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Supporting Information

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Nucleophilic Addition to *N*-Phosphinylimines *Via* Rare Earth Metal Triflate / Trifluoroacetic Anhydride Activation

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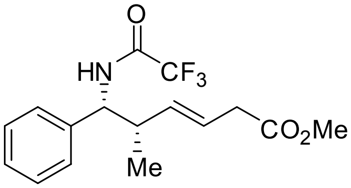
I. General Information

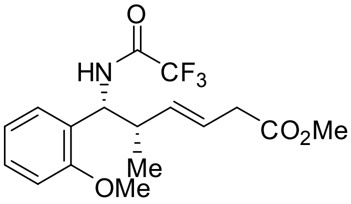
^{1}H NMR spectra were recorded at 400 MHz at ambient temperature with $CDCl_3$ as solvent unless otherwise stated. ^{13}C NMR spectra were recorded at 100.0 MHz at ambient temperature with $CDCl_3$ as solvent unless otherwise stated. Chemical shifts are reported in parts per million relative to $CDCl_3$ (^{1}H, δ 7.24; ^{13}C, δ 77.0). Data for ^{1}H NMR are reported as follows: chemical shift, integration, multiplicity (app = apparent, par obsc = partially obscure, ovrlp = overlapping, s = singlet, d = doublet, t = triplet, q = quartet, qt = quintuplet, m = multiplet) and coupling constants are reported as values in hertz (Hz). ^{31}P NMR spectra were recorded at 400 MHz at ambient temperature with CD_3CN as solvent unless otherwise stated. ^{31}P NMR spectra were recorded at 121.5 MHz at ambient temperature with CD_3CN as solvent unless otherwise stated. Chemical shifts are reported in parts per million using 85% H_3PO_4 as internal standard. The internal standard was taken up into a Stem Coaxial Insert (Wilmad) which was placed within the NMR tube. Infrared spectra were recorded on a Nicolet Nexus 670 FT-IR spectrophotometer. Optical rotations were recorded on an AUTOPOL III digital polarimeter at 589 nm and are recorded as $[\alpha]_D$ (concentration in grams/100 mL solvent). High-resolution mass spectra were obtained in the Boston University Chemical Instrumentation Center using a Waters Q-TOF mass spectrometer. Analytical and preparative HPLC were performed on a Waters FractionLynx System (www.waters.com) with a Waters 600 HPLC pump, MicroMass ZQ 2000 mass spectrometer, Water 996 diode array, and Sedere Sedex 75 ELS detector. A Sunfire 4.6 x 50 mm C18 column was used for analytical HPLC. Analytical thin layer chromatography was performed using 0.25 mm silica gel 60-F plates (VWR). Microwave reactions were carried out using a CEM Explorer/Discover (www.cem.com) system equipped with a dynamic cooling valve. Flash chromatography of starting materials was performed using an Isco CombiFlash Companion using CombiFlash silica gel cartridges (www.isco.com). Alternatively, flash chromatography was performed using 200-400 mesh silica gel (Scientific Absorbents, Inc.). Yields refer to chromatographically and spectroscopically pure materials, unless otherwise stated. Methylene chloride, THF, and toluene were dried by passing through two packed columns of neutral alumina (Innovative Technologies, MA). E.r values were determined using a Waters Breeze high pressure liquid chromatography (HPLC) equipped with a quaternary pump using a Phenomenex Chiradex R-Pgly Column (50 x 4.6 mm) with UV detection monitored at 254 nm or 280 nm. Compounds **8-13** were run using a gradient method, 0-10% IPA:Hexanes, 1.0 mL/min, for 35 min. Mixtures of enantiomers were prepared by mixing equal amounts of *S* and *R* isomers respectively. Karl Fischer titration was carried out using a Metrohm 756 KF Coulometer. Chemical names were generated using CambridgeSoft ChemDraw Ultra 10.0. Chemical reaction planning was performed using the Arthur Suite Reaction Planner (Symyx Technologies Inc., Santa Clara, CA). $La(OTf)_3 \cdot nH_2O$ (n = 8-9) was purchased from Aldrich. Amberlyst OH resin was obtained from Aldrich (loading 4.2 mmol/g) and activated by sequentially washing with 0.5 N HCl, deionized H_2O, and 0.5 N NaOH. All other reagents and solvents were used as supplied by Sigma-Aldrich, Fluka, and Strem Chemicals.

II. Experimental Procedures and Characterization Data for La(OTf)$_3$-TFAA mediated crotylation



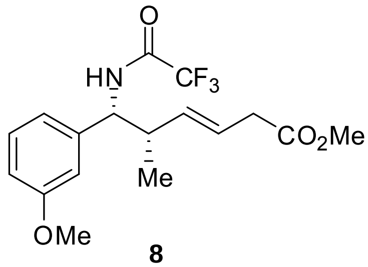
3

Representative Procedure for Crotylation.; (5*S*, 6*R*, E)-Methyl 5-methyl-6-phenyl-6-(2,2,2-trifluoroacetamido)hex-3-enoate (3);
To a round-bottom flask was added hydrated lanthanum triflate (65.3 mg, 0.089 mmol), trifluoroacetic anhydride (150 μL, 0.90 mmol), and ACS-grade acetonitrile (1.6 mL, 0.3 M). The mixture was sonicated and transferred by syringe to a dry flask containing a mixture of phosphinylimine **1** (0.15 g, 0.49 mmol) and crotylsilane **2** (117 mg, 0.45 mmol). The mixture was vortexed until clear and allowed to stir at room temperature under an argon atmosphere for 3 h. The solvent was removed *in vacuo* and the crude material purified by column chromatography (SiO$_2$, CH$_2$Cl$_2$/hexanes, 7:3) to afford trifluoroacetamide **3** (150 mg, 93%, d. r. = >20:1) as a white solid. The e. r. was determined to be 97:3 by Trost mandelamide analysis (see SI-8 for details). m. p. = 50 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.37-7.30 (m, 3H), 7.18 (dd, 2H, *J* = 1.2 Hz, *J* = 7.8 Hz), 7.03 (d, 1H, *J* = 7.7 Hz), 5.62 (m, 1H), 5.30 (dd, 1H, *J* = 8.9 Hz, *J* = 15.4 Hz), 4.95 (dd, 1H, *J* = 5.6 Hz, *J* = 8.9 Hz), 3.71 (s, 3H), 3.06 (m, 2H,) 2.69 (qd, 1H, *J* = 6.7 Hz, *J* = 13.3 Hz), 0.99 (d, 3H, *J* = 6.9 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 172.2, 156.9 (q, $^2J_{\text{F-C}}$ = 37.1 Hz), 137.3, 134.7, 128.4, 127.9, 127.4, 124.8, 115.8 (q, $J_{\text{F-C}}$ = 288.2 Hz), 57.7, 52.0, 41.4, 37.5, 16.8; IR (neat) ν_{max}: 1713, 1202, 1170 cm^{-1}; $[\alpha]^{23}_{D}$ = +88.3 ° (c = 2.52, CH$_2$Cl$_2$); HRMS: Calculated for $C_{16}H_{18}F_3NO_5$: 329.1239, found 352.1128 (M+Na).



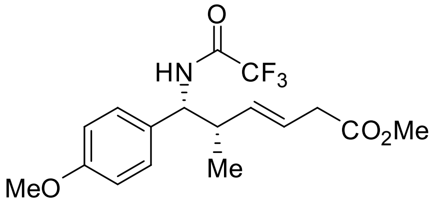
7

(5*S*,6*R*,E)-Methyl 6-(2-methoxyphenyl)-5-methyl-6-(2,2,2-trifluoroacetamido)hex-3-enoate (7);
(75% yield, d. r. = 10:1, e. r. = 93:7). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.63 (d, 1H, *J* = 8.9 Hz), 7.18 (m, 1H), 6.98 (d, 1H, *J* = 7.2 Hz), 6.84 (m, 2H), 5.29 (m, 1H), 5.19 (dd, 1H, *J* = 8.0 Hz, *J* = 15.5 Hz), 4.87 (t, 1H, J = 9.0 Hz), 3.80 (s, 3H), 3.60 (s, 3H), 2.82 (dq, 2H, *J* = 6.7 Hz, *J* = 16.2 Hz), 2.69 (m, 1H), 0.98 (d, 3H, *J* = 6.8 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 171.9, 156.9, 156.2 (q, $^2J_{\text{F-C}}$ = 36.5 Hz), 135.5, 130.1, 129.1, 125.9, 123.0, 116.0 (q, $J_{\text{F-C}}$ = 288.2 Hz), 111.2, 57.1, 55.3, 51.7, 41.3, 37.7, 16.8; IR (neat) ν_{max}: 1724, 1173 cm^{-1}; $[\alpha]^{23}_{D}$ = +44.7 ° (c = 21.0, CH$_3$CN); HRMS: Calculated for $C_{17}H_{20}F_3NO_4$: 359.1344, found 382.1215 (M+Na).



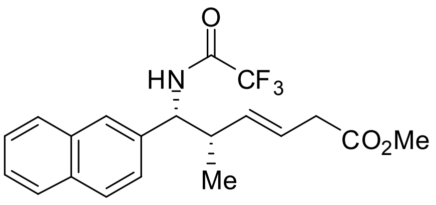
8

(5*S*,6*R*,E)- Methyl6-(3-methoxyphenyl)-5-methyl-6-(2,2,2-trifluoroacetamido)hex-3-enoate (8);
(71% yield, d. r. = >20:1, e. r. = 96:4). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.26 (t, 2H, *J* = 7.9 Hz), 7.20 (s, 1H), 6.85-6.75 (m, 2H), 5.61 (td, 1H, *J* = 7.1 Hz, *J* = 14.6 Hz), 5.34 (dd, 1H, *J* = 8.8 Hz, *J* = 15.5 Hz), 4.92 (dd, 1H, *J* = 6.1Hz, *J* = 8.8Hz), 3.80 (s, 3H), 3.71 (s, 3H), 3.06 (m, 2H), 2.69 (m, 1H), 1.02 (d, 3H, *J* = 6.9 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 172.2, 159.5, 156.2 (q, $^2J_{\text{F-c}}$ = 37.1 Hz), 138.8, 134.8, 129.5, 124.7, 119.8, 115.9 (q, $J_{\text{F-C}}$ = 288.1 Hz), 113.6, 113.0, 57.5, 55.2, 52.0, 41.4, 37.5, 16.8; IR (neat) ν_{max}: 2360, 1716, 1167 cm^{-1}; $[\alpha]^{23}_{D}$ = +104 ° (c = 7.55, CH$_2$Cl$_2$); HRMS: Calculated for $C_{17}H_{20}F_3NO_4$: 359.1344, found 382.1266 (M+Na).



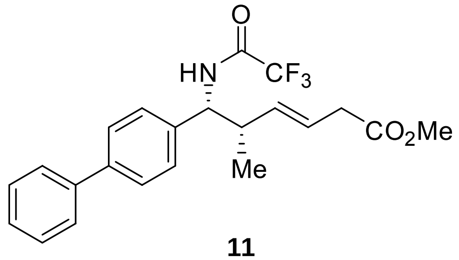
9

(5*S*,6*R*,E)- Methyl 6-(4-methoxyphenyl)-5-methyl-6-(2,2,2-trifluoroacetamido)hex-3-enoate (9);
(87% yield, d. r. = 15:1, e. r. = 89:11). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.31 (d, 1H, *J* = 8.8 Hz), 7.10 (d, 2H, *J* = 8.8 Hz), 6.86 (d, 2H, *J* = 8.6 Hz), 5.61 (m, 1H), 5.29 (dd, 1H, *J* = 8.5 Hz, *J* = 15.8 Hz), 4.89 (dd, 1H, *J* = 5.7 Hz, *J* = 8.7 Hz), 3.76 (s, 3H), 3.66 (s, 3H), 3.05 (m, 2H), 2.66 (m, 1H), 0.98 (d, 3H, *J* = 6.8 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 172.5, 159.4, 156.5 (q, $^2J_{\text{F-C}}$ = 36.9 Hz), 135.2, 123.0, 128.8, 124.7, 116.2 (q, $J_{\text{F-C}}$ = 287.9 Hz), 114.0, 57.6, 55.4, 52.1, 41.6, 37.7, 17.1; IR (neat) ν_{max}: 2360, 1715, 1178 cm^{-1}; $[\alpha]^{23}_{D}$ = +120.0° (c = 10.45, CH$_2$Cl$_2$); HRMS: Calculated for $C_{17}H_{20}F_3NO_4$: 359.1344, found 382.1236 (M+Na).



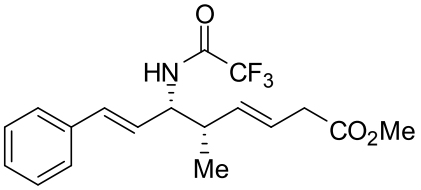
10

(5*S*,6*R*,E)- Methyl 5-methyl-6-(naphthalen-2-yl)-6-(2,2,2-trifluoroacetamido)hex-3-enoate (10); (99% yield, d. r. = 15:1, e. r. = 96:4). m. p. = 87 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-7.81 (m, 3H), 7.69 (s, 1H), 7.51-7.48 (m, 2H), 7.42 (d, 1H, J = 8.6 Hz), 7.33 (d, 1H, J = 8.5 Hz), 5.62 (m, 1H), 5.34 (dd, 1H, J = 8.1 Hz, J = 14.9 Hz), 5.11 (m, 1H), 3,65 (s, 3H), 3.03 (m, 2H), 2.79 (m, 1H), 1.06 (d, 3H, J = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 156.4 (q, $^{2}J_{F\text{-}C}$ = 37.0 Hz), 134.9, 134.8, 132.9, 132.8, 128.2, 127.9, 127.5, 126.7, 126.3, 126.2, 124.9, 124.6, 115.9 (q, $J_{\text{F-C}}$ = 288.0 Hz), 57.9, 51.8, 41.4, 37.4, 16.8; IR (neat) ν_{max}: 1713, 1202, 1170 cm^{-1}; $[\alpha]^{23}_{\text{D}}$ = +151.6 ^{o} (c = 17.60, CH_2Cl_2); HRMS: Calculated for $C_{20}H_{20}F_3NO_3$: 379.1395, found 402.1299 (M+Na).



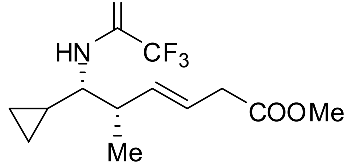
11

(5*S*,6*R*,E)- Methyl 6-(biphenyl-4-yl)-5-methyl-6-(2,2,2-trifluoroacetamido)hex-3-enoate (11); (87% yield, d. r. = 15:1, e. r. = 99:1). m. p. = 115 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (m, 4H), 7.39 (t, 2H, J = 7.4 Hz), 7.30 (t, 1H, J = 7.3 Hz), 7.23-7.21 (m, 3H), 5.59 (m, 1H), 5.30 (dd, 1H, J = 8.9 Hz, J = 15.3 Hz), 4.98 (dd, 1H, J = 6.2 Hz, J = 8.6 Hz), 3.69 (s, 3H), 3.01 (m, 2H), 2.67 (m, 1H), 0.99 (d, 3H, J = 6.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 156.3 (q, $^{2}J_{\text{F-C}}$ = 37.1 Hz), 140.8, 140.4 136.3, 134.8, 128.8, 127.9, 127.4, 127.1, 127.0, 124.9, 116.0 (q, $J_{\text{F-C}}$ = 288.0 Hz), 57.3, 52.0, 41.4, 37.4, 16.8; IR (neat) ν_{max}: 3320, 1731, 1698, 1172 cm^{-1}; $[\alpha]^{23}_{\text{D}}$ = +159.6 ^{o} (c = 8.45, CH_2Cl_2); HRMS: Calculated for $C_{22}H_{22}F_3NO_3$: 405.1552, found 428.1468 (M+Na).



12

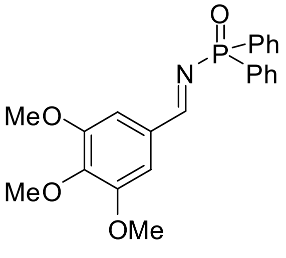
(3*E*,5*S*,6*S*,7*E*)- Methyl 5-methyl-8-phenyl-6-(2,2,2-trifluoroacetamido)octa-3,7-dienoate (12); (80% yield, d. r. = 10:1, e. r. = 97:3). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.14 (m, 5H), 6.68 (s, 1H), 6.46 (d, 1H, J = 15.9 Hz), 5.94 (ddd, 1H, J = 1.0 Hz, J = 7.6 Hz, J = 15.9 Hz), 5.57 (td, 1H, J = 7.3 Hz, J = 14.5 Hz), 5.36 (ddd, 1H, J = 1.0 Hz, J = 9.0 Hz, J = 15.4 Hz), 4.51 (dd, 1H, J = 8.2 Hz, J = 13.3 Hz), 3.60 (s, 3H), 3.05-2.94 (m, 2H), 2.45 (qd, 1H, J = 6.8 Hz, J = 13.4 Hz), 1.01 (d, 3H, J = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 156.2 (q, $^{2}J_{\text{F-C}}$ = 36.9 Hz), 136.0 115.9 (q, $J_{\text{F-C}}$ = 288.2 Hz), 134.6, 133.9, 128.6, 128.1, 126.5, 125.3, 123.8, 55.8, 52.0, 41.4, 37.5, 16.9; IR (neat) ν_{max}: 2360, 1714, 1170 cm^{-1}; $[\alpha]^{23}_{\text{D}}$ = +118.8^{o} (c = 9.92, CH_2Cl_2); HRMS: Calculated for $C_{18}H_{20}F_3NO_3$: 355.1395, found 378.1310 (M+Na).



13

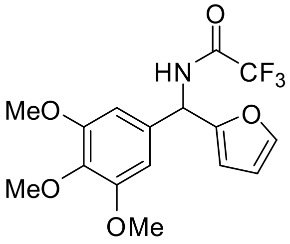
(5*S*,6*S*,*E*)-Methyl-6-cyclopropyl-5-methyl-6-(2,2,2-trifluoroacetamido)hex-3-enoate (13); (53% yield, d. r. = 10:1, e. r. 97:3 by Trost mandelamide analysis, see SI-9 for details). m. p. = 69 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.58 (s, 1H), 5.63-5.51 (m, 2H), 3.67 (s, 3H), 3.25 (dt, 1H, J = 5.1 Hz, J = 9.4 Hz), 3.06 (m, 2H), 2.51 (m, 1H), 1.13 (d, 3H, J = 7.0 Hz), 0.92-0.86 (m, 1H), 0.67-0.61 (m, 1H), 0.50-0.25 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 156.5 (q, $^{2}J_{\text{P-C}}$ = 36.7 Hz), 135.2, 124.2, 116.0 (q, $J_{\text{P-C}}$ = 288.1 Hz), 58.7, 51.9, 41.6, 37.6, 16.9, 11.9, 5.5, 1.8; IR (neat) ν_{max}: 1711, 1200, 1177 cm^{-1}; $[\alpha]^{23}_{\text{D}}$ = -15.4^{o} (c = 12.64, CH_2Cl_2); HRMS: Calculated for $C_{13}H_{18}F_3NO_3$: 293.2821, found 316.1125 (M+Na).

III. Experimental Procedures and Characterization Data for Friedel-Crafts and (*aza*)-ene products



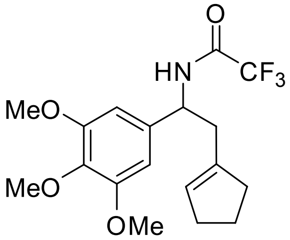
14

(*E*)-P,P-Diphenyl-*N*-(3,4,5-trimethoxybenzylidene)phosphinic amide (14):[1] To a solution of 3,4,5-trimethoxybenzaldehyde (0.45 g, 2.30 mmol), diphenylphosphinamide (0.50 g, 2.30 mmol), triethylamine (0.96 mL, 6.90 mmol) in methylene chloride (15 mL) at -20 ^{o}C was added titanium tetrachloride (0.126 mL, 1.15 mmol) dropwise. The reaction mixture was allowed to stir for 2 h before solvent was removed *in vacuo*. The concentrate was washed with ethyl acetate and the precipitate removed by filtration through Celite. The filtrate containing crude product was concentrated *in vacuo*. Column chromatography (SiO_2, CH_2Cl_2/acetone, 9:1) afforded product **14** (0.76 g, 84%) as a white solid, m. p. = 189 ^{o}C ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (d, 1H, $J_{P\text{-}H}$ = 31.8 Hz), 7.94-7.89 (m, 4H), 7.53-7.43 (m, 6H), 7.26 (s, 2H), 3.95 (s, 6H), 3.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1 (d, $^3J_{P\text{-}C}$ = 7.4 Hz), 153.5, 143.1, 133.5, 131.8 (d, 2C, $^4J_{F\text{-}C}$ = 2.8 Hz), 131.5 (d, 6C, $^3J_{F\text{-}C}$ = 9.4 Hz), 131.1 (d, 2C, $^2J_{F\text{-}C}$ = 25.4 Hz), 128.4 (d, 2C, $J_{F\text{-}C}$ = 12.5 Hz), 107.3, 61.0, 56.3; HRMS: Calculated for $C_{22}H_{22}NO_4P$: 395.1286, found 418.1195 (M+Na).



