Supporting Information for

Sequence-selective Three-component Reactions of Alkyltrifluoroborates, α,β-Unsaturated Carbonyl Compounds, and Vinylphosphonium Salts

Masaki Yoshida,[a] Masaya Sawamura,*[a,b] and Yusuke Masuda*[a]

[a] Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo, Hokkaido 060-0810, Japan.

[b] Institute for Chemical Reaction Design and Discovery (WPI-ICReDD), Hokkaido University, Sapporo, Hokkaido 001-0021, Japan.

Correspondence to: ymasuda@sci.hokudai.ac.jp
sawamura@sci.hokudai.ac.jp

Table of contents

1. General and materials

General

All reactions were carried out under nitrogen atmosphere. Irradiation of photoreactions was carried out using a CCS LED lamp (Controller: PD3-5024-4-PI, Head: LDL2-14630BL2, λ_{max} = 470 nm, light intensity at 10 mm distance form light source: 77 mW/cm^2). NMR spectra were recorded on a JEOL ECX-400, operating at 400 MHz for ^{1}H NMR, 101 MHz for ^{13}C NMR, 376 MHz for^{19}F NMR, and 162 MHz for ^{31}P NMR. Chemical shift values for ^{1}H NMR and ^{13}C NMR are referenced to Me_4Si (0.00 ppm for ^{1}H NMR) and $CDCl_3$ (77.0 ppm for ^{13}C NMR), respectively. Chemical shift values for ^{31}P NMR are referenced to an external reference of H_3PO_4 (0.00 ppm). Chemical shifts are reported in δ ppm. NMR data was analyzed by Delta software (JEOL). High-resolution mass spectra were recorded on Thermo Fisher Scientific Exactive Plus. TLC analyses were performed on commercial glass plates bearing 0.25-mm layer of Merck Silica gel 60F_{254}. Silica gel (Kanto Chemical Co., Silica gel 60 N, spherical, neutral) was used for column chromatography. Silica gel (Merck, Silica Gel60 PF254 for PLC) was used for preparative thin-layer chromatography. Gel permeation chromatography was performed with a Japan Analytical Industry LC-5060P (JAIGEL-2HR Plus). IR spectra were measured with a PerkinElmer Frontier instrument.

Materials

Anhydrous dichloromethane (CH_2Cl_2) was purchased from FUJIFILM Wako Pure Chemical Corporation. [Ir(dFCF_3ppy)$_2$dtbbpy]PF_6 (Ir catalyst) was synthesized according to the reported method.[S1] Tetrahydrofuran (THF) was purchased from Kanto Chemical Co., and purified by passing through activated alumina under positive argon pressure as described by Grubbs *et al*.[S2] CD_2Cl_2 was purchased from Kanto Chemical Co., degassed by argon bubbling, and dehydrated with molecular sieves 4A. Organotrifluoroborates were prepared according to the reported methods.[S3,S4] Phenyl vinyl ketone[S5] and methyl 2-phenylacrylate[S6] were prepared according to the reported methods. The other chemicals were obtained from commercial suppliers and were used as received without further purification. (Note: Commercially available reagents containing polymerization inhibitors were also used without purification. We confirmed that removal of the polymerization inhibitor did not affect the yield of the products.)

2. Photoreaction Setup

Reactions were irradiated using a photo-reactor (CCS, Controller: PD3-5024-4-PI, Head: LDL2-14630BL2, λ_{max} = 470 nm, light intensity at 10 mm distance form light source: 77 mW/cm^2) shown in Figure S1. Ordinary Pyrex® vial was used for the reaction. To keep the reaction temperature at room temperature, a simple cooling fan was installed above the reaction vials. Emission spectrum of the light source is shown in Figure S2.

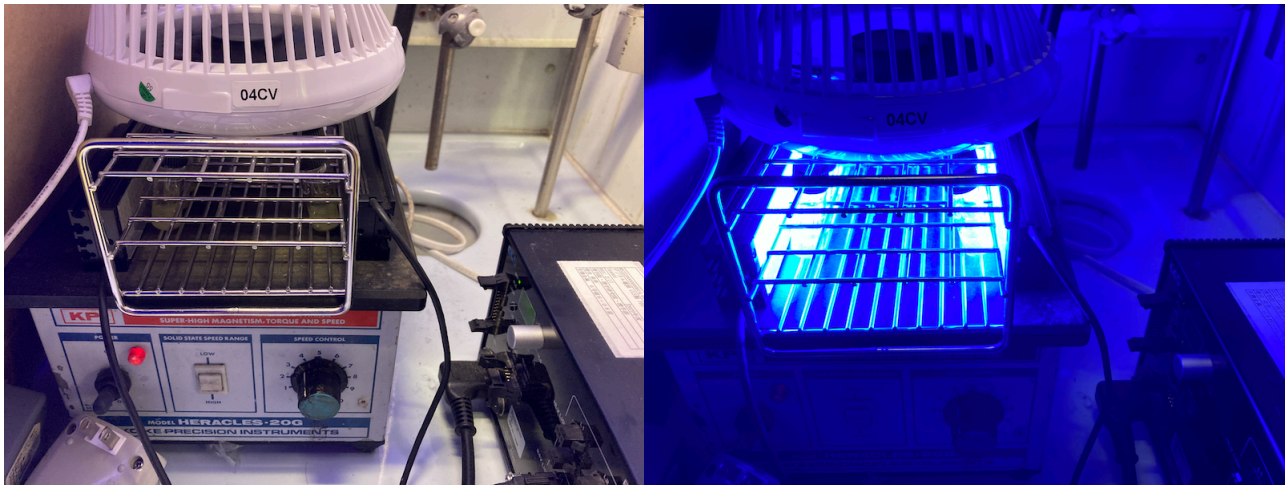


Figure S1. Photoreaction Setup.

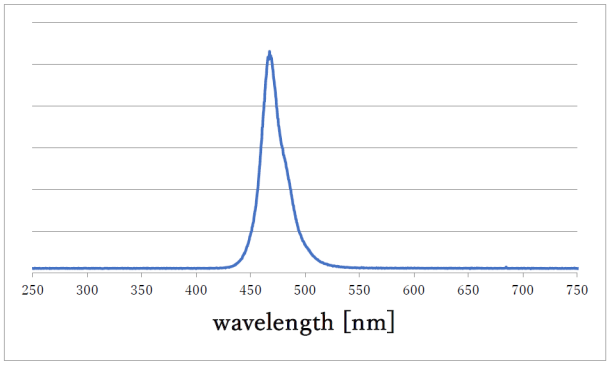
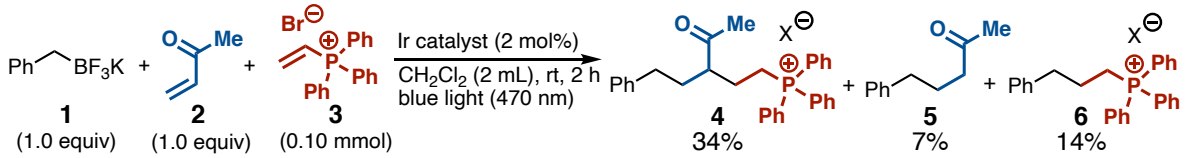


Figure S2. Emission spectrum of blue LEDs

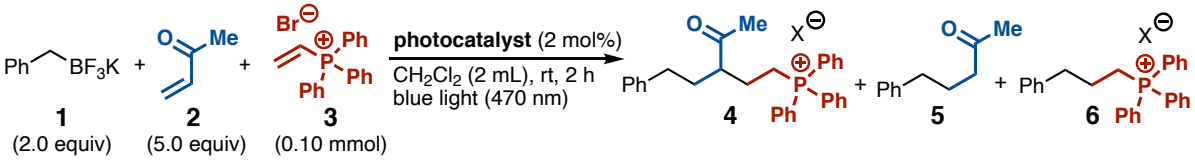
3. Reaction optimization

Scheme S1. Reaction with 1:1:1 ratio of **1**, **2**, and **3**

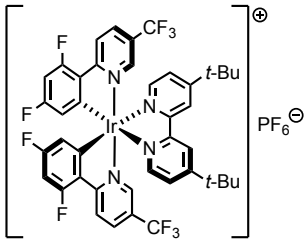


To an oven-dried 4 mL vial equipped with a stirrer bar, Ir catalyst (2.2 mg, 0.002 mmol, 2.0 mol%), potassium benzyltrifluoroborate (**1**, 20.0 mg, 0.10 mmol, 1.0 equiv), and triphenylvinylphosphonium bromide (**3**, 36.9 mg, 0.10 mmol) were added. The vial was purged with argon gas, capped, and taken into a nitrogen-filled glove box. In the glove box, methyl vinyl ketone (**2**, 7.0 mg, 0.10 mmol, 1.0 equiv) and anhydrous CH_2Cl_2 (2.0 mL) was added to the vial. The vial was capped and taken out of the glove box, and the suspension was stirred under photoirradiation (470 nm) at ambient temperature for 2 h. After irradiation, solvent was removed under a reduced pressure. Yields of the products were determined by ^{1}H NMR analysis using triphenylmethane as an internal standard.

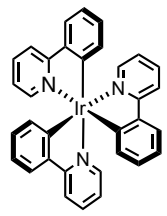
Table S1. Effect of photocatalyst



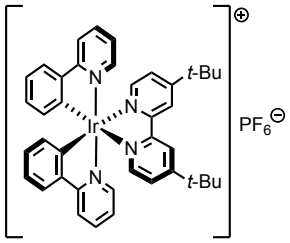
entry	photocatalyst	Yield of **4**	Yield of **5** (based on **3**)	Yield of **6**
1	$[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (Ir catalyst)	73%	32%	8%
2	$Ir(ppy)_3$	0%	not determined	21%
3	$[Ir(ppy)_2dtbbpy]PF_6$	0%	not determined	9%
4	4CzIPN	0%	not determined	13%



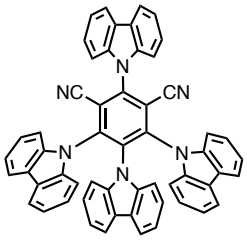
$[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (Ir catalyst)



$Ir(ppy)_3$

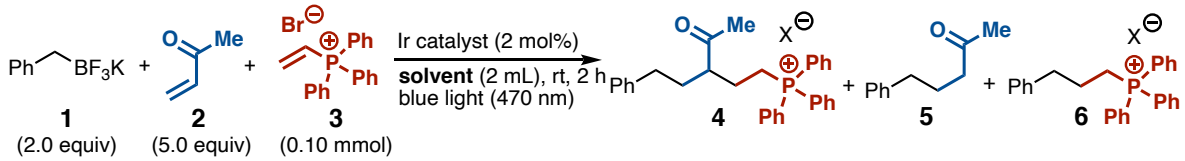


$[Ir(ppy)_2dtbbpy]PF_6$



4CzIPN

Table S2. Effect of solvent



1 (2.0 equiv) 2 (5.0 equiv) 3 (0.10 mmol) 4 5 6

entry	solvent	Yield of **4**	Yield of **5** (based on **3**)	Yield of **6**
1	CH_2Cl_2	73%	32%	8%
2	$CHCl_3$	60%	14%	10%
3	CH_3CN	13%	17%	6%
4	AcOEt	14%	Trace	9%
5	THF	9%	Trace	Trace

Reaction conditions: **1** (0.20 mmol, 2.0 equiv), **2** (0.50 mmol, 5.0 equiv), **3** (0.10 mmol, 1.0 equiv), photocatalyst (0.002 mmol, 2.0 mol%), CH_2Cl_2 (2.0 mL), ambient temperature, 2 h, blue light (470 nm). Yields were determined by ^{1}H NMR analysis using triphenylmethane as an internal standard.

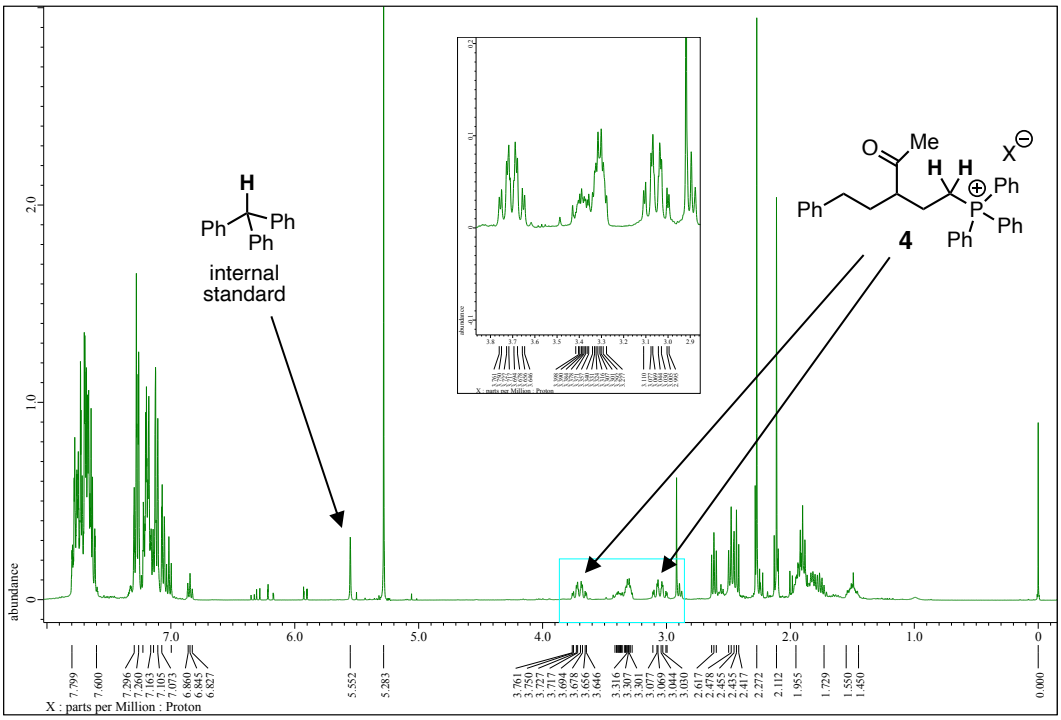


Figure S3. Determination of NMR yield by ^{1}H NMR analysis of the crude reaction mixture.

4. Mechanistic experiments

4.1. Investigation of counter anions

To an oven-dried 4 mL vial equipped with a stirrer bar, Ir catalyst (2.2 mg, 0.002 mmol, 2.0 mol%), potassium benzyltrifluoroborate (**1**, 20.0 mg, 0.10 mmol, 1.0 equiv), and triphenylvinylphosphonium bromide (**3**, 36.9 mg, 0.10 mmol) were added. The vial was purged with argon gas, capped, and taken into a nitrogen-filled glove box. In the glove box, methyl vinyl ketone (**2**, 7.0 mg, 0.10 mmol, 1.0 equiv) and anhydrous CH_2Cl_2 (2.0 mL) were added to the vial. The vial was capped and taken out of the glove box, and the suspension was stirred under photoirradiation (470 nm) at ambient temperature for 2 h. After irradiation, solvent was removed under a reduced pressure. The residue was subjected to mass spectrometry (ESI). The result was shown in Figure S4. $B(OCH_3)F_3^-$ might be formed during the measurement using CH_3OH as a mobile phase solvent. The remaining benzyltrifluoroborate (**1**) was also obtained. These anionic species were identified by HRMS.

HRMS of Br^- (ESI) m/z: [M^-] Calcd for Br^- 78.9189, Found 78.9189.

HRMS of BF_4^- (ESI) m/z: [M^-] Calcd for $^{10}BF_4^-$ 86.0071, Found 86.0072.

HRMS of $B(OCH_3)F_3^-$ (ESI) m/z: [M^-] Calcd for $CH_3O^{10}BF_3^-$ 98.0271, Found 98.0270.

HRMS of $PhCH_2BF_3^-$ (ESI) m/z: [M^-] Calcd for $C_7H_7{}^{10}BF_3^-$ 158.0635, Found 158.0636.

HRMS of $PhCHBF_2^-$ (ESI) m/z: [M^-] Calcd for $C_7H_6{}^{10}BF_2^-$ 138.0572, Found 138.0572.

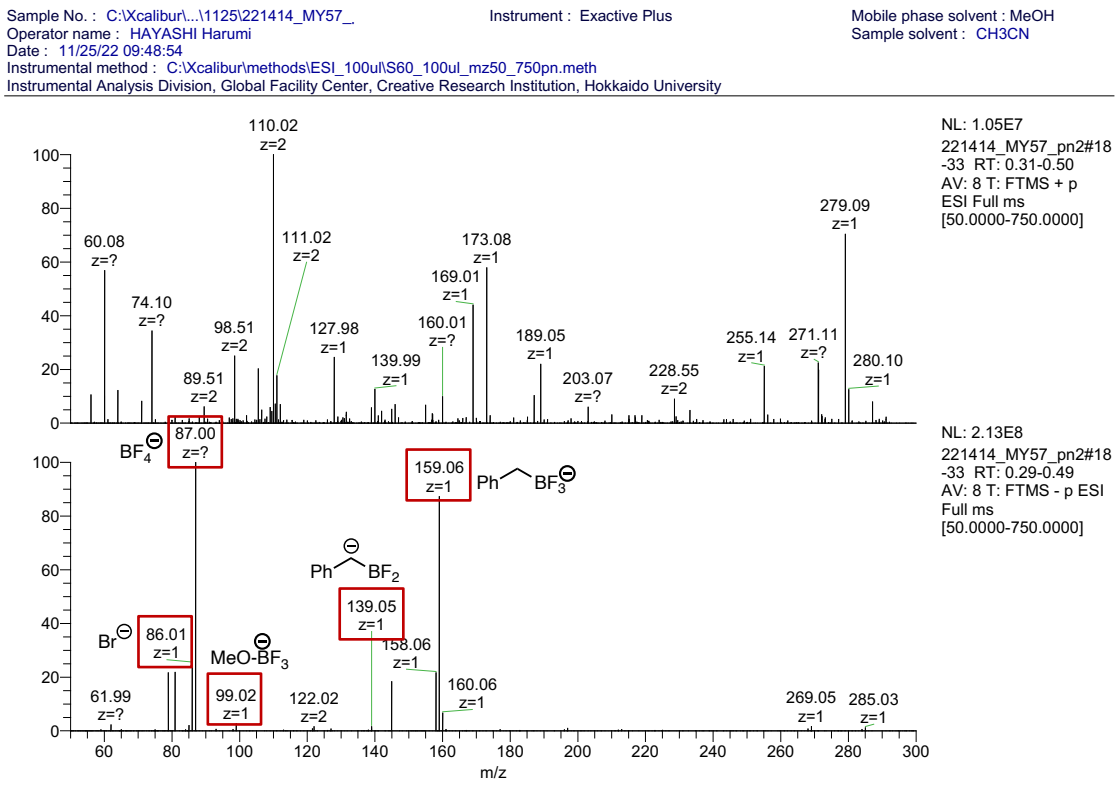
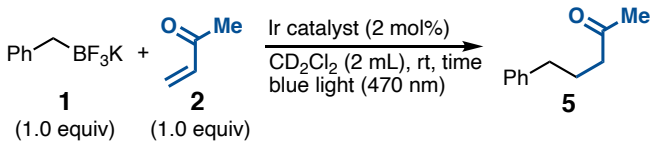


Figure S4. Mass spectrum of the crude reaction mixture.

4.2. Reaction monitoring

(a) Reaction with **1** and **2**

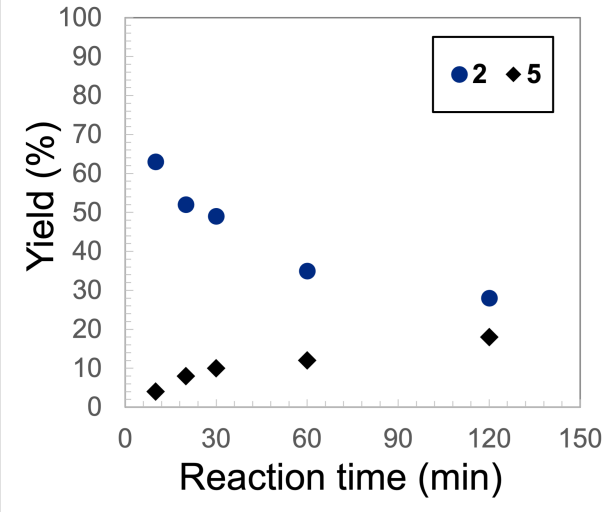


1 (1.0 equiv) **2** (1.0 equiv) **5**

To an oven-dried 4 mL vial equipped with a stirrer bar, Ir catalyst (1.1 mg, 0.001 mmol, 2.0 mol%) and potassium benzyltrifluoroborate (**1**, 10.0 mg, 0.05 mmol, 1.0 equiv) were added. The vial was purged with argon gas, capped, and taken into a nitrogen-filled glove box. In the glove box, methyl vinyl ketone (**2**, 3.5 mg, 0.05 mmol, 1.0 equiv) and anhydrous CD_2Cl_2 (1.0 mL) were added to the vial. The vial was capped and taken out of the glove box, and the suspension was stirred under photoirradiation (470 nm) at ambient temperature for the indicated time. After irradiation, the reaction mixture was directly transferred to an NMR sample tube along with triphenylmethane as an internal standard, and yields of compounds **2** and **5** were determined by ^{1}H NMR analysis.

Table S3. Progress of the reaction with **1** and **2**

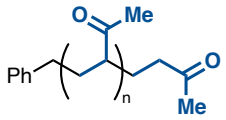
Time / min	Yield of **2**	Yield of **5**
10	63%	4%
20	52%	8%
30	49%	10%
60	35%	12%
120	28%	18%



Oligomers **5-2** and **5-3** were observed by the mass spectrometric analysis of the crude mixture and identified by HRMS.

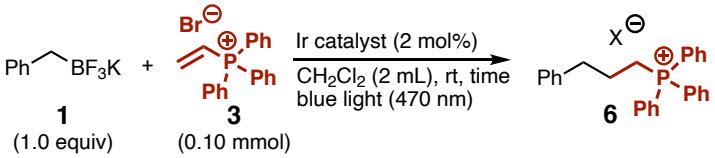
HRMS of **5-2** (ESI) m/z: [M+Na$^+$] Calcd for $C_{15}H_{20}O_2Na$ 255.1356, Found 255.1352.

HRMS of **5-3** (ESI) m/z: [M+Na$^+$] Calcd for $C_{19}H_{26}O_3Na$ 325.1774, Found 325.1770.



5-2 (n = 1)
5-3 (n = 2)

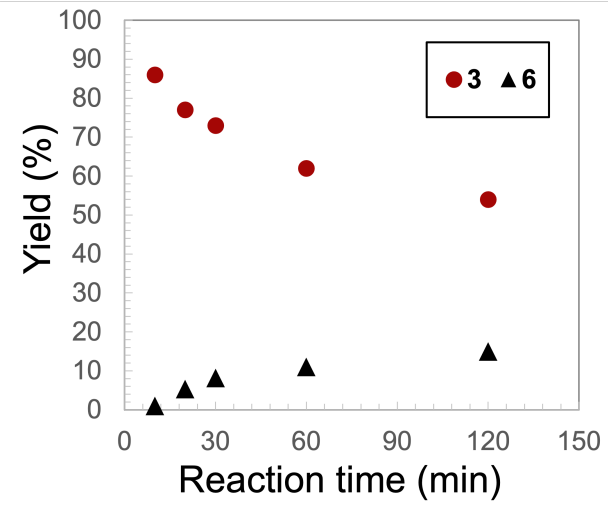
(b) Reaction with **1** and **3**



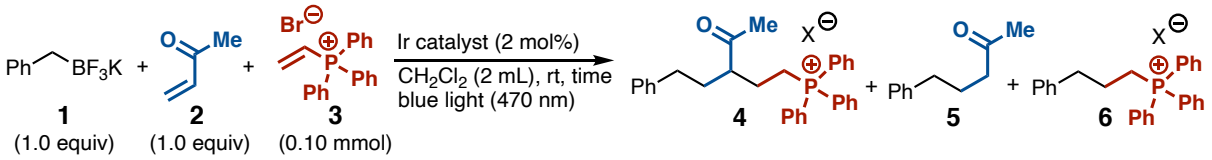
To an oven-dried 4 mL vial equipped with a stirrer bar, Ir catalyst (1.1 mg, 0.001 mmol, 2.0 mol%), potassium benzyltrifluoroborate (**1**, 10.0 mg, 0.05 mmol, 1.0 equiv), and triphenylvinylphosphonium bromide (**3**, 18.5 mg, 0.05 mmol) were added. The vial was purged with argon gas, capped, and taken into a nitrogen-filled glove box. In the glove box, anhydrous CH_2Cl_2 (1.0 mL) was added to the vial. The vial was capped and taken out of the glove box, and the suspension was stirred under photoirradiation (470 nm) at ambient temperature for the indicated time. After irradiation, the solvent was removed under vacuum, and yields of compounds **3** and **6** were determined by ^{1}H NMR analysis using triphenylmethane as an internal standard.

Table S4. Progress of the reaction with **1** and **3**

Time / min	Yield of **3**	Yield of **6**
10	86%	1%
20	77%	5%
30	73%	8%
60	62%	11%
120	54%	15%



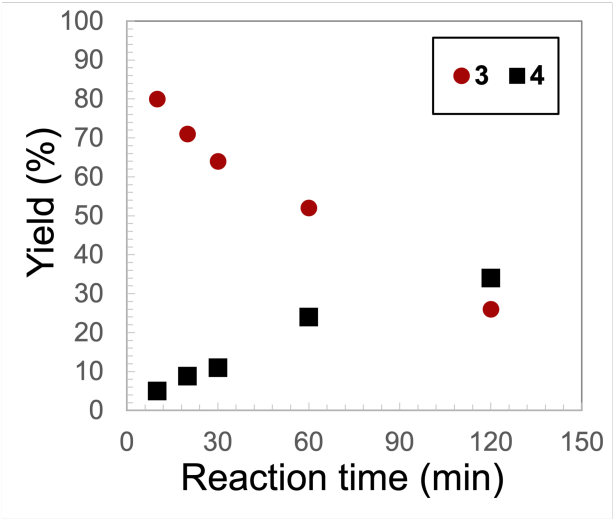
(c) Reaction with **1**, **2**, and **3**



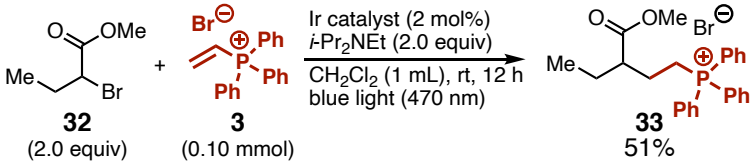
To an oven-dried 4 mL vial equipped with a stirrer bar, Ir catalyst (1.1 mg, 0.001 mmol, 2.0 mol%), potassium benzyltrifluoroborate (**1**, 10.0 mg, 0.05 mmol, 1.0 equiv), and triphenylvinylphosphonium bromide (**3**, 18.5 mg, 0.05 mmol) were added. The vial was purged with argon gas, capped, and taken into a nitrogen-filled glove box. In the glove box, methyl vinyl ketone (**2**, 3.5 mg, 0.05 mmol, 1.0 equiv) and anhydrous CH_2Cl_2 (1.0 mL) were added to the vial. The vial was capped and taken out of the glove box, and the suspension was stirred under photoirradiation (470 nm) at ambient temperature for the indicated time. After irradiation, the solvent was removed under vacuum, and yield of compounds **3** and **4** were determined by ^{1}H NMR analysis using triphenylmethane as an internal standard.

Table S4. Progress of the reaction with **1**, **2**, and **3**

Time / min	Yield of **3**	Yield of **4**
10	80%	5%
20	71%	9%
30	64%	11%
60	52%	24%
120	26%	34%



4.3. Reaction with α-bromoester 32

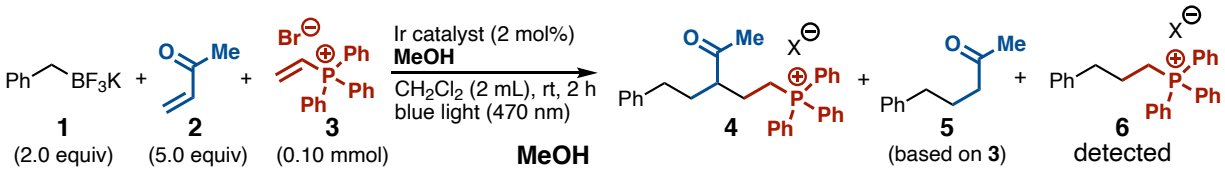


To an oven-dried 4 mL vial equipped with a stirrer bar, Ir catalyst (2.2 mg, 0.002 mmol, 2.0 mol%), and triphenylvinylphosphonium bromide (**3**, 36.9 mg, 0.10 mmol) were added. The vial was purged with argon gas, capped, and taken into a nitrogen-filled glove box. In the glove box, anhydrous CH_2Cl_2 (1.0 mL), methyl 2-bromobutyrate (**32**, 36.2 mg, 0.20 mmol, 2.0 equiv), and diisopropylethylamine (*i*-Pr_2NEt, 34.8 μL, 0.20 mmol, 2.0 equiv) were sequentially added to the vial. The vial was capped and taken out of the glove box, and the mixture was stirred under photoirradiation (470 nm) at ambient temperature for 12 h. After irradiation, the solvent was removed under vacuum, and the crude product was purified with preparative shin-layer chromatography (CH_2Cl_2/CH_3OH = 10:1) to obtain compound **33** in 51% yield (24.7 mg, 0.05 mmol).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91-7.85 (m, 6H), 7.83-7.78 (m, 3H), 7.74-7.69 (m, 6H), 4.42 (dddd, *J* = 15.1, 13.3, 12.8, 4.6 Hz, 1H), 3.69 (s, 3H), 3.34 (dddd, *J* = 15.6, 13.3, 12.8, 3.2 Hz, 1H), 3.09-3.03 (m, 1H), 1.99-1.87 (m, 1H), 1.80-1.59 (m, 3H), 0.82 (t, *J* = 7.3 Hz, 3H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 175.9, 134.9, 133.7 (d, *J* = 11 Hz, 2C), 130.4 (d, *J* = 12 Hz, 2C), 118.1 (d, *J* = 86 Hz), 51.8, 45.6 (d, *J* = 16 Hz), 25.4 23.7, 20.9 (d, *J* = 51 Hz), 10.9 ppm; **^{31}P{^{1}H} NMR** (162 MHz, $CDCl_3$): δ 25.1. **HRMS** (ESI) m/z: [M^+] Calcd for $C_{25}H_{28}O_2P$ 391.1821, Found 391.1824.

4.4. Reaction in the presence of proton source

Scheme S2. Reaction in the presence of methanol

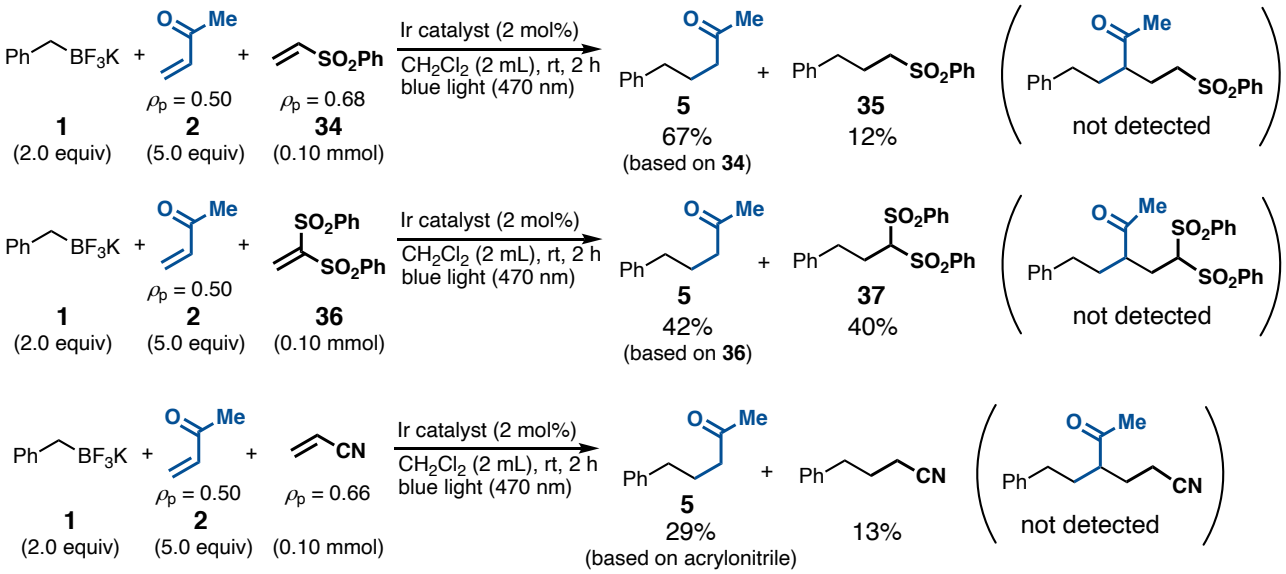


MeOH		
1.0 equiv	64%	53%
5.0 equiv	43%	56%
10.0 equiv	23%	51%

To an oven-dried 4 mL vial equipped with a stirrer bar, Ir catalyst (2.2 mg, 0.002 mmol, 2.0 mol%), potassium benzyltrifluoroborate (**1**, 39.9 mg, 0.20 mmol, 2.0 equiv), and triphenylvinylphosphonium bromide (**3**, 36.9 mg, 0.10 mmol) were added. The vial was purged with argon gas, capped, and taken into a nitrogen-filled glove box. In the glove box, methyl vinyl ketone (**2**, 35.0 mg, 0.50 mmol, 5.0 equiv), methanol (MeOH, 3.2 mg, 0.10 mmol, 1.0 equiv; 16.0 mg, 0.50 mmol, 5.0 equiv; 32.0 mg, 1.0 mmol, 10 equiv) and anhydrous CH_2Cl_2 were added to the vial. The vial was capped and taken out of the glove box, and the suspension was stirred under photoirradiation (470 nm) at ambient temperature for 2 h. After irradiation, the solvent was removed under vacuum, and yield of **4** was determined by ^{1}H NMR analysis using triphenylmethane as an internal standard.

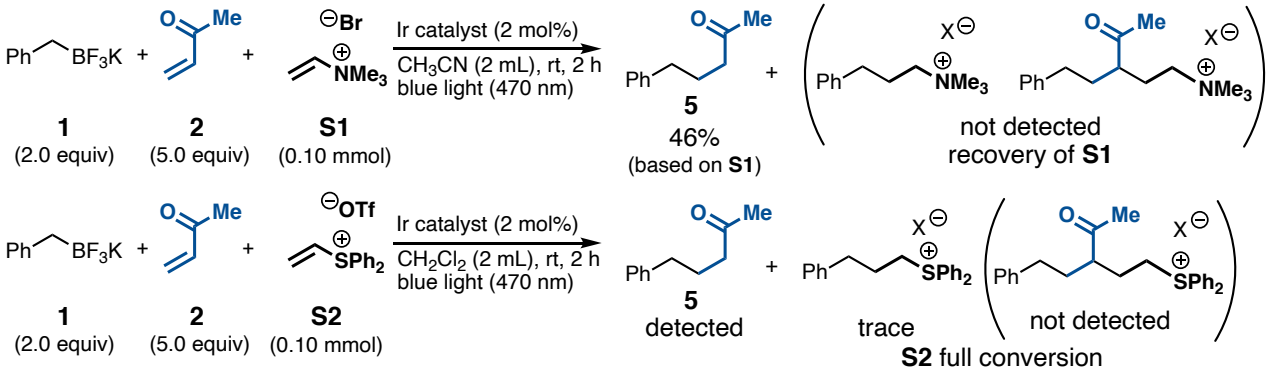
4.5. Reaction with other electron-deficient alkenes

Scheme S3. Reactions with non-ionic alkenes, phenyl vinyl sulfones (**34** and **36**) and acrylonitrile.



To an oven-dried 4 mL vial equipped with a stirrer bar, Ir catalyst (2.2 mg, 0.002 mmol, 2.0 mol%), potassium benzyltrifluoroborate (**1**, 39.9 mg, 0.20 mmol, 2.0 equiv), and *electron-deficient alkene* (**34**, 16.8 mg, 0.10 mmol; **36**, 30.8 mg, 0.10 mmol) were added. The vial was purged with argon gas, capped, and taken into a nitrogen-filled glove box. In the glove box, methyl vinyl ketone (**2**, 35.0 mg, 0.50 mmol, 5.0 equiv), *electron-deficient alkene* (acetonitrile: 5.3 mg, 0.10 mmol), and anhydrous CH_2Cl_2 were added to the vial. The vial was capped and taken out of the glove box, and the suspension was stirred under photoirradiation (470 nm) at ambient temperature for 2 h. After irradiation, the solvent was removed under vacuum, and yields of the products were determined by ^1H NMR analysis using triphenylmethane as an internal standard.

Scheme S4. Reactions with ionic alkenes, vinylammonium **S1** and vinylsulfonium **S2**

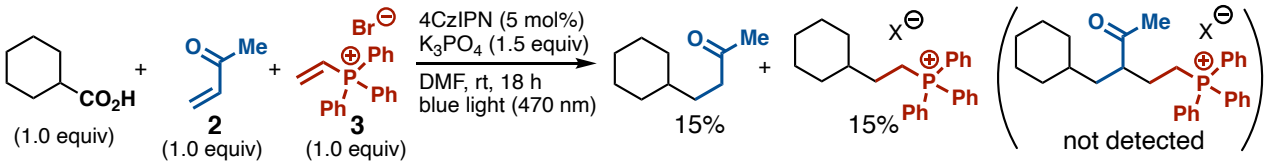


To an oven-dried 4 mL vial equipped with a stirrer bar, Ir catalyst (2.2 mg, 0.002 mmol, 2.0 mol%), potassium benzyltrifluoroborate (**1**, 39.9 mg, 0.20 mmol, 2.0 equiv), and *electron-deficient alkene* (0.10 mmol) were added. The vial was purged with argon gas, capped, and taken into a nitrogen-filled glove box. In the glove box, methyl vinyl ketone (**2**, 35.0 mg, 0.50 mmol, 5.0 equiv) and anhydrous CH_3CN or CH_2Cl_2 were added to the vial. The vial was capped and taken out of the glove box, and the suspension was stirred under photoirradiation (470 nm) at ambient temperature for 2 h. After irradiation, the solvent was removed under vacuum, and yields of the products were determined by ^1H NMR analysis using triphenylmethane as an internal standard.

Ammonium salt **S1** was unreactive toward alkyl radical species, resulting in the recovery of the starting salt. In contrast, sulfonium salt **S2** was labile under the reaction conditions, and only a trace amount of two-component product was observed with full conversion of the starting alkene.

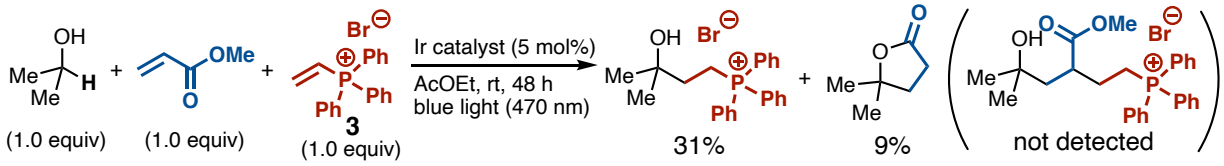
4.6. Reactions of other radical precursors

Scheme S5. Reaction of carboxylic acid



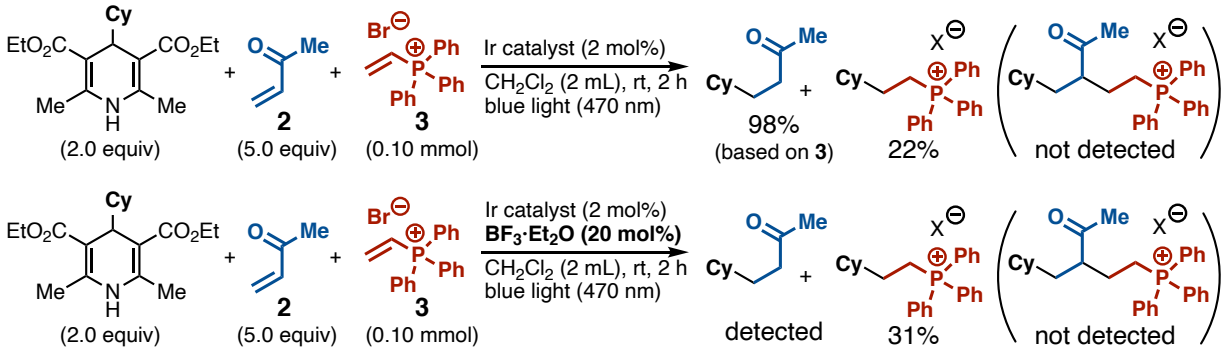
To an oven-dried 4 mL vial equipped with a stirrer bar, 4CzIPN (3.9 mg, 0.005 mmol, 5.0 mol%), cyclohexanecarboxylic acid (12.8 mg, 0.10 mmol, 1.0 equiv), triphenylvinylphosphonium bromide (**3**, 36.9 mg, 0.10 mmol), K_3PO_4 (31.8 mg, 0.15 mmol, 1.5 equiv) were added. The vial was purged with argon gas, capped, and taken into a nitrogen-filled glove box. In the glove box, methyl vinyl ketone (**2**, 7.0 mg, 0.10 mmol, 1.0 equiv) and anhydrous DMF (0.2 mL) were added to the vial. The vial was capped and taken out of the glove box, and the suspension was stirred under photoirradiation (470 nm) at ambient temperature for 18 h. After irradiation, the reaction mixture was diluted with CH_2Cl_2, washed with water (3 times) and brine, dried over $MgSO_4$, and concentrated under reduced pressure. Yields of the products were determined by ^{1}H NMR analysis using triphenylmethane as an internal standard.

