Supporting Information
for
Photocatalytic Defluorocarboxylation Using Formate Salts as Both Reductant and Carbon Dioxide Source

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1. General information

All reactions were set up with glovebox and carried out using Schlenk tubes under a nitrogen atmosphere with dry solvents, unless otherwise noted. All commercially available compounds were purchased from J&K, Across, TCI or Adamas and used as received unless otherwise noted. N_2 (99.999% purity) was commercially available. HCOOK/Li/Na/Cs and $H^{13}COONa$ wree purchased from Sigma-Aldrich. Methylethiosalicylate (98% purity) was purchased from adamas. Na_2CO_3 (99% purity) was purchased from Acros. Anhydrous solvent (99.8% purity, with molecular sieves) was purchased from J&K. The photosensitizer 4DPAIPN and the substrates were synthesized according to the literature procedure. Visible light irradiation was performed with a 30 W LED Light at λir = 450 ± 10 nm) for photocatalytic reactions. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.2±0.03 mm using UV light as a visualizing agent and bromocresol green in EtOH as developing agents.

^1H, ^{13}C and ^{19}F NMR spectra were recorded on a Brüker Advance 400 spectrometer (^1H: 400 MHz, ^{13}C: 101 MHz, ^{19}F: 376 MHz). Chemical shifts (δ) for ^1H and ^{13}C NMR spectra are given in ppm relative to TMS. The residual solvent signals were used as references for ^1H and ^{13}C NMR spectra and the chemical shifts were converted to the TMS scale ($CDCl_3$: 7.26 ppm for ^1H NMR and 77.16 ppm for ^{13}C NMR. DMSO-d_6: 2.50 ppm for ^1H NMR and 39.52 ppm for ^{13}C NMR). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad.

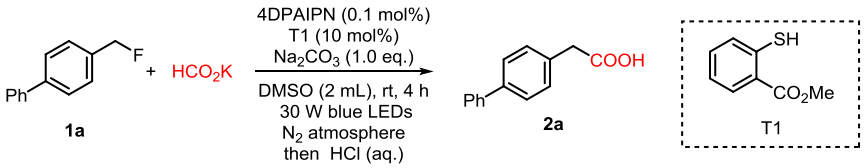
GC-MS was obtained using electron ionization (Agilent Technologies 7890B/GC-System and 5977A/MSD). High-resolution mass spectra (HRMS) were recorded on a Bruker Daltonics MicroTOF-Q. LRMS were obtained on a Thermo-LTQ. Fluorescence quenching experiments were measured on a RF-5301PC Spectrofluorophotometer. Visible light irradiation was performed with a 30 W LED Light at λ_{ir} = 450 ± 10 nm for photocatalytic reactions. TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF254), and visualization was

effected at 254 nm or stained with bromocresol green.

Figure S1: Blue LED photoreactor

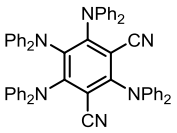
2. Reaction Optimization

Table S1. Reaction Conditions Optimization [a]

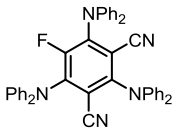


1a **2a** T1

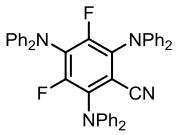
entry	variation from the above conditions	yield of 1b (%) [b]
1	none	87
2	no HCO_2K	trace
3	no 4DPAIPN	trace
4	no HAT	30
5	no Na_2CO_3	73
6	no LEDS	trace
7	3DPAFIPN instead of 4DPAIPN	40
8	3DPA2FBN instead of 4DPAIPN	22
9	4CzIPN instead of 4DPAIPN	20
10	$IrdF(CF_3)ppy_2(Phen)PF_6$ instead of 4DPAIPN	15
11	$HCO_2Li/Na/Cs$ instead of HCO_2K	82/77/70
12	NaOH/KOH instead of Na_2CO_3	65/63
13	Et_3N/pyridine/DMAP/Morpholine instead of HCO_2K	73/47/67/28
14	$Li_2CO_3/K_2CO_3/Cs_2CO_3$ instead of Na_2CO_3	73/75/80
15	0.5/1.5 eq. Na_2CO_3 instead of 1.0 eq. Na_2CO3	77/74
16	Et_3SiH, PMHS and $PhMe_2SiH$ instead of T1	24/24/27
17	CySH instead of T1	38
18	4-methooxybenzenethiol instead of T1	65
19	methyl thioglycolate instead of T1	48
20	5 mol% T1 instead of 10 mol% T1	79
21	under O_2 atmosphere	76
22	4-(chloromethyl)-1,1'-biphenyl instead of **1a**	76
23	4-(bromomethyl)-1,1'-biphenyl instead of **1a**	42
24	NMP instead of DMSO	40
25	DMF instead of DMSO	38
26	CH_3CN instead of DMSO	trace



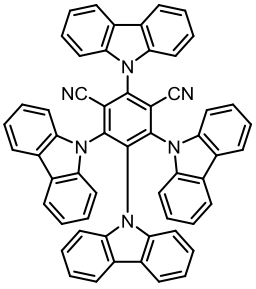
4DPAIPN



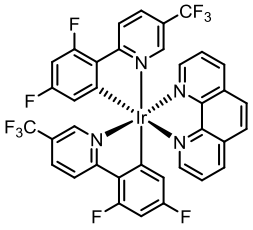
3DPAFIPN



3DPA2FBN



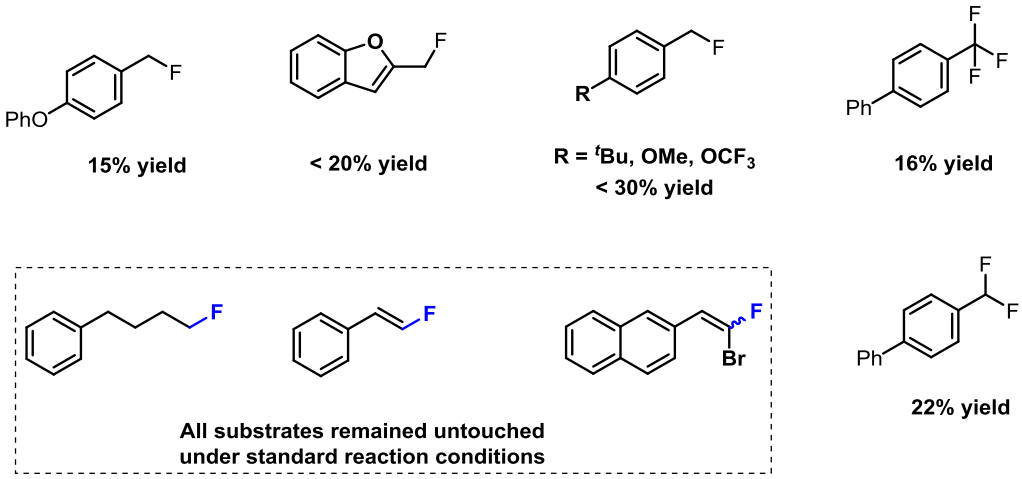
4CzIPN



$IrdF(CF_3)ppy_2(Phen)PF_6$

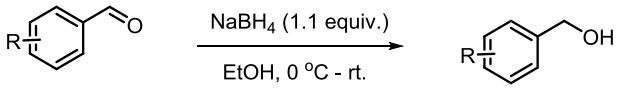
[a] Reaction conditions: 1a (0.2 mmol), 1 atm of N_2, HCO_2K (0.24 mmol), 4DPAIPN (0.1 mol%), T1 (10.0 mol%), Na_2CO_3 (0.2 mmol), DMSO (2 mL), irradiation with 30 W blue LEDs at 25 ºC for 4 h. [b] Isolated yields. 4DPAIPN = 2,4,5,6-tetrakis(diphenylamino)isophthalonitrile. N.D. = not detected. DMSO = dimethyl sulfoxide. NMP = N-methyl-2-pyrrolidone, DMF = N,N-dimeth ylformamide, CySH = cyclohexyl mercaptan·

Table S2. Unsuccessful examples [a]

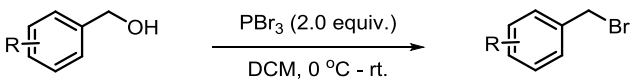


3. Synthesis of Substrates

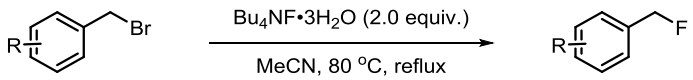
General procedure A for benzylic fluorides (**1a-1t**, **1aa-1ab**)[1-3]:



To a stirred solution of the benzaldehyde (1 equiv.) in ethanol (0.45 M) at 0 ℃ was added sodium borohydride (1.1 equiv.). The resulting solution was stirred for 4 hours at room temperature and then quenched with water. After partial evaporation of the solvents under reduced pressure, the resulting aqueous phase is extracted with EtOAc (4 x 10 mL). The combined organic extracts are dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified by flash chromatography using the appropriate gradient of petroleum ether and EA to afford the desired pure product.

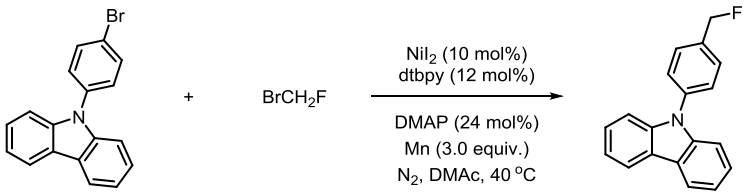


Tribromophosphine (1.2 equiv.) was added dropwise to a stirred solution of benzylic alcohols in freshly distilled CH_2Cl_2 at 0 ^oC. The reaction mixture was stirred for 12 h. Ice water was added to quench the reaction. The solvent was removed in vacuo. The residue was washed with water, and extracted with EtOAc (4 x 10 mL). The combined organic phase was washed with saturated $NaHCO_3$ solution, water and brine, dried (Na_2SO_4), filtered, and evaporated to give benzylic bromides.



To a stirred of the benzylic bromide (1.0 equiv.) in anhydrous CH_3CN (0.45 M) was added tetrabutylammonium trifluoride trihydrate (TBAF·$3H_2O$; 2.0 equiv.). The reaction mixture was stirred and refluxed for 5-18 h at 85 ℃. The reaction was quenched with water, extracted with Et_2O (3 x 10 mL), and washed with brine. The crude was dried with $NaSO_4$, filtered and evaporated under reduced pressure. The residue was purified by silica gel flash column chromatography to afford the desired benzyl fluoride.

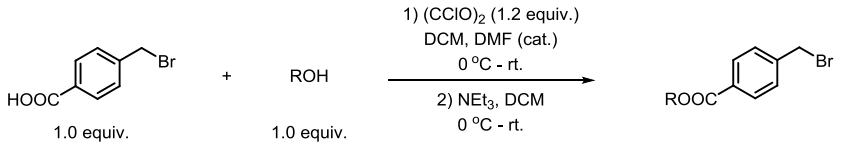
General procedure B for benzylic fluorides (**1u**-**1x**)[4]:



To a 25 mL of Schlenk tube were added NiI_2 (10 mol%), dtbpy (4,4'-Di-tert-butyl-2,2'-bipyridine, 12 mol%), DMAP (4-Dimethylaminopyridine, 24 mol%) and manganese powder (200 mesh, 3.0 equiv). The vessel was evacuated and backfilled with N_2 (repeated for 3 times), after that, aryl bromine (2 mmol, 1.0 equiv) and dry DMAc (1 mL) were added. The solution then premixed for 10 s before $BrCH_2F$ (1.0 M solution in DMAc, 2.5 equiv) was added. The tube was sealed with a Teflon lined cap and heated in a preheated oil bath at 40 ℃ for 24 h. The reaction mixture was then cooled to room temperature, diluted with EtOAc (~20 mL) and

filtered through a pad of celite. The filtrate was added brine (30 mL) and extracted with EtOAc (2×15 mL), the combined organic layer was dried over Na_2SO_4, filtrated and concentrated under vacuum. The residue was then purified by flash column chromatography to give benzyl fluoride substrate as a colorless solid

General procedure C for benzylic fluorides (**1y**-**1z**)[5]:

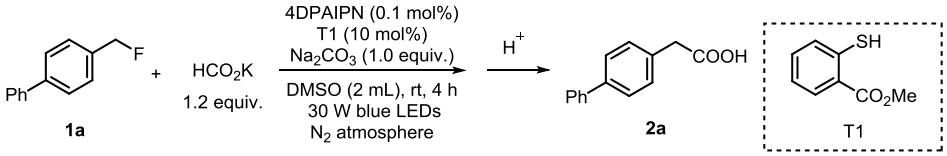


To a stirred solution of 4-bromomethyl benzoic acid (10 mmol, 1.0 eq.) in DCM (20 mL), DMF (cat.), and subsequently $(CClO)_2$ (13 mmol, 1.3 eq.) were added at 0 ℃. The reaction mixture was stirred for 1 h at rt under N_2 atmosphere, and then the solvent was evaporated under reduced pressure to give the carbonyl chloride.

Alcohol (10 mmol, 1.0 eq.) and triethylamine (TEA, 11 mmol, 1.1 equiv) were dissolved in dry dichloromethane (DCM, 10 mL) under 0 ℃ ice bath under N_2 atmosphere. Then carbonyl chloride in 5 mL DCM was added dropwise using a syringe followed by 2 h stirring at 0 ℃. After continuous stirring for 20 h at room temperature, the solvent was concentrated by evaporation, and the crude product was purified by column chromatography with petroleum ether/ethyl acetate as eluent.

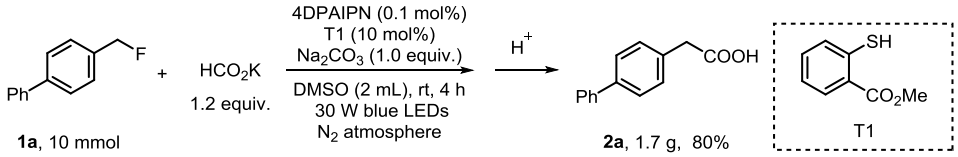
4. Experimental procedures for defluorocarboxylation of benzylic fluorides

General procedure D for Defluorocarboxylation of benzylic fluorides with HCOOK



A flame-dried Schlenk tube (10 mL) containing a stirring bar was charged with 4DPAIPN (0.16 mg, 0.0002 mmol, 0.1 mol%) and benzyl fluoride substrate **1a** (37.2 mg, 0.2 mmol, 1.0 equiv for non-liquid substrates). The reaction tube was transferred to the glovebox and charged with HCO_2K (20.2 mg, 0.24 mmol, 1.2 equiv) and Na_2CO_3 (21.2 mg, 0.2 mmol, 1.0 equiv). After sealing with a Teflon plug, the reaction tube was moved out of the glovebox and the tube was then evacuated and back-filled with nitrogen atmosphere (N_2) for 3 times. Subsequently, anhydrous DMSO (2 mL) was added followed by benzyl fluoride substrate (0.2 mmol, 1.0 equiv for liquid substrates) and methyl thiosalicylate T_1 (2.75 μL, 0.02 mmol, 10 mol%) via syringe under N_2. Once added, the Schlenk tube was sealed at atmospheric pressure of N_2 (1 atm). The reaction was stirred vigorously (1500 r/min) and irradiated with a 30 W blue LED lamp (1-2 cm away, with a cooling fan to keep the reaction temperature at 25~30 ℃) for the indicated time. The resulting mixture was quenched by 2 mL 2N HCl and diluted with 2 mL EtOAc, then stirred for 3 min. The reaction mixture was extracted by EtOAc with four times and the combined organic phases were concentrated in vacuo. The residue was purified by a silica gel flash column chromatography (PE:EA = 10:1, PE:EA = 5:1 ~3:1 +1% AcOH) to give the pure desired product with bromocresol green as chromogenic agent.

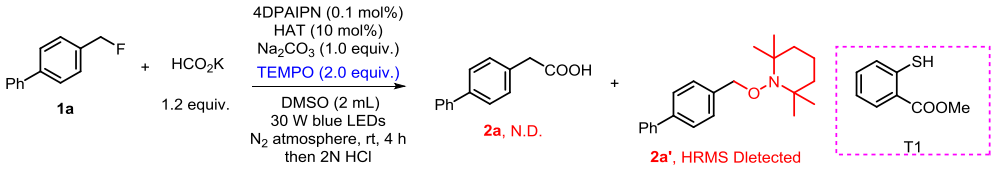
General procedure E for Defluorocarboxylation of benzylic fluorides for gram-scale synthesis of 2a



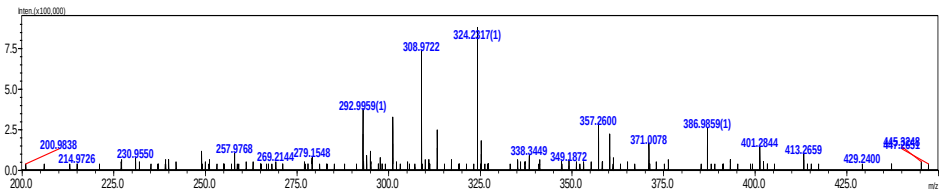
An oven‐dried Schlenk tube (250 mL) containing a stirring bar was charged with benzyl fluoride **1a** (1.86 g, 10.0 mmol, 1.0 equiv.) and 4DPAIPN (8.0 mg, 0.01 mmol, 0.1 mol%). The reaction tube was transferred to the glovebox and charged with HCO_2K (1.0 g, 12.0 mmol, 1.2 equiv) and Na_2CO_3 (1.05 g, 10.0 mmol, 1.0 equiv). After sealing with a Teflon plug, the reaction tube was moved out of the glovebox and the tube was then evacuated and back-filled with nitrogen atmosphere (N_2) for 3 times. Subsequently, anhydrous DMSO (100 mL) was added followed by methyl thiosalicylate T1 (137.5 μL, 1 mmol, 10 mol%) via syringe under N_2 atmosphere. Once added, the Schlenk tube was sealed at atmospheric pressure of N_2 (1 atm). The reaction was stirred vigorously (1500 r/min) and irradiated with a 30 W blue LED lamp (1-2 cm away, with a cooling fan to keep the reaction temperature at 25~30 ℃) for the indicated time. The resulting mixture was quenched by 50 mL 2N HCl and diluted with 50 mL EtOAc, then stirred for 3 min. The reaction mixture was extracted by EtOAc with four times and the combined organic phases were concentrated in vacuo. The residue was purified by a silica gel flash column chromatography (PE:EA = 10:1, PE:EA = 5:1 ~3:1 +1% AcOH) to give the pure desired product **2a** (1.7 g, white solid).

5. Mechanistic Studies

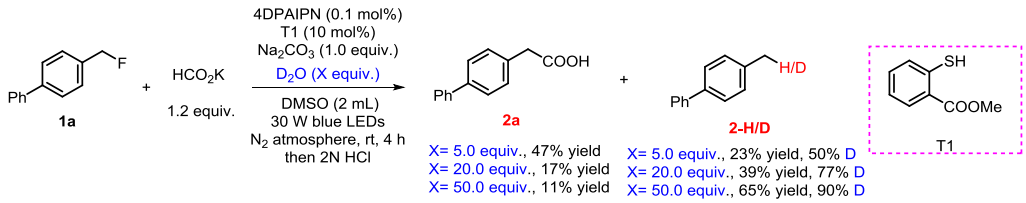
(a) Radical trapping with TEMPO



Following the general procedure D, an oven‐dried Schlenk tube (10 mL) containing a stirring bar was charged with benzyl fluoride **1a** (37.2 mg, 0.2 mmol, 1.0 equiv.), 4DPAIPN (0.16 mg, 0.0002 nmol, 0.1 mol%), TEMPO (62.5 mg, 0.4 mmol, 2.0 equiv.) and transferred to glovebox to add HCOOK (20.2 mg, 0.24 mmol, 1.2 equiv.) and Na_2CO_3 (21.2 mg, 0.2 mmol, 1.0 equiv). The tube was then evacuated and back‐filled with N_2 for 3 times after transferred out of the glovebox. Subsequently, anhydrous DMSO (2 mL) was added followed by methyl thiosalicylate T1 (2.75 μL, 0.02 mmol, 10 mol%) via syringe under N_2 atmosphere. The reaction was stirred in water bath and irradiated with the 30 W blue LED lamp (1 cm away from the reaction tube, with cooling fan to keep the reaction temperature at 25~30 ℃) for 4 h. The reaction mixture was quenched by 2 mL H_2O, diluted with 2 mL EtOAc, then stirred for 3 min. The reaction mixture was extracted by EtOAc for four times and the combined organic phase was concentrated in reduced presure. The obtained residue was analyzed by HRMS and confirmed the formation of **2a'**. HRMS (ESI‐) $[M+H]^+$ calculated m/z for $[C_{22}H_{30}NO]^+$: 324.2322, found: 324.2317. Then, the aqueous phase was acidified with 2 N HCl, added 2 mL EtOAc, and stirred for 3 min. The resulting organic phase was analyzed with TLC and ESI‐MS, compound **2a** was not detected.



(b) Deuterium-labeling experiment



Following the general procedure D, D_2O (18 μL, 1 mmol, 5 equiv) was added via syringe after the addition of T1 under N_2. The reaction afforded **2-H/D** as a white solid in 47% yield and 50% deuterium incorporation.

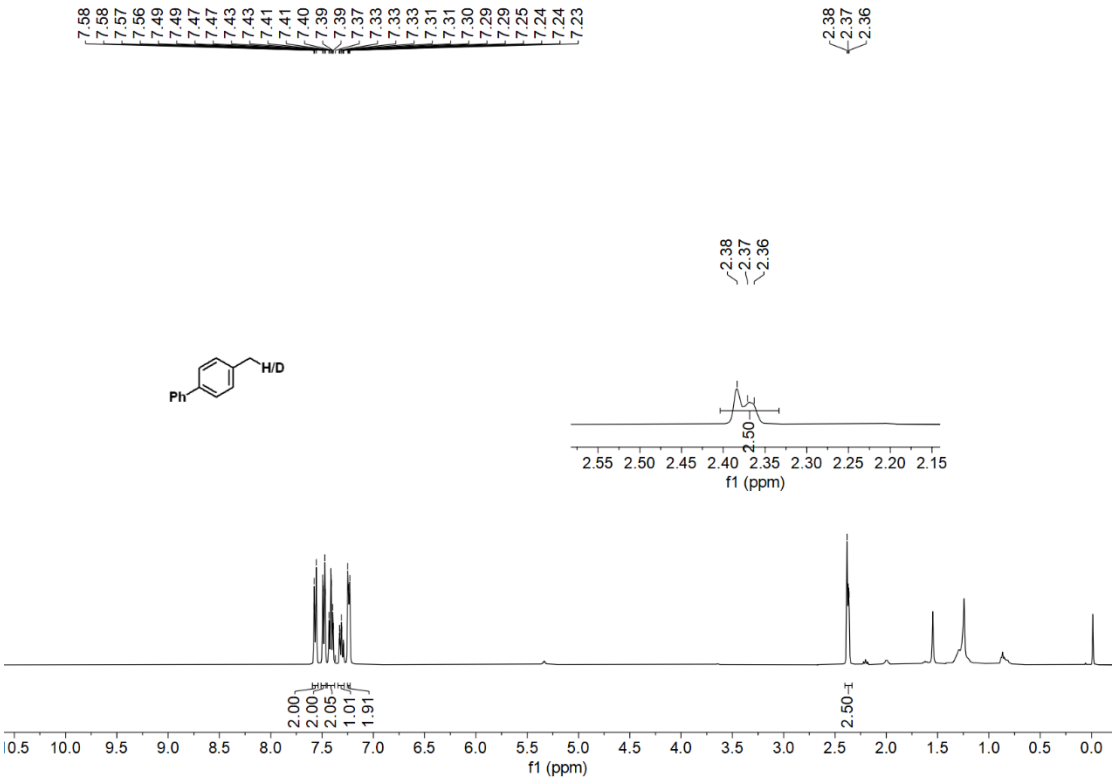


Figure S2. ^{1}H NMR Spectra of compound 2-H/D

Following the general procedure D, D_2O (72 μL, 4 mmol, 20 equiv) was added via syringe after the addition of T1 under N_2. The reaction afforded **2-H/D** as a white solid in 17% yield and 77% deuterium incorporation.

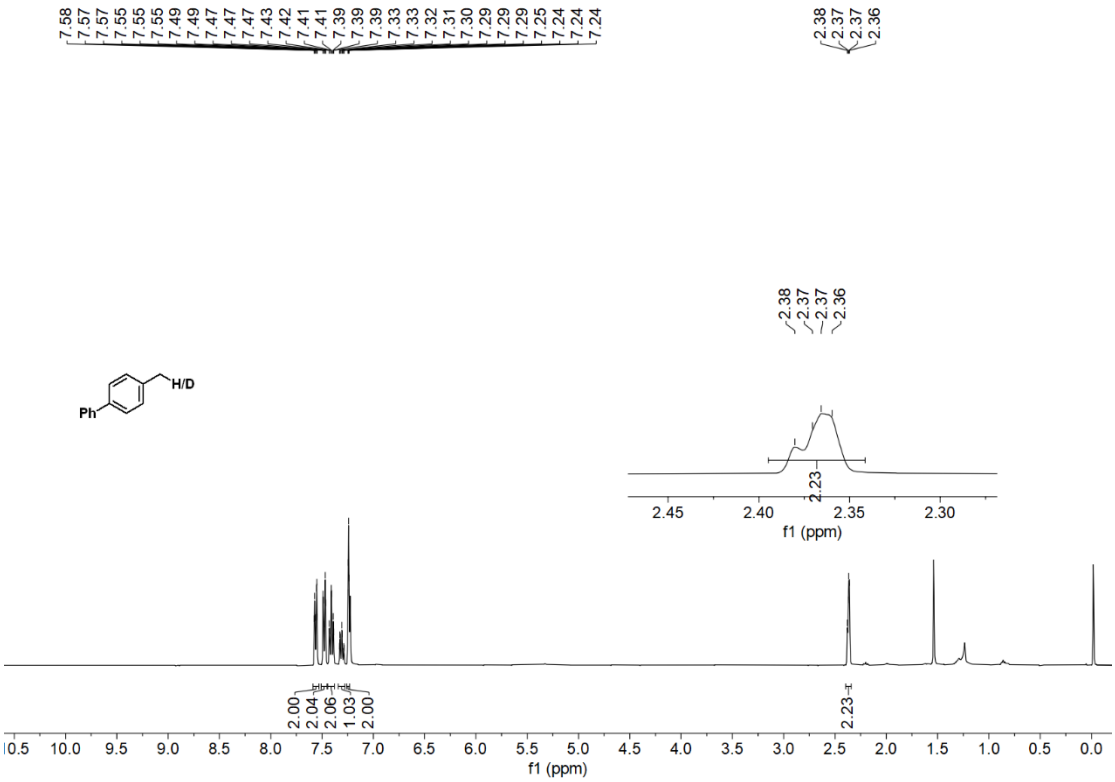


Figure S3. ^{1}H NMR Spectra of compound 2-H/D

Following the general procedure D, D_2O (181 μL, 10 mmol, 50 equiv) was added via syringe after the addition of T1 under N_2. The reaction afforded **2-H/D** as a white solid in 11% yield and 90% deuterium incorporation.

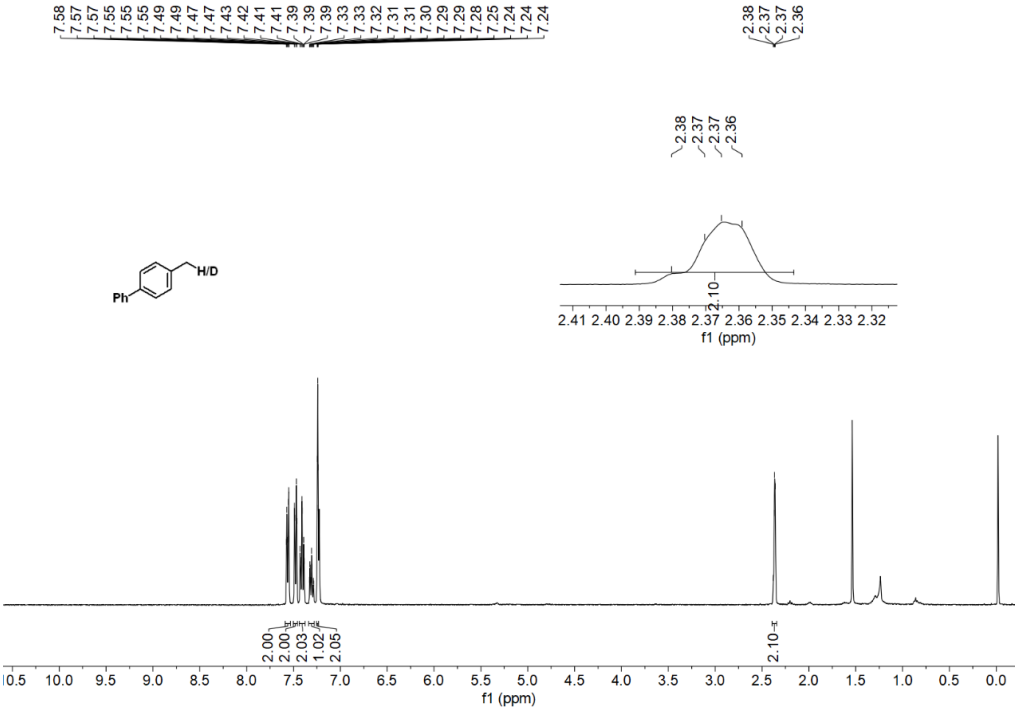
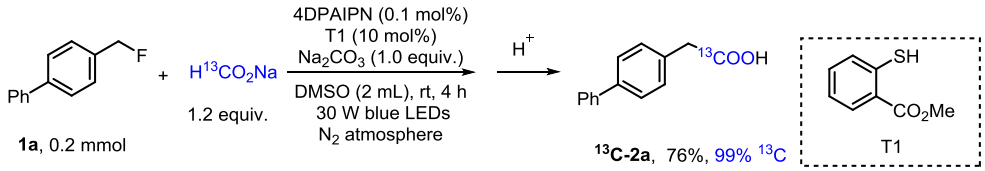
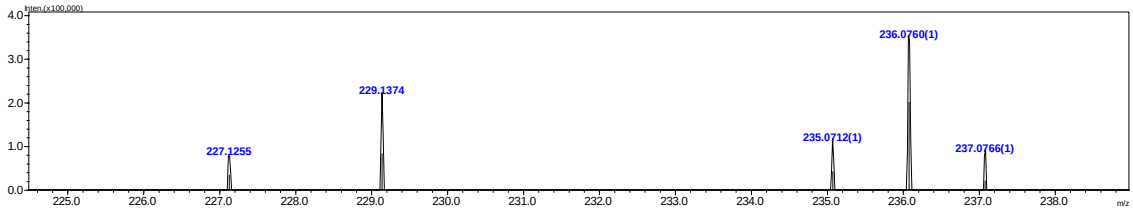


Figure S4. ^{1}H NMR Spectra of compound 2-H/D

(c) ^{13}C-Labeling Experiments



A flame-dried Schlenk tube (10 mL) containing a stirring bar was charged with benzyl fluoride substrate **1a** (37.2 mg, 0.2 mmol, 1.0 equiv) and 4DPAIPN (0.16 mg, 0.0002 mmol, 0.1 mol%) and The reaction tube was transferred to the glovebox and charged with $H^{13}CO_2Na$ (16.5 mg, 0.24 mmol, 1.2 equiv) and Na_2CO_3 (21.2 mg, 0.2 mmol, 1.0 equiv). After sealing with a Teflon plug, the reaction tube was moved out of the glovebox and the tube was then evacuated and back-filled with nitrogen atmosphere (N_2) for 3 times. Subsequently, anhydrous DMSO (2 mL) was added followed by methyl thiosalicylate T1 (2.75 μL, 0.02 mmol, 10 mol%) via syringe under N_2. Once added, the Schlenk tube was sealed at atmospheric pressure of N_2 (1 atm). The reaction was stirred vigorously (1500 r/min) and irradiated with a 30 W blue LED lamp (1-2 cm away, with a cooling fan to keep the reaction temperature at 25~30 ℃) for the indicated time. The resulting mixture was quenched by 2 mL 2N HCl and diluted with 2 mL EtOAc, then stirred for 3 min. The reaction mixture was extracted by EtOAc with four times and the combined organic phases were concentrated in vacuo. The residue was purified by a silica gel flash column chromatography (PE:EA = 10:1, PE:EA = 5:1 ~3:1 +1% AcOH) to give the pure desired product with bromocresol green as chromogenic agent.



m/z	Intensity	Theo. Mass	Composition
n.d	_	235.0730	$C_{14}H_{12}NaO_2^+$
236.0760	202086	236.0763	$C_{13}{}^{13}CH_{12}NaO_2^+$

ESI+

[MS Spectrum]

# of Peaks	34
Raw Spectrum	[0.163],(scan:[29])
Background Spectrum	No Background Spectrum
Base Peak	m/z 236.0760 (Inten: 202,086)

m/z	Abs. Inten.	Rel. Inten.
205.0674	47680	23.59
215.1216	9856	4.88
227.1255	34496	17.07
229.1374	83904	41.52
235.0712	42752	21.16
236.0760	**202086**	**100**
237.0766	21376	10.58
239.1639	28032	13.87
239.1892	13184	6.52
257.0508	39552	19.57
258.0532	146787	72.64
205.0674	47680	23.59

(d) Stern-Volmer emission quenching

Fluorescence quenching experiments were measured on a RF-5301PC Spectrofluorophotometer with a 3 mL quartz cuvette with a cap. Anhydrous DMSO was degassed by N_2 bubbling for 2 hours before using. 4DPAIPN was irradiated at 430 nm and the emission intensity at about 528 nm was observed. In a typical experiment, the emission spectrum of a 5.0 $x10^{-6}$ M solution of 4DPAIPN in DMSO was collected.

