

Supporting Information

Iridium-Catalyzed Enantioselective Ring Opening of Alkenyl Oxiranes by Unactivated Carboxylic Acids

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1. General information:

The catalytic asymmetric epoxide ring opening reaction was performed in oven dried round bottom flask with a Teflon-coated magnetic stirring bar unless otherwise noted. The reactions were run under nitrogen atmosphere. Air-and moisture-sensitive liquids were transferred via a gas-tight syringe and a stainless-steel needle. All work-up and purification procedures were carried out with reagent-grade solvents under ambient atmosphere.

2. Instrumentation:

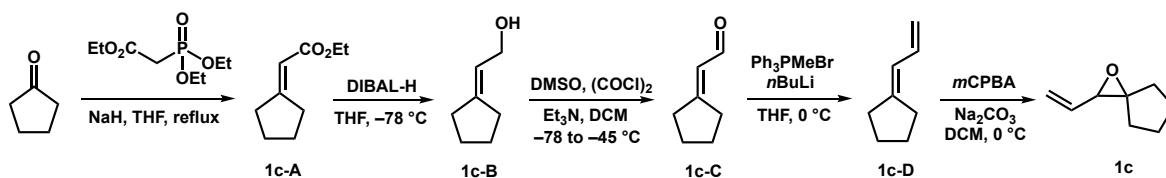
^1H and ^{13}C NMR were recorded on Bruker 400 and 500 MHz spectrometers. Chemical shifts for proton are reported in parts per million downfield from tetramethylsilane and referenced to residual protium in the NMR solvent (CDCl_3 : δ 7.24 ppm). For ^{13}C NMR chemical shifts are reported in the scale relative to NMR solvent (CDCl_3 : δ 77.0 ppm) as an internal reference. NMR data are reported as follows: chemical shifts, multiplicity (s: singlet, d: doublet, dd: doublet of doublets, t: triplet, q: quartet, m: multiplet, br: broad signal), coupling constant (Hz), and integration. Optical rotation was measured using a 1 mL cell with a 1.0 dm path length on a Anton Paar Polarimeter MCP 100. High resolution mass spectra were obtained on Q-TOF (Agilent 6520). HPLC analysis was conducted on Waters and Agilent HPLC systems equipped with Daicel chiral-stationary-phase columns (0.46 cm ϕ x 25 cm).

3. Materials:

All commercially available chemicals were used as received unless otherwise indicated. All solvents were strictly dried prior to use: dichloromethane and acetonitrile were distilled over calcium hydride under nitrogen; tetrahydrofuran and ether were distilled from sodium and benzophenone; benzene and toluene were distilled from sodium under nitrogen. The carboxylic acid substrates were purchased and used without further purification. Vinyl oxirane and isoprene monoxide were purchased from Alfa-Aesar and used as received. The alkenyl epoxides, that are not commercially available, are prepared in the lab as described below. $[\text{Ir}(\text{COD})\text{Cl}]_2$ was purchased from Sigma-Aldrich and used without further purification. Commercially available ligands (**L4**, **L5**) were purchased from Sigma-Aldrich and used as received. Carreira ligand (**S**-**L**) and other phosphoramidite ligands (**L1**, **L2** and **L3**) were synthesized in the lab following the literature procedures.¹ Column chromatography was performed on flash silica gel unless mentioned otherwise. Thin layer chromatography was performed on 0.25 mm thick aluminum-backed silica gel plates purchased from Merck and visualized with ultraviolet light ($\lambda=254$ nm).

4. Preparation of Starting materials:

Synthesis of 2-vinyl-1-oxaspiro[2.4]heptane ((\pm)-1c):



Ethyl 2-cyclopentylideneacetate (1c-A): To a suspension of sodium hydride (60% dispersion in oil, 2.61 g, 65.4 mmol, 1.1 equiv.) in THF (70 mL), was added a solution of triethyl phosphonoacetate (14.7 g, 13.5 mL, 65.4 mmol, 1.1 equiv.) in THF (30 ml), slowly over 30 minutes at 0°C . The reaction mixture was stirred at 0°C for one hour, then cyclopentanone (5 g, 5.26 mL, 59.4 mmol, 1.0 equiv.) was added dropwise at the same temperature. The reaction mixture was then stirred at room temperature for 18 h. After the completion of reaction, the reaction was quenched with water and the resulting mixture was extracted with diethyl ether. The combined organic layer was washed with brine, dried over Na₂SO₄ and evaporated under reduced pressure. The residue was purified by flash column chromatography eluting with a gradient of 0-10% ethyl acetate/hexanes to give compound (**1c-A**) as a clear oil (8.98 g, 58.2 mmol, 98%); R_f = 0.62 (EtOAc/Hex 0.5: 9.5). ¹H NMR (400 MHz, CDCl₃): δ 5.72 (s, 1H), 4.16 – 3.87 (m, 2H), 2.69 (t, J = 6.0 Hz, 2H), 2.36 (t, J = 6 Hz, 2H), 1.66 (q, J = 6 Hz, 2H), 1.58 (q, J = 6 Hz, 2H), 1.27 – 1.13 (m, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 168.9, 166.8, 111.6, 59.3, 35.9, 35.8, 32.5, 26.4, 25.4, 14.3. The analytical data of the compound was in complete agreement with the literature.²

2-Cyclopentylideneethan-1-ol (1c-B): To a cooled (-78°C) solution of ethyl 2-cyclopentylideneacetate (**1d-A**) (3.68 g, 23.9 mmol, 1 equiv.) in dry THF (60 mL) was added a DIBAL-H (1 M in Toluene 72 mL, 71.6 mmol, 3 equiv.). After the reduction was complete (monitored by TLC), the reaction was quenched by the addition of saturated Rochelle's salt (5 ml). The biphasic mixture was stirred overnight and then extracted with EtOAc (4 x 110 mL), dried over Na₂SO₄, and the volatiles were removed under reduced pressure. The crude alcohol was purified by silica gel chromatography (0-20% ethyl acetate/hexanes) to give product (**1c-B**) as a clear oil (2.26 g, 20.5 mmol, 86%); R_f = 0.32 (EtOAc/Hex 2:8). ¹H NMR (400 MHz, CDCl₃): δ 5.50 – 5.48 (m, 1H), 4.11 (d, J = 7.2 Hz, 2H), 2.28 – 2.22 (m, 4H), 1.69 – 1.59 (m, 4H). ¹³C NMR (125 MHz, CDCl₃): δ 147.9, 119.0, 61.0, 33.7, 28.6, 26.3, 26.0. The analytical data of the compound was in complete agreement with the literature.²

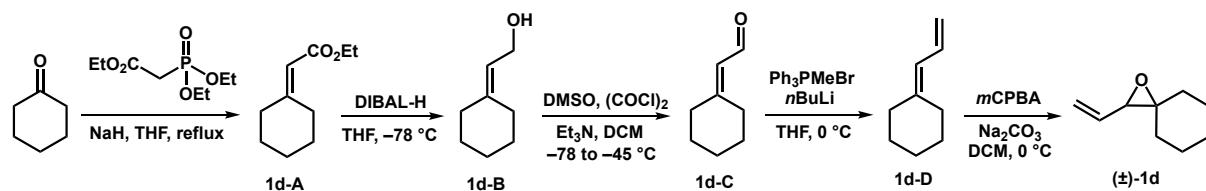
2-cyclopentylideneacetaldehyde (1c-C): To a well stirred solution oxalyl chloride (2.7 g, 1.82 mL, 21.2 mmol, 1.5 equiv.) in anhydrous dichloromethane (25 mL) was added a solution of freshly distilled dimethylsulfoxide (3.32 g, 3.02 ml, 42.5 mmol, 3 equiv.) in dichloromethane (30 mL) dropwise at -78°C . The reaction mixture was stirred for 30 minutes. 2-cyclopentylidene ethan-1-ol (**1c-B**) (1.56 g, 13.9 mmol, 1 equiv.) dissolved in dichloromethane (25 mL) was then added to this solution. After one hour, triethylamine (8.6 g, 11.8 mL, 85 mmol, 6 equiv.) was added. The resulting mixture was stirred at -78°C for one hour and then at -45°C for another one hour. When the starting material was consumed, the reaction was quenched with ice water and extracted with dichloromethane (3 x 50 mL). The combined organic phases were washed with brine, dried over Na₂SO₄, filtered and concentrated in vacuo. The crude mixture was then used in the next step without further purification. The crude product was a pale-yellow oil. R_f = 0.45 (EtOAc/Hex 2:8).

Allylidene cyclopentane (1c-D): To freshly azeotroped methyltriphenylphosphonium bromide (6.98 g, 19.5 mmol, 1.5 equiv.) in THF (55 mL) at 0°C was added nBuLi (1.6 M in hexane, 12.8 mL, 20.4 mmol,

1.57 equiv.). The reaction was allowed to stir at 0 °C for an hour, at which point 2-cyclopentylideneacetaldehyde (**1c-C**) (1.43 g, 13 mmol, 1 equiv.) in THF (10 ml) was added. After 30 minutes, the reaction mixture was quenched with water and the resulting mixture extracted with diethyl ether (3 x 50 mL). The combined organic layer was washed with brine and dried over Na₂SO₄. The solvent was concentrated in vacuo, until the solid began to precipitate out. At this point, pentane was added to further precipitate the solid. The mixture was filtered through celite and the remaining solvent was removed. This crude mixture was then used in the next step without further purification. R_f = 0.70 (pentane).

2-Vinyl-1-oxaspiro[2.4]heptane (1c**):** *m*-Chloroperbenzoic acid (75%, 1.28 g, 7.39 mmol, 1 equiv.) was added portion wise to a stirred slurry of the allylidencyclopentane (**1c-D**) (0.80 g, 7.39 mmol, 1 equiv.) and sodium carbonate (1.96 g, 18.48 mmol, 2.5 equiv.) in methylene chloride (9.0 mL) at 0 °C. The resulting mixture was stirred at 0 °C. After all the allylidencyclopentane (**1c-D**) had been consumed (as shown by TLC) the mixture was filtered through celite pad and the precipitates were washed with dichloromethane. Removal of the solvent from the filtrate gave crude 2-vinyl-1-oxaspiro[2.4]heptane (**1c**) as an oil, which was further purified by column chromatography using neutral alumina eluting with 5% Et₂O/pentane to afford the pure product (0.46 g, 3.70 mmol, yield = 50%); R_f = 0.59 (Ether/Pentane 0.5:9.5). ¹H NMR (300 MHz, CDCl₃): δ 5.63 – 5.51 (m, 1H), 5.45 – 5.35 (m, 1H), 5.26 (ddd, J = 10.2, 1.8, 0.6 Hz, 1H), 3.36 (d, J = 7.5 Hz, 1H), 1.91 – 1.71 (m, 4H), 1.67 – 1.52 (m, 4H). ¹³C NMR (125 MHz, CDCl₃): δ 134.8, 119.6, 71.0, 62.3, 33.5, 29.1, 25.1, 25.0. The analytical data of the compound was in complete agreement with the literature.³

Synthesis of 2-vinyl-1-oxaspiro[2.5]octane ((±)-**1d**):



ethyl 2-cyclohexylideneacetate (1d-A**):** To a suspension of sodium hydride (60% dispersion in oil, 0.89 g, 22.44 mmol, 1.1 equiv.) in THF (50 mL), was added a solution of triethyl phosphonoacetate (4.8 g, 4.36 mL, 21.42 mmol, 1.05 equiv.) in THF (15 ml), slowly over 30 minutes at 0 °C. The reaction mixture was stirred at 0 °C for one hour, then cyclohexanone (2 g, 2.1 mL, 20.4 mmol, 1.0 equiv.) was added dropwise at the same temperature. The reaction mixture was then stirred at room temperature for 18 h. After the completion of reaction, the reaction was quenched with water and the resulting mixture was extracted with diethyl ether. The combined organic layer was washed with brine, dried over Na₂SO₄ and evaporated under reduced pressure. The residue was purified by flash column chromatography eluting with a gradient of 0-10% ethyl acetate/hexanes to give compound (**1d-A**) as a clear oil (3.25 g, 19.38 mmol, 95%); R_f = 0.34 (EtOAc/Hex 0.5: 9.5). ¹H NMR (400 MHz, CDCl₃): δ 5.63 – 5.54 (m, 1H), 4.12 (q, J = 7.2 Hz, 2H), 2.90 – 2.70 (m, 2H), 2.21 – 2.13 (m, 2H), 1.63 – 1.58 (m, 6H), 1.27 – 1.23 (m, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 166.9, 163.5, 113.0, 59.5, 38.0, 29.8, 28.6, 27.8, 26.3, 14.3. The analytical data of the compound was in complete agreement with the literature.⁴

2-cyclohexylideneethan-1-ol (1d-B**):** To a cooled (-78 °C) solution of ethyl 2-cyclohexylideneacetate (**1d-A**) (2 g, 11.90 mmol, 1 equiv.) in dry THF (30 mL) was added a DIBAL-H (1 M in Toluene, 36 mL, 36 mmol, 3 equiv.). After the reduction was complete (monitored by TLC), the reaction was quenched by the addition of saturated Rochelle's salt (5 ml). The biphasic mixture was stirred overnight and then extracted with 4 x 100 mL portions of EtOAc, dried over Na₂SO₄. The volatiles were removed under reduced pressure. The crude alcohol was purified by silica gel flash chromatography (gradient of 0:100 to 20:80 EtOAc/ hexanes) to afford the product (**1d-B**) as a clear oil (1.4 g, 11.09 mmol, 93%); R_f =

0.087 (EtOAc/Hex 1:9). ^1H NMR (400 MHz, CDCl_3): δ 5.26 (t, $J = 7.2$ Hz, 1H), 4.03 (d, $J = 6.8$ Hz, 2H), 2.11 – 2.02 (m, 4H), 1.47 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 143.7, 120.5, 58.2, 37.0, 28.8, 28.3, 27.8, 26.7. The analytical data of the compound was in complete agreement with the literature.⁴

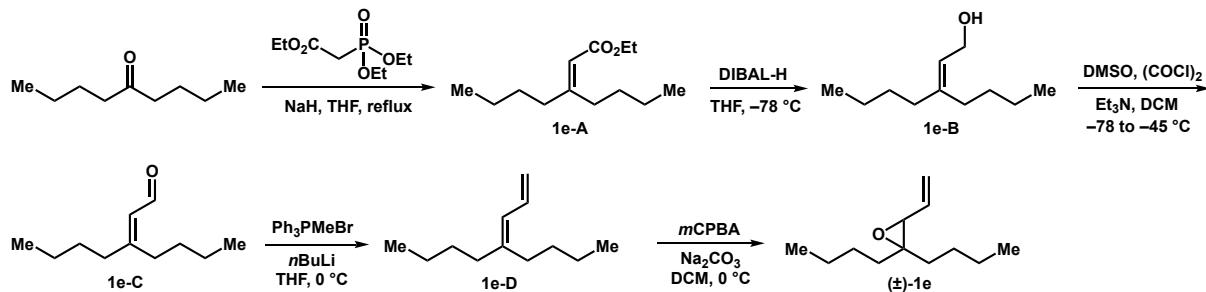
2-cyclohexylideneacetaldehyde (1d-C): In anhydrous dichloromethane (55 mL), freshly distilled anhydrous DMSO (2.78 g, 2.53 ml, 35.70 mmol, 3 equiv.) was treated with oxalyl chloride (2.26 g, 1.53 mL, 17.85 mmol, 1.5 equiv.) under nitrogen at -78°C for 30 minutes. Then a solution of 2-cyclohexylideneethan-1-ol (**1d-B**) (1.50 g, 11.90 mmol, 1 equiv.) in dichloromethane (25 mL) was added and the reaction mixture was stirred for 30 minutes. Triethyl amine (7.22 g, 9.95 mL, 71.40 mmol, 6 equiv.) in DCM (25 mL) was added. The resulting mixture was stirred at -78°C for one hour and then at -45°C for another one hour. After the starting material was consumed (monitored by TLC), the reaction was quenched with ice water. The resulting mixture was extracted with dichloromethane (3 x 50 mL). The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The crude mixture (**1d-C**) was then used in the next step without further purification. $R_f = 0.7$ (EtOAc/ Hex 2:8).

Allylidencyclohexane (1d-D): To freshly azeotroped methyltriphenylphosphonium bromide (12.89 g, 36 mmol, 1.5 equiv.) in THF (90 mL) at 0°C was added *n*-BuLi (2.5 M in hexane, 15 mL, 37.68 mmol, 1.57 equiv.). The reaction was allowed to stir at 0°C for an hour, at which point 2-cyclohexylideneacetaldehyde (**1d-C**) (2.98 g, 24 mmol, 1 equiv.) in THF (20 ml) was added. After 30 minutes, the reaction mixture was quenched with water, and the resulting mixture extracted with diethyl ether (3 x 50 mL). The combined organic layers were washed with brine and dried over Na_2SO_4 . The organic layers were concentrated in vacuo, until the solid began to precipitate out. At this point, hexane was added to further precipitate the solid. The mixture was filtered through celite. The solvent was removed under reduced pressure. This crude mixture was then used in the next step without further purification. $R_f = 0.86$ (Hex).

2-vinyl-1-oxaspiro[2.5]octane ((\pm)-1d): *m*-Chloroperbenzoic acid (*m*CPBA, 75%) (1.92 g, 11.13 mmol, 1 equiv.) (used after purification following the procedure described in the preparation method of compound **1c**) was added portion wise to a stirred slurry of the allylidencyclohexane (**1d-D**) (1.36 g, 1.4 mL, 11.12 mmol, 1 equiv.) and sodium carbonate (2.95 g, 27.82 mmol, 2.5 equiv.) in dichloromethane (14 ml) at 0°C . The reaction mixture was stirred at 0°C for 30 minutes and then monitored by TLC. After completion of the reaction, the mixture was filtered through celite pad and the precipitate was washed with dichloromethane. Removal of the solvent gave crude 2-vinyl-1-oxaspiro[2.5]octane ((\pm)-**1d**), which was further purified by flash chromatography using neutral alumina eluting with 5% Et₂O/pentane to afford the pure product (0.94 g, 6.78 mmol, 61% yield); $R_f = 0.45$ (EtOAc/Hex 0.5:9.5). ^1H NMR (400 MHz, CDCl_3): δ 5.75 – 5.69 (m, 1H), 5.43 – 5.36 (m, 1H), 5.29 – 5.25 (m, 1H), 3.14 (d, $J = 0.8$ Hz, 1H), 1.76 – 1.60 (m, 2H), 1.55 – 1.39 (m, 8H). ^{13}C NMR (100 MHz, CDCl_3): δ 133.2, 119.9, 64.7, 64.4, 35.4, 29.4, 25.6, 25.0, 24.7.

The analytical data of the compound was in complete agreement with the literature.⁵

Synthesis of 2,2-dibutyl-3-vinyloxirane ((\pm)-1e):



Ethyl 3-butylhept-2-enoate (1e-A): In a round bottom flask, sodium hydride (60% dispersion in oil, 1.34 g, 33.61 mmol, 1.1 equiv.) was suspended in THF (50 mL) and cooled to 0 °C. A solution of triethyl phosphonoacetate (7.54 g, 6.44 mL, 33.61 mmol, 1.1 equiv.) in THF (30 ml) was slowly added over 30 minutes. The reaction mixture was stirred at 0 °C for one hour, then nonan-5-one (4.35 g, 5.3 ml, 30.56 mmol, 1.0 equiv.) was added dropwise at the same temperature. The reaction mixture was then refluxed for 18 h. The reaction was quenched with water and the resulting mixture was extracted with diethyl ether (3 x 40 mL). The combined organic layer was washed with brine, dried with Na₂SO₄. After evaporation of the solvent, the residue was purified by silica gel chromatography eluting with a gradient of 0-10% ethyl acetate/hexane to give the product (**1e-A**) as a clear oil (6.30 g, 29.64 mmol, 97%); R_f = 0.62 (EtOAc/Hex 0.5: 9.5). ¹H NMR (400 MHz, CDCl₃): δ 5.58 (s, 1H), 4.10 (q, J = 7.2 Hz, 2H), 2.59 – 2.53 (m, 2H), 2.13 – 2.07 (m, 2H), 1.46 – 1.19 (m, 11H), 0.90 – 0.85 (m, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 166.6, 164.8, 115.1, 59.3, 38.1, 31.9, 30.8, 29.8, 23.0, 22.4, 14.3, 13.9, 13.9. The analytical data of the compound was in complete agreement with the literature.⁶

2,3-butylhept-2-en-1-ol (1e-B): To a cooled (–78 °C) solution of ethyl 3-butylhept-2-enoate (**1e-A**) (3.47 g, 16.33 mmol, 1 equiv.) in dry THF (80 mL) was added a DIBAL-H (1 M in Toluene 49 mL, 48.99 mmol, 3 equiv.). After the reduction was complete (monitored by TLC), the reaction was quenched by the addition of saturated Rochelle's salt (5 ml). The biphasic mixture was stirred overnight and then extracted with EtOAc (4 x 110 mL), dried over Na₂SO₄, and the volatiles were removed under reduced pressure. The crude alcohol was purified by silica gel chromatography (0-20% ethyl acetate/hexanes) to give product (**1e-B**) as a clear oil (2.67 g, 15.67 mmol, 96%); R_f = 0.25 (EtOAc/Hex 1:9). ¹H NMR (400 MHz, CDCl₃): δ 5.35 (t, J = 7.2 Hz, 1H), 4.11 (d, J = 6.4 Hz, 2H), 2.06 – 1.92 (m, 4H), 1.40 – 1.19 (m, 8H), 0.87 (t, J = 7.1 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 144.4, 123.3, 59.2, 36.5, 31.1, 30.2, 30.1, 22.8, 22.5, 14.0, 13.9. The analytical data of the compound was in complete agreement with the literature.⁶

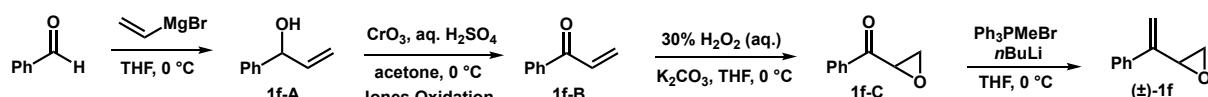
3-butylhept-2-enal (1e-C): To a well stirred solution oxalyl chloride (2.57 g, 1.73 mL, 20.25 mmol, 1.5 equiv.) in anhydrous dichloromethane (40 mL) was added a solution of freshly distilled dimethylsulfoxide (3.16 g, 2.876 mL, 40.50 mmol, 3 equiv.) in dichloromethane (30 mL) dropwise at –78 °C. The reaction mixture was stirred for 30 minutes. 2,3-butylhept-2-en-1-ol (**1e-B**) (2.3 g, 13.50 mmol, 1 equiv.) dissolved in dichloromethane (25 mL) was then added to this solution. After one hour, triethylamine (8.2 g, 11.28 mL, 81 mmol, 6 equiv.) was added. The resulting mixture was stirred at –78°C for one hour and then at –45°C for another one hour. When the starting material was consumed, the reaction was quenched with ice water and extracted with dichloromethane (3 x 50 mL). The combined organic phases were washed with brine, dried over Na₂SO₄, filtered and concentrated in vacuo. The crude mixture was then used in the next step without further purification. The crude product was a pale-yellow oil. R_f = 0.72 (EtOAc/Hex 2:8).

5-allylidenenonane (1e-D): To freshly azeotroped methyltriphenylphosphonium bromide (6.98 g, 19.50 mmol, 1.5 equiv.) in THF (55 mL) at 0 °C was added nBuLi (1.6 M in hexane, 12.75 mL, 20.41 mmol, 1.57 equiv.). The reaction was allowed to stir at 0 °C for an hour, at which point 3-butylhept-2-enal (**1e-C**) (2.18 g, 13 mmol, 1 equiv.) in THF (10 ml) was added. After 30 minutes, the reaction mixture was quenched with water and the resulting mixture extracted with diethyl ether (3 x 50 mL). The combined organic layer was washed with brine and dried over Na₂SO₄. The solvent was concentrated in vacuo, until the solid began to precipitate out. At this point, hexane was added to further precipitate the solid. The mixture was filtered through celite and the remaining solvent was removed. This crude mixture was then used in the next step without further purification. R_f = 0.90 (Hex).

2,2-dibutyl-3-vinyloxirane ((±)-1e): m-Chloroperbenzoic acid (75%, 1.45 g, 8.42 mmol, 1 equiv.) (used after purification following the procedure described in the preparation method of compound **1c**) was added portion wise to a stirred slurry of the 5-allylidenenonane (**1e-D**) (1.4 g, 8.42 mmol, 1 equiv.) and sodium carbonate (2.23 g, 21.06 mmol, 2.5 equiv.) in methylene chloride (9.6 mL) at 0 °C. The resulting

mixture was stirred at 0 °C. After all the 5-allylidenenonane (**1e-D**) had been consumed (as shown by TLC) the mixture was filtered through celite pad and the precipitates were washed with dichloromethane. Removal of the solvent from the filtrate gave crude 2,2-dibutyl-3-vinyloxirane ((\pm)-**1e**) as an oil, which was further purified by column chromatography using neutral alumina eluting with 5% Et₂O/pentane to afford the pure product (0.65 g, 3.53 mmol, yield = 42%); R_f = 0.42 (EtOAc/Hex 0.5:9.5). ¹H NMR (400 MHz, CDCl₃): δ 5.73 (ddd, J = 17.2, 10.4, 7.2 Hz, 1H), 5.39 (ddd, J = 17.2, 1.6, 0.8 Hz, 1H), 5.28 (ddd, J = 10.8, 1.6, 0.8 Hz, 1H), 3.15 (d, J = 7.2 Hz, 1H), 1.62 – 1.20 (m, 12H), 0.87 (td, J = 6.8, 4.0 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 133.5, 119.6, 65.41, 63.4, 34.7, 29.8, 27.3, 26.8, 22.9, 22.8, 14.0, 14.0. The analytical data of the compound was in complete agreement with the literature.⁶

Synthesis of 1,2-Epoxy-3-(phenyl)-3-butene ((\pm)-**1f**):

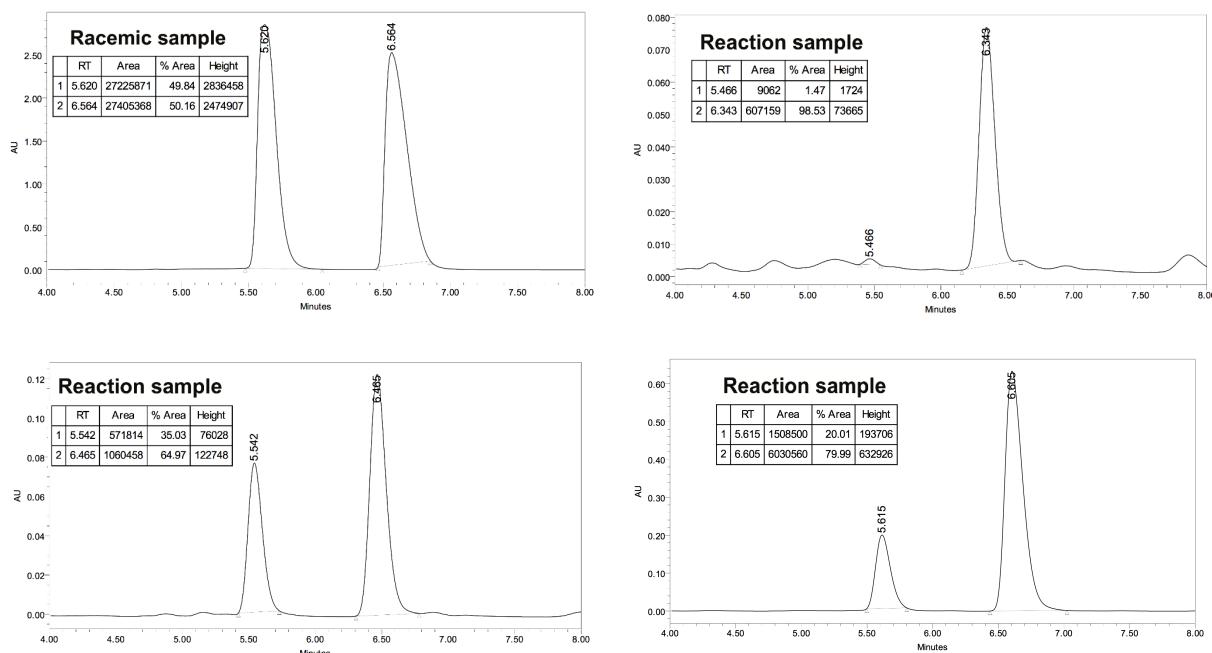


1-phenylprop-2-en-1-ol (1f-A): To a solution of benzaldehyde (5 g, 5 mL, 47.11 mmol, 1 equiv.) in THF (50 mL) at 0 °C was added vinyl magnesium bromide (1.0 M in THF, 94.22 mL, 94.22 mmol, 2 equiv.). The reaction was monitored by TLC. After completion, the reaction was quenched with saturated aqueous NH₄Cl solution and the resulting mixture was extracted with ethyl acetate (3 x 150 mL). The layers were separated and the aqueous layer was extracted with ethyl acetate (3 x 150 mL). The combined organic layers were washed with a saturated brine solution and dried over Na₂SO₄. The organic layers were concentrated in vacuo and After chromatography (10% EtOAc/hexane), product **1f-A** was obtained as a clear oil (6.26 g, 46.66 mmol, 99% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.30 (d, J = 4.4 Hz, 4H), 7.24 (dd, J = 8.4, 4 Hz, 1H), 6.02 – 5.94 (ddd, J = 16.8, 10.4, 6.4 Hz, 1H), 5.29 – 5.25 (m, 1H), 5.14–5.11 (m, 2H), 2.53 (br s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 142.7, 140.3, 128.6, 127.7, 126.4, 115.1, 75.3. The analytical data of the compound was in complete agreement with the literature.⁷

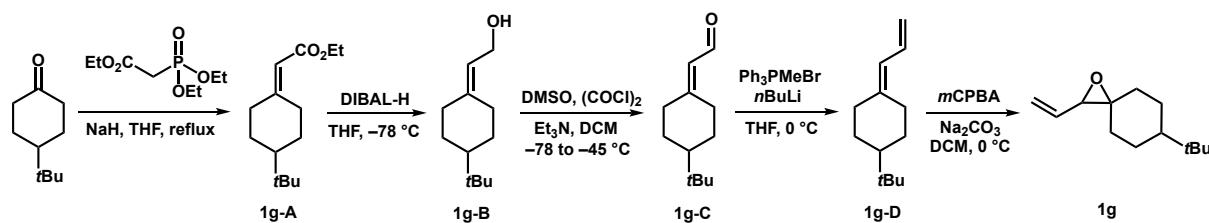
1-phenylprop-2-en-1-one (1f-B): To a solution of 1-phenylprop-2-en-1-ol (**1f-A**) (6.26 g, 46.66 mmol, 1.0 equiv.) in acetone (100 mL) at 0 °C was added Jones reagent (2.5 M, 18.66 mL, 46.66 mmol, 1.0 equiv.). The reaction was monitored by TLC . After completion (20-30 minutes), the reaction was quenched with isopropanol. Water and dichloromethane were added and the layers were separated. The aqueous layer was extracted with dichloromethane (3 x 150 mL), washed with brine and dried over Na₂SO₄. The organic layers were concentrated in vacuo and after purification by column chromatography (5% EtOAc/hexane), product **1f-B** was obtained as a slightly green oil (6.05 g, 45.72 mmol, 98% yield). R_f = 0.6 (EtOAc/Hex 1:9). ¹H NMR (400 MHz, CDCl₃): δ 7.90 (dd, J = 6.4, 0.8 Hz, 2H), 7.53 – 7.49 (m, 1H), 7.44 – 7.40 (m, 2H), 7.24 – 7.05 (m, 1H), 6.39 (ddd, J = 16.8, 2.4, 1.2 Hz, 1H), 5.89 – 5.85 (m, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 191.0, 137.3, 133.0, 132.4, 130.1, 128.7, 128.6. The analytical data of the compound was in complete agreement with the literature.⁸

2,3-Epoxy-1-(phenyl)-1-propanone (1f-C): To a suspension of 1-phenylprop-2-en-1-one (**1f-B**) (6.05 g, 45.78 mmol, 1.0 equiv.) and K₂CO₃ (50.54 g, 366.24 mmol, 8.0 equiv.) in THF (80 mL) at 0 °C was added 30% H₂O₂ solution (140 mL). The reaction mixture was stirred for 9 h at 0 °C and monitored by TLC. After completion, the reaction was quenched with saturated aqueous NH₄Cl solution and the resulting mixture was extracted with ethyl acetate (3 x 150 mL). The combined organic layers were washed with brine and dried over Na₂SO₄. The organic layers were concentrated in vacuo and After chromatography (10% EtOAc/hexane), the product (**1f-C**) was obtained as a white solid (5.97 g, 40.28 mmol, 88% yield); R_f = 0.2 (EtOAc: Hex 1:9). ¹H NMR (500 MHz, CDCl₃): δ 8.03 – 8.00 (m, 2H), 7.62 – 7.59 (m, 1H), 7.48 (m, 2H), 4.21 (dd, J = 4.5, 2.5 Hz, 1H), 3.10 (dd, J = 6.5, 4.5 Hz, 1H), 2.95 (ddd, J = 6.5, 2.5, 1.5 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 194.7, 135.5, 133.9, 128.8, 128.4, 51.1, 47.5. The analytical data of the compound was in complete agreement with the literature.⁹

1,2-Epoxy-3-(phenyl)-3-butene ((\pm)-1f): To freshly azeotroped methyltriphenylphosphonium bromide (17.27 g, 48.35 mmol, 1.2 equiv.) in THF (100 mL) at 0 °C was added *n*BuLi (1.6 M in hexane, 42.80 mL, 68.47 mmol, 1.7 equiv.). The reaction was allowed to stir at 0 °C for an hour, at which point 2,3-Epoxy-1-(phenyl)-1-propanone (**1f-C**) (5.97 g, 40.28 mmol, 1.0 equiv.) was added. The reaction was monitored by TLC and after completion (ca. 30 minutes), the reaction mixture was quenched with water. The resulting mixture was extracted with ethyl acetate (3 x 150 mL). The combined organic layers were washed with brine and dried over Na₂SO₄. The organic layers were concentrated in vacuo, until the solid began to precipitate out. At this point, hexane was added to further precipitate the solid. The mixture was filtered and the remaining solvent was removed. The product ((\pm)-1f) was obtained as a clear oil (2.95 g, 20.14 mmol, 50% yield); R_f = 0.8 (EtOAc : Hex 1:9) after purification by chromatography with hexane using neutral alumina. ¹H NMR (400 MHz, CDCl₃): δ 7.45 – 7.43 (m, 2H), 7.37 – 7.30 (m, 3H), 5.43 (d, J = 1.2 Hz, 1H), 5.36 (t, J = 0.8 Hz, 1H), 3.67 (ddd, J = 4, 2.8, 1.2 Hz, 1H), 3.03 (dd, J = 6, 4 Hz, 1H), 2.62 (dd, J = 6, 2.4 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 144.6, 138.0, 128.5, 128.1, 126.2, 112.7. The analytical data of the compound was in complete agreement with the literature.¹⁰ HPLC: For reaction with [Ir]/(*S*)-L, (with 1 equiv. of ((\pm)-1f)) t_R = 5.5 min (minor), t_R = 6.3 min (major), 97% ee. For reaction with [Ir]/(S)-L, (with 4 equiv. of ((\pm)-1f)) t_R = 5.5 min (minor), t_R = 6.5 min (major), 30% ee. t_R = 5.6 min (minor), t_R = 6.6 min (major), 60% ee (Chiralcel OJ-H, 245 nm, 20% IPA-Hex, 1 ml/min). [α]_D^{28.9} –2.6 (c = 0.5, CHCl₃) for 60% ee of (*R*)-1f. The absolute stereochemistry of this compound was assigned in analogy to **1a**.¹¹



6-(*tert*-Butyl)-2-vinyl-1-oxaspiro[2.5]octane ((\pm)-1g):



Ethyl 2-(4-(*tert*-butyl)cyclohexylidene)acetate (1g-A): To a suspension of sodium hydride (60% dispersion in oil, 0.80 g, 21.0 mmol, 1.3 equiv.) in THF (27 mL), was added a solution of triethyl

phosphonoacetate (4.70 g, 4.30 mL, 21.0 mmol, 1.3 equiv.) in THF (10 ml), slowly over 30 minutes at 0 °C. The reaction mixture was stirred at 0 °C for one hour, then 4-(*tert*-butyl)cyclohexan-1-one (2.5 g, 2.54 mL, 16.2 mmol, 1.0 equiv.) was added dropwise at the same temperature. The reaction mixture was then stirred at room temperature for 18 h. After the completion of reaction, the reaction was quenched with water and the resulting mixture was extracted with diethyl ether. The combined organic layer was washed with brine, dried over Na₂SO₄ and evaporated under reduced pressure. The residue was purified by flash column chromatography eluting with a gradient of 0-10% ethyl acetate/hexanes to give compound (**1g-A**) as a clear oil (3.2 g, 14.7 mmol, 91%); R_f = 0.70 (EtOAc/Hex 1: 9). ¹H NMR (400 MHz, CDCl₃): δ 5.55 (s, 1H), 4.10 (q, J = 0.4 Hz, 2H), 3.84 (ddd, J = 8.4, 5.6, 3.2 Hz, 1H), 2.27 (dd, J = 13.2, 2.0 Hz, 1H), 2.11 (td, J = 13.2, 4.0 Hz, 1H), 1.92 – 1.88 (m, 2H), 1.79 (td, J = 13.6, 4.4 Hz, 1H), 1.25 – 1.19 (m, 4H), 1.14 – 1.07 (m, 2H), 0.82 (s, 9H). ¹³C NMR (125 MHz, CDCl₃): δ 166.9, 163.5, 112.7, 59.4, 47.8, 37.9, 32.4, 29.6, 29.2, 28.5, 27.5, 14.3. The analytical data of the compound was in complete agreement with the literature.¹²

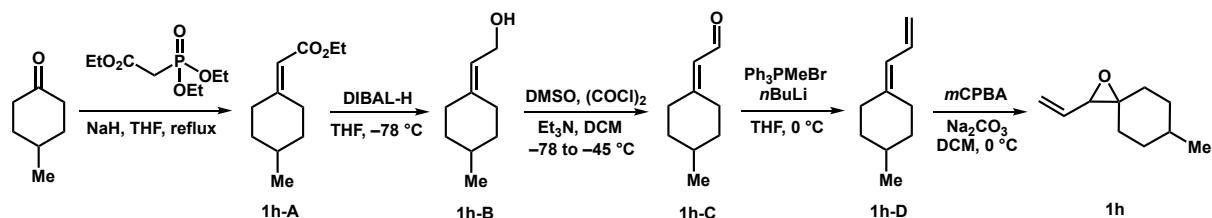
2-(4-(*tert*-Butyl)cyclohexylidene)ethan-1-ol (1g-B**):** To a cooled (-78 °C) solution of ethyl 2-(4-(*tert*-butyl)cyclohexylidene)acetate (**1g-A**) (3.20 g, 14.26 mmol, 1 equiv.) in dry THF (36 mL) was added a DIBAL-H (1 M in Toluene 43.0 mL, 43.0 mmol, 3 equiv.). After the reduction was complete (monitored by TLC), the reaction was quenched by the addition of saturated Rochelle's salt (5 ml). The biphasic mixture was stirred overnight and then extracted with EtOAc (3 x 60 mL), dried over Na₂SO₄, and the volatiles were removed under reduced pressure. The crude alcohol was purified by silica gel chromatography (0-20% ethyl acetate/hexanes) to give product (**1g-B**) as a clear oil (2.58 g, 14.11 mmol, yield = 99%); R_f = 0.41 (EtOAc/Hex 2:8). ¹H NMR (400 MHz, CDCl₃): δ 5.31 (t, J = 7.2 Hz, 1H), 4.09 (d, J = 7.2 Hz, 2H), 2.67 – 2.63 (m, 1H), 2.22 (dd, J = 13.2, 2.0 Hz, 1H), 2.00 (td, J = 13.2, 3.2 Hz, 1H), 1.85 – 1.80 (m, 2H), 1.70 (td, J = 13.2, 3.2 Hz, 1H), 1.18 – 0.9 (m, 4H), 0.81 (s, 9H). ¹³C NMR (125 MHz, CDCl₃): δ 144.2, 120.0, 58.5, 48.3, 36.9, 32.4, 29.0, 28.6, 28.5, 27.6. The analytical data of the compound was in complete agreement with the literature.¹³

2-(4-(*tert*-Butyl)cyclohexylidene)acetaldehyde (1g-C**):** To a well stirred solution oxalyl chloride (2.2 g, 1.48 mL, 17.3 mmol, 1.5 equiv.) in anhydrous dichloromethane (20 mL) was added a solution of freshly distilled dimethylsulfoxide (2.69 g, 2.5 ml, 34.5 mmol, 3 equiv.) in dichloromethane (20 mL) dropwise at -78 °C. The reaction mixture was stirred for 30 minutes. 2-(4-(*tert*-butyl)cyclohexylidene)ethan-1-ol (**1g-B**) (2.10 g, 11.5 mmol, 1 equiv.) dissolved in dichloromethane (20 mL) was then added to this solution. After one hour, triethylamine (6.93 g, 9.6 mL, 68.5 mmol, 6 equiv.) was added. The resulting mixture was stirred at -78°C for one hour and then at -45°C for another one hour. When the starting material was consumed, the reaction was quenched with ice water and extracted with dichloromethane (3 x 50 mL). The combined organic phases were washed with brine, dried over Na₂SO₄, filtered and concentrated in vacuo. The crude mixture was then used in the next step without further purification. The crude product was a pale-yellow oil. R_f = 0.50 (EtOAc/Hex 1:9).

1-Allylidene-4-(*tert*-butyl)cyclohexane (1g-D**):** To freshly azeotroped methyltriphenyl-phosphonium bromide (6.2 g, 17.3 mmol, 1.5 equiv.) in THF (40 mL) at 0 °C was added nBuLi (1.6 M in hexane, 12.2 mL, 19.6 mmol, 1.57 equiv.). The reaction was allowed to stir at 0 °C for an hour, at which point 2-(4-(*tert*-butyl)cyclohexylidene)acetaldehyde (**1g-C**) (2.0 g, 11.5 mmol, 1 equiv.) in THF (17 ml) was added. After 30 minutes, the reaction mixture was quenched with water and the resulting mixture extracted with diethyl ether (3 x 60 mL). The combined organic layer was washed with brine and dried over Na₂SO₄. The solvent was concentrated in vacuo, until the solid began to precipitate out. At this point, hexane was added to further precipitate the solid. The mixture was filtered through celite and the remaining solvent was removed. This crude mixture was then used in the next step without further purification. R_f = 0.95 (EtOAc/Hex 1:9).

6-(tert-butyl)-2-vinyl-1-oxaspiro[2.5]octane (1g**):** *m*-Chloroperbenzoic acid (75%, 1.53 g, 8.86 mmol, 1 equiv.) was added portion wise to a stirred slurry of the 1-allylidene-4-(tert-butyl)cyclohexane (**1g-D**) (1.58 g, 8.86 mmol, 1 equiv.) and sodium carbonate (2.4 g, 22.2 mmol, 2.5 equiv.) in methylene chloride (11.0 mL) at 0 °C. The resulting mixture was stirred at 0 °C. After all the 1-allylidene-4-(tert-butyl)cyclohexane (**1g-D**) had been consumed (as shown by TLC) the mixture was filtered through celite pad and the precipitates were washed with dichloromethane. Removal of the solvent from the filtrate gave crude 6-(*tert*-butyl)-2-vinyl-1-oxaspiro[2.5]octane (**1g**) as an oil, which was further purified by column chromatography using neutral alumina eluting with 5% Et₂O/pentane to afford the pure product (0.98 g, 5.05 mmol, yield = 57%); R_f = 0.4 (EtOAc/Hex 0.5:9.5). ¹H NMR (300 MHz, CDCl₃): δ 5.76 – 5.64 (m, 1H), 5.41 – 5.33 (m, 1H), 5.28 – 5.22 (m, 1H), 3.13 (dd, J = 9.6, 7.2 Hz, 1H), 1.85 – 1.47 (m, 5H), 1.34 – 1.19 (m, 3H), 1.10 – 0.94 (m, 1H), 0.80 (d, J = 6.0 Hz, 9H). ¹³C NMR (125 MHz, CDCl₃): δ 133.3, 119.8, 64.4, 47.7, 35.7, 32.5, 29.3, 27.7, 26.7, 26.1, 24.8. The ¹³C NMR shows extra peaks from the inseparable isomer of (**1g**).¹⁴ HRMS calcd for C₁₃H₂₃O (ESI⁺, [M+H]⁺): 195.1749, found 195.1736.

6-Methyl-2-vinyl-1-oxaspiro[2.5]octane ((±)-1h**):**



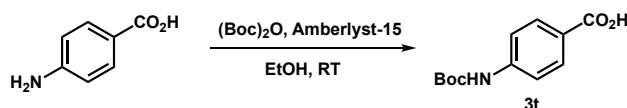
Ethyl 2-(4-methylcyclohexylidene)acetate (1h-A**):** To a suspension of sodium hydride (60% dispersion in oil, 1.37 g, 34.32 mmol, 1.1 equiv.) in THF (50 mL), was added a solution of triethyl phosphonoacetate (7.69 g, 7.05 mL, 34.32 mmol, 1.1 equiv.) in THF (20 mL), slowly over 30 minutes at 0 °C. The reaction mixture was stirred at 0 °C for one hour, then 4-methylcyclohexan-1-one (3.5 g, 3.85 mL, 31.20 mmol, 1.0 equiv.) was added dropwise at the same temperature. The reaction mixture was then stirred at room temperature for 18 h. After the completion of reaction, the reaction was quenched with water and the resulting mixture was extracted with diethyl ether. The combined organic layer was washed with brine, dried over Na₂SO₄ and evaporated under reduced pressure. The residue was purified by flash column chromatography eluting with a gradient of 0-10% ethyl acetate/hexanes to give compound (**1h-A**) as a clear oil (5.4 g, 29.64 mmol, 95%); R_f = 0.66 (EtOAc/Hex 0.5: 9.5). ¹H NMR (300 MHz, CDCl₃): δ 85.57 (s, 1H), 4.10 (q, J = 7.2 Hz, 2H), 3.70 (dt, J = 4.8, 3.6 Hz, 1H), 2.25 – 2.14 (m, 2H), 1.95 – 1.73z (m, 3H), 1.66 – 1.56 (m, 1H), 1.23 (t, J = 7.2 Hz, 3H), 1.16 – 0.96 (m, 2H), 0.87 (d, J = 6.6 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 166.8, 163.1, 113.1, 59.4, 37.3, 36.5, 35.8, 32.2, 29.0, 21.6, 14.3. The analytical data of the compound was in complete agreement with the literature.¹²

2-(4-Methylcyclohexylidene)ethan-1-ol (1h-B**):** To a cooled (-78 °C) solution of ethyl 2-(4-methylcyclohexylidene)acetate (**1h-A**) (3.50 g, 19.2 mmol, 1 equiv.) in dry THF (50 mL) was added a DIBAL-H (1 M in Toluene 57.6 mL, 57.6 mmol, 3 equiv.). After the reduction was complete (monitored by TLC), the reaction was quenched by the addition of saturated Rochelle's salt (5 mL). The biphasic mixture was stirred overnight and then extracted with EtOAc (4 x 90 mL), dried over Na₂SO₄, and the volatiles were removed under reduced pressure. The crude alcohol was purified by silica gel chromatography (0-20% ethyl acetate/hexanes) to give product (**1h-B**) as a clear oil (3.13 g, 20.5 mmol, 89%); R_f = 0.43 (EtOAc/Hex 2:8). ¹H NMR (400 MHz, CDCl₃): δ 5.34 (t, J = 7.2 Hz, 1H), 4.10 (d, J = 7.2 Hz, 2H), 2.62 – 2.52 (m, 1H), 2.18 – 2.15 (m, 1H), 2.09 – 1.96 (m, 1H), 1.86 – 1.69 (m, 3H), 1.57 – 1.52 (m, 1H), 1.37 (s, 1H), 1.01 – 0.93 (m, 2H), 0.87 (d, J = 6.4 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 143.9, 120.5, 58.6, 36.5, 36.3, 36.0, 32.7, 28.1, 21.9. The analytical data of the compound was in complete agreement with the literature.¹⁵

2-(4-Methylcyclohexylidene)acetaldehyde (1h-C**):** To a well stirred solution oxalyl chloride (2.17 g, 1.47 mL, 17.11 mmol, 1.5 equiv.) in anhydrous dichloromethane (20 mL) was added a solution of freshly distilled dimethylsulfoxide (2.67 g, 2.43 mL, 34.23 mmol, 3 equiv.) in dichloromethane (20 mL) dropwise at -78 °C. The reaction mixture was stirred for 30 minutes. 2-(4-methylcyclohexylidene)ethan-1-ol (**1h-B**) (2.08 g, 11.41 mmol, 1 equiv.) dissolved in dichloromethane (20 mL) was then added to this solution. After one hour, triethylamine (6.93 g, 9.6 mL, 68.46 mmol, 6 equiv.) was added. The resulting mixture was stirred at -78°C for one hour and then at -45°C for another one hour. When the starting material was consumed, the reaction was quenched with ice water and extracted with dichloromethane (3 x 50 mL). The combined organic phases were washed with brine, dried over Na₂SO₄, filtered and concentrated in vacuo. The crude mixture was then used in the next step without further purification. The crude product was a pale-yellow oil. R_f = 0.62 (EtOAc/Hex 2:8).

1-Allylidene-4-methylcyclohexane (1h-D**):** To freshly azeotroped methyltriphenyl-phosphonium bromide (4.84 g, 13.5 mmol, 1.5 equiv.) in THF (30 mL) at 0 °C was added nBuLi (1.6 M in hexane, 8.83 mL, 14.1 mmol, 1.57 equiv.). The reaction was allowed to stir at 0 °C for an hour, at which point 2-(4-methylcyclohexylidene)acetaldehyde (**1h-C**) (1.62 g, 9.0 mmol, 1 equiv.) in THF (15 mL) was added. After 30 minutes, the reaction mixture was quenched with water and the resulting mixture extracted with diethyl ether (3 x 50 mL). The combined organic layer was washed with brine and dried over Na₂SO₄. The solvent was concentrated in vacuo, until the solid began to precipitate out. At this point, hexane was added to further precipitate the solid. The mixture was filtered through celite and the remaining solvent was removed. This crude mixture was then used in the next step without further purification. R_f = (EtOAc/Hex 0.5: 9.5)

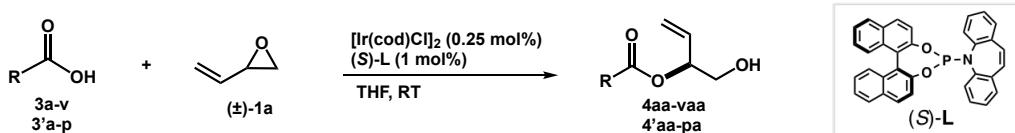
6-Methyl-2-vinyl-1-oxaspiro[2.5]octane (1h**):** m-Chloroperbenzoic acid (75%, 1.45 g, 8.41 mmol, 1 equiv.) was added portion wise to a stirred slurry of the 1-allylidene-4-methylcyclohexane (**1h-D**) (1.5 g, 8.41 mmol, 1 equiv.) and sodium carbonate (2.23 g, 21.0 mmol, 2.5 equiv.) in dichloromethane (10 mL) at 0 °C. The resulting mixture was stirred at 0 °C. After all the 1-allylidene-4-methylcyclohexane (**1h-D**) had been consumed (as shown by TLC) the mixture was filtered through celite pad and the precipitates were washed with dichloromethane. Removal of the solvent from the filtrate gave crude 6-methyl-2-vinyl-1-oxaspiro[2.5]octane (**1h**) as an oil, which was further purified by column chromatography using neutral alumina eluting with 5% Et₂O/pentane to afford the pure product (0.80 g, 5.30 mmol, yield = 63%); R_f = 0.65 (Ether/Pentane 0.5:9.5). ¹H NMR (400 MHz, CDCl₃): δ 5.79 – 5.66 (m, 1H), 5.44 – 5.37 (m, 1H), 5.32 – 5.23 (m, 1H), 3.25 – 3.10 (m, 1H), 1.98 – 1.22 (m, 9H), 1.05 – 0.79 (m, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 133.1, 119.8, 64.2, 63.9, 34.2, 34.0, 32.3, 31.8, 28.4, 22.0. The ¹³C NMR shows extra peaks from the inseparable isomer of (**1h**). ¹⁴ HRMS calcd for C₁₀H₁₆OH (ESI⁺, [M+H]⁺): 153.1279, found 153.1257.



Preparation of 4-((tert-butoxycarbonyl)amino)benzoic acid (3t**):** 4-aminobenzoic acid (0.082 g, 0.6 mmol, 1 equiv.) was added to a magnetically stirred mixture of Amberlyst-15 (0.048 g, 10 mol% 0.1 equiv.) and di-tert-butyl dicarbonate (0.26 g, 1.2 mmol, 2 equiv.) in 0.6 mL EtOH at room temperature. The reaction mixture was stirred until a clear solution was obtained. After completion of the reaction (followed by TLC), the catalyst was separated by filtration through a celite pad. The filtrate was concentrated under reduced pressure, and the residue was washed with hexane (10 mL) to afford the pure product 4-((tert-butoxycarbonyl)amino)benzoic acid (**3t**) as an amorphous solid (0.11 g, 0.48 mmol, 80% yield); R_f = 0.48 (EtOAc/Hex 1:1). ¹H NMR (400 MHz, MeOD): δ 7.79 (d, J = 8.8 Hz, 1H), 7.37 (d, J = 8.8 Hz, 1H), 1.37 (s, 9H). ¹³C NMR (100 MHz, MeOD): δ 168.4, 153.4, 143.9, 130.5, 124.0, 117.3,

117.2, 80.0, 27.3. The analytical data of the compound was in complete agreement with the literature.¹⁶

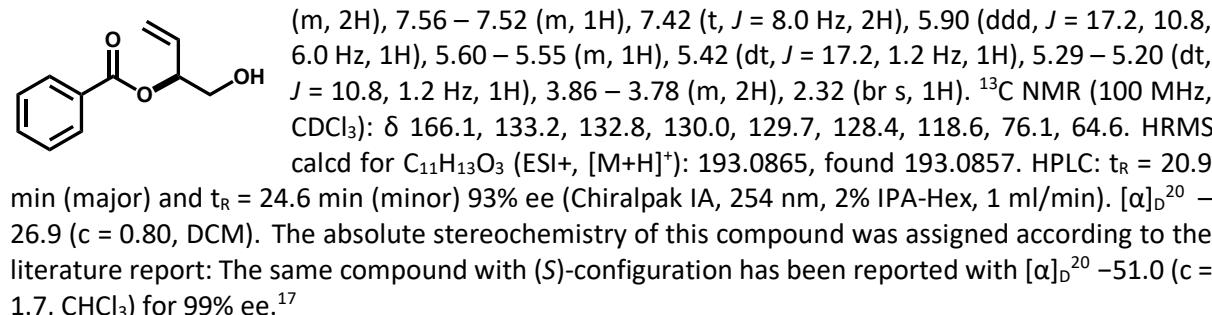
5. General Procedure for Catalytic Asymmetric ring opening of epoxides using carboxylic acids



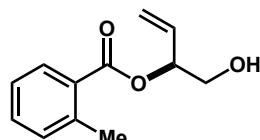
An oven-dried 5 mL screw cap glass vial equipped with a magnetic stirring bar was charged with $[\text{Ir}(\text{COD})\text{Cl}]_2$ (0.34 mg, 0.0005 mmol, 0.0025 equiv., 0.25 mol%), and (S)-L (1.0 mg, 0.002 mmol, 0.01 equiv.) under N_2 atmosphere. To this mixture, dry THF (1 mL) was added via a gas-tight syringe with a stainless steel needle. The mixture was stirred for 15 min to give a clear catalyst solution at room temperature. To this, was added the carboxylic acid (**3a-v**, **3'a-p**) (0.2 mmol) and finally the vinyl oxirane ((\pm)-**1a**) (56 mg, 64 μl , 0.8 mmol). The reaction mixture was stirred at room temperature and was monitored by TLC under ultraviolet light ($\lambda = 254 \text{ nm}$), bromocresol green and KMnO_4 stains. After the reaction was over, the reaction mixture was filtered through a short pad of celite and the volatiles were evaporated to give the desired product in pure form. No further column purification was necessary.

6. Characterization of vinyl oxirane ring opened products:

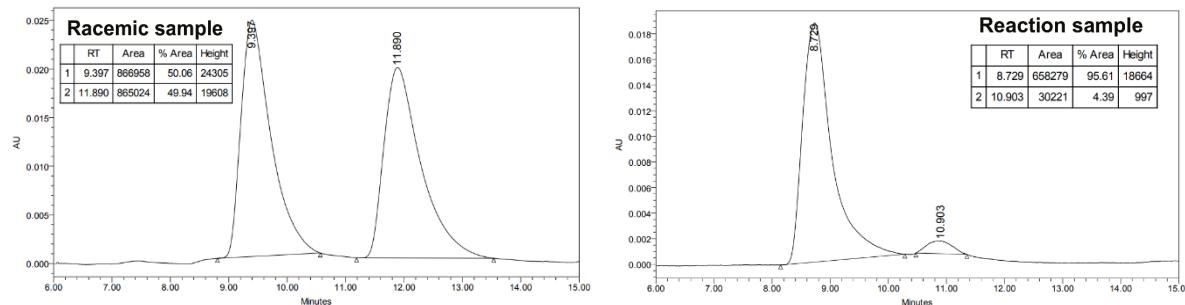
(S)-1-hydroxybut-3-en-2-yl benzoate (4aa): Prepared according to the general procedure from benzoic acid (**3a**) (24.4 mg, 0.2 mmol) and vinyl oxirane ((\pm)-**1a**) (56 mg, 64 μl , 0.8 mmol). Reaction time: 2.5 h. Yield: 97% (37.3 mg, 0.19 mmol). Pale yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 8.06 – 8.04 (m, 2H), 7.56 – 7.52 (m, 1H), 7.42 (t, $J = 8.0 \text{ Hz}$, 2H), 5.90 (ddd, $J = 17.2, 10.8, 6.0 \text{ Hz}$, 1H), 5.60 – 5.55 (m, 1H), 5.42 (dt, $J = 17.2, 1.2 \text{ Hz}$, 1H), 5.29 – 5.20 (dt, $J = 10.8, 1.2 \text{ Hz}$, 1H), 3.86 – 3.78 (m, 2H), 2.32 (br s, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 166.1, 133.2, 132.8, 130.0, 129.7, 128.4, 118.6, 76.1, 64.6. HRMS calcd for $\text{C}_{11}\text{H}_{13}\text{O}_3$ (ESI+, $[\text{M}+\text{H}]^+$): 193.0865, found 193.0857. HPLC: $t_R = 20.9$ min (major) and $t_R = 24.6$ min (minor) 93% ee (Chiralpak IA, 254 nm, 2% IPA-Hex, 1 ml/min). $[\alpha]_D^{20} = -26.9$ ($c = 0.80$, DCM). The absolute stereochemistry of this compound was assigned according to the literature report: The same compound with (S)-configuration has been reported with $[\alpha]_D^{20} = -51.0$ ($c = 1.7$, CHCl_3) for 99% ee.¹⁷



(S)-1-hydroxybut-3-en-2-yl 2-methylbenzoate (4ba): Prepared according to the general procedure from *o*-toluic acid (**3b**) (27.2 mg, 0.2 mmol) and vinyl oxirane ((\pm)-**1a**) (56 mg, 64 μl , 0.8 mmol). Reaction time: 7 h. Yield: 96% (39.6 mg, 0.19 mmol). Pale yellow oil; ^1H NMR (500 MHz, CDCl_3): δ 7.93 – 7.95 (dd, $J = 8.5, 1.5 \text{ Hz}$, 1H), 7.39 (td, $J = 7.5, 1.5 \text{ Hz}$, 1H), 7.25 – 7.20 (m, 2H), 5.91 (ddd, $J = 17.0, 10.5, 6.0 \text{ Hz}$, 1H).

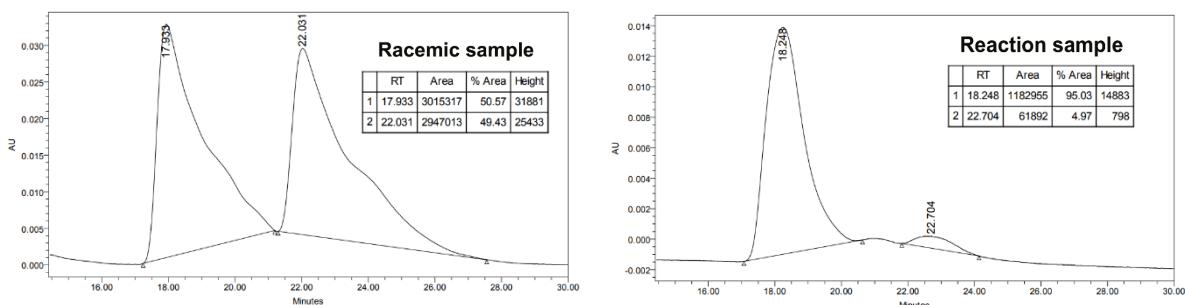


Hz, 1H), 5.60–5.55 (m, 1H), 5.43 (dt, J = 17.0, 1.5 Hz, 1H), 5.31 (dt, J = 10.5, 1.0 Hz, 1H), 3.89 – 3.74 (m, 2H), 2.59 (s, 3H), 2.28 (br s, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ 167.1, 140.4, 133.0, 132.2, 131.8, 130.6, 129.4, 125.8, 118.7, 76.0, 64.6, 21.8. HRMS calcd for $\text{C}_{12}\text{H}_{15}\text{O}_3$ (ESI^+ , $[\text{M}+\text{H}]^+$): 207.1021, found 207.1016. HPLC: $t_{\text{R}} = 8.7$ min (major) and $t_{\text{R}} = 10.9$ min (minor) 91% ee (Chiralpak IA, 254 nm, 5% IPA-Hex, 1 ml/min). $[\alpha]_D^{20} -20.0$ ($c = 0.81$, DCM). The absolute stereochemistry of this compound was assigned in analogy to **4aa**.



(S)-1-hydroxybut-3-en-2-yl 3-methylbenzoate (4ca): Prepared according to the general procedure from *m*-toluic acid (**3c**) (27.2 mg, 0.2 mmol) and vinyl oxirane ((\pm) -**1a**) (56 mg, 64 μl , 0.8 mmol).

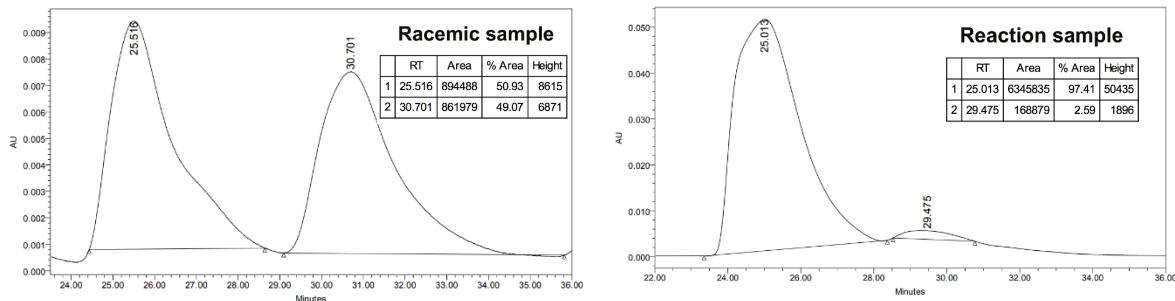
Reaction time: 7 h. Yield: 98% (40.4 mg, 0.196 mmol). Pale yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.90 – 7.80 (m, 2H), 7.39 – 7.28 (m, 2H), 5.91 (ddd, J = 16.8, 10.4, 5.6 Hz, 1H), 5.66 – 5.52 (m, 1H), 5.43 (dt, J = 17.2, 1.2 Hz, 1H), 5.31 (dt, J = 10.4, 1.2 Hz, 1H), 3.92 – 3.74 (m, 2H), 2.39 (s, 3H), 2.06 (br s, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 166.3, 138.3, 134.0, 132.9, 130.2, 129.9, 128.3, 126.9, 118.6, 76.0, 64.6, 21.2. HRMS calcd for $\text{C}_{12}\text{H}_{15}\text{O}_3$ (ESI^+ , $[\text{M}+\text{H}]^+$): 207.1021, found 207.1012. HPLC: $t_{\text{R}} = 18.2$ min (major) and $t_{\text{R}} = 22.7$ min (minor) 90% ee (Chiralpak IA, 254 nm, 2% IPA-Hex, 1 ml/min). $[\alpha]_D^{20} -32.9$ ($c = 0.69$, DCM). The absolute stereochemistry of this compound was assigned in analogy to **4aa**.



(S)-1-hydroxybut-3-en-2-yl 4-methylbenzoate (4da): Prepared according to the general procedure from *p*-toluic acid (**3d**) (27.2 mg, 0.2 mmol) and vinyl oxirane ((\pm) -**1a**) (56 mg, 64 μl , 0.8 mmol).

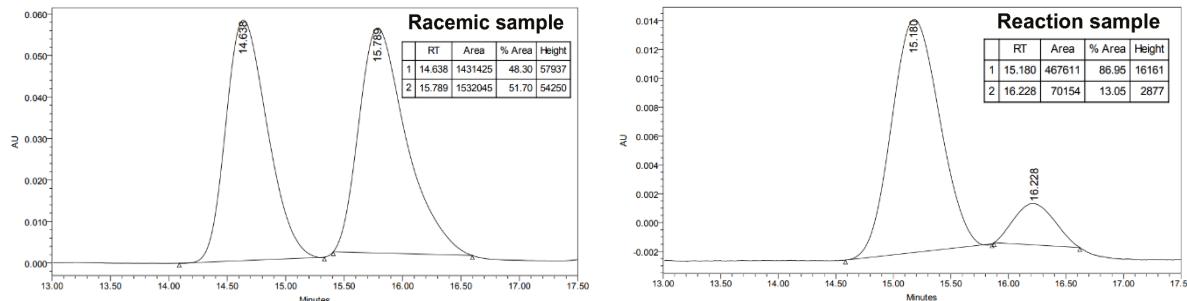
Reaction time: 6.5 h. Yield: 98% (40.4 mg, 0.196 mmol). Pale yellow oil; ^1H NMR (500 MHz, CDCl_3): δ 7.85 (d, J = 8.0 Hz, 2H), 7.12 (d, J = 8.0 Hz, 2H), 5.81 (ddd, J = 17.0, 10.5, 5.5 Hz, 1H), 5.47 (dd, J = 10.5, 5.5 Hz, 1H), 5.32 (d, J = 17.5 Hz, 1H), 5.19 (d, J = 10.5 Hz, 1H), 3.72 (t, J = 6.0 Hz, 2H), 2.29 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 166.2, 144.0, 133.0, 129.8, 129.1, 127.3, 118.5, 75.9, 64.6, 21.7. HRMS calcd for $\text{C}_{12}\text{H}_{15}\text{O}_3$ (ESI^+ , $[\text{M}+\text{H}]^+$): 207.1021, found 207.1015. HPLC: $t_{\text{R}} = 25.0$ min (major) and $t_{\text{R}} = 29.5$ min (minor) 95% ee (Chiralpak IA, 254 nm, 2% IPA-Hex, 1

ml/min). $[\alpha]_D^{20} -31.7$ ($c = 0.81$, DCM). The absolute stereochemistry of this compound was assigned in analogy to **4aa**.

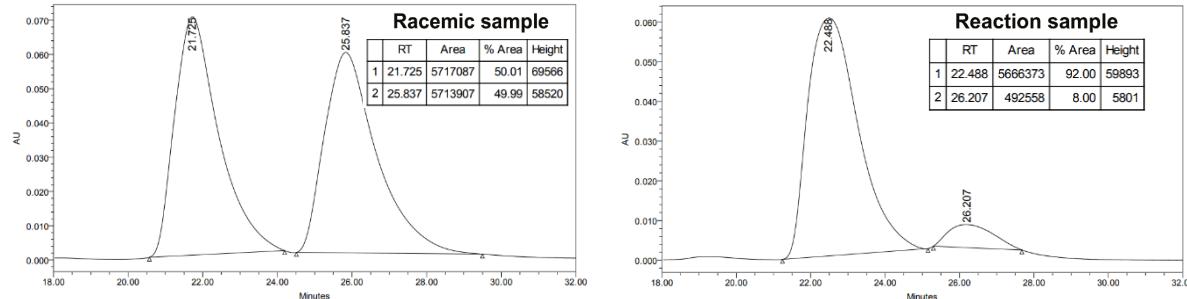


(S)-1-hydroxybut-3-en-2-yl 2-iodobenzoate (4ea): Prepared according to the general procedure from 2-iodobenzoic acid (**3e**) (49.6 mg, 0.2 mmol) and vinyl oxirane ((\pm)-**1a**) (56 mg, 64 μ L, 0.8 mmol).

Reaction time: 5 h. Yield: 95% (60.4 mg, 0.19 mmol). Pale yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.96 (dd, $J = 8.0, 0.8$ Hz, 1H), 7.81 (dd, $J = 7.6, 1.6$ Hz, 1H), 7.39 (td, $J = 7.6, 0.8$ Hz, 1H), 7.14 (td, $J = 7.6, 1.6$ Hz, 1H), 5.92 (ddd, $J = 17.2, 10.8, 6.4$ Hz, 1H), 5.62 – 5.53 (m, 1H), 5.45 (dt, $J = 17.2, 1.2$ Hz, 1H), 5.33 (dt, $J = 10.4, 1.2$ Hz, 1H), 3.92 – 3.76 (m, 2H), 2.22 (br s, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 165.9, 141.3, 135.2, 132.8, 132.4, 131.2, 128.0, 119.3, 93.9, 77.2, 64.3. HRMS calcd for $\text{C}_{11}\text{H}_{12}\text{IO}_3$ ($\text{ESI}^+, [\text{M}+\text{H}]^+$): 318.9831, found 318.9827. HPLC: $t_R = 15.2$ min (major) and $t_R = 16.2$ min (minor) 74% ee (Chiralcel OD-H, 254 nm, 5% IPA-Hex, 1 ml/min). $[\alpha]_D^{28.3} -11.96$ ($c = 1.0$, CHCl_3). The absolute stereochemistry of this compound was assigned in analogy to **4aa**.

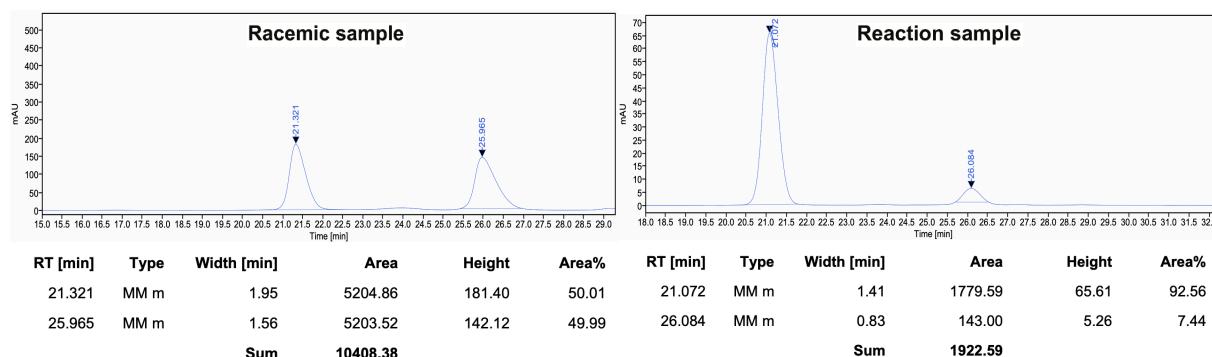


(S)-1-hydroxybut-3-en-2-yl [1,1'-biphenyl]-2-carboxylate (4fa): Prepared according to the general procedure from 2-phenylbenzoic acid (**3f**) (39.4 mg, 0.2 mmol) and vinyl oxirane ((\pm)-**1a**) (56 mg, 64 μ L, 0.8 mmol). Reaction time: 7 h. Yield: 97% (52.0 mg, 0.194 mmol). Pale yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.87 (dd, $J = 7.6, 1.2$ Hz, 1H), 7.52 (td, $J = 7.6, 1.6$ Hz, 1H), 7.45 – 7.37 (m, 4H), 7.35 – 7.31 (m, 3H), 5.58 (ddd, $J = 17.2, 10.8, 6.4$ Hz, 1H), 5.31 – 5.24 (m, 1H), 5.22 – 5.13 (m, 2H), 3.46 – 3.26 (m, 2H), 1.48 (br s, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 168.2, 142.2, 142.0, 132.5, 131.4, 130.9, 130.7, 130.2, 128.4, 128.3, 127.5, 127.4, 118.6, 76.7, 64.2. HRMS calcd for $\text{C}_{17}\text{H}_{17}\text{O}_3$ ($\text{ESI}^+, [\text{M}+\text{H}]^+$): 269.1178, found 269.1175. HPLC: $t_R = 22.5$ min (major) and $t_R = 26.2$ min (minor) 84% ee (Chiralpak IA, 254 nm, 2% IPA-Hex, 1 ml/min). $[\alpha]_D^{20} -20.4$ ($c = 1.20$, DCM). The absolute stereochemistry of this compound was assigned in analogy to **4aa**.



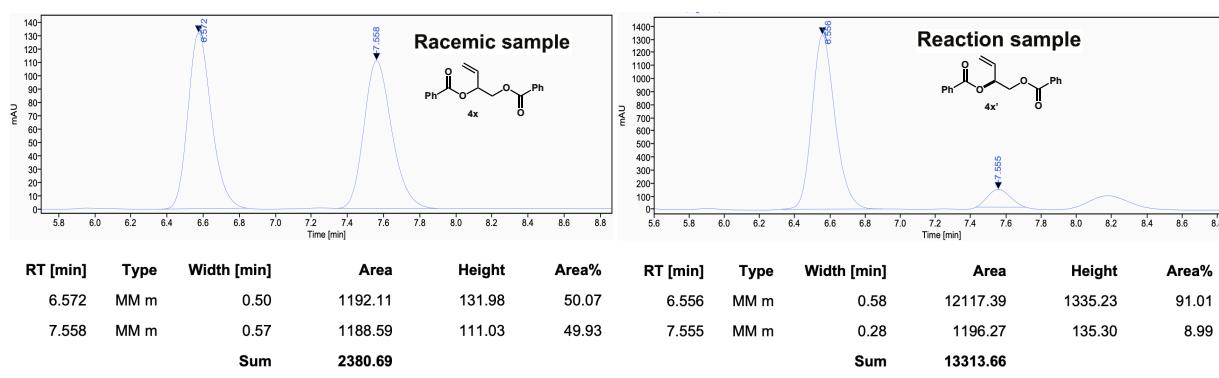
(S)-1-hydroxybut-3-en-2-yl 4-fluorobenzoate (4ga): Prepared according to the general procedure from 4-fluorobenzoic acid (**3g**) (28.0 mg, 0.2 mmol) and vinyl oxirane ((\pm)-**1a**) (56 mg, 64 μ l, 0.8 mmol).

Reaction time: 3 h. Yield: 98% (41.2 mg, 0.196 mmol). Pale yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 8.16 – 7.98 (m, 2H), 7.15 – 7.02 (m, 2H), 5.89 (ddd, J = 16.8, 10.8, 6.0 Hz, 1H), 5.64 – 5.51 (m, 1H), 5.41 (dt, J = 17.2, 1.2 Hz, 1H), 5.31 (dt, J = 10.8, 1.2 Hz, 1H), 3.91 – 3.71 (m, 2H), 2.31 (br s, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 167.2, 165.2, 164.7, 132.7, 132.3, 132.4, 126.3, 118.7, 115.7, 115.5, 76.3, 64.5. HRMS calcd for $\text{C}_{11}\text{H}_{12}\text{FO}_3$ (ESI^+ , [M+H] $^+$): 211.0770, found 211.0759. HPLC: t_{R} = 21.1 min (major) and t_{R} = 26.1 min (minor) 85% ee (Chiralpak IA, 254 nm, 2% IPA-Hex, 1 ml/min). $[\alpha]_D^{20}$ –23.9 (c = 0.81, DCM). The absolute stereochemistry of this compound was assigned in analogy to **4aa**.

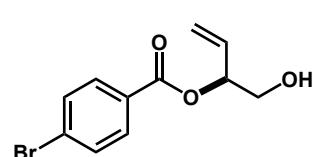


(S)-1-hydroxybut-3-en-2-yl 4-chlorobenzoate (4ha): Prepared according to the general procedure from 4-chlorobenzoic acid (**3h**) (31.3 mg, 0.2 mmol) and vinyl oxirane ((\pm)-**1a**) (56 mg, 64 μ l, 0.8 mmol).

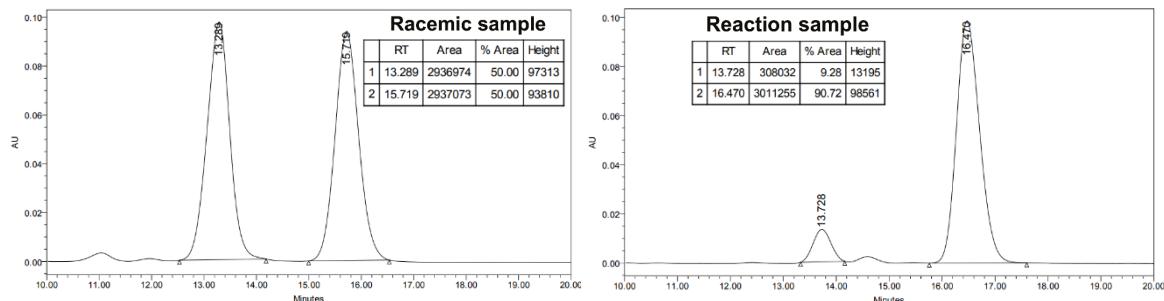
Reaction time: 20 h. Yield: 96% (43.5 mg, 0.192 mmol). Pale yellow oil; ^1H NMR (500 MHz, CDCl_3): δ 7.98 (d, J = 8.5 Hz, 2H), 7.39 (d, J = 8.5 Hz, 2H), 5.89 (ddd, J = 17, 10.5, 5.5 Hz, 1H), 5.59 – 5.55 (m, 1H), 5.41 (d, J = 17 Hz, 1H), 5.30 (d, J = 10.5 Hz, 1H), 3.86 – 3.79 (m, 2H), 2.54 (br s, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ 165.3, 139.7, 132.7, 131.1, 128.8, 128.5, 118.8, 76.4, 64.4. HRMS calcd for $\text{C}_{11}\text{H}_{12}\text{ClO}_3$ (ESI^+ , [M+H] $^+$): 227.0475, found 227.0466. For the determination of enantiomeric excess of **4ha**, the compound **4ha** was converted to the corresponding diol dibenzoylate **4x'**. HPLC: t_{R} = 6.6 min (major) and t_{R} = 7.6 min (minor) 82% ee (Chiralpak IG, 280 nm 20% IPA-Hex, 1 ml/min). $[\alpha]_D^{26.2}$ –32.01 (c = 1.5, CHCl_3). The absolute stereochemistry of this compound was assigned in analogy to **4aa**.



