Supporting information

A Direct Palladium-Catalysed Carbonylative Transformation of Allylic Alcohols and Related Derivatives

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1. General details and materials

Unless otherwise noted, all reactions were carried out under a nitrogen atmosphere. All chemicals were from commercial sources and used as received without further purification. All solvents were dried by standard techniques, and distilled prior to use. Column chromatography was performed on silica gel (200-300 meshes) using petroleum ether (bp. 60~90 ^{o}C) and ethyl acetate as eluent. ^{1}H and ^{13}C NMR spectra were taken on 400 MHz instruments and spectral data were reported in ppm relative to tetramethylsilane (TMS) as internal standard and $CDCl_3$ as solvent. Mass spectra (MS) were measured on spectrometer by direct inlet at 70 eV. The allylic compounds used here were known compounds and synthesized according to the reported methods.[1]

2. Optimization of the reaction conditions

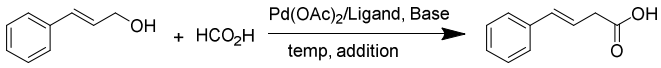


Table 1. Screening of the base.[a]

Entry	Pd	Ligand	Base	Yield (%)
1	$Pd(OAc)_2$	Xantphos	None	46
2	$Pd(OAc)_2$	Xantphos	$NaHCO_3$	53
3	$Pd(OAc)_2$	Xantphos	NaOOCH	35
4	$Pd(OAc)_2$	Xantphos	DIPEA	10
5	$Pd(OAc)_2$	Xantphos	DMAP	8
6	$Pd(OAc)_2$	Xantphos	Et_3N	<5

[a] Reaction condition: Cinnamyl alcohol (0.5 mmol), formic acid (3.5 mmol), $Pd(OAc)_2$ (3 mol%), Xantphos (3 mol%), Base (1.0 mmol), 4Å MS (80 mg), DCC(1.0 mmol), dioxane (2 mL), 50 ^{o}C, 20h.

Table 2. Screening of the Ligand.[a]

Entry	Pd	Ligand	Base	Yield (%)
1	$Pd(OAc)_2$	PPh_3	$NaHCO_3$	8
2	$Pd(OAc)_2$	$P(o\text{-}tolyl)_3$	$NaHCO_3$	<5
3	$Pd(OAc)_2$	$(t\text{-}Bu)_3P{\cdot}HBF_4$	$NaHCO_3$	<5
4	$Pd(OAc)_2$	DPPF	$NaHCO_3$	<5
5	$Pd(OAc)_2$	DPPP	$NaHCO_3$	<5

[a] Reaction condition: Cinnamyl alcohol (0.5 mmol), formic acid (3.5 mmol), $Pd(OAc)_2$ (3 mol%), L (Pd:P=1:2) , $NaHCO_3$ (1.0 mmol), 4Å MS (80 mg), DCC(1.0 mmol), dioxane (2 mL), 50 °C, 20h.

Table 3. Screening of the temperature.[a]

Entry	Pd	Ligand	Temp.(°C)	Yield (%)
1	$Pd(OAc)_2$	Xantphos	50	53
2	$Pd(OAc)_2$	Xantphos	60	67
3	$Pd(OAc)_2$	Xantphos	70	63

[a] Reaction condition: Cinnamyl alcohol (0.5 mmol), formic acid (3.5 mmol), $Pd(OAc)_2$ (3 mol%), Xantphos (3 mol%) , $NaHCO_3$ (1.0 mmol), 4Å MS (80 mg), DCC(1.0 mmol), dioxane (2 mL), 20h.

Table 4. Screening of the addition.[a]

Entry	Pd	L	Addition	Yield (%)
1[b]	$Pd(OAc)_2$	Xantphos	-	59
2[c]	$Pd(OAc)_2$	Xantphos	-	76
3[d]	$Pd(OAc)_2$	Xantphos	-	58
4[e]	$Pd(OAc)_2$	Xantphos	TFA	40
5	$Pd(OAc)_2$	Xantphos	$Cu(OTf)_2$	<5

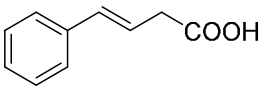
[a] Reaction condition: Cinnamyl alcohol (0.5 mmol), formic acid (3.5 mmol), Pd (3 mol%), Xantphos (3 mol%), $NaHCO_3$ (1.0 mmol), 4Å MS (80 mg), DCC(1.0 mmol), dioxane (2 mL), 60 °C, 20h. [b] $NaHCO_3$ (0.5 mmol). [c] $NaHCO_3$ (1.5 mmol). [d] Pd:P=1:3. [e] TFA (10 mol%) instead of $NaHCO_3$. [f] $Cu(OTf)_2$ (20 mol%) instead of $NaHCO_3$.

3. General Procedure

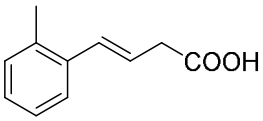
$Pd(OAc)_2$ (3 mol %), ligand (P:Pd=2:1, 6 mol % for monodentate ligands and 3 mol % for bidentate ligand), $NaHCO_3$ (1.5 mmol), DCC (1 mmol), 4 Å MS (80 mg) were transferred into an oven-dried tube which was filled with nitrogen. Dioxane (2.0 mL), formic acid (3.5 mmol), and allylic alcohol (0.5 mmol) were added to the reaction tube. After formic acid (3.5 mmol) were added, the tube was sealed and the mixture was stirred at 60 °C for 20 h. After the reaction finished, the reaction solution was cooled to room temperature and the reaction mixture was filtered and concentrated under vacuum. The crude product was purified column chromatography on silica gel. EtOAc/petroleum ether (1/10 to 2/1) to give the desired product.

Procedure for Table 2, entry 1: $Pd(OAc)_2$ (3 mol %), Xantphos (3 mol %), $NaHCO_3$ (3 mmol), DCC (2 mmol), 4 Å MS (160 mg) were transferred into an oven-dried tube which was filled with nitrogen. 1,4-Dioxane (4.0 mL), formic acid (7 mmol), and cinnamyl alcohol (1 mmol) were added to the reaction tube. After formic acid was added, the tube was sealed and the mixture was stirred at 60 °C for 20 h. After the reaction finished, the reaction solution was cooled to room temperature and the reaction mixture was filtered and concentrated under vacuum. The crude product was purified column chromatography on silica gel. EtOAc/petroleum ether (1/10 to 2/1) to give the desired product.

4.Spectroscopic Data of Products

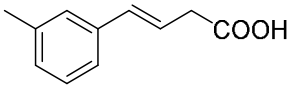


(*E*)-4-Phenylbut-3-enoic acid:[2] (Table 2, entry 1; Table 3, entry 1; Table 4), white solid, 61.6 mg, ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.02 (s, 1H), 7.43 (d, *J* = 7.3 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 2H), 7.29 (dd, *J* = 8.5, 5.8 Hz, 1H), 6.56 (d, *J* = 15.9 Hz, 1H), 6.34 (dt, *J* = 15.8, 7.1 Hz, 1H), 3.35 (dd, *J* = 7.1, 1.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.98, 136.70, 133.99, 128.61, 127.73, 126.37, 120.93, 38.14.

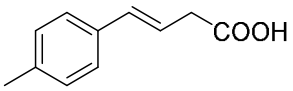


(*E*)-4-(*o*-Tolyl)but-3-enoic acid:[3] (Table 2, entry 2; Table 3, entry 2), white solid, 56.3 mg, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.30 (s, 1H), 7.50 – 7.45 (m, 1H), 7.22 – 7.16 (m, 3H), 6.76 (d, *J* = 15.7

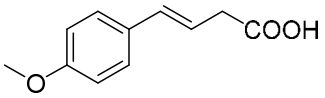
Hz, 1H), 6.28 – 6.12 (m, 1H), 3.36 (dd, *J* = 7.1, 1.3 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.20, 135.83, 135.32, 131.91, 130.28, 127.64, 126.15, 125.79, 122.18, 38.39, 19.81.



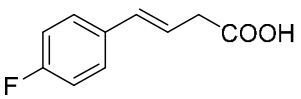
(*E*)-4-(*m*-Tolyl)but-3-enoic acid:[2] (Table 2, entry 3; Table 3, entry 3), white solid, 66.9 mg, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.41 (s, 1H), 7.27 – 7.18 (m, 3H), 7.10 (d, *J* = 7.0 Hz, 1H), 6.53 (d, *J* = 15.9 Hz, 1H), 6.36 – 6.26 (m, 1H), 3.33 (d, *J* = 7.0 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.22, 138.14, 136.62, 134.10, 128.53, 128.49, 127.04, 123.56, 120.61, 38.12, 21.40.



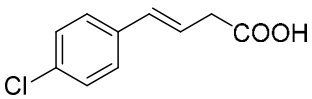
(*E*)-4-(*p*-Tolyl)but-3-enoic acid:[2] (Table 2, entry 4; Table 3, entry 4), white solid, 58.1 mg, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 7.9 Hz, 2H), 6.52 (d, *J* = 15.9 Hz, 1H), 6.32 – 6.21 (m, 1H), 3.36 – 3.28 (m, 2H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.17, 137.52, 133.92, 133.88, 129.27, 126.27, 119.77, 38.10, 21.20.



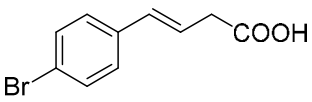
(*E*)-4-(4-Methoxyphenyl)but-3-enoic acid:[2] (Table 2, entry 5; Table 3, entry 5), white solid, 69.1 mg, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.52 (s, 1H), 7.33 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.47 (d, *J* = 15.8 Hz, 1H), 6.16 (d, *J* = 15.8 Hz, 1H), 3.82 (s, 3H), 3.28 (d, *J* = 7.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.27, 159.24, 133.31, 129.55, 127.52, 118.74, 113.98, 55.29, 38.22.



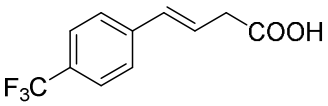
(*E*)-4-(4-Fluorophenyl)but-3-enoic acid:[2] (Table 2, entry 6; Table 3, entry 6), white solid, 63 mg, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.35 (s, 1H), 7.36 (dd, *J* = 8.6, 5.5 Hz, 2H), 7.03 (t, *J* = 8.7 Hz, 2H), 6.50 (d, *J* = 15.9 Hz, 1H), 6.22 (d, *J* = 15.9 Hz, 1H), 3.31 (dd, *J* = 7.1, 0.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.09, 163.62, 161.16, 132.85, 127.90, 127.82, 120.56, 115.61, 115.39, 37.97.



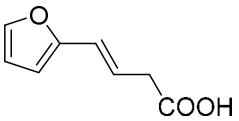
(*E*)-4-(4-Chlorophenyl)but-3-enoic acid:[2] (Table 2, entry 7; Table 3, entry 7), white solid, 67.7 mg, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.17 (s, 1H), 7.34 – 7.28 (m, 4H), 6.49 (d, *J* = 15.9 Hz, 1H), 6.33 – 6.24 (m, 1H), 3.32 (d, *J* = 7.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.96, 135.13, 133.37, 132.80, 128.75, 127.55, 121.55, 38.01.



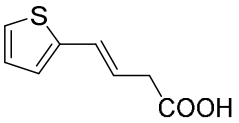
(*E*)-4-(4-Bromophenyl)but-3-enoic acid:[4] (Table 2, entry 8; Table 3, entry 8), light yellow solid, 86.8 mg, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.76 (s, 1H), 7.45 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 8.3 Hz, 2H), 6.47 (d, *J* = 15.9 Hz, 1H), 6.36 – 6.24 (m, 1H), 3.31 (d, *J* = 6.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.95, 135.57, 132.86, 131.70, 127.88, 121.68, 121.52, 38.02.



