

Supporting Information

Remote and Selective C(sp²)-H Olefination for Sequential Regioselective Linkage of Phenanthrenes

Yi Wei,^{†,||} Abing Duan,^{‡,||} Pan-Ting Tang,[†] Jia-Wei Li,[†] Rou-Ming Peng,[†] Zheng-Xin Zhou,[†] Xiao-Peng Luo,[†] Mohamedally Kurmoo,[§] Yue-Jin Liu,^{*,†} Ming-Hua Zeng^{*,†,#}

[†]Hubei Collaborative Innovation Center for Advanced Chemical Materials, Ministry of Education Key Laboratory for the Synthesis and Application of Organic Functional Molecules and College of Chemistry and Chemical Engineering, Hubei University, Wuhan, 430062, China.

[‡]College of Environmental Science and Engineering, Hunan University, Changsha, Hunan 410082, China.

[#]Department Key Laboratory for the Chemistry and Molecular Engineering of Medicinal Resources, School of Chemistry and Pharmaceutical Sciences, Guangxi Normal University, Guilin, 541004, China.

[§]Institut de Chimie de Strasbourg, CNRS-UMR7177, Université de Strasbourg, 4 rue Blaise Pascal, Strasbourg 67070, France.

*liuyuejin@hubu.edu.cn; *zmh@mailbox.gxnu.edu.cn

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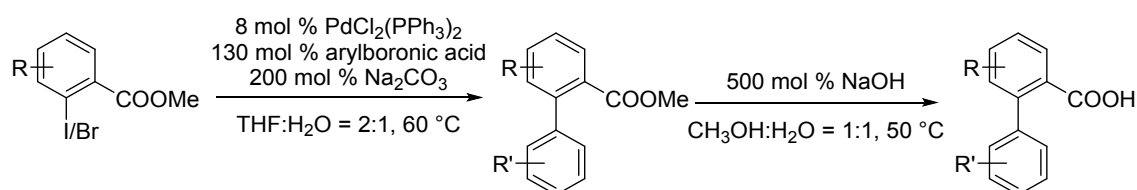
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1. General Information

Unless otherwise noted, all reactions were carried out in a flame-dried tubes under an atmosphere of air. Materials. Unless otherwise noted, materials were purchased from Alfa-Aesar and J&K Scientific Ltd. and used as received. All the solvents were purchased from commercial suppliers and purified by standard procedures as specified in Purification of Laboratory Chemicals, 4th Ed (W. L. F. Armarego, D. D. Perrin, Butterworth-Heinemann: 1997). Analytical thin layer chromatography (TLC) was performed on silica gel plates with F-254 indicator and compounds were visualized by irradiation with UV light. Flash column chromatography was carried out using silica gel (200-300 mesh) at increased pressure. The ^1H , ^{13}C NMR spectroscopic data were recorded on Bruker Mercury Plus 400 MHz NMR spectrometers or Bruker Mercury Plus 500 MHz NMR spectrometers or Bruker Mercury Plus 600 MHz NMR spectrometers. Chemical shifts (δ) for ^1H and ^{13}C are referenced to internal solvent resonances and reported relative to SiMe_4 . ^1H NMR coupling constants were reported in Hz, and multiplicity was indicated as follows: s (singlet); d (doublet); t (triplet); q (quartet); m (multiplet); dd (doublet of doublets); dt (doublet of triplets); td (triplet of doublets). The diffraction data of crystals were collected on a Rigaku XtaLAB Synergy CCD diffractometer with graphite monochromated Cu-K α radiation ($\lambda = 1.54056 \text{ \AA}$) at 293 or 100 K. Absorption corrections were applied by SADABS. All the structures were solved by direct methods and refined by full-matrix least-squares method on F^2 using SHELXTL-2014. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms of the ligand were generated geometrically. High resolution mass spectra (HRMS) were recorded on the Thermo Scientific Exactive Plus equipped with ESI ionization source.

2. Experimental Procedures

2.1 General procedure for preparation of substrate 1



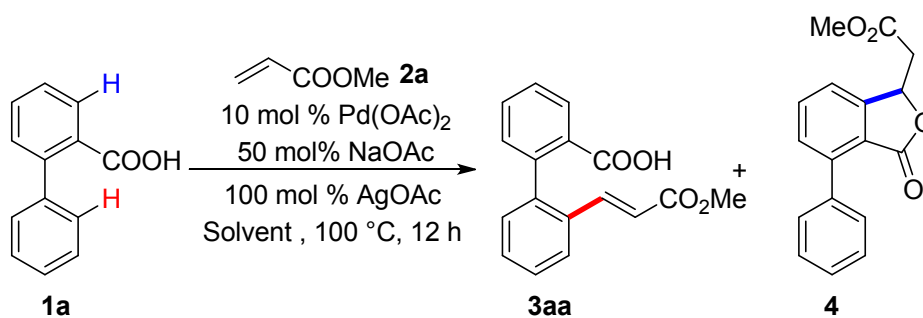
Step 1: Methyl 2-iodobenzoate or Methyl 2-bromobenzoate (17 mmol) was added to arylboronic acid (22 mmol) and Na_2CO_3 (3.6 g, 34 mmol) dissolved in THF (68 mL) and water (34 mL) mixed solvents. The reaction mixture was degassed three times and charged with argon, after which $\text{PdCl}_2(\text{PPh}_3)_2$ (8 mol%, 1 g, 1.4 mmol) was added. The reaction mixture was heated to 60°C in oil bath overnight. The resulting

reaction mixture was cooled to room temperature and added to water, the product was extracted with dichloromethane three times. The combined organic phases were dried with Na₂SO₄ and the solvent was evaporated via vacuo. The product was purified by column chromatography to give a colorless liquid.

Step 2: The methyl 2-arylbenzoate was dissolved in a solution of 3.4 g NaOH in 50 mL H₂O and 50 mL MeOH and stirred at 50 °C in oil bath for 6 h. MeOH was removed under vacuum and the reaction mixture was diluted with H₂O, and washed with Et₂O. The aqueous phase was acidified with 3N HCl, then extracted with Et₂O three times. The combined organic phase was washed with H₂O and brine, dried over Na₂SO₄, filtered and the filtration was evaporated under reduced pressure to give the desired product as a solid.

2.2 Optimization of reaction conditions

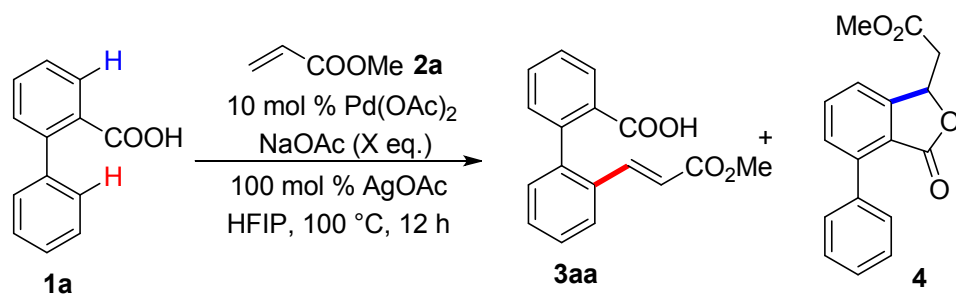
Scheme S1: The screen of solvents.



Entry	Solvent	^a yield(3aa/4)
1	DMF	12/13
2	DCE	16/19
3	Toluene	14/23
4	CH ₃ OH	7/1
5	Dioxone	15/15
6	HFIP	33/8
7	CH ₃ CN	18/8

[a] Reaction conditions: **1a** (0.10 mmol, 1equiv), **2a** (0.5 mmol, 5.0 equiv), Pd(OAc)₂ (10 mol %), NaOAc (50 mol %), AgOAc (100 mol %), solvent (0.5 mL), 100 °C, 12 h in air. ¹H NMR yield using CH₂Br₂ as internal standard.

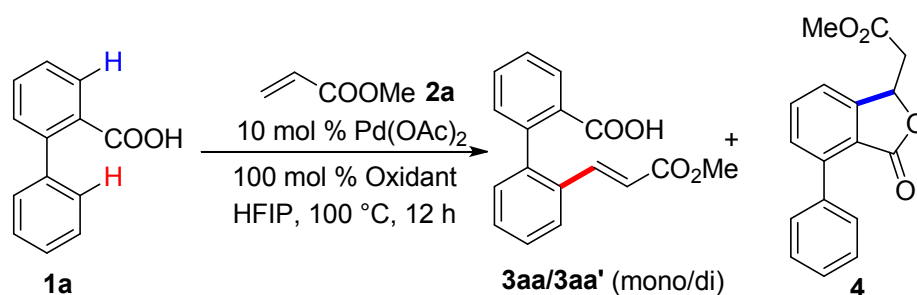
Scheme S2: The screen of amounts of bases.



Entry	equiv of NaOAc	^a yield(3aa/4)
1	0	37/10
2	0.5	33/8
3	1.5	24/9
4	2.0	21/10

[a] Reaction conditions: **1a** (0.10 mmol, 1equiv), **2a** (0.5 mmol, 5.0 equiv), $\text{Pd}(\text{OAc})_2$ (10 mol %), NaOAc (X mol %), AgOAc (100 mol %), HFIP(0.5 mL), $100\text{ }^\circ\text{C}$, 12 h in air. ^1H NMR yield using CH_2Br_2 as internal standard.

Scheme S3: The screen of oxidants.

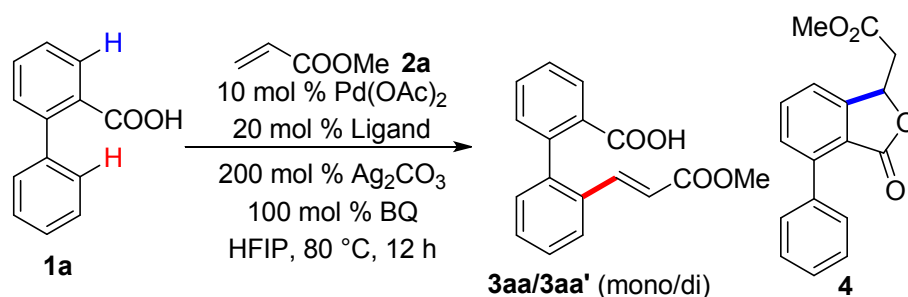


Entry	Oxidant	^a yield(3aa/3aa'/4)
1	AgOAc	37/-/10
2	BQ	15/-/-
3	MnO_2	trace
4	$\text{Cu}(\text{OAc})_2$	trace
5	Ag_3PO_4	12/-/-
6	Ag_2O	11/-/-
7	AgCF_3COO	30/5/14
8	Ag_2CO_3	50/7/10
9	$\text{Ag}_2\text{CO}_3(2)$	20/20/8
10	$\text{Ag}_2\text{CO}_3(2)/\text{BQ}(0.5)$	40/13/8
11	$\text{Ag}_2\text{CO}_3(2)/\text{BQ}(1)$	45/14/8
12	$\text{Ag}_2\text{CO}_3(2)/\text{BQ}(2)$	32/11/8

[a] Reaction conditions: **1a** (0.10 mmol, 1equiv), **2a** (0.5 mmol, 5.0 equiv), $\text{Pd}(\text{OAc})_2$ (10 mol %), oxidant, HFIP(0.5 mL), $100\text{ }^\circ\text{C}$, 12 h

in air. ¹H NMR yield using CH₂Br₂ as internal standard.

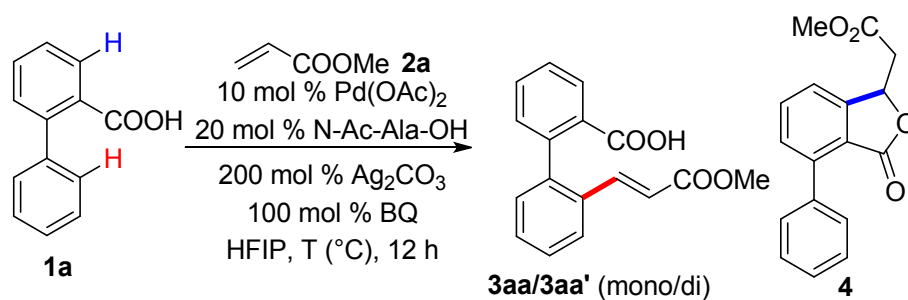
Scheme S4: The screen of ligands.



Entry	Ligand	^a yield(3aa/3aa'/4)
1	-	32/12/trace
2	AcOH	44/14/trace
3	PivOH	32/14/trace
4	AdCOOH	48/14/trace
5	N-Ac-Gly-OH	46/15/trace
6	N-Ac-Ala-OH	64/22/trace
7	N-Ac-Phe-OH	42/11/trace
8	N-Ac-Ile-OH	34/13/trace
9	N-Ac-Val-OH	42/13/trace

[a] Reaction conditions unless specified otherwise: **1a** (0.10 mmol, 1equiv), **2a** (0.5 mmol, 5.0 equiv), Pd(OAc)₂ (10 mol %), Ligand (20 mol %), Ag₂CO₃ (200 mol %), BQ (100 mol%), HFIP (0.5 mL), 80 °C, 12 h in air. ¹H NMR yield using CH₂Br₂ as internal standard.

Scheme S5: The screen of temperature.



Entry	T (°C)	^a yield(3aa/3aa'/4)
1	100	36/6/17
2	120	28/4/19
3	140	19/5/27

[a] Reaction conditions unless specified otherwise: **1a** (0.10 mmol, 1equiv), **2a** (0.5 mmol, 5.0 equiv), Pd(OAc)₂ (10 mol %), Ligand (20 mol %), Ag₂CO₃ (200 mol %), BQ (100 mol%) HFIP (0.5 mL), T °C, 12 h in air. ¹H NMR yield using CH₂Br₂ as internal standard.

2.3 General procedure for Pd(II)-Catalyzed Remote Selective C(sp²)-H Olefination

Procedure A

In a 25 mL sealed tube, 0.5 mL HFIP was added to a mixture of carboxylic acid **1** (0.1 mmol, 1.0 equiv.), Pd(OAc)₂ (2.2 mg, 0.01 mmol, 10 mol%), N-acetylalanine (2.6 mg, 0.02 mmol, 0.2 equiv.), Ag₂CO₃ (55.5 mg, 0.2 mmol, 2.0 equiv.), benzoquinone (10.8 mg, 1.0 equiv.), alkene (0.5 mmol, 5 equiv.) under air. The tube was sealed with a Teflon lined cap and the reaction mixture was stirred at 80 °C by heating metal mantle for 12 h. After cooling to room temperature, the mixture was filtered over celite, concentrated under vacuum and the residue was purified by preparative chromatography with a gradient eluent of petroleum ether, ethyl acetate and acetic acid to give the corresponding products.

Procedure B

In a 25 mL sealed tube, 0.5 mL HFIP was added to a mixture of carboxylic acid **1** (0.1 mmol, 1.0 equiv.), Pd(OAc)₂ (2.2 mg, 0.01 mmol, 10 mol%), N-acetylalanine (2.6 mg, 0.02 mmol, 0.2 equiv.), Ag₂CO₃ (55.5 mg, 0.2 mmol, 2.0 equiv.), benzoquinone (10.8 mg, 1.0 equiv.), alkene (0.5 mmol, 5 equiv.) under air. The tube was sealed with a Teflon lined cap and the reaction mixture was stirred at 60 °C by heating metal mantle for 24 h. After cooling to room temperature, the mixture was filtered over celite, concentrated under vacuum and the residue was purified by preparative chromatography with a gradient eluent of petroleum ether, ethyl acetate and acetic acid to give the corresponding products.

Procedure C

In a 25 mL sealed tube, 0.5 mL HFIP was added to a mixture of carboxylic acid **1** (0.1 mmol, 1.0 equiv.), Pd(OAc)₂ (2.2 mg, 0.01 mmol, 10 mol%), N-acetylalanine (2.6 mg, 0.02 mmol, 0.2 equiv.), Ag₂CO₃ (55.5 mg, 0.2 mmol, 2.0 equiv.), alkene (0.5 mmol, 5 equiv.) under air. The tube was sealed with a Teflon lined cap and the reaction mixture was stirred at 60 °C by heating metal mantle for 24 h. After cooling to room temperature, the mixture was filtered over celite, concentrated under vacuum and the residue was purified by preparative chromatography with a gradient eluent of petroleum ether, ethyl acetate and acetic acid to give the corresponding products.

Procedure D

In a 25 mL sealed tube, 0.5 mL tert-amyl alcohol was added to a mixture of carboxylic acid **1** (0.1 mmol, 1.0 equiv.), Pd(OAc)₂ (2.2 mg, 0.01 mmol, 10 mol%), N-acetylalanine (2.6 mg, 0.02 mmol, 0.2 equiv.), CH₃COOAg (33.4 mg, 0.2 mmol, 2.0 equiv.), alkene (0.5 mmol, 5 equiv.) under air. The tube was sealed with a Teflon lined cap and the reaction mixture was stirred at 60 °C by heating metal mantle for 12 h. After cooling to room temperature, the mixture was filtered over celite, concentrated under

vacuum and the residue was purified by preparative chromatography with a gradient eluent of petroleum ether, ethyl acetate and acetic acid to give the corresponding products.

Procedure E for large scale reaction

In a 50 mL sealed tube, aromatic acid (4 mmol) was added to Pd(OAc)₂ (88 mg, 0.4 mmol), N-acetylalanine (104 mg, 0.8 mmol), Ag₂CO₃ (2.2 g, 8 mmol) and benzoquinone (432 mg, 4 mmol) dissolved in HFIP (10 mL). After Methyl acrylate (1.7 g, 20 mmol) was added. The reaction mixture was heated to 80 °C in oil bath for 12 h. After cooling to room temperature, the mixture was filtered over celite, then dissolved in 50 mL ethyl acetate. The organic phase was washed with H₂O for 3 times and brine for 3 times, dried over Na₂SO₄ and the solvent was evaporated via vacuo. The corresponding product was purified by column chromatography with a gradient eluent of petroleum ether, ethyl acetate and acetic acid (PE/EA/HOAc = 20:1:0.05 to 5:1:0.05) to give corresponding products as white solids.

The general procedure E was applied to **1a** (4 mmol, 1 equiv), **2a** (20 mmol, 5 equiv), Pd(OAc)₂ (10 mol %), N-acetylalanine (104 mg, 0.8 mmol), Ag₂CO₃ (2.2 g, 8 mmol) and benzoquinone (432 mg, 4 mmol) in HFIP (10 mL) was stirred at 80 °C in oil bath for 12 h. Purification of the residue by column chromatography (PE/EA/HOAc = 20:1:0.05 to 5:1:0.05) to afford the **3aa** as white solid (710.0 mg, 63% yield) and di-alkenylated product (307 mg, 21%) .

The general procedure E was applied to **1b** (2 mmol, 1 equiv), **2a** (10 mmol, 5 equiv), Pd(OAc)₂ (10 mol %), N-acetylalanine (52 mg, 0.4 mmol), Ag₂CO₃ (1.1 g, 4 mmol) and benzoquinone (216 mg, 2 mmol) in HFIP (5 mL) was stirred at 80 °C in oil bath for 12 h. Purification of the residue by column chromatography (PE/EA/HOAc = 20:1:0.05 to 5:1:0.05) to afford the **3ba** as white solid (434.0 mg, 70% yield).

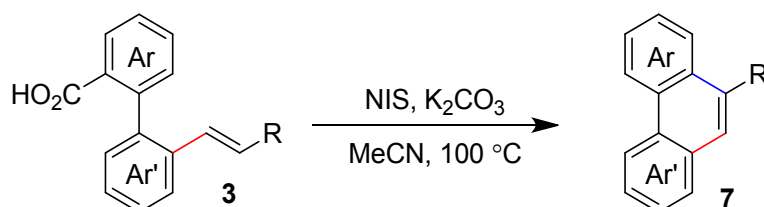
The general procedure E was applied to **1c** (2 mmol, 1 equiv), **2a** (10 mmol, 5 equiv), Pd(OAc)₂ (10 mol %), N-acetylalanine (52 mg, 0.4 mmol), Ag₂CO₃ (1.1 g, 4 mmol) and benzoquinone (216 mg, 2 mmol) in HFIP (5 mL) was stirred at 80 °C in oil bath for 12 h. Purification of the residue by column chromatography (PE/EA/HOAc = 20:1:0.05 to 5:1:0.05) to afford the **3ca** as white solid (481.8 mg, 73% yield).

The general procedure E was applied to **1d** (2 mmol, 1 equiv), **2a** (10 mmol, 5 equiv), Pd(OAc)₂ (10 mol %), N-acetylalanine (52 mg, 0.4 mmol), Ag₂CO₃ (1.1 g, 4 mmol) and benzoquinone (216 mg, 2 mmol) in HFIP (5 mL) was stirred at 80 °C in oil bath for 12 h. Purification of the residue by column chromatography (PE/EA/HOAc = 20:1:0.05 to 5:1:0.05) to afford the **3da** as white solid (489.2 mg, 72% yield).

The general procedure E was applied to **1n** (2 mmol, 1 equiv), **2a** (10 mmol, 5 equiv), Pd(OAc)₂ (10 mol %), N-acetylalanine (52 mg, 0.4 mmol), Ag₂CO₃ (1.1 g, 4 mmol) and benzoquinone (216 mg, 2 mmol) in HFIP (5 mL) was stirred at 60 °C in oil bath for 12 h. Purification of the residue by column

chromatography (PE/EA/HOAc = 20:1:0.05 to 5:1:0.05) to afford the **3na** as white solid (494.5 mg, 67% yield).

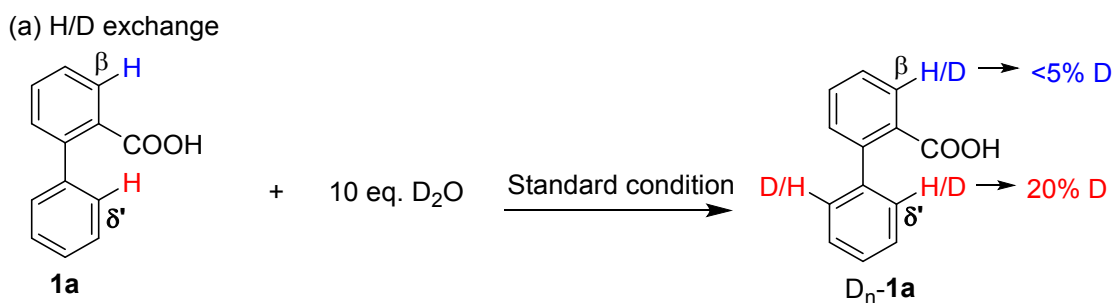
The general procedure E was applied to **1o** (2 mmol, 1 equiv), **2a** (10 mmol, 5 equiv), Pd(OAc)₂ (10 mol %), N-acetylalanine (52 mg, 0.4 mmol), Ag₂CO₃ (1.1 g, 4 mmol) and benzoquinone (216 mg, 2 mmol) in HFIP (5 mL) was stirred at 60 °C in oil bath for 12 h. Purification of the residue by column chromatography (PE/EA/HOAc = 20:1:0.05 to 5:1:0.05) to afford the **3oa** as white solid (493.1 mg, 67% yield).



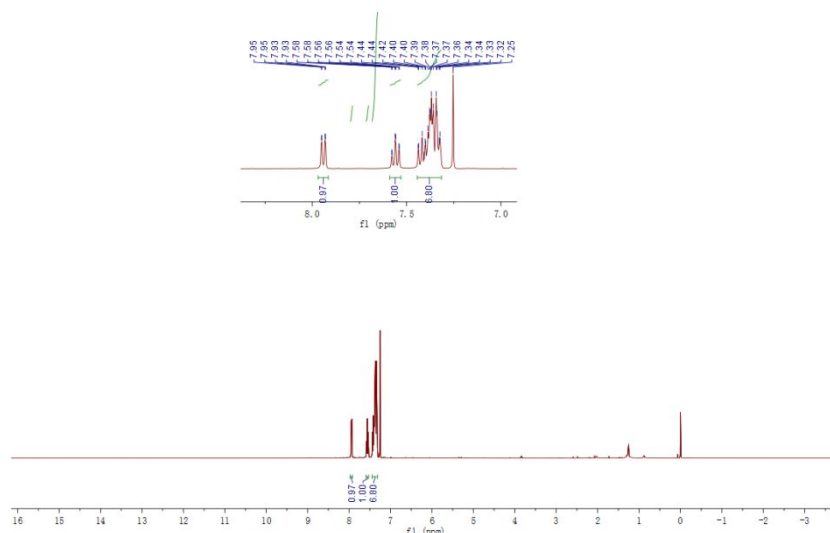
Procedure F

In a 25 mL sealed tube, 1 mL acetonitrile was added to a mixture of alkenylated carboxylic acid **3** (0.1 mmol, 1.0 equiv.), N-iodosuccinimide (90.0 mg, 0.4 mmol, 4 equiv.), K₂CO₃ (27.7 mg, 0.2 mmol, 2.0 equiv.) under air. The tube was sealed with a Teflon lined cap and the reaction mixture was stirred at 100 °C by heating metal mantle for 12 h. After cooling to room temperature, the mixture was filtered over celite, concentrated under vacuum and the residue was purified by preparative chromatography with a gradient eluent of petroleum ether and ethyl acetate to give the corresponding products **7**.

2.4 Mechanism investigation

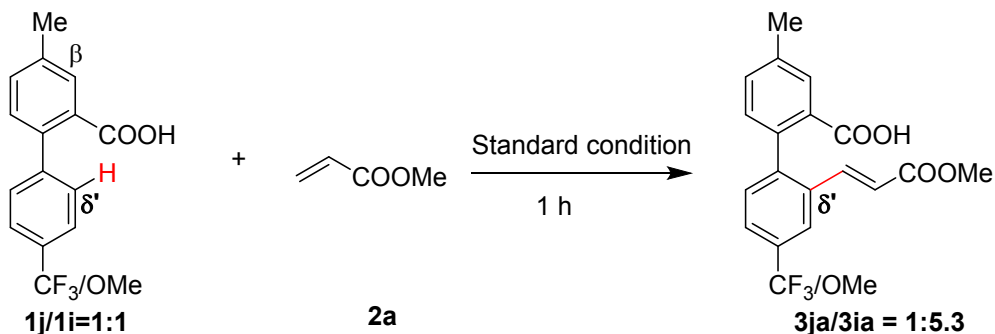


Scheme S5a. The deuteration reaction of [1,1'-biphenyl]-2-carboxylic acid

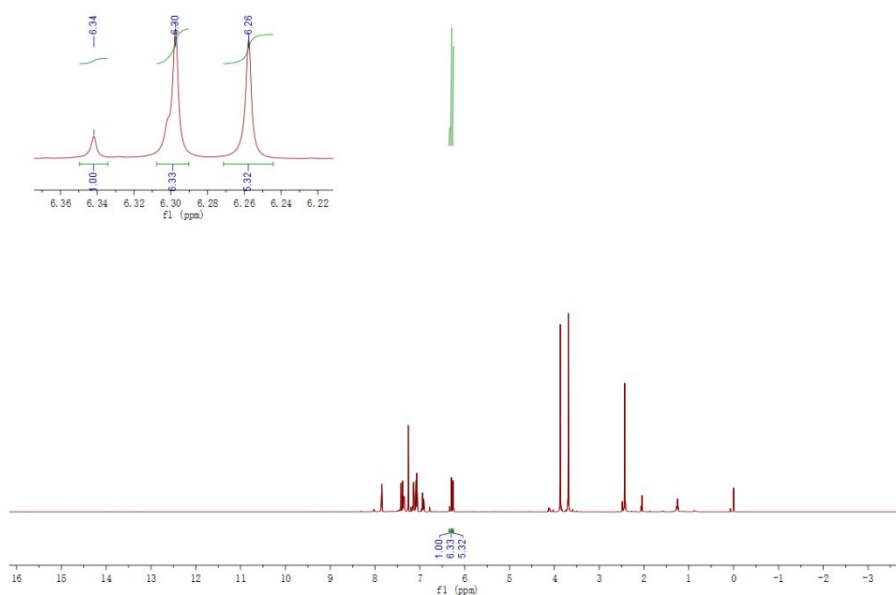


To the suspension of **1a** (19.8 mg, 0.10 mmol), Pd(OAc)₂ (2.3 mg, 0.01 mmol), N-Ac-Ala-OH (2.6 mg, 0.02 mmol), Ag₂CO₃ (55.5 mg, 0.20 mmol), benzoquinone (10.8 mg, 0.10 mmol) and HFIP (0.5 mL) in a sealed tube was added D₂O (1.0 mmol) under air atmosphere. The mixture was stirred at room temperature for 5 min and then reacted at 80 °C by heating metal mantle for further 1 h. After being cooled down to room temperature, it was purified by preparative chromatography to afford the starting material, which was subject to ¹H NMR test to determine the ratio of **1a** and Dn-**1a**.

(b) competition experiment



Scheme S5b. Intermolecular competition between the electron-rich and electron-deficient substrates.

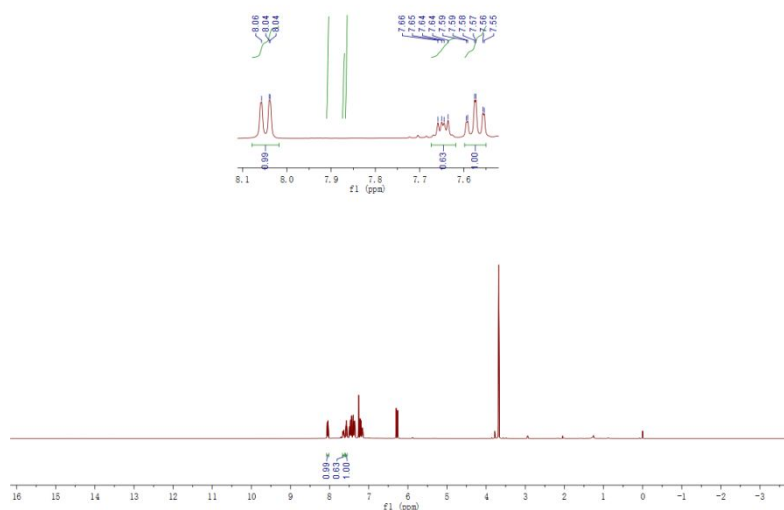


To the suspension of Pd(OAc)₂ (4.6 mg, 0.02 mmol), N-Ac-Ala-OH (5.2 mg, 0.04 mmol), Ag₂CO₃ (110.0 mg, 0.40 mmol), benzoquinone (21.6 mg, 0.20 mmol), methyl acrylate (86.0 mg, 1.0 mmol) and HFIP (1.0 mL) in a sealed tube was added **3j** (0.1 mmol) and **3i** (0.1 mmol) under air atmosphere. The mixture was stirred at room temperature for 5 min and then reacted at 80 °C by heating metal mantle for further 1 h. After being cooled down to room temperature, it was purified by preparative chromatography to afford mixed product, which was subject to ¹H NMR test to determine the ratio of **3ja** and **3ia**.

(c) kinetic isotope effect

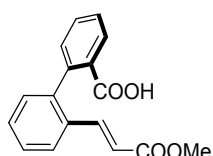


Scheme S5c. Intermolecular competitive kinetic isotope effect



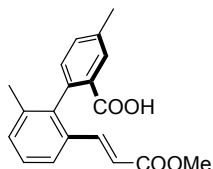
To the suspension of Pd(OAc)₂ (4.4 mg, 0.02 mmol), N-Ac-Ala-OH (5.2 mg, 0.04 mmol), Ag₂CO₃ (111.0 mg, 0.40 mmol), benzoquinone (21.6 mg, 0.20 mmol), methyl acrylate (86.0 mg, 1.0 mmol) and HFIP (1 mL) in a sealed tube was added **1a** (0.1 mmol) and **D₅-1a** (0.1 mmol) under air atmosphere. The mixture was stirred at room temperature for 5 min and then reacted at 80 °C by heating metal mantle for further 1 h. After being cooled down to room temperature, it was purified by preparative chromatography to afford mixed product, which was subject to ¹H NMR test to determine the ratio of **3aa** and **D₄-3aa**.

3. Characterization Data



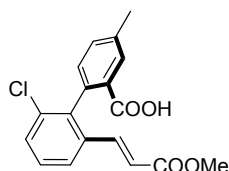
2'-(3-methoxy-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2-carboxylic acid (**3aa**)

Prepared according to general procedure A, purification of the residue by preparative chromatography (PE/EA/ acetic acid = 3/1/0.05) afforded the product as a white solid (17.8 mg, 63% yield), ¹H NMR (501 MHz, CDCl₃) δ 8.05 (d, *J* = 7.5 Hz, 1H), 7.67 – 7.65 (m, 1H), 7.59 - 7.56 (m, 1H), 7.49 - 7.46 (m, 1H), 7.41 (d, *J* = 16.0 Hz, 1H), 7.38 – 7.36 (m, 2H), 7.21 (d, *J* = 7.4 Hz, 1H), 7.18 – 7.14 (m, 1H), 6.28 (d, *J* = 15.9 Hz, 1H), 3.68 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 171.7, 167.3, 143.1, 142.3, 141.6, 132.6, 132.4, 131.8, 131.2, 129.7, 129.5, 128.0, 127.8, 126.2, 118.9, 51.6. HRMS (ESI+) exact mass calculated for [M+Na]⁺ (C₁₇H₁₄NaO₄): 305.0784, found: 305.0787.



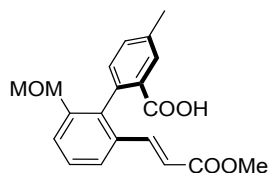
2'-(3-methoxy-3-oxoprop-1-en-1-yl)-4,6'-dimethyl-[1,1'-biphenyl]-2-carboxylic acid (**3ba**)

Prepared according to general procedure A, purification of the residue by preparative chromatography (PE/EA/ acetic acid = 3/1/0.05) afforded the product as a white solid (24.8 mg, 80% yield), ¹H NMR (501 MHz, CDCl₃) δ 7.95 (s, 1H), 7.50 (d, *J* = 7.5 Hz, 1H), 7.42 (d, *J* = 7.5 Hz, 1H), 7.22-7.25 (m, 2H), 6.99 (d, *J* = 7.5 Hz, 1H), 6.24 (d, *J* = 16.0 Hz, 1H), 3.66 (s, 3H), 2.45 (s, 3H), 1.93 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 171.0, 167.4, 143.8, 142.2, 138.0, 137.8, 136.4, 134.0, 132.7, 132.0, 131.2, 128.7, 127.3, 123.5, 118.2, 51.6, 21.1, 20.5. HRMS (ESI+) exact mass calculated for [M+Na]⁺ (C₁₉H₁₈NaO₄): 333.1097, found: 333.1103.



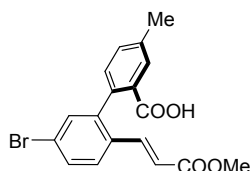
2'-chloro-6'-(3-methoxy-3-oxoprop-1-en-1-yl)-4-methyl-[1,1'-biphenyl]-2-carboxylic acid (3ca)

Prepared according to general procedure A, purification of the residue by preparative chromatography (PE/EA/ acetic acid = 3/1/0.05) afforded the product as a white solid (24.8 mg, 75% yield), ^1H NMR (501 MHz, CDCl_3) δ 7.98 (s, 1H), 7.56 (d, $J = 7.9$ Hz, 1H), 7.42 - 7.45 (m, 2H), 7.29 (t, $J = 7.9$ Hz, 1H), 7.23 (d, $J = 15.9$ Hz, 1H), 7.01 (d, $J = 7.9$ Hz, 1H), 6.26 (d, $J = 15.8$ Hz, 1H), 3.68 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 170.9, 167.0, 142.6, 141.0, 138.5, 135.9, 134.8, 134.0, 133.9, 132.1, 131.4, 130.2, 128.8, 128.3, 124.5, 119.7, 51.7, 21.1. HRMS (ESI+) exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{18}\text{H}_{15}\text{ClNaO}_4$): 353.0551, found: 353.0543.



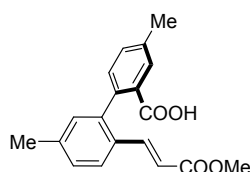
2'-(3-methoxy-3-oxoprop-1-en-1-yl)-6'-(methoxymethyl)-4-methyl-[1,1'-biphenyl]-2-carboxylic acid (3da)

Prepared according to general procedure A, purification of the residue by preparative chromatography (PE/EA/ acetic acid = 3/1/0.05) afforded the product as a white solid (25.8 mg, 76% yield), ^1H NMR (501 MHz, CDCl_3) δ 7.88 (s, 1H), 7.60 (d, $J = 7.5$ Hz, 1H), 7.44 (d, $J = 6.5$ Hz, 1H), 7.41 - 7.32 (m, 2H), 7.22 (d, $J = 16.0$ Hz, 1H), 7.00 (d, $J = 7.5$ Hz, 1H), 6.25 (d, $J = 16.0$ Hz, 1H), 4.01 (m, 2H), 3.66 (s, 3H), 3.10 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 171.0, 167.2, 143.0, 141.6, 138.1, 136.0, 135.7, 133.3, 133.2, 131.6, 131.0, 130.1, 129.7, 127.6, 125.5, 118.7, 72.6, 57.9, 51.6, 21.1. HRMS (ESI+) exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{20}\text{H}_{20}\text{NaO}_5$): 363.1203, found: 363.1197.



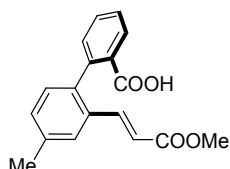
5'-bromo-2'-(3-methoxy-3-oxoprop-1-en-1-yl)-4-methyl-[1,1'-biphenyl]-2-carboxylic acid (3ea)

Prepared according to general procedure A, purification of the residue by preparative chromatography (PE/EA/ acetic acid = 3/1/0.05) afforded the product as a white solid (23.2mg, 62% yield), ^1H NMR (501 MHz, CDCl_3) δ 7.79 (s, 1H), 7.71 (d, $J = 16.1$ Hz, 1H), 7.48 (d, $J = 8.0$ Hz, 1H), 7.46 (s, 1H), 7.30 - 7.39 (m, 3H), 7.23 (d, $J = 8.0$ Hz, 1H), 6.44 (d, $J = 16.0$ Hz, 1H), 3.79 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 173.1, 167.6, 144.9, 141.8, 139.8, 137.6, 134.1, 133.0, 131.4, 131.1, 130.7, 128.9, 128.5, 128.2, 126.8, 117.9, 51.8, 20.9. HRMS (ESI+) exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{18}\text{H}_{15}\text{BrNaO}_4$): 397.0046, found: 397.0041.



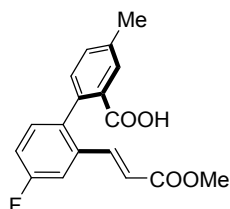
2'-(3-methoxy-3-oxoprop-1-en-1-yl)-4,5'-dimethyl-[1,1'-biphenyl]-2-carboxylic acid (3fa)

Prepared according to general procedure A, purification of the residue by preparative chromatography (PE/EA/ acetic acid = 3/1/0.05) afforded the product as a white solid (22.0 mg, 71% yield), ^1H NMR (400 MHz, CDCl_3) δ 7.85 (s, 1H), 7.54 (d, $J = 8.0$ Hz, 1H), 7.40 (d, $J = 16.0$ Hz, 1H), 7.35 (s, 1H), 7.15 (d, $J = 8.0$ Hz, 1H), 7.08 (d, $J = 8.0$ Hz, 1H), 6.96 (s, 1H), 6.24 (d, $J = 15.9$ Hz, 1H), 3.67 (s, 3H), 2.43 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 171.7, 167.5, 143.2, 142.4, 139.7, 138.7, 137.7, 133.1, 131.7, 131.6, 130.4, 130.0, 129.3, 128.5, 126.0, 117.5, 51.5, 21.4, 21.0. HRMS (ESI+) exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{19}\text{H}_{18}\text{NaO}_4$): 333.1097, found: 333.1088.



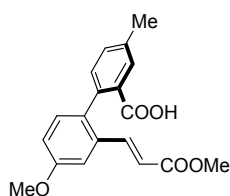
2'-(3-methoxy-3-oxoprop-1-en-1-yl)-4'-methyl-[1,1'-biphenyl]-2-carboxylic acid (3ga)

Prepared according to general procedure A, purification of the residue by preparative chromatography (PE/EA/ acetic acid = 3/1/0.05) afforded the product as a white solid (19.5 mg, 66% yield), ^1H NMR (400 MHz, CDCl_3) δ 8.03 (dd, $J = 7.8, 1.2$ Hz, 1H), 7.54 (td, $J = 7.5, 1.4$ Hz, 1H), 7.46 – 7.38 (m, 3H), 7.20 – 7.15 (m, 2H), 7.06 (d, $J = 7.8$ Hz, 1H), 6.27 (d, $J = 15.9$ Hz, 1H), 3.66 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 171.9, 167.3, 143.2, 141.5, 139.4, 137.3, 132.3, 132.2, 132.0, 131.1, 130.3, 129.6, 129.6, 127.7, 126.7, 118.6, 51.5, 21.2. HRMS (ESI+) exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{18}\text{H}_{16}\text{NaO}_4$): 319.0941, found: 319.0937.



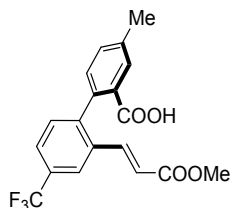
4'-fluoro-2'-(3-methoxy-3-oxoprop-1-en-1-yl)-4-methyl-[1,1'-biphenyl]-2-carboxylic acid (3ha)

Prepared according to general procedure A, purification of the residue by preparative chromatography (PE/EA/ acetic acid = 3/1/0.05) afforded the product as a white solid (19.2 mg, 61% yield), ^1H NMR (400 MHz, CDCl_3) δ 7.88 (s, 1H), 7.41 – 7.29 (m, 3H), 7.15 – 7.03 (m, 3H), 6.27 (d, $J = 15.9$ Hz, 1H), 3.69 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 171.9, 167.0, 163.3, 160.8, 142.1 (d, $J = 2.4$ Hz), 138.3 (d, $J = 3.2$ Hz), 138.2, 137.8, 134.6 (d, $J = 7.7$ Hz), 133.4, 131.9 (d, $J = 2.1$ Hz), 131.4 (d, $J = 8.1$ Hz), 129.2, 119.8, 116.5 (d, $J = 21.6$ Hz), 112.4 (d, $J = 22.3$ Hz), 51.8, 21.0. ^{19}F NMR (377 MHz, CDCl_3) δ -114.71. HRMS (ESI+) exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{18}\text{H}_{15}\text{FNaO}_4$): 337.0847, found: 337.0843.



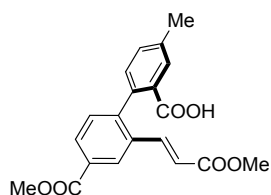
4'-methoxy-2'-(3-methoxy-3-oxoprop-1-en-1-yl)-4-methyl-[1,1'-biphenyl]-2-carboxylic acid (3ia)

Prepared according to general procedure A, purification of the residue by preparative chromatography (PE/EA/ acetic acid = 3/1/0.05) afforded the product as a white solid (23.5 mg, 72% yield), ¹H NMR (501 MHz, CDCl₃) δ 7.84 (s, 1H), 7.41 (d, *J* = 16.0 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.14 (d, *J* = 2.5 Hz, 1H), 7.08 (q, *J* = 8.0 Hz, 2H), 6.93 (dd, *J* = 8.0, 2.5 Hz, 1H), 6.28 (d, *J* = 16.0 Hz, 1H), 3.86 (s, 3H), 3.69 (s, 3H), 2.43 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 171.9, 167.3, 158.8, 143.3, 138.3, 137.6, 135.0, 133.7, 133.0, 132.1, 131.6, 131.00, 129.6, 118.8, 115.7, 110.6, 55.3, 51.6, 21.0. HRMS (ESI+) exact mass calculated for [M+Na]⁺(C₁₉H₁₈NaO₅): 349.1046, found: 349.1051.



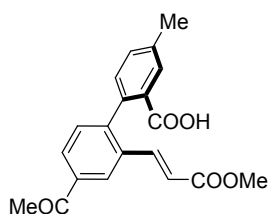
2'-(3-methoxy-3-oxoprop-1-en-1-yl)-4-methyl-4'-(trifluoromethyl)-[1,1'-biphenyl]-2-carboxylic acid (3ja)

Prepared according to general procedure A, purification of the residue by preparative chromatography (PE/EA/ acetic acid = 3/1/0.05) afforded the product as a white solid (24.0 mg, 66% yield), ¹H NMR (400 MHz, CDCl₃) δ 7.93 (s, 1H), 7.86 (s, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.43 – 7.36 (m, 2H), 7.27 (d, *J* = 8.0 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 1H), 6.34 (d, *J* = 16.0 Hz, 1H), 3.70 (s, 3H), 2.45 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 171.5, 166.8, 145.8, 141.7, 138.6, 137.6, 133.6, 133.5, 132.1, 131.3, 130.3, 129.9 (q, *J* = 32.6 Hz), 125.7 (q, *J* = 3.5 Hz), 123.9 (q, *J* = 270.6 Hz), 122.9 (q, *J* = 3.7 Hz), 120.4, 51.8, 21.0. ¹⁹F NMR (377 MHz, CDCl₃) δ -62.63. HRMS (ESI+) exact mass calculated for [M+Na]⁺(C₁₉H₁₅F₃NaO₄): 387.0815, found: 387.0822.



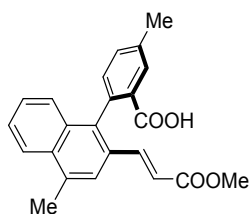
2'-(3-methoxy-3-oxoprop-1-en-1-yl)-4'-(methoxycarbonyl)-4-methyl-[1,1'-biphenyl]-2-carboxylic acid (3ka)

Prepared according to general procedure A, purification of the residue by preparative chromatography (PE/EA/ acetic acid = 3/1/0.05) afforded the product as a white solid (20.3 mg, 54% yield), ¹H NMR (400 MHz, CDCl₃) δ 8.31 (d, *J* = 1.1 Hz, 1H), 7.98 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.88 (s, 1H), 7.42 – 7.36 (m, 2H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.04 (d, *J* = 7.7 Hz, 1H), 6.38 (d, *J* = 15.9 Hz, 1H), 3.94 (s, 3H), 3.68 (s, 3H), 2.43 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 171.6, 167.0, 166.6, 146.9, 142.2, 138.4, 137.9, 133.4, 133.1, 131.9, 131.2, 130.0, 130.0, 129.4, 128.9, 127.4, 119.9, 52.3, 51.7, 21.0. HRMS (ESI+) exact mass calculated for [M+Na]⁺(C₂₀H₁₈NaO₆): 377.0996, found: 377.0994.



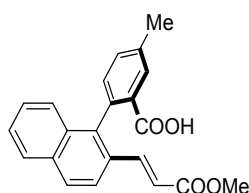
4'-acetyl-2'-(3-methoxy-3-oxoprop-1-en-1-yl)-4-methyl-[1,1'-biphenyl]-2-carboxylic acid (3la)

Prepared according to general procedure A, purification of the residue by preparative chromatography (PE/EA/ acetic acid = 3/1/0.05) afforded the product as a white solid (20.5 mg, 57% yield), ^1H NMR (400 MHz, CDCl_3) δ 8.22 (d, $J = 1.4$ Hz, 1H), 7.94 – 7.89 (m, 2H), 7.43 – 7.37 (m, 2H), 7.25 (d, $J = 9.4$ Hz, 1H), 7.06 (d, $J = 7.7$ Hz, 1H), 6.38 (d, $J = 16.0$ Hz, 1H), 3.70 (s, 3H), 2.66 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 197.6, 171.3, 167.0, 147.1, 142.3, 138.5, 137.9, 136.3, 133.5, 133.3, 132.0, 131.2, 130.2, 128.9, 126.1, 120.1, 51.7, 26.7, 21.1. HRMS (ESI+) exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{20}\text{H}_{18}\text{NaO}_5$): 361.1046, found: 361.1049.



2-(2-(3-methoxy-3-oxoprop-1-en-1-yl)-4-methylnaphthalen-1-yl)-5-methylbenzoic acid (3ma)

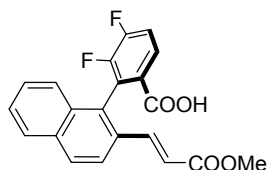
Prepared according to general procedure B, purification of the residue by preparative chromatography (PE/EA/ acetic acid = 3/1/0.05) afforded the product as a yellow solid (24.1 mg, 67% yield), ^1H NMR (400 MHz, CDCl_3) δ 7.96 (d, $J = 8.5$ Hz, 2H), 7.95 (s, 1H), 7.56 (s, 1H), 7.49 – 7.40 (m, 2H), 7.37 (d, $J = 16.0$ Hz, 1H), 7.26 (dd, $J = 4.5, 3.2$ Hz, 1H), 7.19 – 7.14 (m, 1H), 7.06 (d, $J = 7.7$ Hz, 1H), 6.37 (d, $J = 15.9$ Hz, 1H), 3.67 (s, 3H), 2.72 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 170.8, 167.4, 143.3, 139.5, 138.1, 136.7, 133.9, 133.6, 133.2, 132.8, 132.5, 132.0, 129.9, 128.9, 127.3, 126.5, 126.1, 124.1, 123.2, 118.0, 77.3, 77.0, 76.7, 51.5, 21.0, 19.7. HRMS (ESI+) exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{23}\text{H}_{20}\text{NaO}_4$): 383.1254, found: 383.1248.



2-(2-(3-methoxy-3-oxoprop-1-en-1-yl)naphthalen-1-yl)-5-methylbenzoic acid (3na)

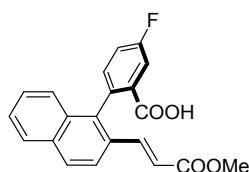
Prepared according to general procedure B, purification of the residue by preparative chromatography (PE/EA/ acetic acid = 3/1/0.05) afforded the product as a yellow solid (21.1 mg, 61% yield), ^1H NMR (400 MHz, CDCl_3) δ 7.95 (s, 1H), 7.79 (t, $J = 7.9$ Hz, 2H), 7.70 (d, $J = 8.4$ Hz, 1H), 7.44 – 7.37 (m, 3H), 7.29 – 7.24 (m, 1H), 7.14 (d, $J = 8.4$ Hz, 1H), 7.07 (d, $J = 7.6$ Hz, 1H), 6.37 (d, $J = 15.9$ Hz, 1H), 3.66 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 171.1, 167.4, 143.2, 141.1, 138.2, 136.6, 133.8,

133.7, 132.7, 132.2, 132.0, 129.7, 129.4, 127.9, 127.8, 126.7, 126.7, 126.4, 122.6, 118.3, 77.3, 77.0, 76.7, 51.6, 21.1. HRMS (ESI+) exact mass calculated for $[M+Na]^+$ ($C_{22}H_{18}NaO_4$): 369.1097, found: 369.1099.



