Supporting Information

Naturally occurring phytic acid: an advanced Brønsted acid catalyst for direct amination reactions of allylic alcohols

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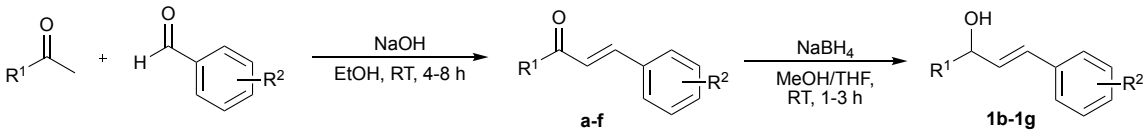
General Experimental Considerations

All reactions were carried out in air using technical solvents without any particular precautions to exclude moisture or oxygen, unless stated otherwise. Commercially available reagents were used as received without further purification. Phytic acid was purchased from Tokyo Chemical Industry with ca. 50% in water, ca. 1.1 mol/L. Allylic alcohols **1a**, **1h, 1i** and **1j** were purchased from Honeywell Fluka. Column chromatography was performed with silica gel (70–230 mesh) of SiliaFlash® G60 (Cananda). Analytical thin layer chromatography (TLC) was performed with precoated Merck silica gel 60 F254 plates (0.25 mm for thick layer) and visualized at 254 nm using an ultraviolet lamp. Infrared spectra were recorded in reciprocal centimetres (cm-1) using a A JASCO FT/IR-460 Plus spectrometer. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded in $CDCl_3$ and DMSO-d_6 on on JEOL JNM–ECZ500R/S1 spectrometers (^{1}H: 500 MHz, ^{13}C: 125 MHz, ^{31}P: 202 MHz). The chemical shifts, δ, are given in ppm relatively to solvents residual peaks or diphenyl phosphate (−11 ppm). The multiplicity is given as br, s, d, t, q, and m for broad, singlet, doublet, triplet, quartet, and multiplet. Assignments of some ^{1}H and ^{13}C NMR signals rely on COSY, HSQC and/or HMBC experiments. High resolution mass spectra were recorded on an Agilent HPLC 1260 series coupled with a QTOF 6540 UHD accurate mass (Agilent Technologies, Waldbronn, Germany) using ESI techniques at Chulalongkorn University. Melting points were determined on a Stuart SMP20 apparatus and are uncorrected.

Experimental Procedures and Characterisations Data

Preparation of Allylic Alcohols



Scheme 1. Synthesis of allylic alcohols **1b**-**1g**.

a,[1] **b**,[2] **c**,[2] **e**,[3] **f**,[4] **g**,[4] **1b**,[6] **1c**,[6] **1d**,[6] **1e**,[7] **1f**,[8] **1g**[9] were prepared by following procedures. Spectroscopic data for these compounds are in accordance with the literature.

General procedure for allylic ketone: Following the reported procedure,[10] a solution of $NaOH_{(aq)}$ (2.75 M, 12 mL) was added to a stirred solution of the chosen ketone (0.03 mol) in EtOH (7.5 mL). Then, the corresponding aldehyde (0.031 mol) was added dropwise, and the resulting solution was stirred at room temperature for 4-8 h. The solution mixture was then neutralized with 10% HCl until pH ≈ 5-6. The obtained solid was filtered and washed with water to give the corresponding allylic ketone.

(*E*)-3-(2-methoxyphenyl)-1-phenylprop-2-en-1-one (a) Yellow oil (60%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ_H (ppm) 8.12 (d, *J* = 16.0 Hz, 1H), 8.03–8.01 (m, 2H), 7.64–7.61(m, 2H) 7.58-7.55 (m, 1H), 7.50-7.47 (m,

2H), 7.39-7.35 (m, 1H), 6.98 (t, *J* = 2.5 Hz, 1H), 6.93 (dd, *J* = 8.5, 1.0 Hz, 1H), and 3.90 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ_C (ppm) 191.2, 158.9, 140.5, 138.6, 132.6, 131.9, 129.3, 124.0, 122.9, 120.8, 120.7, 111.3, and 55.7.

(*E*)-3-(3-methoxyphenyl)-1-phenylprop-2-en-1-one (b) Bright yellow solid (75%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ_H (ppm) 8.03–8.01 (m, 2H), 7.77 (d, *J* = 15.5 Hz, 1H), 7.60–7.57 (m, 1H), 7.53–7.49 (m, 3H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.23 (m, 1H), 7.15 (t, *J* = 2.5 Hz, 1H), 6.98–6.95 (m, 1H), and 3.85 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ_C (ppm) 190.7, 160.0, 144.9, 138.3, 136.3, 132.9, 130.1, 128.7, 128.6, 122.5, 121.2, 116.4, 113.5, and 55.6.

(*E*)-3-(4-methoxyphenyl)-1-phenylprop-2-en-1-one (c) Yellow solid (70%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ_H (ppm) 8.02–8.00 (m, 2H), 7.78 (d, *J* = 15.5 Hz, 1H), 7.60–7.54 (m, 3H), 7.50–7.47 (m, 2H), 7.41 (d, *J* = 15.5 Hz, 1H), 7.92 (d, *J* = 8.5 Hz, 2H), and 3.83 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ_C (ppm) 190.6, 161.8, 144.8, 138.6, 132.6, 130.3, 128.6, 128.5, 127.7, 119.8, 114.5, and 55.5.

(*E*)-3-(4-nitrophenyl)-1-phenylprop-2-en-1-one (d) Dark yellow solid (85%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ_H (ppm) 8.26 (d, *J* = 9.0 Hz, 2H), 8.04–8.03 (m, 2H), 7.83–7.78 (m, 3H), 7.66–7.61 (m, 2H), and 7.54–7.51 (m, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ_C (ppm) 189.8, 148.6, 141.6, 141.1, 137.6, 133.5, 129.1, 128.9, 128.7, 125.7, and 124.3.

(*E*)-4-(4-methoxyphenyl)but-3-en-2-one (e) Yellow solid (30%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ_H (ppm) 7.50–7.46 (m, 3H), 6.91 (d, *J* = 8.5 Hz, 2H), 7.60 (d, *J* = 16.5 Hz, 1H), 3.83 (d, *J* = 1.0 Hz, 3H), and 2.35 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ_C (ppm) 198.6, 161.7, 143.4, 130.1, 127.2, 125.1, 114.6, 55.5, and 27.5.

(*E*)-1-(4-methoxyphenyl)but-2-en-1-one (f) Following the procedure which was modified from the literature,[11] $AlCl_3$ (3.2 g) was added to a stirred solution of crotonoyl chloride (1.5 mL) and anisole (2 mL) in DCM (20 mL) at 0^o C. The reaction mixture was stirred at room temperature. After 15 min, the obtained residue was diluted with water (10 mL) and then extracted with DCM (3 x 20 mL). The combined organic layers were quenched with saturated $NaHCO_{3(aq)}$ (15 mL, 5 M), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to give the title compound as a yellow oil (60%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ_H (ppm) 7.91–7.93 (m, 2H), 6.93–6.91 (m, 3H), 6.89–6.87 (m, 1H), 3.84 (s, 3H), and 1.96 (dd, *J* = 6.5, 1.5 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ_C (ppm) 189.1, 163.3, 144.1, 130.9, 129.5, 127.2, 114.0, 55.5, and 18.6.

General procedure for allylic alcohols: Following the reported procedure,[12] $NaBH_4$ (4.0 mmol) was added to a stirred solution of the chosen allylic ketone (2.0 mmol) in MeOH/THF (6 mL each). The

reaction mixture was stirred at room temperature. After 1-3 h, the residue was diluted with water (10 mL) and then extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was then purified by column chromatography (hexane/EtOAc) to give the corresponding allylic alcohol.

(*E*)-3-(2-methoxyphenyl)-1-phenylprop-2-en-1-ol (1b) Colourless oil (75%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ_H (ppm) 7.47–7.42 (m, 3H), 7.39–7.36 (m, 2H) 7.28–7.31 (m, 1H), 7.25–7.21 (m, 1H), 7.39–7.35 (m, 1H), 7.05 (d, *J* = 16.0 Hz, 1H), 6.93–6.87 (m, 2H), 6.41 (dd, *J* = 16.0, 6.0 Hz, 1H), 5.40 (d, *J* = 6.0 Hz, 1H), and 3.86 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ_C (ppm) 157.0, 143.1, 132.3, 129.0, 128.7, 127.8, 127.2, 126.5, 125.7, 125.6, 120.7, 111.0, 75.7, and 55.6.

(*E*)-3-(3-methoxyphenyl)-1-phenylprop-2-en-1-ol (1c) Colourless oil (75%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ_H (ppm) 7.4–7.43 (m, 2H), 7.40–7.37 (m, 2H), 7.32–7.29 (m, 1H), 7.23 (t, *J* = 8.0 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.94–6.92 (m, 1H), 6.82–6.79 (m, 1H), 6.67 (d, *J* = 16.0 Hz, 1H), 6.38 (dd, *J* = 16.0, 6.5 Hz, 1H), 5.39 (d, *J* = 6.5 Hz, 1H), and 3.80 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ_C (ppm) 159.9, 142.9, 138.1, 132.0, 130.6, 129.7, 128.8, 128.0, 126.5, 119.5, 113.7, 112.0, 75.2, and 55.4.

(*E*)-3-(4-methoxyphenyl)-1-phenylprop-2-en-1-ol (1d) Colourless oil (60%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ_H (ppm) 7.46–7.29 (m, 7H), 6.94–6.91 (m, 2H), 6.61–6.51 (m, 1H), 6.42–6.33 (m, 1H), 5.11–5.01 (m, 1H), and 3.81 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ_C (ppm) 159.2, 141.7, 136.8, 133.4, 131.2, 129.5, 128.6, 127.9, 127.1, 114.0, 79.4, and 55.4.

(*E*)-3-(4-nitrophenyl)-1-phenylprop-2-en-1-ol (1e) Bright yellow oil (85%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ_H (ppm) 8.16 (dd, *J* = 9.0, 1.5 Hz, 2H), 7.51 (dd, *J* = 9.0, 1.5 Hz, 2H), 7.44–7.37 (m, 5H), 6.78 (d, *J* = 16.0 Hz, 1H), 6.56 (dd, *J* = 16.0, 5.5 Hz, 1H), and 5.44 (d, *J* = 5.5 Hz, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ_C (ppm) 150.0, 146.5, 144.2, 136.4, 129.0, 128.4, 128.1, 127.2, 126.6, 124.1, and 74.8.

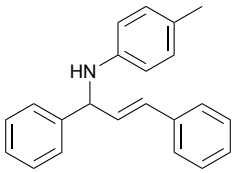
(*E*)-4-(4-methoxyphenyl)but-3-en-2-ol (1f) White solid (90%). ^{1}H-NMR (500 MHz, $(CD_3)_2CO$): δ_H (ppm) 7.34 (d, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 6.49 (dd, *J* = 16.0, 1.5 Hz, 1H), 6.16 (dd, *J* = 16.0, 6.0 Hz, 1H), 4.38–4.35 (m, 1H), 3.78 (s, 3H), and 1.26 (d, *J* = 6.0 Hz, 3H); ^{13}C-NMR (125 MHz, $(CD_3)_2CO$): δ_C (ppm) 160.1, 133.6, 130.8, 128.3, 128.2, 114.7, 68.5, 55.5, and 24.1.

(*E*)-1-(4-methoxyphenyl)but-2-en-1-ol (1g) White solid (20%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ_H (ppm) 7.31 (d, *J* = 9.0 Hz, 2H), 6.85 (d, *J* = 9.0 Hz, 2H), 6.50 (d, *J* = 16.0, Hz, 1H), 6.12 (dd, *J* = 16.0, 6.5 Hz, 1H), 5.11–5.08 (m, 1H), 3.80 (s, 3H), and 1.63 (d, *J* = 6.5 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ_C (ppm) 159.4, 131.5, 129.5, 129.2, 127.8, 114.1, 69.3, 55.4, and 18.3.

Nucleophilic Substitution Reactions of Allylic Alcohols

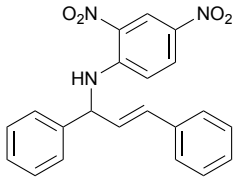
General procedure: An aqueous solution of phytic acid (50 wt% aq. solution, 2.5–5 mol%) was added to a solution of allylic alcohol **1** (1.0 equiv.) in technical toluene (0.5 M). Then, the chosen nucleophile (1.5 equiv.) was added. The reaction mixture stirred for 4-20 h at 110 °C. After completion, the solution was cooled to room temperature and concentrated *in vacuo* using a rotary evaporator. The obtained residue was purified by flash column chromatography.

(*E*)-*N*-(1,3-diphenylallyl)-4-methylaniline (3aa)



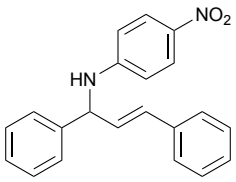
Following the general procedure for 20 h from (*E*)-1,3-diphenylprop-2-en-1-ol **1a** (210 mg, 1 mmol) and *p*-toluidine (160 mg, 1.5 mmol) with phytic acid (23.0 μL, 2.5 mol%), the title compound was isolated by column chromatography (hexane/EtOAc = 80:1) as a dark orange oil (253 mg, 85%). R_f = 0.63 (hexane/EtOAc = 32:1); ^{1}H NMR (500 MHz, $CDCl_3$):δ_H (ppm) 7.45 (dd, *J* = 8.5; 1.5 Hz, 2H), 7.40–7.36 (m, 4H), 7.33–7.29 (m, 3H), 7.24–7.22 (m, 1H), 6.98 (dd, *J* = 6.0; 2.0 Hz, 2H), 6.64 (dd, *J* = 16.0; 1.5 Hz, 1H), 6.60–6.57 (m, 2H), 6.41 (dd, *J* = 16.0; 6.5 Hz, 1H), 5.07 (dd, *J* = 6.5; 1.5 Hz, 1H, NCH), 2.25 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C (ppm) 145.1, 142.4, 136.9, 131.1, 131.0, 129.8, 128.9, 128.7, 127.8, 127.6, 127.3, 127.1, 126.6, 113.9, 61.1 (NCH), and 20.5. Spectroscopic data for this compound are in accordance with the literature.[13]

(*E*)-*N*-(1,3-Diphenylallyl)-2,4-dinitroaniline (3ab)



Following the general procedure for 4 h from (*E*)-1,3-diphenylprop-2-en-1-ol **1a** (210 mg, 1 mmol) and 2,4-dinitroaniline (274 mg, 1.5 mmol) with phytic acid (23.0 μL, 2.5 mol%), the title compound was isolated by column chromatography (hexane/EtOAc = 4:1) as a dark yellow oil (337 mg, 90%). R_f = 0.33 (hexane/EtOAc = 4:1); ^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ_H (ppm) 9.01 (d, *J* = 6.5 Hz, 1H), 8.95 (d, *J* = 2.5 Hz, 1H), 8.19 (dd, *J* = 9.5; 2.5 Hz, 1H), 7.56 (m, 2H), 7.43–7.39 (m, 4H), 7.34–7.31 (m, 1H), 7.29–7.26 (m, 2H), 7.22–7.12 (m, 2H), 6.81 (d, *J* = 16.0 Hz, 1H), 6.65 (dd, *J* = 16.0; 6.5 Hz, 1H), and 5.73 (t, *J* = 6.5 Hz, 1H, NCH); ^{13}C NMR (125 MHz, $(CD_3)_2CO$): δ_C (ppm) 148.3, 141.1, 137.2, 133.2, 132.0, 130.7, 130.1, 129.5, 129.2, 129.1, 129.0, 128.0, 127.6, 124.2, 116.9, and 60.8 (NCH); IR: ν_{max} 3357 (NH), 1612 (C=C), 1518-1493 (NO_2); HRMS (ESI) m/z: Calcd for $C_{21}H_{17}N_3O_4$ $[M+H]^+$ 376.1297, found 376.1290.

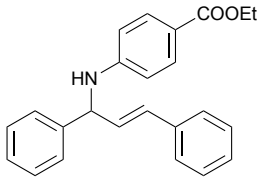
(*E*)-*N*-(1,3-diphenylallyl)-4-nitroaniline (3ac)



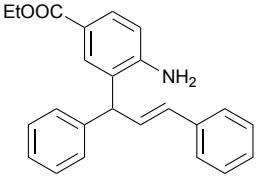
Following the general procedure for 4 h from (*E*)-1,3-diphenylprop-2-en-1-ol **1a** (210 mg, 1 mmol) and 4-nitroaniline (207 mg, 1.5 mmol) with phytic acid (23.0 μL, 2.5 mol%), the title compound was isolated by column chromatography (hexane/EtOAc = 4:1) as a light yellow solid (304 mg, 92%). Mp = 145–146 °C, R_f = 0.15 (hexane/EtOAc = 8:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ_H (ppm) 8.06 (d, *J* = 9.0 Hz, 2H), 7.41–7.30 (m, 10H), 6.62–6.58 (m, 3H), 6.38 (dd, *J* = 15.5; 6.5 Hz, 1H), and 5.21 (d, *J* = 6.5 Hz, 1H, NCH); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C (ppm) 152.2, 140.4, 138.7, 136.1, 132.4, 129.3, 128.8, 128.7, 128.4, 128.3, 127.3, 126.7, 126.4, 112.3, and 60.2 (NCH). Spectroscopic data for this compound are in accordance with the literature.[13]

Ethyl(*E*)-4-((1,3-diphenylallyl)amino)benzoate (3ad)

Following the general procedure for 4 h from (*E*)-1,3-diphenylprop-2-en-1-ol **1a** (210 mg, 1.0 mmol) and ethyl-4-aminobenzoate (247 mg, 1.5 mmol) with phytic acid (23.0 μL, 2.5 mol%), the title compound was isolated by column chromatography (hexane/EtOAc = 8:1) as a light yellow oil (279 mg, 78%). From this reaction, ethyl (*E*)-4-amino-3-(1,3-diphenylallyl)benzoate **4ad** was also isolated as a light yellow oil (49 mg, 14%).

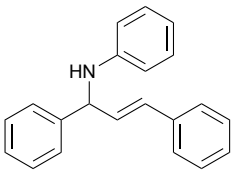


3ad: R_f = 0.5 (hexane/EtOAc = 8:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ_H (ppm) 7.86 (d, *J* = 8.5, 2H), 7.43–7.36 (m, 6H), 7.34–7.30 (m, 3H), 7.25-7.23 (m, 1H), 6.63–6.61 (m, 3H), 6.39 (dd, *J* = 16.0; 6.0 Hz, 1H), 5.18 (t, *J* = 5.5 Hz, 1H, NCH), 4.60 (d, *J* = 5.5 Hz, 1H), 4.31 (q, *J* = 14.5; 7.0 Hz, 2H), and 1.35 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C (ppm) 166.9, 150.9, 141.3, 136.5, 131.8, 131.5, 129.7, 129.1, 128.7, 128.0, 127.9, 127.3, 126.7, 119.4, 112.6, 60.3 (NCH), 60.1, and 14.5; IR: ν_{max} 3357 (NH), 1685 (C=O), 1599 (C=C); HRMS (ESI) m/z: Calcd for $C_{24}H_{23}NO_2$ $[M+H]^+$ 358.1807, found 358.1790.



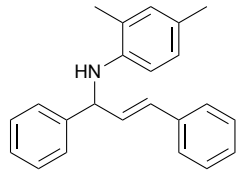
4ad: R_f = 0.35 (hexane/EtOAc = 8:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ_H (ppm) 7.85 (d, *J* = 2.0 Hz, 1H), 7.85 (dd, *J* = 8.5; 2.0 Hz, 1H), 7.39–7.21 (m, 10H), 6.69 (dd, *J* = 16.0; 7.5 Hz, 1H), 6.65 (d, *J* = 8.5 Hz, 1H), 6.33 (dd, *J* = 16.0; 1.5 Hz, 1H), 4.84 (d, *J* = 8.5 Hz, 1H), 4.30 (q, *J* = 7.0 Hz, 2H), and 1.33 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C (ppm) 167.0, 148.9, 141.2, 137.1, 132.2, 131.4, 130.5, 130.0, 129.0, 128.7, 128.6, 127.7, 127.2, 126.9, 126.6, 120.5, 115.5, 60.5, 50.0, and 14.5. Spectroscopic data for this compound are in accordance with the literature.[14]

(*E*)-*N*-(1,3-diphenylallyl)aniline (3ae)



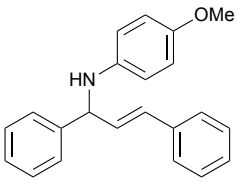
Following the general procedure for 20 h from (*E*)-1,3-diphenylprop-2-en-1-ol **1a** (210 mg, 1.0 mmol) and aniline (137 μL, 1.5 mmol) with phytic acid (23.0 μL, 2.5 mol%), the title compound was isolated by column chromatography (hexane/EtOAc = 32:1) as a dark orange oil (166 mg, 58%). R_f = 0.75 (hexane/EtOAc = 8:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ_H (ppm) 7.47–7.45 (m, 2H), 7.39-7.36 (m, 4H), 7.32–7.29 (m, 3H), 7.26–7.22 (m, 1H), 7.18–7.14 (m, 2H), 6.77–6.73 (m, 1H), 6.69 (dd, *J* = 8.5; 1.0 Hz, 2H), 6.65 (dd, *J* = 16.0; 1.5 Hz, 1H), 6.43 (dd, *J* = 16.0; 6.5 Hz, 1H), and 5.11 (dd, *J* = 6.5; 1.5 Hz, 1H, NCH); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C (ppm) 147.1, 142.0, 136.7, 131.3, 130.7, 129.3, 128.9, 128.7, 127.8, 127.7, 127.4, 126.7, 118.1, 114.0, and 61.0 (NCH). Spectroscopic data for this compound are in accordance with the literature.[13]

(*E*)-*N*-(1,3-diphenylallyl)-2,4-dimethylaniline (3af)



Following the general procedure for 20 h from (*E*)-1,3-diphenylprop-2-en-1-ol **1a** (210 mg, 1.0 mmol) and 2,4-dimethylaniline (182 mg, 1.5 mmol) with phytic acid (23.0 μL, 2.5 mol%), the title compound was isolated by column chromatography (hexane/EtOAc = 16:1) as a yellow oil (197 mg, 63%). R_f = 0.9 (hexane/EtOAc = 8:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ_H (ppm) 7.48–7.46 (m, 2H), 7.42–7.36 (m, 4H), 7.34–7.29 (m, 3H), 7.2 –7.24 (m, 1H), 6.94 (s, 1H), 6.86 (d, *J* = 8.5 Hz, 1H), 6.64 (d, *J* = 16.0 Hz, 1H), 6.51 (d, *J* = 8.0 Hz, 1H), 6.47 (d, *J* = 6.5 Hz, 1H), 6.44 (d, *J* = 6.3 Hz, 1H), 5.13 (d, *J* = 6.5 Hz, 1H), 2.24 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C (ppm) 142.9, 142.4, 136.8, 131.2, 131.1, 131.0, 128.9, 128.7, 127.8, 127.6, 127.4, 127.3, 126.7, 122.4, 111.7, 60.9, 20.5, 17.8. Spectroscopic data for this compound are in accordance with the literature.[15]

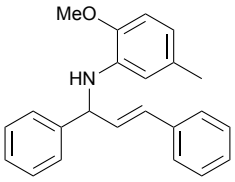
(*E*)-*N*-(1,3-diphenylallyl)-4-methoxyaniline (3ag)



Following the general procedure for 20 h from (*E*)-1,3-diphenylprop-2-en-1-ol **1a** (210 mg, 1.0 mmol) and 4-methoxyaniline (184 mg, 1.5 mmol) with phytic acid (23.0 μL, 2.5 mol%), the title compound was isolated by column chromatography (hexane/EtOAc = 16:1) as a dark brown oil (174 mg, 55%). R_f = 0.5 (hexane/EtOAc = 16:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ_H (ppm) 7.45–7.43 (m, 2H), 7.38–7.35 (m, 4H), 7.32–7.27 (m, 3H), 7.25–7.21 (m, 1H), 6.77–6.73 (m, 2H), 6.65–6.60 (m, 3H), 6.40 (dd, *J* = 16.0, 6.5 Hz, 1H), 5.07 (dd, *J* = 6.5, 1.5 Hz, 1H, NCH), and 3.73 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C (ppm) 152.4,

142.5, 141.7, 136.9, 131.3, 131.1, 129.0, 128.7, 127.8, 127.6, 127.4, 126.7, 115.1, 114.9, 61.7 (NCH), and 55.9. Spectroscopic data for this compound are in accordance with the literature.[13]

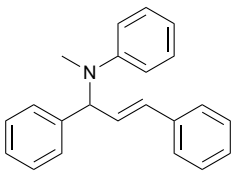
(*E*)-*N*-(1,3-diphenylallyl)-2-methoxy-5-methylaniline (3ah)



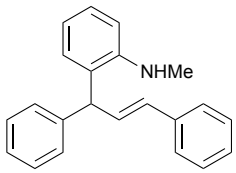
Following the general procedure for 20 h from (*E*)-1,3-diphenylprop-2-en-1-ol **1a** (210 mg, 1.0 mmol) and 2-methoxy-5-methylaniline (206 mg, 1.5 mmol) with phytic acid (23.0 μL, 2.5 mol%), the title compound was isolated by column chromatography (hexane/EtOAc = 16:1) as a yellow oil (135 mg, 41%). R_f = 0.76 (hexane/EtOAc = 8:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ_H (ppm) 7.47–7.45 (m, 2H), 7.41–7.35 (m, 4H), 7.34–7.27 (m, 3H), 7.25–7.22 (m, 1H), 6.69 (d, *J* = 8.0 Hz, 1H), 6.63 (d, *J* = 16.0 Hz, 1H), 6.48 (dd, *J* = 8.0, 2.5 Hz, 1H), 6.44 (dd, *J* = 16.0, 6.0 Hz, 1H), 6.41 (d, *J* = 2.0 Hz, 1H), 5.08 (d, *J* = 6.0 Hz, 1H), 3.85 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C (ppm) 145.0, 142.4, 137.1, 136.9, 131.1, 130.9, 130.6, 128.9, 128.7, 127.7, 127.5, 127.4, 126.7, 117.1, 112.3, 109.4, 60.6, 55.7, 21.3; IR: n_{max} 3420 (NH), 1596 (C=C); HRMS (ESI) m/z: Calcd for $C_{23}H_{23}NO$ $[M+H]^+$ 330.1858, found 330.1857.