1a: A stock solution of **1a** (1.0 x 10^{-3}M) was prepared. Then, different amounts of this stock solution were added to 3.0 mL of 4DPAIPN in DMSO (5.0 $x10^{-6}$ M).

Luminescence Data: **Stern-Volmer Plot with 1a:**

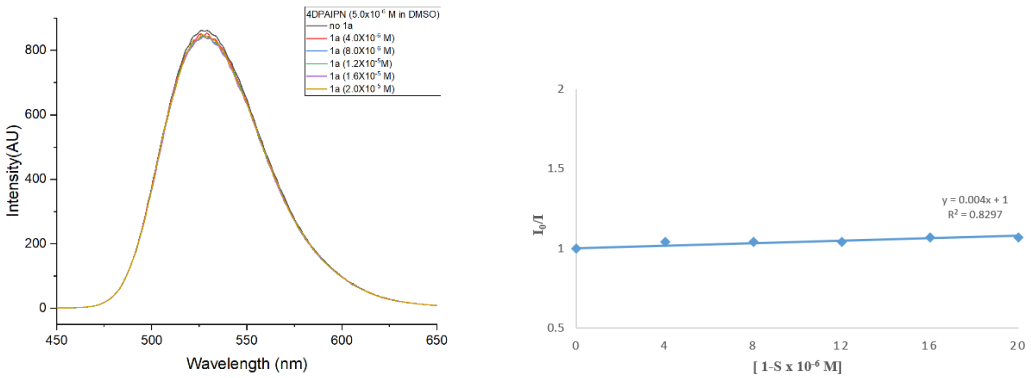


Figure S5: Stern –Volmer fluorescence quenching experiments with **1a**.

HCO_2K: A stock solution of **HCO_2K** (1.0 x10^{-3} M) was prepared. Then, different amounts of this stock solution were added to 3.0 mL of 4DPAIPN in DMSO (5.0 x10^{-6} M).

Luminescence Data: **Stern-Volmer Plot with HCO_2K:**

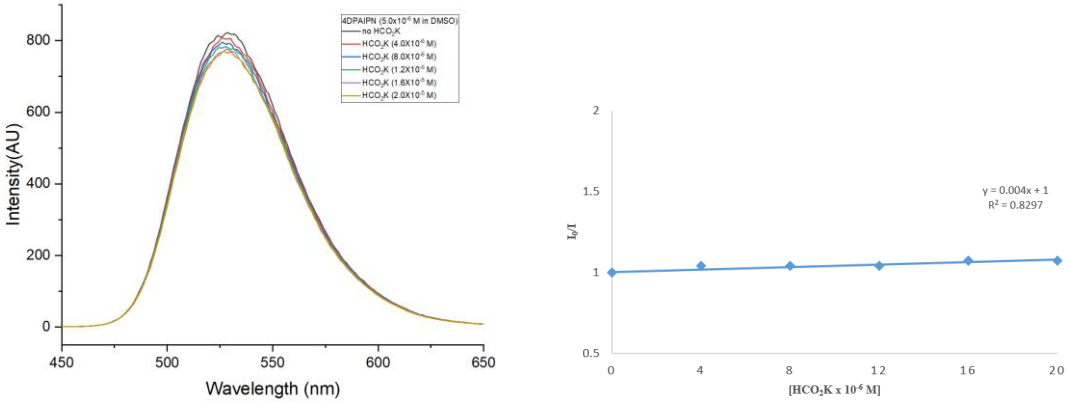


Figure S6: Stern –Volmer fluorescence quenching experiments with **HCO_2K**.

Na_2CO_3: A stock solution of **Na_2CO_3** (1.0 x10^{-3} M) was prepared. Then, different amounts of this stock solution were added to 3.0 mL of 4DPAIPN in DMSO (5.0 x10^{-6} M).

Luminescence Data: **Stern-Volmer Plot with Na_2CO_3:**

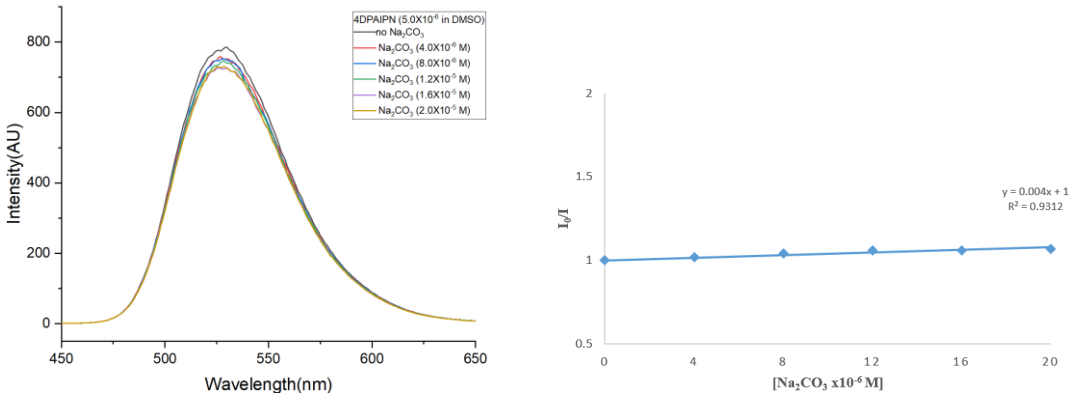


Figure S7: Stern –Volmer fluorescence quenching experiments with **Na_2CO_3**.

T_1 (methyl 2-mercaptobenzoate): A stock solution of **T_1** (1.0 x10^{-3} M) was prepared. Then, different amounts of this stock solution were added to 3.0 mL of 4DPAIPN in DMSO (5.0 x10^{-6} M).

Luminescence Data: **Stern-Volmer Plot with T_1:**

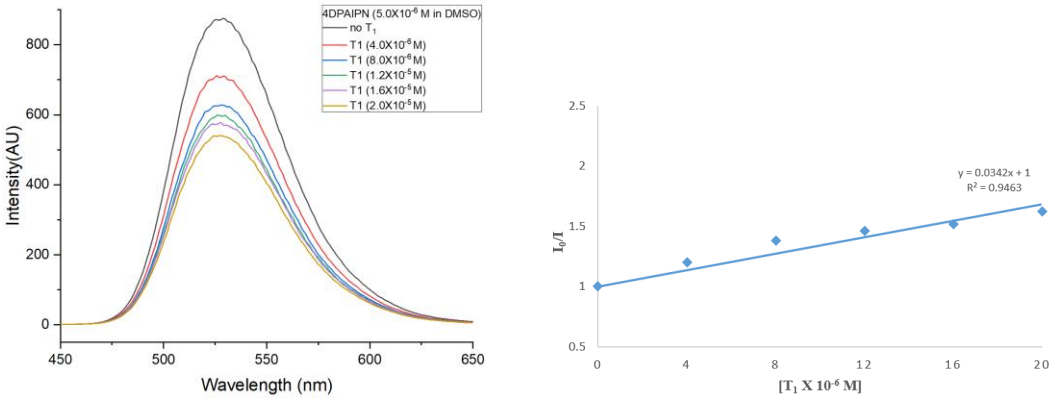


Figure S8: Stern –Volmer fluorescence quenching experiments with **T_1**.

T_1Na (sodium methyl 2-mercaptobenzoate): A stock solution of **T_1Na**: (1.0 x10^{-3} M) was prepared. Then, different amounts of this stock solution were added to 3.0 mL of 4DPAIPN in DMSO (5.0 x10^{-6} M).

Luminescence Data: **Stern-Volmer Plot with T_1Na:**

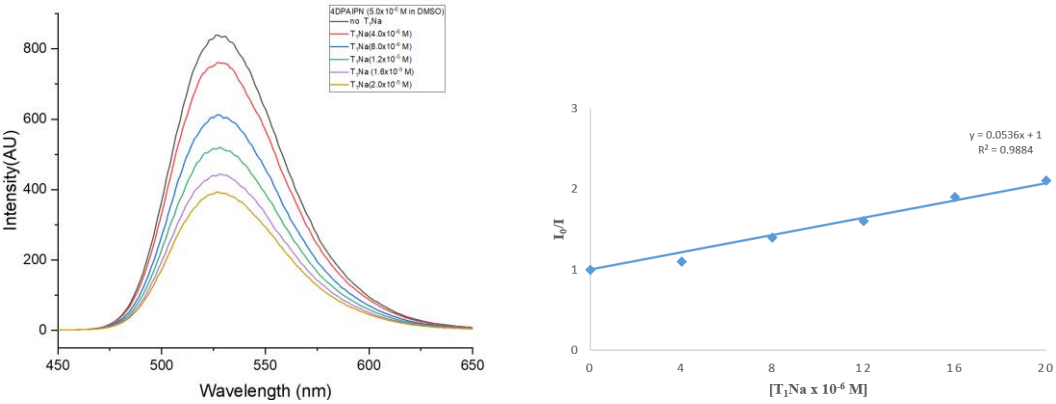
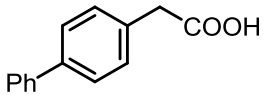


Figure S9: Stern –Volmer fluorescence quenching experiments with **T_1Na**.

6. Characterization data of products

2-([1,1'-biphenyl]-4-yl)acetic acid (2a)



Following General Procedure D, 4-(fluoromethyl)-1,1'-biphenyl (37.2 mg, 0.2 mmol), HCO_2K (20.2 mg, 1.2 eq.), Na_2CO_3 (21.2 mg, 1.0 eq.), 4DPAIPN (0.16 mg, 0.1 mol%), methyl thiosalicylate (2.75 μL, 10 mol%), DMSO (2 mL) were used. The reaction was stirred vigorously (1500 r/min) and irradiated with a 30 W blue LED lamp (1 cm away, with cooling fan to keep the reaction temperature at 25~30 ℃) for 4 h. After completion of the reaction, the reaction mixture was quenched by 2 mL 2N HCl. The reaction mixture was extracted by EtOAc (4 x 10 mL) and the combined organic phases were dried with concentrated in vacuo. The residue was purified by a silica gel flash column chromatography (silica gel, PE:EA = 10:1, PE:EA = 5:1 ~3:1 +1% AcOH) to give the title product (colorless solid., 37 mg, 87% yield.). The compound data was in agreement with the literature (Ref. *Chem*, **2021**, *7*, 3099-3113).

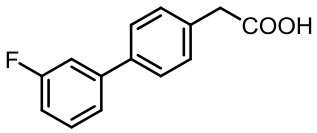
R_f = 0.3 (PE/EA = 1:1).

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.68 – 7.63 (d, 2H), 7.63 – 7.59 (d, 2H), 7.46 (t, *J* = 8.4, 6.9 Hz, 2H), 7.39 – 7.32 (t, 3H), 3.62 (s, 2H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 173.11, 140.41, 138.98, 134.74, 130.42, 129.36, 127.77, 127.02, 127.00, 40.74.

ESI-MS (m/z) calcd for $C_{14}H_{12}O_2$, [M-H^+]: 211.08, found: 210.87

2-(3'-fluoro-[1,1'-biphenyl]-4-yl)acetic acid (2b)



Following General Procedure D, 3-fluoro-4'-(fluoromethyl)-1,1'-biphenyl (40.8 mg, 0.2 mmol), HCO_2K (20.2 mg, 1.2 eq.), Na_2CO_3 (21.2 mg, 1.0 eq.), 4DPAIPN (0.16 mg, 0.1 mol%), methyl thiosalicylate (2.75 μL, 10 mol%), DMSO (2 mL) were used. The reaction was stirred vigorously (1500 r/min) and irradiated with a 30 W blue LED lamp (1 cm away, with cooling fan to keep the

reaction temperature at 25~30 ℃) for 4 h. After completion of the reaction, the reaction mixture was quenched by 2 mL 2N HCl. The reaction mixture was extracted by EtOAc (4 x 10 mL) and the combined organic phases were dried with concentrated in vacuo. The residue was purified by a silica gel flash column chromatography (silica gel, PE:EA = 10:1, PE:EA = 5:1 ~3:1 +1% AcOH) to give the title product (colorless solid, 37.4 mg, 82% yield.). The compound data was in agreement with the literature (Ref. *Tetrahedron Lett*, **1996**, 3*7*, 5491-5494).

R_f = 0.3 (PE/EA = 1:1).

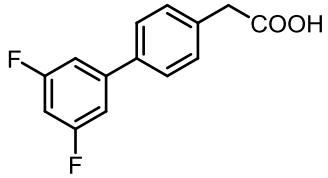
^{1}H NMR (400 MHz, DMSO-d_6) δ 12.35 (brs, 1H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.56 – 7.43 (m, 3H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.18 (ddt, *J* = 9.5, 4.4, 2.5 Hz, 1H), 3.62 (s, 2H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 173.10, 163.16 (d, J = 244.4), 142.87 (d, *J* = 7.1 Hz), 137.51 (d, *J* = 2.0 Hz), 135.51, 131.27 (d, *J* = 8.1 Hz), 130.50, 127.11, 123.05 (d, *J* = 3.0 Hz), 114.45 (d, *J* = 21.2 Hz), 113.68 (d, *J* = 22.2 Hz), 40.77.

^{19}F NMR (376 MHz, DMSO-d_6) δ -112.89.

ESI-MS (m/z) calcd for $C_{14}H_{11}FO_2$, [M-H$^+$]: 229.07, found: 228.78.

2-(3',5'-difluoro-[1,1'-biphenyl]-4-yl)acetic acid (2c)



Following General Procedure D, 3,5-difluoro-4'-(fluoromethyl)-1,1'-biphenyl (44.4 mg, 0.2 mmol), HCO_2K (20.2 mg, 1.2 eq.), Na_2CO_3 (21.2 mg, 1.0 eq.), 4DPAIPN (0.16 mg, 0.1 mol%), methyl thiosalicylate (2.75 μL, 10 mol%), DMSO (2 mL) were used. The reaction mixture was stirred at room temperature for 4 h at 1500 rpm. After completion of the reaction, the reaction mixture was quenched by 2 mL 2N HCl. The reaction mixture was extracted by EtOAc (4 x 10 mL) and the combined organic phases were dried with concentrated in vacuo. The residue was purified by a silica gel flash column chromatography (silica gel, PE:EA = 10:1, PE:EA = 5:1 ~3:1 +1% AcOH) to give the title product (colorless solid, 45.7 mg, 92%

yield.). The compound data was in agreement with the literature (Ref. *J. Chem. Res.*, **2019**, *43*, 50-52).

R_f = 0.3 (PE/EA = 1:1).

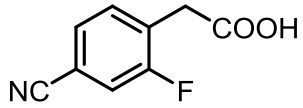
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 7.9 Hz, 2H), 7.11 – 7.02 (m, 2H), 6.82 – 6.70 (m, 1H), 3.69 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.73, 163.40 (d, *J* = 248.5 Hz), 143.99 (t, *J* = 9.6 Hz), 138.05 (t, *J* = 2.5 Hz), 133.58, 130.10, 127.28, 109.92 (m, *J* = 19.2 Hz), 102.61 (t, *J* = 25.4 Hz), 40.67.

^{19}F NMR (376 MHz, CDCl3) δ -109.64.

ESI-MS (m/z) calcd for $C_{14}H_{10}F_2O_2$, $[M\text{-}H^+]$: 247.06, found: 246.73.

2-(4-cyano-2-fluorophenyl)acetic acid (2d)



Following General Procedure D, 3-fluoro-4-(fluoromethyl)benzonitrile (30.6 mg, 0.2 mmol), HCO_2K (20.2 mg, 1.2 eq.), Na_2CO_3 (21.2 mg, 1.0 eq.), 4DPAIPN (0.16 mg, 0.1 mol%), methyl thiosalicylate (2.75 μL, 10 mol%), DMSO (2 mL) were used. The reaction mixture was stirred at room temperature for 4 h at 1500 rpm. After completion of the reaction, the reaction mixture was quenched by 2 mL 2N HCl. The reaction mixture was extracted by EtOAc (4 x 10 mL) and the combined organic phases were dried with concentrated in vacuo. The residue was purified by a silica gel flash column chromatography (silica gel, PE:EA = 10:1, PE:EA = 5:1 ~3:1 +1% AcOH) to give the title product (colorless solid, 32.0 mg, 89% yield.). The compound data was in agreement with the literature (Ref. *Chem*, **2021**, *7*, 3099-3113).

R_f = 0.1 (PE/EA = 1:1)

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.68 (s, 1H), 7.82 (dd, *J* = 9.8, 1.6 Hz, 1H), 7.67 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 3.76 (s, 2H).

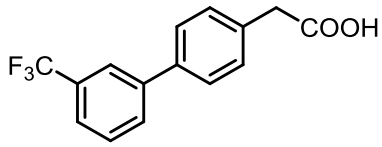
^{13}C NMR (101 MHz, DMSO-d_6) δ 171.36, 160.70 (J = 248.5 Hz), 133.88 (d, *J* = 5.1 Hz), 129.37 (d, *J* = 16.2 Hz), 129.06 (d, *J* = 4.0 Hz), 119.42 (d, *J* = 26.3 Hz), 118.18

(d, *J* = 2.0 Hz), 111.82 (d, *J* = 10.1 Hz), 34.83.

^{19}F NMR (376 MHz, DMSO-d_6) δ -114.26.

ESI-MS (m/z) calcd for $C_9H_6FNO_2$, [M-H^+]: 178.03, found: 177.58.

2-(3'-(trifluoromethyl)-[1,1'-biphenyl]-4-yl)acetic acid (2e)



Following General Procedure D, 4'-(fluoromethyl)-3-(trifluoromethyl)-1,1'-biphenyl (50.8 mg, 0.2 mmol), HCO_2K (20.2 mg, 1.2 eq.), Na_2CO_3 (21.2 mg, 1.0 eq.), 4DPAIPN (0.16 mg, 0.1 mol%), methyl thiosalicylate (2.75 μL, 10 mol%), DMSO (2 mL) were used. The reaction mixture was stirred at room temperature for 4 h at 1500 rpm. After completion of the reaction, the reaction mixture was quenched by 2 mL 2N HCl. The reaction mixture was extracted by EtOAc (4 x 10 mL) and the combined organic phases were dried with concentrated in vacuo. The residue was purified by a silica gel flash column chromatography (silica gel, PE:EA = 10:1, PE:EA = 5:1 ~3:1 +1% AcOH) to give the title product (colorless solid, 48.9 mg, 87% yield.). The compound data was in agreement with the literature (Ref. *Bioorg. Med. Chem.*, **2006**, *14*, 6640-6658).

R_f = 0.4 (PE/EA = 1:1)

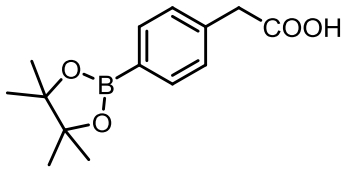
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 1.9 Hz, 1H), 7.81 – 7.73 (m, 1H), 7.67 – 7.55 (m, 4H), 7.43 (d, *J* = 8.1 Hz, 2H), 3.76 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.82, 141.49, 138.93, 133.15, 131.54 (q, *J* = 33.3 Hz),130.37, 130.10, 129.29, 127.48, 124.05 (q, *J* = 3.8 Hz), 123.89 (q, *J* = 3.8 Hz), 121.48 (q, *J* = 273.7 Hz), 40.69.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.59.

ESI-MS (m/z) calcd for $C_{15}H_{11}F_3O_2$, [M-H^+]: 279.06, found: 278.76.

2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acetic acid (2f)



Following General Procedure D, 2-(4-(fluoromethyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dio xaborolane (47.2 mg, 0.2 mmol), HCO_2K (20.2 mg, 1.2 eq.), Na_2CO_3 (21.2 mg, 1.0 eq.), 4DPAIPN (0.16 mg, 0.1 mol%), methyl thiosalicylate (2.75 μL, 10 mol%), DMSO (2 mL) were used. The reaction mixture was stirred at room temperature for 4 h at 1500 rpm. After completion of the reaction, the reaction mixture was quenched by 2 mL 2N HCl. The reaction mixture was extracted by EtOAc (4 x 10 mL) and the combined organic phases were dried with concentrated in vacuo. The residue was purified by a silica gel flash column chromatography (silica gel, PE:EA = 10:1, PE:EA = 5:1 ~3:1 +1% AcOH) to give the title product (colorless solid, 35.5 mg, 68% yield.). The compound data was in agreement with the literature (Ref. *Bioorg. Med. Chem.*, **2015**, *25*, 3436-3441).

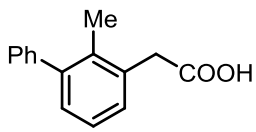
R_f = 0.3 (PE/EA = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 7.5 Hz,2H), 7.27 (d, J = 7.6 Hz, 2H), 3.64 (s, 2H), 1.31 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.80, 136.41, 135.09, 128.75, 83.81, 41.14, 24.80 (The **^{13}C NMR** resonance at 131.25 (aryl carbon signal bonded to Bpin group) has very low intensity due to ^{11}B quadrupolar broadening).

ESI-MS (m/z) calcd for $C_{14}H_{19}BO_4$, $[M-H^+]$: 261.13, found: 260.97.

2-(2-methyl-[1,1'-biphenyl]-3-yl)acetic acid (2g)



Following General Procedure D, 3-(fluoromethyl)-2-methyl-1,1'-biphenyl (40.0 mg, 0.2 mmol), HCO_2K (20.2 mg, 1.2 eq.), Na_2CO_3 (21.2 mg, 1.0 eq.), 4DPAIPN (3.2 mg, 2 mol%), methyl thiosalicylate (2.75 μL, 10 mol%), DMSO (2 mL) were used. The reaction mixture was stirred at room temperature for 96 h at 1500

rpm. After completion of the reaction, the reaction mixture was quenched by 2 mL 2N HCl. The reaction mixture was extracted by EtOAc (4 x 10 mL) and the combined organic phases were dried with concentrated in vacuo. The residue was purified by a silica gel flash column chromatography (silica gel, PE:EA = 10:1, PE:EA = 5:1 ~3:1 +1% AcOH) to give the title product (colorless solid, 20.0 mg, 45% yield.). The compound data was in agreement with the literature (Ref. *Chem*, **2021**, *7*, 3099-3113).

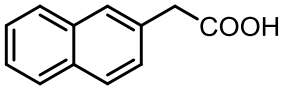
R_f = 0.4 (PE/EA = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.37 (m, 2H), 7.36 – 7.27 (m, 3H), 7.23 – 7.16 (m, 3H), 3.76 (s, 2H), 2.20 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.48, 143.01, 142.16, 134.55, 132.78, 129.61, 129.51, 129.39, 128.06, 126.83, 125.67, 39.58, 16.96.

ESI-MS (m/z) calcd for $C_{15}H_{14}O_2$, [M-H^+]: 225.09, found: 224.92.

2-(naphthalen-2-yl)acetic acid (2h)



Following General Procedure D, 2-(fluoromethyl)naphthalene (32.0 mg, 0.2 mmol), HCO_2K (20.2 mg, 1.2 eq.), Na_2CO_3 (21.2 mg, 1.0 eq.), 4DPAIPN (0.16 mg, 0.1 mol%), methyl thiosalicylate (2.75 μL, 10 mol%), DMSO (2 mL) were used. The reaction mixture was stirred at room temperature for 4 h at 1500 rpm. After completion of the reaction, the reaction mixture was quenched by 2 mL 2N HCl. The reaction mixture was extracted by EtOAc (4 x 10 mL) and the combined organic phases were dried with concentrated in vacuo. The residue was purified by a silica gel flash column chromatography (silica gel, PE:EA = 10:1, PE:EA = 5:1 ~3:1 +1% AcOH) to give the title product (colorless solid, 30.4 mg, 82% yield.). The compound data was in agreement with the literature (Ref. *Chem*, **2021**, *7*, 3099-3113).

R_f = 0.4 (PE/EA = 1:1).

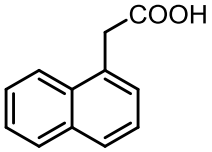
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (t, *J* = 8.3 Hz, 3H), 7.74 (s, 1H), 7.47 (td, *J* = 5.5,

4.7, 2.7 Hz, 2H), 7.41 (dd, *J* = 8.4, 1.8 Hz, 1H), 3.82 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.17, 133.36, 132.52, 130.67, 128.33, 128.17, 127.66, 127.65, 127.28, 126.23, 125.95, 41.08.

ESI-MS (m/z) calcd for $C_{12}H_{10}O_2$, [M-H^+]: 185.06, found: 184.93.

2-(naphthalen-1-yl)acetic acid (2i)



Following General Procedure D, 1-(fluoromethyl)naphthalene (32.0 mg, 0.2 mmol), HCO_2K (20.2 mg, 1.2 eq.), Na_2CO_3 (21.2 mg, 1.0 eq.), 4DPAIPN (0.16 mg, 0.1 mol%), methyl thiosalicylate (2.75 μL, 10 mol%), DMSO (2 mL) were used. The reaction mixture was stirred at room temperature for 4 h at 1500 rpm. After completion of the reaction, the reaction mixture was quenched by 2 mL 2N HCl. The reaction mixture was extracted by EtOAc (4 x 10 mL) and the combined organic phases were dried with concentrated in vacuo. The residue was purified by a silica gel flash column chromatography (silica gel, PE:EA = 10:1, PE:EA = 5:1 ~3:1 +1% AcOH) to give the title product (colorless solid, 28.2 mg, 76% yield). The compound data was in agreement with the literature (Ref. *J. Catal.*, **2016**, *344*, 741-748).

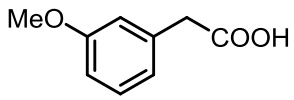
R_f = 0.4 (PE/EA = 1:1.)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.1 Hz, 1H), 7.89 – 7.85 (m, 1H), 7.81 (dd, *J* = 7.2, 2.2 Hz, 1H), 7.57 – 7.39 (m, 4H), 4.09 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.41, 133.77, 131.96, 129.73, 128.77, 128.36, 128.19, 126.50, 125.86, 125.44, 123.65, 38.73.

ESI-MS (m/z) calcd for $C_{12}H_{10}O_2$, [M-H^+]:185.06, found: 184.93.

2-(3-methoxyphenyl)acetic acid (2j)



Following General Procedure D, 1-(fluoromethyl)-3-methoxybenzene (28 mg, 0.2 mmol), HCO_2K (20.2 mg, 1.2 eq.), Na_2CO_3 (21.2 mg, 1.0 eq.), 4DPAIPN (0.16 mg, 0.1 mol%), methyl thiosalicylate (2.75 μL, 10 mol%), DMSO (2 mL) were used. The reaction mixture was stirred at room temperature for 4 h at 1500 rpm. After completion of the reaction, the reaction mixture was quenched by 2 mL 2N HCl. The reaction mixture was extracted by EtOAc (4 x 10 mL) and the combined organic phases were dried with concentrated in vacuo. The residue was purified by a silica gel flash column chromatography (silica gel, PE:EA = 10:1, PE:EA = 5:1 ~3:1 +1% AcOH) to give the title product (colorless solid, 24.8 mg, 75% yield.). The compound data was in agreement with the literature (Ref. *Chem*, **2021**, *7*, 3099-3113).

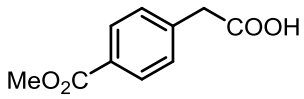
R_f = 0.3 (PE/EA = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.21 (m, 1H), 6.88 – 6.80 (m, 3H), 3.80 (s, 3H), 3.62 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.19, 159.75, 134.69, 129.66, 121.73, 115.06, 112.90, 62.67, 43.75.

ESI-MS (m/z) calcd for $C_9H_{10}O_3$, $[M\text{-}H^+]$: 165.05, found: 164.92.

2-(4-(methoxycarbonyl)phenyl)acetic acid (2k)



Following General Procedure D, methyl 4-(fluoromethyl)benzoate (33.6 mg, 0.2 mmol), HCO_2K (20.2 mg, 1.2 eq.), Na_2CO_3 (21.2 mg, 1.0 eq.), 4DPAIPN (0.16 mg, 0.1 mol%), methyl thiosalicylate (2.75 μL, 10 mol%), DMSO (2 mL) were used. The reaction mixture was stirred at room temperature for 4 h at 1500 rpm. After completion of the reaction, the reaction mixture was quenched by 2 mL 2N HCl. The reaction mixture was extracted by EtOAc (4 x 10 mL) and the combined organic phases were dried with concentrated in vacuo. The residue was purified by a silica gel flash column

chromatography (silica gel, PE:EA = 10:1, PE:EA = 5:1 ~3:1 +1% AcOH) to give the title product (colorless solid, 35.5 mg, 86% yield.). The compound data was in agreement with the literature (Ref. *Chem. Eur. J.*, **2021**, *27*, 6077-6085).

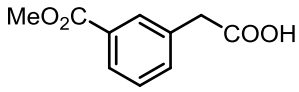
R_f = 0.4 (PE/EA = 1:1).

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.47 (s, 1H), 7.92 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 8.3 Hz, 2H), 3.85 (s, 3H), 3.69 (s, 2H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 172.57, 166.60, 141.14, 130.34, 129.56, 128.47, 52.55, 40.96.

ESI-MS (m/z) calcd for $C_{10}H_{10}O_4$, [M-H^+]: 193.05, found: 192.62.

2-(3-(methoxycarbonyl)phenyl)acetic acid (2l)



Following General Procedure D, methyl 3-(fluoromethyl)benzoate (33.6 mg, 0.2 mmol), HCO_2K (20.2 mg, 1.2 eq.), Na_2CO_3 (21.2 mg, 1.0 eq.), 4DPAIPN (0.16 mg, 0.1 mol%), methyl thiosalicylate (2.75 μL, 10 mol%), DMSO (2 mL) were used. The reaction mixture was stirred at room temperature for 4 h at 1500 rpm. After completion of the reaction, the reaction mixture was quenched by 2 mL 2N HCl. The reaction mixture was extracted by EtOAc (4 x 10 mL) and the combined organic phases were dried with concentrated in vacuo. The residue was purified by a silica gel flash column chromatography (silica gel, PE:EA = 10:1, PE:EA = 5:1 ~3:1 +1% AcOH) to give the title product (colorless solid, 30.9 mg, 80% yield.). The compound data was in agreement with the literature (Ref. *Chem*, **2021**, *7*, 3099-3113).

R_f = 0.4 (PE/EA = 1:1).

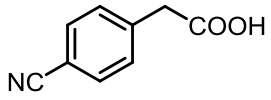
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.10 – 7.77 (m, 2H), 7.64 – 7.30 (m, 2H), 3.86 (s, 3H), 3.69 (s, 2H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 172.87, 166.60, 136.22, 134.88, 130.58, 129.98,

129.11, 127.86, 52.57, 40.53.

ESI-MS (m/z) calcd for $C_{12}H_{10}O_4$, [M-H^+]: 193.05, found: 192.86.

2-(4-cyanophenyl)acetic acid (2m)



Following General Procedure D, 4-(fluoromethyl)benzonitrile (27.0 mg, 0.2 mmol), HCO_2K (20.2 mg, 1.2 eq.), Na_2CO_3 (21.2 mg, 1.0 eq.), 4DPAIPN (0.16 mg, 0.1 mol%), methyl thiosalicylate (2.75 μL, 10 mol%), DMSO (2 mL) were used. The reaction mixture was stirred at room temperature for 4 h at 1500 rpm. After completion of the reaction, the reaction mixture was quenched by 2 mL 2N HCl. The reaction mixture was extracted by EtOAc (4 x 10 mL) and the combined organic phases were dried with concentrated in vacuo. The residue was purified by a silica gel flash column chromatography (silica gel, PE:EA = 10:1, PE:EA = 5:1 ~3:1 +1% AcOH) to give the title product (colorless solid, 29.6 mg, 92% yield.). The compound data was in agreement with the literature (Ref. *Chem*, **2021**, *7*, 3099-3113).

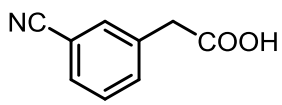
R_f = 0.1 (PE/EA = 1:2)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.62 (m, 2H), 7.44 – 7.39 (m, 2H), 3.73 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.68, 138.43, 132.40, 130.26, 118.52, 111.50, 40.80.

ESI-MS (m/z) calcd for $C_9H_7NO_2$, [M-H^+]: 160.04, found: 159.80.

2-(3-cyanophenyl)acetic acid (2n)



Following General Procedure D, 3-(fluoromethyl)benzonitrile (27.0 mg, 0.2 mmol), HCO_2K (20.2 mg, 1.2 eq.), Na_2CO_3 (21.2 mg, 1.0 eq.), 4DPAIPN (0.16 mg, 0.1 mol%), methyl thiosalicylate (2.75 μL, 10 mol%), DMSO (2 mL) were used. The reaction

mixture was stirred at room temperature for 4 h at 1500 rpm. After completion of the reaction, the reaction mixture was quenched by 2 mL 2N HCl. The reaction mixture was extracted by EtOAc (4 x 10 mL) and the combined organic phases were dried with concentrated in vacuo. The residue was purified by a silica gel flash column chromatography (silica gel, PE:EA = 10:1, PE:EA = 5:1 ~3:1 +1% AcOH) to give the title product (colorless solid, 24.2mg, 75% yield.). The compound data was in agreement with the literature (Ref. *Chem*, **2021**, *7*, 3099-3113).

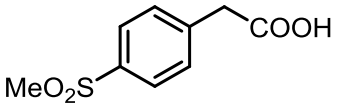
R_f = 0.1 (PE/EA = 1:2)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.57 (m, 2H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.46 (t, *J* = 7.9 Hz, 1H), 3.71 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.02, 134.55, 133.97, 132.97, 131.16, 129.45, 118.46, 112.79, 40.24.

ESI-MS (m/z) calcd for $C_9H_7NO_2$, [M-H^+]:160.04, found: 159.80.

