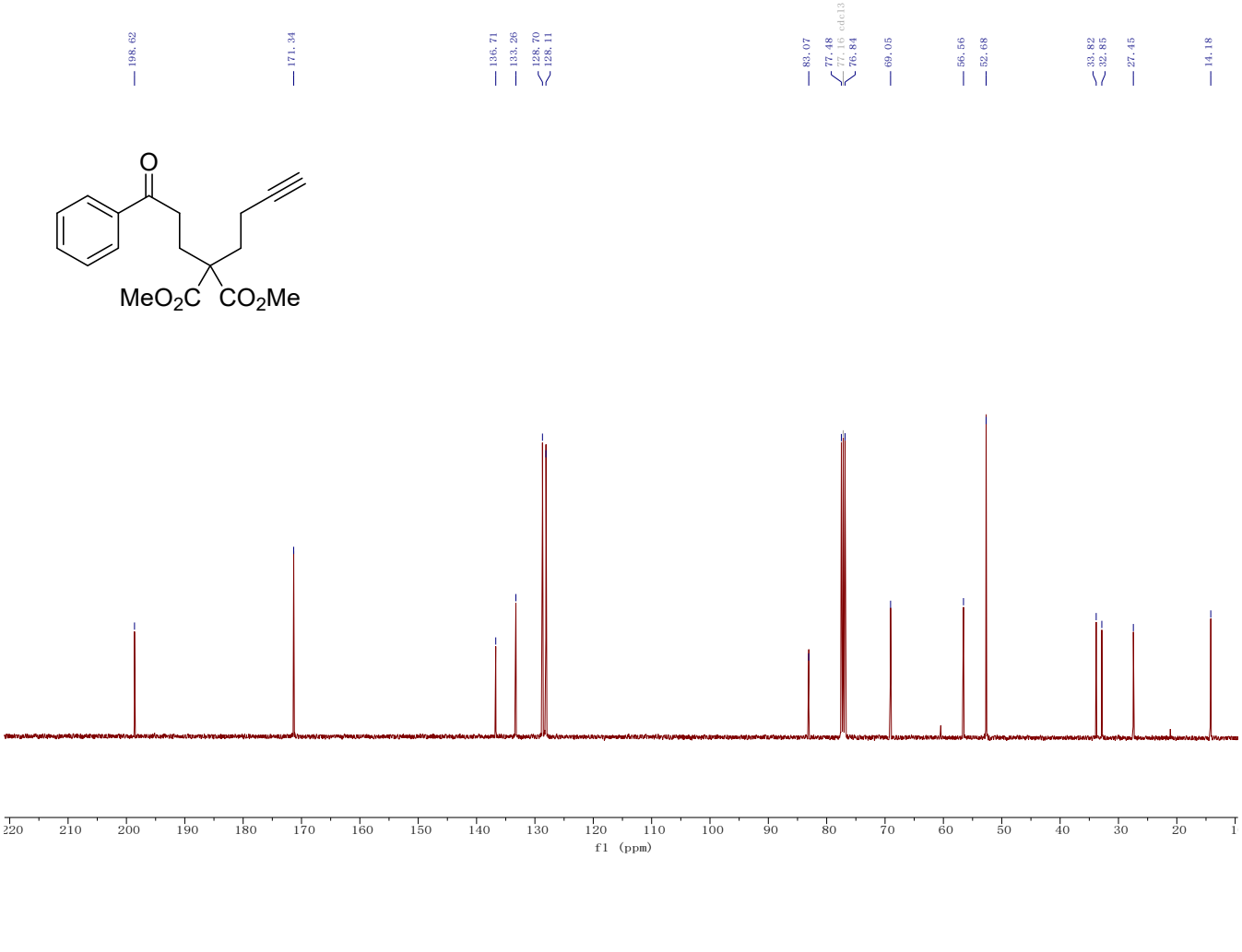
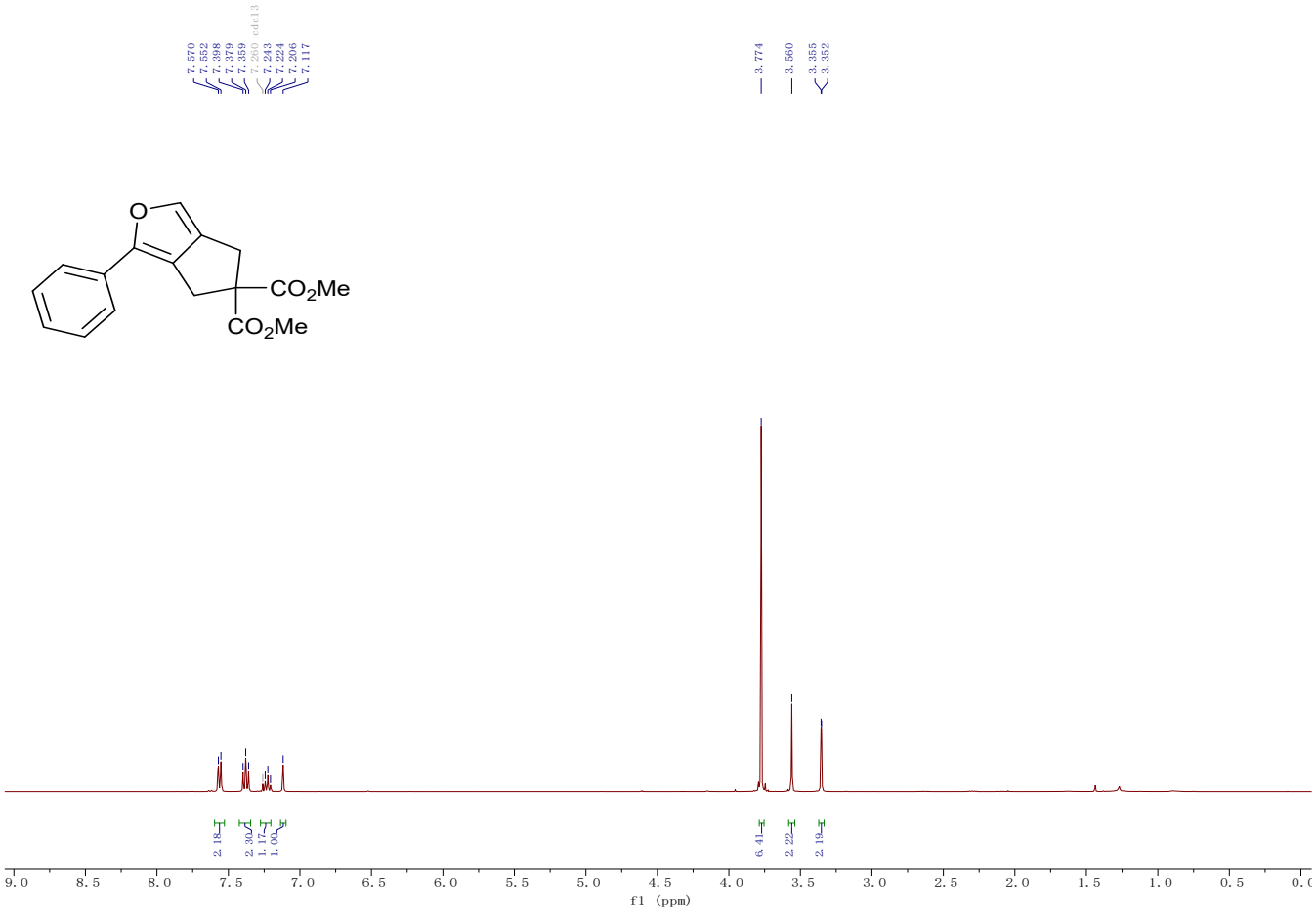
7.914
7.909
7.574
7.571
7.566
7.554
7.546
7.539
7.525
7.522
7.518
7.465
7.438
7.420
7.415
7.260 cdcl3
3.715
3.008
2.982
2.956
2.357
2.330
2.305
2.210
1.956
1.953
1.945
O
MeO2C CO2Me
1.96
1.00
2.01
6.00
2.06
2.11
3.98
0.86
f1 (ppm)


198.62
171.34
136.71
133.26
128.70
128.11
83.07
77.48
77.16 cdcl3
76.84
69.05
56.56
52.68
33.82
32.85
27.45
14.18
O
MeO2C CO2Me
f1 (ppm)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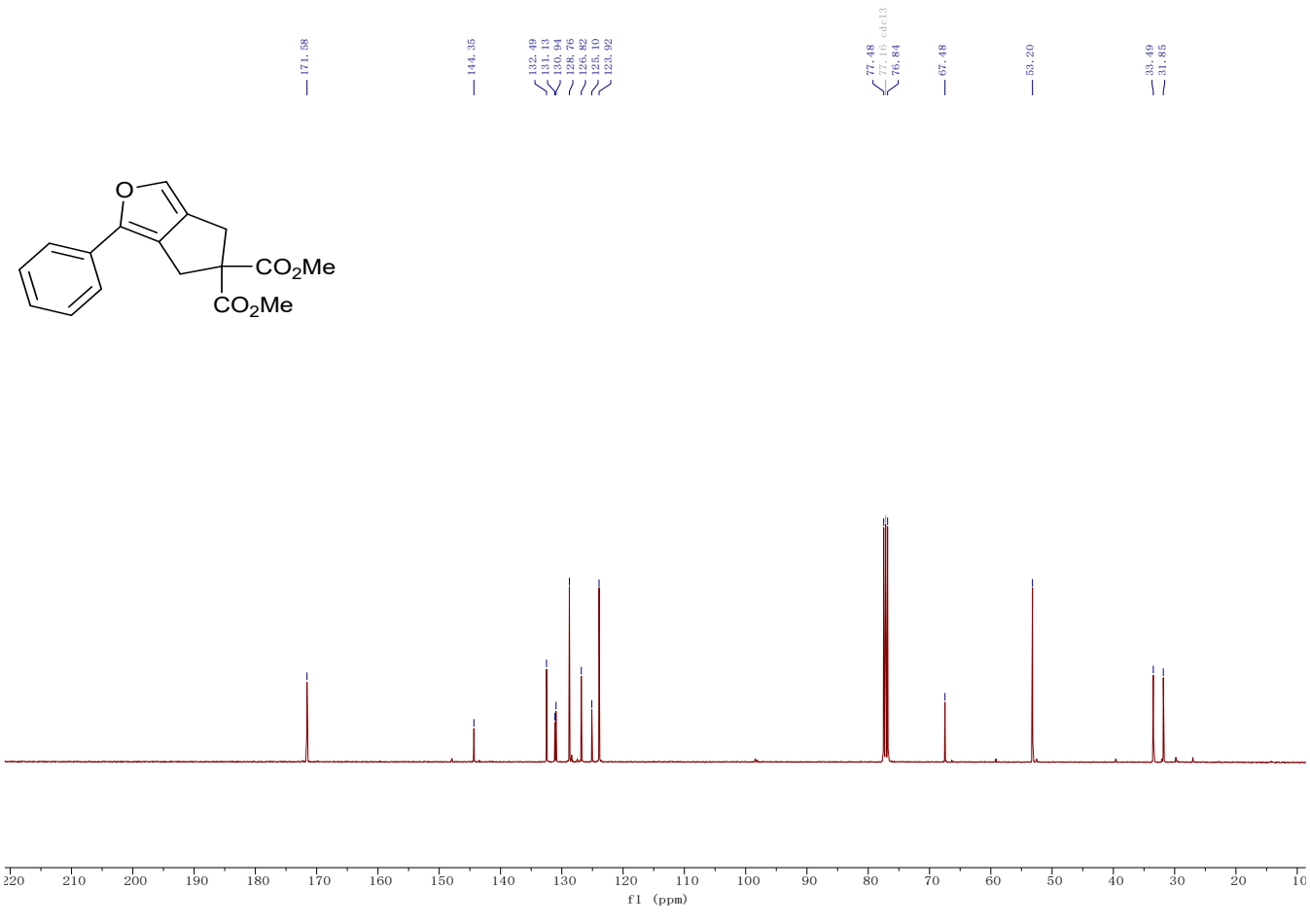
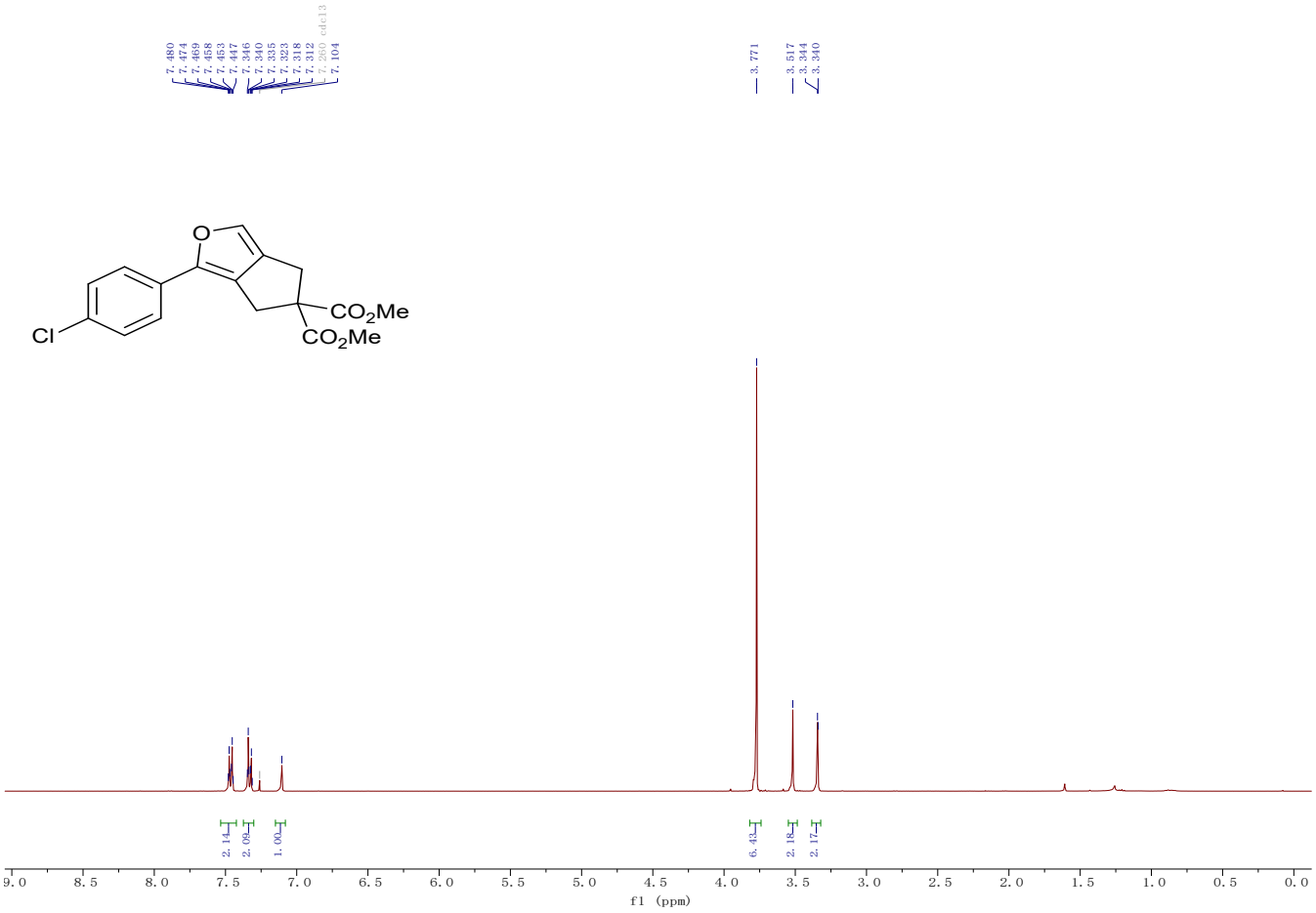
7.552
7.398
7.379
7.359
7.280 cdcl3
7.243
7.224
7.206
7.117
3.774
3.560
3.355
3.352
O
CO2Me
CO2Me
2.18
2.30
1.17
1.00
6.41
2.22
2.19
f1 (ppm)


171.58
144.35
132.49
131.13
130.94
128.76
126.82
125.10
123.92
77.48
77.16 cdcl3
76.84
67.48
53.20
33.49
31.85
O
CO2Me
CO2Me
f1 (ppm)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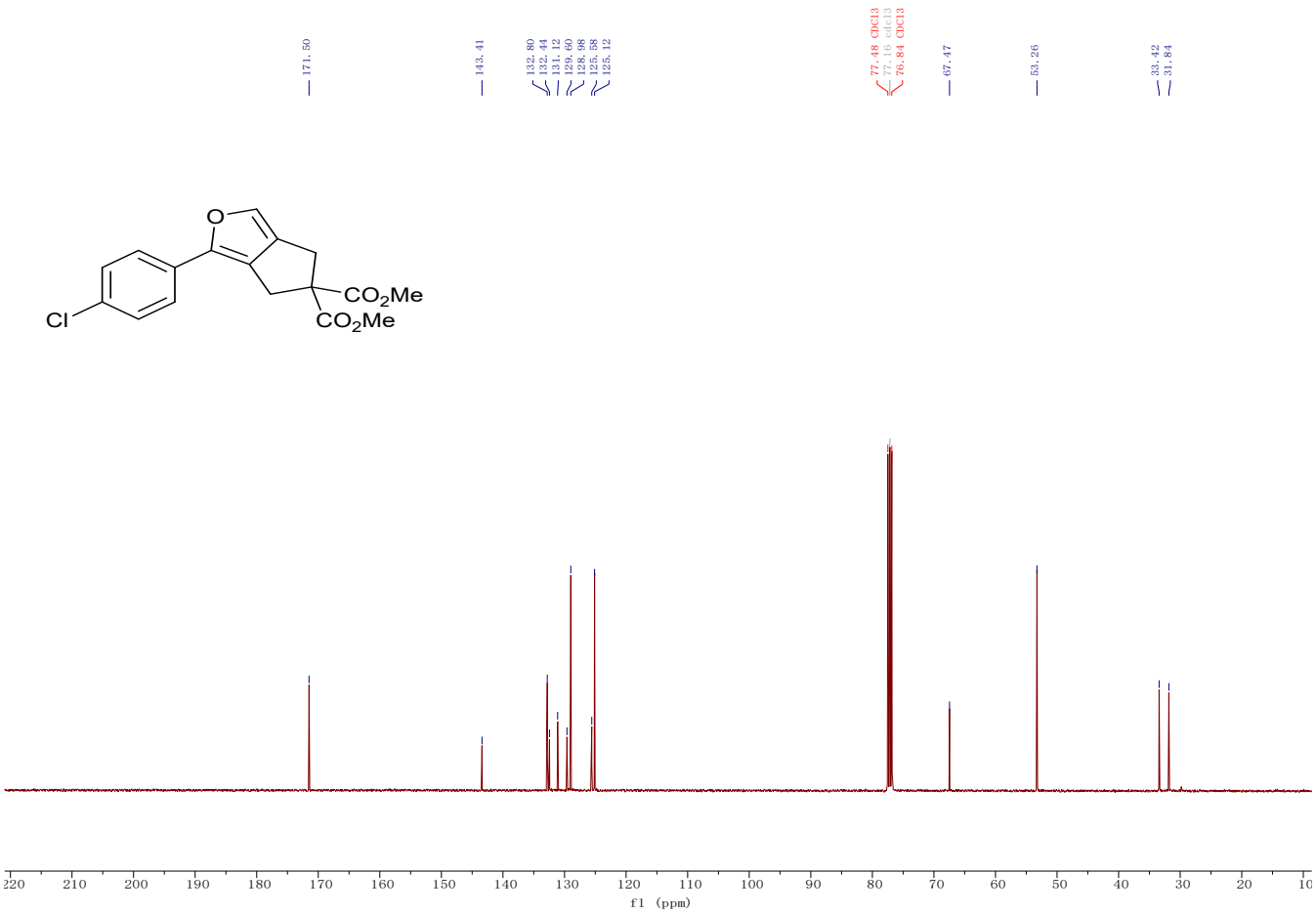
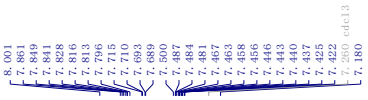
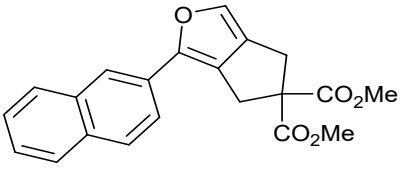
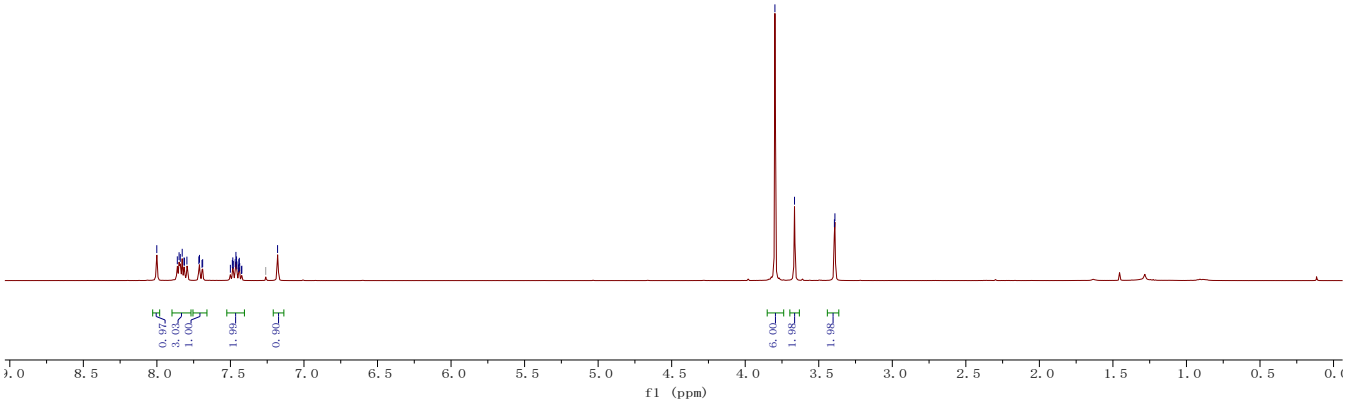
7.469
7.458
7.453
7.447
7.346
7.340
7.335
7.323
7.318
7.312
7.280 cdcl3
7.104
3.771
3.517
3.344
3.340
O
Cl
CO2Me
CO2Me
2.14
2.08
1.00
6.43
2.18
2.17
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


171.50
143.41
132.80
132.44
131.12
129.60
128.98
125.58
125.12
77.48 CDCl3
77.16 cdcl3
76.84 CDCl3
67.47
53.26
33.42
31.84
O
Cl
CO2Me
CO2Me
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


8.001
7.881
7.849
7.841
7.828
7.816
7.813
7.796
7.715
7.710
7.693
7.689
7.500
7.487
7.484
7.481
7.467
7.463
7.458
7.456
7.446
7.443
7.440
7.437
7.425
7.422
7.260 cdcl3
7.180


