

Supporting Information

for

Visible-light-Induced Photoredox-Catalyzed Dearomative

Dicarboxylation of Arenes with Formate and CO₂

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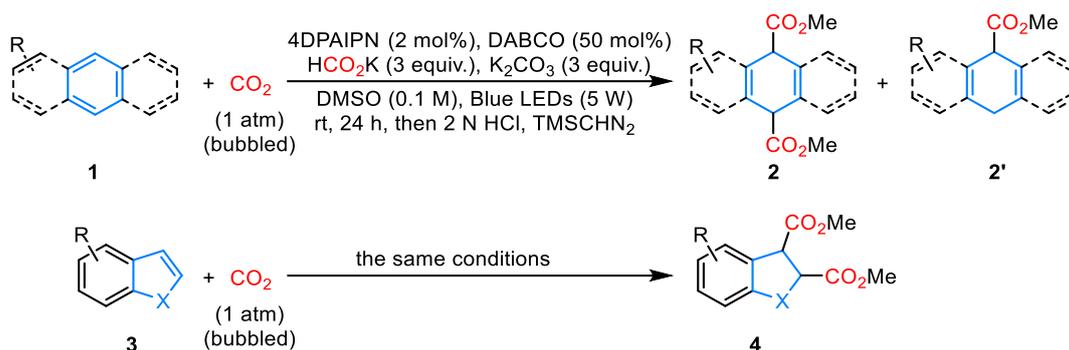
1. General information

All the reactions were carried out in pre-dried Schlenk tube. Boc-indoles in this work were synthesized as the literatures reported.¹ The other reagents were purchased from commercially available suppliers and used without further purification. All of the solvents were dried prior to use. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum ether, ethyl acetate, and alcohol.

All NMR spectra are collected on 400 MHz or 600 MHz spectrometer at ambient temperature with CDCl₃ as the solvent. All chemical shifts are reported in δ -scale as parts per million [ppm] (multiplicity, coupling constant *J*, number of protons) relative to TMS (Me₄Si) and d-solvent peaks, respectively. Coupling constants (*J*) are given in Hertz [Hz]. Abbreviations used for signal multiplicity. ¹H and ¹⁹F NMR: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets, ddd = doublet of doublets of doublets, tt = triplet of triplets, and m = multiplet.

Information about the photoreactor: the photoreactor (Type H106065) used in this research was purchased from GeAo Chem, Wuhan, China. The photoreactor was made up of 8 blue LED bulbs (5 W for each) with a cooler fan to keep room temperature. Spectral distribution: 415 - 430 nm. In the reaction, each Schlenk tube is mainly irradiated by one of the light bulbs. The approximate distance of the tube to the closest light bulb is 2 cm. A magnetic stirrer is placed under the photoreactor to keep the reaction being stirred.

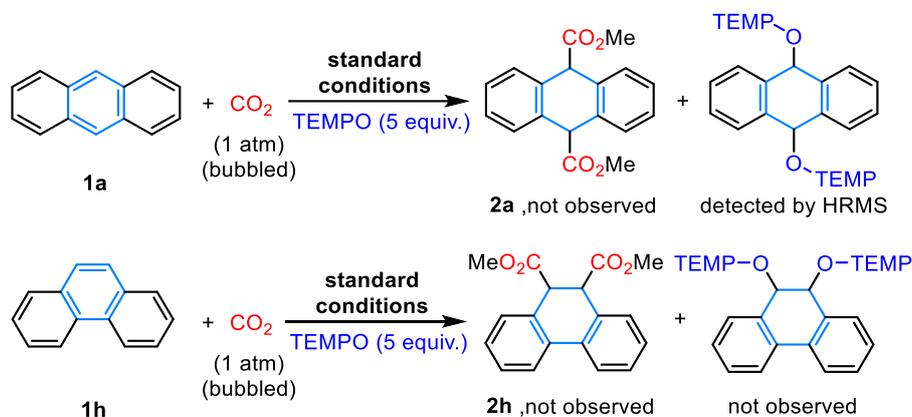
2. General procedure



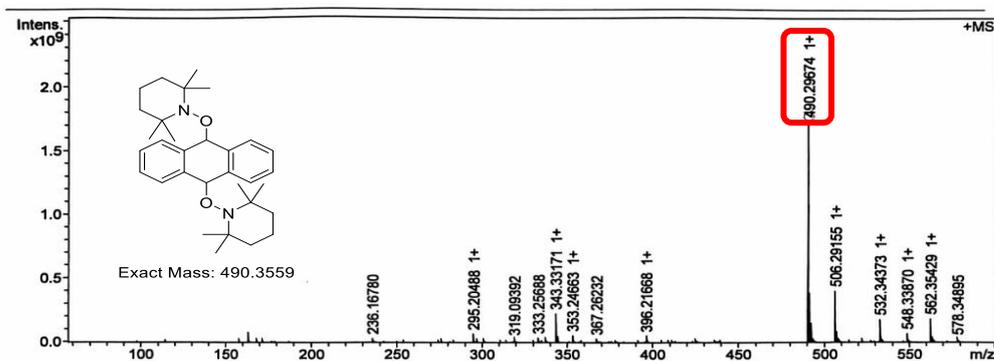
To a 25 mL Schlenk tube equipped with a magnetic stir bar was added **1** or **3** (0.2 mmol), 4DPAIPN (3.2 mg, 0.004 mmol), DABCO (11.2 mg, 0.1 mmol), HCO₂K (50.4 mg, 0.6 mmol) and K₂CO₃ (82.8 mg, 0.6 mmol), the tube was evacuated and filled CO₂ for three times. Then the anhydrous DMSO (2 mL) was added to the tube under the CO₂ atmosphere. The solution was bubbled with CO₂ for 5 min. The reaction tube was sealed and stirred at room temperature under blue LEDs (5 W) for 24 h. After completion, the reaction was carefully quenched with 2 N HCl and the mixture was extracted with 5 mL dichloromethane for 3 times. The combined organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The yields were determined by crude ¹H NMR using dibromomethane (CH₂Br₂) or dichloroethylene (C₂H₂Cl₂) as the internal standard. Then the crude product was esterified to allow for further characterization and isolation.

3. Mechanism studies

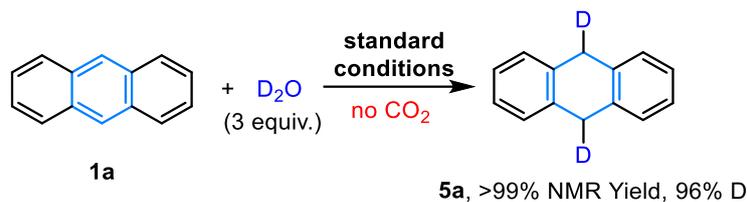
3.1 Radical capture experiment with TEMPO



To a 25 mL Schlenk tube equipped with a magnetic stir bar was added **1a** (35.6 mg, 0.2 mmol), 4DPAIPN (3.2 mg, 0.004 mmol), DABCO (11.2 mg, 0.1 mmol), HCO₂K (50.4 mg, 0.6 mmol) and K₂CO₃ (82.8 mg, 0.6 mmol), the tube was evacuated and filled CO₂ for three times. Then the anhydrous DMSO (2 mL) and TEMPO (157 mg, 1 mmol) were added to the tube under the CO₂ atmosphere. The solution was bubbled with CO₂ for 5 min. The reaction tube was sealed and stirred at room temperature under blue LEDs (5 W) for 24 h. After completion, the reaction was carefully quenched with 2 N HCl and the mixture was extracted with 5 mL dichloromethane for 3 times. The combined organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The yields were determined by crude ¹H NMR using dichloroethylene (C₂H₂Cl₂) as the internal standard. After esterification, the crude product was tested by HRMS(ESI).



3.2 D-labeling experiment with D₂O



To a 25 mL Schlenk tube equipped with a magnetic stir bar was added **1a** (35.6 mg, 0.2 mmol), 4DPAIPN (3.2 mg, 0.004 mmol), DABCO (11.2 mg, 0.1 mmol), HCO₂K (50.4 mg, 0.6 mmol) and K₂CO₃ (82.8 mg, 0.6 mmol), the tube was evacuated and filled N₂ for three times. Then the anhydrous DMSO (2 mL) and D₂O (13.2 μL , 0.6 mmol) were added to the tube under the N₂ atmosphere. The reaction tube was sealed and stirred at room temperature under blue LEDs (5 W) for 24 h. After completion, the reaction was carefully quenched with 2 N HCl and the mixture was extracted with 5 mL dichloromethane for 3 times. The combined organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. After purified by silica gel column chromatography with petroleum ether/ethyl acetate as the eluent, the deuterium ratio was determined by ¹H NMR.

¹H NMR (the reaction system of 3 equiv. of D₂O, **1a**, in standard condition without CO₂):

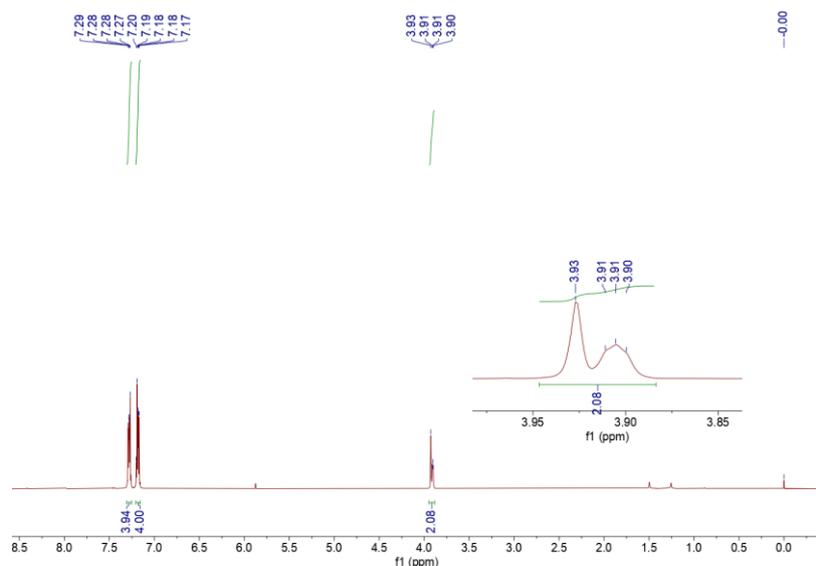


Figure S1

^{13}C NMR (the reaction system of 3 equiv. of D_2O , **1a**, in standard condition without CO_2):

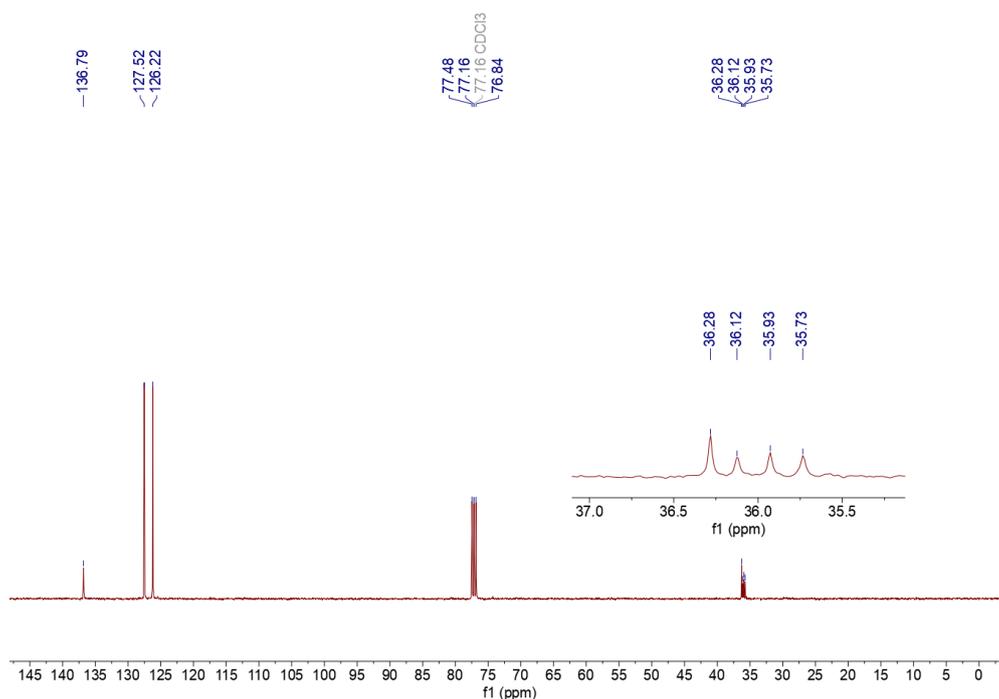
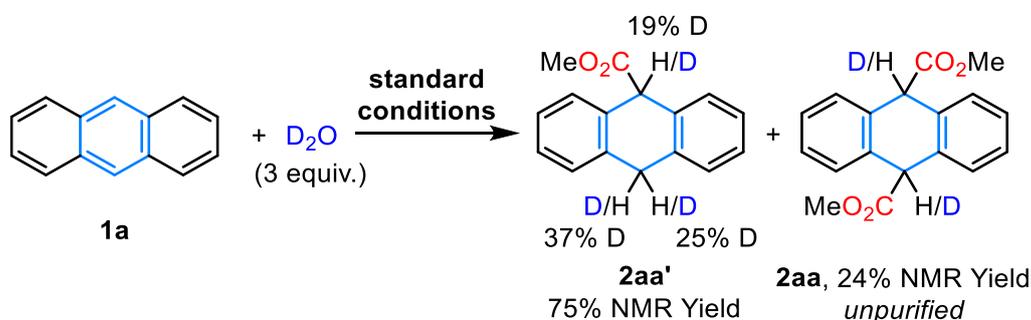


Figure S2



To a 25 mL Schlenk tube equipped with a magnetic stir bar was added **1a** (35.6 mg, 0.2 mmol), 4DPAIPN (3.2 mg, 0.004 mmol), DABCO (11.2 mg, 0.1 mmol), HCO_2K (50.4 mg, 0.6 mmol) and K_2CO_3 (82.8 mg, 0.6 mmol), the tube was evacuated and filled CO_2 for three times. The solution was bubbled with CO_2 for 5 min. Then the anhydrous DMSO (2 mL) and D_2O (13.2 μL , 0.6 mmol) were added to the tube under the CO_2 atmosphere. The reaction tube was sealed and stirred at room temperature under blue LEDs (5 W) for 24 h. After completion, the reaction was carefully quenched with 2 N HCl and the mixture was extracted with 5 mL dichloromethane for 3 times. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated

under reduced pressure. After purified by silica gel column chromatography with petroleum ether/ethyl acetate as the eluent, the deuterium ratio was determined by ^1H NMR.

^1H NMR (the reaction system of 3 equiv. of D_2O , **1a**, in standard condition):

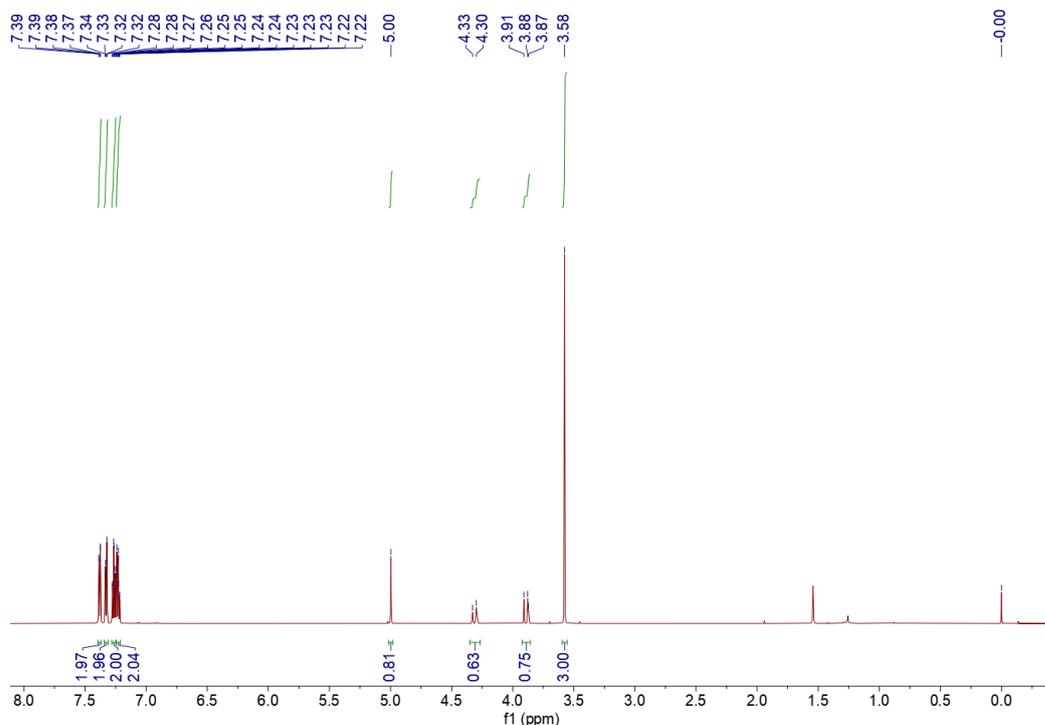
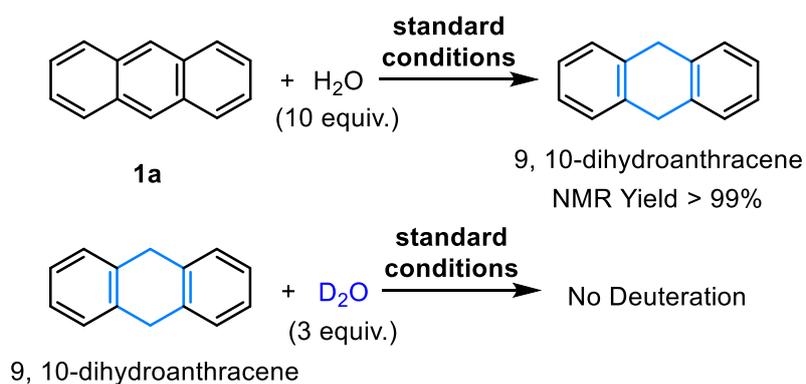


Figure S3

For the validation experiment, the reaction conditions were the same as the labeling experiment, except that D_2O was replaced with more equivalents of H_2O (40 μL , 2 mmol) to gain the reduced product 9, 10-dihydroanthracene. Then 9, 10-dihydroanthracene underwent the D-labeling reaction in the same conditions. The deuterium ratio was determined by ^1H NMR.



^1H NMR (the reaction system in 3 equiv. of D_2O , 9, 10-dihydroanthracene):

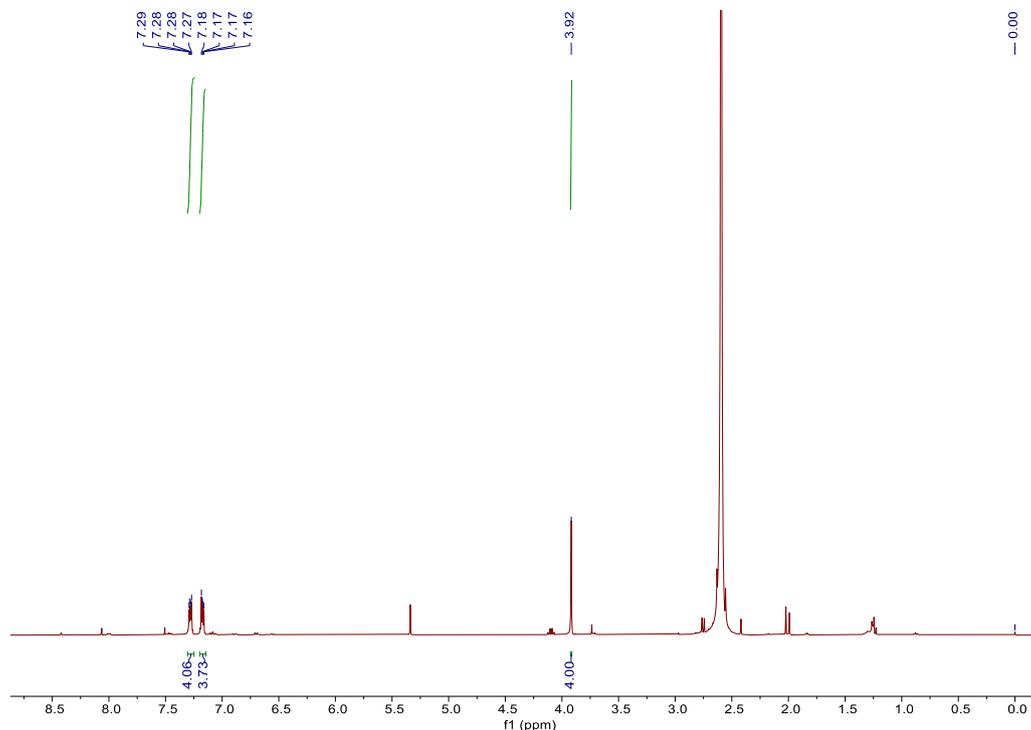
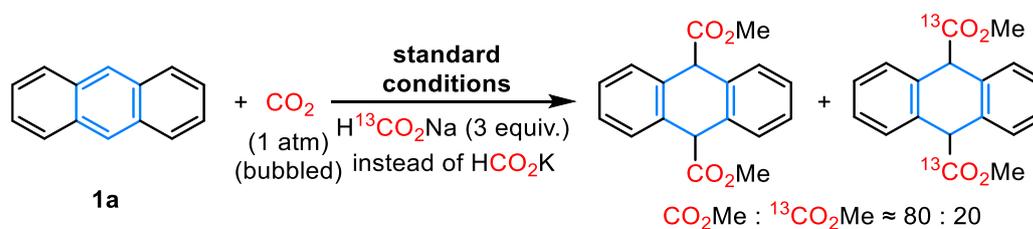


Figure S4

3.3 ^{13}C -labeling experiment with $\text{H}^{13}\text{CO}_2\text{Na}$



To a 25 mL Schlenk tube equipped with a magnetic stir bar was added **1a** (35.6 mg, 0.2 mmol), 4DPAIPN (3.2 mg, 0.004 mmol), DABCO (11.2 mg, 0.1 mmol), $\text{H}^{13}\text{CO}_2\text{Na}$ (41.4 mg, 0.6 mmol) and K_2CO_3 (82.8 mg, 0.6 mmol), the tube was evacuated and filled CO_2 for three times. Then the anhydrous DMSO (2 mL) was added to the tube under the CO_2 atmosphere. The solution was bubbled with CO_2 for 5 min. The reaction tube was sealed and stirred at room temperature under blue LEDs (5 W) for 24 h. After completion, the reaction was carefully quenched with 2 N HCl and the mixture was extracted with 5 mL dichloromethane for 3 times. The combined organic layers were

dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. Then the crude product was esterified to allow for further characterization and isolation. After purified by silica gel column chromatography with petroleum ether/ethyl acetate as the eluent, the ¹³C ratio was determined by quantitative ¹³C NMR.

Quantitative ¹³C NMR (H¹³CO₂Na):

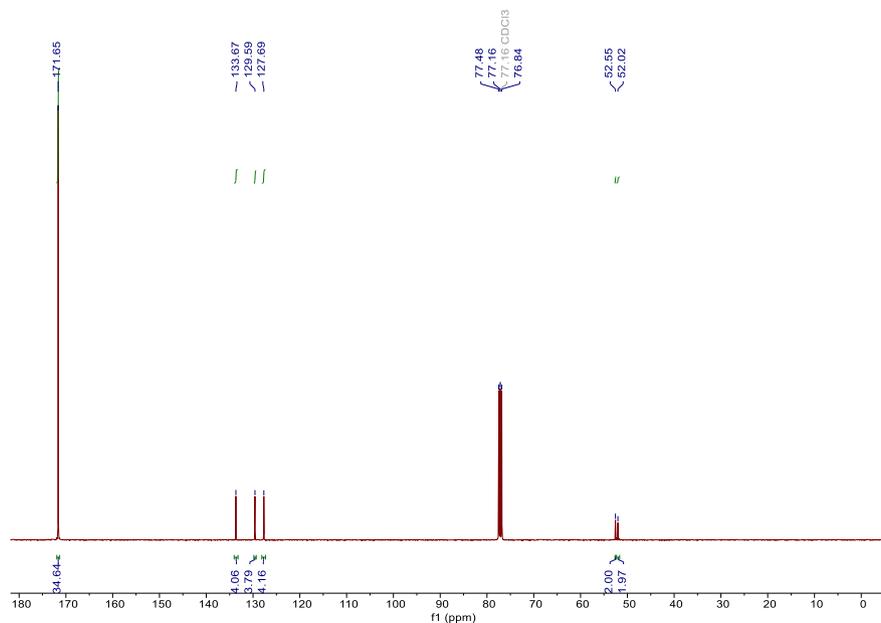


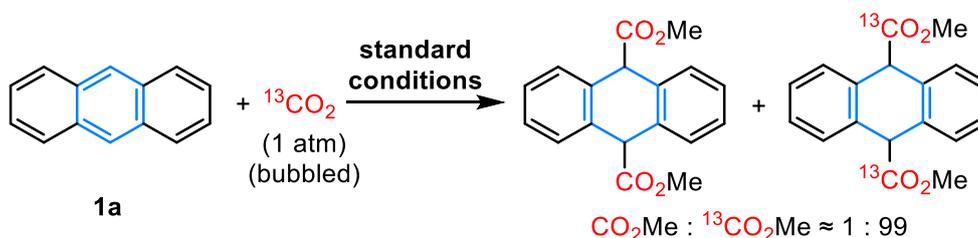
Figure S5

Assume that the ¹³C labeling ratio of the base is x , and the natural abundance of ¹³C is known to be 1.11%, so there are:

$$\frac{1.11\%(1 - x) + x}{1.11\%} = \frac{34.64}{2}$$

Solution $x = 18.3\% \approx 20\%$

3.4 ¹³C-labeling experiment with ¹³CO₂



To a 25 mL Schlenk tube equipped with a magnetic stir bar was added **1a** (35.6 mg, 0.2 mmol), 4DPAIPN (3.2 mg, 0.004 mmol), DABCO (11.2 mg, 0.1 mmol), HCO₂K (50.4 mg, 0.6 mmol) and K₂CO₃ (82.8 mg, 0.6 mmol), the above feeding steps

are all completed in the N₂ atmosphere of the glove box. Then the anhydrous DMSO (2 mL) was added to the tube under the N₂ atmosphere. The solution was bubbled with ¹³CO₂ for 5 min. The reaction tube was sealed and stirred at room temperature under blue LEDs (5 W) for 24 h. After completion, the reaction was carefully quenched with 2 N HCl and the mixture was extracted with 5 mL dichloromethane for 3 times. The combined organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. Then the crude product was esterified to allow for further characterization and isolation. After purified by silica gel column chromatography with petroleum ether/ethyl acetate as the eluent, the ¹³C ratio was determined by quantitative ¹³C NMR.

