Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

One-Pot Chemoenzymatic Reactions in Water Enabled by Micellar Encapsulation

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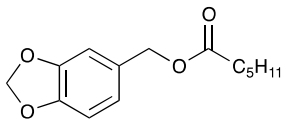
I. General Information

Unless otherwise noted, all metal-catalyzed reactions were carried out under positive argon pressure and all enzyme-catalyzed reactions were carried out under air. Unless otherwise noted, all reagents, catalysts, and solvents were obtained from commercial suppliers and used without further purification. Pig Liver Esterase (PLE), Horse Liver Alcohol Dehydrogenase (HLAD), and ω-Transaminase from aspergillus fumigatus (ω-TA) were obtained from Sigma-Aldrich. CALB lipase was obtained from Strem. Enzyme unit values indicate the rate of enzyme-catalyzed reaction of a standard substrate per unit time at a definted pH and temperature, as reported by the supplier. Solutions of surfactant/H_2O were prepared by dissolving the surfactant in degassed deionized water and storing under argon. Analytical thin-layer chromatography (TLC) was conducted using the indicated solvent systems on Analtech Uniplate Silica Gel TLC plates (250 microns). The developed chromatogram was visualized under UV light (254 nm), followed by aqueous potassium permanganate ($KMnO_4$). HPLC data were collected using an Agilent 1100 liquid chromatograph with a diode array detector equipped with a Discovery C18, 5 µm, 150 x 4.6 mm column (Supelco). GC data were recorded on a Shimadzu GC-2014 Gas Chromatograph with a Supelco SPB-1 Capillary column (15m x 0.32mm x 1.0 µm film thickness). All NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer, except for the 19F spectrum of **24c**, which was recorded on a Bruker Avance 300 MHz spectrometer. Chemical shifts (δ) are quoted in parts per million (ppm) and referenced to residual solvent peaks.[1] Ultra-performance liquid chromatography-high resolution mass spectrometry (UPLC HRMS) analyses were done using a Waters Acquity/Xevo-G2 instrument. Chromatographic separations were carried out on a Waters Acquity BEH UPLC column (ethylene-bridged hybrid C-18 stationary phase, 2.1 mm x 350 mm, 1.7 µm) with HRMS detection using an electrospray ionization (ESI) ion source in positive mode.

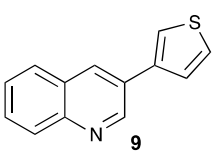
II. Synthetic Procedures and Analytical Data



3

Piperonyl hexanoate (3): A 250 mL round-bottom flask containing a magnetic stir bar was charged with piperonyl alcohol (1.99 g, 13.1 mmol), triethylamine (2.1 mL, 15 mmol), and dichloromethane (100 mL), and was cooled to 0 °C in an ice bath. Hexanoyl chloride (2.0 mL, 14 mmol) was added dropwise to the stirring reaction mixture. The reaction was allowed to warm to room temperature and stir for 3 hours, at which point TLC analysis indicated full conversion of reactant. The reaction mixture was transferred to a separatory funnel and washed sequentially with sat. K_2CO_3 solution (50 mL), 1.0 M HCl (50 mL), and brine (50 mL), dried over sodium sulfate, filtered, and concentrated by rotary evaporation. Purification by silica gel chromatography provided the title compound as a pale yellow liquid (2.95 g, 90%). Analytical data were in agreement with previous reports.[2]

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.85-6.75 (3H, m), 5.95 (2H, s), 5.00 (2H, s), 2.32 (2H, t, J = 7.5 Hz), 1.63 (2H, pent., *J* = 7.5 Hz), 1.37 – 1.21 (4H, m), 0.88 (3H, t, *J* = 7.0 Hz); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 173.6, 147.7, 147.5, 129.9, 122.1, 108.9, 108.1, 101.1, 65.9, 34.2, 31.2, 24.5, 22.2, 13.8; $\mathbf{R_f}$ = 0.68 (1:4 hexanes:EtOAc) UV + $KMnO_4$ stain.

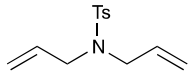


9

3-(thiophen-3-yl)quinolone (9): A 5 mL glass vial containing a magnetic stir bar was charged with 3-thienylboronic acid (64 mg, 0.50 mmol) and Pd(dtbfp)Cl_2 (3.0 mg, 0.0046 mmol). The vial was capped with a rubber septum and flushed with argon. Under positive argon pressure, 3-

bromoquinoline (34 µL, 0.25 mmol), 2 wt % TPGS-750-M/H_2O solution (1.0 mL), and triethylamine (105 µL, 0.75 mmol) were added by syringe, and the reaction mixture was stirred vigorously (600 rpm) at room temperature for 12 hours, at which point TLC analysis indicated the consumption of 3-bromoquinoline. The reaction mixture was quenched by adding 3 mL brine and then extracted with ethyl acetate (3 x 6 mL). The combined organics were washed with brine, dried over sodium sulfate, filtered, and concentrated by rotary evaporation. Purification by silica gel column chromatography using 4:1 hexane:EtOAc as the eluent provided the title compound as a tan solid (46.2 mg, 88%). Analytical data were in agreement with previous reports.[3] Colored impurities that were present in this material could be removed in the following way[4]: The product was dissolved in ~15 mL dichloromethane and 20 µL DMSO, and stirred for 12 hours. This solution was concentrated, purified by silica gel column chromatography, and recrystallized from hot petroleum ether to provide the title compound as a flakey white solid.

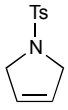
^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.21 (d, *J* = 2.1 Hz, 1H), 8.29 (d, *J* = 2.1 Hz, 1H), 8.13 (d, *J* = 8.3 Hz, 1H), 7.85 (d, *J* = 8.3 Hz, 1H), 7.73-7.68 (m, 1H), 7.66 (dd, *J* = 1.3, 2.9 Hz, 1H), 7.59-7.54 (m, 1H), 7.53 (dd, *J* = 1.4, 5.1 Hz, 1H), 7.49 (dd, *J* = 2.8, 5.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 149.4, 147.2, 138.9, 132.0, 129.3, 129.2, 128.7, 128.0, 127.8, 127.2, 127.1, 126.1, 121.6; **R_f** = 0.39 (1:5 hexanes:EtOAc) UV + $KMnO_4$ stain.



10

***N,N*-diallyl-4-methylbenzenesulfonamide (10):** A 250 mL round-bottom flask containing a magnetic stir bar was charged with diallylamine (1.23 mL, 10.0 mmol), triethylamine (1.80 mL, 12.9 mmol), and dichloromethane (50 mL). The flask was cooled to 0 °C in an ice bath, and tosyl chloride (2.48 g, 13.0 mmol) was added. The reaction was allowed to warm to room temperature and stir for 36 hours, at which point TLC analysis indicated full conversion of reactant. The reaction mixture was transferred to a separatory funnel and washed sequentially with 1.0 M HCl (50 mL), sat. $NaHCO_3$ solution (2 x 50 mL), and brine (50 mL), dried over sodium sulfate, filtered, and concentrated by rotary evaporation. Purification by silica gel chromatography using 9:1 hexane:EtOAc as the eluent provided **10** as a clear, colorless liquid (2.115 g, 84%). Analytical data were in agreement with previous reports.[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.70 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 2H), 5.66-5.55 (m, 2H), 5.16-5.13 (m, 2H), 5.13-5.10 (m, 2H), 3.79 (d, *J* = 6.2 Hz, 4H), 2.42 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 143.1, 137.2, 132.5, 129.5, 126.9, 118.7, 49.2, 21.3; **R_f** = 0.22 (9:1 hexane:EtOAc) UV + $KMnO_4$ stain.

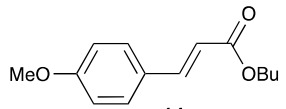


11

***N*-Tosyl-2,5-dihydropyrrole (11):** A 5 mL glass vial containing a magnetic stir bar was charged with N,N-diallyl-4-methylbenzenesulfonamide (**10**, 50 mg, 0.20 mmol) and Hoveyda-Grubbs 2nd Generation catalyst (2.5 mg, 0.004 mmol). The vial was capped with a rubber septum and flushed with argon. Under positive argon pressure 2 wt % TPGS-750-M/H_2O solution (2.0 mL) was added by syringe, and the reaction mixture was stirred vigorously (600 rpm) at room temperature for 4 hours, at which point TLC analysis indicated the consumption of reactant. The reaction mixture was quenched by adding 3 mL brine and then extracted with ethyl acetate (3 x 6 mL). The combined organics were washed with brine, dried over sodium sulfate, filtered, and concentrated by rotary evaporation. Purification by silica gel column chromatography using 4:1 hexane:EtOAc as the eluent provided the title compound as a yellow solid (42.3 mg, 95%). Analytical data were in agreement with previous reports.[6] Colored impurities that were present in this material could be removed using the method of Georg[4]: The product was dissolved in ~15 mL dichloromethane

and 20 µL DMSO, and stirred for 12 hours. This solution was concentrated, filtered through a plug of silica gel, and recrystallized from Et_2O/petroleum ether to yield the product as a white solid.

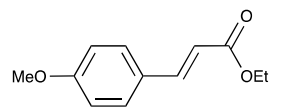
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.72 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 5.65 (s, 2H), 4.12 (s, 4H), 2.42 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 143.4, 134.3, 129.7, 127.4, 125.4, 54.8, 21.5; $\mathbf{R_f}$ = 0.57 (4:1 hexane:EtOAc) $KMnO_4$ stain.



14

(*E*)-Butyl-4-methoxycinnamate (14): A 5 mL glass vial containing a magnetic stir bar was charged with 4-iodoanisole (117 mg, 0.50 mmol), sodium chloride (175 mg, 3.0 mmol) and Pd(*t*Bu_3)$_2$ (5.1 mg, 0.010 mmol). The vial was capped with a rubber septum and flushed with argon. Under positive argon pressure, butyl acrylate (143 µL, 1.0 mmol), 2 wt % TPGS-750-M/H_2O solution (1.0 mL), and triethylamine (209 µL, 1.5 mmol) were added by syringe, and the reaction mixture was stirred vigorously (600 rpm) at room temperature for 16 hours. The reaction mixture was quenched by adding 3 mL brine and then extracted with ethyl acetate (3 x 6 mL). The combined organics were washed with brine, dried over sodium sulfate, filtered, and concentrated by rotary evaporation. Purification by silica gel column chromatography using 5% EtOAc/hexanes as the eluent provided the title compound as a clear liquid (100.6 mg, 86%). Analytical data were in agreement with previous reports.[7,8]

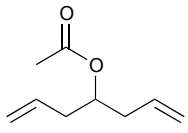
^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.63 (d, *J* = 16.0 Hz, 1H), 7.47 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.31 (d, *J* = 16.0 Hz, 2H), 4.20 (t, *J* = 6.9 Hz, 2H), 3.81 (s, 3H), 1.66 (m, 2H), 1.42 (m, 2H), 0.96 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 167.4, 161.3, 144.2, 129.6, 127.1, 115.7, 114.2, 64.4, 55.4, 30.8, 19.2, 13.7; $\mathbf{R_f}$ = 0.49 (4:1 hexane:EtOAc) UV + $KMnO_4$ stain.



16

(*E*)-Ethyl-4-methoxycinnamate (16): A 5 mL glass vial containing a magnetic stir bar was charged with 4-iodoanisole (117 mg, 0.50 mmol), sodium chloride (175 mg, 3.0 mmol) and Pd(*t*Bu_3)$_2$ (5.1 mg, 0.010 mmol). The vial was capped with a rubber septum and flushed with argon. Under positive argon pressure, ethyl acrylate (109 µL, 1.0 mmol), 2 wt % TPGS-750-M/H_2O solution (1.0 mL), and triethylamine (209 µL, 1.5 mmol) were added by syringe, and the reaction mixture was stirred vigorously (600 rpm) at room temperature for 16 hours. The reaction mixture was quenched by adding 3 mL brine and then extracted with ethyl acetate (3 x 6 mL). The combined organics were washed with brine, dried over sodium sulfate, filtered, and concentrated by rotary evaporation. Purification by silica gel column chromatography using 5% EtOAc/hexanes as the eluent provided the title compound as a clear liquid (90.7 mg, 86%). Analytical data were in agreement with previous reports.[9]

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.69 (d, *J* = 16.2 Hz, 1H), 7.44 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 6.28 (d, *J* = 15.6 Hz, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 167.2, 161.3, 144.2, 129.6, 127.2, 115.7, 114.3, 60.2, 55.3, 14.3; $\mathbf{R_f}$ = 0.55 (4:1 hexane:EtOAc) UV + $KMnO_4$ stain.

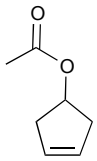


18

1,6-Heptadien-4-yl acetate (18): Compound **18** was prepared by the method described by Ishihara.[10] A 25 mL round-bottom flask containing a magnetic stir bar was charged with 1,6-heptadien-4-ol (3.56 g, 31.7 mmol) and DMAP (19 mg, 0.16 mmol). Acetic anhydride (3.3 mL, 35 mmol) was added dropwise and

the reaction flask was stoppered and heated in an oil bath at 40 °C. The reaction mixture was stirred for 48 hours at which point TLC analysis indicated full conversion of reactant. Et_2O (30 mL) was added to the reaction mixture, and this solution was washed with saturated K_2CO_3 (3 x 10 mL) and brine (1 x 10 mL). The organic layer was dried over sodium sulfate, filtered, and concentrated by rotary evaporation. Purification by silica gel column chromatography using 3:1 hexane:EtOAc as the eluent, followed by Kugelrohr distillation, provided the title compound as a clear liquid (2.66 g, 54%). Analytical data were in agreement with previous reports.[11]

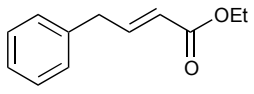
^{1}H-NMR (400 MHz, $CDCl_3$) δ: 5.72(ddt, *J* = 17.4, 10.2, 7.0, 2H), 5.10-5.00 (m, 4H), 4.94 (pent., *J* = 6.1, 1H), 2.29 (m, 4H), 2.00 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 170.3, 133.4, 117.6, 72.1, 37.9, 20.9; $\mathbf{R_f}$ = 0.72 (4:1 hexane:EtOAc) UV + $KMnO_4$ stain.



