

Supporting Information
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Supporting Information

Visible-Light-Catalyzed Regioselective Arylcarboxylation of Allenes with CO₂

Xian-Ming Zhang,^a Zhen-Qiang Zhang*^b and Zhuang-Ping Zhan*^a

^a Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361001 Fujian, People's Republic of China; Email: zpzhan@xmu.edu.cn.

^b Yunnan Precious Metals Laboratory Company, Ltd., Kunming 650106 Yunnan, People's Republic of China; Email: zhenqiang.zhang@163.com.

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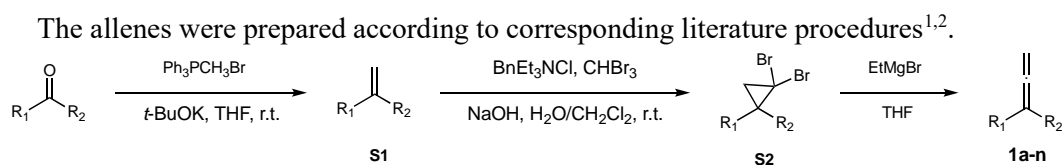
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1. General information

The liquid-state NMR was recorded on a 400 or 500 MHz spectrometer. Chemical shifts were reported in ppm. ^1H 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

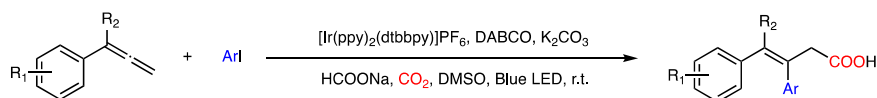


Methyl triphenylphosphonium bromide (1.2 equiv) was added to an oven dried flask followed by THF (2.5 mL/mmol). Then *t*-BuOK (1.5 equiv) was added dropwise to the solution under ice-bath and the resulting yellow suspension was stirred at room temperature for 30 min. To this suspension, a solution of 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 **2a–q**.

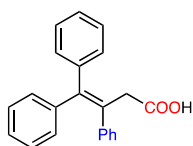
3. General procedure for the arylcarboxylation of allenes



To an oven dried Schlenk tube (10 mL) with a magnetic stir bar, allenes (0.2 mmol, 1 equiv, if solid), DABCO (0.1 mmol, 0.5 equiv), K₂CO₃ (0.5 mmol, 2.5 equiv), HCOONa (0.4 mmol, 2 equiv) and Ir[(ppy)₂dtbbpy]PF₆ (5 mol%) was added. The Schlenk tube was sealed and degassed via vacuum evacuation and subsequent backfilled with CO₂ for three times. Subsequently, allenes (0.2 mmol, if liquid), aryl iodides (0.4 mmol, 2 equiv) 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 r.t.. The mixture was acidified with 1 mL dilute HCl (2 N) and quenched with H₂O. Then extracted with EtOAc three times, the combined organic layers were dried over anhydrous MgSO₄ 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.

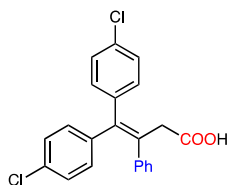
4. Analytical data for compounds

3,4,4-triphenylbut-3-enoic acid (3a)



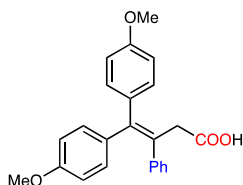
Prepared following the general procedure, purified by column chromatography (3/1 petroleum ether/ ethyl acetate), and isolated as a white solid (27 mg, 43 %). ¹H NMR (400 MHz, CDCl₃) δ 7.38 – 7.27 (m, 5H), 7.19 – 7.10 (m, 5H), 7.09 – 6.99 (m, 3H), 6.96 – 6.88 (m, 2H), 3.58 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 177.23, 143.75, 142.66, 142.21, 141.36, 131.80, 130.75, 129.80, 129.52, 128.58, 128.10, 127.64, 127.42, 126.87, 126.50, 41.57. HRMS (ESI) *m/z* [M+H]⁺ calcd for [C₂₂H₁₉O₂]⁺ 315.1380, found 315.1382.

4,4-bis(4-chlorophenyl)-3-phenylbut-3-enoic acid (3b)



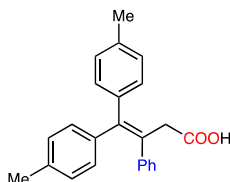
Prepared following the general procedure, purified by column chromatography (3/1 petroleum ether/ ethyl acetate), and isolated as a white solid (31 mg, 41 %). ¹H NMR (400 MHz, CDCl₃) δ 7.32 (d, J = 8.0 Hz, 2H), 7.28 – 7.09 (m, 7H), 7.01 (d, J = 8.2 Hz, 2H), 6.79 (d, J = 8.2 Hz, 2H), 3.54 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 176.75, 141.31, 140.71, 140.59, 140.24, 133.69, 133.14, 132.62, 132.06, 130.97, 129.64, 128.95, 128.38, 128.02, 127.31, 41.63. HRMS (ESI) *m/z* [M+H]⁺ calcd for [C₂₂H₁₇Cl₂O₂]⁺ 383.0600, found 383.0604.

4,4-bis(4-methoxyphenyl)-3-phenylbut-3-enoic acid (3c)



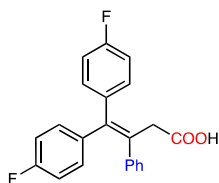
Prepared following the general procedure, purified by column chromatography (3/1 petroleum ether/ ethyl acetate), and isolated as a white solid (33 mg, 45 %). ¹H NMR (400 MHz, CDCl₃) δ 7.22 – 7.07 (m, 7H), 6.83 (dd, J = 29.4, 8.7 Hz, 4H), 6.56 (d, J = 8.7 Hz, 2H), 3.82 (s, 3H), 3.69 (s, 3H), 3.58 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 177.53, 158.86, 158.04, 142.82, 141.85, 135.43, 134.97, 132.09, 130.84, 129.82, 128.14, 126.59, 113.86, 112.96, 55.37, 55.16, 41.73. HRMS (ESI) *m/z* [M+H]⁺ calcd for [C₂₄H₂₃O₄]⁺ 375.1591, found 375.1589.

3-phenyl-4,4-di-p-tolylbut-3-enoic acid (3d)



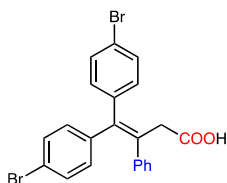
Prepared following the general procedure, purified by column chromatography (3/1 petroleum ether/ ethyl acetate), and isolated as a colorless oil (31 mg, 46 %). ¹H NMR (400 MHz, CDCl₃) δ 7.23 – 7.07 (m, 3H), 6.87 – 6.75 (m, 1H), 3.57 (s, 1H), 2.36 (s, 1H), 2.20 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 177.37, 143.60, 141.74, 140.05, 139.46, 137.00, 136.02, 131.01, 130.68, 129.81, 129.44, 129.22, 128.34, 128.08, 126.67, 41.69, 21.36, 21.23. HRMS (ESI) *m/z* [M+H]⁺ calcd for [C₂₄H₂₃O₂]⁺ 343.1693, found 343.1697.

4,4-bis(4-fluorophenyl)-3-phenylbut-3-enoic acid (3e)



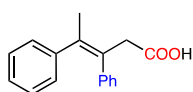
Prepared following the general procedure, purified by column chromatography (3/1 petroleum ether/ ethyl acetate), and isolated as a white solid (29 mg, 42 %). ¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.25 (m, 2H), 7.26 – 7.13 (m, 5H), 7.08 (t, J = 8.7 Hz, 2H), 6.88 (dd, J = 8.6, 5.7 Hz, 2H), 6.77 (t, J = 8.7 Hz, 2H), 3.59 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 177.51, 162.23 (d, J = 247.1 Hz), 161.47 (d, J = 246.8 Hz), 141.64, 141.01, 138.32 (d, J = 3.5 Hz), 137.98 (d, J = 3.5 Hz), 132.41, 132.34 (d, J = 8.0 Hz), 131.25 (d, J = 8.0 Hz), 129.70, 128.29, 127.11, 115.64 (d, J = 21.3 Hz), 114.72 (d, J = 21.4 Hz), 41.66. HRMS (ESI) *m/z* [M+H]⁺ calcd for [C₂₂H₁₇F₂O₂]⁺ 351.1191, found 351.1195.

4,4-bis(4-bromophenyl)-3-phenylbut-3-enoic acid (3f)



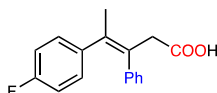
Prepared following the general procedure, purified by column chromatography (3/1 petroleum ether/ ethyl acetate), and isolated as a colorless oil (34 mg, 37 %). ^1H NMR (400 MHz, CDCl_3) δ 7.48 (d, $J = 6.7$ Hz, 2H), 7.24 – 7.01 (m, 9H), 6.74 (d, $J = 6.8$ Hz, 2H), 3.53 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 177.23, 141.39, 140.98, 140.62, 133.11, 132.37, 131.92, 131.27, 130.98, 129.61, 128.40, 127.36, 121.92, 120.92, 41.69. HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $[\text{C}_{22}\text{H}_{17}\text{Br}_2\text{O}_2]^+$ 470.9590, found 470.9590.

(Z)-3,4-diphenylpent-3-enoic acid (3g)



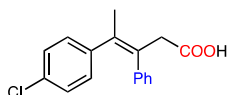
Prepared following the general procedure, purified by column chromatography (3/1 petroleum ether/ ethyl acetate), and isolated as a colorless oil (13 mg, 26 %). ^1H NMR (400 MHz, CDCl_3) δ 7.48 – 7.38 (m, 4H), 7.37 – 7.27 (m, 6H), 3.34 (s, 2H), 1.95 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 178.05, 143.48, 141.71, 138.68, 129.73, 129.01, 128.62, 128.40, 127.92, 127.07, 126.99, 41.10, 22.90. HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $[\text{C}_{22}\text{H}_{19}\text{O}_2]^+$ 253.1223, found 253.1220.

(Z)-4-(4-fluorophenyl)-3-phenylpent-3-enoic acid (3h)



Prepared following the general procedure, purified by column chromatography (3/1 petroleum ether/ ethyl acetate), and isolated as a colorless oil (18 mg, 33 %). ^1H NMR (400 MHz, CDCl_3) δ 7.44 – 7.33 (m, 2H), 7.33 – 7.22 (m, 5H), 7.06 (t, $J = 8.7$ Hz, 2H), 3.28 (s, 2H), 1.89 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 177.99, 161.94 (d, $J = 245.8$ Hz), 141.53, 139.28 (d, $J = 3.5$ Hz), 137.71, 130.27, 129.60 (d, $J = 7.9$ Hz), 128.92, 128.45, 127.10, 115.52 (d, $J = 21.4$ Hz), 41.13, 22.98. HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $[\text{C}_{17}\text{H}_{16}\text{FO}_2]^+$ 271.1129, found 271.1124.

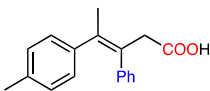
(Z)-4-(4-chlorophenyl)-3-phenylpent-3-enoic acid (3i)



Prepared following the general procedure, purified by column chromatography (3/1 petroleum ether/ ethyl acetate), and isolated as a colorless oil (15 mg, 27 %). ^1H NMR (400 MHz, CDCl_3) δ 7.48 – 7.36 (m, 4H), 7.36 – 7.22 (m, 5H), 3.32 (s, 2H), 1.93 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 177.85, 141.82, 141.38, 137.54, 132.97, 130.42, 129.40, 128.89, 128.85, 128.47, 127.16, 41.11, 22.81. HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for

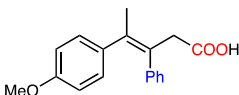
$[C_{17}H_{16}ClO_2]^+$ 287.0833, found 287.0833.

(Z)-3-phenyl-4-(p-tolyl)pent-3-enoic acid (3j)



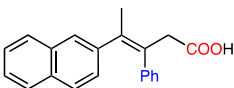
Prepared following the general procedure, purified by column chromatography (3/1 petroleum ether/ ethyl acetate), and isolated as a colorless oil (14 mg, 26 %). 1H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.35 (m, 2H), 7.34 – 7.27 (m, 3H), 7.24 – 7.16 (m, 4H), 3.33 (s, 2H), 2.39 (s, 3H), 1.91 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.25, 141.84, 140.51, 138.59, 136.67, 129.55, 129.29, 129.03, 128.37, 127.81, 126.92, 41.15, 22.92, 21.31. HRMS (ESI) m/z $[M+H]^+$ calcd for $[C_{18}H_{19}O_2]^+$ 267.1380, found 267.1383.