(*E*)-*N*-(1,3-diphenylallyl)-*N*-methylaniline (3ai)

Following the general procedure for 20 h from (*E*)-1,3-diphenylprop-2-en-1-ol **1a** (210 mg, 1.0 mmol) and *N*-methylaniline (162 μL, 1.5 mmol) with phytic acid (46 μL, 5 mol%), the title compound was isolated by column chromatography (hexane/EtOAc = 40:1) as a light brown oil (173 mg, 58%). From this reaction, (*E*)-2-(1,3-diphenylallyl)-*N*-methylaniline **4ag** was also isolated as a light brown oil (21 mg, 7%).



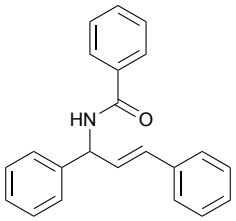
3ai: R_f = 0.38 (hexane/EtOAc = 40:1), ^{1}H NMR (500 MHz, $CDCl_3$): δ_H (ppm) 7.37–7.28 (m, 10H), 7.25–7.22 (m, 2H), 7.10 (dd, *J* = 7.5, 2.0 Hz, 1H), 6.78 (m, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 6.67 (dd, *J* = 16.0, 6.0 Hz, 1H), 6.25 (dd, *J* = 16.0, 2.0 Hz, 1H), 4.89 (d, *J* = 6.0 Hz, 1H, NCH), and 2.76 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C (ppm) 146.5, 141.9, 137.3, 131.8, 131.6, 129.2, 129.0, 128.9, 128.7, 128.0, 127.5, 127.0, 126.5, 117.8, 49.2 (NCH), and 29.8. Spectroscopic data for this compound are in accordance with the literature.[16]



4ai: R_f = 0.28 (hexane/EtOAc = 40:1); ^{1}H NMR (500 MHz, DMSO-d_6): δ_H (ppm) 7.42–7.40 (m, 2H), 7.31–7.28 (m, 4H), 7.26–7.24 (m, 2H), 7.22–7.18 (m, 2H), 7.10–7.06 (m, 1H), 7.03 (dd, *J* = 7.5, 2.0 Hz, 1H), 6.77 (dd, *J* = 16.0, 7.5 Hz, 1H), 6.61-6.58 (m, 1H), 6.53 (dd, *J* = 8.5, 1.5 Hz, 1H), 6.31 (dd, *J* = 16.0, 1.0 Hz, 1H), 5.06 (q, *J* = 5.0 Hz, 1H), 5.02 (d, *J* = 7.5 Hz, 1H), and 2.69 (d, *J* = 5.0, 3H); ^{13}C NMR (125 MHz, DMSO-d_6):

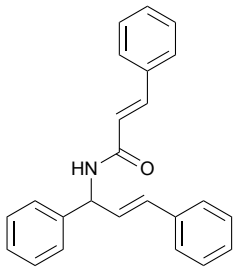
δ_C (ppm) 146.6, 143.0, 137.0, 132.7, 130.0, 128.7, 128.5, 128.4, 128.3, 127.4, 127.3, 127.2, 126.3, 126.2, 115.8, 109.7, 46.8, and 30.4. Spectroscopic data for this compound are in accordance with the literature.[17]

(*E*)-*N*-(1,3-diphenylallyl)benzamide (3aj)



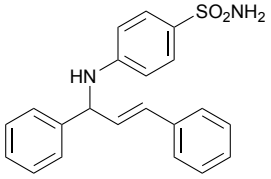
Following the general procedure for 4 h from (*E*)-1,3-diphenylprop-2-en-1-ol **1a** (210 mg, 1.0 mmol) and benzamide (181 mg, 1.5 mmol) with phytic acid (23.0 μL, 2.5 mol%), the title compound was isolated by column chromatography (hexane/EtOAc = 4:1) as a white solid (305 mg, 97%). Mp = 154–155 °C; R_f = 0.18 (hexane/EtOAc = 8:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ_H (ppm) 7.81–7.79 (m, 2H), 7.50–7.46 (m, 1H), 7.42–7.38 (m, 4H), 7.37–7.34 (m, 4H), 7.30–7.27 (m, 2H), 7.23–7.20 (m, 1H), 6.63 (d, *J* = 8.0 Hz, 1H), 6.59 (dd, *J* = 16.0, 1.5 Hz, 1H), 6.41 (dd, *J* = 16.0, 6.5 Hz, 1H), and 6.00 (t, *J* = 6.5 Hz, 1H, NCH); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C (ppm) 166.7, 140.9, 136.5, 134.4, 131.9, 131.8, 129.0, 128.9, 128.7, 128.6, 128.0, 127.9, 127.4, 127.2, 126.7, and 55.4 (NCH). Spectroscopic data for this compound are in accordance with the literature.[18]

***N*-((*E*)-1,3-diphenylallyl)cinnamamide (3ak)**



Following the general procedure for 4 h from (*E*)-1,3-diphenylprop-2-en-1-ol **1a** (210.1 mg, 1.0 mmol) and (*E*)-3-phenylacrylamide (220.8 mg, 1.5 mmol) with phytic acid (23.0 μL, 2.5 mol%), the title compound was obtained after trituration with acetone as a light white solid (324.5 mg, 96%). Mp = 181-183 °C; R_f = 0.1 (hexane/EtOAc = 4:1); ^{1}H NMR (500 MHz, DMSO-d_6): d (ppm) 8.86 (d, *J* = 8.0 Hz, 1H), 7.58 (dd, *J* = 8.5, 1.5 Hz, 2H), 7.48 (d, *J* = 16.0 Hz, 1H), 7.46-7.36 (m, 9H), 7.34-7.31 (m, 2H), 7.30-7.22 (m, 2H), 6.80 (d, *J* = 16.0 Hz, 1H), 6.57 (d, *J* = 16.0 Hz, 1H), 6.49 (dd, *J* = 16.0, 6.5 Hz, 1H), 5.79 (t, *J* = 6.5 Hz, 1H, NCH); ^{13}C NMR (125 MHz, DMSO-d_6): d (ppm) 164.1, 141.9, 139.2, 136.3, 134.9, 130.1, 129.9, 129.6, 129.0, 128.7, 128.6, 127.7, 127.6, 127.2, 127.1, 126.4, 122.1, 54.3 (NCH). Spectroscopic data for the title compound is in accordance with the literature.[13]

(*E*)-4-((1,3-diphenylallyl)amino)benzenesulfonamide (3al)

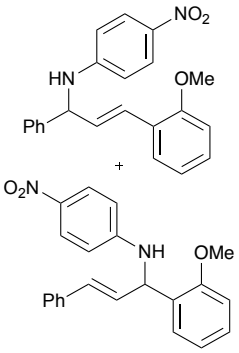


Following the general procedure for 2.5 h from (*E*)-1,3-diphenylprop-2-en-1-ol **1a** (210.1 mg, 1.0 mmol) and 4-aminobenzenesulfonamide (258.3 mg, 1.5 mmol) with phytic acid (23.0 μL, 2.5 mol%), the title compound was isolated by column chromatography (hexane/EtOAc = 2:1) as a light yellow oil (289.0 mg, 79%). R_f = 0.2 (hexane/EtOAc = 2:1); ^{1}H NMR (500 MHz, DMSO-d_6): d (ppm) 7.48-7.44 (m, 4H),

7.42-7.40 (m, 2H), 7.38-7.35 (m, 2H), 7.33-7.30 (m, 2H), 7.27-7.22 (m, 2H), 7.08 (d, *J* = 7.0 Hz, 1H, NH), 6.90 (s, 1H, SO_2NH_2), 6.72-6.70 (m, 2H), 6.61 (d, *J* = 16.0 Hz, 1H), 6.46 (dd, *J* = 16.0, 7.0 Hz, 1H), 5.30 (t, *J* = 7.0 Hz, 1H, NCH); ^{13}C NMR (125 MHz, DMSO-d_6): d (ppm) 150.3, 142.0, 136.4, 130.9 ($C^{Ar}SO_2NH_2$), 130.6, 130.0, 128.7, 128.6, 127.7, 127.2 (NHC^{Ar}), 127.1, 126.4, 111.9 , 58.5 (NCH); IR: n_{max} 3359 (NH_2), 3352 (N-H), 1703 (SO_2NH_2, N-H), 1595 (C=C), 1315 (S=O); HRMS (ESI) m/z: Calcd for $C_{21}H_{20}N_2O_2S$ $[M+Na]^+$ 387.1143, found 387.1138.

(*E*)-*N*-(3-(2-methoxyphenyl)-1-phenylallyl)-4-nitroaniline (3bc)

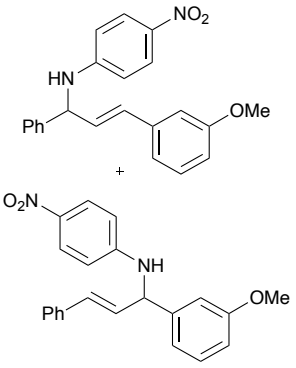
And (*E*)-*N*-(1-(2-methoxyphenyl)-3-phenylallyl)-4-nitroaniline (3bc')



Following the general procedure from for 4 h (*E*)-3-(2-methoxyphenyl)-1-phenylprop-2-en-1-ol **1b** (240 mg, 1.0 mmol) and 4-nitroaniline (207 mg, 1.5 mmol) with phytic acid (23.0 μL, 2.5 mol%), the title compound was isolated by column chromatography (hexane/EtOAc = 4:1) as a mixture of regioisomers as a light yellow oil (332 mg, 92%). R_f = 0.5 (hexane/EtOAc = 4:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ_H (ppm) 8.03–7.93 (m, 4H), 7.40–7.8 (m, 12H), 7.23–7.19 (m, 2H), 6.97–6.94 (m, 3H), 6.89–6.83 (m, 2H), 6.56–6.53 (m, 5H), 6.40 (d, *J* = 5.5 Hz, 1H), 6.38–6.35 (m, 1H), 5.55 (d, *J* = 7.5 Hz, 1H, NCH), 5.17 (d, *J* = 7.5 Hz, 1H, NCH), 3.87 (s, 3H), and 3.80 (s, 3H'); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C (ppm) 156.9, 152.5, 152.4, 140.7, 138.2, 138.1, 136.4, 131.4, 129.3, 129.3, 129.1, 128.7, 128.4, 128.2, 128.0, 127.9, 127.9, 127.3, 127.2, 127.1, 126.6, 126.4, 126.3, 126.0, 125.0, 121.1, 120.7, 112.2, 112.0, 111.2, 111.0, 60.6 (NCH), 55.7, 55.5 (NCH), and 54.4; IR: ν_{max} 3348 (NH), 1597 (C=C), 1489 (NO_2); HRMS (ESI) m/z: Calcd for $C_{22}H_{20}N_2O_3$ $[M+H]^+$ 361.1552, Found 361.1547.

(*E*)-*N*-(3-(3-methoxyphenyl)-1-phenylallyl)-4-nitroaniline (3cc)

and (*E*)-*N*-(1-(3-methoxyphenyl)-3-phenylallyl)-4-nitroaniline (3cc')

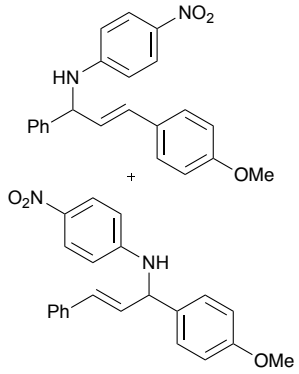


Following the general procedure for 4 h from (*E*)-3-(3-methoxyphenyl)-1-phenylprop-2-en-1-ol **1c** (240 mg, 1.0 mmol) and 4-nitroaniline (207 mg, 1.5 mmol) with phytic acid (23.0 μL, 2.5 mol%), the title compound was isolated by column chromatography (hexane/EtOAc = 4:1) as a mixture of regioisomers as a dark yellow oil (329 mg, 91%). R_f = 0.48 (hexane/EtOAc = 4:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ_H (ppm) 8.06–8.04 (m, 2 x 2H), 7.40 (dd, *J* = 4.5 Hz, 2 x 2H), 7.38–7.30 (m, 2 x 4H), 7.25–7.21 (m, 2 x 1H), 6.97 (dd, J = 15.0; 7.5 Hz 1H), 6.94–6.93 (m, 1H), 6.90–6.89 (m, 1H), 6.88–6.85 (m, 1H), 6.82–6.80 (m, 1H), 6.62–6.56 (m, 7H), 6.39–6.37 (m, 1H), 6.36–6.34 (m, 1H), 5.20 (dd, *J* = 6.0, 1.5 Hz, 1H, NCH), 5.16 (dd, *J* = 6.0, 1.5 Hz, 1H, NCH), 4.97 (br s, 1H), 3.81 (s, 3H), and 3.80 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C

(ppm) 160.3, 159.9, 152.2, 142.1, 140.3, 138.5, 137.5, 136.1, 132.4, 132.2, 130.4, 129.8, 129.3, 129.0, 128.8, 128.6, 128.5, 128.3, 128.3, 127.3, 126.7, 126.4, 126.0, 119.4, 119.3, 113.9, 113.2, 113.1, 112.2, 112.0, 60.1 (NCH), 60.1 (NCH), 55.4, and 55.4. IR: ν_{max} 3371 (NH), 1595 (C=C), 1500 (NO_2); HRMS (ESI) m/z: Calcd for $C_{22}H_{20}N_2O_3$ $[M+H]^+$ 361.1552, found 361.1549.

(*E*)-*N*-(3-(4-methoxyphenyl)-1-phenylallyl)-4-nitroaniline (3dc)

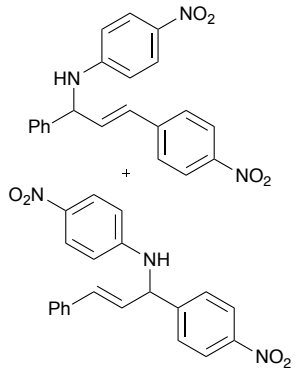
and (*E*)-*N*-(1-(4-methoxyphenyl)-3-phenylallyl)-4-nitroaniline (3dc')



Following the general procedure for 4 h from (*E*)-3-(4-methoxyphenyl)-1-phenylprop-2-en-1-ol **1d** (240 mg, 1.0 mmol) and 4-nitroaniline (207 mg, 1.5 mmol) with phytic acid (23.0 μL, 2.5 mol%), the title compound was isolated by column chromatography (hexane/EtOAc = 4:1) as a mixture of regioisomers as a dark yellow oil (333 mg, 92%). R_f = 0.45 (hexane/EtOAc = 4:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ_H (ppm) 8.05 (dd, *J* = 9.0; 4.5 Hz, 2 x 2H), 7.39 (d, *J* = 4.5 Hz, 2 x 2H), 7.38–7.22 (m, 2 x 5H), 6.92 (d, *J* = 9.0 Hz, 1 x 2H), 6.85 (d, *J* = 9.0 Hz, 2 x 1H), 6.59–6.55 (m, 5H), 6.53 (d, *J* = 16.0 Hz, 1H), 6.37 (dd, *J* = 16.0; 6.0 Hz, 1H), 6.23 (dd, *J* = 16.0; 6.5 Hz, 1H), 5.19–5.16 (m, 2 x 1H, NCH), 4.95 (br s, 1H), 4.91 (br s, 1H), 3.82 (s, 3H), and 3.80 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C (ppm) 159.7, 159.5, 152.3, 140.6, 138.5, 136.2, 132.3, 132.0, 131.9, 129.2, 128.8, 128.5, 128.2, 127.9, 127.2, 126.7, 126.5, 126.4, 114.6, 114.2, 112.2, 60.2 (NCH), 59.5 (NCH), 55.5, 55.4; IR: ν_{max} 3357 (NH), 1595 (C=C), 1508 (NO_2); HRMS (ESI) m/z: Calcd for $C_{22}H_{20}N_2O_3$ $[M+H]^+$ 361.1552, found 361.1537.

(*E*)-4-nitro-*N*-(3-(4-nitrophenyl)-1-phenylallyl)aniline (3ec)

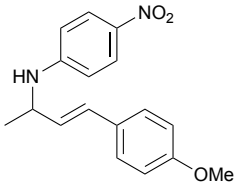
and (*E*)-4-nitro-*N*-(1-(4-nitrophenyl)-3-phenylallyl)aniline (3ec')



Following the general procedure for 4 h from (*E*)-3-(4-nitrophenyl)-1-phenylprop-2-en-1-ol **1e** (255 mg, 1.0 mmol) and 4-nitroaniline (207 mg, 1.5 mmol) with phytic acid (23.0 μL, 2.5 mol%), the title compound was isolated by column chromatography (hexane/EtOAc = 4:1) as a mixture of regioisomers as a dark yellow oil (209 mg, 56%). R_f = 0.2 (hexane/EtOAc = 4:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ_H (ppm) 8.26 (d , *J* = 8.5 Hz, 2H), 8.17 (d, *J* = 9.0 Hz, 2H), 8.07 (dd, *J* = 9.0; 7.5 Hz, 2 x 2H), 7.60 (d, *J* = 9.0 Hz, 2H), 7.50 (d, *J* = 9.0 Hz, 2H), 7.45-7.39 (m, 2 x 2H), 7.37–7.27 (m, 2 x 3H), 6.69–6.59 (m, 5H), 6.54 (d, *J* = 9.0 Hz, 2H), 6.34 (dd, *J* = 16.0, 6.5 Hz, 1H), 5.32 (d, *J* = 7.0 Hz, 1H, NCH), 5.25 (dd, *J* = 7.0 Hz, 1H, NCH), and 4.97 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C (ppm) 151.9, 151.5, 147.8, 147.3, 142.6, 139.5, 139.23, 138.9, 135.5, 134.2, 133.5, 130.0, 129.5, 129.0, 128.9, 128.8, 128.0, 127.4, 127.2, 126.8, 126.4, 124.6, 124.2,

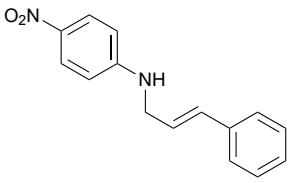
112.4, 112.3, 60.1 (NCH), 59.9 (NCH); IR: ν_{max} 3348 (NH), 1593 (C=C), 1512 (NO_2); HRMS (ESI) m/z: Calcd for $C_{21}H_{17}N_3O_4$ $[M+H]^+$ 376.1297, found 376.1299.

(*E*)-*N*-(4-(4-methoxyphenyl)but-3-en-2-yl)-4-nitroaniline (3fc)



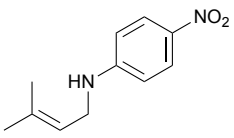
Following the general procedure for 4 h from (*E*)-4-(4-methoxyphenyl)but-3-en-2-ol **1f** or (*E*)-1-(4-methoxyphenyl)but-2-en-1-ol **1g** (178 mg, 1.0 mmol) and 4-nitroaniline (207 mg, 1.5 mmol) with phytic acid (23.0 μL, 2.5 mol%), the title compound was isolated by column chromatography (hexane/EtOAc = 8:1) as a mixture of regioisomers as a dark yellow oil (270 mg, 91% from **1f** or 274 mg, 92% from **1g**). R_f = 0.2 (hexane/EtOAc = 4:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ_H (ppm) 8.06 (d, *J* = 9.0 Hz, 2H), 7.28 (d, *J* = 9.0 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 6.56 (d, *J* = 9.0 Hz, 2H), 6.49 (dd, *J* = 16.0; 1.5 Hz, 1H), 6.01 (dd, *J* = 16.0; 6.0 Hz, 1H), 4.60 (br s, 1H), 4.24–4.21 (m, 1H, NCH), 3.80 (s, 3H), and 1.45 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C (ppm) 159.5, 152.7, 138.1, 130.0, 129.1, 128.7, 127.7, 126.5, 114.2, 111.8, 55.4, 50.8, and 22.0; IR: ν_{max} 3396 (NH), 1595 (C=C), 1498 (NO_2); HRMS (ESI) m/z: Calcd for $C_{17}H_{18}N_2O_3$ $[M+H]^+$ 299.1395, found 299.1385.