3.798
3.665
3.394
3.390


O
CO2Me
CO2Me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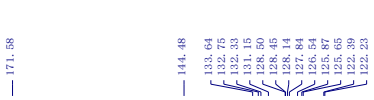
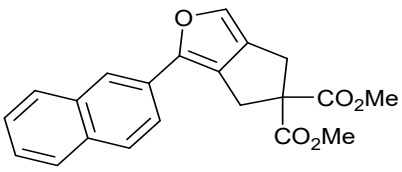
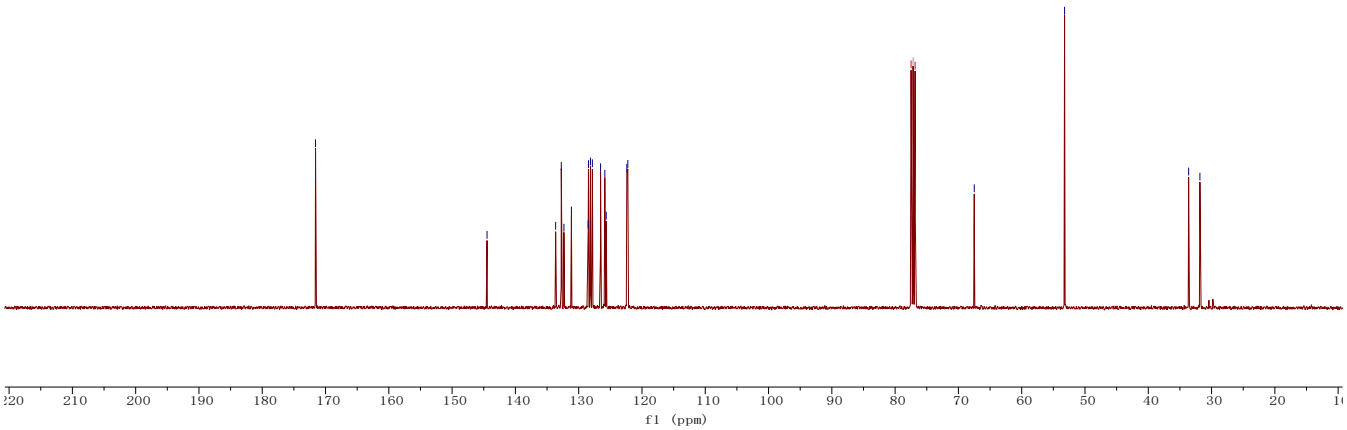
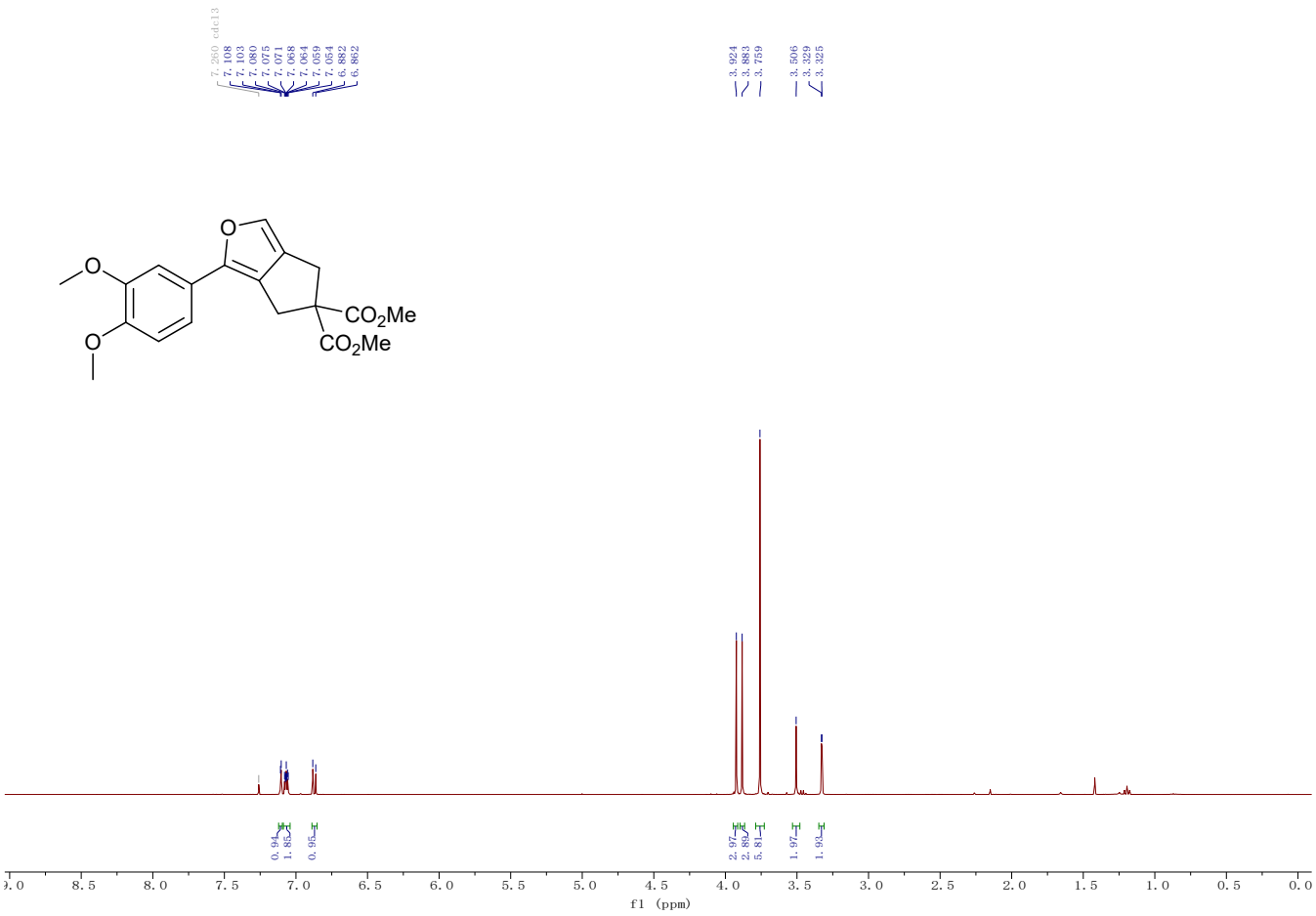
3.05
1.06
1.96
0.90
6.00
1.98
1.98
f1 (ppm)


171.58
144.48
133.64
132.75
132.33
131.15
128.50
128.45
128.14
127.84
126.54
125.87
125.65
122.39
122.23
77.48 CDCl3
77.16 cdcl3
76.84 CDCl3
67.50
53.23
33.62
31.84


O
CO2Me
CO2Me


f1 (ppm)


7.280 cdcl3
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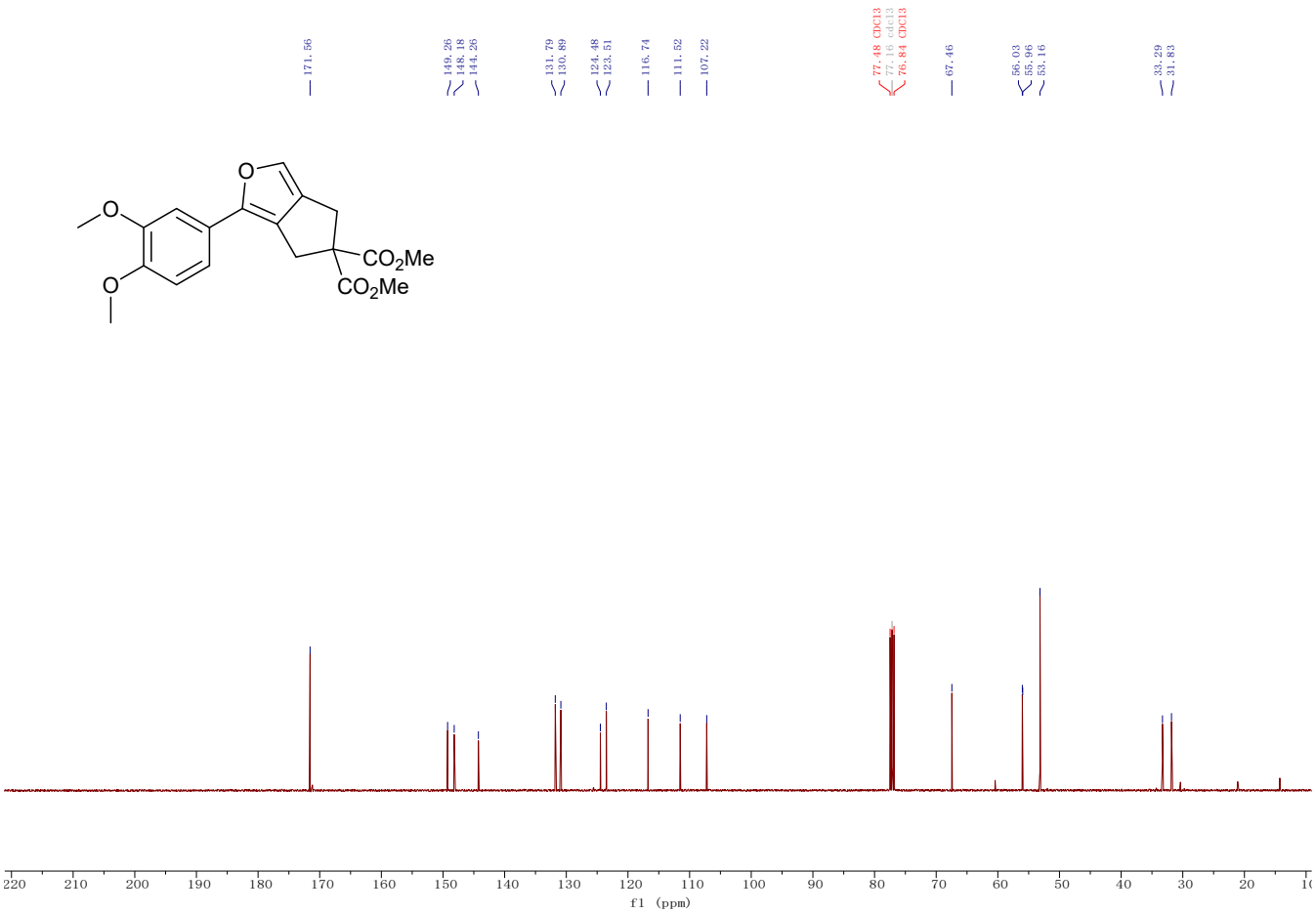
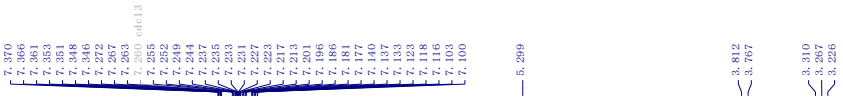
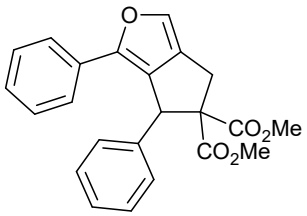
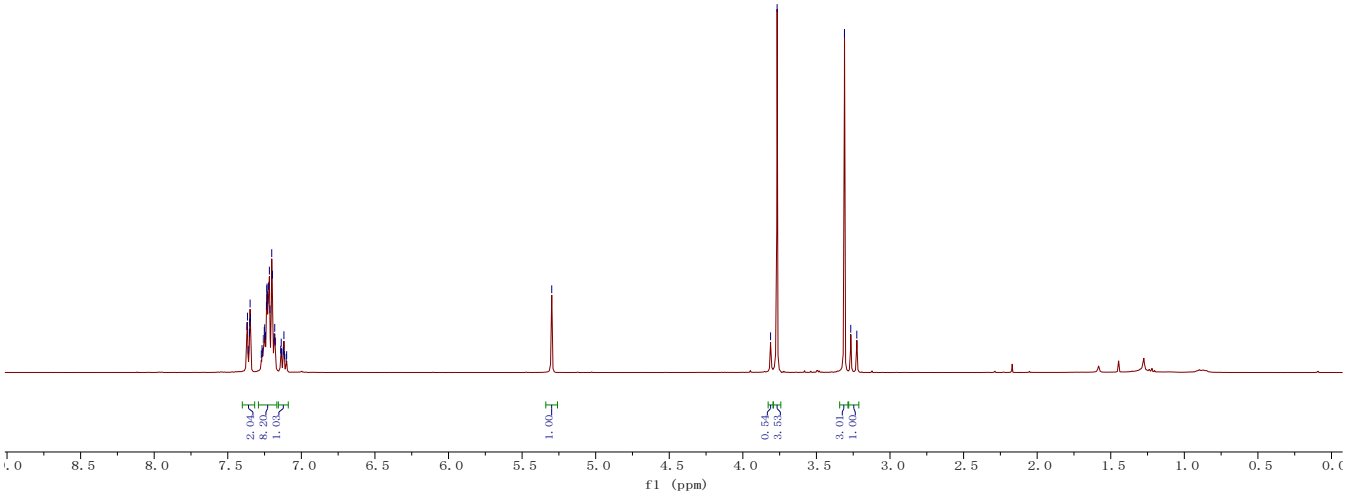
7.103
7.080
7.075
7.071
7.068
7.064
7.059
7.054
6.882
6.862
3.924
3.883
3.759
3.506
3.329
3.325
O
O
O
CO2Me
CO2Me
0.94
1.85
0.96
2.97
2.89
5.81
1.97
1.93
f1 (ppm)

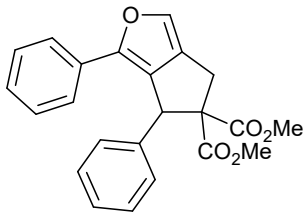

171.56
149.26
148.18
144.26
131.79
130.89
124.48
123.51
116.74
111.52
107.22
77.48 CDCl3
77.16 cdcl3
76.84 CDCl3
67.46
56.03
55.96
53.16
33.29
31.83
O
O
O
CO2Me
CO2Me
f1 (ppm)

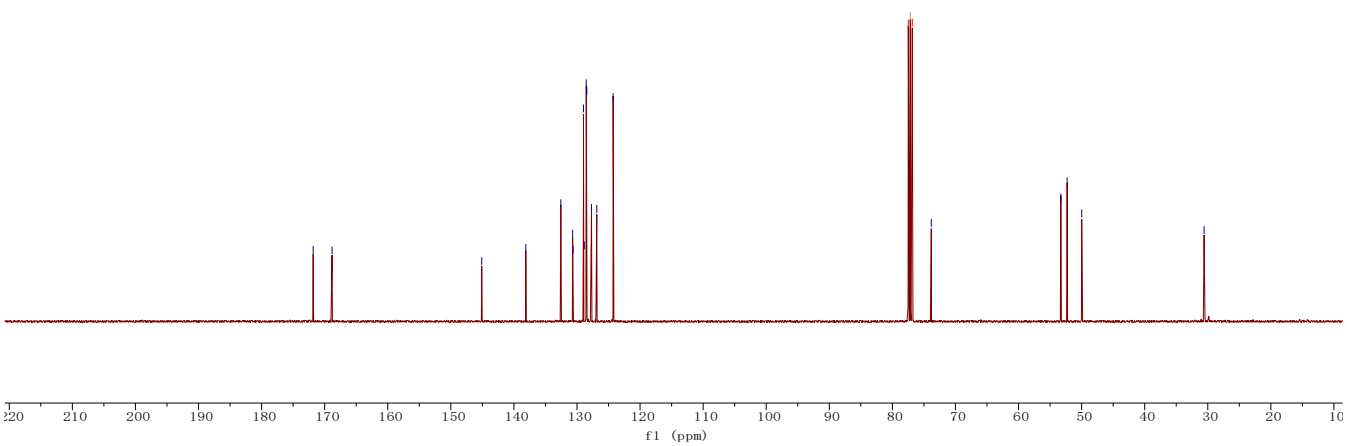

7.370
7.366
7.361
7.353
7.351
7.348
7.346
7.272
7.267
7.263
7.260 cdcl3
7.255
7.252
7.249
7.244
7.237
7.235
7.233
7.231
7.227
7.223
7.217
7.213
7.201
7.196
7.186
7.181
7.177
7.140
7.137
7.133
7.123
7.118
7.116
7.103
7.100
5.299
3.812
3.767
3.310
3.267
3.226

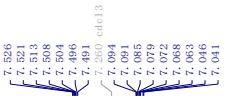

O
CO2Me
CO2Me

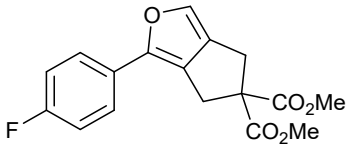

2.04
8.20
1.03
1.00
0.54
3.53
3.01
1.00
f1 (ppm)

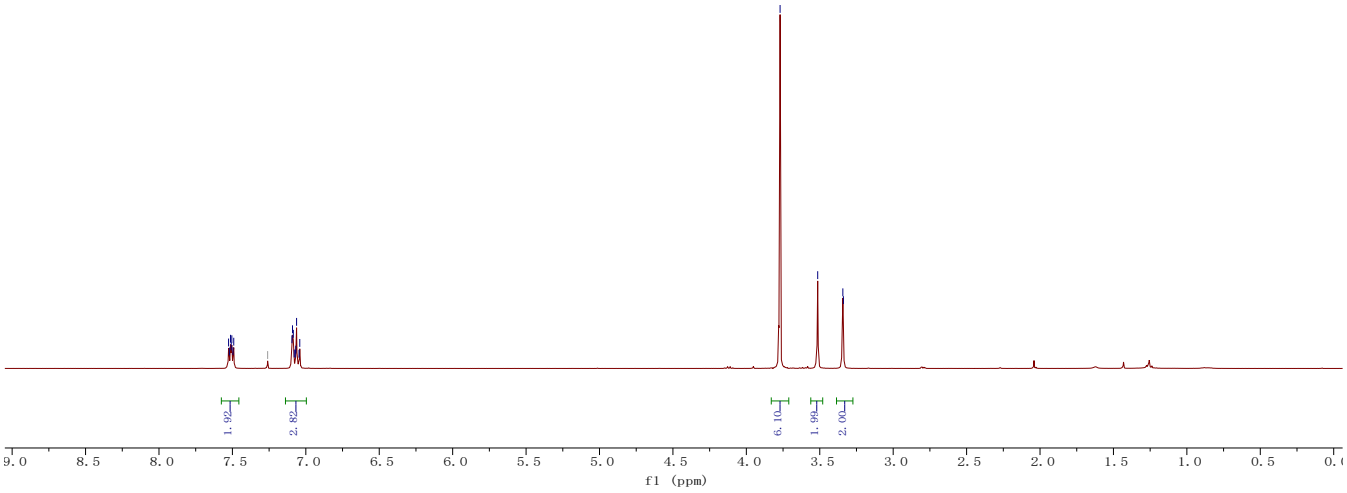

171.82
168.83
145.10
138.12
132.56
130.69
130.62
128.97
128.84
128.53
128.44
127.70
126.86
124.27
77.48 CDCl3
77.16 cdcl3
76.84 CDCl3
73.83
53.30
52.29
49.99
30.58


O
CO2Me
CO2Me

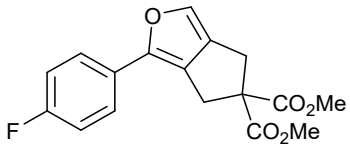

f1 (ppm)

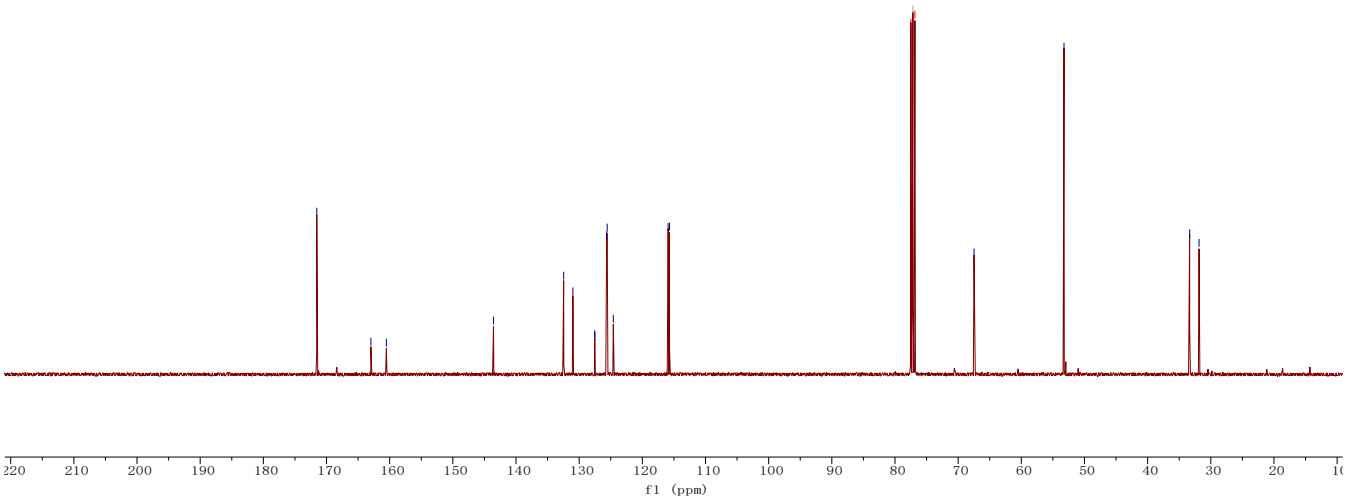

7.526
7.521
7.513
7.508
7.504
7.494
7.491
7.260 cdcl3
7.094
7.091
7.085
7.079
7.072
7.068
7.063
7.046
7.041
3.770
3.514
3.343
3.339