2-(4-(methylsulfonyl)phenyl)acetic acid (2o)



Following General Procedure D, 1-(fluoromethyl)-4-(methylsulfonyl)benzene (37.6 mg, 0.2 mmol), HCO_2K (20.2 mg, 1.2 eq.), Na_2CO_3 (21.2 mg, 1.0 eq.), 4DPAIPN (0.16 mg, 0.1 mol%), methyl thiosalicylate (2.75 μL, 10 mol%), DMSO (2 mL) were used. The reaction mixture was stirred at room temperature for 4 h at 1500 rpm. After completion of the reaction, the reaction mixture was quenched by 2 mL 2N HCl. The reaction mixture was extracted by EtOAc (4 x 10 mL) and the combined organic phases were dried with concentrated in vacuo. The residue was purified by a silica gel flash column chromatography (silica gel, PE:EA = 10:1, PE:EA = 5:1 ~3:1 +1% AcOH) to give the title product (colorless liquid, 33.2 mg, 78% yield.). The compound data was in agreement with the literature (Ref. CN107641089, **2018**, A).

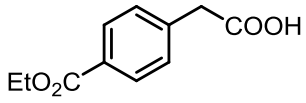
R_f = 0.2 (PE/EA = 1:2)

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.59 (s, 1H), 7.87 (d, *J* = 7.9 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 3.74 (s, 2H), 3.21 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 172.54, 141.65, 139.61, 130.96, 127.37, 44.02, 40.78.

ESI-MS (m/z) calcd for $C_9H_{10}O_4S$, [M-H^+]: 213.02, found: 212.94.

2-(4-(ethoxycarbonyl)phenyl)acetic acid (2p)



Following General Procedure D, ethyl 4-(fluoromethyl)benzoate (36.4 mg, 0.2 mmol), HCO_2K (20.2 mg, 1.2 eq.), Na_2CO_3 (21.2 mg, 1.0 eq.), 4DPAIPN (0.16 mg, 0.1 mol%), methyl thiosalicylate (2.75 μL, 10 mol%), DMSO (2 mL) were used. The reaction mixture was stirred at room temperature for 4 h at 1500 rpm. After completion of the reaction, the reaction mixture was quenched by 2 mL 2N HCl. The reaction mixture was extracted by EtOAc (4 x 10 mL) and the combined organic phases were dried with concentrated in vacuo. The residue was purified by a silica gel flash column chromatography (silica gel, PE:EA = 10:1, PE:EA = 5:1 ~3:1 +1% AcOH) to give the title product (colorless solid., 35.1 mg, 84% yield.). The compound data was in agreement with the literature (Ref. *J. Med. Chem.*, **1998**, *41*, 5219-5246).

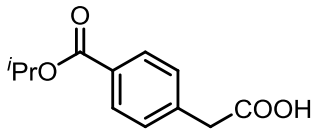
R_f = 0.3 (PE/EA = 1:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.3 Hz, 2H), 4.37 (q, *J* = 7.4 Hz, 2H), 3.72 (s, 2H), 1.39 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.11, 166.33, 138.23, 129.85, 129.59, 129.39, 60.99, 40.85, 14.28.

ESI-MS (m/z) calcd for $C_{11}H_{12}O_4$, [M-H^+]:207.07, found: 206.96.

2-(4-(isopropoxycarbonyl)phenyl)acetic acid (2q)



Following General Procedure D, isopropyl 4-(fluoromethyl)benzoate (39.2 mg, 0.2 mmol), HCO_2K (20.2 mg, 1.2 eq.), Na_2CO_3 (21.2 mg, 1.0 eq.), 4DPAIPN (0.16 mg, 0.1 mol%), methyl thiosalicylate (2.75 μL, 10 mol%), DMSO (2 mL) were used. The reaction mixture was stirred at room temperature for 4 h at 1500 rpm. After completion of the reaction, the reaction mixture was quenched by 2 mL 2N HCl. The reaction mixture was extracted by EtOAc (4 x 10 mL) and the combined organic phases were dried with concentrated in vacuo. The residue was purified by a silica gel flash column chromatography (silica gel, PE:EA = 10:1, PE:EA = 5:1 ~3:1 +1% AcOH) to give the title product (light yellow solid, 35.3 mg, 80% yield.)

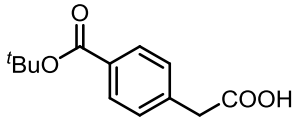
R_f = 0.3 (PE/EA = 1:1)

1H NMR (400 MHz, $CDCl_3$) δ 8.06 – 8.00 (m, 2H), 7.41 – 7.35 (m, 2H), 5.27 (p, *J* = 6.3 Hz, 1H), 3.74 (s, 2H), 1.38 (d, *J* = 6.3 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.52, 165.78, 138.02, 130.02, 129.84, 129.35, 68.40, 40.84, 21.90.

HRMS (ESI+): calculated for $C_{12}H_{14}O_4$, [M+Na^+]: 245.0784, found: 245.0788.

2-(4-(tert-butoxycarbonyl)phenyl)acetic acid (2r)



Following General Procedure D, tert-butyl 4-(fluoromethyl)benzoate (42.0 mg, 0.2 mmol), HCO_2K (20.2 mg, 1.2 eq.), Na_2CO_3 (21.2 mg, 1.0 eq.), 4DPAIPN (0.16 mg, 0.1 mol%), methyl thiosalicylate (2.75 μL, 10 mol%), DMSO (2 mL) were used. The reaction mixture was stirred at room temperature for 4 h at 1500 rpm. After completion of the reaction, the reaction mixture was quenched by 2 mL 2N HCl. The reaction mixture was extracted by EtOAc (4 x 10 mL) and the combined organic phases were dried with concentrated in vacuo. The residue was purified by a silica gel

flash column chromatography (silica gel, PE:EA = 10:1, PE:EA = 5:1 ~3:1 +1% AcOH) to give the title product (light yellow solid, 36.4 mg, 77% yield.). The compound data was in agreement with the literature (Ref. US2010/29772, **2010**, A1).

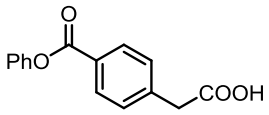
R_f = 0.3 (PE/EA = 1:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 8.3, 1.6 Hz, 2H), 7.33 (dd, *J* = 8.2, 1.6 Hz, 2H), 3.70 (s, 2H), 1.58 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.57, 165.48, 137.89, 131.08, 129.71, 129.25, 81.06, 40.96, 28.15.

ESI-MS (m/z) calcd for $C_{13}H_{16}O_4$, $[M-H^+]$:235.10, found: 234.90.

2-(4-(phenoxycarbonyl)phenyl)acetic acid (2s)



Following General Procedure D, phenyl 4-(fluoromethyl)benzoate (46.0 mg, 0.2 mmol), HCO_2K (20.2 mg, 1.2 eq.), Na_2CO_3 (21.2 mg, 1.0 eq.), 4DPAIPN (0.16 mg, 0.1 mol%), methyl thiosalicylate (2.75 μL, 10 mol%), DMSO (2 mL) were used. The reaction mixture was stirred at room temperature for 4 h at 1500 rpm. After completion of the reaction, the reaction mixture was quenched by 2 mL 2N HCl. The reaction mixture was extracted by EtOAc (4 x 10 mL) and the combined organic phases were dried with concentrated in vacuo. The residue was purified by a silica gel flash column chromatography (silica gel, PE:EA = 10:1, PE:EA = 5:1 ~3:1 +1% AcOH) to give the title product (light yellow solid, 34.7 mg, 68% yield.)

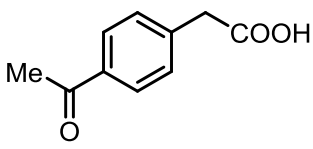
R_f = 0.3 (PE/EA = 1:1)

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.50 (s, 1H), 8.39 – 7.93 (m, 2H), 7.54 – 7.44 (m, 4H), 7.35 – 7.25 (m, 3H), 3.74 (s, 2H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 172.44, 164.90, 151.08, 141.95, 130.49, 130.18, 129.99, 127.76, 126.40, 122.34, 41.02.

HRMS (ESI+): calculated for $C_{15}H_{12}O_4$, [M+H$^+$]: 257.0808, found: 257.0805.

2-(4-acetylphenyl)acetic acid (2t)



Following General Procedure D, 1-(4-(fluoromethyl)phenyl)ethan-1-one (30.4 mg, 0.2 mmol), HCO_2K (20.2 mg, 1.2 eq.), Na_2CO_3 (21.2 mg, 1.0 eq.), 4DPAIPN (0.16 mg, 0.1 mol%), methyl thiosalicylate (2.75 μL, 10 mol%), DMSO (2 mL) were used. The reaction mixture was stirred at room temperature for 4 h at 1500 rpm. After completion of the reaction, the reaction mixture was quenched by 2 mL 2N HCl. The reaction mixture was extracted by EtOAc (4 x 10 mL) and the combined organic phases were dried with concentrated in vacuo. The residue was purified by a silica gel flash column chromatography (silica gel, PE:EA = 10:1, PE:EA = 5:1 ~3:1 +1% AcOH) to give the title product (light yellow solid, 14.7 mg, 43% yield.). The compound data was in agreement with the literature (Ref. *J. Am. Chem. Soc.* **2006**, *128*, 1404–1405).

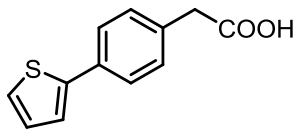
R$_f$ = 0.2 (PE/EA = 1:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 7.9 Hz, 2H), 3.73 (s, 2H), 2.60 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.77, 176.17, 138.54, 136.16, 129.68, 128.69, 40.79, 26.6

ESI-MS (m/z) calcd for $C_{10}H_{10}O_3$, [M-H$^+$]: 177.06, found: 176.70.

2-(4-(thiophen-2-yl)phenyl)acetic acid (2u)



Following General Procedure D, 2-(4-(fluoromethyl)phenyl)thiophene (38.4 mg, 0.2 mmol), HCO_2K (20.2 mg, 1.2 eq.), Na_2CO_3 (21.2 mg, 1.0 eq.),

4DPAIPN (3.2 mg, 2 mol%), methyl thiosalicylate (2.75 μL, 10 mol%), DMSO (2 mL) were used. The reaction mixture was stirred at room temperature for 4 h at 1500 rpm. After completion of the reaction, the reaction mixture was quenched by 2 mL 2N HCl. The reaction mixture was extracted by EtOAc (4 x 10 mL) and the combined organic phases were dried with concentrated in vacuo. The residue was purified by a silica gel flash column chromatography (silica gel, PE:EA = 10:1, PE:EA = 5:1 ~3:1 +1% AcOH) to give the title product (colorless solid, 24.2 mg, 63% yield.). The compound data was in agreement with the literature (Ref. *Chem. Mater.* **2013**, *25*, 90–97).

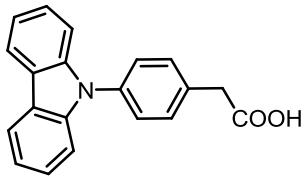
R_f = 0.3 (PE/EA = 1:1)

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.83 (dd, *J* = 2.9, 1.4 Hz, 1H), 7.70 – 7.58 (m, 3H), 7.54 (dd, *J* = 5.1, 1.4 Hz, 1H), 7.33 – 7.23 (m, 2H), 3.59 (s, 2H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 173.17, 141.73, 134.38, 134.04, 130.38, 127.51, 126.63, 126.44, 121.14, 40.80.

ESI-MS (m/z) calcd for $C_{12}H_{10}O_2S$, [M-H^+]: 217.03, found: 216.87.

2-(4-(9H-carbazol-9-yl)phenyl)acetic acid (2v)



Following General Procedure D, 9-(4-(fluoromethyl)phenyl)-9H-carbazole (55.0 mg, 0.2 mmol), HCO_2K (20.2 mg, 1.2 eq.), Na_2CO_3 (21.2 mg, 1.0 eq.), 4DPAIPN (3.2 mg, 2 mol%), methyl thiosalicylate (2.75 μL, 10 mol%), DMSO (2 mL) were used. The reaction mixture was stirred at room temperature for 24 h at 1500 rpm. After completion of the reaction, the reaction mixture was quenched by 2 mL 2N HCl. The reaction mixture was extracted by EtOAc (4 x 10 mL) and the combined organic phases were dried with concentrated in vacuo. The residue was purified by a silica gel flash column chromatography (silica gel, PE:EA = 10:1, PE:EA = 5:1 ~3:1 +1% AcOH) to give the title product (light yellow solid, 35.0 mg,

58% yield.)

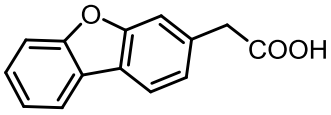
R_f = 0.1 (PE/EA = 1:1)

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.50 (brs, 1H), 8.25 (dt, *J* = 7.8, 1.1 Hz, 2H), 7.57 (s, 4H), 7.41 (dddd, *J* = 15.4, 8.1, 6.9, 1.1 Hz, 4H), 7.29 (ddd, *J* = 7.9, 6.8, 1.3 Hz, 2H), 3.75 (s, 2H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 173.08, 140.62, 135.83, 135.01, 131.66, 126.90, 126.71, 123.18, 120.99, 120.48, 110.11, 40.71.

HRMS (ESI+): calculated for $C_{20}H_{15}NO_2$, [M+H$^+$]: 302.1176, found: 302.1170.

2-(dibenzo[b,d]furan-3-yl)acetic acid (2w)



Following General Procedure D, 3-(fluoromethyl)dibenzo[b,d]furan (40.0 mg, 0.2 mmol), HCO_2K (20.2 mg, 1.2 eq.), Na_2CO_3 (21.2 mg, 1.0 eq.), 4DPAIPN (3.2 mg, 2 mol%), methyl thiosalicylate (2.75 μL, 10 mol%), DMSO (2 mL) were used. The reaction mixture was stirred at room temperature for 24 h at 1500 rpm. After completion of the reaction, the reaction mixture was quenched by 2 mL 2N HCl. The reaction mixture was extracted by EtOAc (4 x 10 mL) and the combined organic phases were dried with concentrated in vacuo. The residue was purified by a silica gel flash column chromatography (silica gel, PE:EA = 10:1, PE:EA = 5:1 ~3:1 +1% AcOH) to give the title product (light yellow solid, 20.2 mg, 44% yield.). The compound data was in agreement with the literature (Ref. *Eur. J. Med. Chem*., **2016**, *108*, 154-165).

R_f = 0.2 (PE/EA = 1:1)

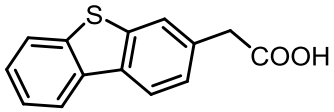
^{1}H NMR (400 MHz, DMSO-d_6) δ 12.39 (s, 1H), 8.13 (dd, *J* = 7.7, 1.3 Hz, 1H), 8.03 (d, *J* = 1.8 Hz, 1H), 7.72 – 7.62 (m, 2H), 7.52 (ddd, *J* = 8.4, 7.3, 1.4 Hz, 1H), 7.45 – 7.37 (m, 2H), 3.75 (s, 2H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 173.43, 156.23, 154.88, 130.48, 129.51, 128.05,

123.99, 123.93, 123.58, 122.32, 121.57, 112.15, 111.76, 40.91.

ESI-MS (m/z) calcd for $C_{14}H_{10}O_3$, [M-H^+]: 225.06, found: 224.95.

2-(dibenzo[b,d]thiophen-3-yl)acetic acid (2x)



Following General Procedure D, 3-(fluoromethyl)dibenzo[b,d]thiophene (43.3 mg, 0.2 mmol), HCO_2K (20.2 mg, 1.2 eq.), Na_2CO_3 (21.2 mg, 1.0 eq.), 4DPAIPN (3.2 mg, 2 mol%), methyl thiosalicylate (2.75 μL, 10 mol%), DMSO (2 mL) were used. The reaction mixture was stirred at room temperature for 24 h at 1500 rpm. After completion of the reaction, the reaction mixture was quenched by 2 mL 2N HCl. The reaction mixture was extracted by EtOAc (4 x 10 mL) and the combined organic phases were dried with concentrated in vacuo. The residue was purified by a silica gel flash column chromatography (silica gel, PE:EA = 10:1, PE:EA = 5:1 ~3:1 +1% AcOH) to give the title product (light yellow solid, 28.0 mg, 58% yield.). The compound data was in agreement with the literature (Ref. US4219657, **1980**, A).

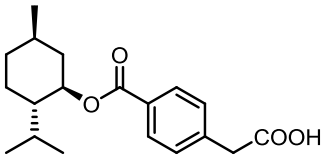
R_f = 0.2 (PE/EA = 1:1)

H NMR (400 MHz, DMSO-d_6) δ 12.42 (brs, 1H), 8.36 – 8.29 (m, 1H), 8.25 (d, *J* = 1.7 Hz, 1H), 8.05 – 7.99 (m, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.55 – 7.48 (m, 2H), 7.43 (dd, *J* = 8.2, 1.7 Hz, 1H), 3.78 (s, 2H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 173.30, 139.39, 137.34, 135.56, 135.32, 132.32, 129.18, 127.54, 125.22, 123.57, 123.29, 123.21, 122.37, 41.03.

ESI-MS (m/z) calcd for $C_{14}H_{10}O_2S$, [M-H^+]: 241.03, found: 240.94.

2-(4-((((*1R,2S,5R*)-2-isopropyl-5-methylcyclohexyl)oxy)carbonyl)phenyl)acetic acid (2y)



Following General Procedure D, (1R,2S,5R)-2-isopropyl-5-methylcyclohexyl 4-(fluoromethyl)benzoate (58.5 mg, 0.2 mmol), HCO_2K (20.2 mg, 1.2 eq.), Na_2CO_3 (21.2 mg, 1.0 eq.), 4DPAIPN (0.16 mg, 0.1 mol%), methyl thiosalicylate (2.75 μL, 10 mol%), DMSO (2 mL) were used. The reaction mixture was stirred at room temperature for 4 h at 1500 rpm. After completion of the reaction, the reaction mixture was quenched by 2 mL 2N HCl. The reaction mixture was extracted by EtOAc (4 x 10 mL) and the combined organic phases were dried with concentrated in vacuo. The residue was purified by a silica gel flash column chromatography (silica gel, PE:EA = 10:1, PE:EA = 5:1 ~3:1 +1% AcOH) to give the title product (light yellow solid, 40.7 mg, 64% yield.)

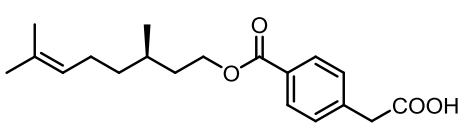
R_f = 0.3 (PE/EA = 1:1)

H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 4.92 (td, *J* = 10.9, 4.4 Hz, 1H), 3.71 (s, 2H), 2.16 – 2.06 (m, 1H), 1.94 (pt, *J* = 7.0, 3.5 Hz, 1H), 1.78 – 1.64 (m, 2H), 1.54 (ddt, *J* = 13.9, 10.7, 2.9 Hz, 2H), 1.26 (s,1H), 1.20 – 1.04 (m, 2H), 0.92 (t, *J* = 6.6 Hz, 6H), 0.78 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.63, 165.82, 138.14, 130.02, 129.92, 129.41, 74.96, 47.30, 40.96, 34.33, 31.45, 26.52, 23.67, 22.03, 20.75, 16.52.

HRMS (ESI+): calculated for $C_{19}H_{26}O_4$, [M+Na^+]: 341.1723, found: 341.1722.

(*R*)-2-(4-(((3,7-dimethyloct-6-en-1-yl)oxy)carbonyl)phenyl)acetic acid (2z)



Following General Procedure D, (R)-3,7-dimethyloct-6-en-1-yl 4-(fluoromethyl)benzoate (58.5 mg, 0.2 mmol), HCO_2K (20.2 mg, 1.2 eq.), Na_2CO_3 (21.2 mg, 1.0 eq.), 4DPAIPN (0.16 mg, 0.1

mol%), methyl thiosalicylate (2.75 μL, 10 mol%), DMSO (2 mL) were used. The reaction mixture was stirred at room temperature for 4 h at 1500 rpm. After completion of the reaction, the reaction mixture was quenched by 2 mL 2N HCl. The reaction mixture was extracted by EtOAc (4 x 10 mL) and the combined organic phases were dried with concentrated in vacuo. The residue was purified by a silica gel flash column chromatography (silica gel, PE:EA = 10:1, PE:EA = 5:1 ~3:1 +1% AcOH) to give the title product (colorless liquid, 56.0 mg, 88% yield.)

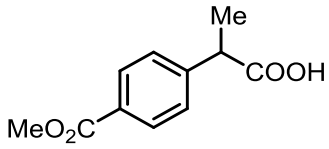
R_f = 0.3 (PE/EA = 1:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.97 (m, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 5.10 (tt, *J* = 7.0, 1.5 Hz,1H), 4.35 (tq, *J* = 7.9, 4.2 Hz, 2H), 3.71 (s, 2H), 1.98 (dp, *J* = 14.9, 9.2, 8.8 Hz, 2H), 1.81 (dtd, *J* = 12.5, 7.1, 4.8 Hz, 1H), 1.70 – 1.58 (m, 6H), 1.55 (dd, *J* = 14.0, 6.7 Hz, 1H), 1.45 – 1.34 (m, 1H), 1.31 – 1.14 (m, 2H), 0.96 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.31, 166.35, 138.16, 131.37, 129.87, 129.68, 129.41, 124.54, 63.55, 40.84, 36.97, 35.48, 29.56, 25.67, 25.38, 19.47, 17.63.

HRMS (ESI+): calculated for $C_{19}H_{26}O_4$, [M+Na^+]: 341.1723, found: 341.1725.

2-(4-(methoxycarbonyl)phenyl)propanoic acid (2aa)



Following General Procedure D, methyl 4-(1-fluoroethyl)benzoate (36.4 mg, 0.2 mmol), HCO_2K (20.2 mg, 1.2 eq.), Na_2CO_3 (21.2 mg, 1.0 eq.), 4DPAIPN (0.16 mg, 0.1 mol%), methyl thiosalicylate (2.75 μL, 10 mol%), DMSO (2 mL) were used. The reaction mixture was stirred at room temperature for 4 h at 1500 rpm. After completion of the reaction, the reaction mixture was quenched by 2 mL 2N HCl. The reaction mixture was extracted by EtOAc (4 x 10 mL) and the combined organic phases were dried with concentrated in vacuo. The residue was purified by a silica gel flash column chromatography (silica gel, PE:EA = 10:1, PE:EA = 5:1 ~3:1 +1%

AcOH) to give the title product (colorless solid, 32.5 mg, 78% yield.). The compound data was in agreement with the literature (Ref. *Chem*, **2021**, *7*, 3099-3113).

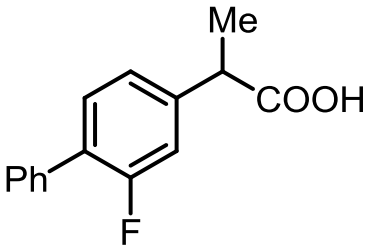
R_f = 0. 2 (PE/EA = 1:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 3.91 (s, 3H), 3.80 (q, *J* = 7.1 Hz, 1H), 1.53 (d, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 179.78, 166.84, 144.77, 129.98, 129.24, 127.70, 52.16, 45.32, 17.98.

ESI-MS (m/z) calcd for $C_{11}H_{12}O_4$, $[M-H^+]$: 207.07, found: 206.77.

2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoic acid (2ab)



Following General Procedure D, 2-fluoro-4-(1-fluoroethyl)-1,1'-biphenyl (43.7 mg, 0.2 mmol), HCO_2K (20.2 mg, 1.2 eq.), Na_2CO_3 (21.2 mg, 1.0 eq.), 4DPAIPN (0.16 mg, 0.1 mol%), methyl thiosalicylate (2.75 μL, 10 mol%), DMSO (2 mL) were used. The reaction mixture was stirred at room temperature for 4 h at 1500 rpm. After completion of the reaction, the reaction mixture was quenched by 2 mL 2N HCl. The reaction mixture was extracted by EtOAc (4 x 10 mL) and the combined organic phases were dried with concentrated in vacuo. The residue was purified by a silica gel flash column chromatography (silica gel, PE:EA = 10:1, PE:EA = 5:1 ~3:1 +1% AcOH) to give the title product (colorless solid, 36.6 mg, 75% yield.). The compound data was in agreement with the literature (Ref. *Synlett*, **2010**, *17*, 2644 - 2648).

R_f = 0.3 (PE/EA = 1:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.49 (m, 2H), 7.46 – 7.32 (m, 4H), 7.20 – 7.10 (m, 2H), 3.78 (q, *J* = 7.1 Hz, 1H), 1.55 (d, *J* = 7.2 Hz, 3H).

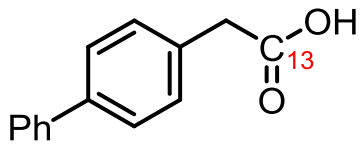
^{13}C NMR (101 MHz, $CDCl_3$) δ 180.12, 159.66 (d, *J* = 249.5 Hz), 140.90 (d, *J* = 8.1 Hz), 135.38, 130.88 (d, *J* = 4.0 Hz), 128.94 (d, *J* = 3.0 Hz), 128.44, 128.14 (d, *J* = 13.1 Hz), 127.70, 123.67 (d, *J* = 3.0 Hz), 115.36 (d, *J* = 24.2 Hz), 44.81 (d, *J* = 2.0

Hz), 17.98.

^{19}F NMR (376 MHz, $CDCl_3$) δ -117.44.

ESI-MS (m/z) calcd for $C_{15}H_{13}FO_2$, [M-H^+]: 243.08, found: 242.76.

2-([1,1'-biphenyl]-4-yl)acetic acid (^{13}C-2a)



Following General Procedure D, 4-(fluoromethyl)-1,1'-biphenyl (37.2 mg, 0.2 mmol), H$^{13}CO_2Na$ (17.0 mg, 1.2 eq.), Na_2CO_3 (21.2 mg, 1.0 eq.), 4DPAIPN (0.16 mg, 0.1 mol%), methyl thiosalicylate (2.75 μL, 10 mol%), DMSO (2 mL) were used. The reaction was stirred vigorously (1500 r/min) and irradiated with a 30 W blue LED lamp (1 cm away, with cooling fan to keep the reaction temperature at 25~30 ℃) for 4 h. After completion of the reaction, the reaction mixture was quenched by 2 mL 2N HCl. The reaction mixture was extracted by EtOAc (4 x 10 mL) and the combined organic phases were dried with concentrated in vacuo. The residue was purified by a silica gel flash column chromatography (silica gel, PE:EA = 10:1, PE:EA = 5:1 ~3:1 +1% AcOH) to give the title product (colorless solid, 32.3 mg, 76% yield.).

R_f = 0.3 (PE/EA = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.53 (m, 4H), 7.48 – 7.40 (m, 2H), 7.40 – 7.30 (m, 3H), 3.71 (d, *J* = 7.8 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.28, 140.69, 140.37, 132.23 (d, *J* = 2.7 Hz), 129.78 (d, *J* = 1.9 Hz), 128.75, 127.41, 127.32, 127.08, 40.58 (d, *J* = 55.4 Hz).

ESI-MS (m/z) calcd for $C_{13}{}^{13}CH_{12}O_2$, [M+Na^+]: 236.0760, found: 236.0763

7. References

[1] J. N. Jaworski, C. V. Kozack, S. J. Tereniak, S. M. M. Knapp, C. R. Landis, J. T. Miller, S. S. Stahl. *J. Am. Chem. Soc.* **2019**, *141*, 10462-10474.

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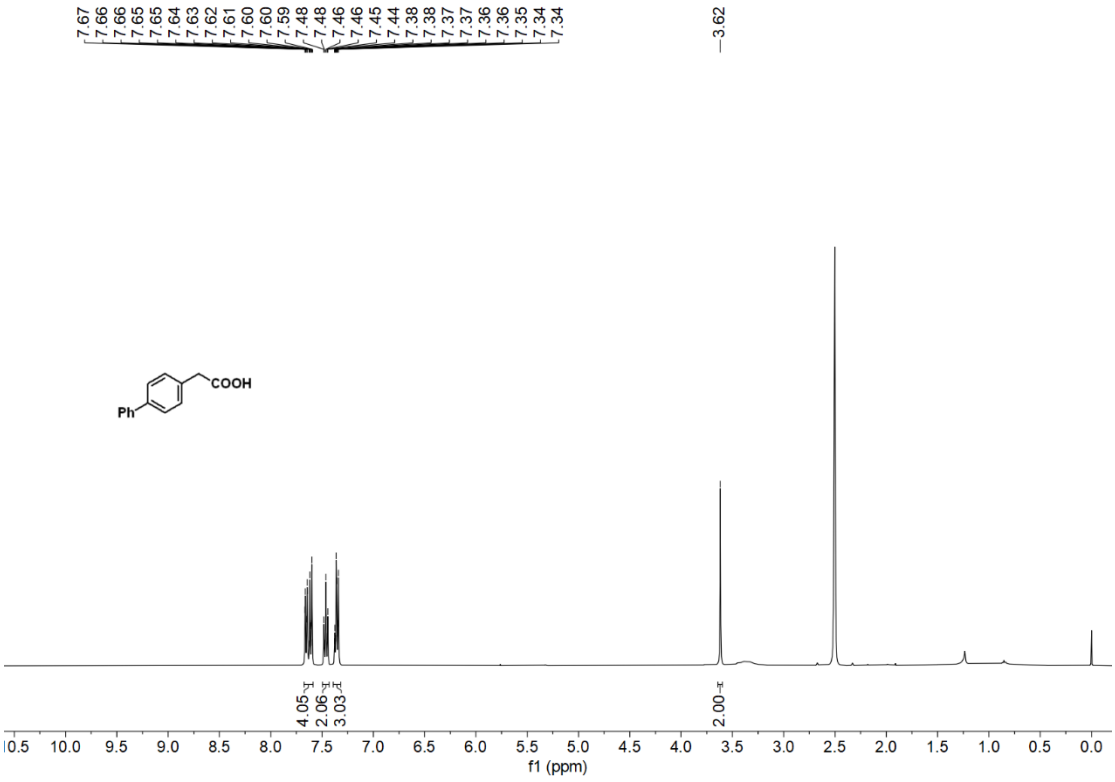
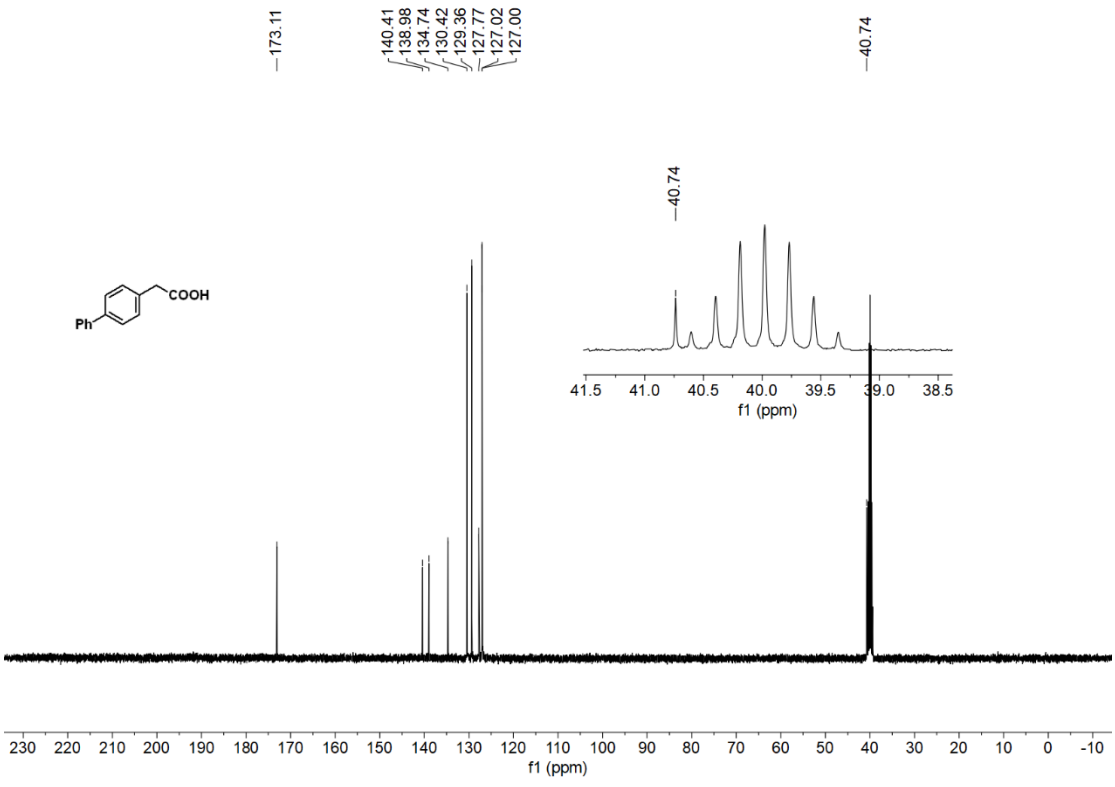
[4] H. Yin, J. Sheng, K.-F. Zhang, Z.-Q. Zhang, K.-J. Biana, X.-S. Wang. *Chem. Commun.* **2019**, *55*, 7635-7638.

[5] K. G. Konya, T. Paul, S.-Q. Lin, J. Lusztyk, K. U. Ingold. *J. Am. Chem. Soc.* **2000**, 122, 7518-7527.