***N*-cinnamyl-4-nitroaniline (3hc)**



Following the general procedure for 20 h from (*E*)-3-phenylprop-2-en-1-ol **1h** (124 μL, 1.0 mmol) and 4-nitroaniline (207 mg, 1.5 mmol) with phytic acid (23.0 μL, 2.5 mol%), the title compound was isolated by column chromatography (hexane/EtOAc = 4:1) as a yellow solid (212 mg, 83%). Mp = 141–142 °C; R_f = 0.38 (hexane/EtOAc = 4:1); ^{1}H NMR (500 MHz, DMSO-d_6): δ_H (ppm) 8.01 (d, *J* = 9.5 Hz, 2H,), 7.59 (t, *J* = 6.0 Hz, 1H), 7.41 (d, *J* = 7.0 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.23 (t, *J* = 7.5 Hz, 1H), 6.69 (d, *J* = 9.5 Hz, 2H), 6.59 (d, *J* = 16.0 Hz, 2H), 6.37-6.32 (m, 1H), and 4.01 (t, *J* = 6.0 Hz, 2H, NCH_2); ^{13}C NMR (125 MHz, DMSO-d_6): δ_C (ppm) 154.5, 136.4, 135.9, 130.9, 128.7, 127.6, 126.3, 126.2, 110.1, 110.9, and 44.3 (NCH_2). Spectroscopic data for these compounds are in accordance with the literature.[19]

***N*-(3-methylbut-2-en-1-yl)-4-nitroaniline (3ic')**

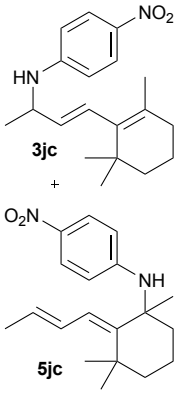


Following the general procedure for 4 h from 2-methylbut-3-en-2-ol **1i** (99 μL, 1.0 mmol) and 4-nitroaniline (207 mg, 1.5 mmol) with phytic acid (46.0 μL, 5 mol%), the title compound was isolated by column chromatography (hexane/EtOAc = 8:1) as a dark yellow oil (70 mg, 34%). R_f = 0.42 (hexane/EtOAc = 4:1); ^{1}H NMR (500 MHz, DMSO-d_6): δ_H (ppm) 7.98 (dd, *J* = 7.0; 2.0 Hz, 2H), 7.35 (t, *J* = 5.0 Hz, 1H), 6.61 (dd, *J* = 7.0; 2.0 Hz,

2H), 5.25—5.21 (m, 1H), 3.74 (t, *J* = 6.0 Hz, 2H, NCH_2), and 1.70 (dd, *J* = 8.0; 1.5 Hz, 6H); ^{13}C NMR (125 MHz, DMSO-d_6): δ_C (ppm) 154.5, 135.6, 135.1, 126.3, 120.7, 112.5, 25.5 (NCH_2), and 18.0. Spectroscopic data for this compound are in accordance with the literature.[20]

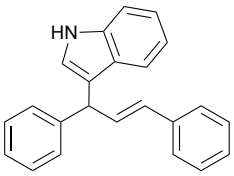
(*E*)-4-nitro-*N*-(4-(2,6,6-trimethylcyclohex-1-en-1-yl)but-3-en-2-yl)aniline (3jc)

and *N*-((*E*)-2-((*E*)-but-2-en-1-ylidene)-1,3,3-trimethylcyclohexyl)-4-nitroaniline (5jc)



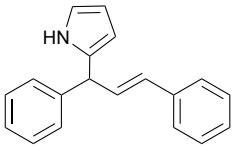
Following the general procedure for 4 h from (E)-4-(2,6,6-trimethylcyclohex-1-en-1-yl)but-3-en-2-ol **1j** (194 mg, 1.0 mmol) and 4-nitroaniline (207 mg, 1.5 mmol) with phytic acid (23.0 μL, 2.5 mol%), the title compound was isolated by column chromatography (hexane/EtOAc = 16:1) as a mixture of regioisomers as a yellow oil (287 mg, 91%). R_f = 0.6 (hexane/EtOAc = 8:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ_H (ppm) 8.07 (d, *J* = 9.0 Hz, 2 x 2H), 6.72—6.67 (m, 1H), 6.62 (d, *J* = 9.0 Hz, 2 x 1H), 6.59 (d, *J* = 9.0 Hz, 1H), 6.06—6.01 (m, 2 x 1H), 5.70—5.69 (m, 1H), 5.67–5.63 (m, 1H, CH=C*H*-CH_3; **5ic**) 5.31 (dd, *J* = 16.0; 6.0 Hz, 1H), 4.13—4.09 (m, 1H, NCH; **3jc**), 2.09—2.05 (m, 2H), 1.96—1.93 (m, 2H), 1.83—1.81 (m, 3 x 3H), 1.59—1.56 (m, 3 x 3H), 1.47 (t , *J* = 6.0 Hz, 2H), 1.43—1.40 (m, 3 x 3H), 1.26 (s, 3 x 3H), 0.94 (s, 3H), and 0.89 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C (ppm) 152.6, 142.6, 138.1, 136.6, 134.8, 134.0, 130.4 (CH=*C*H-CH_3; **5jc**), 130.1, 129.1, 128.9, 127.3, 126.5, 126.4, 124.1, 113.5, 112.2, 51.5 (NCH; **3jc**), 40.6, 39.3, 34.9, 34.0, 32.7, 29.1, 28.8, 28.7, 28.0, 22.9, 22.3, 21.9, 21.5, 19.3, and 18.8; IR: ν_{max} 3357 (NH), 2904 (C–H), 1595 (C=C), 1535 (NO_2); HRMS (ESI) m/z: Calcd for $C_{19}H_{26}N_2O_2$ $[M+H]^+$ 315.2072, found 315.2087.

(*E*)-3-(1,3-diphenylallyl)-1*H*-indole (3am)



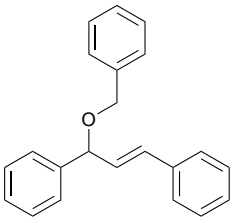
Following the general procedure for 2.5 h from (*E*)-1,3-diphenylprop-2-en-1-ol **1a** (210 mg, 1.0 mmol) and 1*H*-indole (175 mg, 1.5 mmol) with phytic acid (23.0 μL, 2.5 mol%), the title compound was isolated by column chromatography (hexane/EtOAc = 8:1) as a dark brown oil (249 mg, 80%). R_f = 0.25 (hexane/EtOAc = 40:1); ^{1}H NMR (500 MHz, DMSO-d_6): δ_H (ppm) 10.96 (br s, 1H) 7.44 (dd, *J* = 8.5; 1.5 Hz, 2H), 7.37—7.34 (m, 4H), 7.31—7.28 (m, 4H), 7.22—7.17 (m, 3H), 7.06—7.03 (m, 1H), 6.91—6.86 (m, 2H), 6.49 (d, *J* = 15.5 Hz, 1H), and 5.09 (d, *J* = 8.0 Hz, 1H, C^{indole}CH); ^{13}C NMR (125 MHz, DMSO-d_6): δ_C (ppm) 144.2, 137.1, 136.6, 133.1, 129.4, 128.6, 128.4, 128.0, 127.2, 126.3, 126.2, 126.1, 122.9, 121.1, 119.0, 118.4, 117.0, 111.6, and 45.9 (C^{indole}*C*H). Spectroscopic data for this compound are in accordance with the literature.[18]

(*E*)-2-(1,3-diphenylallyl)-1*H*-pyrrole (3an)



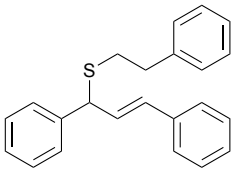
Following the general procedure for 2.5 h from (*E*)-1,3-diphenylprop-2-en-1-ol **1a** (210 mg, 1.0 mmol) and 1*H*-pyrrole (101 μL, 1.5 mmol) with phytic acid (23.0 μL, 2.5 mol%), the title compound was isolated by column chromatography (hexane/EtOAc = 8:1) as a black oil (213 mg, 82%). R_f = 0.5 (hexane/EtOAc = 8:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ_H (ppm) 7.40—7.28 (m, 10H), 6.74—6.72 (m, 1H), 6.61 (dd, *J* = 15.5; 7.5 Hz, 1H), 6.44 (dd, *J* = 15.5; 1.5 Hz, 1H), 6.21—6.18 (m, 1H), 6.00—5.98 (m, 1H), and 4.88 (d, *J* = 6.5 Hz, 1H, $C^{pyrrole}CH$); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C (ppm) 142.2, 137.1, 133.2, 131.4, 131.2, 128.9, 128.7, 128.5, 127.6, 127.1, 126.5, 117.4, 108.5, 106.9, and 48.2 ($C^{pyrrole}$*C*H). Spectroscopic data for this compound are in accordance with the literature.[21]

(*E*)-(3-(benzyloxy)prop-1-ene-1,3-diyl)dibenzene (3ao)



Following the general procedure for 2.5 h from (*E*)-1,3-diphenylprop-2-en-1-ol **1a** (210.1 mg, 1.0 mmol) and phenylmethanol (155.4 μL, 1.5 mmol) with phytic acid (23.0 μL, 2.5 mol%), the title compound was isolated by column chromatography (hexane/EtOAc = 90:1) as a light yellow oil (286.0 mg, 95%). R_f = 0.6 (hexane/EtOAc = 90:5); ^{1}H NMR (500 MHz, $CDCl_3$): δ_H (ppm) 7.51 (dd, *J* = 8.5; 1.5 Hz, 2H), 7.46–7.41 (m, 8H), 7.39–7.35 (m, 4H), 7.31–7.27 (m, 1H), 6.70 (d, *J* = 15.0 Hz, 1H), 6.42 (dd, *J* = 16.0; 7.0 Hz, 1H), 5.09 (d, *J* = 7.0 Hz, 1H, OCH), 4.65 (dd, *J* = 14.5; 12.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C (ppm) 141.2, 138.5, 136.7, 131.7, 131.5, 130.5, 130.4, 128.7, 128.5, 127.8, 127.7, 127.2, 127.1, 126.7, 81.7 (OCH), 70.2. Spectroscopic data for the title compound is in accordance with the literature.[22]

(*E*)-(1,3-diphenylallyl)(phenethyl)sulfane (3ap)



Following the general procedure for 2.5 h from (*E*)-1,3-diphenylprop-2-en-1-ol **1a** (210.1 mg, 1.0 mmol) and 2-phenylethanethiol (200.9 μL, 1.5 mmol) with phytic acid (23.0 μL, 2.5 mol%), the title compound was isolated by column chromatography (hexane/EtOAc = 90:1) as a light yellow oil (306.4 mg, 93%). R_f = 0.65 (hexane/EtOAc = 90:5); ^{1}H NMR (500 MHz, $CDCl_3$): δ_H (ppm) 7.42–7.26 (m, 12H), 7.24–7.21 (m, 1H), 7.16 (d, *J* = 7.0 Hz, 2H), 6.47 (d, *J* = 16.0 Hz, 1H), 6.40 (dd, *J* = 16.0; 8.0 Hz, 1H), 4.55 (d, *J* = 8.0 Hz, 1H, SCH), 2.89 (t, *J* = 8.0 Hz, 2H), 2.80–2.71 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C (ppm) 140.6, 136.6, 131.1, 129.6, 128.8, 128.75, 128.7, 128.6, 128.5, 127.9, 127.8, 127.6, 126.6, 126.5, 52.6 (SCH), 36.4, 33.3; IR: ν_{max} 3024 (S-H), 1599 (C=C); HRMS (ESI) m/z: Calcd for $C_{23}H_{22}S$ $[M+Na]^+$ 353.1340, found 353.1334.

^{31}P NMR study

The ^{31}P NMR spectra of commercially available phytic acid (50 wt% aqueous solution) and the crude mixtures were recorded in DMSO-d_6 with respect to the diphenyl phosphate as an external standard (δ = -11.5 ppm) (Figure 1).

Reaction procedure for model reaction: *p*-Toluidine (1.5 mmol) was added to a solution of allylic alcohol **1a** (1.0 mmol) and phytic acid (23.0 µL, 2.5% mol) in technical toluene (2 mL). The reaction mixture was stirred for 20 h at 110 °C. After completion, the solution was cooled to room temperature and concentrated *in vacuo* using a rotary evaporator.

Reaction procedure for stoichiometric reaction: *p*-Toluidine (1.5 mmol) was added to a solution of phytic acid (1.5 mmol) in technical toluene (2 mL). The reaction mixture was stirred for 20 h at 110 °C. After completion, the solution was cooled to room temperature and concentrated *in vacuo* using a rotary evaporator.

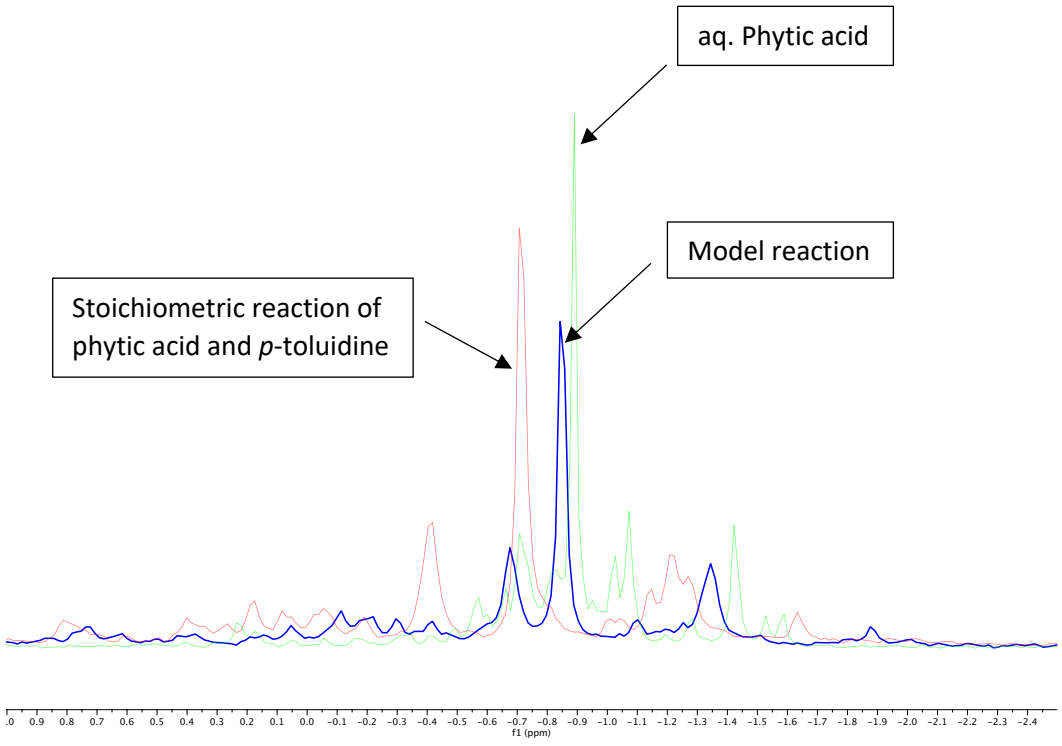
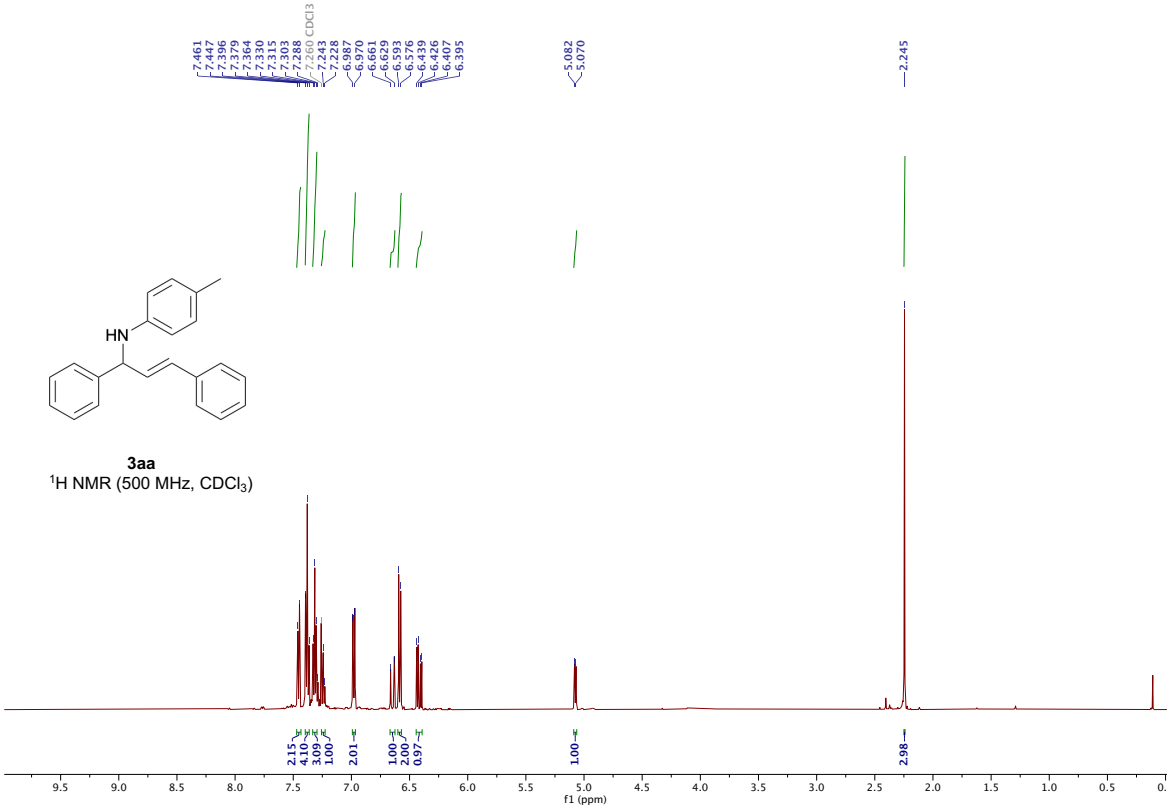


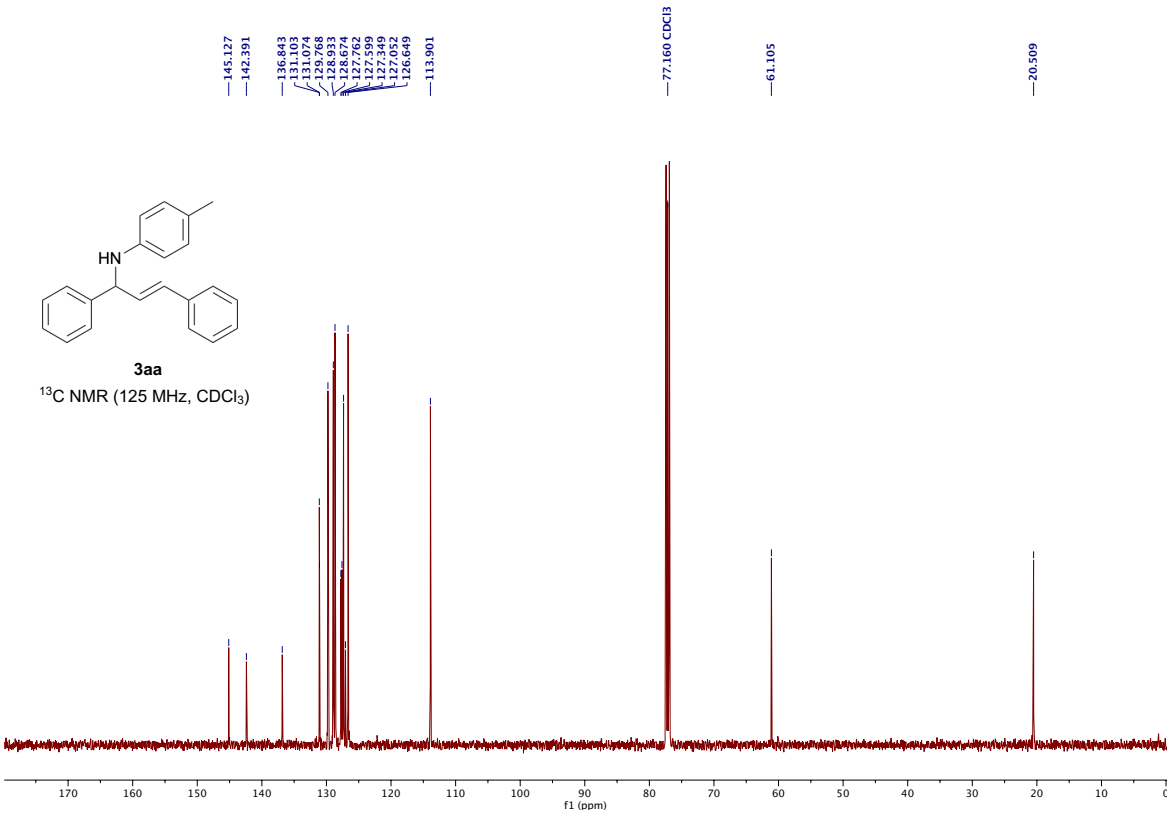
Figure 1. Superimposed ^{31}P NMR spectra.