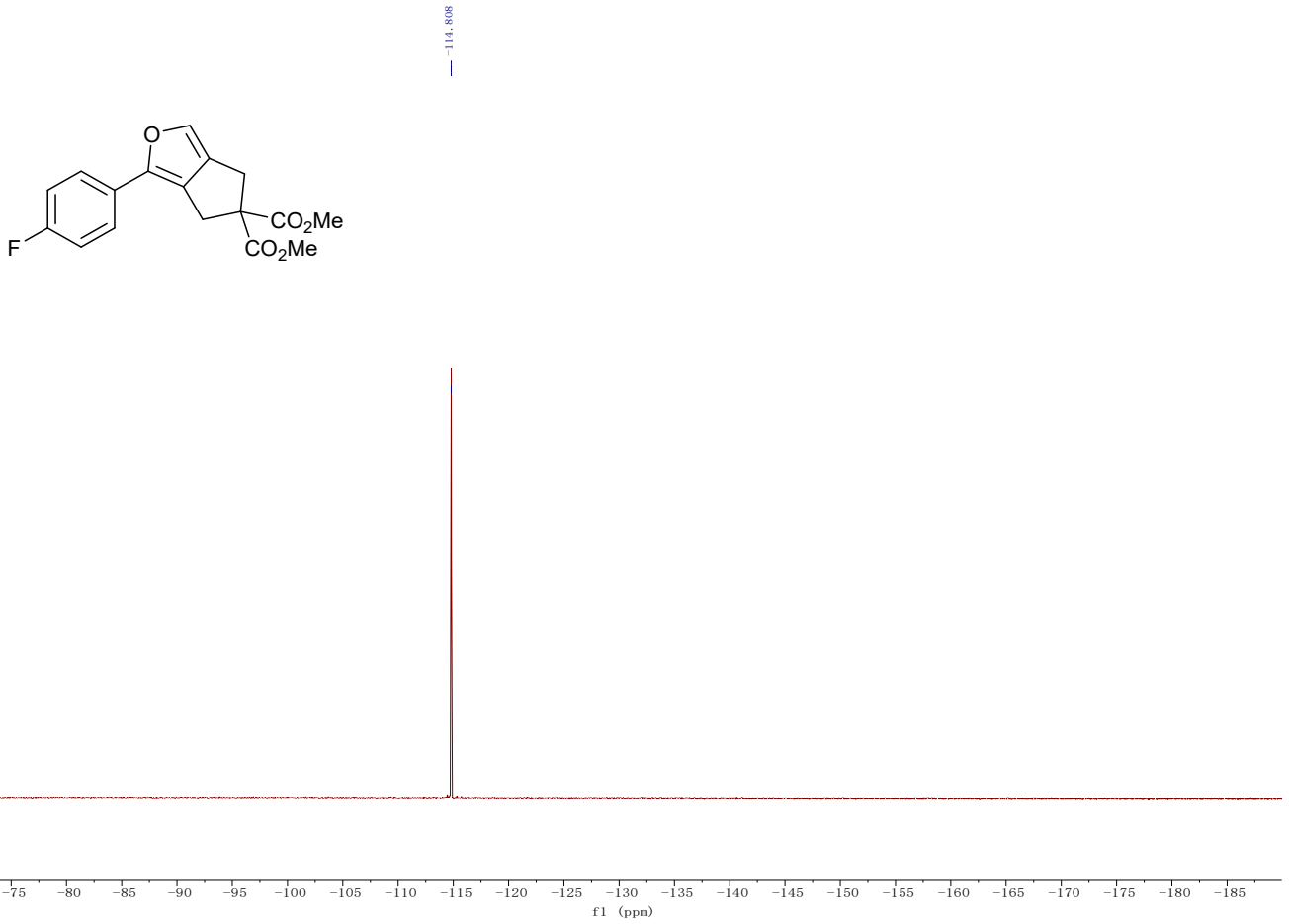

O
F
CO2Me
CO2Me

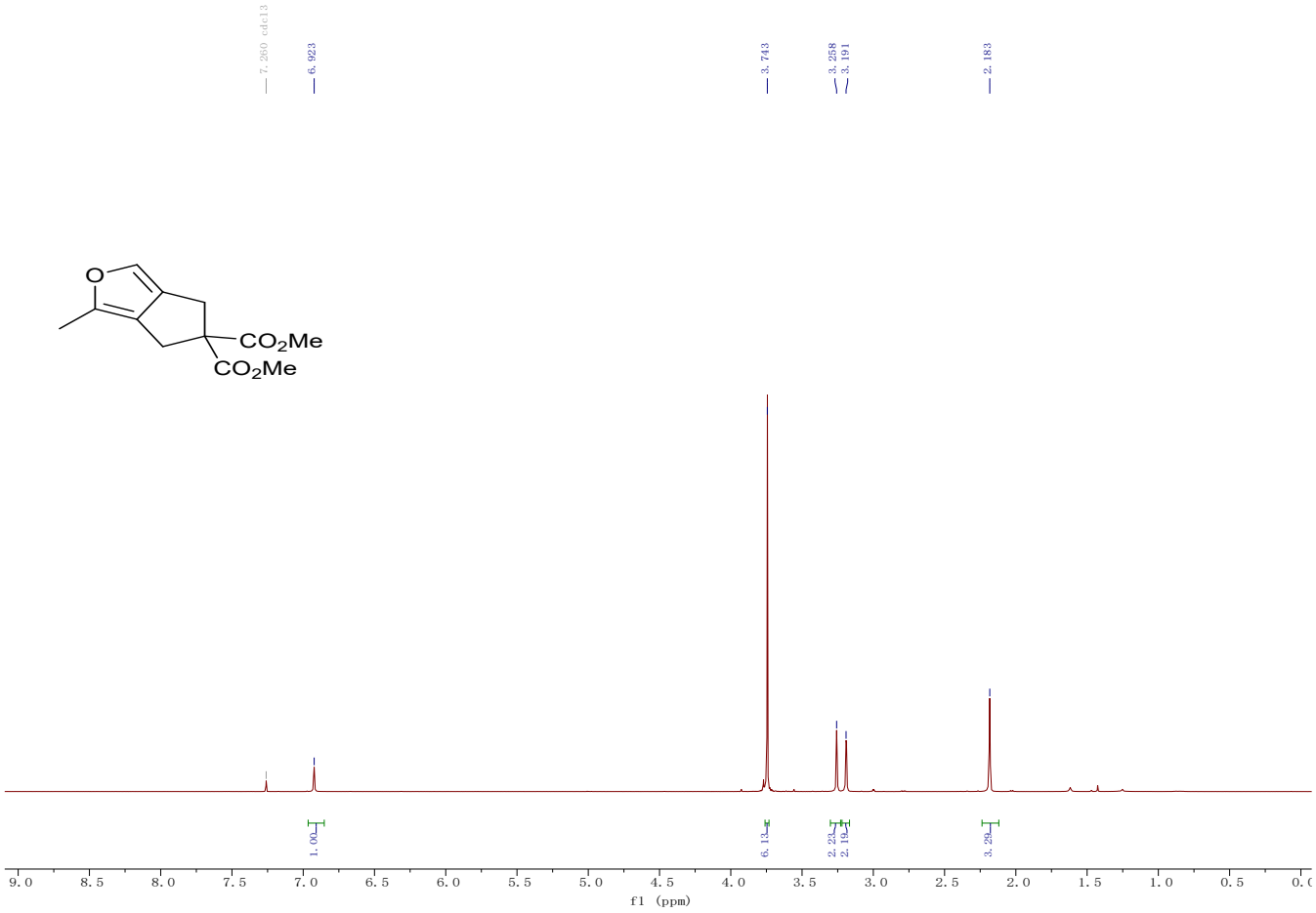

1.92
2.82
6.10
1.99
2.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

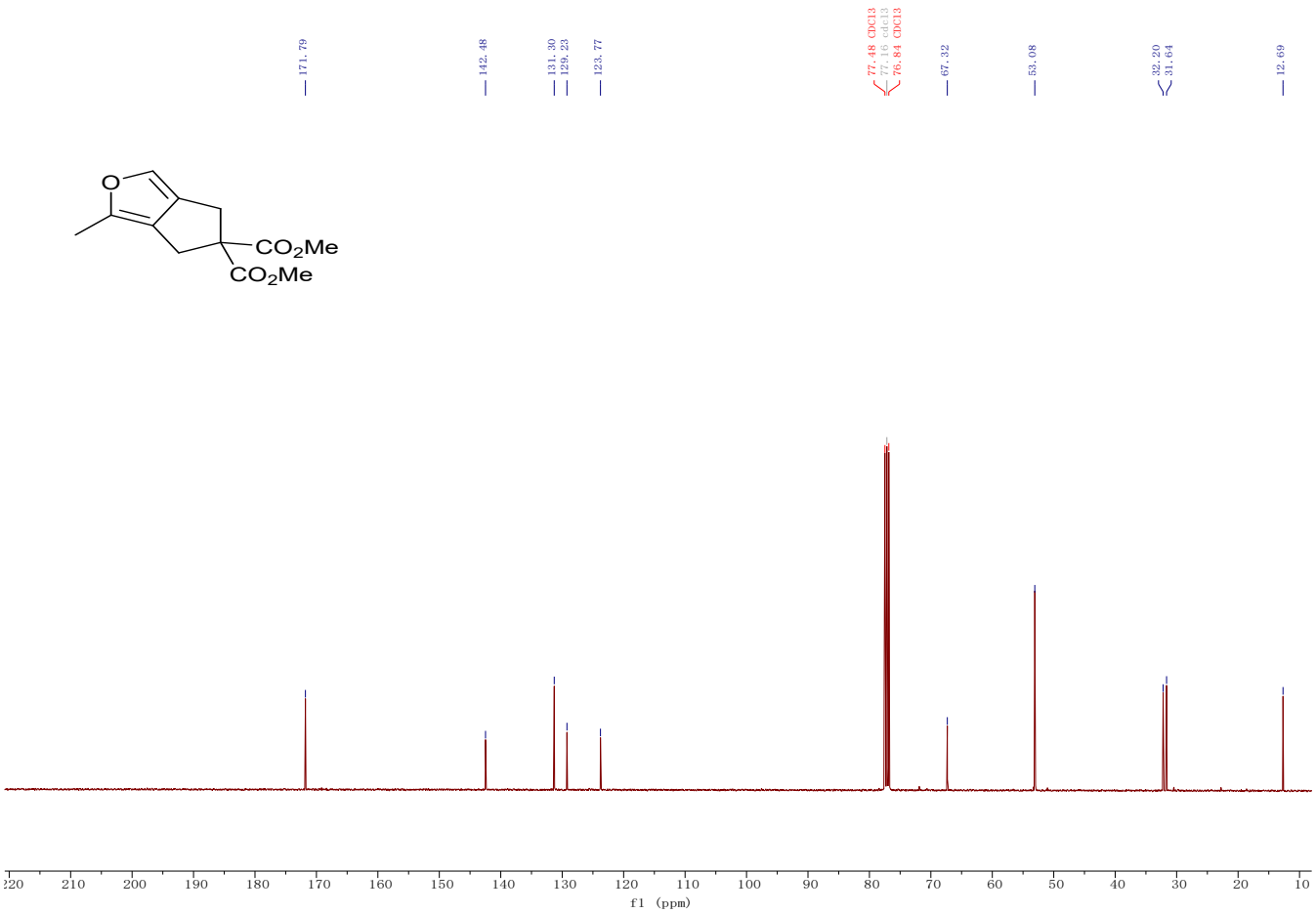

171.54
162.97
160.52
143.57
132.45
130.99
127.54
127.51
125.64
125.56
124.60
115.91
115.70
77.48 CDCl3
77.16 cdcl3
76.84 CDCl3
67.48
53.24
33.35
31.86

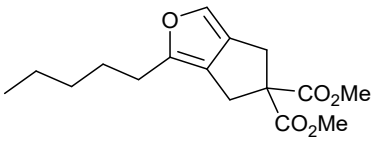

O
F
CO2Me
CO2Me


220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

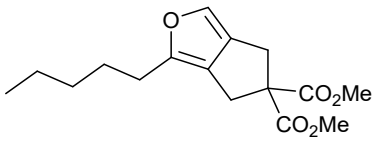

-114.808
O
F
CO2Me
CO2Me
−75 −80 −85 −90 −95 −100 −105 −110 −115 −120 −125 −130 −135 −140 −145 −150 −155 −160 −165 −170 −175 −180 −185
f1 (ppm)


7.260 cdcl3
6.923
3.743
3.258
3.191
2.183
O
CO2Me
CO2Me
1.00
6.13
2.23
2.18
3.29
f1 (ppm)

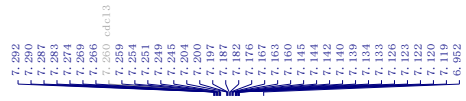

171.79
142.48
131.30
129.23
123.77
77.48 CDCl3
77.16 cdcl3
76.84 CDCl3
67.32
53.08
32.20
31.64
12.69
O
CO2Me
CO2Me
f1 (ppm)

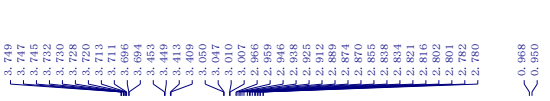

O
CO2Me
CO2Me

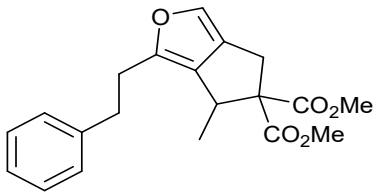
6.934
3.749
3.259
3.254
3.224
3.220
3.216
2.557
2.532
2.506
1.653
1.628
1.603
1.579
1.562
1.340
1.312
1.304
1.288
1.279
1.266
1.253
1.250
0.914
0.892
0.869
0.89
6.00
4.00
2.01
2.86
4.70
3.19
f1 (ppm)

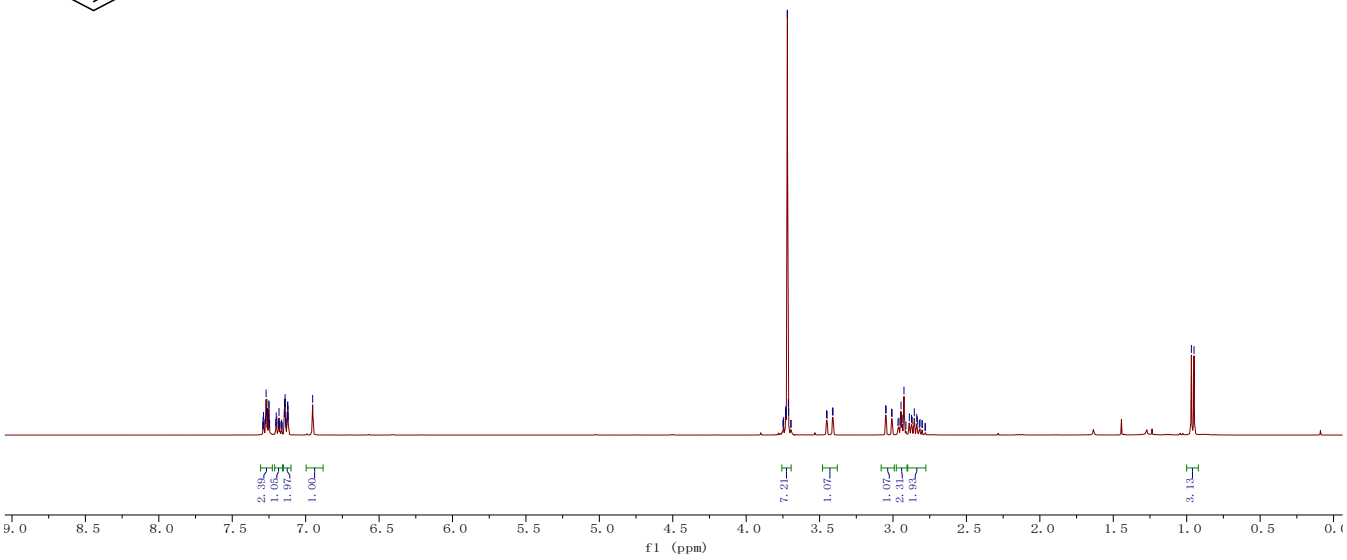

O
CO2Me
CO2Me

171.81
146.76
131.17
129.12
123.26
77.48 CDCl3
77.16 cdcl3
76.84 CDCl3
67.35
53.08
32.01
31.98
31.52
27.44
27.35
22.50
14.15
f1 (ppm)

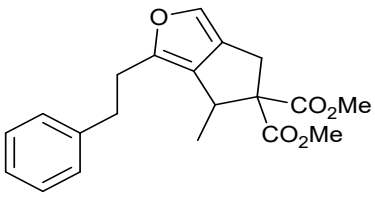

7.292
7.290
7.287
7.283
7.274
7.269
7.266
7.260 cdcl3
7.259
7.254
7.251
7.249
7.245
7.204
7.200
7.197
7.187
7.182
7.176
7.167
7.163
7.160
7.145
7.144
7.142
7.140
7.139
7.134
7.133
7.126
7.123
7.122
7.120
7.119
6.952

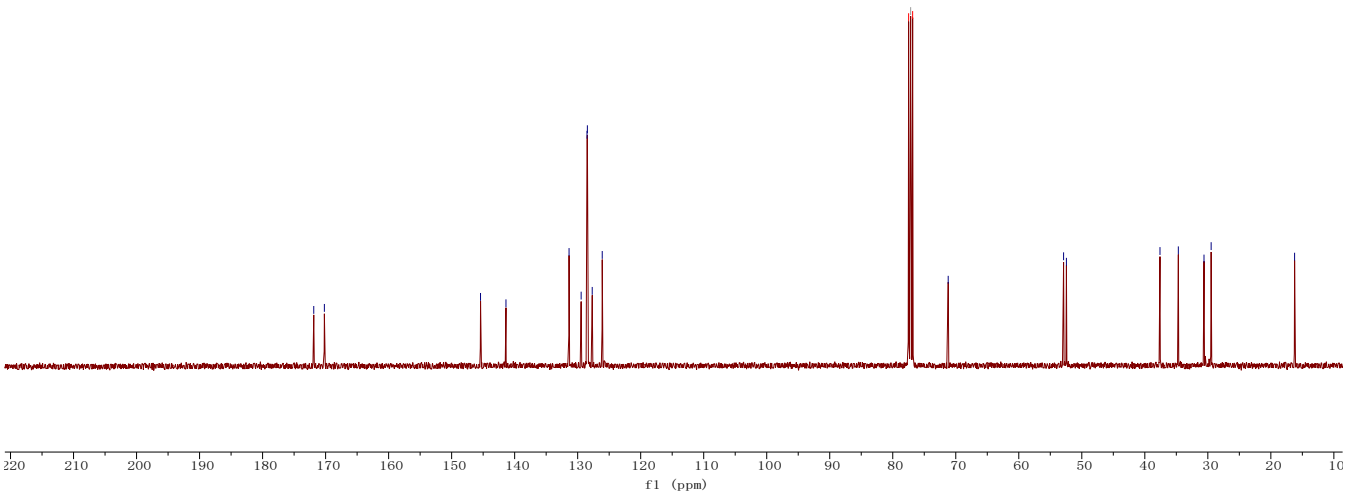

3.749
3.747
3.745
3.732
3.730
3.728
3.720
3.713
3.711
3.696
3.694
3.453
3.449
3.413
3.409
3.050
3.047
3.010
3.007
2.966
2.959
2.946
2.938
2.925
2.912
2.889
2.874
2.870
2.855
2.838
2.834
2.821
2.816
2.802
2.791
2.782
2.780
0.968
0.950


O
CO2Me
CO2Me


2.38
1.05
1.97
1.00
7.21
1.07
1.07
2.31
1.93
3.13
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

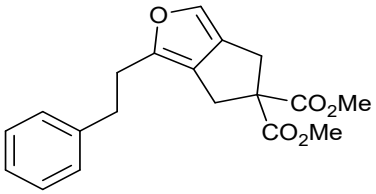

171.88
170.20
145.42
141.38
131.37
129.45
128.52
128.46
127.69
126.10
77.48 CDCl3
77.16 cdcl3
76.84 CDCl3
71.20
52.89
52.44
37.59
34.68
30.61
29.47
16.23

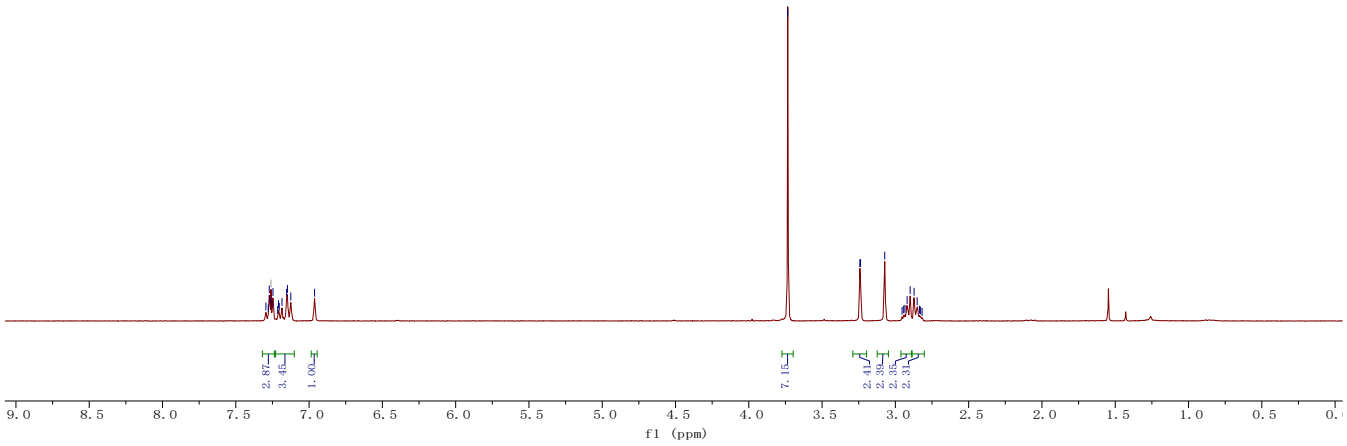

O
CO2Me
CO2Me


220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.295
7.278
7.272
7.266
7.260 cdcl3
7.252
7.246
7.214
7.209
7.204
7.185
7.153
7.148
7.125
6.963

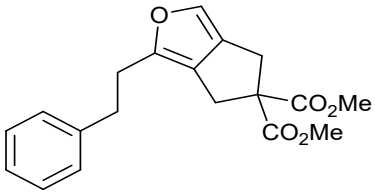

3.735
3.242
3.238
3.073
2.954
2.943
2.935
2.920
2.899
2.872
2.851
2.835
2.828
2.817

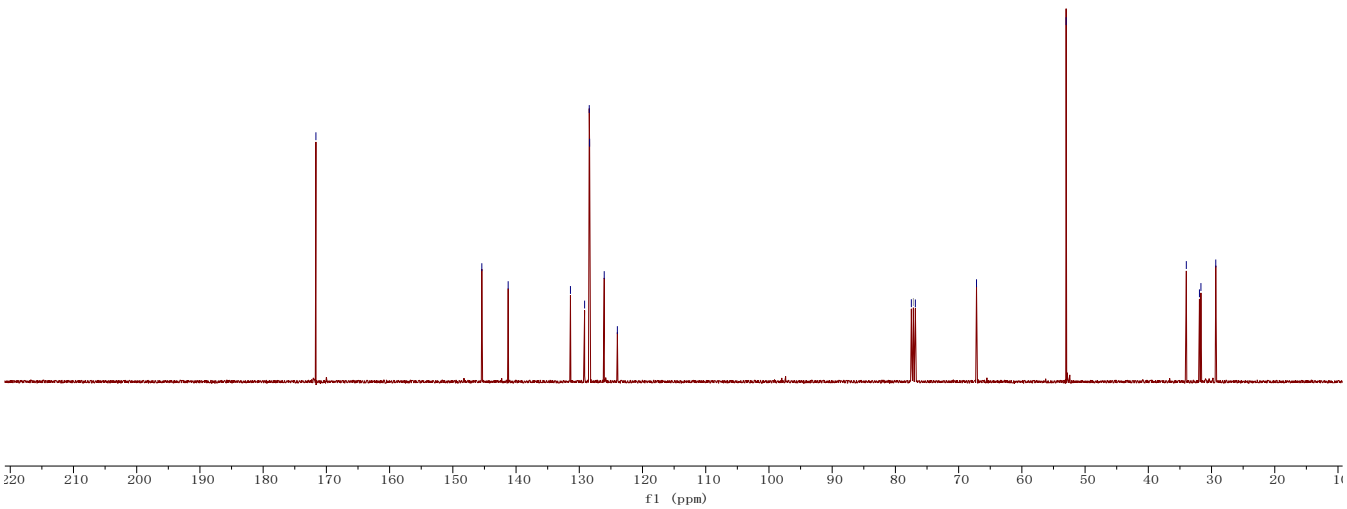

O
CO2Me
CO2Me

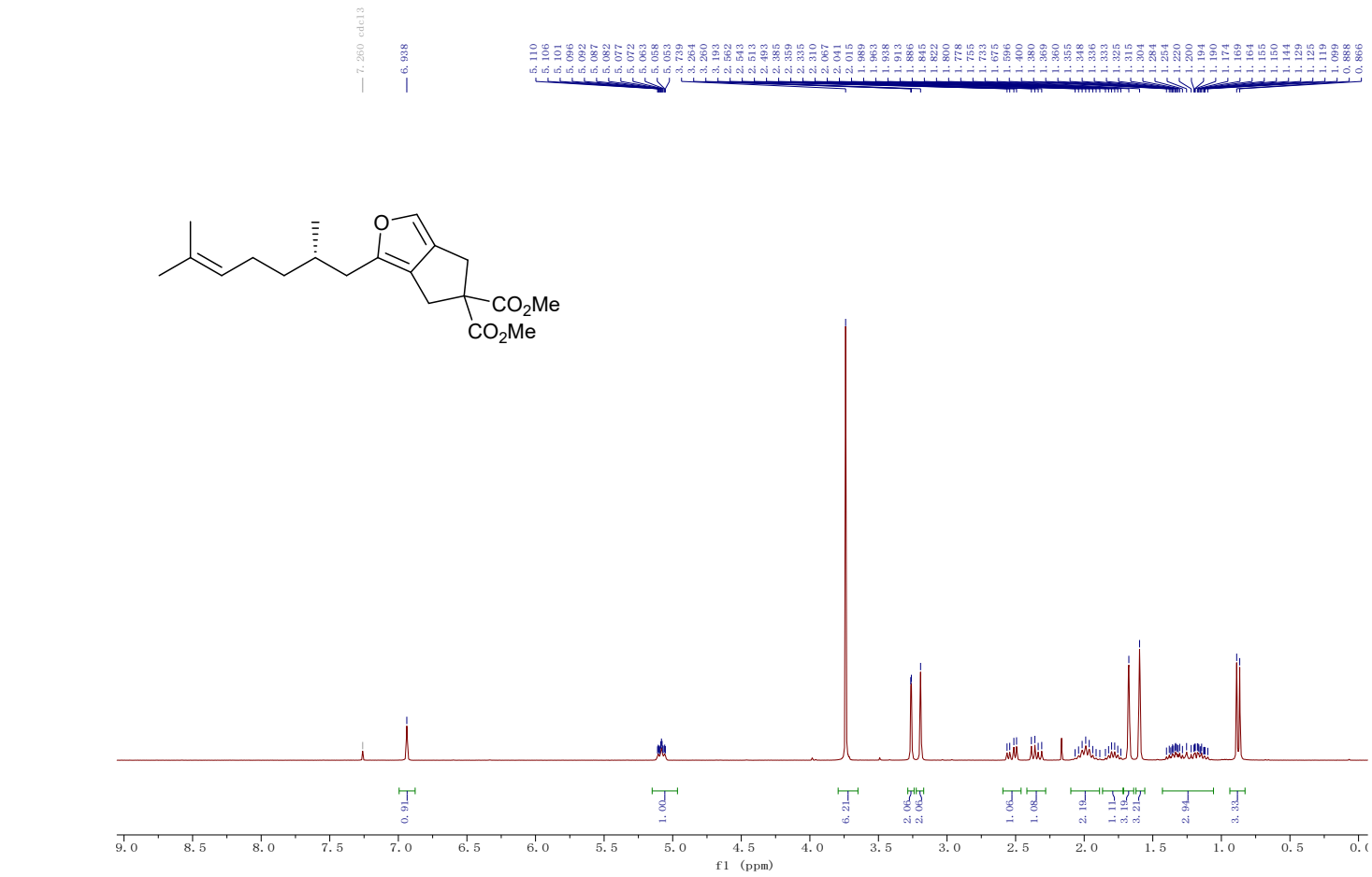

2.87
3.45
1.00
7.15
2.41
2.39
2.35
2.31
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