(S)-1-hydroxybut-3-en-2-yl 4-bromobenzoate (4ia): Prepared according to the general procedure from 4-bromobenzoic acid (**3i**) (40.2 mg, 0.2 mmol) and vinyl oxirane ((\pm)-**1a**) (56 mg, 64 μ l, 0.8 mmol). Reaction time: 3 h. Yield: 95% (51.5 mg, 0.19 mmol). Pale yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.90 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 8.8 Hz, 2H), 5.89 (ddd, J = 17.2, 10.8, 6.0 Hz, 1H), 5.58 – 5.54 (m, 1H), 5.41 (d, J = 17.2 Hz, 1H), 5.31 (d, J = 10.4 Hz, 1H), 3.86 – 3.78 (m, 2H),

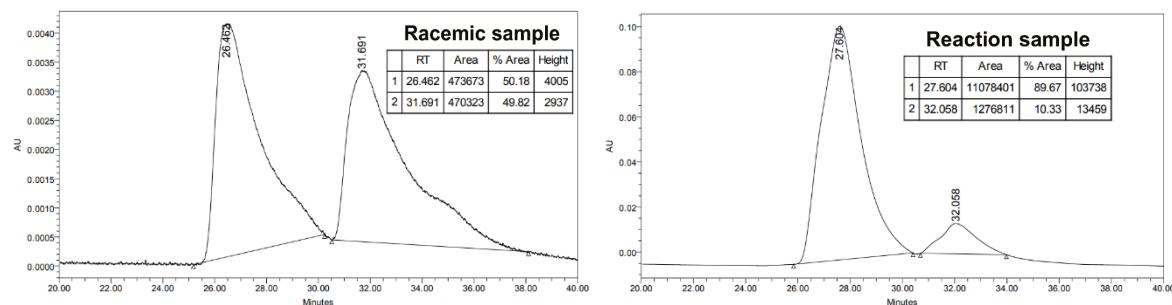


2.31 (br s, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 165.4, 132.6, 131.8, 131.2, 128.9, 128.4, 118.9, 76.4, 64.5. HRMS calcd for $\text{C}_7\text{H}_4\text{BrO}_2$ (ESI^- , $[\text{M}-\text{H}]^-$ -[$\text{C}_4\text{H}_6\text{O}$]): 198.9395, found 198.9401. HPLC: $t_{\text{R}} = 13.7$ min (minor) and $t_{\text{R}} = 16.5$ min (major) 82% ee (Chiralcel OD-H, 254 nm, 5% IPA-Hex, 1 ml/min). $[\alpha]_D^{25.9} -34.9$ ($c = 1.2$, CHCl_3). The absolute stereochemistry of this compound was assigned in analogy to **4aa**.



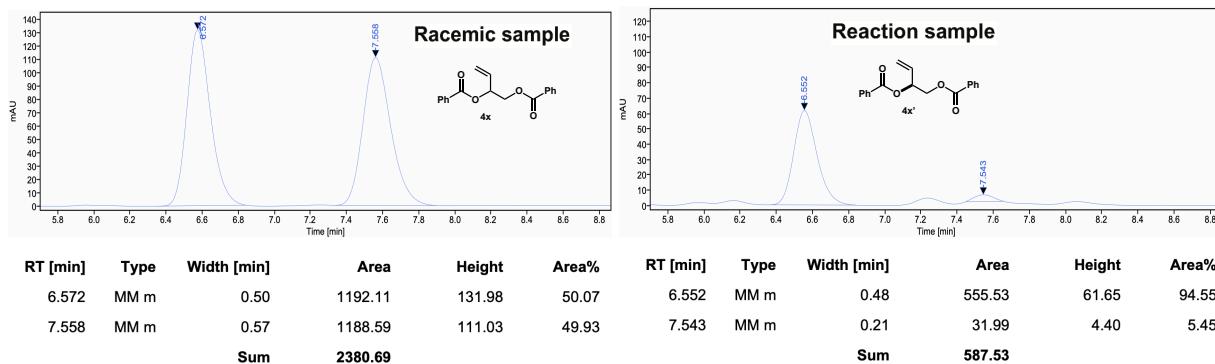
(S)-1-hydroxybut-3-en-2-yl 4-cyanobenzoate (4ja): Prepared according to the general procedure from 4-cyanobenzoic acid (**3j**) (29.4 mg, 0.2 mmol) and vinyl oxirane (**(±)-1a**) (56 mg, 64 μl , 0.8 mmol).

Reaction time: 1 h. Yield: 93% (40.4 mg, 0.186 mmol). Pale yellow oil; ^1H NMR (500 MHz, CDCl_3): δ 8.14 (d, $J = 8.5$ Hz, 2H), 7.71 (d, $J = 8.5$ Hz, 2H), 5.89 (ddd, $J = 17.0, 10.5, 6.0$ Hz, 1H), 5.65 – 5.53 (m, 1H), 5.46 – 5.37 (m, 1H), 5.36 – 5.26 (m, 1H), 3.91 – 3.74 (m, 2H), 2.37 (s, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ 164.5, 133.9, 132.3, 132.3, 130.2, 119.2, 117.9, 116.5, 77.0, 64.2. HRMS calcd for $\text{C}_{12}\text{H}_{11}\text{NO}_3$ (ESI^+ , $[\text{M}+\text{H}]^+$): 218.0817, found 218.0814. HPLC: $t_{\text{R}} = 27.6$ min (major) and $t_{\text{R}} = 32.0$ min (minor) 79% ee (Chiralpak IA, 254 nm, 5% IPA-Hex, 1 ml/min). $[\alpha]_D^{25.6} -5.6$ ($c = 0.35$, CHCl_3). The absolute stereochemistry of this compound was assigned in analogy to **4aa**.

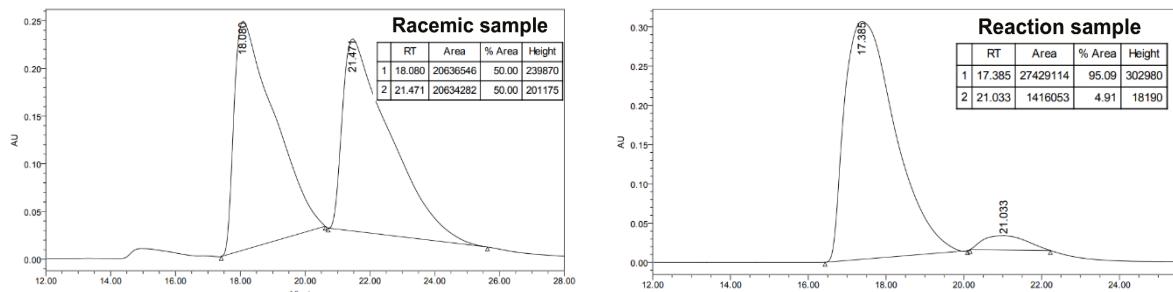


(S)-1-hydroxybut-3-en-2-yl 4-(tert-butyl)benzoate (4ka): Prepared according to the general procedure from 4-tert-butylbenzoic acid (**3k**) (35.6 mg, 0.2 mmol) and vinyl oxirane (**(±)-1a**) (56 mg,

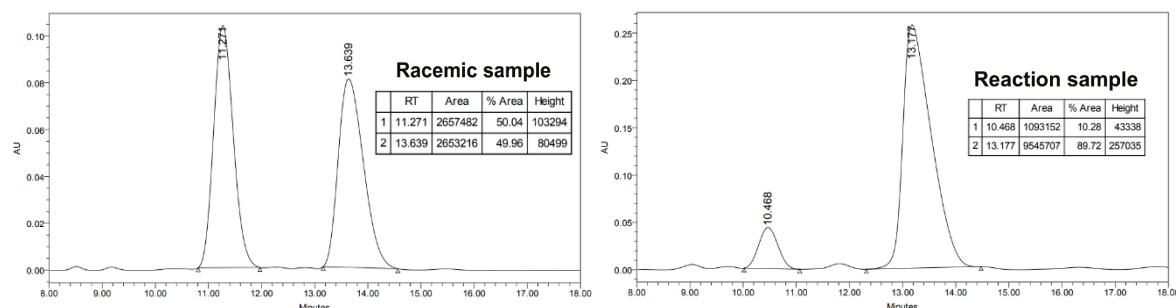
64 μl , 0.8 mmol). Reaction time: 14 h. Yield: 97% (48.2 mg, 0.194 mmol). Pale yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.99 (d, $J = 8.4$ Hz, 2H), 7.44 (d, $J = 8.4$ Hz, 2H), 5.90 (ddd, $J = 17.2, 10.8, 5.6$ Hz, 1H), 5.68 – 5.51 (m, 1H), 5.42 (dt, $J = 17.2, 1.2$ Hz, 1H), 5.29 (dt, $J = 10.8, 1.2$ Hz, 1H), 3.95 – 3.70 (m, 2H), 2.09 (br s, 1H), 1.31 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 166.1, 157.0, 133.0, 129.6, 127.2, 125.4, 118.4, 75.9, 64.7, 35.1, 31.1. HRMS calcd for $\text{C}_{15}\text{H}_{21}\text{O}_3$ (ESI^+ , $[\text{M}+\text{H}]^+$): 249.1491, found 249.1482. For the determination of enantiomeric excess of **4ka**, the compound **4ka** was converted to the corresponding diol dibenzoylate **4x'**. HPLC: $t_{\text{R}} = 6.6$ min (major) and $t_{\text{R}} = 7.5$ min (minor) 89% ee (Chiralpak IG, 280 nm, 20% IPA-Hex, 1 ml/min). $[\alpha]_D^{20} -26.4$ ($c = 0.59$, DCM). The absolute stereochemistry of this compound was assigned in analogy to **4aa**.



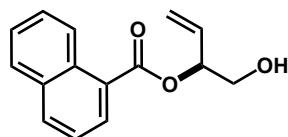
(S)-1-hydroxybut-3-en-2-yl 4-methoxybenzoate (4la): Prepared according to the general procedure from 4-methoxybenzoic acid (**3l**) (30.4 mg, 0.2 mmol) and vinyl oxirane (**(±)-1a**) (56 mg, 64 µl, 0.8 mmol). Reaction time: 14 h. Yield: 98% (43.6 mg, 0.196 mmol). Pale yellow oil; ¹H NMR (400 MHz, CDCl₃): δ 8.00 (d, *J* = 9.2 Hz, 2H), 6.89 (d, *J* = 9.2 Hz, 2H), 5.89 (ddd, *J* = 17.2, 10.8, 6.0 Hz, 1H), 5.60 – 5.48 (m, 1H), 5.40 (dt, *J* = 17.2, 1.2 Hz, 1H), 5.28 (dt, *J* = 10.4, 1.2 Hz, 1H), 3.89 – 3.72 (m, 5H), 2.20 (br s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 165.9, 163.6, 133.1, 131.8, 122.4, 118.3, 113.7, 75.8, 64.6, 55.4. HRMS calcd for C₁₂H₁₅O₄ (ESI⁺, [M+H]⁺): 223.0970, found 223.0965. HPLC: t_R = 19.0 min (major) and t_R = 23.0 min (minor) 90% ee (Chiralpak IA, 254 nm, 5% IPA-Hex, 1 ml/min). [α]_D²⁰ –31.2 (c = 0.81, DCM). The absolute stereochemistry of this compound was assigned in analogy to **4aa**.



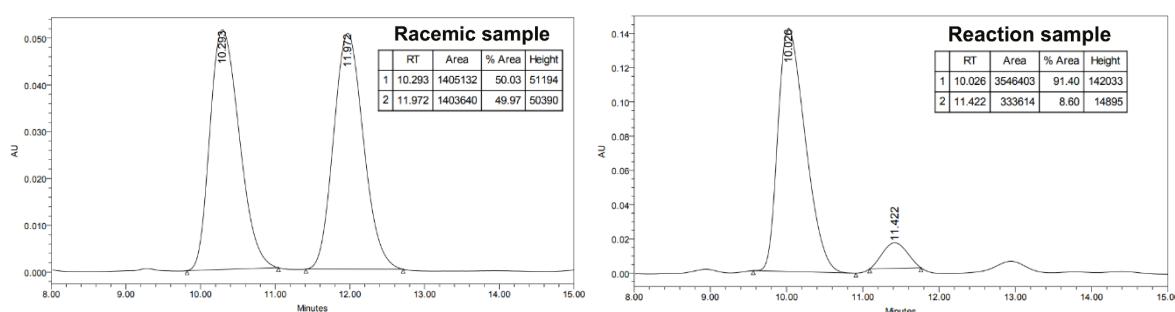
(S)-1-hydroxybut-3-en-2-yl 2-naphthoate (4ma): Prepared according to the general procedure from 2-naphthoic acid (**3m**) (34.4 mg, 0.2 mmol) and vinyl oxirane (**(±)-1a**) (56 mg, 64 µl, 0.8 mmol). Reaction time: 17 h. Yield: 95% (46.0 mg, 0.19 mmol). Pale yellow oil; ¹H NMR (500 MHz, CDCl₃): δ 8.62 (s, 1H), 8.06 (dd, *J* = 9.0, 2.0 Hz, 1H), 7.92 (d, *J* = 8.5 Hz, 1H), 7.84 (d, *J* = 8.5 Hz, 2H), 7.60 – 7.46 (m, 2H), 5.96 (ddd, *J* = 17.0, 11.0, 6.0 Hz, 1H), 5.72 – 5.62 (m, 1H), 5.47 (dd, *J* = 17.5, 1.5 Hz, 1H), 5.33 (dd, *J* = 10.5, 1.0 Hz, 1H), 3.98 – 3.82 (m, 2H), 2.52 (s, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 166.3, 135.6, 132.9, 132.5, 131.3, 129.4, 128.4, 128.2, 127.8, 127.2, 126.7, 125.2, 118.7, 76.3, 64.6. HRMS calcd for C₁₅H₁₅O₃ (ESI⁺, [M+H]⁺): 243.1021, found 243.1017. HPLC: t_R = 10.5 min (minor) and t_R = 13.2 min (major) 80% ee (Chiralcel OD-H, 254 nm, 10% IPA-Hex, 1 ml/min). [α]_D²⁰ –37.0 (c = 0.93, DCM). The absolute stereochemistry of this compound was assigned in analogy to **4aa**.



(S)-1-hydroxybut-3-en-2-yl 1-naphthoate (4na): Prepared according to the general procedure from 1-naphthoic acid (**3n**) (34.4 mg, 0.2 mmol) and vinyl oxirane (**(±)-1a**) (56 mg, 64 μ L, 0.8 mmol). Reaction time: 17 h. Yield: 96% (46.5 mg, 0.192 mmol). Pale yellow oil; ^1H NMR (500 MHz, CDCl_3): δ 8.90 (d, J = 9.0 Hz, 1H), 8.22 (dd, J = 7.5, 1.0 Hz, 1H), 8.00 (d, J = 8.0 Hz, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.62 – 7.55 (m, 1H), 7.54 – 7.44 (m, 2H), 5.96 (ddd, J = 17.0, 10.5, 6.0 Hz, 1H), 5.74 – 5.64 (m, 1H), 5.49 (dt, J = 17.5, 1.0 Hz, 1H), 5.34 (dt, J = 10.5, 1.0 Hz, 1H), 3.94 – 3.81 (m, 2H), 2.47 (br s, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ 167.0, 133.9, 133.6, 133.0, 131.4, 130.3, 128.6, 127.9, 127.0, 126.3, 125.7, 124.5, 118.8, 76.2, 64.6. HRMS calcd for $\text{C}_{15}\text{H}_{15}\text{O}_3$ (ESI^+ , [M+H] $^+$): 243.1021, found 243.1016. HPLC: t_{R} = 10.0 min (major) and t_{R} = 11.4 min (minor) 83% ee (Chiralcel OD-H, 254 nm, 10% IPA-Hex, 1 ml/min). $[\alpha]_D^{20}$ –7.3 (c = 0.98, DCM). The absolute stereochemistry of this compound was assigned in analogy to **4aa**.

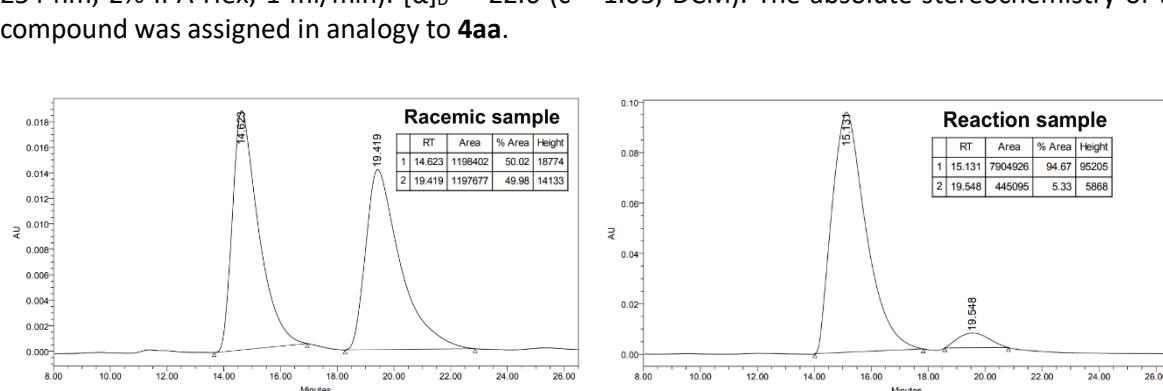


9.0 Hz, 1H), 8.22 (dd, J = 7.5, 1.0 Hz, 1H), 8.00 (d, J = 8.0 Hz, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.62 – 7.55 (m, 1H), 7.54 – 7.44 (m, 2H), 5.96 (ddd, J = 17.0, 10.5, 6.0 Hz, 1H), 5.74 – 5.64 (m, 1H), 5.49 (dt, J = 17.5, 1.0 Hz, 1H), 5.34 (dt, J = 10.5, 1.0 Hz, 1H), 3.94 – 3.81 (m, 2H), 2.47 (br s, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ 167.0, 133.9, 133.6, 133.0, 131.4, 130.3, 128.6, 127.9, 127.0, 126.3, 125.7, 124.5, 118.8, 76.2, 64.6. HRMS calcd for $\text{C}_{15}\text{H}_{15}\text{O}_3$ (ESI^+ , [M+H] $^+$): 243.1021, found 243.1016. HPLC: t_{R} = 10.0 min (major) and t_{R} = 11.4 min (minor) 83% ee (Chiralcel OD-H, 254 nm, 10% IPA-Hex, 1 ml/min). $[\alpha]_D^{20}$ –7.3 (c = 0.98, DCM). The absolute stereochemistry of this compound was assigned in analogy to **4aa**.



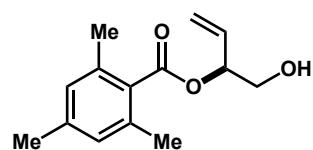
(S)-1-hydroxybut-3-en-2-yl 3,5-dimethylbenzoate (4oa): Prepared according to the general procedure from 3,5-dimethylbenzoic acid (**3o**) (30.0 mg, 0.2 mmol) and vinyl oxirane (**(±)-1a**) (56 mg,

64 μ L, 0.8 mmol). Reaction time: 12 h. Yield: 96% (42.3 mg, 0.192 mmol). Pale yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.66 (s, 2H), 7.17 (s, 1H), 5.90 (ddd, J = 17.2, 10.8, 6.0 Hz, 1H), 5.63 – 5.51 (m, 1H), 5.41 (dt, J = 17.6, 1.2 Hz, 1H), 5.29 (dt, J = 10.8, 1.2 Hz, 1H), 3.90 – 3.75 (m, 2H), 2.49 (br s, 1H), 2.33 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 166.3, 137.9, 134.7, 132.8, 129.7, 127.3, 118.3, 75.8, 64.4, 21.0. HRMS calcd for $\text{C}_{13}\text{H}_{17}\text{O}_3$ (ESI^+ , [M+H] $^+$): 221.1178, found 221.1173. HPLC: t_{R} = 15.1 min (major) and t_{R} = 19.5 min (minor) 89% ee (Chiralpak IA, 254 nm, 2% IPA-Hex, 1 ml/min). $[\alpha]_D^{20}$ –22.6 (c = 1.05, DCM). The absolute stereochemistry of this compound was assigned in analogy to **4aa**.

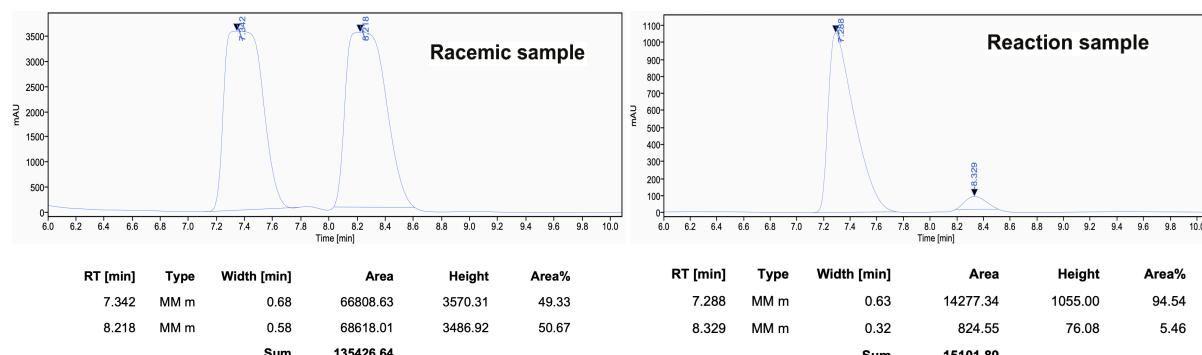


(S)-1-hydroxybut-3-en-2-yl 2,4,6-trimethylbenzoate (4pa): Prepared according to the general procedure from 2,4,6-trimethylbenzoic acid (**3p**) (32.8 mg, 0.2 mmol) and vinyl oxirane (**(±)-1a**) (56

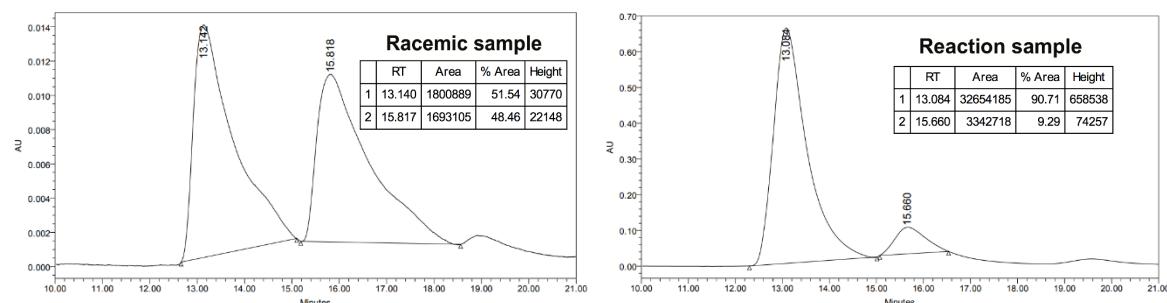
mg, 64 μ L, 0.8 mmol). Reaction time: 14 h. Yield: 99% (46.4 mg, 0.198 mmol). Pale yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 6.84 (s, 2H), 5.89 (ddd, J = 17.2, 10.4, 6.4 Hz, 1H), 5.65 – 5.54 (m, 1H), 5.46 (dt, J = 17.2, 1.2 Hz, 1H), 5.34 (dt, J = 10.8, 1.2 Hz, 1H), 3.89 – 3.69 (m, 2H), 2.29 (s, 6H), 2.27 (s, 3H), 2.17 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 169.7, 139.5, 135.1,



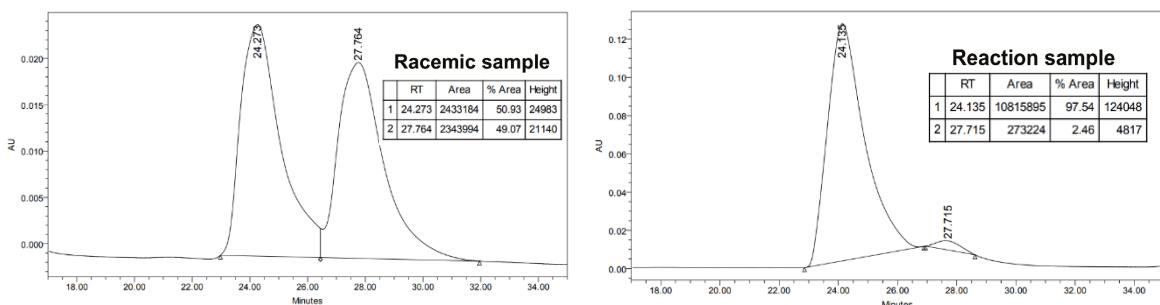
132.8, 130.8, 128.4, 119.5, 76.2, 64.5, 21.1, 19.7. HRMS calcd for $C_{14}H_{19}O_3$ ($ESI^+, [M+H]^+$): 235.1334, found 235.1327. HPLC: $t_R = 7.3$ min (major) and $t_R = 8.3$ min (minor) 89% ee (Chiralcel OD-H, 280 nm, 5% IPA-Hex, 1 ml/min). $[\alpha]_D^{20} -6.9$ ($c = 1.11$, DCM). The absolute stereochemistry of this compound was assigned in analogy to **4aa**.



(S)-1-hydroxybut-3-en-2-yl 3-formylbenzoate (4qa): Prepared according to the general procedure from 3-formylbenzoic acid (**3q**) (30.0 mg, 0.2 mmol) and vinyl oxirane (**(±)-1a**) (56 mg, 64 μ l, 0.8 mmol). Reaction time: 3 h. Yield: 98% (43.2 mg, 0.196 mmol). Pale yellow oil; 1H NMR (400 MHz, $CDCl_3$): δ 10.05 (s, 1H), 8.52 (t, $J = 1.6$ Hz, 1H), 8.30 (dt, $J = 8.0, 1.6$ Hz, 1H), 8.06 (dt, $J = 7.6, 1.6$ Hz, 1H), 7.61 (t, $J = 8.0$ Hz, 1H), 5.92 (ddd, $J = 16.8, 10.4, 6.0$ Hz, 1H), 5.68 – 5.56 (m, 1H), 5.44 (dt, $J = 17.2, 1.2$ Hz, 1H), 5.33 (dt, $J = 10.4, 1.2$ Hz, 1H), 3.97 – 3.77 (m, 2H), 2.26 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.4, 165.0, 136.6, 135.3, 133.5, 132.5, 131.2, 129.4, 119.1, 76.7, 64.4. HRMS calcd for $C_{12}H_{13}O_4$ ($ESI^+, [M+H]^+$): 221.0814, found 221.0806. HPLC: $t_R = 13.1$ min (major) and $t_R = 15.7$ min (minor) 81% ee (Chiralpak IA, 245 nm, 10% IPA-Hex, 1 ml/min). $[\alpha]_D^{20} -15.3$ ($c = 1.04$, DCM). The absolute stereochemistry of this compound was assigned in analogy to **4aa**.

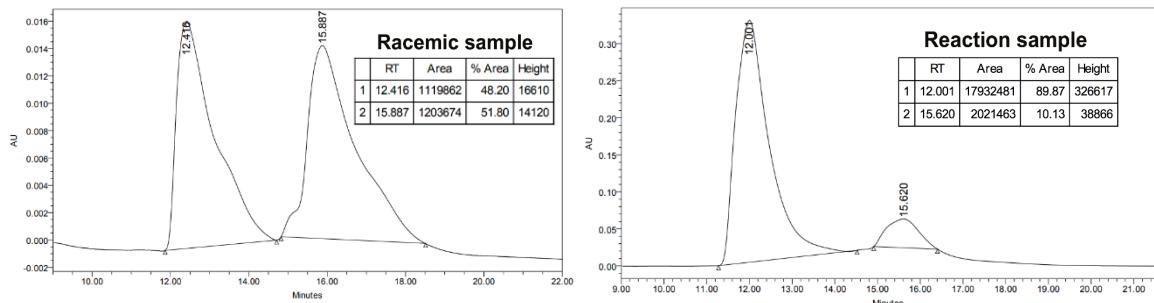


(S)-1-hydroxybut-3-en-2-yl 2-acetylbenzoate (4ra): Prepared according to the general procedure from 2-acetylbenzoic acid (**3r**) (32.8 mg, 0.2 mmol) and vinyl oxirane (**(±)-1a**) (56 mg, 64 μ l, 0.8 mmol). Reaction time: 5.5 h. Yield: 96% (45 mg, 0.192 mmol). Pale yellow oil; 1H NMR (400 MHz, $CDCl_3$): δ 7.83 – 7.74 (m, 1H), 7.58 – 7.41 (m, 3H), 5.84 (ddd, $J = 17.2, 10.8, 6.4$ Hz, 1H), 5.61 – 5.50 (m, 1H), 5.35 (dt, $J = 17.2, 1.2$ Hz, 1H), 5.25 (dt, $J = 10.8, 1.2$ Hz, 1H), 3.88 – 3.65 (m, 2H), 2.77 (br s, 1H), 2.54 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.3, 166.9, 141.0, 132.4, 131.7, 130.8, 129.8, 127.0, 118.7, 76.8, 64.3, 29.7. HRMS calcd for $C_{13}H_{14}O_4Na$ ($ESI^+, [M+Na]^+$): 257.0790, found 257.0785. HPLC: $t_R = 24.1$ min (major) and $t_R = 27.7$ min (minor) 95% ee (Chiralpak IA, 254 nm, 5% IPA-Hex, 1 ml/min). $[\alpha]_D^{20} -32.4$ ($c = 0.96$, DCM). The absolute stereochemistry of (**4ra**) was assigned in analogy to **4aa**.



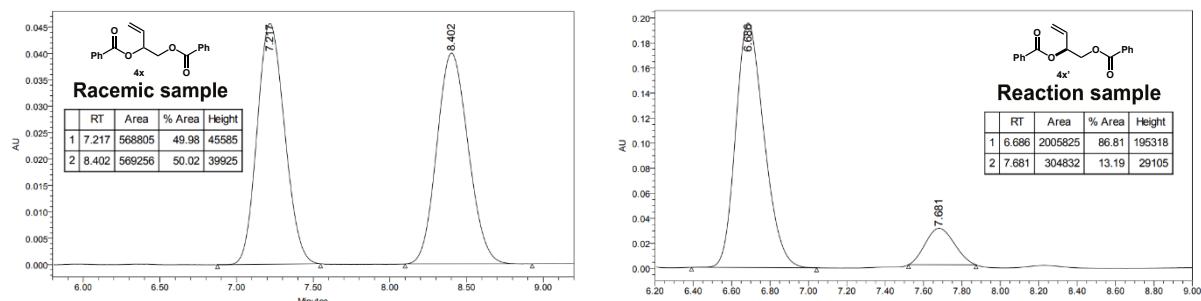
(S)-1-hydroxybut-3-en-2-yl 3-acetylbenzoate (4sa): Prepared according to the general procedure from 3-acetylbenzoic acid (**3s**) (32.8 mg, 0.2 mmol) and vinyl oxirane ((\pm)-**1a**) (56 mg, 64 μ l, 0.8 mmol).

Reaction time: 2.5 h. Yield: 98% (45.9 mg, 0.196 mmol). Pale yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 8.58 (t, J = 1.6 Hz, 1H), 8.23 (dt, J = 8.0, 1.6 Hz, 1H), 8.12 (dt, J = 7.6, 1.6 Hz, 1H), 7.54 (t, J = 7.6 Hz, 1H), 5.92 (ddd, J = 17.2, 10.8, 6.0 Hz, 1H), 5.67 – 5.54 (m, 1H), 5.43 (dt, J = 17.2, 1.2 Hz, 1H), 5.33 (dt, J = 10.4, 1.2 Hz, 1H), 3.97 – 3.75 (m, 2H), 2.62 (s, 3H), 2.24 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 197.3, 165.3, 137.3, 134.0, 132.6, 130.6, 129.6, 128.9, 119.0, 76.7, 64.4, 26.7. HRMS calcd for $\text{C}_{13}\text{H}_{15}\text{O}_4$ (ESI^+ , [M+H] $^+$): 235.0970, found 235.0960. HPLC: t_{R} = 12.0 min (major) and t_{R} = 15.6 min (minor) 80% ee (Chiralpak IA, 245 nm, 10% IPA-Hex, 1 ml/min). $[\alpha]_D^{20}$ –18.8 (c = 0.99, DCM). The absolute stereochemistry of this compound was assigned in analogy to **4aa**.

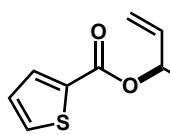


(S)-1-hydroxybut-3-en-2-yl 4-((tert-butoxycarbonyl)amino)benzoate (4ta): Prepared according to the general procedure from 4-((tert-butoxycarbonyl)amino)benzoic acid (**3t**) (47.4 mg, 0.2 mmol) and

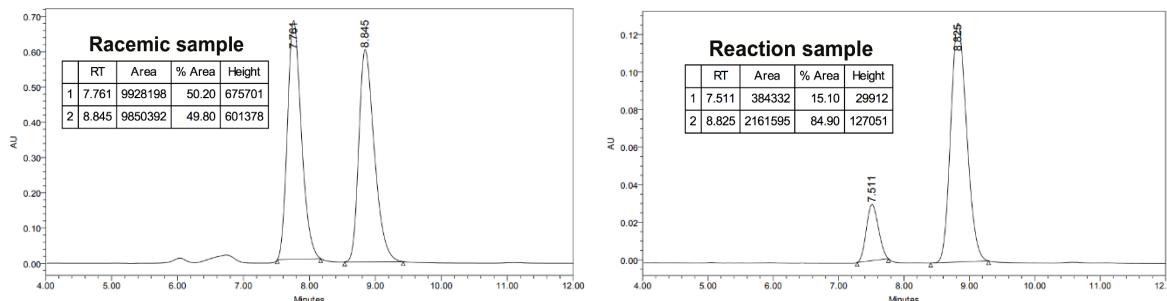
vinyl oxirane ((\pm)-**1a**) (56 mg, 64 μ l, 0.8 mmol). Reaction time: 5 h. Yield: 56% (34.4 mg, 0.112 mmol). Pale yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.96 (d, J = 8.8 Hz, 2H), 7.41 (d, J = 8.8 Hz, 2H), 6.84 (s, 1H), 5.89 (ddd, J = 17.2, 10.8, 6.0 Hz, 1H), 5.63 – 5.48 (m, 1H), 5.40 (dt, J = 17.2, 1.2 Hz, 1H), 5.29 (dt, J = 10.8, 1.2 Hz, 1H), 3.90 – 3.72 (m, 2H), 2.18 (br s, 1H), 1.49 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 165.8, 152.2, 143.1, 133.0, 131.0, 124.1, 118.5, 117.4, 81.3, 75.9, 64.6, 28.3. HRMS calcd for $\text{C}_{16}\text{H}_{22}\text{NO}_5$ (ESI^+ , [M+H] $^+$): 308.1498, found 308.1494. For the determination of enantiomeric excess of **4'ta**, the compound **4'ta** was converted to the corresponding diol dibenzoylate **4x'**. HPLC: t_{R} = 6.7 min (major) and t_{R} = 7.7 min (minor) 74% ee (Chiralpak IG, 280 nm, 20% IPA-Hex, 1 ml/min). $[\alpha]_D^{25}$ –41.6 (c = 0.62, DCM). The absolute stereochemistry of this compound was assigned in analogy to **4aa**.



(S)-1-hydroxybut-3-en-2-yl thiophene-2-carboxylate (4ua): Prepared according to the general procedure from 2-thiophenecarboxylic acid (**3u**) (25.6 mg, 0.2 mmol) and vinyl oxirane (**(±)-1a**) (56 mg, 64 μ L, 0.8 mmol). Reaction time: 1 h. Yield: 96% (38 mg, 0.192 mmol). Pale yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.81 (dd, J = 4.0, 1.6 Hz, 1H), 7.54 (dd, J = 4.8, 1.2 Hz, 1H), 7.07 (dd, J = 5.2, 4.0 Hz, 1H), 5.87 (ddd, J = 17.2, 10.8, 6.0 Hz, 1H), 5.60 – 5.47 (m, 1H), 5.41 (dt, J = 17.2, 1.2 Hz, 1H), 5.29 (dt, J = 10.8, 1.2 Hz, 1H), 3.91 – 3.70 (m, 2H), 2.26 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 161.8, 133.8, 133.5, 132.8, 132.6, 127.9, 118.7, 76.4, 64.5. HRMS calcd for $\text{C}_9\text{H}_{11}\text{SO}_3$ (ESI^+ , [M+H] $^+$): 199.0429, found 199.0420. HPLC: t_{R} = 7.5 min (minor) and t_{R} = 8.8 min (major) 70% ee (Chiralcel OD-H, 254 nm, 10% IPA-Hex, 1 ml/min). $[\alpha]_D^{28.4}$ –28.2 (c = 0.75, CHCl_3). The absolute stereochemistry of this compound was assigned in analogy to **4aa**.

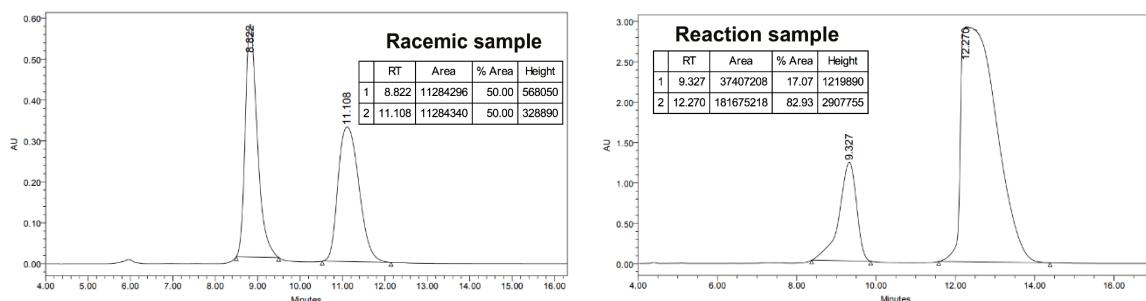


Reaction time: 1 h. Yield: 96% (38 mg, 0.192 mmol). Pale yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.81 (dd, J = 4.0, 1.6 Hz, 1H), 7.54 (dd, J = 4.8, 1.2 Hz, 1H), 7.07 (dd, J = 5.2, 4.0 Hz, 1H), 5.87 (ddd, J = 17.2, 10.8, 6.0 Hz, 1H), 5.60 – 5.47 (m, 1H), 5.41 (dt, J = 17.2, 1.2 Hz, 1H), 5.29 (dt, J = 10.8, 1.2 Hz, 1H), 3.91 – 3.70 (m, 2H), 2.26 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 161.8, 133.8, 133.5, 132.8, 132.6, 127.9, 118.7, 76.4, 64.5. HRMS calcd for $\text{C}_9\text{H}_{11}\text{SO}_3$ (ESI^+ , [M+H] $^+$): 199.0429, found 199.0420. HPLC: t_{R} = 7.5 min (minor) and t_{R} = 8.8 min (major) 70% ee (Chiralcel OD-H, 254 nm, 10% IPA-Hex, 1 ml/min). $[\alpha]_D^{28.4}$ –28.2 (c = 0.75, CHCl_3). The absolute stereochemistry of this compound was assigned in analogy to **4aa**.



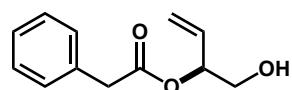
(S)-1-hydroxybut-3-en-2-yl furan-2-carboxylate (4va): Prepared according to the general procedure from 2-furoic acid (**3v**) (22.4 mg, 0.2 mmol) and vinyl oxirane (**(±)-1a**) (56 mg, 64 μ L, 0.8 mmol).

Reaction time: 1 h. Yield: 96% (35.0 mg, 0.192 mmol). Pale yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.57 (dd, J = 1.6, 0.8 Hz, 1H), 7.22 (dd, J = 3.6, 0.8 Hz, 1H), 6.50 (dd, J = 3.2, 1.6 Hz, 1H), 5.88 (ddd, J = 17.2, 10.8, 6.0 Hz, 1H), 5.62 – 5.49 (m, 1H), 5.42 (dt, J = 17.2, 1.2 Hz, 1H), 5.31 (dt, J = 10.8, 1.2 Hz, 1H), 3.92 – 3.70 (m, 2H), 2.05 (br s, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 157.2, 145.5, 143.4, 131.4, 118.0, 117.5, 110.9, 75.1, 63.4. HRMS calcd for $\text{C}_9\text{H}_{11}\text{O}_4$ (ESI^+ , [M+H] $^+$): 183.0657, found 183.0648. HPLC: t_{R} = 9.3 min (minor) and t_{R} = 12.3 min (major) 66% ee (Chiralcel OD-H, 254 nm, 10% IPA-Hex, 1 ml/min). $[\alpha]_D^{25}$ –16.2 (c = 0.82, DCM). The absolute stereochemistry of this compound was assigned in analogy to **4aa**.



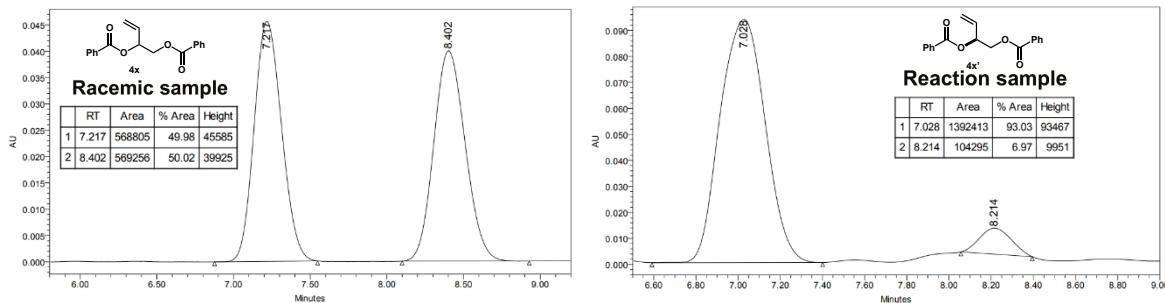
(S)-1-hydroxybut-3-en-2-yl 2-phenylacetate (4'aa): Prepared according to the general procedure from 2-phenylacetic acid (**3'a**) (27.2 mg, 0.2 mmol) and vinyl oxirane (**(±)-1a**) (56 mg, 64 μ L, 0.8 mmol).

Reaction time: 12 h. Yield: 98% (40.4 mg, 0.196 mmol). Pale yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.36 – 7.22 (m, 5H), 5.78 (ddd, J = 17.2, 10.4, 6.0 Hz, 1H), 5.42 – 5.16 (m, 3H), 3.80 – 3.54 (m, 4H), 2.04 (br s, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 171.1, 133.9, 132.6, 129.2, 128.7, 127.2, 118.6, 75.9, 64.4, 41.5. HRMS calcd for $\text{C}_{12}\text{H}_{15}\text{O}_3$ (ESI^+ , [M+H] $^+$): 207.1021, found 207.1012. For the determination of enantiomeric excess of **4'aa**, the compound **4'aa** was converted to the corresponding diol dibenzoylate **4x'**. HPLC: t_{R} = 7.0 min (major) and t_{R} = 8.2 min (minor) 86% ee (Chiraldak IG, 280 nm,

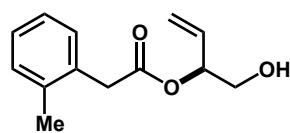


Reaction time: 12 h. Yield: 98% (40.4 mg, 0.196 mmol). Pale yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.36 – 7.22 (m, 5H), 5.78 (ddd, J = 17.2, 10.4, 6.0 Hz, 1H), 5.42 – 5.16 (m, 3H), 3.80 – 3.54 (m, 4H), 2.04 (br s, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 171.1, 133.9, 132.6, 129.2, 128.7, 127.2, 118.6, 75.9, 64.4, 41.5. HRMS calcd for $\text{C}_{12}\text{H}_{15}\text{O}_3$ (ESI^+ , [M+H] $^+$): 207.1021, found 207.1012. For the determination of enantiomeric excess of **4'aa**, the compound **4'aa** was converted to the corresponding diol dibenzoylate **4x'**. HPLC: t_{R} = 7.0 min (major) and t_{R} = 8.2 min (minor) 86% ee (Chiraldak IG, 280 nm,

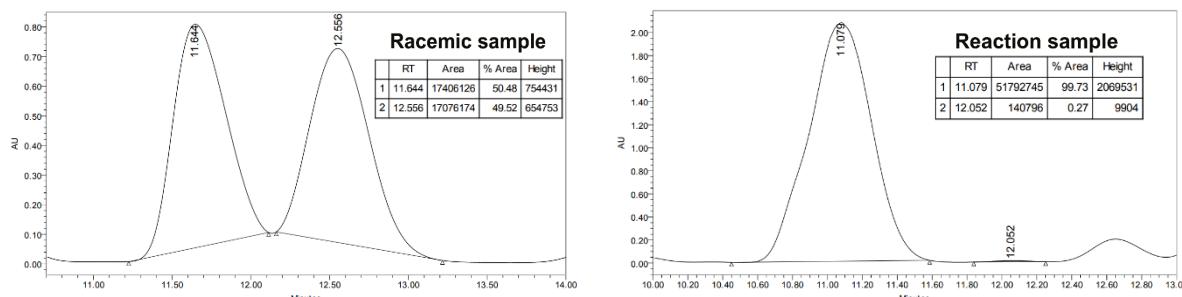
20% IPA-Hex, 1 ml/min). $[\alpha]_D^{25} -72.9$ ($c = 0.88$, DCM). The absolute stereochemistry of this compound was assigned in analogy to **4aa**.



(S)-1-hydroxybut-3-en-2-yl 2-(*o*-tolyl)acetate (4'ba): Prepared according to the general procedure from 2-(*o*-tolyl)acetic acid (**3'b**) (30.0 mg, 0.2 mmol) and vinyl oxirane ((\pm)-**1a**) (56 mg, 64 μ L, 0.8 mmol).

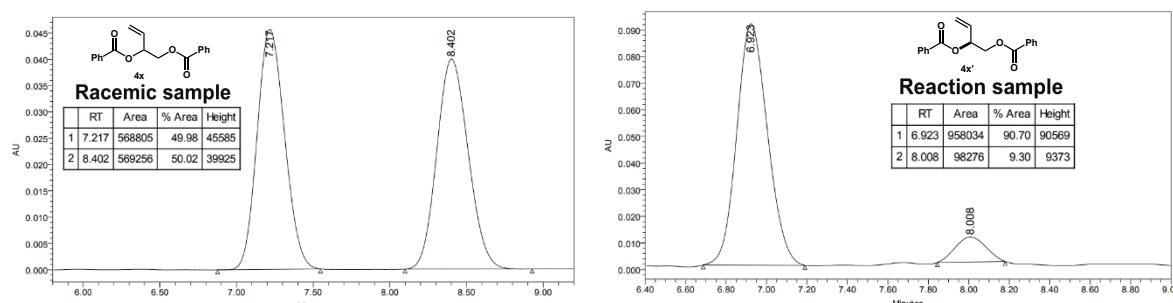


Reaction time: 5 h. Yield: >99% (43.8 mg, 0.199 mmol). Pale yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.23 – 7.04 (m, 4H), 5.76 (ddd, $J = 16.8, 10.4, 6.0$ Hz, 1H), 5.41 – 5.14 (m, 3H), 3.74 – 3.52 (m, 4H), 2.31 (s, 3H), 2.09 (br s, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 171.1, 136.8, 132.6, 130.4, 130.1, 127.5, 126.2, 118.6, 75.8, 64.4, 39.3, 19.6. HRMS calcd for $\text{C}_{13}\text{H}_{16}\text{O}_3\text{Na}$ (ESI $^+$, [M+Na] $^+$): 243.0997, found 243.0992. HPLC: $t_R = 11.1$ min (major) and $t_R = 12.1$ min (minor) 99.5% ee (Chiralcel OD-H, 210 nm, 10% IPA-Hex, 1 ml/min). $[\alpha]_D^{28.0} -31.5$ ($c = 0.5$, CHCl_3). The absolute stereochemistry of this compound was assigned in analogy to **4aa**.

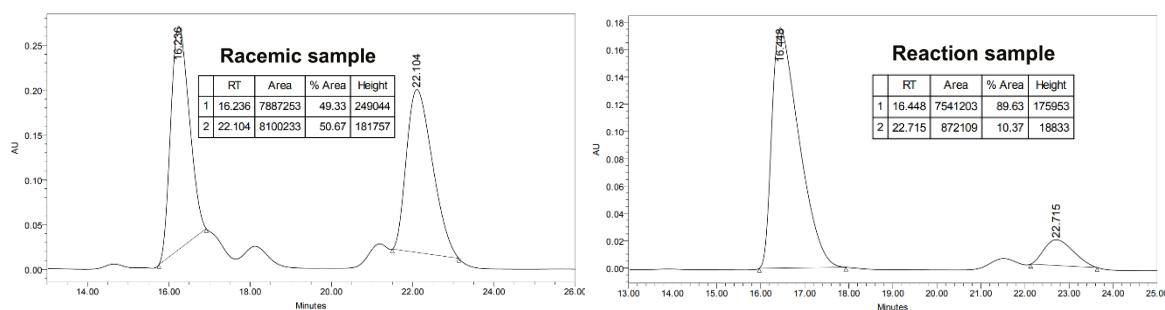


(S)-1-hydroxybut-3-en-2-yl acrylate (4'ca): Prepared according to the general procedure from acrylic acid (**3'c**) (28.8 mg, 27.4 μ L, 0.4 mmol) and vinyl oxirane ((\pm)-**1a**) (112.1 mg, 128.7 μ L, 1.6 mmol).

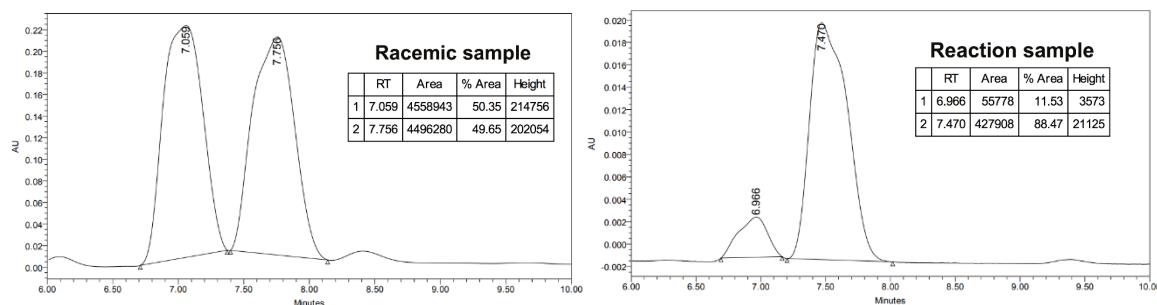
Reaction time: 5 h. Yield: 95% (54.0 mg, 0.38 mmol). Pale yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 6.42 (dd, $J = 17.6, 1.6$ Hz, 1H), 6.18 – 6.08 (m, 1H), 5.88 – 5.74 (m, 2H), 5.45 – 5.22 (m, 3H), 3.81 – 3.62 (m, 2H), 2.17 (br s, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 165.7, 132.7, 131.4, 128.2, 118.6, 75.7, 64.3. HRMS calcd for $\text{C}_7\text{H}_9\text{O}_2$ (ESI $^+$, [M+H] $^+[-\text{H}_2\text{O}]$): 125.0603, found 125.0597. For the determination of enantiomeric excess of **4'ca**, the compound **4'ca** was converted to the corresponding diol dibenzoylate **4x'**. HPLC: $t_R = 6.9$ min (major) and $t_R = 8.0$ min (minor) 81% ee (Chiralpak IG, 280 nm, 20% IPA-Hex, 1 ml/min). $[\alpha]_D^{25} -55.4$ ($c = 0.71$, DCM). The absolute stereochemistry of this compound was assigned in analogy to **4aa**.



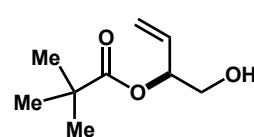
(S)-1-hydroxybut-3-en-2-yl 2-(naphthalen-1-yl)acetate (4'da): Prepared according to the general procedure from 2-(naphthalen-1-yl)acetic acid (**3'd**) (37.2 mg, 0.2 mmol) and vinyl oxirane (**(±)-1a**) (56 mg, 64 µL, 0.8 mmol). Reaction time: 3 h. Yield: 98% (50.2 mg, 0.196 mmol). Pale yellow oil; ¹H NMR (400 MHz, CDCl₃): δ 7.99 (d, J = 8.4 Hz, 1H), 7.90 – 7.83 (m, 1H), 7.79 (dd, J = 6.0, 3.6 Hz, 1H), 7.57 – 7.43 (m, 2H), 7.45 – 7.37 (m, 2H), 5.72 (ddd, J = 17.2, 10.8, 6.4 Hz, 1H), 5.40 – 5.65 (m, 1H), 5.27 – 5.13 (m, 2H), 4.12 (s, 2H), 3.72 – 3.52 (m, 2H), 2.63 (br s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 170.1, 132.8, 131.4, 131.0, 129.3, 127.8, 127.2, 126.9, 125.4, 124.8, 124.5, 122.6, 117.6, 75.0, 63.3, 38.3. HRMS calcd for C₁₆H₁₇O₃ (ESI⁺, [M+H]⁺): 257.1178, found 257.1169. HPLC: t_R = 16.4 min (major) and t_R = 22.7 min (minor) 79% ee (Chiralcel OD-H, 230 nm, 10% IPA-Hex, 1 mL/min). [α]_D^{24.7} –5.2 (c = 0.4, DCM). The absolute stereochemistry of this compound was assigned in analogy to **4aa**.



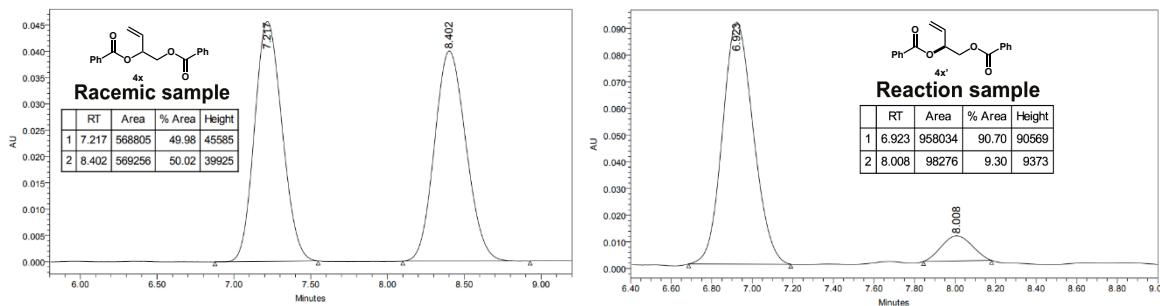
(S)-1-hydroxybut-3-en-2-yl 2-(thiophen-3-yl)acetate (4'ea): Prepared according to the general procedure from 2-(thiophen-2-yl)acetic acid (**3'e**) (28.4 mg, 0.2 mmol) and vinyl oxirane (**(±)-1a**) (56 mg, 64 µL, 0.8 mmol). Reaction time: 5 h. Yield: 96% (40.8 mg, 0.192 mmol). Pale yellow oil; ¹H NMR (400 MHz, CDCl₃): δ 7.27 (dd, J = 4.8, 2.8 Hz, 1H), 7.18 – 7.11 (m, 1H), 7.03 (dd, J = 5.2, 1.2 Hz, 1H), 5.78 (ddd, J = 16.8, 10.8, 6.0 Hz, 1H), 5.42 – 5.17 (m, 3H), 3.77 – 3.61 (m, 4H), 3.06 (br s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 169.7, 132.4, 131.5, 127.4, 124.9, 121.9, 117.7, 74.9, 63.3, 35.0. HRMS calcd for C₁₀H₁₃SO₃ (ESI⁺, [M+H]⁺): 213.0585, found 213.0575. HPLC: t_R = 7.4 min (major) and t_R = 6.9 min (minor) 77% ee (Chiralcel OD-H, 245 nm, 20% IPA-Hex, 1 mL/min). [α]_D²⁵ –140.0 (c = 0.89, DCM). The absolute stereochemistry of this compound was assigned in analogy to **4aa**.



(S)-1-hydroxybut-3-en-2-yl pivalate (4'fa): Prepared according to the general procedure from pivalic acid (**3'f**) (20.4 mg, 22.9 µL, 0.2 mmol) and vinyl oxirane (**(±)-1a**) (56 mg, 64 µL, 0.8 mmol). Reaction time: 8 h. Yield: 98% (33.8 mg, 0.196 mmol). Pale yellow oil; ¹H NMR (400 MHz, CDCl₃): δ 5.79 (ddd, J = 16.8, 10.4, 5.6 Hz, 1H), 5.40 – 5.18 (m, 3H), 3.80 – 3.54 (m, 2H), 2.19 (br s, 1H), 1.21 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): δ 178.1, 133.0, 118.1, 75.1, 64.6, 39.0, 27.1, 27.1. HRMS calcd for C₉H₁₇O₃ (ESI⁺, [M+H]⁺): 173.1178, found 173.1171. For the determination of enantiomeric excess of

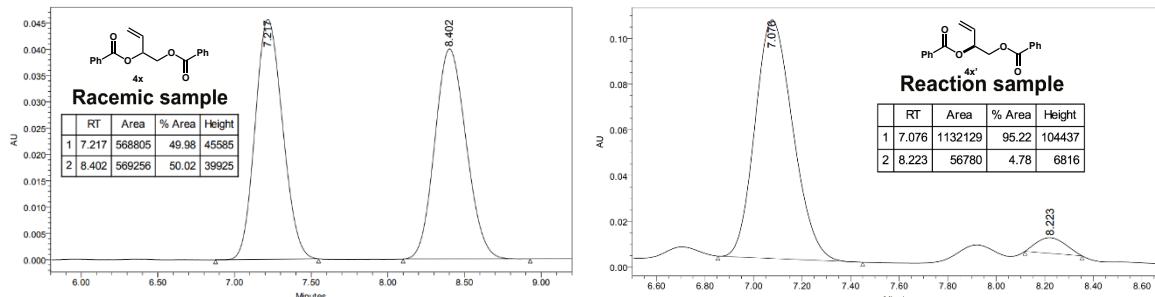


4'fa, the compound **4'fa** was converted to the corresponding diol dibenzoylate **4x'**. HPLC: $t_R = 6.9$ min (major) and $t_R = 8.0$ min (minor) 81% ee (Chiralpak IG, 280 nm, 20% IPA-Hex, 1 ml/min). $[\alpha]_D^{25} -41.2$ ($c = 0.71$, DCM). The absolute stereochemistry of this compound was assigned in analogy to **4aa**.



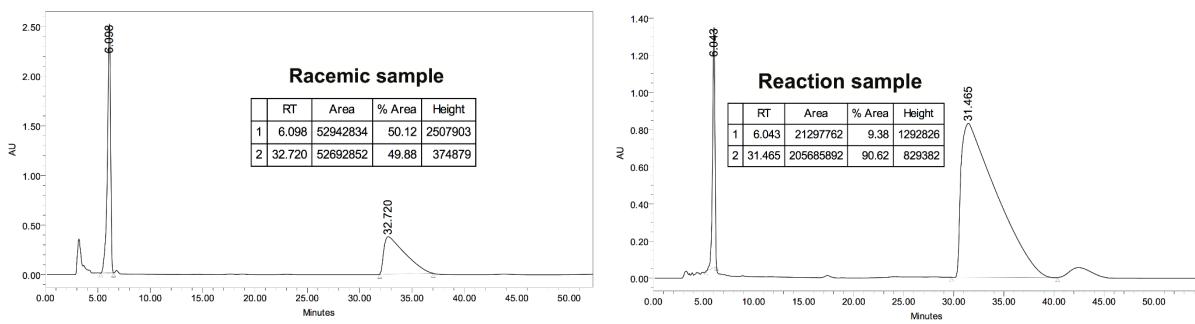
(S)-1-hydroxybut-3-en-2-yl cyclohexanecarboxylate (4'ga): Prepared according to the general procedure from cyclohexanecarboxylic acid (**3'g**) (25.6 mg, 24.7 μ L, 0.2 mmol) and vinyl oxirane ((\pm) -**1a**) (56 mg, 64 μ L, 0.8 mmol). Reaction time: 20 h. Yield: 98% (38.9 mg, 0.196 mmol). Pale yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 5.77 (ddd, $J = 17.2, 10.8, 5.6$ Hz, 1H), 5.37 – 5.18 (m, 3H), 3.79 – 3.55 (m, 2H), 2.41 – 2.26 (m, 1H), 1.94 – 1.82 (m, 2H), 1.79 – 1.67 (m, 2H), 1.76 – 1.70 (m, 1H), 1.29 – 1.25 (m, 2H), 1.24 – 1.20 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 175.7, 133.1, 118.2, 75.0, 64.5, 43.3, 29.1, 29.0, 25.7, 25.4, 25.3. HRMS calcd for $\text{C}_{11}\text{H}_{19}\text{O}_3$ (ESI^+ , $[\text{M}+\text{H}]^+$): 199.1334, found 199.1329. For the determination of enantiomeric excess of **4'ga**, the compound **4'ga** was converted to the corresponding diol dibenzoylate **4x'**. HPLC: $t_R = 7.1$ min (major) and $t_R = 8.2$ min (minor) 90% ee (Chiralpak IG, 280 nm, 20% IPA-Hex, 1 ml/min). $[\alpha]_D^{25} -67.2$ ($c = 0.98$, DCM). The absolute stereochemistry of this compound was assigned in analogy to **4aa**.

Reaction time: 20 h. Yield: 98% (38.9 mg, 0.196 mmol). Pale yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 5.77 (ddd, $J = 17.2, 10.8, 5.6$ Hz, 1H), 5.37 – 5.18 (m, 3H), 3.79 – 3.55 (m, 2H), 2.41 – 2.26 (m, 1H), 1.94 – 1.82 (m, 2H), 1.79 – 1.67 (m, 2H), 1.76 – 1.70 (m, 1H), 1.29 – 1.25 (m, 2H), 1.24 – 1.20 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 175.7, 133.1, 118.2, 75.0, 64.5, 43.3, 29.1, 29.0, 25.7, 25.4, 25.3. HRMS calcd for $\text{C}_{11}\text{H}_{19}\text{O}_3$ (ESI^+ , $[\text{M}+\text{H}]^+$): 199.1334, found 199.1329. For the determination of enantiomeric excess of **4'ga**, the compound **4'ga** was converted to the corresponding diol dibenzoylate **4x'**. HPLC: $t_R = 7.1$ min (major) and $t_R = 8.2$ min (minor) 90% ee (Chiralpak IG, 280 nm, 20% IPA-Hex, 1 ml/min). $[\alpha]_D^{25} -67.2$ ($c = 0.98$, DCM). The absolute stereochemistry of this compound was assigned in analogy to **4aa**.

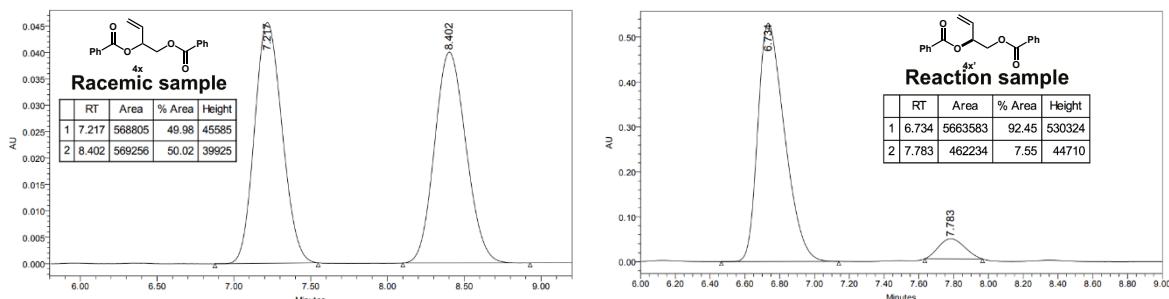


(S)-1-hydroxybut-3-en-2-yl cinnamate (4'ha): Prepared according to the general procedure from cinnamic acid (**3'h**) (29.6 mg, 0.2 mmol) and vinyl oxirane ((\pm) -**1a**) (56 mg, 64 μ L, 0.8 mmol). Reaction time: 24 h. Yield: 98% (42.3 mg, 0.196 mmol). Pale yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.71 (d, $J = 16.0$ Hz, 1H), 7.55 – 7.43 (m, 2H), 7.42 – 7.31 (m, 3H), 6.47 (d, $J = 16.0$ Hz, 1H), 5.86 (ddd, $J = 17.2, 10.8, 6.0$ Hz, 1H), 5.54 – 5.43 (m, 1H), 5.39 (dt, $J = 17.2, 1.2$ Hz, 1H), 5.29 (dt, $J = 10.8, 1.2$ Hz, 1H), 3.88 – 3.68 (m, 2H), 2.27 (br s, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 166.5, 145.6, 134.3, 132.9, 130.5, 128.9, 128.2, 118.5, 117.7, 75.7, 64.5. HRMS calcd for $\text{C}_{13}\text{H}_{15}\text{O}_3$ (ESI^+ , $[\text{M}+\text{H}]^+$): 219.1021, found 219.1016. HPLC: $t_R = 6.0$ min (minor) and $t_R = 31.5$ min (major) 81% ee (Chiralcel OD-H, 254 nm, 30% IPA-Hex, 1 ml/min). $[\alpha]_D^{20} -32.2$ ($c = 0.99$, DCM). The absolute stereochemistry of this compound was assigned in analogy to **4aa**.

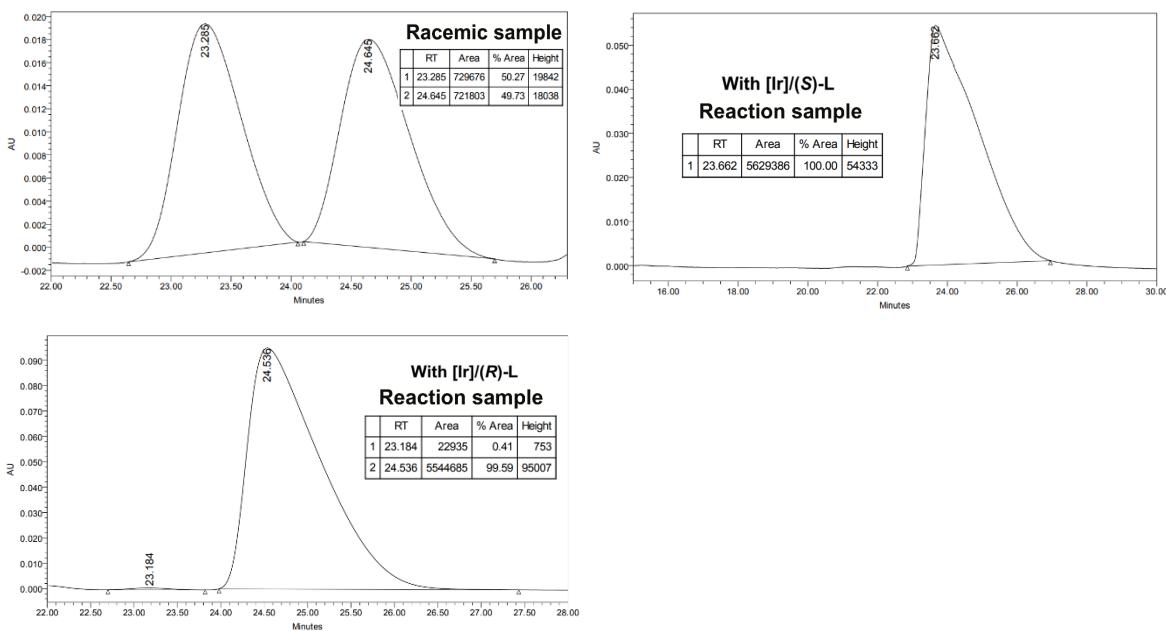
Reaction time: 24 h. Yield: 98% (42.3 mg, 0.196 mmol). Pale yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.71 (d, $J = 16.0$ Hz, 1H), 7.55 – 7.43 (m, 2H), 7.42 – 7.31 (m, 3H), 6.47 (d, $J = 16.0$ Hz, 1H), 5.86 (ddd, $J = 17.2, 10.8, 6.0$ Hz, 1H), 5.54 – 5.43 (m, 1H), 5.39 (dt, $J = 17.2, 1.2$ Hz, 1H), 5.29 (dt, $J = 10.8, 1.2$ Hz, 1H), 3.88 – 3.68 (m, 2H), 2.27 (br s, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 166.5, 145.6, 134.3, 132.9, 130.5, 128.9, 128.2, 118.5, 117.7, 75.7, 64.5. HRMS calcd for $\text{C}_{13}\text{H}_{15}\text{O}_3$ (ESI^+ , $[\text{M}+\text{H}]^+$): 219.1021, found 219.1016. HPLC: $t_R = 6.0$ min (minor) and $t_R = 31.5$ min (major) 81% ee (Chiralcel OD-H, 254 nm, 30% IPA-Hex, 1 ml/min). $[\alpha]_D^{20} -32.2$ ($c = 0.99$, DCM). The absolute stereochemistry of this compound was assigned in analogy to **4aa**.



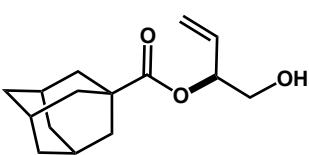
(S)-1-hydroxybut-3-en-2-yl propionate (4'ia): Prepared according to the general procedure from propionic acid (**3'i**) (29.6 mg, 0.4 mmol) and vinyl oxirane (**(±)-1a**) (112.1 mg, 128.7 μ l, 1.6 mmol). Reaction time: 12 h. Yield: 94% (54.2 mg, 0.376 mmol). Pale yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 5.74 (ddd, $J = 17.6, 10.8, 6.0$ Hz, 1H), 5.33 – 5.12 (m, 3H), 3.74 – 3.52 (m, 2H), 2.92 (br s, 1H), 2.33 (qd, $J = 7.6, 1.2$ Hz, 2H), 1.09 (t, $J = 7.6$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 174.1, 133.0, 118.3, 75.3, 64.4, 27.7, 9.1. HRMS calcd for $\text{C}_7\text{H}_{12}\text{O}_3\text{Na}$ (ESI^+ , $[\text{M}+\text{Na}]^+$): 167.0684, found 167.0694. For the determination of enantiomeric excess of **4'ia**, the compound **4'ia** was converted to the corresponding diol dibenzoylate **4x'**. HPLC: $t_{\text{R}} = 6.7$ min (major) and $t_{\text{R}} = 7.8$ min (minor) 85% ee (Chiralpak IG, 280 nm, 20% IPA-Hex, 1 ml/min). $[\alpha]_D^{25} = 60.7$ ($c = 0.67$, DCM). The absolute stereochemistry of this compound was assigned in analogy to **4aa**.



(S)-1-hydroxybut-3-en-2-yl 2-(4-methoxyphenyl)acetate (4'ja): Prepared according to the general procedure from 2-(4-methoxyphenyl)acetic acid (**3'j**) (33.24 mg, 0.2 mmol) and vinyl oxirane (**(±)-1a**) (56 mg, 64 μ l, 0.8 mmol). Reaction time: 5 h. Yield: >99% (46.80 mg, 0.199 mmol). Pale yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.18 (d, $J = 8.8$ Hz, 2H), 6.83 (d, $J = 8.8$ Hz, 2H), 5.75 (ddd, $J = 17.2, 10.4, 5.6$ Hz, 1H), 5.39 – 5.14 (m, 3H), 3.76 (s, 3H), 3.73 – 3.55 (m, 4H), 2.19 (br s, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 170.4, 157.7, 131.6, 129.2, 124.9, 117.5, 113.1, 74.8, 63.3, 54.2, 39.5. HRMS calcd for $\text{C}_{13}\text{H}_{17}\text{O}_4$ (ESI^+ , $[\text{M}+\text{H}]^+$): 237.1127, found 237.1122. HPLC: $t_{\text{R}} = 23.2$ min (minor) and $t_{\text{R}} = 24.5$ min (major) >99% ee (Chiralcel OD-H, 280 nm, 5% IPA-Hex, 1 ml/min). $[\alpha]_D^{25} = -10.5$ ($c = 0.89$, DCM) (for $[\text{Ir}]$ /(S)-L). $[\alpha]_D^{28.7} +32.4$ ($c = 0.9$, CHCl_3) (for $[\text{Ir}]$ /(R)-L). The absolute stereochemistry of (**4'ja**) was assigned in analogy to **4aa**.

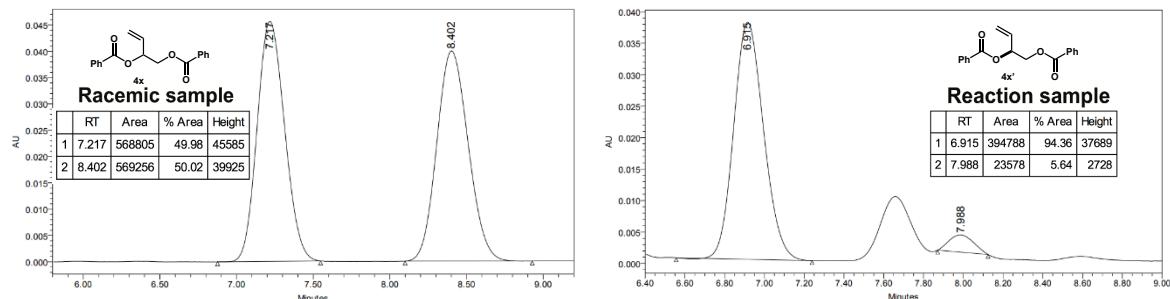


(S)-1-hydroxybut-3-en-2-yl (3r,5r,7r)-adamantane-1-carboxylate (4'ka): Prepared according to the general procedure from 1-Adamantanecarboxylic acid ((±)-1a) (36.0 mg, 0.2 mmol) and vinyl oxirane

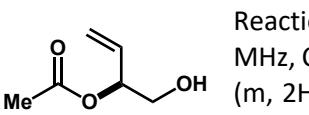


(1a) (56 mg, 64 µL, 0.8 mmol). Reaction time: 8 h. Yield: 98% (49.1 mg, 0.196 mmol). Pale yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 5.78 (ddd, J = 17.2, 10.8, 5.6 Hz, 1H), 5.36 – 5.17 (m, 3H), 3.77 – 3.57 (m, 2H), 2.13 (br s, 1H), 1.99 (s, 3H), 1.89 (d , J = 2.8 Hz, 6H), 1.76 – 1.60 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 177.2, 133.1, 117.9, 74.8, 64.5, 40.9, 38.8, 36.5, 27.9.

HRMS calcd for $\text{C}_{15}\text{H}_{22}\text{O}_3$ (ESI^+ , $[\text{M}+\text{H}]^+$): 251.1647, found 251.1638. For the determination of enantiomeric excess of 4'ka, the compound 4'ka was converted to the corresponding diol dibenzoylate 4x'. HPLC: $t_{\text{R}} = 6.9$ min (major) and $t_{\text{R}} = 8.0$ min (minor) 89% ee (Chiralpak IG, 280 nm, 20% IPA-Hex, 1 mL/min). $[\alpha]_D^{25} -81.4$ ($c = 0.80$, DCM). The absolute stereochemistry of this compound was assigned in analogy to 4aa.



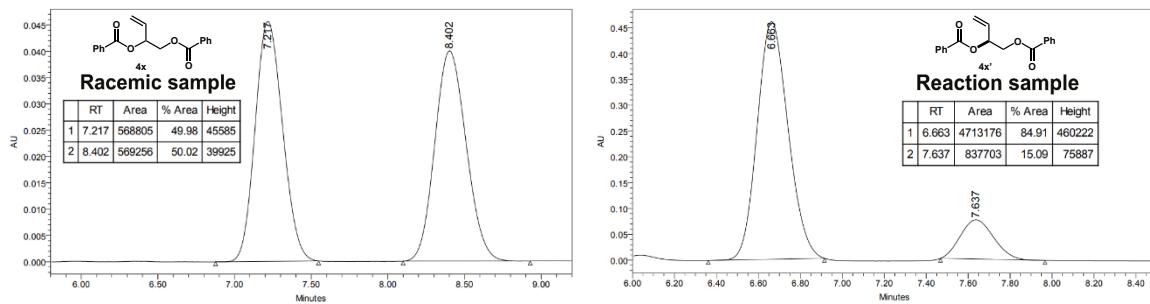
(S)-1-hydroxybut-3-en-2-yl acetate (4'la): Prepared according to the general procedure from acetic acid (3'I) (24.0 mg, 22.8 µL, 0.4 mmol) and vinyl oxirane ((±)-1a) (112.1 mg, 128.7 µL, 1.6 mmol).



Reaction time: 7 h. Yield: 85% (44.2 mg, 0.34 mmol). Pale yellow oil; ^1H NMR (500 MHz, CDCl_3): δ 5.74 (ddd, J = 16.5, 10.5, 6 Hz, 1H), 5.29 – 5.19 (m, 3H), 3.66 – 3.58 (m, 2H), 2.61 (br s, 1H), 2.04 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 170.7, 132.9, 118.3, 75.5, 64.2, 21.1. $\text{C}_6\text{H}_{11}\text{O}_3$ (ESI^+ , $[\text{M}+\text{H}]^+$): 131.0708, found 131.0727.

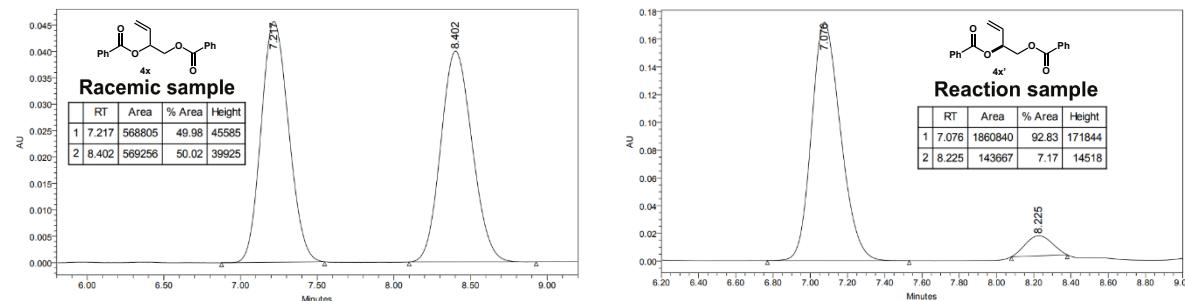
For the determination of enantiomeric excess of 4'la, the compound 4'la was converted to the corresponding diol dibenzoylate 4x'. HPLC: $t_{\text{R}} = 6.7$ min (major) and $t_{\text{R}} = 7.6$ min (minor) 70% ee (Chiralpak IG, 280

nm, 20% IPA-Hex, 1 ml/min). $[\alpha]_D^{26.5} -5.4$ ($c = 0.23$, CHCl_3). The absolute stereochemistry of this compound was assigned in analogy to **4aa**.



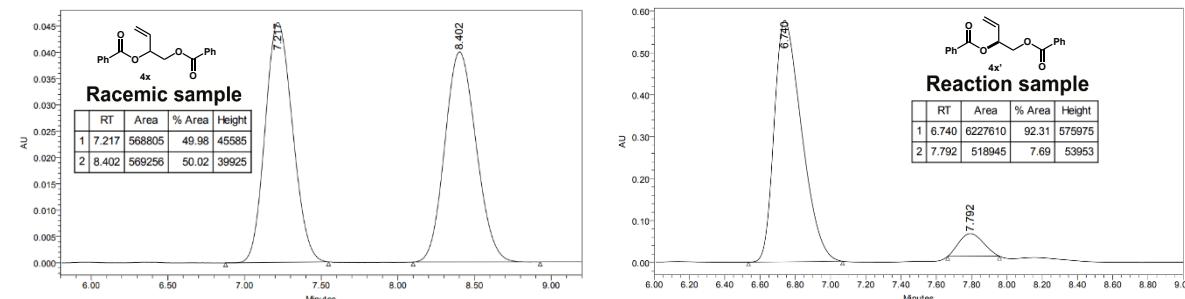
(S)-1-hydroxybut-3-en-2-yl octanoate (4'ma): Prepared according to the general procedure from octanoic acid (**3'm**) (28.8 mg, 31.6 μL , 0.2 mmol) and vinyl oxirane ((\pm) -**1a**) (56 mg, 64 μl , 0.8 mmol).

Reaction time: 12 h. Yield: 97% (41.6 mg, 0.194 mmol). Pale yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 5.77 (ddd, $J = 17.6, 10.8, 6.0$ Hz, 1H), 5.45 – 5.09 (m, 3H), 3.75 – 3.57 (m, 2H), 2.33 (t, $J = 7.6$ Hz, 2H), 1.64 – 1.55 (m, 2H), 1.30 – 1.20 (m, 9H), 0.84 (t, $J = 6.8$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 173.4, 133.0, 118.4, 75.3, 64.5, 34.4, 31.4, 28.7, 24.9, 22.4, 14.0. HRMS calcd for $\text{C}_{12}\text{H}_{21}\text{O}_2$ (ESI^+ , $[\text{M}+\text{H}]^+ - \text{H}_2\text{O}$): 197.1542, found 197.1538. For the determination of enantiomeric excess of **4'ma**, the compound **4'ma** was converted to the corresponding diol dibenzoylate **4x'**. HPLC: $t_R = 7.1$ min (major) and $t_R = 8.2$ min (minor) 86% ee (Chiralpak IG, 280 nm, 20% IPA-Hex, 1 ml/min). $[\alpha]_D^{25} -156.4$ ($c = 0.62$, DCM). The absolute stereochemistry of this compound was assigned in analogy to **4aa**.

