Electronic Supplementary Information

Visible-light-driven alkene dicarboxylation with formate and CO_2 under mild conditions

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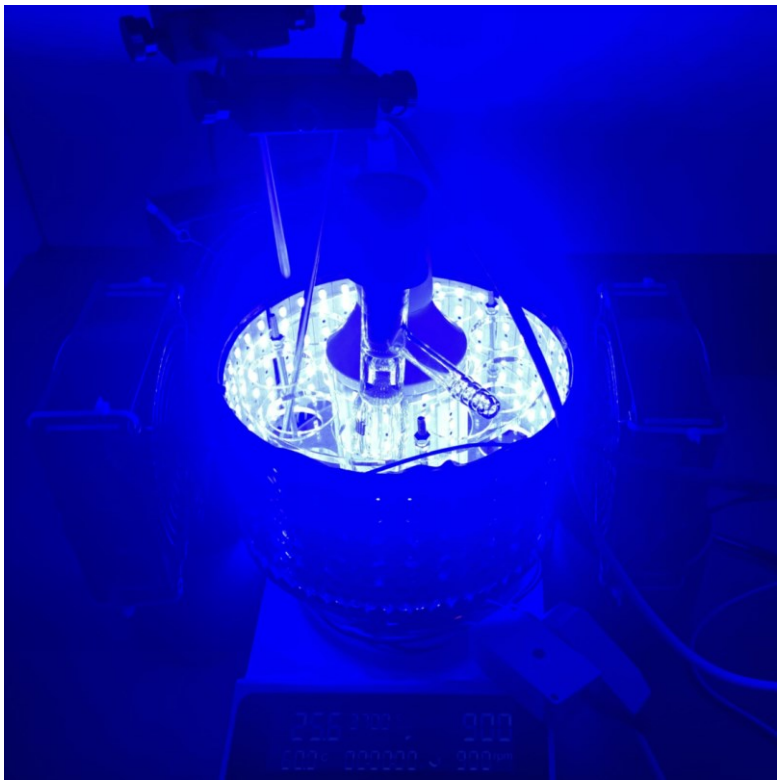
1. General information

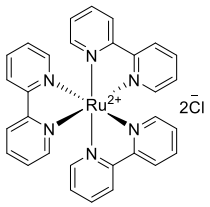
Chemicals were purchased from commercial suppliers and used without further purification unless otherwise stated. Solvents were generally dried over 4 Å molecular sieves. Unless otherwise indicated, all reactions were set up in glovebox in Schlenk tubes. Flash column chromatography was performed using silica gel 60 (200-300 mesh) or preparative thin layer chromatography. Reaction was monitored by thin layer chromatography (TLC) and was visualized by ultraviolet light (254 nm). Melting points were recorded using a SRS Melting Point thermometer. ^{1}H and ^{13}C NMR spectra were recorded on Bruker-BioSpin AVANCE III HD 400MHz spectrometer and Bruker Avance NEO 500MHz. Chemical shifts are reported parts per million (ppm) referenced to $CDCl_3$ (δ 7.26 ppm), tetramethylsilane (TMS, δ 0.00 ppm), DMSO-*d*$_6$ (δ 2.50 ppm), CD_3OD (δ 3.31 ppm) for ^{1}H NMR; $CDCl_3$ (δ 77.16 ppm), DMSO-*d*$_6$ (δ 40.00 ppm), CD_3OD (δ 49.00 ppm) for ^{13}C NMR. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet; d = doublet; t = triplet; q = quarter; p = pentet; m = multiplet; br = broad), coupling constant (Hz), integration. Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). HRMS were obtained on SolariX 7.0T and Waters Micromass Q-Tof Premier and XEVO-G2XSQTOF mass spectrometer. CO_2 gas (Purity: 99.999%) was purchased from Air Liquide. The light source used for the photocatalyzed experiment was a 30 W blue LED strips, purchased from Xuzhou Ai Jia electronic technology Co. LTD. (China) and 30W blue LED purchased from Shenzhen Xin Xing Yuan electronic techn -ology Co. LTD. (China)

2. Optimization of the reaction conditions

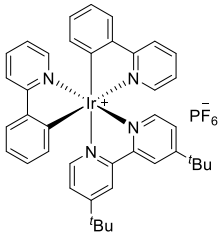
An oven-dried Schlenk tube (25 mL) containing a stirring bar was cooled to room temperature. The Schlenk tube was then introduced in a glovebox, where it was charged with base (0.6 mmol, 3.0 equiv), HCOOK (50.5 mg, 0.6 mmol, 3.0 equiv), photocatalyst (8.0 mg, 6.2 mol %), HAT (30 mol%), alkene (0.20 mmol, 1.0 equiv, if solid). The tube was taken out of the glovebox. Subsequently, the degassed anhydrous DMSO (2 mL, 0.1 M) and the alkene (0.2 mmol, if liquid) were added into the tube via syringe. Then the tube was evacuated and back-filled with CO_2 for 10 times. Finally, the tube was placed under 30 W blue LED strips (λ = 450 - 455 nm, 3.0 cm - 4.5 cm away from the LEDs, with fans to keep the reaction temperature at 25 - 33 °C) and stirred for 24 h. Then, the mixture was quenched with H_2O and 2 mL of HCl (2 N), extracted with EtOAc three times. The resulting solution was concentrated by rotary evaporation and the yield of crude products was determined via ^1H NMR using CH_2Br_2 as internal standard.



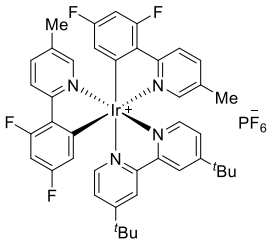
Photocatalysts:



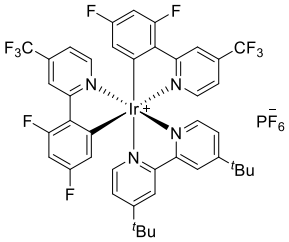
$Ru(bpy)_3Cl_2$



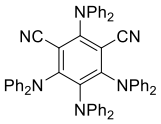
$[Ir(ppy)_2(dtbbpy)]PF_6$



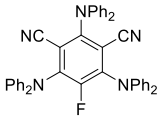
$[Ir(dF(Me)ppy)_2(dtbbpy)]PF_6$



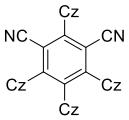
$[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$



4DPAIPN

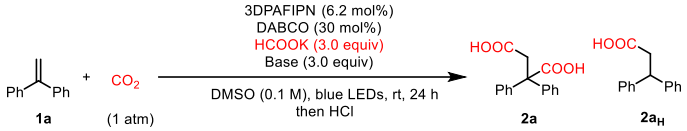


3DPAFIPN



4CzIPN

Table S1. Screening of Bases[a]

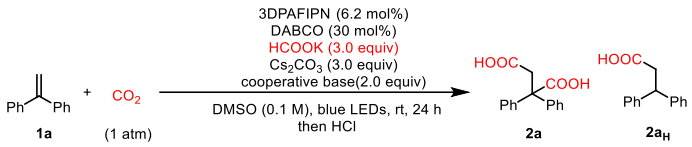


Entry	Base	2a [%][b]	$2a_H$ [%][b]
1	None	11%	66%
2	CsF	23%	54%
3	Cs_2CO_3	40%	12%
4	KF	29%	36%
5	^{t}BuOLi	42%	50%
6	CsOAc	38%	68%
7	NaOAc	44%	31%
8	KOAc	23%	34%
9	LiOAc	13%	40%
10	Na_2CO_3	24%	32%
11	K_3PO_4	44%	50%
12	KOH	27%	54%
13	Na_3PO_4	23%	52%
14	$NaOCH_3$	23%	60%
15	DMAP	26%	34%
16	DBU	--	18%
17	Pyridine	8%	40%
18	1,10-phenanthroline	16%	18%
19[c]	Cs_2CO_3	59%	--
20[d]	K_3PO_4	64%	--

21[e]	NaOAc	43%	48%

[a]Reaction conditions: 1,1-diphenylethylene (0.2 mmol), 3DPAFIPN (6.2 mol%), DABCO (0.06 mmol), Base (0.6 mmol), HCOOK (0.6 mmol) in DMSO (2 mL), 1 atm CO_2, 30 W blue LEDs (450 - 455 nm), rt, 24 h. DABCO = triethylenediamine. [b]Yield was determined by ^1H NMR with CH_2Br_2 as internal standard. [c]Cs_2CO_3 (5.0 equiv). [d]K_3PO_4 (5.0 equiv). [e]NaOAc (5.0 equiv).

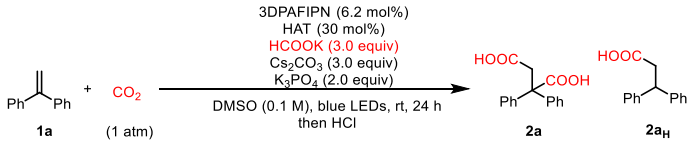
Table S2. Screening of cooperative bases[a]



Entry	cooperative base	2a [%][b]	$2a_H$ [%][b]
1	KPF_6	55%	--
2	KOPiv	31%	38%
3	KF	42%	--
4	K_3PO_4	91%(88%)	--
5[c]	K_3PO_4	74%	--
6[d]	K_3PO_4	65%	--
7[e]	K_3PO_4	71%	

[a]Reaction conditions: 1,1-diphenylethylene (0.2 mmol), 3DPAFIPN (6.2 mol%), DABCO (0.06 mmol), Cs_2CO_3 (0.6 mmol), additive (0.4 mmol), HCOOK (0.6 mmol) in DMSO (2 mL), 1 atm CO_2, 30 W blue LEDs (450 - 455 nm), rt, 24 h. DABCO = triethylenediamine. [b]Yield was determined by ^1H NMR with CH_2Br_2 as internal standard. Numbers in parentheses are referred to isolated yields. [c]K_3PO_4 (1.0 equiv). [d] Cs_2CO_3 (2.0 equiv) and K_3PO_4 (1.0 equiv). [e]Cs_2CO_3 (2.0 equiv).

Table S3. Screening of HATs[a]

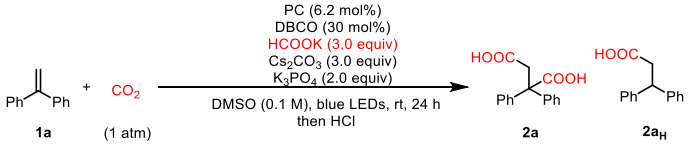


Entry	HAT	2a [%][b]	$2a_H$ [%][b]
1	quinuclidine	40%	--
2	Mesna	56%	20%
3	*p*-Toluenethiol	81%	--
4	2-Mercaptobenzoic Acid Methyl Ester	77%	--
5	L-Cysteine	50%	48%
6[c]	DABCO	65%	--
7[d]	DABCO	71%	--

[a]Reaction conditions: 1,1-diphenylethylene (0.2 mmol), 3DPAFIPN (6.2 mol%), HAT (0.06 mmol), Cs_2CO_3 (0.6 mmol), K_3PO_4 (0.4

mmol), HCOOK (0.6 mmol) in DMSO (2 mL), 1 atm CO_2, 30 W blue LEDs (450 - 455 nm), rt, 24 h. DABCO = triethylenediamine. [b]Yield was determined by ^{1}H NMR with CH_2Br_2 as internal standard. [c]DABCO (10 mol%). [d]DABCO (20 mol%).

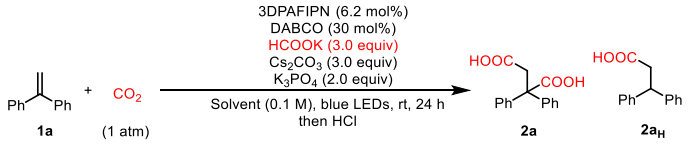
Table S4. Screening of photocatalysts[a]



Entry	Photocatalyst (PC)	2a [%][b]	$2a_H$ [%][b]
1	None	--	--
2	3DPAFIPN	91%(88%)[c]	--
3[d]	$Ru(bpy)_3Cl_2$	--	--
4[d]	$Ir(ppy)_2(dtbbpy)(PF_6)$	7%	--
5[d]	$[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$	--	--
6[d]	$[Ir(dF(Me)ppy)_2(dtbbpy)]PF_6$	20%	--
7	4DPAIPN	65%	--
8	4CzIPN	39%	--
9[e]	3DPAFIPN	70%	--
10[f]	3DPAFIPN	86%	--
11[g]	3DPAFIPN	--	--
12[h]	3DPAFIPN	32%	28%
13[i]	3DPAFIPN	--	76%
14[j]	3DPAFIPN		

[a]Reaction conditions: 1,1-diphenylethylene (0.2 mmol), PC (6.2 mol%), DABCO (0.06 mmol), Cs_2CO_3 (0.6 mmol), K_3PO_4 (0.4 mmol), HCOOK (0.6 mmol) in DMSO (2 mL), 1 atm CO_2, 30 W blue LEDs (450 - 455 nm), rt, 24 h. DABCO = triethylenediamine. [b]Yield was determined by ^{1}H NMR with CH_2Br_2 as internal standard. [c]Isolated yield. [d]PC (5.0 mol%). [e]3DPAFIPN (2.0 mol%). [f]3DPAFIPN (4.0 mol%). [g]In darkness. [h]Without DABCO. [i]In N_2 atmosphere. [j]Without HCOOK.

Table S5. Screening of Solvents

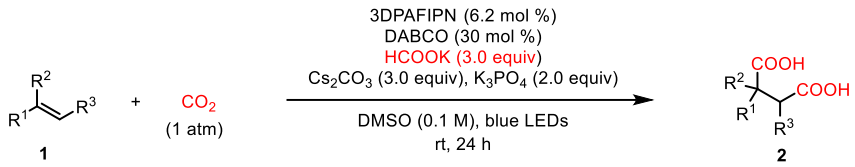


Entry	Solvent	2a [%][b]	$2a_H$ [%][b]
1	DMF	15%	--
2	1,4-dioxane	--	--
3	THF	16%	--
4	MeCN	--	--
5	DMA	17%	--

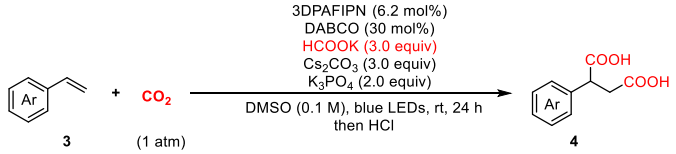
[a]Reaction conditions: 1,1-diphenylethylene (0.2 mmol), 3DPAFIPN (6.2 mol%), DABCO (0.06 mmol), Cs_2CO_3 (0.6 mmol), K_3PO_4 (0.4

mmol), HCOOK (0.6 mmol) in slovent (2 mL), 1 atm CO_2, 30 W blue LEDs (450 - 455 nm), rt, 24 h. DABCO = triethylenediamine. [b]Yield was determined by ^1H NMR with CH_2Br_2 as internal standard.

3. General procedures

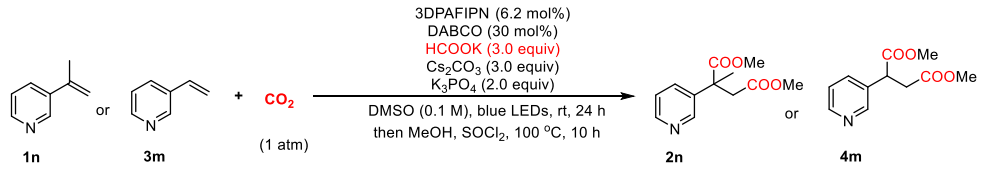


An oven-dried Schlenk tube (25 mL) containing a stirring bar was cooled to room temperature. The Schlenk tube was then introduced in a glovebox, where it was charged with K_3PO_4 (2.0 equiv, 0.4 mmol, 85.5 mg), Cs_2CO_3 (3.0 equiv, 0.6 mmol, 195.5 mg), HCOOK (3.0 equiv, 0.6 mmol, 50.5 mg), 3DPAFIPN (6.2 mol%, 8.0 mg, 3DPAFIPN was synthesized following the literature procedures[1]), DABCO (30 mol%), alkene **1** (0.20 mmol, 1.0 equiv, if solid). The tube was taken out of the glovebox. Subsequently, the degassed anhydrous DMSO (2 mL, 0.1 M) and the alkene (0.2 mmol, if liquid) were added into the tube via syringe. Then the tube was evacuated and back-filled with CO_2 for 10 times. Finally, the tube was placed under 30 W blue LED strips (λ = 450 - 455 nm, 3.0 cm - 4.5 cm away from the LEDs, with fans to keep the reaction temperature at 25 - 33 °C) and stirred for 24 h. Then, the mixture was quenched with H_2O and 2 mL of HCl (2 N), extracted with EtOAc three times. The resulting solution was concentrated by rotary evaporation. The residual was purified by column chromatography on silica gel to give the desired product **2**. If there was traces of DMSO, extraction with H_2O.



An oven-dried Schlenk tube (25 mL) containing a stirring bar was cooled to room temperature. The Schlenk tube was then introduced in a glovebox, where it was charged with K_3PO_4 (2.0 equiv, 0.4 mmol, 85.5 mg), Cs_2CO_3 (3.0 equiv, 0.6 mmol, 195.5 mg), HCOOK (3.0 equiv, 0.6 mmol, 50.5 mg), 3DPAFIPN (6.2 mol%, 8.0 mg),

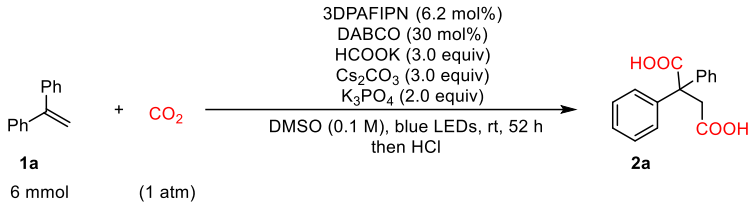
DABCO (30 mol%, 6.8 mg), alkene (0.20 mmol, 1.0 equiv, if solid). The tube was taken out of the glovebox. Subsequently, the degassed anhydrous DMSO (2 mL, 0.1 M) and the alkene **3** (0.2 mmol, if liquid) were added into the tube via syringe. Then the tube was evacuated and back-filled with CO_2 for 10 times. Finally, the tube was placed under 30 W blue LED strips (λ = 450 - 455 nm, 3.0 cm - 4.5 cm away from the LEDs, with fans to keep the reaction temperature at 25 - 33 °C) and stirred for 24 h. Then, the mixture was quenched with H_2O and 2 mL of HCl (2 N), extracted with EtOAc three times, then concentrated in vacuo. The resulting solution was concentrated by rotary evaporation. The residual was purified by column chromatography on silica gel to give the desired product **4** (If traces of DMSO were present with product, extract with H_2O to remove DMSO).



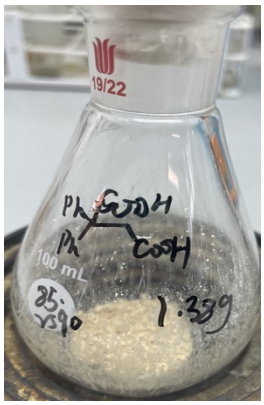
An oven-dried reaction tube (25 mL) containing a stirring bar was cooled to room temperature. The Schlenk tube was then introduced in a glovebox, where it was charged with K_3PO_4 (2.0 equiv, 0.4 mmol, 85.5 mg), Cs_2CO_3 (3.0 equiv, 0.6 mmol, 195.5 mg), HCOOK (3.0 equiv, 0.6 mmol, 50.5 mg), 3DPAFIPN (6.2 mol%, 8.0 mg), DABCO (30 mol%, 6.8 mg). The tube was taken out of the glovebox. Subsequently, the degassed anhydrous DMSO (2 mL, 0.1 M) and the alkene **1n** or **3m** (0.2 mmol) were added into the tube via syringe. Then the tube was evacuated and back-filled with CO_2 for 10 times. Finally, the tube was placed under 30 W blue LED strips (λ = 450 - 455 nm, 3.0 cm - 4.5 cm away from the LEDs, with fans to keep the reaction temperature at 25 - 33 °C) light source and stirred at ambient temperature for 24 h. Upon completion of the reaction, then AcOH (0.2 mL) was added and the system was stirred for 10 min at room temperature. The solvent along with other volatile matter was removed directly under reduced pressure at high temperature. The residue was re-dissolved in MeOH (8 mL) and then $SOCl_2$ (0.8 mL) was added dropwise carefully. The Schlenk tube was capped and stirred at 100 °C for 10 h. After cooled to room

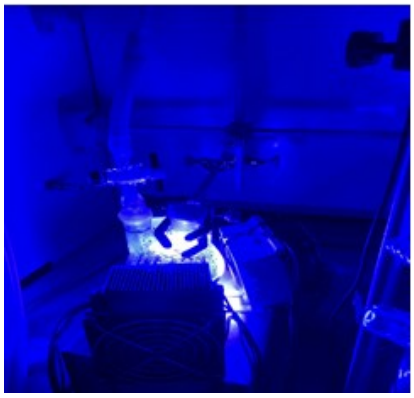
temperature, the mixture was diluted with EtOAc (10 mL) and quenched with saturated aqueous solution of sodium hydrogen carbonate. The reaction was extracted with EtOAc (30 mL ×3) and the organic layers were combined and dried over Na_2SO_4. After concentrated under reduced pressure, crude ^1H NMR spectrum was taken using CH_2Br_2 as internal standard. The resulting residue was purified by flash silica gel chromatography or preparative thin layer chromatography using petroleum ether/EtOAc (3:1-1:1) as the eluent to give the desired products.

Large Scale Reaction Procedure:

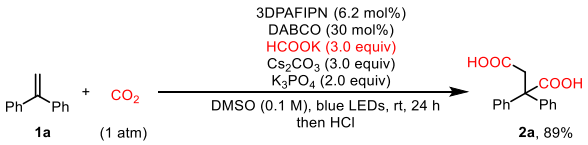


An oven-dried round-bottom flask (250 mL) containing a stirring bar was cooled to room temperature. The round-bottom flask was then introduced in a glovebox, where it was charged with K_3PO_4 (2.0 equiv, 12.0 mmol, 2.55 g), Cs_2CO_3 (3.0 equiv, 18.0 mmol, 5.86 g), HCOOK (3.0 equiv, 18.0 mmol, 1.51 g), 3DPAFIPN (6.2 mol%, 240 mg), DABCO (30 mol%, 202 mg). The flask was taken out of the glovebox. Subsequently, the degassed anhydrous DMSO (10 mL, 0.1 M) and 1,1-diphenylethylene (6.0 mmol, 1.0 equiv, 1.08 g) were added into the flask via syringe. Then the flask was evacuated and back-filled with CO_2 for 10 times. Then the reaction flask was attached with a CO_2 gas bag (about 3 L). Finally, the tube was placed under two 30 W blue LEDs (purchased from Shenzhen Xin Xing Yuan electronic techn-ology Co. LTD. Of China; λ = 450 - 455 nm; 3.0 cm - 4.5 cm away from the LED with a fan to keep the reaction temperature at about 36 °C) light source and stirred at ambient temperature for 52 h. Then, the mixture was quenched with H_2O and 10 mL of HCl (2 N), extracted with EtOAc three times. The resulting solution was concentrated by rotary evaporation. The residual was purified by column chromatography on silica gel to give the desired product in 85% yield (1.38 g).





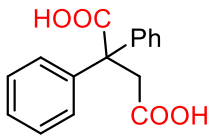
Set-up the reaction outside the glovebox



Take some K_3PO_4, Cs_2CO_3, HCOOK, DABCO and 3DPAFIPN from bottles kept in the glovebox and put them into vials respectively. Then weigh these chemicals using a balance outside the glovebox. To an oven-dried reaction tube containing a stirring bar cooled to room temperature was added K_3PO_4 (2.0 equiv, 0.4 mmol, 85.5 mg), Cs_2CO_3 (3.0 equiv, 0.6 mmol, 195.5 mg), HCOOK (3.0 equiv, 0.6 mmol, 50.5 mg), 3DPAFIPN (6.2 mol%, 8.0 mg) and DABCO (30 mol%, 6.8 mg). Subsequently, the degassed anhydrous DMSO (2 mL, 0.1 M) and 1,1-diphenylethylene (1.0 equiv, 0.2 mmol, 36 mg) were added into the tube via syringe. Then the tube was evacuated and back-filled with CO_2 for 10 times. Finally, the tube was placed under 30 W blue LEDs (λ = 450 - 455 nm, 3.0 cm - 4.5 cm away from the LEDs, with fans to keep the reaction temperature at 28 °C) and stirred for 24 h. Then, the mixture was quenched with H_2O and 2 mL of HCl (2 N), extracted with EtOAc three times. The resulting

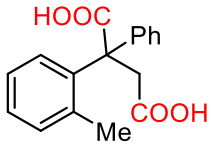
solution was concentrated by rotary evaporation. The residual was purified by column chromatography on silica gel to give the desired product **2a** in 89% yield (48.1 mg).

2,2-diphenylsuccinic acid (2a)[2]



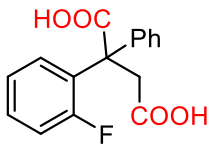
Product **(2a)** was obtained as a white solid (47.4 mg, 88%); R_f = 0.4 (Petroleum ether : Acetone = 3 : 1); ^{1}H NMR (400 MHz, CD_3OD) δ 7.35 - 7.32 (m, 4H), 7.27 - 7.18 (m, 6H), 3.50 (s, 2H). ^{13}C NMR (100 MHz, CD_3OD) δ 176.6, 174.3, 144.4, 129.9, 128.8, 127.8, 58.5, 44.7.

2-phenyl-2-(*o*-tolyl)succinic acid (2b)[2]



Product **(2b)** was obtained as a white solid (43.7 mg, 77%); R_f = 0.5 (Petroleum ether : Acetone = 3 : 1); ^{1}H NMR (400 MHz, CD_3OD) δ 7.51 - 7.47 (m, 1H), 7.40 - 7.37 (m, 2H), 7.26 - 7.15 (m, 5H), 7.09 - 7.07 (m, 1H), 3.62 (d, *J* = 15.6 Hz, 1H), 3.41 (d, *J* = 15.6 Hz, 1H), 1.86 (s, 3H).^{13}C NMR (100 MHz, CD_3OD) δ 176.1, 174.4, 143.7, 141.7, 138.9, 133.5, 130.0, 129.7, 128.8, 128.3, 127.7, 126.4, 58.7, 45.0, 22.0.

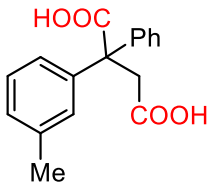
2-(2-fluorophenyl)-2-phenylsuccinic acid (2c)[2]



Product **(2c)** was obtained as a colorless oil (42 mg, 73%); R_f = 0.5 (Petroleum ether : Acetone = 3 : 1); ^{1}H NMR (400 MHz, CD_3OD) δ 7.45 - 7.24 (m, 7H), 7.09 - 6.97 (m, 2H), 3.58 (2H, ABq, *J* = 17.2 Hz). ^{13}C NMR (100 MHz, CD_3OD) δ 176.0, 174.2, 162.3 (d, *J* = 246 Hz), 141.8, 132.5 (d, *J* = 3.6 Hz), 131.4 (d, *J* = 10.8 Hz), 130.2 (d, *J* = 9.0 Hz), 129.2, 129.0, 128.2, 124.2 (d, *J* = 3.3 Hz), 116.7 (d, *J* = 23.2 Hz), 56.6,

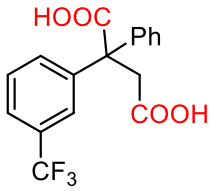
41.6 (d, J = 3.0 Hz).^{19}F NMR (376 MHz, CD_3OD) δ -109.5.

2-phenyl-2-(*m*-tolyl)succinic acid (2d)



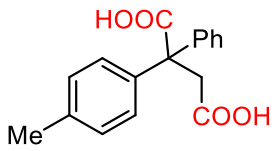
Product **(2d)** was obtained as a white solid (42 mg, 74%); mp: 151-152 ºC; R_f = 0.5 (Petroleum ether : Acetone = 3 : 1); ^{1}H NMR (400 MHz, CD_3OD) δ 7.34 - 7.31 (m, 2H), 7.27 - 7.20 (m, 3H), 7.17 - 7.10 (m, 3H), 7.05 - 7.03 (m, 1H), 3.47 (2H, ABq, J = 16.8 Hz), 2.27 (s, 3H). ^{13}C NMR (100 MHz, CD_3OD) δ 176.7, 174.4, 144.5, 144.4, 138.4, 130.5, 130.0, 128.71, 128.68, 128.5, 127.8, 126.8, 58.4, 44.8, 21.6. HRMS (ESI) m/z calcd for $C_{17}H_{15}O_4^-$ $(M-H)^-$ 283.0976; found 283.0967.

2-phenyl-2-(3-(trifluoromethyl)phenyl)succinic acid (2e)[2]



Product **(2e)** was obtained as a white solid (41 mg, 62%); R_f = 0.4 (Petroleum ether : Acetone = 3 : 1); ^{1}H NMR (400 MHz, CD_3OD) δ 7.52 (s, 1H), 7.35 - 7.29 (m, 2H), 7.24 - 7.20 (m, 1H), 7.15 - 7.03 (m, 5H), 3.46 (d, J = 16.4 Hz, 1H), 3.19 (d, J = 16.8 Hz, 1H). ^{13}C NMR (100 MHz, CD_3OD) δ 176.0, 174.0, 145.9, 144.0, 134.2, 130.9 (q, J = 31.6 Hz), 129.4, 129.31, 129.28, 128.4, 127.4 (q, J = 3.9 Hz), 125.7 (q, J = 270 Hz), 124.5 (q, J = 3.8 Hz), 58.5, 44.5. ^{19}F NMR (376 MHz, CD_3OD) δ -64.0.

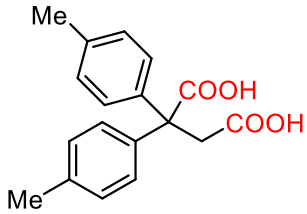
2-phenyl-2-(*p*-tolyl)succinic acid (2f)[2]



Product **(2f)** was obtained as a white solid (35 mg, 62%); R_f = 0.3 (Petroleum ether :

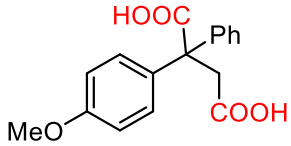
Acetone = 3 : 1); ^{1}H NMR (400 MHz, CD_3OD) δ 7.34 - 7.31 (m, 2H), 7.26 - 7.19 (m, 5H), 7.08 - 7.06 (m, 2H), 3.46 (2H, ABq, J = 16.4 Hz), 2.29 (s, 3H). ^{13}C NMR (100 MHz, CD_3OD) δ 176.8, 174.4, 144.6, 141.5, 137.6, 129.9, 129.7, 129.4, 128.7, 127.7, 58.2, 44.8, 20.9.

2,2-di-*p*-tolylsuccinic acid (2g)



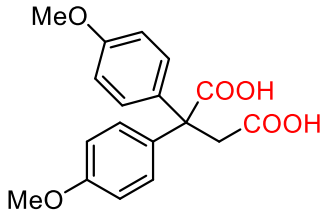
Product **(2g)** was obtained as a white solid (42 mg, 70%); mp: 117-118 ºC; R_f = 0.5 (Petroleum ether : Acetone = 3 : 1); ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.43 (br, 2H), 7.16 - 7.14 (m, 4H), 7.07 - 7.05 (m, 4H), 3.34 (s, 2H), 2.25 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 174.2, 171.9, 140.6, 135.5, 128.4, 128.2, 56.0, 43.5, 20.5. HRMS (ESI) m/z calcd for $C_{18}H_{17}O_4^-$ $(M-H)^-$ 297.1132; found 297.1122.

2-(4-methoxyphenyl)-2-phenylsuccinic acid (2h)[2]



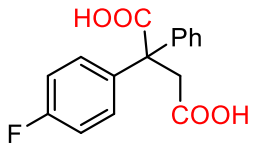
Product **(2h)** was obtained as a white solid (45 mg, 75%); R_f = 0.5 (Petroleum ether : Acetone = 3 : 1); ^{1}H NMR (400 MHz, CD_3OD) δ 7.34 - 7.32 (m, 2H), 7.27 - 7.18 (m, 5H), 6.82 - 6.79 (m, 2H), 3.75 (s, 3H), 3.46 (2H, ABq, J = 16.4 Hz). ^{13}C NMR (100 MHz, CD_3OD) δ 176.9, 174.4, 159.8, 144.7, 136.4, 131.0, 129.9, 128.7, 127.8, 114.1, 57.9, 55.6, 44.9.

2,2-bis(4-methoxyphenyl)succinic acid (2i)



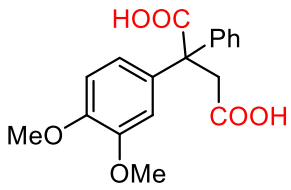
Product **(2i)** was obtained as a colorless oil (48 mg, 74%); R_f = 0.5 (Petroleum ether : Acetone = 3 : 1); ^{1}H NMR (400 MHz, CD_3OD) δ 7.25 - 7.22 (m, 4H), 6.83 - 6.79 (m, 4H), 3.77 (s, 6H), 3.41 (s, 2H). ^{13}C NMR (100 MHz, CD_3OD) δ 177.2, 174.5, 159.8, 136.7, 131.0, 114.0, 57.3, 55.6, 45.1. HRMS (ESI) m/z calcd for $C_{18}H_{17}O_6^-$ $(M-H)^-$ 329.1031; found 329.1018.