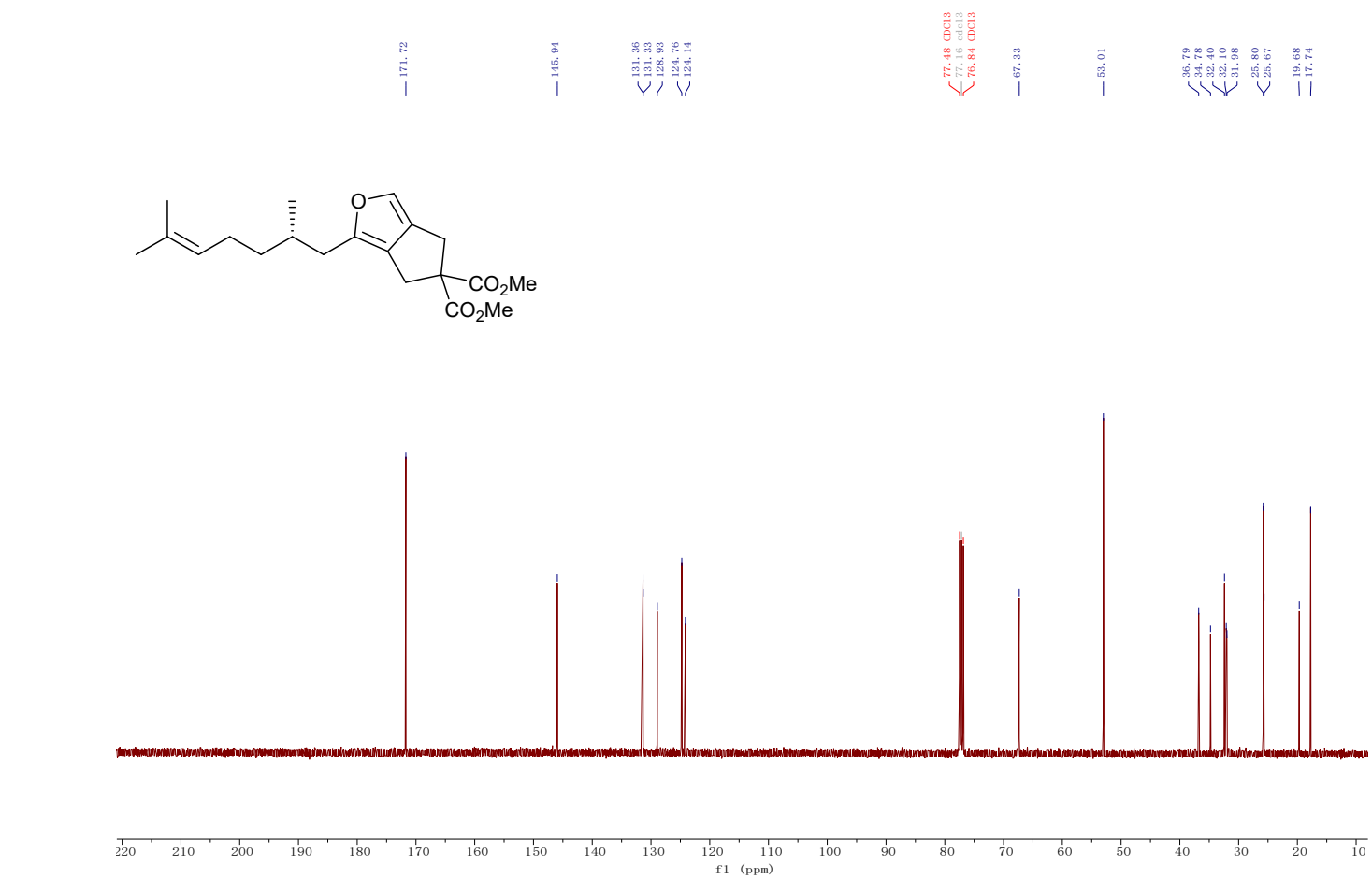

171.66
145.41
141.25
131.40
129.16
128.42
128.37
126.05
123.98

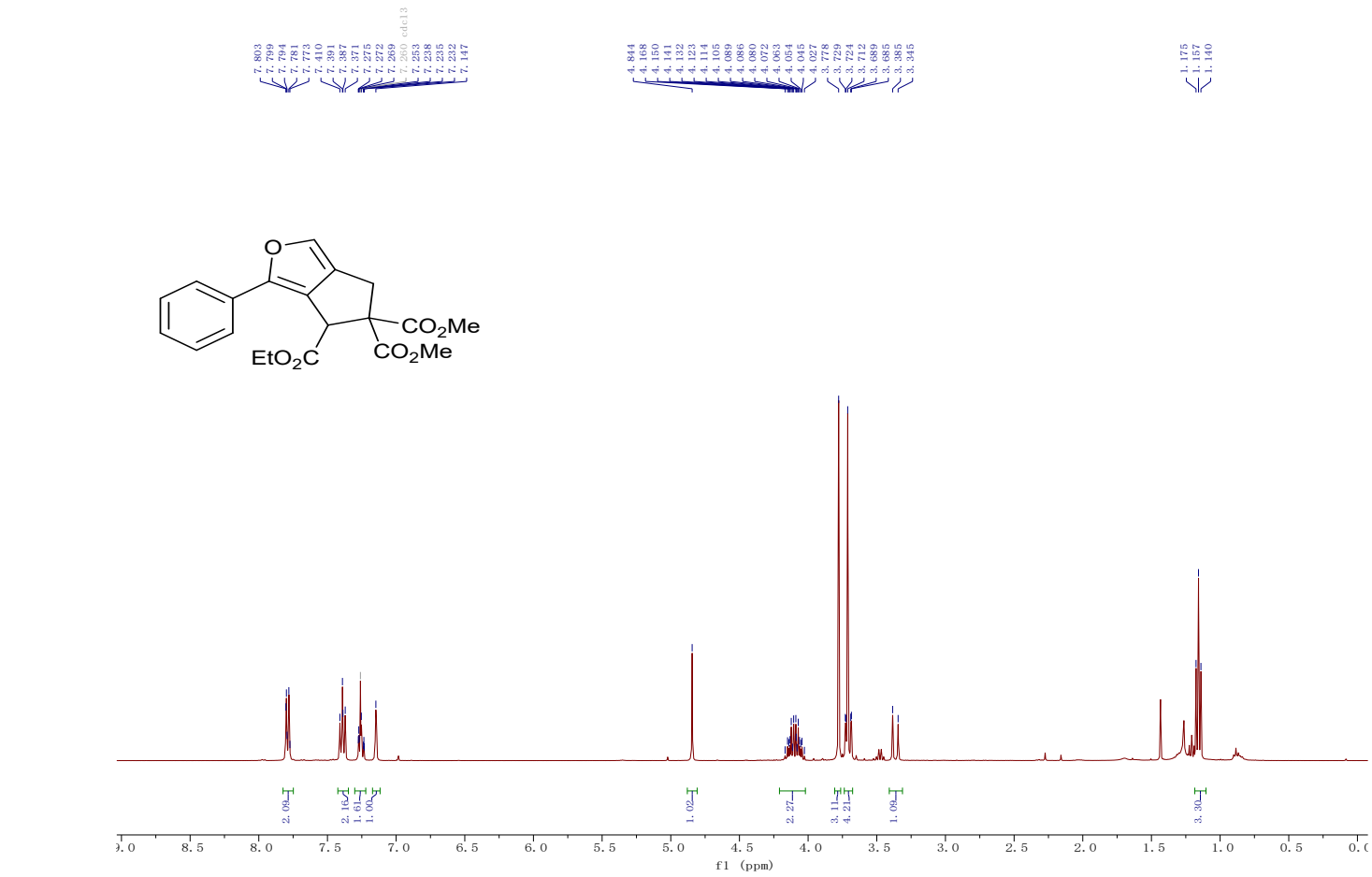

77.48
77.16 cdcl3
76.84
67.17
53.00
33.99
31.91
31.68
29.33

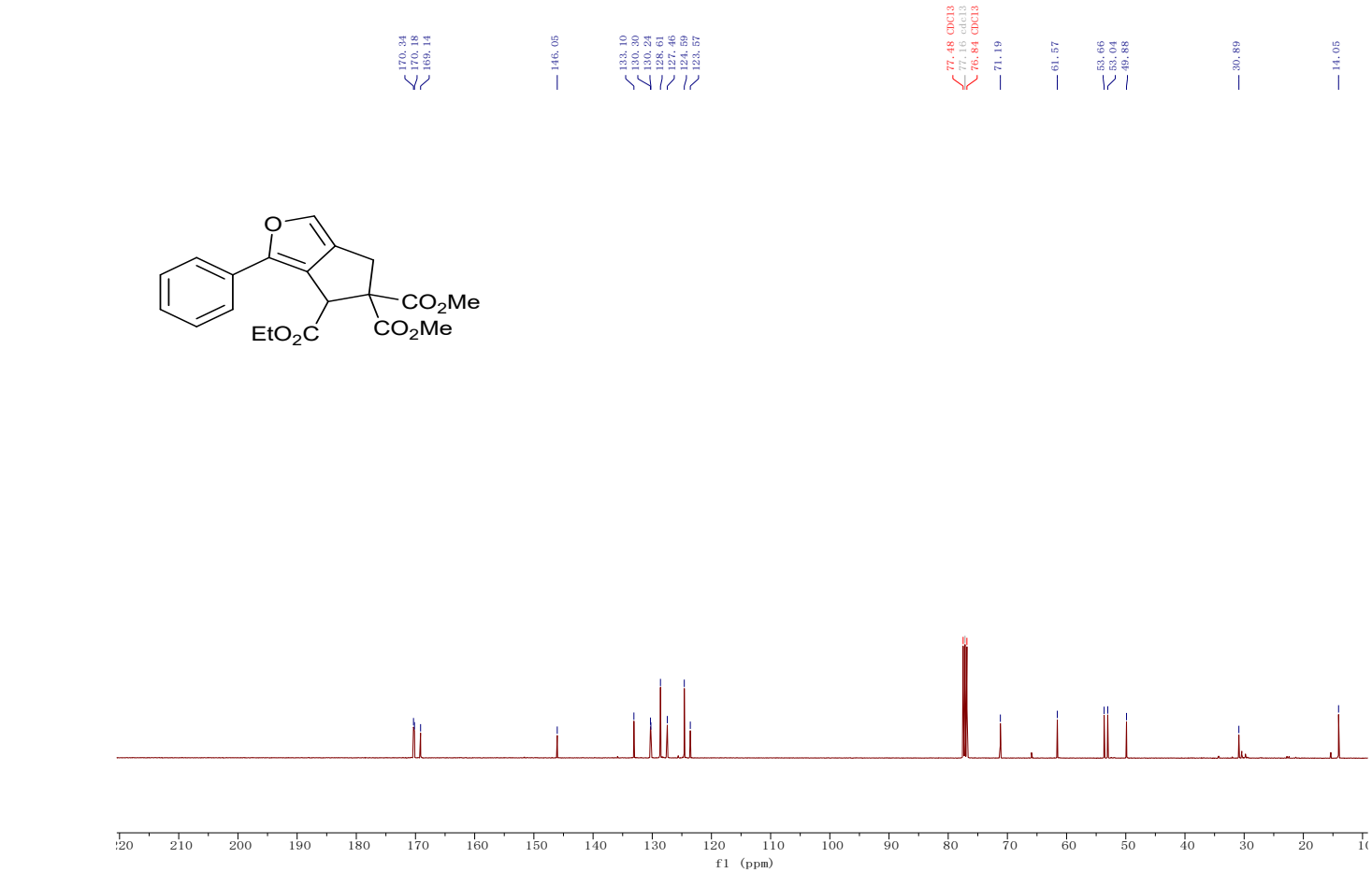

O
CO2Me
CO2Me

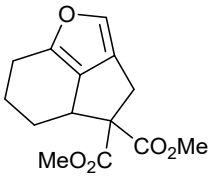

220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

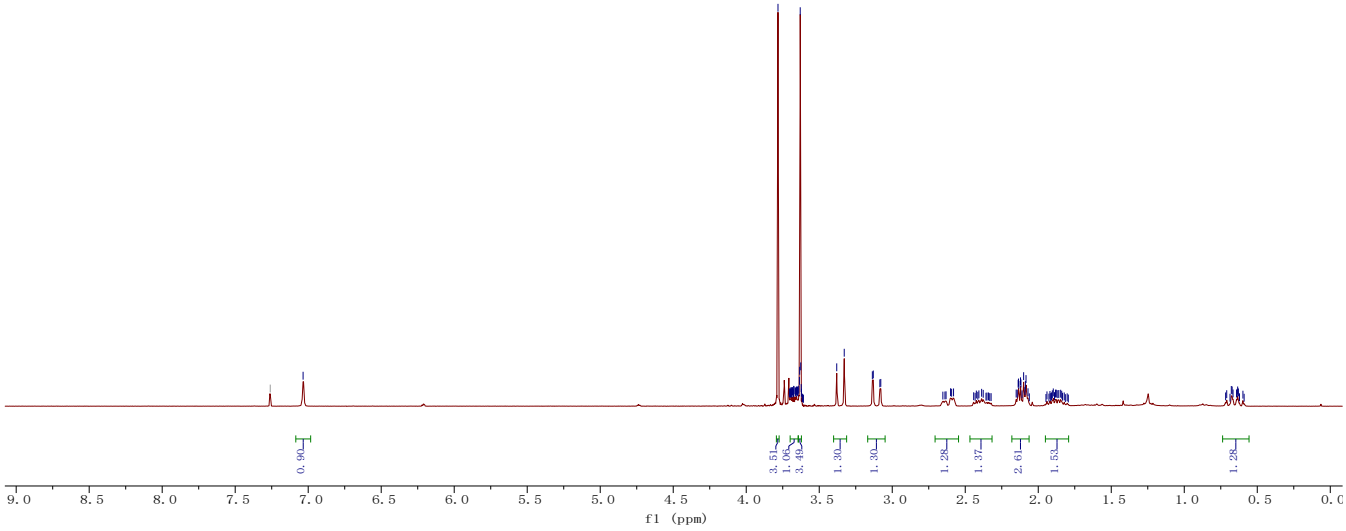

7.260 cdcl3
6.938
5.110
5.106
5.101
5.096
5.092
5.087
5.082
5.077
5.072
5.063
5.058
5.053
3.739
3.264
3.260
3.193
2.562
2.543
2.513
2.493
2.385
2.359
2.335
2.310
2.067
2.041
2.015
1.989
1.963
1.938
1.913
1.886
1.845
1.822
1.800
1.778
1.755
1.733
1.675
1.596
1.400
1.380
1.369
1.360
1.355
1.348
1.336
1.333
1.325
1.315
1.304
1.284
1.254
1.220
1.200
1.194
1.190
1.174
1.169
1.164
1.155
1.150
1.144
1.129
1.125
1.119
1.094
0.888
0.866
O
CO2Me
CO2Me
0.91
1.00
6.21
2.08
2.06
1.06
1.08
2.19
1.11
3.19
3.21
2.94
3.33
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

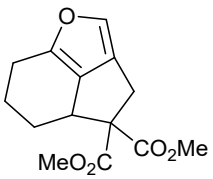

171.72
145.94
131.36
131.33
128.93
124.76
124.14
77.48 CDCl3
77.16 cdcl3
76.84 CDCl3
67.33
53.01
36.79
34.78
32.40
32.10
31.98
25.80
25.67
19.68
17.74
O
CO2Me
CO2Me
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

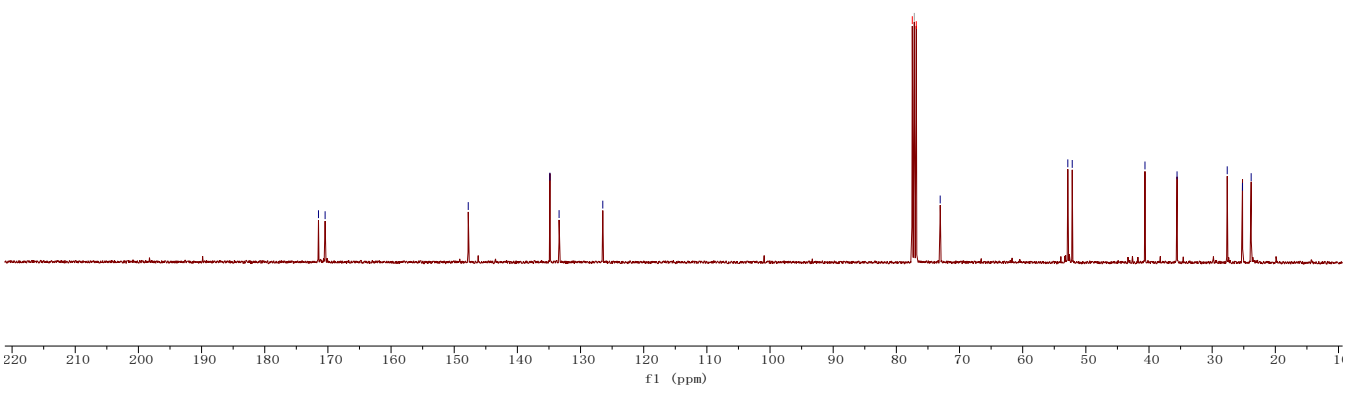

7.803
7.799
7.794
7.781
7.773
7.410
7.391
7.387
7.371
7.275
7.272
7.269
7.260 cdcl3
7.253
7.238
7.235
7.232
7.147
4.844
4.168
4.150
4.141
4.132
4.123
4.114
4.105
4.089
4.086
4.080
4.072
4.063
4.054
4.045
4.027
3.778
3.729
3.724
3.712
3.689
3.685
3.385
3.345
1.175
1.157
1.140
O
CO2Me
CO2Me
EtO2C
2.09
2.16
1.61
1.06
1.02
2.27
3.11
4.21
1.08
3.30
f1 (ppm)

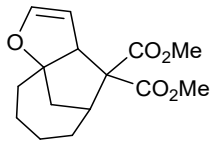

170.34
170.18
169.14
146.05
133.10
130.30
130.24
128.61
127.46
124.69
123.67
77.48 CDCl3
77.16 cdcl3
76.84 CDCl3
71.19
61.57
53.66
53.04
46.88
30.89
14.05
O
CO2Me
CO2Me
EtO2C
f1 (ppm)

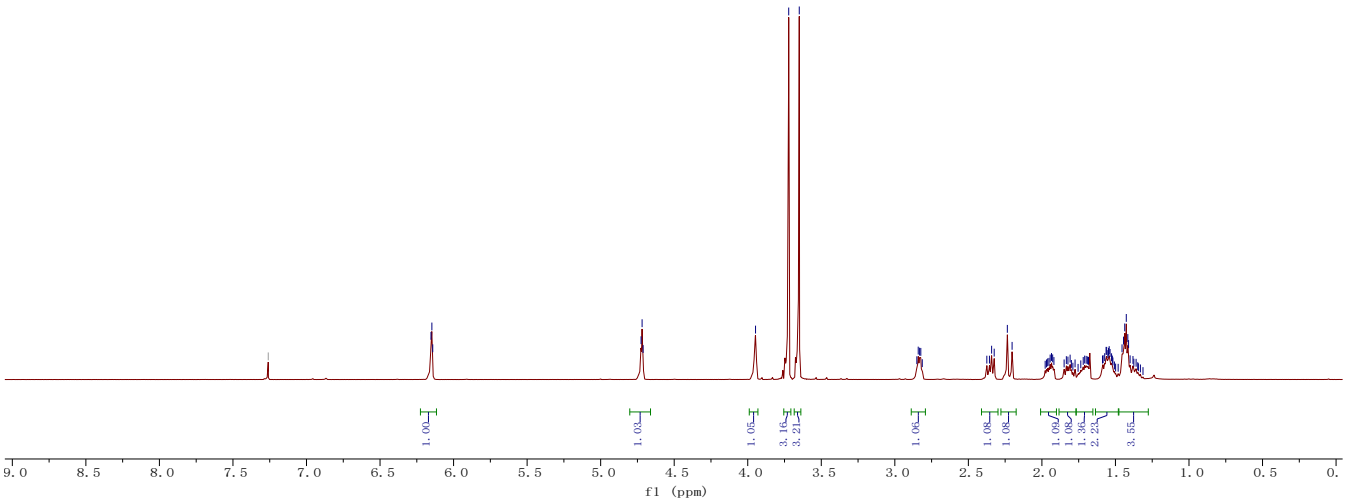

O
MeO2C
CO2Me

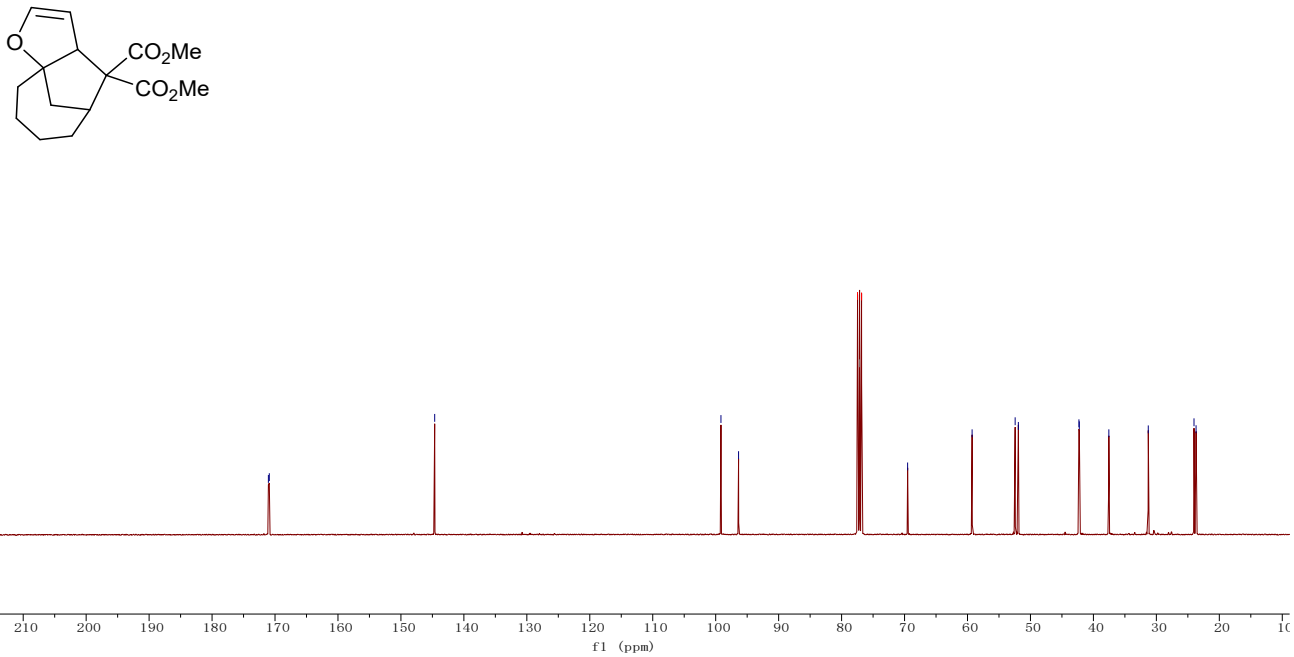

0.90
3.51
1.06
3.48
1.30
1.30
1.28
1.37
2.61
1.53
1.28
f1 (ppm)