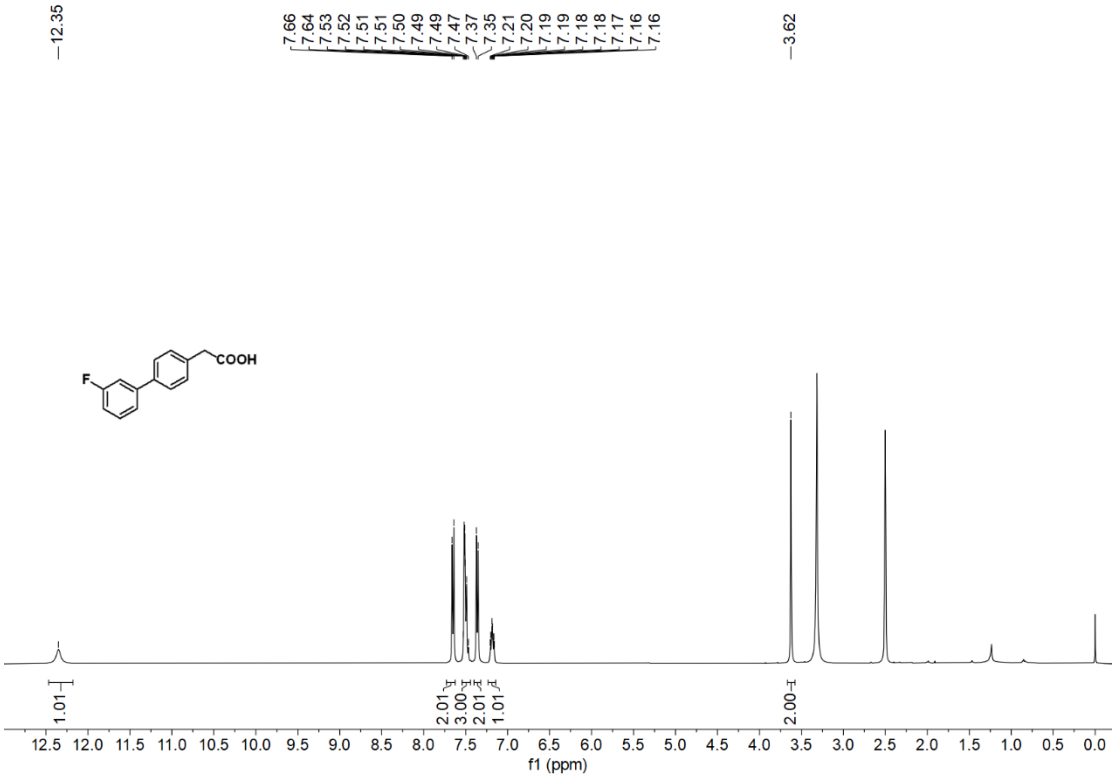
8. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra

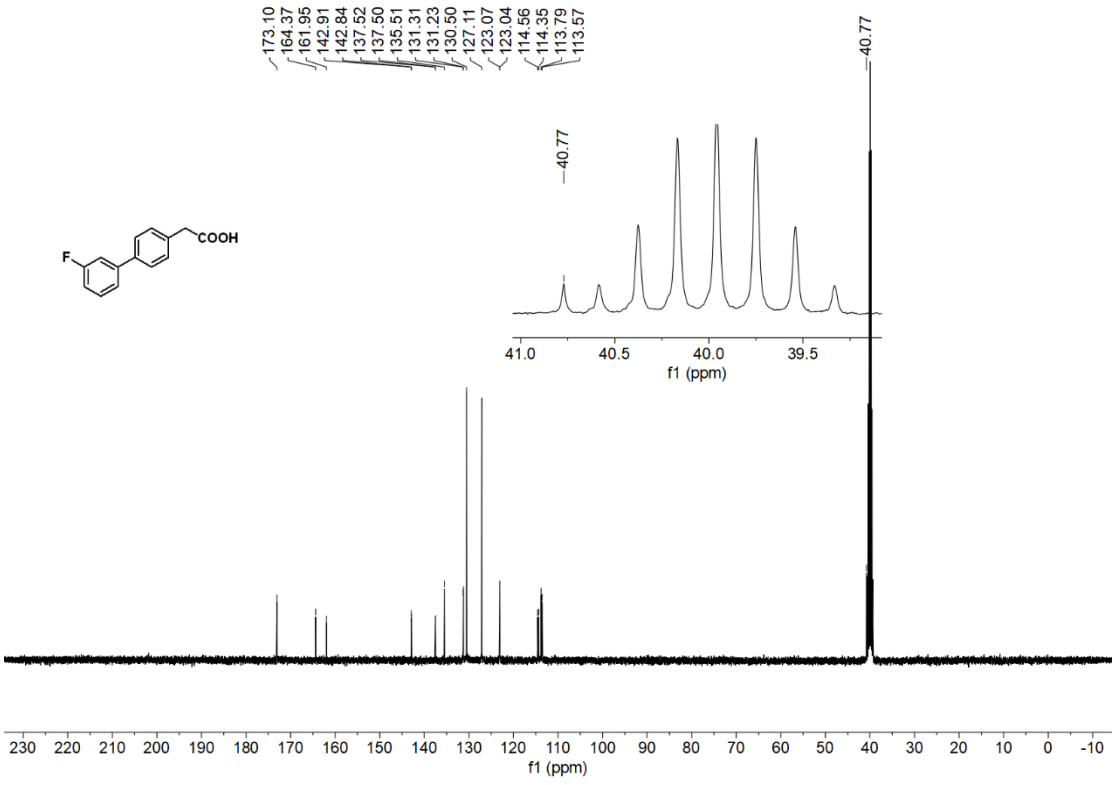
2-([1,1'-biphenyl]-4-yl)acetic acid (2a)

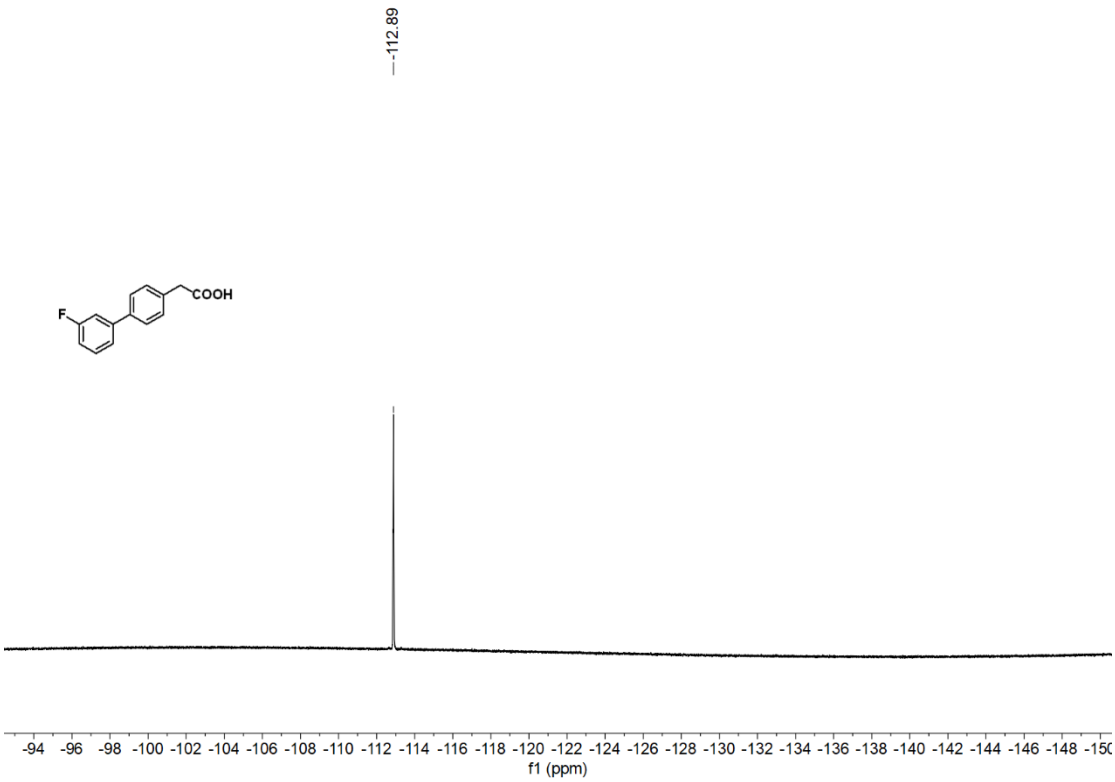




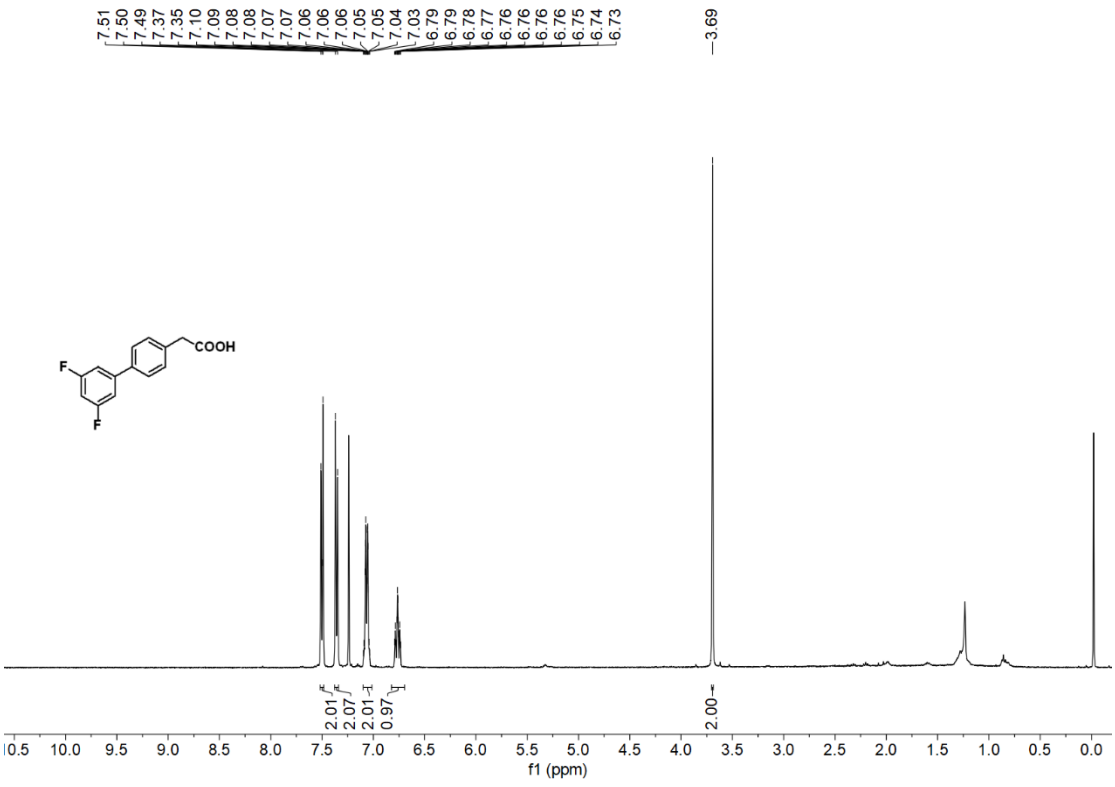
2-(3'-fluoro-[1,1'-biphenyl]-4-yl)acetic acid (2b)

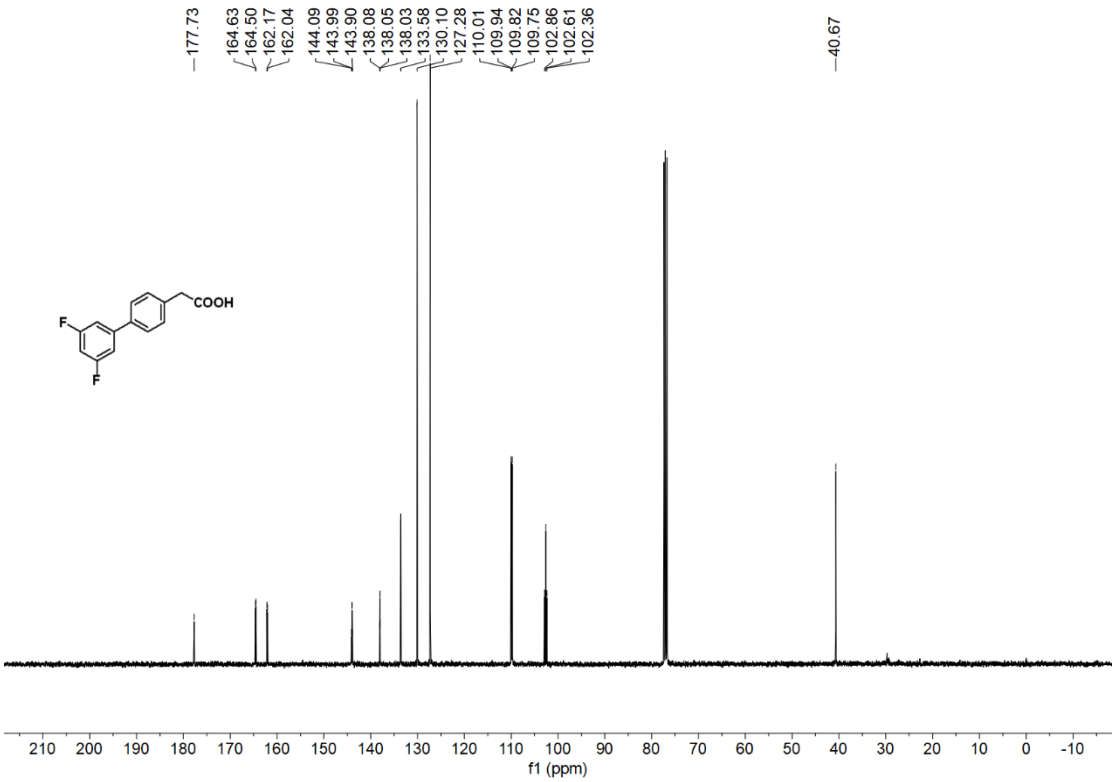






2-(3',5'-difluoro-[1,1'-biphenyl]-4-yl)acetic acid (2c)




177.73
164.63
164.50
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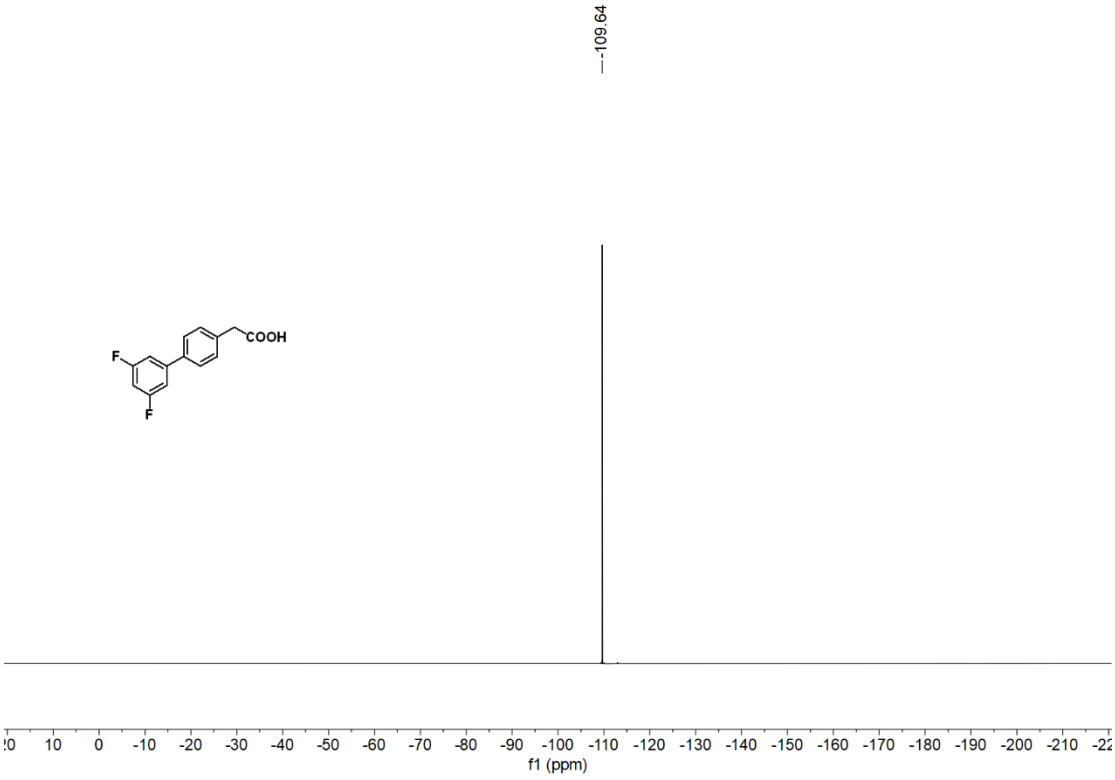
162.04
144.09
143.99
143.90
138.08
138.05
138.03
133.58
130.10
127.28
110.01
109.94
109.82
109.75
102.86
102.61
102.36
40.67
COOH
F
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-109.64
COOH
F
F
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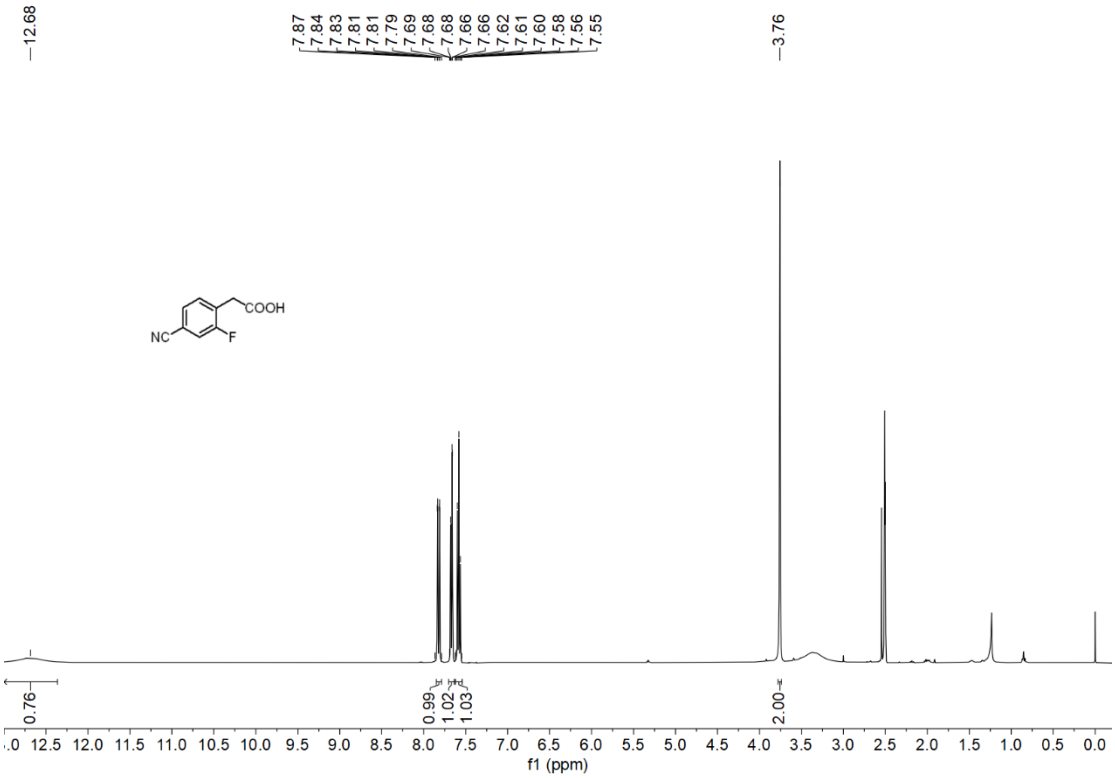
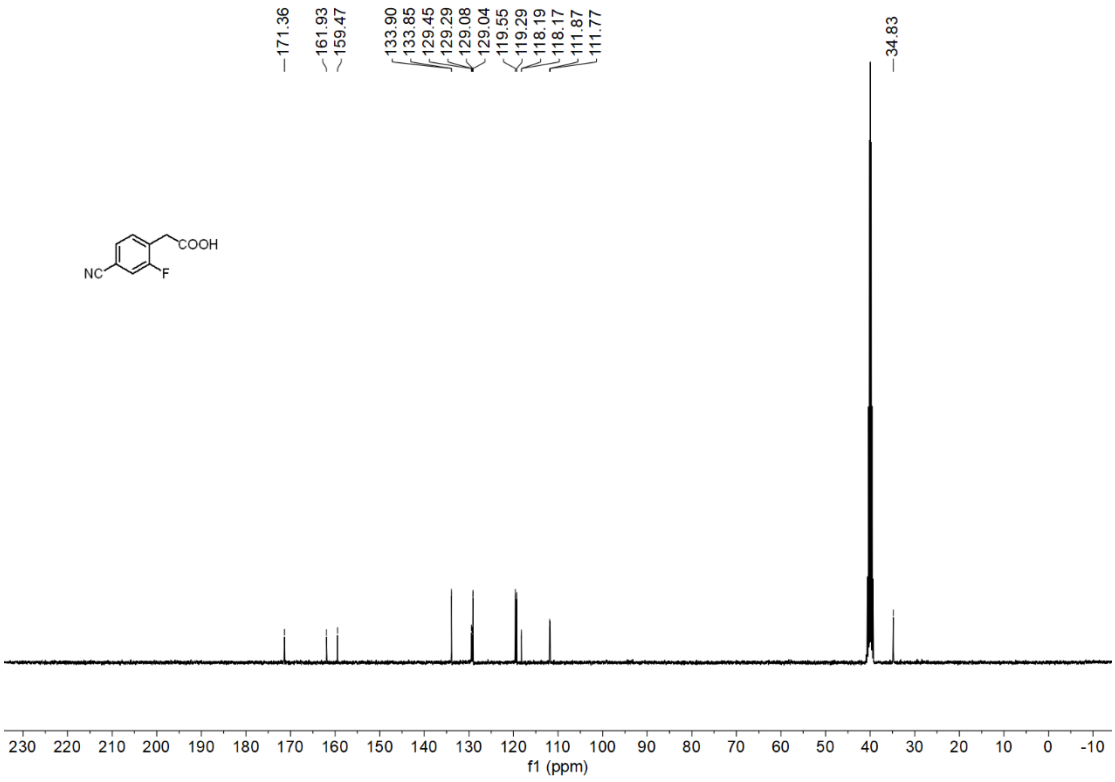
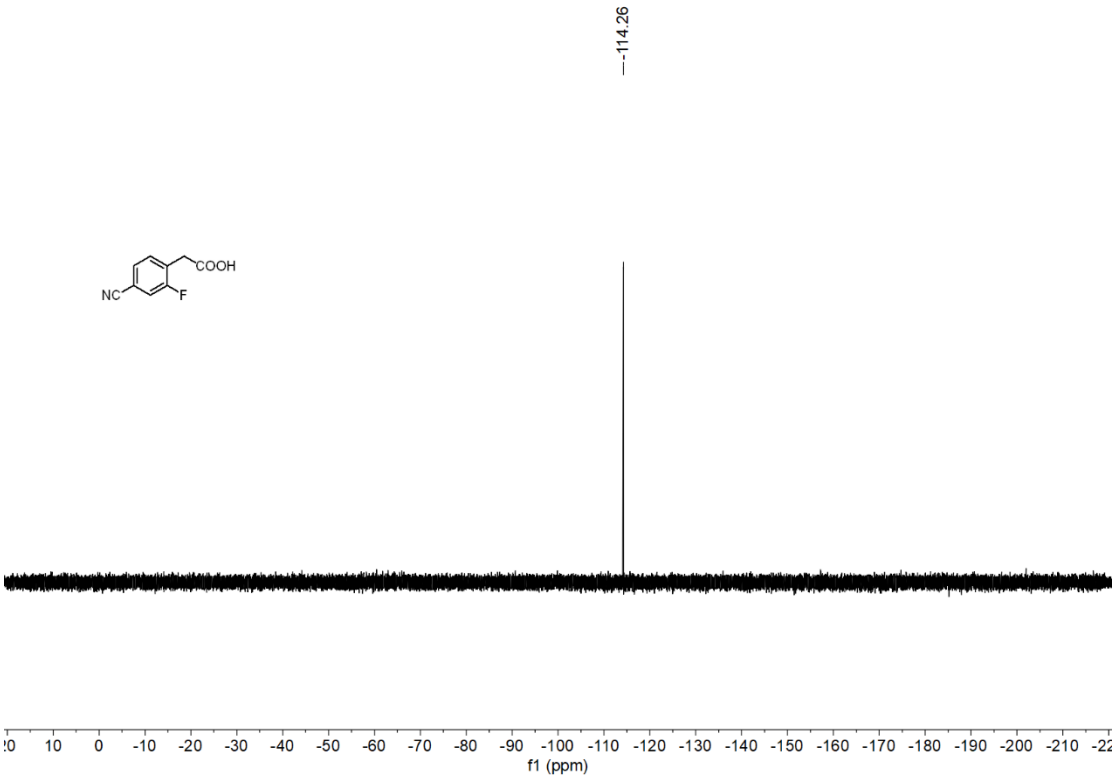
f1 (ppm)

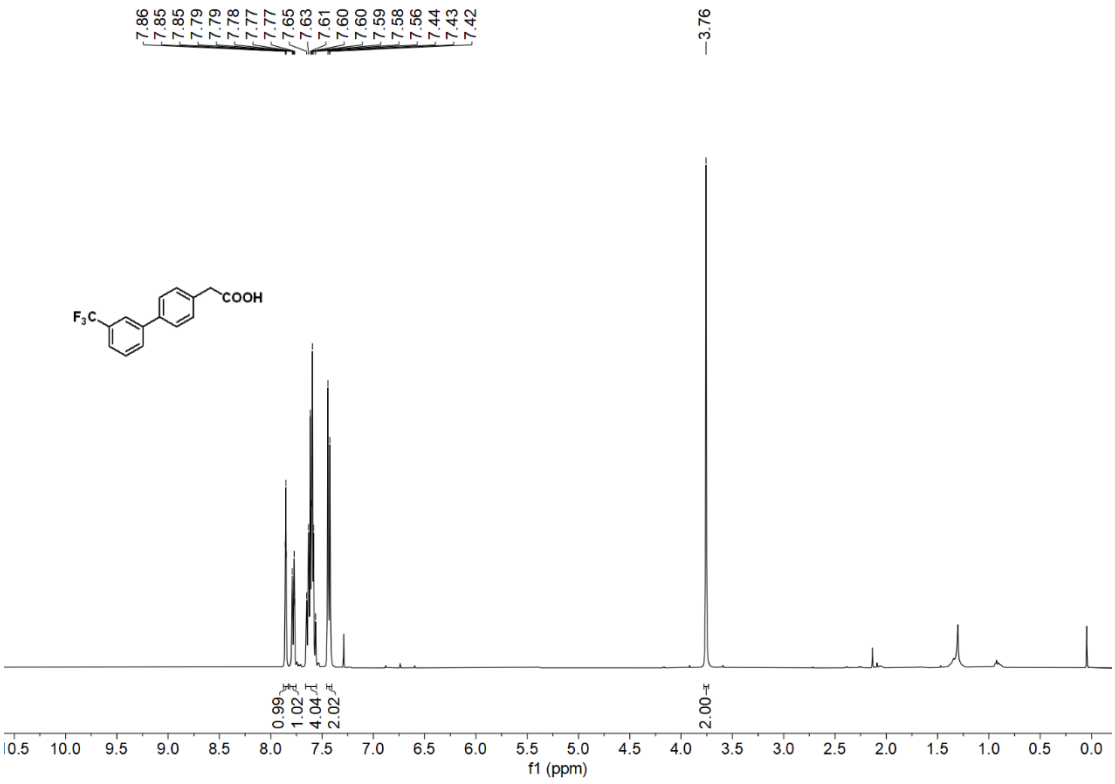
2-(4-cyano-2-fluorophenyl)acetic acid (2d)

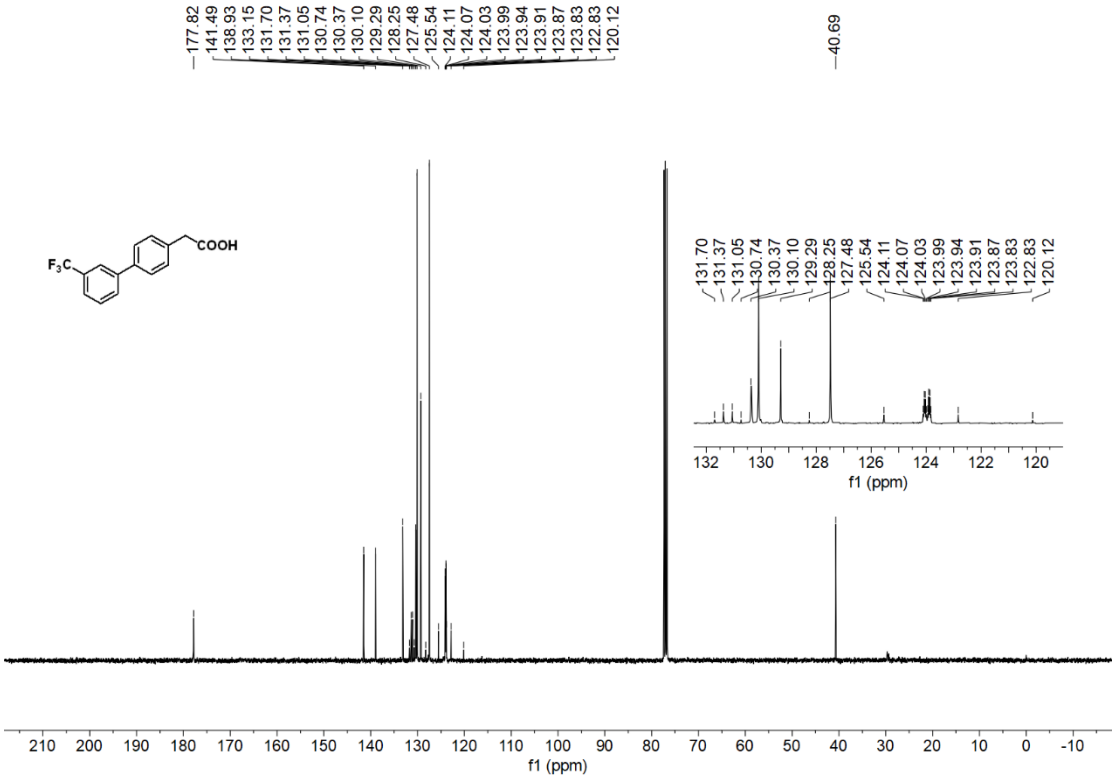






2-(3'-(trifluoromethyl)-[1,1'-biphenyl]-4-yl)acetic acid (2e)