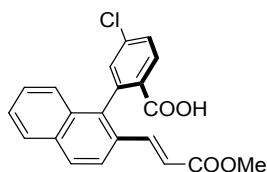
3,4-difluoro-2-(2-(3-methoxy-3-oxoprop-1-en-1-yl)naphthalen-1-yl)benzoic acid (30a)

Prepared according to general procedure B, purification of the residue by preparative chromatography (PE/EA/ acetic acid = 3/1/0.05) afforded the product as a yellow solid (23.2 mg, 63% yield), 1H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, $J = 10.7, 8.1$ Hz, 1H), 7.84 (dd, $J = 8.4, 2.9$ Hz, 2H), 7.69 (d, $J = 8.8$ Hz, 1H), 7.48 (t, $J = 7.4$ Hz, 1H), 7.35 – 7.29 (m, 2H), 7.10 (d, $J = 8.4$ Hz, 1H), 7.04 (dd, $J = 10.0, 7.5$ Hz, 1H), 6.39 (d, $J = 15.9$ Hz, 1H), 3.70 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5, 167.3, 152.9 (dd, $J = 259.7, 12.6$ Hz), 149.6 (dd, $J = 251.9, 12.5$ Hz), 142.2, 138.4, 137.6 (dd, $J = 6.9, 4.1$ Hz), 133.8, 132.2, 129.5, 128.6, 128.1, 127.0 (d, $J = 4.4$ Hz), 126.7 (dd, $J = 5.1, 3.5$ Hz), 126.1, 122.6, 121.5 (d, $J = 17.4$ Hz), 121.1 (d, $J = 18.9$ Hz), 119.3, 51.8. ^{19}F NMR (377 MHz, $CDCl_3$) δ -128.69 (d, $J = 21.6$ Hz), -136.10 (d, $J = 21.9$ Hz). HRMS (ESI+) exact mass calculated for $[M+Na]^+$ ($C_{21}H_{14}F_2NaO_4$): 391.0752, found: 391.0757.



5-fluoro-2-(2-(3-methoxy-3-oxoprop-1-en-1-yl)naphthalen-1-yl)benzoic acid (3pa)

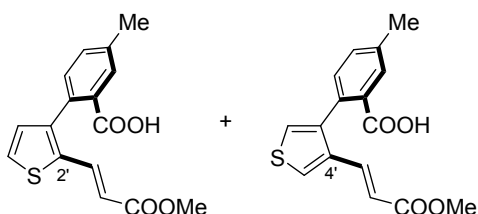
Prepared according to general procedure B, purification of the residue by preparative chromatography (PE/EA/ acetic acid = 3/1/0.05) afforded the product as a yellow solid (24.5 mg, 70% yield), 1H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.81 (m, 3H), 7.72 (d, $J = 8.8$ Hz, 1H), 7.46 (t, $J = 7.5$ Hz, 1H), 7.40 – 7.28 (m, 3H), 7.19 (dd, $J = 8.4, 5.4$ Hz, 1H), 7.11 (d, $J = 8.4$ Hz, 1H), 6.39 (d, $J = 15.9$ Hz, 1H), 3.69 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 167.3, 162.0 (d, $J = 249.1$ Hz), 142.7, 139.6, 135.5 (d, $J = 3.6$ Hz), 134.1 (d, $J = 7.5$ Hz), 133.8, 132.6, 131.8 (d, $J = 7.1$ Hz), 129.6, 128.2, 128.0, 126.8, 126.7, 126.4, 122.6, 120.2 (d, $J = 21.1$ Hz), 118.8, 118.4 (d, $J = 23.4$ Hz), 51.7. ^{19}F NMR (377 MHz, $CDCl_3$) δ -112.48. HRMS (ESI+) exact mass calculated for $[M+Na]^+$ ($C_{21}H_{15}FNaO_4$): 373.0847, found: 373.0855.



4-chloro-2-(2-(3-methoxy-3-oxoprop-1-en-1-yl)naphthalen-1-yl)benzoic acid (3qa)

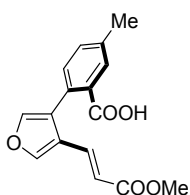
Prepared according to general procedure B, purification of the residue by preparative chromatography

(PE/EA/ acetic acid = 3/1/0.05) afforded the product as a yellow solid (24.5 mg, 67% yield), ^1H NMR (400 MHz, CDCl_3) δ 8.12 (d, $J = 8.5$ Hz, 1H), 7.85 (d, $J = 8.3$ Hz, 2H), 7.72 (d, $J = 8.6$ Hz, 1H), 7.54 (d, $J = 7.0$ Hz, 1H), 7.47 (t, $J = 7.3$ Hz, 1H), 7.38 – 7.30 (m, 2H), 7.23 (d, $J = 1.5$ Hz, 1H), 7.11 (d, $J = 8.4$ Hz, 1H), 6.41 (d, $J = 15.9$ Hz, 1H), 3.70 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 169.1, 167.2, 142.4, 141.6, 139.4, 139.2, 133.8, 133.0, 132.3, 132.2, 129.4, 128.7, 128.4, 128.3, 128.0, 126.9, 126.8, 126.3, 122.6, 119.1, 51.7. HRMS (ESI+) exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{21}\text{H}_{15}\text{ClNaO}_4$): 389.0551, found: 389.0547.



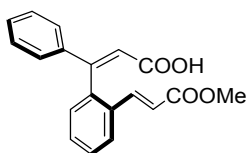
2-(2-(3-methoxy-3-oxoprop-1-en-1-yl) thiophen-3-yl)-5-methylbenzoic acid (3ra) + 2-(4-(3-methoxy-3-oxoprop-1-en-1-yl) thiophen-3-yl)-5-methylbenzoic acid (3ra')

Prepared according to general procedure C, purification of the residue by preparative chromatography (PE/EA/ acetic acid = 3/1/0.05) afforded the product as a yellow solid (16.9 mg, 56% yield), ^1H NMR (400 MHz, CDCl_3) δ 7.88 (s, 0.77H, 3pa), 7.79 – 7.75(m, 0.46H, 3pa'), 7.48 (d, $J = 15.7$ Hz, 0.77H, 3pa), 7.40 (d, $J = 7.6$ Hz, 0.77H, 3pa), 7.35 (d, $J = 7.8$ Hz, 0.23H, 3pa'), 7.30 (d, $J = 5.0$ Hz, 0.77H, 3pa), 7.27 – 7.26(m, 0.23H, 3pa'), 7.26 – 7.24 (m, 0.46H, 3pa'), 7.14 (d, $J = 7.7$ Hz, 0.77H, 3pa), 6.94 (d, $J = 5.1$ Hz, 0.77H, 3pa), 6.24 (d, $J = 15.8$ Hz, 0.23H, 3pa'), 6.20 (d, $J = 15.6$ Hz, 0.77H, 3pa), 3.79 (s, 0.69H, 3pa'), 3.70 (s, 2.31H, 3pa), 2.45 (s, 2.31H, 3pa), 2.41 (s, 0.69H, 3pa'). ^{13}C NMR (101 MHz, CDCl_3) δ 171.4, 167.4, 144.8, 142.2, 138.7, 138.4, 137.8, 137.5, 136.4, 134.7, 133.7, 133.3, 133.0, 132.6, 132.0, 131.9, 131.3, 130.9, 130.8, 129.5, 126.2, 125.4, 116.6, 116.5, 51.8, 51.7, 21.1, 21.0. HRMS (ESI+) exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{16}\text{H}_{14}\text{NaO}_4\text{S}$): 325.0505, found: 325.0499.



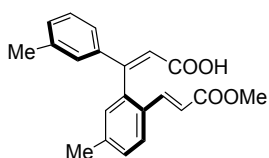
2-(4-(3-methoxy-3-oxoprop-1-en-1-yl)furan-3-yl)-5-methylbenzoic acid (3sa)

Prepared according to general procedure C, purification of the residue by preparative chromatography (PE/EA/ acetic acid = 3/1/0.05) afforded the product as a yellow solid (6.5 mg, 23% yield), ^1H NMR (400 MHz, CDCl_3) δ 7.86 (s, 1H), 7.46 (s, 1H), 7.39 (d, $J = 7.6$ Hz, 1H), 7.27 (d, $J = 15.6$ Hz, 2H), 7.18 (d, $J = 7.7$ Hz, 1H), 6.49 (s, 1H), 6.33 (d, $J = 15.7$ Hz, 1H), 3.72 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 171.1, 167.7, 146.8, 143.5, 138.4, 133.3, 132.0, 131.9, 130.4, 130.0, 129.9, 115.4, 114.9, 51.6, 21.0. HRMS (ESI+) exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{16}\text{H}_{14}\text{NaO}_5$): 309.0733, found: 309.0737.



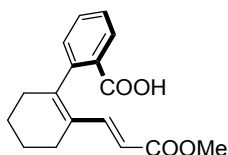
(Z)-3-(2-((E)-3-methoxy-3-oxoprop-1-en-1-yl)phenyl)-3-phenylacrylic acid (3ua)

Prepared according to general procedure A, purification of the residue by preparative chromatography (PE/EA/ acetic acid = 3/1/0.05) afforded the product as a white solid (20.6 mg, 67% yield), ¹H NMR (400 MHz, CDCl₃) δ 7.70 – 7.63 (m, 1H), 7.55 (d, *J* = 15.9 Hz, 1H), 7.41 – 7.25 (m, 7H), 7.13 – 7.09 (m, 1H), 6.55 (s, 1H), 6.33 (d, *J* = 15.9 Hz, 1H), 3.69 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 169.8, 167.2, 156.4, 142.2, 139.4, 139.2, 132.5, 130.1, 129.8, 129.2, 128.7, 128.4, 127.8, 126.2, 119.2, 118.2, 51.7. HRMS (ESI+) exact mass calculated for [M+Na]⁺ (C₁₉H₁₆NaO₄): 331.0941, found: 331.0937.



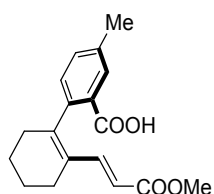
(Z)-3-(2-((E)-3-methoxy-3-oxoprop-1-en-1-yl)-5-methylphenyl)-3-(m-tolyl)acrylic acid (3va)

Prepared according to general procedure A, purification of the residue by preparative chromatography (PE/EA/ acetic acid = 3/1/0.05) afforded the product as a white solid (24.5 mg, 73% yield), ¹H NMR (501 MHz, CDCl₃) δ 7.57 (d, *J* = 8.2 Hz, 1H), 7.55 (d, *J* = 15.9 Hz, 1H), 7.19 (m, 3H), 7.10 (s, 1H), 7.03 (d, *J* = 6.9 Hz, 1H), 6.90 (s, 1H), 6.53 (s, 1H), 6.31 (d, *J* = 15.9 Hz, 1H), 3.69 (s, 3H), 2.35 (s, 3H), 2.31 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 169.8, 167.4, 156.6, 142.3, 140.1, 139.5, 139.4, 138.4, 130.9, 129.8, 129.6, 129.2, 128.6, 128.2, 126.1, 125.2, 118.0, 51.6, 21.5, 21.4. HRMS (ESI+) exact mass calculated for [M+Na]⁺ (C₂₁H₂₀NaO₄): 359.1254, found: 359.1261.



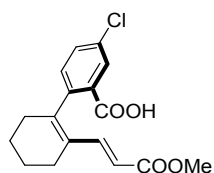
6'-(3-methoxy-3-oxoprop-1-en-1-yl)-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-2-carboxylic acid (3wa)

Prepared according to general procedure D, purification of the residue by preparative chromatography (PE/EA/ acetic acid = 3/1/0.05) afforded the product as a white solid (13.4 mg, 47% yield), ¹H NMR (400 MHz, CDCl₃) δ 8.11 (d, *J* = 7.9 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 7.6 Hz, 1H), 7.04 (d, *J* = 15.7 Hz, 1H), 5.79 (d, *J* = 15.7 Hz, 1H), 3.62 (s, 3H), 2.55 – 2.47 (m, 1H), 2.34 – 2.22 (m, 3H), 1.93 – 1.86 (m, 1H), 1.80 – 1.70 (m, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 171.0, 168.0, 148.5, 144.6, 144.2, 133.1, 131.7, 130.3, 128.5, 127.8, 127.5, 114.9, 51.3, 34.0, 24.9, 22.7, 22.2. HRMS (ESI+) exact mass calculated for [M+Na]⁺ (C₁₇H₁₈NaO₄): 309.1097, found: 309.1101.



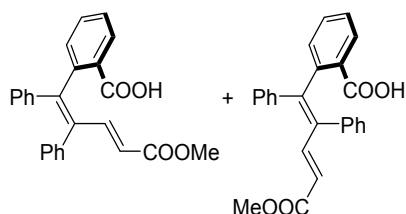
6'-(3-methoxy-3-oxoprop-1-en-1-yl)-4-methyl-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-2-carboxylic acid (3xa)

Prepared according to general procedure D, purification of the residue by preparative chromatography (PE/EA/ acetic acid = 3/1/0.05) afforded the product as a white solid (14.7 mg, 49% yield), ^1H NMR (400 MHz, CDCl_3) δ 7.91 (s, 1H), 7.35 (d, $J = 7.7$ Hz, 1H), 7.07 (d, $J = 15.8$ Hz, 1H), 6.99 (d, $J = 7.7$ Hz, 1H), 5.77 (d, $J = 15.7$ Hz, 1H), 3.63 (s, 3H), 2.41 (s, 3H), 2.31 – 2.19 (m, 4H), 1.90 – 1.73 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 170.7, 168.1, 148.7, 144.4, 141.7, 137.3, 133.8, 132.2, 130.2, 128.5, 127.5, 114.6, 51.3, 34.1, 24.9, 22.7, 22.2, 21.0. HRMS (ESI+) exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{18}\text{H}_{20}\text{NaO}_4$): 323.1254, found: 323.1251.



4-chloro-6'-(3-methoxy-3-oxoprop-1-en-1-yl)-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-2-carboxylic acid (3ya)

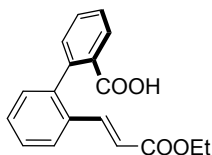
Prepared according to general procedure D, purification of the residue by preparative chromatography (PE/EA/ acetic acid = 3/1/0.05) afforded the product as a white solid (14.4 mg, 45% yield), ^1H NMR (400 MHz, CDCl_3) δ 8.09 (d, $J = 2.2$ Hz, 1H), 7.53 (dd, $J = 8.2, 2.3$ Hz, 1H), 7.07 (d, $J = 8.2$ Hz, 1H), 7.00 (d, $J = 15.7$ Hz, 1H), 5.81 (d, $J = 15.7$ Hz, 1H), 3.64 (s, 3H), 2.50 – 2.43 (m, 1H), 2.31 – 2.19 (m, 3H), 1.90 – 1.84 (m, 1H), 1.78 – 1.69 (m, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 169.4, 168.0, 147.0, 143.7, 142.9, 133.5, 133.1, 131.7, 131.6, 129.3, 129.1, 115.4, 51.4, 33.9, 24.9, 22.6, 22.1. HRMS (ESI+) exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{17}\text{H}_{17}\text{ClNaO}_4$): 343.0708, found: 343.0710.



2-((1E,3E)-5-methoxy-5-oxo-1,2-diphenylpenta-1,3-dien-1-yl)benzoic acid (3za) + 2-((1Z,3E)-5-methoxy-5-oxo-1,2-diphenylpenta-1,3-dien-1-yl)benzoic acid (3za')

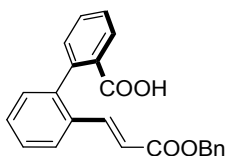
Prepared according to general procedure D, purification of the residue by preparative chromatography (PE/EA/ acetic acid = 3/1/0.05) afforded the product as a white solid (26.1 mg, 68% yield), ^1H NMR (400 MHz, CDCl_3) δ 8.12 (d, $J = 7.8$ Hz, 0.8H, 3xa), 7.87 (d, $J = 15.6$ Hz, 0.2H, 3xa'), 7.77 (d, $J = 7.7$ Hz, 0.2H, 3xa'), 7.63 (td, $J = 7.5, 1.1$ Hz, 0.8H, 3xa), 7.49 (td, $J = 7.7, 1.0$ Hz, 0.8H, 3xa), 7.39 – 7.33

(m, 1.6H, 3xa), 7.27 – 7.09 (m, 6.6H, 3xa + 3xa'), 7.00 – 6.86 (m, 4H, 3xa + 3xa'), 5.63 (d, $J = 15.6$ Hz, 0.2H, 3xa'), 5.57 (d, $J = 15.5$ Hz, 0.8H, 3xa), 3.69 (s, 0.6H, 3xa'), 3.61 (s, 2.4H, 3xa). ^{13}C NMR (101 MHz, CDCl_3) δ 171.6, 171.5, 168.0, 167.8, 149.1, 148.2, 145.7, 145.4, 144.3, 143.0, 140.3, 139.5, 139.1, 138.6, 136.5, 132.9, 132.2, 131.6, 131.1, 130.8, 130.8, 130.5, 128.3, 128.3, 128.0, 127.8, 127.2, 127.1, 125.2, 122.0, 121.4, 51.6, 51.5. HRMS (ESI+) exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{25}\text{H}_{20}\text{NaO}_4$): 407.1254, found: 407.1247.



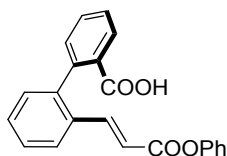
2'-(3-ethoxy-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2-carboxylic acid (3ab)

Prepared according to general procedure A, purification of the residue by preparative chromatography (PE/EA/ acetic acid = 3/1/0.05) afforded the product as a white solid (19.2 mg, 65% yield), ^1H NMR (501 MHz, CDCl_3) δ 8.06 (d, $J = 8.0$ Hz, 1H), 7.67 – 7.65 (m, 1H), 7.59 – 7.56 (m, 1H), 7.49 – 7.46 (m, 1H), 7.43 (d, $J = 15.9$ Hz, 1H), 7.38 – 7.36 (m, 2H), 7.22 (d, $J = 8.0$ Hz, 1H), 7.18 (d, $J = 5.3$ Hz, 1H), 6.29 (d, $J = 15.9$ Hz, 1H), 4.14 (q, $J = 7.1$ Hz, 2H), 1.23 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 171.3, 166.8, 142.8, 142.2, 141.6, 132.6, 132.3, 131.8, 131.1, 129.6, 129.4, 129.3, 127.9, 127.7, 126.0, 119.2, 60.3, 14.2. HRMS (ESI+) exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{18}\text{H}_{16}\text{NaO}_4$): 319.0941, found: 319.0944.



2'-(3-(benzyloxy)-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2-carboxylic acid (3ac)

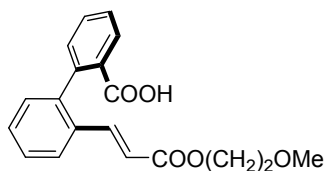
Prepared according to general procedure A, purification of the residue by preparative chromatography (PE/EA/ acetic acid = 3/1/0.05) afforded the product as a white solid (24.7 mg, 69% yield), ^1H NMR (501 MHz, CDCl_3) δ 8.05 (d, $J = 7.1$ Hz, 1H), 7.69 – 7.62 (m, 1H), 7.57 (td, $J = 8.0, 1.2$ Hz, 1H), 7.50 – 7.46 (m, 2H), 7.40 – 7.27 (m, 7H), 7.22 (d, $J = 8.0$ Hz, 1H), 7.18 – 7.16 (m, 1H), 6.35 (d, $J = 15.9$ Hz, 1H), 5.18 – 5.09 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 171.9, 166.7, 143.5, 142.4, 141.6, 136.1, 132.5, 132.4, 131.9, 131.2, 129.7, 129.6, 129.6, 128.5, 128.1, 128.0, 127.9, 127.8, 126.0, 118.8, 66.2. HRMS (ESI+) exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{23}\text{H}_{18}\text{NaO}_4$): 381.1097, found: 381.1089.



2'-(3-oxo-3-phenoxyprop-1-en-1-yl)-[1,1'-biphenyl]-2-carboxylic acid (3ad)

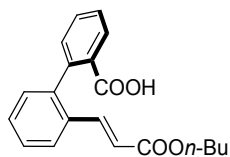
Prepared according to general procedure A, purification of the residue by preparative chromatography (PE/EA/ acetic acid = 3/1/0.05) afforded the product as a white solid (24.4 mg, 71% yield), ^1H NMR

(501 MHz, CDCl₃) δ 8.06 (d, J = 8.1 Hz, 1H), 7.78 – 7.70 (m, 1H), 7.59 (m, 2H), 7.47 (t, J = 7.5 Hz, 1H), 7.44 – 7.38 (m, 2H), 7.35 (t, J = 7.5 Hz, 2H), 7.26 – 7.18 (m, 3H), 7.07 (d, J = 7.8 Hz, 2H), 6.49 (d, J = 15.9 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 171.7, 165.2, 150.7, 144.7, 142.5, 141.4, 132.5, 132.4, 131.8, 131.2, 129.8, 129.7, 129.4, 129.3, 128.0, 127.8, 126.2, 125.7, 121.6, 118.3. HRMS (ESI+) exact mass calculated for [M+Na]⁺ (C₂₂H₁₆NaO₄): 367.0941, found: 367.0937.



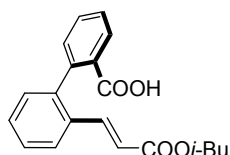
2'-(3-(2-methoxyethoxy)-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2-carboxylic acid (3ae)

Prepared according to general procedure A, purification of the residue by preparative chromatography (PE/EA/ acetic acid = 3/1/0.05) afforded the product as a white solid (20.5 mg, 63% yield), ¹H NMR (501 MHz, CDCl₃) δ 8.03 (d, J = 8.0 Hz, 1H), 7.66 – 7.64 (m, 1H), 7.58 – 7.55 (m, 1H), 7.47 – 7.44 (m, 2H), 7.36 – 7.42 (m, 2H), 7.20 (d, J = 8.0 Hz, 1H), 7.18 – 7.16 (m, 1H), 6.35 (d, J = 15.9 Hz, 1H), 4.24 (t, J = 5.0 Hz, 2H), 3.57 (t, J = 5.0 Hz, 2H), 3.33 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 171.2, 166.8, 143.4, 142.4, 141.5, 132.5, 132.2, 131.8, 131.1, 129.7, 129.5, 128.0, 127.9, 127.7, 126.0, 118.7, 70.4, 63.5, 59.0. HRMS (ESI+) exact mass calculated for [M+Na]⁺ (C₁₉H₁₈NaO₅): 349.1046, found: 349.1039.



2'-(3-butoxy-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2-carboxylic acid (3af)

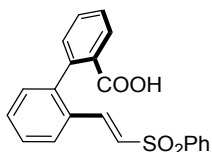
Prepared according to general procedure A, purification of the residue by preparative chromatography (PE/EA/ acetic acid = 3/1/0.05) afforded the product as a white solid (21.4 mg, 66% yield), ¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, J = 7.6 Hz, 1H), 7.68 – 7.61 (m, 1H), 7.58 – 7.55 (m, 1H), 7.48 – 7.33 (m, 4H), 7.25 – 7.11 (m, 2H), 6.29 (d, J = 15.9 Hz, 1H), 4.08 (t, J = 6.5 Hz, 2H), 1.66 – 1.50 (m, 2H), 1.37 – 1.25 (m, 3H), 0.89 (t, J = 7.4 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 171.4, 167.0, 142.8, 142.3, 141.4, 132.5, 132.1, 131.7, 131.0, 129.6, 129.3, 127.8, 127.6, 125.9, 119.0, 64.3, 30.5, 19.0, 13.7. HRMS (ESI+) exact mass calculated for [M+Na]⁺ (C₂₀H₂₀NaO₄): 347.1254, found: 347.1247.



2'-(3-isobutoxy-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2-carboxylic acid (3ag)

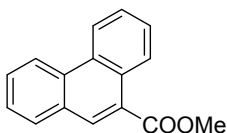
Prepared according to general procedure A, purification of the residue by preparative chromatography (PE/EA/ acetic acid = 3/1/0.05) afforded the product as a white solid (20.1 mg, 62% yield), ¹H NMR (501 MHz, CDCl₃) δ 8.05 (d, J = 7.7 Hz, 1H), 7.69 – 7.64 (m, 1H), 7.58 – 7.55 (m, 1H), 7.48 – 7.36 (m,

4H), 7.23 – 7.16 (m, 2H), 6.30 (d, $J = 15.9$ Hz, 1H), 3.86 (d, $J = 6.4$ Hz, 2H), 1.94 – 1.82 (m, 1H), 0.87 (d, $J = 6.6$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 171.4, 166.9, 142.7, 142.3, 141.6, 132.5, 132.3, 131.8, 131.1, 129.5, 129.4, 129.4, 127.8, 127.7, 125.9, 119.1, 70.4, 27.7, 19.0. HRMS (ESI+) exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{20}\text{H}_{20}\text{NaO}_4$): 347.1254, found: 347.1247.



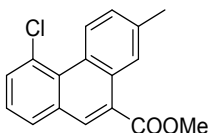
2'-(2-(phenylsulfonyl)vinyl)-[1,1'-biphenyl]-2-carboxylic acid (3ai)

Prepared according to general procedure A, purification of the residue by preparative chromatography (PE/EA/ acetic acid = 3/1/0.05) afforded the product as a white solid (18.6 mg, 51% yield), ^1H NMR (501 MHz, CDCl_3) δ 8.02 (d, $J = 7.5$ Hz, 1H), 7.76 (d, $J = 7.5$ Hz, 2H), 7.59 (t, $J = 7.5$ Hz, 1H), 7.55 – 7.32 (m, 8H), 7.19 (d, $J = 7.5$ Hz, 2H), 6.62 (d, $J = 15.9$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 171.2, 142.6, 141.2, 140.9, 140.4, 133.3, 132.7, 131.8, 131.4, 130.9, 130.3, 129.8, 129.3, 129.2, 128.6, 128.3, 127.9, 127.6, 126.8. HRMS (ESI+) exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{21}\text{H}_{16}\text{NaO}_4\text{S}$): 387.0662, found: 387.0670.



methyl phenanthrene-9-carboxylate (7a)

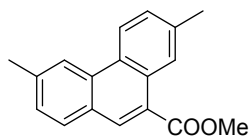
Prepared according to general procedure F, purification of the residue by preparative chromatography (PE/EA = 10/1) afforded the product as a white solid (21.0 mg, 89% yield), ^1H NMR (400 MHz, CDCl_3) δ 8.97 – 8.90 (m, 1H), 8.75 – 8.71 (m, 1H), 8.68 (d, $J = 8.4$ Hz, 1H), 8.48 (s, 1H), 7.96 (d, $J = 8.3$ Hz, 1H), 7.77 – 7.67 (m, 3H), 7.66 – 7.60 (m, 1H), 4.05 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 168.0, 132.4, 132.1, 130.6, 130.0, 129.9, 129.0, 128.9, 127.4, 127.00, 126.9, 126.6, 126.1, 122.8, 122.6, 52.3. HRMS (ESI+) exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{16}\text{H}_{12}\text{NaO}_2$): 259.0730, found: 259.0726.



methyl 4-chloro-7-methylphenanthrene-9-carboxylate (7b)

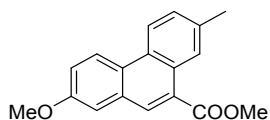
Prepared according to general procedure F, purification of the residue by preparative chromatography (PE/EA = 10/1) afforded the product as a white solid (7.7 mg, 27% yield), ^1H NMR (400 MHz, CDCl_3) δ 9.79 (d, $J = 8.8$ Hz, 1H), 8.61 (s, 1H), 8.31 (s, 1H), 7.85 (dd, $J = 7.8, 1.1$ Hz, 1H), 7.80 (dd, $J = 7.7, 1.4$ Hz, 1H), 7.52 (dd, $J = 8.9, 1.8$ Hz, 1H), 7.48 (t, $J = 7.7$ Hz, 1H), 4.05 (s, 3H), 2.59 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 167.9, 137.7, 132.8, 132.7, 132.0, 131.1, 130.2, 129.4, 129.2, 127.9, 127.7, 127.3, 127.0, 126.3, 125.7, 52.4, 29.7, 21.8. HRMS (ESI+) exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{17}\text{H}_{13}\text{ClNaO}_2$):

307.0496, found: 307.0491.



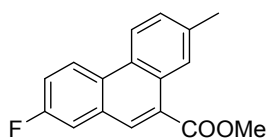
methyl 3,7-dimethylphenanthrene-9-carboxylate (7c)

Prepared according to general procedure F, purification of the residue by preparative chromatography (PE/EA = 10/1) afforded the product as a white solid (16.9 mg, 64% yield), ^1H NMR (400 MHz, CDCl_3) δ 8.72 (s, 1H), 8.59 (d, $J = 8.5$ Hz, 1H), 8.42 (s, 2H), 7.82 (d, $J = 8.2$ Hz, 1H), 7.50 (dd, $J = 8.5$, 1.6 Hz, 1H), 7.42 (d, $J = 7.6$ Hz, 1H), 4.04 (s, 3H), 2.62 (s, 3H), 2.60 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 168.2, 139.0, 137.1, 132.4, 132.3, 129.7, 129.3, 128.4, 128.3, 128.2, 127.6, 126.0, 124.7, 122.6, 122.2, 52.1, 22.3, 21.9. HRMS (ESI+) exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{18}\text{H}_{16}\text{NaO}_2$): 287.1043, found: 287.1038.



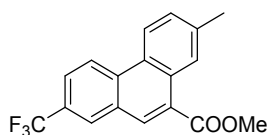
methyl 2-methoxy-7-methylphenanthrene-9-carboxylate (7d)

Prepared according to general procedure F, purification of the residue by preparative chromatography (PE/EA = 10/1) afforded the product as a white solid (16.5 mg, 59% yield), ^1H NMR (400 MHz, CDCl_3) δ 8.65 (s, 1H), 8.52 (d, $J = 9.1$ Hz, 1H), 8.49 (d, $J = 8.5$ Hz, 1H), 8.36 (s, 1H), 7.48 (dd, $J = 8.5$, 1.6 Hz, 1H), 7.34 (dd, $J = 9.1$, 2.7 Hz, 1H), 7.28 (d, $J = 2.7$ Hz, 1H), 4.04 (s, 3H), 3.95 (s, 3H), 2.58 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 168.2, 158.1, 136.2, 131.7, 130.9, 128.7, 128.1, 126.6, 126.4, 126.0, 124.0, 122.2, 119.5, 109.3, 55.4, 52.2, 21.8. HRMS (ESI+) exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{18}\text{H}_{16}\text{NaO}_3$): 303.0992, found: 303.0987.



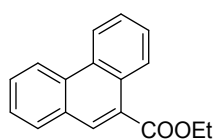
methyl 2-fluoro-7-methylphenanthrene-9-carboxylate (7e)

Prepared according to general procedure F, purification of the residue by preparative chromatography (PE/EA = 10/1) afforded the product as a white solid (13.9 mg, 52% yield), ^1H NMR (400 MHz, CDCl_3) δ 8.64 (s, 1H), 8.59 (dd, $J = 9.1$, 5.2 Hz, 1H), 8.50 (d, $J = 8.5$ Hz, 1H), 8.31 (s, 1H), 7.56 – 7.49 (m, 2H), 7.44 (td, $J = 8.7$, 2.7 Hz, 1H), 4.05 (s, 3H), 2.58 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 167.9, 161.1 (d, $J = 246.7$ Hz), 137.1, 131.1 (d, $J = 3.9$ Hz), 130.9 (d, $J = 8.9$ Hz), 129.0, 128.7 (d, $J = 2.0$ Hz), 128.6, 128.3, 127.3, 126.2, 124.8 (d, $J = 8.5$ Hz), 122.5, 117.7 (d, $J = 23.6$ Hz), 113.6 (d, $J = 20.6$ Hz), 52.3, 21.8. HRMS (ESI+) exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{17}\text{H}_{13}\text{FNaO}_2$): 291.0792, found: 291.0787.



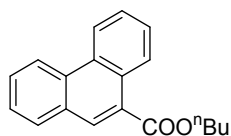
methyl 7-methyl-2-(trifluoromethyl)phenanthrene-9-carboxylate (7f)

Prepared according to general procedure F, purification of the residue by preparative chromatography (PE/EA = 10/1) afforded the product as a white solid (18.4 mg, 58% yield), ¹H NMR (400 MHz, CDCl₃) δ 8.69 (d, *J* = 6.6 Hz, 2H), 8.58 (dd, *J* = 8.5, 1.3 Hz, 1H), 8.43 (s, 1H), 8.19 (s, 1H), 7.87 (d, *J* = 8.7 Hz, 1H), 7.56 (d, *J* = 8.5 Hz, 1H), 4.06 (s, 3H), 2.61 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.7, 138.6, 134.0, 131.7, 129.8, 129.2, 128.9, 128.4 (q, *J* = 32.8 Hz), 127.8, 127.4, 127.0 (q, *J* = 4.2 Hz), 126.3, 124.5 (q, *J* = 3.1 Hz), 124.2 (q, *J* = 272.2 Hz), 123.4, 123.1, 52.4, 22.0. HRMS (ESI⁺) exact mass calculated for [M+Na]⁺ (C₁₈H₁₃F₃NaO₂): 341.0760, found: 341.0756.



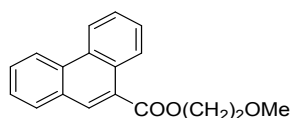
ethyl phenanthrene-9-carboxylate (7g)

Prepared according to general procedure F, purification of the residue by preparative chromatography (PE/EA = 10/1) afforded the product as a white solid (19.5 mg, 78% yield), ¹H NMR (400 MHz, CDCl₃) δ 8.96 – 8.89 (m, 1H), 8.76 – 8.72 (m, 1H), 8.69 (d, *J* = 8.4 Hz, 1H), 8.46 (s, 1H), 7.97 (d, *J* = 7.9 Hz, 1H), 7.77 – 7.73 (m, 1H), 7.72 – 7.67 (m, 2H), 7.66 – 7.61 (m, 1H), 4.53 (q, *J* = 7.1 Hz, 2H), 1.51 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.7, 132.1, 130.7, 130.1, 129.9, 129.0, 128.8, 127.4, 127.0, 126.8, 126.6, 122.8, 122.6, 61.2, 14.4. HRMS (ESI⁺) exact mass calculated for [M+Na]⁺ (C₁₇H₁₄NaO₂): 273.0886, found: 273.0881.



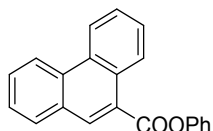
butyl phenanthrene-9-carboxylate (7h)

Prepared according to general procedure F, purification of the residue by preparative chromatography (PE/EA = 10/1) afforded the product as a white solid (13.9 mg, 50% yield), ¹H NMR (400 MHz, CDCl₃) δ 8.96 – 8.89 (m, 1H), 8.76 – 8.71 (m, 1H), 8.69 (d, *J* = 8.4 Hz, 1H), 8.45 (s, 1H), 7.98 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.77 – 7.72 (m, 1H), 7.72 – 7.67 (m, 2H), 7.66 – 7.61 (m, 1H), 4.47 (t, *J* = 6.7 Hz, 2H), 1.92 – 1.82 (m, 2H), 1.59 – 1.52 (m, 2H), 1.04 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.8, 132.1, 130.7, 130.1, 129.9, 129.1, 128.8, 127.3, 127.0, 126.8, 126.7, 126.6, 122.8, 122.6, 65.1, 30.8, 19.4, 13.8. HRMS (ESI⁺) exact mass calculated for [M+Na]⁺ (C₁₉H₁₈NaO₂): 301.1199, found: 301.1195.



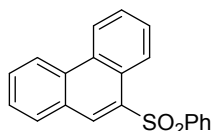
2-methoxyethyl phenanthrene-9-carboxylate (7i)

Prepared according to general procedure F, purification of the residue by preparative chromatography (PE/EA = 10/1) afforded the product as a white solid (12.2 mg, 41% yield), ^1H NMR (400 MHz, CDCl_3) δ 8.96 – 8.90 (m, 1H), 8.75 – 8.71 (m, 1H), 8.69 (d, $J = 8.4$ Hz, 1H), 8.51 (s, 1H), 7.98 (dd, $J = 7.9, 1.2$ Hz, 1H), 7.77 – 7.73 (m, 1H), 7.72 – 7.66 (m, 2H), 7.66 – 7.61 (m, 1H), 4.63 – 4.60 (m, 2H), 3.85 – 3.81 (m, 2H), 3.49 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 167.6, 132.5, 132.2, 130.7, 130.0, 129.9, 129.0, 128.9, 127.4, 127.0, 126.9, 126.6, 126.1, 122.8, 122.6, 70.6, 64.1, 59.1. HRMS (ESI+) exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{18}\text{H}_{16}\text{NaO}_3$): 303.0992, found: 303.0987.



phenyl phenanthrene-9-carboxylate (7j)

Prepared according to general procedure F, purification of the residue by preparative chromatography (PE/EA = 10/1) afforded the product as a white solid (11.9 mg, 40% yield), ^1H NMR (400 MHz, CDCl_3) δ 9.10 – 9.05 (m, 1H), 8.80 – 8.75 (m, 2H), 8.73 (d, $J = 8.3$ Hz, 1H), 8.04 (dd, $J = 7.9, 1.1$ Hz, 1H), 7.83 – 7.78 (m, 1H), 7.76 – 7.71 (m, 2H), 7.70 – 7.66 (m, 1H), 7.53 – 7.48 (m, 2H), 7.37 – 7.31 (m, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 165.8, 151.0, 133.7, 132.5, 130.8, 130.2, 129.9, 129.6, 129.4, 129.1, 127.7, 127.2, 127.1, 126.6, 126.0, 125.0, 122.9, 122.7, 121.9. HRMS (ESI+) exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{21}\text{H}_{14}\text{NaO}_2$): 321.0886, found: 321.0880.



9-(phenylsulfonyl)phenanthrene (7k)

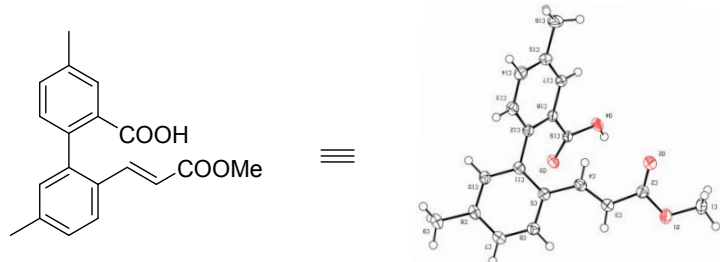
Prepared according to general procedure F, purification of the residue by preparative chromatography (PE/EA = 10/1) afforded the product as a white solid (13.4 mg, 42% yield), ^1H NMR (400 MHz, CDCl_3) δ 8.92 (s, 1H), 8.70 (d, $J = 8.2$ Hz, 1H), 8.67 (d, $J = 8.4$ Hz, 1H), 8.63 (dd, $J = 8.4, 0.9$ Hz, 1H), 8.10 (dd, $J = 7.9, 1.2$ Hz, 1H), 8.03 – 7.98 (m, 2H), 7.82 (ddd, $J = 8.4, 7.1, 1.4$ Hz, 1H), 7.74 – 7.69 (m, 1H), 7.67 (ddd, $J = 8.3, 7.1, 1.4$ Hz, 1H), 7.60 (ddd, $J = 8.3, 7.1, 1.3$ Hz, 1H), 7.55 – 7.50 (m, 1H), 7.49 – 7.44 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 141.6, 134.1, 133.1, 133.0, 132.8, 131.2, 130.8, 130.1, 129.3, 129.1, 127.7, 127.5, 127.4, 125.9, 125.4, 123.3, 122.8. HRMS (ESI+) exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{20}\text{H}_{14}\text{NaO}_2\text{S}$): 341.0607, found: 341.0604.

4. Crystallographic Data

General procedure for the crystal preparation

In a 10 mm × 100 mm tube, 10 mg 3fa or 7a was dissolved in 0.5 mL DCM. Then 5 mL hexane was added carefully and slowly. The tube was placed in a clean and stable environment to let the solvent evaporate naturally until crystals appear.

X-ray data for 3fa (CCDC 1981722)



compound	3fa
formula	C ₁₉ H ₁₈ O ₄
formula weight	310.00
<i>T</i> (K)	100.00(10)
crystal system	triclinic
space group	<i>P</i> -1
<i>a</i> (Å)	7.6320(2)
<i>b</i> (Å)	9.3257(3)
<i>c</i> (Å)	13.0604(4)
α (°)	69.364(3)
β (°)	89.097(2)
γ (°)	72.184(3)
<i>V</i> (Å ³)	823.76(5)
<i>Z</i>	2
<i>D_c</i> (g cm ⁻³)	1.251
μ (mm ⁻¹)	0.713
reflns coll.	8544
unique reflns	3288
<i>R</i> _{int}	0.0230
^a <i>R</i> _I [<i>I</i> ≥ 2σ(<i>I</i>)]	0.0415
^b <i>wR</i> ₂ (all data)	0.1154
GOF	1.076

$${}^a R_I = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, {}^b wR_2 = \left[\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right]^{1/2}$$

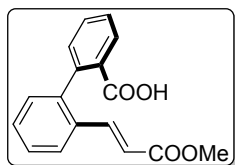
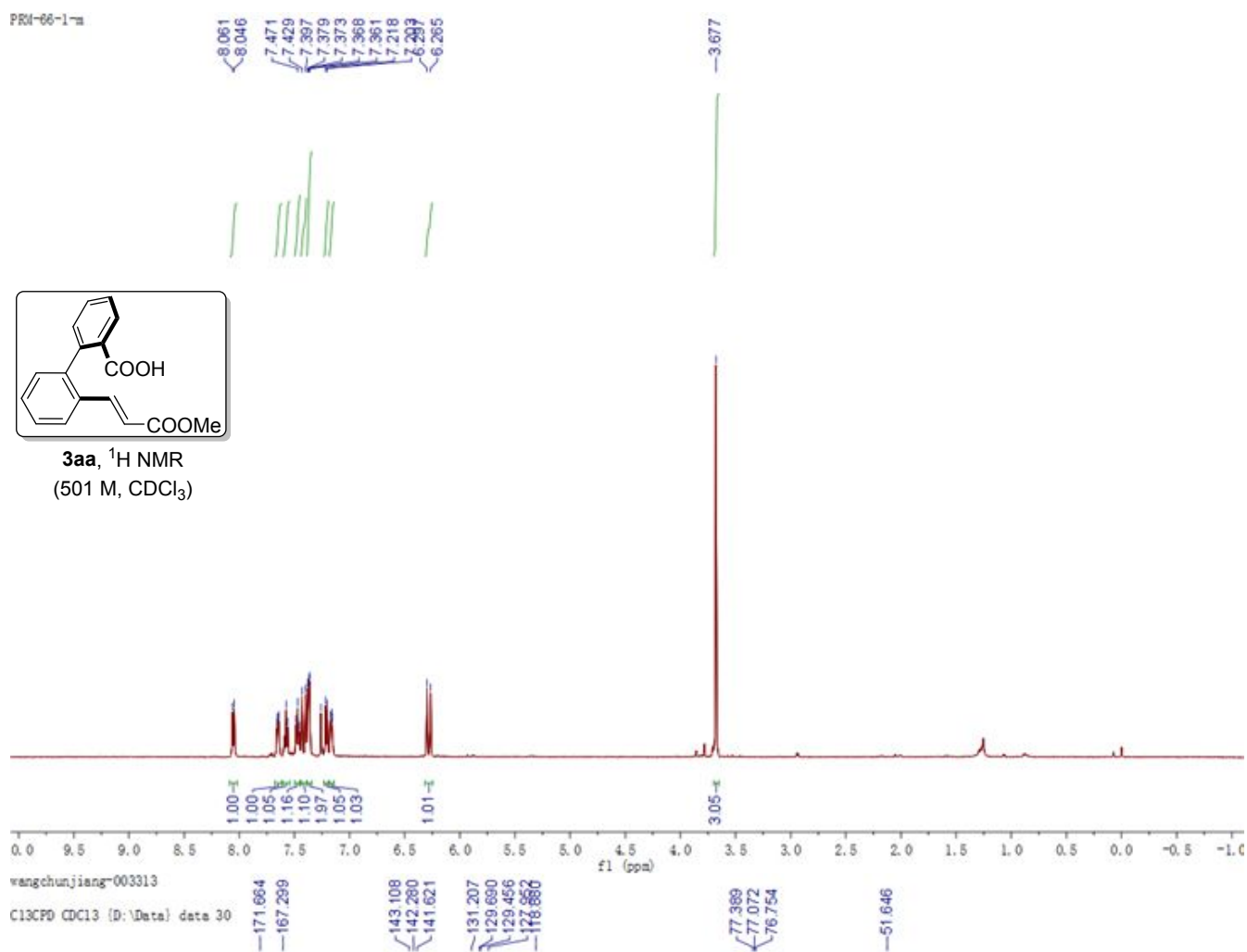
X-ray data for 7a (CCDC 1981706)



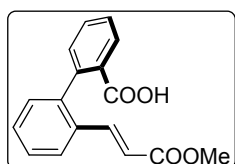
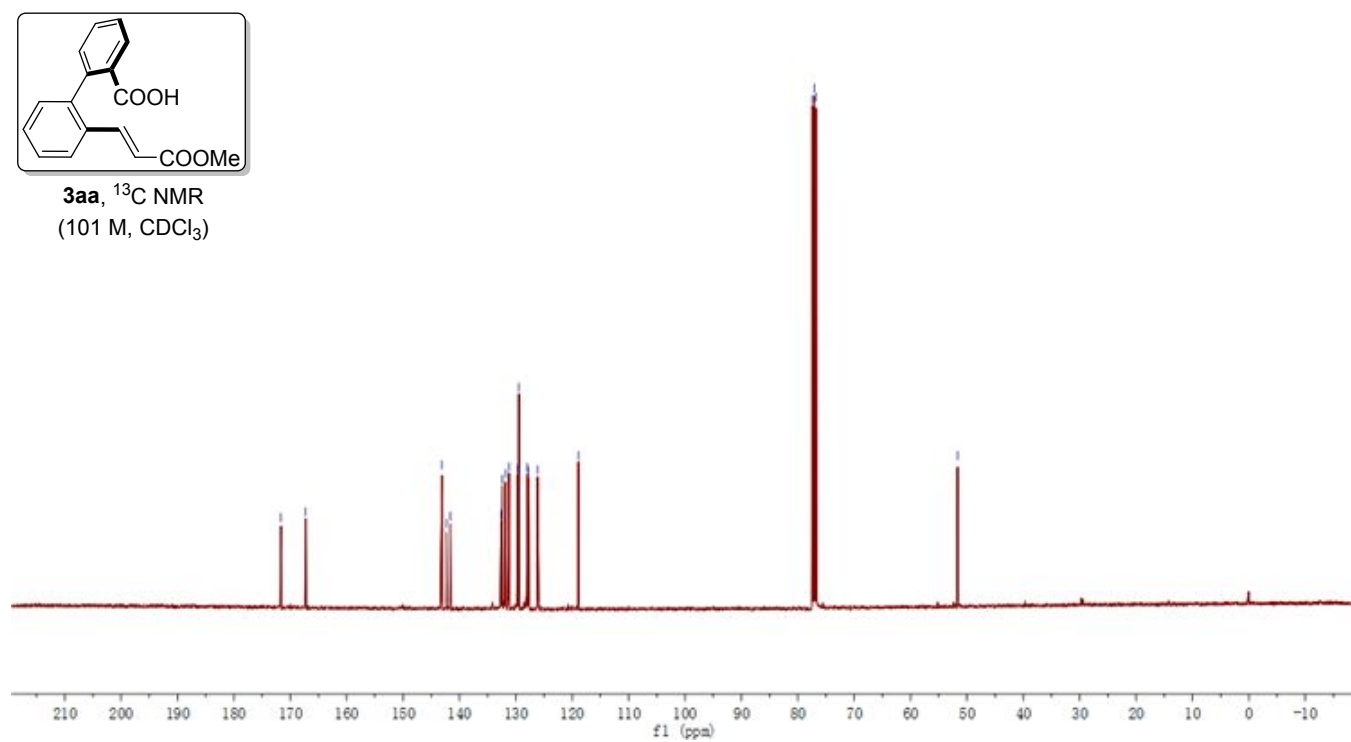
compound	7a
formula	C ₁₆ H ₁₂ O ₂
formula weight	236.26
<i>T</i> (K)	100
crystal system	monoclinic
space group	<i>C</i> 2
<i>a</i> (Å)	21.6144(5)
<i>b</i> (Å)	5.84580(10)
<i>c</i> (Å)	9.2932(2)
<i>α</i> (°)	90
<i>β</i> (°)	100.440(2)
<i>γ</i> (°)	90
<i>V</i> (Å ³)	1154.79(4)
<i>Z</i>	4
<i>D_c</i> (g cm ⁻³)	1.359
<i>μ</i> (mm ⁻¹)	0.712
reflns coll.	2951
unique reflns	1630
<i>R</i> _{int}	0.0238
^a <i>R</i> _I [<i>I</i> ≥ 2σ(<i>I</i>)]	0.0368
^b <i>wR</i> ₂ (all data)	0.1039
GOF	1.078

$${}^a R_I = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \quad {}^b wR_2 = \left[\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right]^{1/2}$$

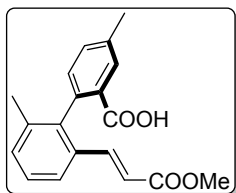
5. NMR Spectra



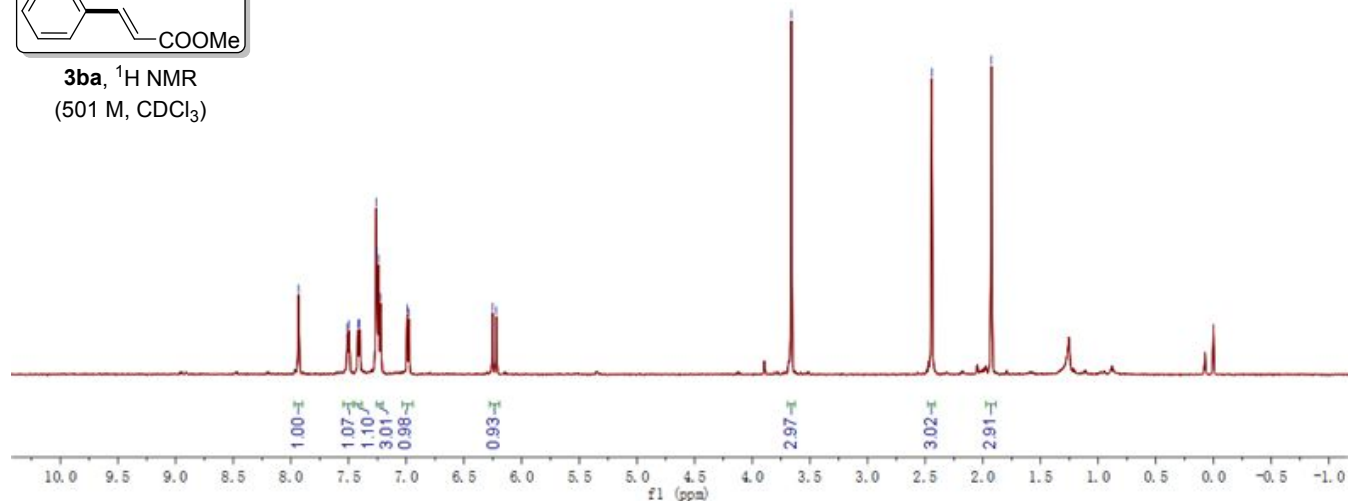
3aa, ^1H NMR
(501 M, CDCl_3)



3aa, ^{13}C NMR
(101 M, CDCl_3)