Scheme S6. Reaction of 2-propanol



To an oven-dried 4 mL vial equipped with a stirrer bar, Ir catalyst (5.5 mg, 0.005 mmol, 5.0 mol%) and **3** (36.3 mg, 0.10 mmol) were added. The vial was purged with argon gas and was taken into a nitrogen-filled glove box. In the glove box, methyl acrylate (8.6 mg, 0.10 mmol, 1.0 equiv), 2-propanol (6.0 mg, 0.10 mmol, 1.0 equiv), and anhydrous ethyl acetate (AcOEt, 1.0 mL) were added to the vial. The vial was capped and taken out of the glove box, and the suspension was stirred under photoirradiation (470 nm) at ambient temperature for 48 h. NMR yields of the products were determined by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard.

Scheme S7. Reactions of dihydropyridine in the absence and presence of BF_3.

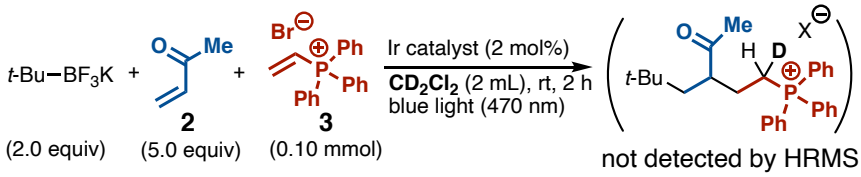


To an oven-dried 4 mL vial equipped with a stirrer bar, Ir catalyst (2.2 mg, 0.002 mmol, 2.0 mol%), dihydropyridine (a precursor of cyclohexyl radical; 67.1 mg, 0.20 mmol, 2.0 equiv), and triphenylvinylphosphonium bromide (**3**, 36.9 mg, 0.10 mmol) were added. The vial was purged with argon gas, capped, and taken into a nitrogen-filled glove box. In the glove box, methyl vinyl ketone (**2**, 35.0 mg, 0.50 mmol, 5.0 equiv) and anhydrous CH_2Cl_2 were added to the vial. [For the reaction in the presence of BF_3, $BF_3{\cdot}Et_2O$ (2.5 μL, 0.02 mmol, 20 mol%) was then added to the vial.] The vial was capped and taken out of the glove box, and the suspension was stirred under photoirradiation (470 nm) at ambient temperature for 2 h. After irradiation, the solvent was removed under vacuum, and yields of the products was determined by ^1H NMR analysis using triphenylmethane as an internal standard.

The three-component product was not obtained when dihydropyridine was used as an alkyl radical precursor with or without BF_3. In particular, the addition of BF_3 caused cloudiness in the solution and complicated the reaction mixture compared to the reaction without BF_3. We also observed polymerization of vinyl ketones in the reaction with BF_3. These results suggested that the gradual *in situ* generation of BF_3 from trifluoroborate salts was crucial for the formation of three-component product. Another reason why dihydropyridine was not suitable substrates is that the proton generated together with alkyl radical in the photoreaction might affect the three-component reaction as shown in Figure 2b.

4.7. Deuterium-labeling experiments

Scheme S8. Reaction in CD_2Cl_2



To an oven-dried 4 mL vial equipped with a stirrer bar, Ir catalyst (2.2 mg, 0.002 mmol, 2.0 mol%), potassium *t*-butyltrifluoroborate (32.8 mg, 0.20 mmol, 2.0 equiv), and triphenylvinylphosphonium bromide (**3**, 36.9 mg, 0.10 mmol) were added. The vial was purged with argon gas, capped, and taken into a nitrogen-filled glove box. In the glove box, methyl vinyl ketone (**2**, 35.0 mg, 0.50 mmol, 5.0 equiv) and anhydrous CD_2Cl_2 (99.8% D, 2.0 mL) were added to the vial. The vial was capped and taken out of the glove box, and the suspension was stirred under photoirradiation (470 nm) at ambient temperature for the indicated time. After irradiation, the solvent was removed under vacuum, and the residue was analyzed by mass spectrometry (ESI). No deuterated product was observed as shown in Figure S5. The spectra were consistent with peak intensities according to the simulated natural abundance ratios.

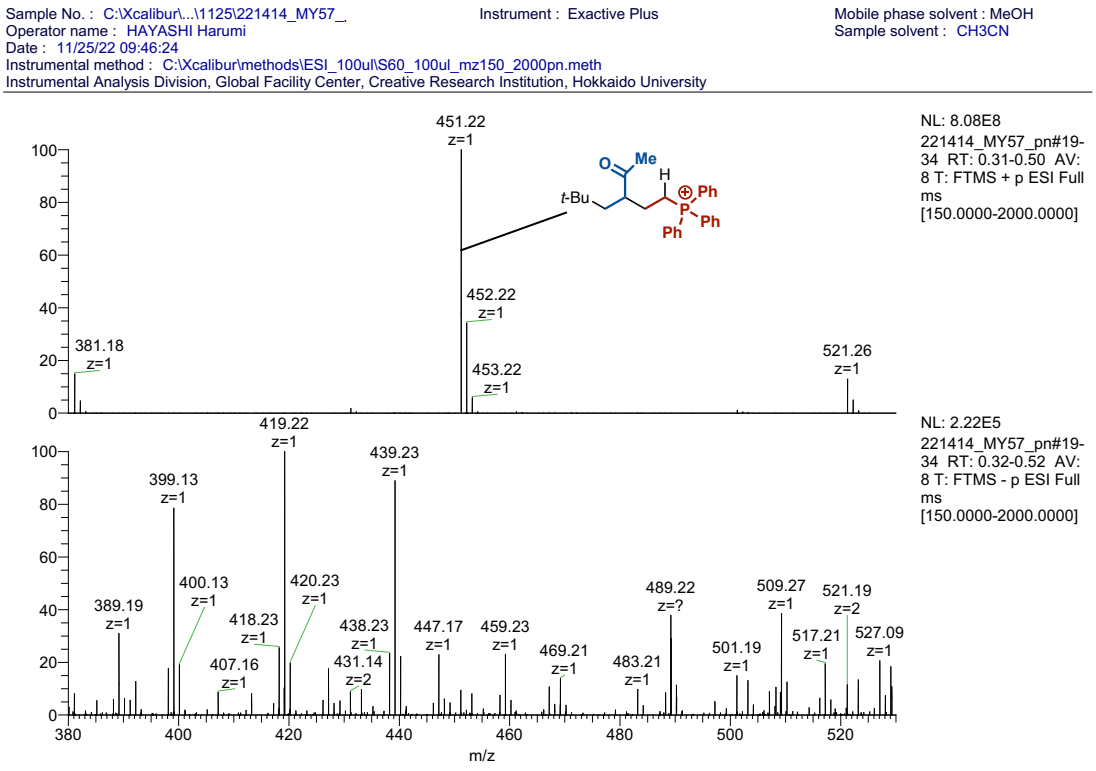
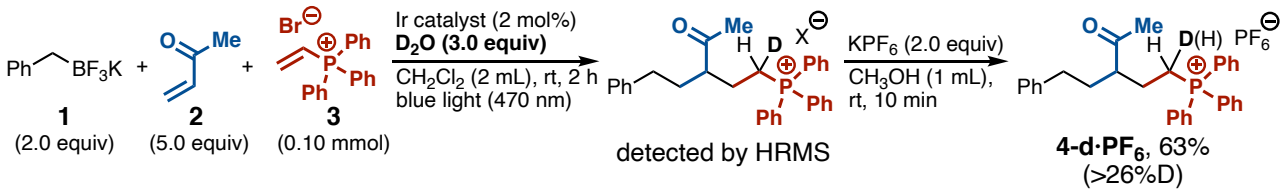


Figure S5. Mass analysis for the reaction in CD_2Cl_2

Scheme S9. Reaction in the presence of D_2O



To an oven-dried 4 mL vial equipped with a stirrer bar, Ir catalyst (2.2 mg, 0.002 mmol, 2.0 mol%), potassium benzyltrifluoroborate (**1**, 40.0 mg, 0.20 mmol, 2.0 equiv), and triphenylvinylphosphonium bromide (**3**, 36.9 mg, 0.10 mmol) were added. The vial was purged with argon gas, capped, and taken into a nitrogen-filled glove box. In the glove box, methyl vinyl ketone (**2**, 35.0 mg, 0.50 mmol, 5.0 equiv), D_2O (6.0 mg, 0.3 mmol, 3 equiv), and anhydrous CH_2Cl_2 (2.0 mL) were added to the vial. The vial was capped and taken out of the glove box, and the suspension was stirred under photoirradiation (470 nm) at ambient temperature for the indicated time. After irradiation, the solvent was removed under vacuum, and the residue was analyzed by mass spectrometry (ESI). The deuterated product was observed and identified by HRMS.

HRMS (ESI) m/z: [M^+] Calcd for $C_{31}H_{31}DOP$ 452.2248, Found 452.2230.

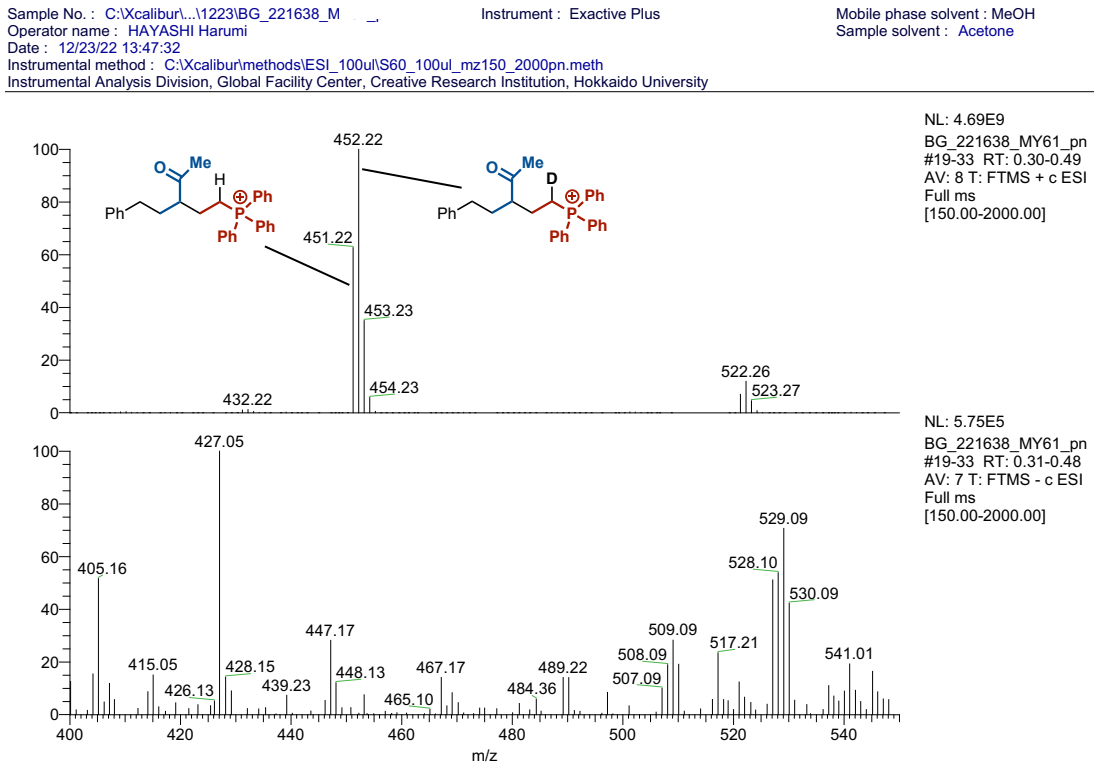


Figure S6. Mass analysis for the reaction in the presence of D_2O

The crude mixture was then treated with KPF_6 (36.8 mg, 0.20 mmol, 2.0 equiv) in CH_3OH (1 mL), and the resulting mixture was purified by silica gel column chromatography ($CHCl_3/CH_3OH$ = 99:1) to obtain a mixture of deuterated phosphonium salts **4-d** and **6-d** (44.0 mg). Yields were calculated based on the molar ratio of **4-d** to **6-d** determined by ^1H NMR spectroscopy (**4-d**: 63% yield, **6-d**: 12% yield). Deuterium incorporation of **4-d** was determined to be more than 26% by comparing the integral of one of the diastereotopic proton signals at the P-adjacent position with that of the proton signal of the methyl group. (The other diastereotopic proton signal at the P-adjacent position overlapped other peaks, so the exact H/D ratio could not be determined.)

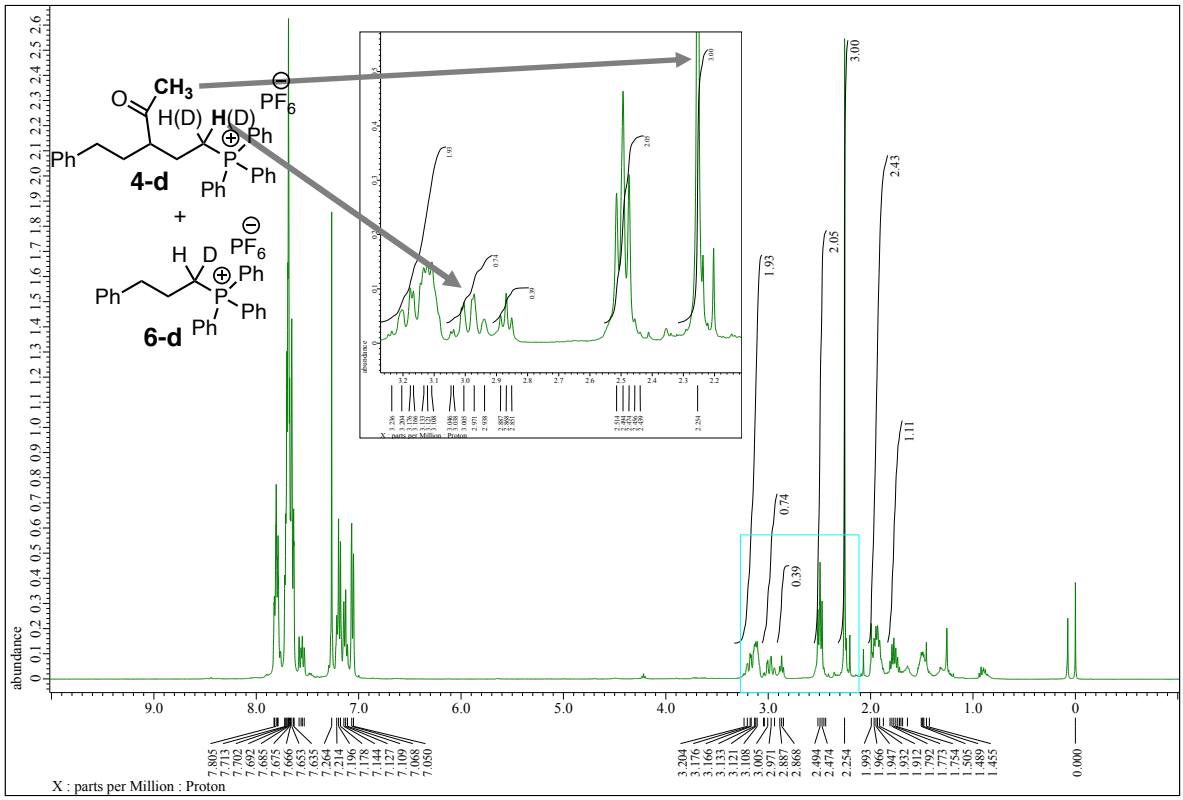
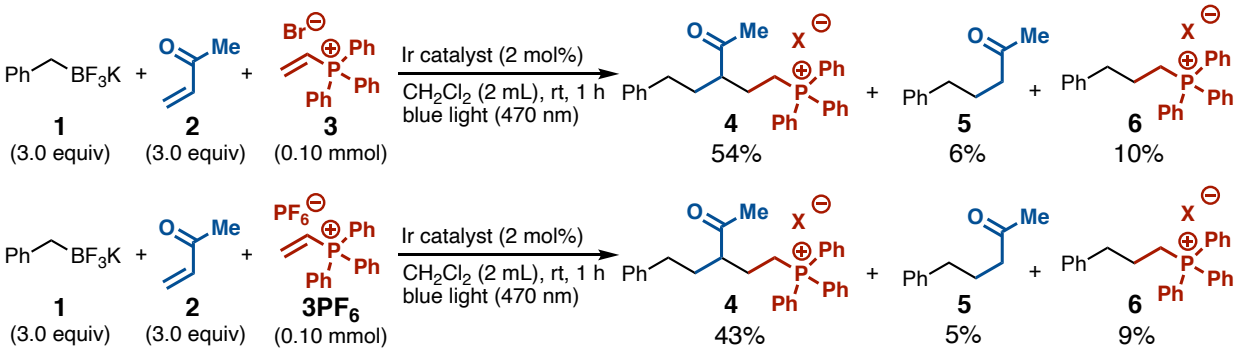


Figure S7. NMR spectrum of a mixture of **4-d** and **6-d**

4.8. Effect of counter anions

Scheme 10. Effect of counter anions of vinylphosphonium salts

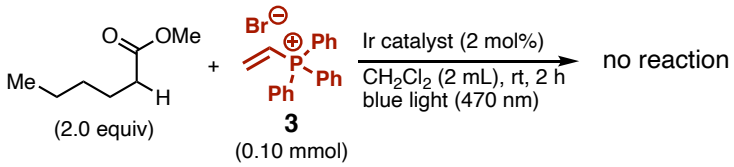


To an oven-dried 4 mL vial equipped with a stirrer bar, Ir catalyst (2.2 mg, 0.002 mmol, 2.0 mol%), potassium benzyltrifluoroborate (**1**, 59.8 mg, 0.30 mmol, 3.0 equiv), and triphenylvinylphosphonium salt (0.10 mmol) were added. The vial was purged with argon gas, capped, and taken into a nitrogen-filled glove box. In the glove box, methyl vinyl ketone (**2**, 21.0 mg, 0.30 mmol, 3.0 equiv), methanol (MeOH, 16.0 mg, 0.50 mmol, 5.0 equiv) and anhydrous CH_2Cl_2 were added to the vial. The vial was capped and taken out of the glove box, and the suspension was stirred under photoirradiation (470 nm) at ambient temperature for 2 h. After irradiation, the solvent was removed under vacuum, and yield of **4** was determined by ^{1}H NMR analysis using triphenylmethane as an internal standard.

Counter anions of vinylphosphonium salts did not affect the reaction efficiency as significantly. We reasoned that counter anions of starting phosphonium salts were easily replaced by other anionic species existing in the reaction mixture such as alkyltrifluoroborate.

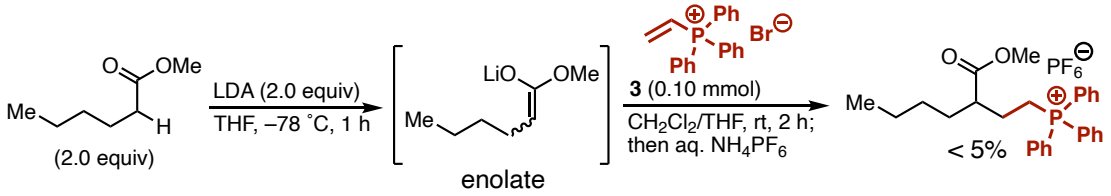
4.9. Reactions of aliphatic ester

Scheme 11. Reaction of methyl hexanoate with 3 under the optimized conditions



To an oven-dried 4 mL vial equipped with a stirrer bar, Ir catalyst (2.2 mg, 0.002 mmol, 2.0 mol%) and triphenylvinylphosphonium salt (0.10 mmol) were added. The vial was purged with argon gas, capped, and taken into a nitrogen-filled glove box. In the glove box, methyl hexanoate (29.0 µL, 0.20 mmol, 2.0 equiv) and anhydrous CH_2Cl_2 (2 mL) were added to the vial. The vial was capped and taken out of the glove box, and the suspension was stirred under photoirradiation (470 nm) at ambient temperature for 2 h. After irradiation, the solvent was removed under vacuum, and yield was determined by ^{1}H NMR analysis using triphenylmethane as an internal standard.

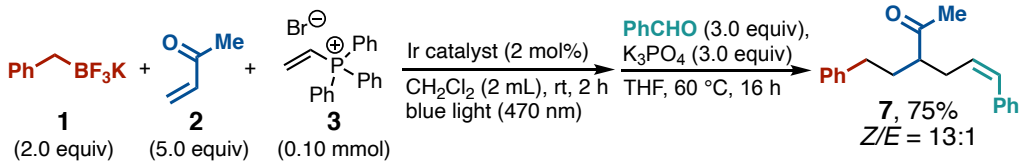
Scheme 12. Reaction of methyl hexanoate with 3 by the aid of base



An oven-dried 10 mL two-neck flask equipped with a stirrer bar was evacuated and filled with argon three times. To the flask, THF (1 mL) and methyl hexanoate (29.0 µL, 0.20 mmol, 2.0 equiv) were added via a syringe. After the reaction was cooled with dry ice-acetone bath, LDA (1.0 M in Et_2O, 200 µL, 0.20 mmol, 2.0 equiv) was added to the reaction mixture, which was stirred for 1 h. To an oven-dried 4 mL vial equipped with a stirrer bar, triphenylvinylphosphonium bromide (**3**, 36.9 mg, 0.10 mmol) was added. The vial was purged with argon gas, capped, and taken into a nitrogen-filled glove box. In the glove box, anhydrous CH_2Cl_2 (1 mL) was added to the vial. The vial was capped and taken out of the glove box, and the solution of enolate was added via a syringe. After stirring at room temperature for 2 h, the reaction was quenched with water, and then, the aqueous layer was extracted with AcOEt (3 times). The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. Yield was determined by ^{1}H NMR analysis using triphenylmethane as an internal standard.

5. Experimental procedures and characterization of products

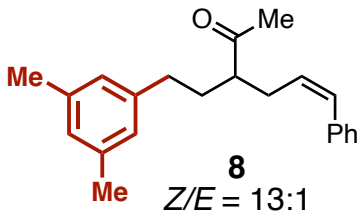
Typical procedure for a sequence of the photocatalytic double Giese-type reaction and Wittig olefination reaction



To an oven-dried 4 mL vial equipped with a stirrer bar, Ir catalyst (2.2 mg, 0.002 mmol, 2.0 mol%), potassium benzyltrifluoroborate (**1**, 39.9 mg, 0.20 mmol, 2.0 equiv), and triphenylvinylphosphonium bromide (**3**, 36.9 mg, 0.10 mmol) were added. The vial was purged with argon gas, capped, and taken into a nitrogen-filled glove box. In the glove box, methyl vinyl ketone (**2**, 35.0 mg, 0.50 mmol, 5.0 equiv) and anhydrous CH_2Cl_2 were added to the vial. The vial was capped and taken out of the glove box, and the suspension was stirred under photoirradiation (470 nm) at ambient temperature for 2 h. After irradiation, the solvent was removed under vacuum. The vial was transferred back into the glove box. After adding potassium phosphate (K_3PO_4, 63.7 mg, 0.30 mmol, 3.0 equiv), benzaldehyde (31.8 mg, 0.30 mmol, 3.0 equiv), and THF (1 mL), the vial was taken out of the glove box and stirred at 60 ˚C for 16 h. The reaction was quenched with water, and then, the aqueous layer was extracted with AcOEt (3 times). The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography and gel permeation chromatography to afford γ,δ-unsaturated ketone **7** as a colorless oil (20.8 mg, 0.075 mmol, 75% yield). The geometry of the alkene moiety (*Z*/*E* = 13:1) was determined by ^{1}H NMR spectroscopy.

Spectral data of the *Z* isomer were reported.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.16 (m, 8H), 7.11 (d, *J* = 6.9 Hz, 2H), 6.50 (d, *J* = 11.5 Hz, 1H), 5.54 (dt, *J* = 11.5, 6.9 Hz, 1H), 2.65-2.49 (m, 5H), 2.08 (s, 3H), 2.02-1.92 (m, 1H), 1.80-1.71 (m, 1H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 211.6, 141.4, 137.0, 130.9, 128.8, 128.7 (2C), 128.4 (2C), 128.3 (2C), 128.2 (2C), 126.8, 126.0, 52.5, 33.3, 32.5, 30.0, 29.0 ppm; **HRMS** (ESI) m/z: [M+Na$^+$] Calcd for $C_{20}H_{22}ONa^+$ 301.1563, Found 301.1558; **IR** (ATR): 3025, 2926, 2859, 1707, 1494, 1352, 1159, 769, 749, 697 cm^{-1}.



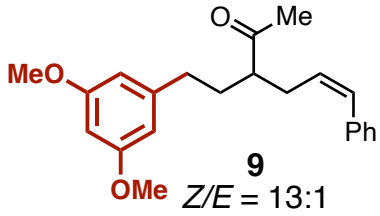
8

Z/*E* = 13:1

Compound **8** was prepared from potassium 3,5-dimethylbenzyltrifluoroborate (45.2 mg, 0.20 mmol), **3** (36.9 mg, 0.10 mmol), methyl vinyl ketone (**2**, 35.0 mg, 0.50 mmol), and benzaldehyde (31.8 mg, 0.30 mmol). The crude mixture was purified by silica gel column chromatography (hexane/EtOAc = 10:0 to 9:1) and gel permeation chromatography to give the titled compound as a colorless oil (19.4 mg, 0.063 mmol, 63% yield, *Z*/*E* = 13:1).

Spectral data of the *Z* isomer were reported.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.31 (m, 2H), 7.26-7.22 (m, 3H), 6.82 (s, 1H), 6.73 (s, 2H), 6.50 (d, *J* = 11.7 Hz, 1H), 5.56 (dt, *J* = 11.7, 7.3 Hz, 1H), 2.68-2.50 (m, 3H), 2.46-2.41 (m, 2H), 2.27 (s, 6H), 2.09 (s, 3H), 1.98-1.89 (m, 1H), 1.77-1.69 (m, 1H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 211.7, 141.4, 137.9 (2C), 137.0, 130.8, 128.9, 128.7 (2C), 128.2 (2C), 127.6, 126.8, 126.1 (2C), 52.6, 33.1, 32.6, 30.0, 28.9, 21.2 (2C) ppm; **HRMS** (ESI) m/z: [M+Na^+] Calcd for $C_{22}H_{26}ONa^+$ 329.1876, Found 329.1869; **IR** (ATR): 3012, 2919, 2858, 1709, 1606, 1352, 1158, 844, 770, 698 cm^{-1}.



9

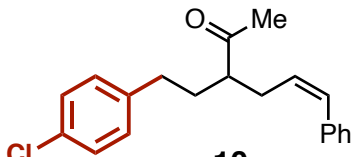
Z/*E* = 13:1

Compound **9** was prepared from potassium 3,5-dimethoxybenzyltrifluoroborate (51.6 mg, 0.20 mmol), **3** (36.9 mg, 0.10 mmol), methyl vinyl ketone (**2**, 35.0 mg, 0.50 mmol), and benzaldehyde (31.8 mg, 0.30 mmol). The crude mixture was purified by silica gel column chromatography (Hexane/EtOAc = 10:0 to 9:1) and gel permeation chromatography to give the titled compound as a colorless oil (17.2 mg, 0.051 mmol, 51% yield, *Z*/*E* = 13:1).

Spectral data of the *Z* isomer were reported.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.31 (m, 2H), 7.25-7.22 (m, 3H), 6.50 (d, *J* = 11.5 Hz, 1H), 6.30 (d, *J* = 2.3 Hz, 1H), 6.27 (d, *J* = 2.3 Hz, 2H), 5.55 (dt, *J* = 11.5, 7.3 Hz, 1H), 3.76 (s, 6H), 2.65-2.40 (m, 5H), 2.09 (s, 3H), 2.01-1.91 (m, 1H), 1.78-1.70 (m, 1H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$):

δ 211.6, 160.7, 143.8, 137.0, 130.9, 128.8, 128.7, 128.2, 126.8, 106.3, 97.9, 55.2, 52.4, 33.6, 32.2, 30.0, 29.0 ppm; **HRMS** (ESI) m/z: [M+Na$^+$] Calcd for $C_{22}H_{26}O_3Na^+$ 361.1774, Found 361.1769; **IR** (ATR): 3000, 2937, 2838, 1708, 1594, 1458, 1428, 1352, 1204, 1148, 1057, 830, 770, 696 cm^{-1}.

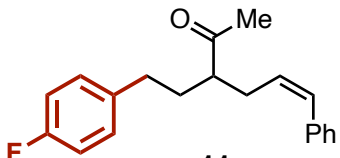


10
Z/*E* = 19:1

Compound **10** was prepared from potassium 4-chlorobenzyltrifluoroborate (46.4 mg, 0.20 mmol), **3** (36.9 mg, 0.10 mmol), methyl vinyl ketone (**2**, 35.0 mg, 0.50 mmol), and benzaldehyde (31.8 mg, 0.30 mmol). The irradiation time was 4 h. The crude mixture was purified by silica gel column chromatography (Hexane/EtOAc = 10:0 to 9:1), gel permeation chromatography, and preparative thin-layer chromatography (Hexane/EtOAc = 20:1) to give the titled compound as a colorless oil (14.6 mg, 0.047 mmol, 47% yield, *Z*/*E* = 19:1).

Spectral data of the *Z* isomer were reported.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.29 (m, 2H), 7.25-7.21 (m, 5H), 7.04-7.01 (m, 2H), 6.51 (d, *J* = 11.9 Hz, 1H), 5.53 (dt, *J* = 11.9, 6.9 Hz, 1H), 2.65-2.41 (m, 5H), 2.09 (s, 3H), 1.98-1.87 (m, 1H), 1.75-1.65 (m, 1H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 211.4, 139.9, 136.9, 131.7, 131.1, 129.7 (2C), 128.7 (2C), 128.6, 128.5 (2C), 128.2 (2C), 126.9, 52.3, 32.6, 32.2, 29.9, 29.0 ppm; **HRMS** (ESI) m/z: [M+Na$^+$] Calcd for $C_{20}H_{21}ClONa^+$ 335.1173, Found 335.1170; **IR** (ATR): 3022, 2930, 2860, 1708, 1491, 1353, 1156, 1091, 1015, 806, 769, 698 cm^{-1}.

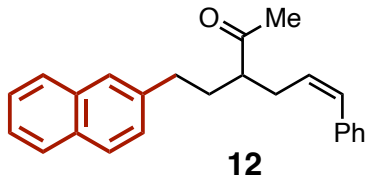


11
Z/*E* = 15:1

Compound **11** was prepared from potassium 4-fluorobenzyltrifluoroborate (43.2 mg, 0.20 mmol), **3** (36.9 mg, 0.10 mmol), methyl vinyl ketone (**2**, 35.0 mg, 0.50 mmol), and benzaldehyde (31.8 mg, 0.30 mmol). The crude mixture was purified by silica gel column chromatography (Hexane/EtOAc = 10:0 to 9:1) and gel permeation chromatography to give the titled compound as a colorless oil (13.1 mg, 0.044 mmol, 44% yield, *Z*/*E* = 15:1).

Spectral data of the *Z* isomer were reported.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.31 (m, 2H), 7.26-7.23 (m, 3H), 7.06-7.02 (m, 2H), 6.98-6.91 (m, 2H), 6.51 (d, *J* = 11.7 Hz, 1H), 5.54 (dt, *J* = 11.7, 7.3 Hz, 1H), 2.66-2.43 (m, 5H), 2.08 (s, 3H), 1.99-1.89 (m, 1H), 1.76-1.67 (m, 1H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 211.5, 161.3 (d, *J* = 243 Hz), 137.02 (d, *J* = 3 Hz), 136.96, 131.0, 129.6 (d, *J* = 8 Hz, 2C), 128.7 (3C), 128.2 (2C), 126.9, 115.1 (d, *J* = 21 Hz, 2C), 52.3, 32.5, 32.4, 30.0, 29.0 ppm; **^{19}F NMR** (376 MHz, $CDCl_3$): δ –117.3 (tt, *J* = 8.7, 5.8 Hz) ppm; **HRMS** (ESI) m/z: [M+Na^+] Calcd for $C_{20}H_{21}FONa^+$ 319.1469, Found 319.1465; **IR** (ATR): 3008, 2931, 2862, 1708, 1599, 1509, 1219, 1205, 1156, 825, 769, 698 cm^{-1}.

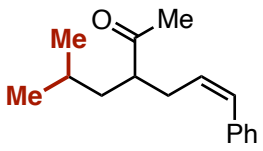


12
Z/*E* = 13:1

Compound **12** was prepared from potassium trifluoro(napthalen-2-ylmethyl)borate (49.6 mg, 0.20 mmol), **3** (36.9 mg, 0.10 mmol), methyl vinyl ketone (**2**, 35.0 mg, 0.50 mmol), and benzaldehyde (31.8 mg, 0.30 mmol). The crude mixture was purified by silica gel column chromatography (Hexane/EtOAc = 10:0 to 9:1) and gel permeation chromatography to give the titled compound as a colorless oil (14.8 mg, 0.045 mmol, 45% yield, *Z*/*E* = 13:1).

Spectral data of the *Z* isomer were reported.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81-7.75 (m, 3H), 7.53 (s, 1H), 7.47-7.40 (m, 2H), 7.35-7.30 (m, 2H), 7.27-7.22 (m, 4H), 6.51 (d, *J* = 11.7 Hz, 1H), 5.55 (dt, *J* = 11.7, 6.9 Hz, 1H), 2.74-2.53 (m, 5H), 2.10 (s, 3H), 2.07-2.01 (m, 1H), 1.89-1.80 (m, 1H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 211.6, 138.9, 137.0, 133.5, 132.0, 131.0, 128.8, 128.7, 128.2, 128.0, 127.6, 127.4, 127.1, 126.8, 126.4, 125.9, 125.2, 52.4, 33.4, 32.2, 30.0, 29.1 ppm; **HRMS** (ESI) m/z: [M+Na^+] Calcd for $C_{24}H_{24}ONa^+$ 351.1719, Found 351.1712; **IR** (ATR): 3052, 3016, 2924, 2858, 1706, 1352, 1159, 855, 816, 770, 747, 698 cm^{-1}.

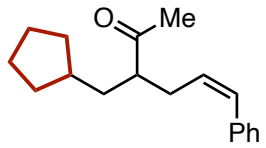


13
Z/*E* = 13:1

Compound **13** was prepared from potassium isopropyltrifluoroborate (30.0 mg, 0.20 mmol), **3** (36.9 mg, 0.10 mmol), methyl vinyl ketone (**2**, 35.0 mg, 0.50 mmol), and benzaldehyde (31.8 mg, 0.30 mmol). The crude mixture was purified by silica gel column chromatography (Hexane/EtOAc = 10:0 to 9:1) and gel permeation chromatography to give the titled compound as a colorless oil (13.8 mg, 0.060 mmol, 60% yield, *Z*/*E* = 13:1).

Spectral data of the *Z* isomer were reported.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.31 (m, 2H), 7.27-7.22 (m, 3H), 6.49 (d, *J* = 11.7 Hz, 1H), 5.56 (dt, *J* = 11.7, 6.9 Hz, 1H), 2.69-2.53 (m, 2H), 2.51-2.43 (m, 1H), 2.07 (s, 3H), 1.58-1.44 (m, 2H), 1.29-1.22 (m, 1H), 0.88 (d, *J* = 6.4 Hz, 3H), 0.86 (d, *J* = 6.4 Hz, 3H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 212.3, 137.1, 130.7, 129.1, 128.7 (2C), 128.2 (2C), 126.8, 51.4, 40.5, 30.8, 28.6, 26.0, 22.9, 22.3 ppm; **HRMS** (ESI) m/z: [M+Na$^+$] Calcd for $C_{16}H_{22}ONa^+$ 253.1563, Found 253.1558; **IR** (ATR): 2955, 2928, 2870, 1709, 1368, 1353, 1163, 771, 698 cm^{-1}.

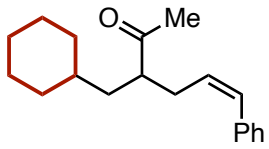


14
Z/*E* = 12:1

Compound **14** was prepared from potassium cyclopentyltrifluoroborate (35.2 mg, 0.20 mmol), **3** (36.9 mg, 0.10 mmol), methyl vinyl ketone (**2**, 35.0 mg, 0.50 mmol), and benzaldehyde (31.8 mg, 0.30 mmol). The crude mixture was purified by silica gel column chromatography (Hexane/EtOAc = 10:0 to 9:1) and gel permeation chromatography to give the titled compound as a colorless oil (14.8 mg, 0.058 mmol, 58% yield, *Z*/*E* = 12:1).

Spectral data of the *Z* isomer were reported.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.30 (m, 2H), 7.26-7.21 (m, 3H), 6.48 (d, *J* = 11.7 Hz, 1H), 5.55 (dt, *J* = 11.7, 7.3 Hz, 1H), 2.67-2.45 (m, 3H), 2.08 (s, 3H), 1.77-1.36 (m, 9H), 1.07-1.01 (m, 2H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 212.4, 137.1, 130.7, 129.2, 128.7 (2C), 128.2 (2C), 126.8, 52.7, 38.0, 37.7, 33.0, 32.6, 30.7, 28.8, 25.04, 24.99 ppm; **HRMS** (ESI) m/z: [M+Na$^+$] Calcd for $C_{18}H_{24}ONa^+$ 279.1719, Found 279.1715; **IR** (ATR): 2946, 2866, 1709, 1448, 1352, 1163, 771, 698 cm^{-1}.



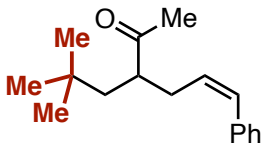
15

Z/*E* = 12:1

Compound **15** was prepared from potassium cyclohexyltrifluoroborate (38.0 mg, 0.20 mmol), **3** (36.9 mg, 0.10 mmol), methyl vinyl ketone (**2**, 35.0 mg, 0.50 mmol), and benzaldehyde (31.8 mg, 0.30 mmol). The crude mixture was purified by silica gel column chromatography (Hexane/EtOAc = 10:0 to 9:1) and gel permeation chromatography to give the titled compound as a colorless oil (13.8 mg, 0.054 mmol, 54% yield, *Z*/*E* = 12:1).

Spectral data of the *Z* isomer were reported.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.31 (m, 2H), 7.27-7.22 (m, 3H), 6.48 (d, *J* = 11.7 Hz, 1H), 5.55 (dt, *J* = 11.7, 7.3 Hz, 1H), 2.71-2.64 (m, 1H), 2.60-2.52 (m, 1H), 2.50-2.42 (m, 1H), 2.07 (s, 3H), 1.72-1.60 (m, 5H), 1.52 (ddd, *J* = 14.2, 7.8, 6.4 Hz, 1H), 1.27 (ddd, *J* = 13.7, 7.8, 6.0 Hz, 1H), 1.21-1.08 (m, 4H), 0.88-0.78 (m, 2H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 212.4, 137.1, 130.7, 129.2, 128.7 (2C), 128.2 (2C), 126.8, 50.7, 39.0, 35.4, 33.6, 33.2, 30.7, 28.6, 26.4, 26.1 (2C) ppm; **HRMS** (ESI) m/z: [M+Na^+] Calcd for $C_{19}H_{26}ONa^+$ 293.1876, Found 293.1874; **IR** (ATR): 2921, 2850, 1709, 1448, 1353, 1161, 770, 698 cm^{-1}.



16

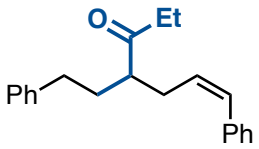
Z/*E* = 12:1

Compound **16** was prepared from potassium *t*-butyltrifluoroborate (32.8 mg, 0.20 mmol), **3** (36.9 mg, 0.10 mmol), methyl vinyl ketone (**2**, 35.0 mg, 0.50 mmol), and benzaldehyde (31.8 mg, 0.30 mmol). The crude mixture was purified by silica gel column chromatography (Hexane/EtOAc = 10:0 to 9:1) and gel permeation chromatography to give the titled compound as a colorless oil (16.3 mg, 0.067 mmol, 67% yield, *Z*/*E* = 12:1).

Spectral data of the *Z* isomer were reported.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.32 (m, 2H), 7.26-7.22 (m, 3H), 6.51 (d, *J* = 11.6 Hz, 1H), 5.55 (ddd, *J* = 11.6, 7.1, 7.1 Hz, 1H), 2.65 (dddd, *J* = 8.8, 7.0, 6.9, 2.5 Hz, 1H), 2.55 (dddd, *J* = 15.1, 7.1, 6.9, 1.8 Hz, 1H), 2.41 (dddd, *J* = 15.1, 7.1, 7.0, 1.8 Hz, 1H), 2.11 (s, 3H), 1.83 (dd, *J* = 14.2, 8.8 Hz,

1H), 1.22 (dd, J = 14.2, 2.5 Hz, 1H), 0.84 (s, 9H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 212.3, 137.0, 131.0, 129.0, 128.7 (2C), 128.2 (2C), 126.8, 49.8, 44.3, 32.6, 30.8, 29.6 (3C), 28.8 ppm; **HRMS** (ESI) m/z: [M+Na$^+$] Calcd for $C_{17}H_{24}ONa^+$ 267.1719, Found 267.1717; **IR** (ATR): 2954, 2927, 2867, 1712, 1366, 1353, 1157, 769, 699 cm^{-1}.