2-(4-fluorophenyl)-2-phenylsuccinic acid (2j)[2]



Product **(2j)** was obtained as a white solid (45 mg, 78%); R_f = 0.5 (Petroleum ether : Acetone = 3 : 1); ^{1}H NMR (400 MHz, CD_3OD) δ 7.38 - 7.32 (m, 4H), 7.30 - 7.20 (m, 3H), 7.00 - 6.94 (m, 2H), 3.55 (d, J = 16.4 Hz, 1H), 3.42 (d, J = 16.4 Hz, 1H). ^{13}C NMR (100 MHz, CD_3OD) δ 176.4, 174.2, 162.9 (d, J = 243.5 Hz), 144.4, 140.5 (d, J = 3.4 Hz), 132.1 (d, J = 7.9 Hz), 129.6, 129.0, 128.0, 115.2 (d, J = 21.3 Hz), 58.0, 44.7. ^{19}F NMR (376 MHz, CD_3OD) δ -118.3.

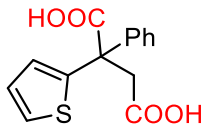
2-(3,4-dimethoxyphenyl)-2-phenylsuccinic acid (2k)



Product **(2k)** was obtained as a colorless oil (29.8 mg, 72%); R_f = 0.5 (Petroleum ether : Acetone = 3 : 1); ^{1}H NMR (400 MHz, CD_3OD) δ 7.36 - 7.34 (m, 2H), 7.28 - 7.19 (m, 3H), 6.97 (s, 1H), 6.88 - 6.82 (m, 2H), 3.80 (s, 3H), 3.69 (s, 3H), 3.47 (s, 2H). ^{13}C NMR (100 MHz, CD_3OD) δ 176.8, 174.3, 149.6, 149.5, 144.6, 137.2, 129.9,

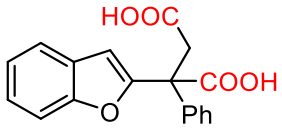
128.8, 127.8, 122.4, 114.9, 112.1, 58.2, 56.4, 44.9. HRMS (ESI) m/z calcd for $C_{18}H_{17}O_6^-$ $(M-H)^-$ 329.1031; found 329.1018.

2-phenyl-2-(thiophen-3-yl)succinic acid (2l)[2]



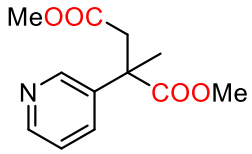
Product **(2l)** was obtained as a white solid (30 mg, 55%); R_f = 0.5 (Petroleum ether : Acetone = 3 : 1); ^{1}H NMR (400 MHz, CD_3OD) δ 7.37 - 7.34 (m, 2H), 7.29 - 7.21 (m, 4H), 7.03 - 7.00 (m, 1H), 6.92 - 6.90 (m, 1H), 3.66 (d, *J* = 16.8 Hz, 1H), 3.47 (d, *J* = 16.8 Hz, 1H). ^{13}C NMR (100 MHz, CD_3OD) δ 175.9, 173.9, 147.5, 144.4, 129.1, 128.4, 128.3, 127.6, 126.7, 126.3, 56.0, 45.6.

2-(benzofuran-2-yl)-2-phenylsuccinic acid(2m)[2]



Product **(2m)** was obtained as a white solid (16 mg, 51.6%); R_f = 0.3 (Petroleum ether : acetone = 3 : 1); ^{1}H NMR (500 MHz, CD_3OD) δ 7.97 (d, *J* = 7.0 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.32 - 7.27 (m, 4H), 7.22 -7.14 (m, 1H), 5.66 - 5.63 (m, 1H), 3.28 (d, *J* = 9.0 Hz, 1H), 3.11 (dd, *J* = 16.0, 7.0 Hz, 1H). ^{13}C NMR (126 MHz, CD_3OD) δ174.7, 166.9, 155.2, 141.8, 129.7, 128.9, 128.2, 127.6, 125.8, 125.0, 123.2, 111.9, 110.0, 41.3, 39.1.

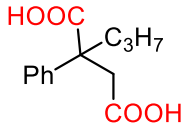
dimethyl 2-methyl-2-(pyridin-3-yl)succinate (2n)



Product **(2n)** was obtained as a yellow oil (18 mg, 38%); R_f = 0.5 (Petroleum ether : ethyl acetate = 1 : 1); ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 8.62 (s, 1H), 8.52 (d, *J* = 5.0 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.29 - 7.26 (m, 1H), 3.72 (s, 3H), 3.68 (s, 3H),

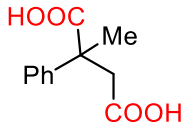
3.25 (d, J = 16.0 Hz, 1H), 2.88 (d, J = 16.5 Hz, 1H), 1.74 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ174.7, 171.1, 148.7, 147.7, 138.0, 133.8, 123.4, 52.8, 51.9, 47.1, 43.24, 23.2. HRMS (ESI) m/z calcd for $C_{12}H_{15}NO_4Na^+$ $(M+Na)^+$ 260.0901; found 260.0899.

2-butyl-2-phenylsuccinic acid (2o)[3]



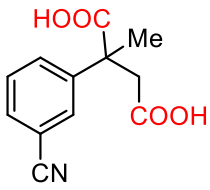
Product **(2o)** was obtained as a white solid (31 mg, 63%); R_f = 0.5 (Petroleum ether : Acetone = 3 : 1); ^{1}H NMR (400 MHz, CD_3OD) δ 7.37 - 7.30 (m, 4H), 7.25 - 7.21 (m, 1H), 3.20 (d, J = 16.0 Hz, 1H), 3.02 (d, J = 16.0 Hz, 1H), 2.24 - 2.09 (m, 2H), 1.20 - 1.01 (m, 2H), 0.87 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, CD_3OD) δ 178.6, 174.7, 143.2, 129.4, 127.9, 127.4, 52.8, 40.0, 38.9, 18.6, 14.8.

2-methyl-2-phenylsuccinic acid (2p)[2]



Product **(2p)** was obtained as a white solid (25 mg, 60%); R_f = 0.5 (Petroleum ether : Acetone = 3 : 1); ^{1}H NMR (400 MHz, CD_3OD) δ 7.42 - 7.40 (m, 2H), 7.35 - 7.31 (m,, 2H), 7.26 - 7.22 (m, 1H), 3.21 (d, J = 16.4 Hz, 1H), 2.82 (d, J = 16.4 Hz, 1H), 1.69 (s, 3H). ^{13}C NMR (100 MHz, CD_3OD) δ 178.8, 174.7, 144.7, 129.5, 128.0, 126.8, 49.2, 44.3, 24.0.

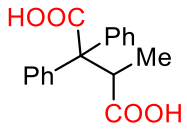
2-(3-cyanophenyl)-2-methylsuccinic acid (2q)



Product **(2q)** was obtained as a white solid (31 mg, 68%); mp: 140-141 °C; R_f = 0.4

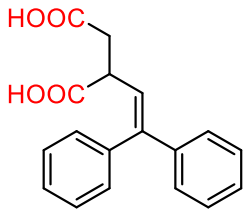
(Petroleum ether : Acetone = 3 : 1); ^{1}H NMR (400 MHz, CD_3OD) δ 7.78 - 7.74 (m, 2H), 7.64 - 7.62 (m, 1H), 7.54 - 7.50 (m, 1H), 3.15 (d, *J* = 16.8 Hz, 1H), 2.93 (d, *J* = 16.8 Hz, 1H), 1.72 (s, 3H). ^{13}C NMR (100 MHz, CD_3OD) δ 177.7, 174.1, 146.3, 132.2, 131.8, 131.0, 130.6, 119.7, 113.5, 44.0, 23.8. HRMS (ESI) m/z calcd for $C_{12}H_{10}NO_4^-$ $(M-H)^-$ 232.0615; found 232.0605.

3-methyl-2,2-diphenylsuccinic acid (2r)



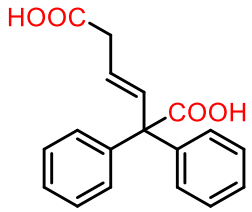
Product **(2r)** was obtained as a white solid (30 mg, 53%); mp: 138-139 ºC; R_f = 0.4 (Petroleum ether : Acetone = 2 : 1); ^{1}H NMR (400 MHz, CD_3OD) δ 7.40 - 7.22 (m, 10H), 4.15 (q, *J* = 7.2 Hz, 1H), 1.12 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, CD_3OD) δ 177.8, 177.3, 143.0, 141.7, 132.5, 130.7, 128.8, 128.1, 127.8, 127.7, 63.5, 45.2, 15.2. HRMS (ESI) m/z calcd for $C_{17}H_{16}O_4Na^+$ $(M+Na)^+$ 307.0941; found 307.0942.

2-(2,2-diphenylvinyl)succinic acid ($2s_a$)



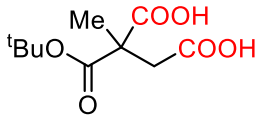
Product **($2s_a$)** was obtained as a white solid (22 mg, 37%); mp: 172-173 ºC; R_f = 0.3 (Petroleum ether : Acetone = 2 : 1); ^{1}H NMR (400 MHz, CD_3OD) δ 7.43 - 7.33 (m, 3H), 7.28 - 7.18 (m, 7H), 6.04 (d, *J* = 10.8 Hz, 1H), 3.59 - 3.53 (m, 1H), 2.81 - 2.75 (m, 1H), 2.54 - 2.49 (m, 1H). ^{13}C NMR (100 MHz, CD_3OD) δ 176.7, 174.9, 146.5, 143.3, 140.6, 130.9, 129.4, 129.2, 128.6, 128.4, 126.1, 43.7, 37.9. HRMS (ESI) m/z calcd for $C_{18}H_{16}O_4Na^+$ $(M+Na)^+$ 319.0941; found 319.0942.

(*E*)-2,2-diphenylhex-3-enedioic acid ($2s_b$)



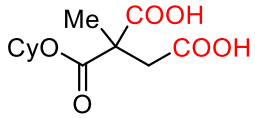
Product **(2sb)** was obtained as a white solid (10 mg, 17%); mp: 155-156 ºC; R_f = 0.4 (Petroleum ether : Acetone = 2 : 1); ^{1}H NMR (400 MHz, CD_3OD) δ 7.32 - 7.24 (m, 6H), 7.20 - 7.18 (m, 4H), 6.58 (d, *J* = 15.8 Hz, 1H), 5.07 - 5.00 (m, 1H), 3.13 (dd, *J* = 7.0, 0.8 Hz, 2H). ^{13}C NMR (100 MHz, CD_3OD) δ 177.2, 175.4, 143.1, 138.8, 130.6, 128.8, 128.1, 127.1, 65.2, 38.8. HRMS (ESI) m/z calcd for $C_{18}H_{15}O_4^-$ $(M-H)^-$ 295.0976; found 295.0961.

2-(tert-butoxycarbonyl)-2-methylsuccinic acid (2t)[2]



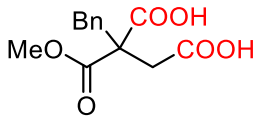
Product **(2t)** was obtained as a white solid (35 mg, 76%); R_f = 0.5 (Petroleum ether : Acetone = 3 : 1); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 3.01 (2H, ABq, *J* = 17.2 Hz), 1.54 (s, 3H), 1.46 (s, 9H).^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 175.6, 172.0, 83.9, 51.2, 40.1, 27.6, 21.9.

2-((cyclohexyloxy)carbonyl)-2-methylsuccinic acid (2u)[2]



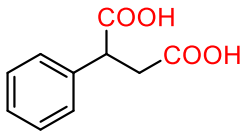
Product **(2u)** was obtained as a white solid (42 mg, 82%); R_f = 0.3 (Petroleum ether : Acetone = 3 : 1); ^{1}H NMR (400 MHz, CD_3OD) δ 4.84 - 4.78 (m, 1H), 2.97 (d, *J* = 16.8 Hz, 1H), 2.83 (d, *J* = 17.2 Hz, 1H), 1.80 - 1.70 (m, 4H), 1.53 - 1.44 (m, 6H), 1.42 - 1.29 (m, 3H). ^{13}C NMR (100 MHz, CD_3OD) δ 174.6, 173.9, 172.4, 74.7, 52.8, 40.9, 32.0, 26.5, 24.2, 20.8.

2-benzyl-2-(methoxycarbonyl)succinic acid (2v)



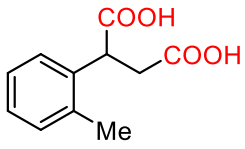
Product **(2v)** was obtained as a white solid (21 mg, 40%); mp: 134-135 ºC; R_f = 0.4 (Petroleum ether : Acetone = 3 : 1); ^{1}H NMR (400 MHz, CD_3OD) δ 7.29 - 7.21 (m, 3H), 7.12 - 7.10 (m, 2H), 3.73 (s, 3H), 3.38 (dd, *J* = 31.6, 14.0 Hz, 2H), 2.76 (dd, *J* = 44.0, 17.6 Hz, 2H). ^{13}C NMR (100 MHz, CD_3OD) δ 174.1, 172.9, 172.5, 137.4, 131.1, 129.4, 128.2, 57.7, 53.1, 39.5, 37.3. HRMS (ESI) m/z calcd for $C_{13}H_{13}O_6^-$ $(M-H)^-$ 265.0718; found 265.0708.

2-phenylsuccinic acid (4a)[2]



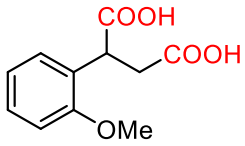
Product **(4a)** was obtained as a white solid (28 mg, 72%); R_f = 0.3 (Petroleum ether : Acetone = 2 : 1); ^{1}H NMR (400 MHz, CD_3OD) δ 7.35 - 7.25 (m, 5H), 4.01 (dd, *J* = 10.0, 5.2 Hz, 1H), 3.10 (dd, *J* = 16.8, 10.4 Hz, 1H), 2.62 (dd, *J* = 16.8, 5.2 Hz, 1H). ^{13}C NMR (100 MHz, CD_3OD) δ 176.6, 175.2, 139.9, 129.8, 128.9, 128.5, 48.7, 38.7.

2-(*o*-tolyl)succinic acid (4b)[2]



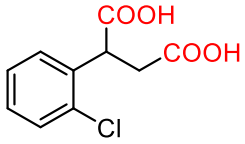
Product **(4b)** was obtained as a white solid (30 mg, 72%); R_f = 0.5 (Petroleum ether : Acetone = 3 : 1); ^{1}H NMR (400 MHz, CD_3OD) δ 7.23 - 7.11(m, 4H), 4.32 (dd, *J* = 10.0, 5.2 Hz, 1H), 3.08 (dd, *J* = 17.2, 10.0 Hz, 1H), 2.57 (dd, *J* = 16.8, 5.2 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, CD_3OD) δ 176.8, 175.4, 138.3, 137.4, 131.7, 128.3, 127.6, 127.4, 44.2, 38.1, 19.8.

2-(2-methoxyphenyl)succinic acid (4c)



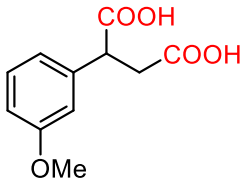
Product **(4c)** was obtained as a white solid (35 mg, 78%) (42 mg, 94%, note：the reaction temperature is 40 to 45°C); mp: 177-178 °C; R_f = 0.5 (Petroleum ether : Acetone = 3 : 1); ^{1}H NMR (400 MHz, CD_3OD) δ 7.27 - 7.23 (m, 1H), 7.18 - 7.16 (m, 1H), 6.98 - 6.96 (m, 1H), 6.92 - 6.88 (m 1H), 4.35 (dd, *J* = 9.6, 5.2 Hz, 1H), 3.83 (s, 3H), 3.01 (dd, *J* = 16.8, 9.6 Hz, 1H), 2.52 (dd, *J* = 16.8, 5.2 Hz, 1H). ^{13}C NMR (100 MHz, CD_3OD) δ 177.0, 175.7, 158.3, 129.8, 128.4, 121.7, 112.1, 56.0, 43.2, 37.5. HRMS (ESI) m/z calcd for $C_{11}H_{11}O_5^-$ $(M-H)^-$ 223.0612; found 223.0602.

2-(2-chlorophenyl)succinic acid (4d)[4]



Product **(4d)** was obtained as a white solid (22 mg, 48%); R_f = 0.5 (Petroleum ether : Acetone = 3 : 1); ^{1}H NMR (400 MHz, CD_3OD) δ 7.44 -7.41 (m, 1H), 7.35 - 7.24 (m, 3H), 4.56 (dd, *J* = 10.0, 5.2 Hz, 1H), 3.05 (dd, *J* = 17.2, 10.0 Hz, 1H), 2.61 (dd, *J* = 16.8, 4.8 Hz, 1H). ^{13}C NMR (100 MHz, CD_3OD) δ 175.7, 174.9, 137.7, 134.9, 130.9, 130.1, 130.0, 128.5, 45.4, 37.6.

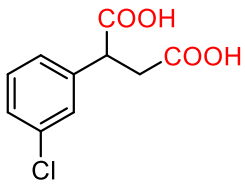
2-(3-methoxyphenyl)succinic acid (4e)[5]



Product **(4e)** was obtained as a white solid (35 mg, 78%); R_f = 0.5 (Petroleum ether : Acetone = 3 : 1); ^{1}H NMR (400 MHz, CD_3OD) δ 7.25 - 7.21 (m, 1H), 6.89 - 6.81 (m, 3H), 3.99 (dd, *J* = 10.0, 5.2 Hz, 1H), 3.77 (s, 3H), 3.09 (dd, *J* = 16.8, 10.0 Hz, 1H), 2.62 (dd, *J* = 16.8, 5.2 Hz, 1H). ^{13}C NMR (100 MHz, CD_3OD) δ 176.5, 175.2, 161.3,

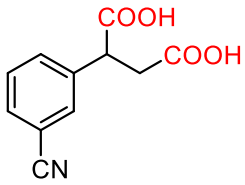
141.2, 130.8, 121.0, 114.6, 113.9, 55.6, 48.6, 38.7.

2-(3-chlorophenyl)succinic acid (4f)[2]



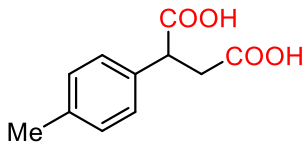
Product **(4f)** was obtained as a white solid (33 mg, 73%); R_f = 0.5 (Petroleum ether : Acetone = 3 : 1); ^{1}H NMR (400 MHz, CD_3OD) δ 7.35 - 7.24 (m, 4H), 4.02 (dd, *J* = 10.0, 5.6 Hz, 1H), 3.09 (dd, *J* = 16.8, 9.6 Hz, 1H), 2.65 (dd, *J* = 16.8, 5.6 Hz, 1H). ^{13}C NMR (100 MHz, CD_3OD) δ 175.9, 174.8, 142.1, 135.5, 131.3, 129.1, 128.6, 127.4, 48.3, 38.4.

2-(3-cyanophenyl)succinic acid (4g)



Product **(4g)** was obtained as a white solid (31 mg, 71%); mp: 180-181 ºC; R_f = 0.3 (Petroleum ether : Acetone = 3 : 1); ^{1}H NMR (400 MHz, CD_3OD) δ 7.70 - 7.63 (m, 3H), 7.53 - 7.49 (m, 1H), 4.11 (dd, *J* = 9.2, 5.6 Hz, 1H), 3.12 (dd, *J* = 17.2, 9.6 Hz, 1H), 2.69 (dd, *J* = 16.8, 5.6 Hz, 1H). ^{13}C NMR (100 MHz, CD_3OD) δ 175.5, 174.7, 141.6, 133.9, 132.8, 132.3, 130.9, 119.5, 113.7, 48.4, 38.2. HRMS (ESI) m/z calcd for $C_{11}H_8NO_4^-$ $(M-H)^-$ 218.0459; found 218.0446.

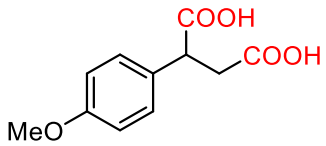
2-(*p*-tolyl)succinic acid (4h)[2]



Product **(4h)** was obtained as a white solid (25 mg, 62%); R_f = 0.4 (Petroleum ether : Acetone = 3 : 1); ^{1}H NMR (400 MHz, CD_3OD) δ 7.20 - 7.12 (m, 4H), 3.97 (dd, *J* =

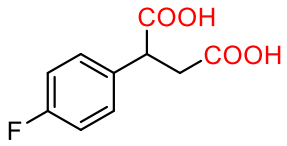
10.0, 5.2 Hz, 1H), 3.08 (dd, *J* = 17.2, 10.4 Hz, 1H), 2.59 (dd, *J* = 16.8, 5.2 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, CD_3OD) δ 176.8, 175.2, 138.3, 136.8, 130.4, 128.7, 48.2, 38.8, 21.1.

2-(4-methoxyphenyl)succinic acid (4i)[6]



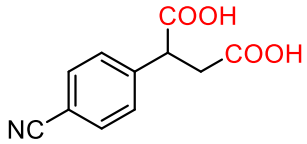
Product **(4i)** was obtained as a white solid (25 mg, 56%); R_f = 0.5 (Petroleum ether : Acetone = 3 : 1); ^{1}H NMR (400 MHz, CD_3OD) δ 7.24 - 7.21 (m, 2H), 6.89 - 6.85 (m, 2H), 3.95 (dd, *J* = 10.0, 5.2 Hz, 1H), 3.76 (s, 3H), 3.07 (dd, *J* = 17.2, 10.0 Hz, 1H), 2.59 (dd, *J* = 17.2, 5.2 Hz, 1H). ^{13}C NMR (100 MHz, CD_3OD) δ 176.9, 175.3, 160.5, 131.7, 129.9, 115.1, 55.7, 47.8, 38.8.

2-(4-fluorophenyl)succinic acid (4j)[2]



Product **(4j)** was obtained as a white solid (25.5 mg, 60%); R_f = 0.3 (Petroleum ether : Acetone = 3 : 1); ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 12.39 (br, 2H), 7.35 - 7.31 (m, 2H), 7.17 - 7.13 (m, 2H), 3.91 (dd, *J* = 10.0, 5.2 Hz, 1H), 2.94 (dd, *J* = 17.2, 10.4 Hz, 1H), 2.57 - 2.53 (m, 1H). ^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 174.0, 172.6, 161.4 (d, *J* = 242 Hz), 134.9 (d, *J* = 3.0 Hz), 129.8 (d, *J* = 8.1 Hz), 115.4 (d, *J* = 21.1 Hz), 46.1, 37.4. ^{19}F NMR (376 MHz, DMSO) δ -115.6.

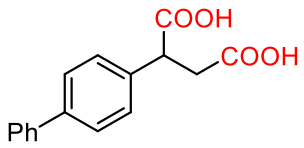
2-(4-cyanophenyl)succinic acid (4k)[2]



Product **(4k)** was obtained as a white solid (28 mg, 65%); R_f = 0.4 (Petroleum ether : Acetone = 3 : 1); ^{1}H NMR (400 MHz, CD_3OD) δ 7.71 - 7.69 (m, 2H), 7.54 - 7.52 (m,

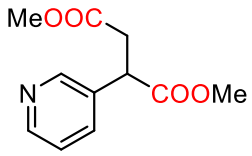
2H), 4.15 - 4.11 (m, 1H), 3.16 - 3.10 (m, 1H), 2.72 - 2.66 (m, 1H). ^{13}C NMR (100 MHz, CD_3OD) δ 175.3, 174.6, 145.5, 133.6, 130.2, 119.5, 112.3, 48.6, 48.4.

2-([1,1'-biphenyl]-4-yl)succinic acid (4l)[2]



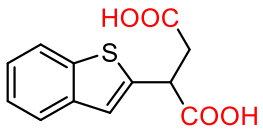
Product **(4l)** was obtained as a white solid (36 mg, 66%); R_f = 0.5 (Petroleum ether : acetone = 3 : 1); ^{1}H NMR (400 MHz, CD_3OD) δ 7.60 - 7.57 (m, 4H), 7.43 - 7.39 (m, 4H), 7.34 - 7.30 (m, 1H), 4.07 (dd, *J* = 10.0, 5.2 Hz, 1H), 3.14 (dd, *J* = 16.8, 10.0 Hz, 1H), 2.67 (dd, *J* = 16.8, 5.2 Hz, 1H). ^{13}C NMR (100 MHz, CD_3OD) δ 176.6, 175.2, 141.9, 141.7, 138.9, 129.9, 129.4, 128.4, 128.3, 127.9, 48.3, 38.7.

dimethyl 2-(pyridin-3-yl)succinate (4m)[7]



Product **(4m)** was obtained as a yellow oil (18 mg, 40%); R_f = 0.5 (Petroleum ether : ethyl acetate = 1 : 1); ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 8.56 - 8.54 (m, 2H), 7.64 - 7.61 (m, 1H), 7.29 - 7.26 (m, 1H), 4.13 (dd, *J* = 9.5, 6.0 Hz, 1H), 3.69 (d, *J* = 9.5 Hz, 6H), 3.22 (dd, *J* = 17.0, 9.5 Hz, 1H), 2.71 (dd, *J* = 17.0, 6.0 Hz, 1H).^{13}C NMR (126 MHz, $CDCl_3$) δ 172.8, 171.6, 149.6, 149.3, 135.2, 133.5, 123.8, 52.7, 52.2, 44.8, 37.3.

2-(benzo[b]thiophen-2-yl)succinic acid (4n)[2]

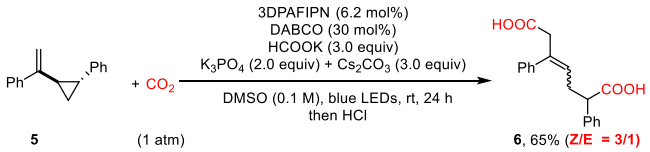


Product **(4n)** was obtained as a colourless oil (16 mg, 32%); R_f = 0.5 (Petroleum ether : acetone = 3 : 1); ^{1}H NMR (400 MHz, CD_3OD) δ 7.83 - 7.71 (m, 2H), 7.36 - 7.22 (m, 3H), 4.39 (dd, *J* = 10.0, 5.2 Hz, 1H), 3.21 (dd, *J* = 16.8, 9.6 Hz, 1H), 2.87 (dd, *J* = 16.8, 5.2 Hz, 1H). ^{13}C NMR (126 MHz, CD_3OD) δ 175.4, 174.7, 142.8, 141.0,

140.8, 125.4, 125.3, 124.4, 123.4, 123.1, 44.9, 39.0. HRMS (ESI) m/z calcd for $C_{12}H_9SO_4^-$ $(M-H)^-$ 249.0224; found 249.0222.

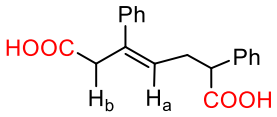
4. Mechanistic Experiments and Product Application

Radical clock experiment



4-(2-(1-phenylvinyl)cyclopropyl)-1,1'-biphenyl was synthesized following the literature procedures[8]. An oven-dried Schlenk tube (25 mL) containing a stirring bar was cooled to room temperature. The Schlenk tube was then introduced in a glovebox, where it was charged with K_3PO_4 (85.5 mg, 0.4 mmol, 2.0 equiv), Cs_2CO_3 (195.5 mg, 0.6 mmol, 3.0 equiv), HCOOK (50.5 mg, 0.6 mmol, 3.0 equiv), 3DPAFIPN (8.0 mg, 6.2 mol%), DABCO (6.8 mg, 30 mol%). The tube was taken out of the glovebox. Subsequently, the degassed anhydrous DMSO (2 mL, 0.1 M) and the 4-(2-(1-phenylvinyl)cyclopropyl)-1,1'-biphenyl (44.1 mg, 0.2 mmol) were added into the tube via syringe. Then the tube was evacuated and back-filled with CO_2 for 10 times. Finally, the tube was placed under 30 W blue LEDs (λ = 450 - 455 nm, 3.0 cm - 4.5 cm away from the LEDs, with fans to keep the reaction temperature at 25 - 33 °C) light source and stirred for 24 h. Then, the mixture was quenched with H_2O and 2 mL of HCl (2 N), extracted with EtOAc three times. The resulting solution was concentrated by rotary evaporation. The residual was purified by column chromatography on silica gel to give the desired product **6** as a colorless oil; R_f = 0.4 (Petroleum ether : ethyl acetate = 1 : 1);. ^{1}H NMR (400 MHz, CD_3OD) δ 7.39 - 7.17 (m, 11.5H), 7.10 - 7.08 (m, 2H), 5.84 (t, *J* = 7.4 Hz, 0.33H), 5.58 (t, *J* = 7.3 Hz, 1H), 3.76 (t, *J* = 7.7 Hz, 0.34H), 3.57 (t, *J* = 7.6 Hz, 1H), 3.48 (0.71H, ABq, *J* = 16.0 Hz), 3.25 (s, 1.9H), 3.01 - 2.94 (m, 0.33H), 2.72 - 2.64 (m, 1.34H), 2.48 - 2.41 (m, 1H). ^{13}C NMR (100 MHz, CD_3OD) δ 177.1, 177.1 , 175.2, 175.1, 143.6, 140.9, 140.5, 140.2, 137.6, 136.1, 129.8, 129.6, 129.5, 129.5, 129.4, 129.2, 129.1, 129.1, 128.3, 128.2,

128.1, 128.0, 127.0, 52.9, 52.6, 36.7, 34.0. HRMS (ESI) m/z calcd for $C_{19}H_{18}NaO_4^+$ $(M+Na)^+$ 333.1097; found 333.1096.



1D selective NOE

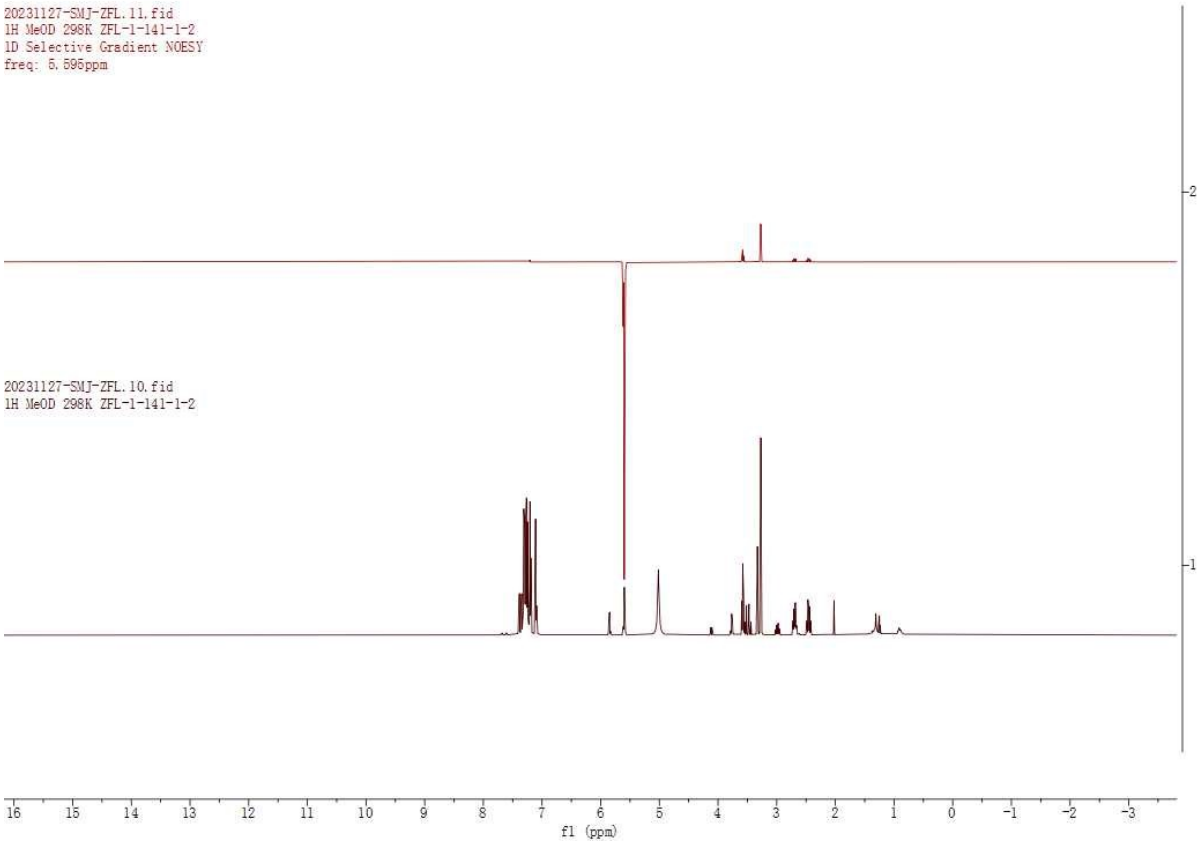
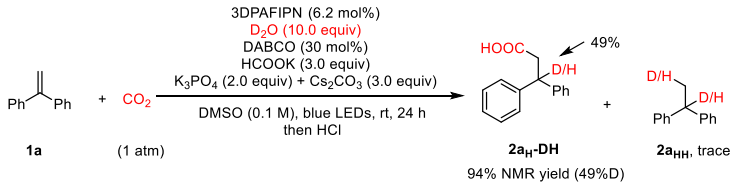


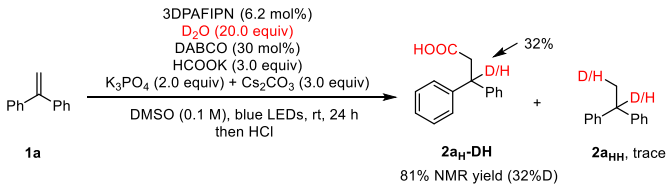
Figure S1. 1D selective NOE of **6**.

