Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Synergistic copper/ppm Pd-catalyzed hydrocarboxylation of alkynes with formic acid as CO surrogate as well as hydrogen source: an alternative indirect utilization of CO_2

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1. General Information

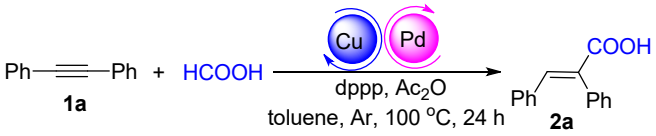
A. Materials:

Unless otherwise noted, all reagents were purchased from commercial sources and used as received. All the solvents used for reactions were distilled under argon after drying over an appropriate drying agent. All reactions were conducted in oven-dried glassware under argon atmosphere (purity ≥ 99.99%). Alkyne compounds were prepared according to literature procedure. DCOOD (99%-D) were purchased from Cambridge Isotope Laboratories and Innochem.

B. Analytical Methods:

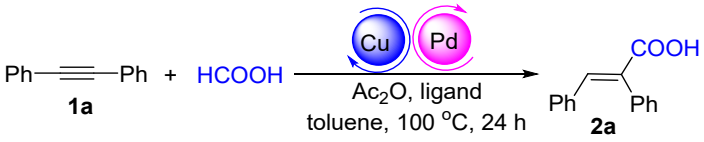
^{1}H-NMR spectra were recorded on Bruker 400 MHz or 600 MHz spectrometer using $CDCl_3$ (7.26 ppm), DMSO (2.50 ppm, 3.33 ppm of water peak), or Acetone (2.09 ppm) as solvent at ambient temperature. Data for ^{1}H-NMR are reported as follows: chemical shift (ppm, scale), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and/or multiplet resonances, br = broad), coupling constant (Hz), and integration. ^{13}C-NMR spectra were recorded at 100.6 MHz in $CDCl_3$ using $CDCl_3$ (77.16 ppm) or DMSO-d_6 (40.45 ppm), Acetone (29.92, 206.68 ppm) as an internal reference. Data for ^{13}C-NMR are reported in terms of chemical shift (ppm, scale), multiplicity, and coupling constants (Hz). Gaseous product CO was analyzed by gas chromatograph FULI 9790 equipped with thermal conductivity detector (TCD) with Ar as carrier gas, and the column oven was maintained at 70 °C for the duration of the analysis. High resolution mass spectral analysis (HRMS) was performed on a Varian 7.0 T FTICR-MS by ESI technique. Infrared (IR) spectra were recorded on a Bruker Tensor 27 FT-IR spectrophotometer with KBr pellets.

2. General procedure for the hydrocarboxylation of alkynes



In an argon gas filled glove box, to an oven-dried 10 mL screw-cap reaction tube equipped with a stir bar was charged with $Pd_2(dba)_3$ (50 ppm, 50 μL of the palladium solution (0.5 mM in toluene)), IPrCuCl (36.6 mg, 15 mol%), dppp (30.9 mg, 15 mol%) and dry toluene (1 mL). The resulting mixture was stirred at room temperature for 15 minutes. Alkyne substrate (0.5 mmol), formic acid (50 μL, 2.7 equiv.), and Ac_2O (60 μL, 1.2 equiv.) were added subsequently and heated at 100 °C (oil bath) for 24 or 36 h. After the reaction mixture was cooled to room temperature, the yield of product was determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. To obtain pure products, the mixture was purified with silica gel chromatography (petroleum ether/ethyl acetate = 50/1 to 2/1). Then the products were determined by NMR and HRMS (ESI).

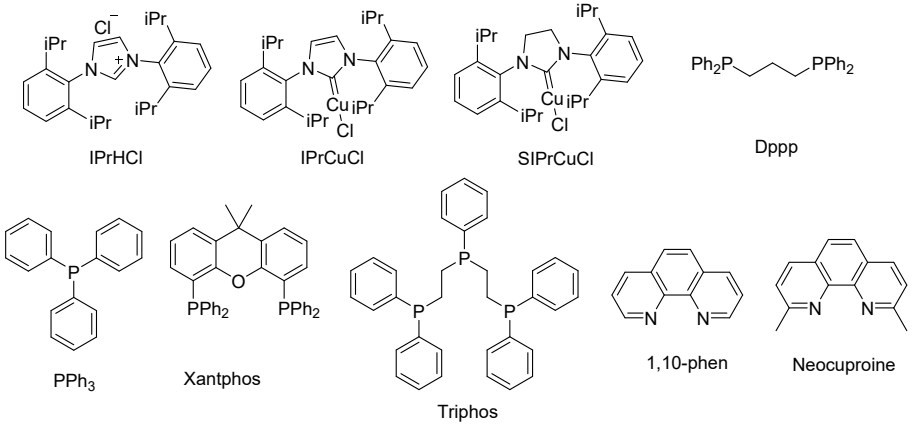
3. Investigation of the key reaction parameters



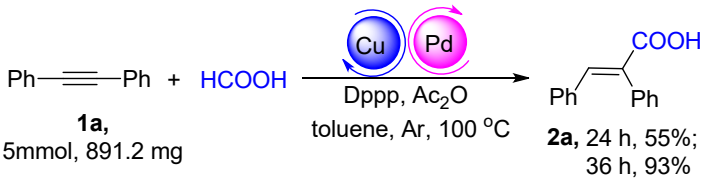
entry	[Pd]/ (x ppm)	[Cu]/ (y mol%)	ligand	L/Cu	solvent	T (°C)	**2a**/yield/%
1	-	CuCl (10)	dppp	1	toluene	100	0
2	-	$Cu_2(CO_3)_2(OH)_2$ (10)	dppp	1	toluene	100	0
3	-	SIPrCuCl (10)	dppp	1	toluene	100	0
4	-	IPrCuCl (10)	dppp	1	toluene	100	0
5	$Pd(OAc)_2$ (200)	$CuCl_2$ (10)	dppp	1	toluene	100	0
6	$Pd(OAc)_2$ (200)	CuCl (10)	dppp	1	toluene	100	73
7	$Pd(OAc)_2$ (200)	$Cu_2(CO_3)_2(OH)_2$ (10)	dppp	1	toluene	100	30
8	$Pd(OAc)_2$ (200)	SIPrCuCl (10)	dppp	1	toluene	100	85
9	$Pd(OAc)_2$ (200)	IPrCuCl (10)	dppp	1	toluene	100	93
10	$Pd(OAc)_2$ (200)	IPrCuCl (10)	PPh_3	2	toluene	100	13
11	$Pd(OAc)_2$ (200)	IPrCuCl (10)	Xantphos	1	toluene	100	89
12	$Pd(OAc)_2$ (200)	IPrCuCl (10)	Triphos	1	toluene	100	Trace
13	$Pd(OAc)_2$ (200)	IPrCuCl (10)	1,10-Phen	1	toluene	100	Trace
14	$Pd(OAc)_2$ (200)	IPrCuCl (10)	Xantphos	1	toluene	100	Trace
15	$Pd(OAc)_2$ (200)	IPrCuCl (10)	Neocuproine	1	toluene	100	Trace
16	$Pd(OAc)_2$ (50)	IPrCuCl (10)	dppp	1	toluene	100	89
17	$Pd(OAc)_2$ (20)	IPrCuCl (10)	dppp	1	toluene	100	72
18	$Pd(OAc)_2$ (50)	IPrCuCl (5)	dppp	1	toluene	100	29
19	$Pd(OAc)_2$ (50)	IPrCuCl (15)	dppp	1	toluene	100	93
20	$Pd_2(dba)_3$ (50)	IPrCuCl (15)	dppp	1	toluene	100	95
21	$Pd(PPh_3)_4$ (50)	IPrCuCl (15)	dppp	1	toluene	100	90
22	Pd/C (50)	IPrCuCl (15)	dppp	1	toluene	100	83
23	$Pd_2(dba)_3$ (50)	IPrCuCl (15)	dppp	0.6	toluene	100	24
24	$Pd_2(dba)_3$ (50)	IPrCuCl (15)	dppp	0.2	toluene	100	6
25	$Pd_2(dba)_3$ (50)	IPrCuCl (15)	dppp	50ppm	toluene	100	Trace
26	$Pd_2(dba)_3$ (50)	IPrCuCl (15)	dppp	-	toluene	100	0
27	-	IPrCuCl (15)	dppp		toluene	100	0
28	$Pd_2(dba)_3$ (50)	-	dppp	-	toluene	100	31
29	$Pd_2(dba)_3$ (50)	IPrCuCl (15)	dppp	1	*p*-xylene	100	90
30	$Pd_2(dba)_3$ (50)	IPrCuCl (15)	dppp	1	*m*-xylene	100	86
31	$Pd_2(dba)_3$ (50)	IPrCuCl (15)	dppp	1	DMF	100	0
32	$Pd_2(dba)_3$ (50)	IPrCuCl (15)	dppp	1	THF	100	0
33	$Pd_2(dba)_3$ (50)	IPrCuCl (15)	dppp	1	MeOH	100	0
34	$Pd_2(dba)_3$ (50)	IPrCuCl (15)	dppp	1	1,4- dioxane	100	90
35	$Pd_2(dba)_3$ (50)	IPrCuCl (15)	dppp	1	H_2O	100	trace
36	$Pd_2(dba)_3$ (50)	IPrCuCl (15)	dppp	1	toluene	110	89
37	$Pd_2(dba)_3$ (50)	IPrCuCl (15)	dppp	1	toluene	80	86

38	$Pd_2(dba)_3$ (50)	IPrCuCl (15)	dppp	1	toluene	25	0

[a] Reaction conditions: diphenylacetylene **1a** (0.5 mmol), [Pd] (x ppm), [Cu] (y mol%), L (x equiv. relative to y mol% of IPrCuCl), HCOOH (50 μL, 2.7 equiv.), Ac_2O (60 μL, 1.2 equiv.), toluene (1 mL) at t °C for 24 h under an argon atmosphere. [b] Yields were determined by ^1H NMR with 1,3,5-trimethoxybenzene as internal standard.



4. General procedure for the gram-scale reactions.



In a argon gas filled glove box, to an oven-dried 135 mL screw-cap reaction flask equipped with a stir bar was charged with $Pd_2(dba)_3$ (100 ppm, 100 μL of the palladium solution (5 mM in toluene)), IPrCuCl (365.6 mg, 15 mol%), dppp (309.3 mg, 15 mol%) and dry toluene (25 mL). The mixture was stirred at room temperature for 15 minutes. Then diphenylacetylene (891.2 mg, 5 mmol), formic acid (509 μL, 13.5 mmol) and Ac_2O (567 μL, 6 mmol) were added through the injection port. The reaction mixture was stirred at 100 °C. After 24 h or 36 h the pressure flask was cooled to the room temperature. The reaction mixture was transferred to a round bottom flask and the solvent was evaporated in vacuo. The ^1H NMR yields were determined with 1,3,5-trimethoxybenzene as internal standard and the ratio of α and β were determined by ^1H NMR. Subsequently, the residue was purified with silica gel chromatography using petroleum ether/EtOAc (50/1 to 5/1, v/v) as an eluent, giving the white solid product.

5. The effect of cooperative catalysis on the release of CO

In an argon gas filled glove box, an oven-dried 10 mL Schlenk tube equipped with a stir bar was charged with $Pd_2(dba)_3$ (50 ppm, 50 μL of the palladium solution (0.5 mM in toluene)), IPrCuCl (36.6 mg, 15 mol%), dppp (30.9 mg, 15 mol%) and dry toluene (1 mL). The resulting mixture was stirred at room temperature for 15 minutes. Then formic acid (50 μL, 2.7 equiv.), and Ac_2O (60 μL, 1.2 equiv.) were added subsequently and then CH_4 (1 mL) as an internal standard was added to the reaction system through the injection port. The reaction mixture was heated at 100 ^oC (oil bath) for t minutes. After the reaction mixture was cooled to room temperature, the mixed gas in tube was detected by GC to give the mount of CO (Table S1).

Table S1. The amount of CO produced under different catalytic systems. [a,b]

t/min	2	20	40	60	80	100		
CO/μmol[c]	18.15	18.77	23.33	29.76	92.95	91.95		
t/min	1	2	3	4	5	10	15	20
CO/μmol[d]	119.80	222.94	318.21	453.17	511.07	635.48	699.67	725.59
t/min	0.5	1	1.5	2	5	10	15	20
CO/μmol[e]	14.55	47.52	219.10	301.43	426.37	530.42	533.43	534.43
t/min	2	5	10	15	20			
CO/μmol[f]	0	0	0	0	0			

[a]Reaction conditions: $Pd_2(dba)_3$ (50 ppm), IPrCuCl (15 mol%), dppp (15 mol%), HCOOH (50 μL, 2.7 equiv.), Ac_2O (60 μL 1.2 equiv.), toluene (1 mL), 100 ^oC, t min. [b]The mount of gas was determined by GC using CH_4 (1 mL) as internal standard. [c]no catalysts. [d] $Pd_2(dba)_3$ (50 ppm), IPrCuCl (15 mol%), dppp (15 mol%). [e]no IPrCuCl. [f]no Ac_2O.

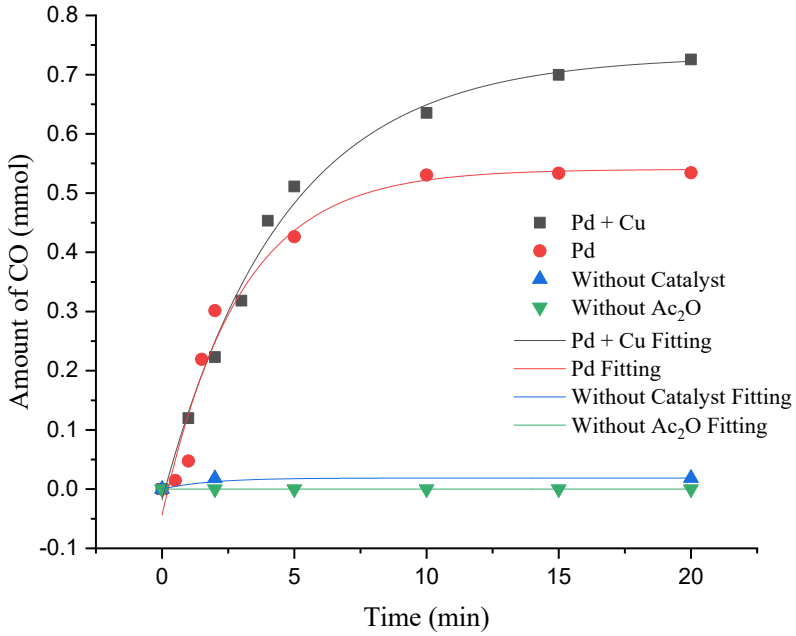
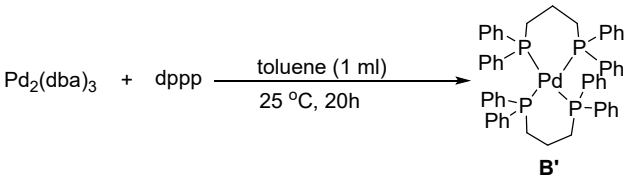


Fig. S1 The effect of cooperative catalysis on the release of CO.

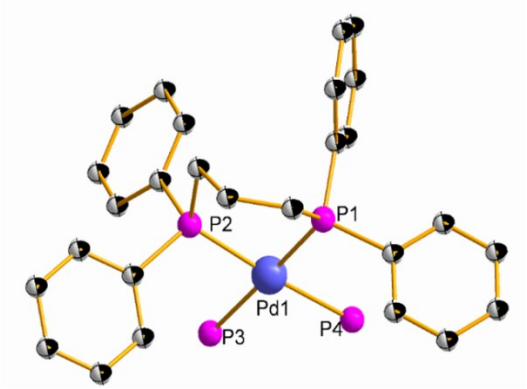
6. Control Experiments

6.1 The coordination model of $Pd_2(dba)_3$ with dppp



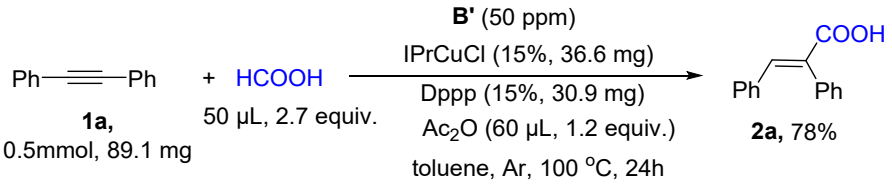
B'

A Schlenk tube with a magnetic stir bar was charged with $Pd_2(dba)_3$ (46 mg, 0.05 mmol), dppp (41.2 mg, 0.1 mmol) and dry toluene (1 mL). Then the reaction allows to stir at 25 °C for 12 h. Removal of volatiles under vacuum and 0.5 mL hexane and 0.5 mL toluene was added and standing the mixture at -20 °C, crystals suitable for X-ray crystallography was obtained and gave analytically pure product **B'**. The complex **B'** was then conducted for the hydrocarboxylation of alkynes under otherwise identical conditions in the absence of $Pd_2(dba)_3$ and dppp. Subsequently, the reaction solution was purified with silica gel chromatography using petroleum ether/EtOAc (50/1 to 5/1, v/v) as an eluent, giving the white solid product in 78%.



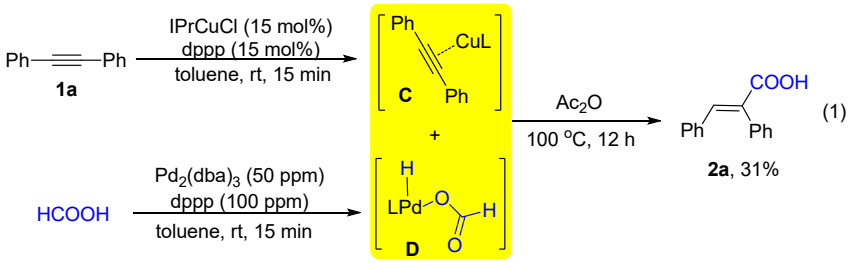
B'-*X*-ray (CCDC:2082526)

Fig. S2 Molecular structure of palladium complex **B'**. H atoms are omitted for clarity.

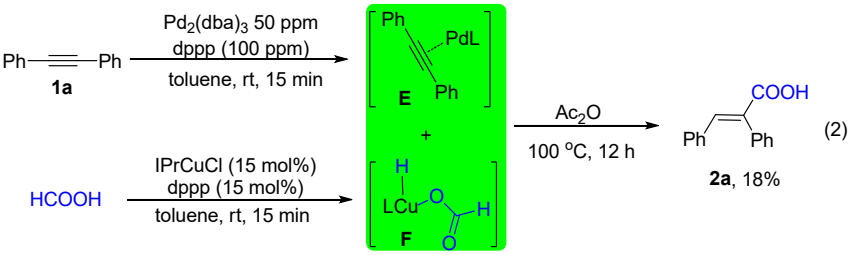


6.2 Separate Experiments

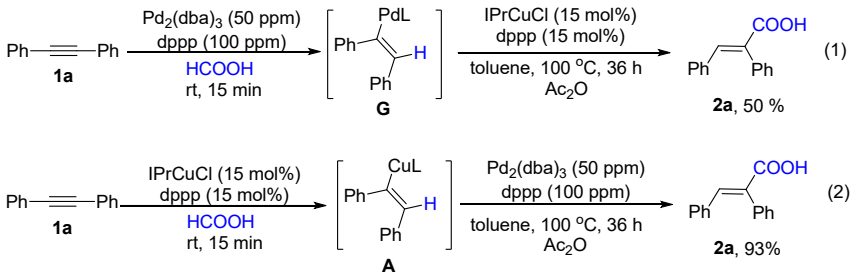
(1) In a argon-filled glove box, an oven-dried 10 mL screw-cap reaction tube equipped with a stir bar was charged with IPrCuCl (36.6 mg, 15 mol%), dppp (30.9 mg, 15 mol%), diphenylacetylene (89.1 mg, 0.5 mmol) and dry toluene (1 mL) at room temperature for about 15 min; Meanwhile, $Pd_2(dba)_3$ (50 ppm, 50 μL of the palladium solution (0.5 mM in toluene)), dppp (100 ppm, 50 μL of the dppp solution (1 mM in toluene)), formic acid (50 μL, 2.7 equiv.) were stirred in toluene (1 mL) in a Schlenk flask at room temperature for 15 min. The Pd complex solution and Ac_2O (60 μL, 1.2 equiv.) were then added into the screw-cap reaction tube equipped with Cu complex. Then the reaction was performed for 12 h at 100 °C. After the reaction was cooled down to room temperature, and the pressure was released carefully, the yield of **2a** determined by ^{1}HNMR analysis using 1,3,5-trimethoxybenzene as internal standard (eq1).



(2) In a argon-filled glove box, an oven-dried 10 mL screw-cap reaction tube equipped with a stir bar was charged with IPrCuCl (36.6 mg, 15 mol%), dppp (30.9 mg, 15 mol%), formic acid (50 μL, 2.7 equiv.), and Ac_2O (60 µL, 1.2 equiv.) and dry toluene (1 mL) at room temperature for about 15 min; Meanwhile, $Pd_2(dba)_3$ (50 ppm, 50 μL of the palladium solution (0.5 mM in toluene)), dppp (100 ppm, 50 μL of the dppp solution (1 mM in toluene)) diphenylacetylene (89.1 mg, 0.5 mmol) were stirred in toluene (1 mL) in a Schlenk flask at room temperature for 15 min. The Pd complex solution and Ac_2O (60 μL, 1.2 equiv.) were then added into the screw-cap reaction tube equipped with Cu complex. Then the reaction was performed for 12 h at 100 °C. After the reaction was cooled down to room temperature, and the pressure was released carefully, the yield of **2a** determined by ^{1}HNMR analysis using 1,3,5- trimethoxybenzene as internal standard (eq 2).



6.3 Study on key intermediates.



(1) In a argon-filled glove box, an oven-dried 10 mL screw-cap reaction tube equipped with a stir bar was charged with IPrCuCl (36.6 mg, 15 mol%), dppp (30.9 mg, 15

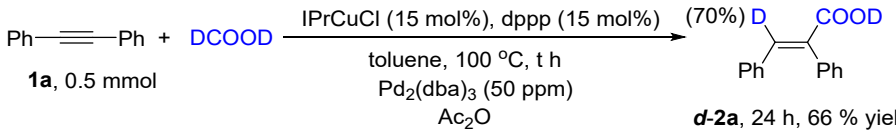
mol%), diphenylacetylene (89.1 mg, 0.5 mmol), HCOOH (50 μL, 2.7 equiv.) and dry toluene (1.5 mL) at room temperature for 15 min. Then $Pd_2(dba)_3$ (50 ppm, 50 μL of the palladium solution (0.5 mM in toluene)), dppp (100 ppm, 50 μL of the dppp solution (1 mM in toluene)) and Ac_2O (60 μL, 1.2 equiv.) were added and the reaction was performed for 36 h at 100 ^oC. After the reaction was cooled down to room temperature, and the pressure was released carefully, 50% yield of **2a** was determined by ^{1}HNMR analysis using 1,3,5-trimethoxybenzene as internal standard (eq1).

(2) In a argon-filled glove box, an oven-dried 10 mL screw-cap reaction tube equipped with a stir bar was charged with $Pd_2(dba)_3$ (50 ppm, 50 μL of the palladium solution (0.5 mM in toluene)), dppp (100 ppm, 50 μL of the dppp solution (1 mM in toluene)), diphenylacetylene (89.1 mg, 0.5 mmol), HCOOH (50 μL, 2.7 equiv.) and dry toluene (1 mL) at room temperature for 15 min. Then IPrCuCl (36.6 mg, 15 mol%), dppp (30.9 mg, 15 mol%) and Ac_2O (60 μL, 1.2 equiv.) were added and the reaction was performed for 36 h at 100 ^oC. After the reaction was cooled down to room temperature, and the pressure was released carefully, 93% yield of **2a** was determined by ^{1}HNMR analysis using 1,3,5-trimethoxybenzene as internal standard (eq2).

6.4 D-labeling experiments under DCOOD.

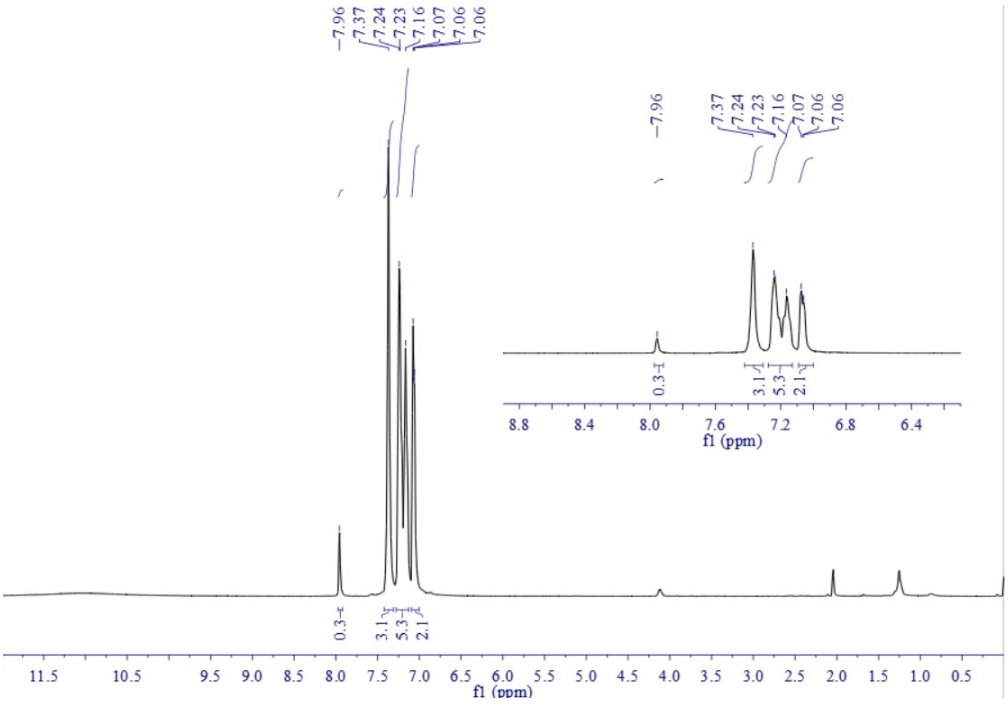
In an argon gas filled glove box, an oven-dried 10 mL screw-cap reaction tube equipped with a stir bar was charged with $Pd_2(dba)_3$ (50 ppm, 50 μL of the palladium solution (0.5 mM in toluene)), IPrCuCl (36.6 mg, 15 mol%), dppp (30.9 mg, 15 mol%) and dry toluene (1 mL). The resulting mixture was stirred at room temperature for 15 minutes. diphenylacetylene (0.5 mmol), DCOOD (50 μL, 2.7 equiv.), and Ac_2O (60 μL, 1.2 equiv.) were added subsequently and heated at 100 ^oC (oil bath) for 36 h. After the reaction mixture was cooled to room temperature, the mixture was purified with silica gel chromatography (petroleum ether/ethyl acetate = 50/1 to 2/1) to give ***d*-2a** as a white solid (74.6 mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 0.3H), 7.37 (s, 3H), 7.28 – 7.16 (m, 5H), 7.09 – 7.05 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.3, 142.4, 135.3, 134.2, 131.5, 130.8, 129.7,

129.5, 128.7, 128.2, 128.0. HRMS (ESI) *calcd.* for ($C_9H_{16}O_2$-H): 155.1072, *found*: 155.1077. IR (KBr): 3500-2900 (br), 1673.3, 1612.9, 1448.3, 1417.2, 1325.8, 1264.6, 1185.3, 917.2, 770.6, 697.4, 600.0, 472.4, 435.3 cm^{-1}



According to the ^{1}H NMR spectrum of D-labeling experiment, the hydrogen of the carboxyl group in the product is completely deuterated (100%) and the deuterium at the *β*-carbon to the carboxyl group was determined to be 46% by **^{1}H** NMR, in which the relative ratio of non-labeled **2a** to D-labeled **2a** is 3:7.