Quantitative ¹³C NMR (¹³CO₂):

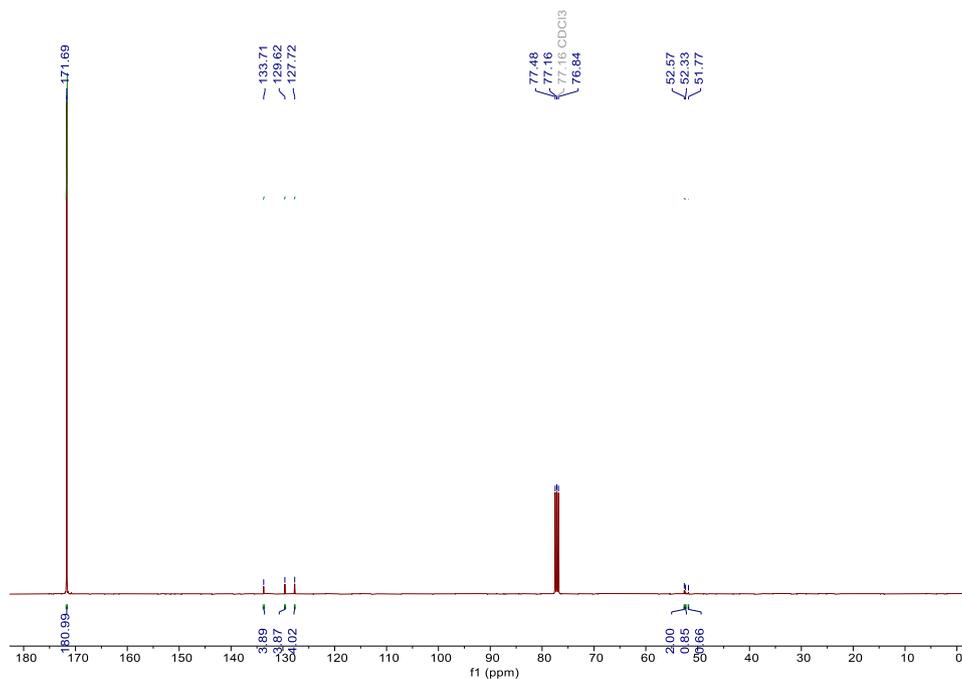


Figure S6

The calculation was performed as follows:

Assume that the ¹³C labeling ratio of the base is x , and the natural abundance of ¹³C is known to be 1.11%, so there are:

$$\frac{1.11\%(1 - x) + x}{1.11\%} = \frac{180.99}{2}$$

Solution $x \approx 1$

3.5 Stern-Volmer fluorescence quenching experiments

Fluorescence quenching experiments were tested on a LS (PERKINELMER(HK)LTD) Spectrofluorophotometer with a 4 mL quartz cuvette with a cap. 4DPAIPN was irradiated at 430 nm and the emission intensity at about 530 nm was observed. In a typical experiment, the emission spectrum of a 10^{-5} M solution of 4DPAIPN in anhydrous DMSO was collected.

DABCO: A stock solution of DABCO (0.05 M) was prepared. Then, different amounts of this stock solution were added to 2 mL of 4DPAIPN in DMSO (10^{-5} M).

1a (anthracene): A stock solution of **1a** (0.02 M) was prepared. Then, different amounts of this stock solution were added to 2 mL of 4DPAIPN in DMSO (10^{-5} M).

HCO₂K: A stock solution of HCO₂K (0.05 M) was prepared. Then, different amounts of this stock solution were added to 2 mL of 4DPAIPN in DMSO (10^{-5} M).

1h (phenanthrene), 1m (naphthalene), 3d (Boc-indole): A stock solution of **1h/1m/3d** (0.02 M) was prepared. Then, different amounts of this stock solution were added to 3 mL of 4DPAIPN in DMSO (10^{-5} M).

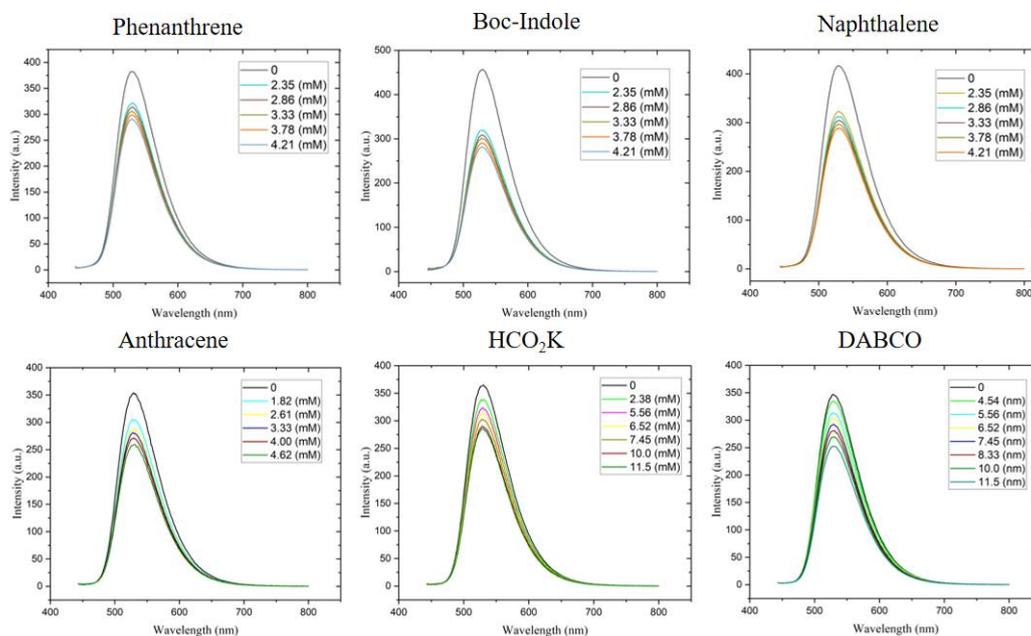


Figure S7

The results of Stern-Volmer fluorescence quenching experiments suggested that **1a**, **1j**, **1p** and **3d** are all able to quench the PC* (4DPAIPN*). Considering that the

phenanthrene ($E_0^{\text{red}} = -2.49$ V in DMSO vs. SCE) , Boc-indole ($E_0^{\text{red}} = -2.70$ V in DMSO vs. SCE), benzothiophene ($E_0^{\text{red}} = -2.80$ V in DMSO vs. SCE) and benzofuran ($E_0^{\text{red}} = -2.87$ V in MeCN vs. SCE) cannot be directly reduced by $\text{PC}^{\bullet-}$ [$E_{1/2}(\text{PC}/\text{PC}^{\bullet-}) = -1.52$ V vs. SCE] or $\text{CO}_2^{\bullet-}$ ($E_{1/2} = -2.21$ V in DMF vs. SCE) because of their high E_0^{red} , we believe that these substrates might quench the PC^* or potentially generated $\text{PC}^{\bullet-}$ (4DPA-Me-IBN*) by energy transfer instead of electron transfer, despite no diradicals detected.

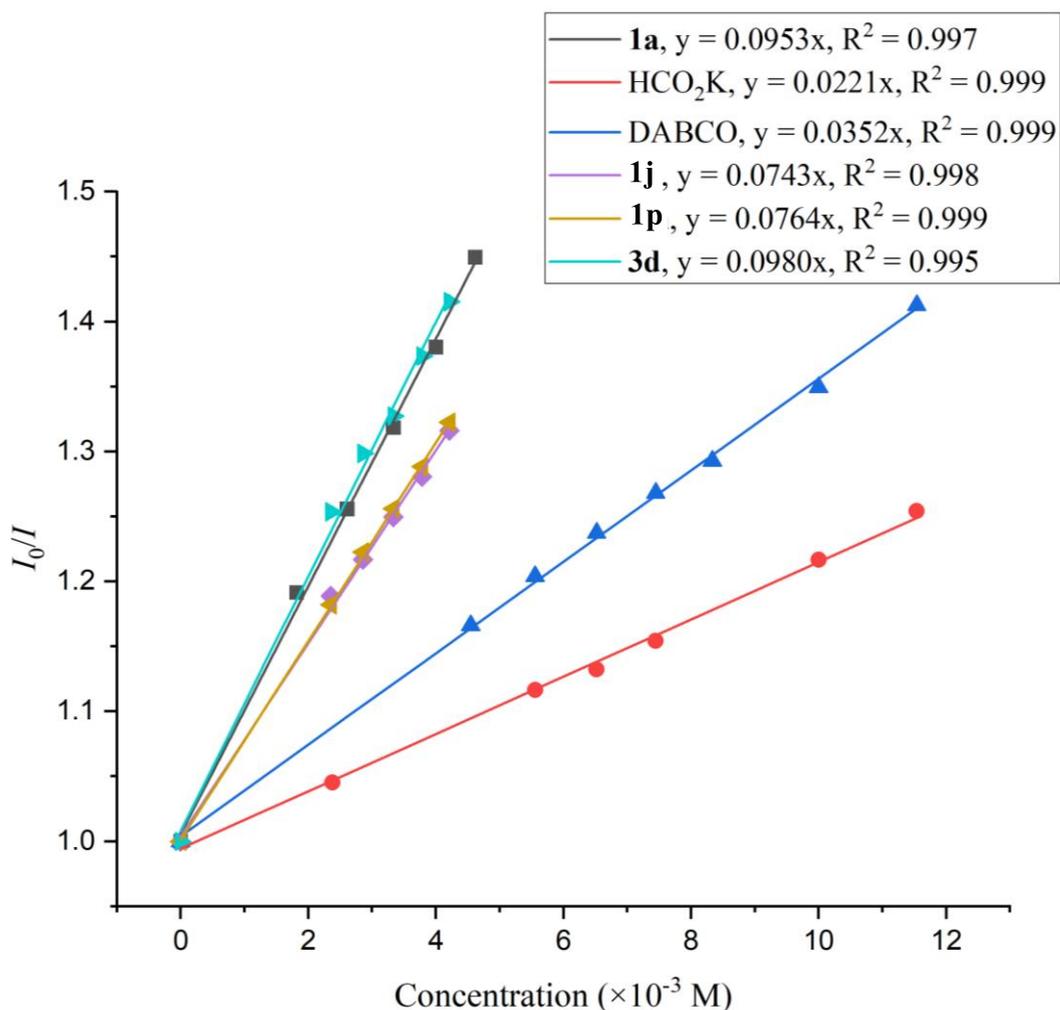
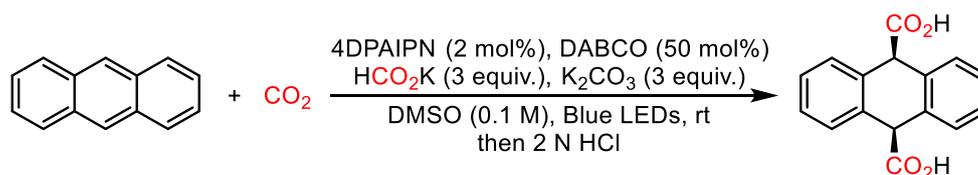


Figure S8

3.6 Light on/off experiments

To a 25 mL Schlenk tube equipped with a magnetic stir bar was added **1a** (35.6 mg, 0.2 mmol), 4DPAIPN (3.2 mg, 0.004 mmol), DABCO (11.2 mg, 0.1 mmol), HCO₂K (50.4 mg, 0.6 mmol) and K₂CO₃ (82.8 mg, 0.6 mmol), the tube was evacuated and filled CO₂ for three times. Then the anhydrous DMSO (2 mL) was added to the tube under the CO₂ atmosphere. The solution was bubbled with CO₂ for 5 min. The reaction tube was sealed and stirred at room temperature under blue LEDs (5 W). Turn on/off the blue LEDs every 2 hours and quenched one reaction with 2 N HCl at the same time until all the reactions were quenched. Each reaction mixture was extracted with 5 mL dichloromethane for 3 times. The combined organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The yields were determined by crude ¹H NMR using dichloroethylene (C₂H₂Cl₂) as the internal standard.

Table S1. Light on/off experiment (**1h**)^a



Entry	time (h)	reaction time (h)	Yield (%) ^b
0	2	2	14
1	4	2	14
2	6	4	37
3	8	4	37
4	10	6	53
5	12	6	53

^aReaction conditions: **1a** (0.2 mmol), 4DPAIPN (2 mol%), DABCO (50 mol%), HCO₂K (3 equiv.), K₂CO₃ (3 equiv.), DMSO (0.1 M), 5 W blue LEDs, room temperature, 1 atm CO₂ atmosphere. ^bCrude ¹H NMR yield.

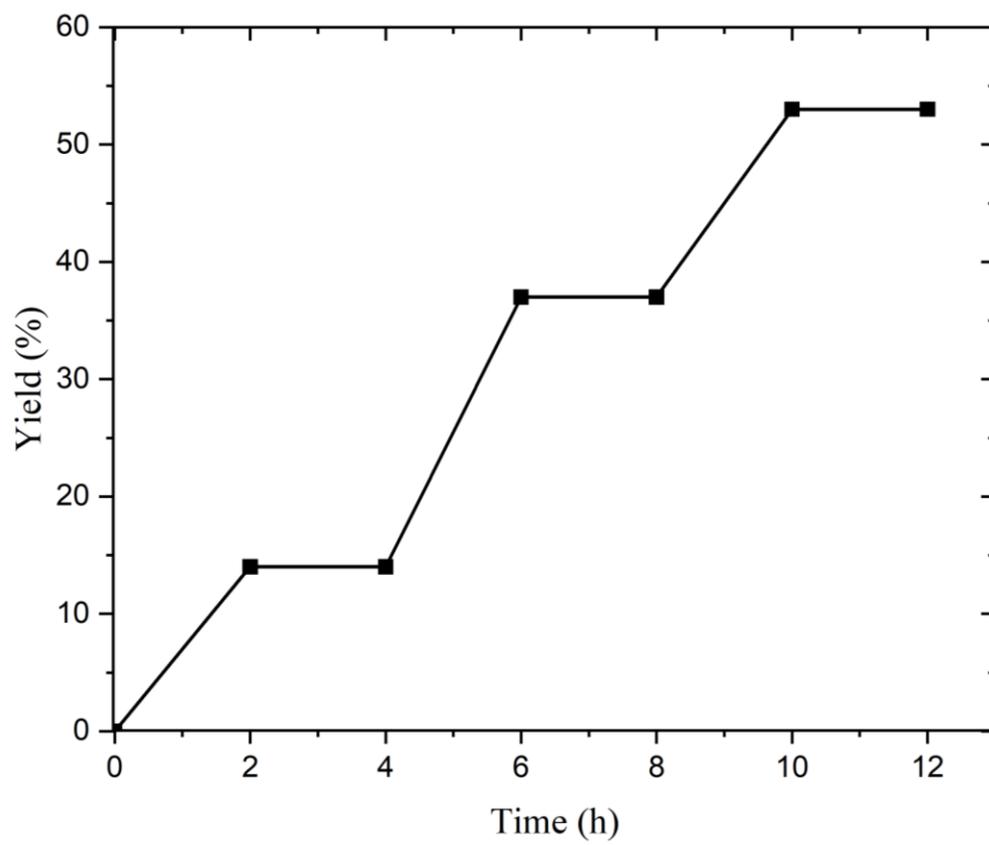
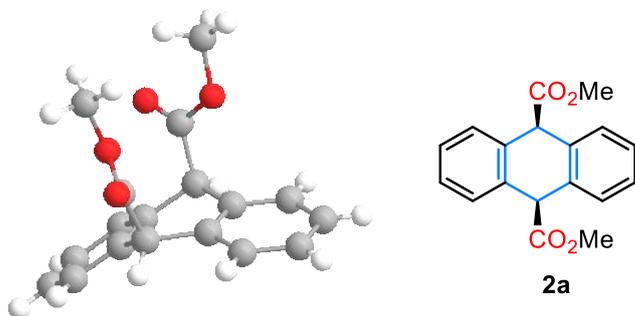


Figure S9

4. X-ray crystallographic data

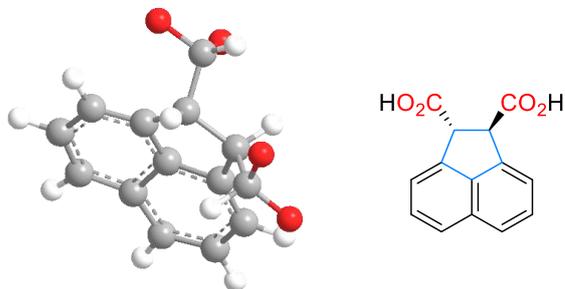
4.1 X-ray crystallographic data of 2a



Crystal data and structure refinement for 2a

Empirical formula	C ₁₈ H ₁₆ O ₄
Formula weight	296.31
Temperature/K	169.9(3)
Crystal system	triclinic
Space group	P-1
a/Å	7.4833(6)
b/Å	8.3504(7)
c/Å	13.1170(8)
α/°	87.703(6)
β/°	79.960(6)
γ/°	63.498(8)
Volume/Å ³	721.64(11)
Z	2
ρ _{calc} /cm ³	1.364
μ/mm ⁻¹	0.788
F(000)	312.0
Crystal size/mm ³	0.42 × 0.35 × 0.25
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/°	6.85 to 151.772
Index ranges	-9 ≤ h ≤ 8, -10 ≤ k ≤ 9, -16 ≤ l ≤ 15
Reflections collected	8294
Independent reflections	2898 [R _{int} = 0.0268, R _{sigma} = 0.0271]
Data/restraints/parameters	2898/0/202
Goodness-of-fit on F ²	1.062
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0381, wR ₂ = 0.1012
Final R indexes [all data]	R ₁ = 0.0410, wR ₂ = 0.1032
Largest diff. peak/hole / e Å ⁻³	0.25/-0.17

4.2 X-ray crystallographic data of (1R,2R)-1,2-dihydroacenaphthylene-1,2-dicarboxylic acid

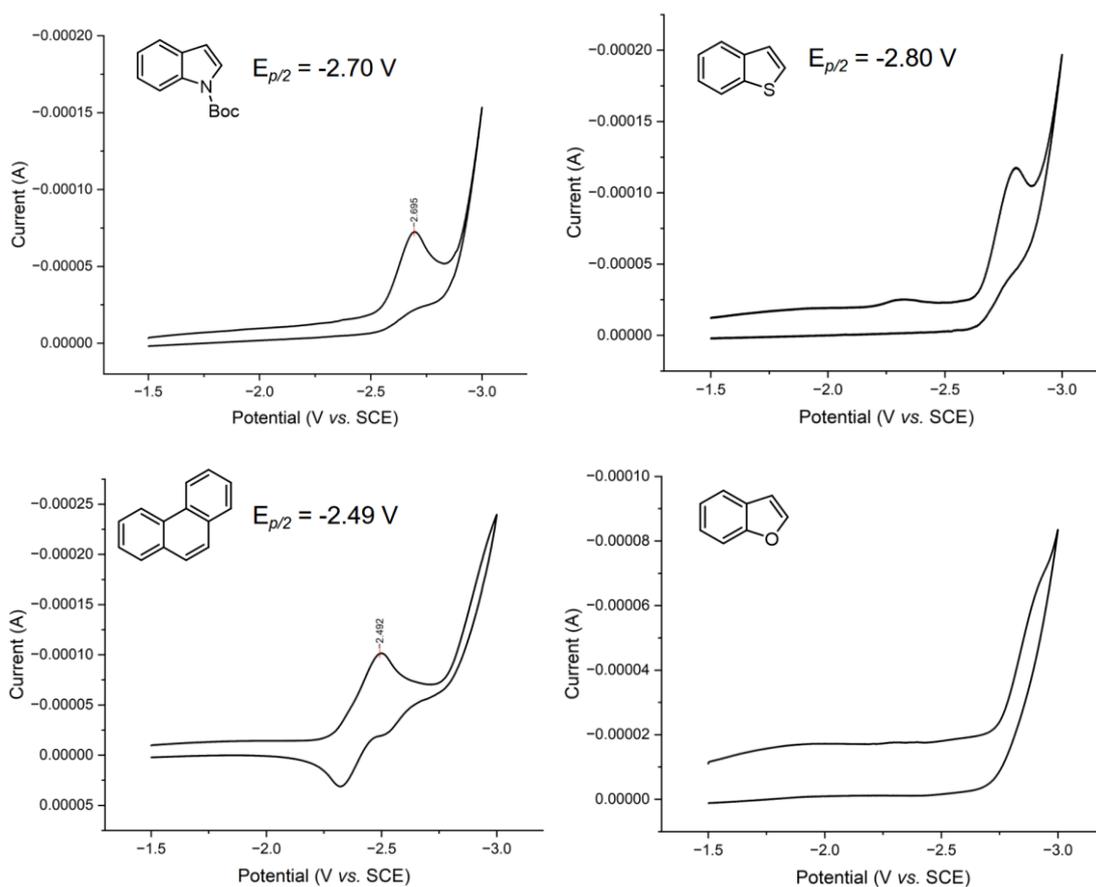


Crystal data and structure refinement for (1R,2R)-1,2-dihydroacenaphthylene-1,2-dicarboxylic acid

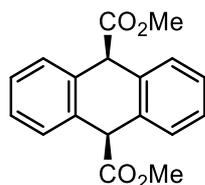
Empirical formula	C ₁₄ H ₁₀ O ₄
Formula weight	121.11
Temperature/K	170.0(4)
Crystal system	orthorhombic
Space group	Pccn
a/Å	5.56956(10)
b/Å	10.83565(18)
c/Å	18.2517(3)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	1101.49(3)
Z	8
ρ _{calc} /cm ³	1.461
μ/mm ⁻¹	0.901
F(000)	504.0
Crystal size/mm ³	0.25 × 0.22 × 0.18
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/°	9.692 to 151.362
Index ranges	-6 ≤ h ≤ 7, -13 ≤ k ≤ 12, -22 ≤ l ≤ 21
Reflections collected	11646
Independent reflections	1135 [R _{int} = 0.0298, R _{sigma} = 0.0146]
Data/restraints/parameters	1135/0/85
Goodness-of-fit on F ²	1.034
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0332, wR ₂ = 0.0890
Final R indexes [all data]	R ₁ = 0.0345, wR ₂ = 0.0900
Largest diff. peak/hole / e Å ⁻³	0.25/-0.16

5. Cyclic Voltammetry Measurements

Cyclic voltammetry (CV) was performed with CHI-660E electrochemical workstation with a three-electrode system. A glassy carbon served as the working electrode, a platinum wire served as the counter electrode and a saturated calomel reference electrode was employed. The scan rate for the experiment was $0.2 \text{ V}\cdot\text{s}^{-1}$. The scan direction was negative. The cyclic voltammetry was carried out with 100 mM DMSO solution of ${}^n\text{Bu}_4\text{N}\cdot\text{ClO}_4$ containing 2 mM of phenanthrene and heteroarenes under a argon gas atmosphere at room temperature.

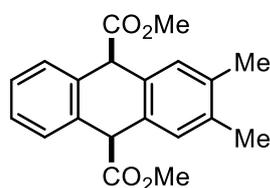


6. NMR data of products



Dimethyl (9S,10S)-9,10-dihydroanthracene-9,10-dicarboxylate (2a)² (d.r. = 8:1):

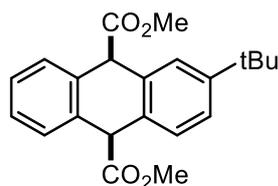
white solid, 52.7 mg, 89% yield, (PE: EA = 5:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.44 (dd, *J* = 5.6, 3.2 Hz, 4H), 7.32 (dd, *J* = 5.6, 3.2 Hz, 4H), 4.97 (s, 2H), 3.57 (s, 6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 171.6, 133.6, 129.6, 127.7, 52.5, 52.0.



Dimethyl (9R,10S)-2,3-dimethyl-9,10-dihydroanthracene-9,10-dicarboxylate (2b)

(d.r. > 20:1): colorless liquid, 55.1 mg, 85% yield, (PE: EA = 5:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.43 (dd, *J* = 5.6, 3.3 Hz, 2H), 7.31 (dd, *J* = 5.6, 3.3 Hz, 2H), 7.21 (s, 2H), 4.91 (s, 2H), 3.57 (s, 6H), 2.27 (s, 6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 172.0, 136.2, 133.9, 130.9, 130.6, 129.6, 127.6, 52.6, 51.6, 19.6.

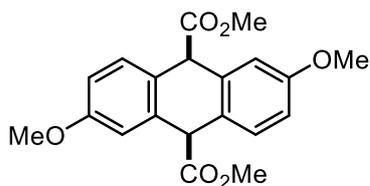
HRMS (ESI) calculated *m/z* [M+Na]⁺ for C₂₀H₂₀NaO₄ 347.1259, found 347.1257.



Dimethyl (9R,10S)-2-(tert-butyl)-9,10-dihydroanthracene-9,10-dicarboxylate (2c)

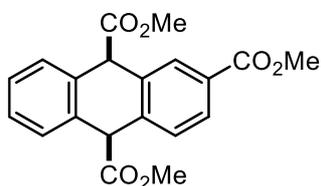
(d.r. > 20:1): colorless liquid, 66.2 mg, 94% yield, (PE: EA = 5:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.40 (m, 3H), 7.40 – 7.33 (m, 2H), 7.30 (dd, *J* = 5.8, 3.3 Hz, 2H), 4.96 (s, 1H), 4.94 (s, 1H), 3.58 (s, 3H), 3.56 (s, 3H), 1.34 (s, 9H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 171.8, 150.5, 133.9, 133.9, 133.2, 130.6, 129.6, 129.4, 129.2, 127.6, 126.4, 124.9, 52.5, 52.4, 52.4, 51.6, 34.6, 31.4.

HRMS (ESI) calculated *m/z* [M+Na]⁺ for C₂₂H₂₄NaO₄ 375.1572, found 375.1569.



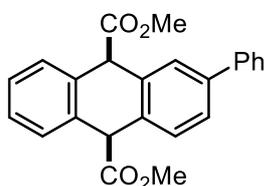
Dimethyl 2,6-dimethoxy-9,10-dihydroanthracene-9,10-dicarboxylate (2d) (d.r. > **20:1**): yellow liquid, 37.0 mg, 52% yield, (PE: EA = 5:1). ¹H NMR (600 MHz, Chloroform-*d*) δ 7.34 (d, *J* = 8.4 Hz, 2H), 6.96 (d, *J* = 2.6 Hz, 2H), 6.88 (dd, *J* = 8.4, 2.6 Hz, 2H), 4.88 (s, 2H), 3.83 (s, 6H), 3.58 (s, 6H). ¹³C NMR (151 MHz, Chloroform-*d*) δ 171.9, 159.0, 135.1, 130.4, 125.8, 114.5, 113.8, 55.5, 52.5, 51.5.

HRMS (ESI) calculated *m/z* [M+Na]⁺ for C₂₀H₂₀NaO₆ 379.1158, found 379.1157.