Reactions in the presence of D_2O



An oven-dried Schlenk tube (25 mL) containing a stirring bar was cooled to room temperature. The Schlenk tube was then introduced in a glovebox, where it was

charged with K_3PO_4 (85.5 mg, 0.4 mmol, 2.0 equiv), Cs_2CO_3 (195.5 mg, 0.6 mmol, 3.0 equiv), HCOOK (50.5 mg, 0.6 mmol, 3.0 equiv), 3DPAFIPN (8.0 mg, 6.2 mol%), DABCO (6.8 mg, 30 mol%). The tube was taken out of the glovebox. Subsequently, D_2O (40 mg, 10 equiv), the degassed anhydrous DMSO (2 mL, 0.1 M) and the **1a** (36.05 mg, 0.2 mmol) were added into the tube via syringe. Then the tube was evacuated and back-filled with CO_2 for 10 times. Finally, the tube was placed under 30 W blue LEDs (λ = 450 - 455 nm, 3.0 cm - 4.5 cm away from the LEDs, with fans to keep the reaction temperature at 25 - 33 °C) light source and stirred for 24 h. Then, the mixture was quenched with H_2O and 2 mL of HCl (2 N), extracted with EtOAc three times. The resulting solution was concentrated by rotary evaporation. The residual was purified by column chromatography on silica gel to give the desired product **$2a_H$-DH (**30 mg, 65%**).** ^{1}H NMR (400 MHz, CD_3OD) δ 7.27 - 7.23 (m, 8H), 7.19 - 7.13 (m, 2H), 4.50 (t, *J* = 8.0 Hz, 0.51H), 3.05 - 3.03 (m, 2H). ^{13}C NMR (100 MHz, CD_3OD) δ 175.7, 145.3, 145.2, 129.5, 128.8, 128.7, 127.4, 48.5, 41.5, 41.4.



An oven-dried Schlenk tube (25 mL) containing a stirring bar was cooled to room temperature. The Schlenk tube was then introduced in a glovebox, where it was charged with K_3PO_4 (85.5 mg, 0.4 mmol, 2.0 equiv), Cs_2CO_3 (195.5 mg, 0.6 mmol, 3.0 equiv), HCOOK (50.5 mg, 0.6 mmol, 3.0 equiv), 3DPAFIPN (8.0 mg, 6.2 mol%), DABCO (6.8 mg, 30 mol%). The tube was taken out of the glovebox. Subsequently, D_2O (80 mg, 20 equiv), the degassed anhydrous DMSO (2 mL, 0.1 M) and the **1a** (36.05 mg, 0.2 mmol) were added into the tube via syringe. Then the tube was evacuated and back-filled with N_2 for 10 times. Finally, the tube was placed under 30 W blue LEDs (λ = 450 - 455 nm, 3.0 cm - 4.5 cm away from the LEDs, with fans to keep the reaction temperature at 25 - 33 °C) light source and stirred for 24 h. Then, the mixture was quenched with H_2O and 2 mL of HCl (2 N), extracted with EtOAc three times. The resulting solution was concentrated by rotary evaporation and the

yield of crude products was determined via ^1H NMR using CH_2Br_2 as internal standard.

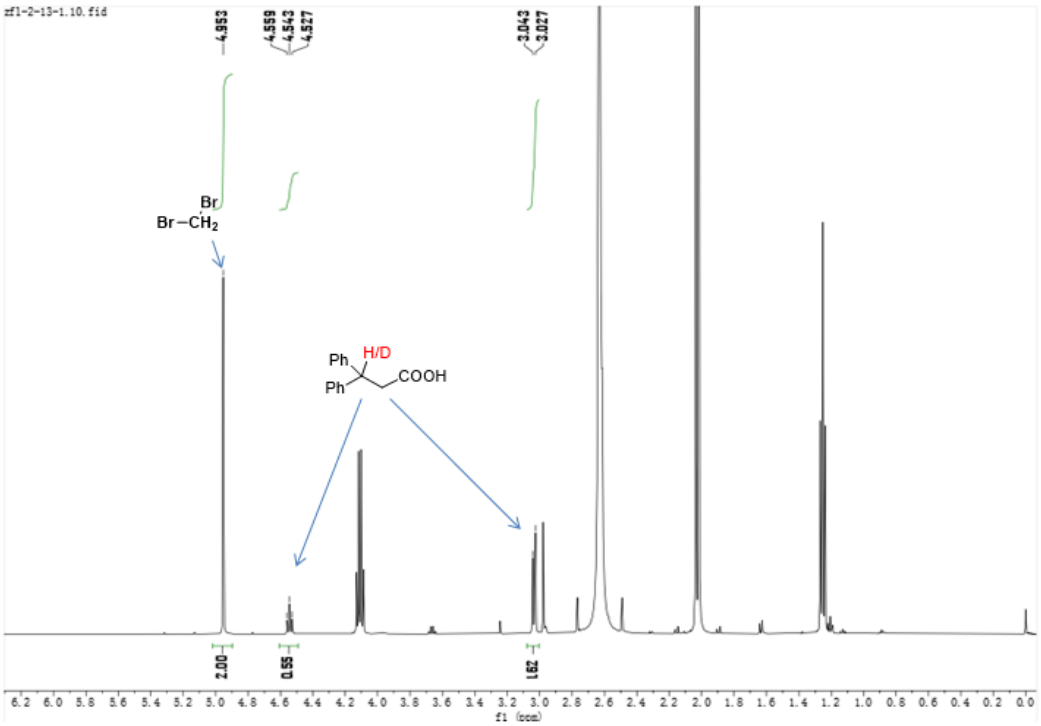
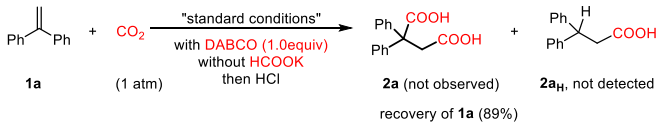


Figure S2. Reaction in the presence of D_2O.

The reaction in the absence of HCOOK



An oven-dried Schlenk tube (25 mL) containing a stirring bar was cooled to room temperature. The Schlenk tube was then introduced in a glovebox, where it was charged with K_3PO_4 (85.5 mg, 0.4 mmol, 2.0 equiv), Cs_2CO_3 (195.5 mg, 0.6 mmol, 3.0 equiv), HCOOK (50.5 mg, 0.6 mmol, 3.0 equiv), 3DPAFIPN (8.0 mg, 6.2 mol%), DABCO (6.8 mg, 30 mol%). The tube was taken out of the glovebox. Subsequently, the degassed anhydrous DMSO (2 mL, 0.1 M) and the **1a** (36.05 mg, 0.2 mmol) were added into the tube via syringe. Then the tube was evacuated and back-filled with CO_2 for 10 times. Finally, the tube was placed under 30 W blue LEDs (λ = 450 - 455 nm, 3.0 cm - 4.5 cm away from the LEDs, with fans to keep the reaction temperature at 25 - 33 °C) light source and stirred at ambient temperature for 24 h. Then, the

mixture was quenched with H_2O and 2 mL of HCl (2 N), extracted with EtOAc three times. The resulting solution was concentrated by rotary evaporation and the yield of crude products was determined via ^1H NMR using CH_2Br_2 as internal standard.

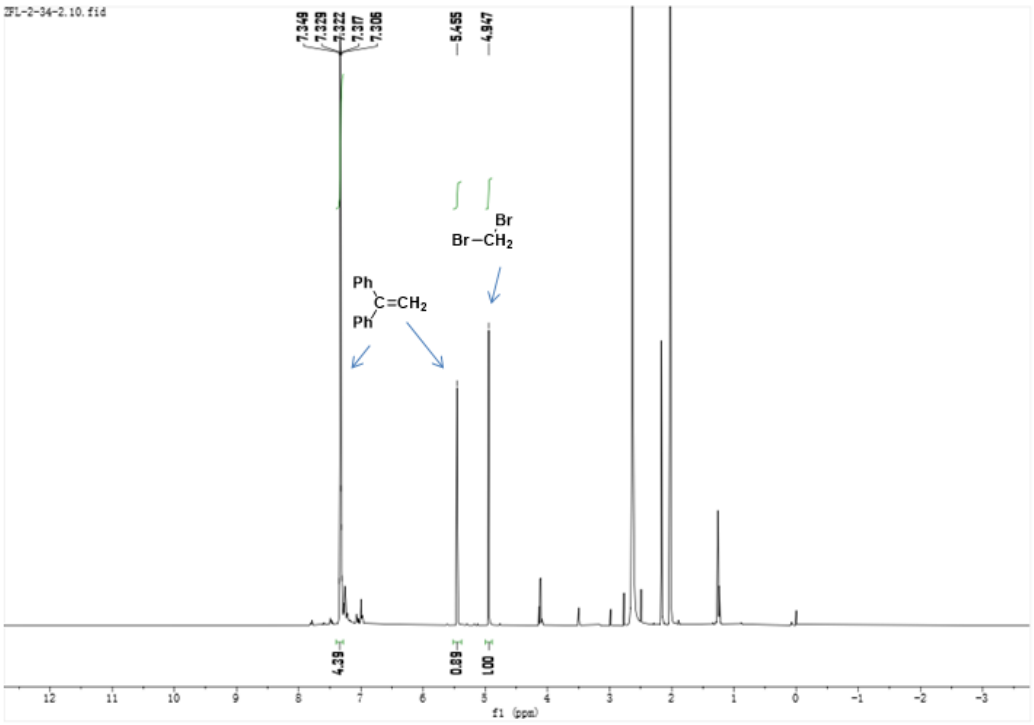
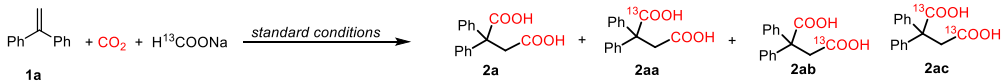


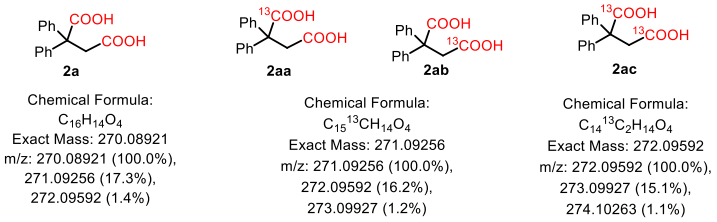
Figure S3. The reaction in the absence of HCOOK.

^{13}C-labelling experiment using commercially available $H^{13}COONa$



An oven-dried Schlenk tube (25 mL) containing a stirring bar was cooled to room temperature. The Schlenk tube was then introduced in a glovebox, where it was charged with K_3PO_4 (85.5 mg, 0.4 mmol, 2.0 equiv), Cs_2CO_3 (195.5 mg, 0.6 mmol, 3.0 equiv), $H^{13}COONa$ (40.8 mg, 0.6 mmol, 3.0 equiv), 3DPAFIPN (8.0 mg, 6.2 mol%), DABCO (6.8 mg, 30 mol%). The tube was taken out of the glovebox. Subsequently, the degassed anhydrous DMSO (2 mL, 0.1 M) and the **1a** (36.05 mg, 0.2 mmol) were added into the tube via syringe. Then the tube was evacuated and back-filled with CO_2 for 10 times. Finally, the tube was placed under 30 W blue LEDs (λ = 450 - 455 nm, 3.0 cm - 4.5 cm away from the LEDs, with fans to keep the

reaction temperature at 25 - 33 °C) light source and stirred for 24 h. Then, the mixture was quenched with H_2O and 2 mL of HCl (2 N), extracted with EtOAc three times. The resulting solution was concentrated by rotary evaporation. The residual was purified by column chromatography on silica gel to give the desired products **2a+(2aa/2ab)+2ac** (37 mg, 68%). ^{1}H NMR (400 MHz, CD_3OD) δ 7.34 - 7.19 (m, 5H), 3.49 (s, 1H). ^{13}C NMR (100 MHz, CD_3OD) δ 176.6, 174.3, 144.5, 129.9, 128.8, 127.8, 58.5, 49.6, 44.7.



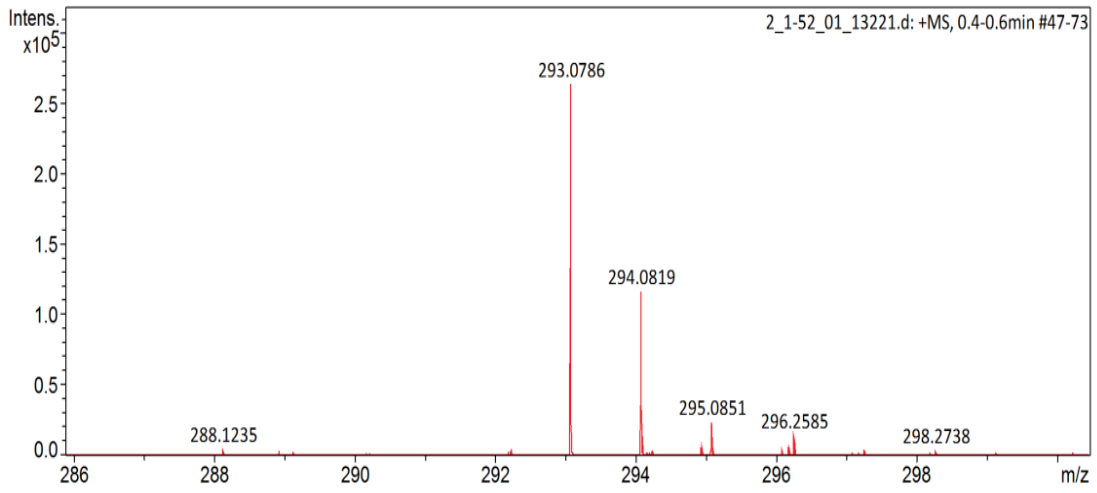
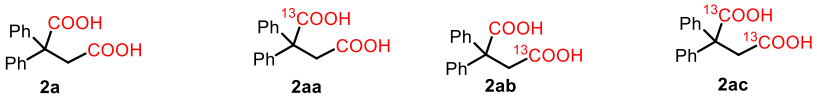


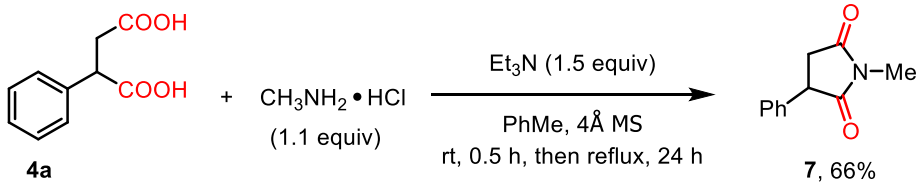
Figure S4. The products were detected by HR-MS.

m/z	Abundance
293.0786	875014
294.0819	388090
295.0851	78504



2a : (**2aa**+**2ab**) : **2ac** = 81 : 14 : 5

The Application of the Reaction



An oven-dried reaction tube (10 mL) containing a stirring bar was charged with **4a** (0.2 mmol, 38.8 mg), CH_3NH_2·HCl (0.22 mmol, 14.9 mg) and 4Å Molecular sieves powder (200 mg). After degassed and filled with dry nitrogen repeated three times, Et_3N (0.3 mmol, 30.4 mg) and toluene (2 mL) were added via syringe. The reaction solution was stirred for 0.5 h at room temperature and then heated to reflux for 24 h. The reaction mixture was filtered through a short pad of celite. After removing the solvent under reduced pressure, the residual was purified by silica gel column chromatography to obtain product **7** (25 mg, 66%).[9] ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.39 - 7.36 (m, 2H), 7.33 - 7.30 (m, 1H), 7.22 (d, J = 7.0 Hz, 2H), 4.03 (dd, J = 9.5, 4.5 Hz, 1H), 3.21 (dd, J = 18.5, 9.5 Hz, 1H), 3.07 (s, 1H), 2.84 (dd, J = 18.5, 5.0 Hz, 1H).^{13}C NMR (126 MHz, $CDCl_3$) δ 177.97, 176.40, 137.18, 129.33, 128.10, 127.51, 46.07, 37.25, 25.35.

Stern-Volmer fluorescence quenching experiments

Fluorescence spectra were collected on Edinburgh FS5 spectrofluorimeter. Samples for the quenching experiments were prepared in a 4 mL glass cuvette with a septum screw cap. 3DPAFIPN was irradiated at 420 nm and the emission intensity at 550 nm was observed. In a typical experiment, the emission spectrum of a 5.0×10^{-5} M solution of 3DPAFIPN in DMSO was collected.

DABCO: A stock solution of DABCO (56.1 mg, 0.5 mmol) in 5 ml of DMSO was prepared. Then, different amounts of this stock solution were added to a solution of the 3DPAFIPN in DMSO (5.0×10^{-5} M).

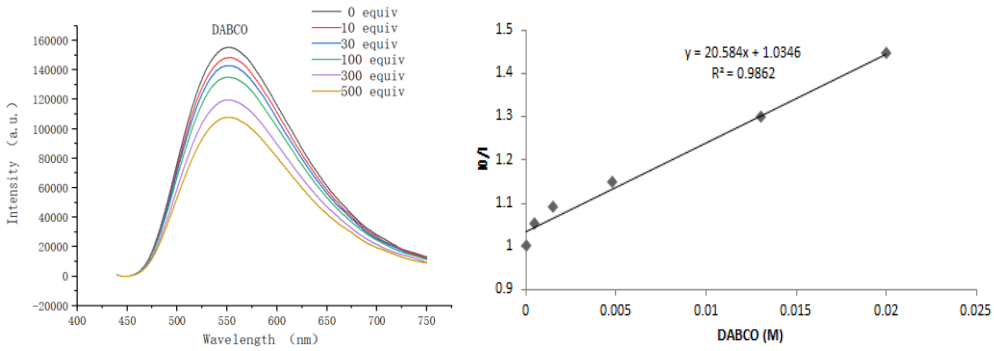


Figure S5. Stern-Volmer quenching by DABCO.

HCOOK: A stock solution of HCOOK (42.1 mg, 0.5 mmol) in 10 ml of DMSO was prepared. Then, different amounts of this stock solution were added to a solution of the 3DPAFIPN in DMSO (5.0×10^{-5} M).

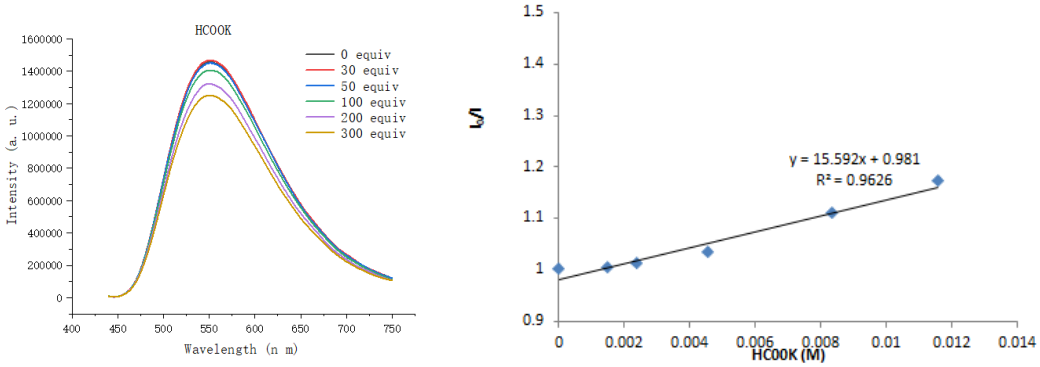


Figure S6. Stern-Volmer quenching by HCOOK.

1a: A stock solution of **1a** (90.1 mg, 0.5 mmol) in 5 ml of DMSO was prepared. Then, different amounts of this stock solution were added to a solution of the 3DPAFIPN in DMSO (5.0×10^{-5} M).

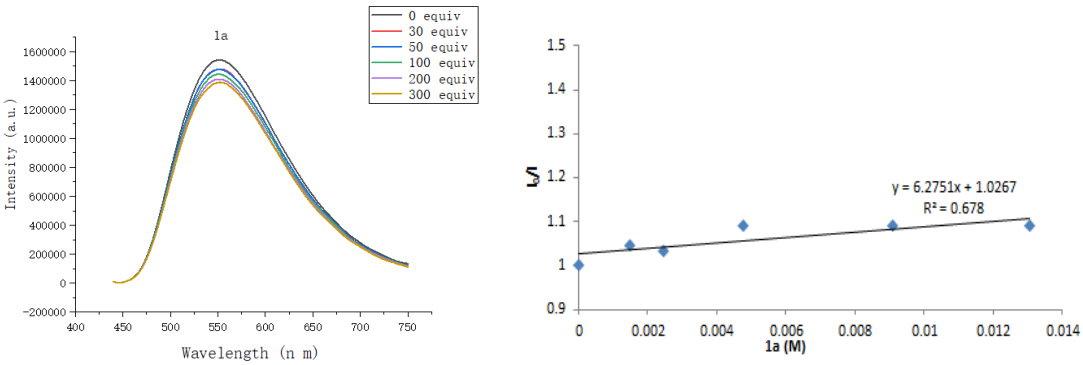


Figure S7. Stern-Volmer quenching by **1a**.

5. References

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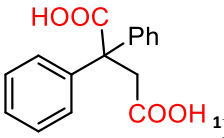
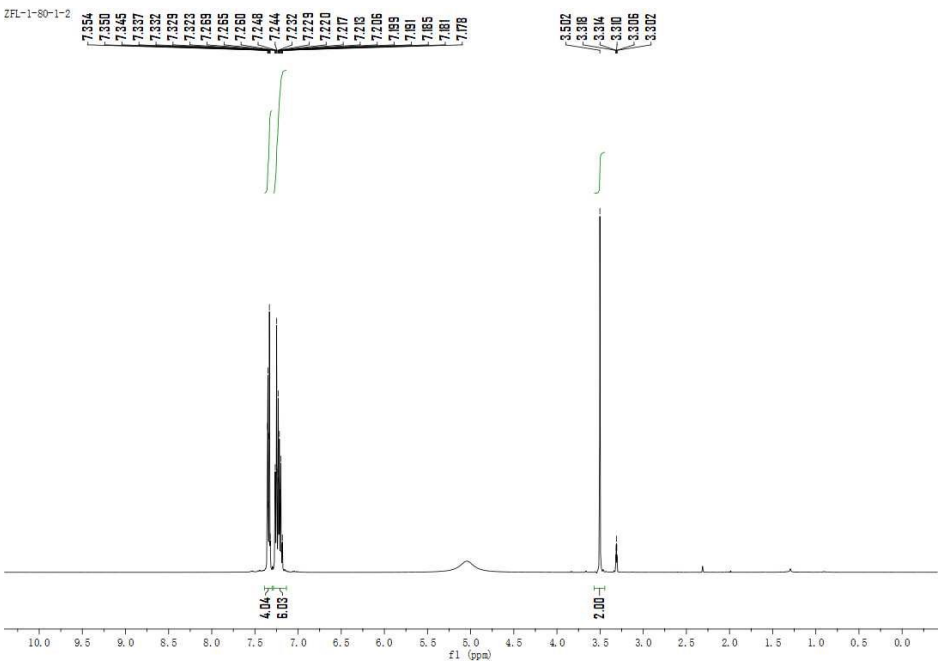
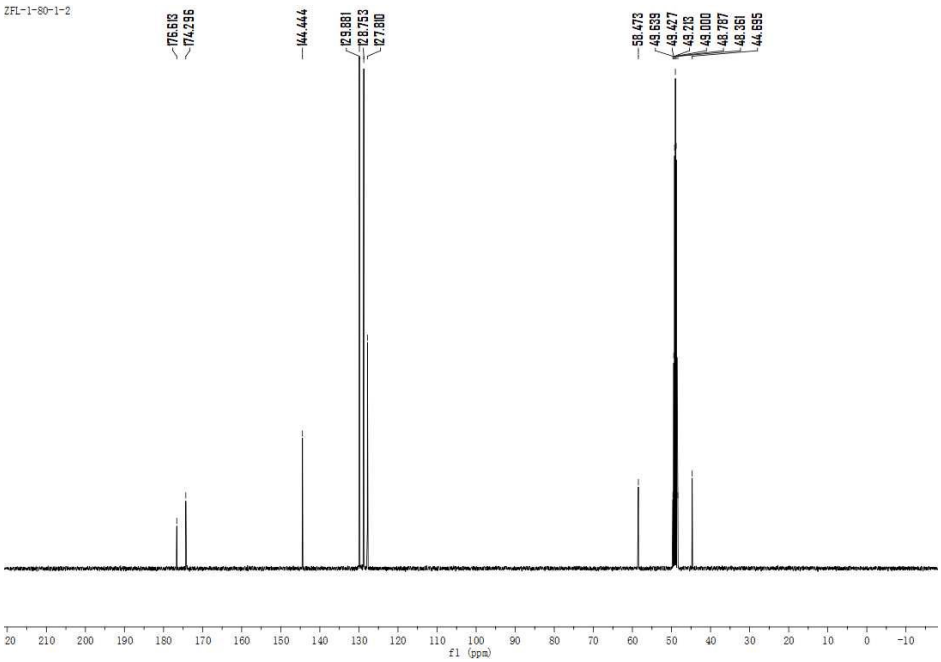
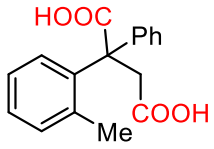
6. Copies of ^{1}H and ^{13}C NMR spectra



^{1}H NMR and ^{13}C NMR spectra of 2a







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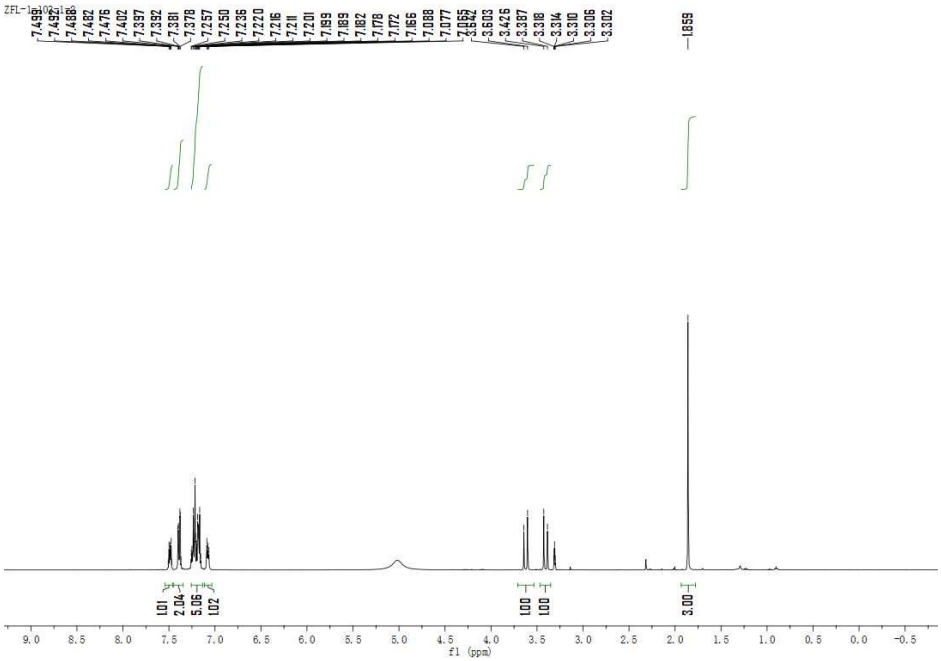
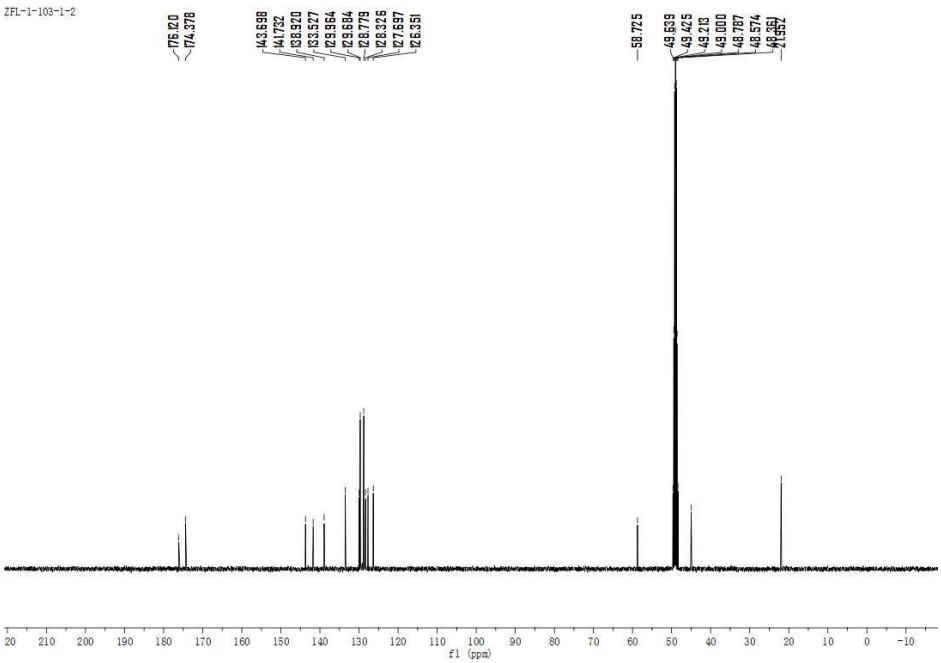
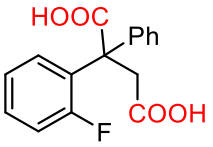
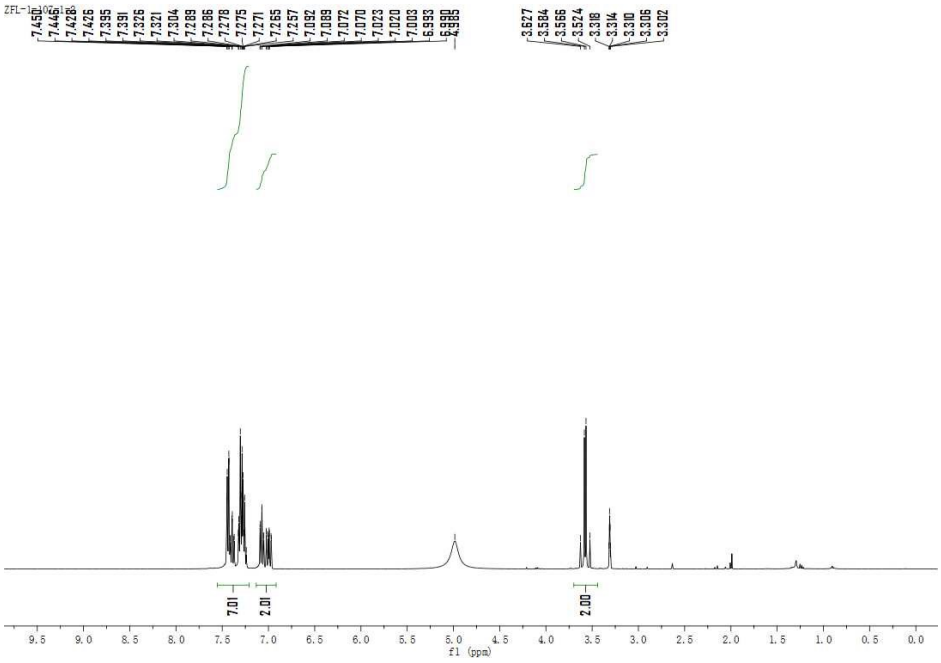
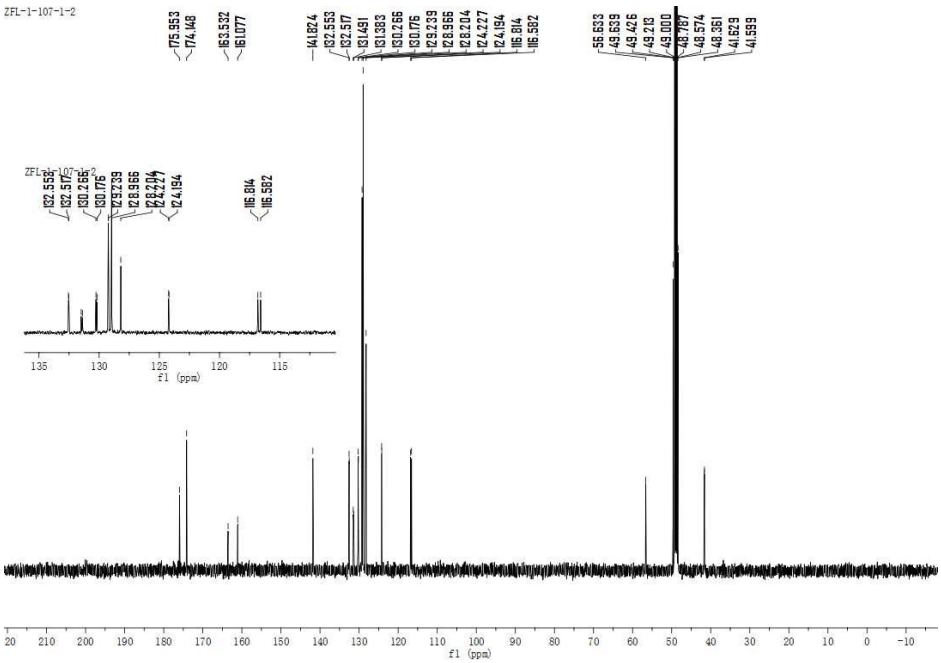


