Supporting Information for

Access to α,β-Unsaturated Carboxylic Acids through Water-Soluble Palladium Catalyzed Hydroxycarbonylation of Alkynes Using Water as the Solvent

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CONTENTS

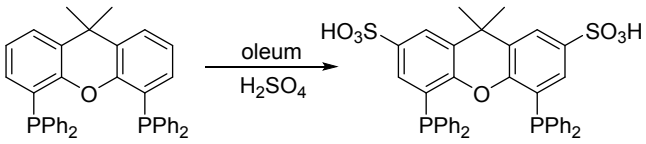
1. General methods

Unless otherwise noted, all manipulations involving air- or moisture-sensitive compounds were performed in a nitrogen-filled glovebox or using standard Schlenk techniques. Solvents were dried according to standard procedures. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker Avance 500 spectrometer or a Varian Mercury 400 MHz spectrometer. Chemical shifts (δ values) were reported in ppm with internal TMS (^{1}H NMR), $CDCl_3$ (^{13}C NMR), or external 85% H_3PO_4 (^{31}P NMR), respectively. The FT-IR spectra were measured on a Thermo (SCIENTIFC) NICOLET iS10 spectrometer. HRMS (ESI) were determined on Waters Micromass GCT Premier spectrometer with a quadrupole time-of-flight mass spectrometer. ICP-OES was determined on Aglient 5110.

2. Synthesis of ligands

Ligand **L1** was purchased from Sigma Aldrich. Ligand **L3** was purchased from Laajoo. Ligand **L2**[1] were prepared by following the reported literature procedure.

Synthesis of ligand **L2**

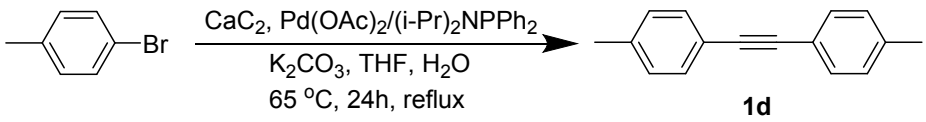


A solution of 9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene (0.35g, 0.6 mmol) in drydichloromethane (2 mL) was cooled to 0 °C. Concentrated sulfuric acid (0.51 mL) was slowly added to the mixture, and the resulting mixture was stirred for 10 minutes. After the dichloromethane was removed by evaporation under vacuum, oleum (0.51 mL) was added to the solution at 0 °C. Subsequently the mixture was warmed to room temperature and stirred for 24 h. After cooling the reaction mixture to 0 °C, degassed ice/water (4 mL) was added slowly to the solution, which resulted in a white precipitate. After stirring, the white precipitate dissolves, then Et_2O (5 mL)

and EtOH (5 mL) were added to the mixture. Three days later, white crystals appeared. After filtration, the white solid Ligands **L2** was obtained in 75% yield (332 mg)**;** ^{1}H NMR (D_2O, 500 MHz): δ 8.00 (s, 2H), 7.00-6.87 (m, 22H), 1.58 (s, 6H) ppm. ^{31}P NMR (D_2O, 202 MHz): -16.2 ppm.

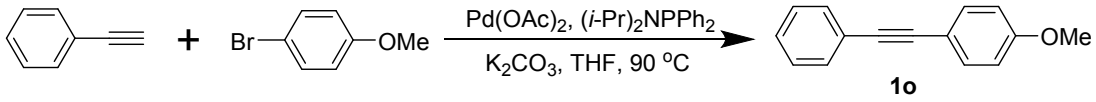
3. General procedure for synthesis of substrates.

Substrates 1a, 1h, 1i, 1j, 1k, 1l and 1r were purchased from commercial suppliers.



Synthesis of 1,2-di-*p*-tolylethyne (1d). Compound **1d** was obtained by following the reported literature procedure. [2] Calcium carbide (0.62 g, 9.7 mmol), *p*-bromotoluene (0.83 g, 4.85 mmol), (i-Pr)$_2$NPPh$_2$ (103.5 mg, 0.36 mmol), Pd(OAc)$_2$ (25 mg, 0.1 mmol) and K_2CO_3 (1.34 g, 9.7 mmol) were added into undried THF (15.0 mL) under N_2 atmosphere in Schlenk flask. The reaction mixture was stirred at 65 °C oil bath for 12 h. The reaction was cooled down to room temperature. The mixture of reaction was purified by flash column chromatography on silica gel using petroleum ether as an eluent. The white solid substrate **1d** was evaporated under reduced pressure and obtained in 69% yield (348.6 mg).

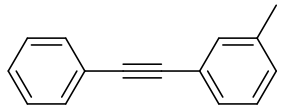
Substrates 1b, 1c, 1e, 1f and 1g were prepared by the same procedure according to **1d**.



Synthesis of Substrates 1-methoxy-4-(phenylethynyl)benzene (1o). Compound **1o** was obtained by following the reported literature procedure. [3] Ethynylbenzene (490 mg, 4.8 mmol), 1-bromo-4-methoxybenzene (900 mg, 4.8 mmol), (i-Pr)$_2$NPPh$_2$ (205 mg, 0.72 mmol), Pd(OAc)$_2$ (55 mg, 0.24 mmol) and K_2CO_3 (1.33 g, 9.6 mmol) were dissolved in undried THF (20.0 mL) under N_2 atmosphere in Schlenk flask. The mixture was heated to 90 °C (oil bath). After 12 h of stirring, the mixture of reaction

was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (10:1, v/v) as an eluent. After removing the solvent by vacuum, the white solid **1o** was obtained in 90% yield (899 mg).

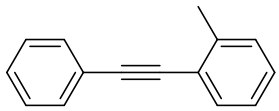
Substrates 1m, 1n, 1p and 1q were prepared by the same procedure according to **1o**.



1-Methyl-3-(2-phenylethynyl)benzene (1m) [4]

Following general procedure of **1o**, **1m** (825.6 mg, 4.3 mmol) was obtained as colorless liquid in 89% yield by column chromatography on silica gel (petroleum ether as an eluent).

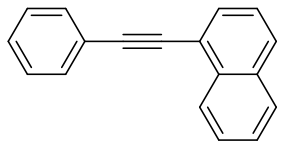
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.53-7.50 (m, 2H), 7.35-7.28 (m, 5H), 7.22-7.19 (m, 1H), 7.12-7.10 (m, 1H), 2.32 (s, 3H) ppm.



1-Methyl-2-(phenylethynyl)benzene (1n) [4]

Following general procedure of **1o**, **1n** (705.0 mg, 3.67 mmol) was obtained as colorless liquid in 76.5% yield by column chromatography on silica gel (petroleum ether as an eluent).

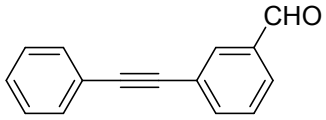
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.52-7.47 (m, 3H), 7.29-7.27 (m, 3H), 7.18-7.17 (m, 2H), 7.12-7.09 (m, 1H), 2.49 (s, 3H) ppm.



1-(Phenylethynyl)naphthalene (1p) [4]

Following general procedure of **1o**, **1p** (912.8 mg, 4.00 mmol) was obtained as white solid in 83.3% yield by column chromatography on silica gel (petroleum ether as an eluent).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.50-8.48 (d, J = 10 Hz, 1H), 7.90-7.86 (m, 2H), 7.81-7.79 (m, 1H), 7.70-7.67 (m, 2H), 7.65-7.61 (m, 1H), 7.58-7.54 (m, 1H), 7.51-7.47 (m, 1H), 7.45-7.39 (m, 3H) ppm.



3-(2-Phenylethyl)benzaldehyde (1q) [5]

Following general procedure of **1o**, **1q** (655.3 mg, 3.18 mmol) was obtained as white solid in 66.2% yield by column chromatography on silica gel (petroleum ether/ethyl acetate = 5: 1).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.00 (s, 1H), 8.01 (s, 1H), 7.83-7.81 (d, *J* = 8 Hz, 1H), 7.76-7.75 (d, *J* = 8 Hz, 1H), 7.55-7.48 (m, 3H), 7.36-7.35 (m, 3H) ppm.

4. General procedure for the hydroxycarbonylation of alkynes.

A glass vial with a magnetic stirring bar was charged with ligand **L2** (0.02 mmol) and $Pd(OAc)_2$ (0.01 mmol) in H_2O (1 mL). After the mixture was stirred for 5 minutes, alkyne (0.5 mmol) was added. The glass vial was transferred to an autoclave. The autoclave was sealed up and purged with CO for three times and subsequently charged with CO (3 bar). The autoclave was then heated to 100 °C (oil bath) and was kept at this temperature for 24 h. The autoclave was cooled in ice water, and the gas was carefully released in a well-ventilated hood. The product was extracted with EtOAc. The collected organic layer was dried over anhydrous $MgSO_4$. After filtration and removing the solvent by vacuum, the residue was directly purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate.

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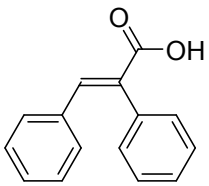
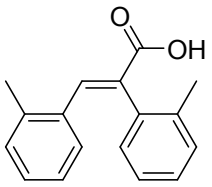


(*E*)-2,3-diphenylacrylaldehyde (2a)[6]

2a (110 mg, 0.49 mmol) was obtained as white solid in 99% yield by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1).

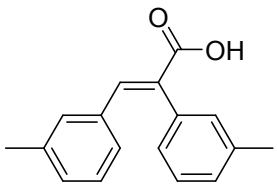
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.88 (s, 1H), 7.32-7.30 (m, 3H), 7.18-7.14 (m, 3H), 7.11-7.08 (m, 2H), 7.00-6.99 (m, 2H) ppm.



(*E*)-2,3-Di-*o*-tolylacrylic acid (2b) [6]

Following general procedure, **2b** (64.4 mg, 0.26 mmol) was obtained as white solid in 51% yield by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1).

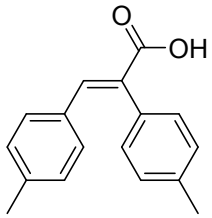
^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.20 (s, 1H), 7.24-7.18 (m, 2H), 7.16-7.08 (m, 3H), 7.05-7.03 (m, 1H), 6.82 (t, *J* = 10 Hz, 1H), 6.66 (d, *J* = 10 Hz, 1H), 2.44 (s, 3H), 2.14 (s, 3H) ppm.