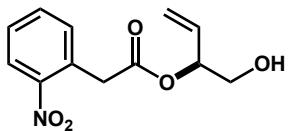


(S)-1-hydroxybut-3-en-2-yl heptanoate (4'na): Prepared according to the general procedure from heptanoic acid (**3'n**) (26.0 mg, 28.3 μL , 0.2 mmol) and vinyl oxirane ((\pm) -**1a**) (56 mg, 64 μl , 0.8 mmol).

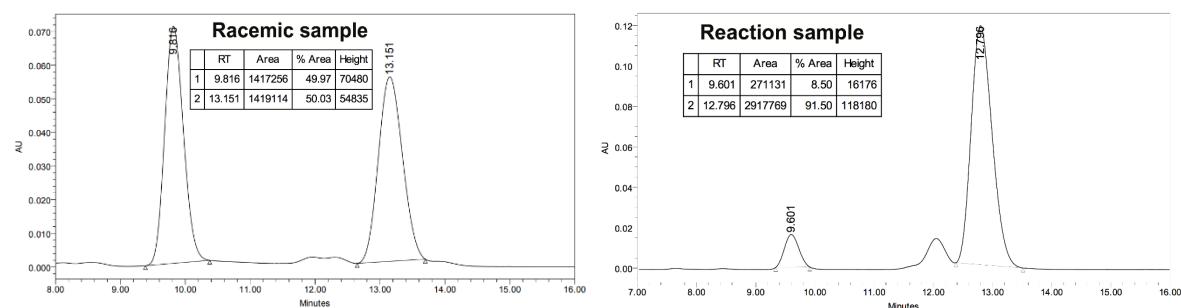
Reaction time: 12 h. Yield: 96% (38.4 mg, 0.192 mmol). Pale yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 5.77 (ddd, $J = 16.8, 10.8, 6.0$ Hz, 1H), 5.46 – 5.10 (m, 3H), 3.79 – 3.58 (m, 2H), 2.41 – 2.26 (m, 2H), 1.69 – 1.53 (m, 2H), 1.35 – 1.23 (m, 6H), 0.86 (t, $J = 6.8$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 172.5, 131.9, 117.4, 74.3, 63.5, 33.4, 30.4, 27.8, 23.9, 21.4, 13.0. HRMS calcd for $\text{C}_{11}\text{H}_{21}\text{O}_3$ (ESI^+ , $[\text{M}+\text{H}]^+$): 201.1491, found 201.1483. For the determination of enantiomeric excess of **4'na**, the compound **4'na** was converted to the corresponding diol dibenzoylate **4x'**. HPLC: $t_R = 6.7$ min (major) and $t_R = 7.8$ min (minor) 85% ee (Chiralpak IG, 280 nm, 20% IPA-Hex, 1 ml/min). $[\alpha]_D^{25} -200.2$ ($c = 0.49$, DCM). The absolute stereochemistry of this compound was assigned in analogy to **4aa**.



(S)-1-hydroxybut-3-en-2-yl 2-(2-nitrophenyl)acetate (4'oa): Prepared according to the general procedure from 2-(2-nitrophenyl)acetic acid (**3'o**) (36.23 mg, 0.2 mmol) and vinyl oxirane (**(±)-1a**) (56

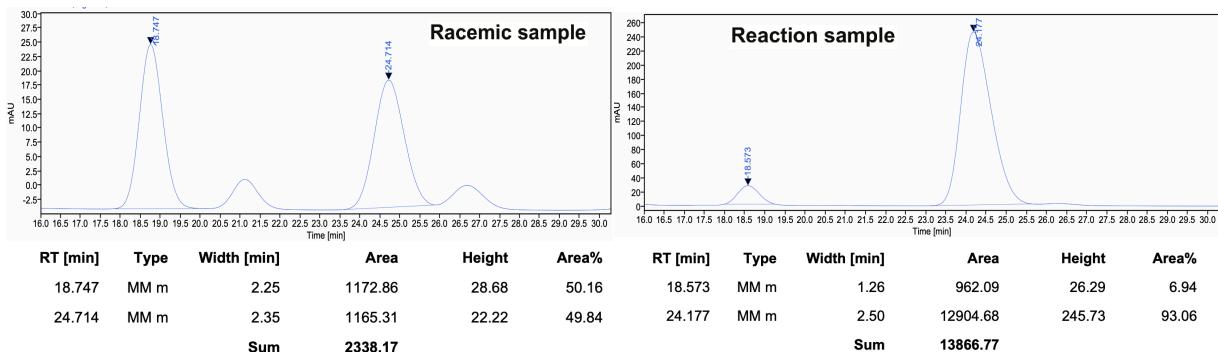


mg, 64 µl, 0.8 mmol). Reaction time: 7 h. Yield: 99% (49.8 mg, 0.198 mmol). Pale yellow oil; ¹H NMR (500 MHz, CDCl₃) δ 8.08 (d, *J* = 8.5 Hz, 1H), 7.60 – 7.57 (m, 1H), 7.47 – 7.44 (m, 1H), 7.36 (d, *J* = 8 Hz, 1H), 5.78 (ddd, *J* = 16.5, 10.5, 6 Hz, 1H), 5.37–5.24 (m, 3H), 4.04 (d, *J* = 2.5 Hz, 2H), 3.73–3.64 (m, 2H), 2.78 (br s, 1H). ¹³C NMR (125 MHz, CDCl₃) δ 169.6, 148.7, 133.7, 133.5, 132.4, 129.6, 128.8, 125.3, 118.8, 76.6, 64.2, 39.9. HRMS calcd for C₁₂H₁₄NO₅ (ESI⁺, [M+H]⁺): 252.0872, found 252.0870. HPLC: t_R = 12.8 min (major) and t_R = 9.6 min (minor) 83% ee (Chiralcel OD-H, 254 nm, 20% IPA-Hex, 1 ml/min). [α]_D²⁵–45.6 (c = 1.06, DCM). The absolute stereochemistry of this compound was assigned in analogy to **4aa**.



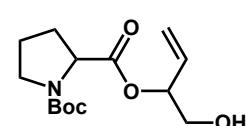
(S)-1-hydroxybut-3-en-2-yl 2-(1H-indol-3-yl)acetate (4'pa): Prepared according to the general procedure from indole-3-acetic acid (**3'p**) (35.0 mg, 0.2 mmol) and vinyl oxirane (**(±)-1a**) (56 mg, 64

µl, 0.8 mmol). Reaction time: 8 h. Yield: 98% (48.1 mg, 0.196 mmol). Pale yellow oil; ¹H NMR (400 MHz, CDCl₃): δ 8.28 (s, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.27 – 7.27 (m, 1H), 7.18 – 7.12 (m, 2H), 7.03 (d, *J* = 2.4 Hz, 1H), 5.76 (ddd, *J* = 17.2, 10.8, 6.0 Hz, 1H), 5.35 – 5.21 (m, 3H), 3.86 – 3.77 (m, 2H), 3.68 – 3.59 (m, 2H), 2.12 (br s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 171.8, 136.1, 132.6, 127.0, 123.3, 122.1, 119.6, 118.5, 111.4, 107.9, 75.8, 64.2, 31.5. HRMS calcd for C₁₄H₁₆NO₃ (ESI⁺, [M+H]⁺): 246.1130, found 246.1128. HPLC: t_R = 24.2 min (major) and t_R = 18.6 min (minor) 86% ee (Chiralcel OD-H, 270 nm, 20% IPA-Hex, 1 ml/min). [α]_D²⁵–70.7 (c = 1.11, DCM). The absolute stereochemistry of this compound was assigned in analogy to **4aa**.



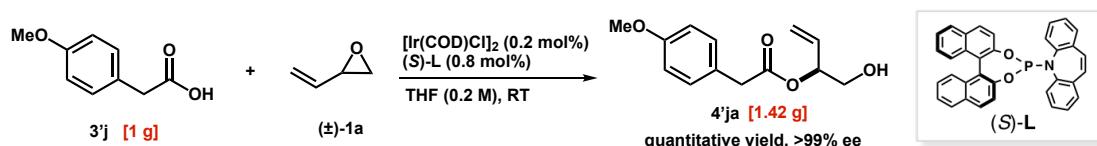
1-(tert-butyl) 2-(1-hydroxybut-3-en-2-yl) pyrrolidine-1,2-dicarboxylate (4'qa): Prepared according to the general procedure from (tert-butoxycarbonyl)proline (**3'q**) (43.05 mg, 0.2 mmol) and vinyl oxirane (**(±)-1a**) (56 mg, 64 µl, 0.8 mmol). Yield: 98% (55.93 mg, 0.196 mmol). Pale yellow oil; ¹H NMR (400

MHz, CDCl₃) δ 5.82 – 5.59 (m, 1H), 5.48 – 5.90 (m, 3H), 4.32–4.22 (m, 1H), 3.73 – 3.62 (m, 1H), 3.51 – 3.34 (m, 3H), 2.27 – 2.15 (m, 1H), 2.03–1.83 (m, 3H), 1.44–1.37 (m, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 172.9, 172.7, 171.6, 155.4, 154.8, 153.8, 135.6, 133.9, 132.6, 132.5, 118.9, 118.3, 117.9, 117.1, 80.5, 80.1, 77.4,



76.5, 75.9, 70.4, 68.5, 64.5, 64.4, 64.3, 59.6, 59.1, 58.3, 46.9, 46.8, 46.3, 30.9, 30.1, 29.9, 29.7, 28.5, 28.4, 28.3, 24.6, 24.5, 23.5. HRMS calcd for $C_{14}H_{24}NO_5$ (ESI $^+$, [M+H] $^+$): 286.1654, found 286.1647.

7. Gram scale preparation of (*S*)-1-hydroxybut-3-en-2-yl 2-(4-methoxyphenyl)acetate (4'ja):



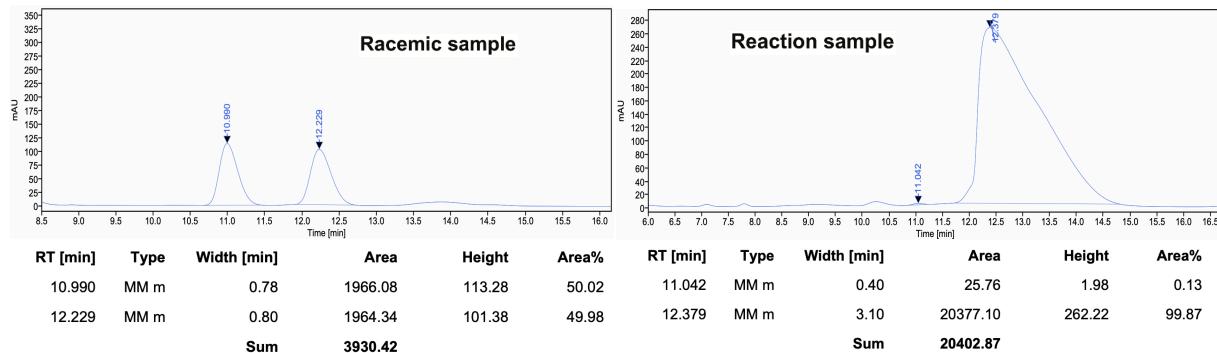
An oven dried 100 mL round bottom flask equipped with a magnetic stirring bar and a three way glass stopcock was charged with $[Ir(COD)Cl]_2$ (8.08 mg, 0.012 mmol, 0.002 equiv., 0.2 mol%) and **(S)-L** (24.4 mg, 0.048 mmol, 0.008 equiv.) under N_2 atmosphere. To this mixture dry THF (30 mL) was added via a gas-tight syringe with a stainless steel needle. The mixture was stirred for 15 min to give a clear catalyst solution. To this, was added 2-(4-methoxyphenyl)acetic acid (**3'j**) (1.0 g, 6.02 mmol, 1 equiv.) and finally vinyl oxirane (**(±)-1a**) (1.69 g, 1.94 mL, 24.1 mmol, 4 equiv.). The reaction was monitored by TLC under ultraviolet light ($\lambda = 254$ nm), bromocresol green and $KMnO_4$ stains. After the reaction was over, the reaction mixture was filtered through a short pad of celite and the volatiles were evaporated to give the desired product (**4'ja**) in pure form in >99% yield (1.42 g, 6.02 mmol) and in >99% ee. No further column purification was necessary.

8. Procedures for the catalytic asymmetric ring opening of the other alkenyl oxiranes and characterization of the products:

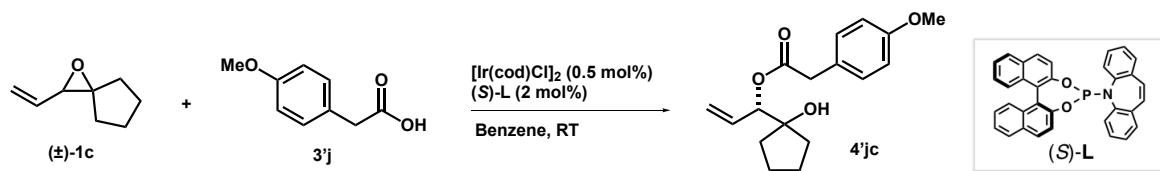
(*S*)-1-hydroxy-2-methylbut-3-en-2-yl 2-(4-methoxyphenyl) acetate (4'jb):



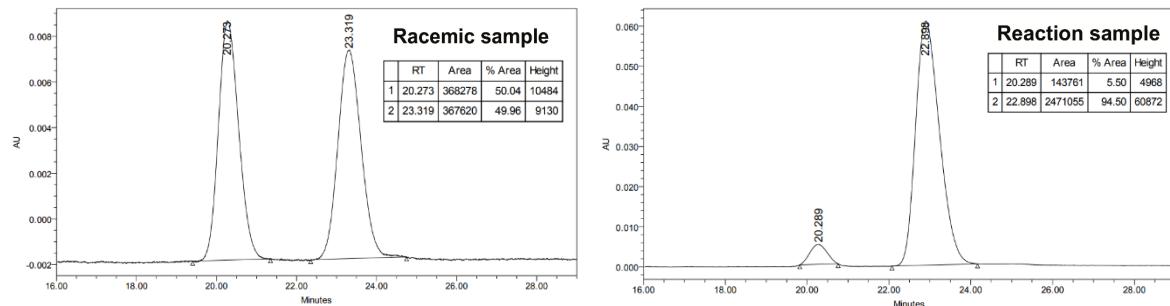
An oven-dried 5 mL screw cap glass vial equipped with a magnetic stirring bar was charged with $[Ir(COD)Cl]_2$ (3.36 mg, 0.005 mmol, 0.025 equiv., 2.5 mol%) and **(S)-L** (10.15 mg, 0.02 mmol, 0.1 equiv.) under N_2 atmosphere. To this mixture, dry benzene (1 mL) was added via a gas-tight syringe with a stainless steel needle. The mixture was stirred for 15 min to give a clear catalyst solution. To this, was added 2-(4-methoxyphenyl)acetic acid (**3'j**) (33.23 mg, 0.2 mmol, 1 equiv.) and finally 2-methyl-2-vinyloxirane (**(±)-1b**) (67.29 mg, 0.078 mL, 0.8 mmol, 4 equiv.). The reaction was monitored by TLC under ultraviolet light ($\lambda = 254$ nm), bromocresol green and $KMnO_4$ stains. After the reaction was over (ca. 1 h), the reaction mixture was filtered through a short pad of celite and the volatiles were evaporated to give desired product (48.0 mg, 0.19 mmol, 96% yield) in pure form. No further column purification was necessary. $R_f = 0.35$ (DCM). 1H NMR (500 MHz, $CDCl_3$): δ 7.16 (d, $J = 8$ Hz, 1H), 6.84 (d, $J = 8.5$ Hz, 1H), 5.90 (dd, $J = 17.5, 11$ Hz, 1H), 5.16 – 5.13 (m, 2H), 3.77 (s, 1H), 3.66 – 3.54 (m, 4H), 1.48 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.7, 158.7, 138.3, 130.2, 126.0, 115.3, 114.1, 84.8, 68.6, 55.3, 41.3, 21.0. HRMS calcd for $C_{14}H_{16}O_3Na$ (ESI $^+$, [M+Na] $^+-H_2O$): 255.0997, found 255.0968. HPLC: $t_R = 11.0$ min (minor) and $t_R = 12.4$ min (major) >99% ee (Chiralpak AS-H, 280 nm, 10% IPA-Hex, 1 ml/min). $[\alpha]_D^{28.8} -27.97$ ($c = 0.7$, $CHCl_3$). The absolute stereochemistry of this compound was assigned in analogy to its diol that is reported. For **4'jb-diol**, $[\alpha]_D^{25} -4.2$ ($c = 0.34$, $CHCl_3$) for (*S*)-isomer.^{18,19}



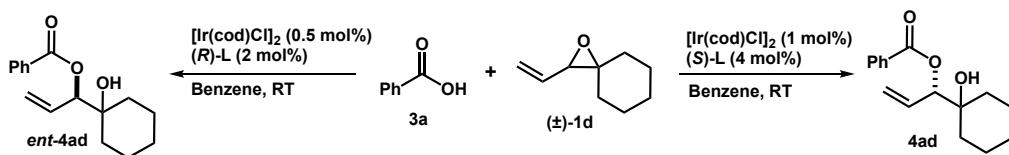
(S)-1-(1-hydroxycyclopentyl)allyl 2-(4-methoxyphenyl)acetate (4'jc**):**



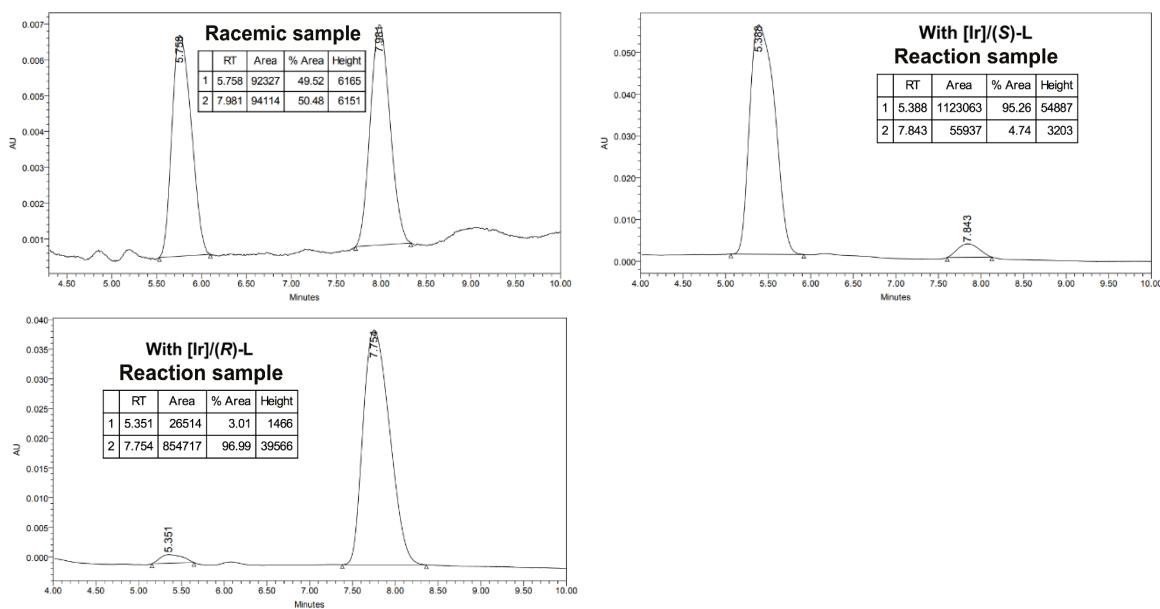
An oven-dried 5 mL screw cap glass vial equipped with a magnetic stirring bar was charged with $[\text{Ir}(\text{cod})\text{Cl}]_2$ (0.67 mg, 0.001 mmol, 0.005 equiv., 0.5 mol%) and **(S)-L** (2.00 mg, 0.004 mmol, 0.02 equiv.) under N_2 atmosphere. To this mixture, dry benzene (1 mL) was added via a gas-tight syringe with a stainless-steel needle. The mixture was stirred for 15 min to give a clear catalyst solution. To this, was added 2-(4-methoxyphenyl)acetic acid (**3'j**) (33.23 mg, 0.2 mmol, 1 equiv.) and finally 2-vinyl-1-oxaspiro[2.4]heptane (**(±)-1c**) (99.20 mg, 0.101 mL, 0.8 mmol, 4 equiv.). The reaction was monitored by TLC under ultraviolet light ($\lambda = 254 \text{ nm}$), bromocresol green and KMnO_4 stains. After the reaction was over (ca. 13 h), the reaction mixture was filtered through a short pad of celite the crude mixture was purified by silica gel column chromatography (0 to 10% $\text{EtOAc}/\text{Hexane}$) to afford the desired product (**4'jc**) as a colorless oil (56.0 mg, 0.19 mmol, 96% yield). $R_f = 0.30$ (DCM). ^1H NMR (400 MHz, CDCl_3): δ 7.17 (d, $J = 8.8 \text{ Hz}$, 2H), 6.83 (d, $J = 8.8 \text{ Hz}$, 2H), 5.85 (ddd, $J = 16.8, 10.8, 6.8 \text{ Hz}$, 1H), 5.26 – 5.19 (m, 2H), 5.19 – 5.13 (m, 1H), 3.75 (s, 3H), 3.57 (s, 2H), 1.79 – 1.72 (m, 3H), 1.58 – 1.50 (m, 5H). ^{13}C NMR (125 MHz, CDCl_3): δ 170.8, 158.6, 132.8, 130.3, 126.1, 119.3, 114.0, 83.1, 80.2, 55.3, 40.8, 37.6, 36.3, 24.1, 23.9. HRMS calcd for $\text{C}_{17}\text{H}_{22}\text{O}_4\text{Na}$ ($\text{ESI}^+, [\text{M}+\text{Na}]^+$): 313.1416, found 313.1401. HPLC: $t_{\text{R}} = 20.3$ min (minor) and $t_{\text{R}} = 22.9$ min (major) 89% ee (Chiralpak IG, 280 nm, 10% IPA-Hex, 1 ml/min). $[\alpha]_D^{28.5} -7.84$ ($c = 0.75$, CHCl_3). The absolute stereochemistry of this compound was assigned in analogy to **4aa**.



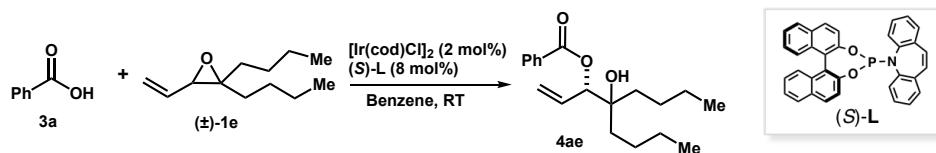
(S)-1-(1-hydroxycyclohexyl)allyl benzoate (4ad):



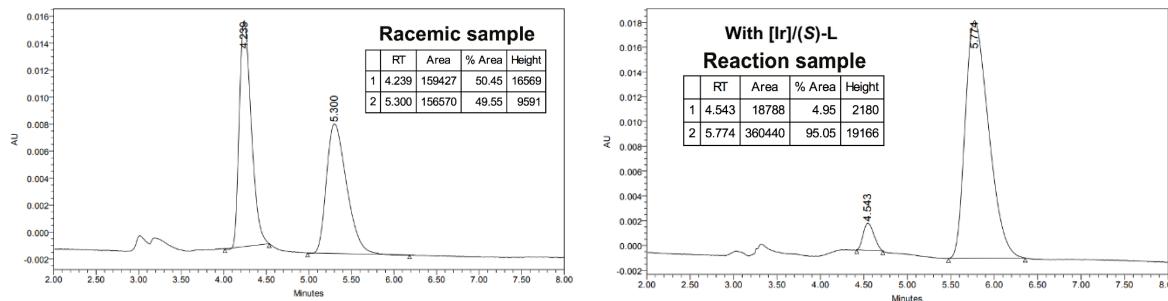
An oven-dried 5 mL screw cap glass vial equipped with a magnetic stirring bar was charged with $[\text{Ir}(\text{COD})\text{Cl}]_2$ (1.34 mg, 0.002 mmol, 0.01 equiv., 1 mol%) and **(S)-L** (4.06 mg, 0.008 mmol, 0.04 equiv.) under N_2 atmosphere. To this mixture dry benzene (1 mL) was added via a gas-tight syringe with a stainless steel needle. The mixture was stirred for 15 min. to give a clear catalyst solution. To this, was added benzoic acid (**3a**) (24.42 mg, 0.2 mmol, 1 equiv.) and finally 2-vinyl-1-oxaspiro[2.5]octane ((\pm) -**1d**) (110.6 mg, 0.8 mmol, 4 equiv.). The reaction was monitored by TLC under ultraviolet light ($\lambda = 254$ nm), bromocresol green and KMnO_4 stains. After the reaction was over (ca. 22 h), the reaction mixture was filtered through a short pad of celite and then the crude mixture was purified by silica gel column chromatography (0 to 10% EtOAc/Hexane) to afford the desired product (**4ad**) as a colorless oil (49.0 mg, 0.19 mmol, 95% yield) in 91% ee. The same reaction was performed with $[\text{Ir}(\text{COD})\text{Cl}]_2$ and **(R)-L** following the same procedure and the product (**ent-4ad**) was obtained in 93% yield and in 94% ee. $R_f = 0.4$ (DCM). ^1H NMR (400 MHz, CDCl_3): δ 8.10 – 8.01 (m, 2H), 7.60 – 7.52 (m, 1H), 7.46 – 7.42 (m, 2H), 6.03 – 5.91 (m, 1H), 5.42 – 5.28 (m, 3H), 1.70 – 1.44 (m, 10H). ^{13}C NMR (100 MHz, CDCl_3): δ 165.6, 133.1, 132.4, 130.2, 129.6, 128.5, 119.8, 81.0, 72.7, 33.9, 33.4, 25.7, 21.4, 21.3. HRMS calcd for $\text{C}_{16}\text{H}_{20}\text{O}_3\text{Na}$ ($\text{ESI}^+, [\text{M}+\text{Na}]^+$): 283.1310, found 283.1315. HPLC: For reaction with $[\text{Ir}]$ /**(S)-L**, $t_R = 5.4$ min (major), $t_R = 7.8$ min (minor), 91% ee. For reaction with $[\text{Ir}]$ /**(R)-L**, $t_R = 5.4$ min (major), $t_R = 7.8$ min (minor), 94% ee. (Chiralpak AS-H, 280 nm, 5% IPA-Hex, 1 mL/min). $[\alpha]_D^{27.9} -11.76$ ($c = 1.0$, CHCl_3) (with $[\text{Ir}]$ /**(S)-L**). $[\alpha]_D^{28.8} +8.71$ ($c = 0.72$, CHCl_3) (with $[\text{Ir}]$ /**(R)-L**). The absolute stereochemistry of **4ad** was assigned in analogy to **4aa**.



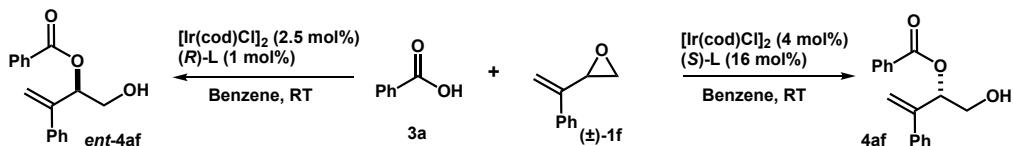
(S)-4-butyl-4-hydroxyoct-1-en-3-yl benzoate (4ae):



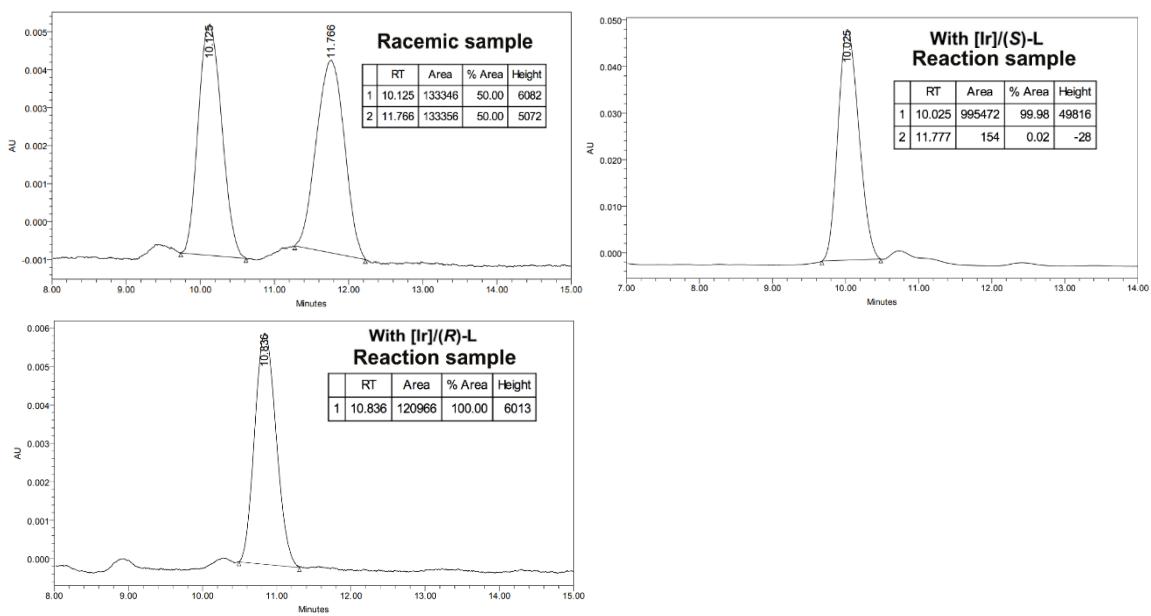
An oven-dried 5 mL screw cap glass vial equipped with a magnetic stirring bar was charged with $[\text{Ir}(\text{COD})\text{Cl}]_2$ (2.68 mg, 0.004 mmol, 0.02 equiv., 2 mol%) and (*S*)-L (8.12 mg, 0.016 mmol, 0.08 equiv.) under N_2 atmosphere. To this mixture, dry benzene (1 mL) was added via a gas-tight syringe with a stainless steel needle. The mixture was stirred for 15 min to give a clear catalyst solution. To this, was added benzoic acid (**3a**) (24.42 mg, 0.2 mmol, 1 equiv.) and finally 2,2-dibutyl-3-vinyloxirane ((\pm)-**1e**) (145.7 mg, 0.8 mmol, 4 equiv.). The reaction was monitored by TLC under ultraviolet light ($\lambda = 254 \text{ nm}$), bromocresol green and KMnO_4 stains. After the reaction was over (ca. 15 h), the reaction mixture was filtered through a short pad of celite and the crude mixture was purified by silica gel column chromatography (0 to 10% EtOAc/Hexane) to afford the desired product (**4ae**) as a colorless oil (59.0 mg, 0.19 mmol, 97% yield). $R_f = 0.56$ (DCM). ^1H NMR (400 MHz, CDCl_3): δ 8.07 – 8.02 (m, 2H), 7.58 – 7.54 (m, 1H), 7.46 – 7.43 (m, 2H), 5.99 (ddd, $J = 17.2, 10.4, 6.8 \text{ Hz}$, 1H), 5.48 – 5.30 (m, 3H), 1.64 (s, 1H), 1.59 – 1.52 (m, 4H), 1.33 – 1.24 (m, 8H), 0.89 – 0.82 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 161.7, 129.2, 128.6, 126.3, 125.7, 124.5, 115.7, 75.4, 71.7, 31.8, 31.1, 21.5, 21.2, 19.4, 19.3, 10.1, 10.1. HRMS calcd for $\text{C}_{19}\text{H}_{28}\text{O}_3\text{Na}$ ($\text{ESI}^+, [\text{M}+\text{Na}]^+$): 327.1936, found 327.1948. HPLC: For reaction with $[\text{Ir}]$ /*(S*)-L, $t_R = 4.5 \text{ min}$ (minor), $t_R = 5.8 \text{ min}$ (major), 90% ee. $[\alpha]_D^{25.6} -14.0$ ($c = 0.6, \text{CHCl}_3$) (with $[\text{Ir}]$ /*(S*)-L). The absolute stereochemistry of this compound was assigned in analogy to **4aa**.



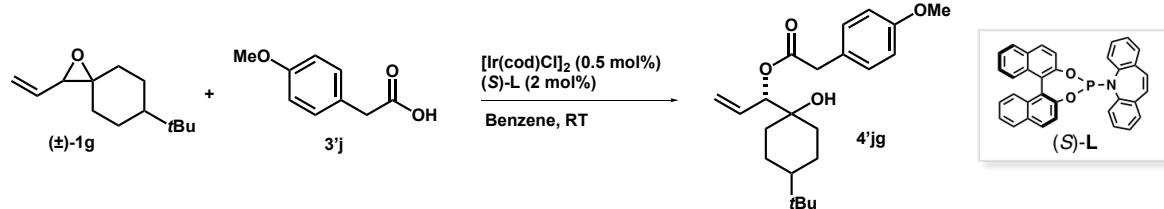
(*S*)-1-hydroxy-3-phenylbut-3-en-2-yl benzoate (**4af**):



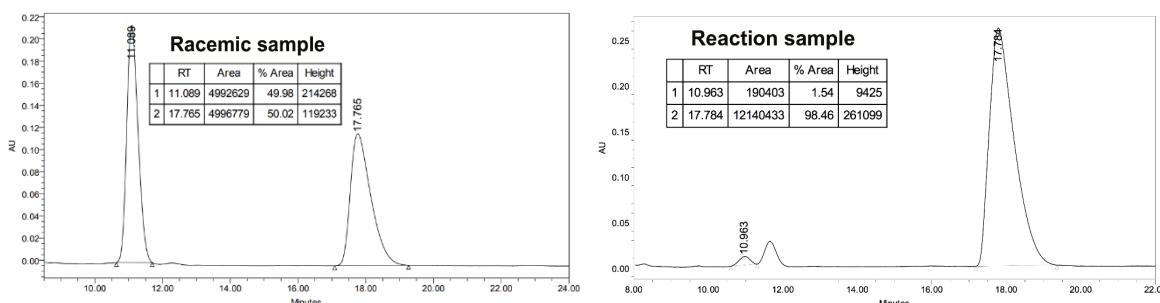
An oven-dried 5 mL screw cap glass vial equipped with a magnetic stirring bar was charged with $[\text{Ir}(\text{COD})\text{Cl}]_2$ (5.37 mg, 0.008 mmol, 0.04 equiv., 4 mol%) and (*S*)-L (16.2 mg, 0.032 mmol, 0.16 equiv.) under N_2 atmosphere. To this mixture, dry benzene (1 mL) was added via a gas-tight syringe with a stainless steel needle. The mixture was stirred for 15 min to give a clear catalyst solution. To this, was added benzoic acid (**3a**) (24.4 mg, 0.2 mmol) and finally 2-(1-phenylvinyl)oxirane ((\pm)-**1f**) (117.0 mg, 0.8 mmol, 4 equiv.). The reaction was monitored by TLC under ultraviolet light ($\lambda = 254 \text{ nm}$), bromocresol green and KMnO_4 stains. After 72 h, the reaction mixture was filtered through a short pad of celite and the crude mixture was purified by silica gel column chromatography (0 to 10% EtOAc/Hexane) to afford the desired product (**4af**) as a colorless oil (45.0 g, 0.17 mmol, 85% yield) in >99% ee. Under the same reaction conditions using (*R*)-L, the product (**ent-4af**) was obtained in 83% yield and in >99% ee. $R_f = 0.38$ (DCM). ^1H NMR (400 MHz, CDCl_3): δ 8.13 – 8.10 (m, 2H), 7.58 (ddd, $J = 8.4, 2.4, 1.2 \text{ Hz}$, 1H), 7.48 (m, 4H), 7.38 – 7.29 (m, 3H), 6.05 – 6.02 (m, 1H), 5.43 (d, $J = 4.0 \text{ Hz}$, 2H), 3.87 – 3.78 (m, 2H), 2.03 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 166.1, 145.1, 138.9, 133.3, 129.8, 128.6, 128.5, 128.2, 126.9, 115.0, 77.1, 64.3, 29.7. HRMS calcd for $\text{C}_{17}\text{H}_{16}\text{O}_3\text{Na}$ ($\text{ESI}^+, [\text{M}+\text{Na}]^+$): 291.0997, found 291.0999. HPLC: $t_R = 10.8 \text{ min}$ (major), minor enantiomer could not be found, >99% ee. (Chiralpak AS-H, 280 nm, 2% IPA-Hex, 1 ml/min). $[\alpha]_D^{28.4} -34.85$ ($c = 2.0, \text{CHCl}_3$) (with $[\text{Ir}]$ /*(S*)-L). $[\alpha]_D^{28.5} +15.2$ ($c = 1.5, \text{CHCl}_3$) (with $[\text{Ir}]$ /*(R*)-L). The absolute stereochemistry of this compound was assigned in analogy to **4aa**.



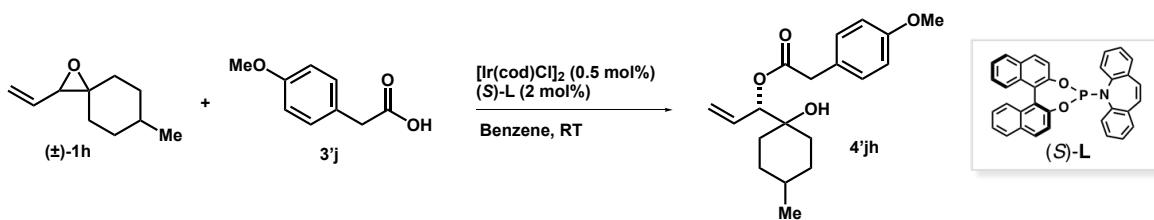
(S)-1-(4-(tert-butyl)-1-hydroxycyclohexyl)allyl 2-(4-methoxyphenyl)acetate (**4'jg**):



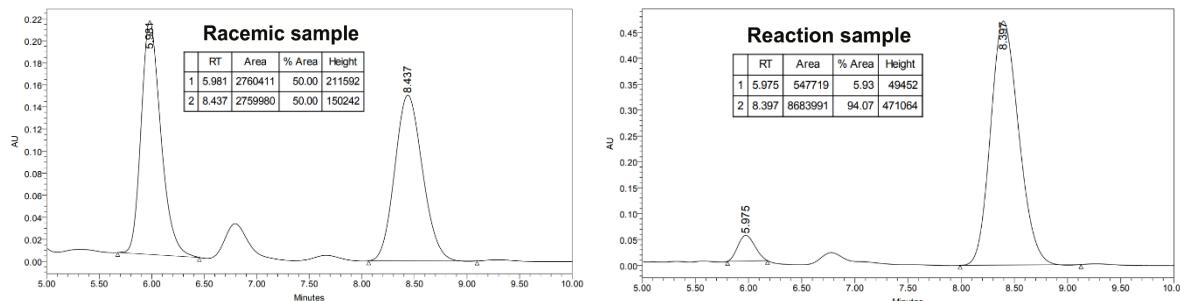
An oven-dried 5 mL screw cap glass vial equipped with a magnetic stirring bar was charged with $[\text{Ir}(\text{COD})\text{Cl}]_2$ (0.67 mg, 0.001 mmol, 0.005 equiv., 0.50 mol%) and $(S)\text{-L}$ (2.0 mg, 0.004 mmol, 0.02 equiv.) under N_2 atmosphere. To this mixture, dry benzene (1 mL) was added via a gas-tight syringe with a stainless-steel needle. The mixture was stirred for 15 min to give a clear catalyst solution. To this, was added 2-(4-methoxyphenyl)acetic acid (**3'j**) (33.23 mg, 0.2 mmol, 1 equiv.) and finally 6-(tert-butyl)-2-vinyl-1-oxaspiro[2.5]octane ($(\pm)\text{-1g}$) (155.20 mg, 0.168 mL, 0.8 mmol, 4 equiv.). The reaction was monitored by TLC under ultraviolet light ($\lambda = 254 \text{ nm}$), bromocresol green and KMnO_4 stains. After the reaction was over (ca. 13 h), the reaction mixture was filtered through a short pad of celite the crude mixture was purified by silica gel column chromatography (0 to 10% EtOAc/Hexane) to afford the desired product (**4'jg**) as a colorless oil (67.8 mg, 0.19 mmol, 94% yield). $R_f = 0.30$ (DCM). ^1H NMR (400 MHz, CDCl_3): δ 7.17 (d, $J = 8.5 \text{ Hz}$, 2H), 6.83 (d, $J = 8.6 \text{ Hz}$, 2H), 5.93 – 5.75 (m, 1H), 5.22 (dd, $J = 13.8, 8.5 \text{ Hz}$, 2H), 4.99 (d, $J = 7.0 \text{ Hz}$, 1H), 3.76 (s, 3H), 3.58 (s, 2H), 1.61 – 1.46 (m, 4H), 1.31 – 1.20 (m, 5H), 0.82 (s, 9H). ^{13}C NMR (125 MHz, CDCl_3): δ 170.9, 158.8, 132.4, 130.3, 126.1, 119.6, 114.0, 81.6, 72.0, 55.3, 47.8, 40.8, 34.0, 33.2, 32.4, 27.5, 21.9, 21.8. HRMS calcd for $\text{C}_{22}\text{H}_{32}\text{O}_4\text{Na}$ (ESI^+ , $[\text{M}+\text{Na}]^+$): 383.2198, found 383.2189. HPLC: $t_R = 11.0 \text{ min}$ (minor) and $t_R = 17.8 \text{ min}$ (major) 97% ee (Chiralpak IG, 220 nm, 10% IPA-Hex, 1 ml/min). $[\alpha]_D^{28.4} -2.93$ ($c = 0.45$, CHCl_3). The absolute stereochemistry of this compound was assigned in analogy to **4aa**.



(S)-1-(1-hydroxy-4-methylcyclohexyl)allyl 2-(4-methoxyphenyl)acetate (4'jh):

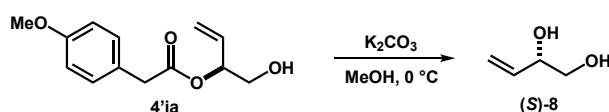


An oven-dried 5 mL screw cap glass vial equipped with a magnetic stirring bar was charged with $[\text{Ir}(\text{COD})\text{Cl}]_2$ (0.67 mg, 0.001 mmol, 0.005 equiv., 0.5 mol%) and **(S)-L** (2.0 mg, 0.004 mmol, 0.02 equiv.) under N_2 atmosphere. To this mixture, dry benzene (1 mL) was added via a gas-tight syringe with a stainless-steel needle. The mixture was stirred for 15 min to give a clear catalyst solution. To this, was added 2-(4-methoxyphenyl)acetic acid (**3'j**) (33.23 mg, 0.2 mmol, 1 equiv.) and finally 6-methyl-2-vinyl-1-oxaspiro[2.5]octane (**(±)-1h**) (122.0 mg, 0.128 mL, 0.8 mmol, 4 equiv.). The reaction was monitored by TLC under ultraviolet light ($\lambda = 254 \text{ nm}$), bromocresol green and KMnO_4 stains. After the reaction was over (ca. 30 h), the reaction mixture was filtered through a short pad of celite the crude mixture was purified by silica gel column chromatography (0 to 10% EtOAc/Hexane) to afford the desired product (**4'jh**) as a colorless oil (54.1 mg, 0.17 mmol, 85% yield). $R_f = 0.30$ (DCM). ^1H NMR (400 MHz, CDCl_3): δ 7.17 (d, $J = 7.2 \text{ Hz}$, 2H), 6.83 (d, $J = 8.4 \text{ Hz}$, 2H), 6.03 – 5.69 (m, 1H), 5.31 – 5.16 (m, 2H), 5.00 (d, $J = 6.8 \text{ Hz}$, 1H), 3.76 (s, 3H), 3.58 (s, 2H), 1.71 – 1.36 (m, 5H), 1.23 (d, $J = 4.8 \text{ Hz}$, 4H), 0.87 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 170.9, 158.8, 132.4, 130.3, 126.1, 119.6, 114.1, 81.6, 72.0, 55.3, 40.8, 33.5, 32.7, 32.1, 29.6, 29.5, 22.2. HRMS calcd for $\text{C}_{19}\text{H}_{26}\text{O}_4\text{Na}$ (ESI^+ , $[\text{M}+\text{Na}]^+$): 341.1729, found 341.1717. HPLC: $t_R = 5.9 \text{ min}$ (minor) and $t_R = 8.4 \text{ min}$ (major) 88% ee (Chiralpak IG, 230 nm, 50% IPA-Hex, 1 ml/min). $[\alpha]_D^{28.7} -7.6$ ($c = 0.6$, CHCl_3). The absolute stereochemistry of this compound was assigned in analogy to **4aa**.



9. Synthetic application of alkenyl diol monoester products:

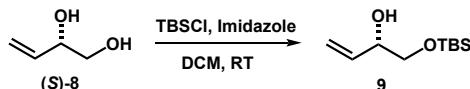
(S)-but-3-ene-1,2-diol ((S)-8):



To a stirred solution of **(S)-1-hydroxybut-3-en-2-yl 2-(4-methoxyphenyl)acetate** (**4'ja**) (0.2 g, 0.84 mmol, 1 equiv.) in methanol (1.7 mL) was added potassium carbonate (0.23 g, 1.68 mmol, 2 equiv.) at 0°C . The mixture was stirred for 1 h and then filtered through sodium sulfate with EtOAc. The reaction mixture was concentrated and the residue was purified by flash chromatography eluting first with DCM and then with EtOAc to give product **((S)-8)** (0.063 g, 0.723 mmol, 86% yield) as a colorless dense oil. $R_f = 0.27$ (Hex/EtOAc 1:1). ^1H NMR (400 MHz, CDCl_3): δ 5.81 (ddd, $J = 17.2, 10.8, 5.6 \text{ Hz}$, 1H), 5.32 (dt, $J = 17.2, 1.6 \text{ Hz}$, 1H), 5.19 (dt, $J = 10.4, 1.6 \text{ Hz}$, 1H), 4.22 – 4.20 (m, 1H), 3.63 (dd, $J = 11.2, 3.2 \text{ Hz}$,

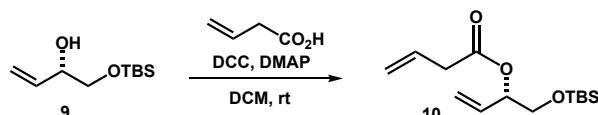
1H), 3.46 (dd, J = 11.2, 7.6 Hz, 1H), 3.40 (br s, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 136.7, 116.7, 73.3, 66.2. The analytical data of the compound was in complete agreement with the literature.²⁰ $[\alpha]_D^{25}$ – 123.9 (c = 0.44, DCM). Reported $[\alpha]_D$ –28.4 (c = 5.0, EtOAc) for (*S*)-isomer.²⁰

(*S*)-1-((tert-butyldimethylsilyl)oxy)but-3-en-2-ol (9):



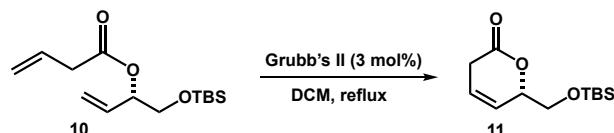
To a solution of (*S*)-but-3-ene-1,2-diol (**(S)-8**) (0.25 g, 2.83 mmol, 1 equiv.) and imidazole (0.39 g, 5.67 mmol, 2 equiv.) in dichloromethane (5 mL) was added *tert*-butyldimethylsilyl chloride (0.43 g, 2.83 mmol, 1 equiv.) and the solution was stirred for 4–8 hours. After completion of reaction (monitored by TLC), the reaction mixture was concentrated and the residue was purified by silica gel chromatography (0 to 10% EtOAc/Hexane) to give compound (**9**) as a colorless oil (0.56 g, 2.75 mmol, 97% yield); R_f = 0.3 (EtOAc/Hex 0.5:9.5). ^1H NMR (500 MHz, CDCl_3): δ 5.78 (ddd, J = 16.5, 11.0, 6.0 Hz, 1H), 5.31 (d, J = 17.0 Hz, 1H), 5.15 (d, J = 11.0 Hz, 1H), 4.13 (s, 1H), 3.63 (dd, J = 10.0, 4.0 Hz, 1H), 3.42 (dd, J = 10.0, 8.0 Hz, 1H), 2.57 (s, 1H), 0.88 (s, 9H), 0.05 (s, 6H). ^{13}C NMR (125 MHz, CDCl_3): δ 136.7, 116.4, 73.0, 67.0, 25.9, 18.3, –5.4, –5.4. The analytical data of the compound was in complete agreement with the literature.¹⁸ $[\alpha]_D^{25}$ –332.4 (c = 0.22, DCM). Reported $[\alpha]_D^{20}$ –5.5 (c = 1.65, CHCl_3).²¹

(*S*)-1-((tert-butyldimethylsilyl)oxy)but-3-en-2-yl but-3-enoate (10):



To a solution of (*S*)-1-((tert-butyldimethylsilyl)oxy)but-3-en-2-ol (**9**) (0.06 g, 0.29 mmol, 1 equiv.) and DCC (0.71 g, 0.35 mmol, 1.2 equiv.) in DCM (2 mL) was added but-3-enoic acid (0.03 g, 0.03 mL, 0.34 mmol, 1.2 equiv.) and DMAP (0.001 g, 0.007 mmol, 0.025 equiv.) respectively at room temperature. After completion, the reaction mixture was concentrated and the residue was purified by silica gel chromatography (0 to 3% EtOAc/Hexane) to give the product (**10**) as a colorless oil (0.06 g, 0.22 mmol, 78% yield); R_f = 0.68 (EtOAc/Hex 1:9). ^1H NMR (400 MHz, CDCl_3): δ 5.94 – 5.75 (m, 2H), 5.34 – 5.27 (m, 2H), 5.22 (dt, J = 18.4, 1.2 Hz, 1H), 5.18 – 5.10 (m, 2H), 3.65 (d, J = 5.6 Hz, 2H), 3.09 (dt, J = 6.8, 1.2 Hz, 2H), 0.85 (s, 9H), 0.02 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 170.6, 133.4, 130.3, 118.5, 117.8, 75.3, 64.6, 39.3, 25.8, 18.2, –5.4, –5.4. The analytical data of the compound was in complete agreement with the literature.²² $[\alpha]_D^{26.3}$ –15.8 (c = 0.13, DCM).

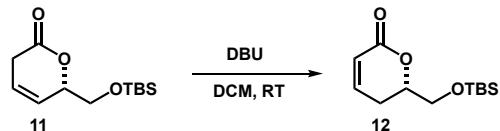
(6*S*)-6-(((tert-butyldimethylsilyl)oxy)methyl)-3,6-dihydro-2*H*-pyran-2-one (11):



(*S*)-1-((tert-butyldimethylsilyl)oxy)but-3-en-2-yl but-3-enoate (**10**) (0.15 g, 0.55 mmol, 1 equiv.) and Grubbs II catalyst (0.014 g, 0.016 mmol, 0.03 equiv., 3 mol%) were combined in 9 mL of degassed and freshly distilled dry dichloromethane. The solution was then refluxed for 18 h. The reaction mixture was concentrated to dryness and the crude product was purified by column chromatography (0 to 10% EtOAc/Hexane) to give product (**11**) as a colorless oil (0.12 g, 0.49 mmol, 88% yield); R_f = 0.28 (EtOAc/Hex 1:9). ^1H NMR (400 MHz, CDCl_3): δ 5.91 – 5.77 (m, 2H), 4.94 – 4.87 (m, 1H), 3.82 (dd, J = 10.8, 4.4 Hz, 1H), 3.71 (dd, J = 10.8, 3.2 Hz, 1H), 3.04 – 2.98 (m, 2H), 0.83 (s, 9H), 0.01 (d, J = 2.4 Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 169.0, 123.5, 123.1, 79.9, 64.9, 30.3, 25.7, 18.2, –5.5, –5.5. The

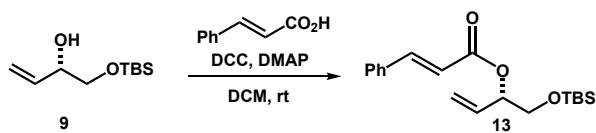
analytical data of the compound was in complete agreement with the literature.²³ $[\alpha]_D^{25} -71.0$ ($c = 0.80$, DCM). Reported $[\alpha]_D^{20} -159.0$ ($c = 1.0$, MeOH).²³

(6*S*)-6-(((*tert*-butyldimethylsilyl)oxy)methyl)-5,6-dihydro-2*H*-pyran-2-one (12):



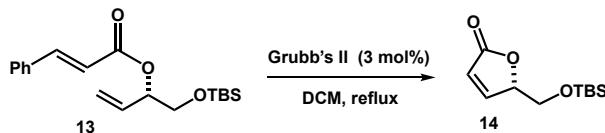
(6*S*)-6-(((*tert*-butyldimethylsilyl)oxy)methyl)-3,6-dihydro-2*H*-pyran-2-one (**11**) (0.10 g, 0.41 mmol, 1 equiv.) and DBU (0.006 g, 10 mol%, 0.006 mL, 0.04 mmol, 0.1 equiv.) were combined in 3 mL dichloromethane. The reaction mixture was stirred at room temperature for 16 h, after which it was concentrated to dryness. The crude product was purified by column chromatography (0 to 10% EtOAc/Hexanes) to yield compound (**12**) as a colorless oil (0.086 g, 0.35 mmol, 86% yield); $R_f = 0.4$ (DCM/Hex 1:1). ¹H NMR (400 MHz, CDCl₃): δ 6.86 (ddd, $J = 9.6, 5.6, 2.8$ Hz, 1H), 5.98 – 5.92 (m, 1H), 4.43 (ddd, $J = 10.8, 10.0, 4.8$ Hz, 1H), 3.77 (dd, $J = 4.8, 2.0$ Hz, 2H), 2.53 – 2.32 (m, 2H), 0.85 (s, 9H), 0.04 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 163.8, 145.0, 121.1, 76.7, 64.2, 25.8, -5.4, -5.4. The analytical data of the compound was in complete agreement with the literature.²⁴ $[\alpha]_D^{28.1} -101.2$ ($c = 0.8$, CHCl₃). Reported $[\alpha]_D^{20} -94.4$ ($c = 1.01$, CHCl₃).²⁴

(S)-1-((*tert*-butyldimethylsilyl)oxy)but-3-en-2-yl cinnamate (13):



To a solution of (S)-1-((*tert*-butyldimethylsilyl)oxy)but-3-en-2-ol (**9**) (0.10 g, 0.49 mmol, 1 equiv.) and DCC (0.13 g, 0.59 mmol, 1.2 equiv.) in DCM (4 mL) was added cinnamic acid (0.087 g, 0.59 mmol, 1.2 equiv.) and DMAP (0.002 g, 0.012 mmol, 0.025 equiv.) respectively at room temperature. After completion of reaction, the reaction mixture was concentrated and the residue was purified by silica gel chromatography (0 to 5% EtOAc/Hexane) to give the product (**13**) as a colorless oil (0.116 g, 0.34 mmol, 71% yield); $R_f = 0.44$ (EtOAc/Hex 1:9). ¹H NMR (400 MHz, CDCl₃): δ 7.70 (d, $J = 16.0$ Hz, 1H), 7.52 – 7.50 (m, 2H), 7.38 – 7.36 (m, 3H), 6.45 (d, $J = 16.0$ Hz, 1H), 5.88 (ddd, $J = 17.2, 10.4, 6.0$ Hz, 1H), 5.46 – 5.41 (m, 1H), 5.34 (dt, $J = 17.2, 1.2$ Hz, 1H), 5.24 (dt, $J = 10.4, 1.2$ Hz, 1H), 3.76 – 3.74 (m, 2H), 0.87 (s, 9H), 0.05 (d, $J = 2.8$ Hz, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 166.1, 145.0, 134.5, 133.6, 130.3, 128.9, 128.1, 118.2, 117.8, 75.3, 64.8, 25.8, 18.3, -5.3, -5.3. HRMS calcd for C₁₉H₂₉O₃Si (ESI⁺, [M+H]⁺): 333.1886, found 333.1878. $[\alpha]_D^{25} -29.3$ ($c = 0.44$, DCM).

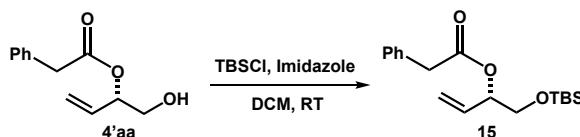
(S)-5-(((*tert*-butyldimethylsilyl)oxy)methyl)dihydrofuran-2(3*H*)-one (14):



(S)-1-((*tert*-butyldimethylsilyl)oxy)but-3-en-2-yl cinnamate (**13**) (0.096 g, 0.28 mmol, 1 equiv.) and Grubbs II catalyst (0.007 g, 0.0086 mmol, 0.03 equiv.) were combined in 5.5 mL degassed and distilled DCM. The solution was then refluxed for 18 h. The reaction mixture was then concentrated to dryness and the crude product was purified by column chromatography (0-10% EtOAc/Hexanes) to yield product (**14**) as a colorless oil (0.053 g, 0.23 mmol, 81% yield); $R_f = 0.11$ (EtOAc/Hex 1:9). ¹H NMR (400 MHz, CDCl₃): δ 7.47 (dd, $J = 6.0, 1.6$ Hz, 1H), 6.13 (dd, $J = 6.0, 2.0$ Hz, 1H), 5.04 – 5.01 (m, 1H), 3.90 (dd,

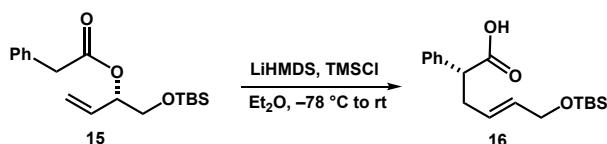
$J = 10.8, 4.4$ Hz, 1H), 3.77 (dd, $J = 10.8, 5.6$ Hz, 1H), 0.84 (s, 9H), 0.03 (d, $J = 4.4$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 173.0, 154.3, 122.5, 83.4, 62.9, 25.7, 18.2, -5.5, -5.5. The analytical data of the compound was in complete agreement with the literature.²⁵ $[\alpha]_D^{26.5} -85.0$ ($c = 0.15$, DCM). Reported $[\alpha]_D^{23} -137$ ($c = 0.9$, CHCl_3).²⁵

(S)-1-((tert-butyldimethylsilyl)oxy)but-3-en-2-yl 2-phenylacetate (15):



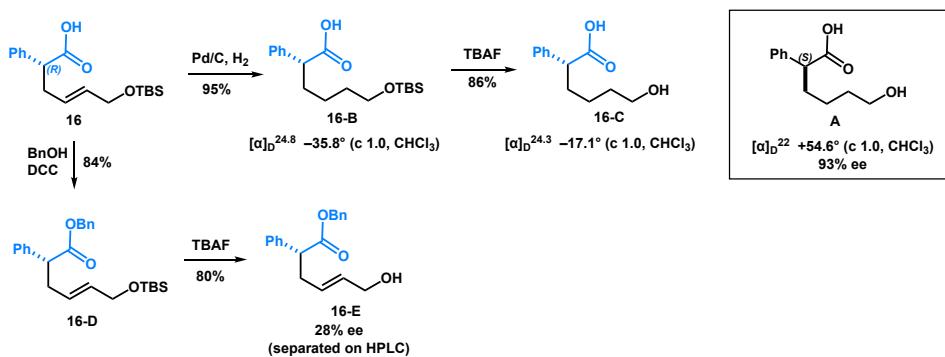
To a solution of (S)-1-hydroxybut-3-en-2-yl 2-phenylacetate (**4'aa**) (0.20 g, 1.0 mmol, 1 equiv.) and imidazole (0.12 g, 1.8 mmol, 1.8 equiv.) in dichloromethane (13 mL) was added *tert*-butyldimethylsilyl chloride (0.27 g, 1.8 mmol, 1.8 equiv.) and the solution stirred for 4-8 hours. When the starting material was consumed, the reaction mixture was concentrated to dryness and the crude mixture was purified by column chromatography (0 to 5% EtOAc/Hexane) to yield product (**15**) as a colorless oil (0.31 g, 0.967 mmol, 97% yield); $R_f = 0.52$ (EtOAc/Hex 1:9). ^1H NMR (400 MHz, CDCl_3): δ 7.31 – 7.24 (m, 5H), 5.78 (ddd, $J = 17.2, 10.8, 6.0$ Hz, 1H), 5.34 – 5.29 (m, 1H), 5.18 (ddd, $J = 12.0, 11.2, 1.2$ Hz, 2H), 3.67 – 3.64 (m, 4H), 0.86 (s, 9H), 0.02 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 170.7, 134.0, 133.3, 129.3, 128.5, 127.0, 117.8, 75.6, 64.6, 41.5, 25.8, 18.3, -5.4, -5.4. HRMS calcd for $\text{C}_{18}\text{H}_{29}\text{O}_3\text{Si}$ (ESI^+ , $[\text{M}+\text{H}]^+$): 321.1886, found 321.1879. $[\alpha]_D^{25} -106.0$ ($c = 0.23$, DCM).

(R,E)-6-((tert-butyldimethylsilyl)oxy)-2-phenylhex-4-enoic acid (16):

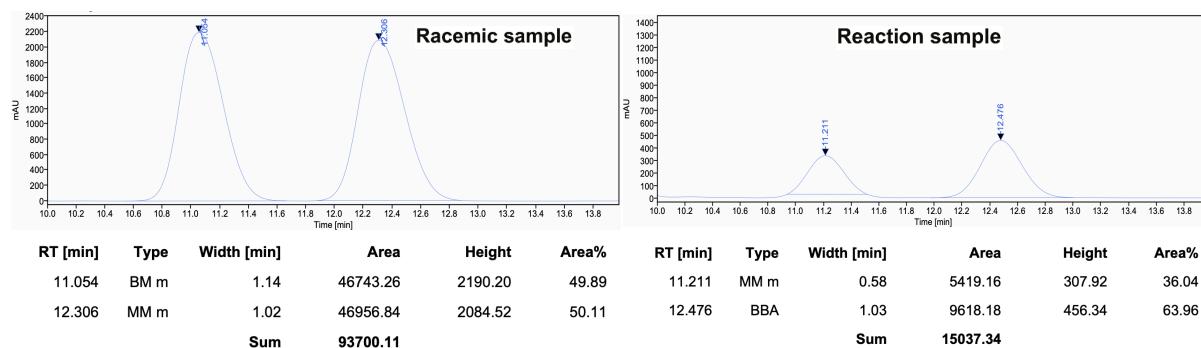


To a well stirred solution of (S)-1-((tert-butyldimethylsilyl)oxy)but-3-en-2-yl 2-phenylacetate (**15**) (0.15 g, 0.47 mmol, 1 equiv.) in anhydrous diethyl ether (6 mL) was added LiHMDS (1 M in THF, 0.94 mL, 0.94 mmol, 2 equiv.) dropwise at -78°C under nitrogen. Then, TMSCl (0.12 ml, 0.94 mmol, 2 equiv.) was added dropwise. The resulting mixture was stirred at -78°C for 2 h and then at room temperature for 24 h. After complete consumption of the starting material (**15**), as observed by TLC analysis (typically 24 h), the reaction was quenched with sat. NH_4Cl (aq.). The resulting mixture was extracted with diethyl ether (3 x 30 mL) and the combined organics were evaporated under reduced pressure. The residue was purified by silica gel chromatography eluting with a gradient of 0 to 20% ethyl acetate/hexane to give product (**16**) as a clear oil (0.087 g, 0.27 mmol, 58% yield); $R_f = 0.21$ (EtOAc/Hex 2:8). ^1H NMR (500 MHz, CDCl_3): δ 7.27 (d, $J = 24.0$ Hz, 5H), 5.57 – 5.53 (m, 2H), 4.05 (d, $J = 3.0$ Hz, 2H), 3.60 (t, $J = 7.0$ Hz, 1H), 2.81 – 2.76 (m, 1H), 2.51 – 2.48 (m, 1H), 0.84 (s, 9H), -0.01 (s, 6H). ^{13}C NMR (125 MHz, CDCl_3): δ 179.1, 137.9, 132.1, 128.7, 128.1, 127.5, 126.8, 63.6, 51.5, 35.6, 25.9, 18.4, -5.2. HRMS calcd for $\text{C}_{18}\text{H}_{29}\text{O}_3\text{Si}$ (ESI^+ , $[\text{M}+\text{H}]^+$): 321.1886, found 321.1884. $[\alpha]_D^{25} -112.6$ ($c = 0.55$, DCM) for **16**; $[\alpha]_D^{24.8} -35.8^\circ$ ($c = 1.0$, CHCl_3) for **16-B**; $[\alpha]_D^{24.3} -17.1^\circ$ ($c = 1.0$, CHCl_3) for **16-C**. $[\alpha]_D^{23} +77.2^\circ$ ($c = 1.0$, CHCl_3) for (*S*)-isomer of reported compound **A**.²⁶

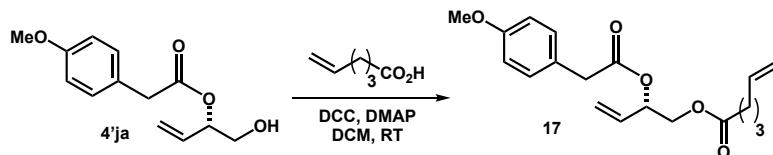
The enantioselectivity of **16** has been determined by converting it to compound **16-E**. HPLC: $t_R = 12.5$ min (major) and $t_R = 11.2$ min (minor) 28% ee (Chiralcel OD-H, 210 nm, 10% IPA-Hex, 1 ml/min).



HPLC of compound 16-E:

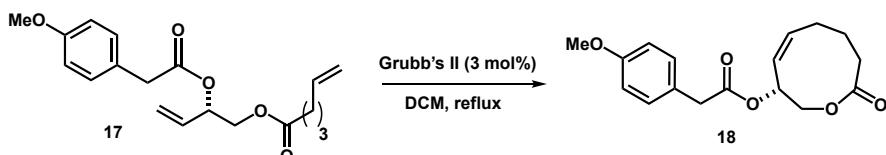


(S)-2-(2-(4-methoxyphenyl)acetoxy)but-3-en-1-yl but-3-enoate (17):



To a solution of (S)-1-hydroxybut-3-en-2-yl 2-(4-methoxyphenyl)acetate (**4'ja**) (0.40 g, 1.69 mmol, 1 equiv.) and DCC (0.42 g, 2.03 mmol, 1.2 equiv.) in DCM (14 mL) was added hex-5-enoic acid (0.23 g, 0.24 mL, 2.03 mmol, 1.2 equiv.) and DMAP (0.005 g, 0.042 mmol, 0.025 equiv.) respectively at room temperature. After completion of reaction, the reaction mixture was concentrated and the residue was purified by silica gel chromatography (0 to 5% EtOAc/Hexane) to give the product (**17**) as a colorless oil (0.48 g, 1.44 mmol, 85% yield); $R_f = 0.625$ (EtOAc/Hex 1:9). ^1H NMR (400 MHz, CDCl_3): δ 7.19 – 7.17 (m, 2H), 6.84 – 6.82 (m, 2H), 5.79 – 5.69 (m, 2H), 5.50 – 5.46 (m, 1H), 5.29–5.21 (m, 2H), 5.03 – 4.96 (m, 2H), 4.22 (dd, $J = 12, 4$ Hz, 1H), 4.07 (dd, $J = 12, 7.6$ Hz, 1H), 3.77 (s, 3H), 3.56 (s, 2H), 2.25 – 2.21 (m, 2H), 2.07 – 2.02 (m, 2H), 1.65 (p, $J = 15.2, 7.6$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 173.1, 170.9, 158.7, 137.6, 132.1, 130.3, 125.9, 118.9, 115.2, 114.0, 72.3, 64.5, 55.2, 40.5, 33.3, 33.0, 23.9. HRMS calcd for $\text{C}_{19}\text{H}_{25}\text{O}_5$ ($\text{ESI}^+, [\text{M}+\text{H}]^+$): 333.1702, found 333.1697. $[\alpha]_D^{25} -69.3$ (c = 0.60, DCM).

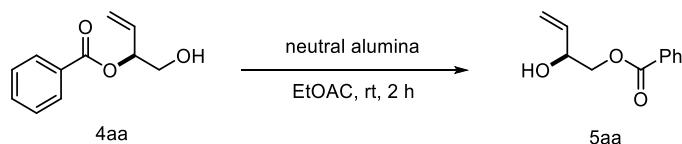
(S,Z)-9-oxo-2,3,6,7,8,9-hexahydrooxonin-3-yl 2-(4-methoxyphenyl)acetate (18):



(S)-2-(2-(4-methoxyphenyl)acetoxy)but-3-en-1-yl but-3-enoate (**17**) (0.20 g, 0.60 mmol, 1 equiv.) and Grubbs II catalyst (0.015 g, 0.018 mmol, 0.03 equiv., 3 mol%) were combined in 12 mL of degassed

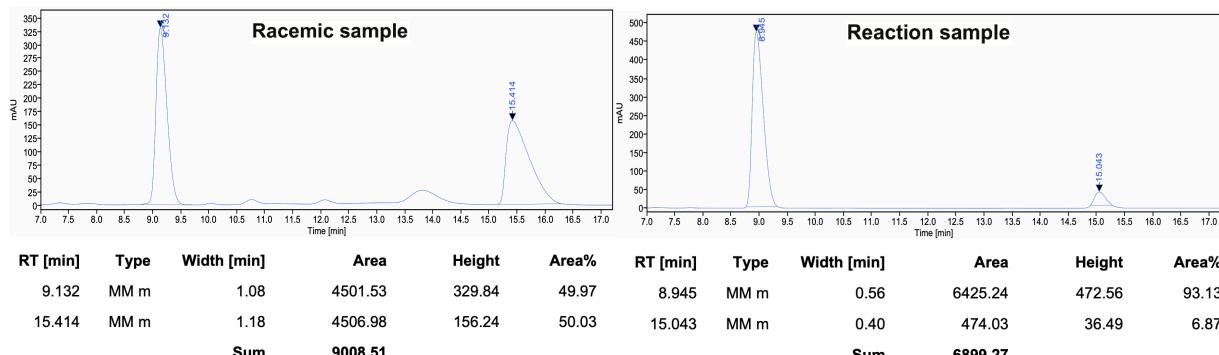
and freshly distilled dry dichloromethane. The solution was then refluxed for 18 h. The reaction mixture was concentrated to dryness and the crude product was purified by column chromatography (10 to 20% EtOAc/Hexane) to give 9-membered lactone compound (**18**) as a white solid after recrystallization from *n*-hexane/DCM (3:1) (0.10 g, 0.33 mmol, 55% yield); R_f = 0.1 (EtOAc/Hex 2:8). M. Pt. 135 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.16 (d, J = 8.4 Hz, 2H), 6.83 (d, J = 8.8 Hz, 2H), 5.61 (dt, J = 14.0, 6.8 Hz, 1H), 5.41 – 5.36 (m, 2H), 4.21 (dt, J = 11.2, 5.6 Hz, 1H), 4.14 – 4.08 (m, 1H), 3.77 (s, 3H), 3.55 (s, 2H), 2.23 (dd, J = 13.2, 5.5 Hz, 2H), 2.12 – 2.01 (m, 2H), 1.70 – 1.63 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3): δ 172.9, 170.8, 158.8, 134.7, 130.3, 126.1, 125.8, 114.0, 71.9, 63.7, 55.3, 40.5, 33.1, 31.2, 23.8. HRMS calcd for $\text{C}_{17}\text{H}_{19}\text{O}_4$ (ESI^+ , $[\text{M}+\text{H}]^+(-\text{H}_2\text{O})$): 343.0948, found 343.0962. $[\alpha]_D^{28.4}$ –31.2 (c = 0.6, CHCl_3).

Conversion of 1-hydroxybut-3-en-2-yl benzoate (**4aa**) to 2-hydroxybut-3-en-1-yl benzoate (**5aa**):

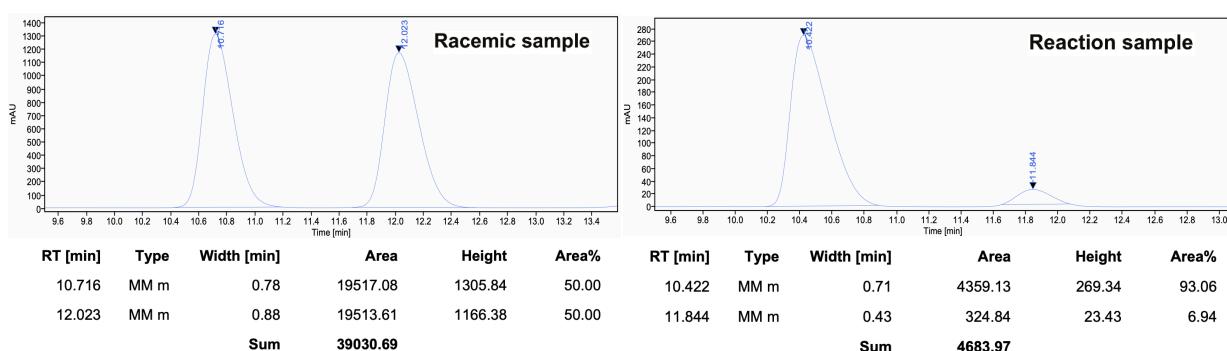


Neutral alumina (40 mg) was added to a stirred mixture of 1-hydroxybut-3-en-2-yl benzoate (**4aa**) (38.4 mg, 0.2 mmol, 86% ee) in EtOAc (1 ml) at room temperature. After >90% conversion (ca. 2 h) the product was isolated by preparative TLC (10% EtOAc/Hex, 3 times run) to give the desired product 2-hydroxybut-3-en-1-yl benzoate **5aa** (32.6 mg, 85% yield) as transparent oil. R_f = 0.2 (EtOAc/Hex 1:9). ^1H NMR (500 MHz, CDCl_3) δ 8.09 – 7.96 (m, 2H), 7.58 – 7.48 (m, 1H), 7.41 (dd, J = 14.0, 4.8 Hz, 2H), 5.92 (ddd, J = 16.5, 10.5, 5.5 Hz, 1H), 5.42 (dt, J = 17.5, 1.5 Hz, 1H), 5.25 (dt, J = 11.0, 1.5 Hz, 1H), 4.55 – 4.46 (m, 1H), 4.39 (dd, J = 11.5, 4.0 Hz, 1H), 4.27 (dd, J = 11.5, 7.0 Hz, 1H), 2.54 (br s, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 166.7, 136.3, 133.2, 129.8, 129.7, 128.4, 117.1, 71.1, 68.3. HPLC for **4aa**: t_R = 8.9 min (major) and t_R = 15.0 min (minor) 86% ee (Chiralpak AS-H, 280 nm, 5% IPA-Hex, 1 ml/min). HPLC for **5aa**: t_R = 10.4 min (major) and t_R = 11.8 min (minor) 86% ee (Chiralpak AS-H, 254 nm, 5% IPA-Hex, 1 ml/min). HRMS calcd for $\text{C}_{11}\text{H}_{13}\text{O}_3$ (ESI^+ , $[\text{M}+\text{H}]^+$): 193.0865, found 193.0874. $[\alpha]_D^{25.1}$ –5.2 (c = 0.5, CHCl_3).