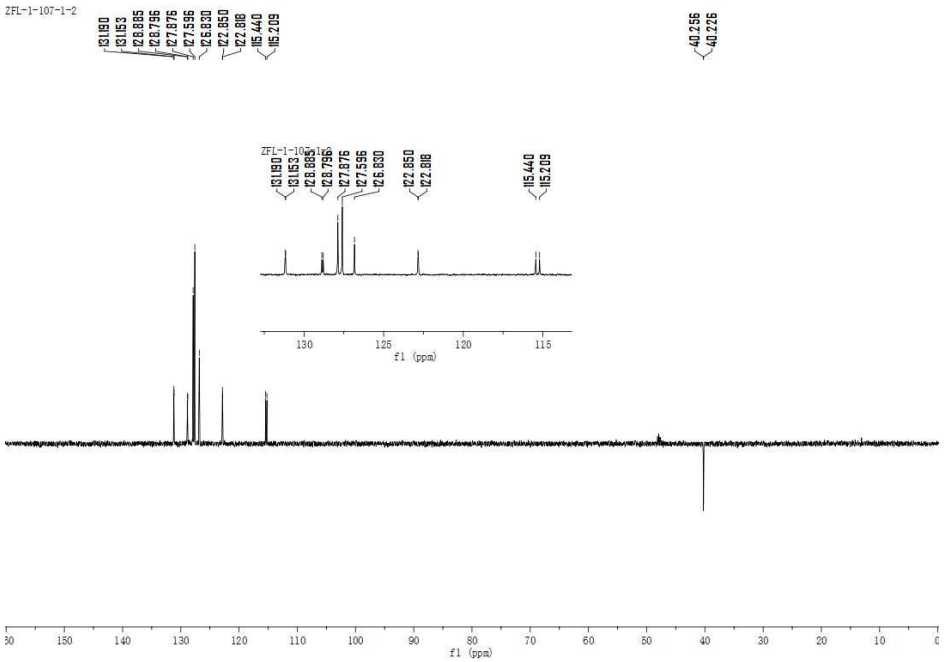




^{1}H NMR and ^{13}C NMR, DEPT-135^{o}, ^{19}F NMR spectra of 2c



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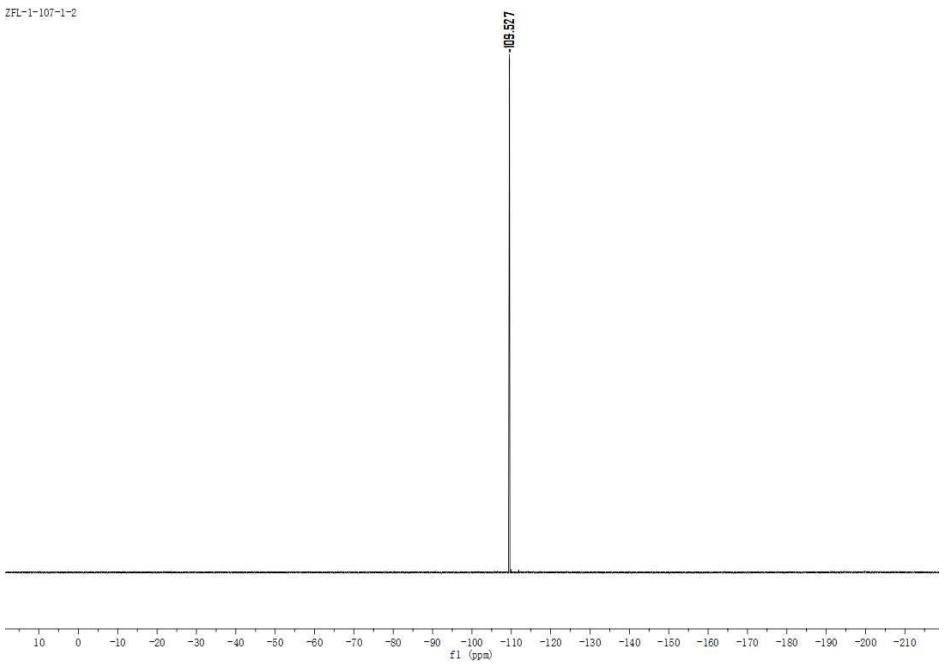
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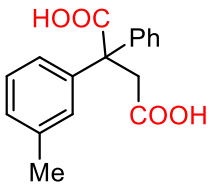

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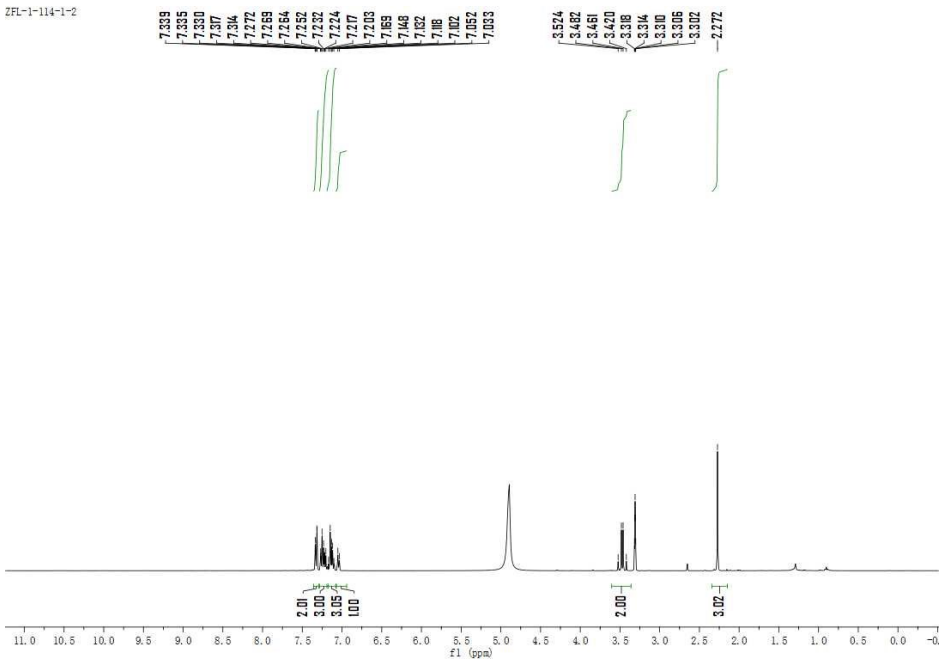
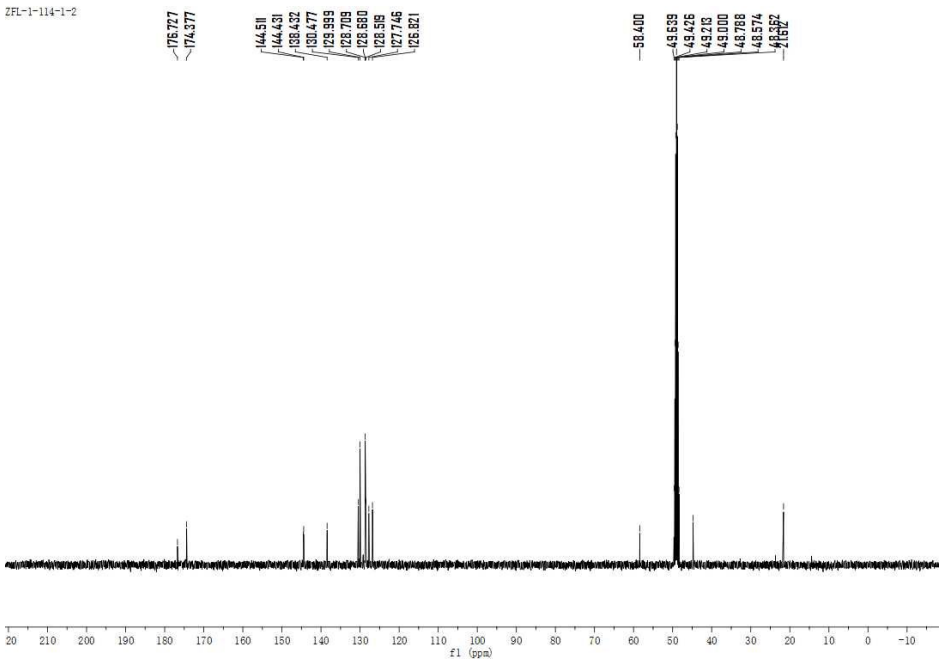
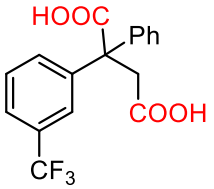
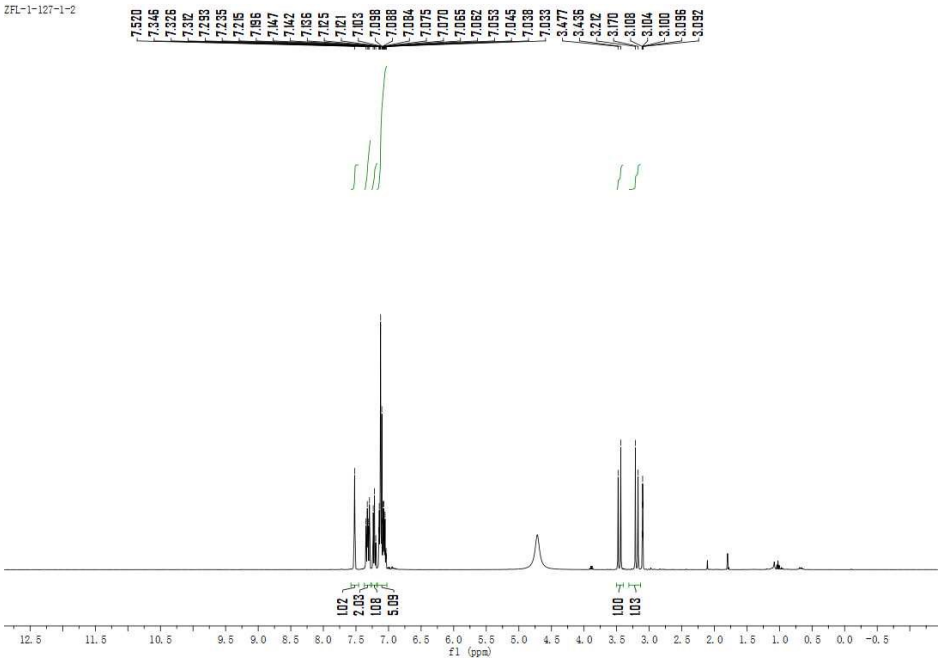
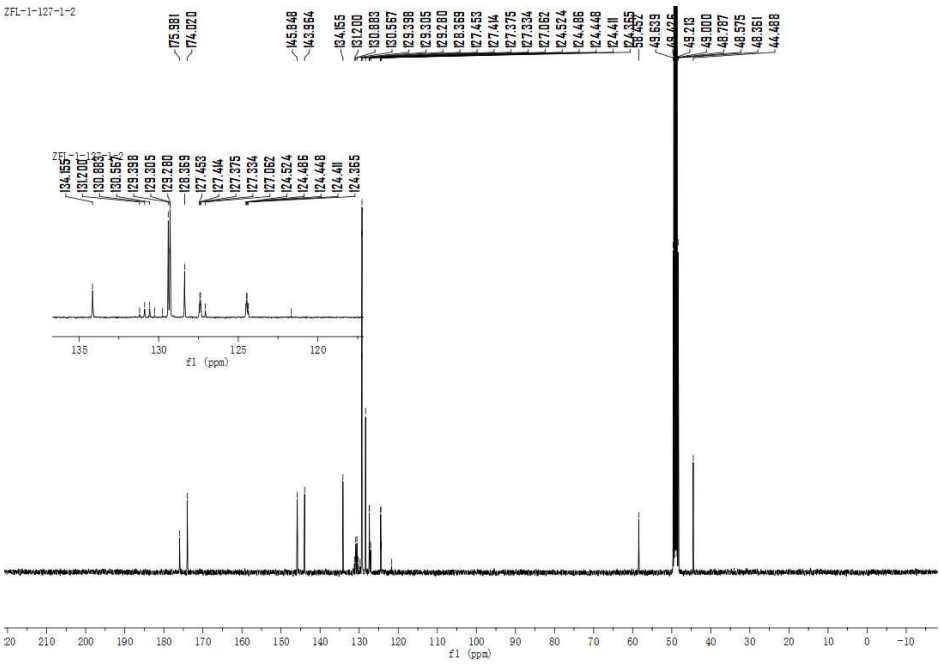


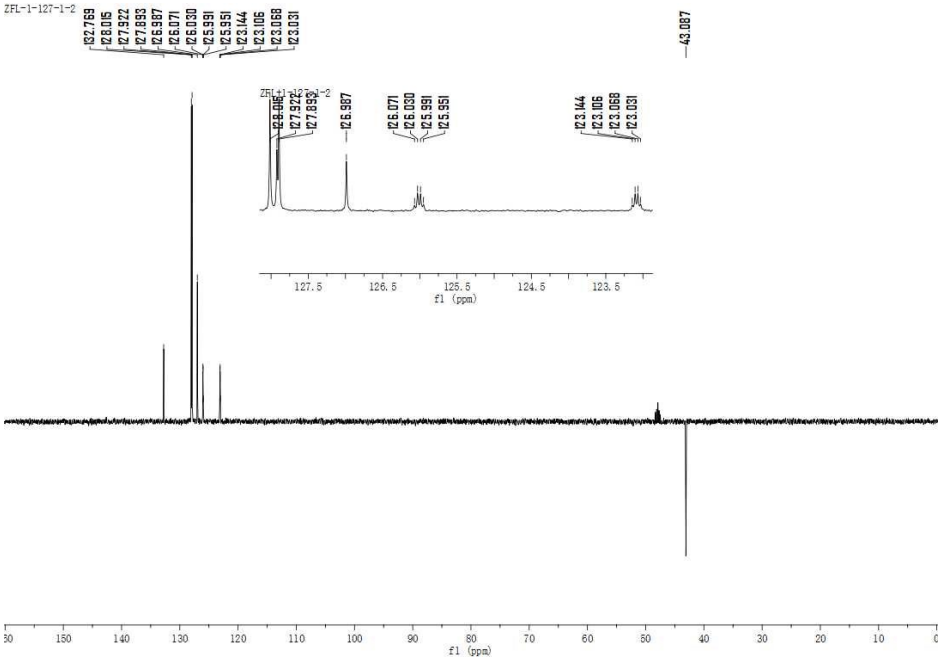




^{1}H NMR and ^{13}C NMR, DEPT-135^{o}, ^{19}F NMR spectra of 2e



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124.5
123.5
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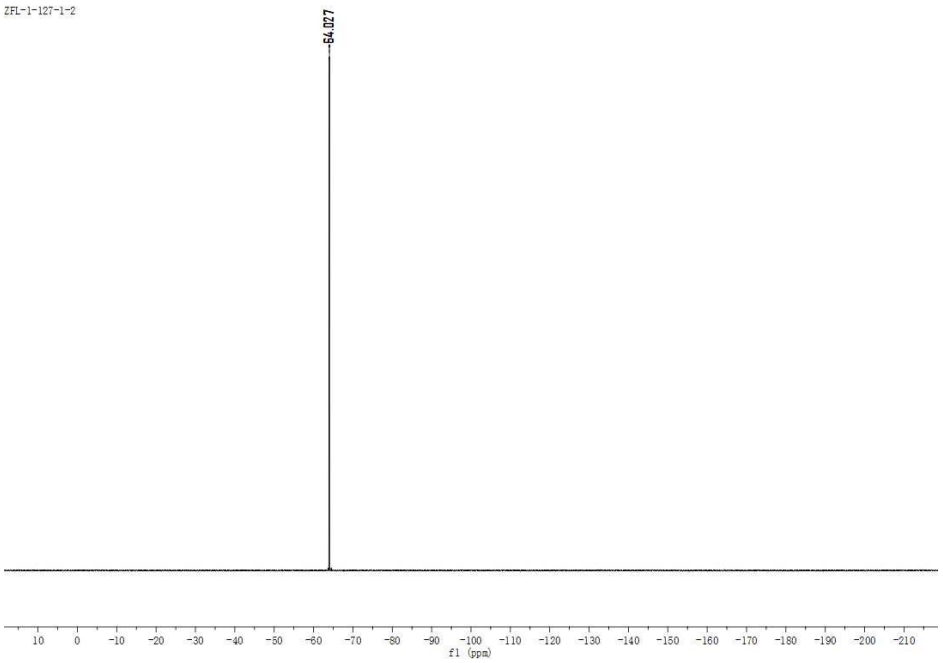
f1 (ppm)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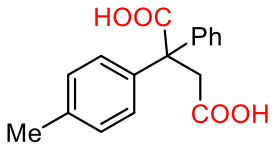
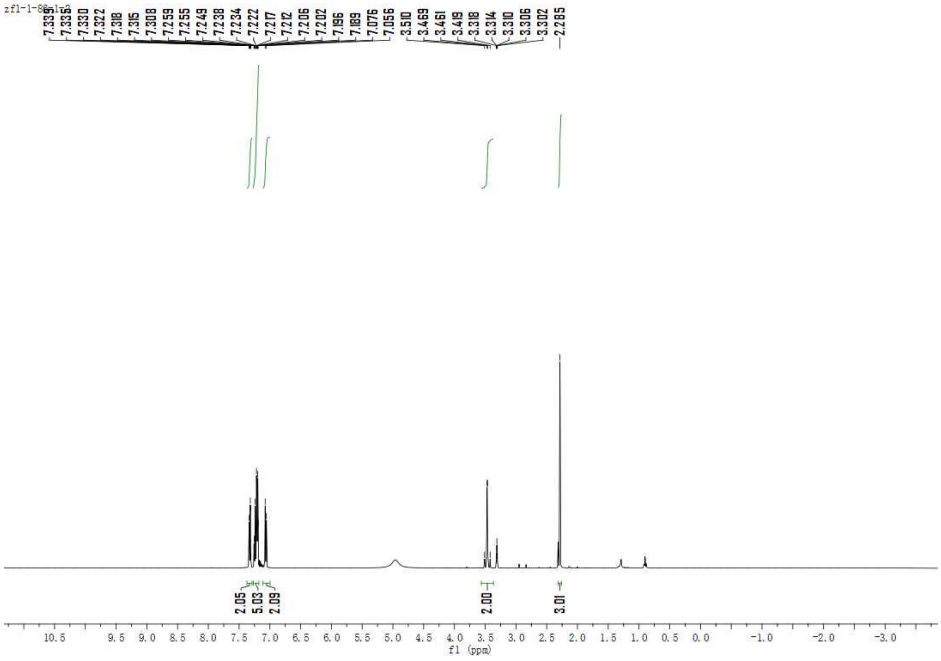
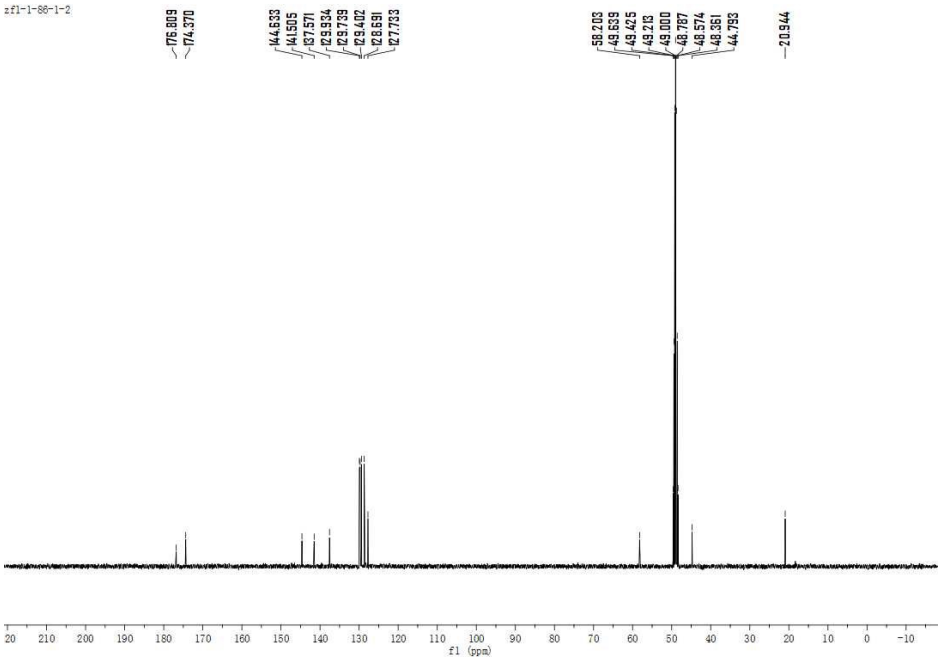
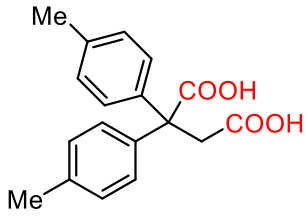
f1 (ppm)