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131.37
131.05
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127.48
125.54
124.11
124.07
124.03
123.99
123.94
123.91
123.87
123.83
122.83
120.12
40.69
COOH
F3C
131.70
131.37
131.05
130.74
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130.10
129.29
128.25
127.48
125.54
124.11
124.07
124.03
123.99
123.94
123.91
123.87
123.83
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132 130 128 126 124 122 120
f1 (ppm)
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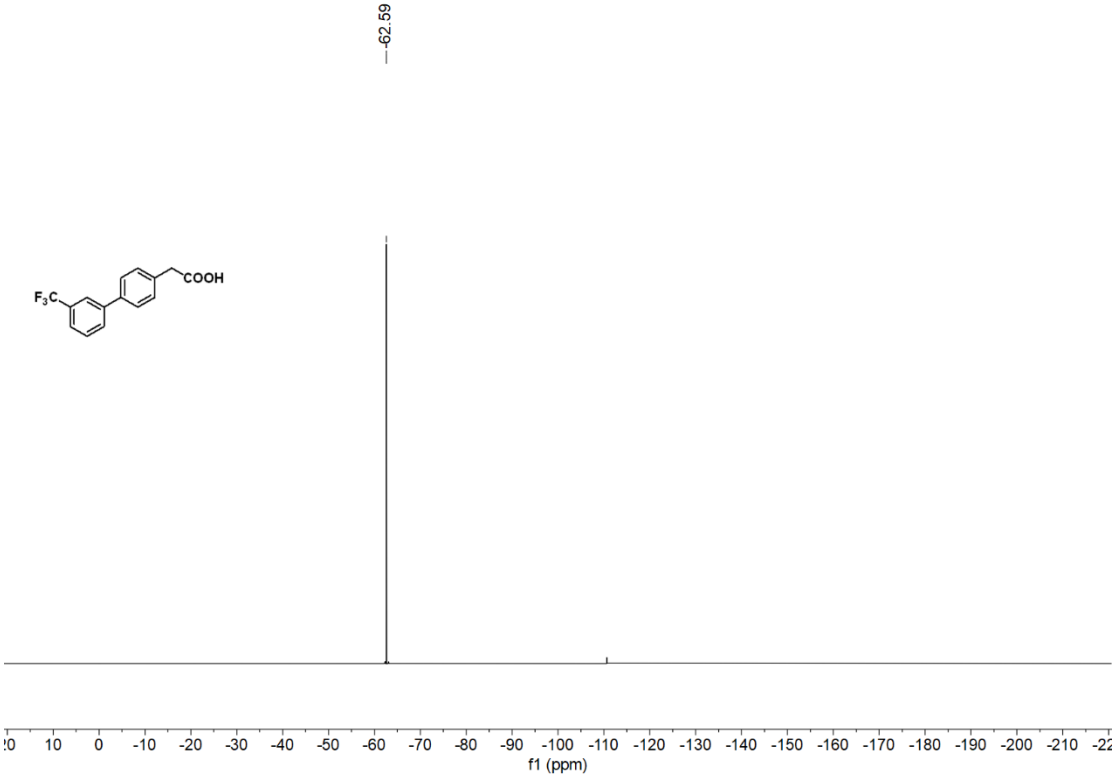
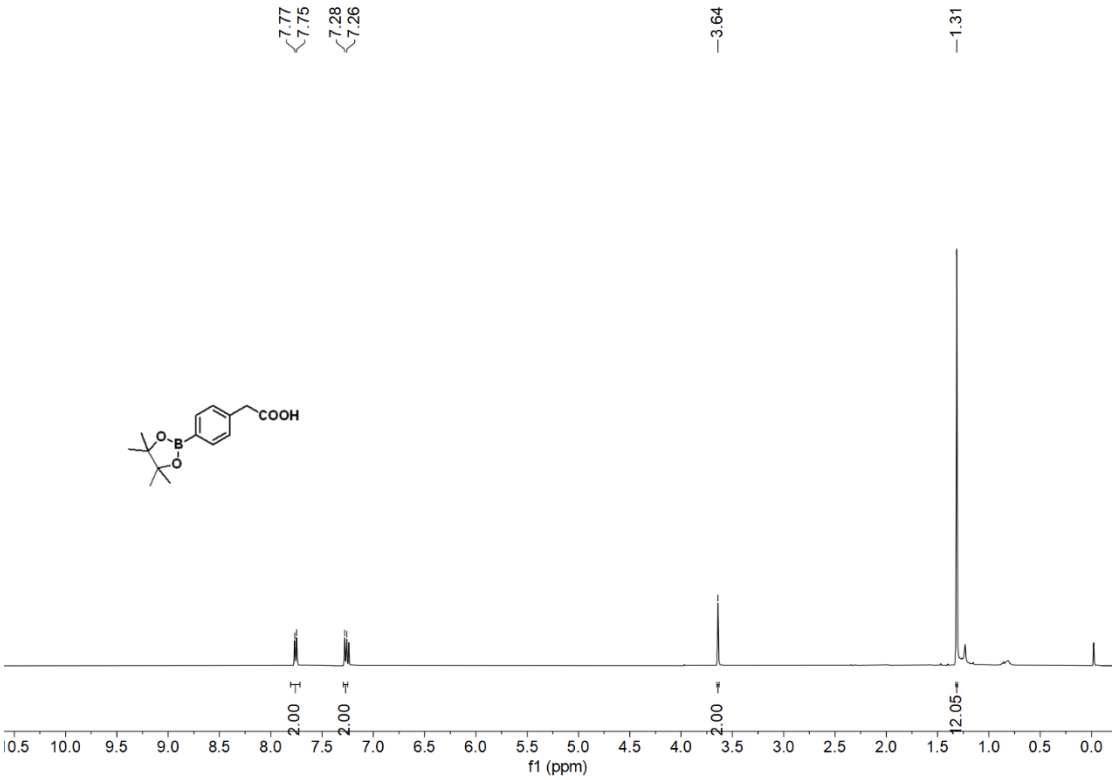
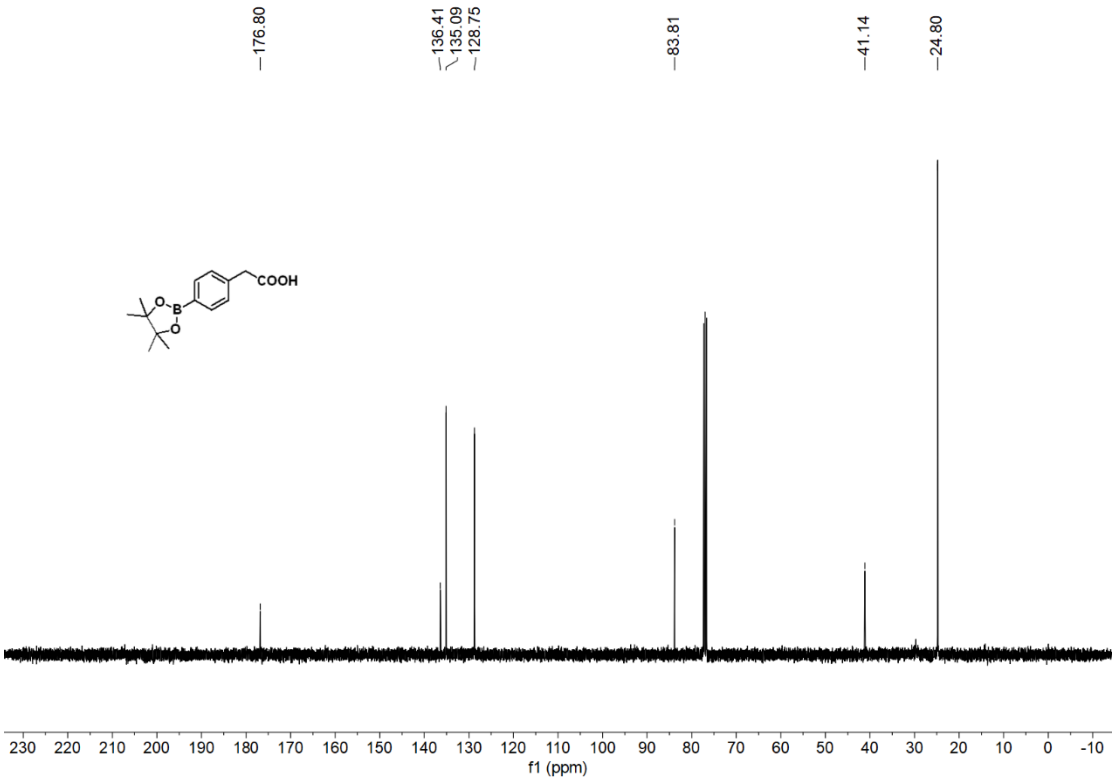
f1 (ppm)

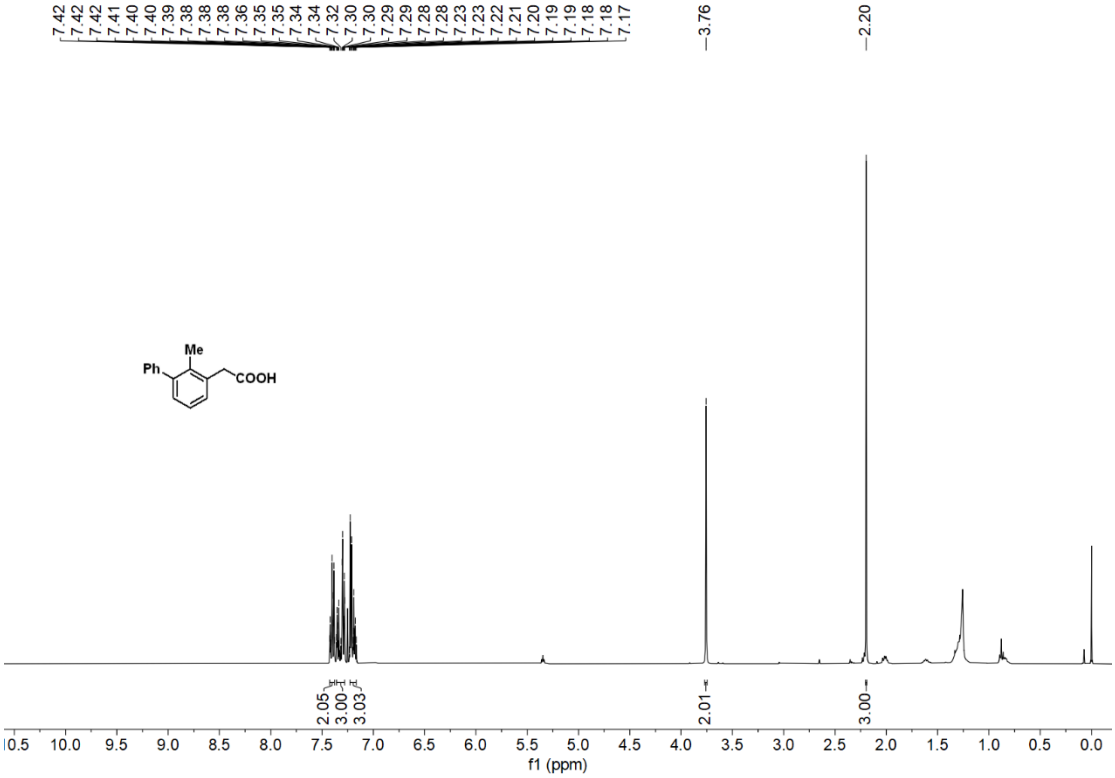

62.59
COOH
F3C
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22
f1 (ppm)

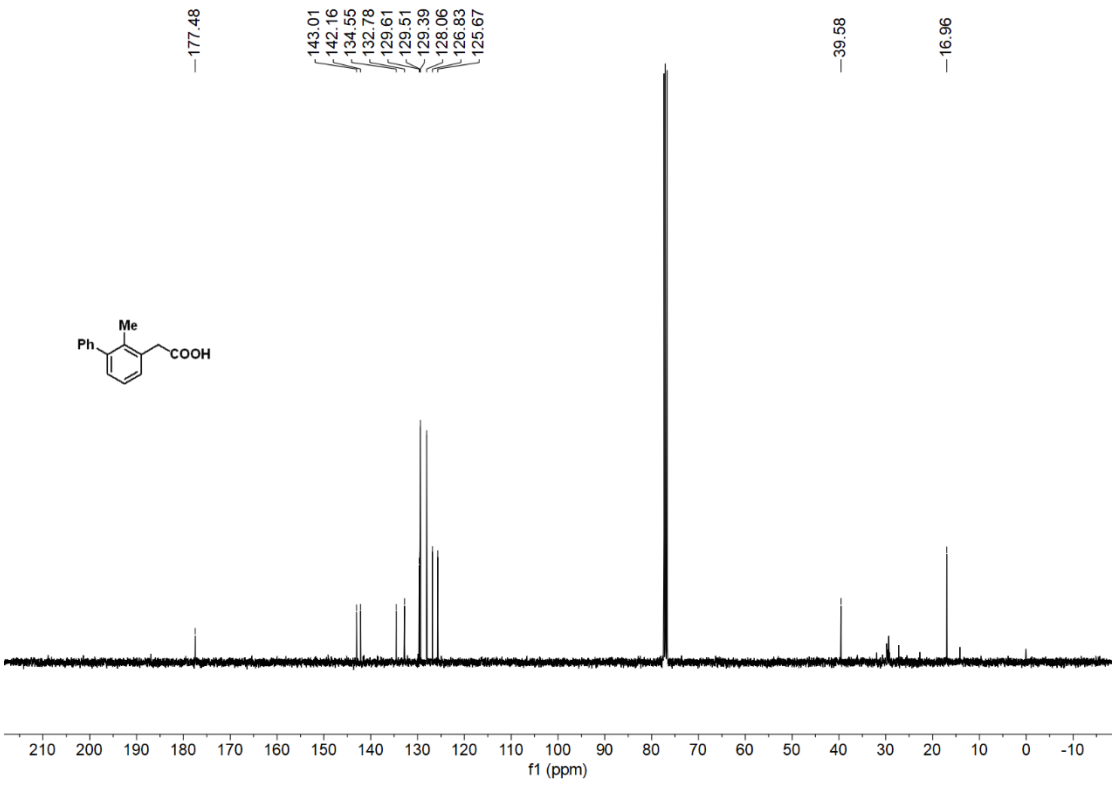
2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acetic acid (2f)



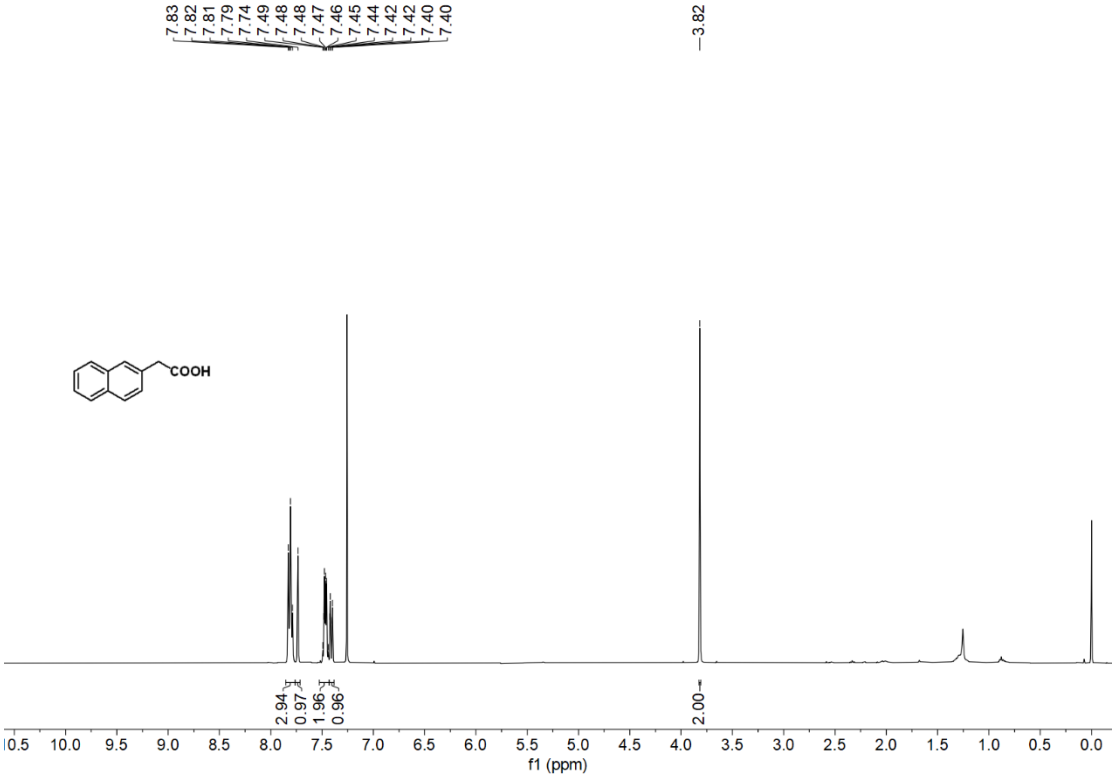


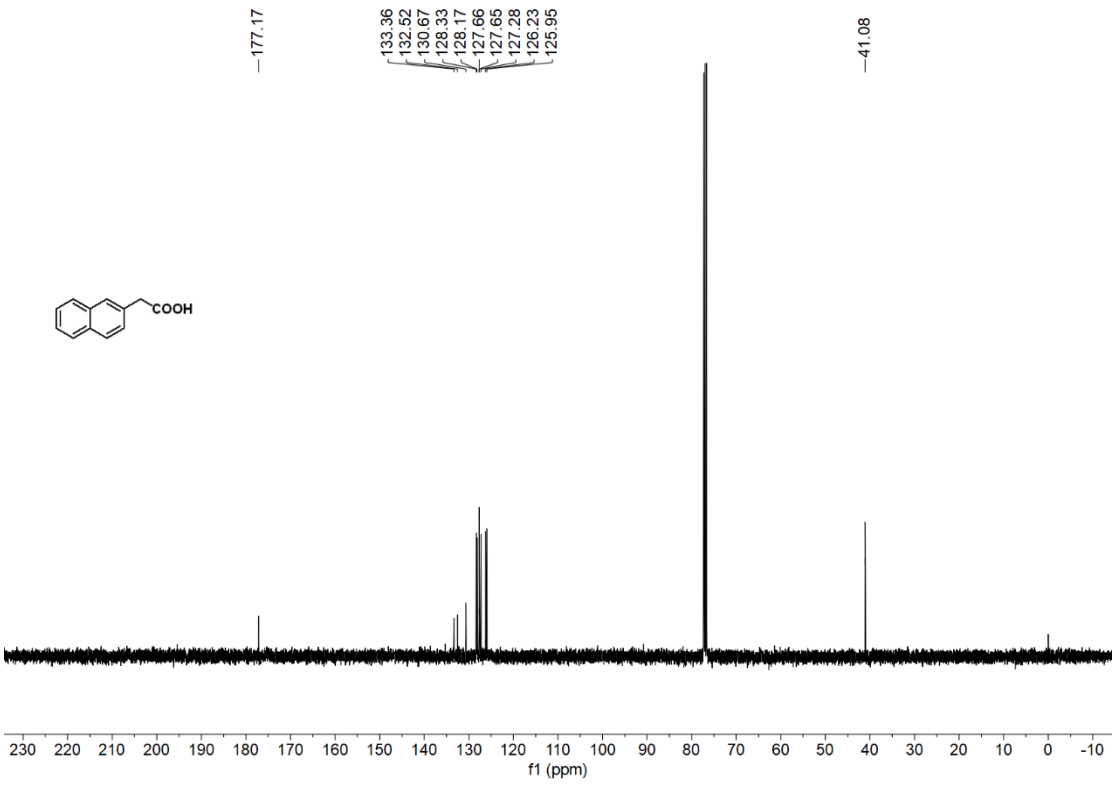
2-(2-methyl-[1,1'-biphenyl]-3-yl)acetic acid (2g)



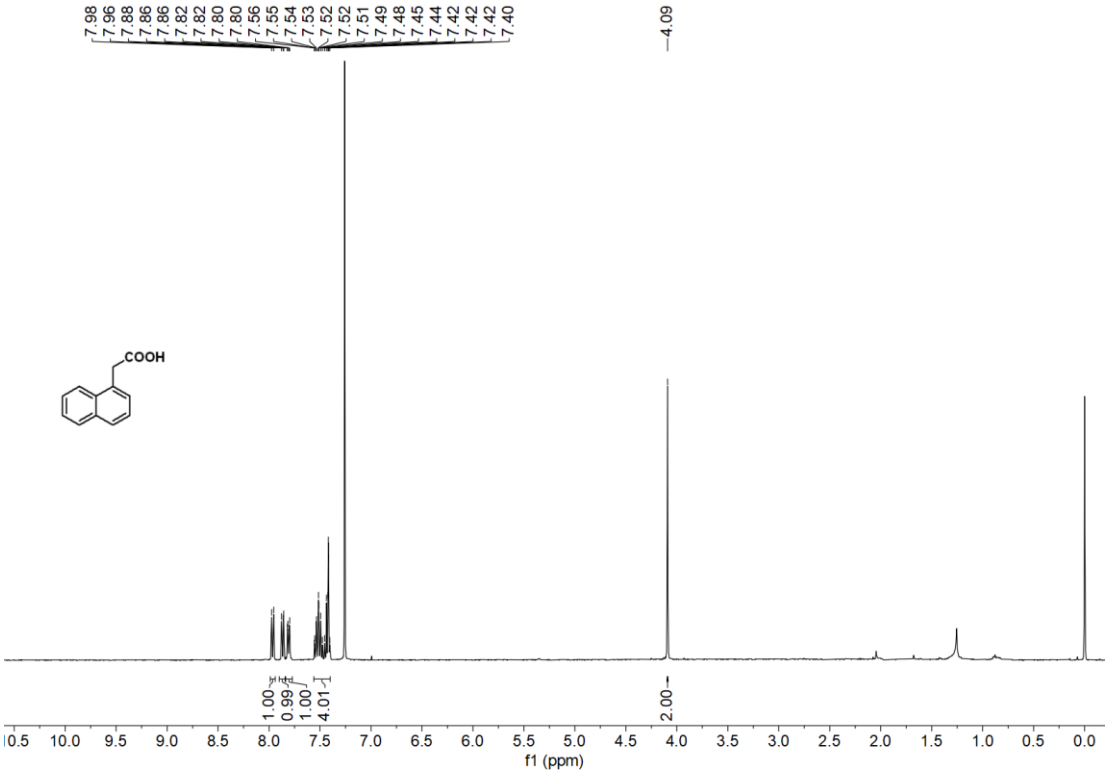


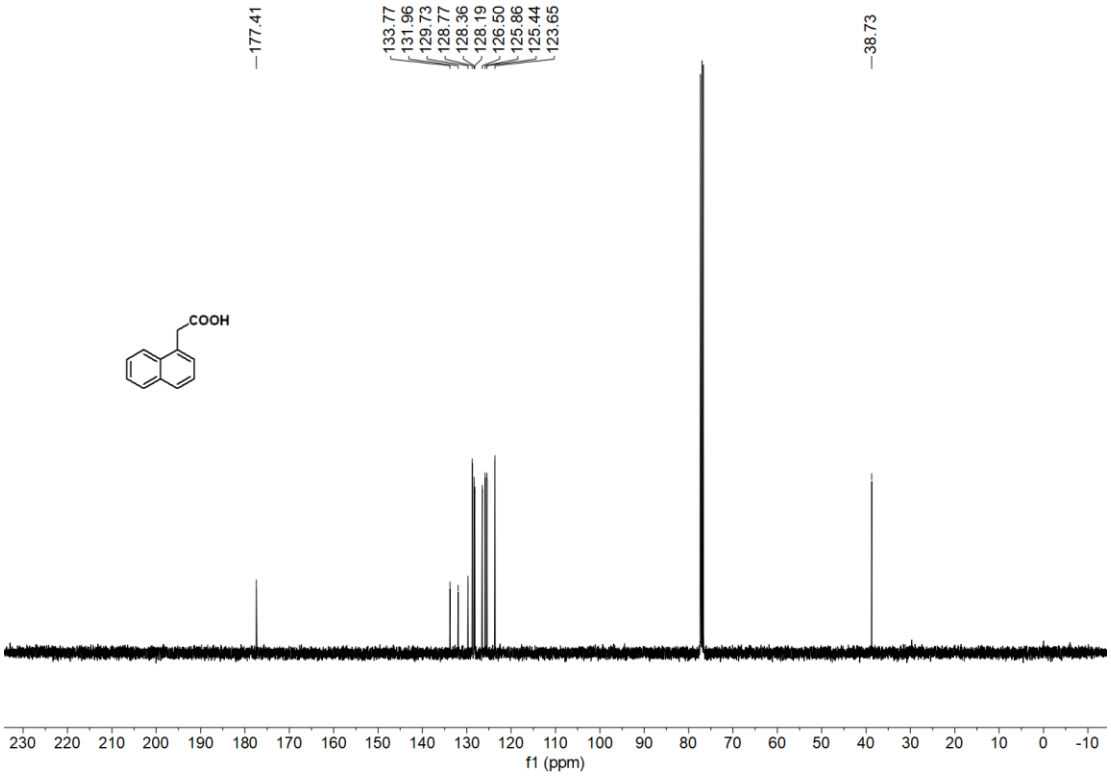
2-(naphthalen-2-yl)acetic acid (2h)



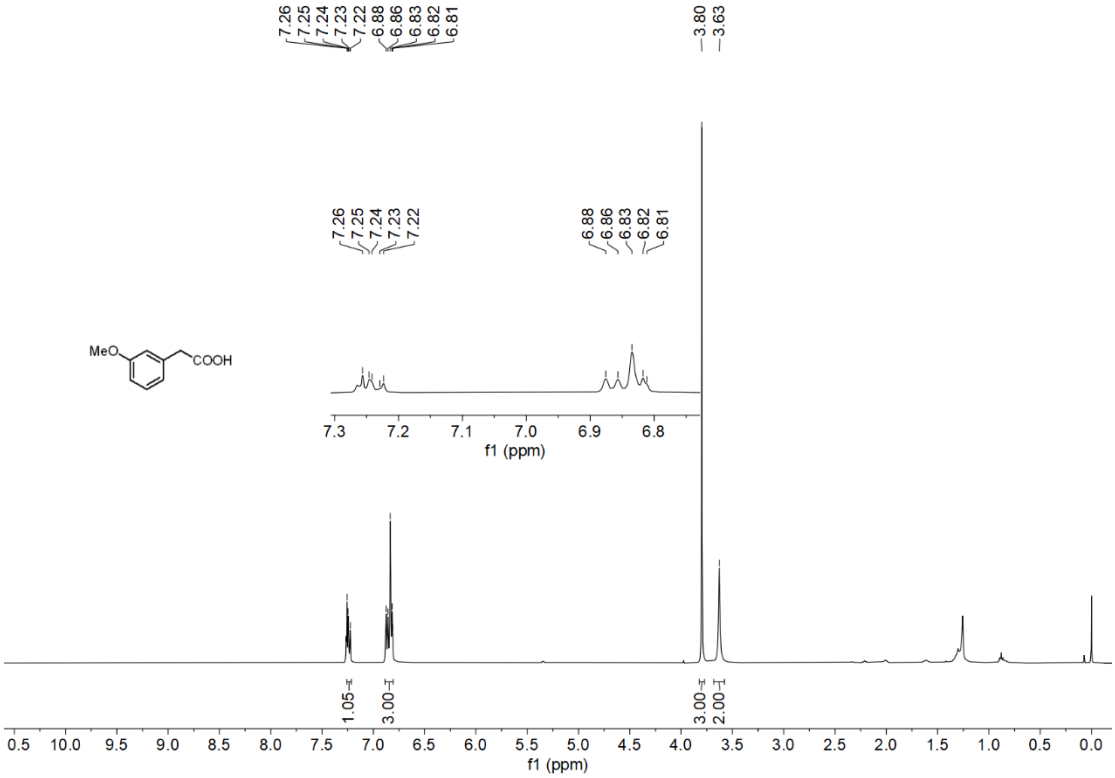


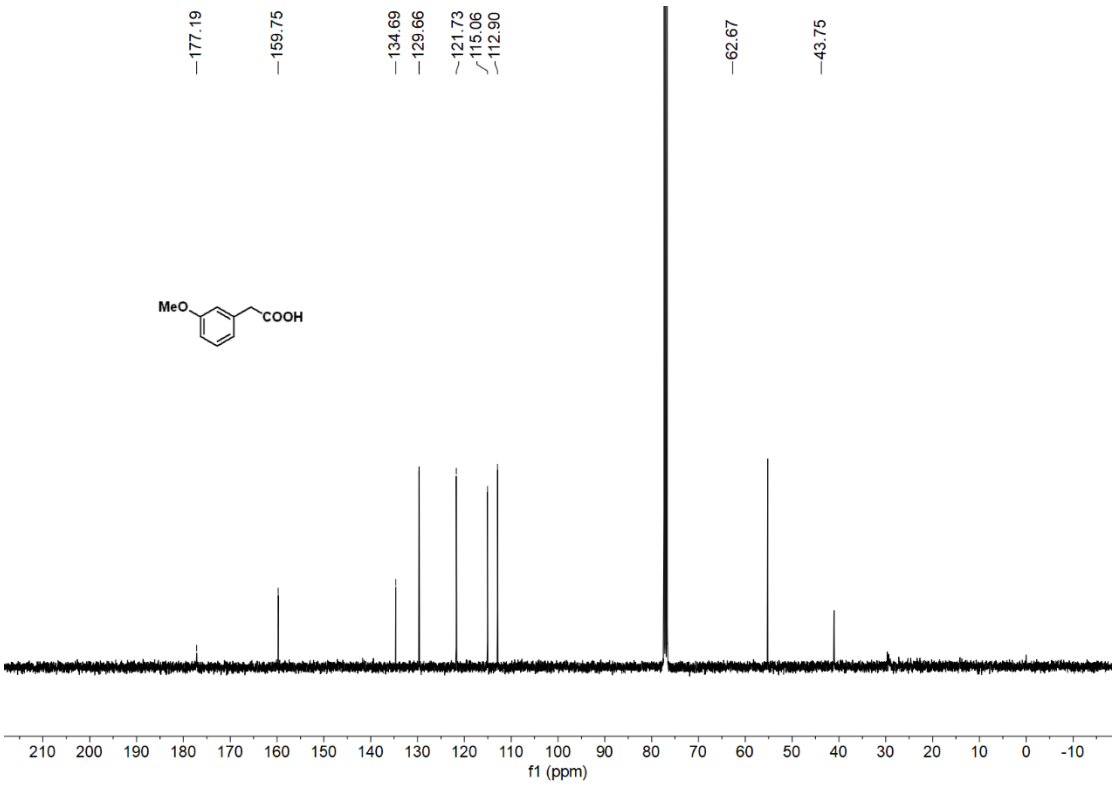
2-(naphthalen-1-yl)acetic acid (2i)



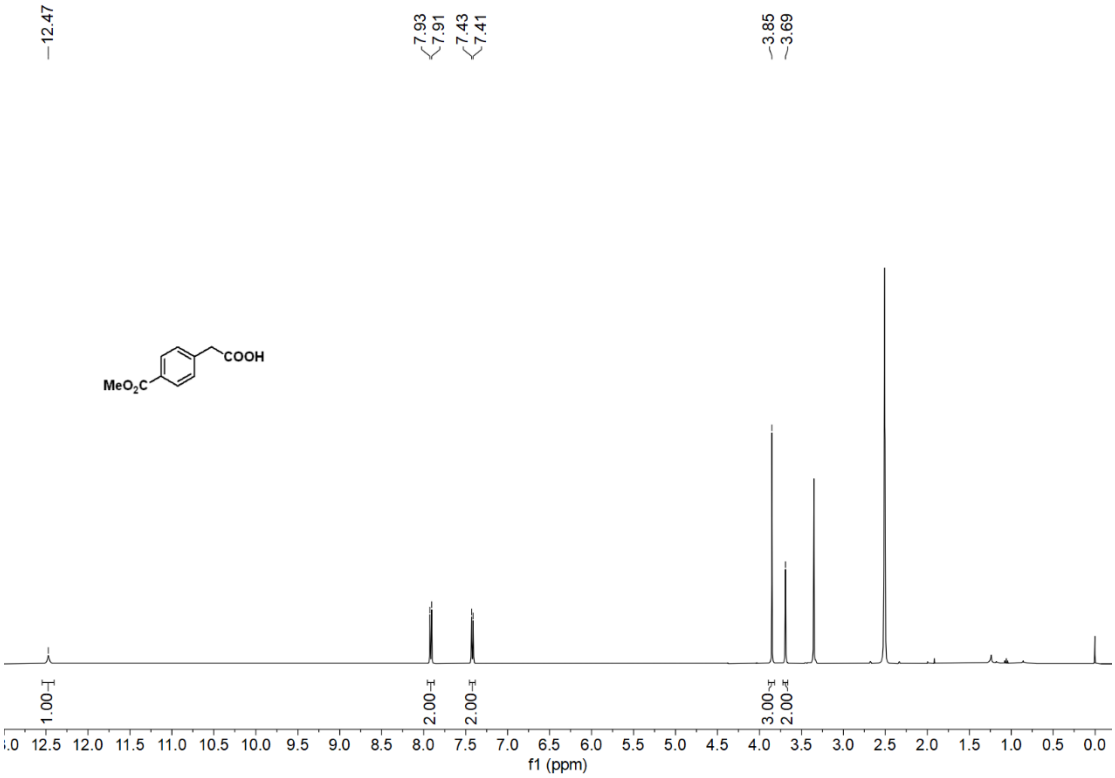


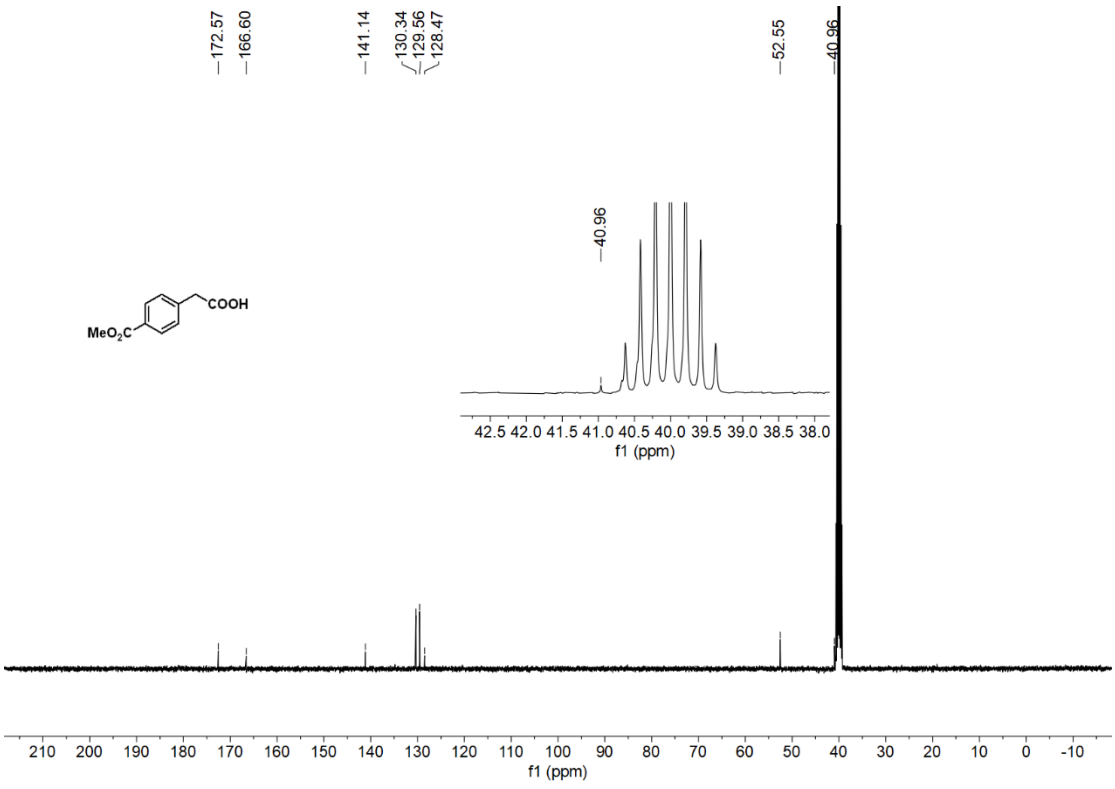
2-(3-methoxyphenyl)acetic acid (2j)