(Z)-4-(4-methoxyphenyl)-3-phenylpent-3-enoic acid (3k)



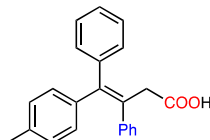
Prepared following the general procedure, purified by column chromatography (3/1 petroleum ether/ ethyl acetate), and isolated as a colorless oil (16 mg, 28 %). 1H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.38 (m, 2H), 7.37 – 7.24 (m, 5H), 6.95 (d, $J = 6.9$ Hz, 2H), 3.87 (s, 3H), 3.37 (s, 2H), 1.93 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.26, 158.63, 141.91, 138.22, 135.73, 129.61, 129.08, 129.01, 128.38, 126.91, 113.98, 55.39, 41.18, 22.95. HRMS (ESI) m/z $[M+H]^+$ calcd for $[C_{18}H_{19}O_3]^+$ 283.1329, found 283.1324.

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



Prepared following the general procedure, purified by column chromatography (3/1 petroleum ether/ ethyl acetate), and isolated as a colorless oil (16 mg, 26 %). 1H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.78 (m, 4H), 7.56 – 7.22 (m, 9H), 3.36 (s, 2H), 2.01 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.71, 141.68, 140.95, 138.59, 133.53, 132.52, 130.24, 129.03, 128.45, 128.31, 128.10, 127.80, 127.06, 126.54, 126.44, 126.31, 125.98, 41.16, 22.91. HRMS (ESI) m/z $[M+H]^+$ calcd for $[C_{21}H_{19}O_2]^+$ 303.1380, found 303.1377.

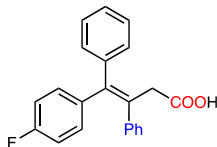
3,4-diphenyl-4-(p-tolyl)but-3-enoic acid (3m)



Prepared following the general procedure, purified by column chromatography (3/1 petroleum ether/ ethyl acetate), and isolated as a colorless oil (24 mg, 37 %). 1H NMR (400 MHz, $CDCl_3$) δ 7.77 – 6.34 (m, 28H), 3.60 (s, 2H), 3.56 (s, 2H), 2.37 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.80, 143.72, 143.61, 142.92, 142.42, 141.58, 141.50,

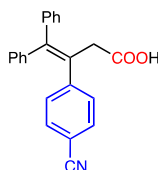
139.78, 139.24, 137.10, 136.11, 131.52, 131.24, 130.76, 130.66, 129.81, 129.79, 129.52, 129.42, 129.26, 128.54, 128.37, 128.11, 128.06, 127.59, 127.32, 126.76, 126.40, 41.69, 21.37, 21.24. HRMS (ESI) m/z $[M+H]^+$ calcd for $[C_{23}H_{21}O_2]^+$ 329.1536, found 329.1538.

4-(4-fluorophenyl)-3,4-diphenylbut-3-enoic acid (3n)



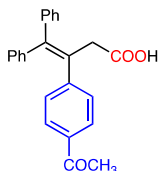
Prepared following the general procedure, purified by column chromatography (3/1 petroleum ether/ ethyl acetate), and isolated as a colorless oil (25 mg, 38 %). 1H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.28 (m, 4H), 7.24 – 7.09 (m, 5H), 7.08 – 6.99 (m, 2H), 6.96 – 6.82 (m, 2H), 6.73 (t, J = 8.6 Hz, 1H), 3.57 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.71, 162.17 (d, J = 246.8 Hz), 161.41 (d, J = 246.4 Hz), 142.73, 142.66, 142.42, 142.04, 141.18, 138.55 (d, J = 3.3 Hz), 138.15 (d, J = 3.5 Hz), 132.34 (d, J = 7.9 Hz), 132.16, 132.04, 131.26 (d, J = 7.9 Hz), 130.71, 129.75, 129.47, 128.66, 128.24, 128.14, 127.71, 127.58, 127.00, 126.97, 126.64, 115.53 (d, J = 21.3 Hz), 114.62 (d, J = 21.3 Hz), 41.66. HRMS (ESI) m/z $[M+H]^+$ calcd for $[C_{22}H_{18}FO_2]^+$ 333.1285, found 333.1283.

3-(4-cyanophenyl)-4,4-diphenylbut-3-enoic acid (3o)



Prepared following the general procedure, purified by column chromatography (3/1 petroleum ether/ ethyl acetate), and isolated as a colorless oil (22 mg, 33 %). 1H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 8.3 Hz, 2H), 7.44 – 7.29 (m, 7H), 7.15 – 7.08 (m, 3H), 6.91 (dd, J = 7.4, 2.2 Hz, 2H), 3.63 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.60, 146.67, 146.08, 141.79, 141.28, 131.95, 130.63, 130.60, 130.13, 129.30, 128.72, 128.02, 127.96, 127.26, 118.96, 110.44, 41.06. HRMS (ESI) m/z $[M+H]^+$ calcd for $[C_{23}H_{18}NO_2]^+$ 340.1332, found 340.1333.

3-(4-acetylphenyl)-4,4-diphenylbut-3-enoic acid (3p)



Prepared following the general procedure, purified by column chromatography (3/1 petroleum ether/ ethyl acetate), and isolated as a colorless oil (18 mg, 25 %). 1H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.3 Hz, 2H), 7.44 – 7.27 (m, 7H), 7.14 – 7.03 (m, 3H), 6.97 – 6.90 (m, 2H), 3.64 (s, 2H), 2.57 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.99, 176.02, 146.79, 145.23, 142.19, 141.70, 135.40, 130.87, 130.71, 130.08, 129.43, 128.66, 128.26,

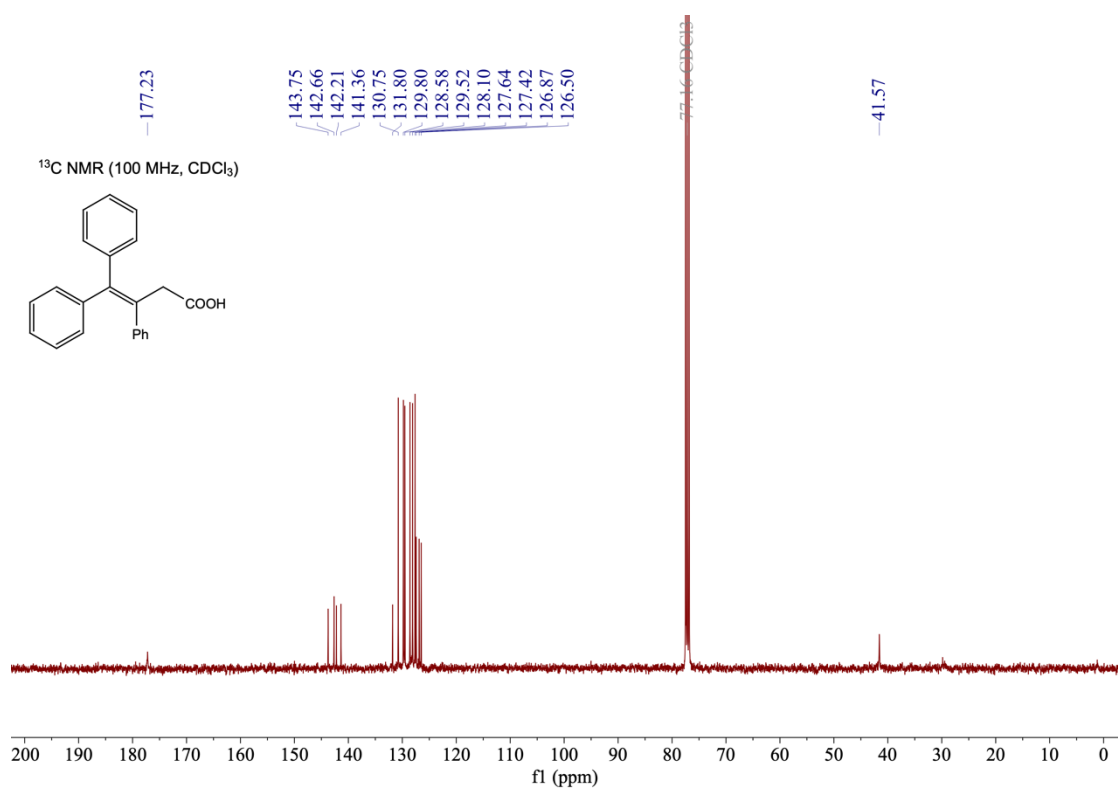
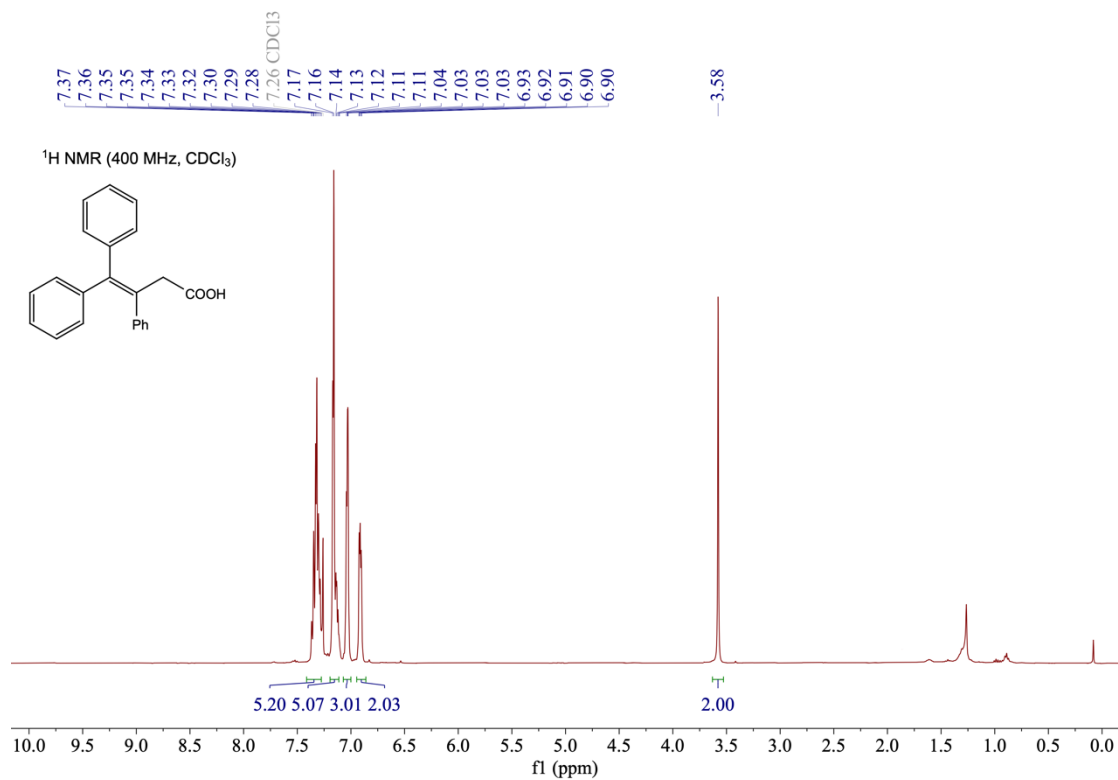
127.89, 127.75, 126.98, 41.17, 26.69. HRMS (ESI) m/z $[M+H]^+$ calcd for $[C_{24}H_{21}O_3]^+$ 357.1485, found 357.1487.

