Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Thianthrenation-Promoted Photoinduced Alkene Difunctionalization and Aryl Allylation with Morita-Baylis-Hillman Adducts

Biplab Mondal,[1] Ayan Chatterjee,[1] Nitis Chandra Saha,[2] Manoranjan Jana,[2] and Jaideep Saha[3]*

[1]Department of Biological and Synthetic Chemistry, Centre of Biomedical Research, Lucknow. [2]Department of Chemistry, University of Kalyani. [3]Department of Medicinal Chemistry, National Institute of Pharmaceutical Education and Research (NIPER), Mohali, India.

*E-mail: jdsaha2000@gmail.com, jsaha@niper.ac.in

Table of contents

1. General Experimental

Unless otherwise noted, all new reactions reported here in were performed using oven-dried or flame-dried glassware under argon atmosphere and stirred magnetically. Solvents received from commercial sources were dried using standard protocols before using in this study and for THF, it was used as freshly distilled. Unless noted, all the reagents and catalysts were used as it was received from commercial sources and no further purification was made on those. Reaction monitoring was performed via TLC, using Merck silica gel 60 F 254 plates. TLC plates were visualized either under UV light (254 nm) or by using 10% ethanolic phosphomolybdic acid (PMA) or 1% aqueous $KMnO_4$ or iodine. Silica gel of 230-400 mesh size was used for the flash column chromatography. ^{1}H, ^{13}C NMR spectra were recorded on Avance III, Bruker at 400 MHz NMR spectrometer. In the experimental section, the ^{1}H NMR chemicals shift are expressed in the form of ppm (δ) relative to δ = 7.26 for $CDCl_3$ whereas ^{13}C NMR chemical shift are expressed relative to δ = 77.16. All coupling constants are apparent J values measured in Hertz. The following abbreviations were used to refer to multiplicities: s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet. HRMS and Electron Spray Ionization (ESI) (m/z) spectra were recorded on Agilent Technologies 6530 Accurate Mass Q-TOF LC/MS at the Centre of Biomedical Research Mass Spectrometry Service. Photoluminescence emissions were acquired on a spectrofluorometer (Shimadzu) at room temperature.

2. *Preparation of the starting materials*

2.1 Thianthrenium salts (TT^+) used in the current study

Following compounds are known in the literature and were prepared following the reported procedure[2] and characterized via NMR/MS.

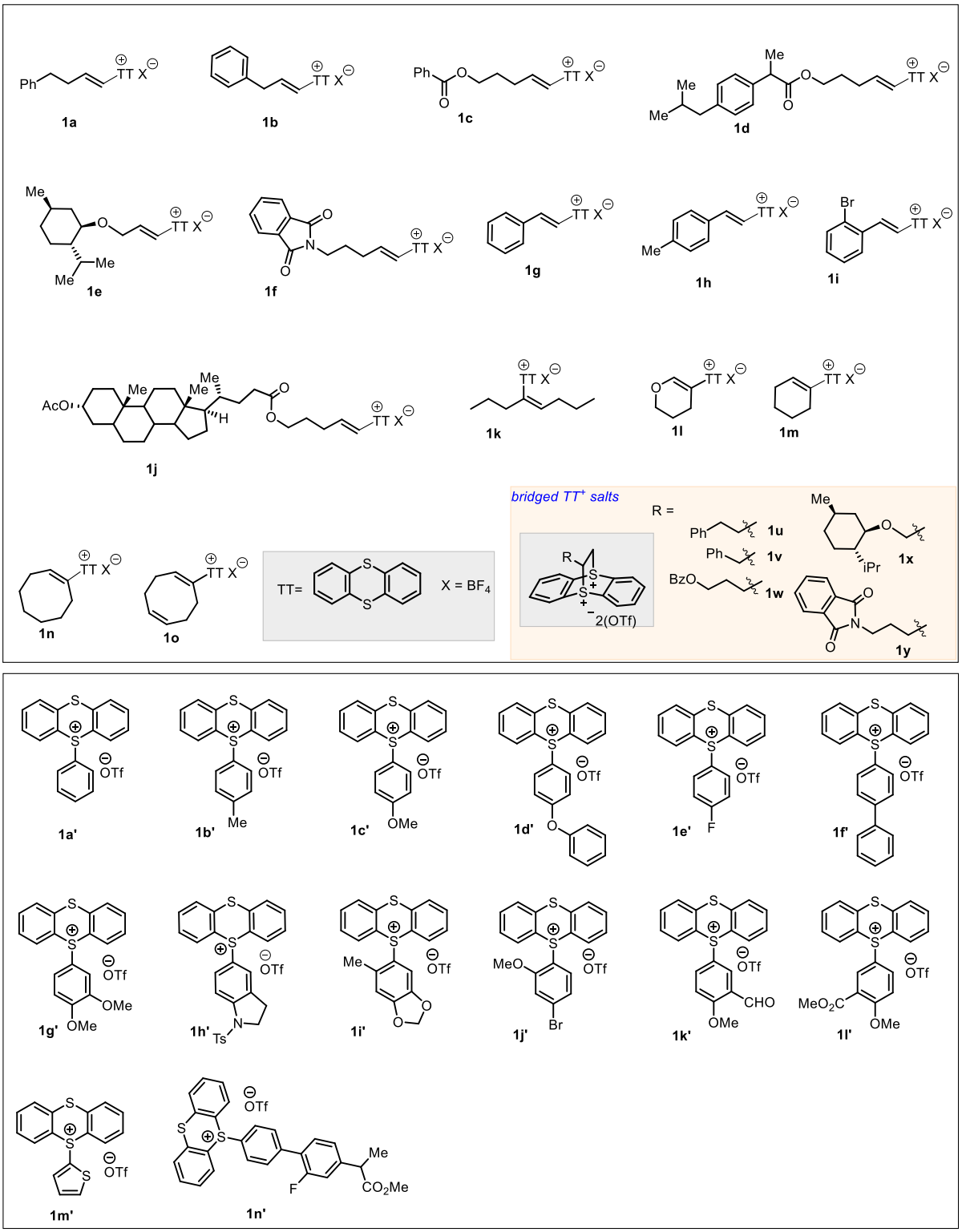


Figure S1. List of various aryl and alkenyl thianthrenium salts used in the current study

2.2. *List of Morita–Baylis–Hillman (MBH) adduct used in the study*[1]

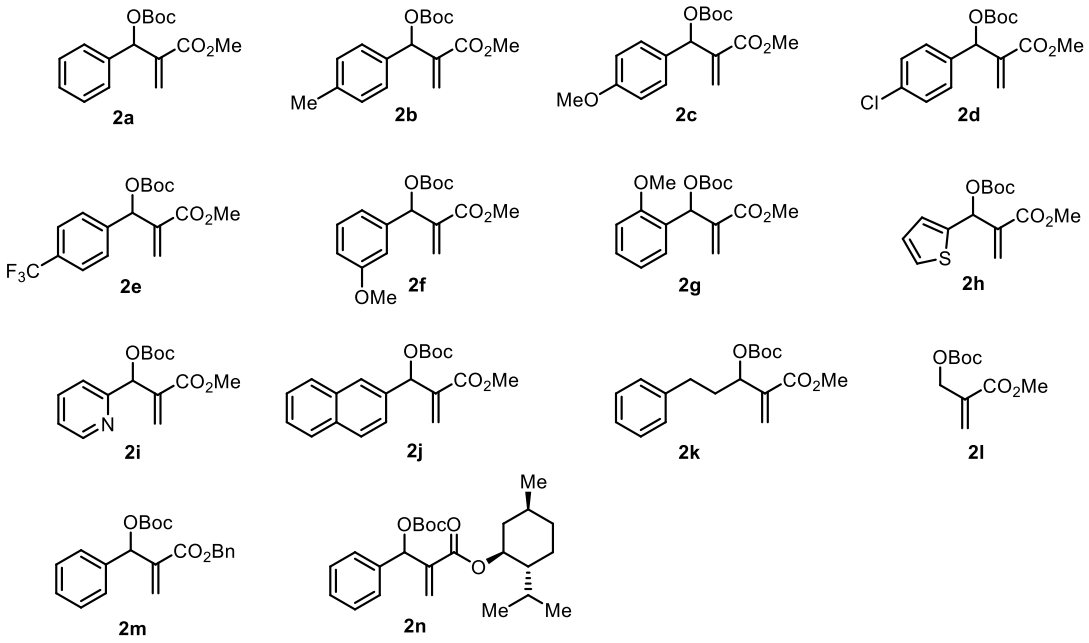


Figure S2. List of various MBH adducts used in the current study

3. Optimization studies for alkene difunctionalization [a]

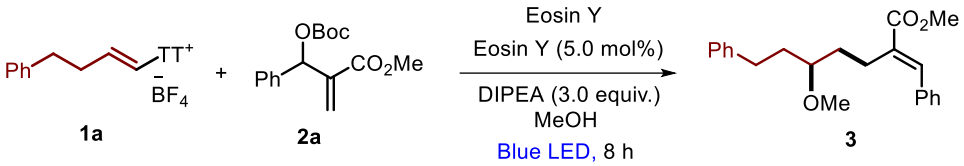


Table S1[a]

Entry	Deviation from standard conditions	Yield [%][b]
1	none	67
2	Rhodamine B instead of Eosin Y	<10
3	$Ru(bpy)_3(PF_6)_2$ instead of Eosin Y	55
4	$Ir[\{dF(CF_3)ppy\}_2(dtbpy)]PF_6$ (IV) instead of Eosin Y	<5
5	no Eosin Y	0
6	without blue LED	0
7	DIPA instead of DIPEA	0
8	no base	0
9[c]	EtOH	CM
10	DCM: MeOH (5:1)	49

[a]Reaction Conditions: Alkene TT-salt (0.1 mmol, 1.0 equiv.), MBH adduct (0.1 mmol, 1.0 equiv.), DIPEA (0.3 mmol, 3.0 equiv.), PC (5.0 mol%), MeOH (0.5 mL), Blue LED (427nm), 12 hours; [b]isolated yields. [c]CM: complex mixture;

4. Control experiments

4.1. Radical trapping with TEMPO (as radical scavenger)

Reactions from the Scheme 4 (main text) of the manuscript.

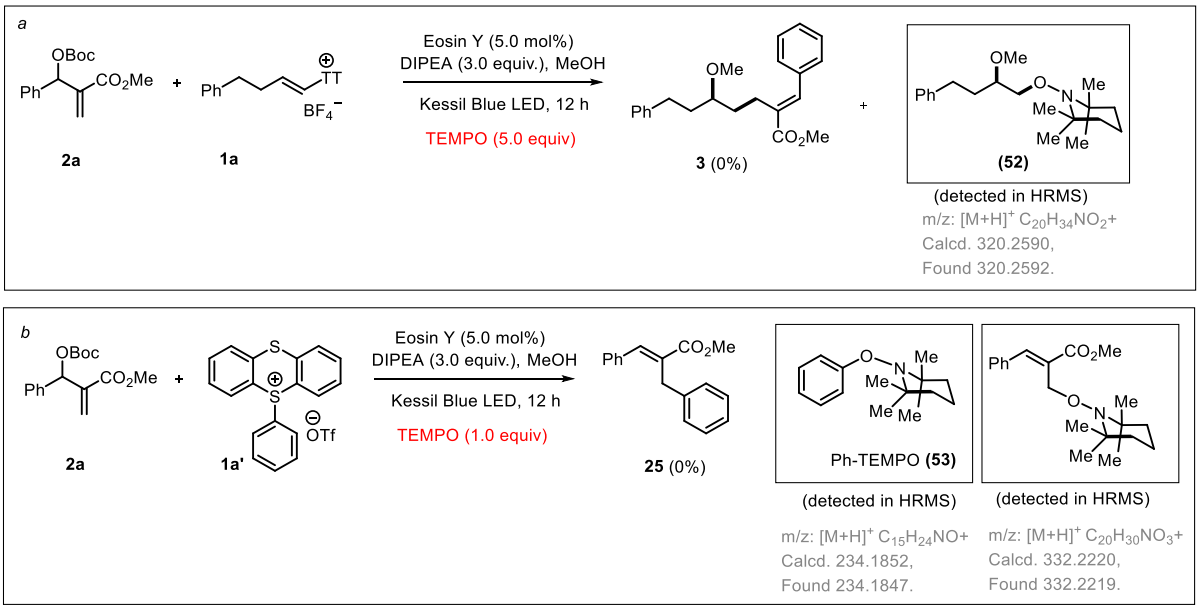


Figure S3. Radical trapping experiment and MS analysis of crude reaction mixture.

4.2. Deuterium labelling experiments

Above reaction was performed according to general procedure, except CD_3OD was used as a solvent.

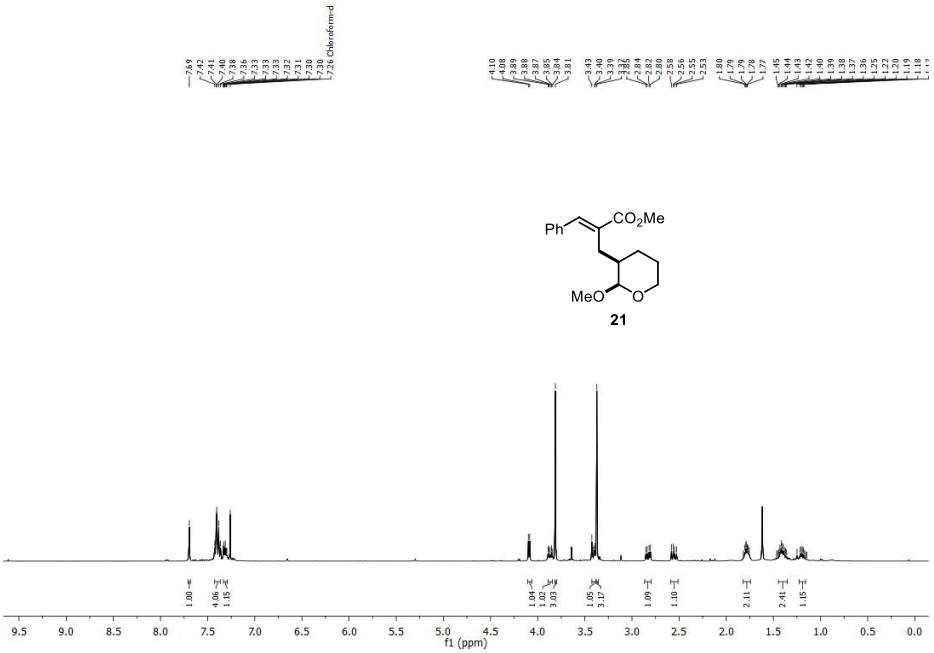


Figure S4: ^1H NMR (400 MHz, $CDCl_3$) of compound **21** (*provided as reference*)

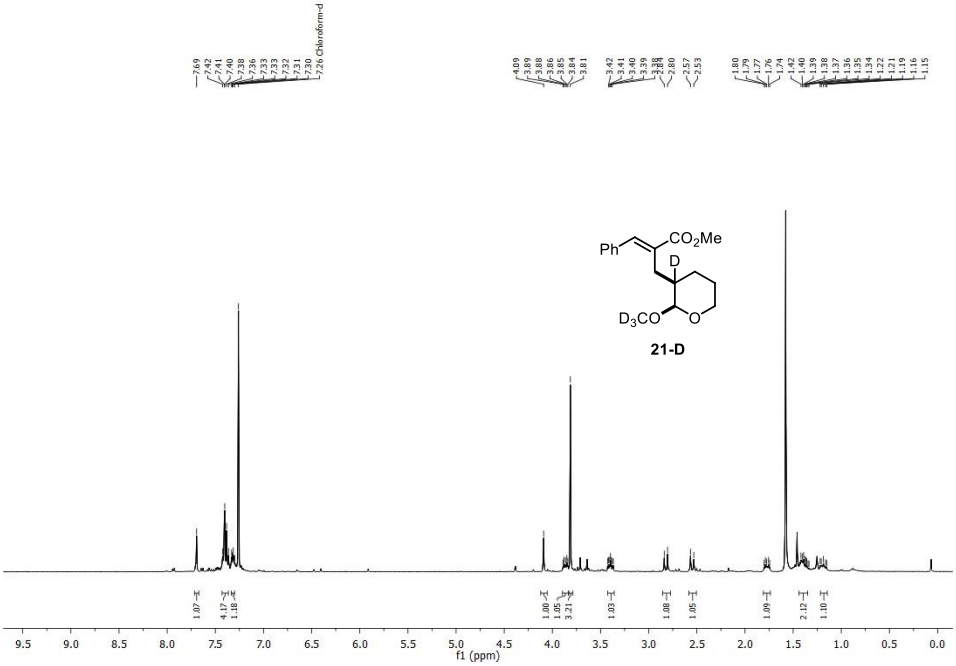


Figure S5: ^1H NMR (400 MHz, $CDCl_3$) of the crude reaction mixture using CD_3OD used as a solvent.

(From Scheme 4 in the main text)

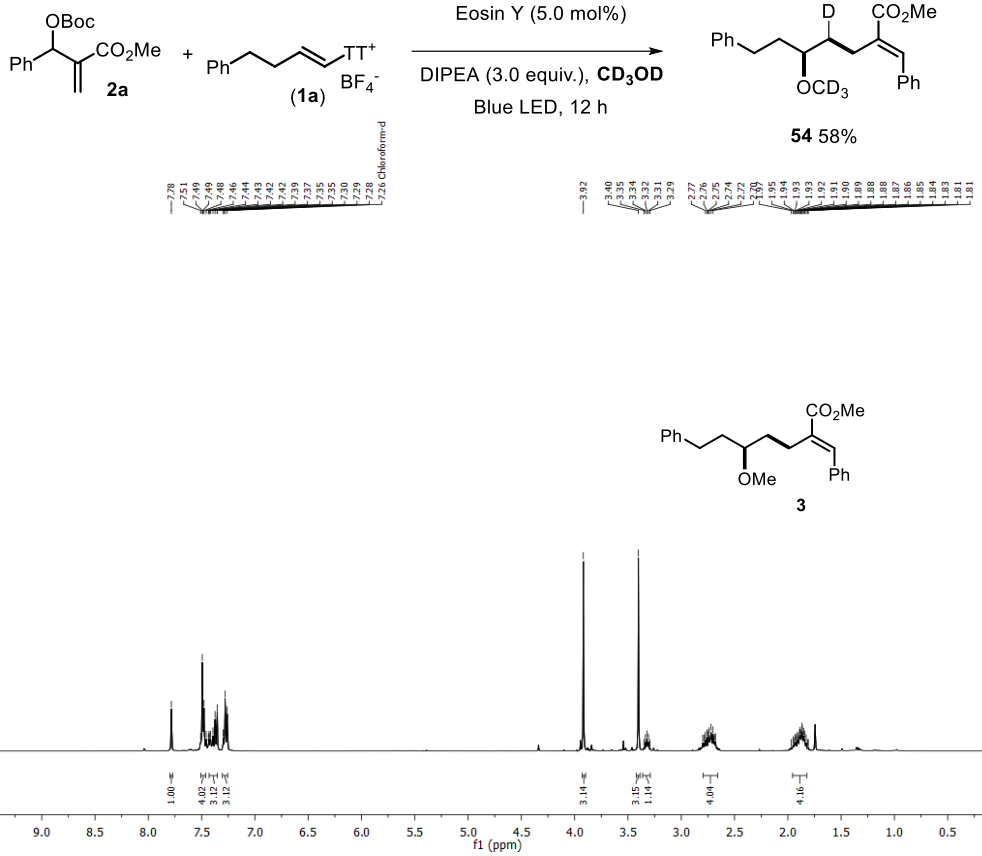


Figure S6: ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3** (*provided as reference*)

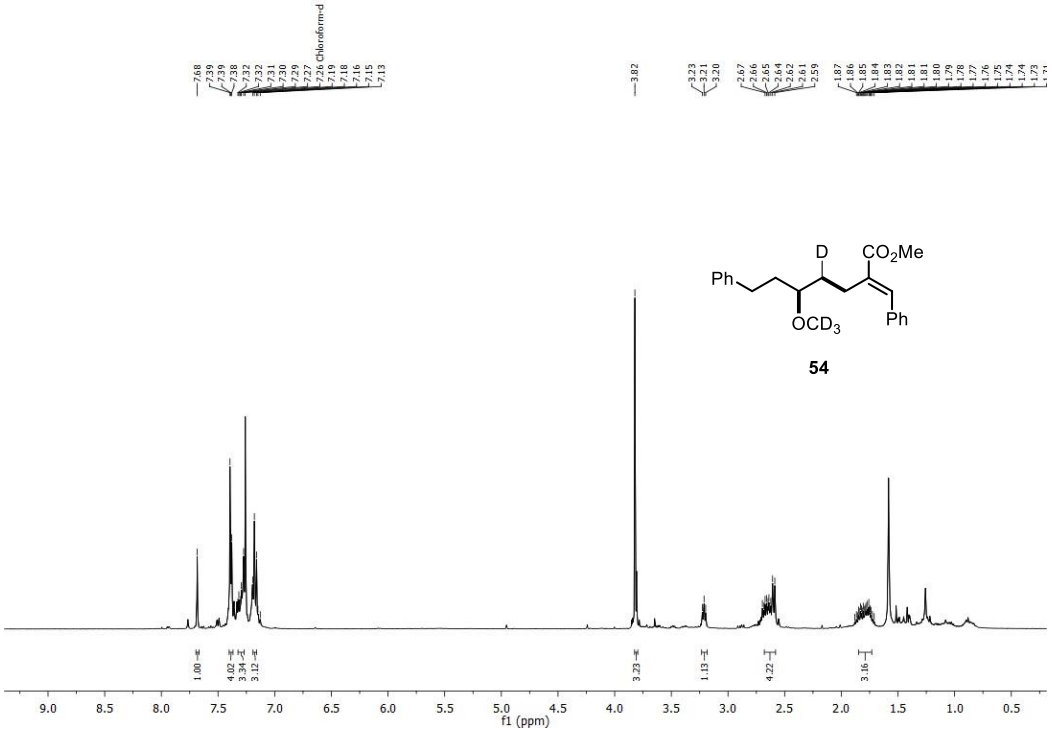


Figure S7: ^{1}H NMR (400 MHz, $CDCl_3$) of the crude reaction mixture using CD_3OD used as a solvent.

4.3. Additional Control experiments

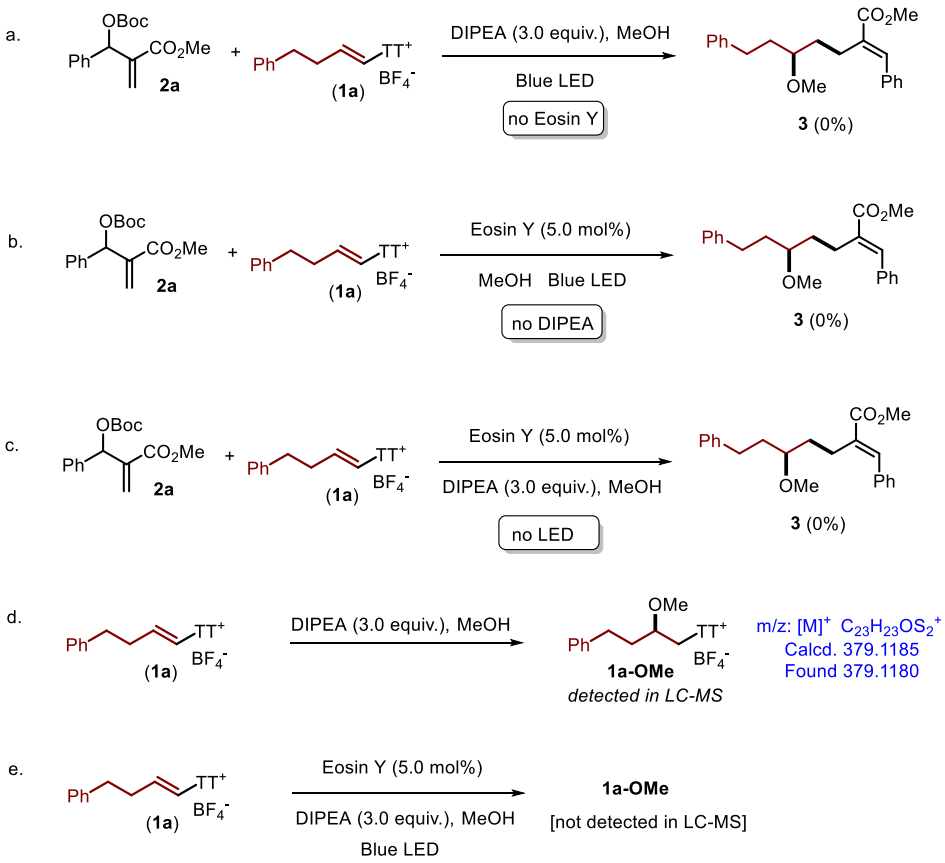
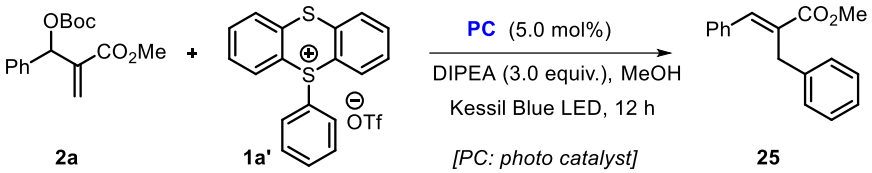


Figure S8: Control experiments a-c were conducted similar to the developed reaction conditions excepts varying one parameter at a time. Experiments d-e were performed with the TT salt (**1a**) itself.

5. Optimization studies for aryl allylation

5.1. *Screening of Photocatalysts*



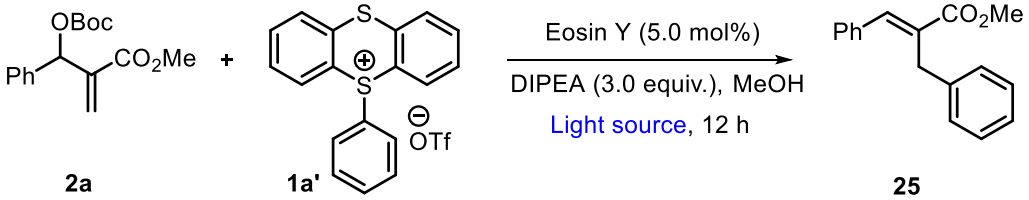
2a **1a'** **25**

Table S2[a]

Entry	***Photocatalyst***	***Yield (%)***[b]
1	4CzIPN	53
2	Rose Bengal	63
3	$Ir[(ppy)_2(dtbbpy)]PF_6$	trace
4	$Ru(bpy)_3Cl_2$	trace
5	Fluorescein	32
6	Rhodamine B	36
7	No photocatalyst	0
8	Eosin Y	71

[a]Reaction Conditions: MBH adduct (0.1 mmol, 1.0 equiv.), TT-salt (0.1 mmol, 1.0 equiv.), DIPEA (0.3 mmol, 3.0 equiv.), PC (5.0 mol%), MeOH (0.5 mL), Blue LED (427nm), 12 hours; [b]isolated yields.

5.2. *Effect of the Light Source*[a]



2a **1a'** **25**

Table S3[a]

Entry	***Light***	***Yield(%)***[b]
1	Kessil Blue LED	71
2	Blue strip	70
3	Green strip	67
4	White CFL	68

[a]Reaction Conditions: MBH adduct (0.1 mmol, 1.0 equiv.), TT-salt (0.1 mmol, 1.0 equiv.), DIPEA (0.3 mmol, 3.0 equiv.), Eosin Y (5.0 mol%), MeOH (0.5 mL), 12 h; [b]isolated yields.

***5.3**. Optimization of wavelength under Kessil Blue LED irradiation*

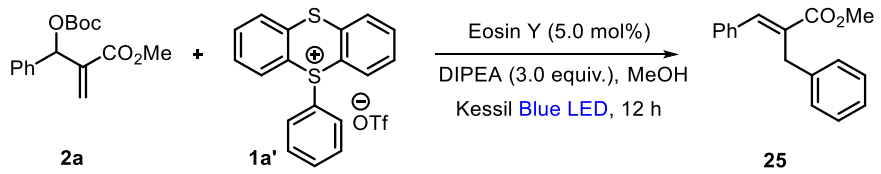


Table S4[a]

Entry	*Wavelength (nm)*	*Yield(%)*[b]
1	456	43
2	440	67
3	427	71
4	390	65

[a]Reaction Conditions: MBH adduct (0.1 mmol, 1.0 equiv.), TT salt (0.10 mmol, 1.0 equiv.), Base (0.3 mmol, 3.0 equiv.), Eosin Y (5.0 mol%), MeOH (0.5 mL), 12 h; [b]isolated yields.

5.4. *Effect of the Base*

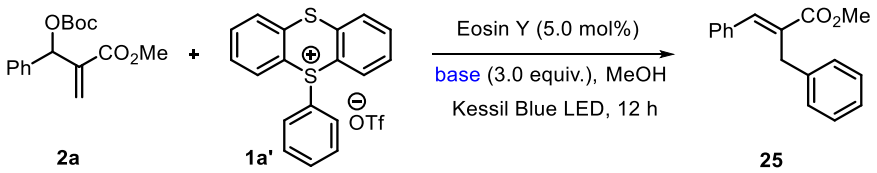


Table S5[a]

Entry	*Base*	*Yields(%)*[b]
1	Cs_2CO_3	0
2	Na_2CO_3	0
3	KOAc	0
4	KO^tBu	0
5	Piperidine	0
6	Diisopropylamine(DIPA)	Trace
7	Et_3N	28
8	DIPEA	71
9	$^nBu_3N$	20

[a]Reaction Conditions: MBH adduct (0.1 mmol, 1.0 equiv.), TT-salt (0.15 mmol, 1.5 equiv.), Base (0.3 mmol, 3.0 equiv.), Eosin Y (5.0 mol%), MeOH (0.5 mL), 12 h; [b]isolated yields.

5.5. Loading of Base

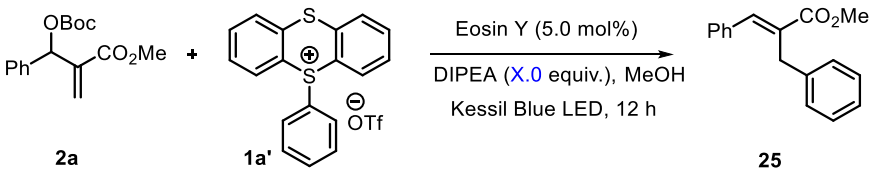


Table S6[a]

Entry	*DIPEA (equiv.)*	*Yields(%)*[b]
1	0.0	0
2	1.0	41
3	2.0	56
4	3.0	71
5	4.0	70
6	5.0	68
7	6.0	68

[a]Reaction Conditions: MBH adduct (0.1 mmol, 1.0 equiv), TT salt (0.15 mmol, 1.5 equiv.), DIPEA (X equiv.), Eosin Y (5.0 mol%), MeOH (0.5 mL), Blue LED (427nm), 12 h; [b]isolated yields.

5.6. Screening of the solvent

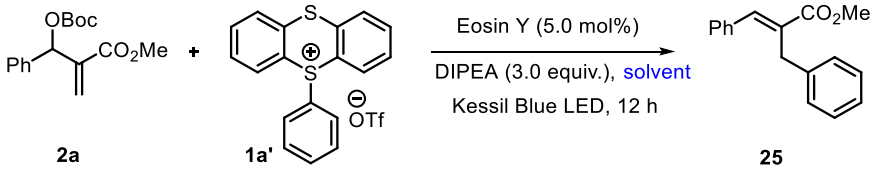


Table S7[a]

Entry	*Solvent*	*Yields(%)*[b]
1	1,4-dioxane	0
2	Et_2O	0
3	THF	0
4	toluene	0
5	DCM	trace
6	acetone	0
7	MeCN	0
8	MeOH	71
9	EtOH	52
10	IPA	48
11	HFIP	0
12	TFE	33
13	MeOH/HFIP (3/2)	67
14	DMSO	0

[a]Reaction Conditions: MBH adduct (0.1 mmol, 1.0 equiv.), TT salt (0.1 mmol, 1.0 equiv.), DIPEA (0.3 mmol, 3.0 equiv.), Eosin Y (5.0 mol%), Solvent (0.5 mL; 0.2 M), Kessil Blue LED (427 nm), 12 h; [b]isolated yields.

5.7. Variations in MBH adduct or TT-salts

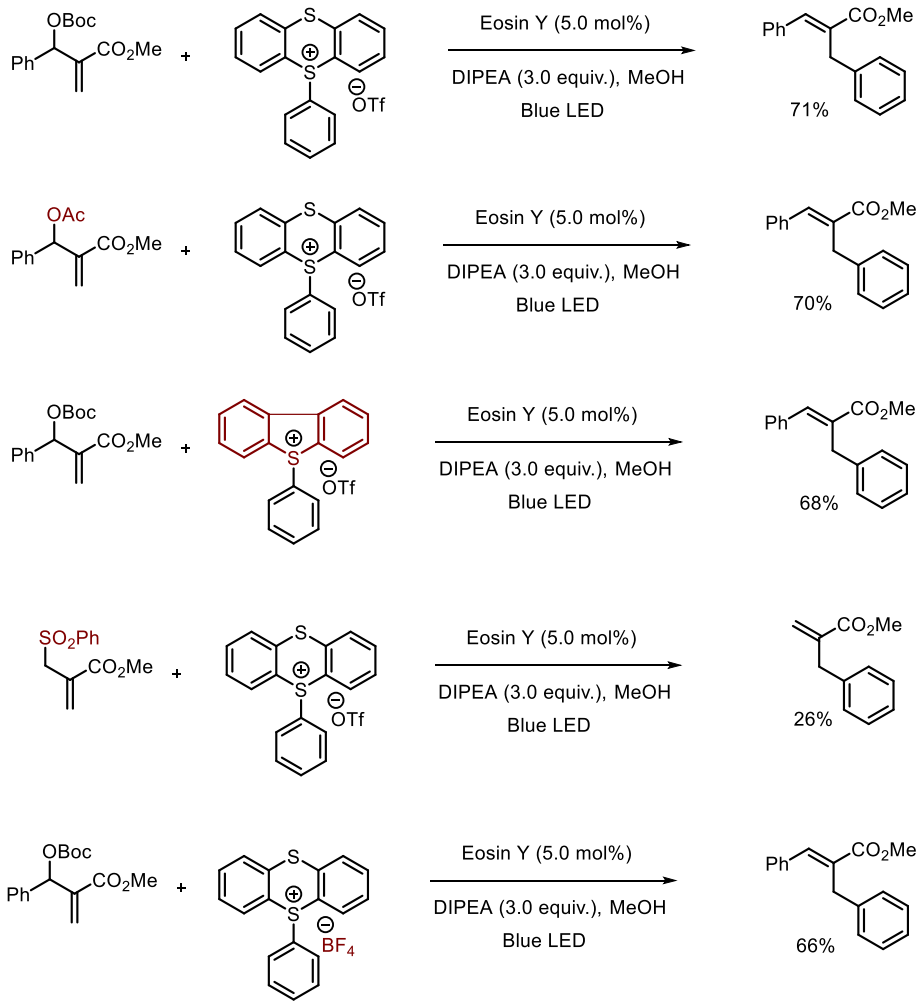


Figure S9. Different variation of MBH adduct and TT salts used under optimized conditions

6. Reaction set up and TLC analysis

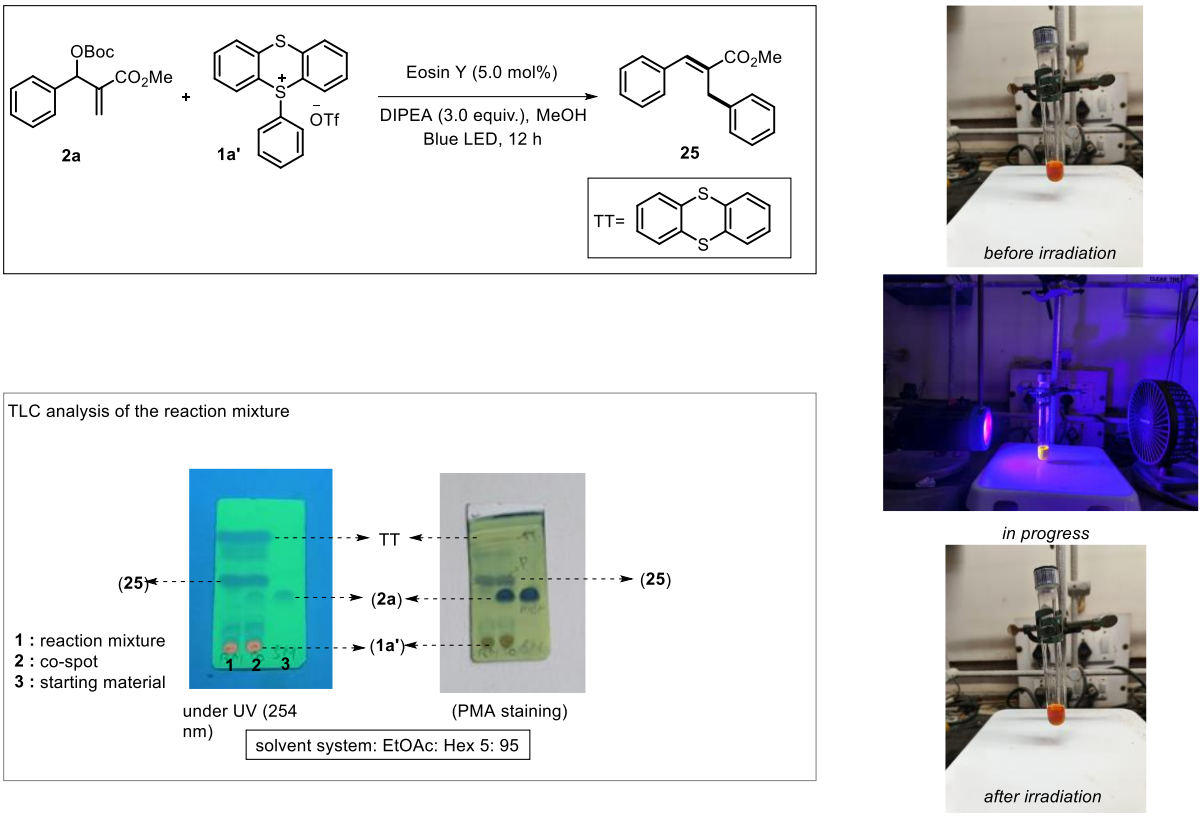
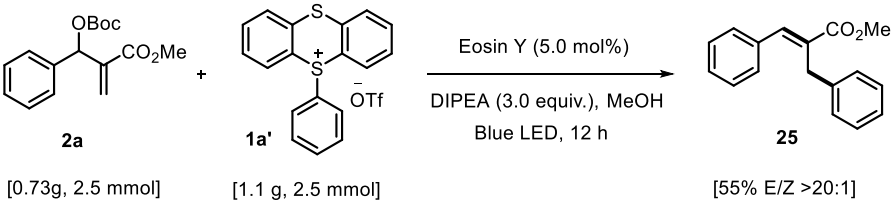


Figure S10. Pictorial description of reaction set-up and TLC analysis

7. Scale-up reaction (gram scale)



A 10 mL oven dried round-bottom flask was charged with MBH adduct (**2a**, 0.73 g, 2.5 mmol 1.0 equiv.), thianthrenium salt (**1a'**, 1.1g, 2.5 mmol, 1.0 equiv.), Eosin-Y (0.081g, 0.125 mmol). The flask was evacuated and backfilled with argon (two times) and capped with a rubber septum (or screw cap). Then degassed MeOH (0.2 M) and N, N-diisopropylethylamine (3.0 equiv.) were added using a syringe under argon atmosphere. The flask was placed 10 cm (approx.) away from a 427 nm Kessil lamp (Blue LED: 427nm) at room temperature (a cooling fan was placed near the reaction vessel) and irradiated for 16 h. The reaction mixture diluted with DCM and solvent was removed under reduced pressure. The crude residue was purified by silica-gel column chromatography (EtOAc: Hexane 3:97) to furnish the title compound **25** as a colorless oil in 55% (0.344g) yield (*E/Z* >20:1). R_f 0.4 (EtOAc: Hexane 5:95).