15

2,2,2-Trifluoro-*N*-(furan-2-yl(3,4,5-trimethoxyphenyl)methyl)acetamide (15); To a round-bottom flask was added hydrated lanthanum triflate (23 mg, 0.030 mmol), trifluoroacetic anhydride (107 µL, 0.76 mmol), and ACS-grade acetonitrile (0.7 mL, 0.3 M). The mixture was sonicated and transferred by syringe to a 10 mL microwave reaction vessel containing a mixture of phosphinylimine **14** (60 mg, 0.20 mmol) and furan (56 µL, 0.76 mmol). The mixture was vortexed until clear and then microwaved at 60 ^{o}C (10 W) for 20 min. The solvent was removed *in vacuo* and the crude material purified by column chromatography (SiO_2, EtOAc/hexanes, 9:1) to afford Friedel-Crafts product **15** (44 mg, 88%) as a yellow solid. m. p. = 132 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, 1H, J = 1.8 Hz), 6.97 (br s, 1H), 6.50 (s, 2H), 6.37 (dd, 1H, J = 1.8, 3.2 Hz), 6.23 (d, 1H, J = 3.2Hz), 6.18 (d, 1H, J = 8.2 Hz), 3.83 (s, 3H), 3.82 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3 (q, $^2J_{F\text{-}C}$ = 37.6 Hz), 153.6, 151.1, 143.1, 138.1, 133.0, 115.7 (q, $J_{F\text{-}C}$ = 288.1 Hz), 110.6, 108.7, 104.3, 60.8, 56.1, 52.0; HRMS: Calculated for $C_{18}H_{20}F_3NO_3$: 359.0981, found 382.0894 (M+Na).



16

***N*-(2-Cyclopentenyl-1-(3,4,5-trimethoxyphenyl)ethyl)-2,2,2-trifluoroacetamide (16);** To a round-bottom flask was added hydrated lanthanum triflate (23 mg, 0.030 mmol), trifluoroacetic anhydride (107 µL, 0.076 mmol), and ACS-grade acetonitrile (0.5 mL, 0.3 M). The mixture was sonicated and transferred by syringe to a 10 mL microwave reaction vessel containing a mixture of phosphinylimine **14** (60 g, 0.152 mmol) and methylenecyclopentane (80 µL, 0.076 mmol)). The mixture was vortexed until clear and then microwaved at 60 ^{o}C (10W) for 20 min. The solvent was removed *in vacuo* and the crude material purified by column chromatography (SiO_2, EtOAc/hexanes, 9:1) to afford *aza*-ene product **16** (52 mg, 91%) as an oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.49 (s, 2H), 5.48 (s, 1H), 5.05 (dd, 1H, J = 7.9Hz, J = 14.9Hz), 3.84 (s, 3H), 3.82 (s, 6H), 2.64 (d, 1H, J = 8.6Hz), 2.29 (t, 2H, J = 7.4Hz), 2.20 (m, 2H), 1.84 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4 (q, $^2J_{F\text{-}C}$ = 36.9 Hz), 153.5, 139.4, 137.7, 135.9, 128.3, 115.8 (q, $J_{F\text{-}C}$ = 288.2 Hz), 103.4, 60.8, 56.1, 52.5, 37.6, 34.7, 32.4, 23.5; HRMS: Calculated for $C_{18}H_{20}F_3NO_3$: 373.1501, found 396.1428 (M+Na).

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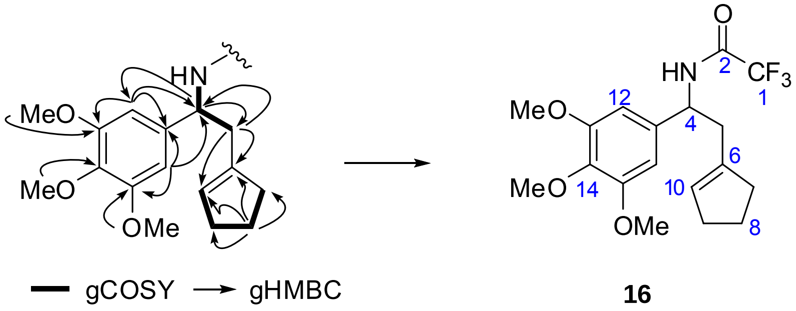
[1] W. B. Jennings, C. J. Lovely, *Tetrahedron Lett.* **1988**, *29*, 3725.

NMR Structure Elucidation for Trifluoroacetamide 16.

The structure elucidation of **16** began with a side-by-side comparison of its ^{1}H and ^{13}C NMR spectra with that of precursor **14** and methylenecyclopentane. This analysis indicated the presence of the tetrasubtituted phenyl moiety as well as a cyclopentyl ring in the aza-ene product **16** which was corraborated by the gHMBC and gCOSY correlations as shown in Figure 1. Further, key gHMBC correlations from δ_H 5.05 and 2.64 to δ_C 37.6 and 52.5 respectively, as well as a gCOSY correlation between these two protons, connect the terminal olefenic carbon of **16** to the iminium carbon of **14** in the aza-ene product. Other gHMBC correlations between the methylene protons at δ_H 1.84 to the olefenic carbons at δ_C 139.4 and 128.3 supported the endocyclic nature of the double bond in the product. All these correlations along with the observed ^{1}H and ^{13}C chemical shifts of **16** supports connectivity of the partial structure shown below. Finally, the two quartets observed at δ_C 156.4 ($^{2}J_{F\text{-}C}$ 36.9 Hz) and 115.8 ($J_{F\text{-}C}$ 115.8 Hz) in the ^{13}C NMR characterized the trifluoroacetyl moiety while the upfield shift of the carbonyl at at δ_C 156.4, indicates its attachment to the nitrogen as depicted in the complete structure of *aza*-ene product **16**.



16

Figure 1. gHMBC and gCOSY correlations observed for **16.**

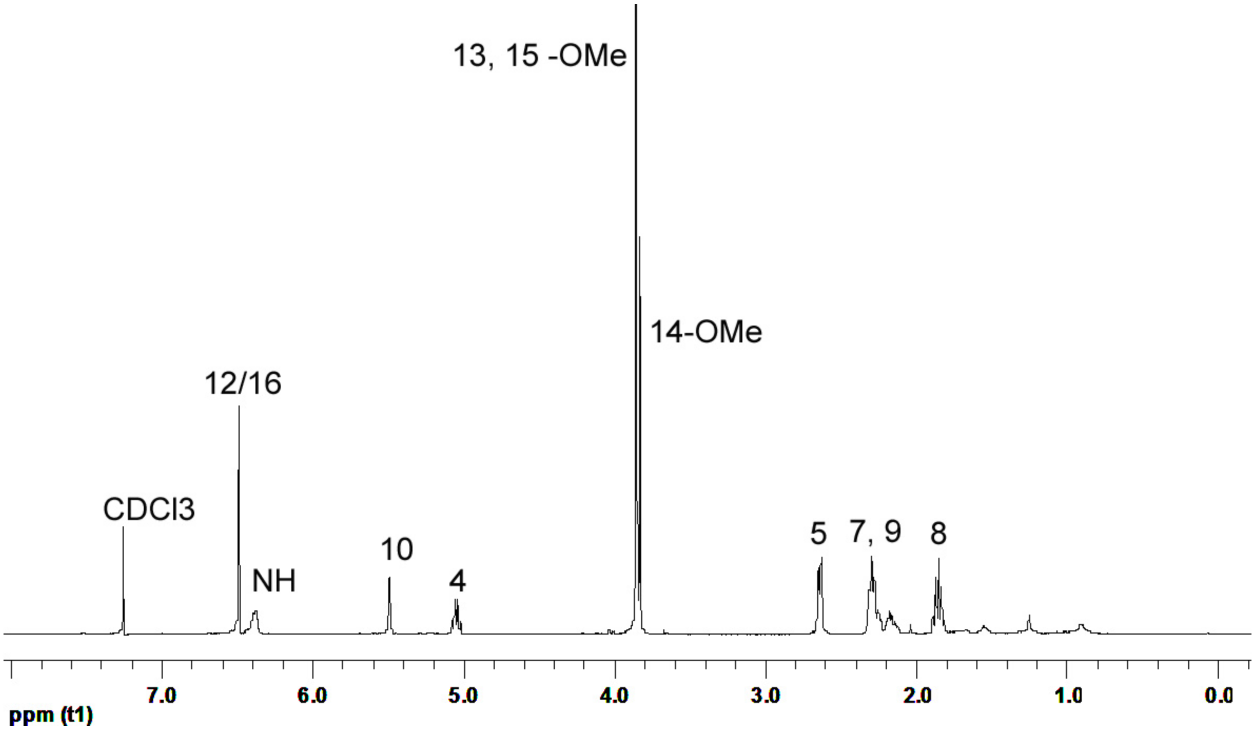


Figure 2. ^{1}H NMR of **16** (400 MHz, CDCl$_3$).

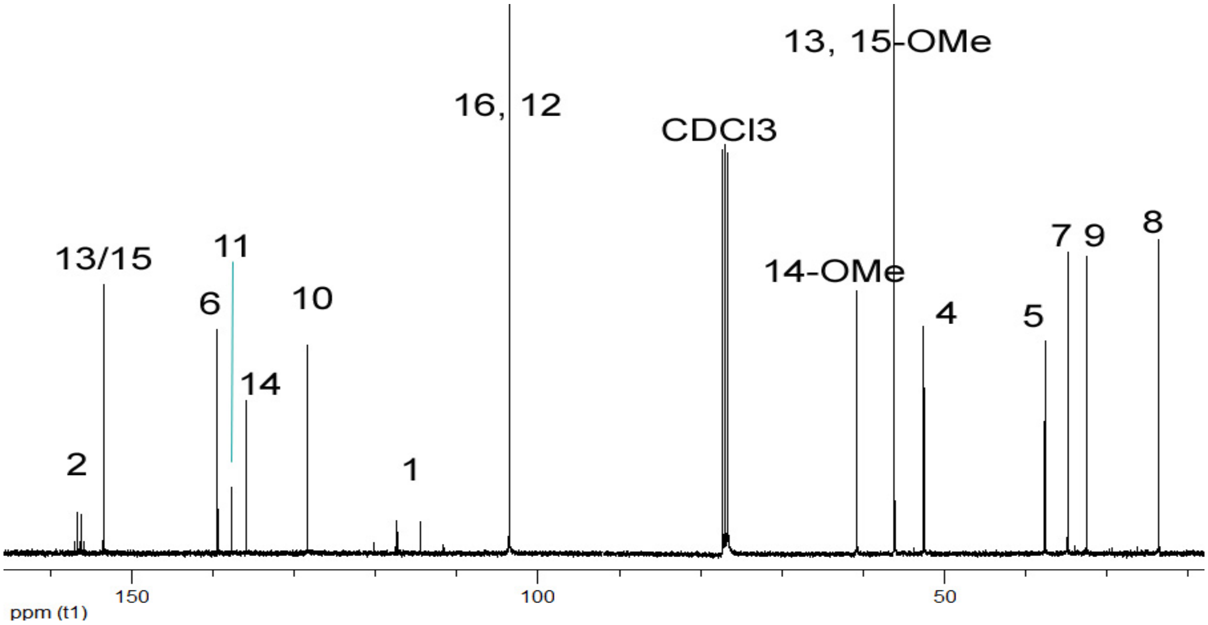


Figure 3. ^{13}C NMR of **16** (100 MHz, CDCl$_3$).

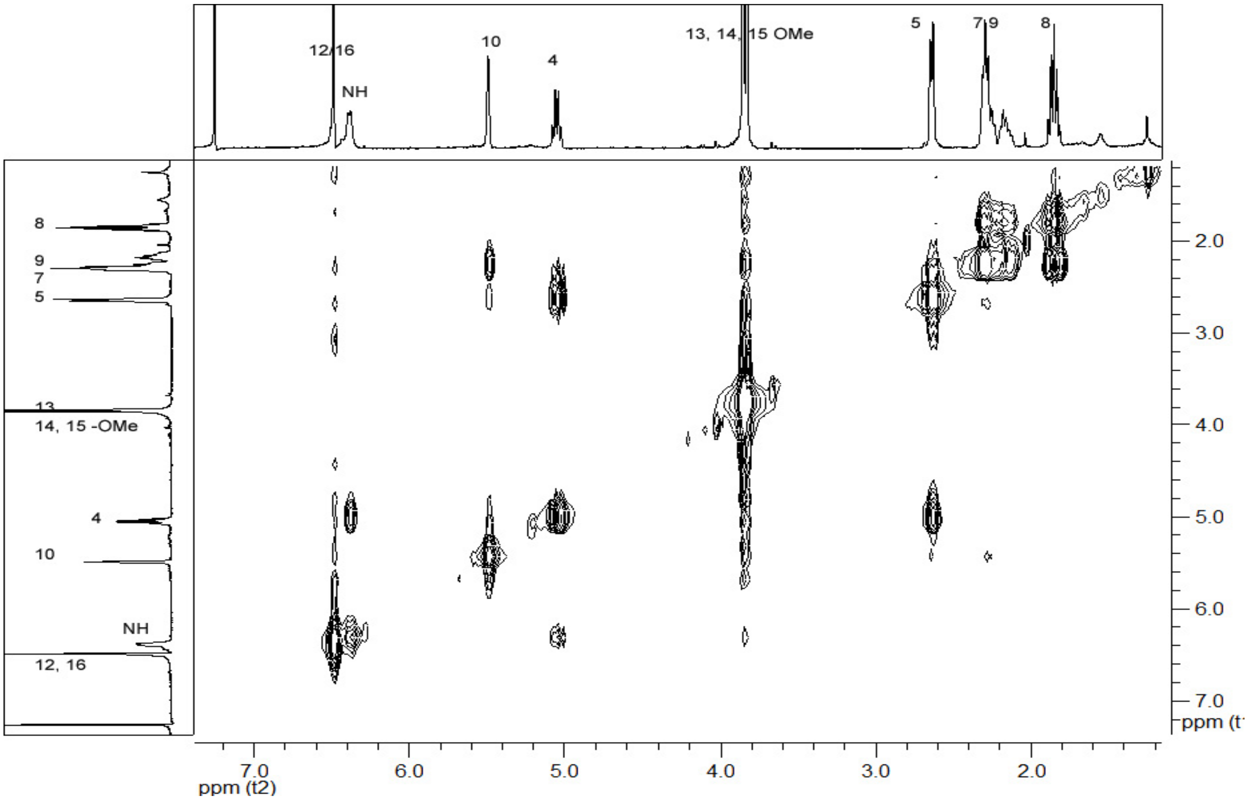


Figure 4. gCOSY NMR of **16** (400 MHz, CDCl$_3$).

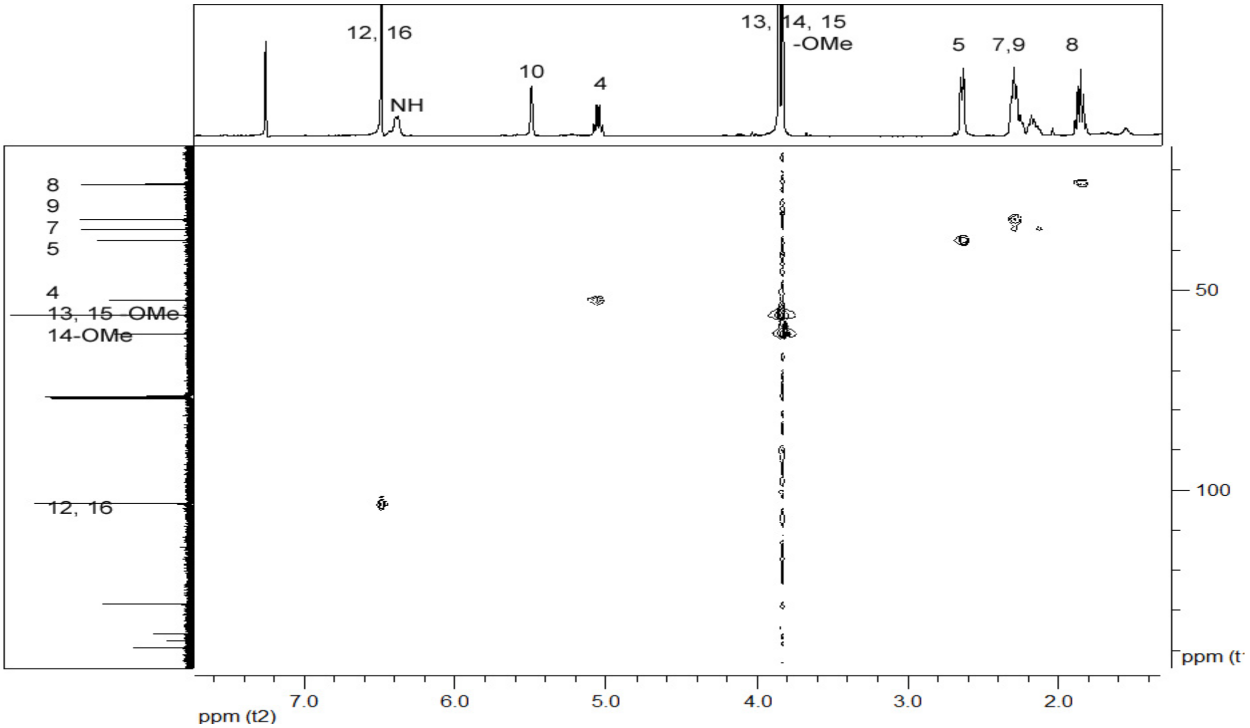


Figure 5. gHMQC NMR of **16** ($CDCl_3$).

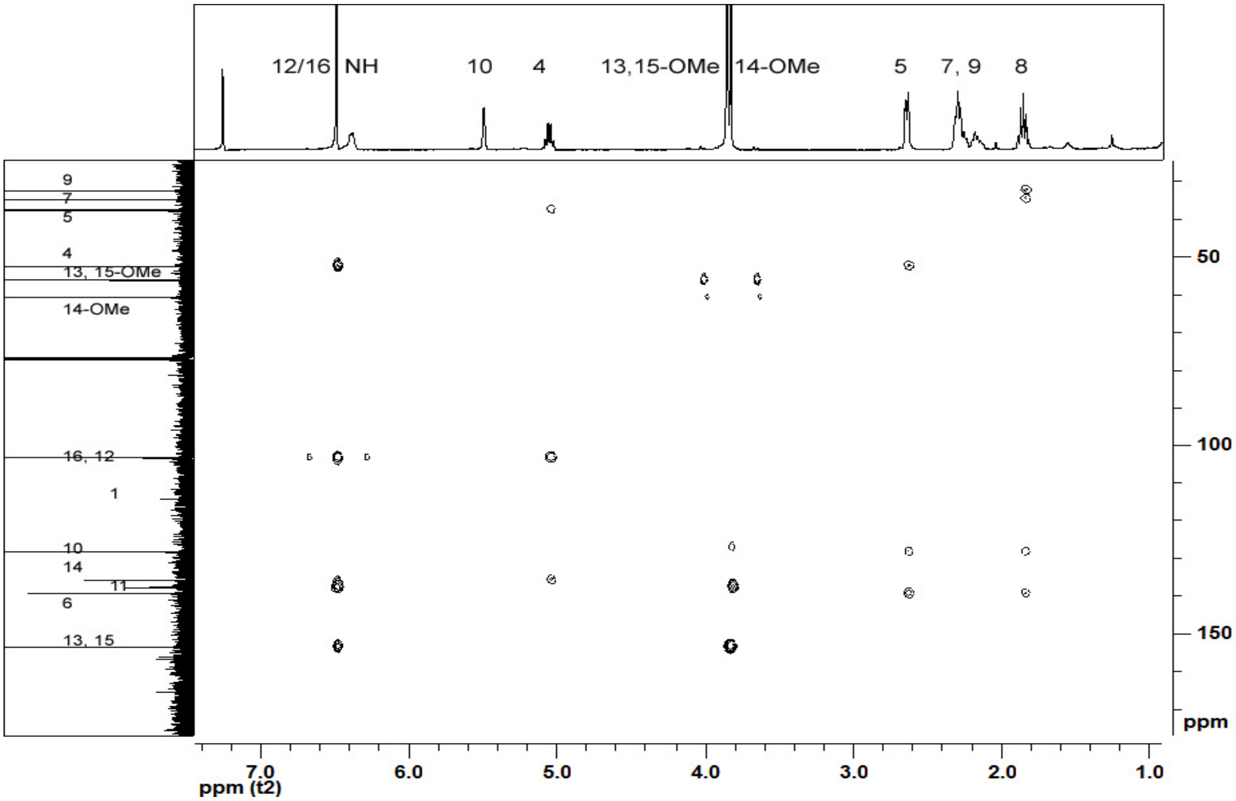
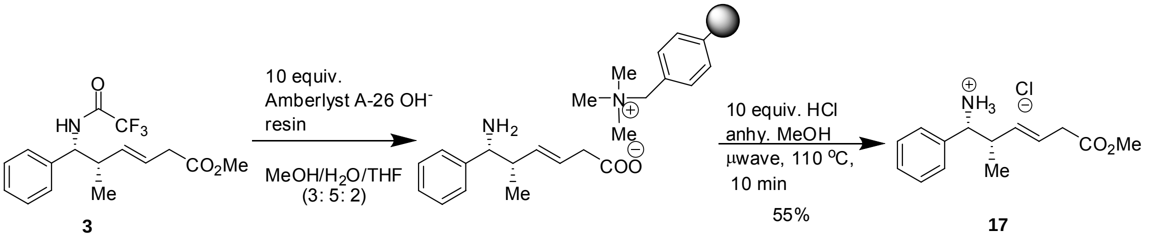
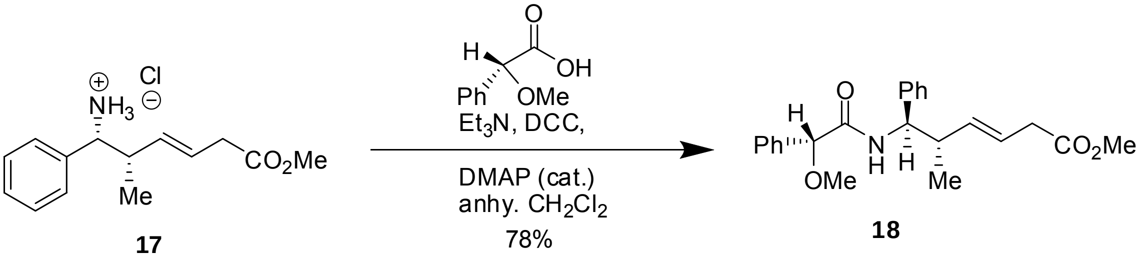


Figure 6. gHMBC NMR of **16** ($CDCl_3$).