5. References

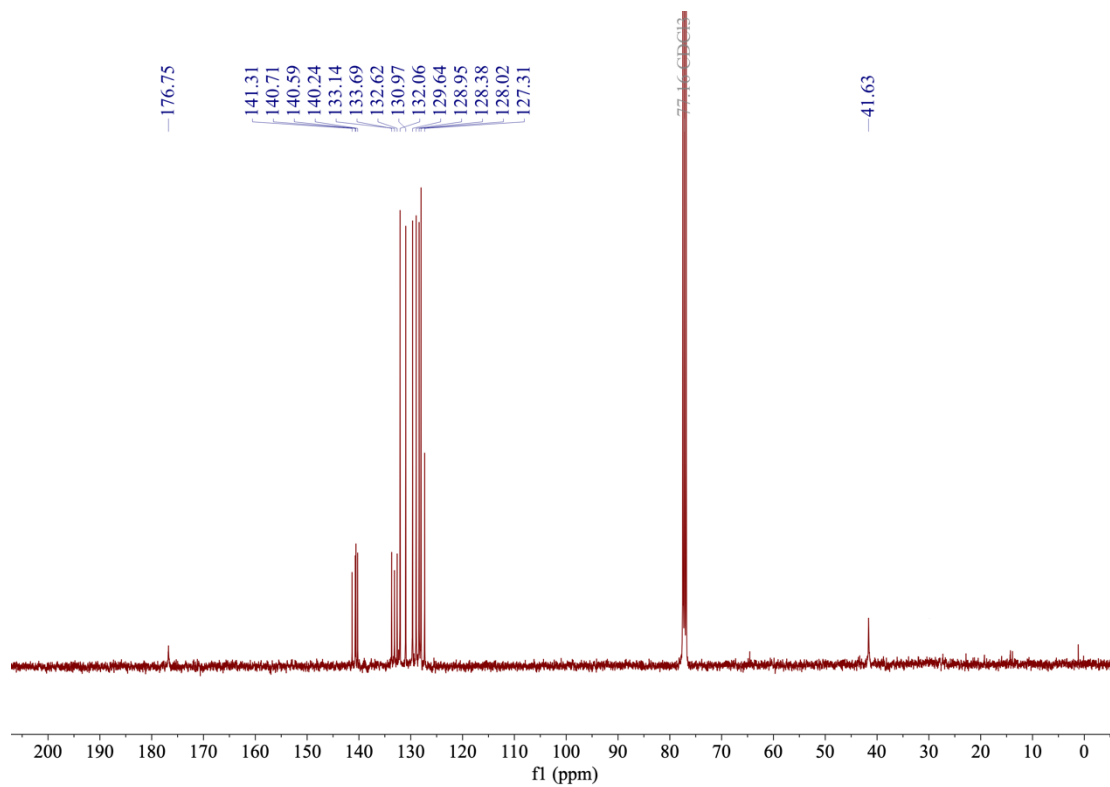
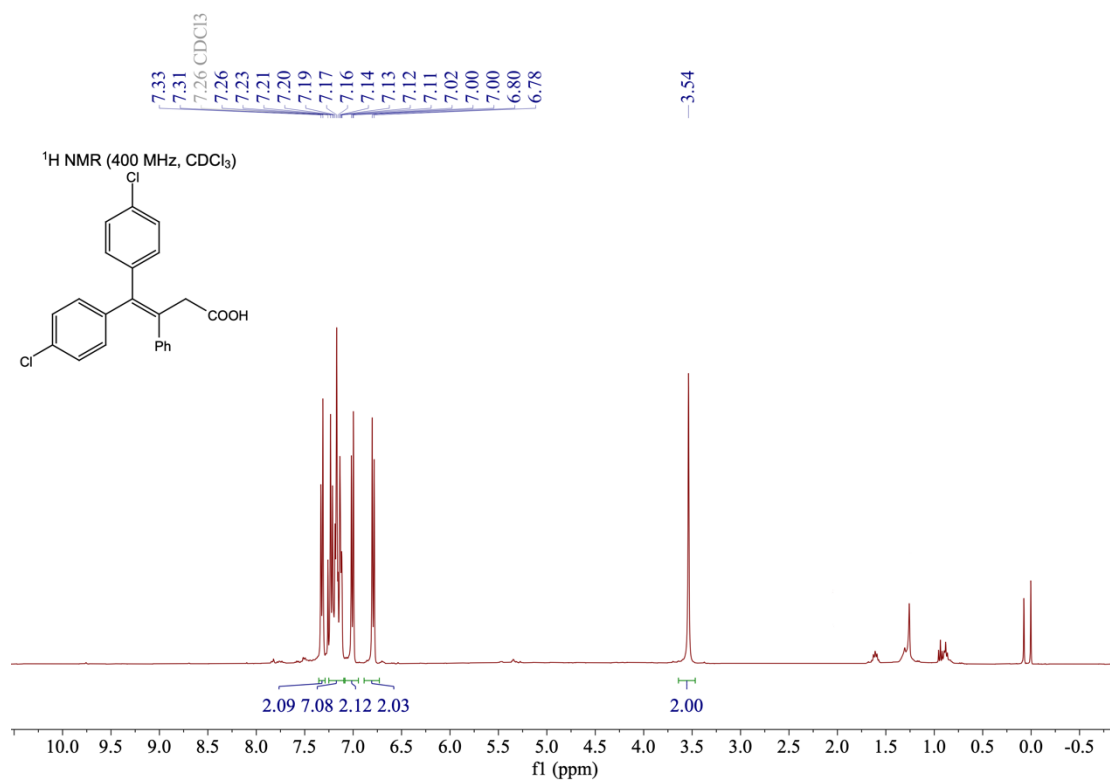
- (1) Ye, F.; Wang, C.; Ma, X.; Hossain, M. L.; Xia, Y.; Zhang, Y.; Wang, J. *J. Org. Chem.* **2015**, 80, 1, 647–652
- (2) Zhao, Z.; Murphy, G. K. *Beilstein J. Org. Chem.* **2018**, 14, 796-802.

6. NMR spectra

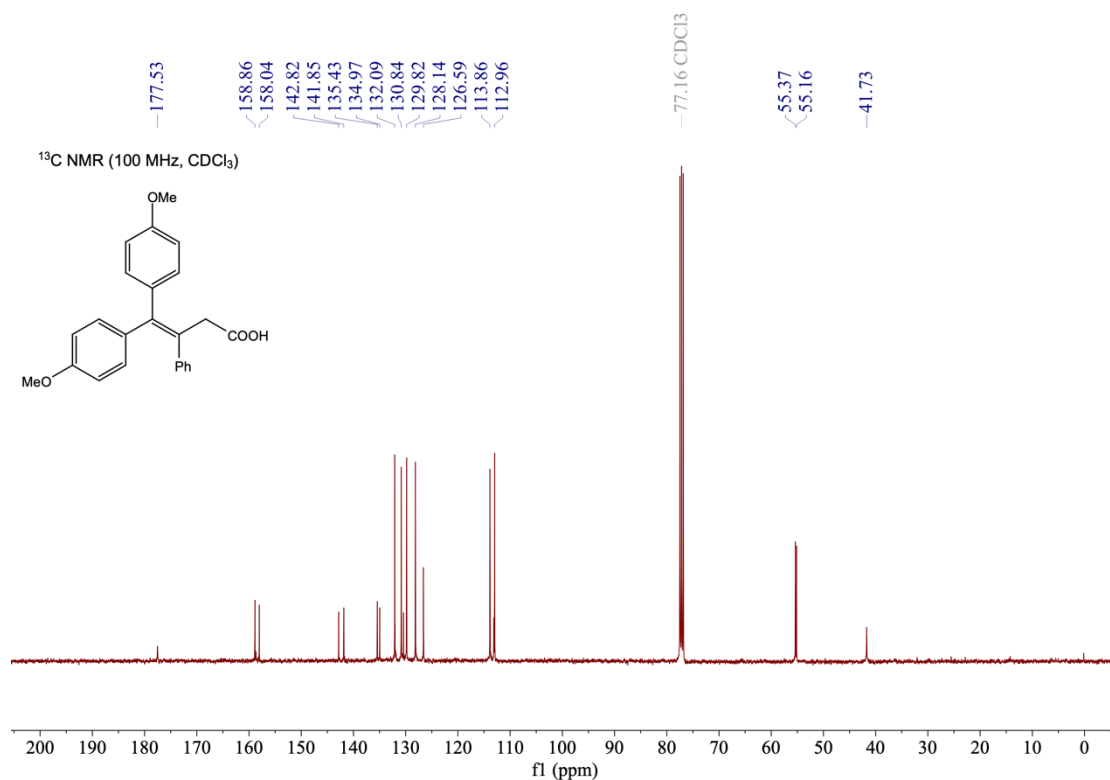
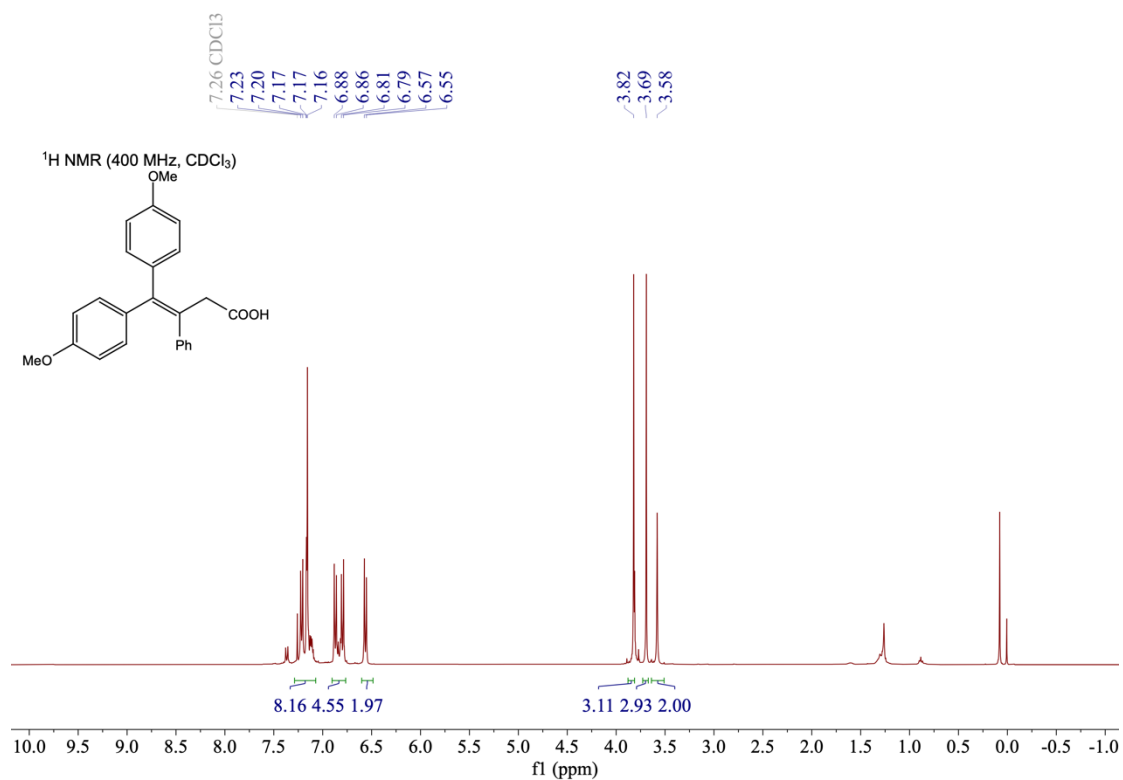
3,4,4-triphenylbut-3-enoic acid (3a)



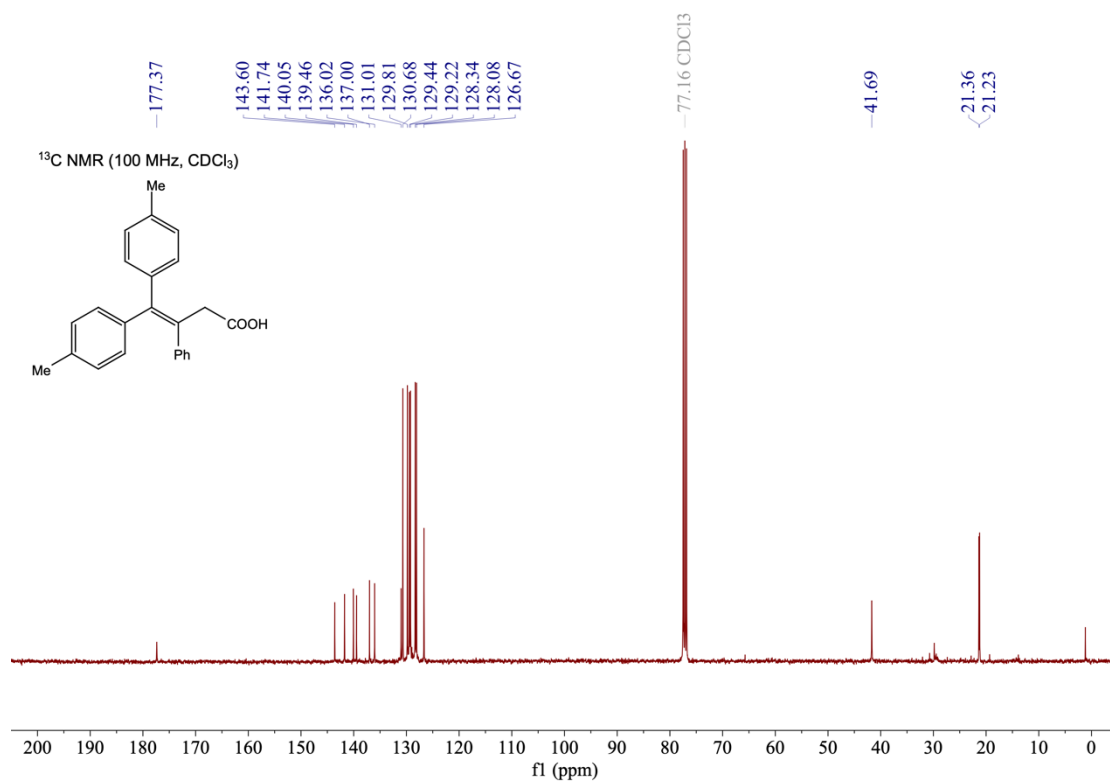
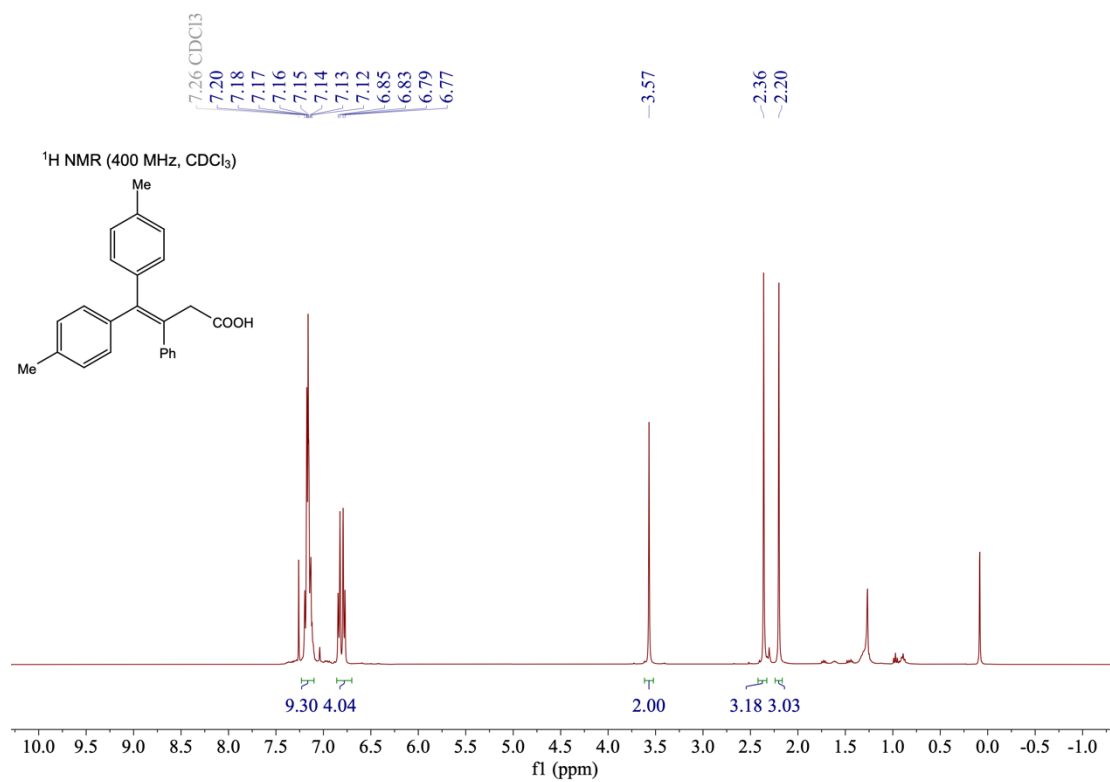
4,4-bis(4-chlorophenyl)-3-phenylbut-3-enoic acid (3b)