^{1}H NMR and ^{31}C NMR Spectra of Substituted Products



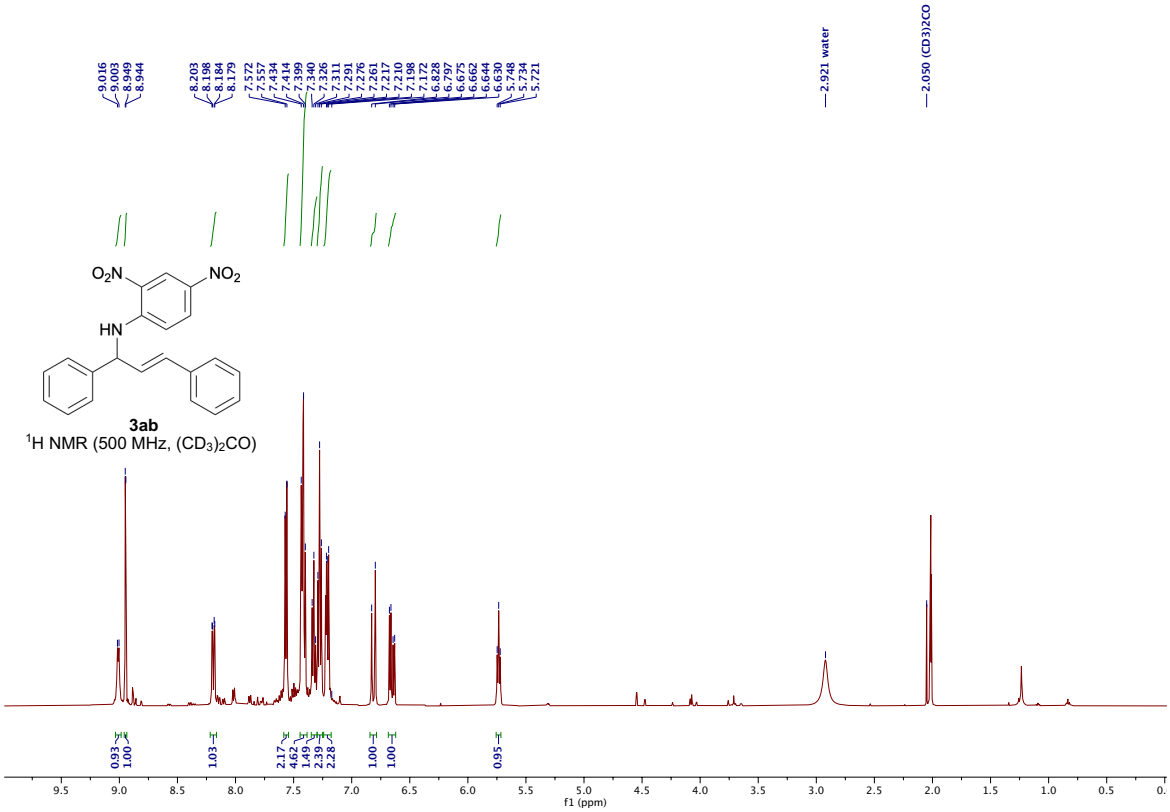
3aa

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



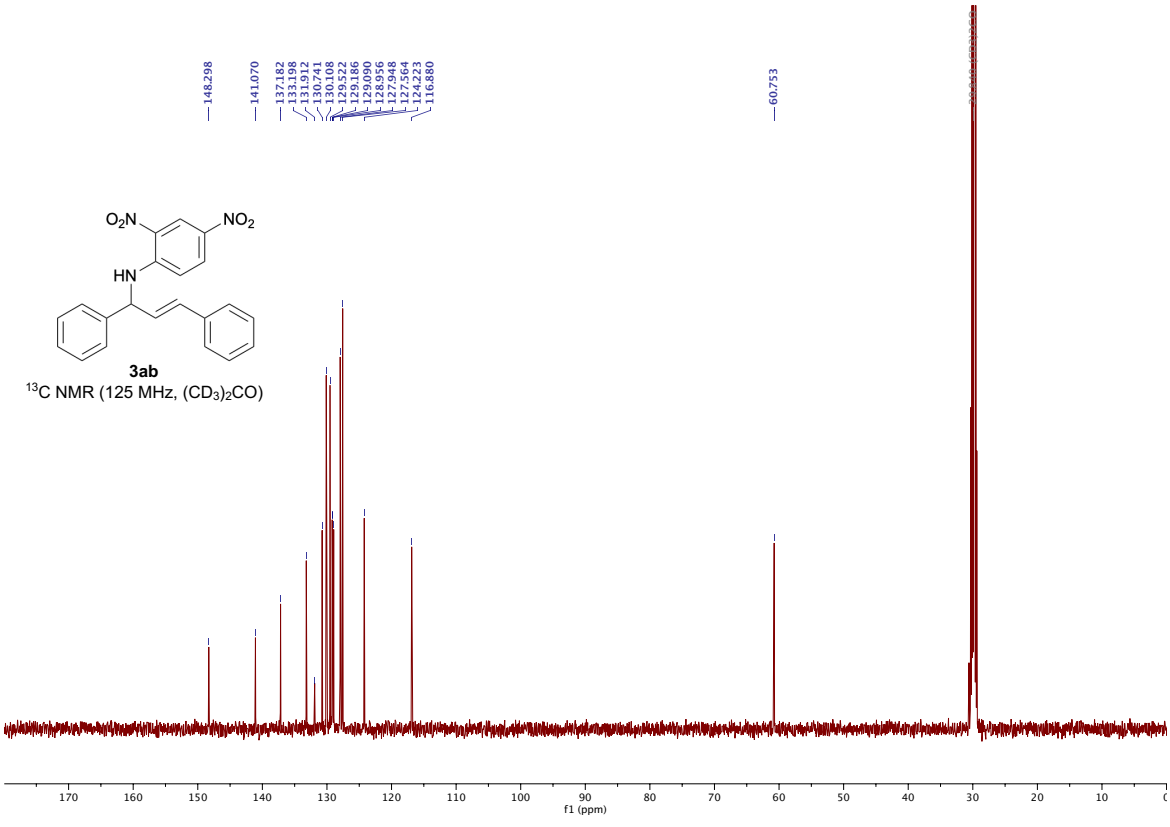
3aa

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



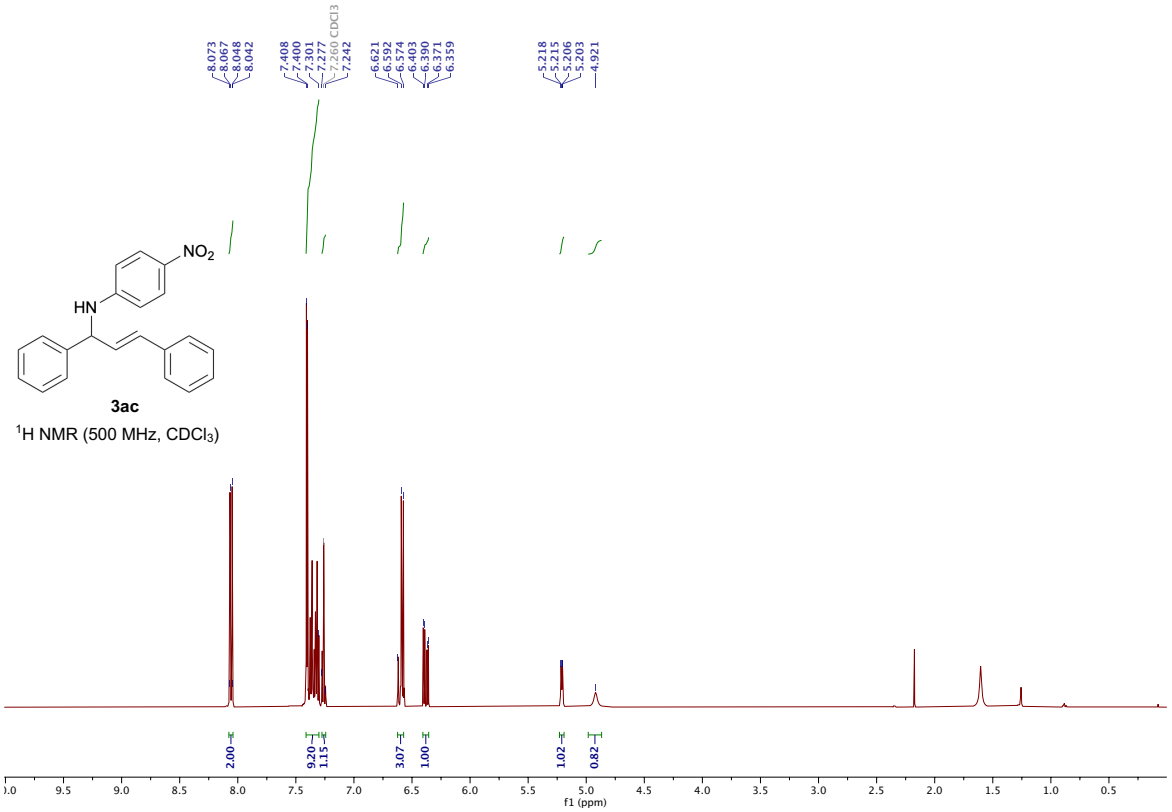
3ab

^{1}H NMR (500 MHz, $(CD_3)_2CO$)



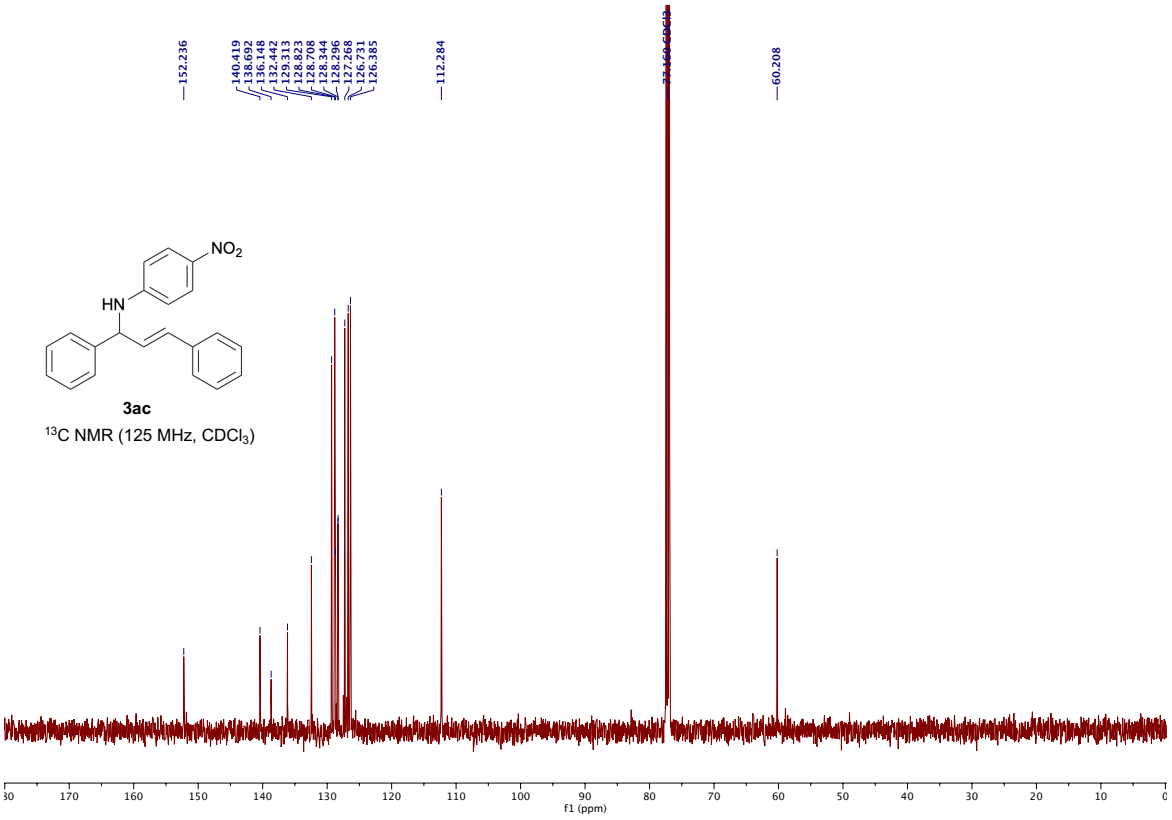
3ab

^{13}C NMR (125 MHz, $(CD_3)_2CO$)