8. Luminescence Quenching Experiments[9]

Luminescence quenching studies were carried out using a 5.0 μM solution of Eosin Y and 10 mM solution of each, TT^+ salt (**1a'**), N,N-diisopropylethylamine (DIPEA), and MBH adduct (**2a**) prepared separately by dissolving the requisite amount of chemical in dry, degassed MeOH. Luminescence was measured at 540 nm.

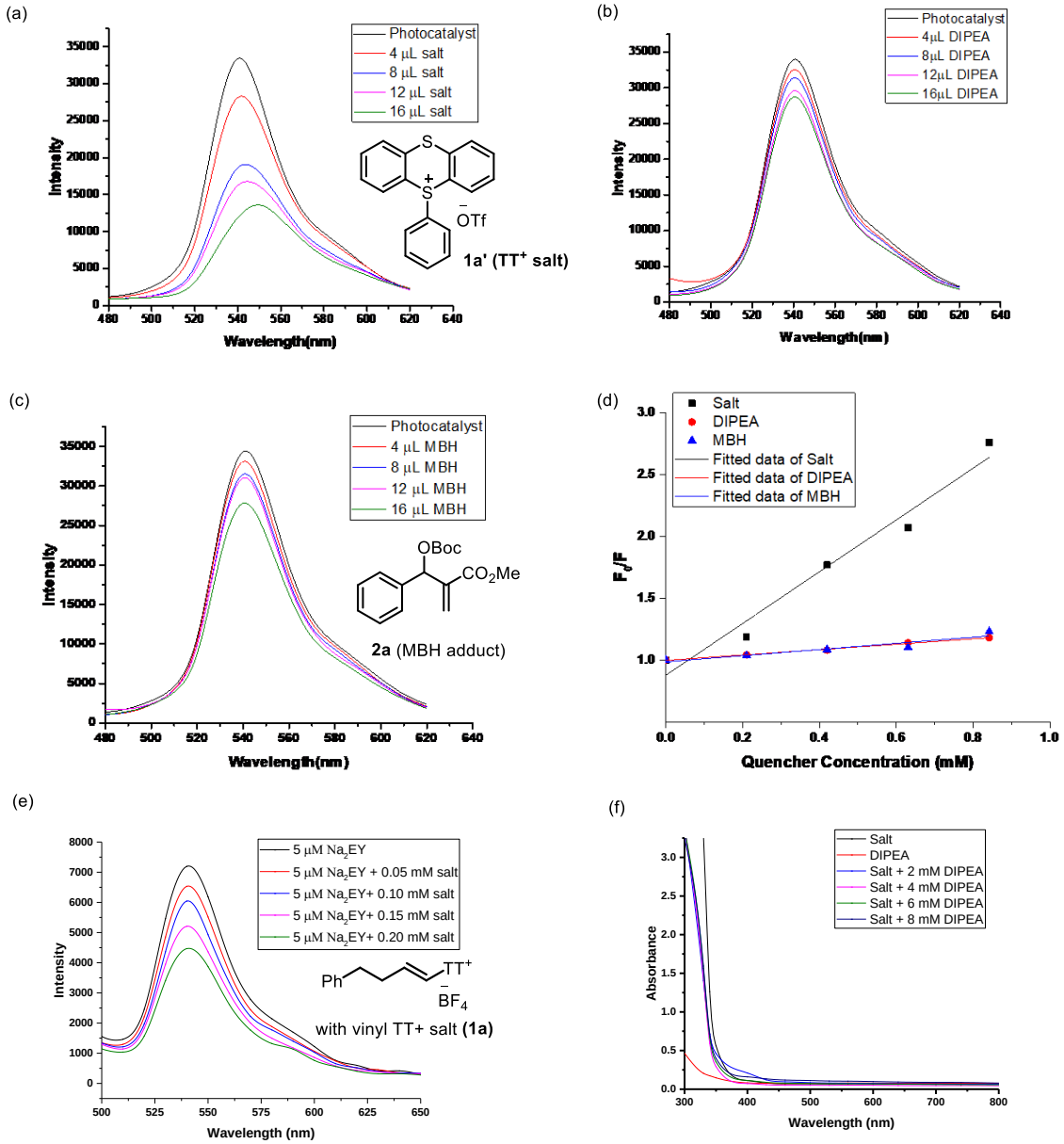
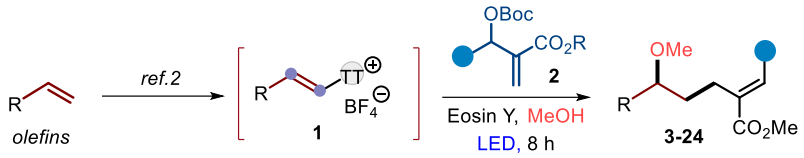


Figure S11. (a) Luminescence spectra of Eosin Y (photocatalyst) with TT^+ salt (**1a'**); (b) Luminescence spectra of Eosin Y with DIPEA; (c) Luminescence spectra of Eosin Y with MBH adduct (**2a**); (d) Stern-Volmer Plot of Eosin Y in presence of TT^+ salt, DIPEA and MBH adduct separately; (e) Luminescence spectra of Eosin Y (photocatalyst) with TT^+ salt (**1a**); (f) Study related to EDA-complex.

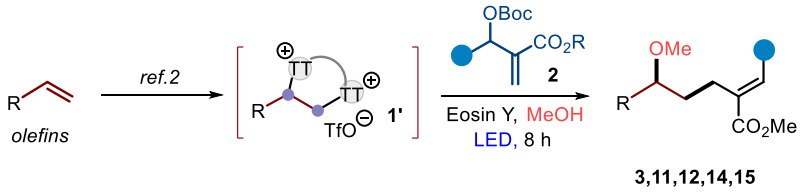
Experimental data suggest that no quenching is observed with respect to MBH adduct and DIPEA. Quenching of the photocatalyst, Eosin-Y was observed with TT^+ salt.

9. General procedure for olefin difunctionalization via thianthrenation



General Procedure [A] [*using alkenyl TT$^+$ salts*]**:**

In an oven dried sealed tube, various feed-stock alkenes were transformed into the corresponding thianthrenium salt (**1,** 1.0 equiv.) *in situ* and charged with charged with MBH adduct (**2**, 1.0 equiv.) and Eosin-Y (0.05 equiv.). The tube was evacuated and backfilled with argon two times and it was capped with a rubber septum. Then degassed MeOH (0.2 M) and DIPEA (3.0 equiv) were added using a syringe under argon atmosphere. The resulting solution was irradiated by a Blue LED (Kessil lamp, 427 nm) at room temperature (using one cooling fan placed at approx. 6 cm away from the vessel) for 8 h. Upon complete consumption of the starting material (TLC monitored), the reaction mixture diluted with DCM and transfer to a round bound flask. The organic solvent was removed under reduced pressure and the crude residue was purified by silica-gel flash column chromatography (using EtOAc /hexanes as eluent) to provide desire product.

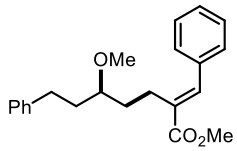


General Procedure [B] [*using bridged TT$^+$ salts*]**:**

A 10 mL oven dried sealed tube was charged with TTSO (1.5 equiv.), and alkene (1.5 equiv.) in MeCN. After cooling to 0^{o}C, trifluoroacetic anhydride (3.0 equiv.) was added dropwise, followed by trifouromethane sulfonic acid (TfOH, 3.0 equiv.). The reaction mixture was stirred for 1h and concentrated under reduced pressure. The crude product was washed with Et_2O (2.0 mL) and further dried in *vacuo*. The resulted solid was dissolved in degassed MeOH, followed by addition of MBH adduct (1.0 equiv.), DIPEA and Eosin Y. The reaction mixture was irradiated by a 427 nm Blue LED (Kessil lamp, 427 nm) at room temperature (using one cooling fan placed at approx. 6 cm away from the vessel) for 8 hours. Upon complete consumption of the starting material (TLC monitored), the reaction mixture diluted with DCM and transfer to a round bound flask. The organic solvent was removed under reduced pressure and the crude residue was purified by silica-gel flash column chromatography (using EtOAc /hexanes as eluent) to provide desire products.

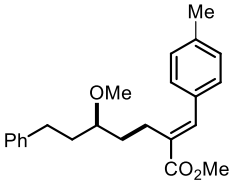
10. Procedure and Characterization of compounds (3-24)

*Methyl (E)-2-benzylidene-5-methoxy-7-phenylheptanoate (**3**)*



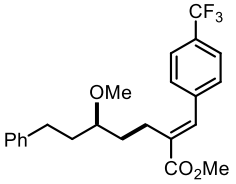
Following the general procedure, reaction of MBH adduct (**2a**; 0.058 g, 0.2 mmol) and thianthrenium salt (**1a**; 0.087 g, 0.2 mmol) in presence of Eosin-Y (0.007 g, 0.01 mmol) and $^{i}Pr_2NEt$ (0.078 g, 0.6 mmol) delivered compound **3**, which was purified by silica gel column chromatography (EtOAc: Hexane 5:95) to furnish the title compound **3** as a colorless oil in 67% (0.045 g) yield (*E/Z* >20:1). R_f 0.3 (EtOAc: Hexane 1:9); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.51 – 7.46 (m, 4H), 7.44 – 7.35 (m, 3H), 7.30 – 7.28 (m, 3H), 3.92 (s, 3H), 3.40 (s, 3H), 3.35 – 3.29 (m, 1H), 2.80 – 2.68 (m, 4H), 1.97 – 1.81 (m, 4H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 169.0, 142.4, 139.4, 135.8, 133.1, 129.4, 128.6, 128.5(2), 125.9, 80.0, 56.5, 52.2, 35.2, 32.5, 31.7, 23.3. **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{22}H_{27}O_3^+$ Calcd. 339.1955, Found 339.1955.

Methyl (E)-5-methoxy-2-(4-methylbenzylidene)-7-phenylheptanoate **(4)**



Following the general procedure, reaction of MBH adduct (**2b**; 0.062 g, 0.2 mmol) and thianthrenium salt (**1a**; 0.087 g, 0.2 mmol) in presence of Eosin-Y (0.013 g, 0.01 mmol) and $^{i}Pr_2NEt$ (0.078 g, 0.6 mmol) delivered compound **4**, which was purified by silica gel column chromatography (EtOAc: Hexane 5:95) to furnish the title compound **4** as a colorless oil in 82% (0.058 g) yield (*E/Z* >20:1). R_f 0.3 (EtOAc: Hexane 1:9); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.28 (d, J = 8.0 Hz, 2H), 7.23 (d, J = 7.3 Hz, 2H), 7.15 (m, 5H), 3.77 (s, 3H), 3.29 (s, 3H), 3.24 – 3.17 (m, 1H), 2.62 (m, 4H), 2.32 (s, 3H), 1.83 – 1.72 (m, 4H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 169.0, 142.4, 139.4, 138.7, 132.8, 132.2, 129.4, 129.3, 128.5, 128.4 125.8, 80.0, 56.5, 52.0, 35.1, 32.4, 31.6, 23.3, 21.4; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ $C_{23}H_{28}NaO_3^+$ Calcd. 375.1931, Found 375.1920.

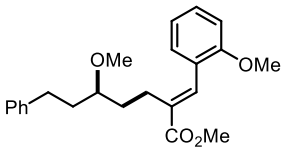
Methyl (E)-5-methoxy-7-phenyl-2-(4-(trifluoromethyl)benzylidene)heptanoate **(5)**



Following the general procedure, reaction of MBH adduct (**2e**; 0.072 g, 0.2 mmol) and thianthrenium salt (**1a**; 0.087 g, 0.2 mmol) in presence of Eosin-Y (0.013 g, 0.01 mmol) and $^{i}Pr_2NEt$ (0.078 g, 0.6 mmol) delivered compound **5**, which was purified by silica gel column chromatography (EtOAc: Hexane 5:95) to furnish the title compound **5** as a colorless oil in 65% (0.053 g) yield (*E/Z* >20:1). R_f 0.3 (EtOAc: Hexane 1:9); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.62 (d, *J* = 8.1 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.26 (m, 2H), 7.16 (m, 3H), 3.82 (s, 3H), 3.27 (s, 3H), 3.23 – 3.16 (m, 1H), 2.68 – 2.53 (m, 4H), 1.77 (m, 4H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 168.4, 142.3, 139.4, 137.6, 135.3, 130.3 (q, J = 32.4 Hz)), 129.5,

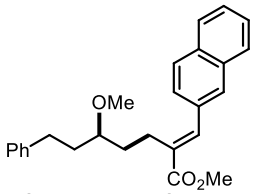
128.5 (2),125.9, 125.6 (q, J = 3.7 Hz), 124.1 (q, J = 265.5 Hz), 79.9, 56.5, 52.3, 35.05 (s), 32.54 (s), 31.58 (s), 23.35 (s); **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{23}H_{26}F_3O_3^+$ Calcd. 407.1829, Found 407.1825

methyl (E)-5-methoxy-2-(2-methoxybenzylidene)-7-phenylheptanoate **(6)**



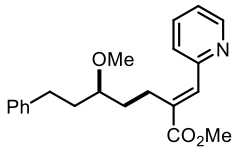
Following the general procedure, reaction of MBH adduct (**2g**; 0.065 g, 0.2 mmol) and thianthrenium salt (**1a**; 0.087 g, 0.2 mmol) in presence of Eosin-Y (0.013 g, 0.01 mmol) and $^{i}Pr_2NEt$ (0.078 g, 0.6 mmol) delivered compound **6**, which was purified by silica gel column chromatography (EtOAc: Hexane 5:95) to furnish the title compound **6** as a colorless oil in 65% (0.048 g) yield (*E/Z* >20:1). R_f 0.2 (EtOAc: Hexane 1:9); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.30 – 7.24 (m, 3H), 7.17 (m, 3H), 6.98 (d, *J* = 7.6 Hz, 1H), 6.93 (m, 1H), 6.86 (dd, *J* = 8.2, 2.3 Hz, 1H), 3.81 (s, 3H), 3.78 (s, 3H), 3.30 (s, 3H), 3.26 – 3.19 (m, 1H), 2.71 – 2.55 (m, 4H), 1.85 – 1.72 (m, 4H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 168.9, 159.7, 142.4, 139.3, 137.0, 133.3, 129.6, 128.5, 128.4 125.8, 121.8, 114.6, 114.2, 80.0, 56.4, 55.3, 52.1, 35.1, 32.5, 31.6, 23.4; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{23}H_{29}O_4^+$ Calcd. 369.2060, Found 369.2052.

Methyl (E)-5-methoxy-2-(naphthalen-2-ylmethylene)-7-phenylheptanoate **(7)**



Following the general procedure, reaction of MBH adduct (**2j**; 0.069 g, 0.2 mmol) and thianthrenium salt (**1a**; 0.087 g, 0.2 mmol) in presence of Eosin-Y (0.013 g, 0.01 mmol) and $^{i}Pr_2NEt$ (0.078 g, 0.6 mmol) delivered compound **7**, which was purified by silica gel column chromatography (EtOAc: Hexane 5:95) to furnish the title compound **7** as a colorless oil in 76% (0.059 g) yield (*E/Z* >20:1). R_f 0.35 (EtOAc: Hexane 1:9); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.86 – 7.80 (m, 4H), 7.54 – 7.48 (m, 3H), 7.26 (t, *J* = 8 Hz, 2H), 7.17 (m, 3H), 3.86 (s, 3H), 3.34 (s, 3H), 3.26 (m, 1H), 2.79 – 2.61 (m, 4H), 1.92 – 1.76 (m, 4H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 169.0, 142.4, 139.4, 133.3, 133.2, 133.1 129.1, 128.5 (2), 128.2, 127.8, 126.9, 126.8 126.6, 125.9, 80.1, 56.6, 52.2, 35.3, 32.6, 31.7, 23.5; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{26}H_{29}O_3^+$ Calcd. 389.2111, Found 389.2108.

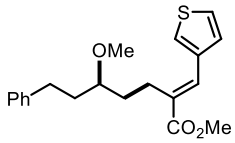
*Methyl (E)-5-methoxy-7-phenyl-2-(pyridin-2-ylmethylene) heptanoate (**8**)*



Following the general procedure, reaction of MBH adduct (**2i**; 0.059 g, 0.2mmol) and thianthrenium salt (**1a**; 0.087 g, 0.2mmol) in presence of Eosin-Y (0.007 g, 0.01mmol) and $^{i}Pr_2NEt$ (0.078 g, 0.6 mmol) delivered compound **8**, which was purified by silica gel column chromatography (EtOAc: Hexane 1:9) to furnish the title compound **8** as a colorless oil in 46% (0.031 g) yield (*E/Z* >20:1). R_f 0.3 (EtOAc: Hexane 3:7); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.62 (d,

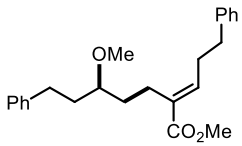
J = 4.0 Hz, 1H), 7.72 – 7.65 (m, 1H), 7.60 (s, 1H), 7.37 (d, *J* = 7.8 Hz, 1H), 7.30 – 7.26 (m, 2H), 7.27-7.17 (m, 4H), 3.83 (s, 3H), 3.34 (s, 3H), 3.32 – 3.26 (m, 1H), 2.98 – 2.94 (m, 2H), 2.79 – 2.63 (m, 2H), 1.89 – 1.77 (m, 4H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 169.0, 154.8, 149.5, 142.7, 137.2, 136.6,136.5, 128.6, 128.4, 126.1, 125.8, 122.8, 80.1, 56.1, 52.3, 35.1, 31.9, 31.7, 23.2; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{21}H_{26}NO_3$ Calcd. 340.1913, Found 340.1902.

*Methyl (E)-5-methoxy-7-phenyl-2-(thiophen-3-ylmethylene) heptanoate (**9**)*



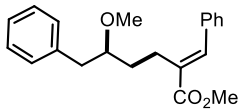
Following the general procedure, reaction of MBH adduct (**2h**; 0.029 g, 0.1 mmol) and thianthrenium salt (**1a**; 0.038 g, 0.1 mmol) in presence of Eosin-Y (0.0035 g, 0.005 mmol) and $^{i}Pr_2NEt$ (0.039 g, 0.3 mmol) delivered compound **9**, which was purified by silica gel column chromatography (EtOAc: Hexane 1:99) to furnish the title compound **9** as a colorless oil in 39% (0.013 g) yield (*E/Z* 7:1). R_f 0.4 (EtOAc: Hexane 5:95); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.46 (d, J = 5.1 Hz, 1H), 7.31-7.27 (m, 3H), 7.22 – 7.17 (m, 3H), 7.09 (dd, J = 5.1, 3.7 Hz, 1H), 3.81 (s, 3H), 3.40 (s, 3H), 3.35-3.29 (m, 1H), 2.81 – 2.65 (m, 4H), 1.95 – 1.83 (m, 2H), 1.80 – 1.72 (m, 2H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 168.9, 142.5, 138.5, 132.3, 131.7, 129.4, 129.2, 128.6, 128.5, 127.5, 125.9, 80.2, 56.6, 52.2, 35.3, 31.8, 31.6, 24.1; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{20}H_{25}O_3S$ Calcd. 345.1524, Found 345.1495.

*Methyl (E)-5-methoxy-7-phenyl-2-(3-phenylpropylidene) heptanoate (**10**)*



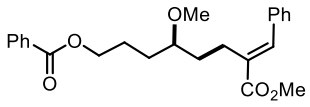
Following the general procedure, reaction of MBH adduct (**2k**; 0.064 g, 0.2 mmol) and thianthrenium salt (**1a**; 0.087 g, 0.2mmol) in presence of Eosin-Y (0.007 g, 0.01mmol) and $^{i}Pr_2NEt$ (0.078 g, 0.6 mmol) delivered compound **10**, which was purified by silica gel column chromatography (EtOAc: Hexane 5:95) to furnish the title compound **10** as a colorless oil in 83% (0.061 g) yield (*E/Z* >20:1). R_f 0.25 (EtOAc: Hexane 1:9); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33-7.28 (m, 4H), 7.24 – 7.19 (m, 6H), 6.83 (t, *J* = 7.5 Hz, 1H), 3.76 (s, 3H), 3.35 (s, 3H), 3.23 – 3.17 (m, 1H), 2.78 (t, *J* = 7.6 Hz, 2H), 2.74 – 2.61 (m, 2H), 2.56-2.51 (m, 2H), 2.38 – 2.30 (m, 2H), 1.91-1.74 (m, 2H), 1.59 – 1.52 (m, 2H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 168.3, 142.4, 141.7, 141.2, 132.7, 128.5 (3), 128.4, 126.2, 125.8, 79.6, 56.1, 51.8, 35.1 (2), 32.4, 31.6, 30.5, 22.4; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{24}H_{31}O_3$ Calcd. 367.2273, Found 367.226.

*Methyl (E)-2-benzylidene-5-methoxy-6-phenylhexanoate (**11**)*



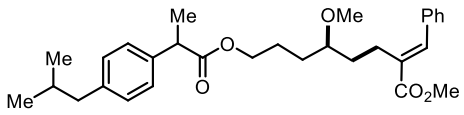
Following the general procedure, reaction of MBH adduct (**2a**; 0.029 g, 0.1 mmol) and thianthrenium salt (1**b**; 0.042 g, 0.1 mmol) in presence of Eosin-Y (0.035 g, 0.005 mmol) and $^{i}Pr_2NEt$ (0.039 g, 0.3 mmol) delivered compound **11**, which was purified by silica gel column chromatography (EtOAc: Hexane 5:95) to furnish the title compound **11** as a colorless oil in 80% (0.026 g) yield (*E/Z* 3:1). R_f 0.3 (EtOAc: Hexane 1:9);**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.39 – 7.31 (m, 5H), 7.30 – 7.28 (m, 4H), 7.22 – 7.17 (m, 5H), 6.60 (s, 0.4H), 3.78 (s, 3H), 3.58 (s, 1H), 3.46 – 3.36 (m, 1.4H), 3.36 (s, 1H), 3.28 (s, 3H), 2.94 – 2.85 (m, 1.4H), 2.75 – 2.67 (m, 2H), 2.63 – 2.54 (m, 1.6H), 2.49 – 2.42 (m, 0.4H), 1.80 – 1.64 (m, 2.8H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 170.4, 169.0, 139.4, 139.0, 138.8, 136.2, 135.8, 134.4, 133.3, 133.1, 129.6, 129.5, 129.4, 128.6, 128.5, 128.4(2), 128.3, 128.1, 127.9, 126.3, 126.2, 82.3, 81.3, 57.1, 57.0, 52.1, 51.7, 40.1, 40.0, 32.6, 32.2, 31.5, 23.4; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{21}H_{25}O_3^+$ Calcd.325.1798, Found 325.1791.

(*E)-4-Methoxy-7-(methoxycarbonyl)-8-phenyloct-7-en-1-yl benzoate (**12**)*



Following the general procedure, reaction of MBH adduct (**2a**; 0.058 g, 0.2mmol) and thianthrenium salt (**1c**; 0.098 g, 0.2mmol) in presence of Eosin-Y (0.007 g, 0.01mmol) and $^{i}Pr_2NEt$ (0.078 g, 0.6mmol) delivered compound **12**, which was purified by silica gel column chromatography (EtOAc: Hexane 5:95) to furnish the title compound **12** as a colorless oil in 73% (0.058 g) yield (*E/Z* >20:1). R_f 0.25 (EtOAc: Hexane 1:9); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 – 7.94 (m, 2H), 7.60 (s, 1H), 7.47 – 7.43 (m, 1H), 7.35 – 7.28 (m, 6H), 7.23 – 7.18 (m, 1H), 4.23 (t, J = 6.6 Hz, 2H), 3.72 (s, 3H), 3.21 (s, 3H), 3.19 – 3.16 (m, 1H), 2.58 – 2.48 (m, 2H), 1.79-1.63 (m, 4H), 1.57-1.52 (m, 2H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 168.8, 166.6, 139.3, 135.7, 133.0, 132.9, 130.4, 129.6, 129.3, 128.5(2),128.4, 80.2, 65.1, 56.5, 52.0, 32.5, 29.7, 24.6, 23.2; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{24}H_{29}O_5$ Calcd. 397.2015, Found 397.2020.

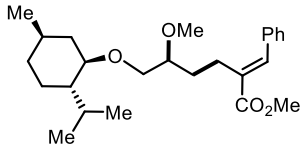
*Methyl (E)-2-benzylidene-8-((2-(4-isobutylphenyl)propanoyl)oxy)-5-methoxyoctanoate (**13**)*



Following the general procedure, reaction of MBH adduct (**2a**; 0.029 g, 0.1mmol) and thianthrenium salt (**1d**; 0.057 g, 0.1mmol) in presence of Eosin-Y (0.0035 g, 0.005mmol) and $^{i}Pr_2NEt$ (0.039 g, 0.3mmol) delivered compound **13**, which was purified by silica gel column chromatography (EtOAc: Hexane 5:95) to furnish the title compound **13** as a colorless oil in 83% (0.040 g) yield (*E/Z* >20:1). R_f 0.25 (EtOAc: Hexane 3:7); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.38 (d, *J* = 4.4 Hz, 4H), 7.36 – 7.29 (m, 1H), 7.19-7.17 (m, 2H), 7.06 (d, *J* = 6.8

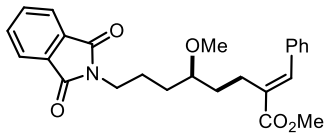
Hz, 2H), 4.05 (t, *J* = 6.5 Hz, 2H), 3.81 (s, 3H), 3.69 – 3.65 (m, 1H), 3.23 (s, 3H), 3.15 (t, *J* = 5.3 Hz, 1H), 2.61 – 2.48 (m, 2H), 2.41 (d, *J* = 7.2 Hz, 2H), 1.85 – 1.78 (m, 1H), 1.67 – 1.57 (m, 4H), 1.48 (d, *J* = 7.2 Hz, 3H), 1.45 – 1.43 (m, 2H), 0.87 (d, *J* = 6.6 Hz, 6H);**^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 174.9, 168.9, 140.6, 139.4, 137.9, 135.7, 133.1, 129.4 (2), 128.6 (2), 127.3, 80.1, 64.8, 56.4, 52.1, 45.3, 45.2, 32.5, 30.3, 29.4, 24.4, 23.3, 22.5, 18.6; **HRMS (ESI-TOF)** m/z: $[M+H]^+C_{30}H_{41}O_5^+$ Calcd. 481.2949, Found 481.2949.

*Methyl 2-((E)-benzylidene)-6-(((2S,5R)-2-isopropyl-5-methylcyclohexyl)oxy)-5-methoxyhexanoate (**14**)*



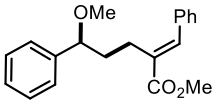
Following the general procedure, reaction of MBH adduct (**2a**; 0.058 g, 0.2 mmol) and thianthrenium salt (**1e**; 0.100 g, 0.2mmol) in presence of Eosin-Y (0.007 g, 0.01 mmol) and $^{i}Pr_2NEt$ (0.078 g, 0.6mmol) delivered compound **14**, which was purified by silica gel column chromatography (EtOAc: Hexane 5:95) to furnish the title compound **14** as a colorless oil in 71% (0.057 g) yield (*E/Z* >20:1). R_f 0.25 (EtOAc: Hexane 3:7); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.43-7.36 (m, 4H), 7.33 – 7.29 (m, 1H), 3.81 (s, 3H), 3.67 – 3.60 (m, 1H), 3.34 (d, 3H), 3.31 – 3.22 (m, 2H), 3.04-2.96 (m, 1H), 2.73-2.57 (m, 2H), 2.25 – 2.16 (m, 1H), 2.08-2.03 (m, 1H), 1.88 – 1.58 (m, 5H), 1.37-1.19 (m, 3H), 0.91 – 0.86 (m, 6H), 0.82 – 0.81 (m, 1H), 0.77-0.73 (m, 3H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 169.0, 139.3 (2), 135.7, 133.1 (2), 129.5 (2), 128.6, 128.5, 80.5 (2), 80.0 (2), 70.1 (2), 57.5 (2), 52.1, 48.3 (2), 40.4, 40.3, 34.7, 31.6 (2), 31.4, 31.0, 25.7, 23.7, 23.6, 23.5, 23.4, 22.5, 21.1, 16.3 (2). **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{25}H_{39}O_4$ Calcd. 403.2848, Found 403.2843.

*Methyl (E)-2-benzylidene-8-(1,3-dioxoisoindolin-2-yl)-5-methoxyoctanoate (**15**)*



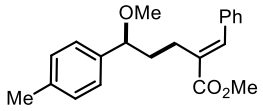
Following the general procedure, reaction of MBH adduct (**2a**; 0.058 g, 0.2mmol) and thianthrenium salt (**1f**; 0.106 g, 0.2mmol) in presence of Eosin-Y (0.007 g, 0.01mmol) and $^{i}Pr_2NEt$ (0.078 g, 0.6 mmol) delivered compound **15**, which was purified by silica gel column chromatography (EtOAc: Hexane 1:9) to furnish the title compound **15** as a colorless oil in 71% (0.060 g) yield (*E/Z* >20:1). R_f 0.3 (EtOAc: Hexane 3:7); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (dd, J = 5.4, 3.1 Hz, 2H), 7.61 (dd, J = 5.4, 3.0 Hz, 2H), 7.57 (s, 1H), 7.29 (d, J = 4.4 Hz, 4H), 7.23 – 7.18 (m, 1H), 3.71 (s, 3H), 3.59 (t, J = 7.2 Hz, 2H), 3.18 (s, 3H), 3.16 – 3.08 (m, 1H), 2.58 – 2.39 (m, 2H), 1.72 – 1.54 (m, 4H), 1.50 – 1.37 (m, 2H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 168.8, 168.4, 139.3, 135.6, 133.9, 132.9, 132.2, 129.3, 128.5 (2), 123.2, 80.1, 56.6, 52.0, 38.0, 32.6, 30.6, 24.6, 23.3. **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{25}H_{28}NO_5$ Calcd. 422.1967, Found 422.1953.

*Methyl (E)-2-benzylidene-5-methoxy-6-phenylhexanoate (**16**)*



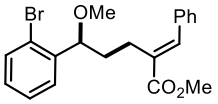
Following the general procedure, reaction of MBH adduct (**2a**; 0.029 g, 0.1 mmol) and thianthrenium salt (**1g**; 0.041 g, 0.1 mmol) in presence of Eosin-Y (0.0035 g, 0.005 mmol) and $^{i}Pr_2NEt$ (0.039 g, 0.3 mmol) delivered compound **16**, which was purified by silica gel column chromatography (EtOAc: Hexane 5:95) to furnish the title compound **16** as a colorless oil in 74% (0.023 g) yield (*E/Z* >20:1). R_f 0.3 (EtOAc: Hexane 1:9); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.37 – 7.33 (m, 2H), 7.29 – 7.28 (m, 8H), 4.13 (t, *J* = 6.5 Hz, 1H), 3.79 (s, 3H), 3.17 (s, 3H), 2.71 – 2.63 (m, 1H), 2.56 - 2.49 (m, 1H), 2.10 – 2.01(m, 1H), 1.95 – 1.86 (m, 1H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 169.0, 142.1, 139.4, 135.6, 132.7, 129.6, 128.6, 128.5, 128.1, 127.7, 126.9, 83.7, 56.7, 52.1, 37.1, 24.0; **HRMS (ESI-TOF) m/z:** $[M+Na]^+$ $C_{20}H_{22}NaO_3^+$ Calcd. 333.1461, Found 333.1455.

*Methyl (E)-2-benzylidene-5-methoxy-5-(p-tolyl)pentanoate (**17**)*



Following the general procedure, reaction of MBH adduct (**2a**; 0.058 g, 0.2mmol) and thianthrenium salt (**1h**; 0.84 g, 0.2mmol) in presence of Eosin-Y (0.007 g, 0.01mmol) and $^{i}Pr_2NEt$ (0.078 g, 0.6 mmol) delivered compound **17**, which was purified by silica gel column chromatography (EtOAc: Hexane 5:95) to furnish the title compound **17** as a colorless oil in 41% (0.027 g) yield (*E/Z* >20:1). R_f 0.25 (EtOAc: Hexane 1:9); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.29 (brs, 5H), 7.20 – 7.14 (m, 4H), 4.11 (t, J = 6.5 Hz, 1H), 3.80 (s, 3H), 3.17 (s, 3H), 2.7-2.64 (m, 1H), 2.56-2.49 (m, 1H), 2.37 (s, 3H), 2.11-2.02 (m, 1H), 1.94-1.85 (m, 1H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 169.0, 139.3, 138.9, 137.3, 135.6, 132.7, 129.5, 129.2, 128.5, 128.4, 126.8, 83.5, 56.5, 52.1, 37.1, 24.1, 21.3. **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{21}H_{25}O_3$ Calcd. 325.1804, Found 325.1820.

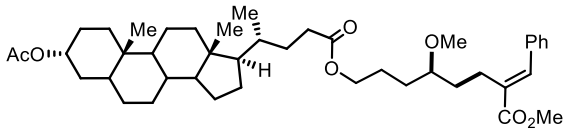
*Methyl (E)-2-benzylidene-5-(2-bromophenyl)-5-methoxypentanoate (**18**)*



Following the general procedure, reaction of MBH adduct (**2a**; 0.058 g, 0.2mmol) and thianthrenium salt (**1i**; 0.097 g, 0.2mmol) in presence of Eosin-Y (0.007 g, 0.01mmol) and $^{i}Pr_2NEt$ (0.078 g, 0.6mmol) delivered compound **18**, which was purified by silica gel column chromatography (EtOAc: Hexane 5:95) to furnish the title compound **18** as a colorless oil in 55% (0.043 g) yield (*E/Z* >20:1). R_f 0.3 (EtOAc: Hexane 1:9); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.51 (dd, J = 8.0, 0.9 Hz, 1H), 7.44 (dd, J = 7.7, 1.6 Hz, 1H), 7.37-7.28 (m, 6H), 7.11 (td, J = 7.9, 1.7 Hz, 1H), 4.59-4.56 (m, 1H), 3.79 (s, 3H), 3.15 (s, 3H), 2.78 – 2.66 (m,

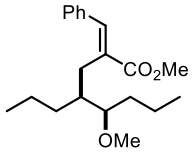
2H), 1.97 – 1.84 (m, 2H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 168.9, 141.2, 139.5, 135.6, 132.8, 132.6, 129.5, 128.9, 128.5 (2), 127.8, 127.6, 123.1, 81.9, 57.0, 52.1, 36.0, 24.0. **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{20}H_{22}BrO_3$ Calcd. 389.0747, Found 389.0713.

*Methyl 8-(((R)-4-((3R,5R,8R,9S,10S,13R,14S,17R)-3-acetoxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoyl)oxy)-2-((E)-benzylidene)-5-methoxyoctanoate (**19**)*



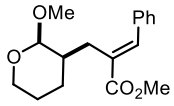
Following the general procedure, reaction of MBH adduct (**2a**; 0.058 g, 0.2mmol) and thianthrenium salt (**1j**; 0.158 g, 0.2mmol) in presence of Eosin-Y (0.007 g, 0.01mmol) and $^{i}Pr_2NEt$ (0.078 g, 0.6 mmol) delivered compound **19**, which was purified by silica gel column chromatography (EtOAc: Hexane 1:9) to furnish the title compound **19** as a colorless oil in 77% (0.107 g) yield (*E/Z* 10:1). R_f 0.2 (EtOAc: Hexane 1:9); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.37 – 7.28 (m, 5H), 4.73 – 4.65 (m, 1H), 4.03 (t, *J* = 6.5 Hz, 2H), 3.79 (s, 3H), 3.26 (s, 3H), 3.22-3.17 (m, 1H), 2.63 – 2.52 (m, 2H), 2.35-227 (m, 1H), 2.22 – 2.14 (m, 1H), 2.00 (s, 3H), 1.93 (d, *J* = 11.7 Hz, 1H), 1.84 – 1.76 (m, 5H), 1.74 – 1.62 (m, 5H), 1.54-1.49 (m, 5H), 1.40-1.34 (m, 7H), 1.29-1.18 (m, 4H), 1.12 – 0.99(m, 5H), 0.90 (s, 6H), 0.61 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.4, 170.7, 168.8, 139.3, 135.9, 133.0, 129.3, 128.6, 128.5, 80.2, 77.5, 76.8, 74.4, 64.4, 56.5 (2), 56.1, 52.0, 42.8, 42.0, 40.5, 40.2, 35.9, 35.4, 35.1, 34.6, 32.5, 32.3, 31.4, 31.1, 29.6, 28.3, 27.1, 26.7, 26.4, 24.6, 24.2, 23.4, 23.3, 21.5, 20.9, 18.3, 12.1; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{43}H_{65}O_7$Calcd. 693.4730, Found 693.4750.

*Methyl (4R)-2-((E)-benzylidene)-5-methoxy-4-propyloctanoate (**20**)*



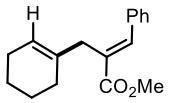
Following the general procedure, reaction of MBH adduct (**2a**; 0.058 g, 0.2mmol) and thianthrenium salt (**1k**; 0.083 g, 0.2 mmol) in presence of Eosin-Y (0.007 g, 0.01mmol) and $^{i}Pr_2NEt$ (0.078 g, 0.6mmol) delivered compound **20**, which was purified by silica gel column chromatography (EtOAc: Hexane 5:95) to furnish the title compound **20** as a colorless oil in 40% (0.025 g) yield (*E/Z* >20:1, *dr* 1:1). R_f 0.25 (EtOAc: Hexane 3:7); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.69 (s, 1H), 7.43-7.38 (m, 2H), 7.37 – 7.35 (m, 6H), 7.32-7.29 (m, 2H), 3.81 (s, 3H), 3.80 (s, 3H), 3.20 (s, 3H), 3.07 (s, 3H), 2.98 – 2.91 (m, 2H), 2.81-2.76 (m, 1H), 2.66-2.61 (m, 1H), 2.56-2.50 (m, 2H), 1.88 – 1.84 (m, 2H), 1.39 – 1.21 (m, 12H), 1.39 – 1.21 (m, 4H), 0.87 – 0.75 (m, 12H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 169.4, 169.2, 139.8, 139.6, 136.0(2), 133.3, 133.1, 129.5, 129.2, 128.5 (2), 128.2(2), 83.0, 82.6, 57.3, 57.0, 52.1, 52.0, 38.9, 38.8, 32.1, 31.9, 31.7,31.6, 27.6, 27.4, 20.9, 20.71 (s), 19.7(2), 14.5, 14.4, 14.3(2); **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{20}H_{31}O_3$ Calcd. 319.2273, Found 319.2272.