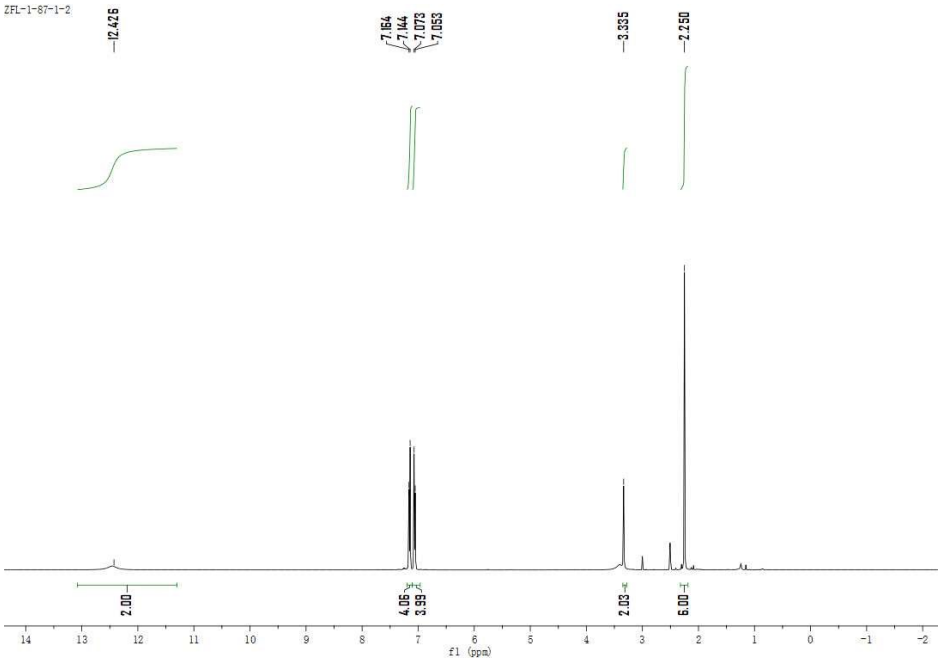
^{1}H NMR and ^{13}C NMR of 2f

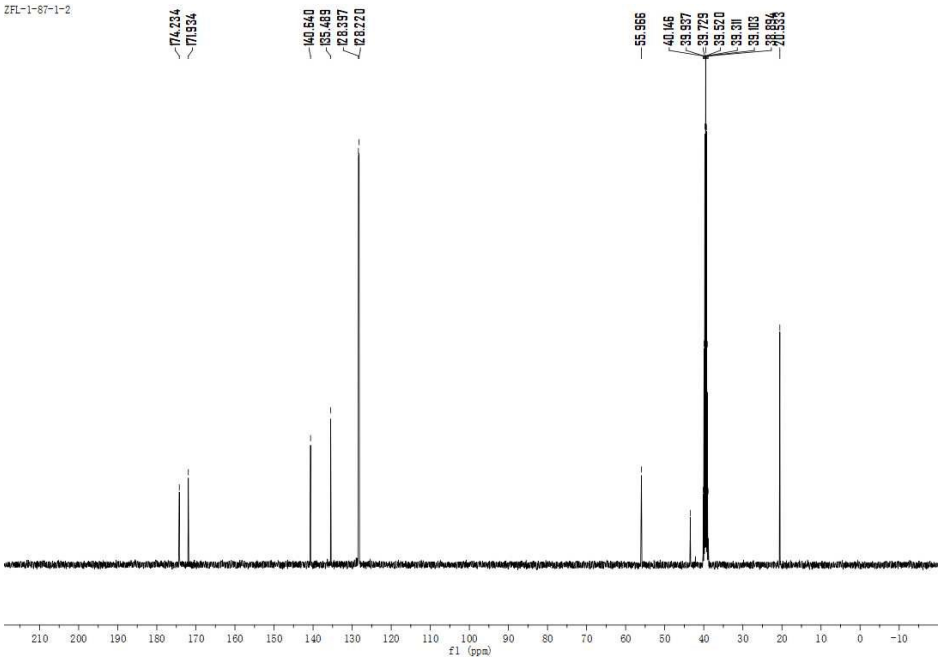


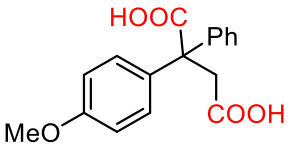




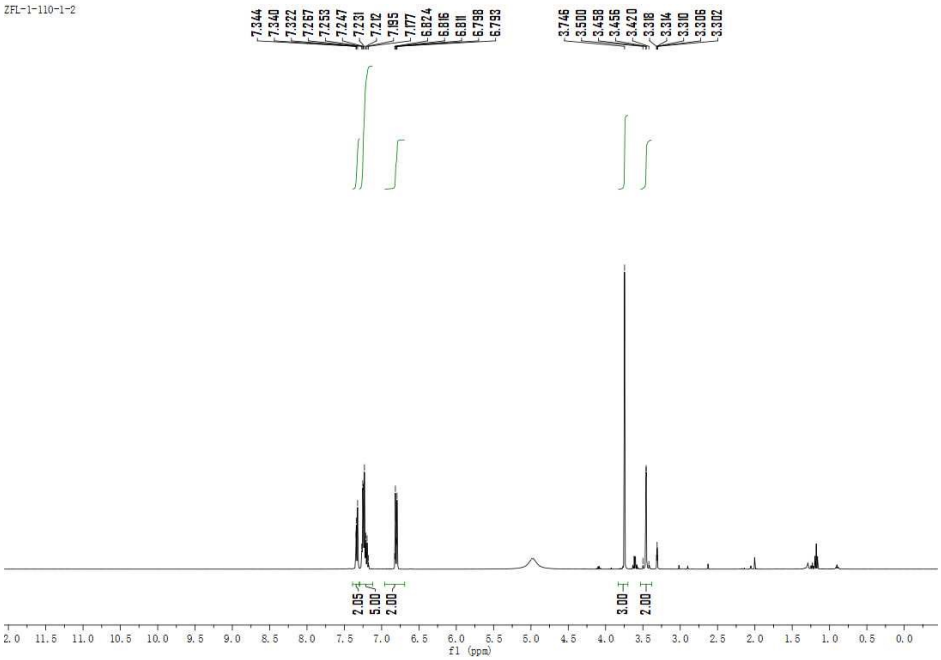
^{1}H NMR and ^{13}C NMR spectra of 2g

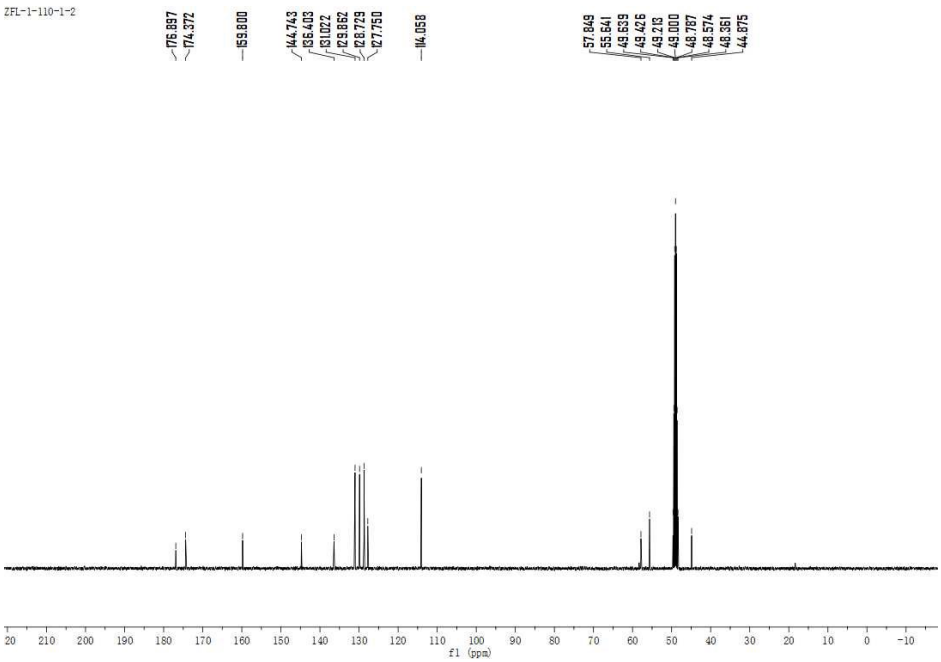


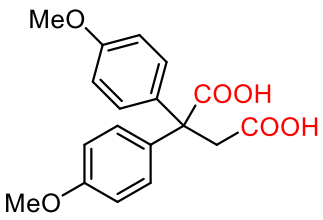




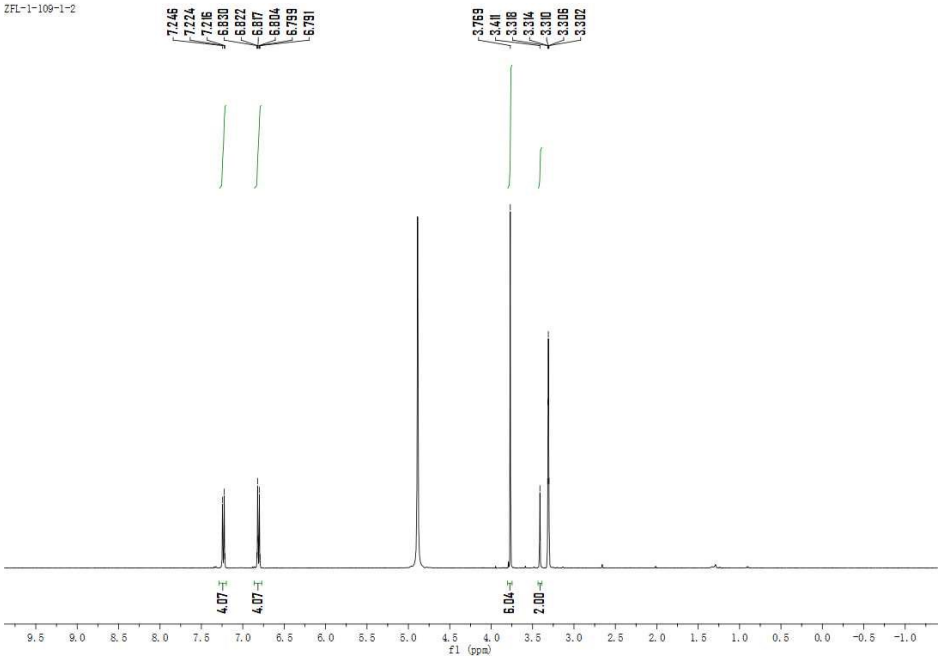
^{1}H NMR and ^{13}C NMR spectra of 2h

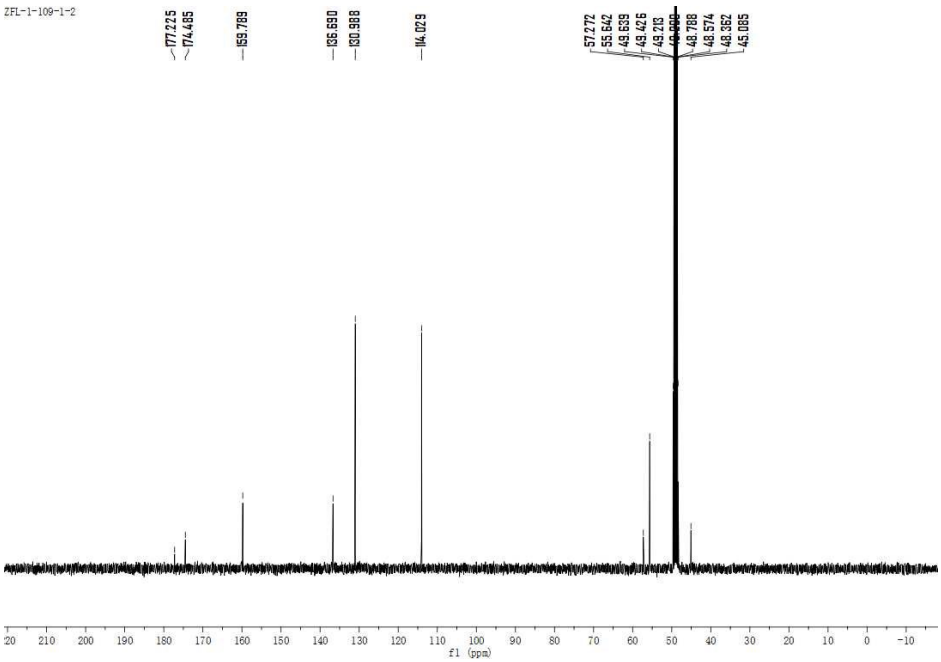


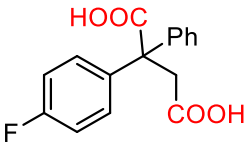




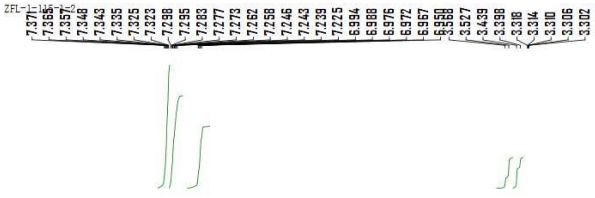
^{1}H NMR and ^{13}C NMR spectra of 2i

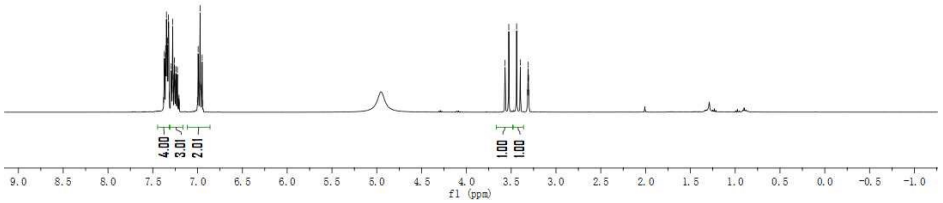


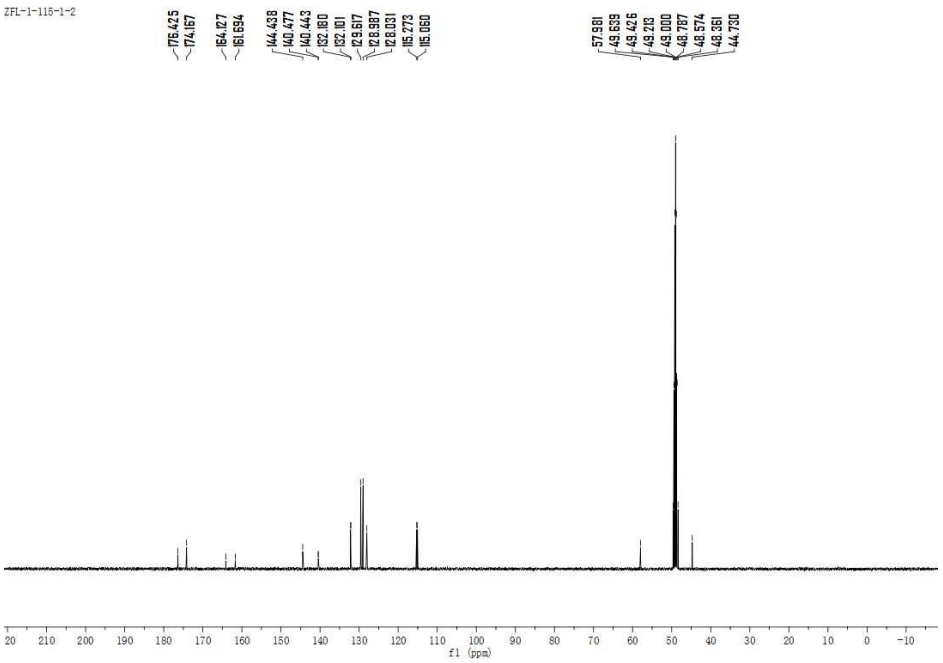


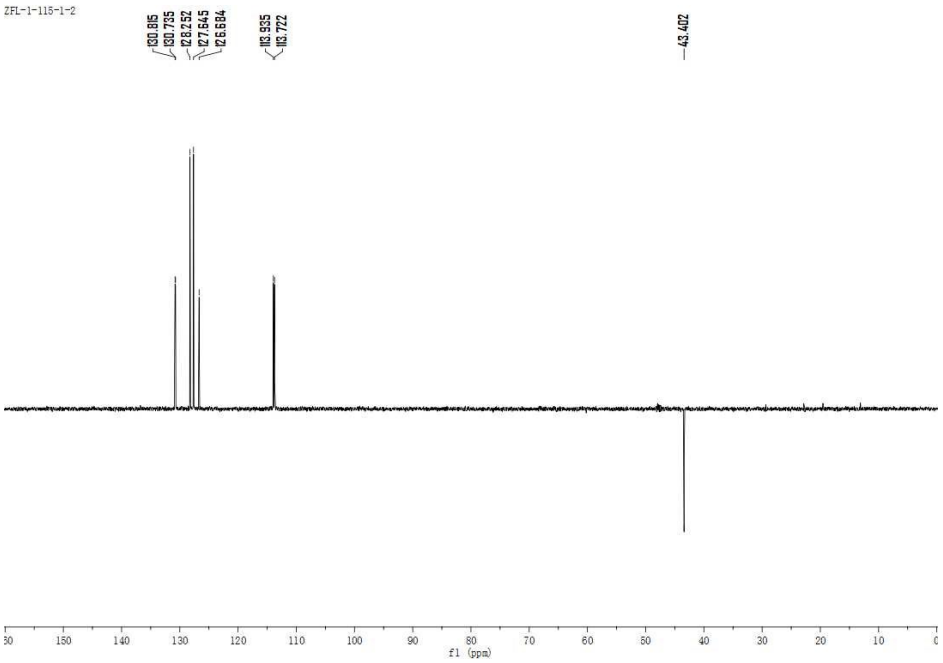


^{1}H NMR and ^{13}C NMR, DEPT-135^{o}, ^{19}F NMR spectra of 2j





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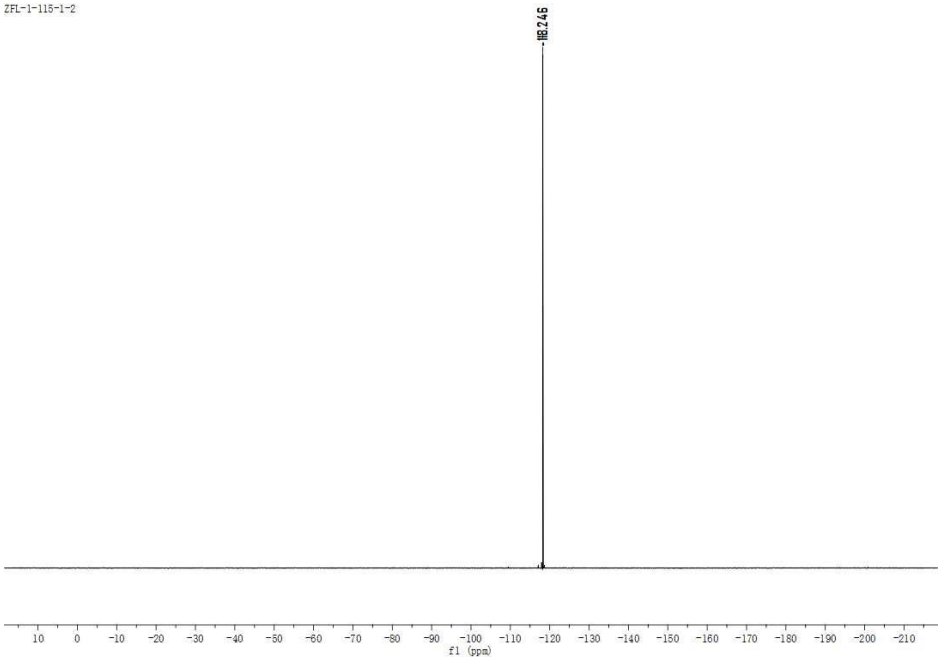
43.402
f1 (ppm)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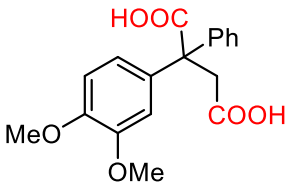
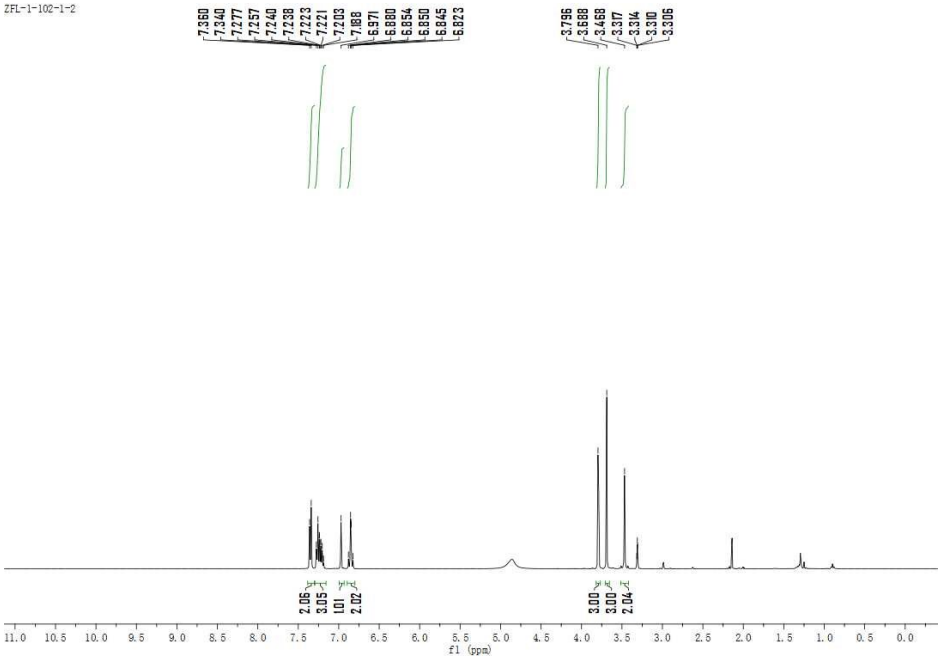
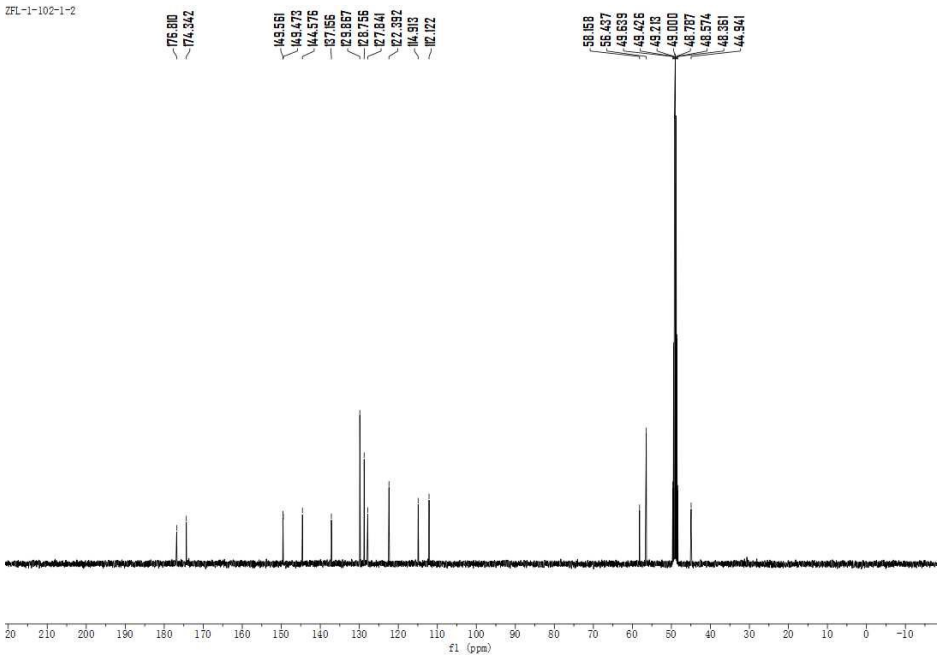
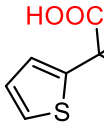


