Supporting Information

Visible-Light-Promoted Regioselective Hydrocarboxylation of Allenes with Formate Salt and CO_2

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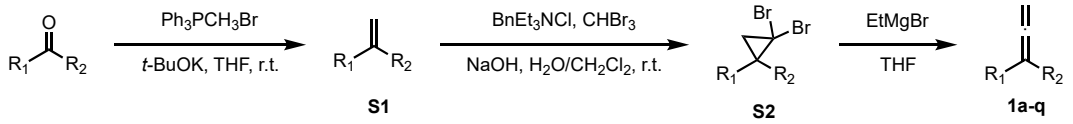
1. General information

The liquid-state NMR was recorded on a 400 or 500 MHz spectrometer. Chemical shifts were reported in ppm. ^{1}H NMR spectra were referenced to $CDCl_3$ (7.260 ppm), and ^{13}C NMR spectra were referenced to $CDCl_3$ (77.160 ppm). All ^{13}C NMR spectra were measured with complete proton decoupling. Peak multiplicities were designated by the following abbreviations: s = singlet; d = doublet; t = triplet; dd = doublet of doublets; td = triplet of doublets; q = quartet; dq = doublet of quartet; m = multiplet and *J* = coupling constant in Hz. High resolution mass spectra were recorded on Ultra-High Resolution Hybrid Qh-Fourier Transform Mass Spectrometer (En Apex ultra 7.0 FT-MS).

Unless otherwise noted, all reagents and solvents were obtained commercially and used without further purification.

2. Preparation of allenes

The allenes were prepared according to corresponding literature procedures[1].



Methyl triphenylphosphonium bromide (1.2 equiv) was added to an oven dried flask followed by THF (2.5 mL/mmol). Then *t*-BuOK (1.5 equiv) was added dropwise to the solution under ice-bath and the resulting yellow suspension was stirred at room temperature for 30 min. To this suspension, a solution of ketone (1.0 equiv) was added and the resulting mixture was further stirred at room temperature overnight. Upon completion, water and DCM were added to the reaction mixture, and the aqueous phase was extracted with DCM. The combined organic phases were washed with brine, dried over anhydrous $MgSO_4$ and the solvent removed under reduced pressure. The reaction mixture was purified by column chromatography over silica gel (200–300 mesh) using hexanes as eluent afforded alkenes **S1**.

To a solution of alkene S1 (1.0 equiv), bromoform (2.5 equiv) and $BnNEt_3Cl$ (10 mol %) was added a solution of 50% NaOH (25 equiv), and the mixture was stirred at room temperature overnight. Upon completion, water and DCM were added and the aqueous phase was extracted with DCM. The combined organic phases were washed with brine, dried over anhydrous $MgSO_4$ and the solvent removed under reduced pressure. The reaction mixture was purified by column chromatography afforded **S2**.

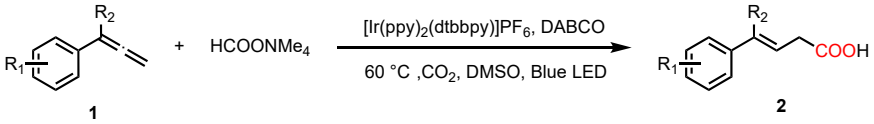
To a pre-cooled (ice-bath) solution of S2 (1.0 equiv) in dry THF (1.0 mL/mmol), EtMgBr (3.0 M in THF, 1.5 equiv) was added dropwise. The mixture was then slowly warmed to room temperature and stirred at room temperature for an additional 3 hours. Then the reaction was quenched by water and the mixture extracted with DCM. The combined organic layers were washed with brine, dried with anhydrous $MgSO_4$. After removing the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel to afford

allenes **1a–q**.

The substrate **1a-e** in Table 2 was prepared according to the procedures described in the literature reported before[1].

The substrate **1f-q** in Table 2 was prepared according to the procedures described in the literature reported before[2].

3. General procedure for the hydrocarboxylation of allenes

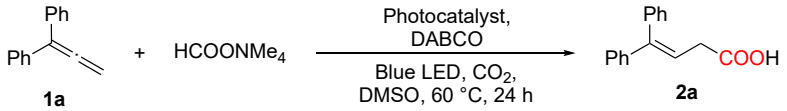


1 **2**

To an oven dried Schlenk tube (10 mL) with a magnetic stir bar, allenes (0.2 mmol, 1 equiv, if solid), $HCOONMe_4$ (2 mmol, 10 equiv), DABCO (0.1 mmol, 0.5 equiv) and $[Ir(ppy)_2dtbbpy]PF_6$ (5 mol%) was added. The Schlenk tube was sealed and degassed via vacuum evacuation and subsequent backfilled with CO_2 for three times. Subsequently, allenes (0.2 mmol, if liquid) and anhydrous DMSO (2 mL) were added. Then the reaction was placed under a blue LED (wavelength 450 nm, 20 W) and irradiated for 24 h at 60 °C. The mixture was acidified with 1 mL dilute HCl (2 N) and quenched with H_2O. Then extracted with EtOAc three times, the combined organic layers were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography isolation on silica gel (eluent: hexane:EA = 5:1 to 1:1 v/v) or prepared TLC (hexane:EA = 1:1 v/v) to give the pure desired product.

4. Optimization of reaction conditions

Table S1. Photocatalyst optimization[a]



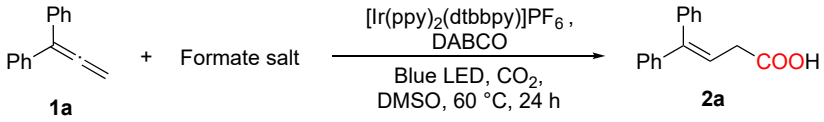
1a **2a**

Entry	Photocatalyst	Yield[b]
1	$[Ir(ppy)_2(dtbbpy)]PF_6$	62 %
2	*fac*-$Ir(ppy)_3$	trace
3	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	45 %
4	$[Ru(bpy)_3]PF_6$	22%
5	Eosin B	trace
6	Eosin Y	trace
7	4CzIPN	12 %
8	3,6-MeO-4CzIPN	9 %
9	3,6-^{t}Bu-4CzIPN	trace
10	3,6-Cl-4CzIPN	trace
11	3,6-Br-4CzIPN	trace
12	$[Ir(ppy)_2(dtbbpy)]PF_6$ (2 mol%)	44 %

[a]Reaction conditions: **1a** (0.2 mmol), $HCOONMe_4$ (2 mmol, 10 eq), photocatalyst (5 mol%), DABCO (0.1 mmol, 0.5 eq), DMSO (2 mL), 60 °C, 24 h, 20 W blue LED (450 nm). [b]Yield was

determined by ^{1}H NMR with 1,3,5-trimethoxybenzene as internal standard.

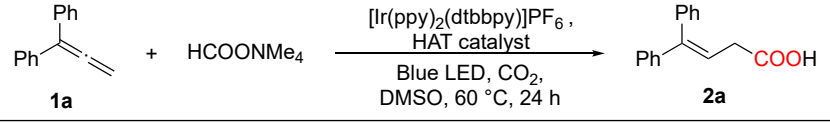
Table S2. Formate salt optimization[a]



Entry	Formate salt	Yield[b]
1	$HCOONMe_4$	62 %
2	$HCOONH_4$	trace
3	$HCOONBnMe_3$	44 %
4	$HCOON^nBu_4$	49%
5	HCOOH	N.R.
6	HCOONa	31 %
7	HCOOCs	57 %
8	$HCOONMe_4$ (5 eq)	47 %
9	$HCOONMe_4$ (2 eq)	32 %

[a]Reaction conditions: **1a** (0.2 mmol), formate salt (2 mmol, 10 eq), $[Ir(ppy)_2(dtbbpy)]PF_6$ (5 mol%), DABCO (0.1 mmol, 0.5 eq), DMSO (2 mL), 60 °C, 24 h, 20 W blue LED (450 nm). [b]Yield was determined by ^{1}H NMR with 1,3,5-trimethoxybenzene as internal standard.

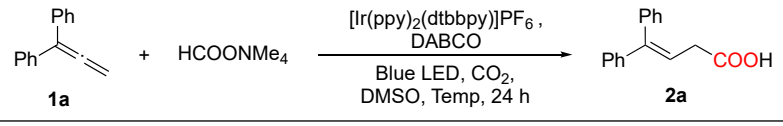
Table S3. HAT catalyst optimization[a]



Entry	HAT catalyst	Yield[b]
1	DABCO	62 %
2	quinuclidine	50 %
3	quinuclidin-3-yl	45 %

[a]Reaction conditions: **1a** (0.2 mmol), $HCOONMe_4$ (2 mmol, 10 eq), $[Ir(ppy)_2(dtbbpy)]PF_6$ (5 mol%), HAT catalyst (0.1 mmol, 0.5 eq), DMSO (2 mL), 60 °C, 24 h, 20 W blue LED (450 nm). [b]Yield was determined by ^{1}H NMR with 1,3,5-trimethoxybenzene as internal standard.

Table S3. Reaction temperature optimization[a]

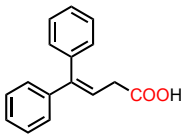


Entry	Temperature	Yield[b]
1	r.t.	23 %
2	50 °C	36 %
3	60 °C	62 %
4	70 °C	43 %
5	90 °C	29 %
6	100 °C	31 %
7	120 °C	trace

[a]Reaction conditions: **1a** (0.2 mmol), $HCOONMe_4$ (2 mmol, 10 eq), $[Ir(ppy)_2(dtbbpy)]PF_6$ (5 mol%), DABCO (0.1 mmol, 0.5 eq), DMSO (2 mL), 24 h, 20 W blue LED (450 nm). [b]Yield was determined by ^1H NMR with 1,3,5-trimethoxybenzene as internal standard.

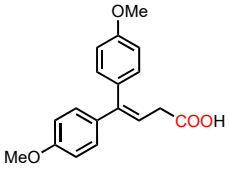
5. Analytical data for compounds

4,4-diphenylbut-3-enoic acid(2a)



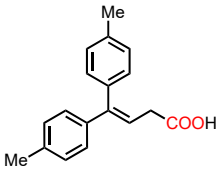
Prepared following the general procedure, purified by column chromatography (3/1 petroleum ether/ ethyl acetate), and isolated as a white solid (30mg, 58%).^1H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.31 (m, 3H), 7.30 – 7.21 (m, 5H), 7.21 – 7.16 (m, 2H), 6.24 (t, J = 7.4 Hz, 1H), 3.21 (d, J = 7.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.52, 145.42, 141.92, 139.23, 129.86, 128.59, 128.31, 127.66, 127.58, 119.67, 35.22. HRMS (ESI) *m/z* $[M+H]^+$ calcd for $[C_{16}H_{15}O_2]^+$ 239.1067, found 239.1069. mp 110-112 °C.

4,4-bis(4-methoxyphenyl)but-3-enoic acid(2b)



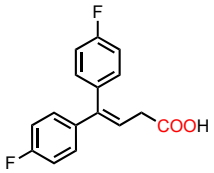
Prepared following the general procedure, purified by column chromatography (1/1 petroleum ether/ ethyl acetate), and isolated as a white solid (35mg, 59%).^1H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, J = 8.5 Hz, 2H), 7.11 (d, J = 8.3 Hz, 2H), 6.92 (d, J = 8.4 Hz, 2H), 6.81 (d, J = 8.4 Hz, 2H), 6.09 (t, J = 7.4 Hz, 1H), 3.84 (s, 3H), 3.79 (s, 3H), 3.21 (d, J = 7.3 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.21, 159.29, 159.05, 144.50, 135.03, 131.70, 131.06, 128.79, 117.59, 113.92, 113.64, 55.41, 35.34. HRMS (ESI) *m/z* $[M+H]^+$ calcd for $[C_{18}H_{19}O_4]^+$ 299.1278, found 299.1273. mp 85-87 °C.

4,4-di-p-tolylbut-3-enoic acid(2c)



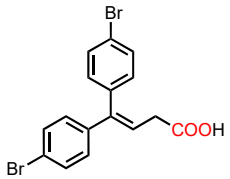
Prepared following the general procedure, purified by column chromatography (3/1 petroleum ether/ ethyl acetate), and isolated as a white solid (32mg, 62%).^1H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.12 (m, 4H), 7.12 – 7.03 (m, 4H), 6.17 (t, J = 7.3 Hz, 1H), 3.21 (d, J = 7.3 Hz, 2H), 2.39 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.15, 145.19, 139.36, 137.37, 137.24, 136.39, 129.76, 129.21, 128.97, 127.50, 118.55, 35.30, 21.37, 21.22. HRMS (ESI) *m/z* $[M+H]^+$ calcd for $[C_{18}H_{19}O_2]^+$ 267.1380, found 267.1377. mp 134-135 °C.

4,4-bis(4-fluorophenyl)but-3-enoic acid(2d)



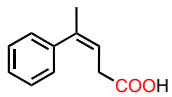
Prepared following the general procedure, purified by column chromatography (3/1 petroleum ether/ ethyl acetate), and isolated as a colorless oil (28mg, 52%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.04 (m, 6H), 7.02 – 6.92 (m, 2H), 6.16 (t, J = 7.4 Hz, 1H), 3.19 (d, J = 7.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.96, 162.59 (d, J = 247.4 Hz), 162.40 (d, J = 247.2 Hz), 143.55, 137.90 (d, J = 3.4 Hz), 134.83 (d, J = 3.5 Hz), 131.49 (d, J = 8.0 Hz), 129.17 (d, J = 8.0 Hz), 119.79, 115.71 (d, J = 21.4 Hz), 115.26 (d, J = 21.4 Hz), 35.24. HRMS (ESI) *m/z* $[M+H]^+$ calcd for $[C_{16}H_{13}F_2O_2]^+$ 275.0878, found 275.0880.

4,4-bis(4-bromophenyl)but-3-enoic acid(2e)



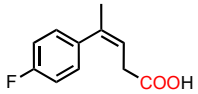
Prepared following the general procedure, purified by column chromatography (3/1 petroleum ether/ ethyl acetate), and isolated as a colorless oil (22mg, 28%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.31 (m, 3H), 7.29 – 7.24 (m, 3H), 7.22 – 7.11 (m, 2H), 6.24 (t, J = 7.3 Hz, 1H), 3.21 (d, J = 7.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.92, 145.26, 141.82, 139.11, 129.76, 128.48, 128.20, 127.55, 127.48, 119.62, 35.28. HRMS (ESI) *m/z* $[M+H]^+$ calcd for $[C_{16}H_{13}Br_2O_2]^+$ 394.9277, found 394.9271.