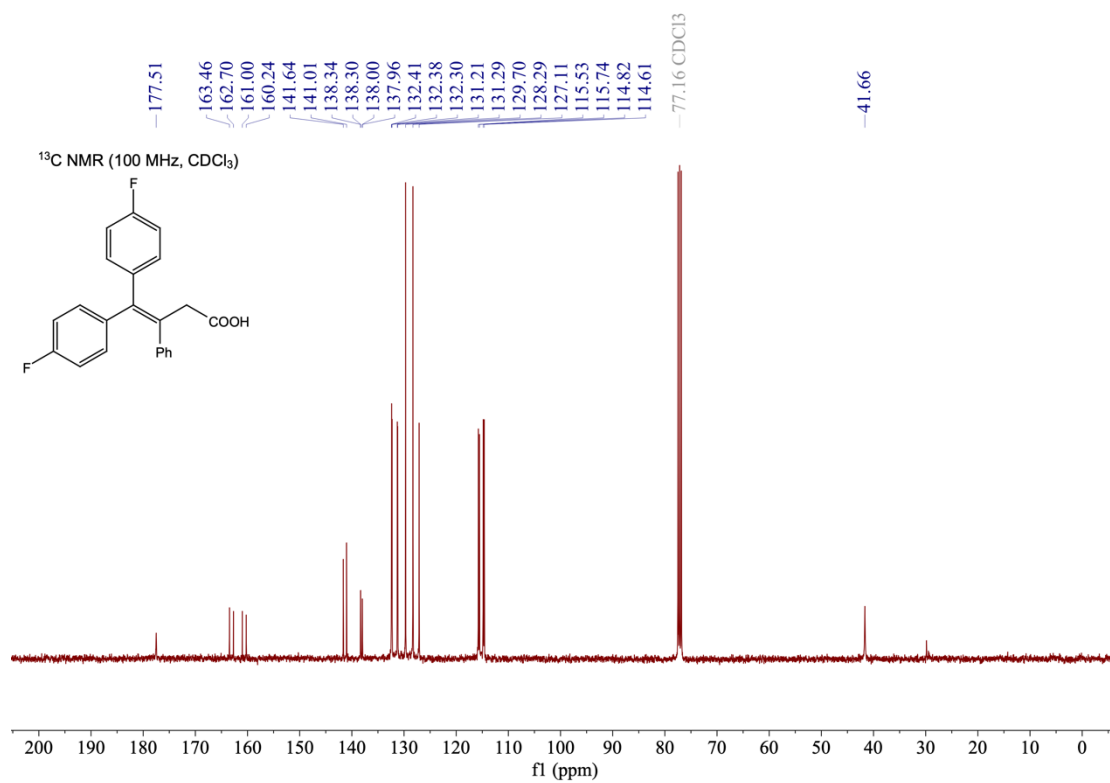
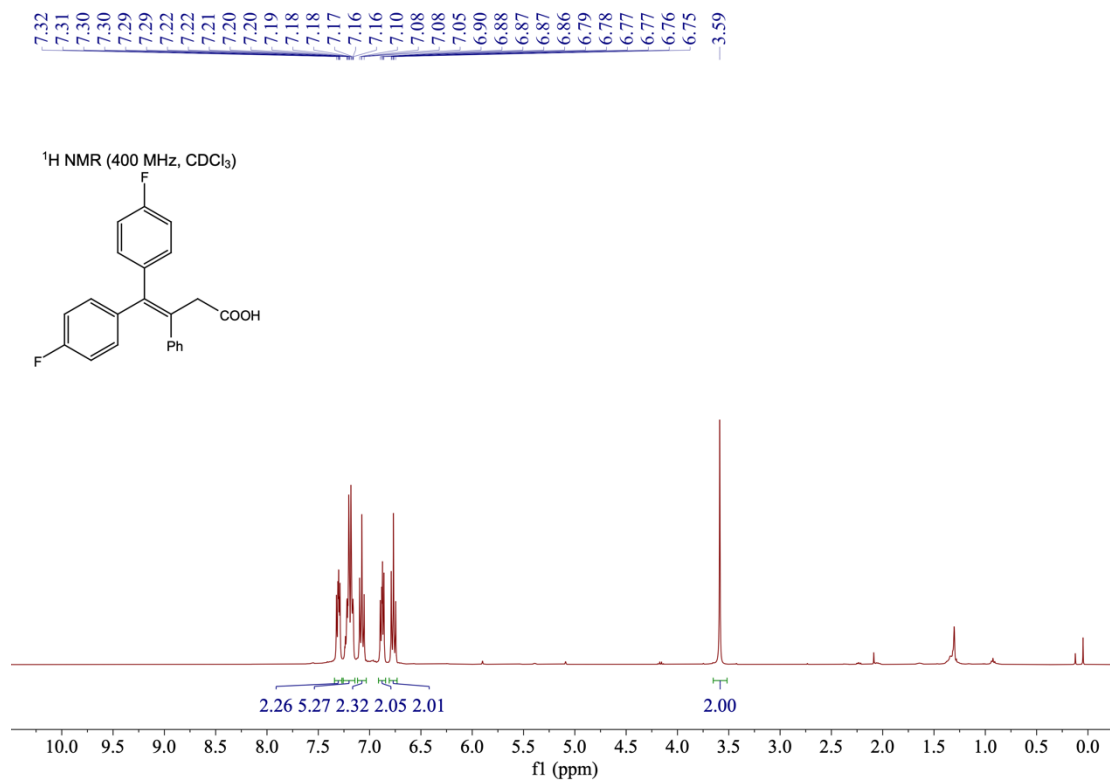
4,4-bis(4-methoxyphenyl)-3-phenylbut-3-enoic acid (3c)



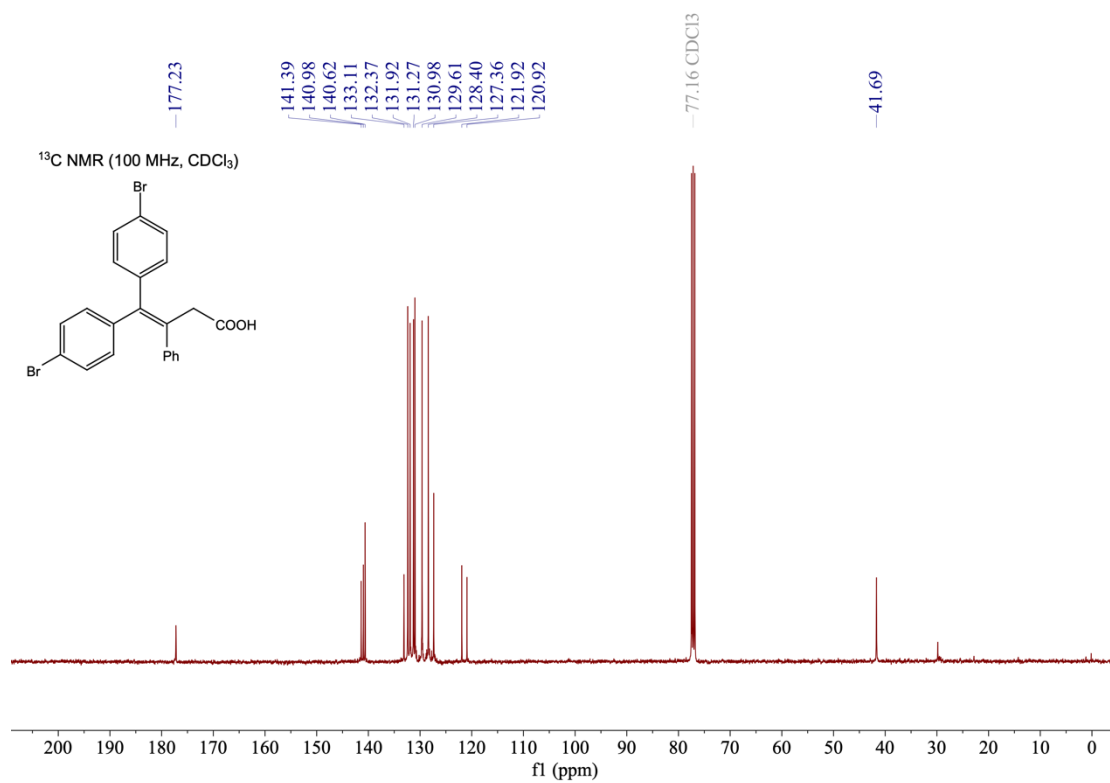
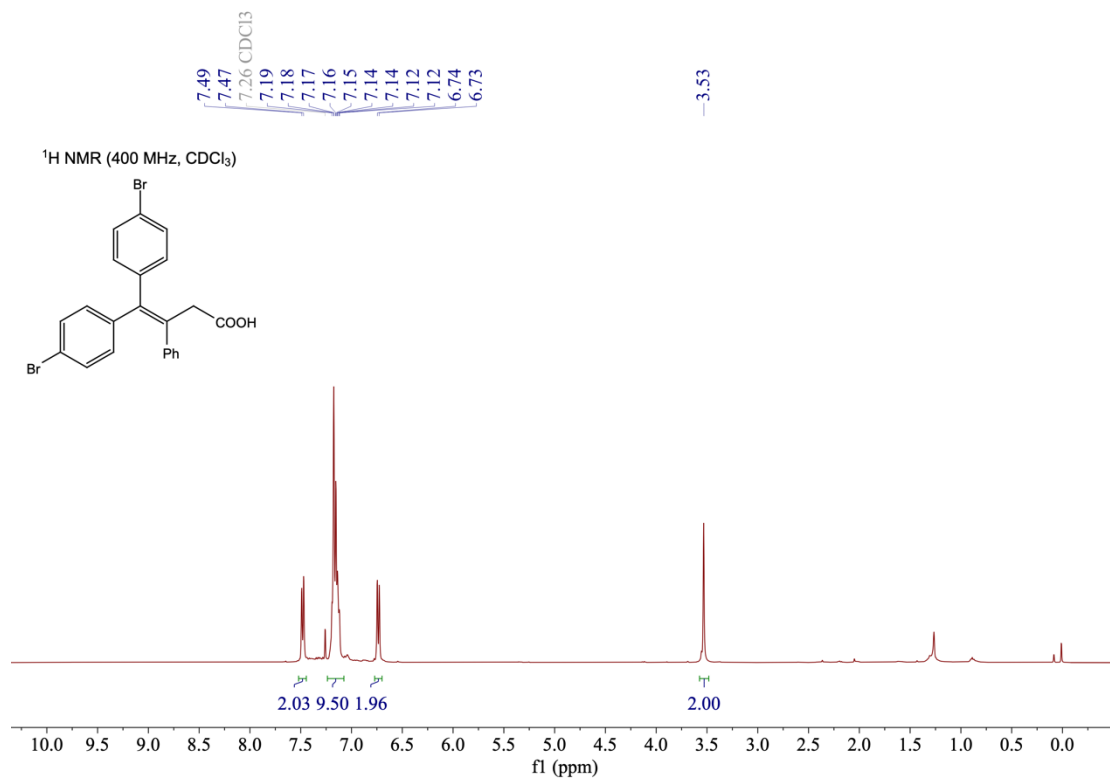
3-phenyl-4,4-di-p-tolylbut-3-enoic acid (3d)