Dimethyl (9R,10S)-2,6-dimethoxy-9,10-dihydroanthracene-9,10-dicarboxylate (2e) (d.r. > **20:1**): colorless liquid, 43.9 mg, 62% yield, (PE: EA = 2:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.14 (d, *J* = 1.8 Hz, 1H), 8.01 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.46 (td, *J* = 6.0, 3.3 Hz, 2H), 7.36 (dd, *J* = 6.0, 3.3 Hz, 2H), 5.04 (s, 1H), 5.03 (s, 1H), 3.93 (s, 3H), 3.59 (s, 3H), 3.58 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 171.2, 138.8, 133.3, 133.1, 130.9, 129.9, 129.7, 128.8, 128.0, 52.7, 52.4, 52.1, 52.0, 29.8.

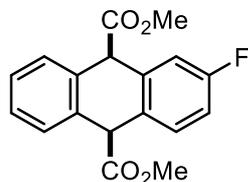
HRMS (ESI) calculated *m/z* [M+Na]⁺ for C₂₀H₁₈NaO₆ 377.1001, found 377.1000.



Dimethyl (9R,10S)-2-phenyl-9,10-dihydroanthracene-9,10-dicarboxylate (2f) (d.r. > **20:1**): colorless liquid, 43.2 mg, 58% yield, (PE: EA = 5:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 1.9 Hz, 1H), 7.61 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.55 (dd, *J* = 7.9, 1.9 Hz, 1H), 7.50 (d, *J* = 7.9 Hz, 1H), 7.47 – 7.40 (m, 4H), 7.37 – 7.31 (m, 3H), 5.03 (s, 1H), 5.00 (s, 1H), 3.59 (d, *J* = 7.8 Hz, 6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 171.6, 171.6, 140.7, 140.7, 134.1, 133.6, 132.7, 130.0, 129.7, 129.6, 128.9, 128.2,

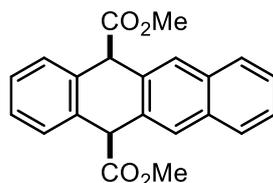
127.8, 127.5, 127.3, 126.5, 52.6, 52.6, 52.2, 51.7.

HRMS (ESI) calculated m/z $[M+Na]^+$ for $C_{24}H_{20}NaO_4$ 395.1259, found 395.1256.



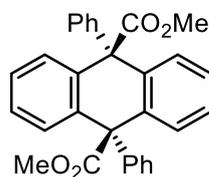
Dimethyl (9R,10S)-2-fluoro-9,10-dihydroanthracene-9,10-dicarboxylate (2g)²

(d.r. > 20:1): white solid, 51.5 mg, 82% yield, (PE: EA = 5:1). ¹H NMR (600 MHz, Chloroform-*d*) δ 7.44 (dt, J = 6.0, 3.2 Hz, 2H), 7.40 (dd, J = 8.4, 6.0 Hz, 1H), 7.34 (dd, J = 6.0, 3.2 Hz, 2H), 7.16 (dd, J = 6.0, 2.7 Hz, 1H), 7.03 (td, J = 8.4, 2.7 Hz, 1H), 4.95 (s, 1H), 4.93 (s, 1H), 3.60 (s, 3H), 3.58 (s, 3H). ¹³C NMR (151 MHz, Chloroform-*d*) δ 171.5, 171.1, 162.1 (d, J = 246.13 Hz), 135.8 (d, J = 7.6 Hz), 133.5, 133.0, 131.0 (d, J = 7.6 Hz), 129.6, 129.5, 127.9 (d, J = 6.0 Hz), 116.4, 116.2, 115.0, 114.8, 52.7, 52.6, 52.0, 51.4. ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -114.9.



Dimethyl (5R,12S)-5,12-dihydrotetracene-5,12-dicarboxylate (2h)² **(d.r. > 20:1):**

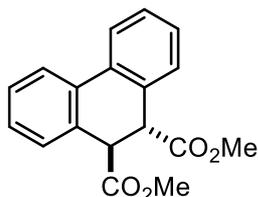
white solid, 49.1 mg, 71% yield, (PE: EA = 5:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.91 (s, 2H), 7.86 (dd, J = 5.9, 3.3 Hz, 2H), 7.50 (ddd, J = 9.4, 5.9, 3.3 Hz, 4H), 7.38 (dd, J = 5.9, 3.3 Hz, 2H), 5.14 (s, 2H), 3.60 (s, 6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 171.7, 133.9, 132.7, 131.6, 129.8, 128.5, 127.8, 127.6, 126.2, 52.6, 52.3.



Dimethyl (9S,10S)-9,10-diphenyl-9,10-dihydroanthracene-9,10-dicarboxylate (2i)

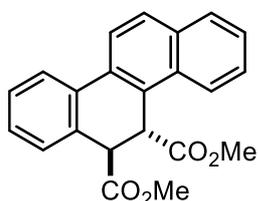
(d.r. > 20:1): white solid, 38.5 mg, 43% yield, (PE: EA = 5:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.28 (m, 6H), 7.18 (dd, J = 7.9, 2.0 Hz, 4H), 7.14 (dd, J = 6.0, 3.4 Hz, 4H), 6.94 (dd, J = 6.0, 3.4 Hz, 4H), 3.63 (s, 6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 172.9, 145.7, 138.7, 131.1, 130.1, 128.2, 127.0, 61.7, 52.8.

HRMS (ESI) calculated m/z $[M+Na]^+$ for $C_{30}H_{24}NaO_4$ 471.1572, found 471.1566.



Dimethyl 9,10-dihydrophenanthrene-9,10-dicarboxylate (2j)³ (d.r. > 20:1):

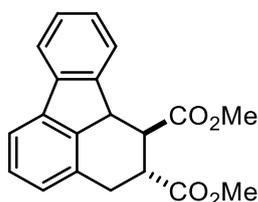
colorless liquid, 41.5 mg, 70% yield, (PE: EA = 5:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.74 (dd, $J = 7.7, 1.5$ Hz, 2H), 7.38 – 7.34 (m, 4H), 7.31 – 7.26 (m, 2H), 4.41 (s, 2H), 3.55 (s, 6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 172.1, 133.3, 131.6, 130.2, 128.6, 128.1, 124.1, 52.6, 47.1.



Dimethyl 5,6-dihydrochrysen-5,6-dicarboxylate (2k) (d.r. > 20:1):

colorless liquid, 54.7 mg, 79% yield, (PE: EA = 5:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.55 – 8.49 (m, 1H), 7.92 (d, $J = 7.6$ Hz, 1H), 7.88 – 7.84 (m, 1H), 7.78 (d, $J = 8.3$ Hz, 1H), 7.51 – 7.44 (m, 4H), 7.41 (td, $J = 7.6, 1.6$ Hz, 1H), 7.36 – 7.31 (m, 1H), 4.50 (d, $J = 3.2$ Hz, 1H), 4.42 (d, $J = 3.2$ Hz, 1H), 3.52 (s, 3H), 3.49 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 171.8, 171.8, 134.6, 133.8, 133.0, 131.2, 131.2, 130.0, 129.8, 129.2, 128.8, 128.4, 127.7, 127.6, 127.4, 126.5, 125.9, 125.8, 52.6, 48.4, 47.6.

HRMS (ESI) calculated m/z $[M+Na]^+$ for $C_{22}H_{18}NaO_4$ 369.1103, found 369.1101.

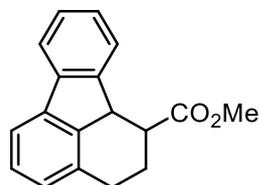


Dimethyl 1,2,3,10b-tetrahydrofluoranthene-1,2-dicarboxylate (2l) (d.r. = 1.2:1):

colorless liquid, 21.9 mg, 34% yield, (PE: EA = 5:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, $J = 7.4$ Hz, 1H), 7.63 (d, $J = 7.4$ Hz, 1H), 7.45 (t, $J = 7.7$ Hz, 1H), 7.40 – 7.37 (m, 2H), 7.29 – 7.26 (m, 1H), 7.26 – 7.22 (m, 1H), 4.14 (t, $J = 9.7$ Hz, 1H), 4.05 – 3.96 (m, 1H), 3.89 (m, 3H), 3.78 – 3.70 (m, 3H), 2.84 – 2.67 (m, 1H), 2.59 – 2.49 (m, 1H), 2.42 (dtd, $J = 27.4, 11.2, 4.1$ Hz, 1H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 176.1,

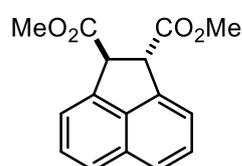
175.4, 174.0, 145.5, 143.7, 141.4, 140.2, 130.9, 128.4, 127.7, 127.2, 126.0, 125.3, 120.6, 118.9, 52.2, 46.3, 43.6, 42.1, 40.9, 31.4.

HRMS (ESI) calculated m/z $[M+Na]^+$ for $C_{20}H_{18}NaO_4$ 345.1103, found 345.1095.

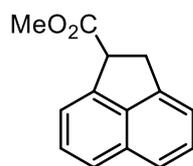


Methyl 1,2,3,10b-tetrahydrofluoranthene-1-carboxylate (2l'): colorless liquid, 16.4 mg, 31% yield, (PE: EA = 30:1). 1H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, J = 7.7 Hz, 1H), 7.55 (d, J = 7.5 Hz, 1H), 7.44 (d, J = 7.4 Hz, 1H), 7.36 (t, J = 7.5 Hz, 1H), 7.31 (t, J = 7.6 Hz, 1H), 7.25 (t, J = 6.3 Hz, 1H), 7.07 (d, J = 7.6 Hz, 1H), 4.00 (d, J = 10.7 Hz, 1H), 3.87 (s, 3H), 3.15 (dt, J = 16.7, 4.8 Hz, 1H), 2.90 – 2.79 (m, 1H), 2.38 – 2.26 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.6, 145.9, 143.4, 141.7, 139.7, 134.1, 128.0, 127.6, 126.9, 125.6, 125.1, 120.6, 117.5, 52.1, 46.7, 43.2, 28.4, 26.2.

HRMS (ESI) calculated m/z $[M+Na]^+$ for $C_{18}H_{16}NaO_2$ 287.1048, found 287.1045.



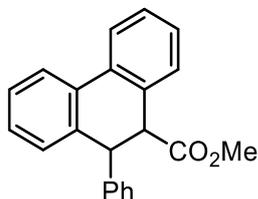
Dimethyl 1,2-dihydroacenaphthylene-1,2-dicarboxylate (2m)² (d.r. > 20:1): yellow solid, 30.2 mg, 56% yield, (PE: EA = 10:1). 1H NMR (400 MHz, Chloroform-*d*) δ 7.70 (d, J = 8.1 Hz, 2H), 7.59 (d, J = 7.0 Hz, 2H), 7.51 (dd, J = 8.1, 7.0 Hz, 2H), 5.13 (s, 2H), 3.83 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.2, 139.8, 136.8, 31.6, 28.2, 124.4, 121.0, 52.8, 51.8.



Methyl 1,2-dihydroacenaphthylene-1-carboxylate (2m'): colorless liquid, 7.6 mg, 18% yield, (PE: EA = 30:1). 1H NMR (400 MHz, Chloroform-*d*) δ 7.67 (dd, J = 6.7, 2.2 Hz, 1H), 7.62 (d, J = 8.3 Hz, 1H), 7.51 – 7.44 (m, 3H), 7.32 (d, J = 6.9 Hz, 1H), 4.59 (dd, J = 8.8, 4.1 Hz, 1H), 3.87 (dd, J = 17.4, 4.1 Hz, 1H), 3.79 (s, 3H), 3.62 (dd, J

= 17.4, 8.8 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.5, 143.4, 142.3, 138.3, 131.7, 128.2, 128.0, 124.1, 122.8, 120.5, 119.7, 52.5, 48.5, 34.3.

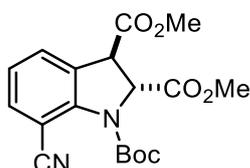
HRMS (ESI) calculated m/z $[\text{M}+\text{Na}]^+$ for $\text{C}_{14}\text{H}_{12}\text{NaO}_2$ 235.0735, found 235.0730.



Methyl 10-phenyl-9,10-dihydrophenanthrene-9-carboxylate (2o') (d.r. > 20:1):

colorless liquid, 20.1 mg, 32% yield, (PE: EA = 15:1). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.83 (ddd, $J = 7.9, 4.3, 1.3$ Hz, 2H), 7.35 (qd, $J = 7.5, 1.4$ Hz, 2H), 7.24 – 7.19 (m, 2H), 7.17 (d, $J = 2.2$ Hz, 1H), 7.17 – 7.13 (m, 2H), 7.13 – 7.07 (m, 2H), 7.06 – 7.02 (m, 2H), 4.69 (d, $J = 5.0$ Hz, 1H), 4.11 (d, $J = 5.0$ Hz, 1H), 3.55 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.2, 142.0, 137.0, 134.2, 133.8, 132.0, 129.7, 129.5, 128.6, 128.5, 128.3, 128.0, 127.9, 126.9, 124.0, 52.8, 52.3, 47.1.

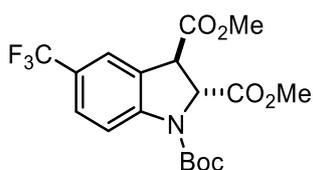
HRMS (ESI) calculated m/z $[\text{M}+\text{Na}]^+$ for $\text{C}_{22}\text{H}_{18}\text{NaO}_2$ 337.1204, found 337.1199.



1-(tert-Butyl) 2,3-dimethyl 7-cyanoindoline-1,2,3-tricarboxylate (4a) (d.r. > 20:1):

yellow liquid, 39.6 mg, 55% yield, (PE: EA = 10:1). ^1H NMR (600 MHz, Chloroform-*d*) δ 7.58 – 7.56 (m, 2H), 7.11 (t, $J = 7.7$ Hz, 1H), 5.51 (d, $J = 2.8$ Hz, 1H), 4.19 (d, $J = 2.8$ Hz, 1H), 3.79 – 3.77 (m, 6H), 1.59 (d, $J = 1.7$ Hz, 9H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.6, 169.6, 151.5, 143.2, 134.6, 130.0, 129.9, 124.1, 117.2, 102.1, 84.3, 64.5, 53.4, 53.2, 49.5, 28.2.

HRMS (ESI) calculated m/z $[\text{M}+\text{Na}]^+$ for $\text{C}_{18}\text{H}_{20}\text{N}_2\text{NaO}_6$ 383.1219, found 383.1213.

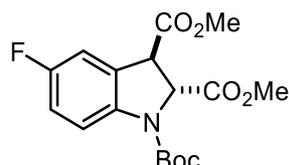


1-(tert-Butyl) 2,3-dimethyl 5-(trifluoromethyl) indoline-1,2,3-tricarboxylate (4b)

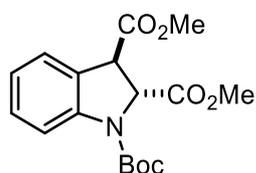
(d.r. > 20:1): yellow liquid, 67.7 mg, 84% yield, (PE: EA = 10:1). ^1H NMR (400 MHz,

Chloroform-*d*) δ 8.01 (s, 1H), 7.60 – 7.52 (m, 2H), 5.48 – 5.34 (m, 1H), 4.20 (d, $J = 4.0$ Hz, 1H), 3.82 (s, 3H), 3.78 (s, 3H), 1.54 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.8, 169.8, 151.2, 145.3, 127.3, 127.3, 125.0 (q, $J = 32.3$ Hz), 124.3 (q, $J = 272.7$ Hz), 122.6, 114.9, 82.7, 63.0, 53.4, 52.8, 49.4, 28.2. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -61.8.

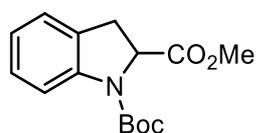
HRMS (ESI) calculated m/z $[\text{M}+\text{Na}]^+$ for $\text{C}_{18}\text{H}_{20}\text{F}_3\text{NNaO}_6$ 426.1140, found 426.1136.



1-(*tert*-Butyl) 2,3-dimethyl 5-fluoroindoline-1,2,3-tricarboxylate (4c)⁴ (d.r. > 20:1): yellow liquid, 55.1 mg, 78% yield, (PE: EA = 10:1). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.87 (s, 1H), 7.06 (dd, $J = 8.1, 2.8$ Hz, 1H), 6.97 (td, $J = 8.9, 2.8$ Hz, 1H), 5.36 (s, 1H), 4.15 (d, $J = 4.1$ Hz, 1H), 3.81 (s, 3H), 3.77 (s, 3H), 1.51 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.1, 169.9, 158.8 (d, $J = 242.4$ Hz), 151.3, 138.5, 126.6, 116.0 (d, $J = 23.2$ Hz), 115.7 (d, $J = 7.1$ Hz), 112.6 (d, $J = 25.3$ Hz), 82.0, 62.9, 53.3, 52.7, 49.6, 28.2. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -120.6.

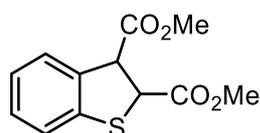


1-(*tert*-Butyl) 2,3-dimethyl indoline-1,2,3-tricarboxylate (4d)⁵ (d.r. > 20:1): colorless liquid, 20.8 mg, 31% yield, (PE: EA = 10:1). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.92 (s, 1H), 7.36 – 7.31 (m, 1H), 7.30 – 7.24 (m, 1H), 6.98 (td, $J = 7.5, 1.1$ Hz, 1H), 5.35 (s, 1H), 4.17 (d, $J = 4.1$ Hz, 1H), 3.79 (s, 3H), 3.76 (s, 3H), 1.52 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.6, 129.6, 125.2, 122.9, 115.1, 62.8, 53.2, 52.7, 29.8, 28.4.



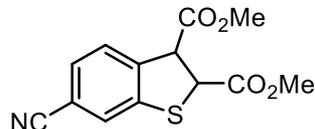
1-(*tert*-butyl) 2-methyl indoline-1,2-dicarboxylate (4d')⁶: colorless liquid, 15.0 mg,

27% yield, (PE: EA = 20:1). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.89 (s, 1H), 7.19 (t, $J = 7.8$ Hz, 1H), 7.10 (dd, $J = 7.5, 1.3$ Hz, 1H), 6.94 (td, $J = 7.5, 1.1$ Hz, 1H), 4.87 (s, 1H), 3.75 (s, 3H), 3.50 (dd, $J = 16.6, 11.4$ Hz, 1H), 3.11 (dd, $J = 16.6, 4.7$ Hz, 1H), 1.50 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.6, 128.0, 124.5, 122.7, 114.8, 81.4, 60.5, 52.4, 32.8, 29.8, 28.4.



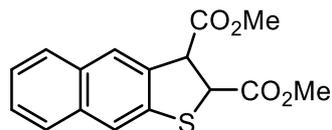
Dimethyl 2,3-dihydrobenzo[b]thiophene-2,3-dicarboxylate (4e) (d.r. > 20:1): colorless liquid, 21.2 mg, 42% yield, (PE: EA = 10:1). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.39 (d, $J = 7.5$ Hz, 1H), 7.20 (t, $J = 7.5$ Hz, 1H), 7.17 – 7.13 (m, 1H), 7.09 (td, $J = 7.5, 1.4$ Hz, 1H), 4.99 (d, $J = 6.1$ Hz, 1H), 4.81 (d, $J = 6.1$ Hz, 1H), 3.80 (s, 3H), 3.78 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.4, 171.0, 139.3, 135.3, 129.1, 126.0, 125.1, 121.9, 54.7, 53.2, 53.0, 50.2.

HRMS (ESI) calculated m/z $[\text{M}+\text{Na}]^+$ for $\text{C}_{12}\text{H}_{12}\text{NaO}_4\text{S}$ 275.0354, found 275.0351.



Dimethyl 6-cyano-2,3-dihydrobenzo[b]thiophene-2,3-dicarboxylate (4f) (d.r. > 20:1): yellow liquid, 17.2 mg, 31% yield, (PE: EA = 10:1). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.68 (s, 1H), 7.50 – 7.46 (d, $J = 8.1$ Hz, 1H), 7.24 (d, $J = 8.1$ Hz, 1H), 5.04 (d, $J = 5.5$ Hz, 1H), 4.86 (d, $J = 5.5$ Hz, 1H), 3.83 (s, 3H), 3.80 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.7, 169.8, 146.5, 136.6, 132.8, 129.5, 122.4, 118.8, 108.7, 54.1, 53.5, 50.3, 45.8.

HRMS (ESI) calculated m/z $[\text{M}+\text{Na}]^+$ for $\text{C}_{13}\text{H}_{11}\text{NNaO}_4\text{S}$ 300.0306, found 300.0301.

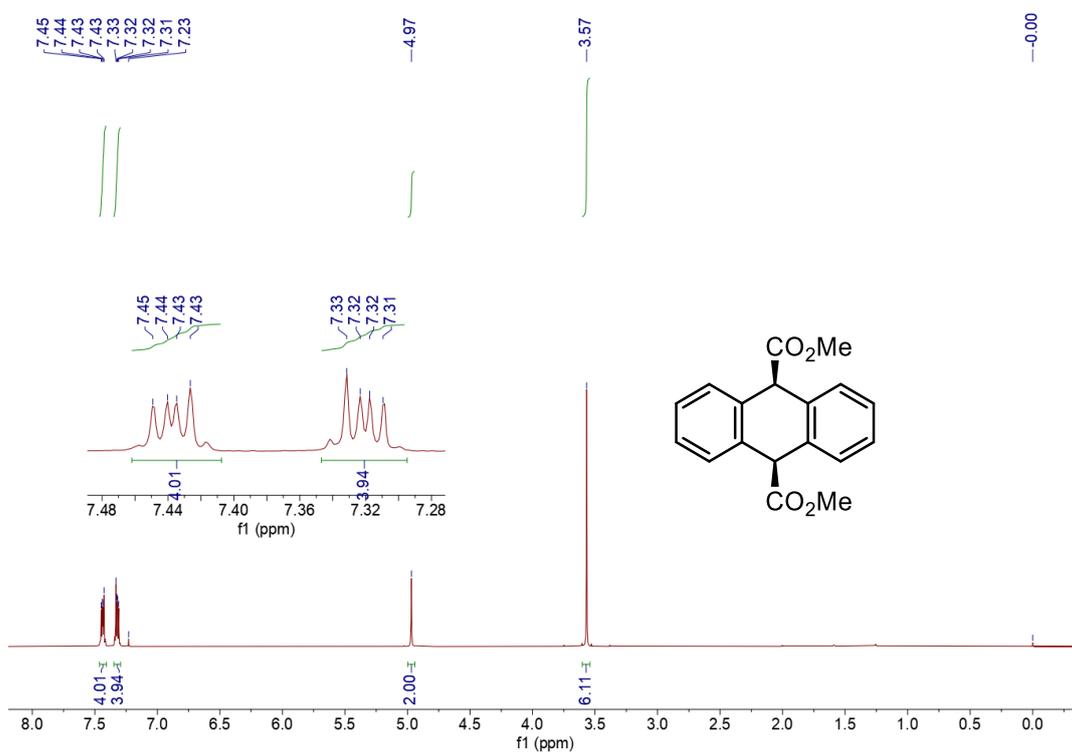


Dimethyl 2,3-dihydronaphtho[2,3-b] thiophene-2,3-dicarboxylate (4g) (d.r. > 20:1): colorless liquid, 25.4 mg, 42% yield, (PE: EA = 15:1). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.42 (m, 2H), 7.34 – 7.32 (m, 2H), 7.28 (d, $J = 5.2$ Hz, 1H),

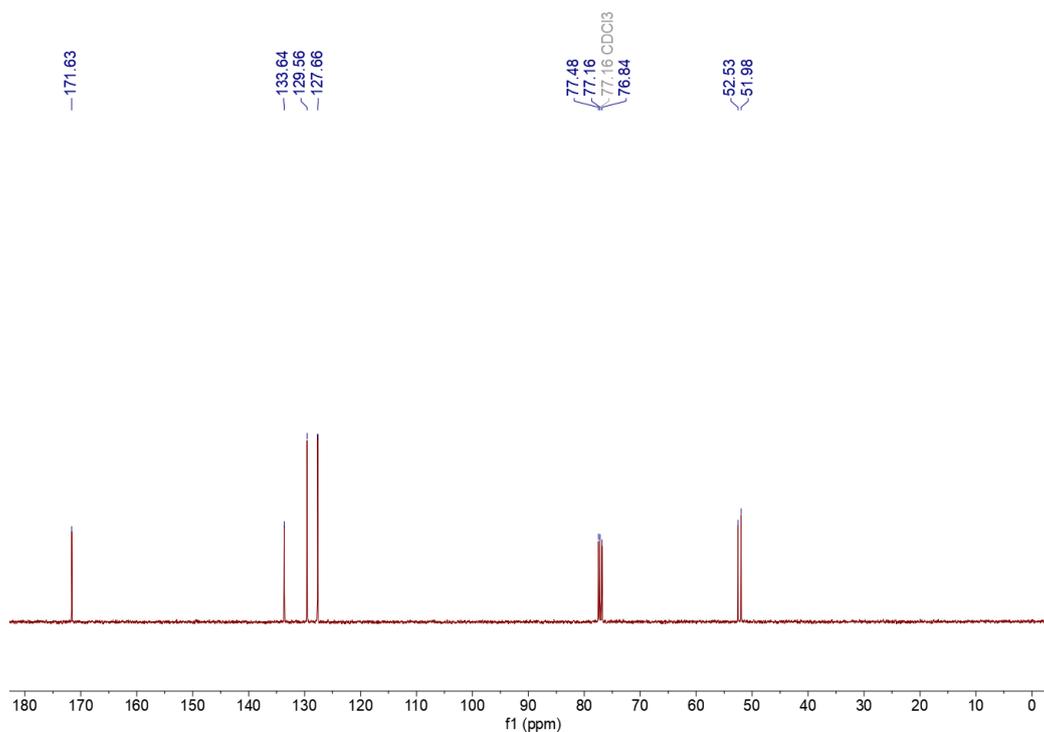
7.06 (d, $J = 5.2$ Hz, 1H), 5.14 (d, $J = 1.9$ Hz, 1H), 5.05 (d, $J = 1.9$ Hz, 1H), 3.64 (s, 3H), 3.61 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.5, 171.2, 133.3, 133.0, 132.8, 132.5, 129.8, 129.6, 127.9, 127.7, 126.9, 125.1, 52.8, 52.6, 48.2, 47.4.

HRMS (ESI) calculated m/z $[\text{M}+\text{Na}]^+$ for $\text{C}_{16}\text{H}_{14}\text{NaO}_4\text{S}$ 325.0510, found 325.0505.