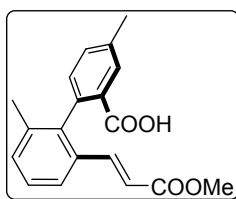


3ba, ¹H NMR
(501 M, CDCl₃)

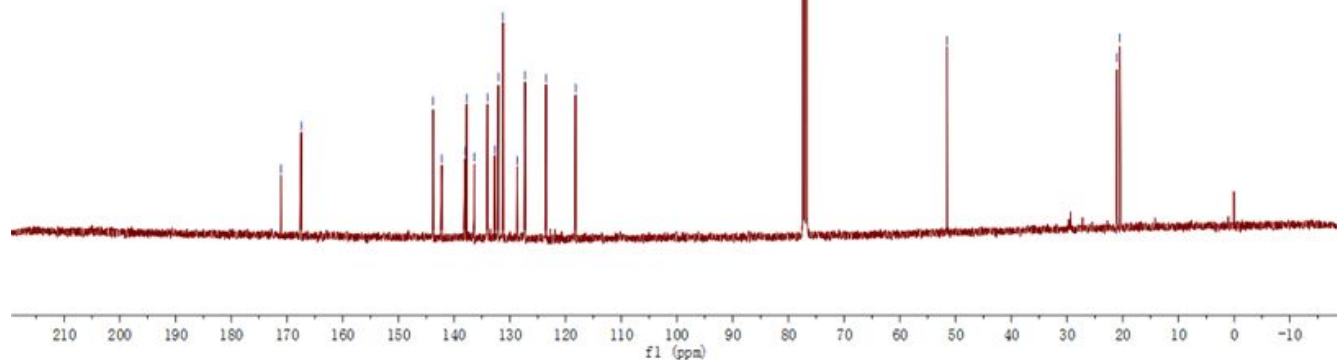


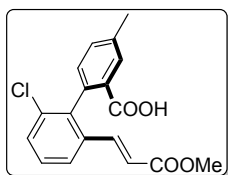
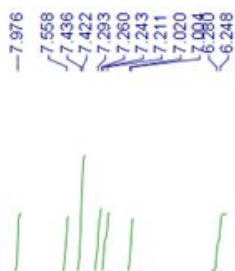
wangchunjiang-003313

C13CPD CDCl3 [D:\Data] data 36

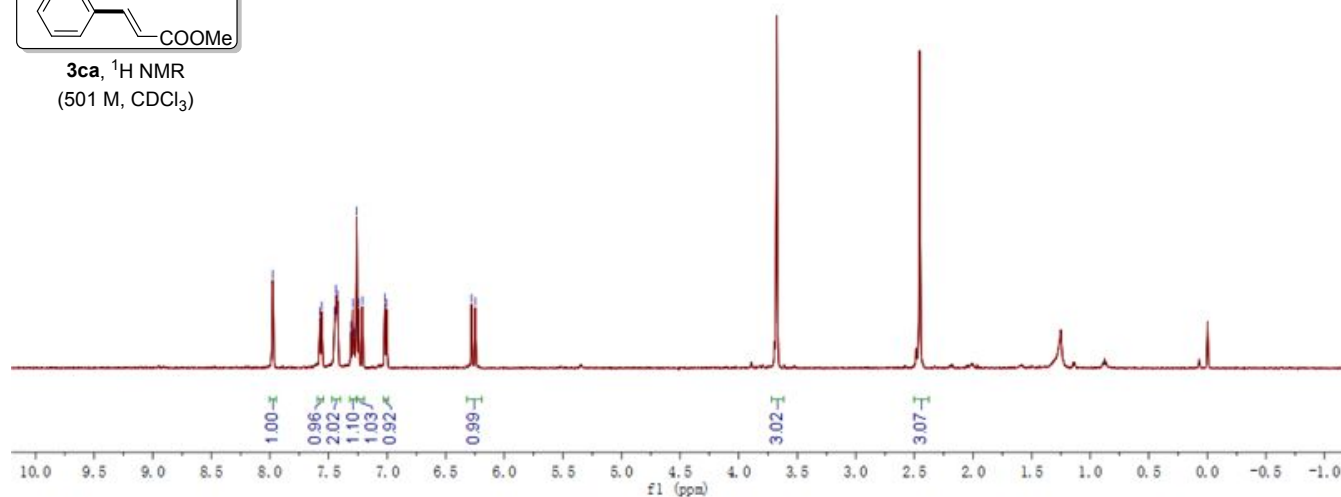


3ba, ¹³C NMR
(101 M, CDCl₃)



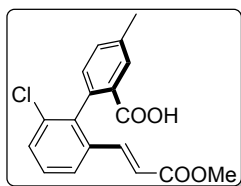


3ca, ¹H NMR
(501 M, CDCl₃)

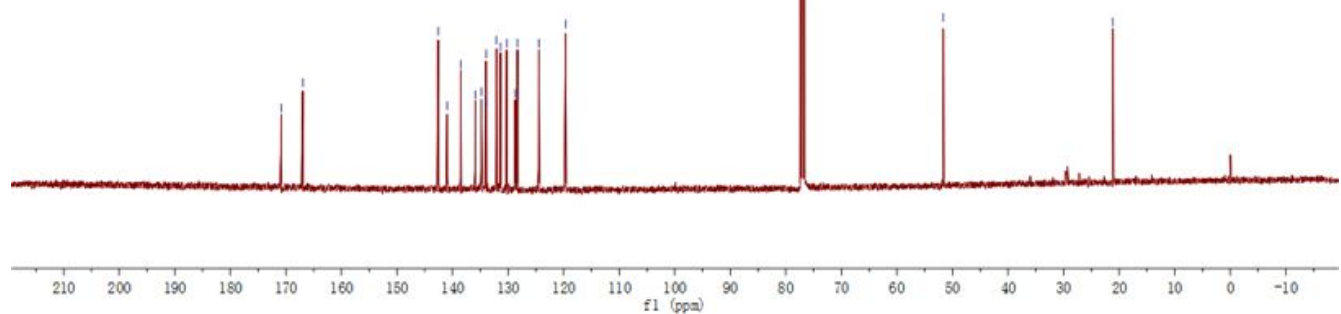


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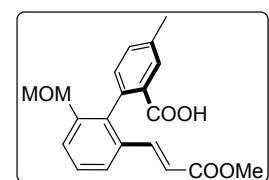
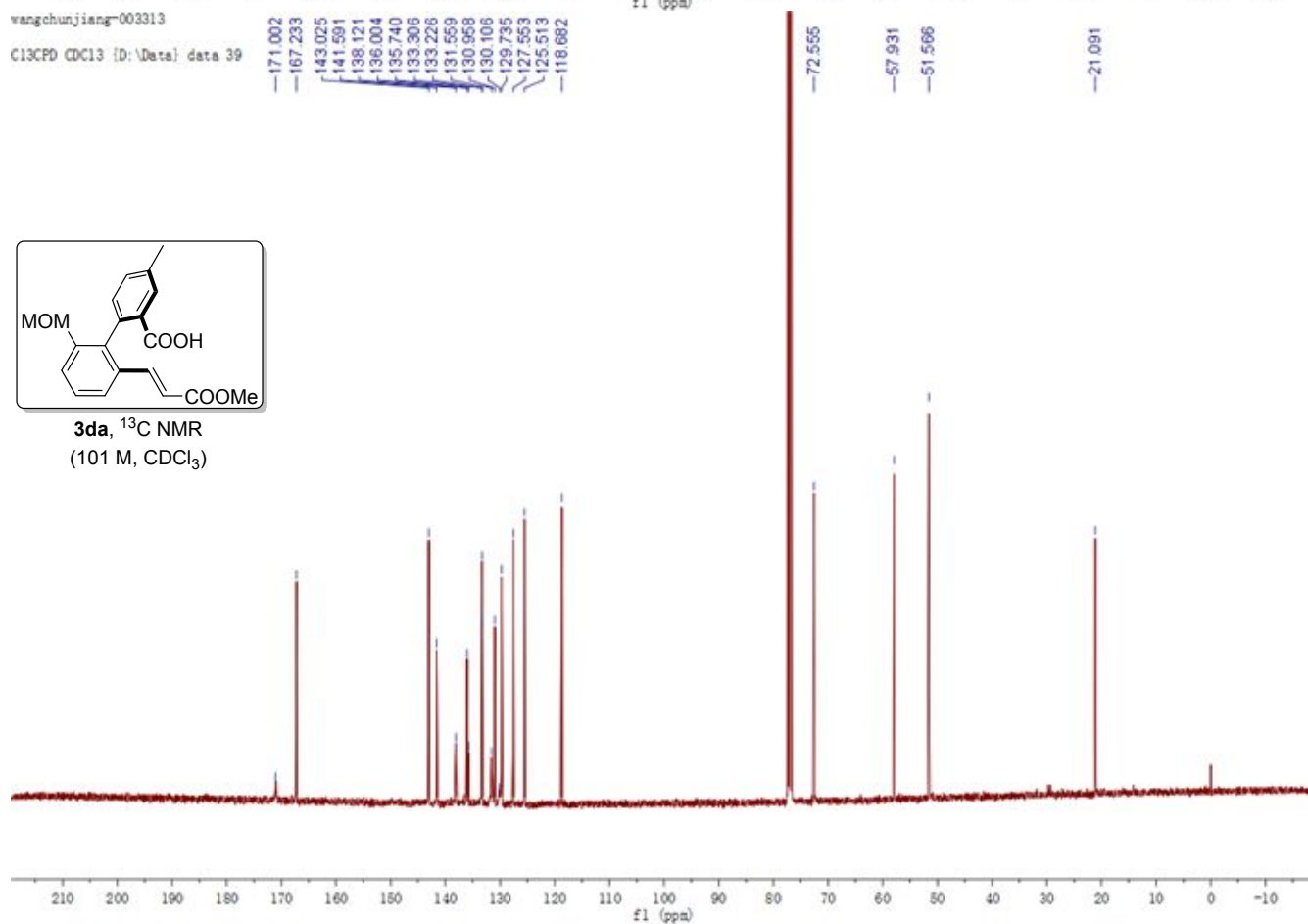
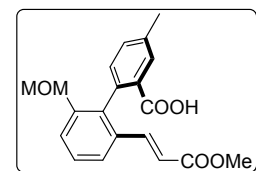
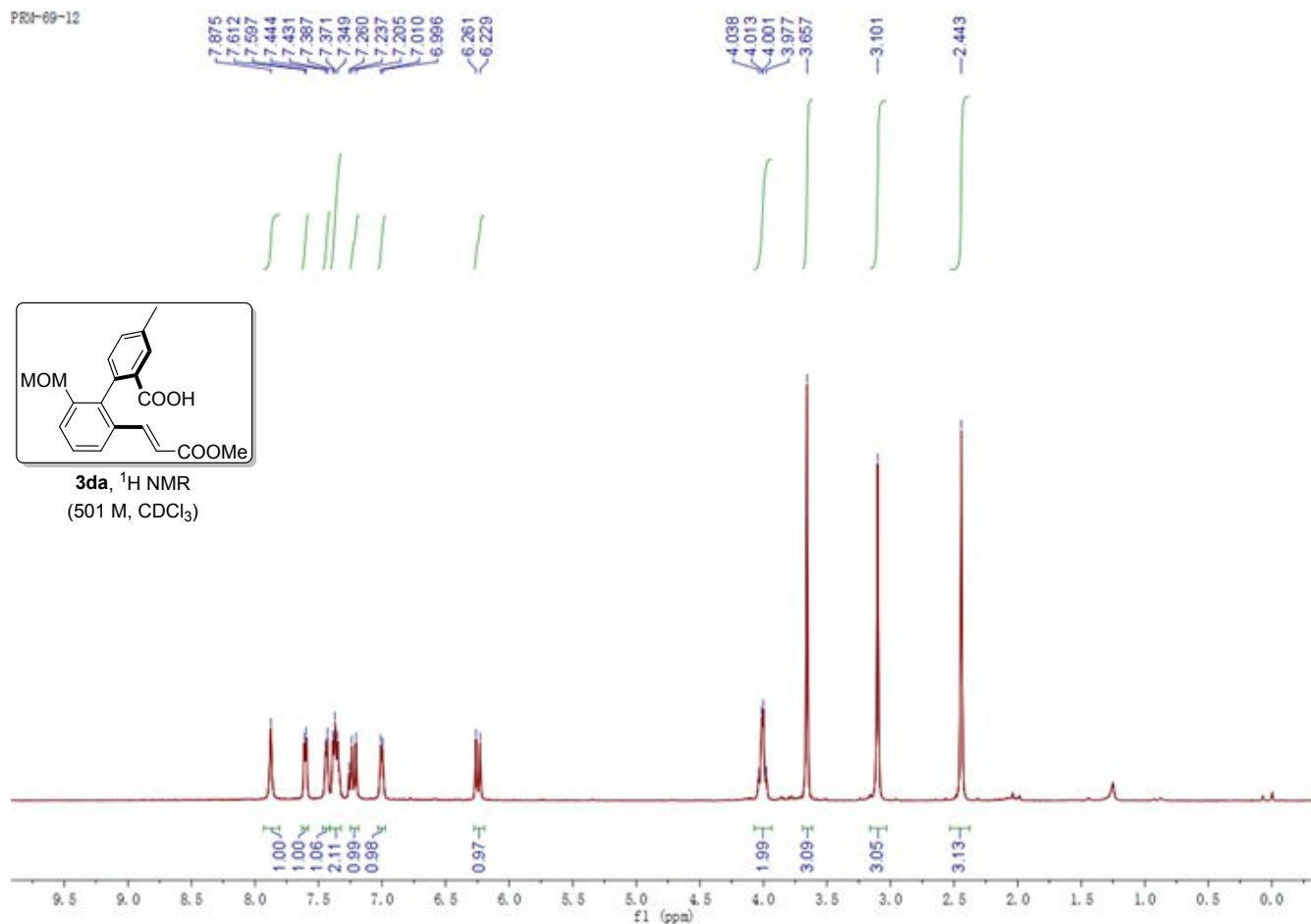
C13CPD CDCl3 [D:\Data] data 37



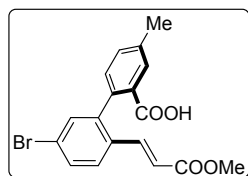
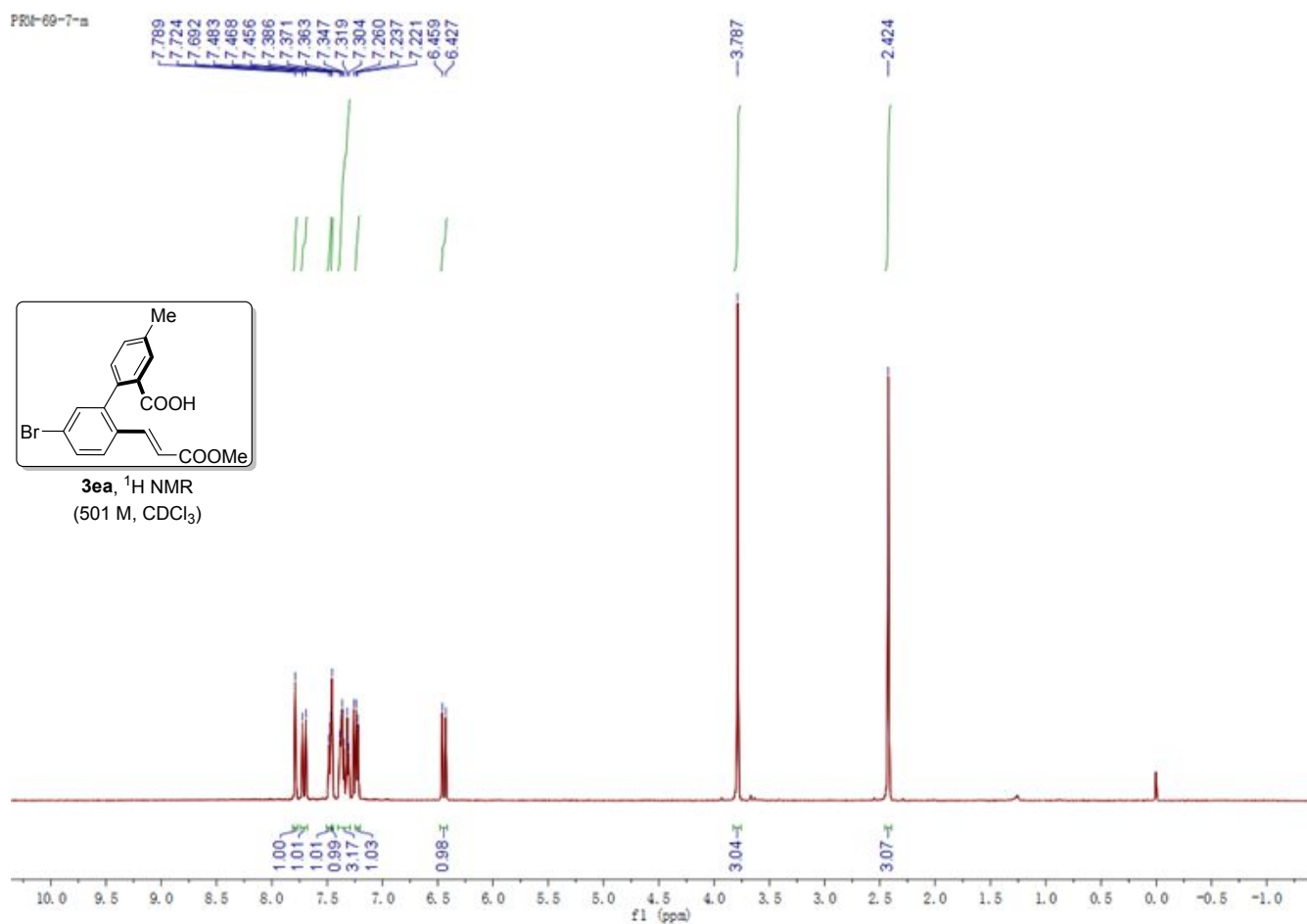
3ca, ¹³C NMR
(101 M, CDCl₃)



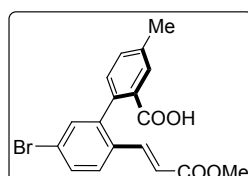
PR1-69-12



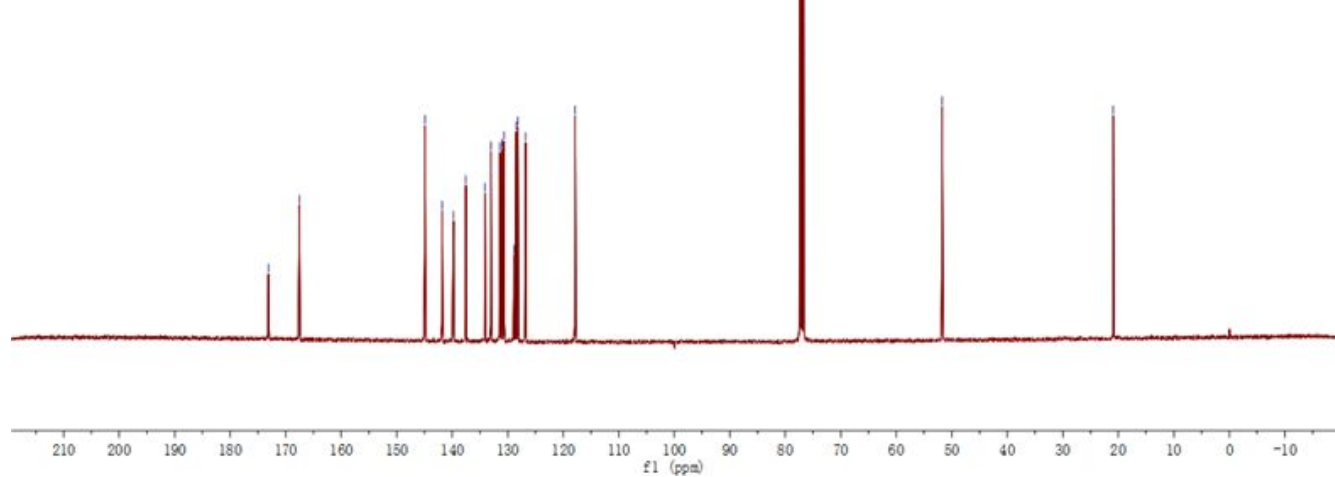
3da, ¹³C NMR
(101 M, CDCl₃)



3ea, ^1H NMR
(501 M, CDCl_3)

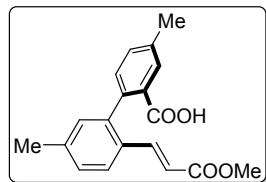


3ea, ^{13}C NMR
(101 M, CDCl_3)

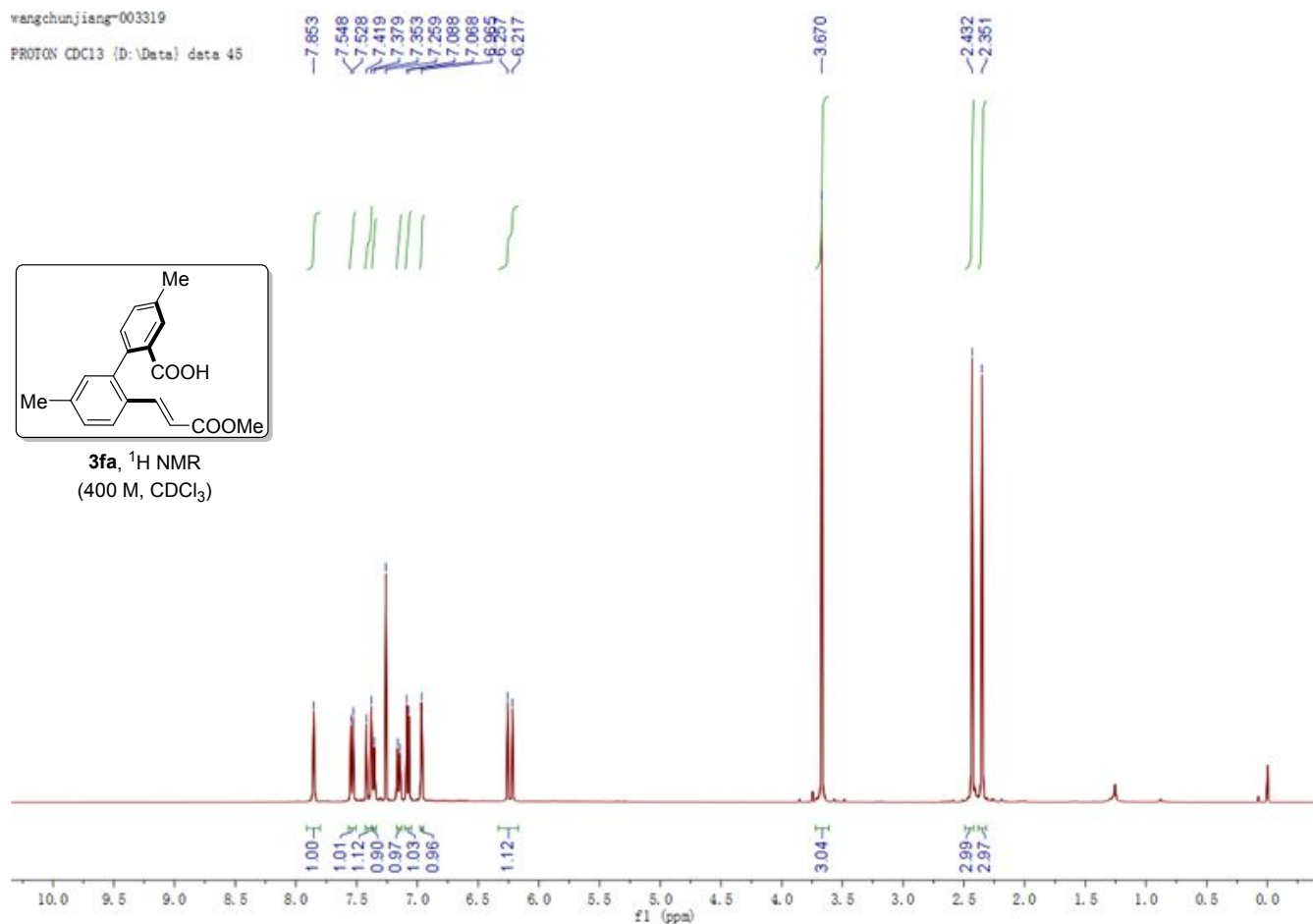


wangchunjiang-003319

PROTON CDC13 [D:\Data] data 45

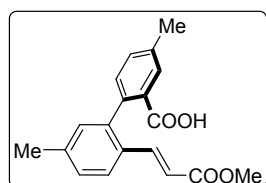


3fa, ^1H NMR
(400 M, CDCl_3)

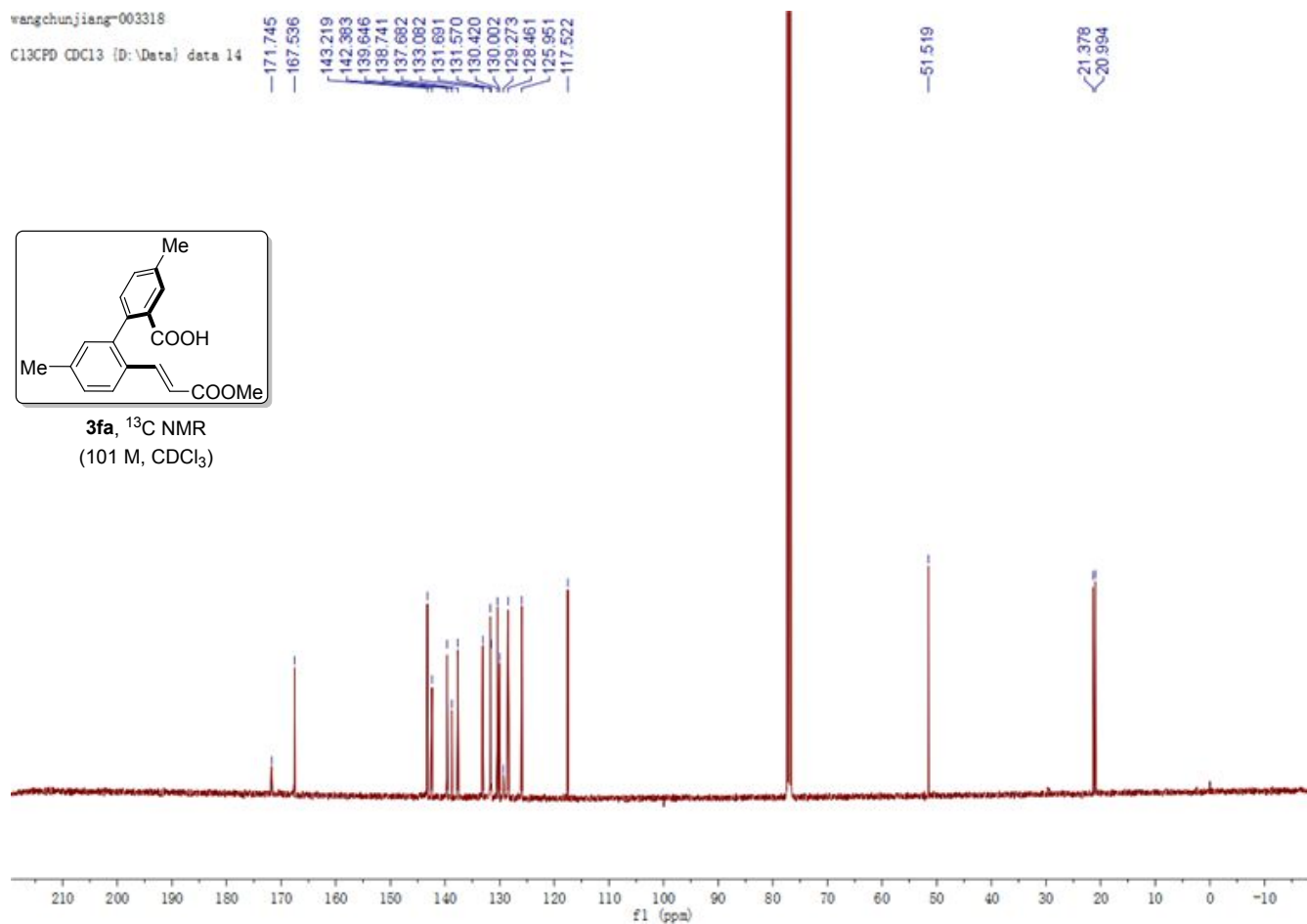


wangchunjiang-003318

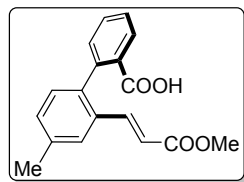
^{13}C CPD CDC13 [D:\Data] data 14



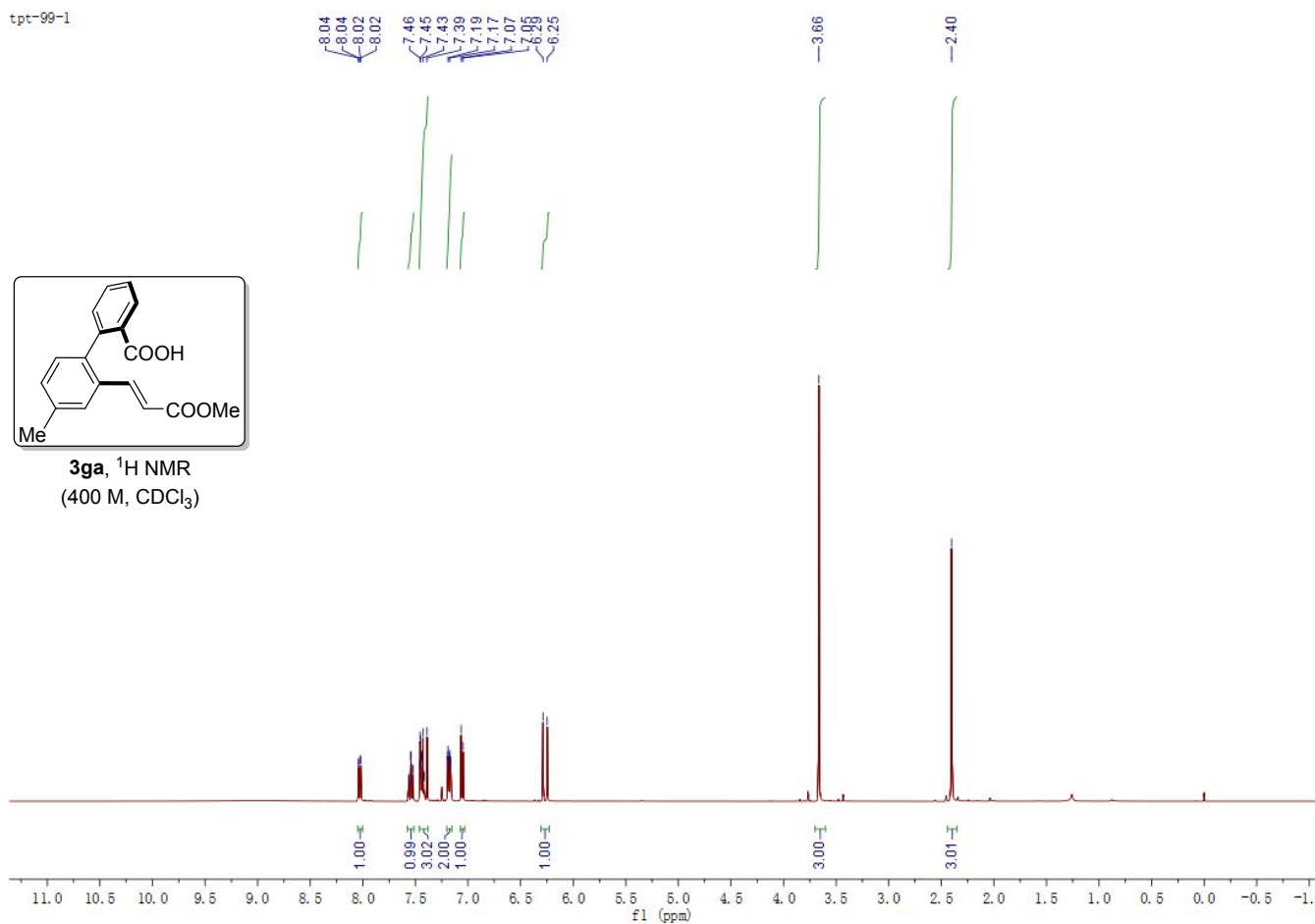
3fa, ^{13}C NMR
(101 M, CDCl_3)



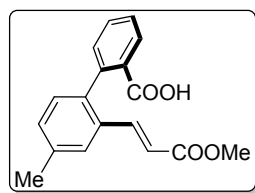
tpt-99-1



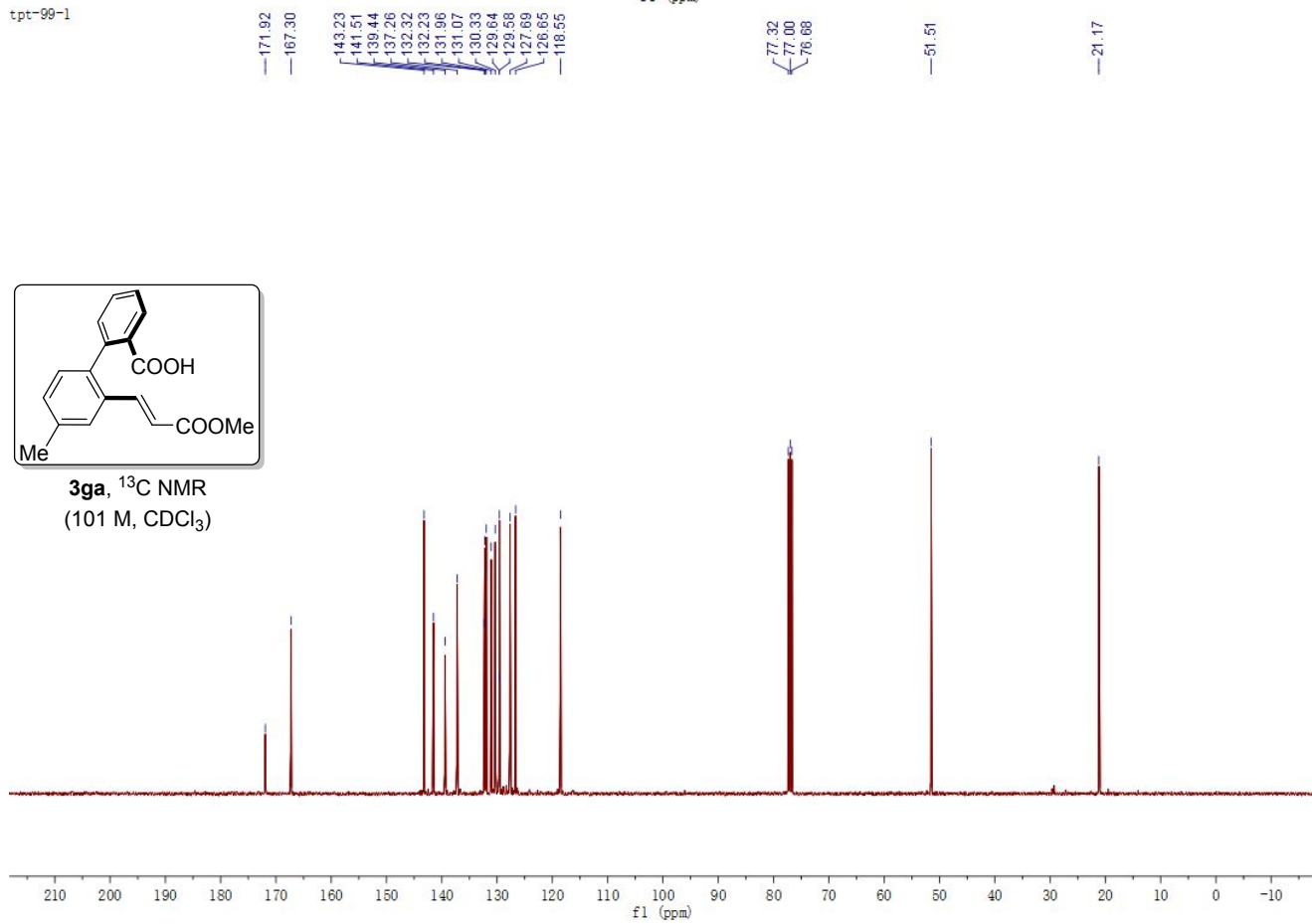
3ga, ^1H NMR
(400 M, CDCl_3)



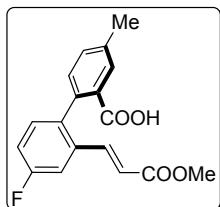
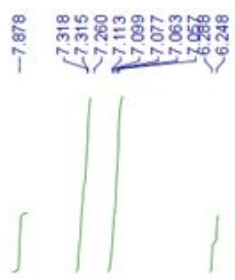
tpt-99-1



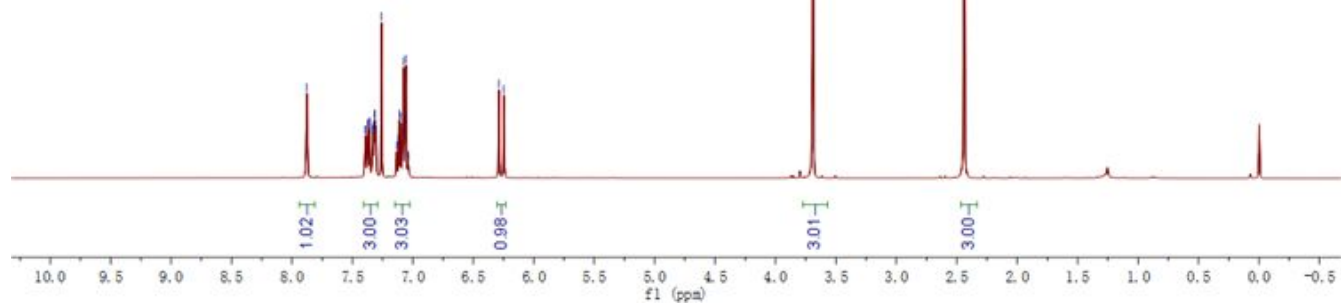
3ga, ^{13}C NMR
(101 M, CDCl_3)



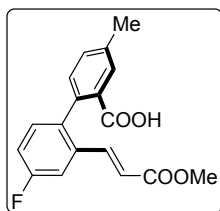
wangchunjiang-003319
PROTON CDCl3 [D:\Data] data 37



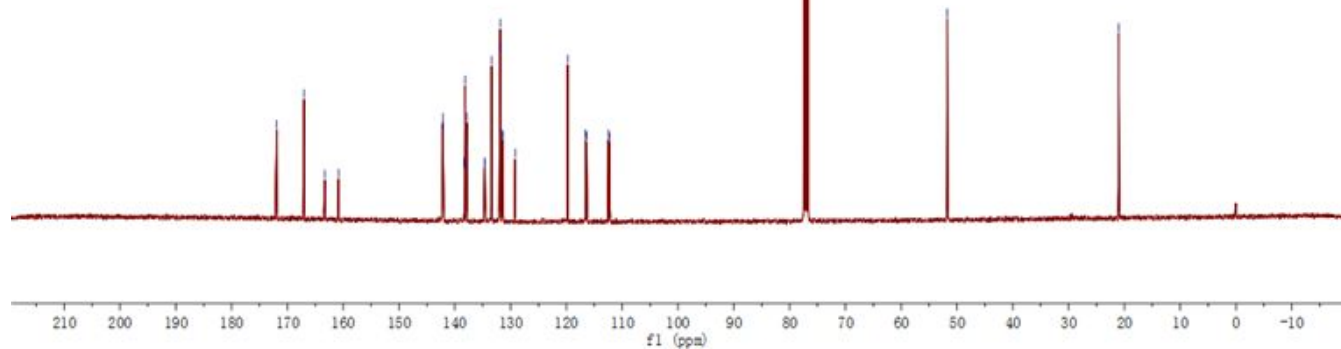
3ha, ^1H NMR
(400 M, CDCl_3)

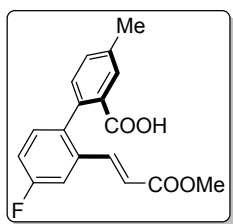


wangchunjiang-003318
C13CPD CDCl3 [D:\Data] data 16

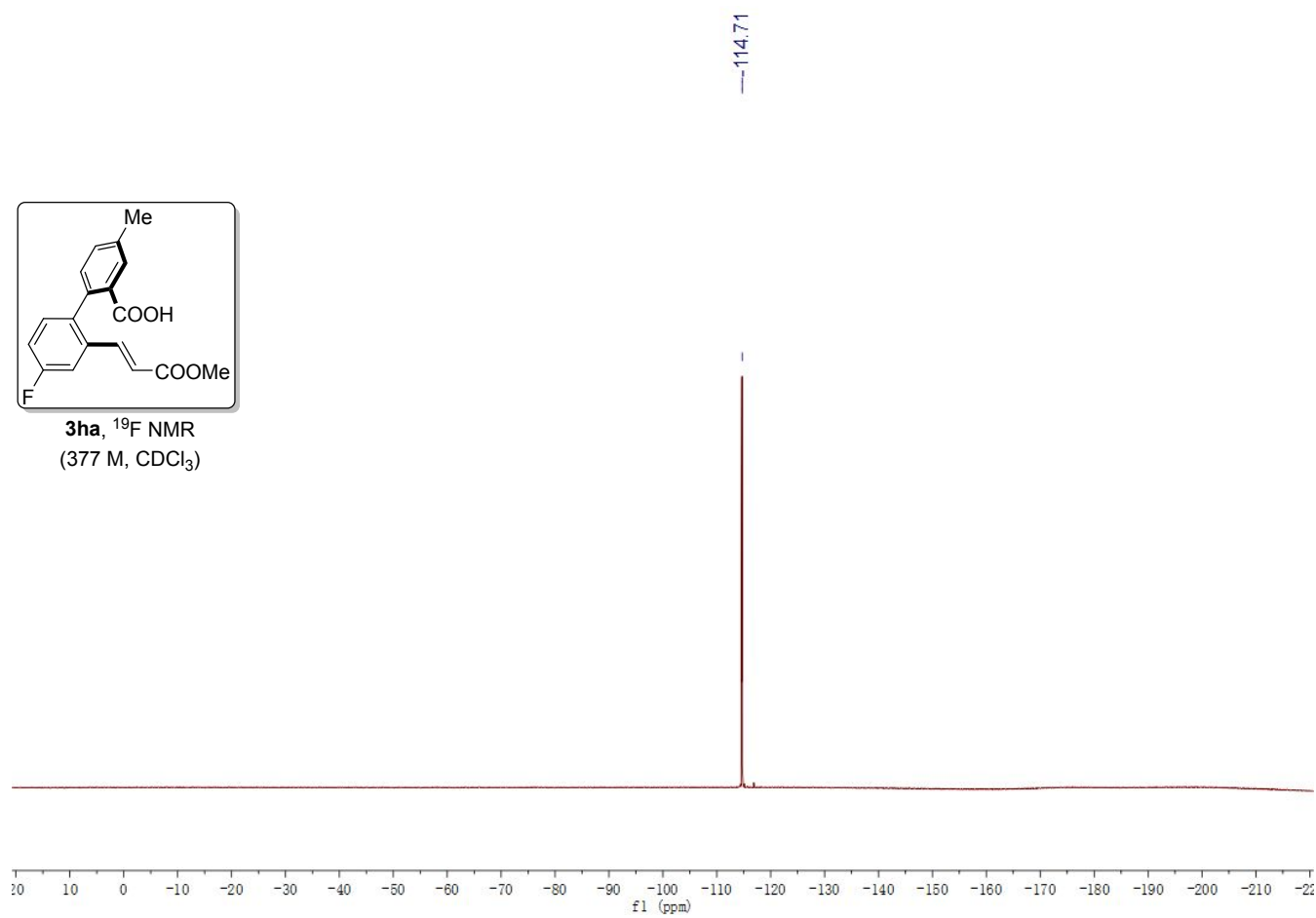


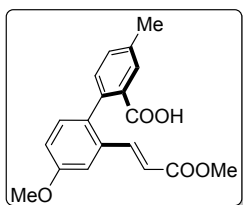
3ha, ^{13}C NMR
(101 M, CDCl_3)



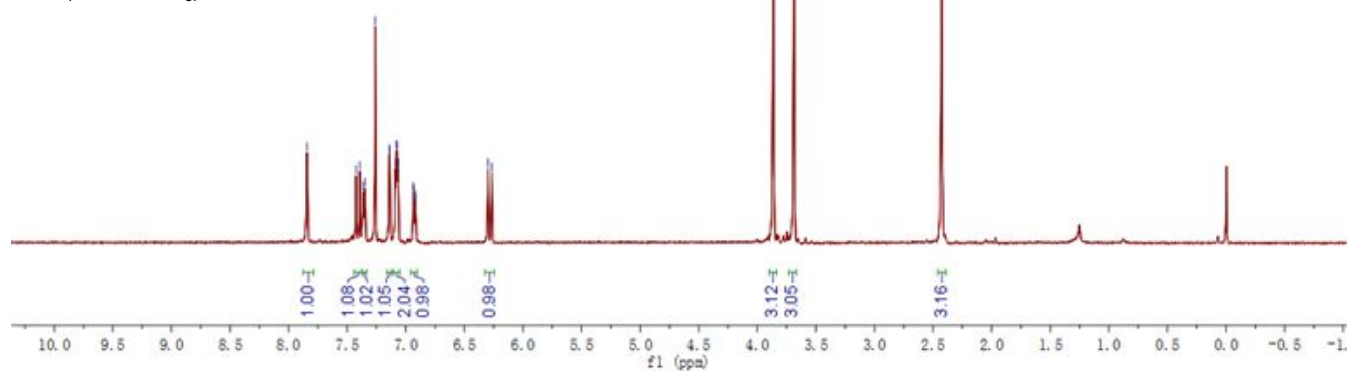


3ha, ^{19}F NMR
(377 M, CDCl_3)



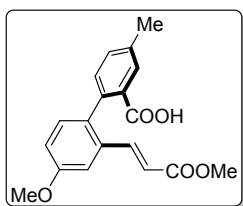


3ia, ¹H NMR
(501 M, CDCl₃)

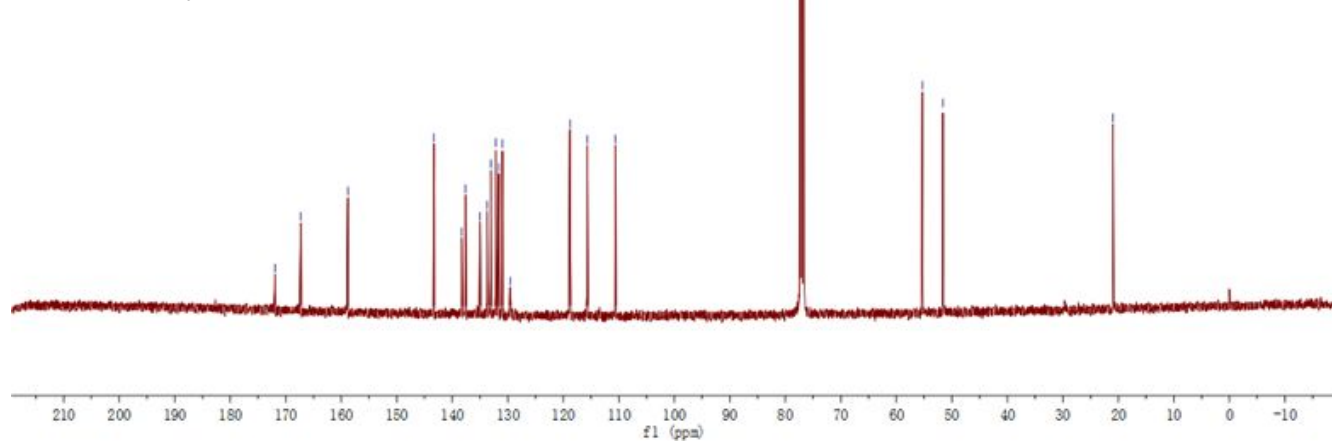


wangchunjiang-003318

C13CPD CDC13 [D:\Data] data 45



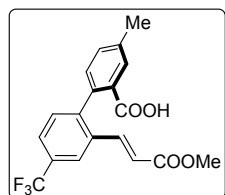
3ia, ¹³C NMR
(101 M, CDCl₃)



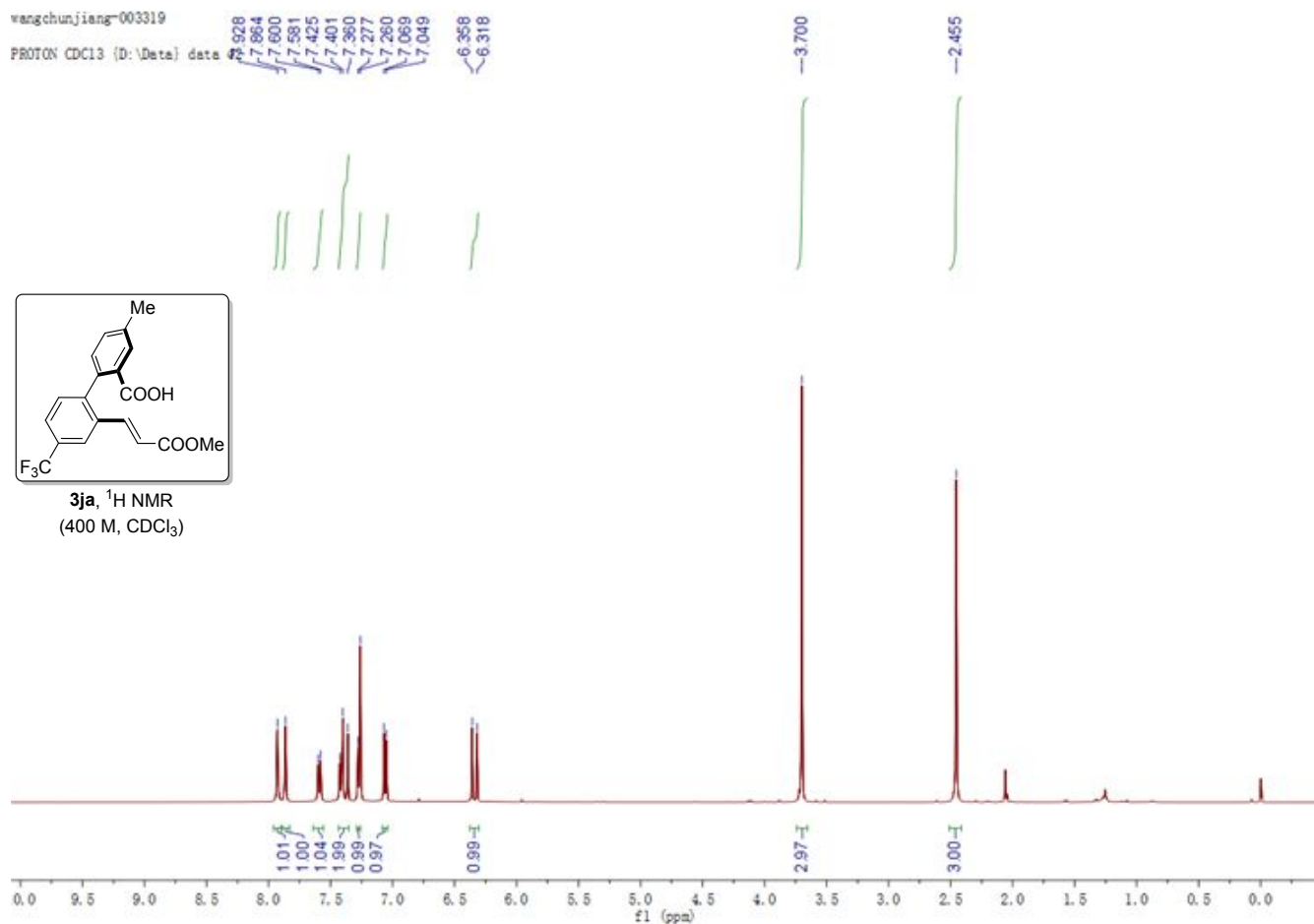
wangchunjiang-003319

PROTON CDC13 [D:\Data] data 4

7.928
7.864
7.600
7.581
7.425
7.401
7.380
7.277
7.260
7.089
7.049
6.358
6.318



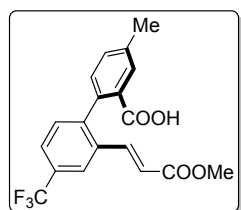
3ja, ¹H NMR
(400 M, CDCl₃)