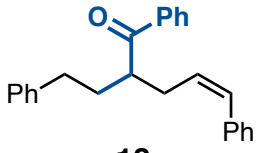


17
Z/*E* = 16:1

Compound **17** was prepared from potassium benzyltrifluoroborate (**1**, 39.9 mg, 0.20 mmol), **3** (36.9 mg, 0.10 mmol), ethyl vinyl ketone (42.1 mg, 0.50 mmol), and benzaldehyde (31.8 mg, 0.30 mmol). The crude mixture was purified by silica gel column chromatography (Hexane/EtOAc = 10:0 to 9:1) and gel permeation chromatography to give the titled compound as a colorless oil (15.6 mg, 0.053 mmol, 53% yield, *Z*/*E* = 16:1).

Spectral data of the *Z* isomer were reported.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.16 (m, 8H), 7.12-7.10 (m, 2H), 6.48 (d, J = 11.4 Hz, 1H), 5.54 (d, J = 11.4, 7.3 Hz, 1H), 2.65-2.48 (m, 5H), 2.46-2.33 (m, 2H), 2.04-1.92 (m, 1H), 1.80-1.70 (m, 1H), 1.01 (t, J = 7.3 Hz, 3H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 214.1, 141.5, 137.0, 130.8, 129.0, 128.7 (2C), 128.4 (2C), 128.3 (2C), 128.2 (2C), 126.8, 125.9, 51.5, 35.5, 33.4, 32.7, 30.3, 7.6 ppm; **HRMS** (ESI) m/z: [M+Na$^+$] Calcd for $C_{21}H_{24}ONa^+$ 315.1719, Found 315.1715; **IR** (ATR): 3025, 2973, 2936, 1708, 1494, 1454, 769, 748, 697 cm^{-1}.

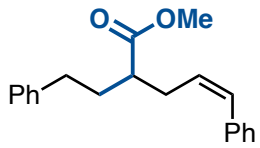


18
Z/*E* = 14:1

Compound **18** was prepared from potassium benzyltrifluoroborate (**1**, 39.9 mg, 0.20 mmol), **3** (36.9 mg, 0.10 mmol), phenyl vinyl ketone (66.1 mg, 0.50 mmol), and benzaldehyde (31.8 mg, 0.30 mmol). The crude mixture was purified by silica gel column chromatography (Hexane/EtOAc = 10:0 to 9:1) and gel permeation chromatography to give the titled compound as a colorless oil (17.8 mg, 0.052 mmol, 52% yield, *Z*/*E* = 14:1).

Spectral data of the *Z* isomer were reported.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88-7.85 (m, 2H), 7.59-7.55 (m, 1H), 7.47-7.42 (m, 2H), 7.34-7.31 (m, 2H), 7.27-7.18 (m, 6H), 7.06 (d, *J* = 8.7 Hz, 2H), 6.46 (d, *J* = 11.4 Hz, 1H), 5.60 (dt, *J* = 11.4, 6.9 Hz, 1H), 3.58-3.51 (m, 1H), 2.81-2.73 (m, 1H), 2.69-2.47 (m, 3H), 2.20-2.11 (m, 1H), 1.91-1.82 (m, 1H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 203.3, 141.5, 137.1, 137.0, 133.0, 130.8, 129.2, 128.7 (2C), 128.6 (2C), 128.4 (2C), 128.33 (2C), 128.28 (2C), 128.2 (2C), 126.7, 125.9, 45.5, 33.3, 33.2, 30.8 ppm; **HRMS** (ESI) m/z: [M+Na$^+$] Calcd for $C_{25}H_{24}ONa^+$ 363.1719, Found 363.1715; **IR** (ATR): 3059, 3024, 2926, 1677, 1495, 1447, 1228, 769, 749, 696 cm^{-1}.

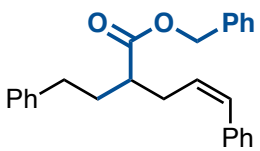


19
Z/*E* = 12:1

Compound **19** was prepared from potassium benzyltrifluoroborate (**1**, 39.9 mg, 0.20 mmol), **3** (36.9 mg, 0.10 mmol), methyl acrylate (43.0 mg, 0.50 mmol), and benzaldehyde (31.8 mg, 0.30 mmol). The irradiation time was 7 h. The crude mixture was purified by silica gel column chromatography (Hexane/EtOAc = 10:0 to 9:1) and gel permeation chromatography to give the titled compound as a colorless oil (12.8 mg, 0.044 mmol, 44% yield, *Z*/*E* = 12:1).

Spectral data of the *Z* isomer were reported.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.12 (m, 10H), 6.49 (d, *J* = 11.9 Hz, 1H), 5.57 (dt, *J* = 11.5, 6.9 Hz, 1H), 3.67 (s, 3H), 2.70-2.51 (m, 5H), 2.03-1.93 (m, 1H), 1.84-1.76 (m, 1H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 175.8, 141.4, 137.1, 130.8, 128.8, 128.7 (2C), 128.4 (2C), 128.3 (2C), 128.2 (2C), 126.8, 125.9, 51.6, 45.2, 33.5, 33.3, 30.9 ppm; **HRMS** (ESI) m/z: [M+Na$^+$] Calcd for $C_{20}H_{22}O_2Na^+$ 317.1512, Found 317.1508; **IR** (ATR): 3025, 2949, 1732, 1495, 1447, 1193, 1159, 770, 748, 697 cm^{-1}.

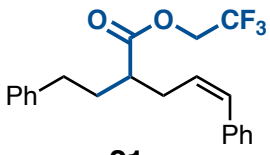


20
Z/*E* = 16:1

Compound **20** was prepared from potassium benzyltrifluoroborate (**1**, 39.9 mg, 0.20 mmol), **3** (36.9 mg, 0.10 mmol), benzyl acrylate (81.1 mg, 0.50 mmol), and benzaldehyde (31.8 mg, 0.30 mmol). The irradiation time was 7 h. The crude mixture was purified by silica gel column chromatography (Hexane/EtOAc = 10:0 to 9:1) and gel permeation chromatography to give the titled compound as a colorless oil (12.8 mg, 0.035 mmol, 35% yield, *Z*/*E* = 16:1).

Spectral data of the *Z* isomer were reported.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.30 (m, 7H), 7.27-7.21 (m, 5H), 7.19-7.14 (m, 1H), 7.07 (d, *J* = 6.9 Hz, 2H), 6.47 (d, *J* = 11.4 Hz, 1H), 5.58 (dt, *J* = 11.9, 6.9 Hz, 1H), 5.11 (s, 2H), 2.73-2.66 (m, 1H), 2.63-2.46 (m, 4H), 2.04-1.95 (m, 1H), 1.85-1.77 (m, 1H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 175.1, 141.4, 137.1, 136.0, 130.8, 128.8, 128.7 (2C), 128.5 (2C), 128.4 (2C), 128.3 (2C), 128.25 (2C), 128.19 (3C), 126.8, 125.9, 66.2, 45.3, 33.4 (2C), 30.9 ppm; **HRMS** (ESI) m/z: [M+Na^+] Calcd for $C_{26}H_{26}O_2Na^+$ 393.1825, Found 393.1820; **IR** (ATR): 3026, 2928, 1729, 1496, 1455, 1146, 770, 747, 695 cm^{-1}.

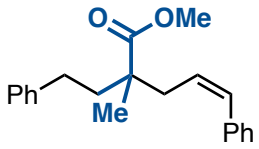


21
Z/*E* = 16:1

Compound **21** was prepared from potassium benzyltrifluoroborate (**1**, 39.9 mg, 0.20 mmol), **3** (36.9 mg, 0.10 mmol), 2,2,2-trifluoroethyl acrylate (77.0 mg, 0.50 mmol), and benzaldehyde (31.8 mg, 0.30 mmol). The irradiation time was 7 h. The crude mixture was purified by silica gel column chromatography (Hexane/EtOAc = 10:0 to 9:1) and gel permeation chromatography to give the titled compound as a colorless oil (17.9 mg, 0.049 mmol, 49% yield, *Z*/*E* = 16:1).

Spectral data of the *Z* isomer were reported.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.16 (m, 8H), 7.13-7.11 (m, 2H), 6.52 (d, *J* = 11.4 Hz, 1H), 5.56 (dt, *J* = 11.9, 6.9 Hz, 1H), 4.46 (dq, *J* = 8.2, 1.1 Hz, 1H), 4.41 (dq, *J* = 8.2, 1.1 Hz, 1H), 2.75-2.49 (m, 5H), 2.06-1.96 (m, 1H), 1.89-1.80 (m, 1H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 173.7, 141.0, 136.9, 131.3, 128.6 (2C), 128.41 (2C), 128.38 (2C), 128.2 (2C), 128.0, 126.9, 126.1, 122.9 (q, *J* = 277 Hz), 60.1 (q, *J* = 36 Hz), 44.8, 33.3, 33.1, 30.6 ppm; **^{19}F NMR** (376 MHz, $CDCl_3$): δ –73.5 (t, *J* = 8.7 Hz) ppm; **HRMS** (ESI) m/z: [M+Na^+] Calcd for $C_{21}H_{21}F_3O_2Na^+$ 385.1386, Found 385.1381; **IR** (ATR): 3026, 2931, 1752, 1496, 1456, 1410, 1280, 1164, 1135, 1074, 974, 770, 749, 697 cm^{-1}.



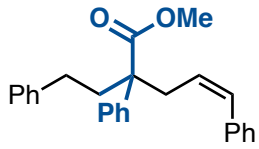
22

Z/*E* = 10:1

Compound **22** was prepared from potassium benzyltrifluoroborate (**1**, 39.9 mg, 0.20 mmol), **3** (36.9 mg, 0.10 mmol), methyl methacrylate (50.0 mg, 0.50 mmol), and benzaldehyde (31.8 mg, 0.30 mmol). The irradiation time was 7 h. The crude mixture was purified by silica gel column chromatography (Hexane/EtOAc = 10:0 to 9:1) and gel permeation chromatography to give the titled compound as a colorless oil (14.8 mg, 0.048 mmol, 48% yield, *Z*/*E* = 10:1).

Spectral data of the *Z* isomer were reported.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.30 (m, 2H), 7.27-7.21 (m, 5H), 7.18-7.11 (m, 3H), 6.54 (d, *J* = 11.9 Hz, 1H), 5.61 (dt, *J* = 11.9, 7.3 Hz, 1H), 3.65 (s, 3H), 2.72 (ddd, *J* = 15.1, 6.9, 1.8 Hz, 1H), 2.60 (ddd, *J* = 15.1, 7.3, 1.8 Hz, 1H), 2.50 (ddd, *J* = 13.3, 12.4, 5.0 Hz, 1H), 2.40 (ddd, *J* = 12.8, 12.8, 5.0 Hz, 1H), 1.96 (ddd, *J* = 13.3, 12.4, 5.0 Hz, 1H), 1.77 (ddd, *J* = 13.7, 12.4, 5.5 Hz, 1H), 1.23 (s, 3H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 177.2, 142.0, 137.3, 131.3, 128.7 (2C), 128.32 (2C), 128.28 (2C), 128.2 (2C), 127.4, 126.7, 125.8, 51.8, 46.2, 40.8, 37.1, 31.1, 21.5 ppm; **HRMS** (ESI) m/z: [M+Na$^+$] Calcd for $C_{21}H_{24}O_2Na^+$ 331.1669, Found 331.1664; **IR** (ATR): 3025, 2949, 1727, 1496, 1455, 1196, 1174, 1112, 1071, 763, 747, 697 cm^{-1}.



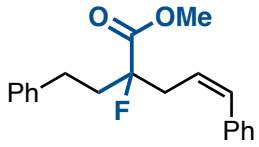
23

Z/*E* = 4:1

Compound **23** was prepared from potassium benzyltrifluoroborate (**1**, 39.9 mg, 0.20 mmol), **3** (36.9 mg, 0.10 mmol), methyl 2-phenylacrylate (81.0 mg, 0.50 mmol), and benzaldehyde (31.8 mg, 0.30 mmol). The irradiation time was 7 h. The crude mixture was purified by silica gel column chromatography (Hexane/EtOAc = 10:0 to 9:1) and gel permeation chromatography to give the titled compound as a colorless oil (16.5 mg, 0.045 mmol, 45% yield, *Z*/*E* = 4:1).

Spectral data of the *Z* isomer were reported.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.20 (m, 12H), 7.17-7.11 (m, 1H), 6.99-6.97 (m, 2H), 6.55 (d, *J* = 11.9 Hz, 1H), 5.41 (ddd, *J* = 11.9, 7.8, 6.4 Hz, 1H), 3.64 (s, 3H), 3.29 (ddd, *J* = 15.6, 7.8, 1.8 Hz, 1H), 3.10 (ddd, *J* = 15.1, 6.9, 1.8 Hz, 1H), 2.37-2.09 (m, 4H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 175.8, 142.0, 141.7, 137.2, 131.7, 128.7 (2C), 128.5 (2C), 128.30 (2C), 128.26 (4C), 127.0 (2C), 126.8, 126.5 (2C), 125.8, 53.9, 52.2, 36.8, 33.2, 30.6 ppm; **HRMS** (ESI) m/z: [M+Na^+] Calcd for $C_{26}H_{26}O_2Na^+$ 393.1825, Found 393.1819; **IR** (ATR): 2968, 1726, 1496, 1446, 1173, 1057, 751, 697cm^{-1}.

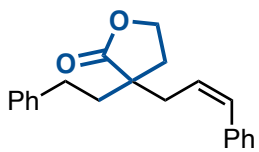


24
Z/*E* = 18:1

Compound **24** was prepared from potassium benzyltrifluoroborate (**1**, 39.9 mg, 0.20 mmol), **3** (36.9 mg, 0.10 mmol), methyl 2-fluoroacrylate (52.0 mg, 0.50 mmol), and benzaldehyde (31.8 mg, 0.30 mmol). The irradiation time was 7 h. The crude mixture was purified by silica gel column chromatography (Hexane/EtOAc = 10:0 to 9:1) and gel permeation chromatography to give the titled compound as a colorless oil (12.5 mg, 0.042 mmol, 42% yield, *Z*/*E* = 18:1).

Spectral data of the *Z* isomer were reported.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.32 (m, 2H), 7.30-7.24 (m, 5H), 7.21-7.14 (m, 3H), 6.63 (d, *J* = 11.4 Hz, 1H), 5.71 (d, *J* = 11.9, 7.3 Hz, 1H), 3.70 (s, 3H), 3.03-2.86 (m, 2H), 2.81 (ddd, *J* = 13.7, 11.0, 6.0 Hz, 1H), 2.53 (ddd, *J* = 13.7, 11.0, 6.0 Hz, 1H), 2.30-2.13 (m, 2H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 171.4 (d, *J* = 26 Hz), 140.6, 136.7, 132.9, 128.6 (2C), 128.44 (2C), 128.35 (2C), 128.3 (2C), 127.0, 126.1, 123.5 (d, *J* = 4 Hz), 96.8 (d, *J* = 191 Hz), 52.4, 38.7 (d, *J* = 22 Hz), 36.2 (d, *J* = 22 Hz), 29.5 ppm; **^{19}F NMR** (376 MHz, $CDCl_3$): δ –166.0 (m) ppm; **HRMS** (ESI) m/z: [M+Na^+] Calcd for $C_{20}H_{21}FO_2Na^+$ 335.1418, Found 335.1413; **IR** (ATR): 3026, 2955, 1759, 1737, 1496, 1439, 1260, 1206, 1088, 1060, 750, 697 cm^{-1}.

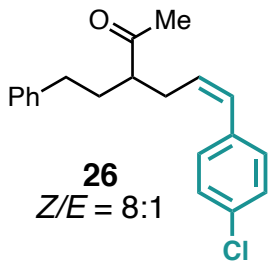


25
Z/*E* = 10:1

Compound **25** was prepared from potassium benzyltrifluoroborate (**1**, 39.9 mg, 0.20 mmol), **3** (36.9 mg, 0.10 mmol), α-methylene-γ-butyrolactone (49.1 mg, 0.50 mmol), and benzaldehyde (31.8 mg, 0.30 mmol). The irradiation time was 7 h. The crude mixture was purified by silica gel column chromatography (Hexane/EtOAc = 10:0 to 9:1), gel permeation chromatography, and preparative thin-layer chromatography (Hexane/EtOAc = 20:1) to give the titled compound as white solids (16.6 mg, 0.054 mmol, 54% yield, *Z*/*E* = 10:1).

Spectral data of the *Z* isomer were reported.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.33 (m, 2H), 7.28-7.24 (m, 5H), 7.20-7.16 (m, 1H), 7.11 (d, *J* = 7.3 Hz, 2H), 6.67 (d, *J* = 11.9 Hz, 1H), 5.66 (ddd, *J* = 11.9, 8.2, 6.4 Hz, 1H), 4.29-4.20 (m, 2H), 2.79 (ddd, *J* = 15.1, 8.2, 1.4 Hz, 1H), 2.67-2.59 (m, 2H), 2.56-2.46 (m, 1H), 2.23-2.11 (m, 2H), 1.97-1.84 (m, 2H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 180.5, 141.2, 136.7, 132.8, 128.7 (2C), 128.5 (2C), 128.3 (2C), 128.2 (2C), 127.0, 126.1, 126.0, 65.3, 46.2, 37.8, 34.0, 32.0, 30.6 ppm; **HRMS** (ESI) m/z: [M+Na^+] Calcd for $C_{21}H_{22}O_2Na^+$ 329.1512, Found 329.1507; **IR** (ATR): 2974, 2904, 1733, 1541, 1057, 696, 607 cm^{-1}.



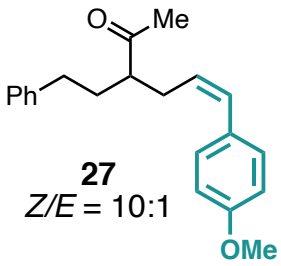
26
Z/*E* = 8:1

Compound **26** was prepared from potassium benzyltrifluoroborate (**1**, 39.9 mg, 0.20 mmol), **3** (36.9 mg, 0.10 mmol), methyl vinyl ketone (**2**, 35.0 mg, 0.50 mmol), and 4-chlorobenzaldehyde (42.2 mg, 0.30 mmol). The crude mixture was purified by silica gel column chromatography (Hexane/EtOAc = 10:0 to 9:1) and gel permeation chromatography to give the titled compound as a colorless oil (20.5 mg, 0.066 mmol, 66% yield, *Z*/*E* = 8:1).

Spectral data of the *Z* isomer were reported.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.23 (m, 4 H), 7.21-7.15 (m, 3H), 7.11 (d, *J* = 6.9 Hz, 2H), 6.43 (d, *J* = 11.9 Hz, 1H), 5.56 (dt, *J* = 11.5, 6.9 Hz, 1H), 2.64-2.46 (m, 5H), 2.08 (s, 3H), 2.01-1.92 (m, 1H), 1.79-1.70 (m, 1H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 211.4, 141.3, 135.4, 132.6, 130.0 (2C), 129.7, 129.6, 128.44 (2C), 128.41 (2C), 128.3 (2C), 126.0, 52.3, 33.2, 32.5, 29.9, 29.1 ppm;

HRMS (ESI) m/z: [M+Na$^+$] Calcd for $C_{20}H_{21}ClONa^+$ 335.1170, Found 335.1173; **IR** (ATR): 3024, 2926, 1708, 1490, 1352, 1159, 1090, 1012, 843, 748, 698 cm^{-1}.

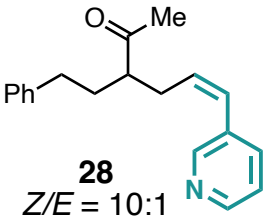


27
Z/*E* = 10:1

Compound **27** was prepared from potassium benzyltrifluoroborate (**1**, 39.9 mg, 0.20 mmol), **3** (36.9 mg, 0.10 mmol), methyl vinyl ketone (**2**, 35.0 mg, 0.50 mmol), and 4-methoxybenzaldehyde (40.8 mg, 0.30 mmol). The crude mixture was purified by silica gel column chromatography (Hexane/EtOAc = 10:0 to 9:1) and gel permeation chromatography to give the titled compound as a colorless oil (10.1 mg, 0.033 mmol, 33% yield, *Z*/*E* = 10:1).

Spectral data of the *Z* isomer were reported.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.25 (m, 2H), 7.20-7.18 (m, 3H), 7.12 (d, *J* = 7.3 Hz, 2H), 6.88-6.82 (m, 2H), 6.43 (d, *J* = 11.4 Hz, 1H), 5.48-5.41 (m, 1H), 3.81 (s, 3H), 2.64-2.50 (m, 5H), 2.09 (s, 3H), 2.02-1.92 (m, 1H), 1.80-1.71 (m, 1H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 211.7, 158.4, 141.5, 130.3, 129.9 (2C), 129.7, 128.4 (2C), 128.3 (2C), 127.3, 126.0, 113.6 (2C), 55.2, 52.5, 33.3, 32.5, 30.1, 29.0 ppm; **HRMS** (ESI) m/z: [M+Na$^+$] Calcd for $C_{21}H_{24}O_2Na^+$ 331.1669, Found 331.1662; **IR** (ATR): 3004, 2932, 2836, 1707, 1607, 1509, 1245, 1175, 1032, 839, 750, 699 cm^{-1}.

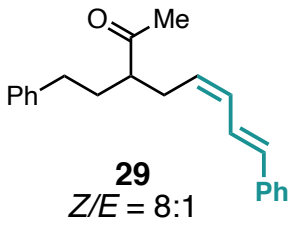


28
Z/*E* = 10:1

Compound **28** was prepared from potassium benzyltrifluoroborate (**1**, 39.9 mg, 0.20 mmol), **3** (36.9 mg, 0.10 mmol), methyl vinyl ketone (**2**, 35.0 mg, 0.50 mmol), and 3-pyridinecarboxaldehyde (32.1 mg, 0.30 mmol). The crude mixture was purified by silica gel column chromatography (Hexane/EtOAc = 10:0 to 5:5) and gel permeation chromatography to give the titled compound as an yellowish oil (18.6 mg, 0.067 mmol, 67% yield, *Z*/*E* = 10:1).

Spectral data of the *Z* isomer were reported.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.62 (broad s, 2H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.36 (s, 1H), 7.29-7.25 (m, 2H), 7.22-7.15 (m, 1H), 7.12-7.10 (m, 2H), 6.46 (d, *J* = 11.4 Hz, 1H), 5.71 (d, *J* = 11.9, 6.9 Hz, 1H), 2.67-2.44 (m, 5H), 2.10 (s, 3H), 2.02-1.93 (m, 1H), 1.79-1.70 (m, 1H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 211.1, 149.1, 147.1, 141.2, 136.3, 131.8, 128.4 (2C), 128.34, 128.30 (2C), 127.0, 126.1, 123.9, 52.1, 33.2, 32.5, 29.9, 29.2 ppm; **HRMS** (ESI) m/z: [M+Na$^+$] Calcd for $C_{19}H_{21}NONa^+$ 302.1515, Found 302.1510; **IR** (ATR): 3025, 2925, 2855, 1706, 1353, 1160, 1025, 826, 750, 699, 619 cm^{-1}.

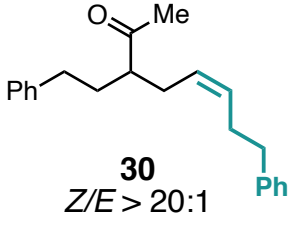


29
Z/*E* = 8:1

Compound **29** was prepared from potassium benzyltrifluoroborate (**1**, 39.9 mg, 0.20 mmol), **3** (36.9 mg, 0.10 mmol), methyl vinyl ketone (**2**, 35.0 mg, 0.50 mmol), and trans-cinnamaldehyde (39.6 mg, 0.30 mmol). The crude mixture was purified by silica gel column chromatography (Hexane/EtOAc = 10:0 to 9:1) and gel permeation chromatography to give the titled compound as a colorless oil (16.2 mg, 0.053 mmol, 53% yield, *Z*/*E* = 8:1).

Spectral data of the *Z* isomer were reported.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.40 (m, 2H), 7.34-7.15 (m, 8H), 7.01 (ddd, *J* = 15.6, 11.1, 1.0 Hz, 1H), 6.55 (d, *J* = 15.6 Hz, 1H), 6.22 (dd, *J* = 11.0, 11.0 Hz, 1H), 5.40 (dt, *J* = 10.5, 7.8 Hz, 1H), 2.68-2.53 (m, 4H), 2.51-2.43 (m, 1H), 2.15 (s, 3H), 2.07-1.98 (m, 1H), 1.83-1.75 (m, 1H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 211.7, 141.4, 137.2, 133.3, 130.7, 128.6 (3C), 128.4 (2C), 128.3 (2C), 127.6, 126.4 (2C), 126.0, 123.6, 52.1, 33.4, 32.6, 29.8, 29.6 ppm; **HRMS** (ESI) m/z: [M+Na$^+$] Calcd for $C_{22}H_{24}ONa^+$ 327.1719, Found 327.1711; **IR** (ATR): 3026, 2925, 1707, 1493, 1451, 1351,1158, 987, 948, 746, 692 cm^{-1}.



30
Z/*E* > 20:1

Compound **30** was prepared from potassium benzyltrifluoroborate (**1**, 39.9 mg, 0.20 mmol), **3** (36.9 mg, 0.10 mmol), methyl vinyl ketone (**2**, 35.0 mg, 0.50 mmol), and 3-phenylpropionaldehyde (40.2 mg, 0.30 mmol). The crude mixture was purified by silica gel column chromatography (Hexane/EtOAc = 10:0 to 9:1) and gel permeation chromatography to give the titled compound as a colorless oil (15.4 mg, 0.050 mmol, 50% yield, *Z/E* > 20:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.24 (m, 4H), 7.21-7.13 (m, 6H), 5.51-5.44 (m, 1H), 5.31-5.24 (m, 1H), 2.68-2.61 (m, 2H), 2.59-2.40 (m, 3H), 2.37-2.23 (m, 3H), 2.17-2.09 (m, 1H), 2.07 (s, 3H), 1.96-1.87 (m, 1H), 1.71-1.62 (m, 1H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 212.0, 141.7, 141.6, 131.0, 128.5 (2C), 128.4 (2C), 128.32 (2C), 128.27 (2C), 126.7, 126.0, 125.8, 52.1, 35.7, 33.4, 32.6, 29.5, 29.2 (2C) ppm; **HRMS** (ESI) m/z: [M+Na^+] Calcd for $C_{22}H_{26}ONa^+$ 329.1876, Found 329.1871; **IR** (ATR): 3062, 3026, 2924, 2858, 1709, 1496, 1454, 748, 697 cm^{-1}.

6. Unsuccessful substrates

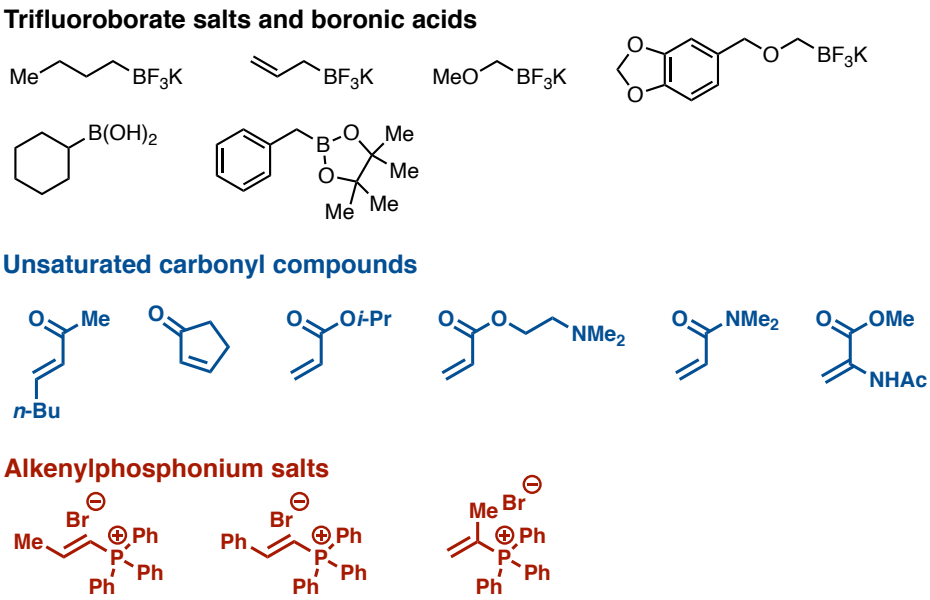


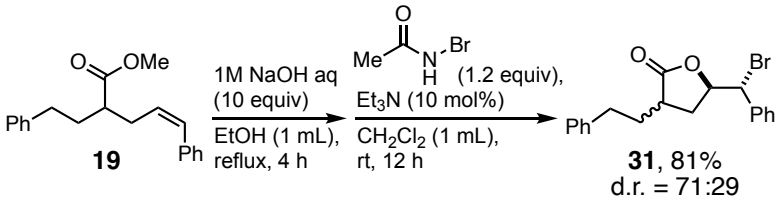
Figure S8. Unsuccessful substrates

7. Synthetic application

1 mmol Scale reaction for synthesis of 16

To an oven-dried 50 mL two-neck round-bottom flask equipped with a stirrer bar, Ir catalyst (22 mg, 0.02 mmol, 2.0 mol%), potassium *t*-butyltrifluoroborate (330 mg, 2.0 mmol, 2.0 equiv), and triphenylvinylphosphonium bromide (**3**, 370 mg, 1.0 mmol) were added. The flask was capped with a septum, and was evacuated and filled with argon gas three times. Methyl vinyl ketone (**2**, 350 mg, 5.0 mmol, 5.0 equiv) and anhydrous CH_2Cl_2 (20 mL) were sequentially added to the flask via syringe. The resulting suspension was stirred under photoirradiation (470 nm) at ambient temperature for 3 h. After irradiation, the solvent was removed under vacuum, and potassium phosphate (K_3PO_4, 640 mg, 3.0 mmol, 3.0 equiv) was added to the same flask, which was evacuated and refilled with argon three times. To the flask, benzaldehyde (320 mg, 3.0 mmol, 3.0 equiv) and THF (10 mL) were added, and the reaction mixture was stirred at 60 ˚C for 16 h. The reaction was quenched with water, and then, the aqueous layer was extracted with AcOEt (3 times). The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography and gel permeation chromatography to afford γ,δ-unsaturated ketone **16** as a colorless oil (115 mg, 0.47 mmol, 47% yield). The geometry of the alkene moiety (*Z/E* = 12:1) was determined by ^{1}H NMR spectroscopy.

Procedure for a sequence of hydration and bromolactonization of 19.



In a round-bottom flask equipped with a condenser, a solution of γ,δ-unsaturated ester **19** (17.6 mg, 0.06 mmol) in ethanol (EtOH, 1.0 mL) was treated with a 1M aqueous solution of NaOH (0.60 mL, 0.60 mmol, 10 equiv), and the resulting mixture was stirred at 110 ℃ for 4 h. After cooling to room temperature, the reaction was quenched with 1M HCl aq, and aqueous layer was extracted with CH_2Cl_2 (3 times). The combined organic phase was washed with brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. To a mixture of the resulting crude carboxylic acid and triethylamine (Et_3N, 0.83 μL, 0.006 mmol, 10 mol%) in CH_2Cl_2 (1.0 mL), *N*-bromoacetamide (9.9 mg, 0.07 mmol, 1.2 equiv) was added. The mixture was stirred at room temperature for 12 h. The reaction was quenched with saturated aqueous $Na_2S_2O_3$, and then, the aqueous layer was extracted with CH_2Cl_2 (3 times). The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (AcOEt/hexane = 1/4) to afford the corresponding bromolactone as a colorless oil (**31**, 17.4 mg, 0.048 mmol, 81% yield), A ratio of diastereomers was determined by ^{1}H NMR analysis (d.r. = 71:29).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45-7.25 (m, 9.8H), 7.23-7.12 (m, 4.2H), 4.98 (d, *J* = 5.0 Hz, 0.4H), 4.94-4.89 (m, 1.4H), 4.77 (ddd, *J* = 10.1, 6.4, 6.0 Hz, 1H), 2.76-2.67 (m, 1.4H), 2.64-2.56 (m, 2.4H), 2.37-2.16 (m, 2.4H), 2.15-2.06 (m, 0.4H), 2.02-1.95 (m, 0.4H), 1.73-1.59 (m, 2.8H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): (Several peaks of the minor diastereomer were overlapped with those of the major diastereomer.) δ 178.3 (minor), 177.2 (Major), 140.4 (Major), 140.3 (minor), 137.0 (Major), 136.5 (minor), 129.2 (Major), 129.1 (minor), 128.9 (Major, 2C), 128.8 (minor), 128.5 (Major, 2C), 128.41 (minor), 128.35 (Major, 2C), 128.3 (Major, 2C), 126.2 (Major), 80.3 (Major), 80.1 (minor), 55.0 (minor), 54.7 (Major), 39.8 (Major), 38.1 (minor), 33.13 (Major), 33.08 (minor), 33.0 (Major), 32.8 (minor), 31.7 (Major), 31.2 (minor) ppm; **HRMS** (ESI) m/z: [M+Na$^+$] Calcd for $C_{19}H_{19}O_2BrNa^+$ 381.0461, Found 381.0456; **IR** (ATR): 3028, 2925, 1769, 1496, 1453, 1159, 1028, 734, 696, 663 cm^{-1}.

8. References

S1 T. Rossolini, J. A. Leitch, R. Grainger, D. J. Dixon, *Org. Lett.* 2018, **20**, 6794–6798.

S2 A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, F. J. Timmers, *Organometallics* 1996, **15**, 1518–1520.

S3 H. Huo, K. Harms, E. Meggers, *J. Am. Chem. Soc.* 2016, **138**, 6936–6939.

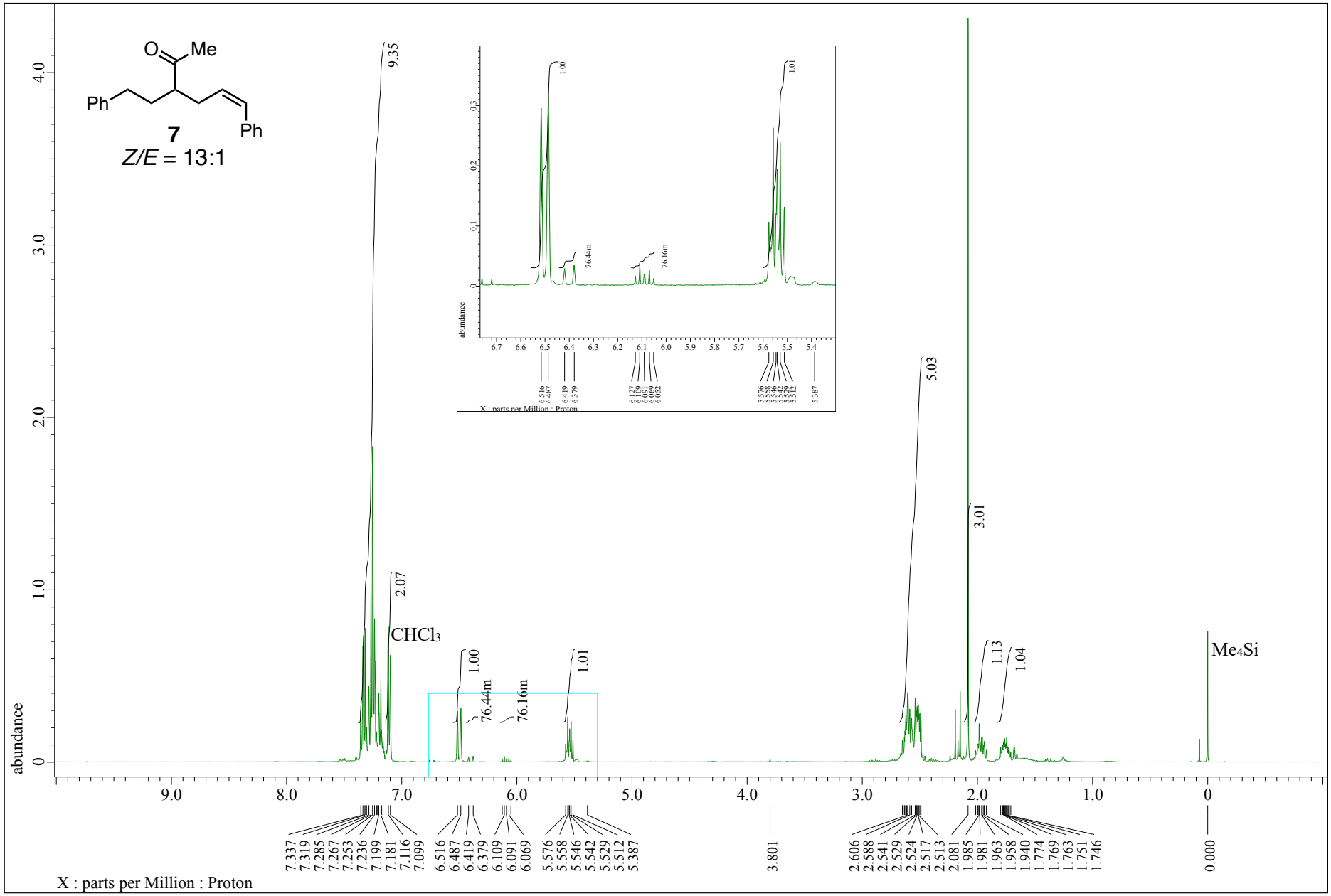
S4 B. Chen, C.-S. Kuai, J.-X. Xu, X.-F. Wu, *Adv. Synth. Catal.* 2022, **364**, 487–492.

S5 B. Zhang, P. Chakma, M. P. Shulman, J. Ke, Z. A. Digby, D. Konkolewicz, *Org. Biomol. Chem.* 2018, **16**, 2725–2734.

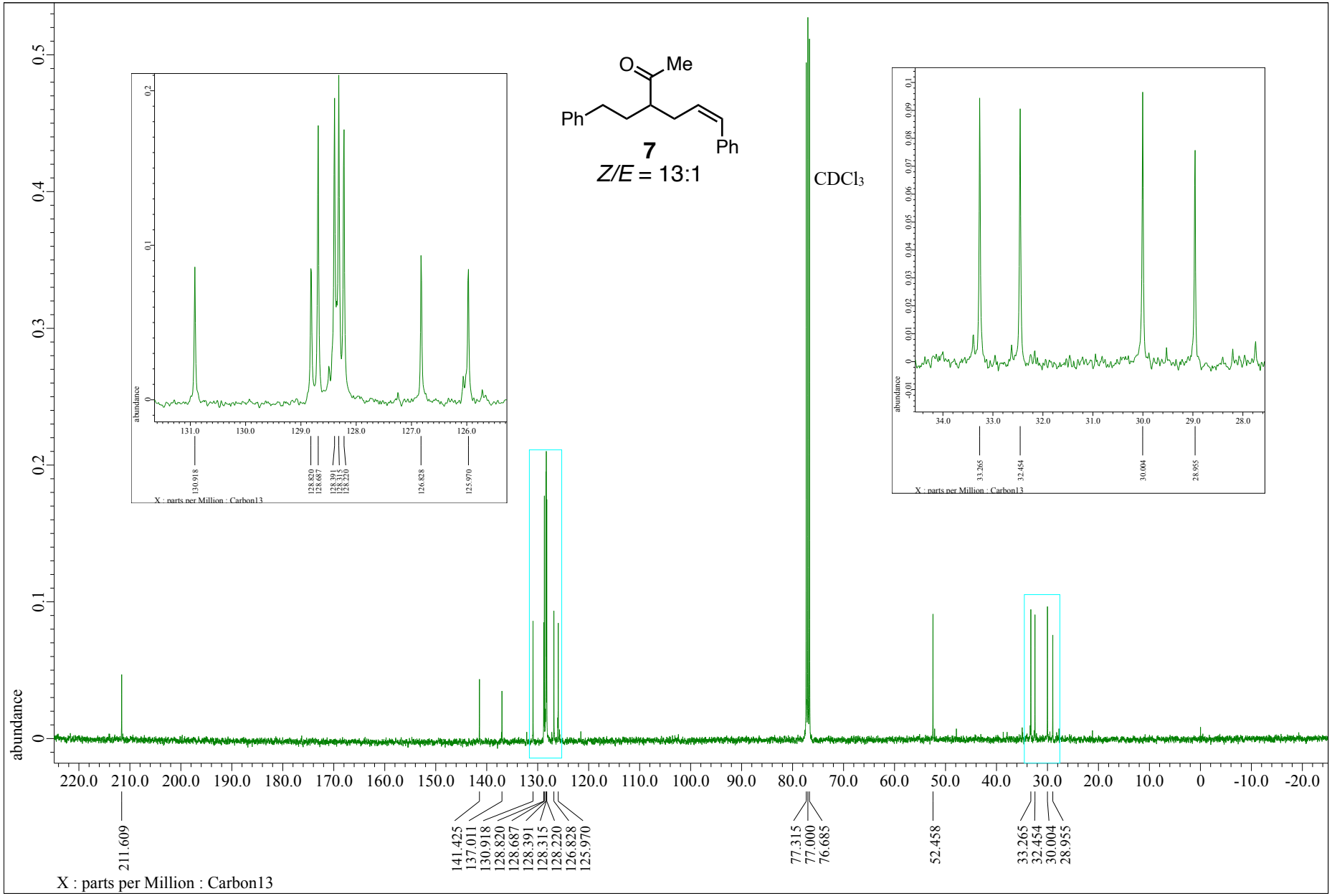
S6 J. Harnedy, M. D. Hareram, G. J. Tizzard, S. J. Colesb, L. C. Morrill, *Chem. Commun.* 2021, **57**, 12643–12646.