19

3-Cyclopenten-1-yl acetate (19): Compound **19** was prepared by the method described by Ishihara.[10] A 10 mL round-bottom flask containing a magnetic stir bar was charged with 3-cyclopenten-1-ol (1.00 g, 11.9 mmol) and DMAP (7 mg, 0.06 mmol). Acetic anhydride (1.3 mL, 13 mmol) was added dropwise and the reaction flask was stoppered and heated in an oil bath at 40 °C. The reaction mixture was stirred for 16 hours at which point TLC analysis indicated full conversion of reactant. The reaction was quenched by addition of 2 mL H_2O and 0.5 mL sat. $NaHCO_3$, followed by stirring at room temperature for 30 minutes. The mixture was transferred to a separatory funnel and 1 mL brine was added to facilitate the separation of product. The organic layer was washed sequentially with 1 M NaOH (5 mL) and brine (2 x 5 mL), and the final separation of the aqueous layer from the product was accomplished by centrifugation (3400 RPM, 1300 x g). The organic layer was dried over sodium sulfate and filtered to provide the product the title compound as a clear liquid (954 mg, 64% yield). Analytical data were in agreement with previous reports.[11]

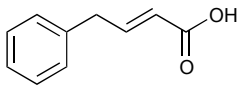
^{1}H-NMR (400 MHz, $CDCl_3$) δ: 5.65 (s, 2H), 5.33-5.27 (m, 1H), 2.67 (dd, *J* = 7.0, 16.6 Hz, 2H), 2.32 (dd, *J* = 2.2, 16.6 Hz, 2H), 1.96 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 170.7, 127.9, 73.9, 39.3, 20.9; $\mathbf{R_f}$ = 0.59 (4:1 hexane:EtOAc) $KMnO_4$ stain.



23

(*E*)-Ethyl 4-phenylbut-2-enoate (23): A 5 mL glass vial containing Grubbs 2nd Generation catalyst (17 mg, 0.020 mmol) a magnetic stir bar was capped with a rubber septum and flushed with argon. Under positive argon pressure, 2 wt % TPGS-750-M/H_2O solution (2.0 mL) allylbenzene (132 µL, 1.0 mmol), ethyl acrylate (232 µL, 2.0 mmol) were added by syringe, and the reaction mixture was stirred vigorously (600 rpm) at room temperature for 12 hours. The reaction mixture was quenched by adding 3 mL brine and then extracted with ethyl acetate (2 x 10 mL). The combined organics were washed with brine, dried over sodium sulfate, filtered, and concentrated by rotary evaporation. Purification by silica gel column chromatography using 5% EtOAc/hexanes as the eluent provided the title compound as a clear liquid (166 mg, 86%). Analytical data were in agreement with previous reports.[12]

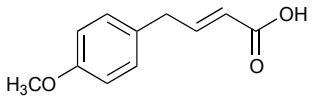
^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.33-7.29 (m, 2H), 7.25-7.22 (m, 1H), 7.18-7.16 (m, 2H), 7.10 (dt, *J* = 15.5, 7.0 Hz, 1H), 5.81 (dt, *J* = 15.5, 1.6 Hz, 1H), 4.17 (q, *J* = 7.0 Hz, 2H), 3.51 (2H, dd, *J* = 7.0, 1.5 Hz, 2H), 1.27 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 166.4, 147.2, 137.6, 128.7, 128.6, 126.6, 122.3, 60.2, 38.4, 14.2; $\mathbf{R_f}$ = 0.38 (9:1 hexane:EtOAc) UV + $KMnO_4$ stain.



24a

(*E*)-4-phenylbut-2-enoic acid (24a): A 5 mL glass vial containing Grubbs 2nd Generation catalyst (17 mg, 0.020 mmol), $NaHCO_3$ (100 mg, 1.2 mmol), a magnetic stir bar was capped with a rubber septum and flushed with argon. Under positive argon pressure, 2 wt % TPGS-750-M/H_2O solution (2.0 mL) allylbenzene (132 µL, 1.0 mmol), ethyl acrylate (232 µL, 2.0 mmol) were added by syringe, and the reaction mixture was stirred vigorously (600 rpm) at room temperature for 12 hours. Pig liver esterase (12 mg, 216 units) was added, and the reaction mixture stirred for an additional 24 hours at room temperature. The reaction mixture was quenched by adding 1.0 M HCl (2.0 mL) and brine (2.0 mL) and then extracted with ethyl acetate (3 x 6 mL). Due to the formation of emulsions, it was necessary to separate the layers by centrifugation for several minutes in a 15 mL falcon tube (3400 RPM, 1300 x g). The combined organics were washed with brine, dried over sodium sulfate, filtered, and concentrated by rotary evaporation. This material was purified by silica gel column chromatography using 20 to 40% EtOAc/hexanes with 1% AcOH as the eluent, followed by recrystallization from petroleum ether to yield the title compound as white crystals (92 mg, 57%). Analytical data were in agreement with previous reports.[13]

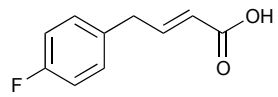
^{1}H-NMR (400 MHz, $CDCl_3$) δ: 11.66 (broad s, 1H), 7.36-7.29 (m, 2H), 7.28-7.15 (m, 4H), 5.82 (dt, *J* = 15.5, 1.6 Hz, 1H), 3.55 (dd, *J* = 6.7, 1.3 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 172.1, 150.2, 137.2, 128.8, 128.7, 126.7, 121.7, 38.5; **R_f** = 0.40 (1% AcOH in 3:2 hexane:EtOAc) UV + $KMnO_4$ stain.



24b

(*E*)-4-(4-Methoxyphenyl)but-2-enoic acid (24b): A 5 mL glass vial containing Grubbs 2nd Generation catalyst (8.5 mg, 0.010 mmol), $NaHCO_3$ (50 mg, 0.6 mmol), a magnetic stir bar was capped with a rubber septum and flushed with argon. Under positive argon pressure, 2 wt % TPGS-750-M/H_2O solution (1.0 mL) 4-allylanisole (77 µL, 0.5 mmol), ethyl acrylate (116 µL, 1.0 mmol) were added by syringe, and the reaction mixture was stirred vigorously (600 rpm) at room temperature for 12 hours. Pig liver esterase (12 mg, 216 units) was added, and the reaction mixture stirred for an additional 24 hours at room temperature. The reaction mixture was quenched by adding 1.0 M HCl (2.0 mL) and brine (1.0 mL) and then extracted with ethyl acetate (3 x 6 mL). Due to the formation of emulsions, it was necessary to separate the layers by centrifugation for several minutes in a 15 mL falcon tube (3400 RPM, 1300 x g). The combined organics were washed with brine, dried over sodium sulfate, filtered, and concentrated by rotary evaporation. This material was purified by silica gel column chromatography using 20 to 40% EtOAc/hexanes with 1% AcOH as the eluent, followed by recrystallization from petroleum ether to yield the title compound as white crystals (41.4 mg, 43%). Analytical data were in agreement with previous reports.[14]

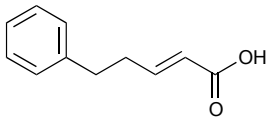
^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.19 (dt, *J* = 15.6, 6.7 Hz, 1H), 7.08 (d, *J* = 8.6 Hz, 2H), 6.86 (dt, *J* = 8.6, 2.0 Hz, 2H), 5.79 (dt, *J* = 15.5, 1.5 Hz, 1H), 3.80 (s, 3H), 3.49 (dd, *J* = 6.8, 1.2 Hz, 2H), (OH signal not observed); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 171.9, 158.7, 150.8, 130.0, 129.4, 121.5, 114.4, 55.5, 37.9; **R_f** = 0.32 (1% AcOH in 3:2 hexane:EtOAc) UV + $KMnO_4$ stain.



24c

(*E*)-4-(4-Fluorophenyl)but-2-enoic acid (24c): A 5 mL glass vial containing Grubbs 2nd Generation catalyst (8.5 mg, 0.010 mmol), $NaHCO_3$ (50 mg, 0.6 mmol), a magnetic stir bar was capped with a rubber septum and flushed with argon. Under positive argon pressure, 2 wt % TPGS-750-M/H_2O solution (1.0 mL) 1-allyl-4-fluorobenzene (68 µL, 0.5 mmol), ethyl acrylate (116 µL, 1.0 mmol) were added by syringe, and the reaction mixture was stirred vigorously (600 rpm) at room temperature for 12 hours. Pig liver esterase (12 mg, 216 units) was added, and the reaction mixture stirred for an additional 24 hours at room temperature. The reaction mixture was quenched by adding 1.0 M HCl (2.0 mL) and brine (1.0 mL) and then extracted with ethyl acetate (3 x 6 mL). Due to the formation of emulsions, it was necessary to separate the layers by centrifugation for several minutes in a 15 mL falcon tube (3400 RPM, 1300 x g). The combined organics were washed with brine, dried over sodium sulfate, filtered, and concentrated by rotary evaporation. This material was purified by silica gel column chromatography using 20 to 40% EtOAc/hexanes with 1% AcOH as the eluent, followed by recrystallization from petroleum ether to yield the title compound as a white solid (35.9 mg, 40%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.22-7.09 (m, 3H), 7.01 (m, 2H), 6.86 (dt, J = 8.6, 2.0 Hz, 2H), 5.80 (dt, J = 15.6, 1.6 Hz, 1H), 3.52 (d, J = 6.6 Hz, 2H), (OH signal not observed); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 171.5, 162.2 (d, J_{CF} = 245.0 Hz), 150.2, 133.3 (d, J_{CF} = 3.0 Hz), 130.7 (d, J_{CF} = 8.1 Hz), 122.0, 116.0 (d, J_{CF} = 21.1 Hz), 38.1; **^{19}F NMR** (282 MHz, $CDCl_3$) δ: -115.55 (tt, J_{FH} = 8.6, 5.3 Hz); **HRMS** (ESI) *m/z*: $[M+H]^+$ calculated for $C_{10}H_{10}FO_2^+$ 181.0660, found 181.0658; **R_f** = 0.33 (1% AcOH in 3:2 hexane:EtOAc) UV + $KMnO_4$ stain.



24d

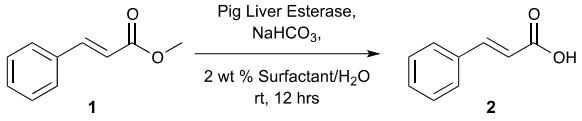
(*E*)-4-phenylbut-2-enoic acid (24d): A 5 mL glass vial containing Grubbs 2nd Generation catalyst (8.5 mg, 0.010 mmol), $NaHCO_3$ (50 mg, 0.6 mmol), a magnetic stir bar was capped with a rubber septum and flushed with argon. Under positive argon pressure, 2 wt % TPGS-750-M/H_2O solution (1.0 mL) 4-phenyl-1-butene (75 µL, 0.5 mmol), ethyl acrylate (116 µL, 1.0 mmol) were added by syringe, and the reaction mixture was stirred vigorously (600 rpm) at room temperature for 12 hours. Pig liver esterase (12 mg, 216 units) was added, and the reaction mixture stirred for an additional 24 hours at room temperature. The reaction mixture was quenched by adding 1.0 M HCl (2.0 mL) and brine (1.0 mL) and then extracted with ethyl acetate (3 x 6 mL). Due to the formation of emulsions, it was necessary to separate the layers by centrifugation for several minutes in a 15 mL falcon tube (3400 RPM, 1300 x g). The combined organics were washed with brine, dried over sodium sulfate, filtered, and concentrated by rotary evaporation. This material was purified by silica gel column chromatography using 20 to 40% EtOAc/hexanes with 1% AcOH as the eluent, followed by recrystallization from petroleum ether to yield the title compound as an off-white solid (30.7 mg, 35%). Analytical data were in agreement with previous reports.[15,16]

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.34-7.27 (m, 2H), 7.25-7.16 (m, 3H), 7.12 (dt, J = 15.6, 6.9 Hz, 1H), 5.85 (dt, J = 15.6, 1.4 Hz, 1H), 2.80 (t, J = 7.4 Hz, 2H), 2.57 (m, 2H) 3.55 (dd, J = 6.7, 1.3 Hz, 2H) (OH signal not observed); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 172.1, 151.4, 141.0, 128.9, 128.7, 126.6, 121.6, 34.6, 34.4; **R_f** = 0.43 (1% AcOH in 3:2 hexane:EtOAc) UV + $KMnO_4$ stain.

III. Effect of Surfactant on Enzymatic Reaction Conversion

Data from experiments in this section are reported as the average of duplicate experiments.