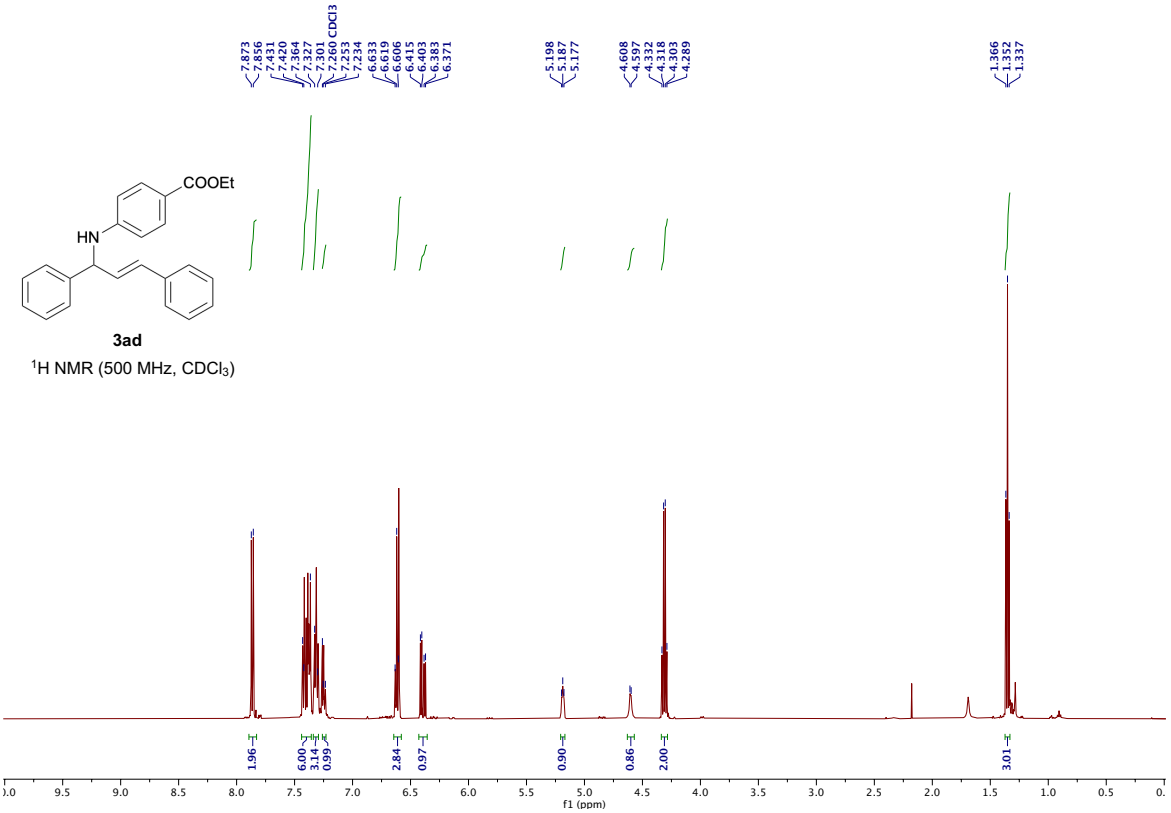
3ac

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



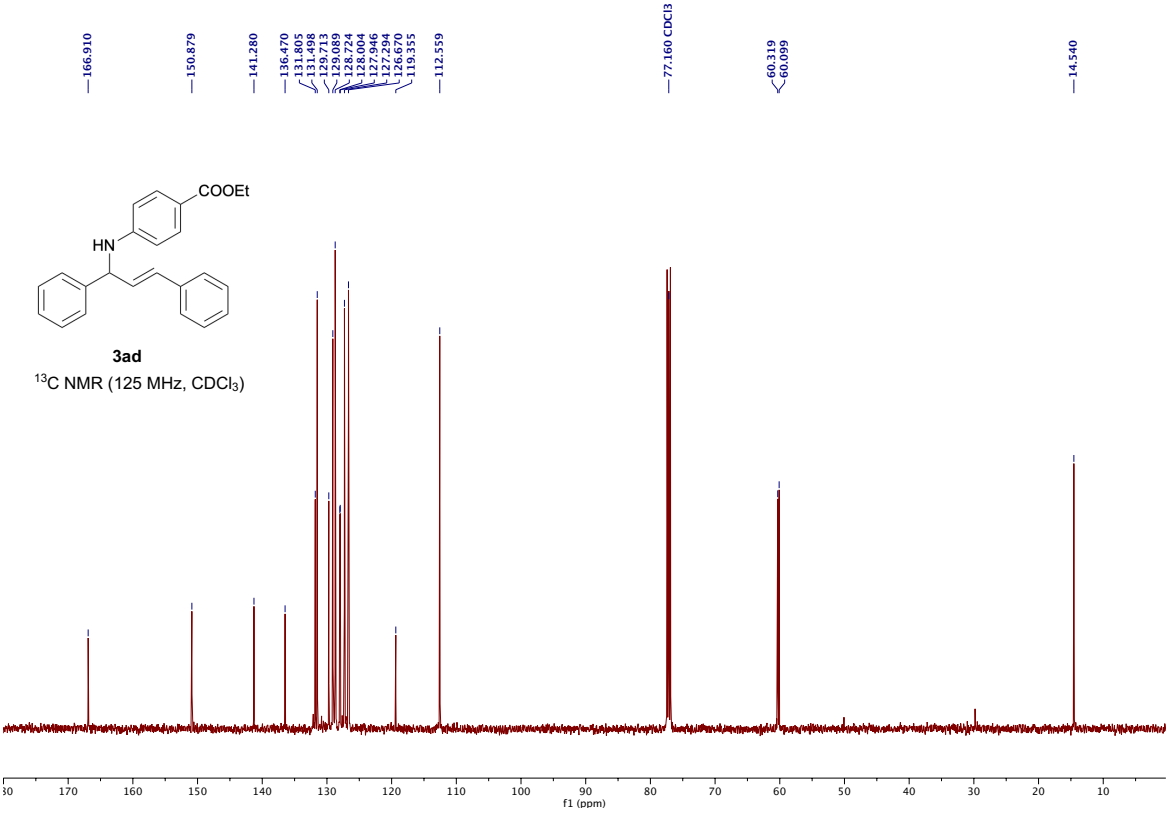
3ac

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



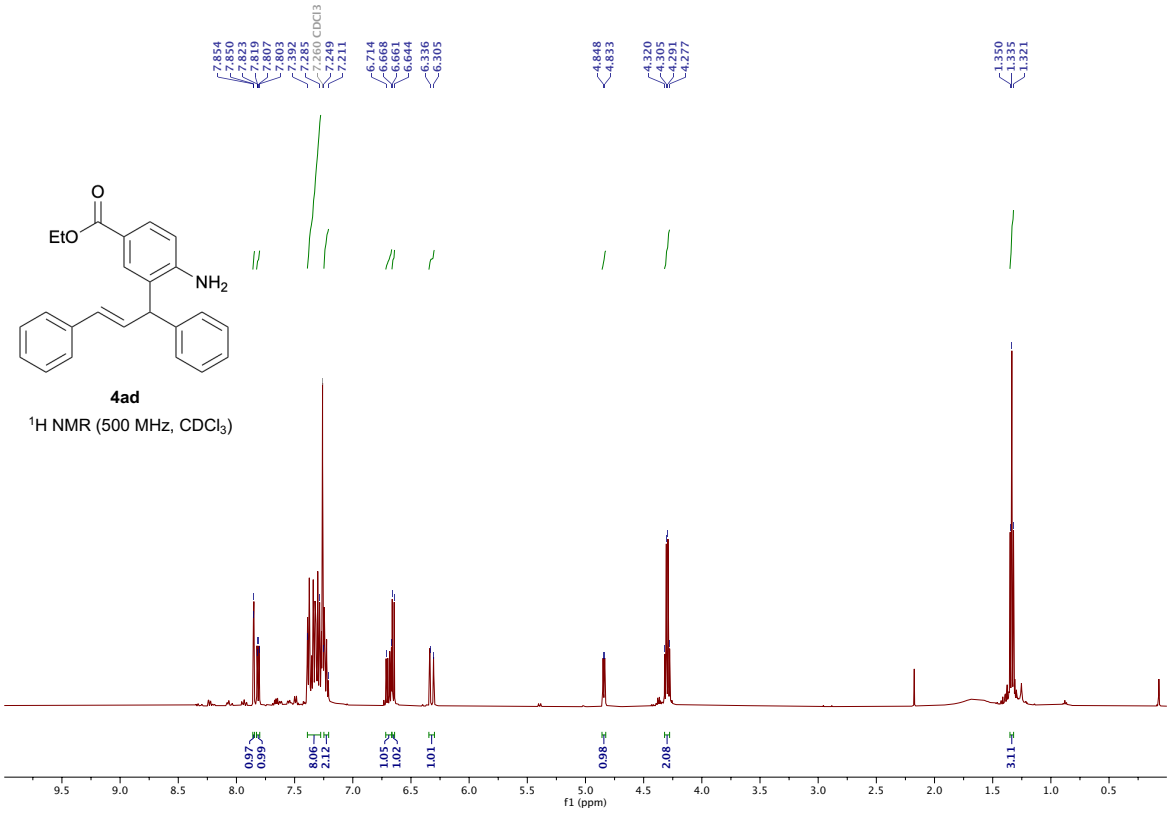
3ad

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



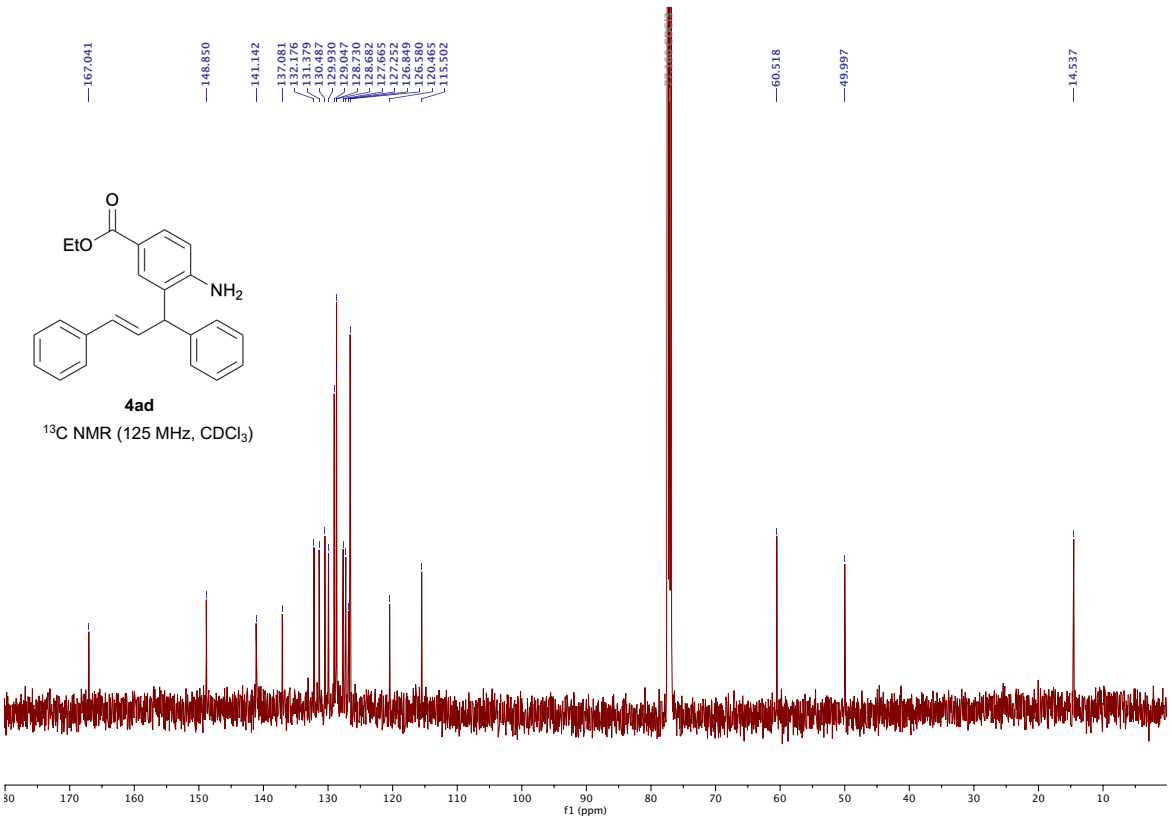
3ad

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



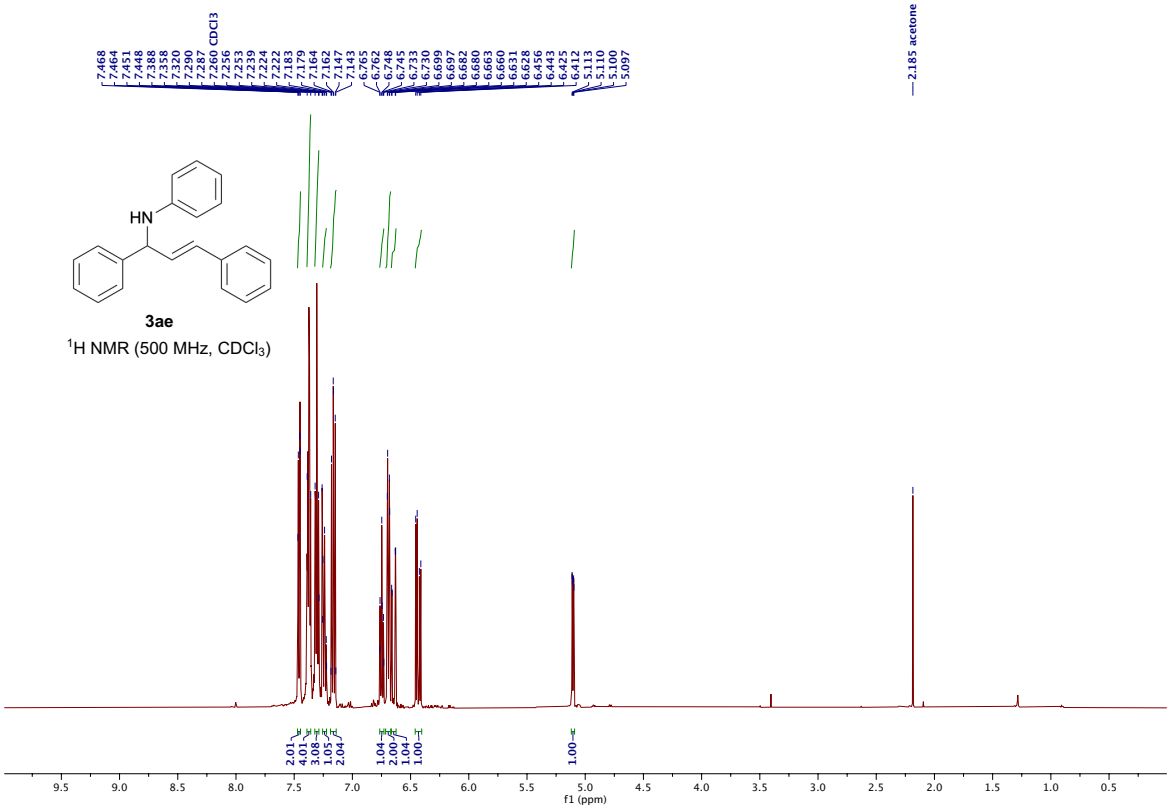
4ad

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



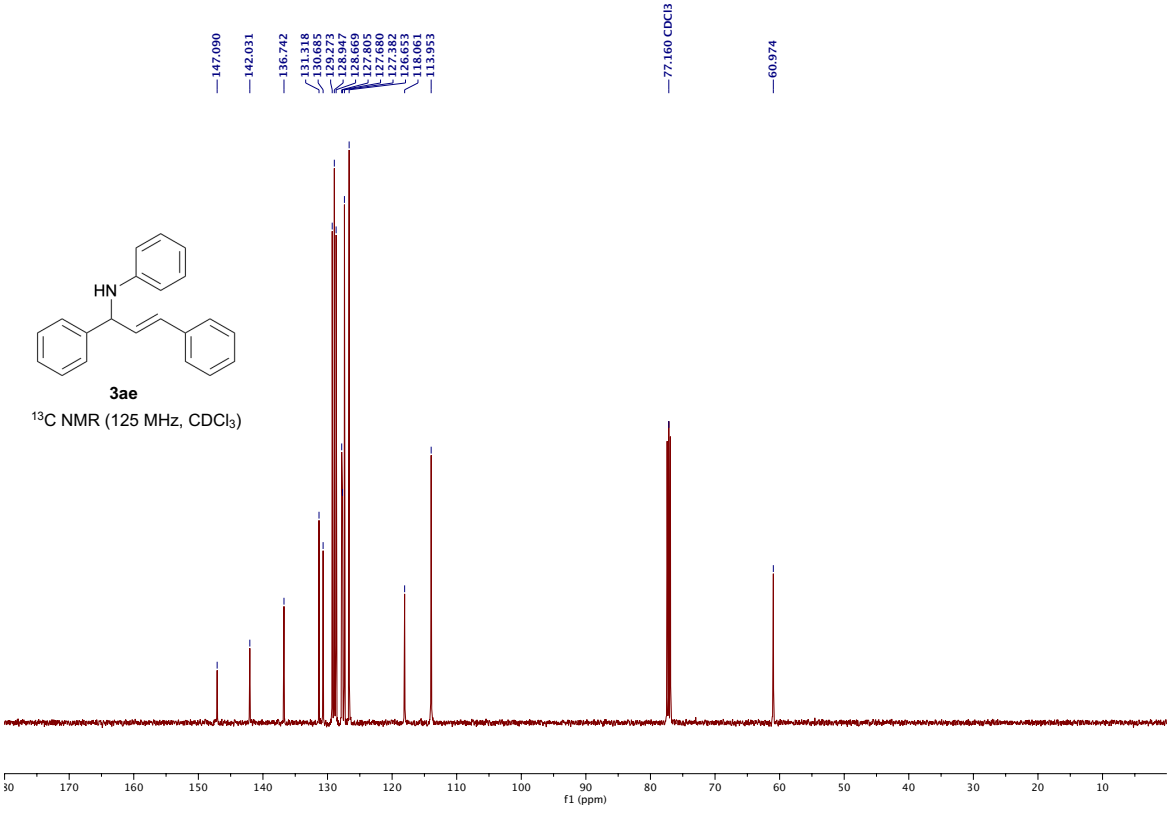
4ad

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



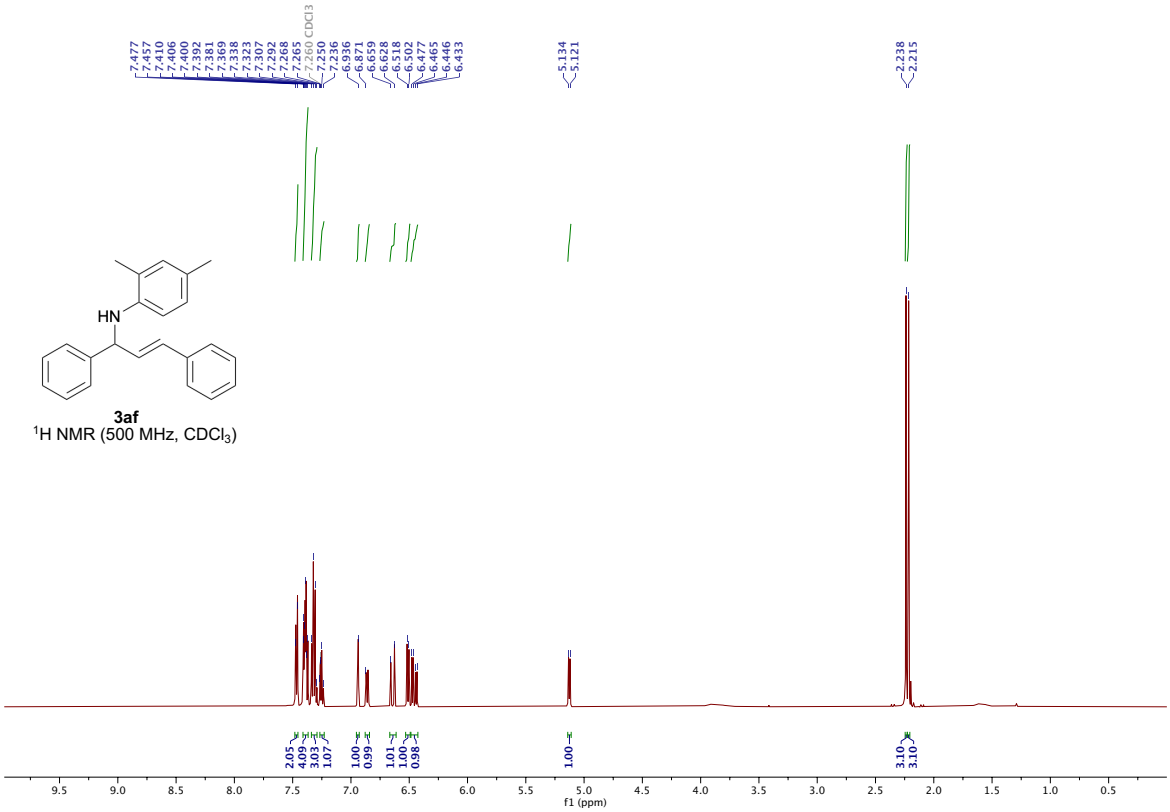
3ae

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



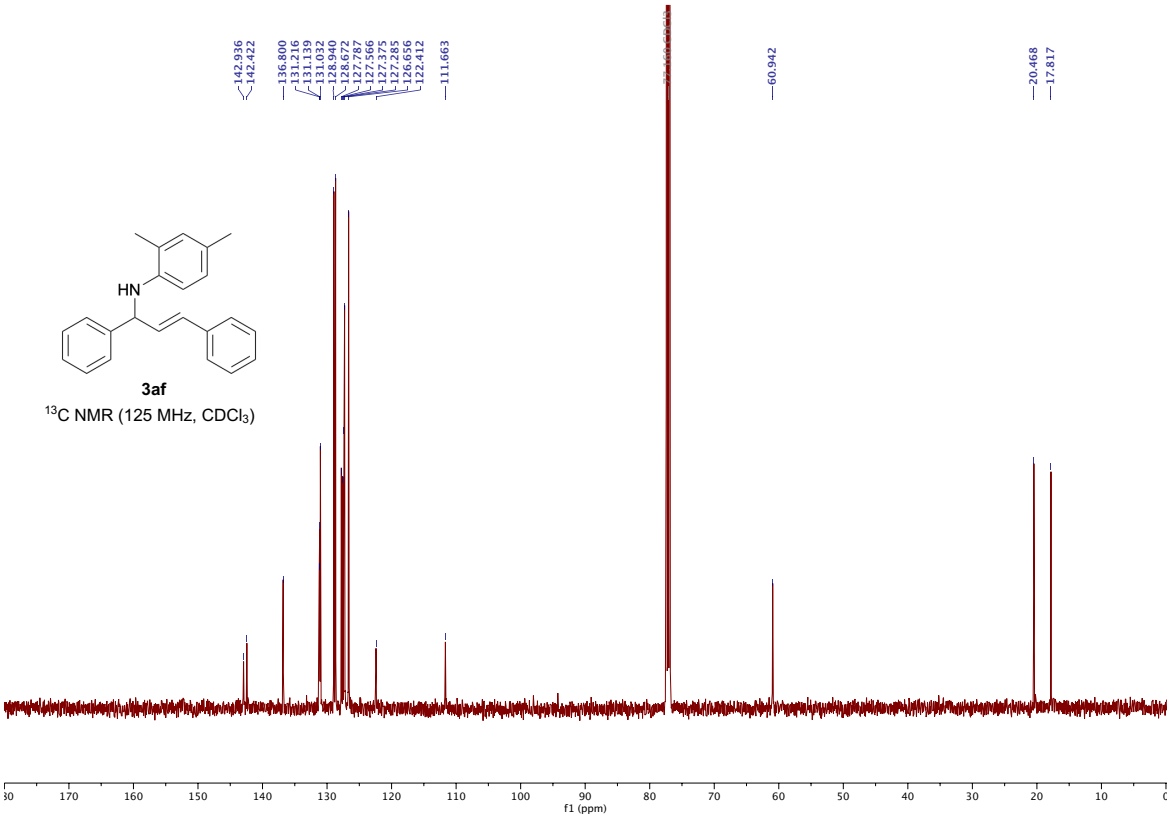
3ae

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



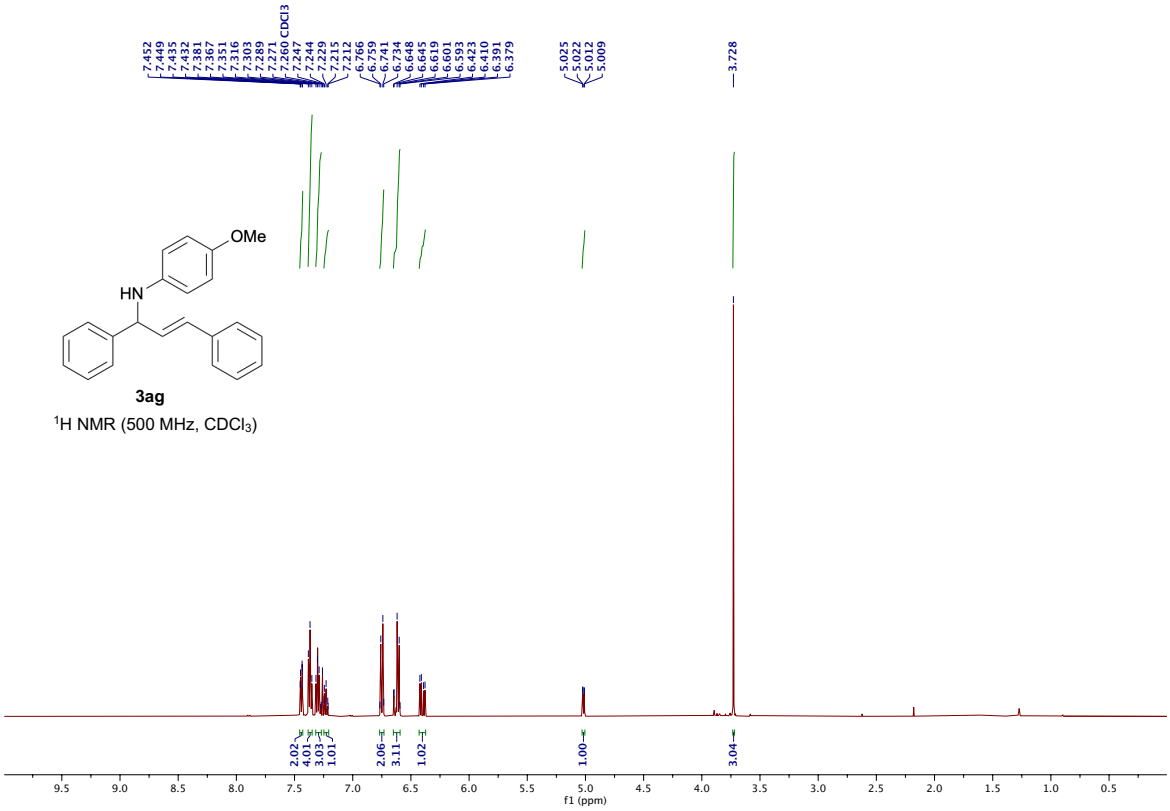
3af

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



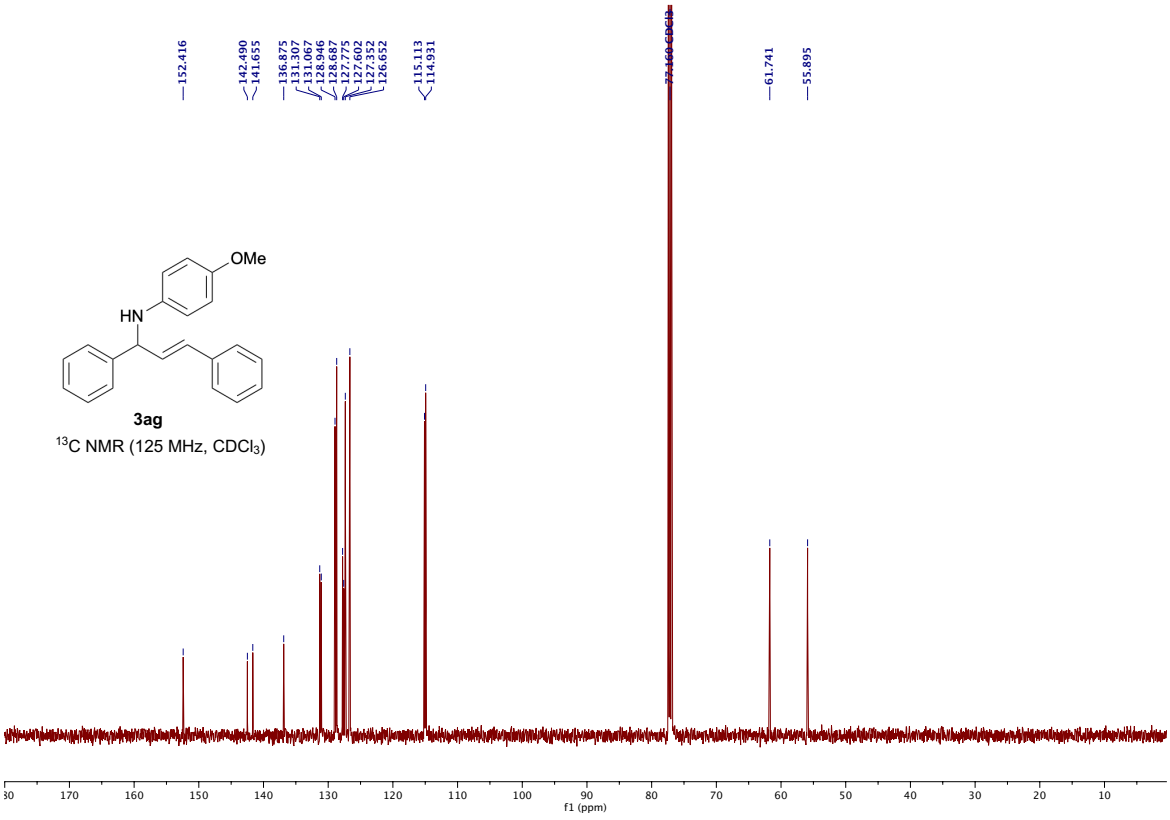
3af

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



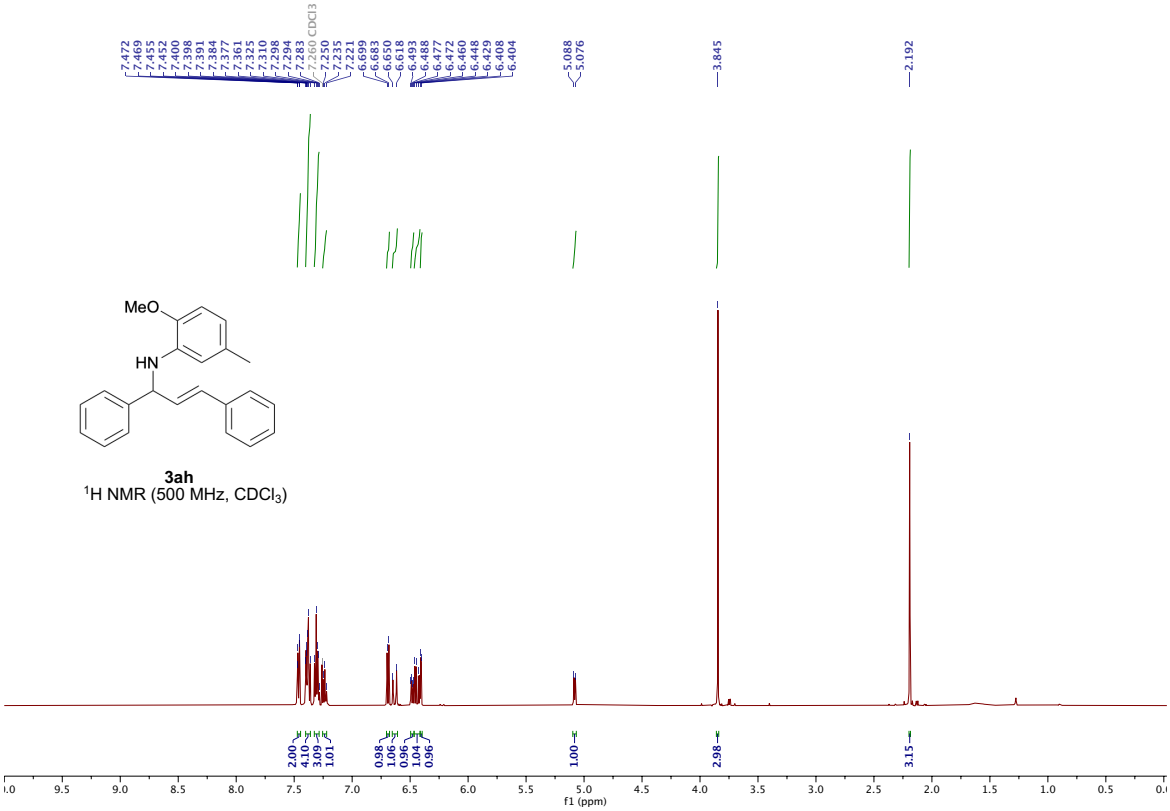
3ag

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



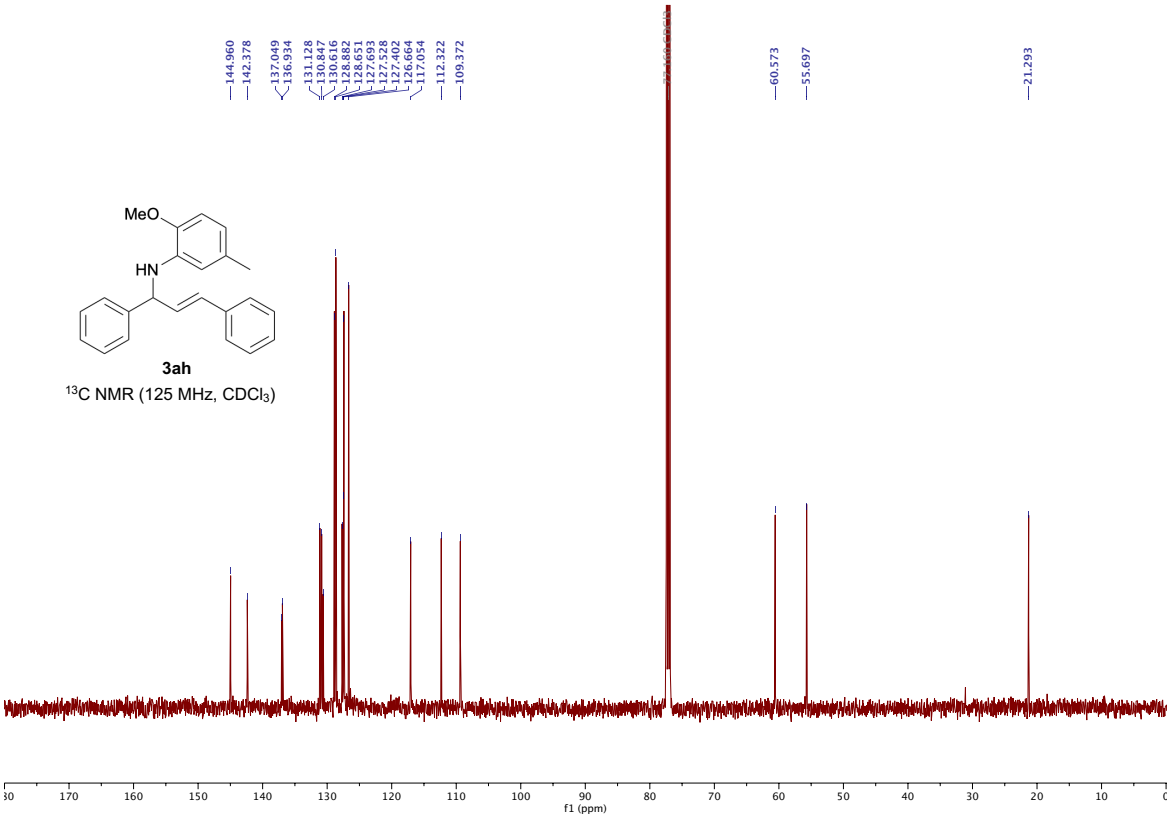
3ag