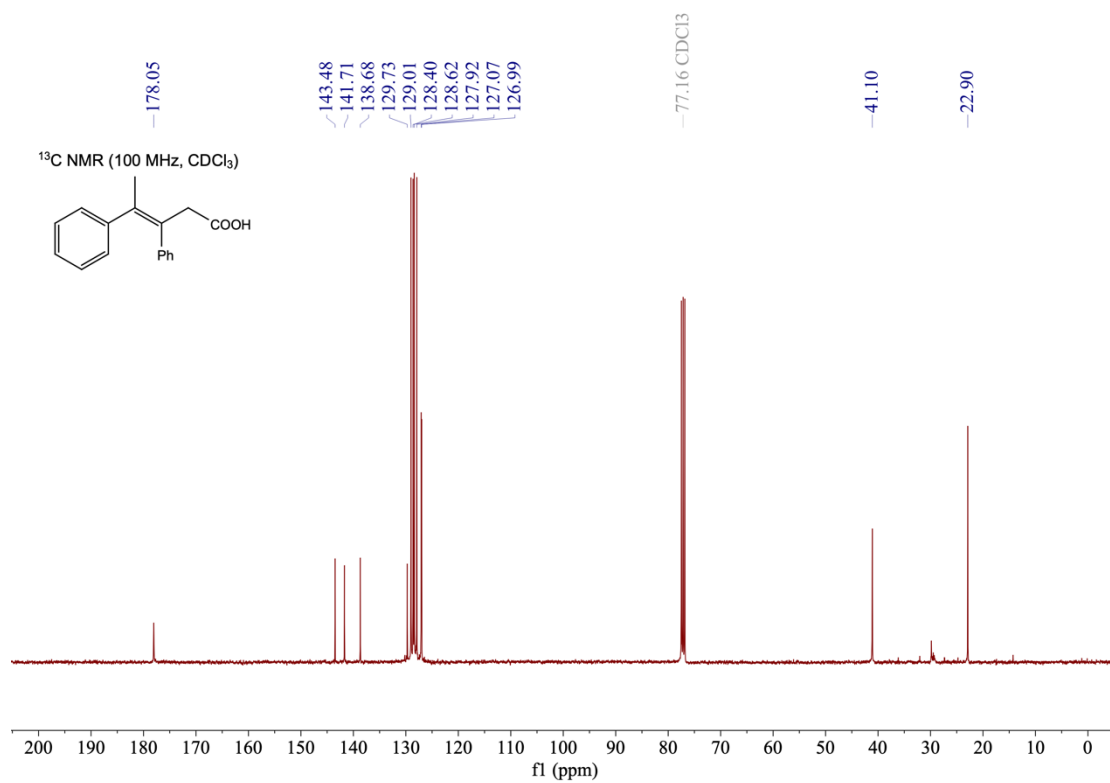
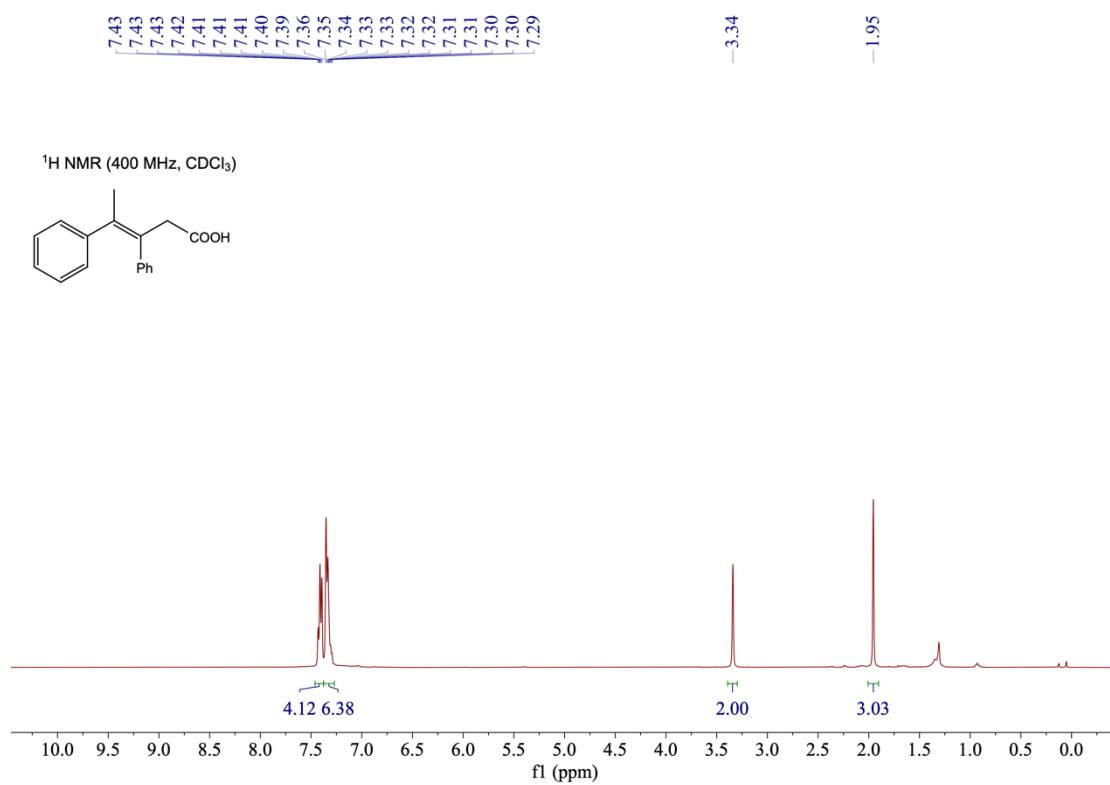
4,4-bis(4-fluorophenyl)-3-phenylbut-3-enoic acid (3e)



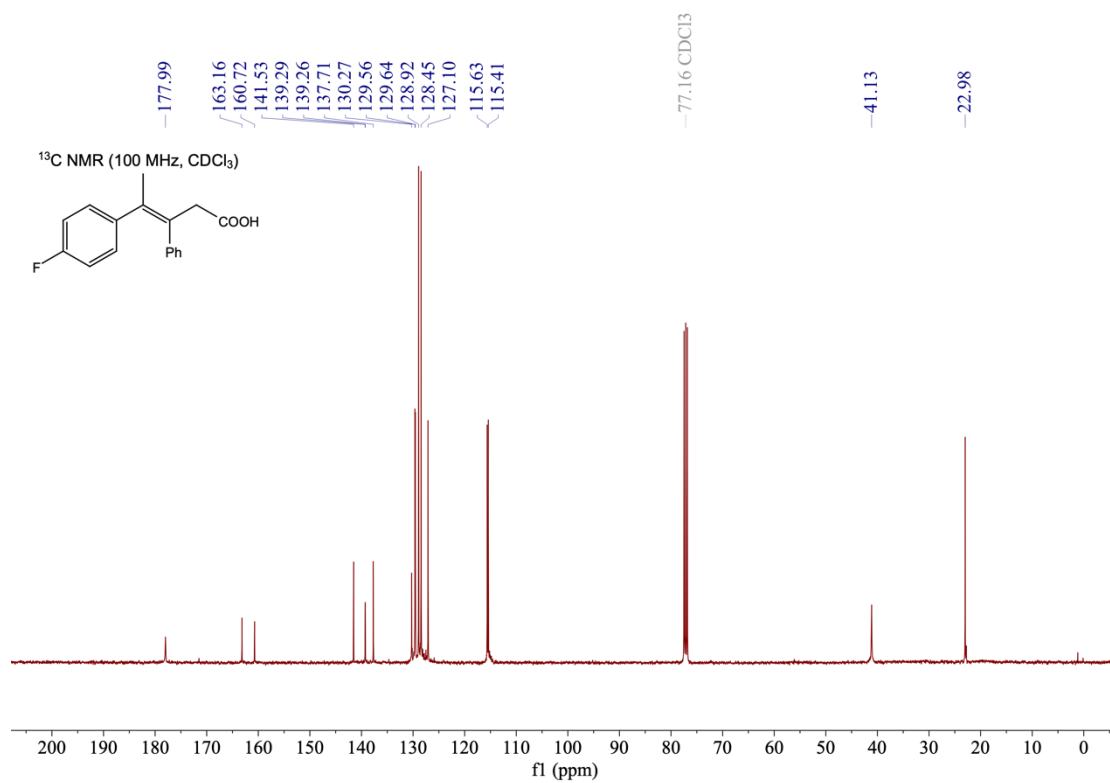
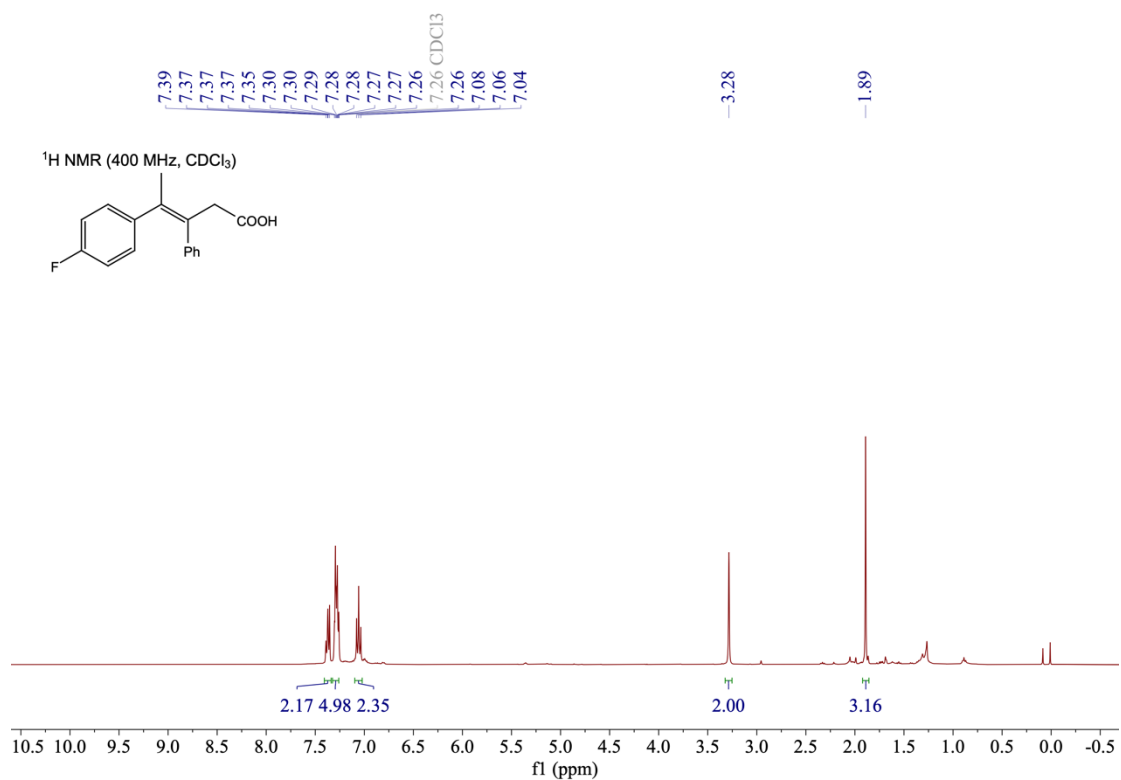
4,4-bis(4-bromophenyl)-3-phenylbut-3-enoic acid (3f)