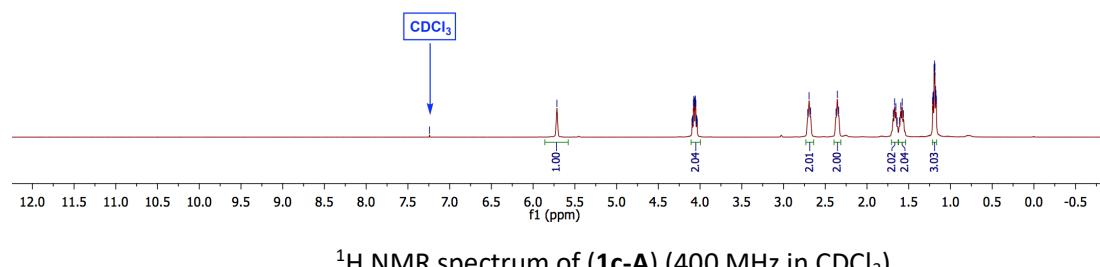
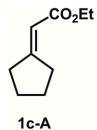
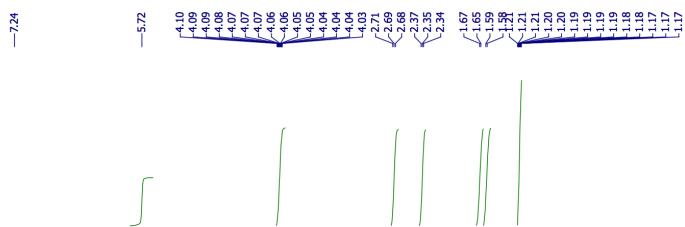
HPLC of **4aa**:



HPLC of **5aa**:

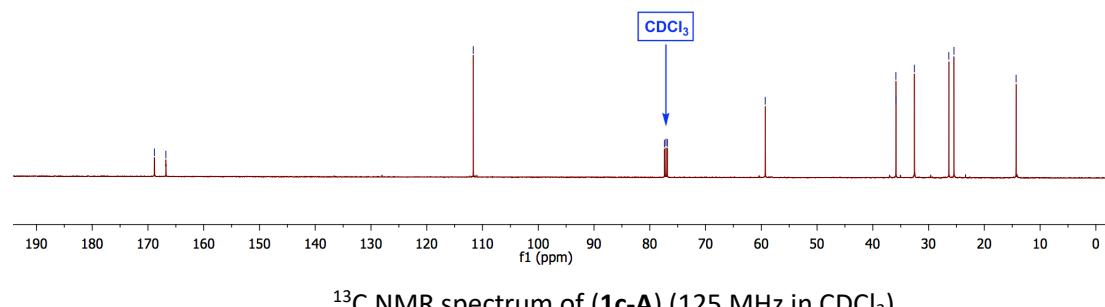
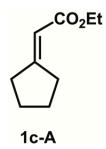


10. ^1H NMR, ^{13}C NMR and HPLC data for the starting materials

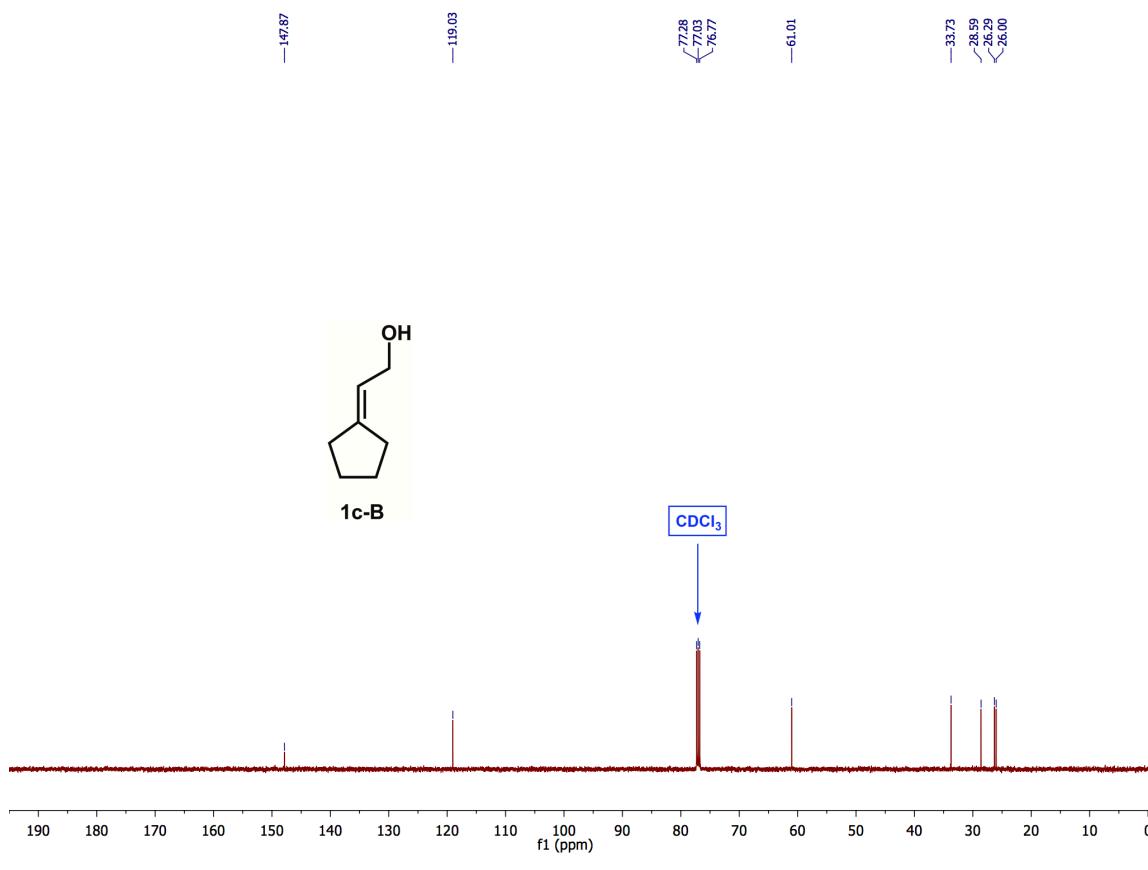
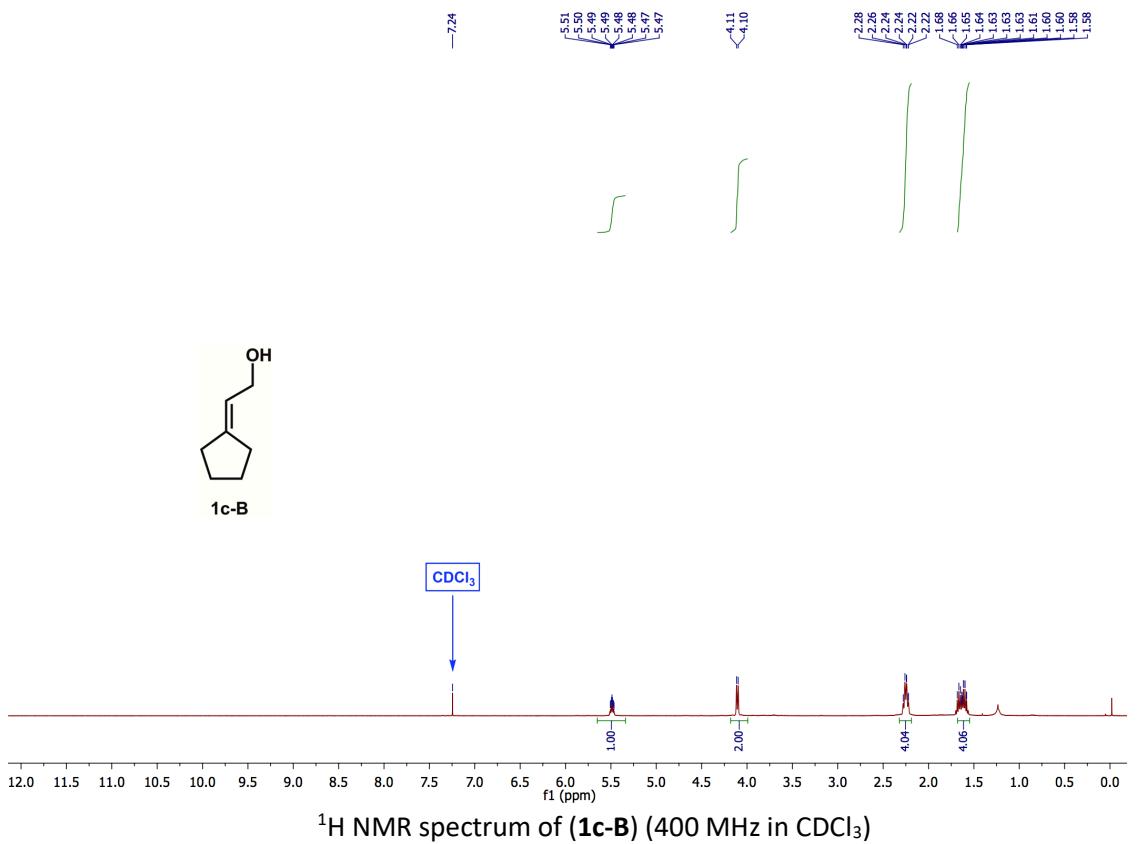


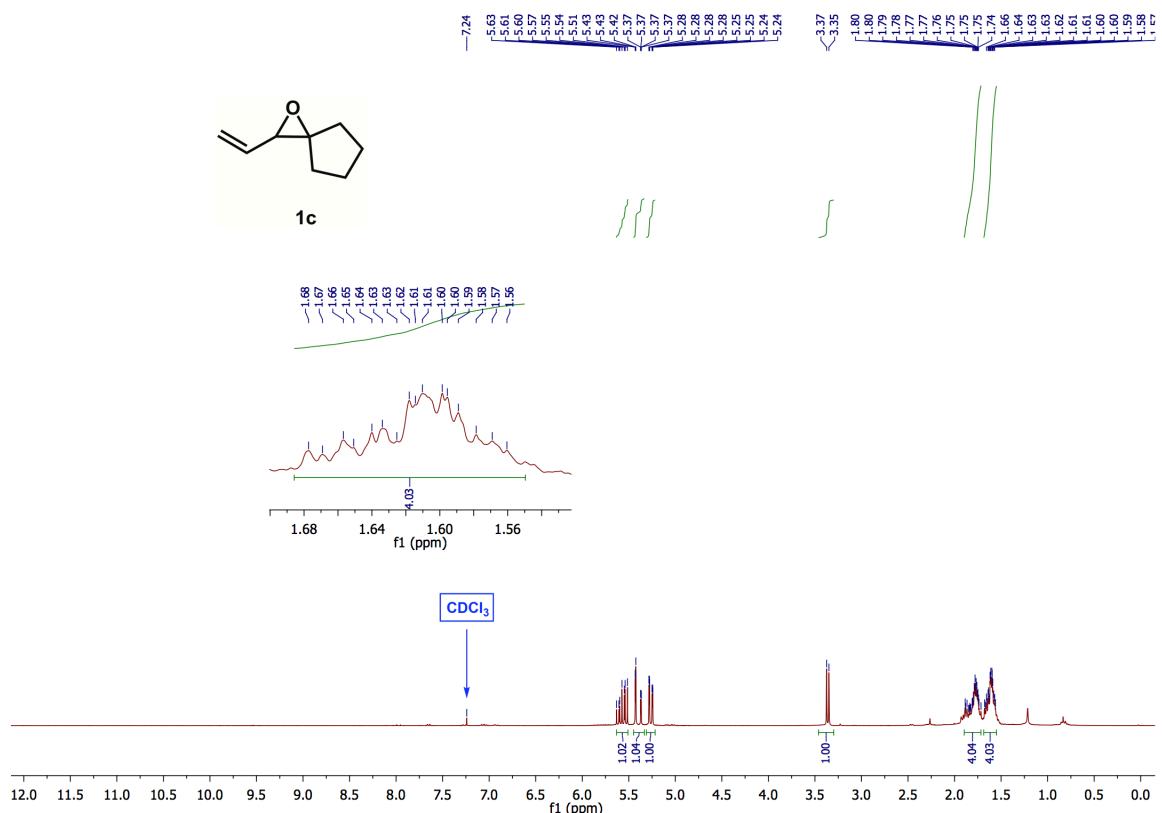
^1H NMR spectrum of (**1c-A**) (400 MHz in CDCl_3)

— 169.86
— 166.79
— 111.65
— 77.36
— 77.10
— 76.85
— 59.30
— 35.86
— 35.85
— 32.54
— 26.37
— 25.45
— 14.31

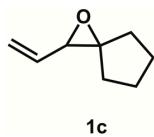


^{13}C NMR spectrum of (**1c-A**) (125 MHz in CDCl_3)

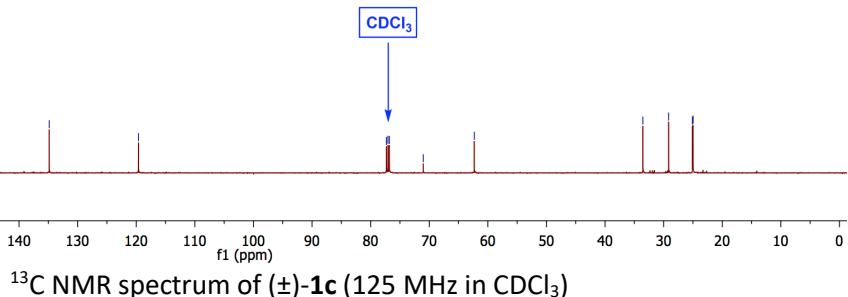


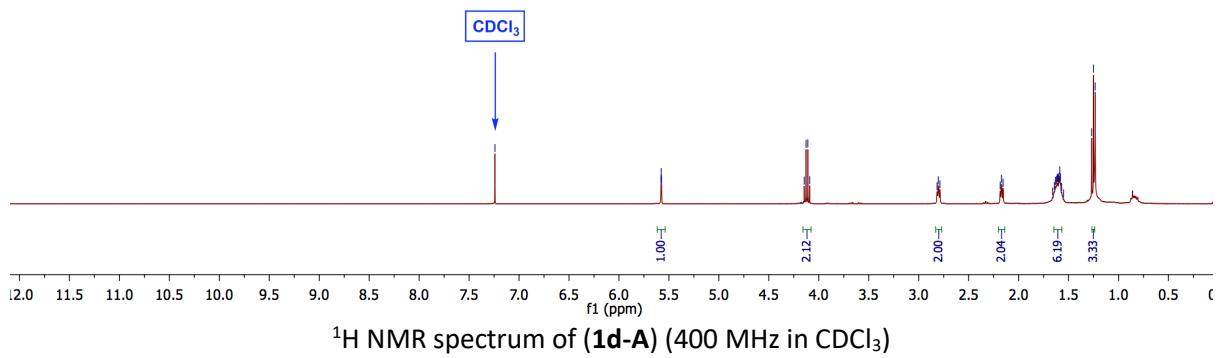
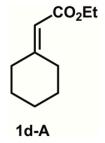


¹H NMR spectrum of (\pm)-1c (300 MHz in CDCl₃)

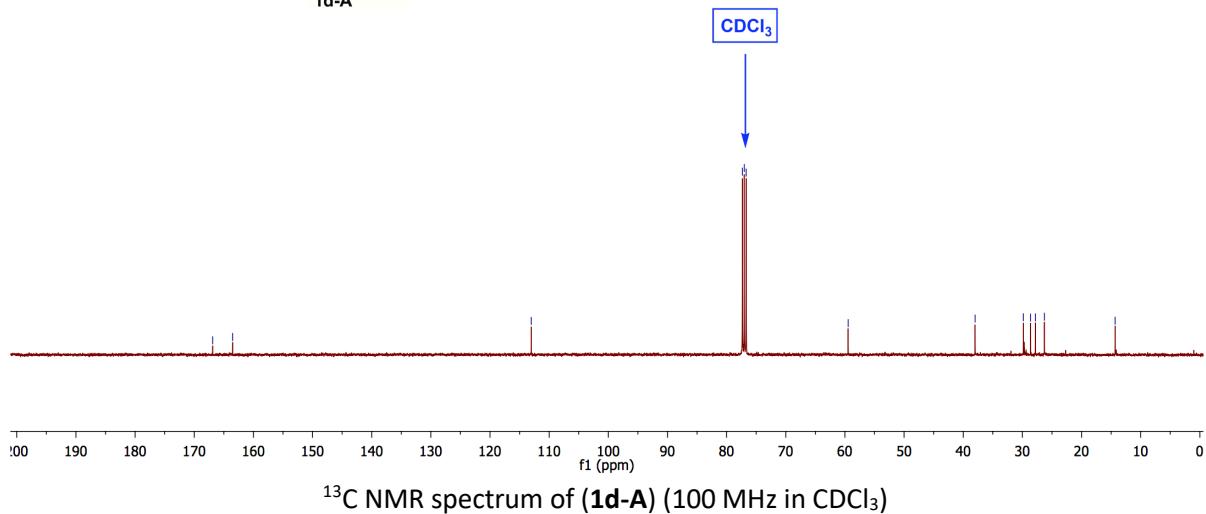
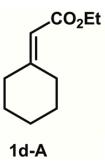


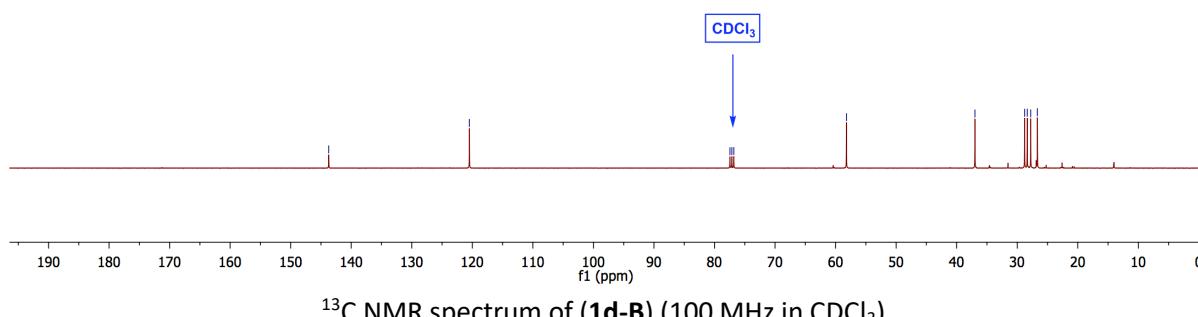
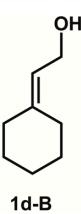
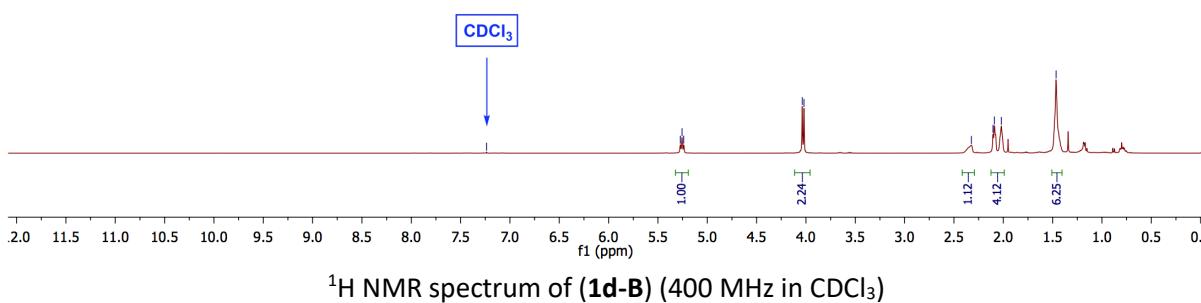
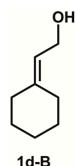
1c

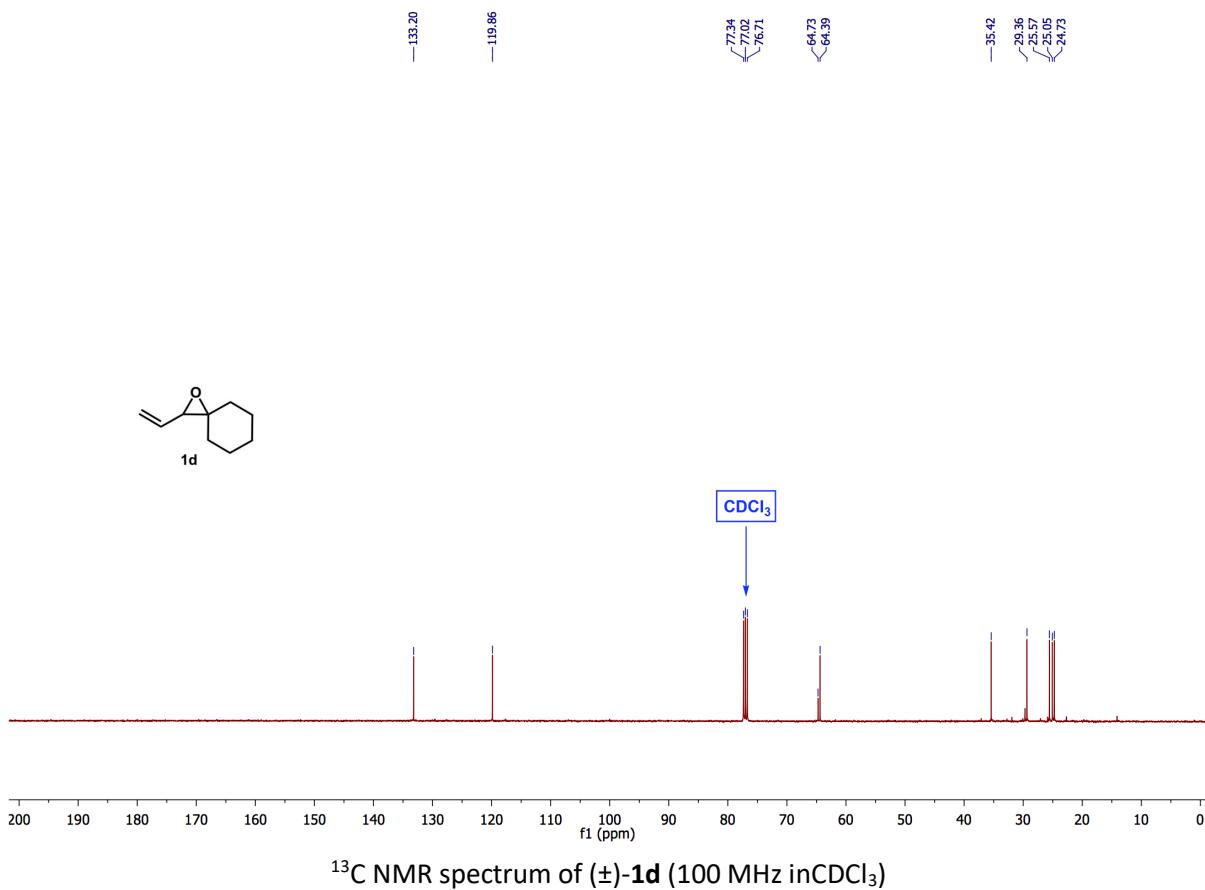
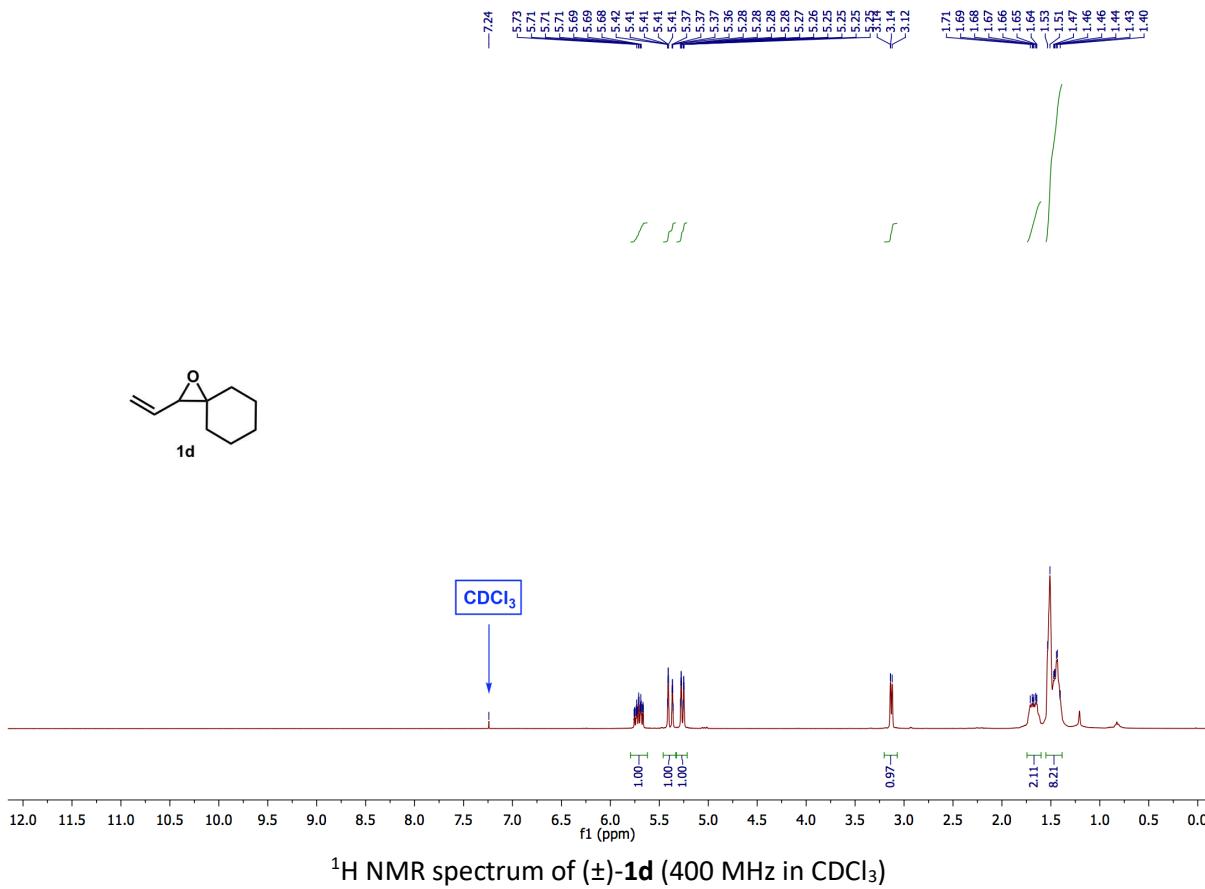


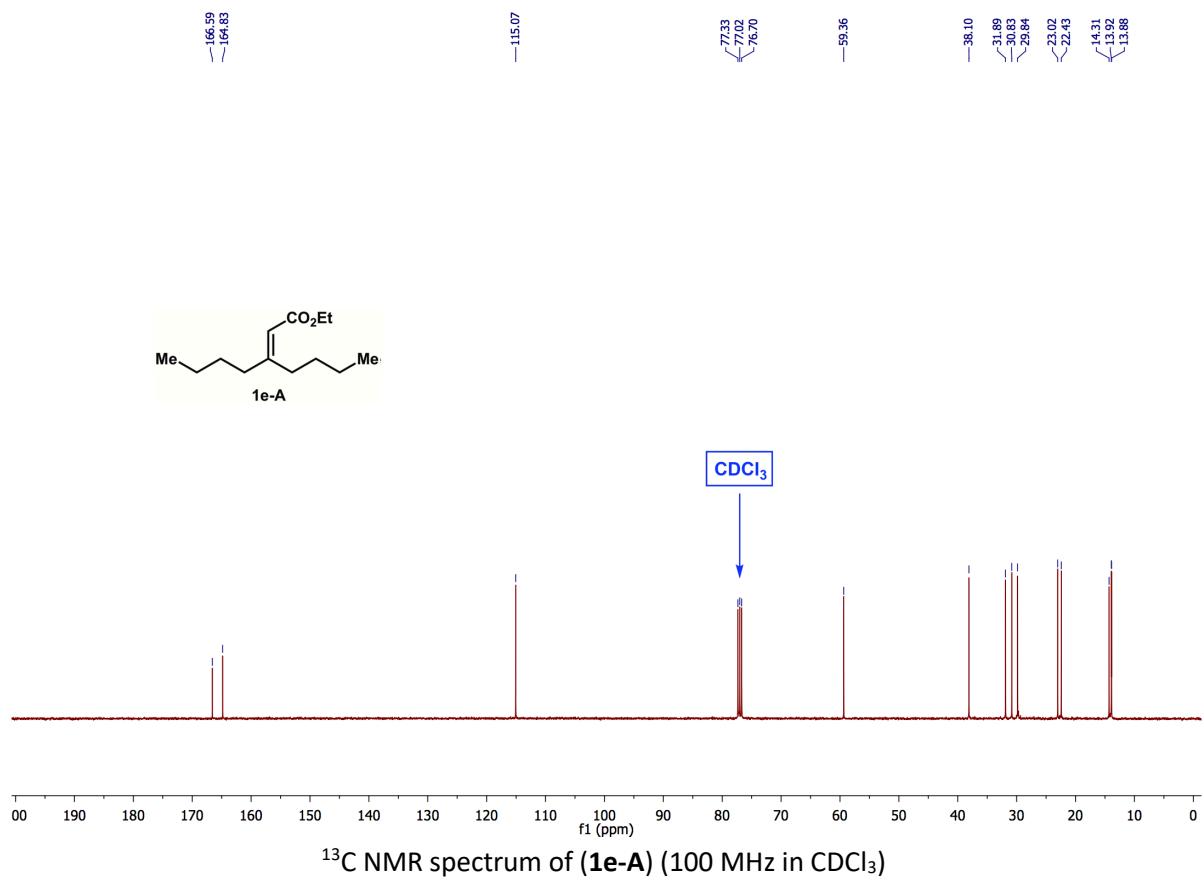
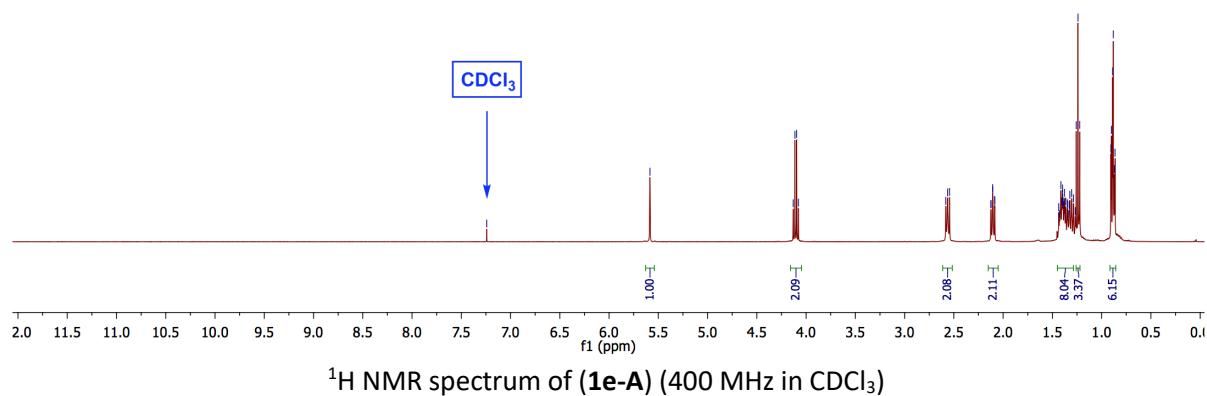
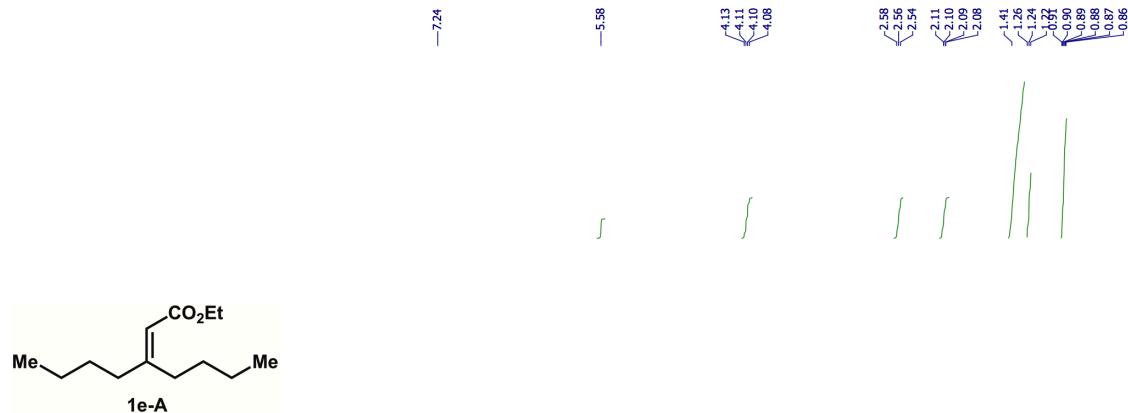


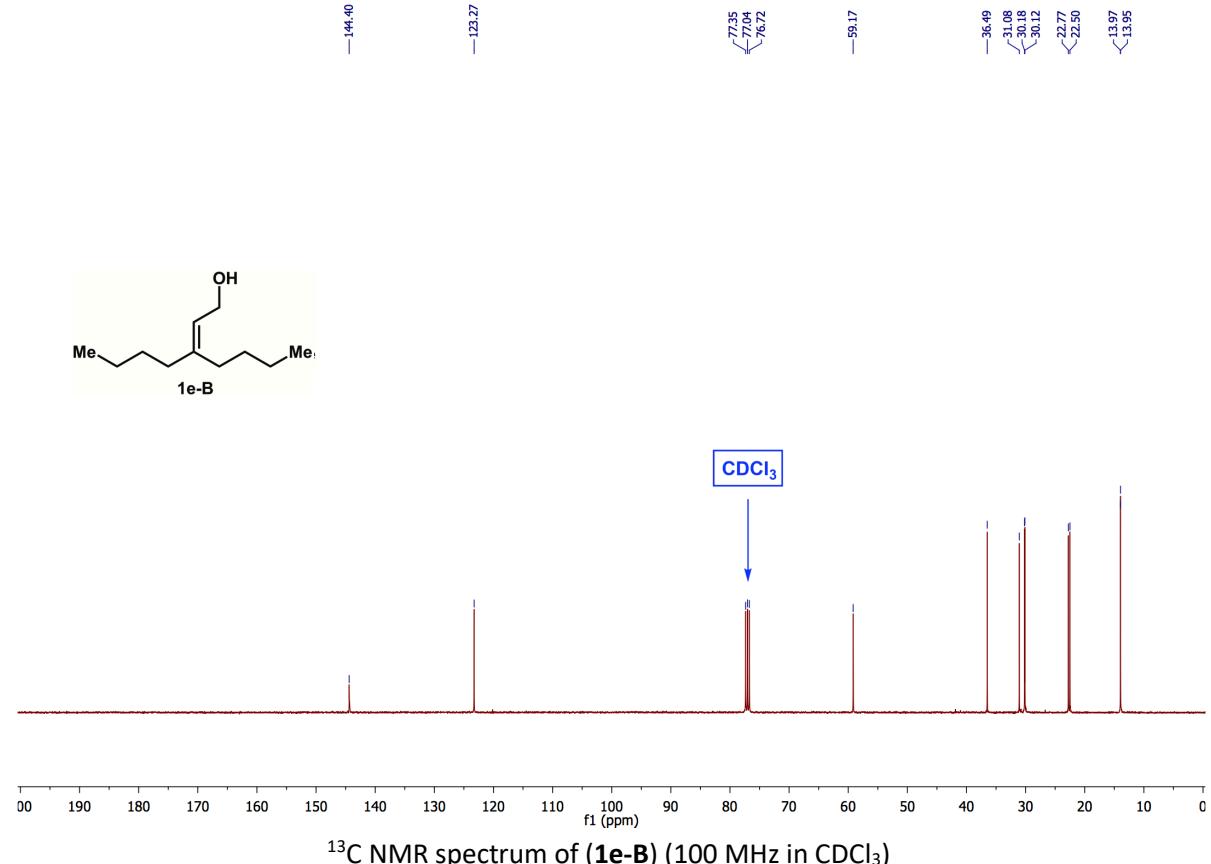
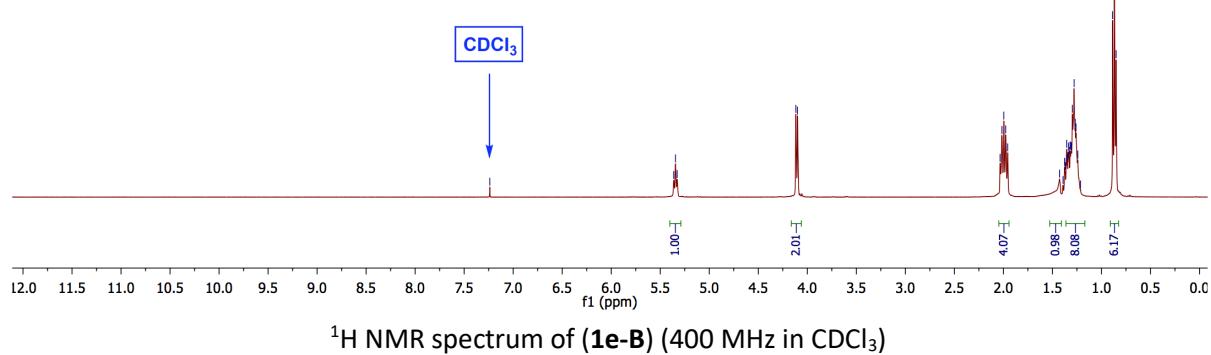
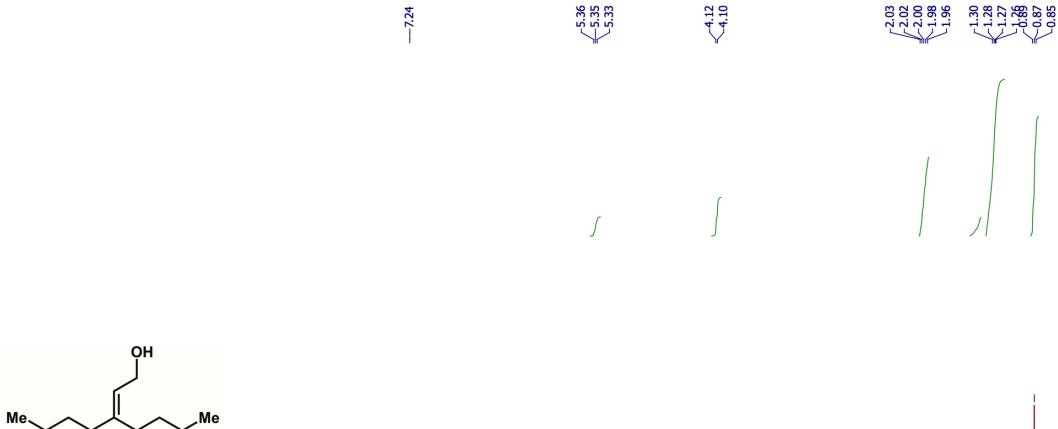
—166.88
—163.52
—113.03
—77.33
—77.01
—76.70
—59.46
—37.99
—29.94
—28.62
—27.80
—26.27
—14.32

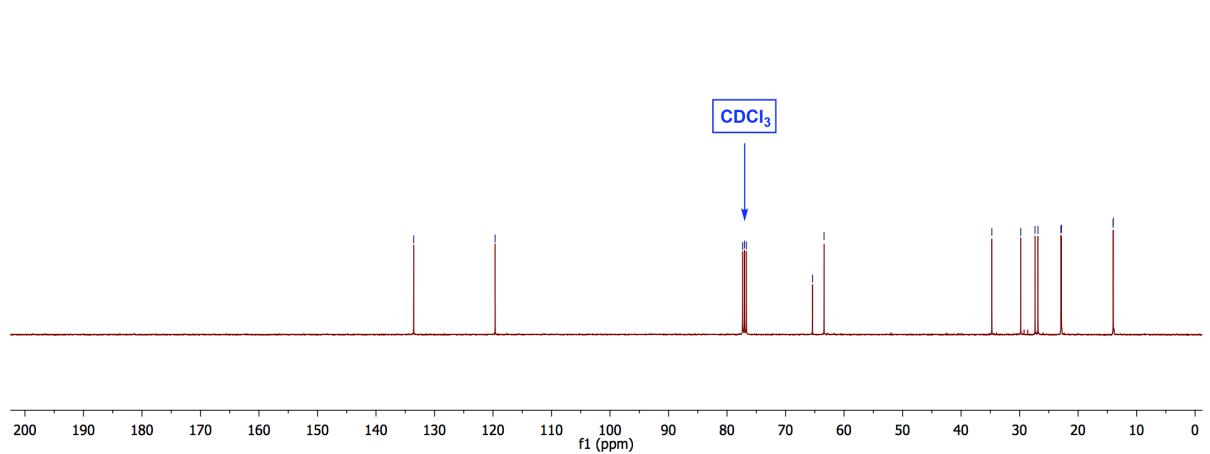
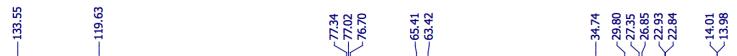
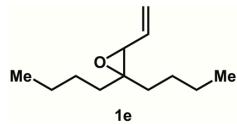
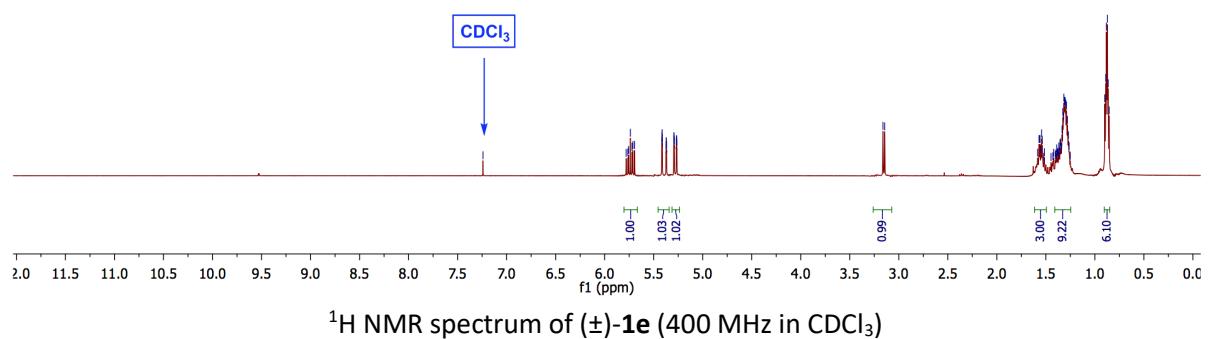
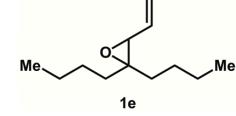


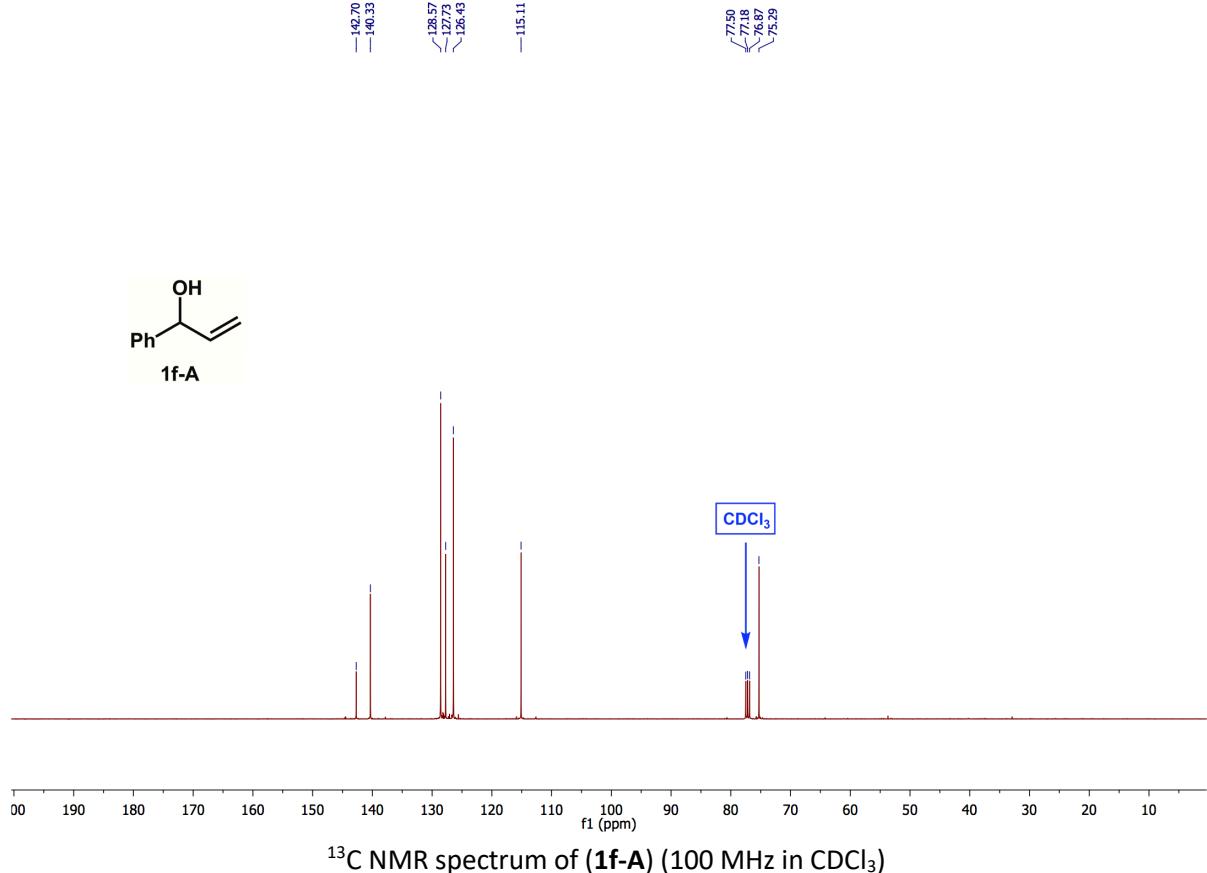
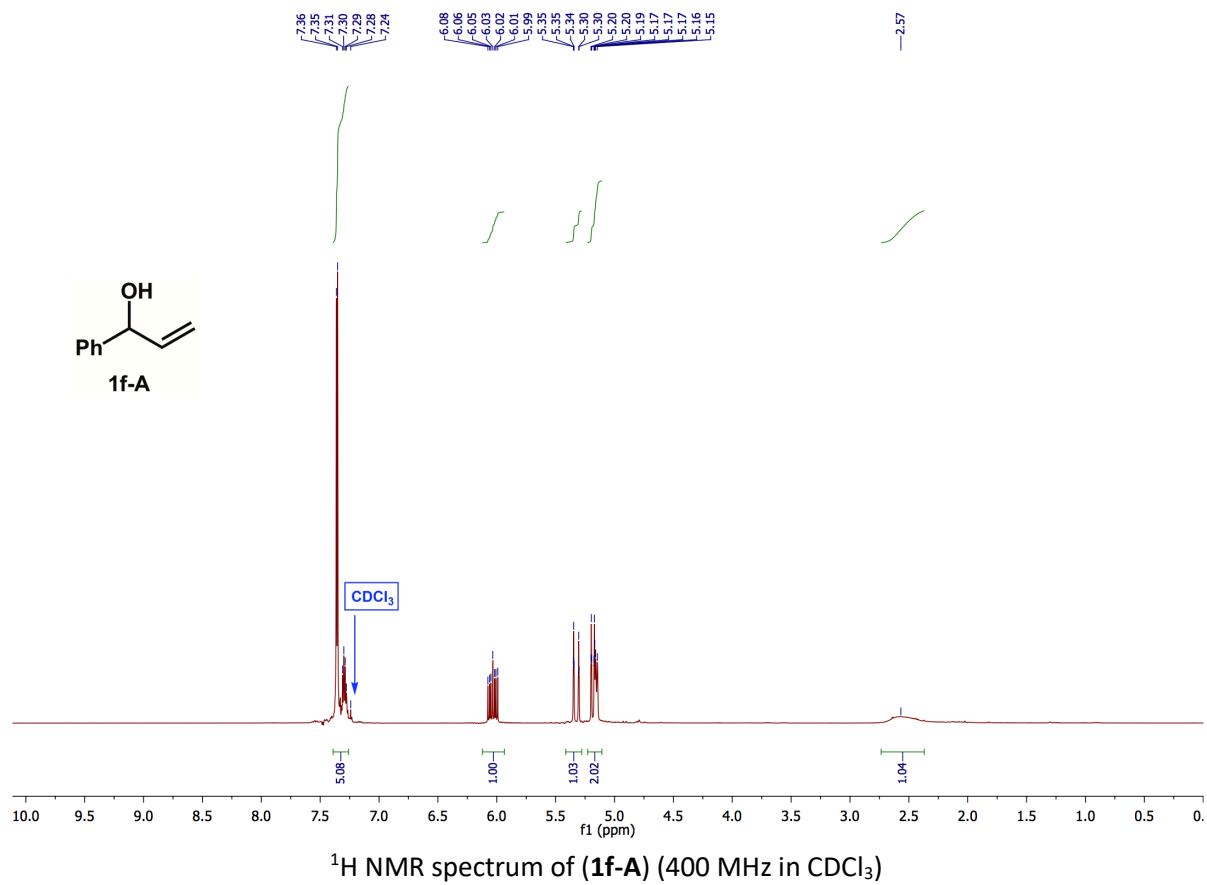


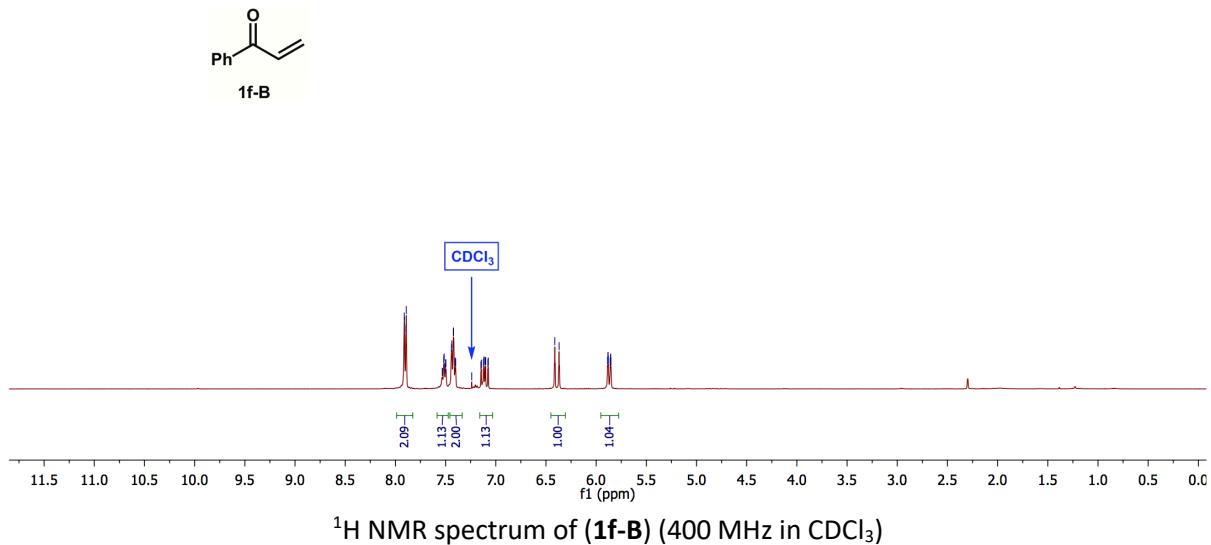
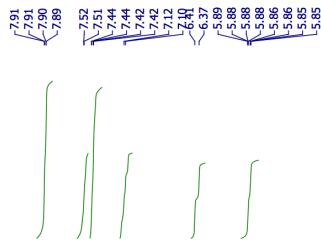




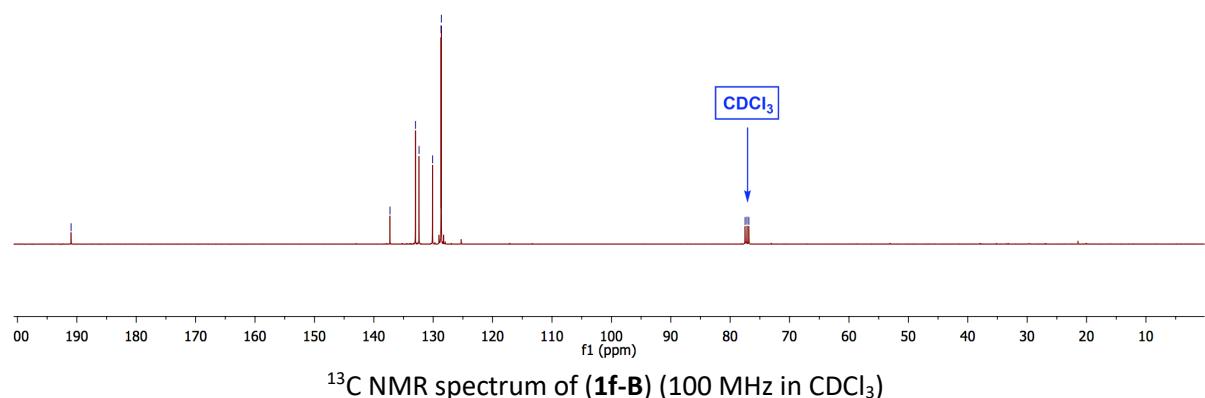
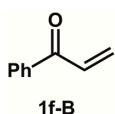


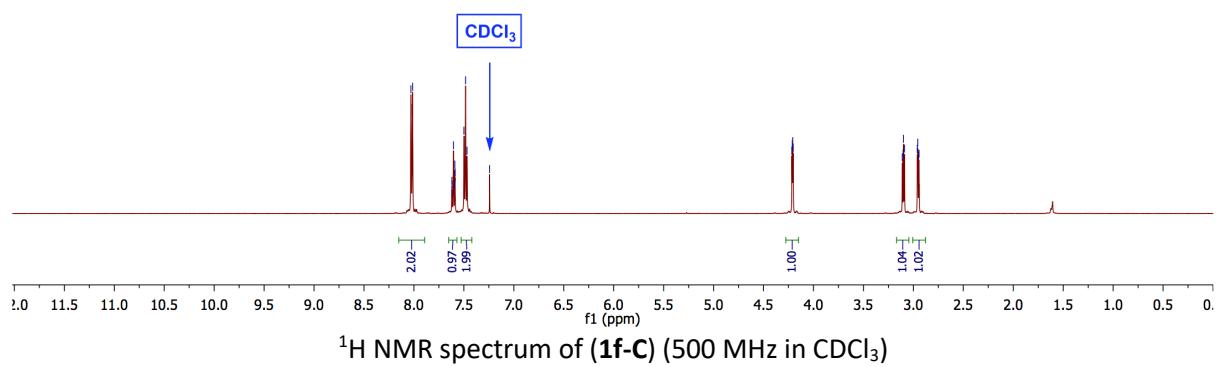
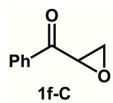
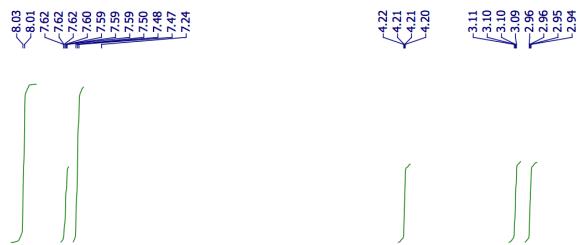




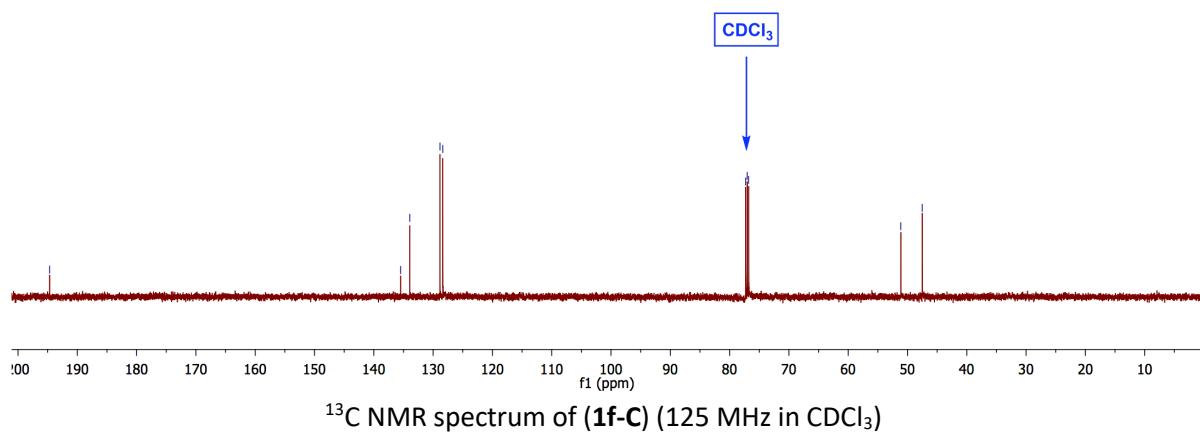
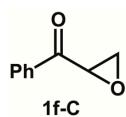


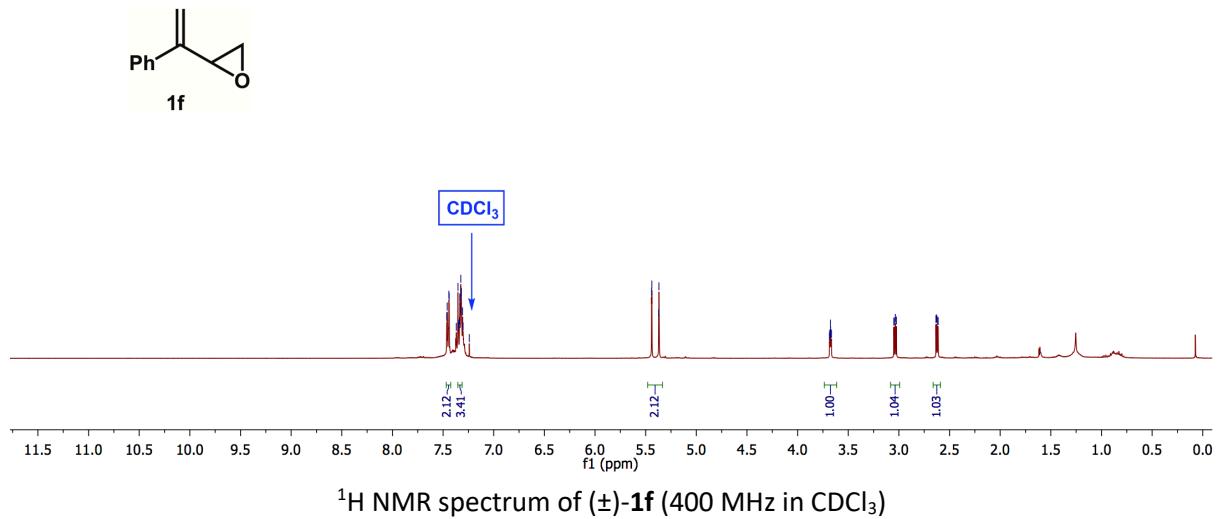
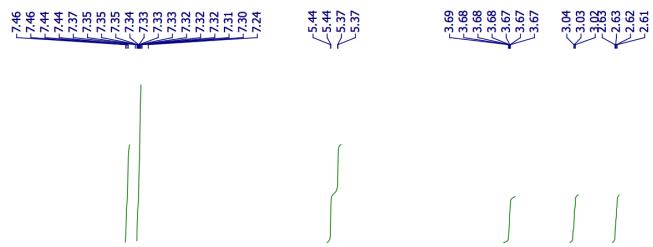
— 190.97
 ↘ 137.27
 ↘ 132.99
 ↘ 132.38
 ↘ 130.11
 ↘ 128.69
 ↘ 128.63
 ↘ 77.49
 ↘ 77.17
 ↘ 76.85



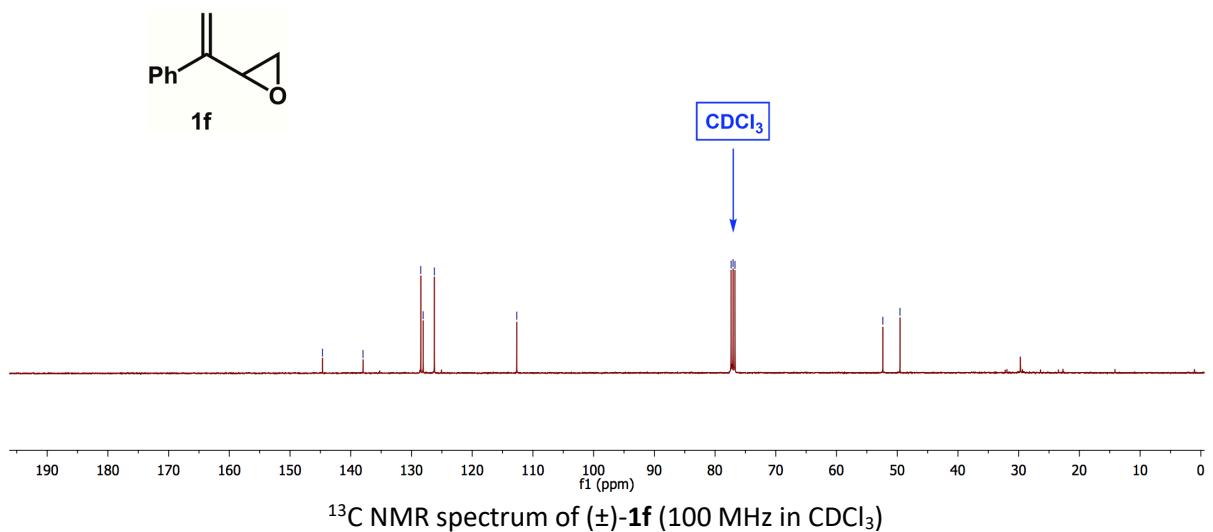


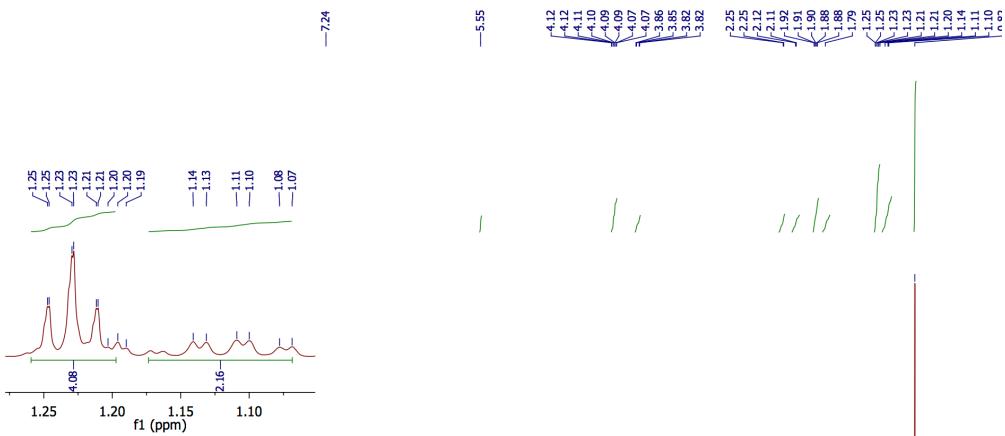
—194.98
—155.47
—133.94
—128.84
—128.36
—77.29
—77.04
—76.79
—51.13
—47.52



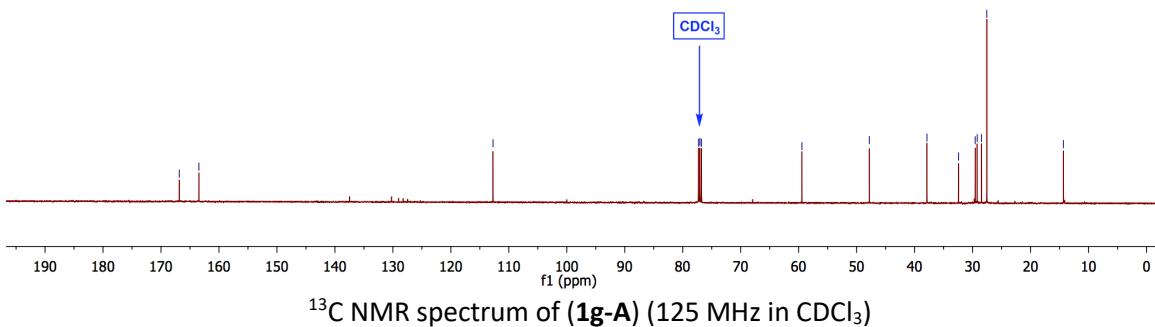
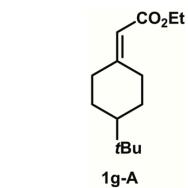
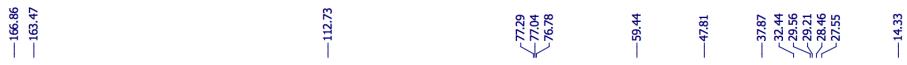


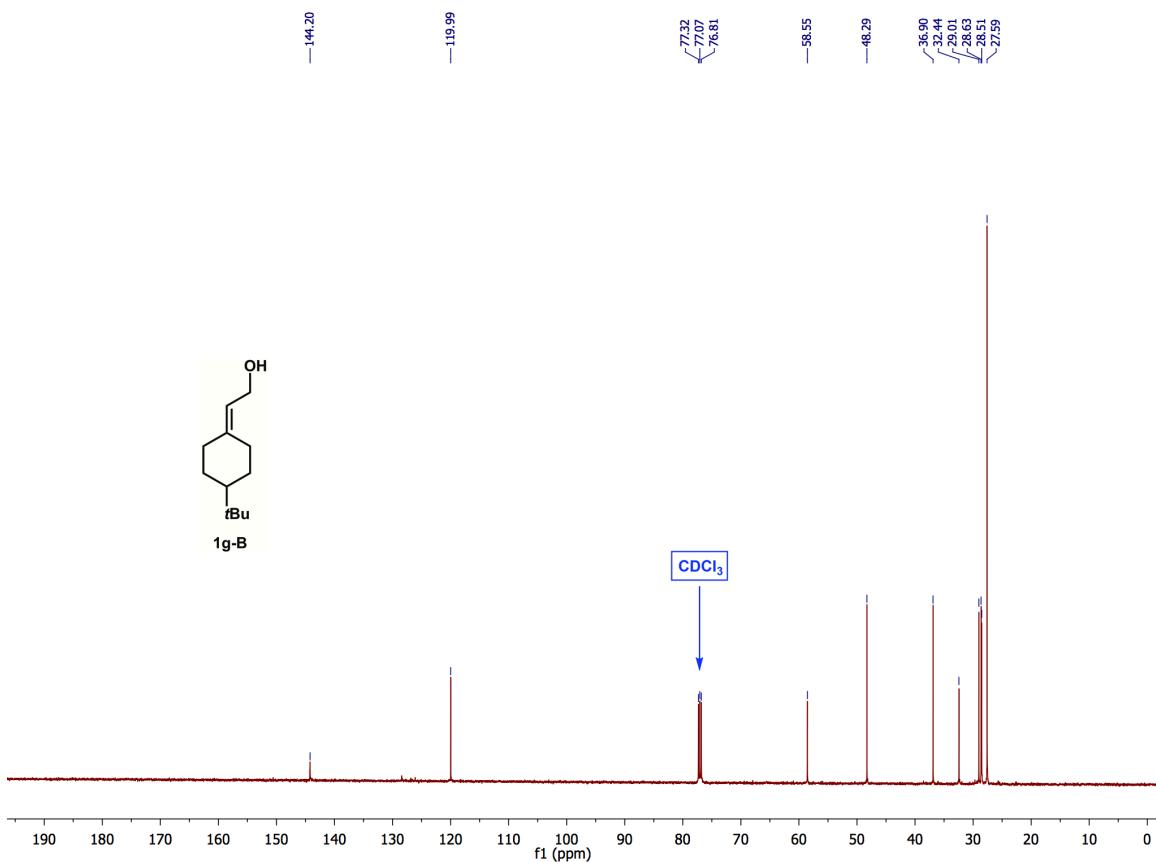
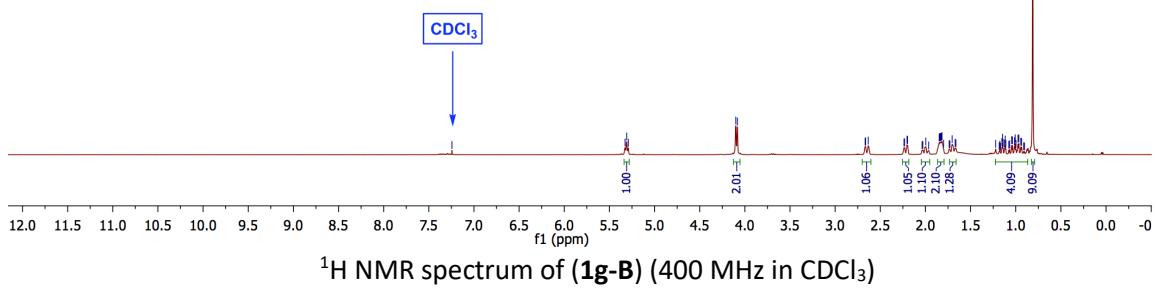
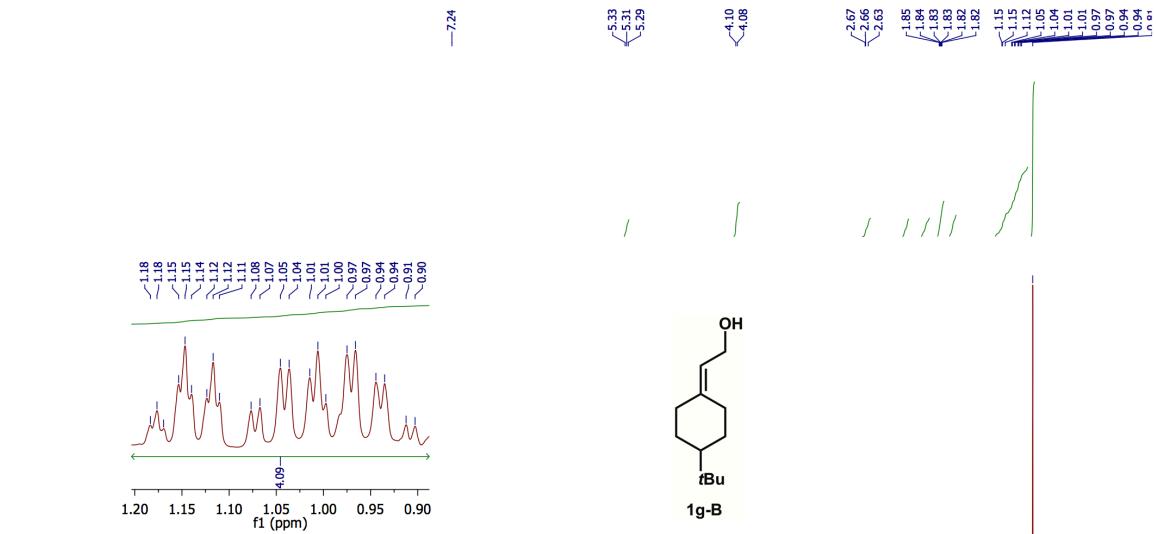
—144.64 —137.98 —128.47 —128.08 —126.23 —112.67 —77.95 —77.94 —76.72 —52.37 —49.55



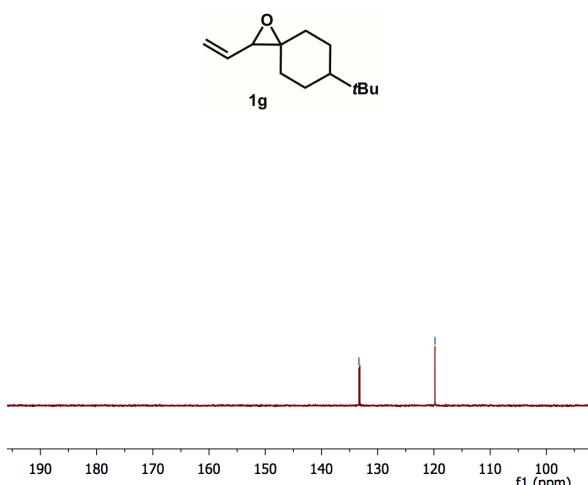
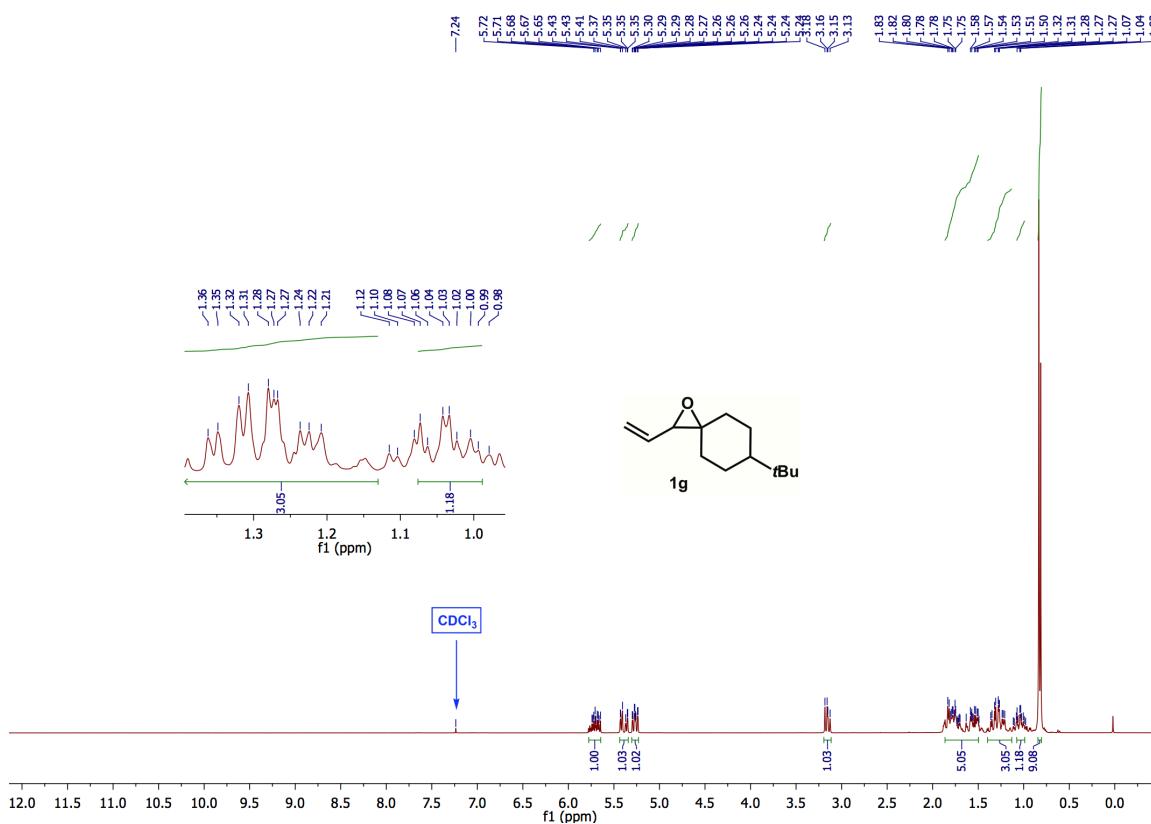


^1H NMR spectrum of (**1g-A**) (400 MHz in CDCl_3)

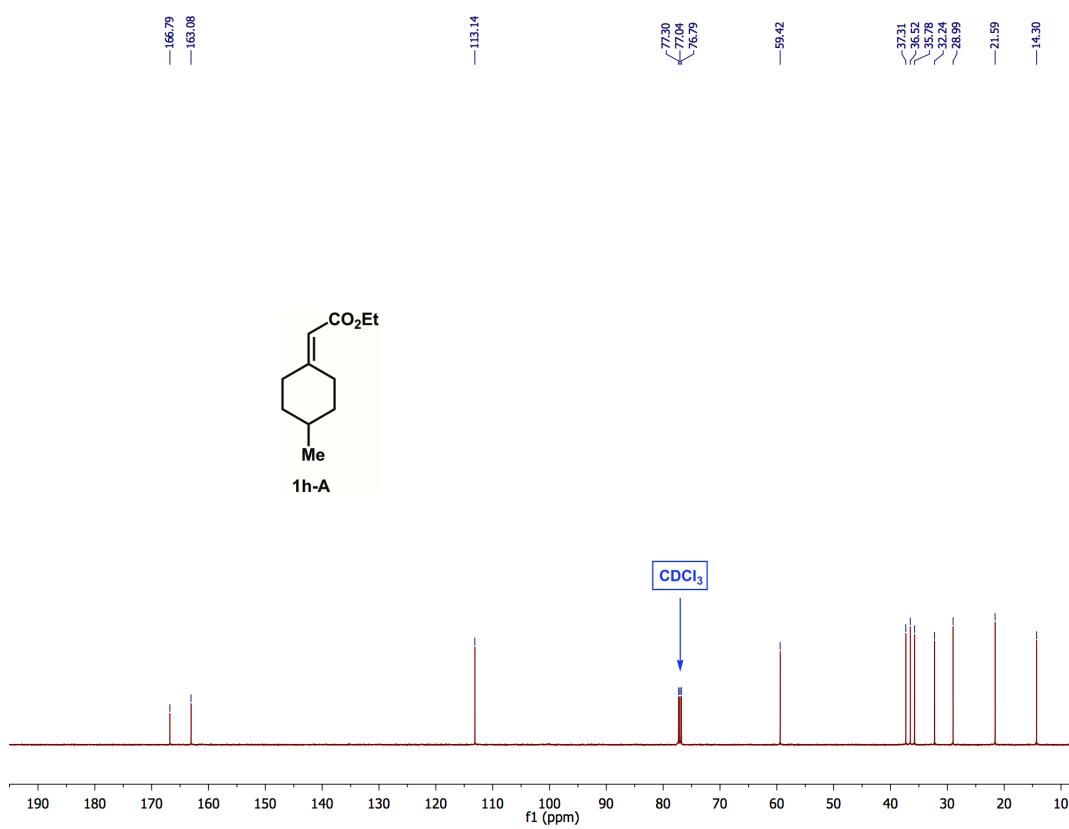
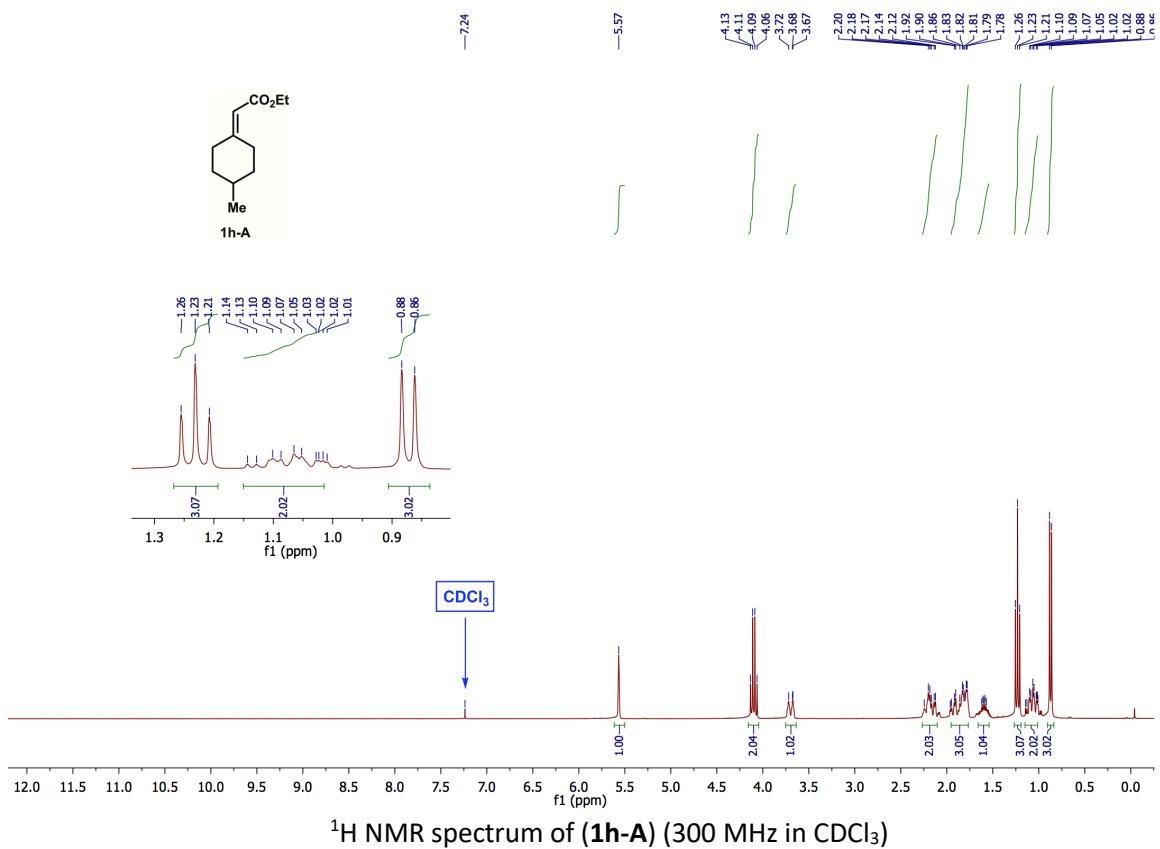


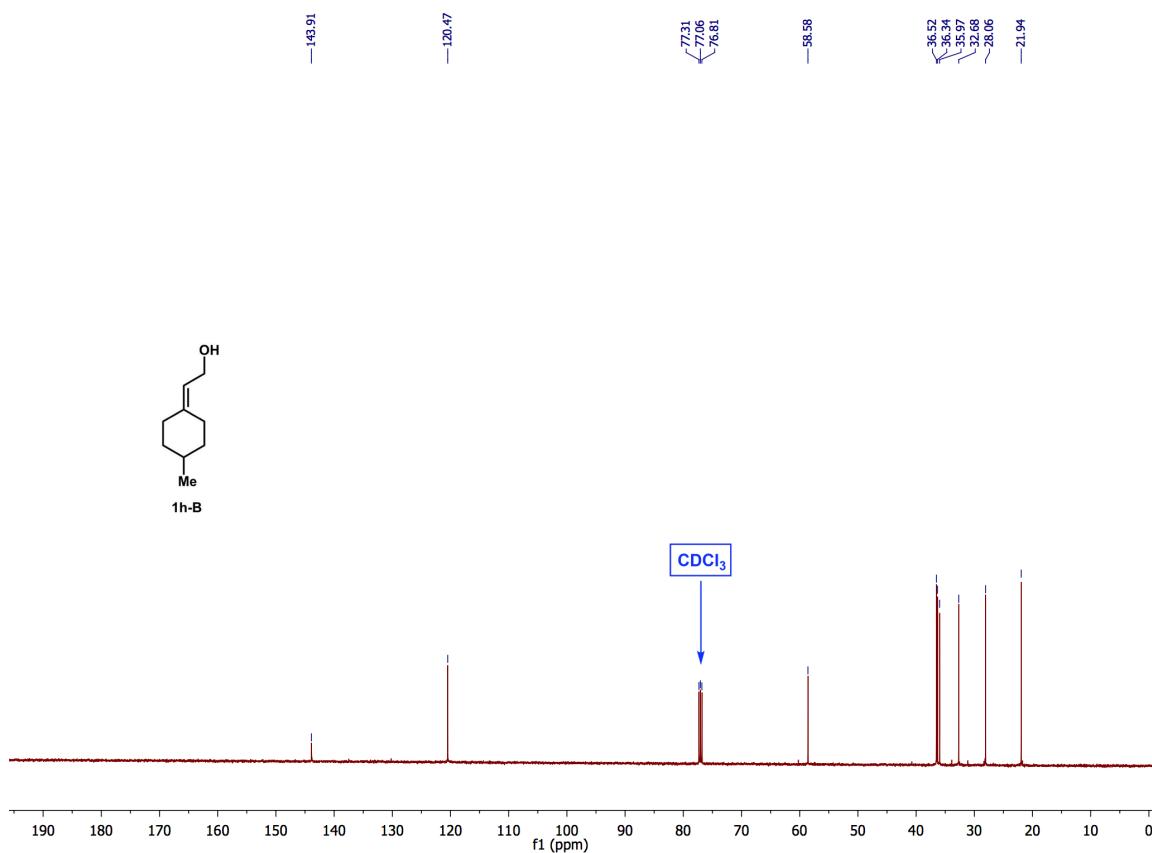
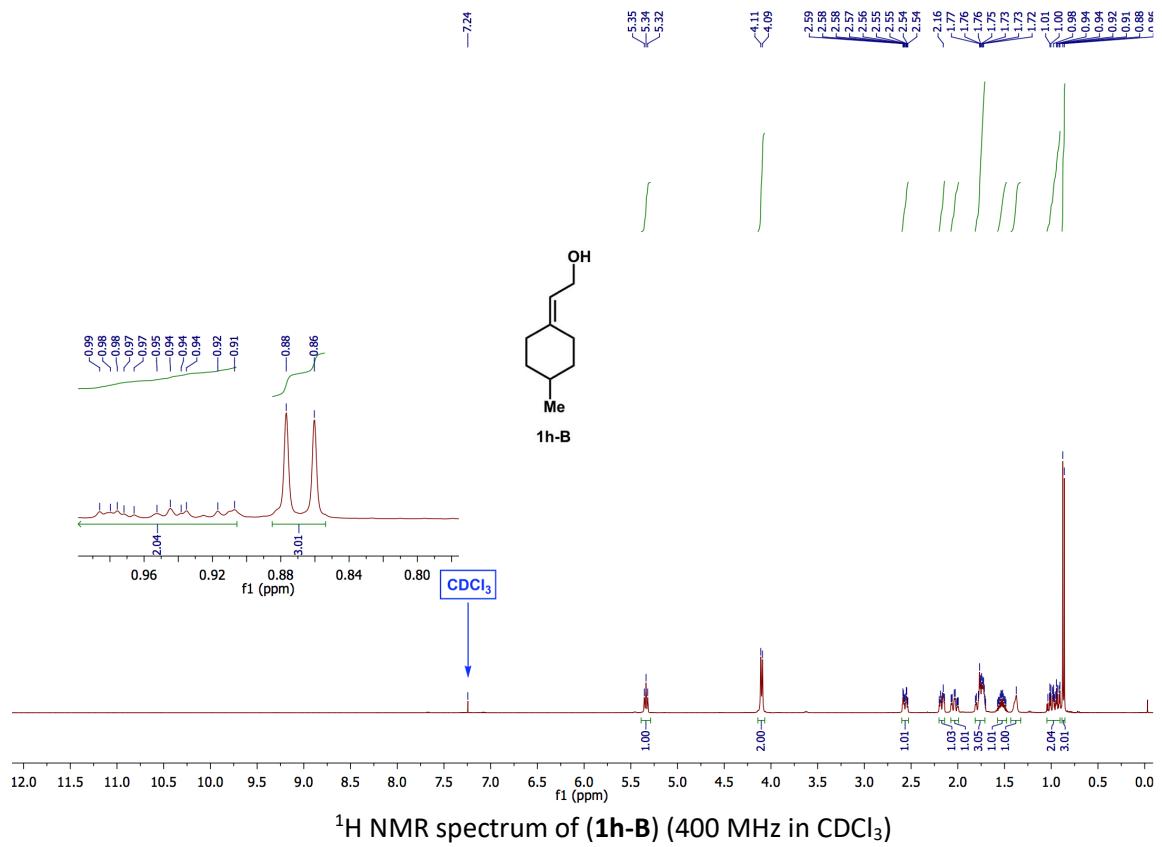