PLE Conversion Surfactant Screen

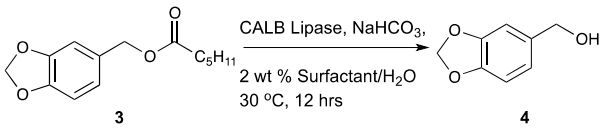


1 2

Entry	Surfactant	Conversion (%)
1	none	98
2	TPGS-750-M	100
3	PTS	94
4	SPGS-550-M (Nok)	80
5	Triton X	100
6	Brij L23	100
7	Tween 80	97
8	Kolliphor EL	95
9	SDS	trace
10	CTAB	trace

Stock solutions of surfactant (5 wt% in H_2O, 200 µL), $NaHCO_3$ (800 mM, 250 µL), and Pig Liver Esterase (600 units/mL, 50 µL) were added to a 5 mL glass vial containing methyl cinnamate (30 mg, 0.185 mmol) and a magnetic stir bar. The vials were capped with a rubber septum pierced with a needle to provide an outlet for the CO_2 that evolves during the reaction. The reaction mixture was stirred vigorously (600 rpm) for 12 hours and then quenched by addition of 350 µL 1.0 M HCl and 1.50 mL benzoic acid in methanol (0.41 M, added as internal standard). The resulting homogeneous solution was diluted 200-fold in methanol, passed through a 0.2 µm syringe filter, and analyzed on an Agilent 1100 HPLC equipped with a Discovery C18, 5 µm, 150 x 4.6 mm column (Supelco). Injections of 25 µL were separated using an isocratic method of 40% H_2O and 60% MeOH (mobile phase contained 0.5% acetic acid) with a 1.0 mL min^{-1} flow rate. Peak areas were monitored at 280 nm at the following retention times: Benzoic acid internal standard (3.45 minutes), cinnamic acid (4.56 minutes), and methyl cinnamate (7.94 minutes).

Lipase Conversion Surfactant Screen

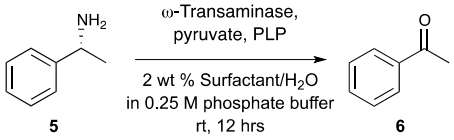


3 4

Entry	Surfactant	Conversion (%)
11	none	99
12	TPGS-750-M	98
13	PTS	99
14	SPGS-550-M (Nok)	100
15	Triton X	99
16	Brij L23	99
17	Tween 80	99
18	Kolliphor EL	98
19	SDS	99
20	CTAB	72

Stock solutions of surfactant (5 wt% in H_2O, 200 µL), $NaHCO_3$ (800 mM, 250 µL), CALB Lipase (5000 LU/g, 35 µL), and water (15 µL) were added to a 5 mL glass vial containing piperonyl hexanoate (37.5 mg, 0.150 mmol) and a magnetic stir bar. The vials were capped with a rubber septum pierced with a needle to provide an outlet for the CO_2 that evolves during the reaction. The reaction mixture was stirred vigorously (600 rpm) for 12 hours and then quenched by addition of 300 µL 1.0 M HCl, 1.0 mL acetonitrile, and 60 µL cinnamyl alcohol in DMSO (1.00 M, added as am internal standard). The resulting homogeneous solution was diluted 30-fold in acetonitrile, passed through a 0.2 µm syringe filter, and analyzed on an Agilent 1100 HPLC equipped with a Discovery C18, 5 µm, 150 x 4.6 mm column (Supelco). The mobile phase (acetonitrile and water) contained 0.5% (v/v) acetic acid and the flow rate was 1.0 mL min^{-1}. Injections of 10 µL were separated using a gradient method of 30-80% ACN over 8 minutes followed by a 4-min hold at 80% ACN before column re-equilibration. Peak areas were monitored at 255 nm at the following retention times: Piperonyl alcohol (3.8 minutes), cinnamyl alcohol internal standard (5.5 minutes), and piperonyl hexanoate (10.7 minutes).

Transaminase Conversion Surfactant Screen



5 6

Entry	Surfactant	Conversion (%)
21	none	96
22	TPGS-750-M	100
23	PTS	98
24	SPGS-550-M (Nok)	93
25	Triton X	100
26	Brij L23	100
27	Kolliphor EL	92
28	SDS	82
29	CTAB	72

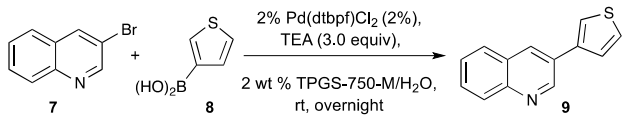
Stock solutions of surfactant (5 wt% in H_2O, 200 µL), phosphate buffer (0.50 M, pH = 7.5, 90 µL), ω-Transaminase from aspergillus fumigatus (4 units/mL, 50 µL), and pyruvate/PLP/phosphate (0.5 M pyruvate, 1.14 mM PLP, 0.50 M phosphate, pH = 7.5, 110 µL) were combined in a 1.5 mL microcentrifuge tube. (*R*)-(+)-1-Phenylethylamine (0.047 mmol, 6 µL) and water (44 µL) were added, the tube was briefly vortexed, and the reactions incubated at room temperature for 12 hours. The reaction tube was vortexed and a 50 µL aliquot of reaction mixture was combined with 47 µL cinnamyl alcohol in DMSO (100 mM, added as internal standard) and 903 µL acetonitrile. This solution was mixed thoroughly and diluted 4.7-fold in acetonitrile, passed through a 0.2 µm syringe filter, and analyzed on an Agilent 1100 HPLC equipped with a Discovery C18, 5 µm, 150 x 4.6 mm column (Supelco). Injections of 10 µL were separated using a gradient method (acetonitrile and water) of 30-70% ACN over 8 minutes followed by a 1-min hold at 80% ACN before column re-equilibration (1.0 mL min^{-1} flow rate). Peak areas were monitored at 255 nm at the following retention times: Cinnamyl alcohol internal standard (6.06 minutes), and acetophenone (6.53 minutes).

IV. Effect of Enzyme Additive on Transition Metal-Catalyzed Reaction Conversion

Data from experiments in this section are reported as the average of duplicate experiments. For each experiment in this section, a stock solution of each enzyme additive in 2% TPGS-750-M was prepared by adding enzyme to a 5 mL glass vial containing a magnetic stir bar, capping with a rubber septum, and flushing with argon. Under positive argon pressure, 2.5 mL of degassed 2 wt % TPGS-750-M was added by syringe, and the contents of the vial were stirred for several minutes until dissolved.

Enzyme	Amount of Enzyme used to make 2.5 mL stock solution	Amount of Enzyme added to each coupling reaction
Pig Liver Esterase	5 mg (90 Units)	2 mg (36 Units)
Horse Liver Alcohol Dehydrogenase	5 mg (1.5 Units)	2 mg (0.6 Units)
CALB Lipase	15 µL (75 Units)	6 µL (30 Units)

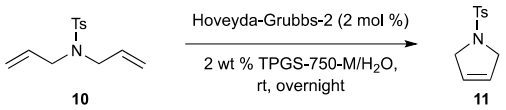
Suzuki Reaction Conversion with Added Enzyme



Entry	Additive	Conversion (%)
1	none	96
2	PLE	95
3	CALB Lipase	96
4	HLAD	95

A 5 mL glass vial containing a magnetic stir bar was charged with 3-thienylboronic acid (64 mg, 0.50 mmol) and Pd(dtbfp)Cl_2 (3.3 mg, 0.005 mmol). The vial was capped with a rubber septum and flushed with argon. Under positive argon pressure, 2 wt % TPGS-750-M/H_2O solution containing the enzyme additive (1.0 mL), 3-bromoquinoline (34 µL, 0.25 mmol), and triethylamine (105 µL, 0.75 mmol) were added by syringe, and the reaction mixture was stirred vigorously (600 pm) at room temperature for 18 hours. The reaction mixture was quenched by addition of 1.0 mL acetonitrile and 1.0 mL cinnamyl alcohol in acetonitrile (625 mM, added as an internal standard), and mixed thoroughly. A 9.6 µL aliquot of this mixture was diluted 150-fold in acetonitrile to 1000 µL, passed through a 0.2 µm syringe filter, and analyzed on an Agilent 1100 HPLC equipped with a Discovery C18, 5 µm, 150 x 4.6 mm column (Supelco). Injections of 10 µL were separated using a gradient method (acetonitrile and water) of 40-80% ACN over 11 minutes followed by a 1-min hold at 80% ACN before column re-equilibration (1.0 mL min^{-1} flow rate). Peak areas were monitored at 255 nm at the following retention times: 3-thienylboronic acid (2.74 minutes), cinnamyl alcohol internal standard (4.50 minutes), 3-bromoquinoline (7.82 minutes), and product **9** (8.44 minutes).

Ring-Closing Metathesis Conversion with Added Enzyme

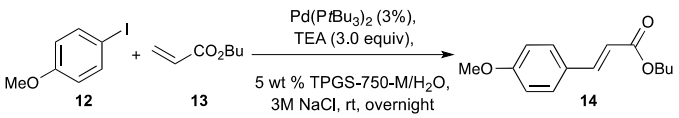


10 11

Entry	Additive	Conversion (%)
5	none	98
6	PLE	98
7	CALB Lipase	99
8	HLAD	95

A 5 mL glass vial containing a magnetic stir bar was charged with N,N-diallyl-4-methylbenzenesulfonamide (**10**, 25 mg, 0.10 mmol) and Hoveyda-Grubbs 2nd Generation catalyst (1.2 mg, 0.002 mmol). The vial was capped with a rubber septum and flushed with argon. Under positive argon pressure 2 wt % TPGS-750-M/H_2O solution containing the enzyme additive (1.0 mL) was added by syringe, and the reaction mixture was stirred vigorously (600 rpm) at room temperature for 18 hours. The reaction mixture was quenched by addition of 1.0 mL piperonyl alcohol in acetonitrile (150 mM, added as an internal standard), and mixed thoroughly. A 67 µL aliquot of this mixture was diluted 150-fold in acetonitrile to 1000 µL, passed through a 0.2 µm syringe filter, and analyzed on an Agilent 1100 HPLC equipped with a Discovery C18, 5 µm, 150 x 4.6 mm column (Supelco). Injections of 10 µL were separated using a gradient method (acetonitrile and water) of 30-80% ACN over 8 minutes followed by a 3-min hold at 80% ACN before column re-equilibration to 30% ACN (1.0 mL min^{-1} flow rate). Peak areas were monitored at 235 nm at the following retention times: Piperonyl alcohol internal standard (3.05 minutes), product **11** (6.57 minutes), and N,N-diallyl-4-methylbenzenesulfonamide **10** (9.00 minutes).

Heck Reaction Conversion with Added Enzyme



12 13 14

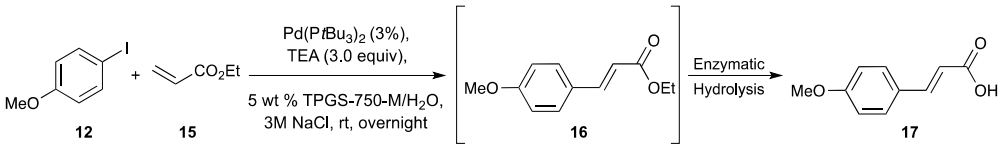
Entry	Additive	Conversion (%)
9	none	99
10	PLE	98
11	CALB Lipase	99
12	HLAD	74

A 5 mL glass vial containing a magnetic stir bar was charged with 4-iodoanisole (58.5 mg, 0.25 mmol), sodium chloride (88 mg, 1.5 mmol) and Pd(tBu$_3$)$_2$ (4.0 mg, 0.008 mmol). The vial was capped with a rubber septum and flushed with argon. Under positive argon pressure, 2 wt % TPGS-750-M/H_2O solution containing the enzyme additive (0.5 mL), butyl acrylate (72 µL, 1.0 mmol), and triethylamine (105 µL, 0.75 mmol) were added by syringe, and the reaction mixture was stirred vigorously (600 rpm) at room temperature for 18 hours. The reaction mixture was quenched by addition of 0.5 mL brine and 1.0 mL methyl toluate in ethyl acetate (625 mM, added as an internal standard), and stirred for 5 minutes. The biphasic mixture was transferred to a 15 mL conical tube and centrifuged for 2 minutes to clear any emulsions (3400 RPM, 1300 x g). A 6.5 µL aliquot of the organic layer was diluted 155-fold in acetonitrile to 1000 µL, passed through a 0.2 µm syringe filter, and analyzed on an Agilent 1100 HPLC equipped with a Discovery C18, 5 µm, 150 x 4.6 mm column (Supelco). Injections of 10 µL were separated using a gradient method (acetonitrile and water) of 40-80% ACN over 8 minutes followed by a 4-min hold at 80% ACN before column re-equilibration (1.0 mL min^{-1} flow rate). Peak areas were monitored at 255 nm at the following retention times: methyl toluate internal standard (7.6 minutes), 4-iodoanisole (9.5 minutes), and (*E*)-butyl 4-methoxycinnamate **14** (11.1 minutes).

V. One-Pot Chemoenzymatic Reaction Conversion

Data from experiments in this section are reported as the average of duplicate experiments.