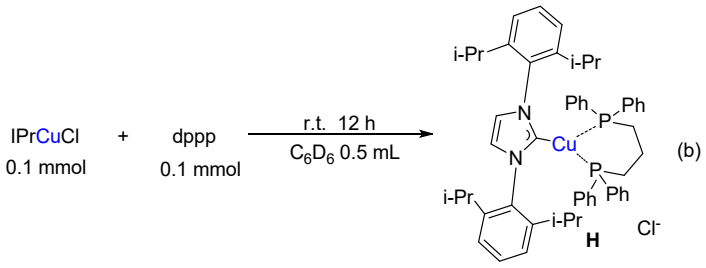
The ^{1}H NMR chart of D-labeling experiment is given as bellow:



7. ^{31}P NMR Investigation

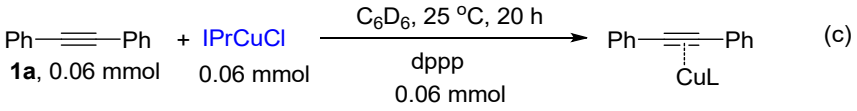
(a) 0.1 mmol of dppp was dissolved in 0.5 ml of C_6D_6 in a NMR tube. The reaction was complete after standing the mixture at room temperature for 6 h as indicated from ^{31}P NMR spectra. ^{31}P NMR (160 MHz, C_6D_6): δ -17.74.

(b)



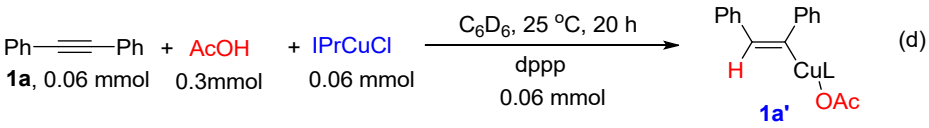
0.1 mmol of IPrCuCl and 0.1 mmol of dppp were dissolved in 0.5 mL of C_6D_6 in a NMR tube. The reaction was complete after standing the mixture at room temperature for 6 h as indicated from ^{31}P NMR spectra. ^{31}P NMR (160 MHz, C_6D_6): δ -13.68, -17.74.

(c)



0.06 mmol of IPrCuCl, 0.06 mmol of dppp and 0.06 mmol diphenylacetylene **1a** were dissolved in 0.5 mL of C_6D_6 in a NMR tube. The reaction was complete after standing the mixture at room temperature for 6 h as indicated from ^{31}P NMR spectra. ^{31}P NMR (160 MHz, C_6D_6): δ -3.89, -13.66, -17.74.

(d)



0.06 mmol of 1,2-diphenylethyne (**1a**), 0.06 mmol of IPrCuCl and 0.06 mmol of dppp were dissolved in 0.5 mL of C_6D_6 in NMR tube. 0.3 mmol of AcOH was then injected. The reaction was complete after standing the mixture at room temperature for 20 h and indicated by ^{31}P NMR spectra. ^{31}P NMR (160 MHz, C_6D_6): δ -4.22, -13.66.

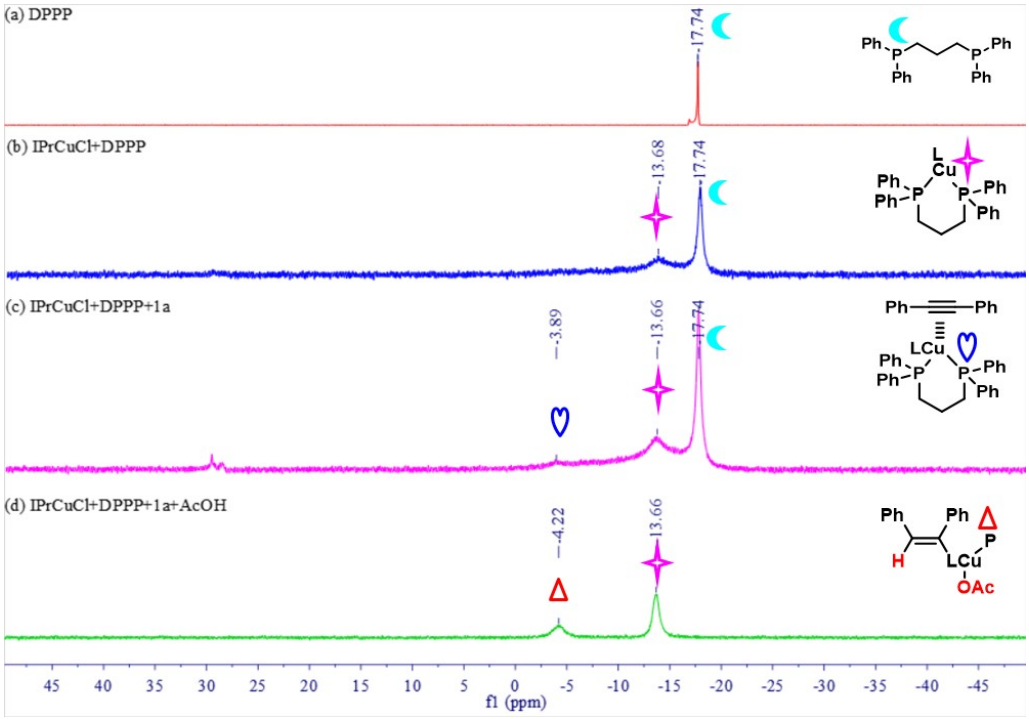


Fig. S3 ^{31}P NMR investigation (161 MHz).

To further verify our hypothesis that the carbon-carbon triple bond of alkyne could be activated by the coordinate chelation of IPrCuCl with dppp,[5] control experiments in the absence of Pd species were examined and monitored by ^{31}P NMR technique. As depicted in Fig. S3, the ^{31}P signal of dppp appeared at δ = -17.74 ppm in accordance with the reported literature (Fig. S3a);[5b,c] a broad signal emerged at δ = -13.68 ppm when IPrCuCl reacted with dppp in C_6D_6 for 6 h, being assigned to the formation of [IPrCu(dppp)]Cl chelate complex **H**, locating in the range of copper (I) diphosphine complexes typically observed[5a] (Fig. S3b). After the input of model substrate **1a**, IPrCuCl and dppp were consumed for 6 h at room temperature, and subsequently a characteristic ^{31}P signal could be observed at -3.89 ppm, indicative of the possible intermediates between C≡C bond and copper species (Fig. S3c). According to the reported literature,[5f] the facile decomposition of alkenylmetal complex with HCOOH

lead to poor detection, so acetic acid was added to the mixture of IPrCuCl and diphenylacetylene **1a** instead of formic acid **(**Fig. S3d**)**, giving rise to one singlet at -4.22 ppm, being attributed to the formation of the corresponding alkenyl copper complex **1a**'.

8. DFT Calculation

Theoretical calculations were performed with the Gaussian 09 program[6]. Geometry optimizations and frequency calculations were carried out at the DFT-D3(BJ) functional with B3LYP [7-10]/LANL2DZ for Pd atom and 6-31G(d) for other atoms. Single point energy calculations for optimized structures were performed at DFT-D3(BJ) functional with def2-TZVP level and SMD(toluene)[11] solvation model was used to account for solvent effects.

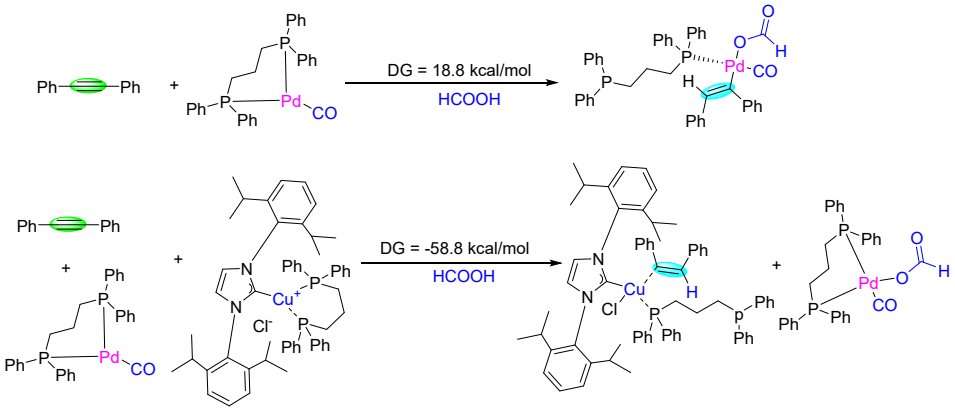
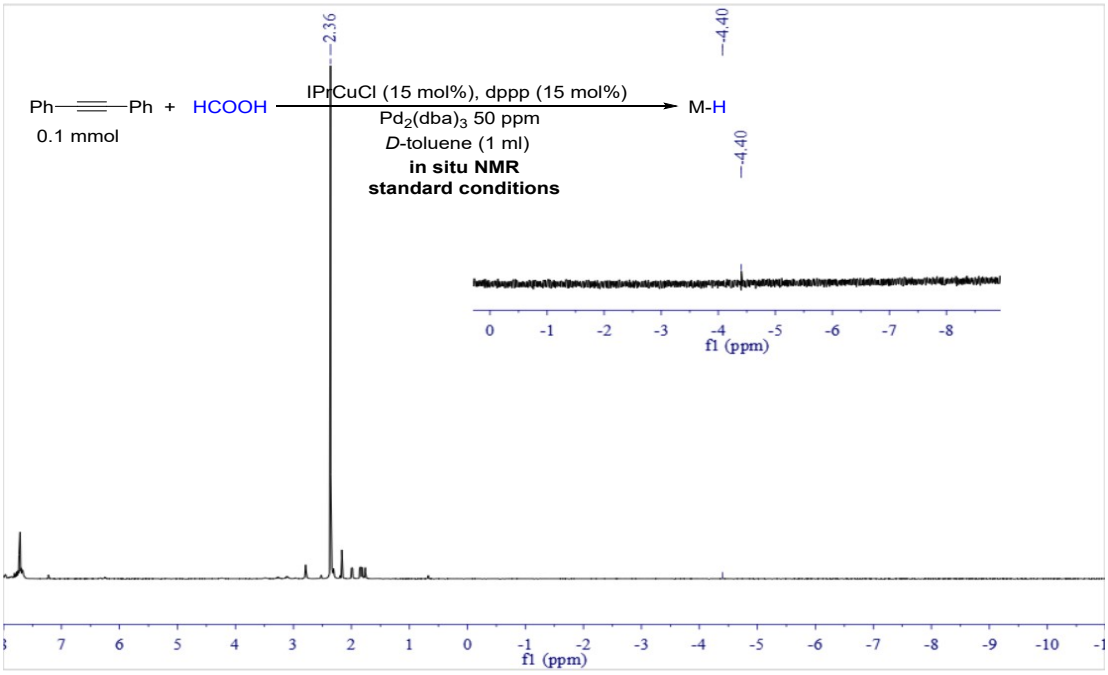


Fig. S4 DFT-D3(BJ) calculations on Cu/Pd (ppm) synergistic effects at SMD (toluene)-B3LYP/def2-TZVP//B3LYP/6-31G(d)+LANL2DZ(Pd) level.

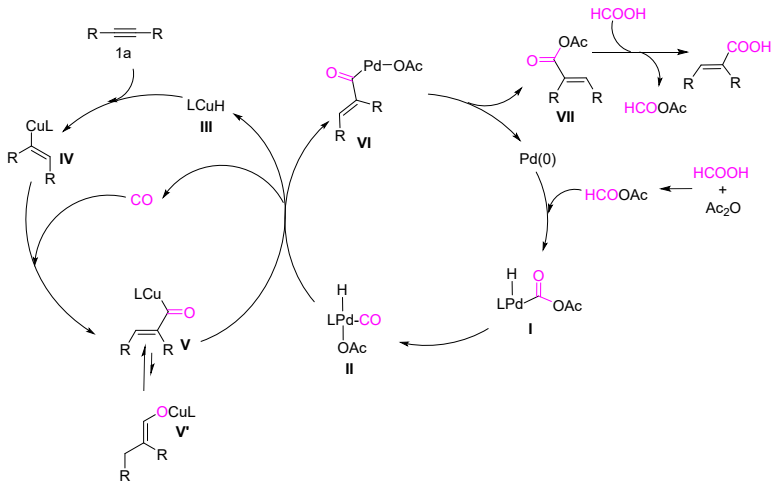
9. Hydride Species Detecting Experiment

In a argon gas filled glove box, an oven-dried 10 mL screw-cap reaction tube equipped with a stir bar was charged with $Pd_2(dba)_3$ (50 ppm, 50 μL of the palladium solution (0.5 mM in toluene)), IPrCuCl (7.3 mg, 15 mol%), dppp (6.2 mg, 15 mol%) and dry toluene (1 ml). The resulting mixture was stirred at room temperature for 15 minutes. Alkyne substrate (0.1 mmol), formic acid (10 μL, 2.7 equiv.), and Ac_2O (12

μL, 1.2 equiv.) were added subsequently and stirred at room temperature for 15 minutes. Then, the mixture was transferred to NMR tube before being sealed. The NMR tube was placed into pre-heated NMR spectrometer (25 °C). We could also find that the hydride species could be clearly observed via ^{1}H NMR after the NMR spectrometer temperature rised to 80 °C.



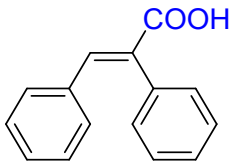
10. Another possible mechanism



The mechanism may also undergo another Pd-catalyzed cycle. Firstly, oxidative insertion of Pd(0) to HCOOAc (generated from HCOOH and Ac_2O) gives H-Pd-OOAc complex **I**, which subsequently undergoes rearrangement to give H-Pd-CO species **II**. At the same time, *syn*-addition of the Cu-H species **III** with alkyne leads to the formation of the alkenyl copper complex **IV.** Then the insertion of CO generated *in situ* from Pd-CO species **II** into the C-Cu bond of complex **IV** to provide an acryloylcopper species **V** with the rearrangement to the complex **V'**. Transmetallation with H-Pd-CO species **II**, ensues to give the corresponding acyl palladium species **VI** and regenerate the Cu-H species **III** for the Cu-catalyzed cycle. The reductive elimination of complex **VI** produces the anhydride **VII**, which finally undergoes hydrolyzation with HCOOH to give the desired product and HCOOAc, and simultaneously regenerates the Pd^0 species for the Pd-catalyzed cycle.

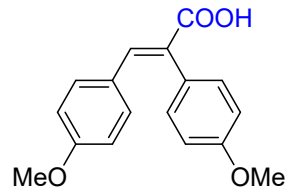
11. Analytical data of the hydrocarboxylation products

11.1 Structure characterization results



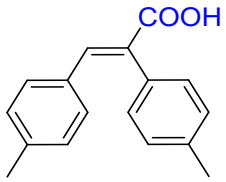
(*E*)-2,3-diphenylacrylic acid (**2a**)[1]

White solid, m.p. 167-171 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.43-7.31 (m, 3H), 7.27-7.12 (m, 5H), 7.07-7.05 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 142.6, 135.4, 134.5, 131.8, 131.0, 129.9, 129.6, 128.9, 128.4, 128.2. HRMS (ESI) *calcd.* for ($C_{15}H_{12}O_2$-H): 223.0759, *found*: 223.0764. IR (KBr): 3500-2900 (br), 1678.8, 1621.7, 1456.1, 1268.8, 753.6, 617.3, 479.3 cm^{-1}



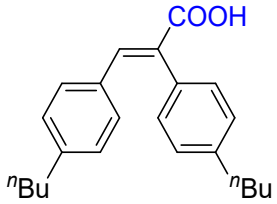
(*E*)-2,3-bis(4-methoxyphenyl)acrylic acid (**2b**)[2]

Light yellow solid, m.p. 210-214 °C**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.18 (d, *J* = 6.5 Hz, 2H), 7.06 (d, *J* = 6.8 Hz, 2H), 6.94 (d, *J* = 8.6 Hz, 2H), 6.71 (d, *J* = 6.7 Hz, 2H), 3.85 (s, 3H), 3.77 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.6, 160.6, 159.3, 142.1, 132.8, 131.1, 128.8, 127.9, 127.2, 114.4, 113.9, 55.4, 55.3. HRMS (ESI) *calcd.* for ($C_{17}H_{16}O_4$-H): 283.0970, *found*: 283.0980. IR (KBr): 3700-2900 (br), 1699.2, 1505.1, 1458.7, 1356.6, 1269.7, 1014.2, 754.7, 617.0 cm^{-1}.



(*E*)-2,3-di-*p*-tolylacrylic acid (**2c**)[1]

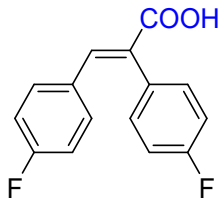
White solid, m.p. 178-182 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.17 (dd, *J* = 24.9, 7.8 Hz, 2H), 7.00 (s, 1H), 2.40 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.8, 142.4, 139.9, 137.8, 132.6, 131.8, 131.0, 130.8, 129.7, 129.6, 129.1, 21.5. HRMS (ESI) *calcd.* for ($C_{17}H_{16}O_2$-H): 251.1072, *found*: 251.1077. IR (KBr): 3600-2900(br), 1682.6, 1630.9, 1459.9, 1267.4, 1093.9, 752.9 621.2 cm^{-1}.



(*E*)-2,3-bis(4-butylphenyl)acrylic acid (**2d**)[1]

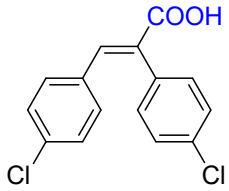
White solid, m.p. 73-77 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.43 (s, 1H), 7.90 (s, 1H), 7.21 – 7.10 (m, 4H), 7.00 – 6.92 (m, 4H), 2.64 (t, *J* = 7.7 Hz, 2H), 2.51 (t, *J* = 7.7 Hz, 2H), 1.63 (dt, *J* = 15.3, 7.6 Hz, 2H), 1.52 (dt, *J* = 15.3, 7.6 Hz, 2H), 1.38 (dt, *J* = 14.8, 7.4 Hz, 2H), 1.33 – 1.23 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H), 0.88 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.8, 144.8, 142.6, 142.2, 132.9, 131.9, 131.1, 130.9, 129.6, 128.8, 128.4, 35.6, 35.5, 33.5, 33.3, 22.5, 22.4, 14.1,

14.0. HRMS (ESI) *calcd.* for ($C_{23}H_{28}O_2$-H): 335.2011, *found*: 335.2011. IR (KBr): 3400-2800 (br), 1691.3, 1643.0, 1463.7, 1420.1, 1268.3, 1018.4, 753.2, 630.6 cm^{-1}.



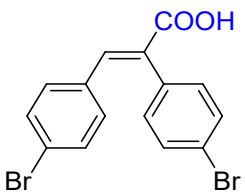
(*E*)-2,3-bis(4-fluorophenyl)acrylic acid (**2e**)

White solid, m.p. 169-171 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.21 (m, 2H), 7.14 – 7.02 (m, 4H), 6.89 (t, J = 8.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1 (s), 164.1 (d, J^F = 253.4 Hz), 162.4 (d, J^F = 249.1 Hz), 141.8 (s), 132.9 (d, J^F = 8.4 Hz), 131.8 (d, J^F = 8.0 Hz), 130.9 (d, J^F = 3.5 Hz), 130.4 (d, J^F = 3.7 Hz), 116.1 (d, J^F = 21.5 Hz), 115.7 (d, J^F = 21.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.51, -113.24. HRMS (ESI) *calcd.* for ($C_{15}H_{10}F_2O_2$-H): 259.0571, *found*: 259.0580. IR (KBr): 3700-2900 (br), 1688.9, 1624.5, 1513.3, 1463.9, 1268.4, 1020.8, 754.4, 616.5 cm^{-1}.



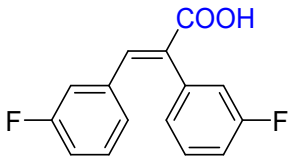
(*E*)-2,3-bis(4-chlorophenyl)acrylic acid (**2f**)[1]

Light yellow solid, m.p. 178-181 °C . ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.40 – 7.35 (m, 2H), 7.21 – 7.15 (m, 4H), 7.03 – 6.98 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6, 141.7, 135.9, 134.5, 133.4, 132.5, 132.0, 131.3, 131.1, 129.3, 128.9. HRMS (ESI) *calcd.* for ($C_{15}H_{10}Cl_2O_2$-H): 290.9980, *found*: 290.9988. IR (KBr): 3500-2900 (br), 1625.6, 1458.0, 1383.5, 1300.4, 1224.7, 1088.1, 793.5, 720.5, 621.6 cm^{-1}.



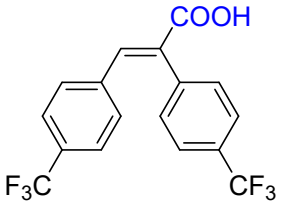
(*E*)-2,3-bis(4-bromophenyl)acrylic acid (**2g**)[1]

Light yellow solid, m.p. 188-190 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 7.10 (d, *J* = 8.3 Hz, 2H), 6.94 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 141.8, 133.8, 132.9, 132.2, 131.8, 131.6, 131.2, 124.3, 122.7. HRMS (ESI) *calcd.* for ($C_{15}H_{10}Br_2O_2$-H): 378.8969, *found*: 378.8968. IR (KBr): 3600-2900 (br), 1626.3, 1267.5, 1149.7, 1080.4, 945.9, 753.9, 616.3, 478.8 cm^{-1}.



(*E*)-2,3-bis(3-fluorophenyl)acrylic acid (**2h**)[1]

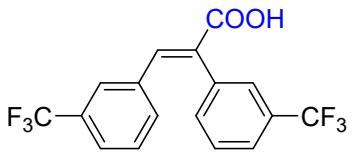
White solid, m.p. 160-161 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.34 (d, *J* = 2.8 Hz, 1H), 7.17 (d, *J* = 2.8 Hz, 1H), 7.07 (m, 1H), 7.03-6.92 (m, 3H), 6.89 (d, *J* = 7.6 Hz, 1H), 6.70 (d, *J* = 9.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.2, 164.3,163.7, 161.8, 161.3, 141.5, 137.0 (d, J^F = 8.1 Hz), 136.1 (d, J^F = 8.1 Hz), 132.0, 130.6 (d, J^F = 8.2 Hz), 130.0 (d, J^F = 8.2 Hz), 126.8 (d, J^F = 2.9 Hz), 125.6 (d, J^F = 2.9 Hz), 117.0 (t, J^F = 22.1Hz), 115.5 (d, J^F = 20.9 Hz). HRMS (ESI) *calcd.* for ($C_{15}H_{10}F_2O_2$-H): 259.0571, found: 259.0577. IR (KBr): 3100-2900 (br), 1688.7, 1624.7, 1514.2, 1463.9, 1268.4, 1020.1, 754.4, 615.0, 480.5 cm^{-1}.



(*E*)-2,3-bis(4-(trifluoromethyl)phenyl)acrylic acid (**2i**)[1]

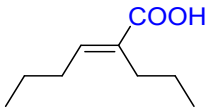
White solid, m.p. 227-230 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.66 (d, *J* = 7.9 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 7.8 Hz, 2H), 7.16 (d, *J* = 7.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ172.1, 142.0, 138.3, 137.2, 132.7, 131.5 (d, J^F= 33.3 Hz), 130.9, 130.8 (d, J^F= 32.3 Hz), 130.5, 125.9 (q, J^F= 4.0 Hz), 125.6 (q, J^F= 4.0 Hz), 124.1 (d, J^F= 273.7 Hz), 123.8 (d, J^F = 273.7 Hz). HRMS (ESI) *calcd.* for ($C_{17}H_{10}F_6O_2$-H): 359.0507, *found*: 359.0502. IR (KBr): 3100-2500(br), 1685.2,

1614.1, 1418.7, 1328.9, 1301.6, 1167.61, 1128.5, 1068.9, 913.4, 843.5, 700.0, 654.9, 598.3 cm^{-1}.



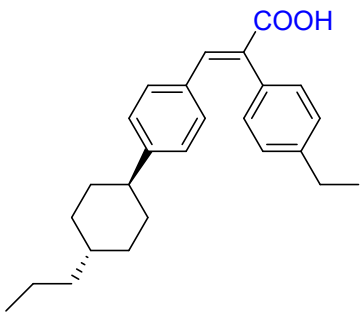
(*E*)-2,3-bis(3-(trifluoromethyl)phenyl)acrylic acid (**2j**)[1]

White solid, m.p. 87-88 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.31 (s, 1H), 8.05 (s, 1H), 7.66 (d, J = 7.6 Hz, 1H), 7.57 – 7.48 (m, 3H), 7.43 (d, J = 7.5 Hz, 1H), 7.32 (t, J = 7.8 Hz, 1H), 7.27 (s, 1H), 7.21 (d, J = 7.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.7, 142.1, 135.4, 134.6, 133.7, 133.5, 132.3, 131.6 (d, J^F = 32.3 Hz), 131.1 (d, J^F = 32.3 Hz), 129.6, 129.2, 127.4 (q, J^F = 11.3 Hz), 126.9 (d, J^F= 3.7 Hz), 126.5 (d, J^F = 3.4 Hz), 125.4 (d, J^F = 3.7 Hz), 125.1 (d, J^F = 31.3 Hz), 122.4 (d, J^F = 31.2 Hz). HRMS (ESI) *calcd.* for ($C_{17}H_{10}F_6O_2$-H): 359.0507, *found*: 359.0504. IR (KBr): 3100-2500 (br), 1696.0, 1620.5, 1424.1, 1329.7, 1295.8, 1201.4, 1175.8, 1167.6, 1124.4, 1073.2, 919.3, 808.5, 688.4, 654.5 cm^{-1}.

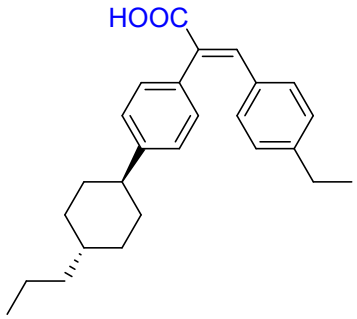


(*E*)-2-propylhex-2-enoic acid **(2o)**[3]

Colourless Oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (t, *J* = 7.5 Hz, 1H), 2.32-2.24 (m, 2H), 2.19 (m, 2H), 1.54 -1.38 (m, 4H), 0.98-0.89 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.6, 145.6, 131.8, 30.9, 28.5, 22.6, 22.1, 14.1, 14.1. HRMS (ESI) *calcd.* for ($C_9H_{16}O_2$-H): 155.1072, *found*: 155.1077. IR (KBr): 3400-2900 (br), 1745.7, 1625.8, 1464.2, 1414.2, 1268.3, 1057.3, 1020.9, 753.5, 616.8, 480.7 cm^{-1}.