(*E*)-2,3-di-*m*-tolylacrylic acid (2c) [6]

Following general procedure, **2c** (108.5 mg, 0.43 mmol) was obtained as white solid in 86% yield by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.86 (s, 1H), 7.24-7.22 (m, 1H), 7.16-7.13 (m, 1H), 7.04-6.96 (m, 4H), 6.89 (s, 1H), 6.81-3.79 (m, 1H), 2.31 (s, 3H), 2.16 (s, 3H) ppm.

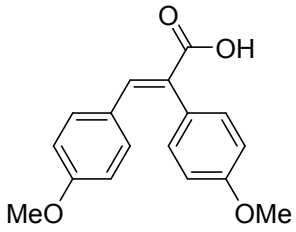


(*E*)-2,3-di-*p*-tolylacrylic acid(2d) [6]

Following general procedure, **2d** (123.5 mg, 0.49 mmol) was obtained as white solid in 98% yield by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.81 (s, 1H), 7.11-7.09 (m, 2H), 7.06-7.03 (m, 2H),

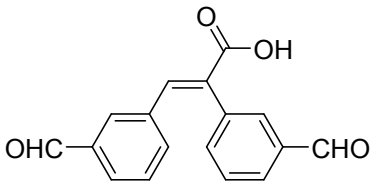
6.90 (s, 4H), 2.31 (s, 3H), 2.20 (s, 3H) ppm.



(*E*)-2,3-bis(4-methoxyphenyl)acrylic acid (2e) [6]

Following general procedure, **2e** (122.2 mg, 0.43 mmol) was obtained as light yellow solid in 86% yield by column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1).

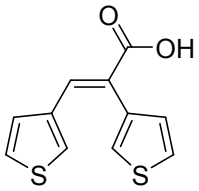
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.87 (s, 1H), 7.18 (d, *J* = 15 Hz, 2H), 7.06 (d, *J* = 10 Hz, 2H), 6.94 (d, *J* = 15 Hz, 2H), 6.71 (d, *J* = 10 Hz, 2H), 3.85 (s, 3H), 3.77 (s, 3H) ppm.



(*E*)-2,3-bis(3-formylphenyl)acrylic acid (2f)

Following general procedure, **2f** (116.2 mg, 0.41 mmol) was obtained as yellow solid in 83% yield by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1).

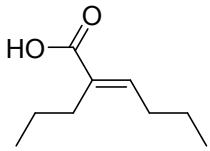
M.P. 144-145 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.00 (s, 1H), 9.81 (s, 1H), 8.08 (s, 1H), 7.94-7.91 (m, 1H), 7.79-7.75 (m, 2H), 7.60-7.56 (m, 2H), 7.53-7.51 (m, 1H), 7.37-7.33 (t, *J* = 9.5 Hz, 1H), 7.28 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ 191.7, 191.3, 171.6, 141.7, 136.9, 136.5, 135.9, 135.8, 135.7, 134.8, 132.1, 131.2, 131.1, 130.4, 129.7, 129.6, 129.2 ppm. FTIR (KBr): 3056, 2955, 2924, 2853, 1701, 1621, 1598, 1495, 1465, 1379, 1249, 1154, 1084, 941, 803, 706 cm^{-1}. HRMS (ESI) m/z: Calcd. For $C_{17}H_{12}O_4Na^+$: 303.0628 [M+Na^+], found: 303.0632.



(*E*)-2,3-di(thiophen-3-yl)acrylic acid (2g) [7]

Following general procedure, **2g** (107.7 mg, 0.46 mmol) was obtained as yellow solid in 91% yield by column chromatography on silica gel (petroleum ether/ethyl acetate = 6:1).

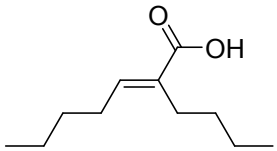
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.95 (s, 1H), 7.42-7.40 (m, 1H), 7.26-7.23 (m, 2H), 7.15-7.13 (m, 1H), 7.01 (dd, J_1 = 6 Hz, J_2 = 1.5 Hz, 1H), 6.60 (dd, J_1 = 6.5 Hz, J_2 = 1 Hz, 1H) ppm.



(*E*)-2-propylhex-2-enoic acid (2h) [8]

Following general procedure, **2h** (60.9 mg, 0.39 mmol) was obtained as colorless liquid in 78% yield by column chromatography on silica gel (*n*-pentane/ether = 6:1).

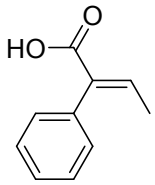
^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.90 (t, J = 10 Hz, 1H), 2.29-2.26 (m, 2H), 2.21-2.17 (m, 2H), 1.50-1.43 (m, 4H), 0.96-0.88 (m, 6H) ppm.



(*E*)-2-butylhept-2-enoic acid (2i) [9]

Following general procedure, **2i** (65.4 mg, 0.35 mmol) was obtained as colorless liquid in 71% yield by column chromatography on silica gel (*n*-pentane/ether = 6:1).

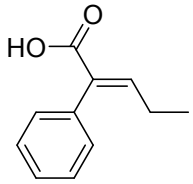
^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.89 (t, J = 9.5 Hz, 1H), 2.30-2.66 (t, J = 9.5 Hz, 2H), 2.23-2.18 (m, 2H), 1.45-1.32 (m, 8H), 0.96-0.89 (m, 6H) ppm.



(*E*)-2-phenylbut-2-enoic acid (2j) [8]

Following general procedure, **2j** (74.6 mg, 0.46 mmol) was obtained as white solid in 92% yield by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1).

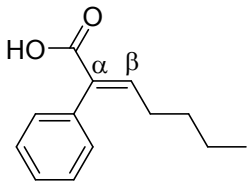
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.40-7.37 (m, 2H), 7.35-7.31 (m, 2H), 7.21-7.19 (m, 2H), 1.79 (d, J = 9 Hz, 3H) ppm.



(*E*)-2-phenylpent-2-enoic acid (2k) [8]

Following general procedure, **2k** (62.4 mg, 0.35 mmol) was obtained as white solid in 95% yield by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.38-7.28 (m, 3H), 7.20-7.16 (m, 3H), 2.13-2.09 (m, 2H), 1.01 (t, J = 10 Hz, 3H) ppm.



(*E*)-2-phenylhept-2-enoic acid (α-2l) [8]

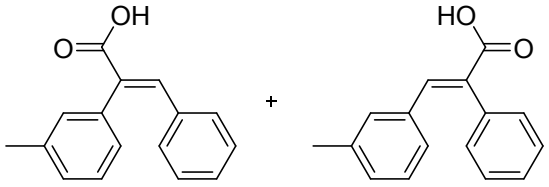
Following general procedure, **α-2l** (82.6 mg, 0.40 mmol) was obtained as white solid in 80.9% yield by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.39-7.31 (m, 3H), 7.25-7.17 (m, 3H), 2.14-2.08 (m, 2H), 1.44-1.37 (m, 2H), 1.32-1.24 (m, 2H), 0.83 (t, J = 10 Hz, 3H) ppm.

(*E*)-2-benzylidenehexanoic acid (β-2l) [8]

Following general procedure, **β-2l** (12.3 mg, 0.06 mmol) was obtained as white solid in 12.1% yield by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1).

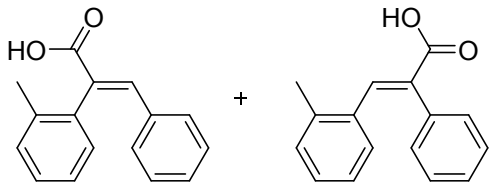
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.77 (s, 1H), 7.31-7.24 (m, 5H), 2.51 (t, *J* = 10 Hz, 2H), 1.59-1.51 (m, 2H), 1.35-1.32 (m, 2H), 0.91 (t, *J* = 10 Hz, 3H) ppm.



(*E*)-3-Phenyl-2-(*m*-tolyl)acrylic acid (α-2m) and **(*E*)-2-Phenyl-3-(*m*-tolyl)acrylic acid (β-2m)** [6]

Following general procedure, **α-2m** and **β-2m** (78.5 mg, 0.33 mmol) was obtained as white solid in 72% yield by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.92 (s, 1H), 7.38-7.35 (m, 1H), 7.26-7.20 (m, 2H), 7.18-7.14 (m, 2H), 7.09-7.06 (m, 2H), 7.04-7.02 (m, 1H), 6.89-6.83 (m, 1H), 2.33 (s, 2H), 2.17(s, 1H) ppm.

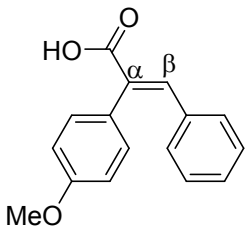


(*E*)-3-Phenyl-2-(*o*-tolyl)acrylic acid (α-2n) and **(*E*)-2-Phenyl-3-(*o*-tolyl)acrylic acid (β-2n)** [6]

Following general procedure, **α-2n** and **β-2n** (66.5 mg, 0.28 mmol) was obtained as white solid in 61% yield by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.14-7.98 (m, 1H), 7.32-7.23 (m, 4H), 7.20-7.14 (m, 2H), 7.11-7.08 (m, 1H), 7.03-7.01 (d, *J* = 9.5 Hz, 1H), 6.86-6.73 (m, 1H), 3.38-2.16

(m, 3H) ppm.



(*E*)-2-(4-Methoxyphenyl)-3-phenylacrylic acid (α-2o) [6]

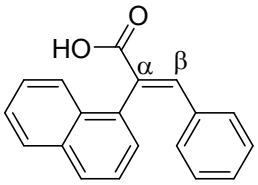
Following general procedure, **α-2o** (70.3 mg, 0.28 mmol) was obtained as white solid in 55.3% yield by column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.84 (s, 1H), 7.43-7.33 (m, 1H), 7.20-7.16 (m, 2H), 7.11-7.10 (m, 2H), 7.05-7.03 (m, 2H), 6.84 (d, *J* = 11 Hz, 2H), 3.77 (s, 3H) ppm.