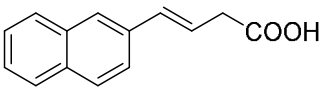
(*E*)-4-(4-(Trifluoromethyl)phenyl)but-3-enoic acid:[2] (Table 2, entry 9), white solid, 85.1 mg, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.81 (s, 1H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 6.58 (d, *J* = 16.0 Hz, 1H), 6.42 (dt, *J* = 15.9, 7.0 Hz, 1H), 3.39 – 3.34 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.59, 140.06, 132.71, 129.71, 129.39, 126.49, 125.53, 123.64, 122.81, 37.94.



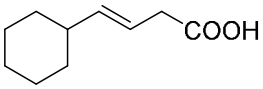
(*E*)-4-(Furan-2-yl)but-3-enoic acid:[2] (Table 2, entry 10; Table 3, entry 9), light brown solid, 61.6 mg, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.16 (s, 1H), 7.36 (s, 1H), 6.40 – 6.33 (m, 2H), 6.29 – 6.18 (m, 2H), 3.28 (d, *J* = 7.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.89, 152.12, 142.06, 122.37, 119.44, 111.22, 107.88, 37.77.



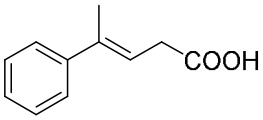
(*E*)-4-(Thiophen-2-yl)but-3-enoic acid:[5] (Table 2, entry 11; Table 3, entry 10), yellow solid, 63 mg, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 7.23 – 7.10 (m, 1H), 7.01 – 6.94 (m, 2H), 6.66 (d, *J* = 15.7 Hz, 1H), 6.17 – 6.09 (m, 1H), 3.28 (d, *J* = 7.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.54, 141.63, 127.31, 127.04, 125.65, 124.33, 120.53, 38.09.



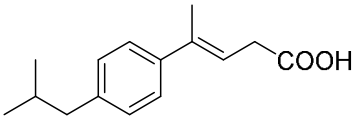
(*E*)-4-(Naphthalen-2-yl)but-3-enoic acid:[2] (Table 2, entry 12; Table 3, entry 11), white solid, 82.7 mg, ^{1}H NMR (400 MHz, DMSO) δ 12.39 (s, 1H), 7.87 (d, *J* = 3.3 Hz, 3H), 7.83 (s, 1H), 7.68 (d, *J* = 8.5 Hz, 1H), 7.53 – 7.44 (m, 2H), 6.67 (d, *J* = 15.9 Hz, 1H), 6.56 – 6.40 (m, 1H), 3.27 (d, *J* = 6.5 Hz, 2H). ^{13}C NMR (101 MHz, DMSO) δ 173.13, 134.77, 133.69, 132.89, 132.75, 128.60, 128.30, 128.01, 126.83, 126.33, 126.04, 124.31, 123.94, 38.43.



(*E*)-4-Cyclohexylbut-3-enoic acid:[6] (Table 2, entry 13; Table 3, entry 12), colorless oil, 53 mg, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (s, 1H), 5.59 – 5.45 (m, 2H), 3.08 (d, *J* = 6.3 Hz, 2H), 2.03 – 1.92 (m, 1H), 1.73 (d, *J* = 10.5 Hz, 4H), 1.31 – 1.25 (m, 2H), 1.25 – 1.03 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.60, 141.19, 118.35, 40.59, 37.92, 32.74, 26.13, 25.98.



(*E*)-4-Phenylpent-3-enoic acid:[2] (Table 3, entry 13), white solid, 52.8 mg, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.3 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.30 (d, *J* = 7.3 Hz, 1H), 5.97 (t, *J* = 7.1 Hz, 1H), 3.35 (d, *J* = 7.1 Hz, 2H), 2.11 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.33, 142.93, 138.74, 128.28, 127.22, 125.84, 118.39, 34.19, 16.29.



(*E*)-4-(4-Isobutylphenyl)pent-3-enoic acid:[7] (Table 3, entry 14), white solid, 60.3 mg, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 5.95 (t, *J* = 7.0 Hz, 1H), 3.32 (d, *J* = 7.1 Hz, 2H), 2.48 (d, *J* = 7.1 Hz, 2H), 2.08 (s, 3H), 1.91 – 1.85 (m, 1H), 0.93 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.63, 140.77, 138.45, 128.99, 126.92, 125.47, 117.64, 45.04, 34.12, 30.21, 22.38, 16.19.

5. References

[1] a) Jiang, T.; Livinghouse, T.; Lovick, H. M. *Chem. Commun*. **2011**, 47, 12861; b) Zhang, P.; Le, H.; Kyne, R. E.; Morken, J. P. *J. Am. Chem. Soc*. **2011**, 133, 9716. c) Ardolino, M. J.; Morken, J. P. *J. Am. Chem. Soc.* **2014**, 136, 7092.

[2] Fu, M.-C.; Shang, R.; Cheng, W.-M.; Fu, Y. *Chem. Eur. J.* **2017**, *23*, 8818-8822.

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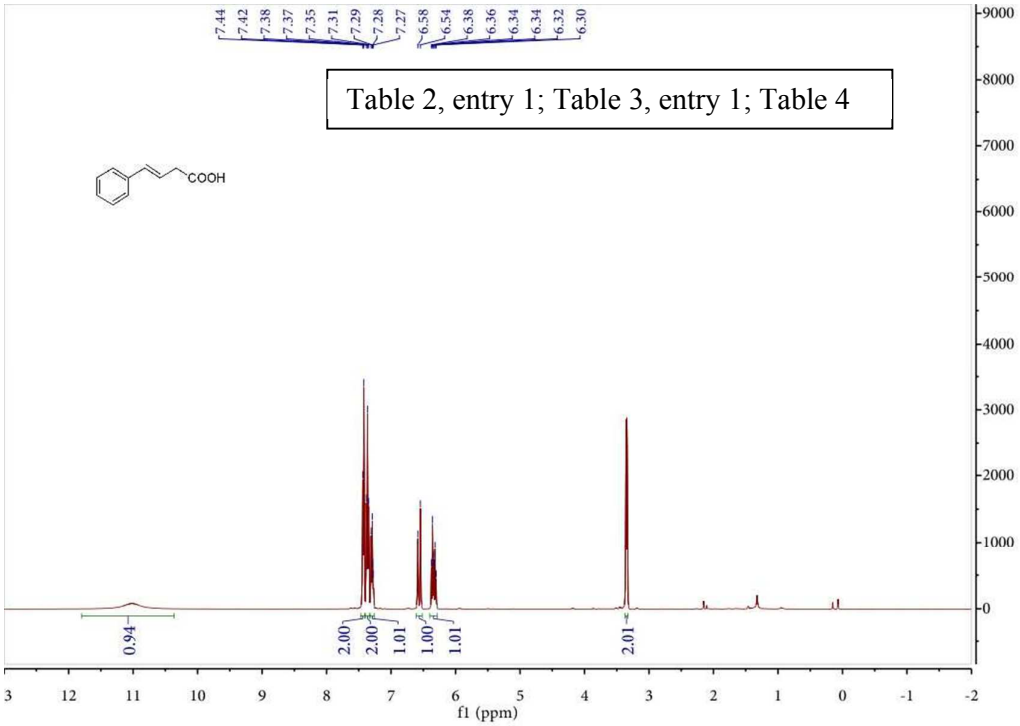
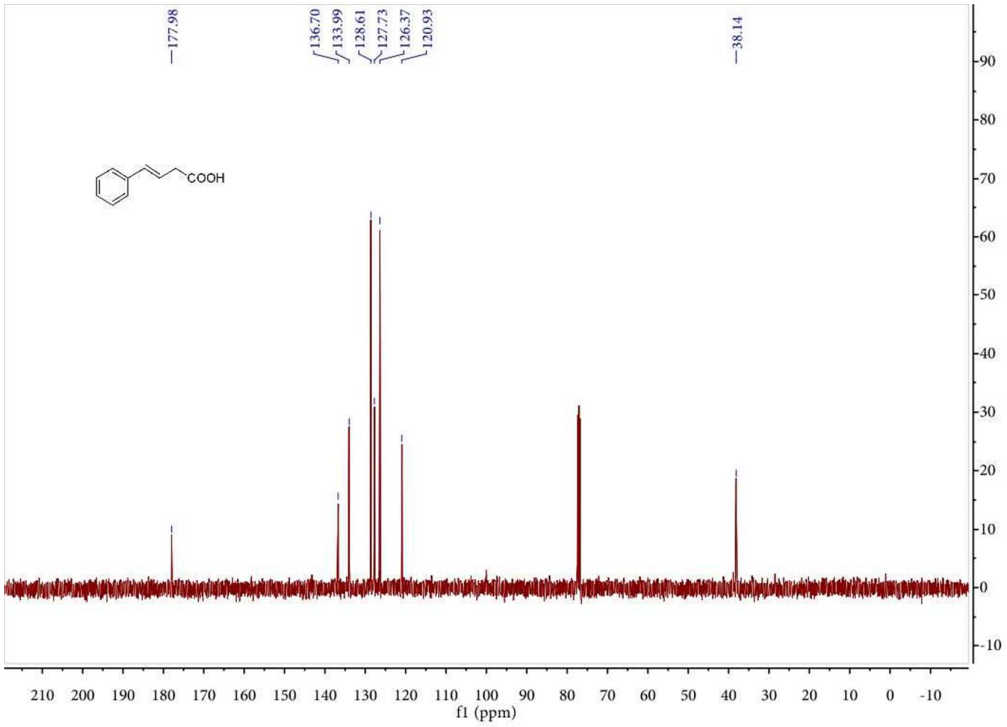
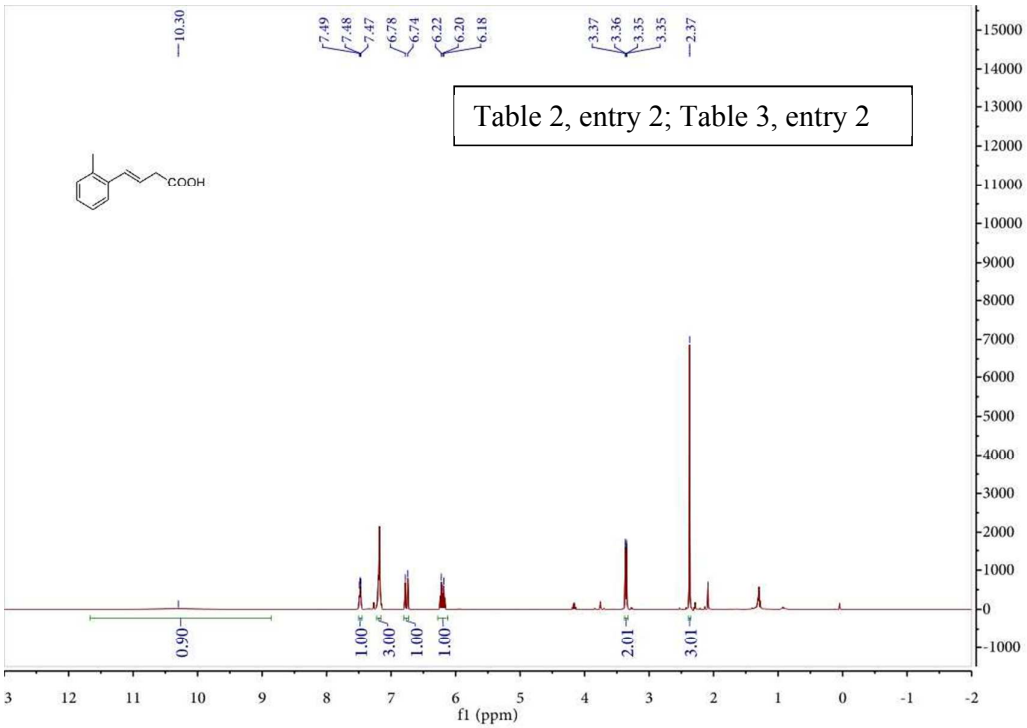
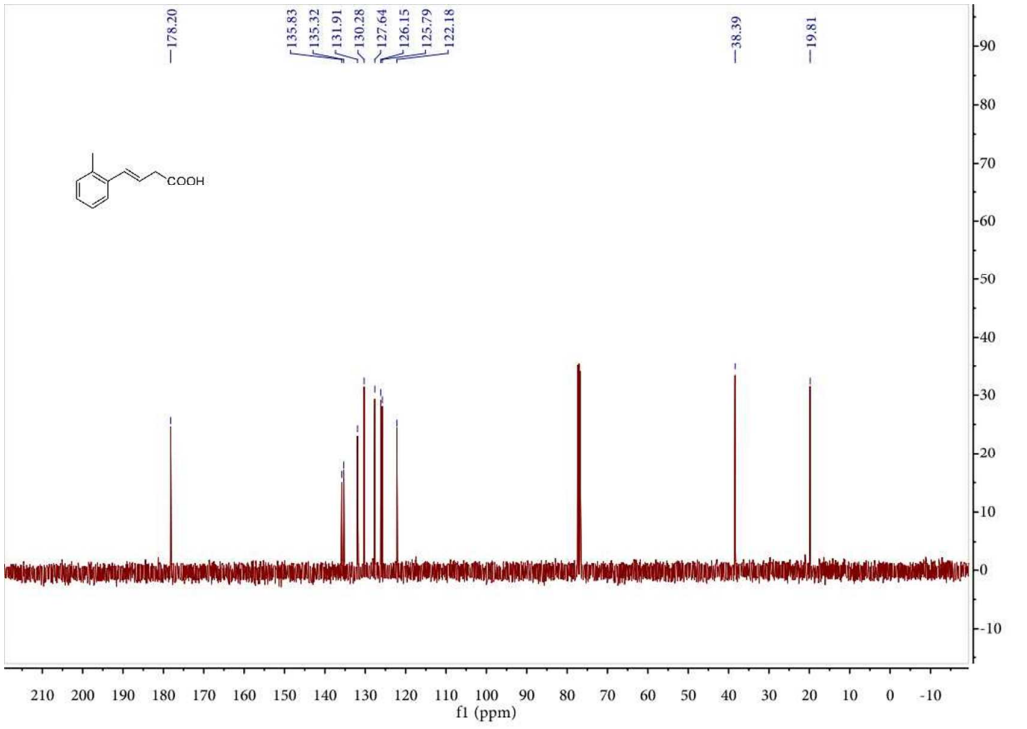
[7] (a) K. Thomae, Patent: DE2223562 , **1973**; (b) K. Thomae, *Chem.Abstr.,* **1974**, *80*, 59713.