9. NMR spectra of new compounds

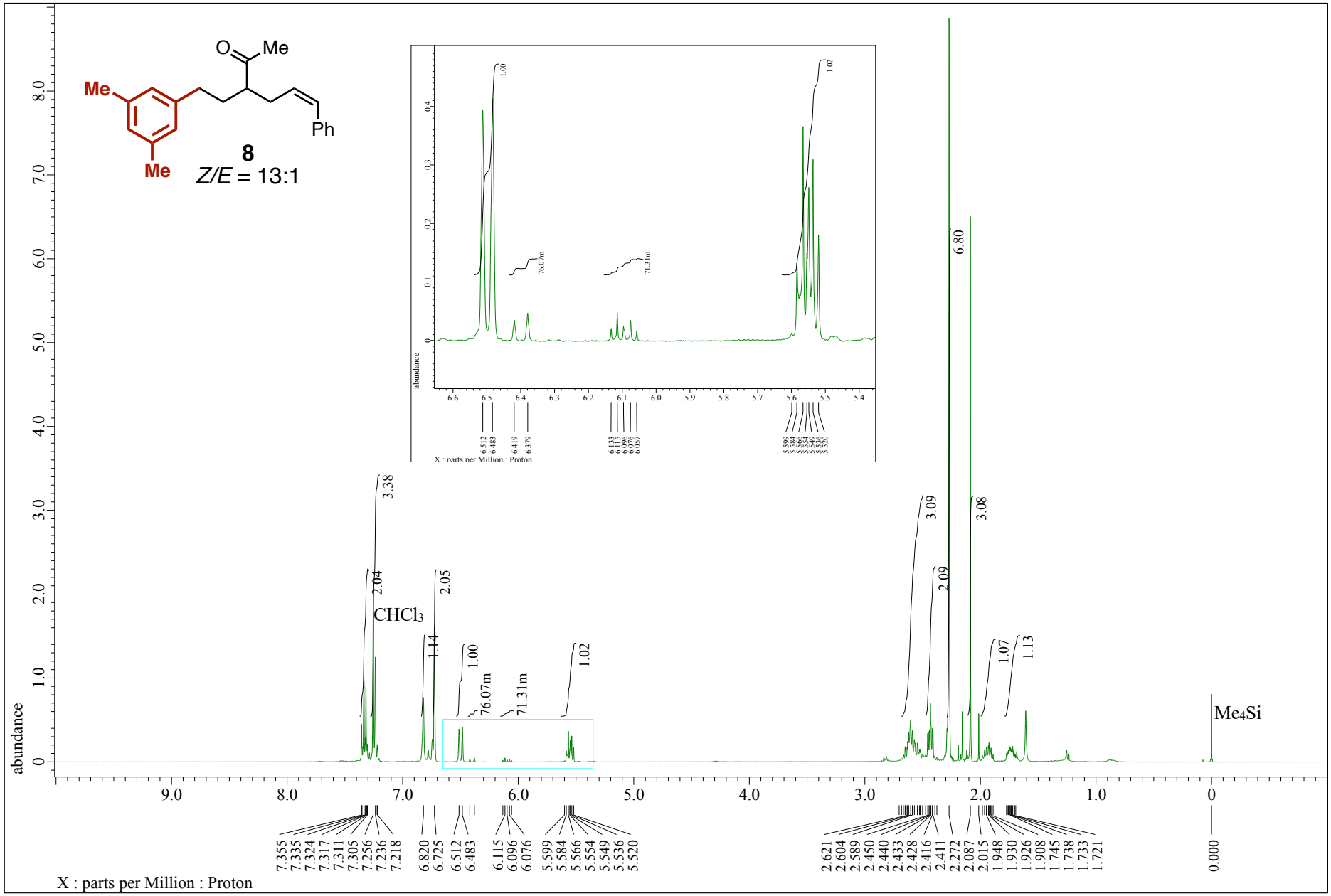
^{1}H NMR spectrum of **7** ($CDCl_3$, 400 MHz)



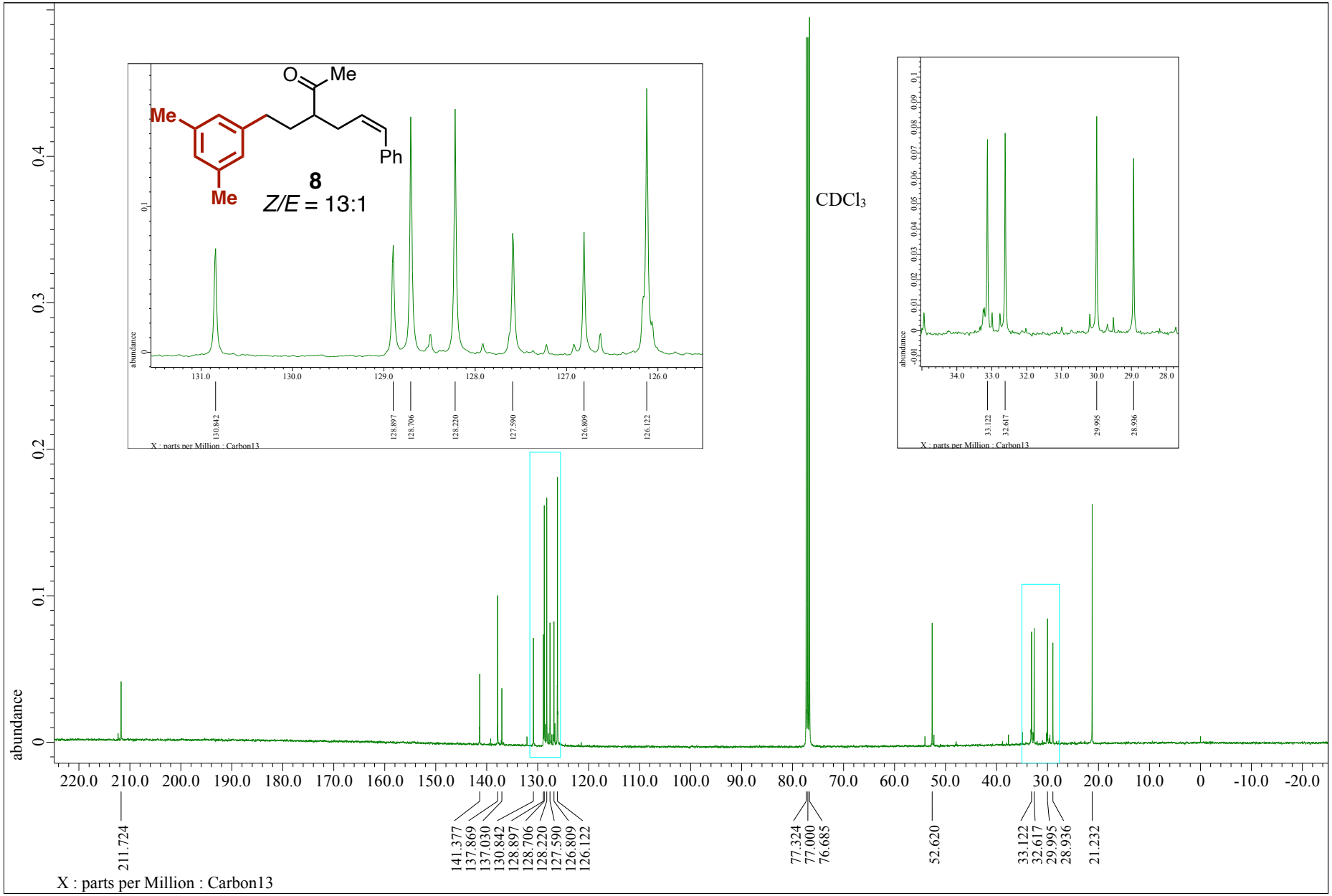
^{13}C NMR spectrum of **7** ($CDCl_3$, 101 MHz)



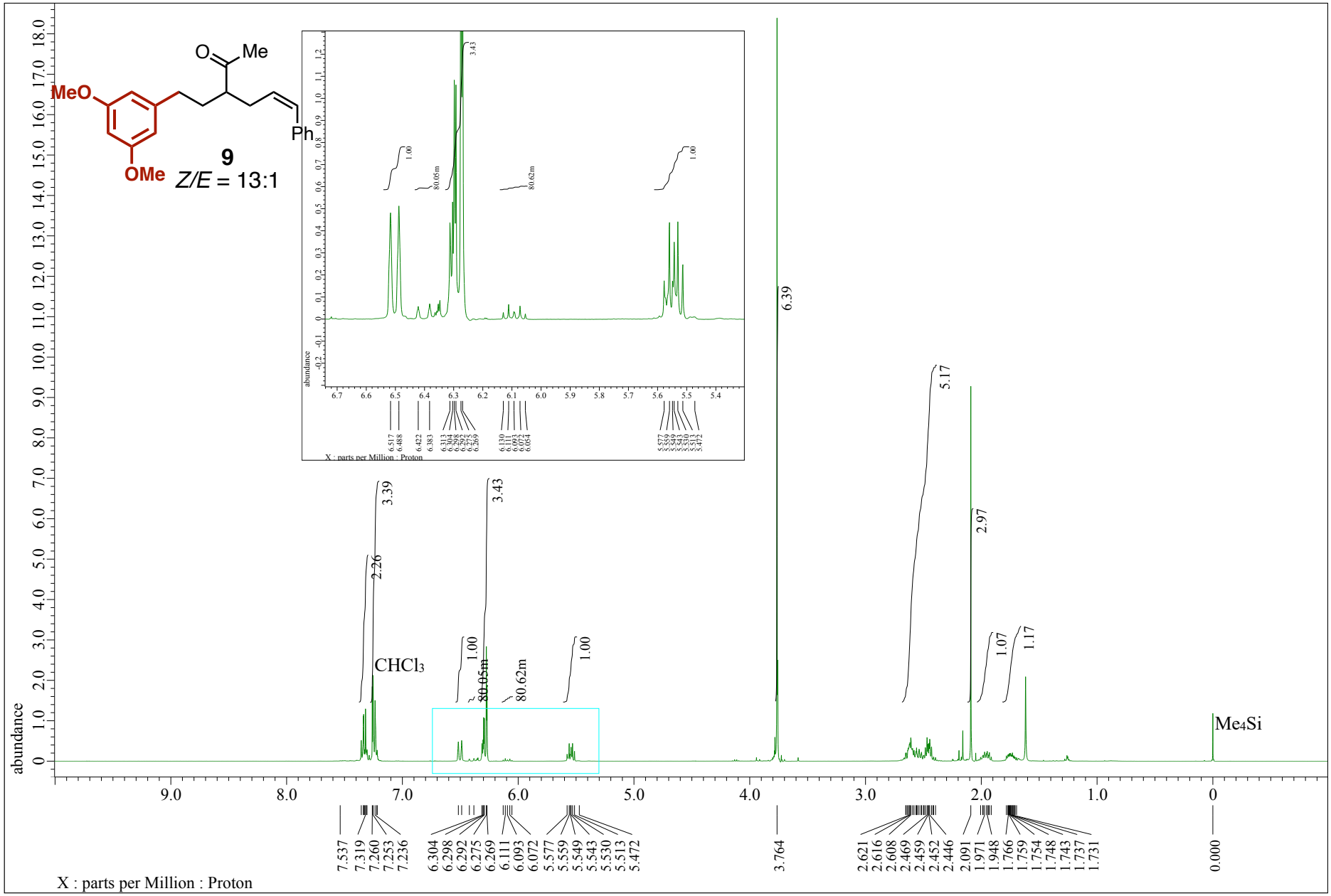
^{1}H NMR spectrum of **8** ($CDCl_3$, 400 MHz)



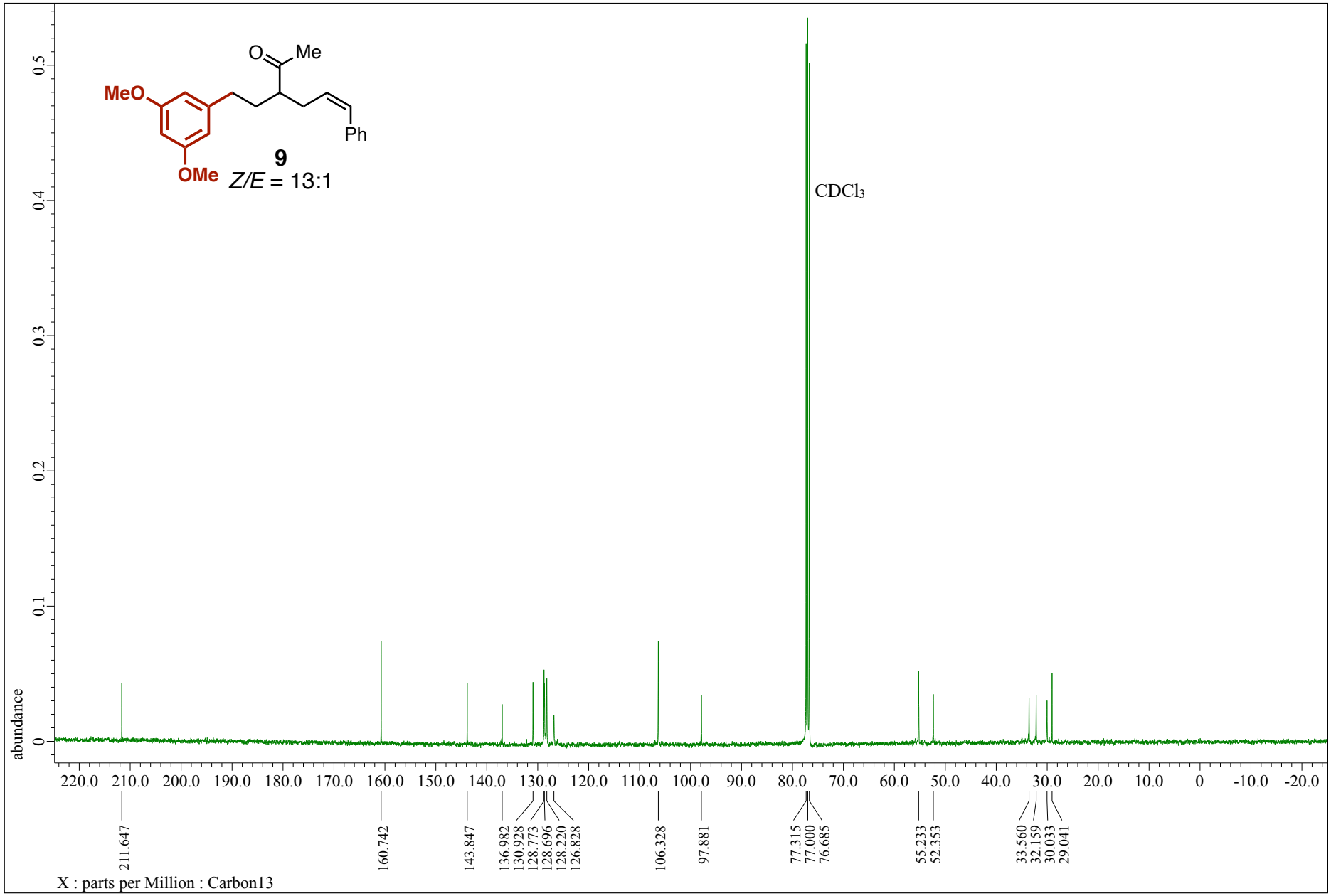
^{13}C NMR spectrum of **8** ($CDCl_3$, 101 MHz)



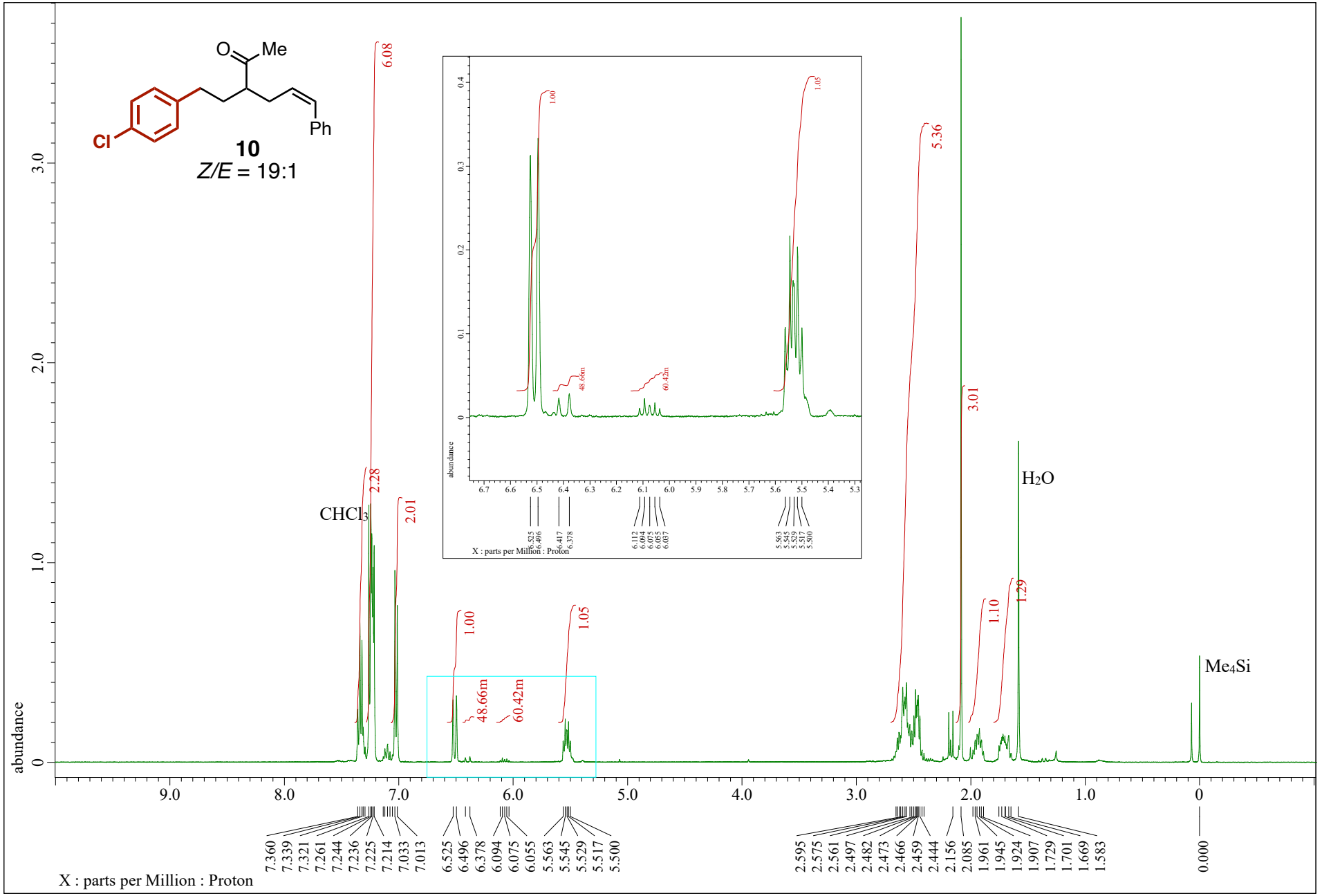
^{1}H NMR spectrum of **9** ($CDCl_3$, 400 MHz)



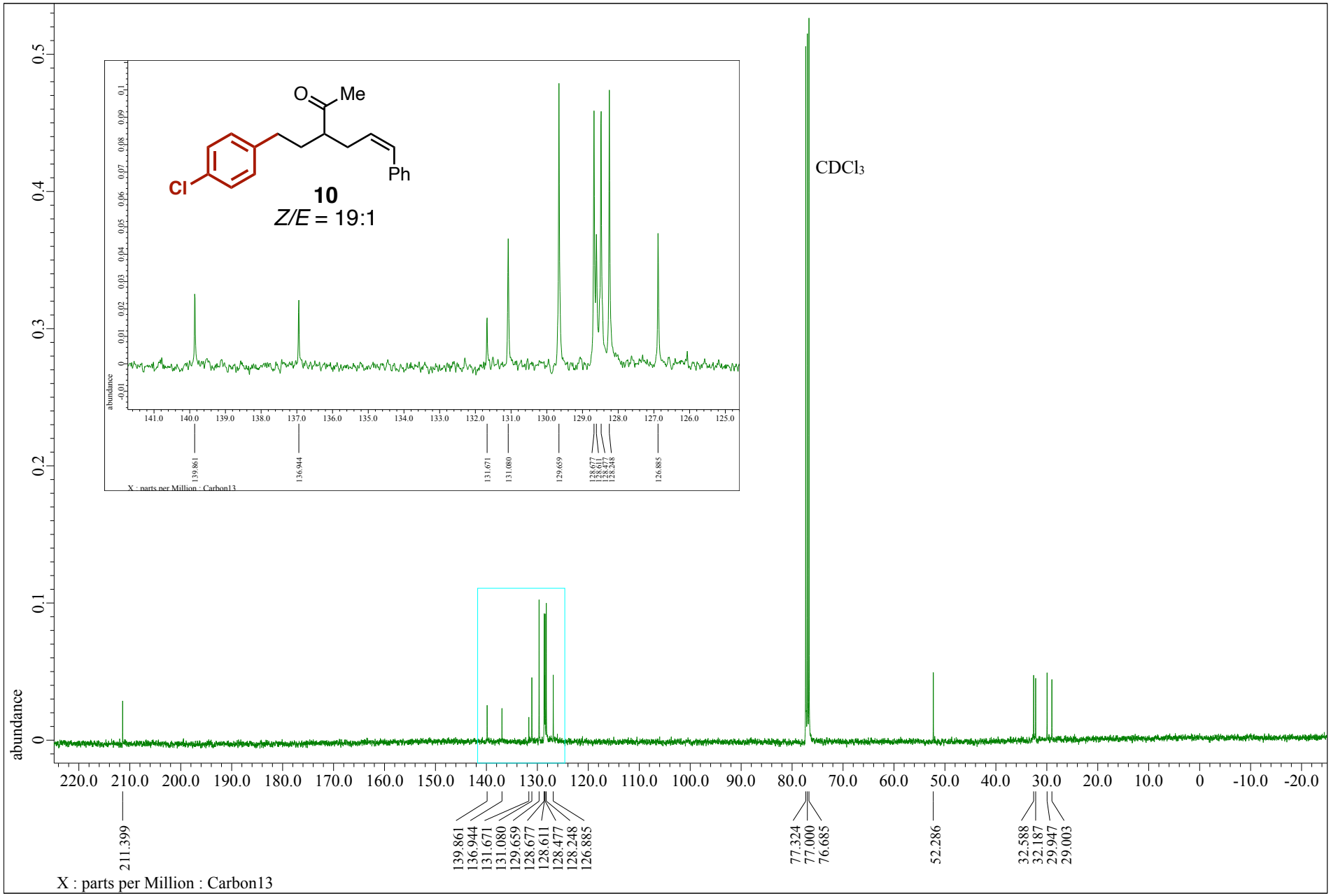
^{13}C NMR spectrum of **9** ($CDCl_3$, 101 MHz)



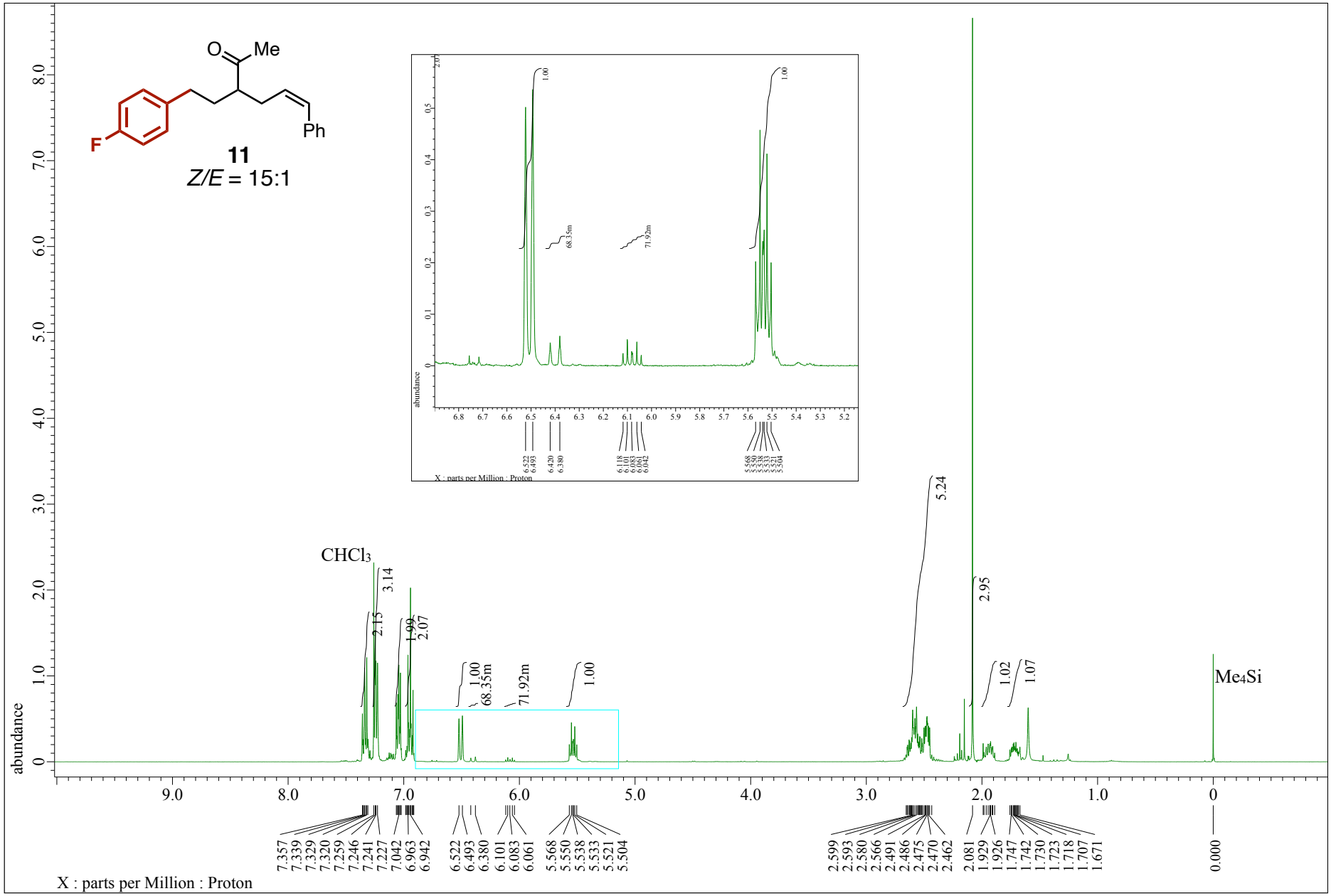
^{1}H NMR spectrum of **10** ($CDCl_3$, 400 MHz)



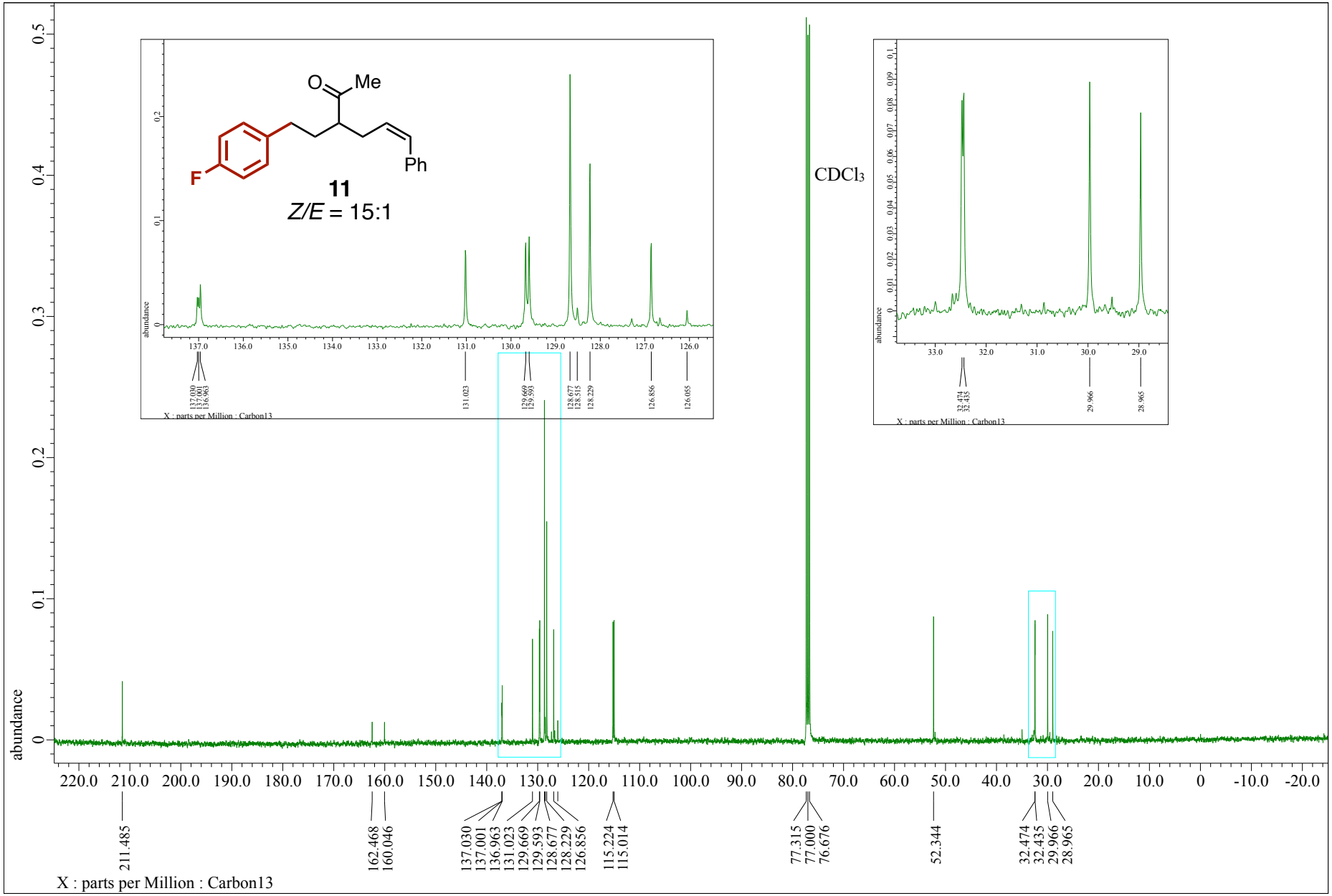
^{13}C NMR spectrum of **10** ($CDCl_3$, 101 MHz)



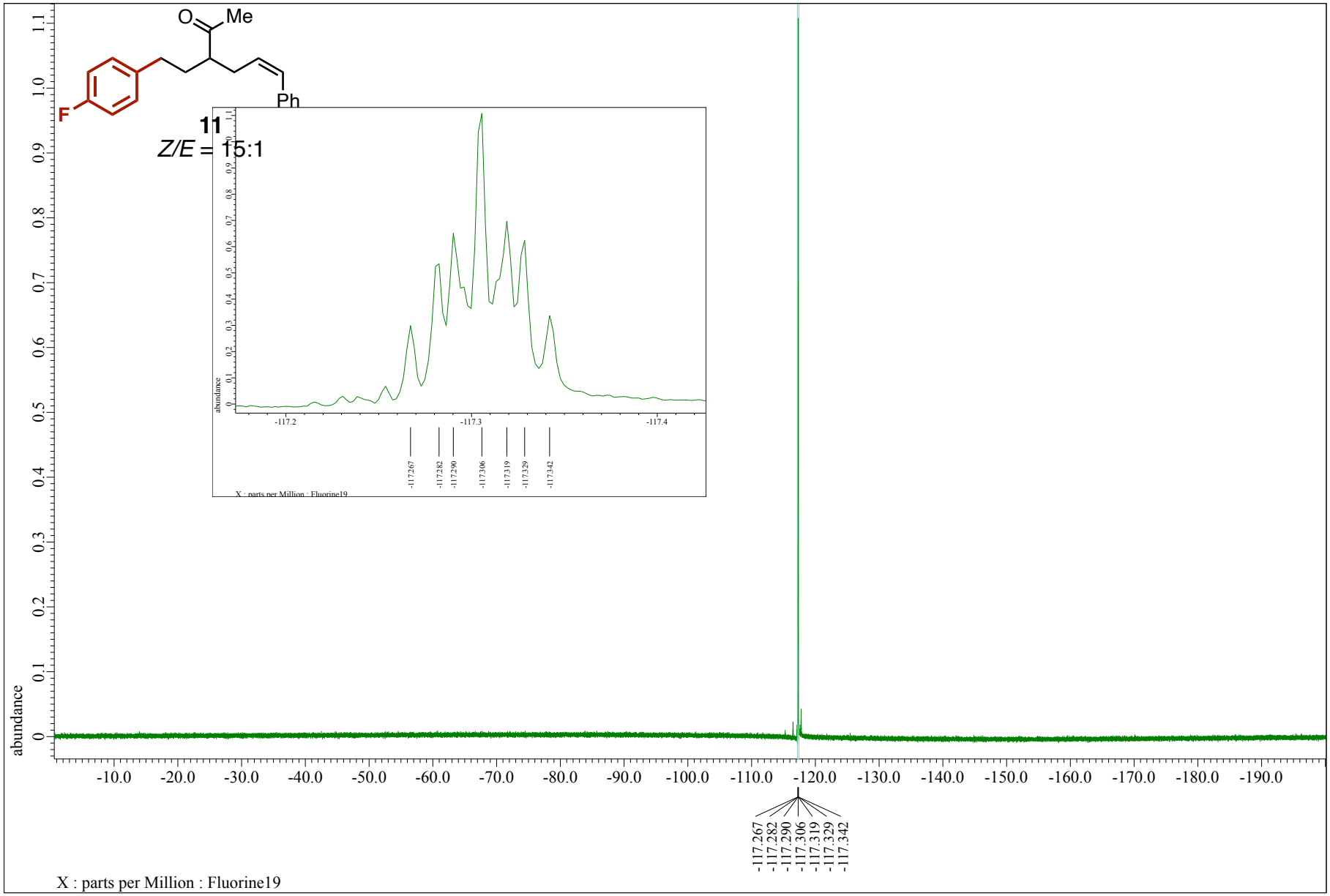
^{1}H NMR spectrum of **11** ($CDCl_3$, 400 MHz)



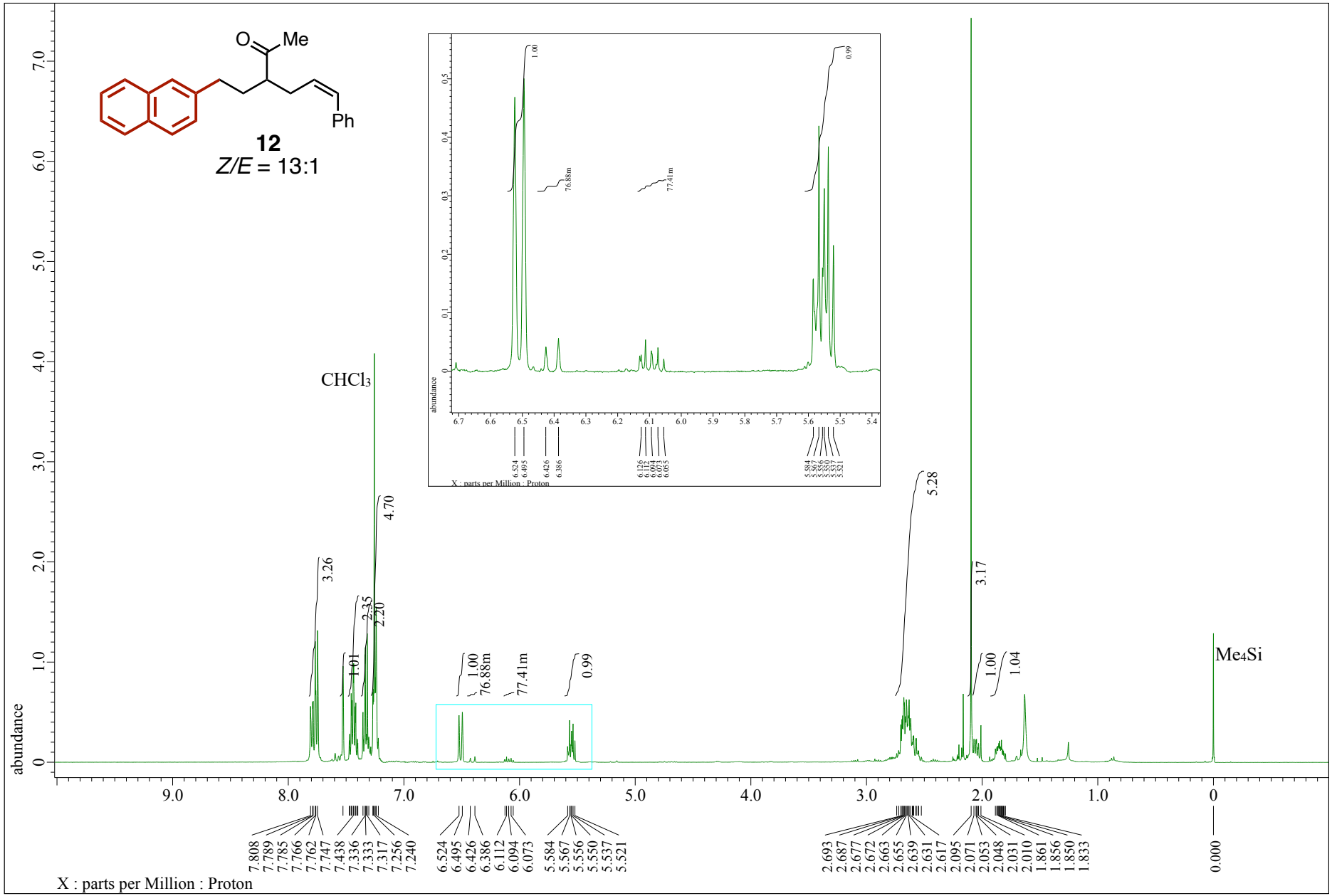
^{13}C NMR spectrum of **11** ($CDCl_3$, 101 MHz)



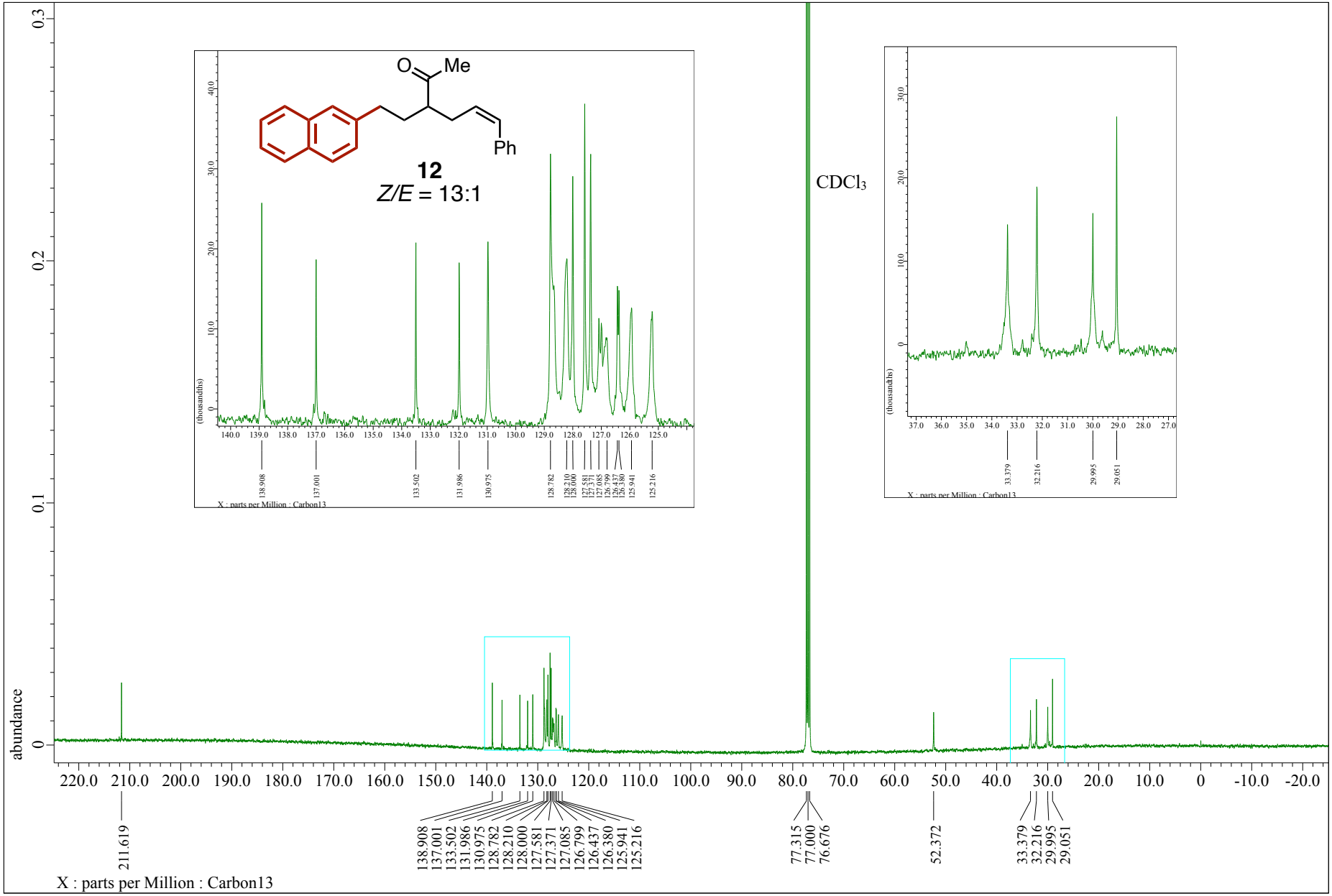
^{19}F NMR spectrum of **11** ($CDCl_3$, 376 MHz)