IV. Experimental Procedures and Characterization Data for aminoester 17 and mandelamide 18.



General Procedure for Aminoester Formation: (1*R*, 2*S*, *E*)-6-methoxy-2-methyl-6-oxo-1-phenylhex-3E-1-aminium chloride (17). To a 10 mL microwave reaction vessel was added trifluoroacetamide **3** (100 mg, 0.30 mmol) and Amberlyst A-26 OH$^-$ resin (723 mg, 3.00 mmol) in a solution of methanol/water/THF (3: 5: 2) (11.6 mL, 0.03 M). The resulting mixture was agitated in an Autochem Miniblock for 1 day. The resin was filtered, washed twice with methanol (30 mL), and dried *in vacuo*. Anhydrous methanol (0.61 mL, 0.5 M) and acetyl chloride (0.22 mL, 3.0 mmol) were added under argon and the reaction was incubated in a microwave at 110 ^{o}C (300 W) for 10 minutes. The resin was filtered and washed with methanol (2 x 10 mL), and the solvent evaporated *in vacuo* to afford aminoester **17** (39 mg, 55 %, dr = 10:1) as a white solid after recrystallization from diethyl ether. m. p. = 199 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (s, 5H), 5.65 (m, 1H), 5.21 (dd, 1H, *J* = 8.4 Hz, *J* = 15.4 Hz), 4.19 (d, 1H, *J* = 5.7 Hz), 3.59 (s, 3H), 3.06 (ddd, 1H, *J* = 1.4 Hz, *J* = 6.4 Hz, *J* = 16.6 Hz), 2.92 (ddd, 1H, *J* = 1.4 Hz, *J* = 6.4 Hz, *J* = 16.6 Hz, par. obsc.), 2.94-2.92 (m, 1H), 1.05 (d, 3H, *J* = 6.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 135.2, 132.3, 128.5, 127.9, 126.2, 60.4, 51.7, 40.6, 37.8, 17.1; IR (neat) ν_{max}: 2947, 2620, 2339, 1741, 1523 cm^{-1}; $[\alpha]^{23}_D$ = +27.5 ^{o} (c = 2.00, CH_2Cl_2); HRMS: Calculated for $C_{14}H_{20}NO_2$: 234.1183, found 256.1293 (M+Na).



(5*S*,6*R*,7*E*)-methyl 6-((*R*)-2-methoxy-2-phenylacetamido)-5-methyl-6-phenylhex-3-enoate (18). [2] To a solution of aminoester **17** (15 mg, 0.064 mmol) in CH_2Cl_2 (0.32 mL, 0.2 M) was added Et_3N (35.7 μL, 0.26 mmol), (*R*)-*O*-methylmandelic acid (11.8 mg, 0.071 mmol), DCC (17.2 mg, 0.084 mmol), and DMAP (0.40 mg, 0.0032 mmol). The reaction mixture was stirred overnight at room temperature. The reaction mixture was then filtered to remove dicyclohexylurea and concentrated *in vacuo*. The crude material was purified by chromatography (SiO_2, EtOAc/Hexanes, 1:9) (19 mg, 78 %) to afford amide **18** as a white solid. m. p. = 97 ^{o}C; ^{1}H NMR (400 MHz, CDCl3) δ 7.46-7.24 (m, 10H), 5.49 (m, 1H), 5.32 (dd, 1H, *J* = 8.0 Hz, *J* = 15.5 Hz), 4.93 (dd, 1H, *J* = 6.1 Hz, *J* = 9.1Hz), 4.62 (s, 1H), 3.70 (s, 3H), 3.38 (s, 3H), 3.06 (ddd, 1H, *J* = 1.4 Hz, *J* = 6.4 Hz, *J* = 16.6 Hz), 2.97 (d, 2H, *J* = 6.9 Hz), 2.64 (m, 1H), 0.95 (d, 3H, *J* = 6.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 169.6, 139.6, 137.2, 135.5, 128.5, 128.3, 128.2, 127.4, 127.2, 126.8, 123.3, 83.9, 57.3, 56.4, 51.8, 41.7, 37.8, 16.3; IR (neat) ν_{max}: 1731, 1653, 1525 cm^{-1}; $[\alpha]^{23}_D$ = +11.3^{o} (c = 5.28, CH_2Cl_2); HRMS: Calculated for $C_{14}H_{20}NO_2$: 381.1940, found 404.1856 (M+Na).

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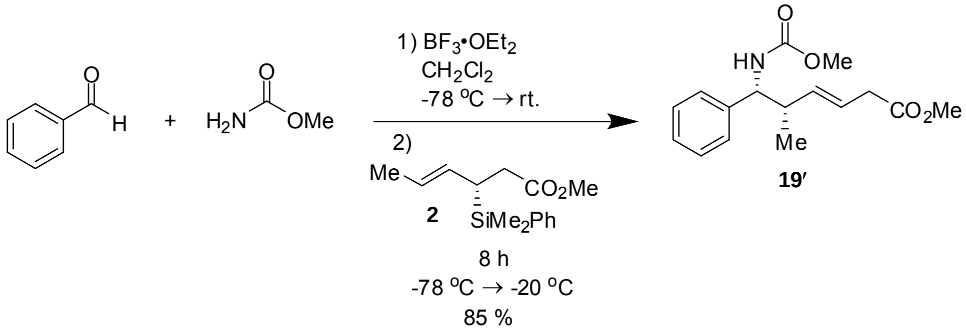
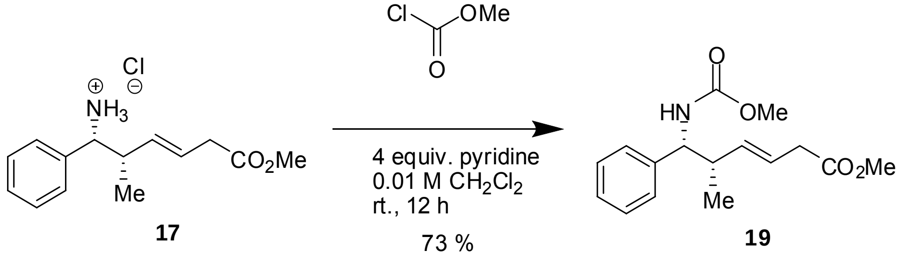
[2] B. Trost, R. C. Bunt, S. R. Pulley, *J. Org. Chem.* **1994**, *59*, 4202.

V. Synthesis of methyl carbamate 19'[3]



To a reaction vessel was added benzaldehyde (41 μL, 0.40 mmol) and methyl carbamate (50 mg, 0.40 mmol) in anhydrous CH_2Cl_2 (2.0 mL, 0.5 M). The reaction was cooled to -78 °C and $BF_3 \cdot OEt_2$ (99 μL, 0.80 mmol) was added dropwise under an argon atmosphere. The mixture was warmed to room temperature and stirred for 10 min. at which time a yellow, homogeneous solution was observed. The reaction mixture was then recooled to -78 °C and a solution of crotylsilane **2** (100 mg, 0.38 mmol) in CH_2Cl_2 (0.5 mL) was added dropwise over a 10 min. period. The reaction mixture was quickly warmed to -25 °C and was monitored by TLC analysis (EtOAc/hexanes, 4:1). After 8 h, the reaction mixture was quenched with a saturated solution of $NaHCO_3$ (20 mL) and extracted with EtOAc (3 x 20 mL). The organic layers were dried over Na_2SO_4 and concentrated *in vacuo* to afford a crude yellow oil. Purification by column chromatography (SiO_2, EtOAc/hexanes, 4:1) afforded carbamate **19'** (d.r. = 15:1, 99.1 mg, 85 %)as a colorless oil.

Observed $[\alpha]^{23}_{D}$ for **21'**= +62° (c = 3.0, CH_2Cl_2)



To a solution of aminoester **17** (20 mg, 0.086 mmol) in CH_2Cl_2 (0.17 mL, 0.50 M) was added pyridine (28 μL, 0.34 mmol). The reaction mixture was cooled to 0 °C before methyl chloroformate (0.066 mL, 0.086 mmol) was added dropwise, then warmed to room temperature and allowed to stir for 14 h. Iced water was added slowly to the mixture and allowed to stir for 15 min. The organic layer was removed and the aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL). The organic extracts were combined, washed with 3N HCl (10 mL), brine (20 mL), and dried over anhydrous Na_2SO_4. The mixture was concentrated *in vacuo* and purified by column chromatography (SiO_2, EtOAc/hexanes, 4:1) to afford carbamate **19** (d. r. = >25:1, 18.3 mg, 73 %) as a colorless oil.

Observed $[\alpha]^{23}_{D}$ for **19** = +55° (c = 6.2, CH_2Cl_2)

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[3] (a) J. Schaus, N. Jain, J. S. Panek, *Tetrahedron*. **2000**, *56*, 10263.

VI. ^{1}H NMR analysis of *O*-methylmandelamide 18 and 18'

The absolute configuration of aminoester **5** was further confirmed by preparation of *O*-methylmandelamide derivatives **18** and **18'**. The difference in chemical shifts in the ^{1}H NMR spectra resulting from differential anisotropic magnetic shielding due to the phenyl ring on the diasteromic *O*-methylmandelamide was used to assign the absolute stereochemistry. In **18**, the proximity of proton H_a (**18a**, 2.60 ppm) to the phenyl ring results in an upfield proton shift compared to H_b (**18'a**, 2.69 ppm) thus confirming the relative stereochemistry of the carbon α to the amine with respect to the stereogenic center present in the *O*-methylmandelic acid. The data was used to assign the absolute configuration of **18** and **18'**as shown in **Figure 1**. The diastereromic purity (d.r. = >95:1) of mandelamide **18** also provides a quantitive measure for enantiomeric excess of aminoester **17**.

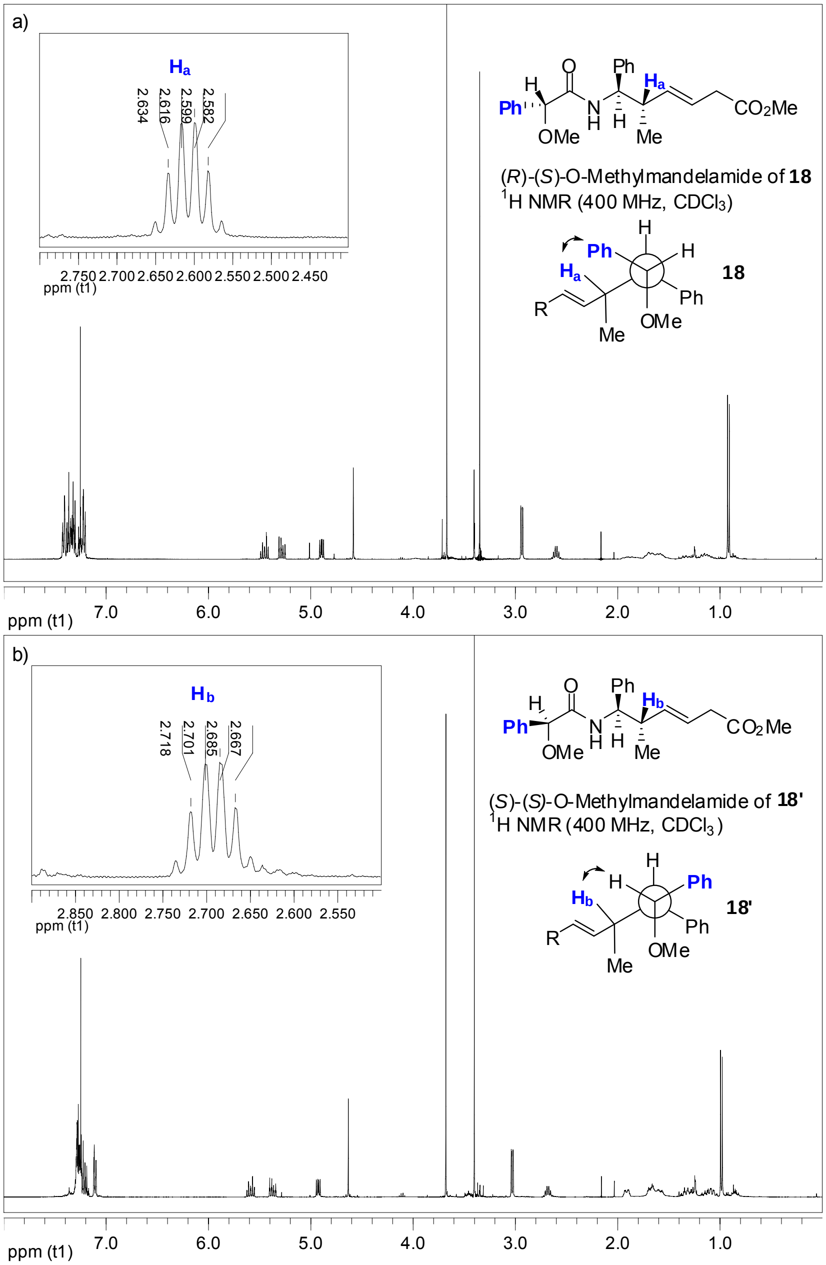


Figure 7. (a) ^{1}H NMR (400 MHz, $CDCl_3$) of (*S*)-(*S*)-*O*-methylmandelamide **18**. (b) ^{1}H NMR (400 MHz, $CDCl_3$) of (*R*)-(*S*)-*O*-methylmandelamide **18'**.

VII. ^{1}H NMR analysis of *O*-methylmandelamide 20 and 20’

The absolute configuration of trifluoroacetamide **13** was further confirmed by preparation of *O*-methylmandelamide derivatives **20** and **20’**. The difference in chemical shifts in the ^{1}H NMR spectra resulting from differential anisotropic magnetic shielding due to the phenyl ring on the diasteromic *O*-methylmandelamide was used to assign the absolute stereochemistry. In **20**, the proximity of proton H_a (**20a**, 2.60 ppm) to the phenyl ring results in an upfield proton shift compared to H_b (**20’a**, 2.69 ppm) thus confirming the relative stereochemistry of the carbon α to the amine with respect to the stereogenic center present in the *O*-methylmandelic acid. The data was used to assign the absolute configuration of **20** and **20’**as shown in **Figure 1**. The diastereromic purity (d.r. = >95:1) of mandelamide **20’** provides a quantitive measure for enantiomeric excess of trifluoroacetamide **13**.

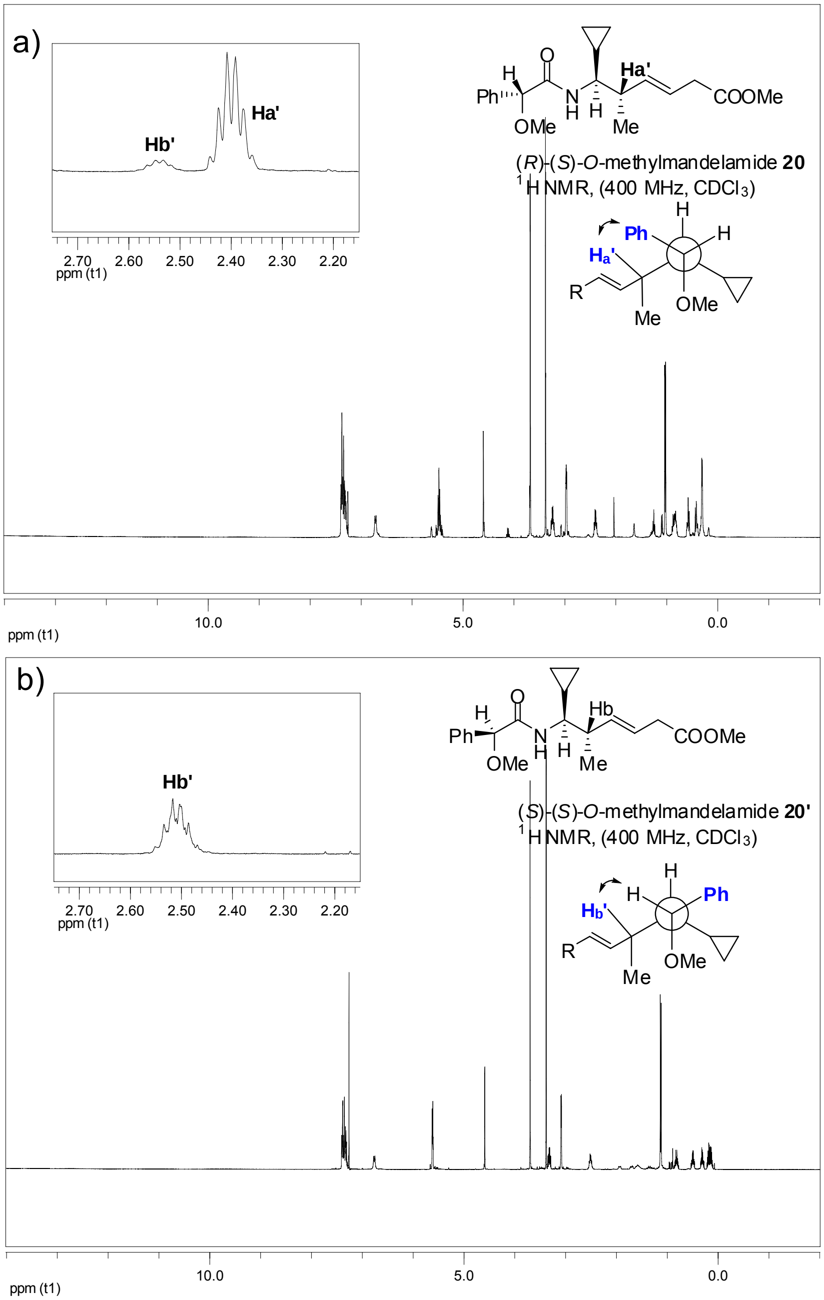
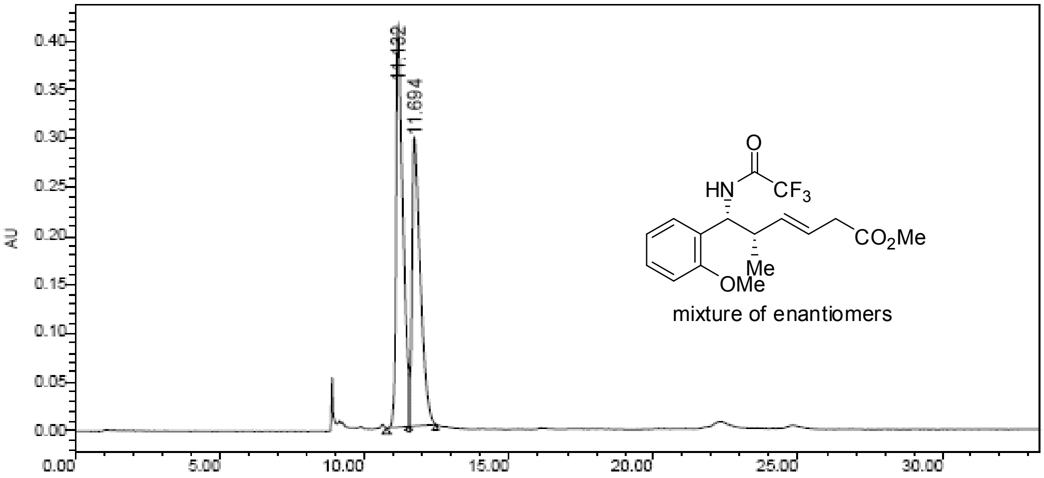


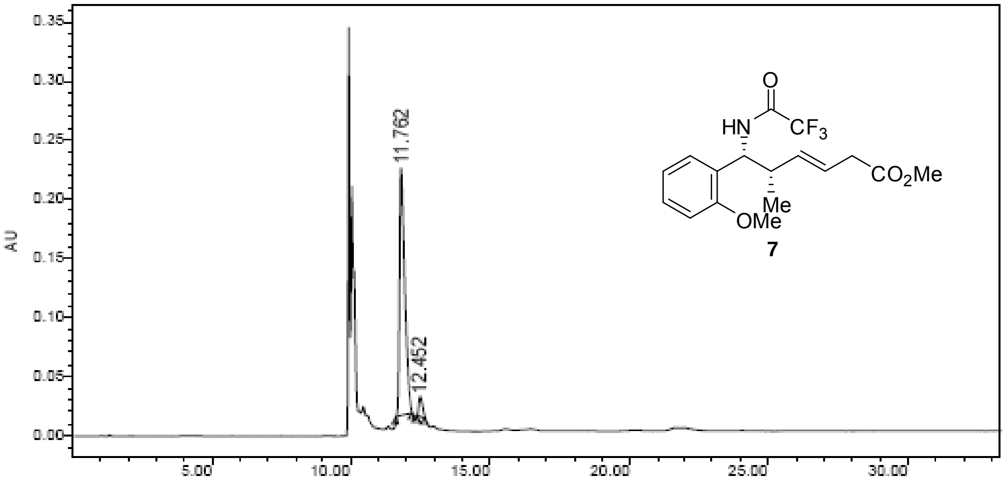
Figure 8. (a) ^{1}H NMR (400 MHz, $CDCl_3$) of (*R*)-(*S*)-*O*-methylmandelamide **20**. (b) ^{1}H NMR (400 MHz, $CDCl_3$) of (*S*)-(*S*)-*O*-methylmandelamide **20’**.