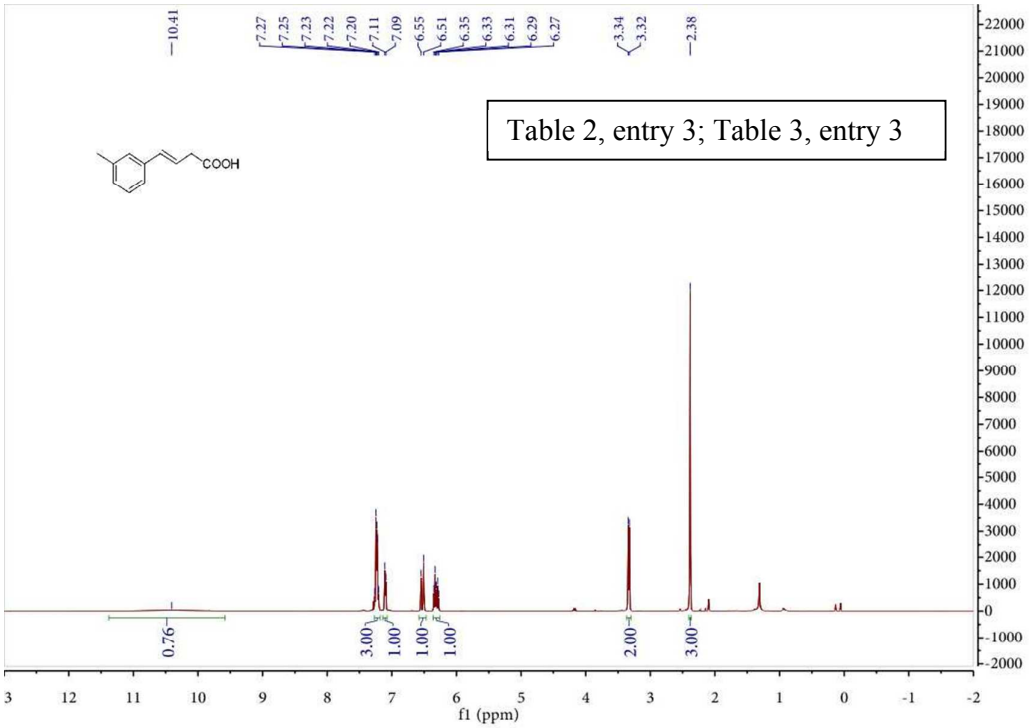
6.Copy of ^{1}H and ^{13}C NMR Spectra of Products

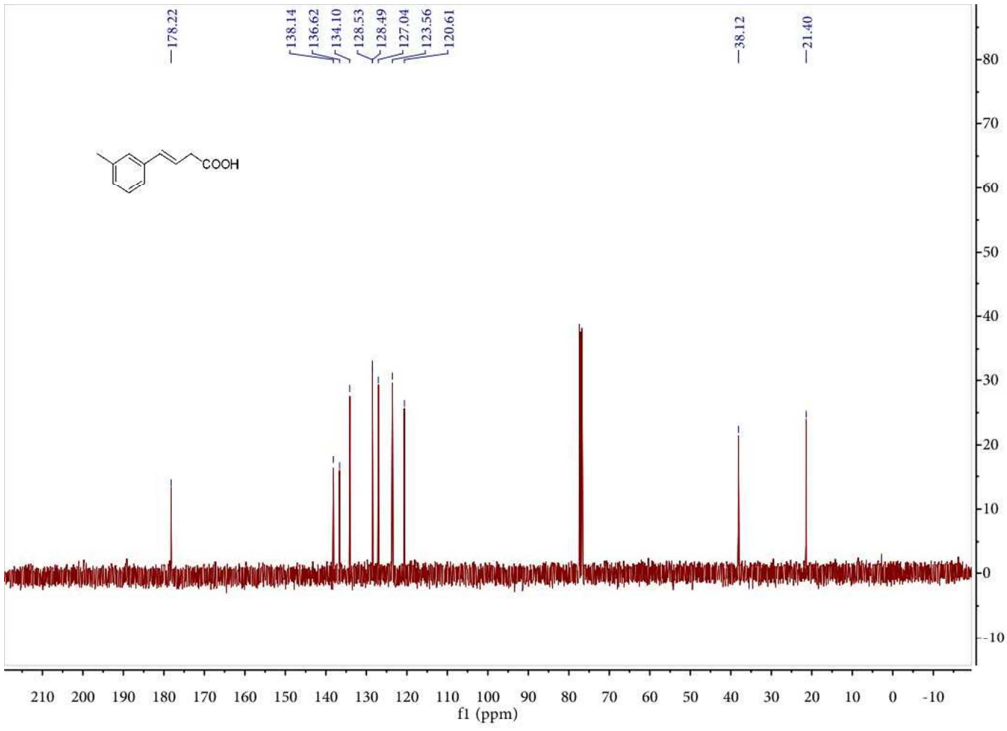


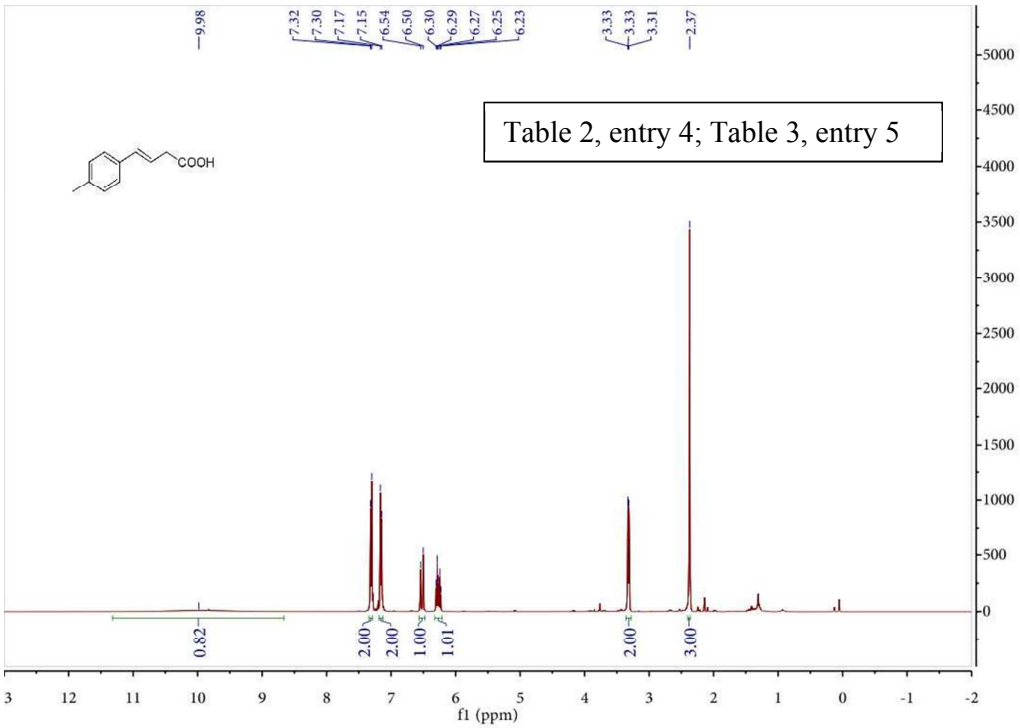


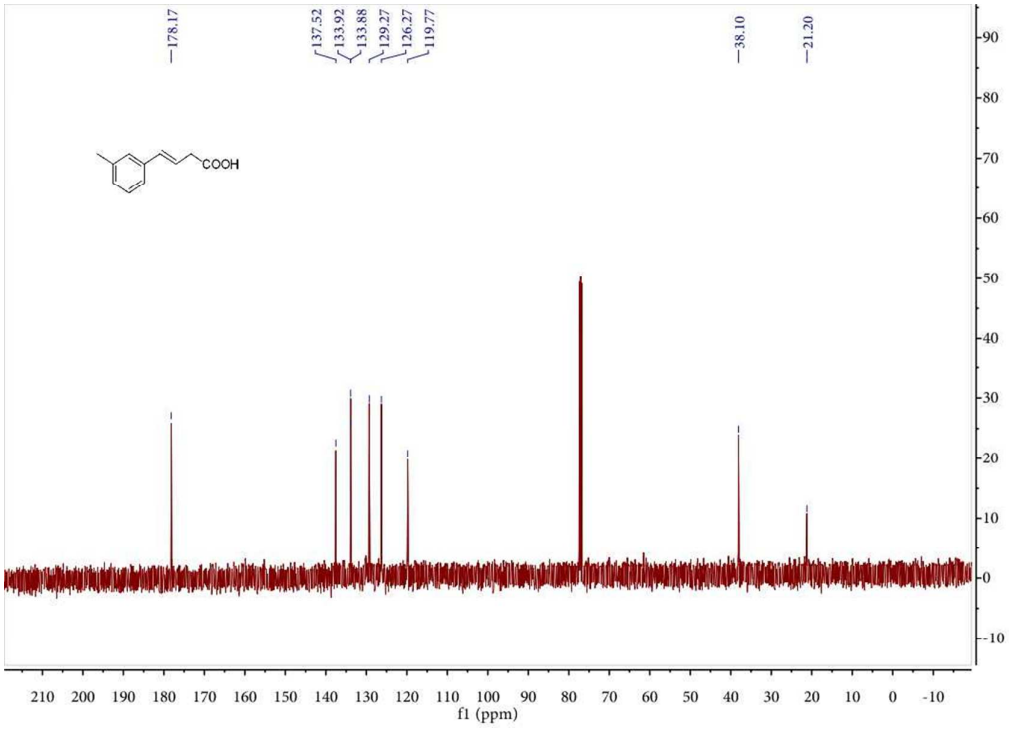

10.30
7.49
7.48
7.47
6.78
6.74
6.22
6.20
6.18
3.37
3.36
3.35
3.35
2.37
Table 2, entry 2; Table 3, entry 2
COOH
0.90
1.00
3.00
1.00
1.00
2.01
3.01
f1 (ppm)