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



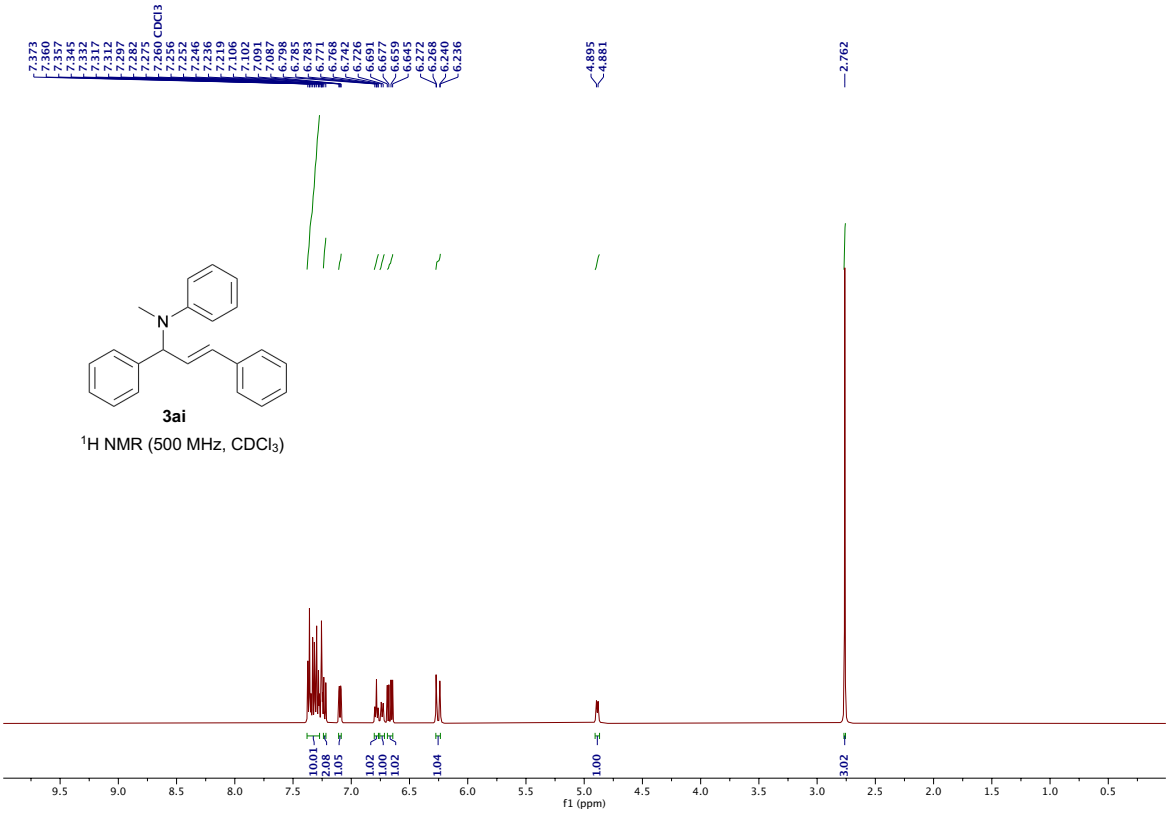
3ah

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



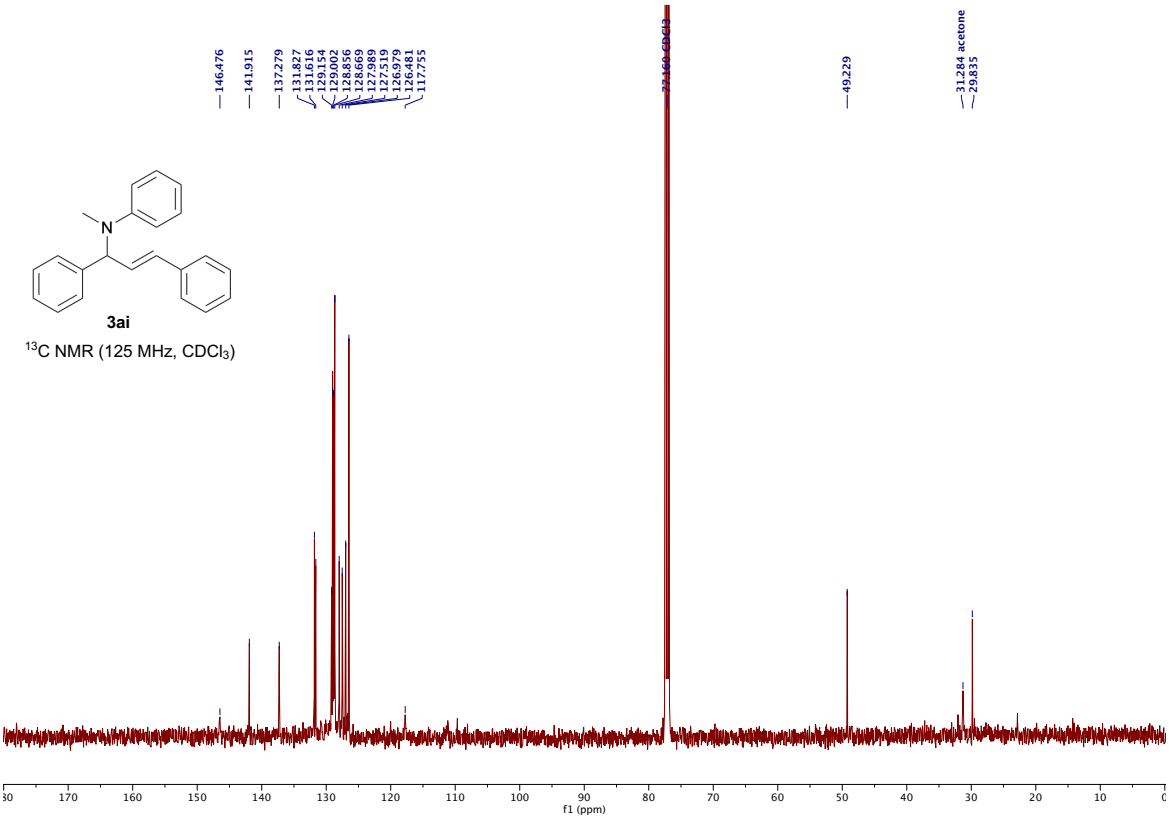
3ah

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



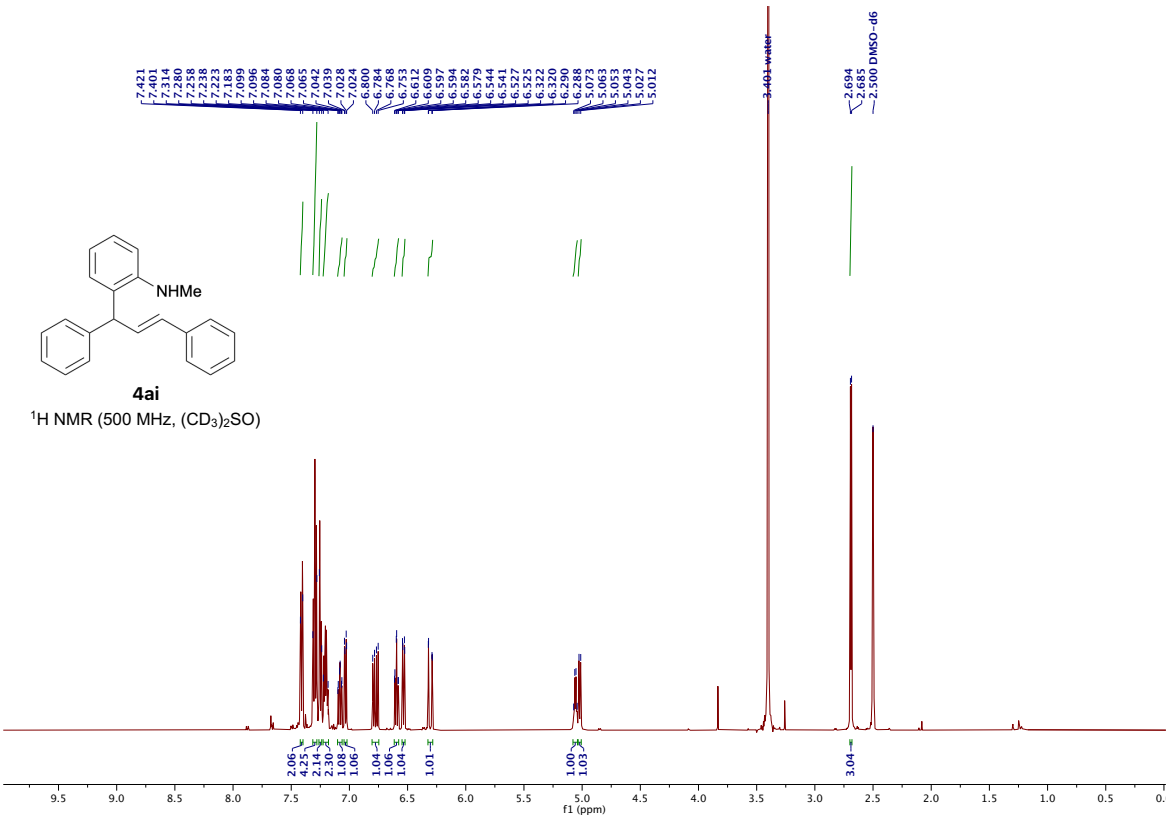
3ai

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



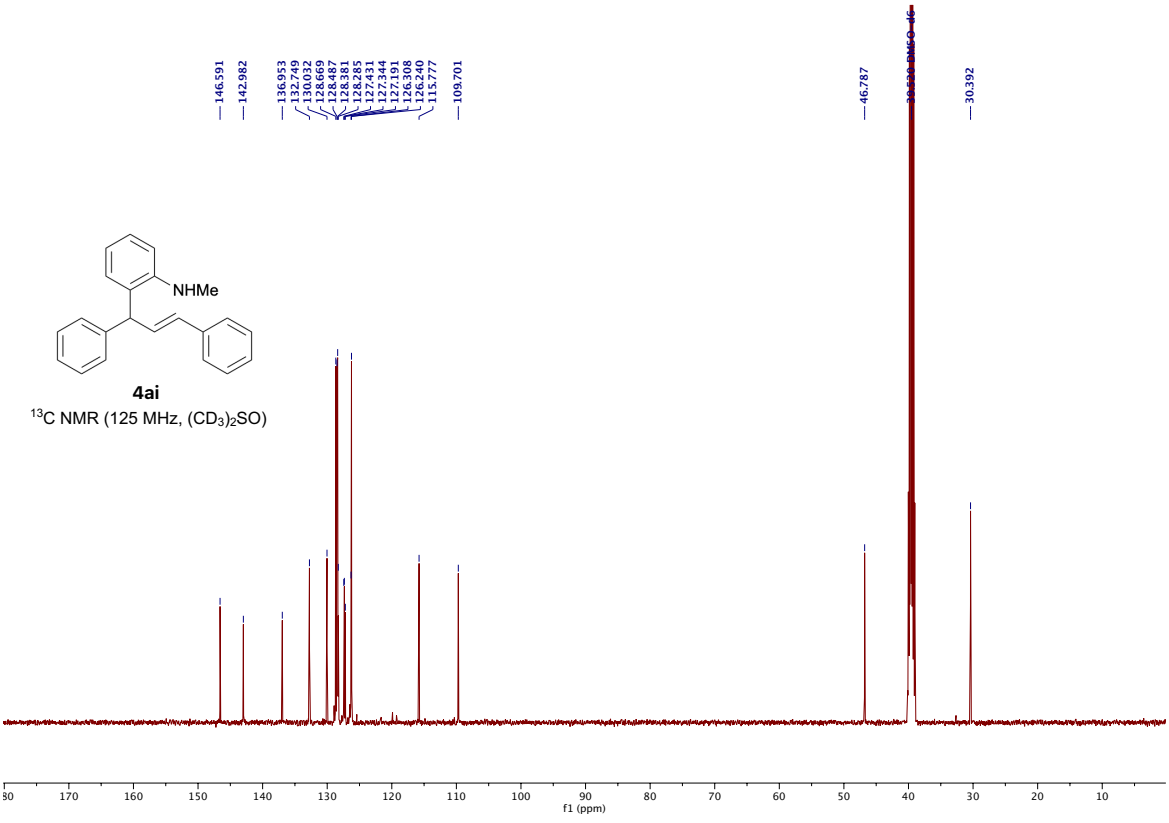
3ai

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



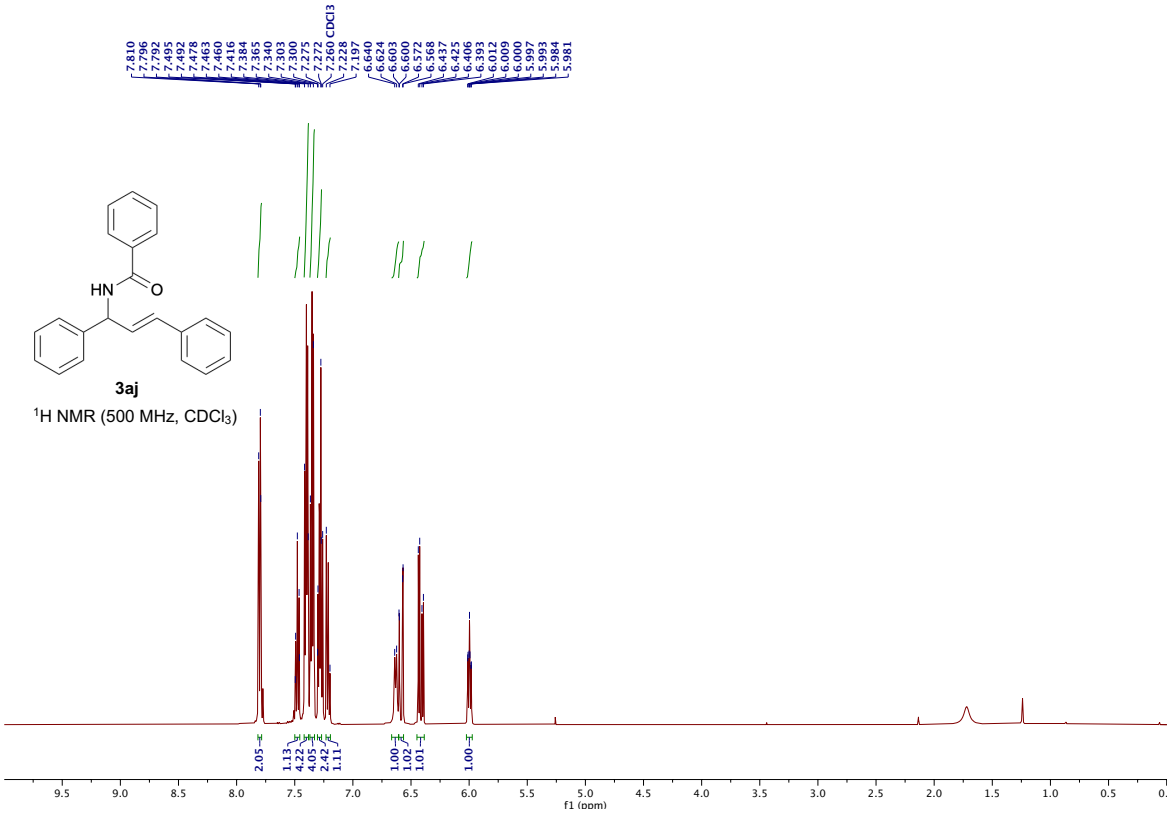
4ai

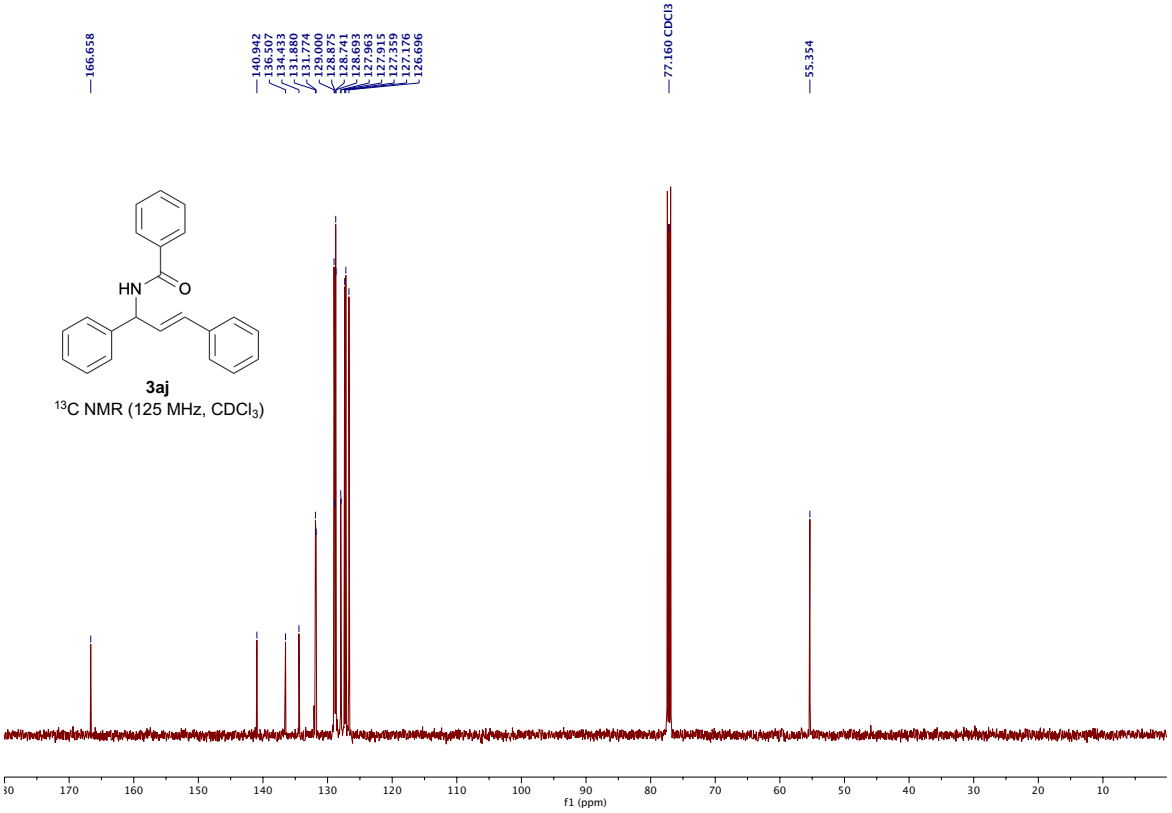
^{1}H NMR (500 MHz, $(CD_3)_2SO$)

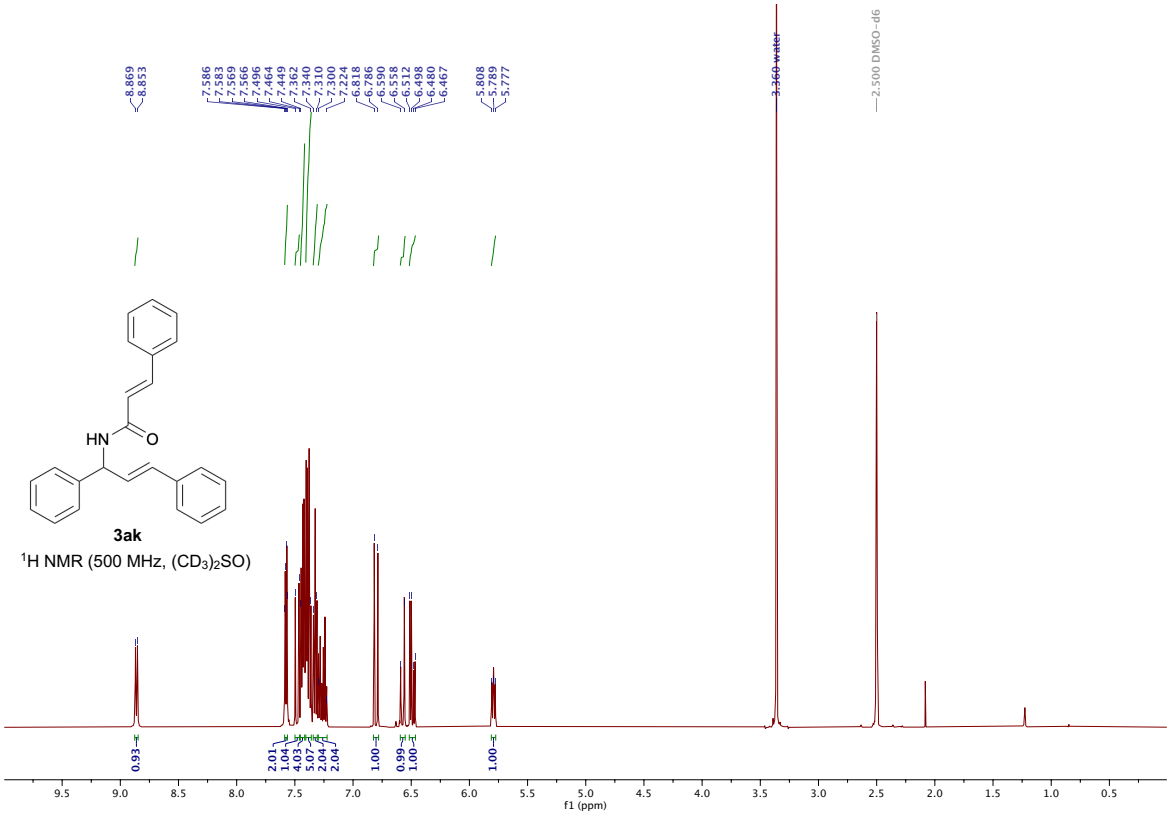


4ai

^{13}C NMR (125 MHz, $(CD_3)_2SO$)

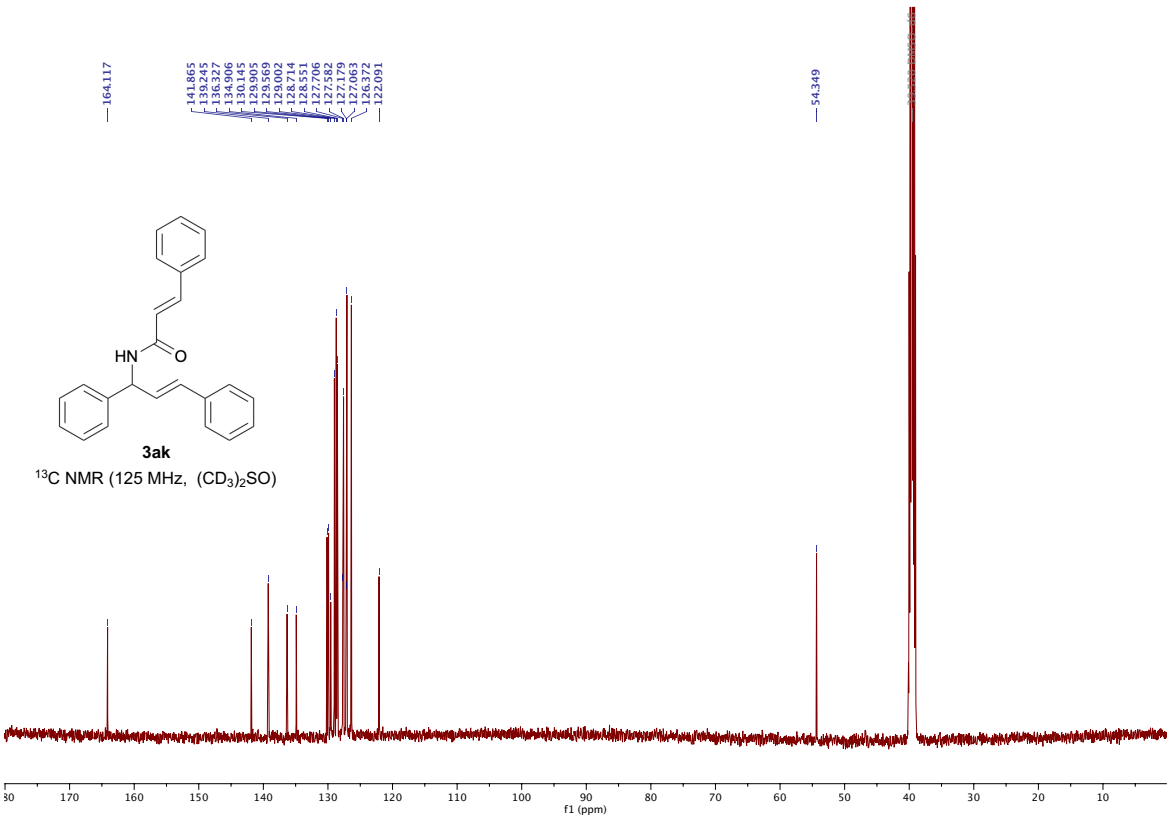

7.810
7.796
7.792
7.495
7.492
7.478
7.463
7.460
7.416
7.384
7.365
7.340
7.301
7.300
7.275
7.272
7.260 CDCl3
7.228
7.197
6.640
6.604
6.603
6.600
6.572
6.568
6.437
6.425
6.406
6.393
6.012
6.009
6.000
5.997
5.993
5.984
5.981
HN
O
3aj
1H NMR (500 MHz, CDCl3)
2.05
1.13
4.22
4.05
2.42
1.11
1.00
1.02
1.01
1.00
f1 (ppm)


166.658
140.942
136.507
134.433
131.880
131.774
129.000
128.875
128.741
128.693
127.963
127.915
127.359
127.176
126.696
77.160 CDCl3
55.354
HN
O
3aj
13C NMR (125 MHz, CDCl3)
f1 (ppm)