VIII. Chiral HPLC analyses of homoallylic trifluoroacetamide products.



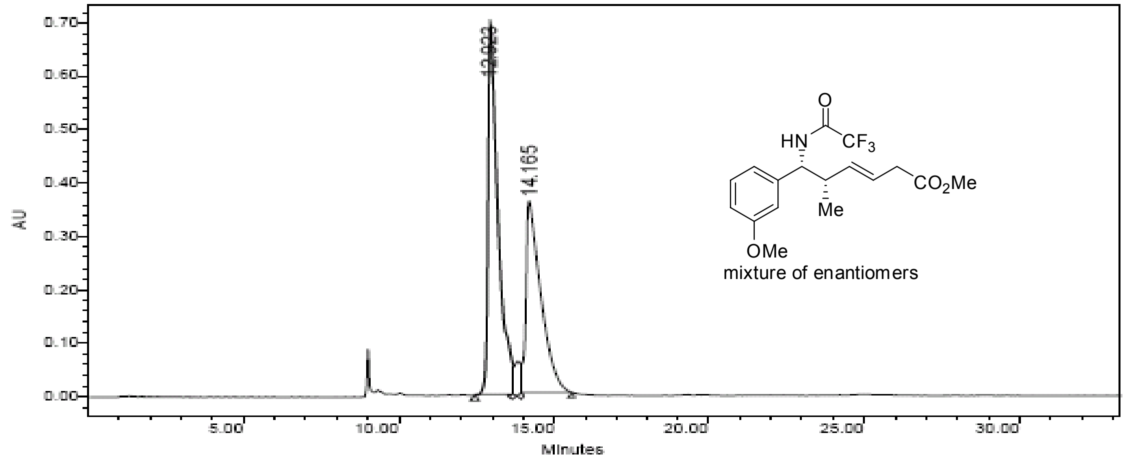
	RT (min)	Peak Type	Area (V*sec)	% Area	Height (V)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	11.132	Unknown	6797875	53.60	412866	58.04	BV	45	10.767	11.533
2	11.694	Unknown	5885077	46.40	298530	41.96	VB	56	11.533	12.467

Chiral HPLC analysis for **(E)-methyl 6-(2-methoxyphenyl)-5-methyl-6-(2,2,2-trifluoroacetamido)hex-3-enoate** (mixture of enantiomers)
Column: Phenomenex Chiradex R-Pgly
Conditions: gradient 0-10% IPA:Hexanes for 35 min, 1.0 mL/min, λ 280 nm, t = 11.1 min, t = 11.7 min



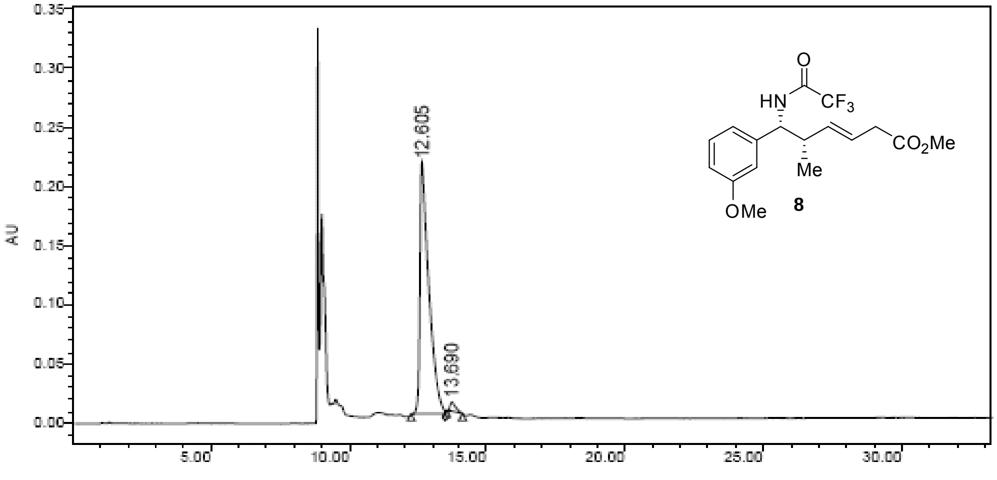
	RT (min)	Peak Type	Area (V*sec)	% Area	Height (V)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	11.762	Unknown	2715212	94.42	213711	92.51	bb	33	11.600	12.167
2	12.452	Unknown	160373	5.58	17305	7.49	bb	16	12.350	12.633

Chiral HPLC analysis for **7**
Column: Phenomenex Chiradex R-Pgly
Conditions: gradient 0-10% IPA:Hexanes for 35 min, 1.0 mL/min, λ 280 nm, t (major) = 11.8 min, t (minor) = 12.5 min



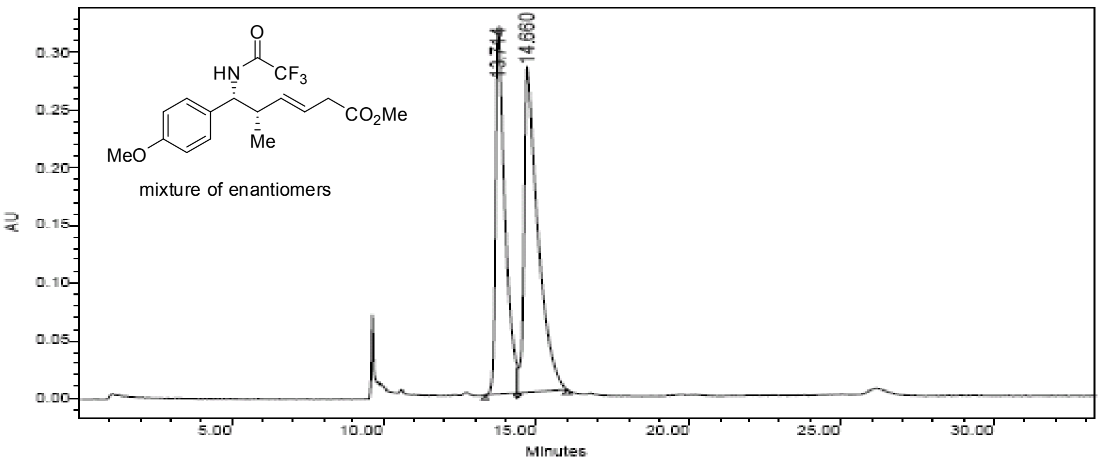
	RT (min)	Peak Type	Area (V*sec)	% Area	Height (V)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	12.923	Unknown	15665653	56.49	695148	65.82	BV	73	12.450	13.683
2	14.165	Unknown	12064093	43.51	361038	34.18	vB	97	13.933	15.567

Chiral HPLC analysis for **(E)-methyl 6-(2-methoxyphenyl)-5-methyl-6-(2,2,2-trifluoroacetamido)hex-3-enoate** (mixture of enantiomers)
Column: Phenomenex Chiradex R-Pgly
Conditions: gradient 0-10% IPA:Hexanes for 35 min, 1.0 mL/min, λ 280 nm, t = 12.9 min, t = 14.2 min



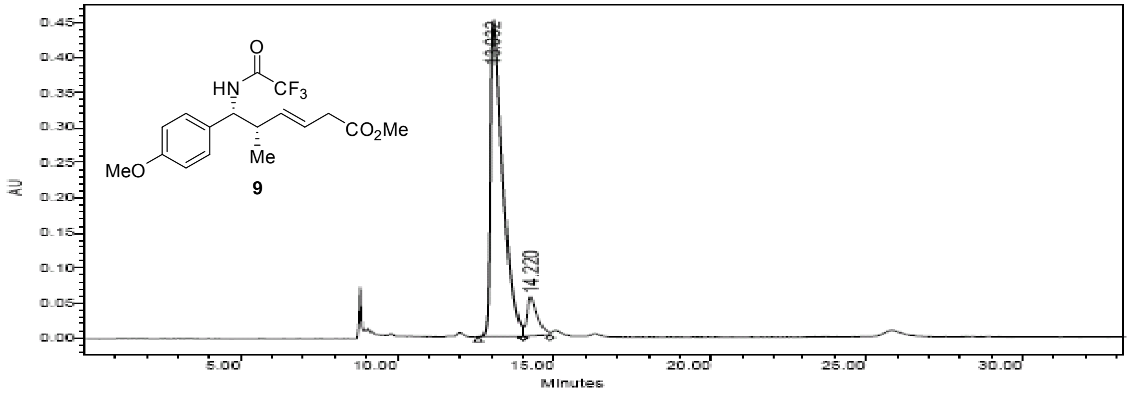
	RT (min)	Peak Type	Area (V*sec)	% Area	Height (V)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	12.605	Unknown	4904116	97.26	214119	96.14	BV	75	12.250	13.500
2	13.690	Unknown	137939	2.74	8596	3.86	bb	33	13.550	14.117

Chiral HPLC analysis for **8**
Column: Phenomenex Chiradex R-Pgly
Conditions: gradient 0-10% IPA:Hexanes for 35 min, 1.0 mL/min, λ 280 nm, t (major) = 12.6 min, t (minor) = 13.7 min



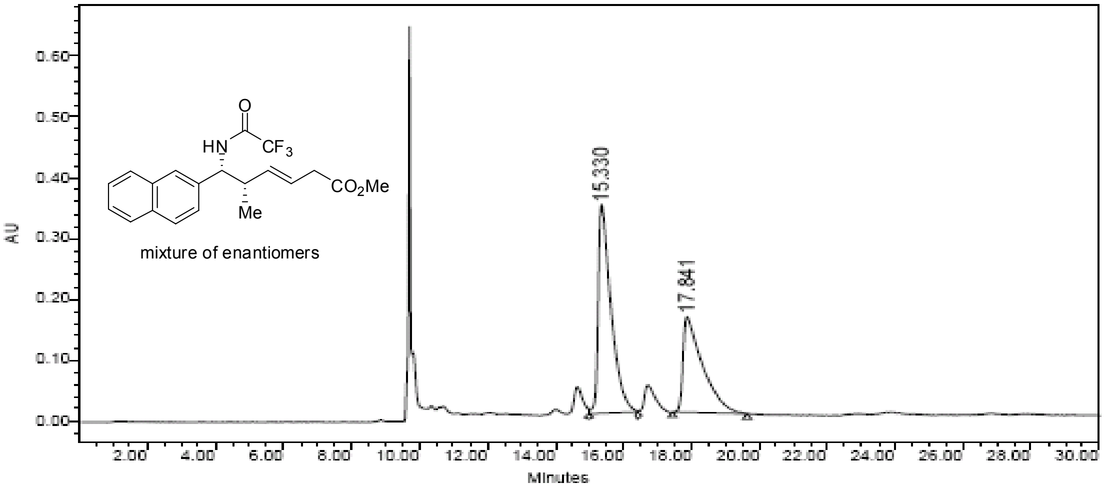
	RT (min)	Peak Type	Area (V*sec)	% Area	Height (V)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	13.714	Unknown	6884481	43.51	318157	52.91	BV	64	13.317	14.383
2	14.660	Unknown	8936783	56.49	283182	47.09	VB	96	14.383	16.000

Chiral HPLC analysis for **(E)-methyl 6-(4-methoxyphenyl)-5-methyl-6-(2,2,2-trifluoroacetamido)hex-3-enoate** (mixture of enantiomers)
Column: Phenomenex Chiradex R-Pgly
Conditions: gradient 0-10% IPA:Hexanes for 35 min, 1.0 mL/min, λ 280 nm, t = 13.7 min, t = 14.7 min



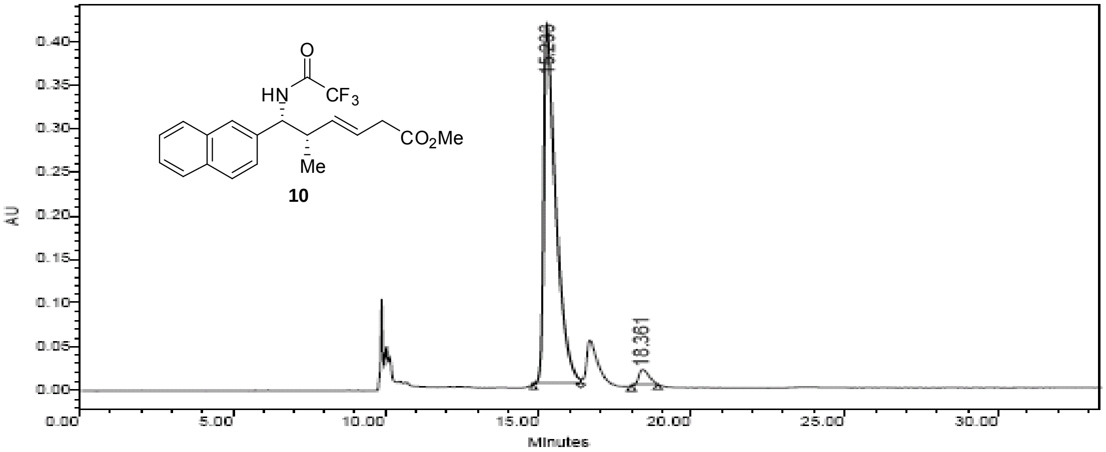
	RT (min)	Peak Type	Area (V*sec)	% Area	Height (V)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	13.032	Unknown	12176063	90.27	449499	88.89	BV	86	12.567	14.017
2	14.220	Unknown	1312581	9.73	56161	11.11	VV	52	14.017	14.883

Chiral HPLC analysis for **9**
Column: Phenomenex Chiradex R-Pgly
Conditions: gradient 0-10% IPA:Hexanes for 35 min, 1.0 mL/min, λ 280 nm, t (major) = 15.3 min, t (minor) = 17.8 min



	RT (min)	Peak Type	Area (V*sec)	% Area	Height (V)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	15.330	Unknown	9101836	58.97	342914	68.47	VV	86	15.000	16.433
2	17.841	Unknown	6334083	41.03	157940	31.53	Bb	131	17.450	19.650

Chiral HPLC analysis for **(E)-methyl 5-methyl-6-(naphthalen-2-yl)-6-(2,2,2-trifluoroacetamido)hex-3-enoate** (mixture of enantiomers)
Column: Phenomenex Chiradex R-Pgly
Conditions: gradient 0-10% IPA:Hexanes for 35 min, 1.0 mL/min, λ 280 nm, t = 15.3 min, t = 17.8 min



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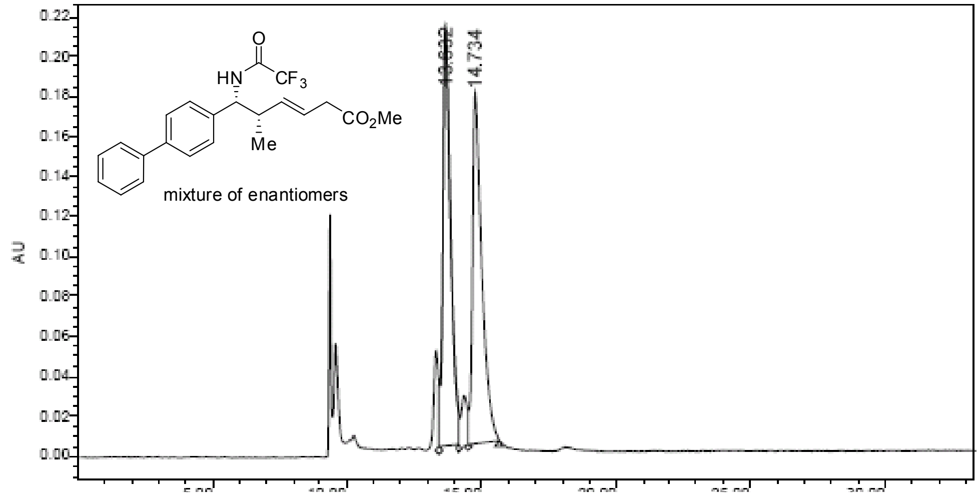
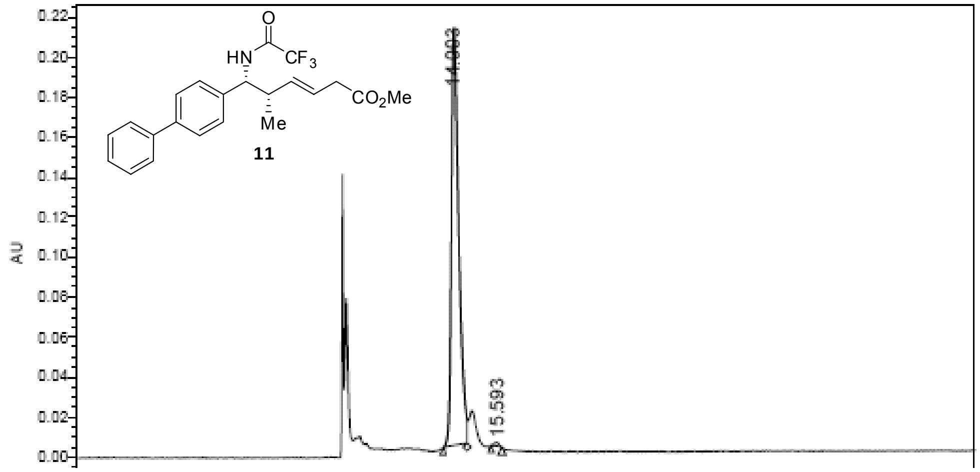
1	15.233	Unknown	11371343	96.31	412590	95.75	BV	93	14.817	16.367
2	18.361	Unknown	435433	3.69	18314	4.25	bb	52	18.033	18.900

Chiral HPLC analysis for **10**
Column: Phenomenex Chiradex R-Pgly
Conditions: gradient 0-10% IPA:Hexanes for 35 min, 1.0 mL/min, λ 280 nm, t (major) = 15.2 min, t (minor) = 18.4 min



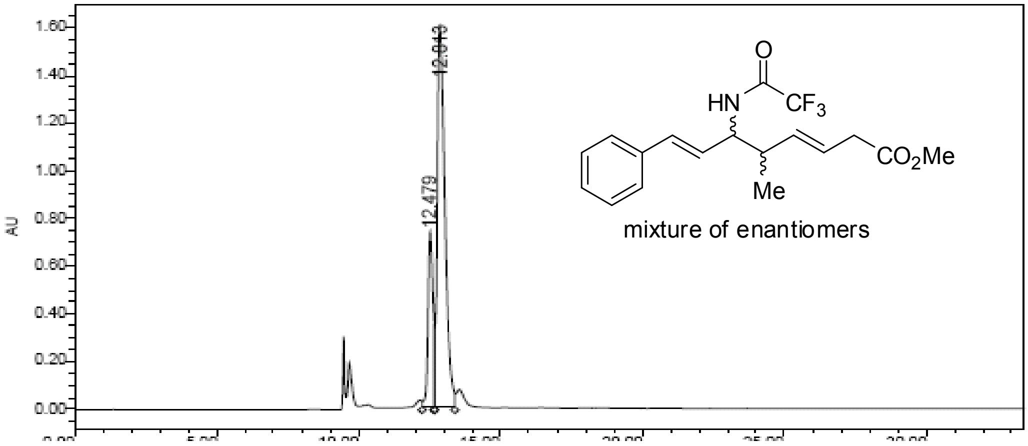
	RT (min)	Peak Type	Area (V*sec)	% Area	Height (V)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	13.632	Unknown	4161106	49.35	209626	54.39	VV	45	13.417	14.167
2	14.734	Unknown	4271204	50.65	175781	45.61	VB	69	14.483	15.650

Chiral HPLC analysis for **(E)-methyl 6-(biphenyl-4-yl)-5-methyl-6-(2,2,2-trifluoroacetamido)hex-3-enoate** (mixture of enantiomers)
Column: Phenomenex Chiradex R-Pgly
Conditions: gradient 0-10% IPA:Hexanes for 35 min, 1.0 mL/min, λ 280 nm, t = 13.6 min, t = 14.7 min



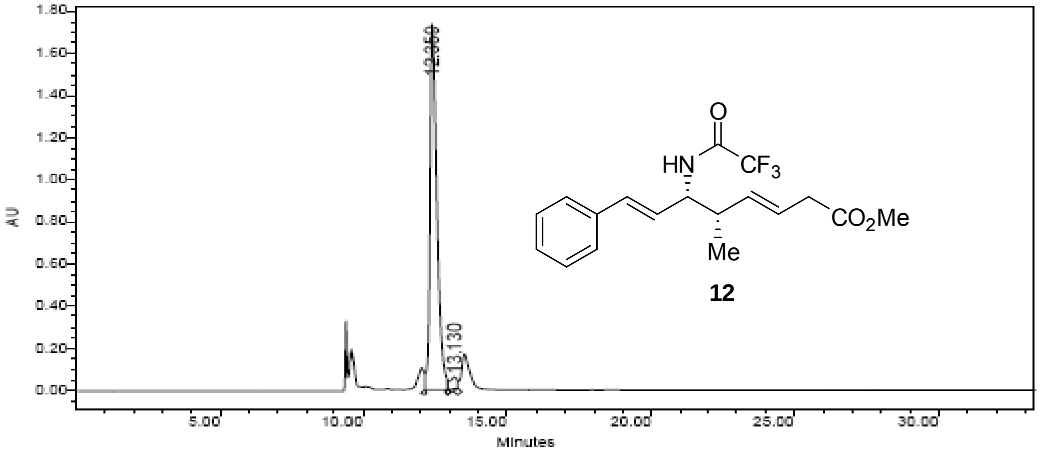
	RT (min)	Peak Type	Area (V*sec)	% Area	Height (V)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	14.003	Unknown	4001121	99.28	209304	98.91	BV	53	13.633	14.533
2	15.593	Unknown	29123	0.72	2310	1.09	bb	23	15.417	15.817

Chiral HPLC analysis for **11**
Column: Phenomenex Chiradex R-Pgly
Conditions: gradient 0-10% IPA:Hexanes for 35 min, 1.0 mL/min, λ 280 nm, t (major) = 14.0 min, t (minor) = 15.6 min



	RT (min)	Peak Type	Area (V*sec)	% Area	Height (V)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	12.479	Unknown	9388891	23.69	740900	31.54	VV	26	12.217	12.650
2	12.813	Unknown	30240712	76.31	1608068	68.46	VV	44	12.650	13.383

Chiral HPLC analysis for **(3E,7E)-methyl 5-methyl-8-phenyl-6-(2,2,2-trifluoroacetamido)octa-3,7-dienoate** (mixture of enantiomers)
Column: Phenomenex Chiradex R-Pgly
Conditions: gradient 0-10% IPA:Hexanes for 35 min, 1.0 mL/min, λ 280 nm, t = 12.5 min, t = 12.8 min