(*E*)-3-(4-Methoxyphenyl)-2-phenylacrylic acid (β-2o) [6]

Following general procedure, **β-2o** (35.1 mg, 0.14 mmol) was obtained as white solid in 27.7% yield by column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.83 (s, 1H), 7.31 (s, 1H), 7.15-7.13 (m, 2H), 7.09-7.08 (m, 2H), 6.94 (d, *J* = 11 Hz, 2H), 6.62 (d, *J* = 11 Hz, 2H), 3.68 (s, 3H) ppm.



(*E*)-2-(naphthalen-2-yl)-3-phenylacrylic acid (α-2p)[10]

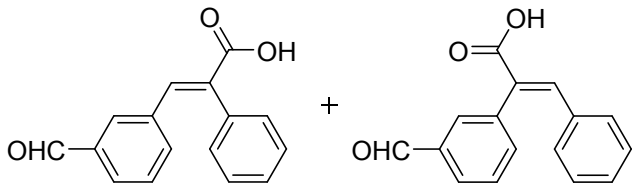
Following general procedure of **2a**, **α-2p** (79.2 mg, 0.29 mmol) was obtained as white solid in 58% yield by column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.20 (s, 1H), 7.89 (d, *J* = 10.5 Hz, 2H), 7.79 (d, *J* = 10.5 Hz, 1H), 7.49-7.45 (m, 2H), 7.32 (d, *J* = 10 Hz, 1H), 7.16-7.13 (m, 2H), 7.04 (t, *J* = 9.5 Hz, 2H), 6.95-6.93 (m, 2H) ppm.

(*E*)-3-(naphthalen-2-yl)-2-phenylacrylic acid (β-2p)[11]

Following general procedure, **β-2p** (20.8 mg, 0.08 mmol) was obtained as white solid in 15% yield by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1).

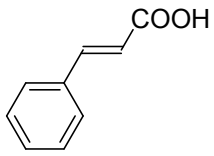
^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.61 (s, 1H), 8.11-8.09 (d, J = 10 Hz, 1H), 7.83 (d, J = 10.5 Hz, 1H), 7.71 (d, J = 10.5 Hz, 1H), 7.58-7.51 (m, 2H), 7.43-7.40 (m, 4H), 7.22-7.20 (m, 2H), 6.99 (d, J = 10 Hz, 1H) ppm.



(*E*)-2-(3-formylphenyl)-3-phenylacrylic acid (α-2q) and **(*E*)-3-(3-formylphenyl)-2-phenylacrylic acid (β-2q)**.

Following general procedure, **α-2q** and **β-2q** (80.7 mg, 0.32 mmol) was obtained as white solid in 63.7% yield by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.99-9.78 (m, 1H), 8.04-7.99 (m, 1H), 7.91-7.74 (m, 1H), 7.57-7.50 (m, 1H), 7.41-7.37 (m, 2H), 7.33-7.23 (m, 3H), 7.20-7.16 (m, 1H), 7.06-7.04 (m, 1H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ 191.9, 191.6, 172.3, 172.2, 143.6, 140.6, 136.8, 136.4, 136.3, 136.1, 135.4, 134.6, 133.8, 133.6, 132.5, 131.8, 130.7, 130.2, 129.9, 129.6, 129.4, 129.0, 128.9, 128.5 ppm. FTIR (KBr): 3432, 3056, 2925, 2852, 1698, 1671, 1620, 1598, 1577, 1421, 1289, 1269, 1157, 1139, 806, 684 cm^{-1}. HRMS (ESI) m/z: Calcd. For $C_{16}H_{11}O_3Na^+$: 274.0600 [M-H+Na$^+$], found: 274.0604.



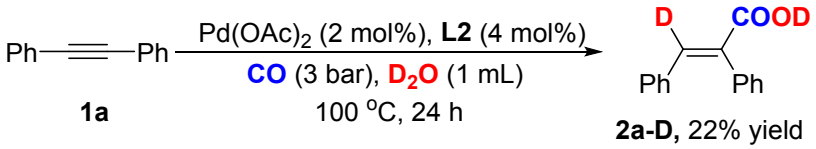
Cinnamic acid (2r)

Following general procedure, **2r** (37.2 mg, 0.25 mmol) was obtained as white solid in

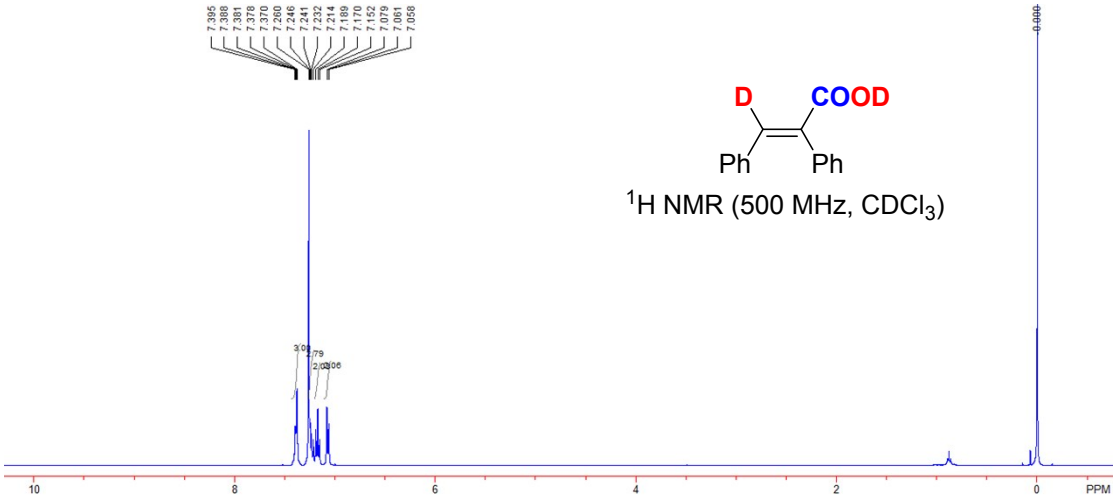
50.2% yield by column chromatography on silica gel (petroleum ether/ethyl acetate = 6:1).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.78 (d, J = 20 Hz, 1H), 7.57-7.54 (m, 2H), 7.42-7.40 (m, 3H), 6.45 (d, J = 20 Hz, 1H) ppm.

5. The experiment of isotope-labeling studies of hydrocarboxylation.



A glass vial with a magnetic stirring bar was charged with ligand **L2** and $Pd(OAc)_2$ (2.2 mg, 0.01 mmol) , then D_2O (1 mL) was added into the vial. After stirring for 5 minutes, alkyne (0.5 mmol) was added. The glass vial was transferred to an autoclave. The autoclave was sealed and purged with CO for three times and subsequently charged with CO (3 bar). Then the autoclave was heated to 100 °C (oil bath) and was kept at this temperature for 24 h. The autoclave was placed in ice water to cool, and the gas was carefully released in a well-ventilated hood. The product was extracted with EtOAc. The collected organic layer was dried over anhydrous $MgSO_4$. After filtration and removing the solvent by vacuum, the residue was directly purified by flash chromatography on silica gel to give the desired product. The reaction afforded a deuterated product in 22% isolated yield (24.5 mg).



6. NMR studies on catalytically active complex.

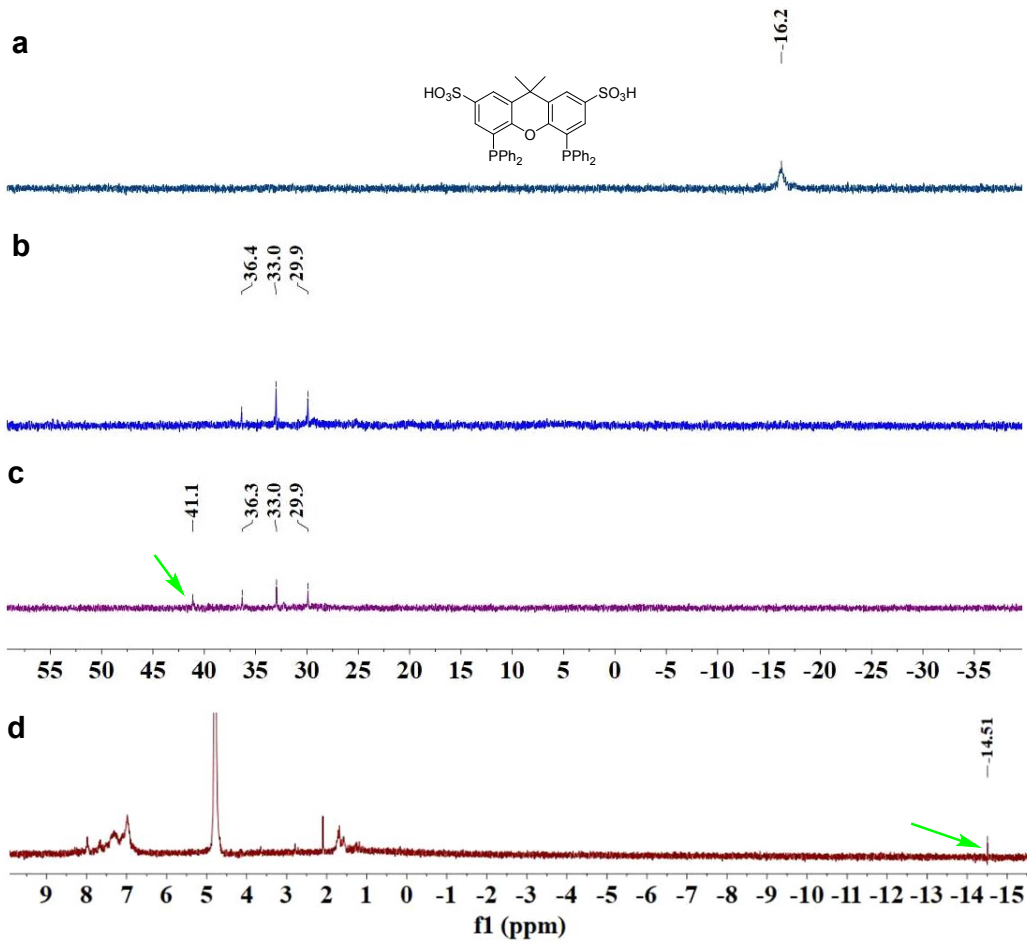


Figure S1. The NMR spectra of **L2**, $Pd(OAc)_2$/**L2** and $Pd(OAc)_2$/**L2**/CO. (a) ^{31}P NMR spectra of **L2** in D_2O at 25 °C; (b) ^{31}P NMR spectra of $Pd(OAc)_2$/**L2** (1:1) in D_2O at 25 °C; (c) ^{31}P NMR spectra of $Pd(OAc)_2$/**L2** (1:1) under CO (1bar) in D_2O/H_2O (4:1) at 25 °C for 2 h. (d) ^{1}H NMR spectra of $Pd(OAc)_2$/**L2** (1:1) under CO (1bar) in D_2O/H_2O (4:1) at 25 °C for 2 h.