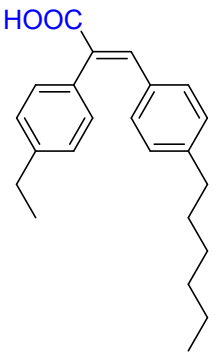


(*E*)-2-(4-ethylphenyl)-3-(4-((1*s*,4*r*)-4-propylcyclohexyl)phenyl)acrylic acid **(2p-*α*)**

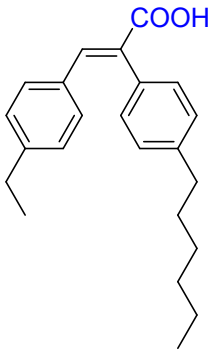


(*E*)-3-(4-ethylphenyl)-2-(4-((1*s*,4*r*)-4-propylcyclohexyl)phenyl)acrylic acid **(2p-*β*)**

White solid, m.p. 161-163°C. The α/β mixture cannot be separated (**2p, *α*:*β*=46:54**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.09 (s, 1H), 7.89 (s, 1H), 7.20 (d, *J* = 7.9 Hz, 2H), 7.17-7.10 (m, 2H), 6.98 (d, *J* = 8.7 Hz, 4H), 2.68 (d, *J* = 7.6 Hz, 1H), 2.55 (dd, *J* = 15.2, 7.6 Hz, 1H), 2.36 (t, *J* = 12.1 Hz, 1H), 1.99-1.74 (m, 5H), 1.38 - 1.12 (m, 11H), 1.11- 0.95 (m, 3H), 0.89 (dt, *J* = 10.9, 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.0, 149.8, 147.6, 146.1, 143.9, 142.4, 132.9, 132.1, 132.0, 131.2, 131.1, 130.8, 130.6, 129.7, 129.6, 128.3, 127.9, 127.3, 126.9, 44.6, 44.5, 39.9, 39.8, 37.1, 37.0, 34.4, 34.1, 33.7, 33.5, 28.8, 20.2, 20.1, 15.4, 15.2, 14.6, 14.5. HRMS (ESI) *calcd.* for ($C_{26}H_{32}O_2$-H): 375.2324, *found*: 375.2325. IR (KBr): 3500-2900 (br), 1745.7, 1677.8, 1605.2, 1413.8, 1414.2, 1262.2, 1176.9, 827.5, 715.9, 570.7, 524.5, 445.6 cm^{-1}.



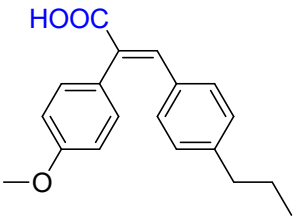
(*E*)-2-(4-ethylphenyl)-3-(4-hexylphenyl)acrylic acid (**2q-*α***)



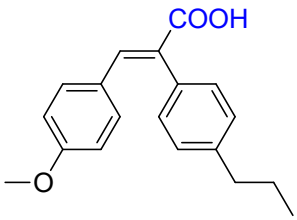
(*E*)-3-(4-ethylphenyl)-2-(4-hexylphenyl)acrylic acid (**2q-*β***)

White solid, m.p. 75-78°C. The α/β mixture cannot be separated (**2q, *α*:*β*=54:46**). ^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.24 – 7.12 (m, 5H), 6.99 (d, *J* = 1.1 Hz, 4H), 2.74 – 2.45 (m, 5H), 1.69 – 1.48 (m, 3H),

1.29 (dd, J = 18.0, 10.4 Hz, 10H), 1.17 (t, J = 7.6 Hz, 2H), 0.94 – 0.79 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ174.0, 146.1, 144.9, 143.9, 142.7, 142.4, 132.8, 131.9, 131.1, 131.1, 130.8, 130.7, 129.7, 129.6, 128.9, 128.4, 128.3, 127.9, 35.9, 31.8, 31.7, 31.3, 31.1, 29.1, 28.8, 22.8, 22.7, 15.4, 15.2, 14.2, 14.1. HRMS (ESI) *calcd.* for ($C_{23}H_{28}O_2$-H): 335.2011, *found*: 335.2019. IR (KBr): 3100-2800(br), 1681.3, 1604.9, 1508.86, 1456.94, 1418.2, 1268.7, 1213.5, 1182.9, 1116.2, 997.9, 833.1, 736.2, 569.2 cm^{-1}.

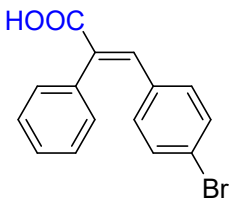


(*E*)-2-(4-methoxyphenyl)-3-(4-propylphenyl)acrylic acid **2r-*α***

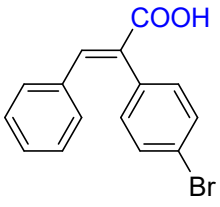


(*E*)-3-(4-methoxyphenyl)-2-(4-propylphenyl)acrylic acid **2r-*β***

White solid, m.p. 172-174°C. The α/β mixture cannot be separated (**2r, *α*:*β*=77:23**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.75 (s, 1H), 7.89 (d, J = 6.1 Hz, 1H), 7.23 – 7.11 (m, 3H), 7.03-7.00 (q, J = 8.0 Hz, 5H), 6.92 (d, J = 8.4 Hz, 2H), 6.68 (d, J = 8.5 Hz, 1H), 3.84 (s, 3H), 3.75 (s, 1H), 2.62 (t, J = 7.5 Hz, 1H), 2.51 (t, J = 7.5 Hz, 2H), 1.68 (dd, J = 14.8, 7.4 Hz, 1H), 1.57 (dt, J = 14.3, 7.2 Hz, 2H), 0.96 (t, J = 7.2 Hz, 1H), 0.89 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.9, 159.4, 144.7, 142.5, 132.8, 132.1, 131.2, 131.0, 130.3, 129.7, 129.0, 128.6, 127.8, 114.3, 113.8, 55.3, 38.0, 24.3, 13.9. HRMS (ESI) *calcd.* for ($C_{19}H_{20}O_3$-H): 295.1334, *found*: 295.1340. IR (KBr): 3000-2837 (br), 1675.0, 1609.9, 1502.5, 1416.7, 1258.4, 1236.7, 1179.2, 1035.9, 928.4, 827.6, 741.8, 684.3, 569.3, 426.1 cm^{-1}.

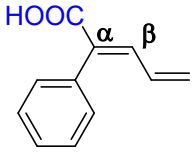


(*E*)-3-(4-bromophenyl)-2-phenylacrylic acid (**2s-*α***)



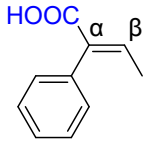
(*E*)-2-(4-bromophenyl)-3-phenylacrylic acid (**2s-*β***)

White solid, m.p. 179-182 °C. The α/β mixture cannot be separated (**2s, *α*:*β*=59:41**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.86 (s, 1H), 7.51 (d, *J* = 8.1 Hz, 1H), 7.38 (s, 3H), 7.34 – 7.19 (m, 7H), 7.11 (dd, *J* = 16.4, 7.5 Hz, 2H), 6.92 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.10, 172.94, 143.27, 141.25, 134.95, 134.26, 134.06, 133.30, 132.47, 132.32, 131.69, 130.94, 129.93, 129.76, 129.00, 128.59, 128.44, 124.06, 122.48. HRMS (ESI) *calcd.* for ($C_{15}H_{11}BrO_2$-H): 300.9864, 300.9844, *found*: 300.9869, 300.9848. IR (KBr): 2926.1, 2847.1, 2349.5, 1678.5, 1654.9, 1481.5, 1387.1, 1259.9, 1079.3, 1000.3, 976.7, 913.1, 825.9, 707.9, 549.9, 486.3 cm^{-1}.

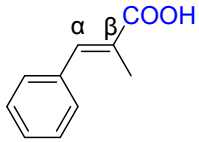


(*E*)-2-phenylpenta-2,4-dienoic acid (2t-*α*)

Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.48-7.41 (d, *J* = 6.8 Hz, 2H), 7.43-7.34 (m, 3H), 6.68-6.61 (dd, *J* = 17.8, 11.9 Hz, 1H), 5.94 (d, *J* = 17.8 Hz, 1H), 5.51 (d, *J* = 11.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ173.4, 141.9, 135.0, 130.4, 129.3, 129.0, 128.5, 121.8. HRMS (ESI) *calcd.* for ($C_{11}H_{10}O_2$-H): 173.0603, *found*: 173.0600. IR (KBr): 3500-3000, 2358.2, 1683.3, 1447.7, 1266.4, 1214.8, 1154.9, 1006.4, 912.2, 755.3, 731.5, 695.4, 607.8cm^{-1}.

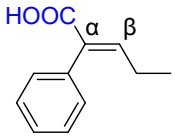


(*E*)-2-phenylbut-2-enoic acid (2u-*α*)

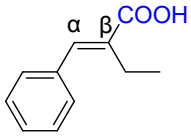


(*E*)-2-methyl-3-phenylacrylic acid (2u-*β*)

White solid, m.p. 92-94 °C. The α/β mixture cannot be separated (**2u, *α*:*β*=71:29**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.34 (s, 1H), 7.81 (s, 1H), 7.45-7.28 (m, 6H), 7.24 (s, 1H), 7.19 (d, *J* = 7.2 Hz, 2H), 2.13 (*β*-product, s, 1H, CH_3), 1.78 (*α*-product, d, *J* = 7.1 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.5, 172.8, 142.9, 141.3, 135.7, 134.5, 129.9, 128.8, 128.5, 128.2, 127.7, 15.9, 13.8. HRMS (ESI) *calcd.* for ($C_{10}H_{10}O_2$-H): 161.0603, found: 161.0608. IR (KBr): 3500-2500 (br), 1636.7, 1458.6, 1384.6, 1300.5, 1230.5, 1084.0, 791.2, 723.0, 618.5 cm^{-1}.

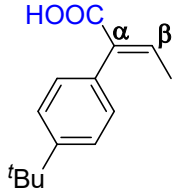


(*E*)-2-phenylpent-2-enoic acid (2v-*α*)

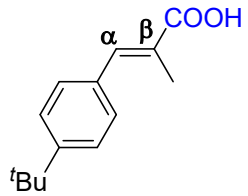


(*E*)-2-benzylidenebutanoic acid (*E*)-2-phenylpent-2-enoic acid (2v-*β*)

Colorless oil liquid. The *α*/*β* mixture cannot be separated (**2v, *α*:*β*=71:29**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.41-7.32 (m, 4H), 7.22-7.16 (m, 3H), 2.56 (*β*-product, q, *J* = 7.5 Hz, 1H, CH_2), 2.18-2.08 (*α*-product, m, 2H, CH_2), 1.20 (s, 1H), 1.03 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.1, 172.8, 149.3, 140.8, 135.4, 134.7, 133.9, 132.7, 129.7, 129.4, 128.7, 128.5, 128.0, 127.6, 23.1, 20.5, 13.7, 13.2. HRMS (ESI) *calcd.* for ($C_{11}H_{12}O_2$-H): 175.0759, found: 175.0766. IR (KBr): 3000-2700 (br), 1685.1, 1630.5, 1457.4, 1407.5, 1378.2, 1266.0, 1165.4, 1093.8, 1023.0, 749.4, 622.4 cm^{-1}.

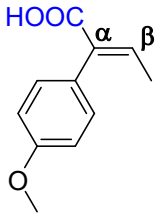


(*E*)-2-(4-(*tert*-butyl)phenyl)but-2-enoic acid, **2w-*α***

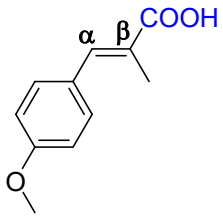


(*E*)-3-(4-(*tert*-butyl)phenyl)-2-methylacrylic acid **2w-*β***

White solid, m.p. 103-106 °C. The *α*/*β* mixture cannot be separated (**2w, *α*:*β*=59:41**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.44-7.38 (dd, *J* = 16.6, 8.1 Hz, 5H), 7.34 -7.29 (m, 1H), 7.14 (d, *J* = 8.1 Hz, 2H), 2.15 (*β*-product, s, 2H, C=C-CH_3), 1.80 (*α*-product, d, *J* = 7.2 Hz, 3H, C=C-CH_3), 1.33 (s, 16H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.8, 173.1, 152.2, 150.4, 142.6, 141.1, 134.1, 132.9, 131.4, 130.0, 129.6, 126.8, 125.5, 125.0, 34.9, 34.7, 31.4, 31.3, 16.0, 13.8. HRMS (ESI) *calcd.* for ($C_{14}H_{18}O_2$-H): 217.1229, *found*: 217.1230. IR (KBr): 3000-2800 (br), 1667.2, 1518.5, 1425.1, 1362.5, 1268.1, 1198.3, 1127.6, 917.2, 822.8, 761.3, 698.7, 627.9, 565.3, 463.7 cm^{-1}.

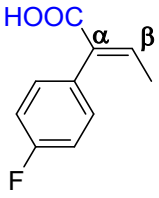


(*E*)-2-(4-methoxyphenyl)but-2-enoic acid **2x-*α***

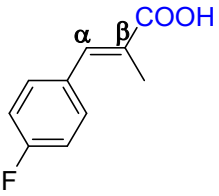


(*E*)-3-(4-methoxyphenyl)-2-methylacrylic acid **2x-*β***

White solid, m.p. 123-126 °C. The *α*/*β* mixture cannot be separated **(2x, *α*:*β*=57:43)**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.8 (s, 1H), 7.77 (s, 1H), 7.42 (d, *J* = 8.7 Hz, 2H), 7.29 (d, *J* = 7.2 Hz, 1H), 7.13 (d, *J* = 8.6 Hz, 2H), 6.93 (t, *J* = 8.0 Hz, 4H), 3.84 (s, 2H), 3.82 (s, 3H), 2.14 (*β*-product, s, 2H, C=C-CH_3), 1.79 (*α*-product, d, *J* = 7.2 Hz, 3H, C=C-CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.8, 173.1, 160.1, 159.1, 142.5, 141.0, 138.8, 133.8, 131.9, 131.1, 129.2, 128.3, 126.7, 125.2, 114.0, 113.7, 55.4, 55.3, 15.9, 13.8. HRMS (ESI) *calcd.* for ($C_{11}H_{12}O_3$-H): 191.0708, *found*: 191.0706. IR (KBr): 3100-2500 (br), 1671.5, 1603.2, 1513.3, 1416.7, 1281.0, 1246.9, 1178.7, 1026.3, 918.9, 828.2, 799.9, 754.9, 731.6, 635.9, 567.7, 533.6, 476.9 cm^{-1}.



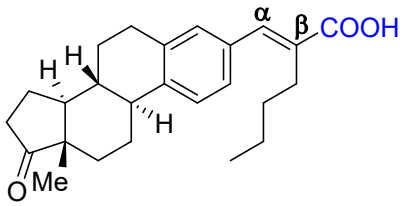
(*E*)-2-(4-fluorophenyl)but-2-enoic acid **2y-*α***



(*E*)-3-(4-fluorophenyl)-2-methylacrylic acid **2y-*β***

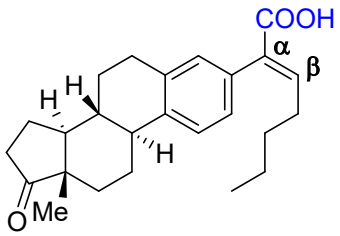
White solid, m.p. 120-123 °C. The *α*/*β* mixture cannot be separated **(2y, *α*:*β*=57:43)**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.42 (s, 1H), 7.78 (s, 1H), 7.46 – 7.39 (m, 2H), 7.35 (dd, *J* = 14.4, 7.1 Hz, 1H), 7.21 – 7.14 (m, 1H), 7.09 (dd, *J* = 17.7, 8.9 Hz, 3H), 2.12 (*β*-product, s, 3H, CH_3), 1.79 (*α*-product, d, J = 7.1 Hz, 2H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.4, 172.7, 163.8 (d, J^F = 49.7 Hz), 161.4 (d, J^F = 46.4 Hz), 143.5, 140.1, 132.6 (d, J^F = 158.6 Hz), 131.9 (d, J^F = 8.3 Hz), 131.7 (d, J^F = 8.0 Hz), 130.4 (dd, J^F = 9.0, 5.7 Hz), 115.7 (d, J^F = 21.7 Hz), 115.3 (d, J^F = 21.5 Hz). HRMS (ESI) *calcd.* for ($C_{10}H_9FO_2$-H): 179.0508, *found*: 179.0507. IR

(KBr): 1663.7, 1625.3, 1505.1, 1422.7, 1292.8, 1220.8, 1158.0, 936.6, 835.3, 738.9, 627.8, 526.6, 435.1 cm^{-1}.



(*E*)-2-(((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)methylene)hexanoic acid (**2aa-*β***)

White solid. m.p. 104-106 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.23 (t, *J* = 9.5 Hz, 1H), 7.16 (s, 1H), 2.94 (d, *J* = 4.8 Hz, 2H), 2.55 – 1.96 (m, 9H), 1.65 – 1.37 (m, 10H), 0.93 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.0, 174.3, 140.9, 136.8, 133.2, 132.3, 130.5, 127.1, 125.7, 50.6, 48.1, 44.6, 38.2, 36.0, 32.1, 31.7, 29.5, 29.0, 26.6, 25.8, 22.5, 21.7, 14.2, 14.0.

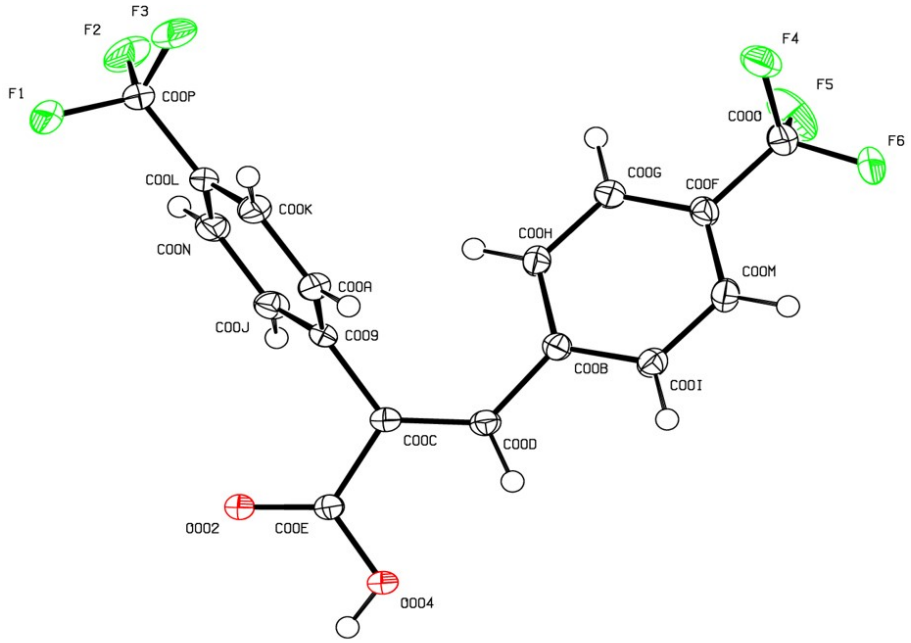


(*E*)-2-((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)hept-2-enoic acid (**2aa-*α***)

Orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.1 Hz, 1H), 7.17 (t, *J* = 7.3 Hz, 1H), 7.02 – 6.84 (m, 2H), 2.91 (d, *J* = 4.7 Hz, 2H), 2.55 – 1.97 (m, 9H), 1.65 – 1.25 (m, 10H), 0.92 (s, 3H), 0.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.2, 172.8, 148.0, 139.1, 136.1, 132.3, 130.3, 127.2, 125.1, 50.7, 48.1, 44.5, 38.1, 36.0, 31.7, 31.5, 29.9, 29.5, 28.5, 25.7, 22.5, 21.7, 14.1, 14.0.

HRMS (ESI) *calcd.* for ($C_{25}H_{32}O_3$-H): 379.2273, *found*: 379.2279. IR (KBr): 3500-2800(br), 2238.5, 2075.6, 1737.8, 1683.3, 1633.1, 1499.9, 1455.2, 1274.8, 1260.42, 1118.7, 975.8, 822.7, 765.4, 676.5, 650.5, 580.6 cm^{-1}.

11.2. X-Ray crystallographic data



(*E*)-2,3-bis(4-(trifluoromethyl)phenyl)acrylic acid (2i-*X*-ray)
CCDC：2082527

Table S2 Crystal data and structure refinement for 2i.

Identification code	**(*E*)-2,3-bis(4-(trifluoromethyl)phenyl)acrylic acid (2i)**
Empirical formula	$C_{17}H_{10}F_6O_2$
Formula weight	360.25
Temperature/K	100.00(10)
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	5.5094(3)
b/Å	15.2120(8)
c/Å	18.2863(9)
α/°	90
β/°	96.429(6)
γ/°	90
Volume/Å^3	1522.92(14)
Z	4
ρ_{calc}g/cm^3	1.571
μ/mm^{-1}	0.151
F(000)	728.0
Crystal size/mm^3	0.22 × 0.15 × 0.14
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.242 to 60.778

Index ranges	$-7 \le h \le 7, -21 \le k \le 21, -26 \le l \le 22$
Reflections collected	10535
Independent reflections	4010 [R_{int} = 0.0294, R_{sigma} = 0.0371]
Data/restraints/parameters	4010/0/227
Goodness-of-fit on F^2	1.073
Final R indexes [I>=2σ (I)]	R_1 = 0.0404, wR_2 = 0.0977
Final R indexes [all data]	R_1 = 0.0524, wR_2 = 0.1026
Largest diff. peak/hole / e $Å^{-3}$	0.37/-0.37

Table S3 Bond Lengths for (*E*)-2,3-bis(4-(trifluoromethyl)phenyl)acrylic acid (2i).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F4	C00O	1.3356(16)	C00B	C00H	1.4014(18)
O002	C00E	1.2241(15)	C00B	C00I	1.3979(17)
F1	C00P	1.3450(17)	C00C	C00D	1.3447(17)
O004	C00E	1.3168(15)	C00C	C00E	1.4902(16)
F6	C00O	1.3288(16)	C00F	C00G	1.3912(18)
F5	C00O	1.3385(17)	C00F	C00M	1.3859(19)
F3	C00P	1.3348(19)	C00F	C00O	1.4975(17)
F2	C00P	1.336(2)	C00G	C00H	1.3844(18)
C009	C00A	1.3915(17)	C00I	C00M	1.3898(18)
C009	C00C	1.4879(16)	C00J	C00N	1.3868(19)
C009	C00J	1.3956(17)	C00K	C00L	1.3889(19)
C00A	C00K	1.3894(18)	C00L	C00N	1.383(2)
C00B	C00D	1.4722(16)	C00L	C00P	1.4999(18)

Table S4 Bond Angles for (*E*)-2,3-bis(4-(trifluoromethyl)phenyl)acrylic acid (2i).

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C00A	C009	C00C	119.49(11)	C00N	C00J	C009	120.64(12)
C00A	C009	C00J	119.29(11)	C00L	C00K	C00A	119.70(12)
C00J	C009	C00C	121.20(11)	C00K	C00L	C00P	119.08(13)
C00K	C00A	C009	120.23(12)	C00N	C00L	C00K	120.69(12)
C00H	C00B	C00D	123.01(11)	C00N	C00L	C00P	120.23(13)
C00I	C00B	C00D	118.36(11)	C00F	C00M	C00I	119.50(12)
C00I	C00B	C00H	118.46(11)	C00L	C00N	C00J	119.45(12)
C009	C00C	C00E	114.79(10)	F4	C00O	F5	105.19(12)

C00D	C00C	C009	126.15(11)	F4	C00O	C00F	112.78(10)
C00D	C00C	C00E	119.05(11)	F6	C00O	F4	106.45(11)
C00C	C00D	C00B	128.96(11)	F6	C00O	F5	107.45(11)
O002	C00E	O004	123.32(11)	F6	C00O	C00F	113.23(12)
O002	C00E	C00C	121.33(11)	F5	C00O	C00F	111.24(11)
O004	C00E	C00C	115.33(10)	F1	C00P	C00L	112.25(11)
C00G	C00F	C00O	118.32(12)	F3	C00P	F1	106.28(14)
C00M	C00F	C00G	120.27(12)	F3	C00P	F2	106.49(12)
C00M	C00F	C00O	121.35(12)	F3	C00P	C00L	112.35(12)
C00H	C00G	C00F	120.09(12)	F2	C00P	F1	106.26(12)
C00G	C00H	C00B	120.56(12)	F2	C00P	C00L	112.72(13)
C00M	C00I	C00B	121.10(12)				

B'-*X*-ray (CCDC:2082526)

Table S5 Crystal data and structure refinement for compound B'.

Identification code	compound **B'**
Empirical formula	$C_{27}H_{26}P_4Pd$
Formula weight	580.76
Temperature/K	113.15
Crystal system	triclinic
Space group	P-1
a/Å	8.4671(5)
b/Å	10.5451(6)
c/Å	14.4131(7)
α/°	88.379(4)
β/°	80.098(4)
γ/°	73.608(5)
Volume/Å^3	1215.92(12)
Z	2

ρ_{calc}g/cm^3	1.586
μ/mm^{-1}	1.041
F(000)	588.0
Crystal size/mm^3	0.2 × 0.18 × 0.16
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.028 to 52.74
Index ranges	-10 ≤ h ≤ 10, -13 ≤ k ≤ 13, -18 ≤ l ≤ 17
Reflections collected	12663
Independent reflections	4961 [R_{int} = 0.0540, R_{sigma} = 0.0603]
Data/restraints/parameters	4961/0/289
Goodness-of-fit on F^2	1.057
Final R indexes [I>=2σ (I)]	R_1 = 0.0439, wR_2 = 0.1112
Final R indexes [all data]	R_1 = 0.0536, wR_2 = 0.1177
Largest diff. peak/hole / e Å^{-3}	0.94/-0.69

Table S6 Bond Lengths for compound B'.