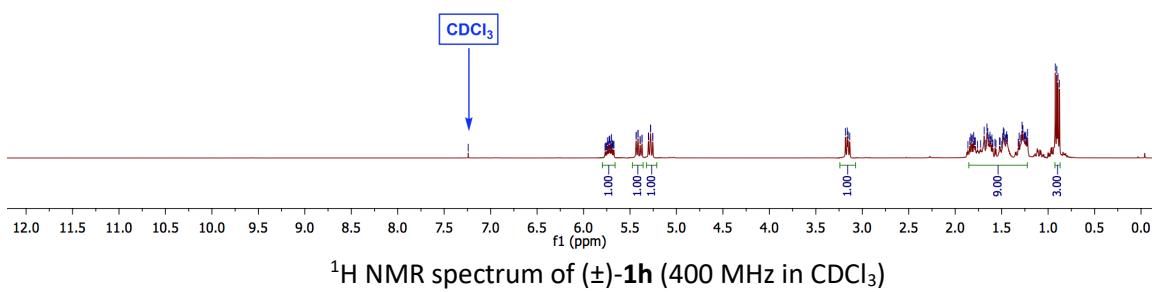
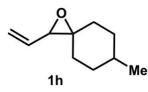
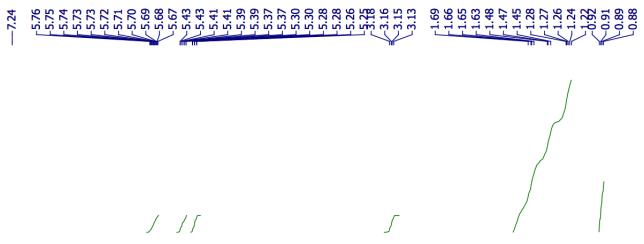
^{13}C NMR spectrum of (1g-B) (125 MHz in CDCl_3)



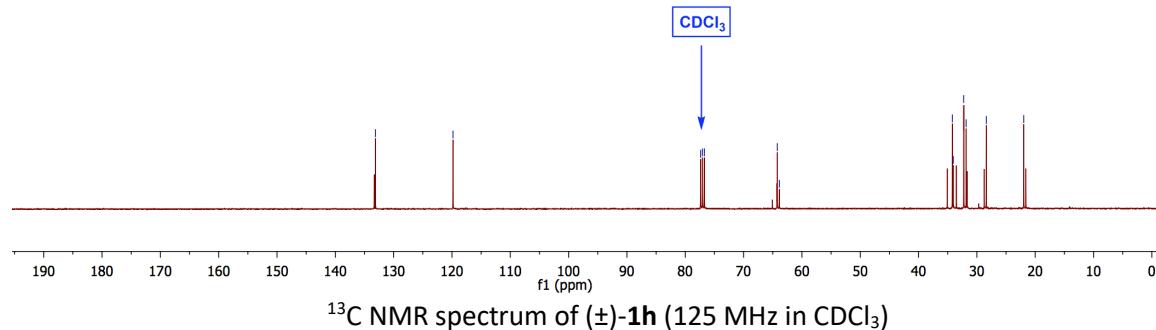
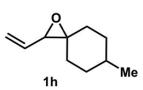
¹³C NMR spectrum of (±)-1g (125MHz in CDCl₃)

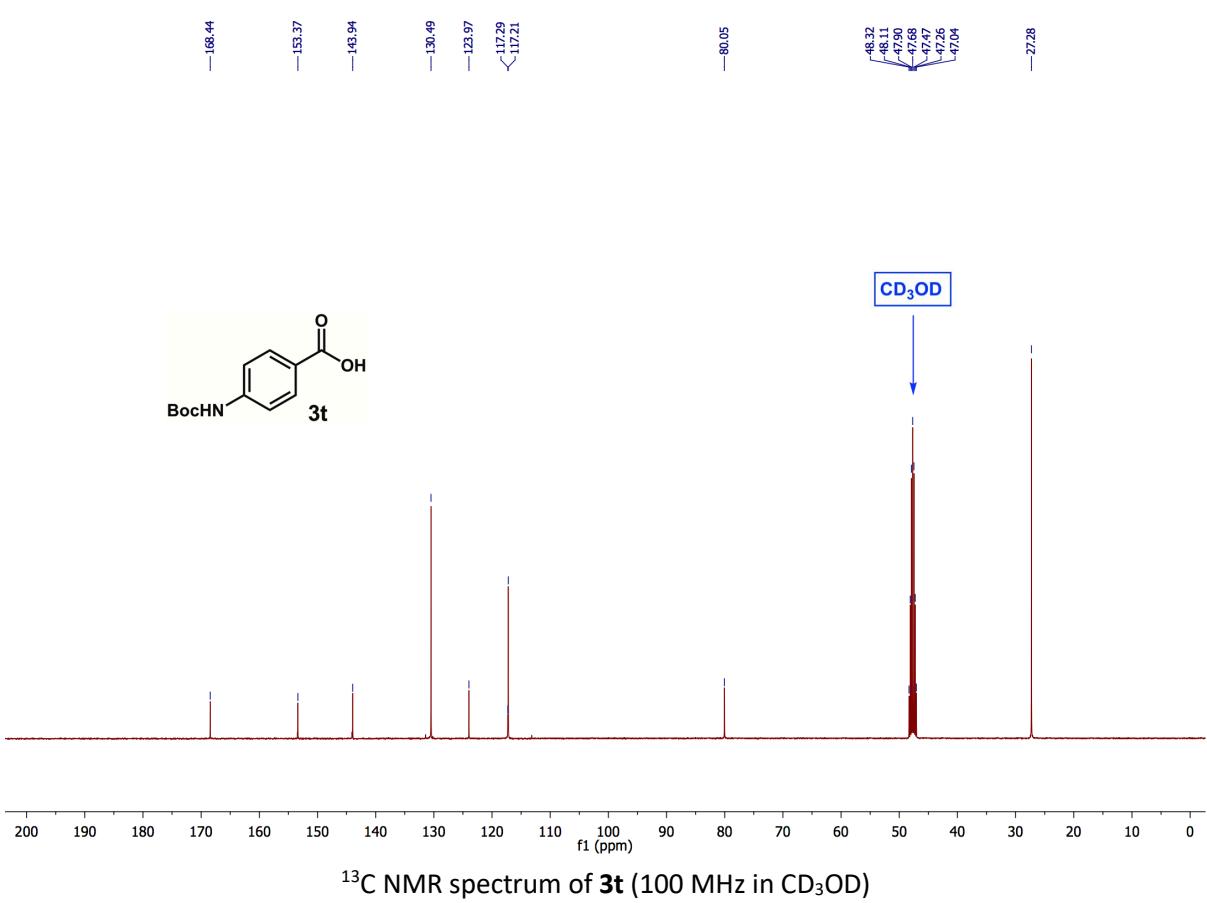
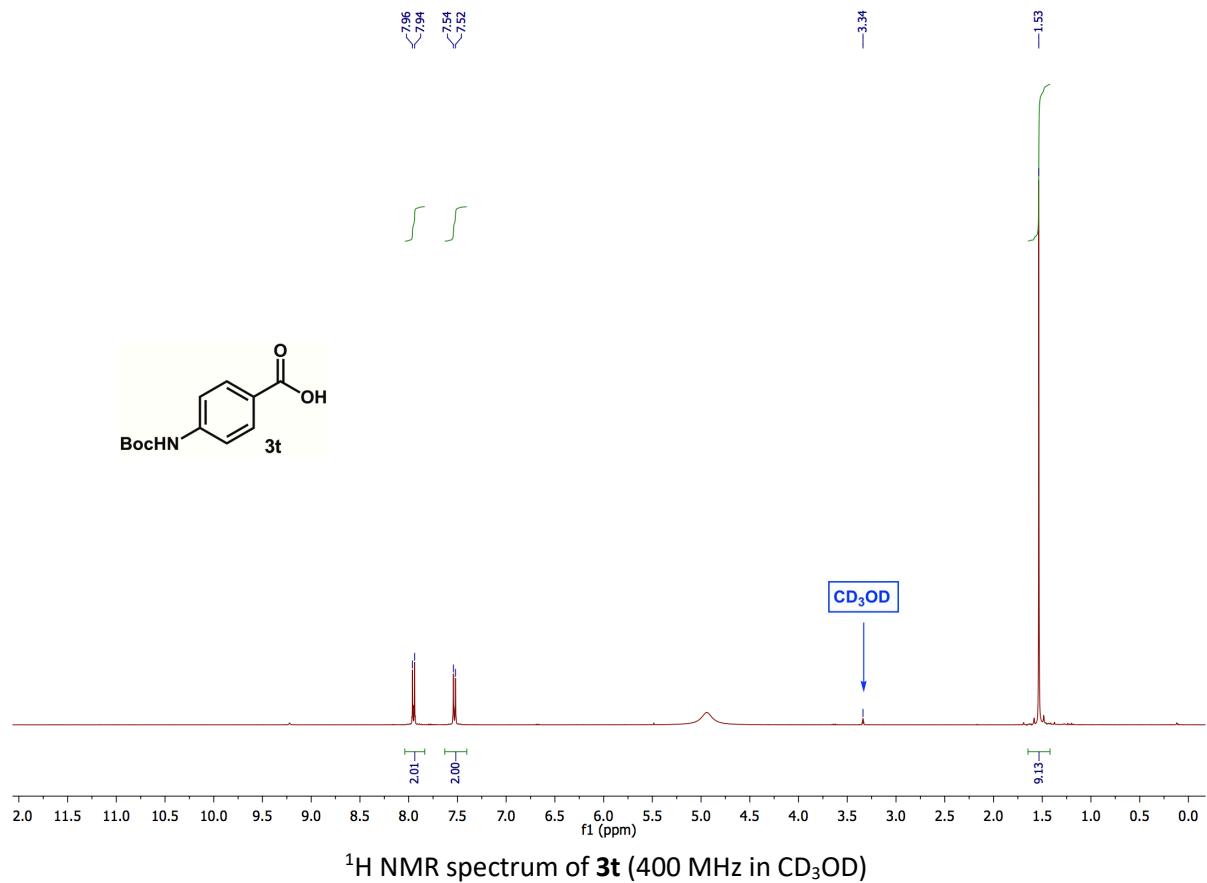




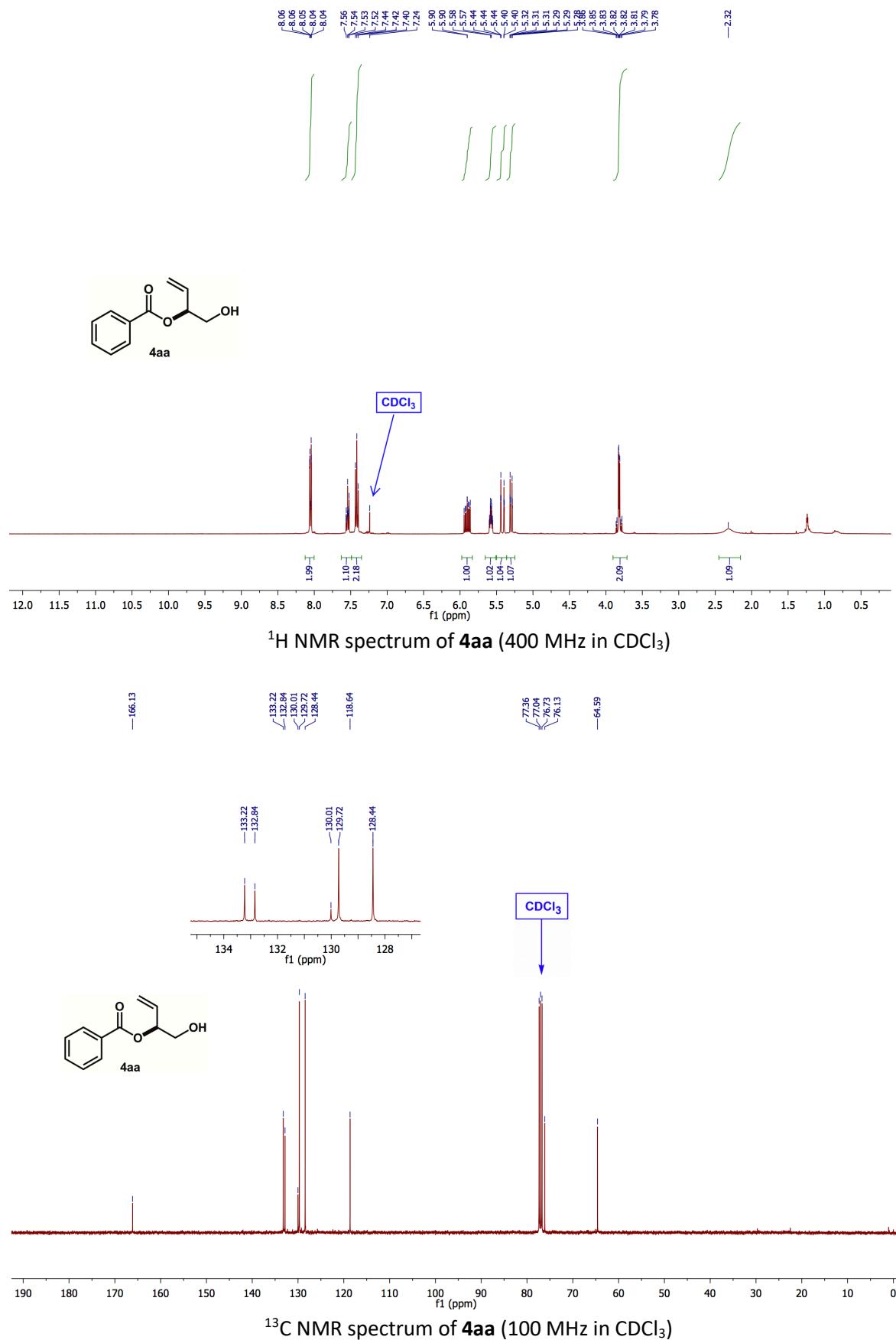


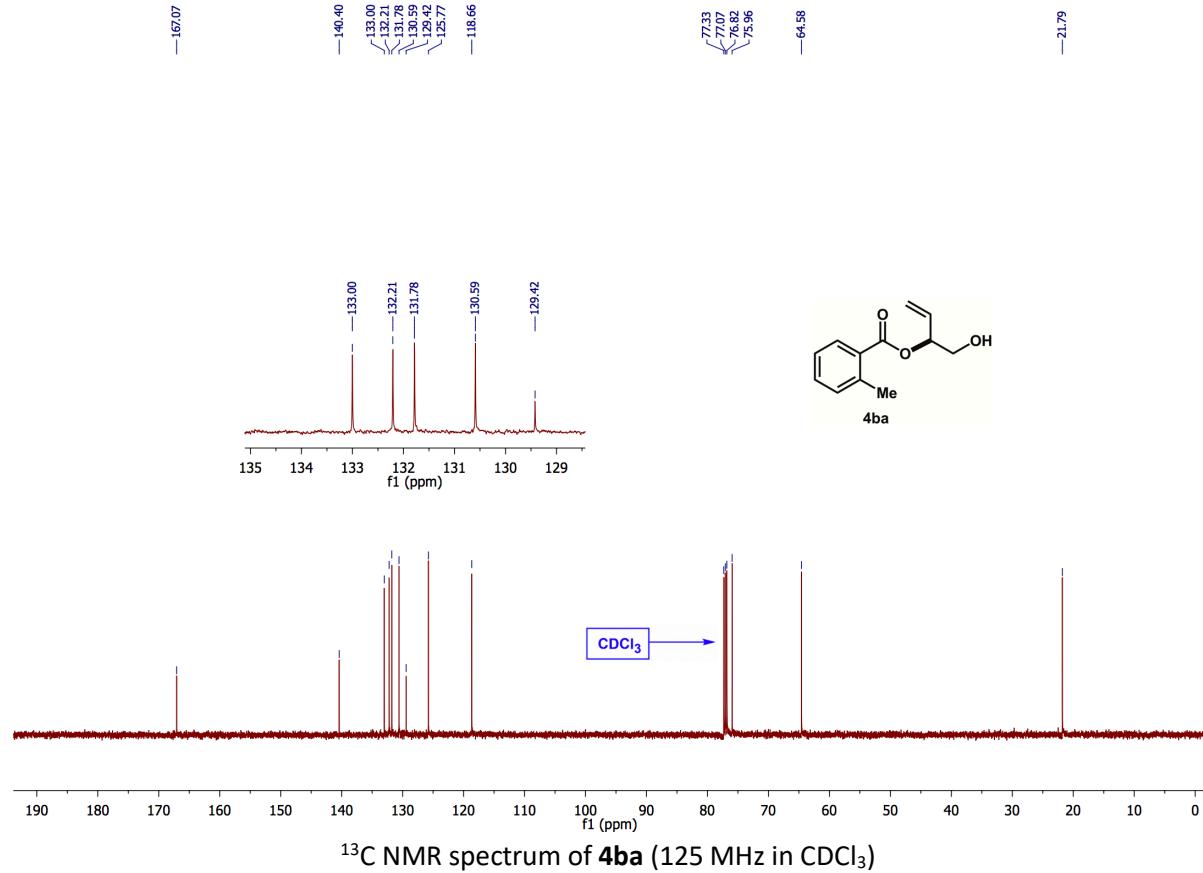
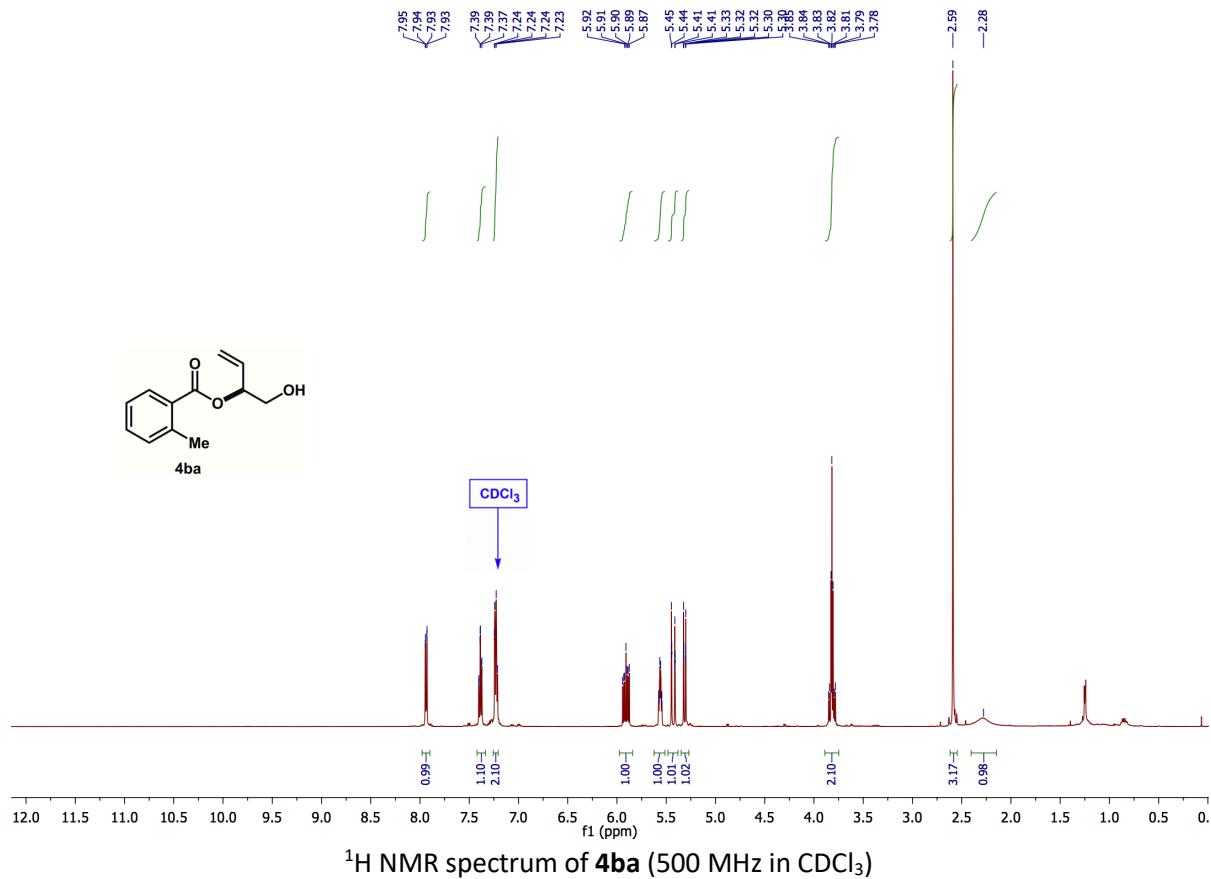
—133.13
—119.82
—77.36
—77.05
—76.73
—64.22
—63.88
—34.22
—34.05
—32.26
—31.84
—28.39
—21.96
—0.91
—0.89
—0.88

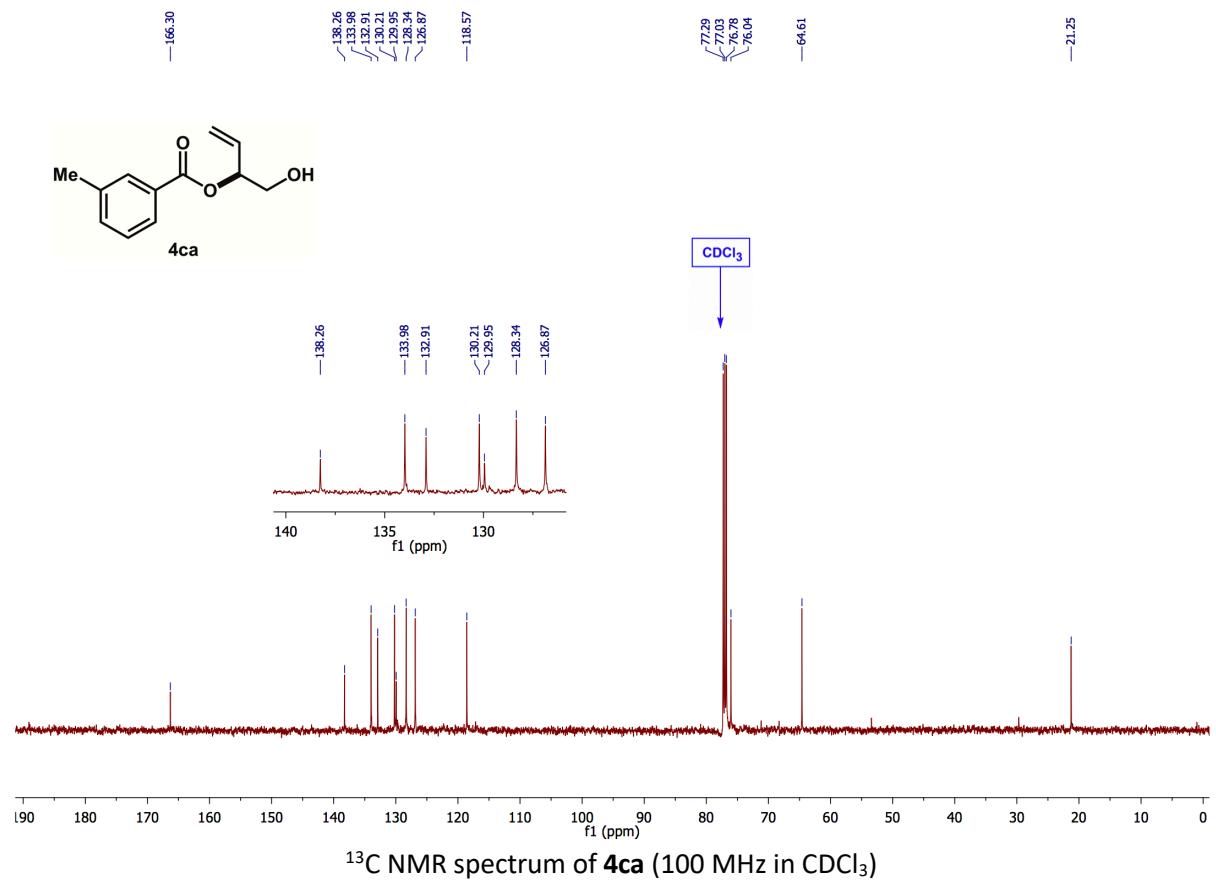
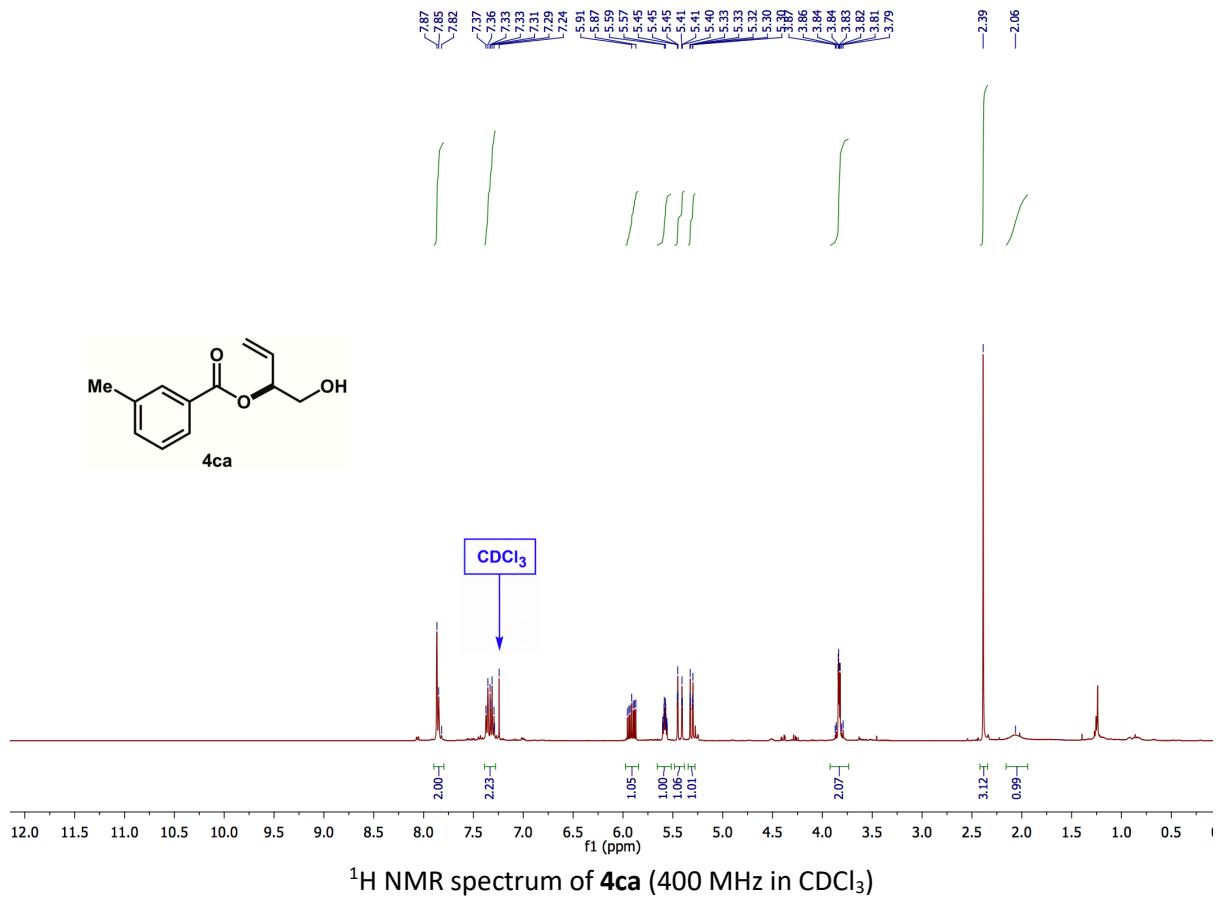
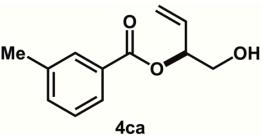


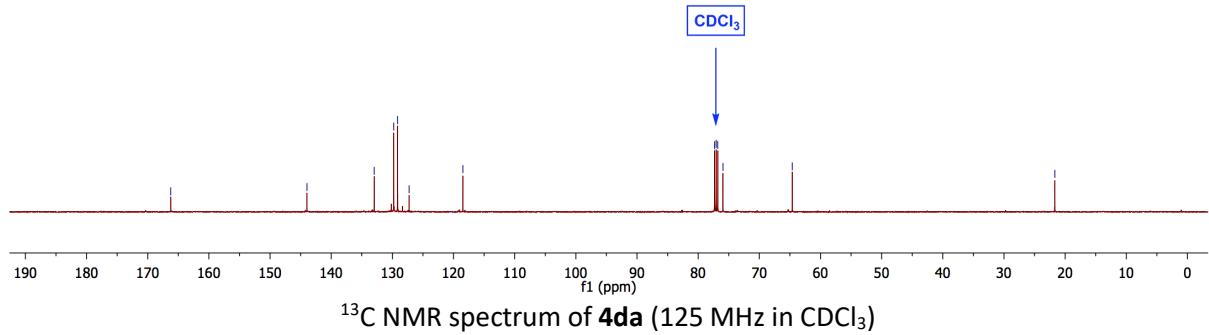
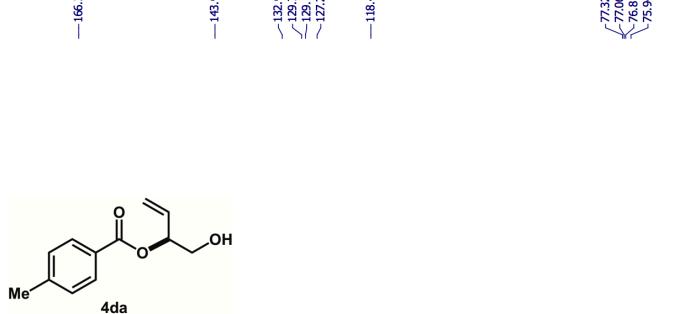
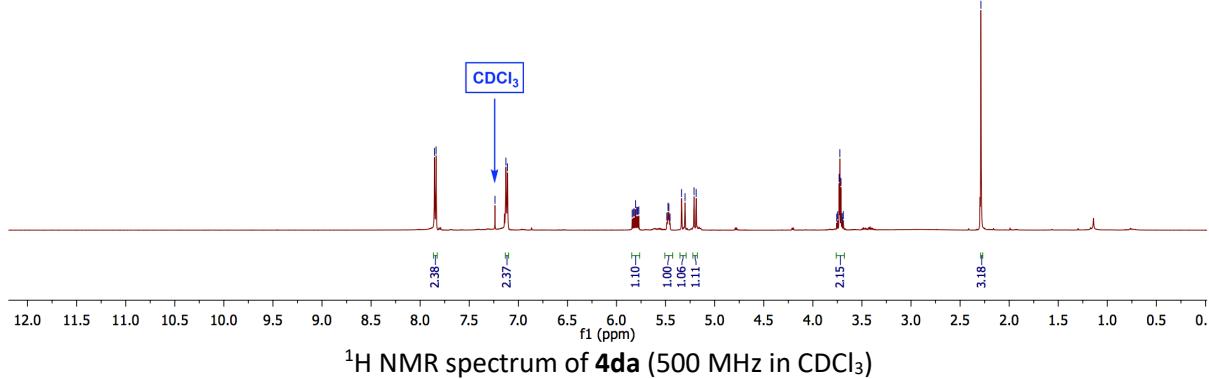
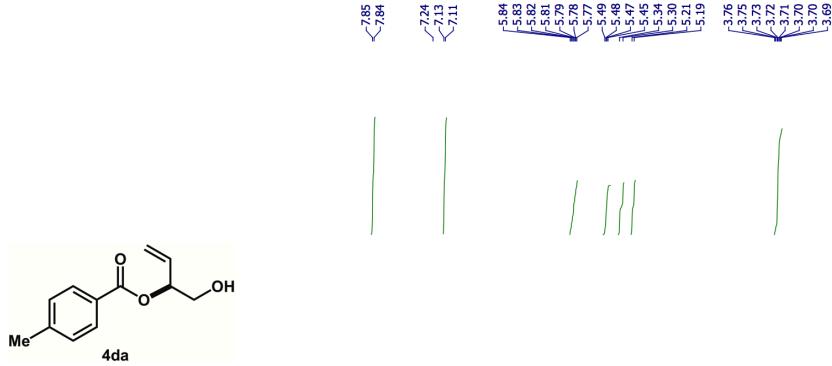


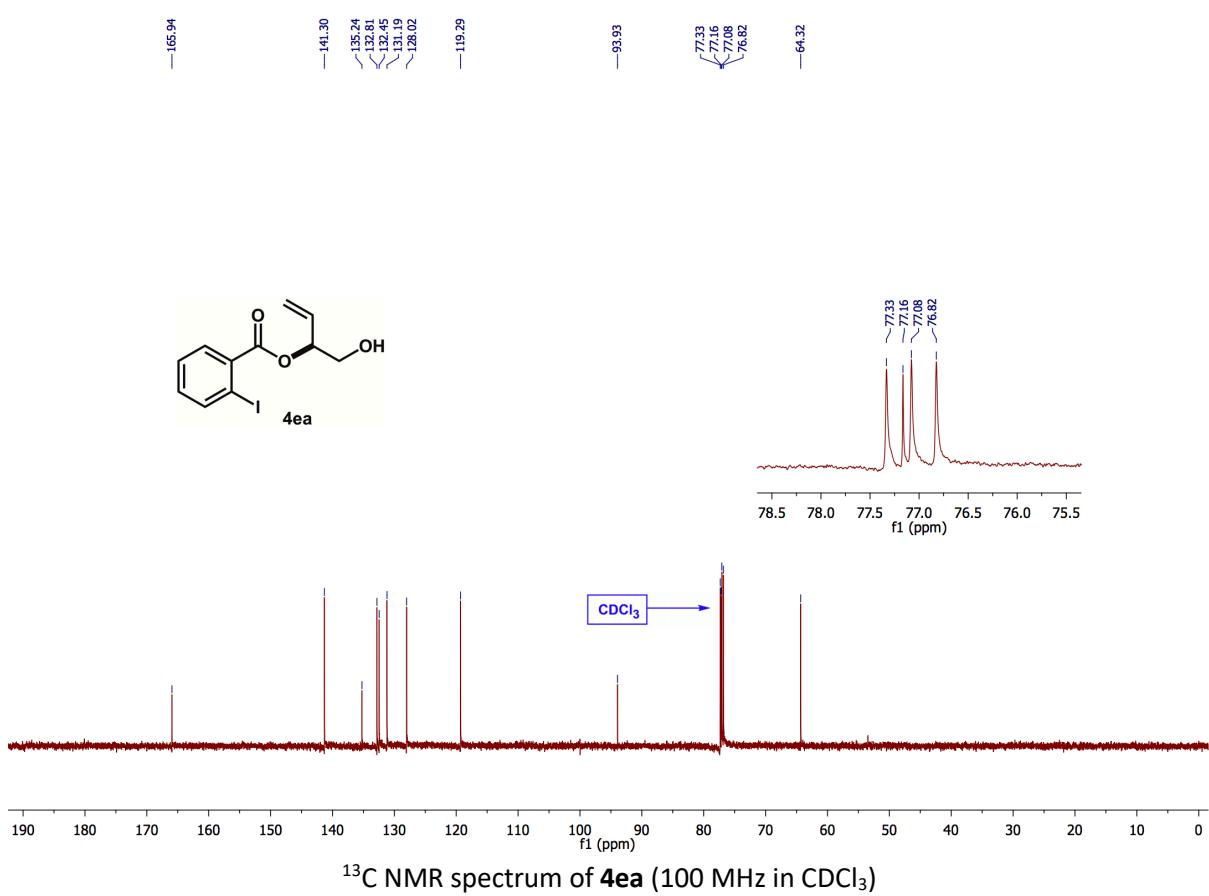
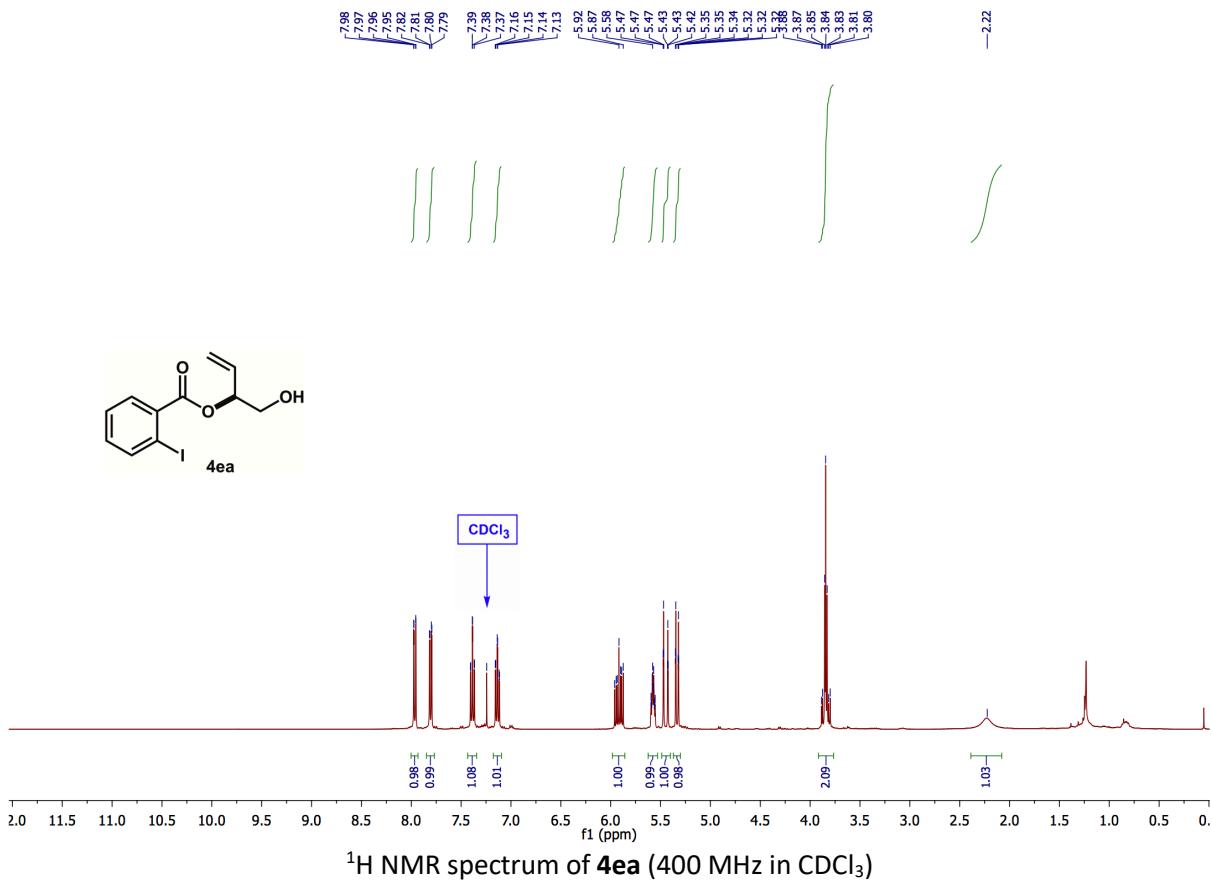
11. ^1H NMR, ^{13}C NMR and HPLC data for the ring opened products:

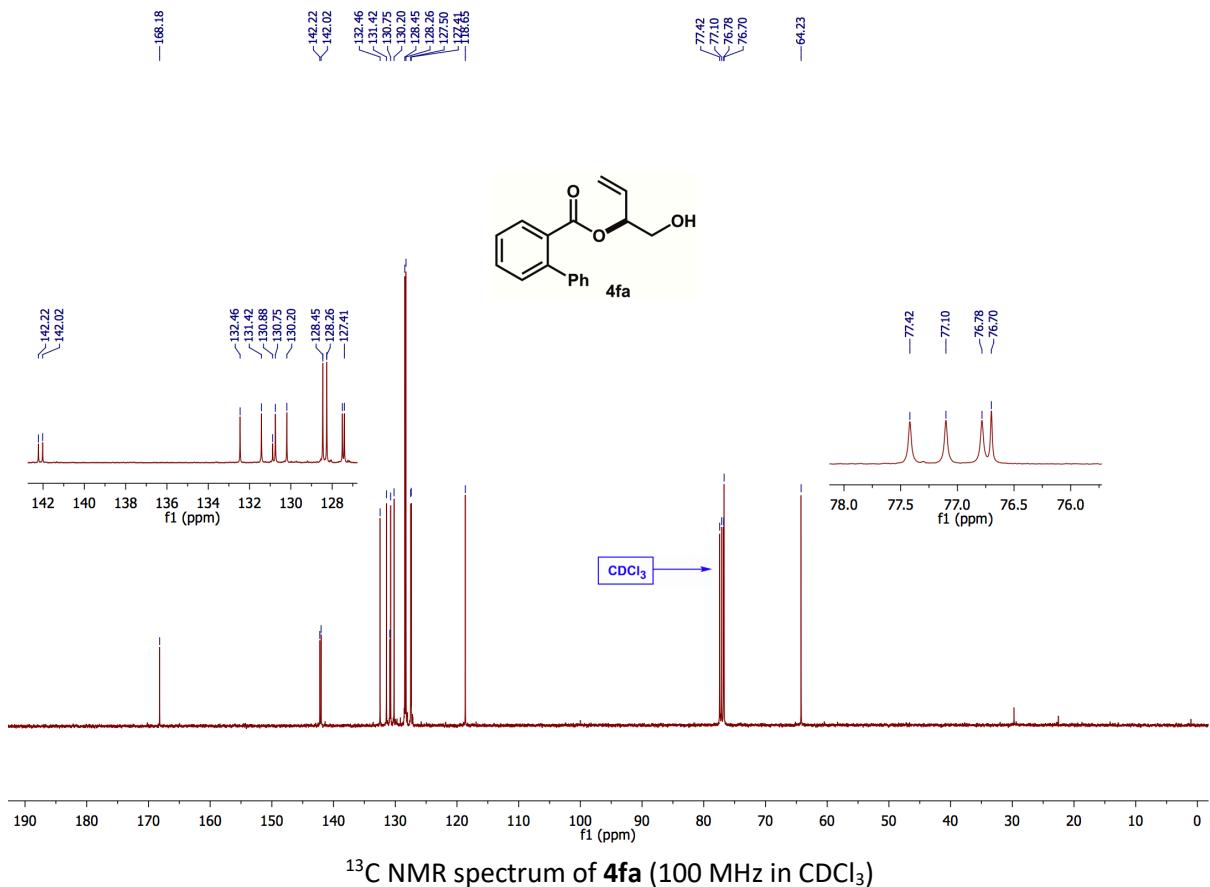
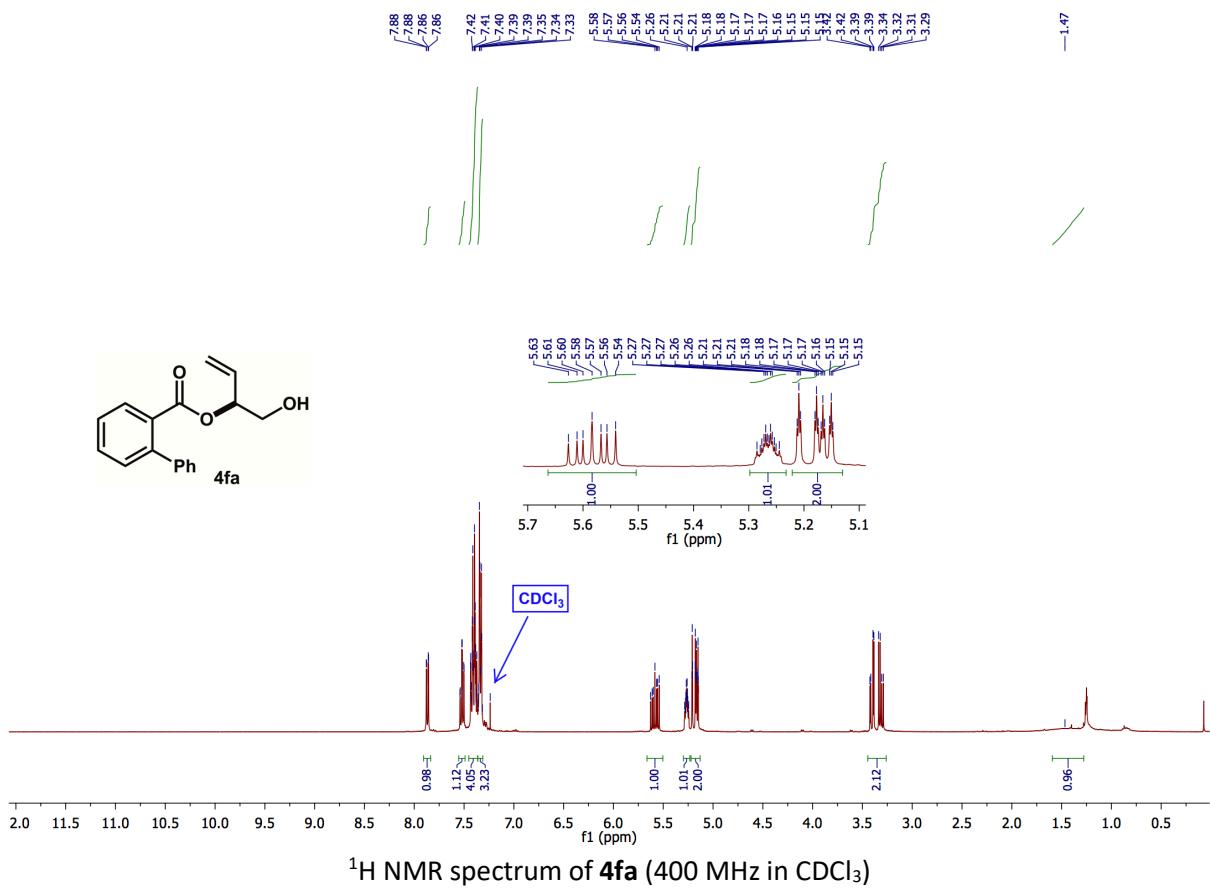


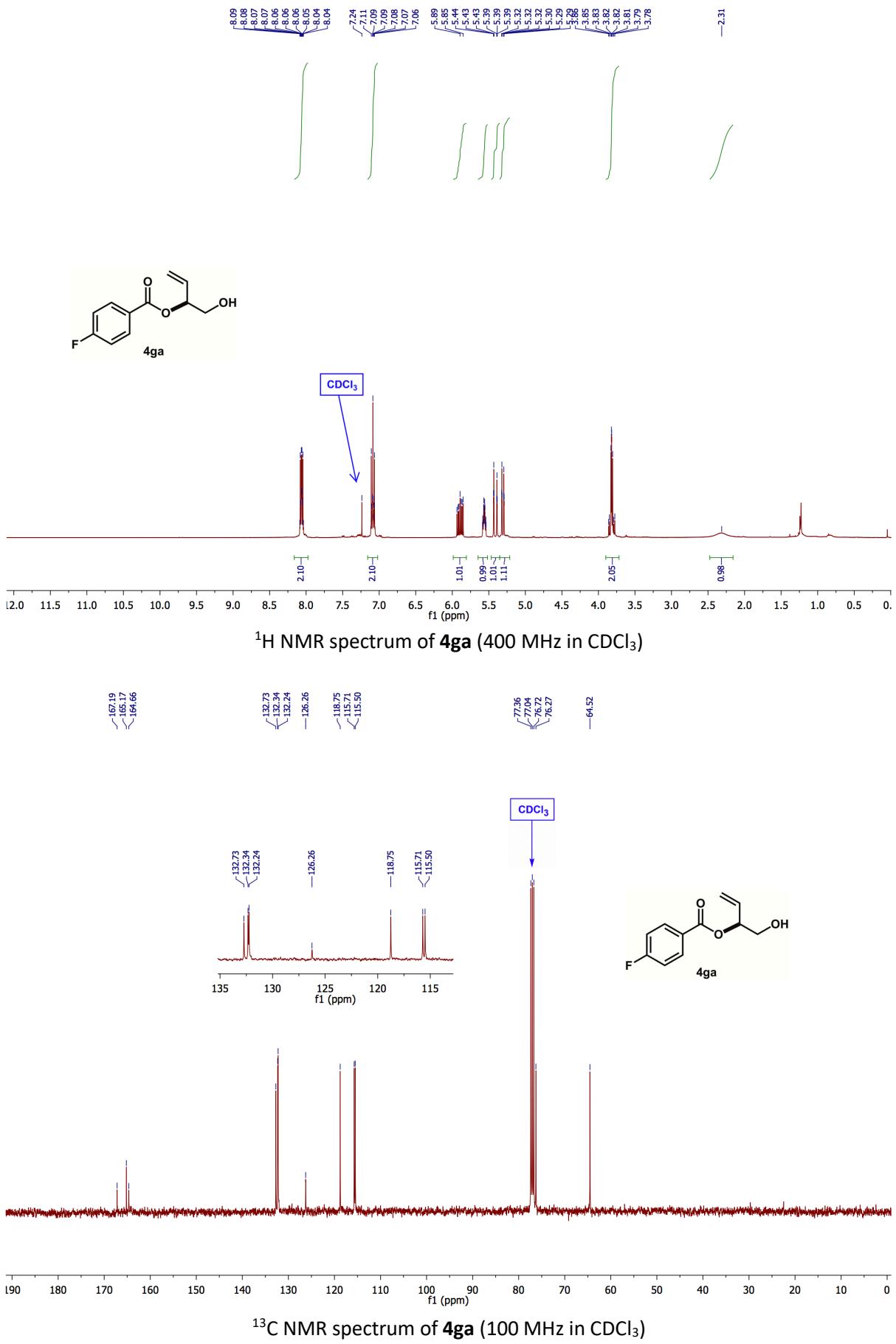


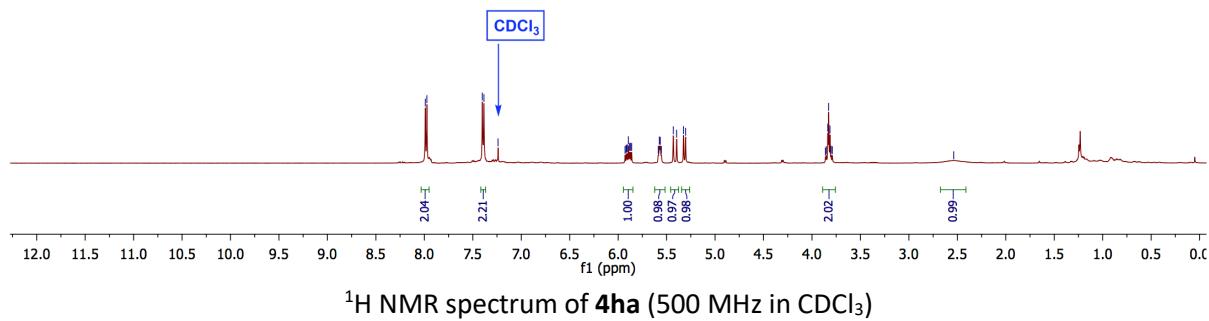
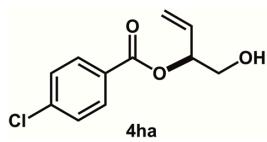
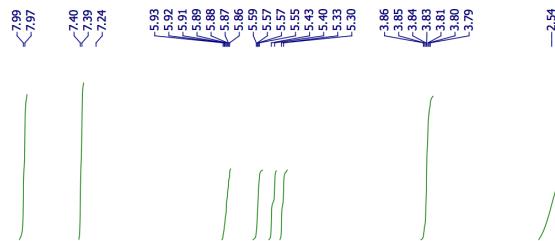




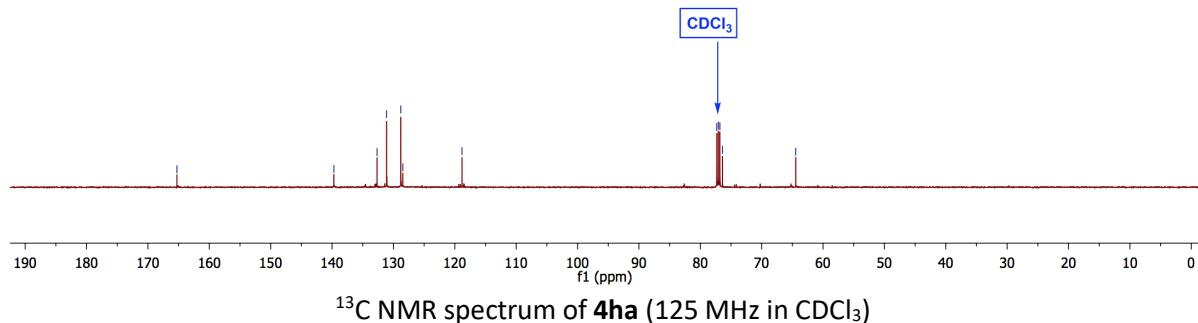
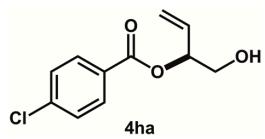




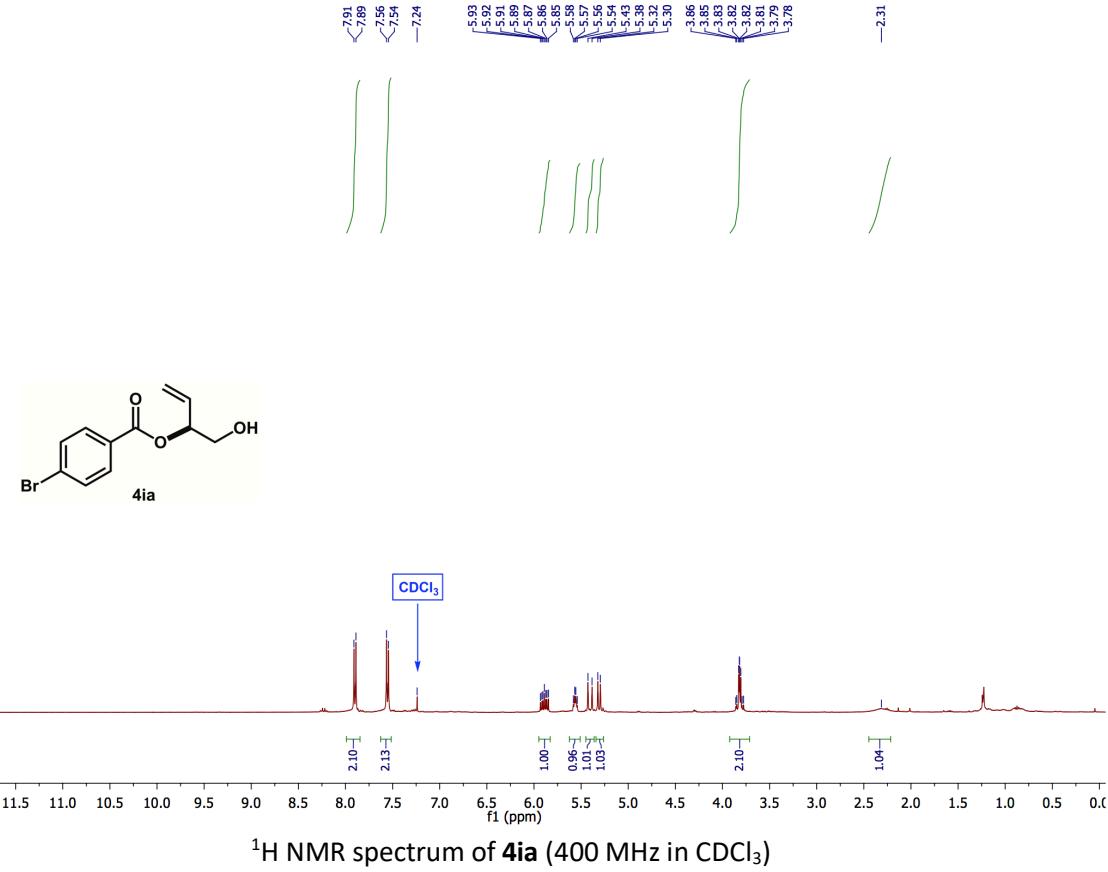




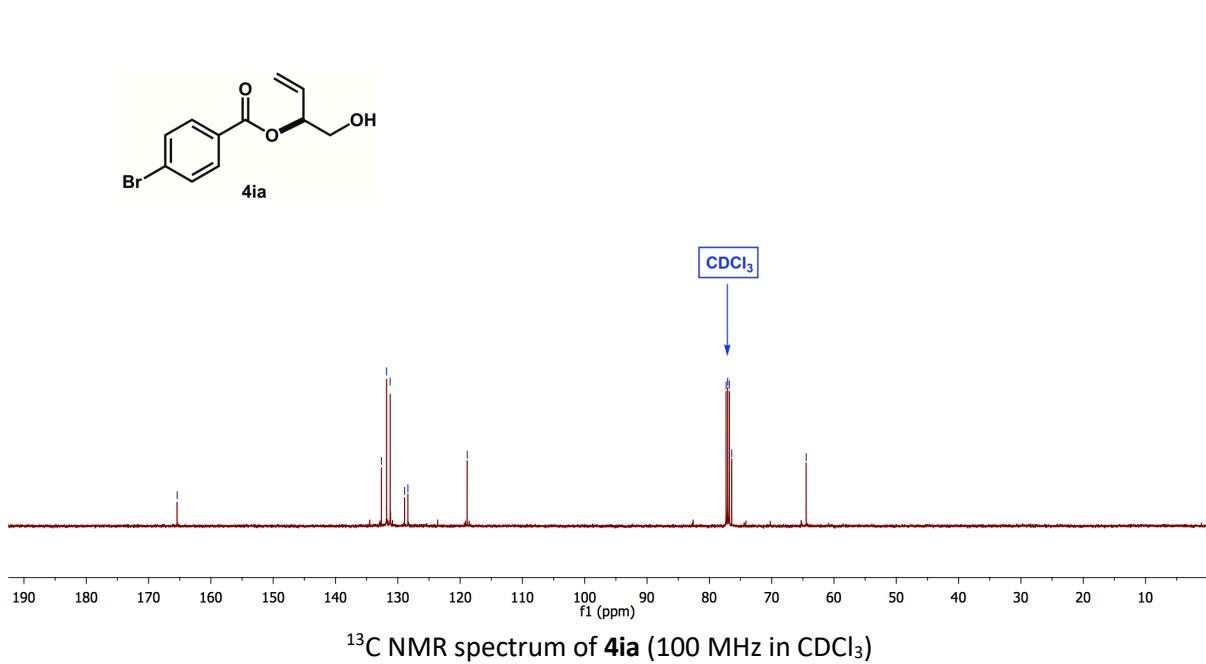
¹H NMR spectrum of **4ha** (500 MHz in CDCl₃)



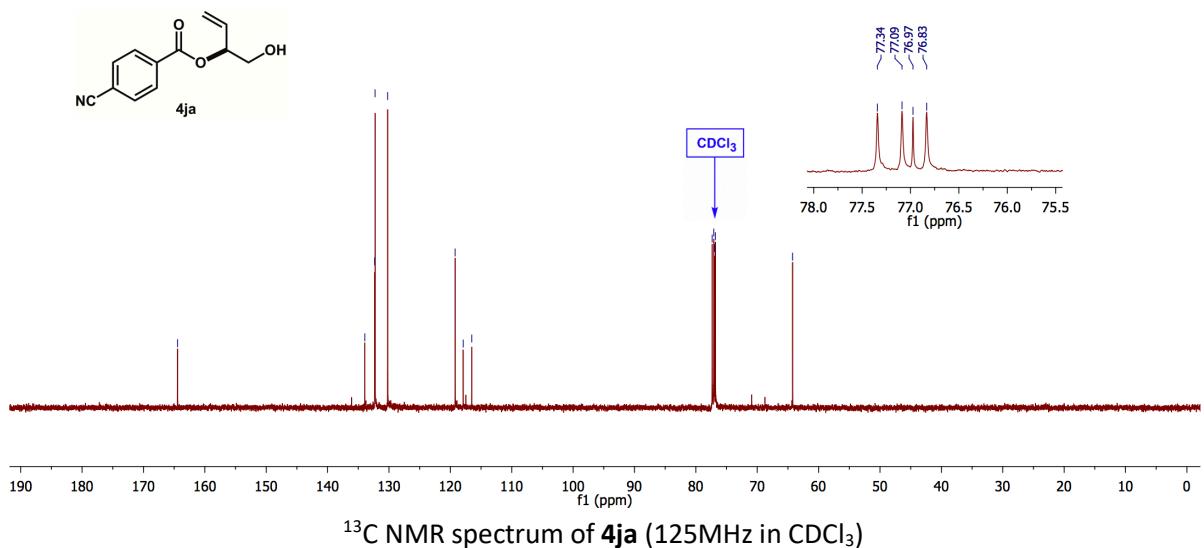
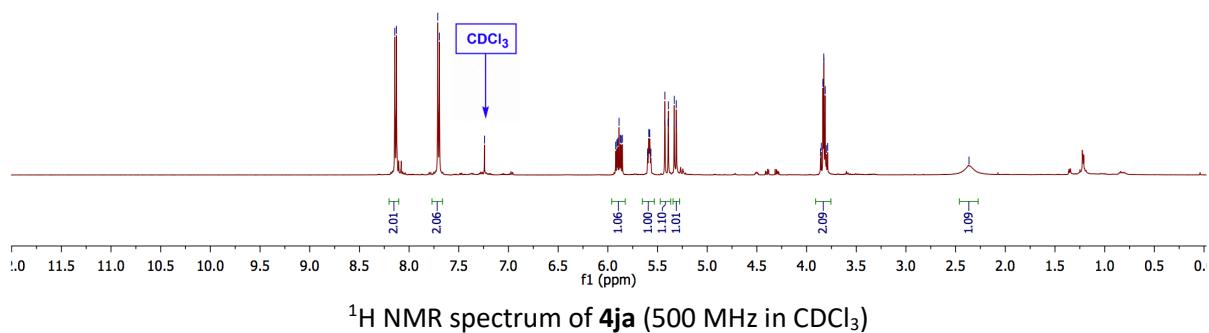
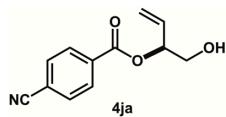
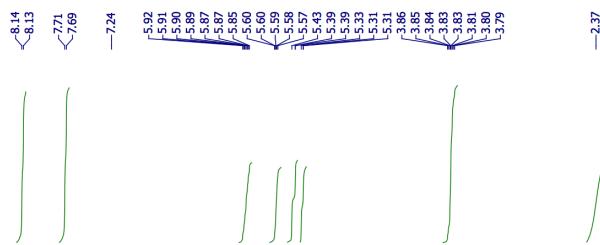
¹³C NMR spectrum of **4ha** (125 MHz in CDCl₃)

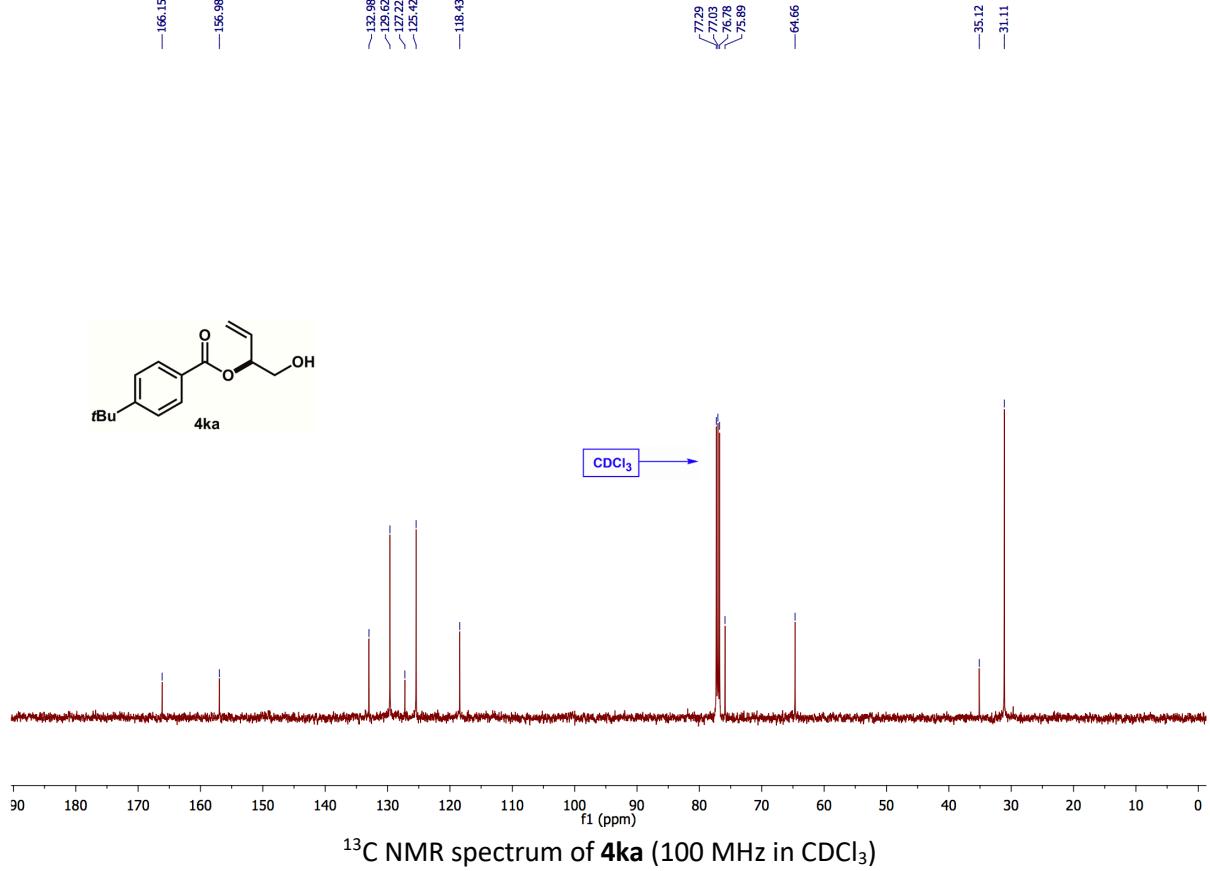
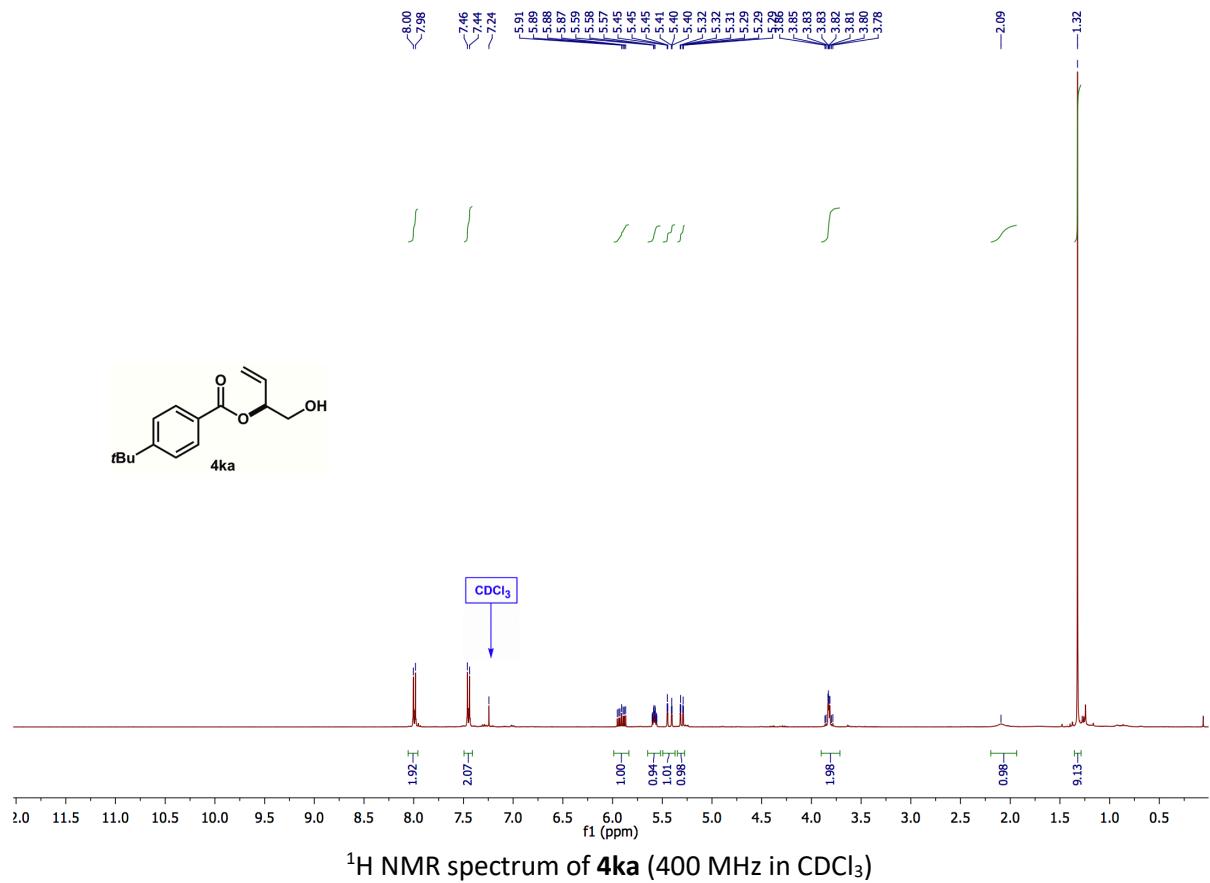


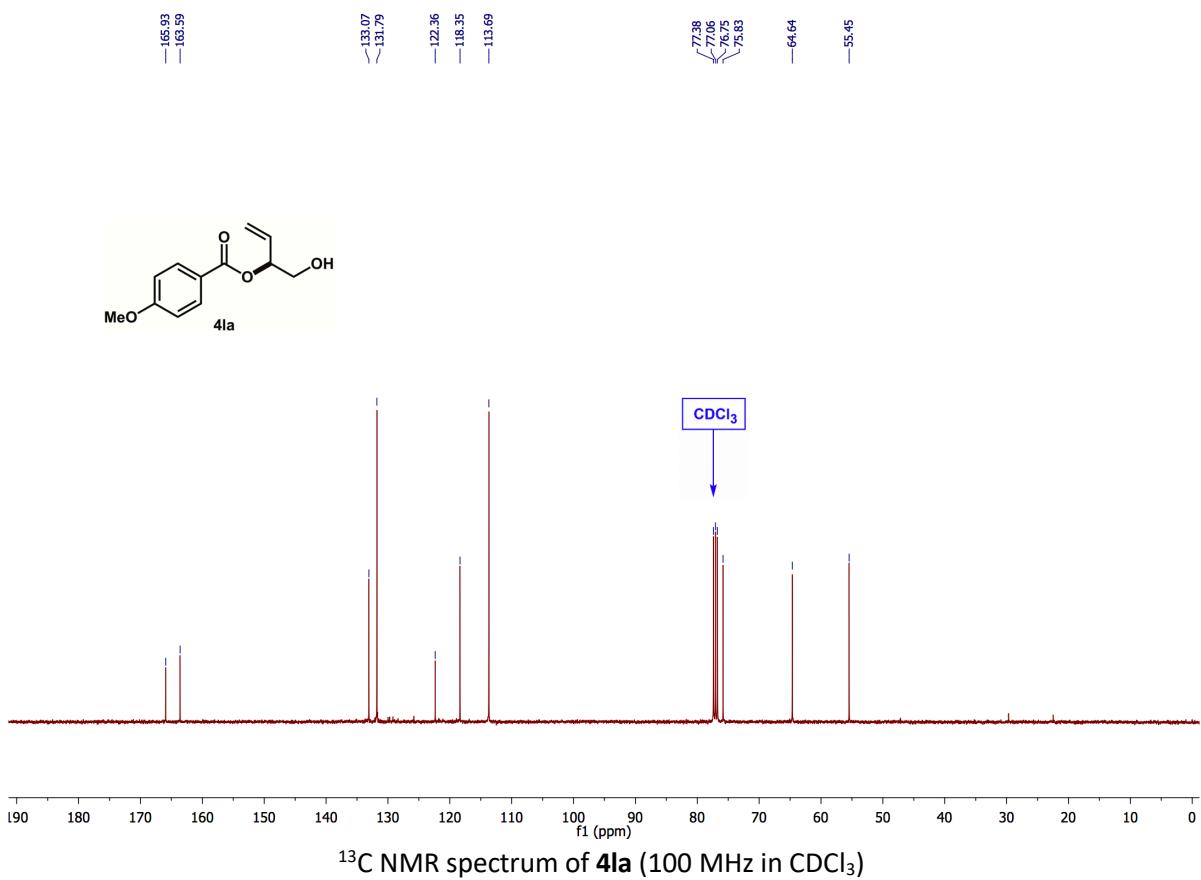
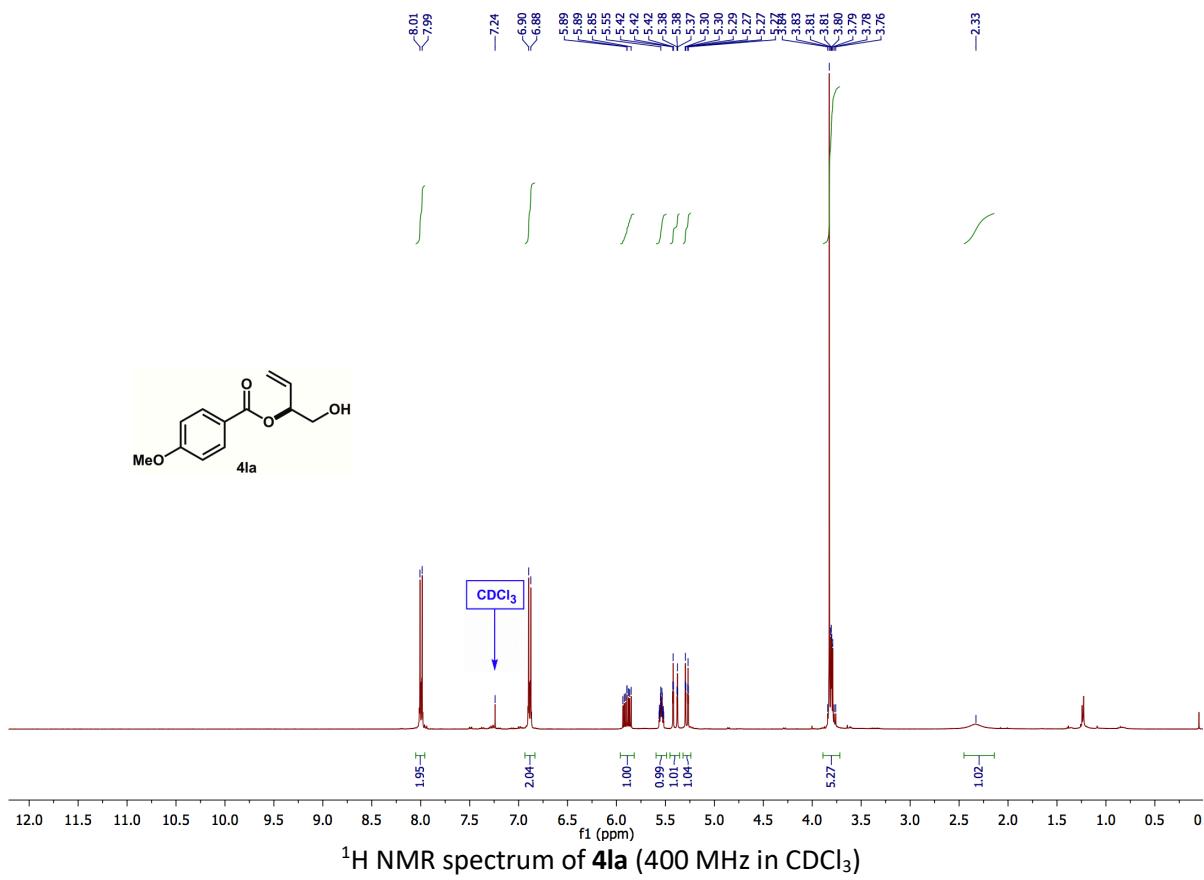
^1H NMR spectrum of **4ia** (400 MHz in CDCl_3)