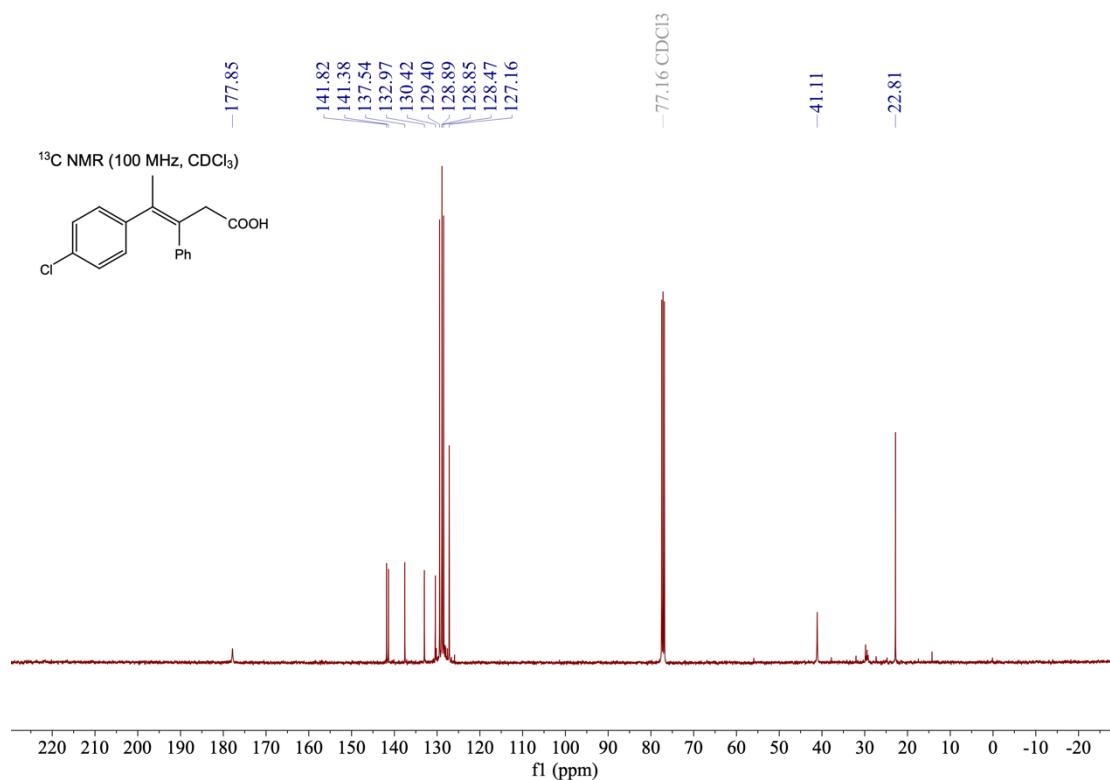
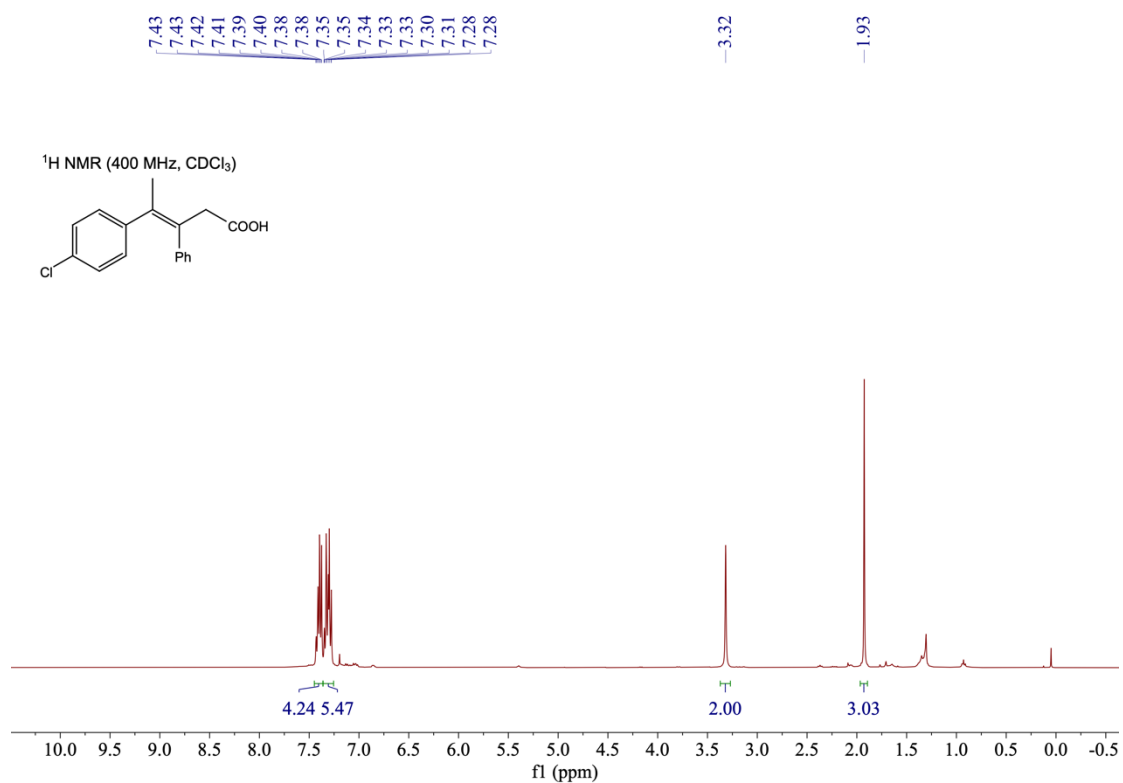
(Z)-3,4-diphenylpent-3-enoic acid (3g)



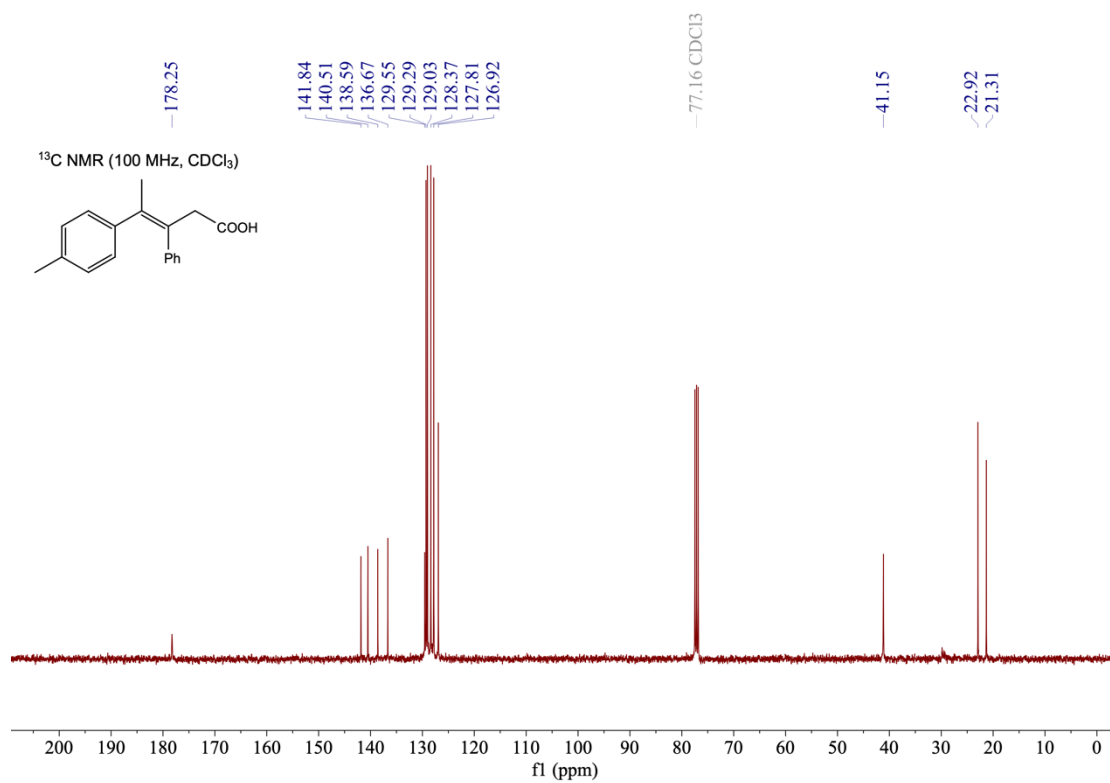
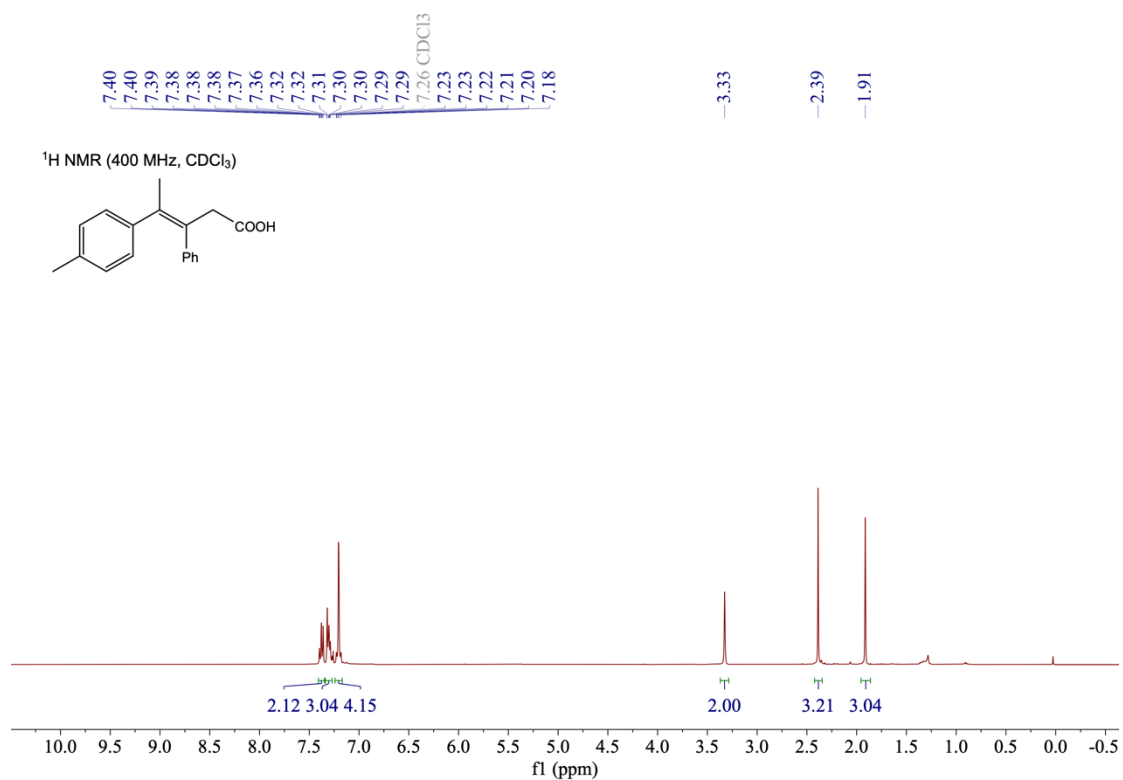
(Z)-4-(4-fluorophenyl)-3-phenylpent-3-enoic acid (3h)