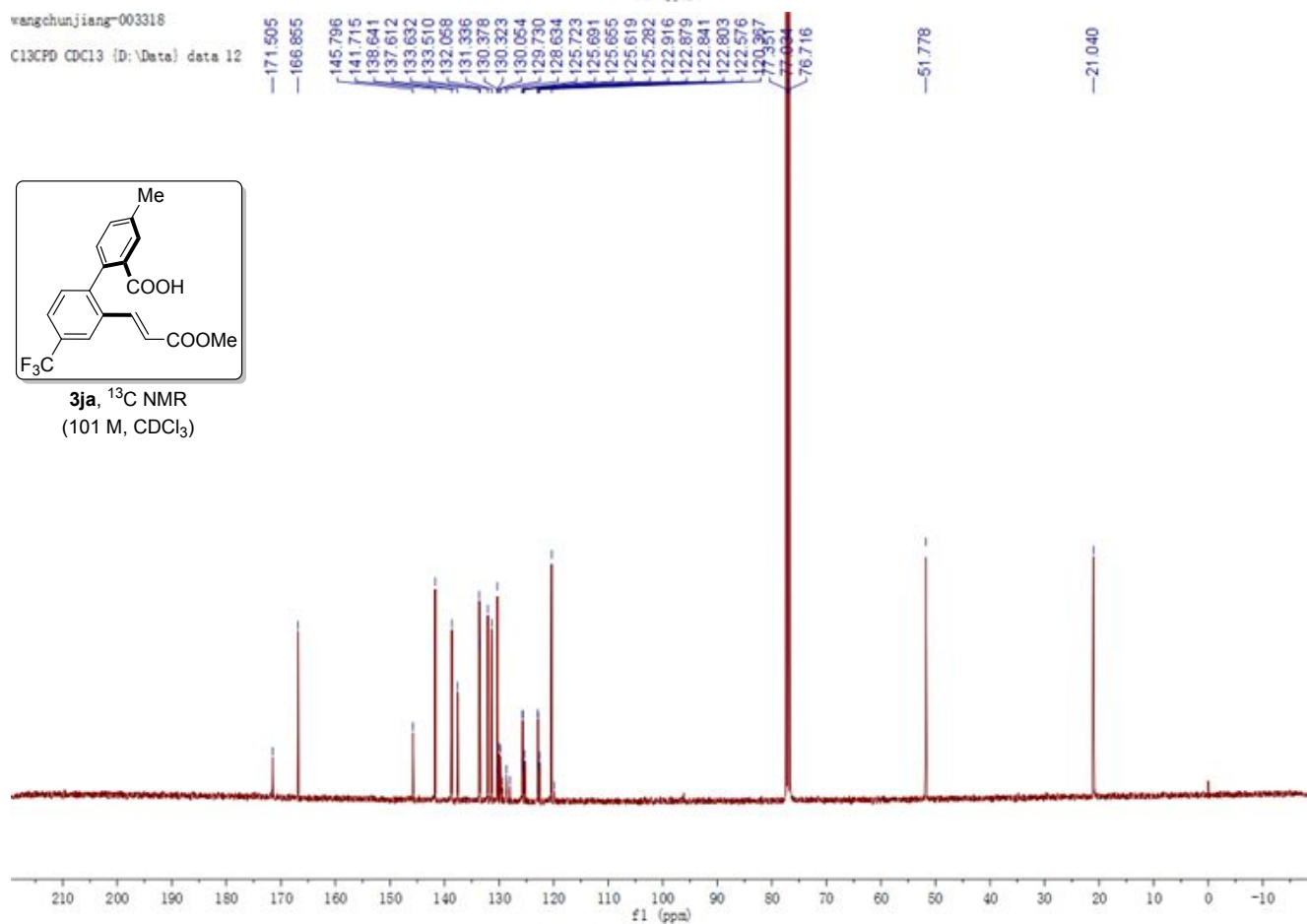
wangchunjiang-003318

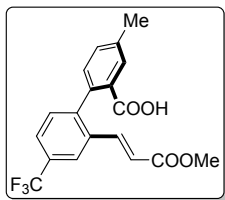
C13CPD CDC13 [D:\Data] data 12

171.505
166.855
145.796
141.715
138.641
137.612
133.632
133.510
132.058
131.336
130.378
130.323
130.054
129.730
128.634
125.723
125.691
125.655
125.619
125.282
122.916
122.879
122.841
122.803
122.576
120.987
77.034
76.716
51.778
21.040



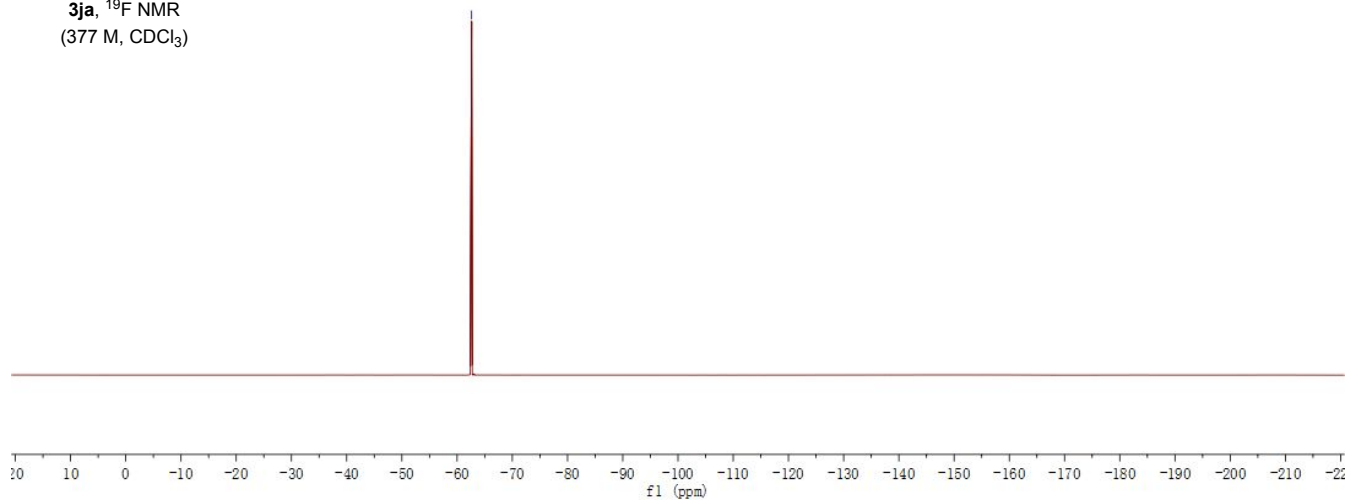
3ja, ¹³C NMR
(101 M, CDCl₃)

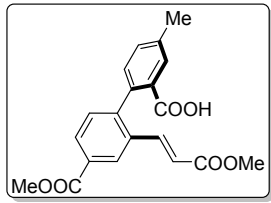




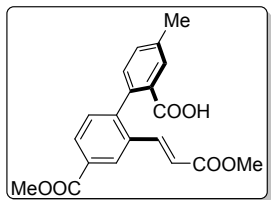
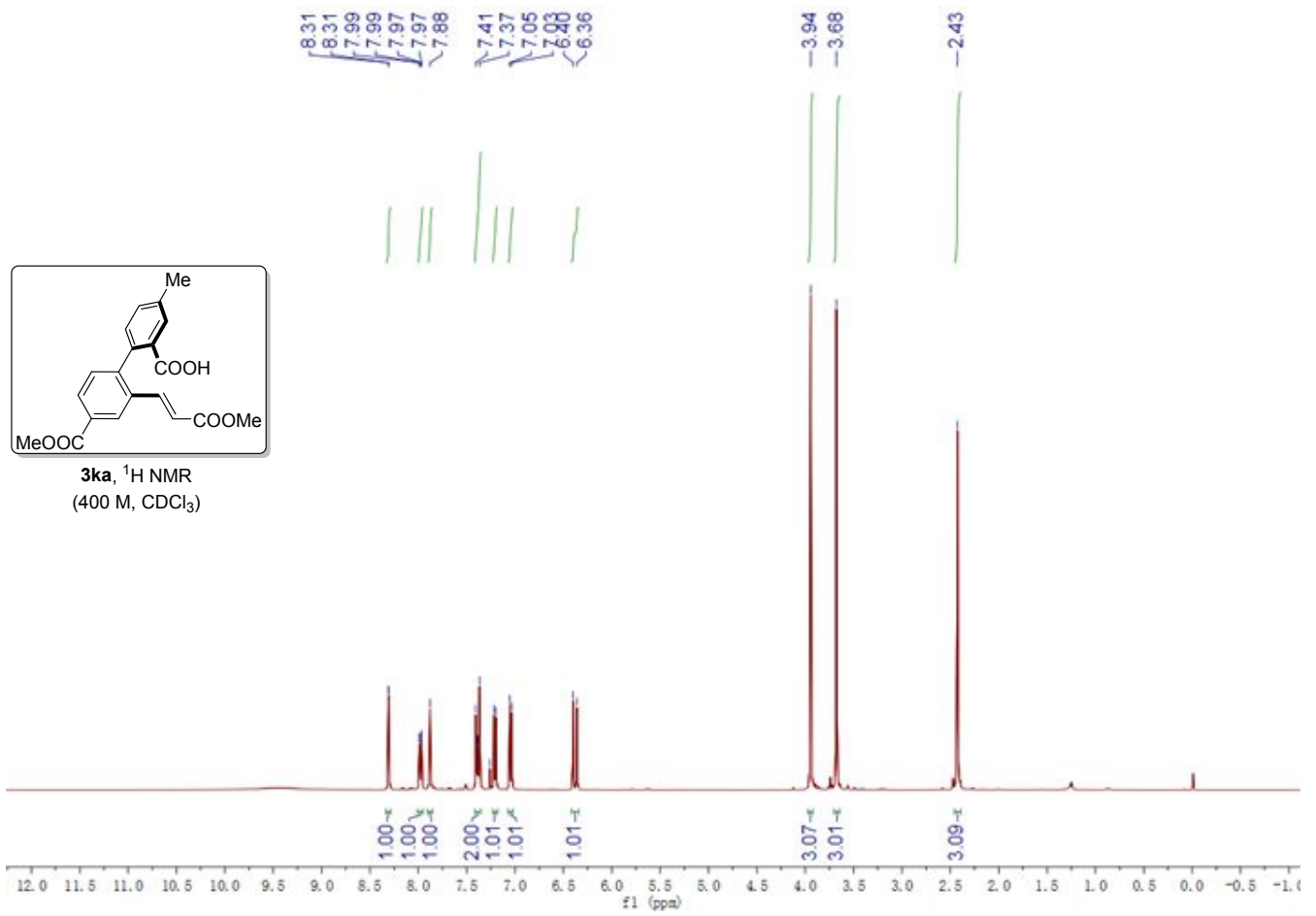
3ja, ^{19}F NMR
(377 M, CDCl_3)

--62.63

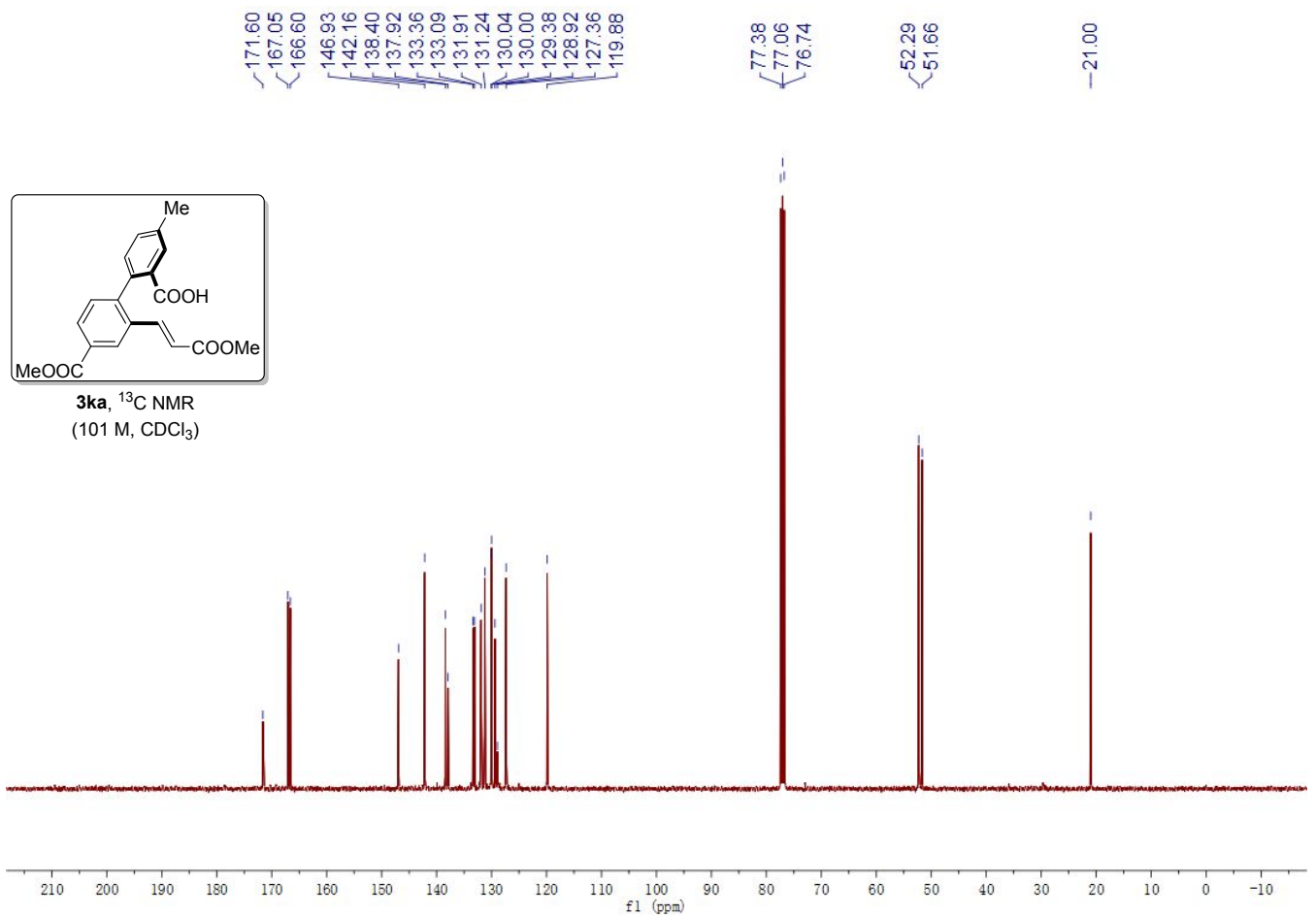


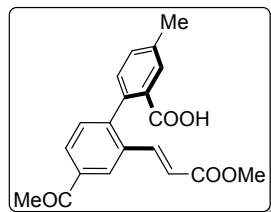


3ka, $^1\text{H NMR}$
(400 M, CDCl_3)

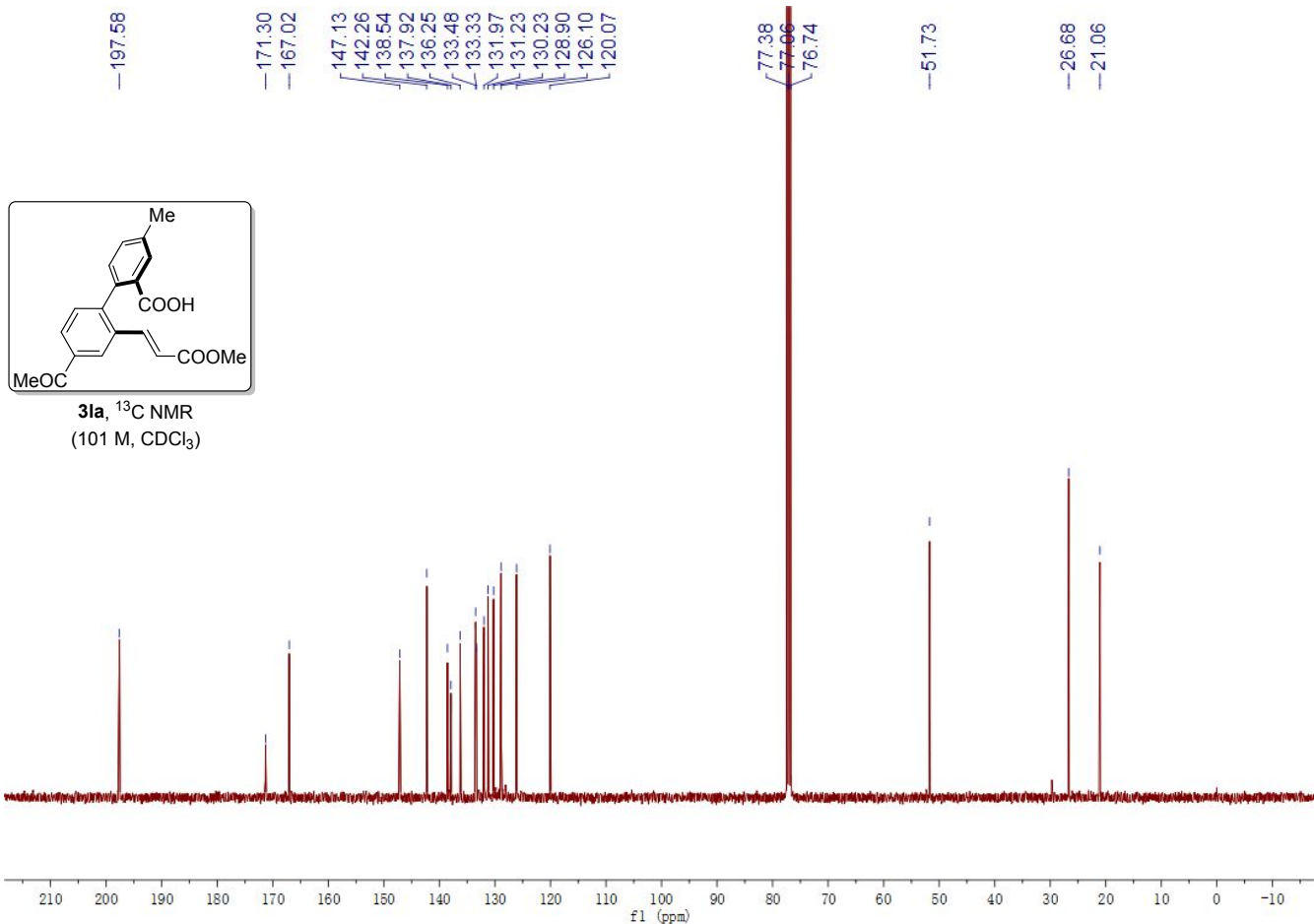
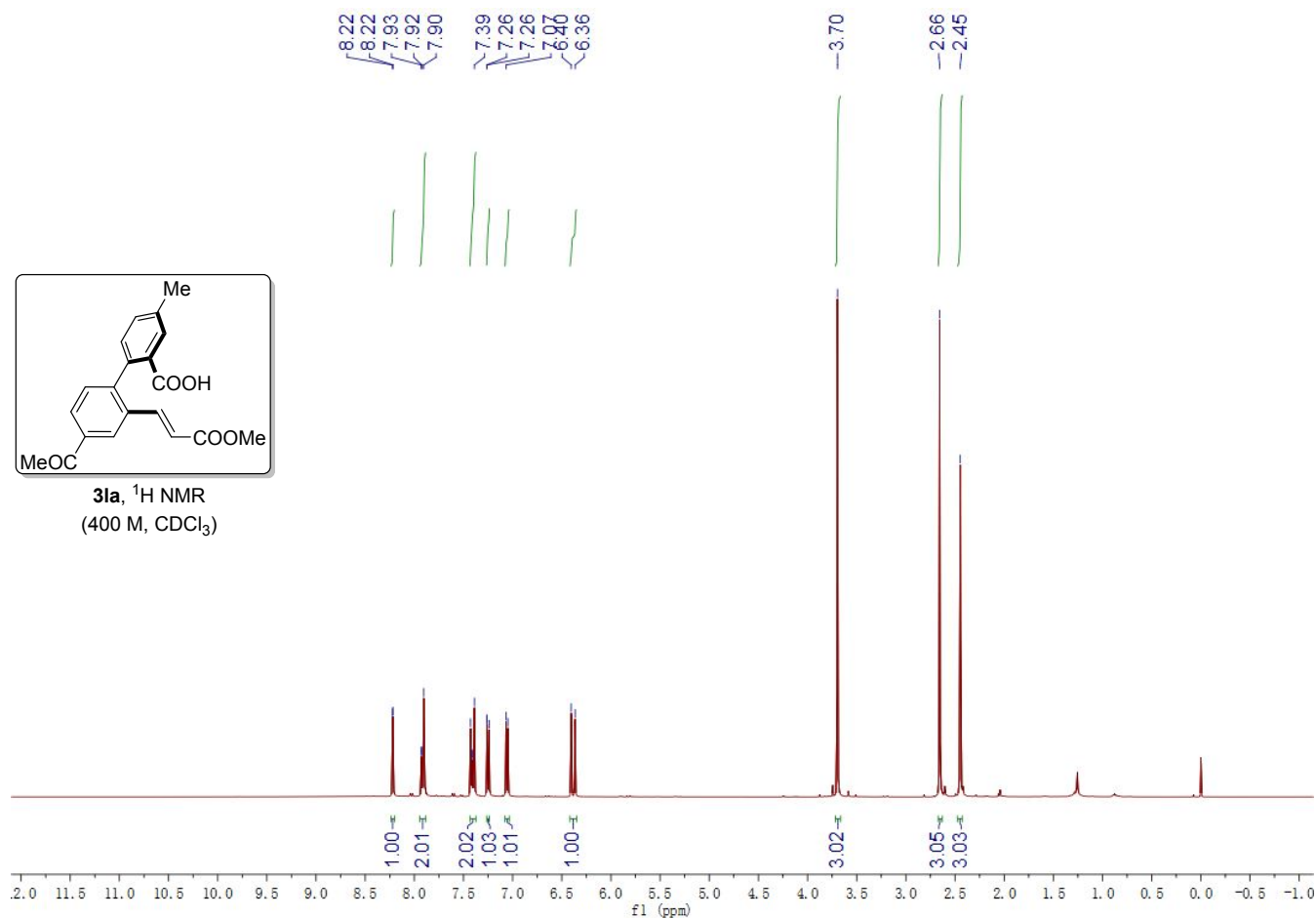


3ka, $^{13}\text{C NMR}$
(101 M, CDCl_3)

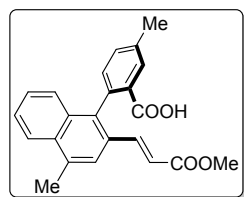




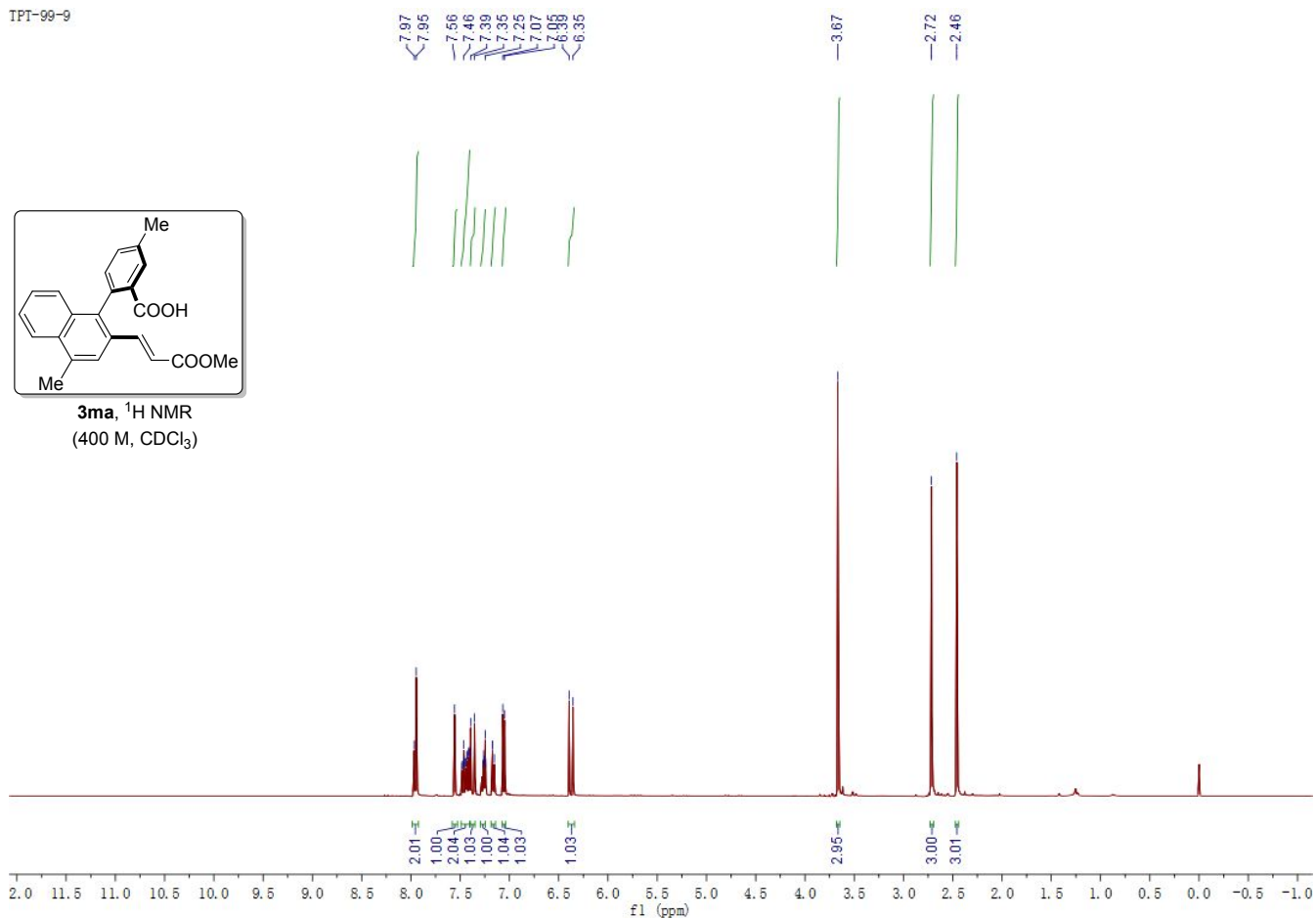
3la, ^1H NMR
(400 M, CDCl_3)



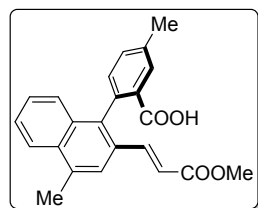
IPT-99-9



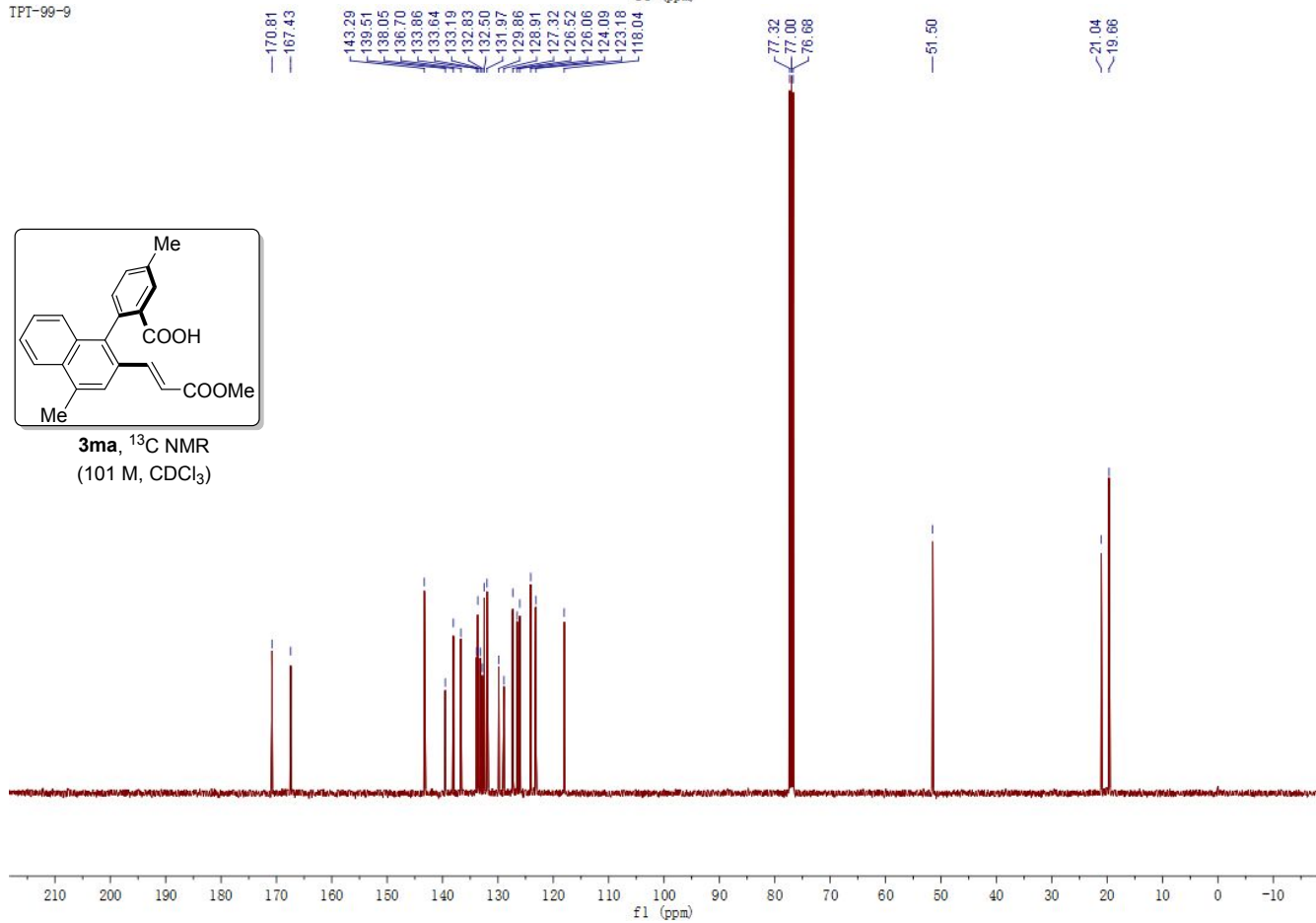
3ma, $^1\text{H NMR}$
(400 M, CDCl_3)



IPT-99-9

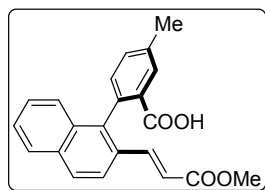


3ma, $^{13}\text{C NMR}$
(101 M, CDCl_3)

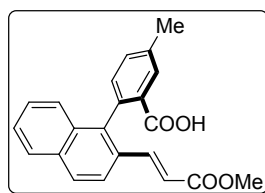
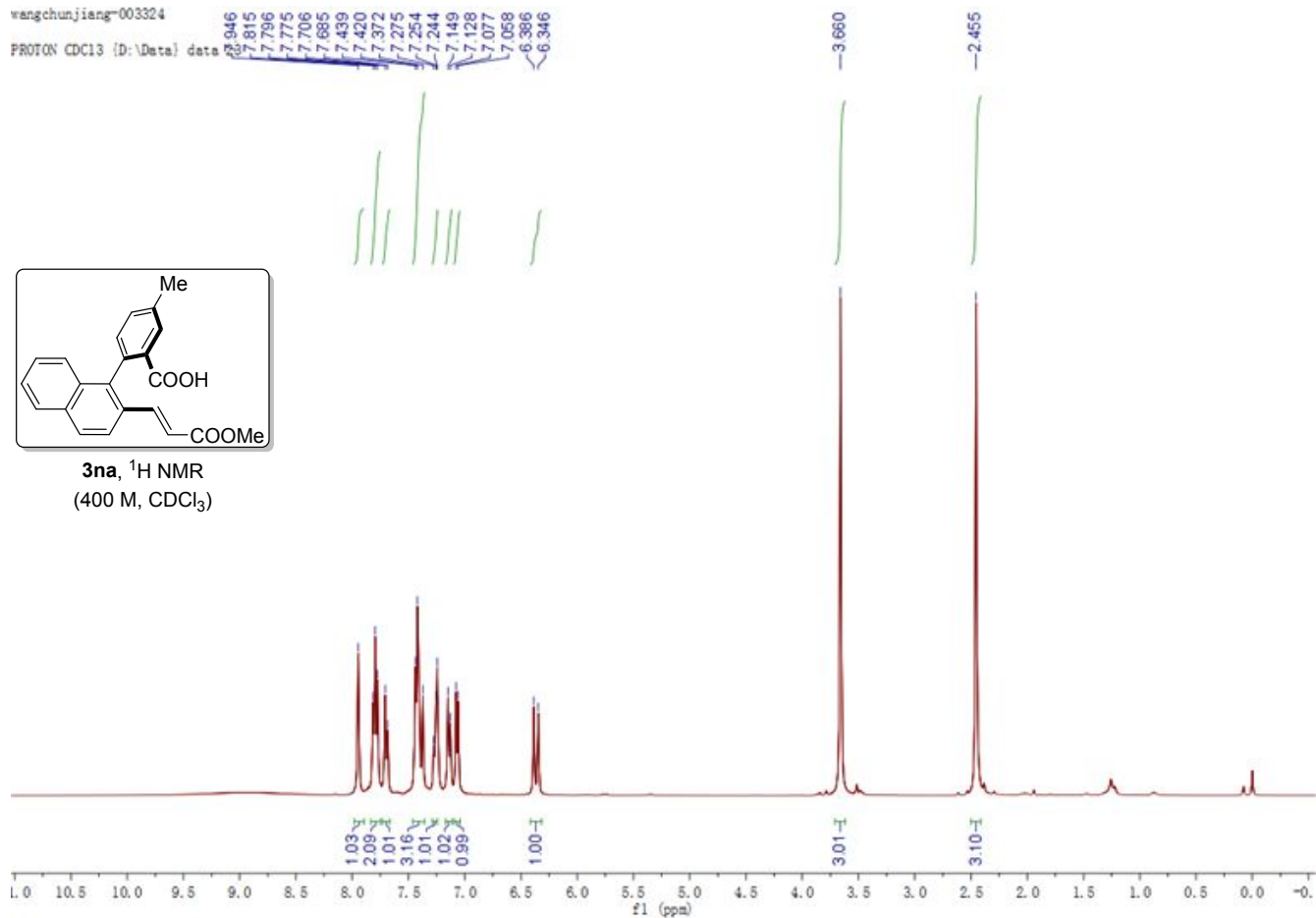


wangchunjiang-003324

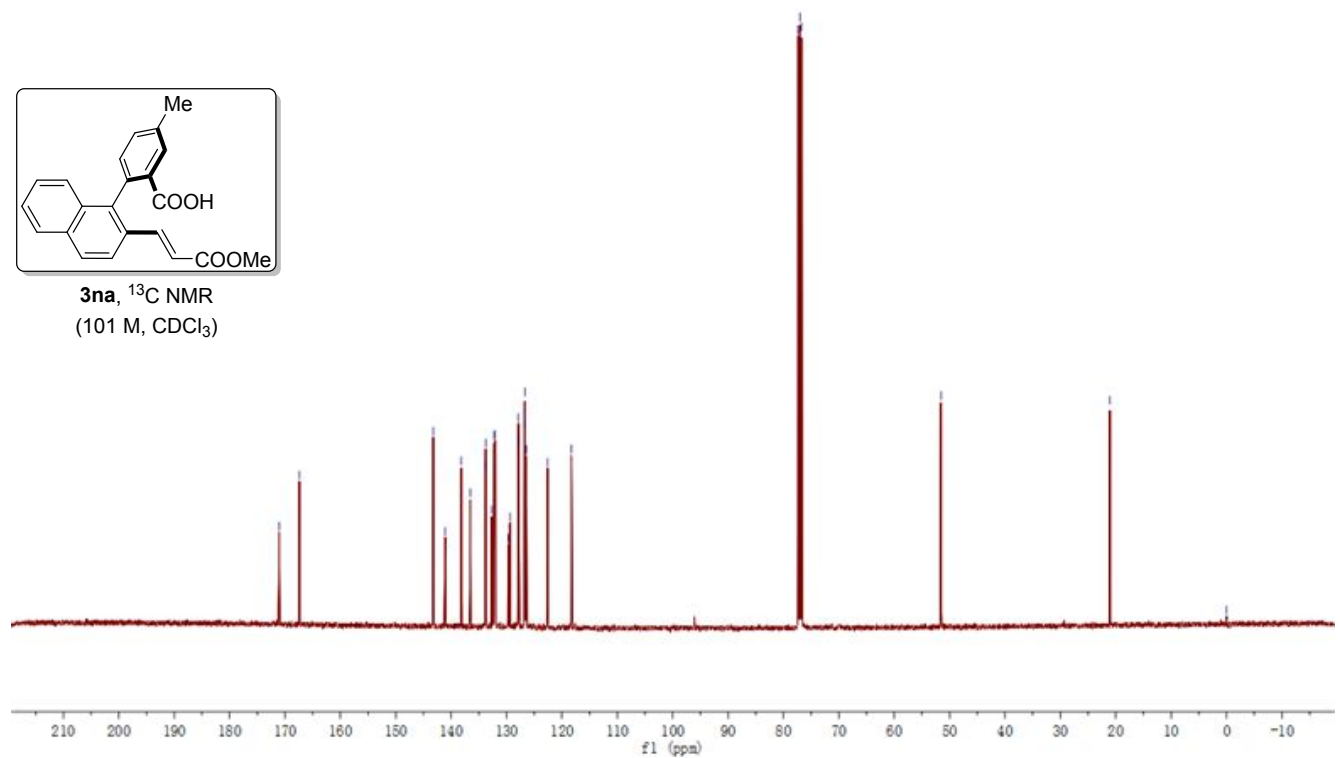
PROTON CDCl3 [D:\Data] data 8.946
7.815
7.796
7.775
7.706
7.685
7.439
7.420
7.372
7.275
7.254
7.244
7.149
7.128
7.077
7.058
6.386
6.346

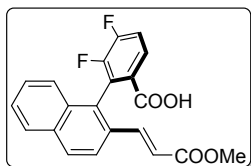
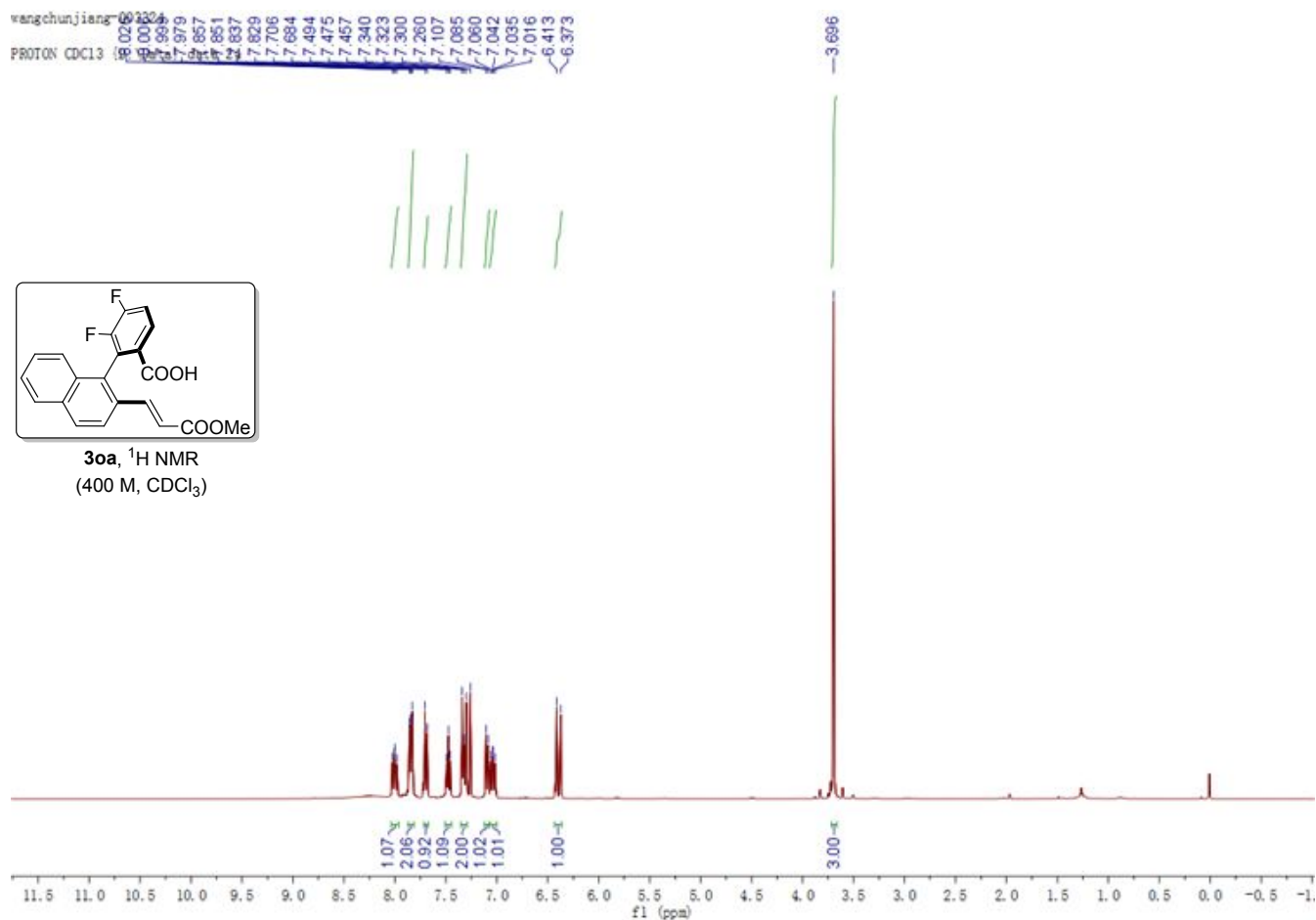


3na, ¹H NMR
(400 M, CDCl₃)

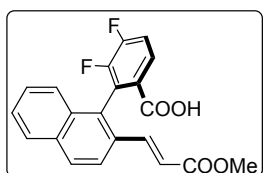
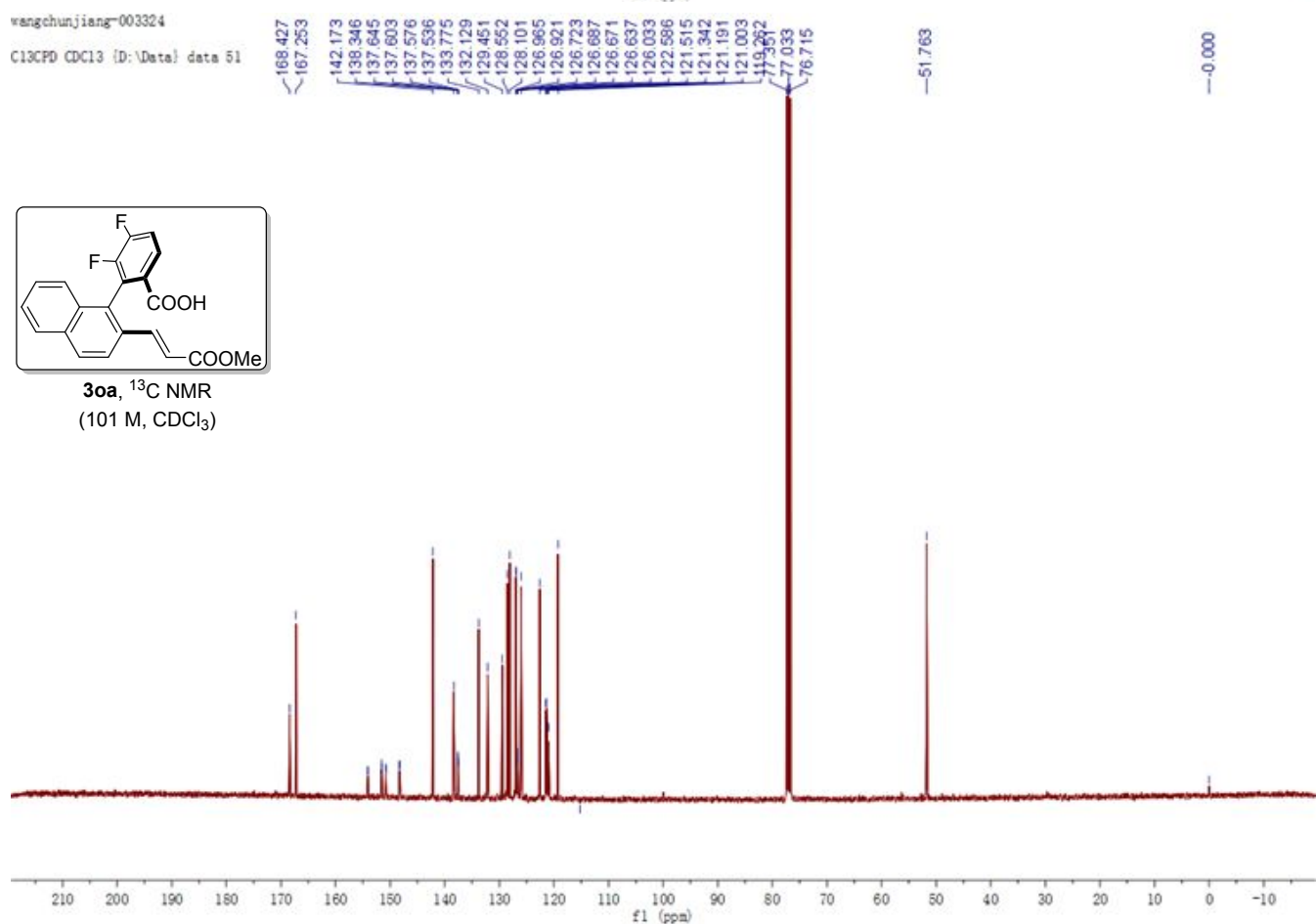


3na, ¹³C NMR
(101 M, CDCl₃)

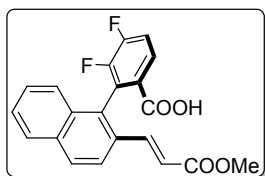




3oa, ^1H NMR
 (400 M, CDCl_3)

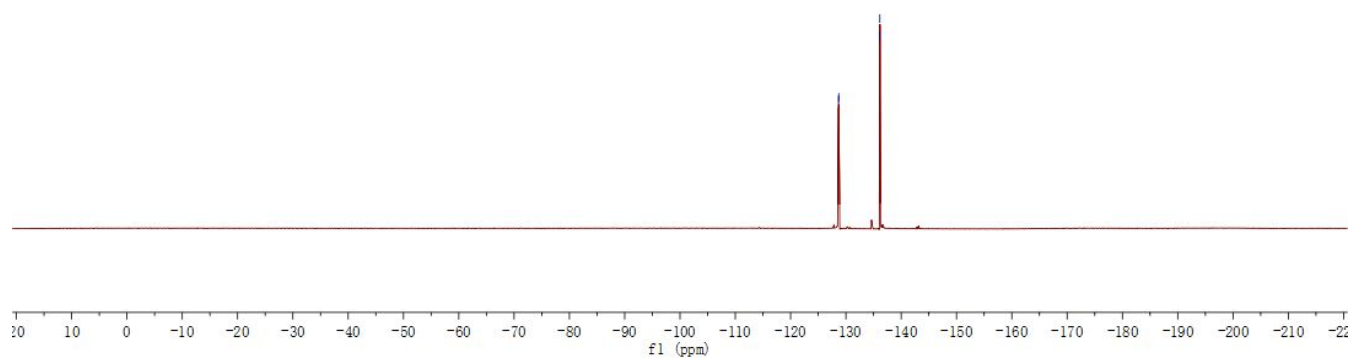


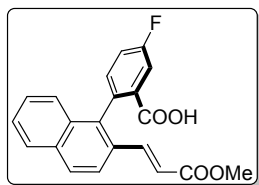
3oa, ^{13}C NMR
 (101 M, CDCl_3)



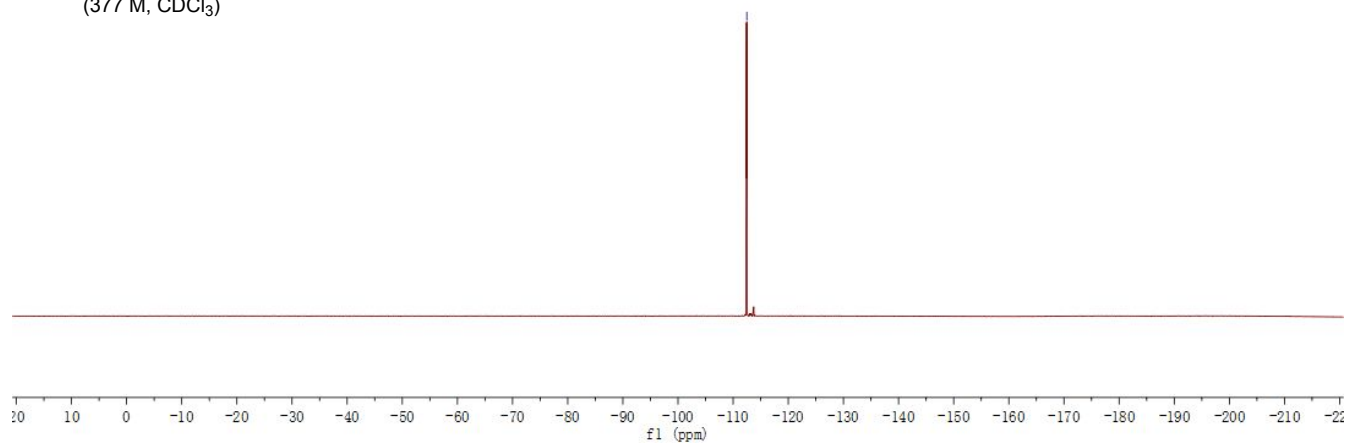
3oa, ^{19}F NMR
(377 M, CDCl_3)