*Methyl (E)-2-((2-methoxytetrahydro-2H-pyran-3-yl)methyl)-3-phenylacrylate(**21**)*



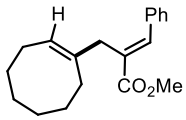
Following the general procedure, reaction of MBH adduct (**2a**; 0.029 g, 0.1 mmol) and thianthrenium salt (**1l**; 0.039 g, 0.1 mmol) in presence of Eosin-Y (0.0035 g, 0.005 mmol) and $^{i}Pr_2NEt$ (0.039 g, 0.3 mmol) delivered compound **21**, which was purified by silica gel column chromatography (EtOAc: Hexane 1:9) to furnish the title compound **21** as a colorless oil in 83% (0.024 g) yield (*E/Z* 13:1, *d/r*>20:1). R_f 0.3 (EtOAc: Hexane 1:5);**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.42 – 7.36 (m, 4H), 7.33 – 7.30 (m, 1H), 4.09 (d, *J* = 5.7 Hz, 1H), 3.89 – 3.84 (m, 1H), 3.81 (s, 3H), 3.43 – 3.39 (m, 1H), 3.37 (s, 3H), 2.83 (dd, *J* = 13.8, 5.9 Hz, 1H), 2.55 (dd, *J* = 13.8, 8.1 Hz, 1H), 1.82 – 1.76 (m, 2H), 1.47-1.36 (m, 2H), 1.25 – 1.15 (m, 1H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 169.4, 139.9, 135.8, 131.9, 129.5, 128.6, 128.5, 105.3, 64.0, 55.7, 52.2, 39.6, 28.6, 26.6, 23.9; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ $C_{17}H_{22}NaO_4^+$Calcd. 313.1410, Found 313.1404.

*Methyl (E)-2-(cyclohex-1-en-1-ylmethyl)-3-phenylacrylate (**22**)*



Following the general procedure, reaction of MBH adduct (**2a**; 0.029 g, 0.1 mmol) and thianthrenium salt (**1m**; 0.038 g, 0.1 mmol) in presence of Eosin-Y (0.0035 g, 0.005 mmol) and $^{i}Pr_2NEt$ (0.039 g, 0.3 mmol) delivered compound **22**, which was purified by silica gel column chromatography (EtOAc: Hexane 1:99) to furnish the title compound **22** as a colorless oil in 76% (0.019 g) yield (*E/Z* 5:1). R_f 0.6 (EtOAc: Hexane 5:95); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.40 – 7.28 (m, 6H), 5.37 – 5.36 (m, 1H), 3.81 (s, 3H), 3.12 (s, 2H), 2.05 – 1.98 (m, 5H), 1.70 – 1.66 (m, 2H), 1.64- 1.54 (m, 3H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 169.2, 140.4, 135.7, 135.4, 130.8, 129.5, 128.7, 128.5, 121.2, 52.2, 35.3, 29.6, 25.4, 23.2, 22.6; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{17}H_{21}O_2^+$Calcd. 257.1536, Found 257.1523.

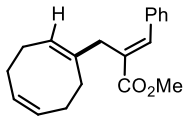
*Methyl (E)-2-(((E)-cyclooct-1-en-1-yl)methyl)-3-phenylacrylate (**23**)*



Following the general procedure, reaction of MBH adduct (**2a**; 0.058 g, 0.2mmol) and thianthrenium salt (**1n**; 0.082 g, 0.2mmol) in presence of Eosin-Y (0.007 g, 0.01mmol) and $^{i}Pr_2NEt$ (0.078 g, 0.6mmol) delivered compound **23**, which was purified by silica gel column chromatography (EtOAc: Hexane 5:95) to furnish the title compound **23** as a colorless oil in 62% (0.035 g) yield (*E/Z* 12:1). R_f 0.4 (EtOAc: Hexane 1:9); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.35-7.33 (m, 2H), 7.30 – 7.21 (m, 3H), 5.21 (t, J = 8.1 Hz, 1H), 3.71 (s, 3H), 3.14 (brs, 2H), 2.15 – 2.12 (m, 2H), 2.07 – 2.05 (m, 2H), 1.51 – 1.36 (m, 9H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 169.1, 140.6, 138.3, 135.7, 130.7, 129.3, 128.7,128.5, 123.8, 52.1, 34.9, 30.5, 30.3,

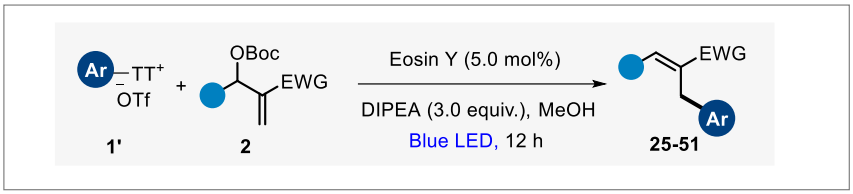
28.4, 26.5(2), 26.4; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{19}H_{25}O_2$ Calcd. 285.1855, Found 285.1859.

*Methyl (E)-2-(((1E,5Z)-cycloocta-1,5-dien-1-yl)methyl)-3-phenylacrylate(**24**)*



Following the general procedure, reaction of MBH adduct (**2a**; 0.058 g, 0.2mmol) and thianthrenium salt (**1o**; 0.082 g, 0.2mmol) in presence of Eosin-Y (0.007 g, 0.01mmol) and $^{i}Pr_2NEt$ (0.078 g, 0.6 mmol) delivered compound **24**, which was purified by silica gel column chromatography (EtOAc: Hexane 5:95) to furnish the title compound **24** as a colorless oil in 53% (0.030 g) yield (*E/Z* >20:1). R_f 0.4 (EtOAc: Hexane 1:9); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.41-7.39 (m, 2H), 7.35 – 7.30 (m, 3H), 5.64-5.52 (m, 2H), 5.25-5.22 (m, 1H), 3.77 (s, 3H), 3.14 (s, 2H), 2.42 – 2.33 (m, 8H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 169.0, 140.7, 136.9, 135.6, 130.8, 129.6, 128.8, 128.6, 128.5, 128.4, 122.7, 52.1, 36.7, 32.7, 28.5, 27.6, 27.5. **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{19}H_{23}O_2$ Calcd. 283.1698, Found 283.1700.

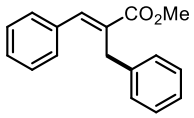
11. General procedure for photo-induced aryl allylation



A 10 mL oven dry sealed tube was charged with MBH adduct (**1**, 1.0 equiv.), thianthrenium salt (**2**, 1.0 equiv.), catalyst Eosin-Y (0.05 equiv.). The tube was evacuated and backfilled with argon two times and it was capped with a rubber septum (or screw cap). Then degassed MeOH (0.2 M) and N, N-diisopropylethylamine (3.0 equiv.) were added using a syringe under argon atmosphere. The resulting solution was placed 10 cm away from a 427 nm Blue LED (Kessil lamp, 427 nm) at room temperature (using one cooling fan) and irradiated for 10-16 h. Upon complete consumption of the starting material (TLC monitored), the reaction mixture diluted with DCM and transfer to a round bound flask. The organic solvent was removed under reduced pressure and the crude residue was purified by silica-gel flash column chromatography (using EtOAc /hexanes as eluent) to provide the desire products (**25-51**).

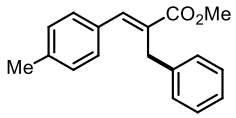
12. Characterization of compounds 25-51 (from Scheme 3: main text)

*Methyl (E)-2-benzyl-3-phenylacrylate (**25**)*[3]



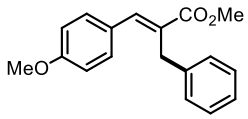
Following the general procedure, reaction of MBH adduct (**2a**; 0.029 g, 0.1 mmol) and thianthrenium salt (**1a'**; 0.044 g, 0.1 mmol) in presence of Eosin-Y (0.0035 g, 0.005 mmol) and $^{i}Pr_2NEt$ (0.039 g, 0.3 mmol) delivered compound **25**, which was purified by silica gel column chromatography (EtOAc: Hexane 3:97) to furnish the title compound **25** as a colorless oil in 71% (0.018 g) yield (*E/Z* >20:1). R_f 0.4 (EtOAc: Hexane 5:95); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.39 – 7.33 (m, 5H), 7.31 – 7.28 (m, 2H), 7.22 -7.19 (t, *J* = 6.0 Hz, 3H), 3.97 (s, 2H), 3.76 (s, 3H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 168.8, 141.1, 139.6, 135.5, 130.9, 129.3, 128.9, 128.7(2), 128.1, 126.3, 52.2, 33.3; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{17}H_{17}O_2^+$Calcd. 253.1223, Found 253.1218.

*Ethyl (E)-2-benzyl-3-(p-tolyl) acrylate (**26**)*[3]



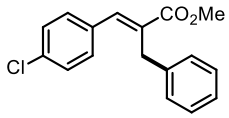
Following the general procedure, reaction of MBH adduct (**2b**; 0.058 g, 0.2 mmol) and thianthrenium salt (**1a'**; 0.088 g, 0.2 mmol) in presence of Eosin-Y (0.007 g, 0.01 mmol) and $^{i}Pr_2NEt$ (0.078 g, 0.6 mmol) delivered compound **26**, which was purified by silica gel column chromatography (EtOAc: Hexane 3:97) to furnish the title compound **26** as a colorless oil in 67% (0.036 g) yield (*E/Z* 13:1). R_f 0.4 (EtOAc: Hexane 5:95); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.30 – 7.24 (m, 4H), 7.20 – 7.17 (m, 3H), 7.14 (d, *J* = 8.0 Hz, 2H), 3.96 (s, 2H), 3.73 (s, 3H), 2.33 (s, 3H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 168.9, 141.2, 139.6, 139.1, 132.6, 129.8, 129.5, 128.7, 128.0, 126.2, 52.2, 33.3, 21.5; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{18}H_{19}O_2^+$ Calcd. 267.1380, Found 267.1376.

*Methyl (E)-2-benzyl-3-(4-methoxyphenyl) acrylate (**27**)*[3]



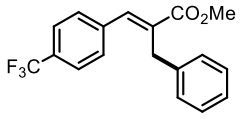
Following the general procedure, reaction of MBH adduct (**2c**; 0.029 g, 0.1 mmol) and thianthrenium salt (**1a'**; 0.044 g, 0.1mmol) in presence of Eosin-Y (0.0035 g, 0.005 mmol) and $^{i}Pr_2NEt$ (0.039 g, 0.3 mmol) delivered compound **27**, which was purified by silica gel column chromatography (EtOAc: Hexane 1:9) to furnish the title compound **27** as a colorless oil in 67% (0.019 g) yield (*E/Z* 16:1). R_f 0.25 (EtOAc: Hexane 1:9); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.35 (d, *J* = 8.7 Hz, 2H), 7.31-7.28 (m, 2H), 7.22 – 7.20 (m, 3H), 6.86 (d, *J* = 8.8 Hz, 2H), 3.98 (s, 2H), 3.80 (s, 3H), 3.75 (s, 3H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 169.1, 160.3, 141.0, 139.6, 131.3, 128.7, 128.4, 128.0(2), 126.2, 114.2, 55.4, 52.2, 33.3; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{18}H_{19}O_3^+$ Calcd. 283.1329, Found 283.1322.

*Methyl (E)-2-benzyl-3-(4-chlorophenyl)acrylate (**28**)*[3]



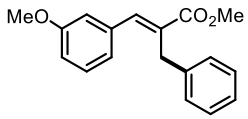
Following the general procedure, reaction of MBH adduct (**2d**; 0.033 g, 0.1 mmol) and thianthrenium salt (**1a'**; 0.044 g, 0.1 mmol) in presence of Eosin-Y (0.0035 g, 0.005 mmol) and $^{i}Pr_2NEt$ (0.039 g, 0.3 mmol) delivered compound **28**, which was purified by silica gel column chromatography (EtOAc: Hexane 3:97) to furnish the title compound **28** as a colorless oil in 52% (0.015 g) yield (*E/Z* >20:1). R_f 0.25 (EtOAc: Hexane 5:95); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.33 – 7.28 (m, 6H), 7.23 – 7.16 (m, 3H), 3.93 (s, 2H), 3.76 (s, 3H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 168.6, 139.8, 139.2, 134.9, 133.9, 131.4, 130.6, 129.0, 128.8, 128.0, 126.4, 52.4, 33.3; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{17}H_{16}ClO_2^+$ Calcd. 287.0833, Found 287.0839.

*Methyl (E)-2-benzyl-3-(4-(trifluoromethyl) phenyl) acrylate (**29**)*



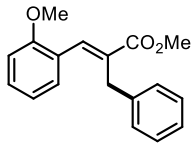
Following the general procedure, reaction of MBH adduct (**2e**; 0.036 g, 0.1 mmol) and thianthrenium salt (**1a'**; 0.044 g, 0.1 mmol) in presence of Eosin-Y (0.0035 g, 0.005 mmol) and $^{i}Pr_2NEt$ (0.039 g, 0.3 mmol) delivered compound **29**, which was purified by silica gel column chromatography (EtOAc: Hexane 3:97) to furnish the title compound **29** as a colorless oil in 50% (0.016 g) yield (*E/Z* >20:1). R_f 0.4(EtOAc: Hexane 5:95); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.60 (d, *J* = 8.2 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 7.17 (d, *J* = 7.1 Hz, 2H), 3.92 (s, 2H), 3.77 (s, 3H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 168.3, 139.3, 139.0, 133.0, 130.0 (q, *J* = 32.4 Hz), 129.4, 128.8, 128.0, 126.5, 125.7 (q, *J* = 3.7 Hz), 52.5, 33.3; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{18}H_{16}F_3O_2^+$ Calcd. 321.1097, Found 321.1112.

*Methyl (E)-2-benzyl-3-(3-methoxyphenyl)acrylate (**30**)*[4]



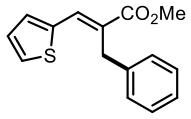
Following the general procedure, reaction of MBH adduct (**2f**; 0.032 g, 0.1 mmol) and thianthrenium salt (**1a'**; 0.044 g, 0.1 mmol) in presence of Eosin-Y (0.0035 g, 0.005 mmol) and $^{i}Pr_2NEt$ (0.039 g, 0.3 mmol) delivered compound **30**, which was purified by silica gel column chromatography (EtOAc: Hexane 5:95) to furnish the title compound **30** as a colorless oil in 60% (0.017 g) yield (*E/Z* >20:1). R_f 0.25 (EtOAc: Hexane 5:95); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.31 – 7.27 (m, 3H), 7.21 – 7.19 (m, 3H), 6.97 (d, *J* = 7.5 Hz, 1H), 6.88 – 6.86 (m, 2H), 3.97 (s, 2H), 3.76 (s, 3H), 3.66 (s, 3H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 168.8, 159.7, 141.1, 139.6, 136.8, 130.9, 129.7, 128.7, 128.0, 126.3, 121.8, 115.02, 114.3, 55.2, 52.3, 33.4; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{18}H_{19}O_3^+$ Calcd. 283.1329, Found 283.1312.

*Methyl (E)-2-benzyl-3-(2-methoxyphenyl)acrylate (**31**)*



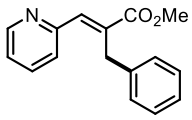
Following the general procedure, reaction of MBH adduct (**2g**; 0.032 g, 0.1 mmol) and thianthrenium salt (**1a'**; 0.044 g, 0.1 mmol) in presence of Eosin-Y (0.0035 g, 0.005 mmol) and $^{i}Pr_2NEt$ (0.039 g, 0.3 mmol) delivered compound **31**, which was purified by silica gel column chromatography (EtOAc: Hexane 3:97) to furnish the title compound **31** as a colorless oil in 43% (0.0096 g) yield (*E/Z* 15:1). R_f 0.25 (EtOAc: Hexane 5:95); **^{1}H NMR** (400 MHz, $CDCl_3$) δ8.06 (s, 1H), 7.33 – 7.27 (m, 2H), 7.23-7.17 (m, 4H), 6.92 – 6.85 (m, 3H), 3.88 (s, 2H), 3.86 (s, 3H), 3.74 (s, 3H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 168.8, 157.8, 140.1, 137.1, 130.9, 130.4, 129.5, 128.6, 128.1, 126.1, 124.6, 120.5, 110.7, 55.6, 52.2, 33.6; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{18}H_{19}O_3^+$Calcd. 283.1329, Found 283.1325.

*Methyl (E)-2-benzyl-3-(thiophen-2-yl) acrylate (**32**)*



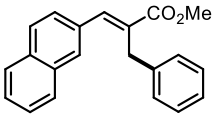
Following the general procedure, reaction of MBH adduct (**2h**; 0.030 g, 0.1mmol) and thianthrenium salt (**1a'**; 0.044 g, 0.1mmol) in presence of Eosin-Y (0.0035 g, 0.005mmol) and $^{i}Pr_2NEt$ (0.039 g, 0.3 mmol) delivered compound **32**, which was purified by silica gel column chromatography (EtOAc: Hexane 5:95) to furnish the title compound **32** as a colorless oil in 70% (0.018 g) yield (*E/Z* 10:1). R_f 0.4 (EtOAc: Hexane 1:9); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.43 (d, *J* = 5.1 Hz, 1H), 7.30 – 7.27 (m, 2H), 7.25 – 7.23 (m, 3H), 7.21 – 7.17 (m, 1H), 7.07 (dd, *J* = 5.1, 3.7 Hz, 1H), 4.12 (s, 2H), 3.77 (s, 3H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 168.8, 138.4, 138.3, 133.4, 132.6, 129.5, 128.6, 128.2, 127.6, 127.4, 126.3, 52.3, 33.8; **HRMS (ESI-TOF)** m/z: $[M+H]^+C_{15}H_{15}O_2S^+$Calcd. 259.0787, Found 259.0785.

*Methyl (E)-2-benzyl-3-(pyridin-2-yl) acrylate (**33**)*



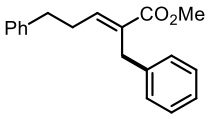
Following the general procedure, reaction of MBH adduct (**2i**; 0.029 g, 0.1 mmol) and thianthrenium salt (**1a'**; 0.044 g, 0.1 mmol) in presence of Eosin-Y (0.0035 g, 0.005 mmol) and $^{i}Pr_2NEt$ (0.039 g, 0.3 mmol) delivered compound **33**, which was purified by silica gel column chromatography (EtOAc: Hexane 1:9) to furnish the title compound **33** as a colorless oil in 59% (0.015 g) yield (*E/Z* >20:1) R_f 0.4 (EtOAc: Hexane 1:5); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 4.7 Hz, 1H), 7.75 (s, 1H), 7.69 (td, *J* = 7.7, 1.8 Hz, 1H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.29 - 7.28 (m, 2H), 7.25 – 7.20 (m, 3H), 7.18 – 7.14 (m, 1H), 4.43 (s, 2H), 3.75 (s, 3H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 168.8, 154.7, 149.8, 140.0, 137.7, 136.5, 135.1, 128.7, 128.4, 126.2, 126.1, 123.2, 52.3, 32.7; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{16}H_{16}NO_2^+$Calcd. 254.1176, Found 254.1167.

*Methyl (E)-2-benzyl-3-(naphthalen-2-yl)acrylate (**34**)* [5]



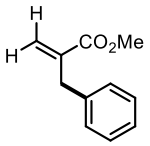
Following the general procedure, reaction of MBH adduct (**2j**; 0.034 g, 0.1 mmol) and thianthrenium salt (**1a'**; 0.044 g, 0.1 mmol) in presence of Eosin-Y (0.0035 g, 0.005 mmol) and $^{i}Pr_2NEt$ (0.039 g, 0.3 mmol) delivered compound **34**, which was purified by silica gel column chromatography (EtOAc: Hexane 2:98) to furnish the title compound **34** as a colorless oil in 53% (0.016 g) yield (*E/Z* 5:1). R_f 0.4 (EtOAc: Hexane 5:95); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.85 – 7.74 (m, 6H), 7.52 – 7.45 (m, 4H), 7.36 – 7.30 (m, 2H), 7.25-7.21 (m, 2H), 4.04 (s, 2H), 3.79 (s, 3H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 168.9, 141.2, 139.7, 133.3, 133.2, 133.0, 131.0, 129.3, 128.7, 128.5, 128.3, 128.1, 127.8, 127.0, 126.7, 126.6, 126.3, 52.3, 33.4; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{21}H_{19}O_2^+$ Calcd. 303.1380, Found 303.1377.

*Methyl (E)-2-benzyl-5-phenylpent-2-enoate (**35**)* [6]



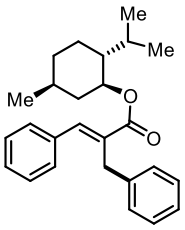
Following the general procedure, reaction of MBH adduct (**2k**; 0.032 g, 0.1 mmol) and thianthrenium salt (**1a'**; 0.044 g, 0.1 mmol) in presence of Eosin-Y (0.0035 g, 0.005 mmol) and $^{i}Pr_2NEt$ (0.039 g, 0.3 mmol) delivered compound **35**, which was purified by silica gel column chromatography (EtOAc: Hexane 1:99) to furnish the title compound **35** as a colorless oil in 54% (0.015 g) yield (*E/Z* >20:1). R_f 0.3 (EtOAc: Hexane 5:95); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 – 7.28 (m, 2H), 7.24 – 7.19 (m, 3H), 7.18 – 7.13 (m, 3H), 7.10 (d, *J* = 7.1 Hz, 2H), 6.98 (t, *J* = 7.4 Hz, 1H), 3.68 (s, 3H), 3.63 (s, 2H), 2.75 (t, *J* = 7.7 Hz, 2H), 2.62 - 2.56 (m, 2H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 168.2, 143.1, 141.1, 139.7, 131.6, 128.5 (2), 126.3, 126.1, 51.9, 34.9, 32.5, 31.1; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{19}H_{21}O_2^+$ Calcd. 281.1536, Found 281.1535.

*Methyl 2-benzylacrylate (**36**)*[7]



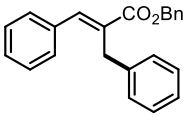
Following the general procedure, reaction of MBH adduct (**2l**; 0.022 g, 0.1 mmol) and thianthrenium salt (**1a'**; 0.044 g, 0.1 mmol) in presence of Eosin-Y (0.0035 g, 0.005 mmol) and $^{i}Pr_2NEt$ (0.039 g, 0.3 mmol) delivered compound **36**, which was purified by silica gel column chromatography (EtOAc: Hexane 3:97) to furnish the title compound **36** as a colorless oil in 33% (0.0058 g) yield. R_f 0.6 (EtOAc: Hexane 1:99); Compound **14** is a reported compound and characterized based on the reported NMR data. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34-7.28 (m, 2H), 7.23 – 7.19 (m, 3H), 6.23 (s, 1H), 5.46 (s, 1H), 3.74 (s, 3H), 3.63 (s, 1H).

*2-Isopropyl-5-methylcyclohexyl (E)-2-benzyl-3-phenylacrylate (**37**)*



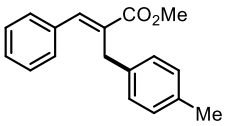
Following the general procedure, reaction of MBH adduct (**2n**; 0.042 g, 0.1 mmol) and thianthrenium salt (**1a'**; 0.044 g, 0.1 mmol) in presence of Eosin-Y (0.0035 g, 0.005 mmol) and $^{i}Pr_2NEt$ (0.039 g, 0.3 mmol) delivered compound **37**, which was purified by silica gel column chromatography (EtOAc: Hexane 2:98) to furnish the title compound **37** as a colorless oil in 51% (0.019 g) yield (*E/Z* 16:1). R_f 0.3 (EtOAc: Hexane 5:95); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.40 – 7.35 (m, 4H), 7.33 – 7.28 (m, 3H), 7.20 – 7.18 (m, 3H), 4.72 (td, *J* = 10.8, 4.3 Hz, 1H), 3.95 (q, *J* = 15.7 Hz, 2H), 1.98 – 1.95 (m, 1H), 1.67 – 1.61 (m, 2H), 1.49 – 1.42 (m, 2H), 1.33 – 1.26 (m, 1H), 1.06 – 0.97 (m, 1H), 0.94 – 0.91 (m, 1H), 0.88 (d, *J* = 6.5 Hz, 3H), 0.83 – 0.78 (m, 1H), 0.74 (d, *J* = 7.0 Hz, 3H), 0.62 (d, *J* = 6.9 Hz, 3H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 167.9, 140.6, 139.8, 135.7, 131.6, 129.2, 128.7(2), 128.6, 128.0, 126.1, 74.9, 47.2, 40.9, 34.4, 33.4, 31.5, 25.9, 23.3, 22.2, 21.0, 16.1; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{26}H_{33}O_2^+$ Calcd.377.2475, Found 377.2472.

*Benzyl (E)-2-benzyl-3-phenylacrylate (**38**)*



Following the general procedure, reaction of MBH adduct (**2m**; 0.037 g, 0.1 mmol) and thianthrenium salt (**1a'**; 0.044 g, 0.1 mmol) in presence of Eosin-Y (0.0035 g, 0.005 mmol) and $^{i}Pr_2NEt$ (0.039 g, 0.3 mmol) delivered compound **38**, which was purified by silica gel column chromatography (EtOAc: Hexane 3:97) to furnish the title compound **38** as a colorless oil in 55% (0.018 g) yield (*E/Z* 14:1). R_f 0.3 (EtOAc: Hexane 5:95); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.38 – 7.32 (m, 5H), 7.30 – 7.28 (m, 4H), 7.25 – 7.18 (m, 6H), 5.18 (s, 2H), 3.97 (s, 2H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 168.1, 141.5, 139.5, 135.5, 130.9, 129.3, 128.9, 128.7(2), 128.6, 128.1, 128.0, 66.8, 33.4; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{23}H_{21}O_2^+$Calcd. 329.1536, Found 329.1530.

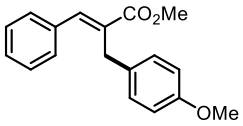
*Methyl (E)-2-(4-methylbenzyl)-3-phenylacrylate (**39**)*[3]



Following the general procedure, reaction of MBH adduct (**2a**; 0.029 g, 0.1 mmol) and thianthrenium salt (**1b'**; 0.046 g, 0.1 mmol) in presence of Eosin-Y (0.0035 g, 0.005 mmol) and $^{i}Pr_2NEt$ (0.039 g, 0.3 mmol) delivered compound **39**, which was purified by silica gel column chromatography (EtOAc: Hexane 3:97) to furnish the title compound **39** as a colorless oil in 64% (0.017 g) yield (*E/Z* >20:1). R_f 0.3 (EtOAc: Hexane 5:95); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.39 – 7.31 (m, 5H), 7.14 – 7.10 (m, 4H), 3.91 (s, 2H), 3.75 (s, 3H), 2.32 (s,

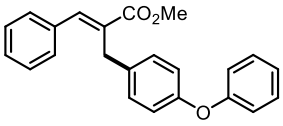
3H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ168.9, 140.9, 136.4, 135.7, 135.5, 131.0, 129.4 (2), 128.9, 128.7,127.9, 52.3, 32.9, 21.2; **HRMS (ESI-TOF)** m/z: $[M+H]^+C_{18}H_{19}O_2^+$ Calcd. 267.1380, Found 267.1377.

*Methyl (E)-2-(4-methoxybenzyl)-3-phenylacrylate (**40**)*



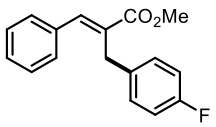
Following the general procedure, reaction of MBH adduct (**2a**; 0.029 g, 0.1 mmol) and thianthrenium salt (**1c'**; 0.0 g, 0.1 mmol) in presence of Eosin-Y (0.0035 g, 0.005 mmol) and $^{i}Pr_2NEt$ (0.039 g, 0.3 mmol) delivered compound **40**, which was purified by silica gel column chromatography (EtOAc: Hexane 3:97) to furnish the title compound **40** as a colorless oil in 63% (0.018 g) yield (*E/Z* >20:1). R_f 0.25 (EtOAc: Hexane 5:95); **^{1}H NMR** (800 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.38 – 7.32 (m, 5H), 7.11 (d, J = 8.6 Hz, 2H), 6.84 (d, J = 8.7 Hz, 2H), 3.89 (s, 2H), 3.79 (s, 3H), 3.76 (s, 3H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 200 MHz) δ 168.9, 158.1, 140.8, 135.5, 131.4, 131.1, 129.4, 129.0, 128.9, 128.7, 114.1, 55.4, 52.3, 32.4; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ $C_{18}H_{18}NaO_3^+$ Calcd. 305.1148, Found 305.1133.

*Methyl (E)-2-(4-phenoxybenzyl)-3-phenylacrylate (**41**)*



Following the general procedure, reaction of MBH adduct (**2a**; 0.029 g, 0.1 mmol) and thianthrenium salt (**1d'**; 0.029 g, 0.1 mmol) in presence of Eosin-Y (0.0035 g, 0.005 mmol) and $^{i}Pr_2NEt$ (0.039 g, 0.3 mmol) delivered compound **41**, which was purified by silica gel column chromatography (EtOAc: Hexane 5:95) to furnish the title compound **41** as a colorless oil in 52% (0.018 g) yield (*E/Z* >20:1). R_f 0.2 (EtOAc: Hexane 5:95); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.38 – 7.30 (m, 7H), 7.15 (d, *J* = 8.6 Hz, 2H), 7.08 (t, *J* = 7.4 Hz, 1H), 7.01 – 6.99 (m, 2H), 6.93 (d, *J* = 8.6 Hz, 2H), 3.93 (s, 2H), 3.78 (s, 3H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 168.8, 157.6, 155.6, 141.0, 135.5, 134.4, 131.0, 129.8, 129., 128.9, 128.8, 123.2, 119.2, 118.9, 52.3, 32.6. **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{23}H_{21}O_3^+$ Calcd. 345.1485, Found 345.1475.

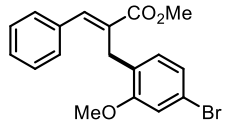
*Methyl (E)-2-(4-fluorobenzyl)-3-phenylacrylate (**42**)* [8]



Following the general procedure, reaction of MBH adduct (**2a**; 0.029 g, 0.1 mmol) and thianthrenium salt (**1e'**; 0.046 g, 0.1 mmol) in presence of Eosin-Y (0.0035 g, 0.05 mmol) and $^{i}Pr_2NEt$ (0.039 g, 0.3 mmol) delivered compound **42**, which was purified by silica gel column chromatography (EtOAc: Hexane 2:98) to furnish the title compound **42** as a colorless oil in 52% (0.014 g) yield (*E/Z* >20:1). R_f 0.25 (EtOAc: Hexane 3:97); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.36 – 7.33 (m, 5H), 7.16 -7.12 (m, 2H), 6.99 – 6.95 (m, 2H), 3.91 (s, 2H), 3.76 (s, 3H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 168.6, 161.6 (d, *J* = 242.4 Hz), 141.2, 135.4, 135.1

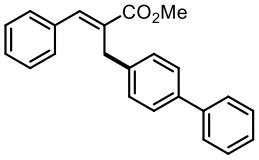
(d, *J* = 3.2 Hz), 130.8, 129.5(d, *J* = 7.8 Hz), 129.3, 129.0, 128.8, 115.4(d, *J* = 21.1 Hz), 52.3, 32.5; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{17}H_{16}FO_2^+$ Calcd. 271.1129, Found 271.1136.

*Methyl (E)-2-(4-bromo-2-methoxybenzyl)-3-phenylacrylate (**43**)*



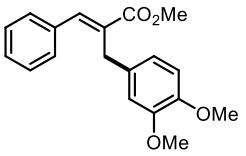
Following the general procedure, reaction of MBH adduct (**2a**; 0.029 g, 0.1mmol) and thianthrenium salt (**1j'**; 0.055 g, 0.1mmol) in presence of Eosin-Y (0.0035 g, 0.005mmol) and $^{i}Pr_2NEt$ (0.039 g, 0.3 mmol) delivered compound **43**, which was purified by silica gel column chromatography (EtOAc: Hexane 5:95) to furnish the title compound **43** as a colorless oil in 47% (0.017 g) yield (*E/Z* 15:1). R_f 0.2 (EtOAc: Hexane 5:95);**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.34 – 7.28 (m, 6H), 7.13 (d, *J* = 2.4 Hz, 1H), 6.74 (d, *J* = 8.7 Hz, 1H), 3.85 (s, 2H), 3.79 (s, 3H), 3.78 (s, 3H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 168.7, 156.6, 142.1, 135.4, 130.7, 130.4, 130.1, 129.6, 129.4, 129.0, 128.7, 113.1, 111.9, 55.7, 52.4, 27.7; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{18}H_{18}BrO_3^+$Calcd. 361.0434, Found 361.0428.

*Methyl (E)-2-([1,1'-biphenyl]-4-ylmethyl)-3-phenylacrylate (**44**)*



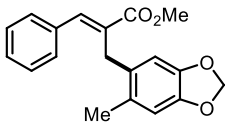
Following the general procedure, reaction of MBH adduct (**2a**; 0.029 g, 0.1 mmol) and thianthrenium salt (**1f'**; 0.052 g, 0.1 mmol) in presence of Eosin-Y (0.0035 g, 0.005 mmol) and $^{i}Pr_2NEt$ (0.039 g, 0.3 mmol) delivered compound **44**, which was purified by silica gel column chromatography (EtOAc: Hexane 2:98) to furnish the title compound **44** as a colorless oil in 58% (0.019 g) yield (*E/Z* >20:1). R_f 0.35 (EtOAc: Hexane 5:95); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.58 (dd, *J* = 8.1, 1.0 Hz, 2H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.44 – 7.30 (m, 8H), 7.28 – 7.25 (m, 2H), 4.00 (s, 2H), 3.78 (s, 3H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 168.8, 141.2, 141.1, 139.2, 138.7, 135.5, 130.8, 129.4, 129.0, 128.5, 127.4, 127.2,127.1, 52.3, 33.0; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{23}H_{21}O_2^+$ Calcd. 329.1536, Found 329.1536.

*Methyl (E)-2-(3,4-dimethoxybenzyl)-3-phenylacrylate (**45**)*



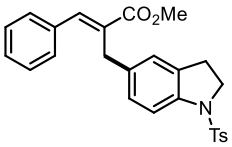
Following the general procedure, reaction of MBH adduct (**2a**; 0.029 g, 0.1 mmol) and thianthrenium salt (**1g'**; 0.050 g, 0.1 mmol) in presence of Eosin-Y (0.0035 g, 0.005 mmol) and $^{i}Pr_2NEt$ (0.039 g, 0.3 mmol) delivered compound **45**, which was purified by silica gel column chromatography (EtOAc: Hexane 1:5) to furnish the title compound **45** as a colorless oil in 64% (0.020 g) yield (*E/Z* >20:1). R_f 0.2 (EtOAc: Hexane 1:5); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.40 – 7.32 (m, 5H), 6.79 (d, *J* = 8.6 Hz, 1H), 6.72 (d, *J* = 7.2 Hz, 2H), 3.89 (s, 2H), 3.85 (s, 3H), 3.82 (s, 3H), 3.77 (s, 3H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 168.8, 149.1, 147.6, 140.9, 135.5, 132.0, 131.1, 129.3, 128.9, 128.7,119.7, 111.6, 111.4, 56.0, 55.9, 52.3, 32.7; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{19}H_{21}O_4^+$ Calcd. 313.1434, Found 313.1427.

*Methyl (E)-2-((6-methylbenzo[d][1,3]dioxol-5-yl)methyl)-3-phenylacrylate (**46**)*



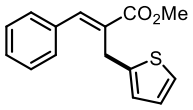
Following the general procedure, reaction of MBH adduct (**2a**; 0.029 g, 0.1 mmol) and thianthrenium salt (**1i'**; 0.050 g, 0.1 mmol) in presence of Eosin-Y (0.0035 g, 0.005 mmol) and $^{i}Pr_2NEt$ (0.039 g, 0.3 mmol) delivered compound **46**, which was purified by silica gel column chromatography (EtOAc: Hexane 1:9) to furnish the title compound **46** as a colorless oil in 42% (0.013 g) yield (*E/Z* 10:1). R_f 0.3 (EtOAc: Hexane 1:5); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.34 – 7.29 (m, 5H), 6.70 (s, 1H), 6.60 (s, 1H), 5.88 (s, 2H), 3.78 (s, 3H), 3.74 (s, 2H), 2.22 (s, 3H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 168.8, 146.0, 141.5, 135.3, 130.6, 130.5, 129.4 (2), 129.0, 128.7, 110.7, 107.5, 100.8, 52.4, 30.9, 19.8; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{19}H_{19}O_4^+$ Calcd. 311.1278, Found 311.1273.

*Methyl (E)-3-phenyl-2-((1-tosylindolin-5-yl)methyl)acrylate (**47**)*



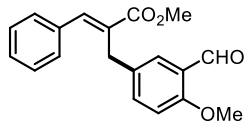
Following the general procedure, reaction of MBH adduct (**2a**; 0.029 g, 0.1 mmol) and thianthrenium salt (**1h'**; 0.064 g, 0.1 mmol) in presence of Eosin-Y (0.0035 g, 0.005 mmol) and $^{i}Pr_2NEt$ (0.039 g, 0.3 mmol) delivered compound **47**, which was purified by silica gel column chromatography (EtOAc: Hexane 1:5) to furnish the title compound **47** as a semi-solid in 47% (0.021 g) yield (*E/Z* 16:1). R_f 0.3 (EtOAc: Hexane 3:7); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.66 (d, *J* = 8.3 Hz, 2H), 7.53 (d, *J* = 8.3 Hz, 1H), 7.34 (brs, 5H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 8.3 Hz, 1H), 6.89 (s, 1H), 3.89 (t, *J* = 8.4 Hz, 2H), 3.86 (s, 2H), 3.75 (s, 3H), 2.83 (t, *J* = 8.4 Hz, 2H), 2.37 (s, 3H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 168.7, 144.1, 141.1, 140.4, 135.3, 135.1, 134.1, 132.4, 130.8, 129.7, 129.3, 129.0, 128.7, 127.5, 127.4, 124.7, 115.1, 52.3, 50.2, 32.7, 28.0, 21.7; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{26}H_{26}NO_4S^+$ Calcd.448.1577, Found 448.1578.

*Methyl (E)-3-phenyl-2-(thiophen-2-ylmethyl)acrylate (**48**)* [3]



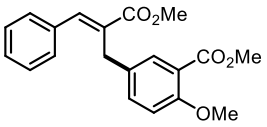
Following the general procedure, reaction of MBH adduct (**2a**; 0.029 g, 0.1 mmol) and thianthrenium salt (**1m'**; 0.045 g, 0.1 mmol) in presence of Eosin-Y (0.0035 g, 0.005 mmol) and $^{i}Pr_2NEt$ (0.039 g, 0.3 mmol) delivered compound **48**, which was purified by silica gel column chromatography (EtOAc: Hexane 3:97) to furnish the title compound **48** as a colorless oil in 46% (0.012 g) yield (*E/Z* 5:1). R_f 0.4 (EtOAc: Hexane 5:95);**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.44 – 7.29 (m, 6H), 7.15 (dd, *J* = 5.1, 1.1 Hz, 1H), 6.96 – 6.90 (m, 1H), 6.84 – 6.83 (m, 1H), 4.06 (s, 2H), 3.81 (s, 3H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 168.4, 142.4, 141.0, 135.2, 130.7, 129.4, 129.1, 128.8, 127.0, 124.8, 123.8, 52.3, 28.3; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{15}H_{15}O_2S^+$ Calcd. 259.0787, Found 259.0793.