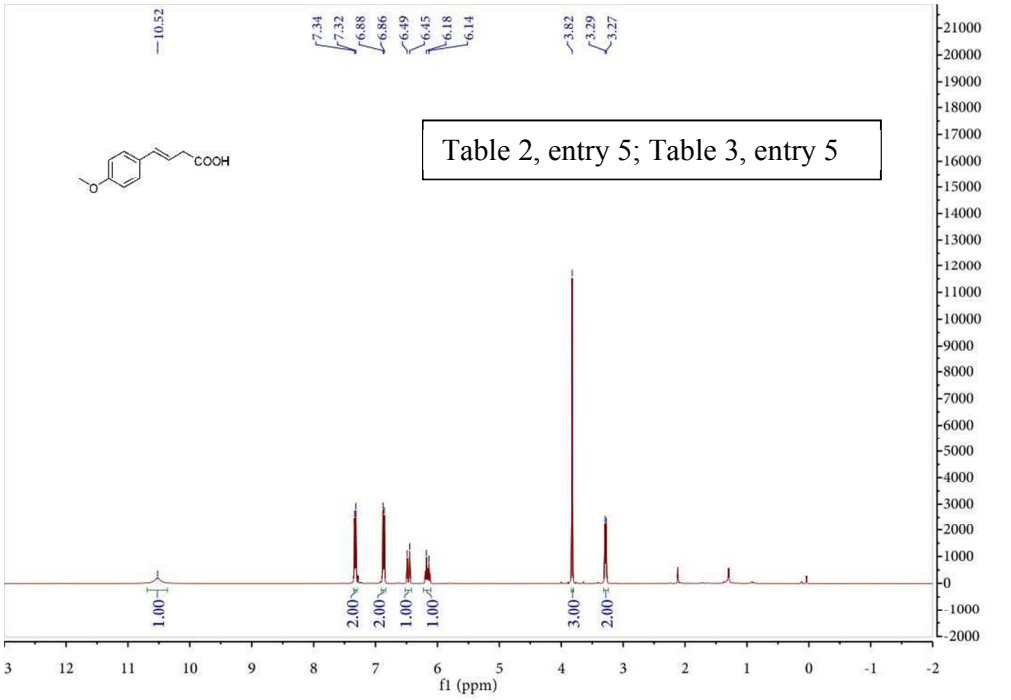

178.20
135.83
135.32
131.91
130.28
127.64
126.15
125.79
122.18
38.39
19.81
COOH
f1 (ppm)

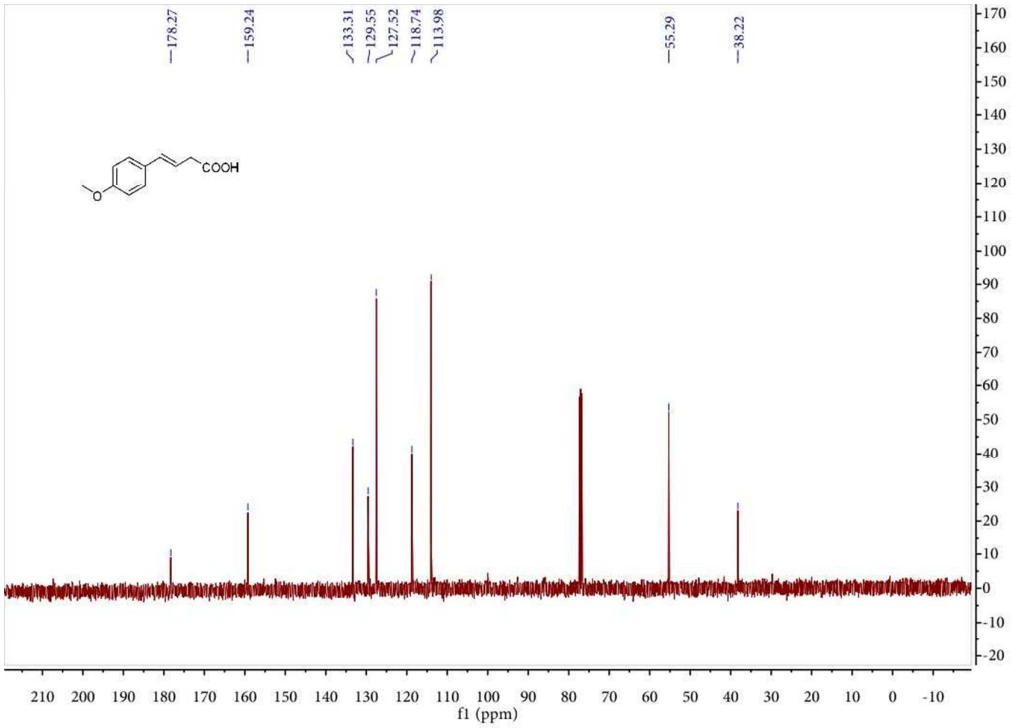

10.41
7.27
7.25
7.23
7.22
7.20
7.11
7.09
6.55
6.51
6.35
6.33
6.31
6.29
6.27
3.34
3.32
2.38
COOH
Table 2, entry 3; Table 3, entry 3
0.76
3.00
1.00
1.00
1.00
2.00
3.00
f1 (ppm)

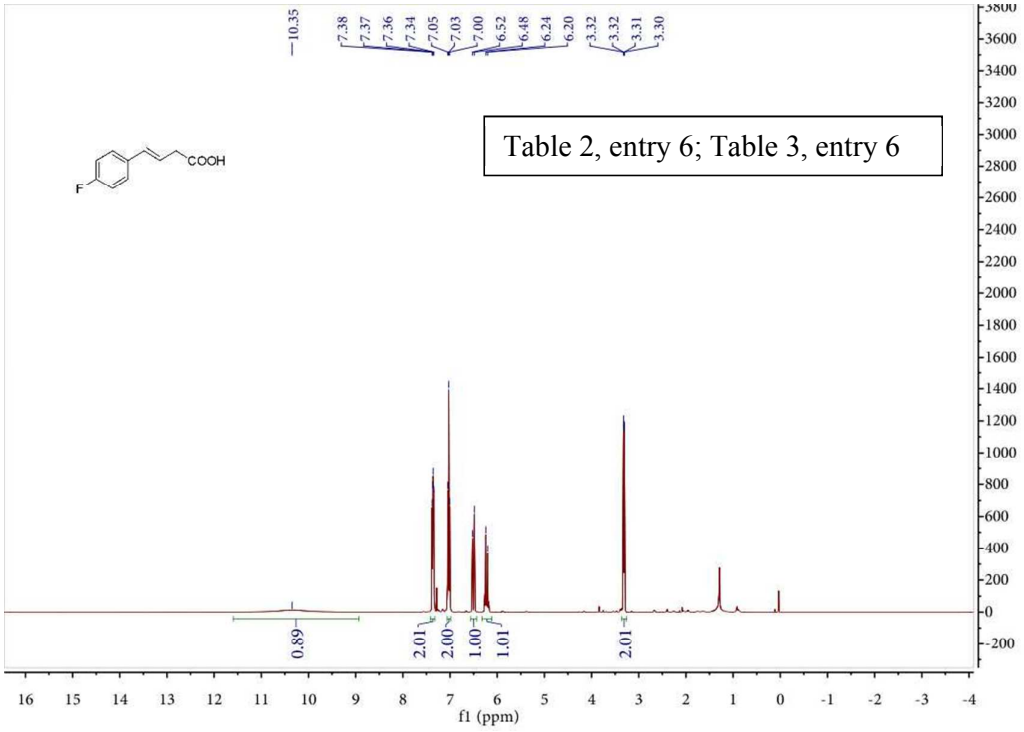

178.22
138.14
136.62
134.10
128.53
128.49
127.04
123.56
120.61
38.12
21.40
COOH
f1 (ppm)

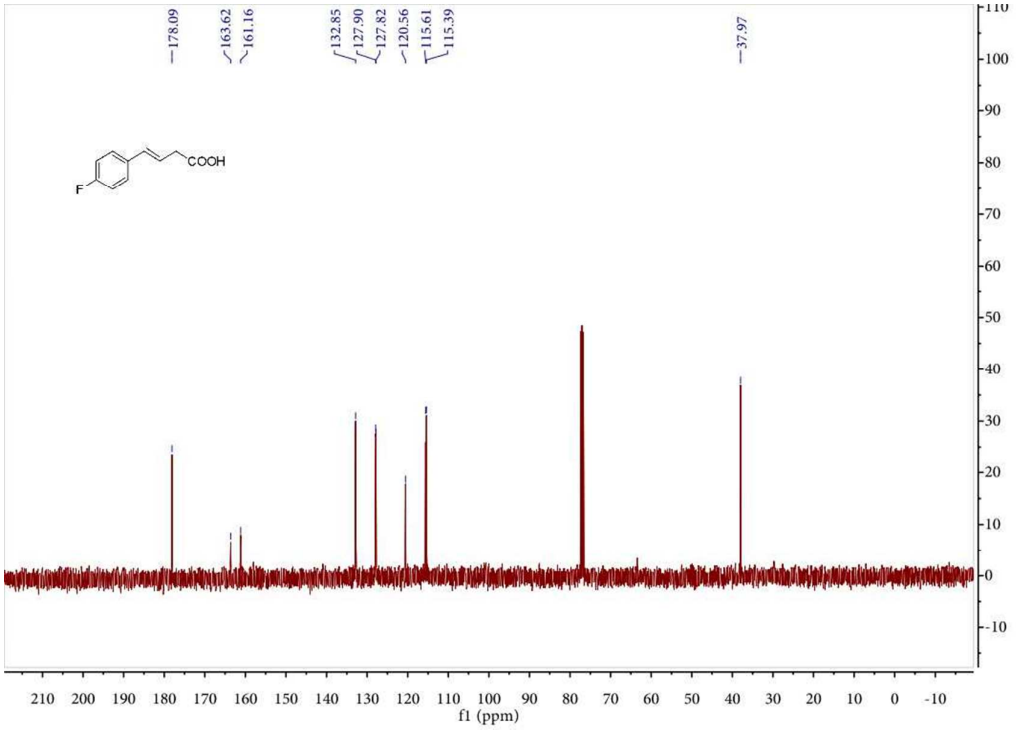

9.98
7.32
7.30
7.17
7.15
6.54
6.50
6.30
6.29
6.27
6.25
6.23
3.33
3.33
3.31
2.37
COOH
Table 2, entry 4; Table 3, entry 5
0.82
2.00
2.00
1.00
1.01
2.00
3.00
f1 (ppm)


178.17
137.52
133.92
133.88
129.27
126.27
119.77
38.10
21.20
COOH
f1 (ppm)


10.52
7.34
7.32
6.88
6.86
6.49
6.45
6.18
6.14
3.82
3.29
3.27
COOH
Table 2, entry 5; Table 3, entry 5
1.00
2.00
2.00
1.00
1.00
3.00
2.00
f1 (ppm)