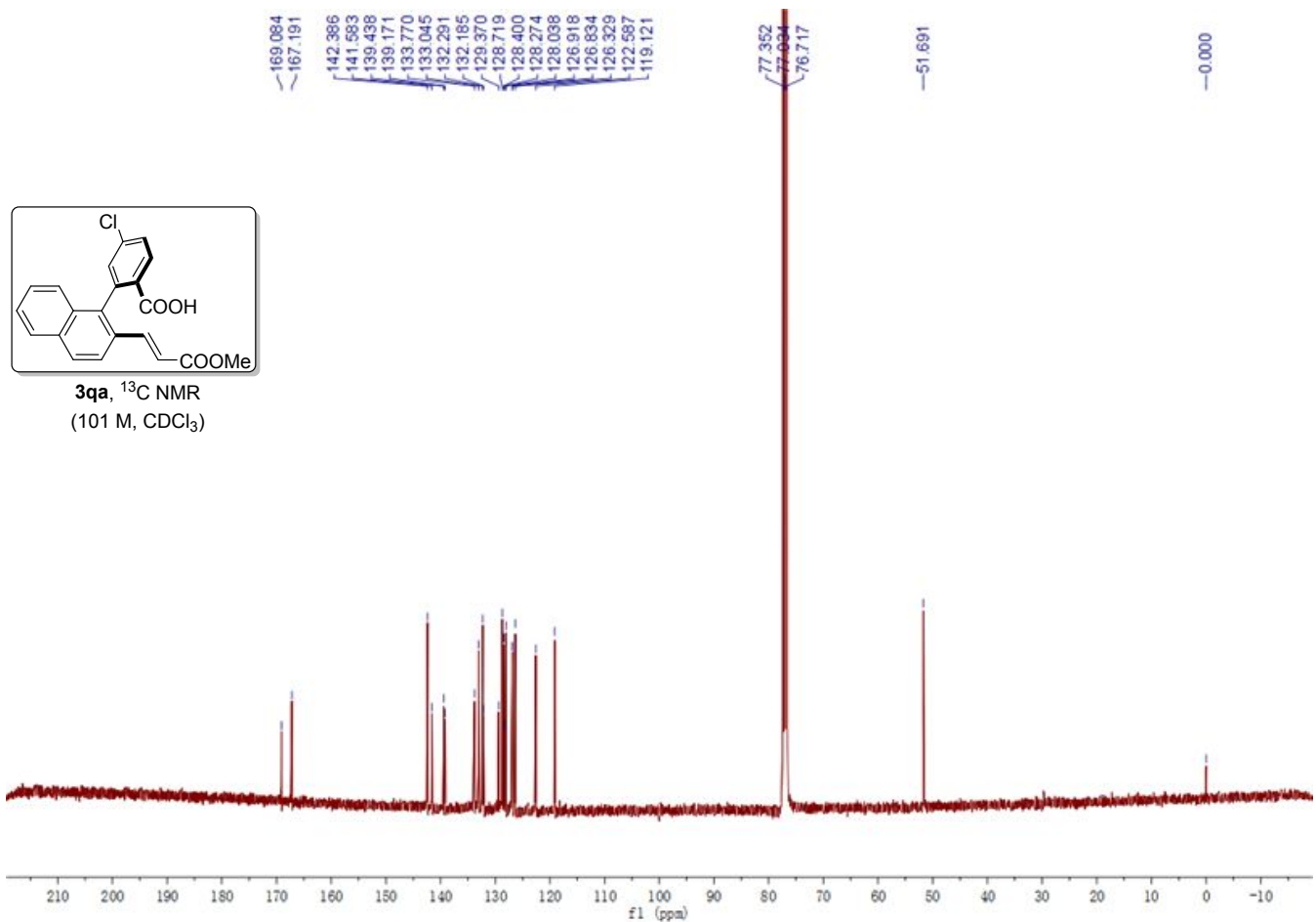
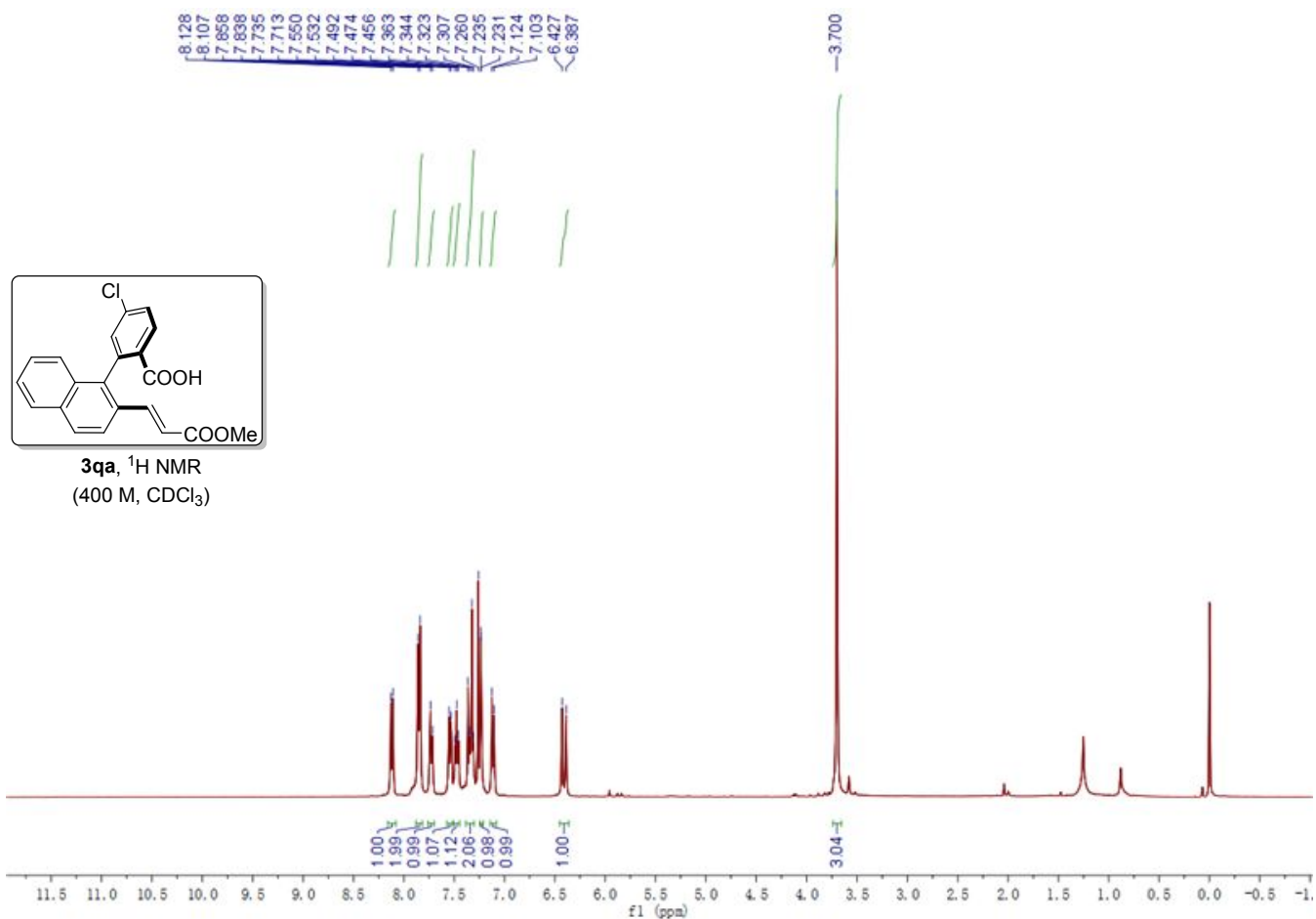
128.66
128.71
136.07
136.13

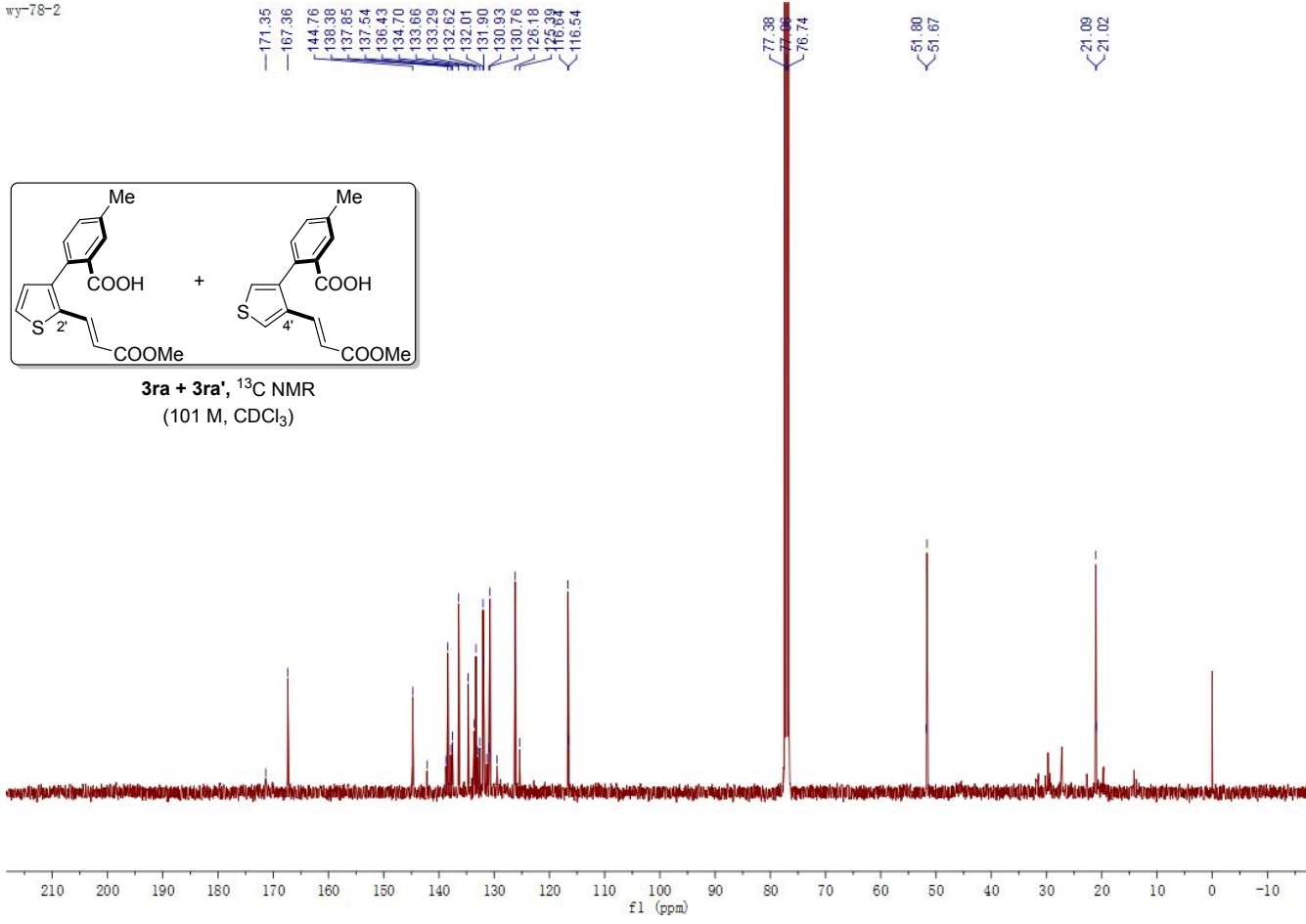
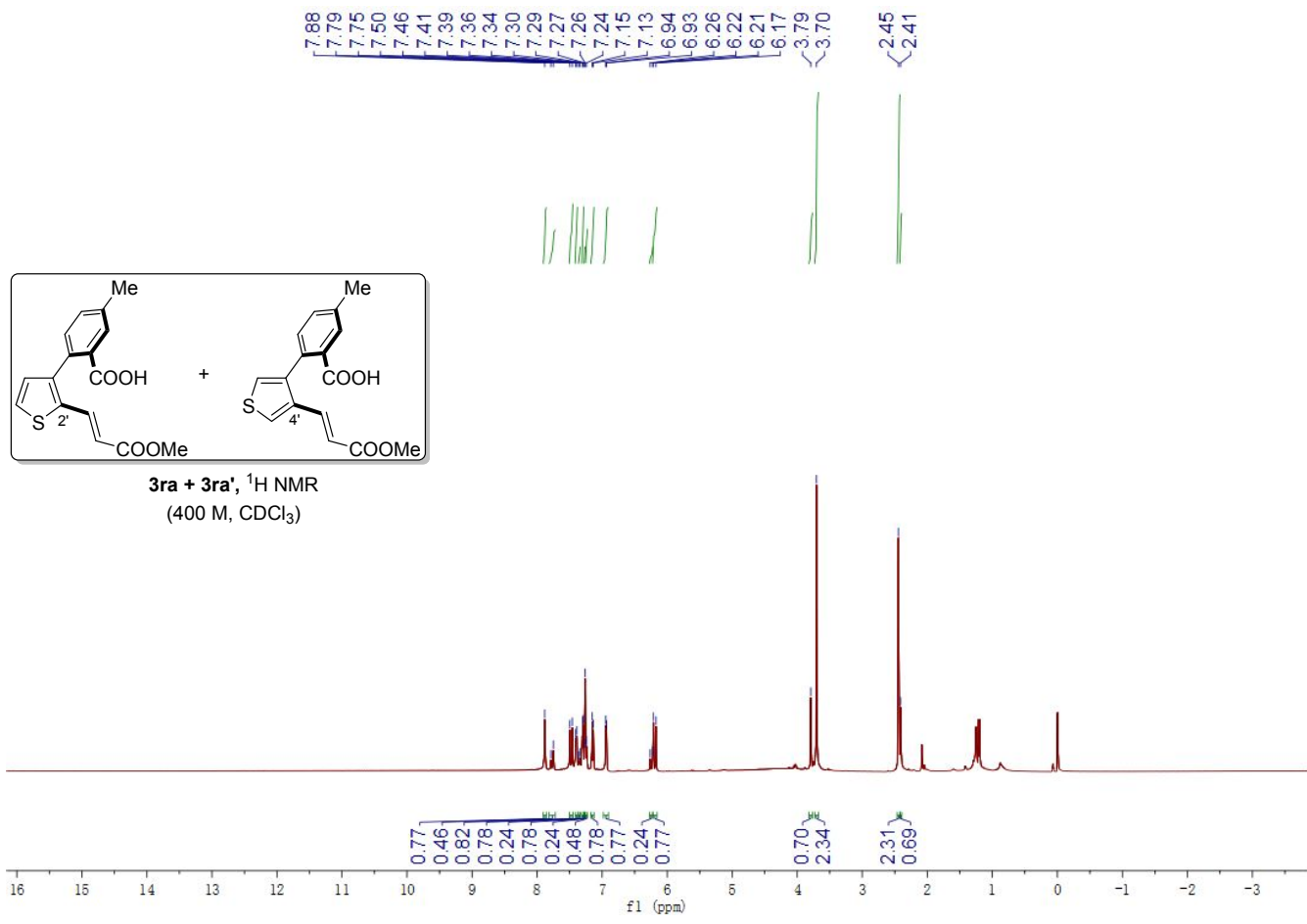




3pa, ^{19}F NMR
(377 M, CDCl_3)

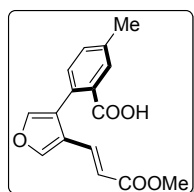




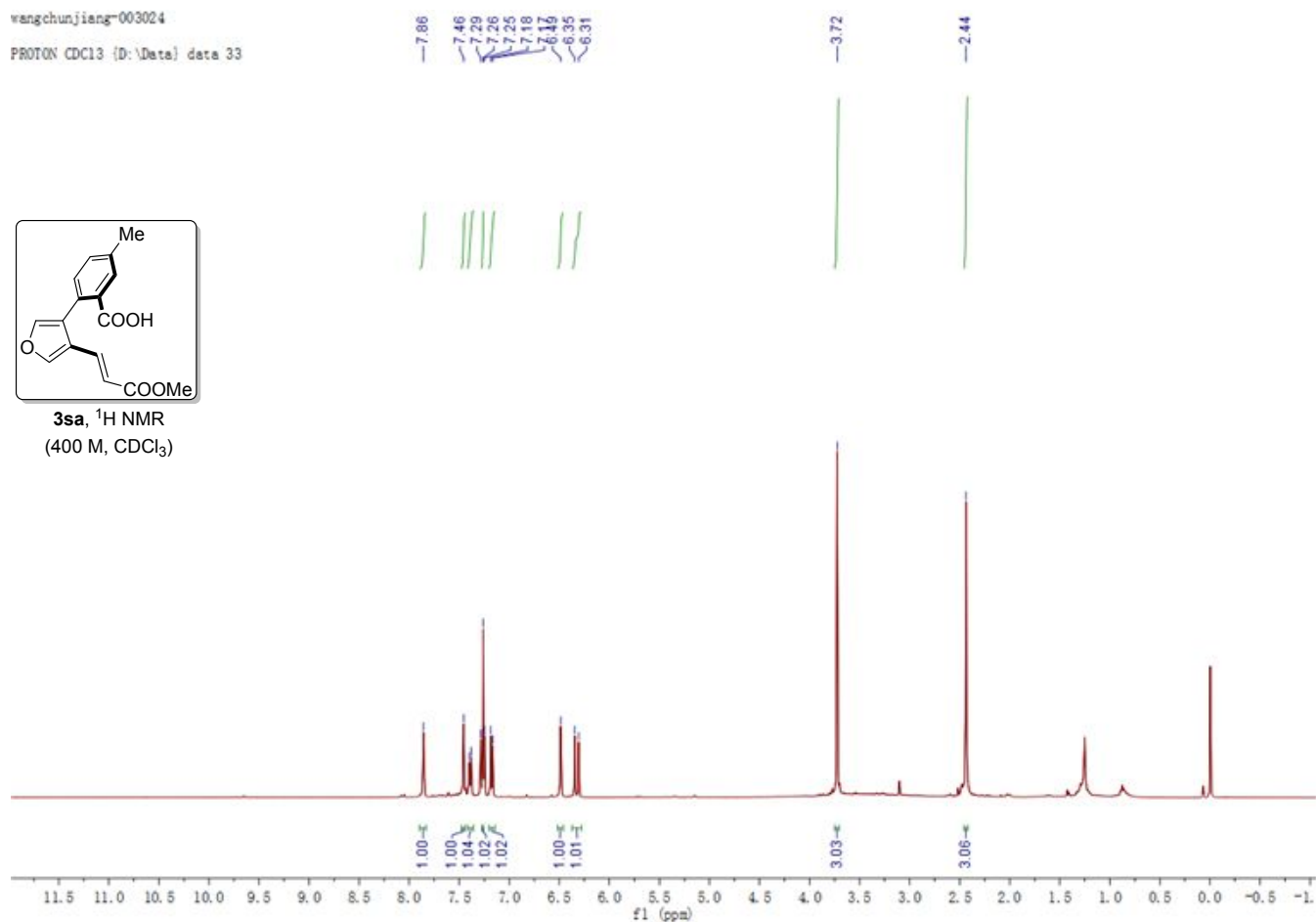


wangchunjiang-003024

PROTON CDCl3 [D:\Data] data 33

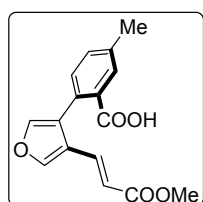


3sa, ^1H NMR
(400 M, CDCl_3)

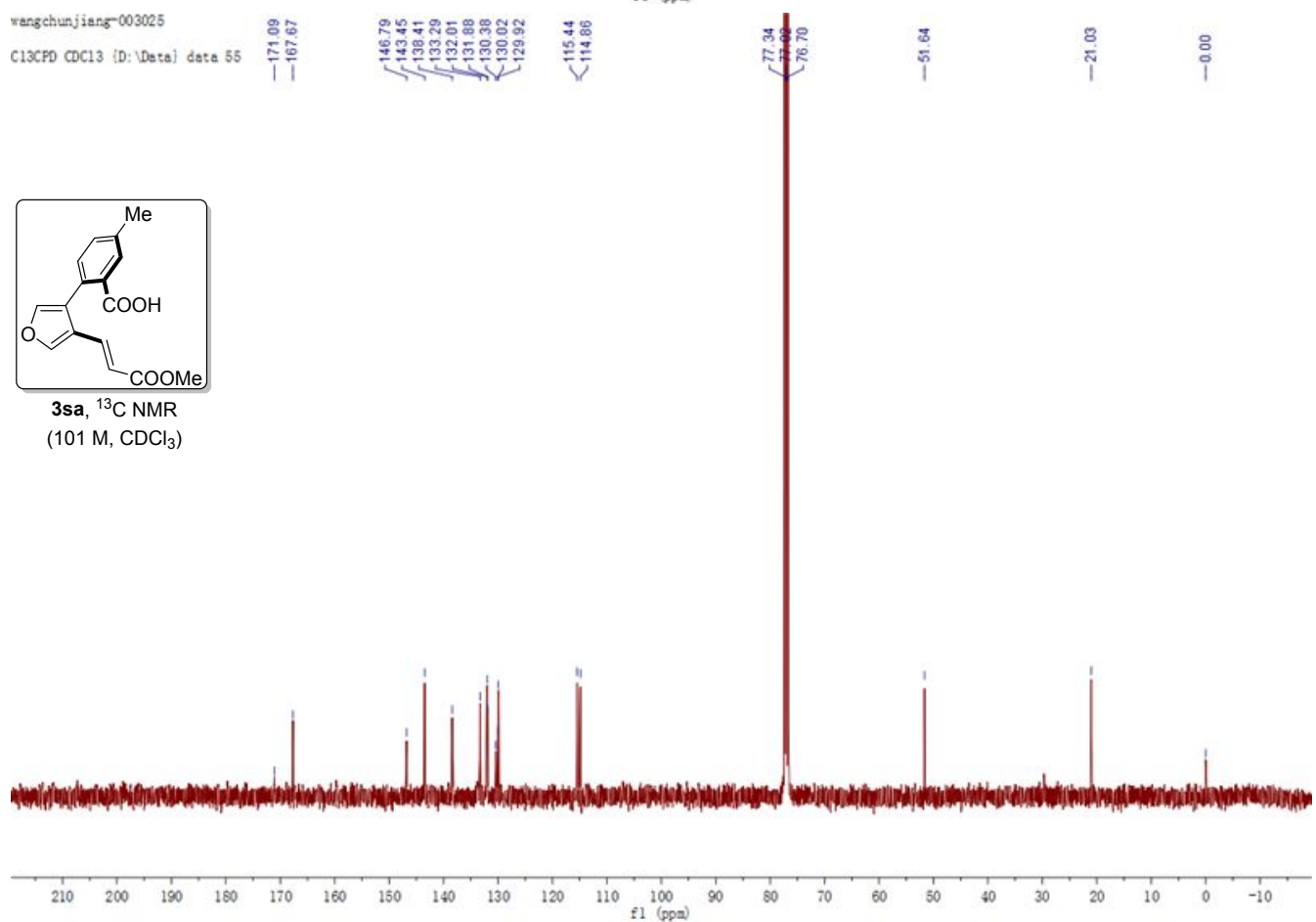


wangchunjiang-003025

^{13}C CPD CDCl3 [D:\Data] data 55



3sa, ^{13}C NMR
(101 M, CDCl_3)

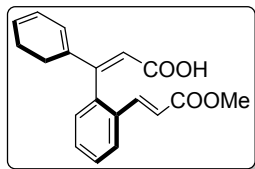


wangchunjiang-003024

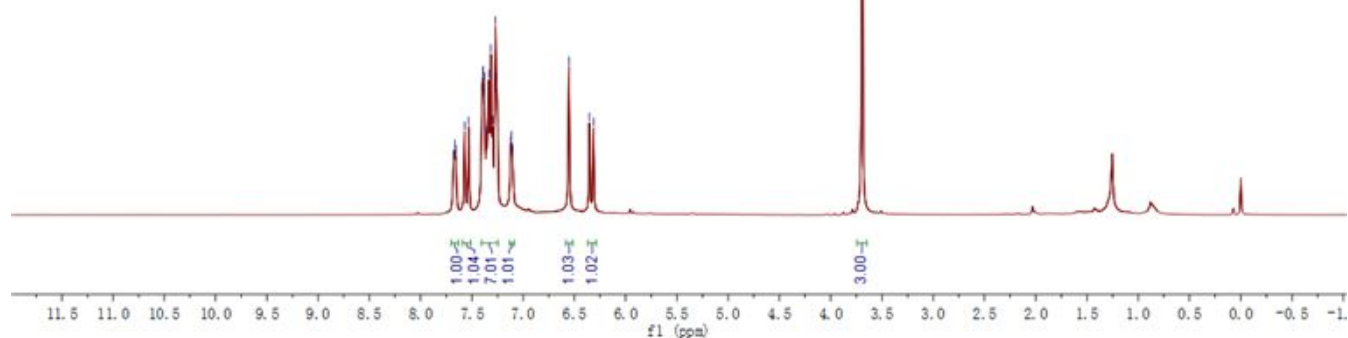
PROTON CDCl3 [D:\Data] data 35

7.68
7.67
7.66
7.57
7.53
7.40
7.39
7.38
7.36
7.33
7.31
7.30
7.27
7.26
7.12
7.11
6.55
6.31

3.89



3ua, ^1H NMR
(400 M, CDCl_3)



wangchunjiang-003025

C13CPD CDCl3 [D:\Data] data 56

169.79
167.16

156.39

142.23
139.39
139.17

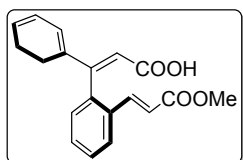
129.77
128.73
127.75

118.79
118.22

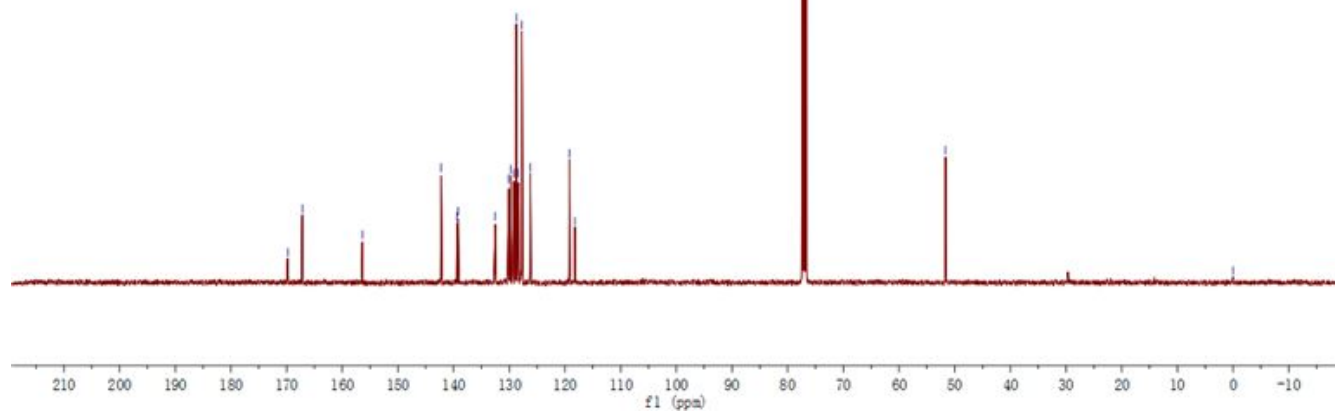
77.35
77.03
76.71

51.85

0.00



3ua, ^{13}C NMR
(101 M, CDCl_3)

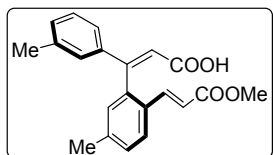


PR1-7-5
PR1-7-6

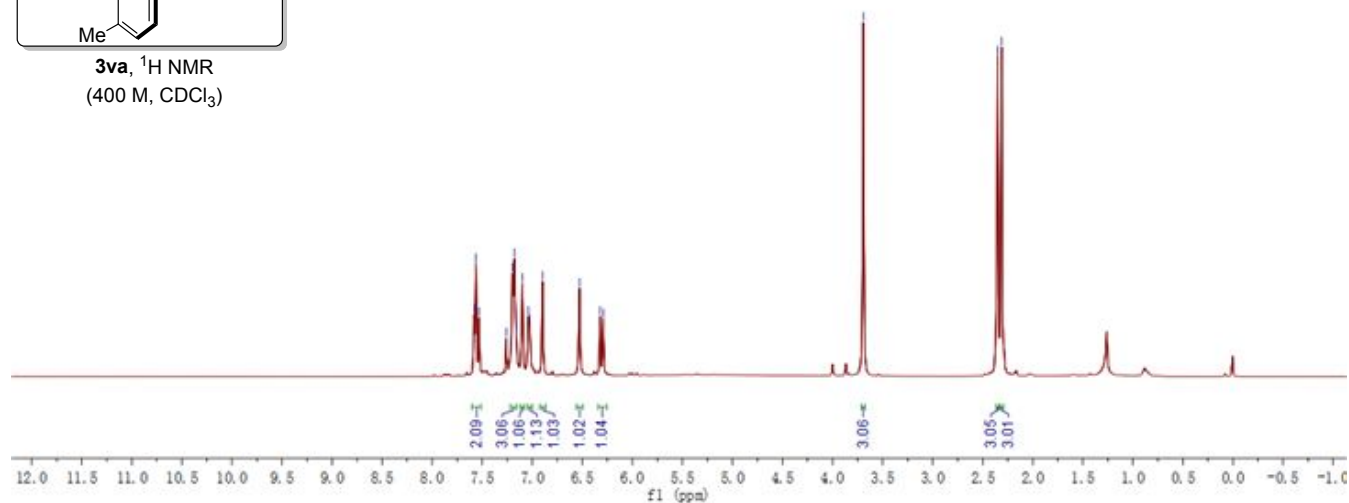
7.50
7.36
7.53
7.26
7.21
7.20
7.18
7.10
7.04
7.03
6.90
6.53
6.32
6.29

3.89

2.35
2.31



3va, ¹H NMR
(400 M, CDCl₃)



wangchunjiang-003034

C13CPD CDCl3 [D:\Data] data 12

169.75
167.40

156.64

142.29
140.08

139.50
138.35
136.36

128.57
128.23

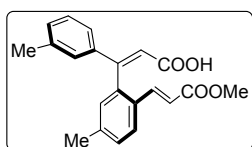
126.05
125.05

77.35
77.00
76.71

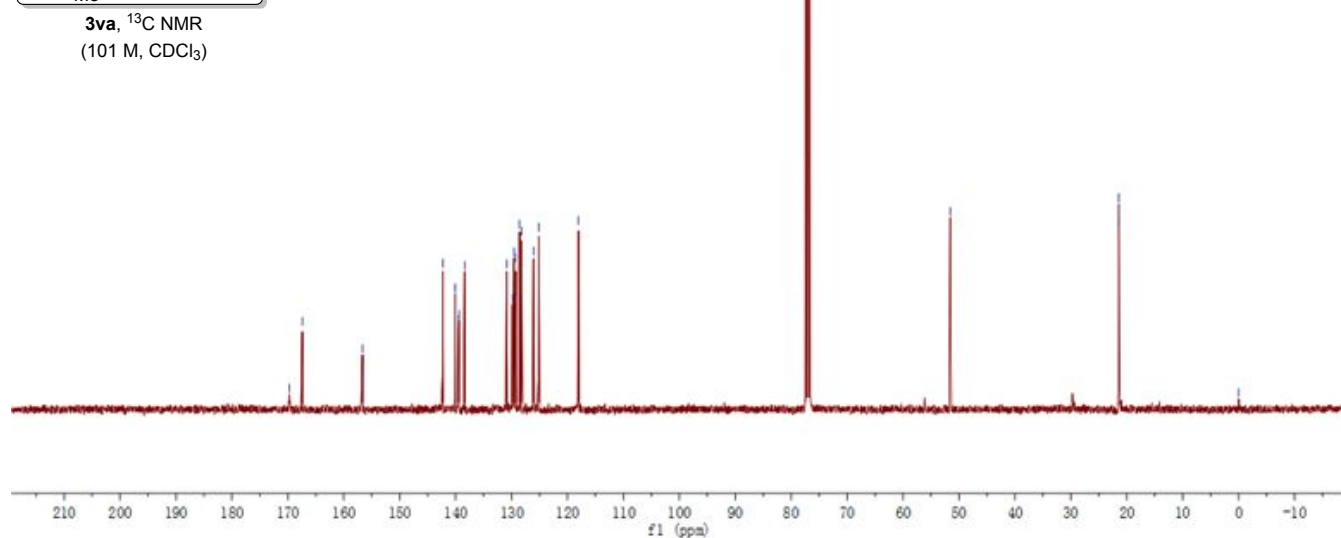
51.57

21.45
21.42

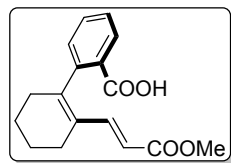
0.00



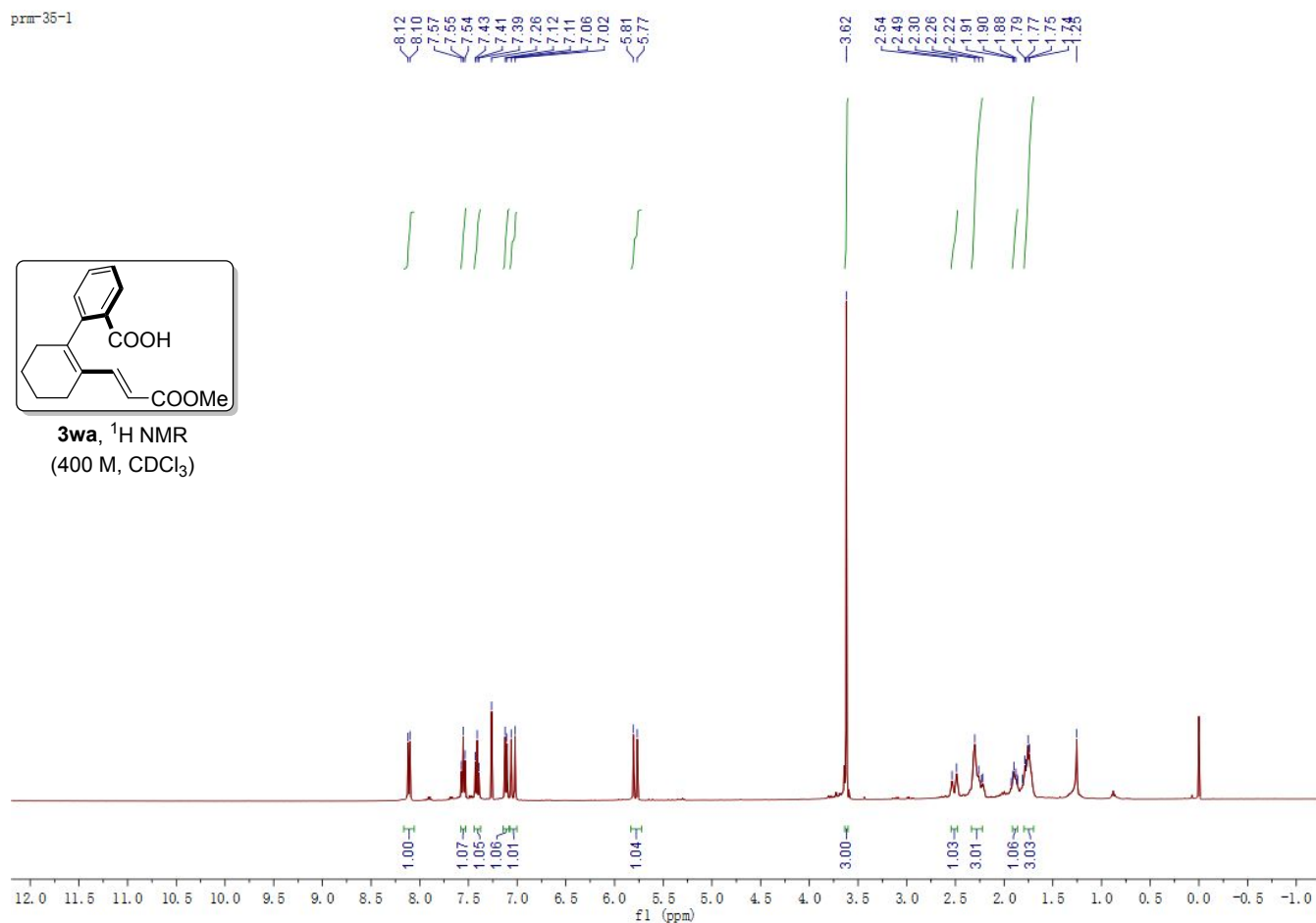
3va, ¹³C NMR
(101 M, CDCl₃)



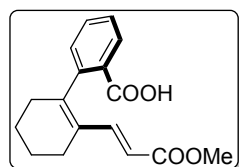
prn-35-1



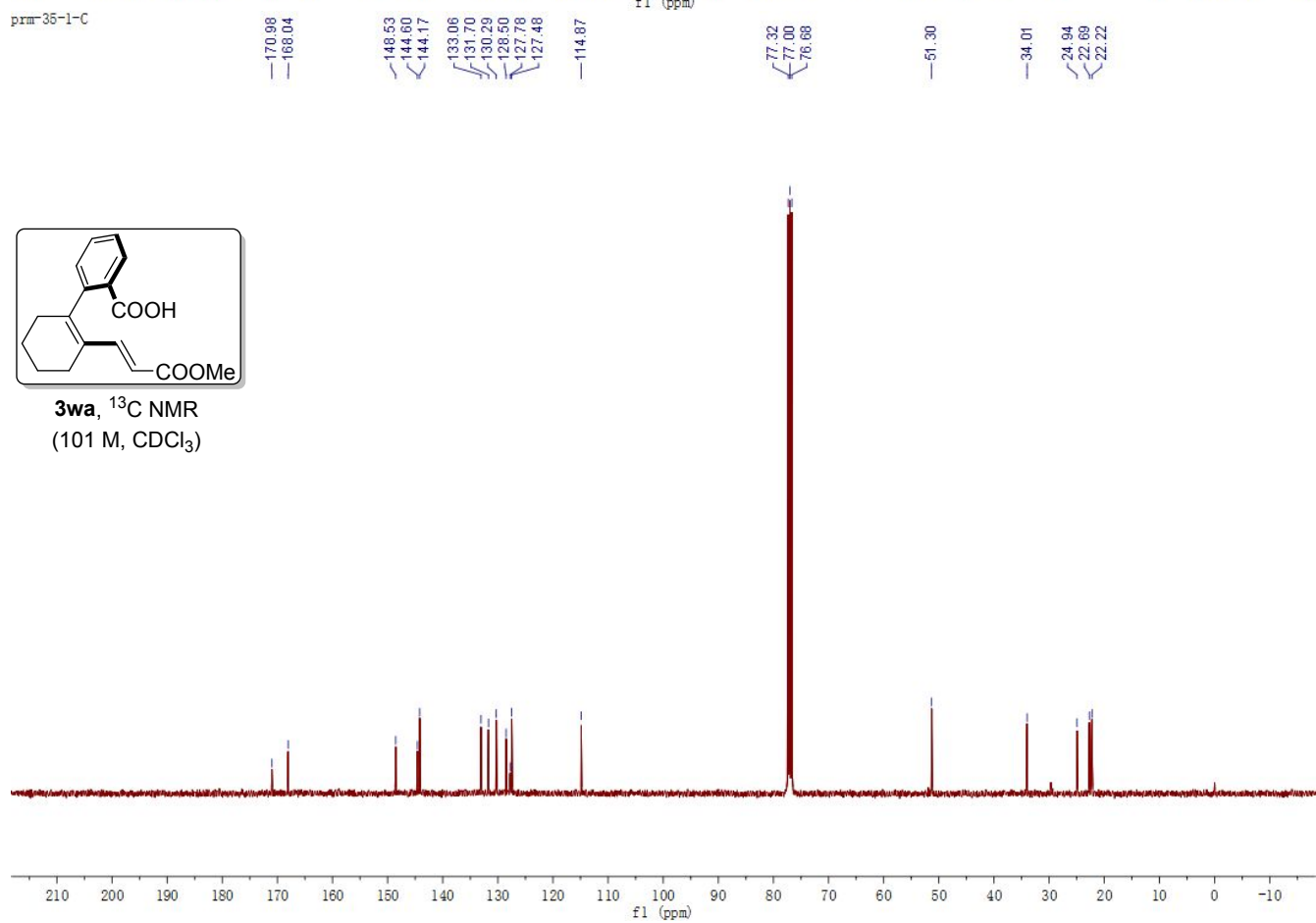
3wa, ^1H NMR
(400 M, CDCl_3)

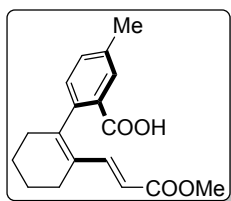


prn-35-1-C

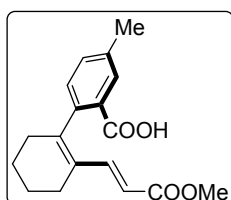
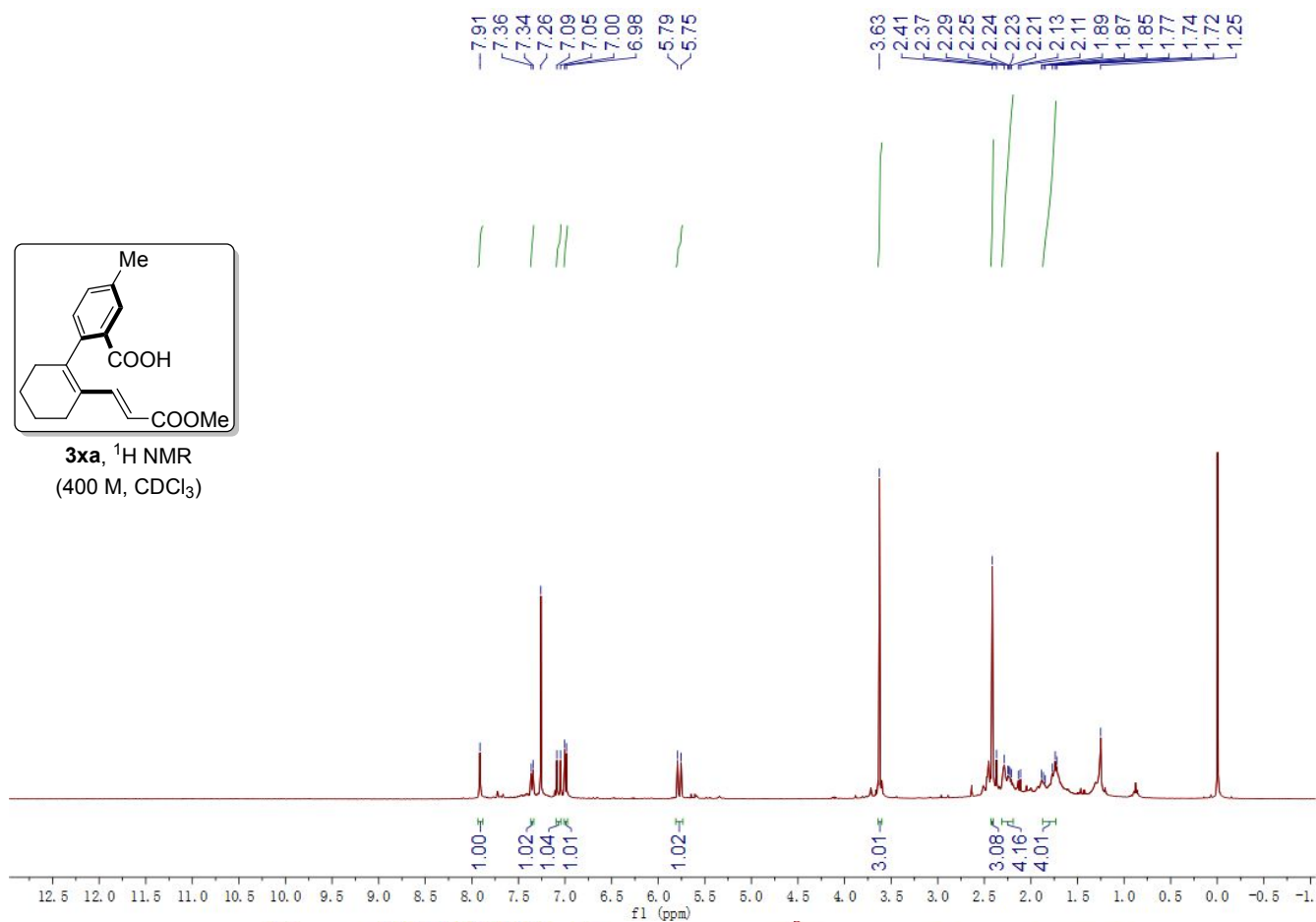


3wa, ^{13}C NMR
(101 M, CDCl_3)

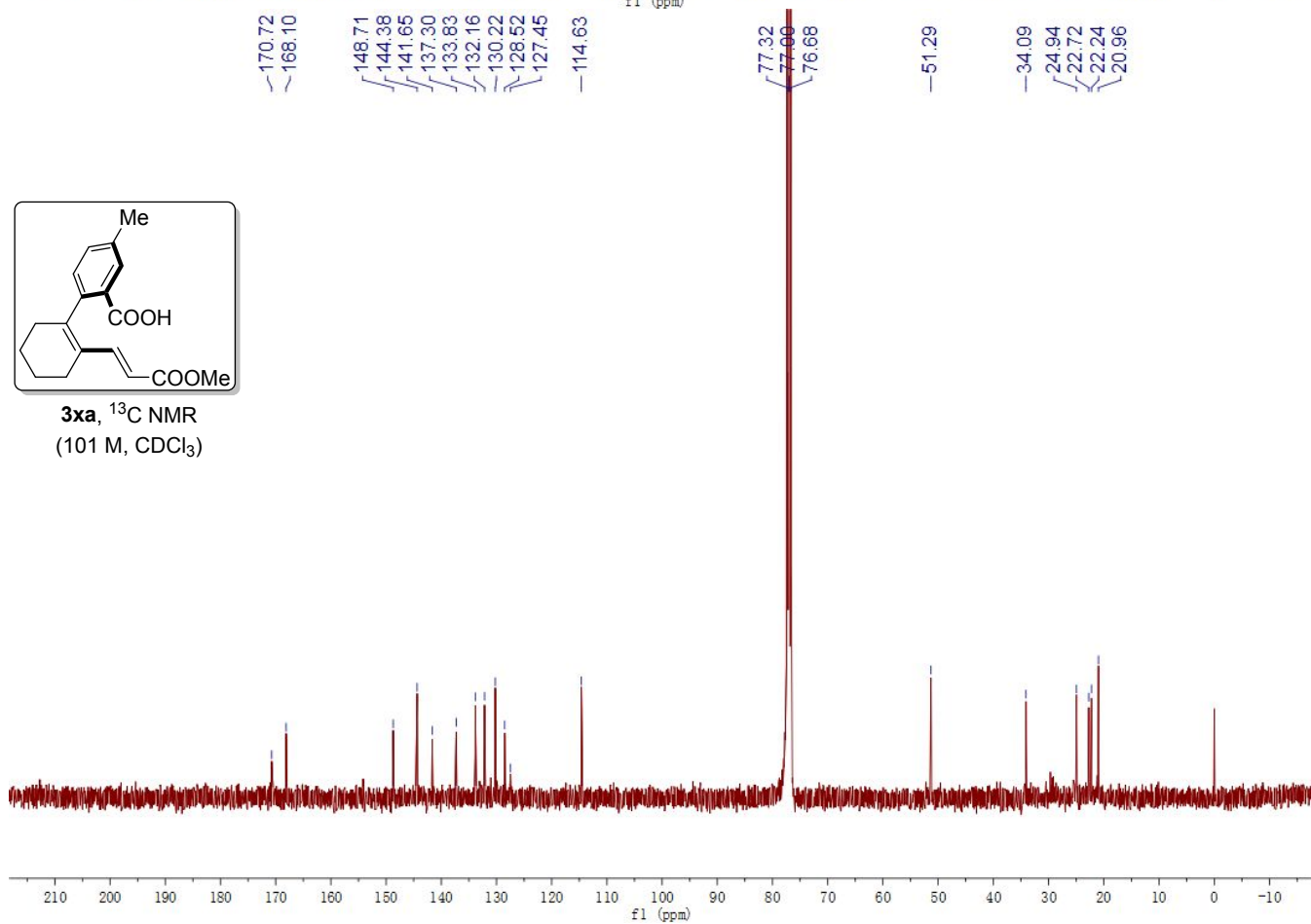




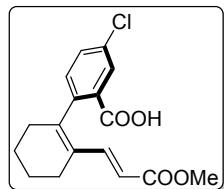
3xa, ¹H NMR
(400 M, CDCl₃)



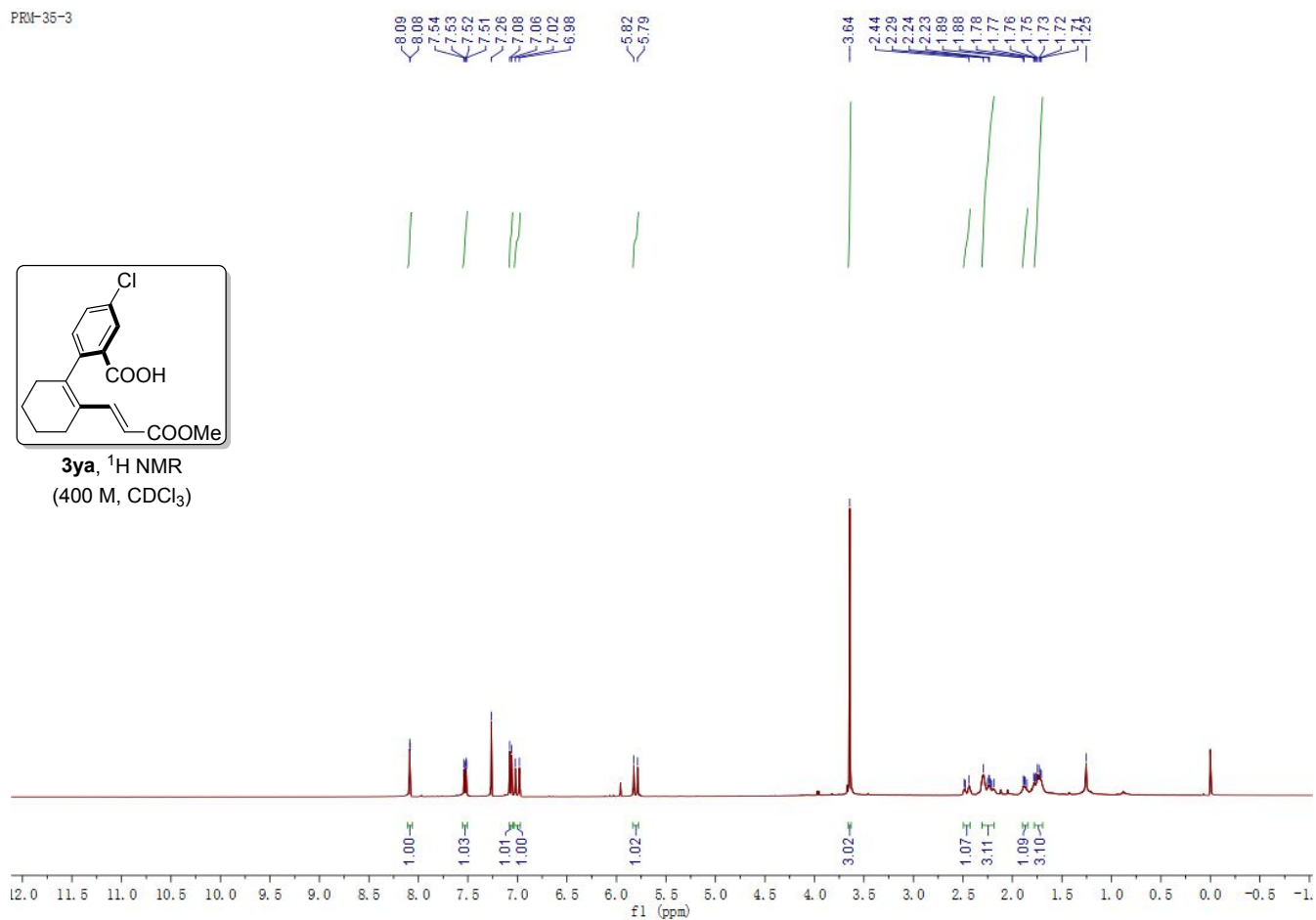
3xa, ¹³C NMR
(101 M, CDCl₃)