*Methyl (E)-2-(3-formyl-4-methoxybenzyl)-3-phenylacrylate (**49**)*



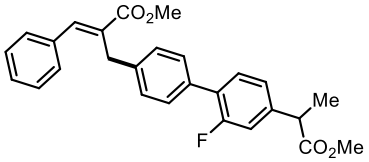
Following the general procedure, reaction of MBH adduct (**2a**; 0.029 g, 0.1 mmol) and thianthrenium salt (**1k'**; 0.050 g, 0.1 mmol) in presence of Eosin-Y (0.0035 g, 0.005 mmol) and $^{i}Pr_2NEt$ (0.039 g, 0.3 mmol) delivered compound **49**, which was purified by silica gel column chromatography (EtOAc: Hexane 1:9) to furnish the title compound **49** as a colorless oil in 42% (0.013 g) yield (*E/Z* 20:1). R_f 0.2 (EtOAc: Hexane 1:9); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.43 (s, 1H), 7.94 (s, 1H), 7.65 (d, *J* = 2.3 Hz, 1H), 7.39 – 7.34 (m, 6H), 6.92 (d, *J* = 8.6 Hz, 1H), 3.90 (s, 5H), 3.75 (s, 3H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 189.9, 168.5, 160.6, 141.5, 135.5, 135.3, 131.9, 130.4, 129.3, 129.0, 128.8, 128.0, 124.9, 112.1, 55.9, 52.3, 32.3; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{19}H_{19}O_4^+$ Calcd.311.1278, Found 311.1270.

*Methyl (E)-2-methoxy-5-(2-(methoxycarbonyl)-3-phenylallyl)benzoate (**50**)*



Following the general procedure, reaction of MBH adduct (**2a**; 0.029 g, 0.1 mmol) and thianthrenium salt (**1l'**; 0.047 g, 0.1 mmol) in presence of Eosin-Y (0.0035 g, 0.005 mmol) and $^{i}Pr_2NEt$ (0.039 g, 0.3 mmol) delivered compound **50**, which was purified by silica gel column chromatography (EtOAc: Hexane 1:9) to furnish the title compound **50** as a colorless oil in 56% (0.019 g) yield (*E/Z* 8:1). R_f 0.2 (EtOAc: Hexane 1:9);**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.61 (d, *J* = 2.3 Hz, 1H), 7.39 – 7.28 (m, 6H), 6.90 (d, *J* = 8.6 Hz, 1H), 3.89 (s, 2H), 3.87 (s, 3H), 3.87 (s, 3H), 3.75 (s, 3H);**^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 168.6, 166.8, 157.7, 141.4, 135.3, 131.3, 131.2, 130.6, 129.3, 129.0, 128.8, 120.1, 112.4, 56.2, 52.3, 52.2, 32.2;**HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{20}H_{21}O_5^+$Calcd. 341.1384, Found 341.1384.

*Methyl (E)-2-((2'-fluoro-4'-(1-methoxy-1-oxopropan-2-yl)-[1,1'-biphenyl]-4-yl)methyl)-3 phenylacrylate (**51**)*

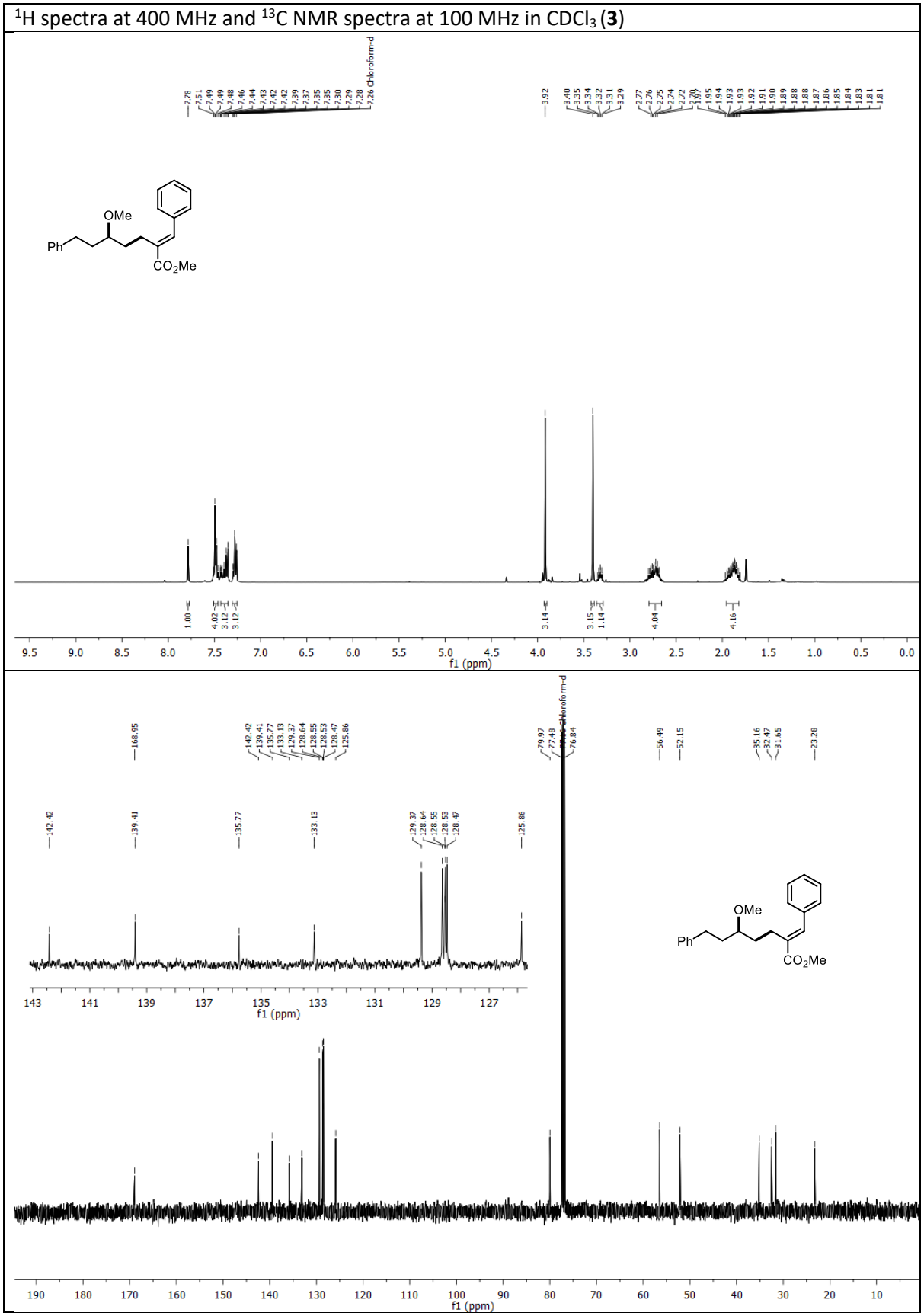


Following the general procedure, reaction of MBH adduct (**2a**; 0.029 g, 0.1 mmol) and thianthrenium salt (**1n'**; 0.062 g, 0.1 mmol) in presence of Eosin-Y (0.0035 g, 0.005 mmol) and $^{i}Pr_2NEt$ (0.039 g, 0.3 mmol) delivered compound **51**, which was purified by silica gel column chromatography (EtOAc: Hexane 1:9) to furnish the title compound **51** as a colorless oil in 49% (0.021 g) yield (*E/Z* >20:1). R_f 0.25 (EtOAc: Hexane 3:7); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.46 – 7.44 (m, 2H), 7.39-7.31 (m, 6H), 7.24-7.23 (m, 2H), 7.12-7.07 (m, 2H), 3.98 (s, 2H), 3.76 (s, 3H), 3.75 – 3.71 (m, 1H), 3.68 (s, 3H), 1.51 (d, *J* = 7.2 Hz, 3H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 174.6, 168.7, 159.8(d, *J* = 246.7 Hz), 141.7 (d, *J* = 7.5 Hz), 141.3, 139.1, 135.4, 133.4, 130.8 (d, *J* = 4.0 Hz), 130.6, 129.3, 129.2(d, *J* = 2.9 Hz) 129.0, 128.8,

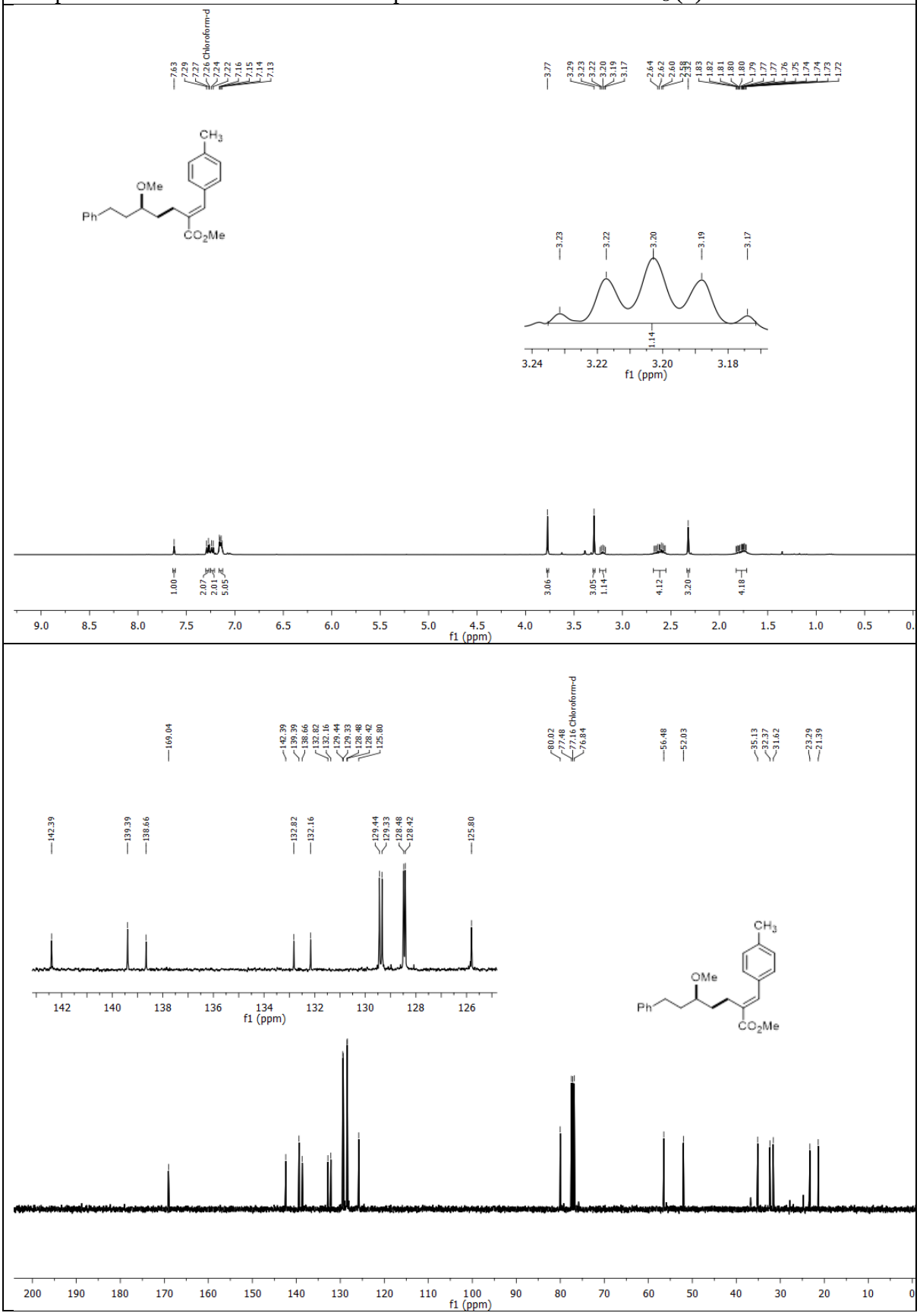
128.1, 123.6 (d, *J* = 3.3 Hz), 115.3 (d, *J* = 23.5 Hz), 52.3(d), 45.0, 33.0, 18.5; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ $C_{27}H_{25}FNaO_4^+$ Calcd.455.1629, Found 455.1638.

13. Spectral Data

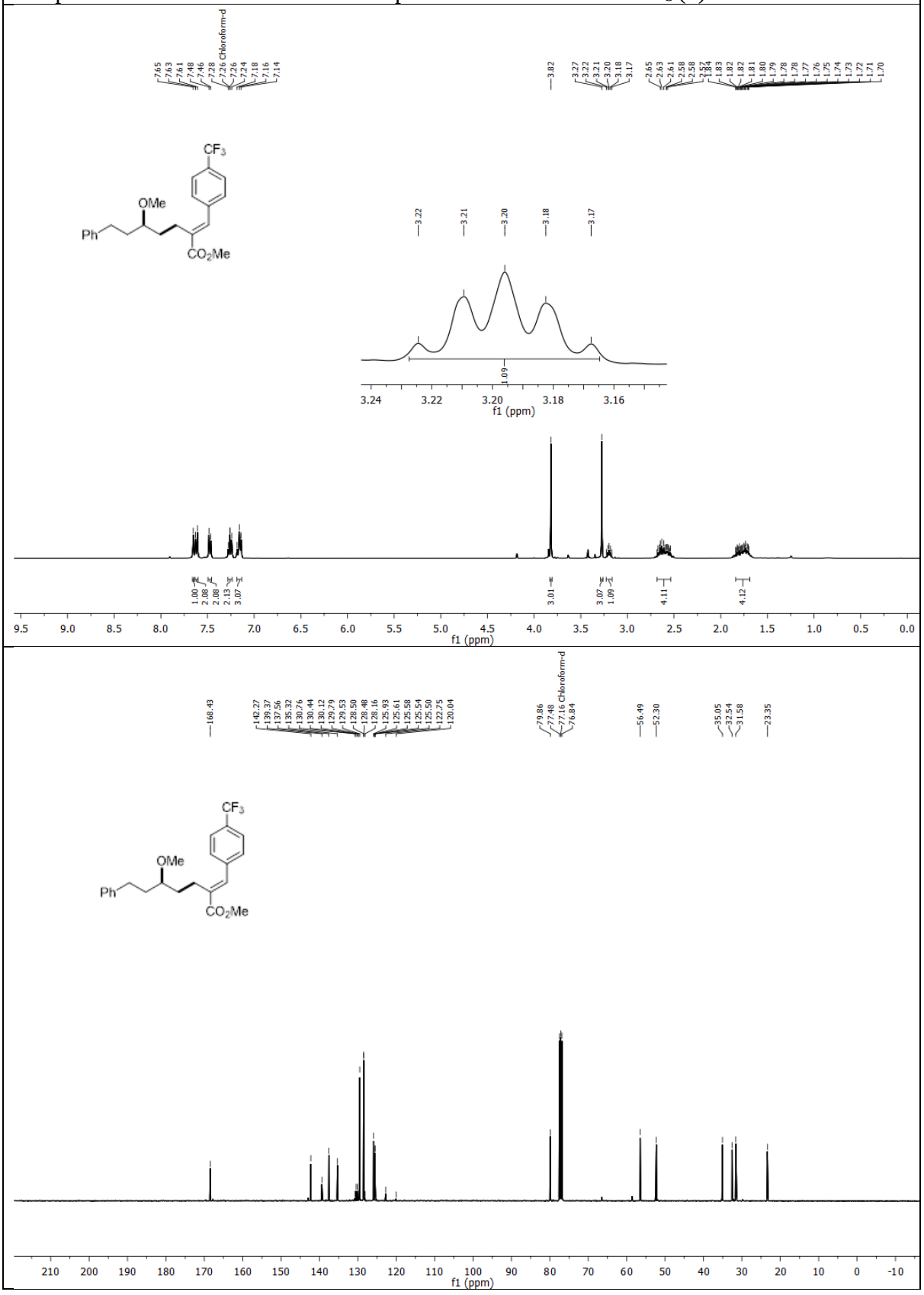
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ (**3**)



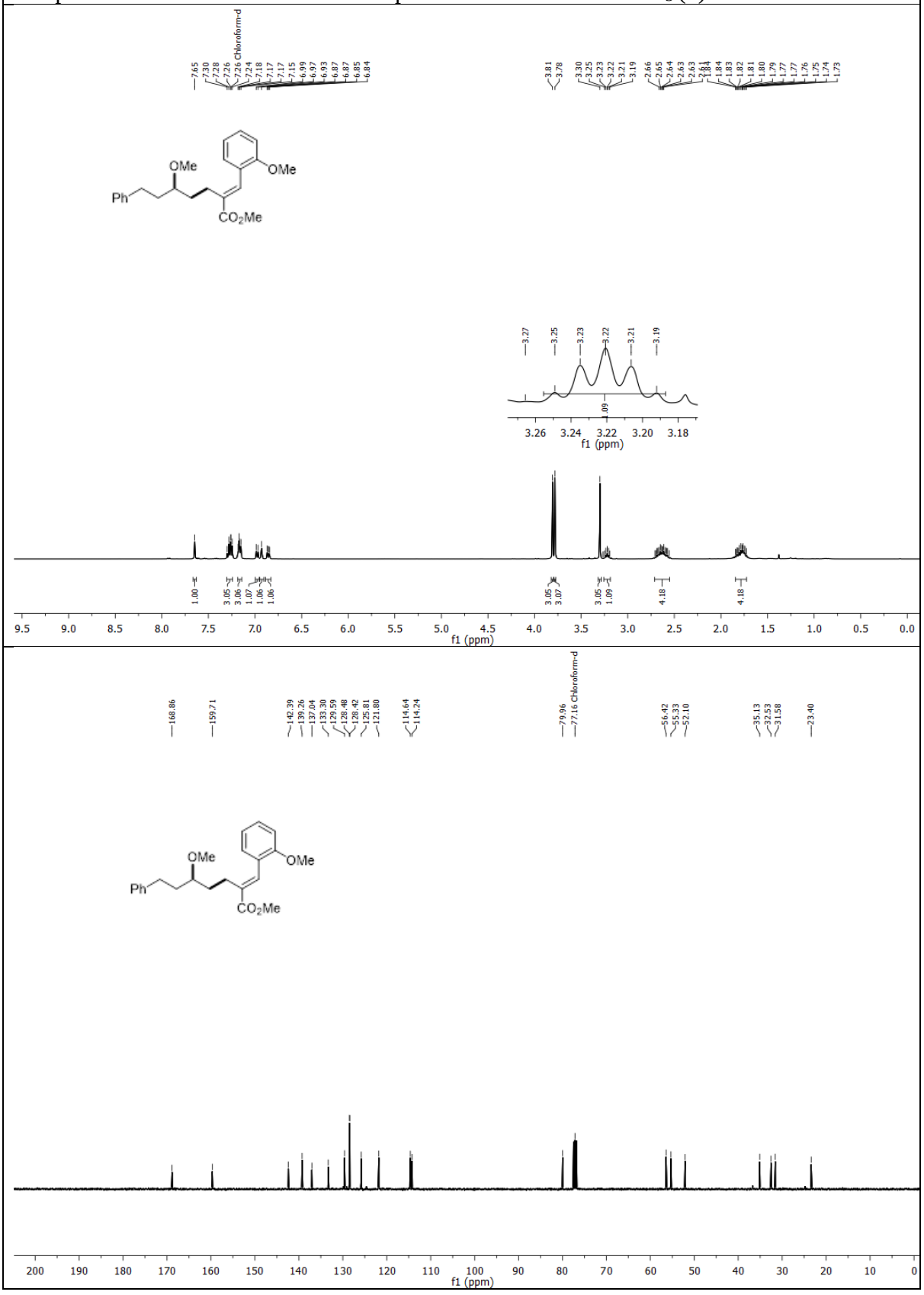
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ (4)



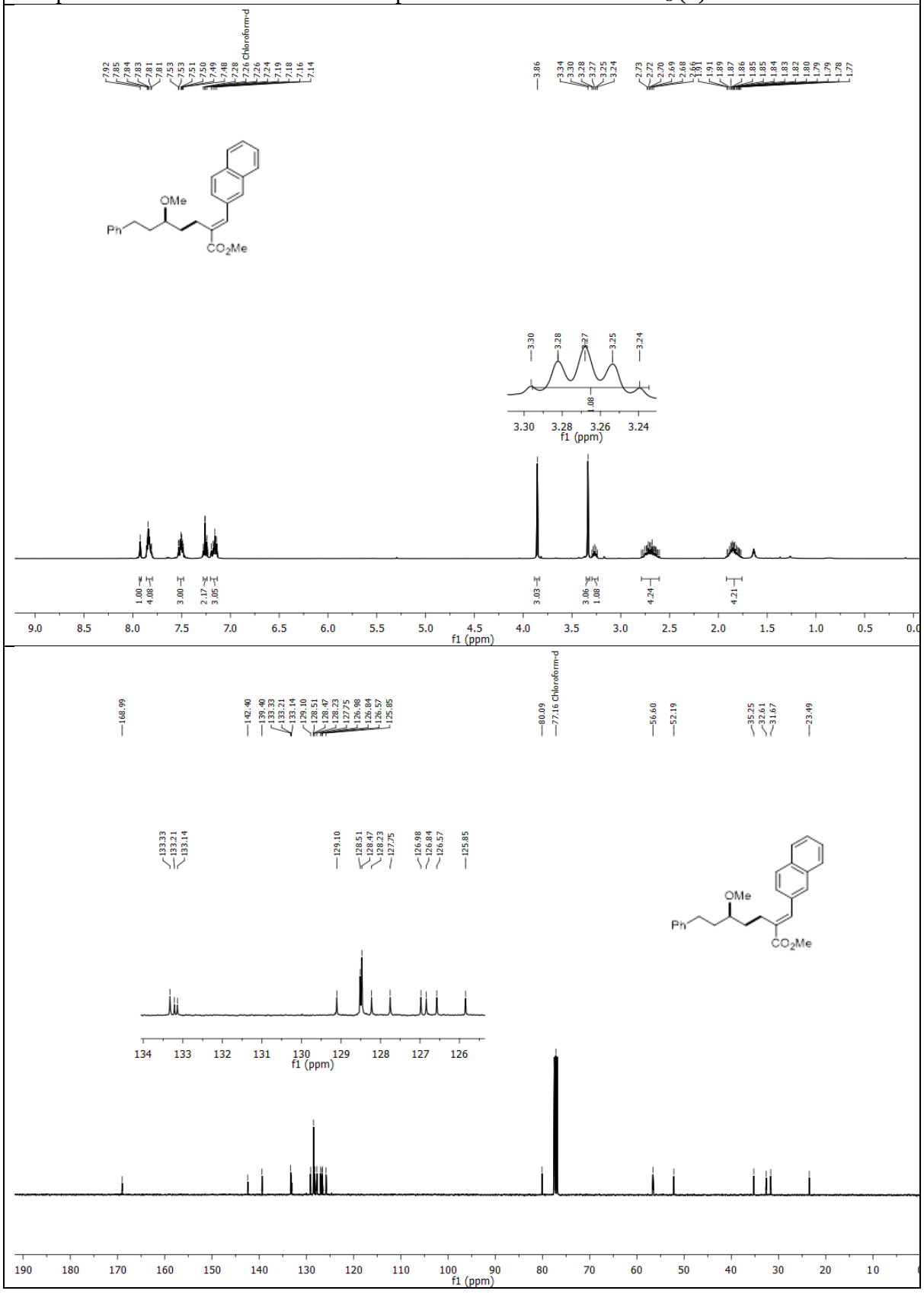
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ (5)



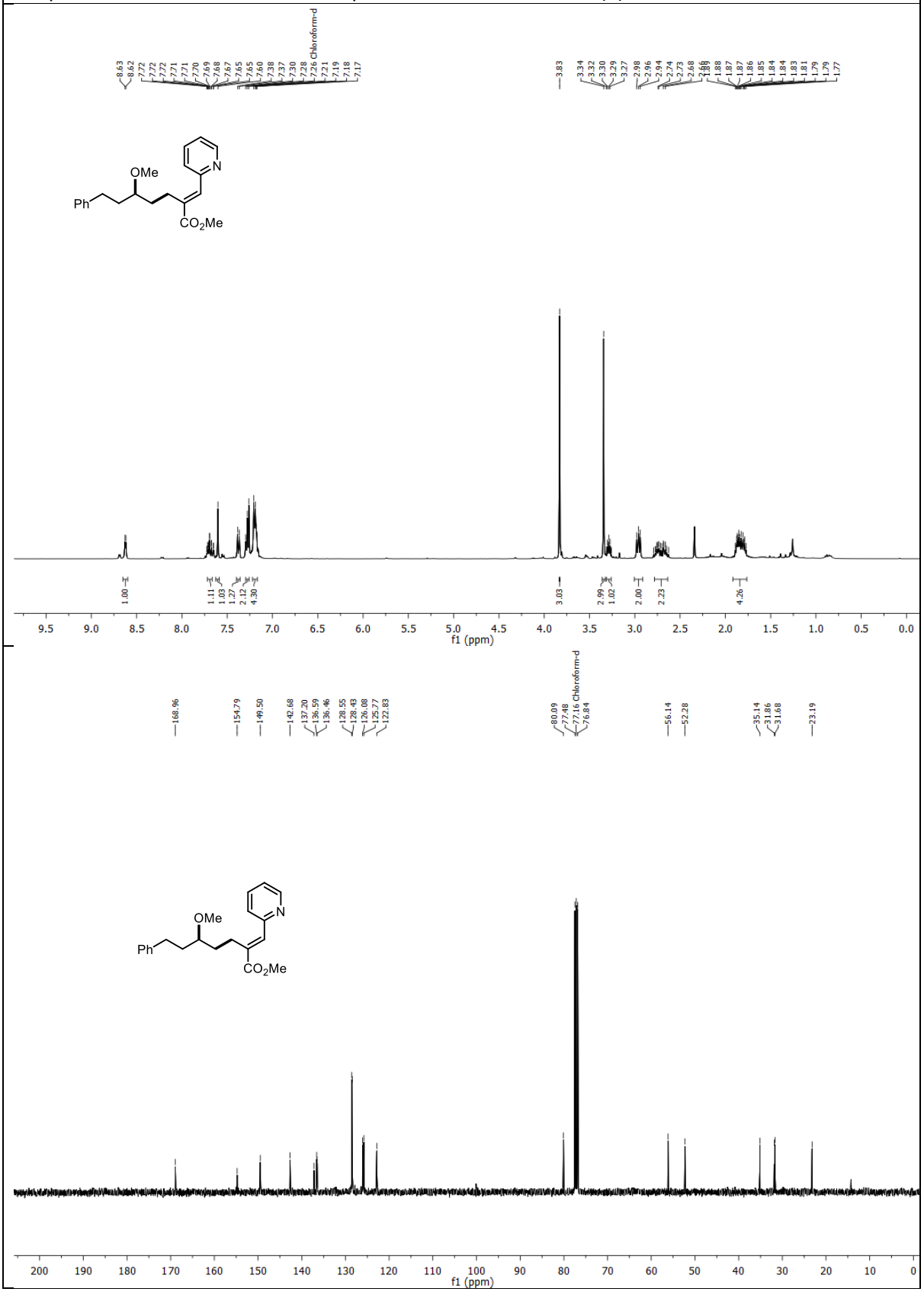
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ (6)



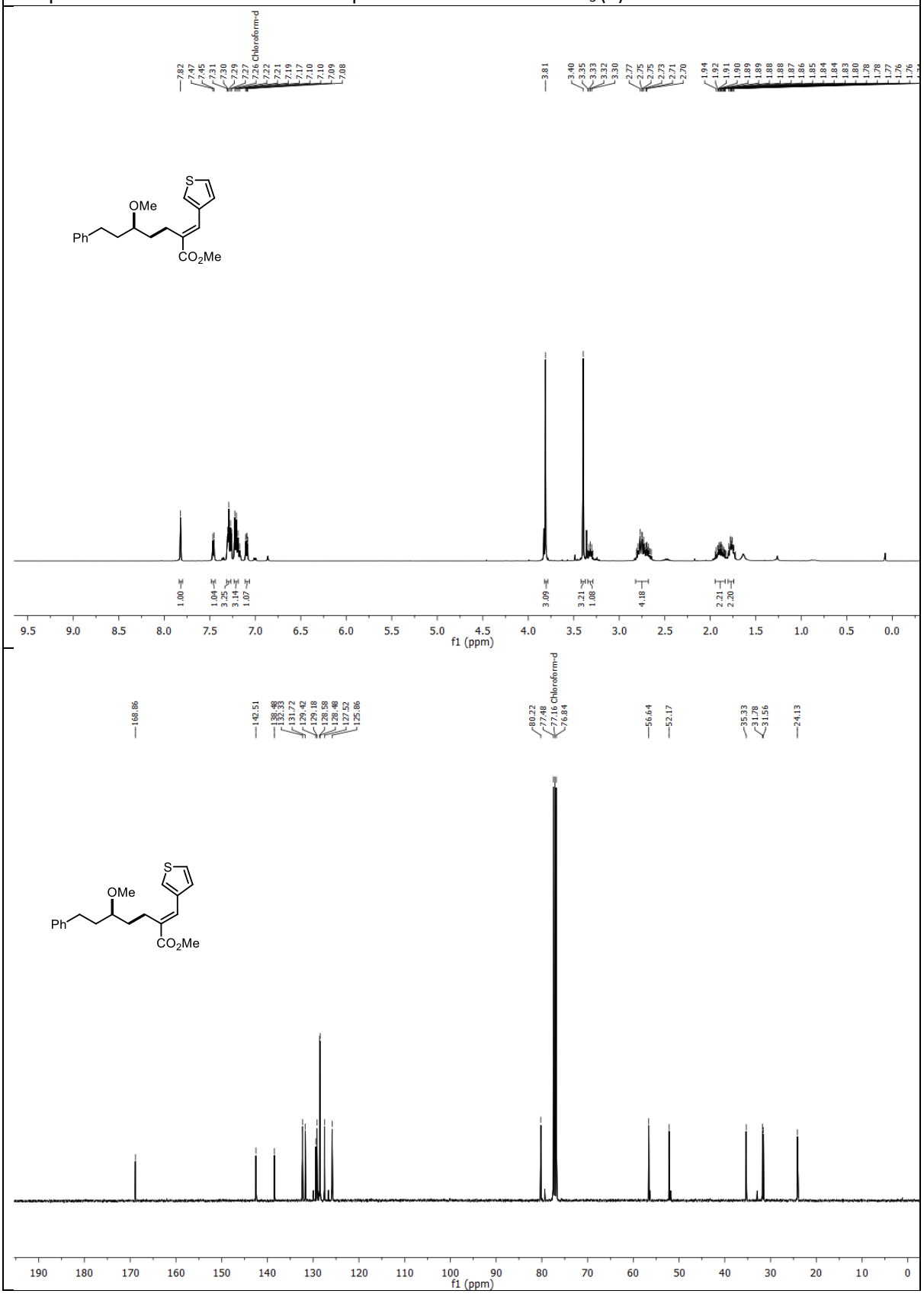
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ (7)



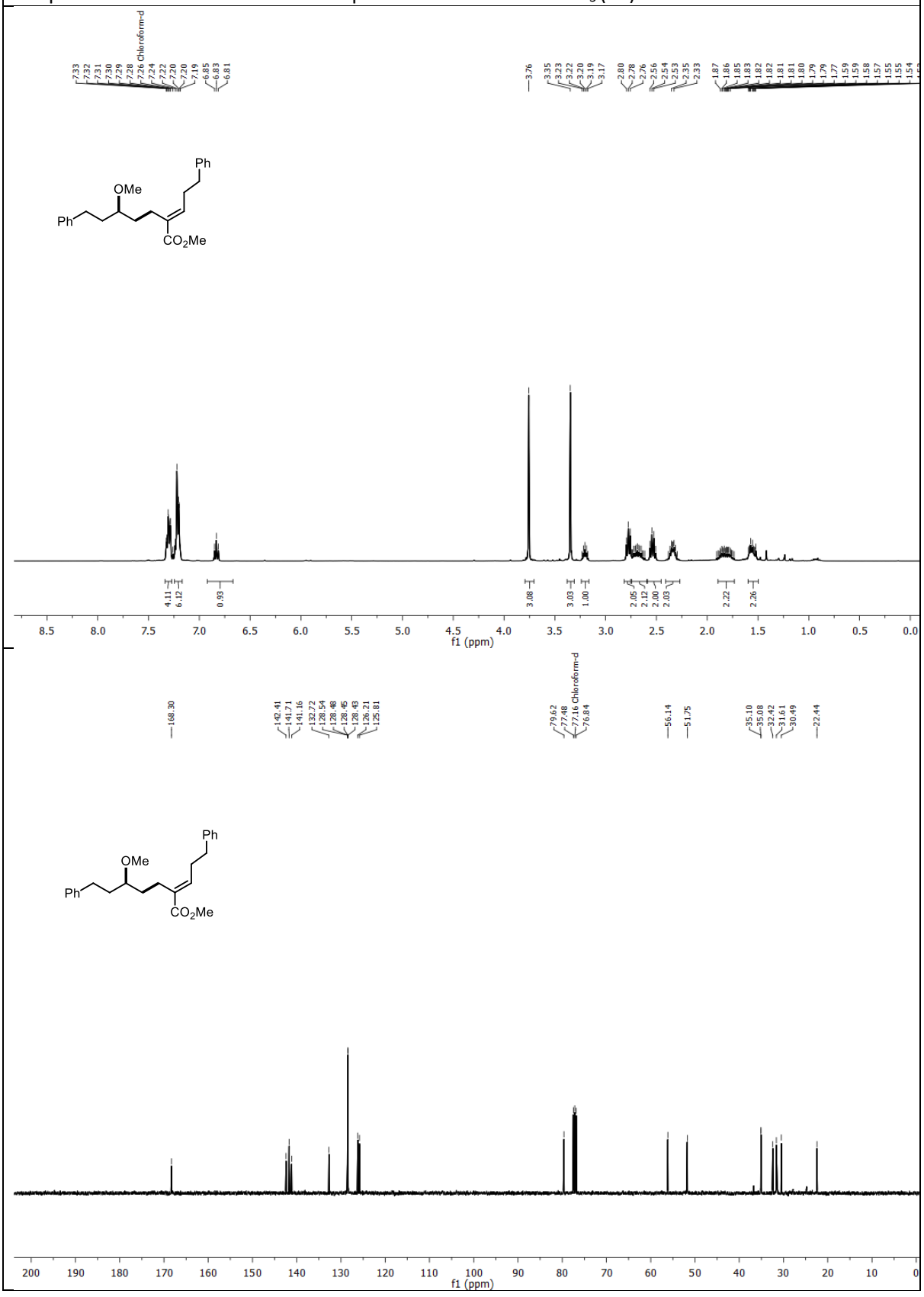
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ (8)



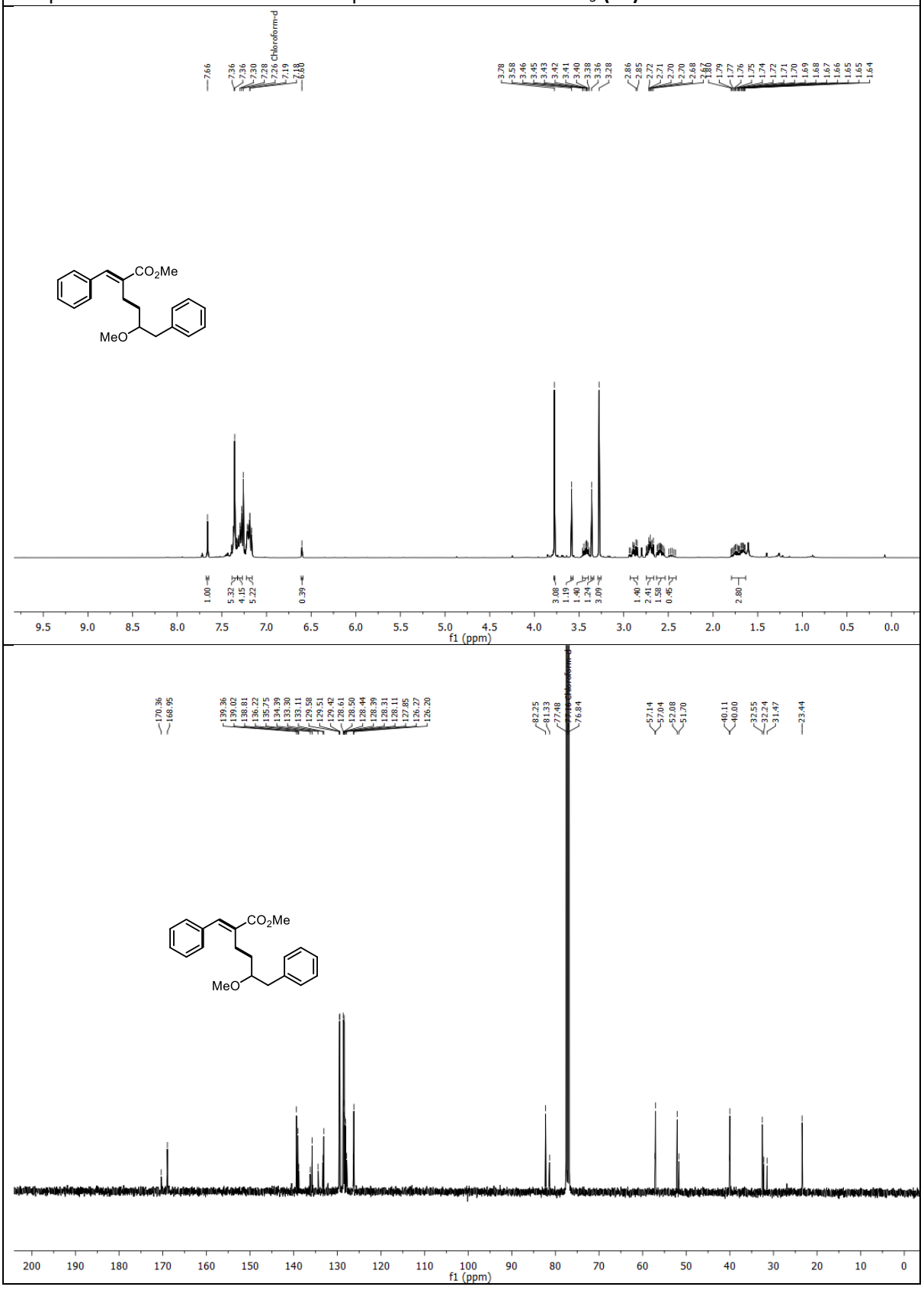
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ (**9**)