Heck/Lipase Optimization

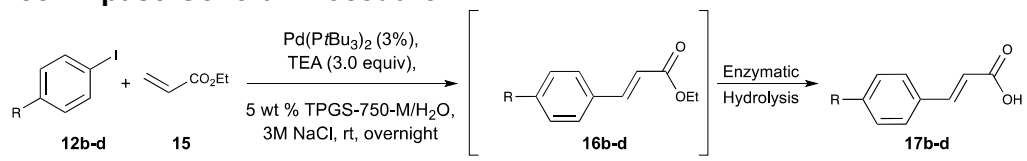


A 5 mL glass vial containing a magnetic stir bar was charged with 4-iodoanisole (58.5 mg, 0.25 mmol), sodium chloride (88 mg, 1.5 mmol) and Pd(tBu$_3$)$_2$ (4.0 mg, 0.008 mmol). The vial was capped with a rubber septum and flushed with argon. Under positive argon pressure, 2 wt % TPGS-750-M/H_2O (0.5 mL), ethyl acrylate (55 µL, 0.5 mmol), and triethylamine (105 µL, 0.75 mmol) were added by syringe, and the reaction mixture was stirred vigorously (600 rpm) at room temperature for 18 hours. At this point enzyme was added in one of the following ways:

Entry	Enzyme addition method:
1	180 units of pig liver esterase (10 mg) was added to the reaction mixture
2	The reaction mixture was neutralized by addition of 40 µL 1.0 M HCl, then 180 units of pig liver esterase (10 mg) and 25 mg $NaHCO_3$ were added.
3	75 units of CALB lipase (15 µL) was added to the reaction mixture
4	The reaction mixture was neutralized by addition of 40 µL 1.0 M HCl, then 75 units of CALB lipase (15 µL) and 25 mg $NaHCO_3$ were added
5	0.5 mL H_2O was added to the reaction mixture, followed by 75 units of CALB lipase (15 µL)
6	1.0 mL H_2O was added to the reaction mixture, followed by 75 units of CALB lipase (15 µL)

After addition of enzyme, the vial was capped with a rubber stopper under air and stirred vigorously (600 rpm) for 24 hours. The reaction mixture was quenched by addition of 0.5 mL brine, 0.5 mL 1M HCl, 1.0 mL methyl toluate in ethyl acetate (625 mM, added as an internal standard), and 4.0 mL ethyl acetate, then stirred for 5 minutes. The biphasic mixture was transferred to a 15 mL conical tube and centrifuged for 2 minutes to clear any emulsions (3400 RPM, 1300 x g). A 16 µL aliquot of the organic layer was diluted 63-fold in acetonitrile to 1000 µL, passed through a 0.2 µm syringe filter, and analyzed on an Agilent 1100 HPLC equipped with a Discovery C18, 5 µm, 150 x 4.6 mm column (Supelco). The mobile phase (acetonitrile and water) contained 0.5% (v/v) acetic acid and the flow rate was 1.0 mL min^{-1}. Injections of 10 µL were separated using a gradient method of 30-80% ACN over 8 minutes followed by a 4-min hold at 80% ACN before column re-equilibration. Peak areas were monitored at 255 nm at the following retention times: (*E*)-4-methoxycinnamic acid product (4.4 minutes), methyl toluate internal standard (7.6 minutes), 4-iodoanisole (9.5 minutes), and (*E*)-ethyl 4-methoxycinnamate **14** (8.6 minutes).

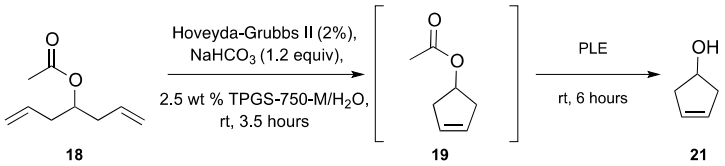
Heck/Lipase General Procedure



A 5 mL glass vial containing a magnetic stir bar was charged with aryl iodide (0.25 mmol), sodium chloride (88 mg, 1.5 mmol) and Pd(*t*Bu$_3$)$_2$ (4.0 mg, 0.008 mmol). The vial was capped with a rubber septum and flushed with argon. Under positive argon pressure, 2 wt % TPGS-750-M/H_2O (0.5 mL), ethyl acrylate (55 µL, 0.5 mmol), and triethylamine (105 µL, 0.75 mmol) were added by syringe, and the reaction mixture was stirred vigorously (600 rpm) at room temperature for 18 hours. Water (0.5 mL) and then 75 units of CALB lipase (15 µL) were added to the reaction mixture, the vial was capped with a rubber stopper under air and stirred vigorously (600 rpm) for 24 hours. The reaction mixture was quenched by addition of 0.5 mL brine, 0.5 mL 1M HCl, 1.0 mL methyl toluate in ethyl acetate (625 mM, added as an internal standard), and 4.0 mL ethyl acetate, then stirred for 5 minutes. The biphasic mixture was transferred to a 15 mL conical tube and centrifuged for 2 minutes to clear any emulsions (3400 RPM, 1300 x g). A 16 µL aliquot of the organic layer was diluted 63-fold in acetonitrile to 1000 µL, passed through a 0.2 µm syringe filter, and analyzed on an Agilent 1100 HPLC equipped with a Discovery C18, 5 µm, 150 x 4.6 mm column (Supelco). The mobile phase (acetonitrile and water) contained 0.5% (v/v) acetic acid and the flow rate was 1.0 mL min^{-1}. Injections of 10 µL were separated using a gradient method of 30-80% ACN over 8 minutes followed by a 4-min hold at 80% ACN before column re-equilibration. Peak areas were monitored at 255 nm at the following retention times:

R = H	Cinnamic Acid (**17b**)	Internal Standard (methyl toluate)	Iodobenzene (**12b**)
Retention Time	4.4 minutes	7.6 minutes	9.5 minutes
R = CH_3	4-Methylcinnamic Acid (**17c**)	Internal Standard (methyl toluate)	4-Iodotoluene (**12c**)
Retention Time	5.5 minutes	7.6 minutes	11.0 minutes
R = F	4-Fluorocinnamic Acid (**17d**)	Internal Standard (methyl toluate)	4-Fluoroiodobenzene (**12d**)
Retention Time	4.7 minutes	7.6 minutes	9.4 minutes

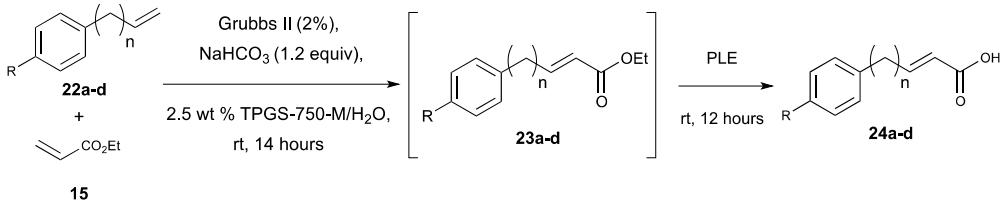
Ring-Closing Metathesis/Esterase Conversion



A 5 mL glass vial containing a magnetic stir bar was charged with 1,6-heptadienyl acetate, (**12**, 32 mg, 0.21 mmol), $NaHCO_3$ (21 mg, 0.25 mmol) and Hoveyda-Grubbs 2nd Generation catalyst

(2.5 mg, 0.004 mmol). The vial was capped with a rubber septum and flushed with argon. Under positive argon pressure 2.5 wt % TPGS-750-M/H_2O (1.3 mL) was added by syringe, and the reaction mixture was stirred vigorously (600 rpm) at room temperature for 3.5 hours. Pig liver esterase (8.0 mg, 144 units) was added and the reaction mixture was stirred under air for an additional 6 hours. The reaction mixture was quenched by addition of 5.0 mL methanol and 24.3 µL acetophenone (added as an internal standard), then stirred for 5 minutes. A 200 µL aliquot of this mixture was diluted with 800 µL ethyl ether, passed through a 0.2 µm syringe filter, and analyzed on Shimadzu GC-2014 Gas Chromatograph with a Supelco SPB-1 Capillary column (15m x 0.32mm x 1.0 µm film thickness). The inlet temperature was 240 °C, the detector temperature was 280 °C, and the column temperature was held at 70 °C. Peak areas were integrated at the following retention times: 3-Cyclopentenol (1.1 minutes), 1,6-heptadien-4-ol (1.9 minutes), 3-cyclopentenyl acetate (3.1 minutes), 1,6-heptadienyl acetate (5.2 minutes), and acetophenone internal standard (7.7 minutes).

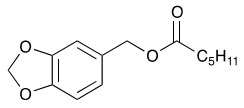
Cross Metathesis/Esterase General Procedure



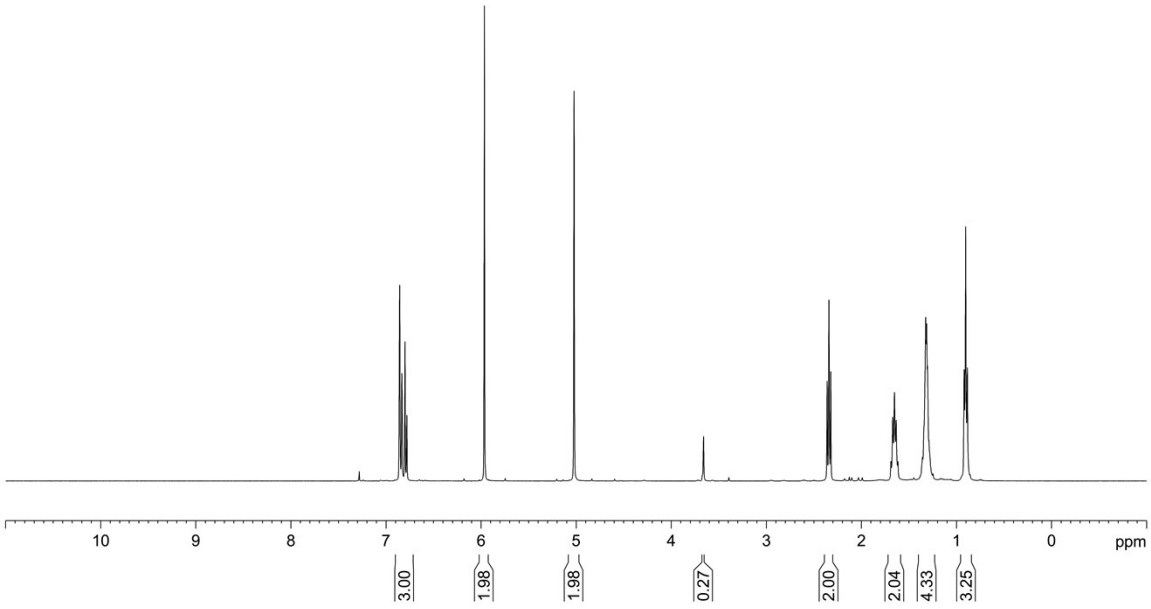
A 5 mL glass vial containing a magnetic stir bar was charged with $NaHCO_3$ (25 mg, 0.30 mmol) and Grubbs 2nd Generation catalyst (4.2 mg, 0.005 mmol). The vial was capped with a rubber septum and flushed with argon. Under positive argon pressure 2.5 wt % TPGS-750-M/H_2O (0.5 mL), aryl alkene (**22a-d**, 0.25 mmol), and ethyl acrylate (58 µL, 0.50 mmol) were added by syringe, and the reaction mixture was stirred vigorously (600 rpm) at room temperature for 20 hours. Pig liver esterase (6 mg, 108 units) was added and the reaction mixture was stirred under air for an additional 24 hours. The reaction mixture was quenched by addition of 0.5 mL brine, 1.0 mL 1M HCl, and 1.0 mL methyl toluate in ethyl acetate (20 mM, added as an internal standard), and 4.0 mL ethyl acetate, then stirred for 5 minutes. The biphasic mixture was transferred to a 15 mL conical tube and centrifuged for 2 minutes to clear any emulsions (3400 RPM, 1300 x g). A 40 µL aliquot of the organic layer was diluted 25-fold in acetonitrile to 1000 µL, passed through a 0.2 µm syringe filter, and analyzed on an Agilent 1100 HPLC equipped with a Discovery C18, 5 µm, 150 x 4.6 mm column (Supelco). The mobile phase (acetonitrile and water) contained 0.5% (v/v) acetic acid and the flow rate was 1.0 mL min^{-1}. Injections of 10 µL were separated using a gradient method of 30-80% ACN over 8 minutes followed by a 4-min hold at 80% ACN before column re-equilibration. Peak areas were monitored at 255 nm at the following retention times:

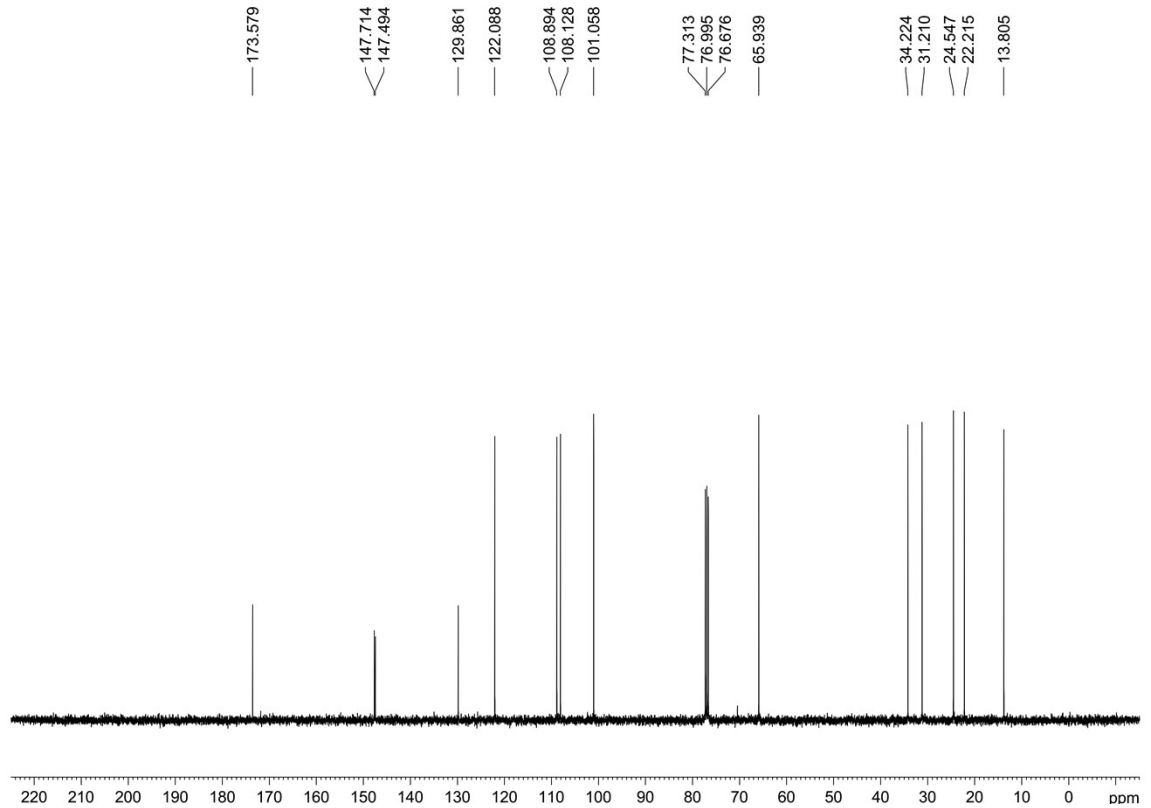
R = H, n = 1	(*E*)-4-phenyl-2-butenoic acid (**24a**)	(*E*)-Ethyl 4-phenyl-2-butenoate (**23a**)	Internal Standard (methyl toluate)
Retention Time	5.0 minutes	9.0 minutes	7.5 minutes
R = OCH_3, n = 1	(E)-4-(4-Methoxyphenyl)but-2-enoic acid (**24b**)	(E)-Ethyl 4-(4-Methoxyphenyl)but-2-enoate (**23b**)	Internal Standard (methyl toluate)
Retention Time	4.8 minutes	8.7 minutes	7.5 minutes
R = F n = 1	(E)-4-(4-Fluorophenyl)but-2-enoic acid (**24c**)	(E)-Ethyl 4-(4-Fluorophenyl)but-2-enoic acid (**23c**)	Internal Standard (methyl toluate)
Retention Time	5.2 minutes	9.0 minutes	7.5 minutes
R = H n = 2	(E)-4-phenylbut-2-enoic acid (**24d**)	(E)-Ethyl 4-phenylbut-2-enoic acid (**24d**)	Internal Standard (methyl toluate)
Retention Time	5.8 minutes	9.9 minutes	7.5 minutes