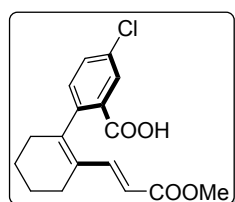
PRM-35-3



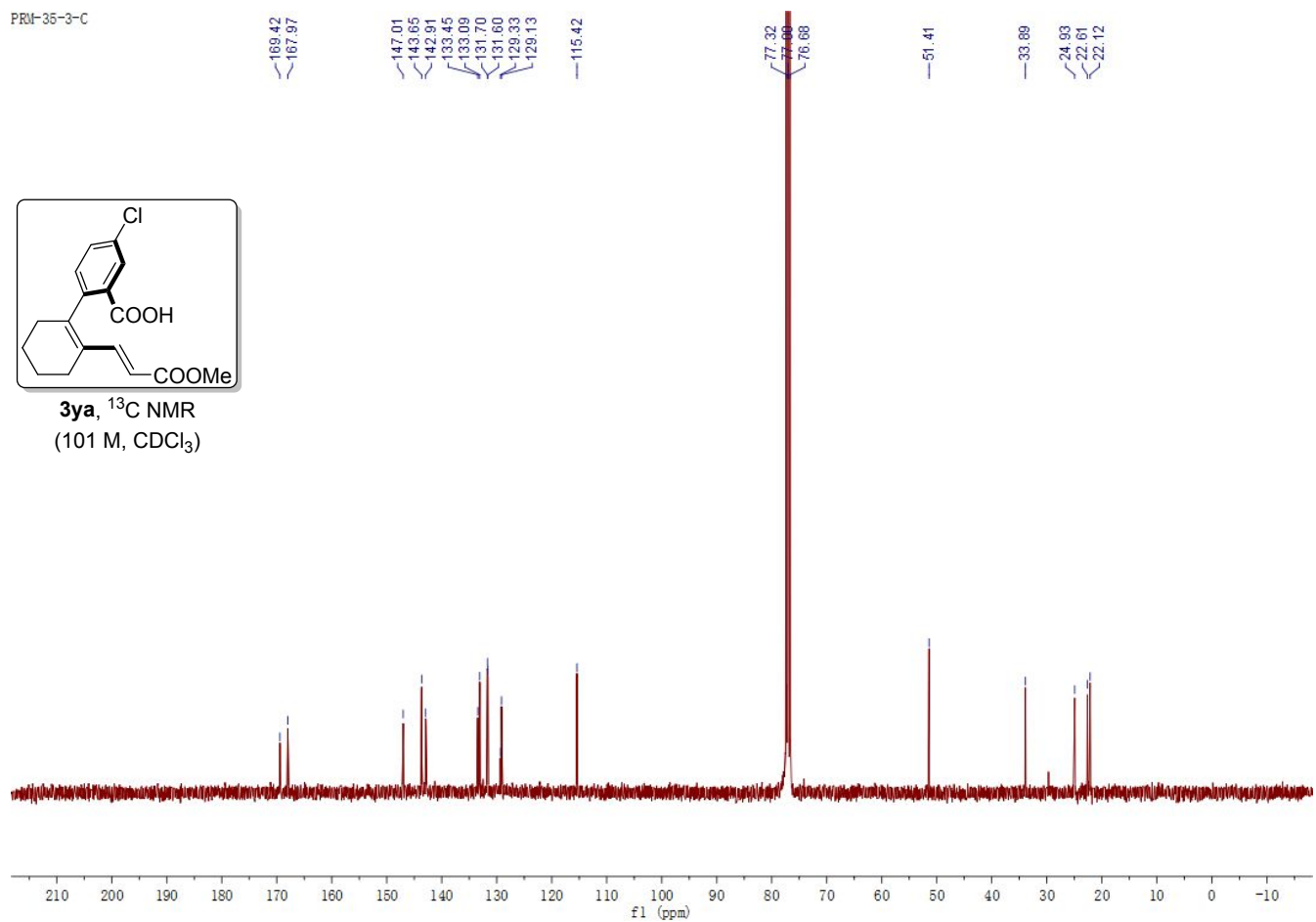
3ya, ^1H NMR
(400 M, CDCl_3)

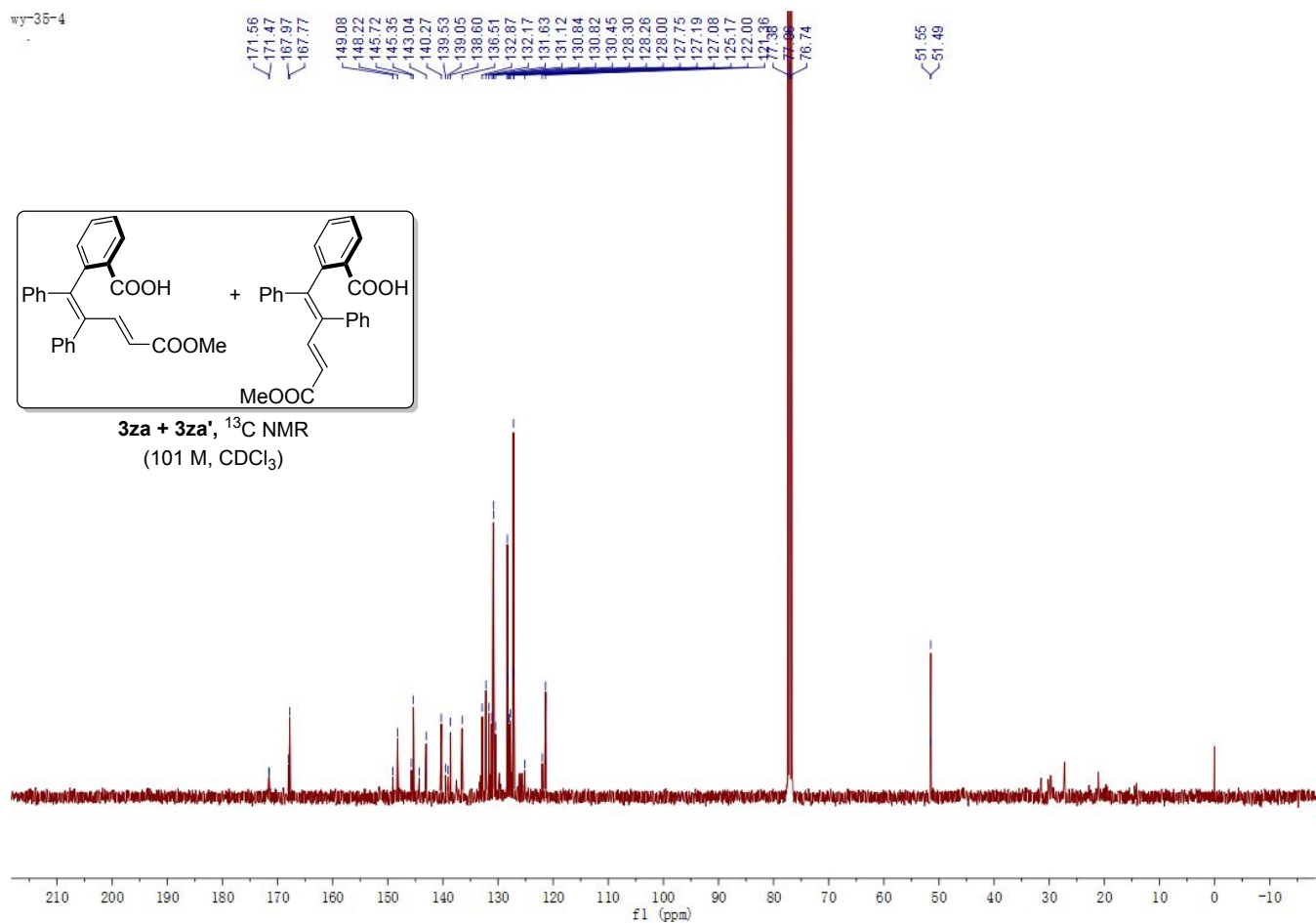
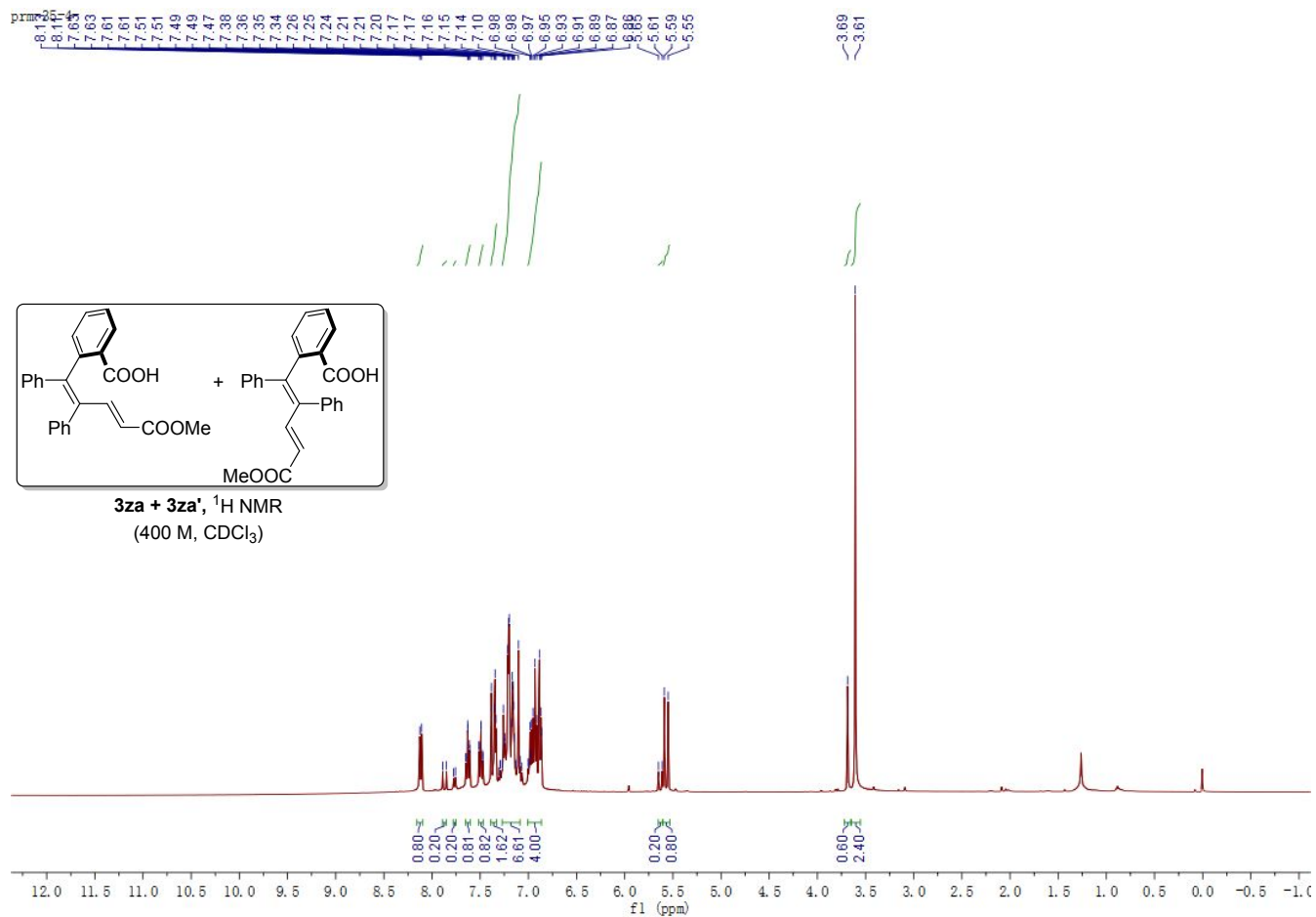


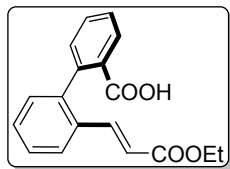
PRM-35-3-C



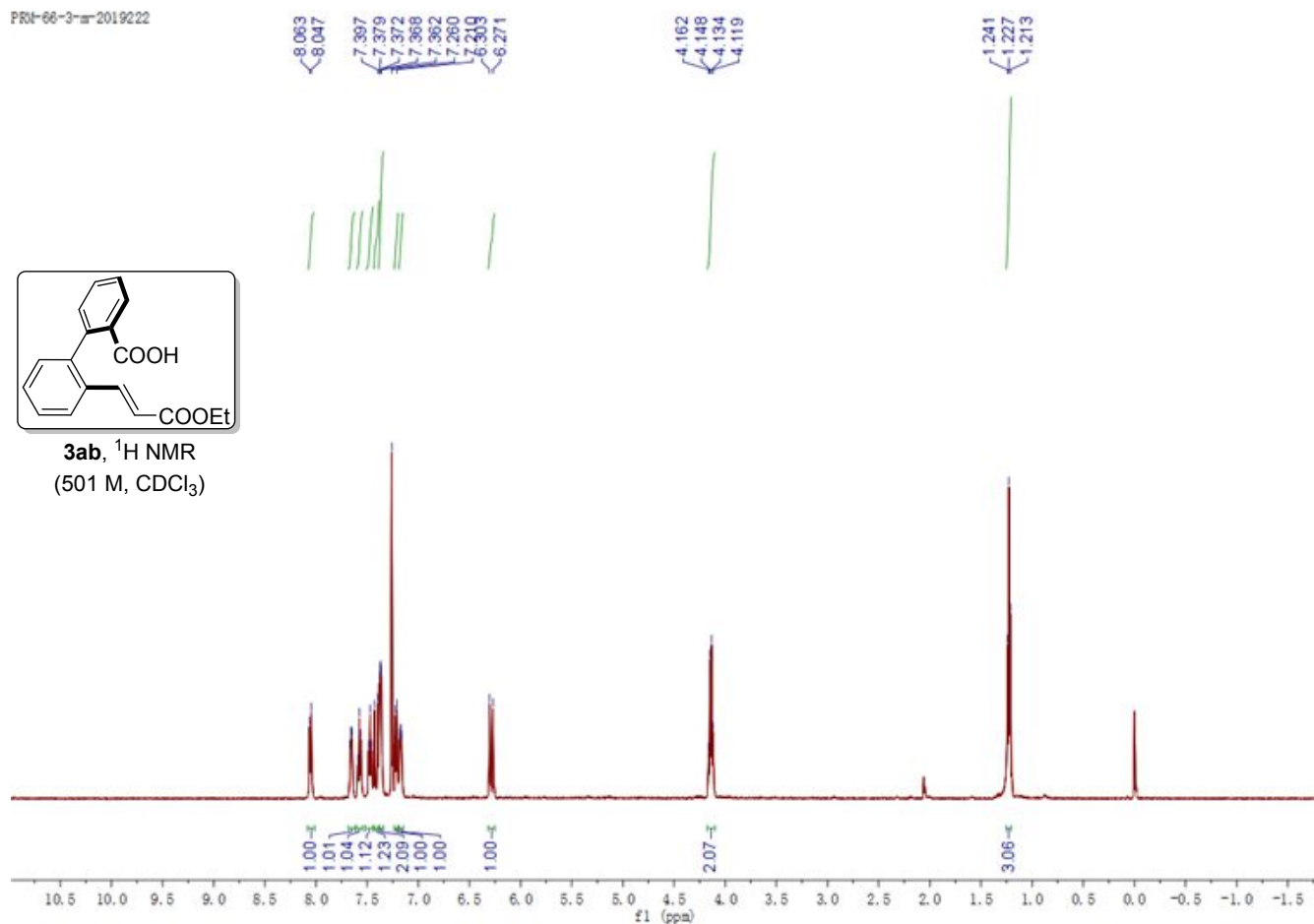
3ya, ^{13}C NMR
(101 M, CDCl_3)





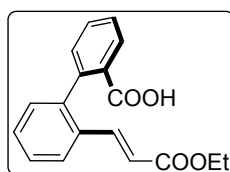


3ab, ¹H NMR
(501 M, CDCl₃)

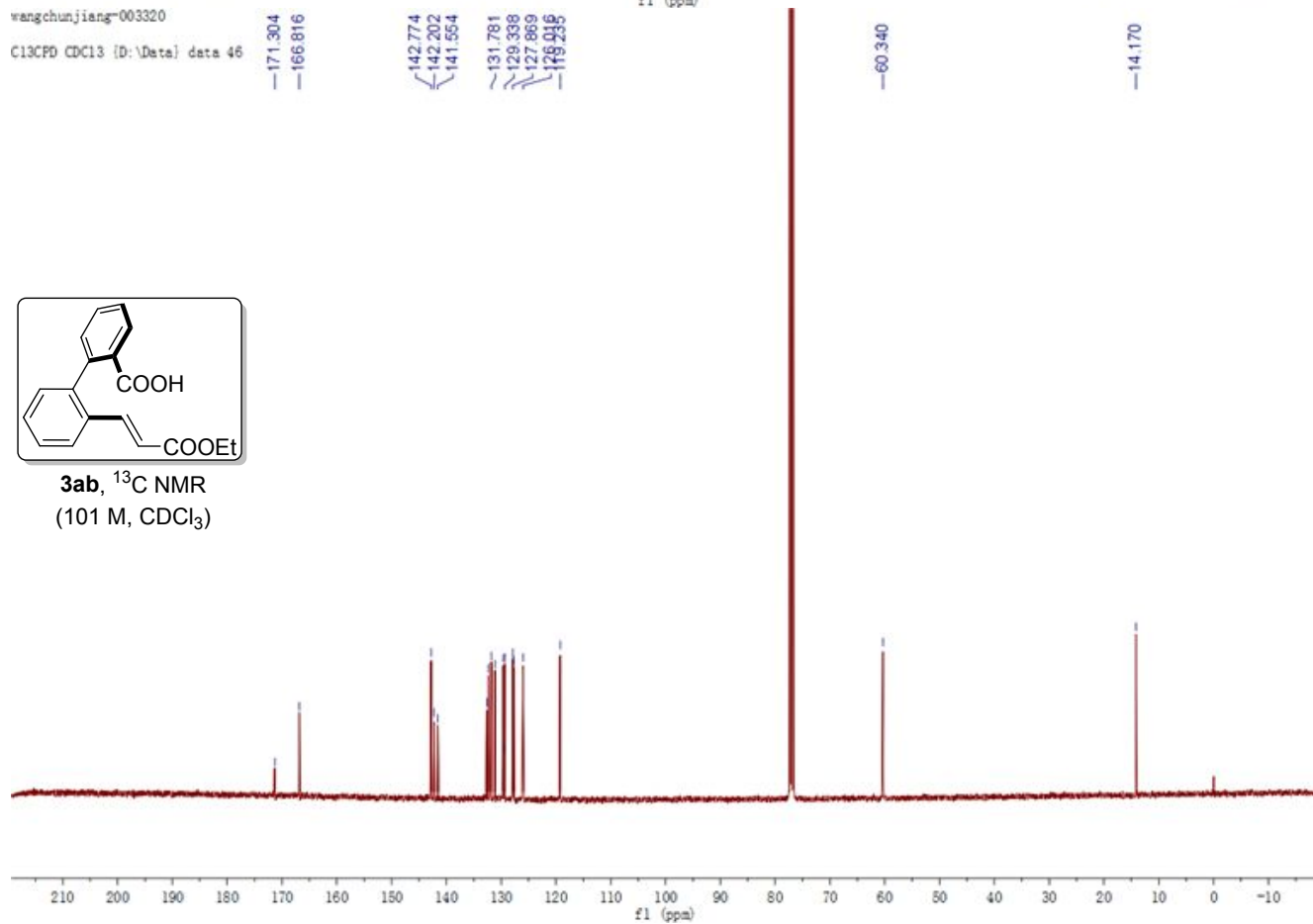


wangchunjiang-003320

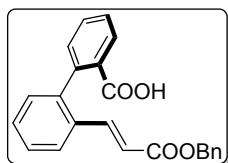
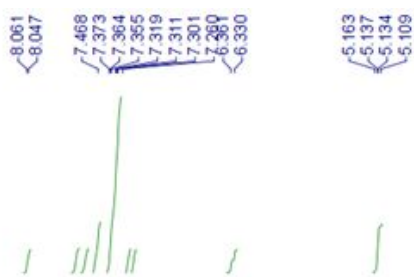
C13CPD CDCl3 [D:\Data] data 46



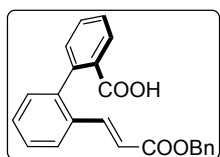
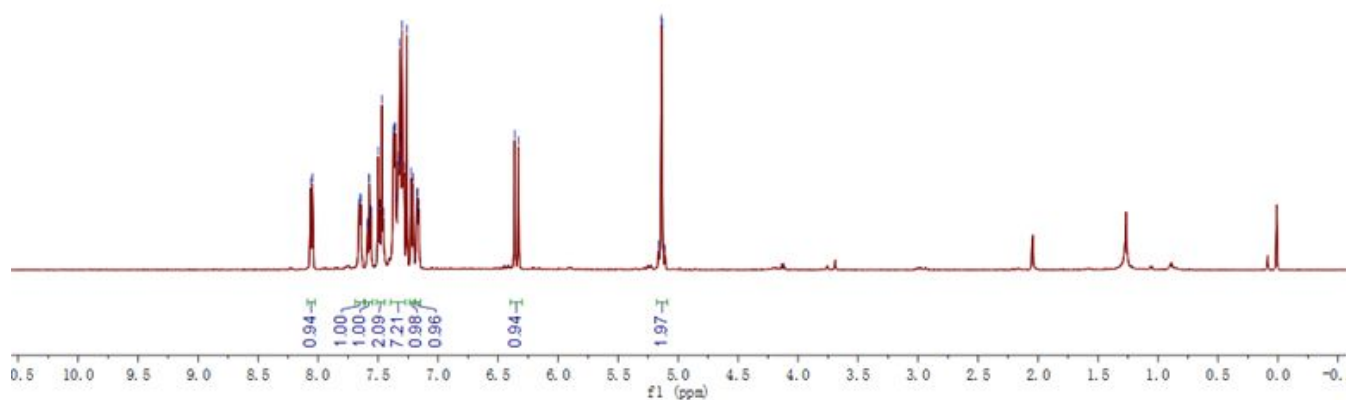
3ab, ¹³C NMR
(101 M, CDCl₃)



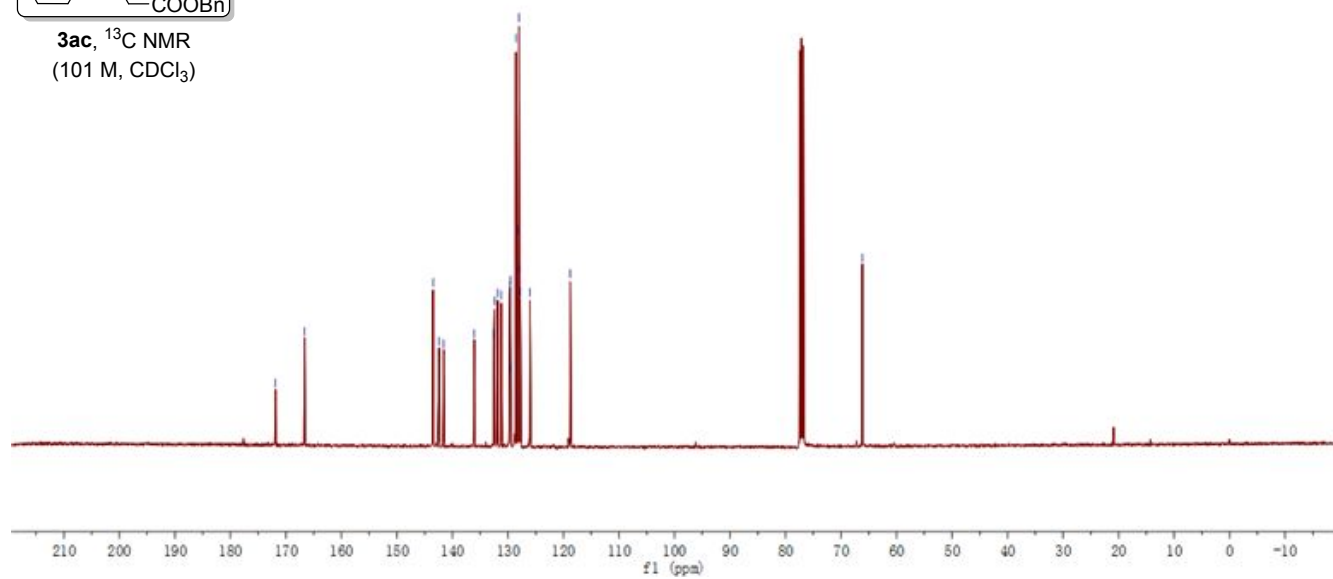
PR1-66-3-m

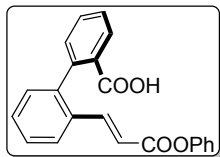
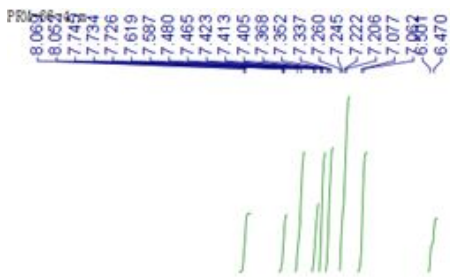


3ac, ^1H NMR
(501 M, CDCl_3)

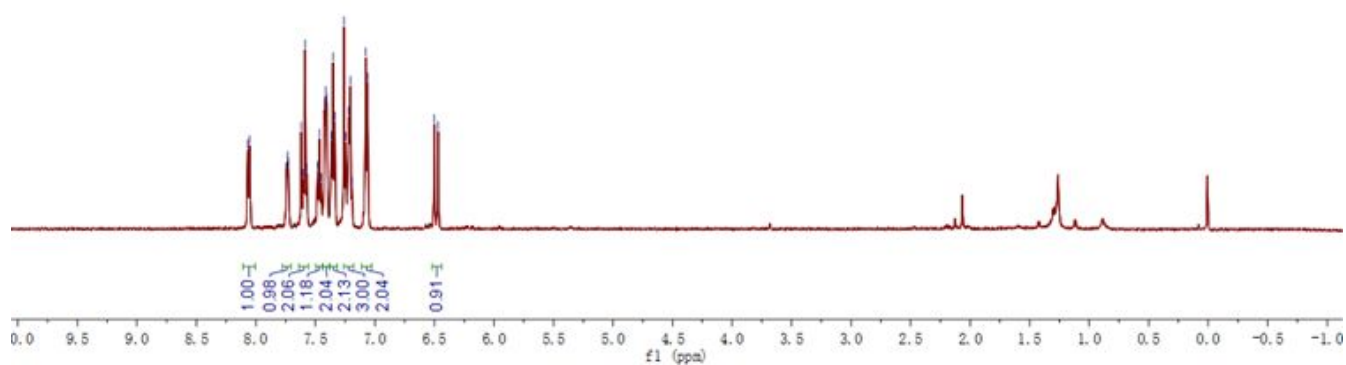


3ac, ^{13}C NMR
(101 M, CDCl_3)



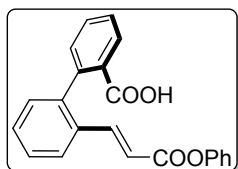


3ad, ^1H NMR
(501 M, CDCl_3)

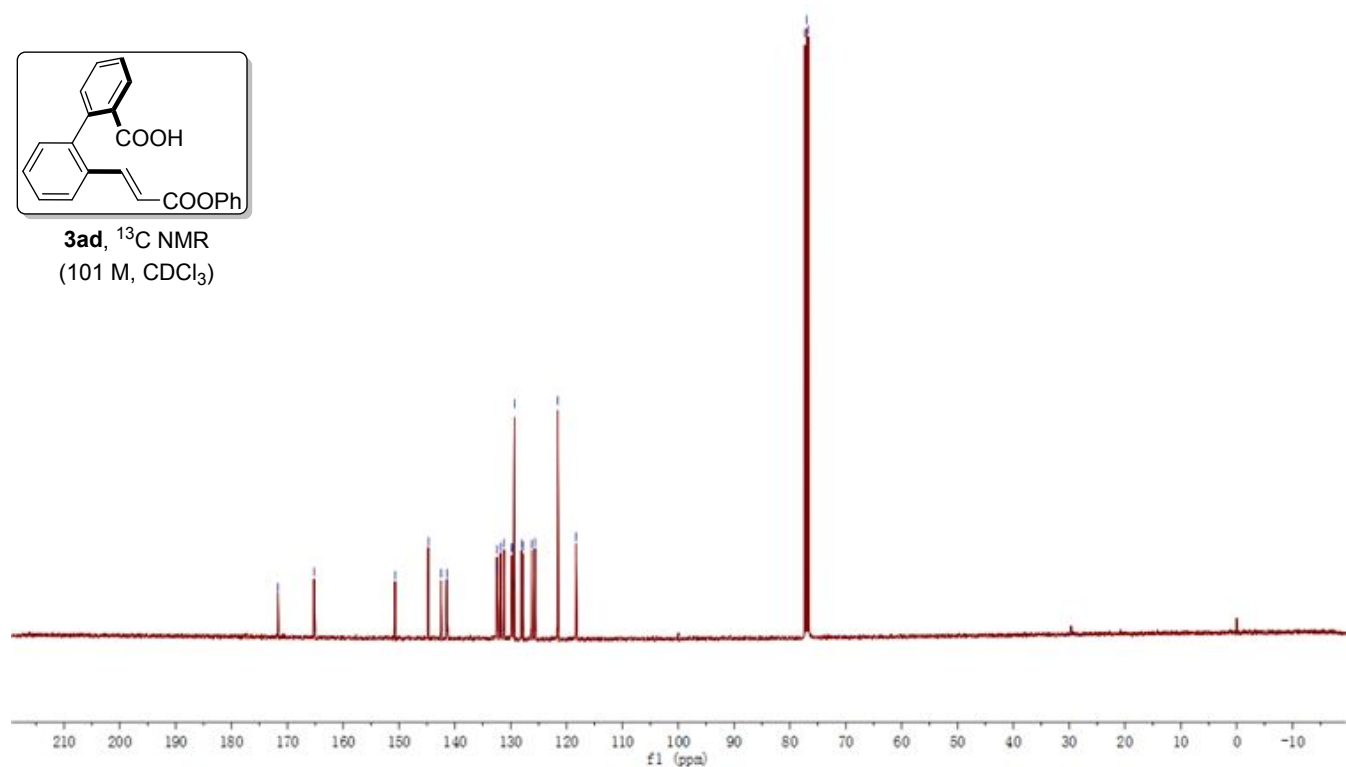


wangchunjiang-003313

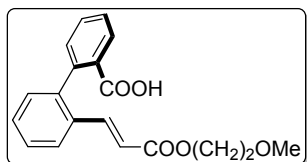
C13CPD CDCl3 [D:\Data] data 33



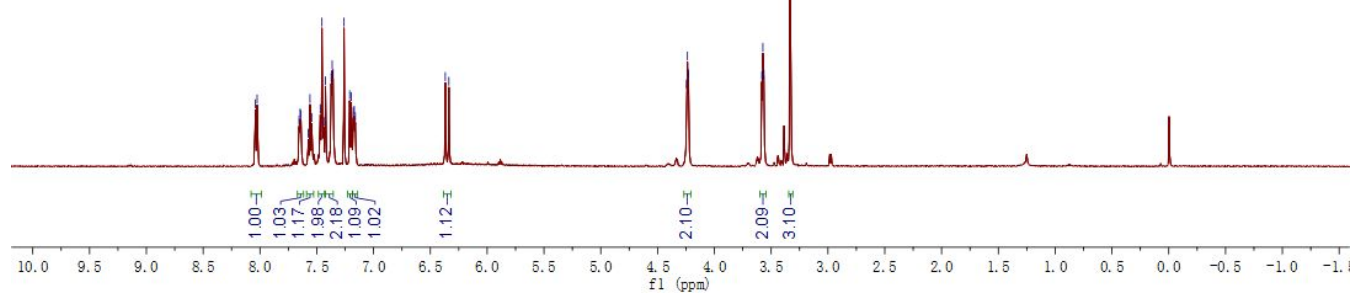
3ad, ^{13}C NMR
(101 M, CDCl_3)



8.041
7.454
7.423
7.373
7.364
7.260
7.210
6.385
6.337
4.246
4.237
4.227
3.582
3.573
3.564
3.334



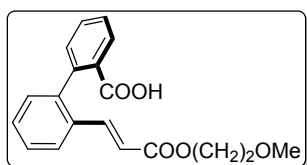
3ae, ¹H NMR
(501 M, CDCl₃)



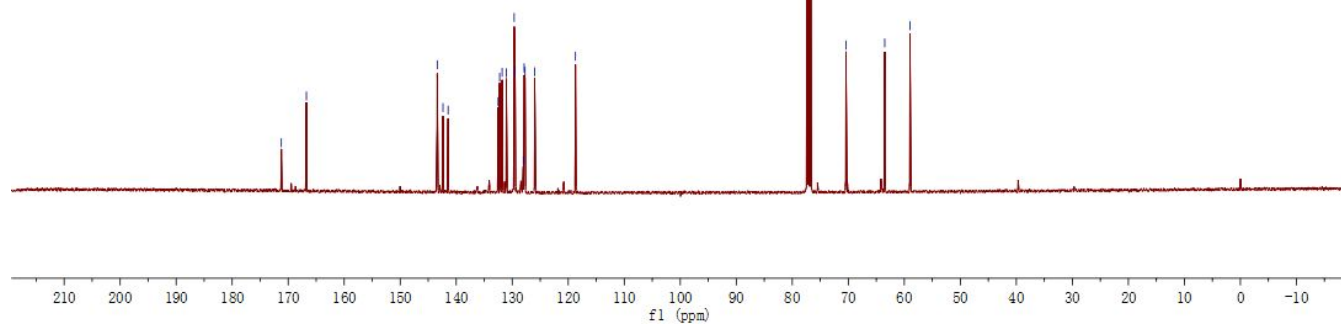
wangchunjiang-003318

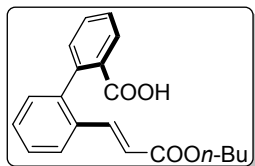
C13CPD CDCl3 {D:\Data} data 42

171.219
166.748
143.388
142.360
141.448
129.651
129.484
127.876
127.712
125.988
118.707
70.421
63.494
58.994

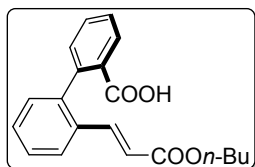
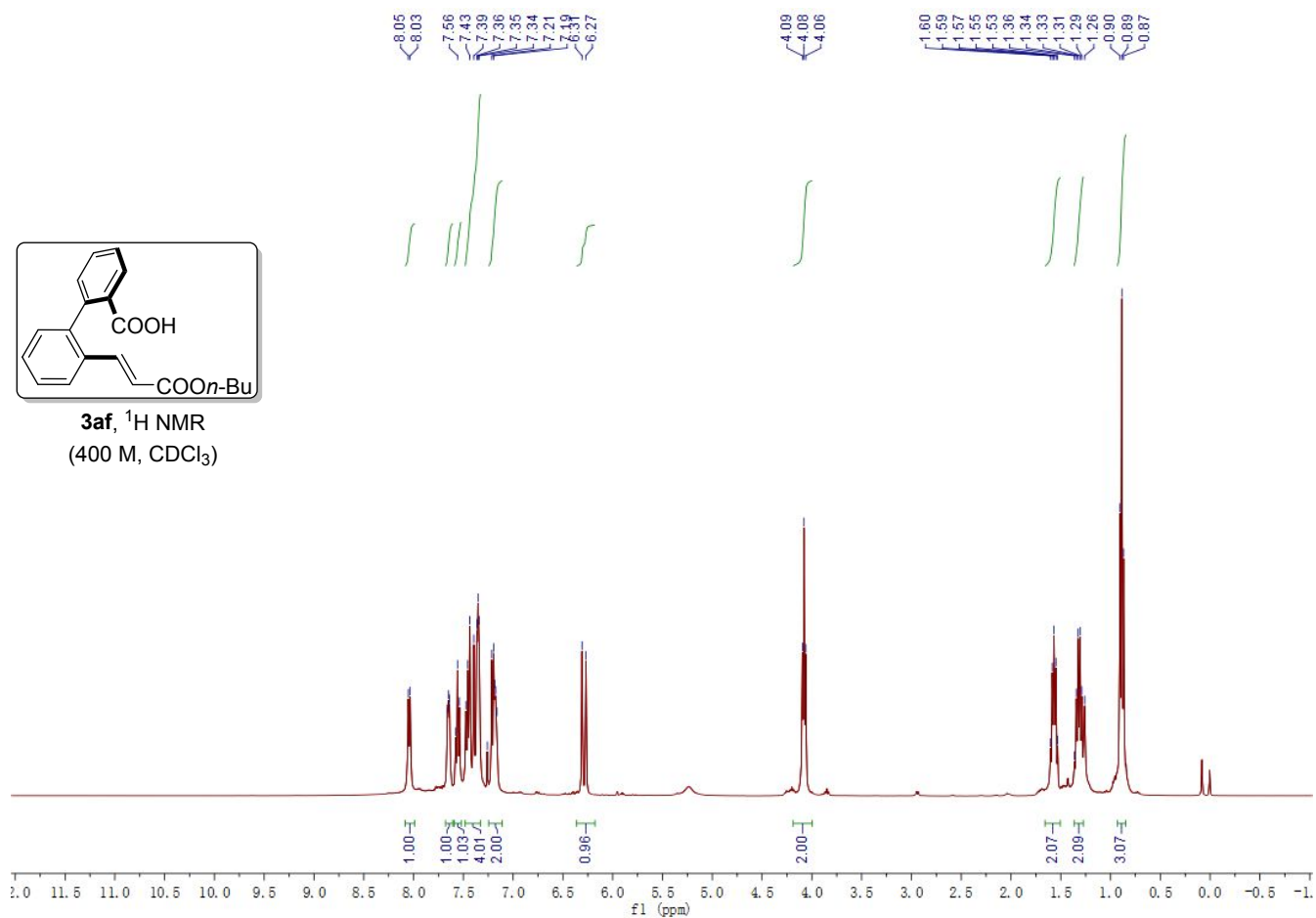


3ae, ¹³C NMR
(101 M, CDCl₃)

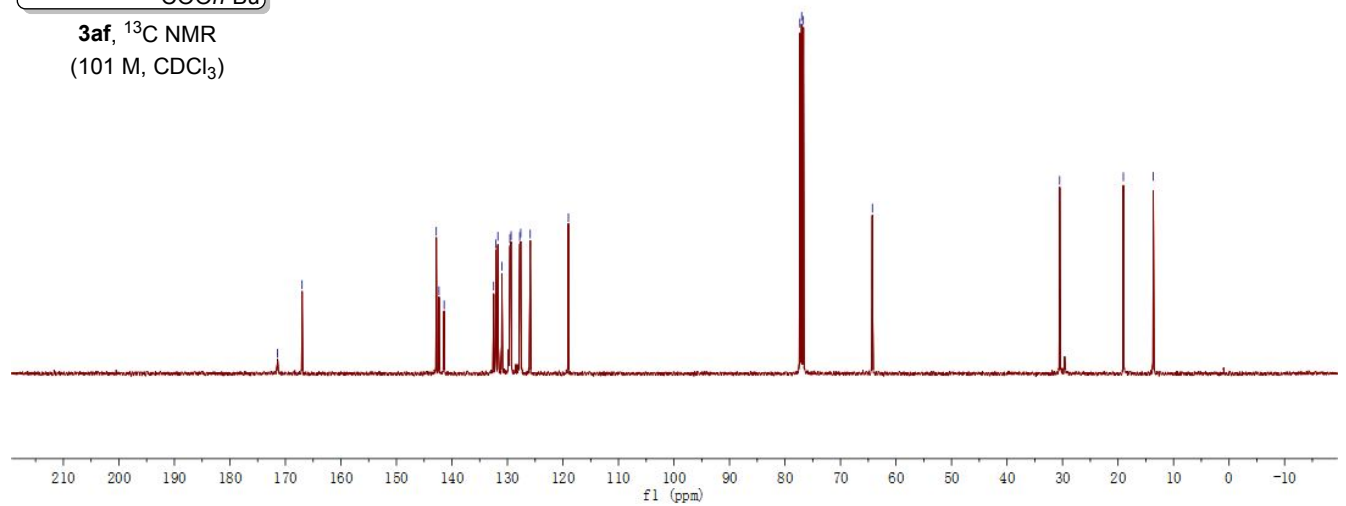


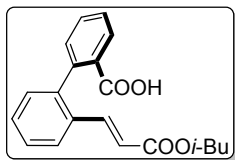


3af, ^1H NMR
(400 M, CDCl_3)

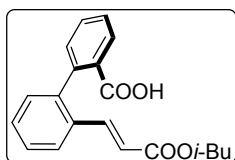
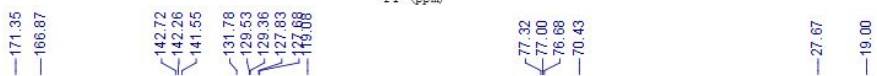
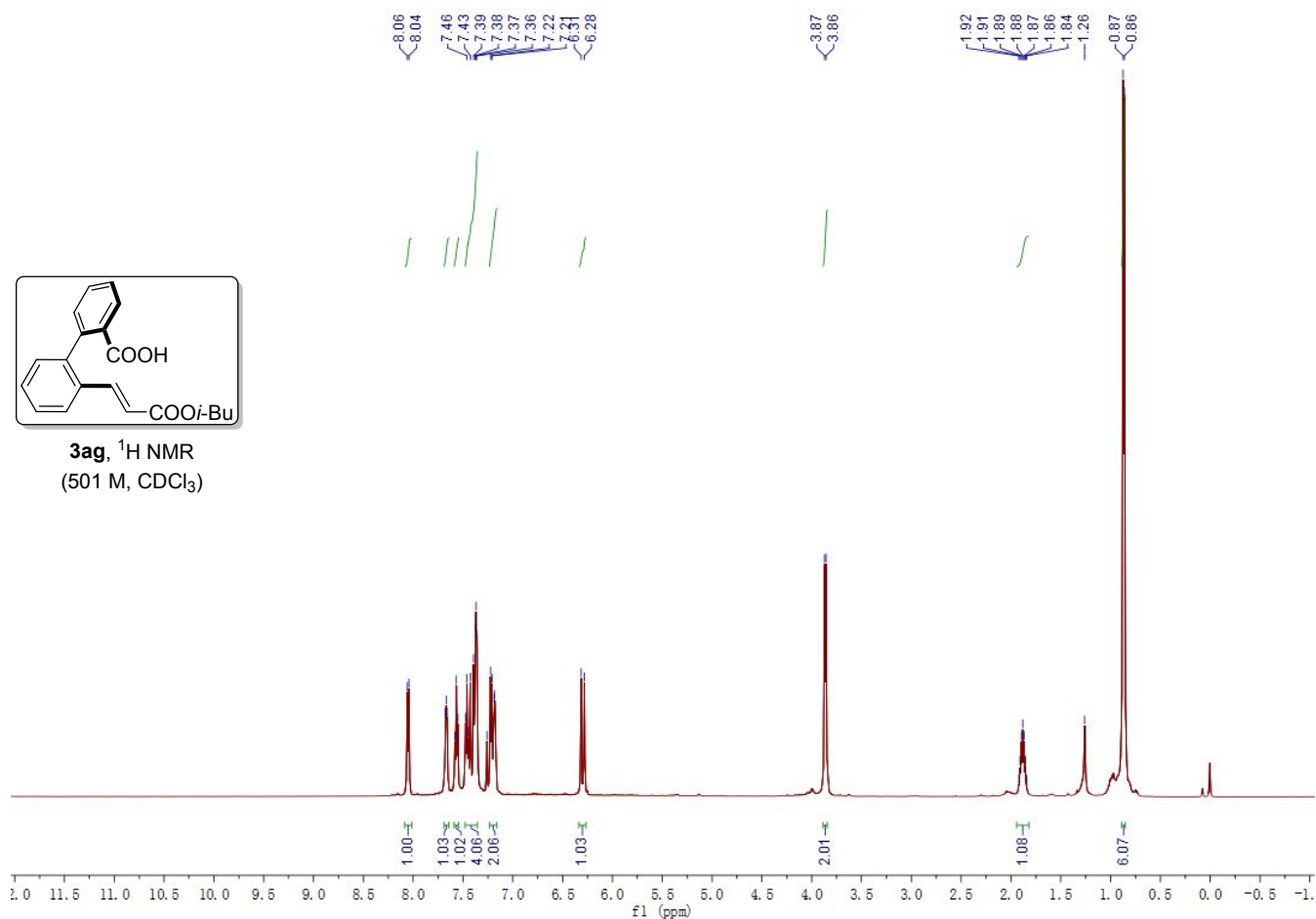


3af, ^{13}C NMR
(101 M, CDCl_3)

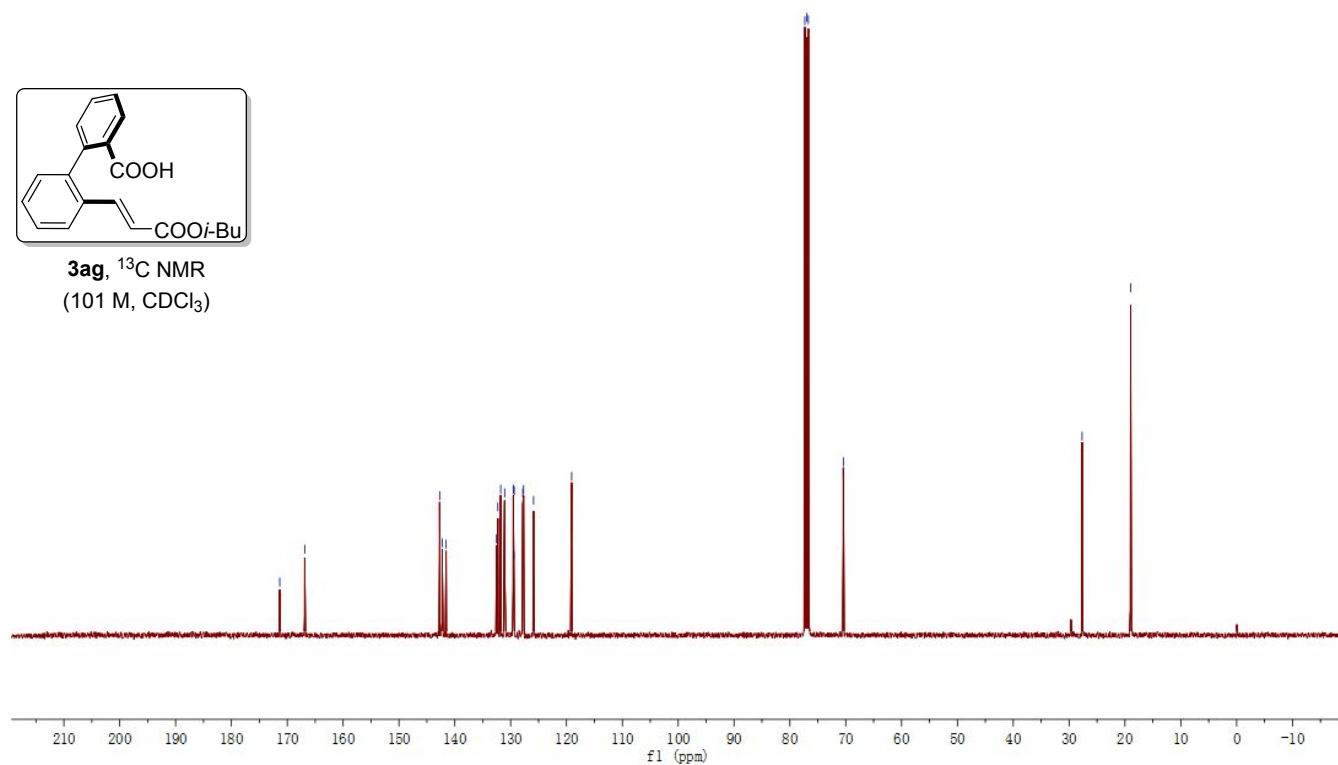


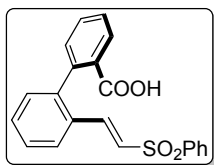
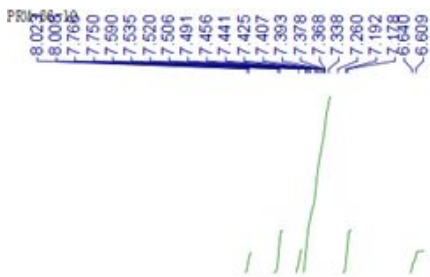


3ag, ^1H NMR
(501 M, CDCl_3)

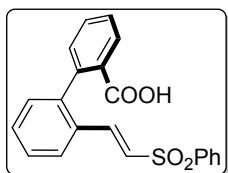
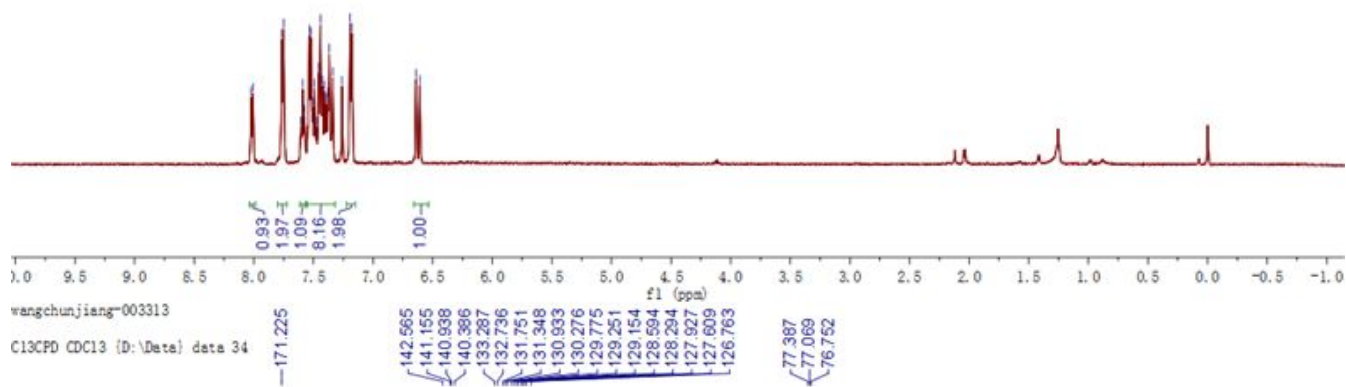


3ag, ^{13}C NMR
(101 M, CDCl_3)