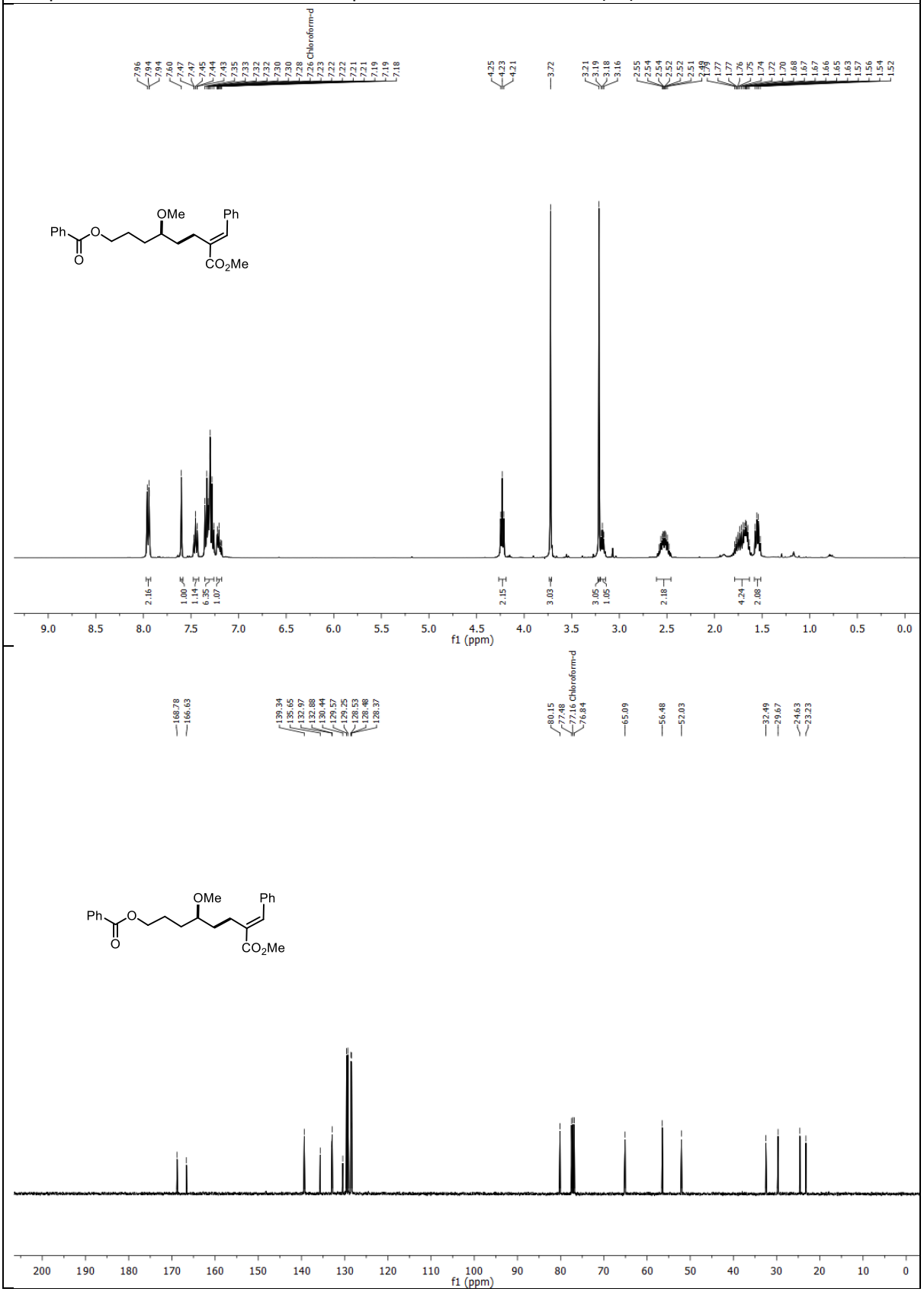
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ (**10**)



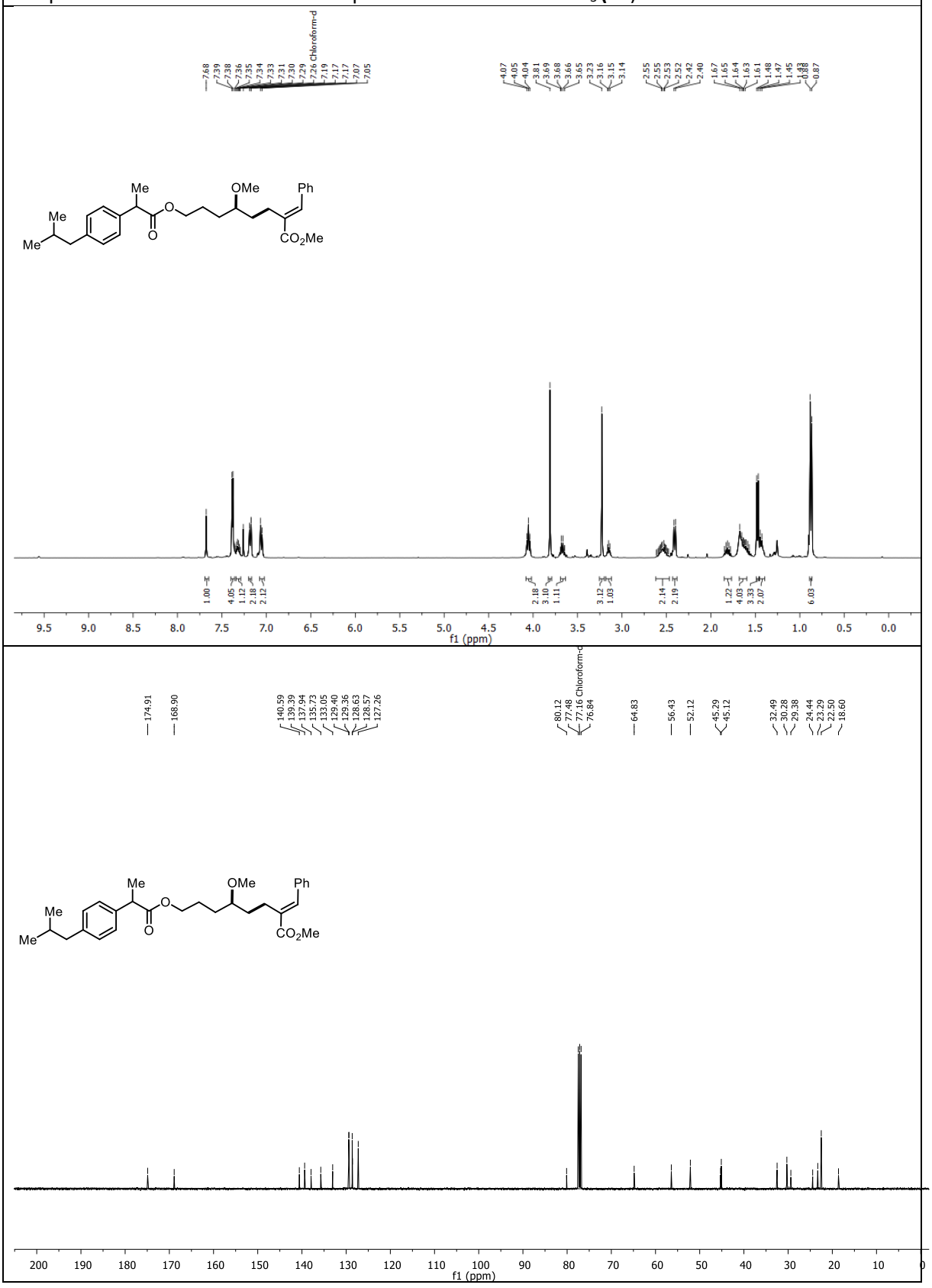
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ **(11)**



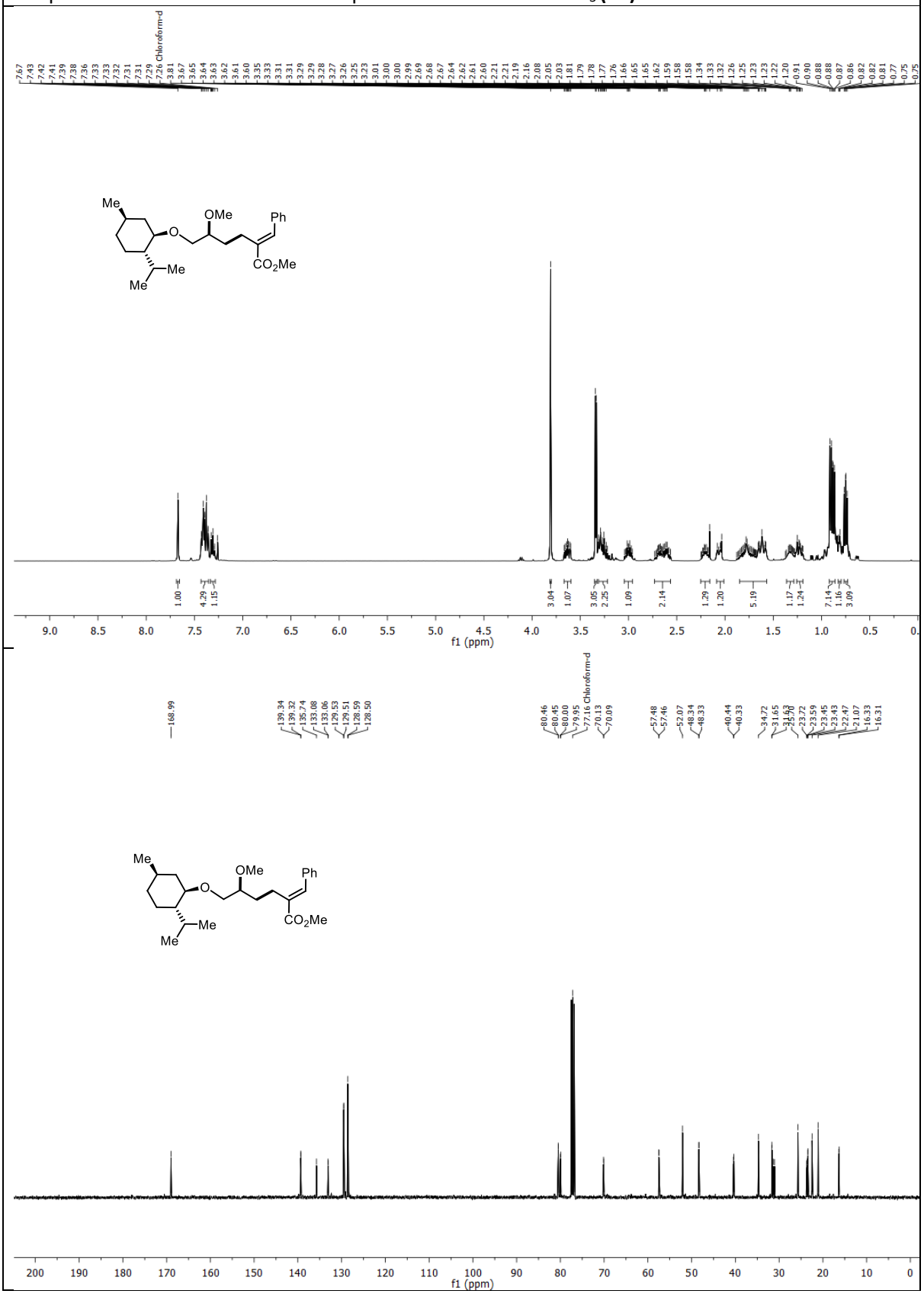
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ (**12**)



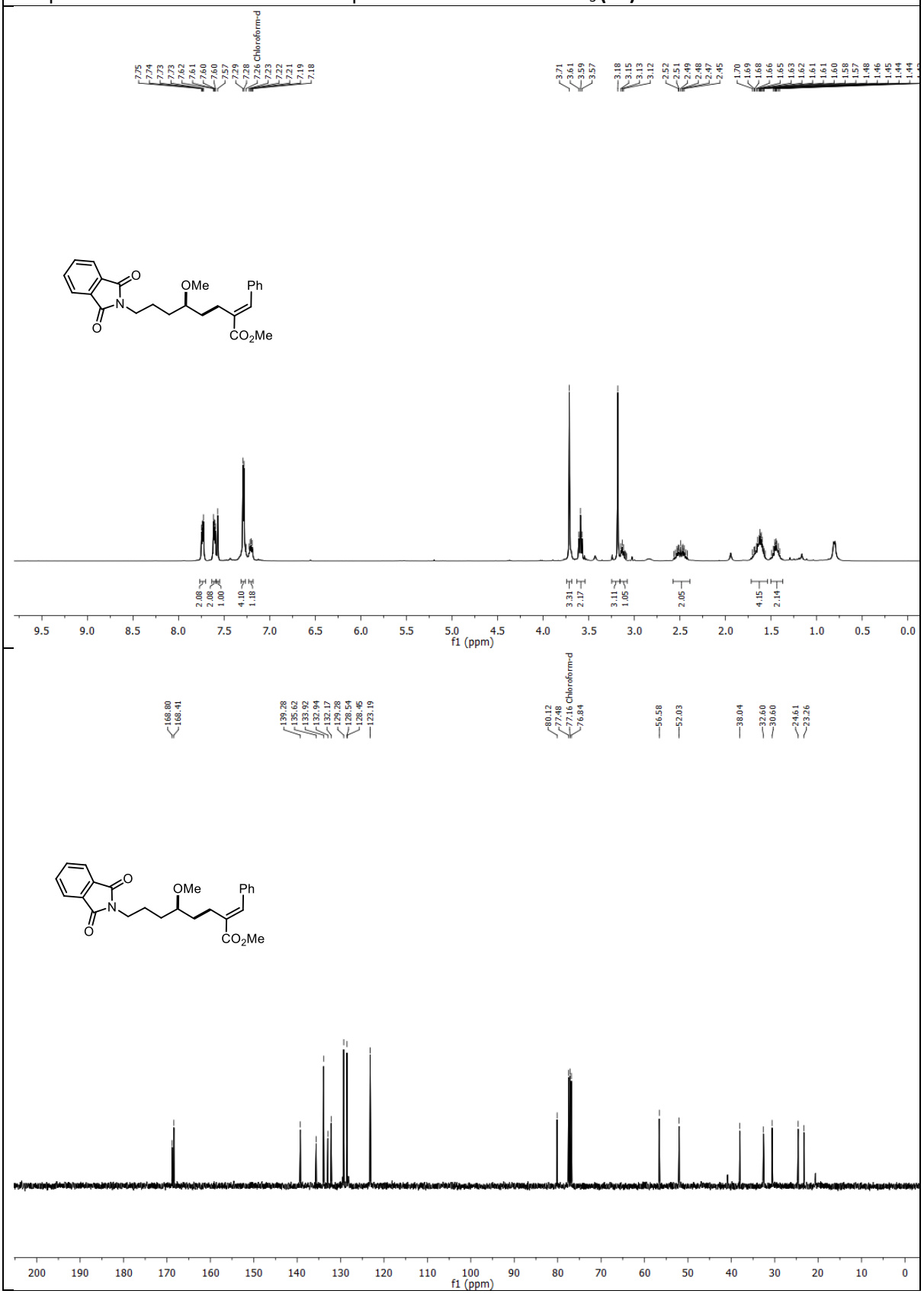
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ **(13)**



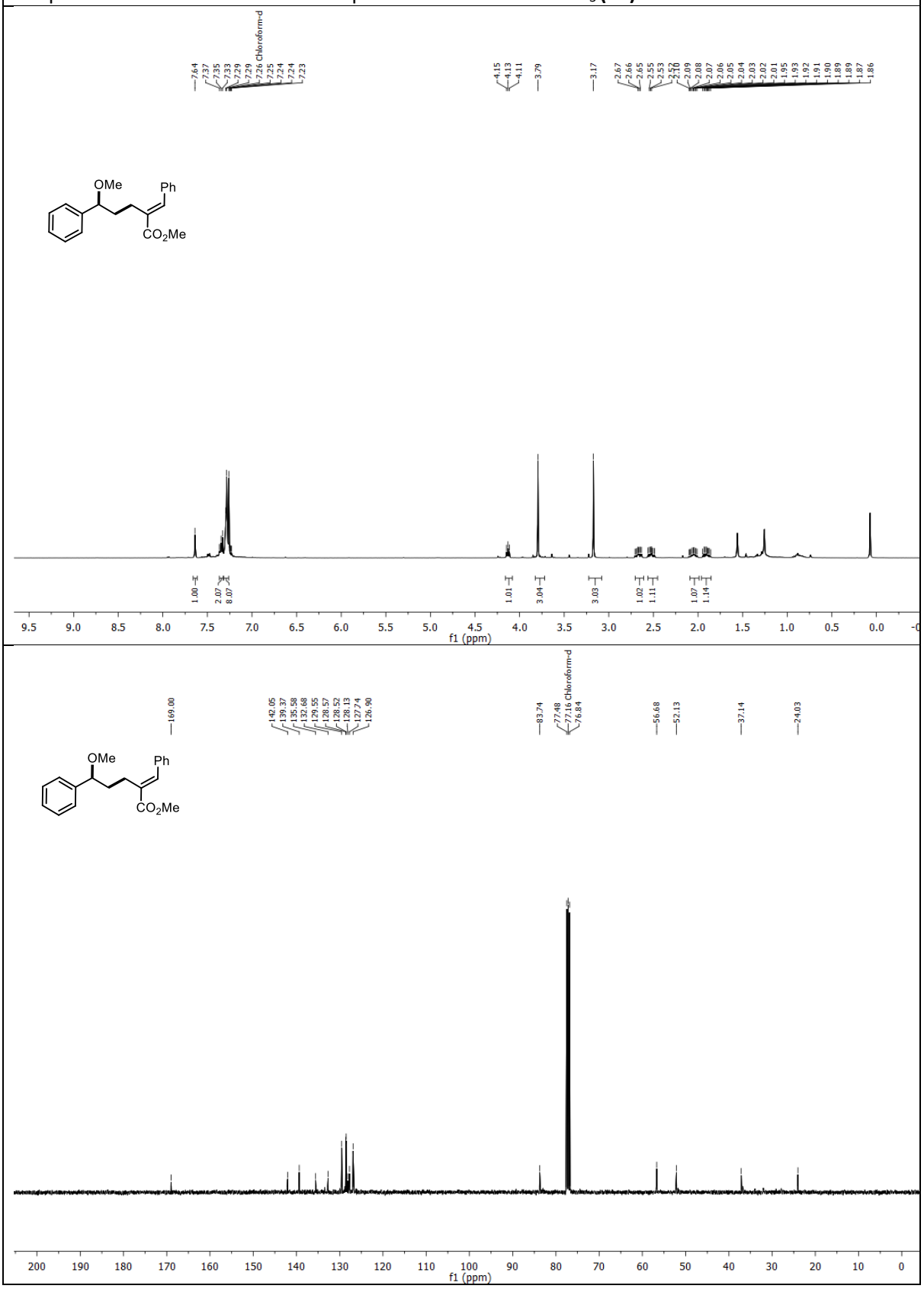
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ **(14)**



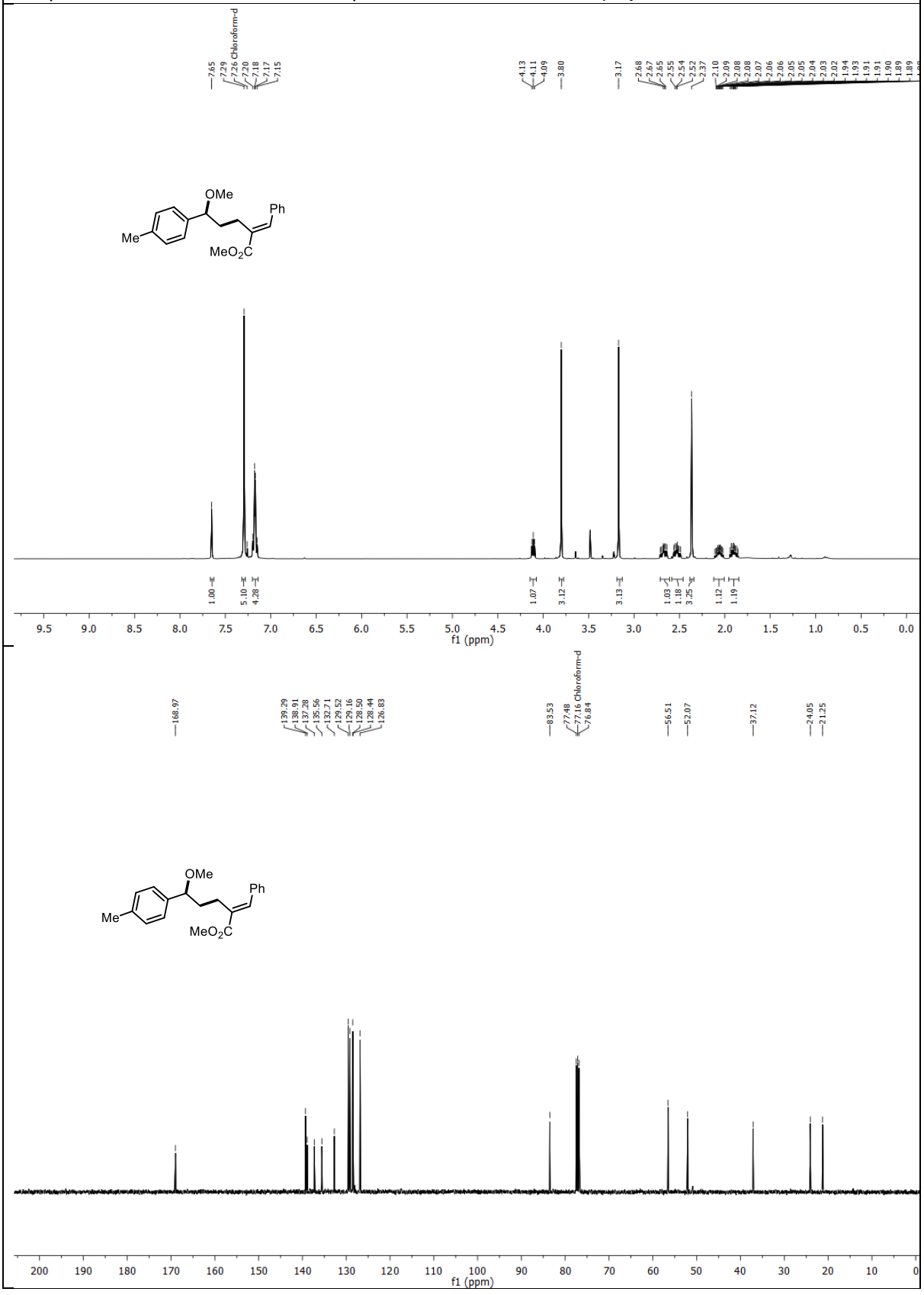
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ **(15)**



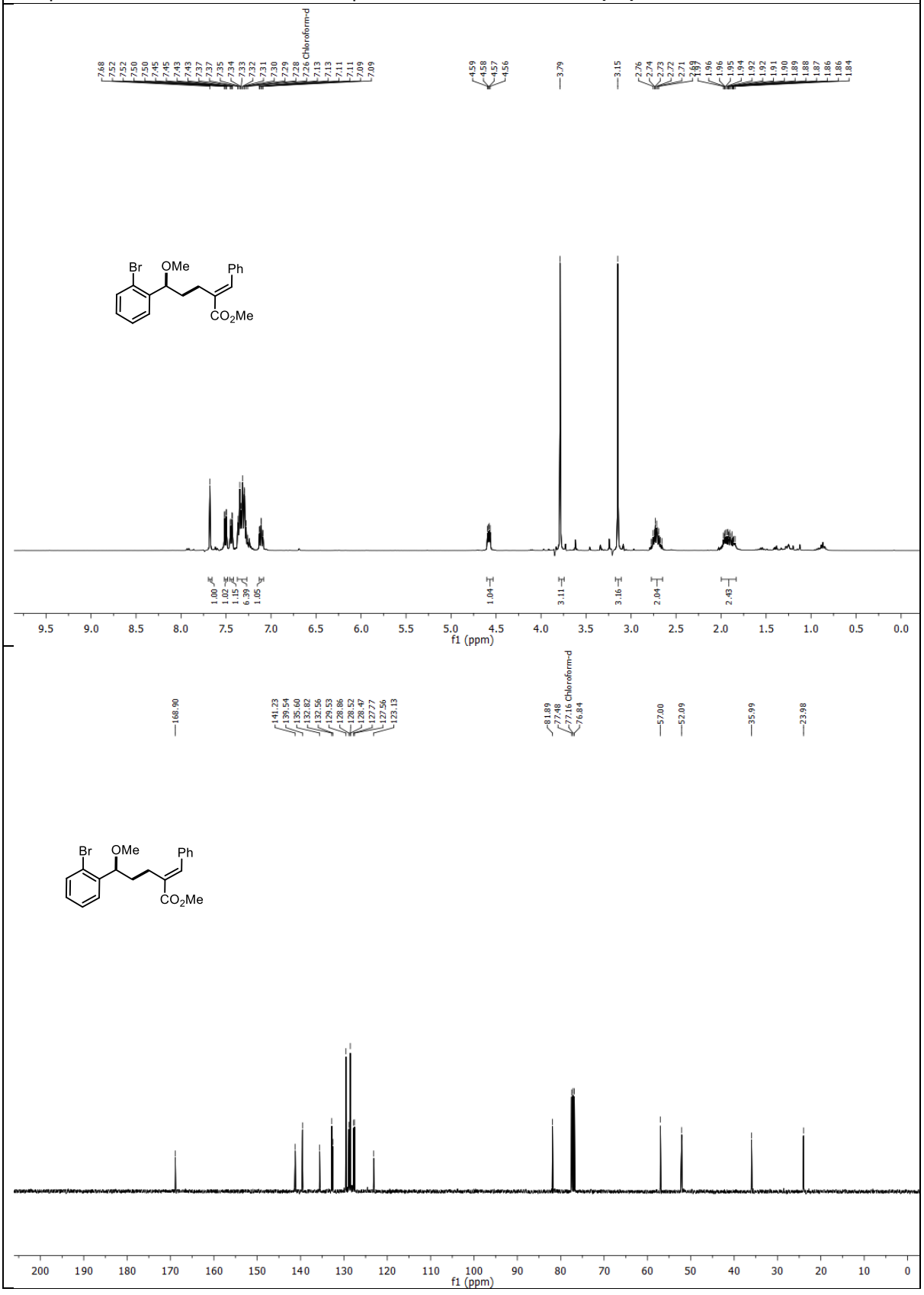
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ **(16)**



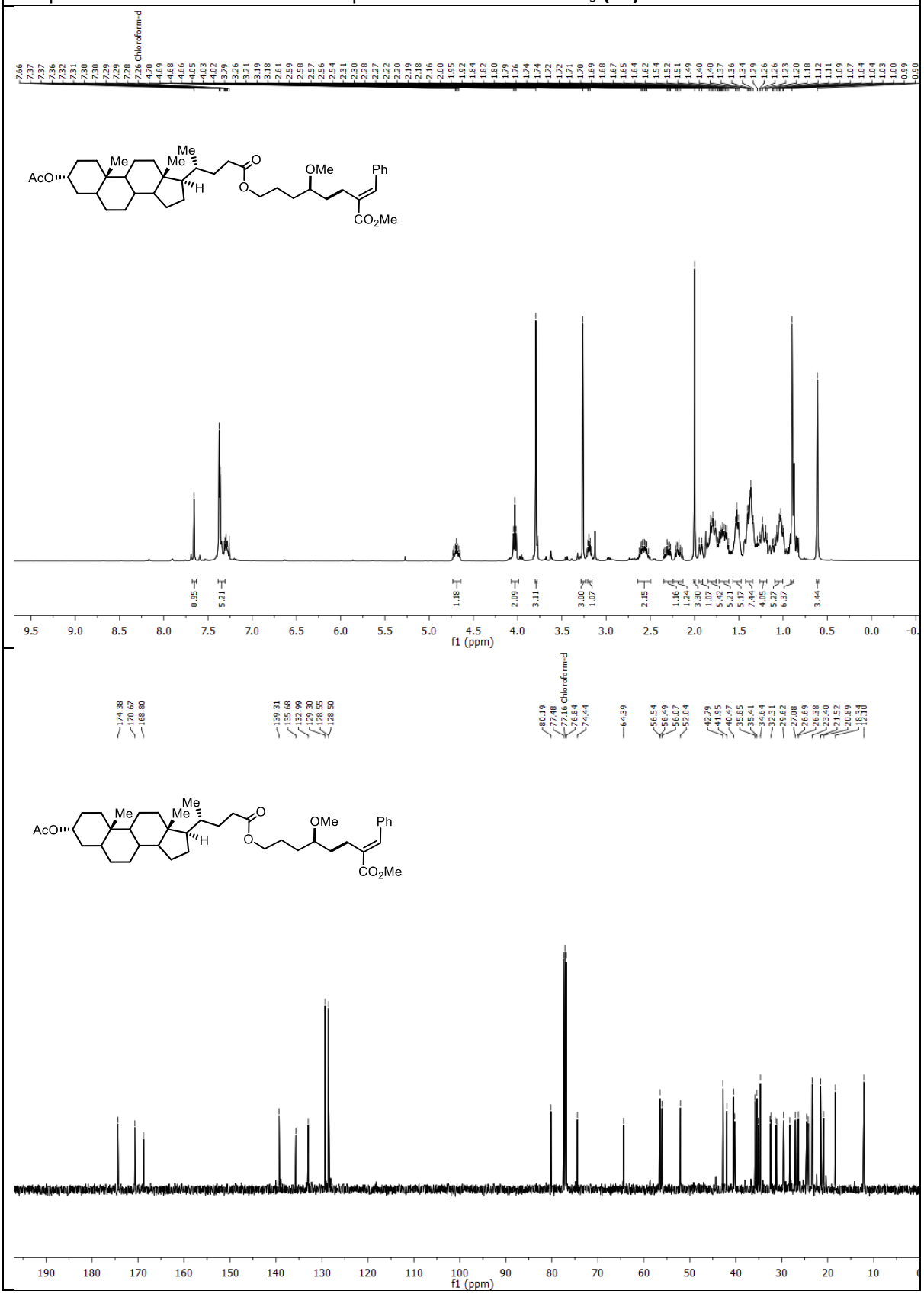
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ (**17**)



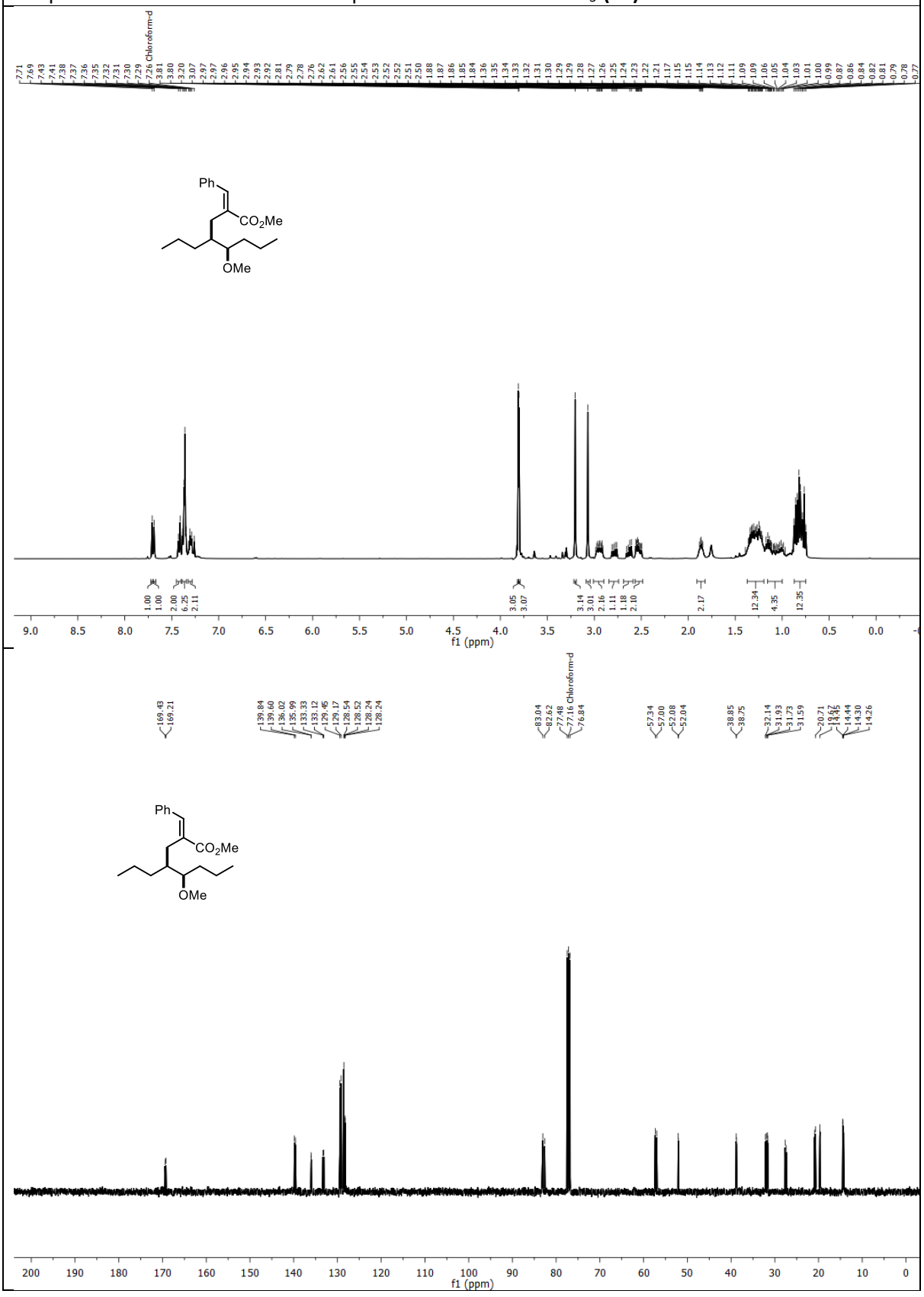
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ **(18)**



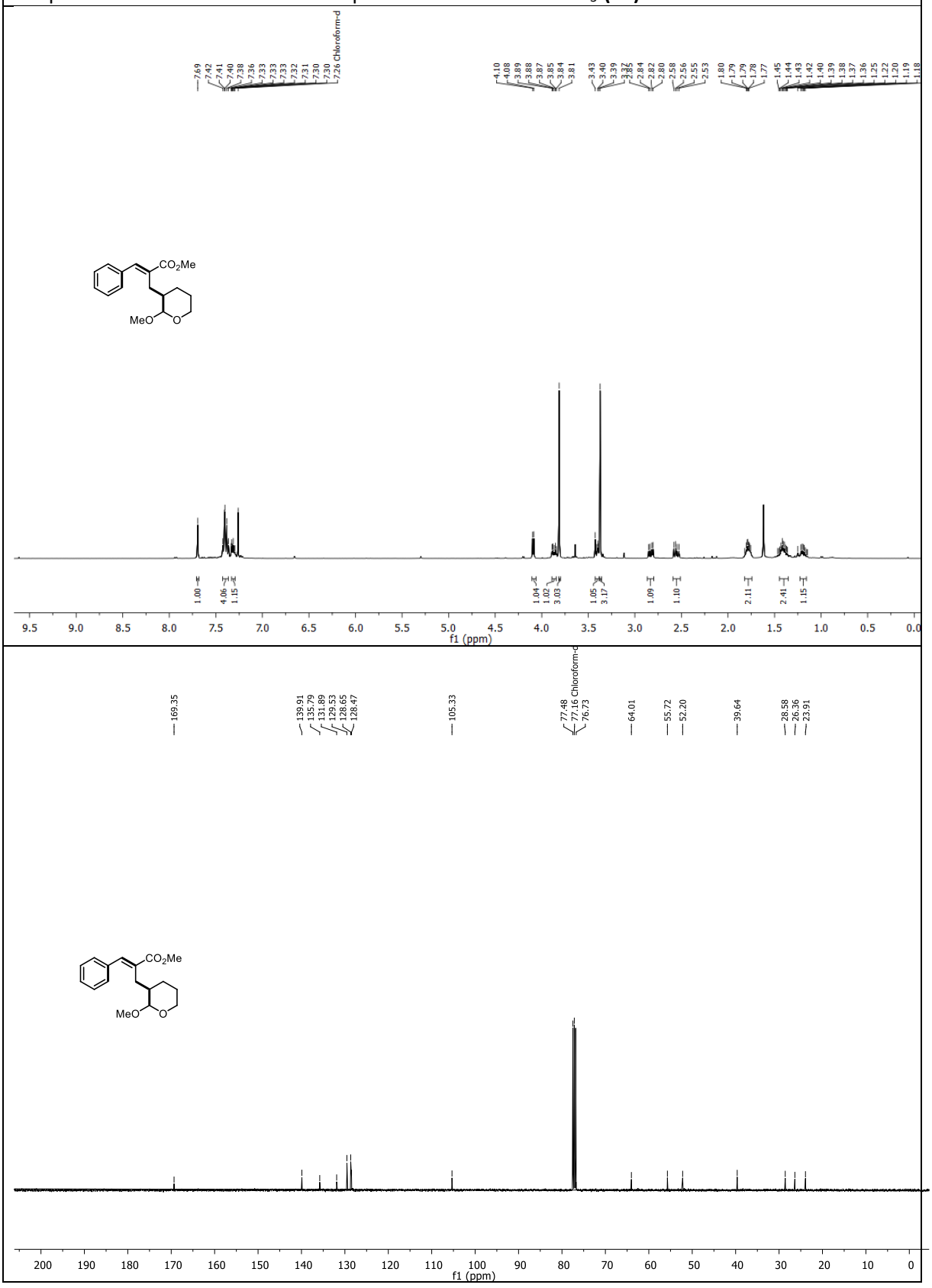
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ **(19)**



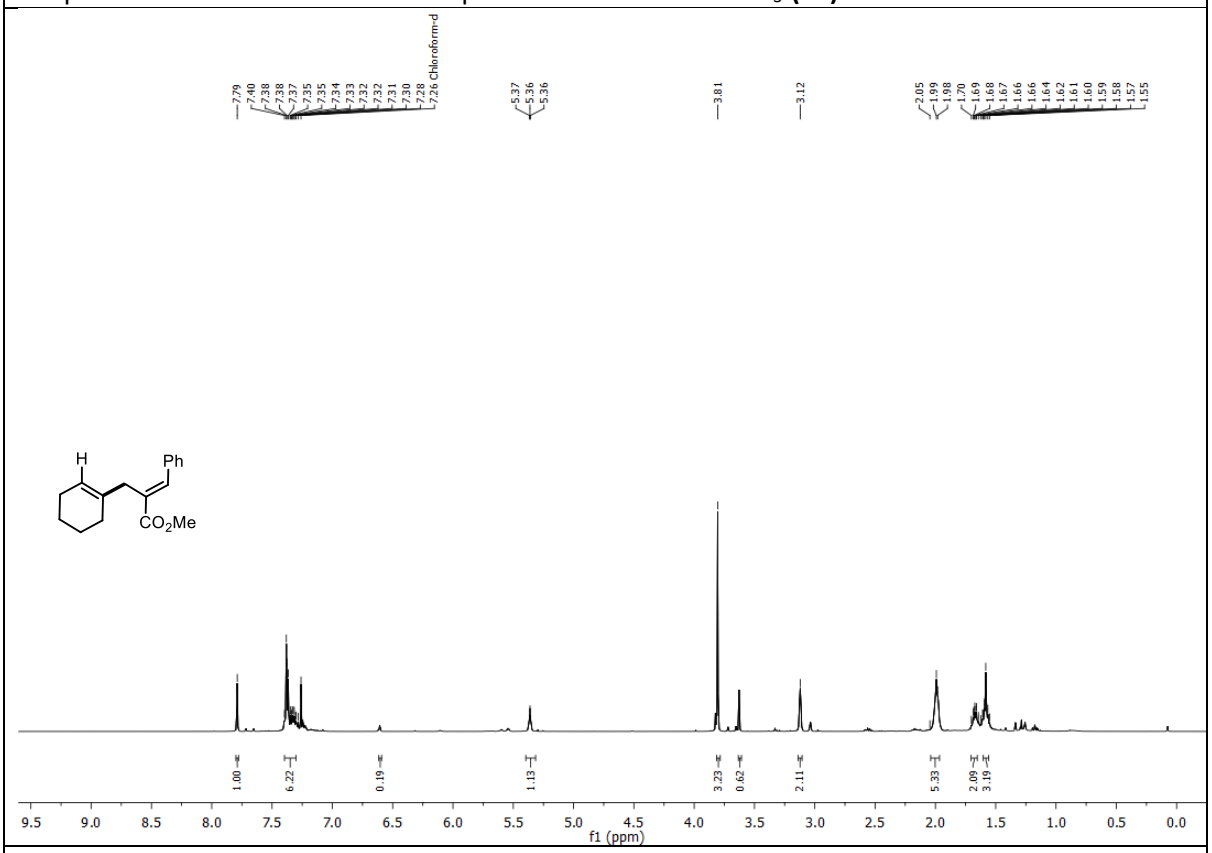
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ **(20)**