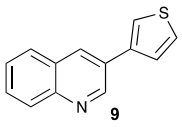
VI. NMR spectra


O
O
O
O
C_5H_{11}

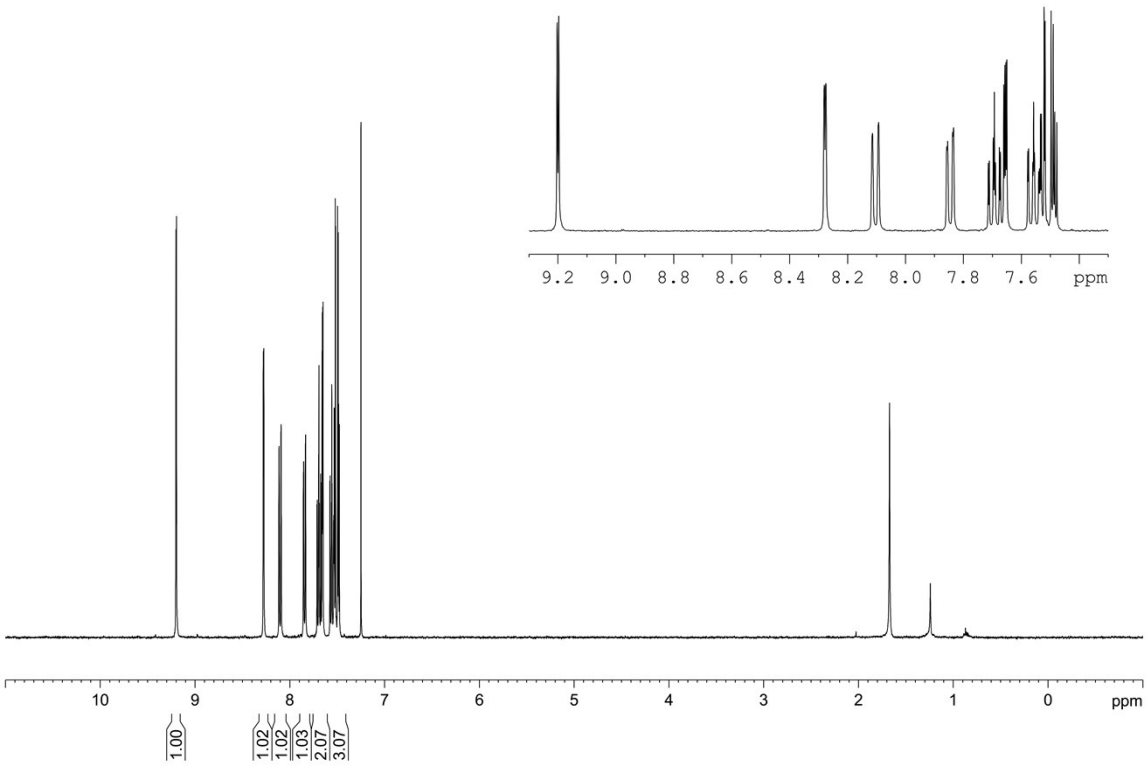
3

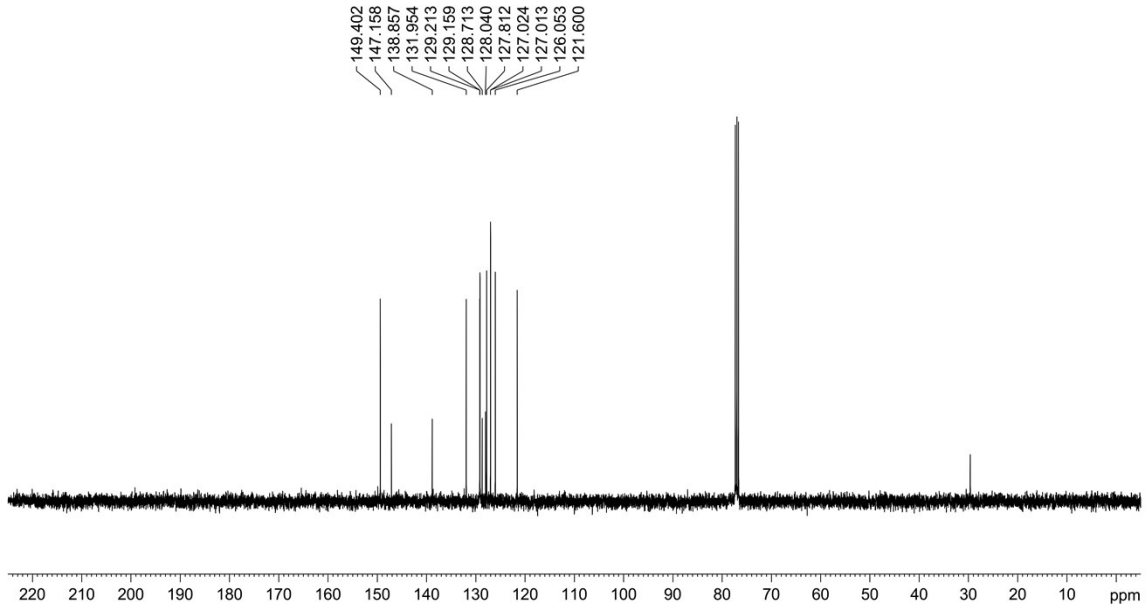

10
9
8
7
6
5
4
3
2
1
0
ppm
3.00
1.98
1.98
0.27
2.00
2.04
4.33
3.25

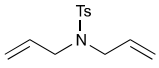

173.579
147.714
147.494
129.861
122.088
108.894
108.128
101.058
77.313
76.995
76.676
65.939
34.224
31.210
24.547
22.215
13.805
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


S
N

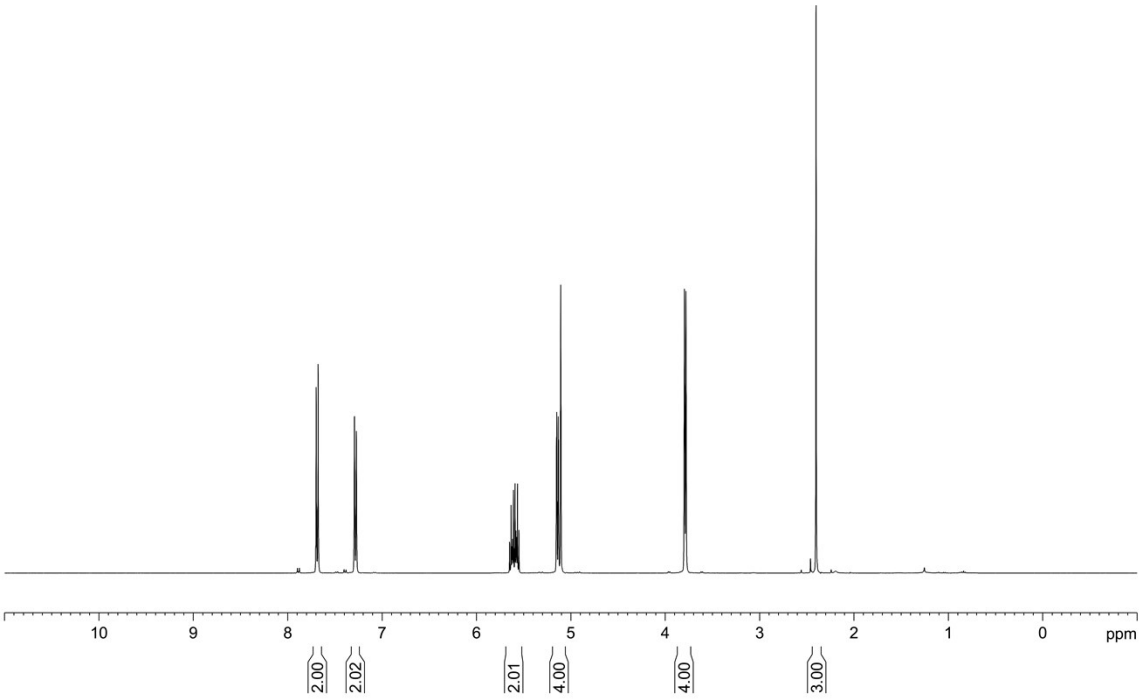
9

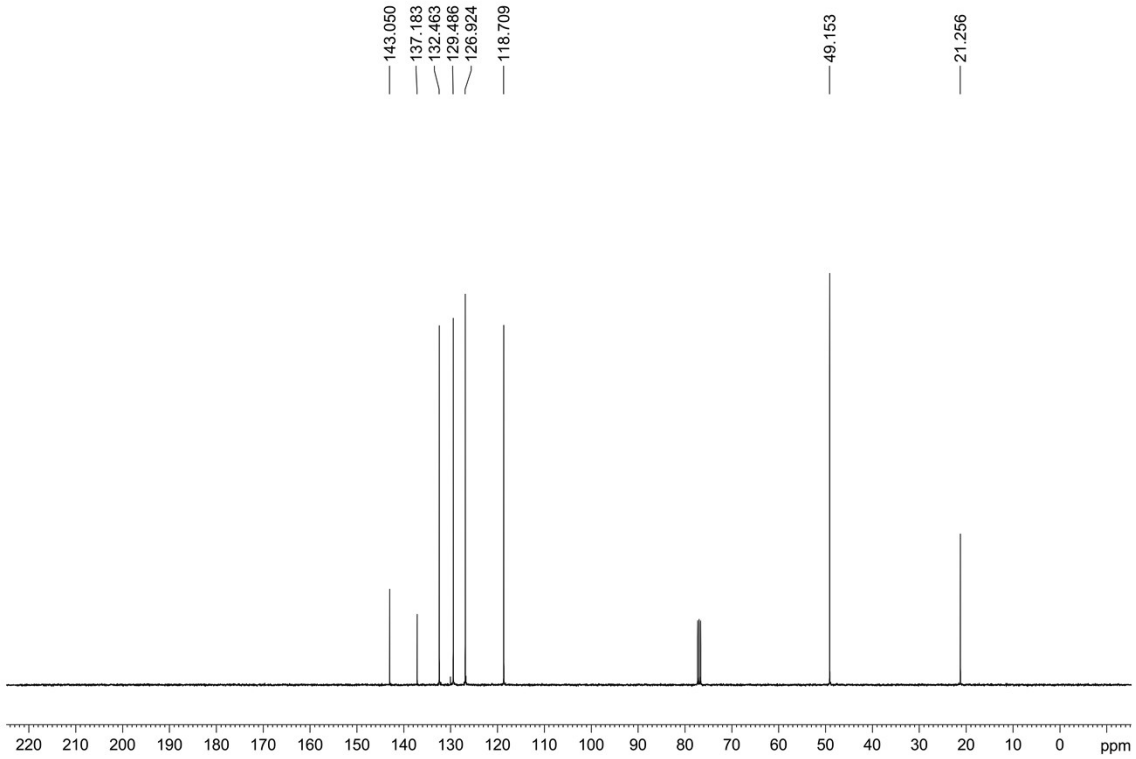

9.2 9.0 8.8 8.6 8.4 8.2 8.0 7.8 7.6 ppm
10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
1.02
1.02
1.03
2.07
3.07


149.402
147.158
138.857
131.954
129.213
129.159
128.713
128.040
127.812
127.024
127.013
126.053
121.600
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