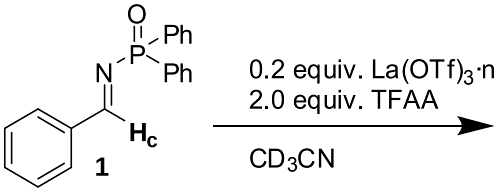


	RT (min)	Peak Type	Area (V*sec)	% Area	Height (V)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	12.359	Unknown	29147370	96.64	1734616	96.58	VV	50	12.100	12.950
2	13.130	Unknown	1012928	3.36	61414	3.42	VV	19	12.950	13.283

Chiral HPLC analysis for **12**
Column: Phenomenex Chiradex R-Pgly
Conditions: gradient 0-10% IPA:Hexanes for 35 min, 1.0 mL/min, λ 280 nm, t (major) = 12.4 min, t (minor) = 13.5 min

IX. Mechanistic Studies:
i. Reaction monitoring using ^{1}H NMR

Experimental Procedure: To a round-bottomed flask was added $La(OTf)_3{\cdot}nH_2O$ (65.3 mg, 0.089 mmol), TFAA (150 µL, 0.90 mmol), and CD_3CN (0.4 mL, 0.3 M). The mixture was sonicated and transferred by syringe to a dry NMR tube containing phosphinylimine **1** (0.15 g, 0.49 mmol) and CD_3CN (0.4 mL, 0.3 M). The mixture was vortexed until the solution was clear and ^{1}H NMR experiments were taken at time intervals to monitoring disappearance of H_c proton (8.93 ppm, $^3J_{P\text{-}H} = 32.8$ Hz).[4]



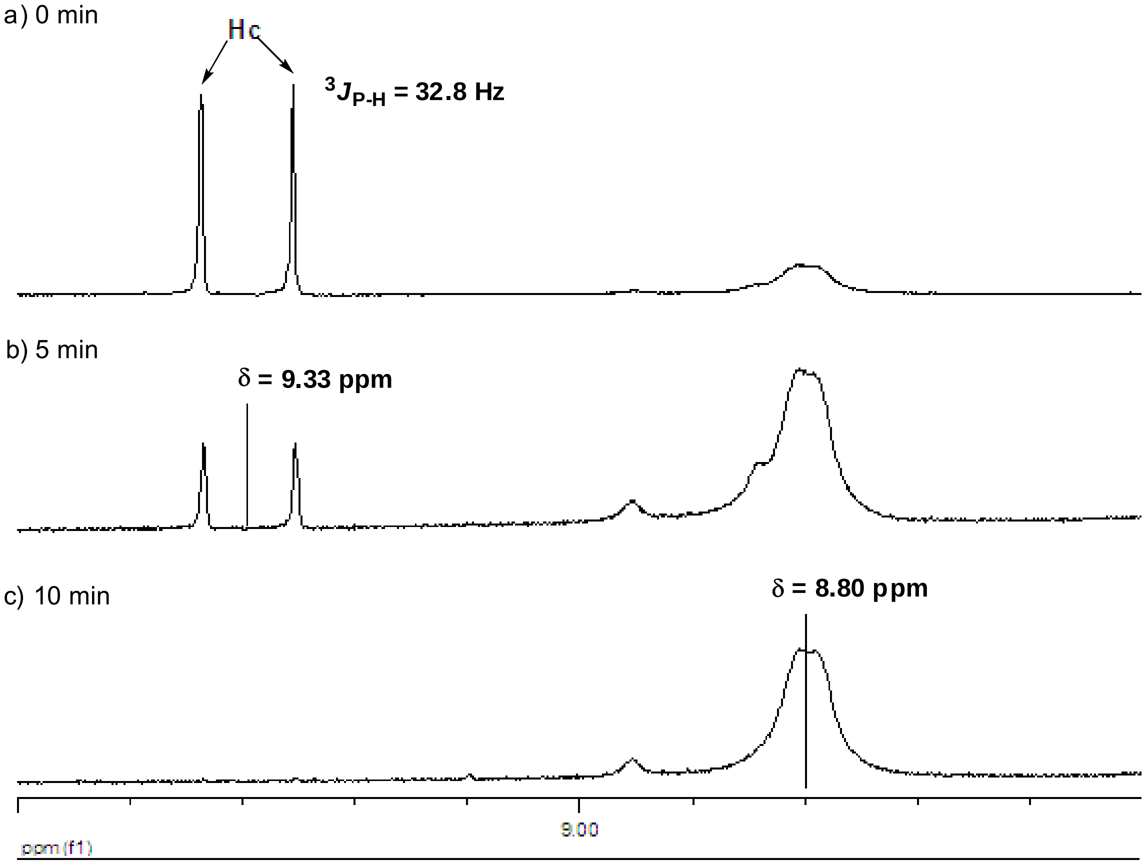


Figure 9. ^{1}H NMR (400 MHz, CD_3CN) experiments ((a), 0 min, (b) 5 min, and (c), 10 min) showing the disappearance of the phosphinylimine **1** doublet (H_c) within 10 minutes of $La(OTf)_3{\cdot}nH_2O$/TFAA addition.

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[4] W. B. Jennings, C. J. Lovely, *Tetrahedron.* **1991**, *47*, 5561.

IX. Mechanistic Studies:

ii. ESI+ Analysis without added crotyl silane 2

Experimental Procedure: To a flask was added hydrated lanthanum triflate (29 mg, 0.040 mmol), trifluoroacetic anhydride (56 µL, 0.40 mmol), and ACS-grade acetonitrile (0.7 mL, 0.3 M). The mixture was sonicated and transferred by syringe to a dry flask containing a mixture of phosphinylimine **1** (60 mg, 0.20 mmol). Direct injections into a mass spectrometer (MicroMass ZQ 2000) were taken immediately and at 15 min. to obtain the following ESI+ spectra (**Figure 7**).

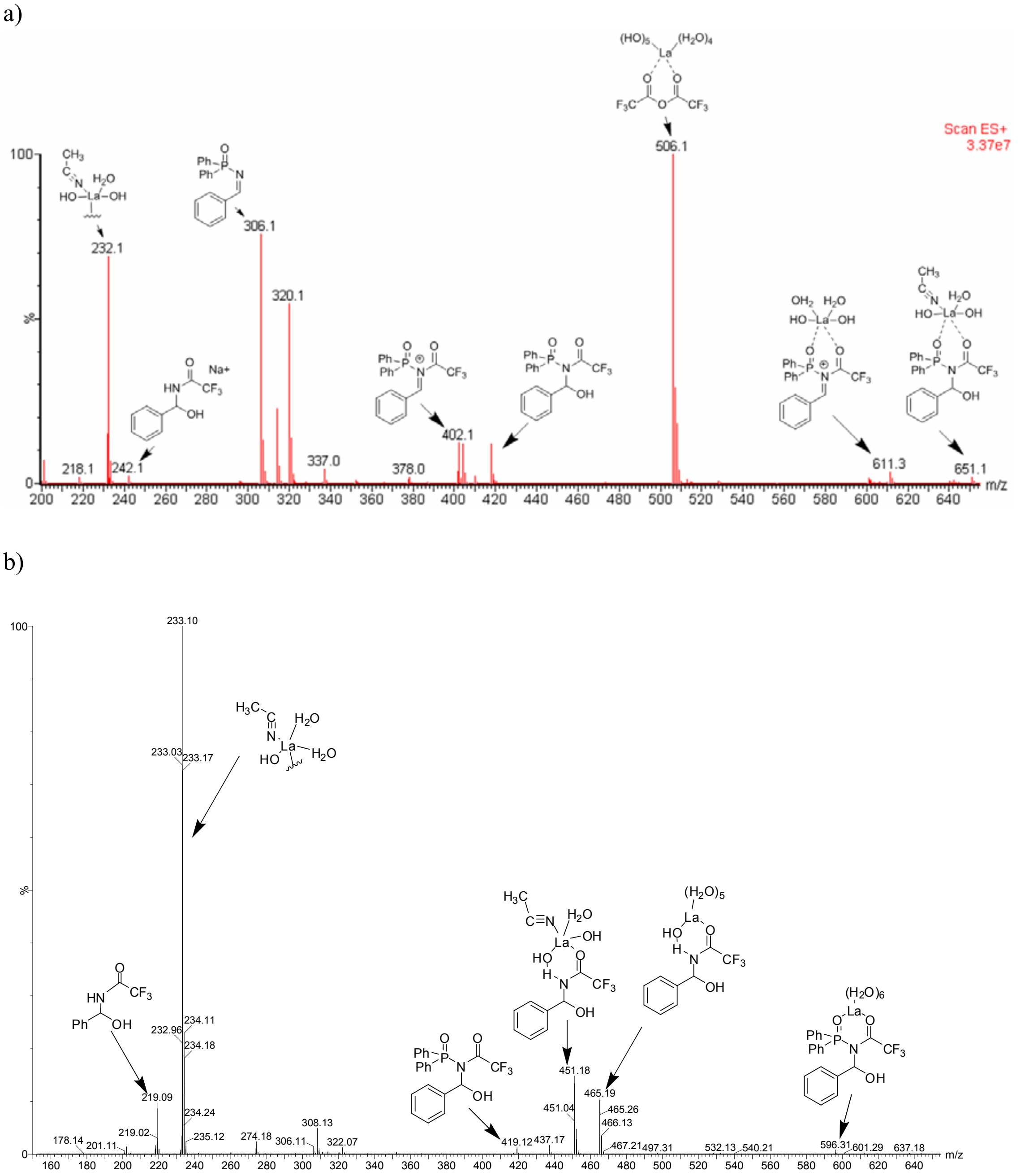


Figure 10. (a) LC-MS direct injection: ESI+ analysis of the crotylation at t = 1 min. (b) (a) LC-MS direct injection: ESI+ analysis of the crotylation at t = 15 min.

IX. Mechanistic Studies:
iii. ESI+ Analysis with added crotyl silane 2

Experimental Procedure: To a flask was added hydrated lanthanum triflate (29 mg, 0.040 mmol), trifluoroacetic anhydride (56 μL, 0.40 mmol), and ACS-grade acetonitrile (0.7 mL, 0.3 M). The mixture was sonicated and transferred by syringe to a dry flask containing a mixture of phosphinylimine **1** (60 mg, 0.20 mmol). Direct injections into a mass spectrometer (MicroMass ZQ 2000) were taken at 0 min. Crotylsilane **2** (51.6 mg, 0.20 mmol) was then added and samples directly injected to the mass spectrometer to obtain the following ESI+ spectra (**Figure 9**).

a)

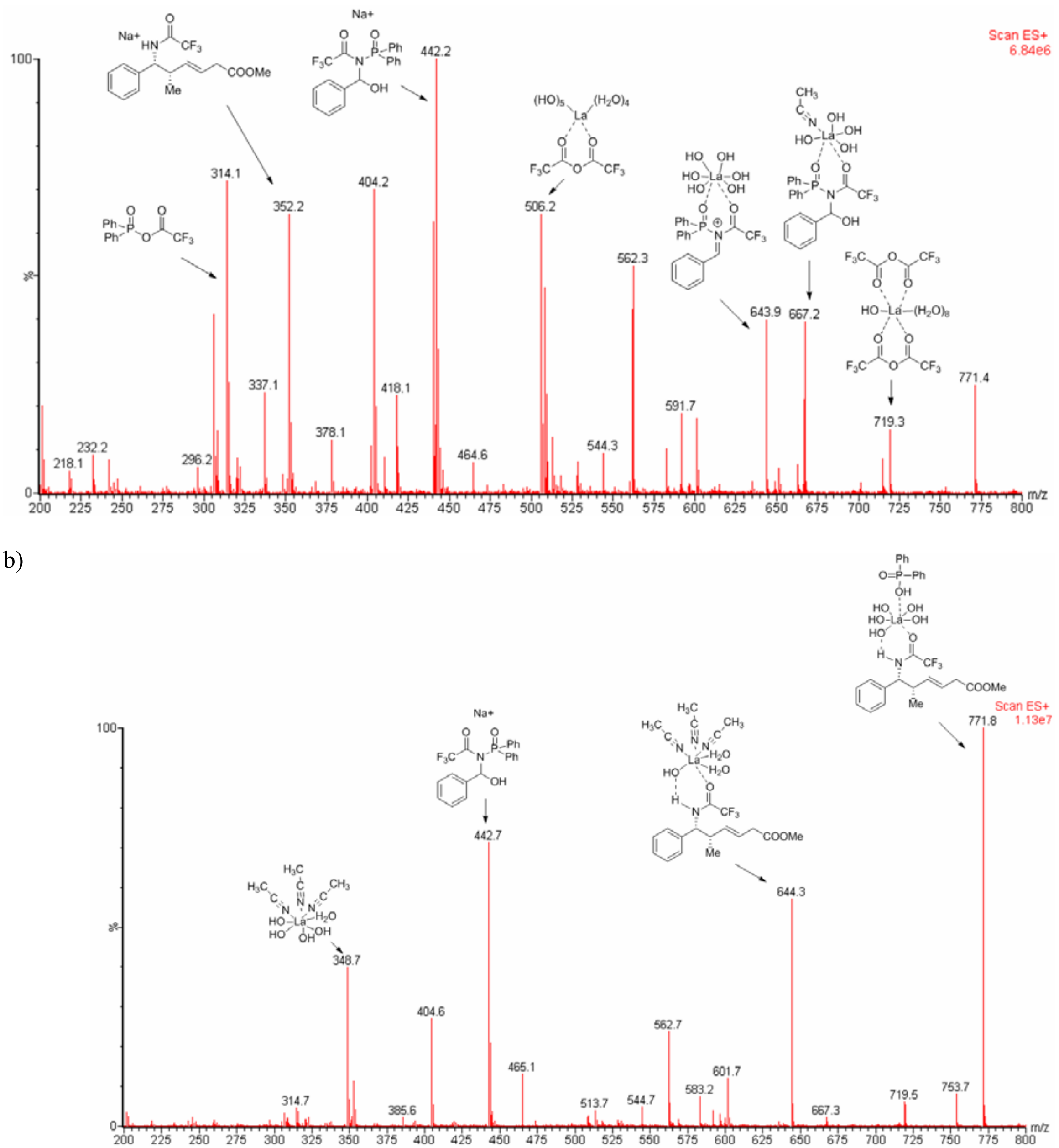


Figure 11. (a) Subsequent LC-MS direct injection: ESI+ analysis of the crotylation at t_1 = 1 min. (b) LC-MS direct injection: ESI+ analysis of the crotylation at t_1 = 15 min.

IX. Mechanistic Studies:
iv. Reaction monitoring using ^{31}P NMR

Experimental Procedure: To a round-bottomed flask was added La(OTf)$_3$·nH$_2$O (65.3 mg, 0.089 mmol), TFAA (150 µL, 0.90 mmol), and CD$_3$CN (0.4 mL, 0.3 M). The mixture was sonicated and transferred by syringe to a dry NMR tube containing phosphinylimine **1** (0.15 g, 0.49 mmol), crotylsilane **2** (117 mg, 0.45 mmol), and CD$_3$CN (0.4 mL, 0.3 M). The mixture was vortexed until clear and ^{31}P NMR spectra were taken at different time intervals to monitor the appearance of multiple peaks in the 36-38 ppm range, and finally, the coalescence of these peaks to a major peak at 37 ppm (15 min).

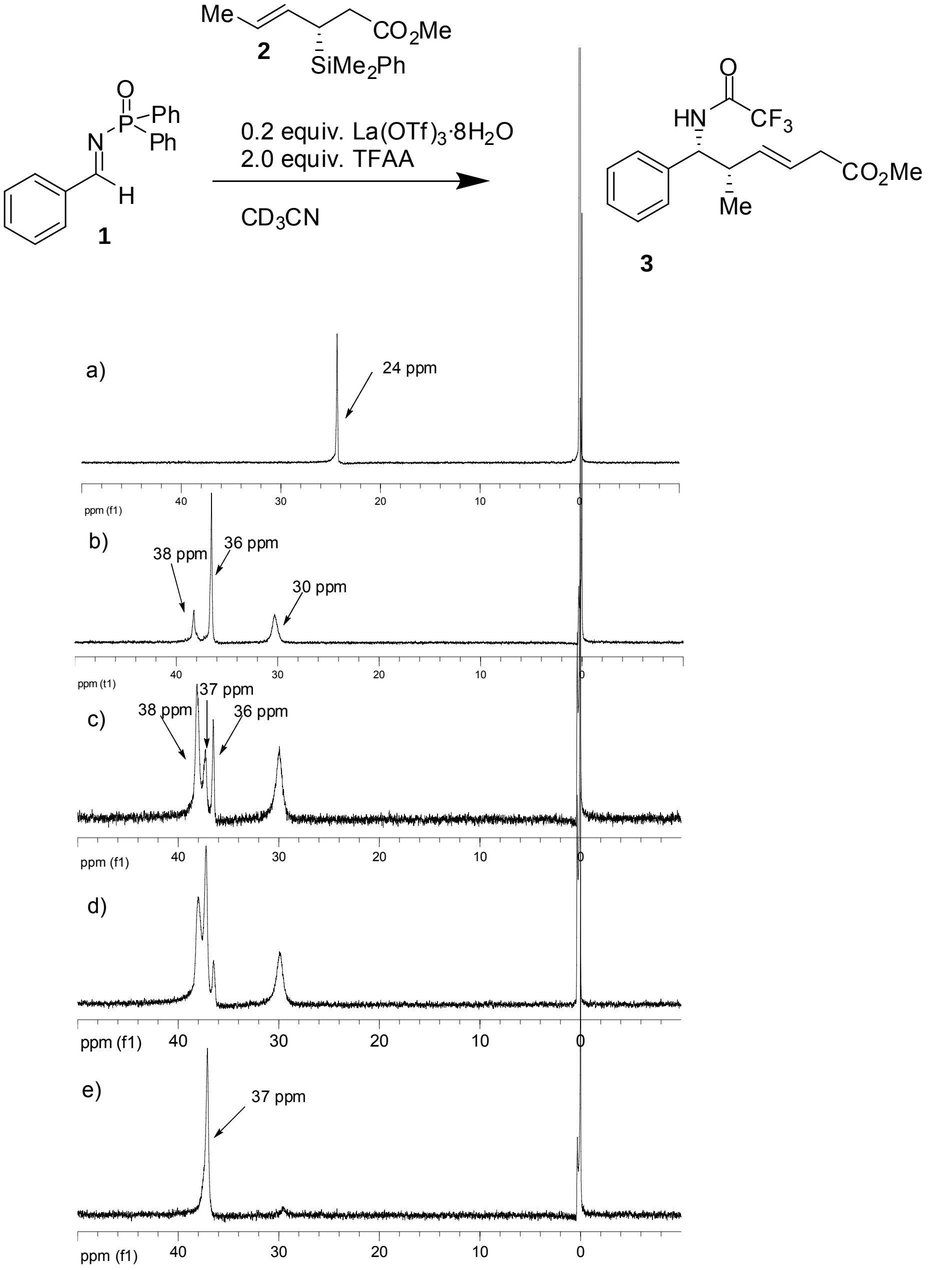


Figure 12. (a) ^{31}P NMR (121.50 MHz, CD$_3$CN) of phophinylimine **1**. (b) ^{31}P NMR (121.50 MHz, CD$_3$CN) of phosphinylimine **1**, La(OTf)$_3$·8H$_2$O and TFAA. (c) ^{31}P NMR (121.50 MHz, CD$_3$CN) of the crotylation reaction (t = 5 min). (d) ^{31}P NMR (121.50 MHz, CD$_3$CN) of the crotylation reaction (t = 10 min). (e) ^{31}P NMR (121.50 MHz, CD$_3$CN) of the crotylation reaction (t = 15 min).

IX. Mechanistic Studies:
v. ^{31}P NMR experiments to probe ligand exchange

^{31}P NMR spectra were taken in order to further probe the nature of phosphorous-containing intermediates observed in the reaction monitoring study (see page SI-10). The experiment in panel f) shows that $La((Ph_2P{=}O)_2O)_m(TFAA)_n(H_2O)_o$ or the corresponding mixed anhydride complexes $(La(Ph_2PO_2OTFA)_mH_2O_n)$ correlate well to the species observed in crotylation experiments by ^{31}P NMR (Figure 4, panel c)).