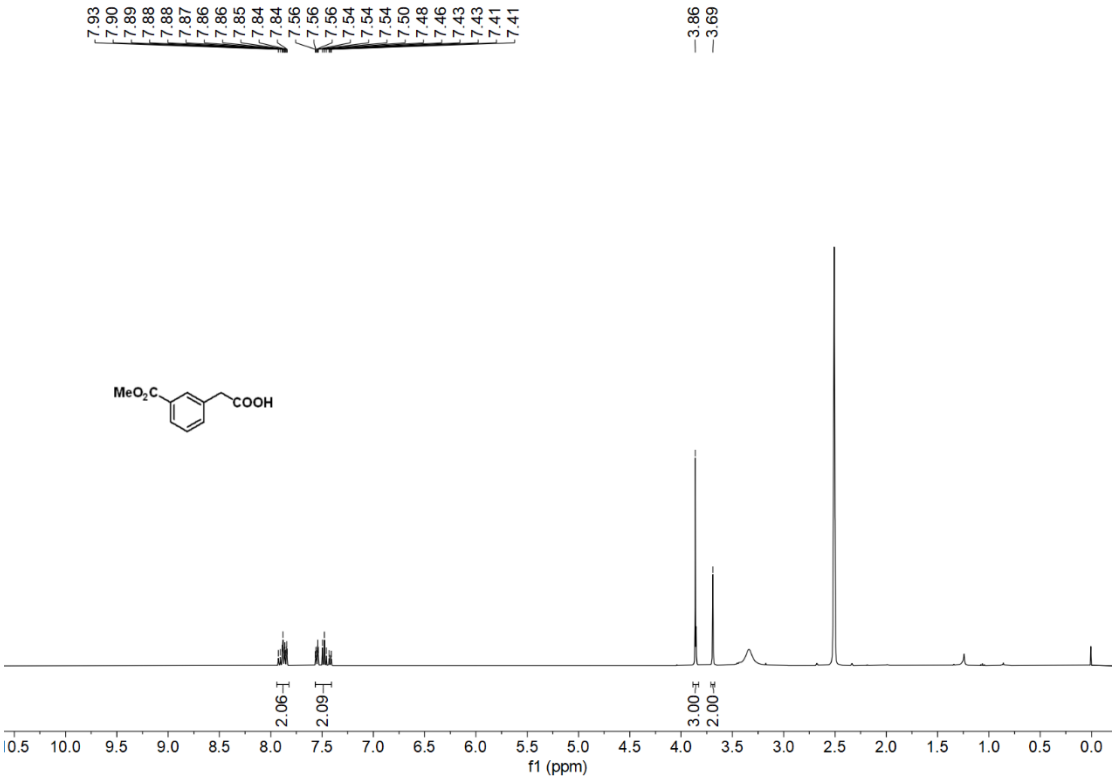


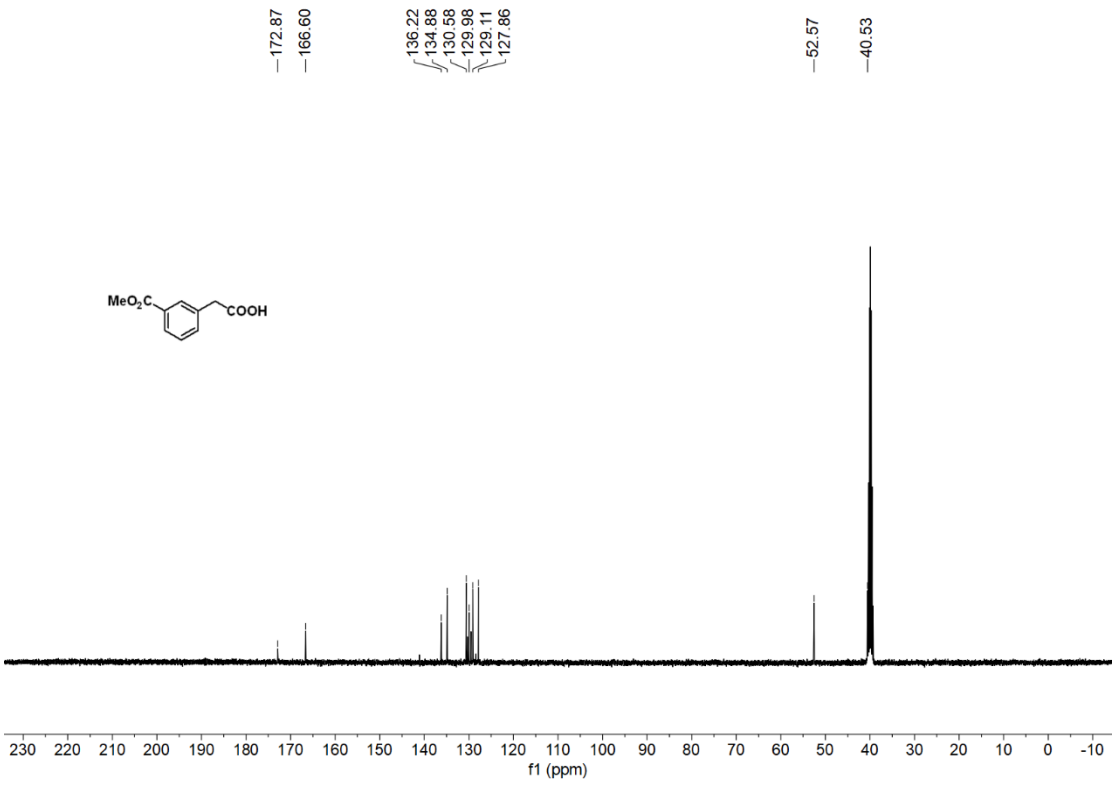
2-(4-(methoxycarbonyl)phenyl)acetic acid (2k)



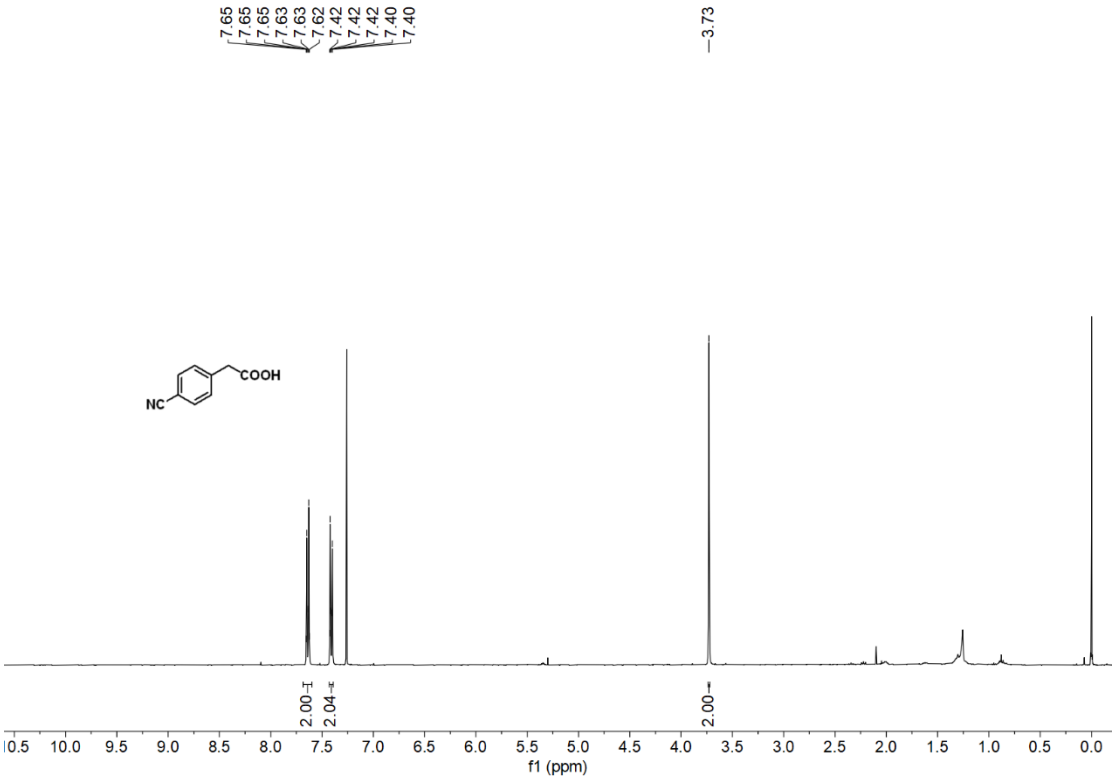


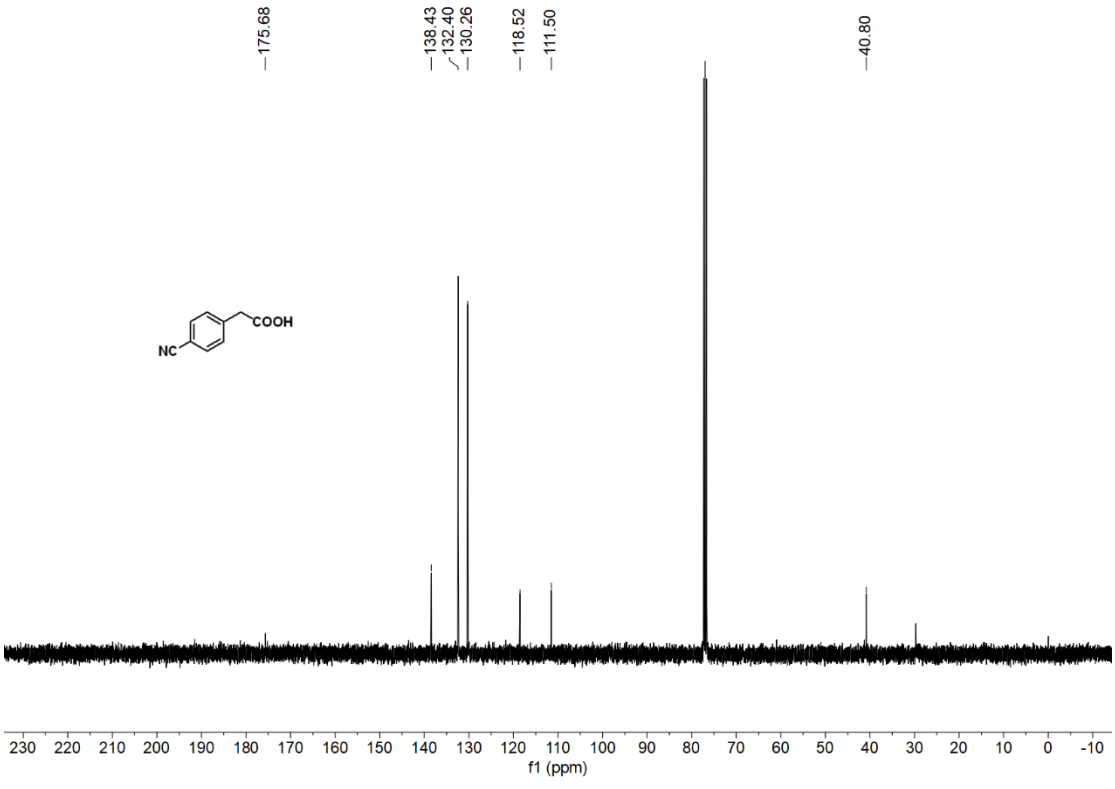
2-(3-(methoxycarbonyl)phenyl)acetic acid (2l)



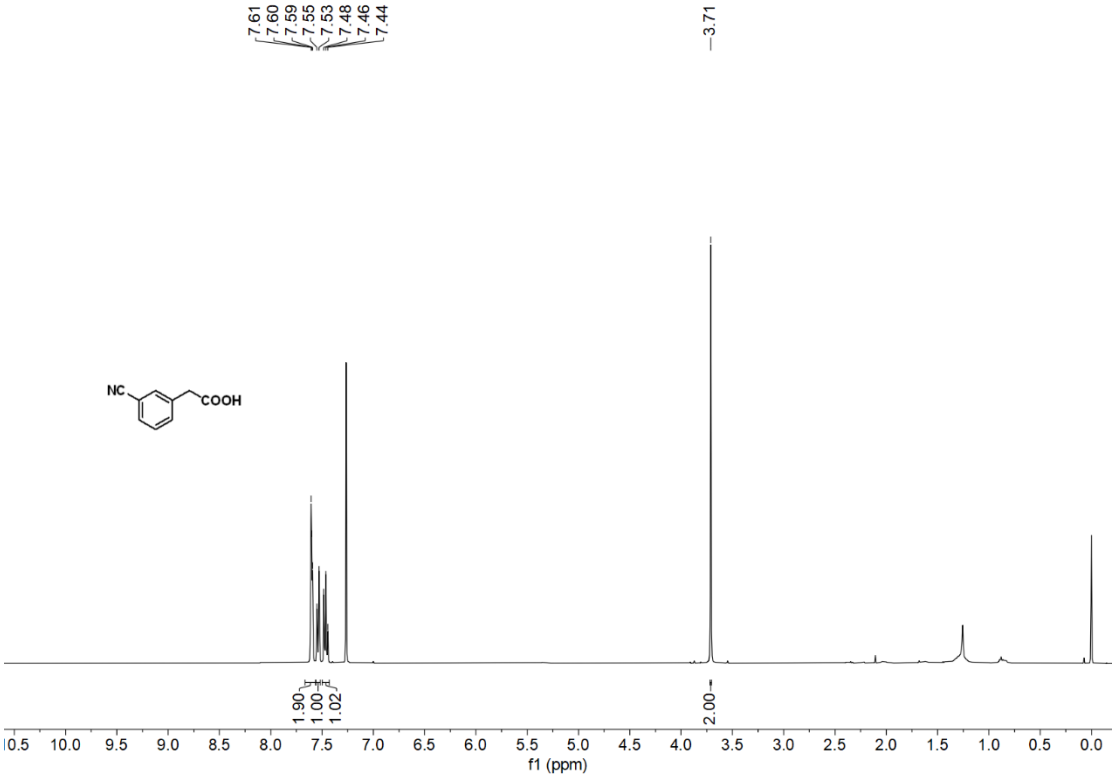


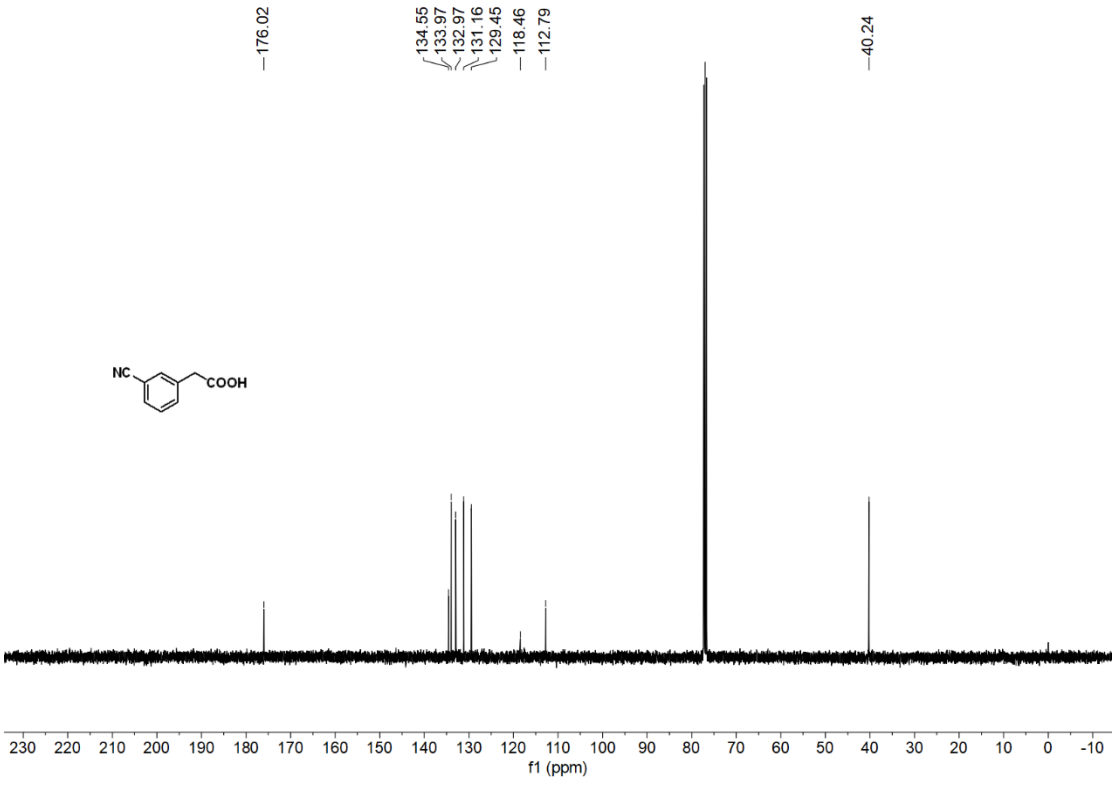
2-(4-cyanophenyl)acetic acid (2m)



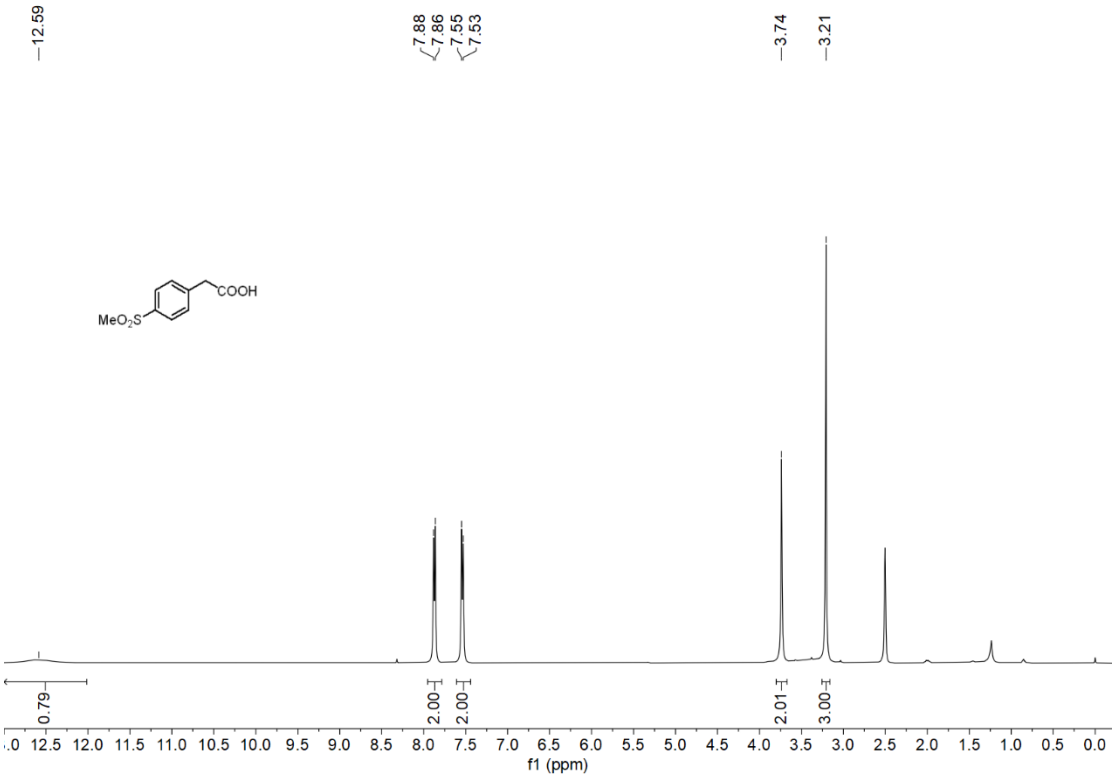


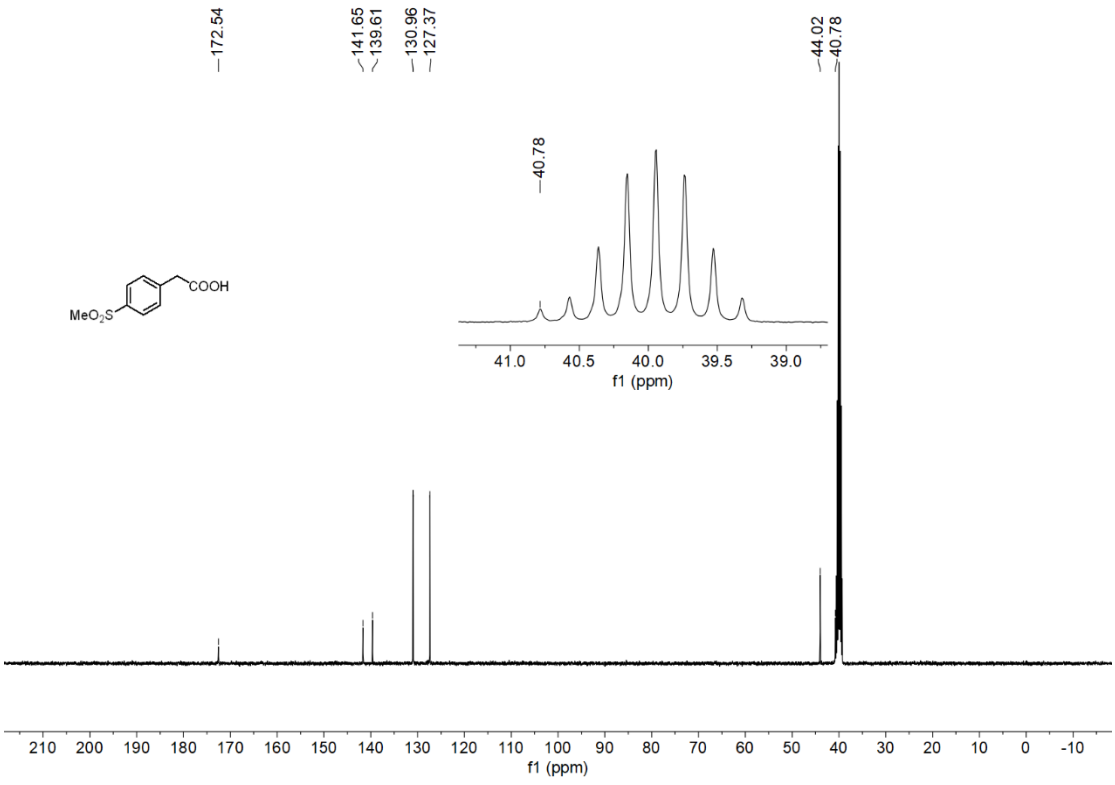
2-(3-cyanophenyl)acetic acid (2n)



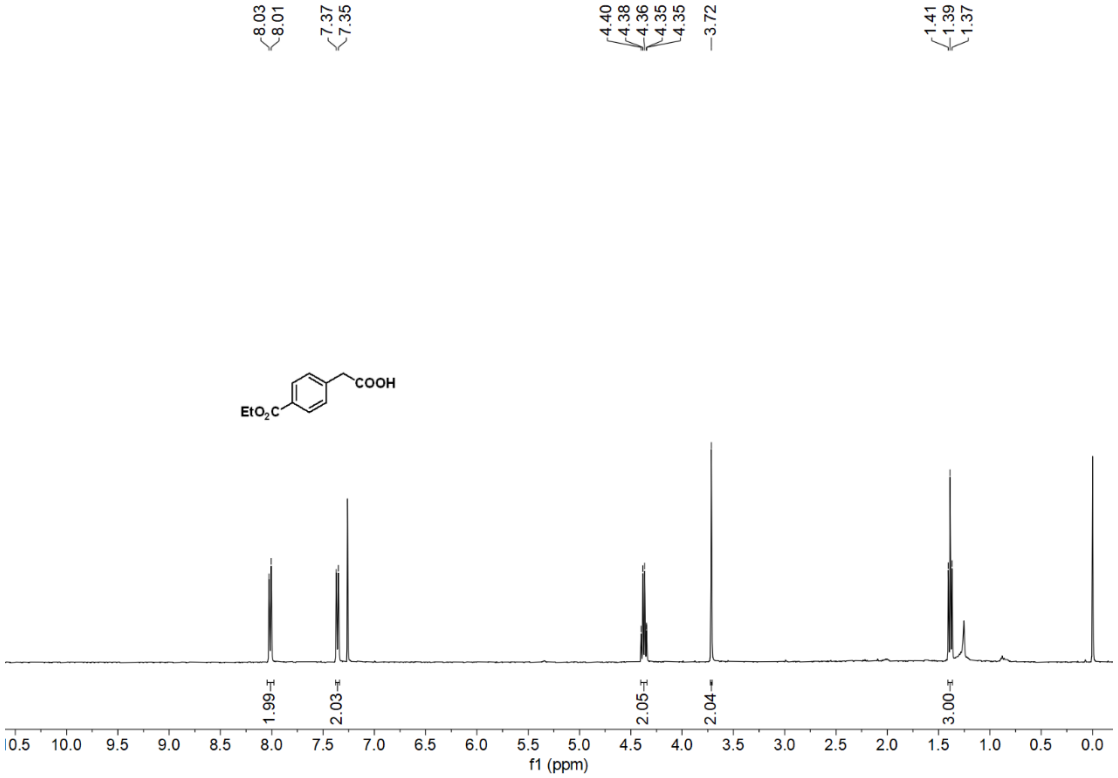


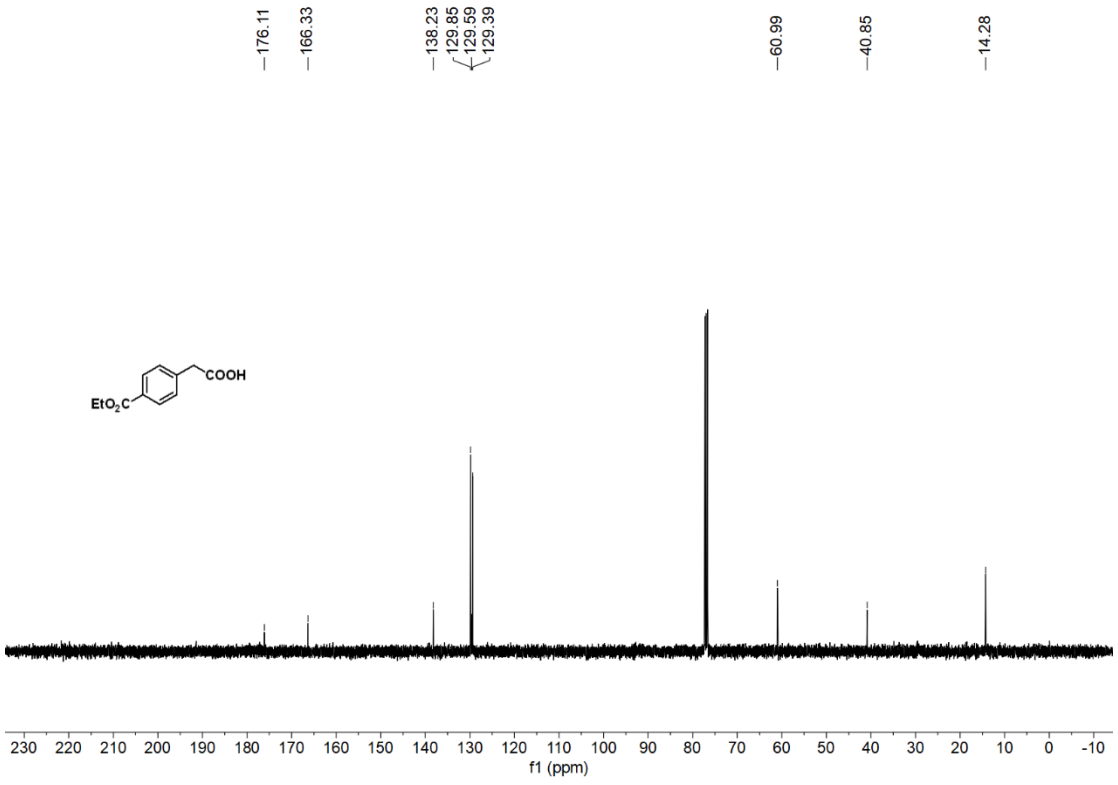
2-(4-(methylsulfonyl)phenyl)acetic acid (2o)



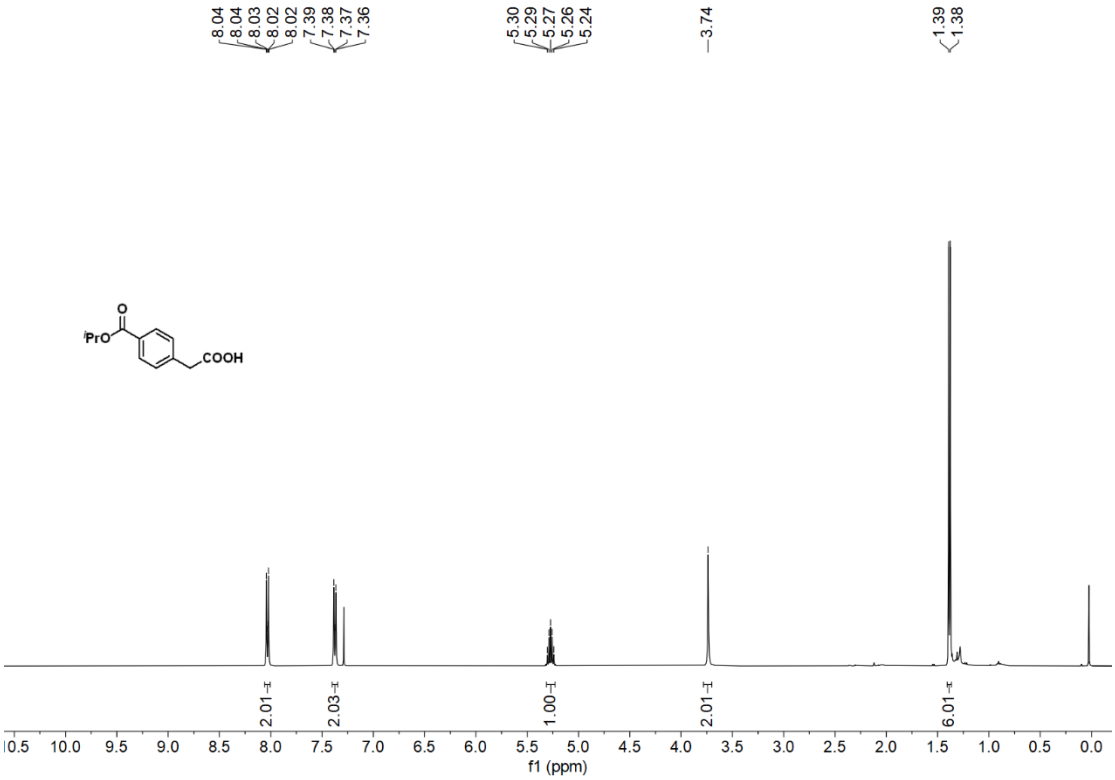


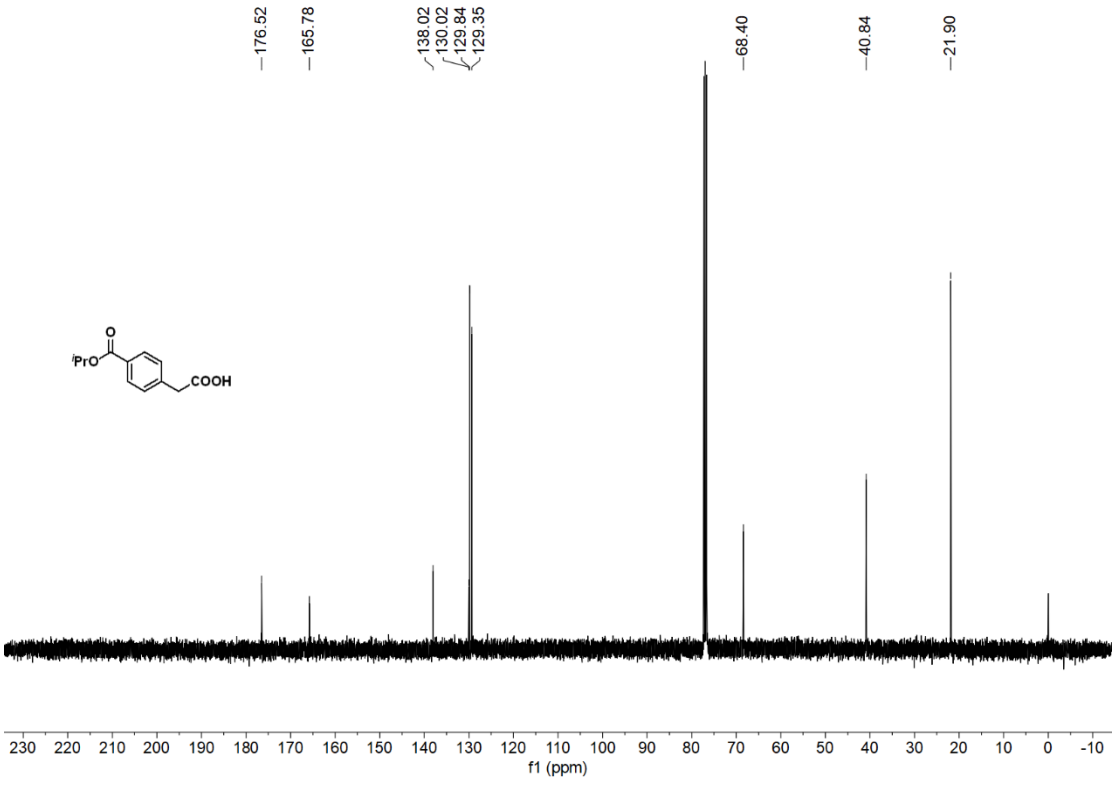
2-(4-(ethoxycarbonyl)phenyl)acetic acid (2p)