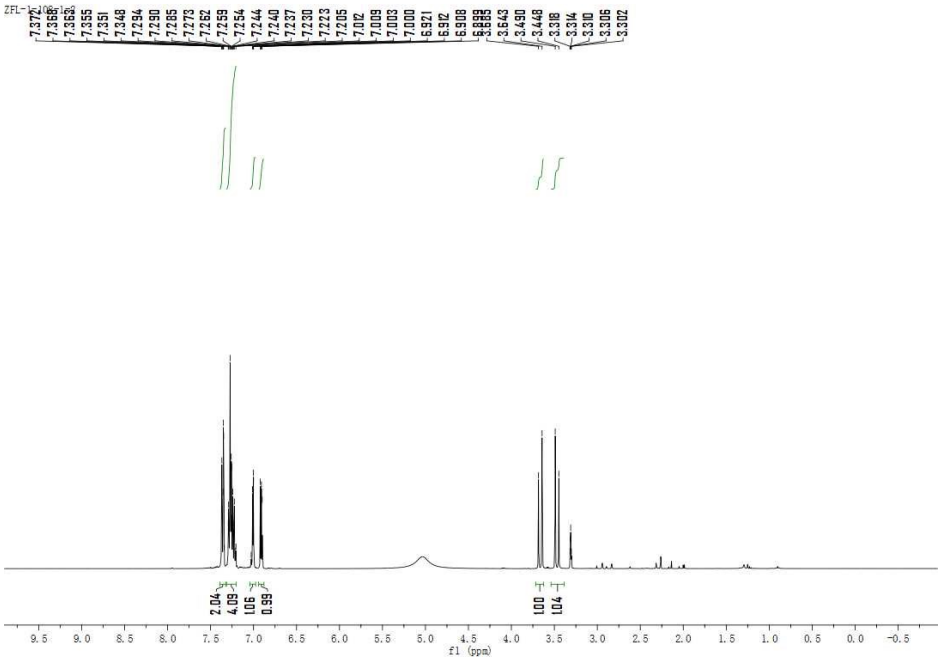
^{1}H NMR and ^{13}C NMR spectra of 2k

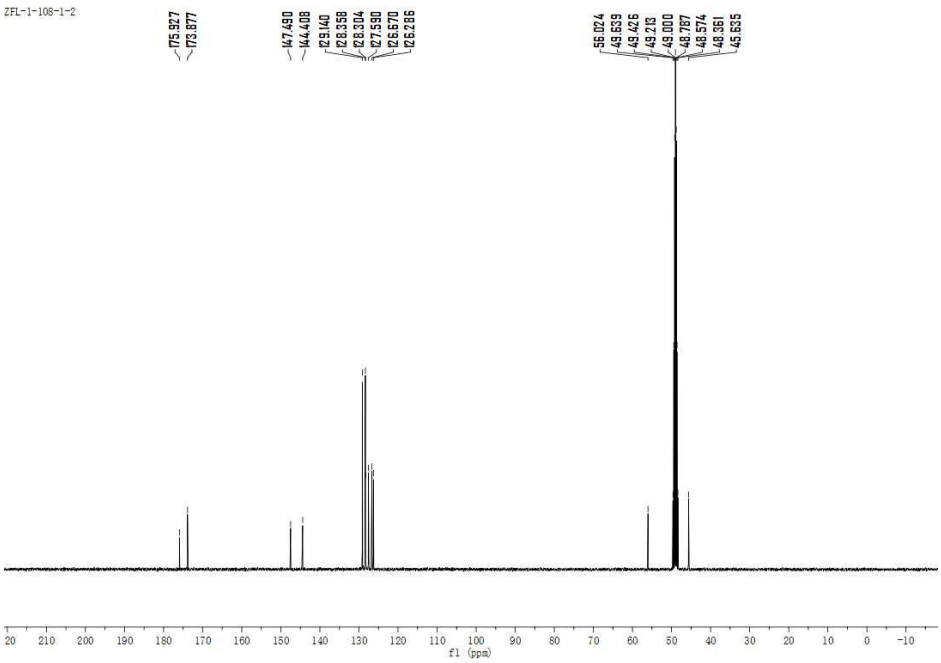


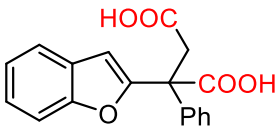




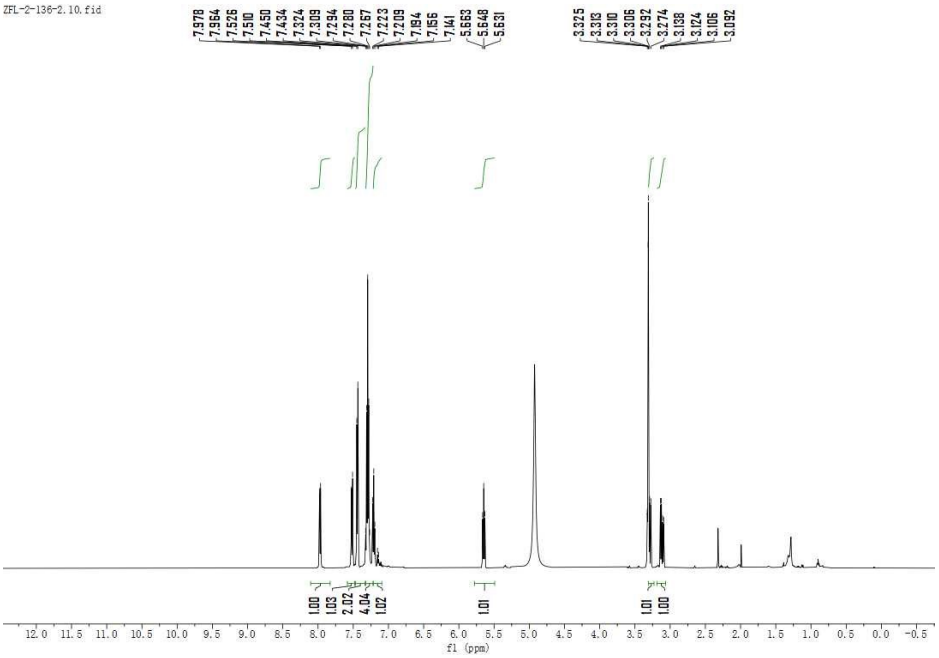
^{1}H NMR and ^{13}C NMR spectra of 2l

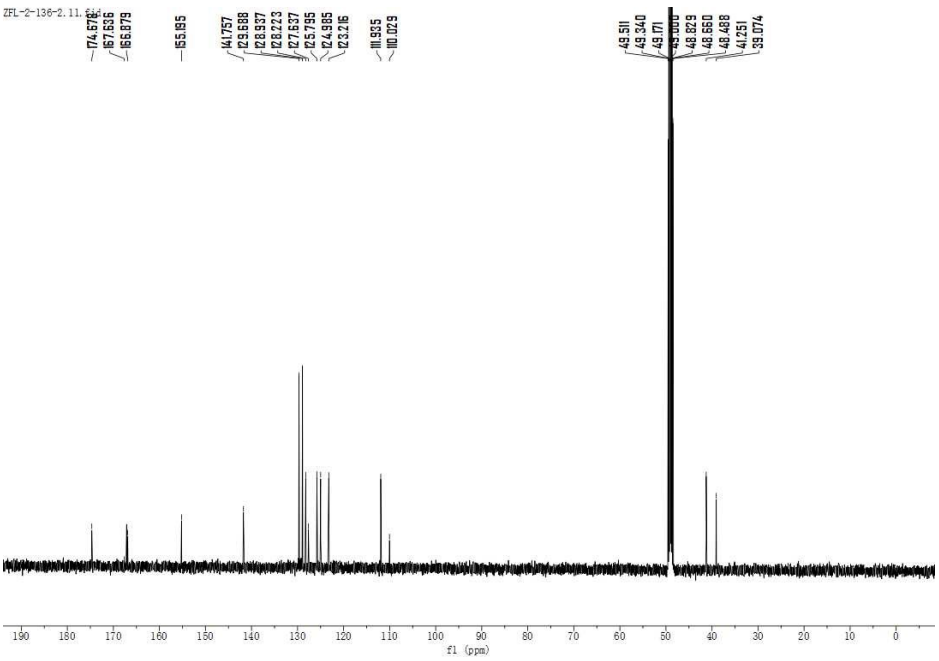


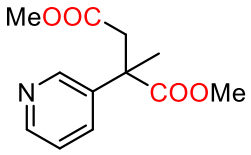




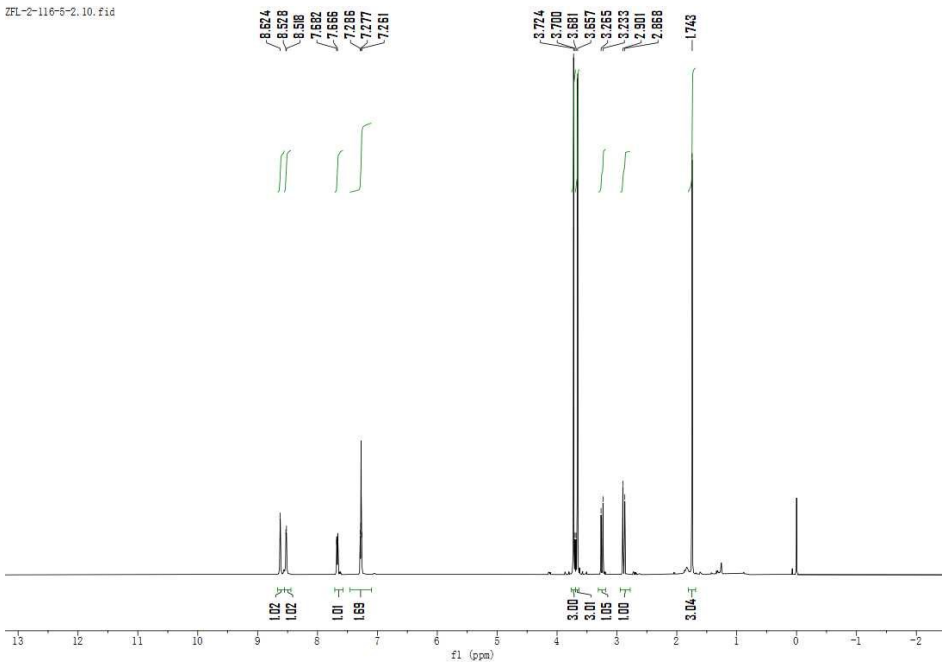
^{1}H NMR and ^{13}C NMR spectra of 2m

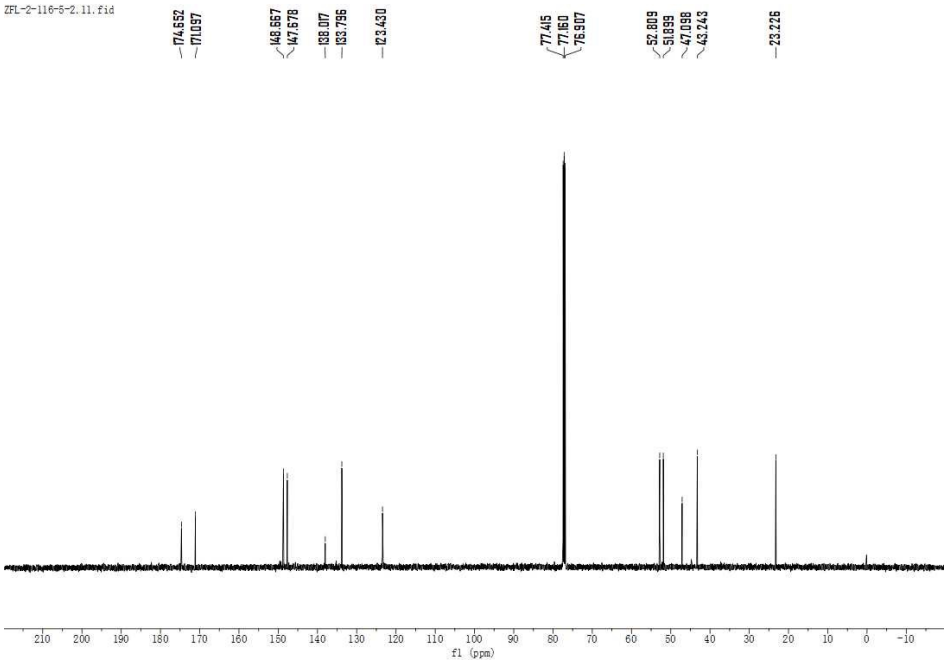


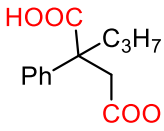




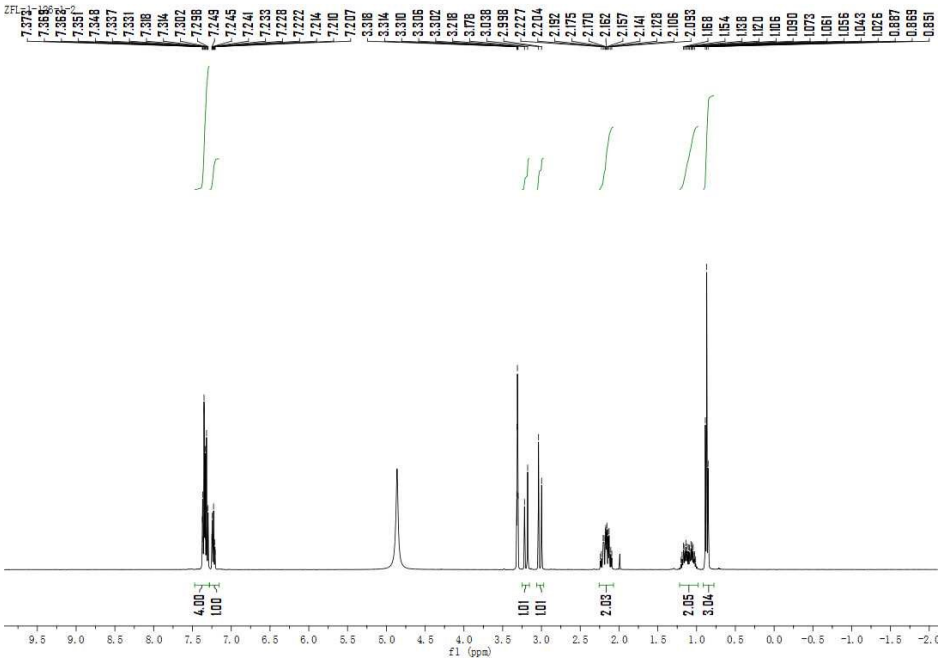
^{1}H NMR and ^{13}C NMR spectra of 2n

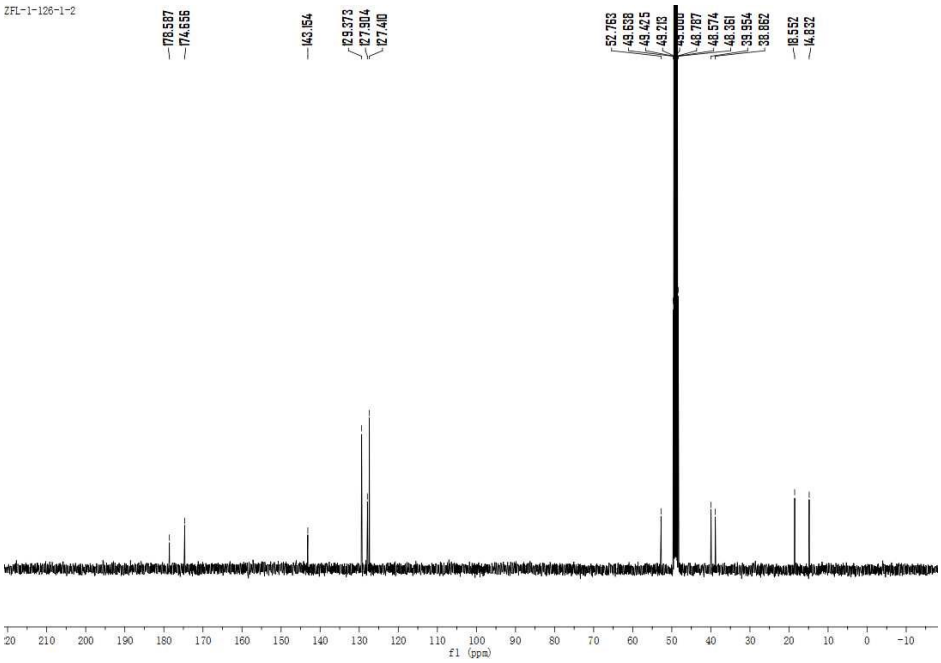


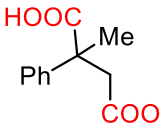




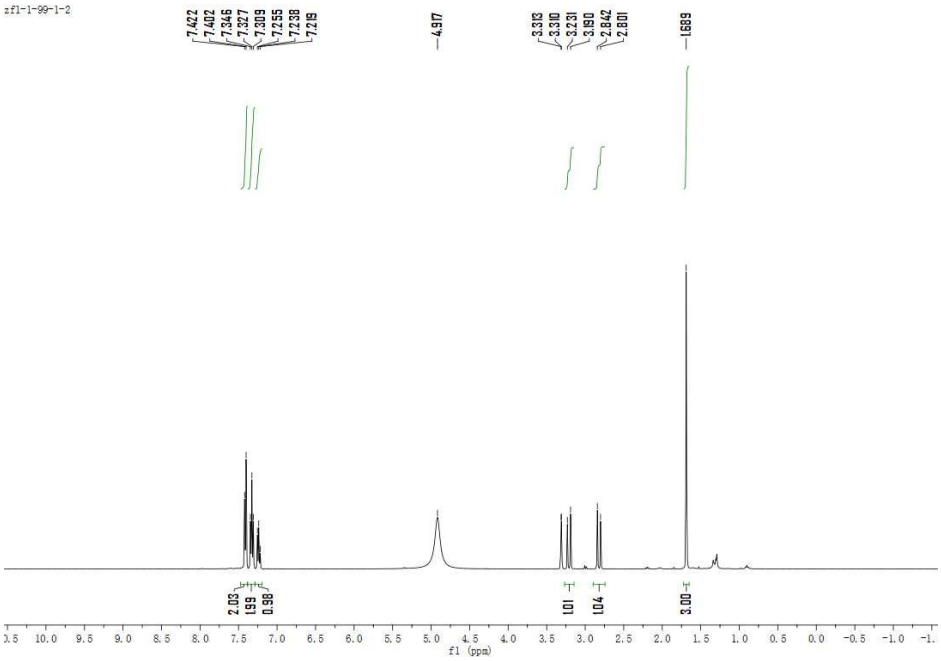
^{1}H NMR and ^{13}C NMR spectra of 2o

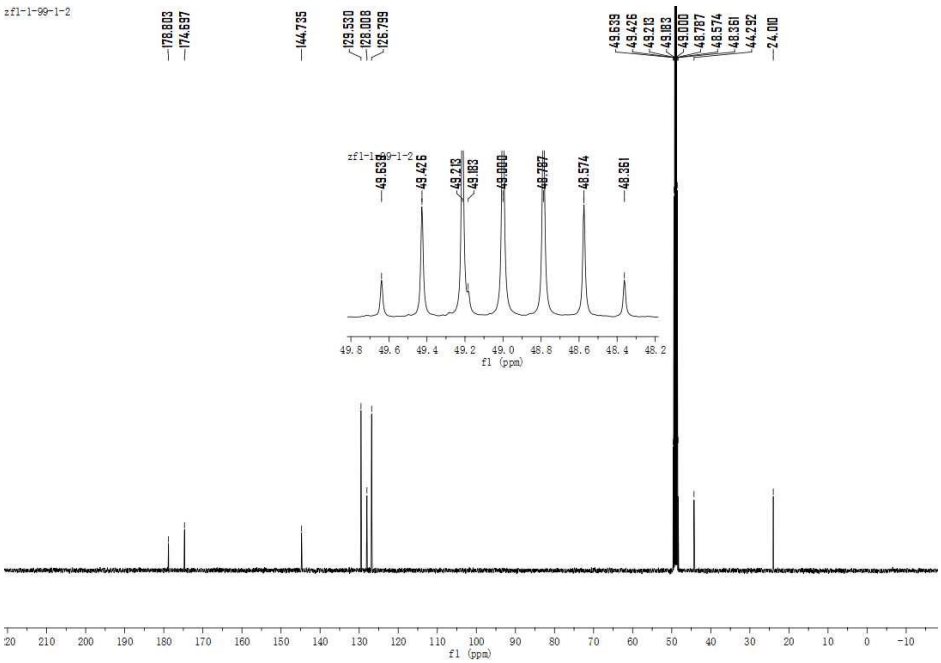


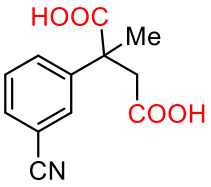




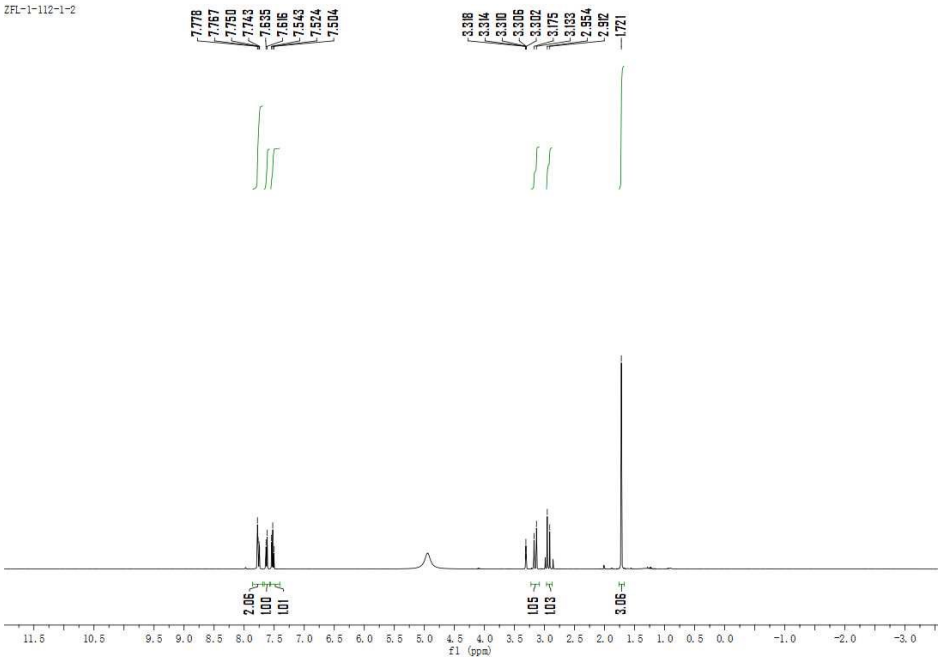
^{1}H NMR and ^{13}C NMR spectra of 2p

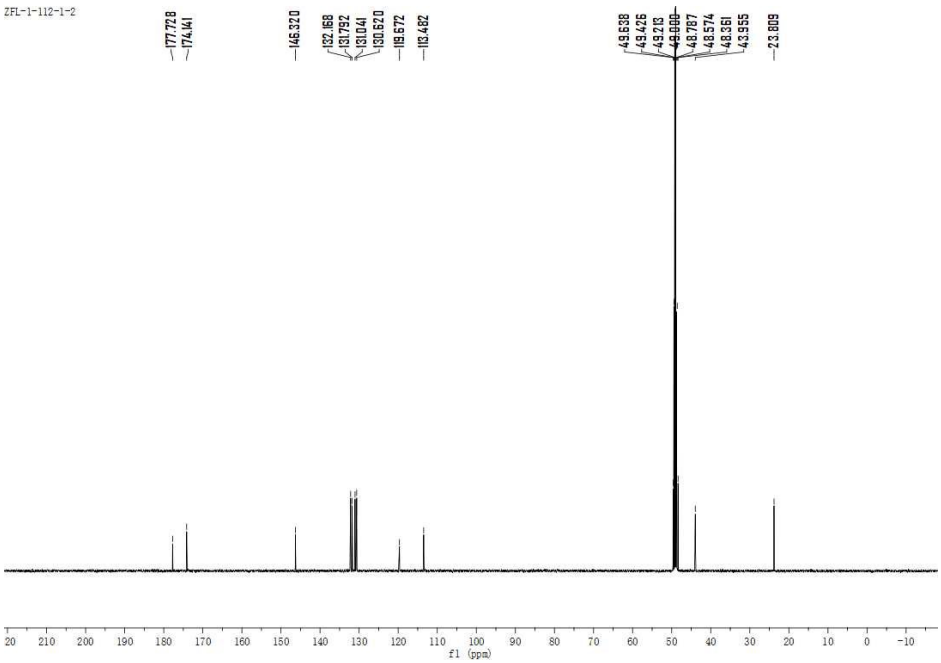


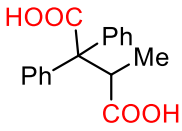




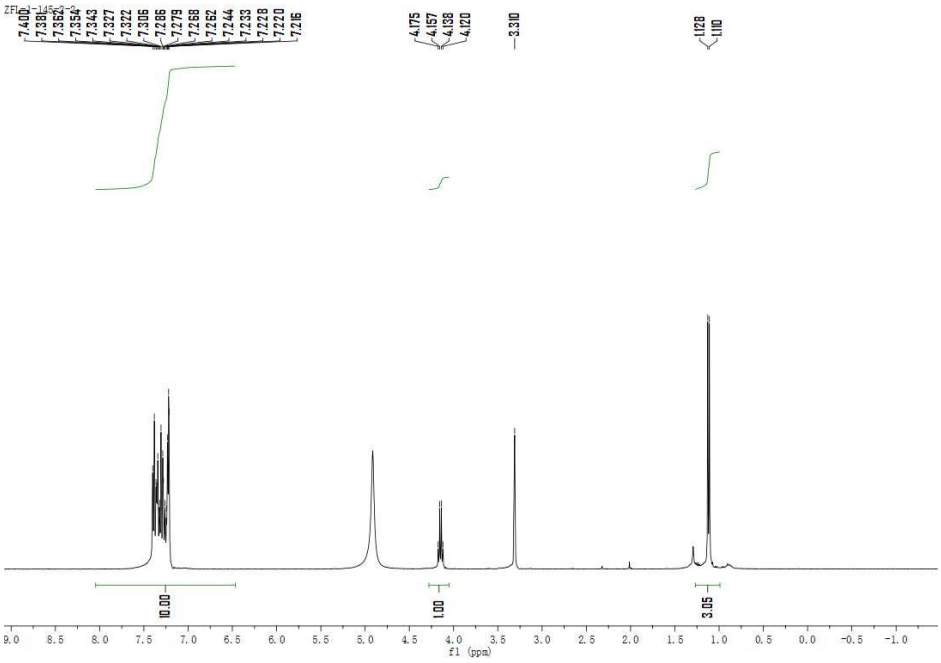
^{1}H NMR and ^{13}C NMR spectra of 2q

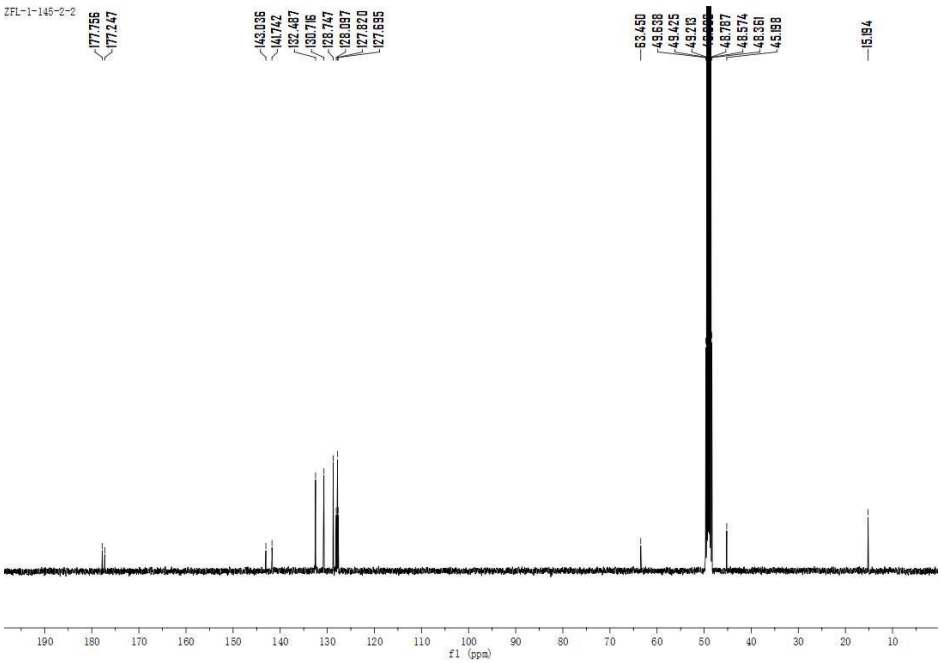


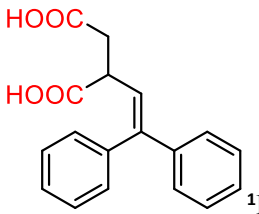




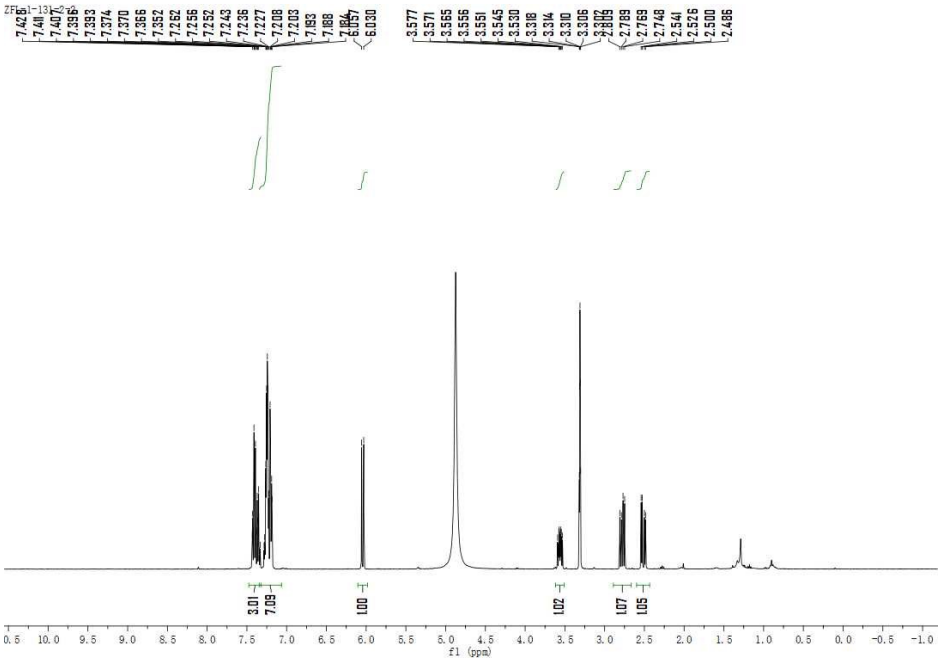
^{1}H NMR and ^{13}C NMR spectra of 2r

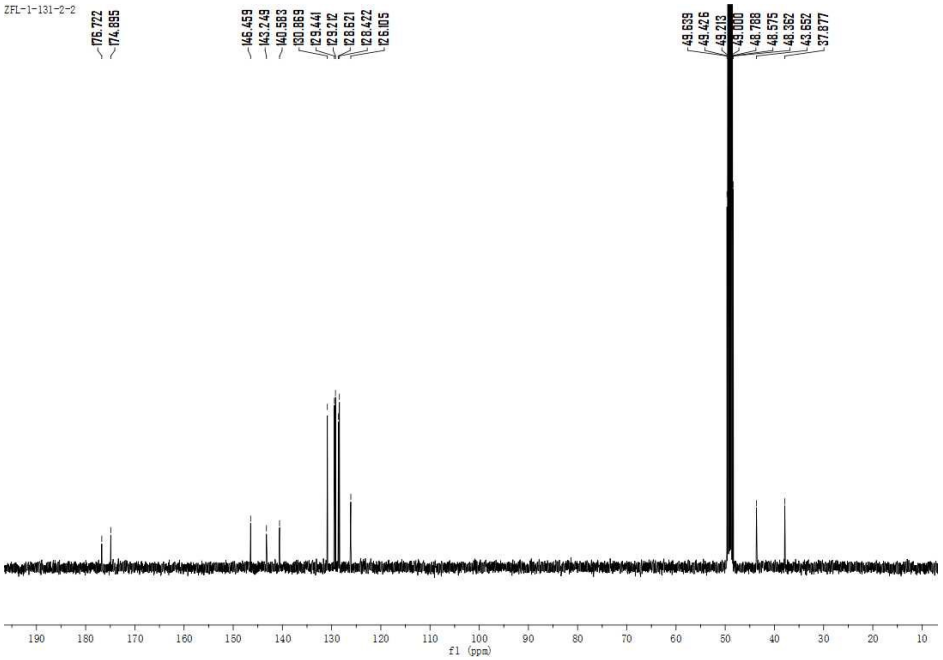


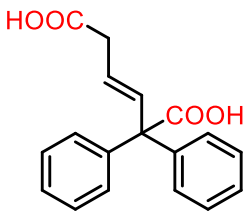




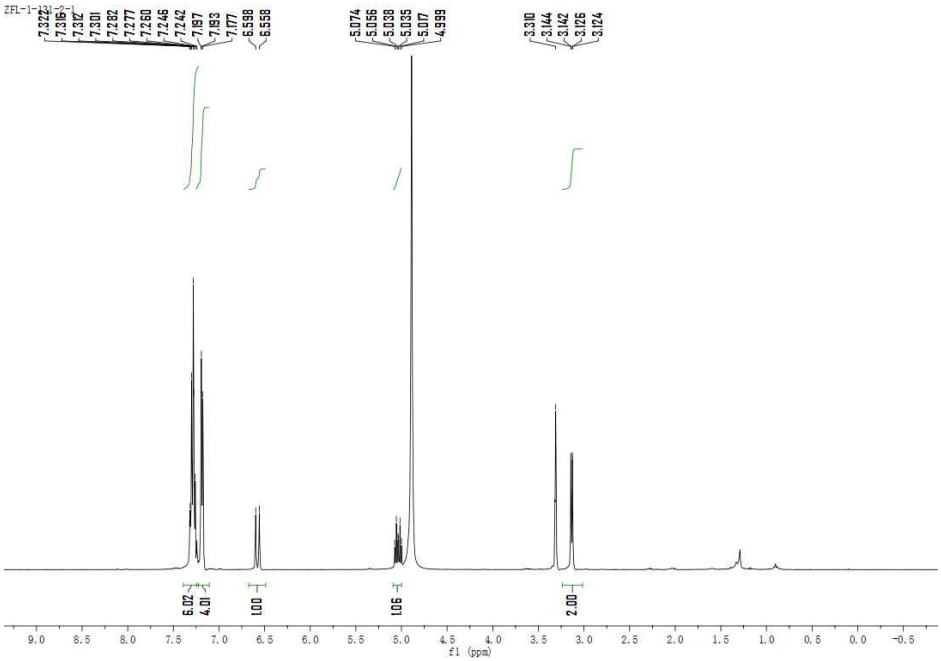
^{1}H NMR and ^{13}C NMR spectra of $2s_a$

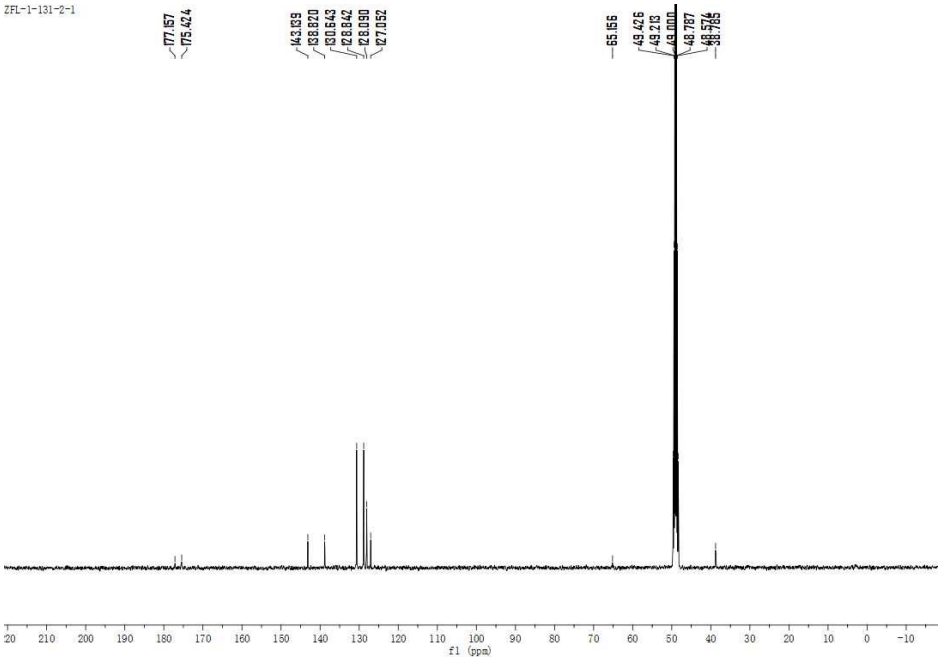


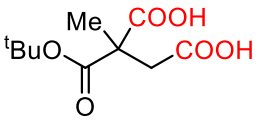




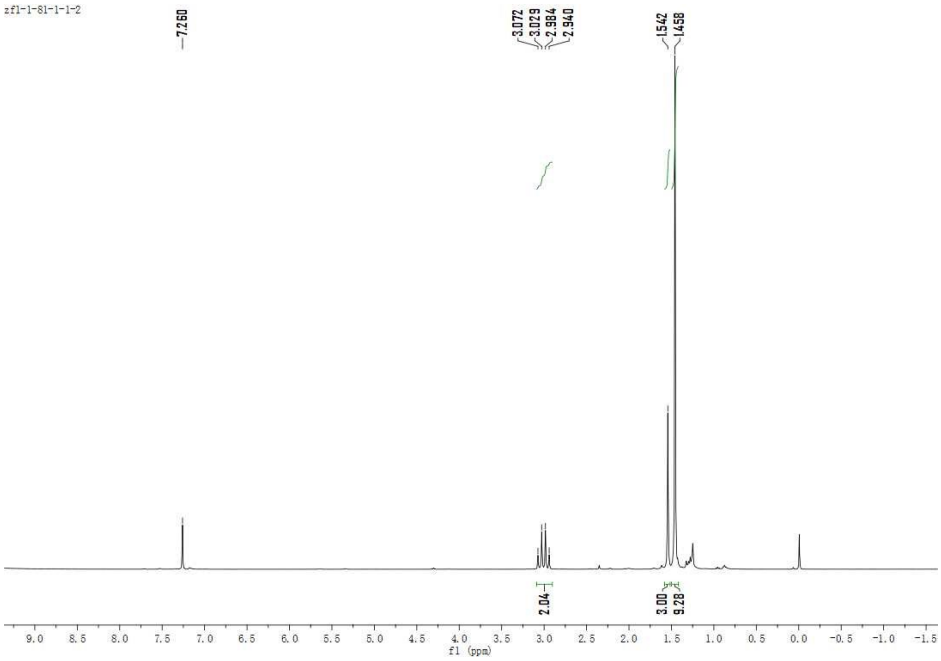
^{1}H NMR and ^{13}C NMR spectra of 2s$_b$