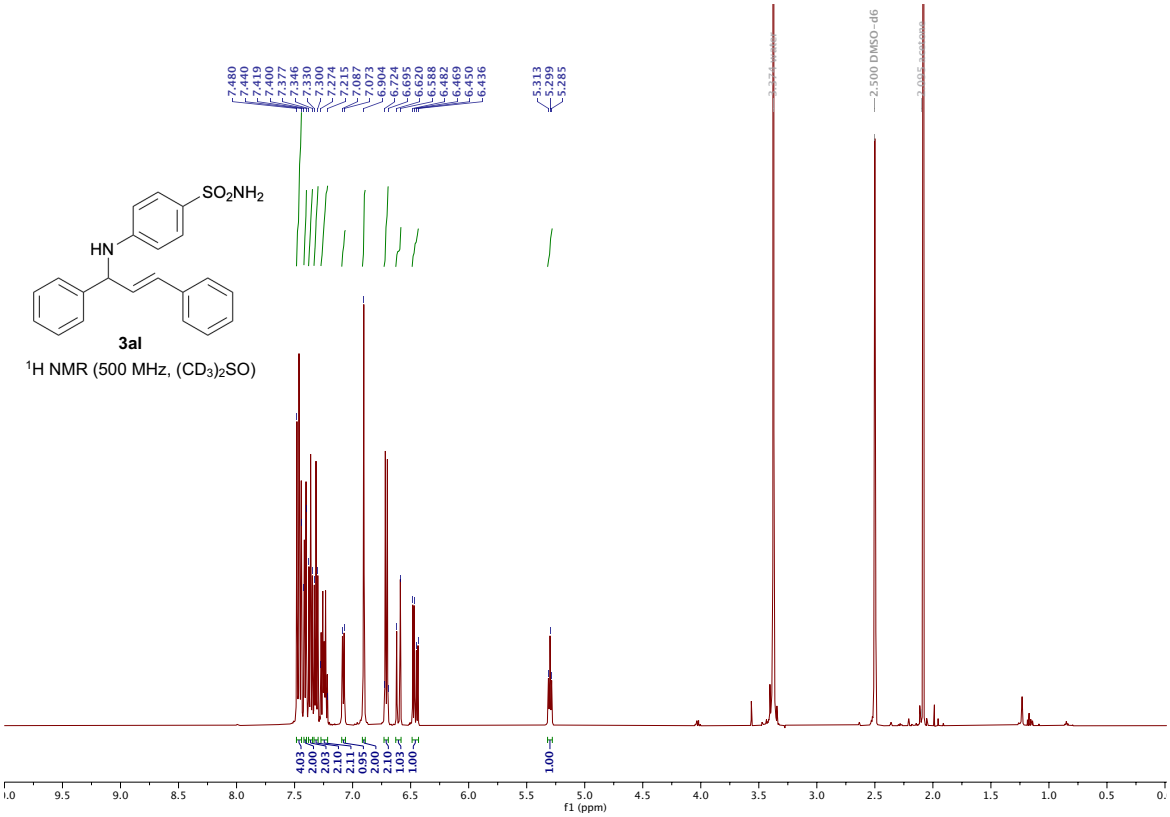
3ak

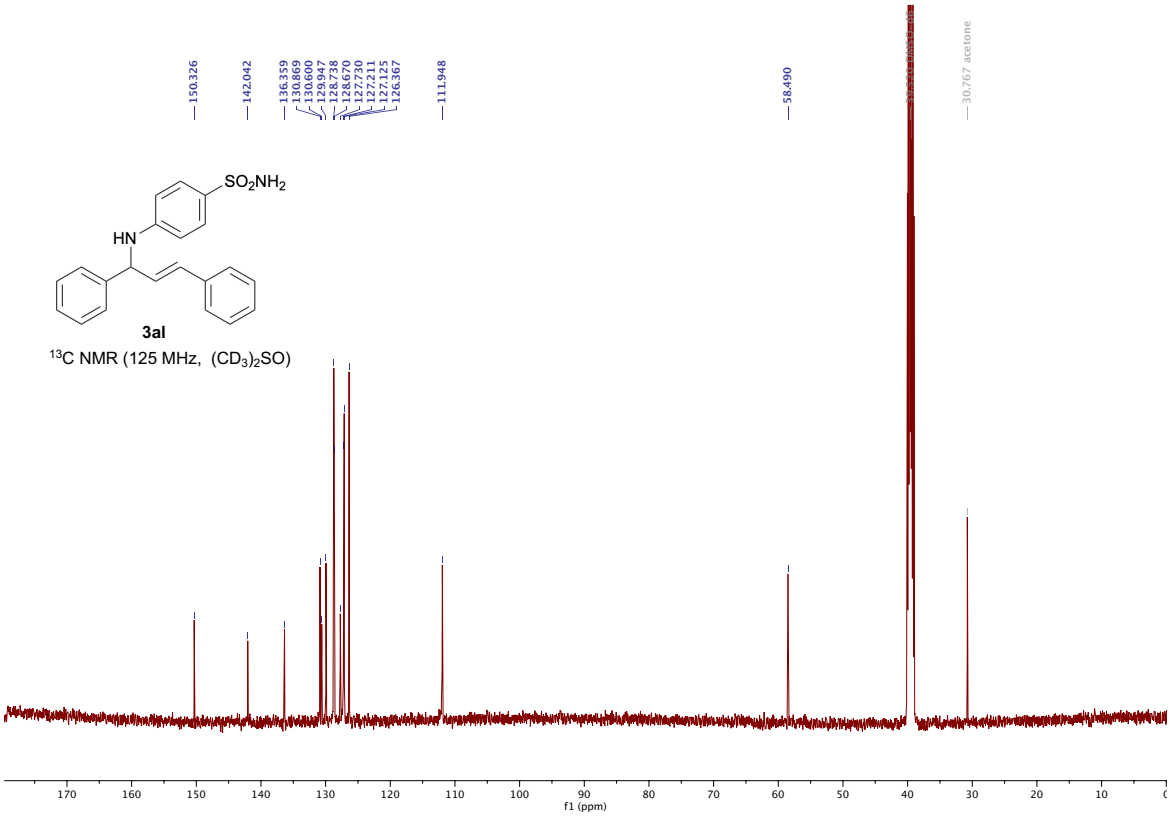
^{1}H NMR (500 MHz, $(CD_3)_2SO$)

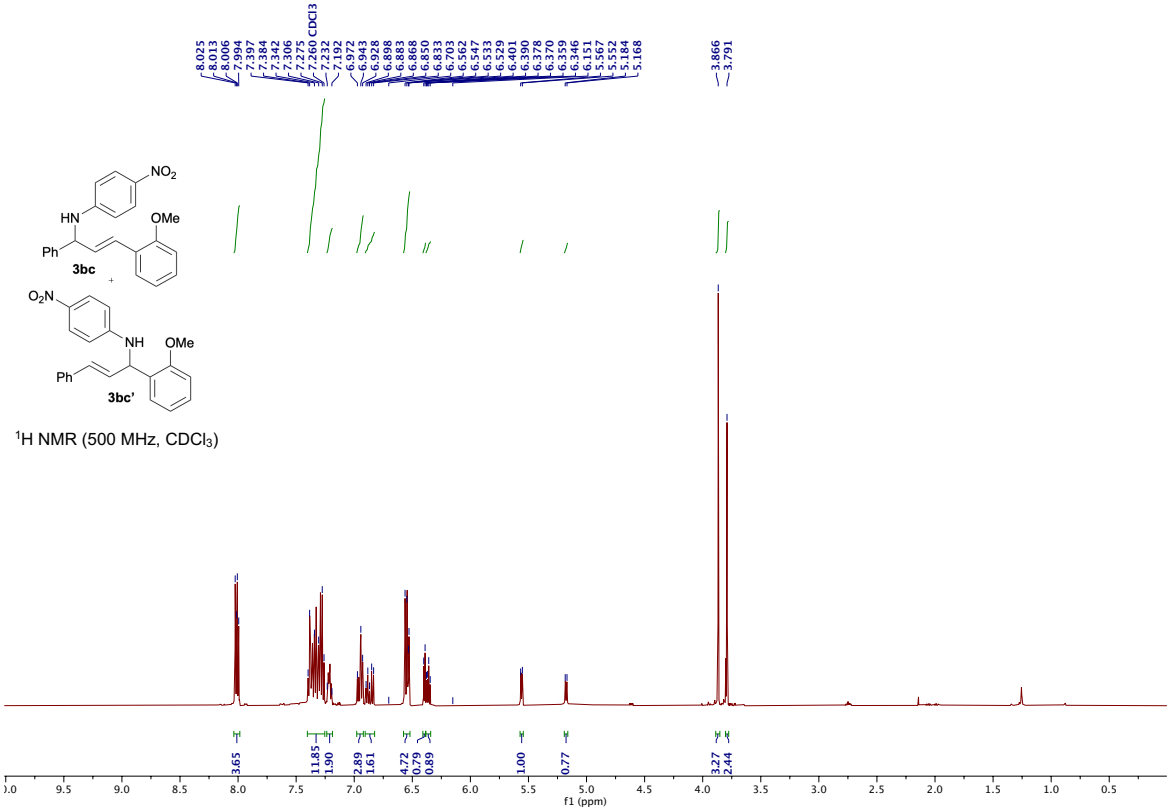


3ak

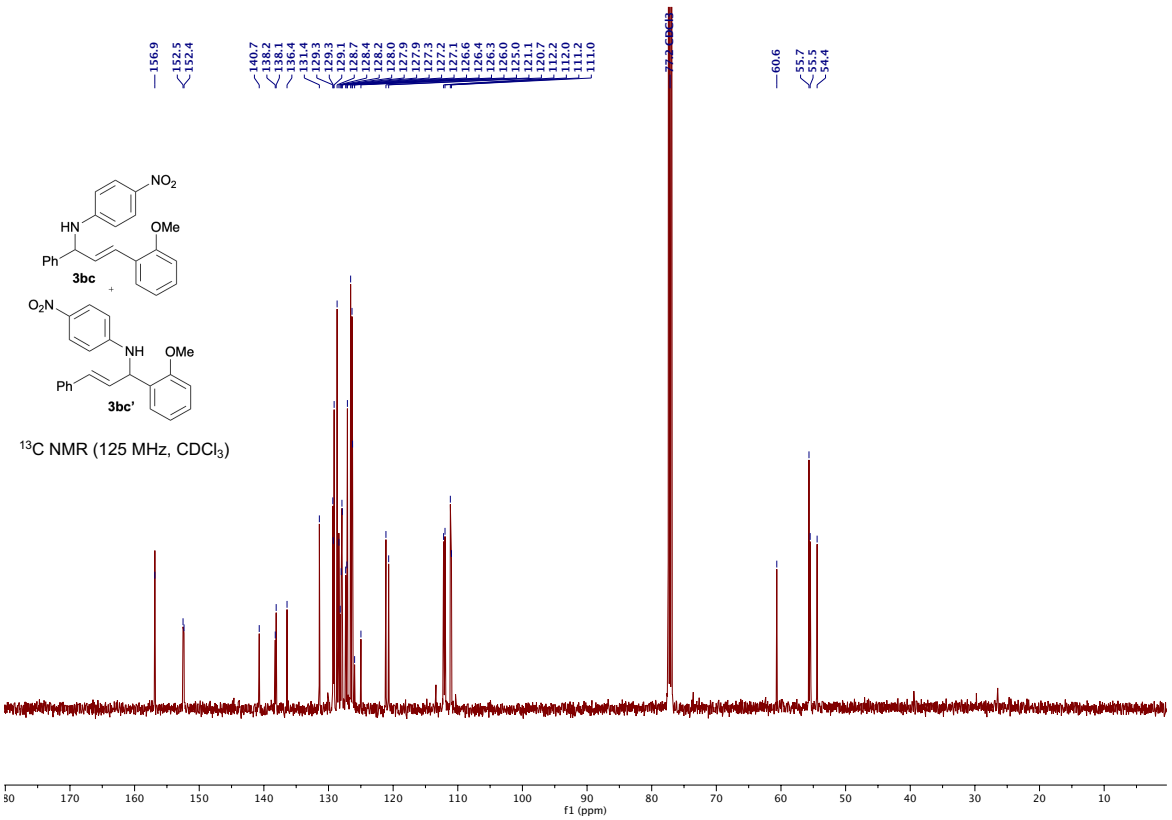
^{13}C NMR (125 MHz, $(CD_3)_2SO$)


7.480
7.440
7.419
7.400
7.377
7.346
7.330
7.300
7.274
7.215
7.087
7.073
6.904
6.774
6.655
6.620
6.588
6.482
6.469
6.450
6.436
5.313
5.299
5.285
3.334 water
2.500 DMSO-d6
3.005 acetone
SO2NH2
HN
3al
1H NMR (500 MHz, (CD3)2SO)
4.03
2.00
2.03
2.10
2.11
0.95
2.00
2.10
1.03
1.00
1.00
f1 (ppm)

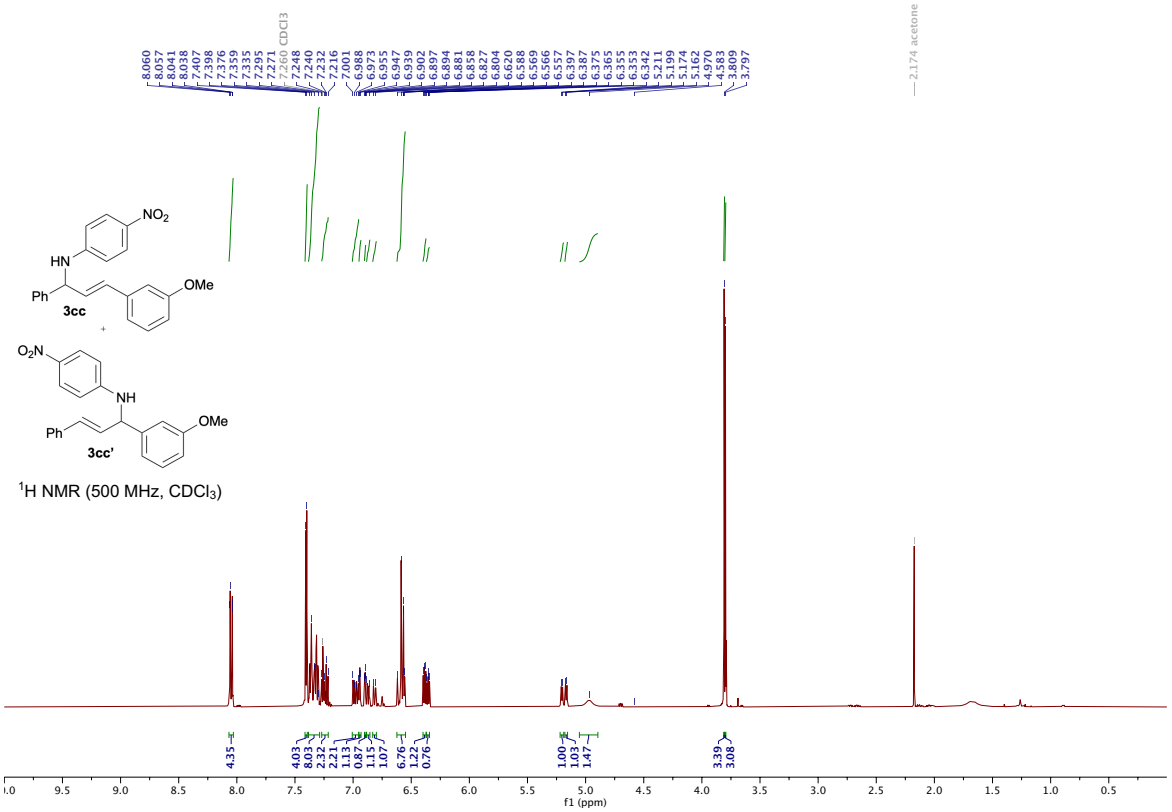

150.326
142.042
136.359
130.869
130.600
129.947
128.738
128.670
127.730
127.211
127.125
126.367
111.948
58.490
39.520 DMSO-d6
30.767 acetone
SO2NH2
HN
3al
13C NMR (125 MHz, (CD3)2SO)
f1 (ppm)

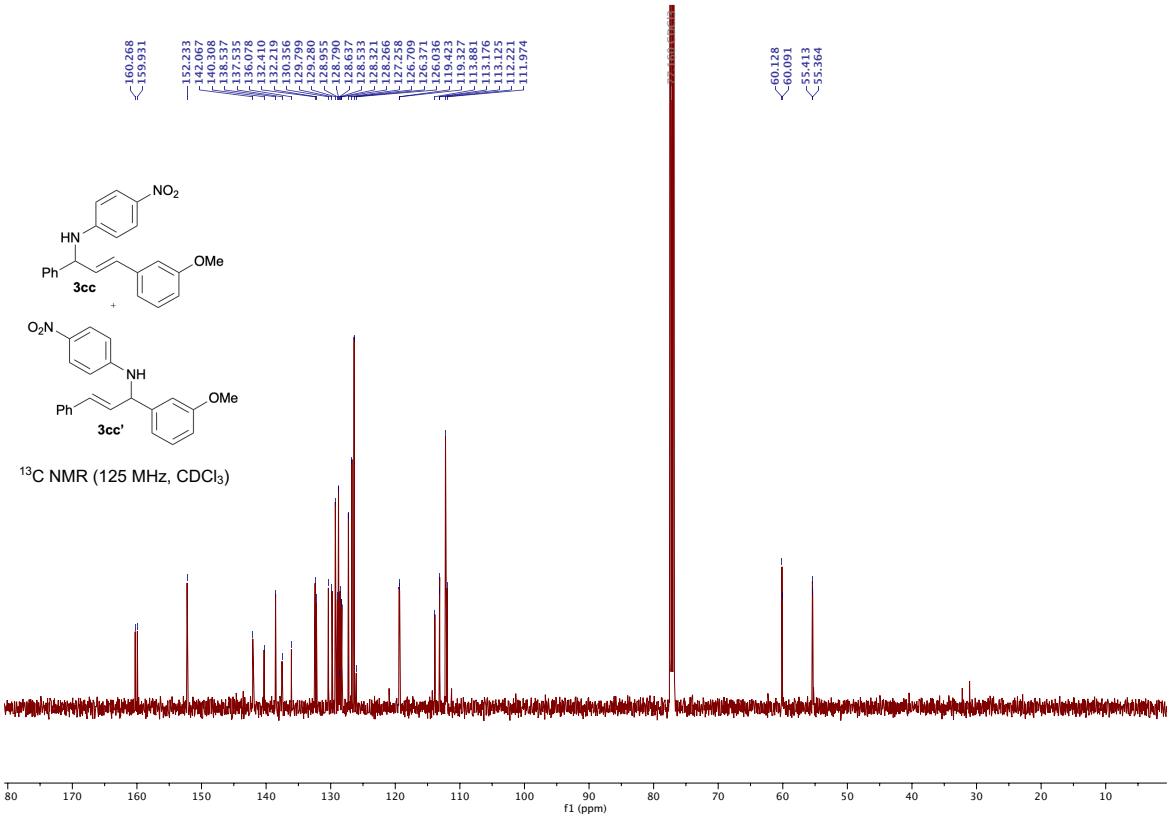


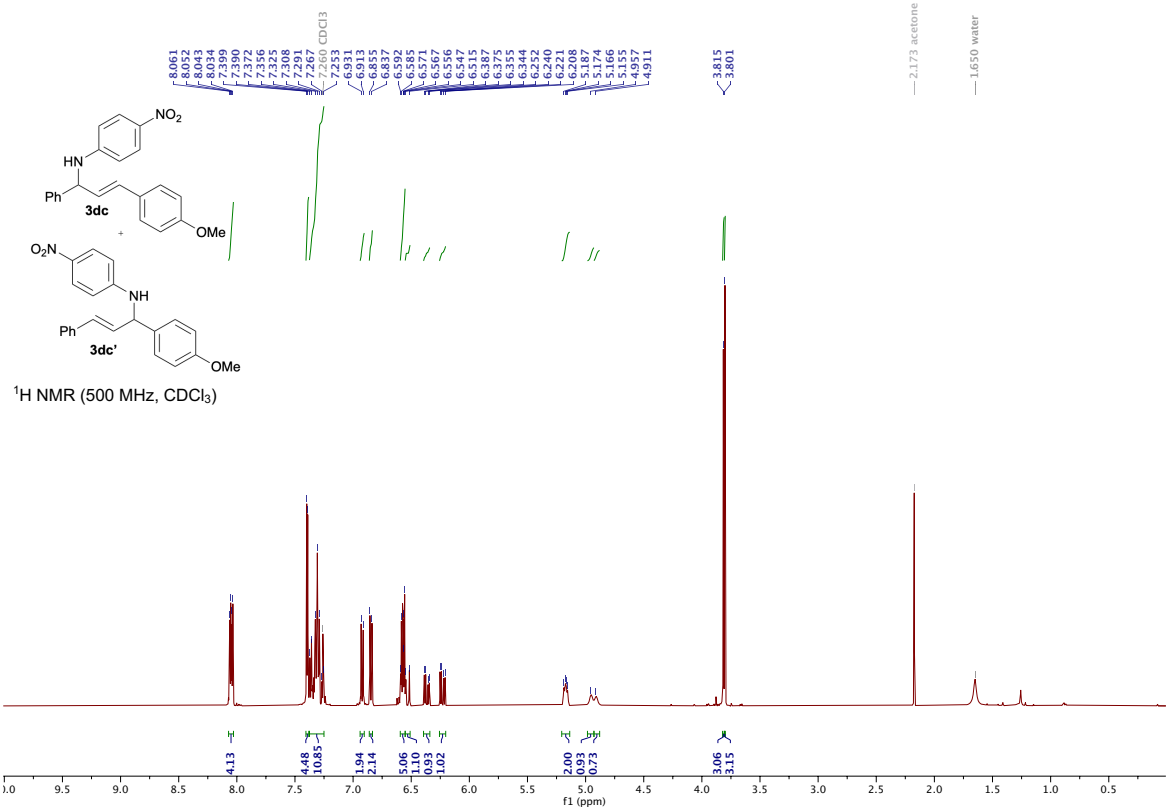
^{1}H NMR (500 MHz, $CDCl_3$)



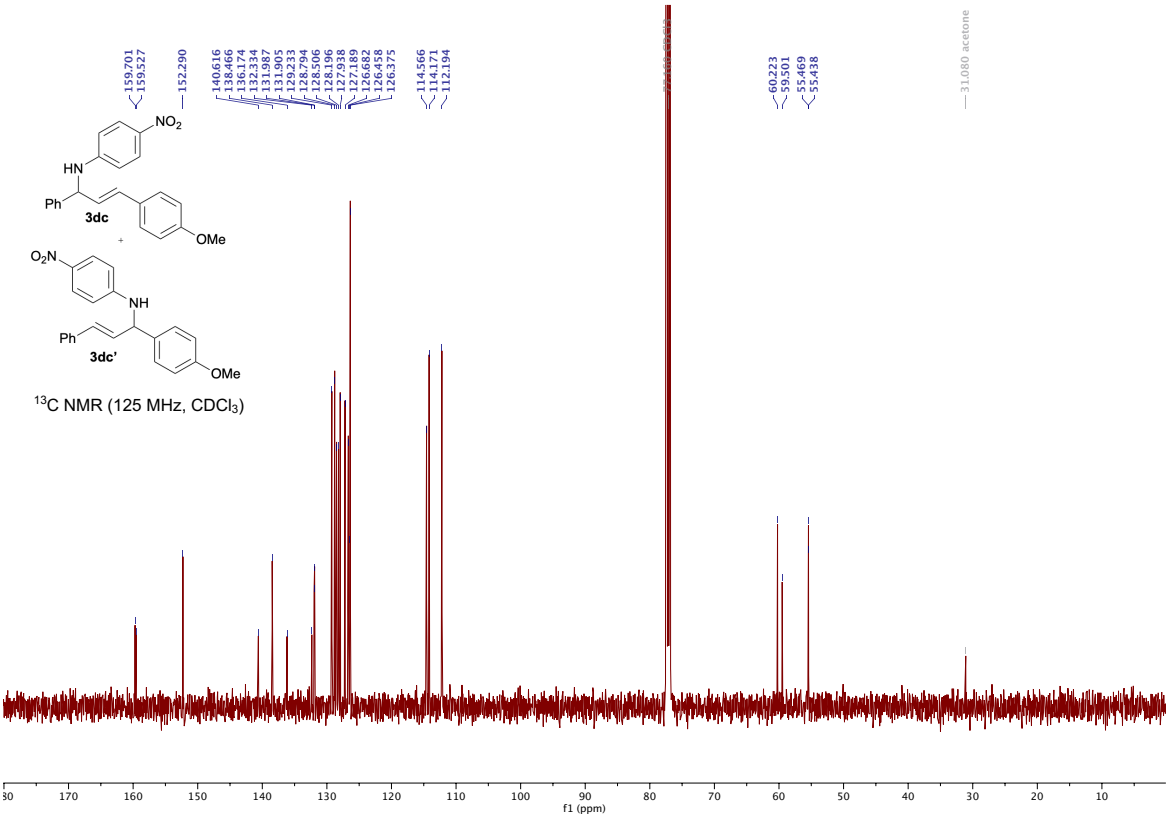
^{13}C NMR (125 MHz, $CDCl_3$)