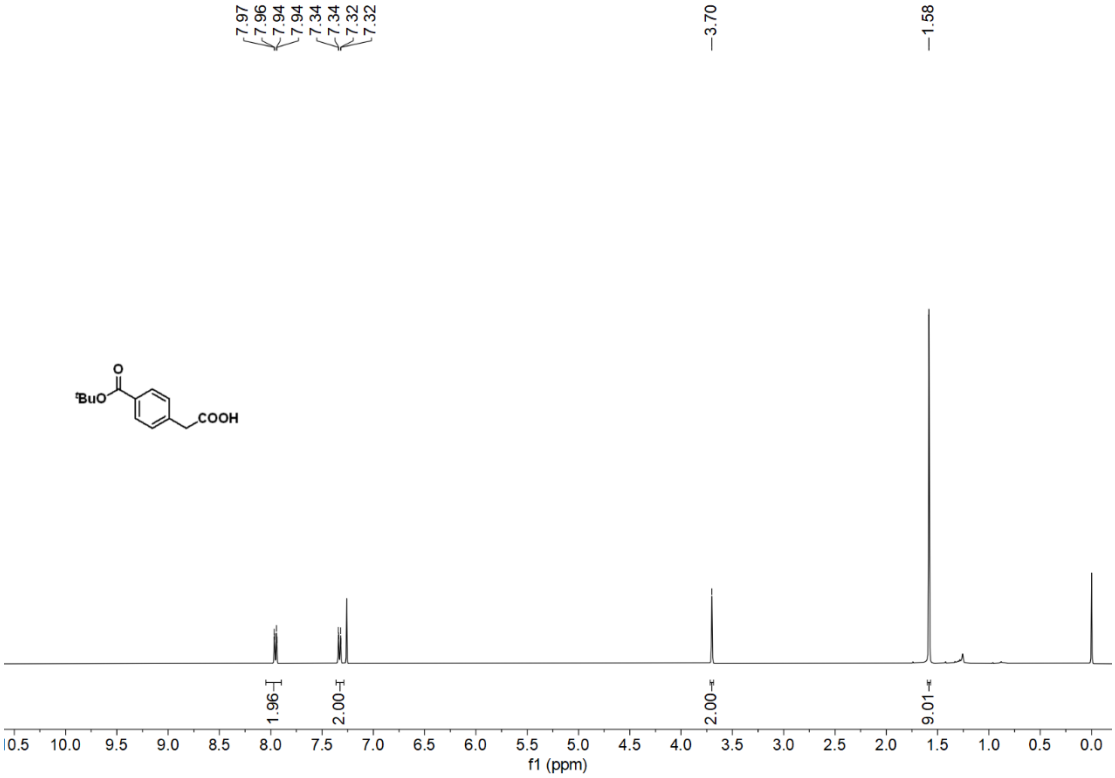


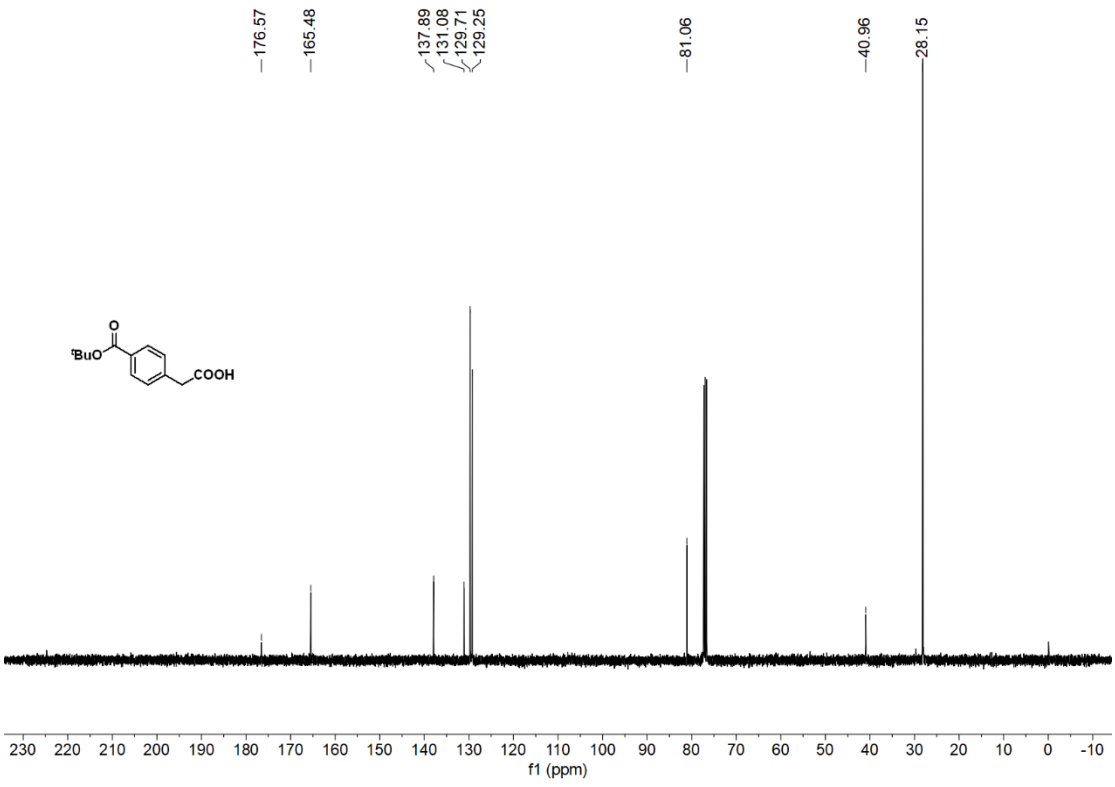
2-(4-(isopropoxycarbonyl)phenyl)acetic acid (2q)



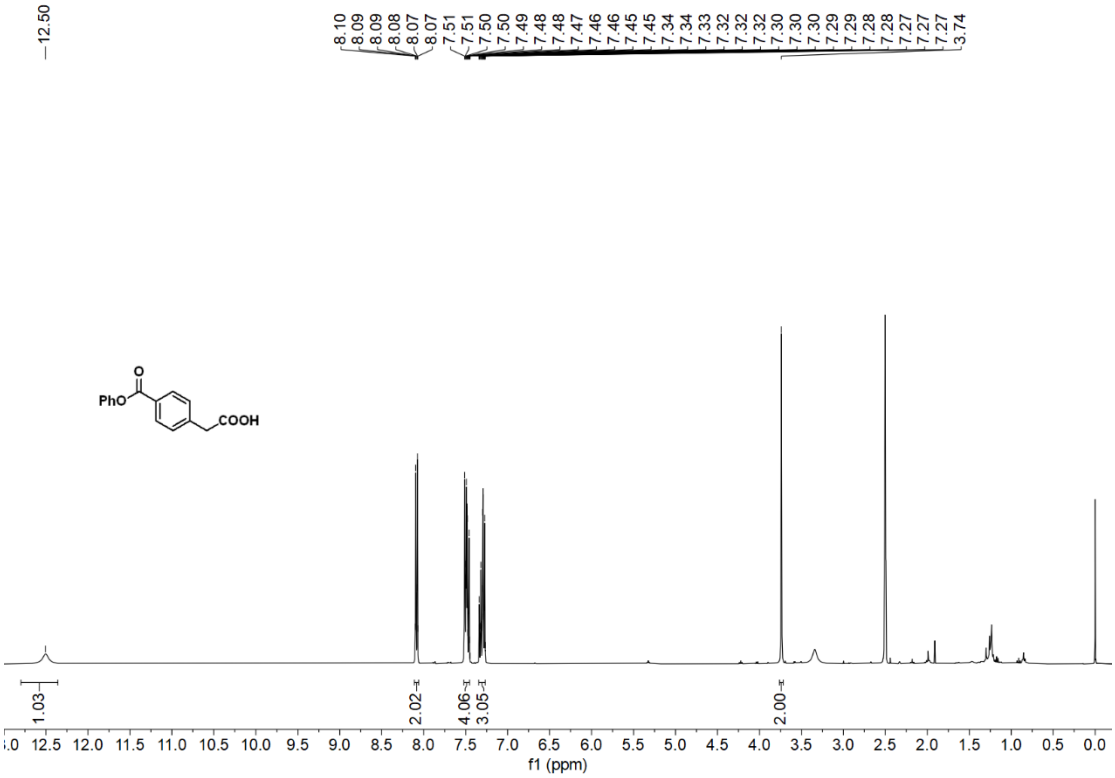


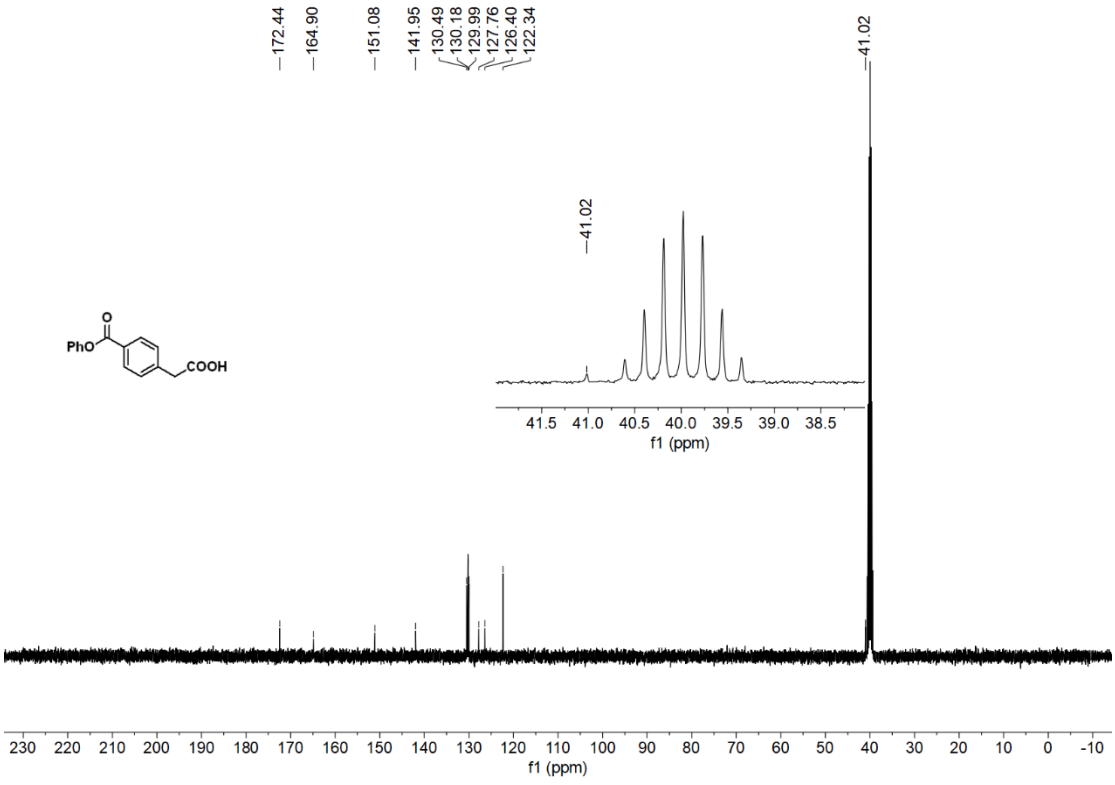
2-(4-(tert-butoxycarbonyl)phenyl)acetic acid (2r)



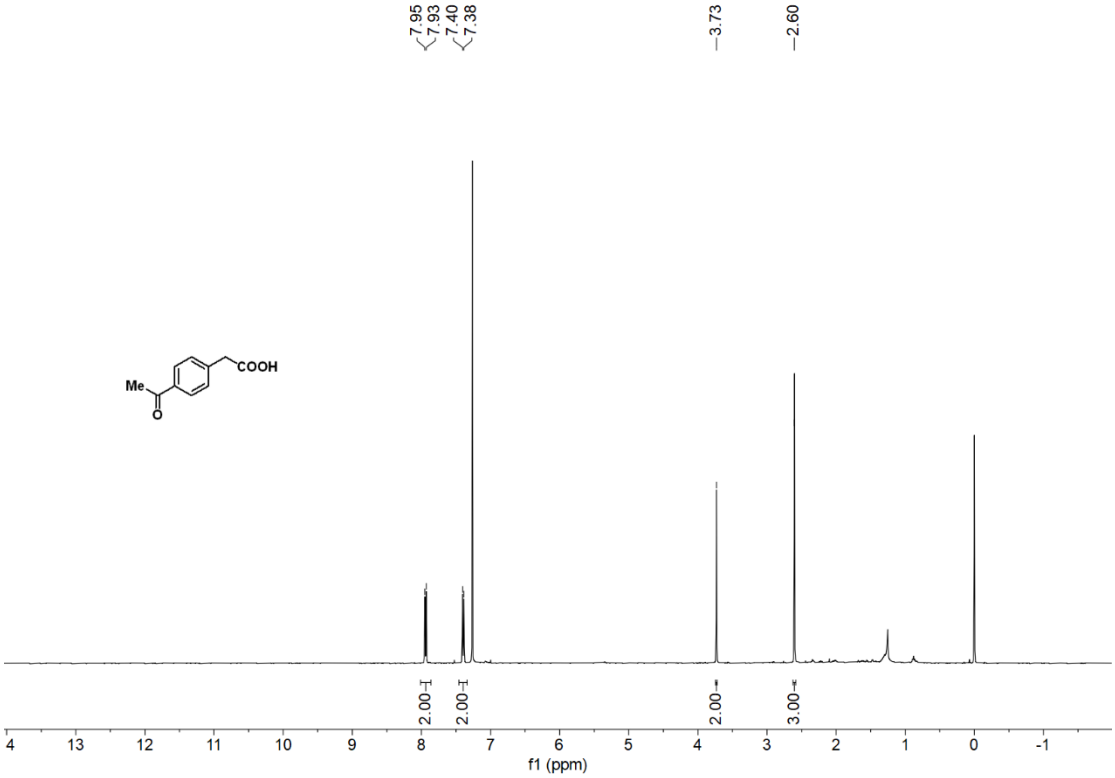


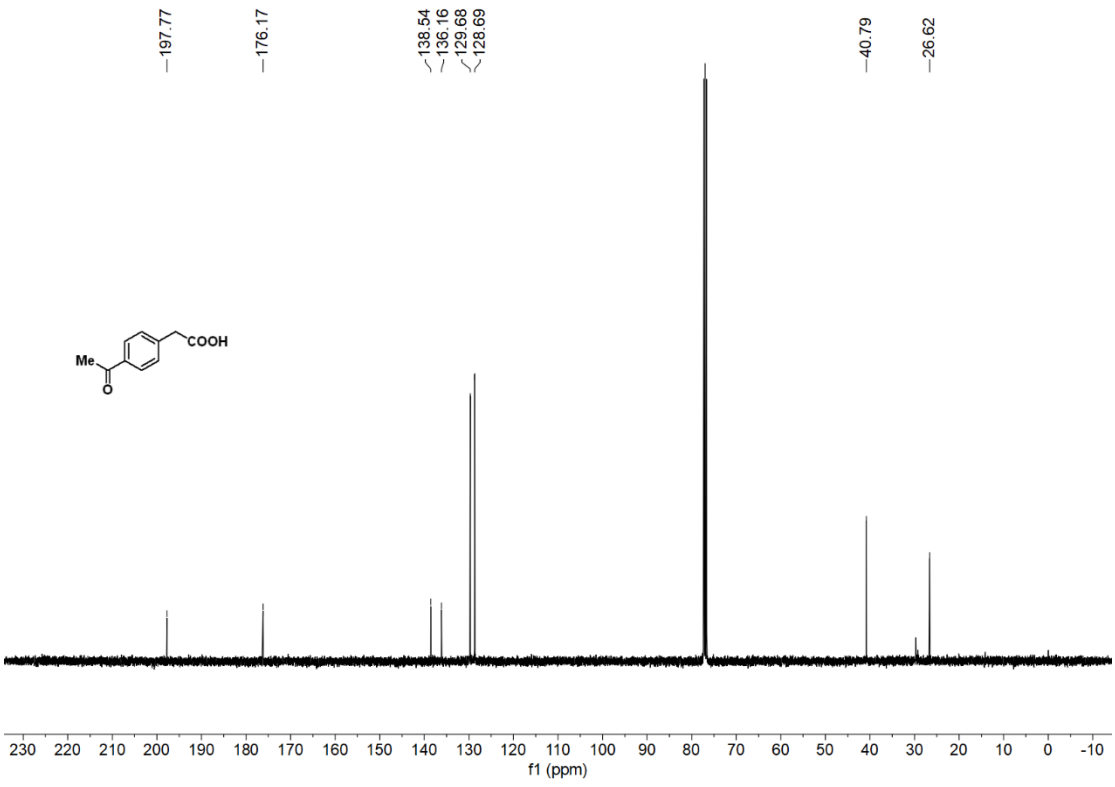
2-(4-(phenoxycarbonyl)phenyl)acetic acid (2s)



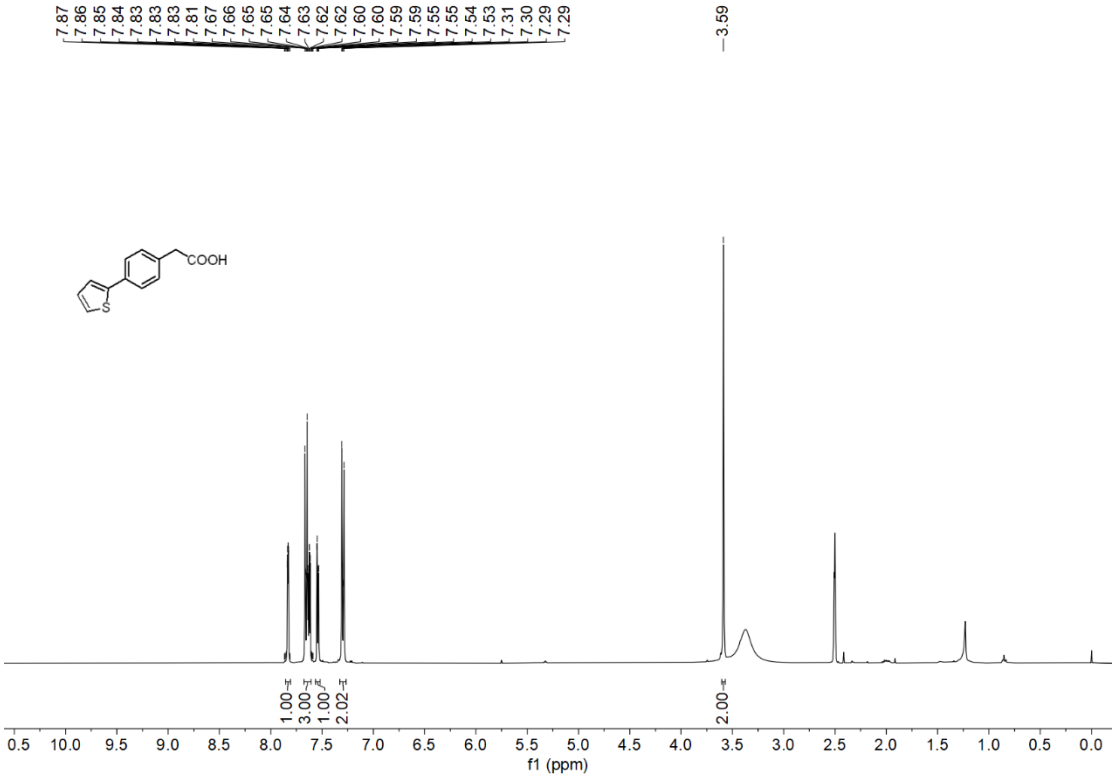


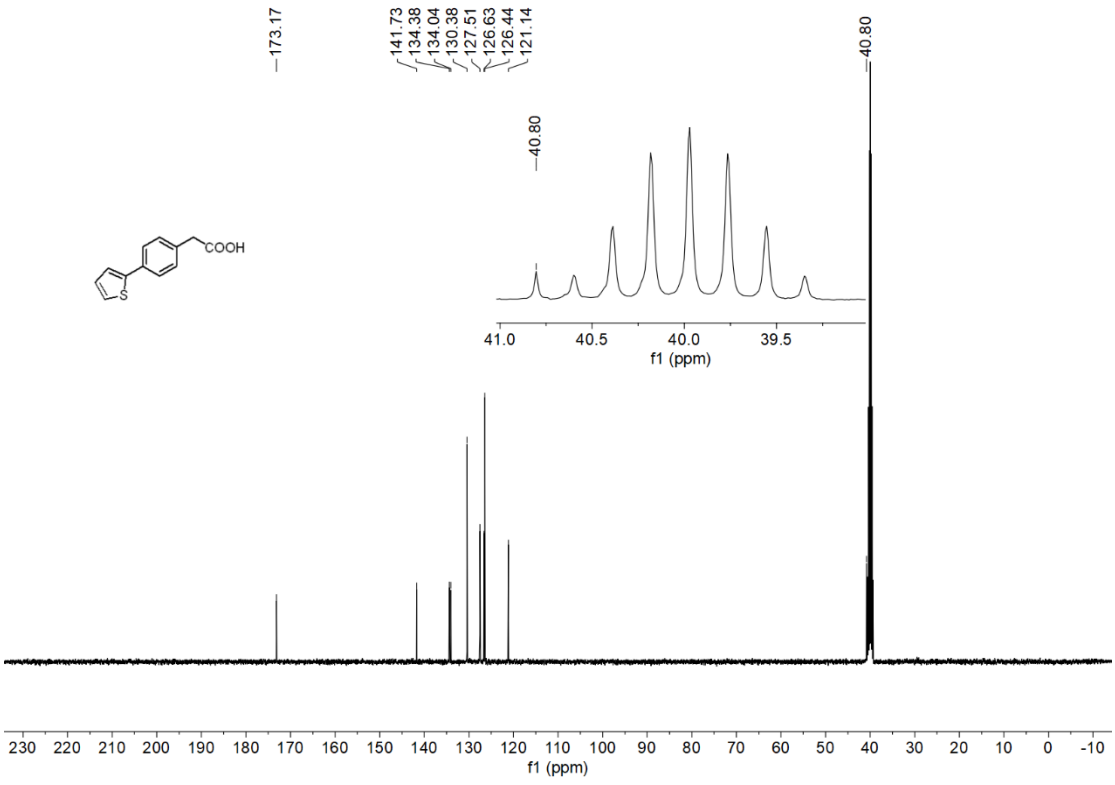
2-(4-acetylphenyl)acetic acid (2t)



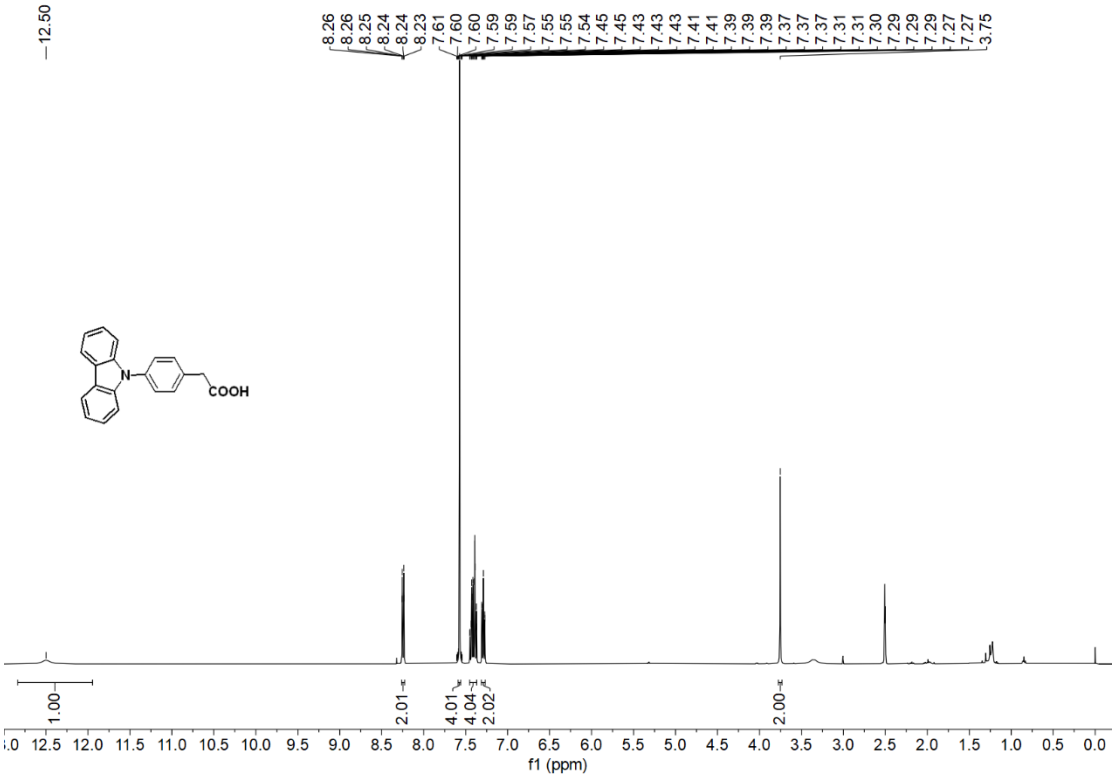


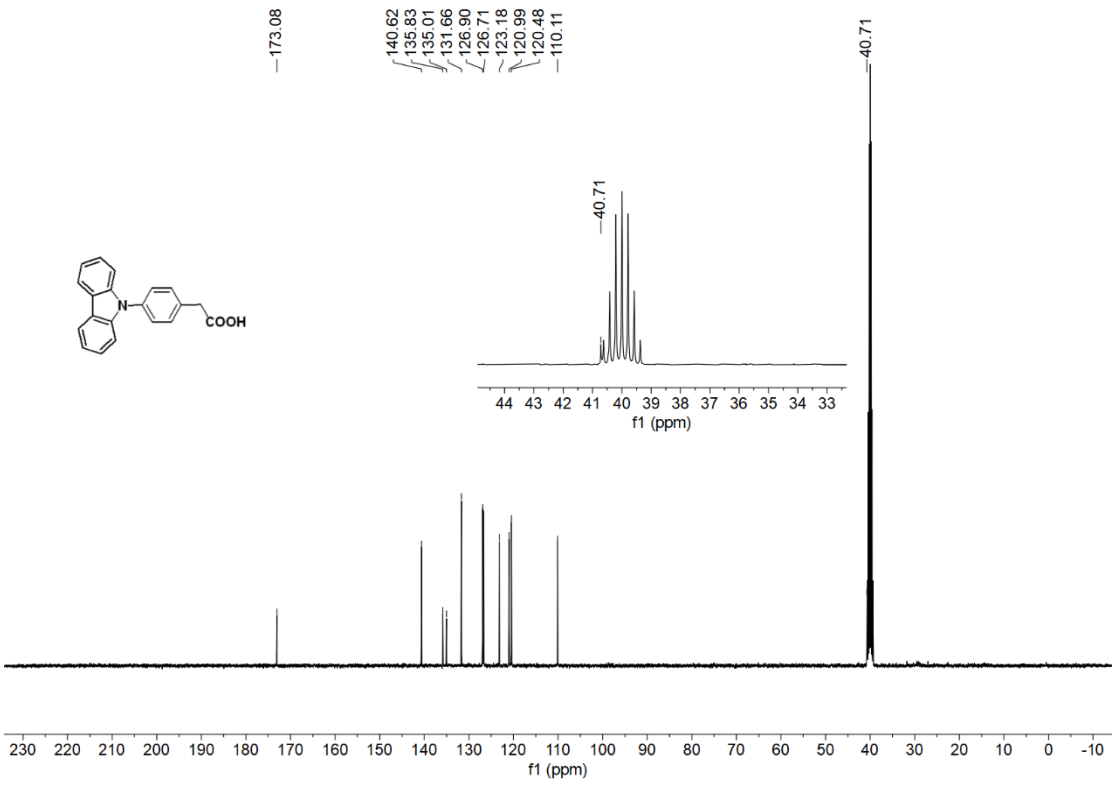
2-(4-(thiophen-2-yl)phenyl)acetic acid (2u)



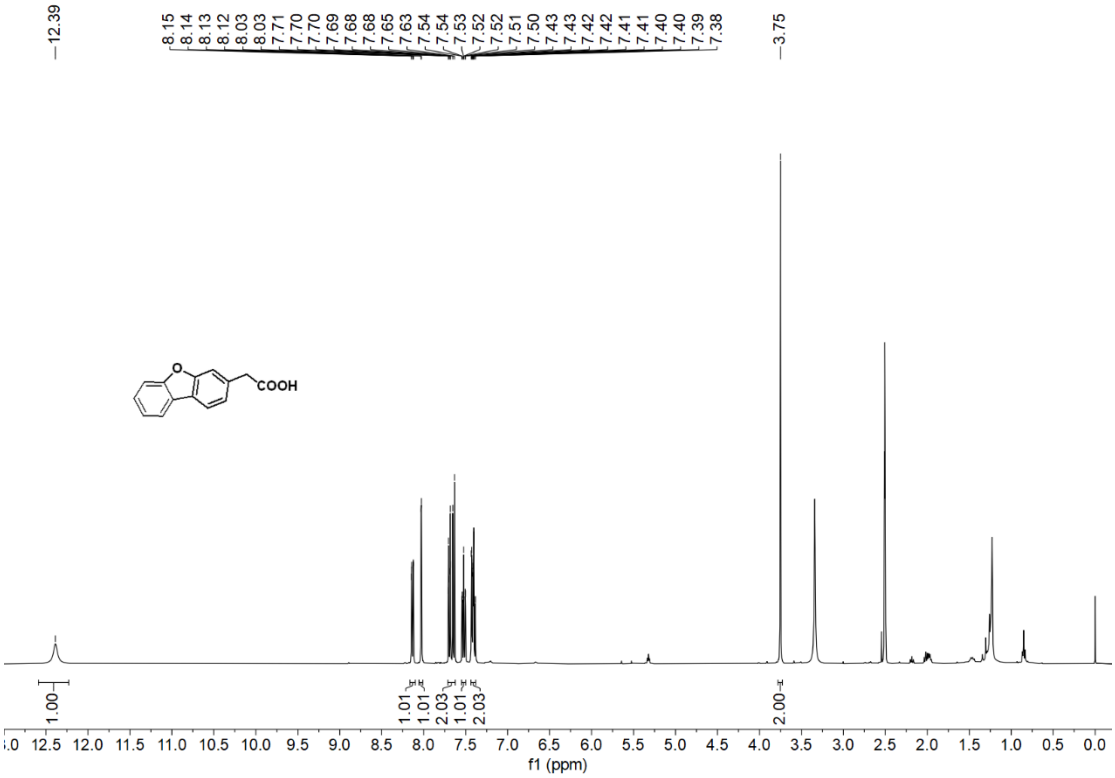


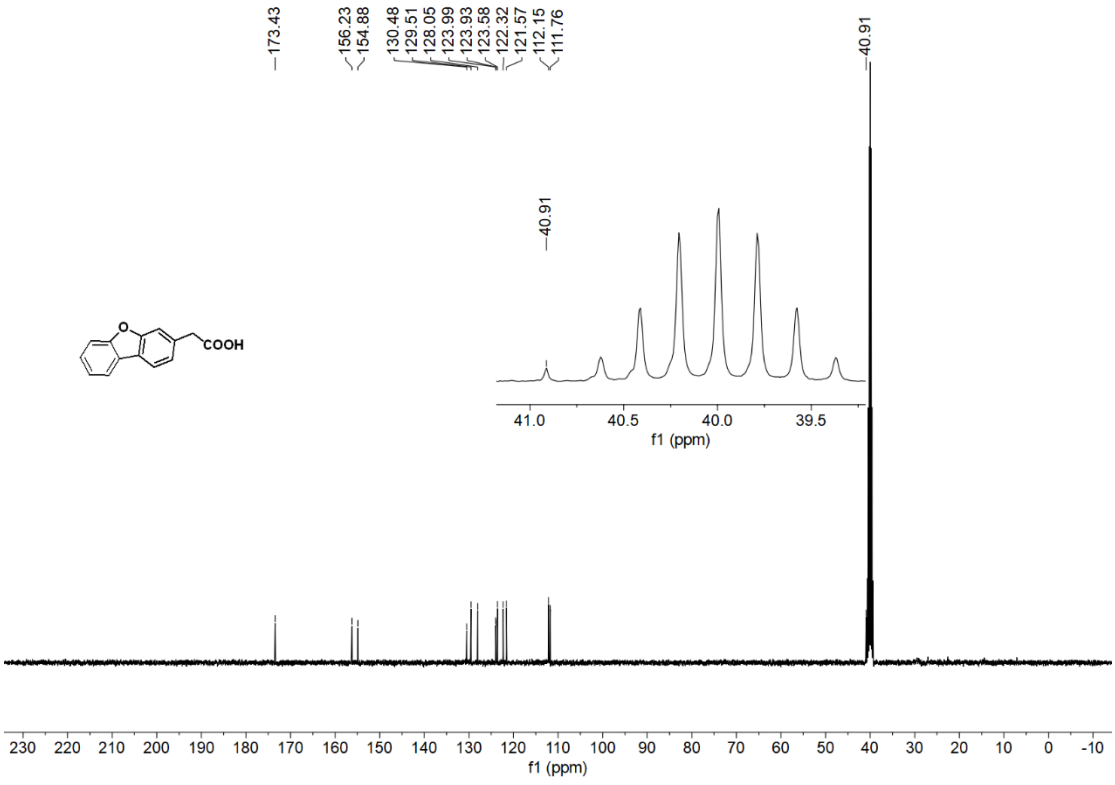
2-(4-(9H-carbazol-9-yl)phenyl)acetic acid (2v)