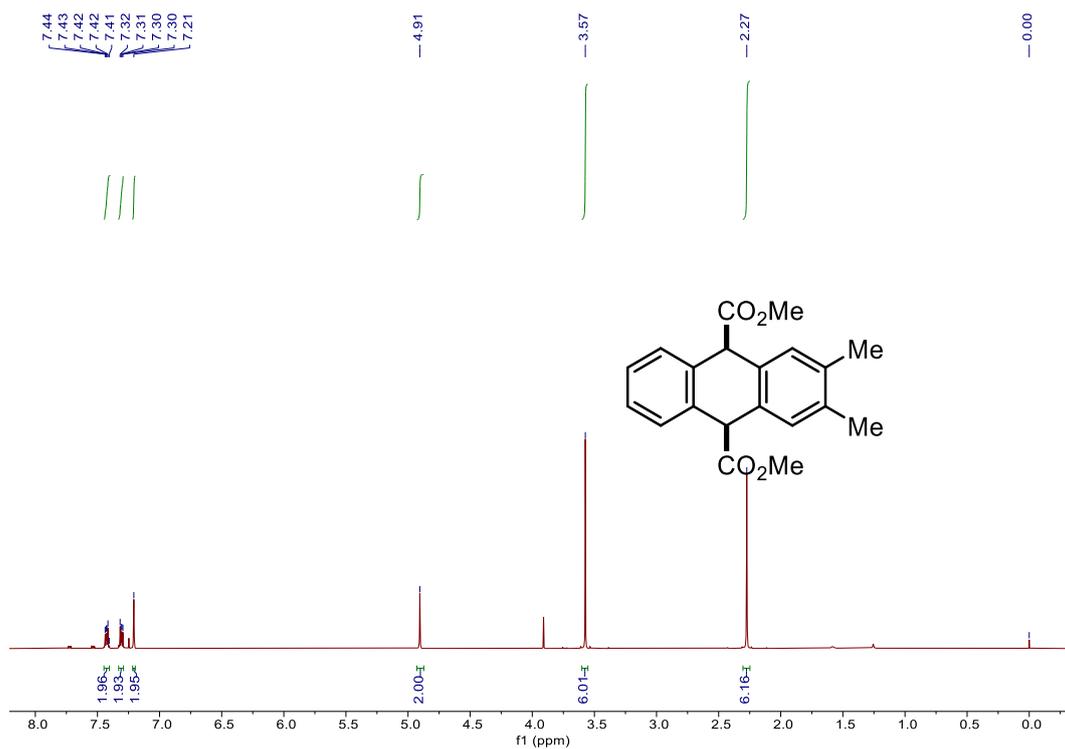
7. NMR spectra of products



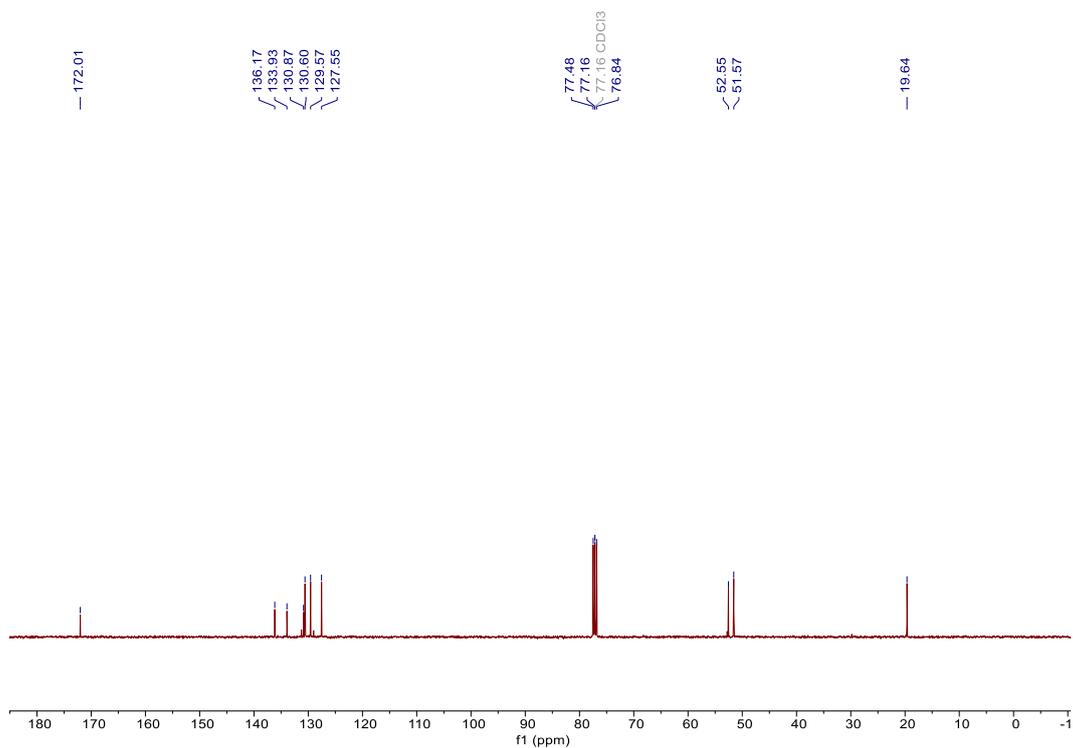
¹H NMR (400 MHz, Chloroform-*d*) spectrum of **2a**



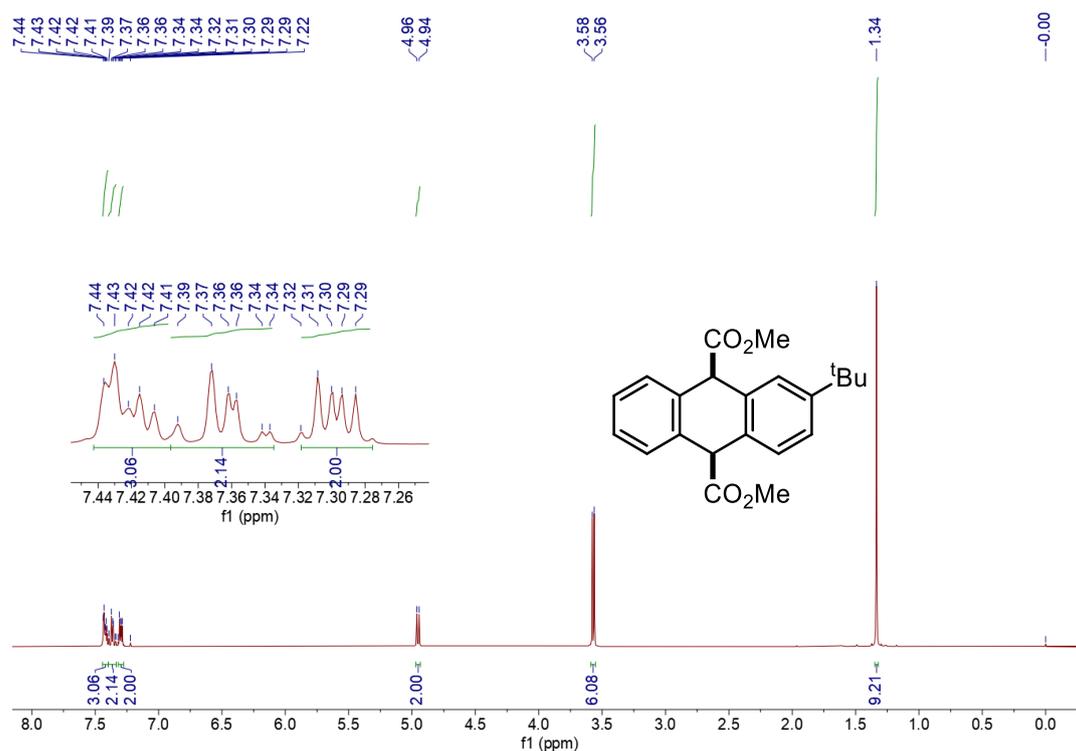
¹³C{¹H} NMR (101 MHz, Chloroform-*d*) spectrum of **2a**



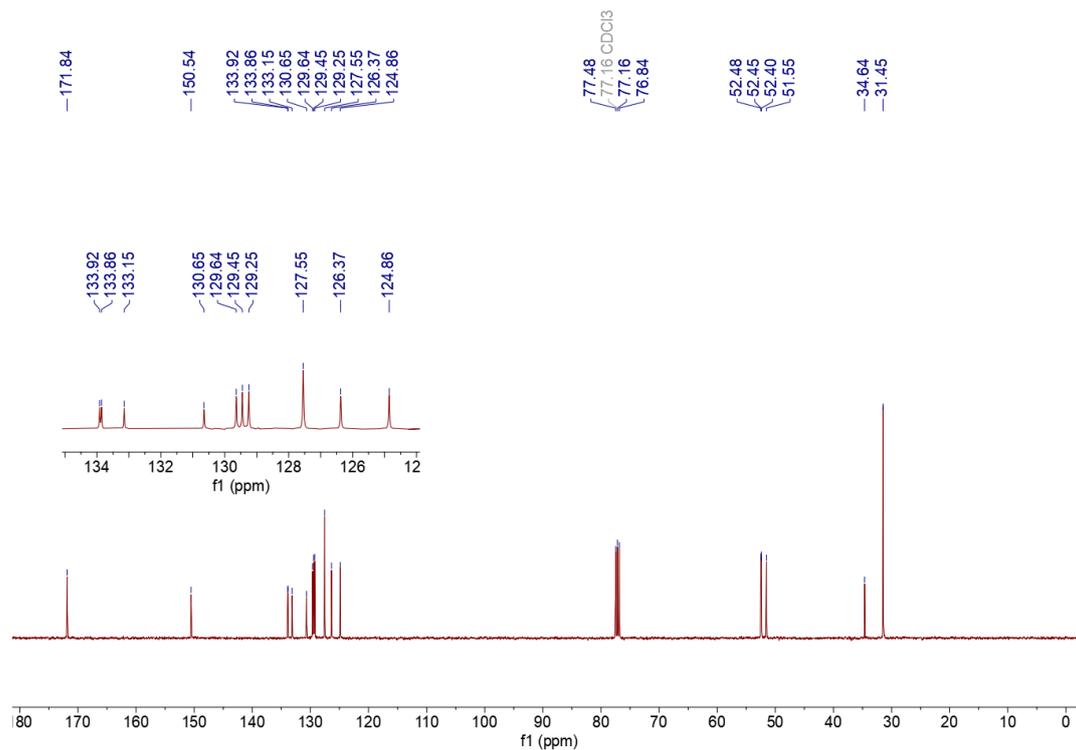
^1H NMR (400 MHz, Chloroform-*d*) spectrum of **2b**



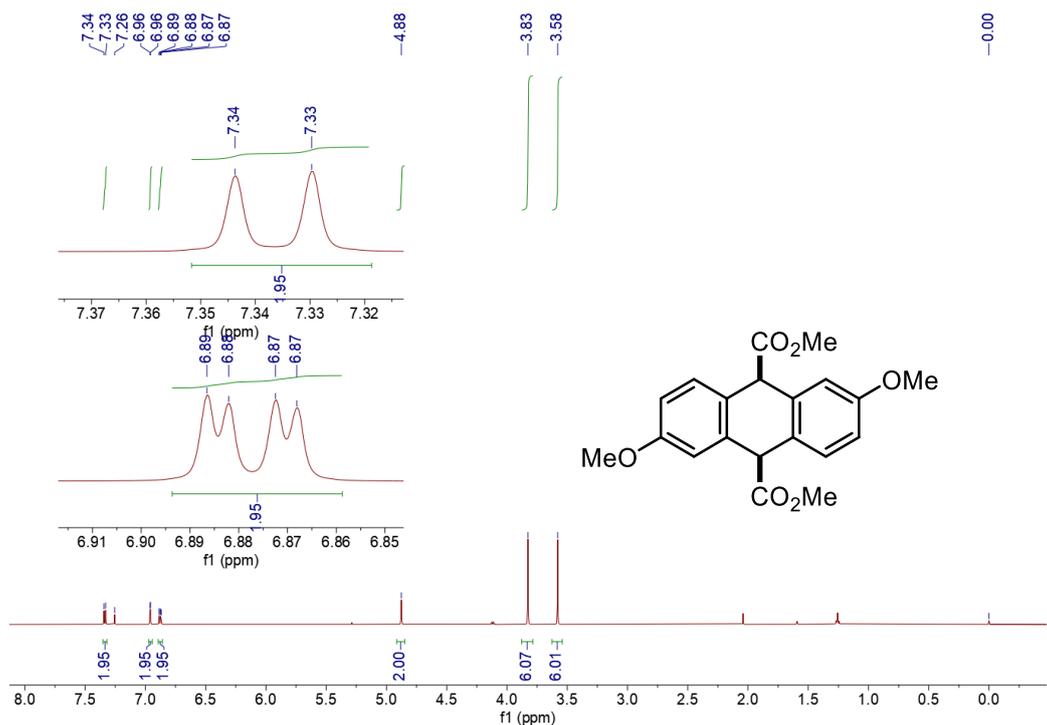
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*) spectrum of **2b**



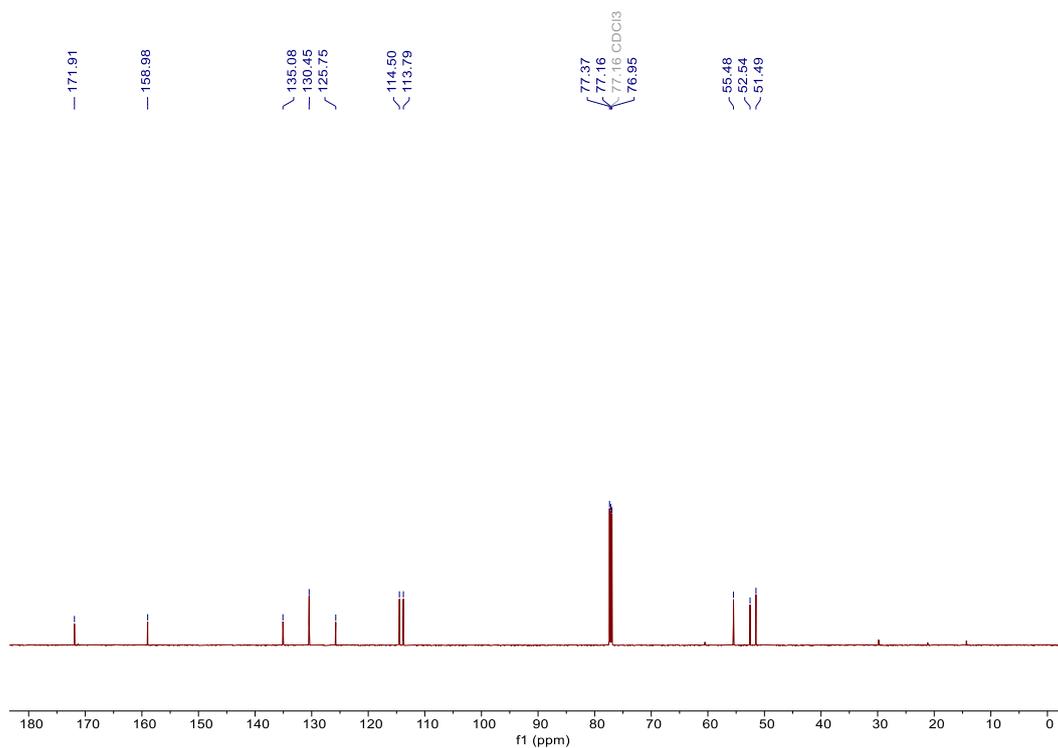
¹H NMR (400 MHz, Chloroform-*d*) spectrum of **2c**



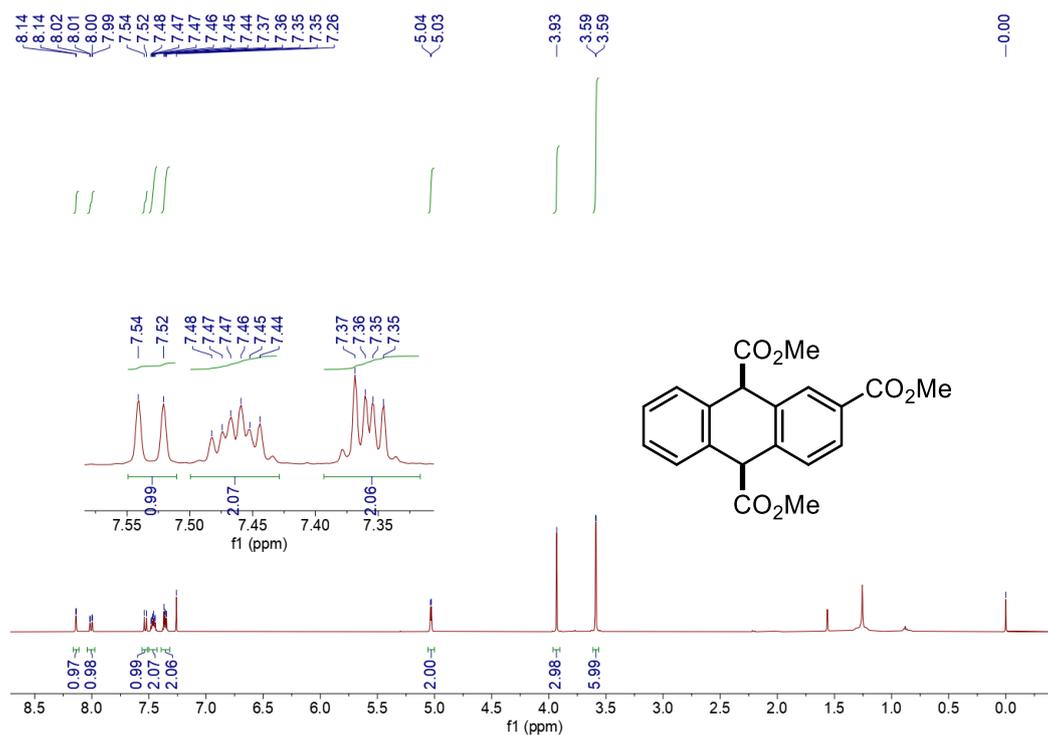
¹³C{¹H} NMR (101 MHz, Chloroform-*d*) spectrum of **2c**



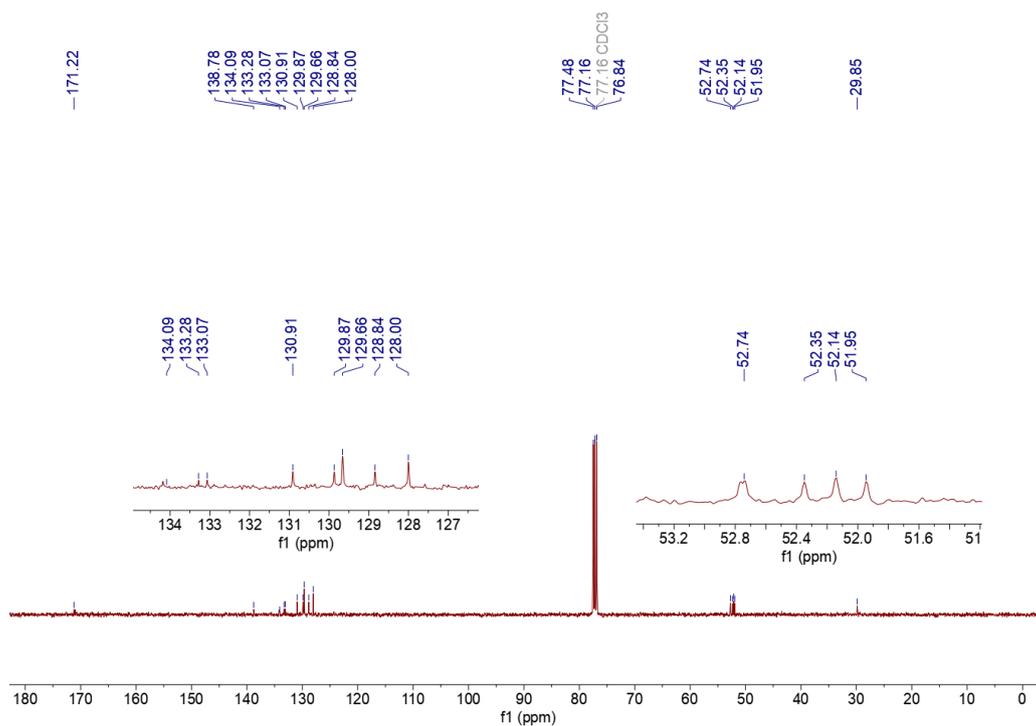
¹H NMR (400 MHz, Chloroform-*d*) spectrum of **2d**



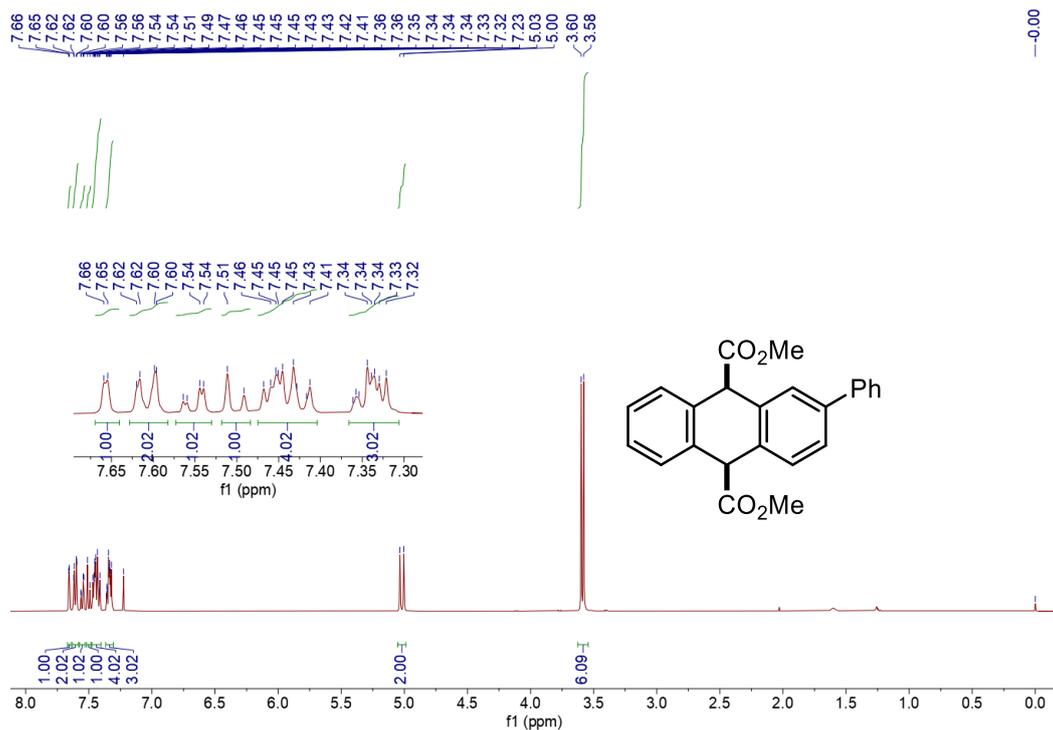
¹³C{¹H} NMR (101 MHz, Chloroform-*d*) spectrum of **2d**



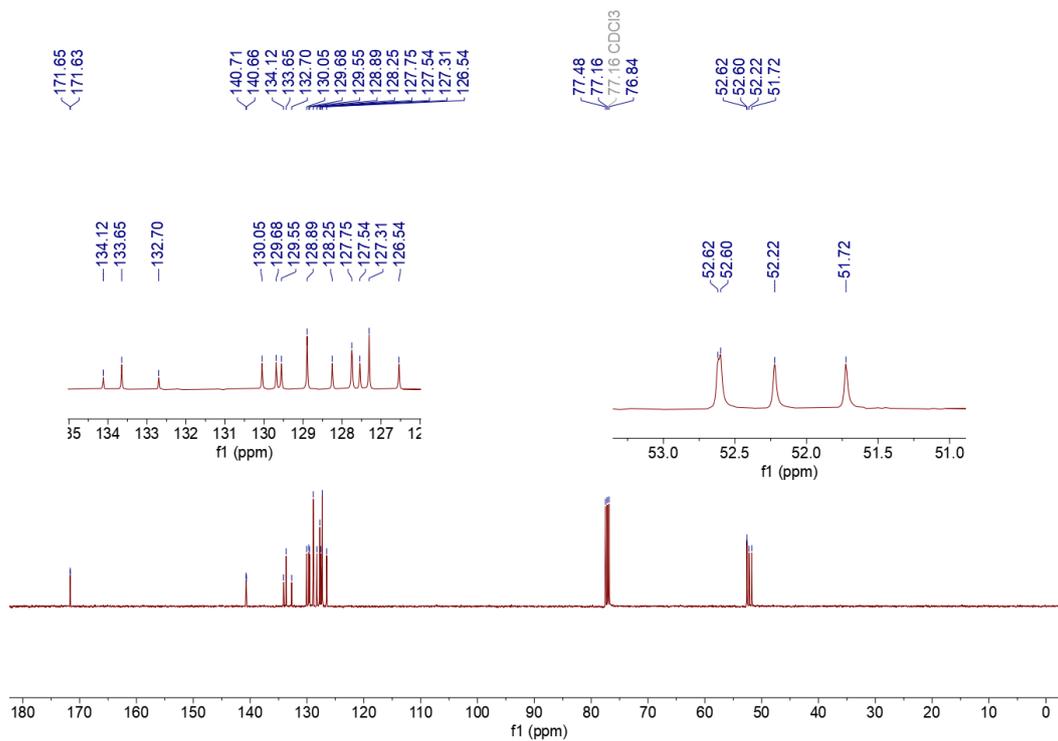
$^1\text{H NMR}$ (400 MHz, Chloroform-*d*) spectrum of **2e**



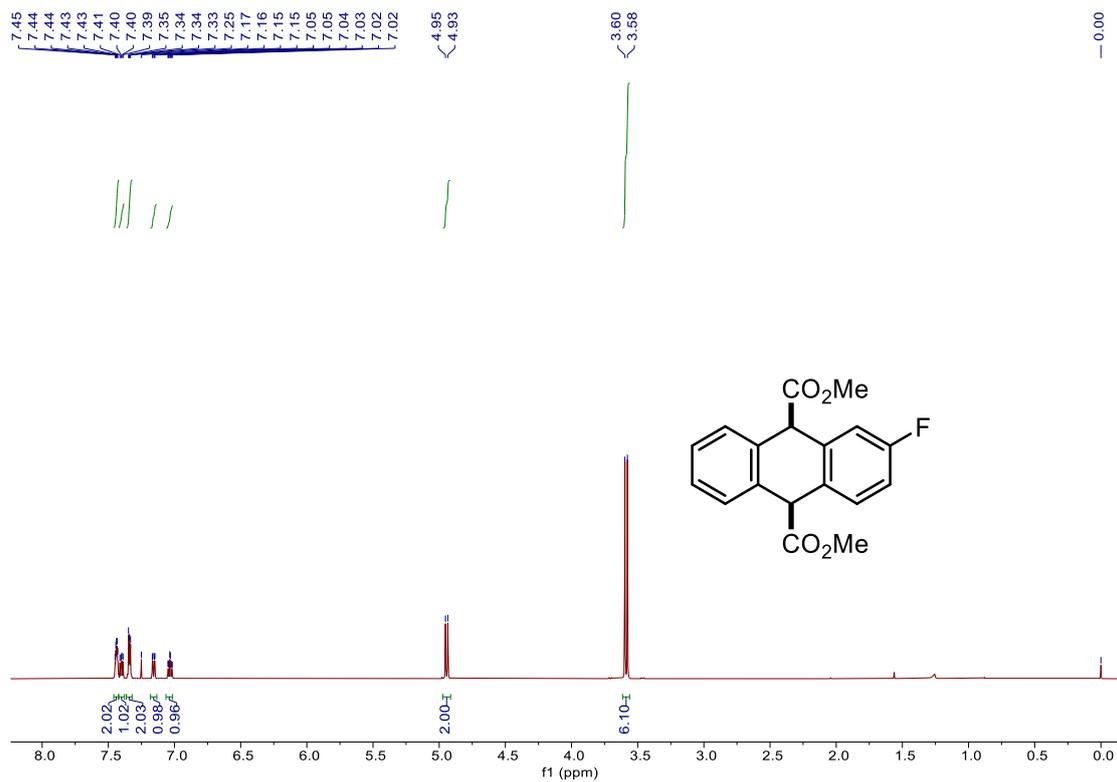
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*) spectrum of **2e**