(Z)-4-phenylpent-3-enoic acid(2f)



Prepared following the general procedure, purified by prepared TLC (1/1 petroleum ether/ ethyl acetate), and isolated as a colorless oil (9mg, 24%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.26 (m, 3H), 7.25 – 7.14 (m, 2H), 5.68 (t, J = 7.3 Hz, 1H), 3.10 (d, J = 7.3 Hz, 2H), 2.13 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.02, 141.03, 140.92, 128.38, 127.77, 127.13, 126.99, 117.66, 34.47, 25.65. HRMS (ESI) *m/z* $[M+H]^+$ calcd for $[C_{11}H_{12}O_2]^+$ 177.0910, found 177.0915.

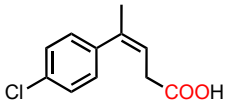
(Z)-4-(4-fluorophenyl)pent-3-enoic acid(2g)



Prepared following the general procedure, purified by prepared TLC (1/1 petroleum ether/ ethyl acetate), and isolated as a colorless oil (10mg, 27%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 6.95 (m, 4H), 5.64 (t, J = 7.5 Hz, 1H), 3.03 (d, J = 7.3 Hz, 2H), 2.07 (s, 3H). ^{13}C NMR (101

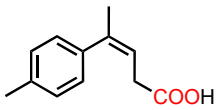
MHz, $CDCl_3$) δ 178.49, 162.00 (d, J = 245.9 Hz), 140.17, 136.84 (d, J = 3.3 Hz), 129.51 (d, J = 7.9 Hz), 118.19, 115.40 (d, J = 21.2 Hz), 34.68, 25.82. HRMS (ESI) *m/z* $[M+H]^+$ calcd for $[C_{11}H_{12}FO_2]^+$ 195.0816, found 195.0818.

(Z)-4-(4-chlorophenyl)pent-3-enoic acid(2h)



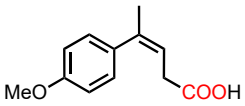
Prepared following the general procedure, purified by prepared TLC (1/1 petroleum ether/ ethyl acetate), and isolated as a colorless oil (15mg, 35%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 2H), 7.14 – 7.10 (m, 2H), 5.64 (t, J = 7.4 Hz, 1H), 3.02 (d, J = 7.4 Hz, 2H), 2.06 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.53, 140.00, 139.36, 133.10, 129.28, 128.71, 118.45, 34.67, 25.61. HRMS (ESI) *m/z* $[M+H]^+$ calcd for $[C_{11}H_{12}ClO_2]^+$ 211.0520, found 211.0522.

(Z)-4-(p-tolyl)pent-3-enoic acid(2i)



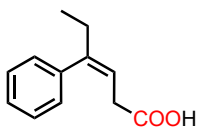
Prepared following the general procedure, purified by prepared TLC (1/1 petroleum ether/ ethyl acetate), and isolated as a colorless oil (15mg, 40%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, J = 7.8 Hz, 2H), 7.09 (d, J = 8.1 Hz, 2H), 5.63 (t, J = 7.3 Hz, 1H), 3.08 (d, J = 8.7 Hz, 2H), 2.37 (s, 3H), 2.09 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.07, 141.00, 138.00, 136.88, 129.14, 127.77, 117.45, 34.74, 25.77, 21.27. HRMS (ESI) *m/z* $[M+H]^+$ calcd for $[C_{12}H_{15}O_2]^+$ 191.1067, found 191.1066.

(Z)-4-(4-methoxyphenyl)pent-3-enoic acid(2j)



Prepared following the general procedure, purified by prepared TLC (1/1 petroleum ether/ ethyl acetate), and isolated as a colorless oil (16mg, 38%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, J = 8.7 Hz, 2H), 6.89 (d, J = 8.8 Hz, 2H), 5.60 (t, J = 7.3 Hz, 1H), 3.82 (s, 3H), 3.08 (d, J = 7.3 Hz, 2H), 2.07 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.86, 158.64, 140.51, 133.15, 128.94, 117.23, 113.75, 55.29, 34.66, 25.72. HRMS (ESI) *m/z* $[M+H]^+$ calcd for $[C_{12}H_{15}O_3]^+$ 207.1016, found 207.1019.

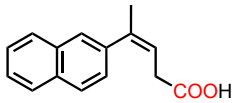
(Z)-4-phenylhex-3-enoic acid(2k)



Prepared following the general procedure, purified by prepared TLC (1/1 petroleum ether/ ethyl acetate), and isolated as a colorless oil (9mg, 24%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.26 (m, 3H), 7.20 – 7.14 (m, 2H), 5.64 (t, J = 7.3 Hz, 1H), 3.05 (d, J = 7.2 Hz, 2H), 2.44 (q, J

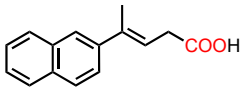
= 7.4 Hz, 2H), 1.03 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.72, 147.28, 140.44, 128.42, 128.28, 127.11, 116.20, 34.48, 32.21, 12.85. HRMS (ESI) *m/z* $[M+H]^+$ calcd for $[C_{12}H_{15}O_2]^+$ 191.1067, found 191.1070.

(Z)-4-(naphthalen-2-yl)pent-3-enoic acid(2l-Z)



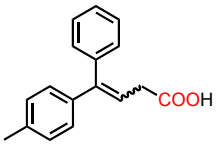
Prepared following the general procedure, purified by column chromatography (3/1 petroleum ether/ ethyl acetate), and isolated as a colorless oil (19mg, 43%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, J = 8.6, 4.5 Hz, 3H), 7.65 (s, 1H), 7.49 (h, J = 5.3 Hz, 2H), 7.33 (dd, J = 8.5, 1.8 Hz, 1H), 5.74 (t, J = 7.3 Hz, 1H), 3.13 (d, J = 7.3 Hz, 2H), 2.19 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.79, 141.09, 138.48, 133.38, 132.59, 128.14, 128.06, 127.78, 126.60, 126.33, 126.20, 126.04, 118.21, 34.75, 25.77. HRMS (ESI) *m/z* $[M+H]^+$ calcd for $[C_{15}H_{15}O_2]^+$ 227.1067, found 227.1065.

(E)-4-(naphthalen-2-yl)pent-3-enoic acid(2l-E)



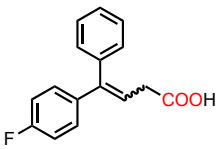
Prepared following the general procedure, purified by column chromatography (3/1 petroleum ether/ ethyl acetate), and isolated as a colorless oil (10mg, 21%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (td, J = 7.6, 5.6 Hz, 4H), 7.60 (dd, J = 8.6, 1.9 Hz, 1H), 7.46 (tt, J = 6.9, 5.2 Hz, 2H), 6.11 (t, J = 6.4 Hz, 1H), 3.38 (d, J = 7.0 Hz, 2H), 2.19 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.94, 140.19, 138.66, 133.51, 132.80, 128.26, 127.90, 127.64, 126.27, 125.88, 124.57, 124.40, 119.10, 34.35, 16.44. HRMS (ESI) *m/z* $[M+H]^+$ calcd for $[C_{15}H_{15}O_2]^+$ 227.1067, found 227.1064.

4-phenyl-4-(p-tolyl)but-3-enoic acid(2m)



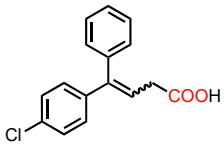
Prepared following the general procedure, purified by column chromatography (3/1 petroleum ether/ ethyl acetate), and isolated as a colorless oil (25mg, 50%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 6.93 (m, 18H), 6.20 (t, J = 7.3 Hz, 2H), 3.22 (d, J = 7.3 Hz, 2H), 3.20 (d, J = 7.4 Hz, 2H), 2.39 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.37, 145.36, 145.23, 142.14, 139.37, 139.11, 137.46, 137.34, 136.18, 129.84, 129.76, 129.25, 129.00, 128.53, 128.26, 127.62, 127.58, 127.46, 119.39, 118.71, 35.33, 21.38, 21.23. HRMS (ESI) *m/z* $[M+H]^+$ calcd for $[C_{17}H_{17}O_2]^+$ 253.1223, found 253.1228.

4-(4-fluorophenyl)-4-phenylbut-3-enoic acid(2n)



Prepared following the general procedure, purified by column chromatography (3/1 petroleum ether/ ethyl acetate), and isolated as a colorless oil (27mg, 53%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 6.85 (m, 18H), 6.27 (t, J = 7.4 Hz, 1H), 6.21 (t, J = 7.3 Hz, 1H), 3.25 (d, J = 2.6 Hz, 2H), 3.23 (d, J = 2.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.05, 162.42 (d, J = 246.9 Hz), 162.24 (d, J = 246.8 Hz), 144.41, 144.35, 141.65, 138.89, 137.96 (d, J = 3.2 Hz), 134.93 (d, J = 3.5 Hz), 131.46 (d, J = 8.1 Hz), 129.67, 129.10 (d, J = 8.0 Hz), 128.58, 128.29, 127.73, 127.44, 119.89, 119.34, 115.50 (d, J = 21.4 Hz), 115.06 (d, J = 21.5 Hz), 35.19. 19F NMR (376 MHz, CDCl3) δ -114.40, -114.93. HRMS (ESI) *m/z* $[M+H]^+$ calcd for $[C_{16}H_{14}FO_2]^+$ 244.0894, found 244.0891.

(Z)-4-(4-chlorophenyl)-4-phenylbut-3-enoic acid(2o)



Prepared following the general procedure, purified by column chromatography (3/1 petroleum ether/ ethyl acetate), and isolated as a colorless oil (21mg, 40%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 6.83 (m, 18H), 6.24 (t, J = 7.5 Hz, 2H), 3.43 – 3.01 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.86, 177.56, 145.34, 144.28, 141.79, 141.37, 139.09, 137.50, 133.60, 131.16, 129.75, 129.67, 128.77, 128.63, 128.49, 128.32, 128.22, 127.80, 127.57, 127.45, 120.06, 119.48, 35.14. HRMS (ESI) *m/z* $[M+H]^+$ calcd for $[C_{16}H_{14}ClO_2]^+$ 273.0677, found 273.0674.

6. Stern-Volmer Fluorescence Quenching Analysis

Stern-Volmer fluorescence quenching experiments were measured on a SHIMADZU RF-5301 PC Spectrophotometer. At first, the emission spectrum of $Ir(ppy)_2(dtbbpy)PF_6$ solution (5.0 x 10^{-5} M in DMSO) was collected in a blank experiment. The solution was irradiated at 450 nm.

DABCO: Different amounts of DABCO solution (0.5 M in DMSO) were added sequentially to the 10 mL of $Ir(ppy)_2(dtbbpy)PF_6$ solution (5.0 x 10^{-5} M in DMSO). As shown in Figure S1, a significant decrease of $Ir(ppy)_2(dtbbpy)PF_6$ luminescence was observed, which indicates that the excited $Ir(ppy)_2(dtbbpy)PF_6$ prefers to undergo single-electron transfer with DABCO.

$HCOONMe_4$: Different amounts of $HCOONMe_4$ solution (0.5 M in DMSO) were added sequentially to the 10 mL of $Ir(ppy)_2(dtbbpy)PF_6$ solution (2.5 x 10^{-5} M in DMSO). As shown in Figure S2, a slight decrease of $Ir(ppy)_2(dtbbpy)PF_6$ luminescence was observed, which indicates that the excited $Ir(ppy)_2(dtbbpy)PF_6$ can undergo single-electron transfer with $HCOONMe_4$.

Propa-1,2-diene-1,1-diyldibenzene: Different amounts of propa-1,2-diene-1,1-

diyldibenzene solution (0.5 M in DMSO) were added sequentially to the 10 mL of $Ir(ppy)_2(dtbbpy)PF_6$ solution (5.0 x 10^{-5} M in DMSO). As shown in Figure S3, a inapparent decrease of $Ir(ppy)_2(dtbbpy)PF_6$ luminescence was observed.

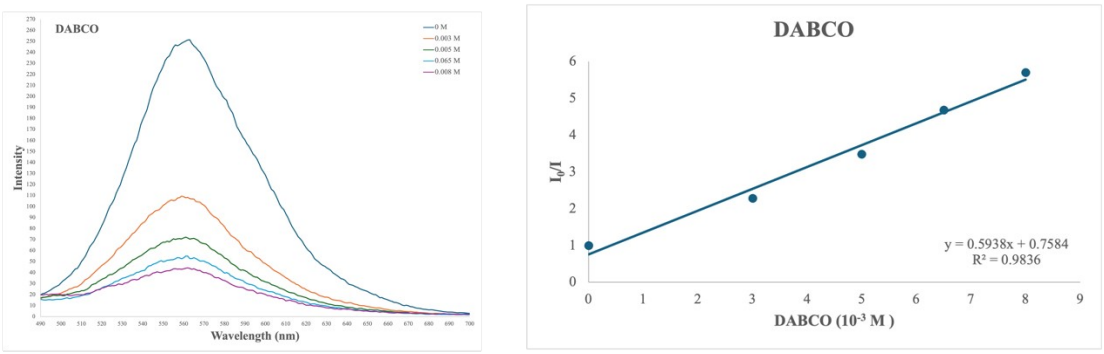


Figure S1 Fluorescence quenching experiments of $Ir[(ppy)_2dtbbpy]PF_6$ in the presence of DABCO.

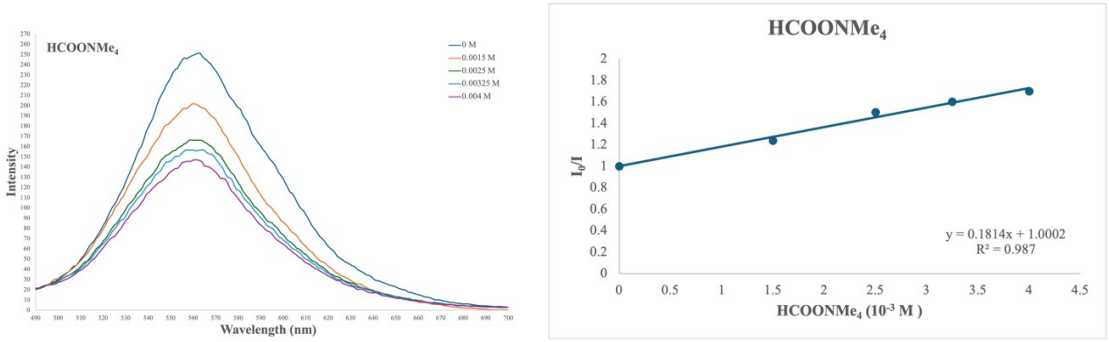


Figure S2 Fluorescence quenching experiments of $Ir[(ppy)_2dtbbpy]PF_6$ in the presence of $HCOONMe_4$.