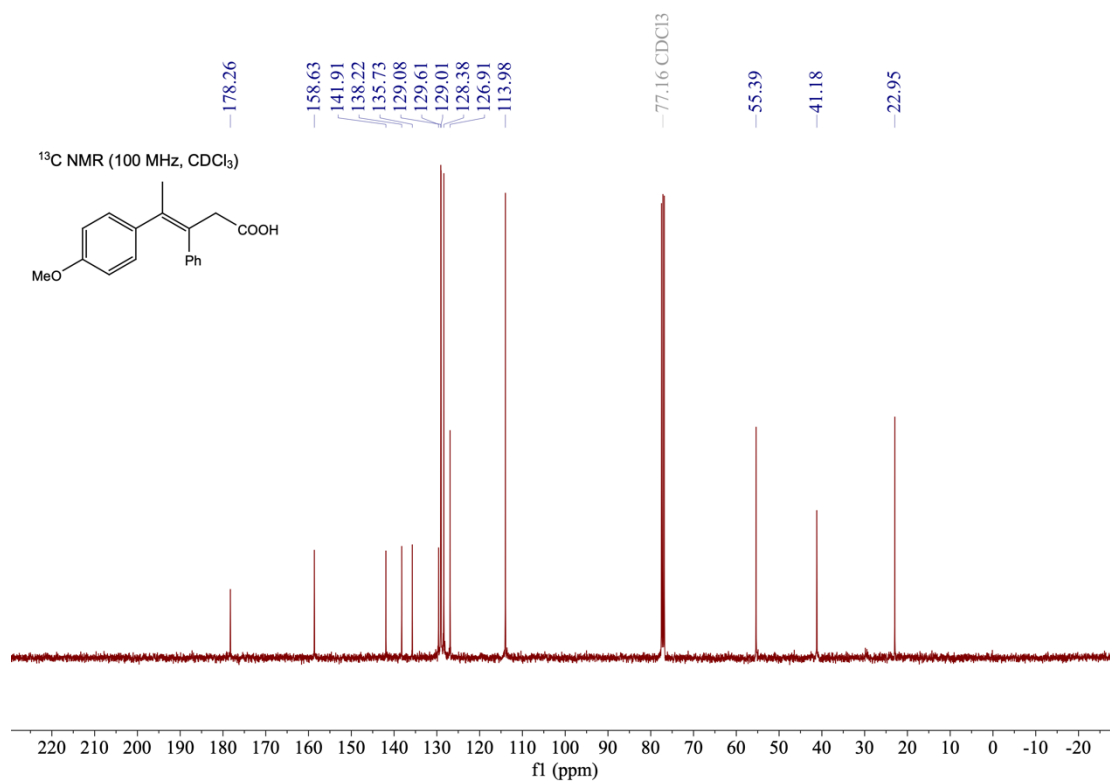
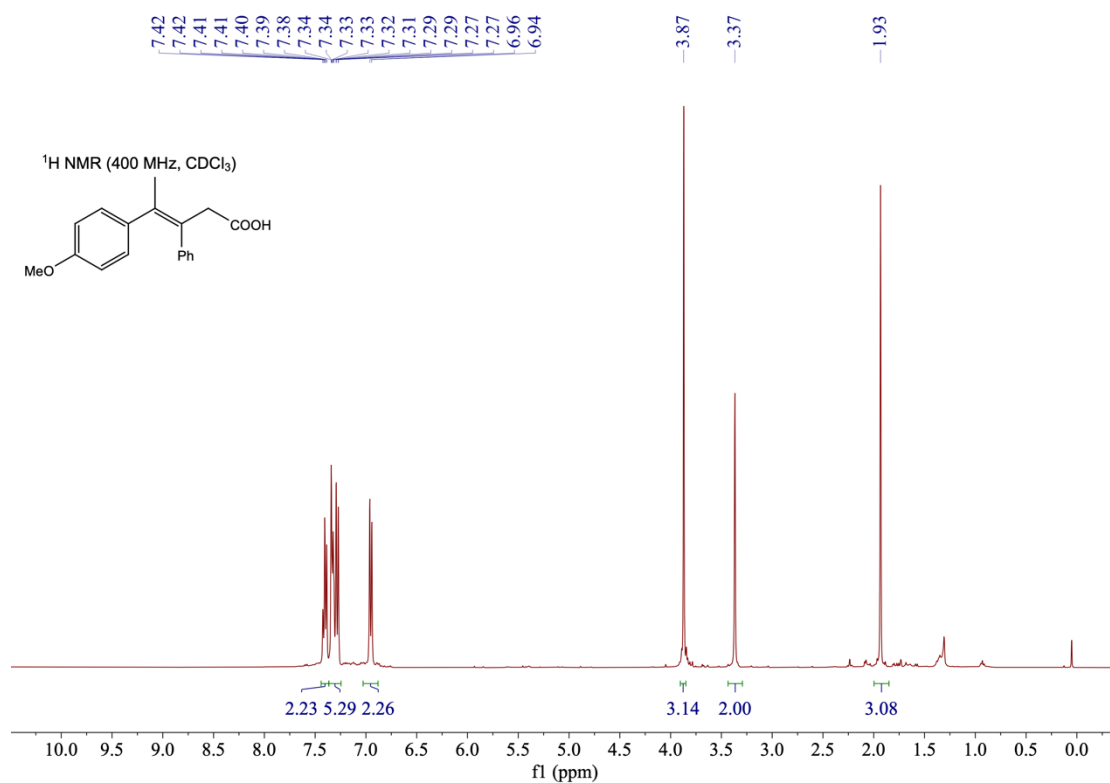
(Z)-4-(4-chlorophenyl)-3-phenylpent-3-enoic acid (3i)



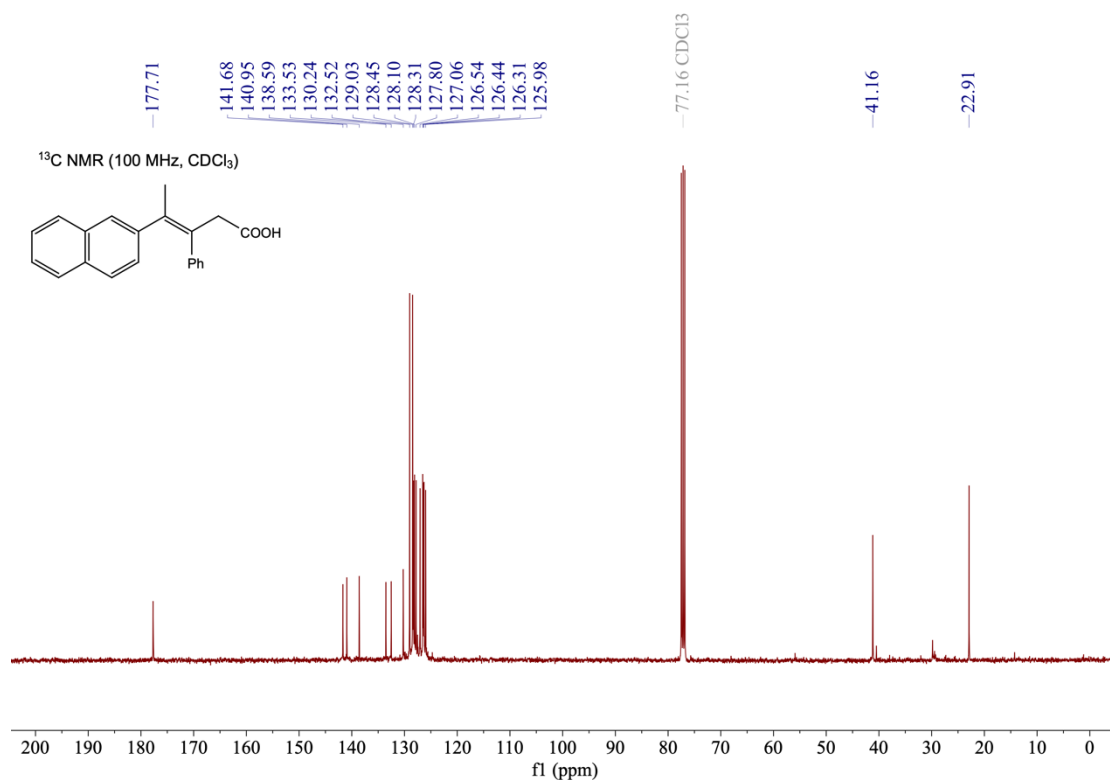
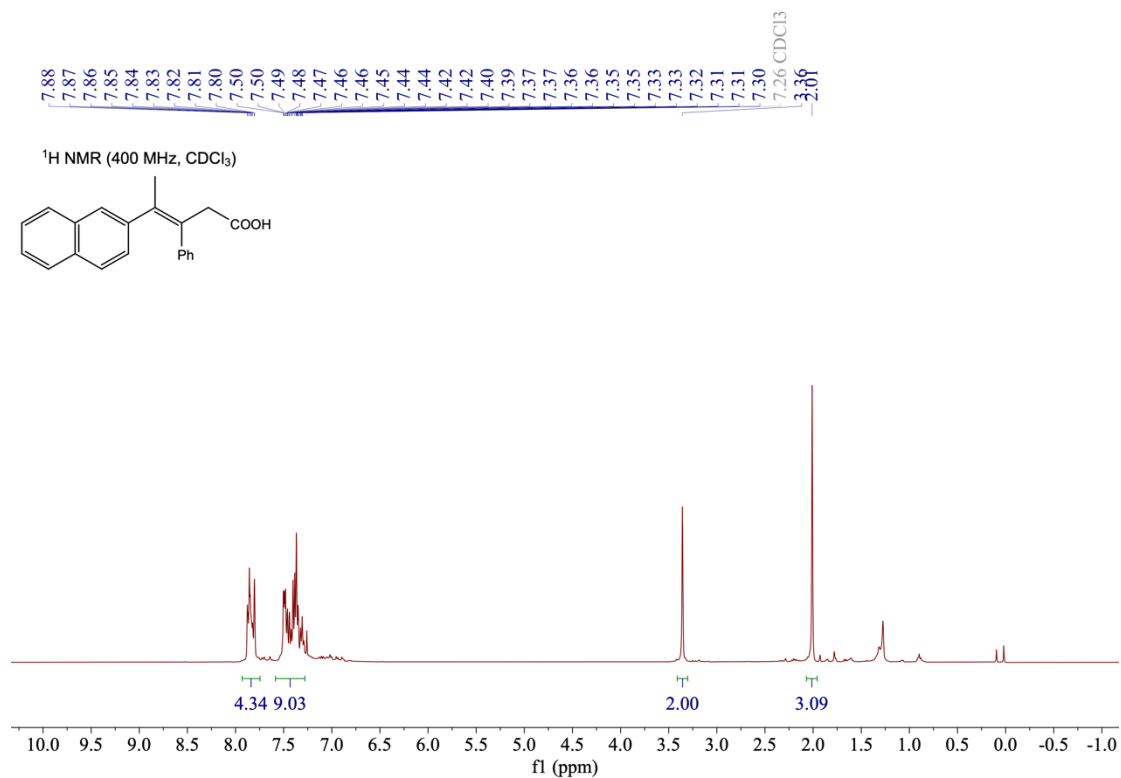
(Z)-3-phenyl-4-(p-tolyl)pent-3-enoic acid (3j)



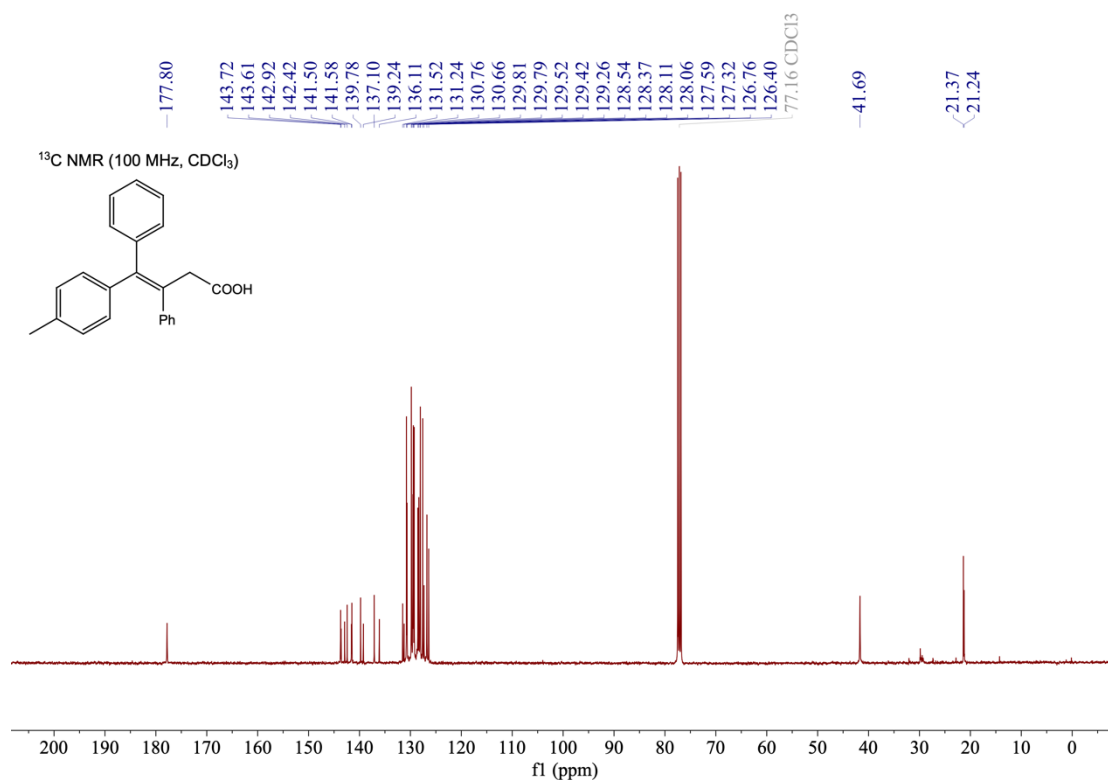
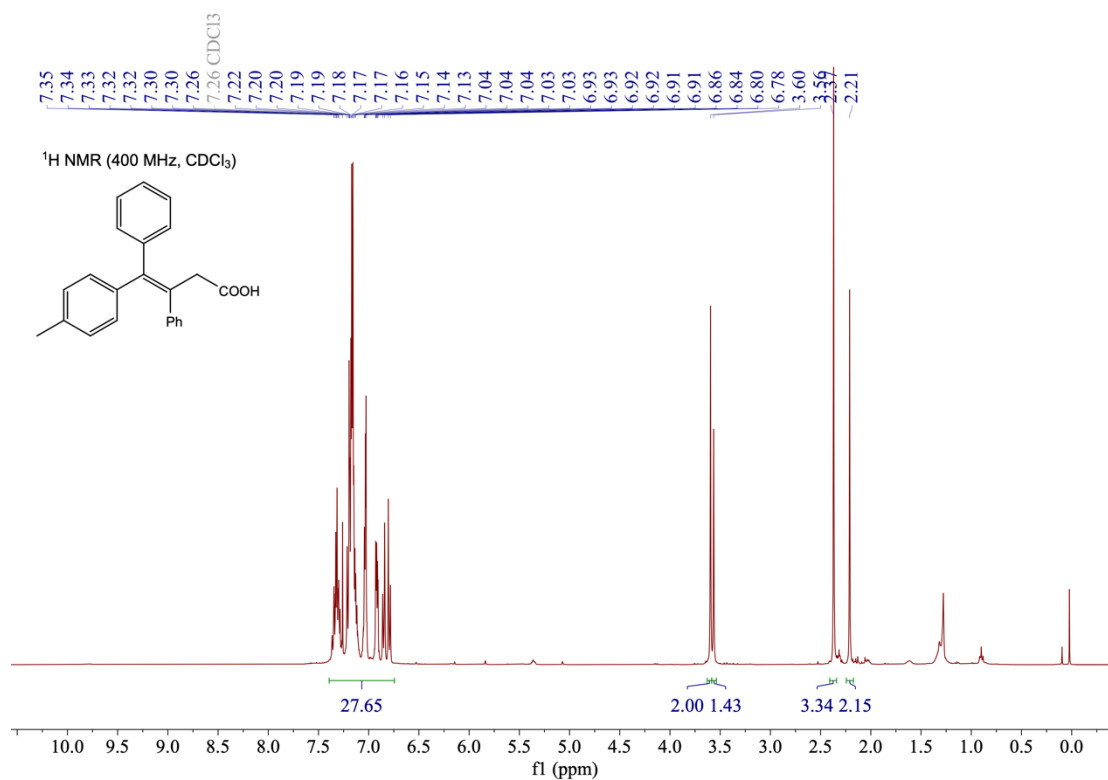
(Z)-4-(4-methoxyphenyl)-3-phenylpent-3-enoic acid (3k)