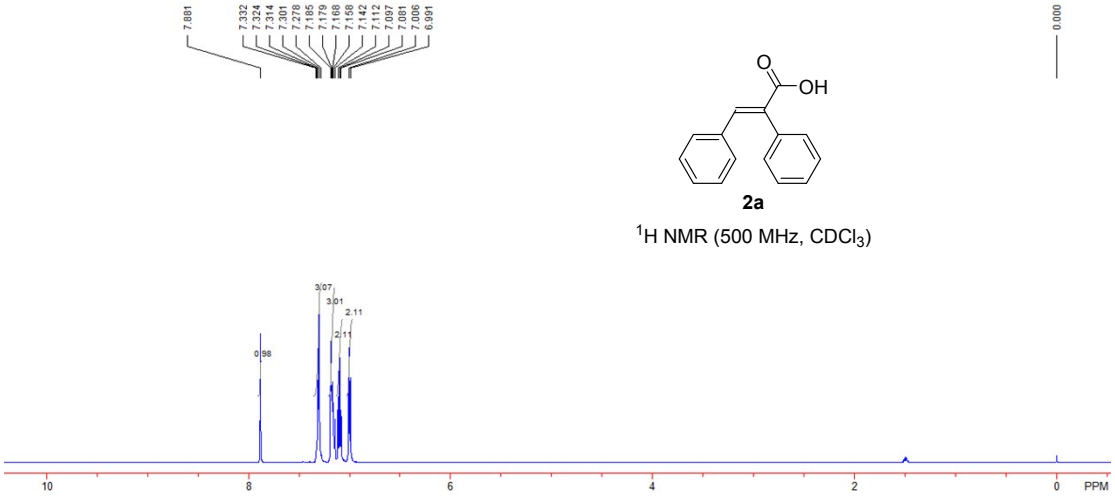
The procedure for preparation and characterization of of Pd-H species.

In a glove box, a NMR tube was charged with $Pd(OAc)_2$ (1.5 mg, 0.007 mmol) and ligand **L2** (5.1 mg, 0.007 mmol) in D_2O/H_2O (V/V = 0.4/0.1 mL). Removed the N_2 in the NMR tube under vacuum, then charged CO (1 bar). After 2 hour at 25 °C, the mixture was analyzed by ^{1}H NMR and ^{31}P NMR.

7. Recycling tests of the $Pd(OAc)_2$/L2 in 1,2-diphenylethyne hydroxycarbonylation.

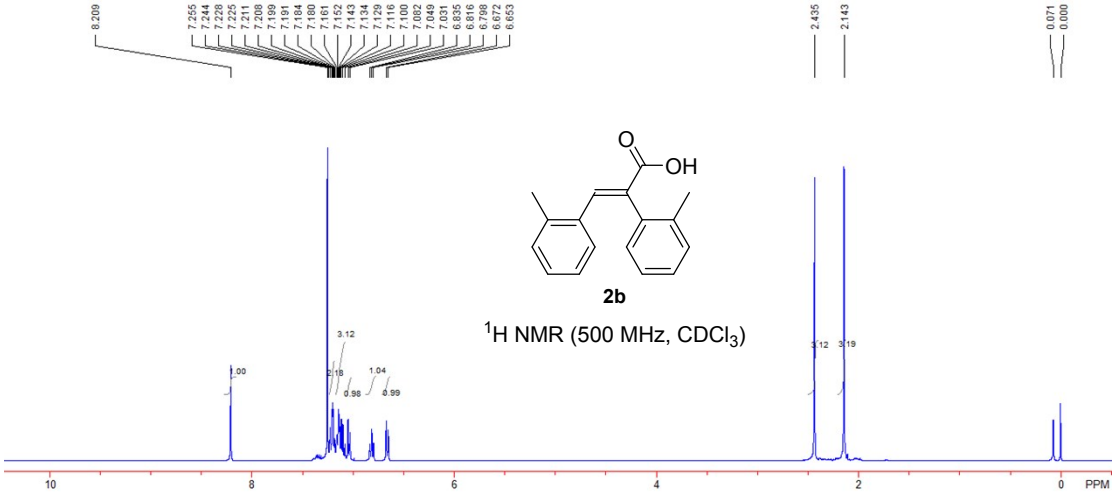
In a glove box, a glass vial with a magnetic stirring bar was charged with $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), **L2** (51.5 mg, 0.07 mmol) and H_2O (2 mL) as the internal standard, after that the mixture was stirred for three minutes, then diphenylacetylene (178.2 mg, 1 mmol) was added to the mixture. The vial was then transferred to an autoclave, which was purged with carbon monoxide for three times and subsequently charged with CO (3 bar). The autoclave was then heated to 100 °C (oil bath) and was kept at this temperature for 24 h. The autoclave was cooled in ice water, and the gas was carefully released in a well-ventilated hood. The mixture was extracted three times with ethyl acetate (2 mL), the organic phase was separated and the water phase which contains the catalyst was used to test next recycling reaction with the same condition and procedure. The product in the organic phase was purified by silica gel column chromatography (PE:EA = 5:1).

8. NMR spectra of compounds 2a-2r.



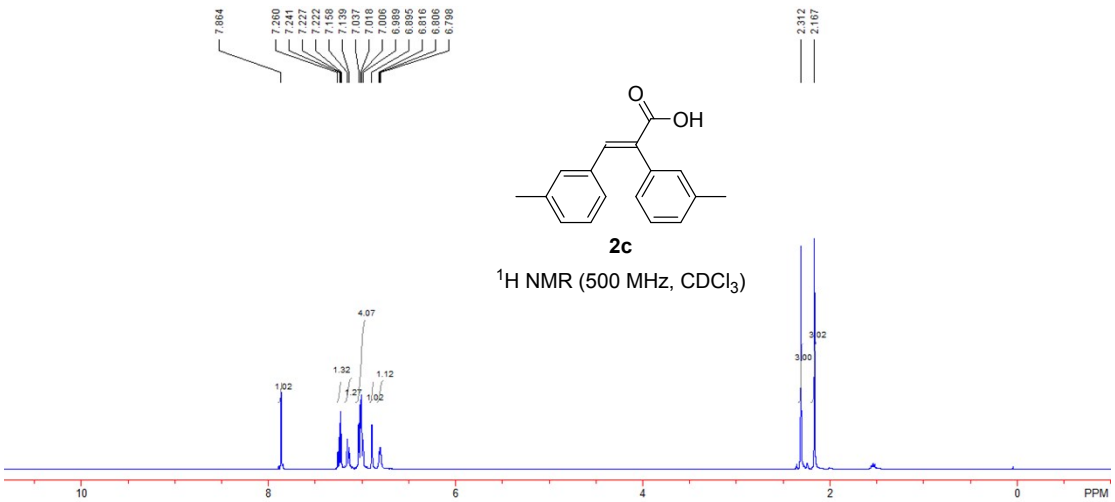
2a

^{1}H NMR (500 MHz, $CDCl_3$)



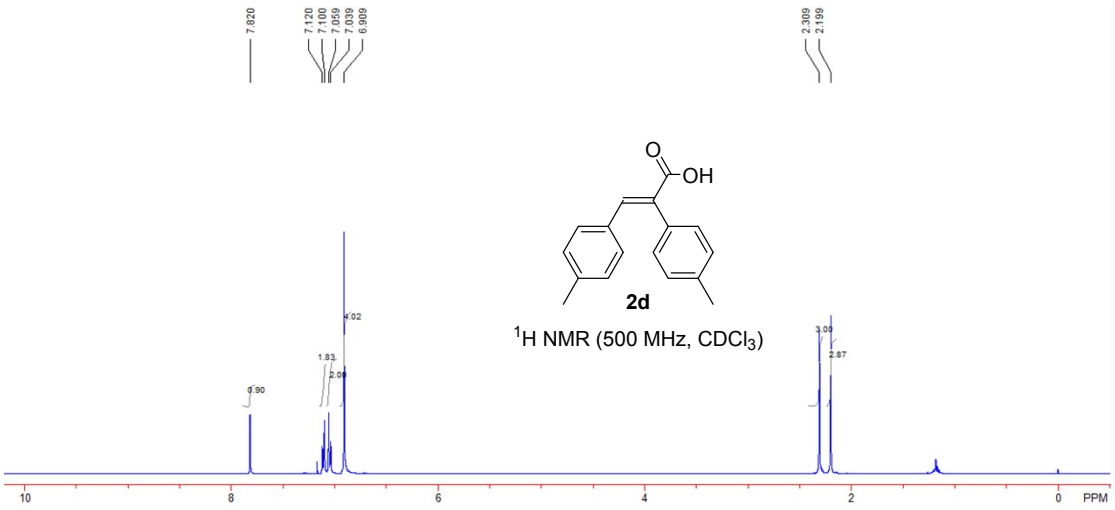
2b

^{1}H NMR (500 MHz, $CDCl_3$)