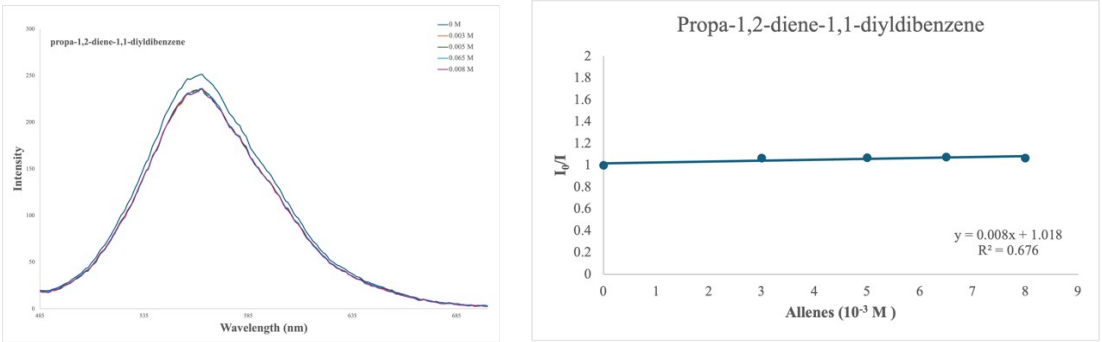


Figure S3 Fluorescence quenching experiments of $Ir[(ppy)_2dtbbpy]PF_6$ in the presence of propa-1,2-diene-1,1-diyldibenzene.

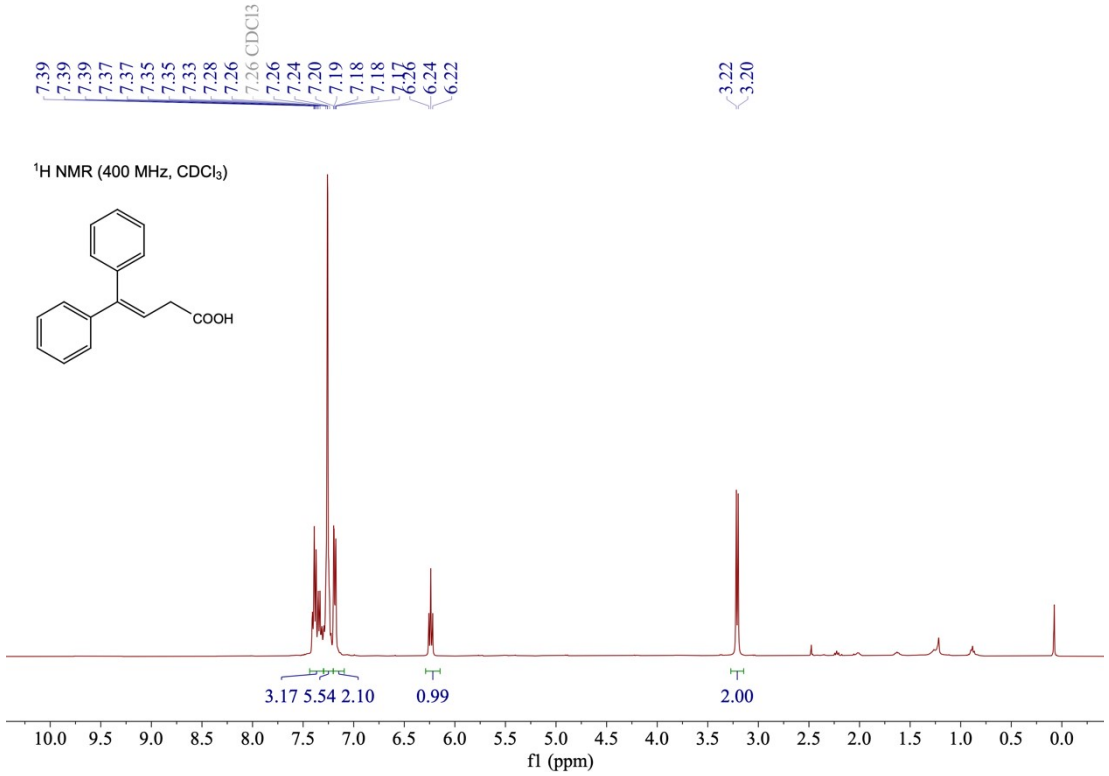
7. References

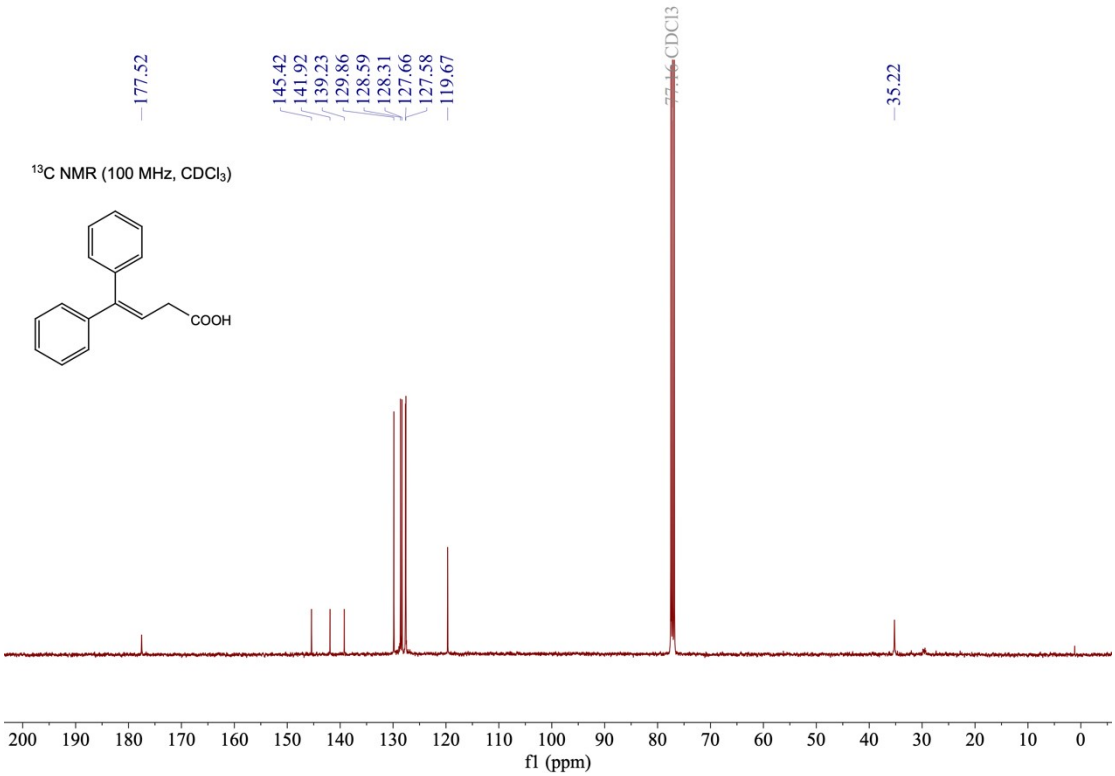
(1) Ye, F.; Wang, C.; Ma, X.; Hossain, M. L.; Xia, Y.; Zhang, Y.; Wang, J. *J. Org. Chem.* **2015**, 80, 1, 647–652

(2) Zhao, Z.; Murphy, G. K. *Beilstein J. Org. Chem*. **2018**, 14, 796-802.

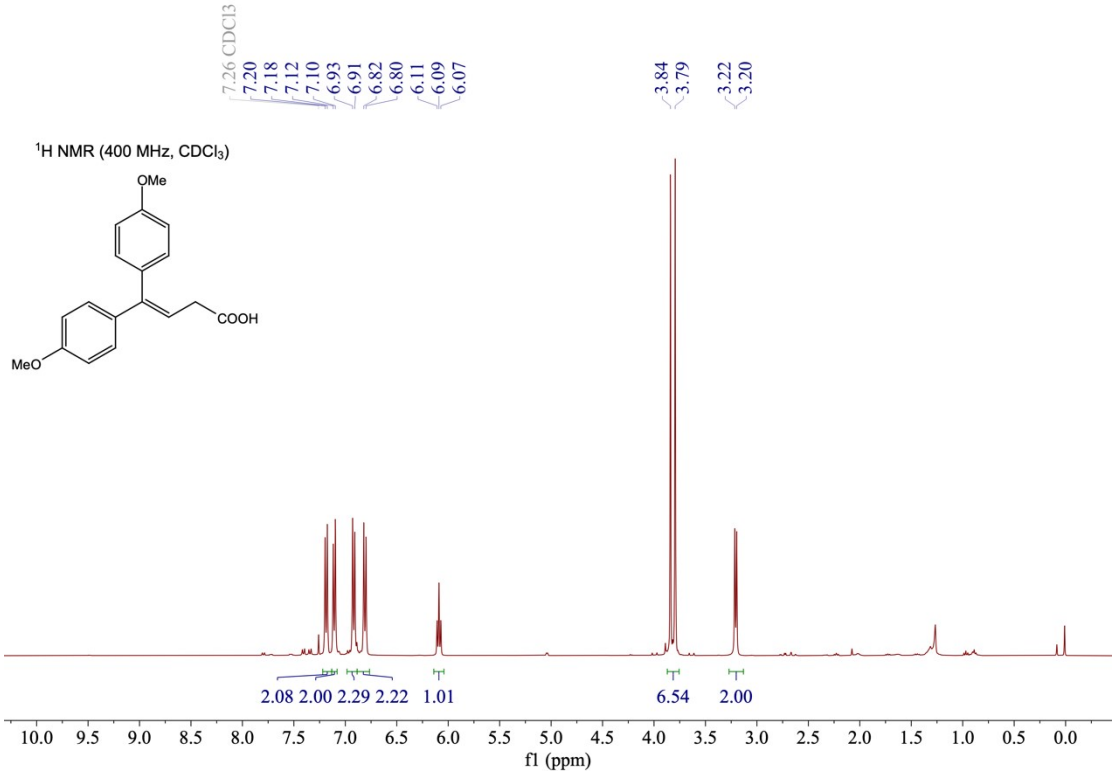
8. NMR spectra

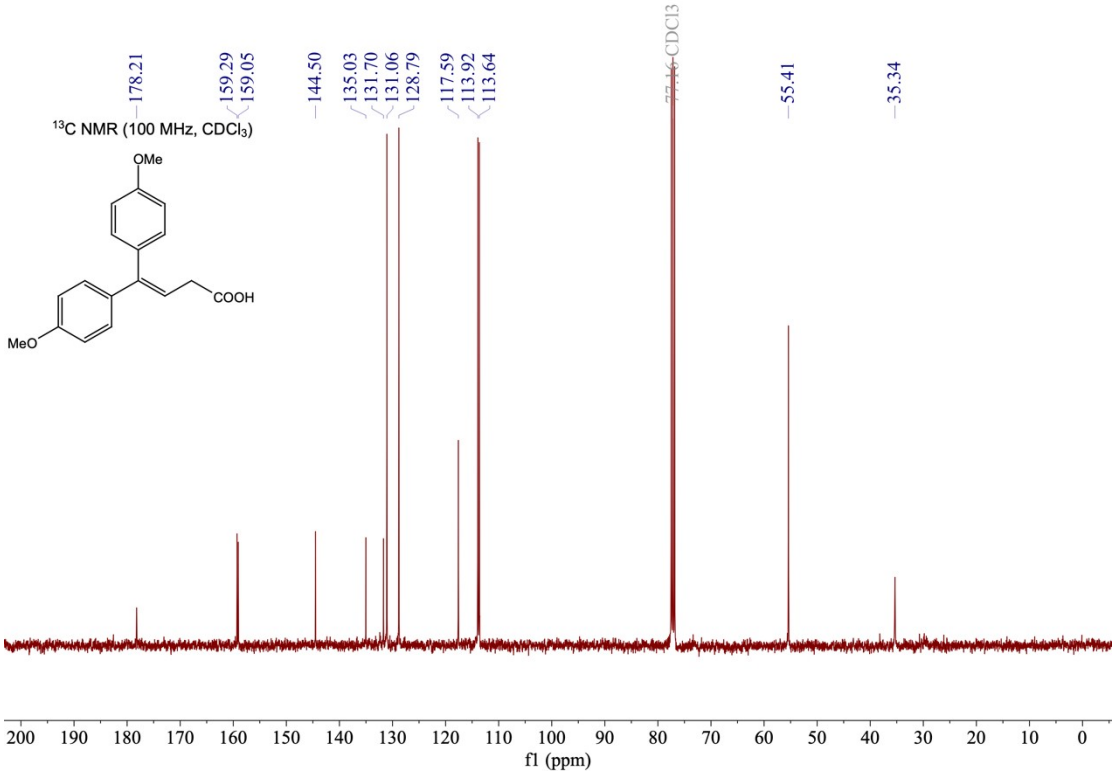
4,4-diphenylbut-3-enoic acid(2a)