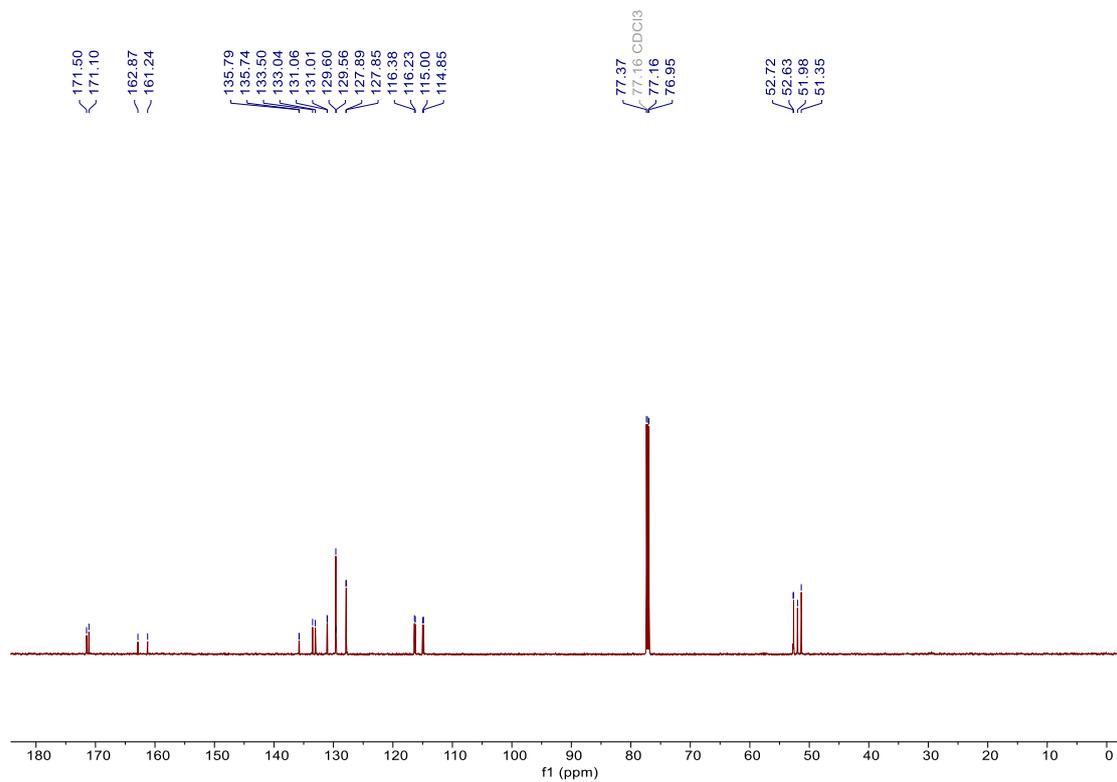
¹H NMR (400 MHz, Chloroform-*d*) spectrum of **2f**



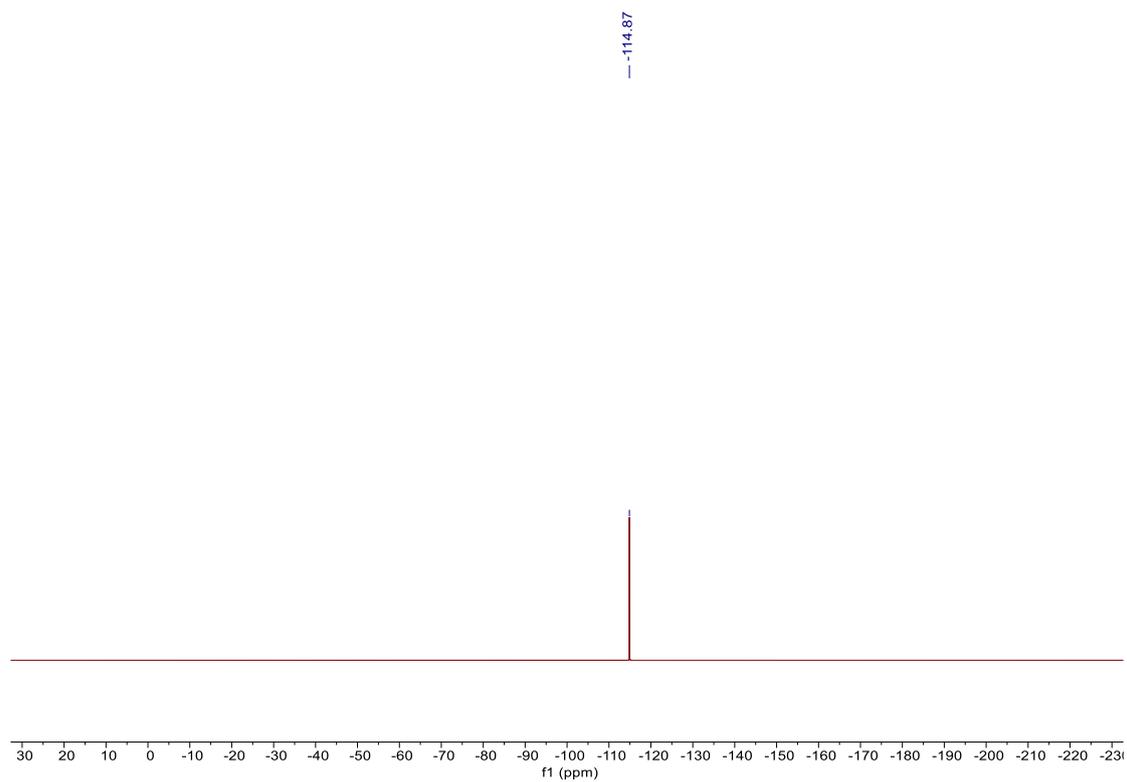
¹³C {¹H} NMR (101 MHz, Chloroform-*d*) spectrum of **2f**



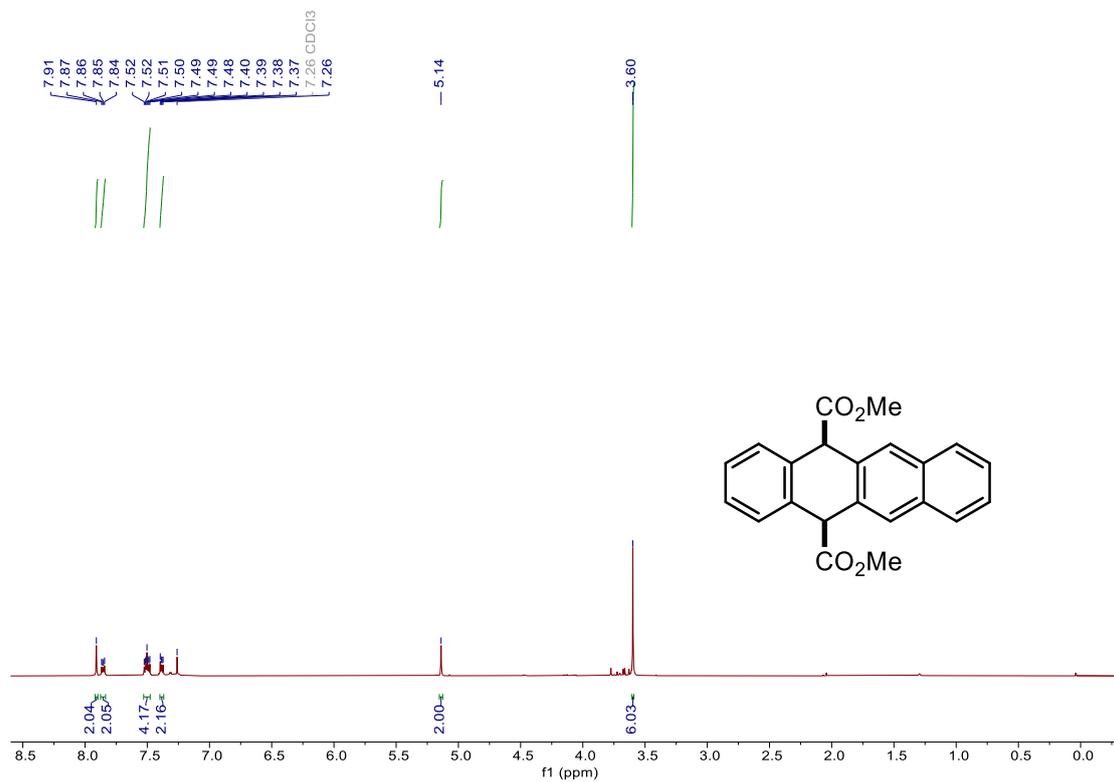
^1H NMR (600 MHz, Chloroform-*d*) spectrum of **2g**



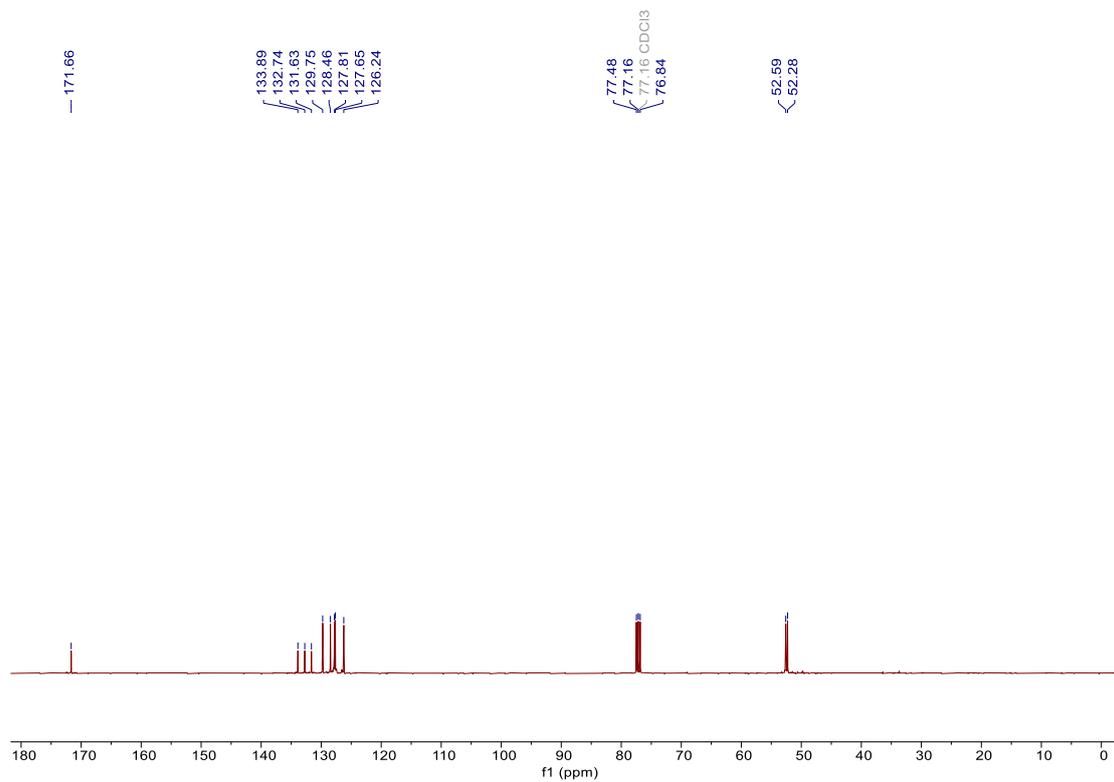
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, Chloroform-*d*) spectrum of **2g**



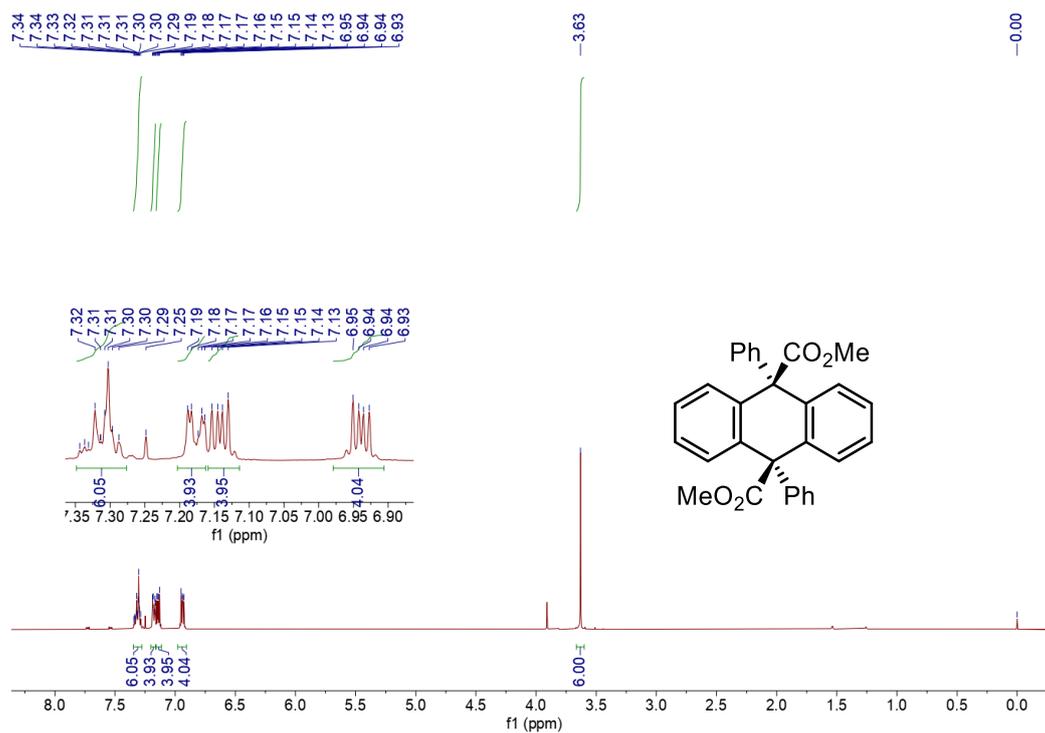
^{19}F NMR (565 MHz, Chloroform-*d*) spectrum of **2g**



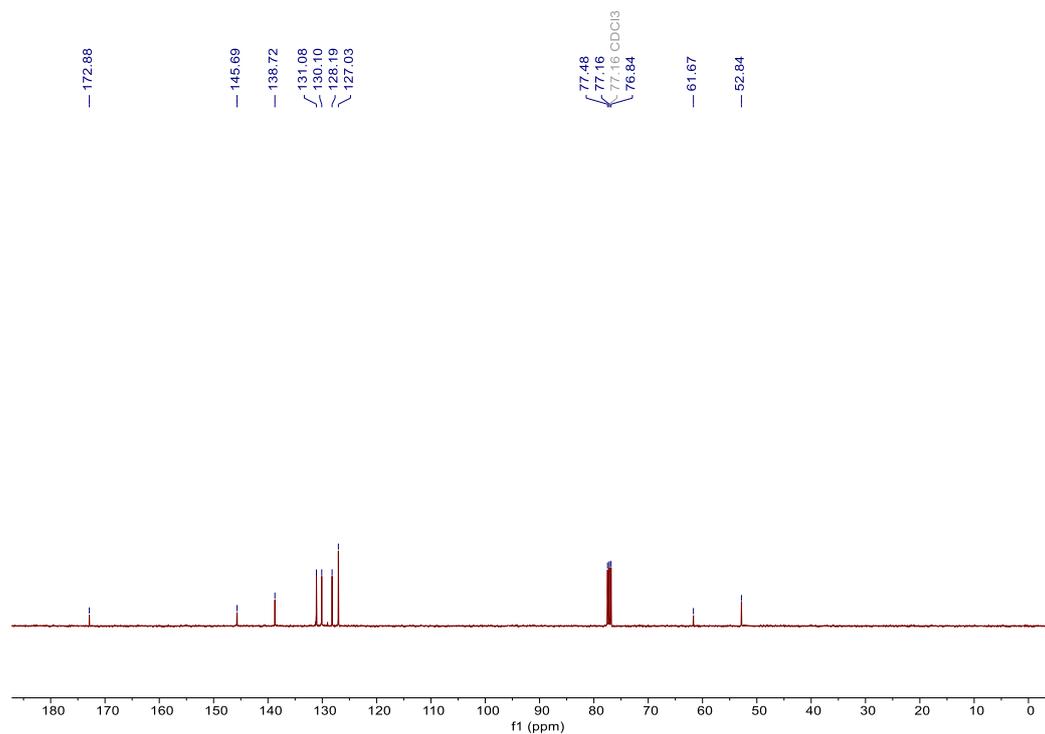
^1H NMR (400 MHz, Chloroform-*d*) spectrum of **2h**



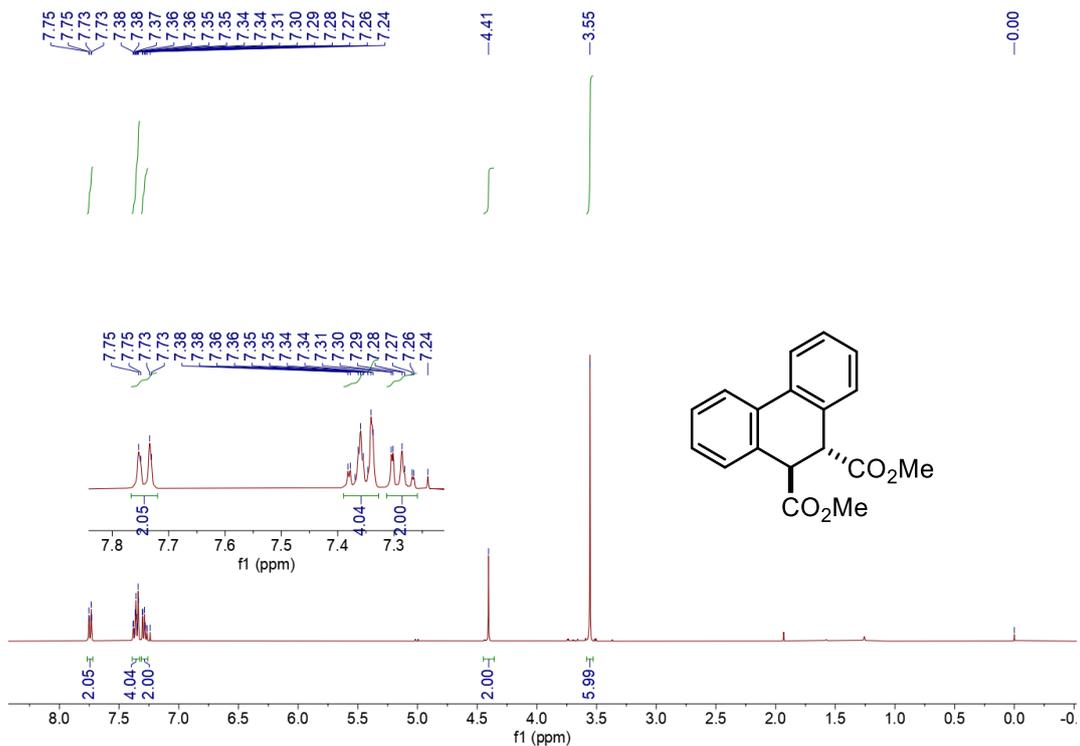
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*) spectrum of **2h**



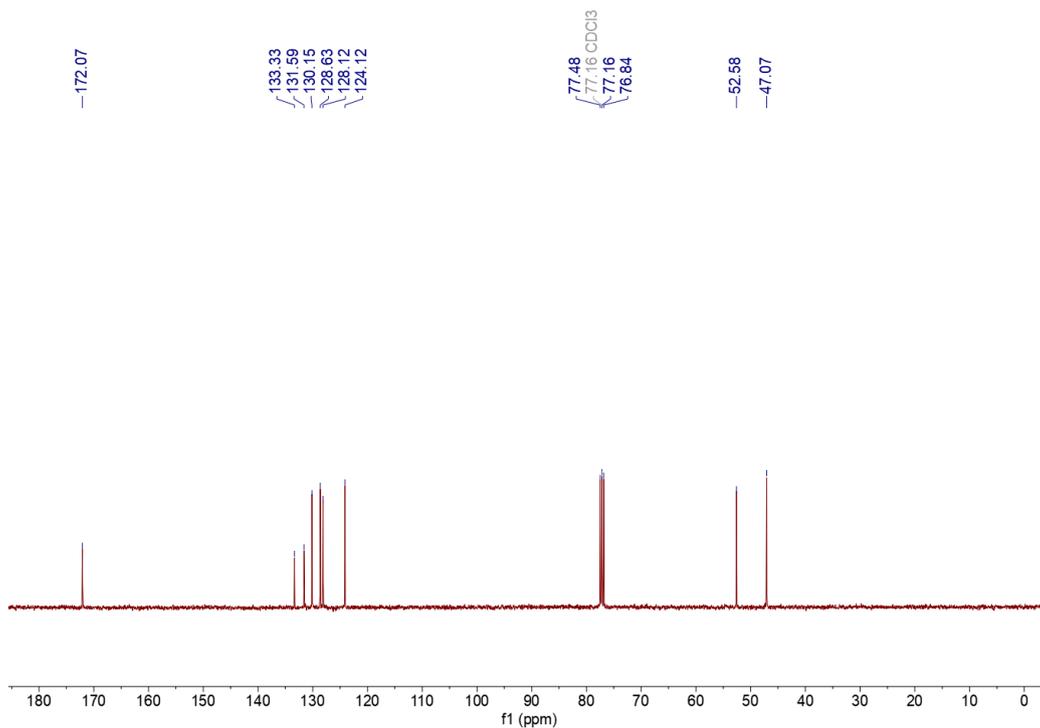
^1H NMR (400 MHz, Chloroform-*d*) spectrum of **2i**



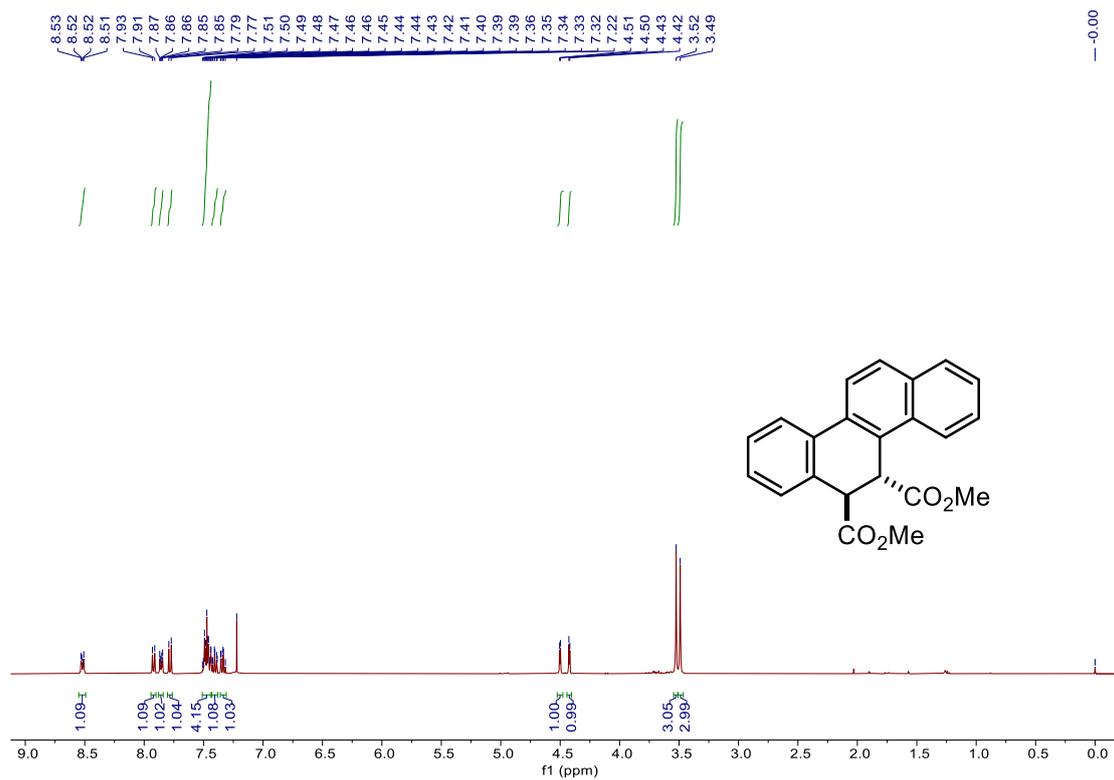
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*) spectrum of **2i**