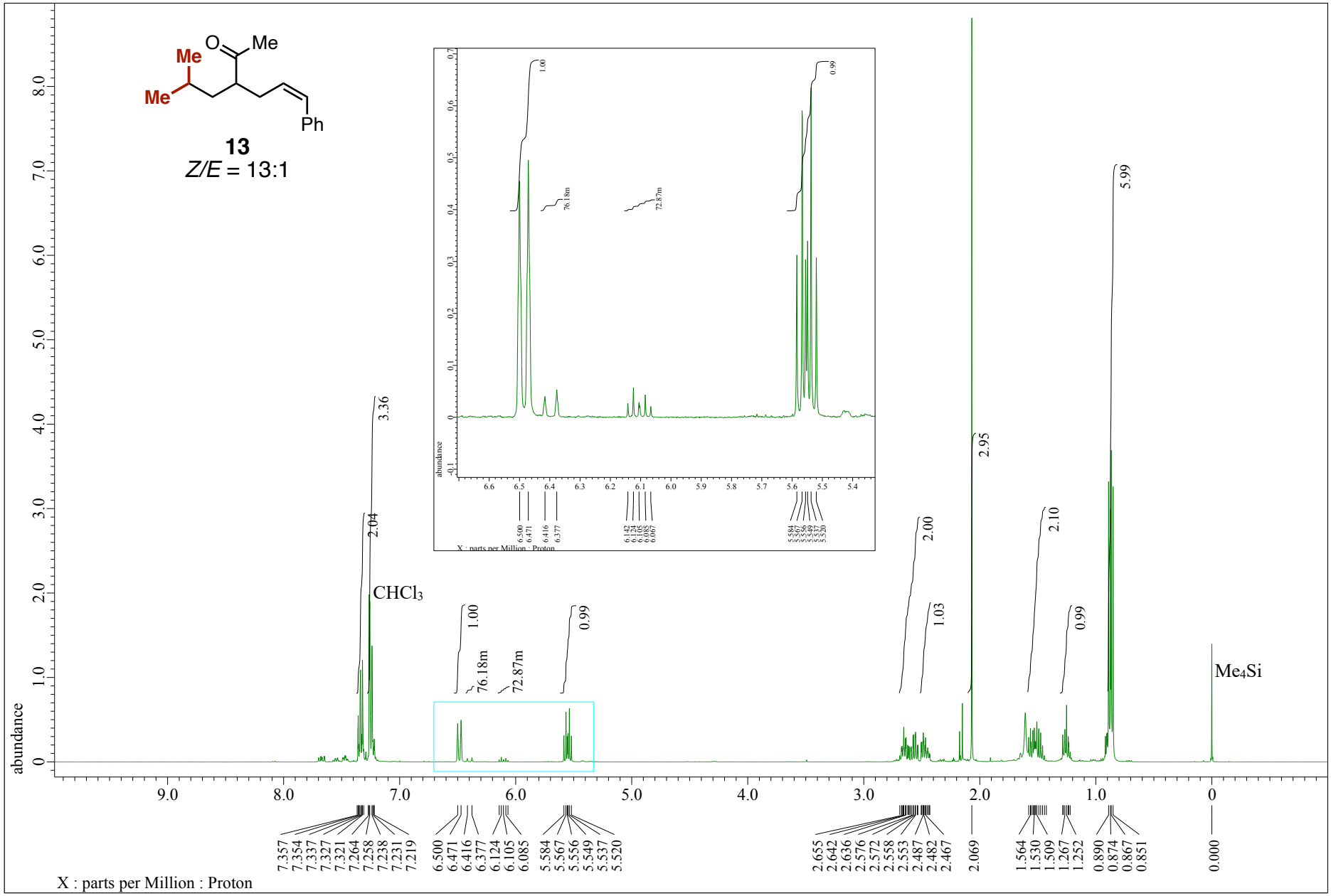
^{1}H NMR spectrum of **12** ($CDCl_3$, 400 MHz)



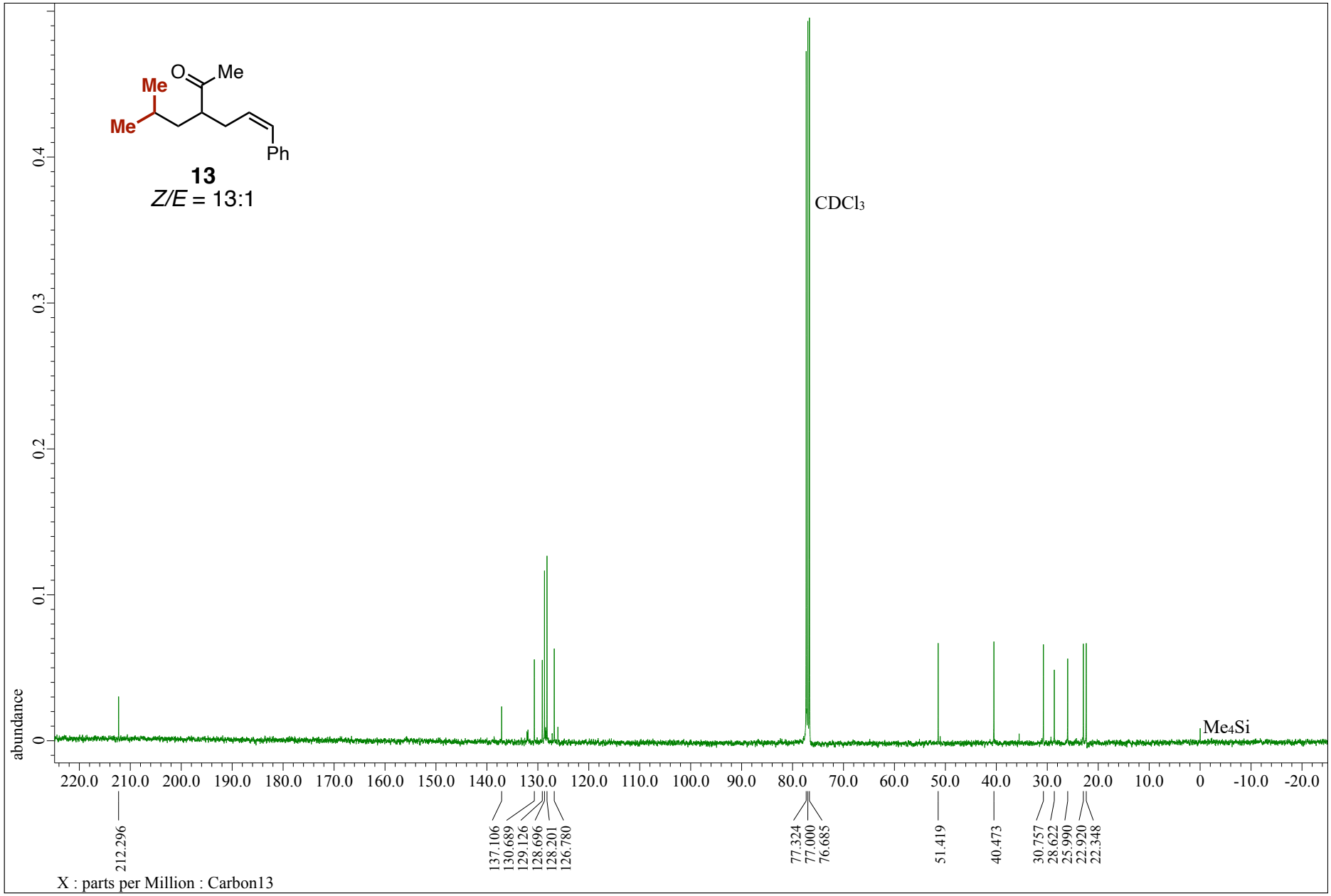
^{13}C NMR spectrum of **12** ($CDCl_3$, 101 MHz)



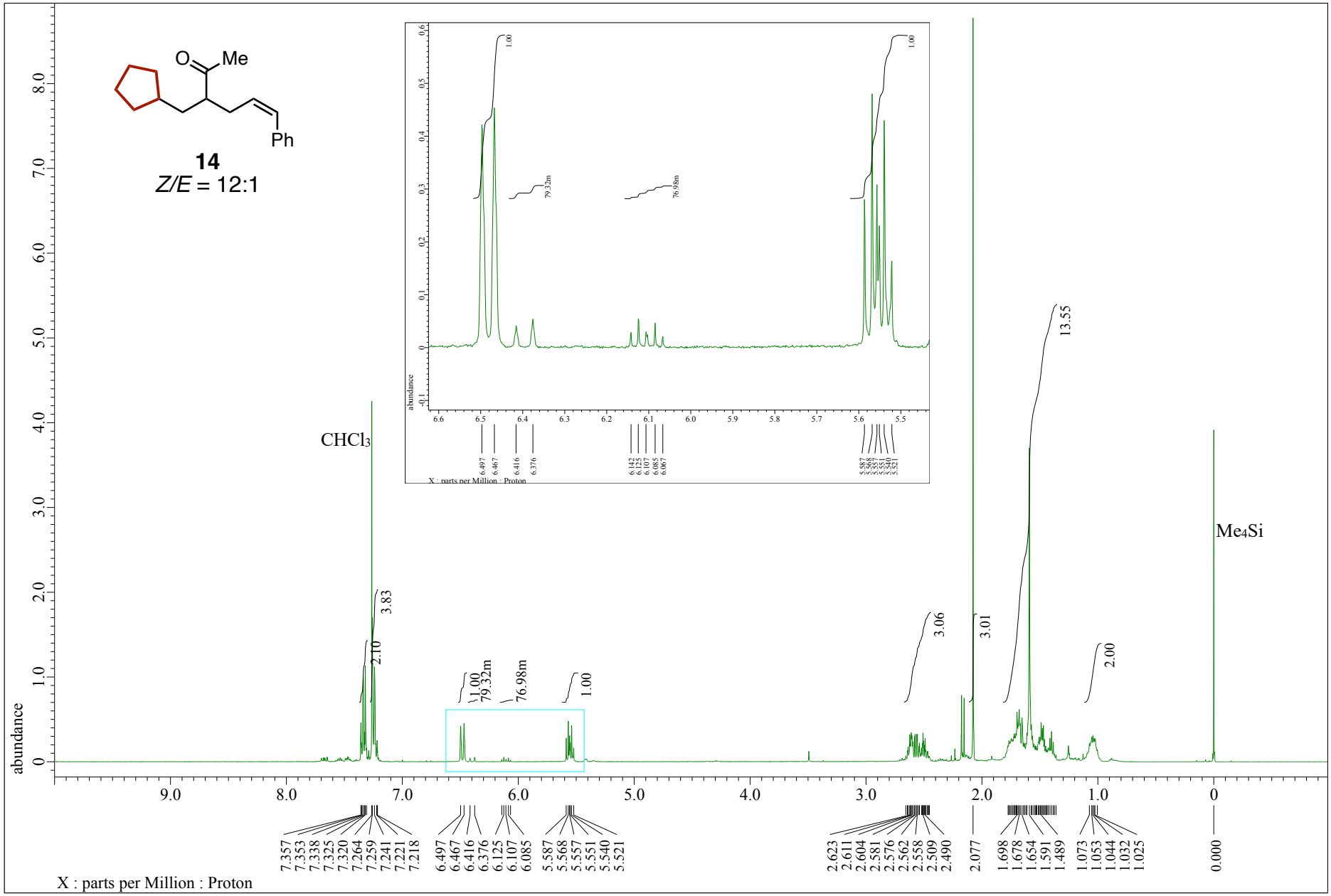
^{1}H NMR spectrum of **13** ($CDCl_3$, 400 MHz)



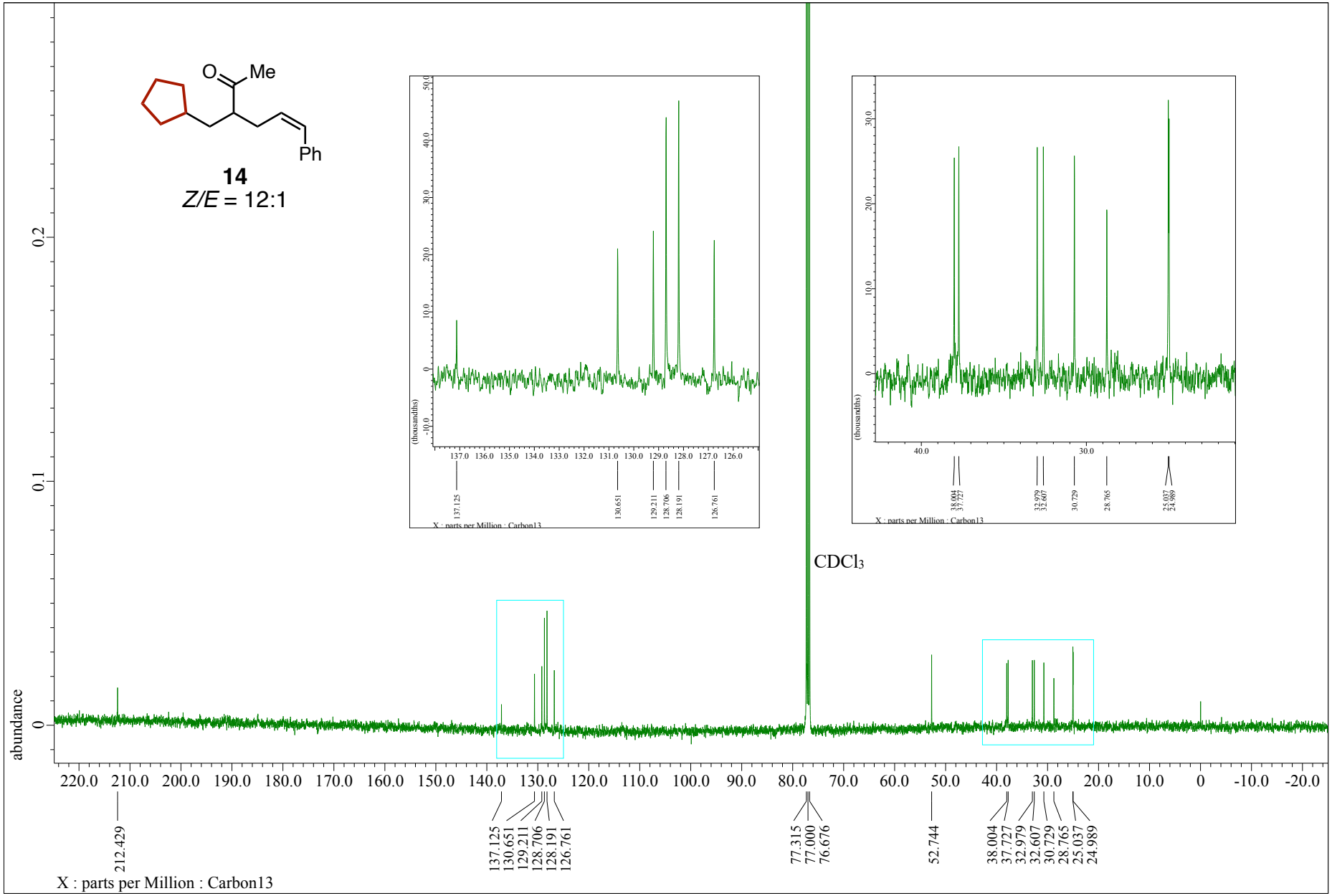
^{13}C NMR spectrum of **13** ($CDCl_3$, 101 MHz)



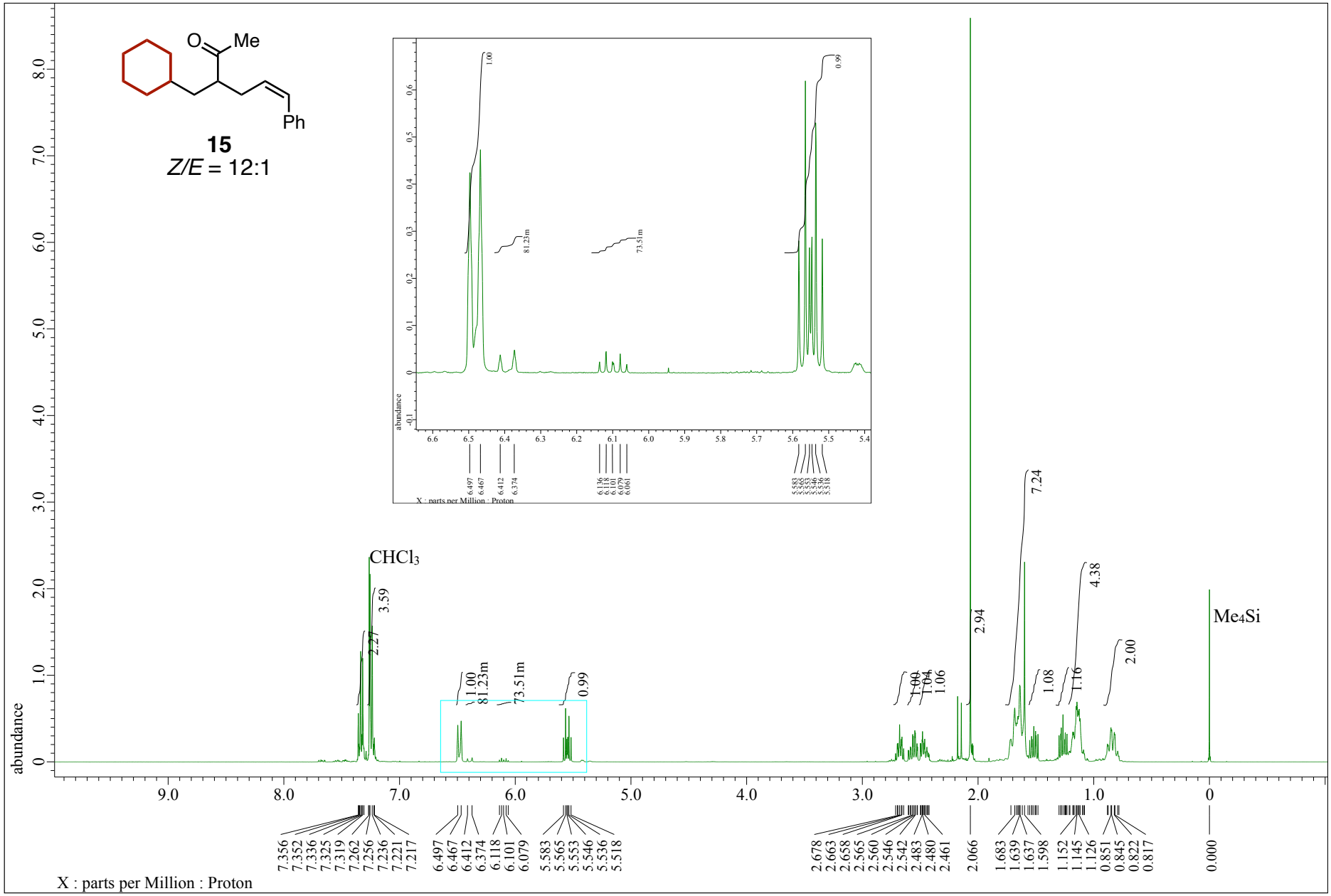
^{1}H NMR spectrum of **14** ($CDCl_3$, 400 MHz)



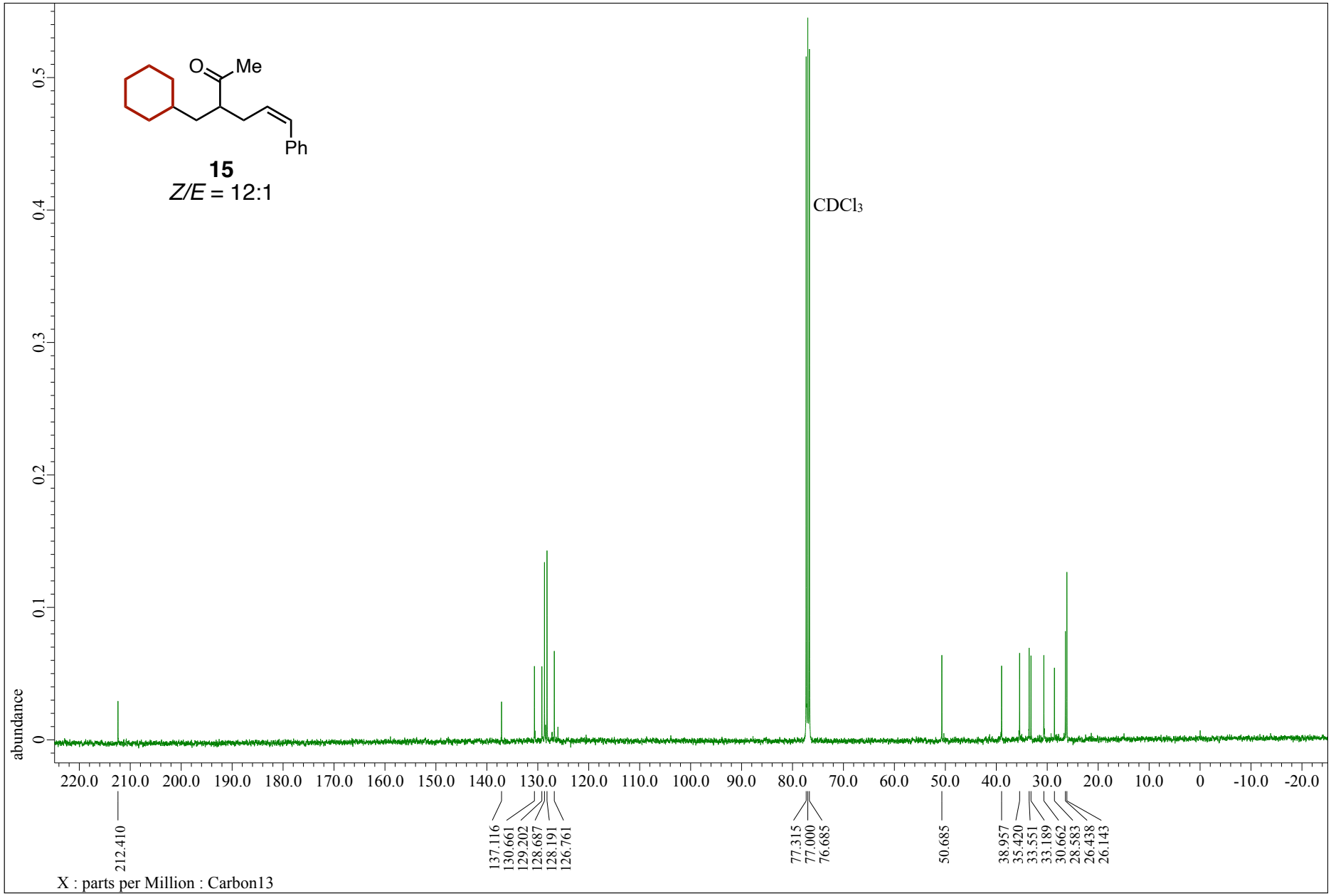
^{13}C NMR spectrum of **14** ($CDCl_3$, 101 MHz)



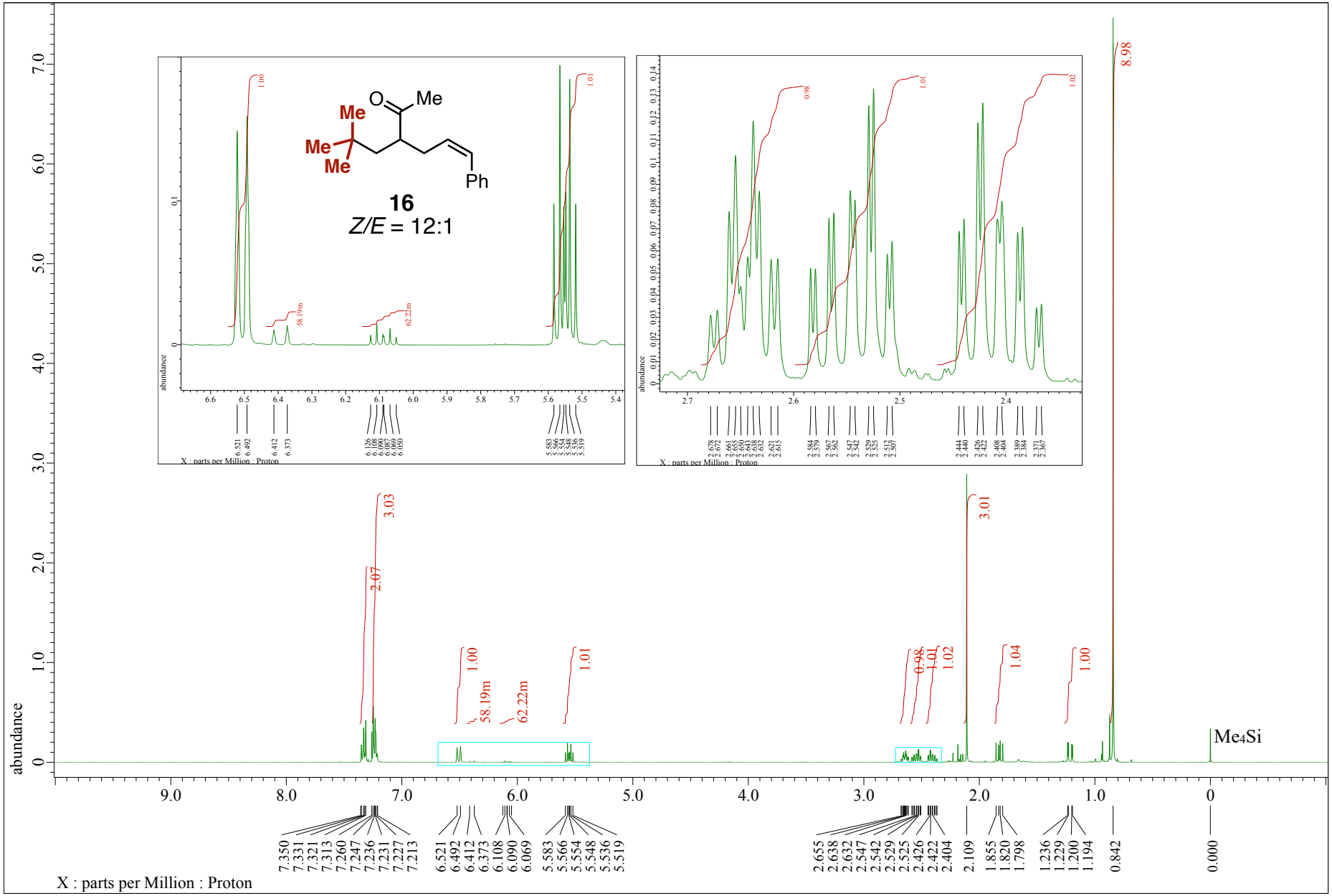
^{1}H NMR spectrum of **15** ($CDCl_3$, 400 MHz)



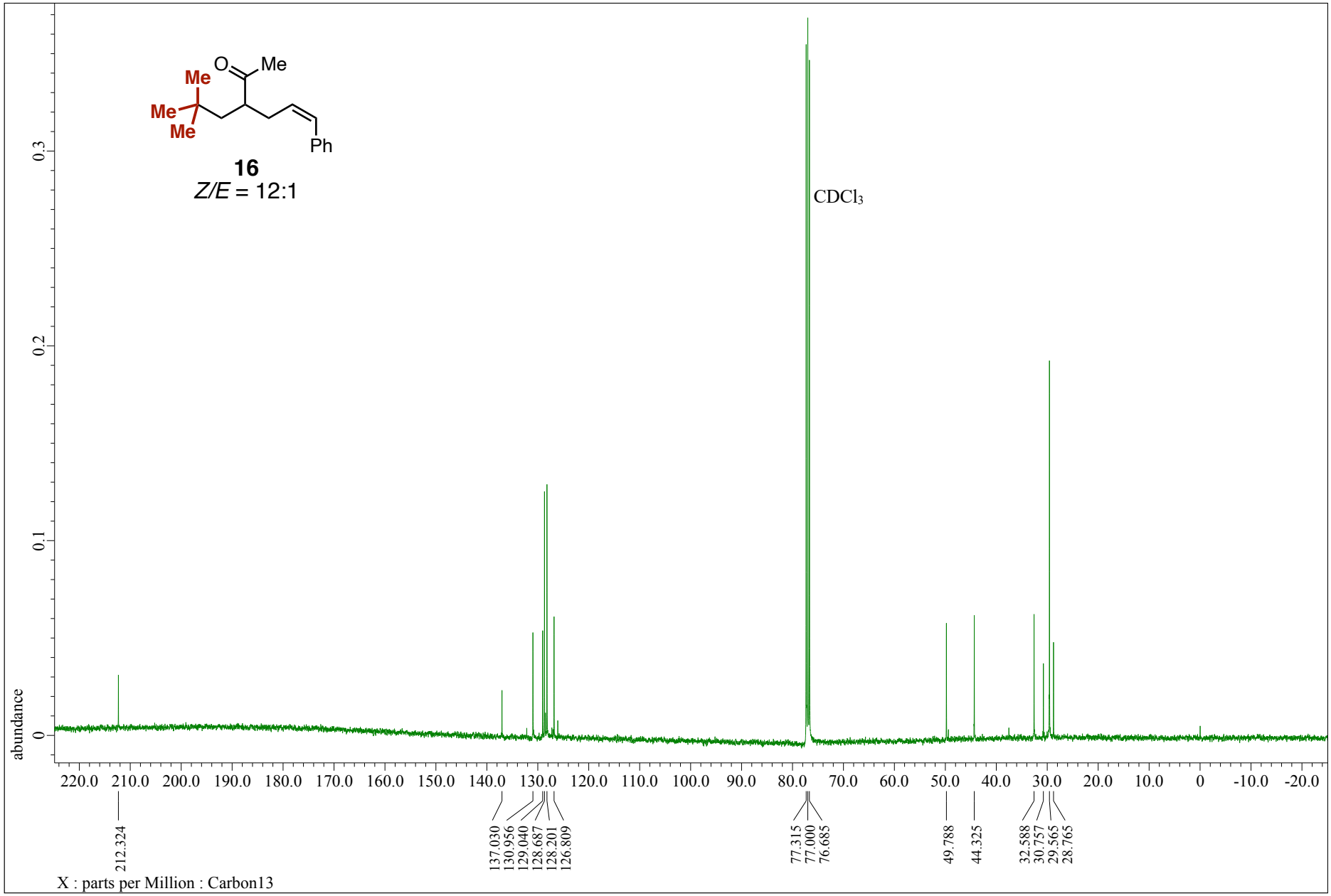
^{13}C NMR spectrum of **15** ($CDCl_3$, 101 MHz)



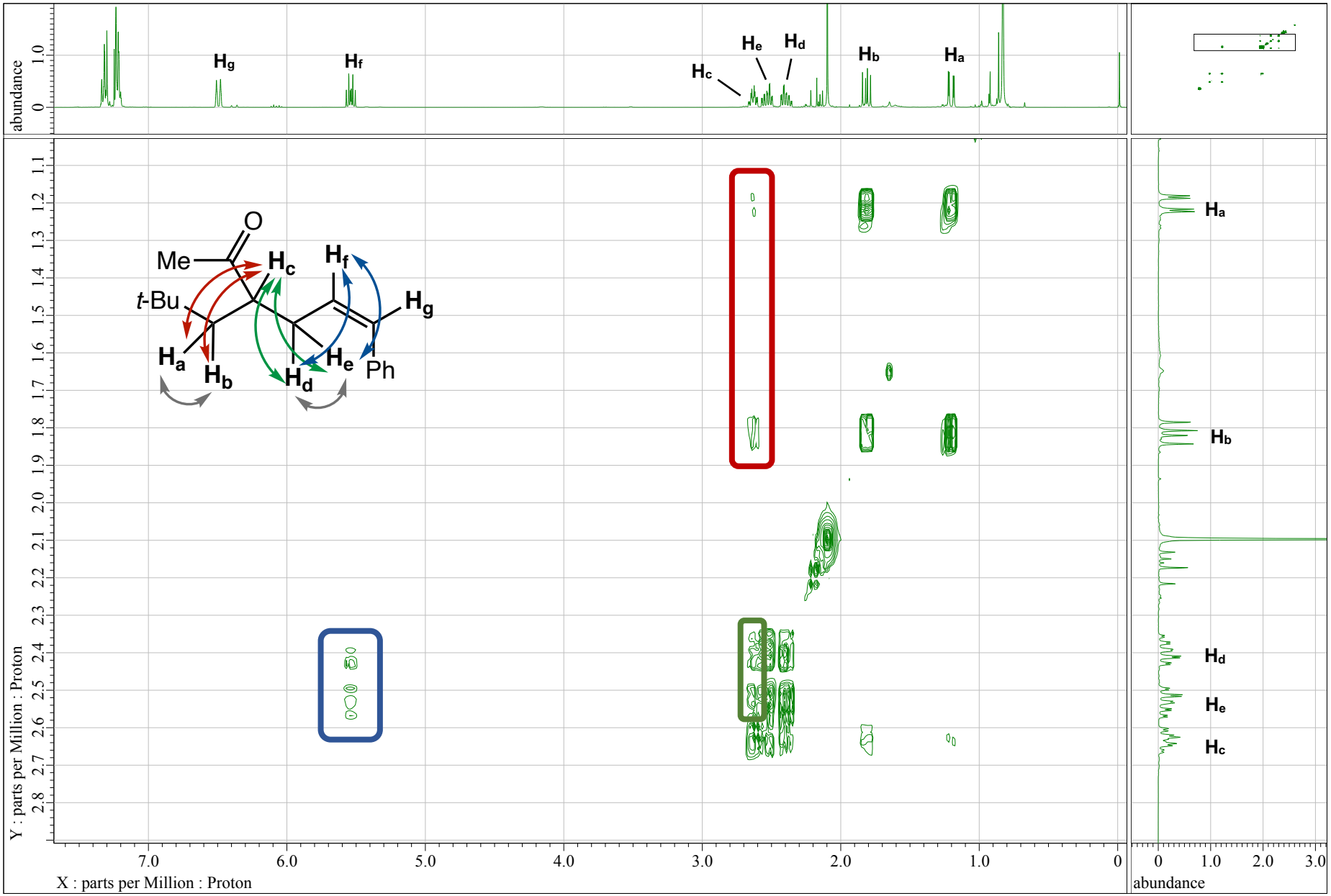
^{1}H NMR spectrum of **16** ($CDCl_3$, 400 MHz)



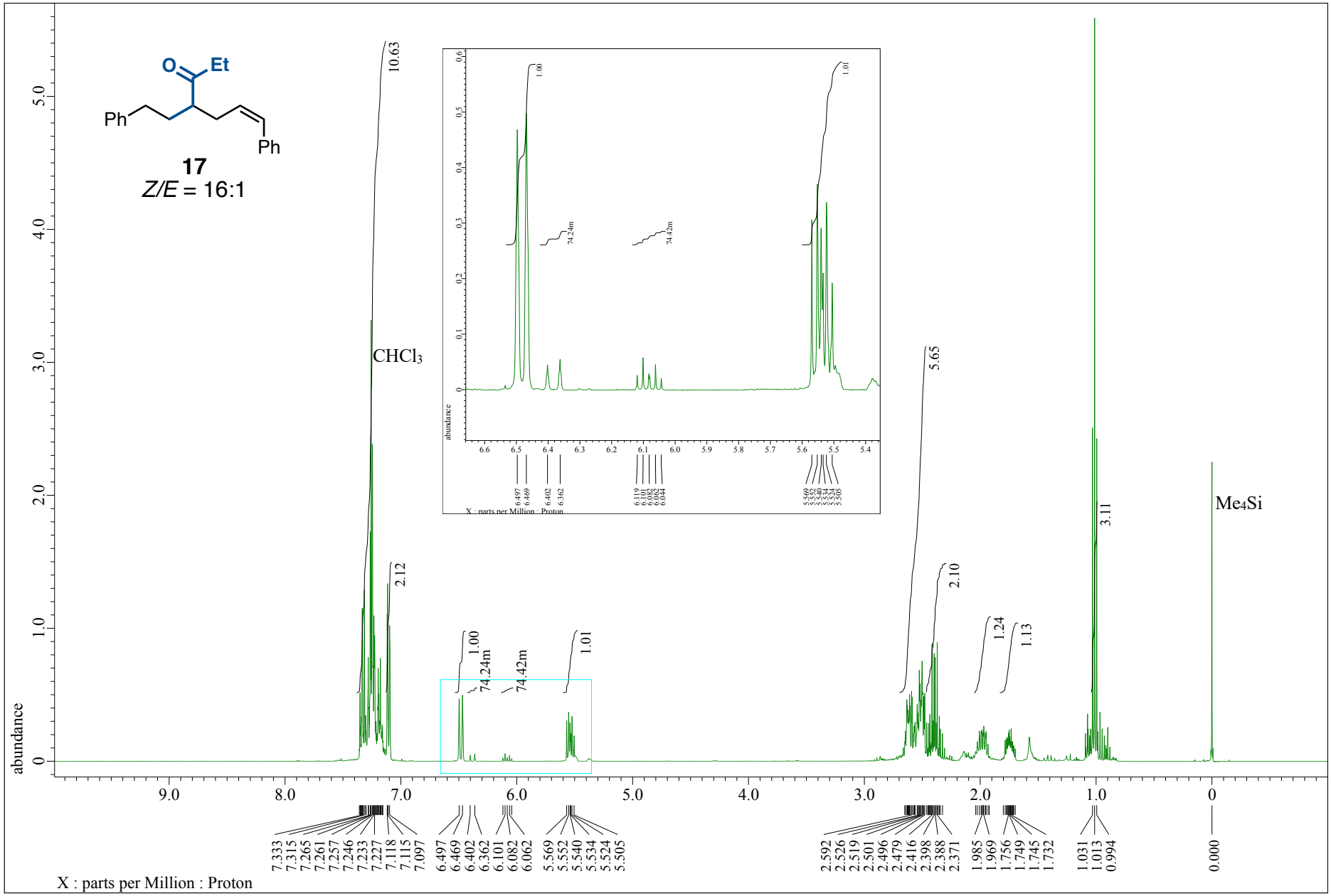
^{13}C NMR spectrum of **16** ($CDCl_3$, 101 MHz)