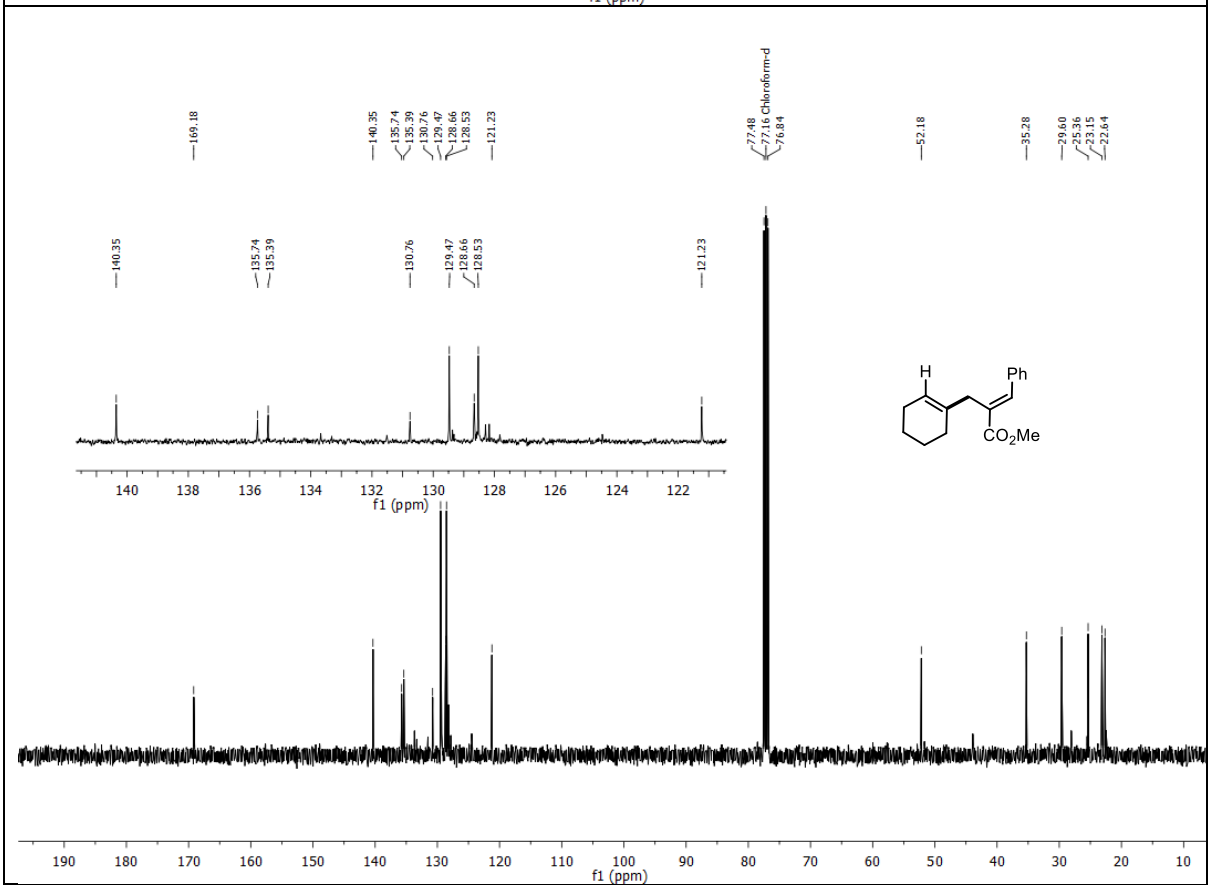


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ **(21)**

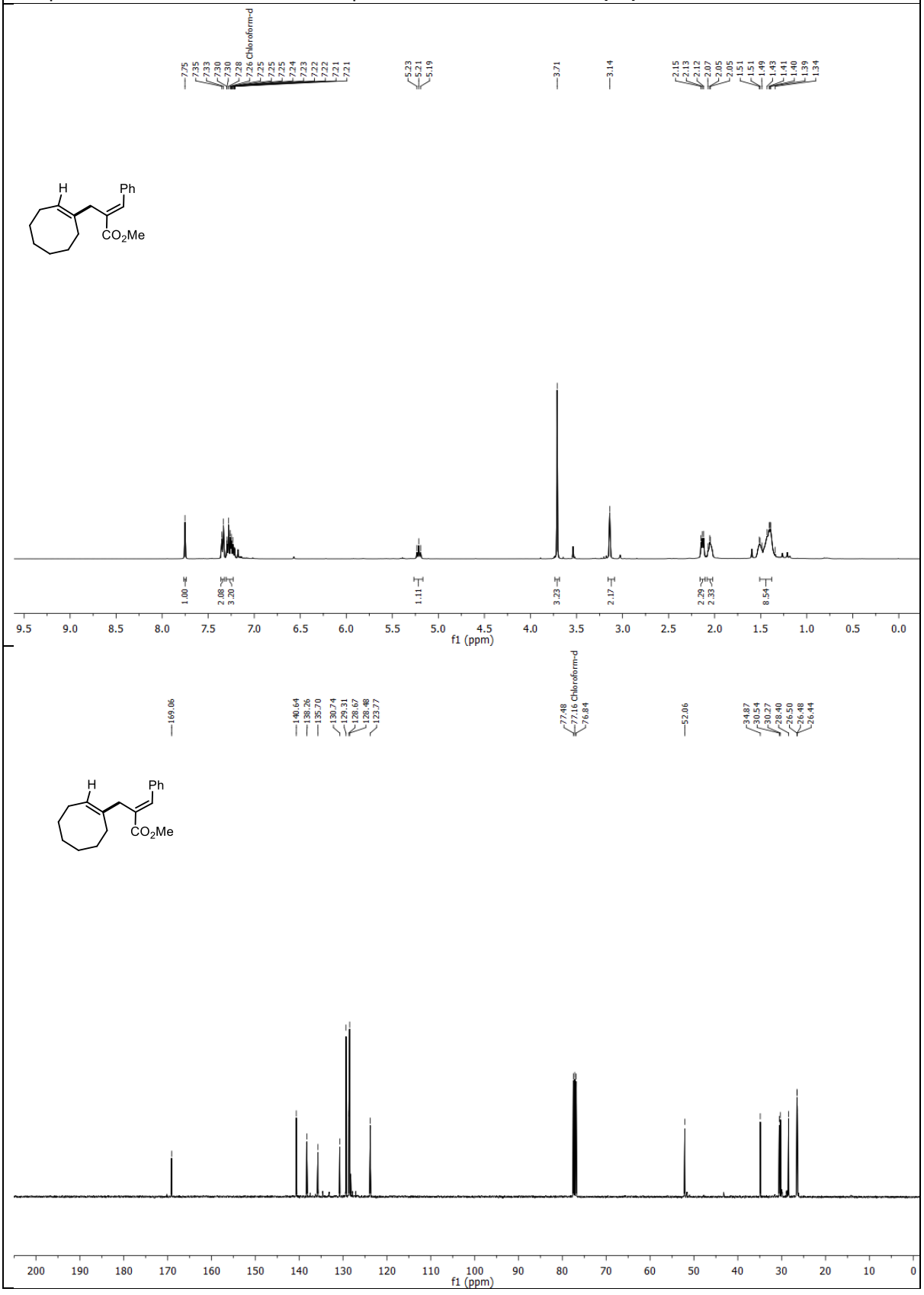


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ **(22)**

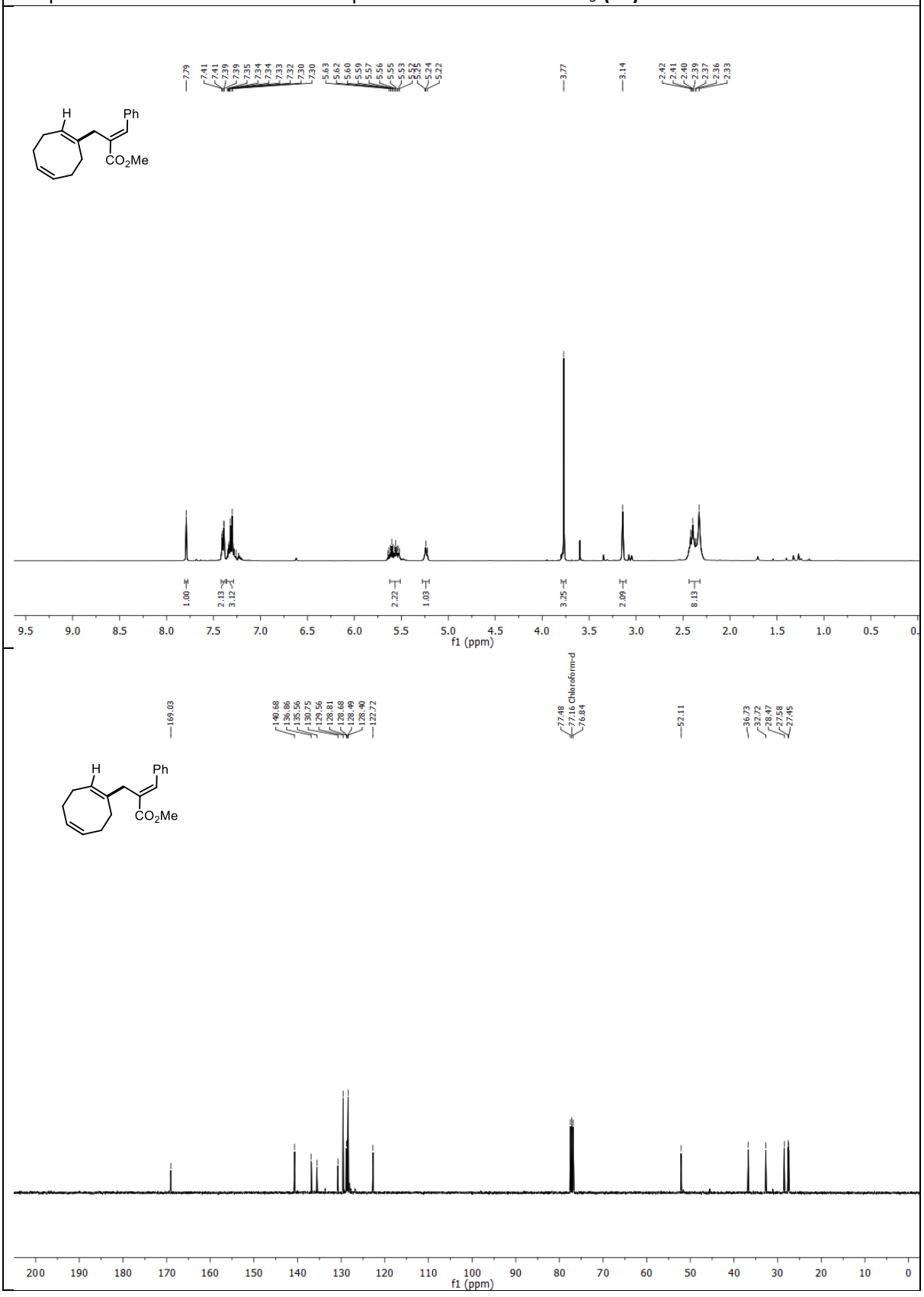




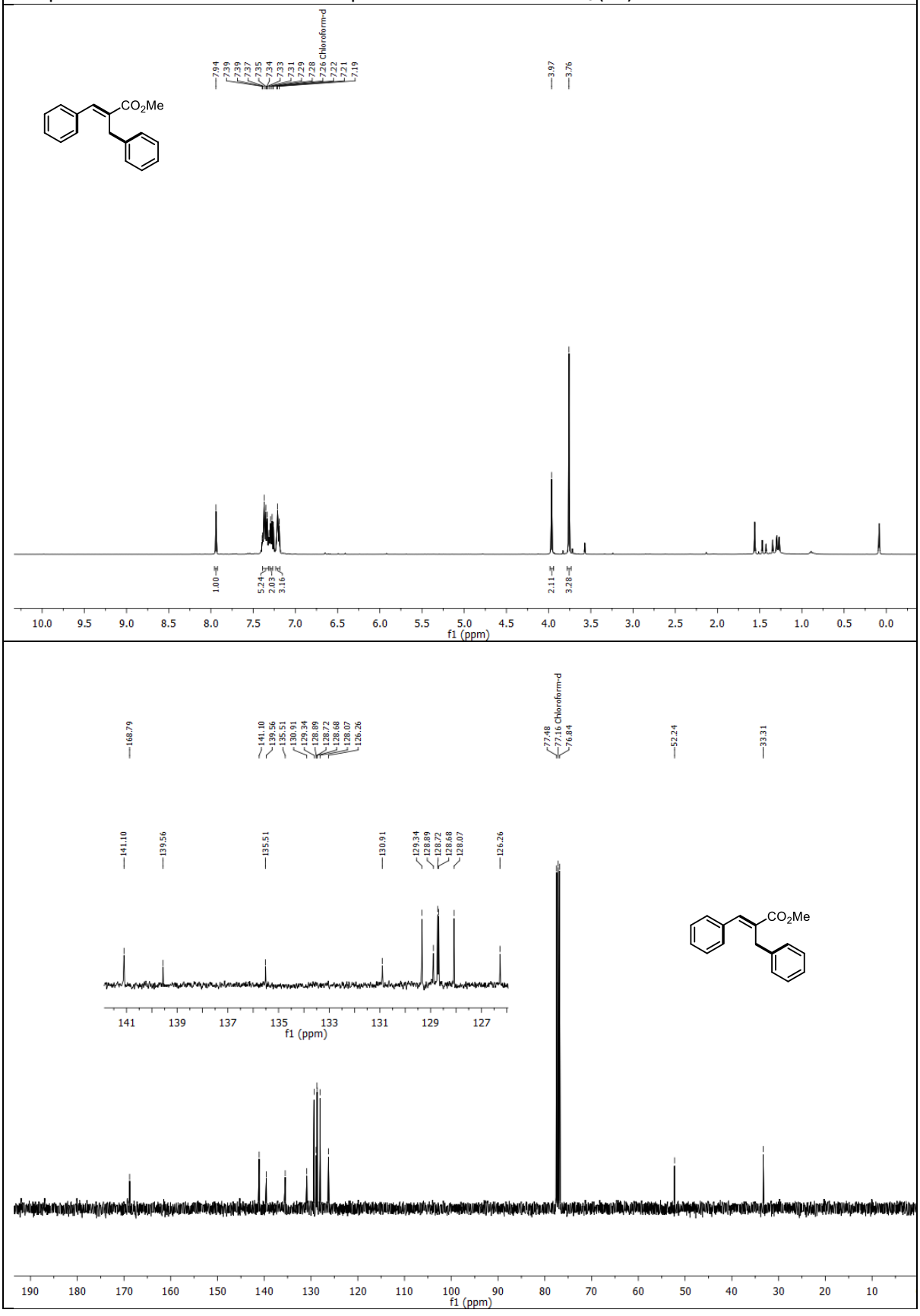
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ **(23)**



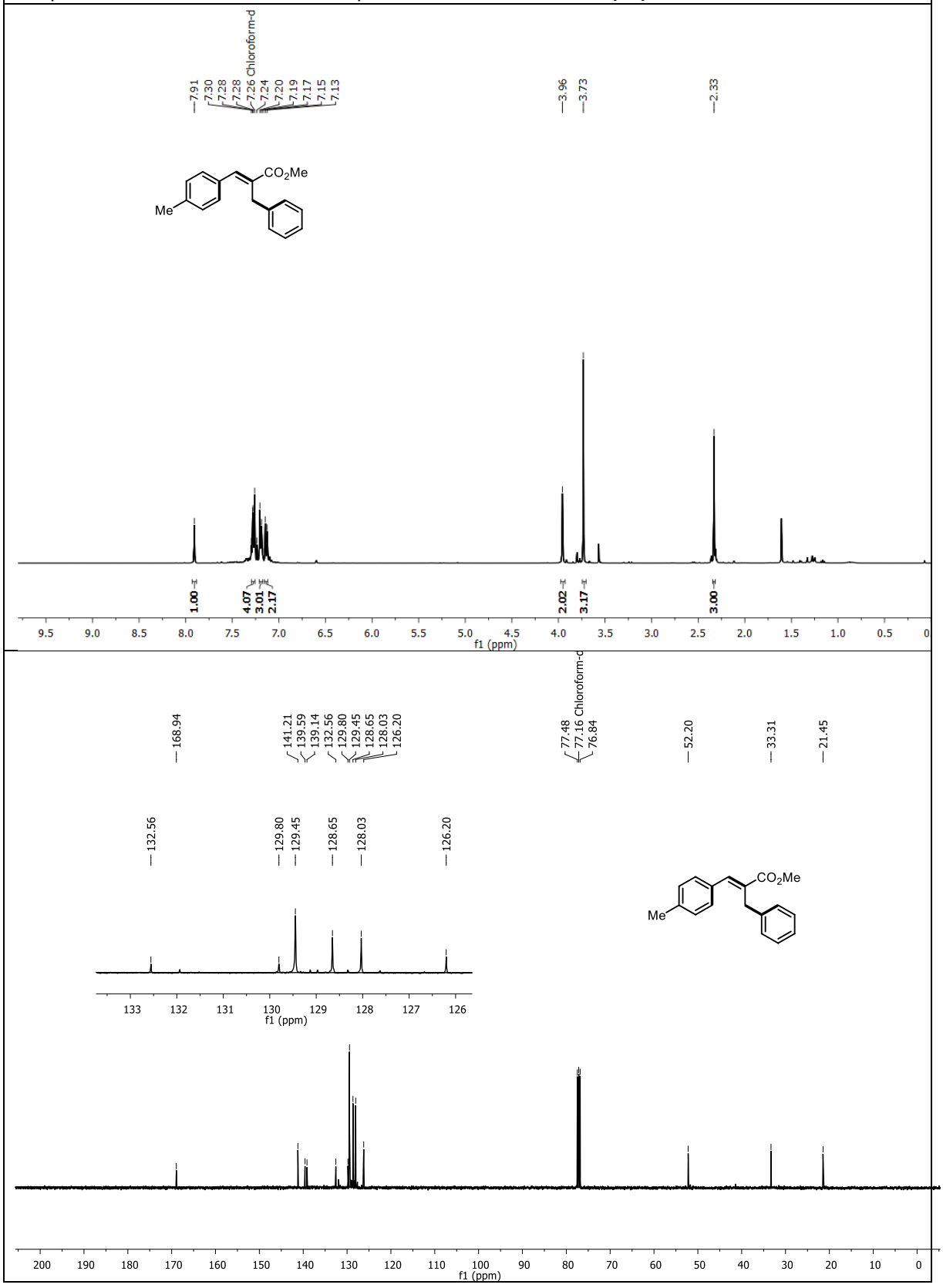
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ **(24)**



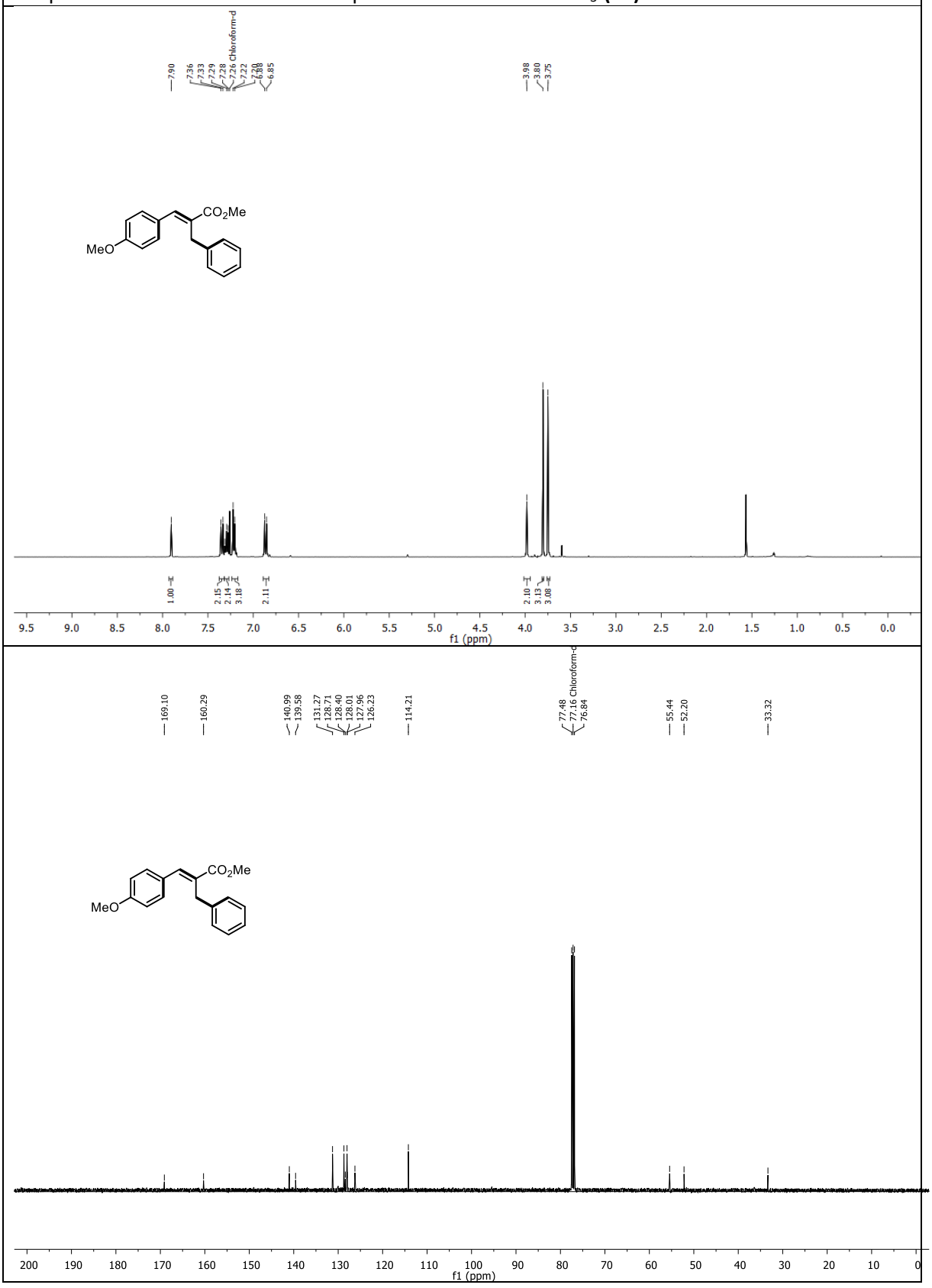
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ (**25**)



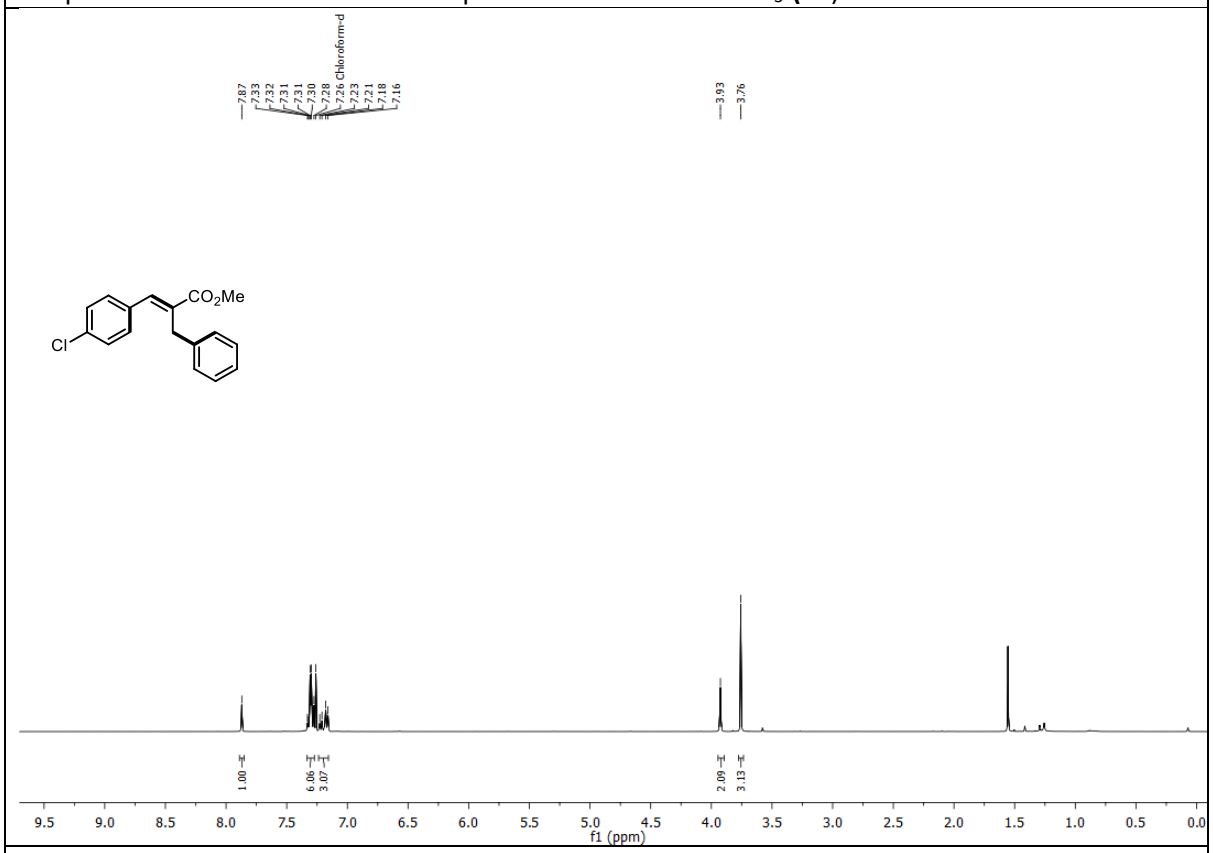
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ **(26)**

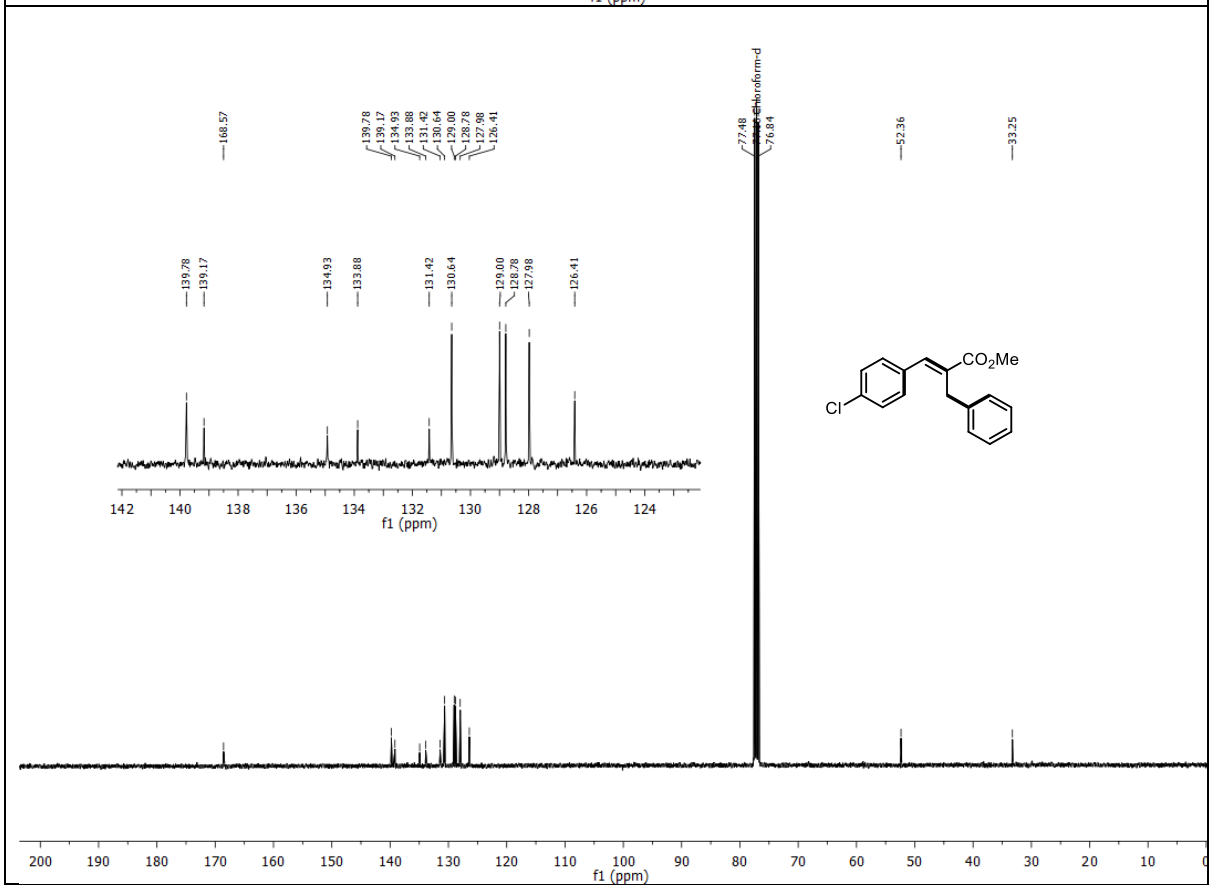


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ **(27)**

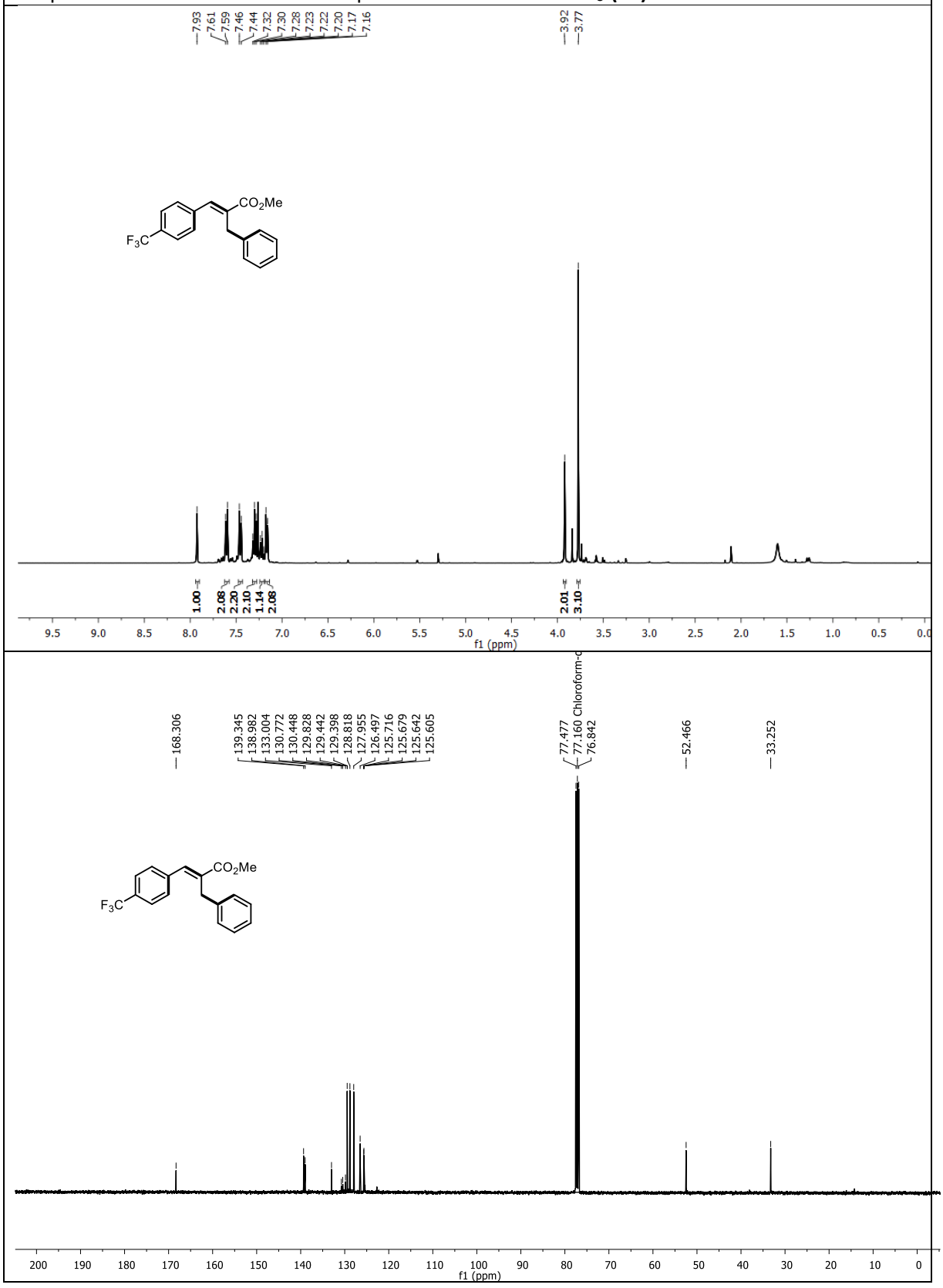


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ **(28)**

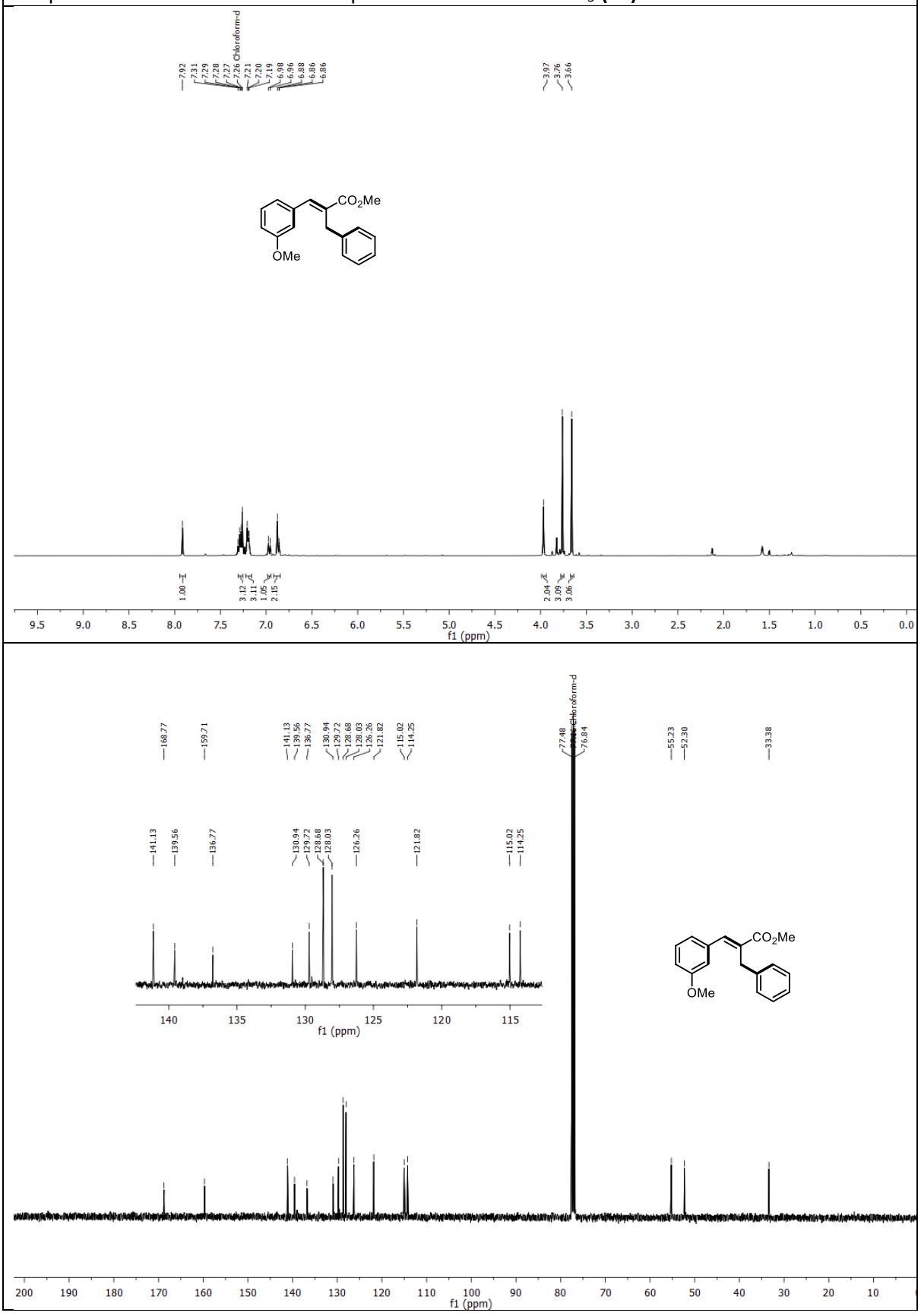




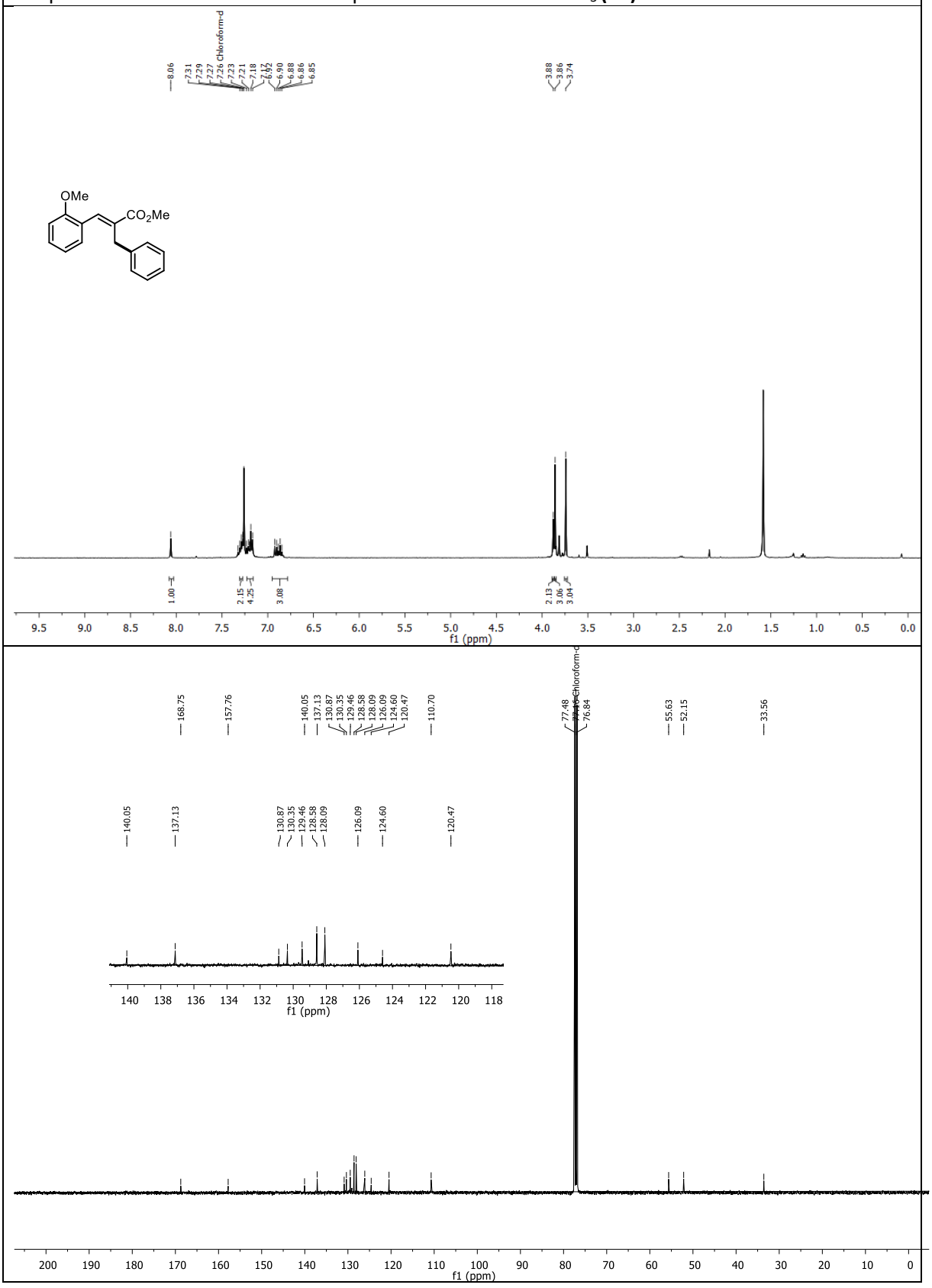
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ **(29)**