178.27
159.24
133.31
129.55
127.52
118.74
113.98
55.29
38.22
COOH
f1 (ppm)


10.35
7.38
7.37
7.36
7.34
7.05
7.03
7.00
6.52
6.48
6.24
6.20
3.32
3.32
3.31
3.30
COOH
F
Table 2, entry 6; Table 3, entry 6
0.89
2.01
2.00
1.00
1.01
2.01
f1 (ppm)


178.09
163.62
161.16
132.85
127.90
127.82
120.56
115.61
115.39
37.97
COOH
F
f1 (ppm)

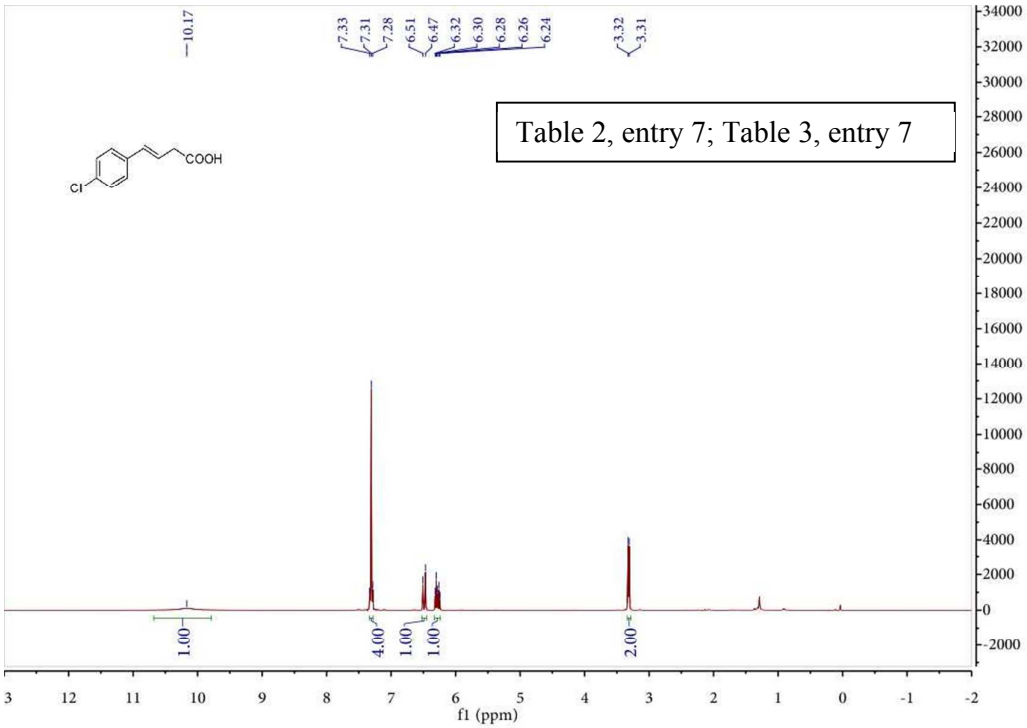
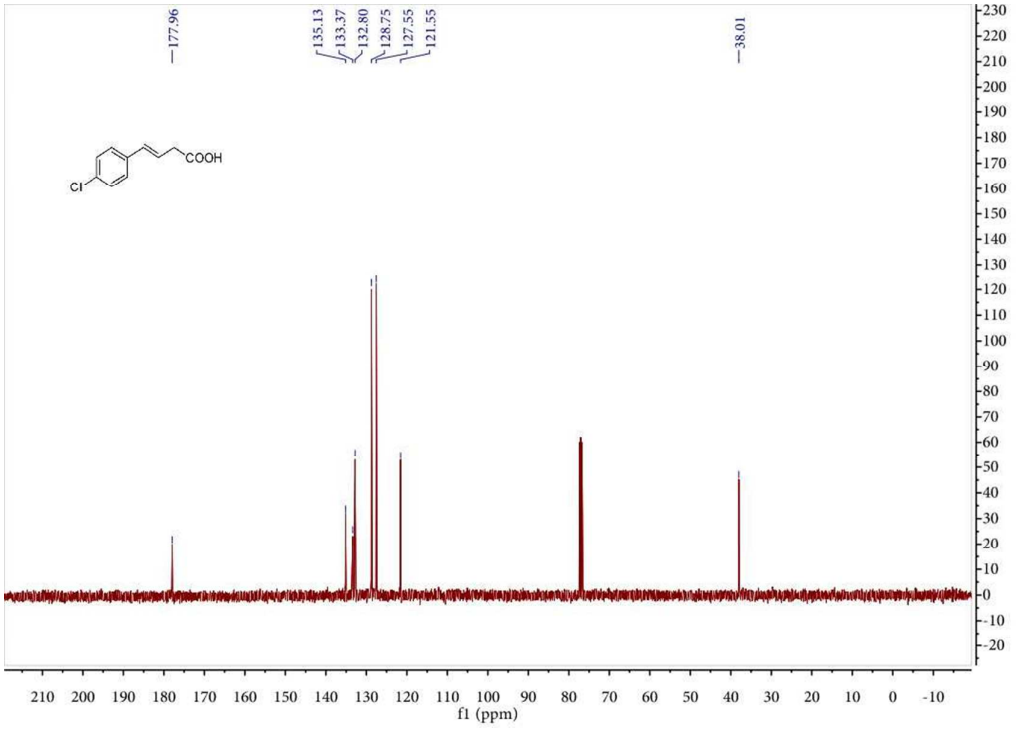


Table 2, entry 7; Table 3, entry 7



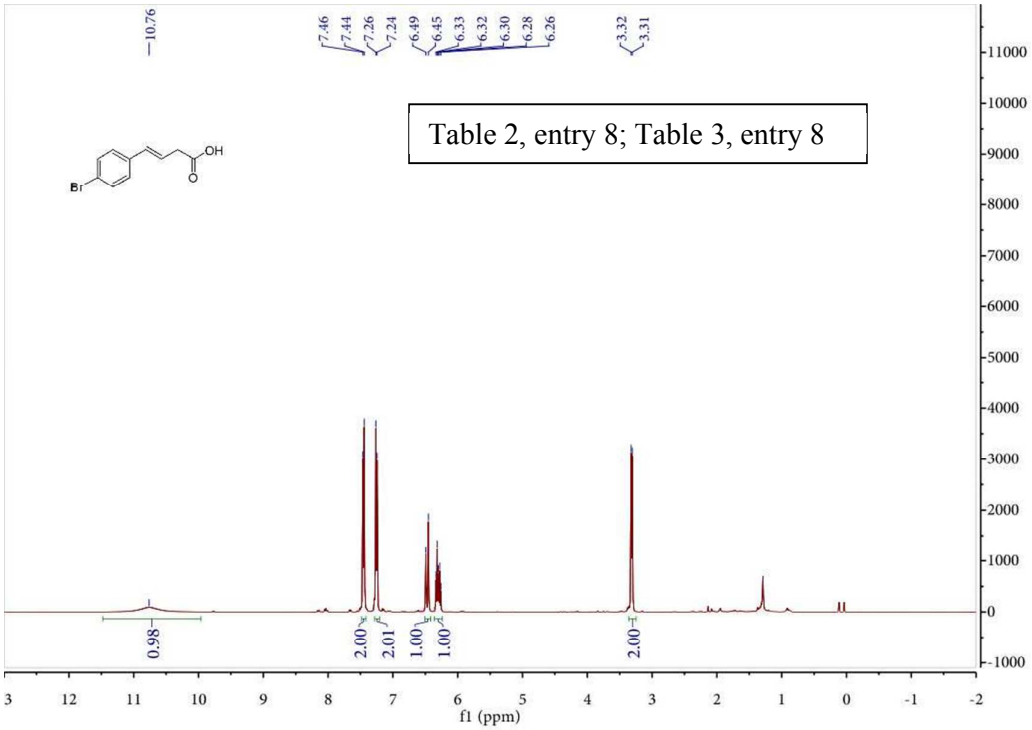
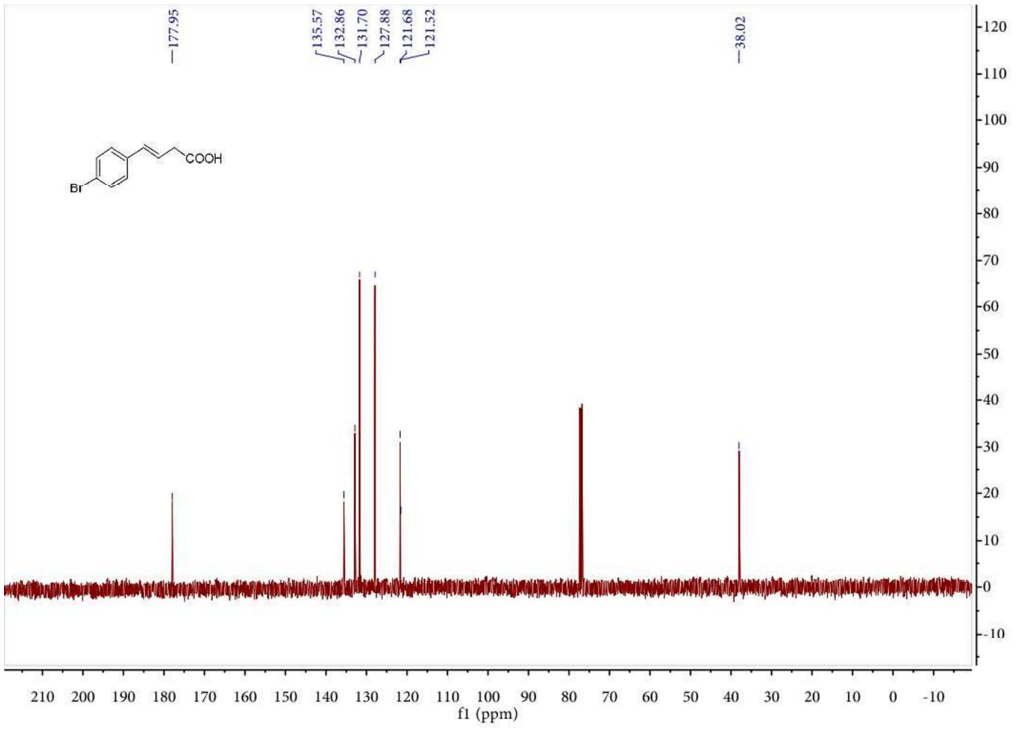
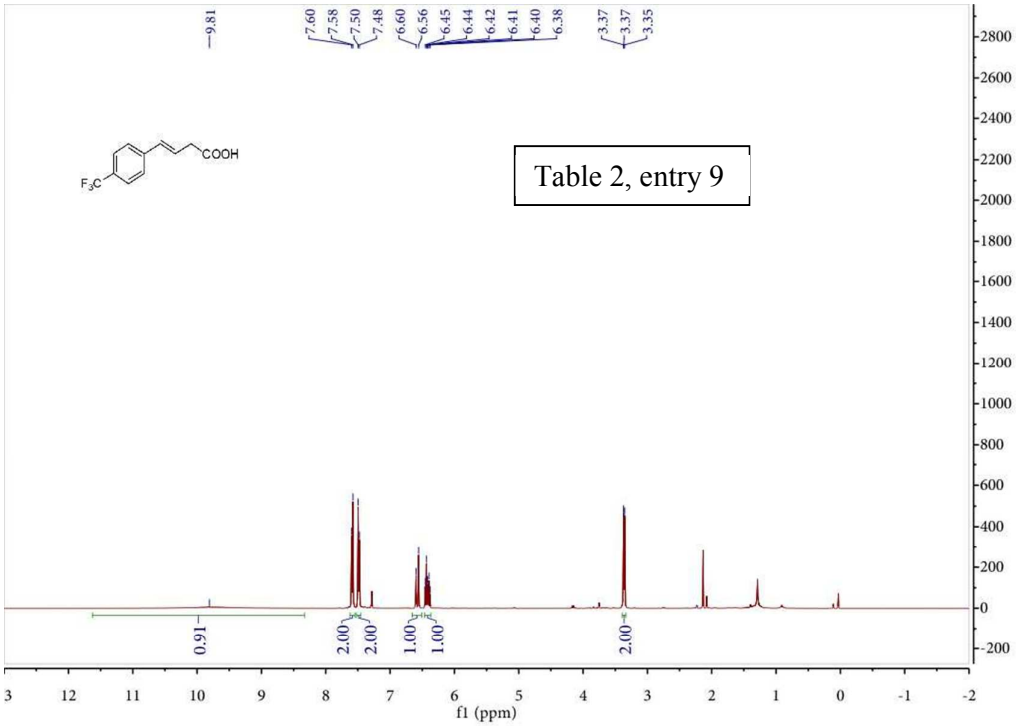
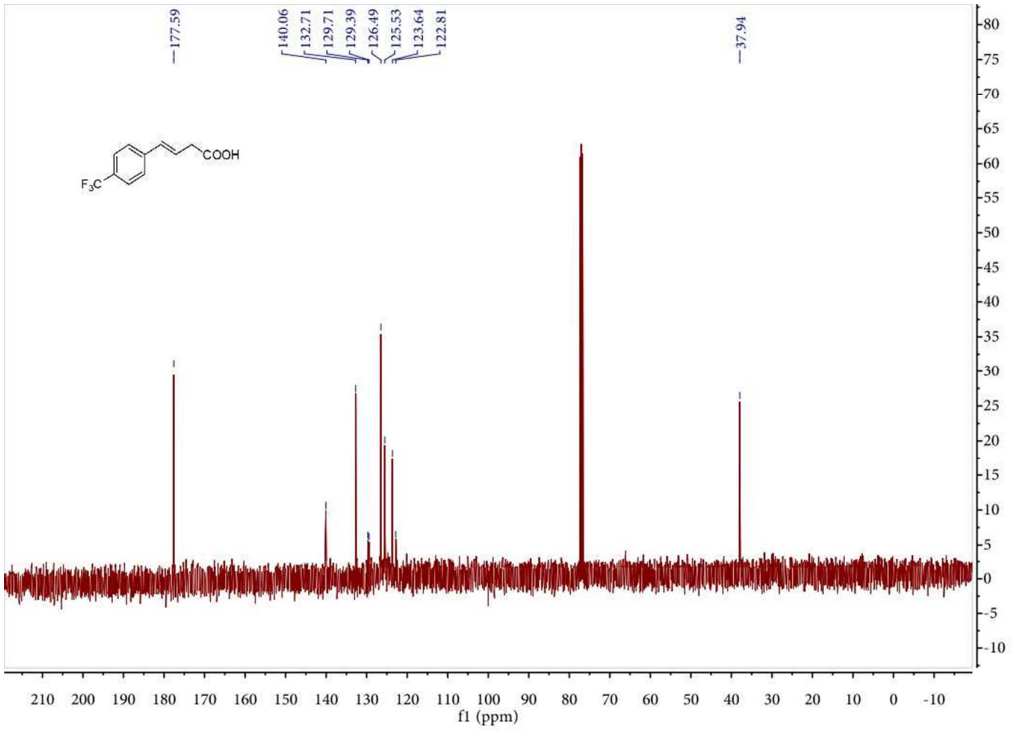