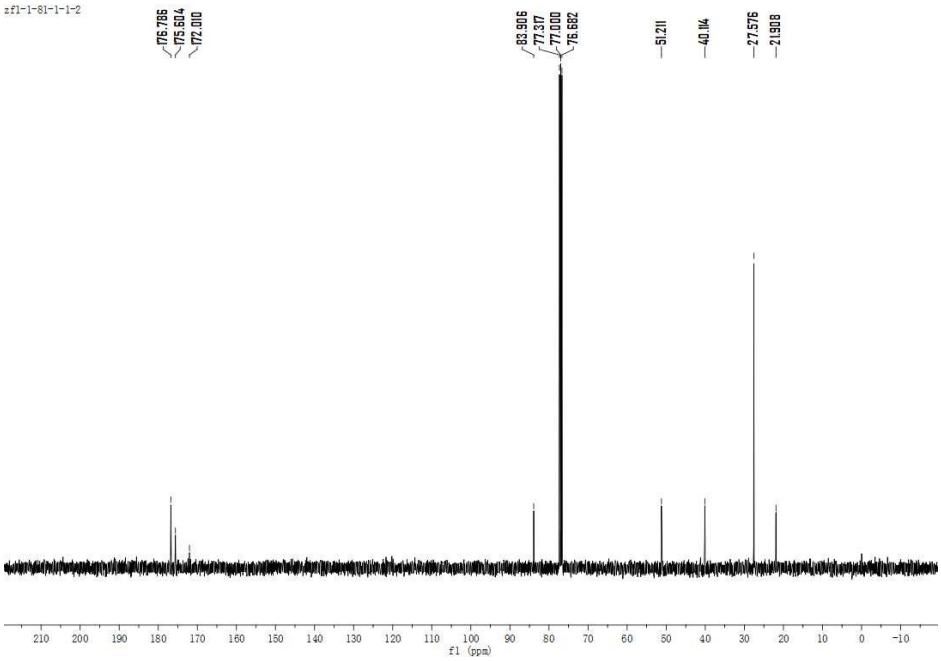


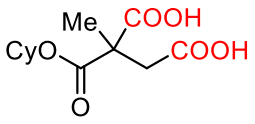




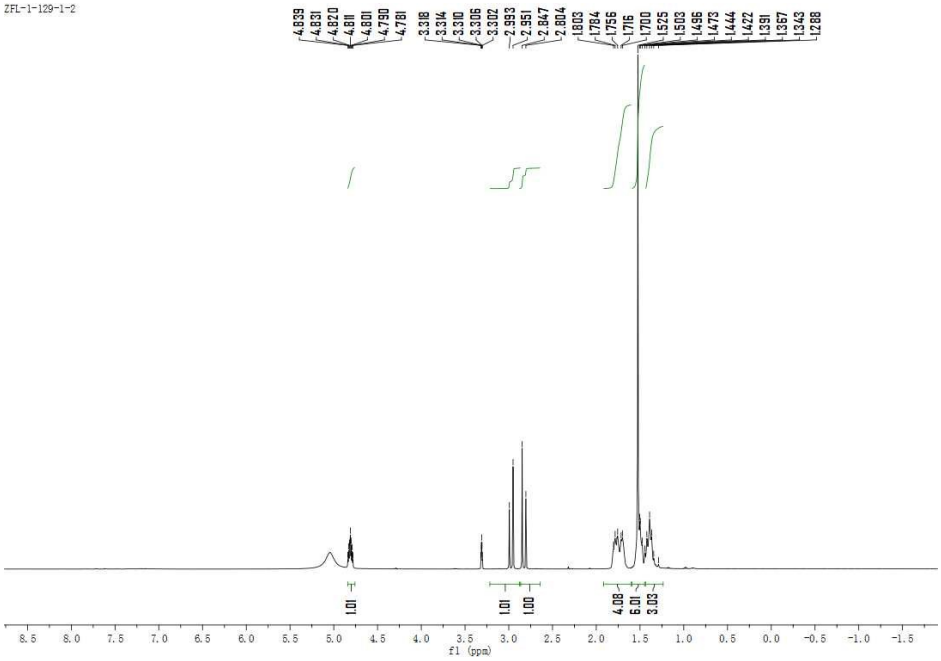
^{1}H NMR and ^{13}C NMR spectra of 2t

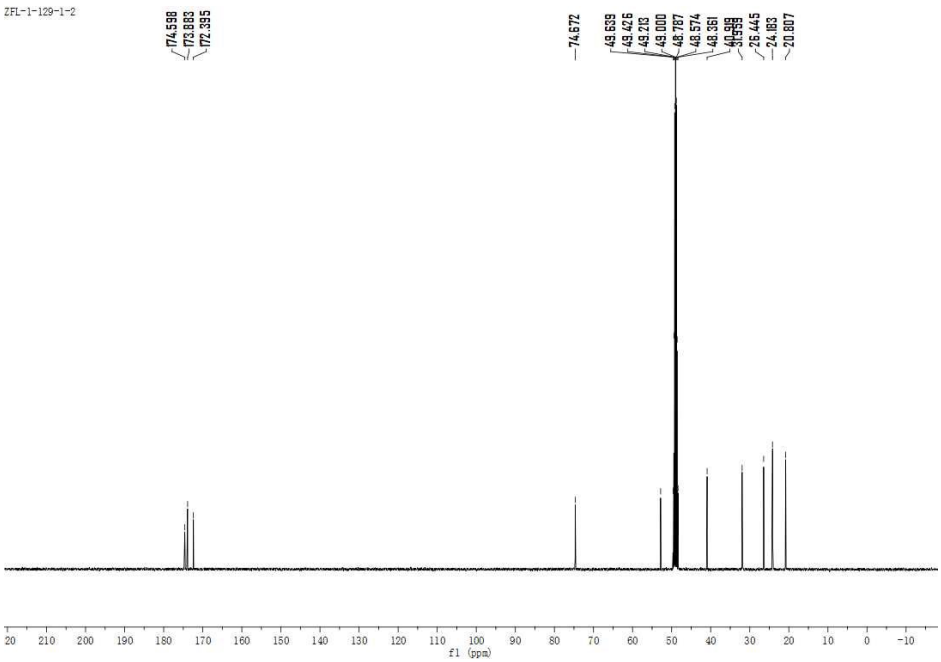


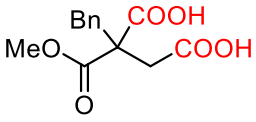




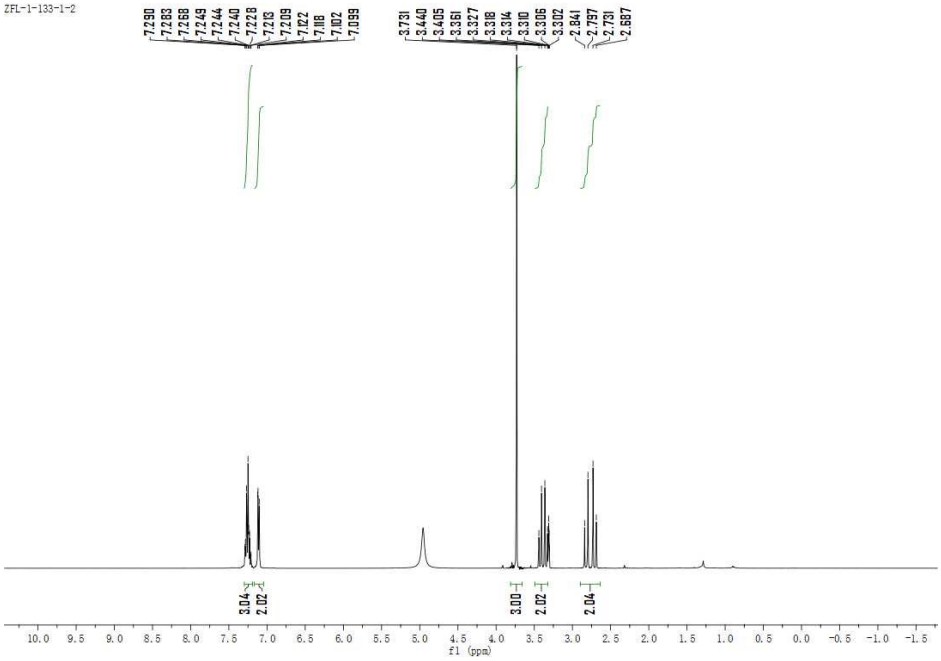
^{1}H NMR and ^{13}C NMR of 2u

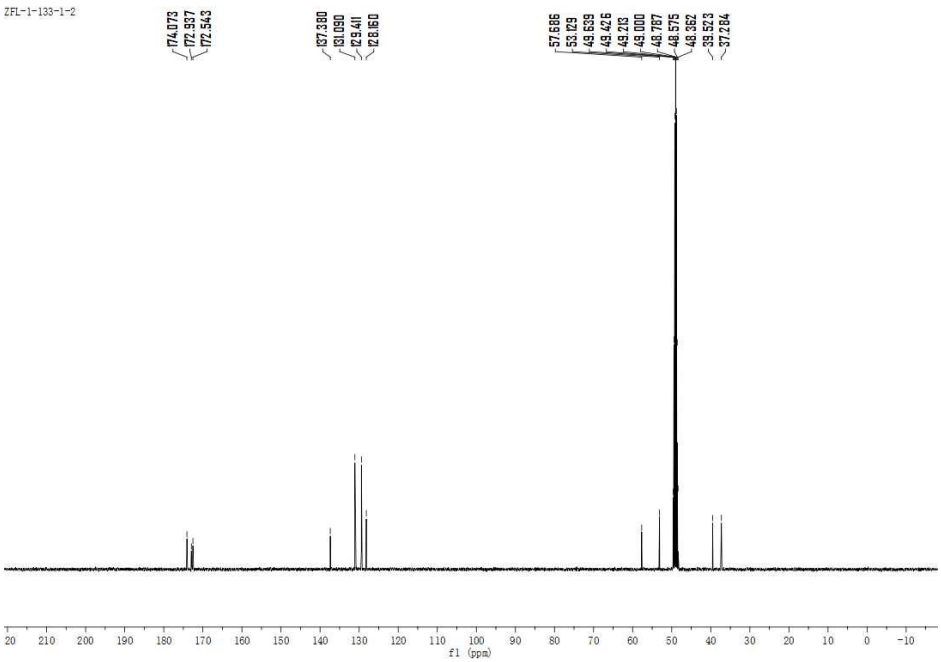


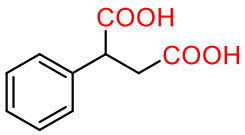




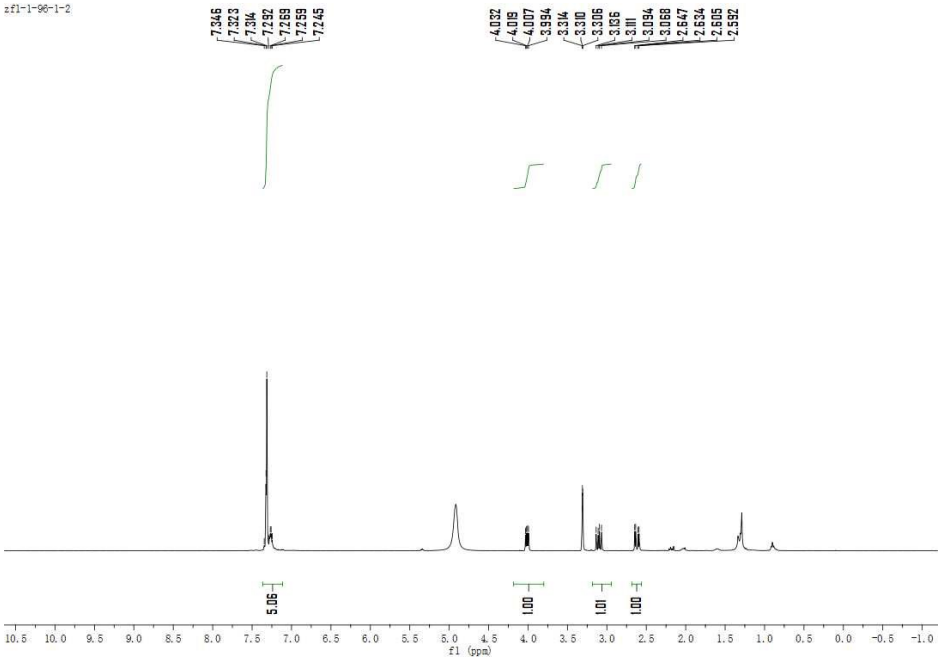
^{1}H NMR and ^{13}C NMR spectra of 2v

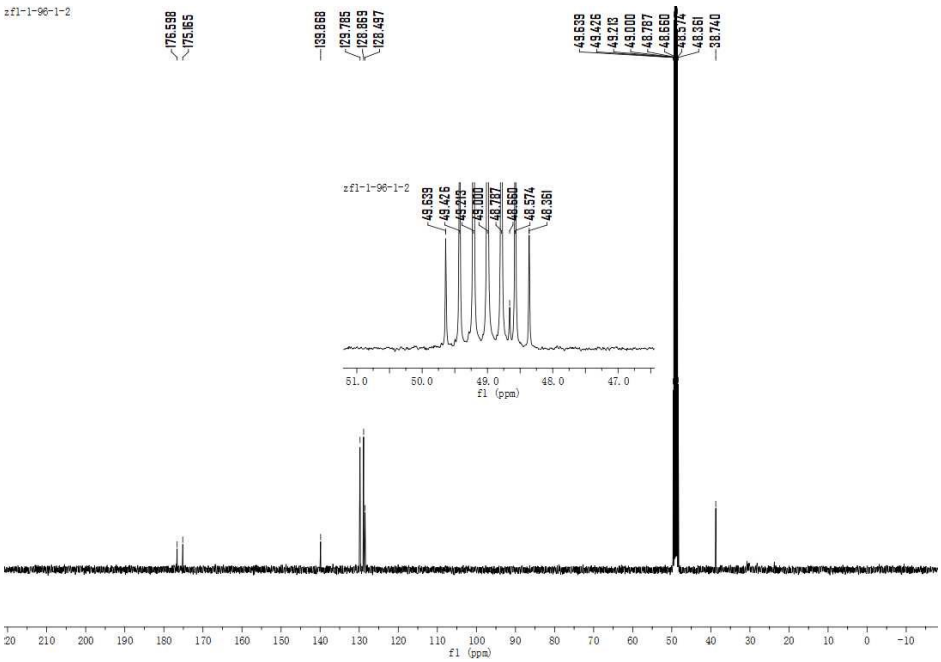


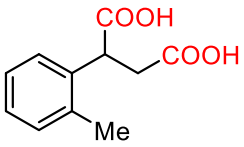




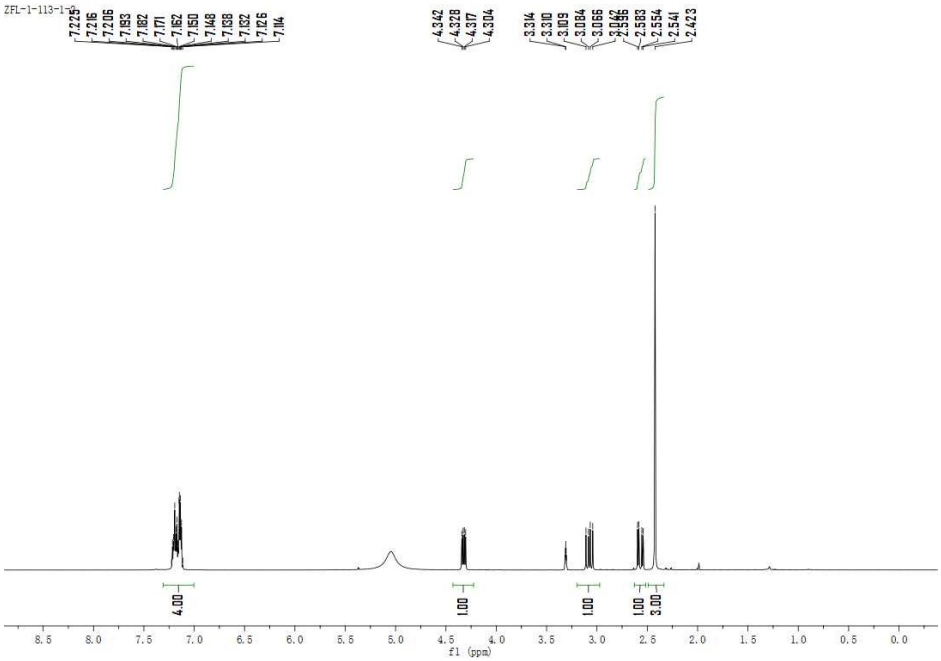
^{1}H NMR and ^{13}C NMR spectra of 4a

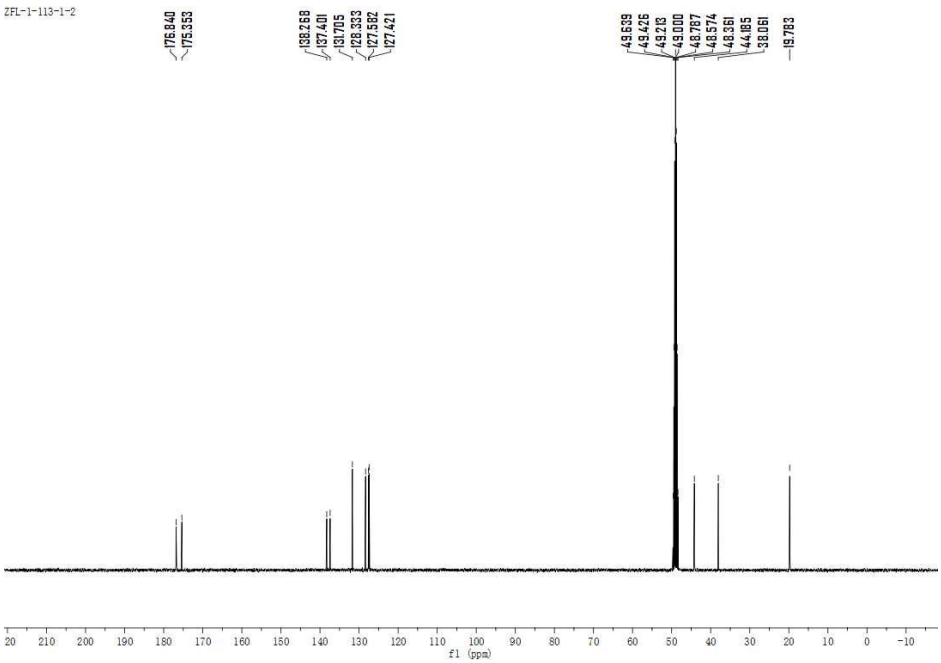


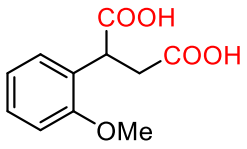




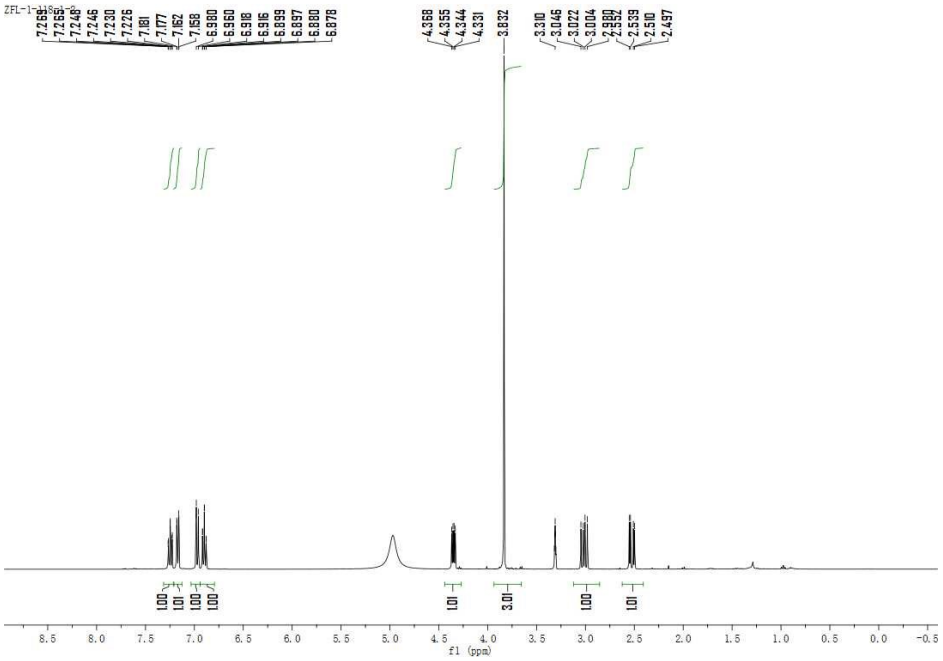
^{1}H NMR and ^{13}C NMR spectra of 4b

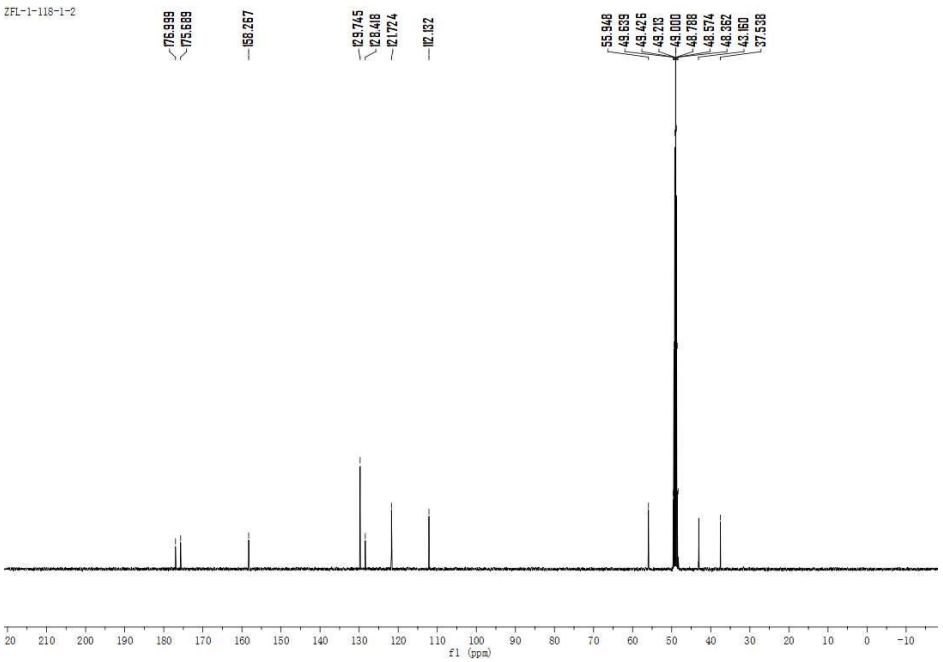


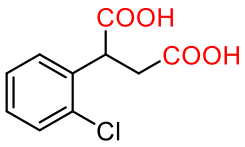




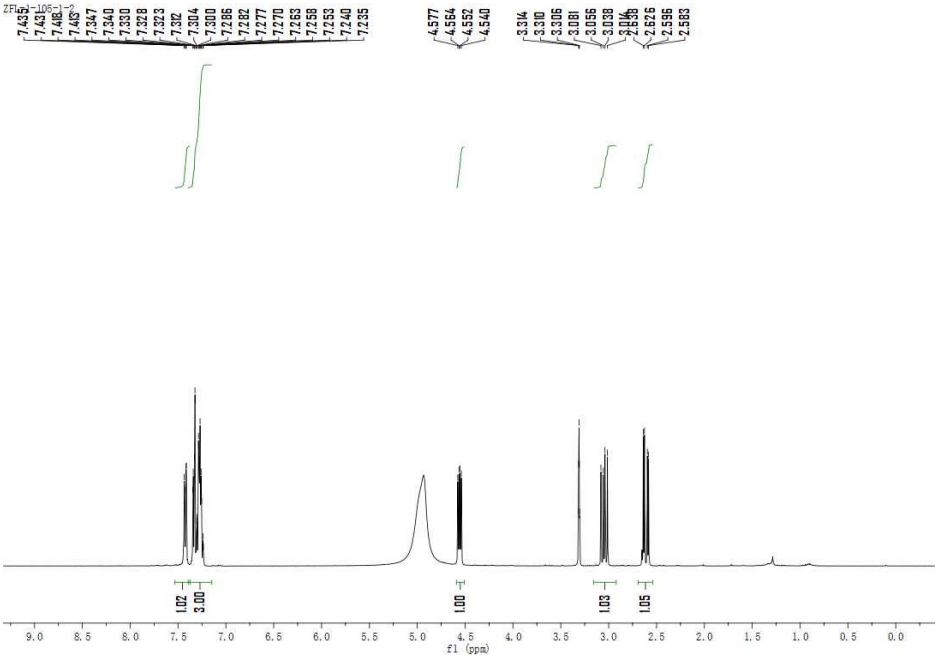
^{1}H NMR and ^{13}C NMR spectra of 4c

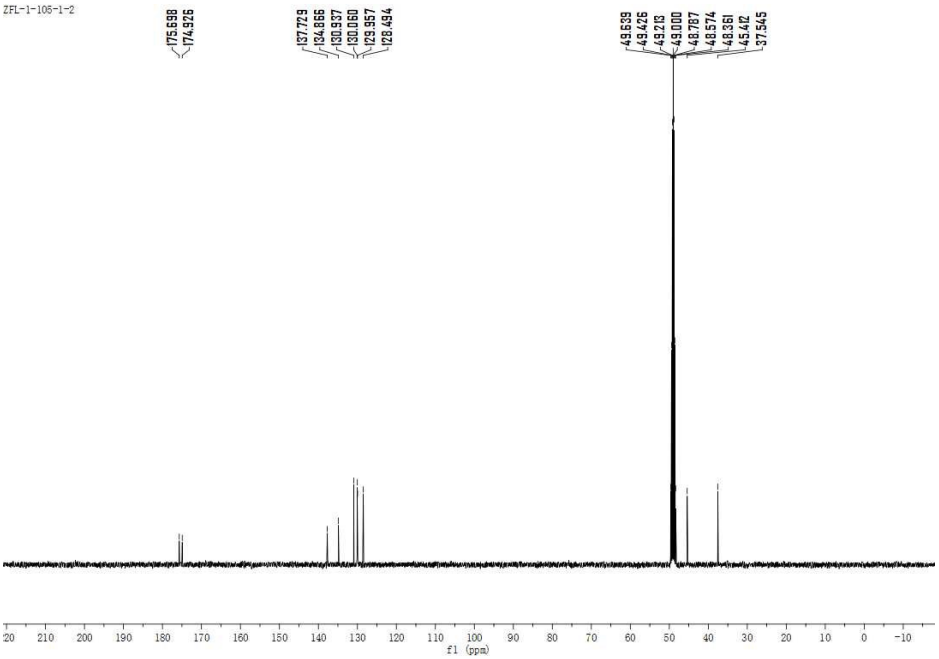


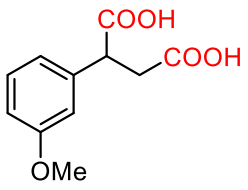




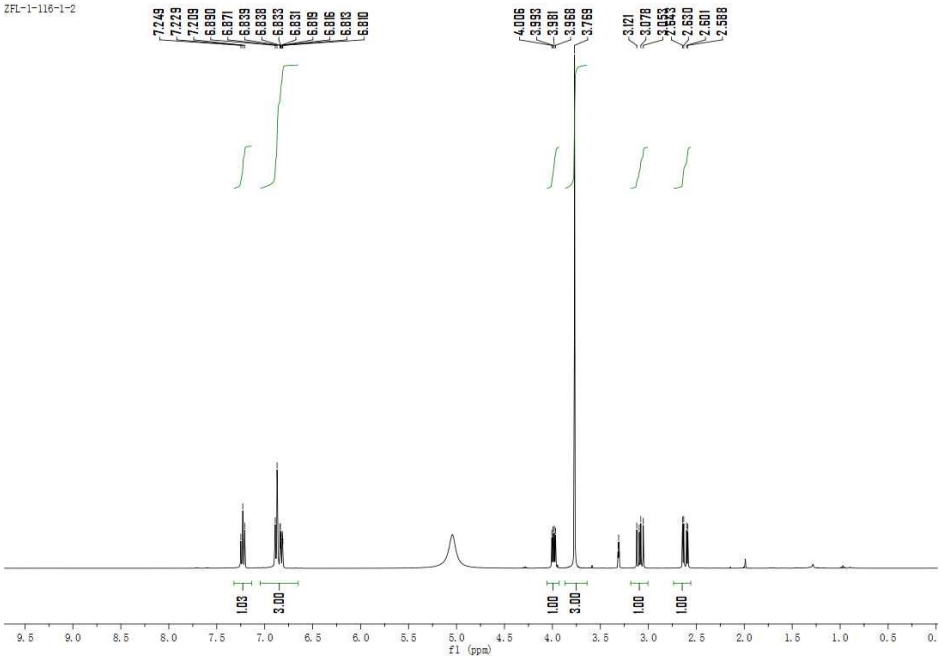
^{1}H NMR and ^{13}C NMR spectra of 4d

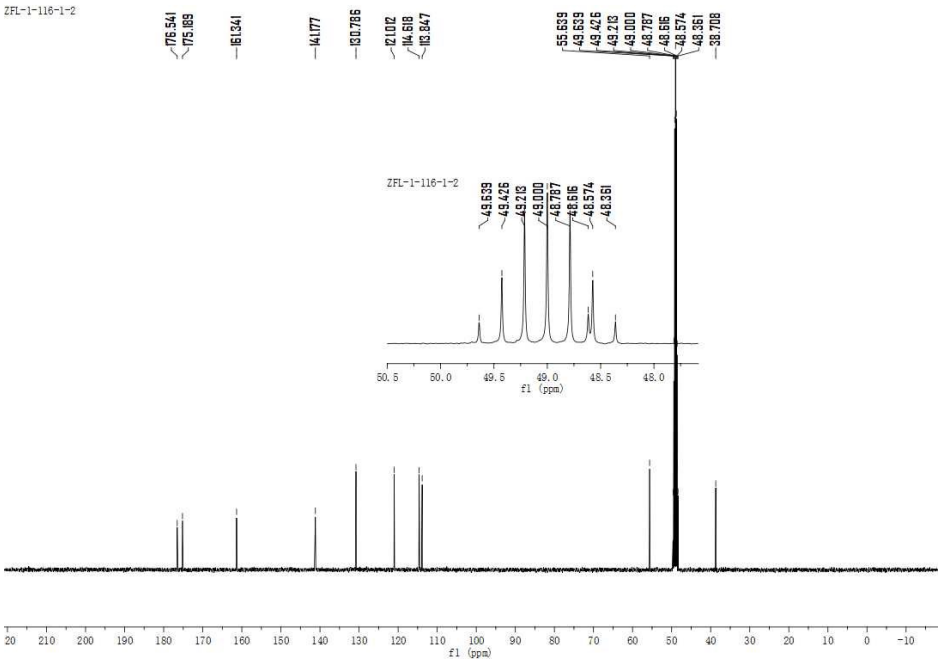


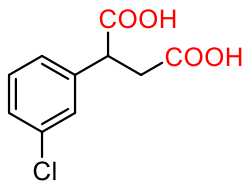




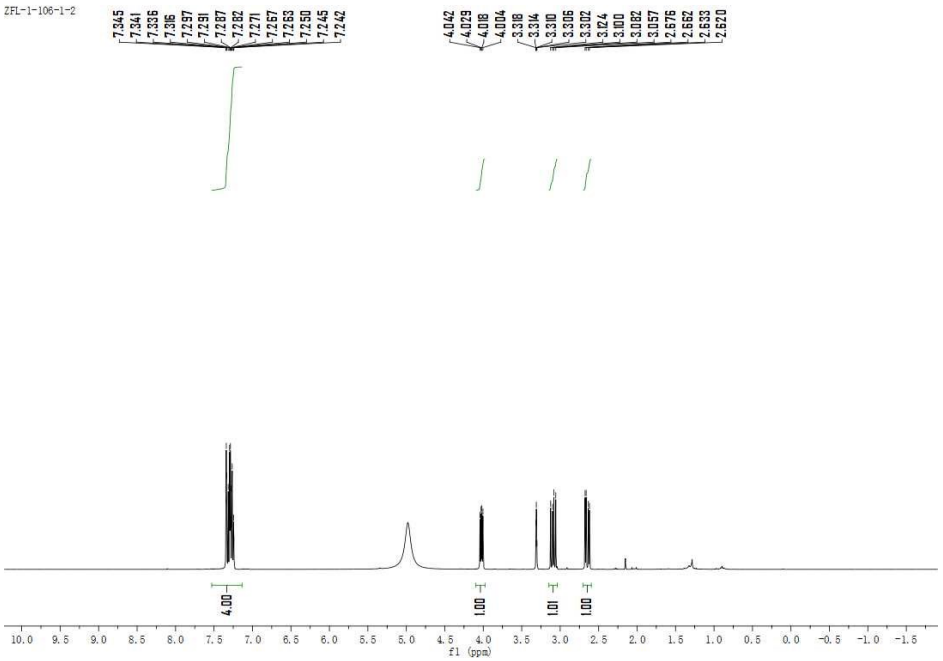
^{1}H NMR and ^{13}C NMR spectra of 4e

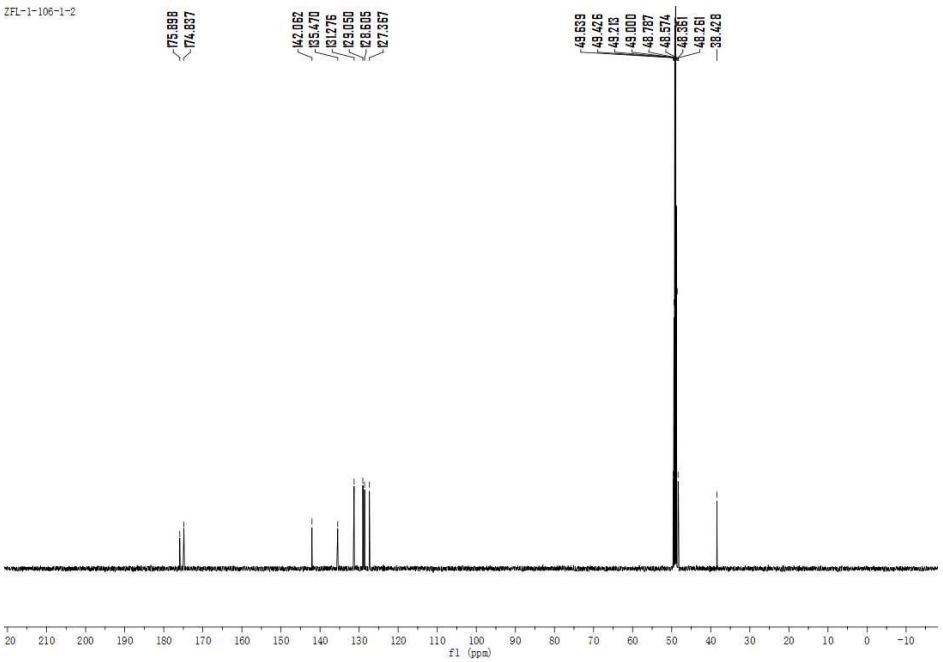


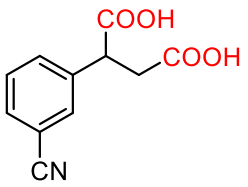




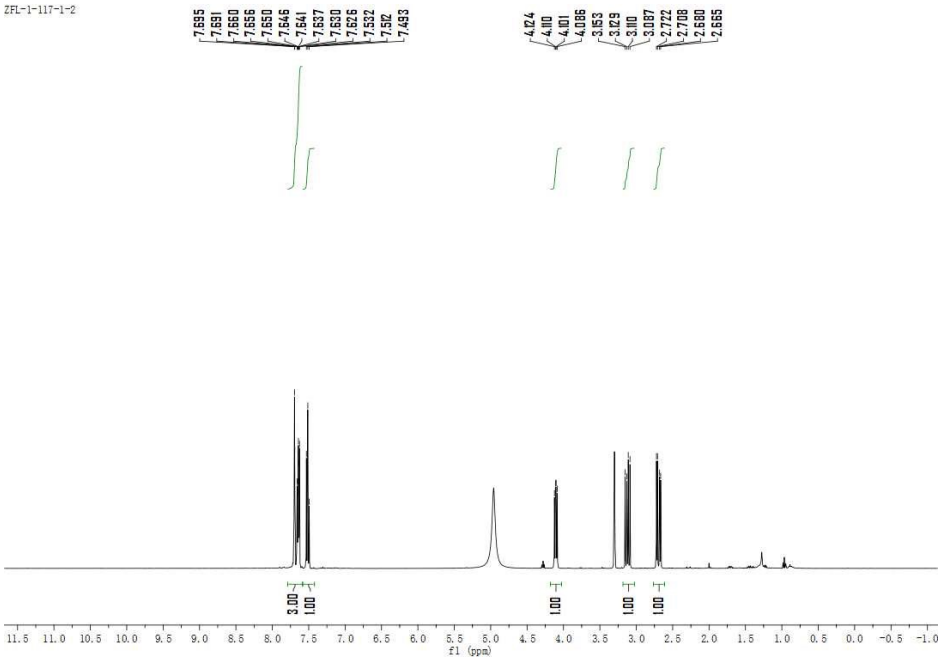
^{1}H NMR and ^{13}C NMR spectra of 4f

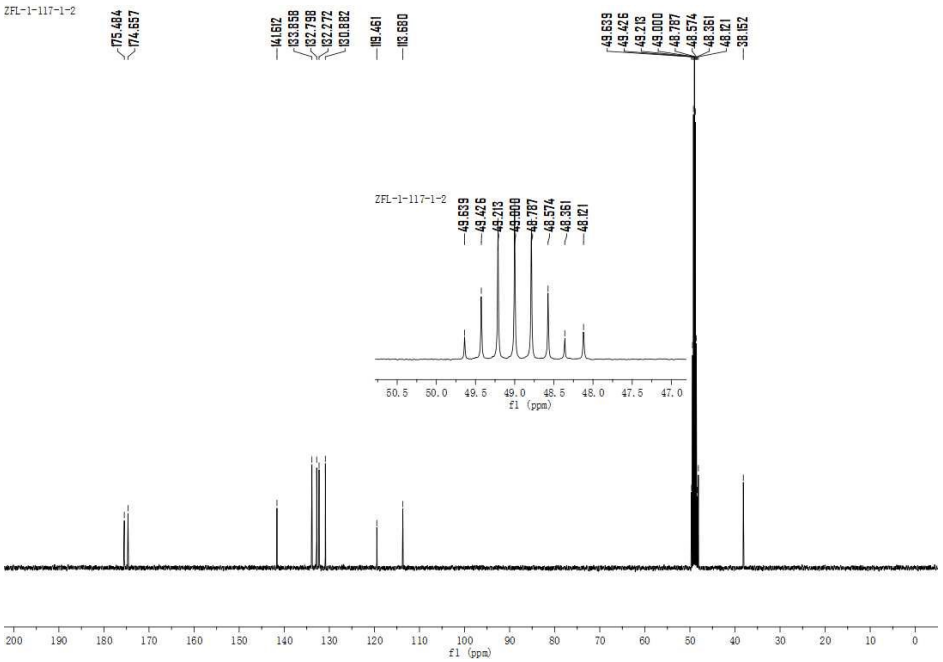


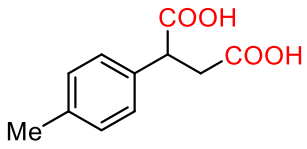




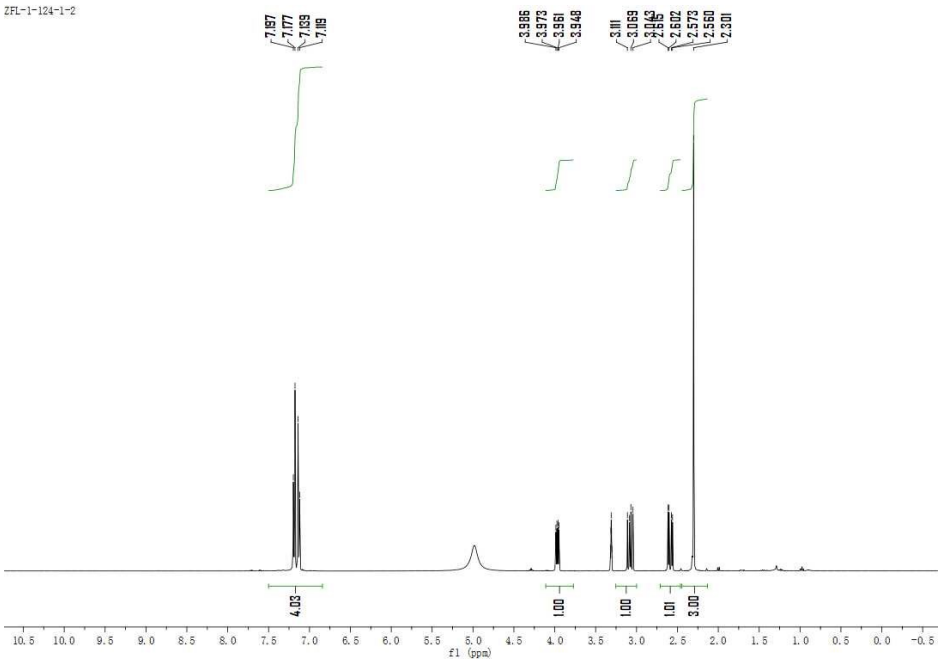
^{1}H NMR and ^{13}C NMR spectra of 4g

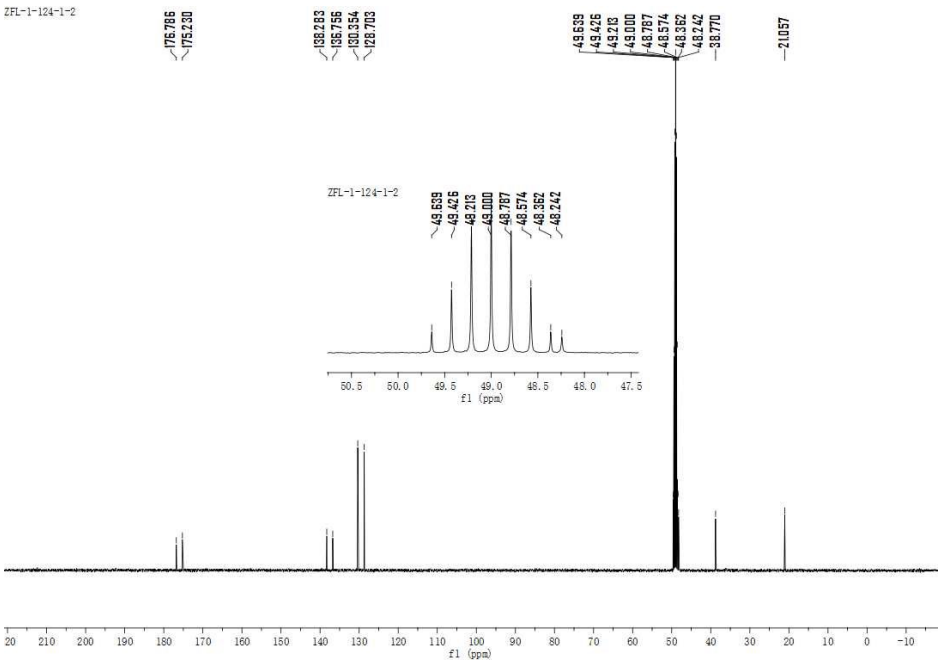


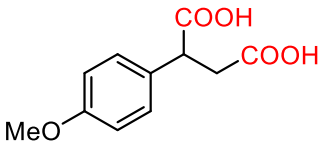




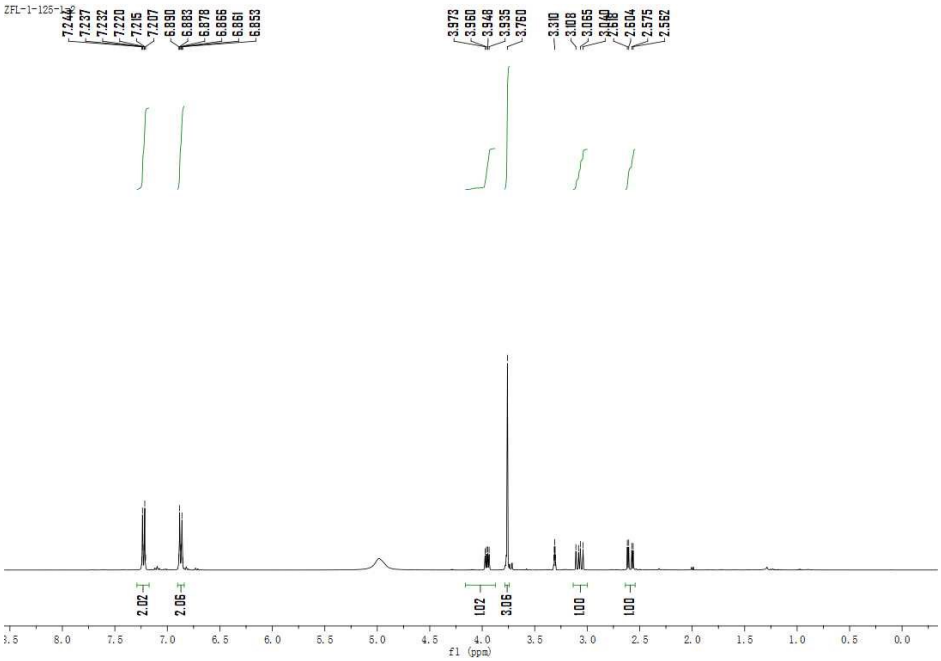
^{1}H NMR and ^{13}C NMR spectra of 4h

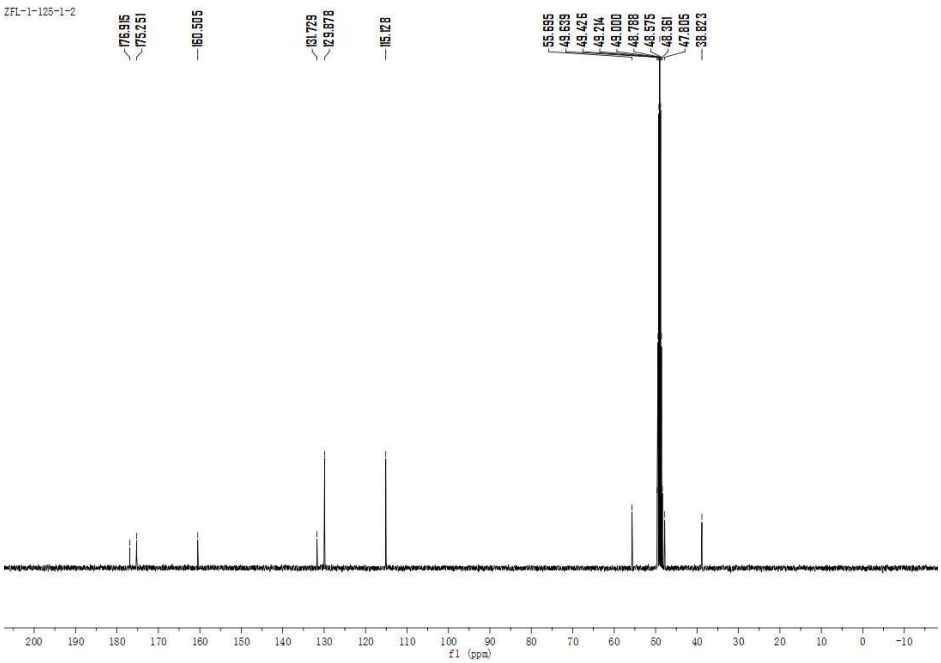


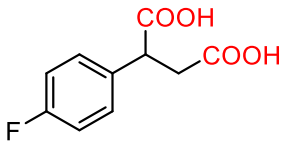




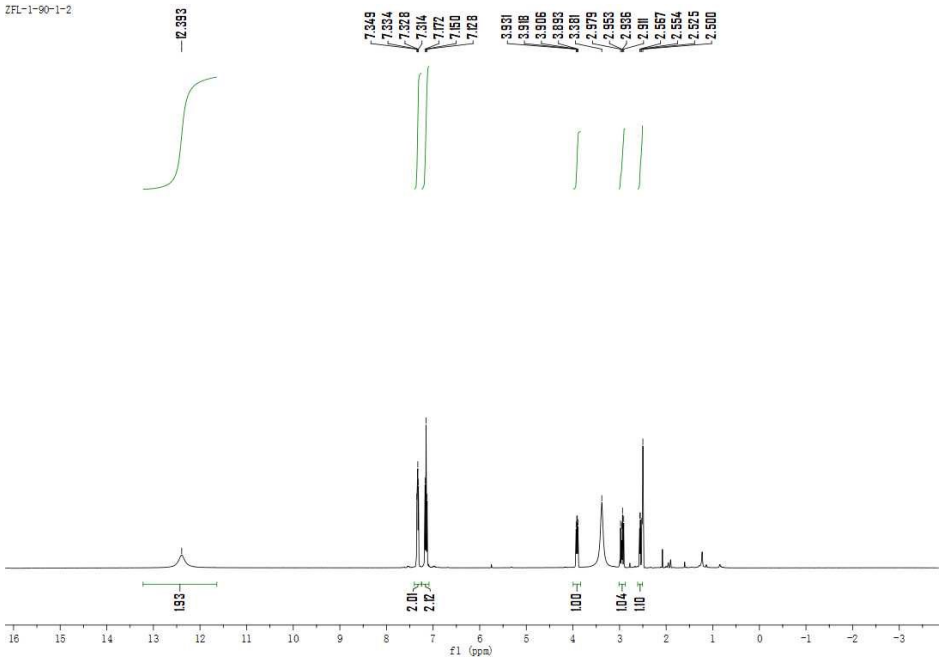
^{1}H NMR and ^{13}C NMR spectra of 4i

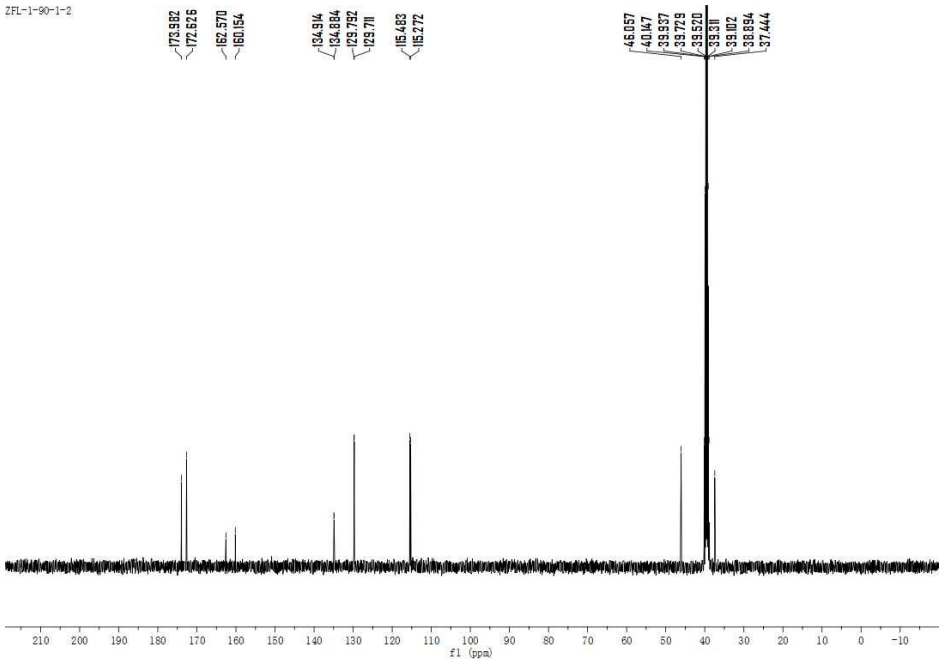


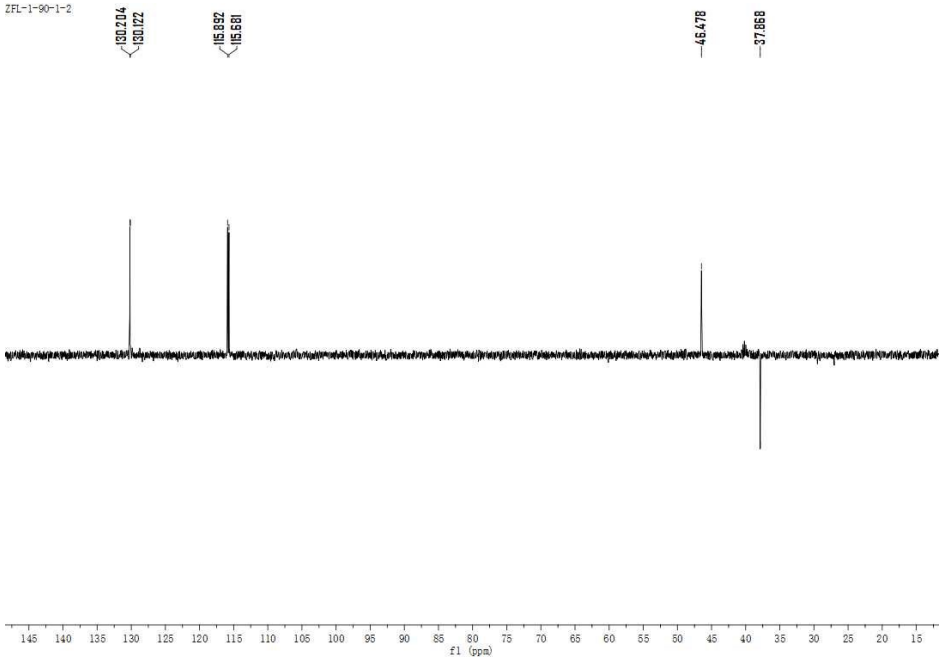




^{1}H NMR and ^{13}C NMR, DEPT-135^{o}, ^{19}F NMR spectra of 4j



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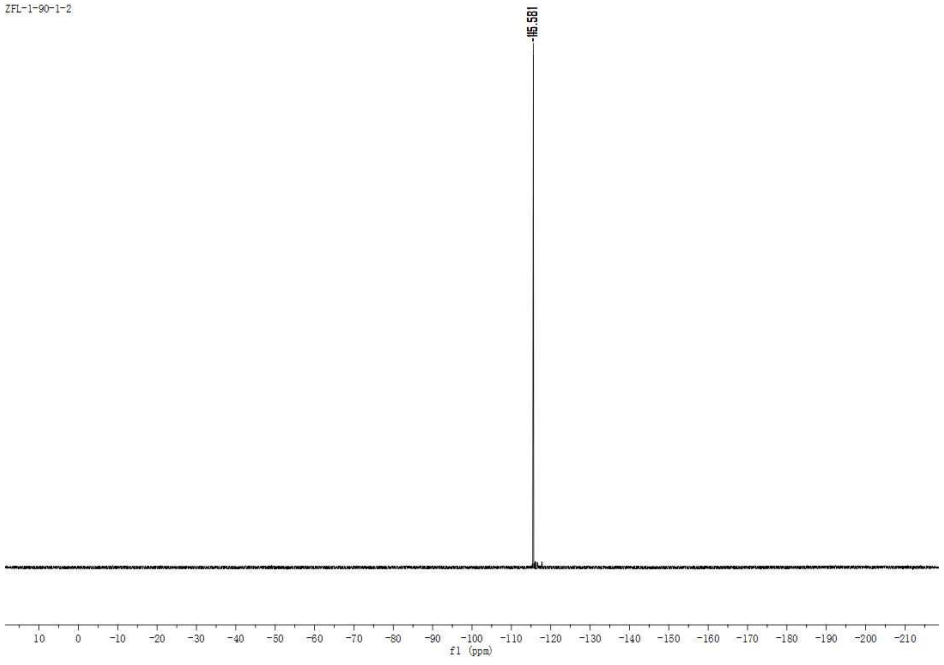
130.122
115.892
115.681
46.478
37.868
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15
f1 (ppm)