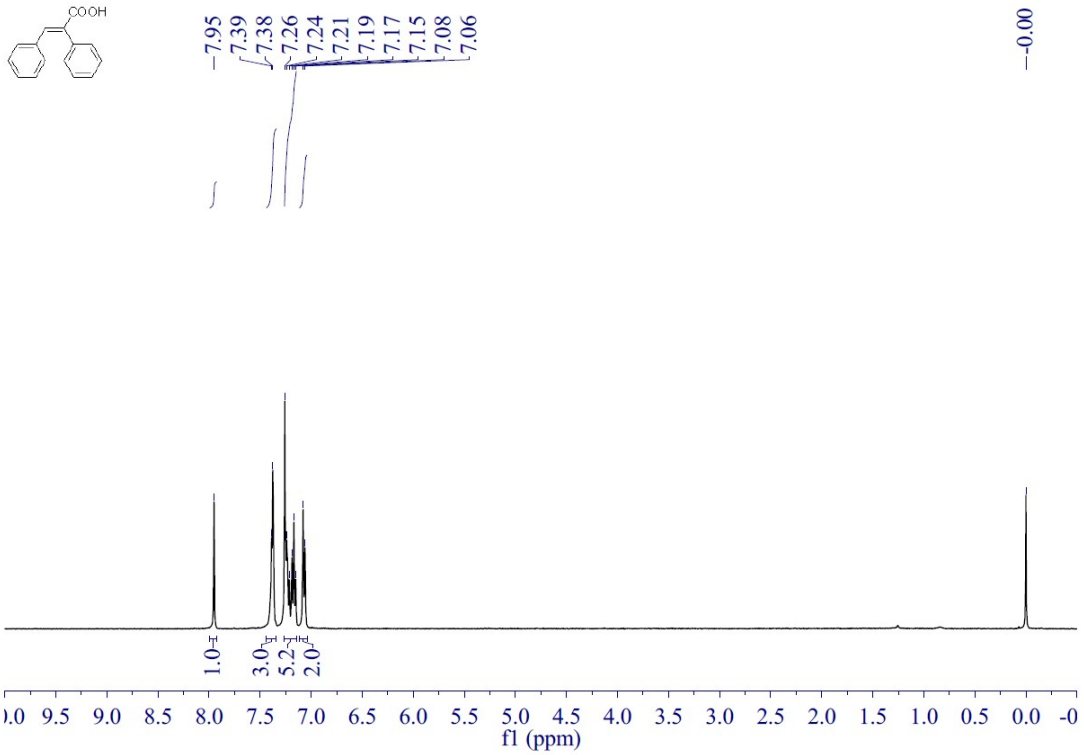
Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pd1	P1	2.2529(11)	C8	C9	1.380(8)
Pd1	P2	2.2445(11)	C9	C10	1.349(9)
Pd1	P3	2.3589(10)	C10	C11	1.354(8)
Pd1	P4	2.3558(11)	C11	C12	1.389(8)
P1	C1	1.814(5)	C13	C14	1.528(6)
P1	C7	1.816(5)	C14	C15	1.522(6)
P1	C13	1.834(5)	C16	C17	1.381(7)
P2	C15	1.823(4)	C16	C21	1.386(6)
P2	C16	1.816(4)	C17	C18	1.377(7)
P2	C22	1.814(5)	C18	C19	1.384(8)
C1	C2	1.397(7)	C19	C20	1.363(8)
C1	C6	1.379(7)	C20	C21	1.394(7)
C2	C3	1.386(7)	C22	C23	1.387(6)
C3	C4	1.384(8)	C22	C27	1.386(7)
C4	C5	1.375(8)	C23	C24	1.378(7)
C5	C6	1.399(7)	C24	C25	1.367(7)
C7	C8	1.374(7)	C25	C26	1.379(7)
C7	C12	1.370(7)	C26	C27	1.401(7)

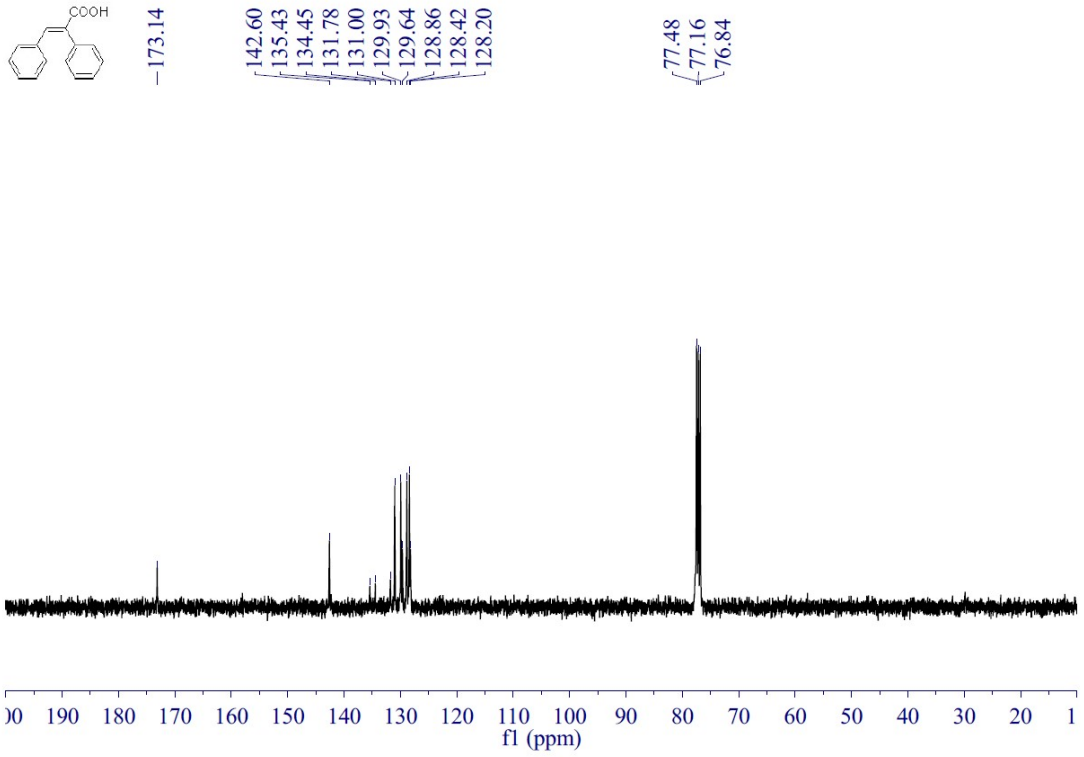
Table S7 Bond Angles for compound B'.

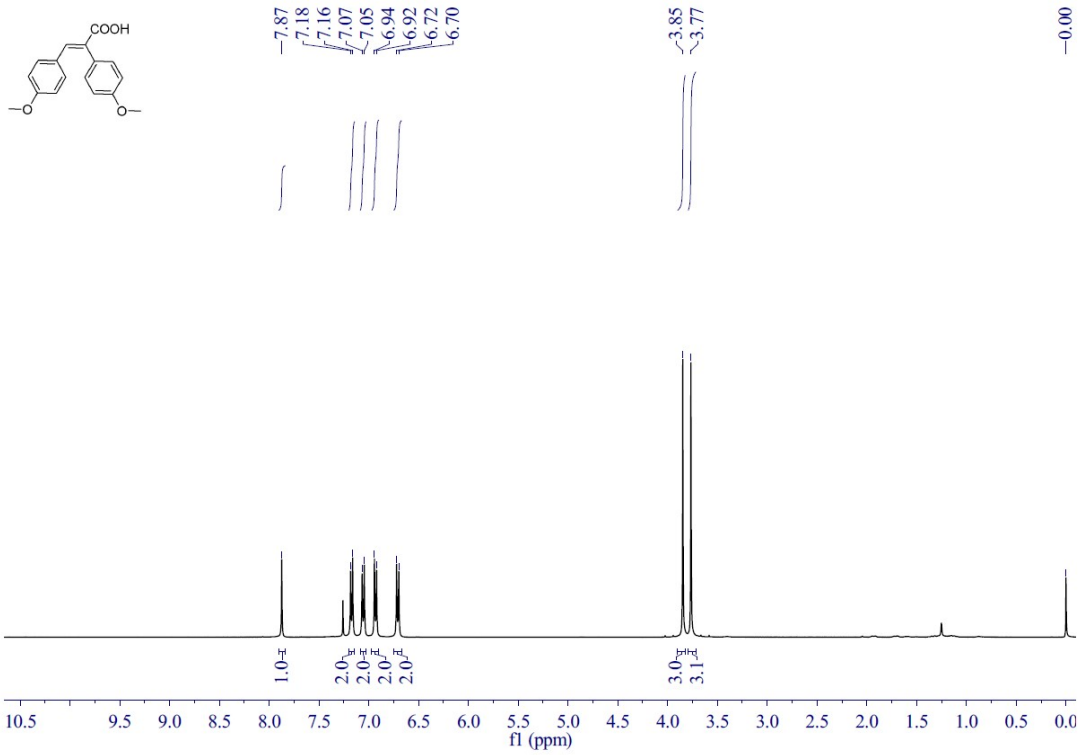
Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
P1	Pd1	P3	177.99(4)	C12	C7	P1	118.6(4)

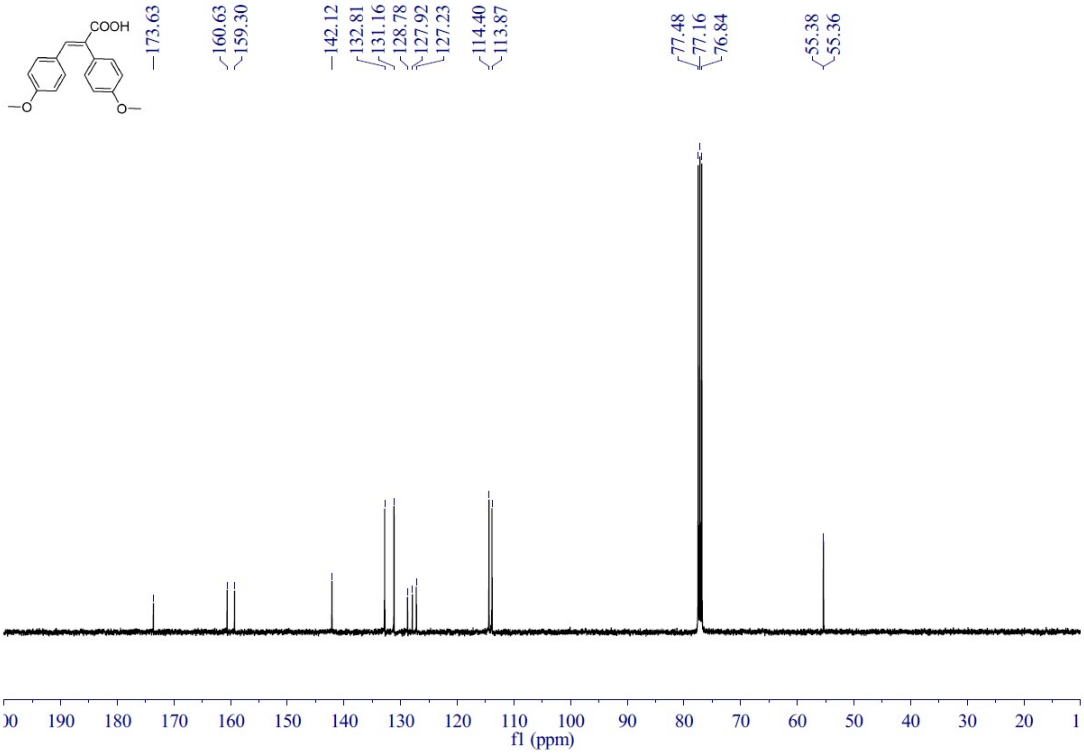
P1	Pd1	P4	91.36(4)	C12	C7	C8	118.2(5)
P2	Pd1	P1	90.62(4)	C7	C8	C9	119.8(5)
P2	Pd1	P3	87.68(4)	C10	C9	C8	122.1(6)
P2	Pd1	P4	172.25(5)	C9	C10	C11	118.4(5)
P4	Pd1	P3	90.47(4)	C10	C11	C12	120.8(5)
C1	P1	Pd1	114.40(15)	C7	C12	C11	120.6(5)
C1	P1	C7	106.6(2)	C14	C13	P1	117.9(3)
C1	P1	C13	102.6(2)	C15	C14	C13	116.2(4)
C7	P1	Pd1	109.42(15)	C14	C15	P2	111.3(3)
C7	P1	C13	107.2(2)	C17	C16	P2	121.1(3)
C13	P1	Pd1	115.92(15)	C17	C16	C21	119.2(4)
C15	P2	Pd1	116.54(15)	C21	C16	P2	119.5(4)
C16	P2	Pd1	114.74(15)	C18	C17	C16	120.4(5)
C16	P2	C15	102.7(2)	C17	C18	C19	120.0(5)
C22	P2	Pd1	109.41(14)	C20	C19	C18	120.2(5)
C22	P2	C15	105.2(2)	C19	C20	C21	119.9(5)
C22	P2	C16	107.4(2)	C16	C21	C20	120.1(5)
C2	C1	P1	118.2(4)	C23	C22	P2	121.5(4)
C6	C1	P1	121.9(4)	C27	C22	P2	119.1(4)
C6	C1	C2	119.8(4)	C27	C22	C23	119.2(4)
C3	C2	C1	120.4(5)	C24	C23	C22	120.4(5)
C4	C3	C2	119.0(5)	C25	C24	C23	120.4(5)
C5	C4	C3	121.2(5)	C24	C25	C26	120.5(5)
C4	C5	C6	119.7(5)	C25	C26	C27	119.4(5)
C1	C6	C5	119.7(5)	C22	C27	C26	120.1(5)
C8	C7	P1	123.2(4)				

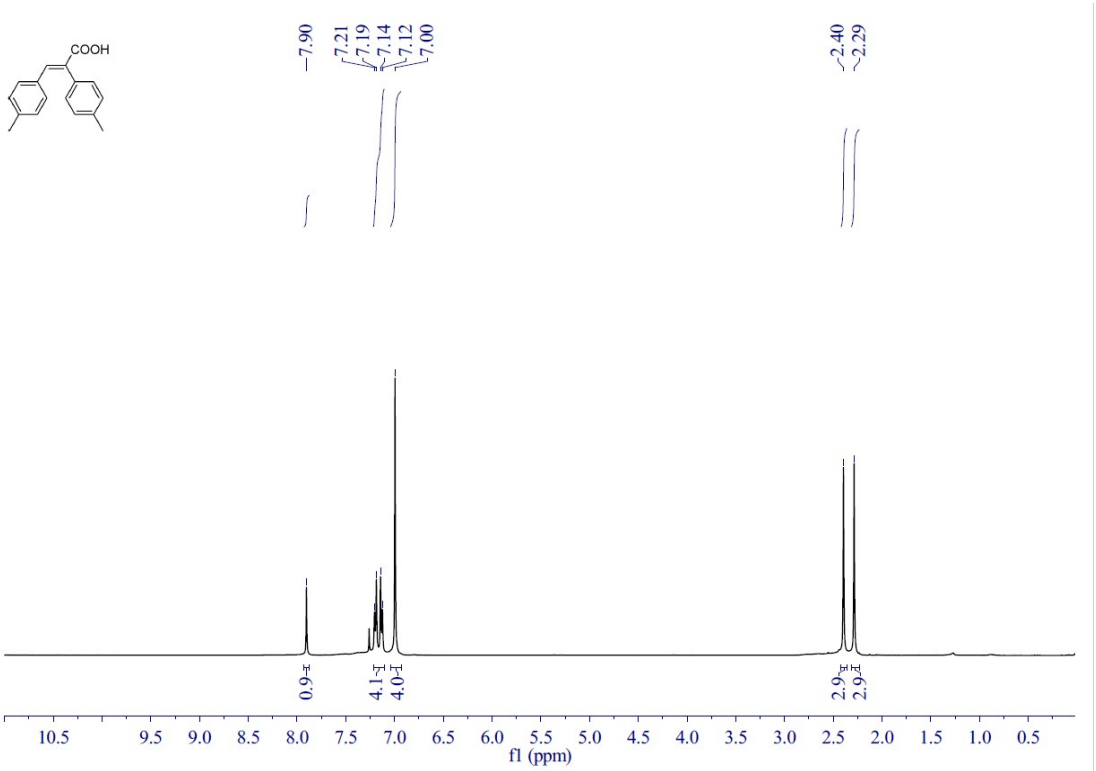
11.3. **NMR Charts**

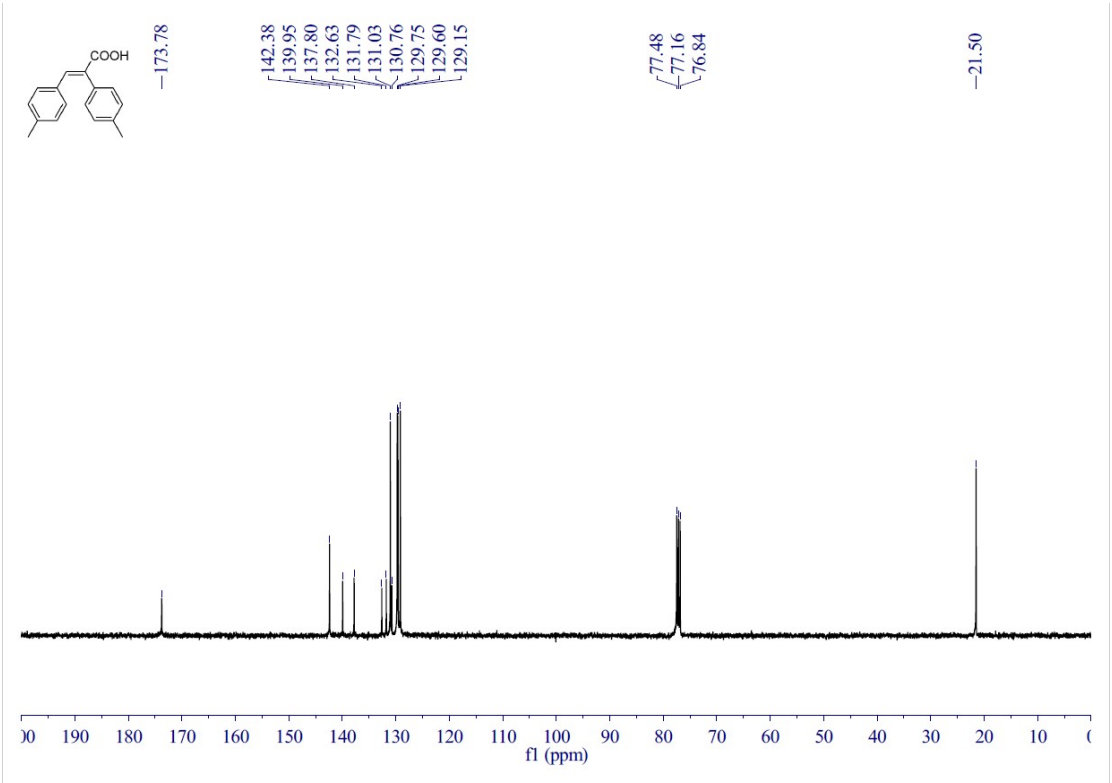


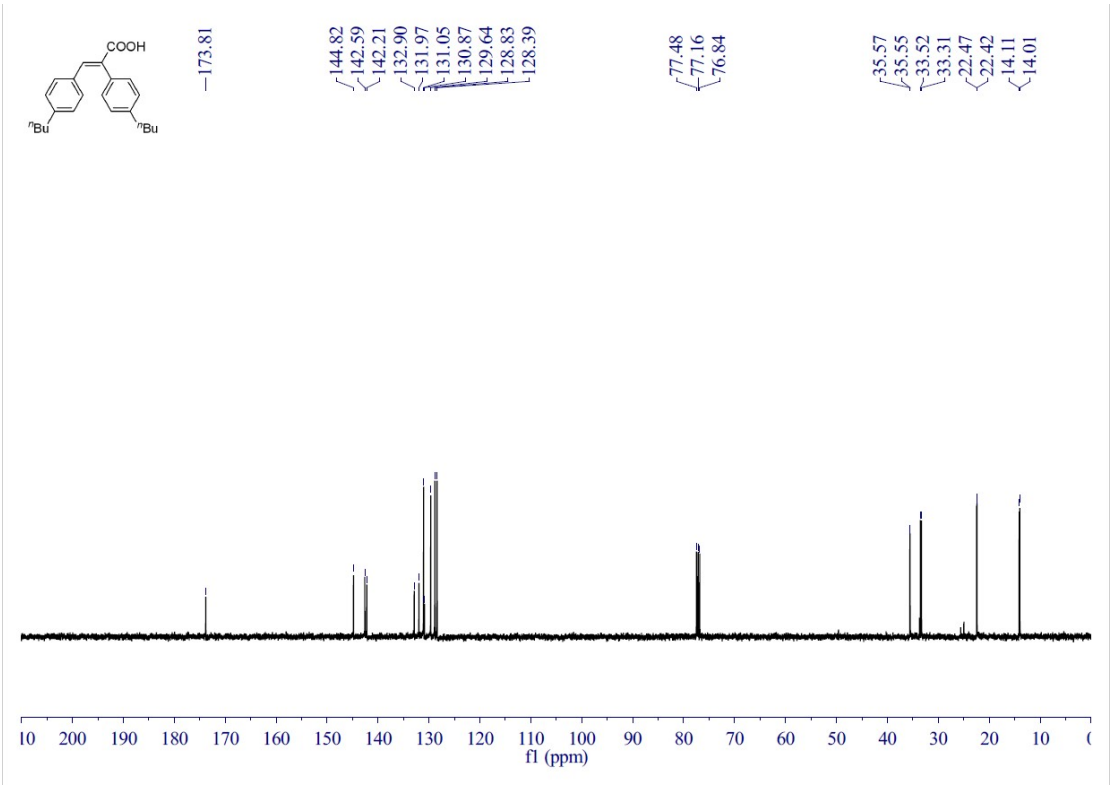


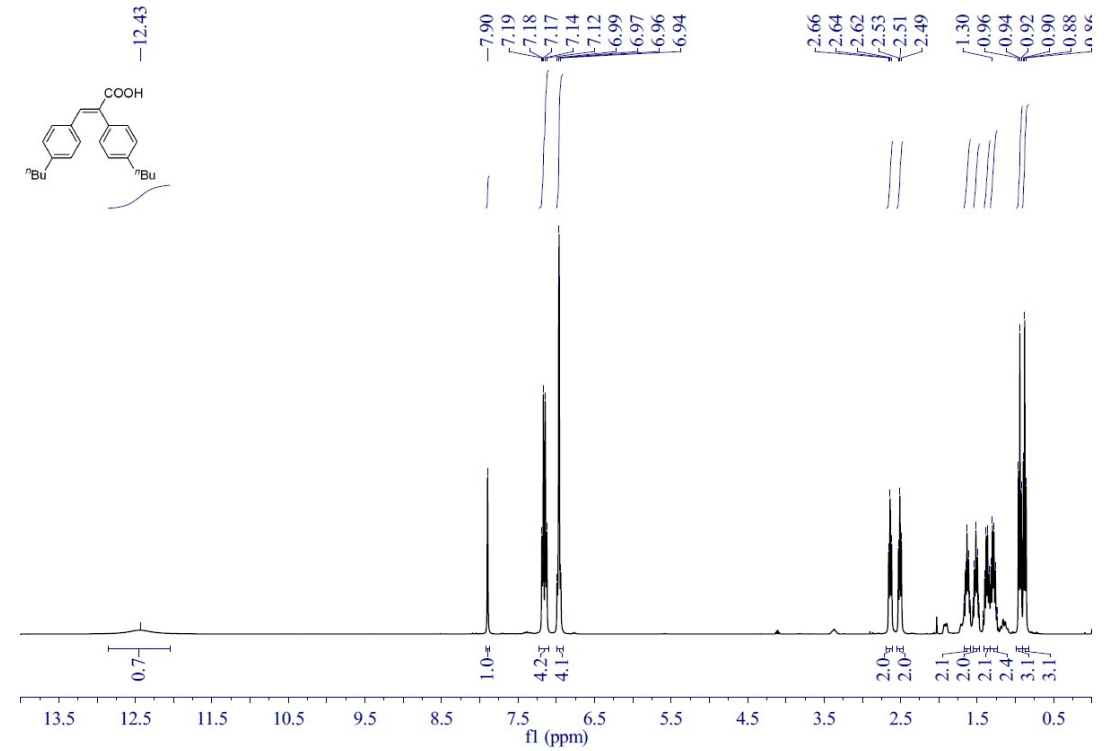

COOH
7.87
7.18
7.16
7.07
7.05
6.94
6.92
6.72
6.70
3.85
3.77
0.00
1.0
2.0
2.0
2.0
2.0
3.0
3.1
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

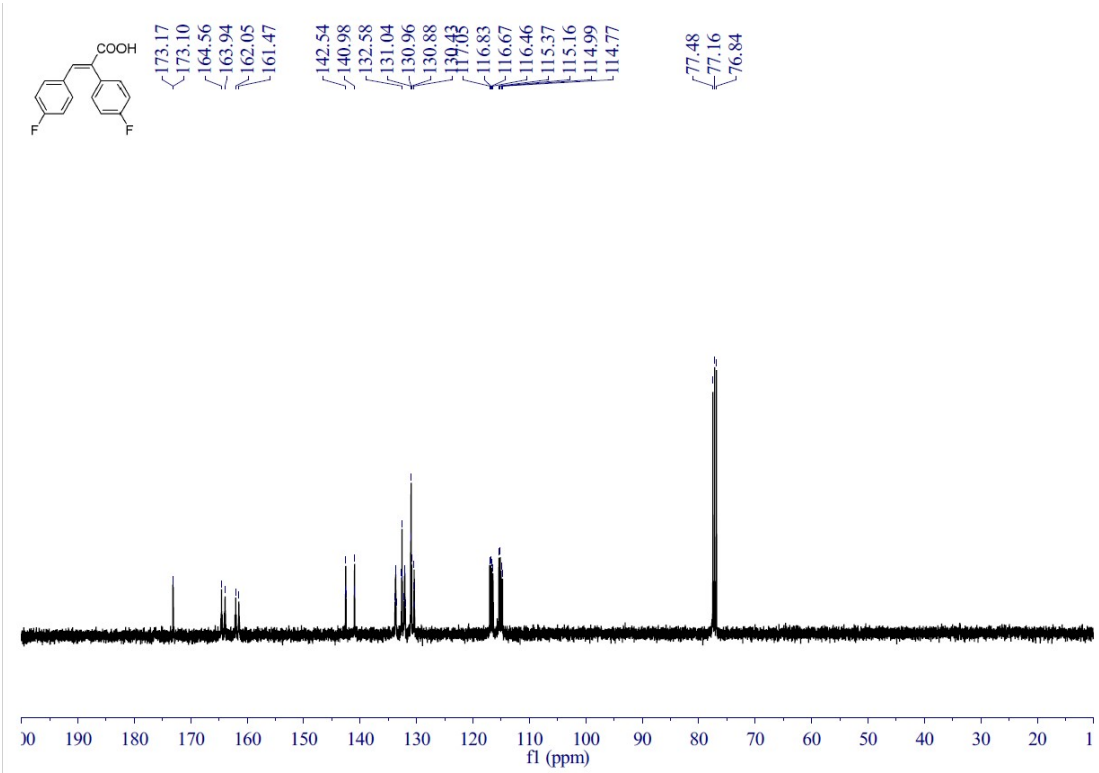

COOH
173.63
160.63
159.30
142.12
132.81
131.16
128.78
127.92
127.23
114.40
113.87
77.48
77.16
76.84
55.38
55.36
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