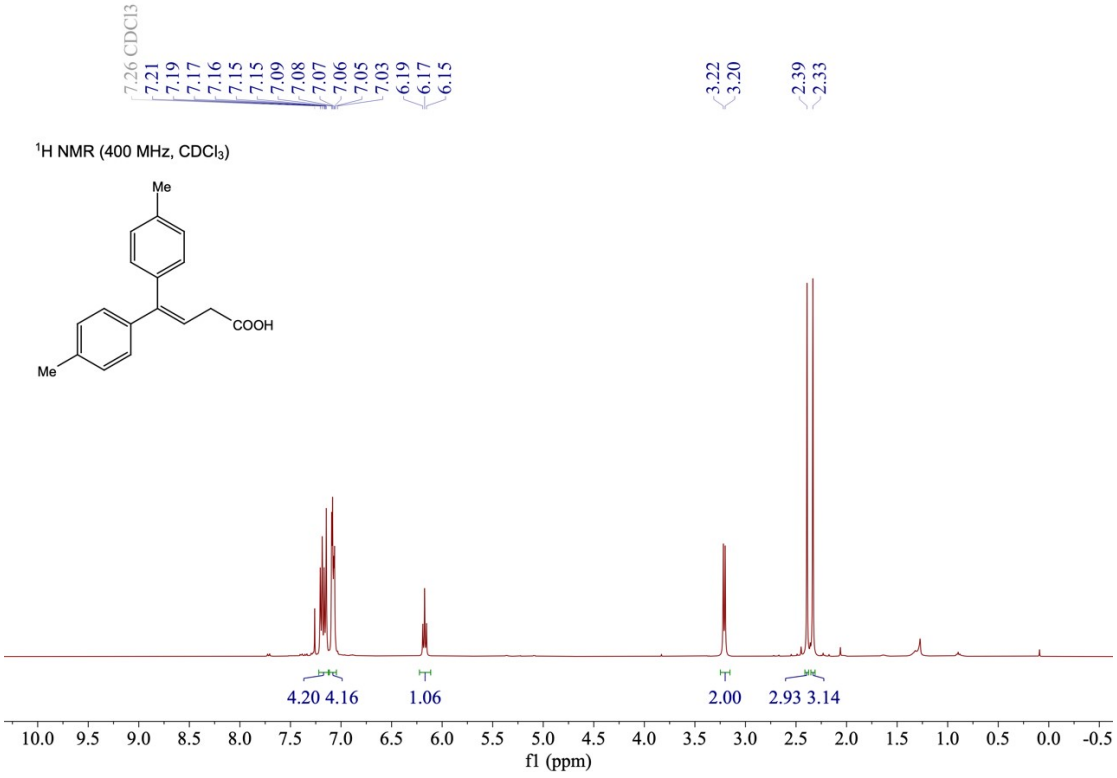


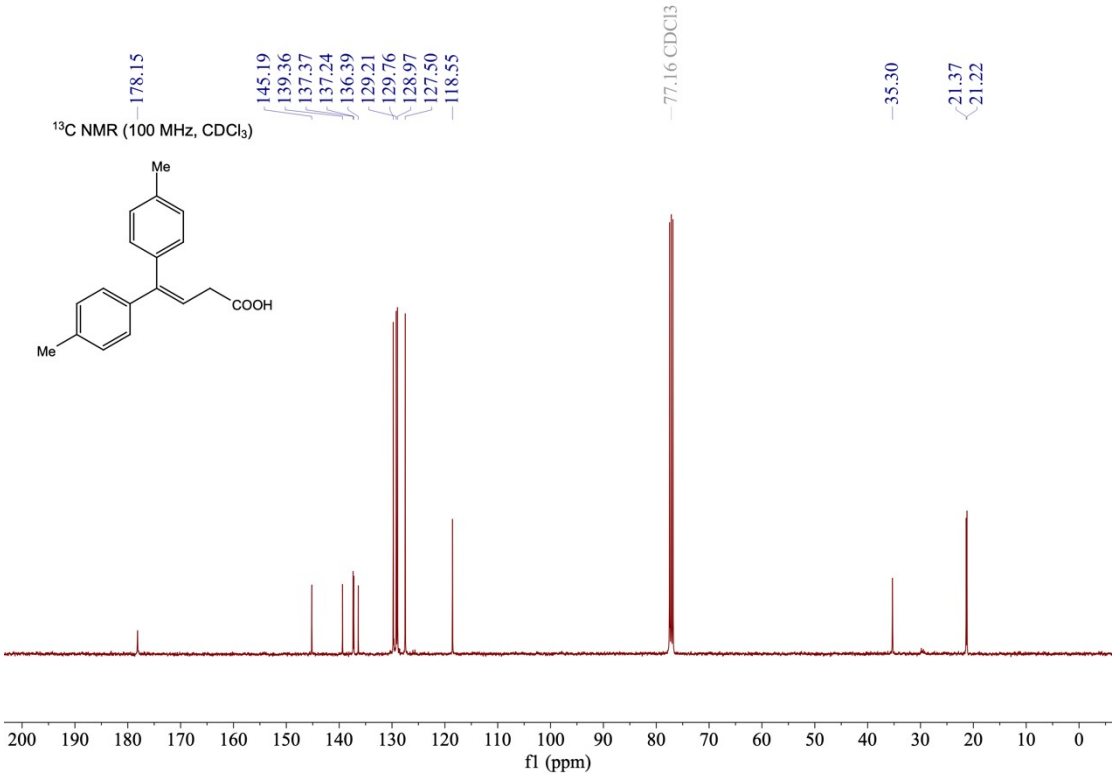
4,4-bis(4-methoxyphenyl)but-3-enoic acid(2b)



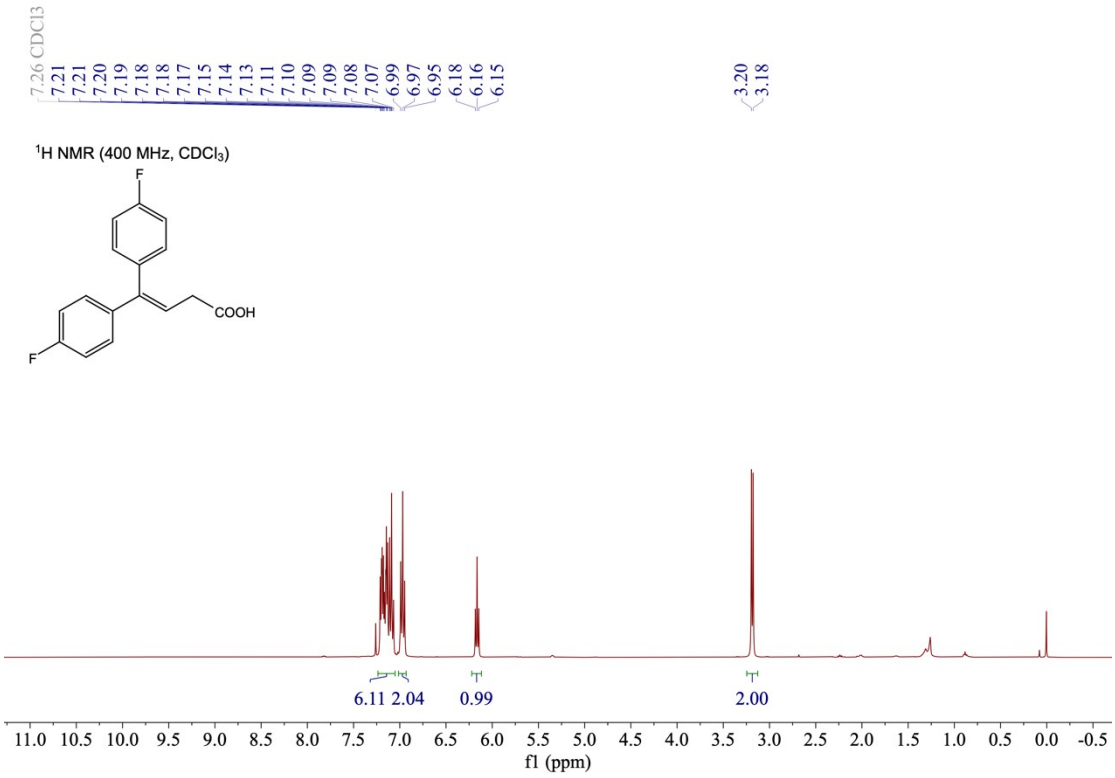


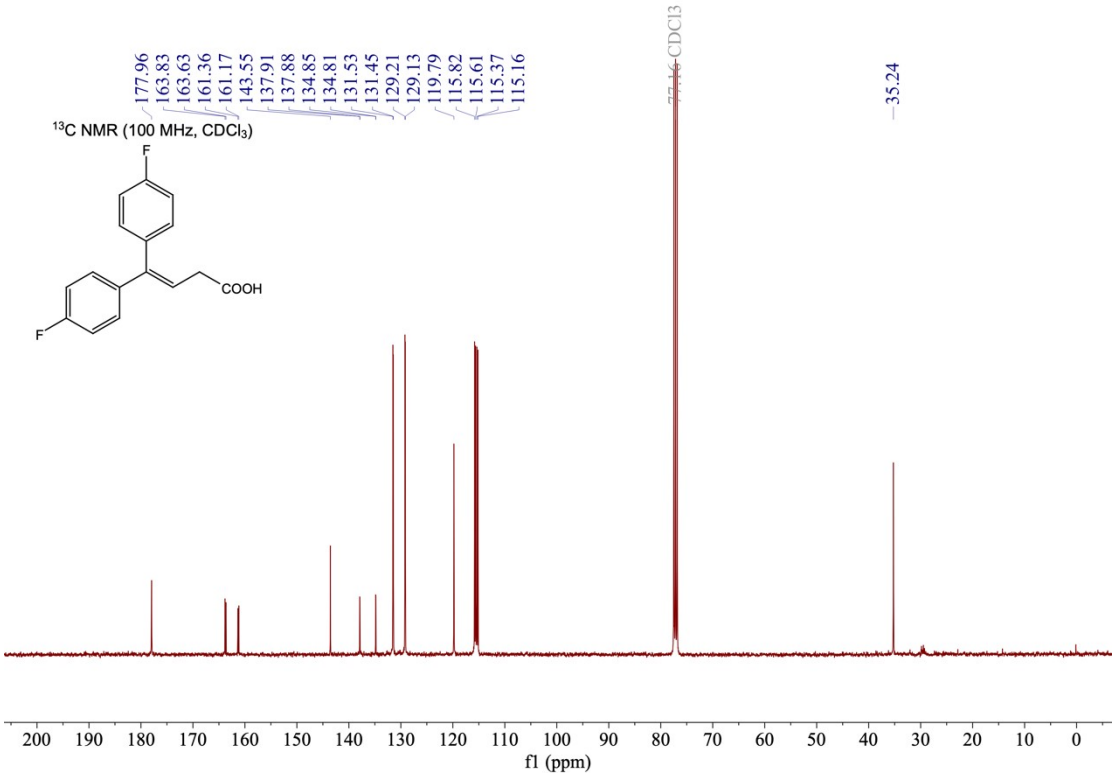
4,4-di-p-tolylbut-3-enoic acid(2c)



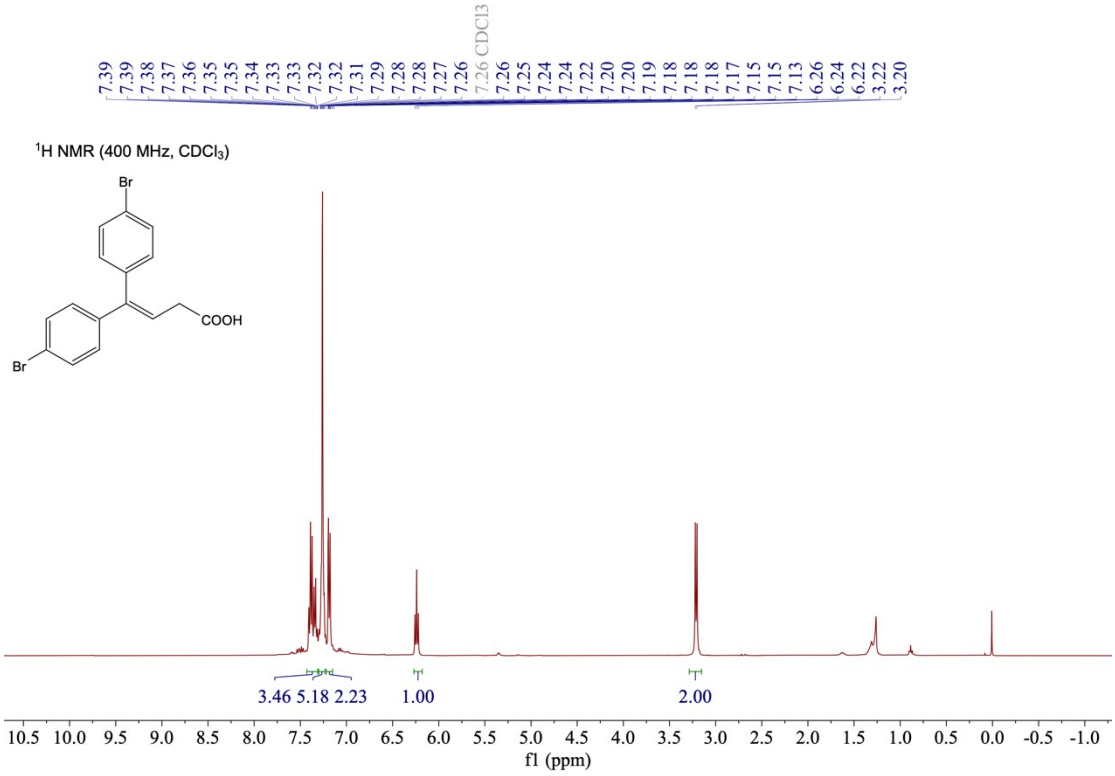


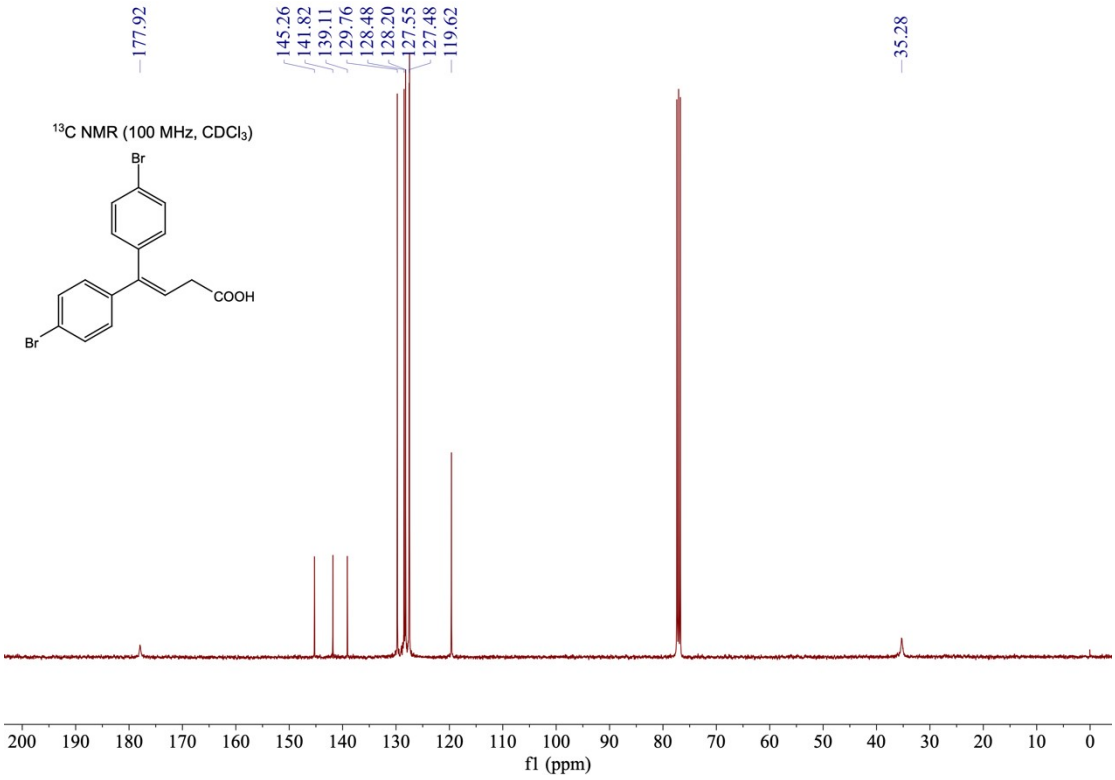
4,4-bis(4-fluorophenyl)but-3-enoic acid(2d)