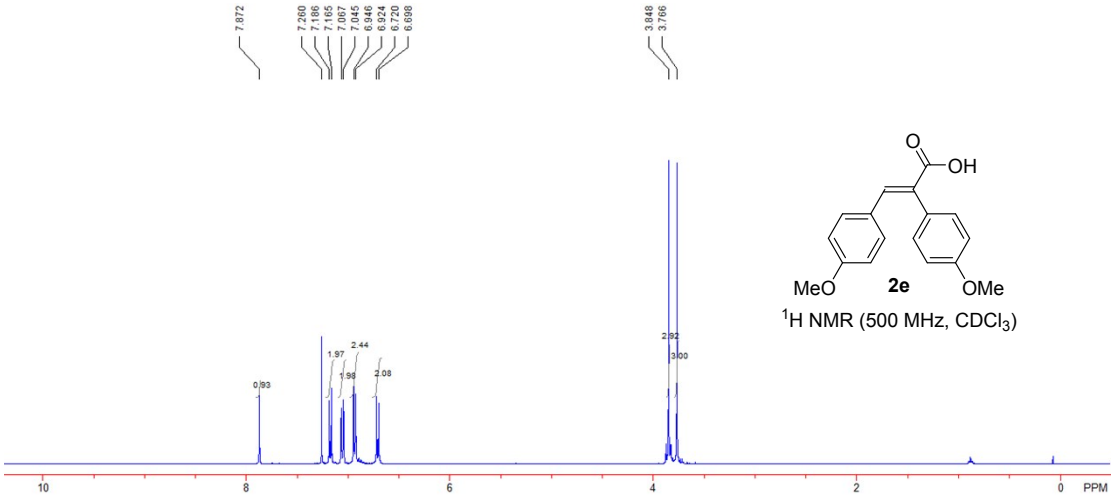
2c

^{1}H NMR (500 MHz, $CDCl_3$)



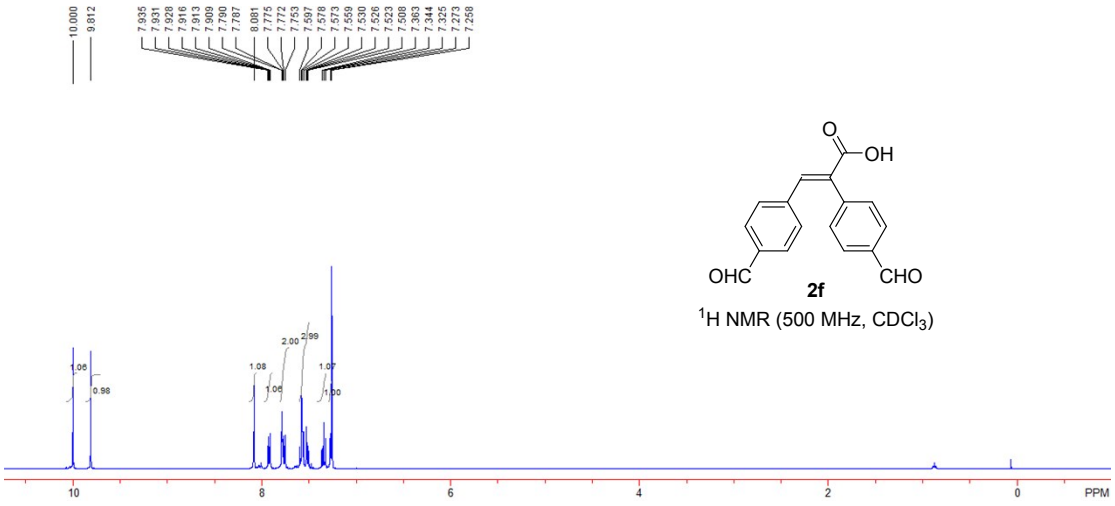
2d

^{1}H NMR (500 MHz, $CDCl_3$)



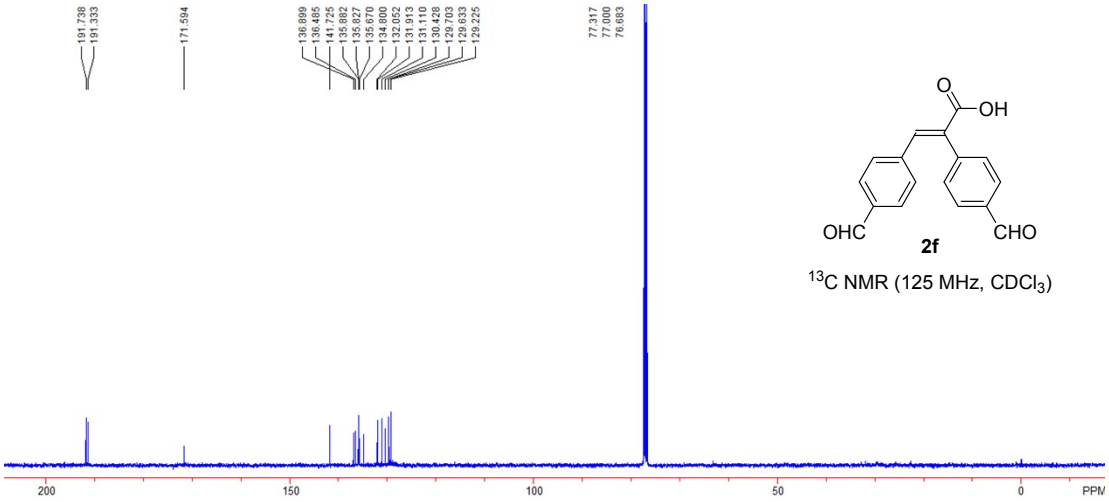
2e

^{1}H NMR (500 MHz, $CDCl_3$)



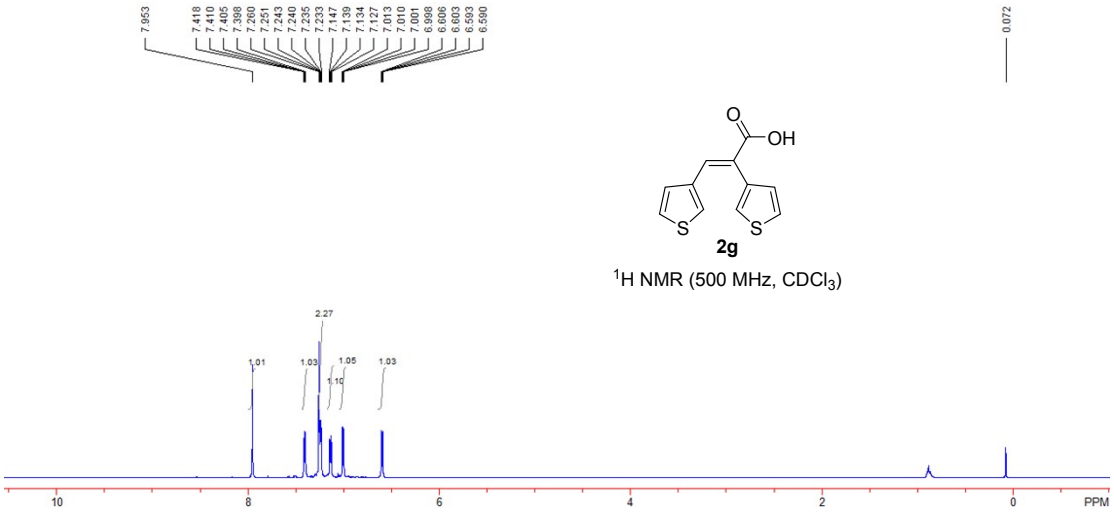
2f

^{1}H NMR (500 MHz, $CDCl_3$)



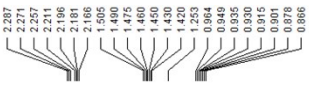
2f

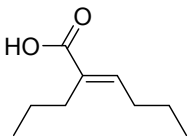
^{13}C NMR (125 MHz, $CDCl_3$)



2g

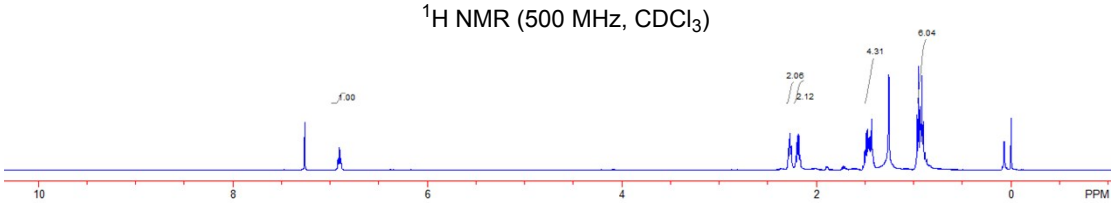
^{1}H NMR (500 MHz, $CDCl_3$)

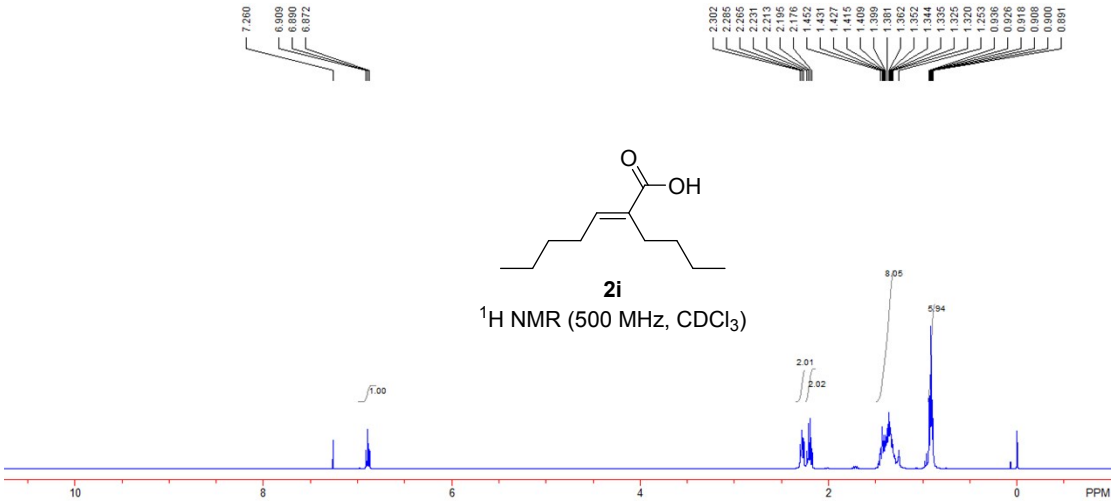




2h

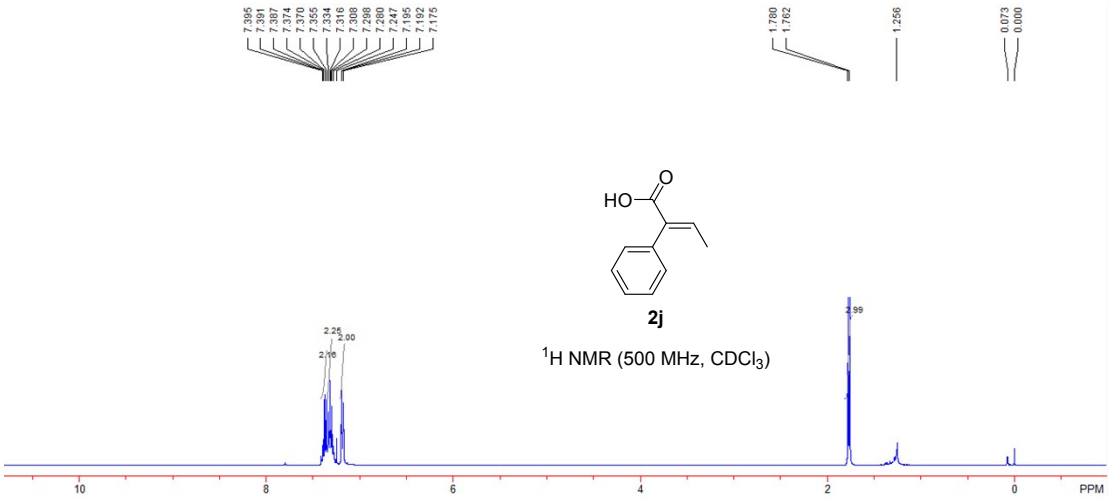
^{1}H NMR (500 MHz, $CDCl_3$)