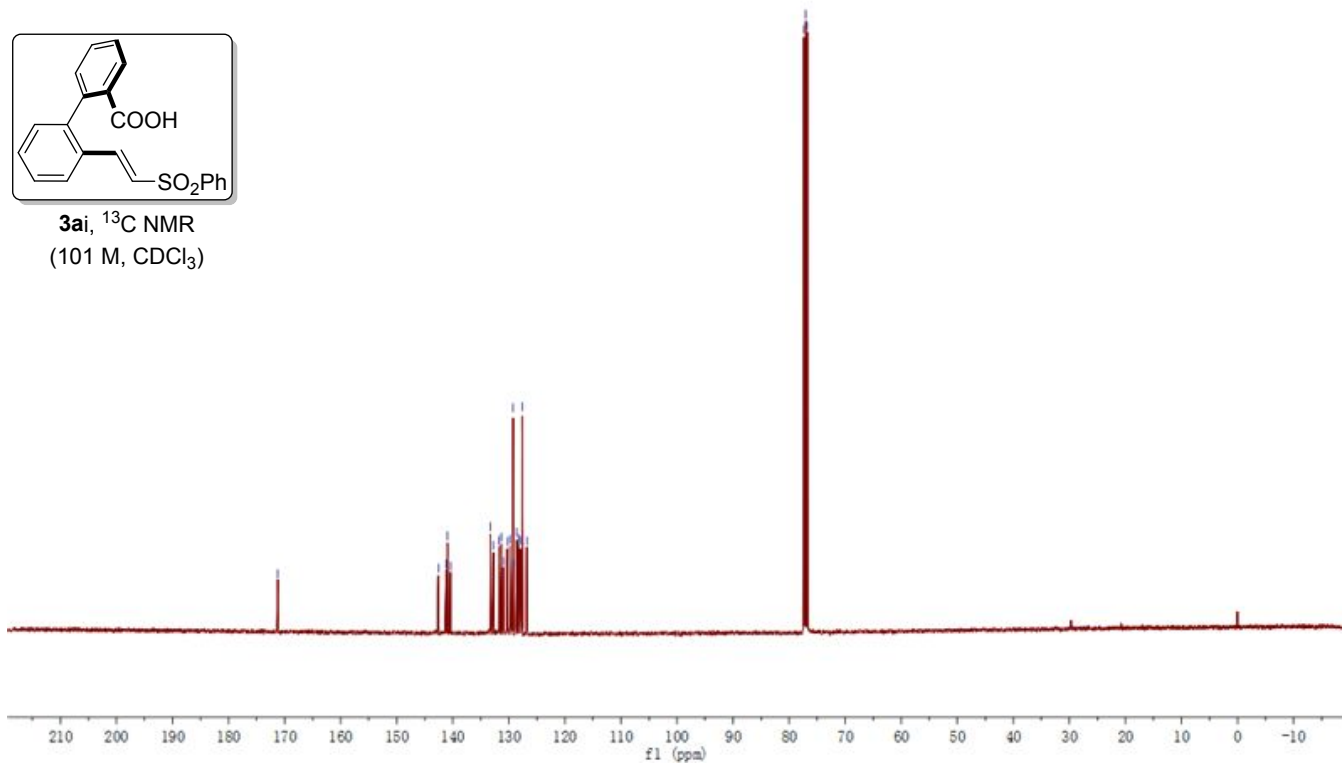


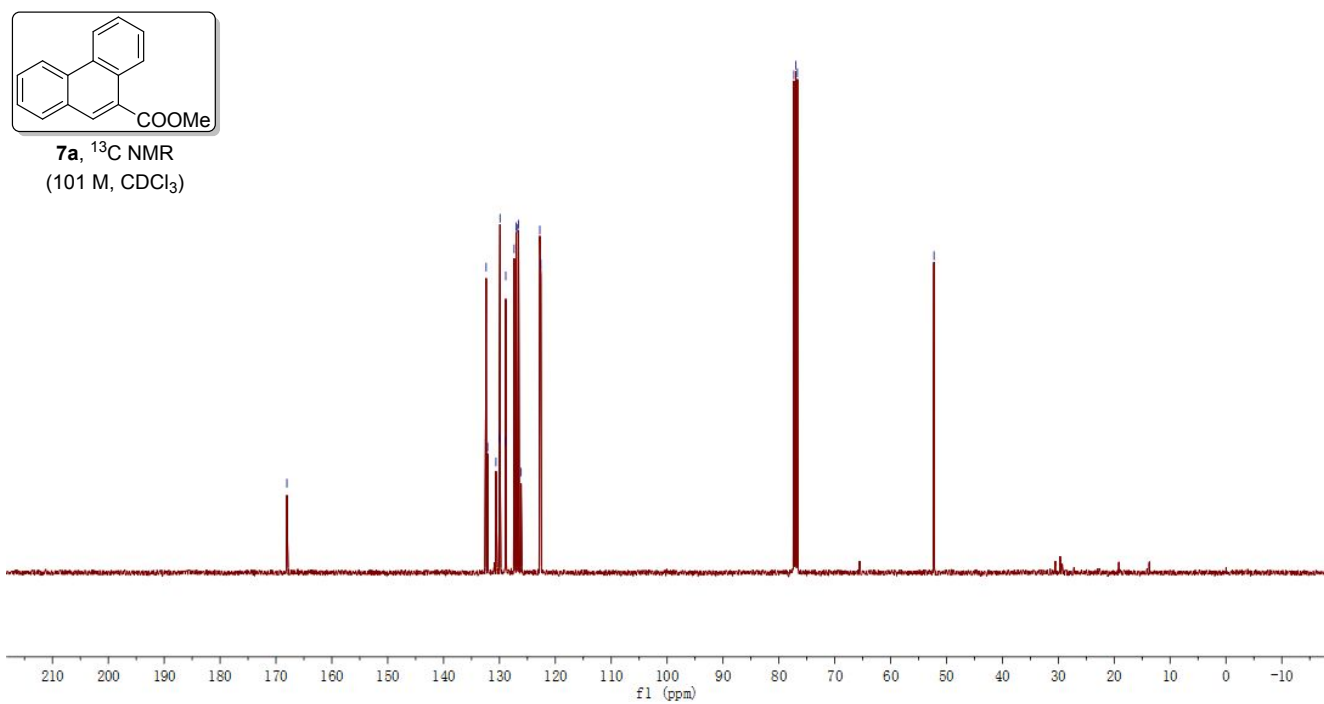
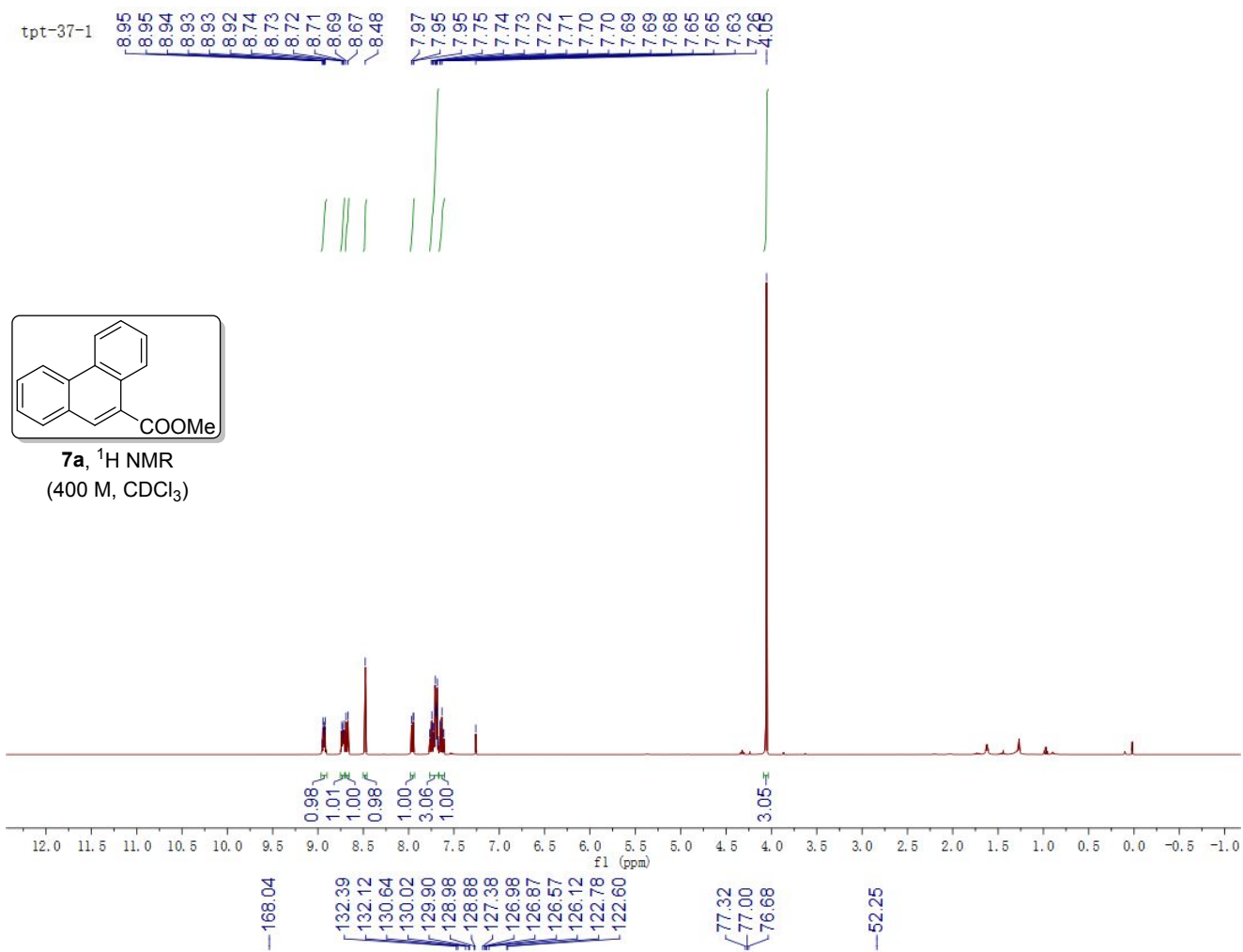


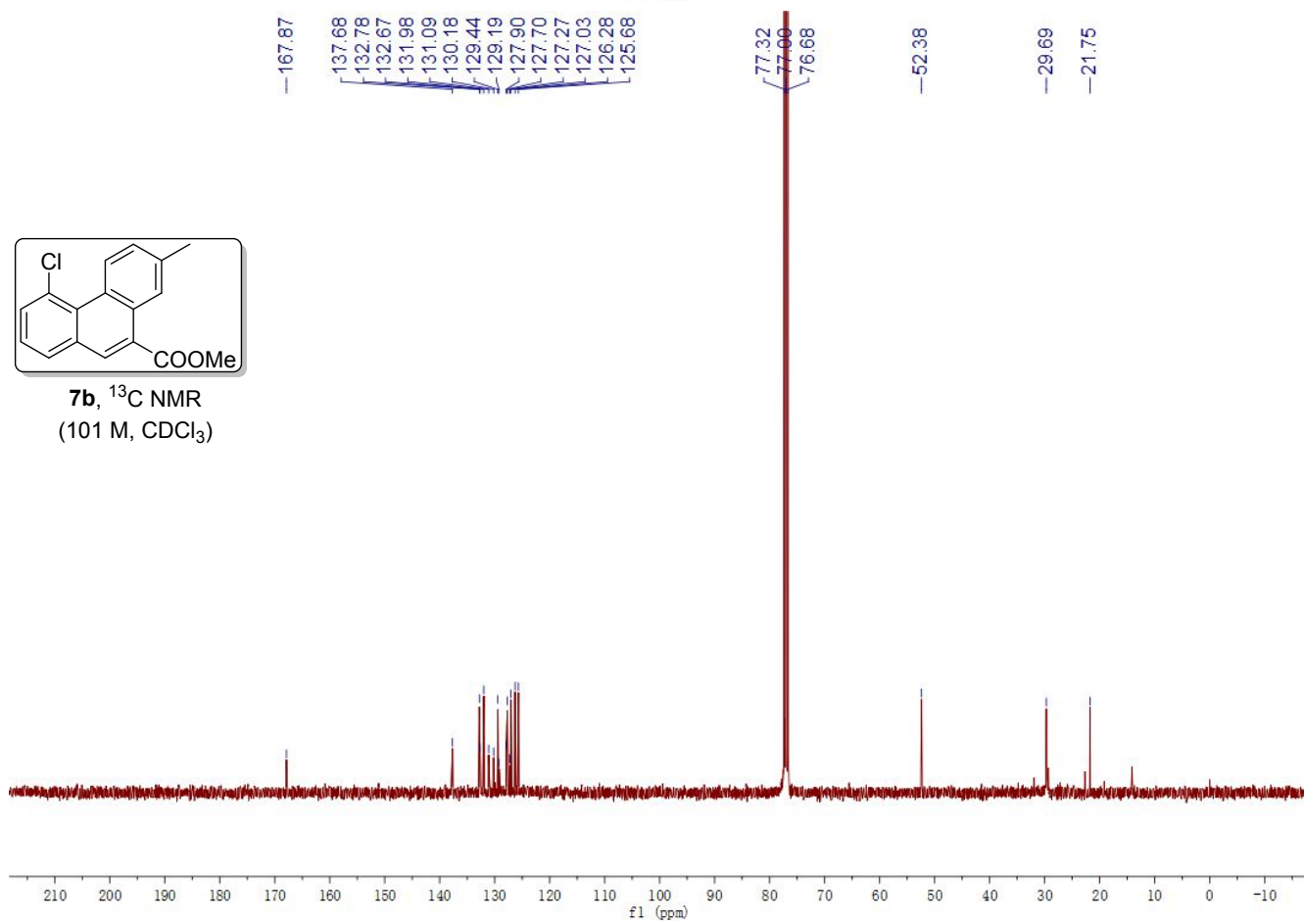
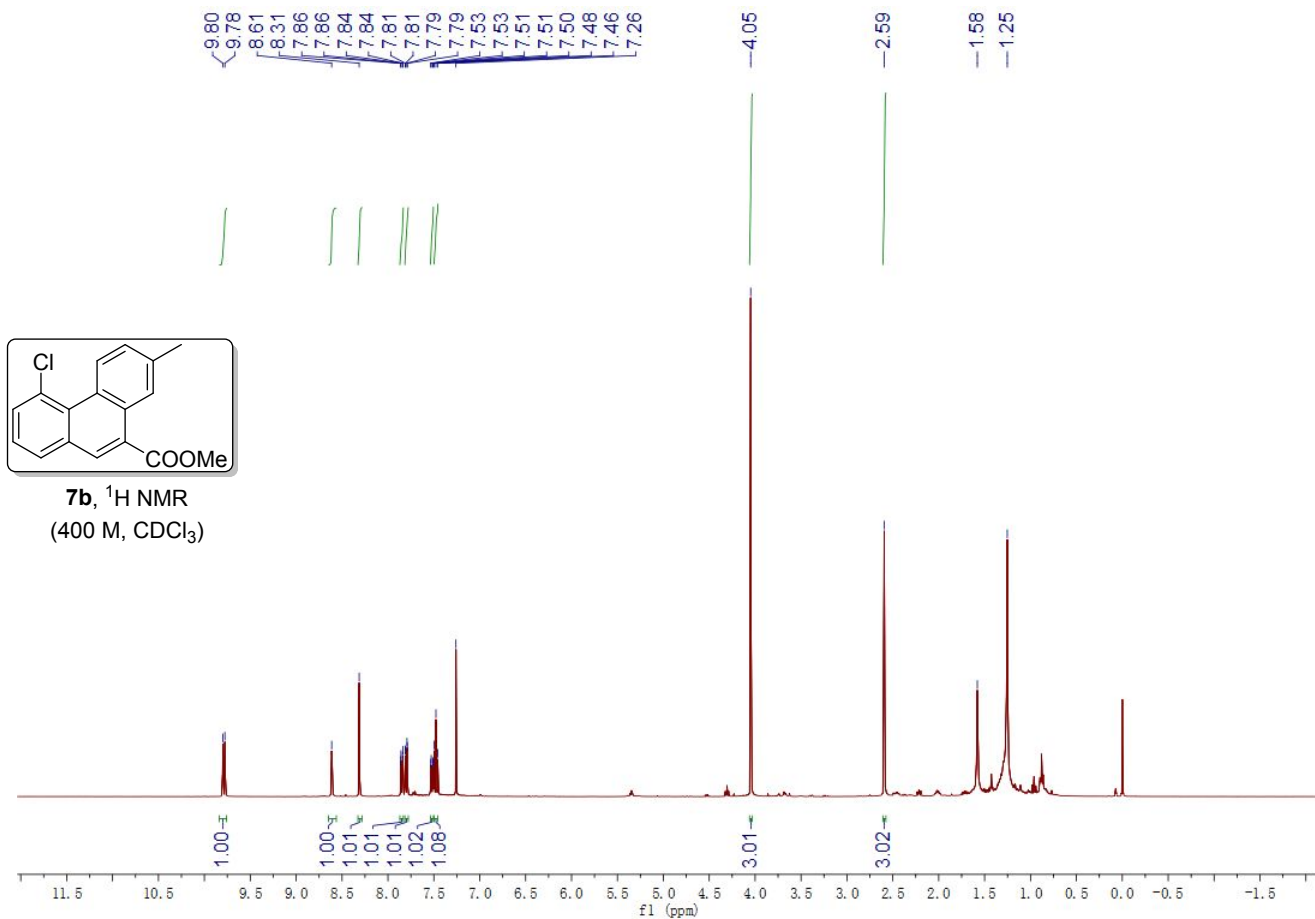
3ai, $^1\text{H NMR}$
(501 M, CDCl_3)

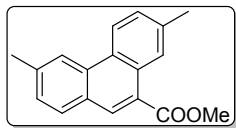


3ai, $^{13}\text{C NMR}$
(101 M, CDCl_3)

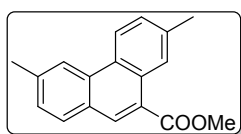
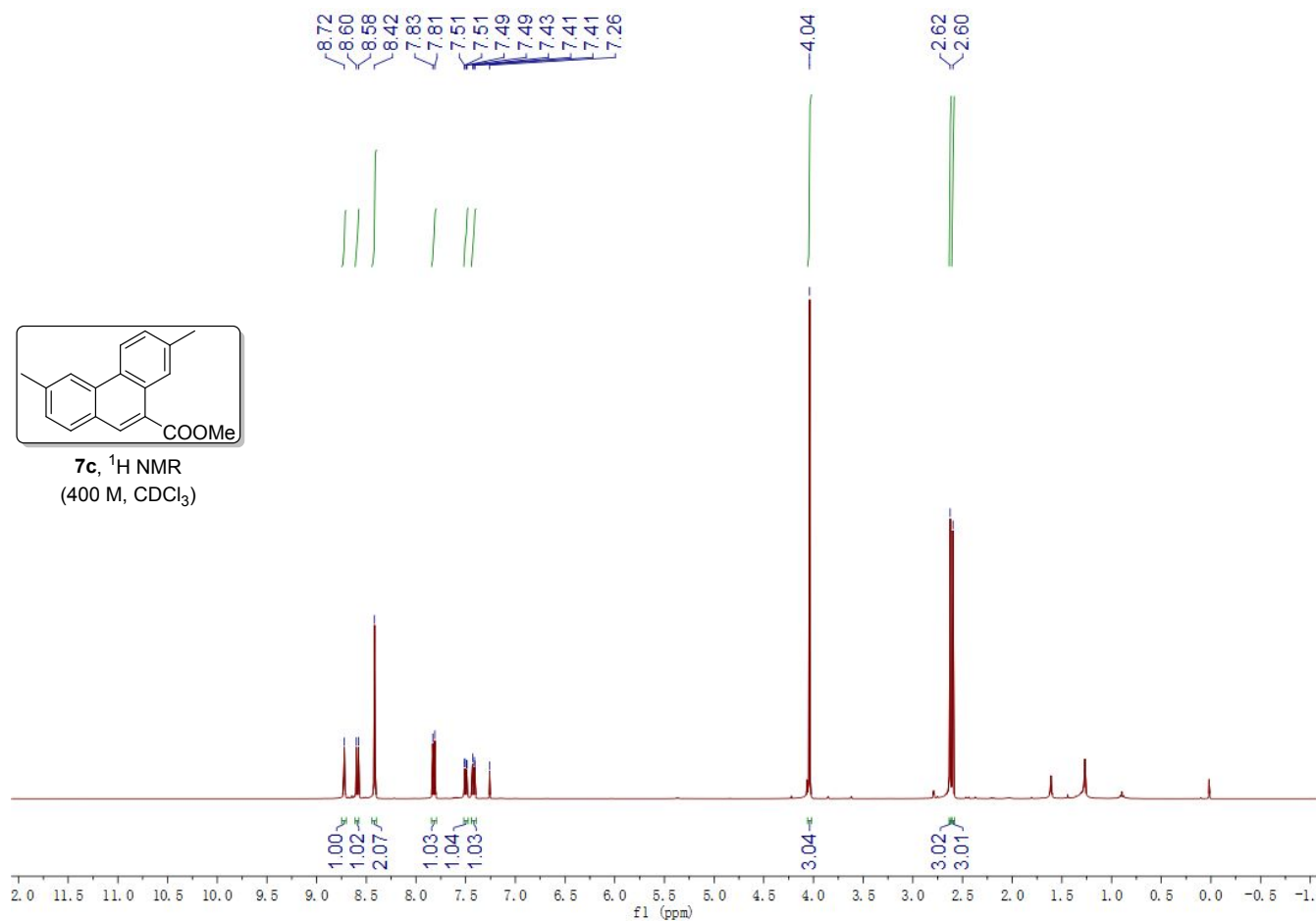




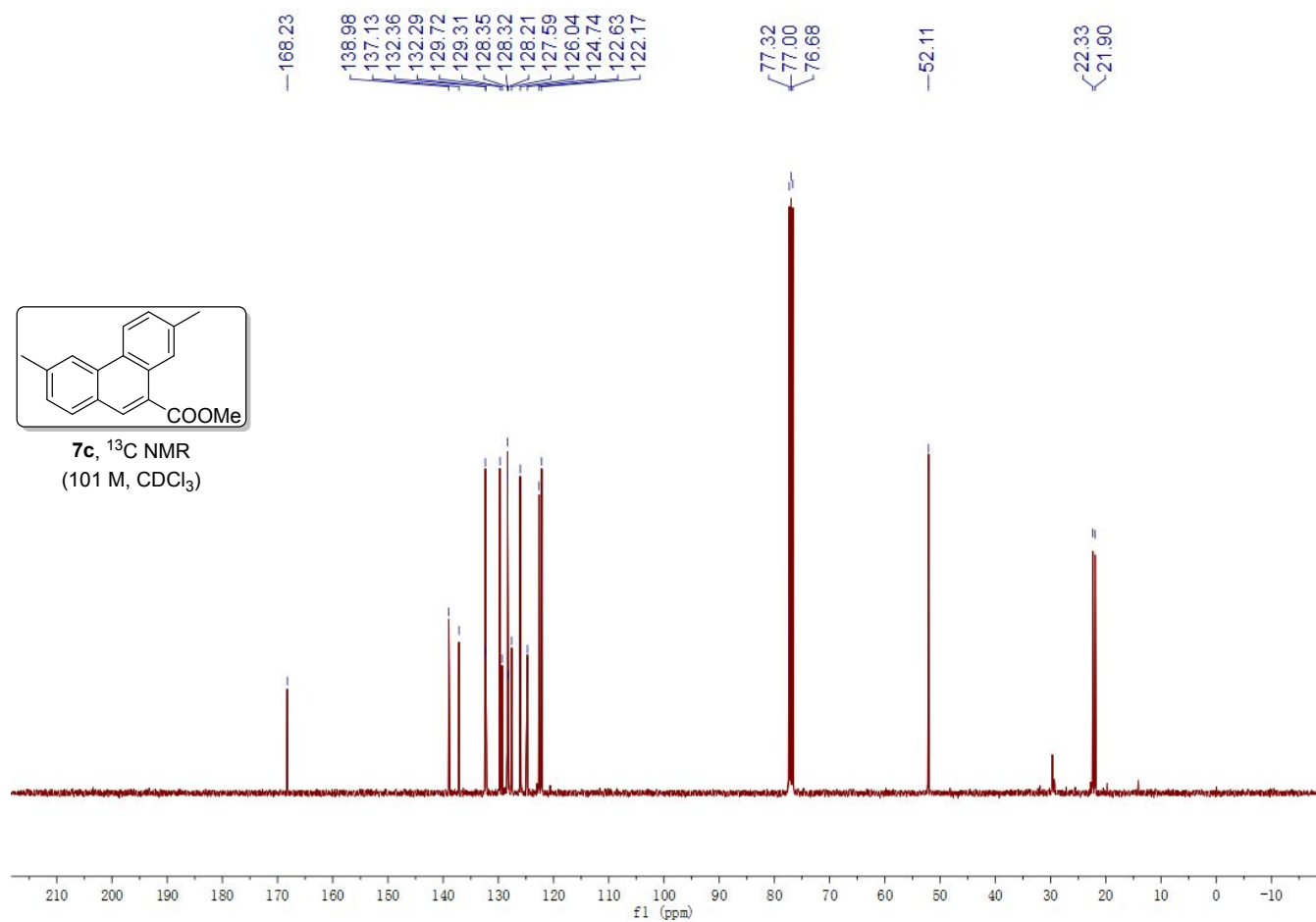


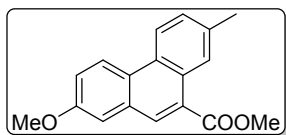


7c, $^1\text{H NMR}$
(400 M, CDCl_3)

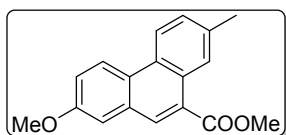
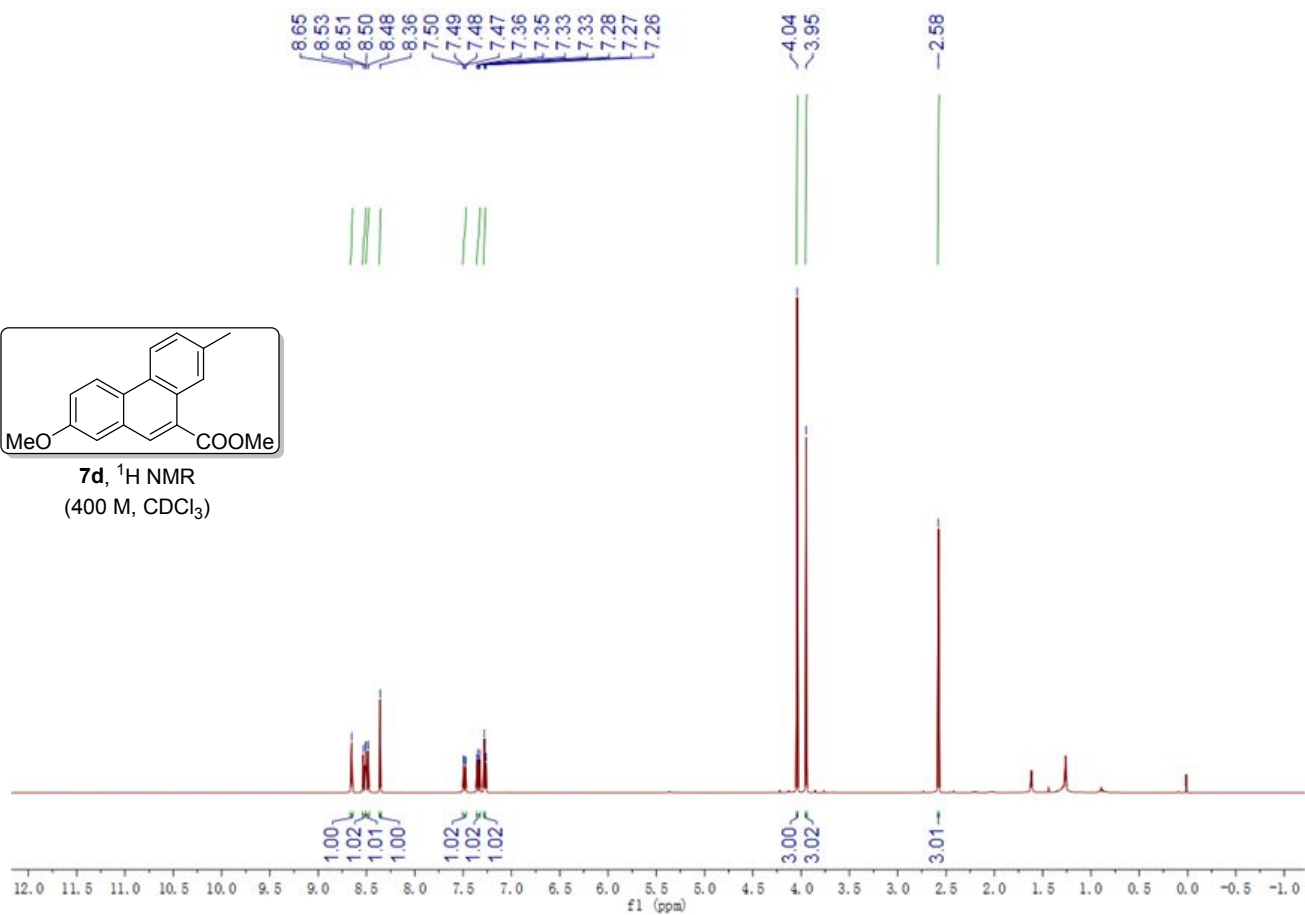


7c, $^{13}\text{C NMR}$
(101 M, CDCl_3)

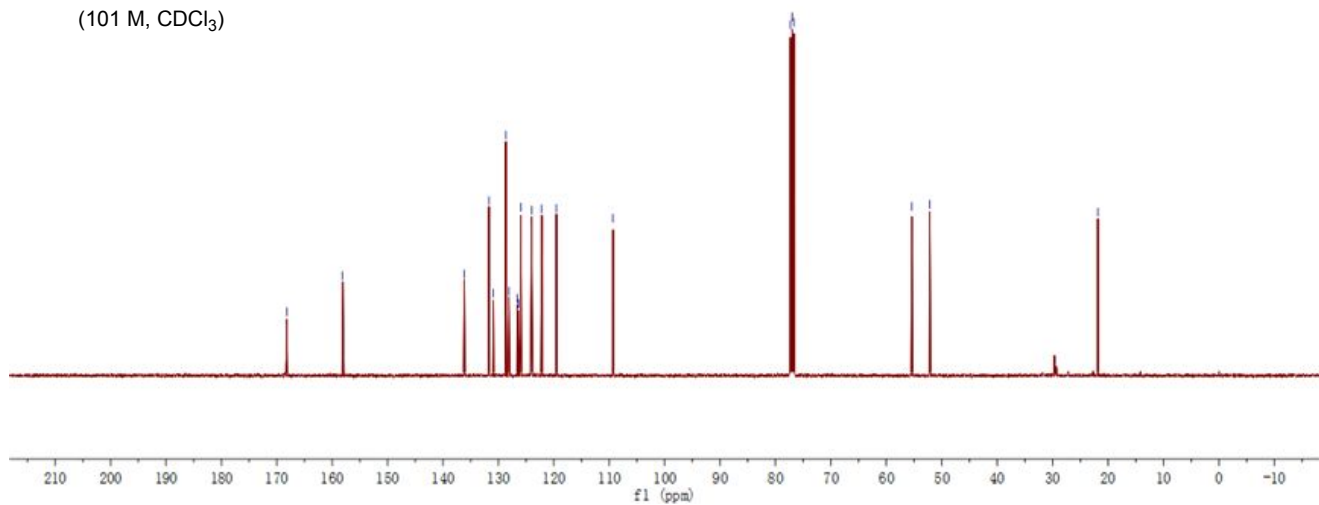


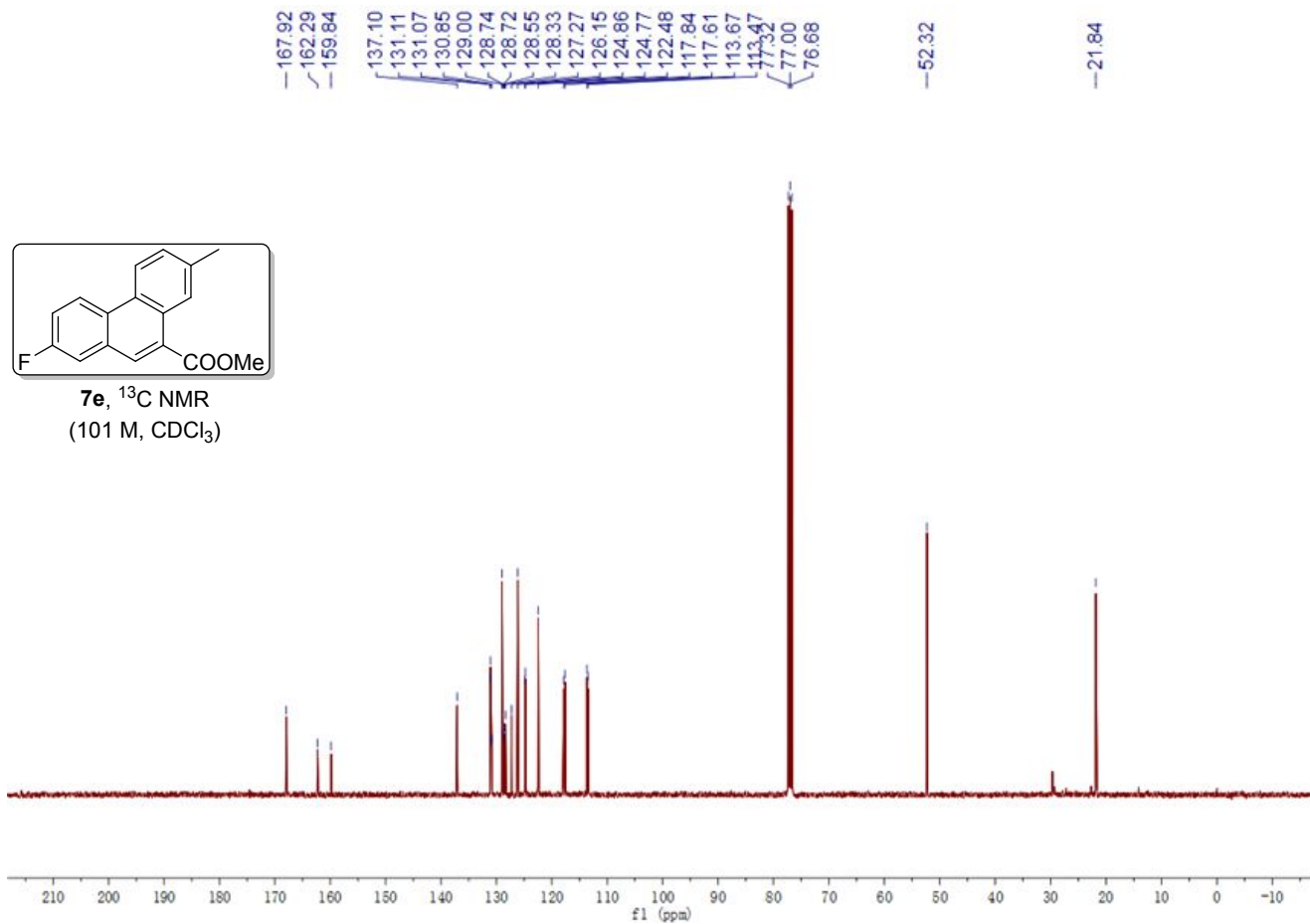
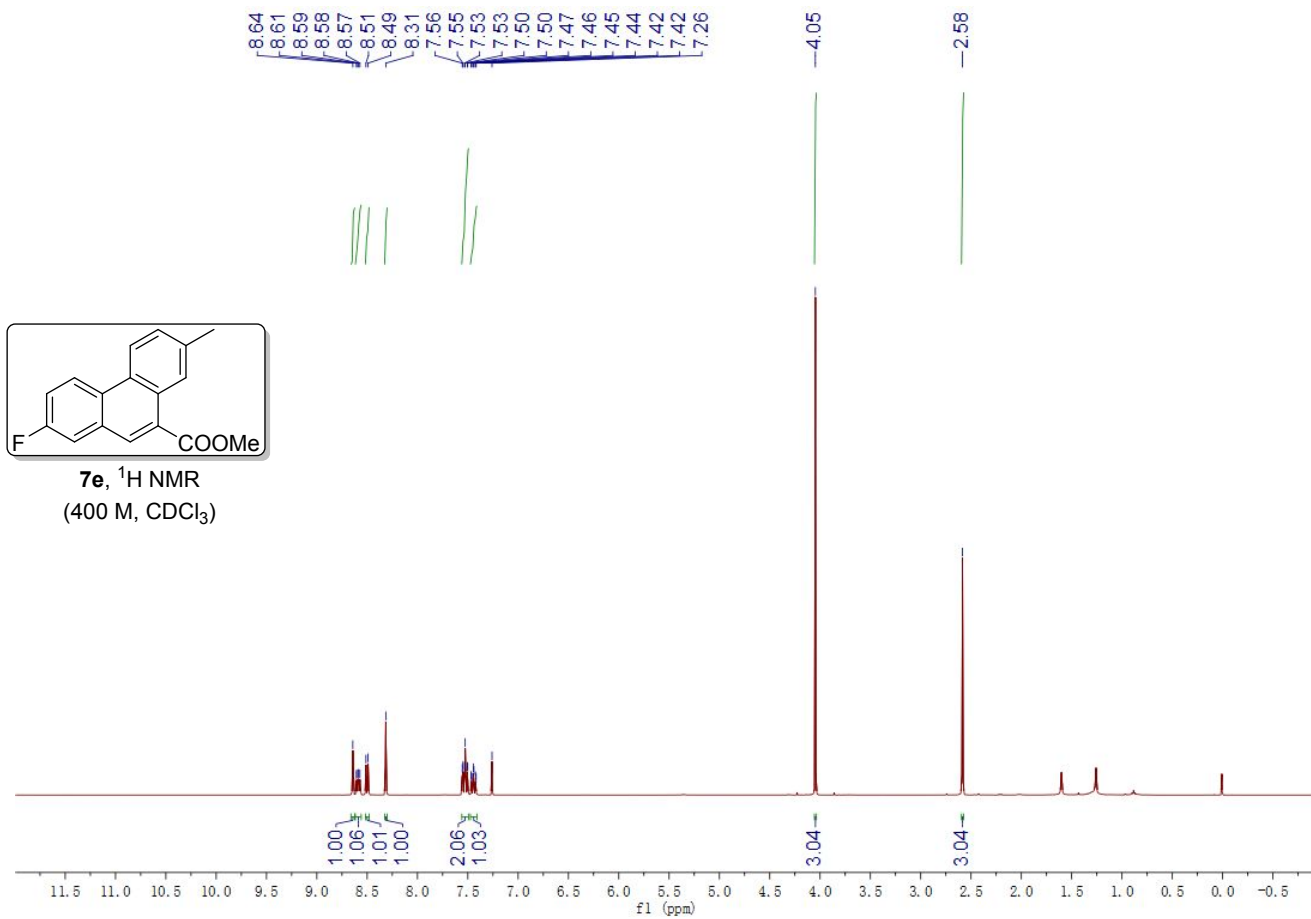


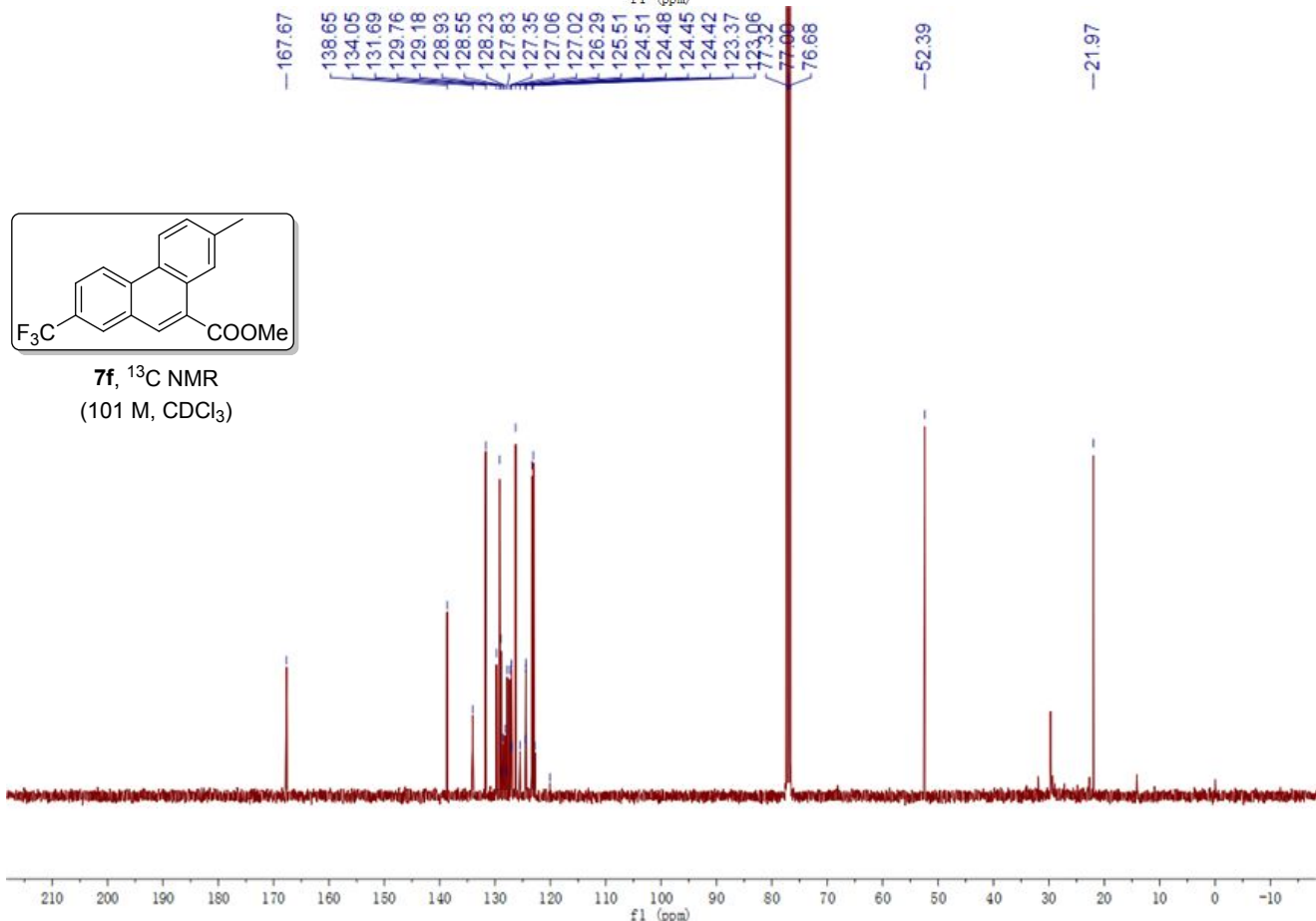
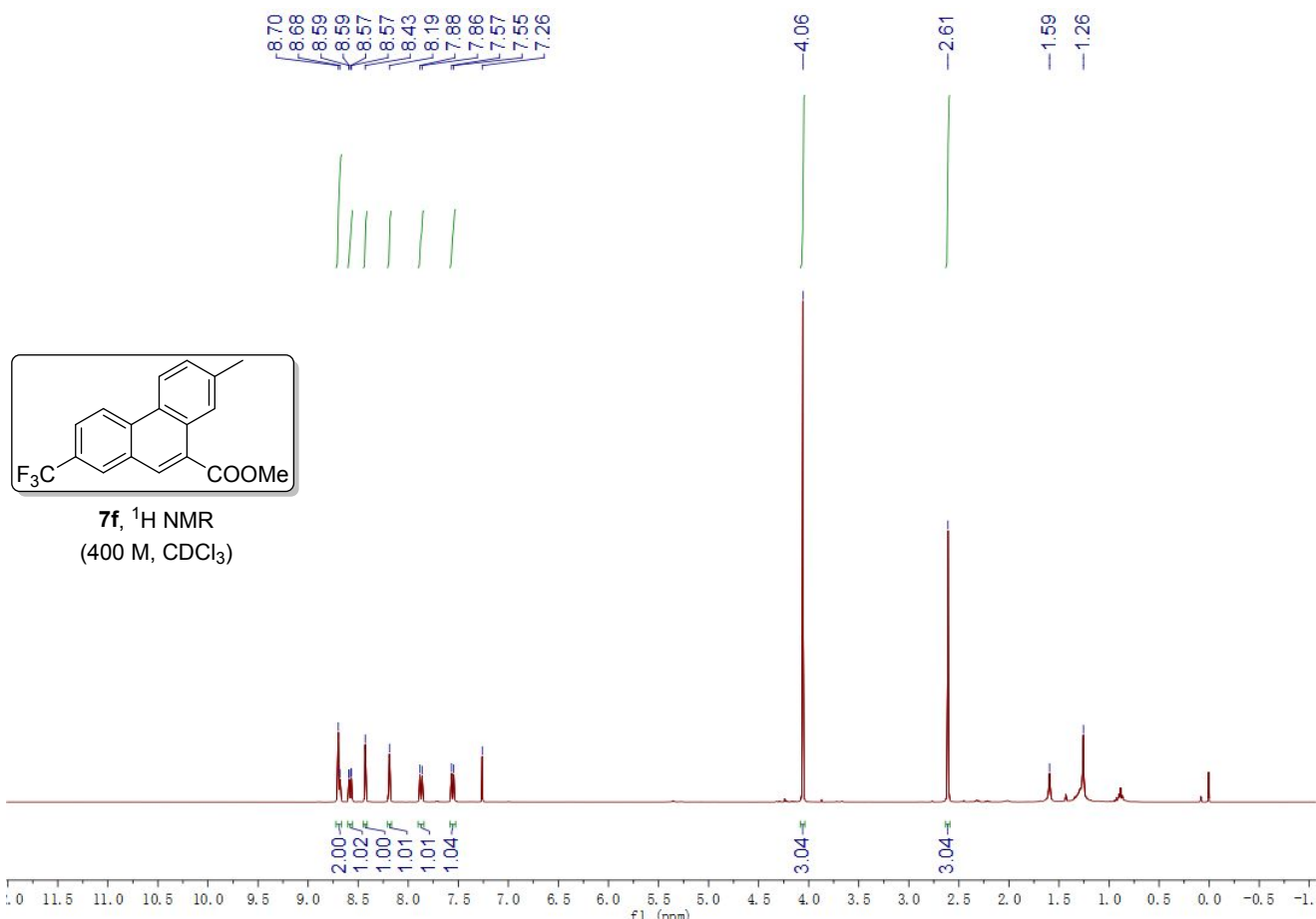
7d, ^1H NMR
(400 M, CDCl_3)

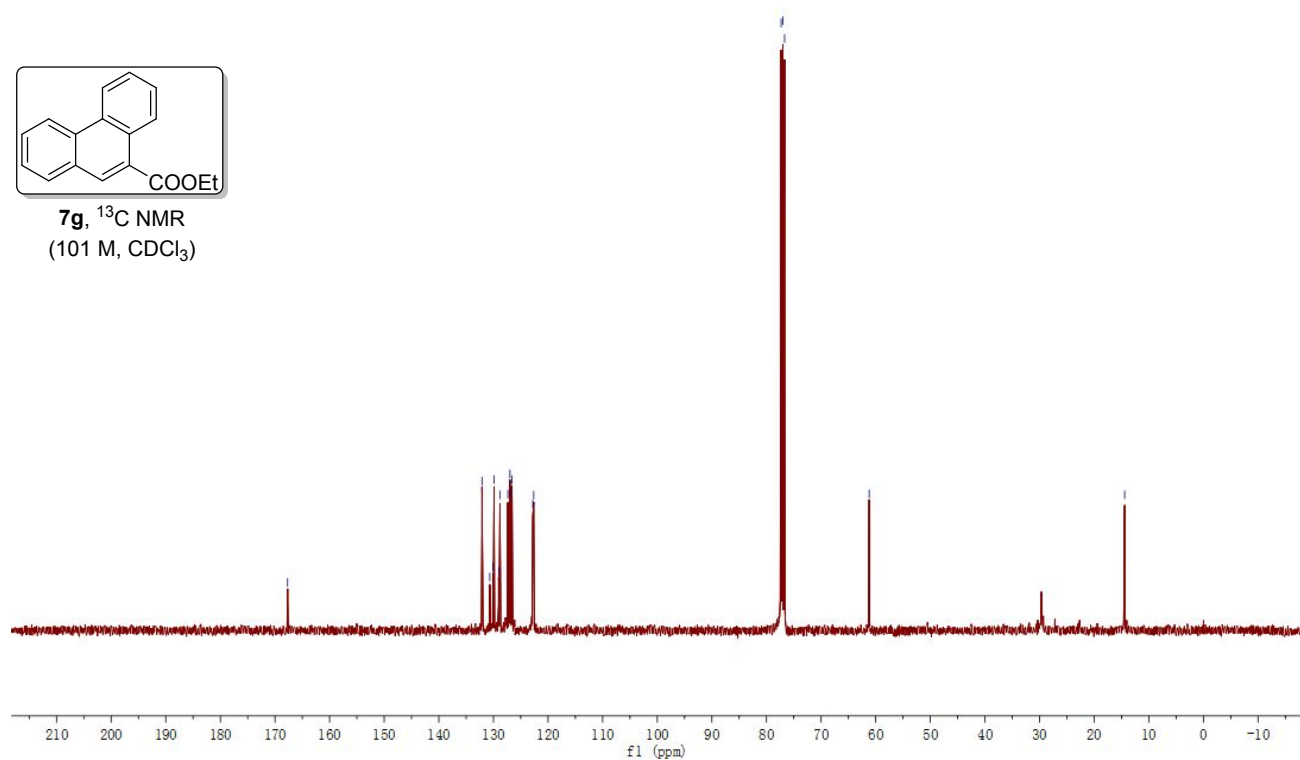
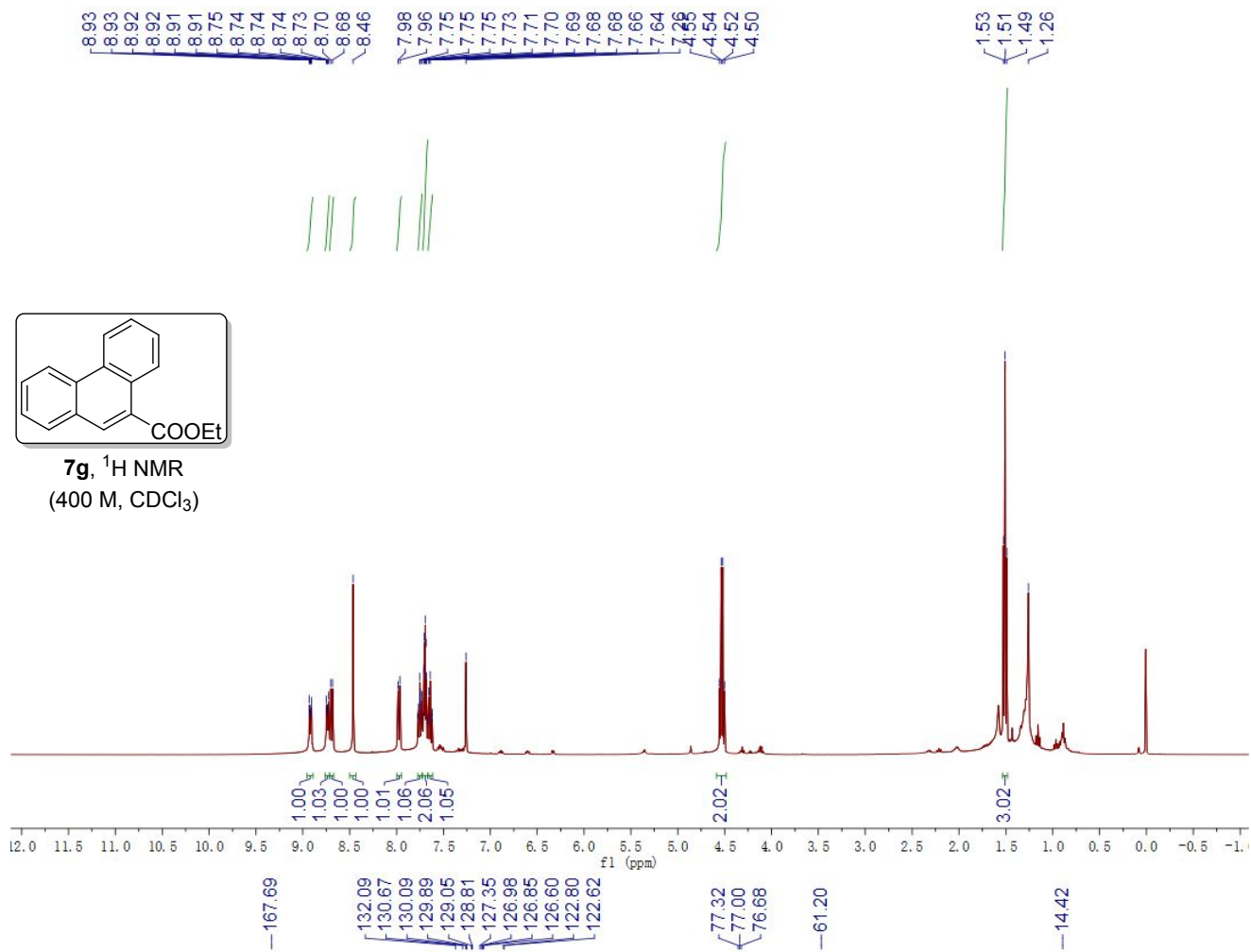