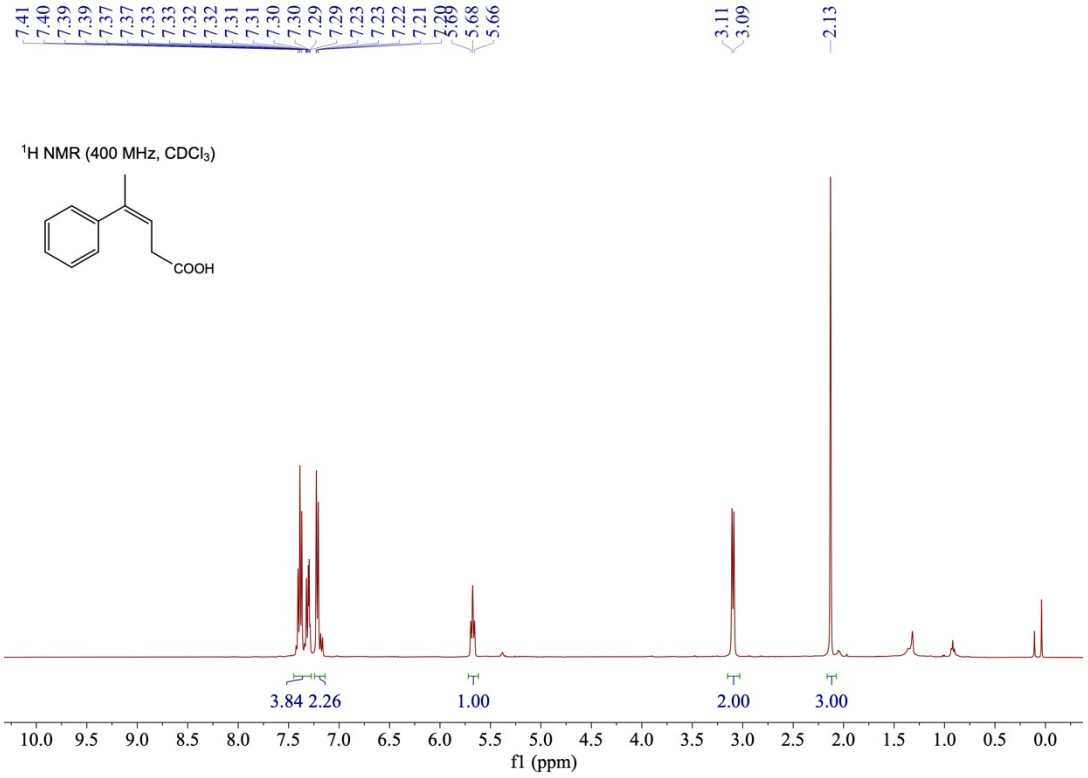


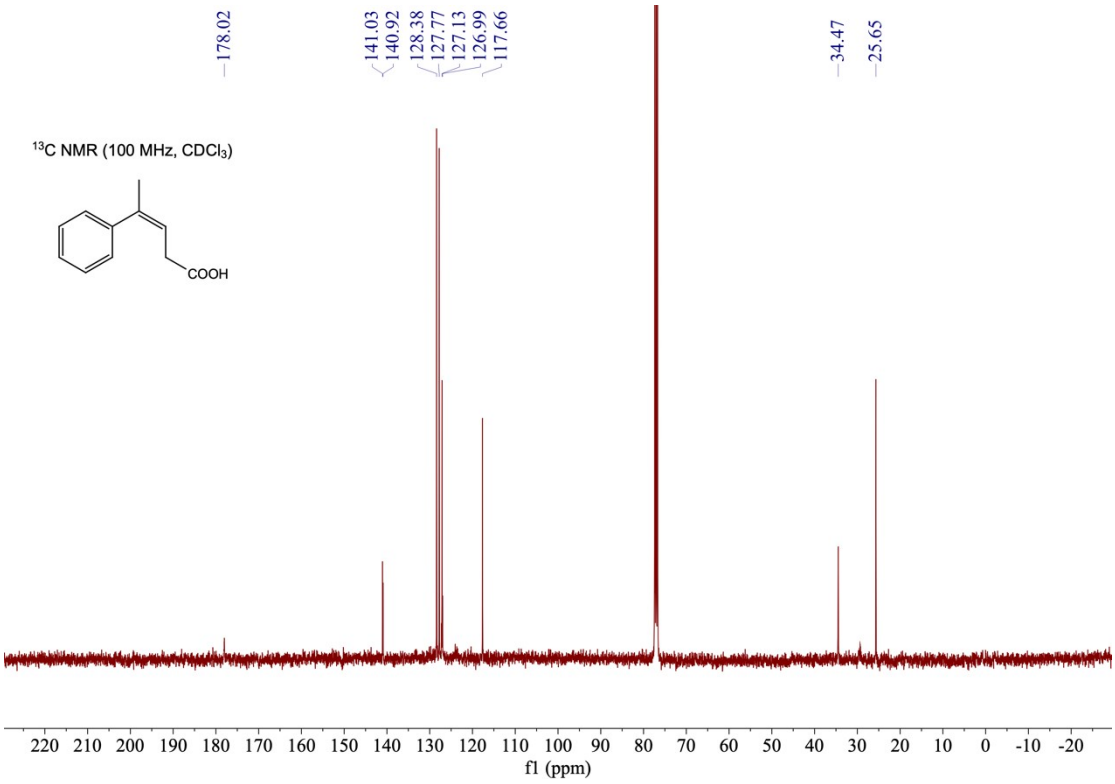
4,4-bis(4-bromophenyl)but-3-enoic acid(2e)



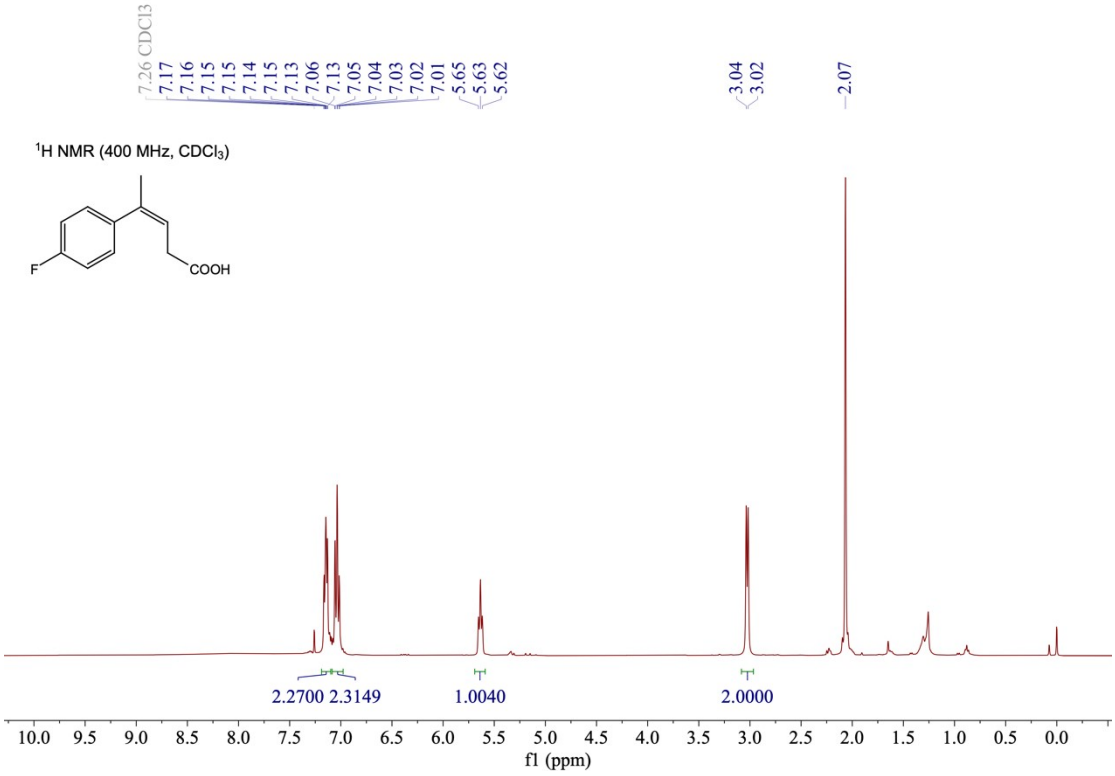


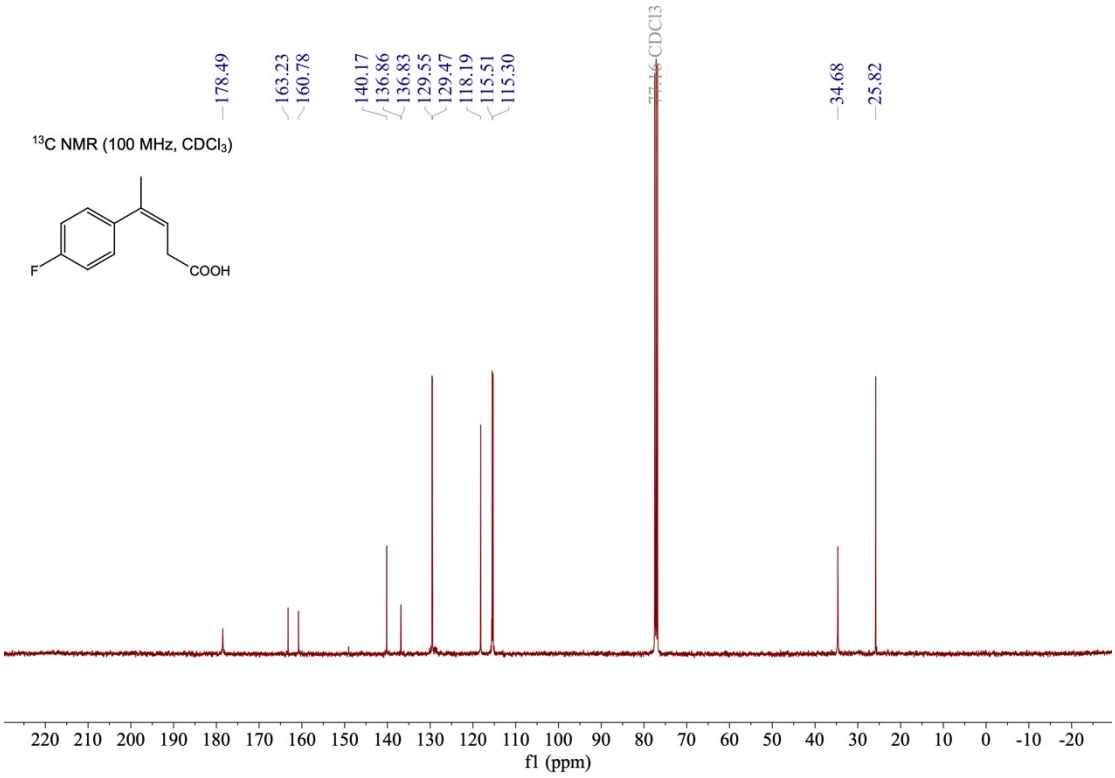
(Z)-4-phenylpent-3-enoic acid(2f)



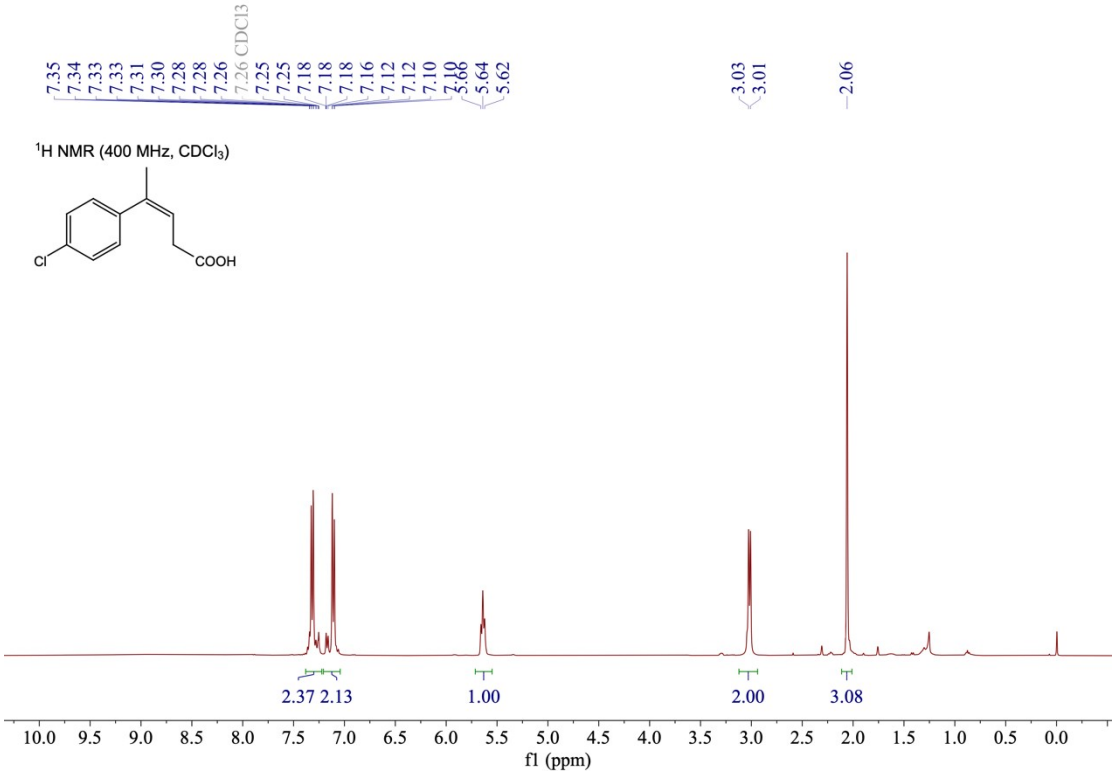


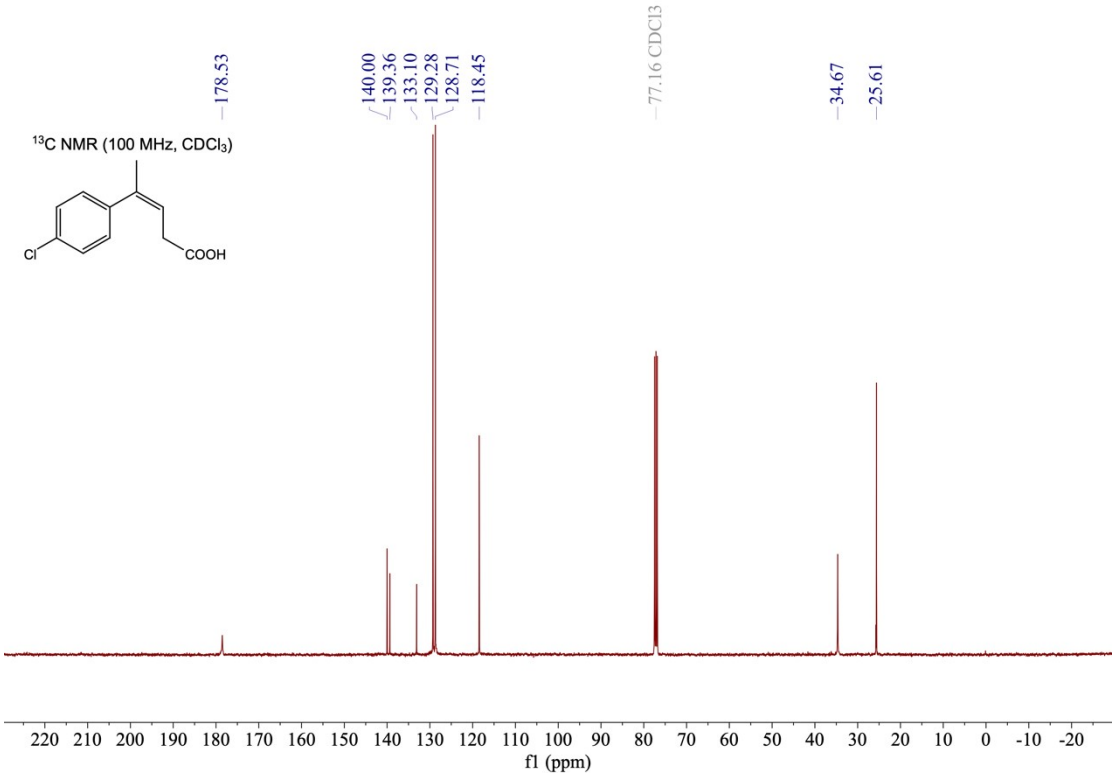
(Z)-4-(4-fluorophenyl)pent-3-enoic acid(2g)