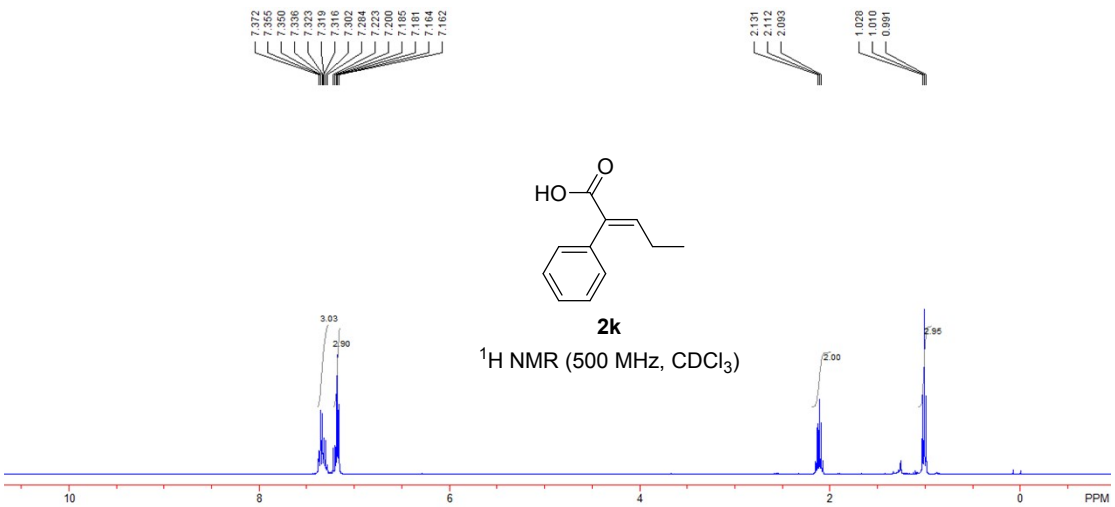
2i

^{1}H NMR (500 MHz, $CDCl_3$)



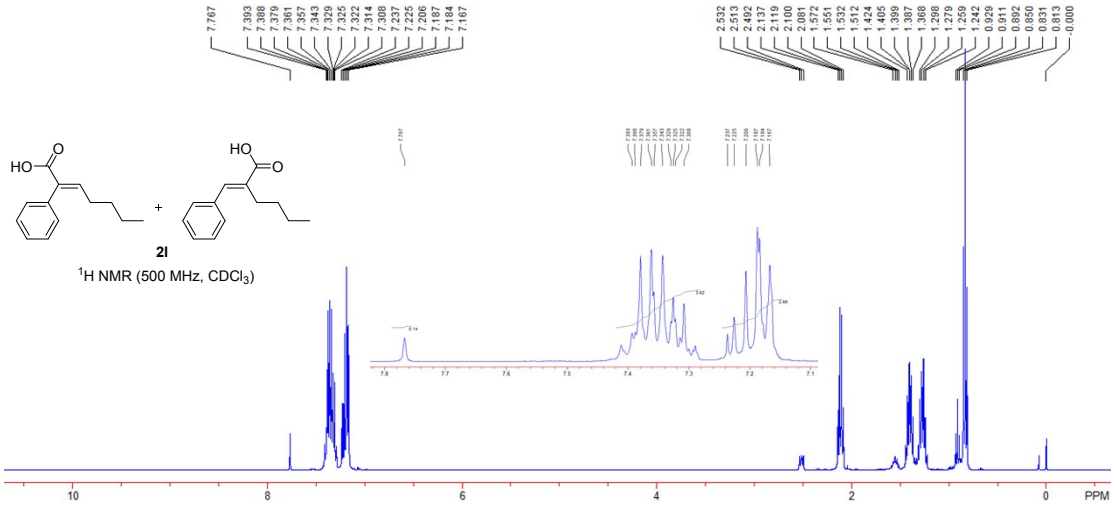
2j

^{1}H NMR (500 MHz, $CDCl_3$)



2k

^{1}H NMR (500 MHz, $CDCl_3$)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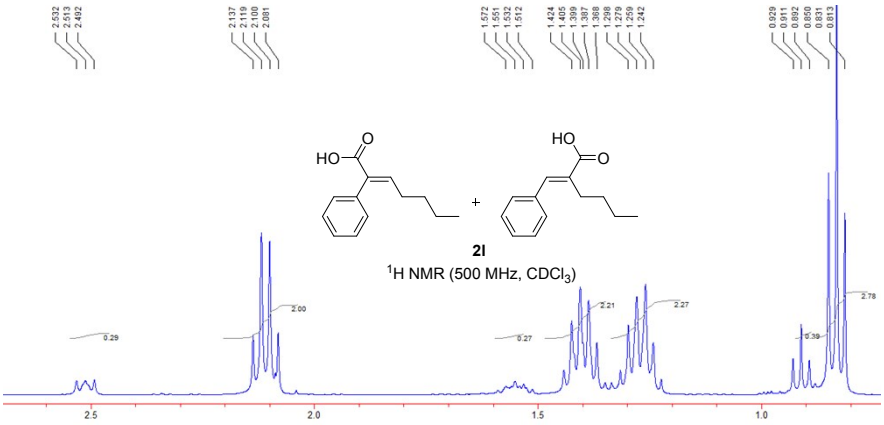
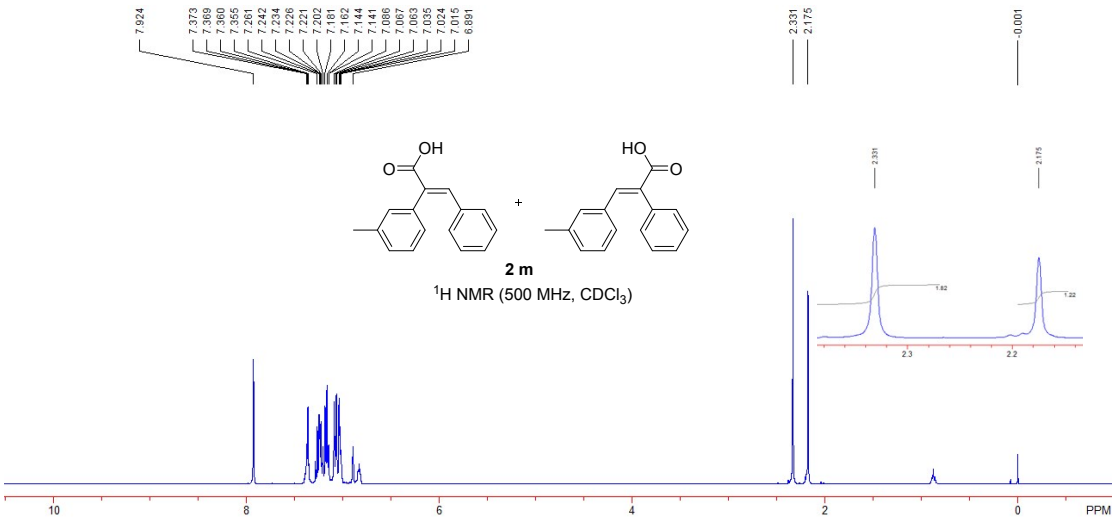
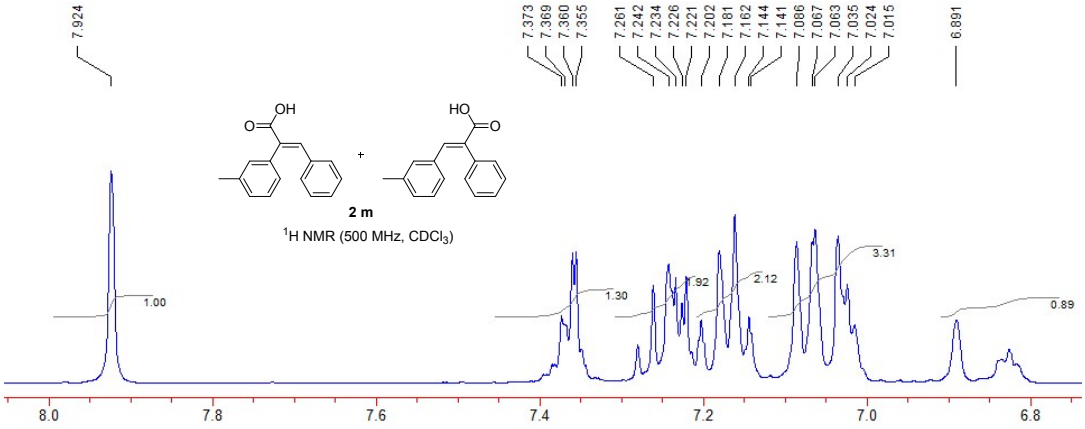
O
HO
O
2l
1H NMR (500 MHz, CDCl3)
PPM


HO
O
HO
O
2l
1H NMR (500 MHz, CDCl3)