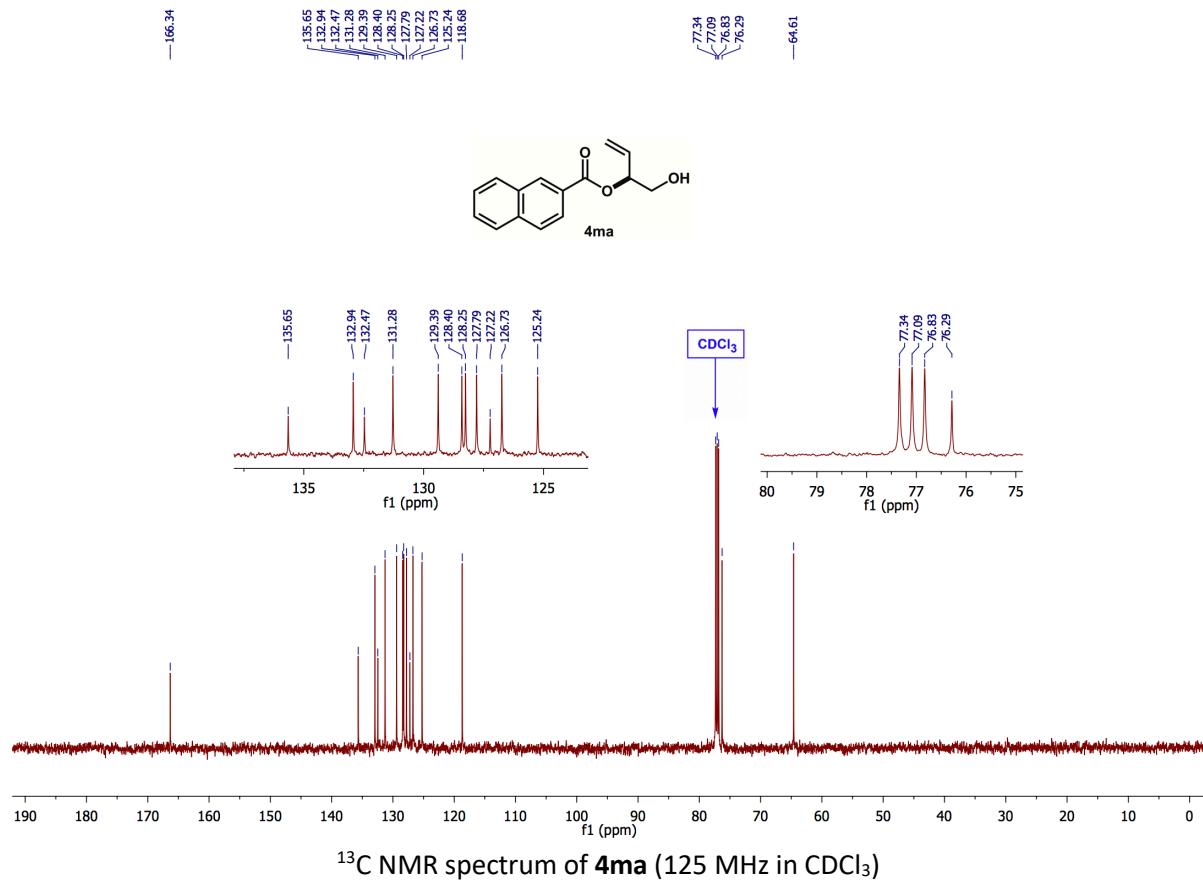
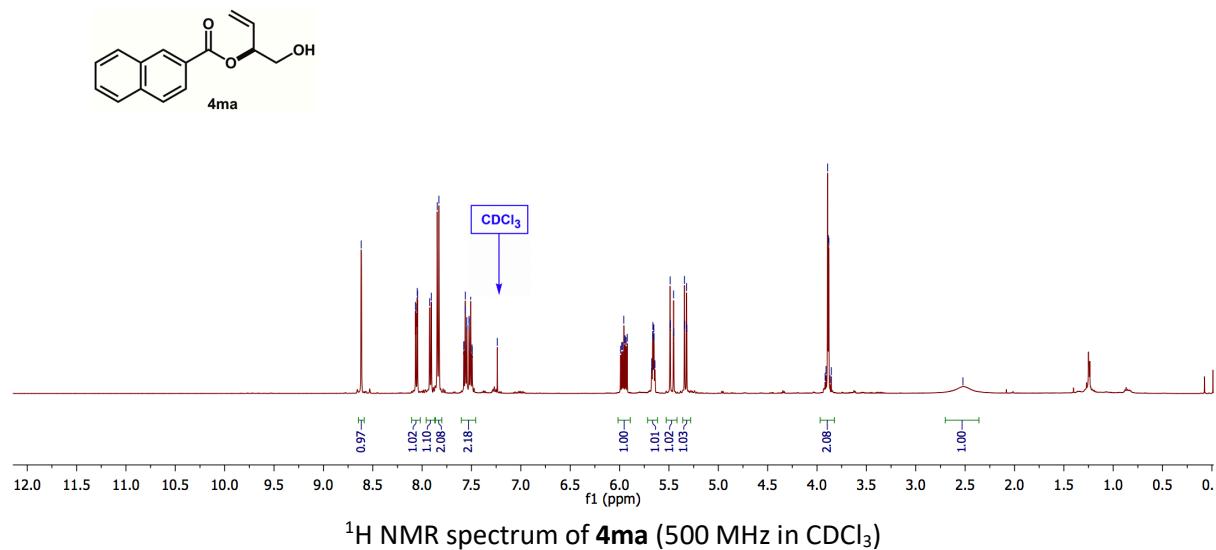
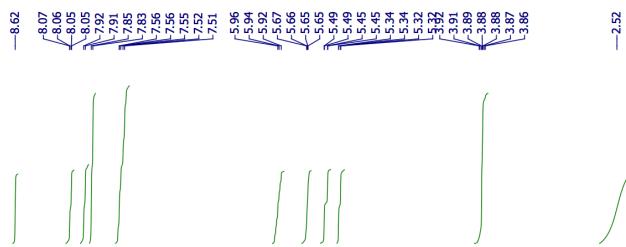


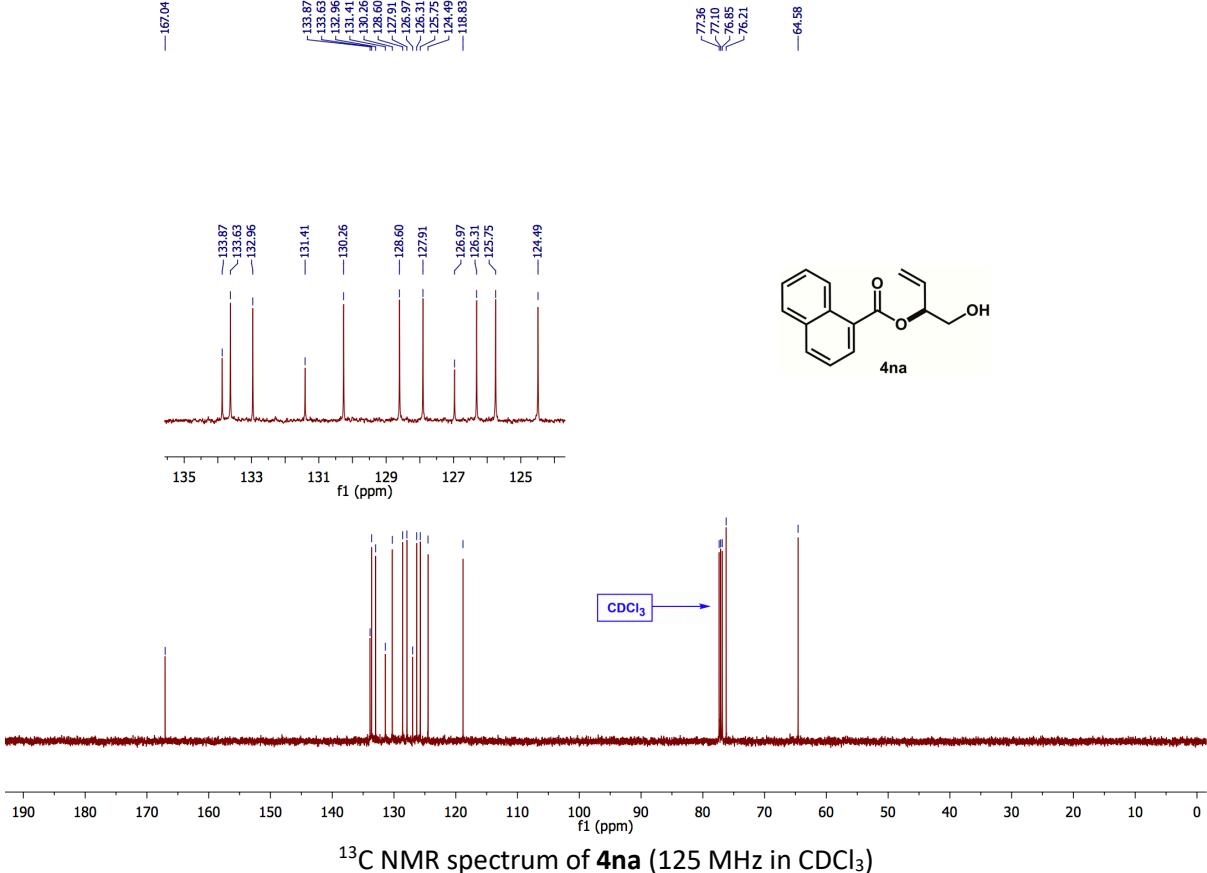
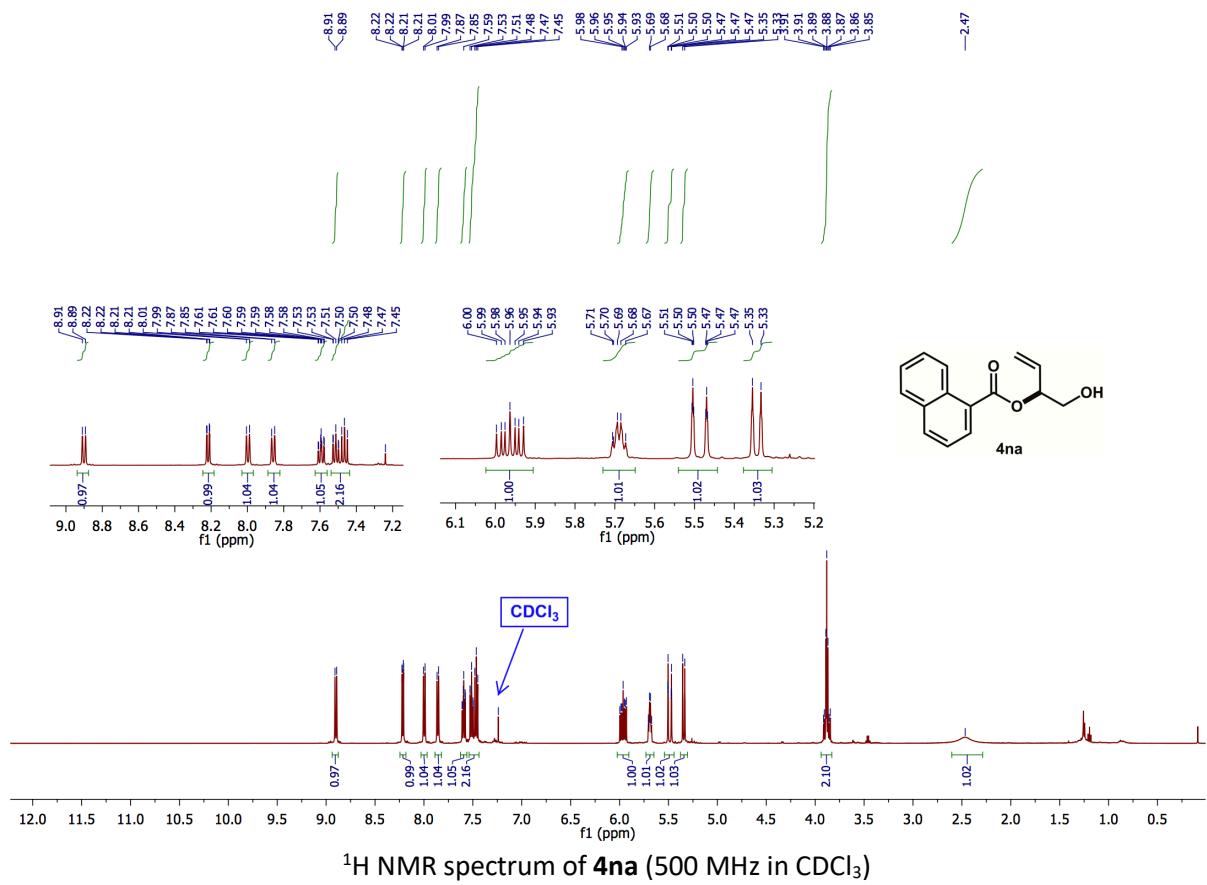
^{13}C NMR spectrum of **4ia** (100 MHz in CDCl_3)

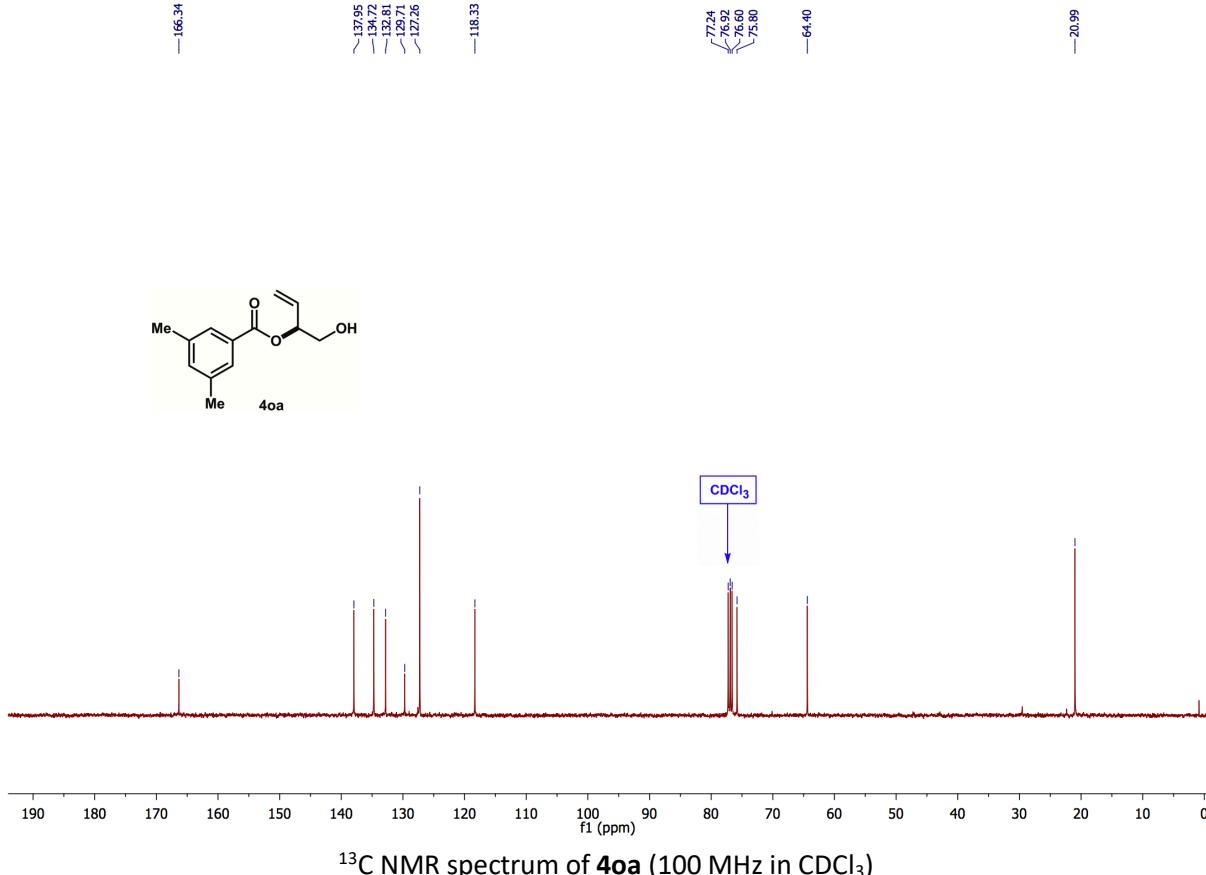
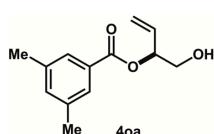
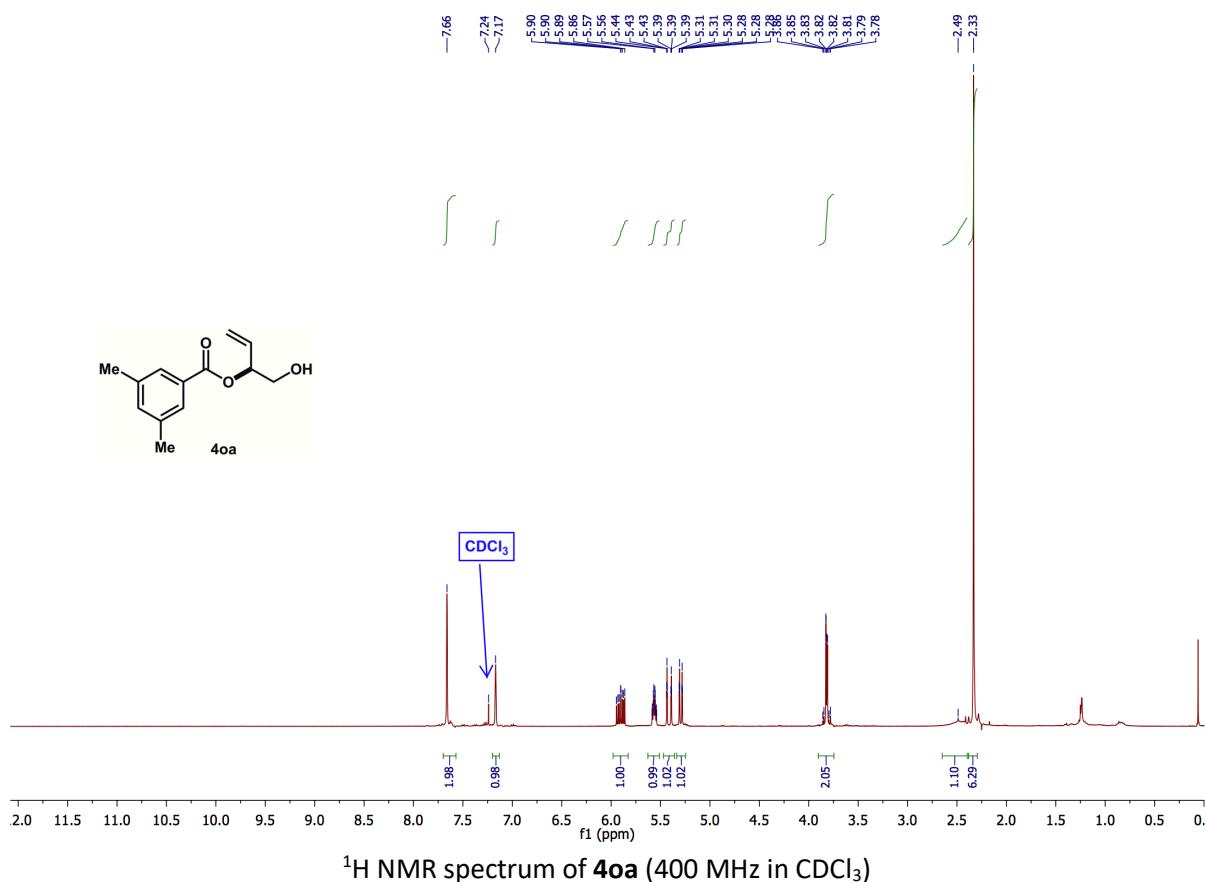
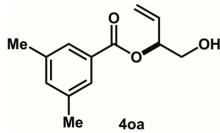


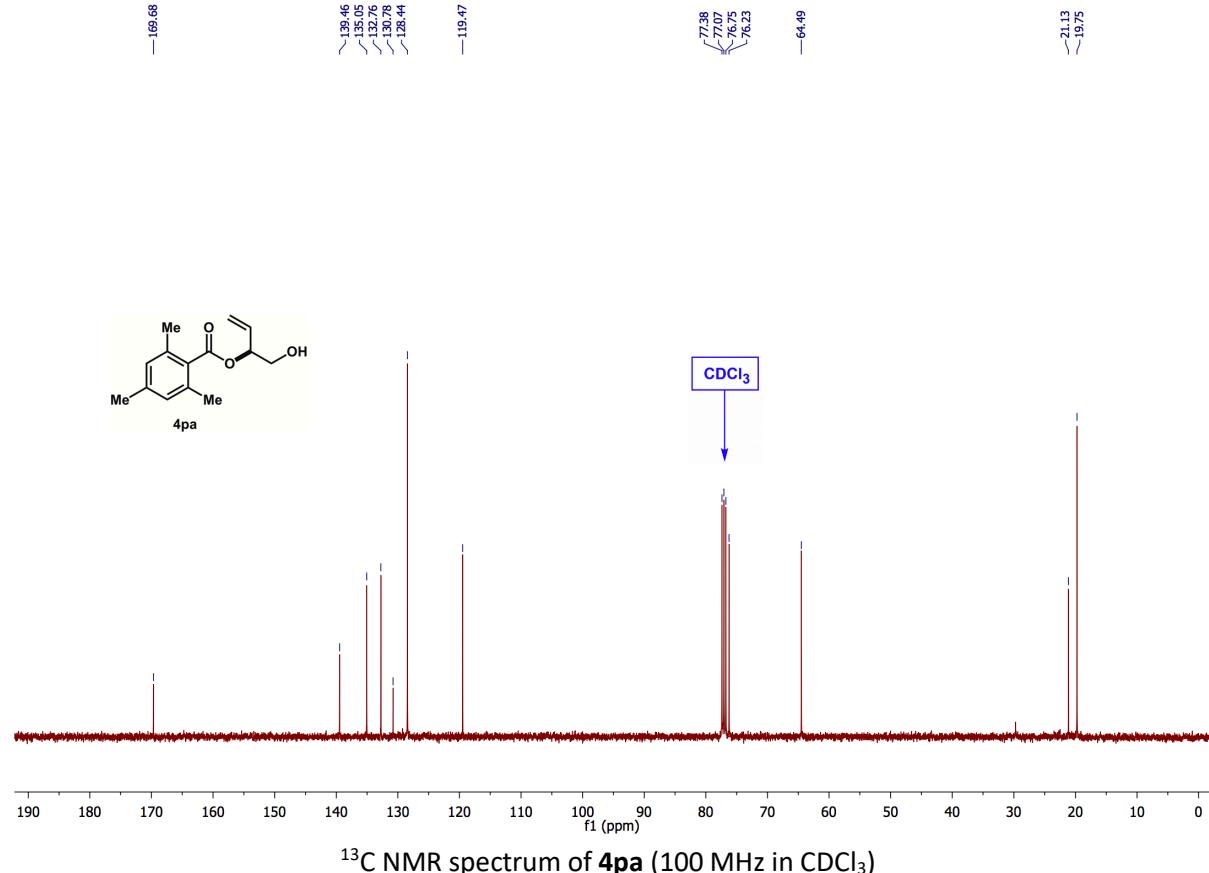
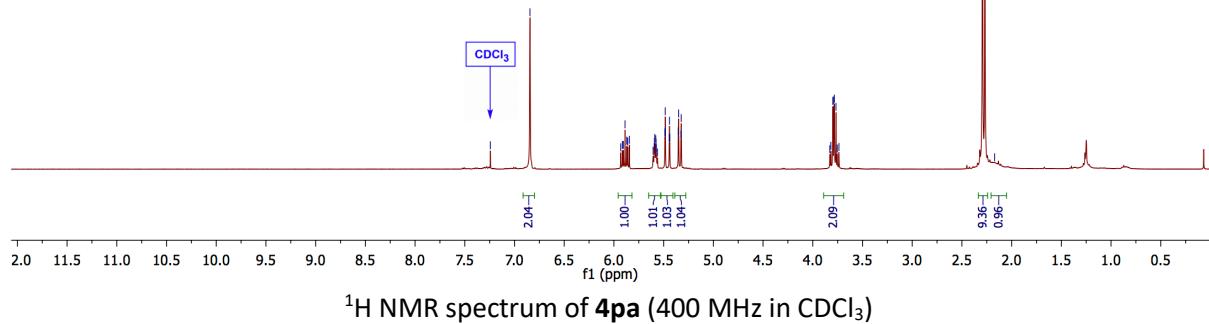
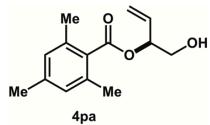


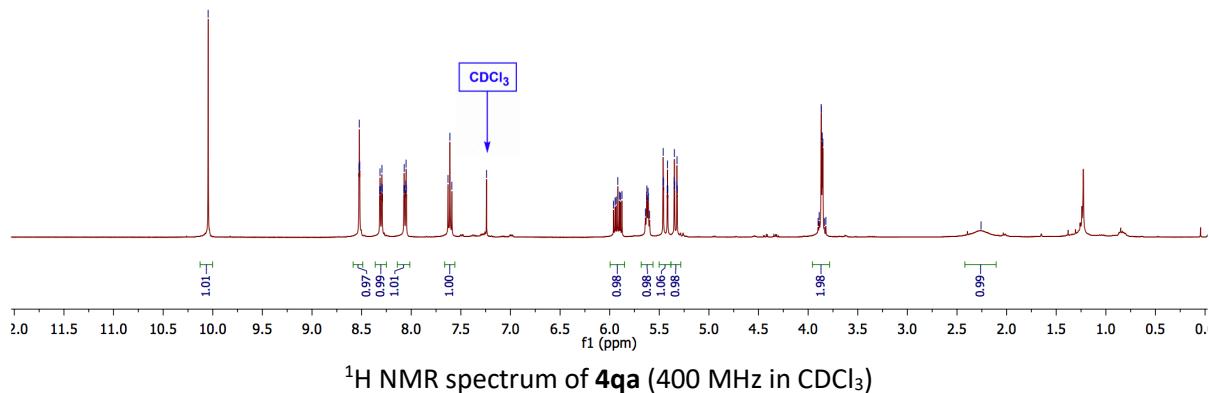
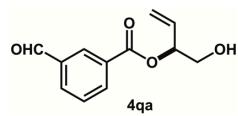
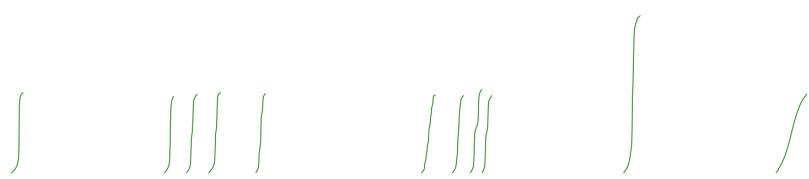




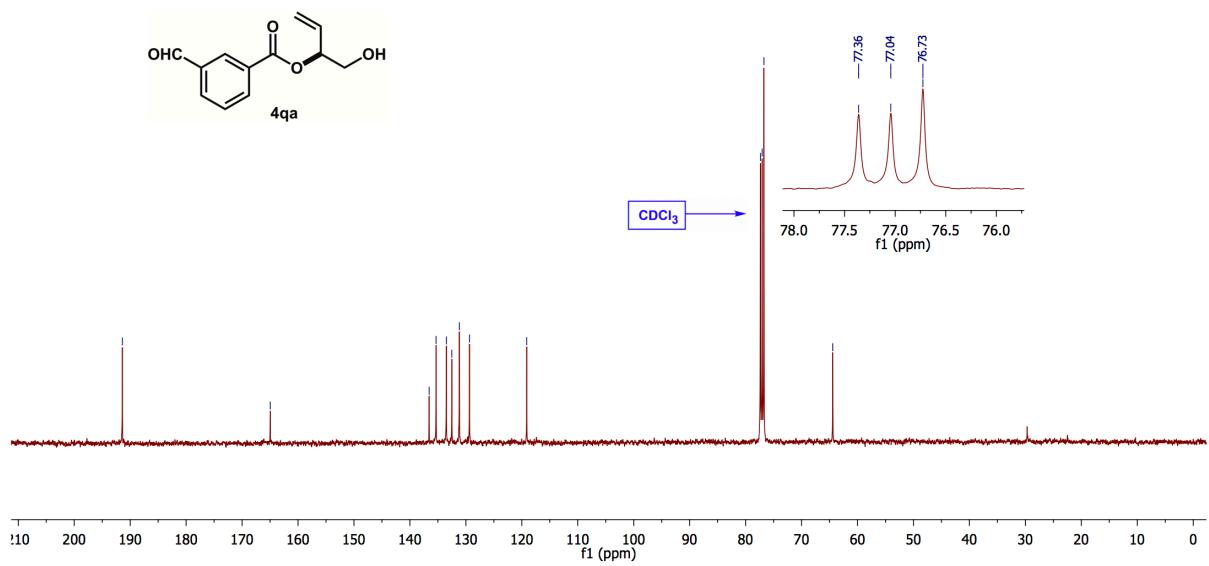




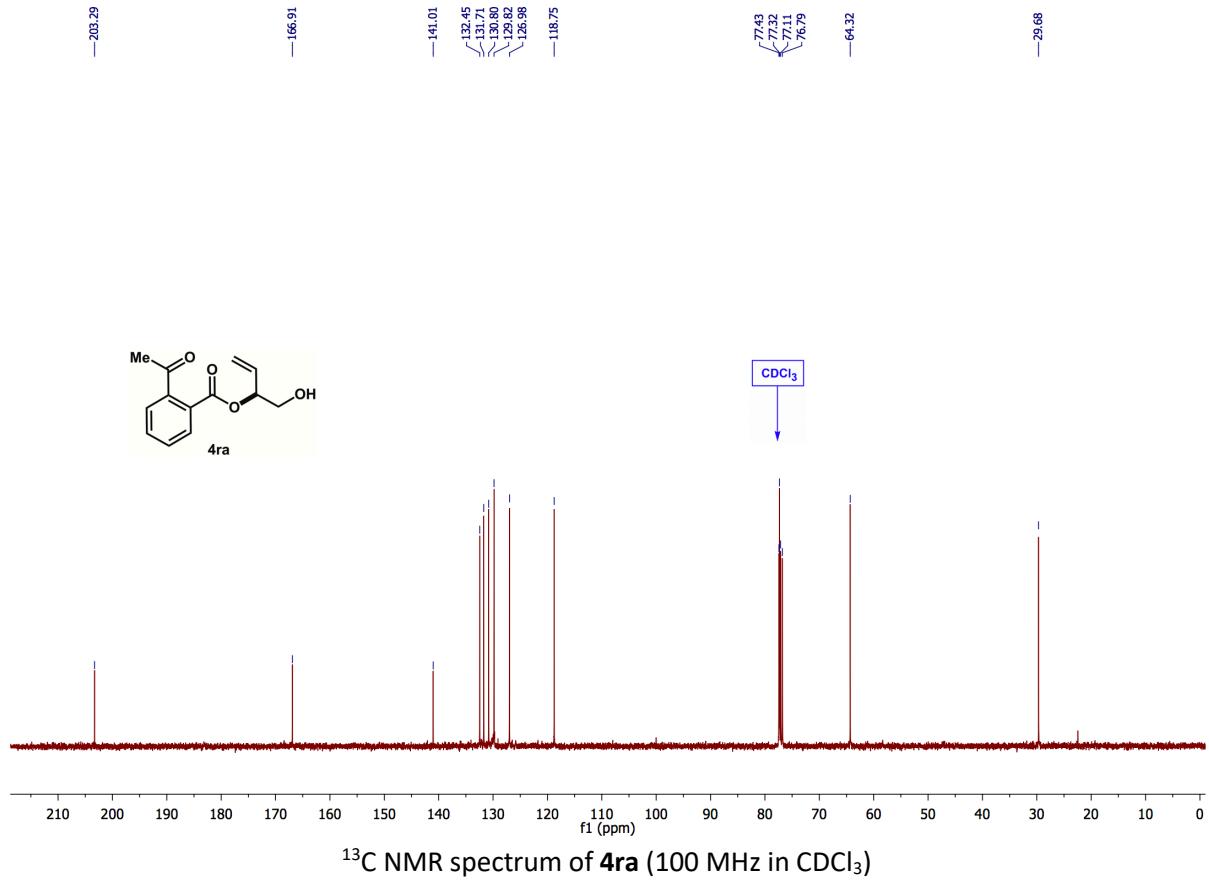
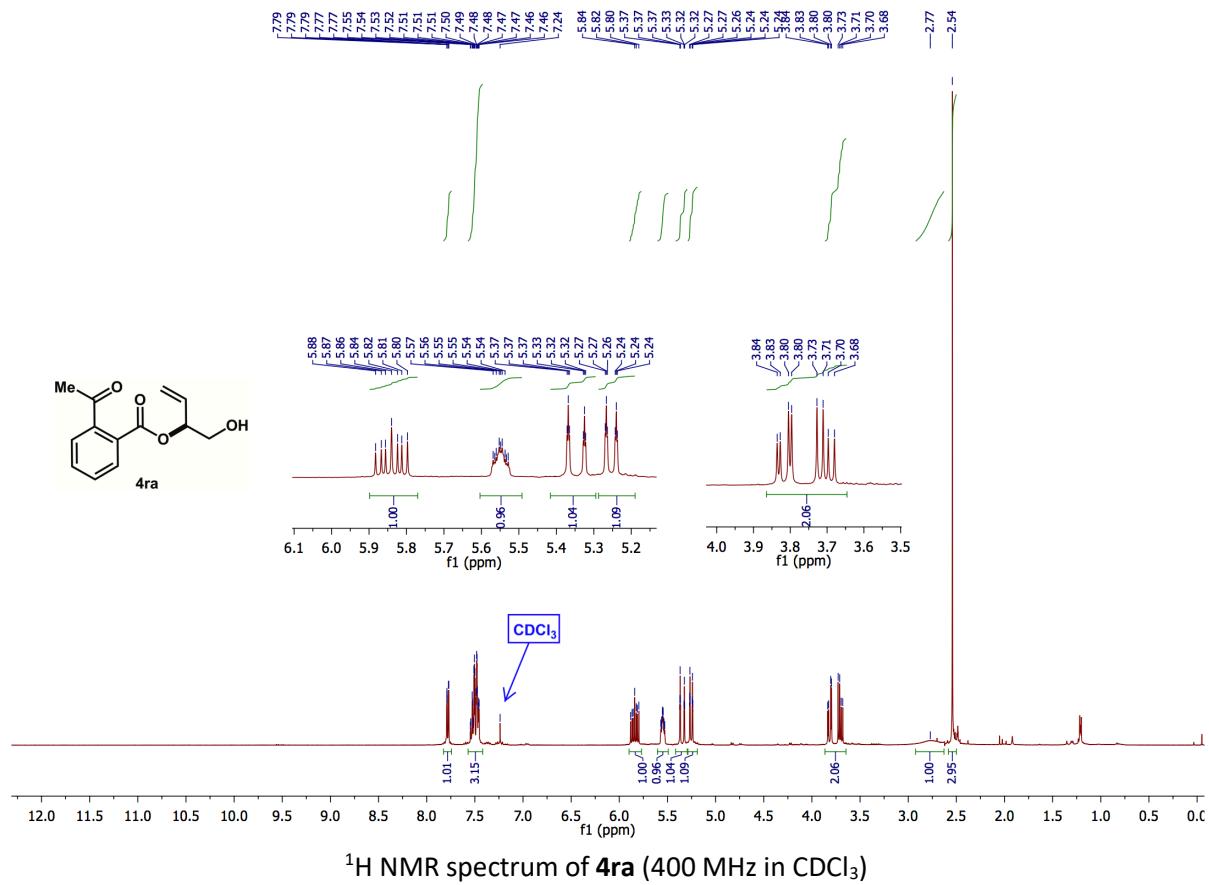


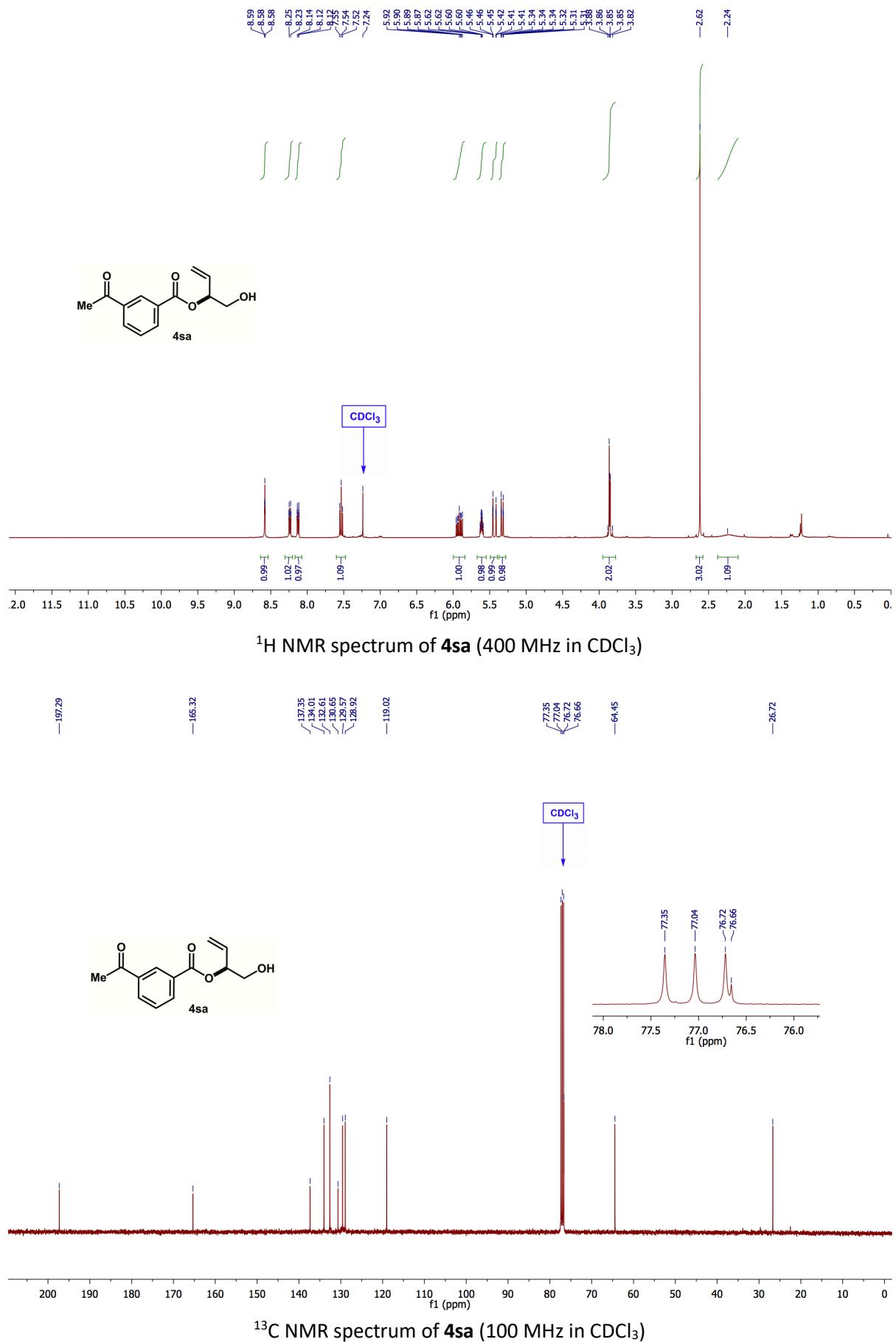


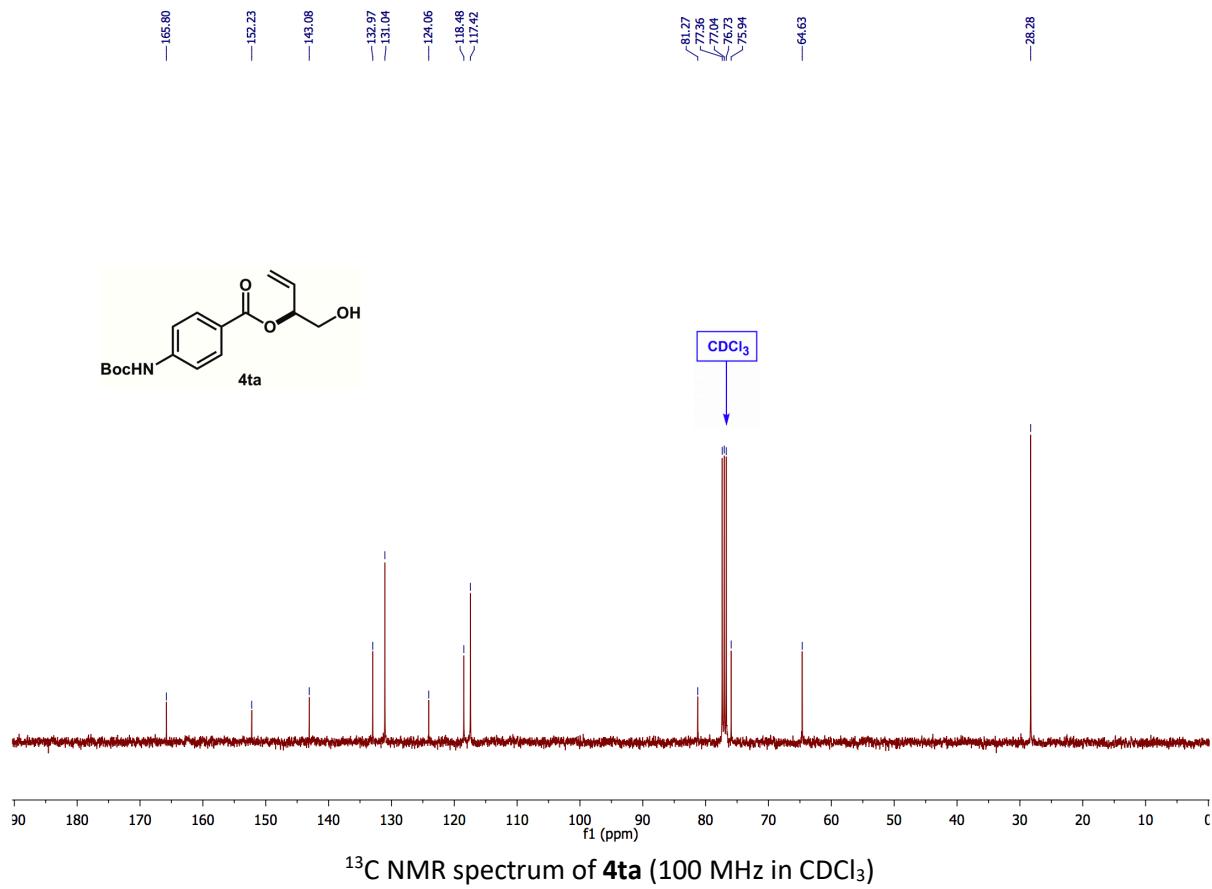
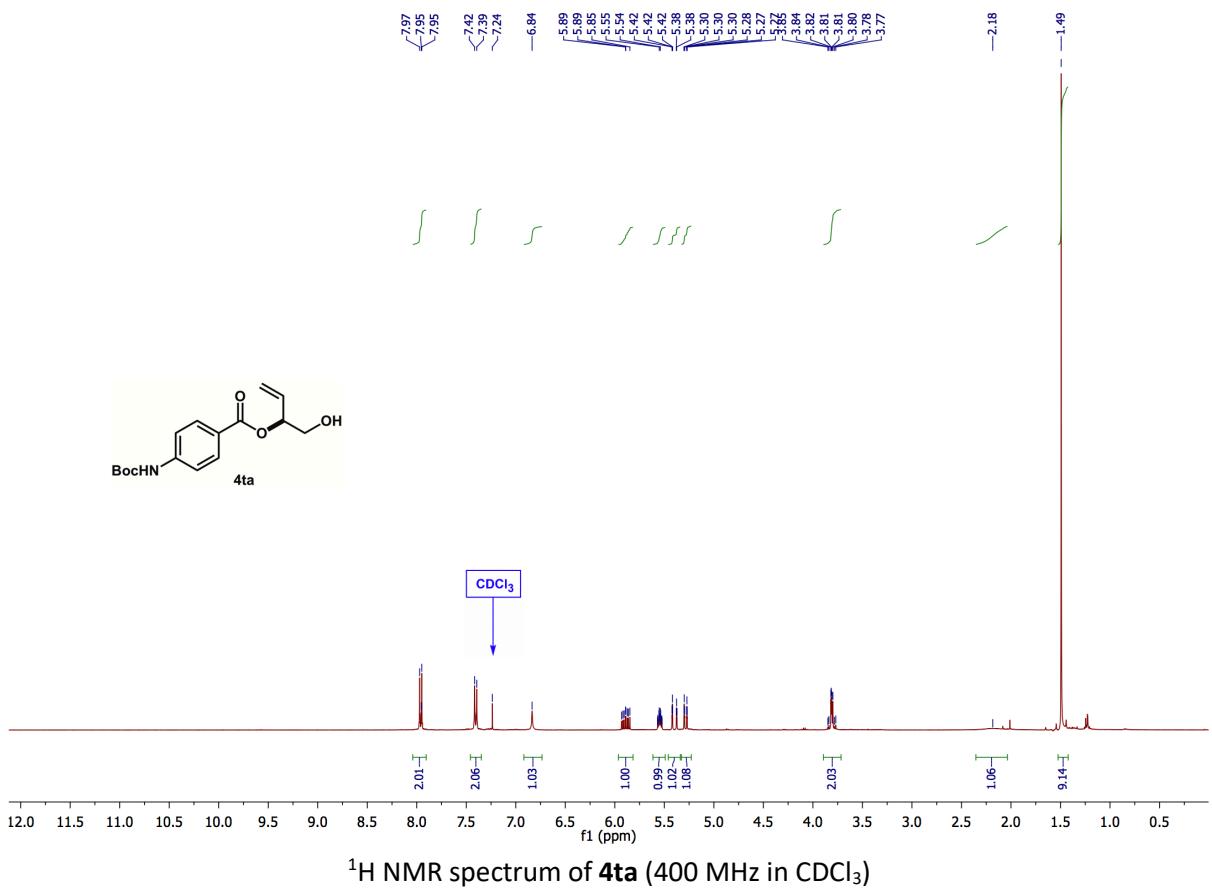
¹H NMR spectrum of **4qa** (400 MHz in CDCl₃)

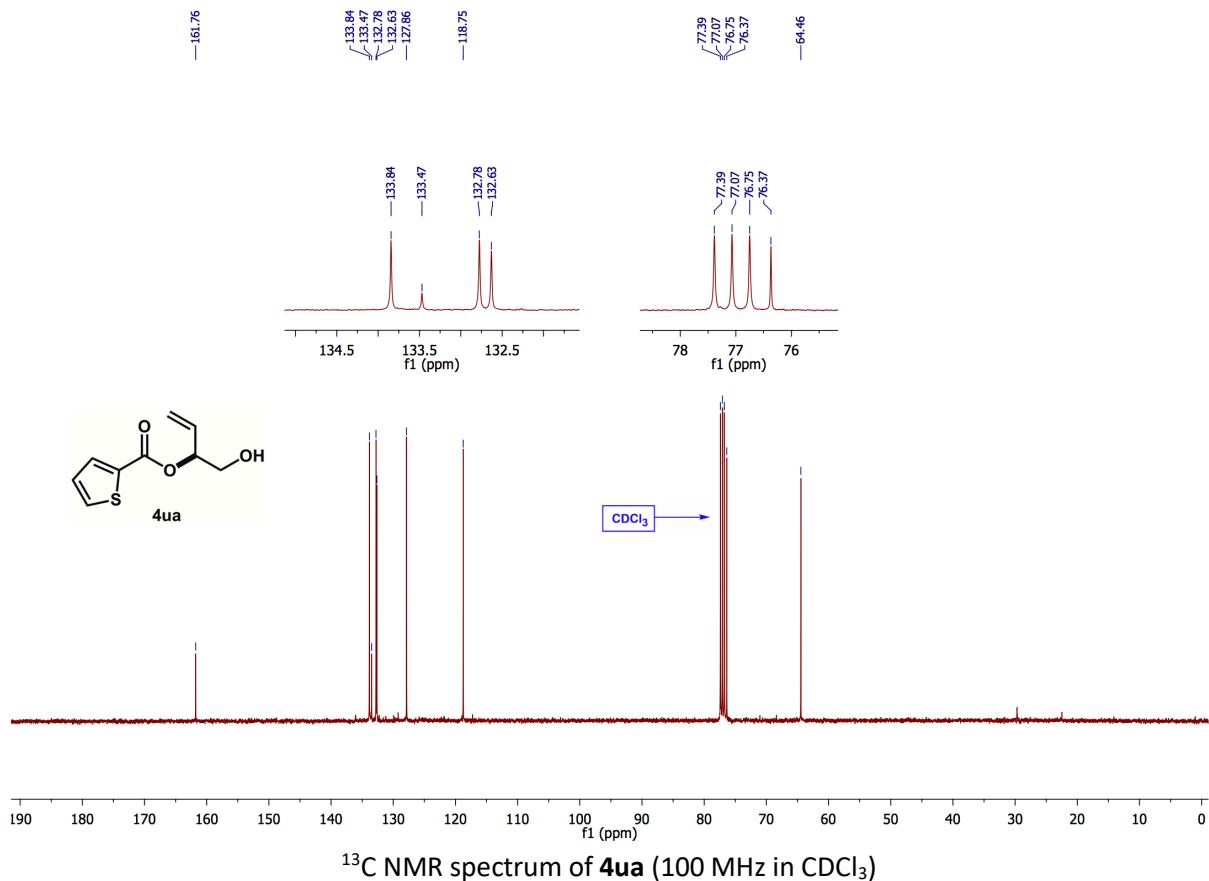
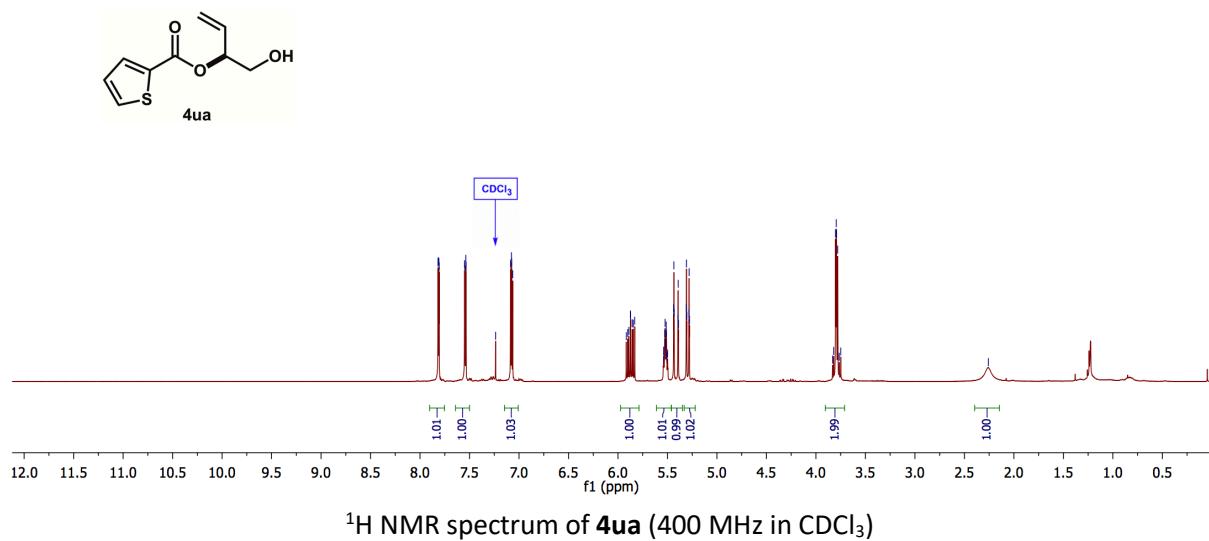


¹³C NMR spectrum of **4qa** (100 MHz in CDCl₃)



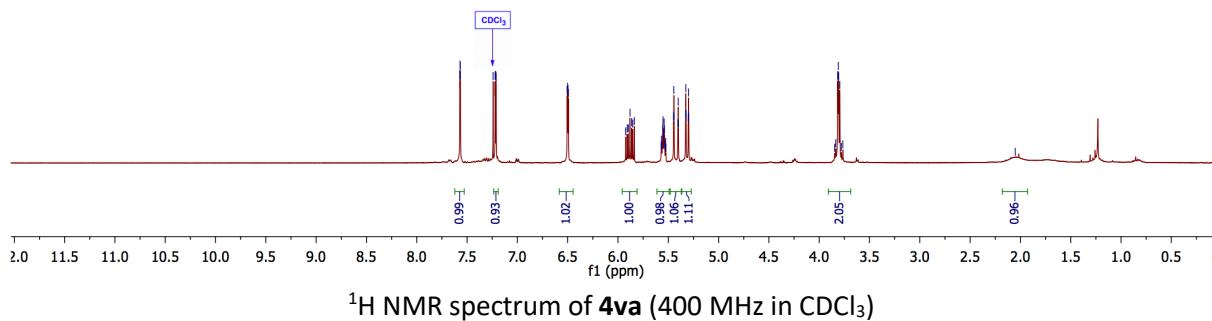
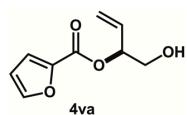
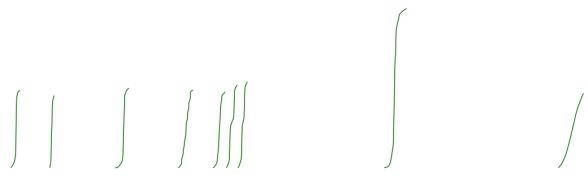






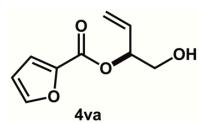


—2.05

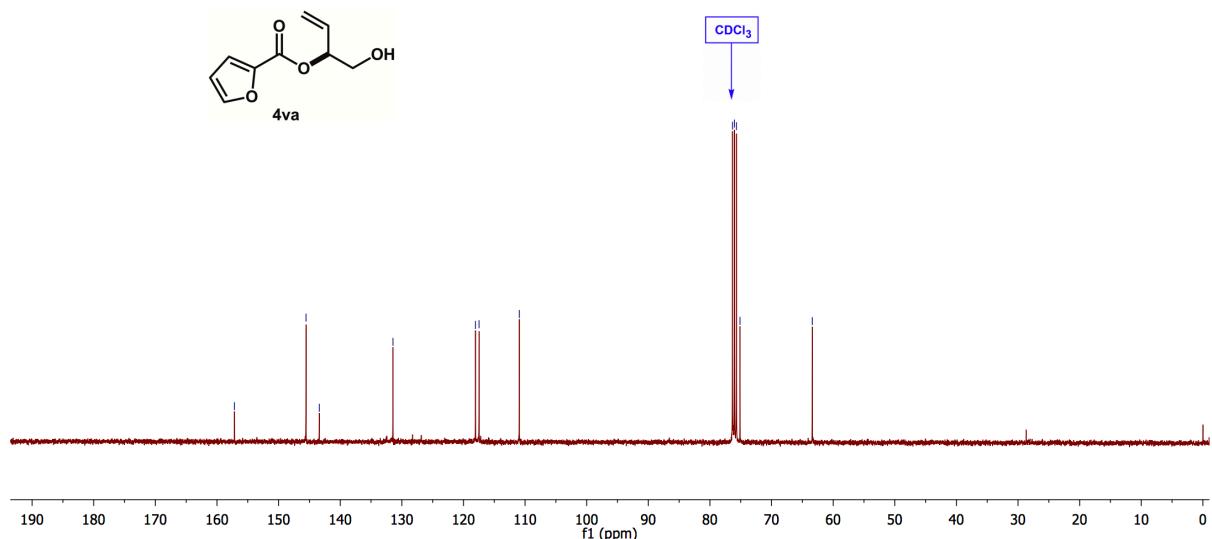


¹H NMR spectrum of 4va (400 MHz in CDCl₃)

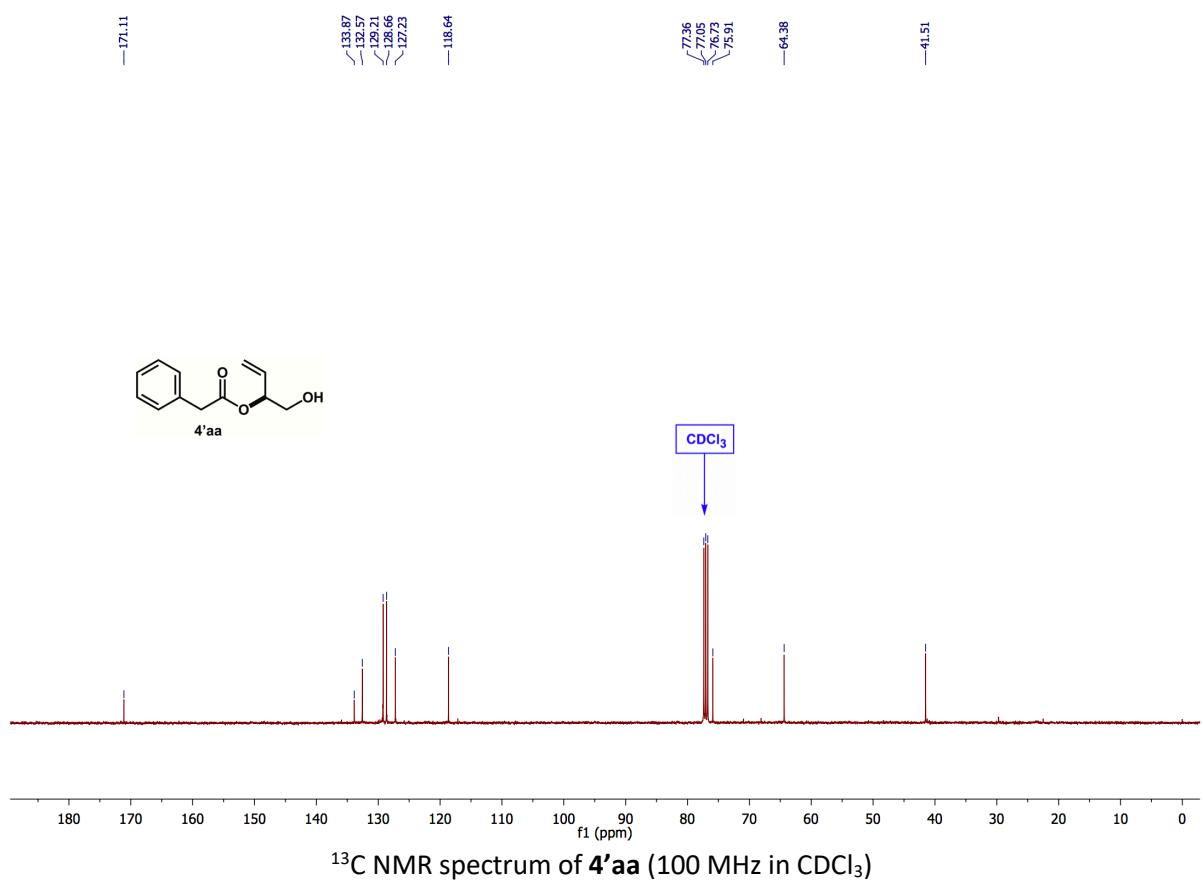
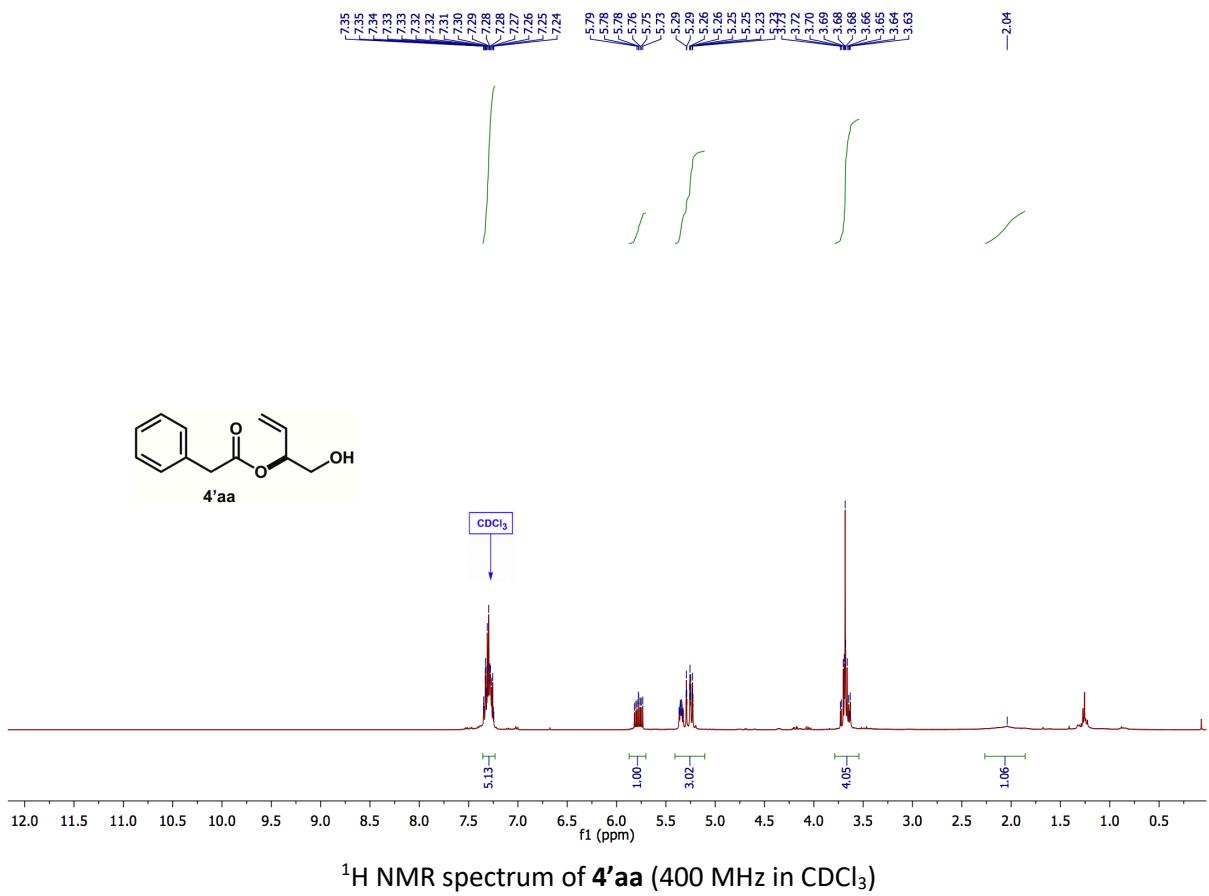
—157.16
—145.55
—143.40
—131.44
—118.04
—117.47
—110.94
—63.40

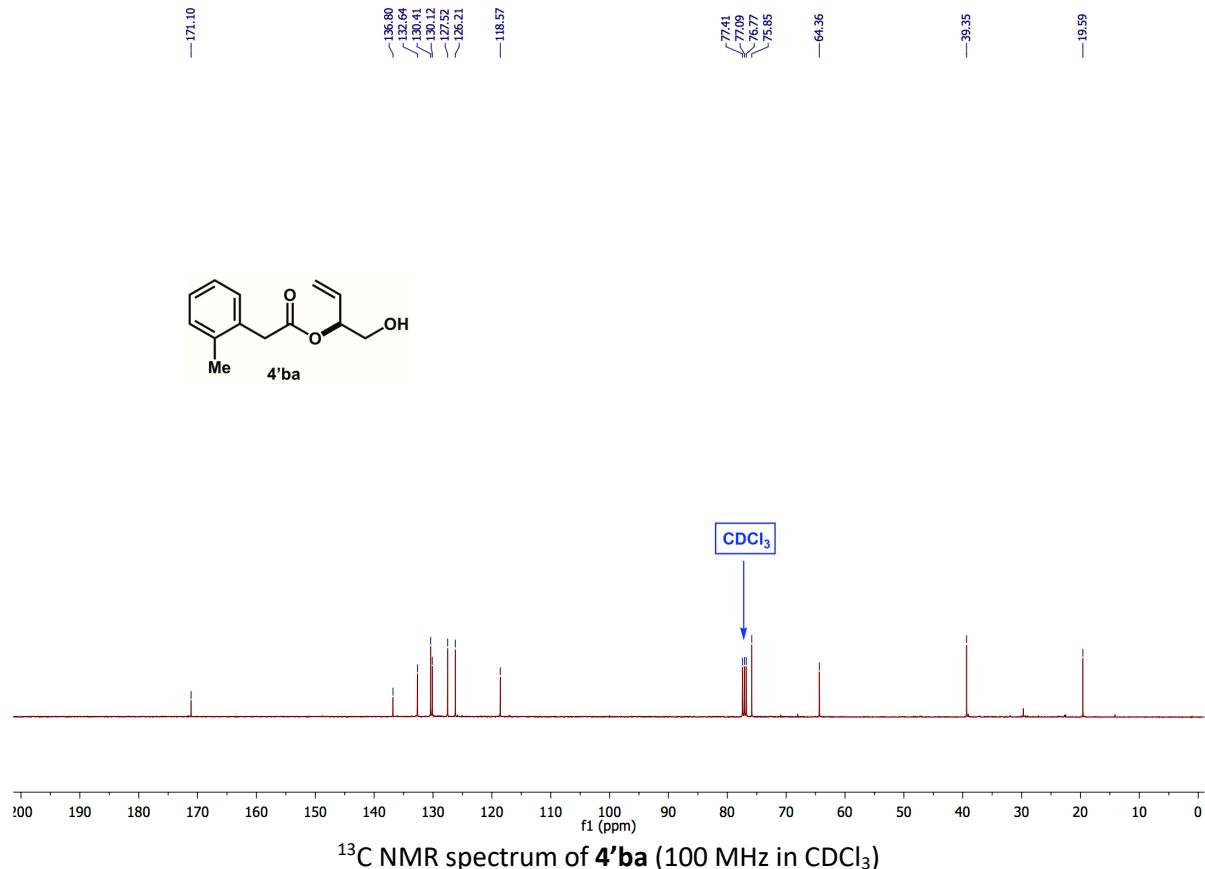
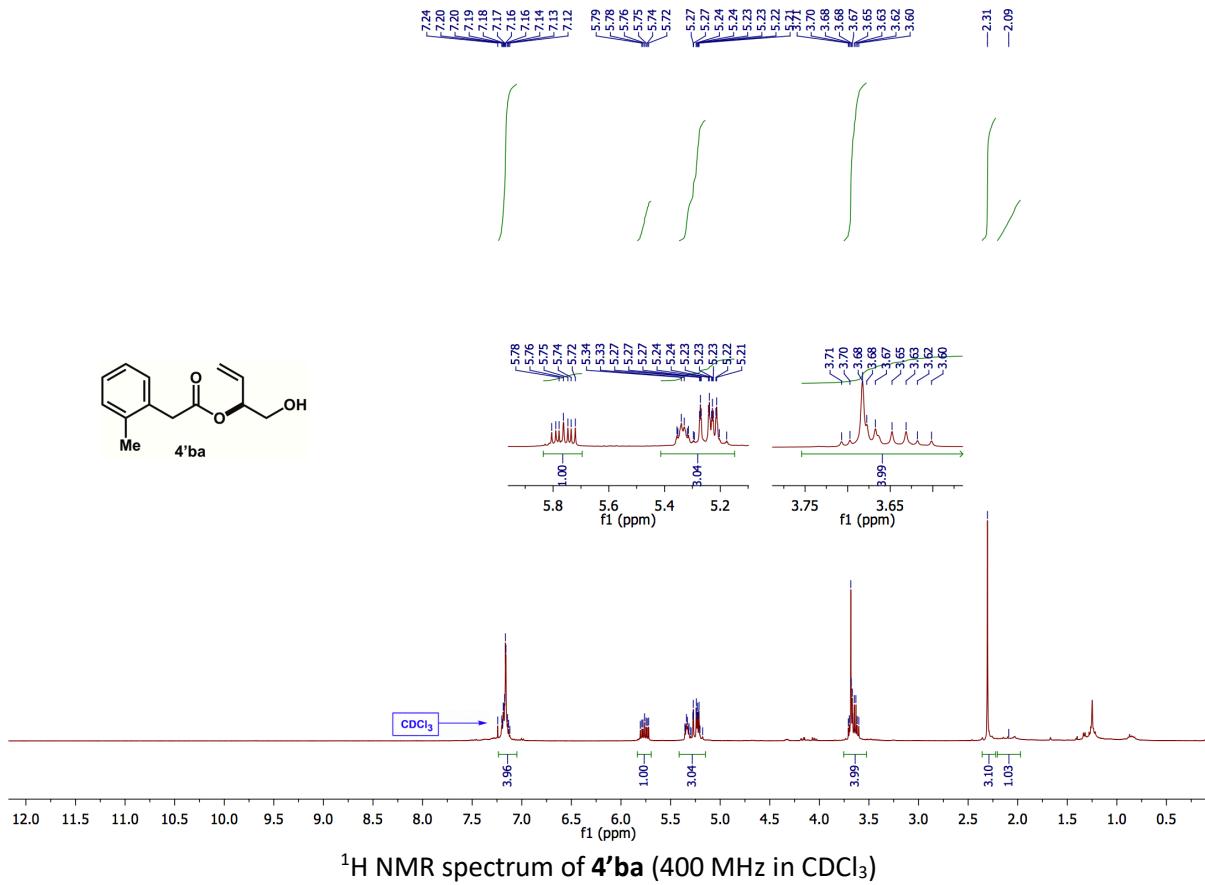


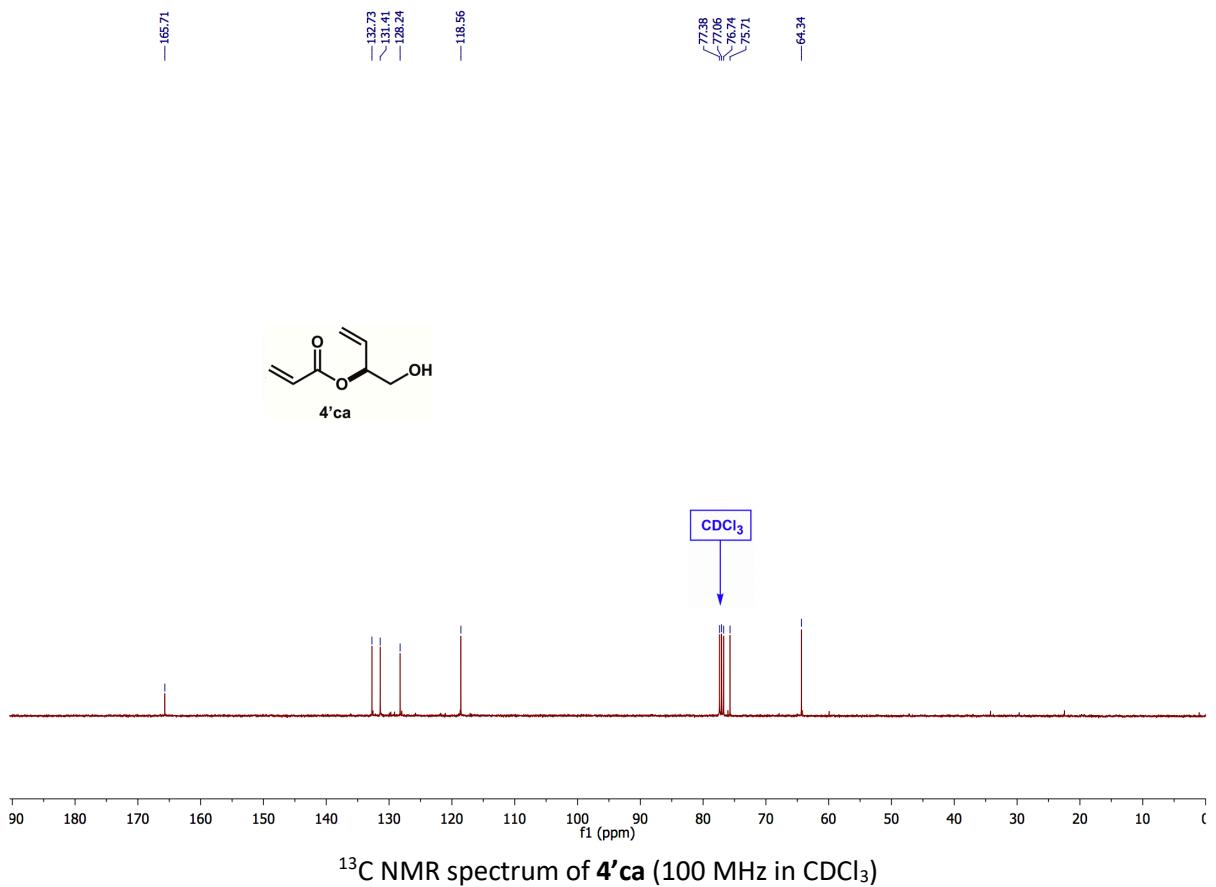
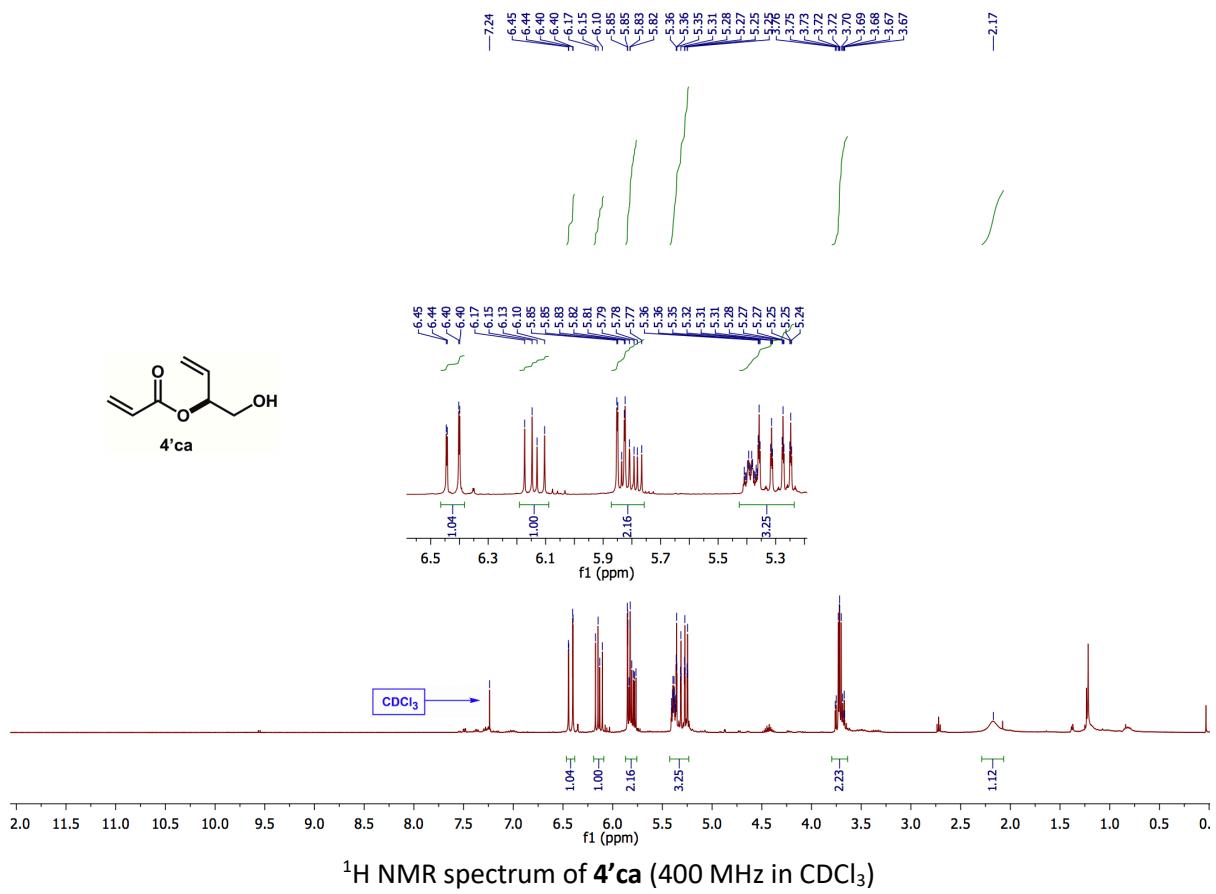
CDCl₃



¹³C NMR spectrum of 4va (100 MHz in CDCl₃)

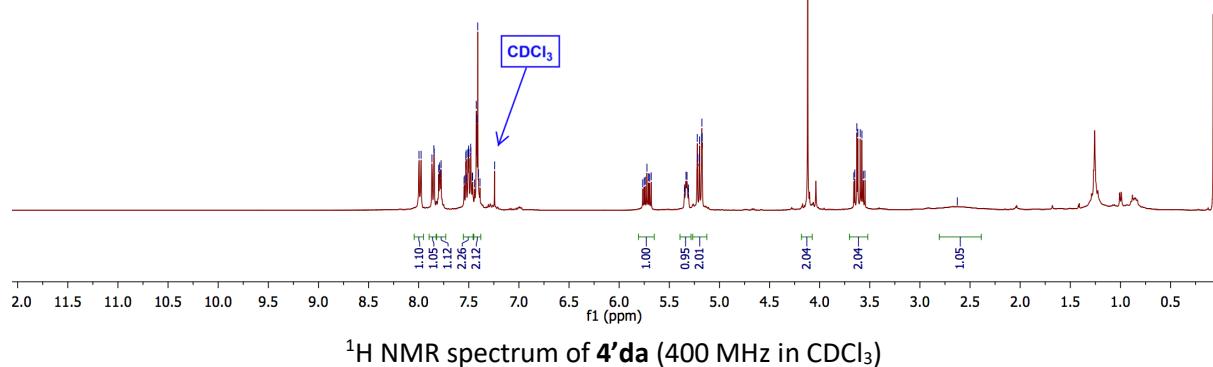
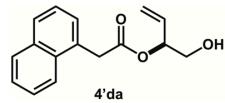






8.00
7.98
7.87
7.85
7.84
7.80
7.79
7.78
7.76
7.55
7.54
7.53
7.53
7.52
7.51
7.44
7.43
7.42
7.41
7.40
7.39
7.24

-2.63



-170.07

-132.61

-131.44

-130.97

-129.35

-127.80

-127.16

-126.95

-125.39

-124.83

-124.46

-122.60

-117.59

76.33

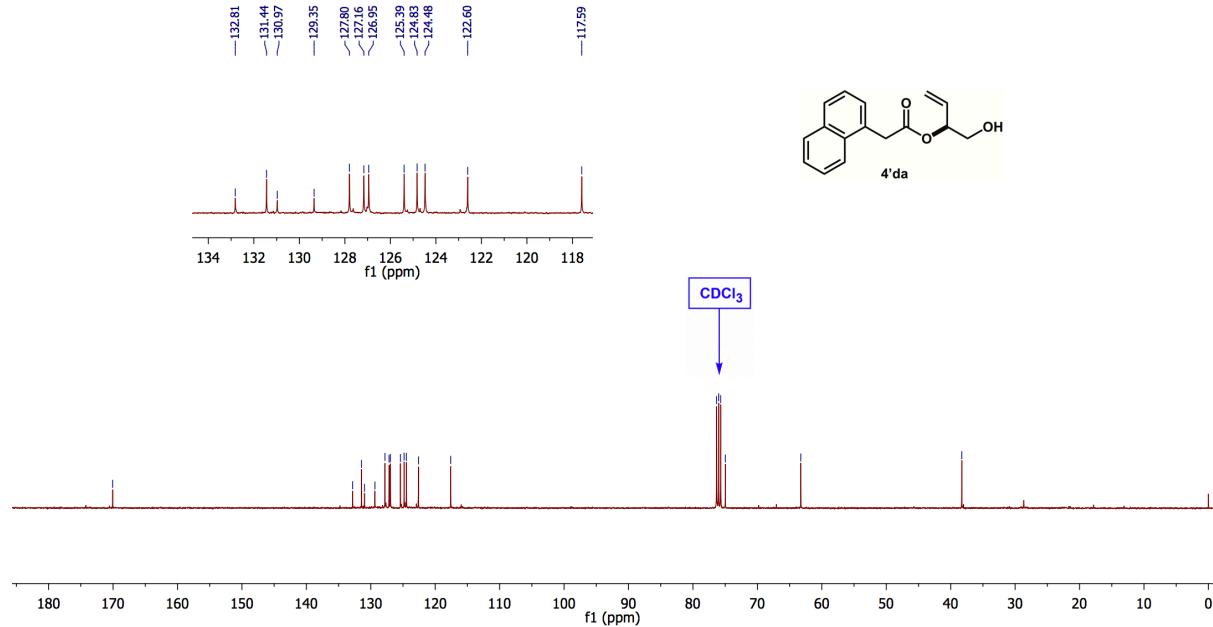
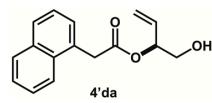
76.02

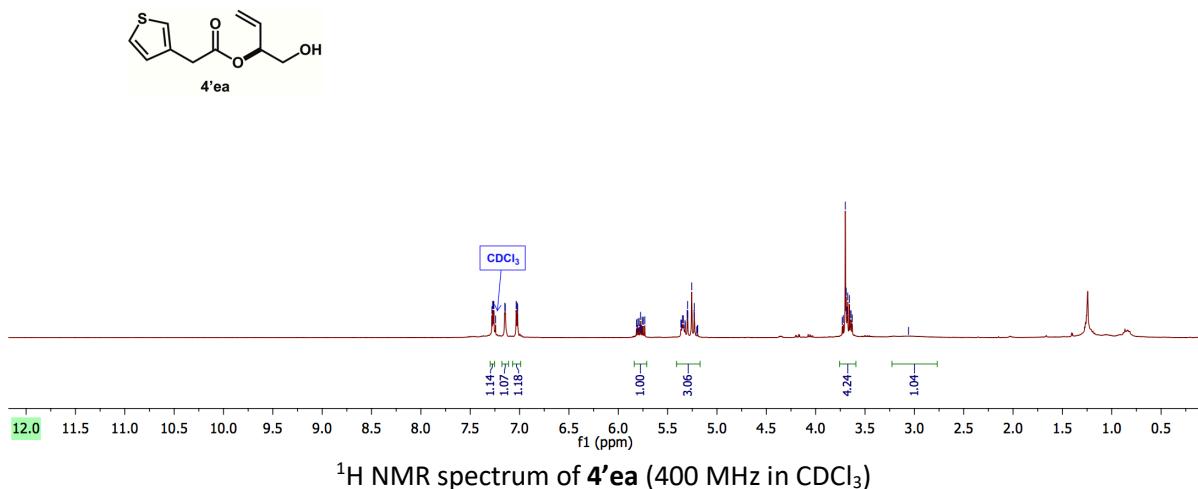
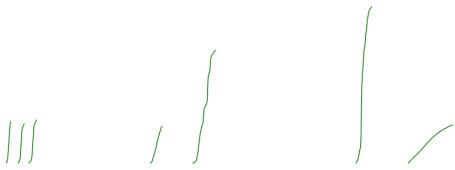
75.70