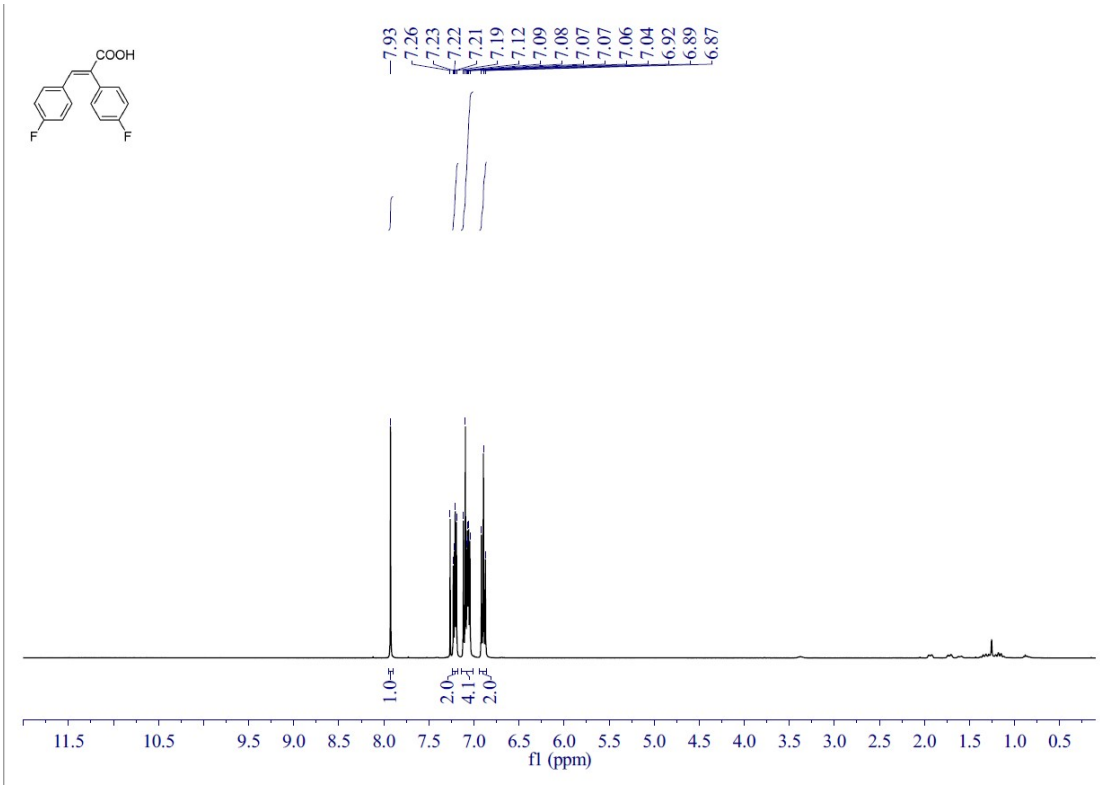

COOH
7.90
7.21
7.19
7.14
7.12
7.00
2.40
2.29
0.9
4.1
4.0
2.9
2.9
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

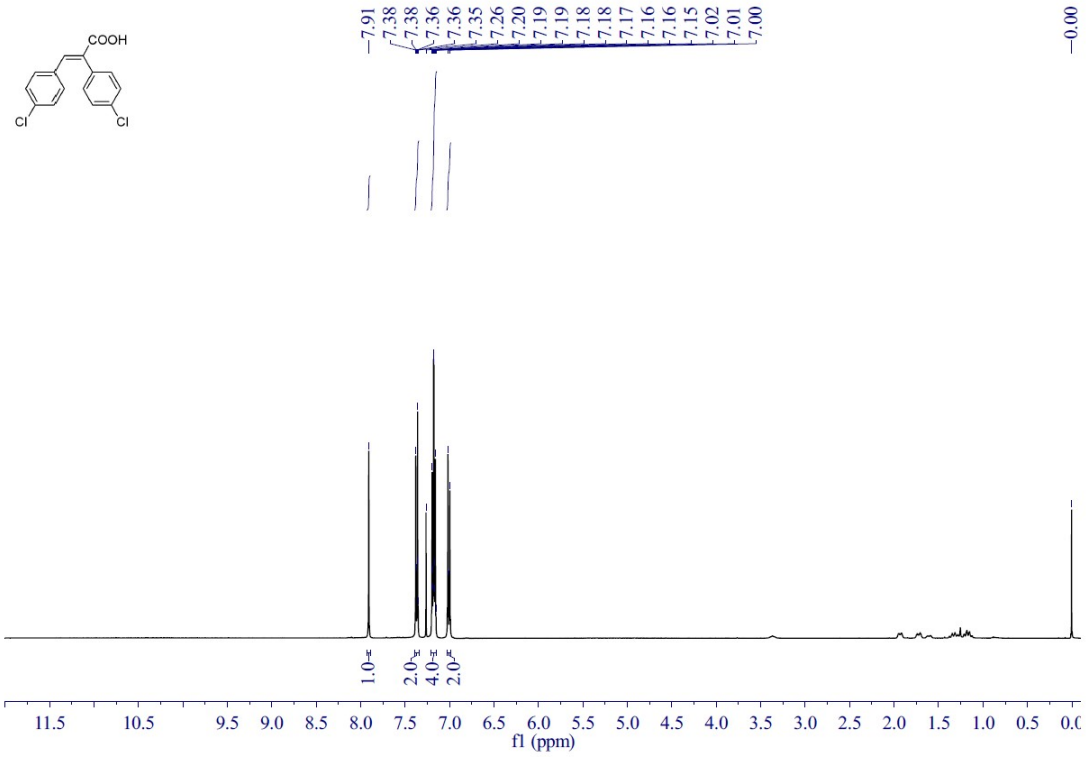

COOH
173.78
142.38
139.95
137.80
132.63
131.79
131.03
130.76
129.75
129.60
129.15
77.48
77.16
76.84
21.50
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

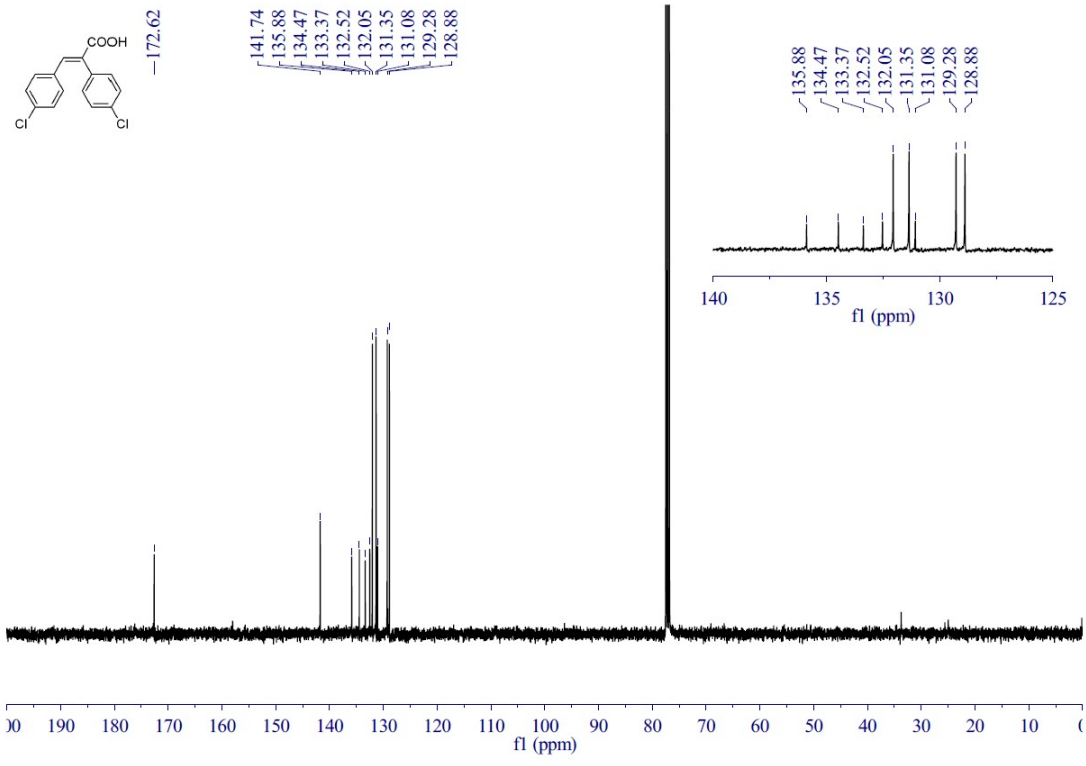

COOH
nBu
nBu
173.81
144.82
142.59
142.21
132.90
131.97
131.05
130.87
129.64
128.83
128.39
77.48
77.16
76.84
35.57
35.55
33.52
33.31
22.47
22.42
14.11
14.01
fl (ppm)

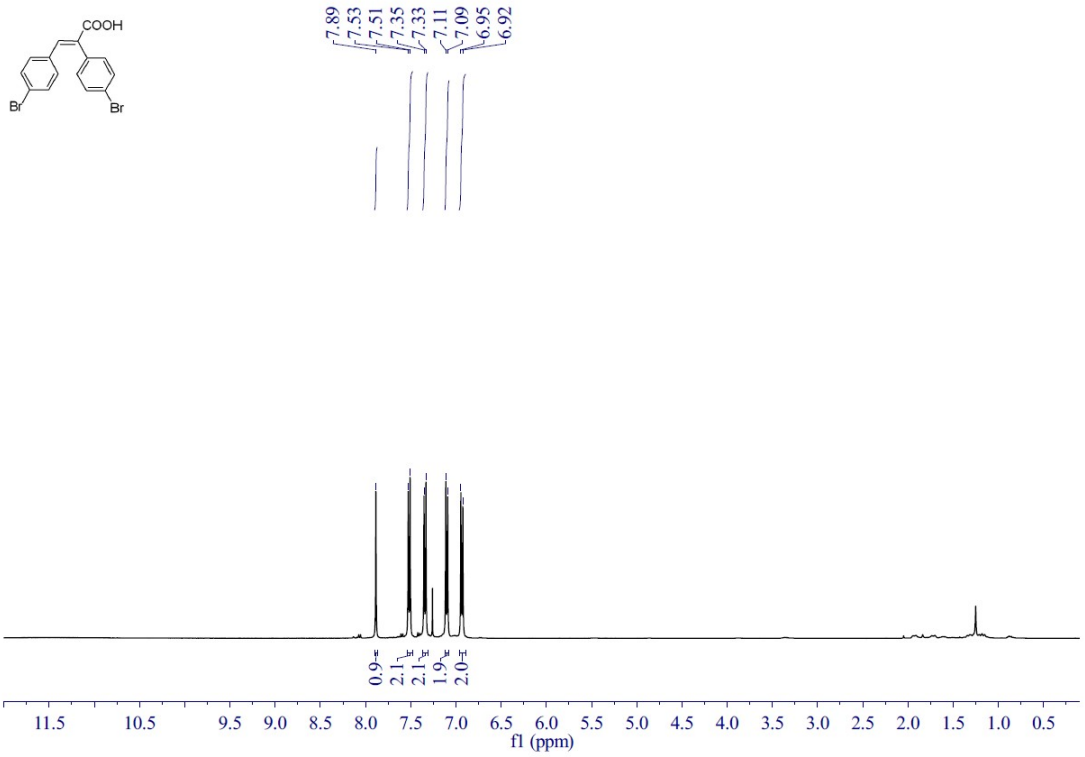

12.43
COOH
nBu
nBu
7.90
7.19
7.18
7.17
7.14
7.12
6.99
6.97
6.96
6.94
2.66
2.64
2.62
2.53
2.51
2.49
1.30
0.96
0.94
0.92
0.90
0.88
0.7
1.0
4.2
4.1
2.0
2.0
2.1
2.0
2.1
2.4
3.1
3.1
fl (ppm)

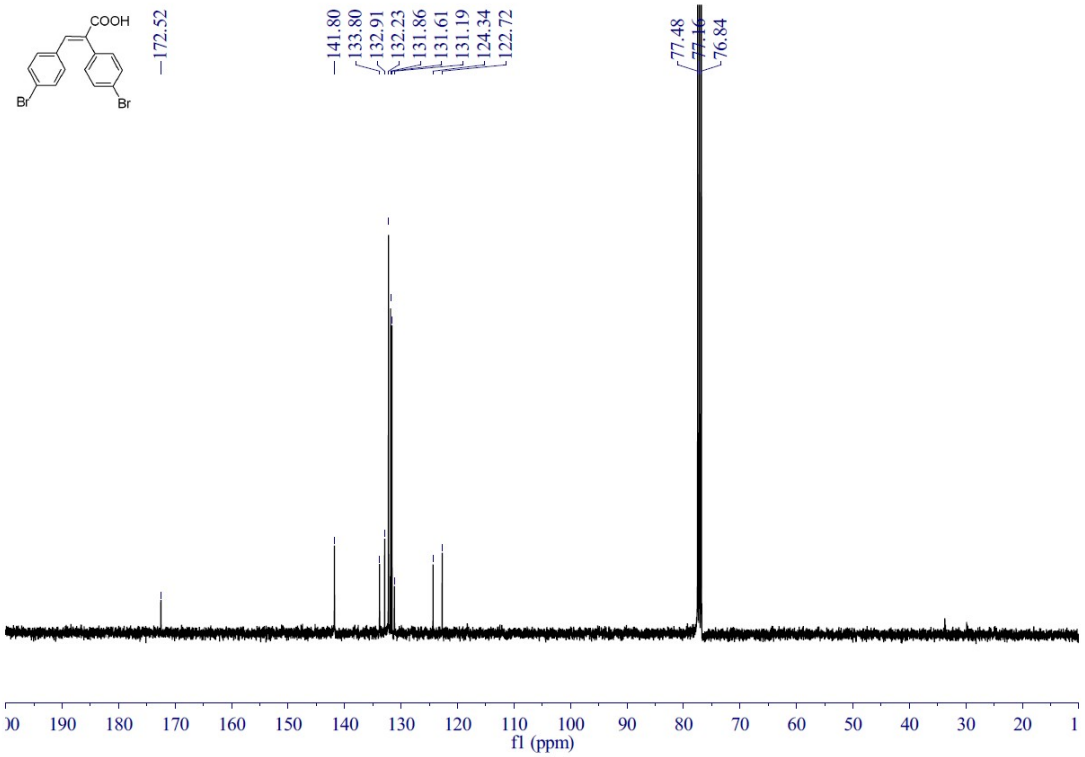

COOH
F
F
173.17
173.10
164.56
163.94
162.05
161.47
142.54
140.98
132.58
131.04
130.96
130.88
116.83
116.67
116.46
115.37
115.16
114.99
114.77
77.48
77.16
76.84
fl (ppm)


COOH
F
F
7.93
7.26
7.23
7.22
7.21
7.19
7.12
7.09
7.08
7.07
7.07
7.06
7.04
6.92
6.89
6.87
1.0
2.0
4.1
2.0
fl (ppm)


COOH
Cl
Cl
7.91
7.38
7.38
7.36
7.36
7.35
7.26
7.20
7.19
7.19
7.18
7.18
7.17
7.16
7.16
7.15
7.02
7.01
7.00
0.00
1.0
2.0
4.0
2.0
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


COOH
Cl
Cl
172.62
141.74
135.88
134.47
133.37
132.52
132.05
131.35
131.08
129.28
128.88
135.88
134.47
133.37
132.52
132.05
131.35
131.08
129.28
128.88
140
135
130
125
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


COOH
Br
Br
7.89
7.53
7.51
7.35
7.33
7.11
7.09
6.95
6.92
0.9
2.1
2.1
1.9
2.0
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


COOH
Br
Br
172.52
141.80
133.80
132.91
132.23
131.86
131.61
131.19
124.34
122.72
77.48
77.16
76.84
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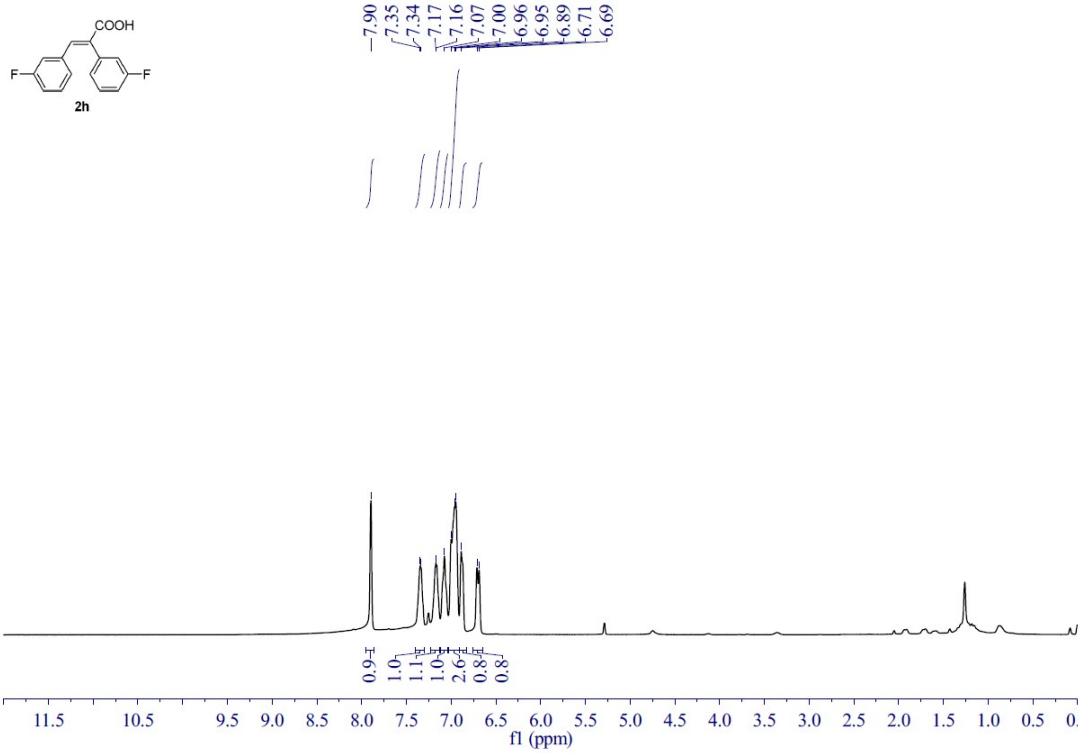
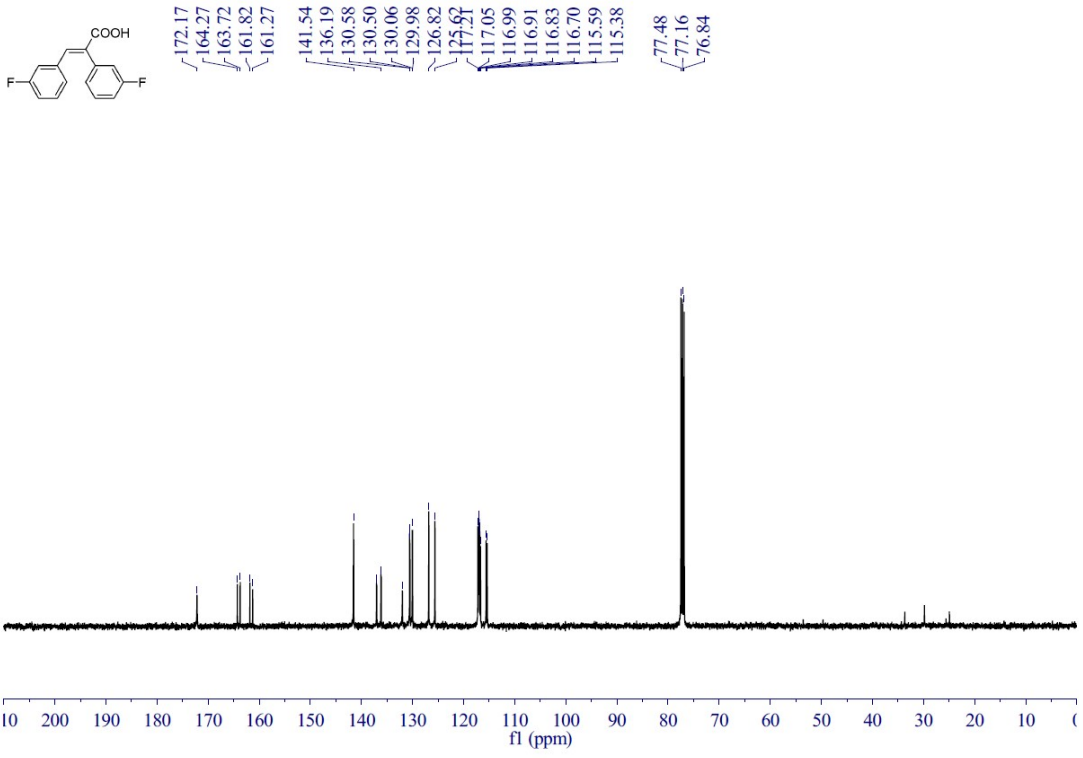
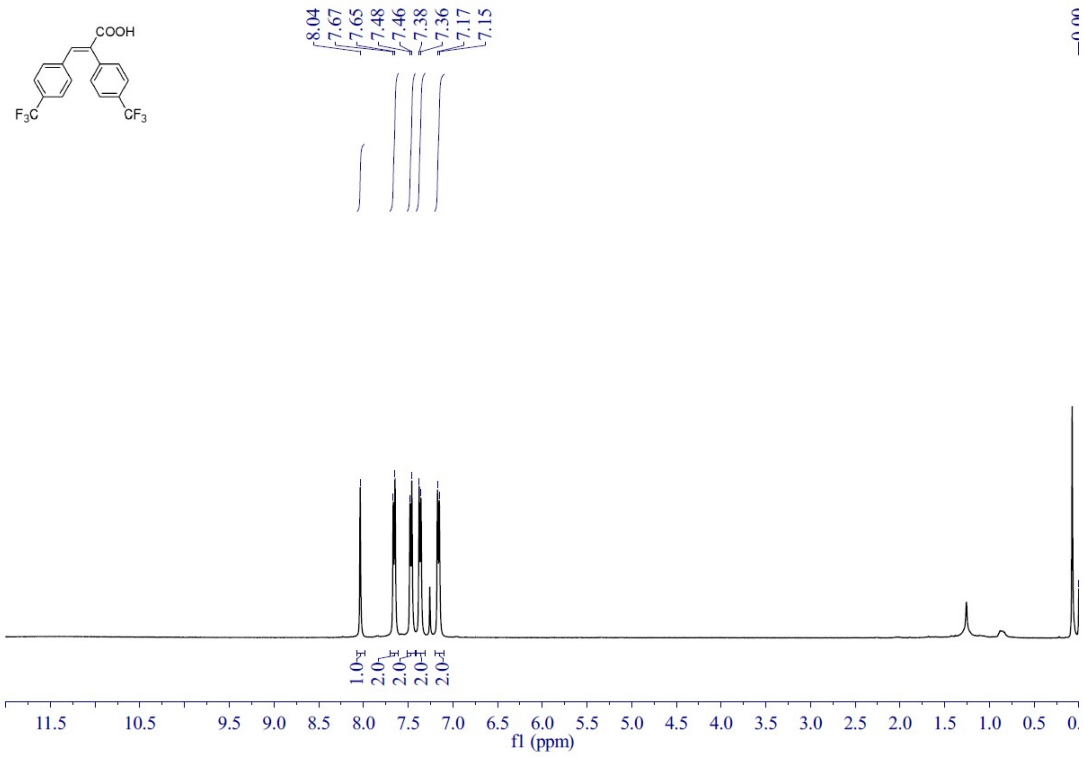
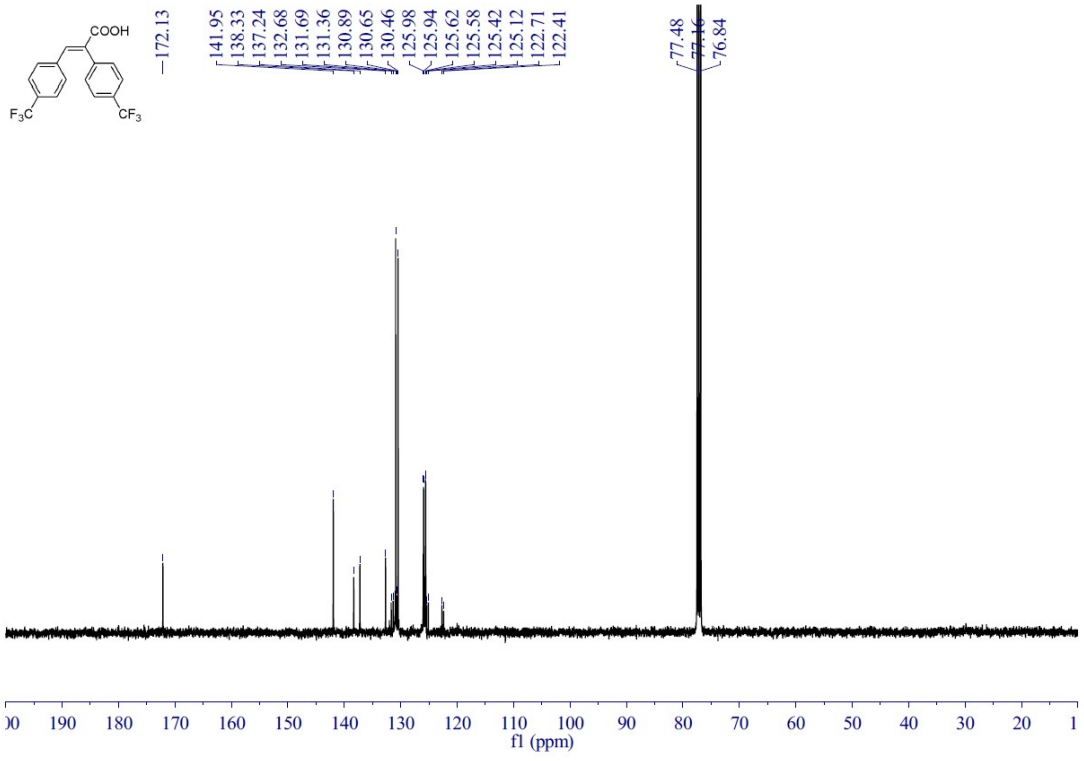
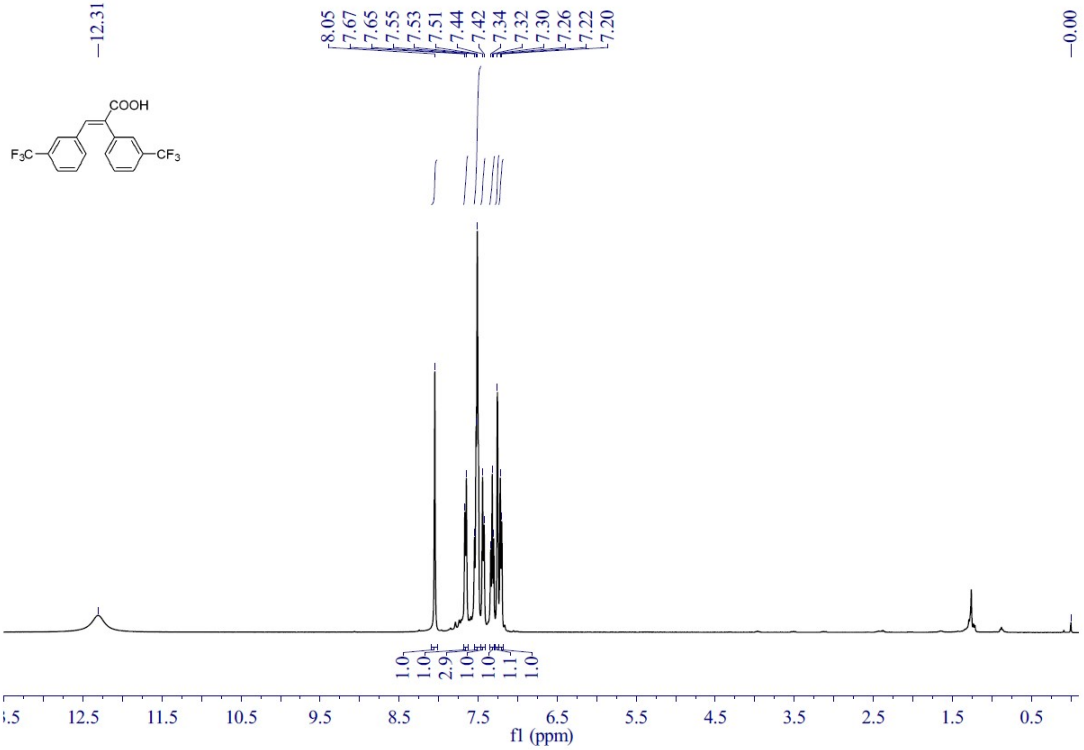
80
70
60
50
40
30
20
f1 (ppm)