OH
O
HO
O
2 m
1H NMR (500 MHz, CDCl3)
PPM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7.221
7.202
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7.162
7.144
7.141
7.086
7.067
7.063
7.035
7.024
7.015
6.891
OH
O
HO
O
2 m
1H NMR (500 MHz, CDCl3)
1.00
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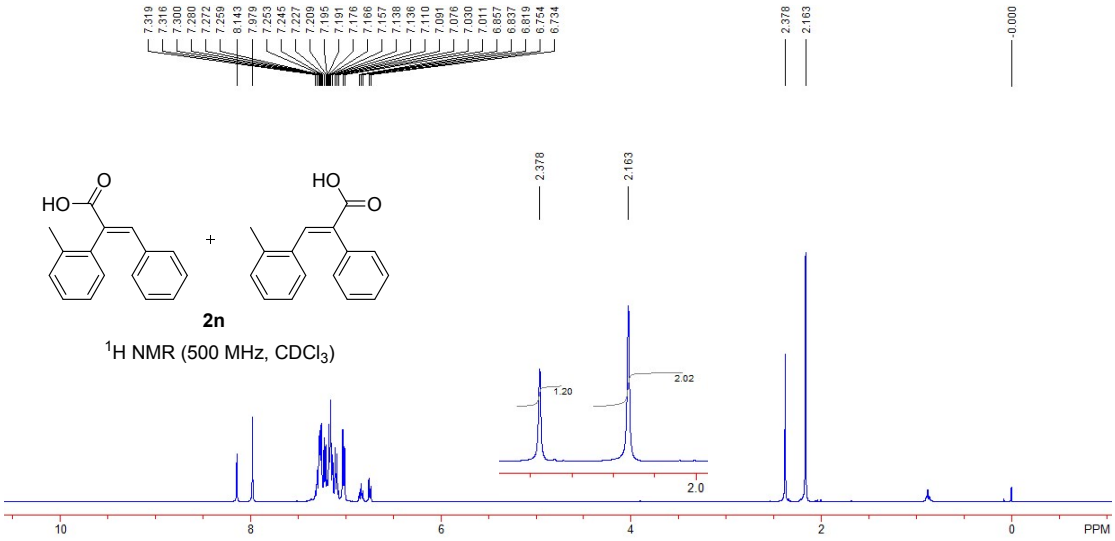
2.12
3.31
0.89
8.0
7.8
7.6
7.4
7.2
7.0
6.8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7.280
7.272
7.259
8.143
7.979
7.253
7.245
7.227
7.209
7.195
7.191
7.176
7.166
7.157
7.138
7.136
7.110
7.091
7.076
7.030
7.011
6.857
6.837
6.819
6.754
6.734
2.378
2.163
0.000
HO
O
HO
O
2n
1H NMR (500 MHz, CDCl3)
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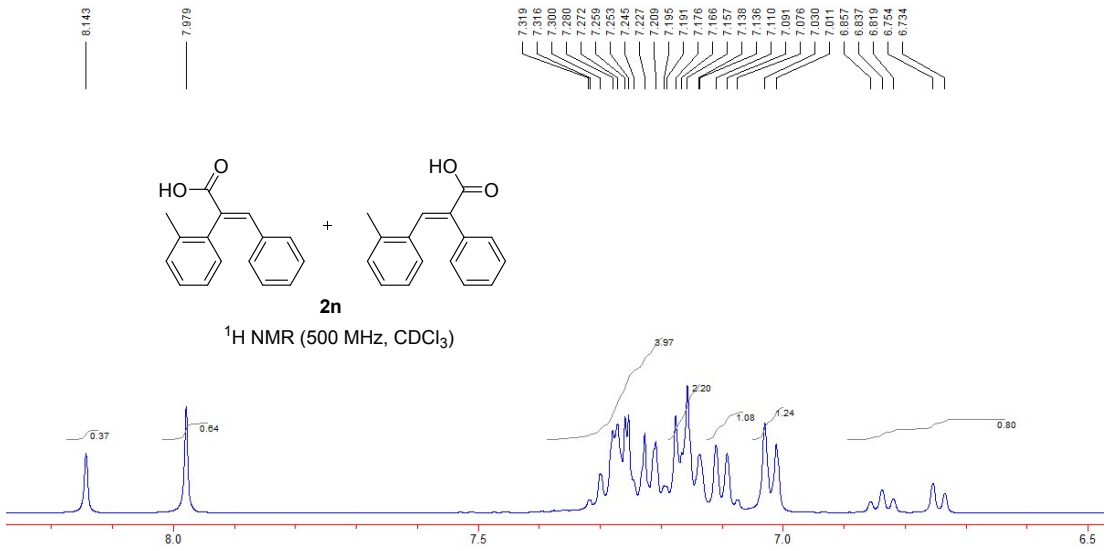
2.02
2.0
10
8
6
4
2
0
PPM


8.143
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7.316
7.300
7.280
7.272
7.259
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7.195
7.191
7.176
7.166
7.157
7.138
7.136
7.110
7.091
7.076
7.030
7.011
6.857
6.837
6.819
6.754
6.734
HO
O
HO
O
2n
1H NMR (500 MHz, CDCl3)
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0.80
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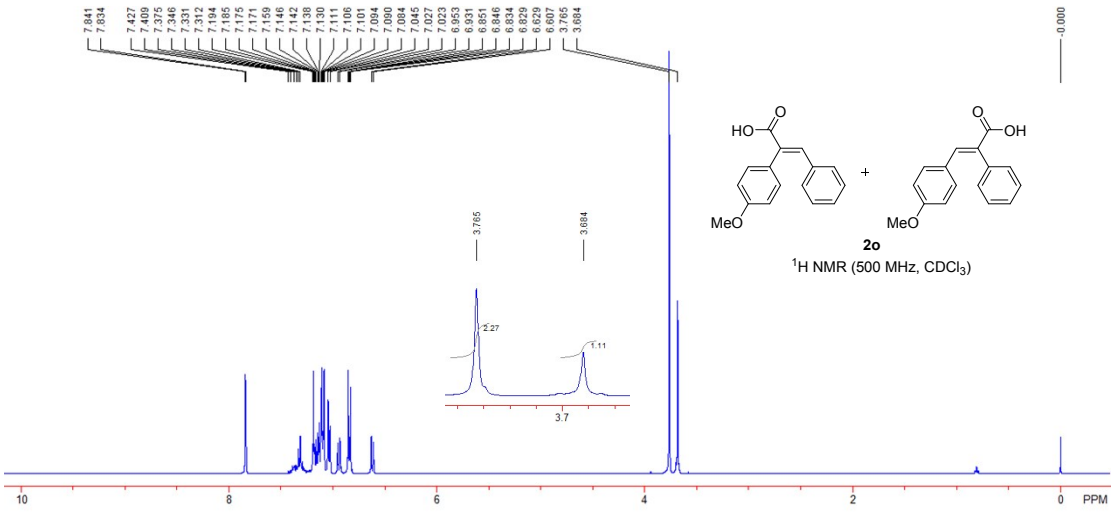
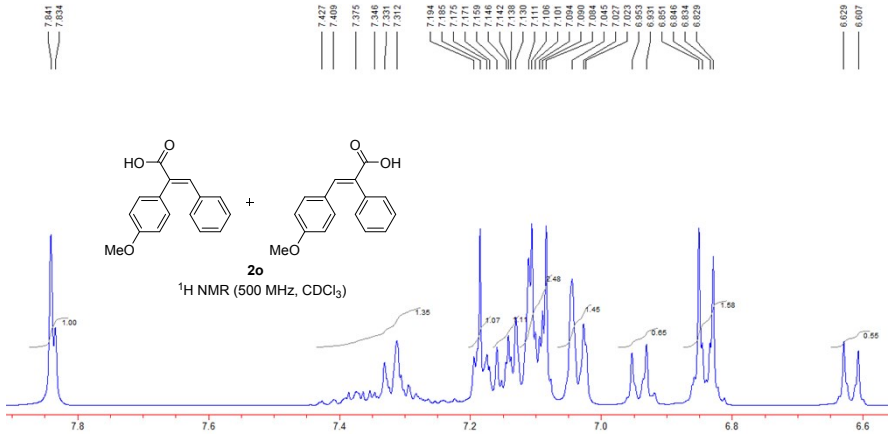
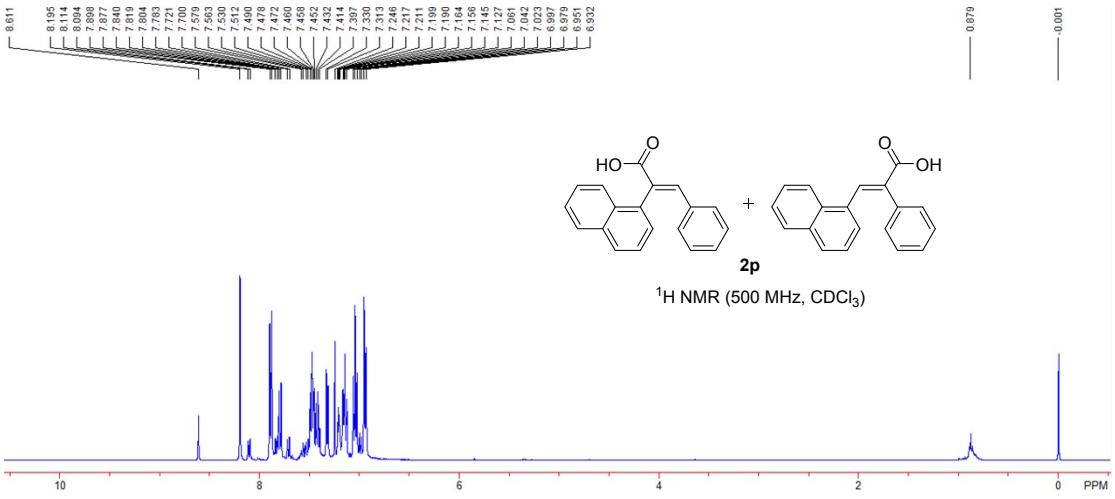
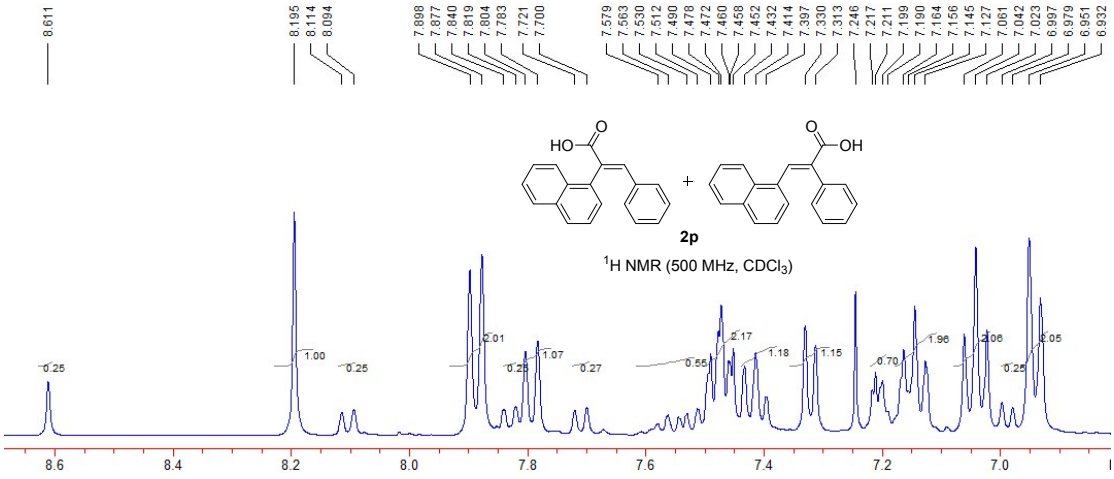
6.5