74.97

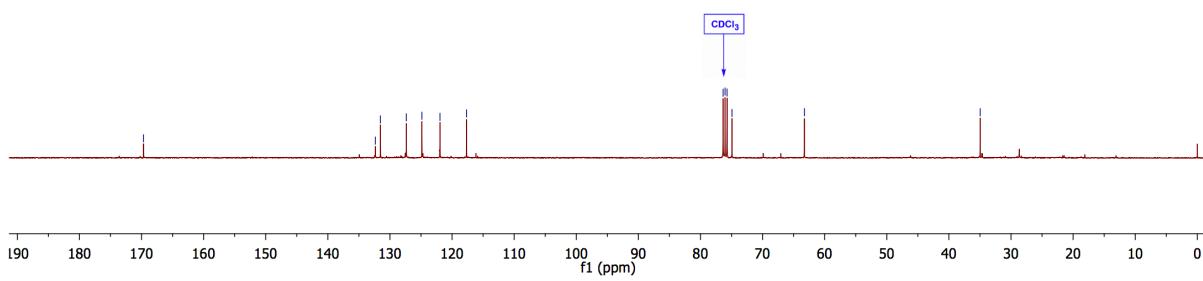
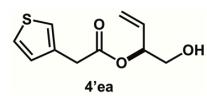
-63.26

-38.28

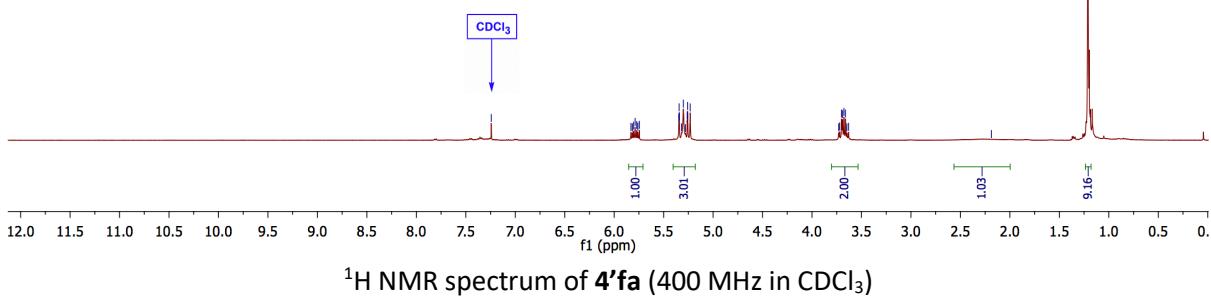
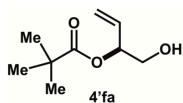




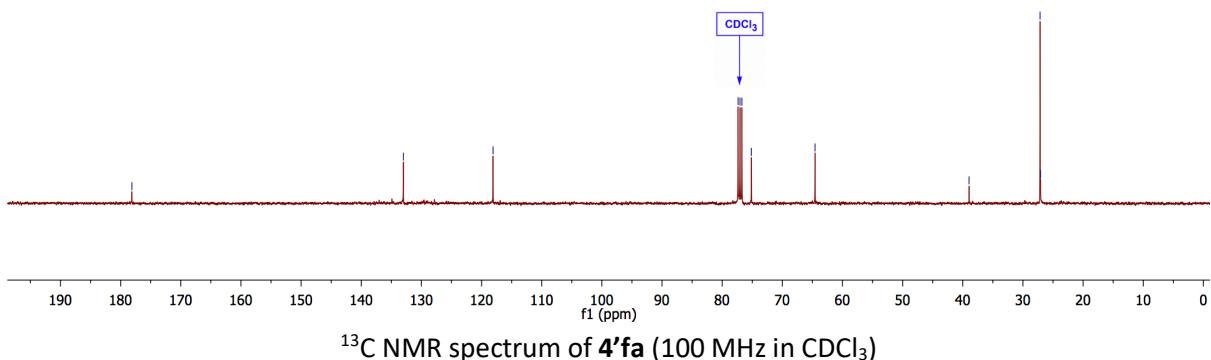
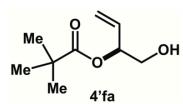
—169.67
—132.36
—131.53
—127.36
—124.66
—121.94
—117.67
—76.26
—76.04
—75.72
—74.93
—63.27
—34.96

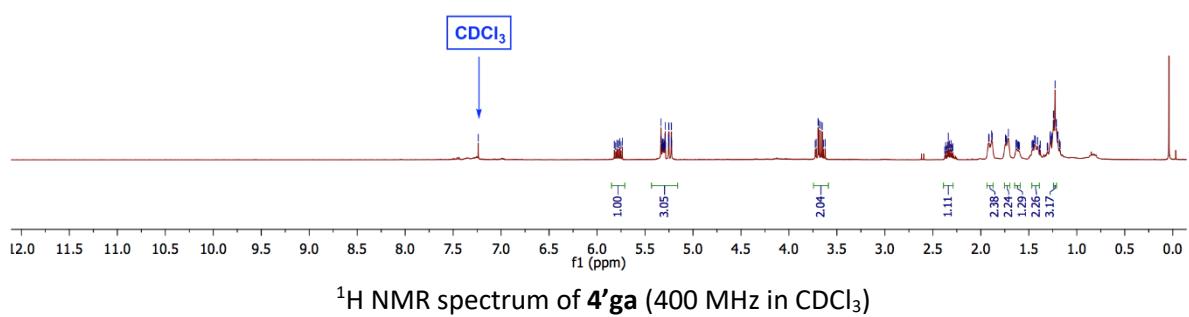
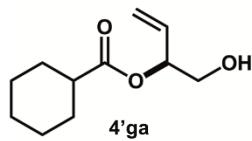
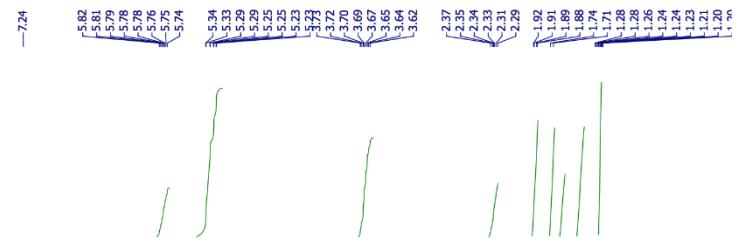


^{13}C NMR spectrum of **4'ea** (100 MHz in CDCl_3)



—178.13
—133.00
—118.09
—77.35
—77.04
—76.72
—75.14
—64.56
—38.96
—27.15
—27.08





¹H NMR spectrum of **4'ga** (400 MHz in CDCl₃)

—175.69

—133.05

—118.17

—43.27

—64.48

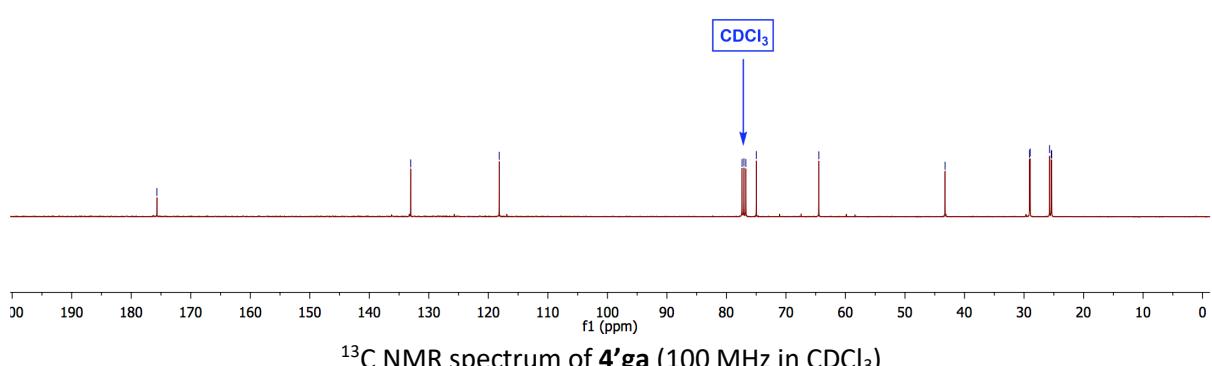
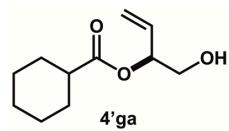
—29.08

—28.97

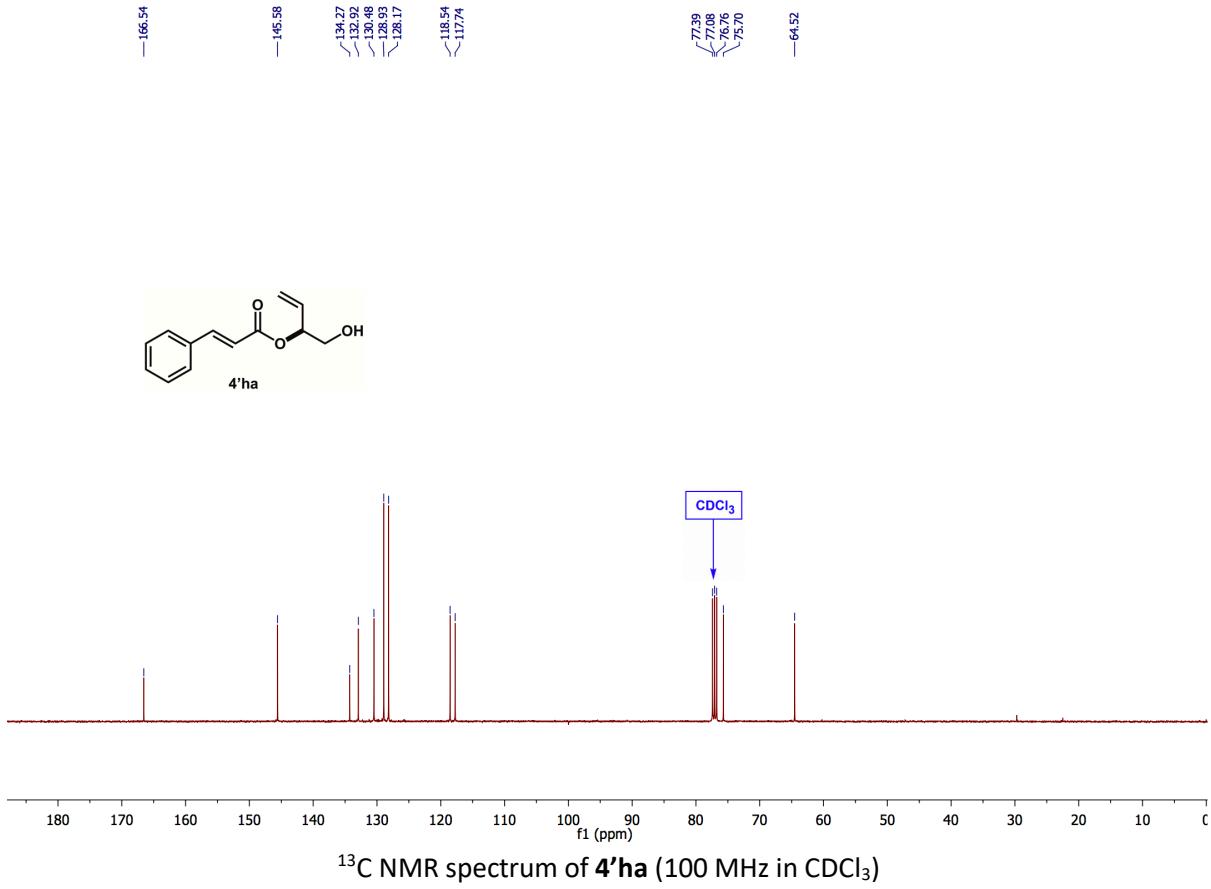
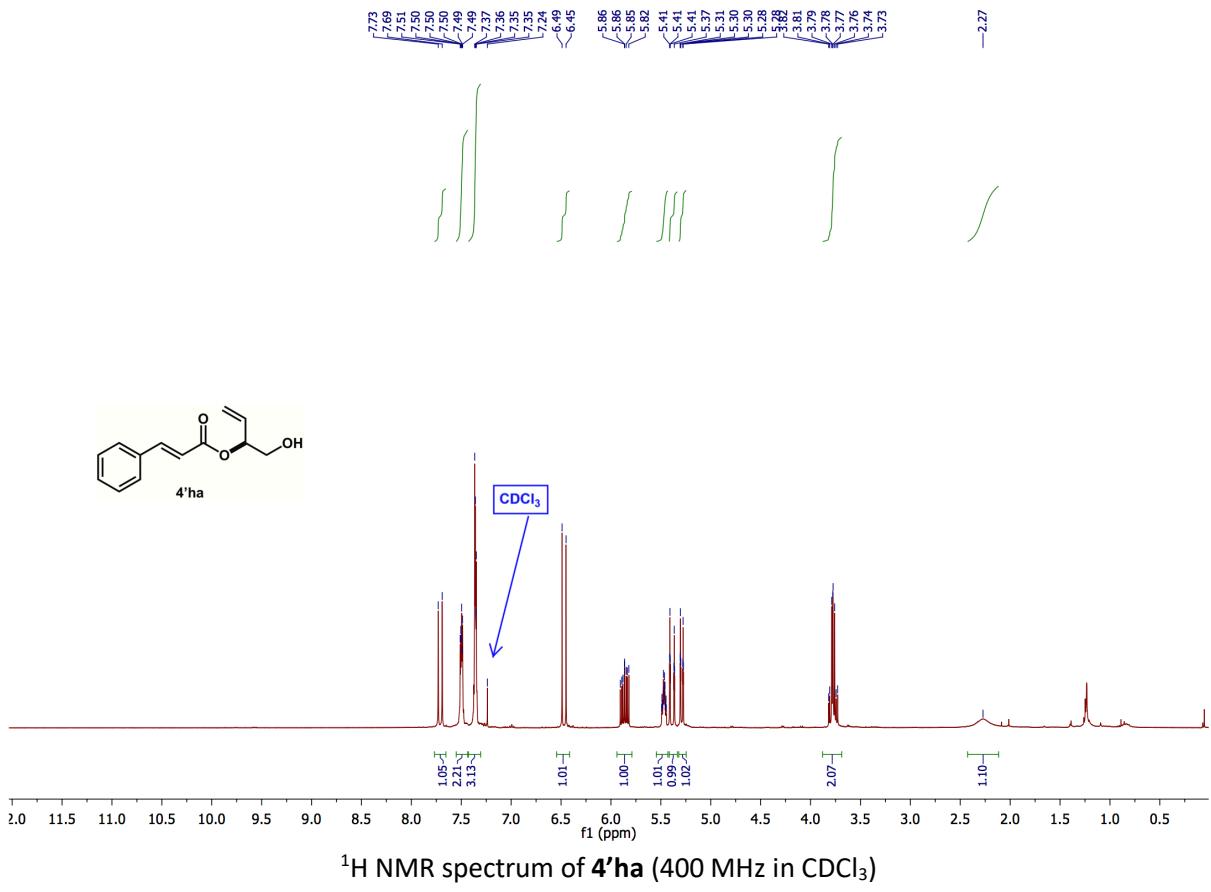
—25.71

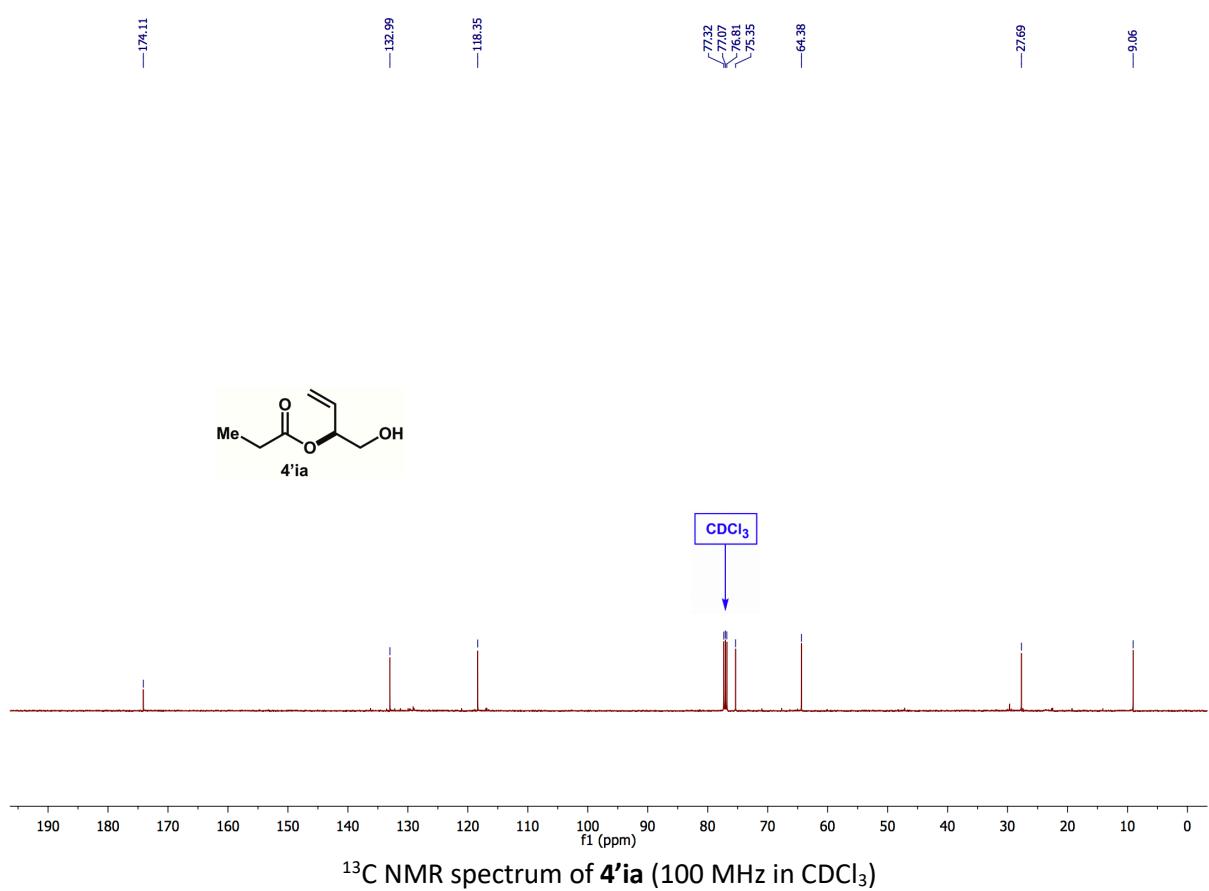
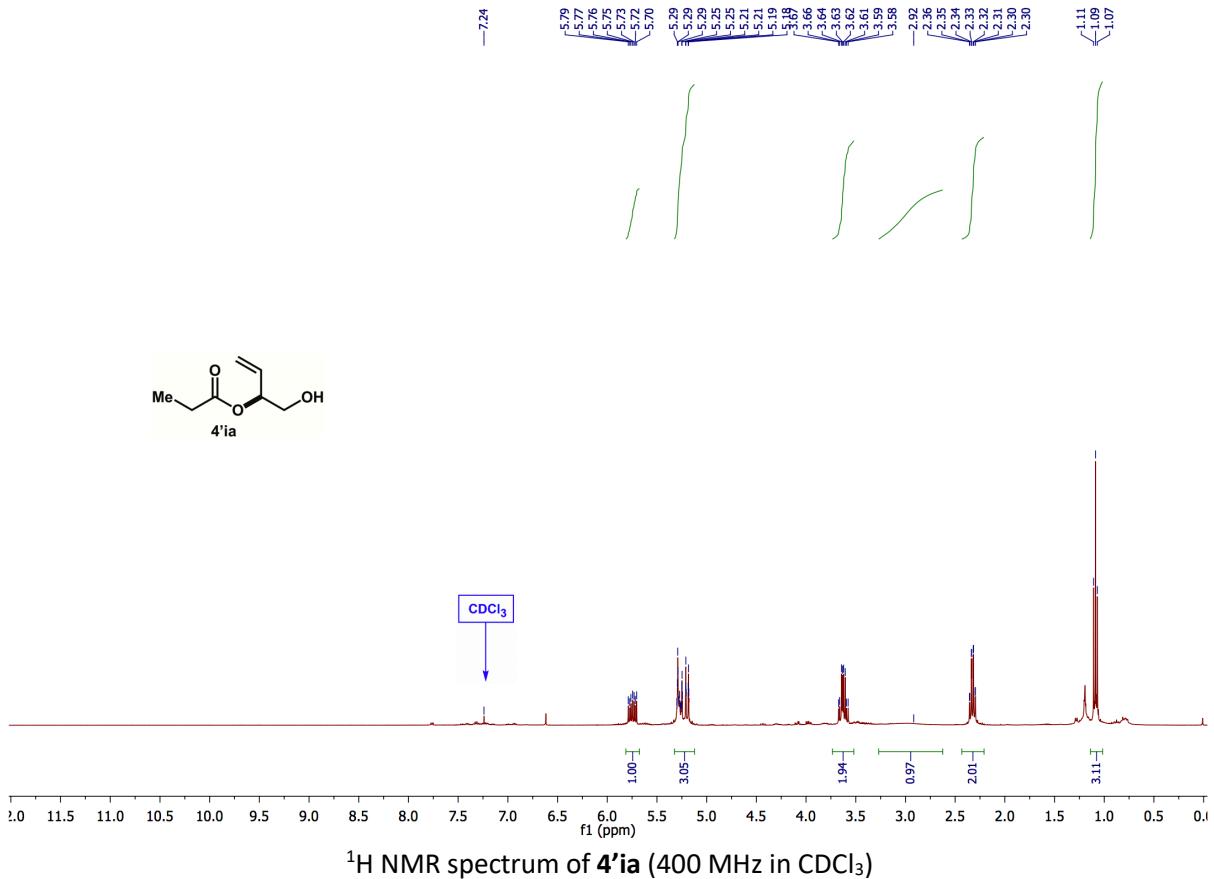
—25.42

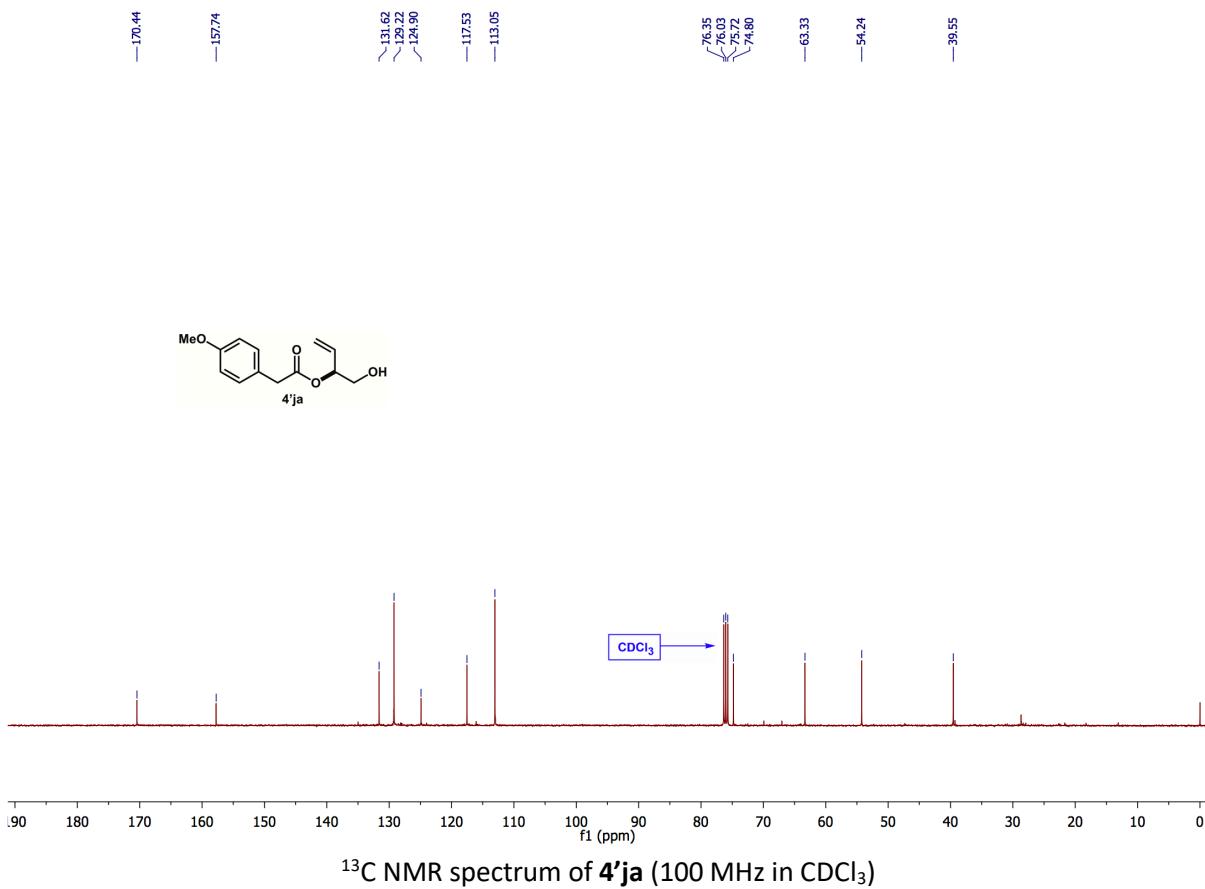
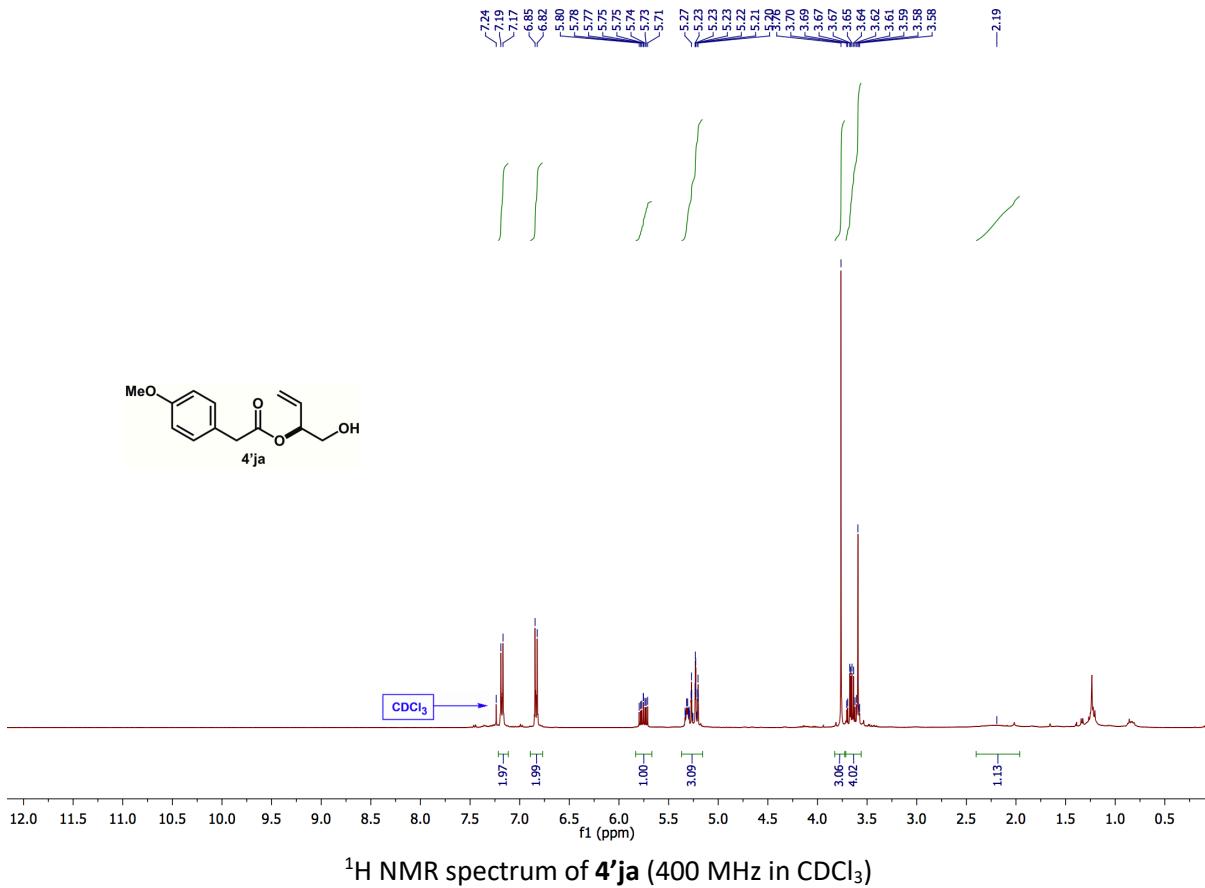
—25.35

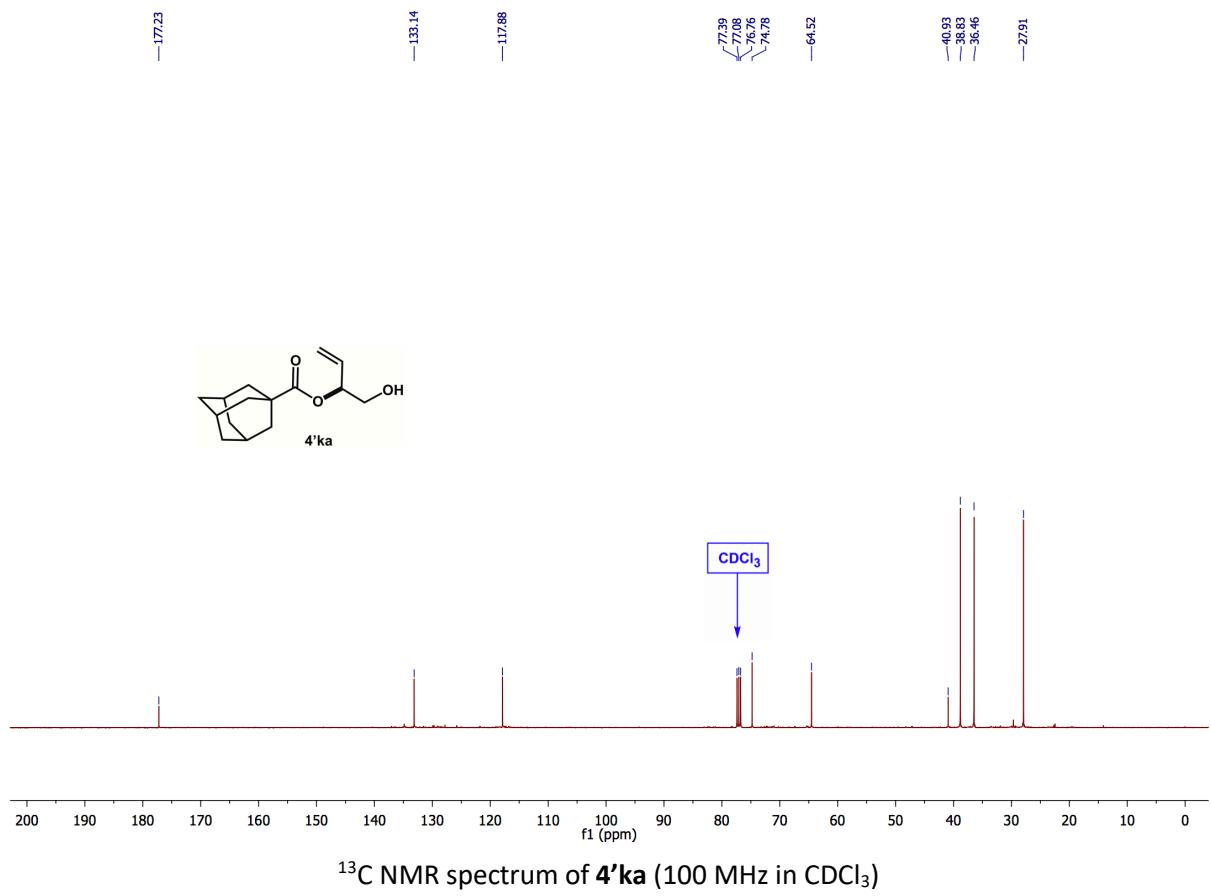
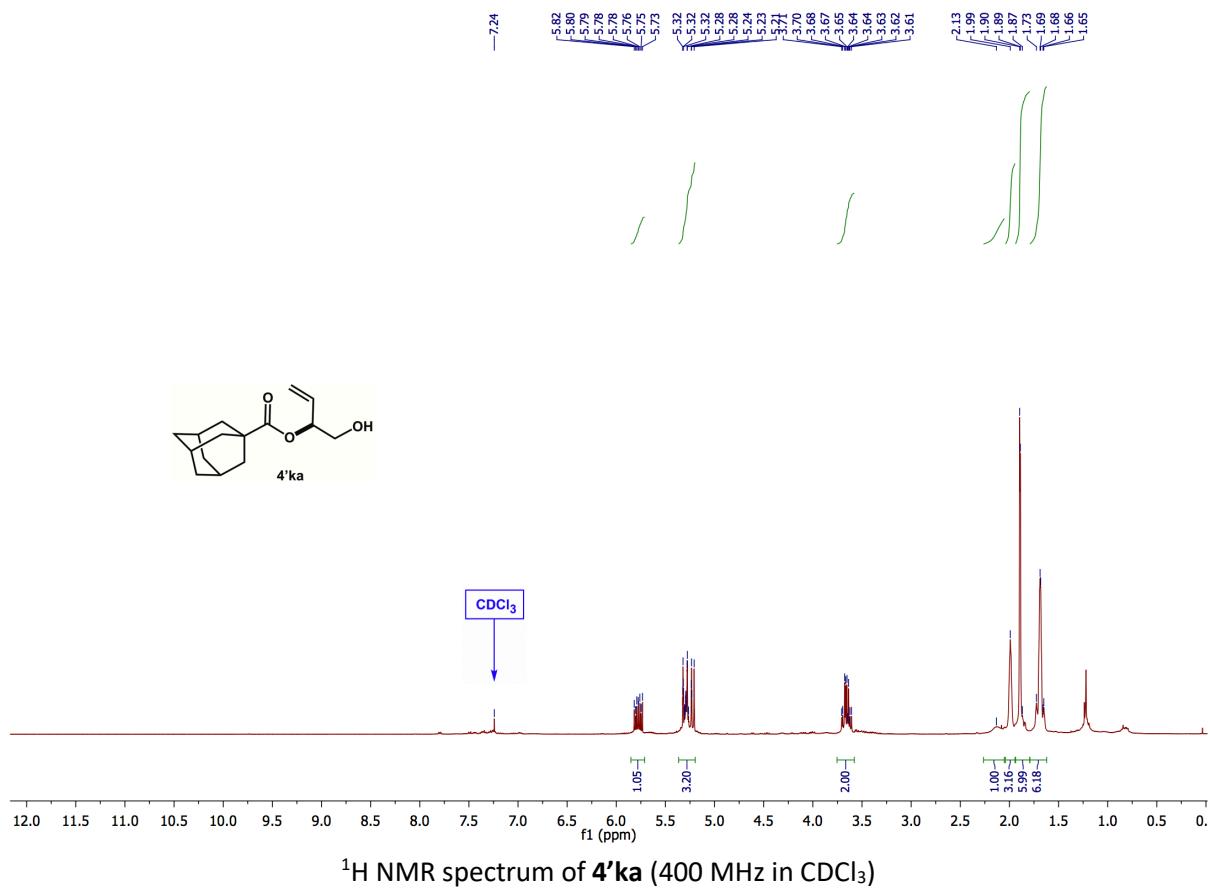


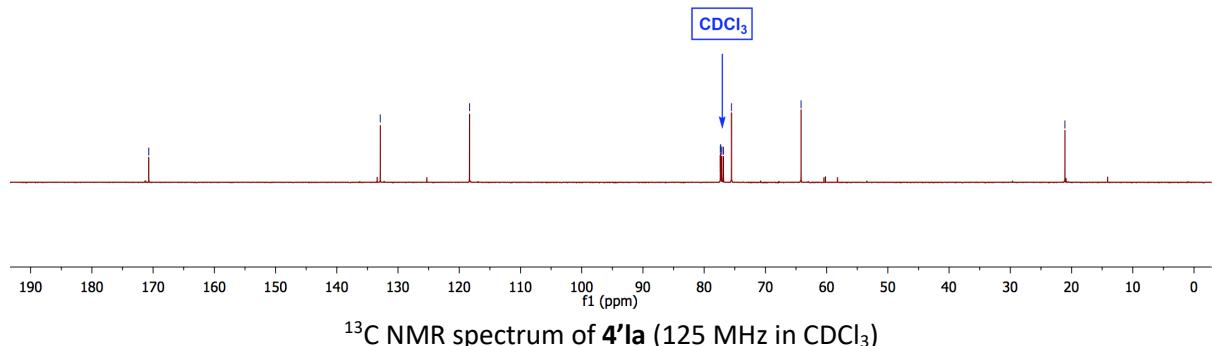
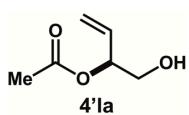
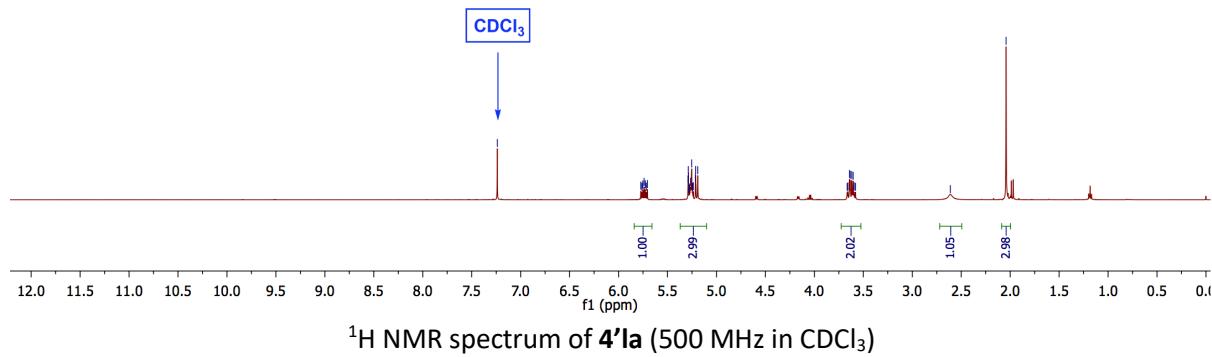
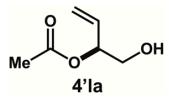
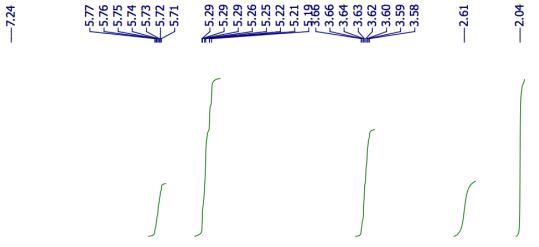
¹³C NMR spectrum of **4'ga** (100 MHz in CDCl₃)

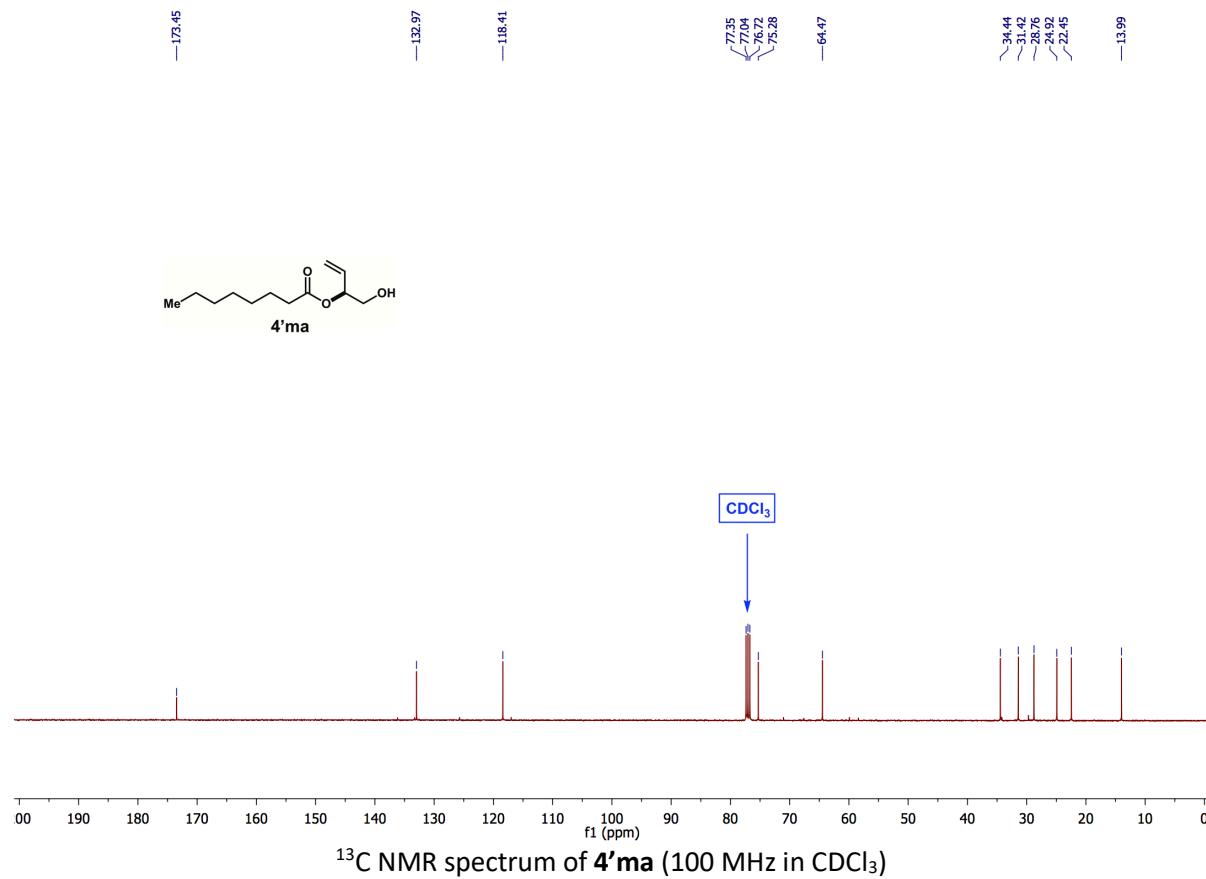
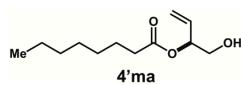
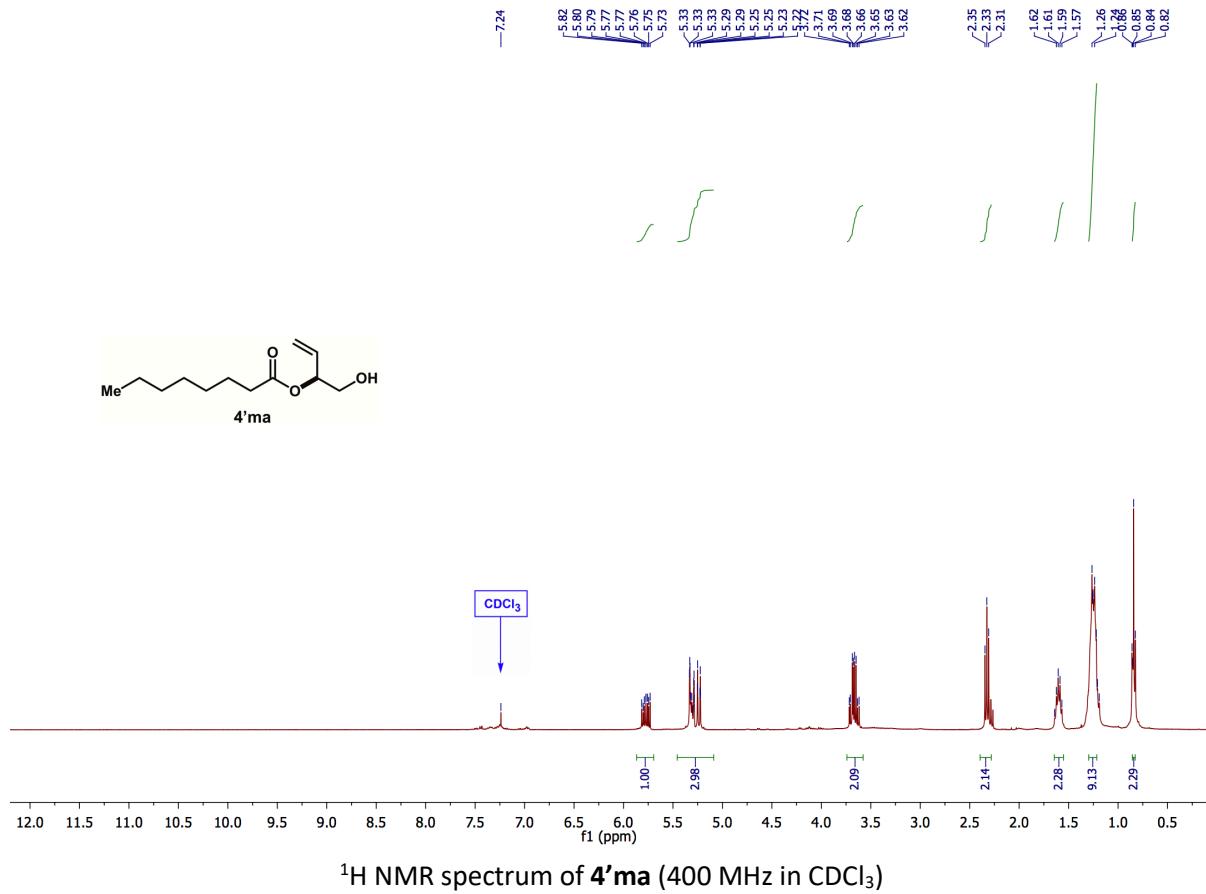
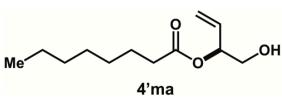


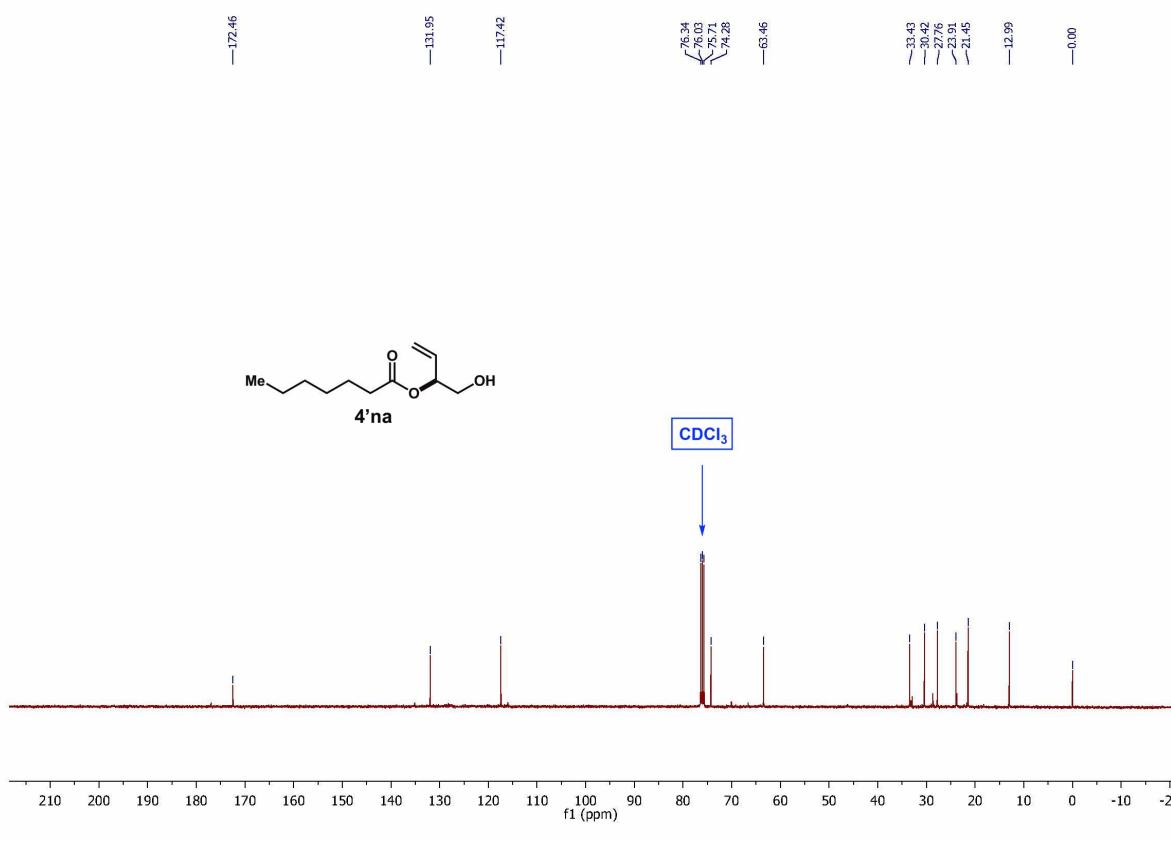
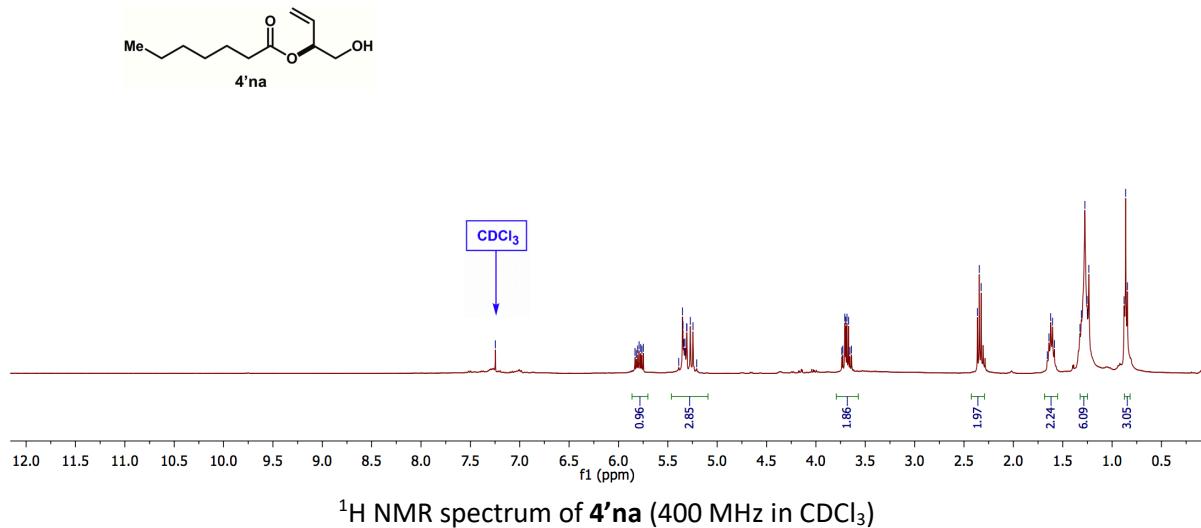
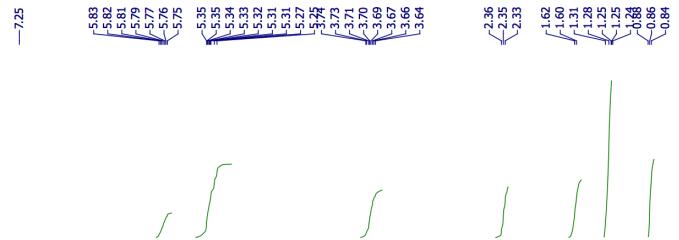


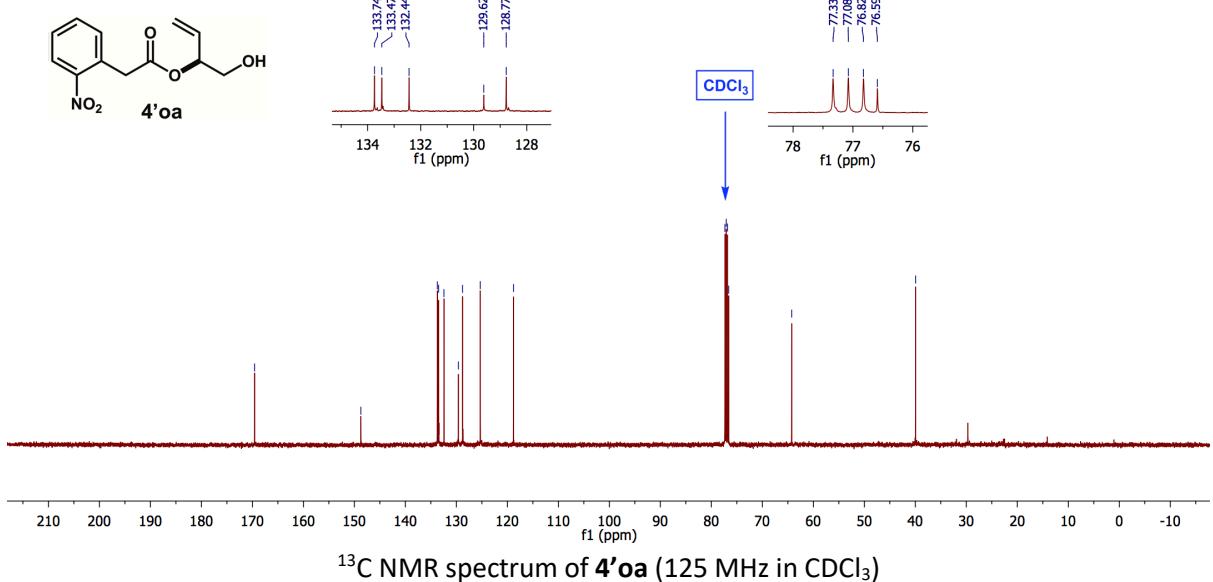
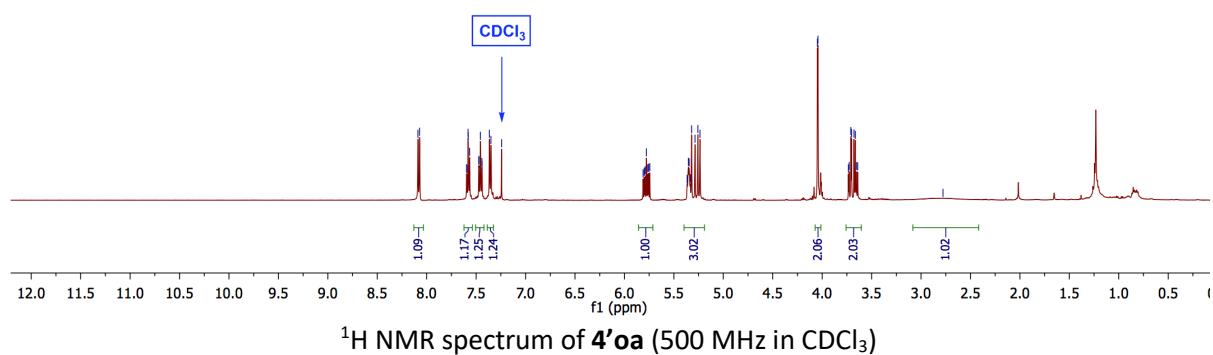
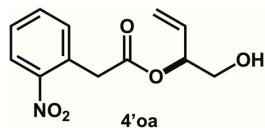
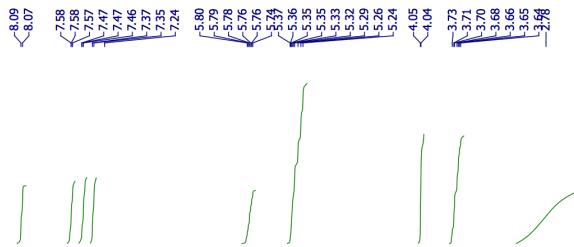


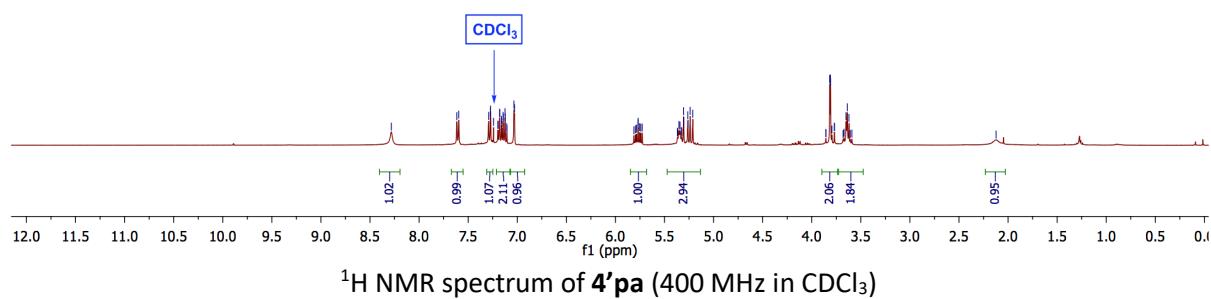
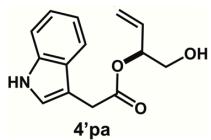
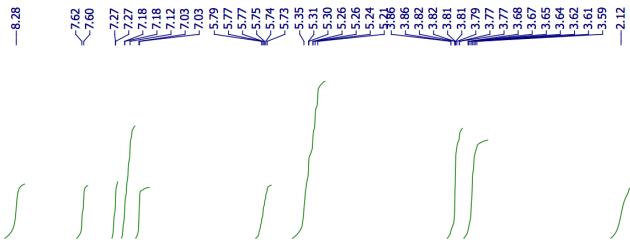












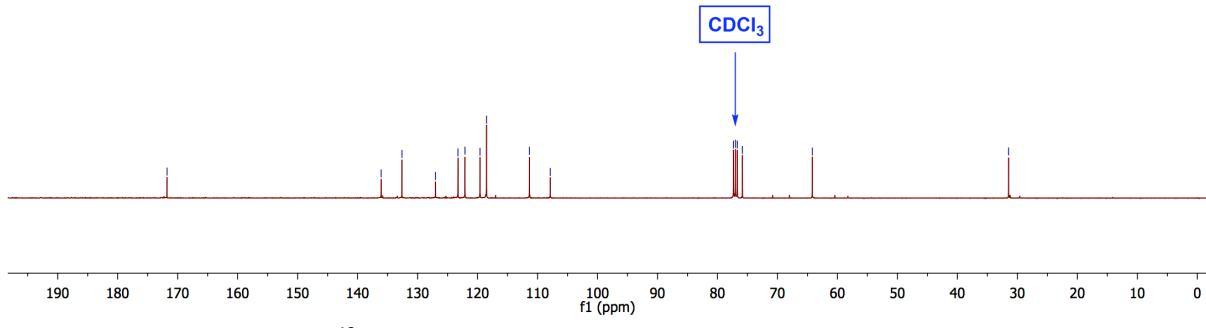
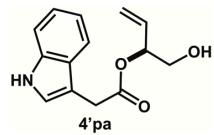
¹H NMR spectrum of **4'pa** (400 MHz in CDCl₃)

—171.77
—136.08
—132.60
—127.00
—123.26
—122.10
—119.59
—118.50
—111.36
—107.88

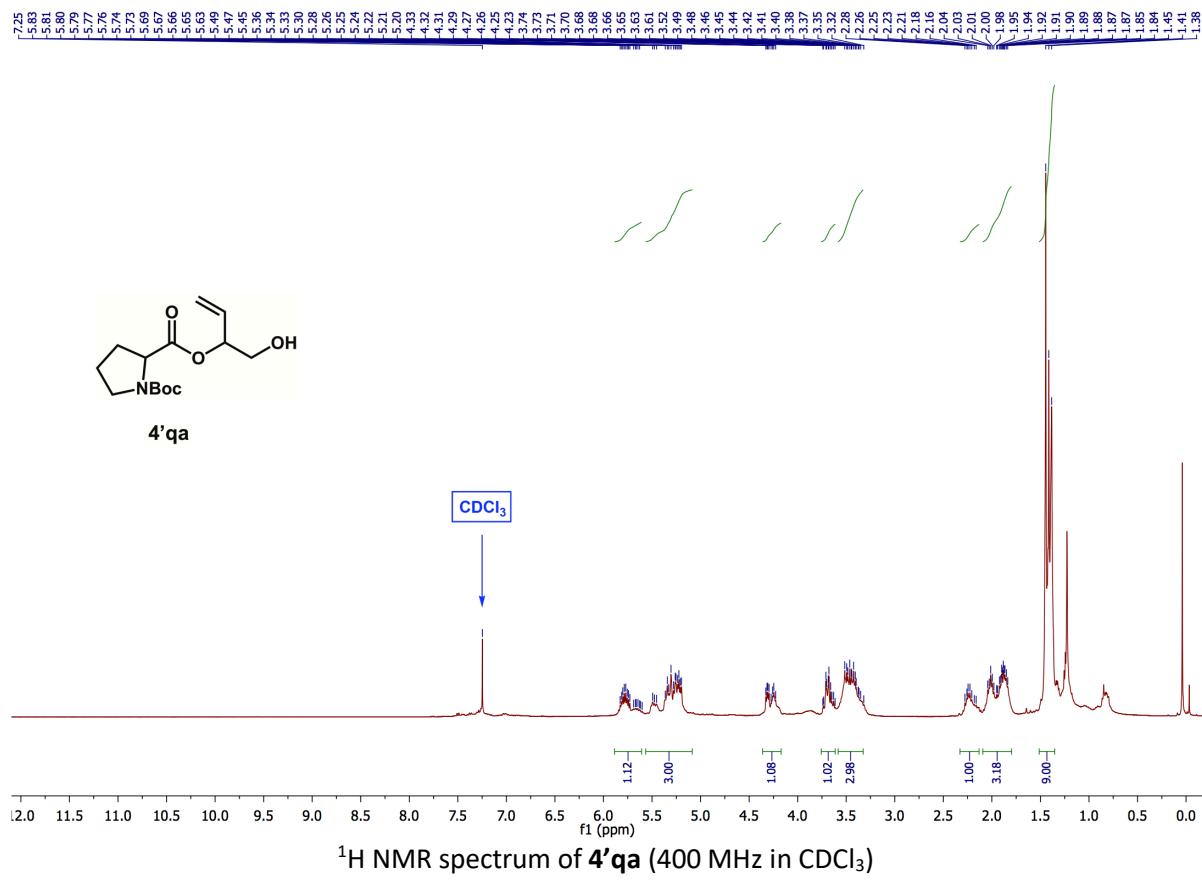
1.02
0.99
1.07
2.11
0.96
1.00
2.94
0.95
0.95

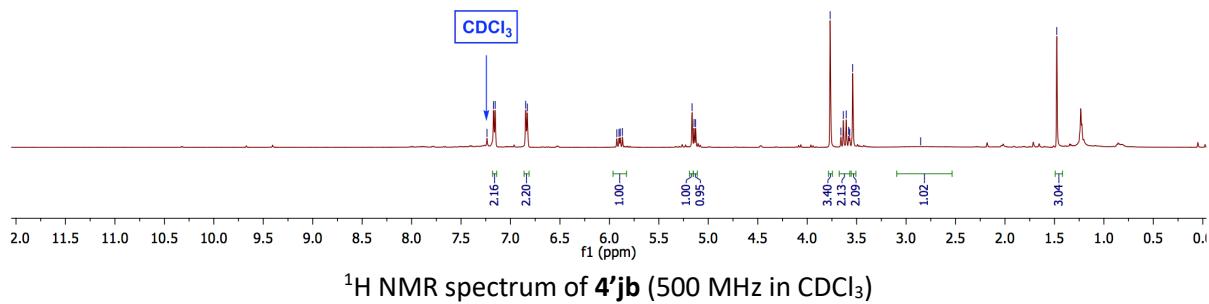
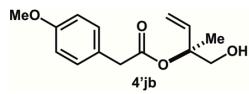
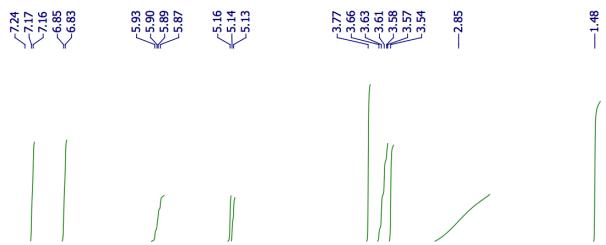
5.31
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5.03
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0.19
0.17
0.15
0.13
0.11
0.09
0.07
0.05
0.03
0.01
0.00.

—64.19
—31.47

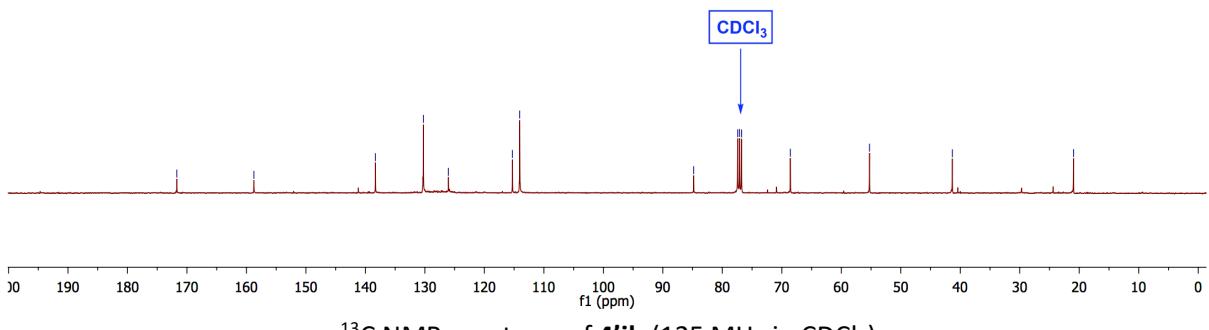
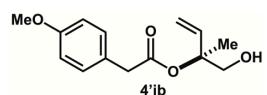


¹³C NMR spectrum of **4'pa** (100 MHz in CDCl₃)





—171.70 —158.74 —138.31 —130.25 —126.04 —115.28 ~114.06 —84.81 77.41 77.10 76.78 —68.56 —55.26 —41.34 —20.96

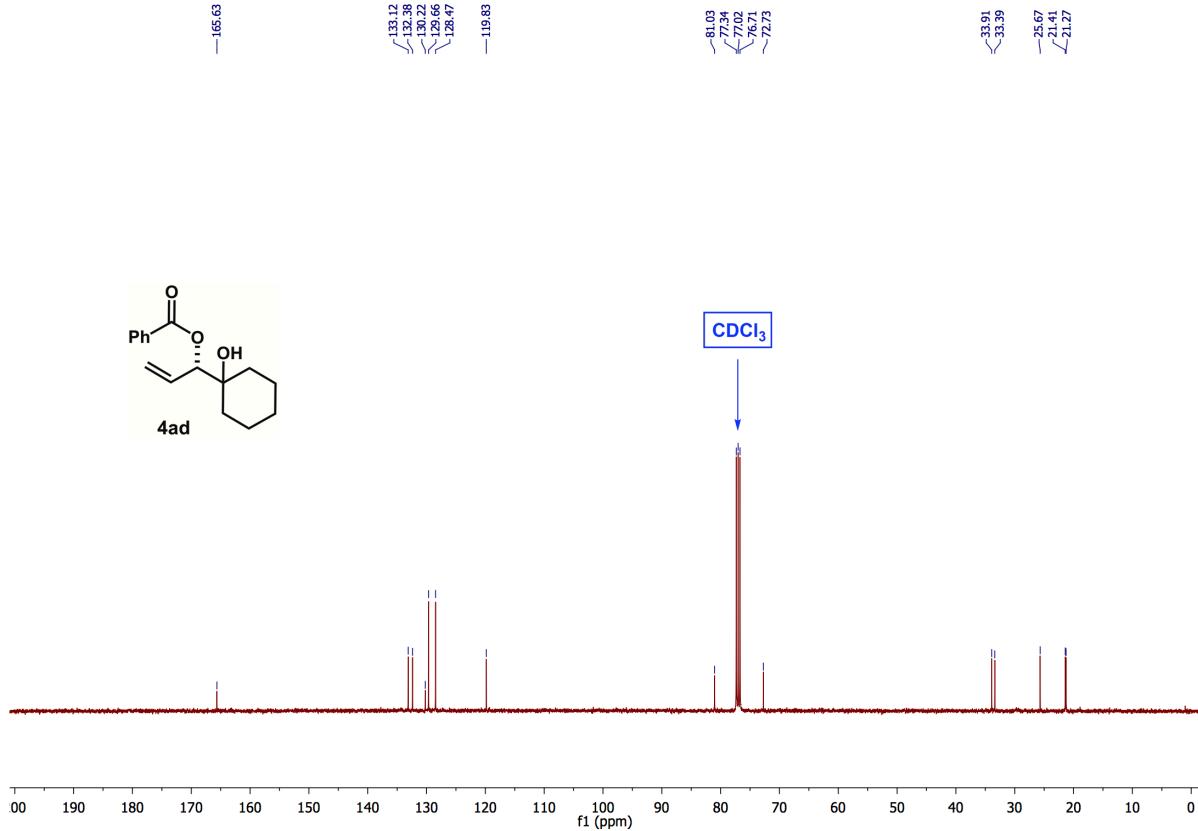
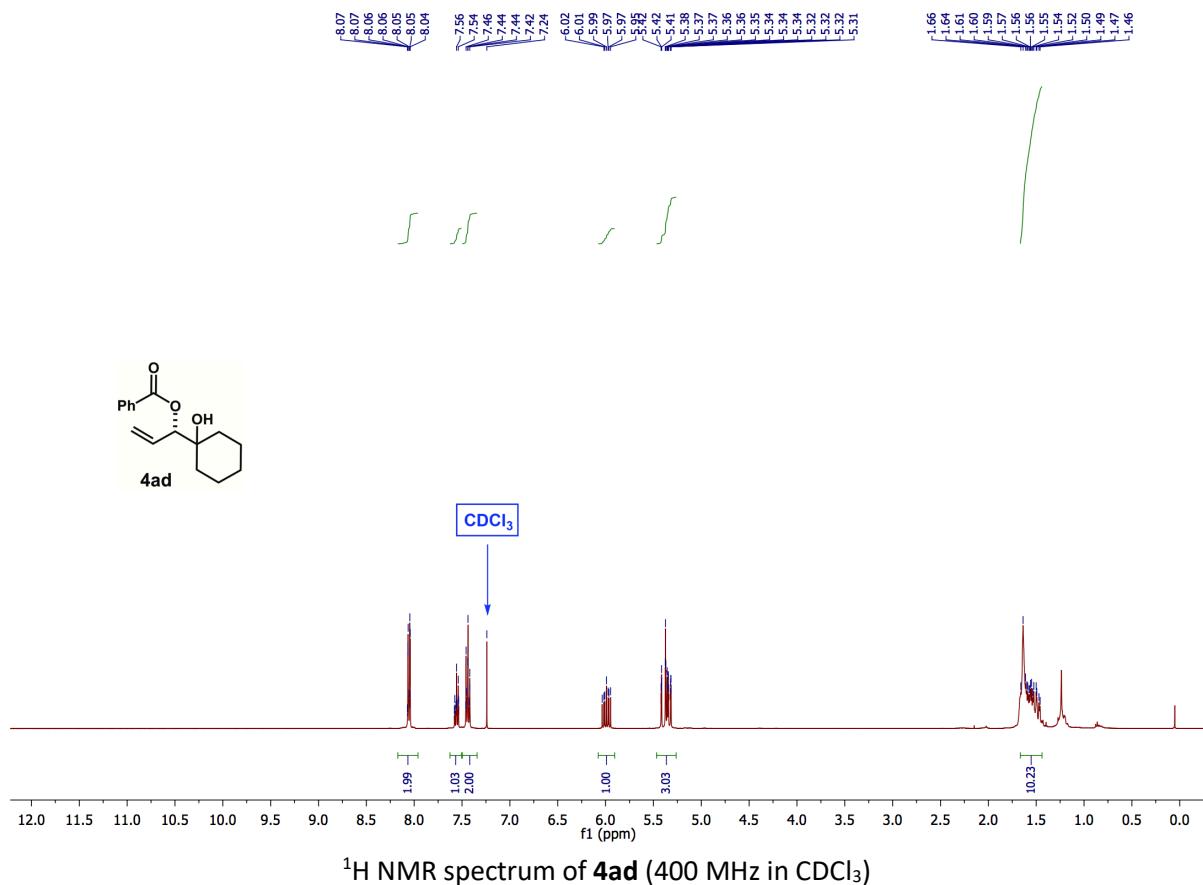




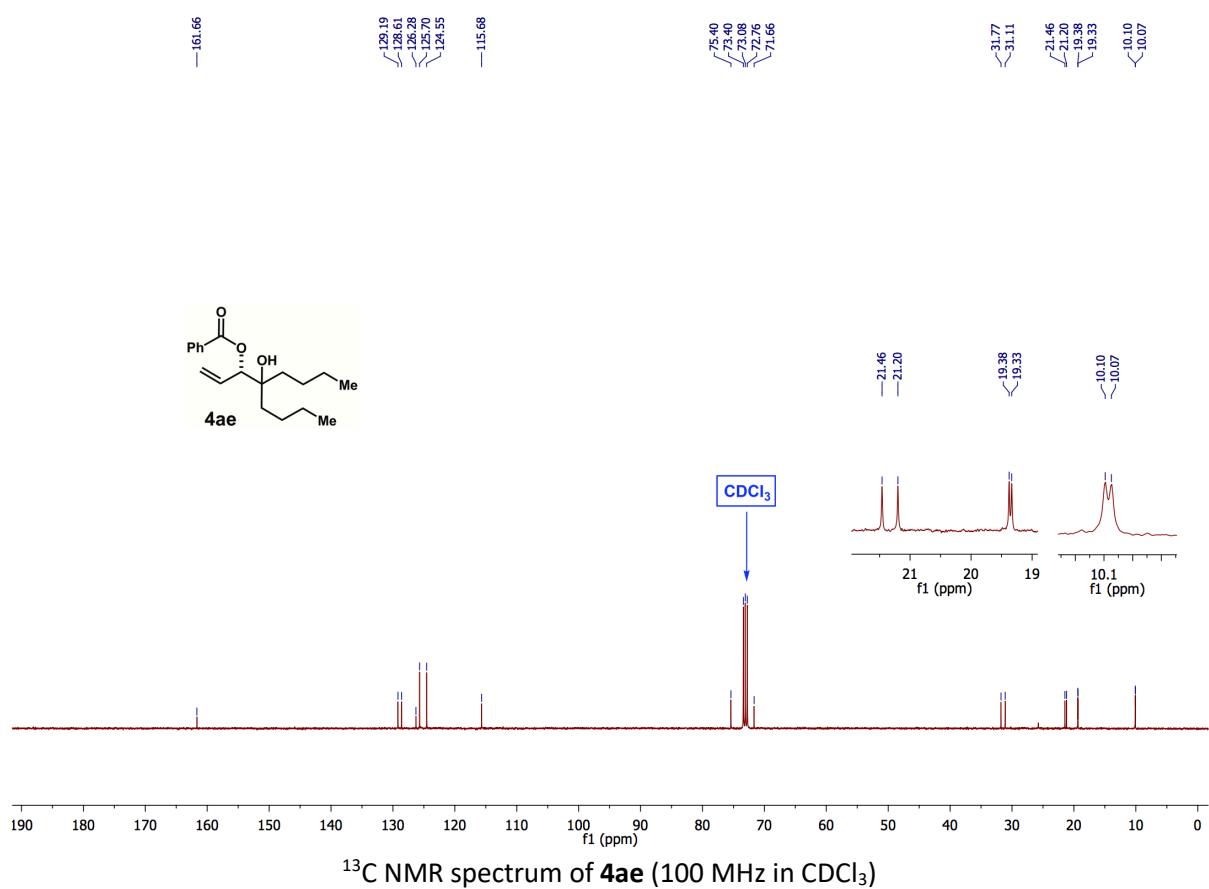
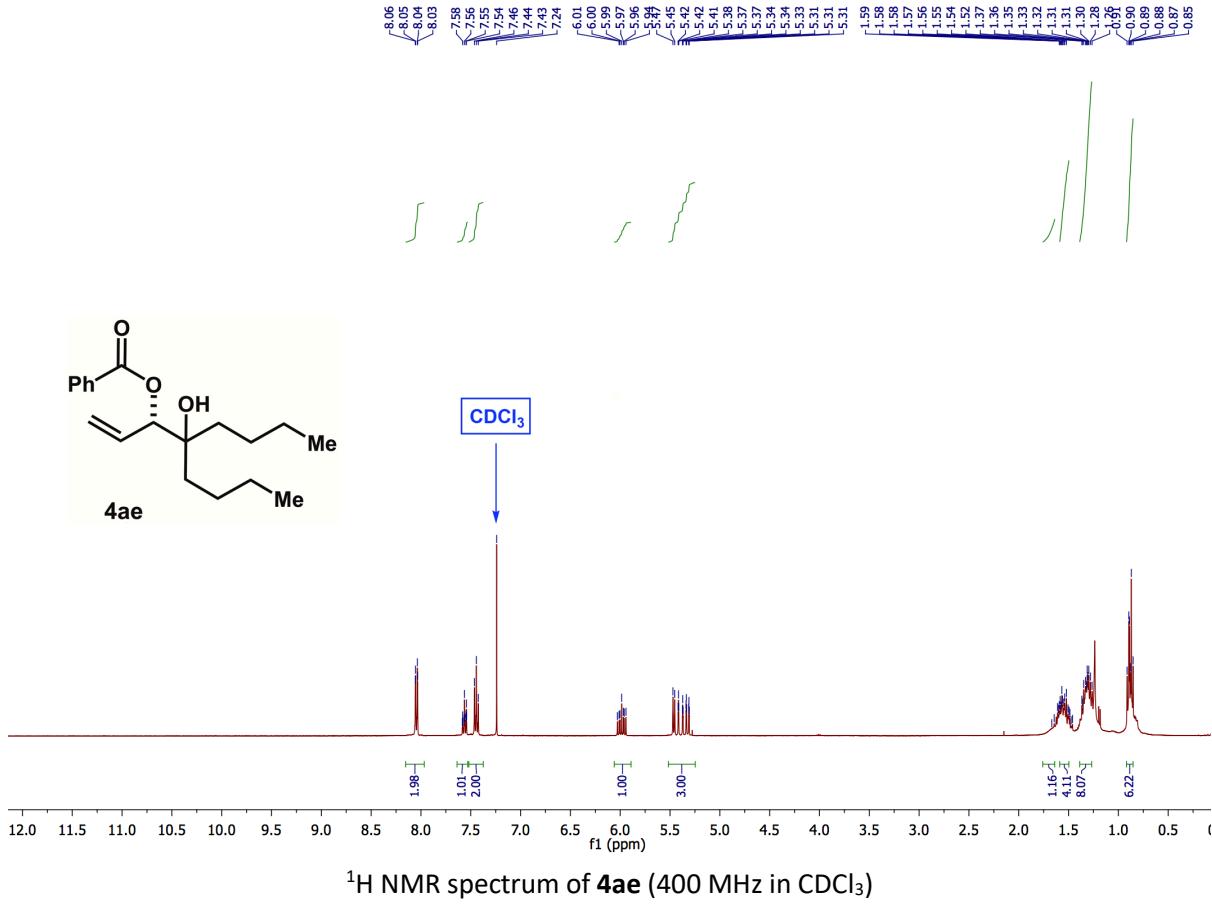
¹H NMR spectrum of **4'jc** (400 MHz in CDCl₃)