Table 2, entry 8; Table 3, entry 8




9.81
7.60
7.58
7.50
7.48
6.60
6.56
6.45
6.44
6.42
6.41
6.40
6.38
3.37
3.37
3.35
COOH
F3C
Table 2, entry 9
0.91
2.00
2.00
1.00
1.00
2.00
f1 (ppm)


177.59
140.06
132.71
129.71
129.39
126.49
125.53
123.64
122.81
37.94
COOH
F3C
f1 (ppm)

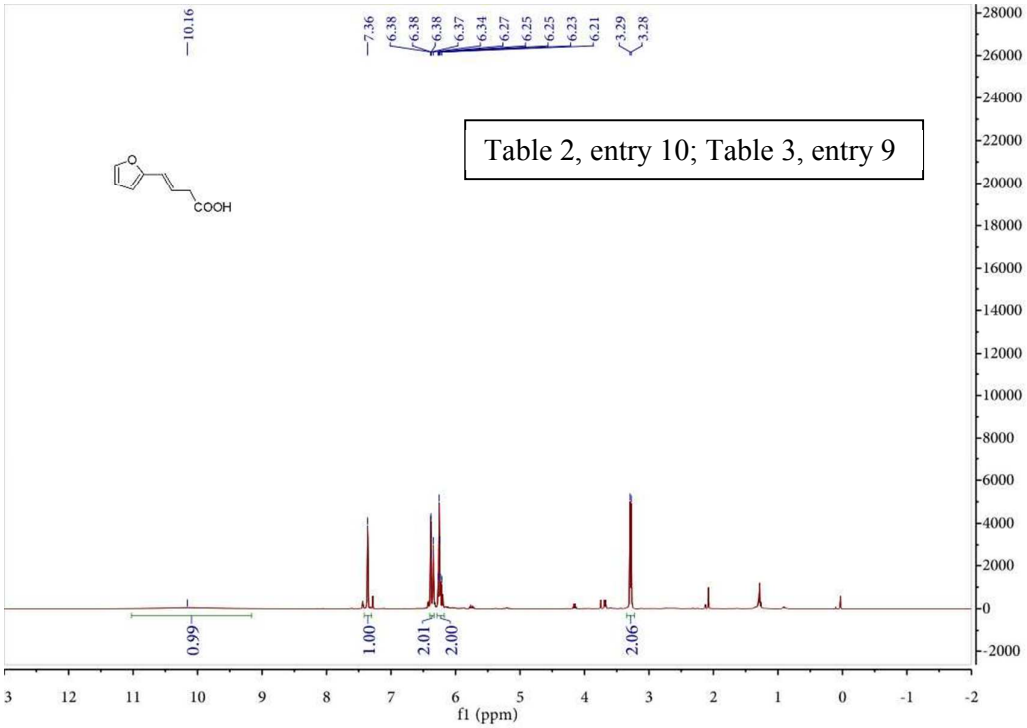
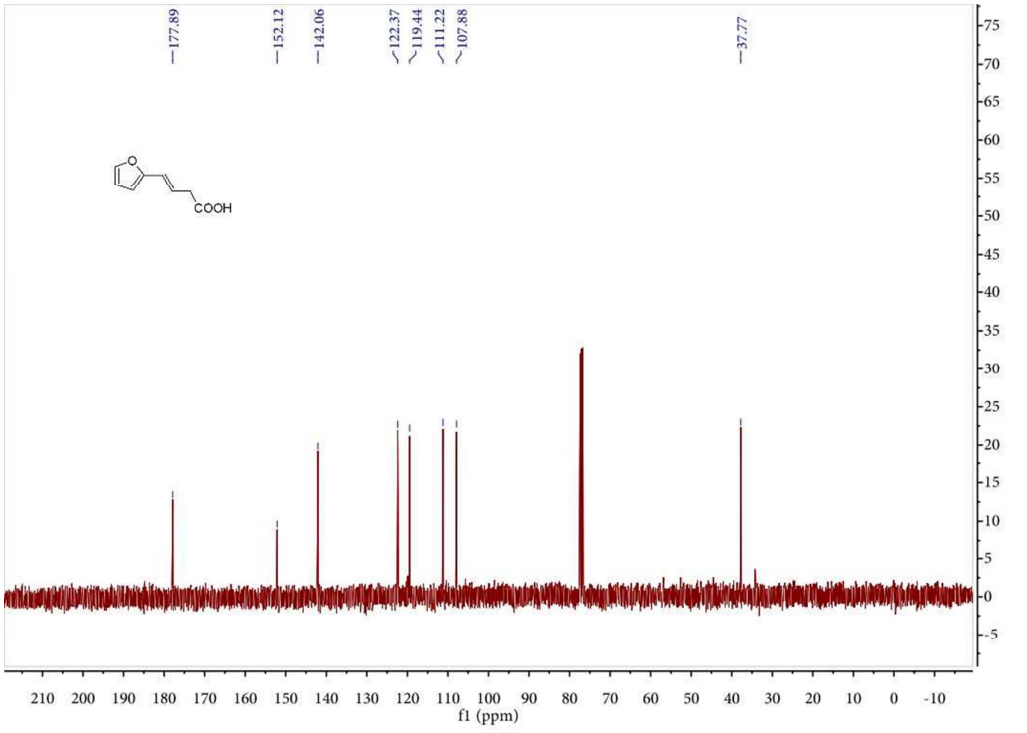
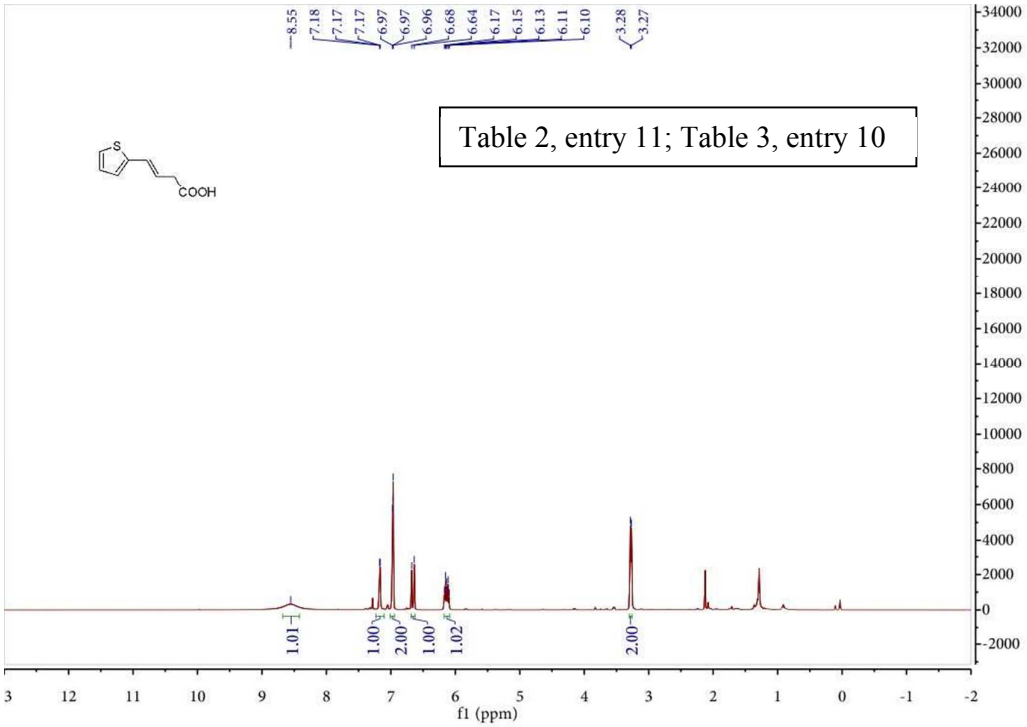
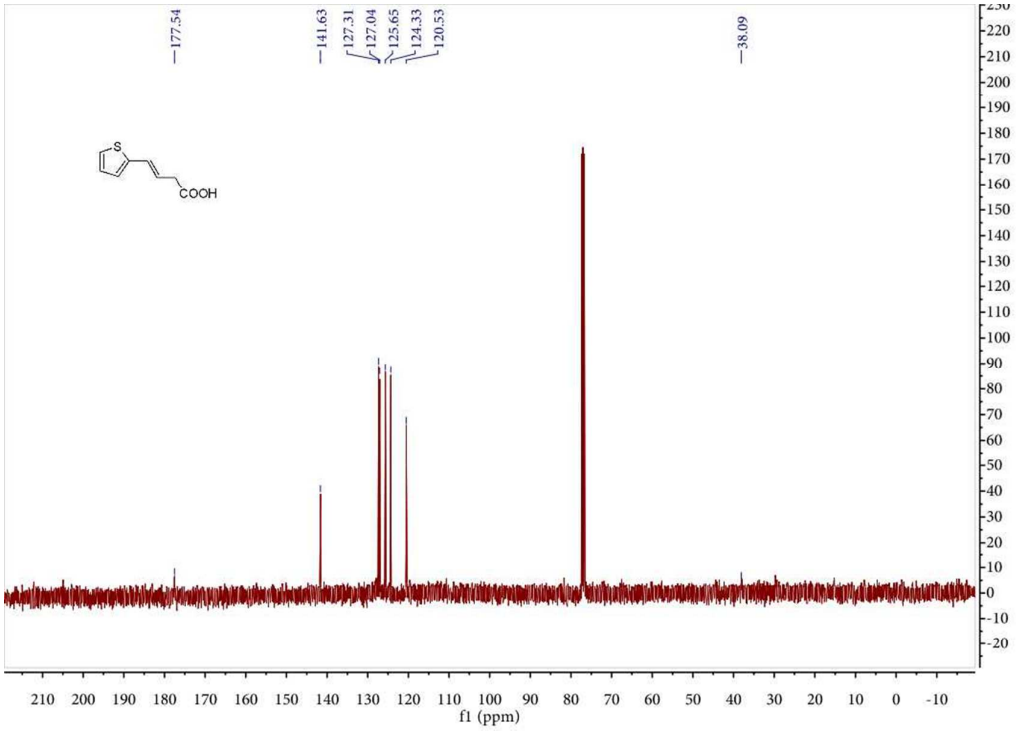
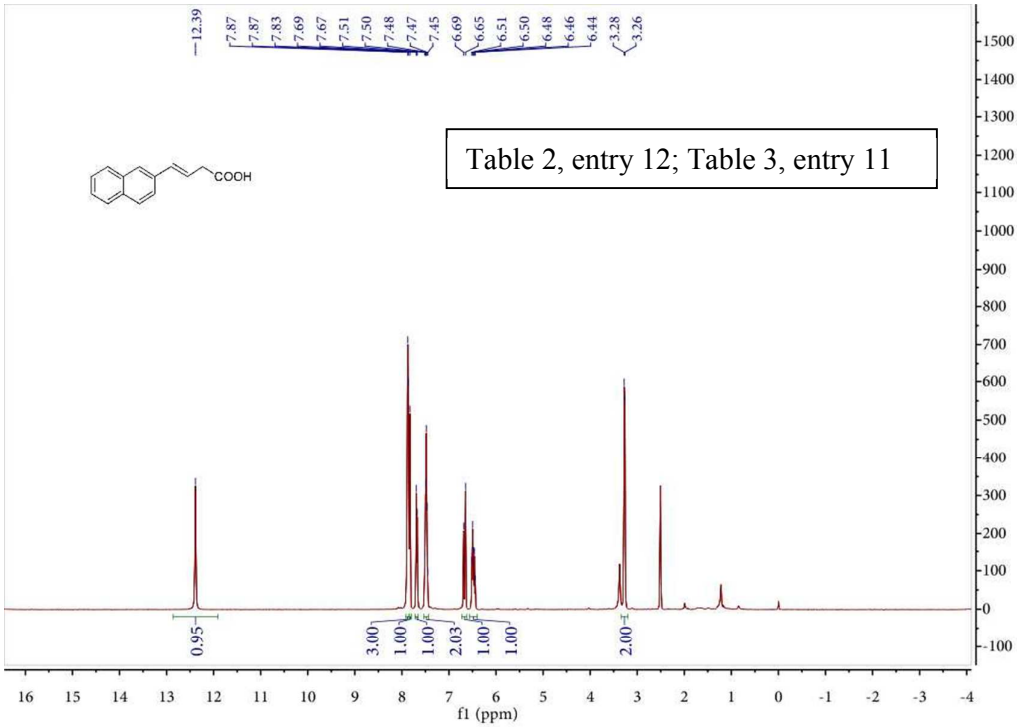