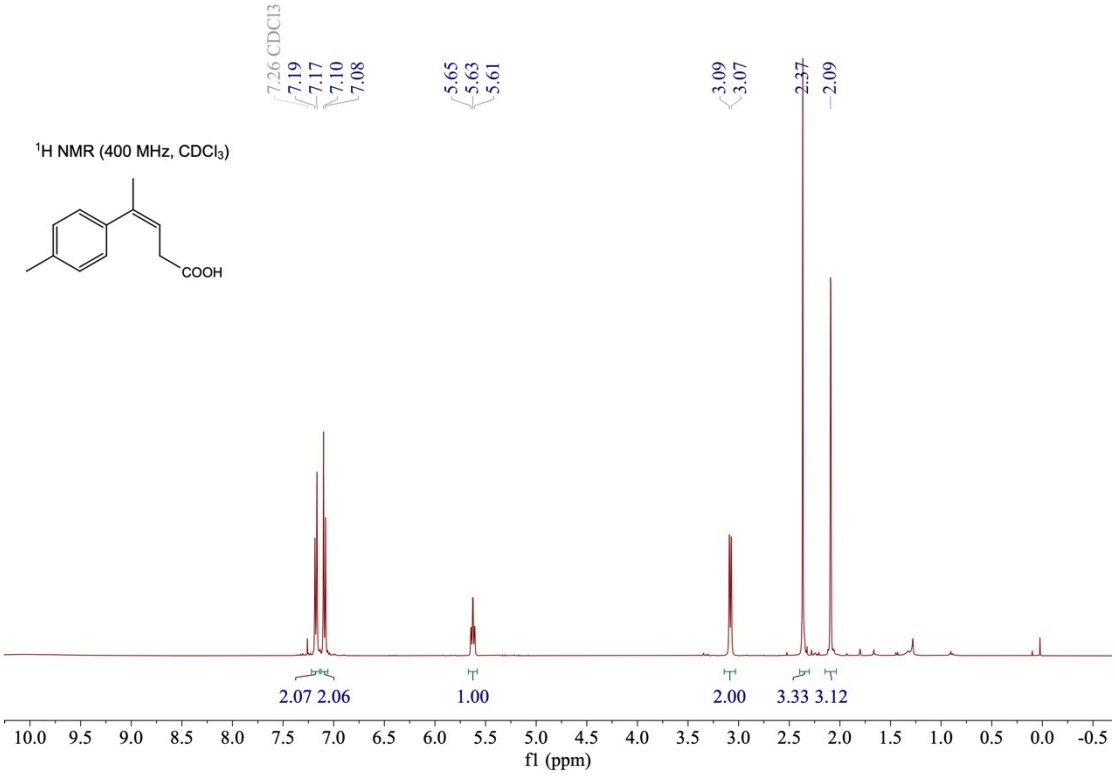


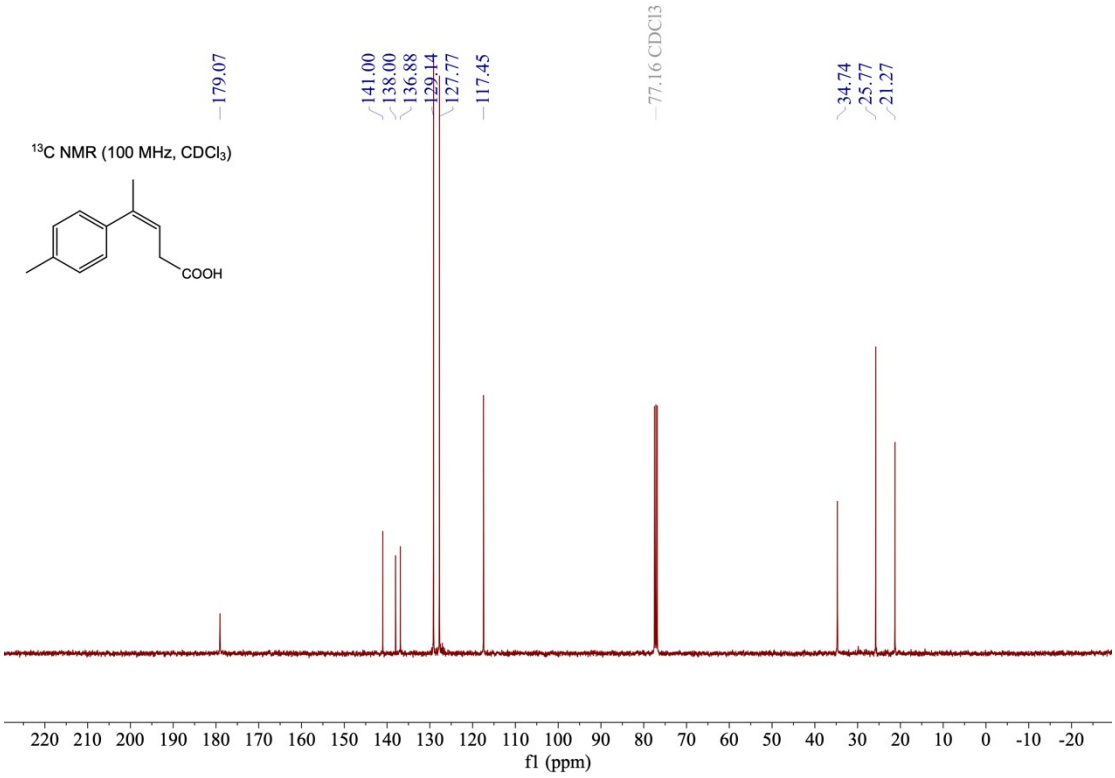
(Z)-4-(4-chlorophenyl)pent-3-enoic acid(2h)



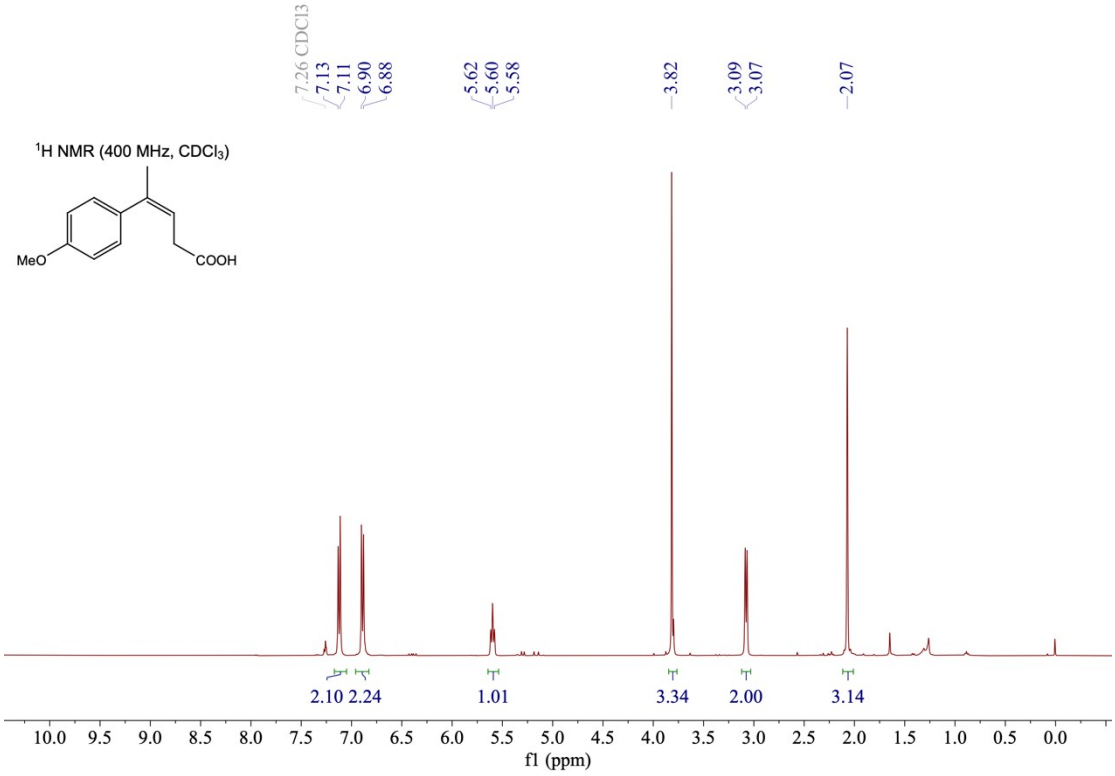


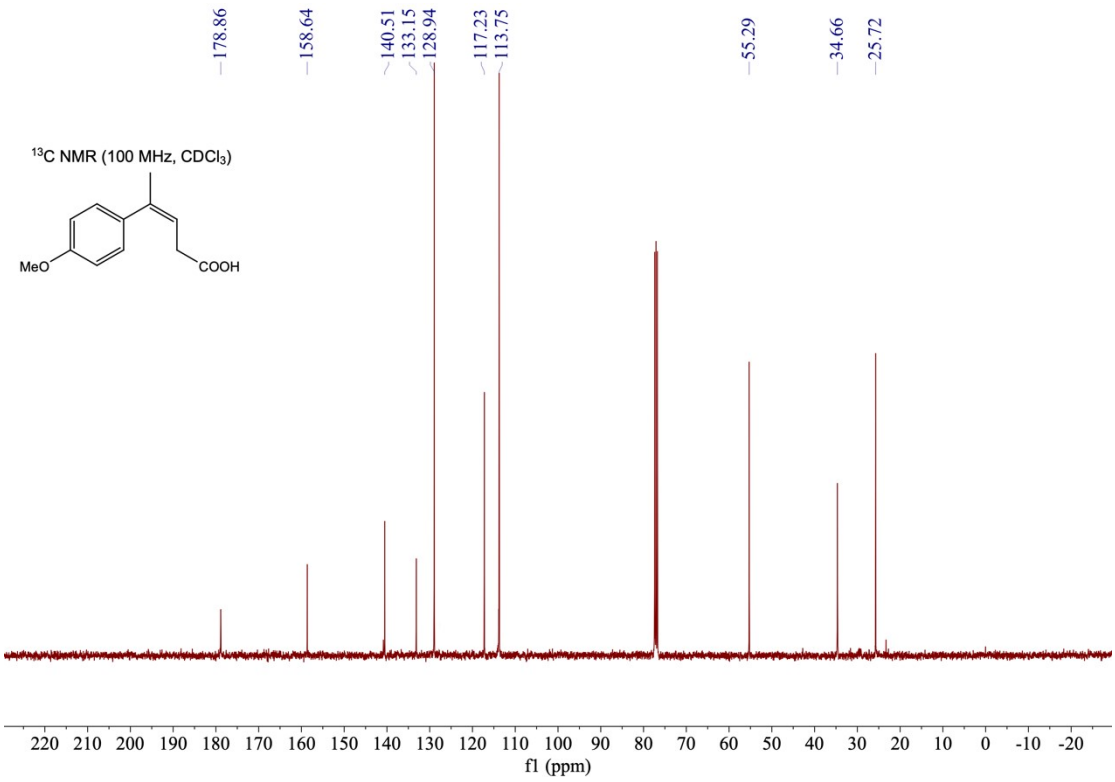
(Z)-4-(p-tolyl)pent-3-enoic acid(2i)