O
MeO2C
CO2Me

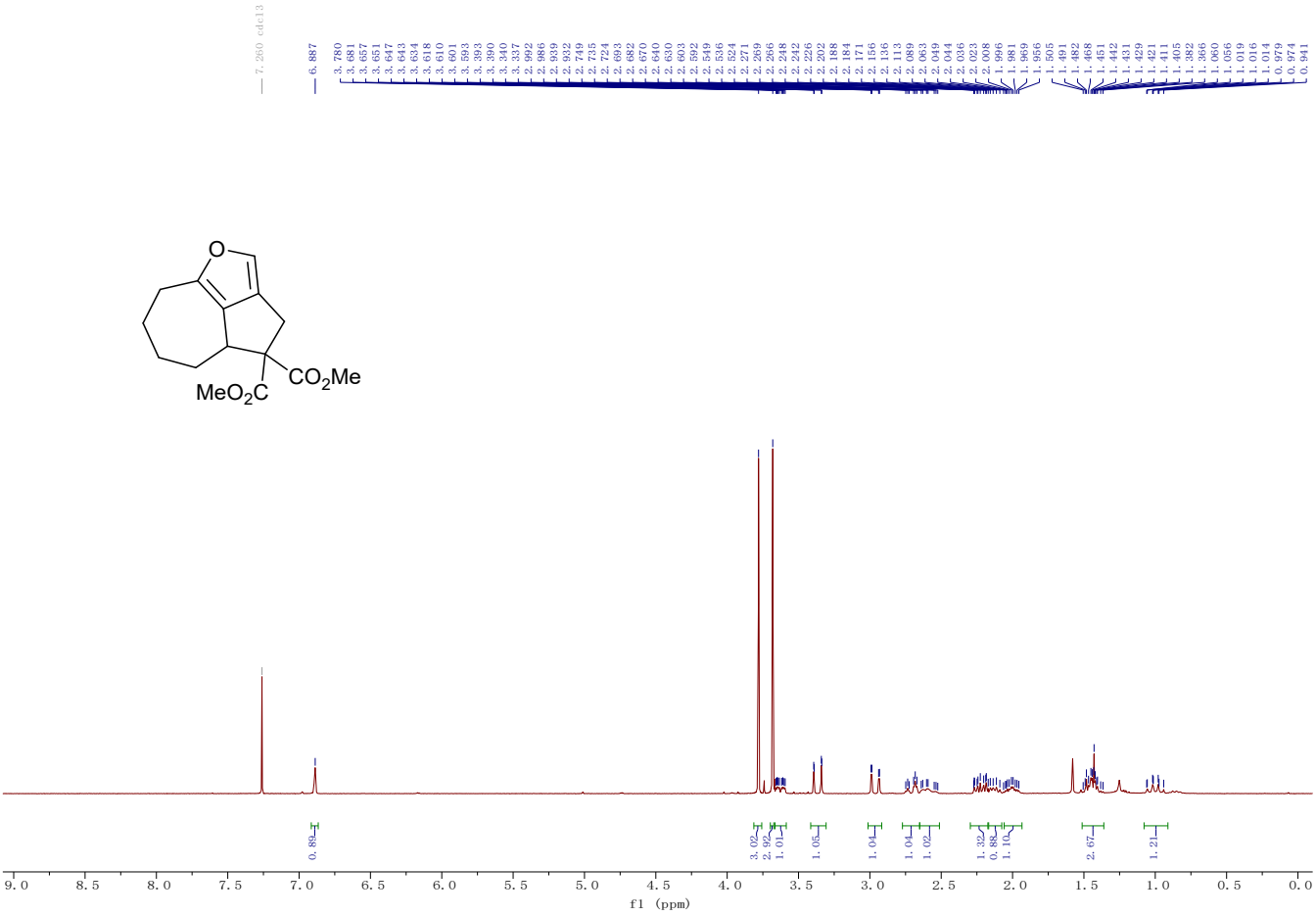

f1 (ppm)


O
CO2Me
CO2Me


f1 (ppm)


f1 (ppm)

O
CO2Me
CO2Me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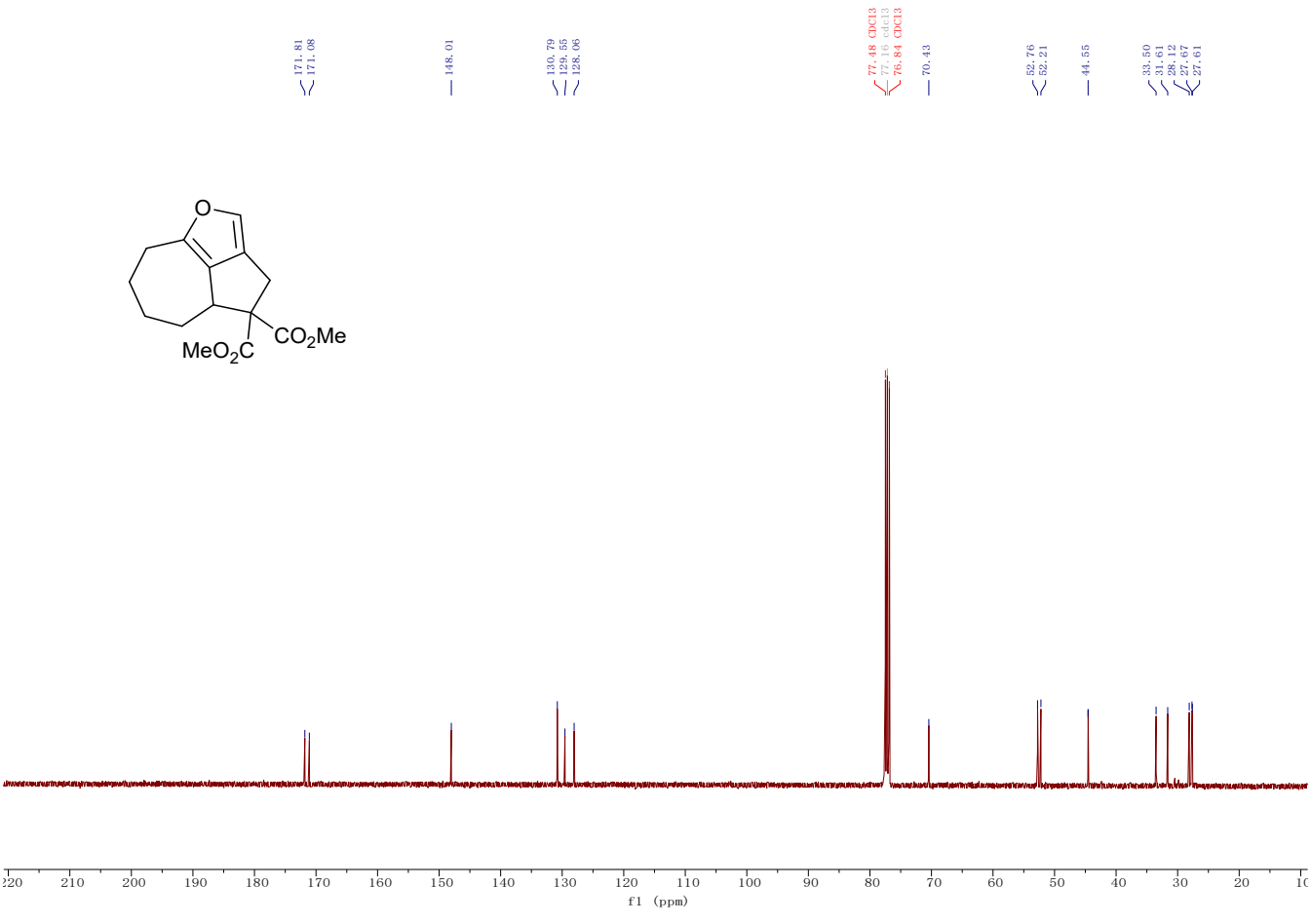
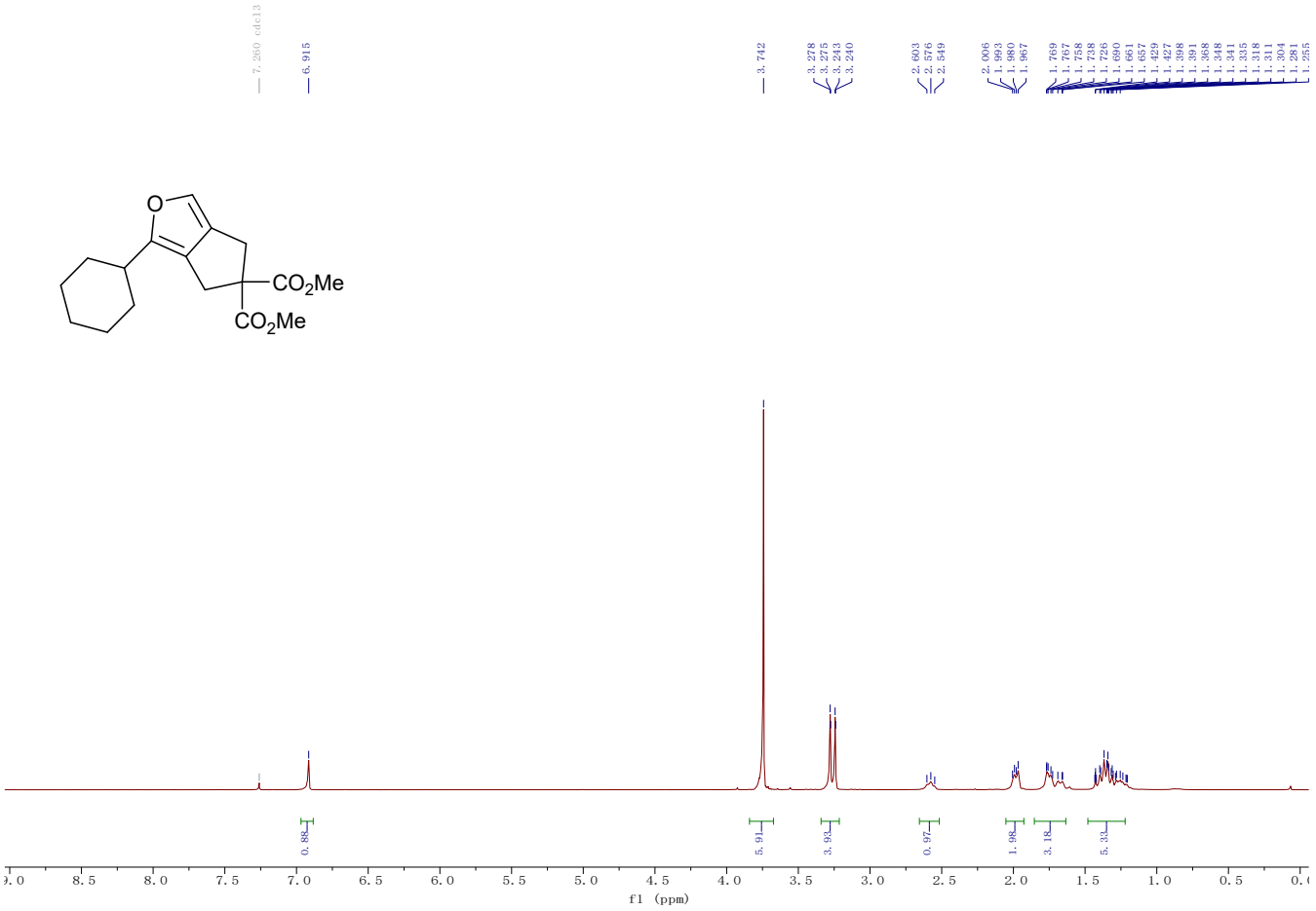
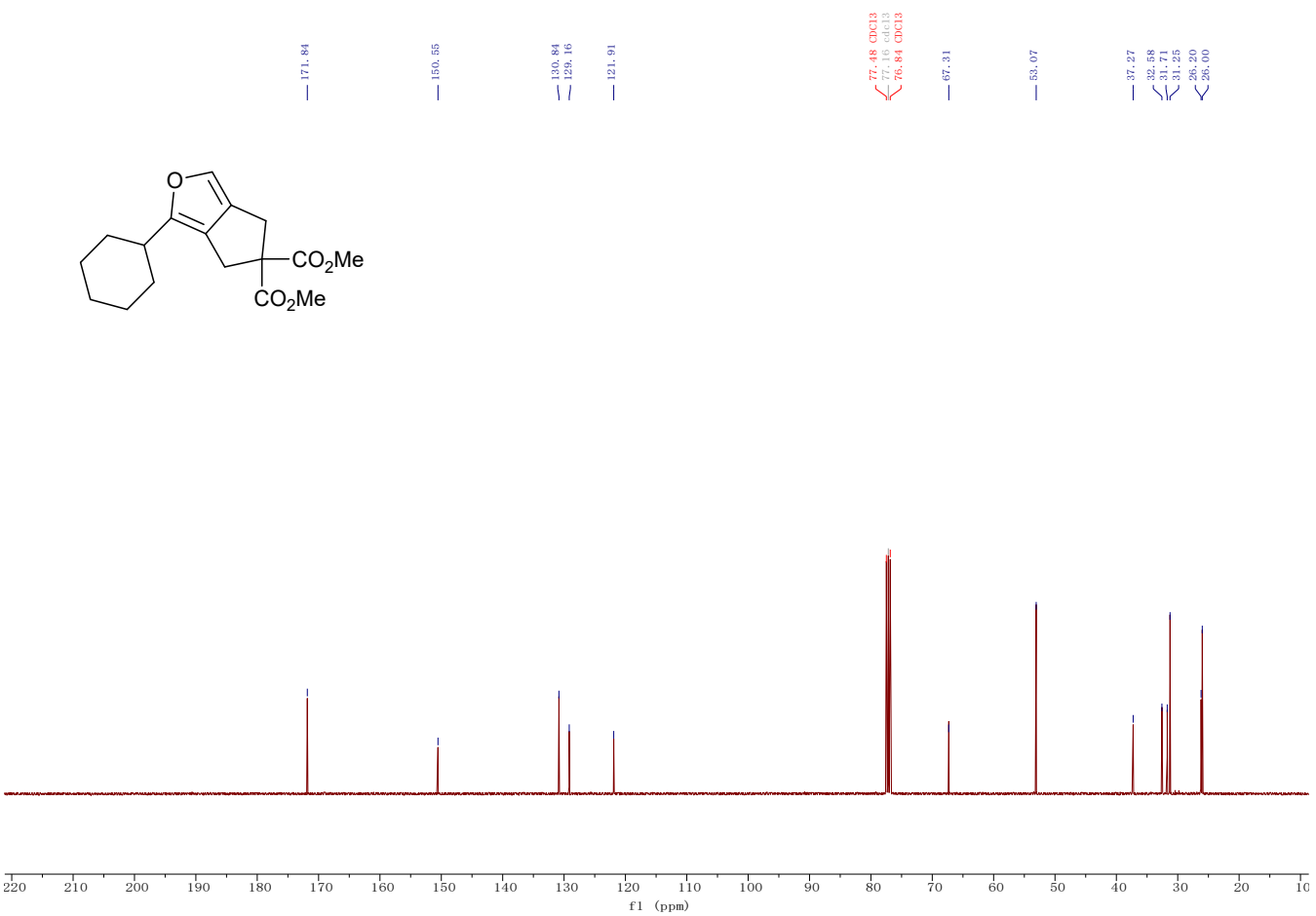
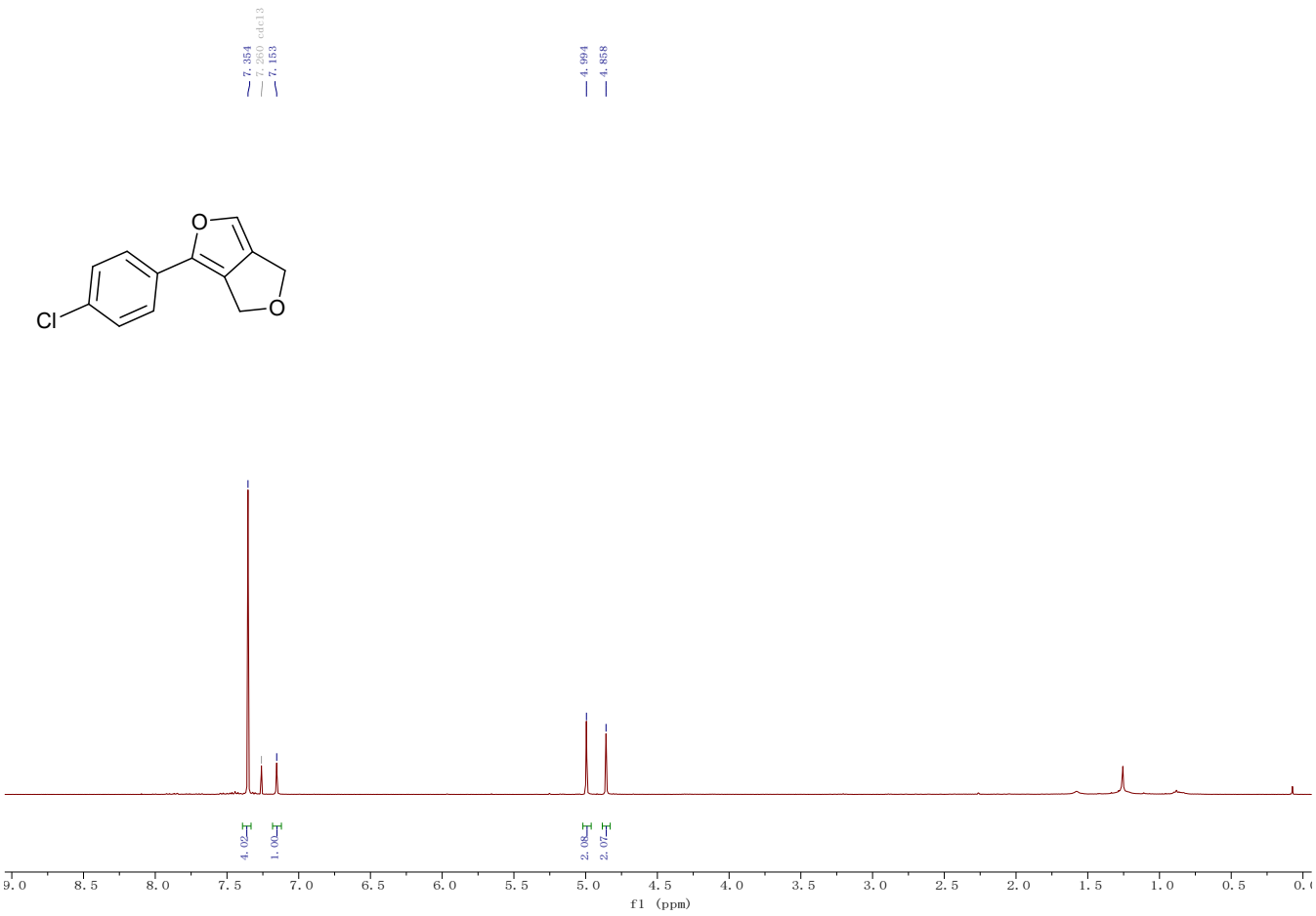
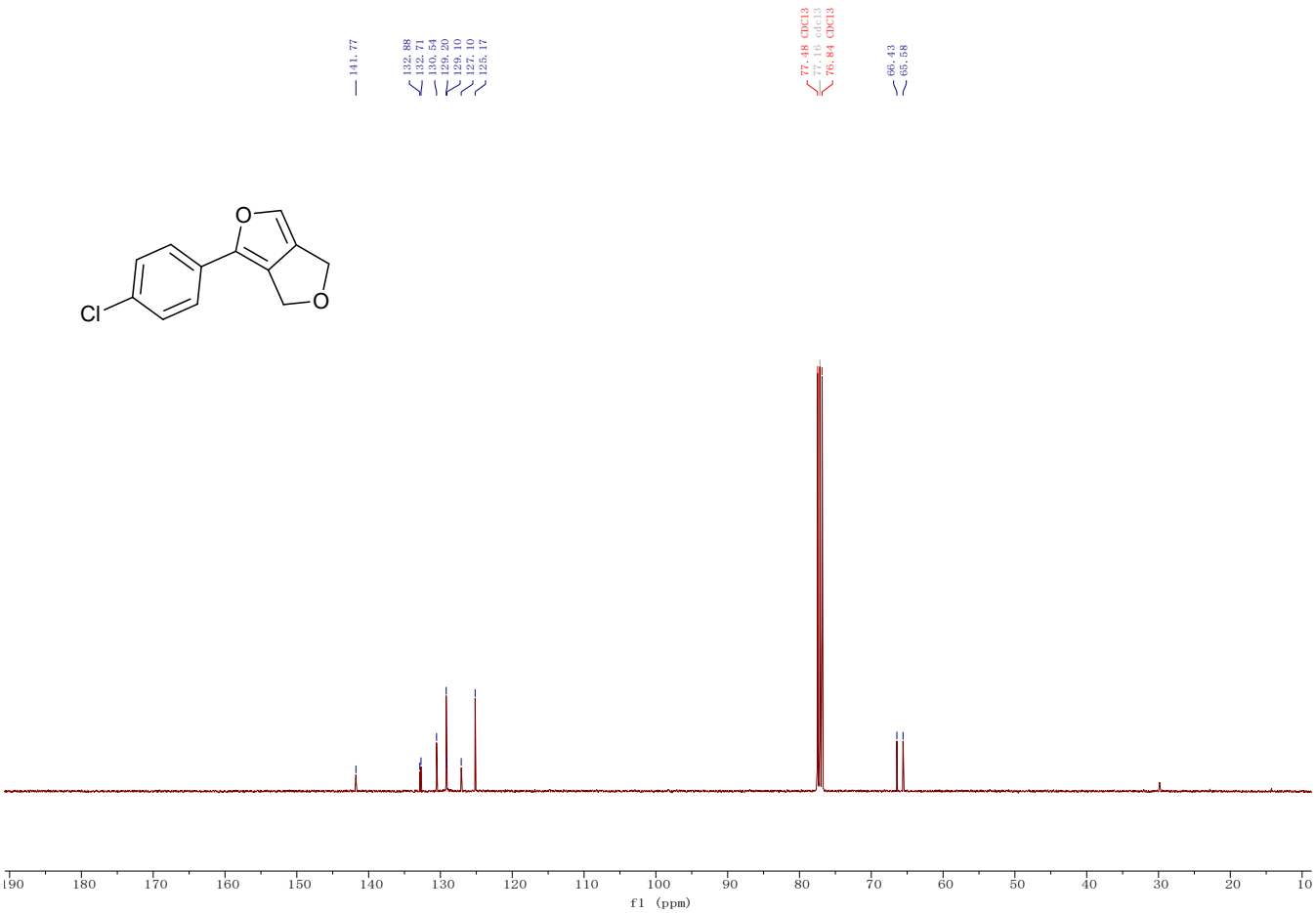
6.887
3.780
3.681
3.657
3.651
3.647
3.643
3.634
3.618
3.610
3.601
3.593
3.393
3.390
3.340
3.337
2.992
2.986
2.939
2.932
2.749
2.735
2.724
2.693
2.682
2.670
2.640
2.630
2.603
2.592
2.549
2.536
2.524
2.271
2.268
2.248
2.242
2.226
2.202
2.188
2.184
2.171
2.156
2.136
2.113
2.089
2.063
2.049
2.044
2.036
2.023
2.008
1.996
1.981
1.969
1.956
1.505
1.491
1.482
1.468
1.451
1.442
1.431
1.429
1.421
1.411
1.405
1.382
1.366
1.060
1.056
1.019
1.016
1.014
0.979
0.974
0.941
O
CO2Me
MeO2C
0.88
3.02
2.92
1.01
1.06
1.04
1.04
1.02
1.32
0.88
1.10
2.67
1.21
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

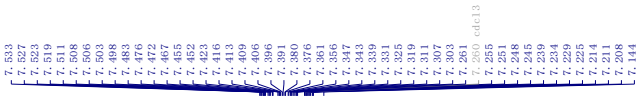

171.81
171.08
148.01
130.79
129.55
128.06
77.48 CDCl3
77.16 cdcl3
76.84 CDCl3
70.43
52.76
52.21
44.55
33.50
31.61
28.12
27.67
27.61
O
CO2Me
MeO2C
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