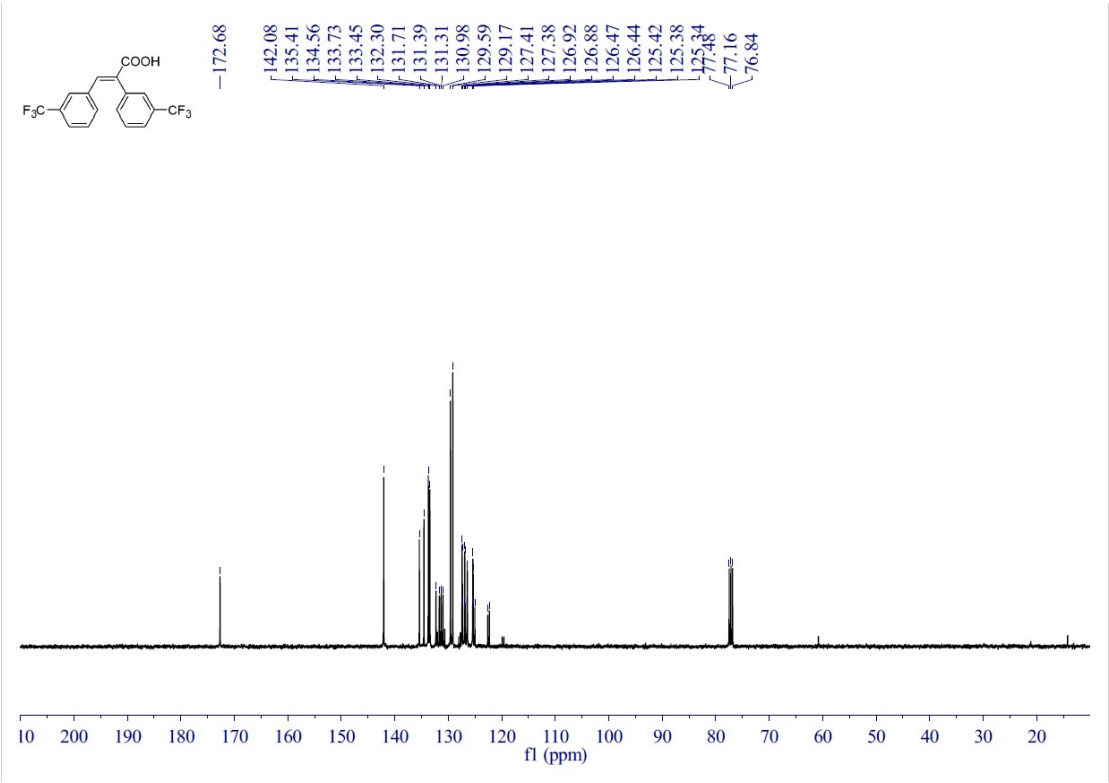

COOH
F
F
2h
7.90
7.35
7.34
7.17
7.16
7.07
7.00
6.96
6.95
6.89
6.71
6.69
0.9
1.0
1.1
1.0
2.6
0.8
0.8
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

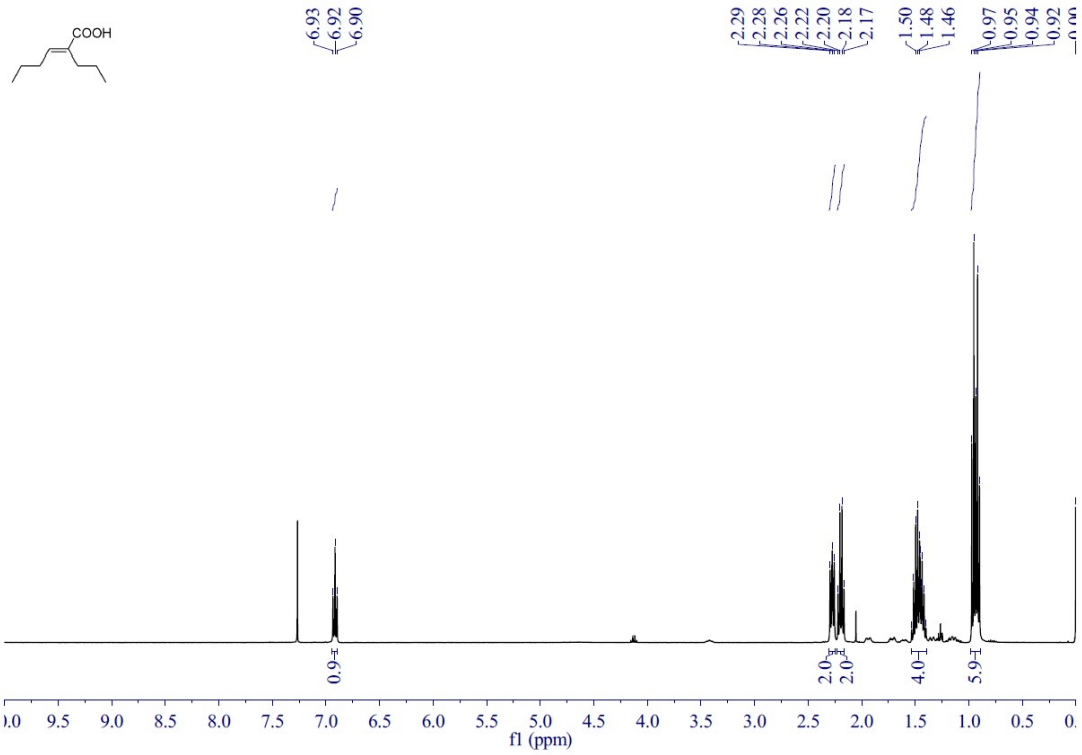

COOH
F
F
172.17
164.27
163.72
161.82
161.27
141.54
136.19
130.58
130.50
130.06
129.98
126.82
125.62
117.21
117.05
116.99
116.91
116.83
116.70
115.59
115.38
77.48
77.16
76.84
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

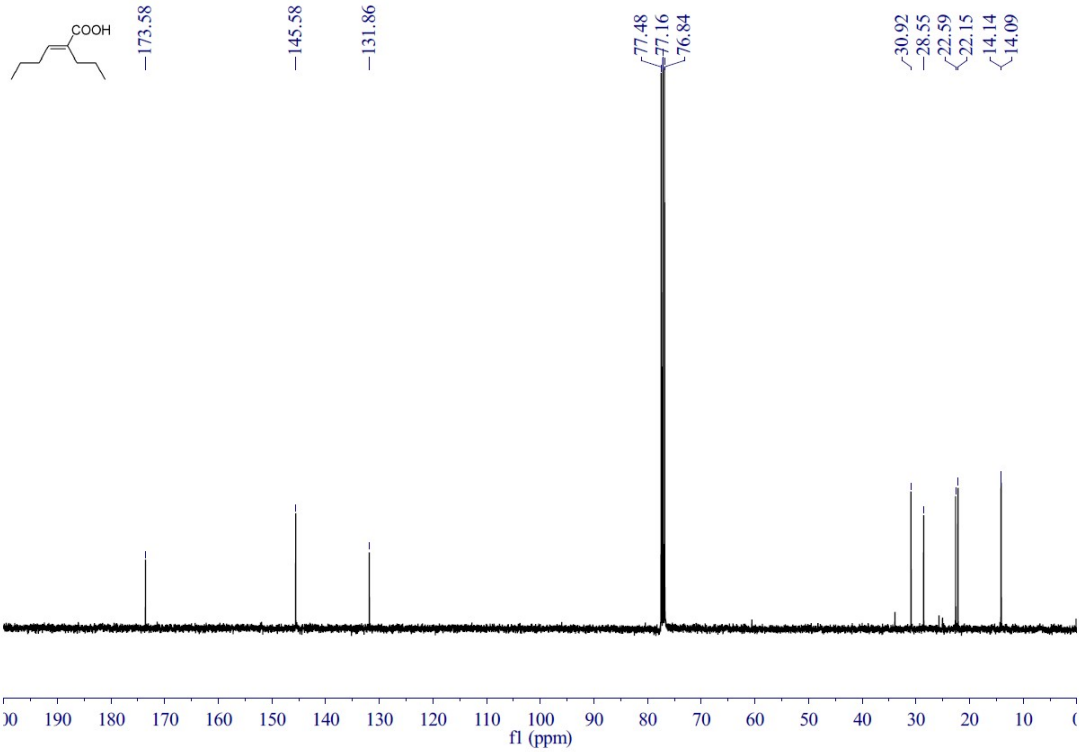

COOH
F3C
CF3
8.04
7.67
7.65
7.48
7.46
7.38
7.36
7.17
7.15
1.0
2.0
2.0
2.0
2.0
fl (ppm)

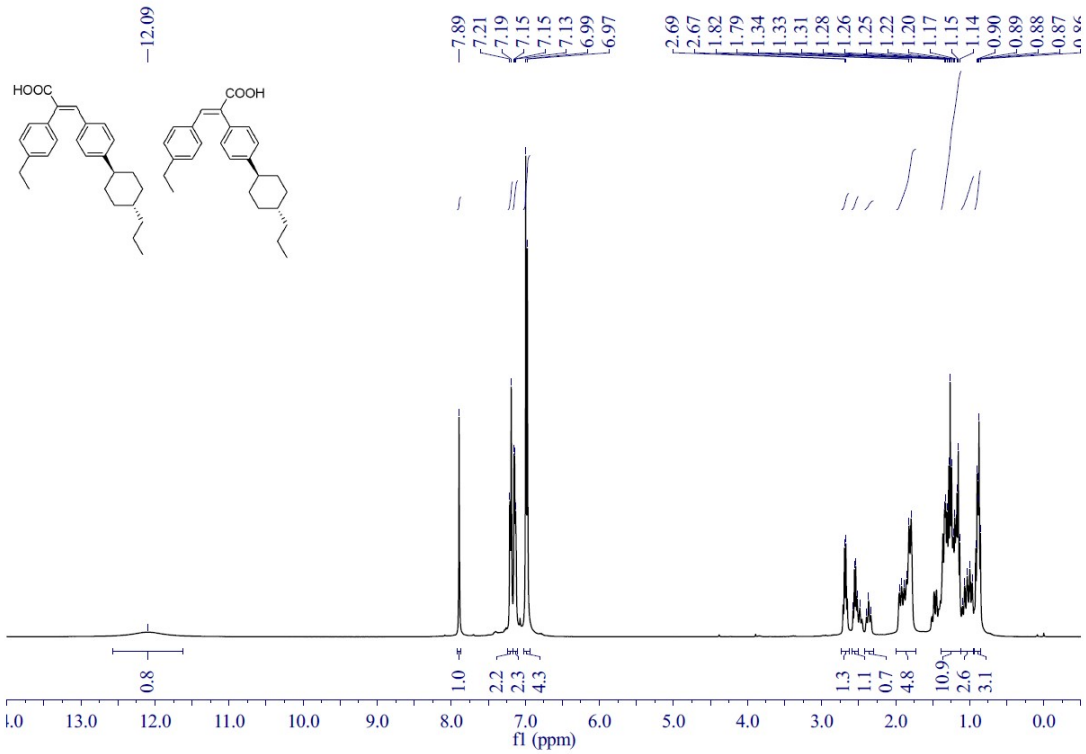

COOH
F3C
CF3
172.13
141.95
138.33
137.24
132.68
131.69
131.36
130.89
130.65
130.46
125.98
125.94
125.62
125.58
125.42
125.12
122.71
122.41
77.48
76.84
fl (ppm)


12.31
8.05
7.67
7.65
7.55
7.53
7.51
7.44
7.42
7.34
7.32
7.30
7.26
7.22
7.20
0.00
COOH
F3C
CF3
1.0
1.0
2.9
1.0
1.0
1.1
1.0
f1 (ppm)


172.68
142.08
135.41
134.56
133.73
133.45
132.30
131.71
131.39
131.31
130.98
129.59
129.17
127.41
127.38
126.92
126.88
126.47
126.44
125.42
125.38
125.34
77.48
77.16
76.84
COOH
F3C
CF3
f1 (ppm)


COOH
6.93
6.92
6.90
2.29
2.28
2.26
2.22
2.20
2.18
2.17
1.50
1.48
1.46
0.97
0.95
0.94
0.92
0.9
2.0
2.0
4.0
5.9
fl (ppm)


COOH
173.58
145.58
131.86
77.48
77.16
76.84
30.92
28.55
22.59
22.15
14.14
14.09
fl (ppm)


HOOC
COOH
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7.89
7.21
7.19
7.15
7.15
7.13
6.99
6.97
2.69
2.67
1.82
1.79
1.34
1.33
1.31
1.28
1.26
1.25
1.22
1.20
1.17
1.15
1.14
0.90
0.89
0.88
0.87
0.8
1.0
2.2
2.3
4.3
1.3
1.1
0.7
4.8
10.9
2.6
3.1
13.0
12.0
11.0
10.0
9.0
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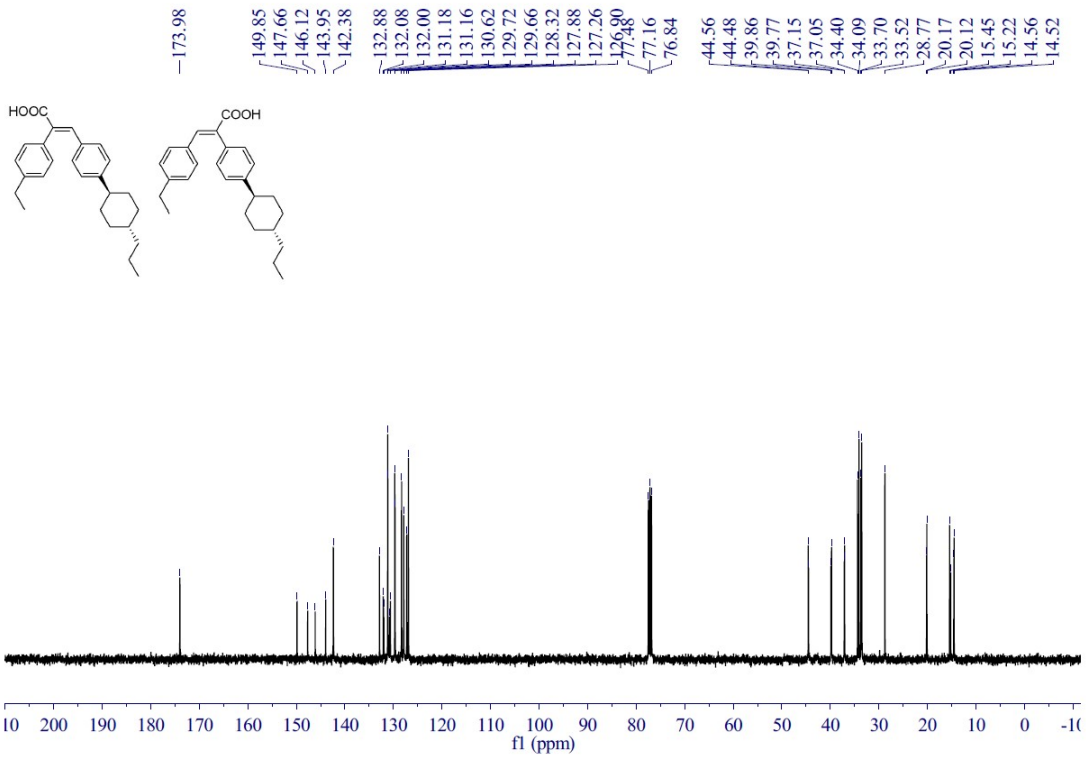
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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COOH
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146.12
143.95
142.38
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132.08
132.00
131.18
131.16
130.62
129.72
129.66
128.32
127.88
127.26
126.90
77.48
77.16
76.84
44.56
44.48
39.86
39.77
37.15
37.05
34.40
34.09
33.70
33.52
28.77
20.17
20.12
15.45
15.22
14.56
14.52
200
190
180
170
160
150
140
130
120
110
100
90
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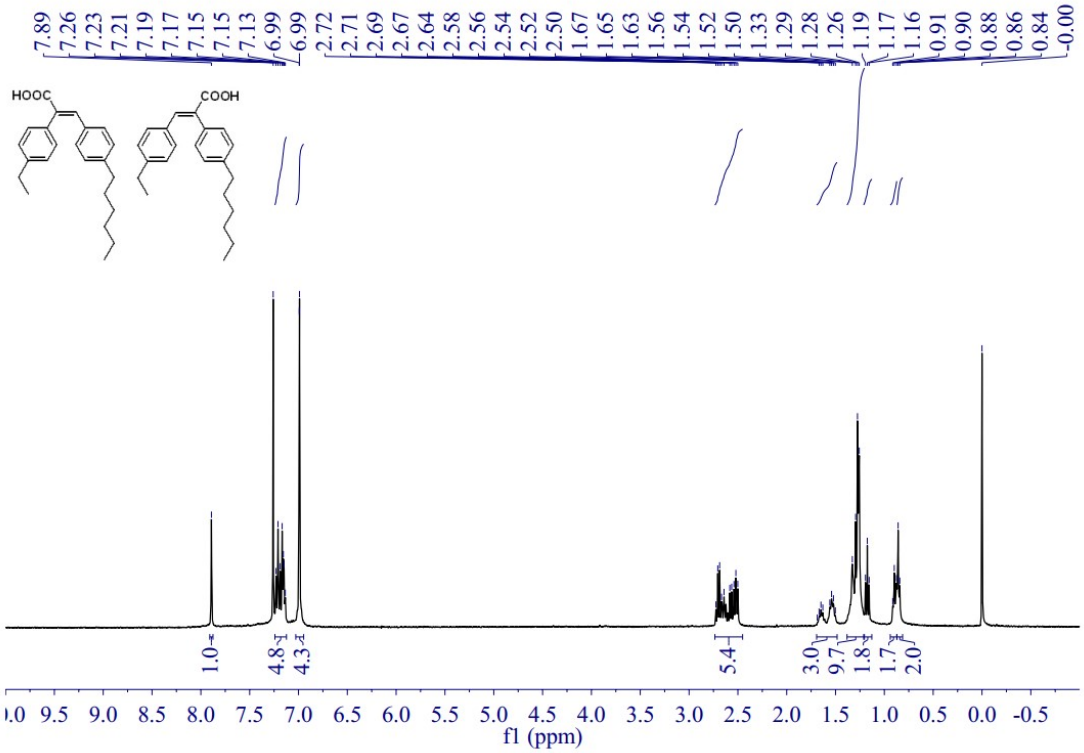
70
60
50
40
30
20
10
0
f1 (ppm)