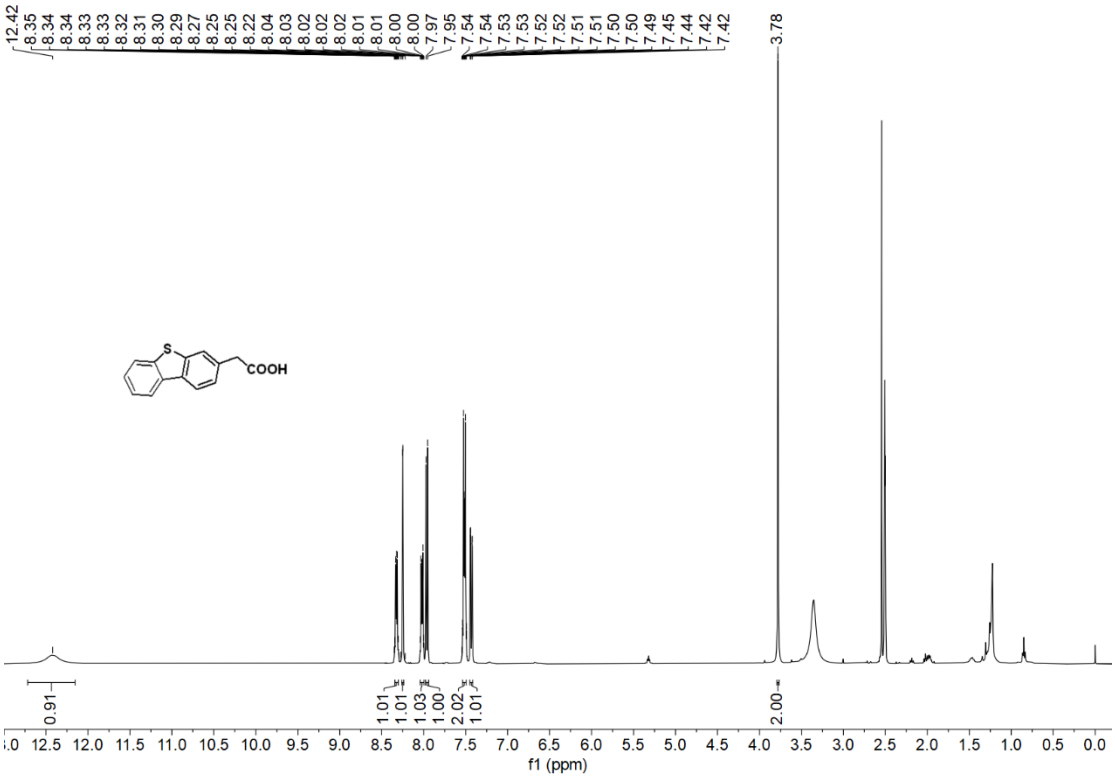


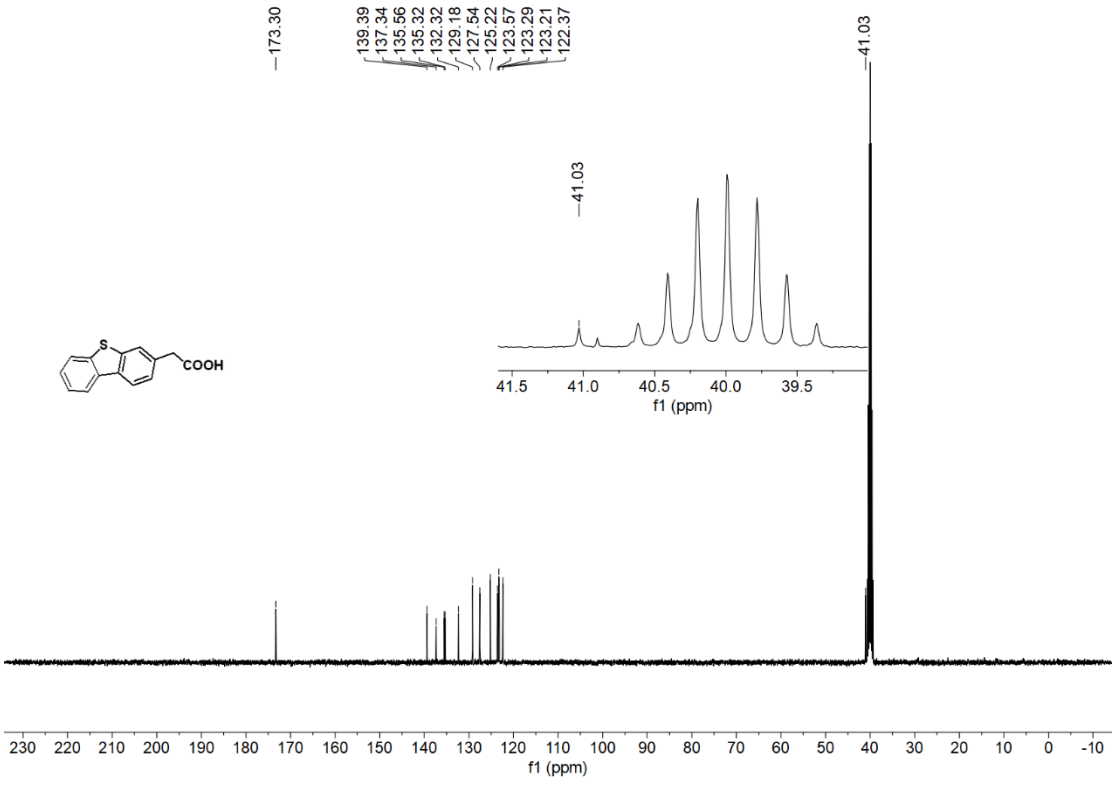
2-(dibenzo[b,d]furan-3-yl)acetic acid (2w)



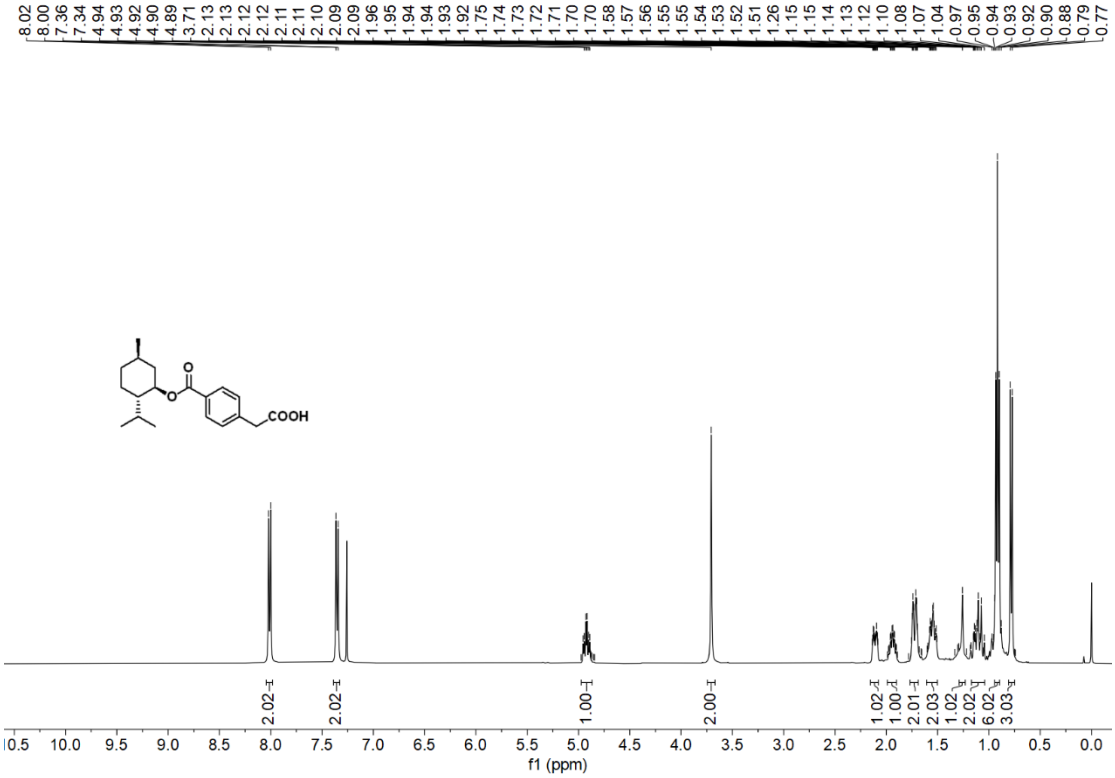


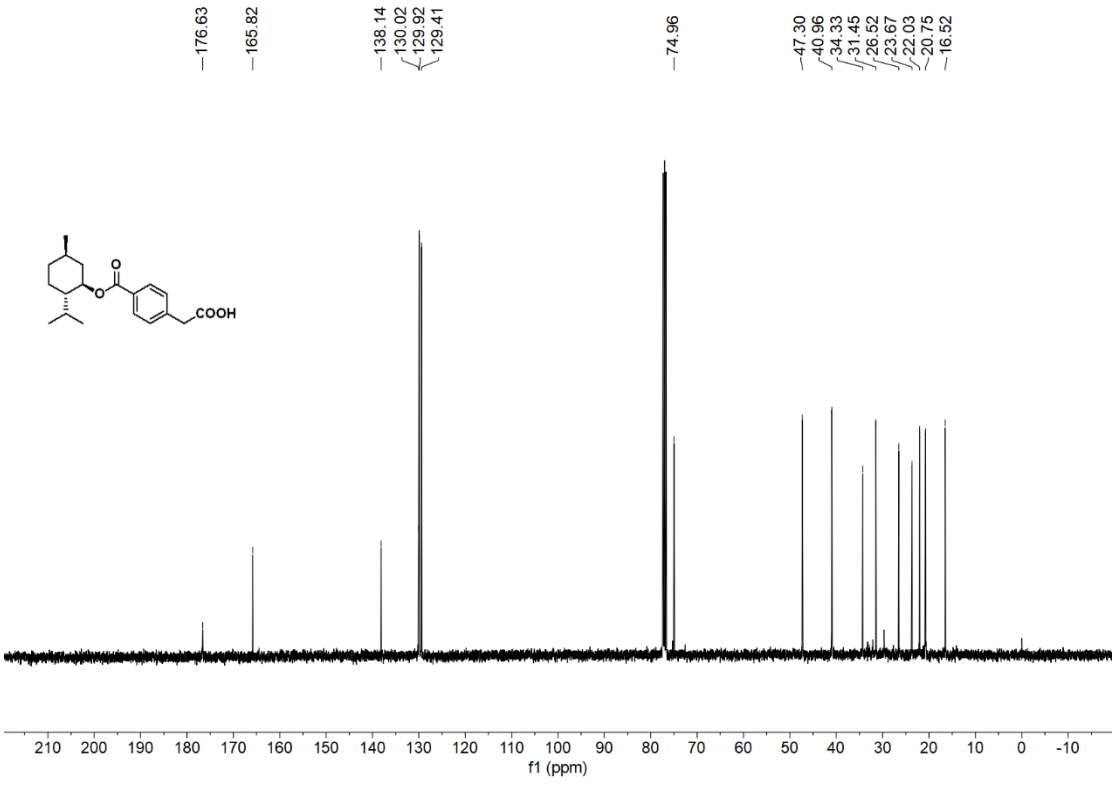
2-(dibenzo[b,d]thiophen-3-yl)acetic acid (2x)



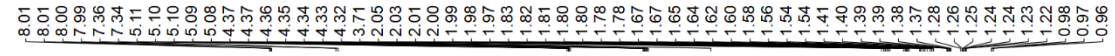


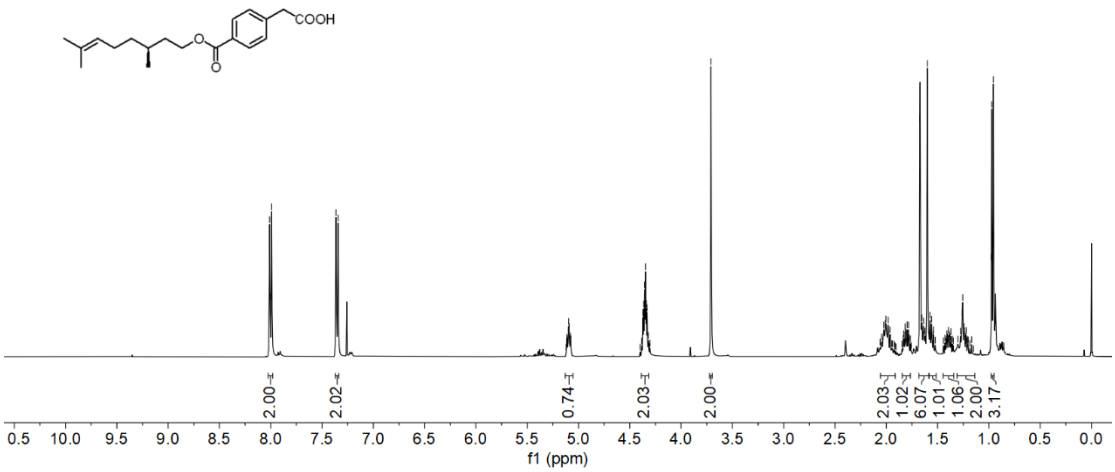
2-(4-((((1R,2S,5R)-2-isopropyl-5-methylcyclohexyl)oxy)carbonyl)phenyl)acetic acid (2y)

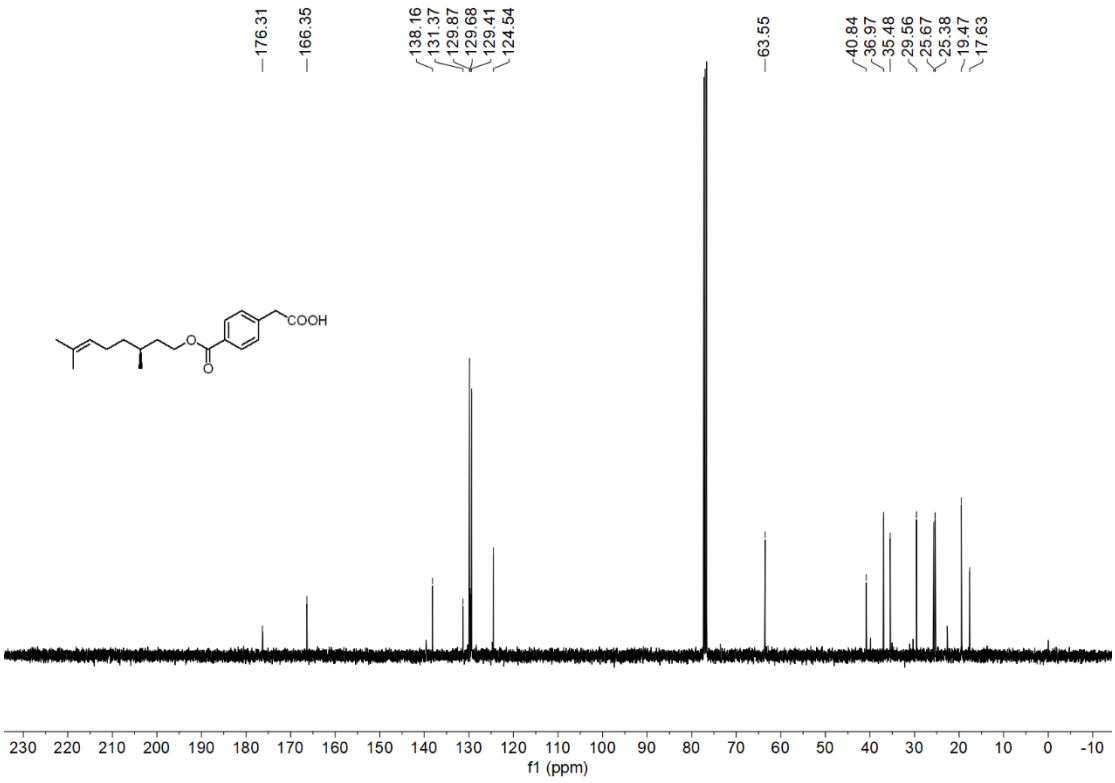




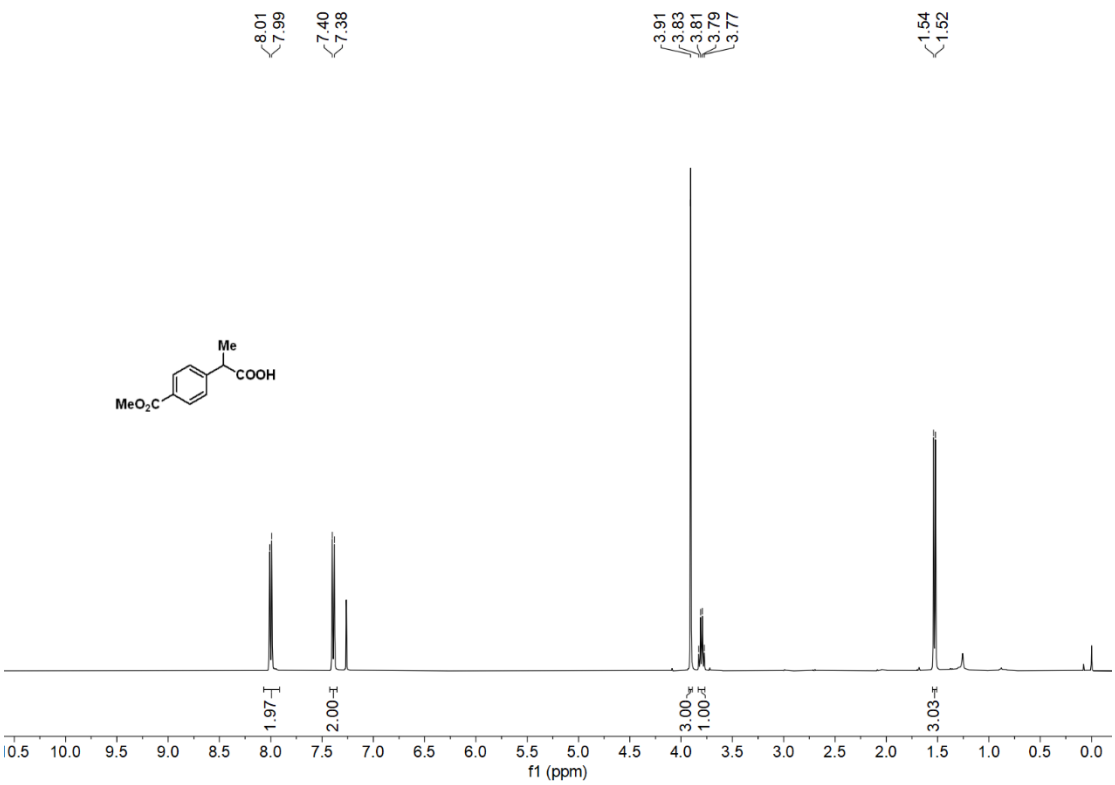
(*R*)-2-(4-(((3,7-dimethyloct-6-en-1-yl)oxy)carbonyl)phenyl)acetic acid (2z)

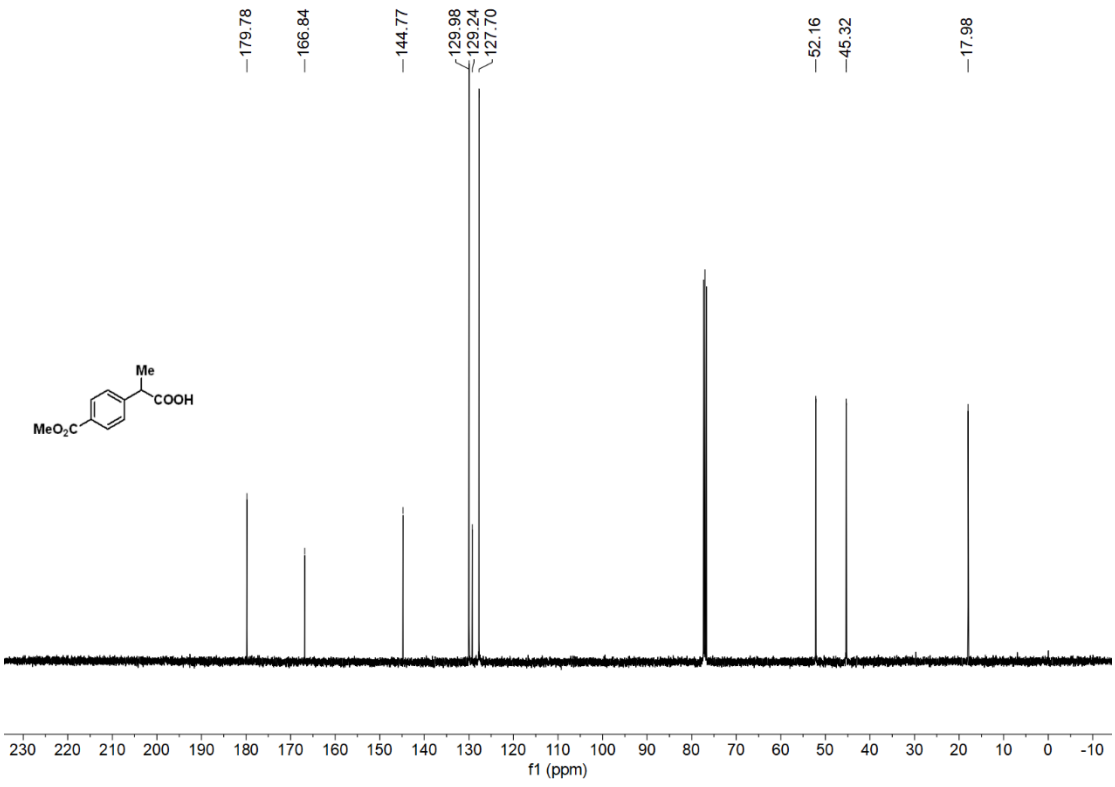




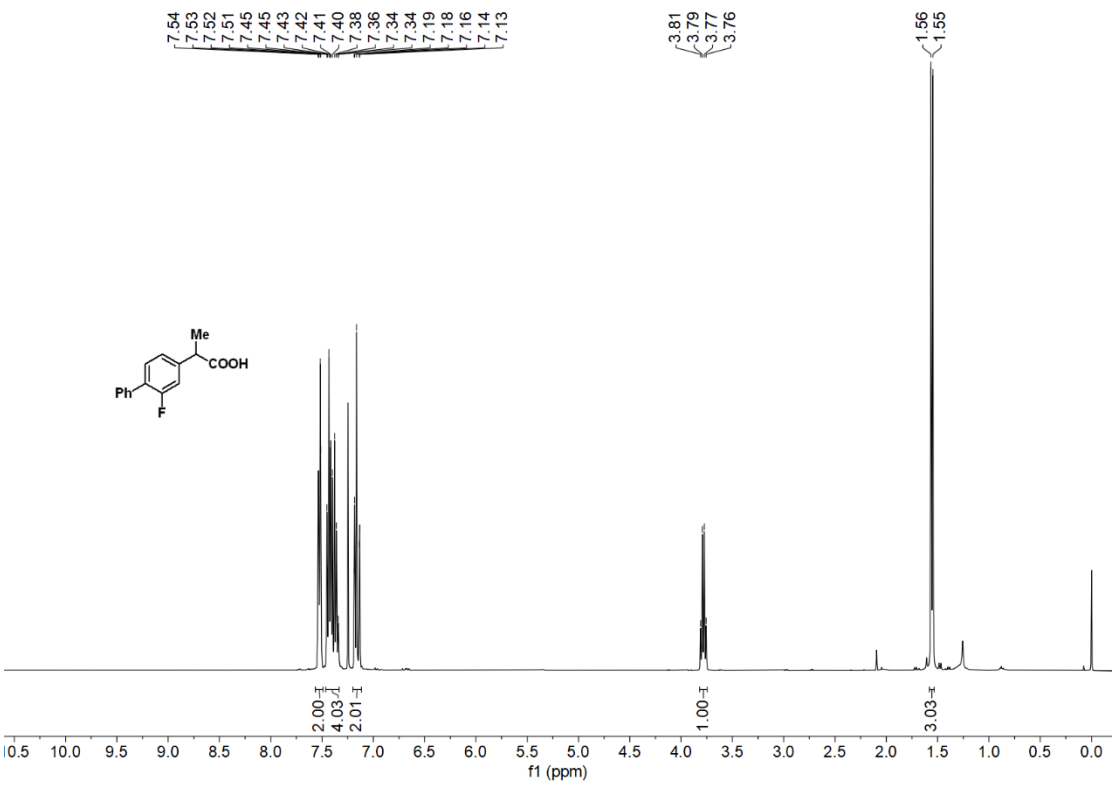


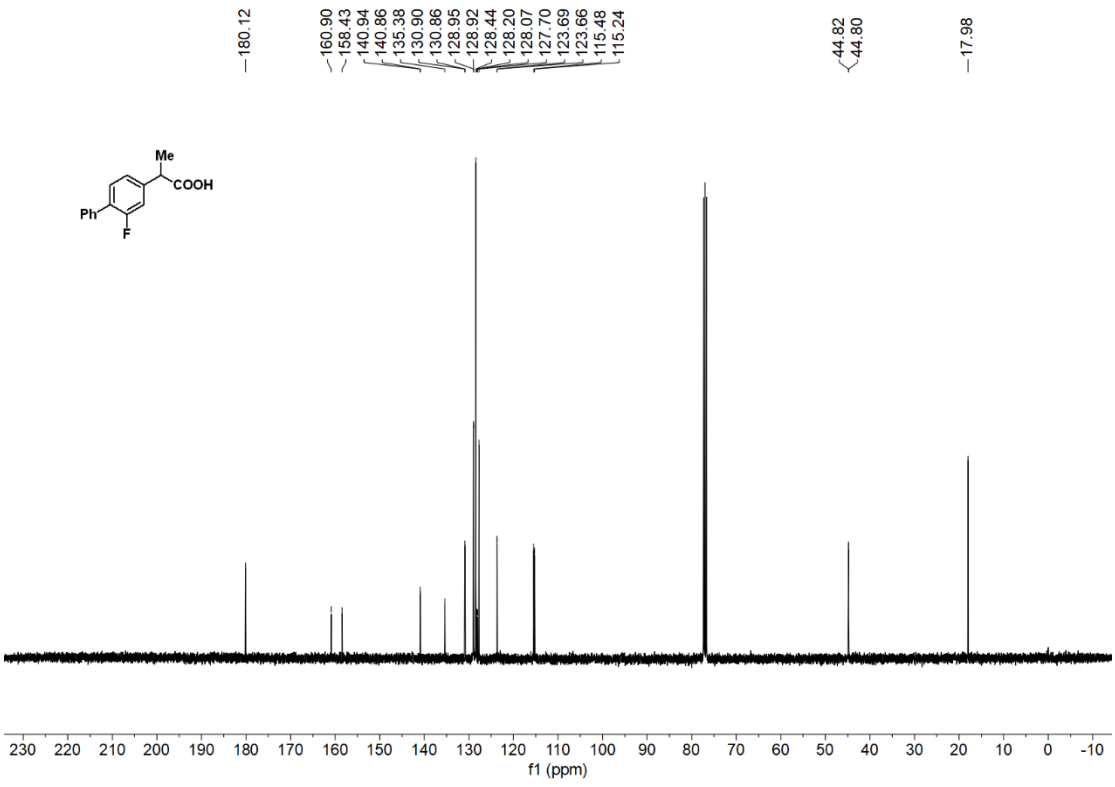
2-(4-(methoxycarbonyl)phenyl)propanoic acid (2aa)

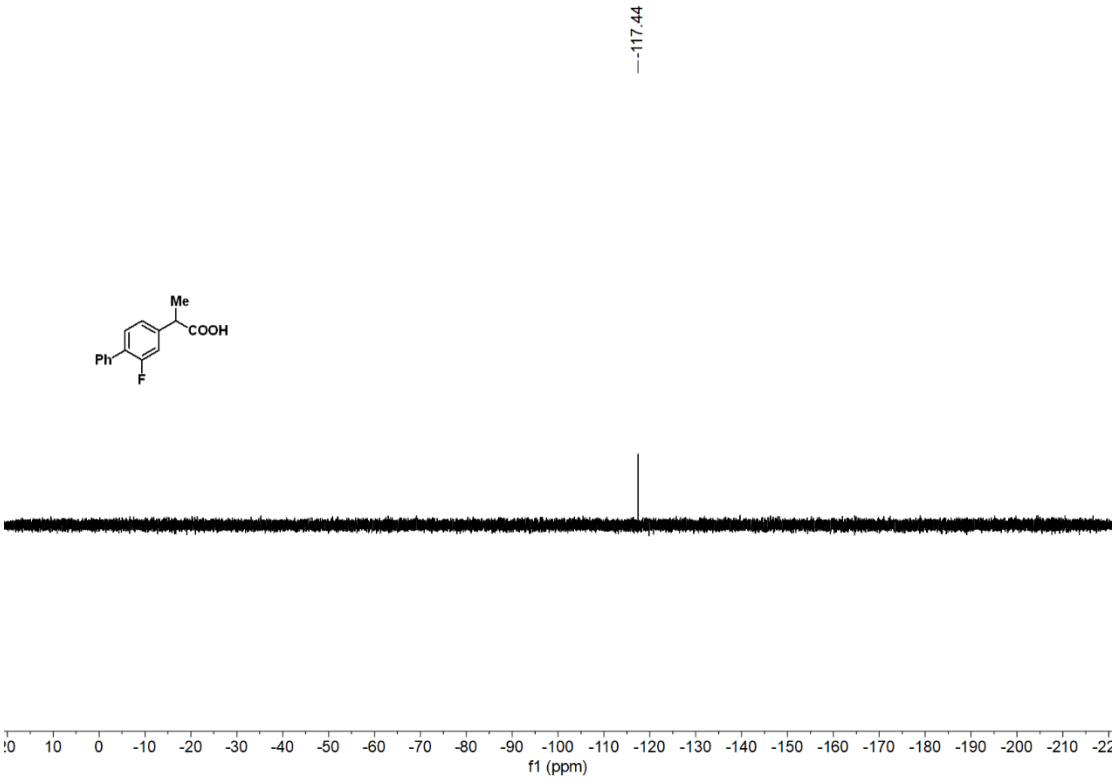




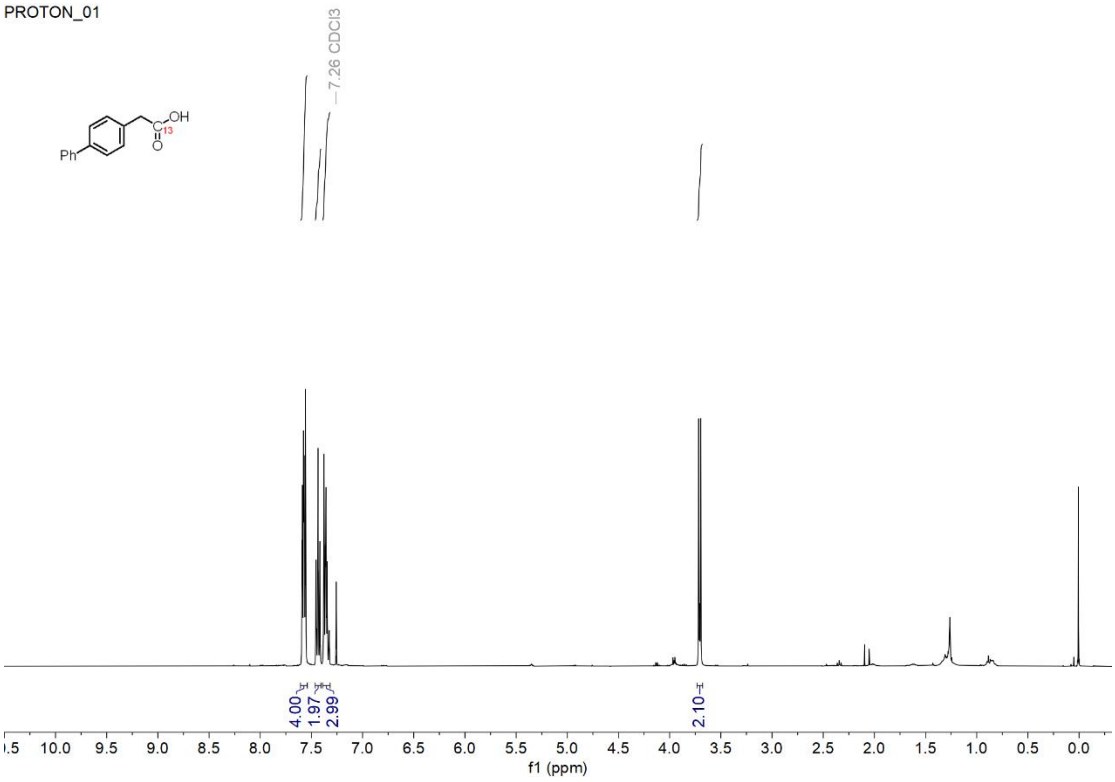
2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoic acid (2ab)

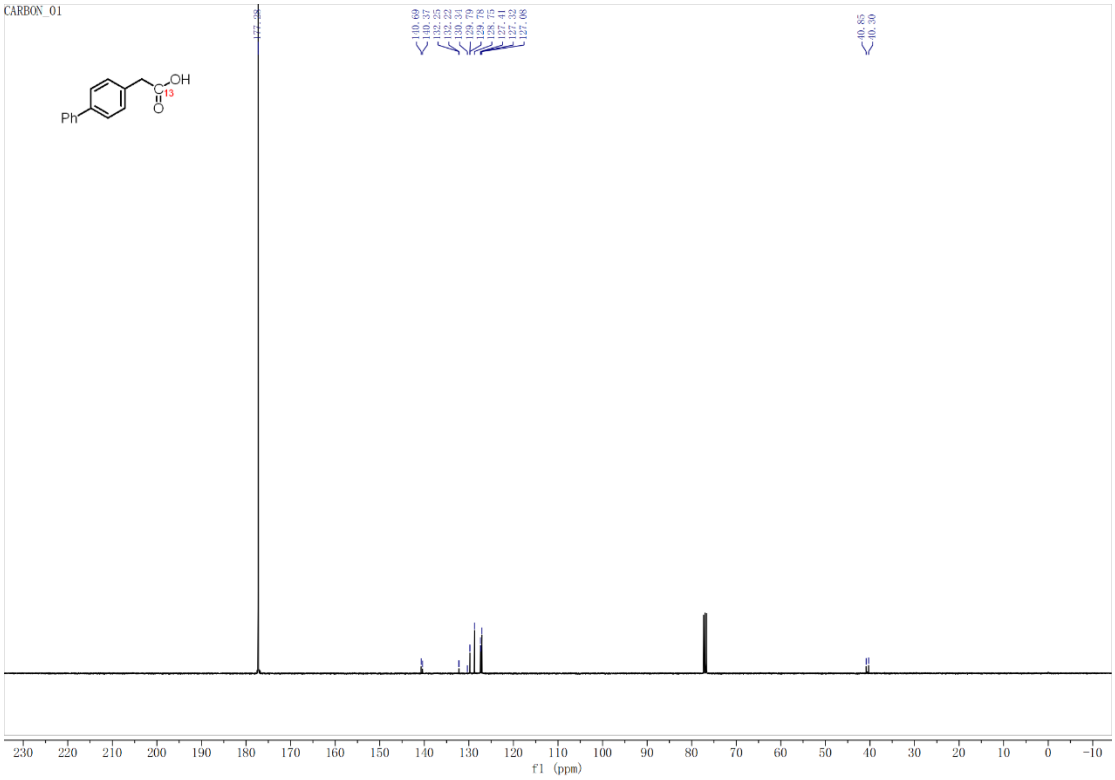






2-([1,1'-biphenyl]-4-yl)acetic acid (^{13}C-2a)

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40.85
40.30
OH
13
O
Ph
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)