Ts
N

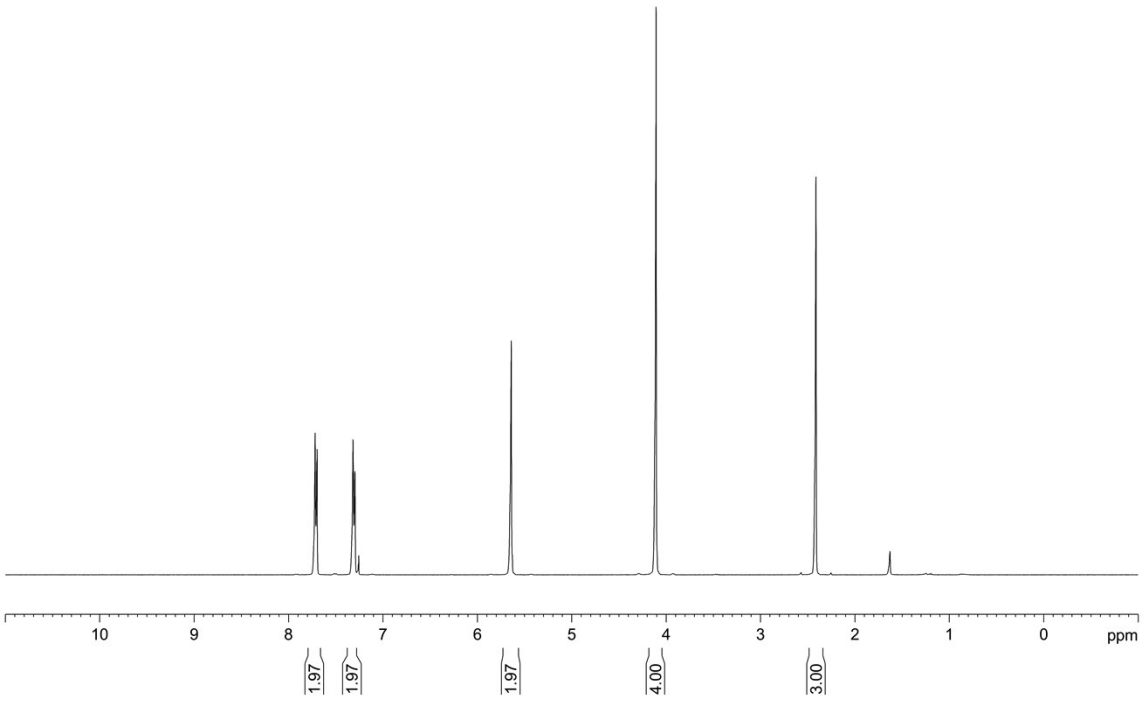
10

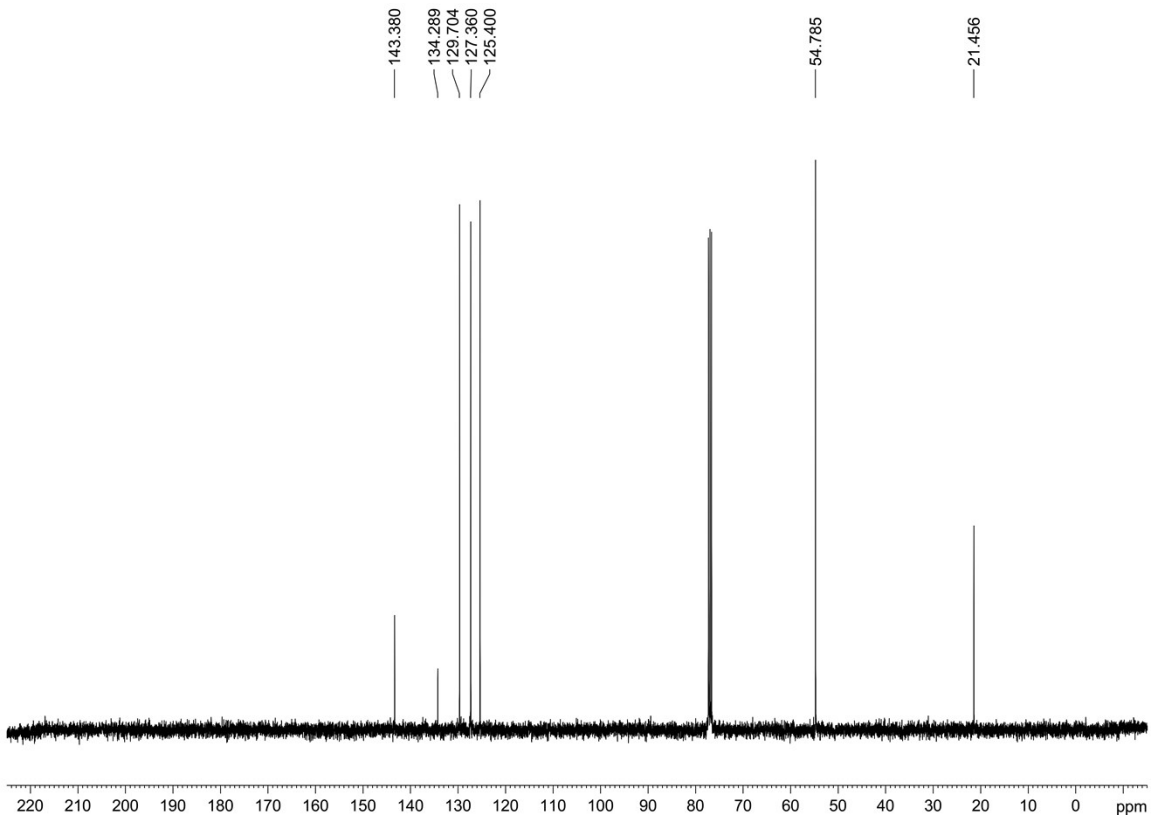

10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.02
2.01
4.00
4.00
3.00

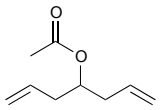

143.050
137.183
132.463
129.486
126.924
118.709
49.153
21.256
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


Ts
N

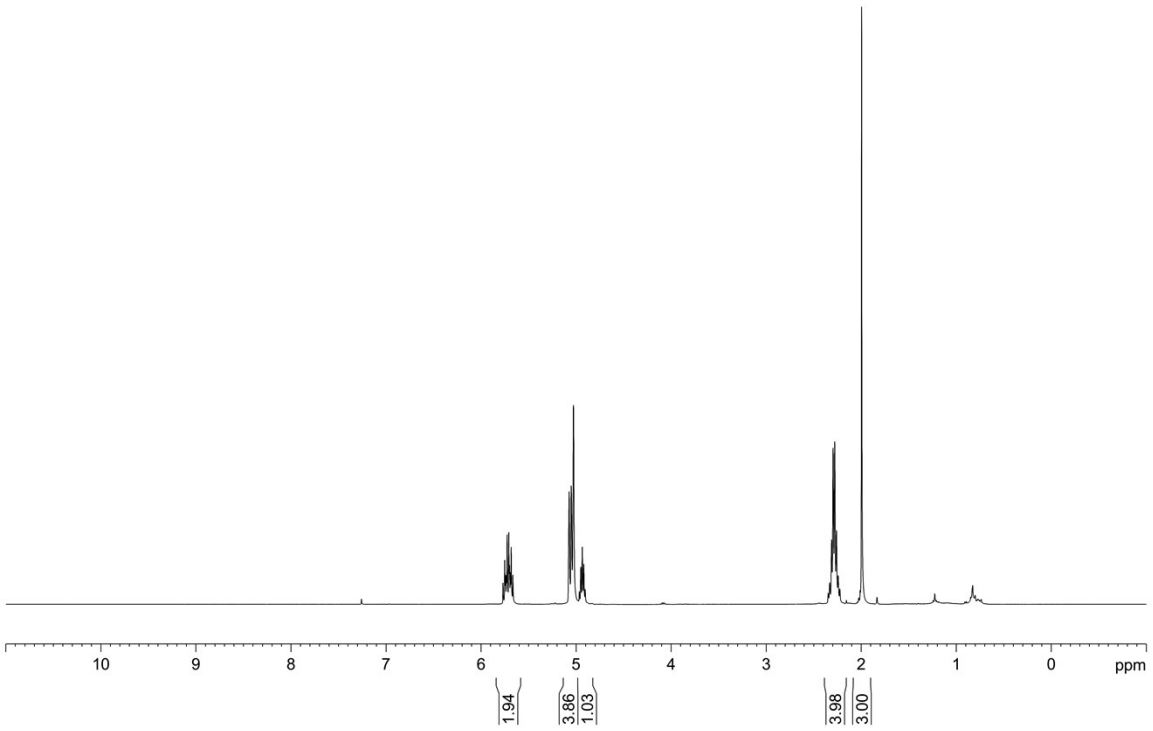
11

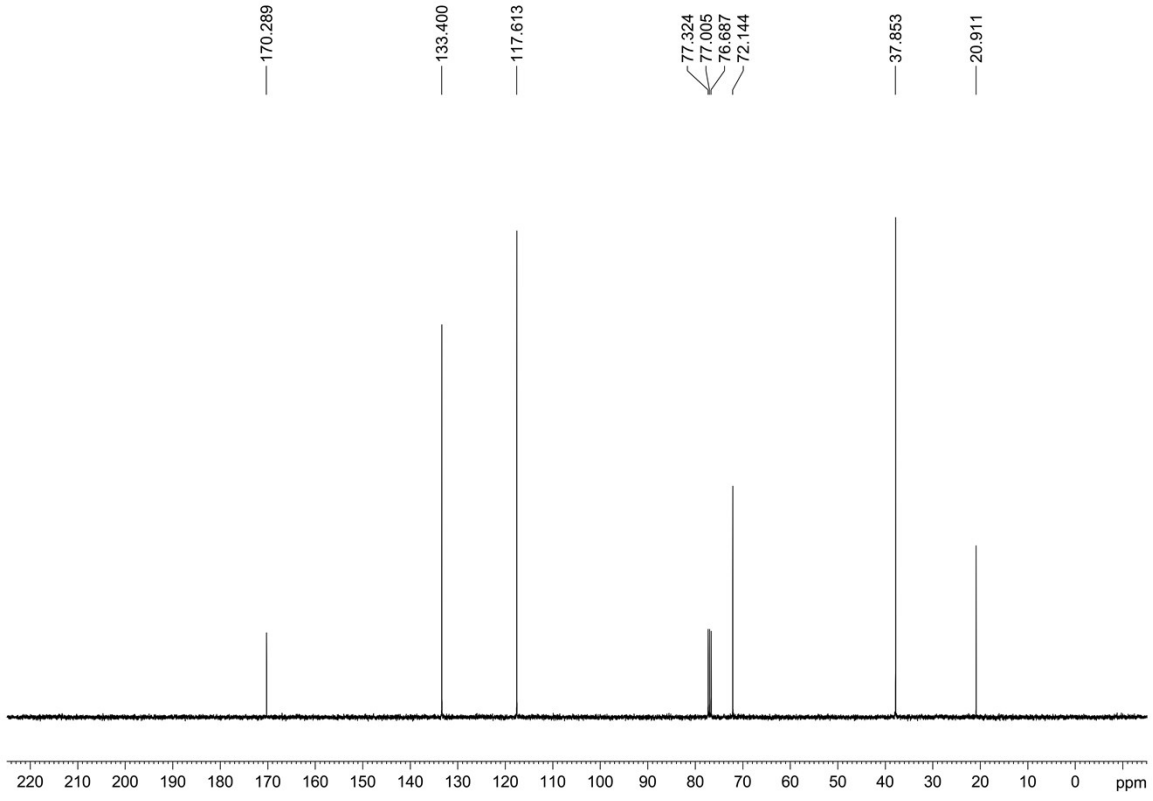

10
9
8
7
6
5
4
3
2
1
0
ppm
1.97
1.97
1.97
4.00
3.00

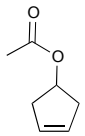

143.380
134.289
129.704
127.360
125.400
54.785
21.456
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