7.89
7.26
7.23
7.21
7.19
7.17
7.15
7.15
7.13
6.99
6.99
2.72
2.71
2.69
2.67
2.64
2.58
2.56
2.54
2.52
2.50
1.67
1.65
1.63
1.56
1.54
1.52
1.50
1.33
1.29
1.28
1.26
1.19
1.17
1.16
0.91
0.90
0.88
0.86
0.84
-0.00
HOOC
COOH
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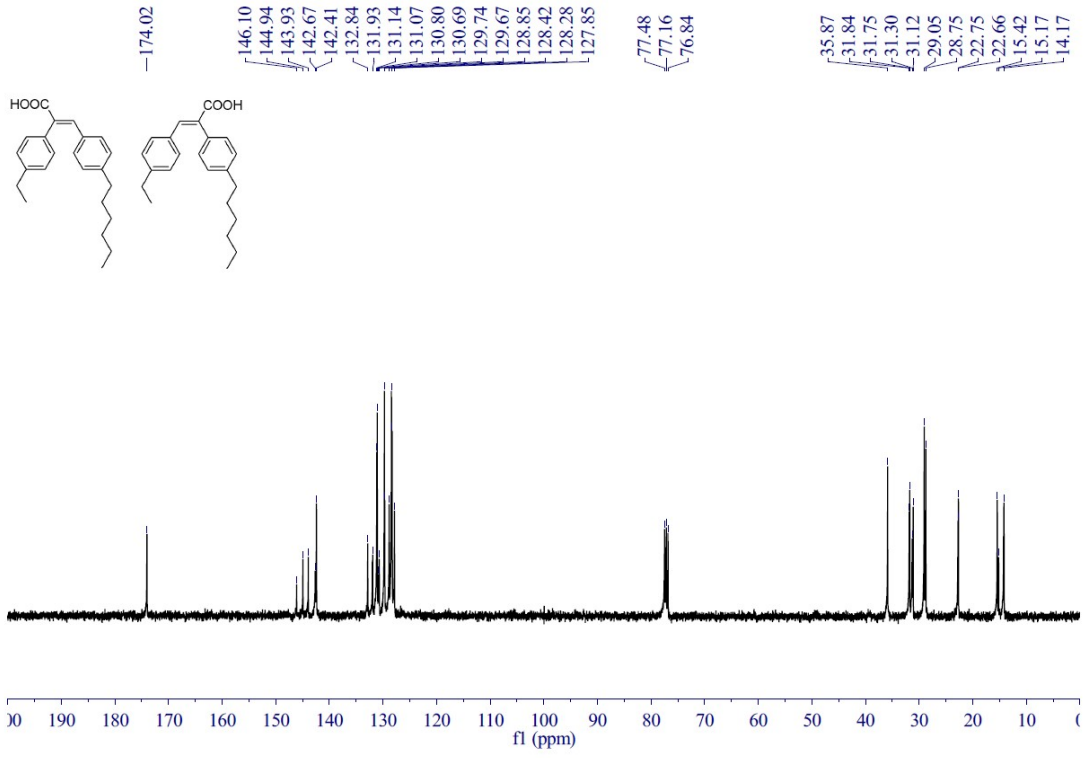
4.8
4.3
5.4
3.0
9.7
1.8
1.7
2.0
fl (ppm)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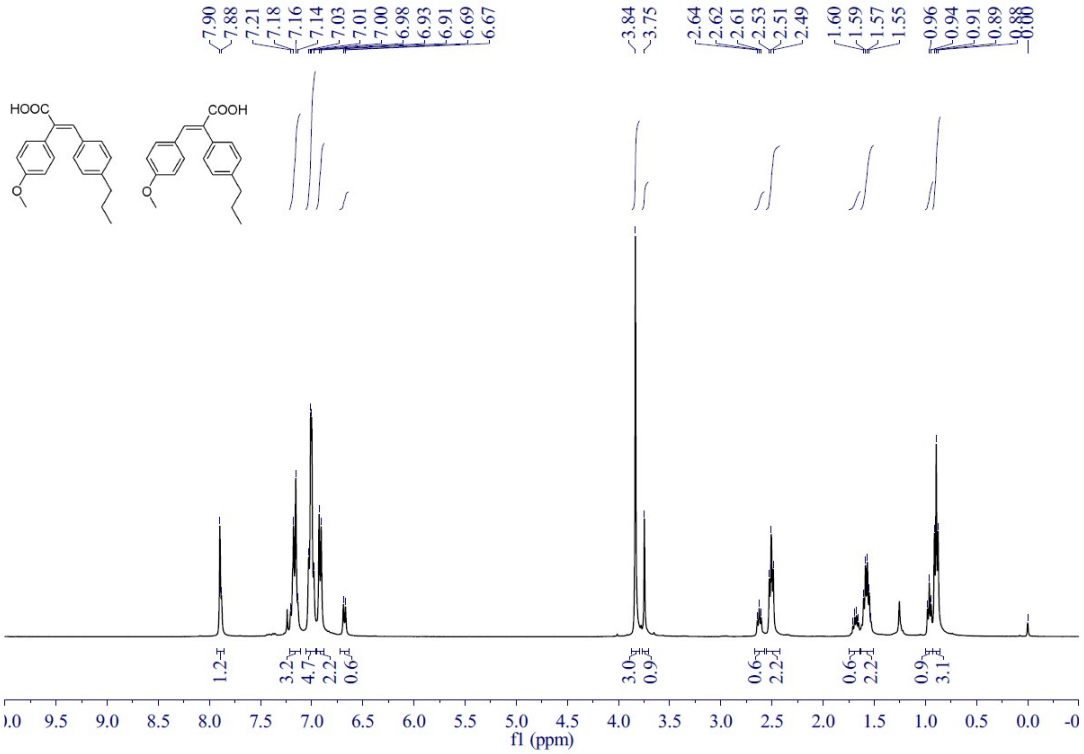
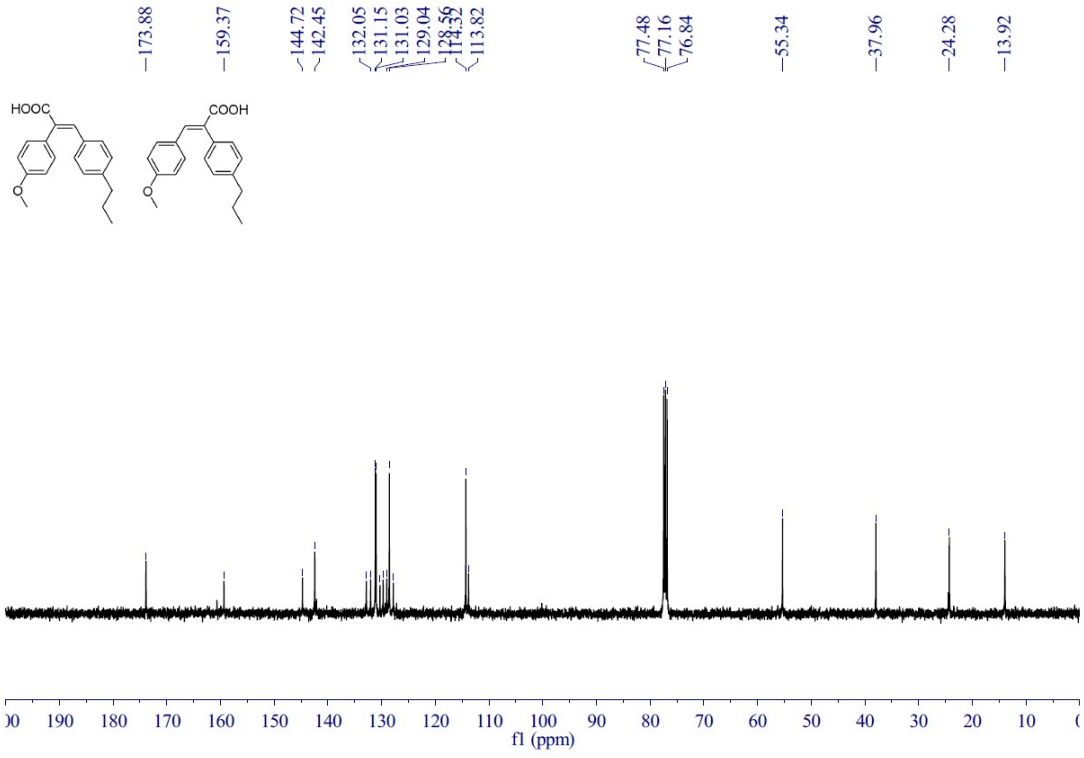
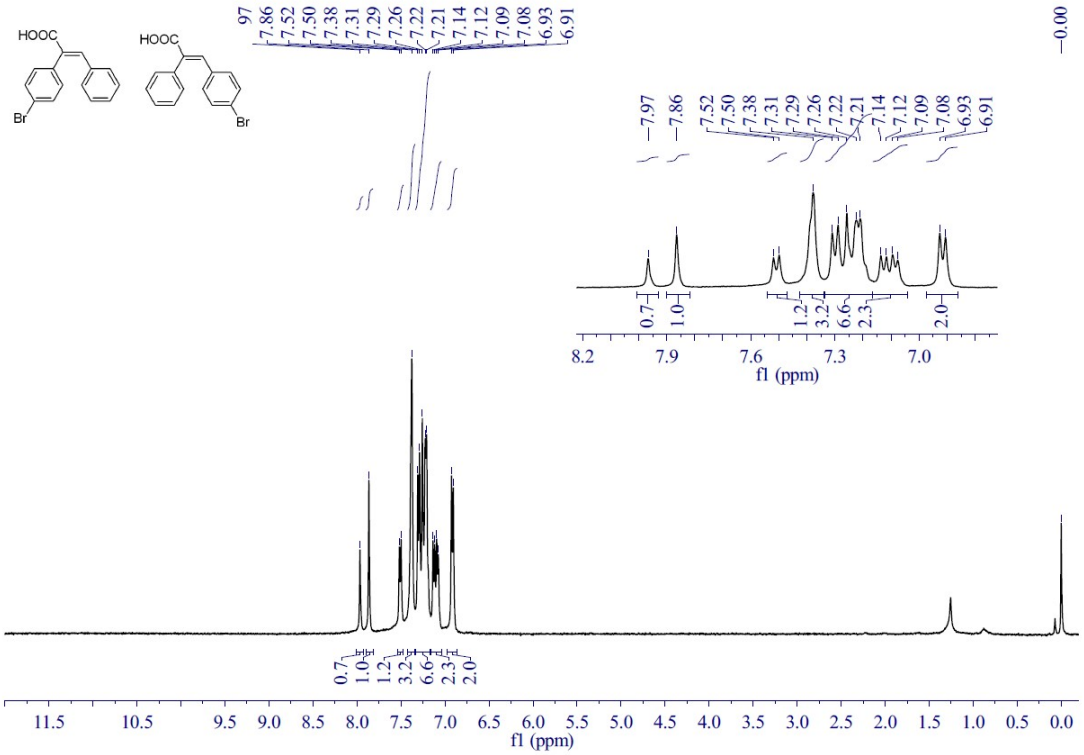
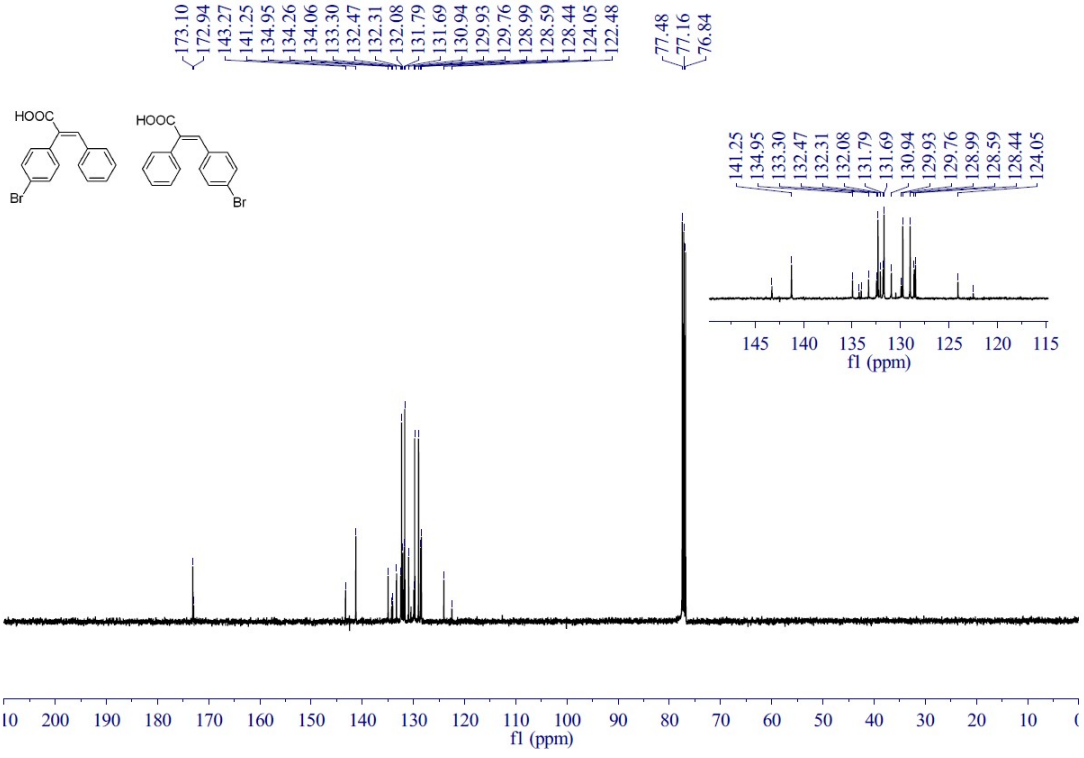
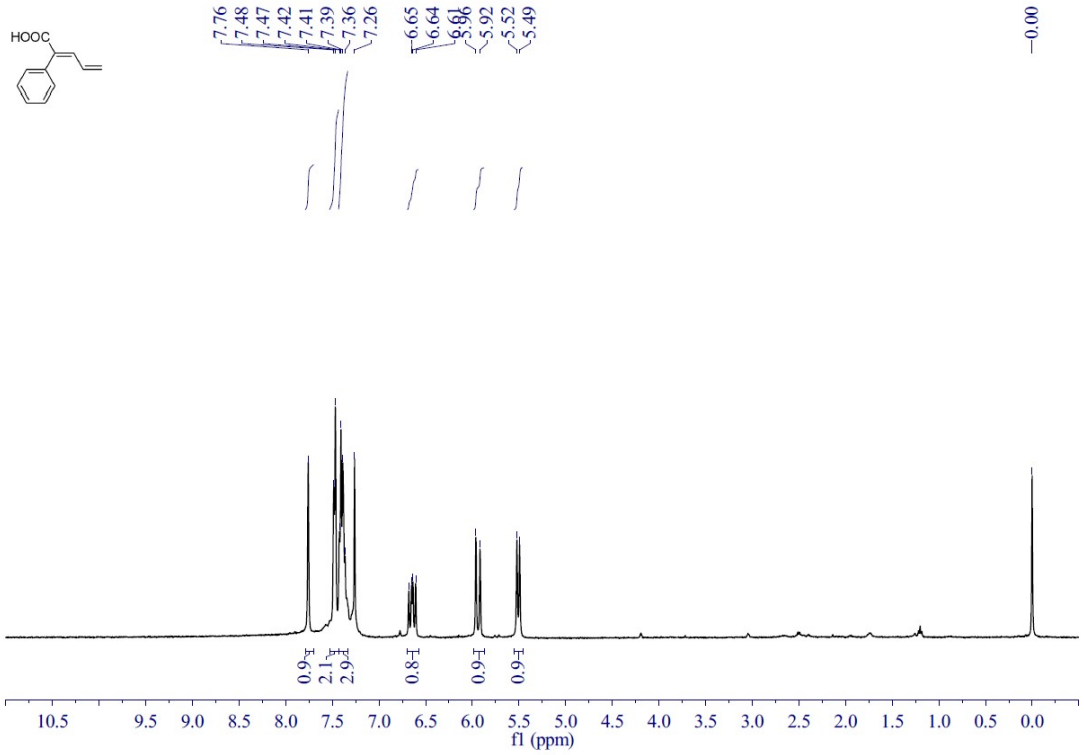
129.67
128.85
128.42
128.28
127.85
77.48
77.16
76.84
35.87
31.84
31.75
31.30
31.12
29.05
28.75
22.75
22.66
15.42
15.17
14.17
HOOC
COOH
fl (ppm)

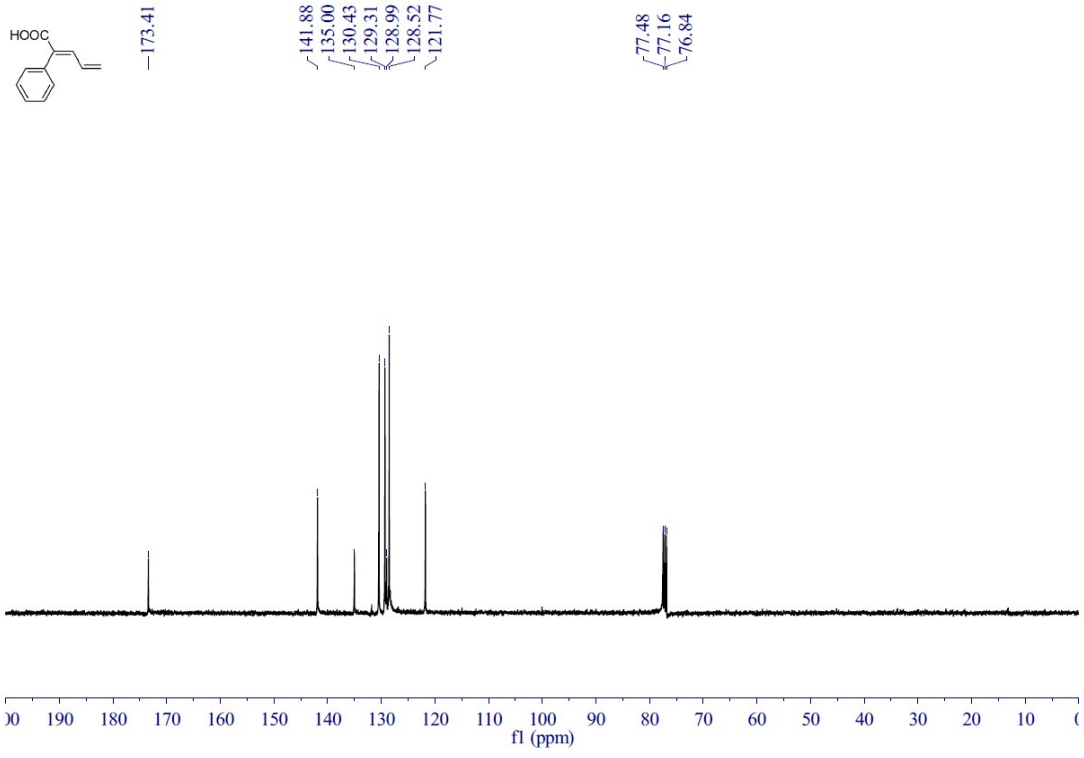

HOOC
COOH
7.90
7.88
7.21
7.18
7.16
7.14
7.03
7.01
7.00
6.98
6.93
6.91
6.69
6.67
3.84
3.75
2.64
2.62
2.61
2.53
2.51
2.49
1.60
1.59
1.57
1.55
0.96
0.94
0.91
0.89
1.2
3.2
4.7
2.2
0.6
3.0
0.9
0.6
2.2
0.6
2.2
0.9
3.1
f1 (ppm)

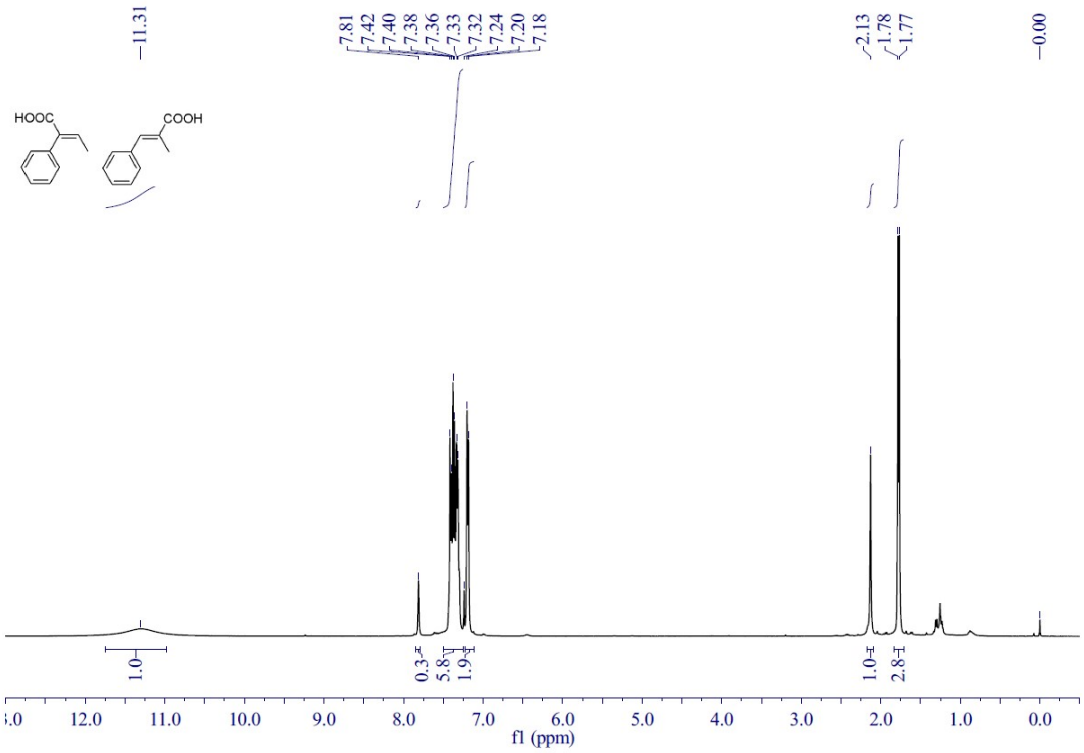

HOOC
COOH
173.88
159.37
144.72
142.45
132.05
131.15
131.03
129.04
128.56
114.32
113.82
77.48
77.16
76.84
55.34
37.96
24.28
13.92
f1 (ppm)

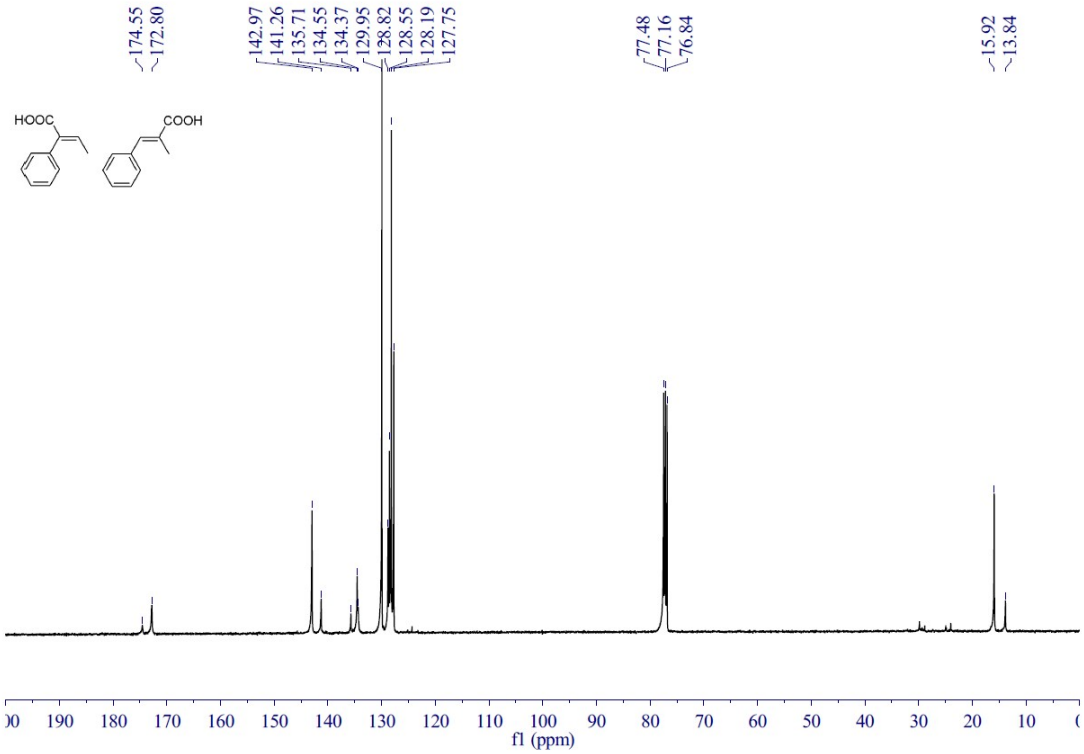

HOOC
Br
HOOC
Br
7.97
7.86
7.52
7.50
7.38
7.31
7.29
7.26
7.22
7.21
7.14
7.12
7.09
7.08
6.93
6.91
0.00
0.7
1.0
1.2
3.2
6.6
2.3
2.0
fl (ppm)


173.10
172.94
143.27
141.25
134.95
134.26
134.06
133.30
132.47
132.31
132.08
131.79
131.69
130.94
129.93
129.76
128.99
128.59
128.44
124.05
122.48
77.48
77.16
76.84
HOOC
Br
HOOC
Br
fl (ppm)


HOOC
7.76
7.48
7.47
7.42
7.41
7.39
7.36
7.26
6.65
6.64
6.61
6.60
5.92
5.52
5.49
0.00
0.9
2.1
2.9
0.8
0.9
0.9
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


HOOC
173.41
141.88
135.00
130.43
129.31
128.99
128.52
121.77
77.48
77.16
76.84
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


11.31
7.81
7.42
7.40
7.38
7.36
7.33
7.32
7.24
7.20
7.18
2.13
1.78
1.77
0.00
HOOC
COOH
1.0
0.3
5.8
1.9
1.0
2.8
fl (ppm)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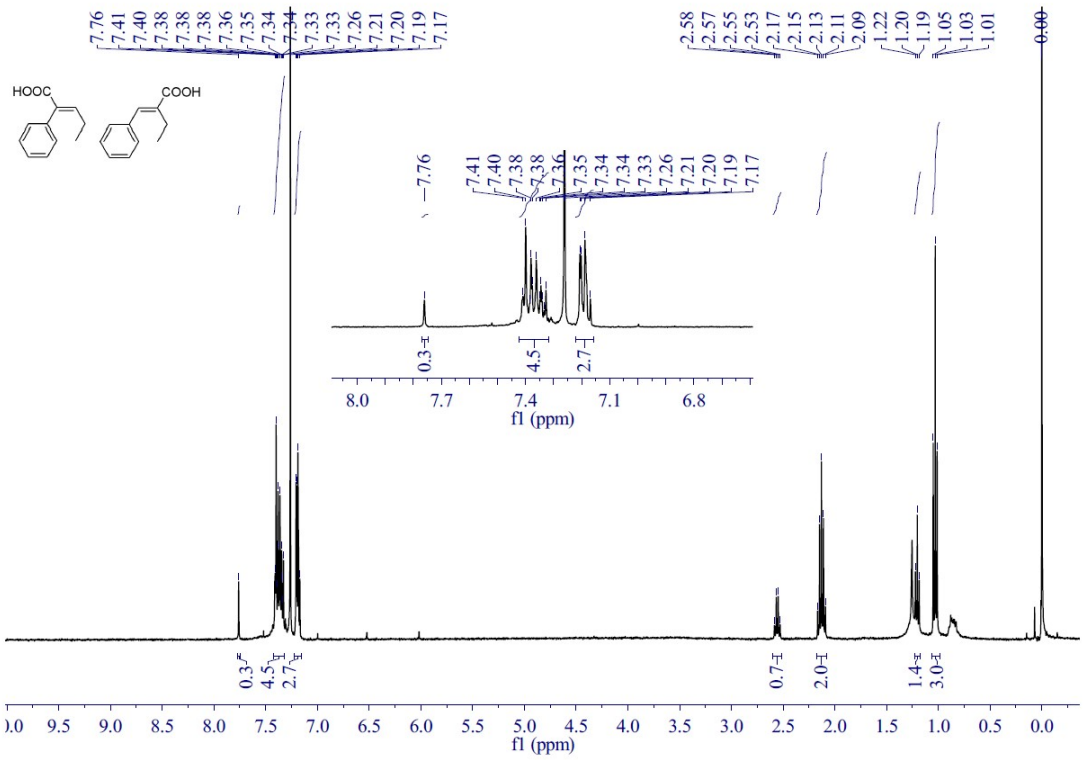
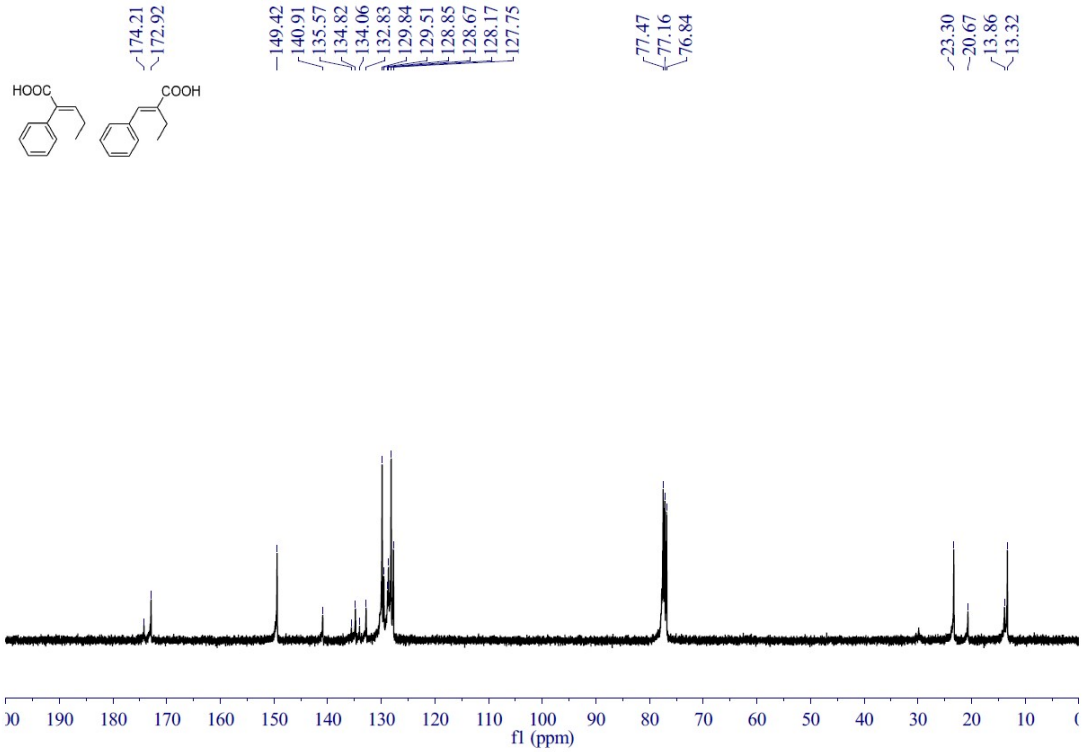
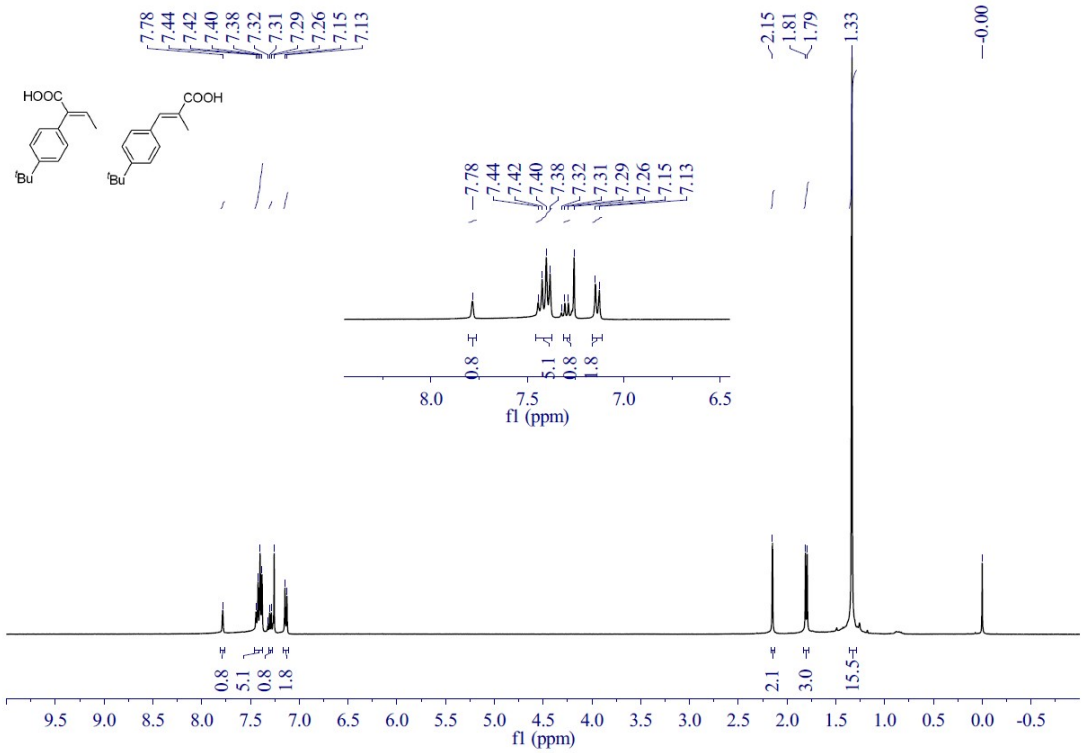
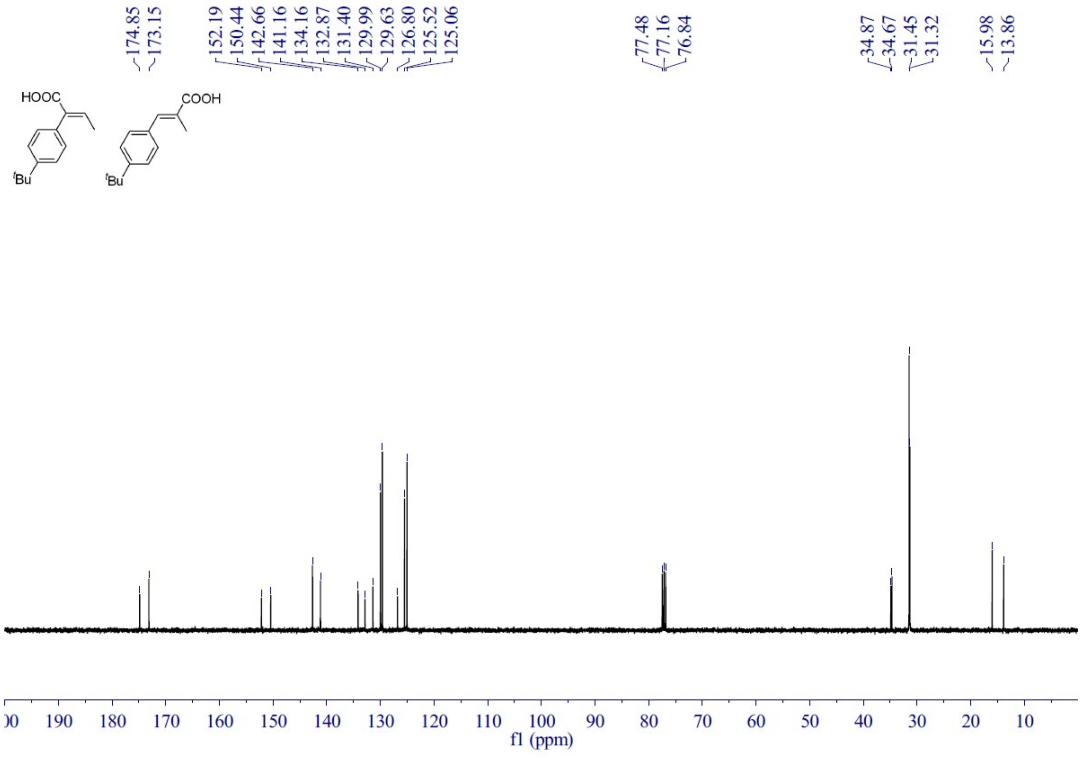
172.80
142.97
141.26
135.71
134.55
134.37
129.95
128.82
128.55
128.19
127.75
77.48
77.16
76.84
15.92
13.84
HOOC
COOH
fl (ppm)