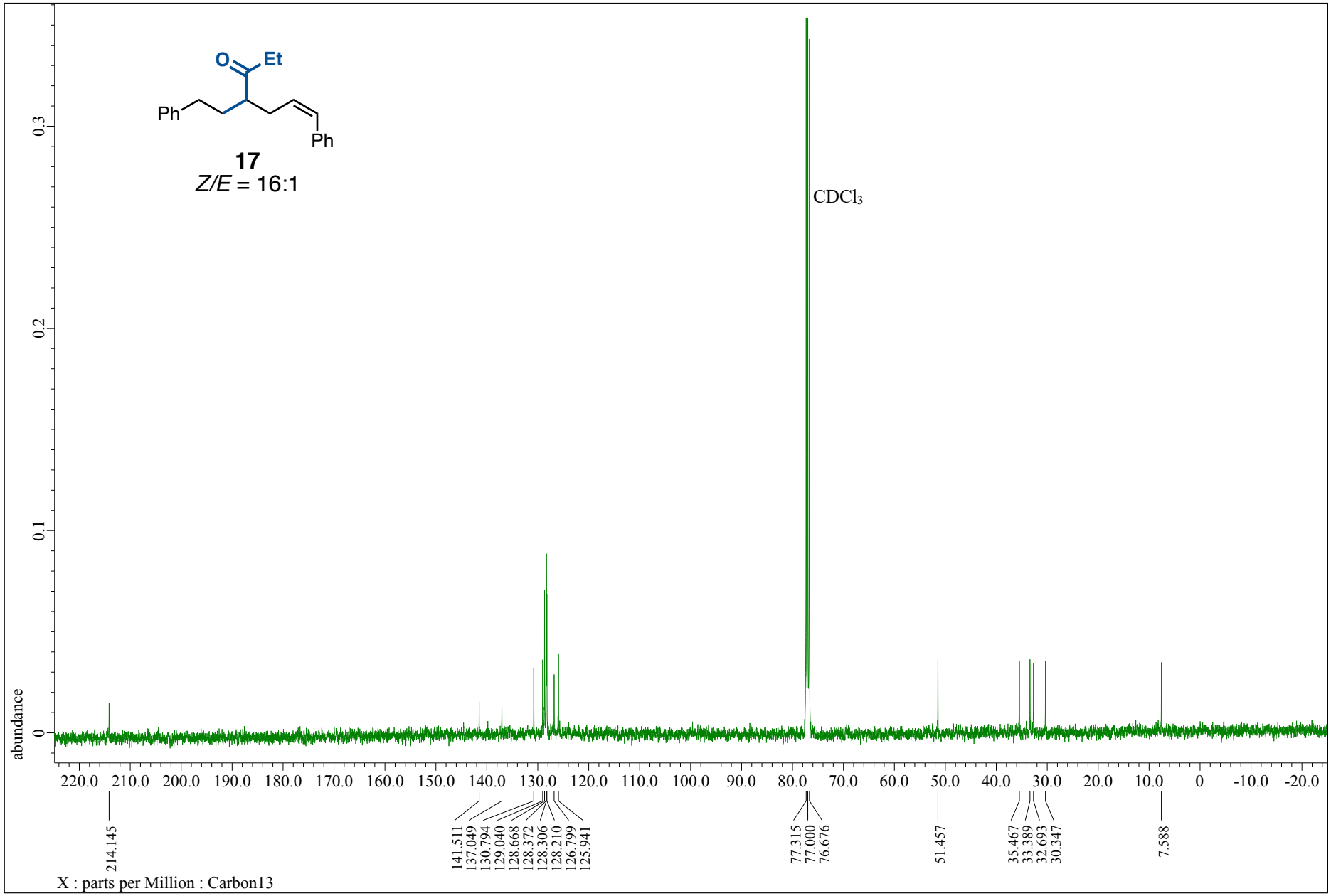
H-H COSY NMR spectrum of **16** ($CDCl_3$, 400 MHz)



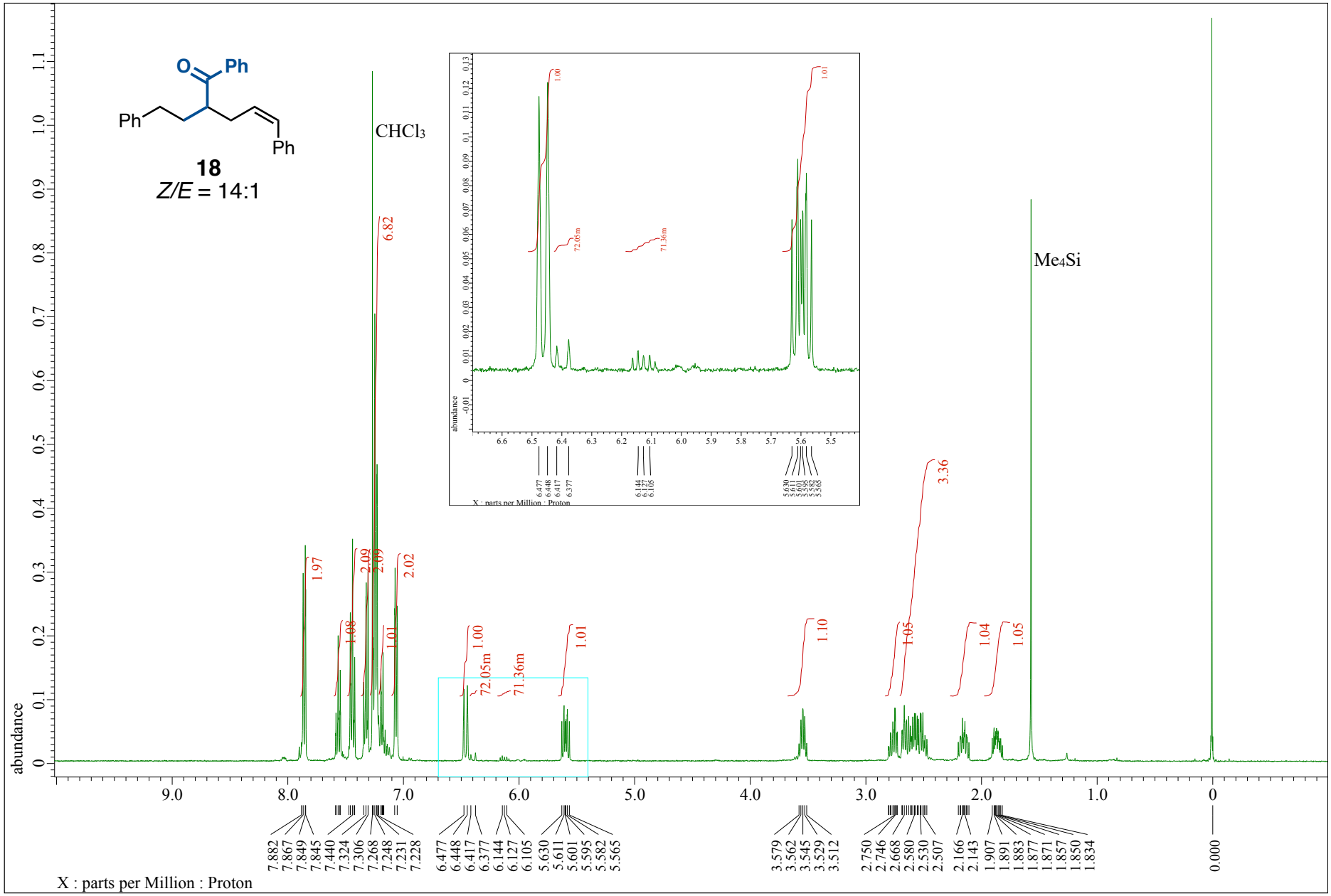
^{1}H NMR spectrum of **17** ($CDCl_3$, 400 MHz)



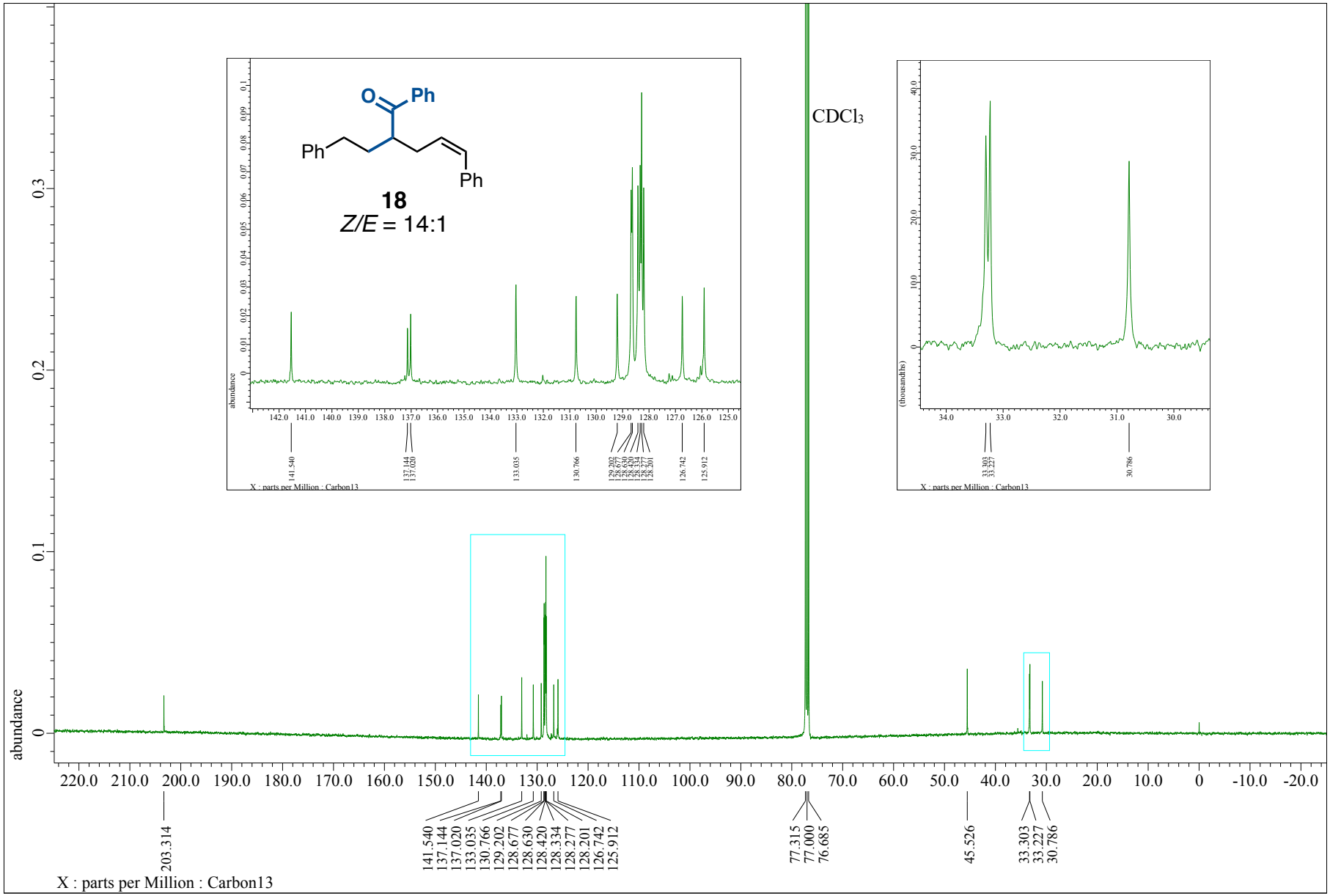
^{13}C NMR spectrum of **17** ($CDCl_3$, 101 MHz)



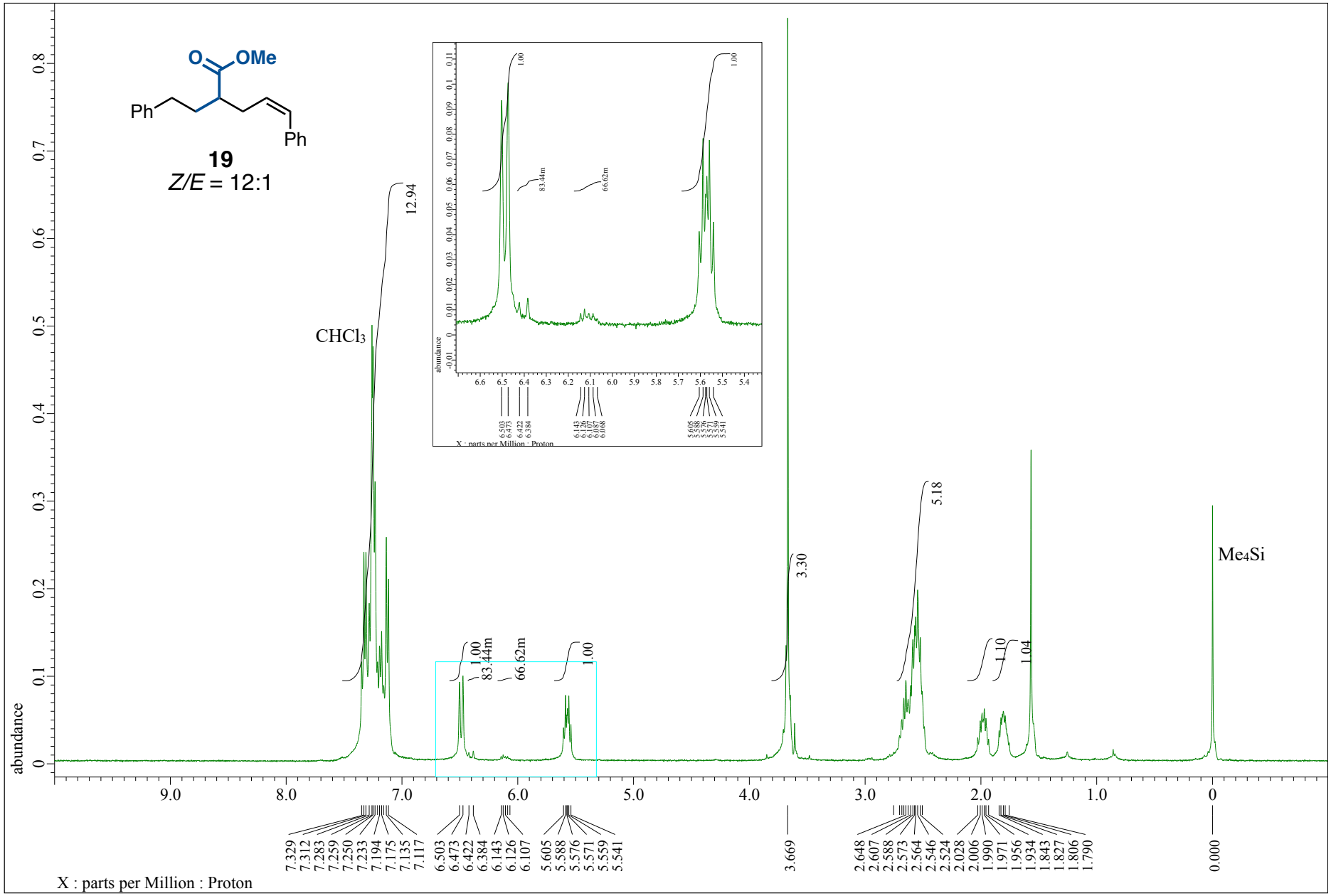
^{1}H NMR spectrum of **18** ($CDCl_3$, 400 MHz)



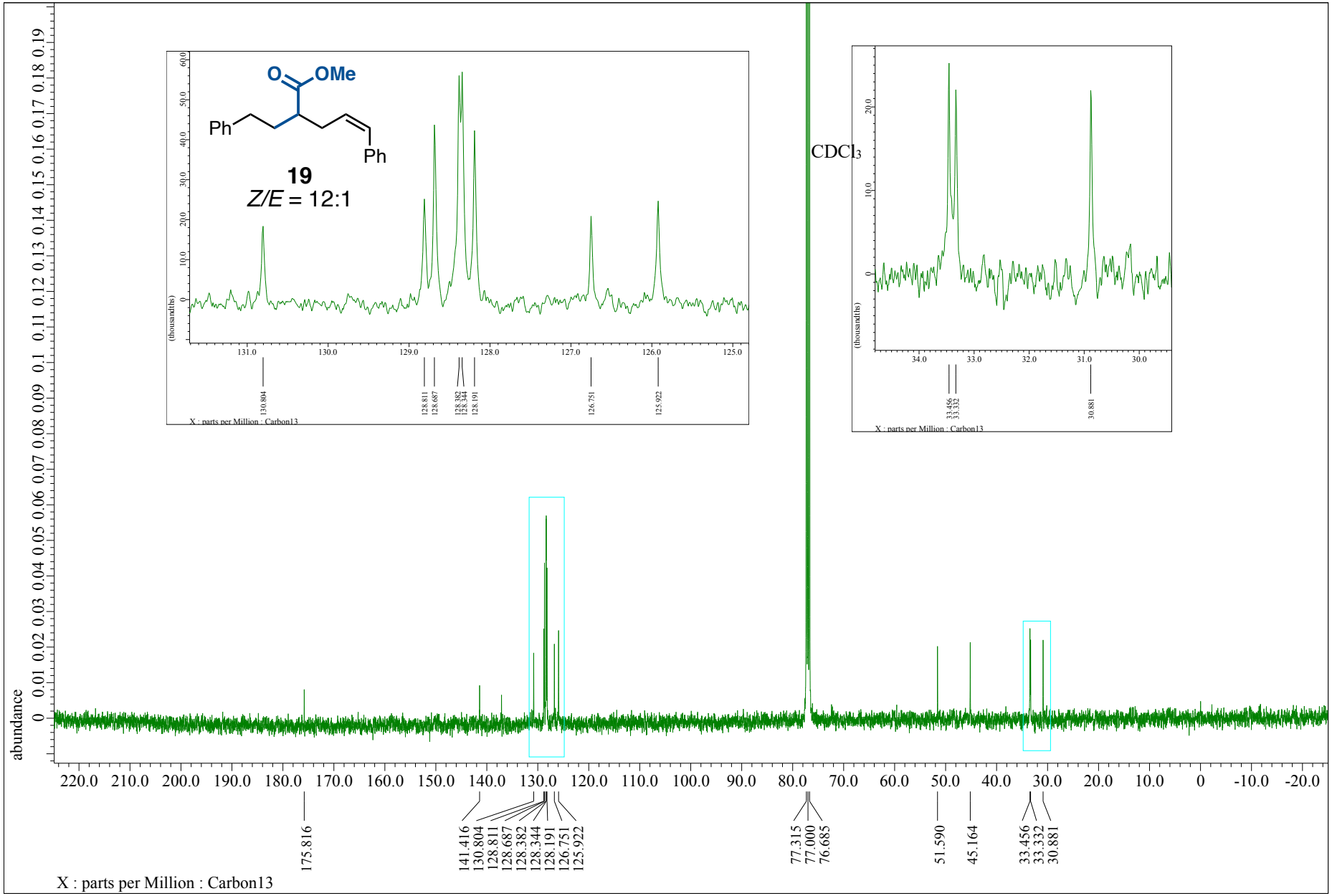
^{13}C NMR spectrum of **18** ($CDCl_3$, 101 MHz)



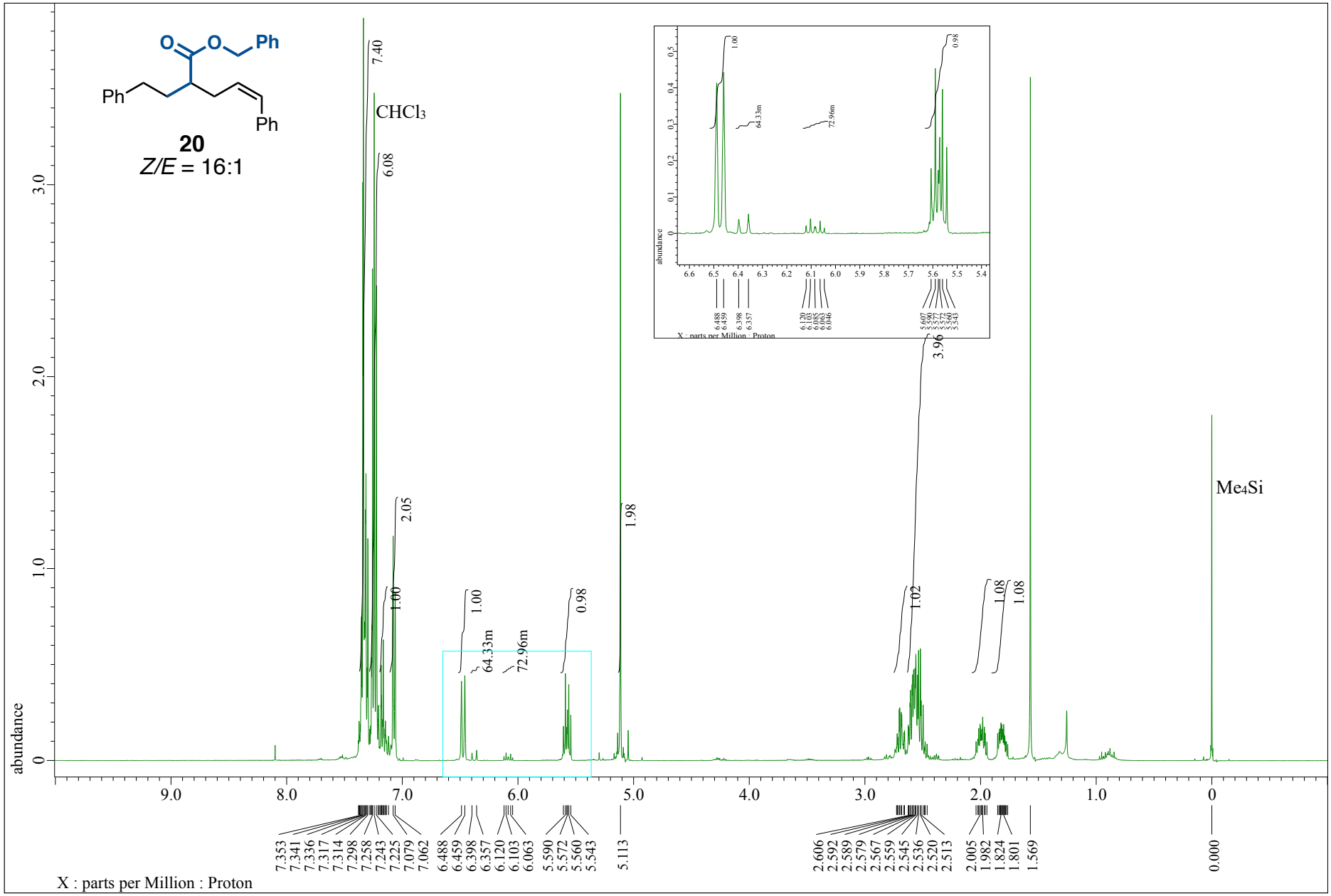
^{1}H NMR spectrum of **19** ($CDCl_3$, 400 MHz)



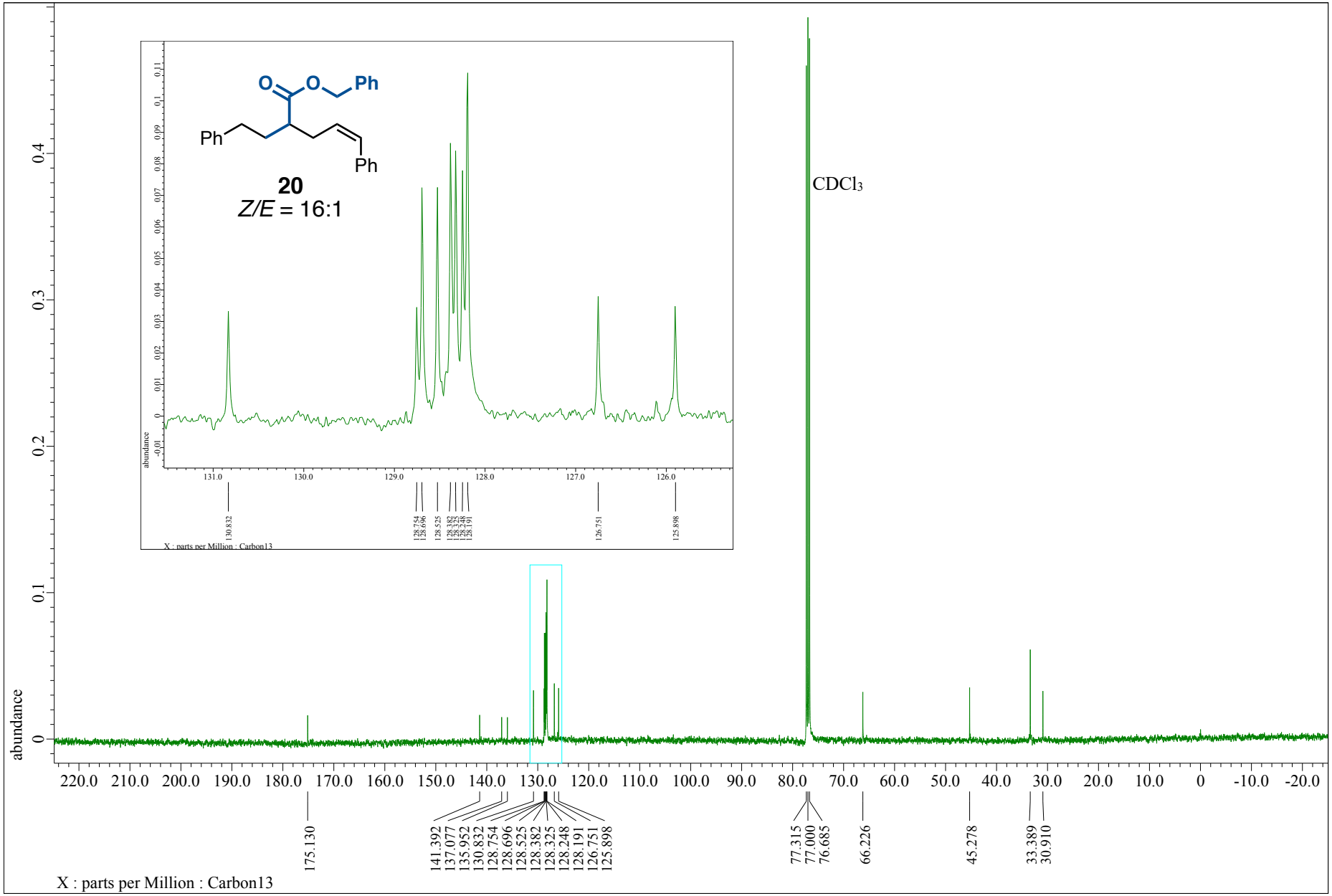
^{13}C NMR spectrum of **19** ($CDCl_3$, 101 MHz)



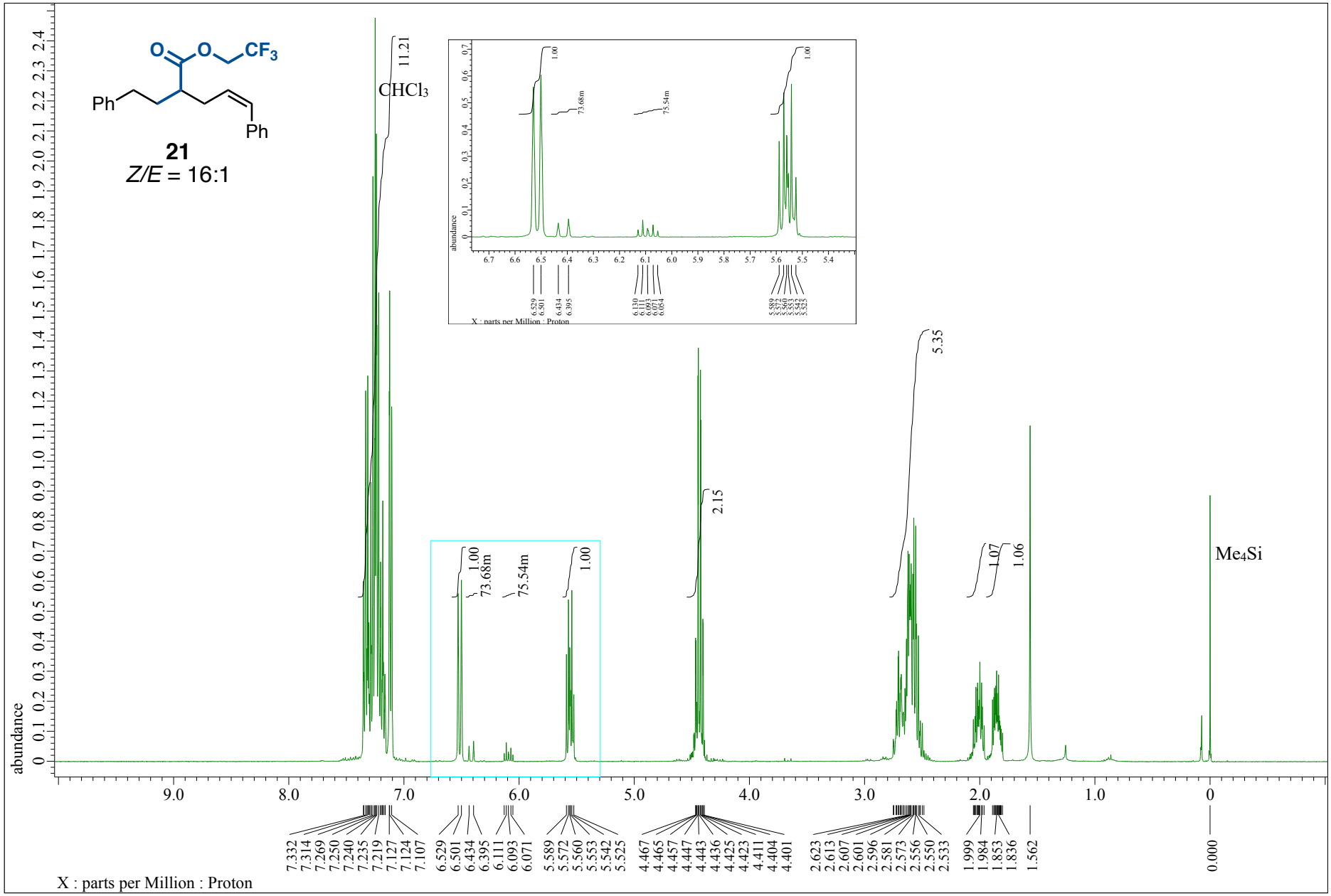
^{1}H NMR spectrum of **20** ($CDCl_3$, 400 MHz)



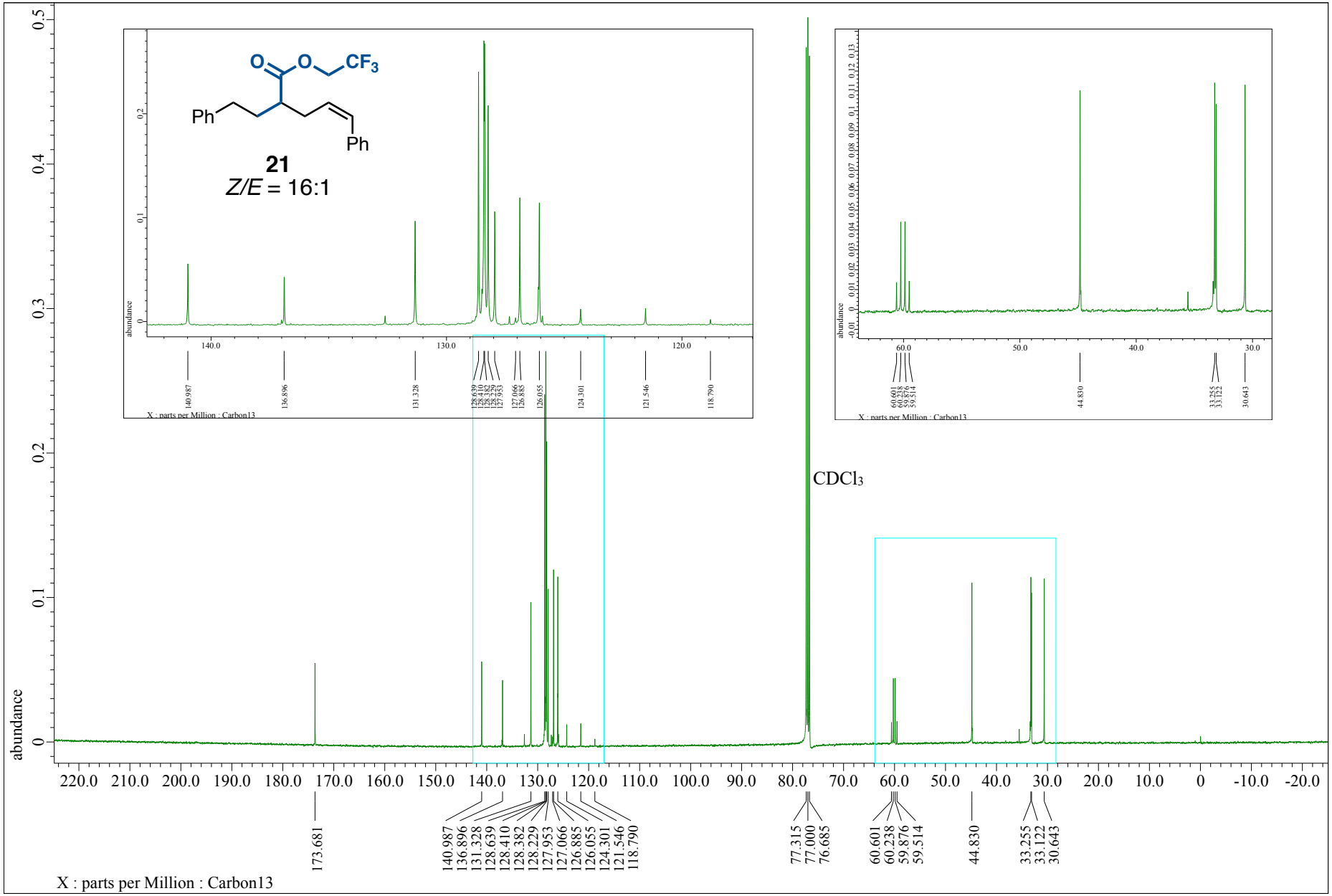
^{13}C NMR spectrum of **20** ($CDCl_3$, 101 MHz)



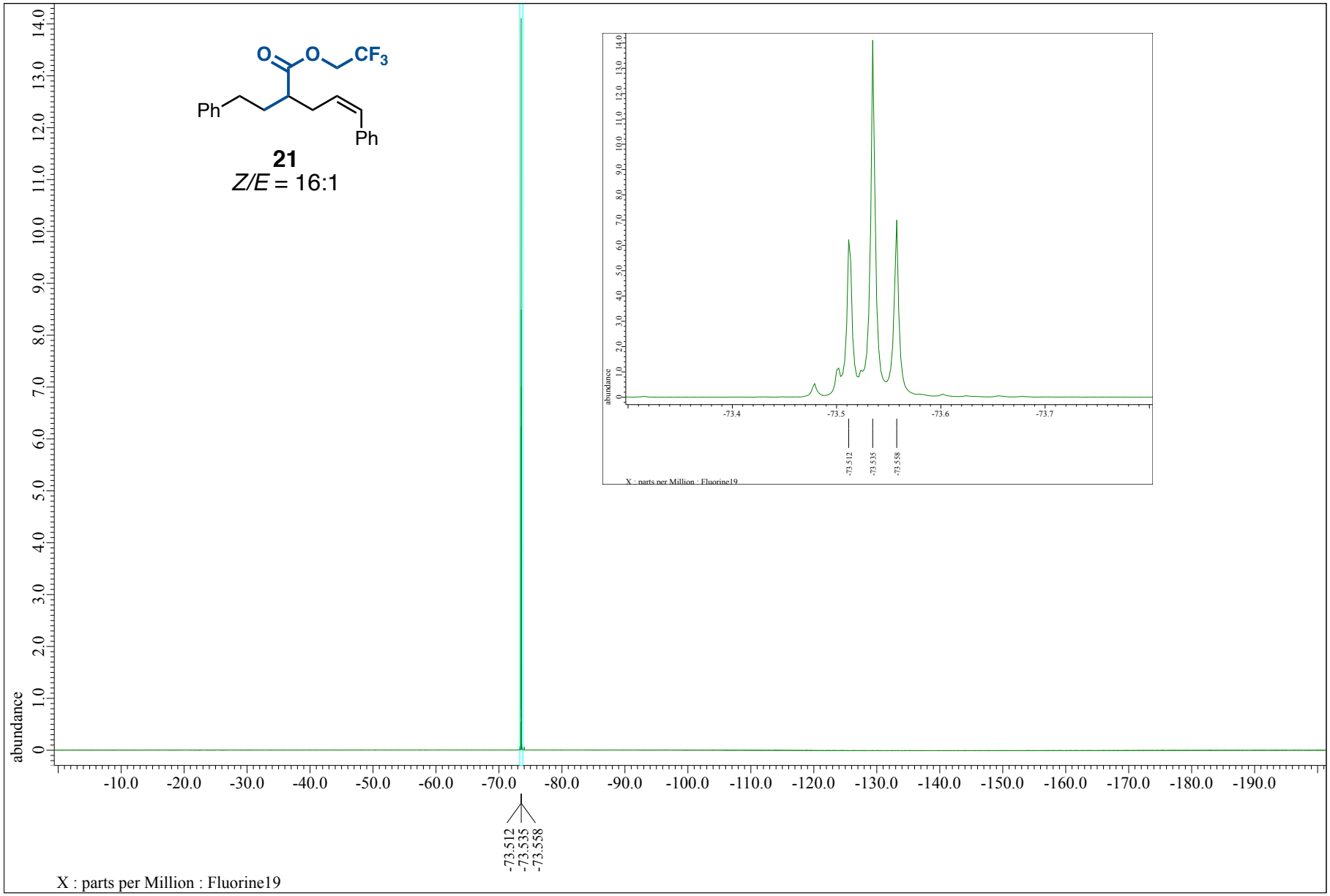
^{1}H NMR spectrum of **21** ($CDCl_3$, 400 MHz)



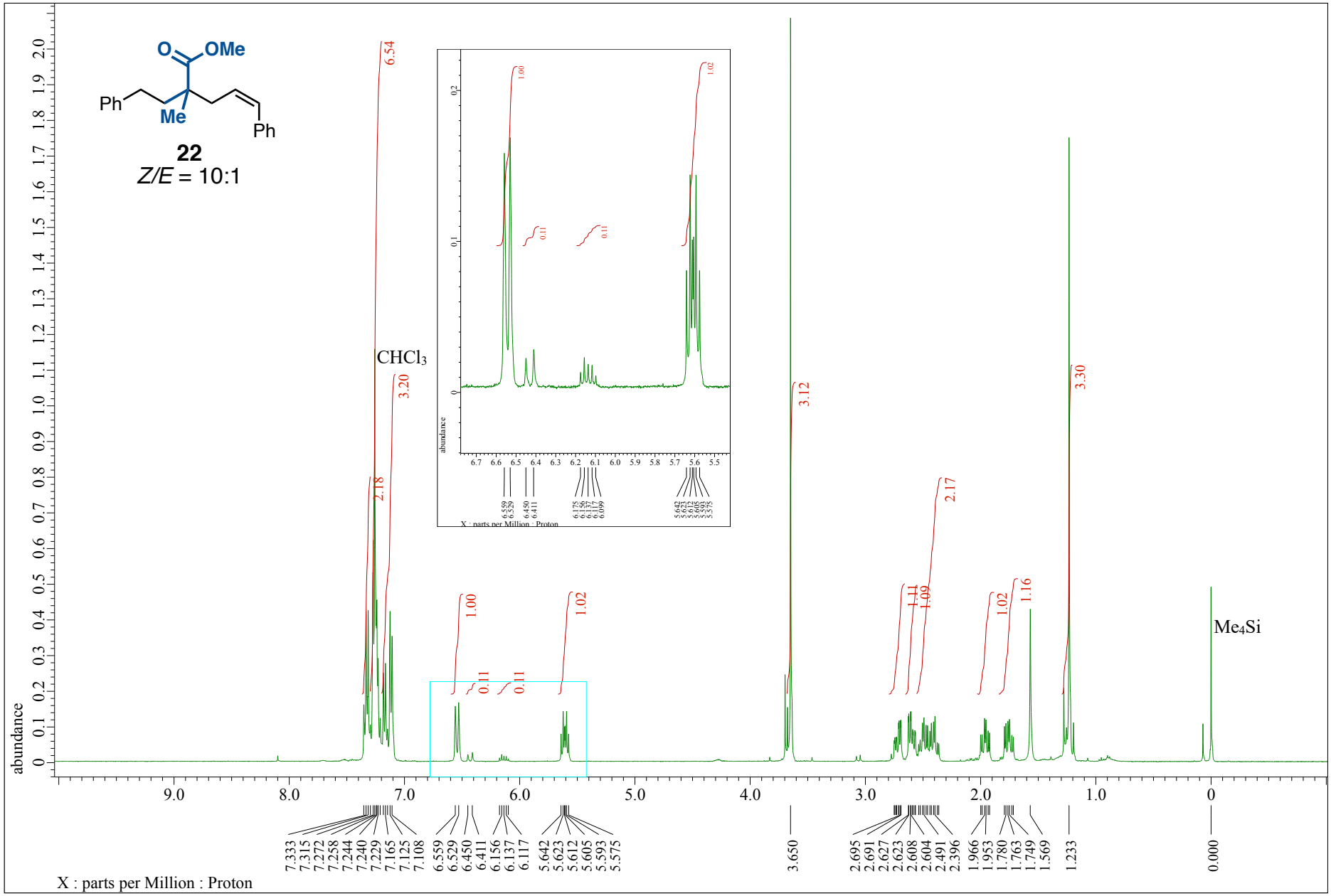
^{13}C NMR spectrum of **21** ($CDCl_3$, 101 MHz)