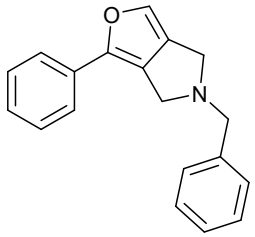

7.260 cdcl3
6.915
3.742
3.278
3.275
3.243
3.240
2.603
2.576
2.549
2.006
1.993
1.980
1.967
1.769
1.767
1.758
1.738
1.726
1.690
1.661
1.657
1.429
1.427
1.398
1.391
1.368
1.348
1.341
1.335
1.318
1.311
1.304
1.281
1.255
O
CO2Me
CO2Me
0.88
5.91
3.98
0.97
1.98
3.18
5.33
f1 (ppm)

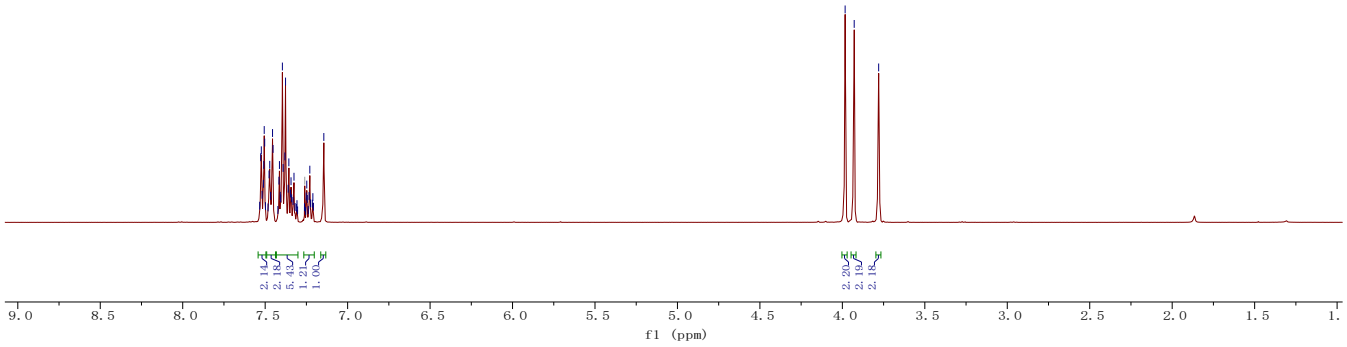

171.84
150.55
130.84
129.16
121.91
77.48 CDCl3
77.16 cdcl3
76.84 CDCl3
67.31
53.07
37.27
32.58
31.71
31.25
26.20
26.00
O
CO2Me
CO2Me
f1 (ppm)


7.354
7.260 cdcl3
7.153
4.994
4.858
O
Cl
O
4.02
1.00
2.08
2.07
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

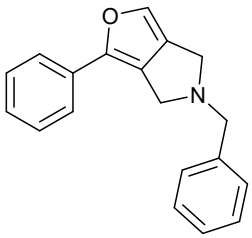

141.77
132.88
132.71
130.54
129.20
129.10
127.10
125.17
77.48 CDCl3
77.16 cdcl3
76.84 CDCl3
66.43
65.58
O
Cl
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

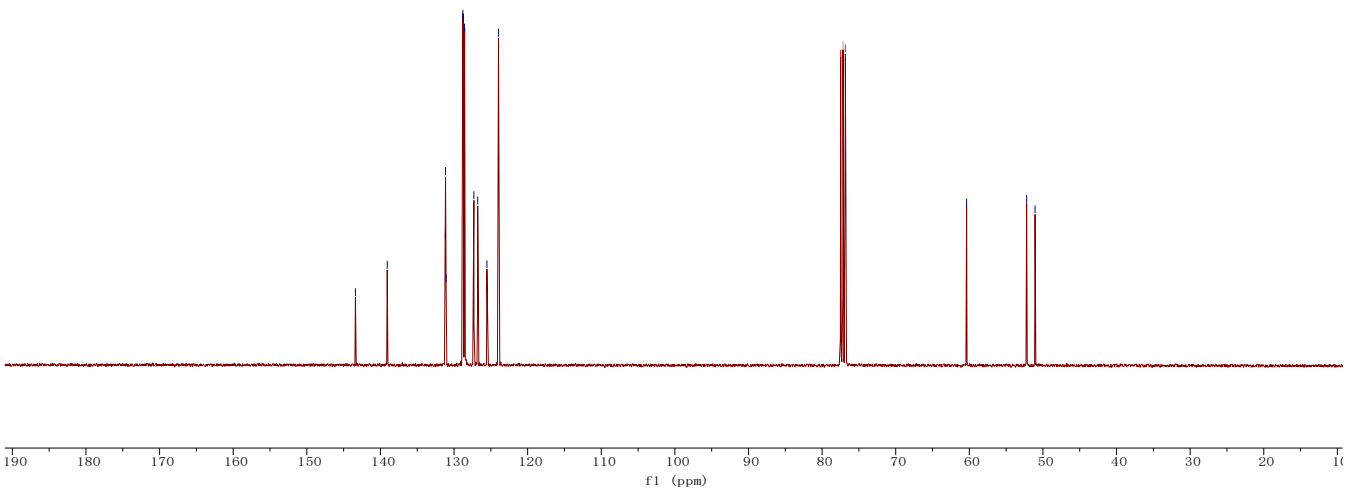

7.533
7.527
7.523
7.519
7.511
7.508
7.506
7.503
7.498
7.483
7.476
7.472
7.467
7.455
7.452
7.423
7.416
7.413
7.409
7.406
7.396
7.391
7.380
7.376
7.361
7.356
7.347
7.343
7.339
7.331
7.325
7.319
7.311
7.307
7.303
7.261
7.260 cdcl3
7.255
7.251
7.248
7.245
7.239
7.234
7.229
7.225
7.214
7.211
7.208
7.144
3.983
3.923
3.780

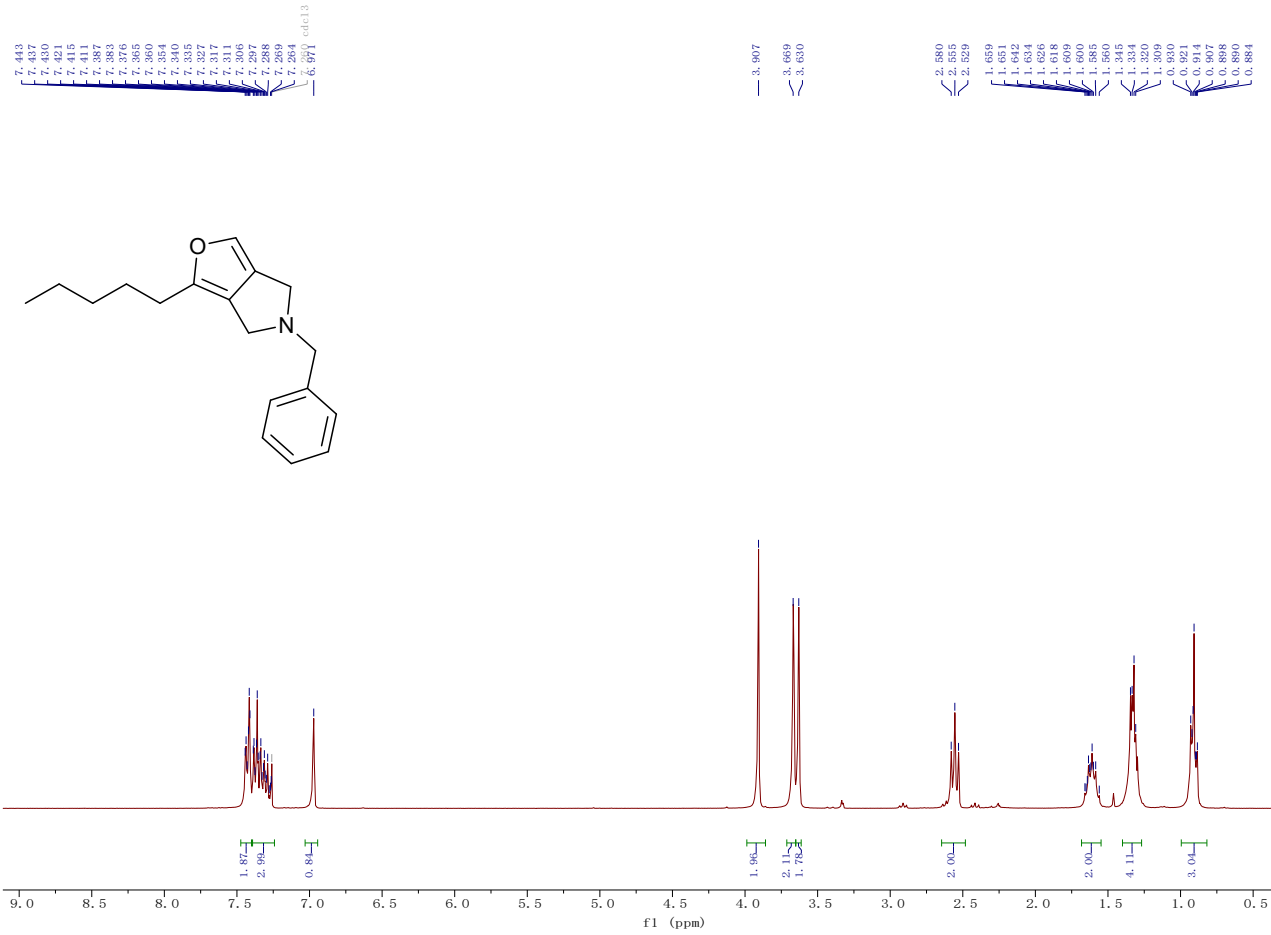

O
N

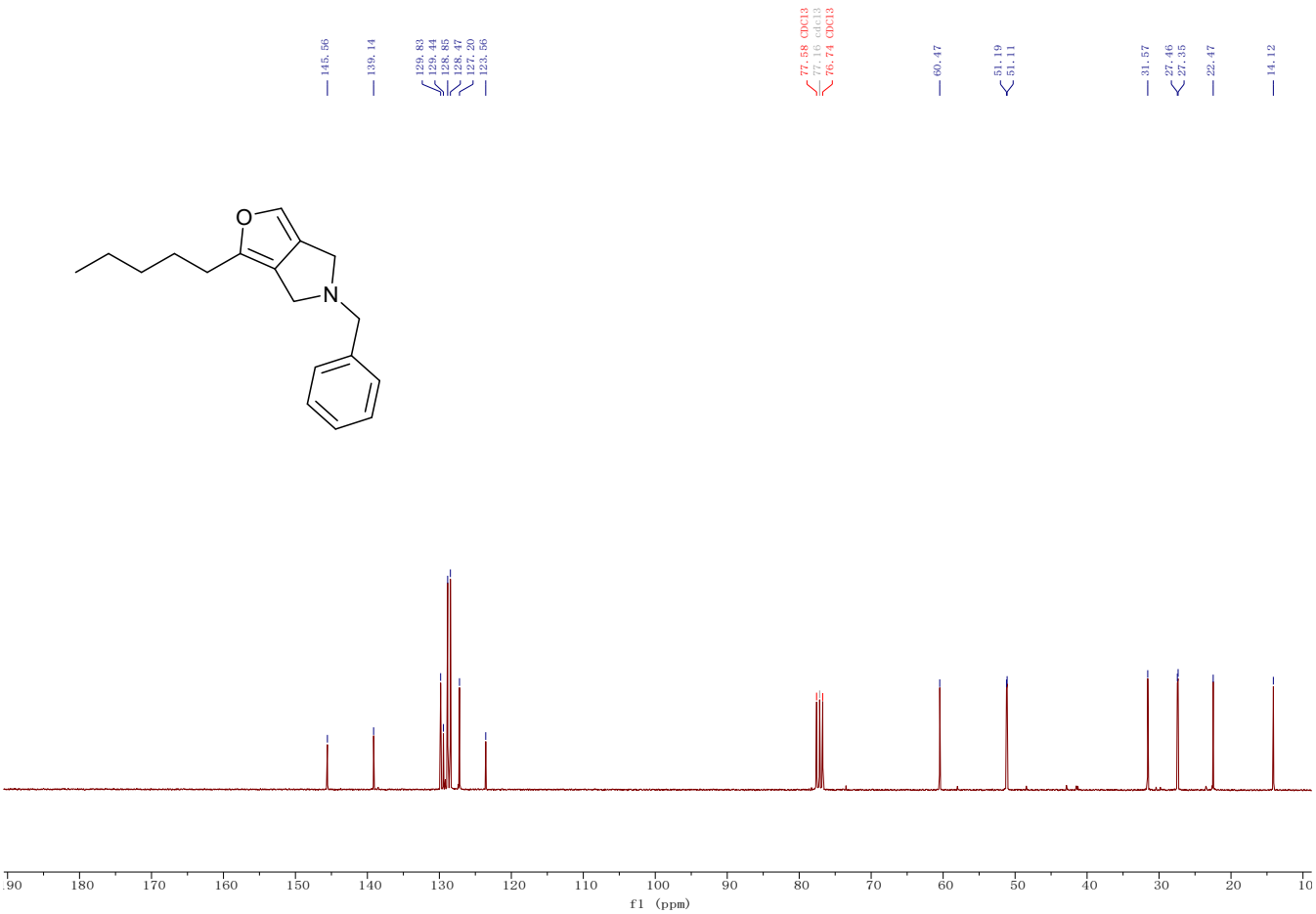

2.14
2.18
5.43
1.21
1.00
2.20
2.11
2.18
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

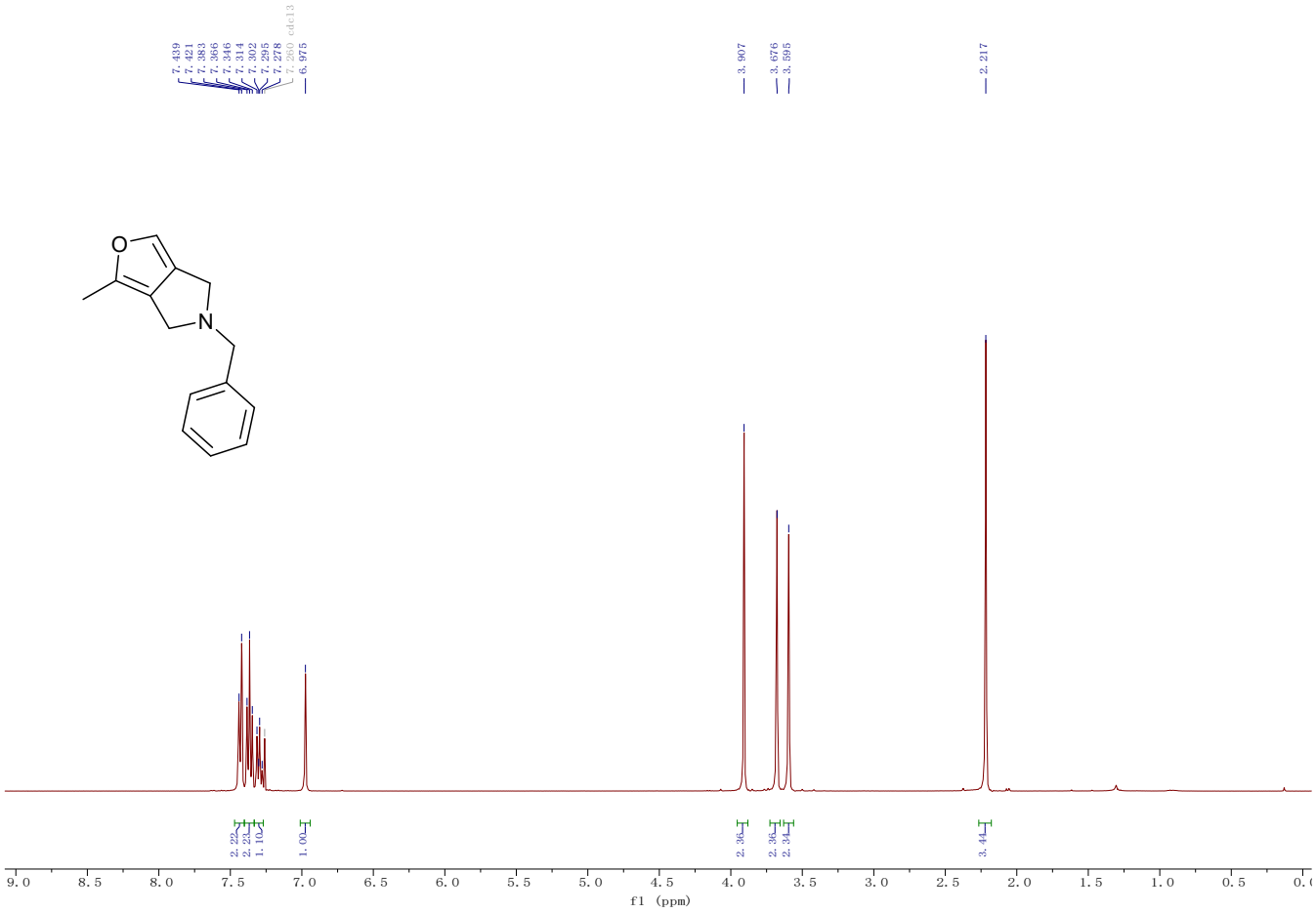

143.40
139.07
131.17
131.16
131.08
128.80
128.76
128.57
127.31
126.78
125.53
123.95
77.48 CDCl3
77.16 cdcl3
76.84 CDCl3
60.37
52.21
51.07

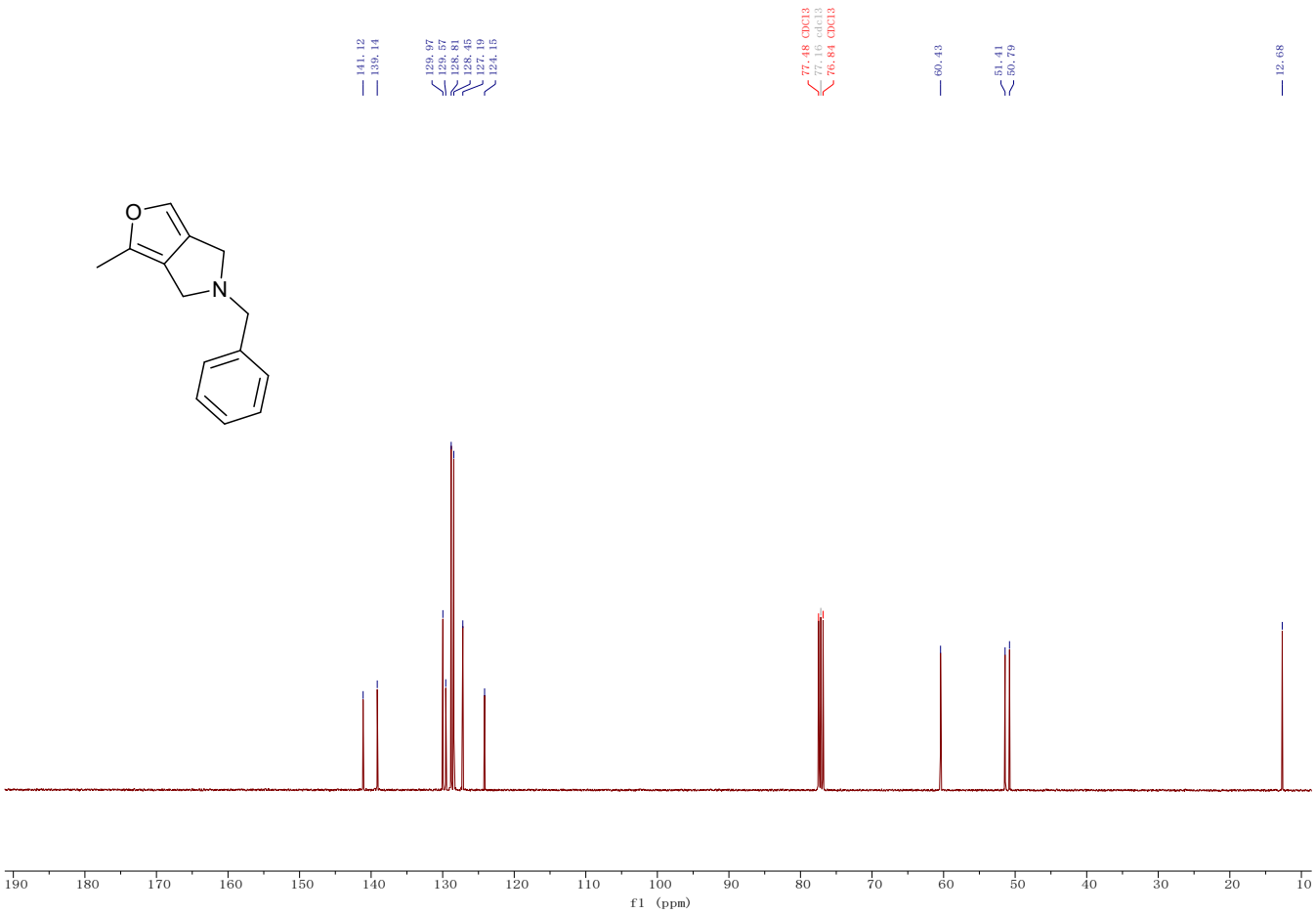

O
N


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


7.443
7.437
7.430
7.421
7.415
7.411
7.387
7.383
7.376
7.365
7.360
7.354
7.340
7.335
7.327
7.317
7.311
7.306
7.297
7.288
7.269
7.264
6.891
3.907
3.669
3.630
2.580
2.555
2.529
1.659
1.651
1.642
1.634
1.626
1.618
1.609
1.600
1.585
1.560
1.345
1.334
1.320
1.309
0.930
0.921
0.914
0.907
0.898
0.890
0.884
O
N
1.87
2.96
0.84
1.96
2.11
1.78
2.00
2.00
4.11
3.04
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

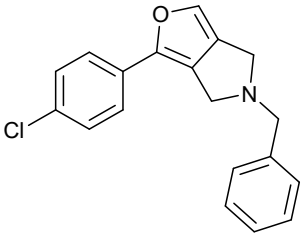

145.56
139.14
129.83
129.44
128.85
128.47
127.20
123.56
77.58 CDCl3
77.16
76.74 CDCl3
60.47
51.19
51.11
31.57
27.46
27.35
22.47
14.12
O
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

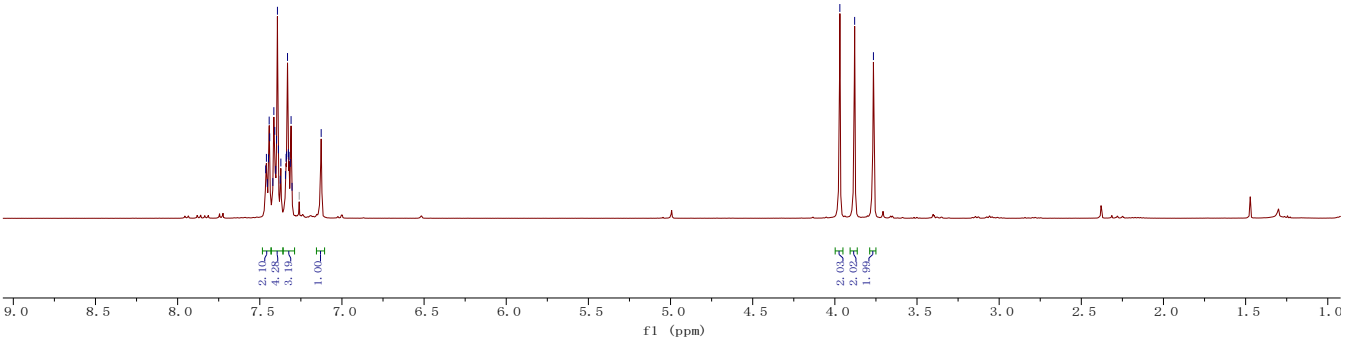

7.439
7.421
7.383
7.366
7.346
7.314
7.302
7.298
7.278
7.260 cdcl3
6.975
3.907
3.676
3.695
2.217
O
N
2.22
2.23
1.10
1.00
2.36
2.36
2.34
3.44
f1 (ppm)


141.12
139.14
129.97
129.57
128.81
128.45
127.19
124.15
77.48 CDCl3
77.16 cdcl3
76.84 CDCl3
60.43
51.41
50.79
12.68
O
N
f1 (ppm)