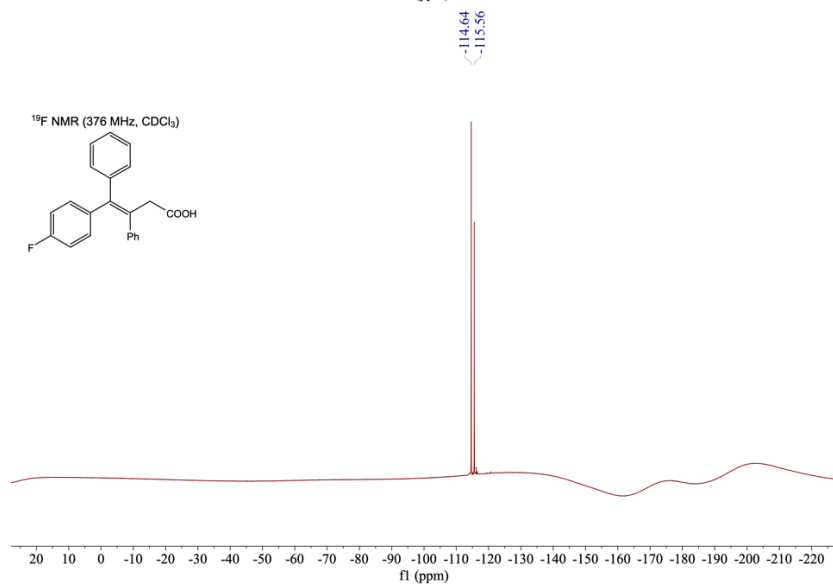
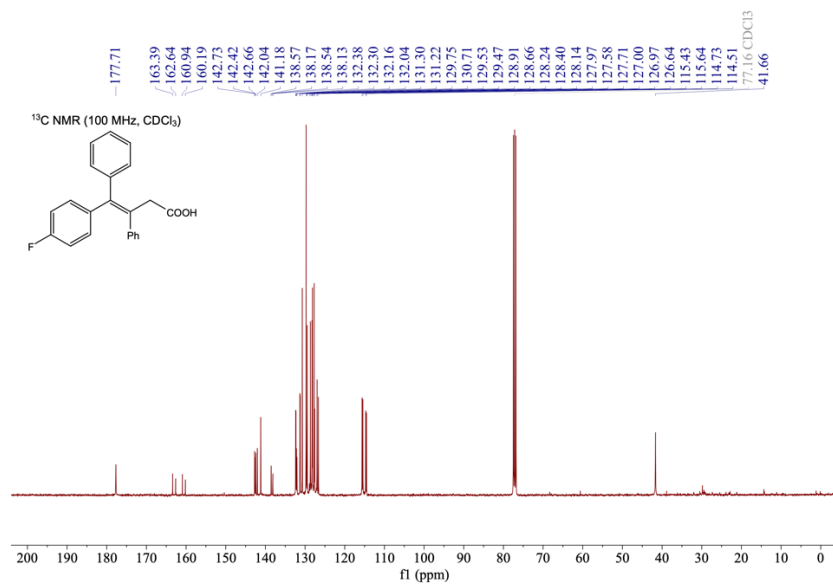
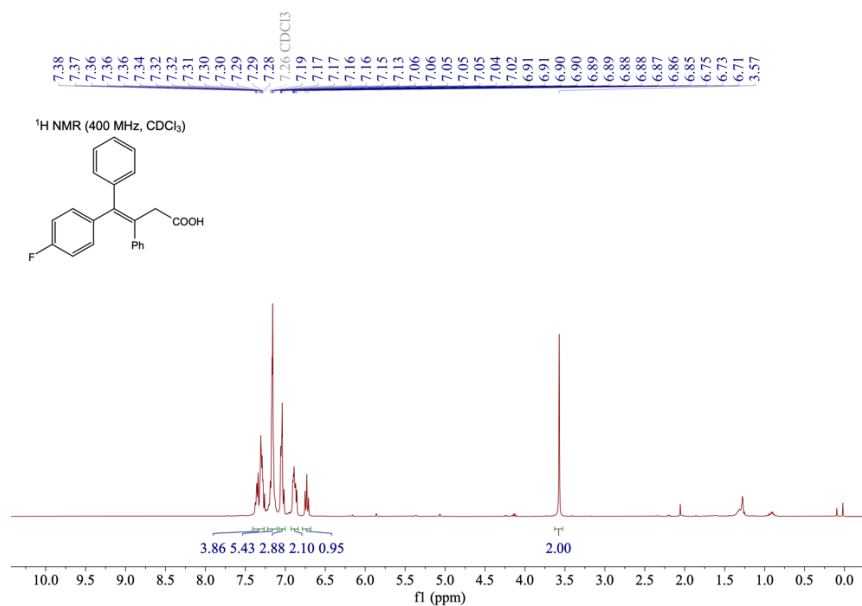
(Z)-4-(naphthalen-2-yl)-3-phenylpent-3-enoic acid (31)



3,4-diphenyl-4-(p-tolyl)but-3-enoic acid (3m)

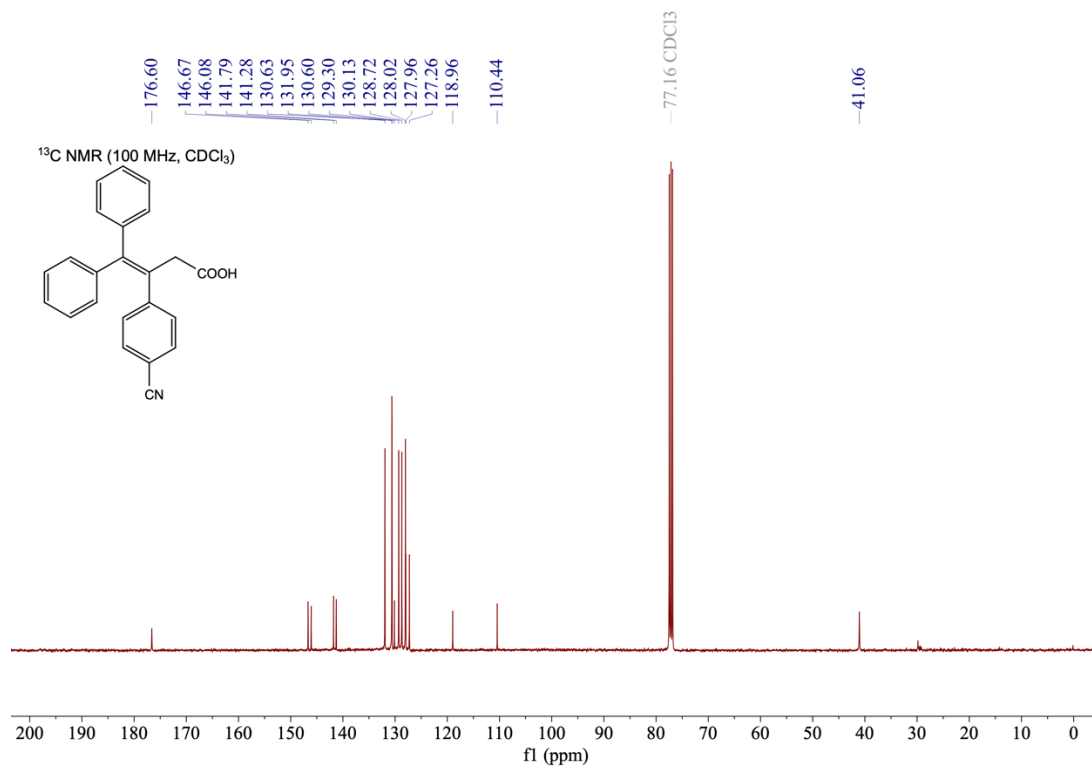
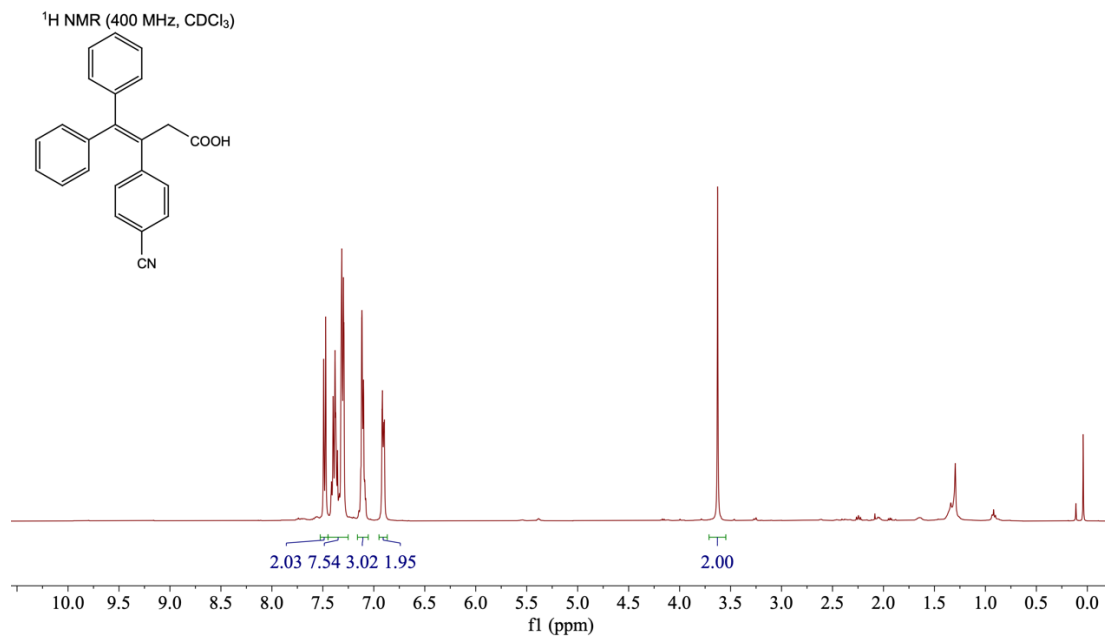


4-(4-fluorophenyl)-3,4-diphenylbut-3-enoic acid (3n)



3-(4-cyanophenyl)-4,4-diphenylbut-3-enoic acid (3o)

7.49
7.47
7.42
7.42
7.41
7.40
7.39
7.38
7.37
7.37
7.36
7.36
7.34
7.34
7.32
7.32
7.31
7.30
7.30
7.29
7.15
7.13
7.13
7.12
7.12
7.11
7.10
7.09
7.09
7.08
6.94
6.93
6.92
6.92
6.90
6.90
3.63



3-(4-acetylphenyl)-4,4-diphenylbut-3-enoic acid (3p)