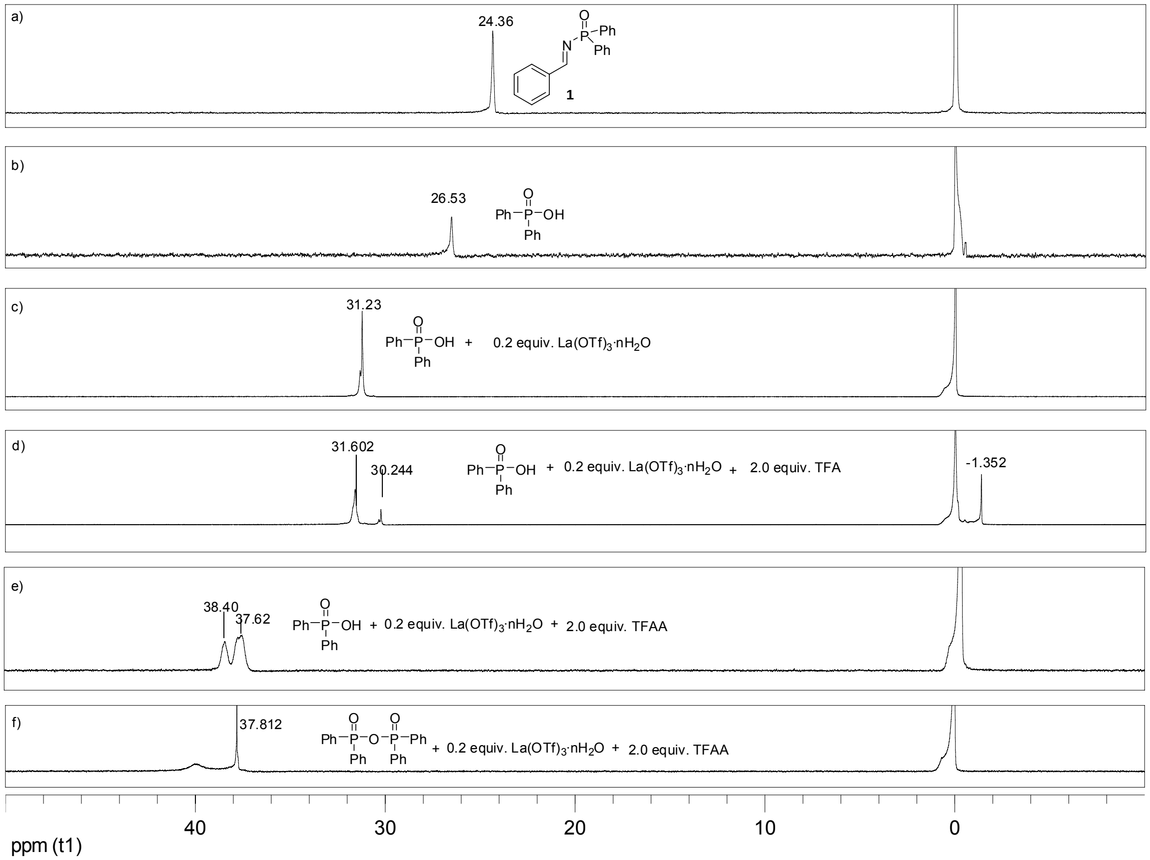


Figure 13. (a) ^{31}P NMR (121.50 MHz, CD_3CN) of N-diphenylphosphinylimine **1**. (b) ^{31}P NMR (121.50 MHz, CD_3CN) of diphenylphosphinic acid. (c) ^{31}P NMR (121.50 MHz, CD_3CN) of a mixture of diphenylphosphinic acid and $La(OTf)_3{\cdot}nH_2O$. (d) ^{31}P NMR (121.50 MHz, CD_3CN) of a mixture of diphenylphosphinic acid, $La(OTf)_3{\cdot}nH_2O$ and TFA. (e) ^{31}P NMR (121.50 MHz, CD_3CN) of a mixture of diphenylphosphinic acid, $La(OTf)_3{\cdot}nH_2O$ and TFAA. (f) ^{31}P NMR (121.50 MHz, CD_3CN) of a mixture of diphenylphosphinyl anhydride, $La(OTf)_3{\cdot}nH_2O$ and TFAA.

IX. Mechanistic Studies:
vi. ESI+ Analysis to probe exchange

Experimental Procedure: To a flask was added hydrated lanthanum triflate (29 mg, 0.040 mmol), trifluoroacetic anhydride (56 µL, 0.40 mmol), and ACS-grade acetonitrile (0.7 mL, 0.3 M). The mixture was sonicated and transferred by syringe to a dry flask containing a mixture of phosphinylimine **1** (60 mg, 0.20 mmol) and crotylsilane **2** (51.6 mg, 0.20 mmol). The mixture was vortexed until clear and allowed to stir at room temperature for 1 h before direct injection into a mass spectrometer (MicroMass ZQ 2000) to obtain the following ESI+ analysis (**Figure 6**). The ESI+ data shows peaks corresponding to different combinations of La, diphenylphosphinic acid, TFA and H_2O, suggesting the possible formation of various $La(DPPOTFA)_m(H_2O)_n$ species from ligand exchange of diphenylphosphinic acid and TFAA with $La(OTf)_3{\cdot}nH_2O$.

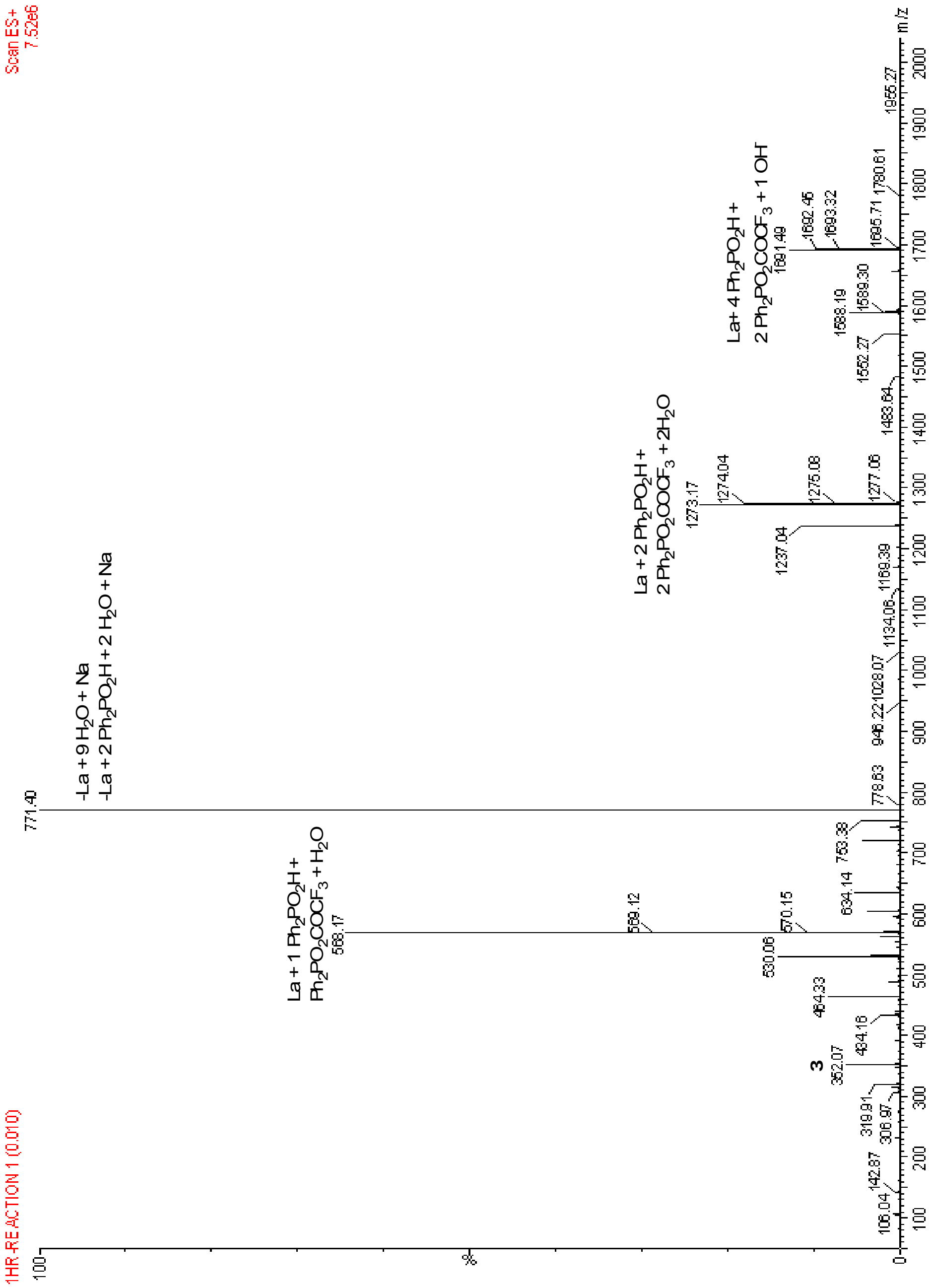
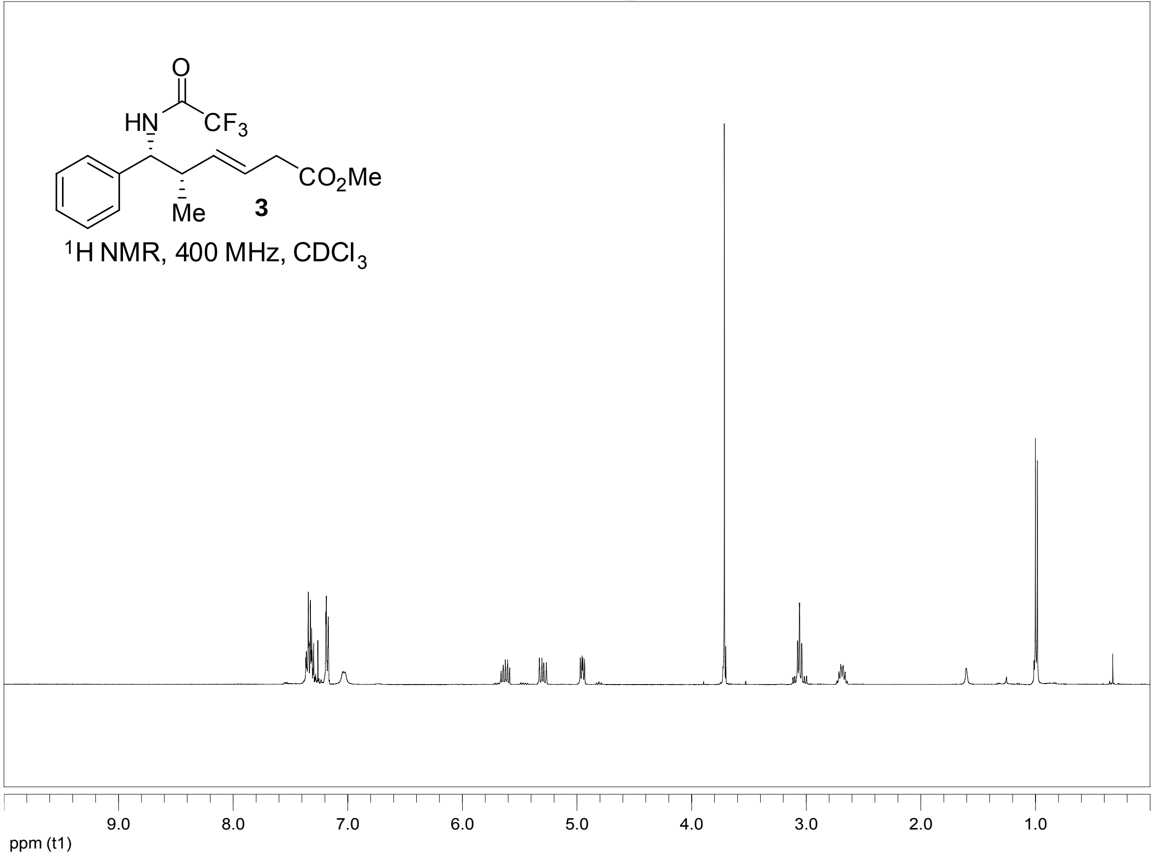
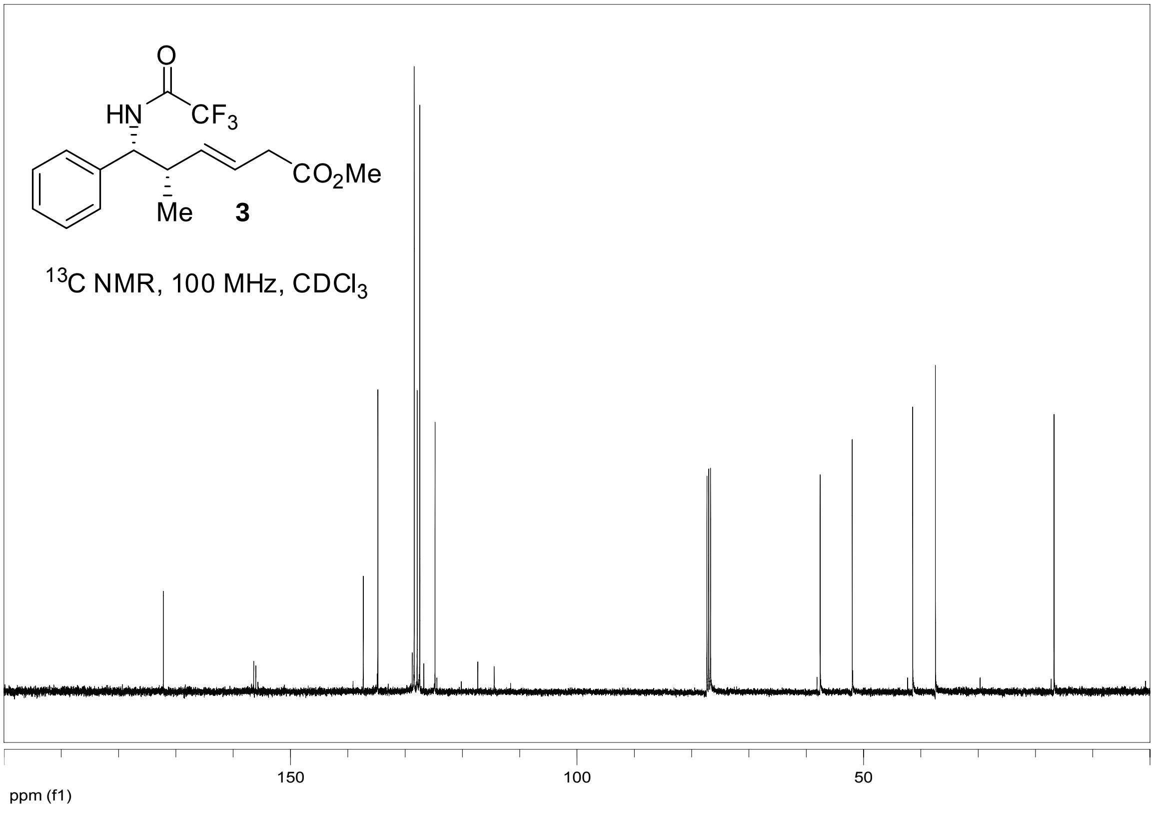
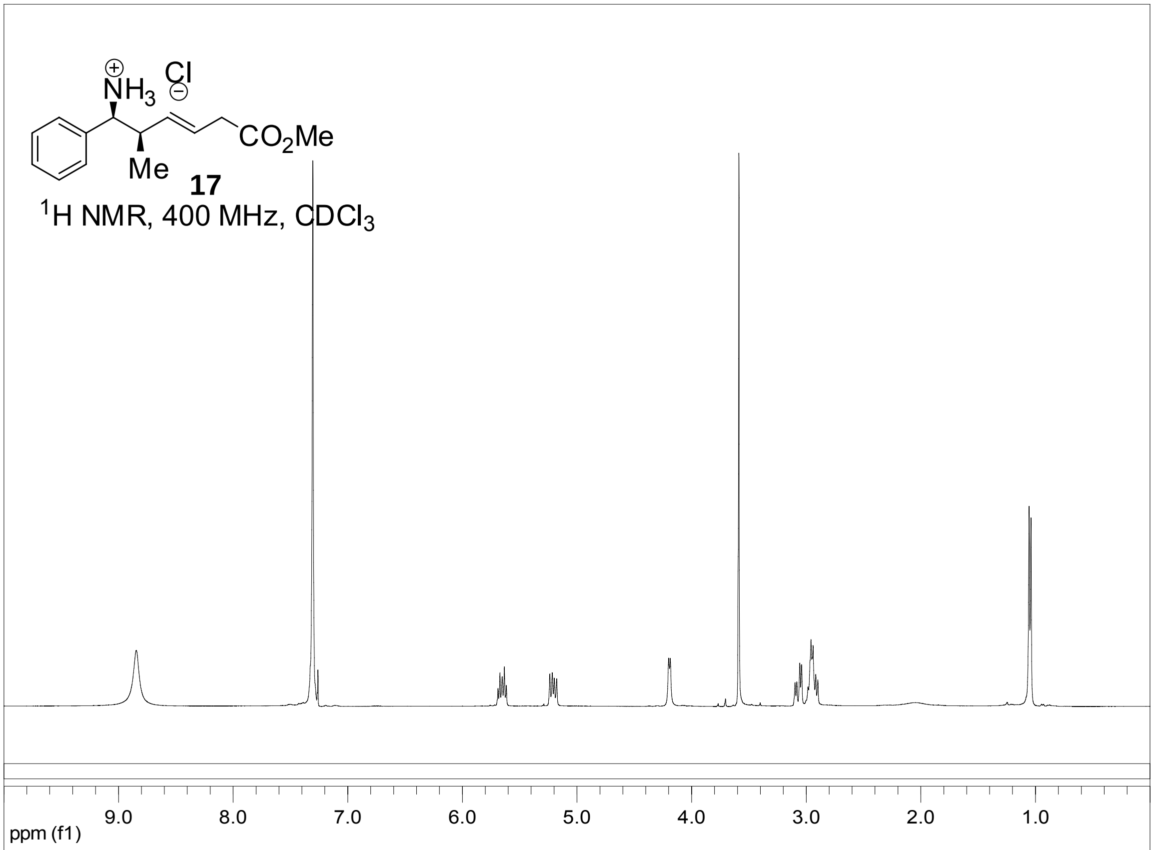


Figure 14. LC-MS direct injection: ESI+ analysis of the crotylation after 1 h.