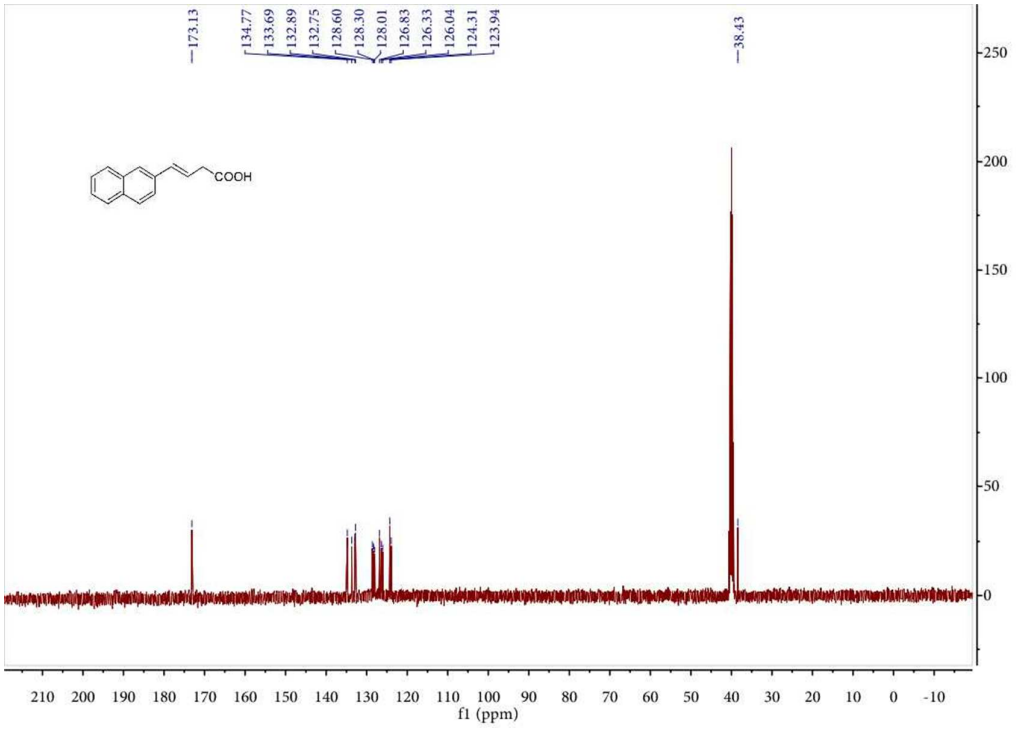
Table 2, entry 10; Table 3, entry 9

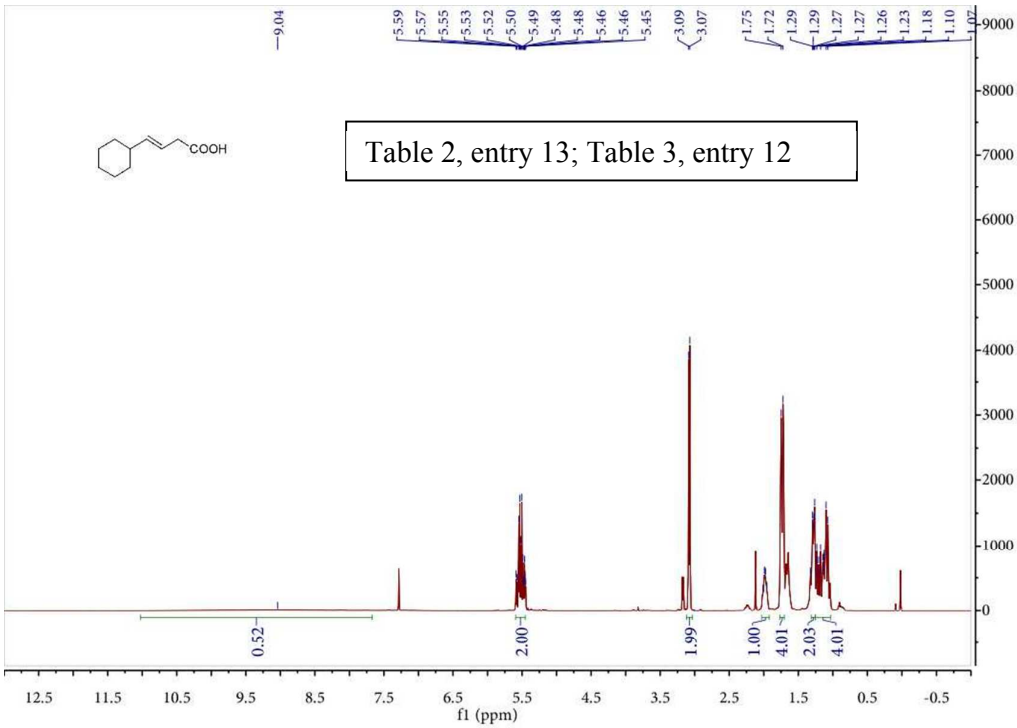


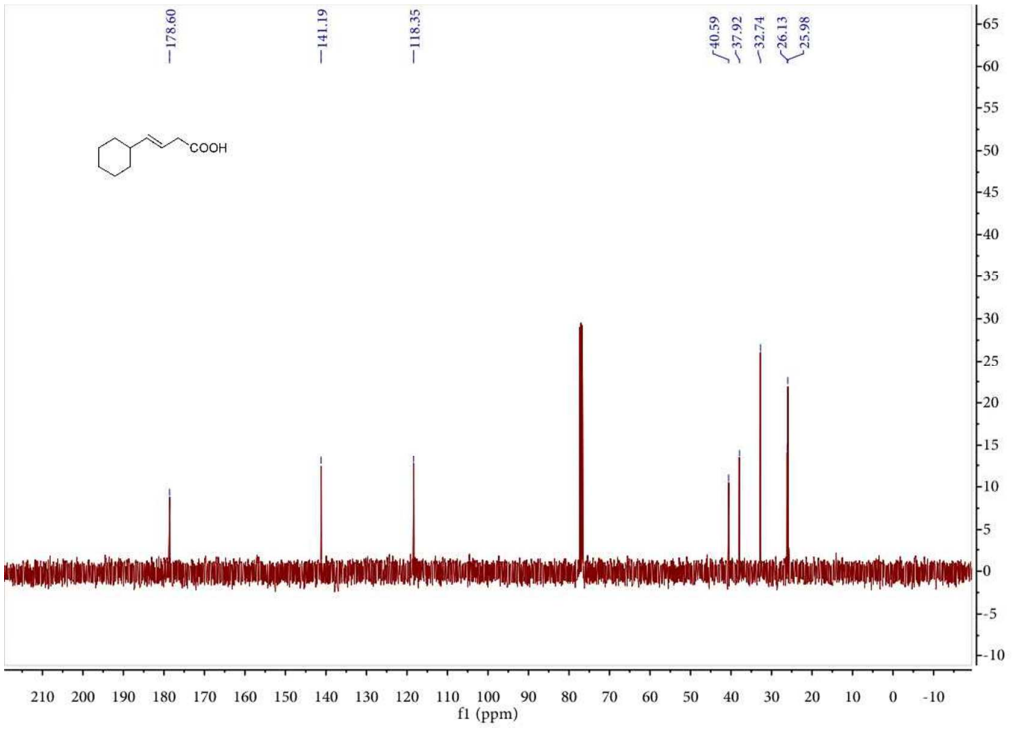

8.55
7.18
7.17
7.17
6.97
6.97
6.96
6.68
6.64
6.17
6.15
6.13
6.11
6.10
3.28
3.27
Table 2, entry 11; Table 3, entry 10
COOH
1.01
1.00
2.00
1.00
1.02
2.00
f1 (ppm)