HOOC
COOH
fl (ppm)


HOOC
COOH
fl (ppm)


7.78
7.44
7.42
7.40
7.38
7.32
7.31
7.29
7.26
7.15
7.13
2.15
1.81
1.79
1.33
-0.00
HOOC
COOH
tBu
tBu
0.8
5.1
0.8
1.8
2.1
3.0
15.5
fl (ppm)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173.15
152.19
150.44
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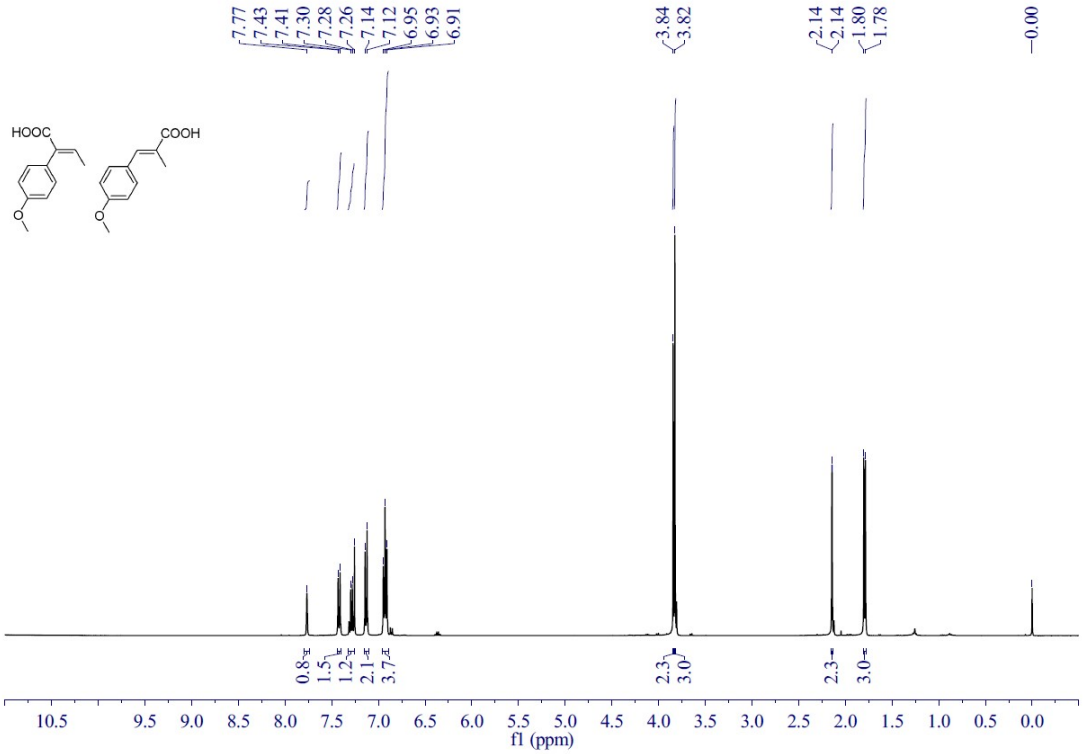
134.16
132.87
131.40
129.99
129.63
126.80
125.52
125.06
77.48
77.16
76.84
34.87
34.67
31.45
31.32
15.98
13.86
HOOC
COOH
tBu
tBu
fl (ppm)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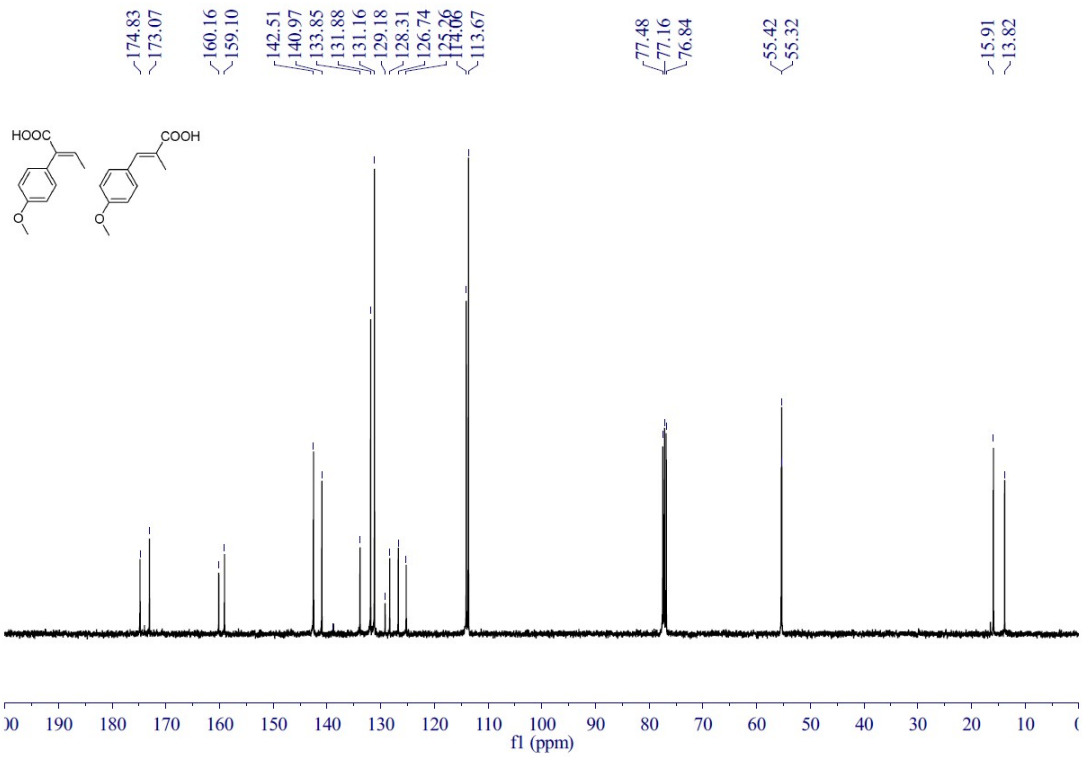
7.26
7.14
7.12
6.95
6.93
6.91
3.84
3.82
2.14
2.14
1.80
1.78
0.00
HOOC
COOH
0.8
1.5
1.2
2.1
3.7
2.3
3.0
2.3
3.0
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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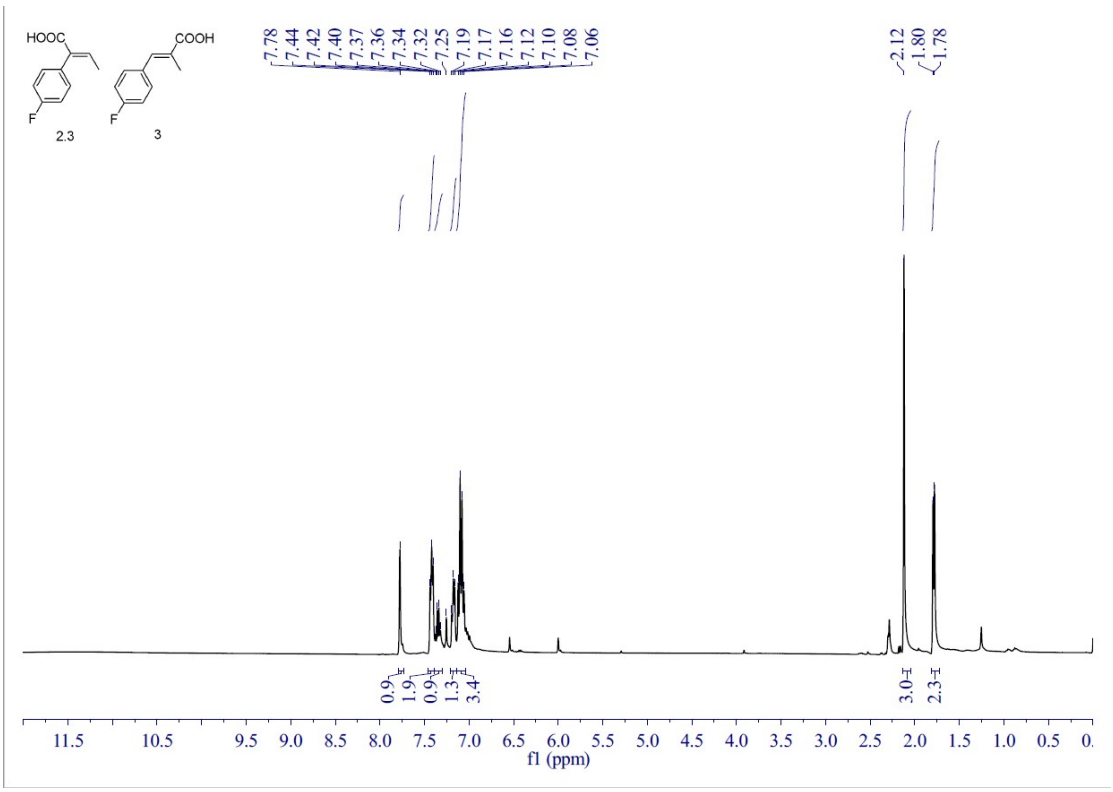
159.10
142.51
140.97
133.85
131.88
131.16
129.18
128.31
126.74
125.26
114.06
113.67
77.48
77.16
76.84
55.42
55.32
15.91
13.82
HOOC
COOH
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


HOOC
COOH
F
F
2.3
3
7.78
7.44
7.42
7.40
7.37
7.36
7.34
7.32
7.25
7.19
7.17
7.16
7.12
7.10
7.08
7.06
2.12
1.80
1.78
0.9
1.9
0.9
1.3
3.4
3.0
2.3
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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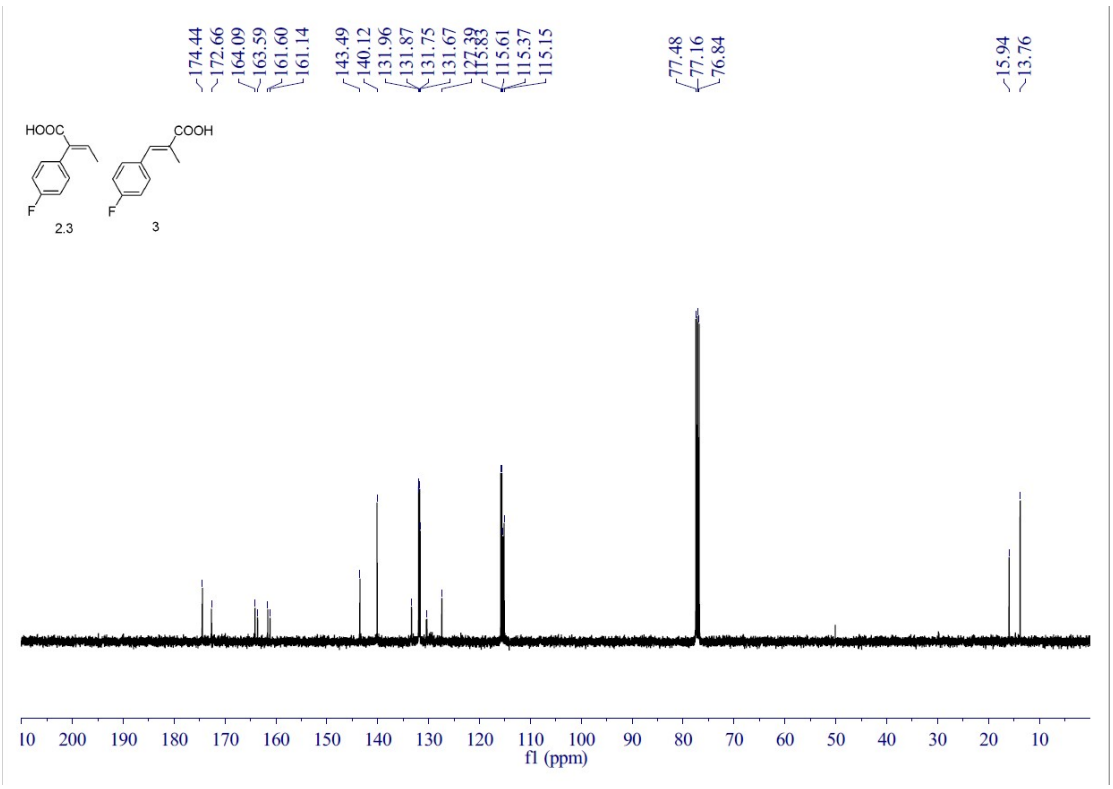
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


174.44
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161.60
161.14
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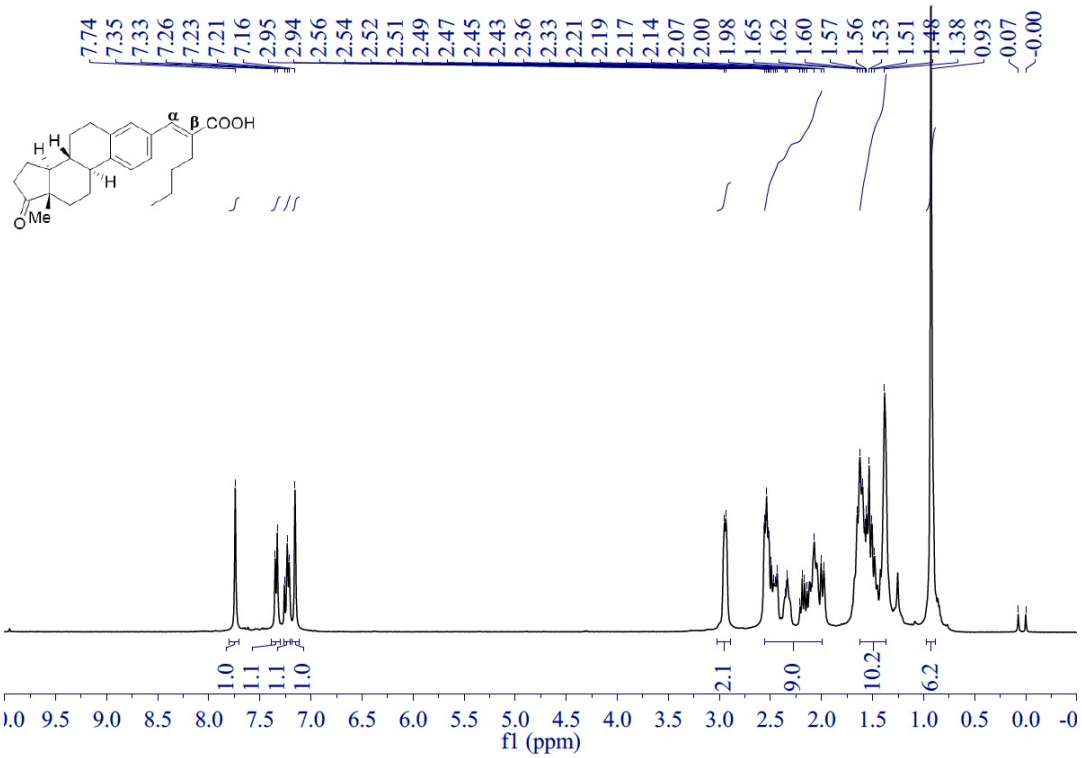
140.12
131.96
131.87
131.75
131.67
127.39
115.83
115.61
115.37
115.15
77.48
77.16
76.84
15.94
13.76
HOOC
COOH
F
F
2.3
3
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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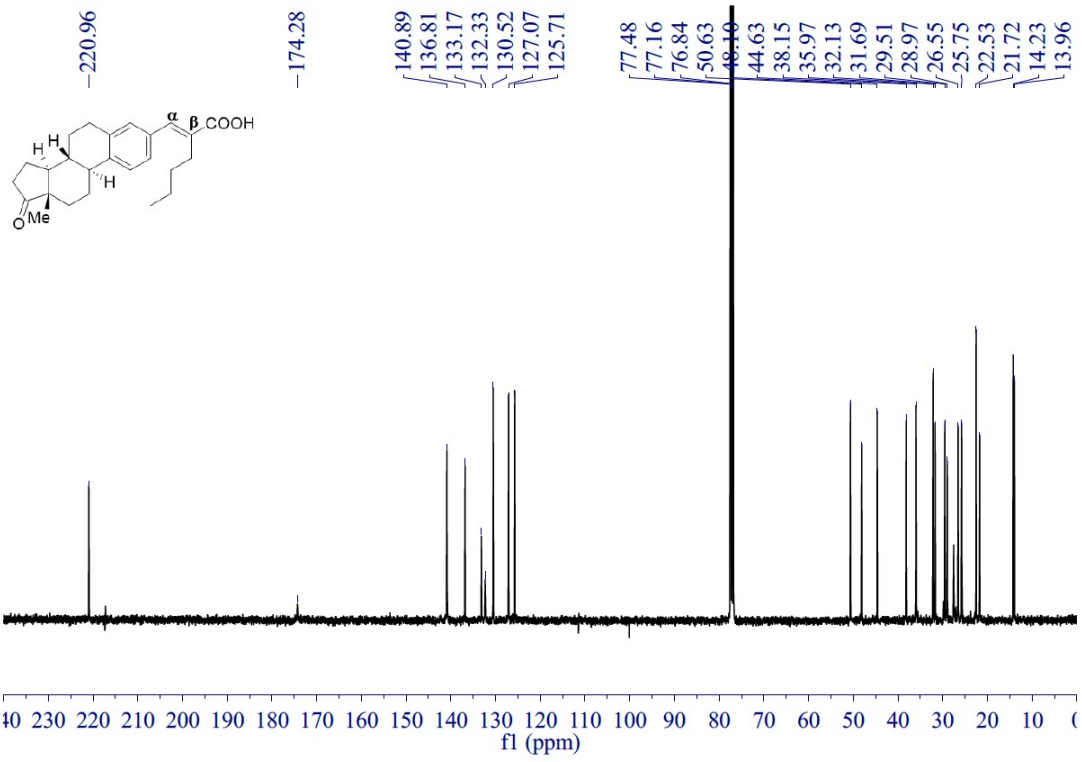
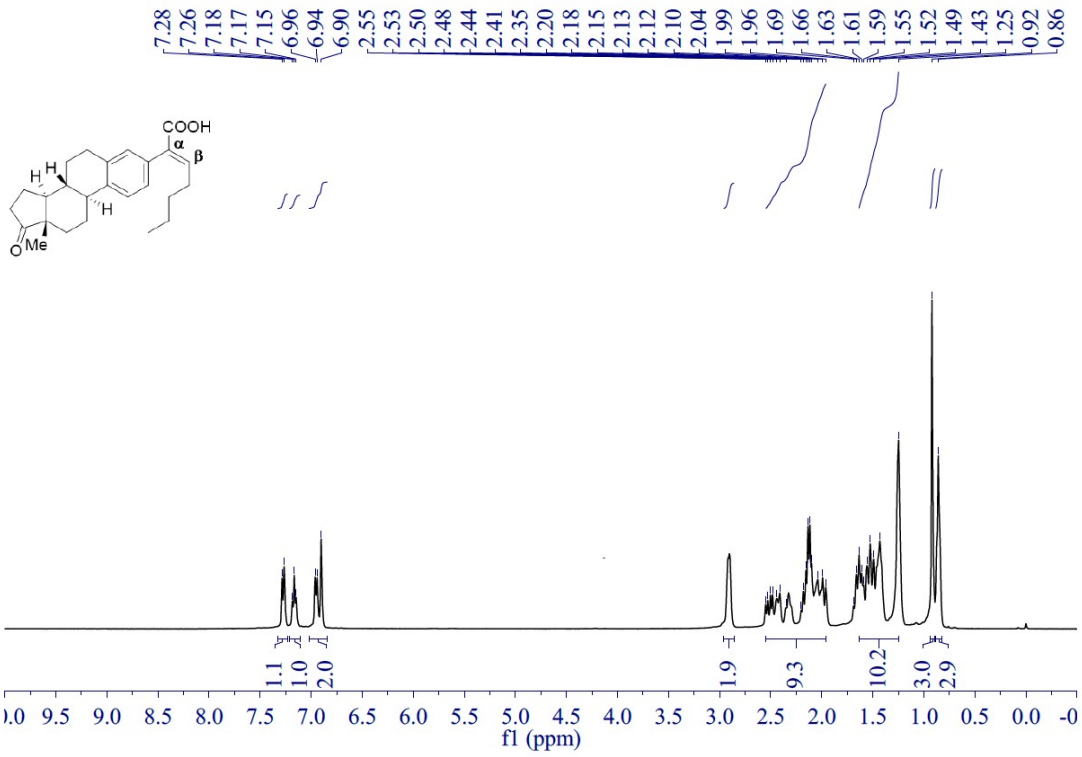
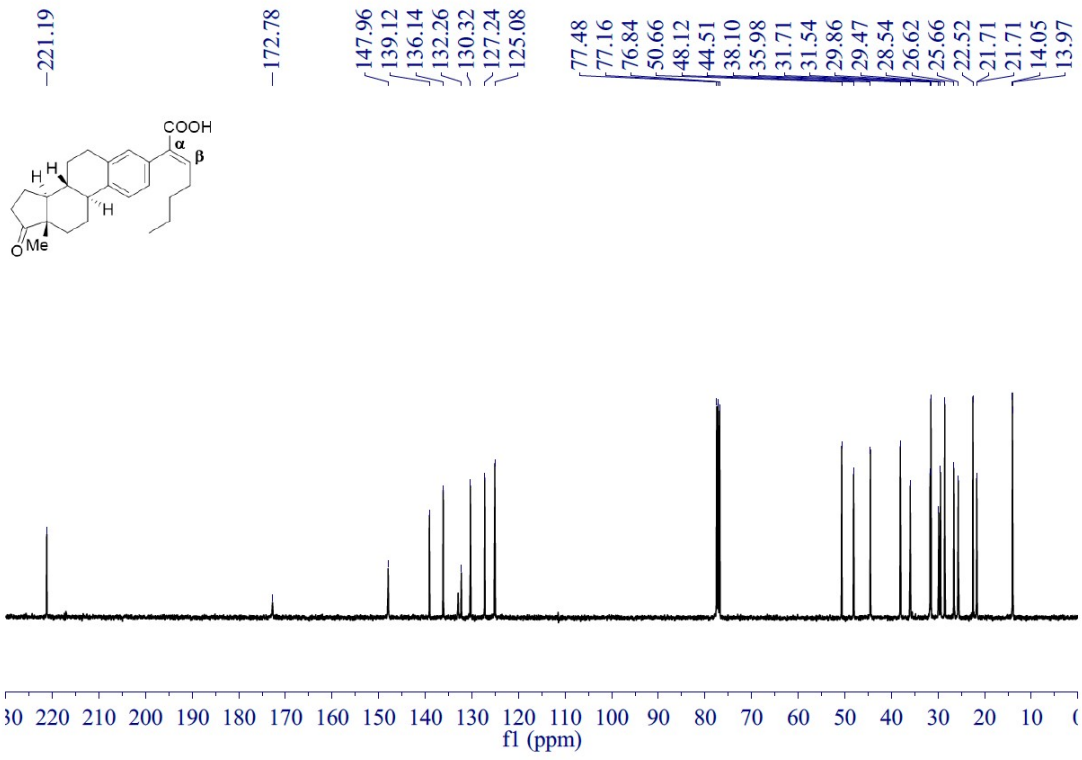
7.21
7.16
2.95
2.94
2.56
2.54
2.52
2.51
2.49
2.47
2.45
2.43
2.36
2.33
2.21
2.19
2.17
2.14
2.07
2.00
1.98
1.65
1.62
1.60
1.57
1.56
1.53
1.51
1.48
1.38
0.93
0.07
-0.00
α
β COOH
H
H
H
O
Me
1.0
1.1
1.1
1.0
2.1
9.0
10.2
6.2
f1 (ppm)


220.96
174.28
140.89
136.81
133.17
132.33
130.52
127.07
125.71
77.48
77.16
76.84
50.63
48.10
44.63
38.15
35.97
32.13
31.69
29.51
28.97
26.55
25.75
22.53
21.72
14.23
13.96
α
β COOH
H
H
H
O
Me
f1 (ppm)


7.28
7.26
7.18
7.17
7.15
6.96
6.94
6.90
2.55
2.53
2.50
2.48
2.44
2.41
2.35
2.20
2.18
2.15
2.13
2.12
2.10
2.04
1.99
1.96
1.69
1.66
1.63
1.61
1.59
1.55
1.52
1.49
1.43
1.25
0.92
0.86
COOH
α
β
H
H
H
O
Me
1.1
1.0
2.0
1.9
9.3
10.2
3.0
2.9
fl (ppm)


221.19
172.78
147.96
139.12
136.14
132.26
130.32
127.24
125.08
77.48
77.16
76.84
50.66
48.12
44.51
38.10
35.98
31.71
31.54
29.86
29.47
28.54
26.62
25.66
22.52
21.71
21.71
14.05
13.97
COOH
α
β
H
H
H
O
Me
fl (ppm)

12. References

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