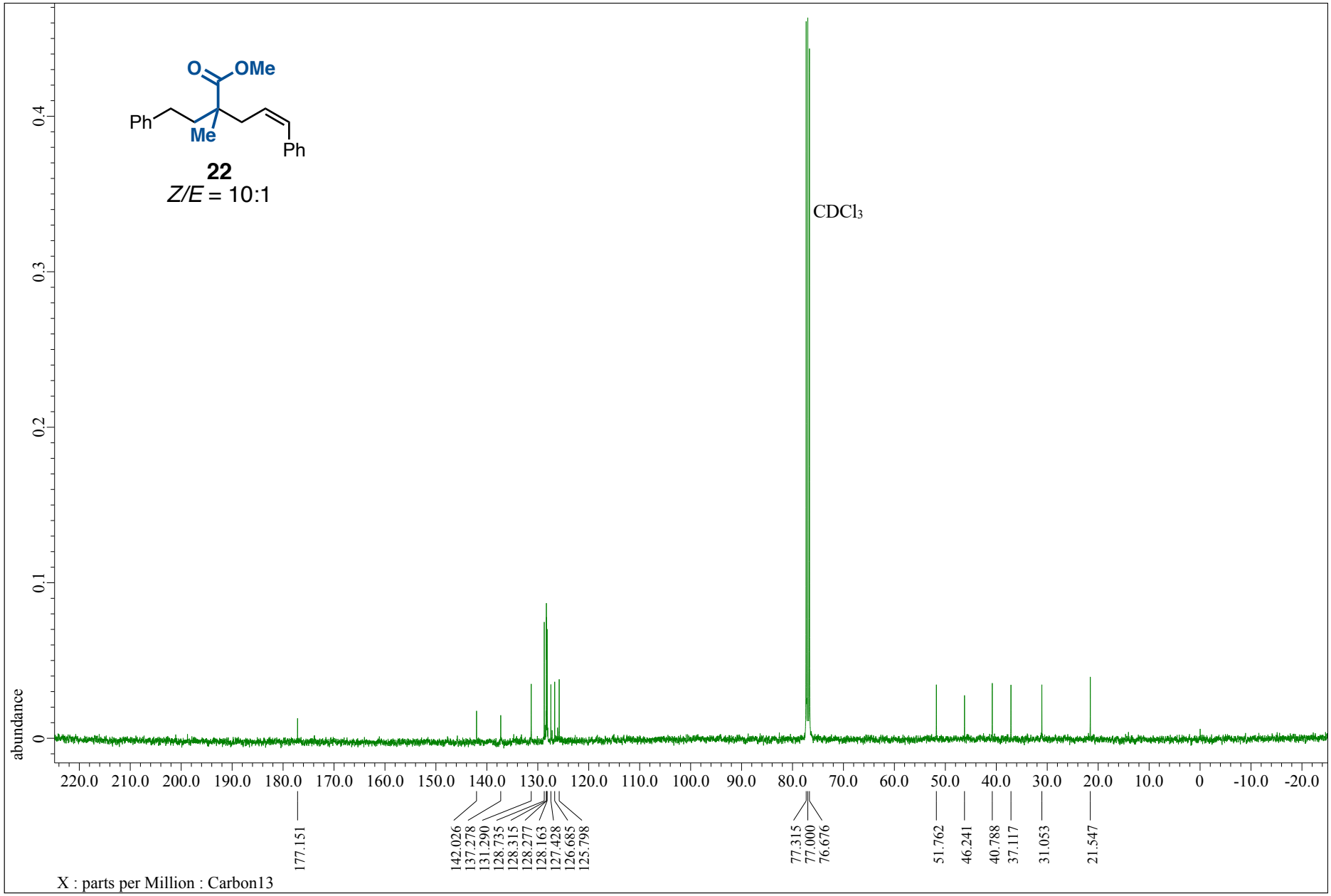
^{19}F NMR spectrum of **21** ($CDCl_3$, 376 MHz)



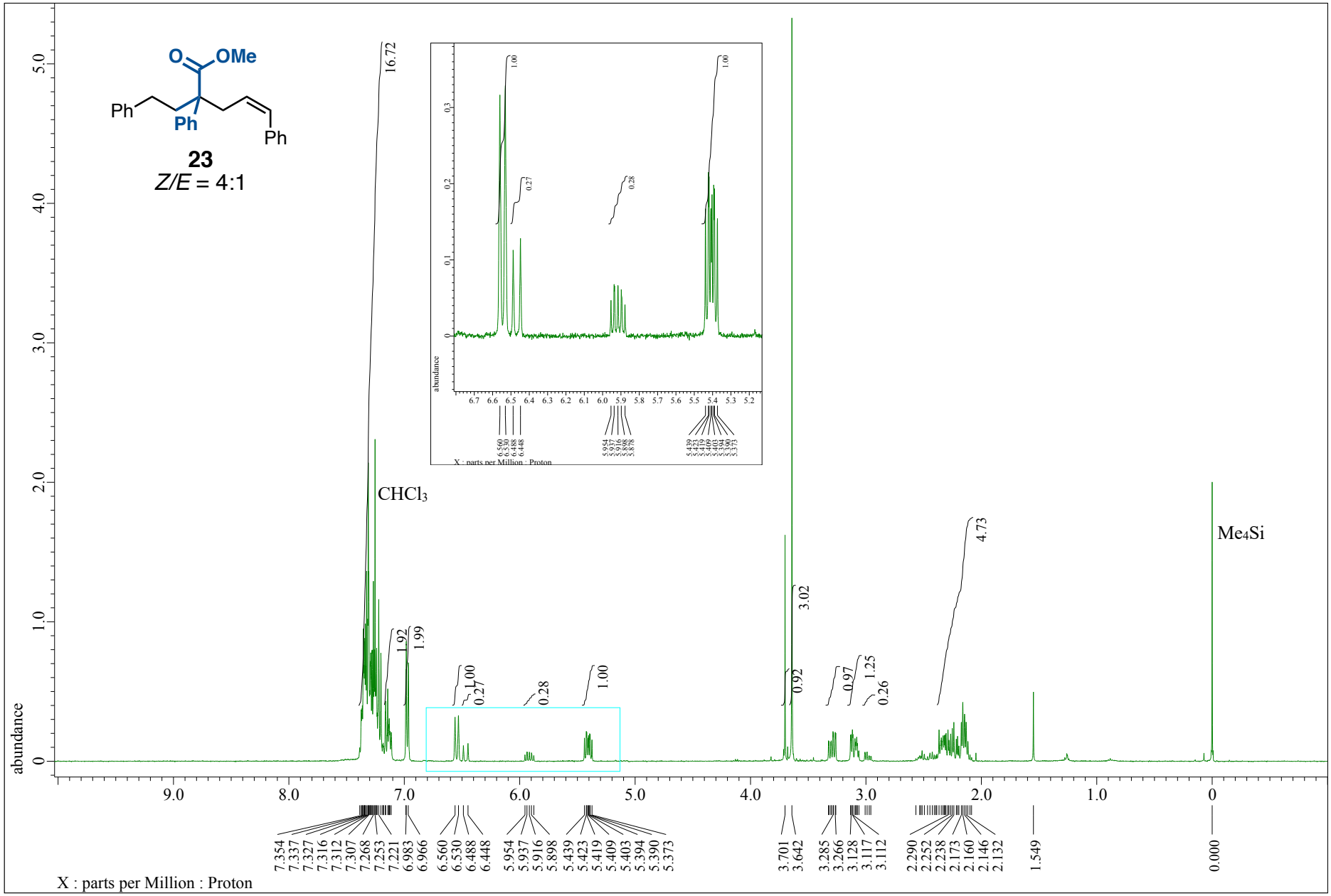
^{1}H NMR spectrum of **22** ($CDCl_3$, 400 MHz)



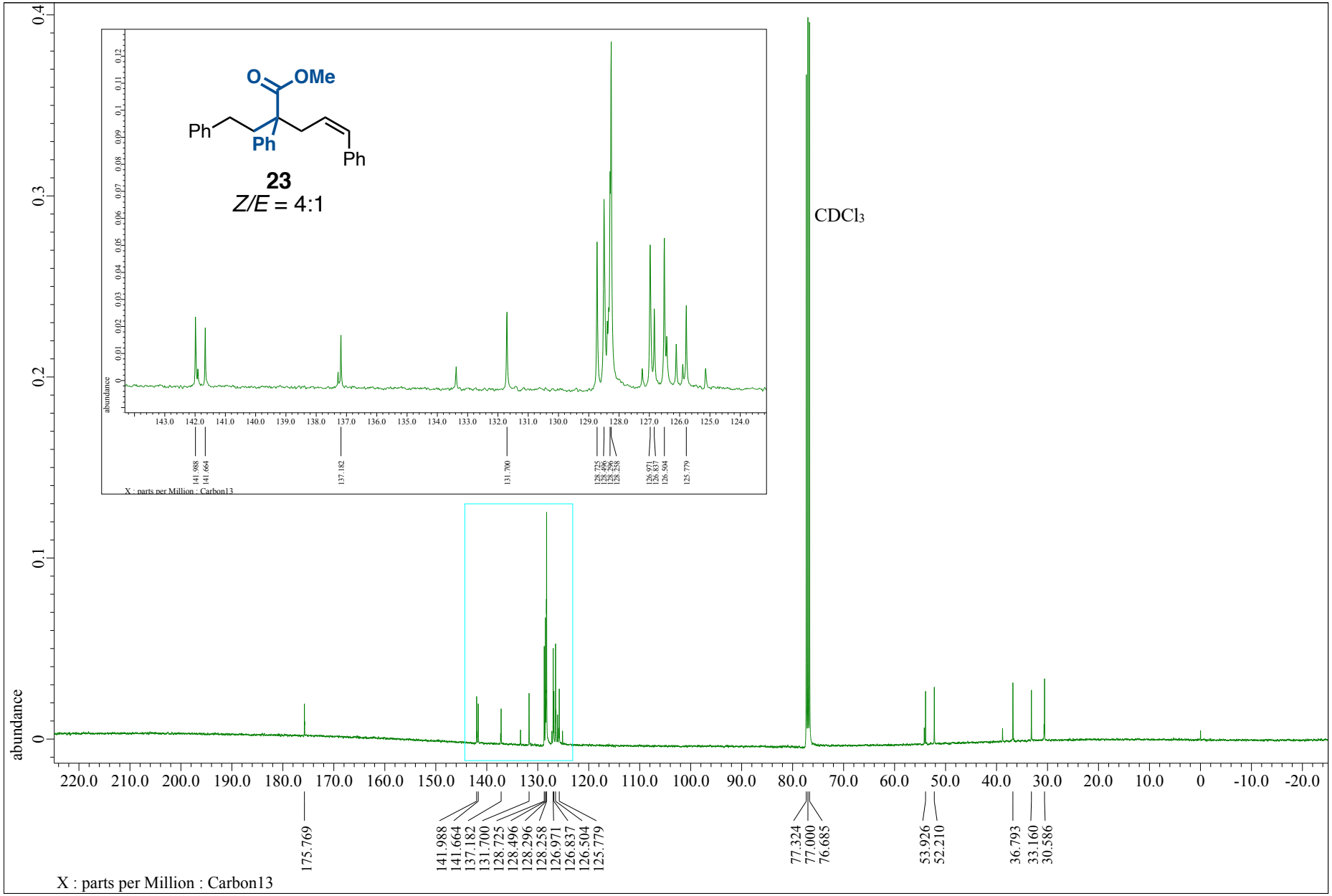
^{13}C NMR spectrum of **22** ($CDCl_3$, 101 MHz)



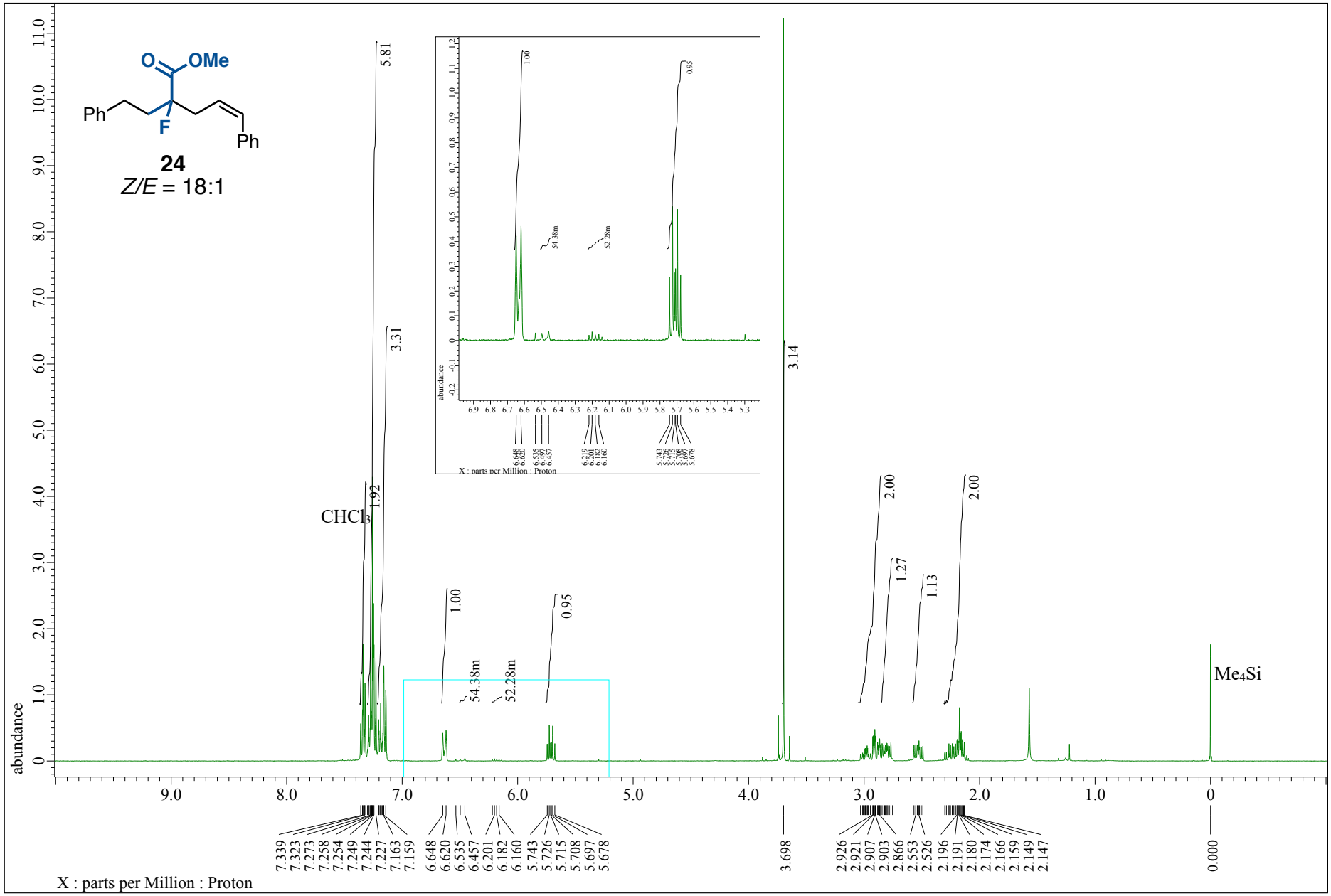
^{1}H NMR spectrum of **23** ($CDCl_3$, 400 MHz)



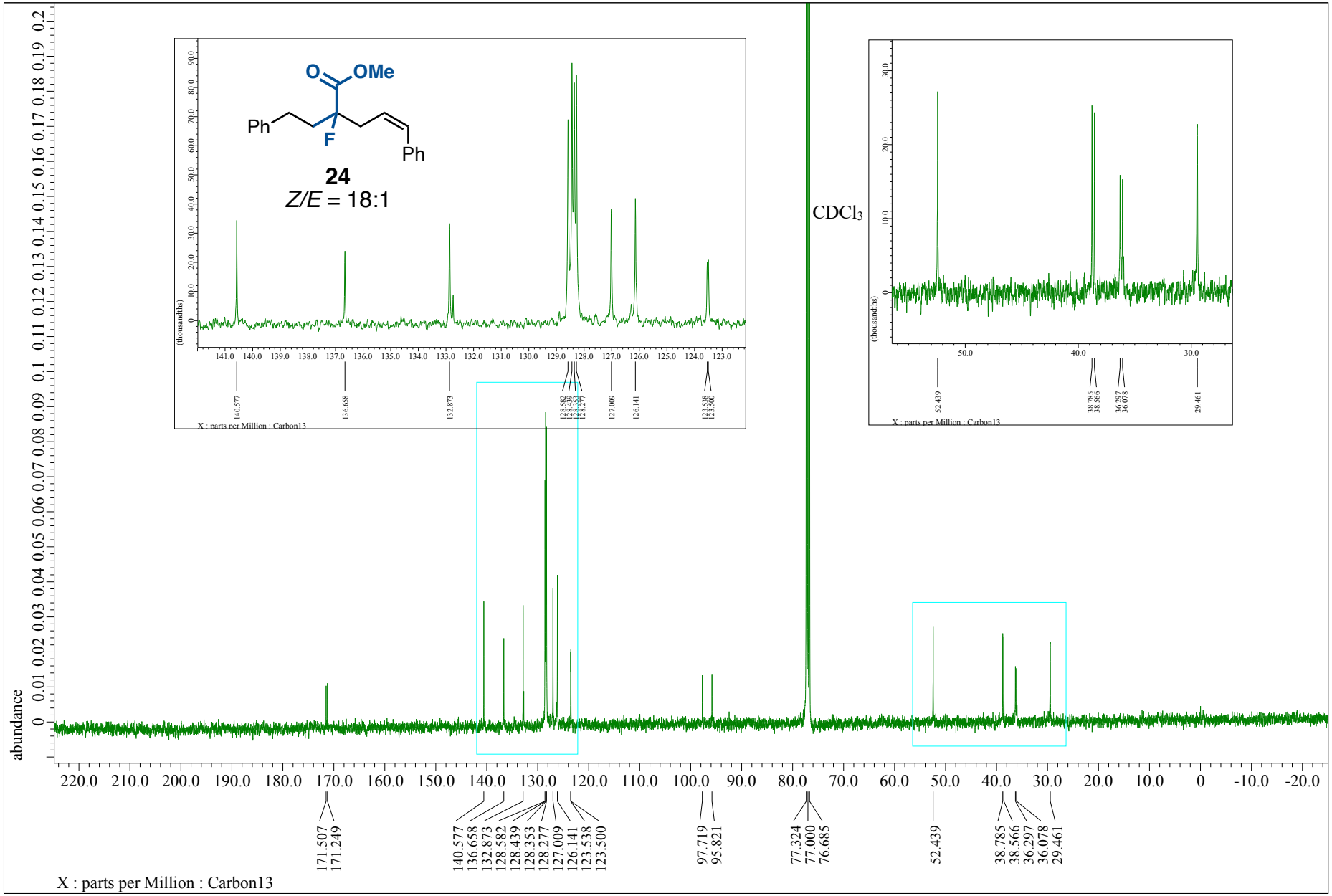
^{13}C NMR spectrum of **23** ($CDCl_3$, 101 MHz)



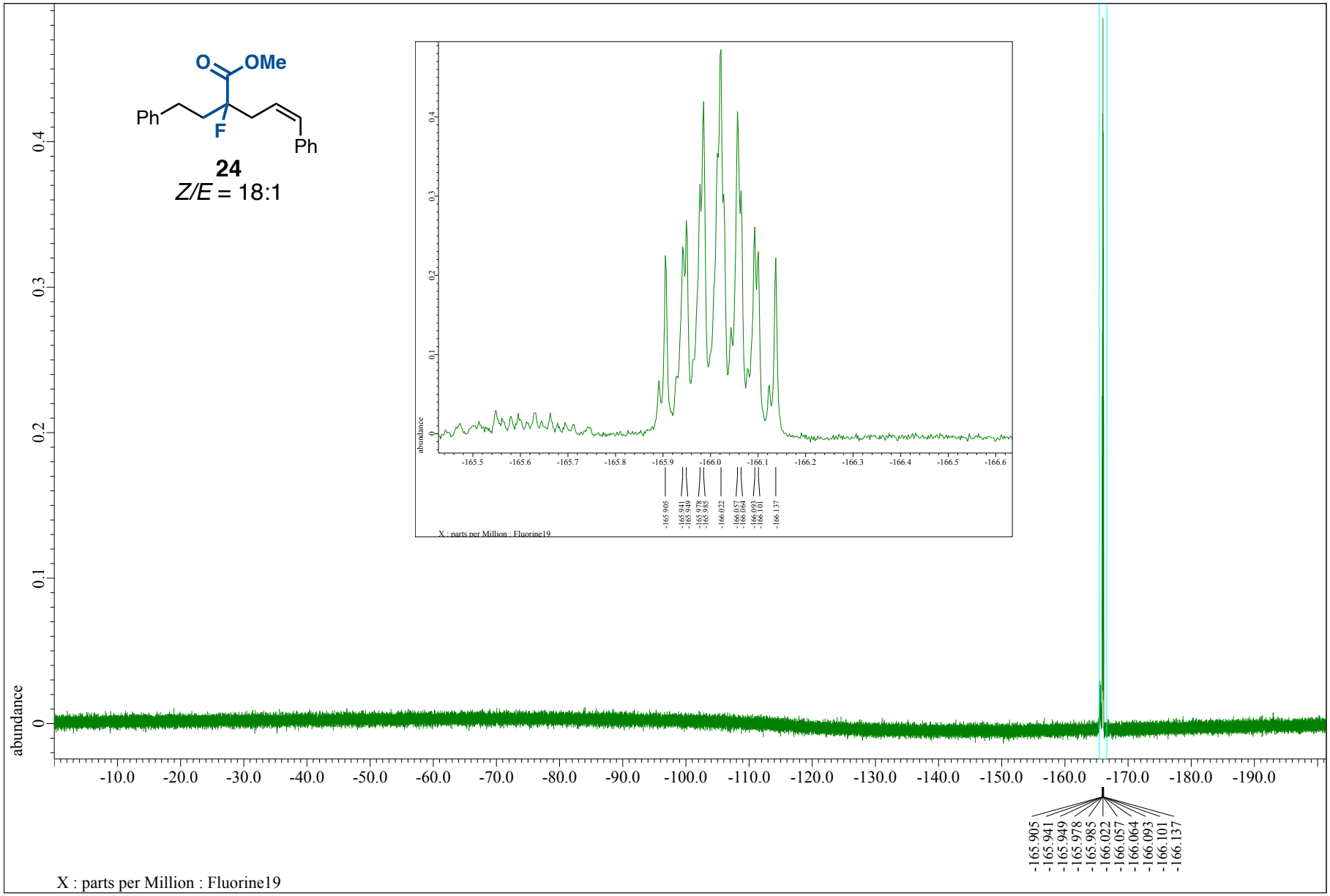
^{1}H NMR spectrum of **24** ($CDCl_3$, 400 MHz)



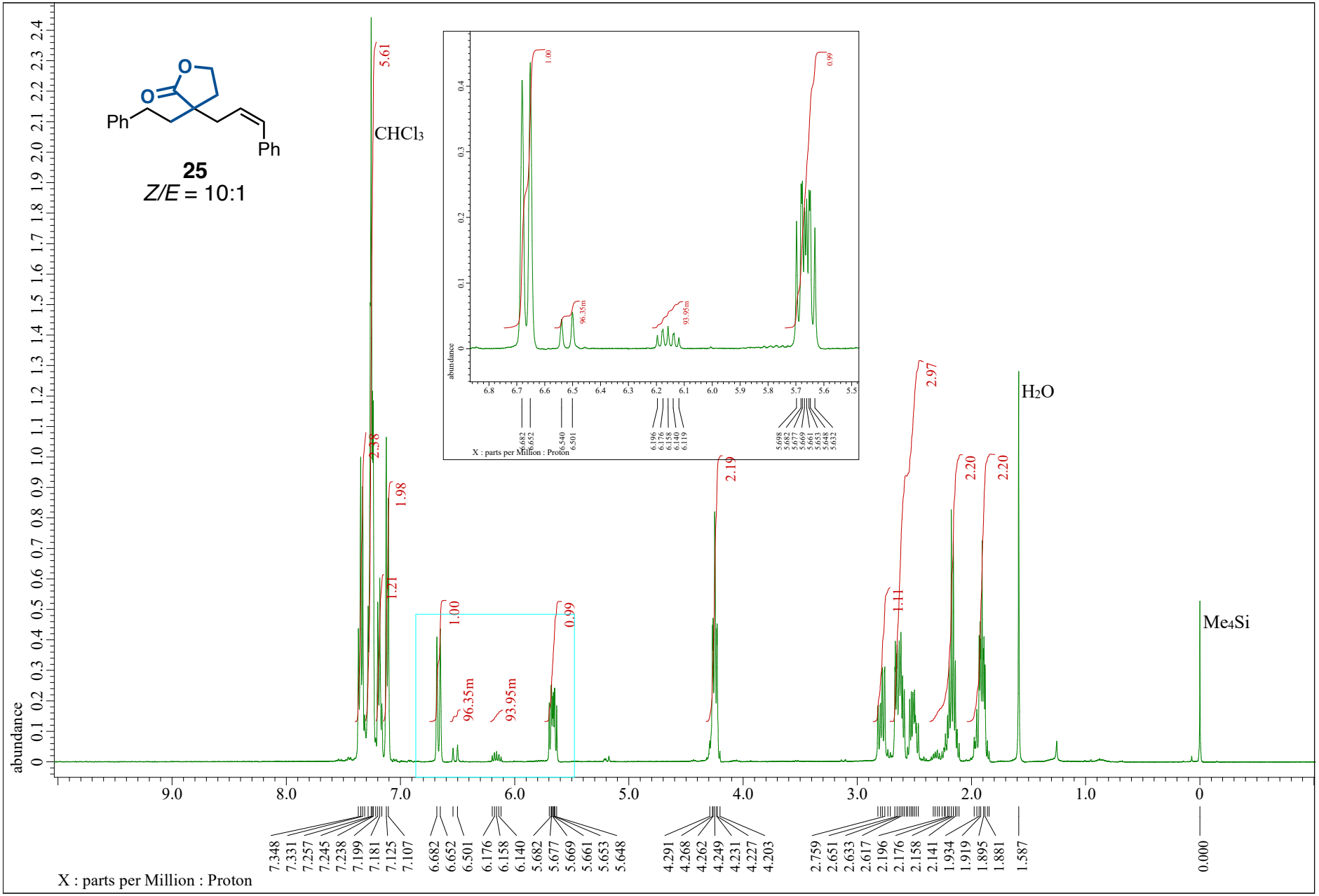
^{13}C NMR spectrum of **24** ($CDCl_3$, 101 MHz)



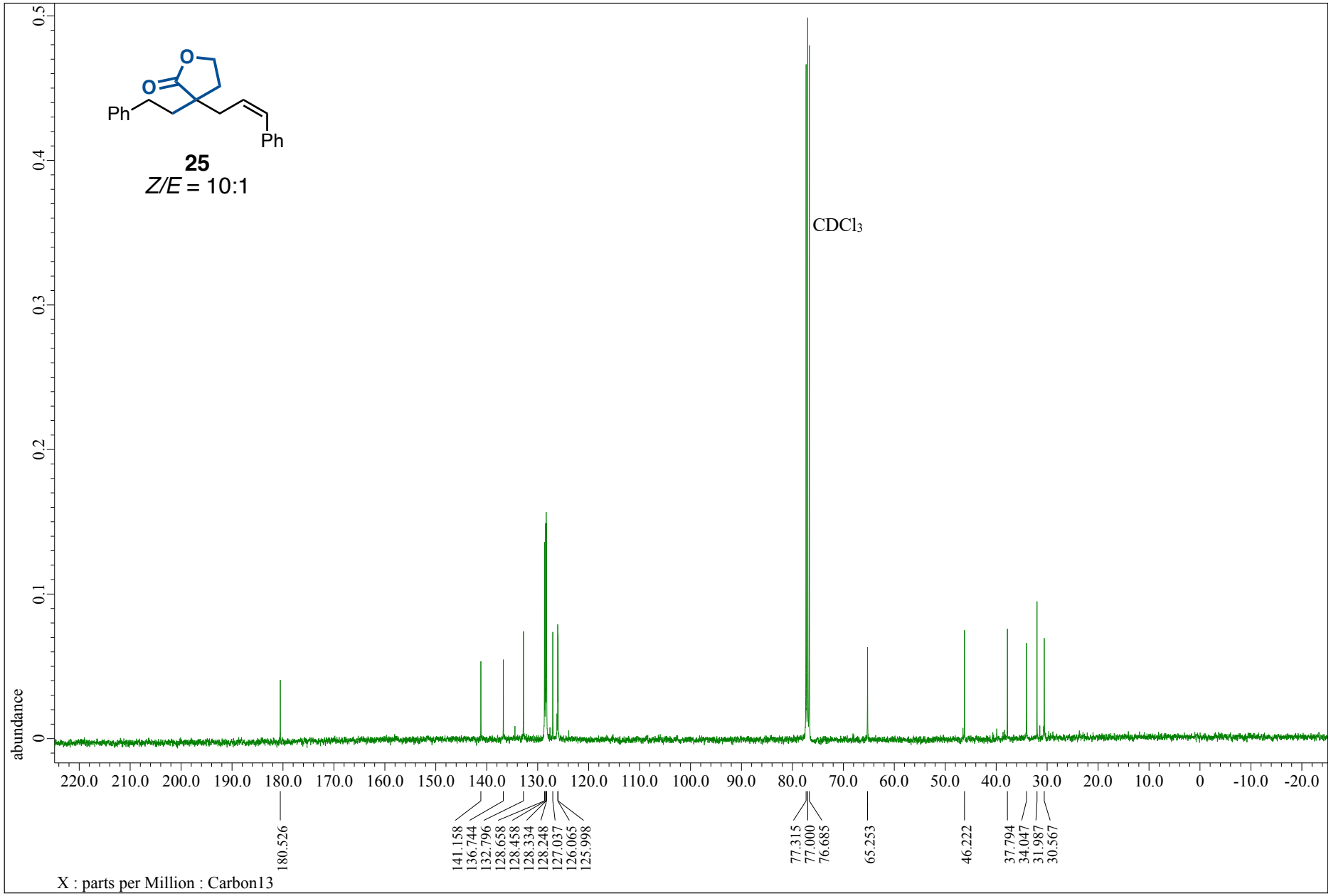
^{19}F NMR spectrum of **24** ($CDCl_3$, 376 MHz)



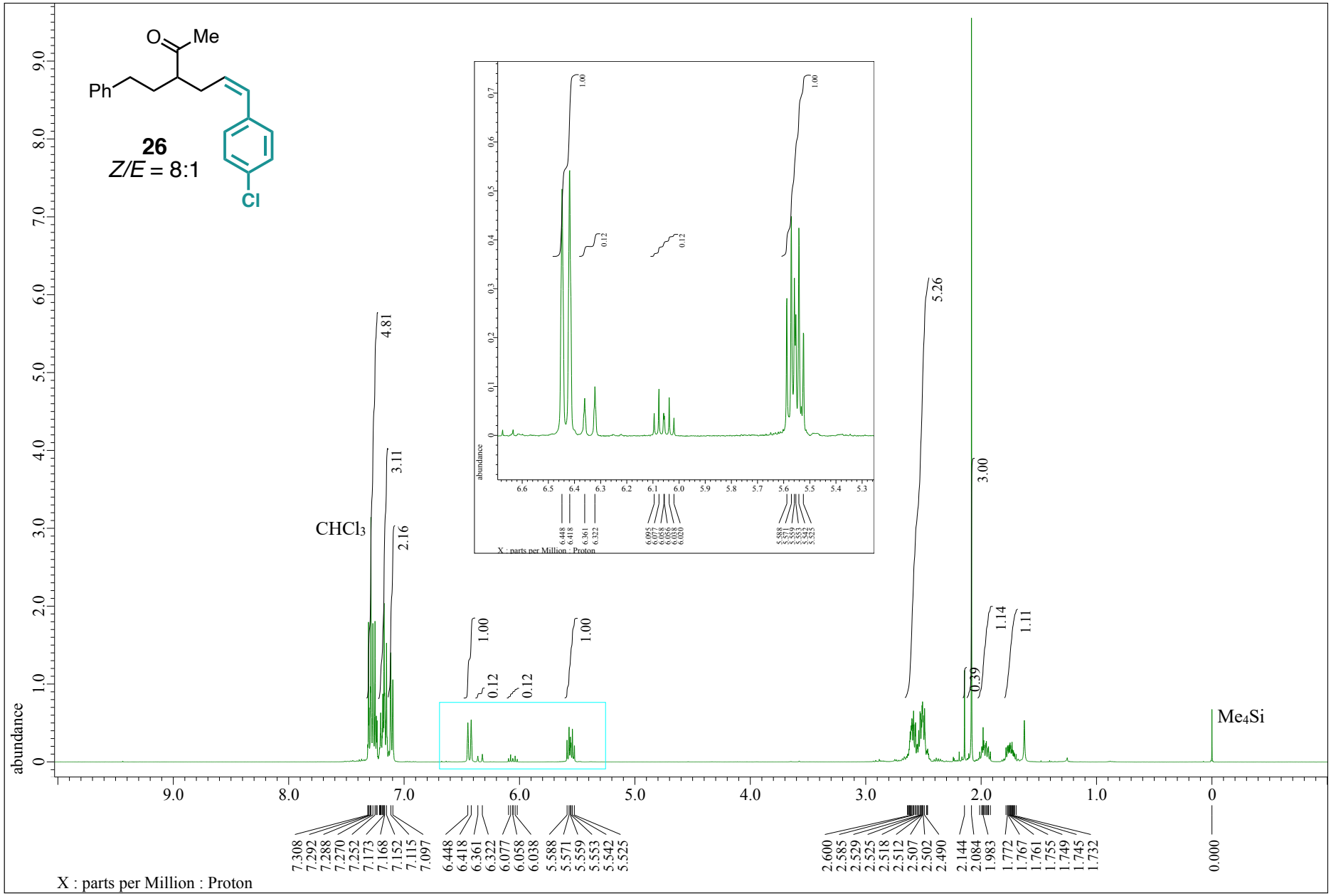
^{1}H NMR spectrum of **25** ($CDCl_3$, 400 MHz)



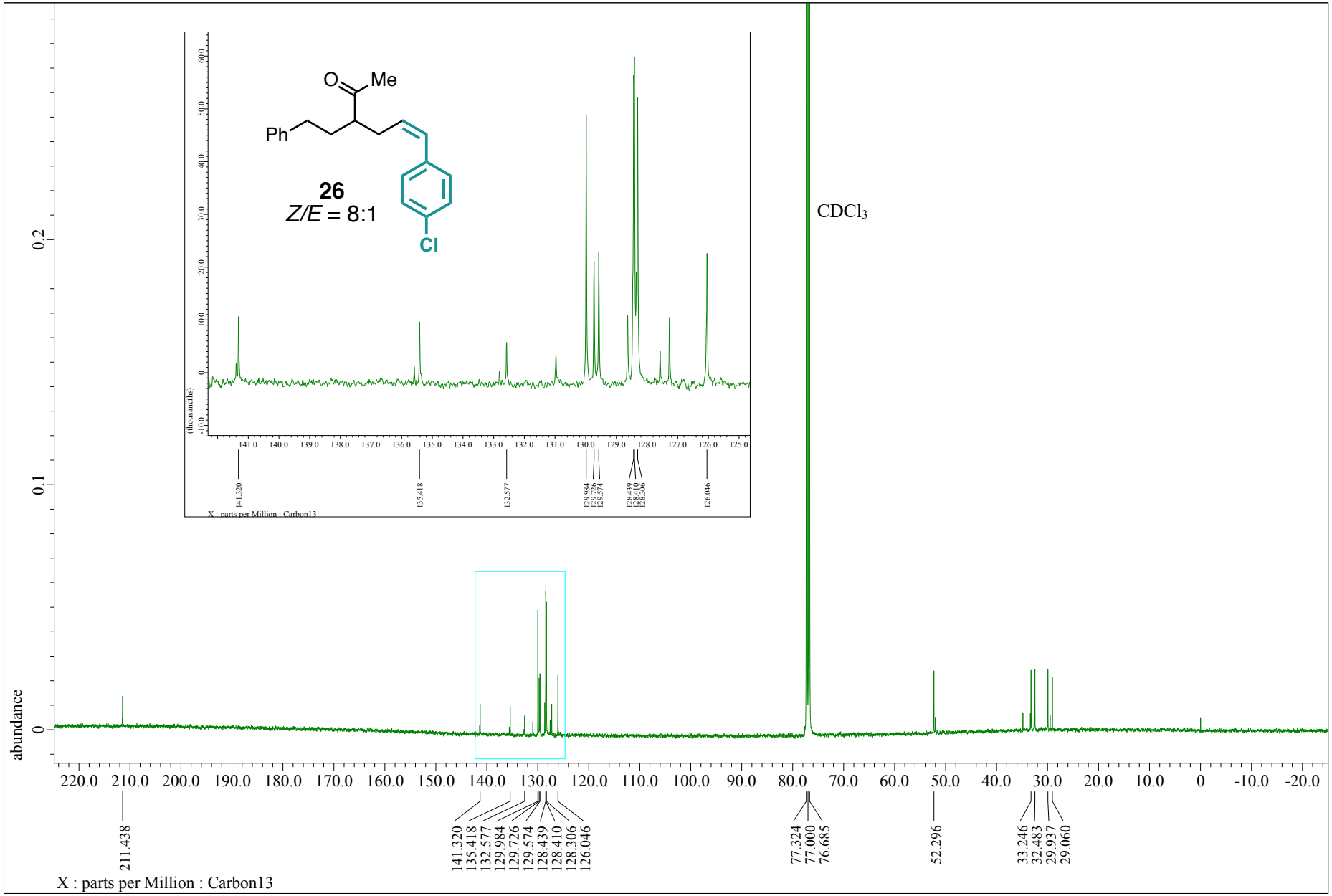
^{13}C NMR spectrum of **25** ($CDCl_3$, 101 MHz)



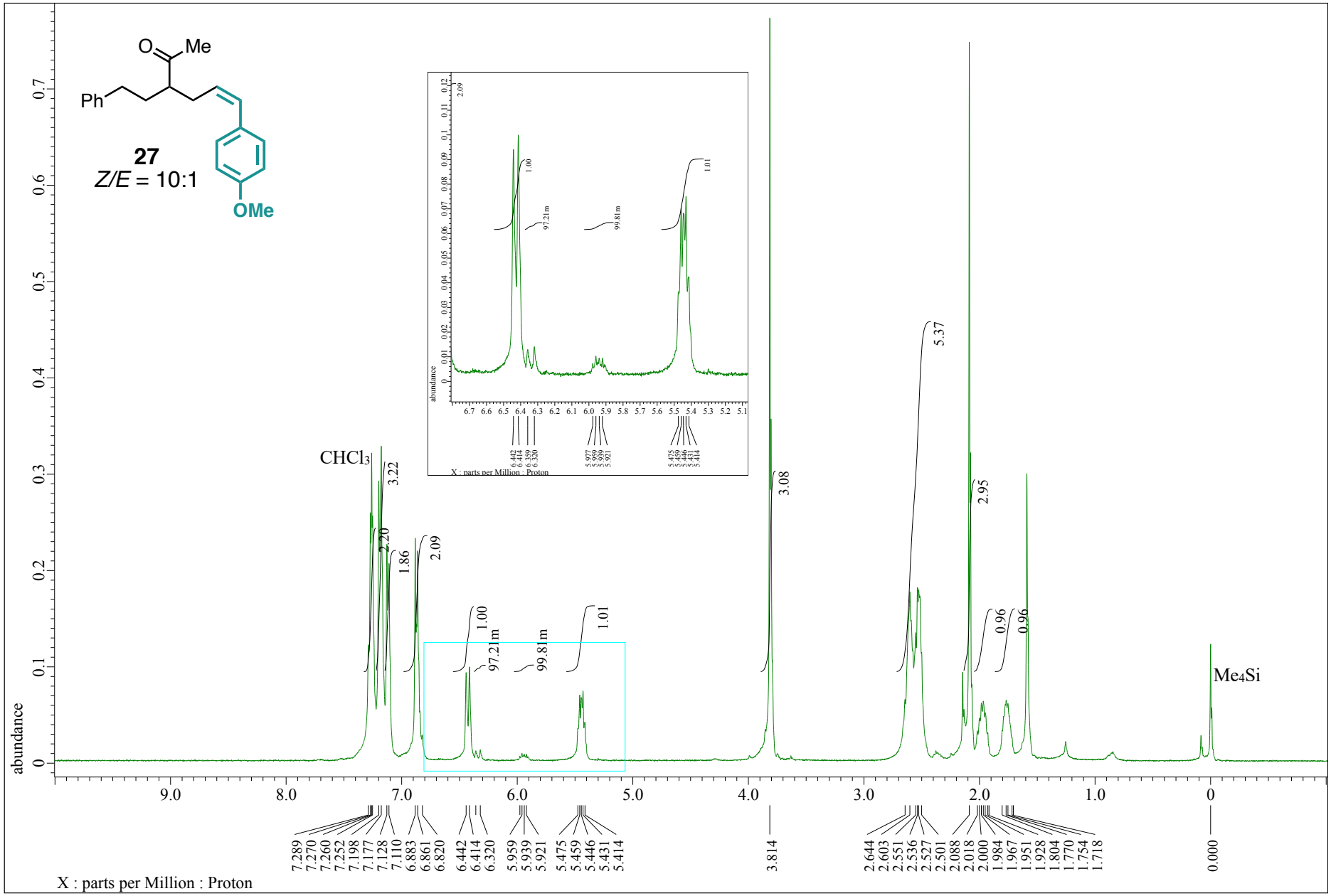
^{1}H NMR spectrum of **26** ($CDCl_3$, 400 MHz)