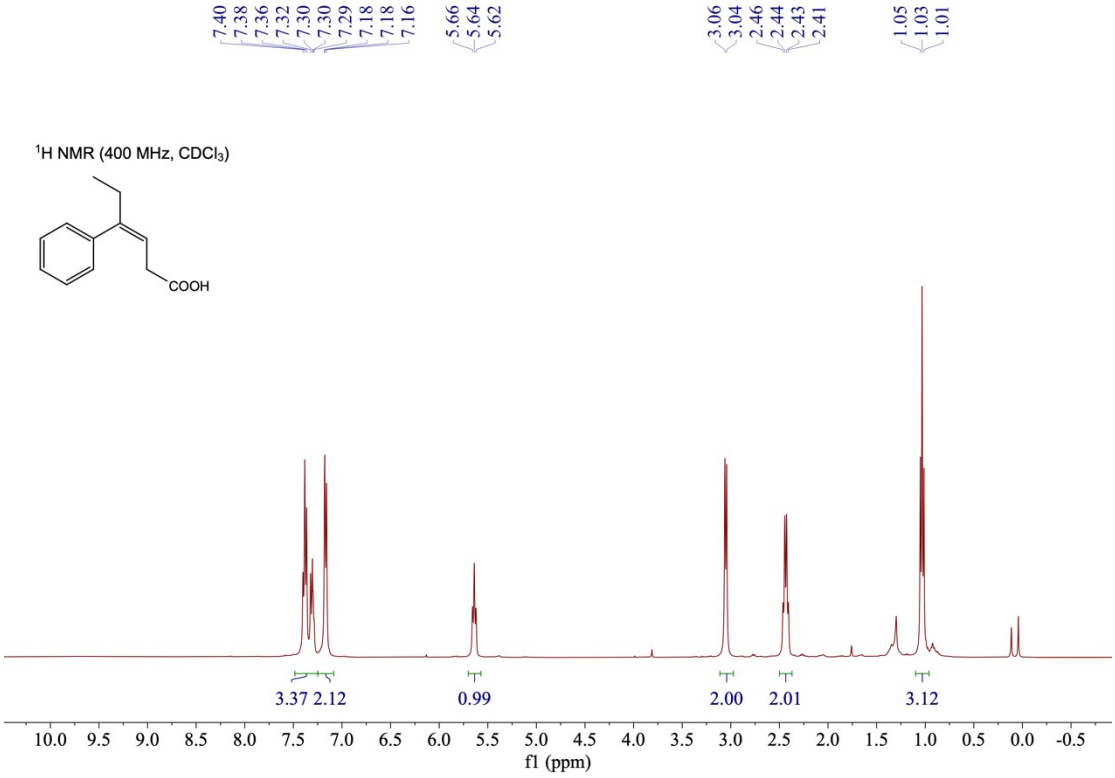


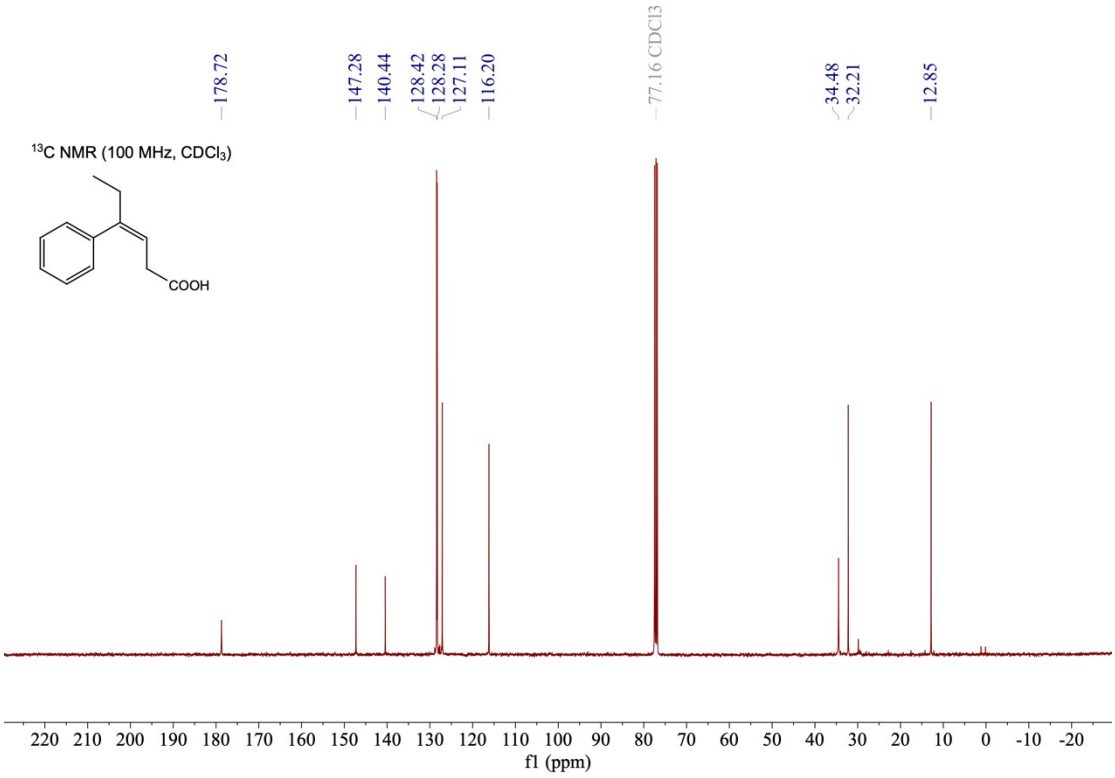
(Z)-4-(4-methoxyphenyl)pent-3-enoic acid(2j)



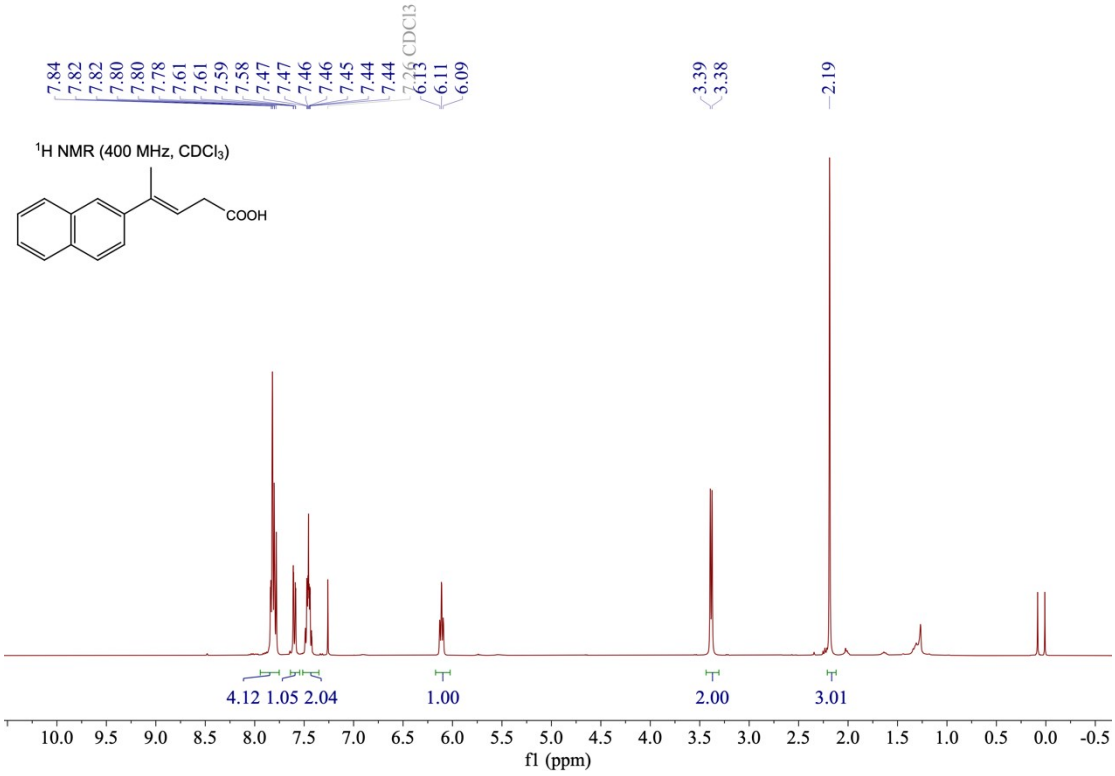


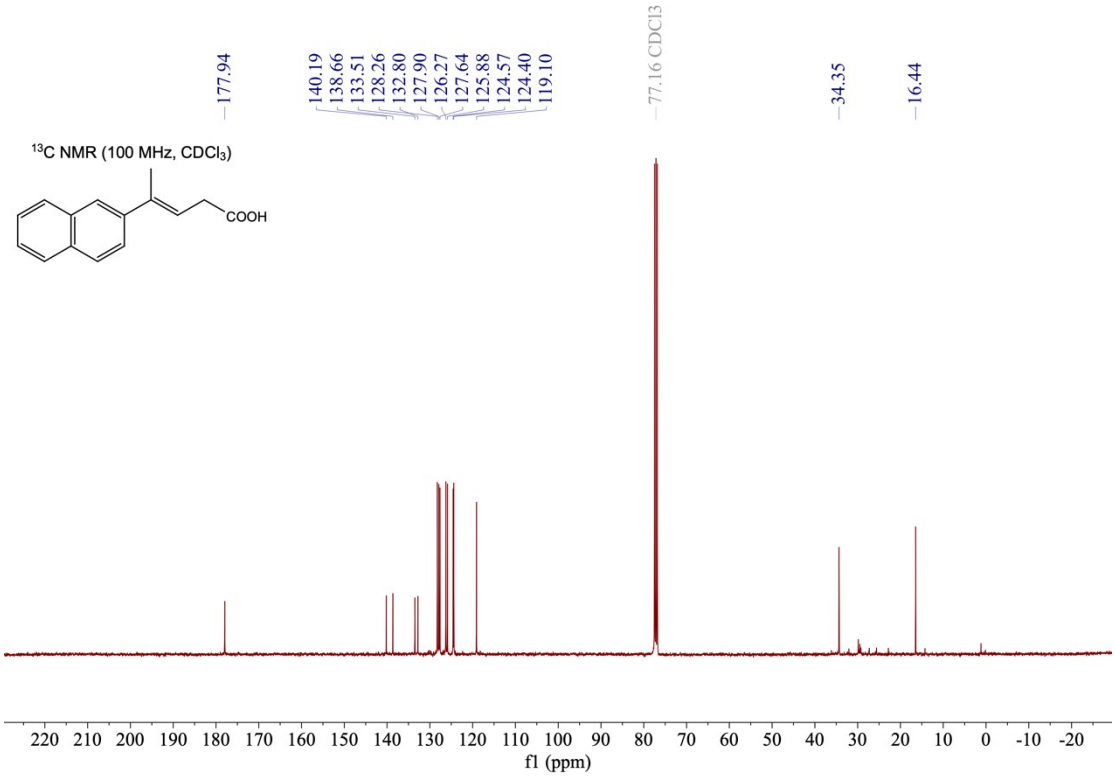
(Z)-4-phenylhex-3-enoic acid(2k)

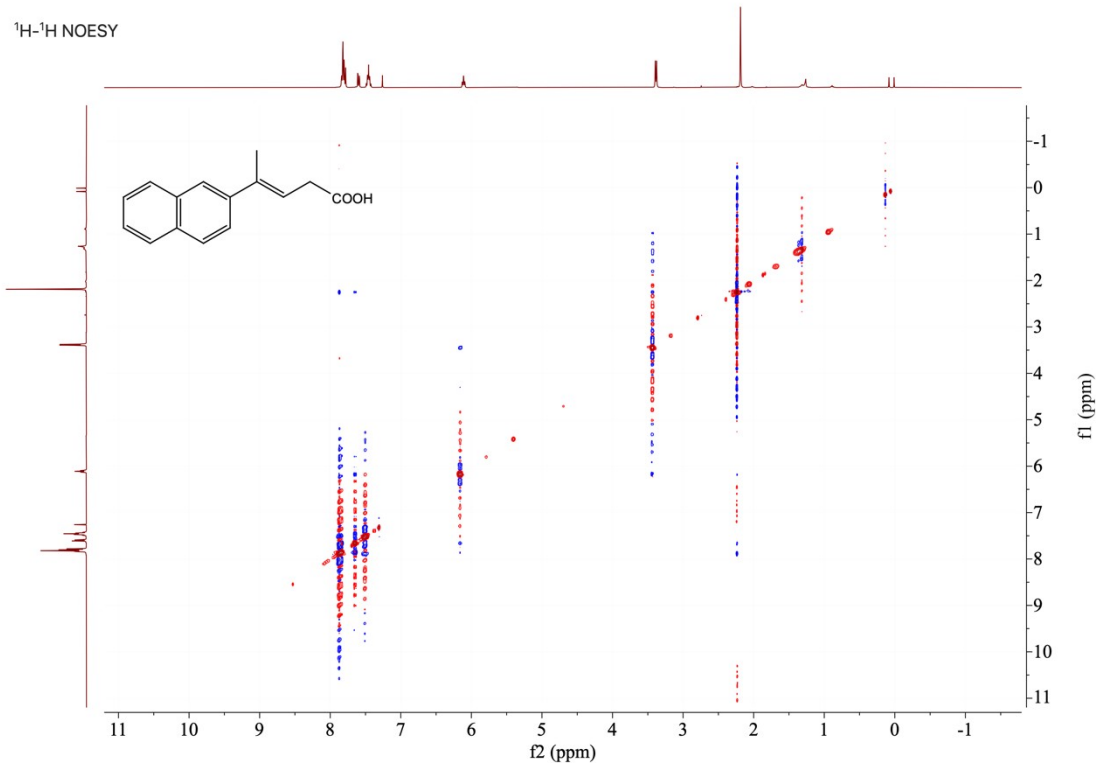




4-(naphthalen-2-yl)pent-3-enoic acid(2l)