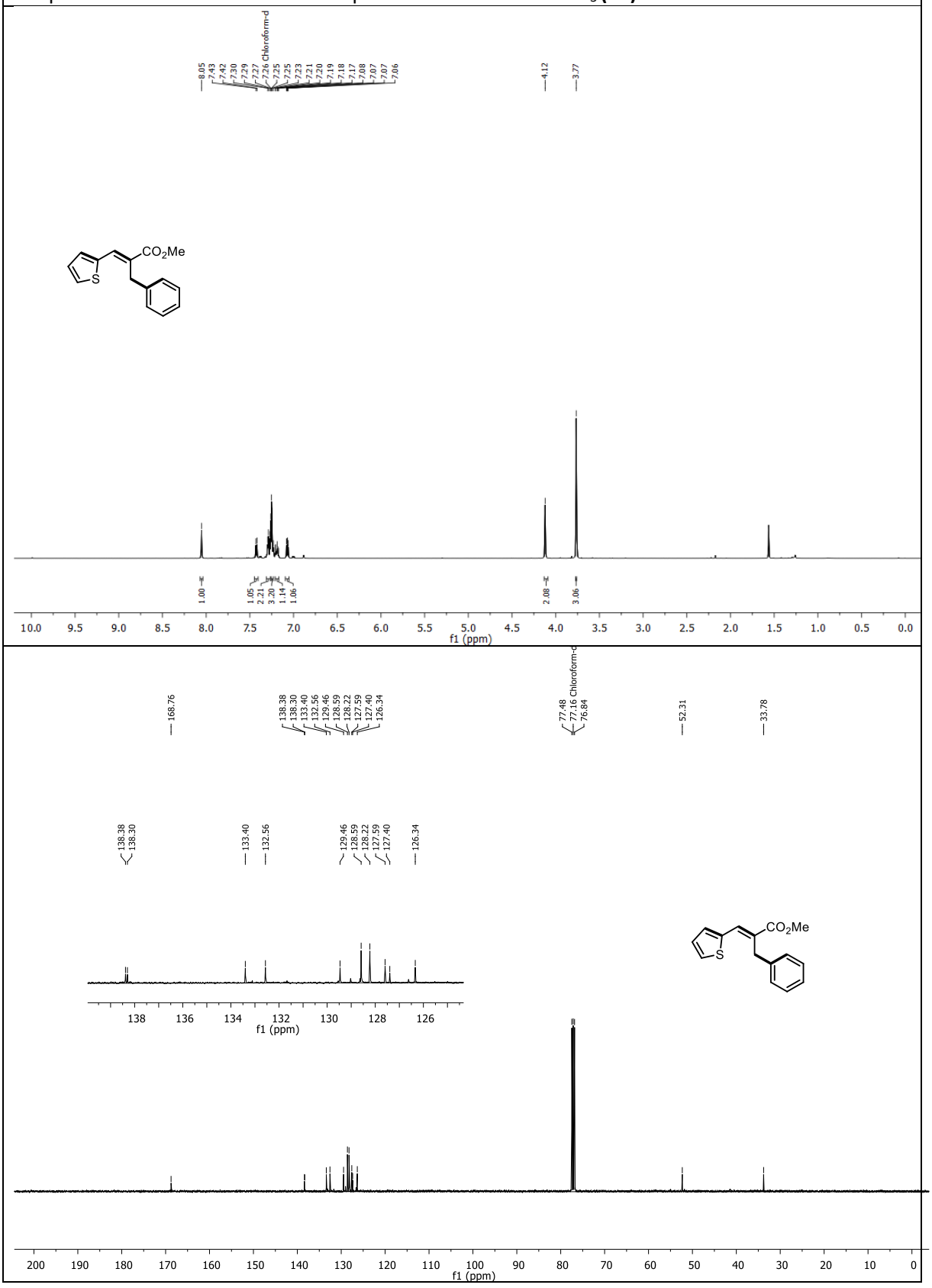
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ **(30)**



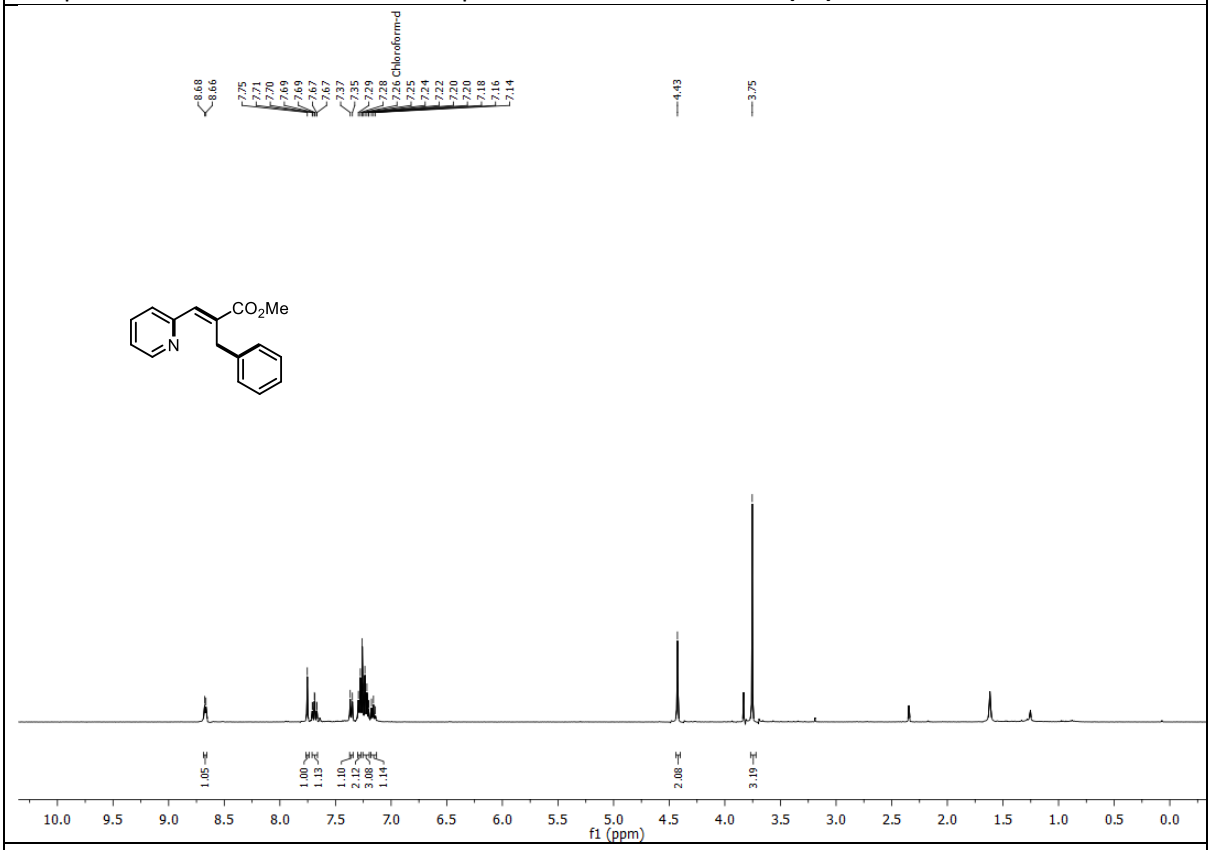
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ **(31)**

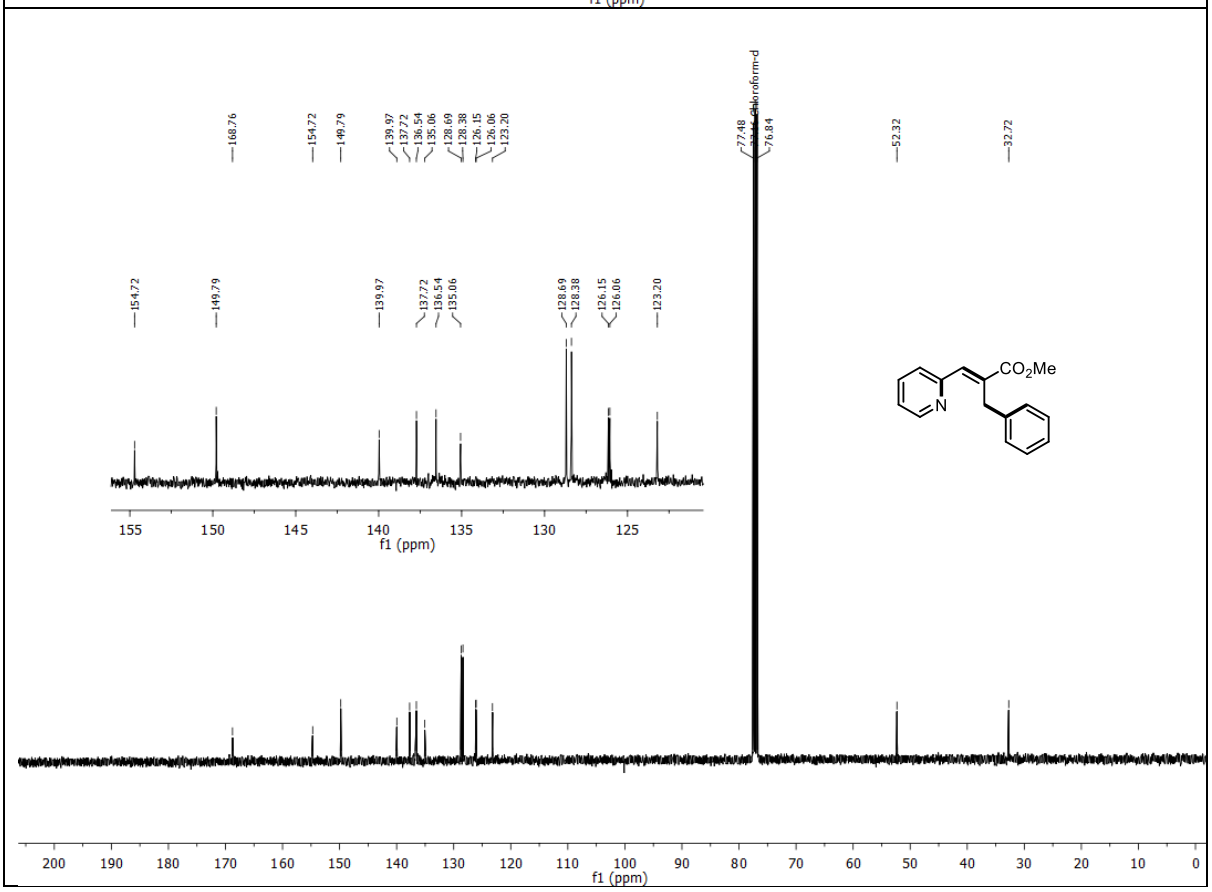


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ **(32)**

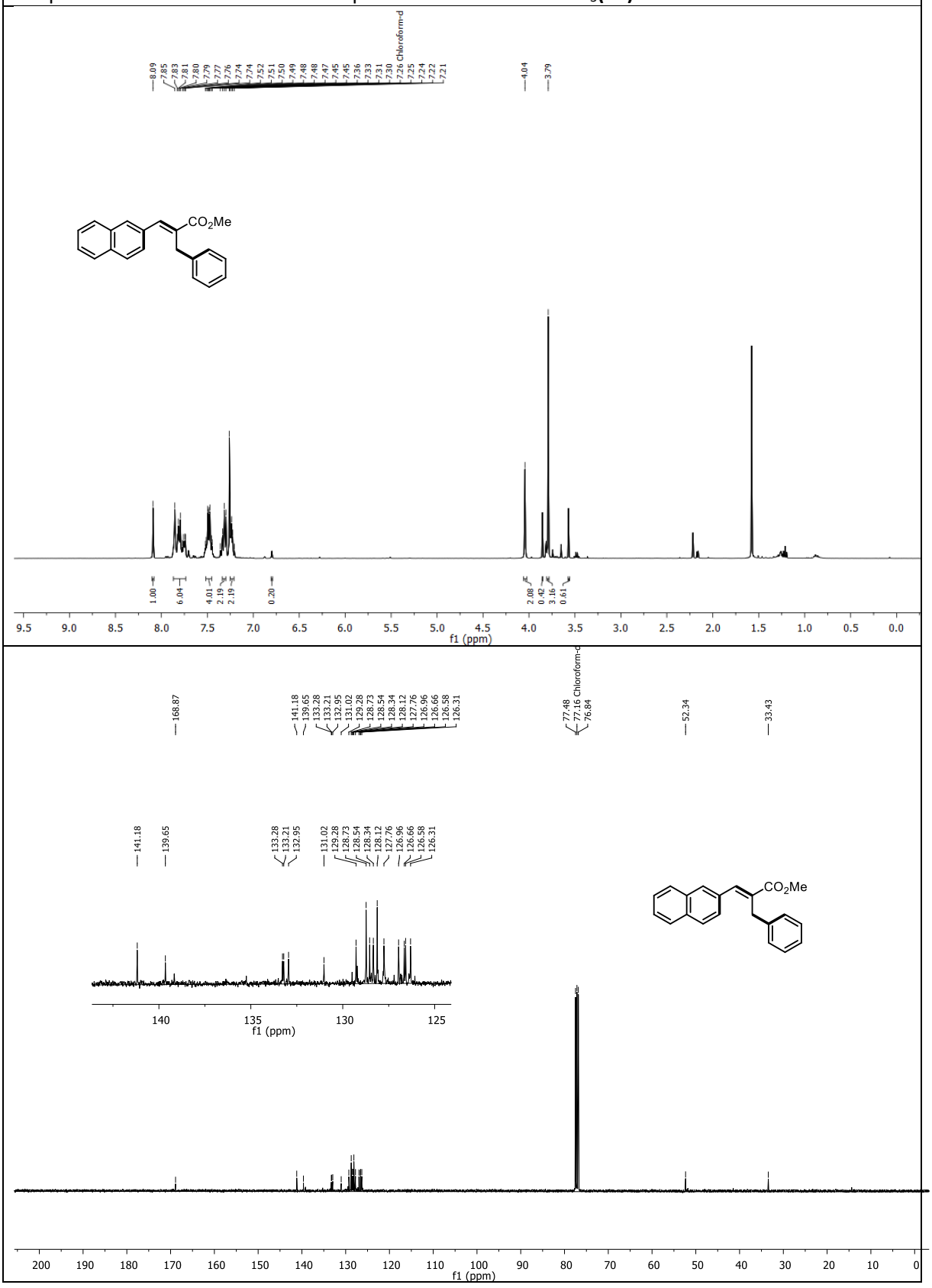


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ **(33)**

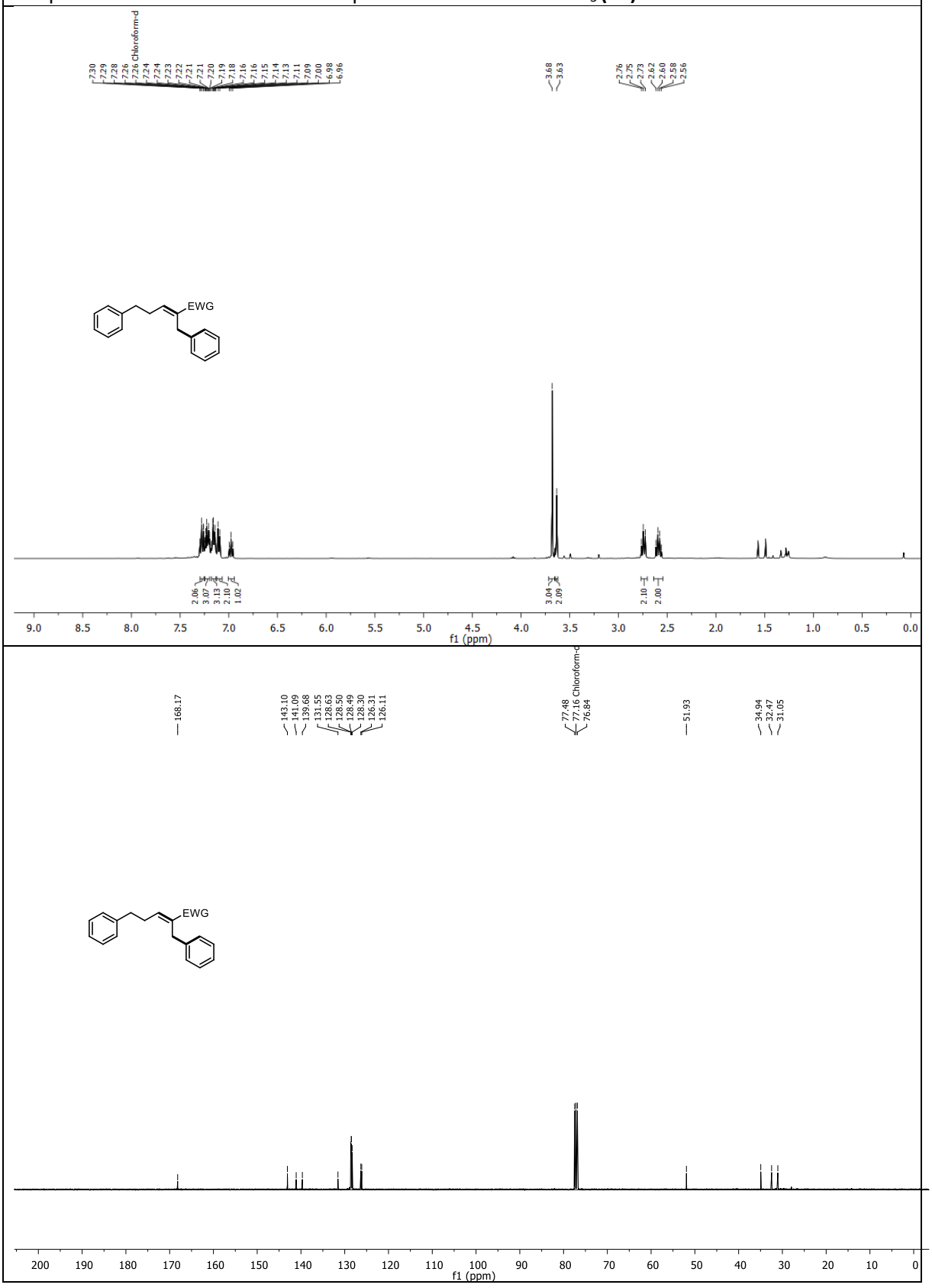




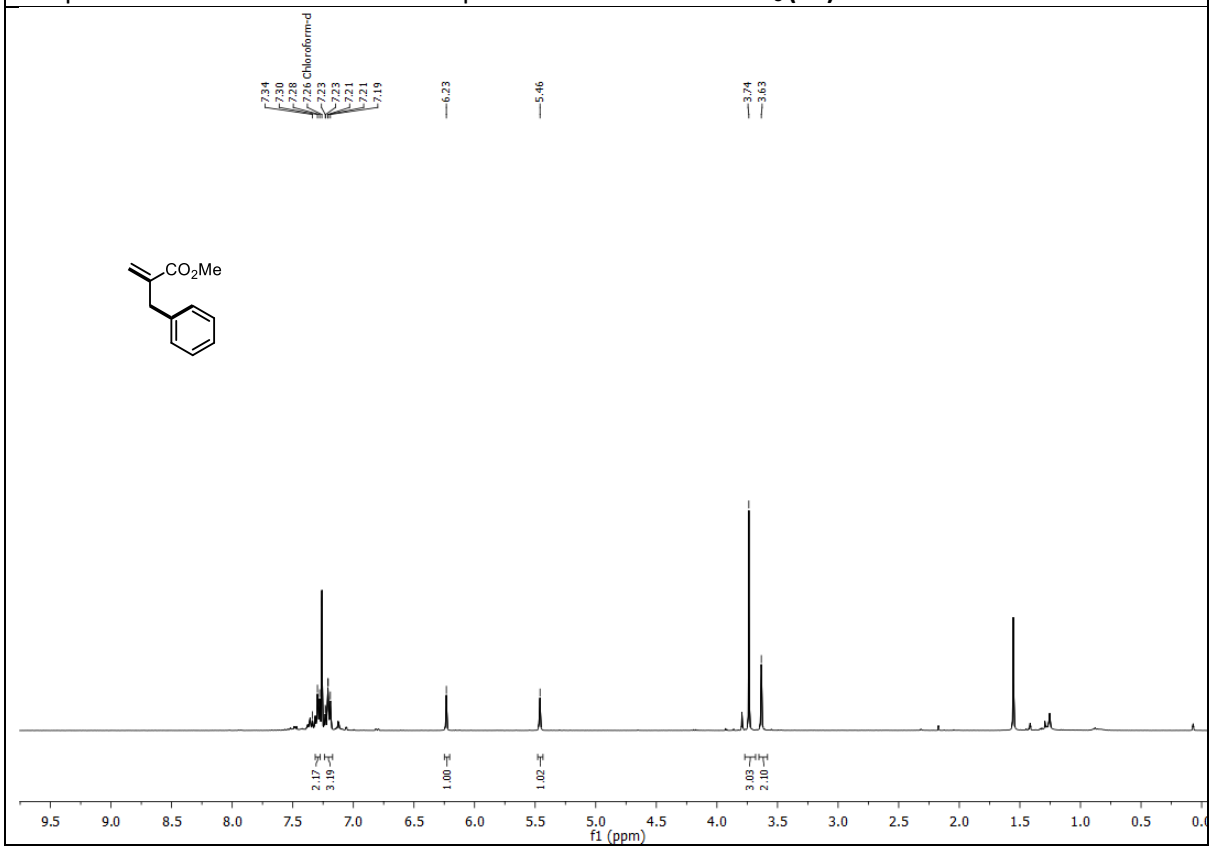
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$**(34)**



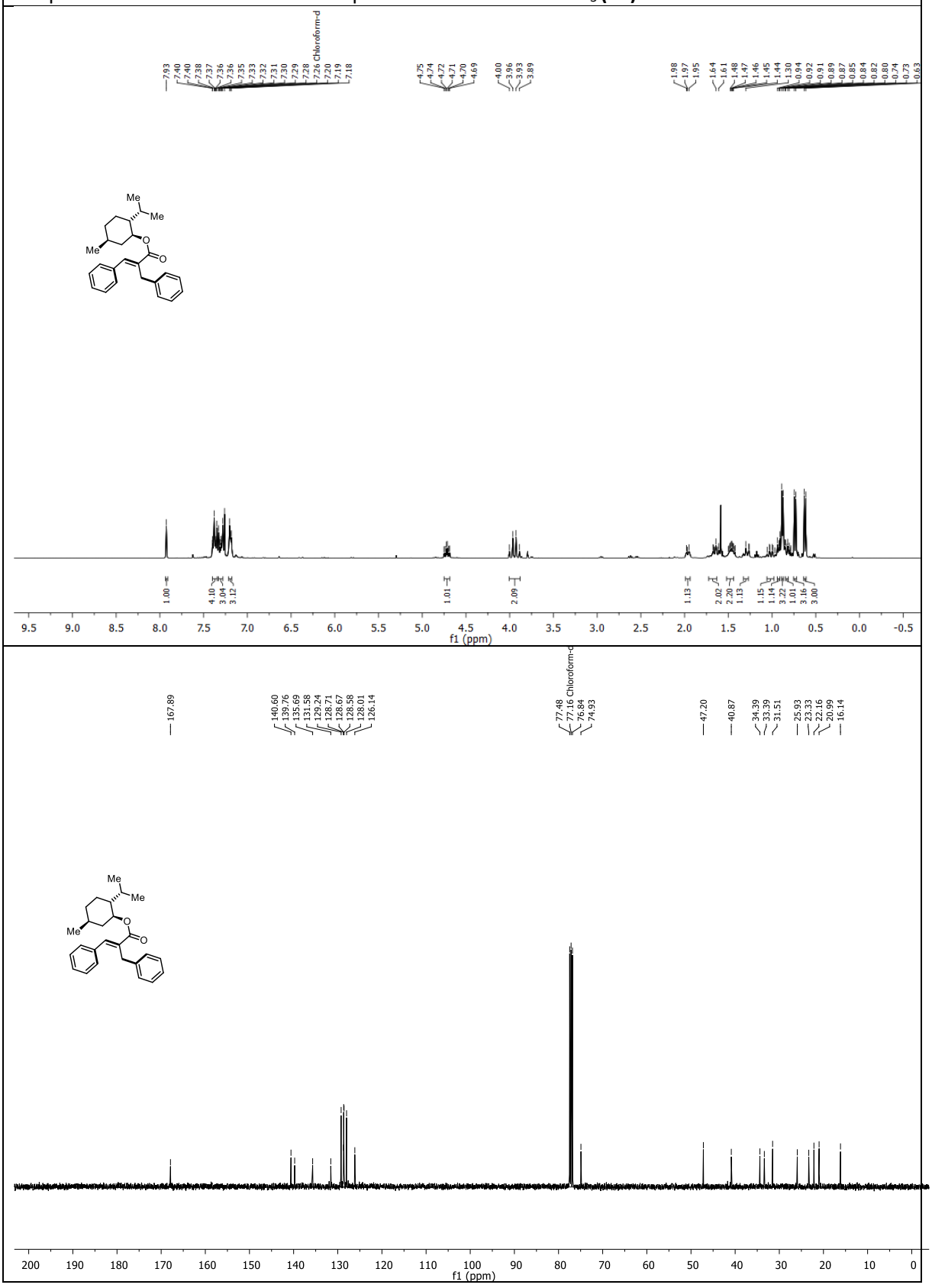
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ **(35)**



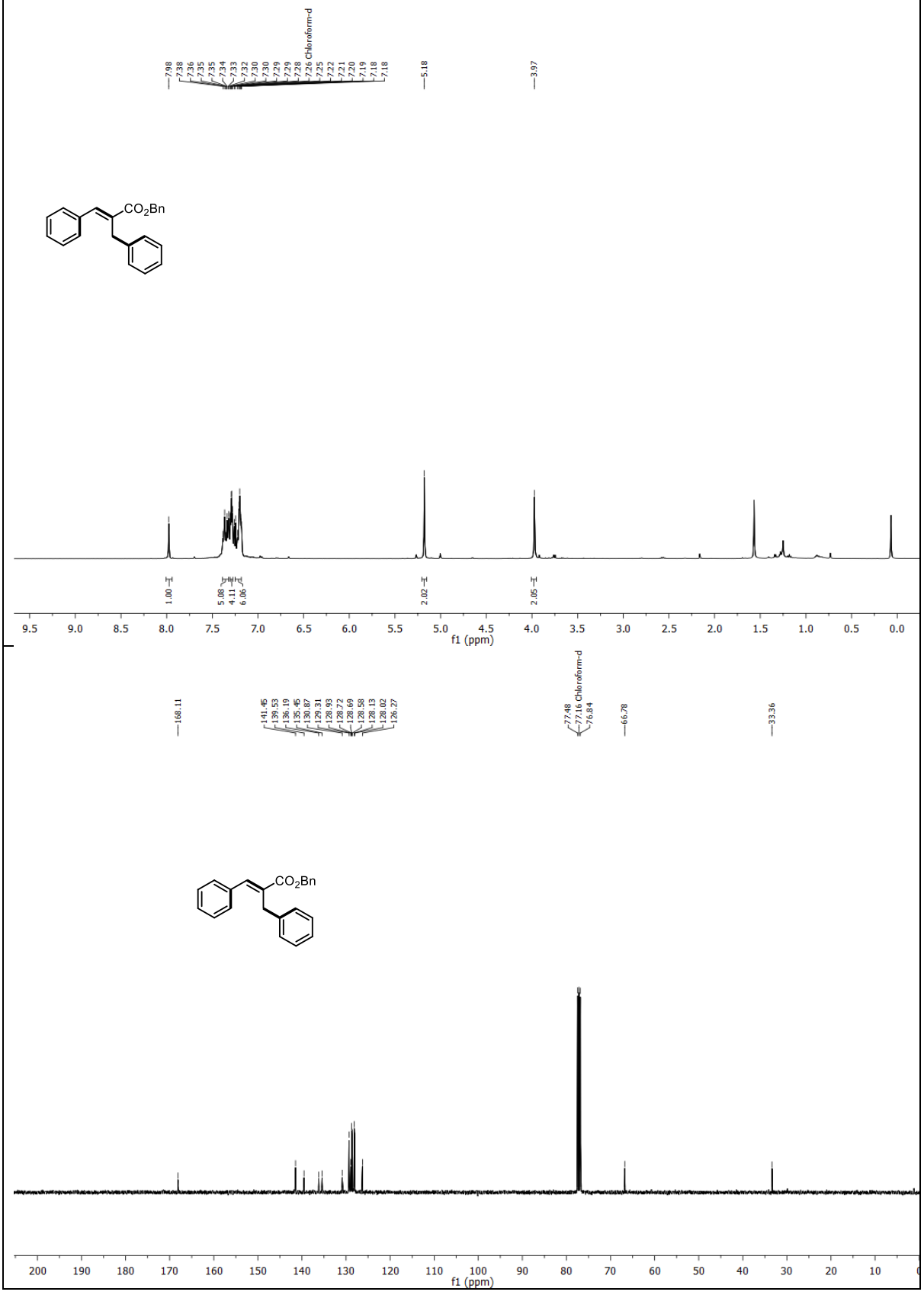
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ **(36)**



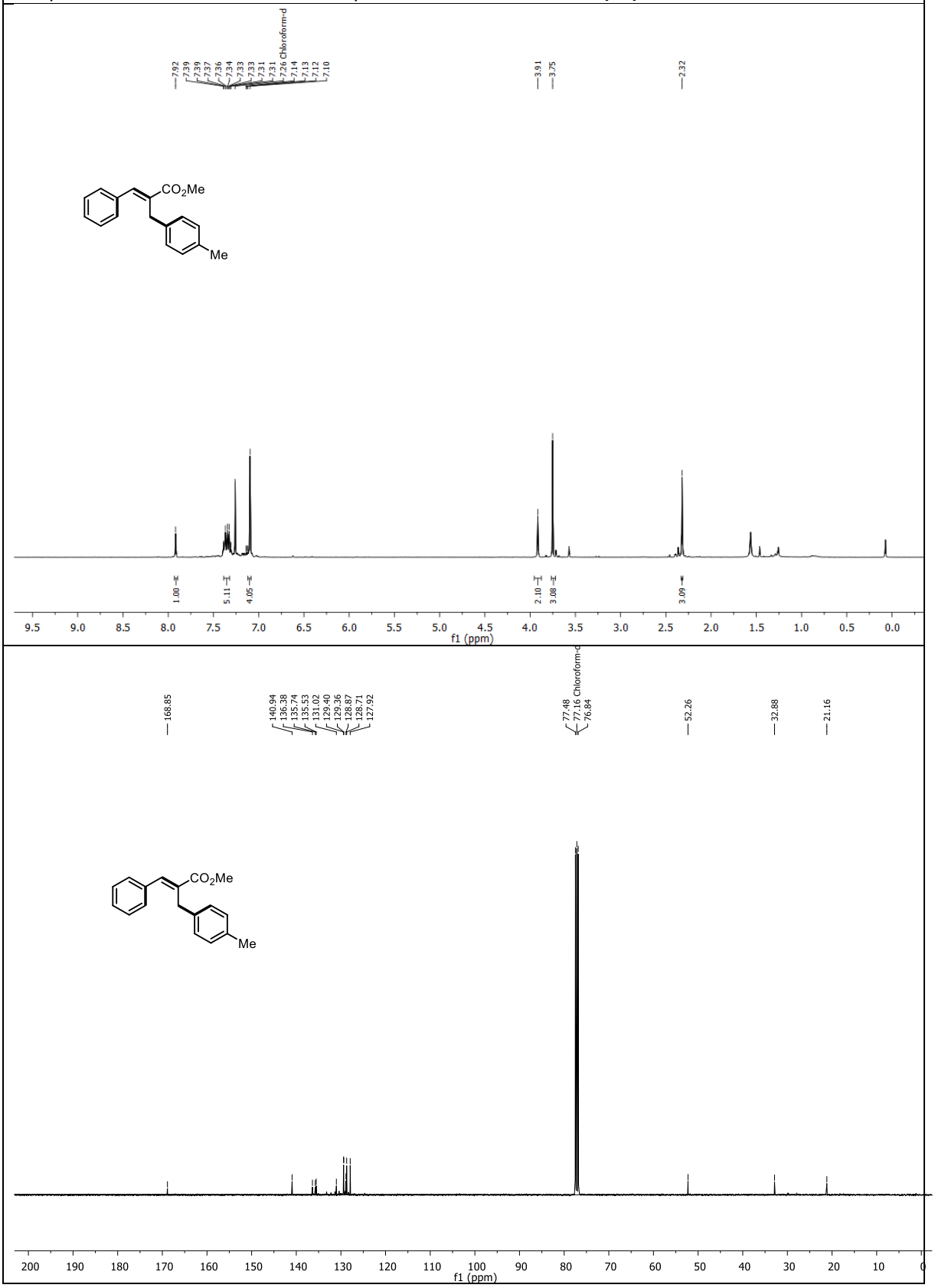
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ **(37)**



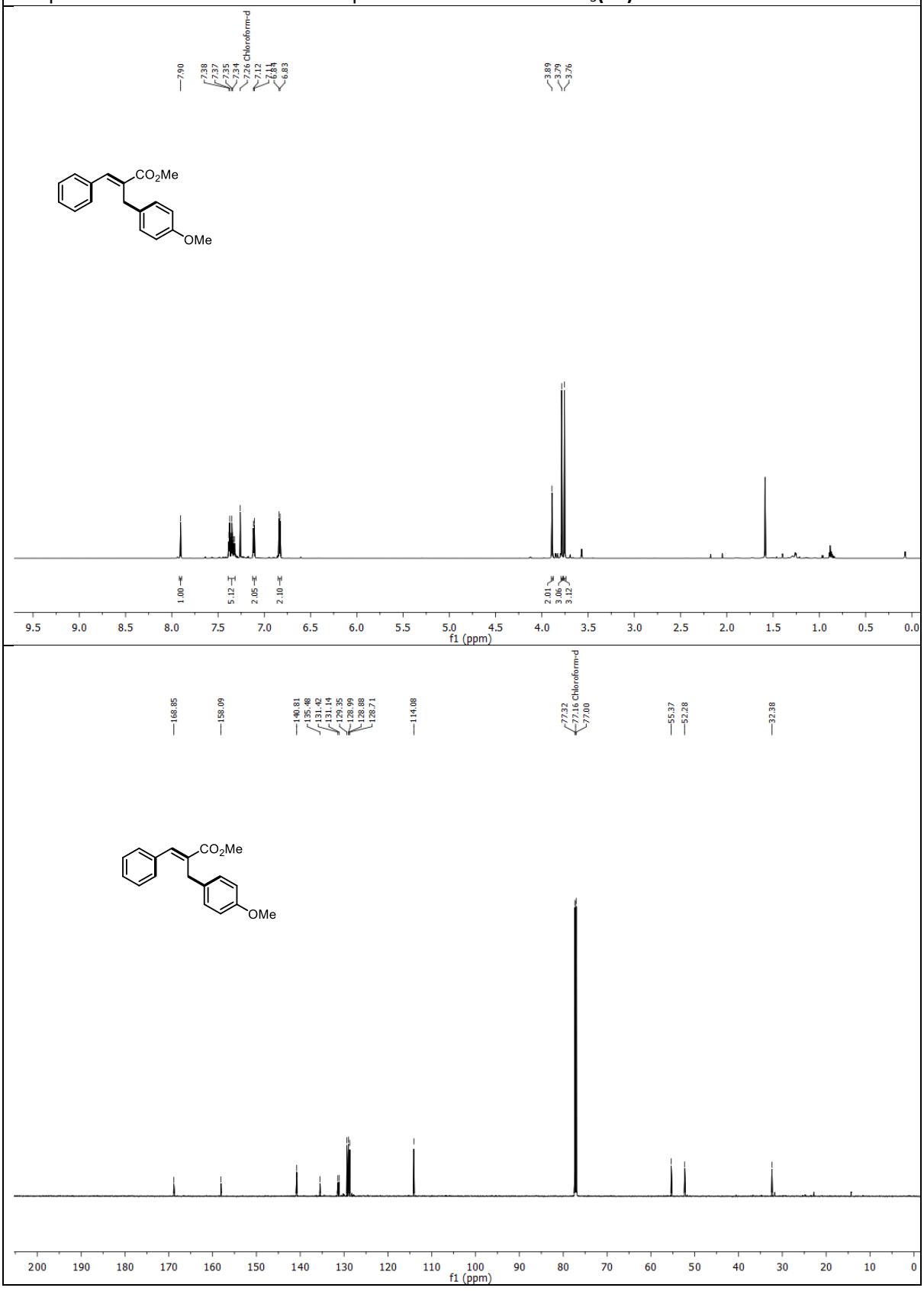
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ **(38)**



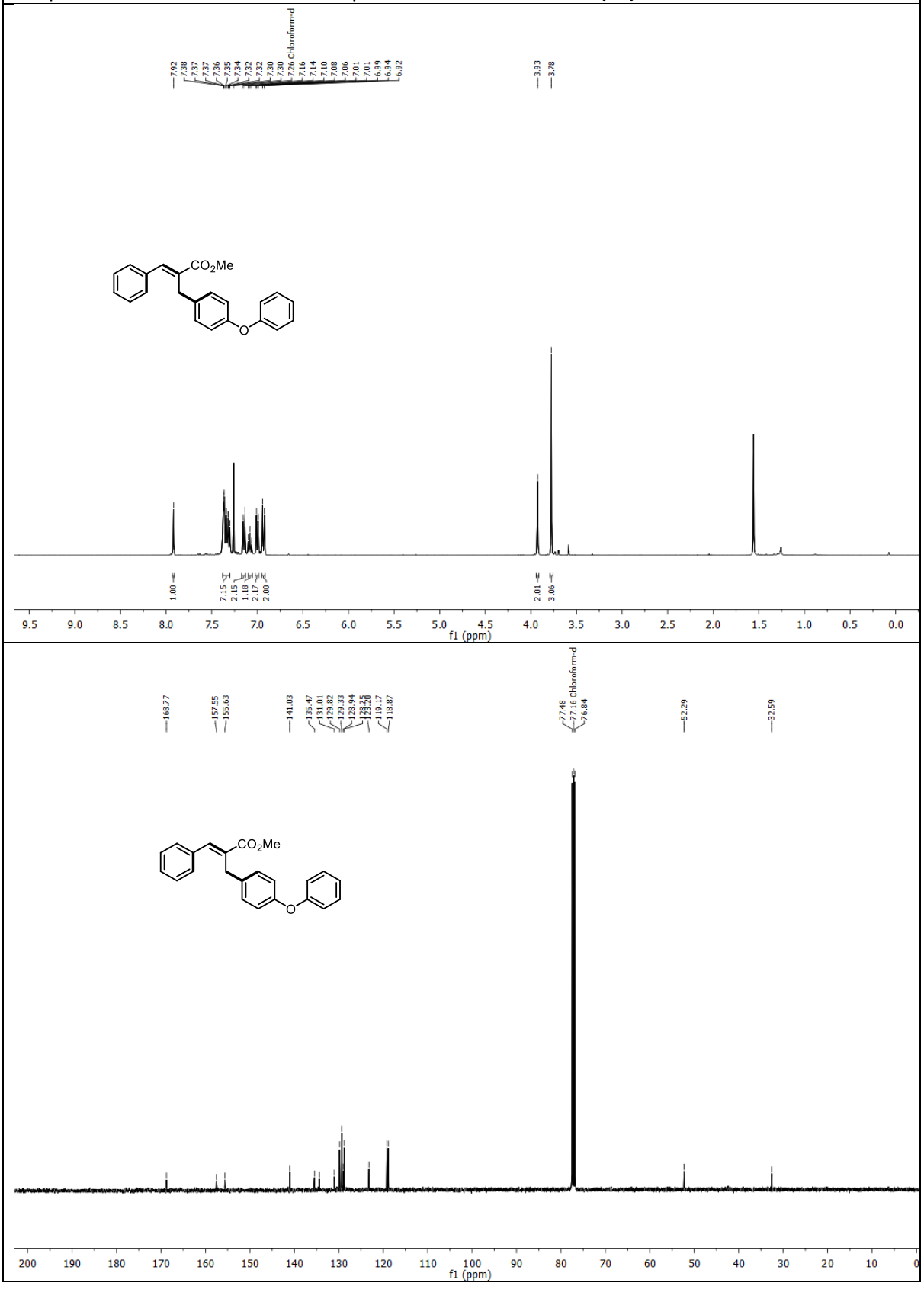
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ **(39)**