7.464
7.460
7.454
7.447
7.443
7.440
7.421
7.414
7.409
7.403
7.398
7.393
7.387
7.375
7.372
7.344
7.340
7.336
7.331
7.326
7.322
7.315
7.310
7.304
7.290 cdcl3
7.126


3.970
3.880
3.765

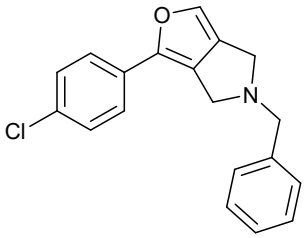

O
N
Cl

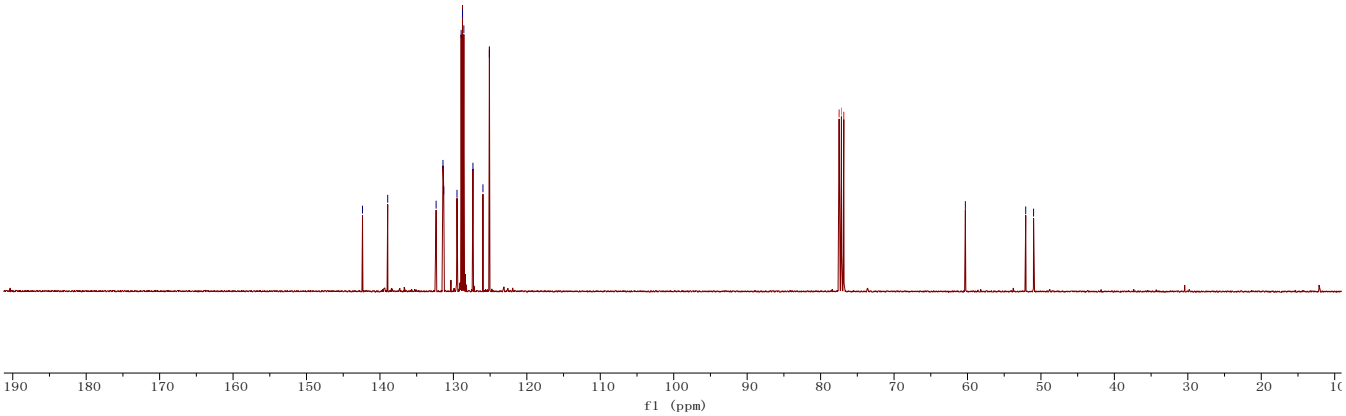

2.10
4.28
3.18
1.00
2.03
2.02
1.99
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

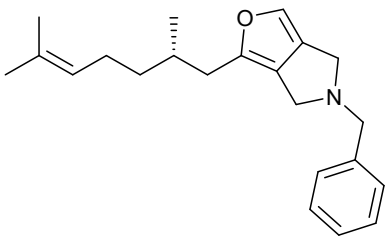

142.37
138.94
132.35
131.42
131.32
129.61
128.94
128.76
128.58
127.34
125.98
125.10

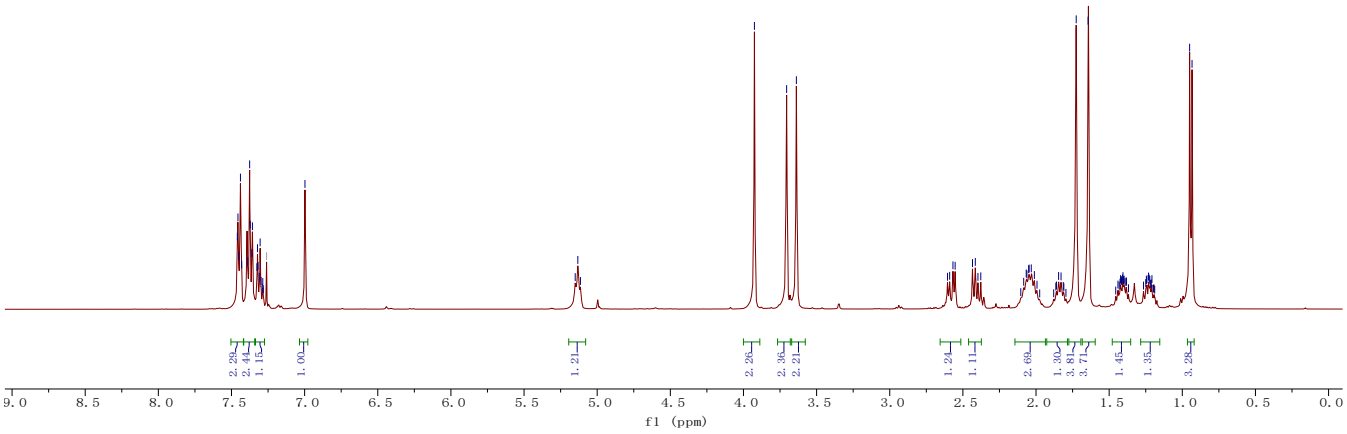

77.48 CDCl3
77.16 cdcl3
76.84 CDCl3

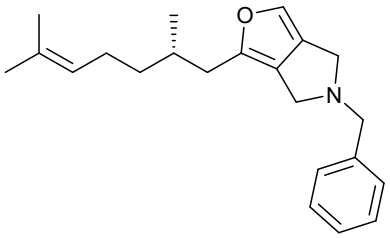

60.29
52.07
51.00

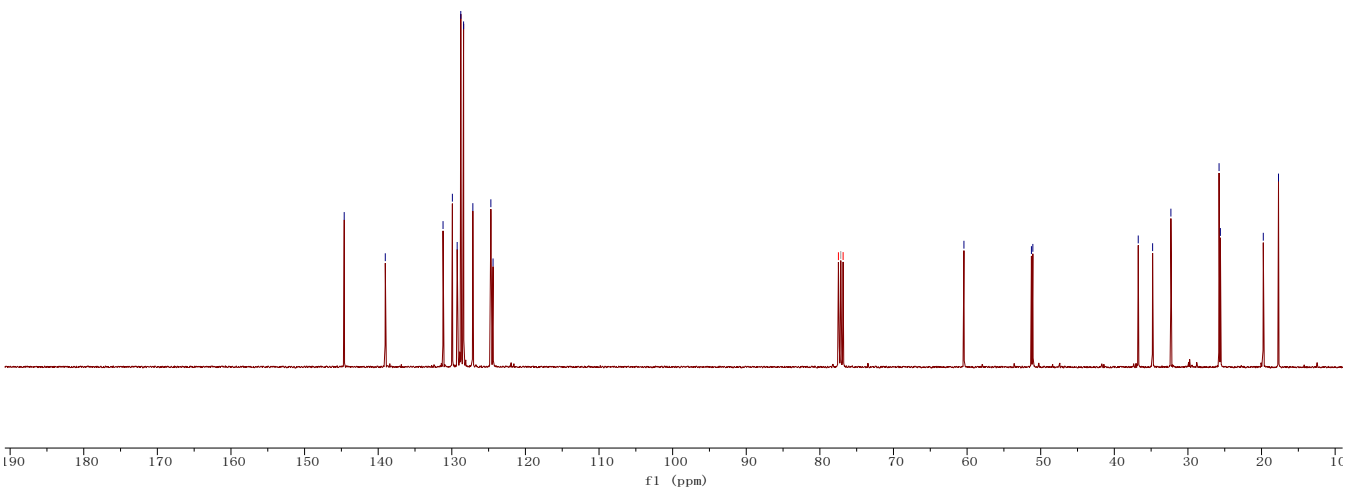

O
N
Cl

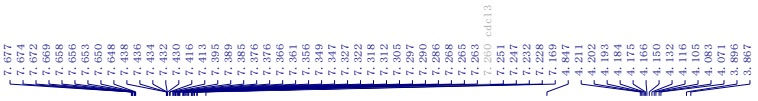

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

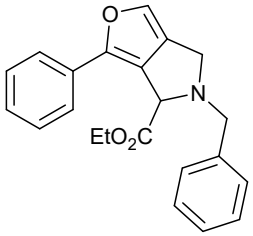


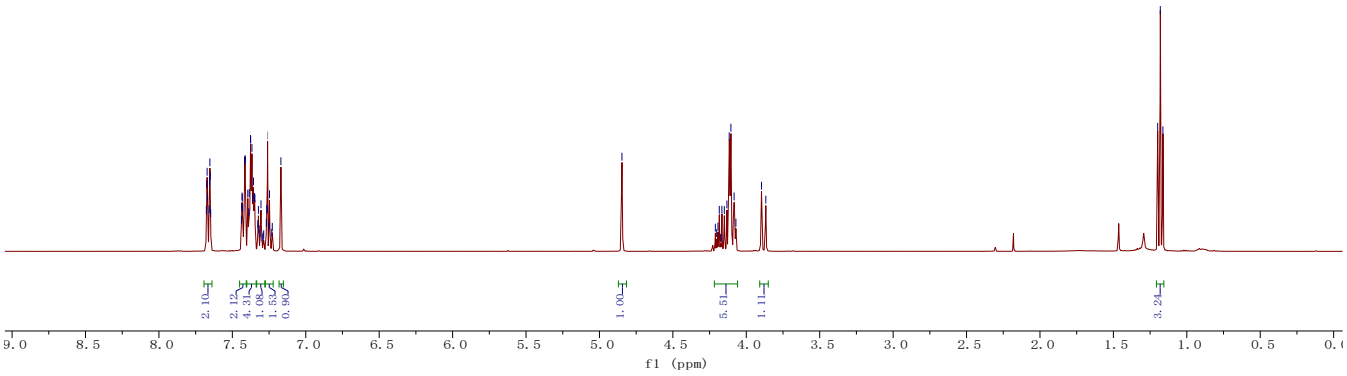

f1 (ppm)

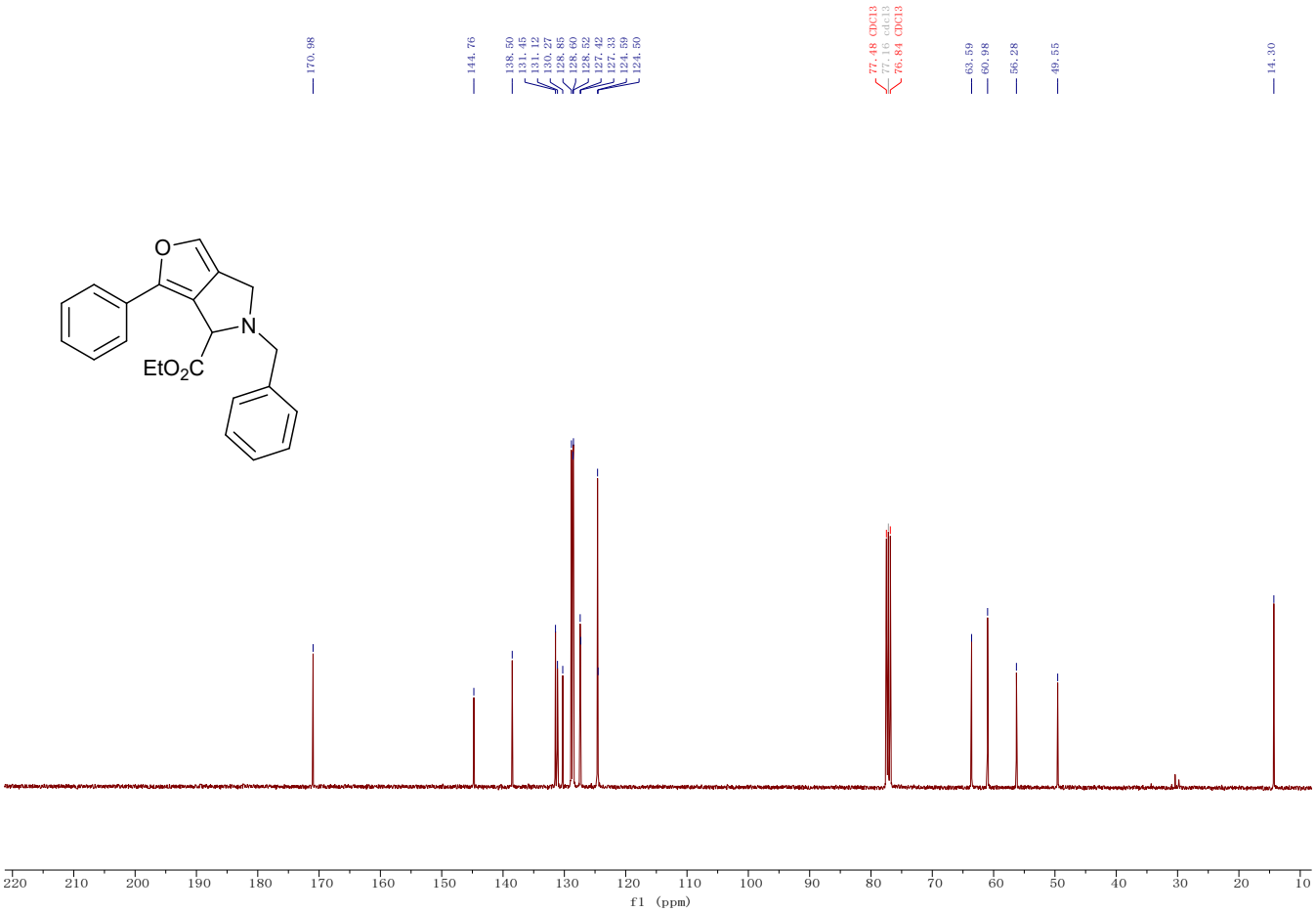



f1 (ppm)


7.677
7.674
7.672
7.669
7.658
7.656
7.653
7.650
7.648
7.438
7.436
7.434
7.432
7.430
7.416
7.413
7.395
7.389
7.385
7.376
7.366
7.361
7.356
7.349
7.347
7.327
7.322
7.318
7.312
7.305
7.297
7.290
7.286
7.268
7.265
7.263
7.260 cdcl3
7.251
7.247
7.232
7.228
7.169
4.847
4.211
4.202
4.193
4.184
4.175
4.166
4.150
4.132
4.116
4.105
4.083
4.071
3.896
3.867
1.198
1.181
1.163

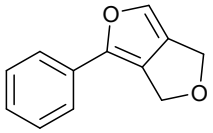

O
N
EtO2C

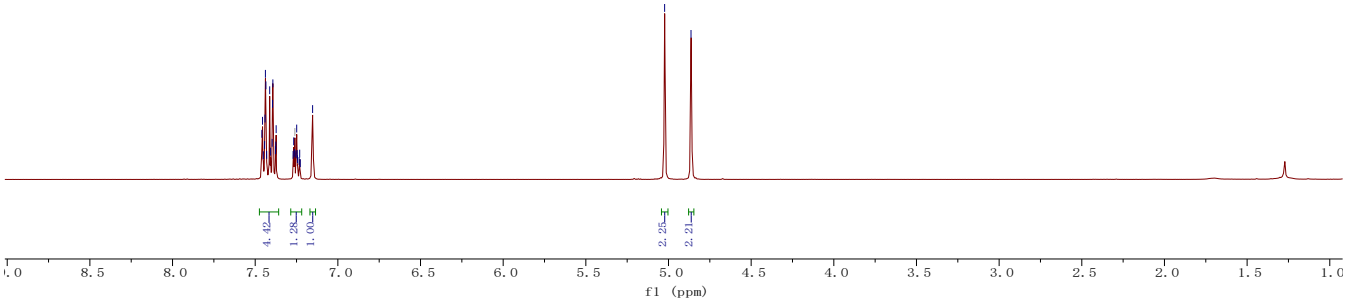

2.10
2.12
4.31
1.08
1.53
0.90
1.00
5.51
1.11
3.24
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


170.98
144.76
138.50
131.45
131.12
130.27
128.85
128.60
128.52
127.42
127.33
124.69
124.50
77.48 CDCl3
77.16 cdcl3
76.84 CDCl3
63.59
60.98
56.28
49.55
14.30
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

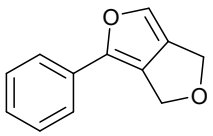
O
N
EtO2C

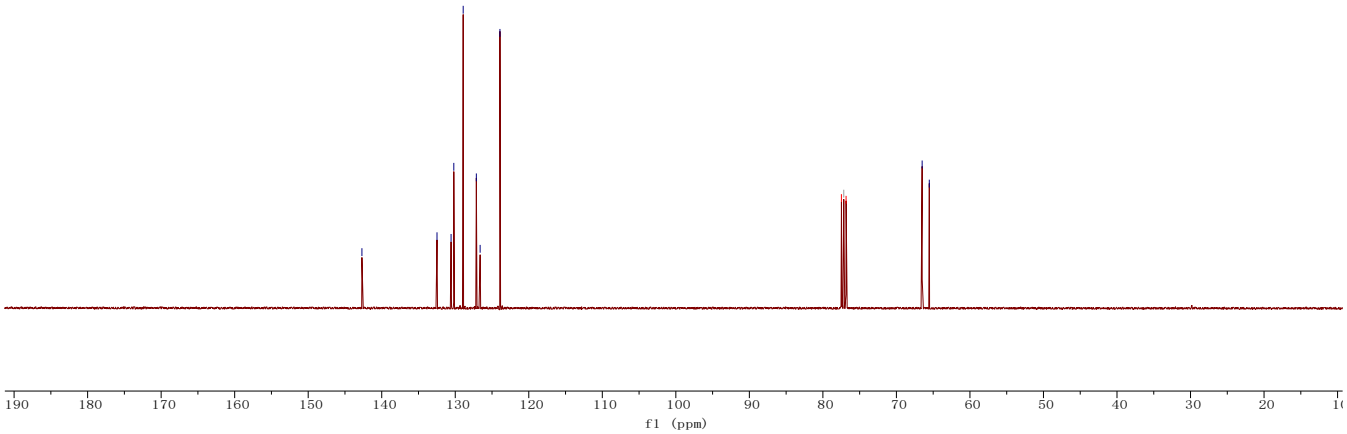

7.459
7.456
7.451
7.443
7.441
7.438
7.435
7.431
7.412
7.407
7.398
7.395
7.393
7.378
7.375
7.373
7.271
7.267
7.263
7.260 cdcl3
7.254
7.249
7.246
7.244
7.234
7.231
7.227
7.153
5.023
4.864

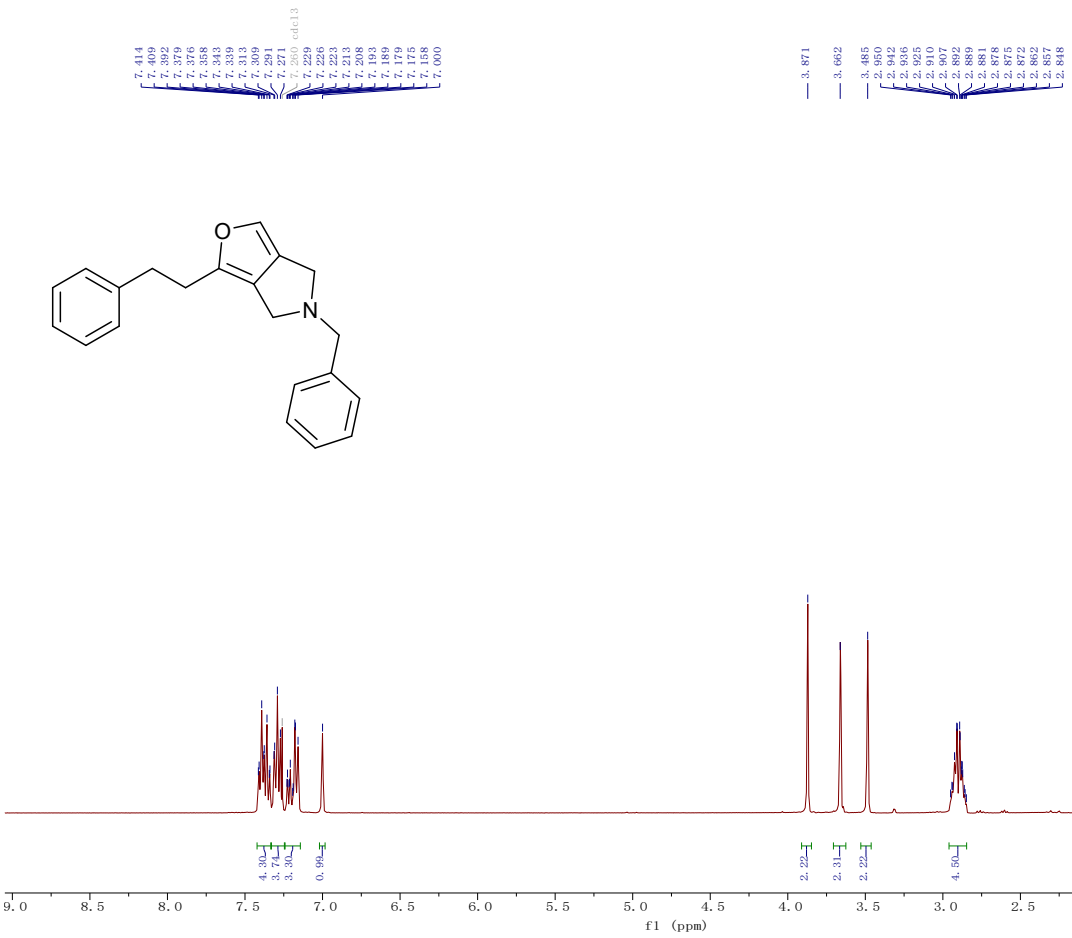


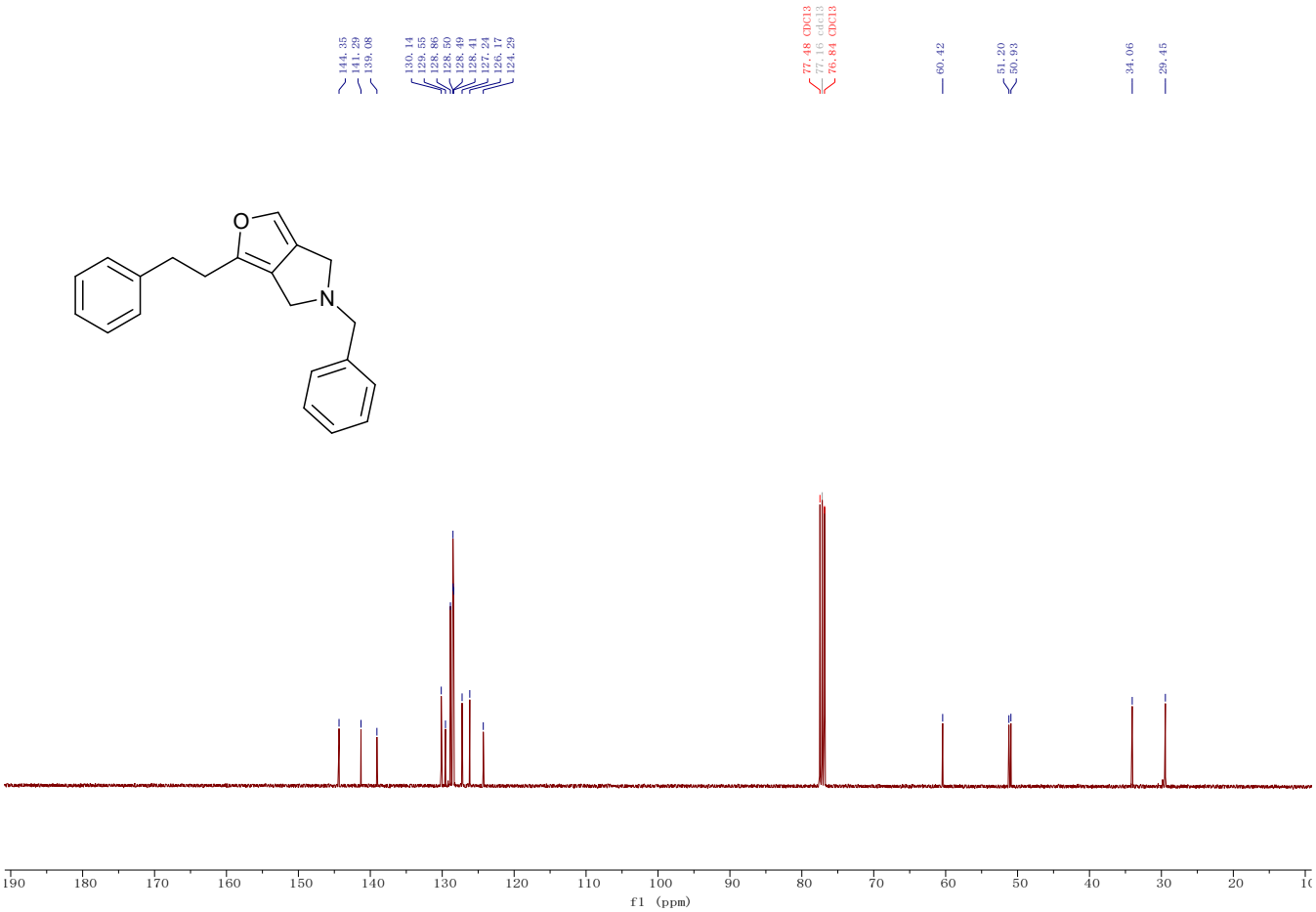

4.42
1.28
1.00
2.25
2.21
f1 (ppm)