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COOH
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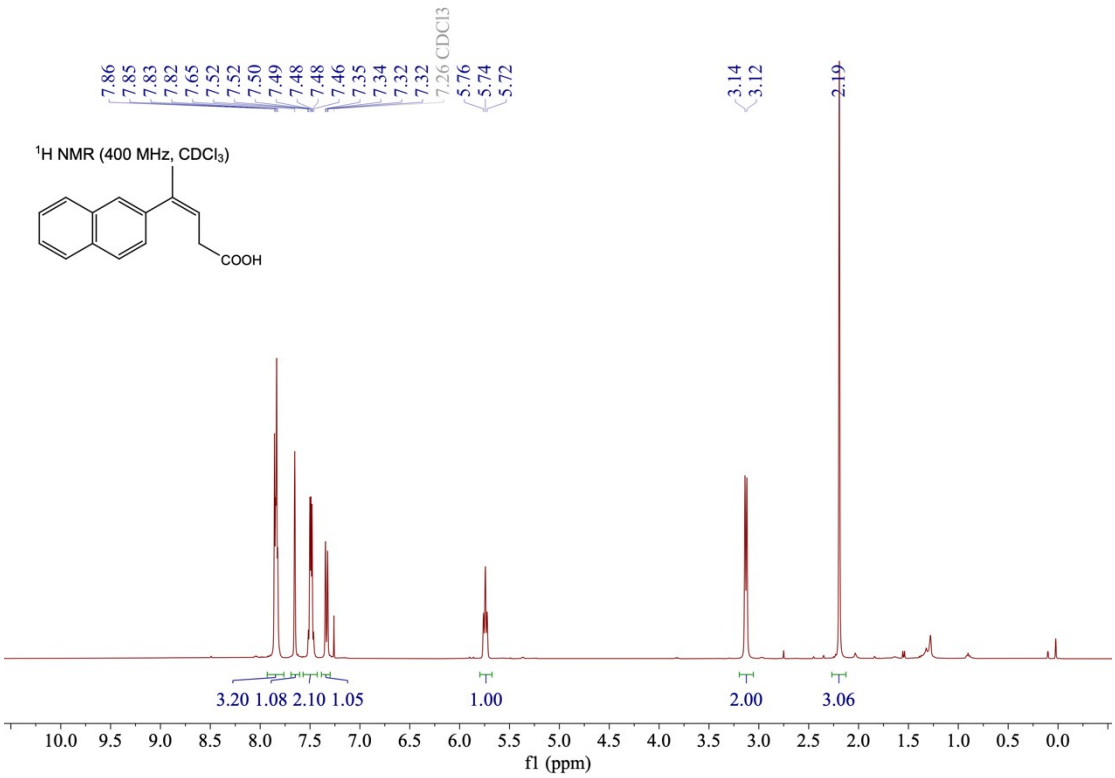
f1 (ppm)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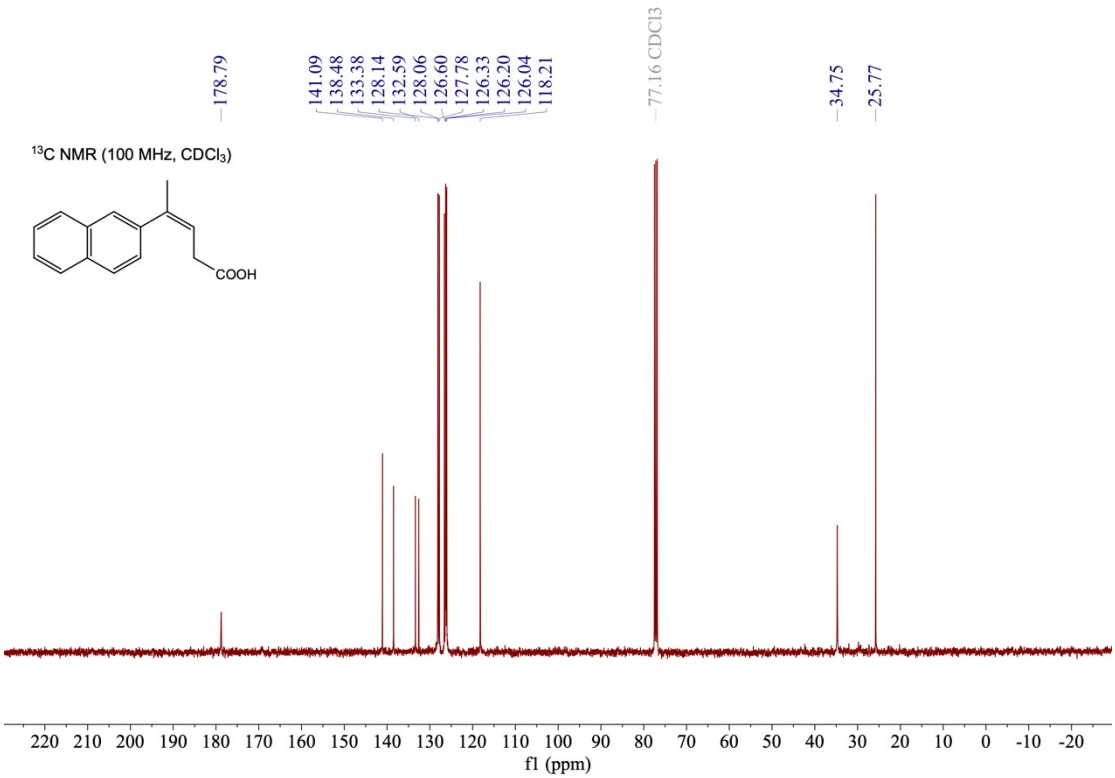
7.34
7.32
7.32
7.26 CDCl3
5.76
5.74
5.72
3.14
3.12
2.19
^{1}H NMR (400 MHz, CDCl$_3$)
COOH
3.20 1.08 2.10 1.05
1.00
2.00
3.06
f1 (ppm)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126.60
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126.33
126.20
126.04
118.21
77.16 CDCl3
34.75
25.77
13C NMR (100 MHz, CDCl3)
COOH
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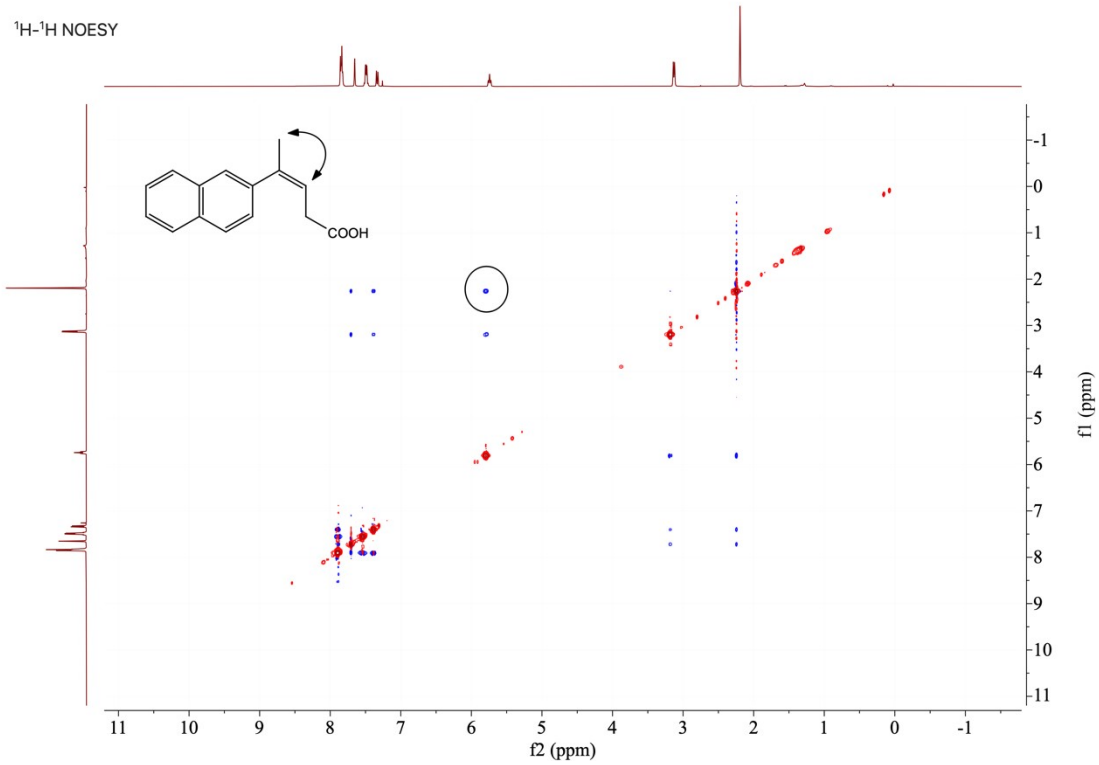
f1 (ppm)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f2 (ppm)
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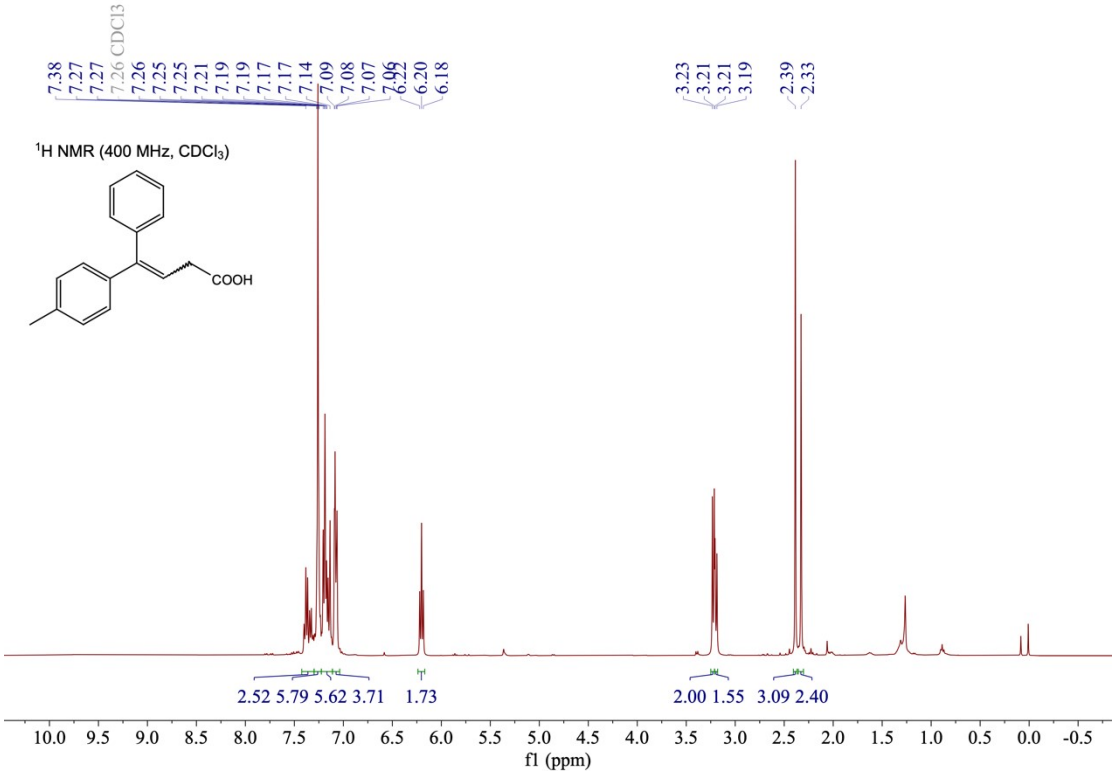
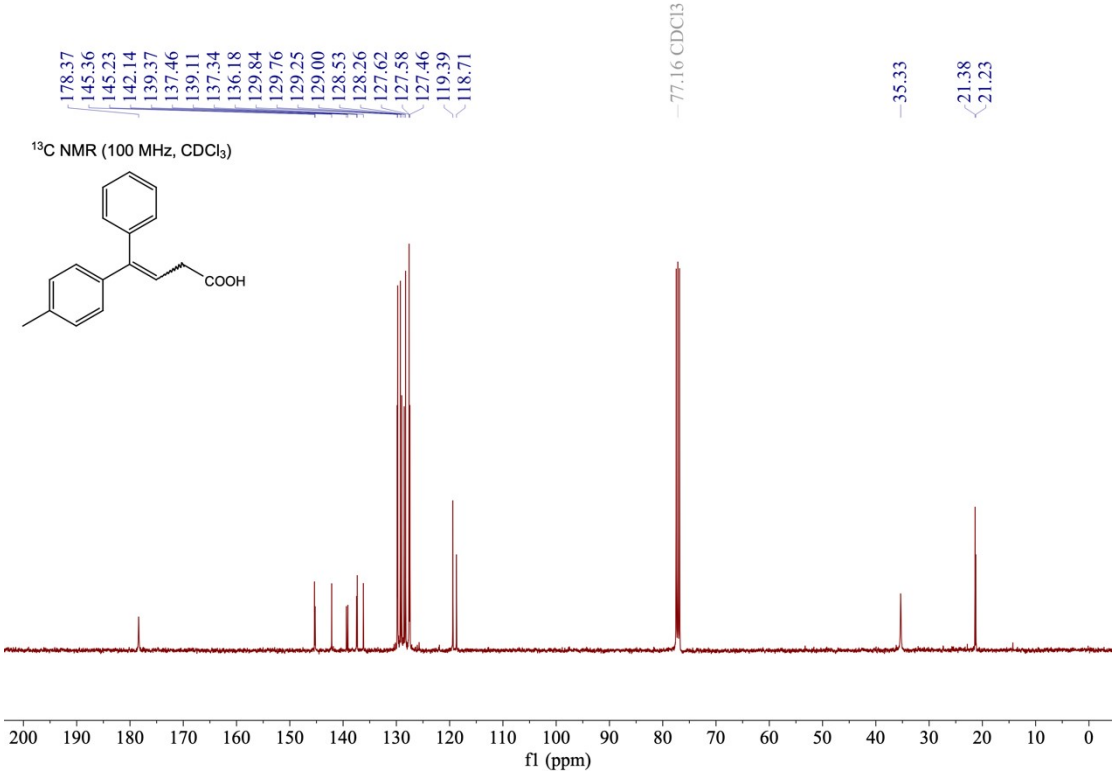
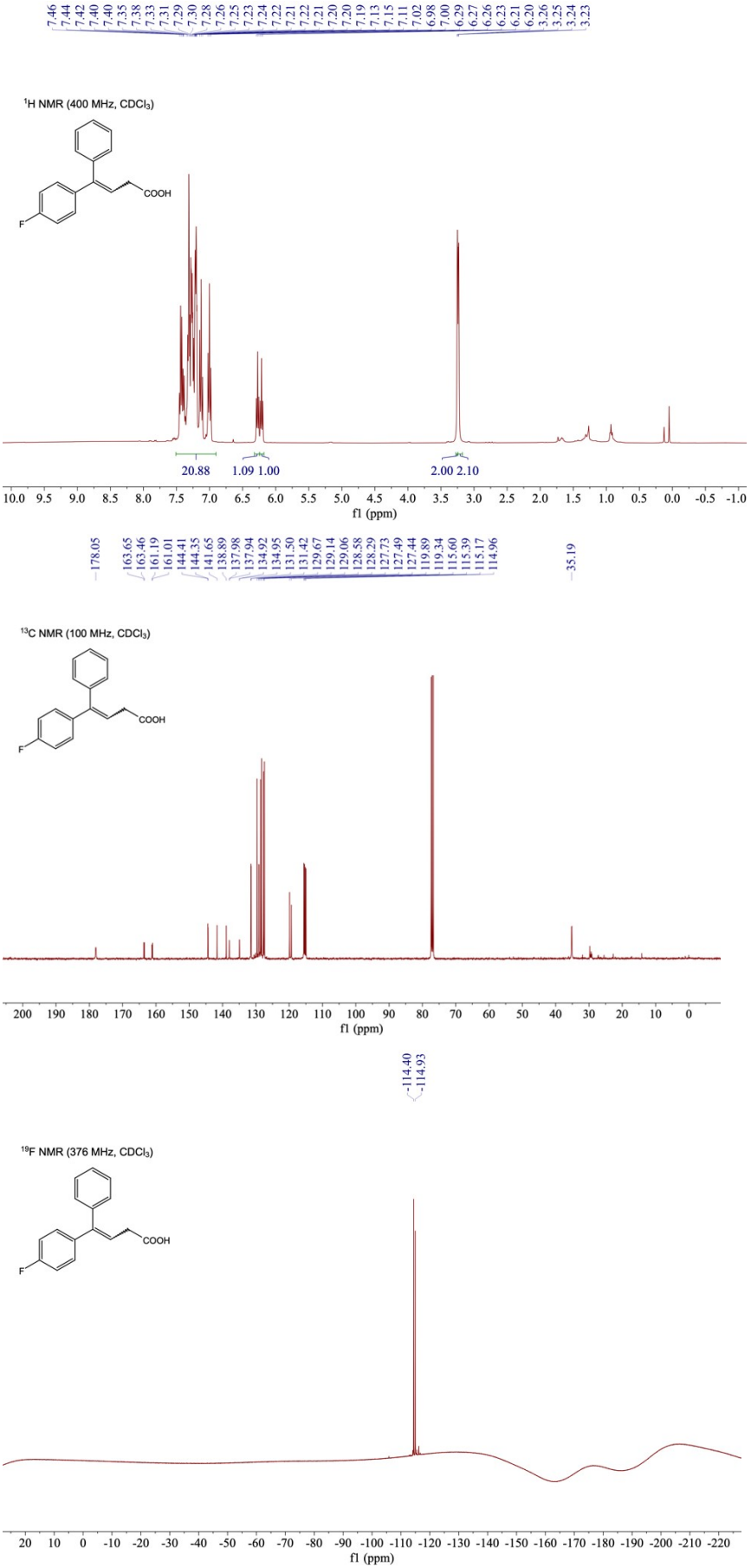
f1 (ppm)

4-phenyl-4-(p-tolyl)but-3-enoic acid(2m)





4-(4-fluorophenyl)-4-phenylbut-3-enoic acid(2n)



4-(4-chlorophenyl)-4-phenylbut-3-enoic acid(2o)