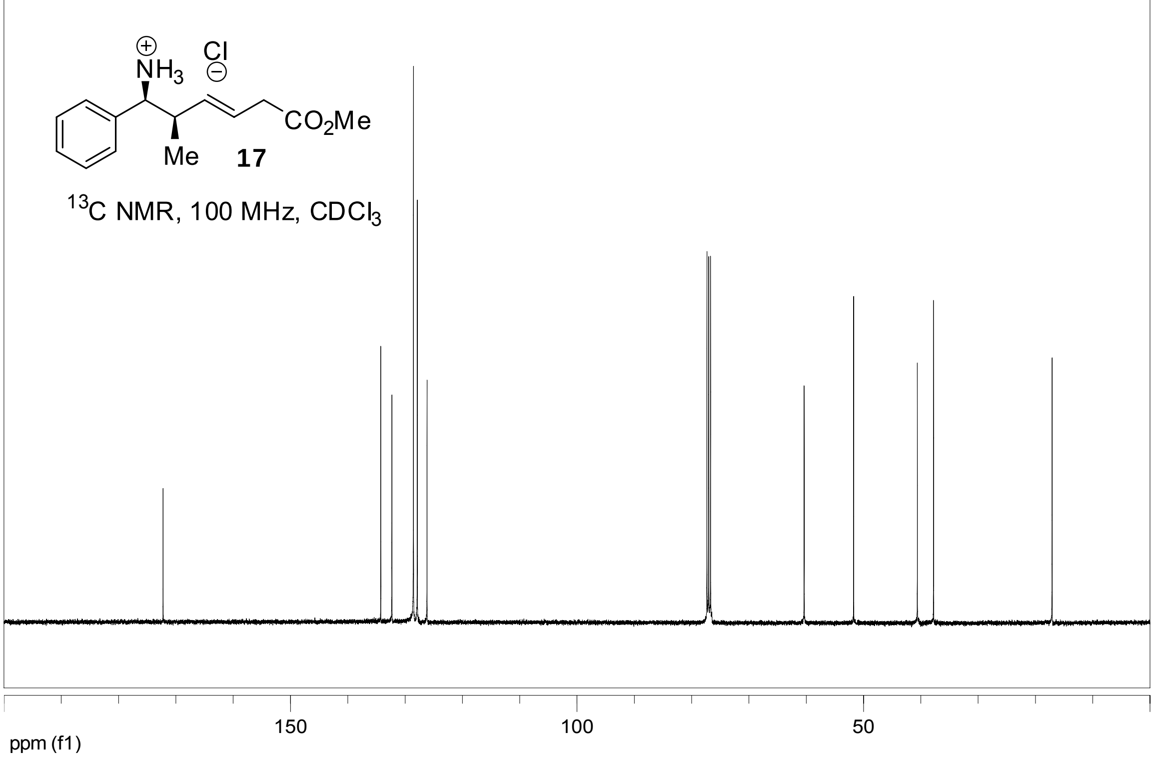
X. Select NMR Spectra



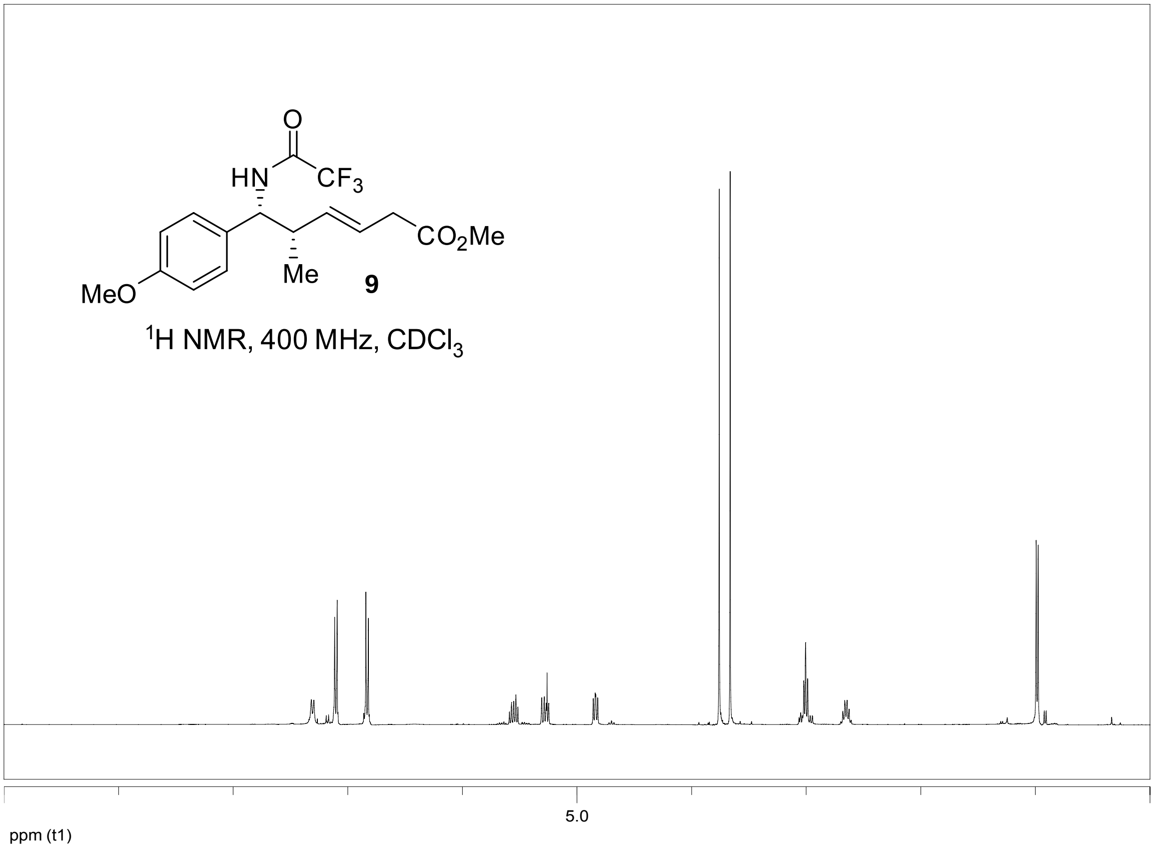


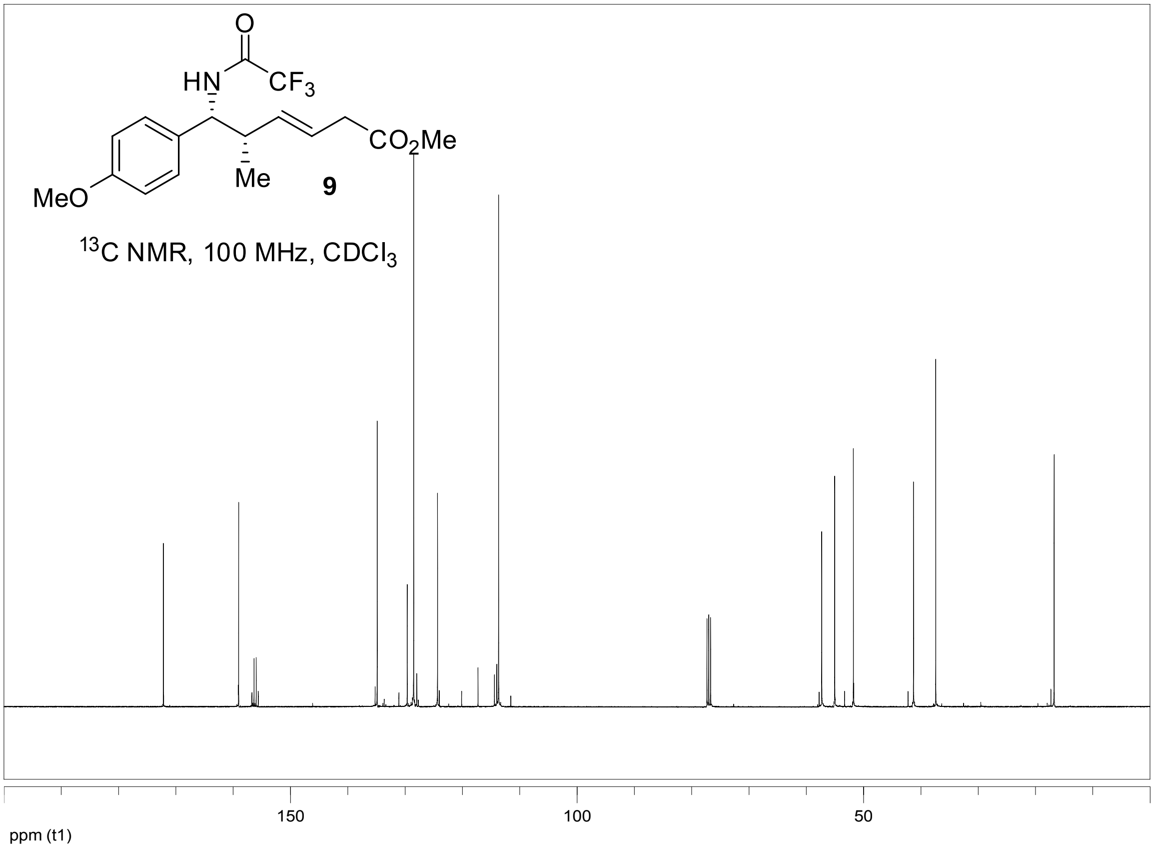


Me
CO2Me
Cl
NH3
17
1H NMR, 400 MHz, CDCl3
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)



Me
CO2Me
Cl
NH3
17
13C NMR, 100 MHz, CDCl3
150
100
50
ppm (f1)


HN
O
CF3
CO2Me
Me
MeO
9
1H NMR, 400 MHz, CDCl3
5.0
ppm (t1)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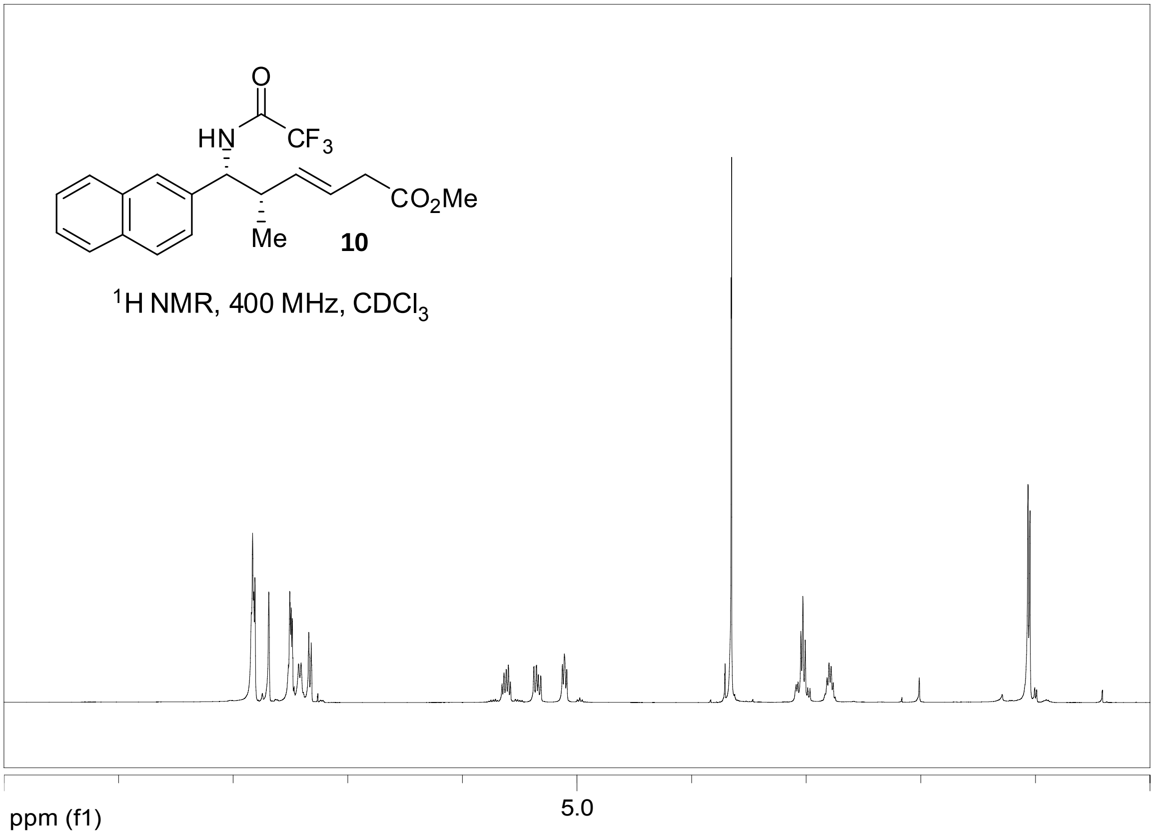
O
CF3
CO2Me
Me
MeO
9
13C NMR, 100 MHz, CDCl3
150
100
50
ppm (t1)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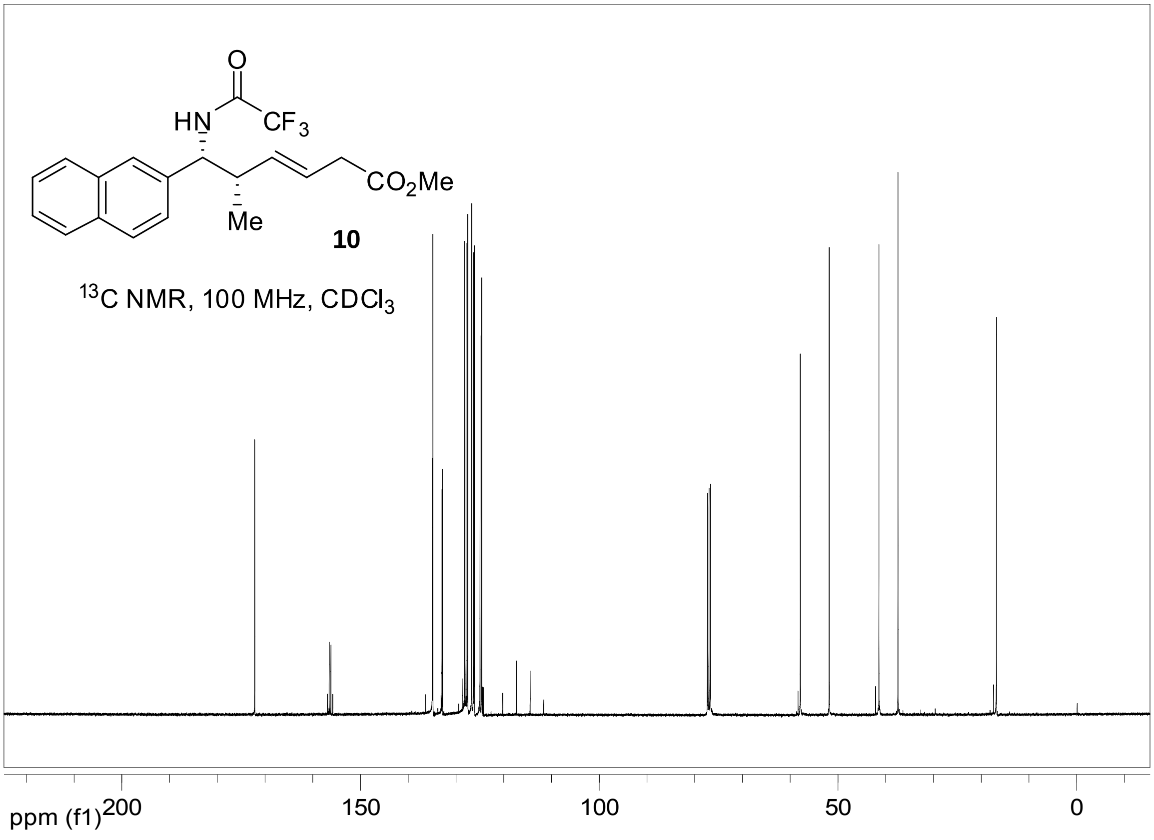
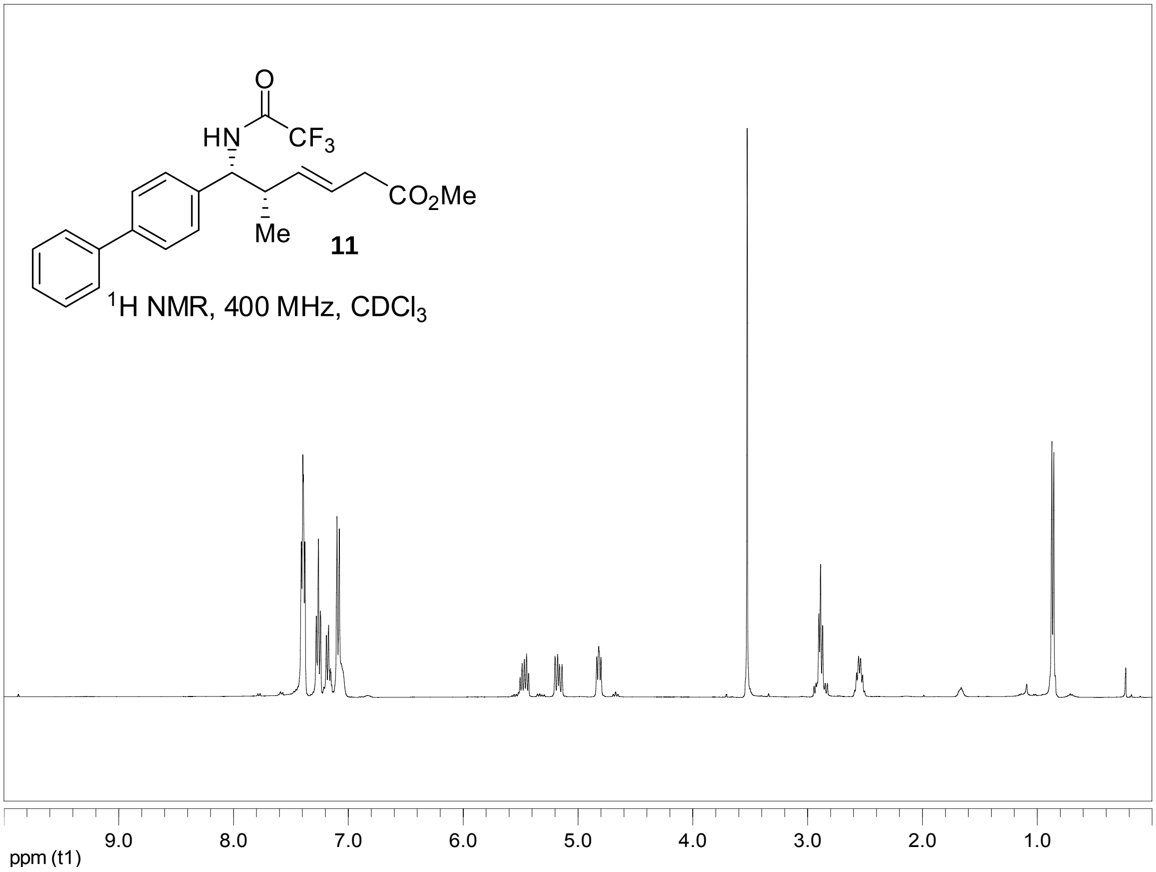
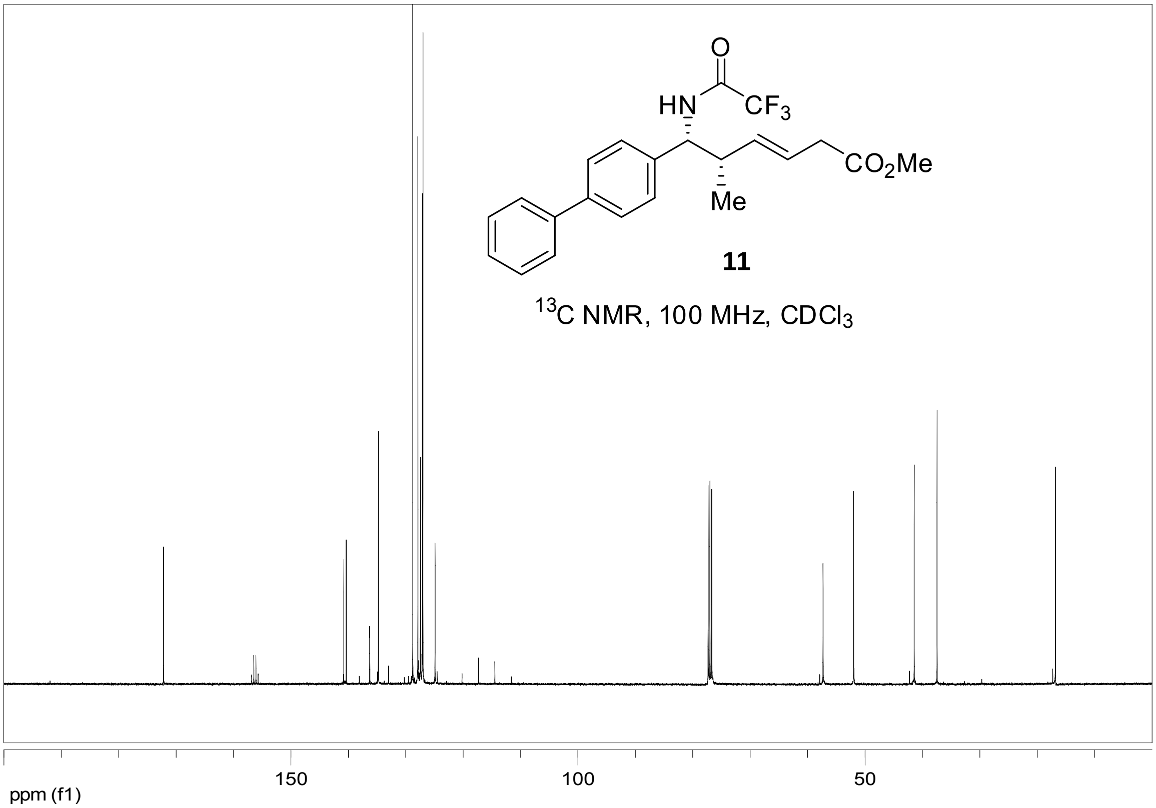
CF3
CO2Me
Me
10
1H NMR, 400 MHz, CDCl3
ppm (f1)
5.0

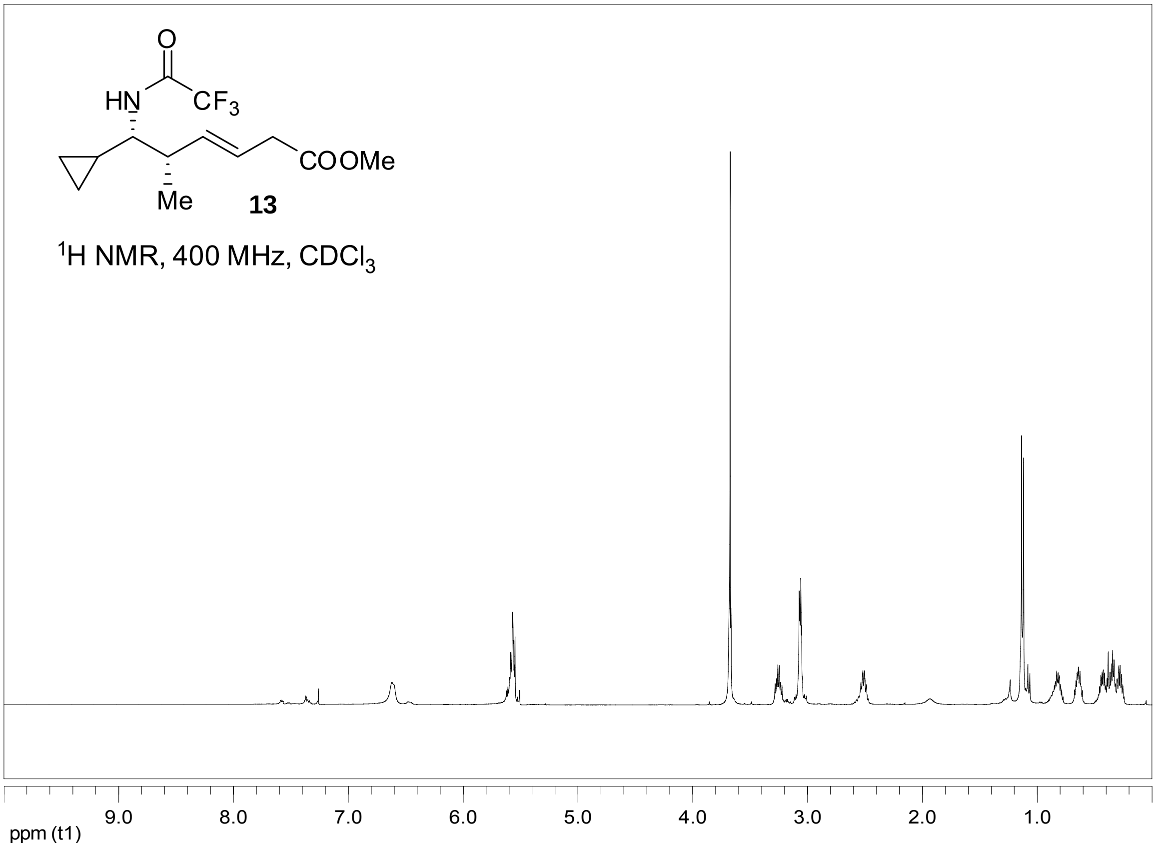

O
HN
CF3
CO2Me
Me
10
13C NMR, 100 MHz, CDCl3
ppm (f1)
200
150
100
50
0



O
HN
CF$_3$
CO$_2$Me
Me
11
^{1}H NMR, 400 MHz, CDCl$_3$
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