ZFL-1-90-1-2
-115.581
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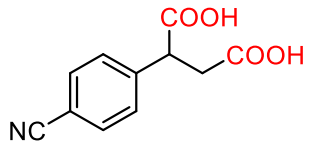
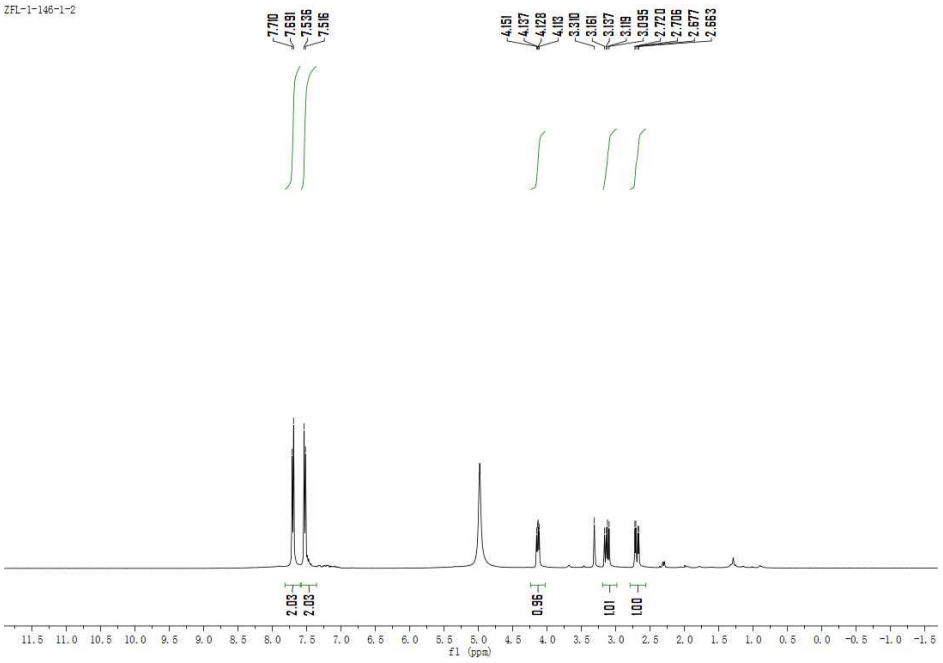
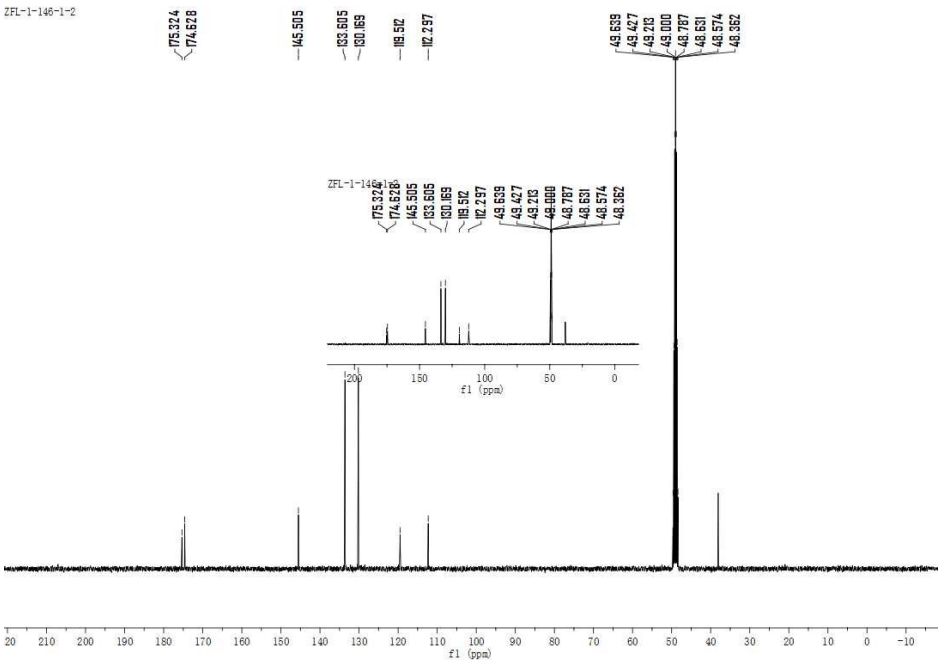
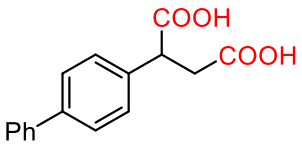
f1 (ppm)



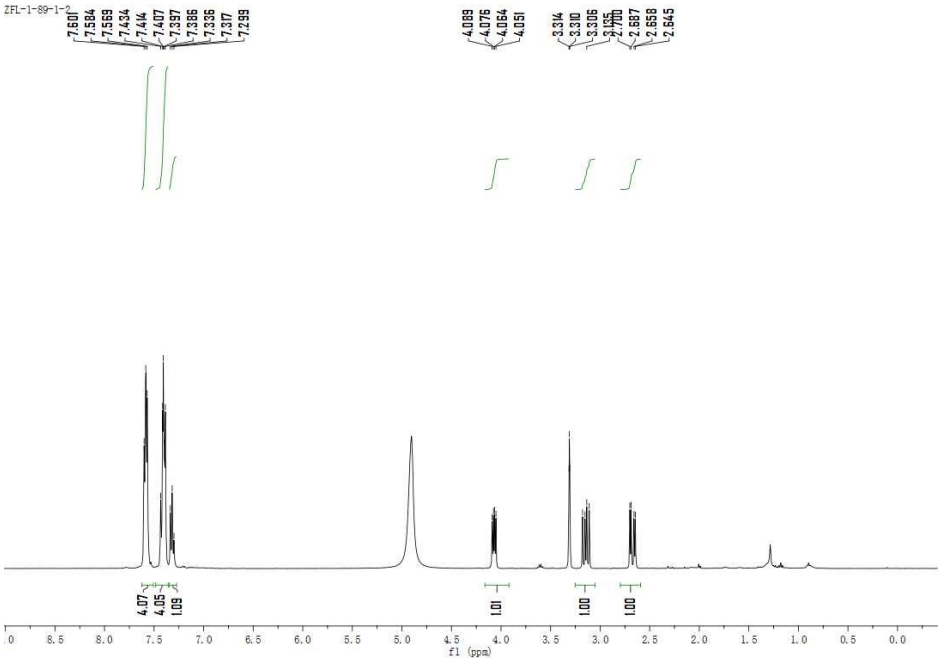
^{1}H NMR and ^{13}C NMR spectra of 4k

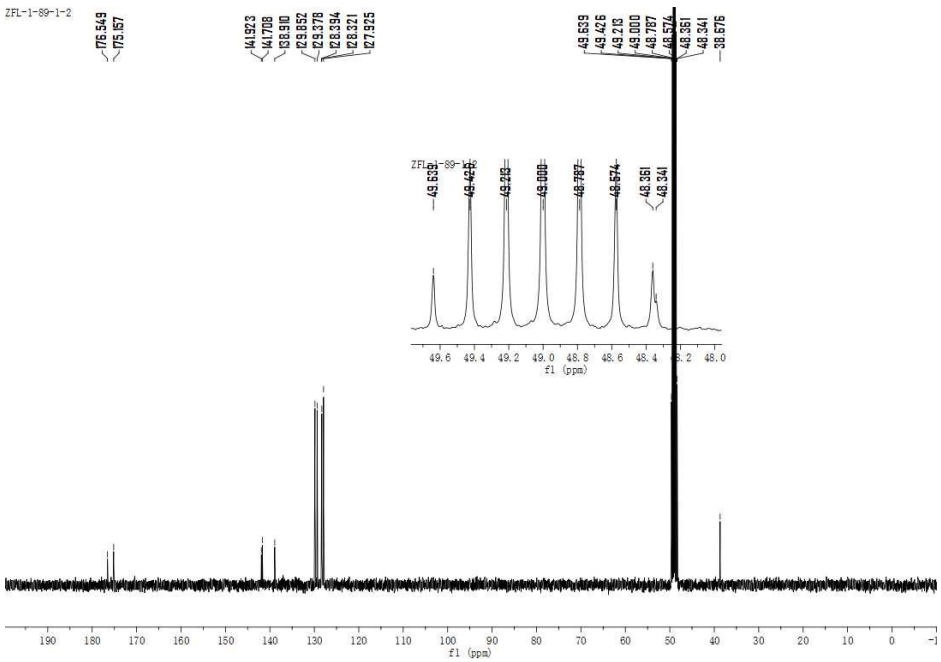


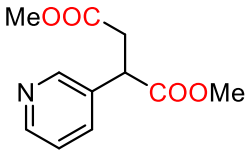




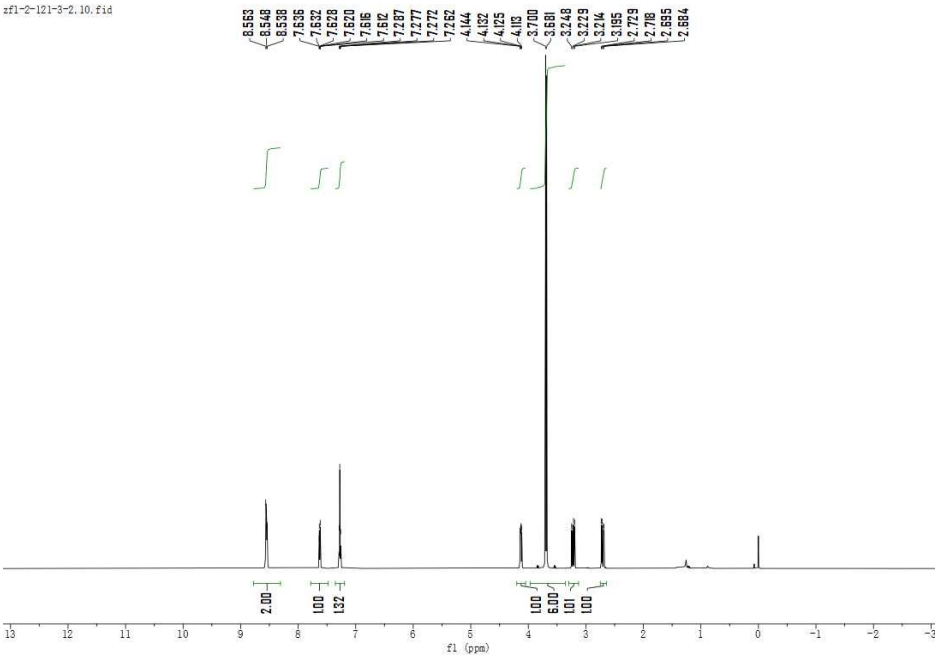
^{1}H NMR and ^{13}C NMR spectra of 4l

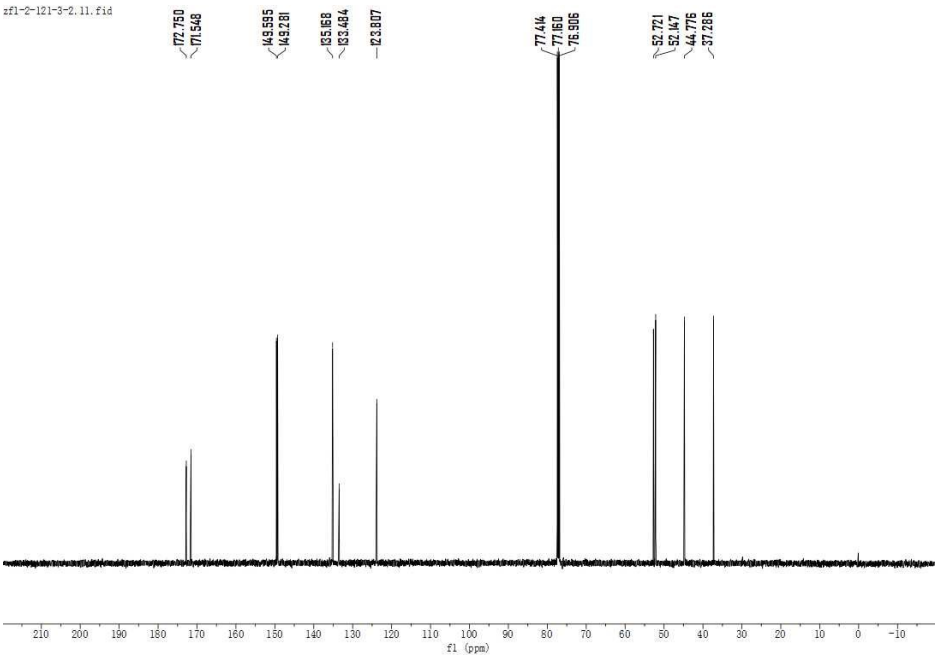


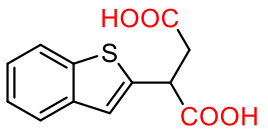




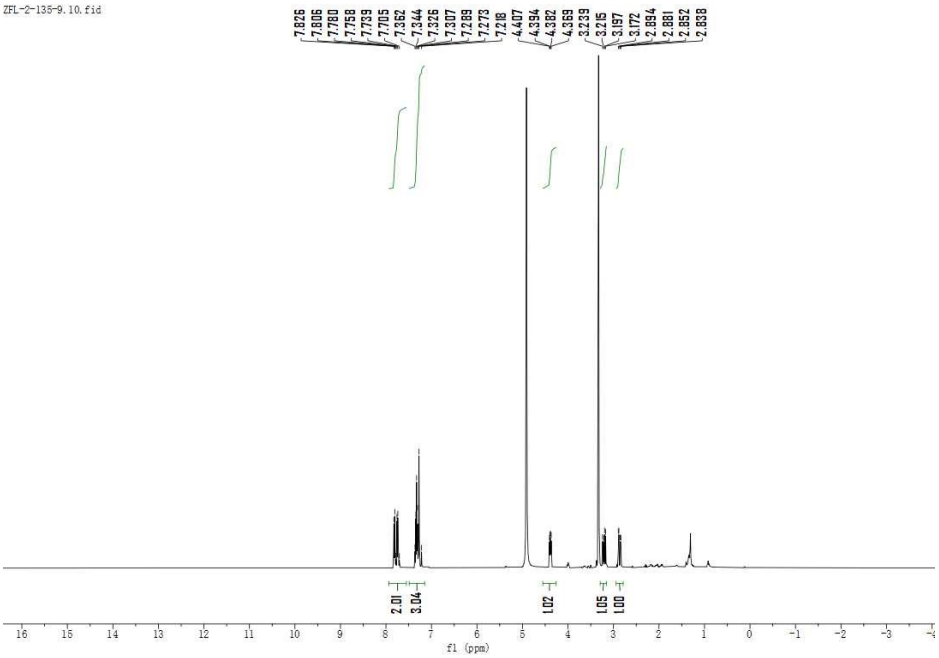
^{1}H NMR and ^{13}C NMR spectra of 4m

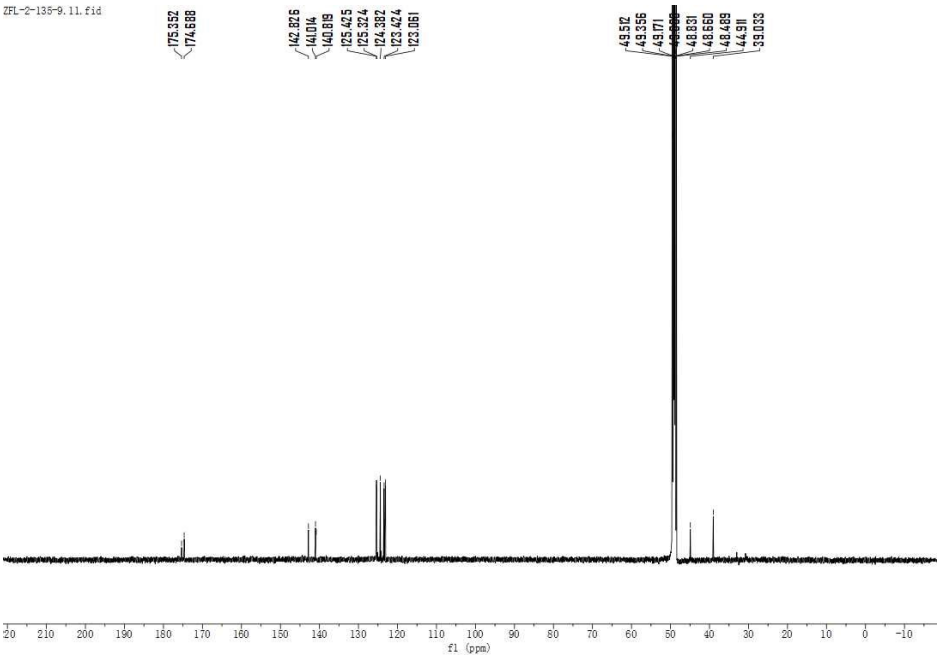


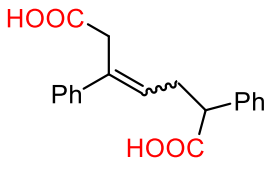




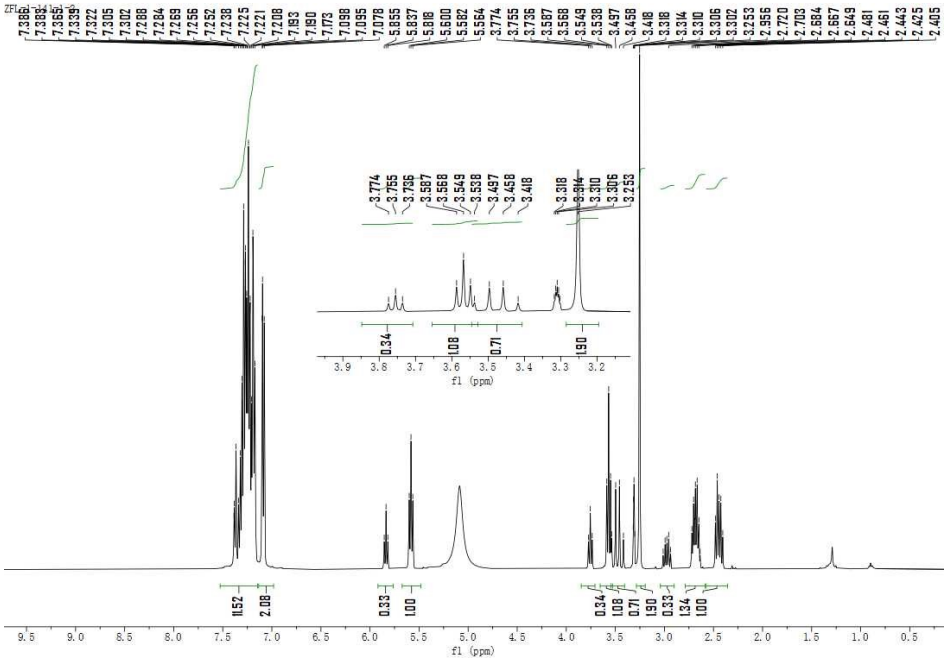
^{1}H NMR and ^{13}C NMR spectra of 4n

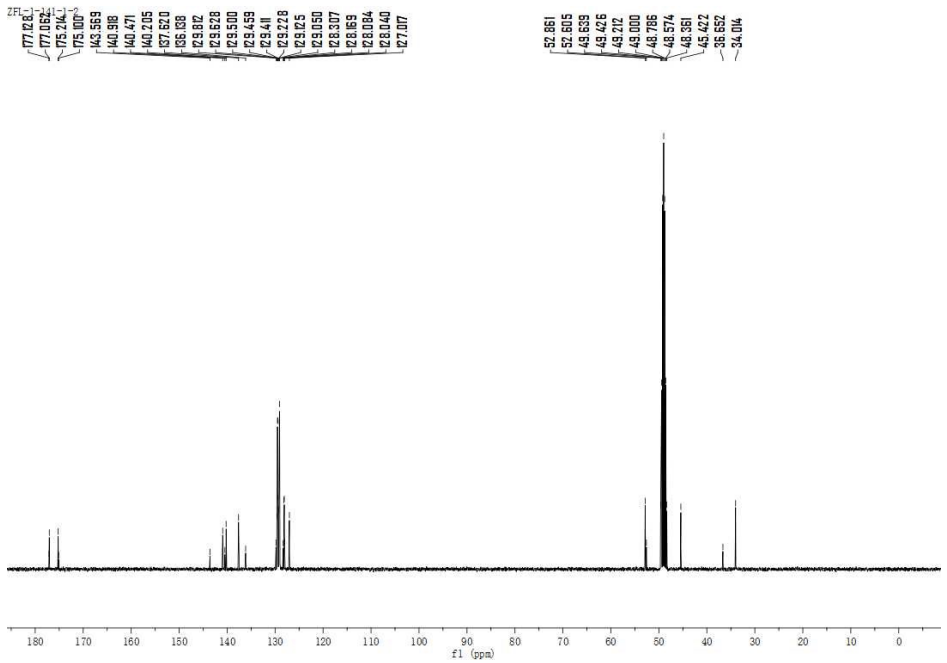


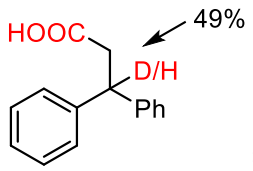




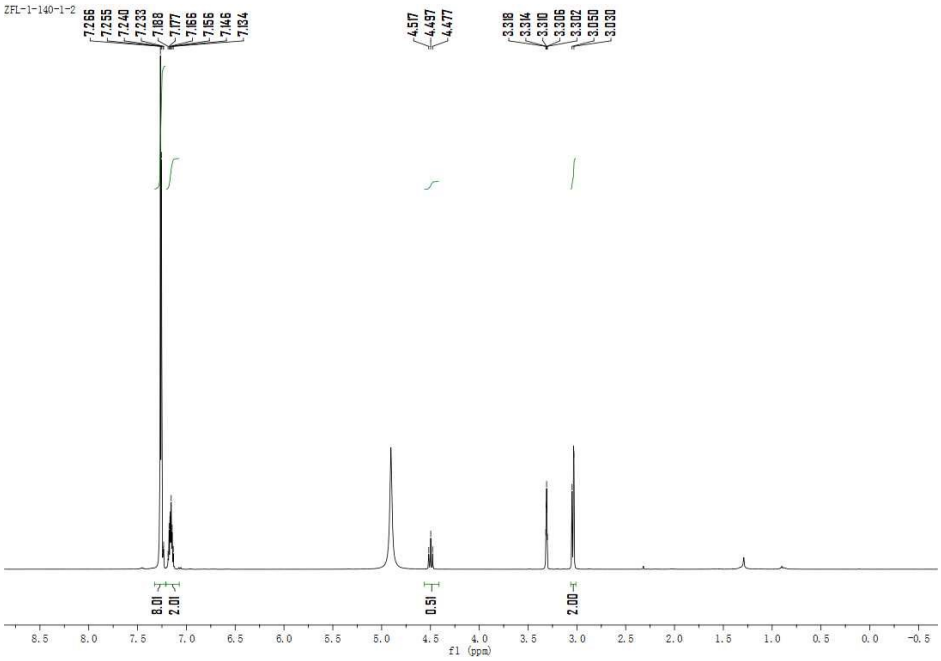
^{1}H NMR and ^{13}C NMR spectra of 6

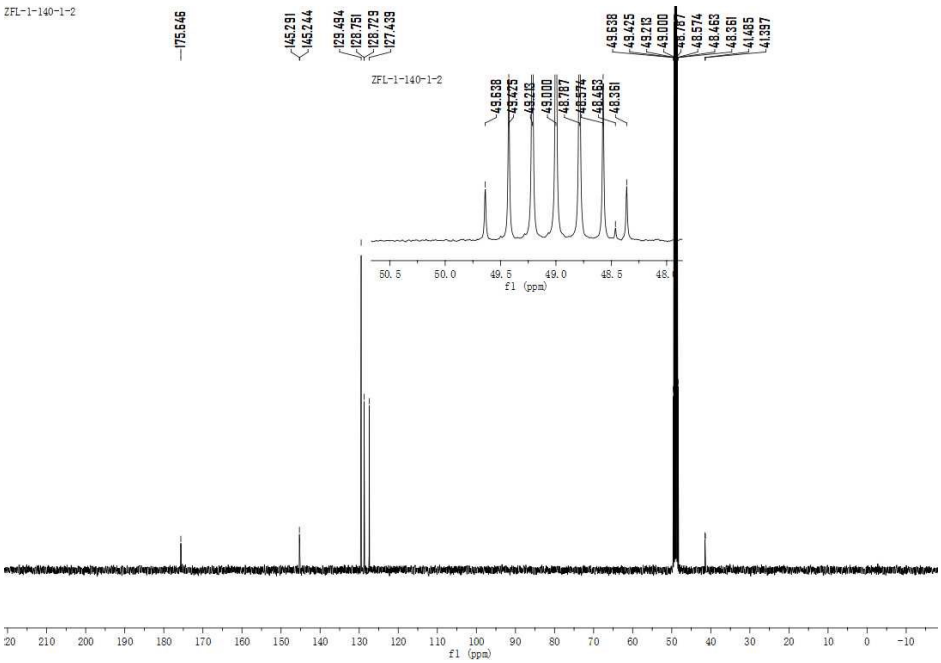


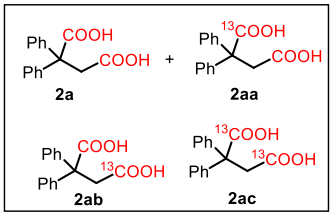




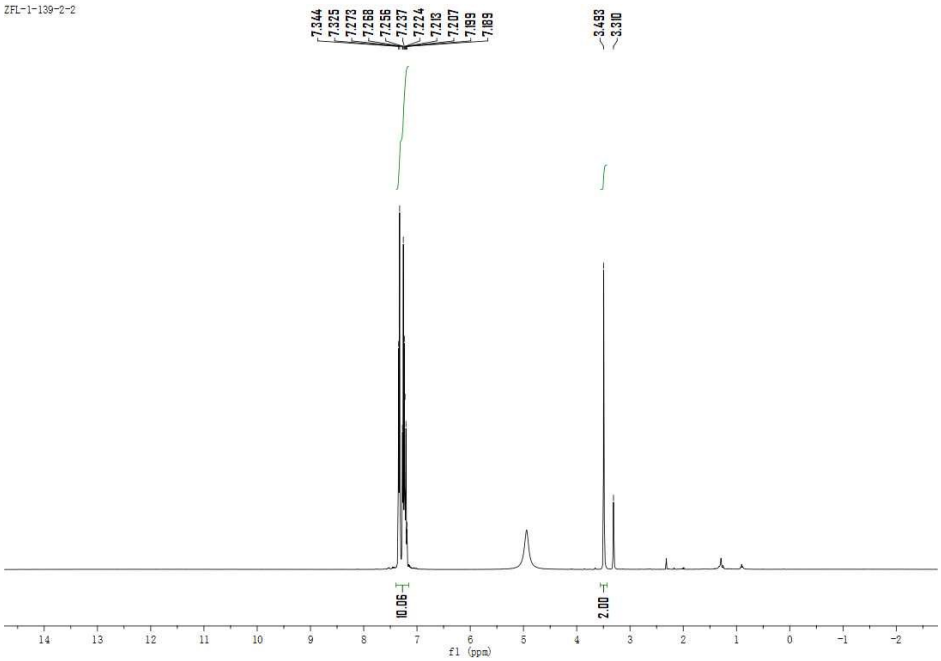
^{1}H NMR and ^{13}C NMR spectra of 2a$_{H}$-DH

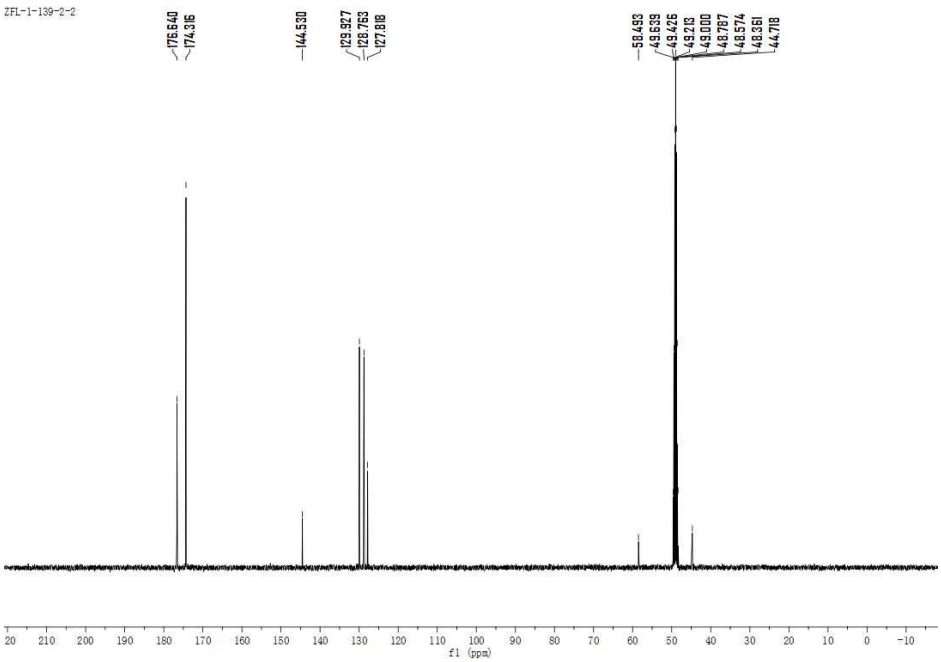


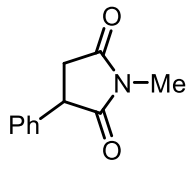




^{1}H NMR and ^{13}C NMR spectra of 2a+(2aa/2ab)+2ac







^{1}H NMR and ^{13}C NMR spectra of 7