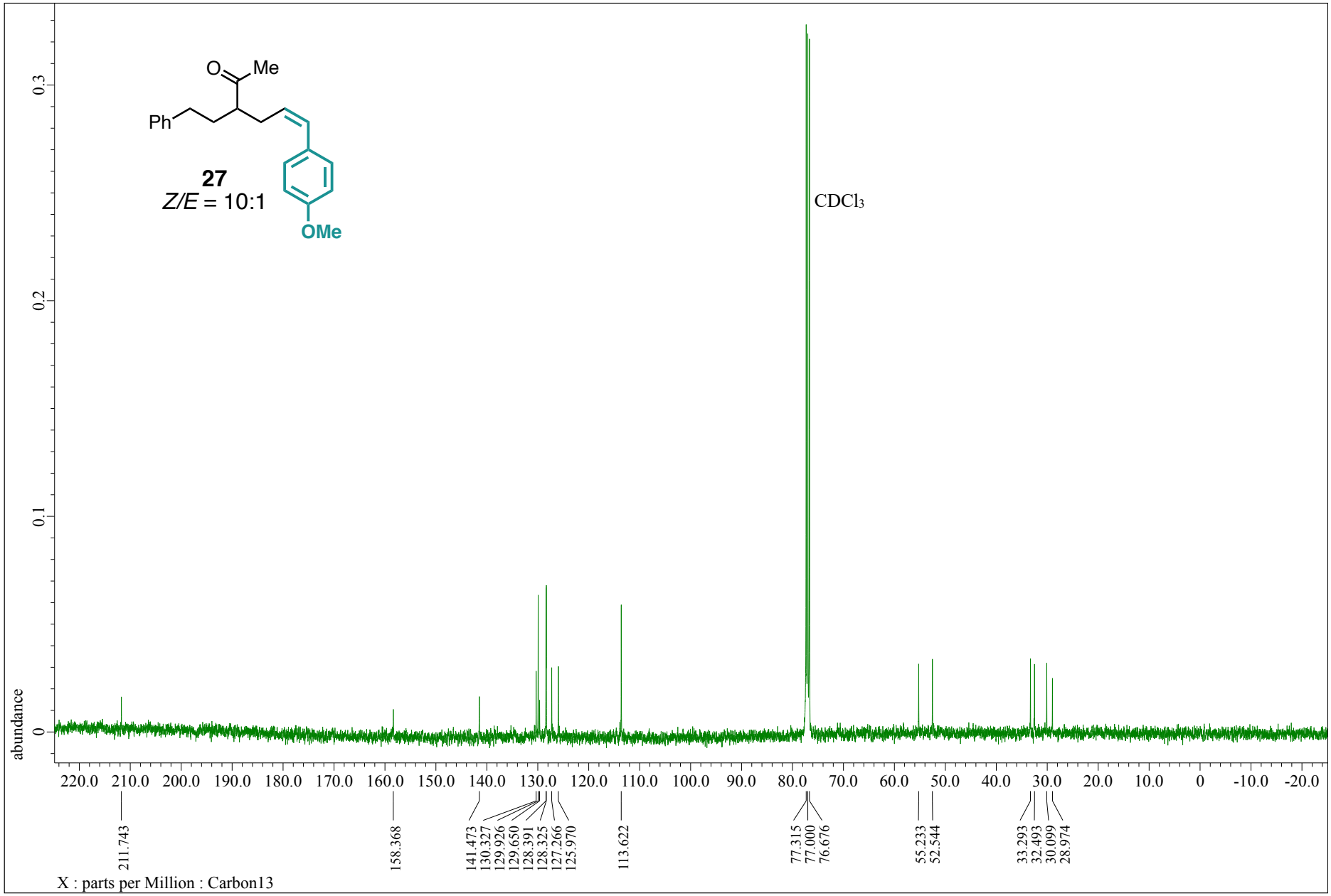
^{13}C NMR spectrum of **26** ($CDCl_3$, 101 MHz)



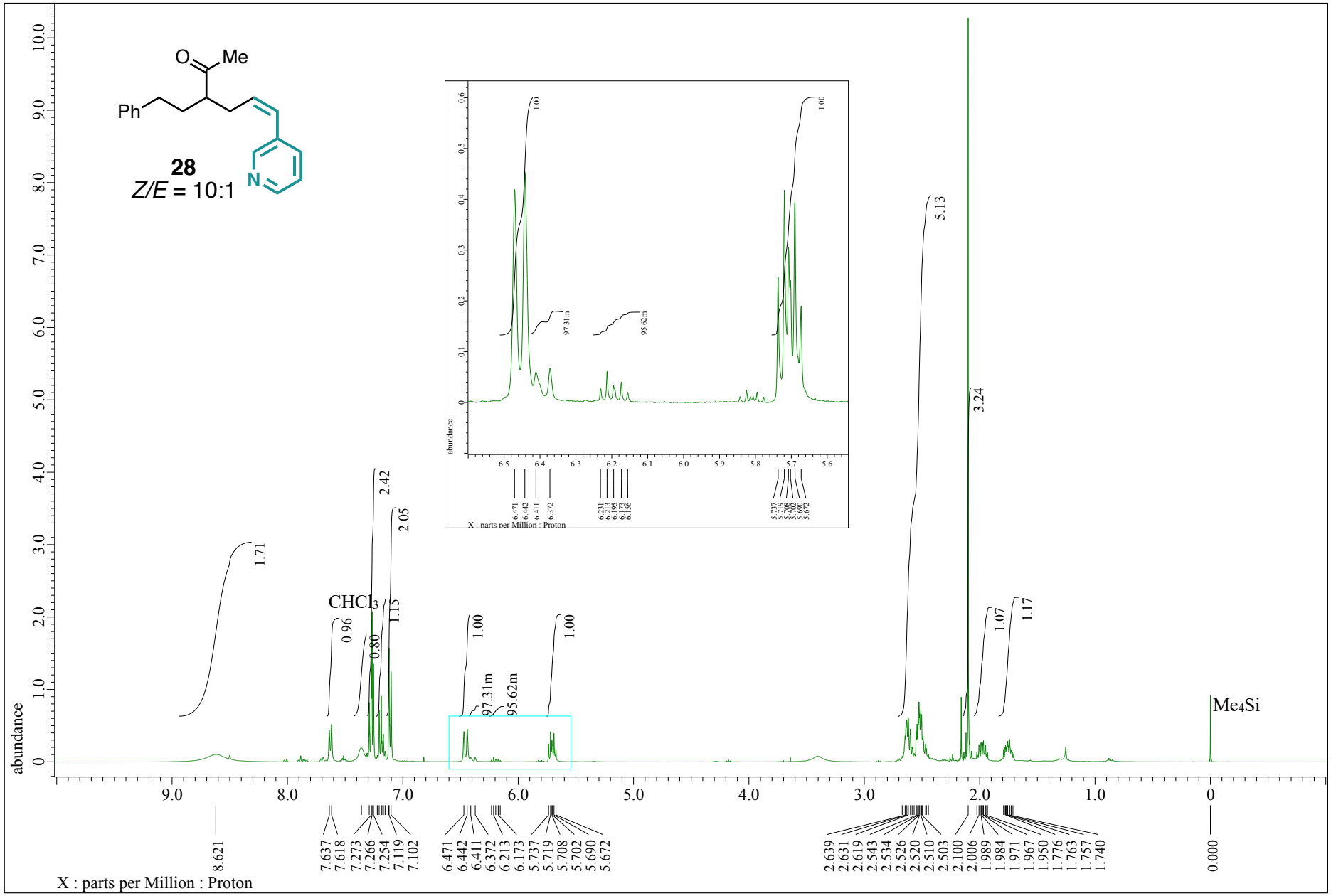
^{1}H NMR spectrum of **27** ($CDCl_3$, 400 MHz)



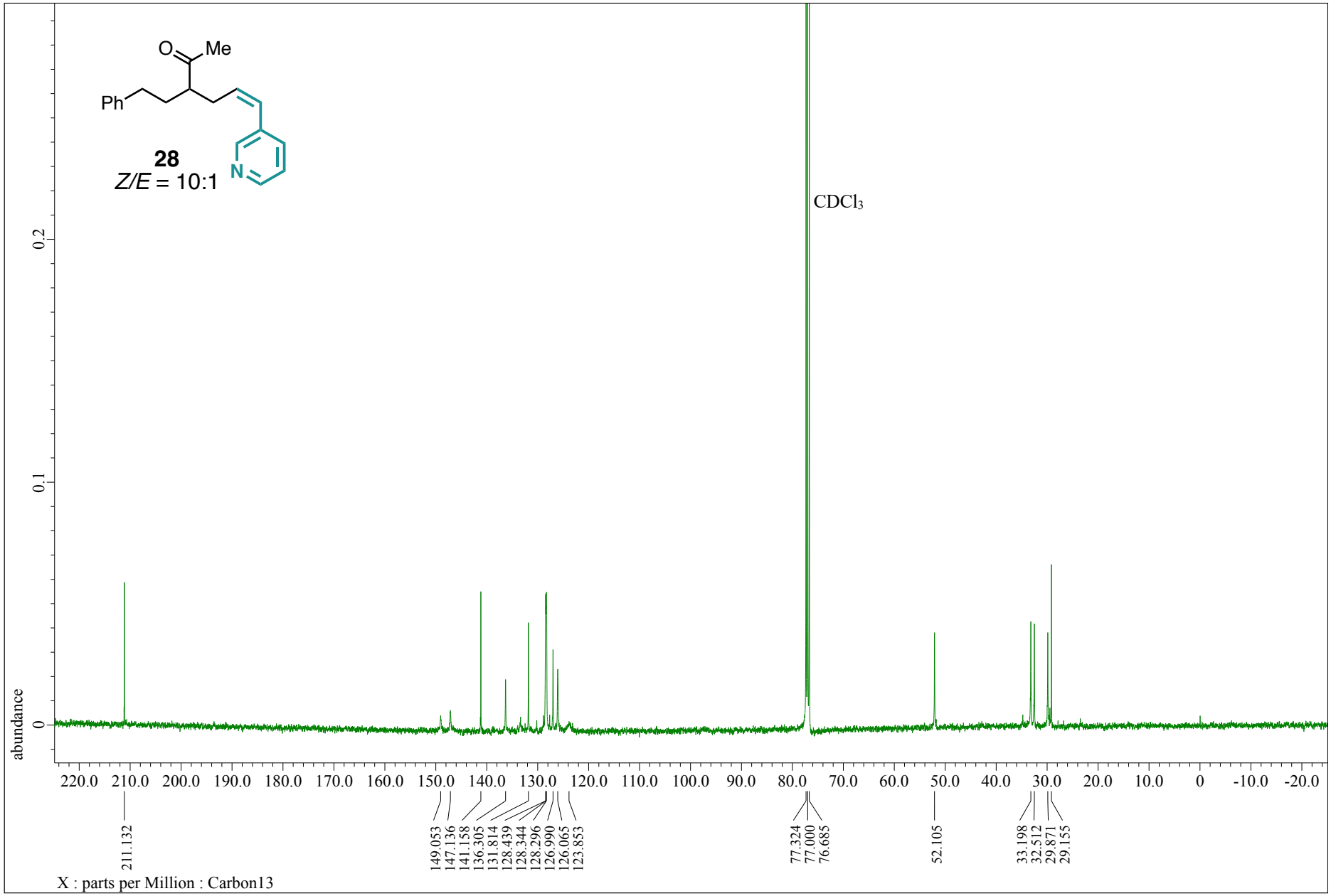
^{13}C NMR spectrum of **27** ($CDCl_3$, 101 MHz)



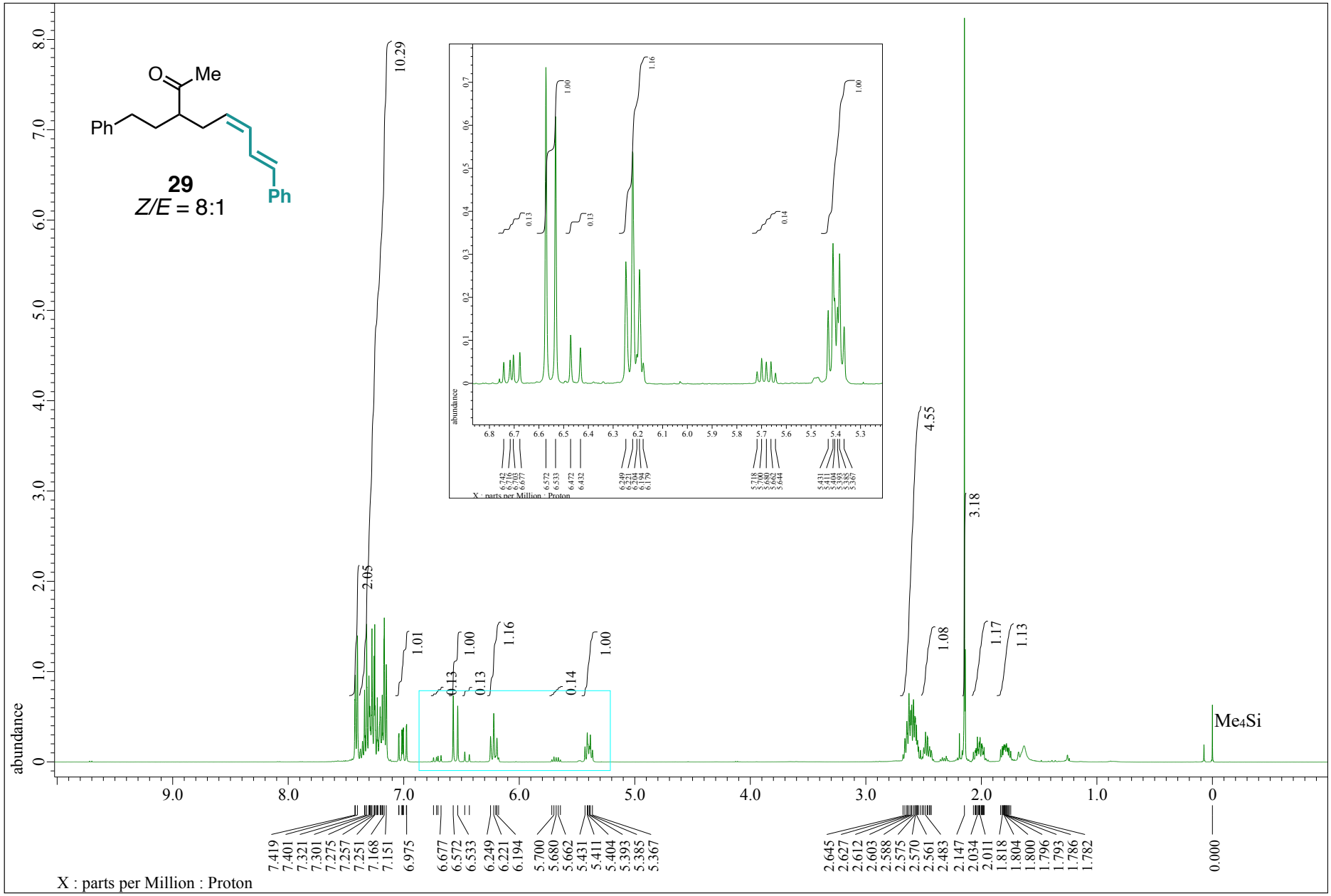
^{1}H NMR spectrum of **28** ($CDCl_3$, 400 MHz)



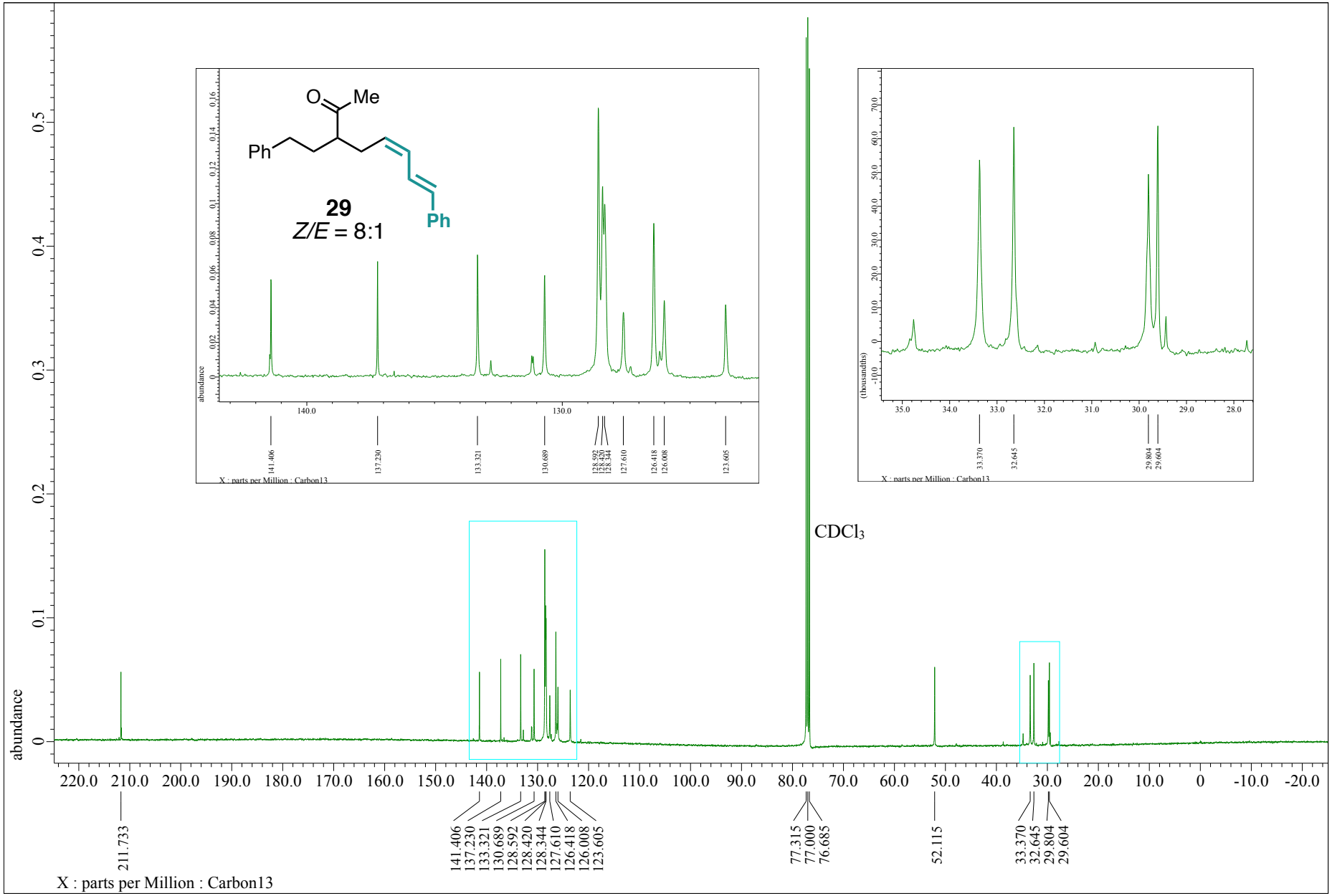
^{13}C NMR spectrum of **28** ($CDCl_3$, 101 MHz)



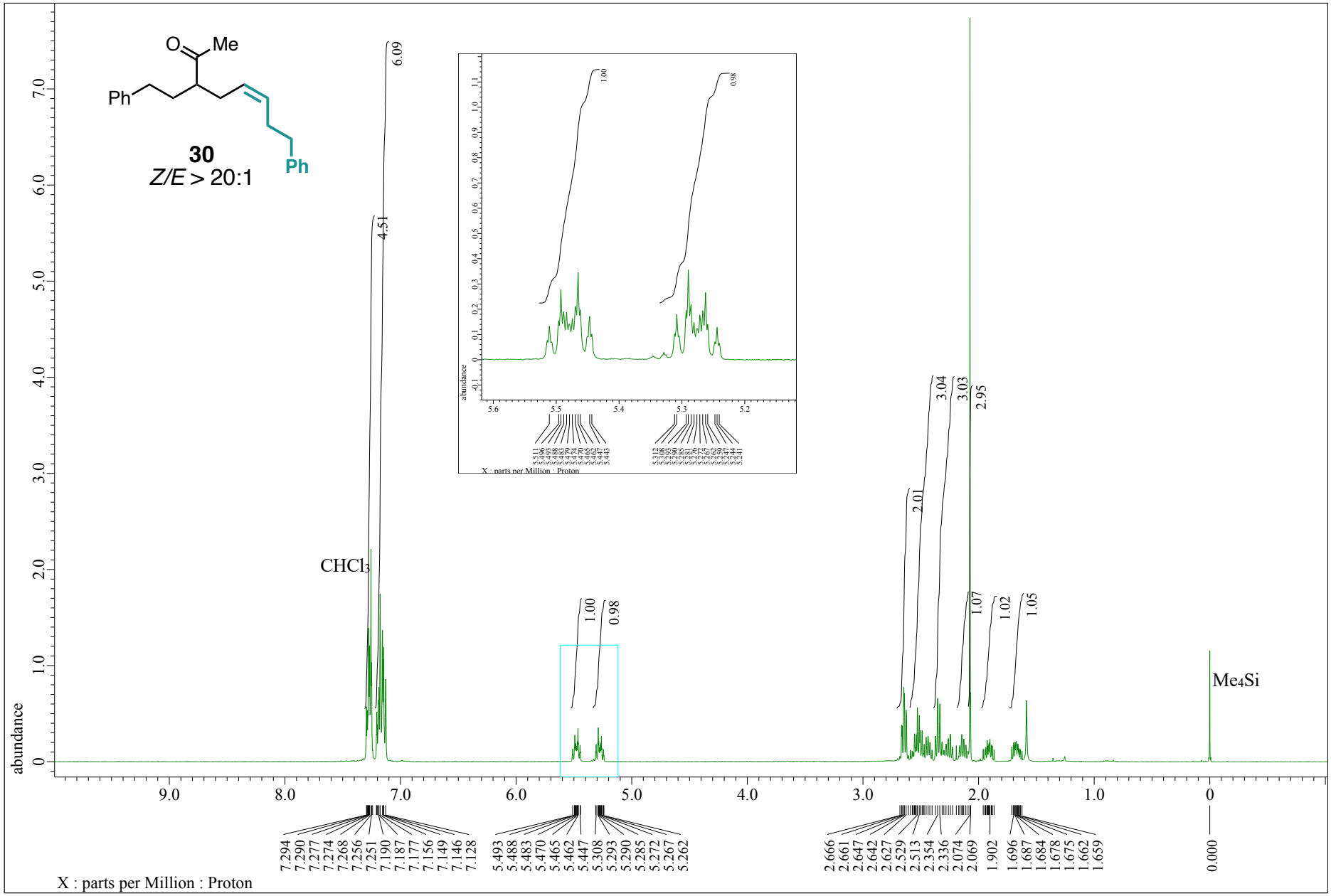
^{1}H NMR spectrum of **29** ($CDCl_3$, 400 MHz)



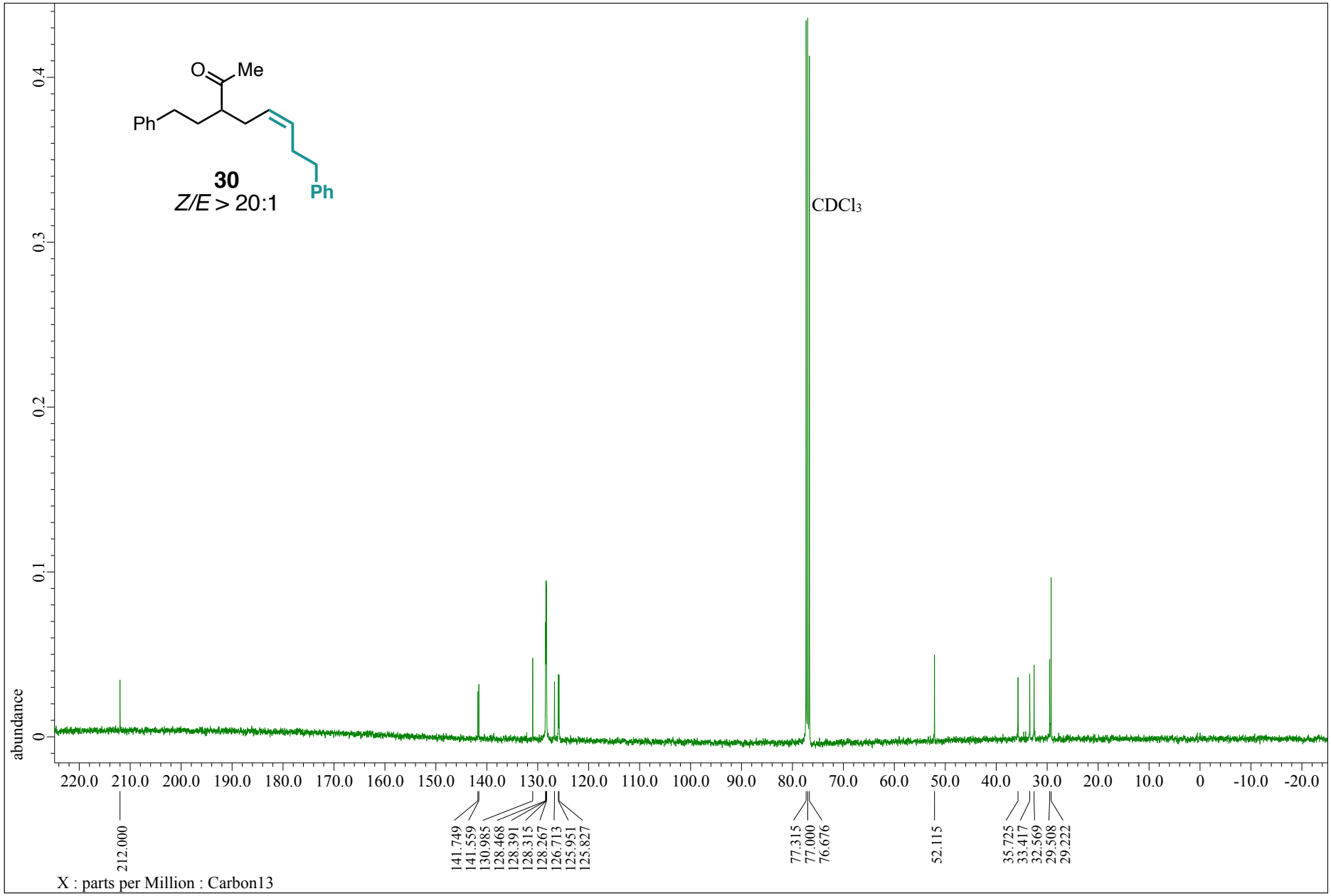
^{13}C NMR spectrum of **29** ($CDCl_3$, 101 MHz)



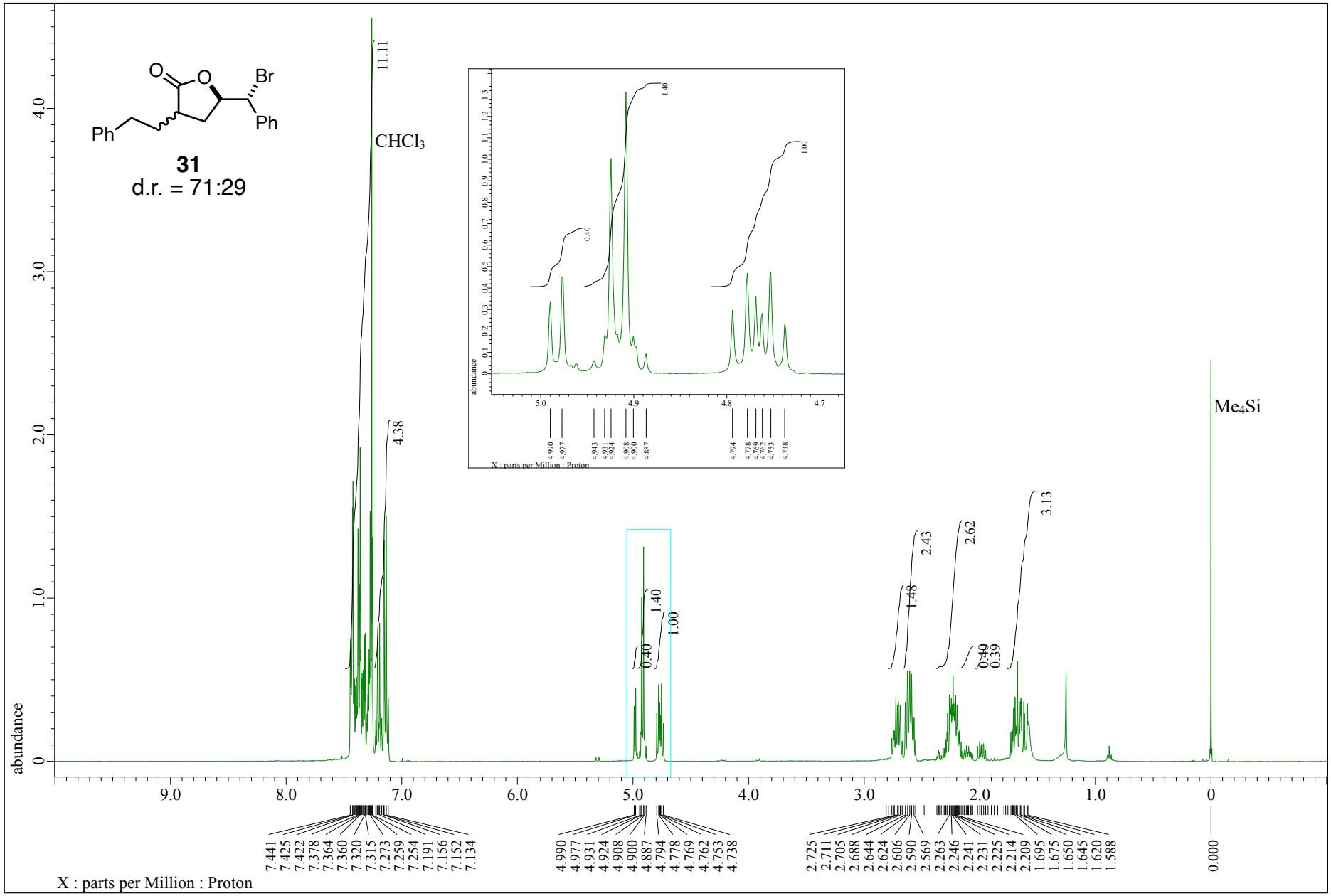
^{1}H NMR spectrum of **30** ($CDCl_3$, 400 MHz)



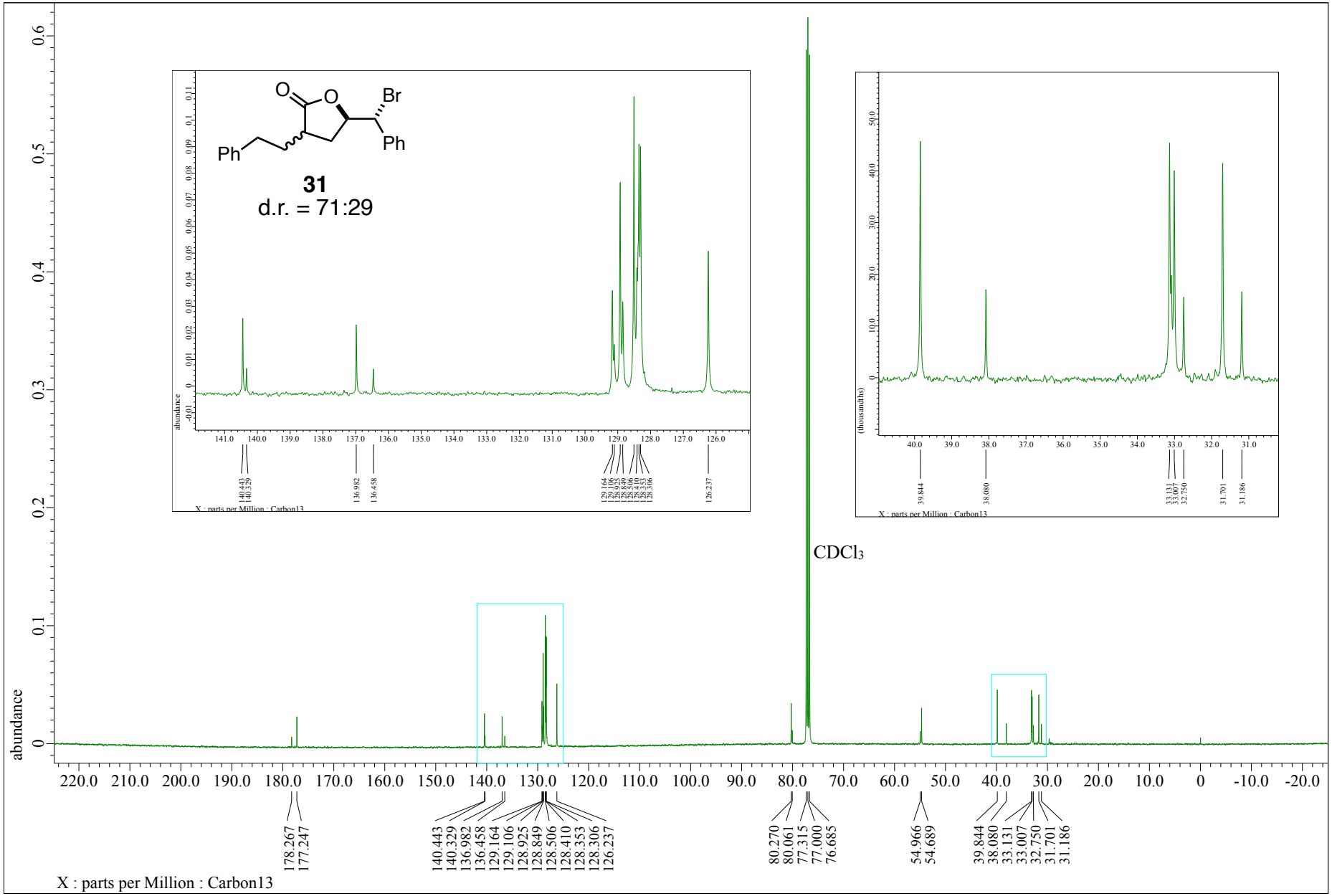
^{13}C NMR spectrum of **30** ($CDCl_3$, 101 MHz)



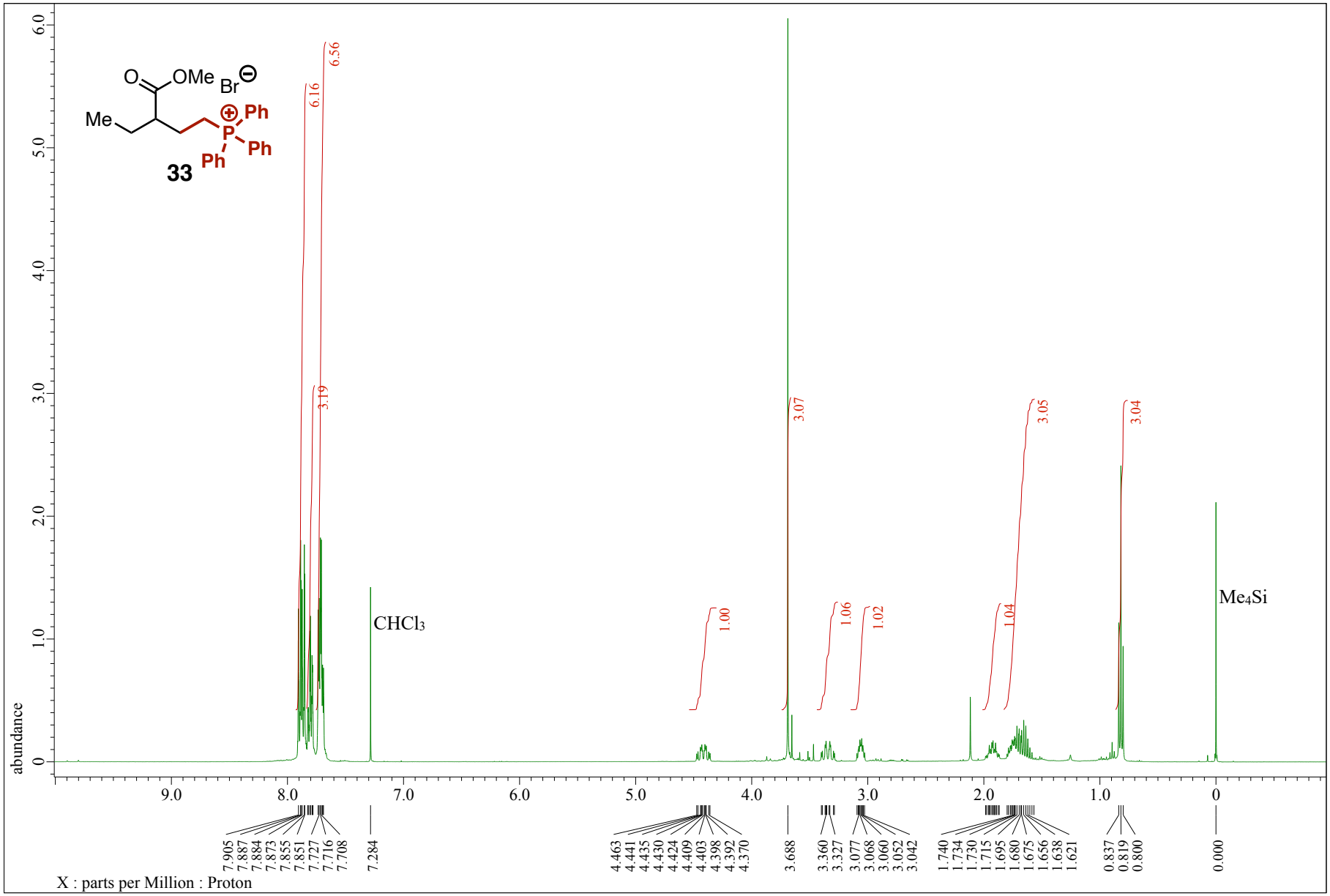
^{1}H NMR spectrum of **31** ($CDCl_3$, 400 MHz)



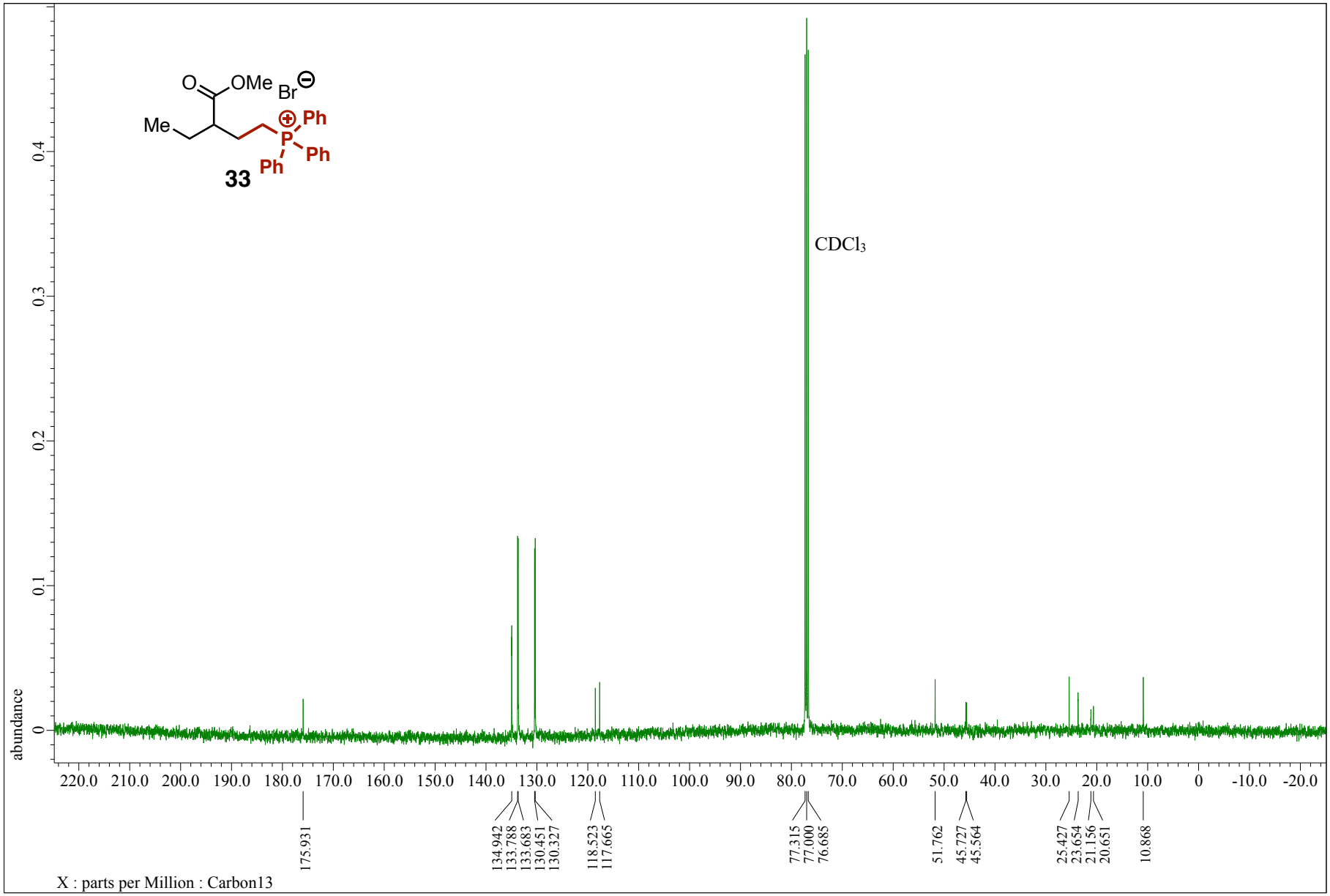
^{13}C NMR spectrum of **31** ($CDCl_3$, 101 MHz)



^{1}H NMR spectrum of **33** ($CDCl_3$, 400 MHz)



^{13}C NMR spectrum of **33** ($CDCl_3$, 101 MHz)



^{31}P NMR spectrum of **33** ($CDCl_3$, 162 MHz)