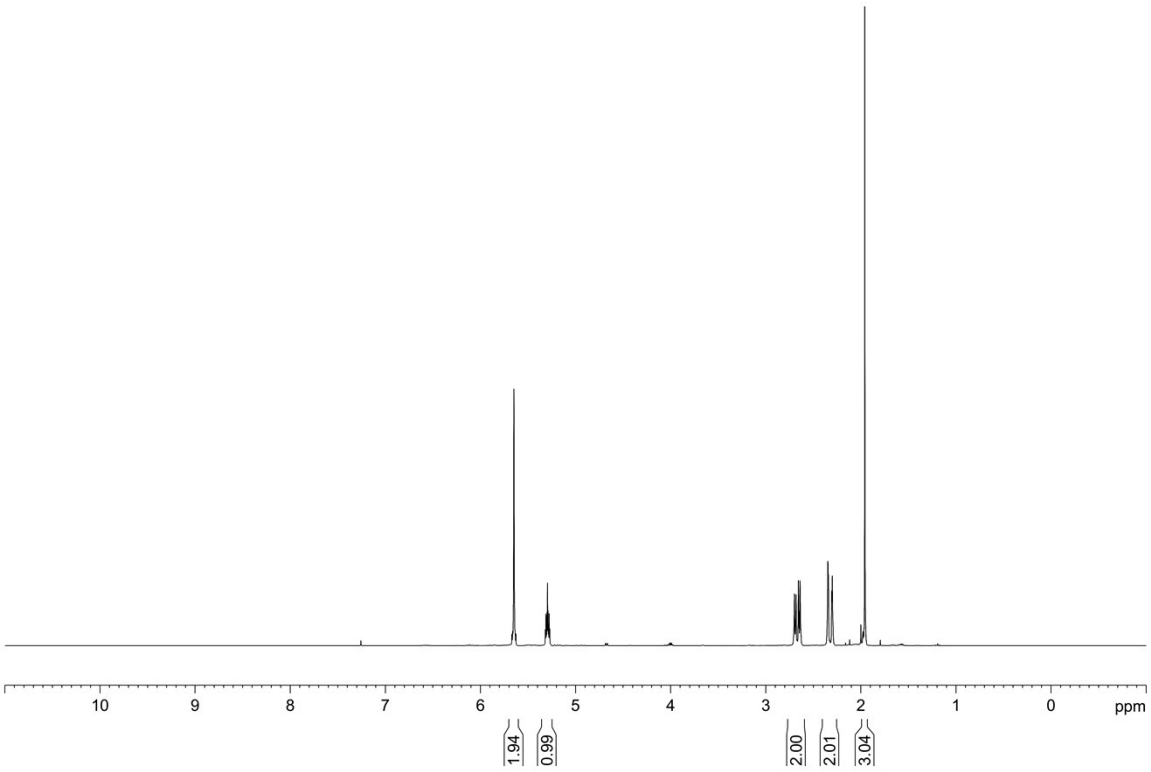
18

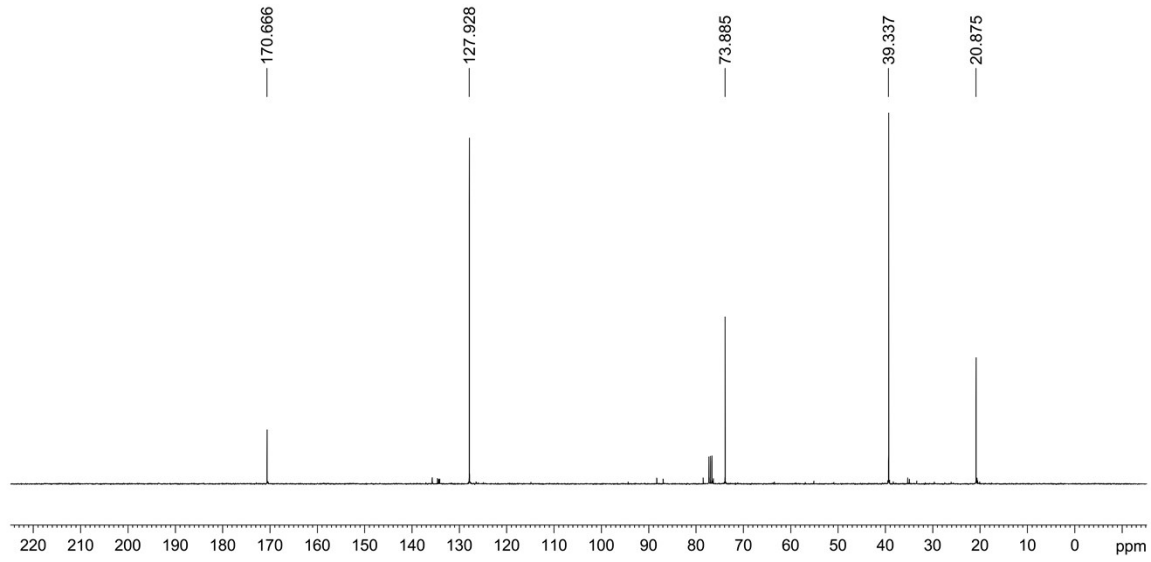

10
9
8
7
6
5
4
3
2
1
0
ppm
1.94
3.86
1.03
3.98
3.00

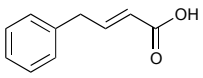

170.289
133.400
117.613
77.324
77.005
76.687
72.144
37.853
20.911
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



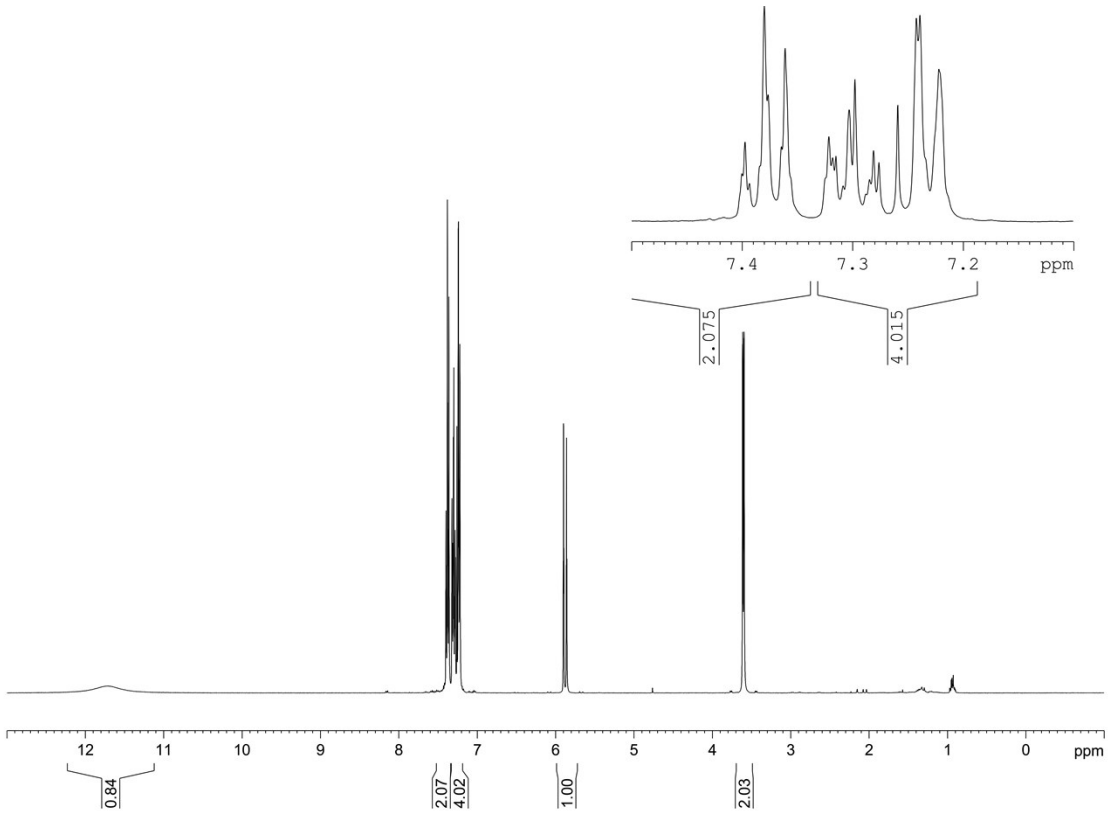
19

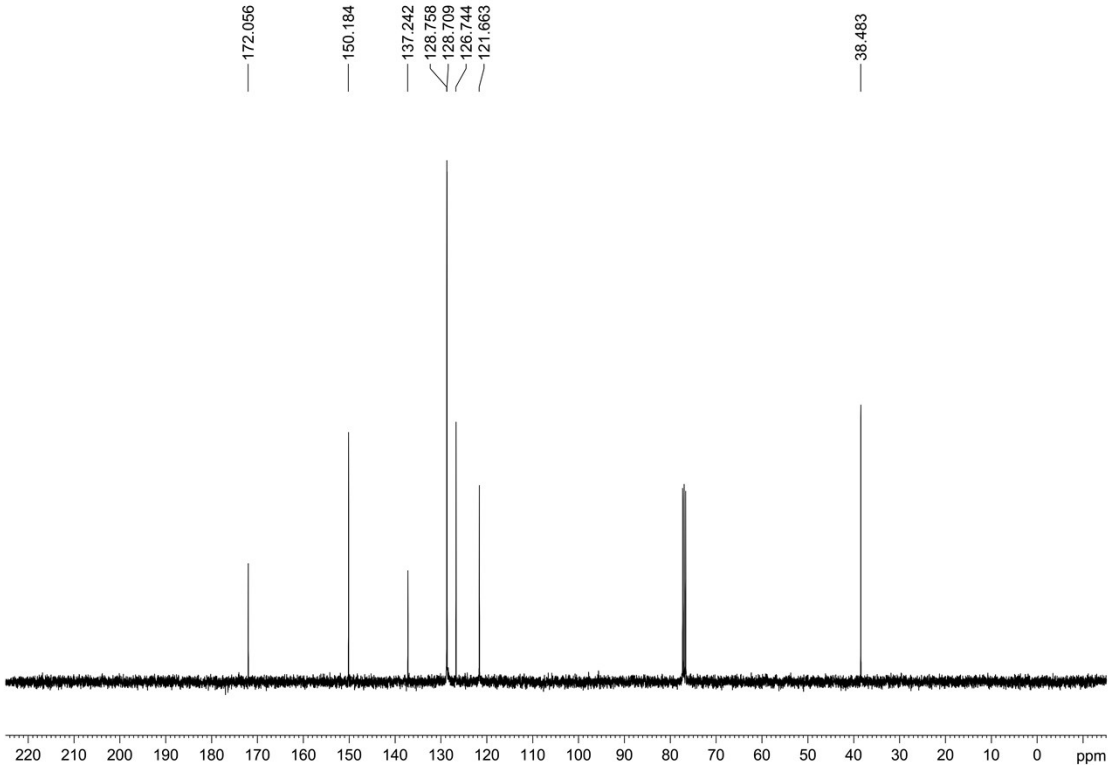

10
9
8
7
6
5
4
3
2
1
0
ppm
1.94
0.99
2.00
2.01
3.04

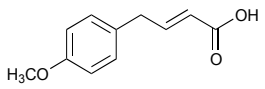

170.666
127.928
73.885
39.337
20.875
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


OH
O

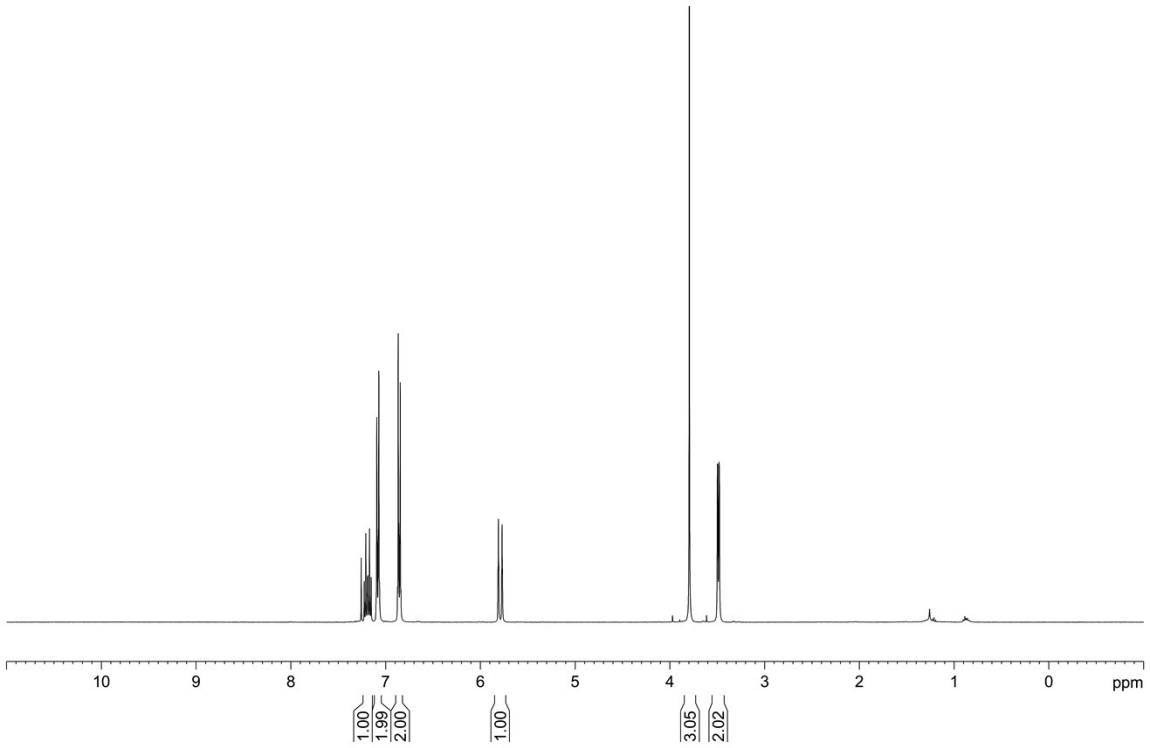
24

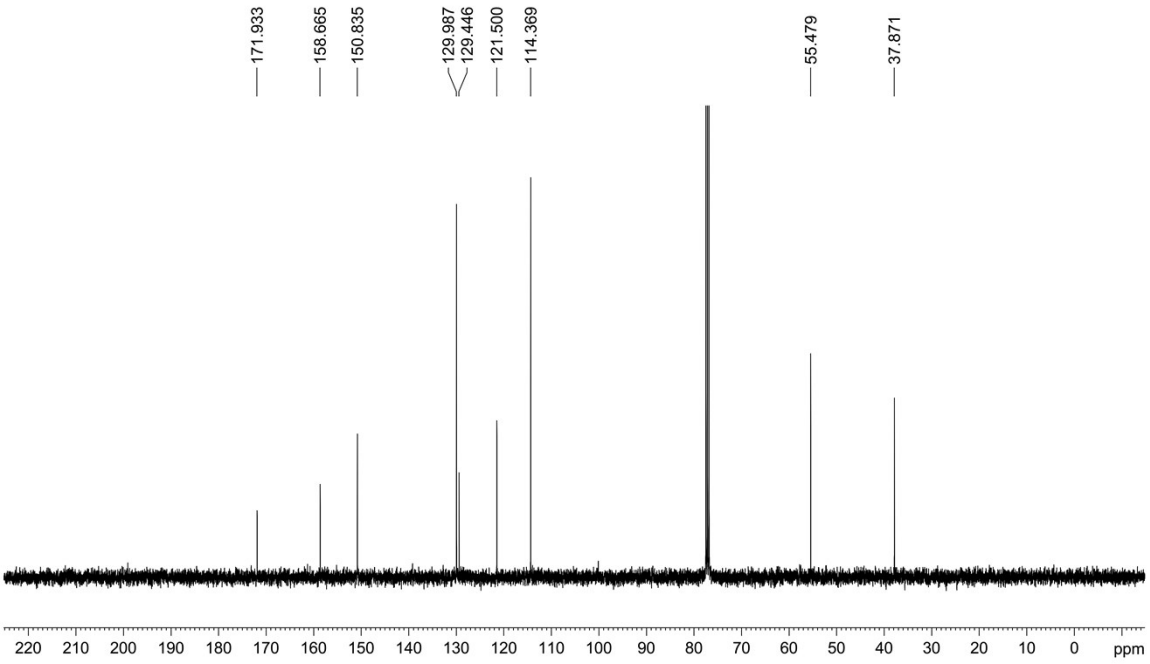

7.4
7.3
7.2
ppm
2.075
4.015
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.84
2.07
4.02
1.00
2.03