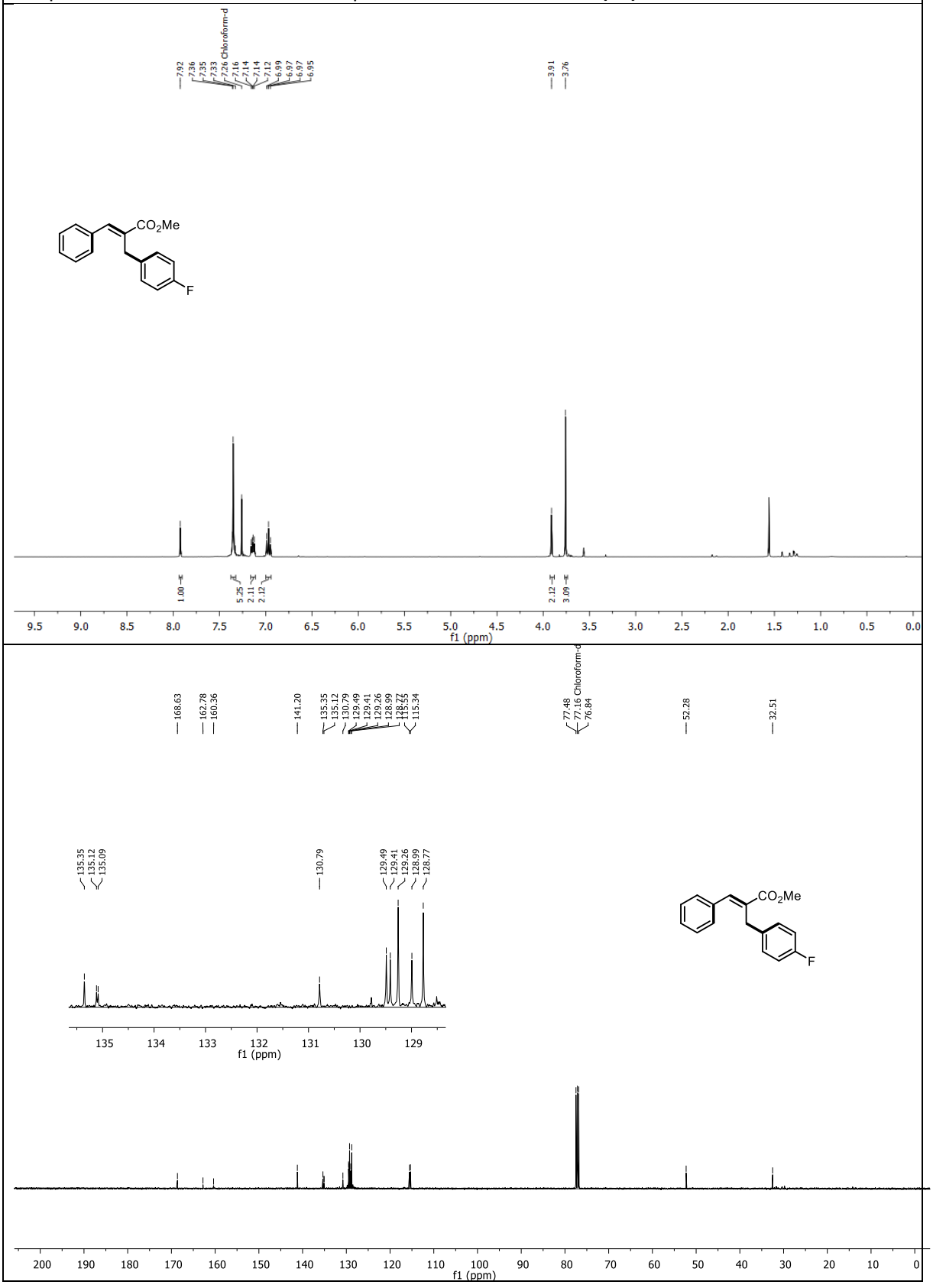
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$**(40)**



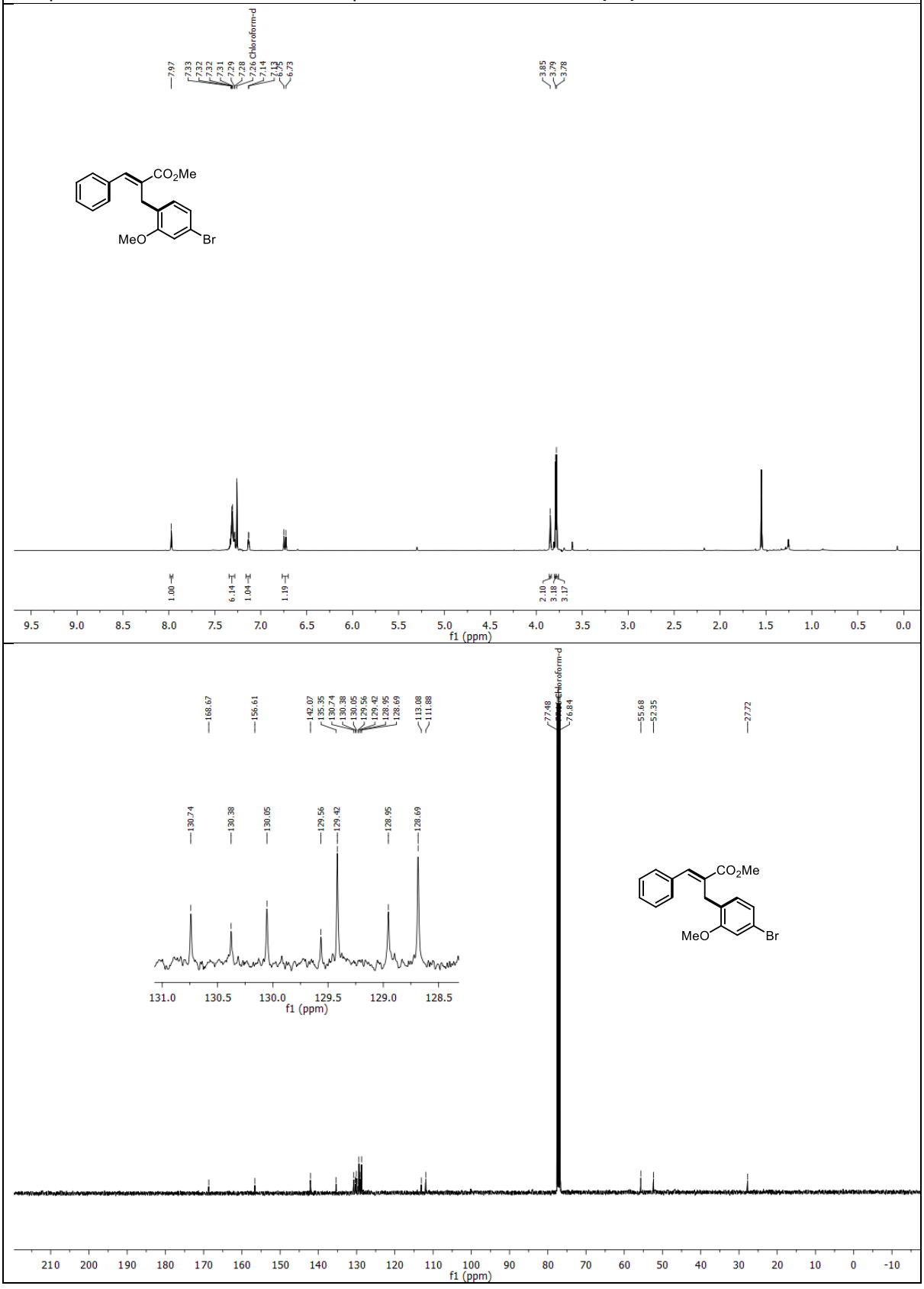
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ **(41)**



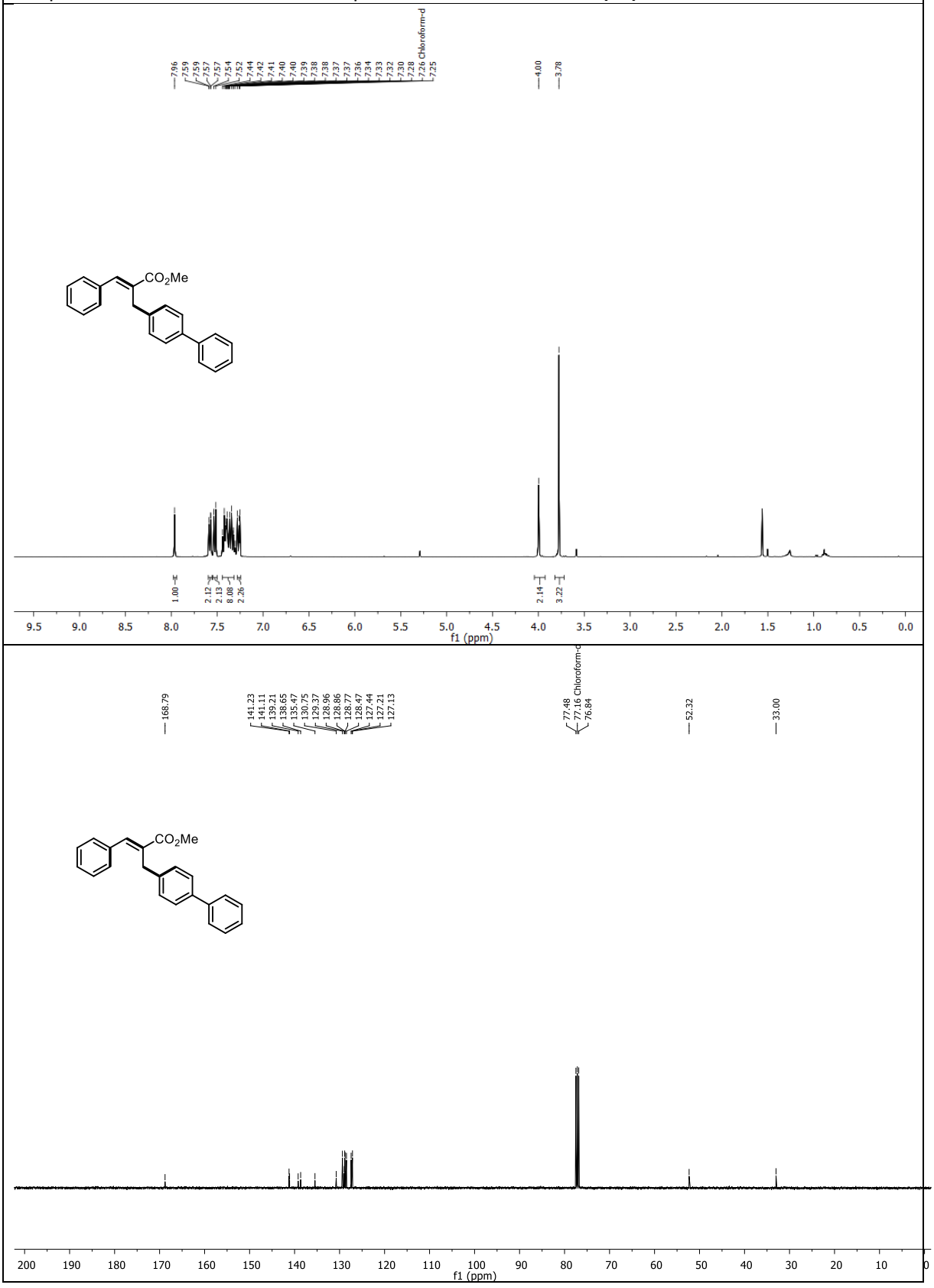
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ **(42)**



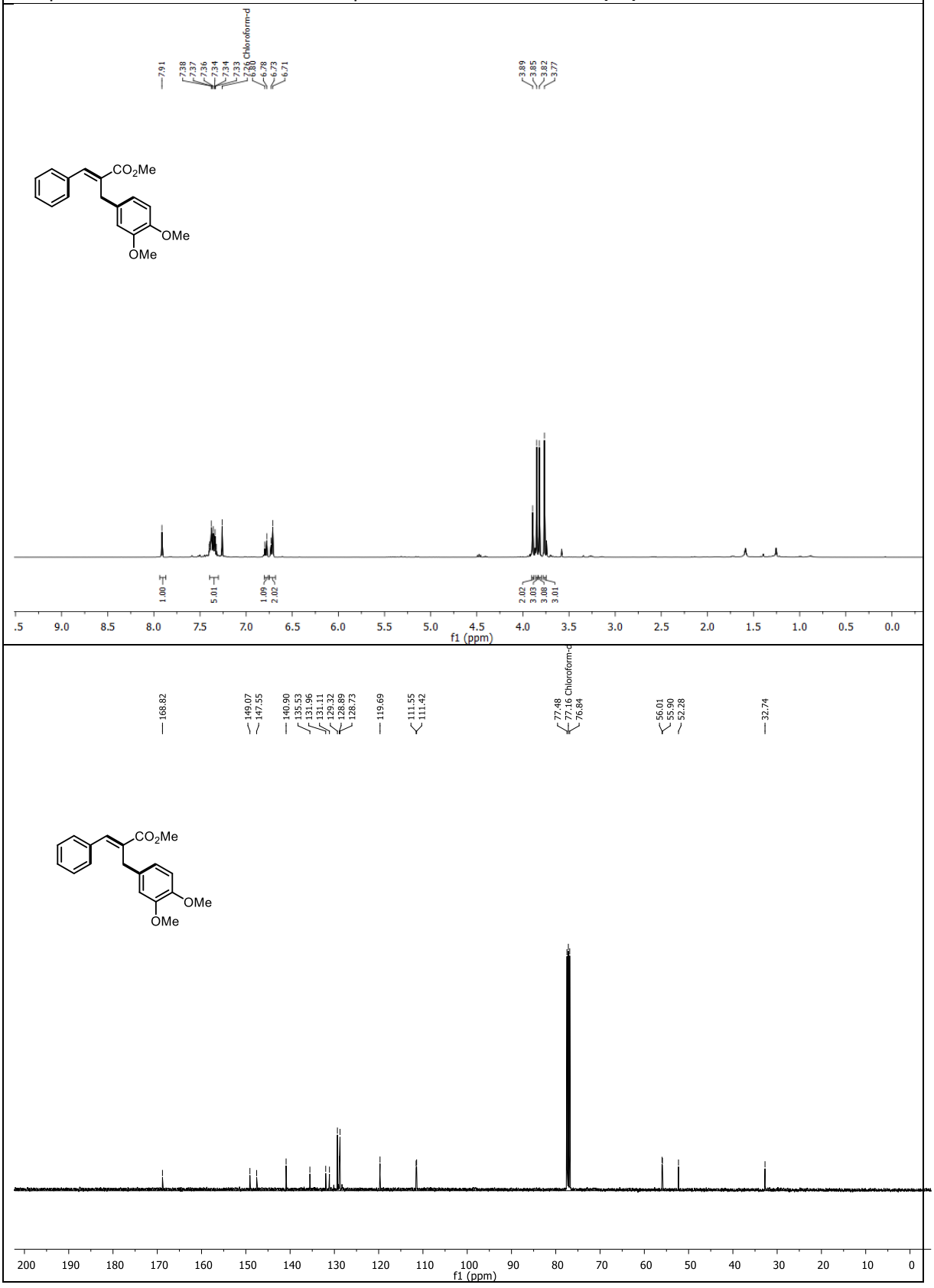
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ **(43)**



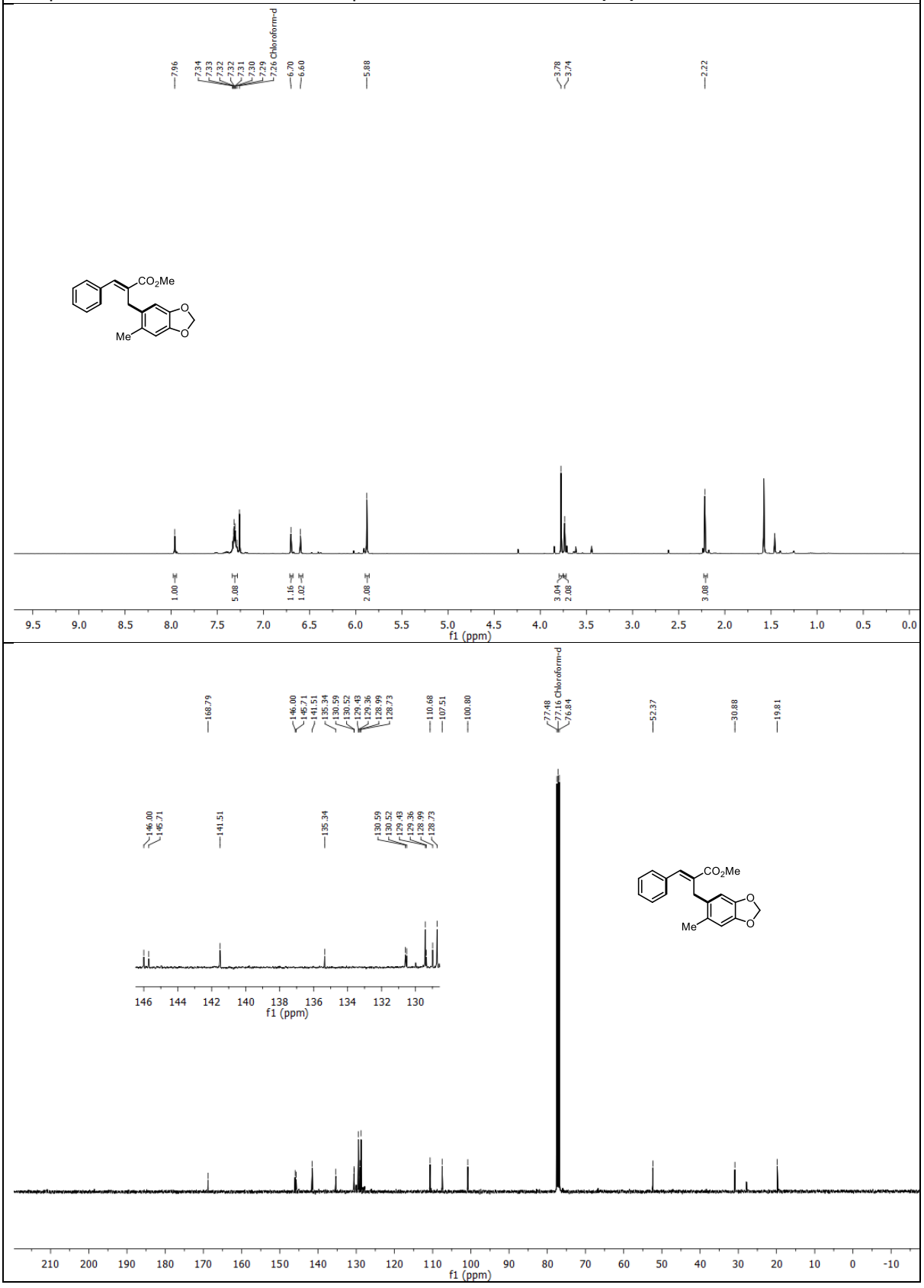
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ **(44)**



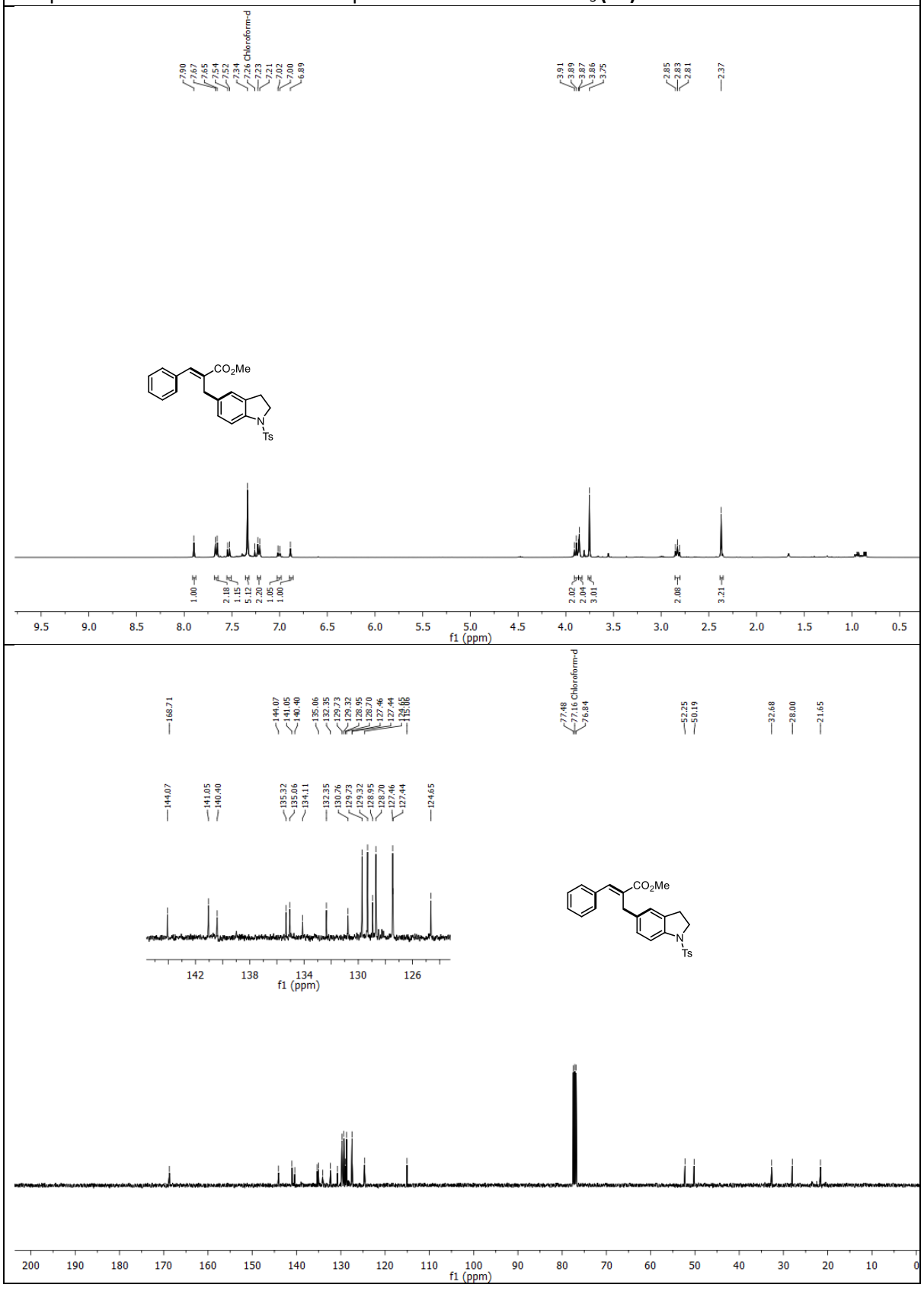
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ **(45)**



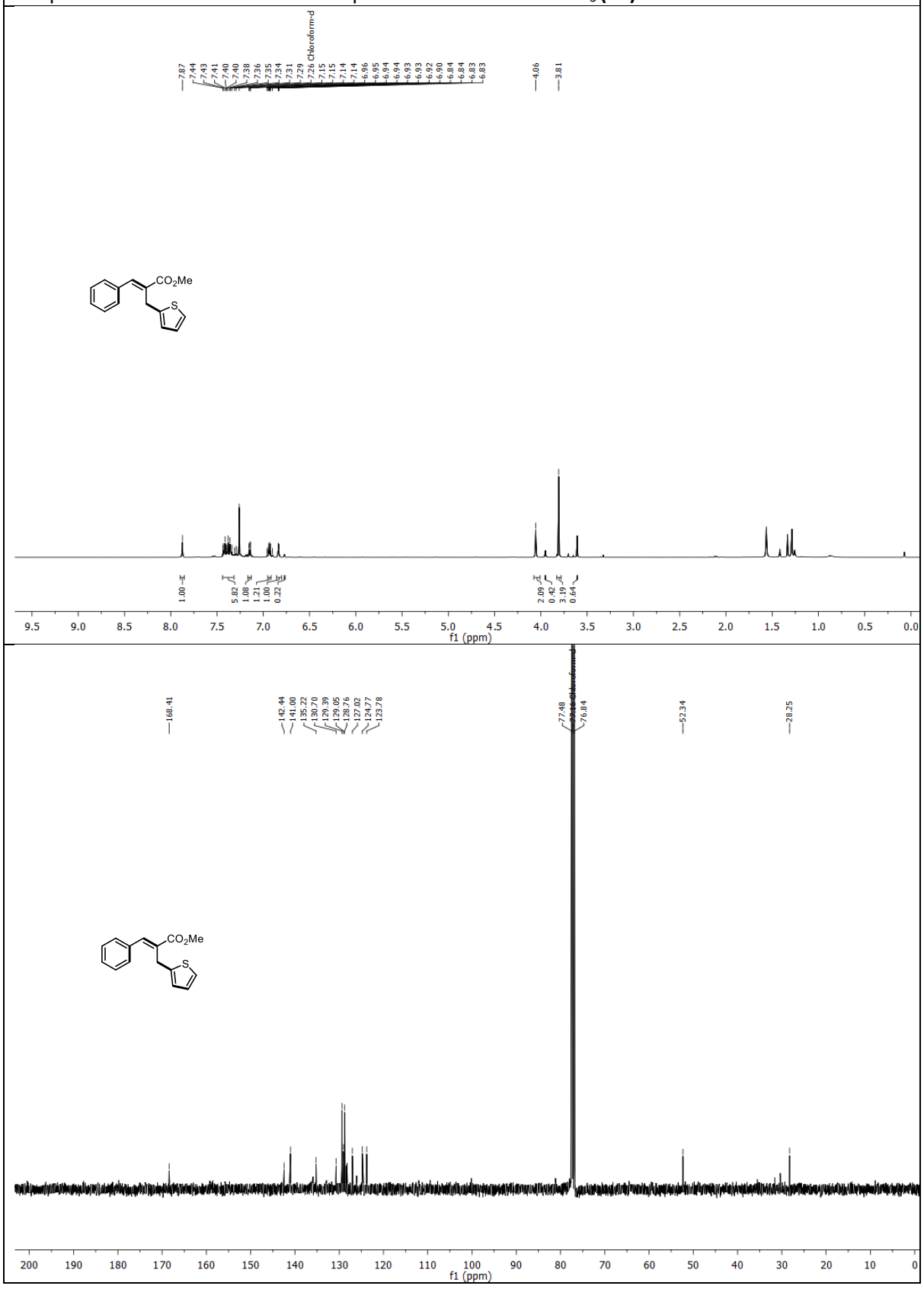
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ **(46)**



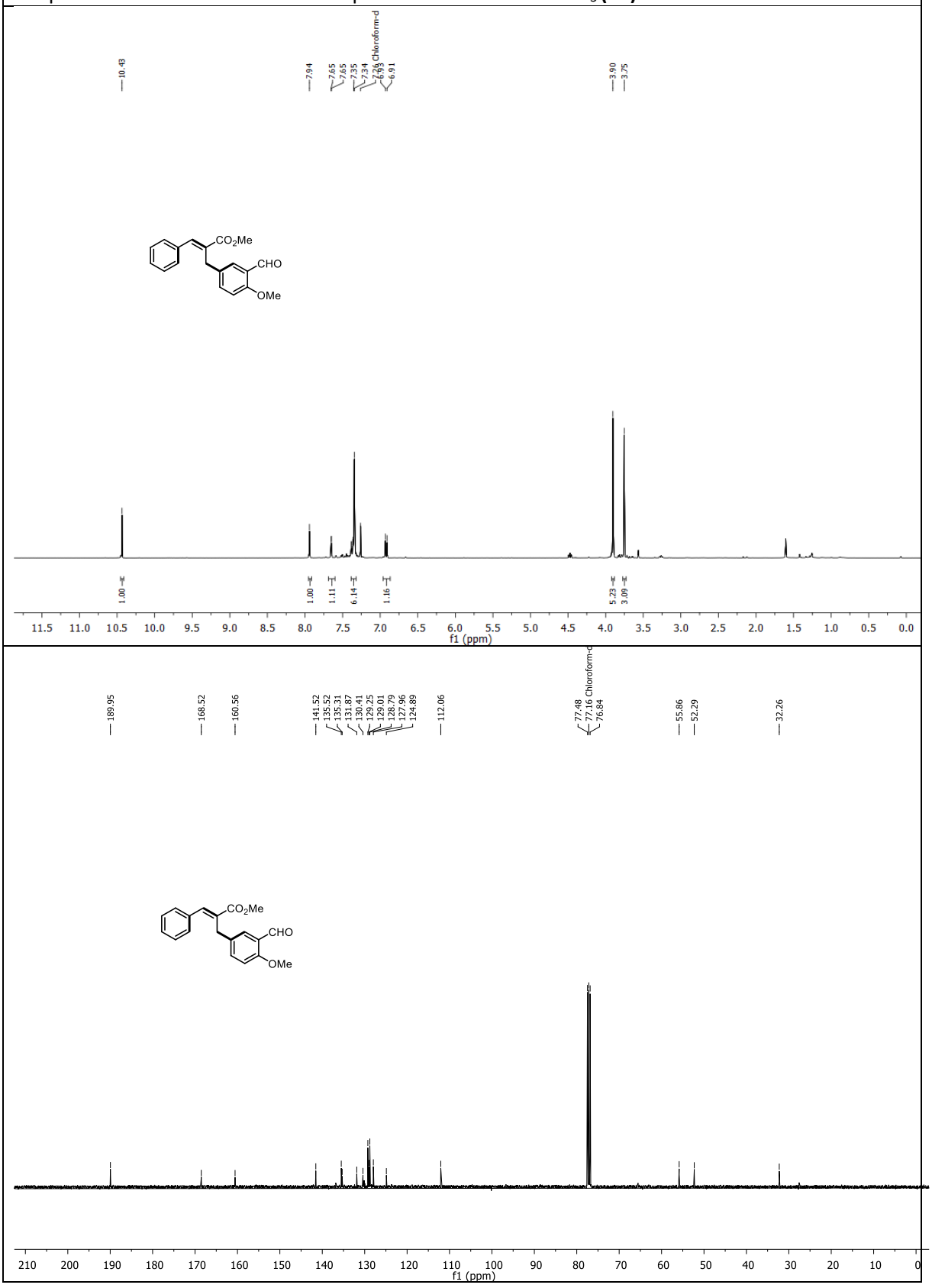
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ **(47)**



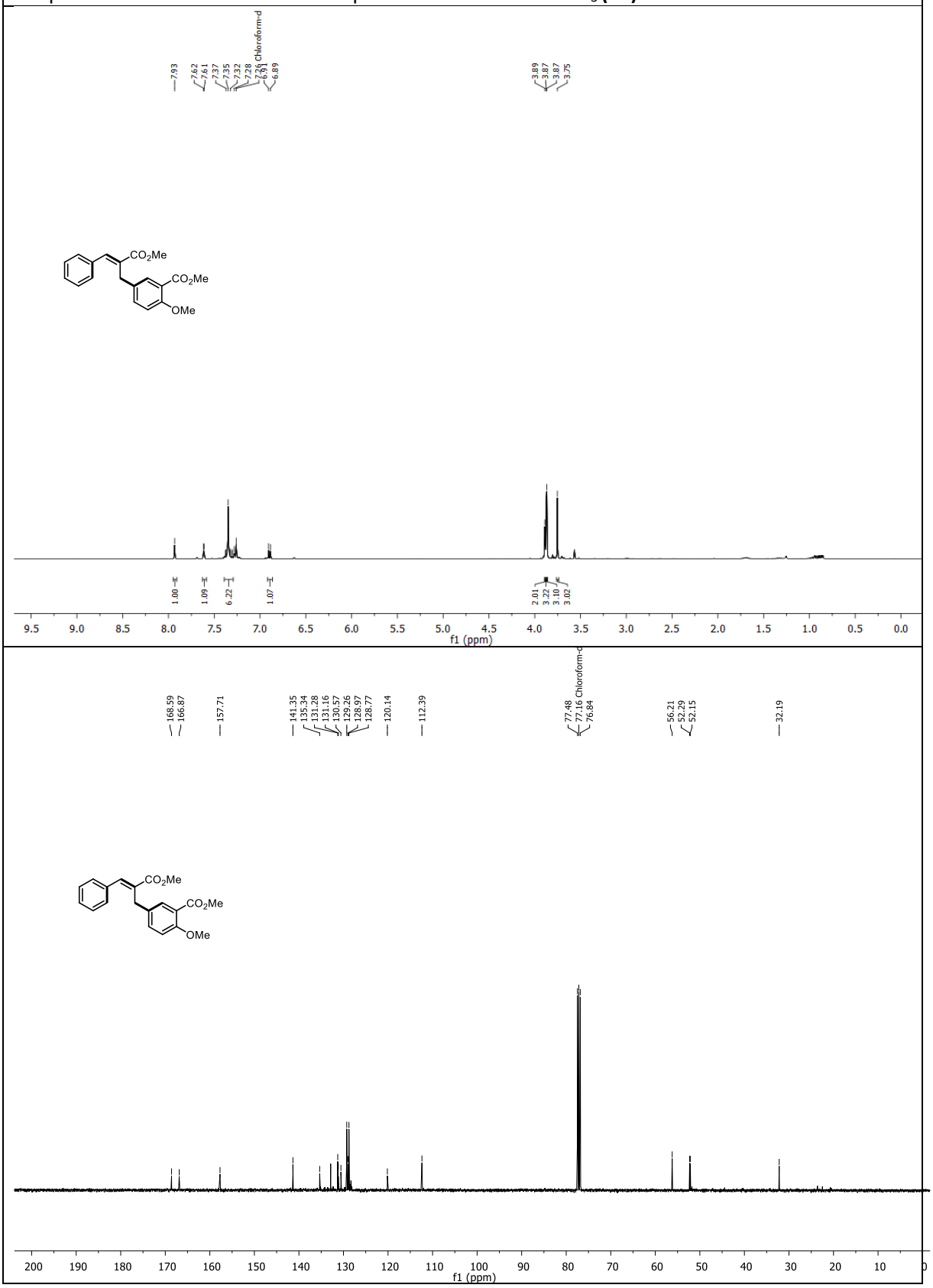
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ **(48)**



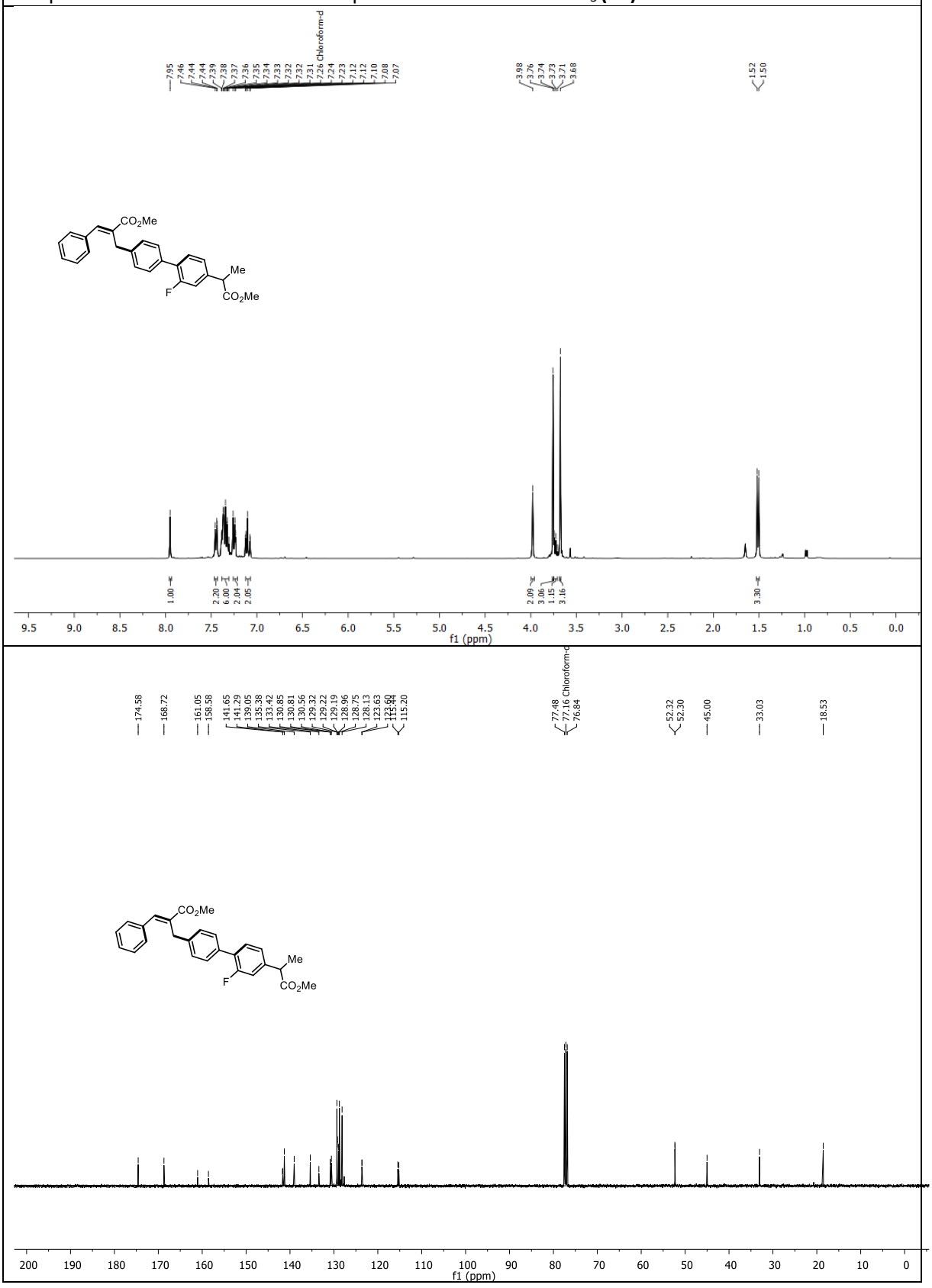
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ **(49)**



^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ **(50)**



^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ **(51)**



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