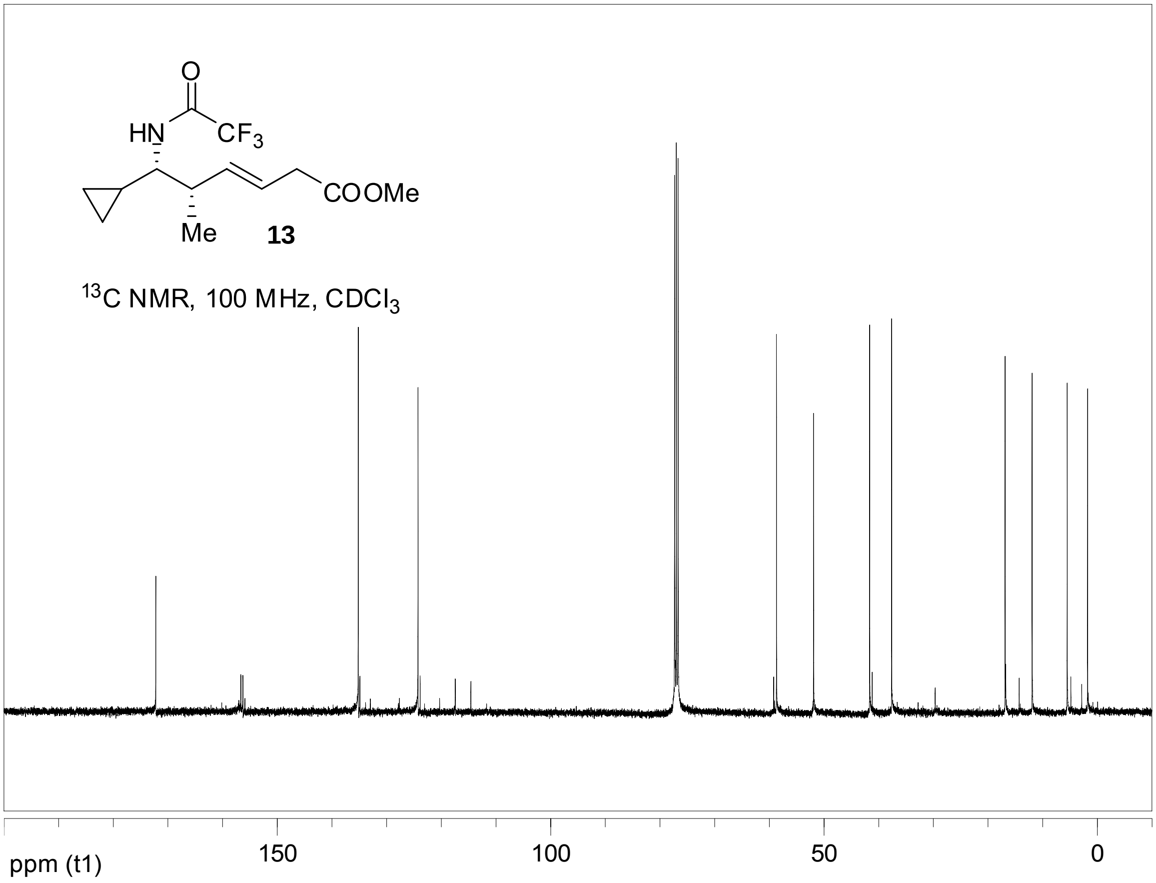


O
HN
CF$_3$
CO$_2$Me
Me
11
^{13}C NMR, 100 MHz, CDCl$_3$
150
100
50
ppm (f1)



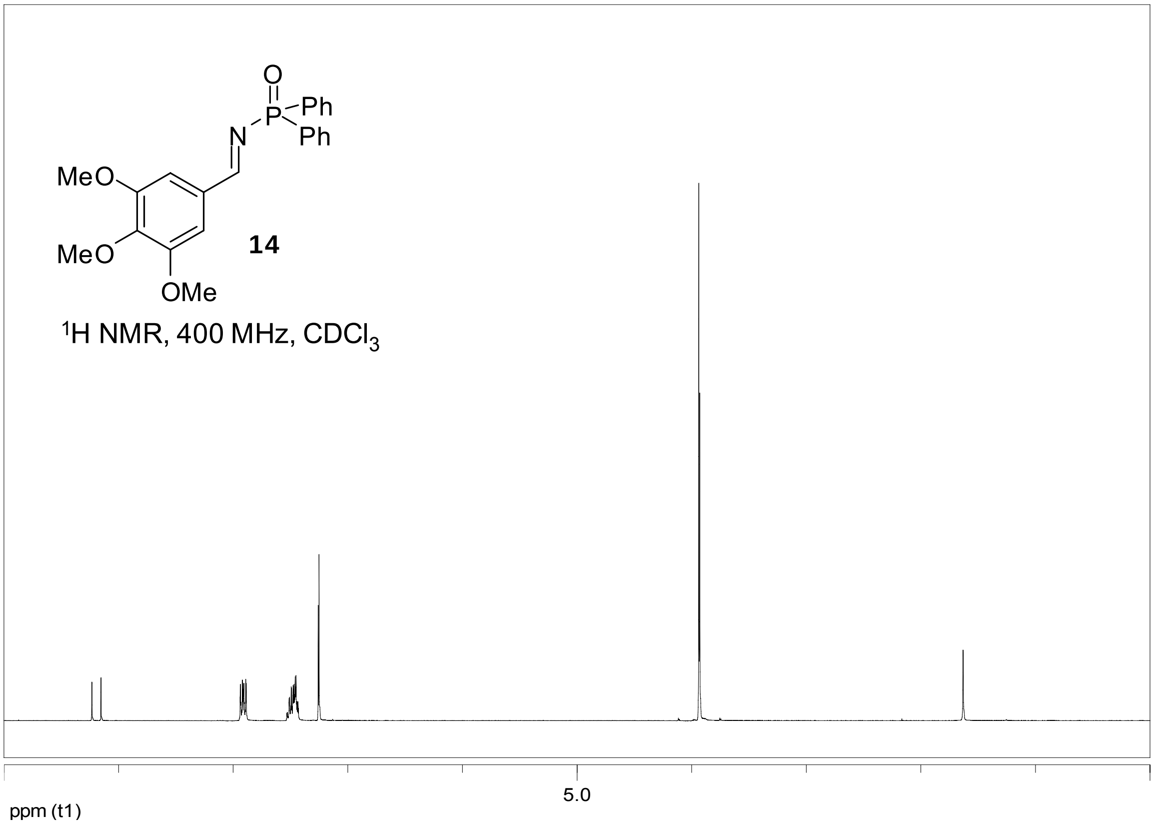
13

^{1}H NMR, 400 MHz, CDCl$_3$

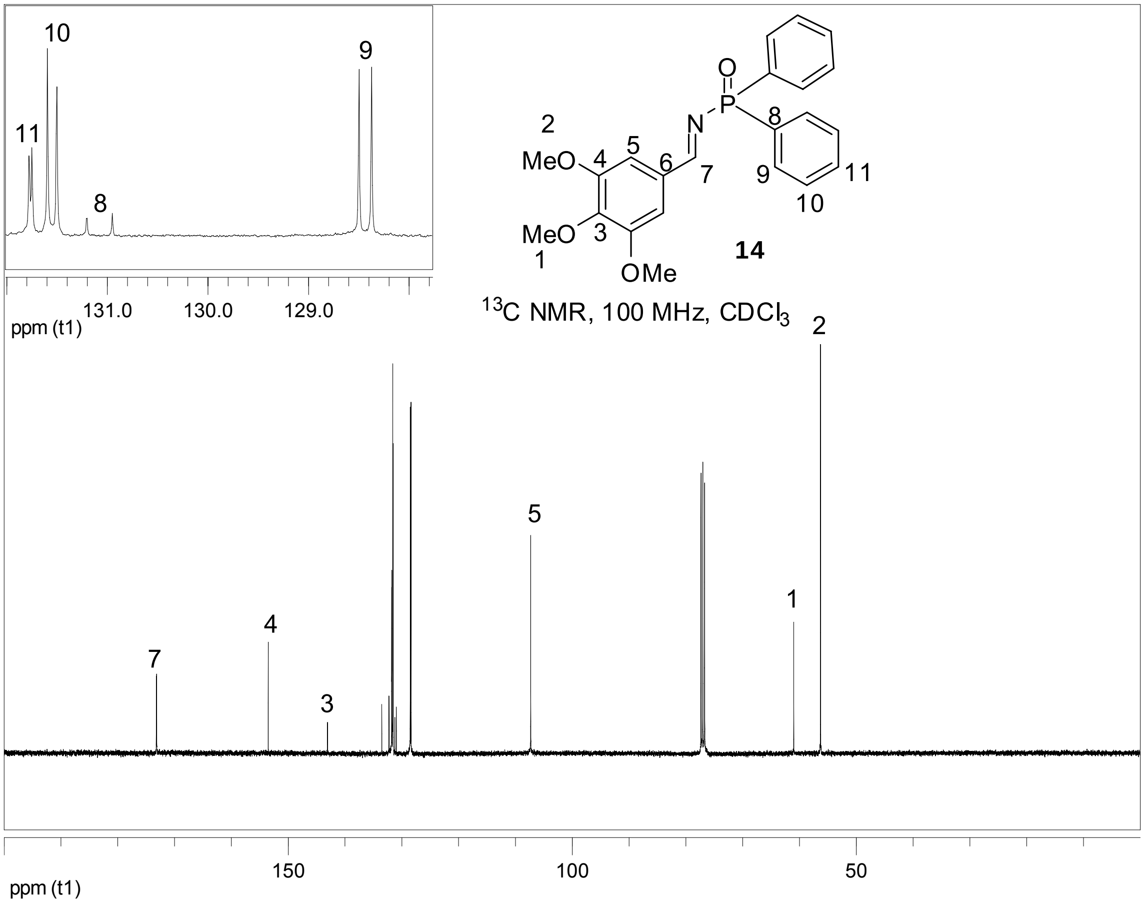


13

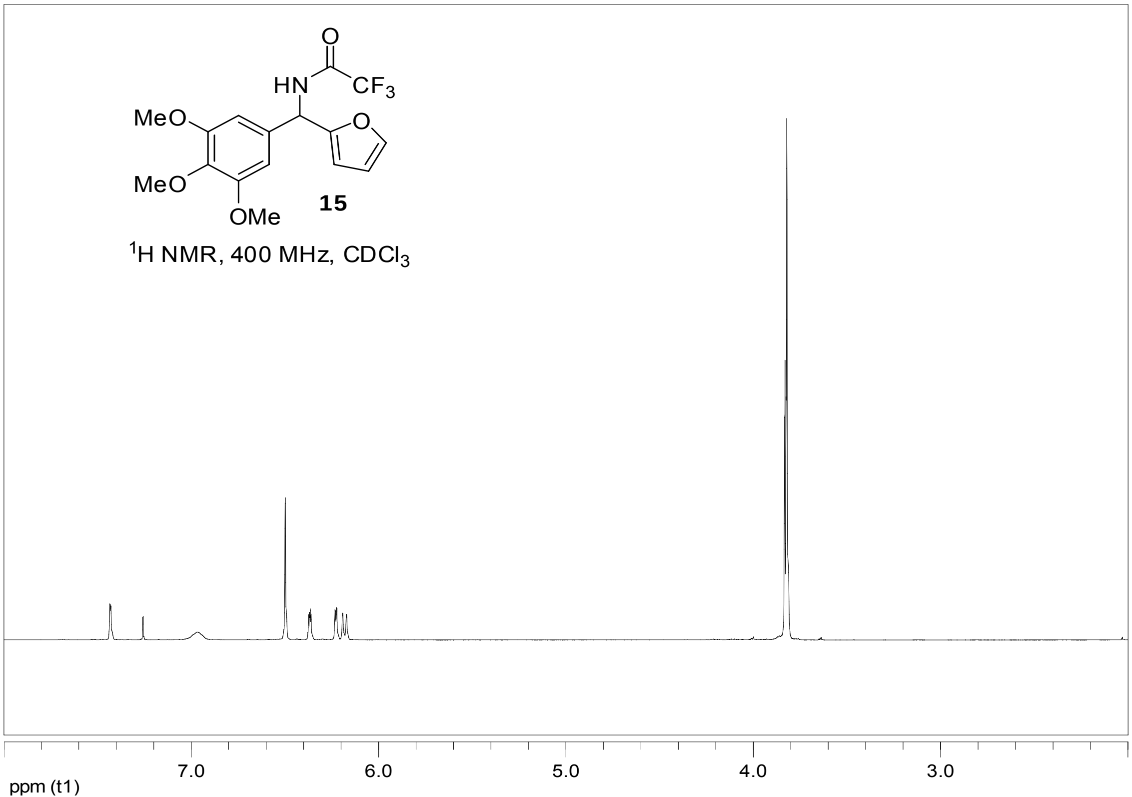
^{13}C NMR, 100 MHz, CDCl$_3$

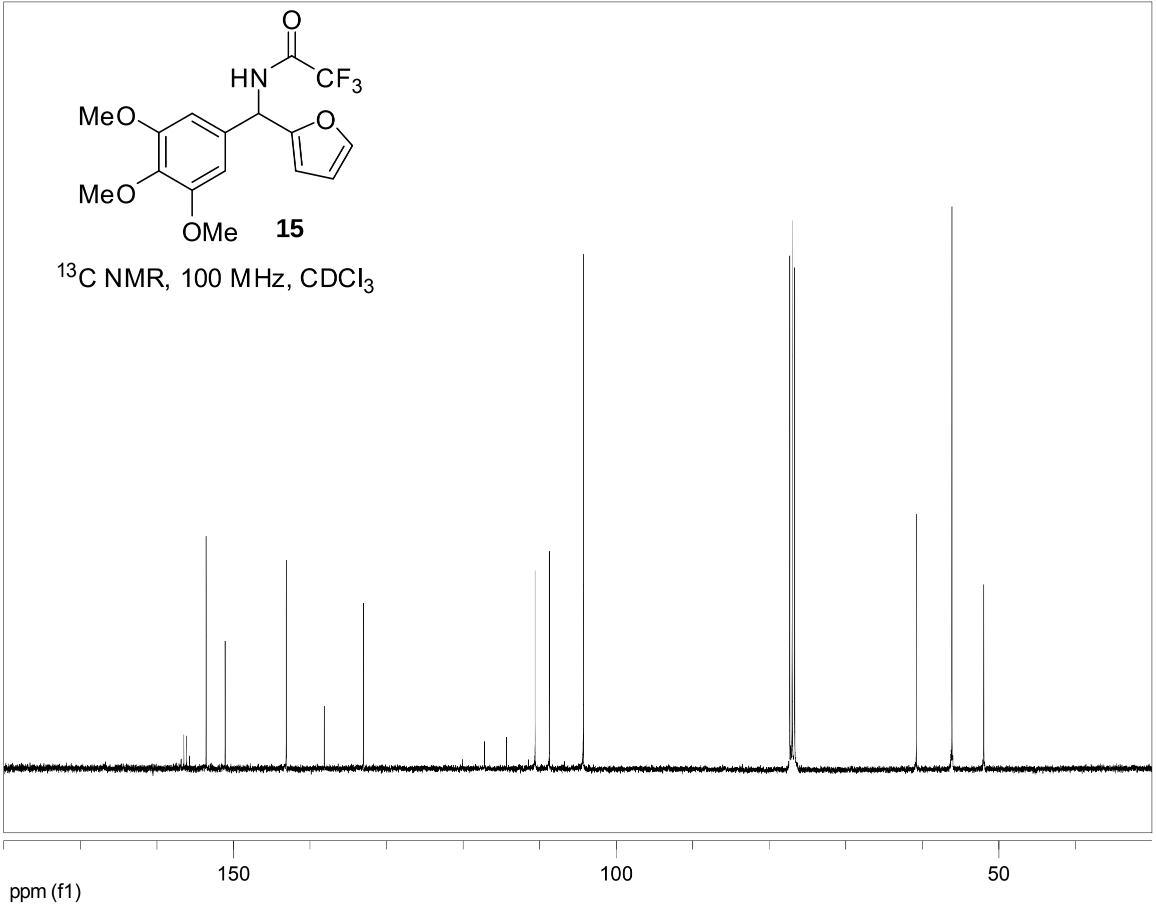


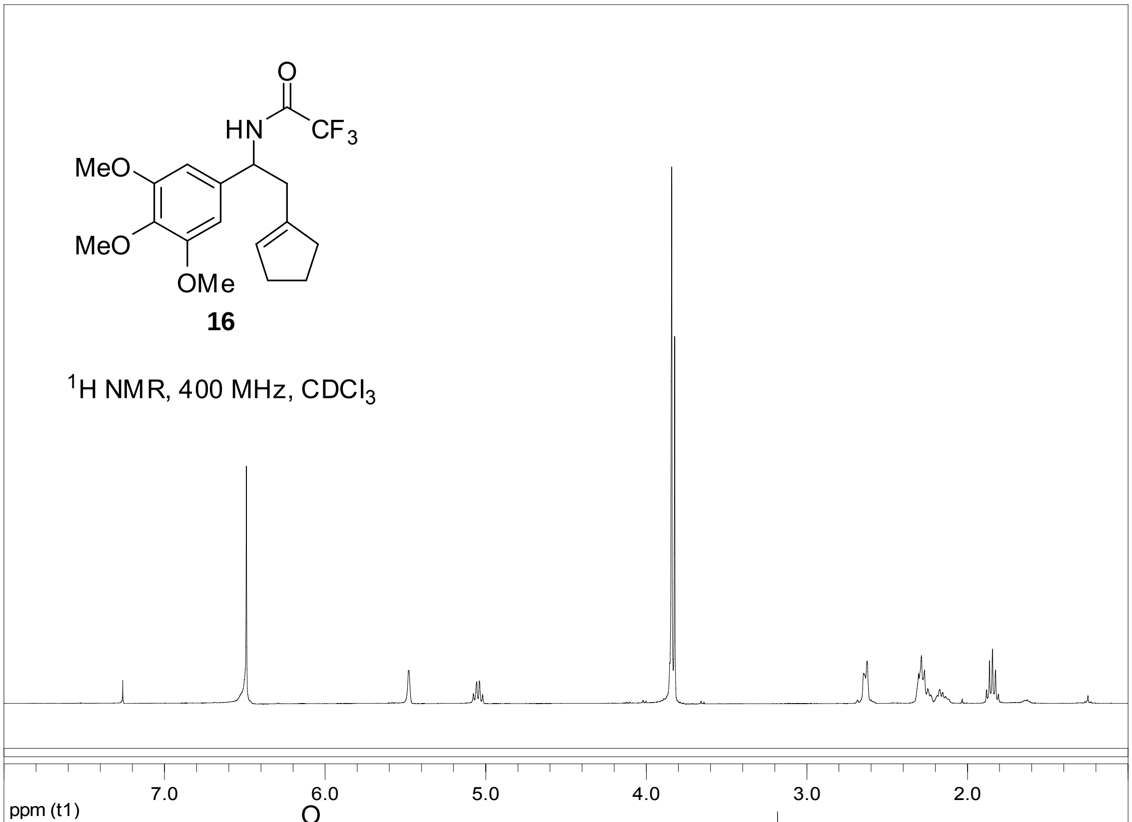
O
P
Ph
Ph
N
MeO
MeO
OMe
14
^{1}H NMR, 400 MHz, CDCl$_3$
5.0
ppm (t1)

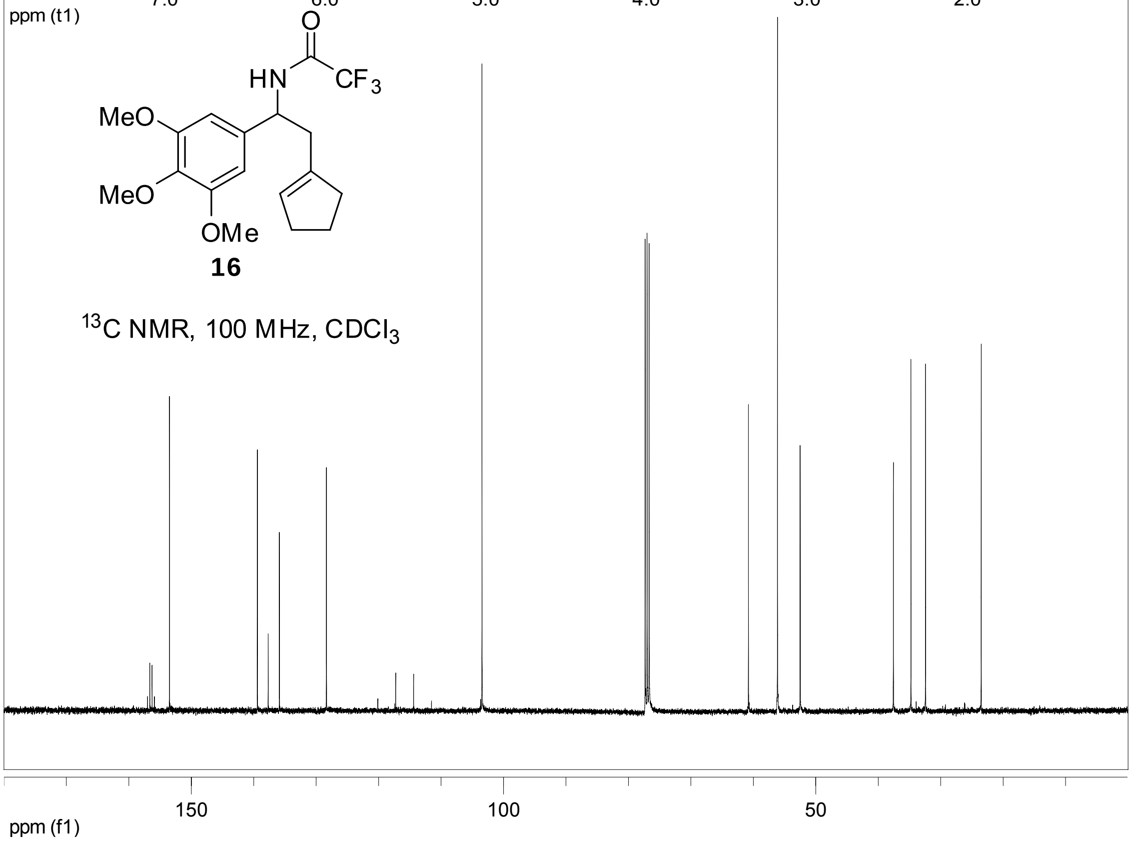


10
11
8
9
131.0
130.0
129.0
ppm (t1)
O
P
N
8
2
MeO
4
5
6
7
9
11
10
MeO
3
1
OMe
14
^{13}C NMR, 100 MHz, CDCl$_3$
2
5
1
4
7
3
150
100
50
ppm (t1)


HN
O
CF3
MeO
MeO
OMe
O
15
1H NMR, 400 MHz, CDCl3
7.0
6.0
5.0
4.0
3.0
ppm (t1)


HN
O
CF3
MeO
MeO
OMe
O
15
13C NMR, 100 MHz, CDCl3
150
100
50
ppm (f1)


16
^{1}H NMR, 400 MHz, CDCl$_3$
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)


16
^{13}C NMR, 100 MHz, CDCl$_3$
150
100
50
ppm (f1)