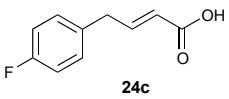

172.056
150.184
137.242
128.758
128.709
126.744
121.663
38.483
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


OH
O
H3CO

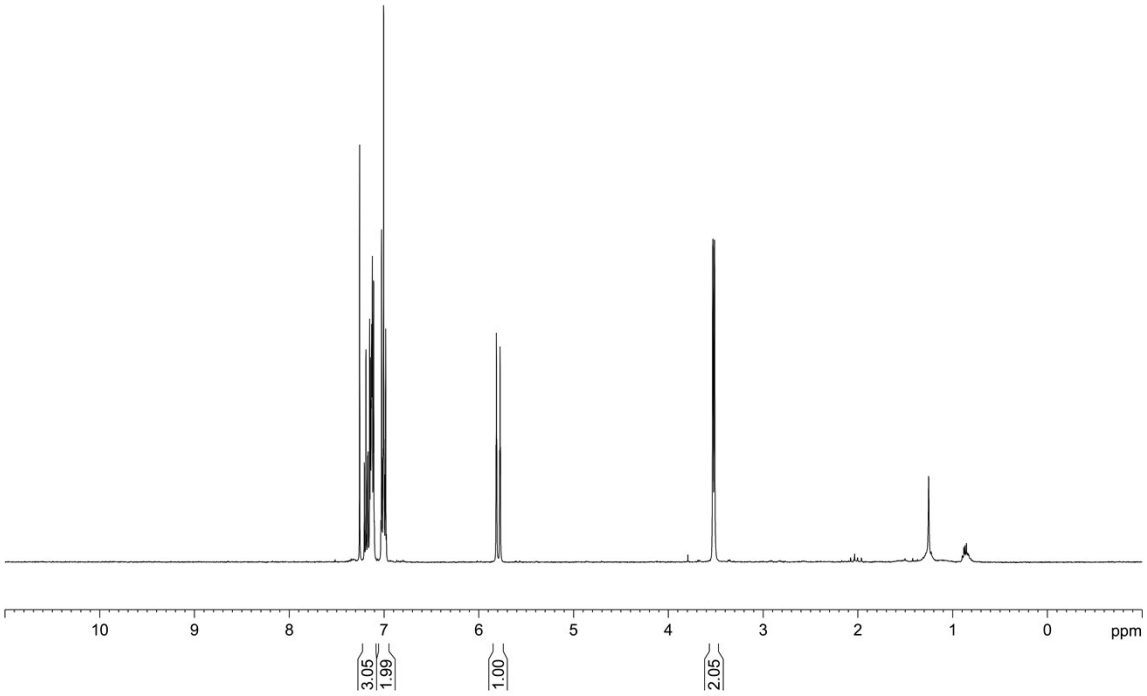
24b

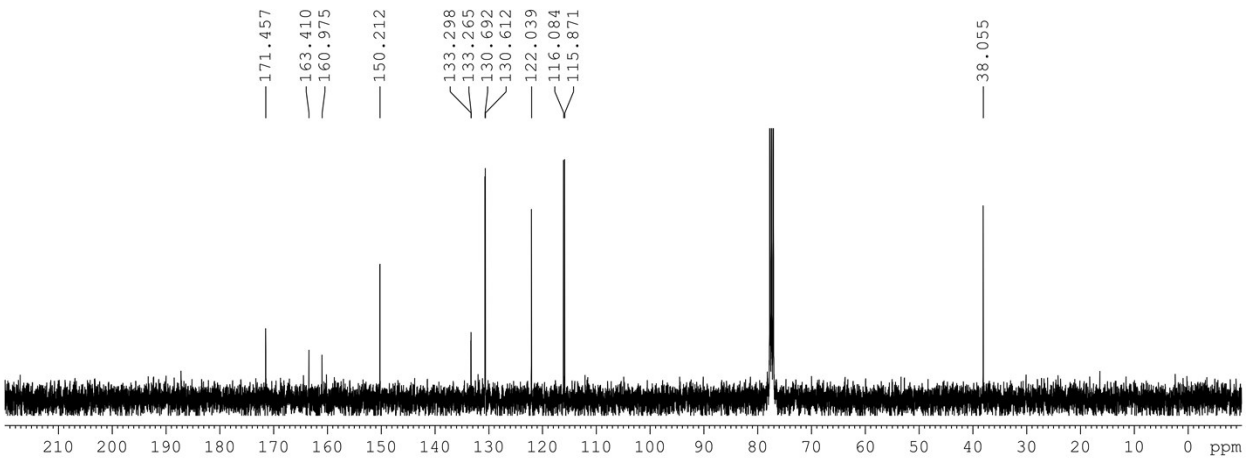

10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.99
2.00
1.00
3.05
2.02

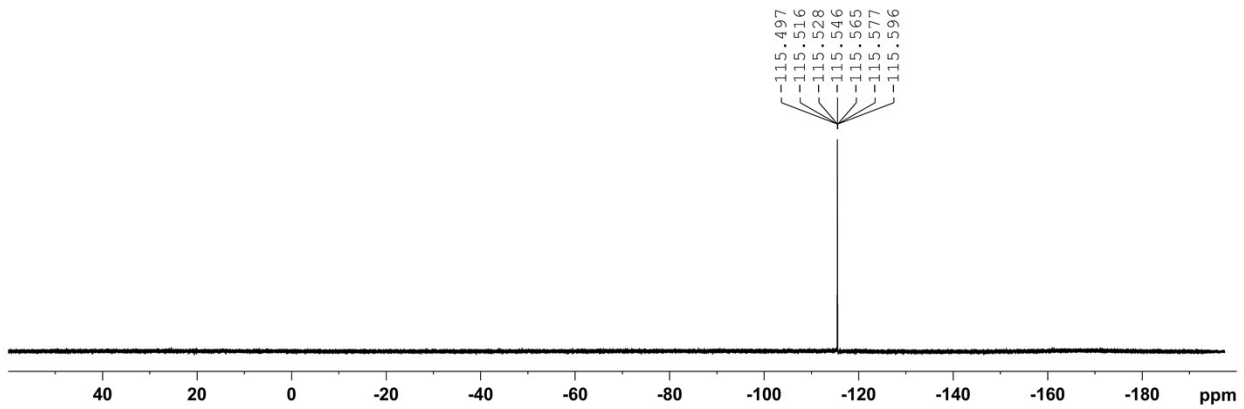

171.933
158.665
150.835
129.987
129.446
121.500
114.369
55.479
37.871
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

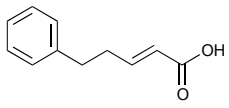

OH
O
F

24c

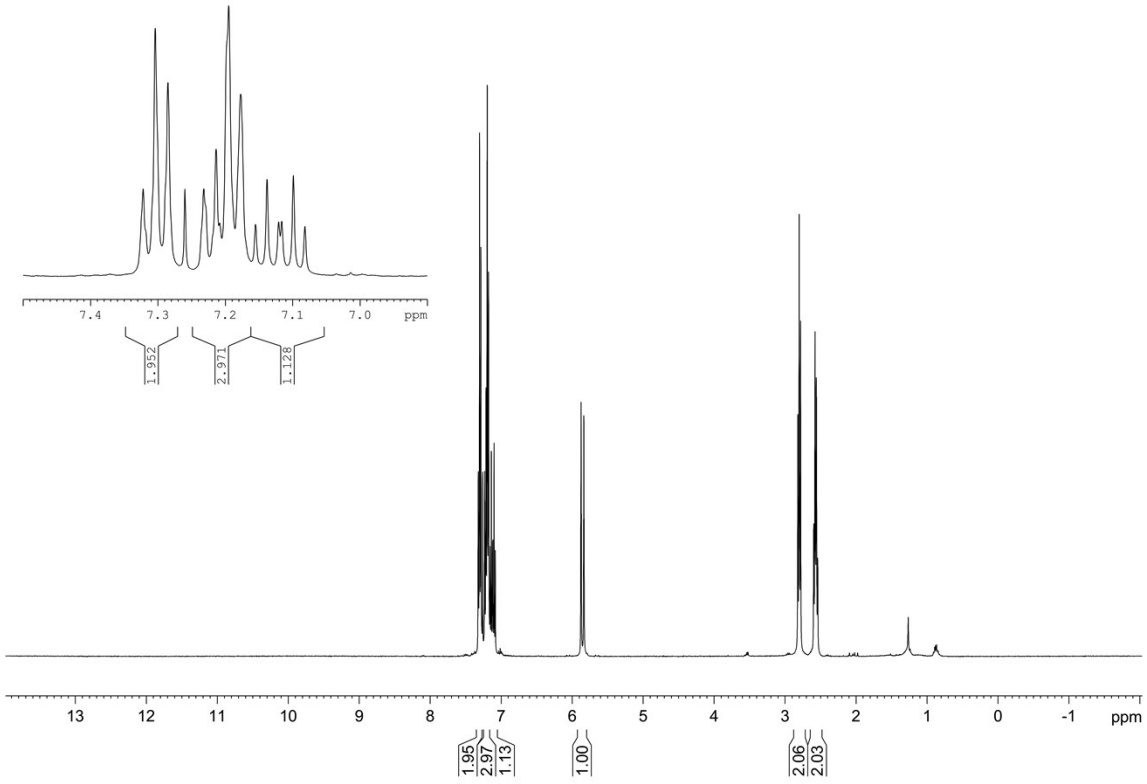

10
9
8
7
6
5
4
3
2
1
0
ppm
3.05
1.99
1.00
2.05

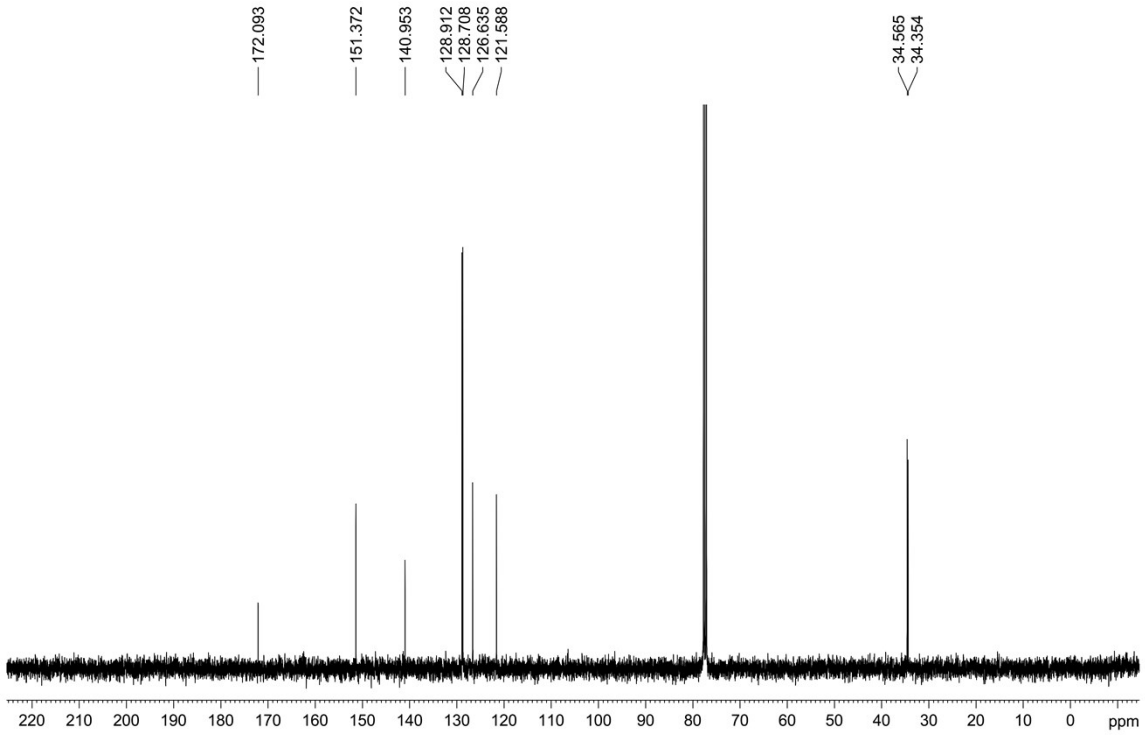

171.457
163.410
160.975
150.212
133.298
133.265
130.692
130.612
122.039
116.084
115.871
38.055
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


-115.497
-115.516
-115.528
-115.546
-115.565
-115.577
-115.596
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm


OH
O

24d


7.4
7.3
7.2
7.1
7.0
ppm
1.952
2.971
1.128
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.95
2.97
1.13
1.00
2.06
2.03


172.093
151.372
140.953
128.912
128.708
126.635
121.588
34.565
34.354
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

VII. Supplementary References

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