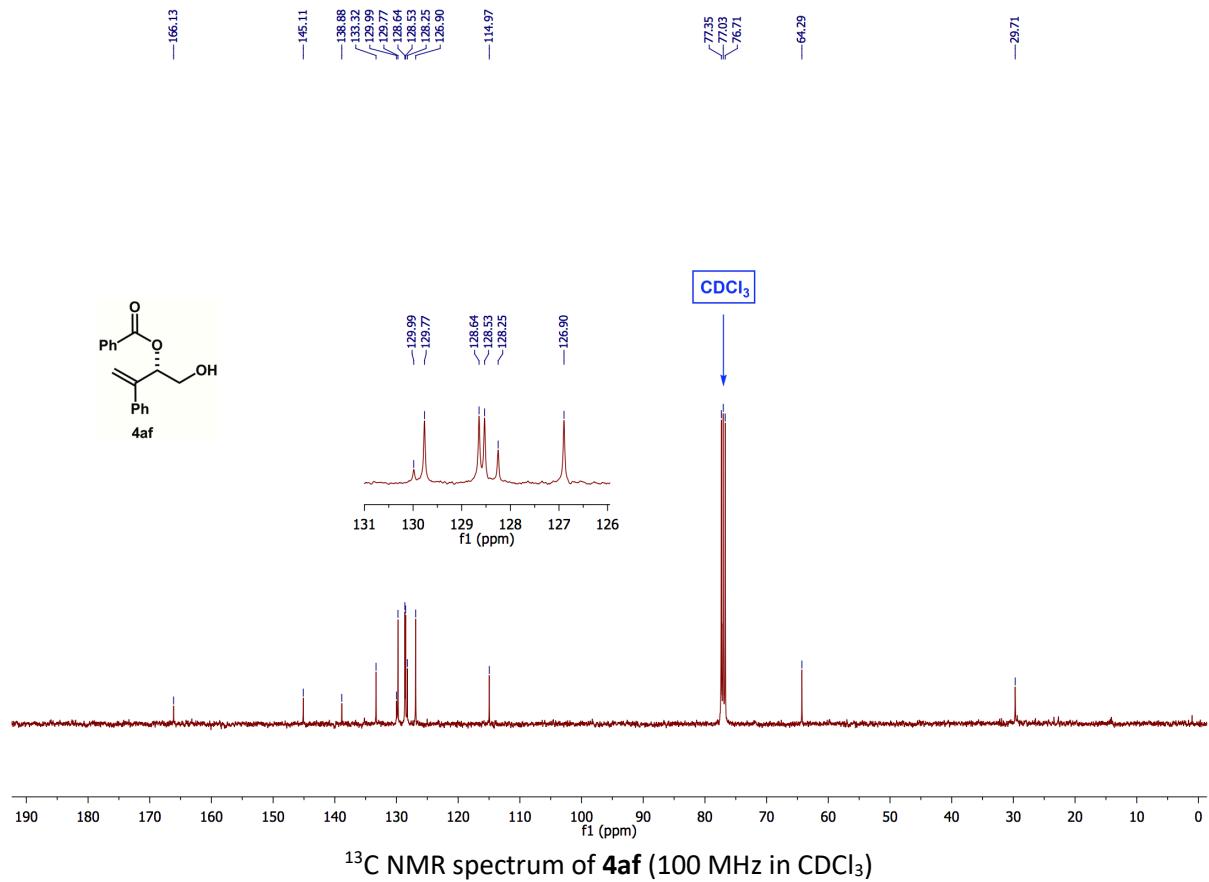
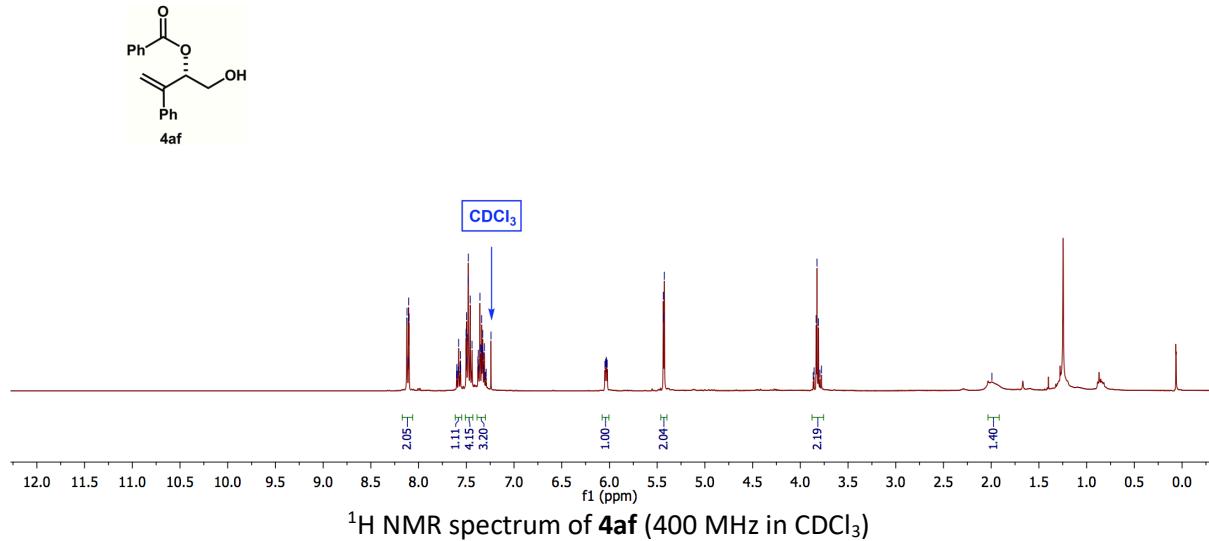
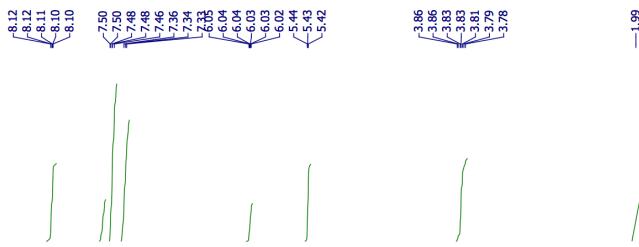


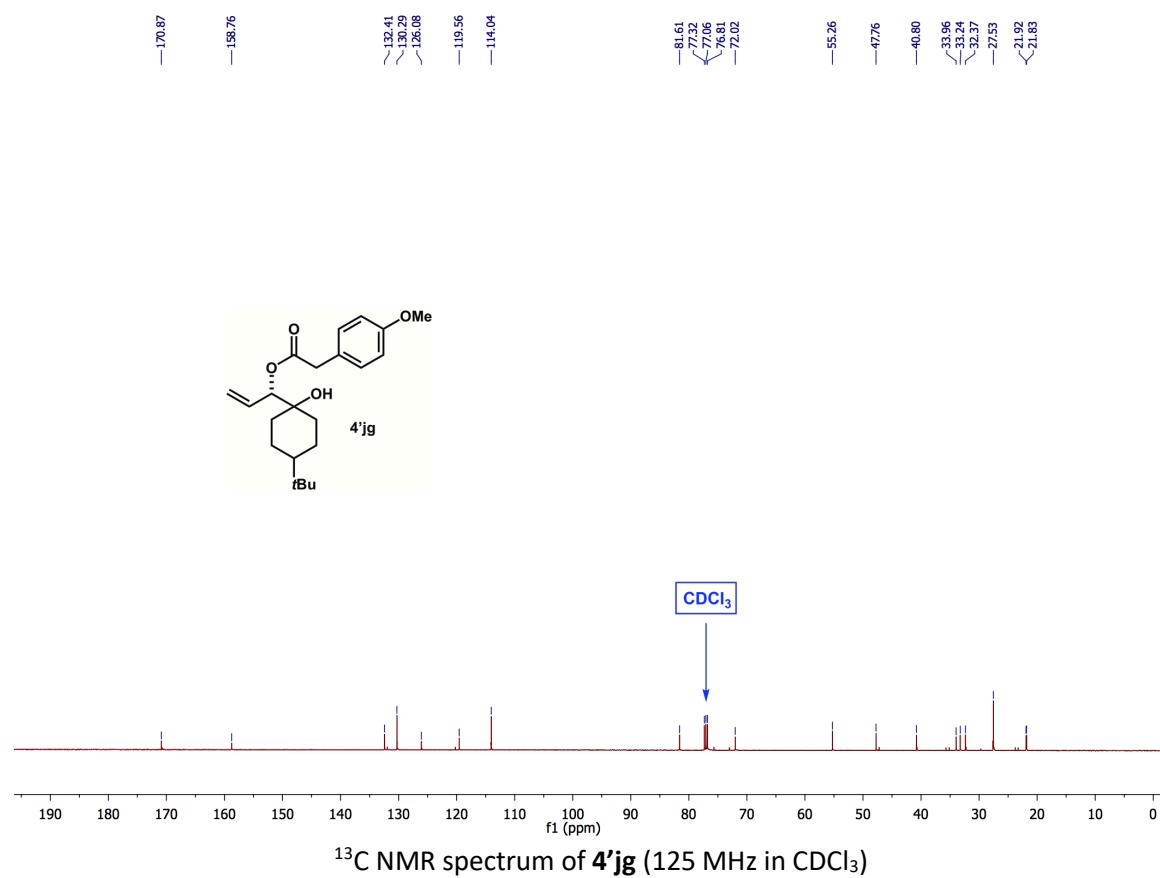
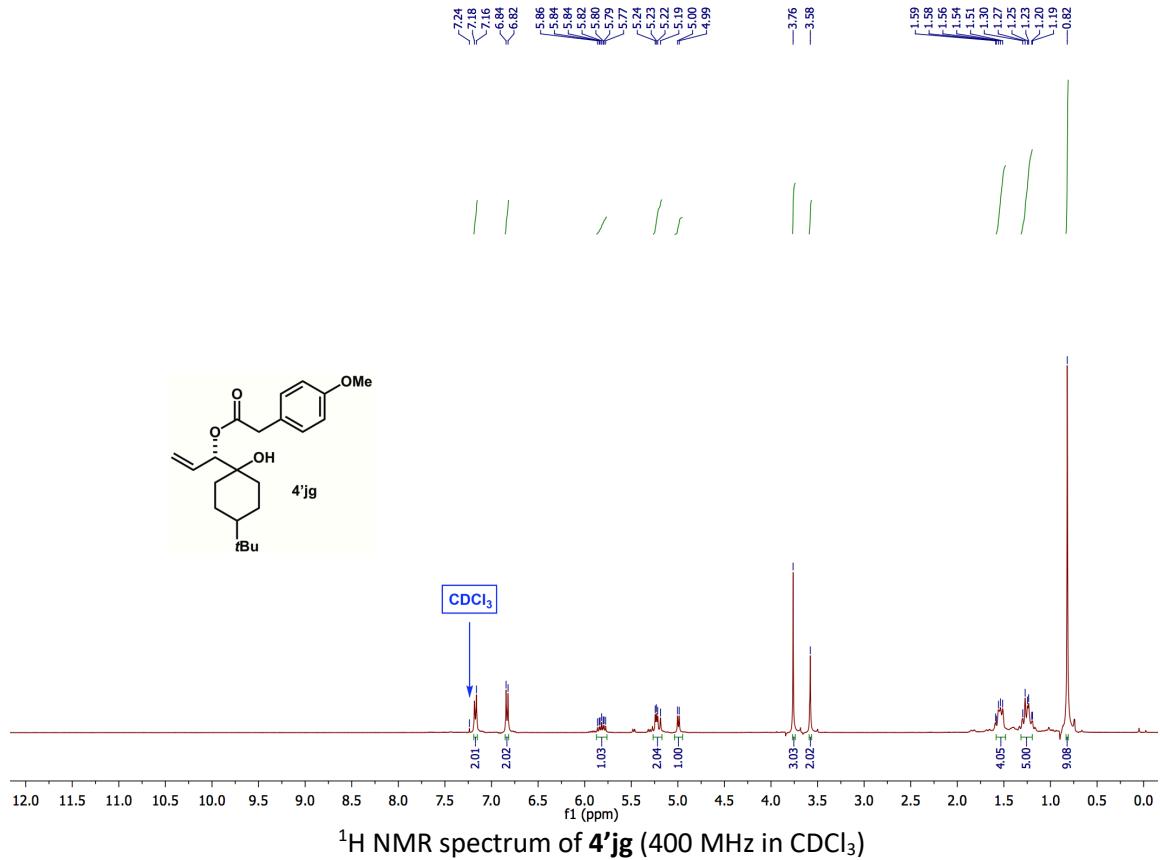
¹³C NMR spectrum of **4'jc** (125 MHz in CDCl₃)

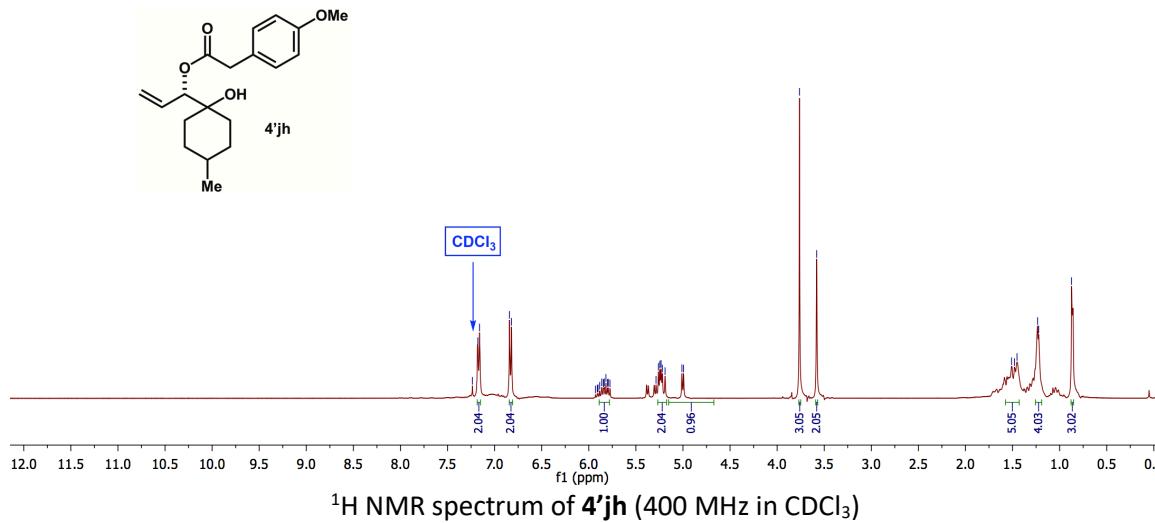
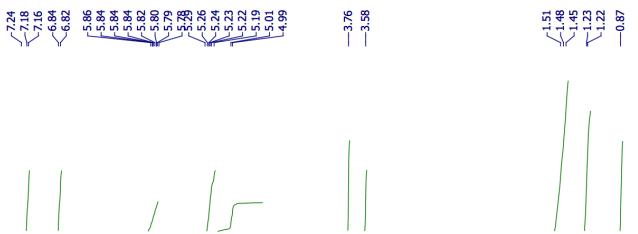


^{13}C NMR spectrum of **4ad** (100 MHz in CDCl_3)







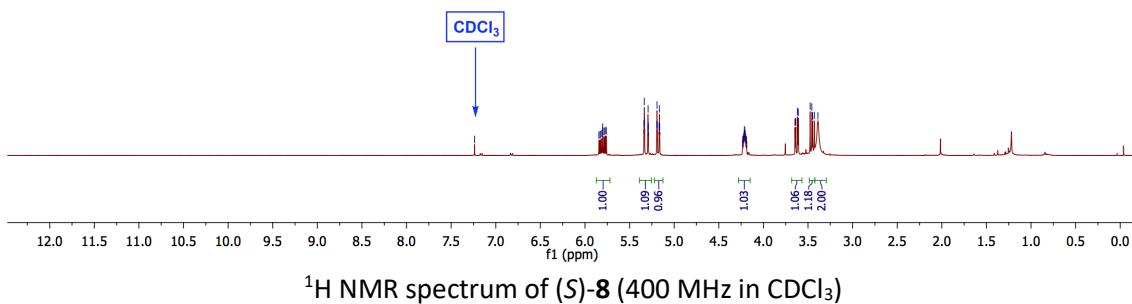
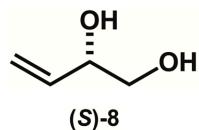
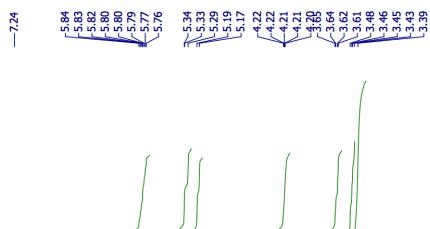


¹H NMR spectrum of **4'jh** (400 MHz in CDCl₃)

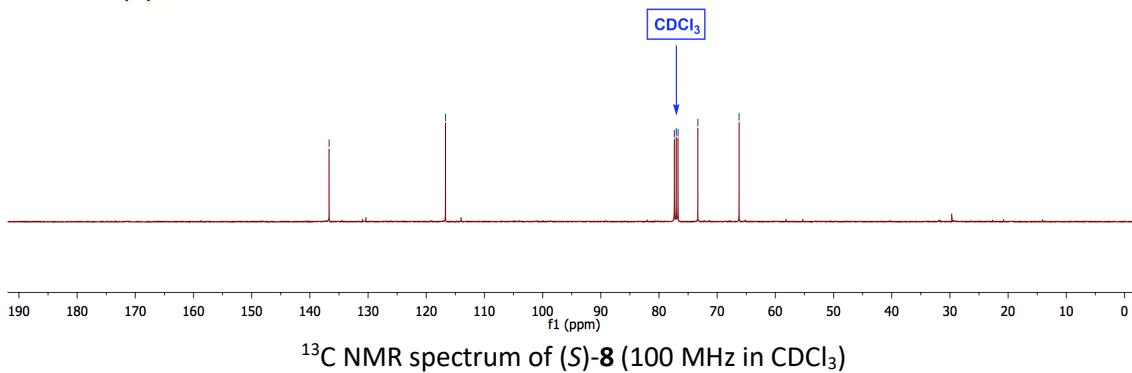
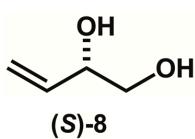


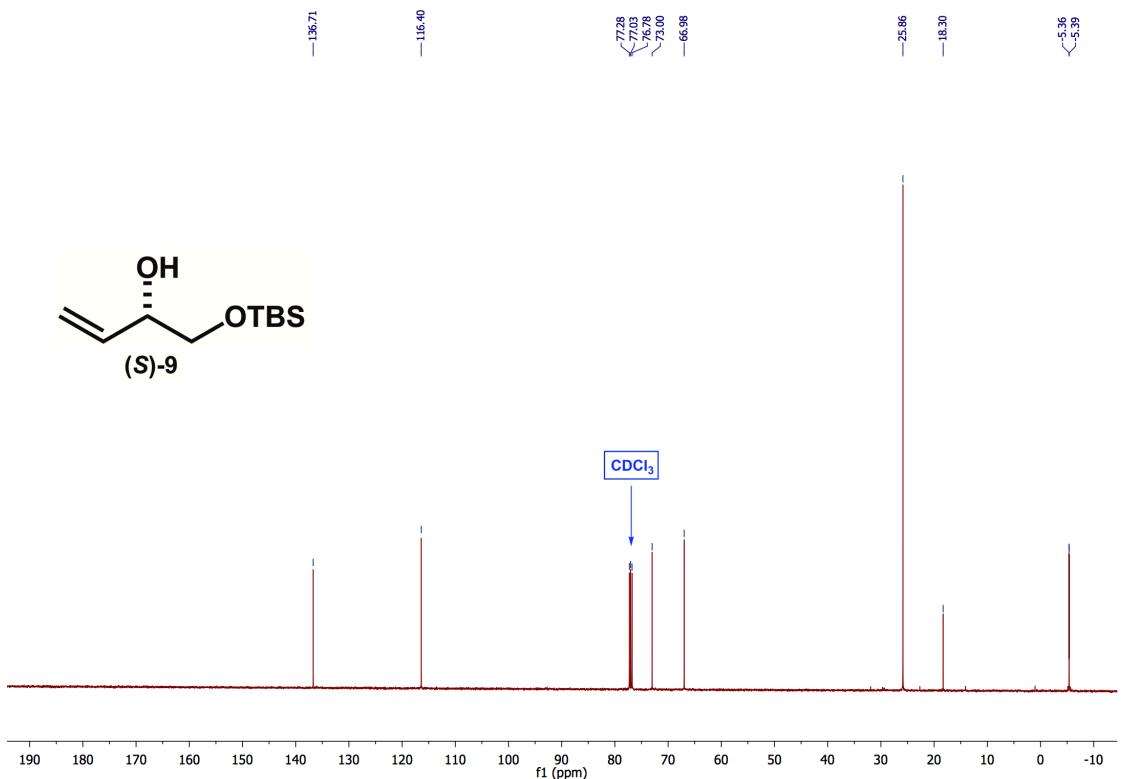
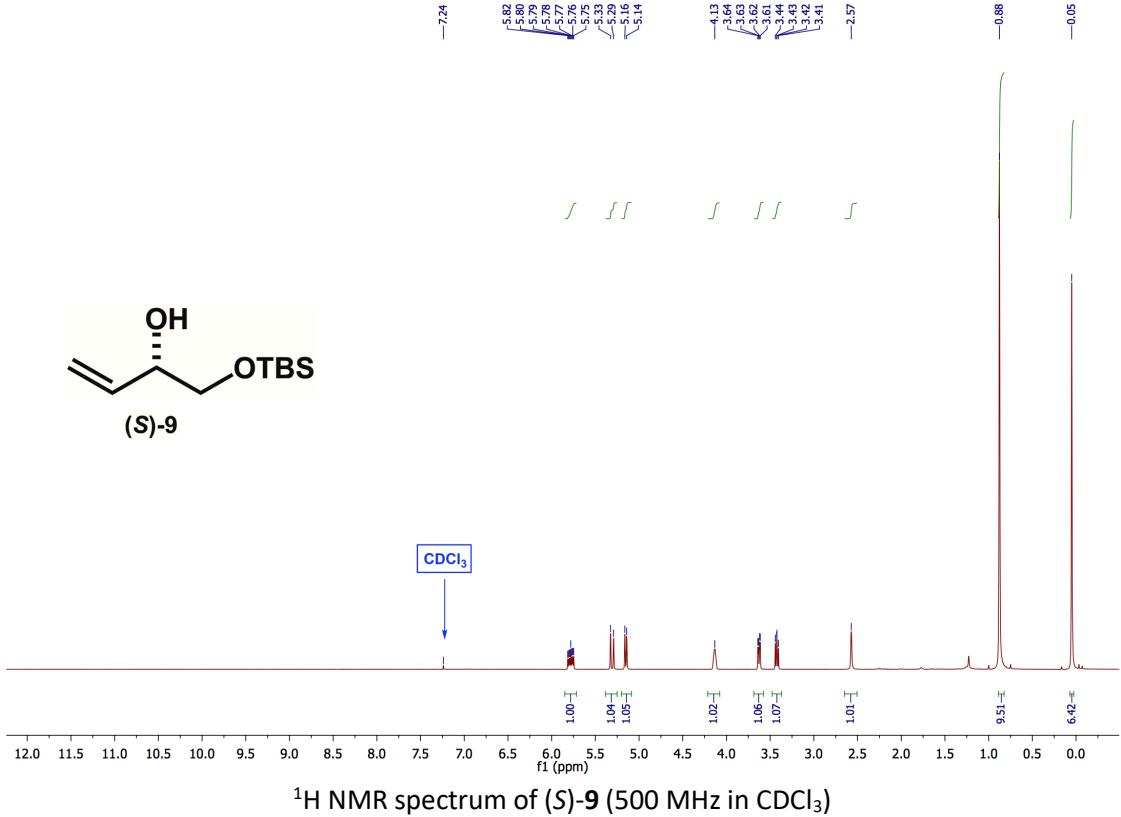
¹³C NMR spectrum of **4'jh** (125 MHz in CDCl₃)

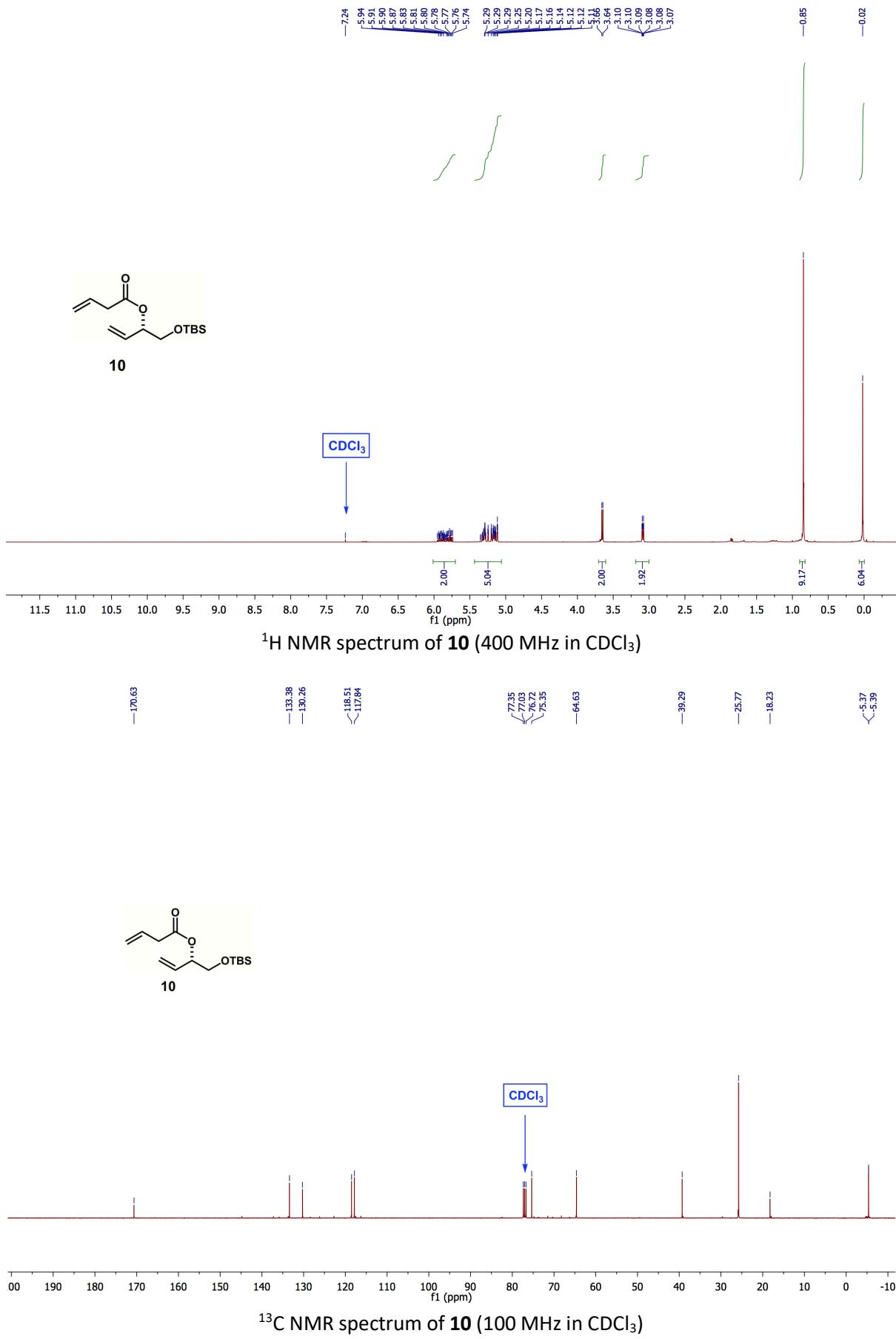
12. ^1H NMR, ^{13}C NMR and HPLC data for the synthetic application:

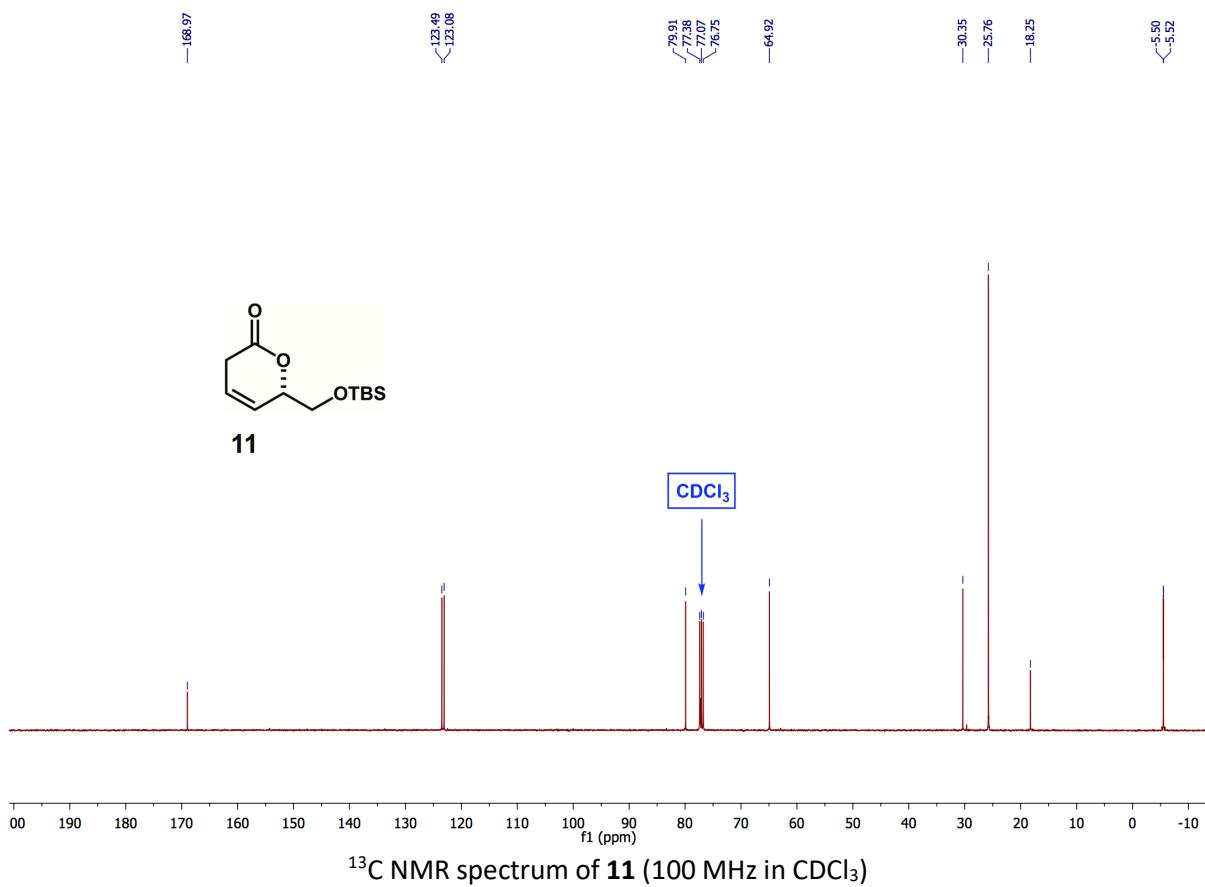
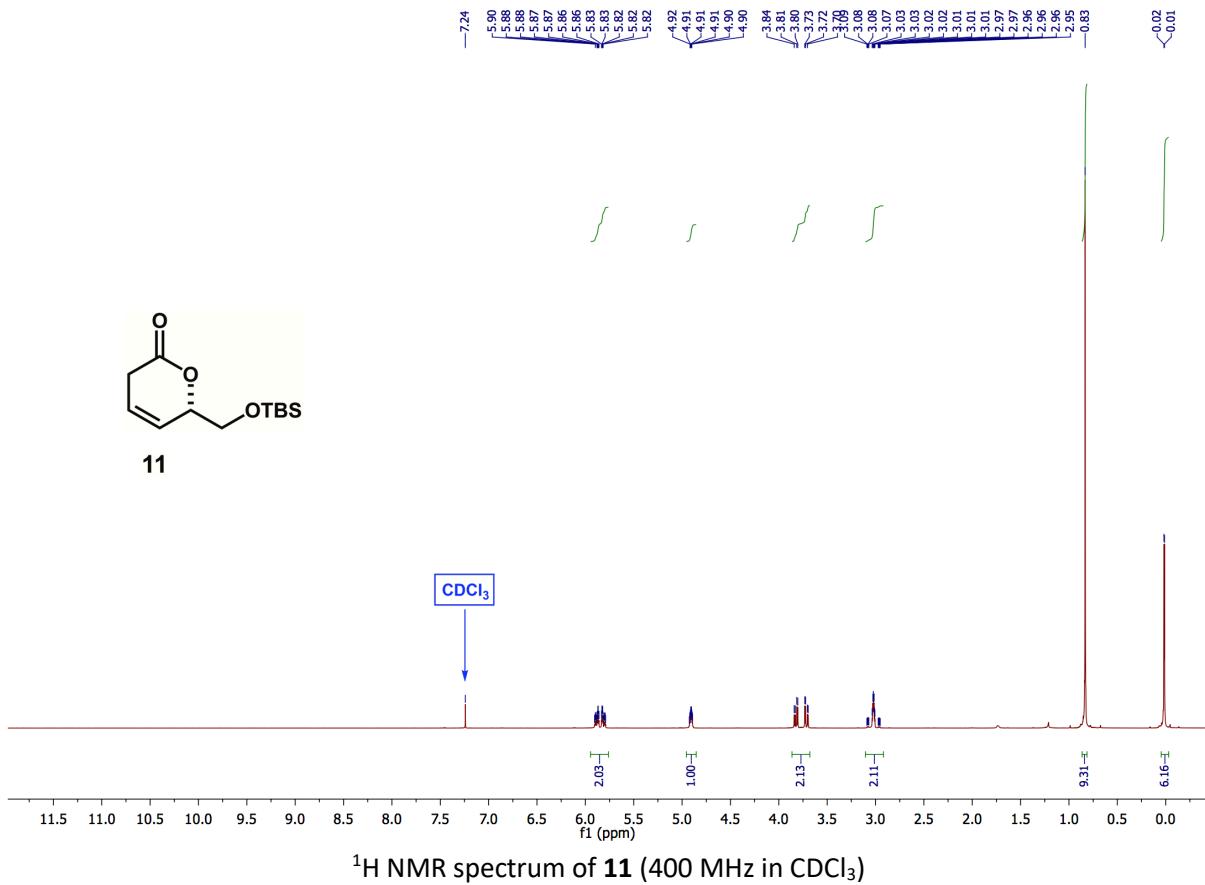


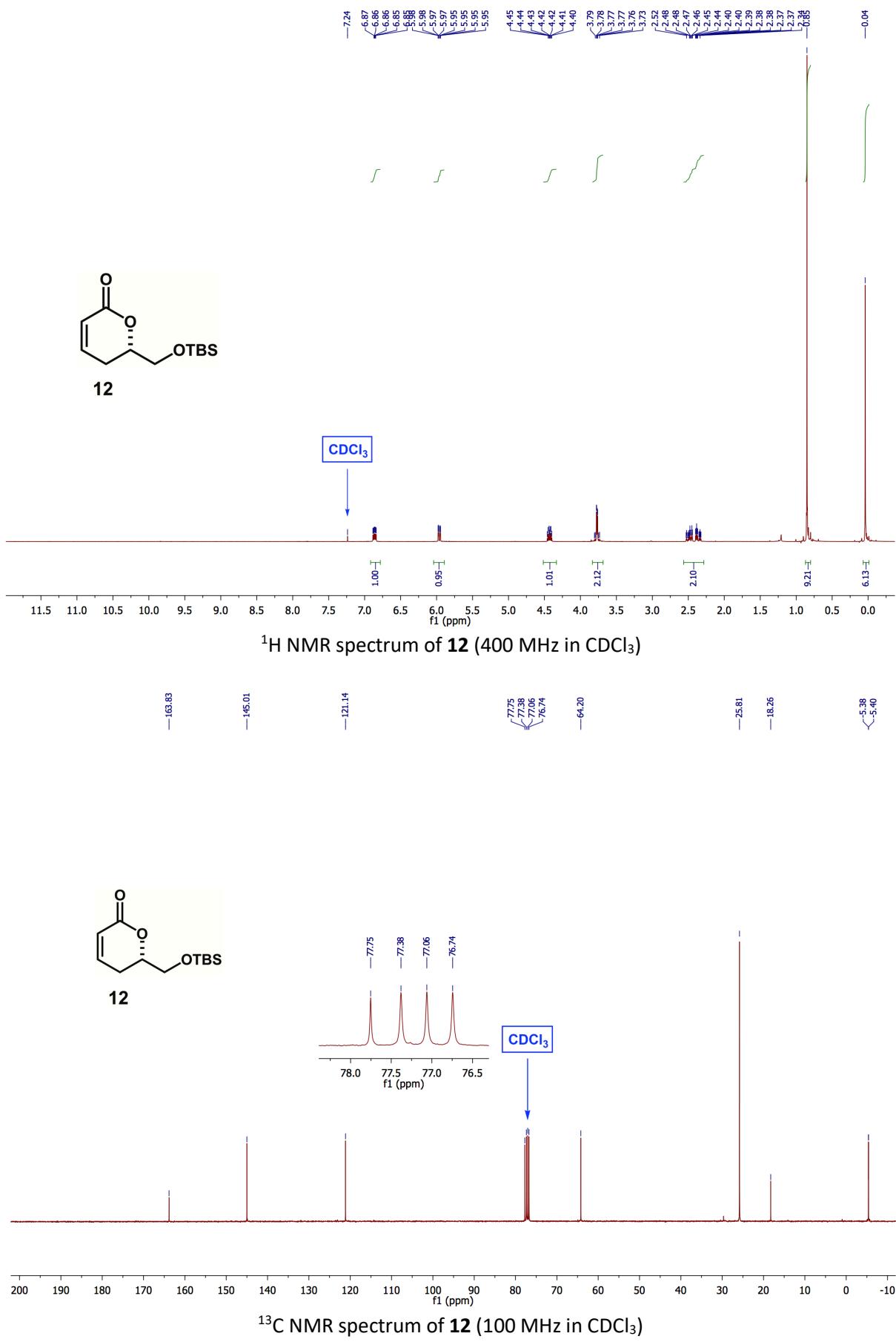
—136.69
—116.69
—77.36
—77.04
—76.72
—73.32
—66.23

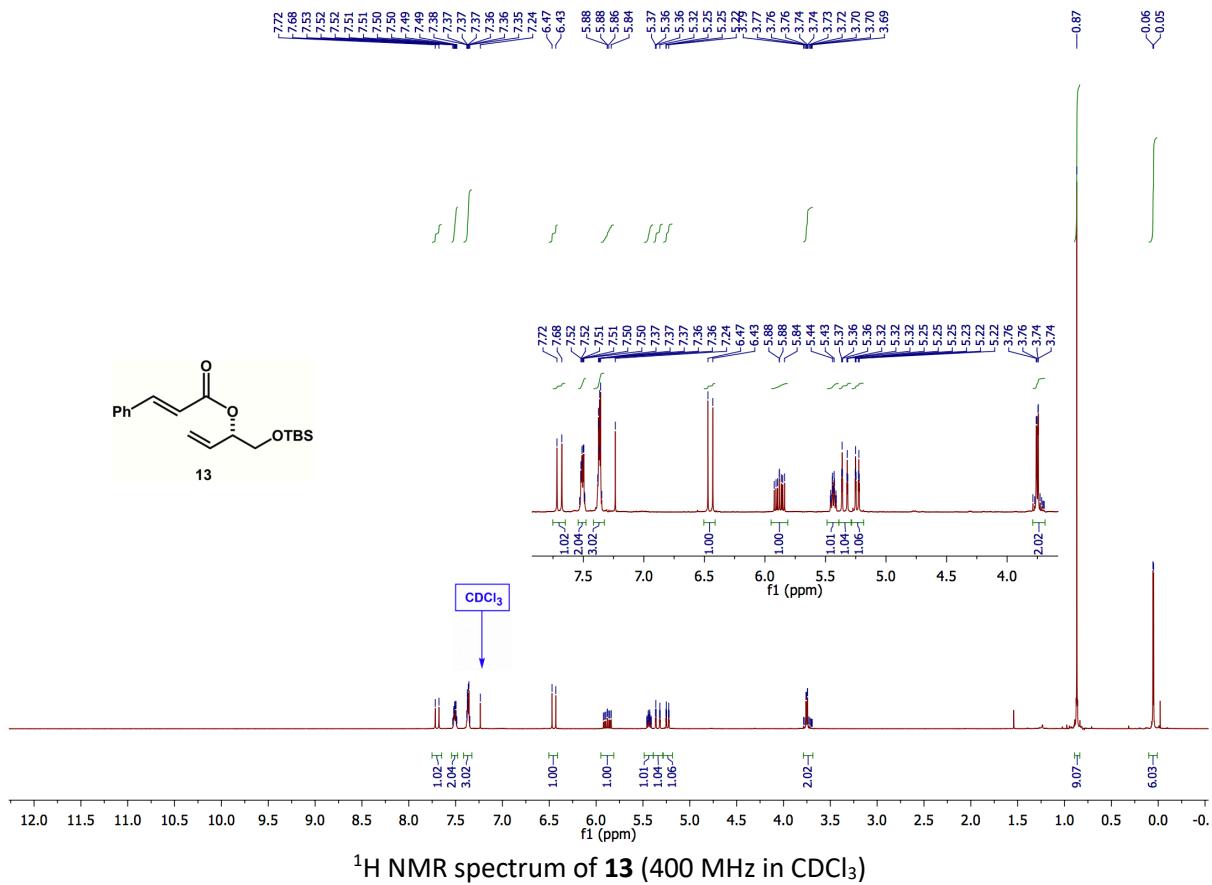




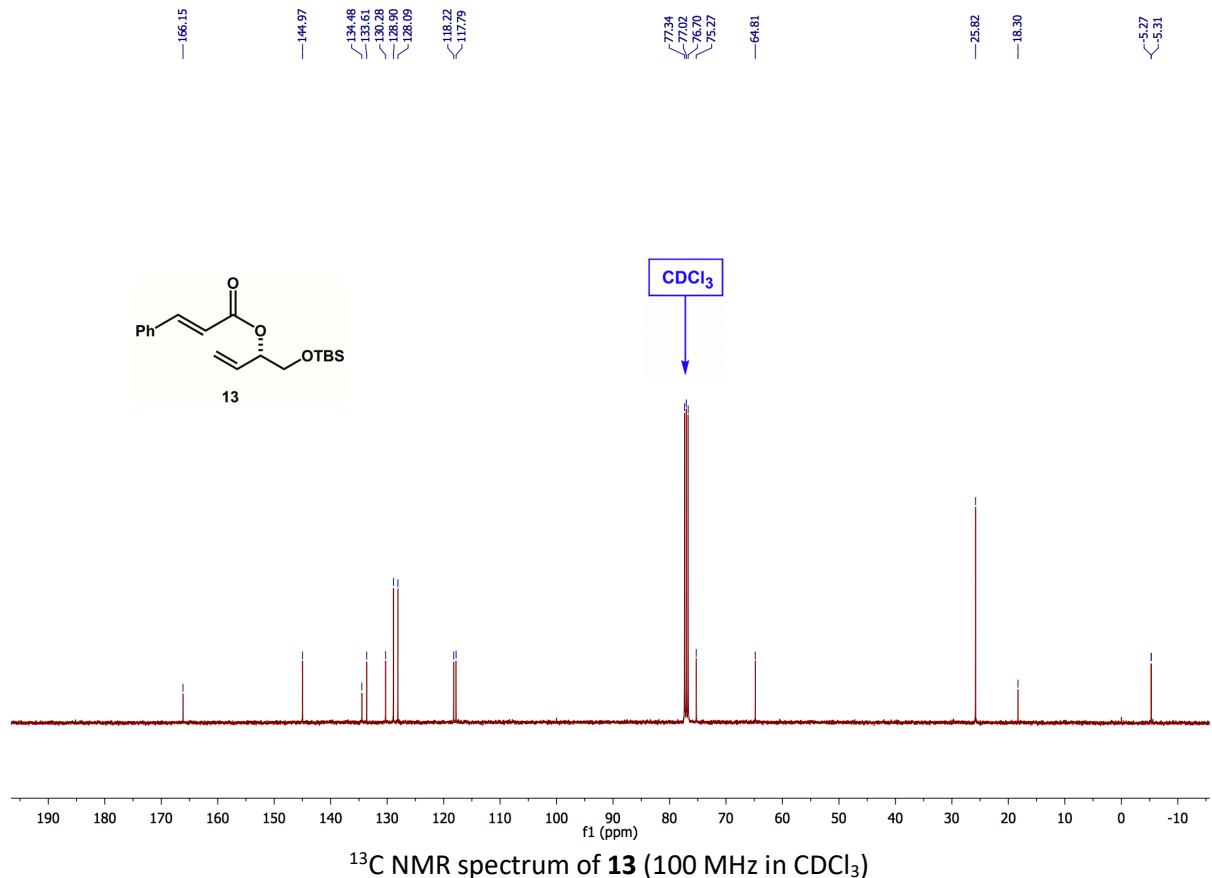


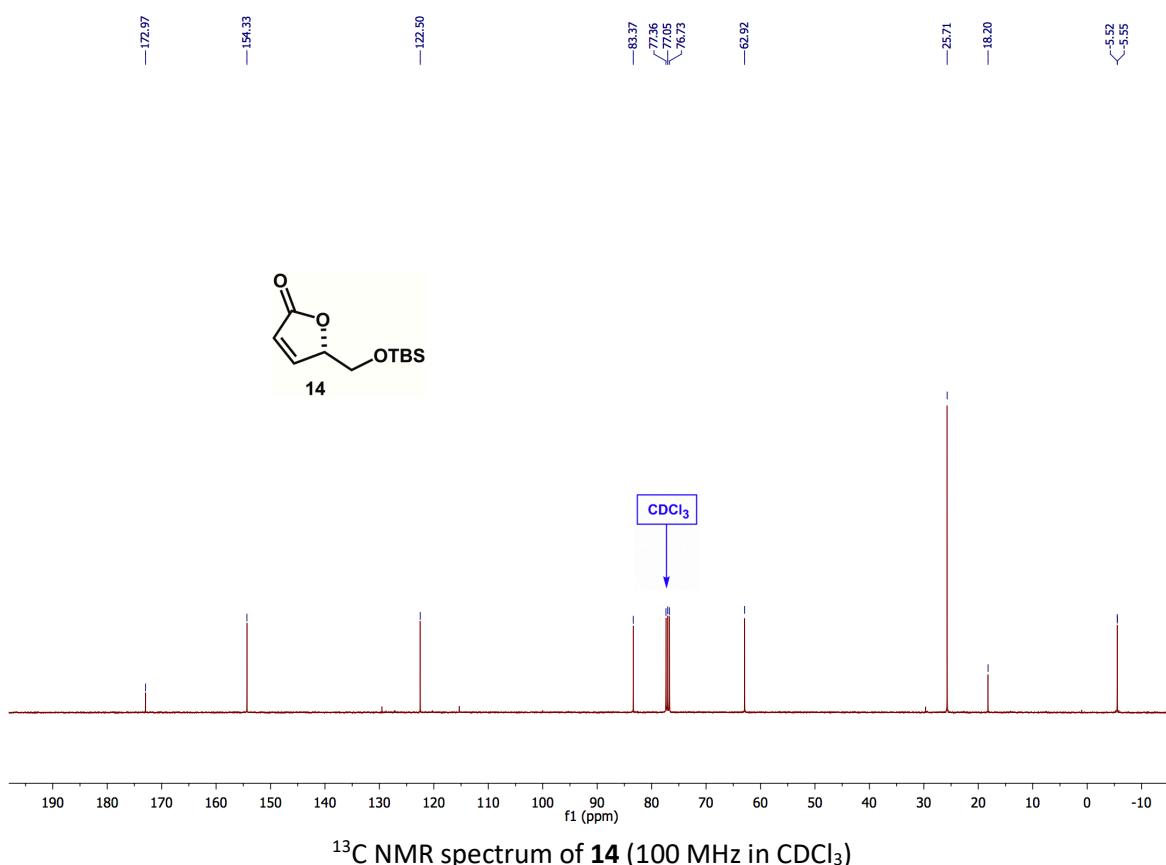
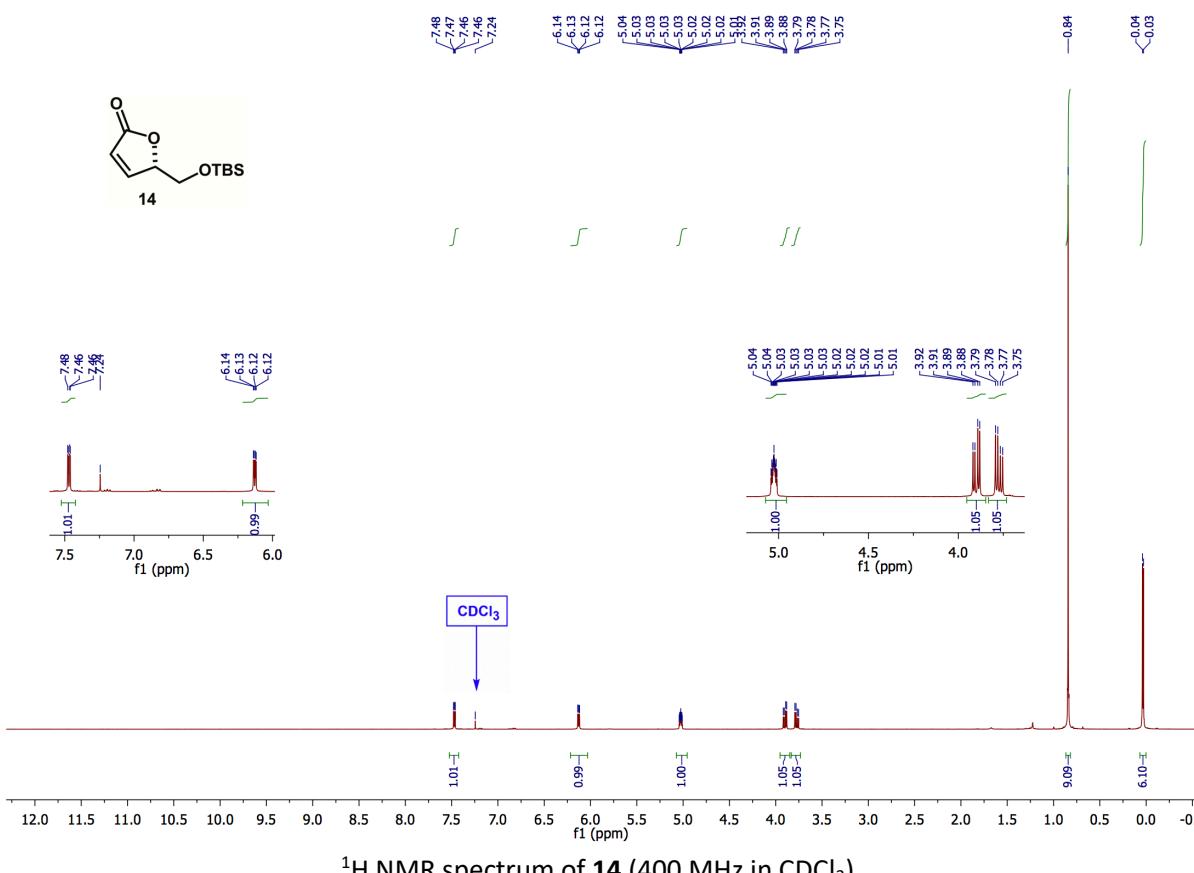


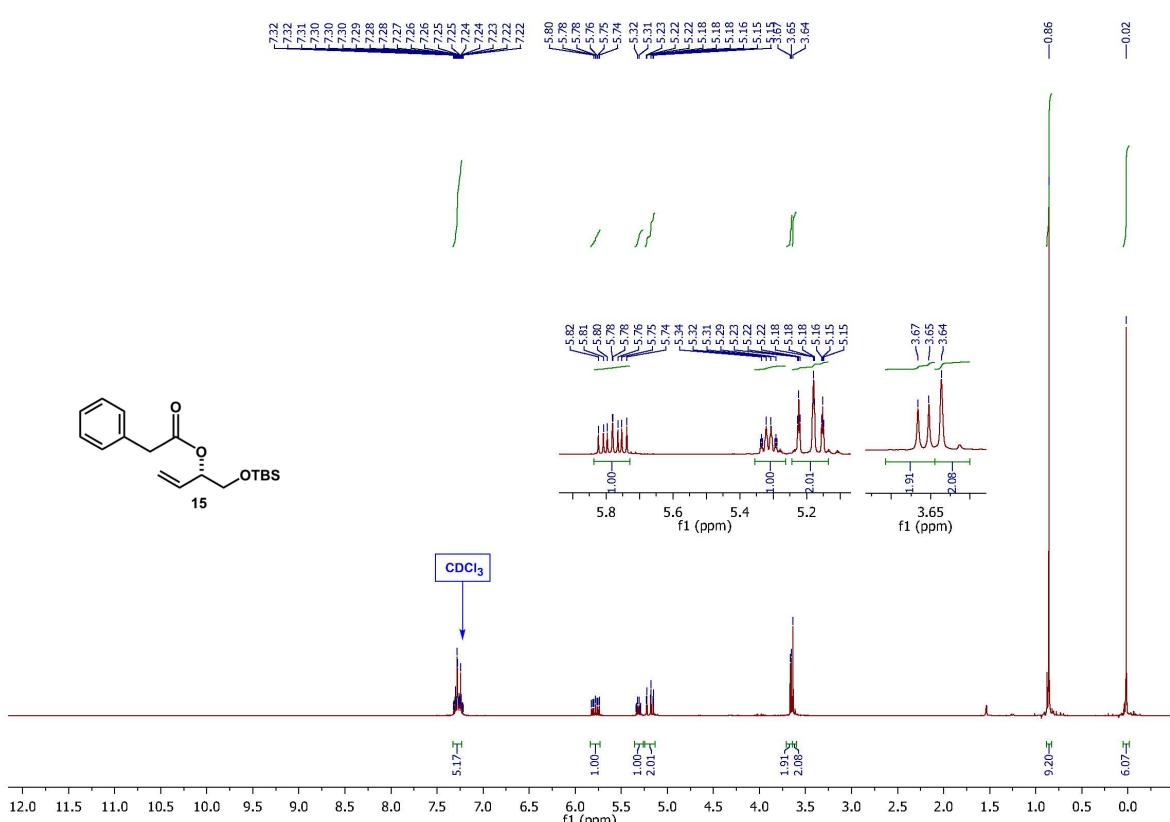




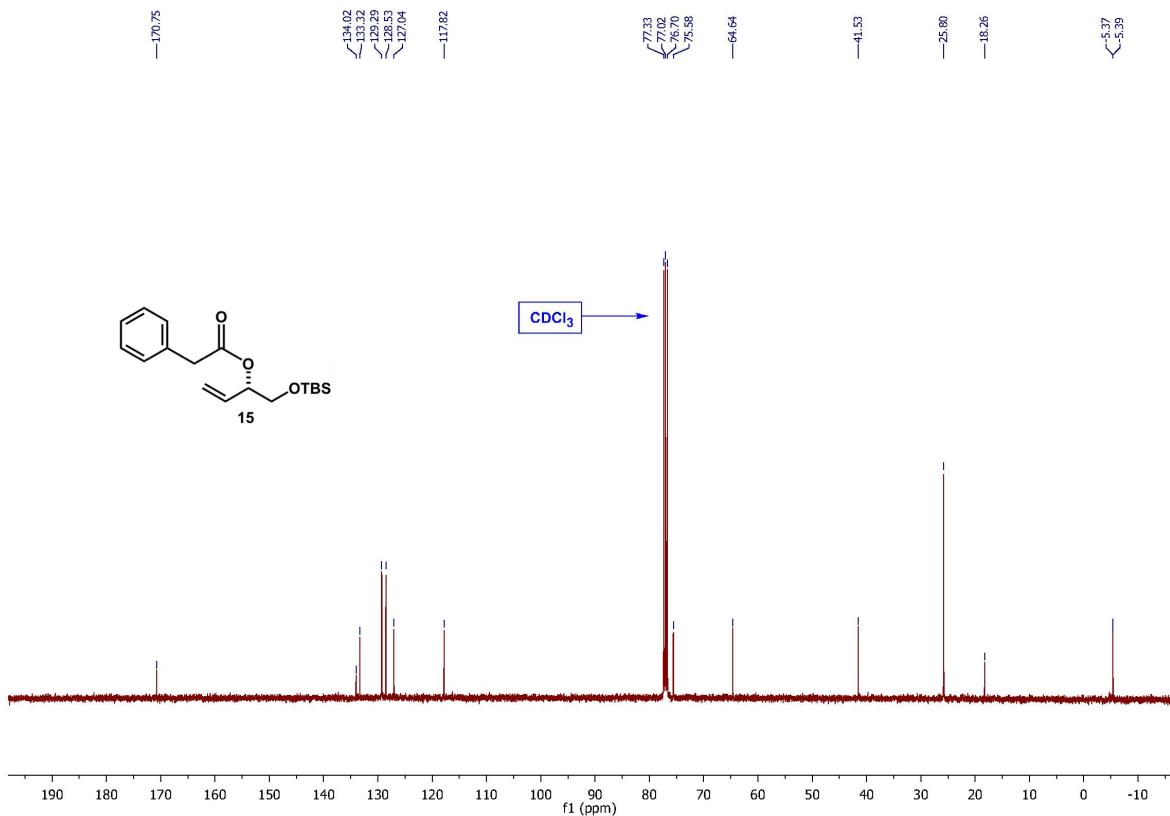
^1H NMR spectrum of **13** (400 MHz in CDCl_3)

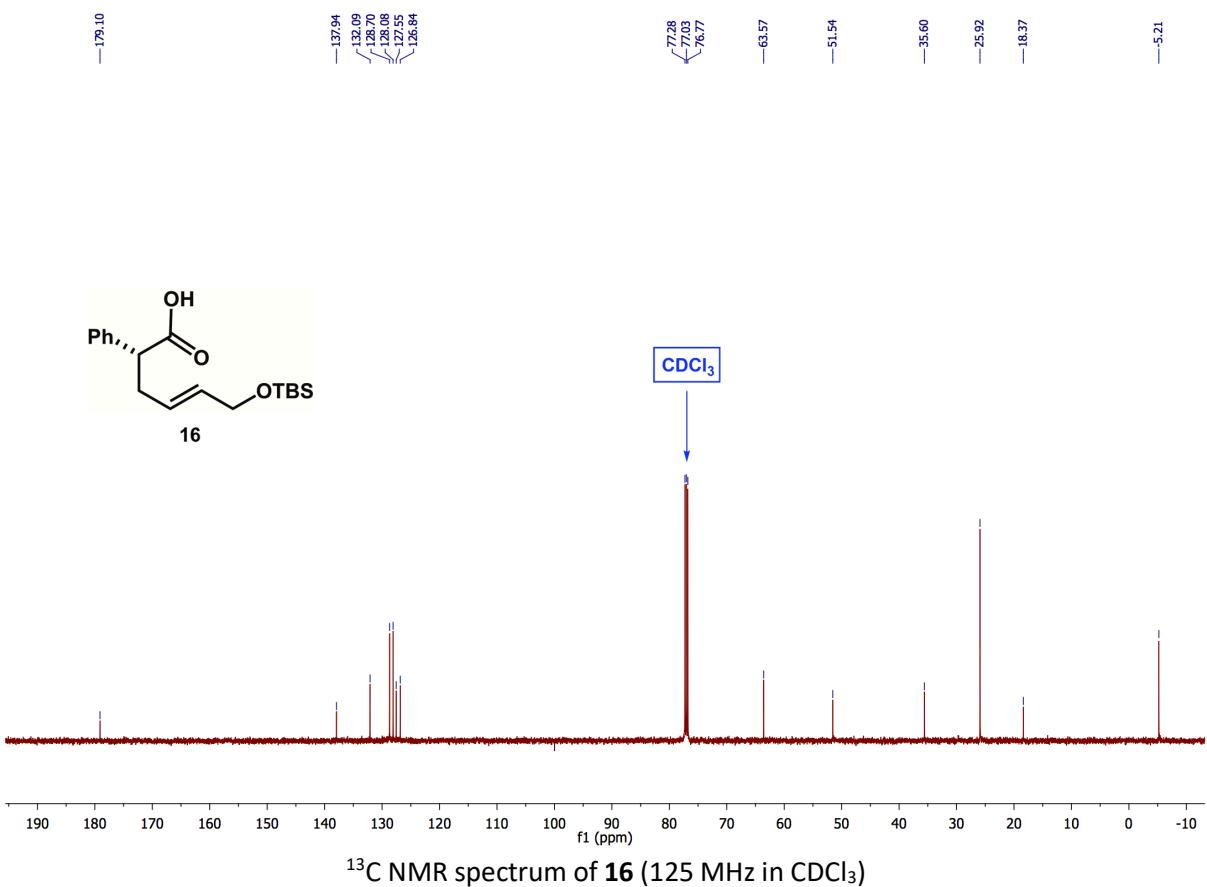
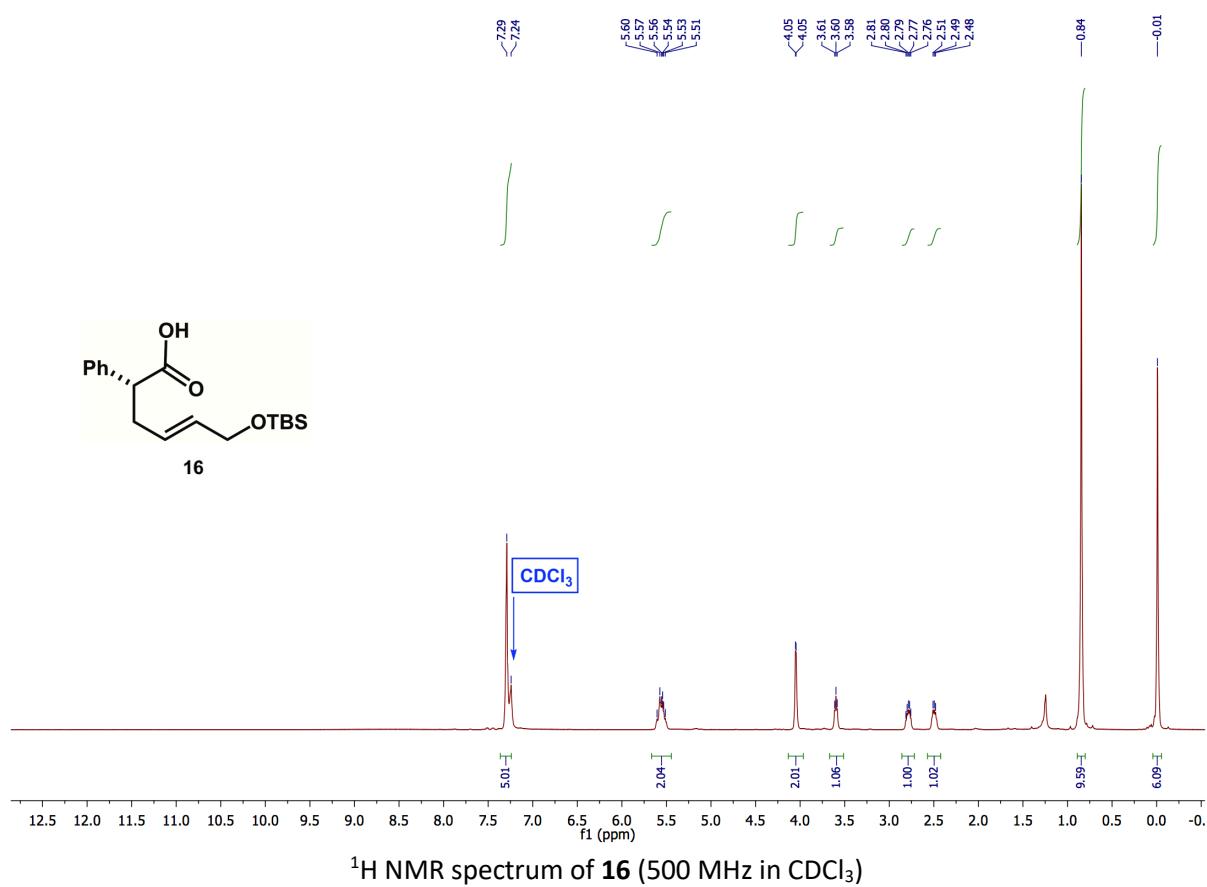
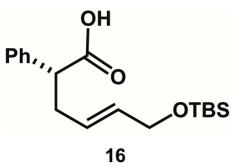


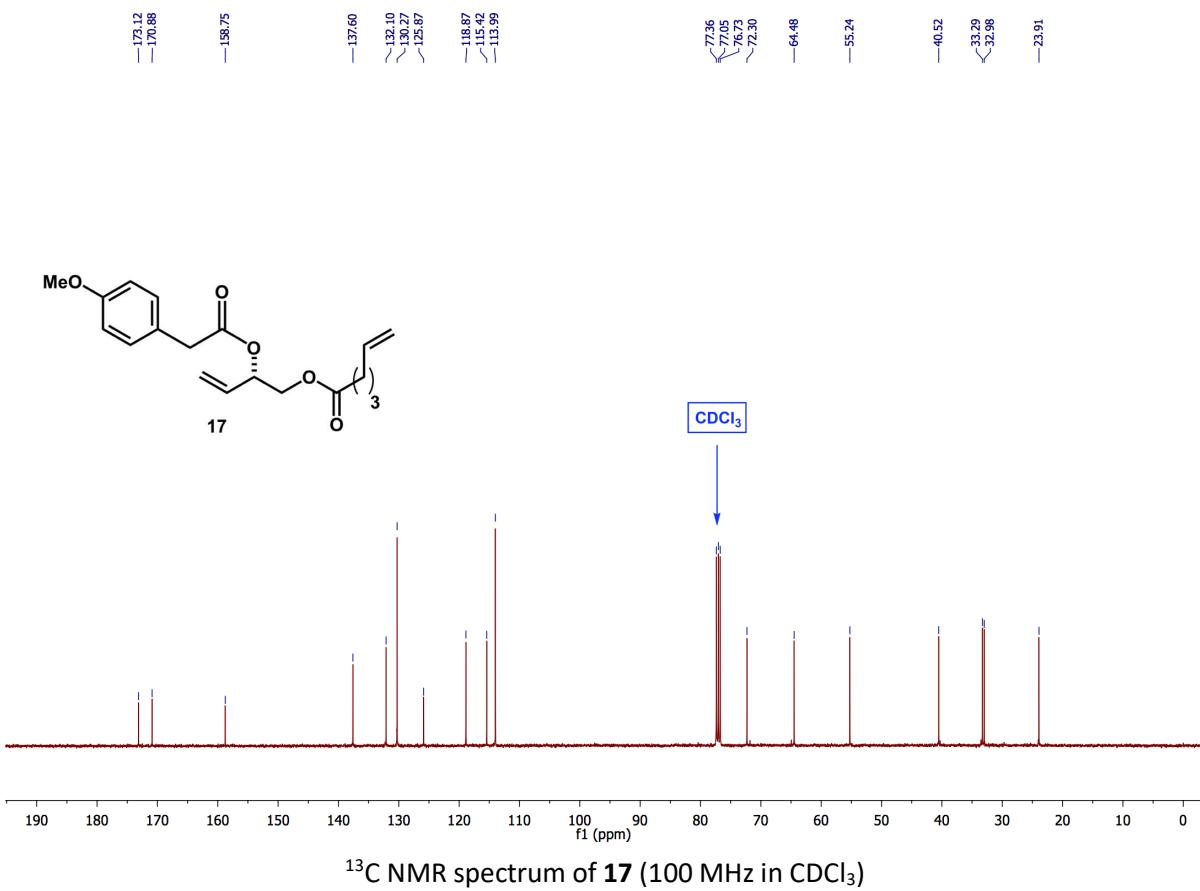
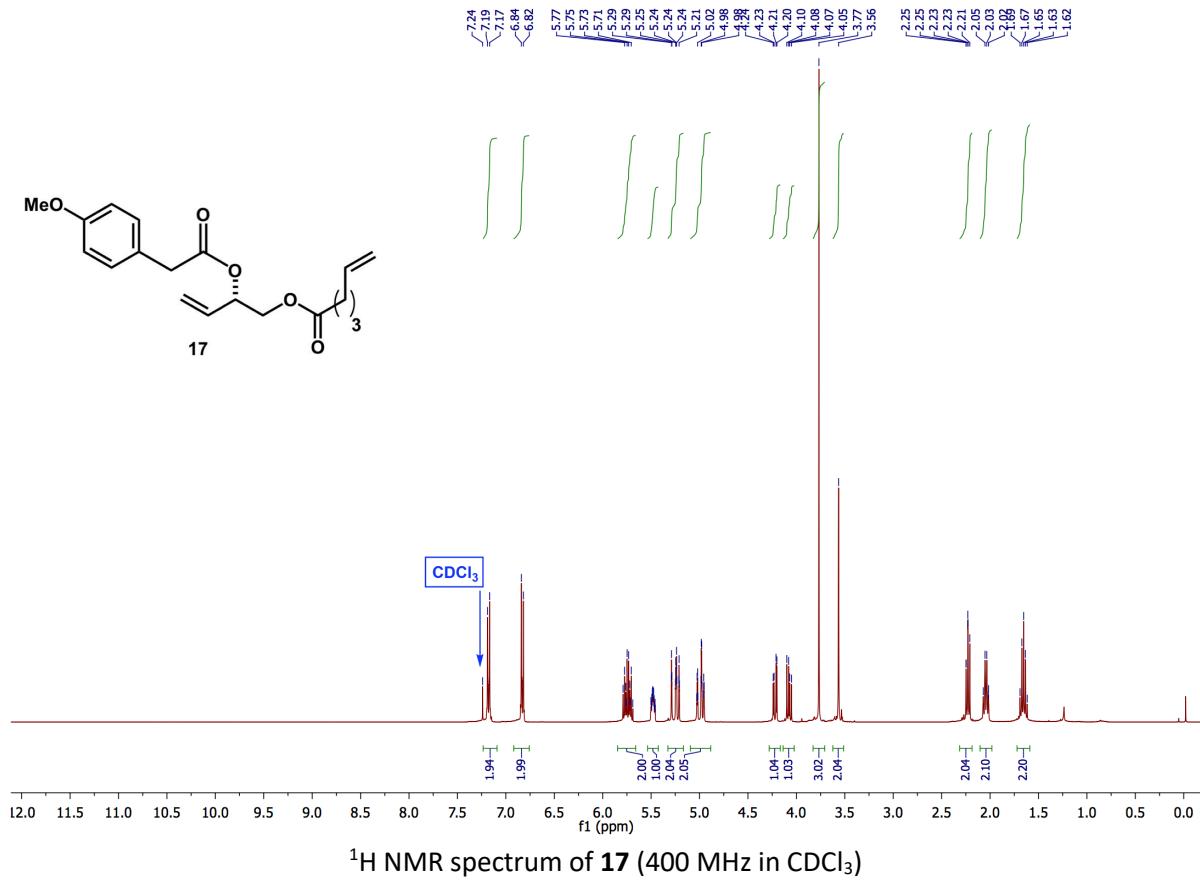


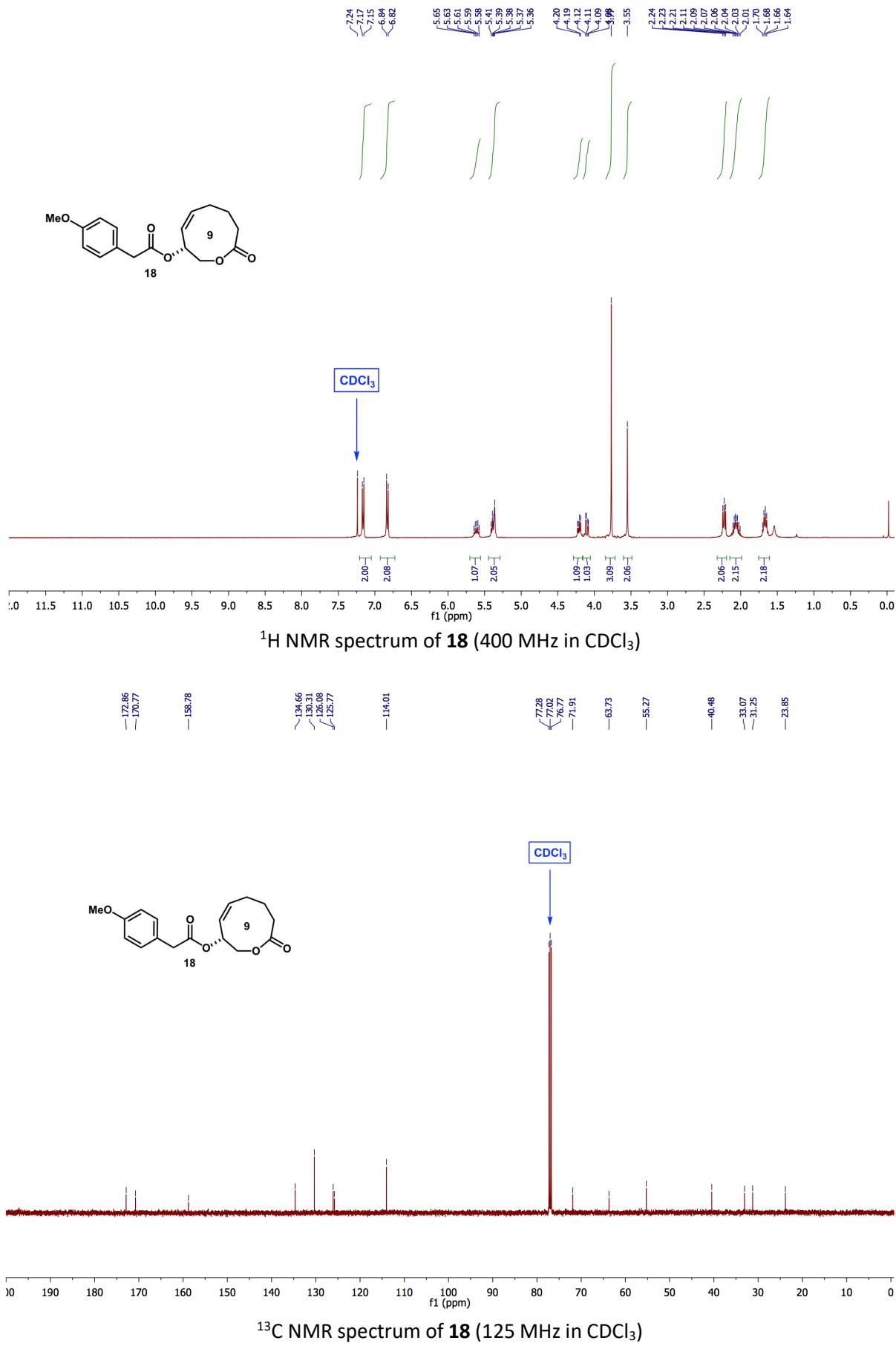


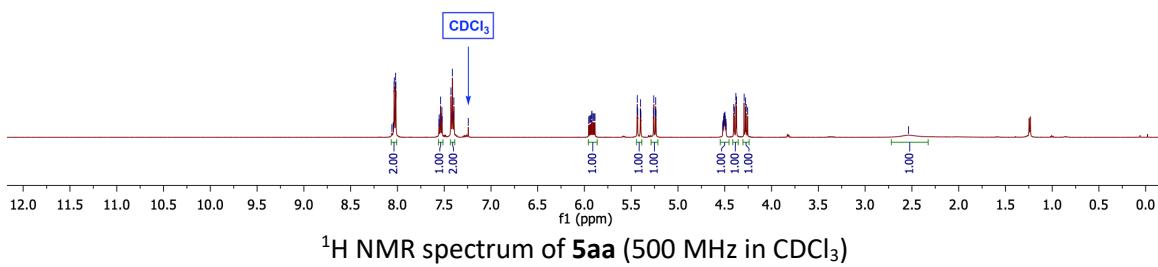
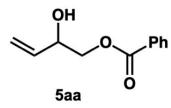
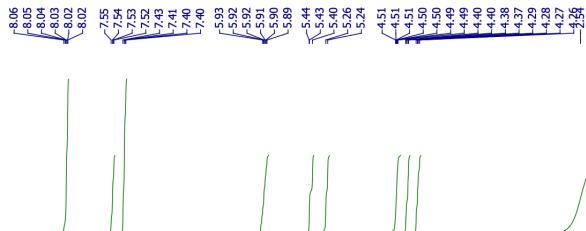
¹H NMR spectrum of **15** (400 MHz in CDCl_3)



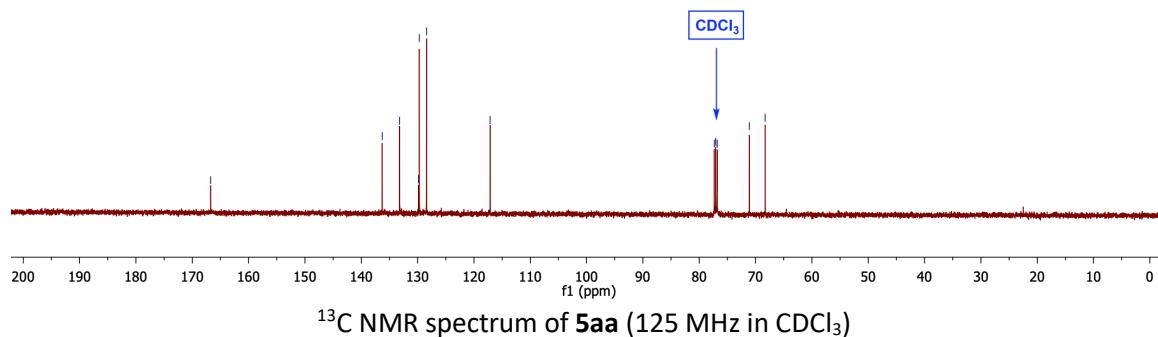
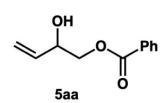






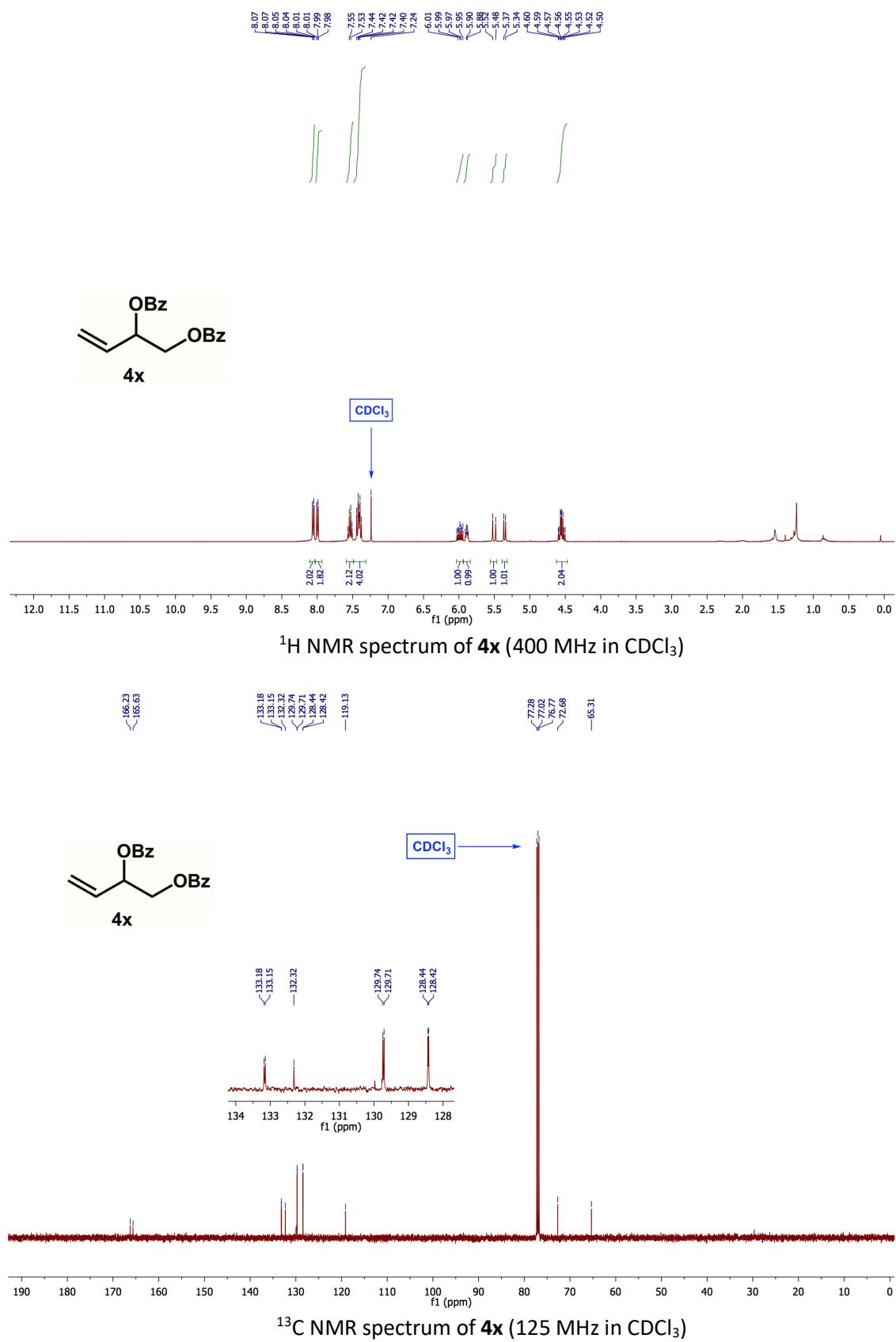


¹H NMR spectrum of **5aa** (500 MHz in CDCl₃)



¹³C NMR spectrum of **5aa** (125 MHz in CDCl₃)

13. ^1H NMR and ^{13}C NMR data for 4x



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