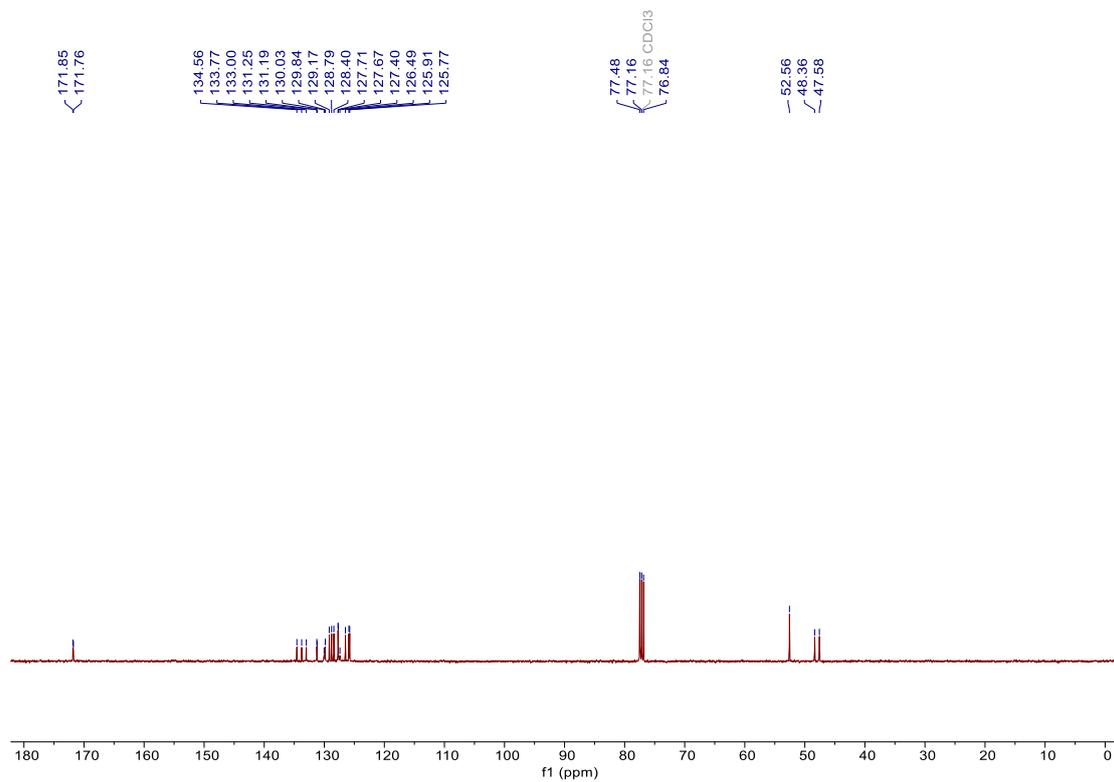
¹H NMR (400 MHz, Chloroform-*d*) spectrum of **2j**



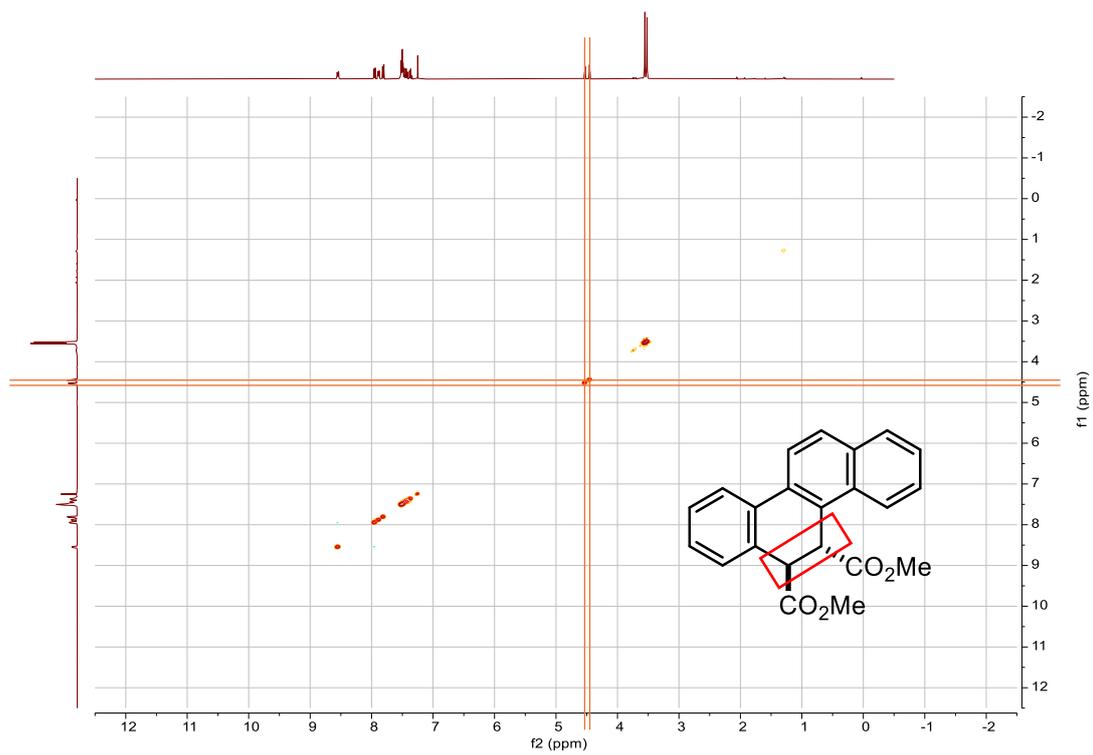
¹³C{¹H} NMR (101 MHz, Chloroform-*d*) spectrum of **2j**



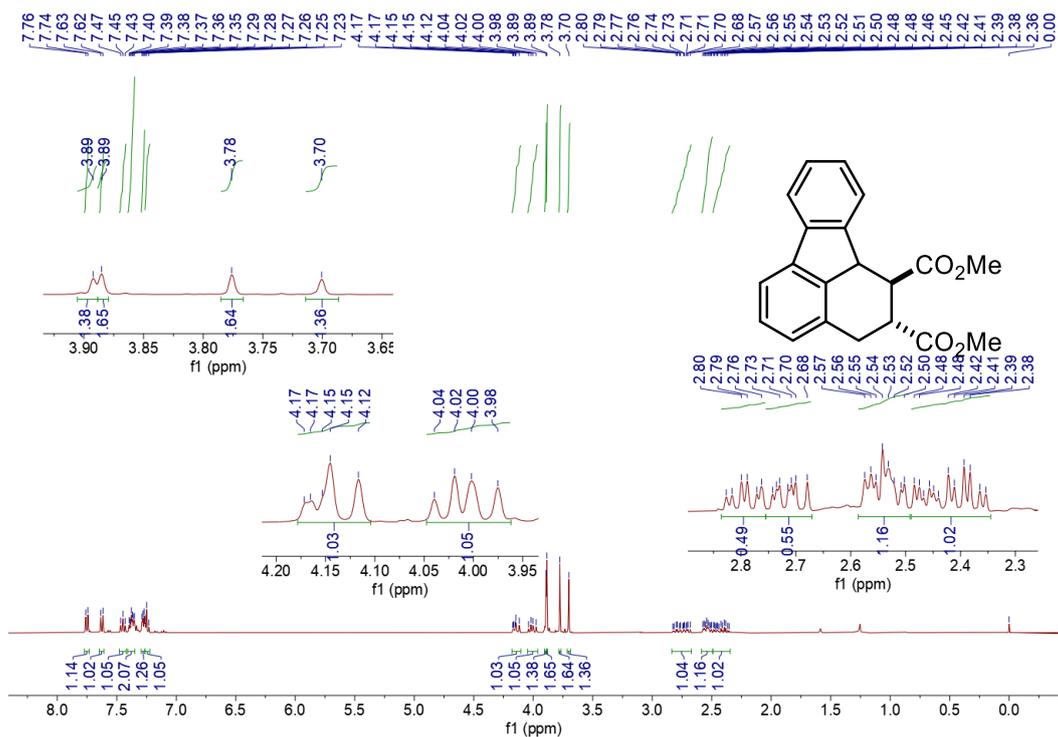
^1H NMR (400 MHz, Chloroform-*d*) spectrum of **2k**



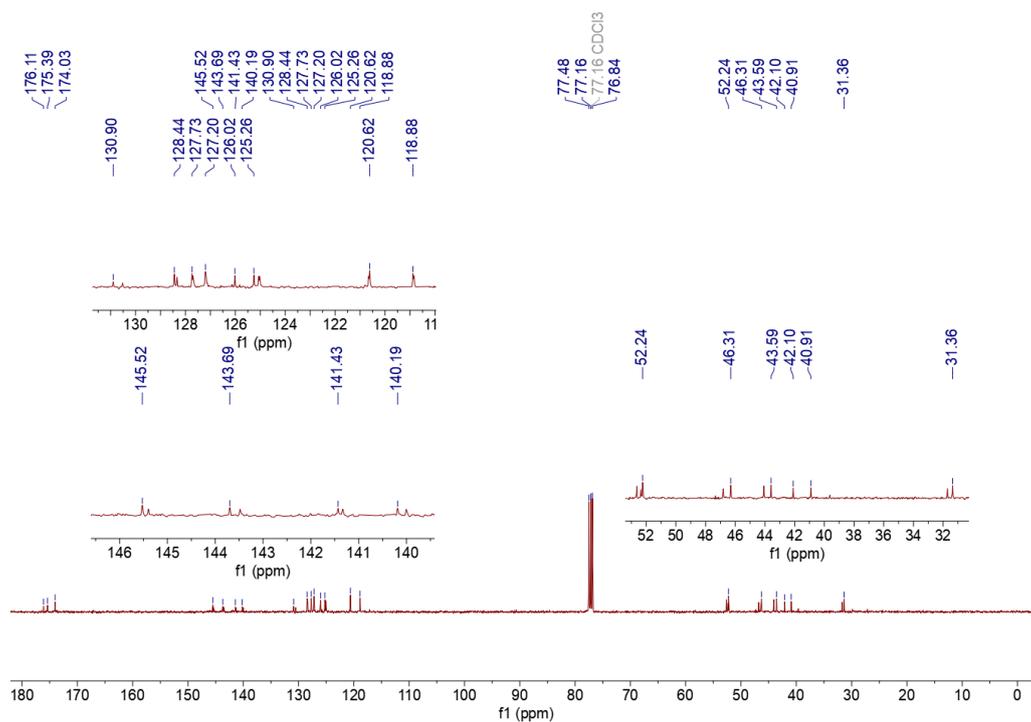
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*) spectrum of **2k**



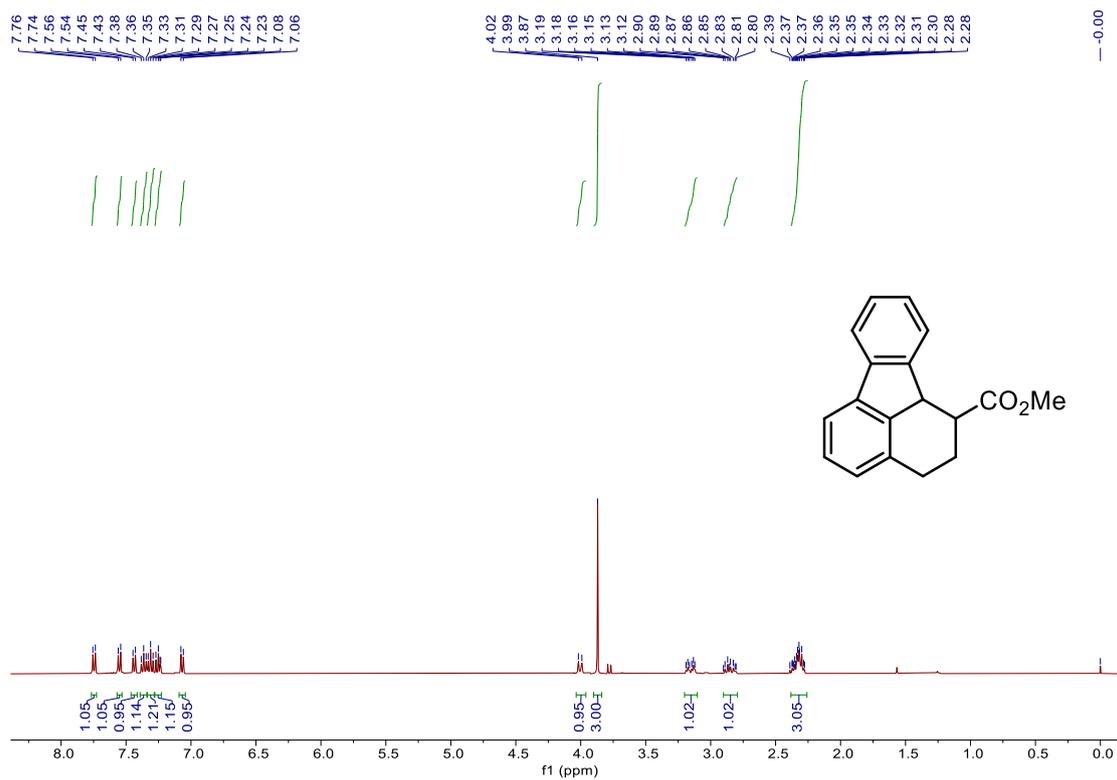
2D NOE spectrum of **2k**



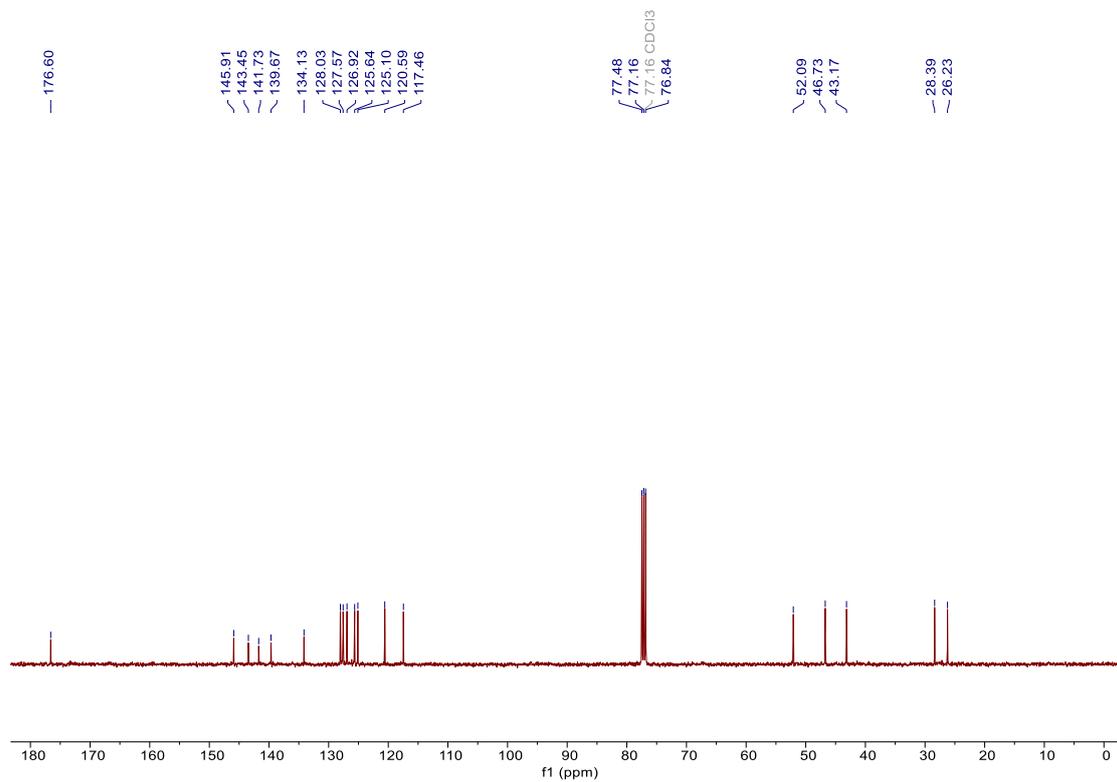
¹H NMR (400 MHz, Chloroform-*d*) spectrum of **21**



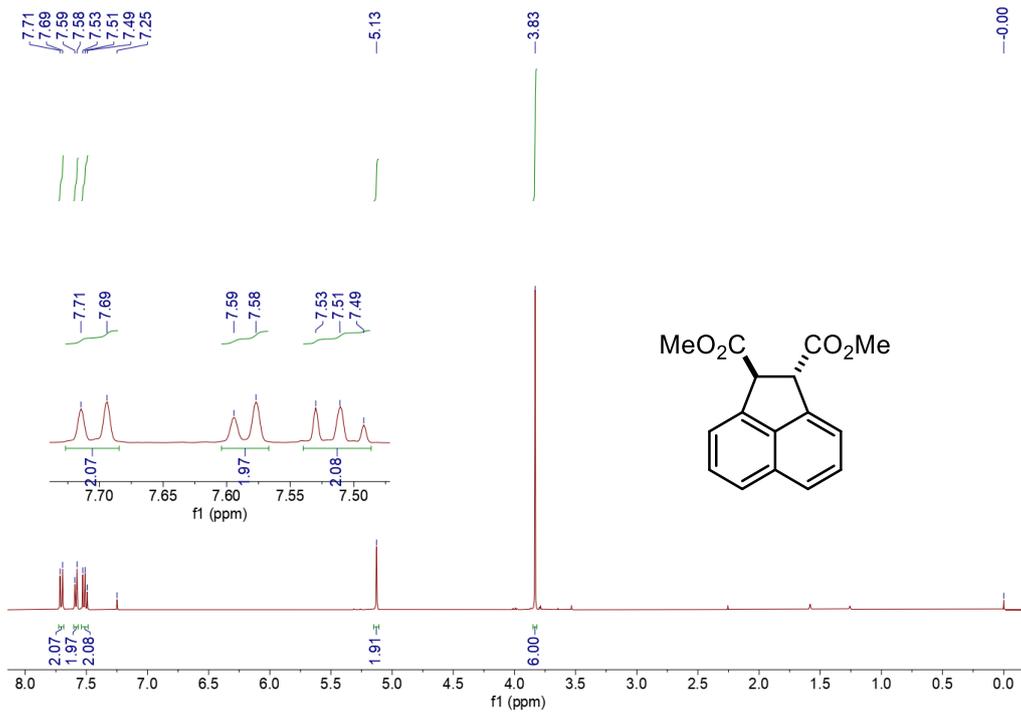
¹³C{¹H} NMR (101 MHz, Chloroform-*d*) spectrum of **21**



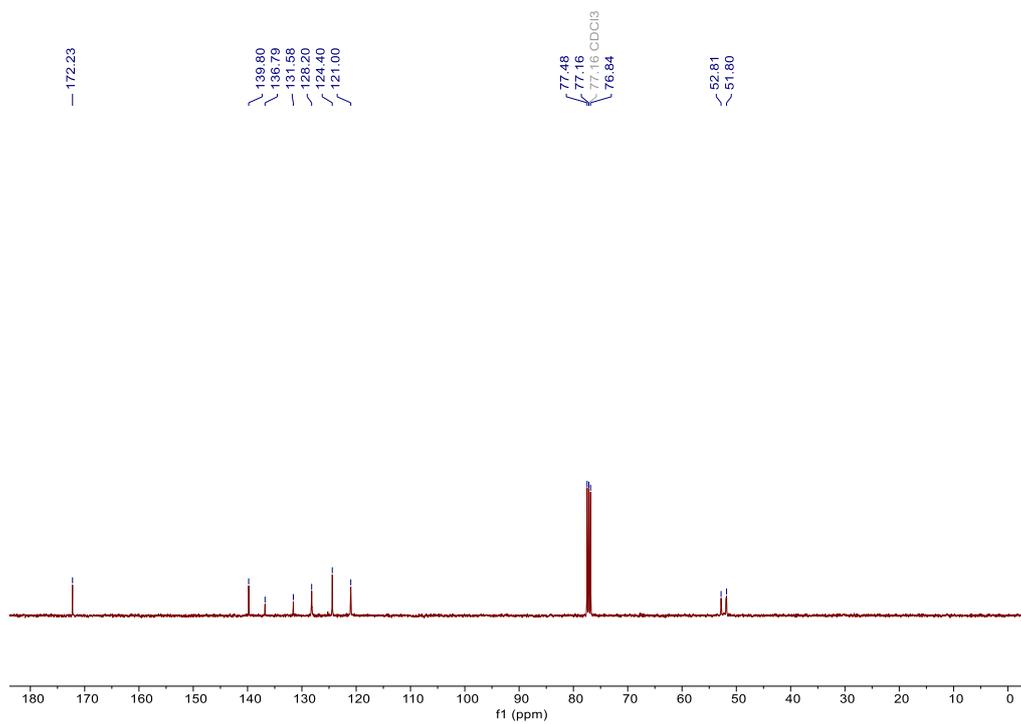
¹H NMR (400 MHz, Chloroform-*d*) spectrum of **21'**



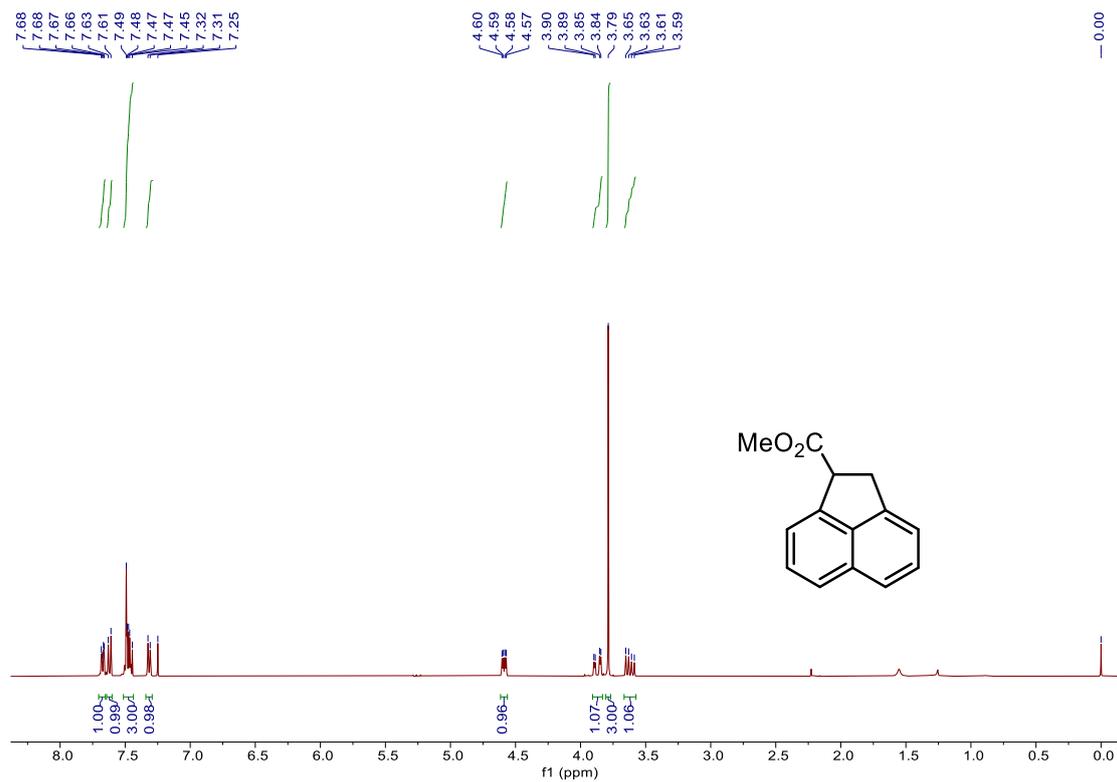
¹³C{¹H} NMR (101 MHz, Chloroform-*d*) spectrum of **21'**



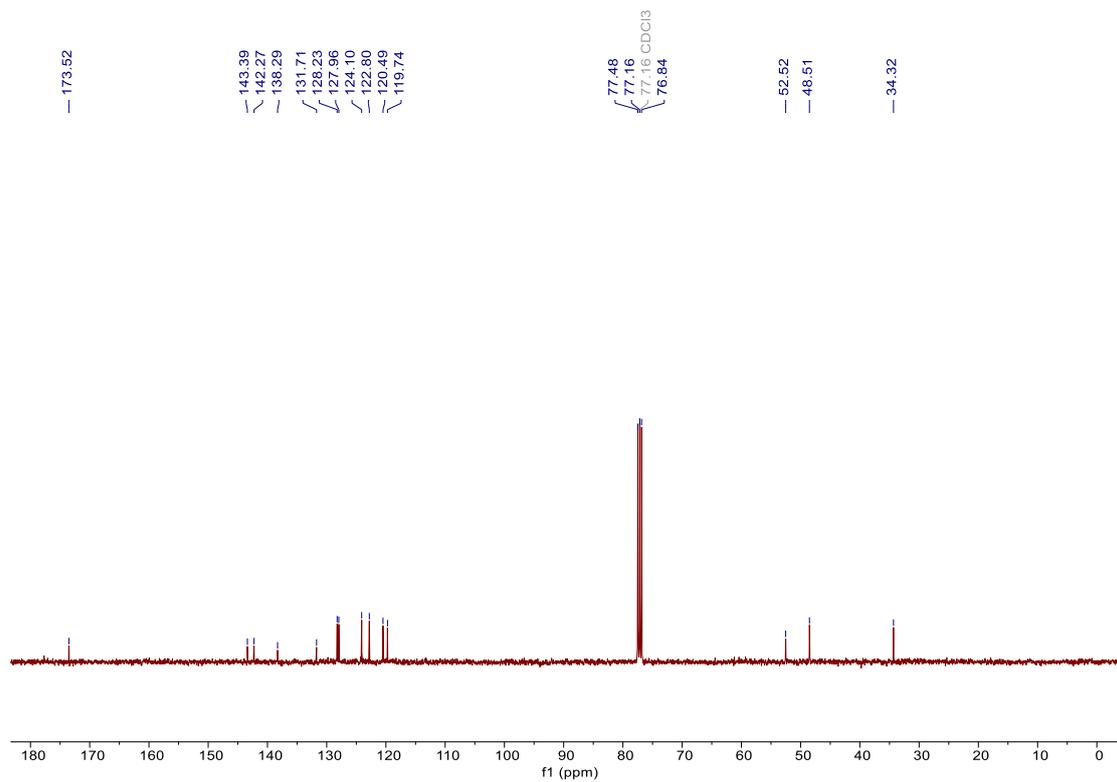
$^1\text{H NMR}$ (400 MHz, Chloroform-*d*) spectrum of **2m**



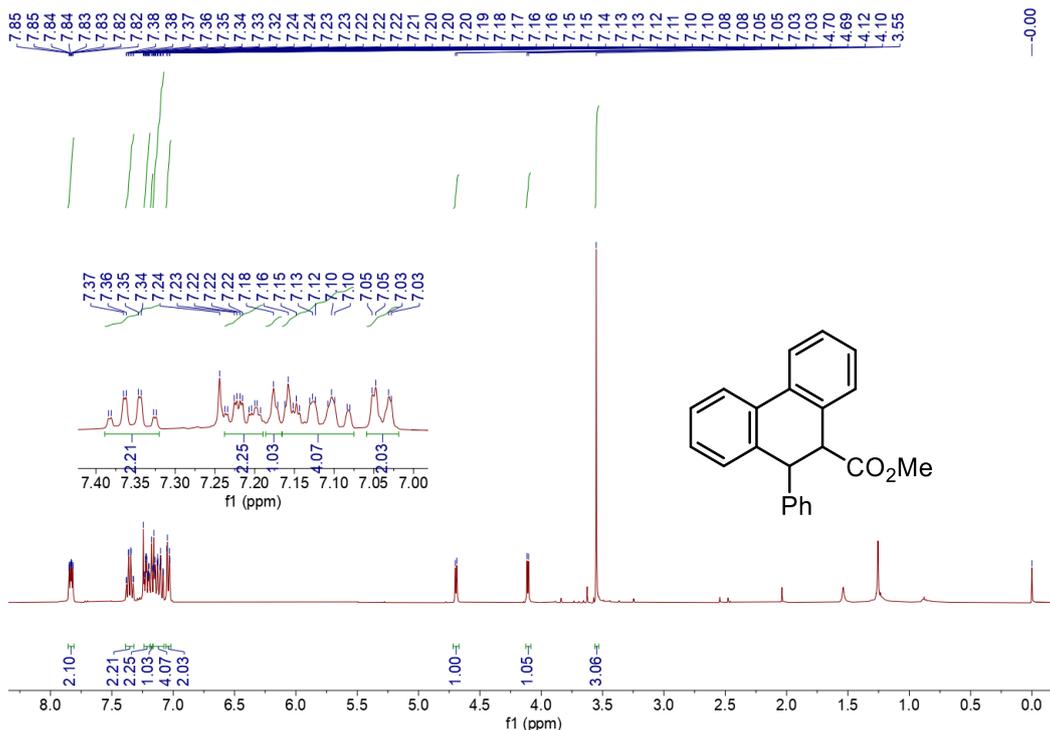
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*) spectrum of **2m**