HO
O
MeO
OH
2o
^{1}H NMR (500 MHz, CDCl$_3$)
PPM


HO
O
MeO
OH
2o
^{1}H NMR (500 MHz, CDCl$_3$)


HO
O
OH
2p
^{1}H NMR (500 MHz, CDCl$_3$)
PPM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7.877
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7.721
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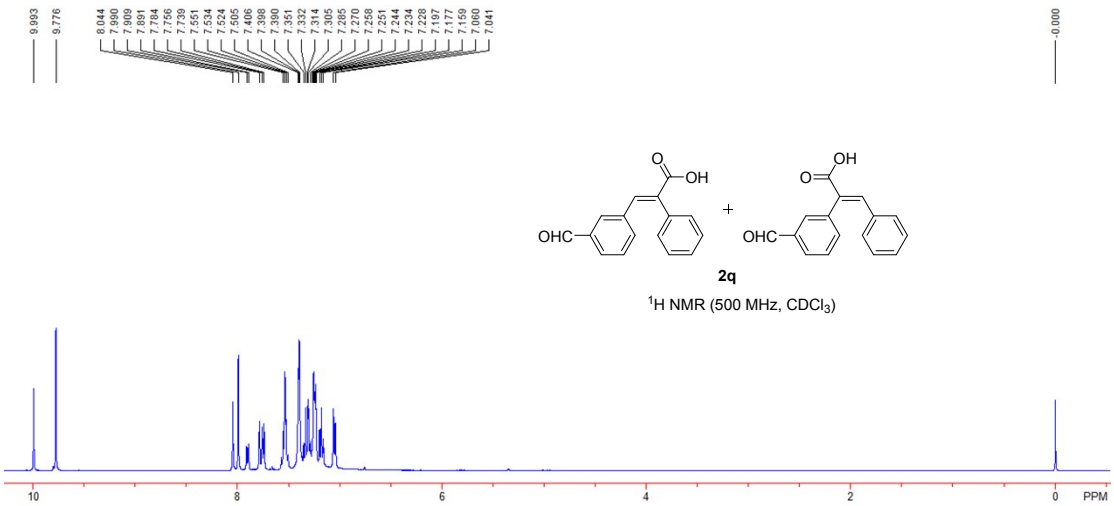
7.563
7.530
7.512
7.490
7.478
7.472
7.460
7.458
7.452
7.432
7.414
7.397
7.330
7.313
7.246
7.217
7.211
7.199
7.190
7.164
7.156
7.145
7.127
7.061
7.042
7.023
6.997
6.979
6.951
6.932
HO
O
OH
2p
1H NMR (500 MHz, CDCl3)
0.25
1.00
0.25
2.01
0.28
1.07
0.27
0.55
2.17
1.18
1.15
0.70
1.96
2.06
0.25
2.05
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0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7.756
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7.534
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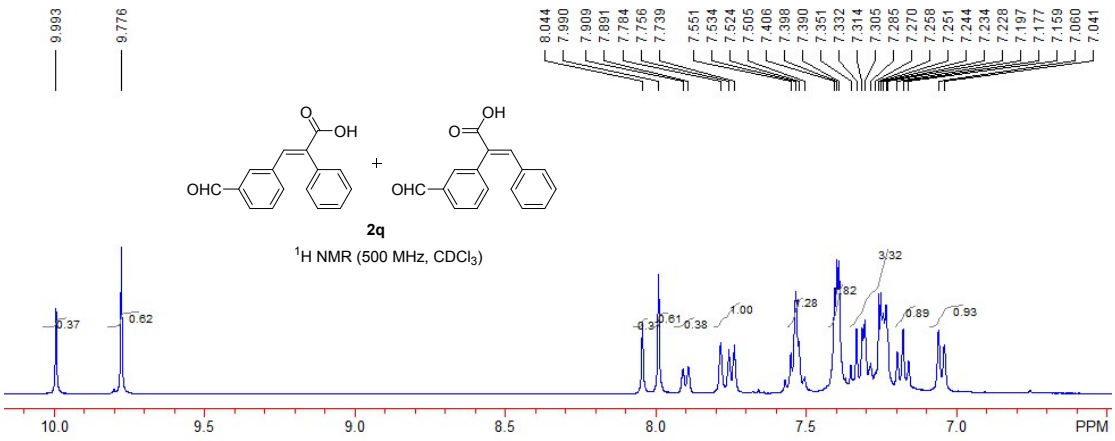
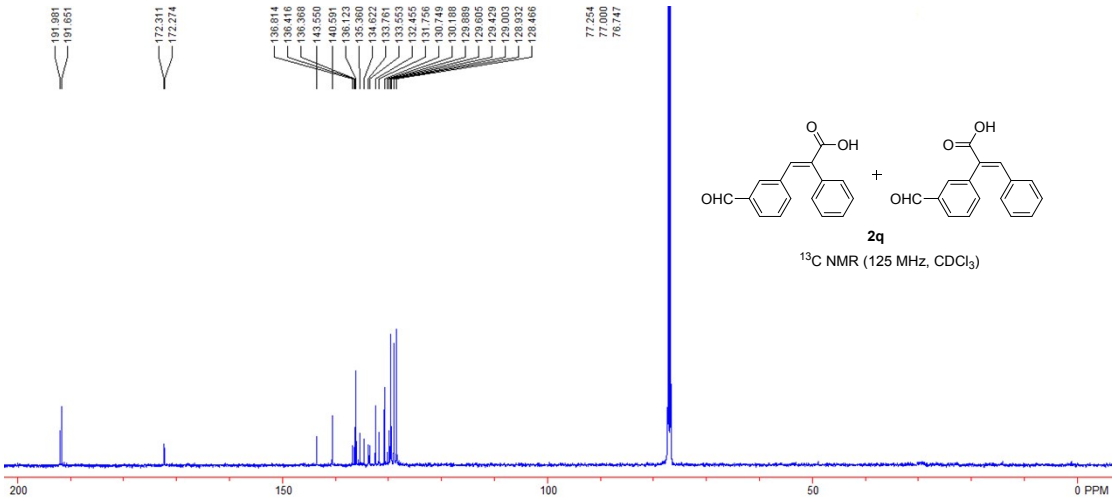
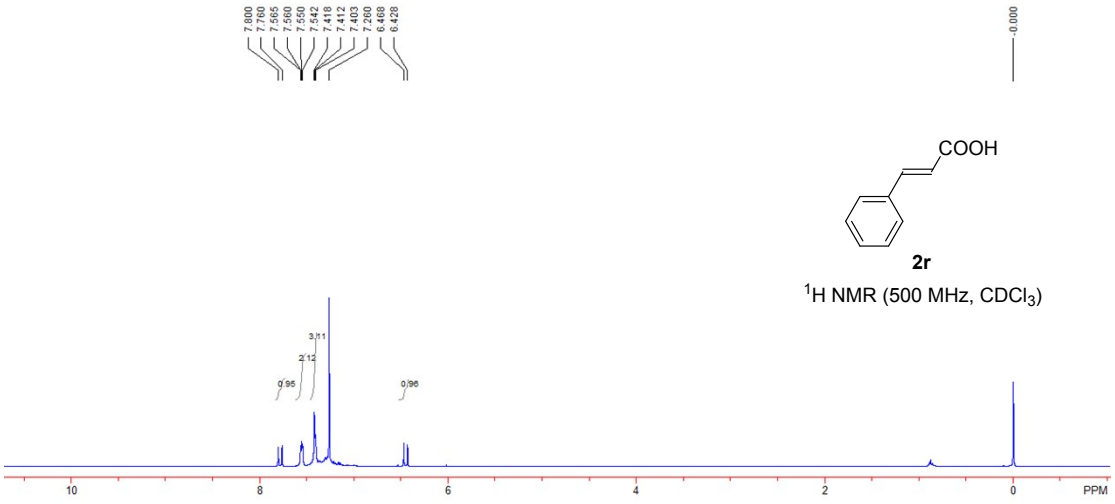
7.406
7.398
7.390
7.351
7.332
7.314
7.305
7.285
7.270
7.258
7.251
7.244
7.234
7.228
7.197
7.177
7.159
7.060
7.041
0.000
O
OH
OHC
2q
1H NMR (500 MHz, CDCl3)
10
8
6
4
2
0
PPM


9.993
9.776
8.044
7.990
7.909
7.891
7.784
7.756
7.739
7.551
7.534
7.524
7.505
7.406
7.398
7.390
7.351
7.332
7.314
7.305
7.285
7.270
7.258
7.251
7.244
7.234
7.228
7.197
7.177
7.159
7.060
7.041
O
OH
OHC
2q
1H NMR (500 MHz, CDCl3)
0.37
0.62
0.34
0.61
0.38
1.00
1.28
3.32
1.82
0.89
0.93
10.0
9.5
9.0
8.5
8.0
7.5
7.0
PPM





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