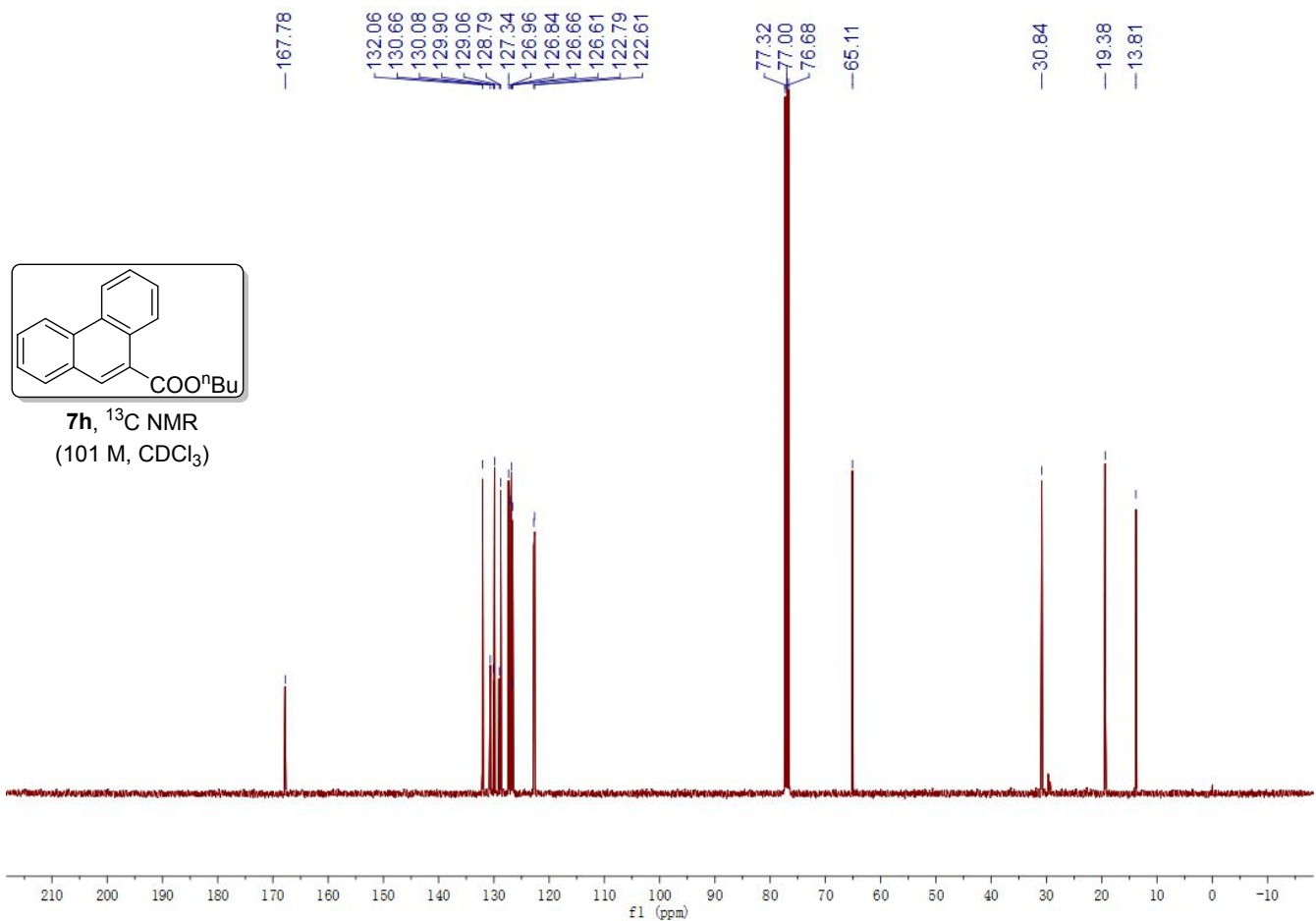
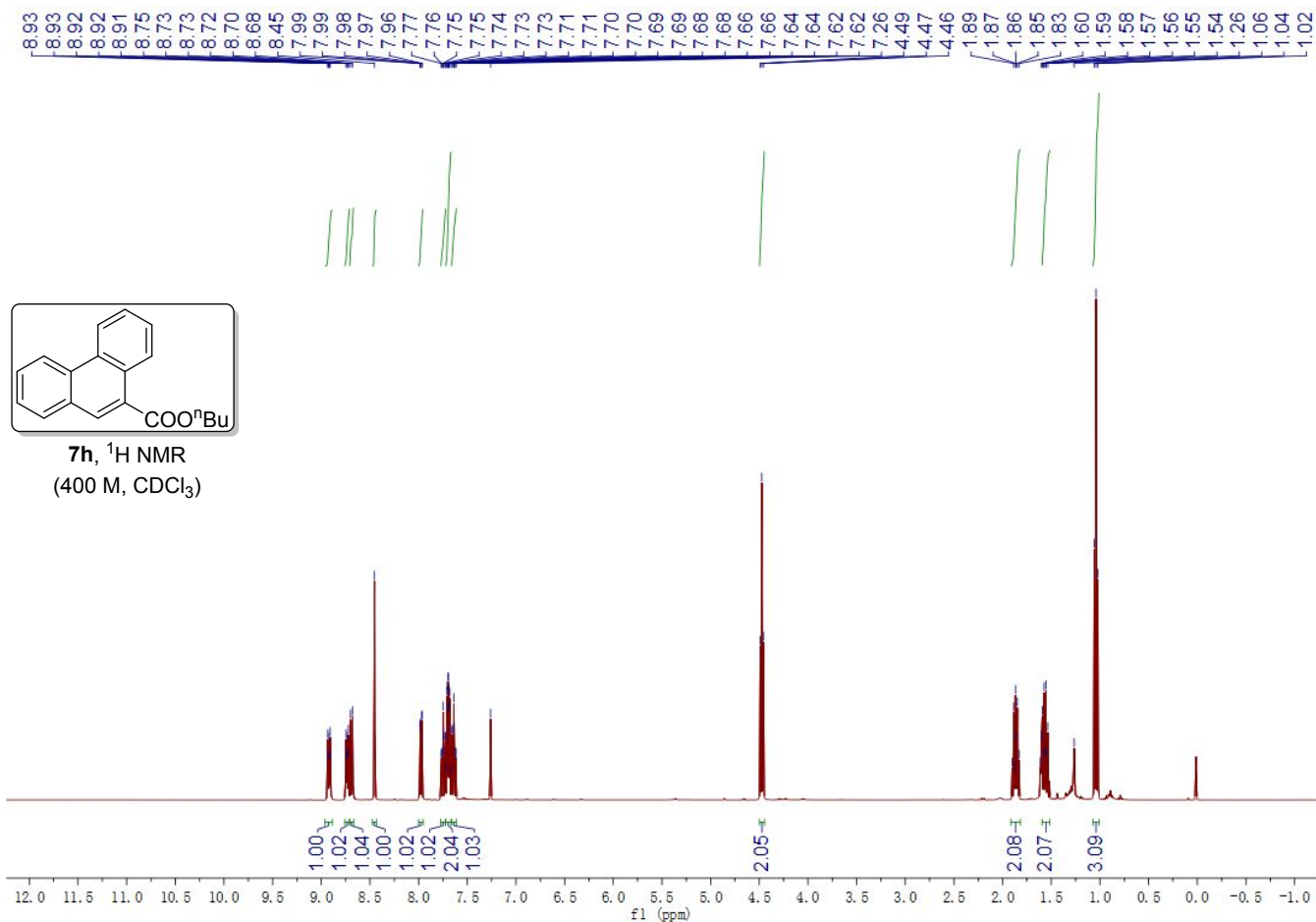
7d, ^{13}C NMR
(101 M, CDCl_3)

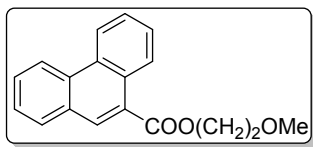
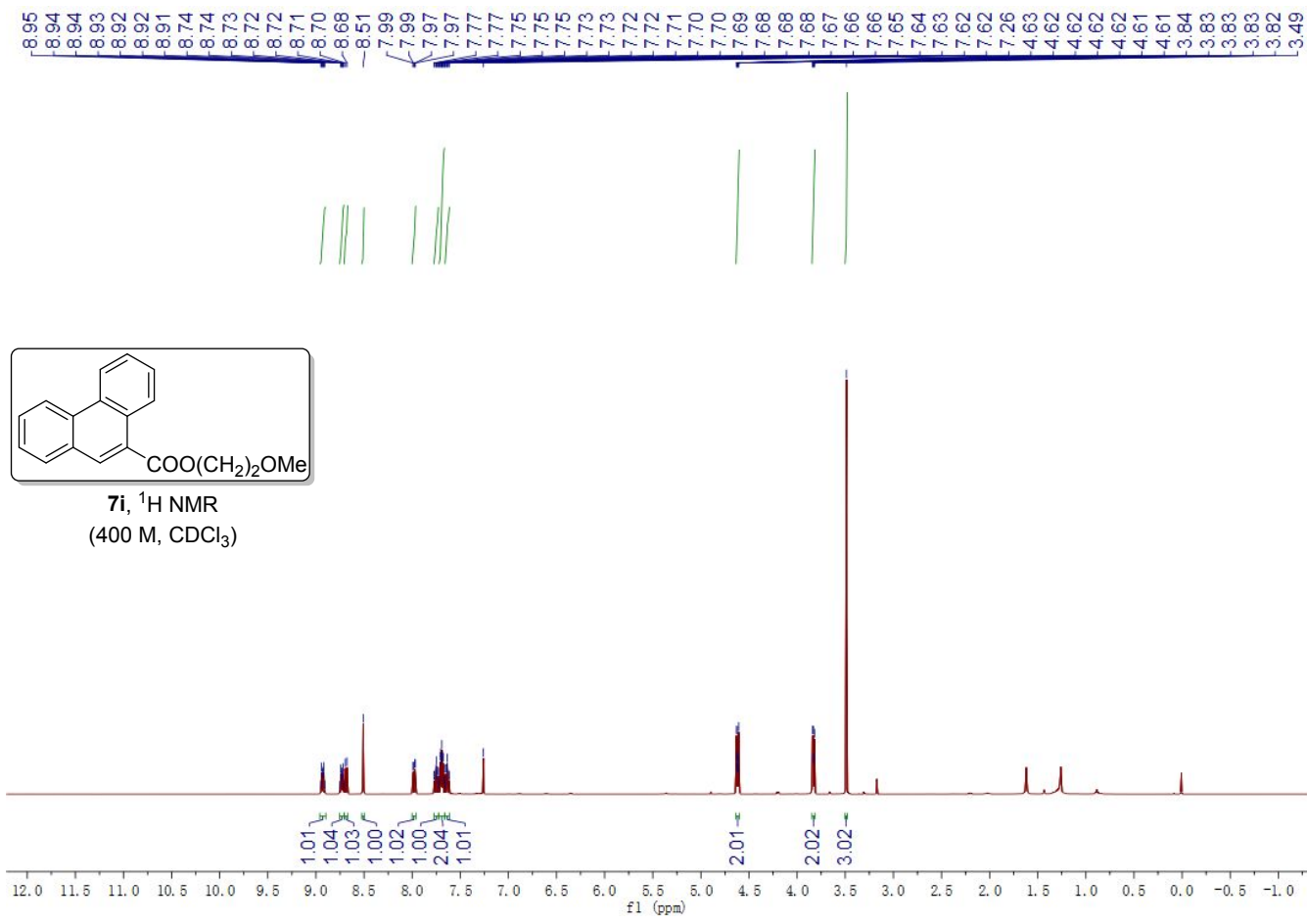




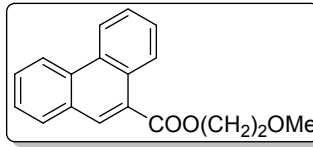
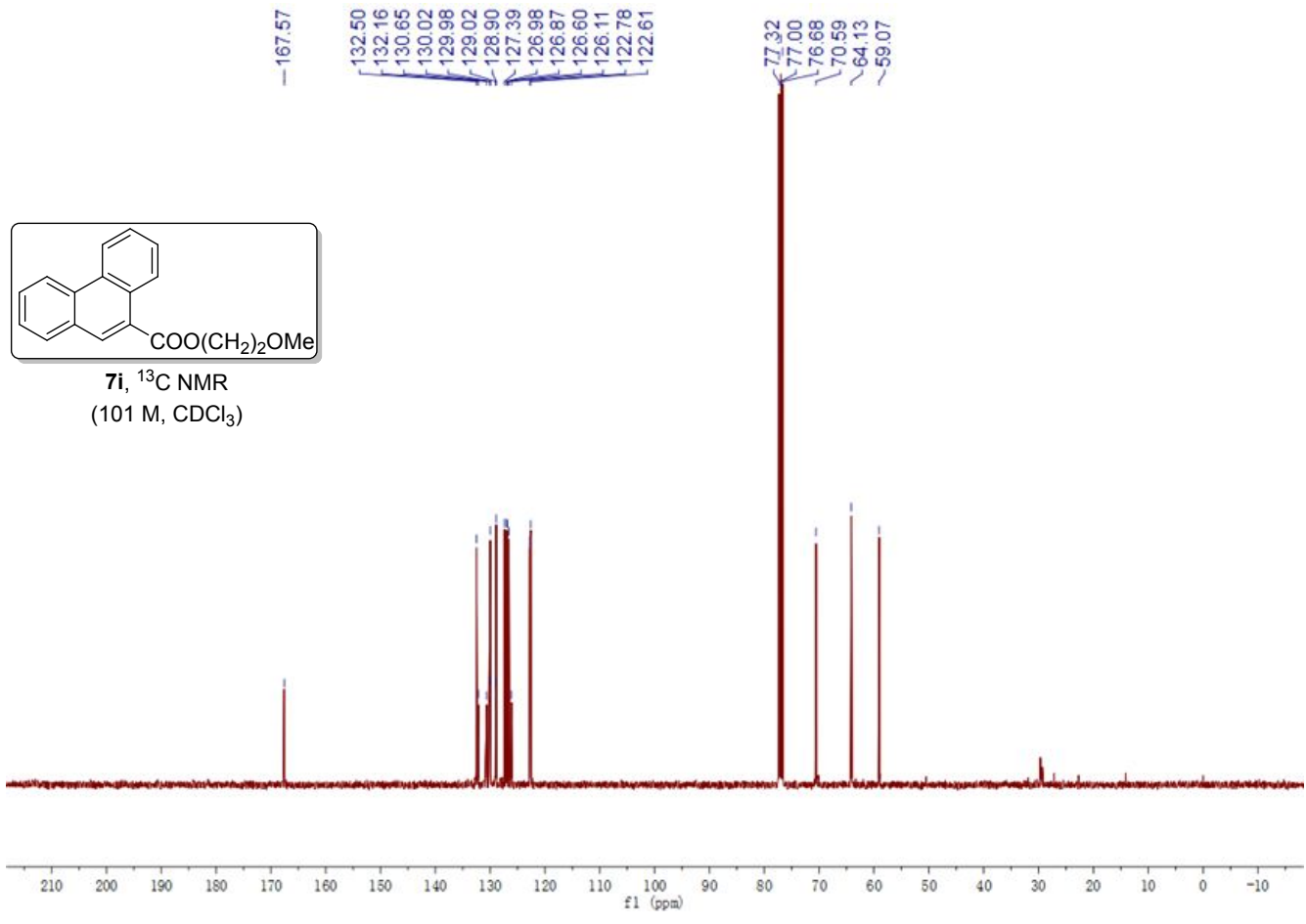




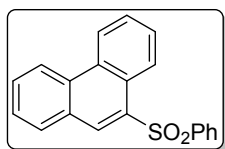




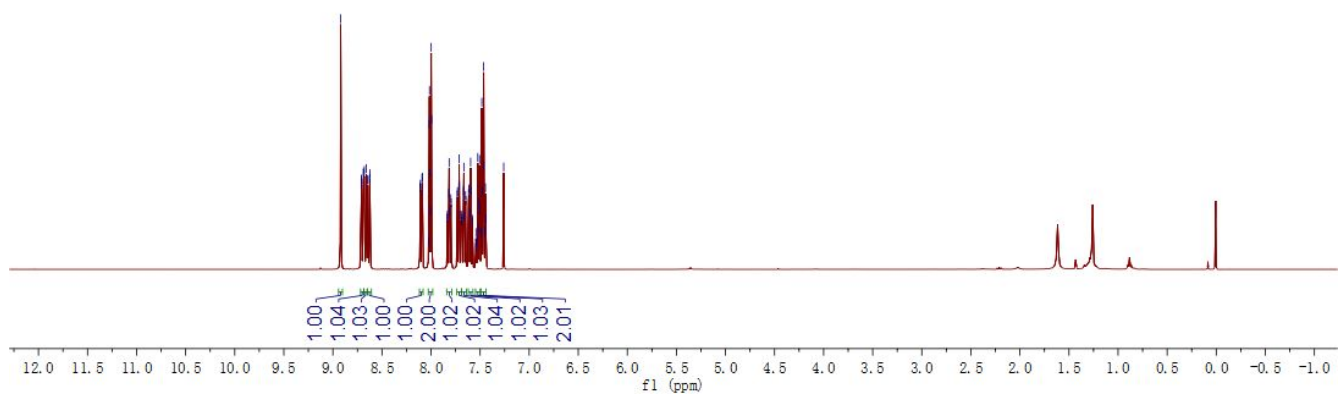
7i, ¹H NMR
(400 M, CDCl₃)



7i, ¹³C NMR
(101 M, CDCl₃)

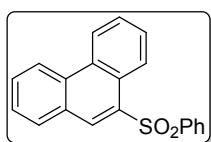


7k, ^1H NMR
(400 M, CDCl_3)

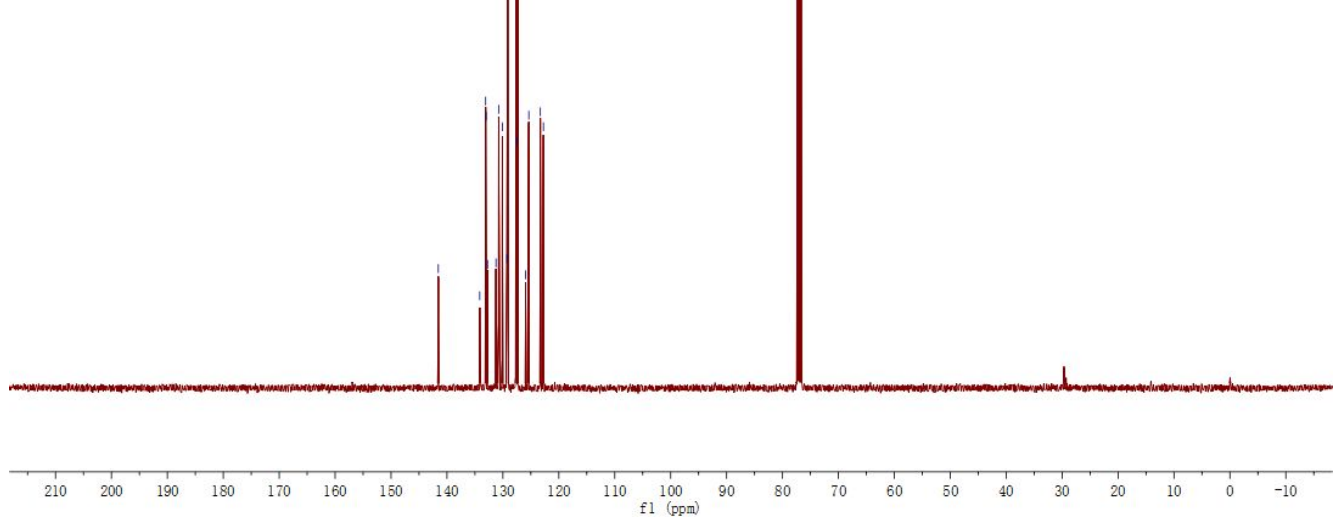


141.55
134.14
133.09
133.00
132.75
131.24
130.76
130.10
129.28
129.12
127.67
127.51
127.35
125.94
125.37
123.30
122.75

77.32
77.00
76.68



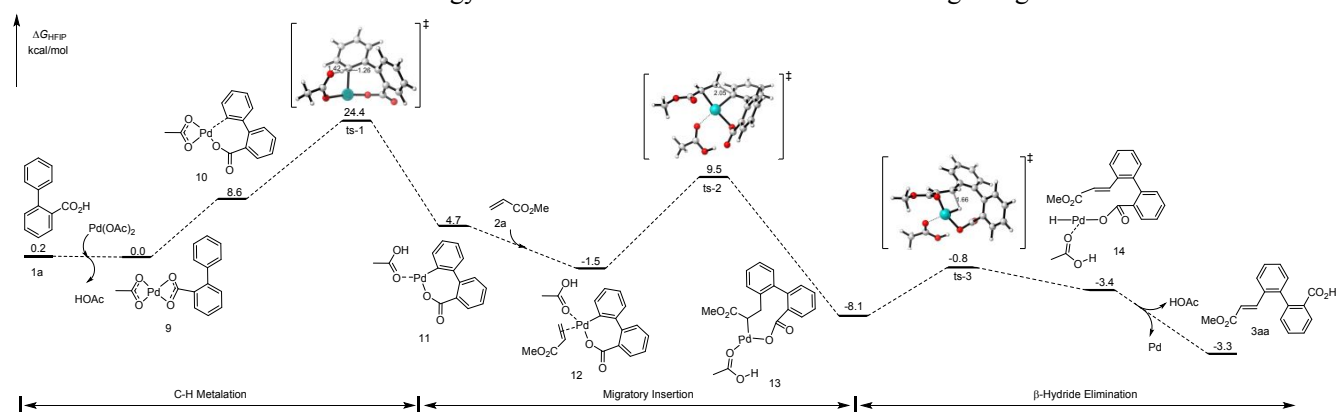
7k, ^{13}C NMR
(101 M, CDCl_3)



6. Computational method

The density functional theory (DFT) calculations were performed using Gaussian 16, Revision B.01^[1]. The geometry optimizations were conducted using the B3LYP functional^[2], with Lanl2dz basis set^[3] for Palladium and 6-31G(d,p) basis set for the other atoms. To confirm whether each optimized stationary point is an energy minimum or a transition state, as well as evaluate the zero-point vibrational energy and thermal corrections at 298 K, the vibrational frequencies were computed at the same level of theory as for the geometry optimizations. On the basis of the gas-phase optimized structures, the single-point energies and solvent effects were evaluated with the M06 functional^[4], SDD basis set^[3] for Palladium, and 6-311+G(2d,p) basis set for other atoms. The solvation energies were calculated using the self-consistent reaction field (SCRF) with the SMD model^[5], and hexafluoroisopropanol was chosen as the solvent for consistency with the experiment. Intrinsic reaction coordinate (IRC) calculations were undertaken to ensure transitions states connected the correct reactants and products. Energies reported are free energies in kcal/mol. Geometries of the optimized structures shown were displayed with CYLview^[6].

Scheme S6. Relative Gibbs free energy measured in kcal mol⁻¹ for DFT modelling using HFIP solvent correction.



Supplementary Computation Data

Cartesian coordinates, electronic energies and free energies of all stationary points. Numbers (and values) of imaginary frequencies of all transition structures.

9

B3LYP/6-31G(d,p)(lanl2dz)(gas) Energy =	-1006.52781
B3LYP/6-31G(d,p)(lanl2dz)(gas) Free Energy =	-1006.340807
M06/6-311+G(2d,p)(sdd)/SMD (HFIP) Energy =	-1007.375437
B3LYP/6-31G(d,p)(lanl2dz)(gas) Geometry	
C	2.14078 2.99392 1.21569
C	2.1556 1.60355 1.13199
C	2.7528 0.95992 0.03706
C	3.3429 1.74383 -0.96541

C	3.3208	3.13657	-0.88525
C	2.7205	3.76567	0.20583
H	1.6784	3.47581	2.07229
H	1.71228	1.00991	1.92597
H	3.80302	1.25699	-1.82062
H	3.77126	3.7285	-1.67688
H	2.70499	4.84975	0.27075
C	2.84512	-0.52643	-0.02781
C	4.12118	-1.10238	-0.13188
C	1.73603	-1.40299	0.05806
C	4.30552	-2.484	-0.13367
H	4.98217	-0.44328	-0.18492
C	1.93115	-2.79476	0.07563
C	3.20722	-3.33786	-0.01882
H	5.30924	-2.89196	-0.21235
H	1.05921	-3.43589	0.14413
H	3.34319	-4.41476	-0.01086
C	0.33037	-0.94675	0.05324
O	-0.61526	-1.73395	0.43069
O	-0.03923	0.20851	-0.35964
Pd	-2.02379	-0.28378	-0.02327
O	-4.01879	-0.7802	0.31122
O	-3.44893	1.171	-0.47213
C	-4.3793	0.37427	-0.10558
C	-5.82307	0.75916	-0.18531
H	-6.39694	0.21479	0.56666
H	-5.93145	1.8371	-0.05196
H	-6.20875	0.49364	-1.17555

10

B3LYP/6-31G(d,p)(lanl2dz)(gas) Energy = -1006.501507

B3LYP/6-31G(d,p)(lanl2dz)(gas) Free Energy = -1006.314072

M06/6-311+G(2d,p)(sdd)/SMD (HFIP) Energy = -1007.362167

B3LYP/6-31G(d,p)(lanl2dz)(gas) Geometry

C	0.44397	3.27791	-0.76274
C	1.51084	2.36383	-0.76603

C	1.52387	1.26544	0.08849
C	0.44165	1.11404	1.0083
C	-0.62331	2.03843	1.00875
C	-0.62842	3.11502	0.10218
H	0.45902	4.11454	-1.45532
H	2.32745	2.49535	-1.4691
H	0.52476	0.38147	1.80712
H	-1.40018	1.96352	1.76283
H	-1.4539	3.81897	0.10508
C	2.64774	0.29277	0.06385
C	3.97002	0.75075	0.16551
C	2.41539	-1.09791	-0.03479
C	5.03817	-0.14548	0.17244
H	4.1565	1.81643	0.26474
C	3.49098	-1.98989	0.00392
C	4.79942	-1.51979	0.09515
H	6.0547	0.22878	0.25199
H	3.27924	-3.05302	-0.04792
H	5.62951	-2.21991	0.1102
C	1.01224	-1.6347	-0.16939
O	0.65677	-2.64493	0.41856
O	0.25984	-0.8837	-0.96451
Pd	-1.35929	-0.14428	-0.06141
O	-2.96435	-1.36665	-0.7123
O	-3.27882	0.32607	0.63595
C	-3.76821	-0.66638	-0.01449
C	-5.22438	-1.00528	0.06882
H	-5.36289	-1.79465	0.81542
H	-5.7999	-0.12909	0.3721
H	-5.57417	-1.38457	-0.89361

TS-1

B3LYP/6-31G(d,p)(lanl2dz)(gas) Energy =	-1006.474611
B3LYP/6-31G(d,p)(lanl2dz)(gas) Free Energy=	-1006.290443
M06/6-311+G(2d,p)(sdd)/SMD (HFIP) Energy =	-1007.333742
Number of Imaginary Frequencies =	1(-652.81)

B3LYP/6-31G(d,p) (lanl2dz)(gas) Geometry

C	0.25407	3.73828	0.35363
C	1.13109	2.68859	0.636
C	0.71078	1.35823	0.53289
C	-0.6587	1.09181	0.2259
C	-1.52432	2.17929	-0.07553
C	-1.0755	3.49004	-0.00987
H	0.61424	4.76177	0.41112
H	2.16276	2.90062	0.89892
H	-1.24831	0.29508	1.01166
H	-2.56469	1.96962	-0.30587
H	-1.74746	4.31489	-0.22523
C	1.67534	0.26157	0.82244
C	2.13045	0.11727	2.14399
C	2.1871	-0.59405	-0.1767
C	3.03381	-0.88587	2.48623
H	1.7498	0.78906	2.90785
C	3.12487	-1.57503	0.17788
C	3.53048	-1.73939	1.49828
H	3.35224	-0.99596	3.51871
H	3.54108	-2.18738	-0.61476
H	4.24522	-2.51589	1.75433
C	1.90854	-0.44176	-1.6604
O	2.79842	-0.66556	-2.46577
O	0.70282	-0.06327	-2.0466
Pd	-0.937	-0.53035	-1.05176
O	-2.69127	-1.20942	-0.23668
O	-2.1654	-0.4324	1.81092
C	-2.88522	-1.10487	1.02521
C	-4.06469	-1.87356	1.58435
H	-4.34127	-1.48557	2.56457
H	-4.90828	-1.82293	0.8933
H	-3.77854	-2.9257	1.68579

TS-1'

B3LYP/6-31G(d,p)(lanl2dz)(gas) Energy =

-1006.460317

B3LYP/6-31G(d,p)(lanl2dz)(gas) Free Energy= -1006.277259
M06/6-311+G(2d,p)(sdd)/SMD (HFIP) Energy = -1007.322599
Number of Imaginary Frequencies = 1(-944.02)

B3LYP/6-31G(d,p) (lanl2dz)(gas) Geometry

C	5.37361	0.89254	-0.8369
C	4.02922	1.24939	-0.72809
C	3.13709	0.45834	0.01056
C	3.62233	-0.69123	0.65054
C	4.96656	-1.04201	0.54827
C	5.8461	-0.25347	-0.19702
H	6.0487	1.50926	-1.42318
H	3.66245	2.13733	-1.23595
H	2.94773	-1.30912	1.23445
H	5.32734	-1.93437	1.05119
H	6.89272	-0.53204	-0.27859
C	1.72089	0.90284	0.16935
C	1.49267	2.17966	0.7184
C	0.59855	0.11673	-0.1457
C	0.21146	2.65553	1.00529
H	2.35525	2.79331	0.96147
C	-0.7191	0.62336	0.06953
C	-0.89505	1.86875	0.71692
H	0.08529	3.63687	1.45236
H	-1.68097	0.64089	-0.78921
H	-1.89794	2.23837	0.89941
C	0.69126	-1.33581	-0.55915
O	-0.27387	-2.06226	-0.01234
O	1.56316	-1.80106	-1.26569
Pd	-1.93113	-1.04368	0.39432
O	-2.96454	1.08399	-1.35039
O	-3.74011	-0.06499	0.42883
C	-3.89034	0.72802	-0.57161
C	-5.29488	1.23918	-0.81333
H	-5.26947	2.14591	-1.41777
H	-5.85601	0.47054	-1.35527

H	-5.80261	1.41615	0.13653
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B3LYP/6-31G(d,p)(lanl2dz)(gas) Energy =	-1006.503338
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B3LYP/6-31G(d,p)(lanl2dz)(gas) Free Energy=	-1006.31512
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M06/6-311+G(2d,p)(sdd)/SMD (HFIP) Energy =	-1007.369115
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B3LYP/6-31G(d,p)(lanl2dz)(gas) Geometry

C	-0.28214	3.67137	-0.66526
C	0.68146	2.86931	-0.05685
C	0.57109	1.46452	-0.04186
C	-0.56452	0.89962	-0.65057
C	-1.53071	1.69733	-1.27526
C	-1.39298	3.0888	-1.27521
H	-0.15919	4.75036	-0.67053
H	1.55635	3.32595	0.39635
H	-1.8186	0.72921	1.05214
H	-2.38838	1.23905	-1.75843
H	-2.1463	3.70548	-1.75683
C	1.61941	0.66223	0.65357
C	1.97395	1.04833	1.95895
C	2.30977	-0.41765	0.05765
C	2.96611	0.38251	2.67414
H	1.44711	1.87966	2.41897
C	3.33438	-1.05188	0.77604
C	3.65217	-0.67616	2.07788
H	3.20412	0.69385	3.68726
H	3.88722	-1.83995	0.27631
H	4.43789	-1.19663	2.61772
C	2.11915	-0.91873	-1.36384
O	3.10215	-1.2095	-2.0284
O	0.8986	-1.07938	-1.83874
Pd	-0.7513	-1.06754	-0.75288
O	-2.57516	-1.35205	0.30708
O	-2.55793	0.46112	1.64782
C	-3.04159	-0.69891	1.24916
C	-4.2254	-1.17295	2.03871

H	-4.55985	-2.13904	1.66451
H	-3.9502	-1.2507	3.09464
H	-5.03238	-0.43809	1.96497

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B3LYP/6-31G(d,p)(lanl2dz)(gas) Energy = -1006.503545

B3LYP/6-31G(d,p)(lanl2dz)(gas) Free Energy = -1006.31678

M06/6-311+G(2d,p)(sdd)/SMD (HFIP) Energy = -1007.371023

B3LYP/6-31G(d,p)(lanl2dz)(gas) Geometry

C	5.56064	0.7152	-0.58885
C	4.20821	0.97691	-0.81012
C	3.22798	0.49299	0.07085
C	3.63724	-0.25595	1.18478
C	4.98813	-0.50715	1.41164
C	5.95488	-0.0248	0.52597
H	6.30325	1.08836	-1.28854
H	3.90429	1.54566	-1.68448
H	2.89301	-0.64287	1.87102
H	5.28676	-1.0864	2.28062
H	7.00731	-0.22815	0.70273
C	1.79995	0.86016	-0.14782
C	1.49594	2.22086	-0.34787
C	0.72799	-0.0609	-0.16787
C	0.19348	2.66308	-0.55967
H	2.30748	2.94129	-0.32149
C	-0.58068	0.4131	-0.35317
C	-0.87307	1.75603	-0.56141
H	0.00054	3.72101	-0.71683
H	-2.53545	0.47996	1.51479
H	-1.88645	2.1006	-0.73858
C	0.83502	-1.56488	-0.12099
O	-0.34786	-2.16554	-0.24637
O	1.86375	-2.20421	-0.01043
Pd	-1.94475	-1.01574	-0.36678
O	-3.39819	0.93154	1.66501
O	-3.7967	0.07927	-0.38035

C	-4.15937	0.74076	0.60133
C	-5.50152	1.4021	0.67877
H	-5.36984	2.48134	0.80061
H	-6.07163	1.19159	-0.22443
H	-6.03765	1.03792	1.55995

C2H3CO₂Me

B3LYP/6-31G(d,p)(lanl2dz)(gas) Energy = -306.475324

B3LYP/6-31G(d,p)(lanl2dz)(gas) Free Energy= -306.410378

M06/6-311+G(2d,p)(sdd)/SMD (HFIP) Energy = -306.379739

B3LYP/6-31G(d,p) (lanl2dz)(gas) Geometry

C	2.03933	-0.6714	0.00001
H	2.36986	-1.7099	0.00035
H	2.40763	-0.1514	0.88787
H	2.40767	-0.15202	-0.88821
O	0.60466	-0.72083	-0.00002
C	-0.0109	0.48493	0.00001
O	0.58868	1.54213	0.00001
C	-1.49088	0.38254	-0.00002
H	-1.98897	1.34707	-0.00002
C	-2.17373	-0.7643	0.00002
H	-1.66661	-1.72306	0.00002
H	-3.25926	-0.77169	0.00001

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B3LYP/6-31G(d,p)(lanl2dz)(gas) Energy = -1312.981115

B3LYP/6-31G(d,p)(lanl2dz)(gas) Free Energy= -1312.703757

M06/6-311+G(2d,p)(sdd)/SMD (HFIP) Energy = -1313.782931

B3LYP/6-31G(d,p) (lanl2dz)(gas) Geometry

C	-2.8237	-3.44139	-1.29004
C	-3.22111	-2.20724	-0.77794
C	-2.29046	-1.25005	-0.32435
C	-0.92898	-1.59576	-0.40721
C	-0.52151	-2.82546	-0.92452
C	-1.46951	-3.75724	-1.36177
H	-3.57277	-4.14603	-1.64054
H	-4.27786	-1.95691	-0.75144

H	0.5151	3.02331	-1.36167
H	0.53481	-3.063	-1.01383
H	-1.14258	-4.71275	-1.76347
C	-2.83548	0.01427	0.26811
C	-3.87673	-0.15185	1.20254
C	-2.43642	1.34335	-0.03822
C	-4.51851	0.92676	1.80583
H	-4.17472	-1.1614	1.4692
C	-3.09923	2.41995	0.57438
C	-4.13286	2.2274	1.48412
H	-5.31235	0.74701	2.52613
H	-2.77449	3.41877	0.30659
H	-4.62478	3.08141	1.94123
C	-1.31227	1.72841	-0.97243
O	-1.08347	2.93773	-1.17693
O	-0.58476	0.80463	-1.52206
Pd	0.44817	-0.21293	-0.06929
O	1.92265	1.49659	0.01628
O	1.51025	3.25729	-1.36388
C	2.27418	2.49847	-0.62148
C	3.71223	2.96098	-0.58644
H	4.28626	2.33143	0.09418
H	4.13562	2.91075	-1.59579
H	3.75961	4.007	-0.2679
C	5.14257	-1.64422	0.05806
H	5.68419	-1.75213	1.00157
H	5.29003	-0.63066	-0.32441
H	5.48322	-2.3811	-0.66932
O	3.74332	-1.90863	0.24846
C	3.12581	-1.12445	1.15907
O	3.67805	-0.25669	1.79929
C	0.80068	-0.77344	2.03736
C	1.68602	-1.51401	1.27788
H	1.44038	-2.52442	0.96905
H	1.1389	0.14478	2.51038

H	-0.1413	-1.19555	2.37045
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TS-2

B3LYP/6-31G(d,p)(lanl2dz)(gas) Energy =	-1312.958777
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B3LYP/6-31G(d,p)(lanl2dz)(gas) Free Energy=	-1312.681302
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M06/6-311+G(2d,p)(sdd)/SMD (HFIP) Energy =	-1313.765503
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Number of Imaginary Frequencies =	-287.47
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B3LYP/6-31G(d,p) (lanl2dz)(gas) Geometry

C	-3.70446	-2.46819	-1.21941
C	-3.62841	-1.16155	-0.7377
C	-2.45305	-0.64843	-0.16259
C	-1.34593	-1.52137	-0.05557
C	-1.42889	-2.84027	-0.53239
C	-2.59727	-3.31284	-1.12574
H	-4.62764	-2.82288	-1.66923
H	-4.48516	-0.50121	-0.83744
H	1.43657	2.05191	-2.00398
H	-0.57527	-3.50411	-0.42093
H	-2.64505	-4.33255	-1.49743
C	-2.48058	0.76611	0.32121
C	-3.44259	1.07034	1.30068
C	-1.65748	1.81406	-0.16099
C	-3.59256	2.35997	1.80703
H	-4.07474	0.26947	1.67488
C	-1.82034	3.10615	0.36098
C	-2.77646	3.38661	1.33226
H	-4.34154	2.5573	2.56937
H	-1.17355	3.88543	-0.02552
H	-2.88193	4.39732	1.71659
C	-0.58493	1.6385	-1.21654
O	0.15409	2.62235	-1.46733
O	-0.44564	0.49964	-1.80124
Pd	0.50157	-0.67716	-0.31536
O	2.47137	0.0003	-0.92059
O	2.40072	1.79837	-2.32215
C	2.96406	0.77007	-1.76798

C	4.3759	0.52718	-2.25248
H	4.87205	-0.21078	-1.62112
H	4.33614	0.15289	-3.28208
H	4.93811	1.46498	-2.26678
C	4.21067	-0.04633	2.6368
H	3.97002	0.16985	3.68109
H	4.18993	0.8859	2.06596
H	5.1881	-0.52318	2.55815
O	3.27775	-0.98863	2.08603
C	1.98637	-0.59932	2.11418
O	1.60187	0.44208	2.61141
C	-0.298	-1.55908	1.71036
C	1.11265	-1.6208	1.46809
H	1.57817	-2.58705	1.28628
H	-0.66712	-0.6827	2.23664
H	-0.82275	-2.47908	1.93174

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B3LYP/6-31G(d,p)(lanl2dz)(gas) Energy = -1313.030121

B3LYP/6-31G(d,p)(lanl2dz)(gas) Free Energy= -1312.751135

M06/6-311+G(2d,p)(sdd)/SMD (HFIP) Energy = -1313.795106

B3LYP/6-31G(d,p) (lanl2dz)(gas) Geometry

C	-3.68483	-1.67217	-2.51944
C	-3.5882	-0.53278	-1.72433
C	-2.76899	-0.48872	-0.58207
C	-2.02593	-1.63805	-0.23843
C	-2.16366	-2.7872	-1.02971
C	-2.97565	-2.81672	-2.16128
H	-4.31874	-1.66653	-3.40138
H	-4.15374	0.35549	-1.98992
H	1.65643	2.62697	-0.15119
H	-1.62058	-3.68642	-0.74612
H	-3.05376	-3.72472	-2.7523
C	-2.88295	0.75334	0.25714
C	-4.16479	0.99648	0.78621
C	-1.87711	1.71814	0.51262

C	-4.45869	2.13706	1.52918
H	-4.9425	0.26068	0.60622
C	-2.18758	2.86686	1.26062
C	-3.46329	3.08527	1.76573
H	-5.46197	2.28152	1.92029
H	-1.39018	3.57953	1.43551
H	-3.67731	3.98159	2.34021
C	-0.44637	1.58485	0.07204
O	0.39573	2.38828	0.54664
O	-0.16997	0.63211	-0.74742
Pd	1.52689	-0.41766	-0.2397
O	3.13069	0.85867	-1.03971
O	2.51206	2.99499	-0.62873
C	3.30262	2.08814	-1.11556
C	4.51131	2.64402	-1.82895
H	5.19007	1.83982	-2.11049
H	4.18198	3.17793	-2.72595
H	5.02033	3.36879	-1.18813
C	3.80038	-2.00355	1.70144
H	4.62807	-1.75272	1.04012
H	3.94535	-2.988	2.15009
H	3.68634	-1.25483	2.48823
O	2.62402	-2.03463	0.86341
C	1.38453	-2.25327	1.52171
O	1.317	-2.52378	2.6907
C	-1.07006	-1.7062	0.94172
C	0.36703	-1.93012	0.48981
H	0.44329	-2.62363	-0.35544
H	-1.13941	-0.81208	1.56583
H	-1.35319	-2.54858	1.5907

TS-3

B3LYP/6-31G(d,p)(lanl2dz)(gas) Energy = -1312.968105

B3LYP/6-31G(d,p)(lanl2dz)(gas) Free Energy= -1312.693761

M06/6-311+G(2d,p)(sdd)/SMD (HFIP) Energy = -1313.778852

Number of Imaginary Frequencies = -572.34

B3LYP/6-31G(d,p) (lanl2dz)(gas) Geometry

C	2.61978	-0.39019	3.52109
C	3.00026	-0.22867	2.18861
C	2.1693	-0.63549	1.13858
C	0.90484	-1.1976	1.44707
C	0.53649	-1.35997	2.79164
C	1.387	-0.96661	3.82305
H	3.28501	-0.06715	4.31675
H	3.95473	0.22845	1.947
H	-0.57684	3.00071	-0.39834
H	-0.4199	-1.81493	3.03164
H	1.08309	-1.10884	4.85627
C	2.65388	-0.4712	-0.27222
C	3.4161	-1.50089	-0.84506
C	2.3703	0.67643	-1.04484
C	3.9015	-1.40226	-2.14924
H	3.63188	-2.38596	-0.25187
C	2.84941	0.75948	-2.3583
C	3.61687	-0.26659	-2.908
H	4.49584	-2.2094	-2.56843
H	2.6151	1.64033	-2.94936
H	3.98657	-0.18028	-3.92609
C	1.57673	1.8524	-0.4989
O	2.0756	2.64171	0.28248
O	0.34309	1.9614	-0.9899
Pd	-0.85522	0.2823	-0.42762
O	-2.47518	1.60993	0.13987
O	-1.37319	3.57807	-0.05303
C	-2.41338	2.85296	0.23426
C	-3.60892	3.63912	0.70854
H	-4.42612	2.96691	0.97095
H	-3.32649	4.24812	1.57318
H	-3.92892	4.32597	-0.08214
C	-4.51245	-3.04005	-0.87591
H	-5.49979	-2.88254	-0.44153

H	-4.25609	-4.10282	-0.87756
H	-4.47912	-2.66396	-1.90202
O	-3.60385	-2.30312	-0.04173
C	-2.30476	-2.37634	-0.3998
O	-1.8938	-3.03365	-1.33686
C	-0.04241	-1.62696	0.3712
C	-1.46052	-1.54359	0.50007
H	-1.91734	-1.21636	1.42935
H	0.31975	-2.37274	-0.33832
H	0.25726	-0.66973	-0.95659

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B3LYP/6-31G(d,p)(lanl2dz)(gas) Energy = -1312.975697

B3LYP/6-31G(d,p)(lanl2dz)(gas) Free Energy = -1312.699847

M06/6-311+G(2d,p)(sdd)/SMD (HFIP) Energy = -1313.784533

B3LYP/6-31G(d,p)(lanl2dz)(gas) Geometry

C	2.19231	1.52145	3.15708
C	2.63707	0.66163	2.15066
C	1.7492	-0.1805	1.47495
C	0.36968	-0.13354	1.81326
C	-0.06506	0.74302	2.82189
C	0.83909	1.55803	3.49724
H	2.90278	2.16257	3.67134
H	3.6857	0.6473	1.8708
H	0.32933	2.36631	-1.92491
H	-1.11733	0.76692	3.08867
H	0.48809	2.21957	4.28416
C	2.26377	-1.09064	0.39818
C	2.68409	-2.38298	0.74464
C	2.32081	-0.69489	-0.95551
C	3.15312	-3.27353	-0.22179
H	2.64027	-2.68813	1.78716
C	2.78753	-1.59706	-1.91914
C	3.20279	-2.87862	-1.55877
H	3.47564	-4.26904	0.07028
H	2.82545	-1.28546	-2.9593

H	3.56481	-3.56421	-2.32004
C	1.96179	0.71111	-1.40259
O	2.74494	1.63132	-1.24323
O	0.78153	0.85813	-2.00415
Pd	-0.78176	0.061	-0.81888
O	-1.35138	2.16378	-0.2274
O	-0.10151	3.2814	-1.74538
C	-0.99097	3.21157	-0.79115
C	-1.57221	4.54594	-0.39892
H	-2.38601	4.41017	0.31389
H	-0.78568	5.16312	0.04889
H	-1.92981	5.07105	-1.2899
C	-5.09965	-2.3807	-0.01236
H	-6.0604	-1.86551	-0.01226
H	-5.10942	-3.21622	0.69268
H	-4.86656	-2.76061	-1.01077
O	-4.13453	-1.39455	0.38794
C	-2.85975	-1.83546	0.46619
O	-2.52352	-2.98034	0.24072
C	-0.58965	-0.99235	1.08929
C	-1.95122	-0.72547	0.87133
H	-2.42454	0.17195	1.2587
H	-0.2564	-1.99857	0.84775
H	-0.53573	-1.33743	-1.36352

3aa

B3LYP/6-31G(d,p)(lanl2dz)(gas) Energy = -1312.977045

B3LYP/6-31G(d,p)(lanl2dz)(gas) Free Energy = -1312.702143

M06/6-311+G(2d,p)(sdd)/SMD (HFIP) Energy = -1313.783388

B3LYP/6-31G(d,p)(lanl2dz)(gas) Geometry

C	3.33856	-2.86241	-2.52274
C	3.10817	-2.64594	-1.16379
C	2.79205	-1.37712	-0.66342
C	2.73056	-0.2781	-1.55903
C	2.94093	-0.52596	-2.92906
C	3.2475	-1.79407	-3.41331

H	3.57427	-3.86105	-2.87976
H	3.15132	-3.48152	-0.47069
H	-4.67221	0.40036	1.18621
H	2.87582	0.30971	-3.62148
H	3.41209	-1.94503	-4.47643
C	2.56168	-1.26522	0.81194
C	3.68043	-1.40606	1.64726
C	1.30211	-1.04567	1.42235
C	3.57792	-1.31229	3.03519
H	4.65016	-1.57374	1.18777
C	1.21221	-0.93896	2.82052
C	2.33765	-1.06953	3.62628
H	4.46737	-1.42157	3.64962
H	0.23622	-0.75881	3.2569
H	2.24633	-0.98605	4.70505
C	0.01896	-0.92642	0.68748
O	-1.00208	-0.48777	1.23704
O	0.004	-1.34393	-0.57271
O	-4.63159	-0.31274	-0.96988
O	-5.6126	0.52672	0.87054
C	-5.63228	0.11939	-0.39425
C	-6.97548	0.23176	-1.05538
H	-6.91075	-0.11807	-2.08575
H	-7.71089	-0.36252	-0.50308
H	-7.31348	1.27303	-1.03311
C	1.62057	5.21028	-0.71674
H	1.22276	5.55329	-1.67271
H	2.5368	5.75227	-0.46554
H	0.88905	5.36631	0.08096
O	1.88909	3.81319	-0.89018
C	2.39137	3.1839	0.20228
O	2.60841	3.75488	1.25496
C	2.46758	1.12091	-1.19228
H	2.12466	1.73918	-2.01942
C	2.65028	1.74518	-0.01269

H	3.02963	1.24515	0.86933
H	-0.93133	-1.19785	-0.89321
Pd	-2.80748	-0.40256	0.12965

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