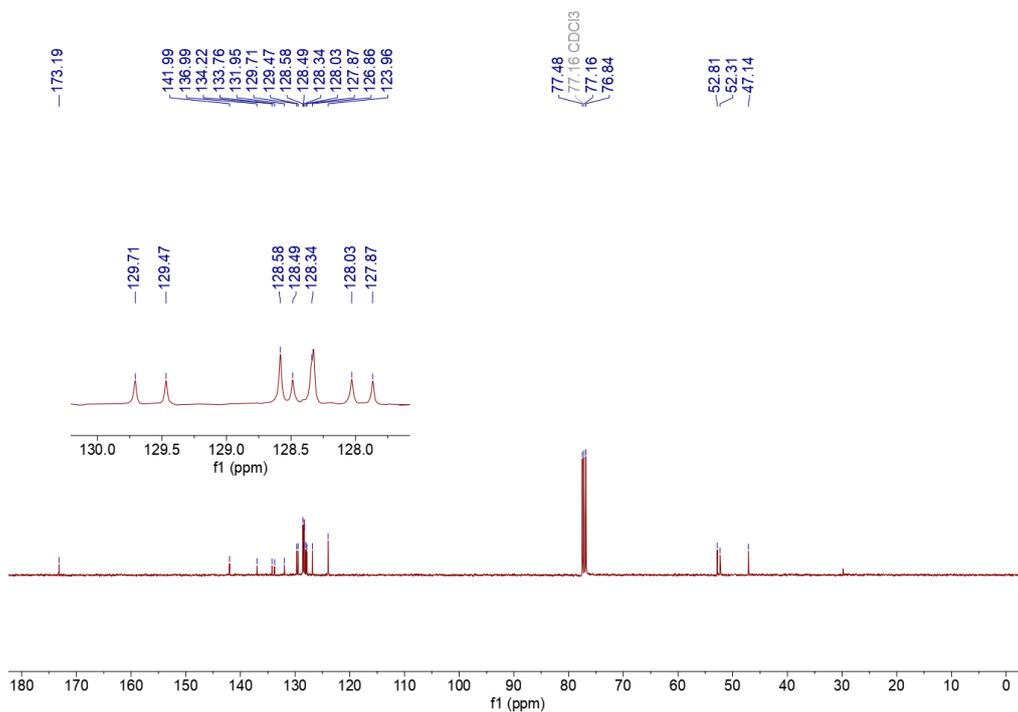
^1H NMR (400 MHz, Chloroform-*d*) spectrum of **2m'**



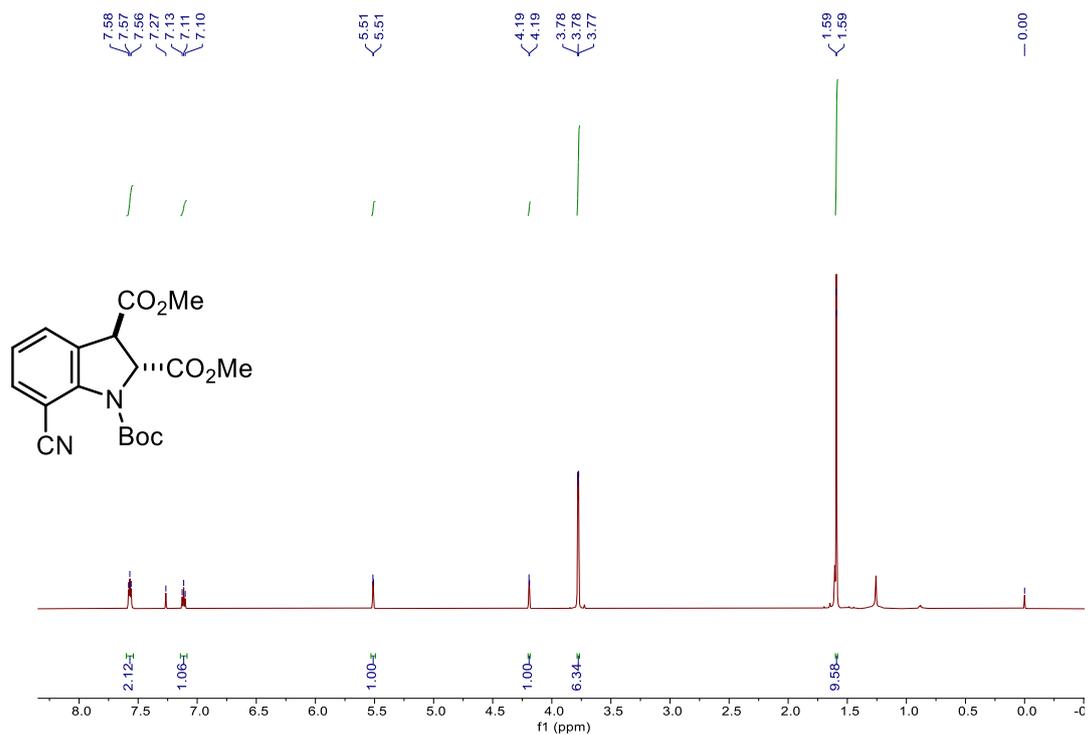
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*) spectrum of **2m'**



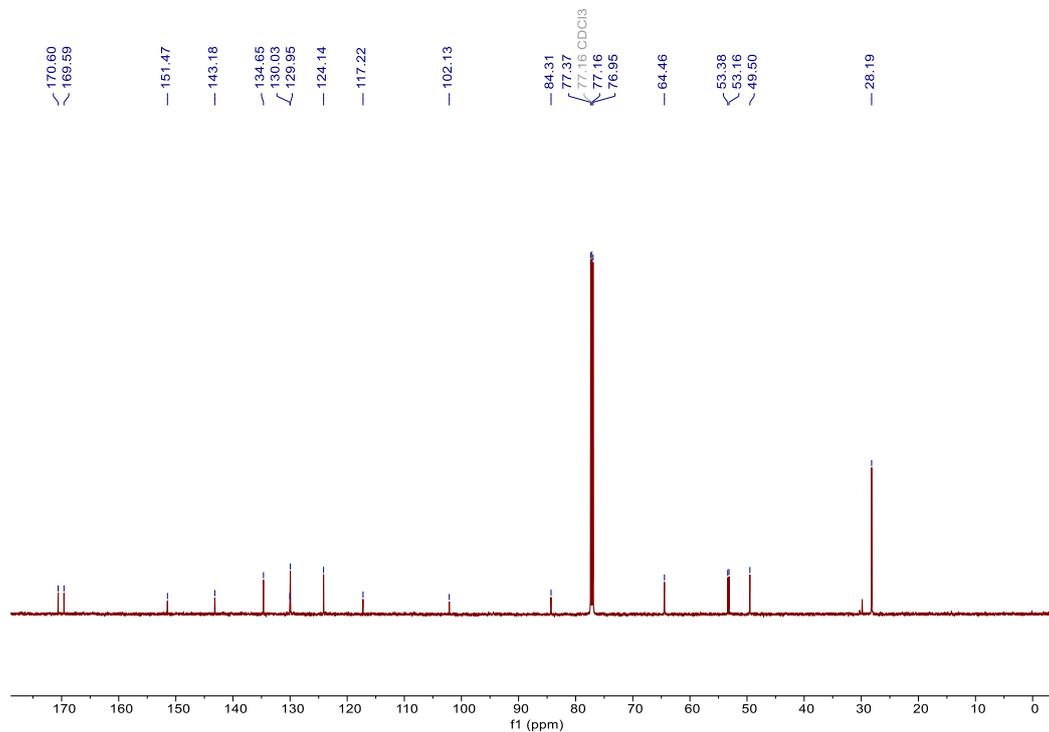
^1H NMR (400 MHz, Chloroform-*d*) spectrum of **2o'**



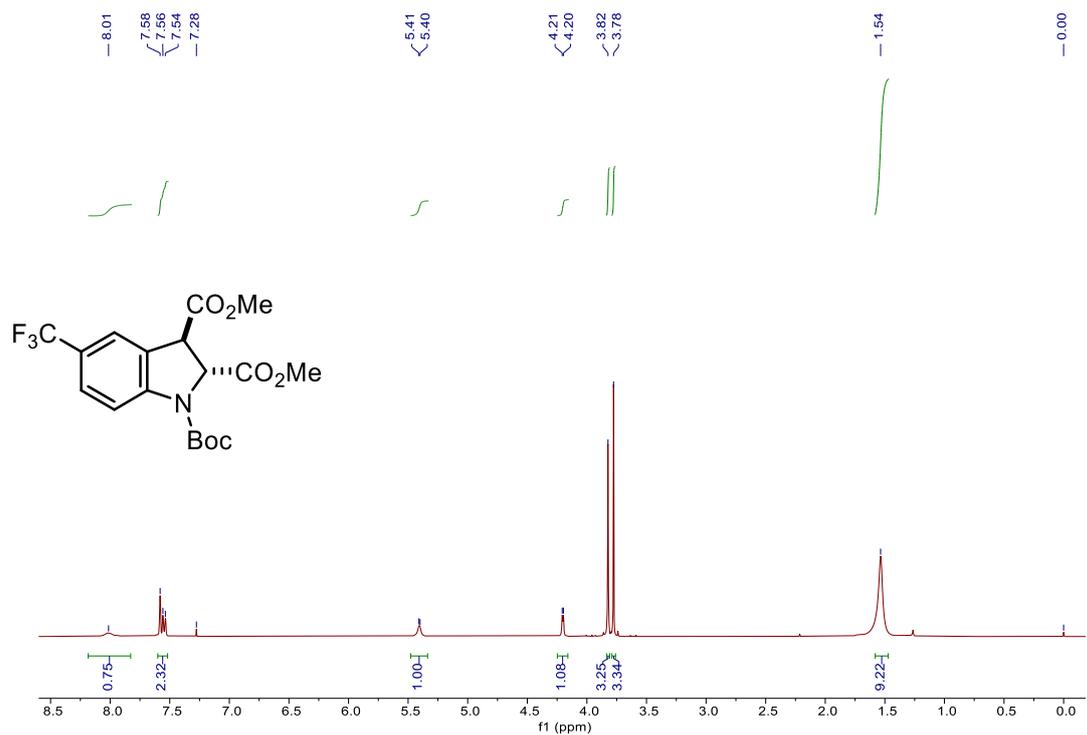
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*) spectrum of **2o'**



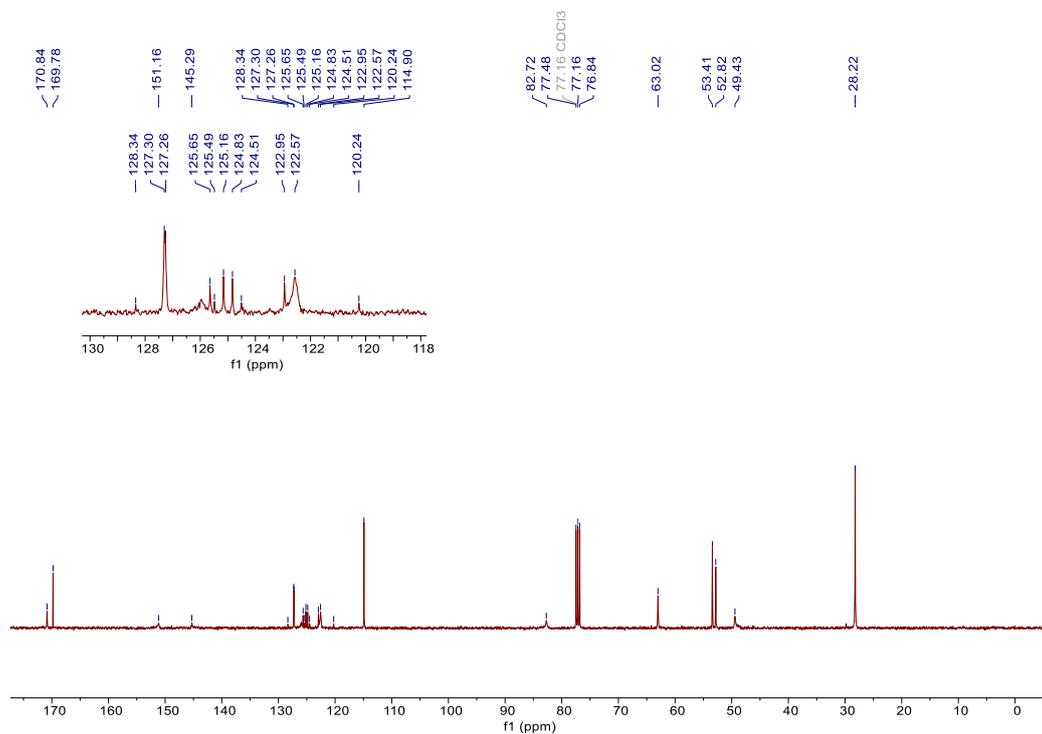
$^1\text{H NMR}$ (400 MHz, Chloroform-*d*) spectrum of **4a**



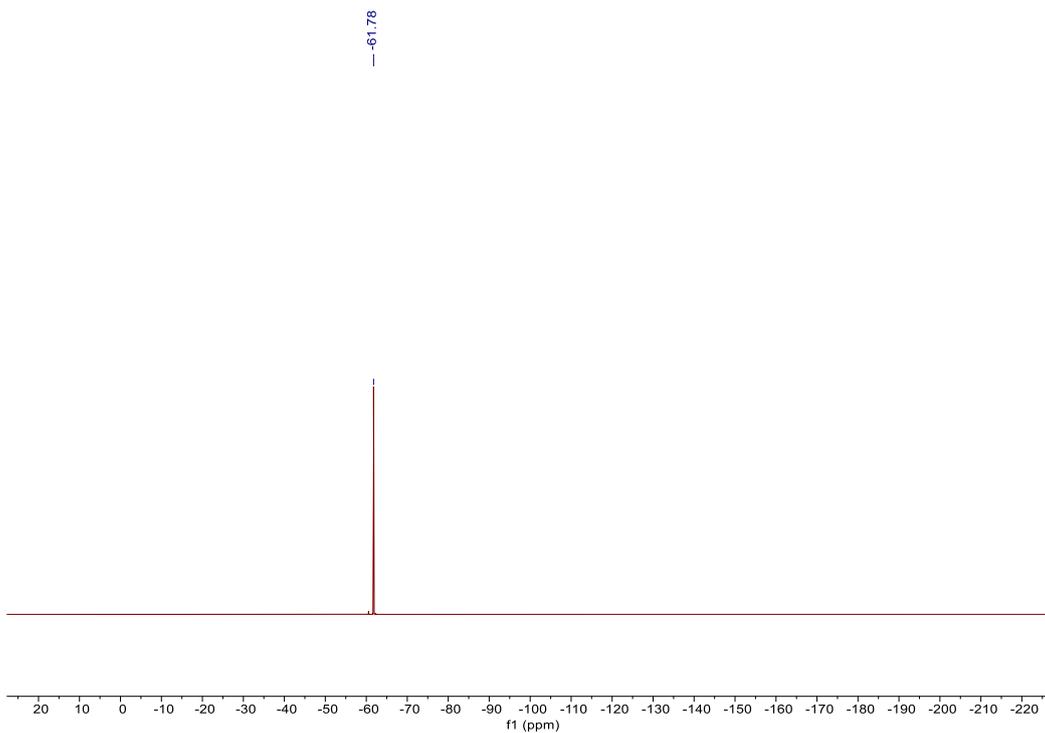
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*) spectrum of **4a**



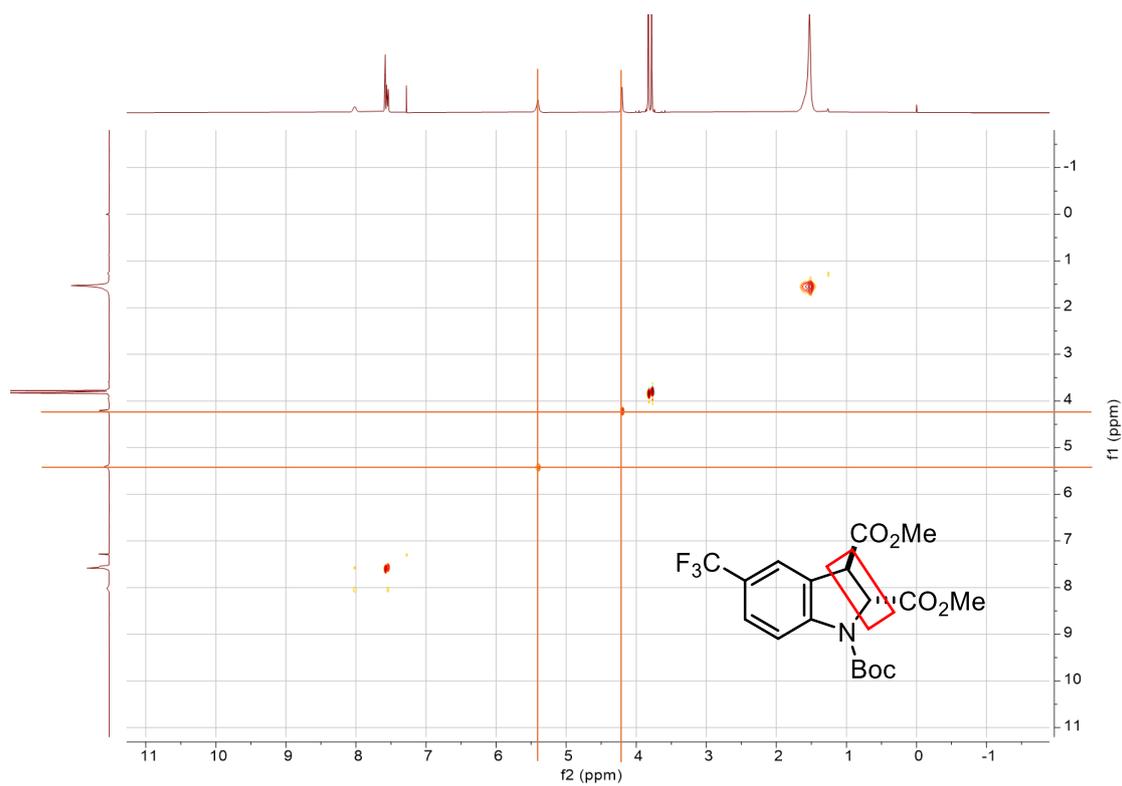
$^1\text{H NMR}$ (400 MHz, Chloroform-*d*) spectrum of **4b**



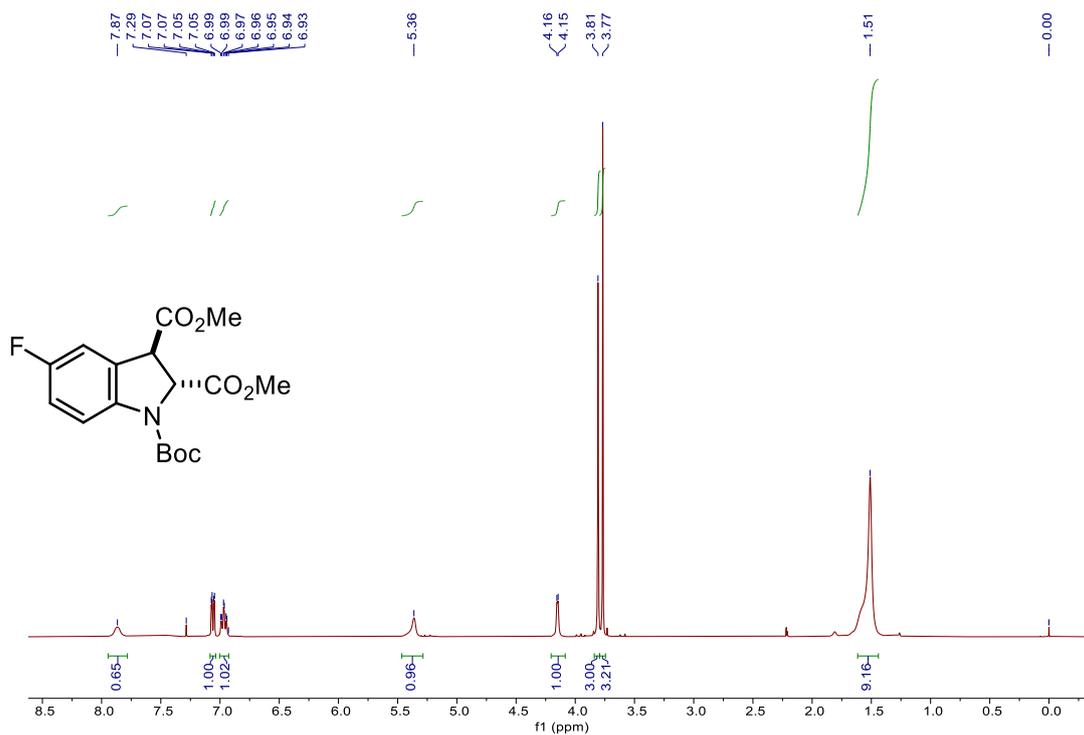
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*) spectrum of **4b**



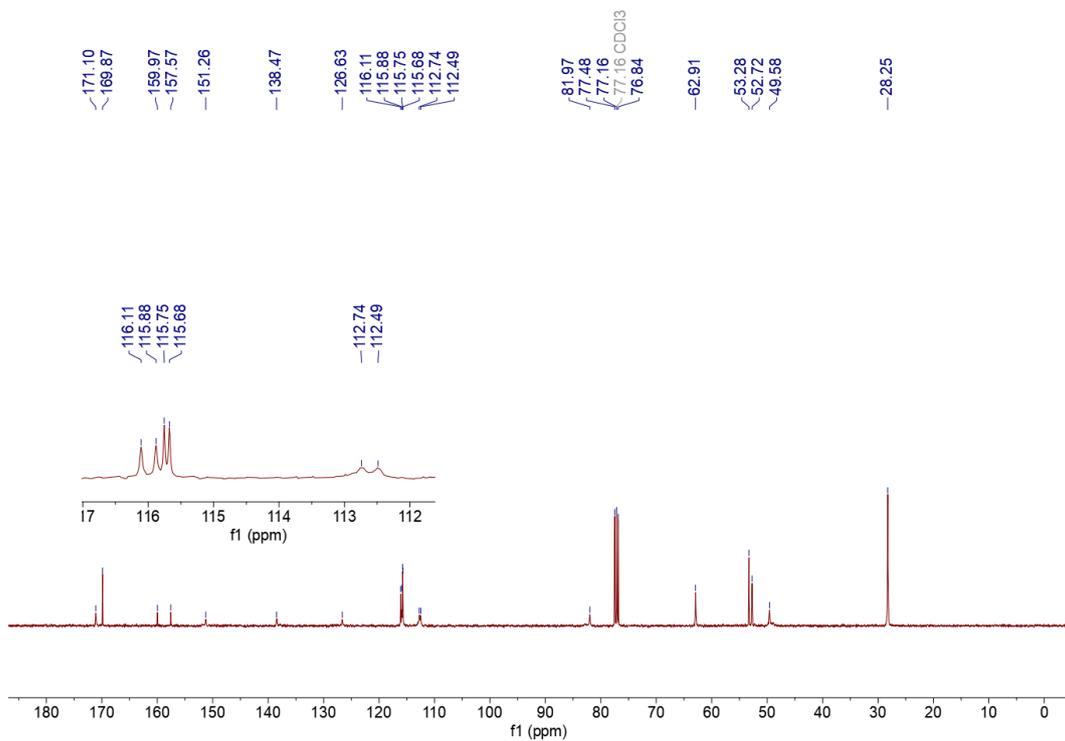
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of **4b**