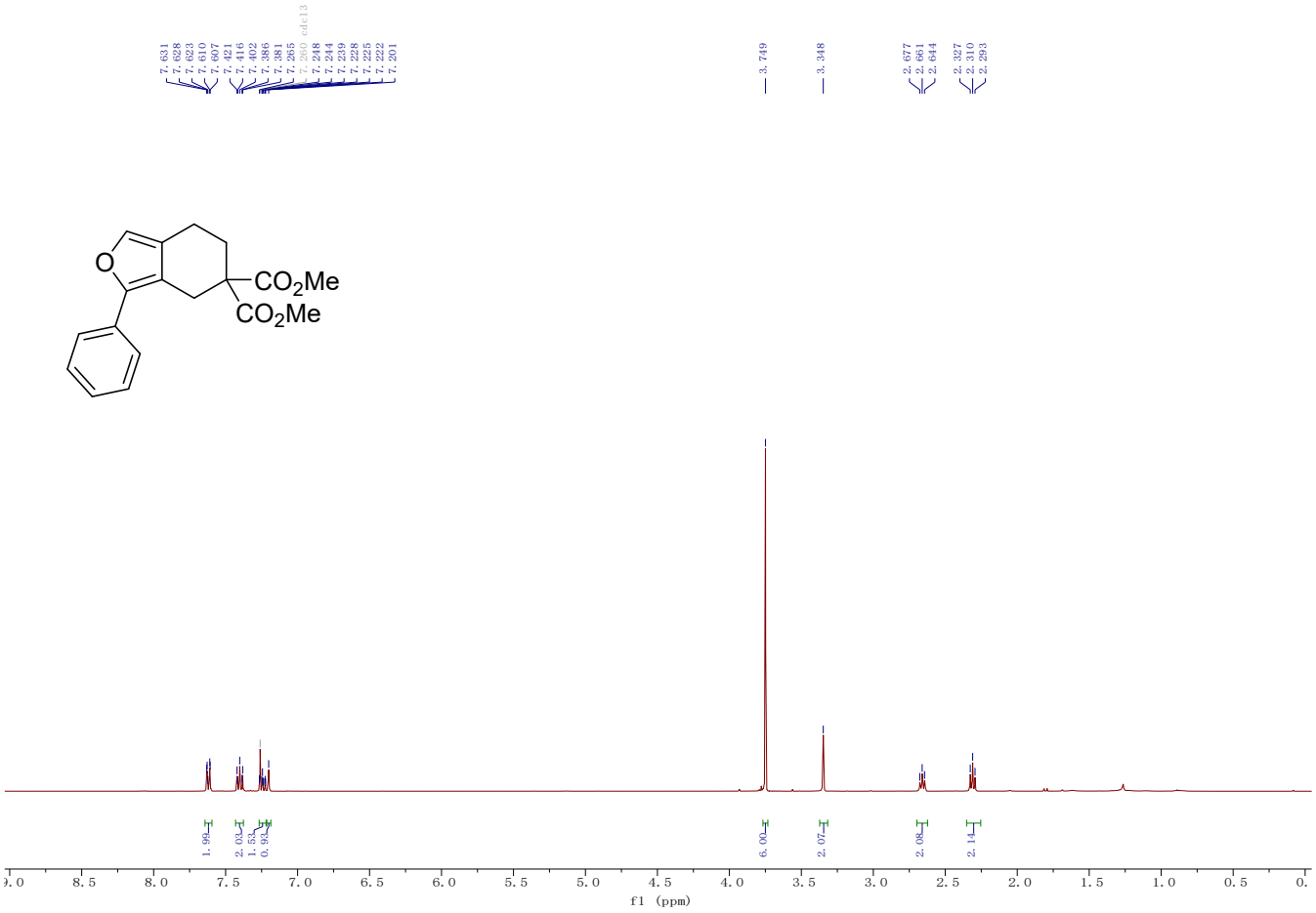

142.69
132.48
131.57
130.20
128.92
127.13
126.62
123.92
77.48 CDCl3
77.16 cdcl3
76.85 CDCl3
66.50
65.53

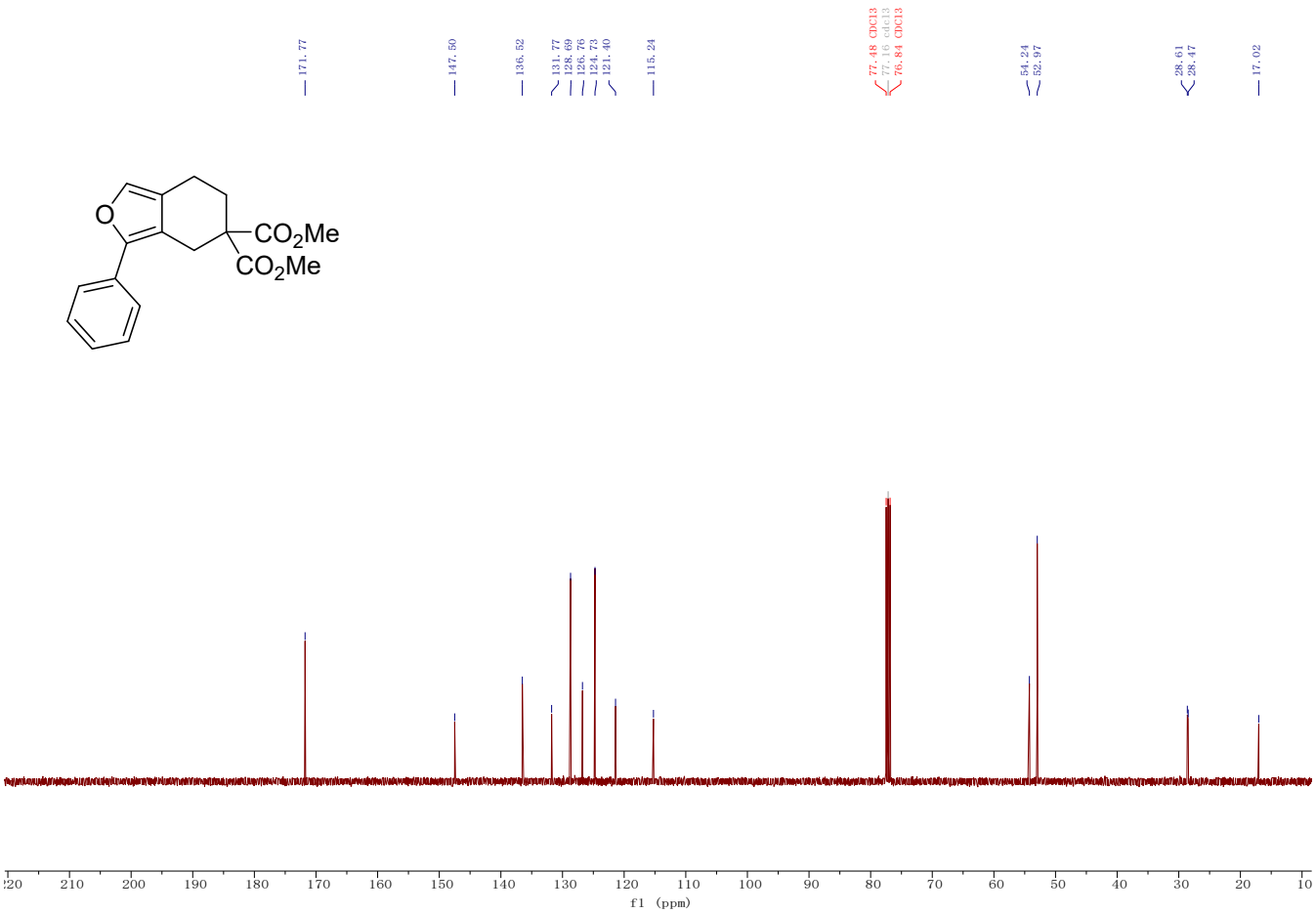


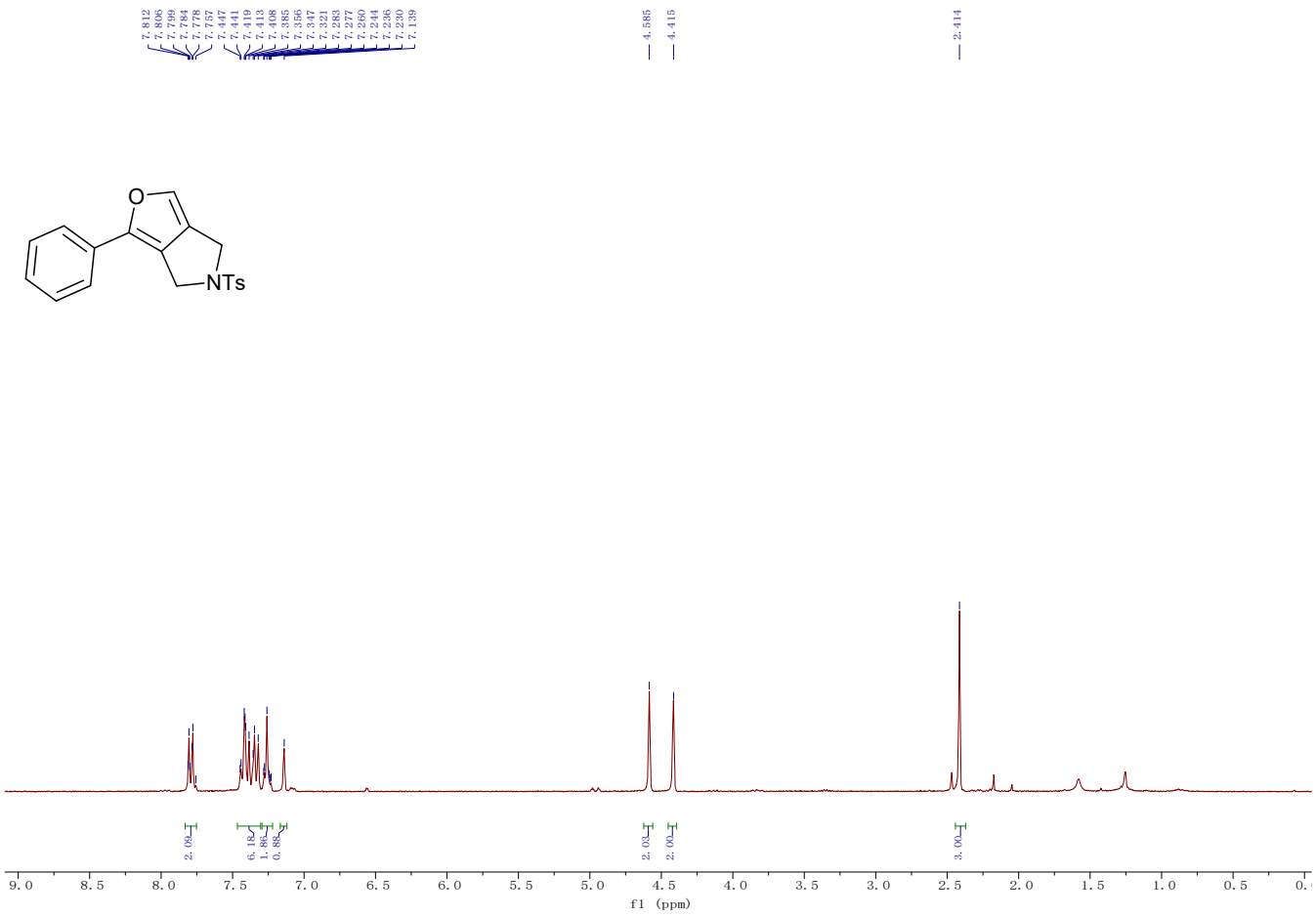

f1 (ppm)


7.414
7.409
7.392
7.379
7.376
7.358
7.343
7.339
7.313
7.309
7.291
7.271
7.260 cdcl3
7.229
7.226
7.223
7.213
7.208
7.193
7.189
7.179
7.175
7.158
7.000
3.871
3.662
3.485
2.950
2.942
2.936
2.925
2.910
2.907
2.892
2.889
2.881
2.878
2.875
2.872
2.862
2.857
2.848
O
N
4.30
3.74
3.30
0.99
2.22
2.31
2.22
4.50
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)


144.35
141.29
139.08
130.14
129.55
128.86
128.50
128.49
128.41
127.24
126.77
124.29
77.48 CDCl3
77.16 cdcl3
76.84 CDCl3
60.42
51.20
50.93
34.06
29.45
O
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

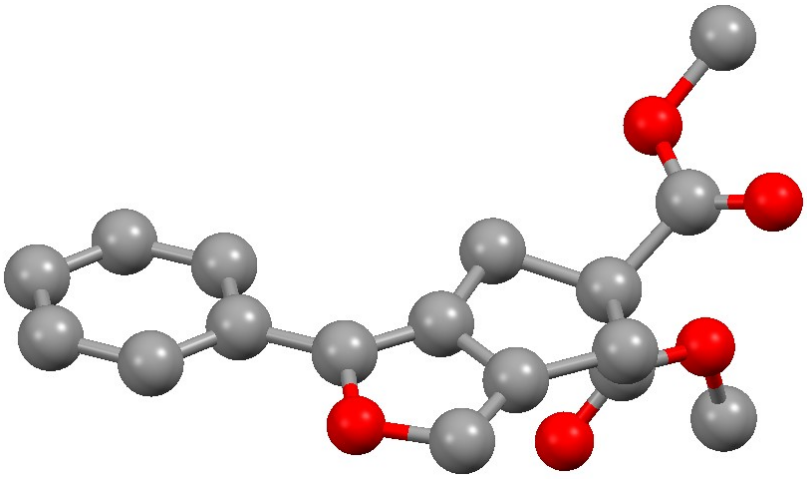

7.631
7.628
7.623
7.610
7.607
7.421
7.416
7.402
7.386
7.381
7.285
7.280 cdcl3
7.248
7.244
7.239
7.228
7.225
7.222
7.201
3.749
3.348
2.677
2.661
2.644
2.327
2.310
2.293
O
CO2Me
CO2Me
1.96
2.03
1.52
0.92
6.00
2.07
2.08
2.14
f1 (ppm)


171.77
147.50
136.52
131.77
128.69
126.76
124.73
121.40
115.24
77.48 CDCl3
77.16 cdcl3
76.84 CDCl3
54.24
52.97
28.61
28.47
17.02
O
CO2Me
CO2Me
f1 (ppm)


7.812
7.806
7.799
7.794
7.778
7.757
7.447
7.441
7.419
7.413
7.408
7.385
7.356
7.347
7.321
7.283
7.277
7.249
7.244
7.236
7.230
7.139
4.585
4.415
2.414
O
NTs
2.08
6.18
1.86
0.88
2.03
2.00
3.00
f1 (ppm)
144.27
143.98
134.18
131.90
130.13
130.08
129.03
127.74
127.62
127.57
123.96
121.57
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
47.55
46.31
21.67
O
NTs
f1 (ppm)

6. Single crystal X-Ray diffraction data

Molecule 2a



checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: shelx

```
Bond precision:   C-C = 0.0010 A          Wavelength=0.71073

Cell:           a=8.4783(3)       b=9.2024(3)       c=10.0482(3)
                alpha=73.376(1)   beta=69.531(1)    gamma=88.284(1)
Temperature:    296 K

                Calculated                Reported
Volume          701.62(4)                 701.62(4)
Space group     P -1                      P -1
Hall group      -P 1                      -P 1
Moiety formula  C17 H16 O5                ?
Sum formula     C17 H16 O5                C17 H16 O5
Mr              300.30                    300.30
Dx,g cm-3       1.421                     1.421
Z               2                         2
Mu (mm-1)       0.105                     0.102
F000            316.0                     316.0
F000'           316.18
h,k,lmax        13,14,15                  13,14,15
Nref            5629                      5302
Tmin,Tmax       0.967,0.975               0.902,0.947
Tmin'           0.962

Correction method= # Reported T Limits: Tmin=0.902 Tmax=0.947
AbsCorr = MULTI-SCAN

Data completeness= 0.942          Theta(max)= 33.755

R(reflections)= 0.0345( 4799)                wR2(reflections)=
                                             0.1030( 5302)
S = 1.039                 Npar= 201
```

```
The following ALERTS were generated. Each ALERT has the format
      test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.
```

Alert level C

```
ABSMU01_ALERT_1_C  The ratio of given/expected absorption coefficient lies
               outside the range 0.99 <> 1.01
           Calculated value of mu =     0.105
           Value of mu given      =     0.102
ABSTY02_ALERT_1_C  An _exptl_absorpt_correction_type has been given without
           a literature citation. This should be contained in the
           _exptl_absorpt_process_details field.
           Absorption correction given as multi-scan
```

Alert level G

```
PLAT154_ALERT_1_G The s.u.'s on the Cell Angles are Equal ..(Note)      0.001 Degree
PLAT398_ALERT_2_G Deviating  C-O-C    Angle From 120 for O1            107.5 Degree
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary .    Please Do !
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity ...........      3.2 Low
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   2 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   4 ALERT level G = General information/check it is not something unexpected

   4 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   1 ALERT type 2 Indicator that the structure model may be wrong or deficient
   1 ALERT type 3 Indicator that the structure quality may be low
   0 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

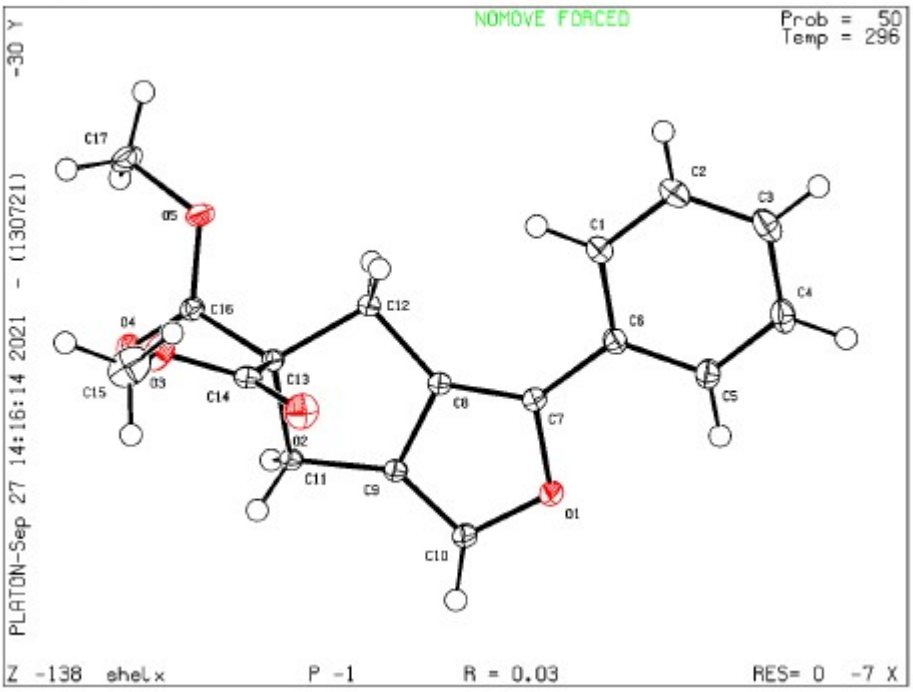
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

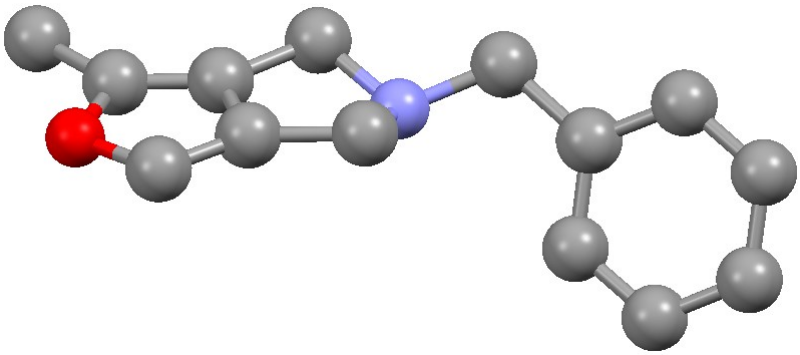
Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 13/07/2021; check.def file version of 13/07/2021

Datablock shelx - ellipsoid plot



Molecule 5g



checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: by660_bis

```
Bond precision:   C-C = 0.0019 A          Wavelength=1.54178

Cell:           a=6.4404(4)       b=9.0870(6)       c=9.8469(7)
                alpha=96.339(4)   beta=93.280(4)    gamma=102.199(4)
Temperature:    100 K

                 Calculated                Reported
Volume           557.90(7)                 557.90(6)
Space group      P -1                      P-1
Hall group       -P 1                      ?
Moiety formula   C14 H15 N O               ?
Sum formula      C14 H15 N O               C14 H15 N O
Mr               213.27                    213.27
Dx,g cm-3        1.270                     1.270
Z                2                         2
Mu (mm-1)        0.626                     0.600
F000             228.0                     228.0
F000'            228.63
h,k,lmax         7,10,11                   7,10,11
Nref             1849                      1839
Tmin,Tmax        0.958,0.982               0.661,0.752
Tmin'            0.892

Correction method= # Reported T Limits: Tmin=0.661 Tmax=0.752
AbsCorr = MULTI-SCAN

Data completeness= 0.995          Theta(max)= 63.590

R(reflections)= 0.0387( 1685)                wR2(reflections)=
                                             0.0977( 1839)
S = 1.062                 Npar= 146
```

```
The following ALERTS were generated. Each ALERT has the format
       test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.
```

Alert level C

```
ABSMU01_ALERT_1_C  The ratio of given/expected absorption coefficient lies
                   outside the range 0.99 <> 1.01
            Calculated value of mu =     0.626
            Value of mu given      =     0.600
ABSTY02_ALERT_1_C  An _exptl_absorpt_correction_type has been given without
            a literature citation. This should be contained in the
            _exptl_absorpt_process_details field.
            Absorption correction given as multi-scan
THETM01_ALERT_3_C  The value of sine(theta_max)/wavelength is less than 0.590
            Calculated sin(theta_max)/wavelength =    0.5809
```

Alert level G

```
PLAT005_ALERT_5_G No Embedded Refinement Details Found  in the CIF     Please Do !
PLAT093_ALERT_1_G No s.u.'s on H-positions, Refinement Reported as      mixed Check
PLAT154_ALERT_1_G The s.u.'s on the Cell Angles are Equal ..(Note)      0.004 Degree
PLAT398_ALERT_2_G Deviating  C-O-C    Angle From 120 for O1            107.6 Degree
PLAT899_ALERT_4_G SHELXL97  is Deprecated and Succeeded by SHELXL/      2018 Note
PLAT982_ALERT_1_G The  C-f'=    0.0192 Deviates from  IT-value =      0.0181 Check
PLAT982_ALERT_1_G The  N-f'=    0.0330 Deviates from  IT-value =      0.0311 Check
PLAT982_ALERT_1_G The  O-f'=    0.0517 Deviates from  IT-value =      0.0492 Check
PLAT983_ALERT_1_G The  O-f"=    0.0336 Deviates from  IT-Value =      0.0322 Check
```

```
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   3 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   9 ALERT level G = General information/check it is not something unexpected

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   1 ALERT type 3 Indicator that the structure quality may be low
   1 ALERT type 4 Improvement, methodology, query or suggestion
   1 ALERT type 5 Informative message, check
```

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PLATON version of 13/07/2021; check.def file version of 13/07/2021

Datablock by660_bis - ellipsoid plot