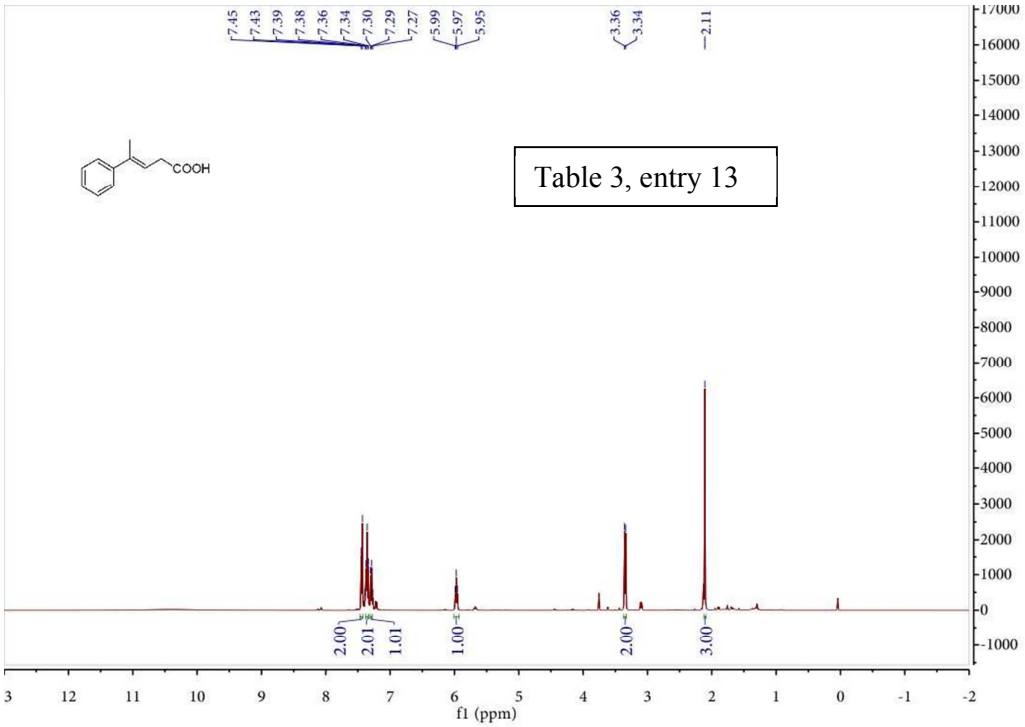

177.54
141.63
127.31
127.04
125.65
124.33
120.53
38.09
COOH
f1 (ppm)

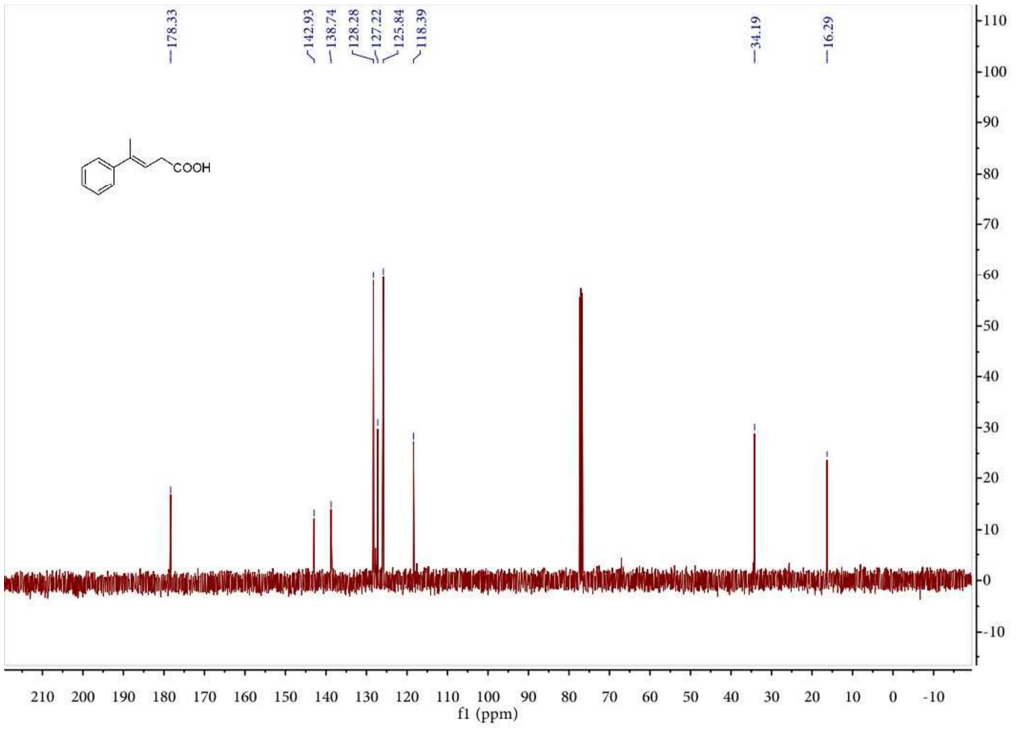

12.39
7.87
7.87
7.83
7.69
7.67
7.51
7.50
7.48
7.47
7.45
6.69
6.65
6.51
6.50
6.48
6.46
6.44
3.28
3.26
COOH
Table 2, entry 12; Table 3, entry 11
0.95
3.00
1.00
1.00
2.03
1.00
1.00
2.00
f1 (ppm)

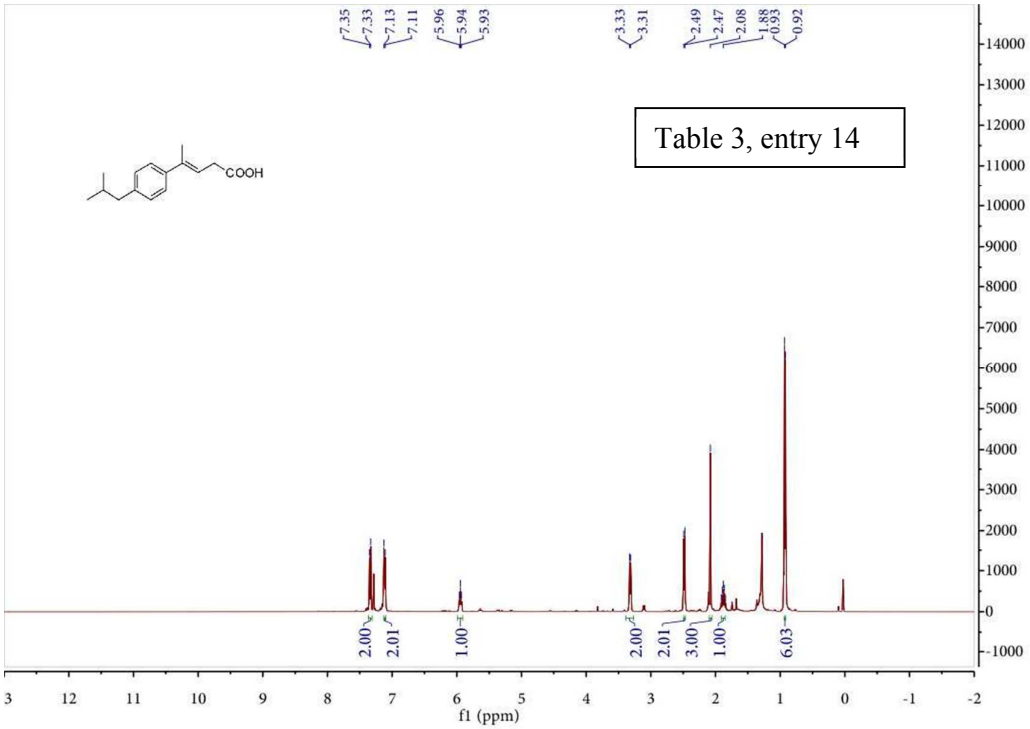

173.13
134.77
133.69
132.89
132.75
128.60
128.30
128.01
126.83
126.33
126.04
124.31
123.94
38.43
COOH
f1 (ppm)

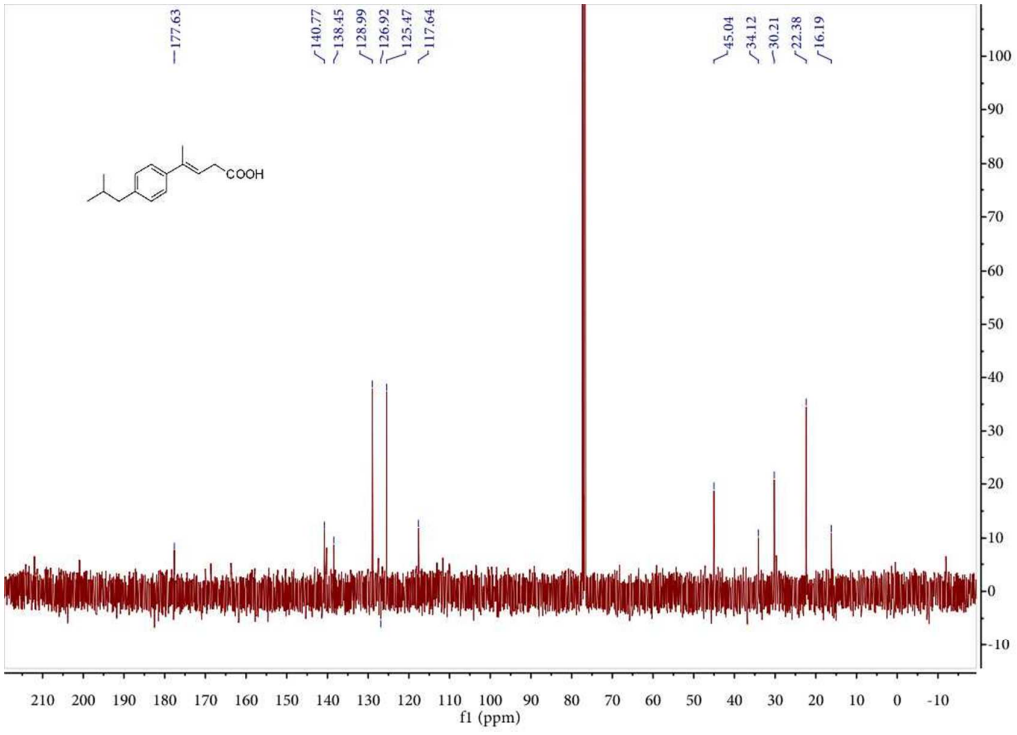

9.04
5.59
5.57
5.55
5.53
5.52
5.50
5.49
5.48
5.48
5.46
5.46
5.45
3.09
3.07
1.75
1.72
1.29
1.29
1.27
1.27
1.26
1.23
1.18
1.10
1.07
COOH
Table 2, entry 13; Table 3, entry 12
0.52
2.00
1.99
1.00
4.01
2.03
4.01
f1 (ppm)


178.60
141.19
118.35
40.59
37.92
32.74
26.13
25.98
COOH
f1 (ppm)


7.45
7.43
7.39
7.38
7.36
7.34
7.30
7.29
7.27
5.99
5.97
5.95
3.36
3.34
2.11
COOH
Table 3, entry 13
2.00
2.01
1.01
1.00
2.00
3.00
f1 (ppm)


178.33
142.93
138.74
128.28
127.22
125.84
118.39
34.19
16.29
COOH
f1 (ppm)


7.35
7.33
7.13
7.11
5.96
5.94
5.93
3.33
3.31
2.49
2.47
2.08
1.88
0.93
0.92
COOH
Table 3, entry 14
2.00
2.01
1.00
2.00
2.01
3.00
1.00
6.03
f1 (ppm)


177.63
140.77
138.45
128.99
126.92
125.47
117.64
45.04
34.12
30.21
22.38
16.19
COOH
f1 (ppm)