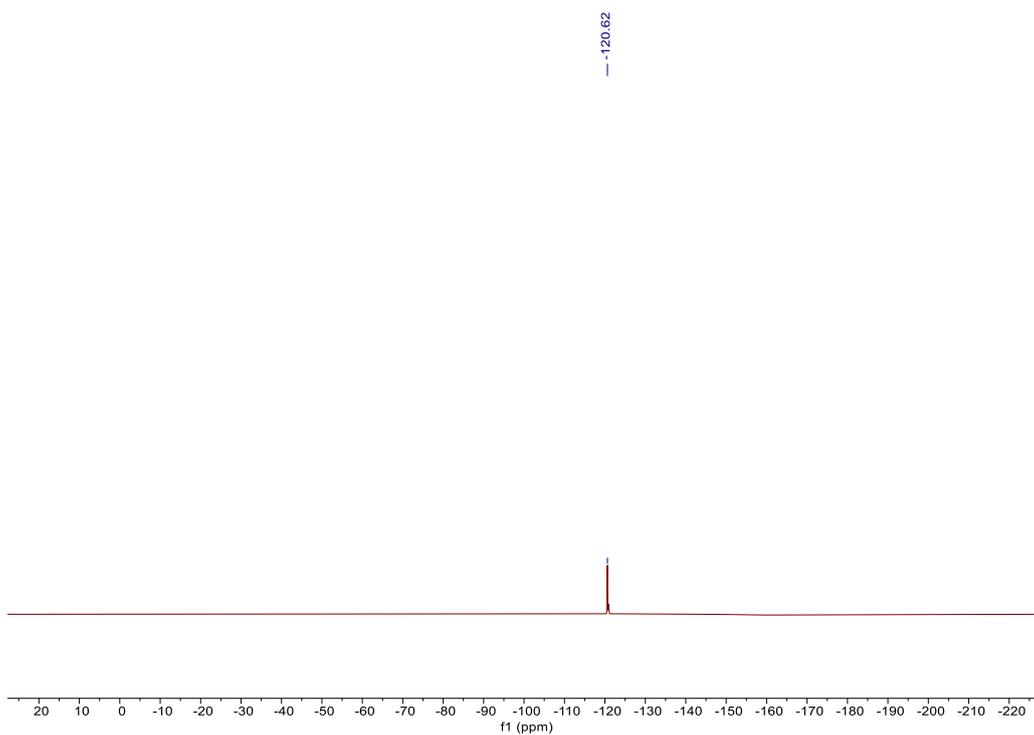
2D NOE spectrum of **4b**



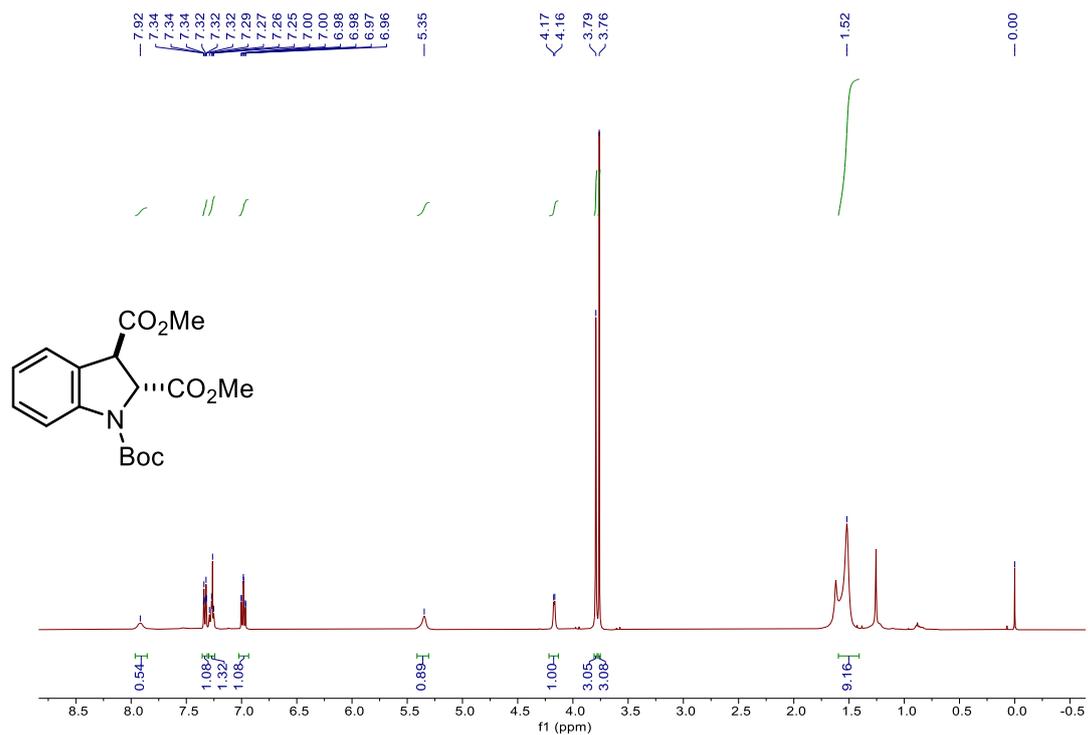
^1H NMR (400 MHz, Chloroform-*d*) spectrum of **4c**



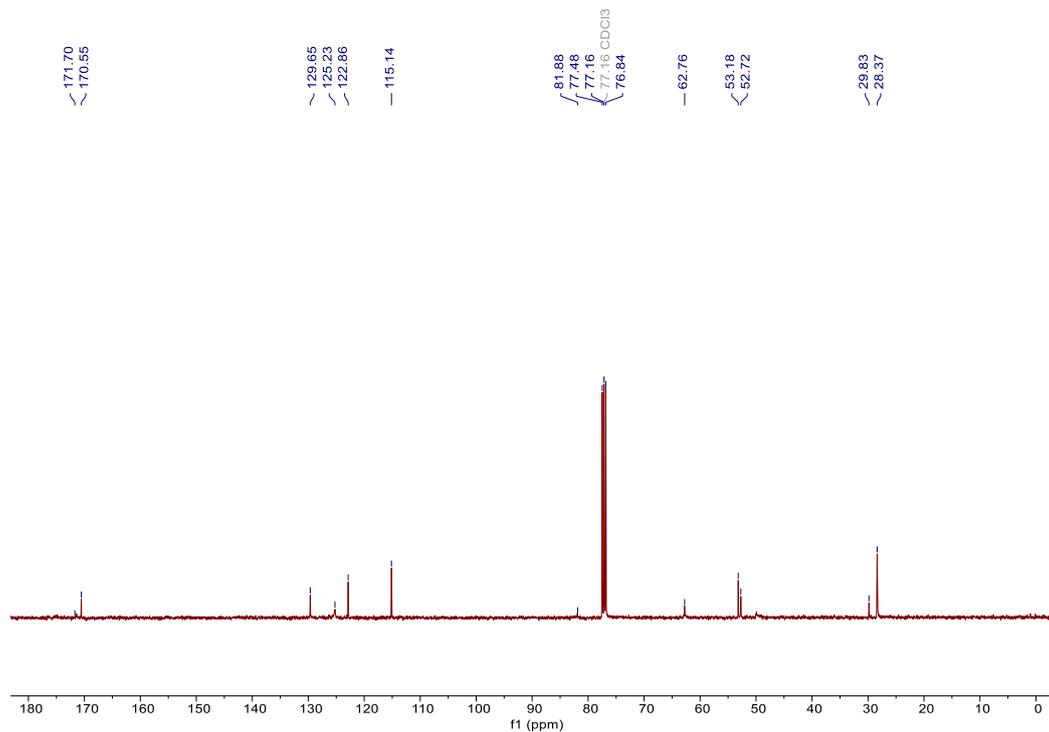
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*) spectrum of **4c**



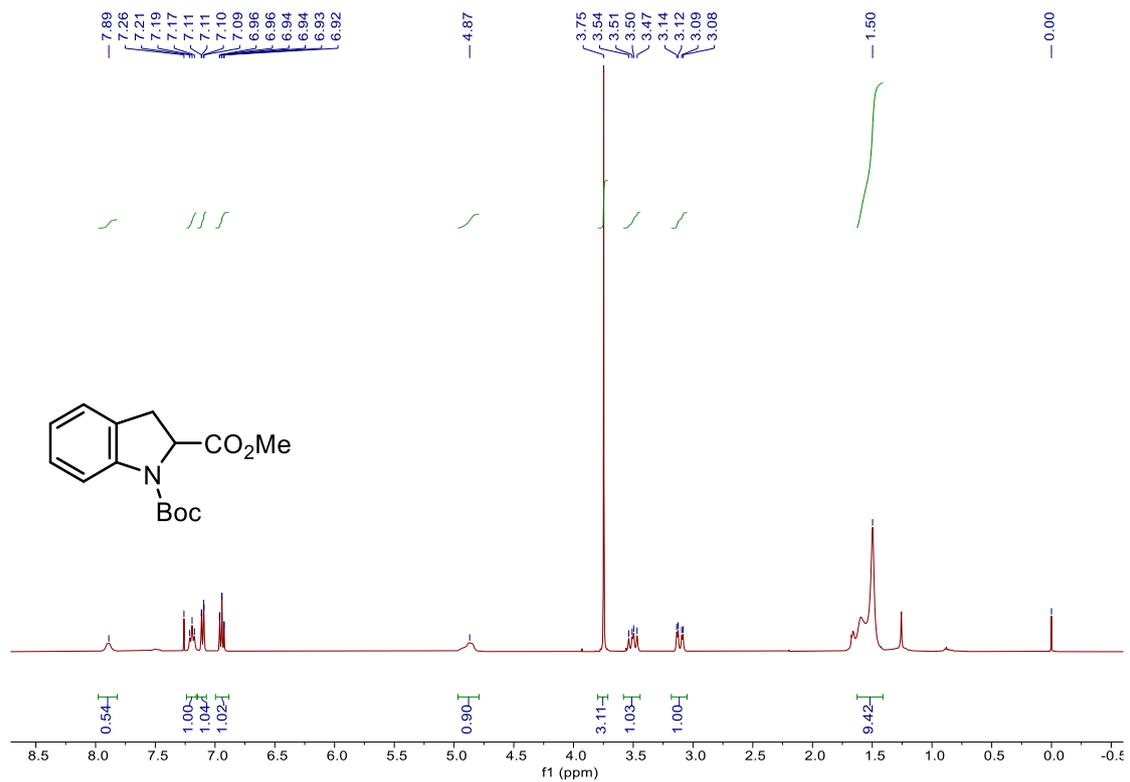
^{19}F NMR (376 MHz, Chloroform-*d*) spectrum of **4c**



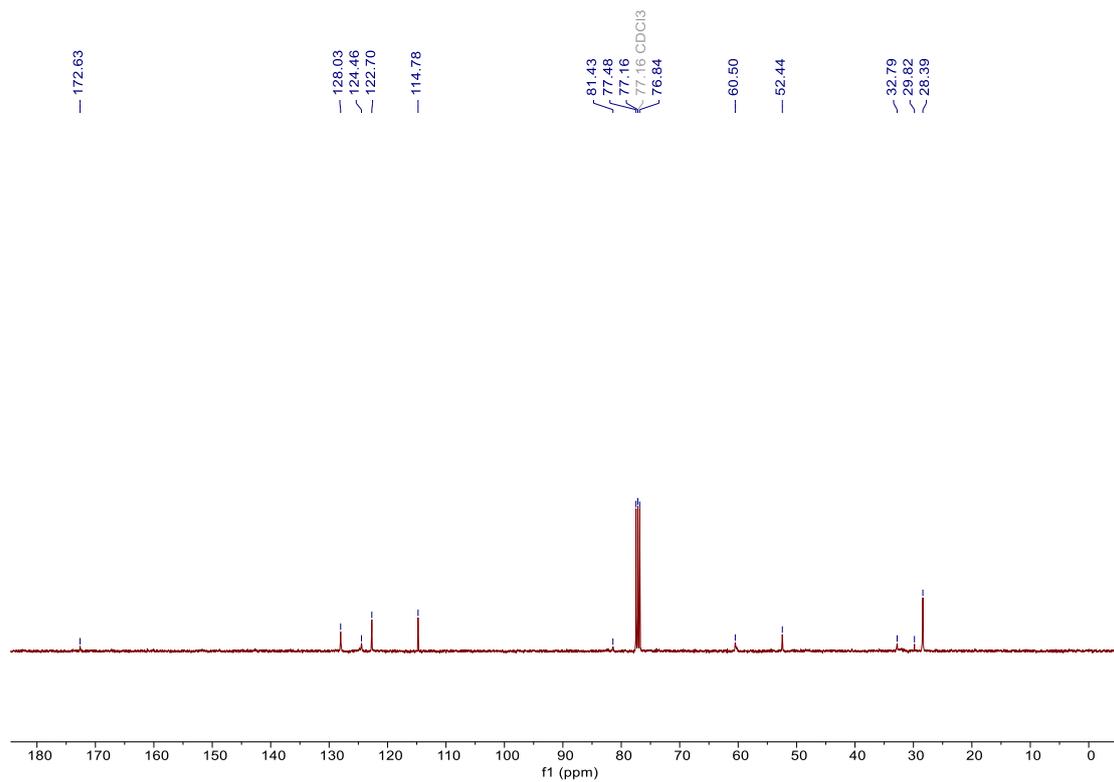
^1H NMR (400 MHz, Chloroform-*d*) spectrum of **4d**



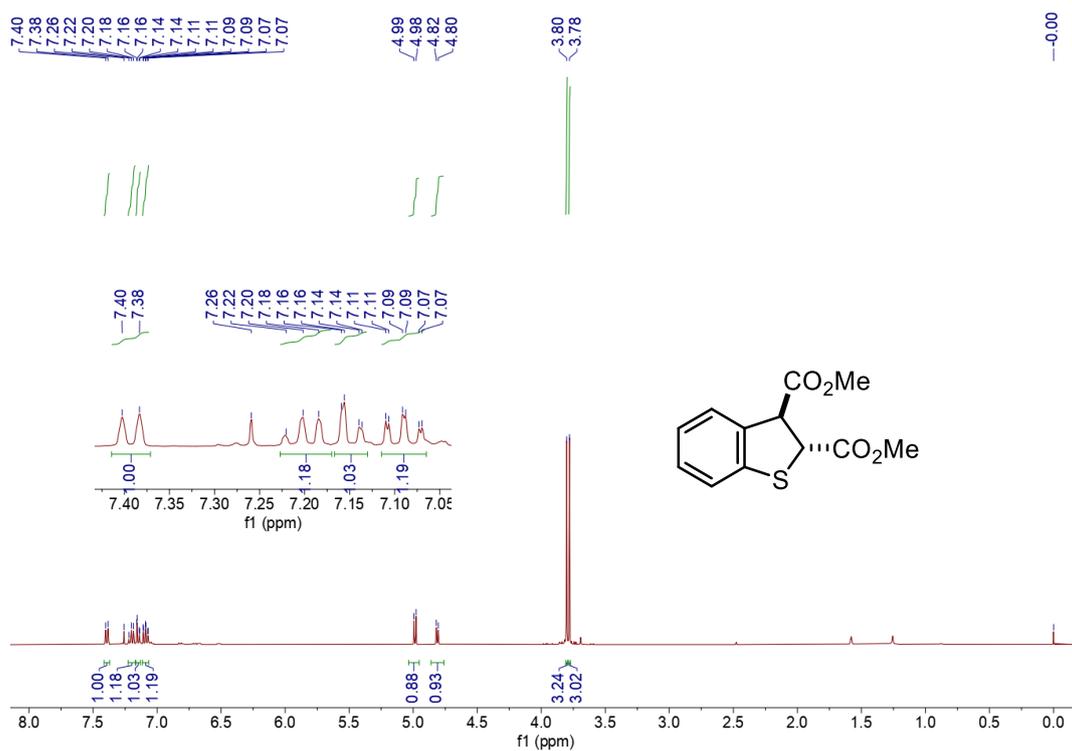
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*) spectrum of **4d**



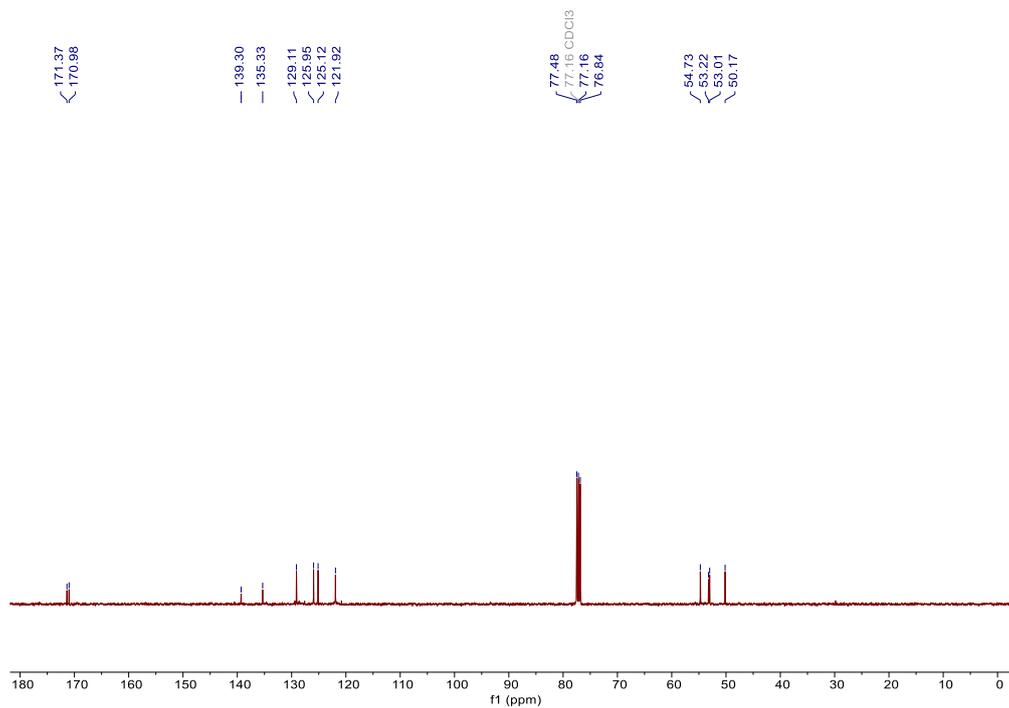
^1H NMR (400 MHz, Chloroform-*d*) spectrum of **4d'**



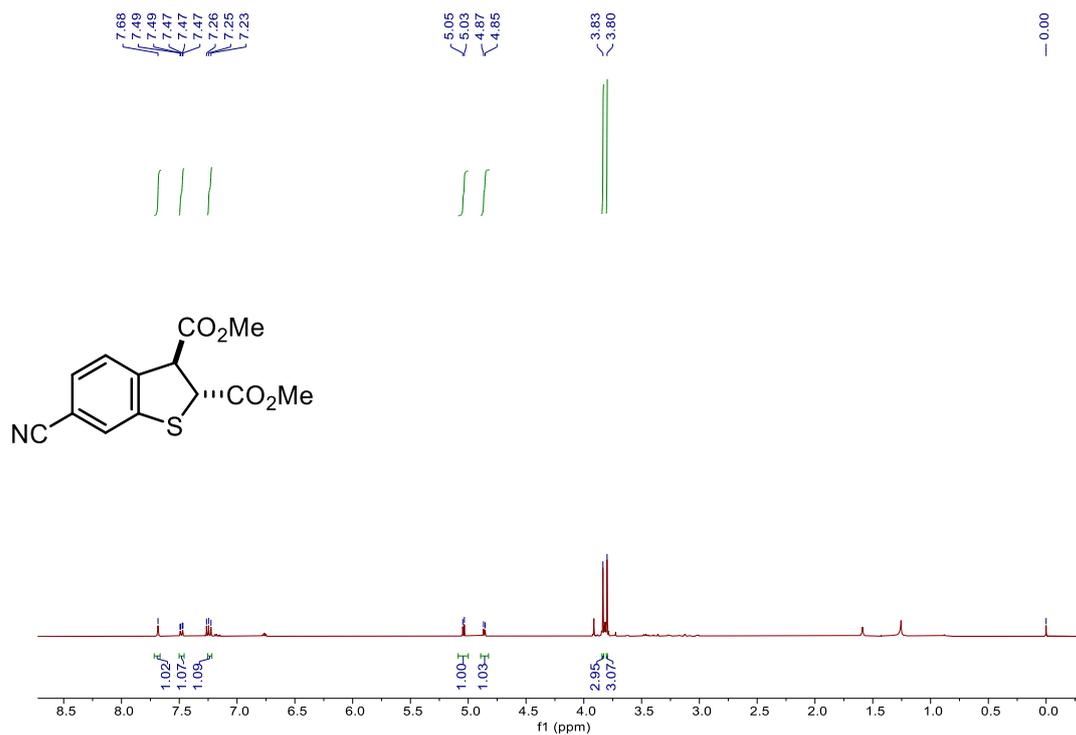
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*) spectrum of **4d'**



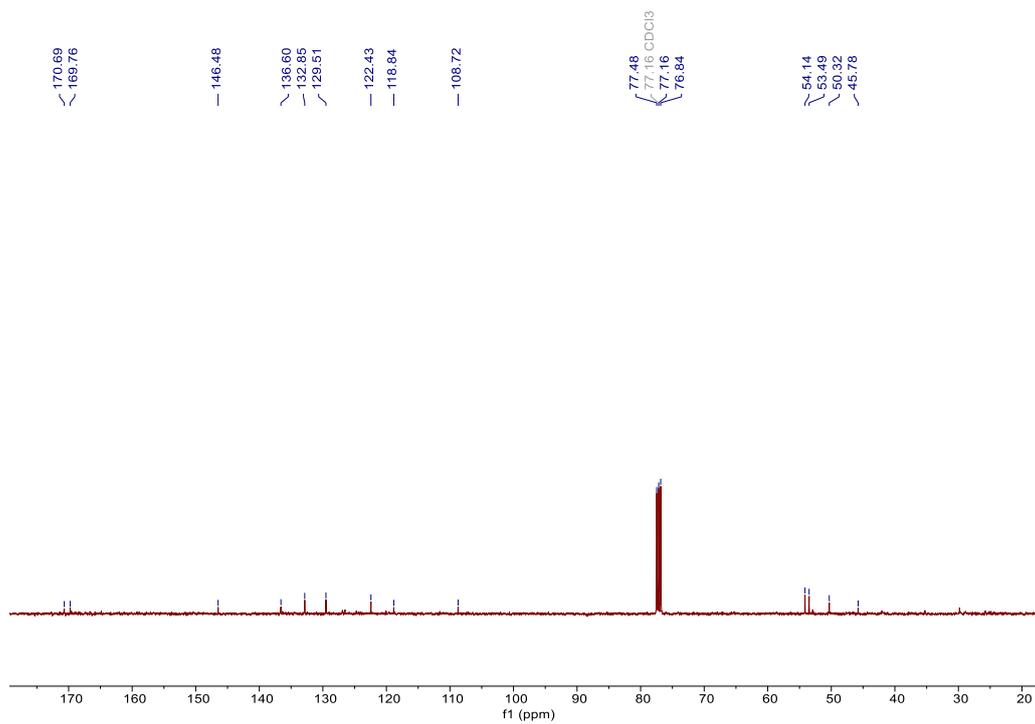
¹H NMR (400 MHz, Chloroform-*d*) spectrum of **4e**



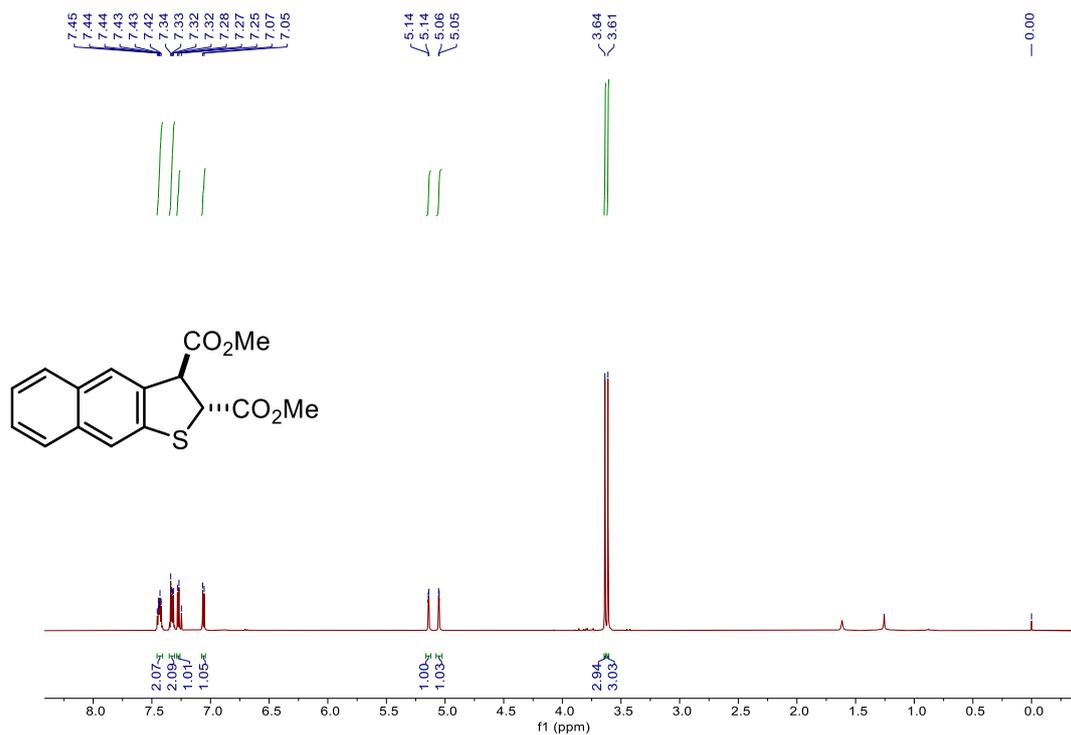
¹³C {¹H} NMR (101 MHz, Chloroform-*d*) spectrum of **4e**



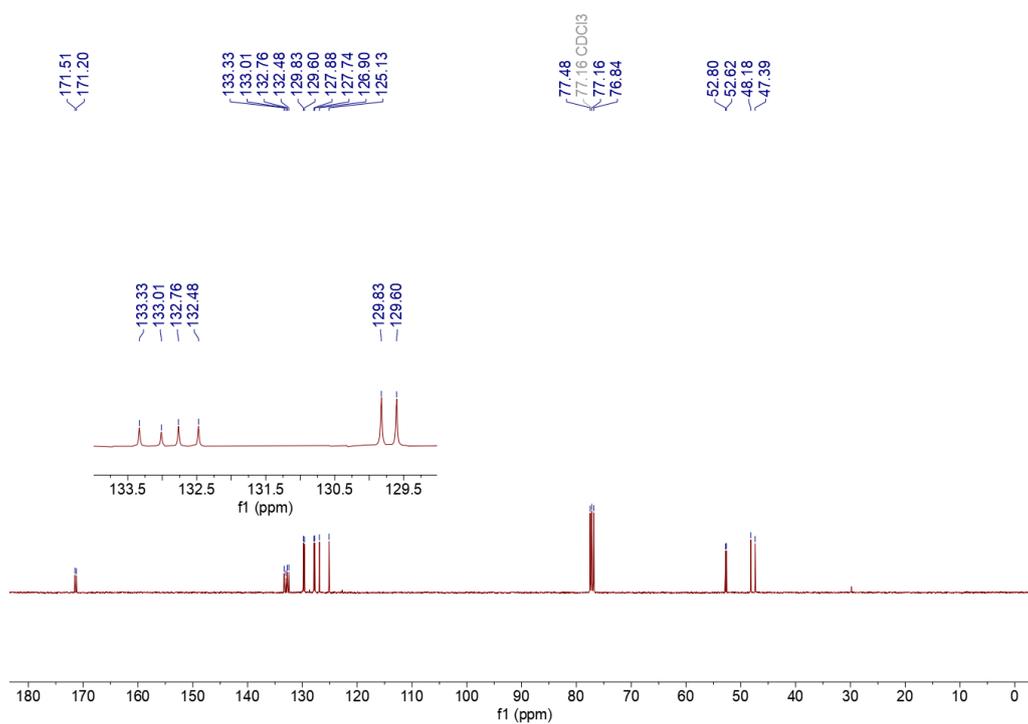
^1H NMR (400 MHz, Chloroform-*d*) spectrum of **4f**



$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*) spectrum of **4f**



^1H NMR (400 MHz, Chloroform-*d*) spectrum of **4g**



$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*) spectrum of **4g**

8. References

1. Yi, Y.; Fan, Z.; Xi, C., Photoredox-catalyzed intermolecular dearomative trifluoromethylcarboxylation of indoles and heteroanalogues with CO₂ and fluorinated radical precursors. *Green Chemistry* **2022**, *24*, 7894-7899.
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3. Quintana, I.; Boersma, A. J.; Peña, D.; Pérez, D.; Guitián, E., Metal-Catalyzed Cotrimerization of Arynes and Alkenes. *Organic Letters* **2006**, *8*, 3347-3349.
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6. Mangaonkar, S. R.; Hayashi, H.; Takano, H.; Kanna, W.; Maeda, S.; Mita, T., Photoredox/HAT-Catalyzed Dearomative Nucleophilic Addition of the CO₂ Radical Anion to (Hetero)Aromatics. *ACS Catalysis* **2023**, *13*, 2482-2488.