3cc
3cc'
^{1}H NMR (500 MHz, $CDCl_3$)
f1 (ppm)

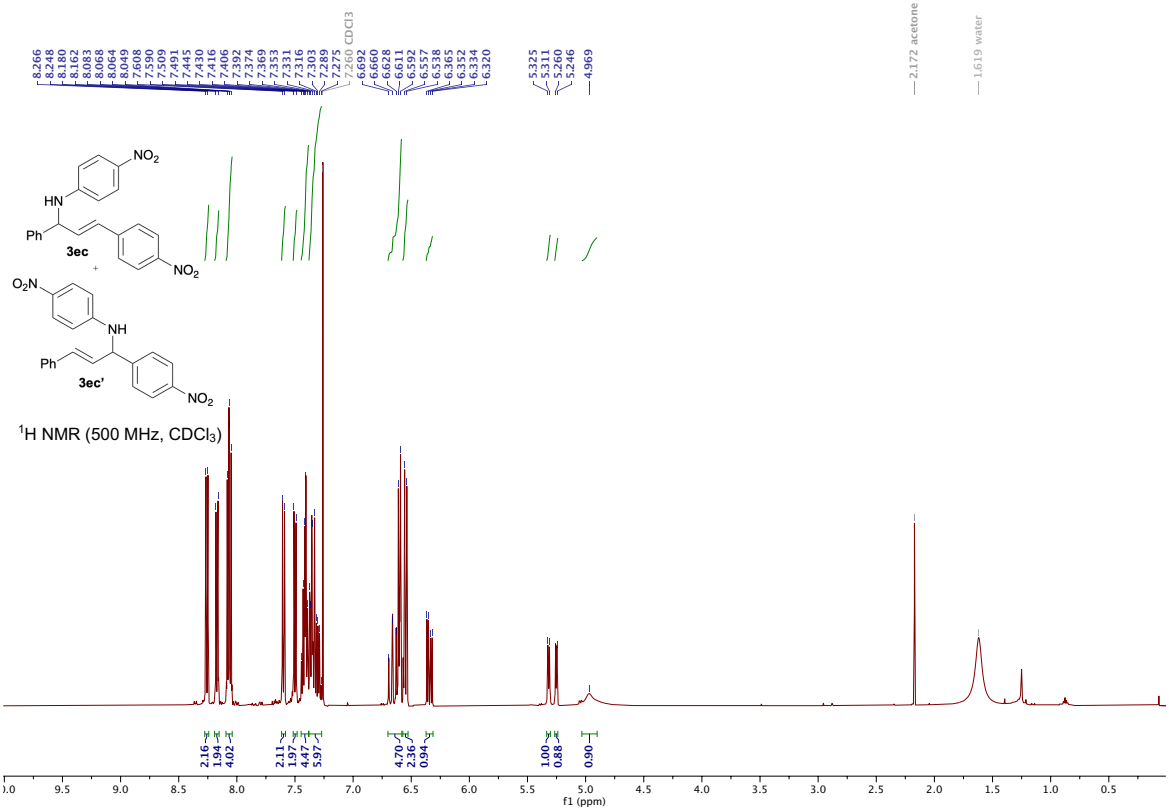

3cc
3cc'
^{13}C NMR (125 MHz, $CDCl_3$)
f1 (ppm)

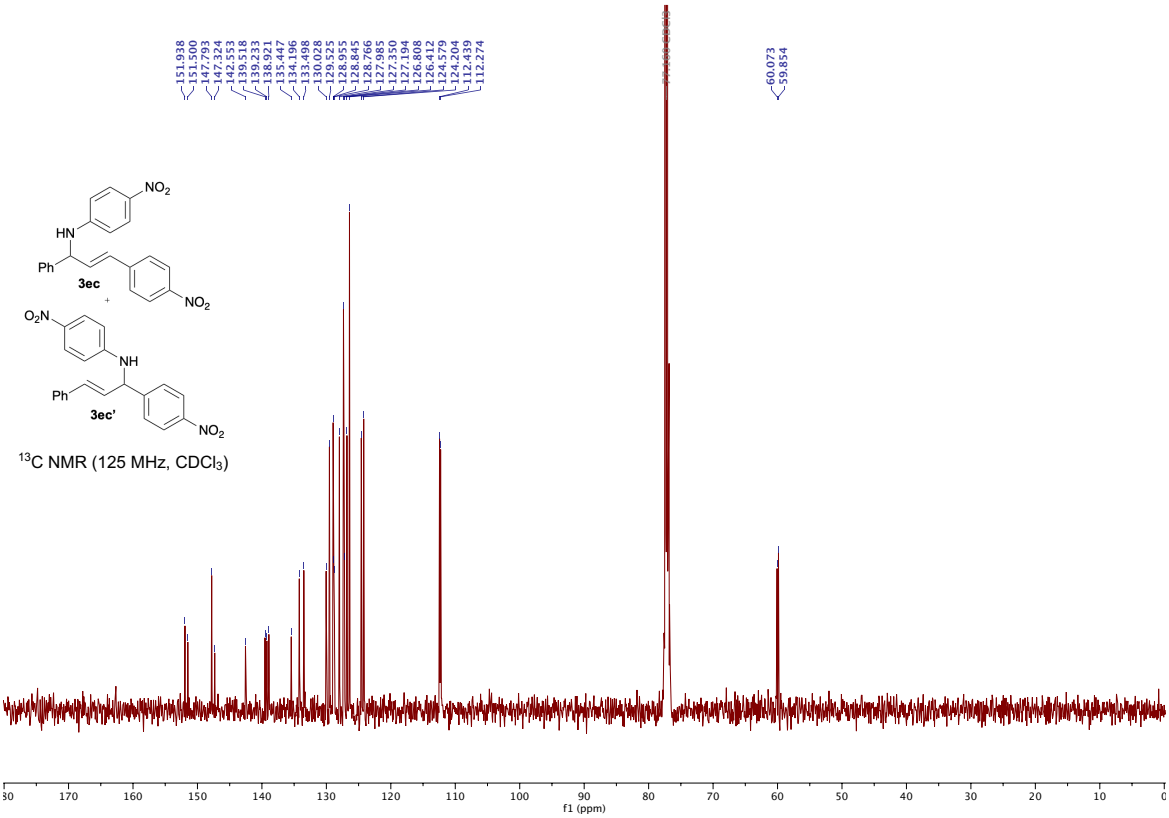


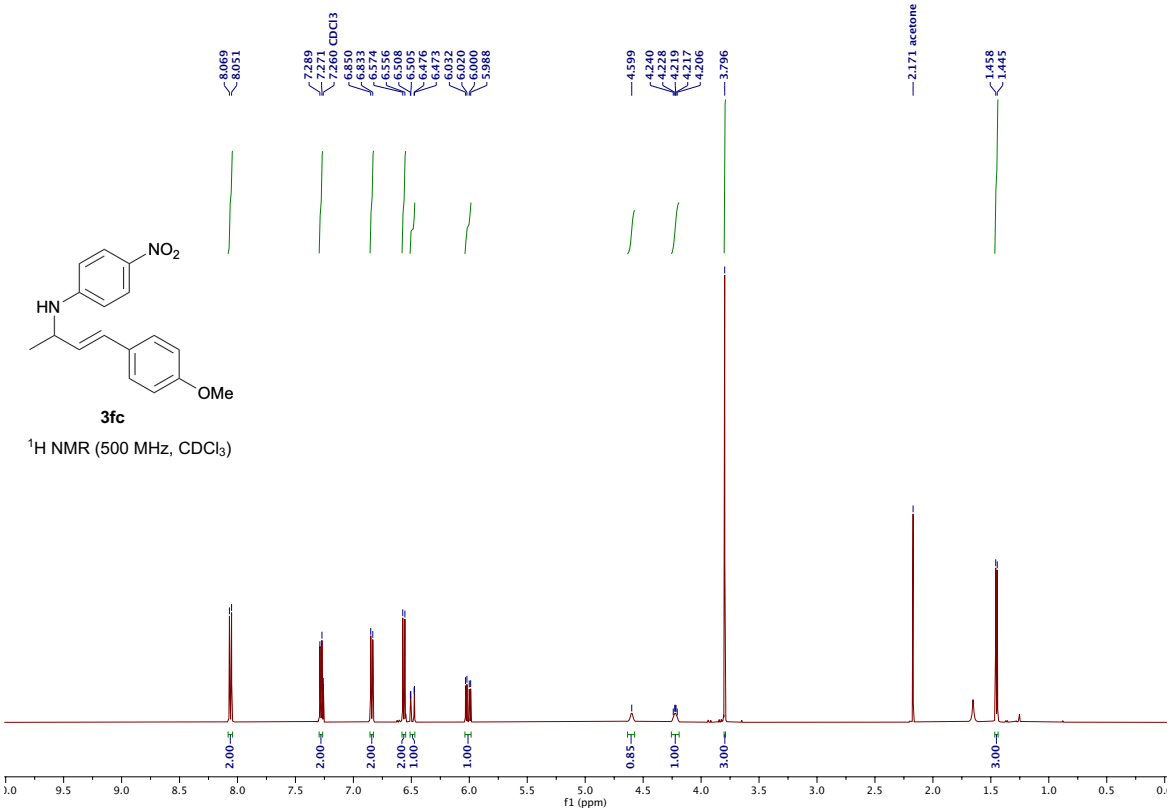
^{1}H NMR (500 MHz, $CDCl_3$)



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

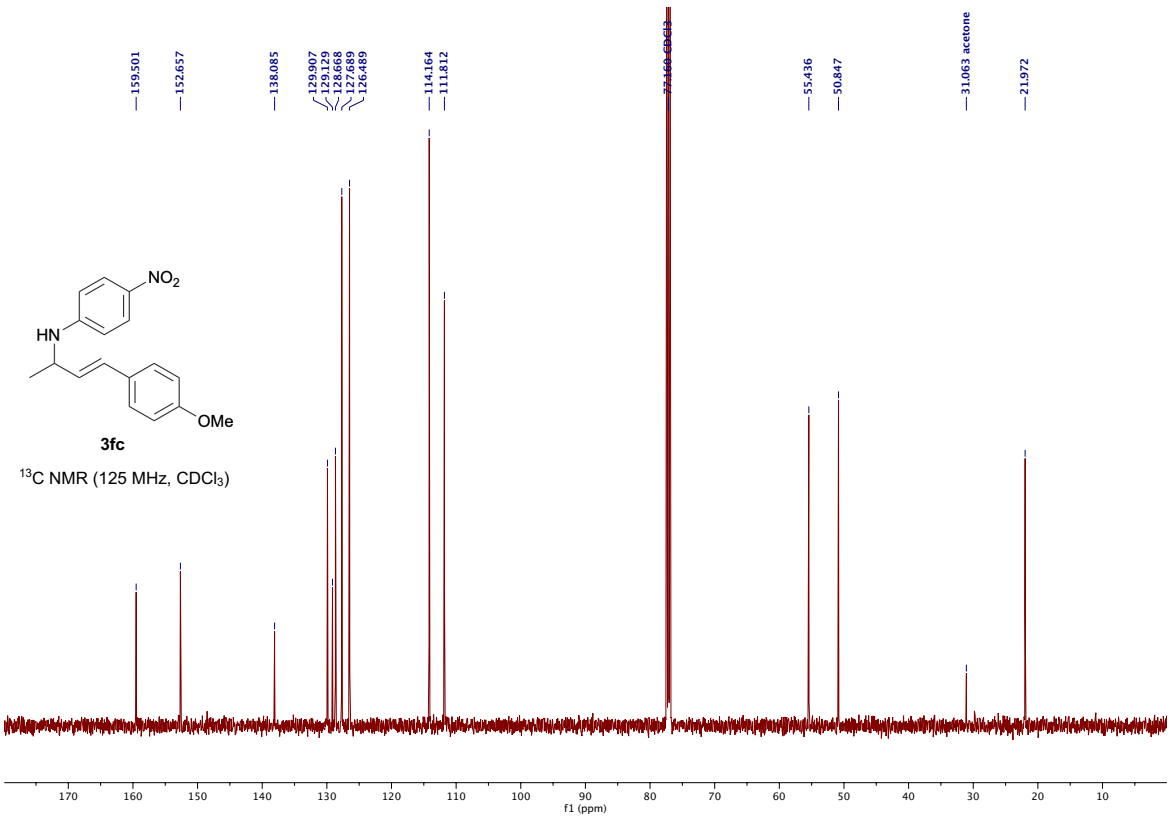

8.266
8.248
8.180
8.162
8.083
8.068
8.064
8.049
7.608
7.590
7.509
7.491
7.445
7.430
7.416
7.406
7.392
7.374
7.369
7.353
7.331
7.316
7.303
7.289
7.275
7.260 CDCl3
6.692
6.660
6.628
6.611
6.592
6.557
6.538
6.365
6.352
6.334
6.320
5.325
5.311
5.260
5.246
4.969
2.172 acetone
1.619 water
NO2
HN
Ph
3ec
NO2
O2N
NH
Ph
3ec'
NO2
1H NMR (500 MHz, CDCl3)
2.16
1.94
4.02
2.11
1.97
4.47
5.97
4.70
2.36
0.94
1.00
0.88
0.90
f1 (ppm)


151.938
151.500
147.793
147.324
142.553
139.518
139.233
138.921
138.447
134.196
133.498
130.028
129.525
128.955
128.845
128.766
127.985
127.550
127.194
126.808
126.412
124.579
124.204
112.439
112.274
77.260 CDCl3
60.073
59.854
NO2
HN
Ph
3ec
NO2
O2N
NH
Ph
3ec'
NO2
13C NMR (125 MHz, CDCl3)
f1 (ppm)



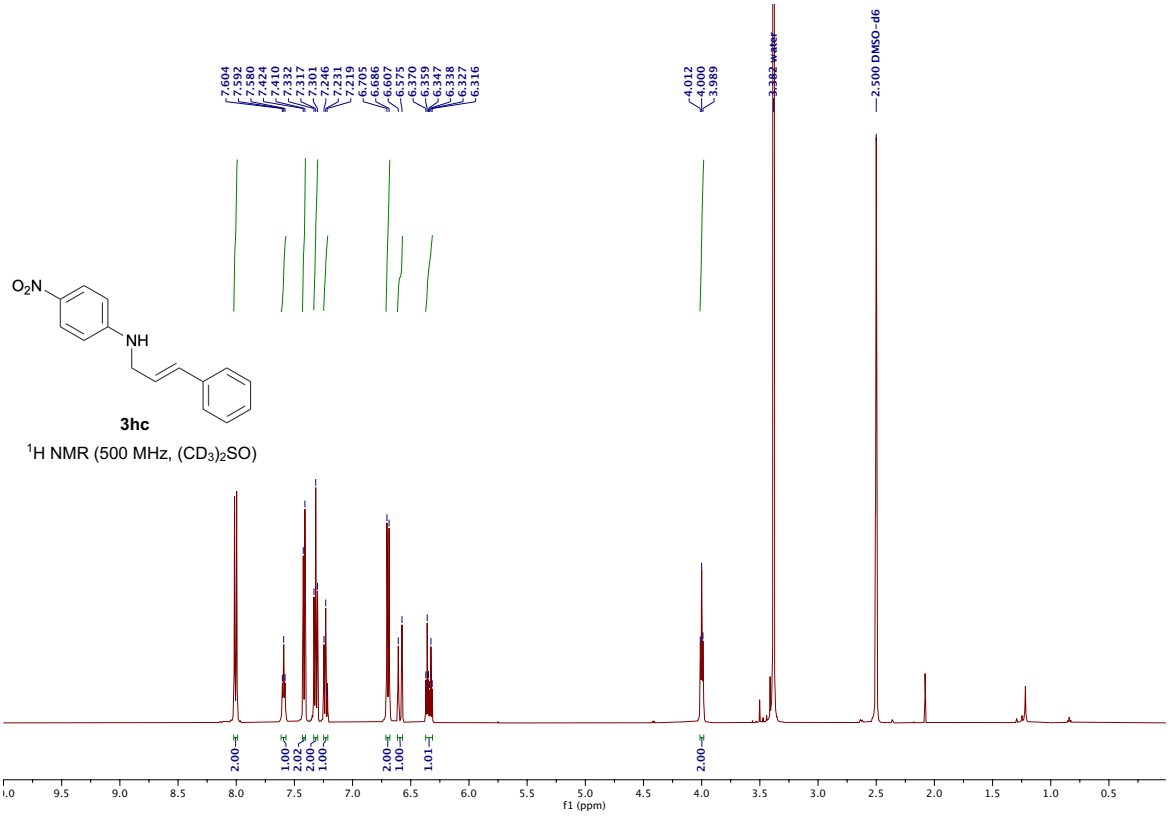
3fc

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



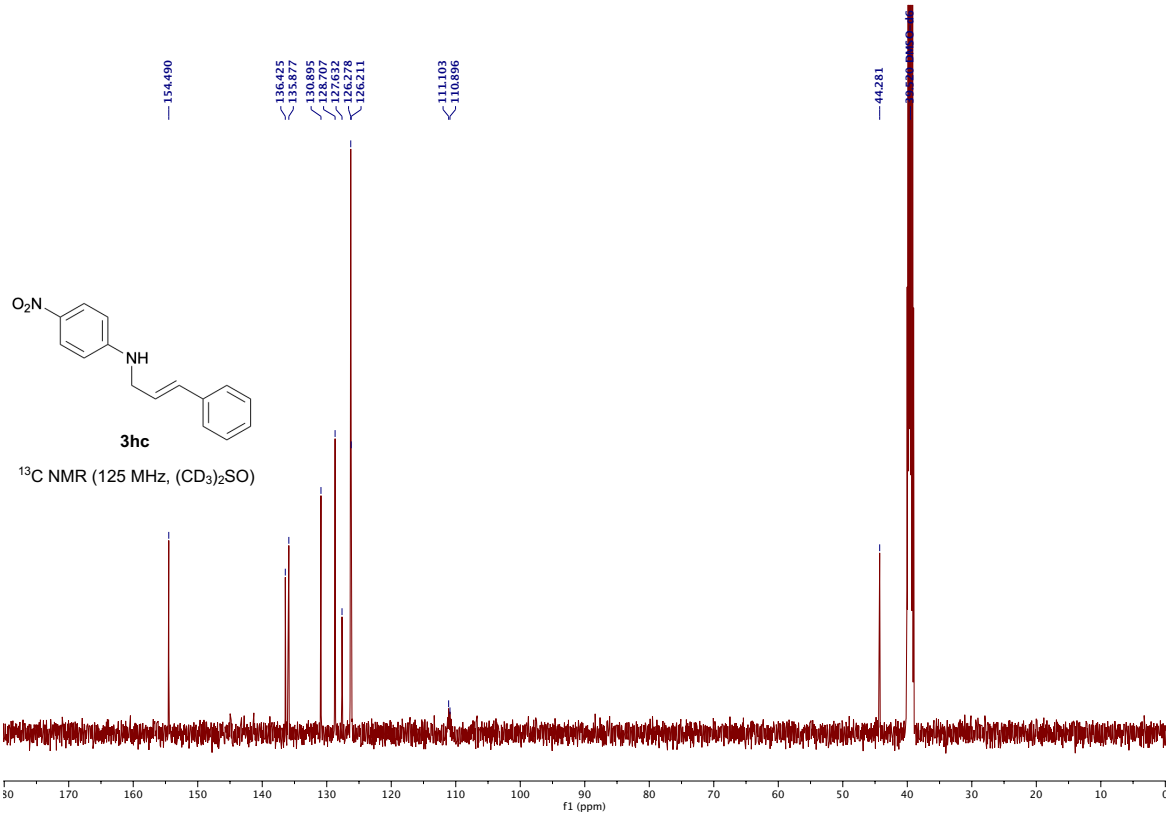
3fc

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



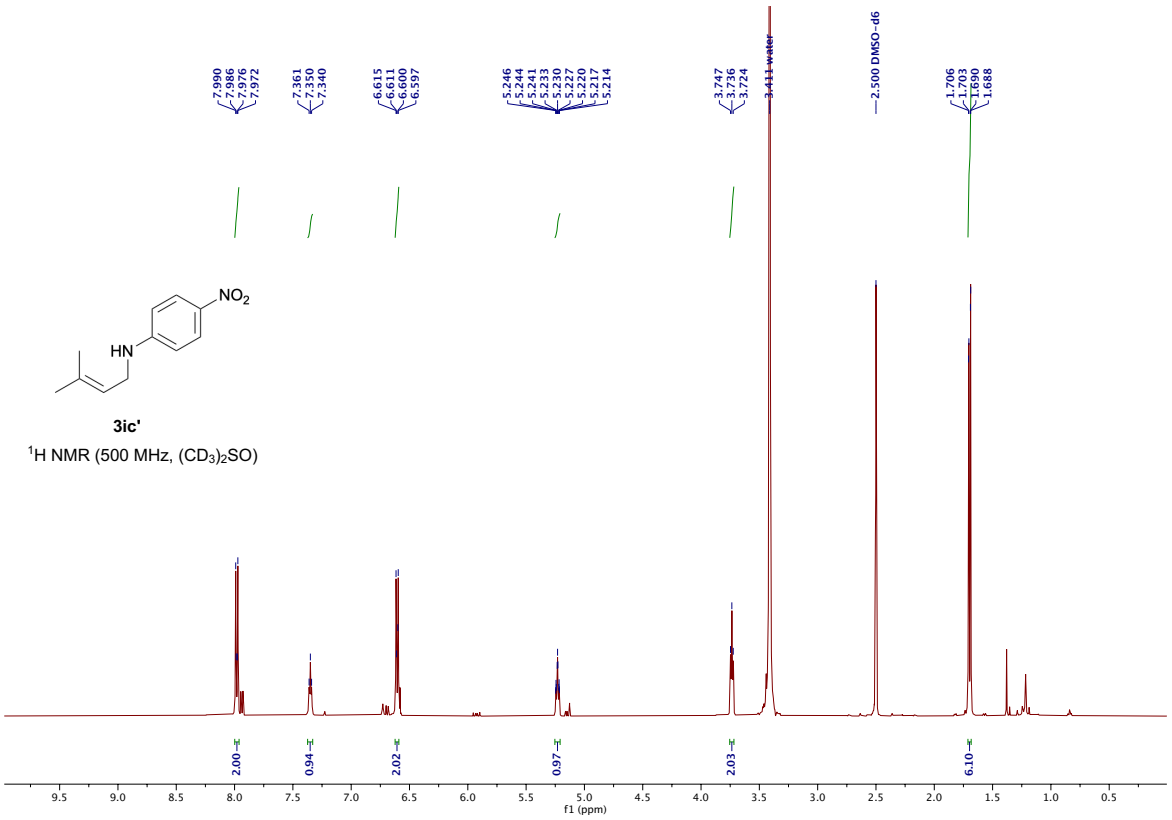
3hc

^{1}H NMR (500 MHz, $(CD_3)_2SO$)



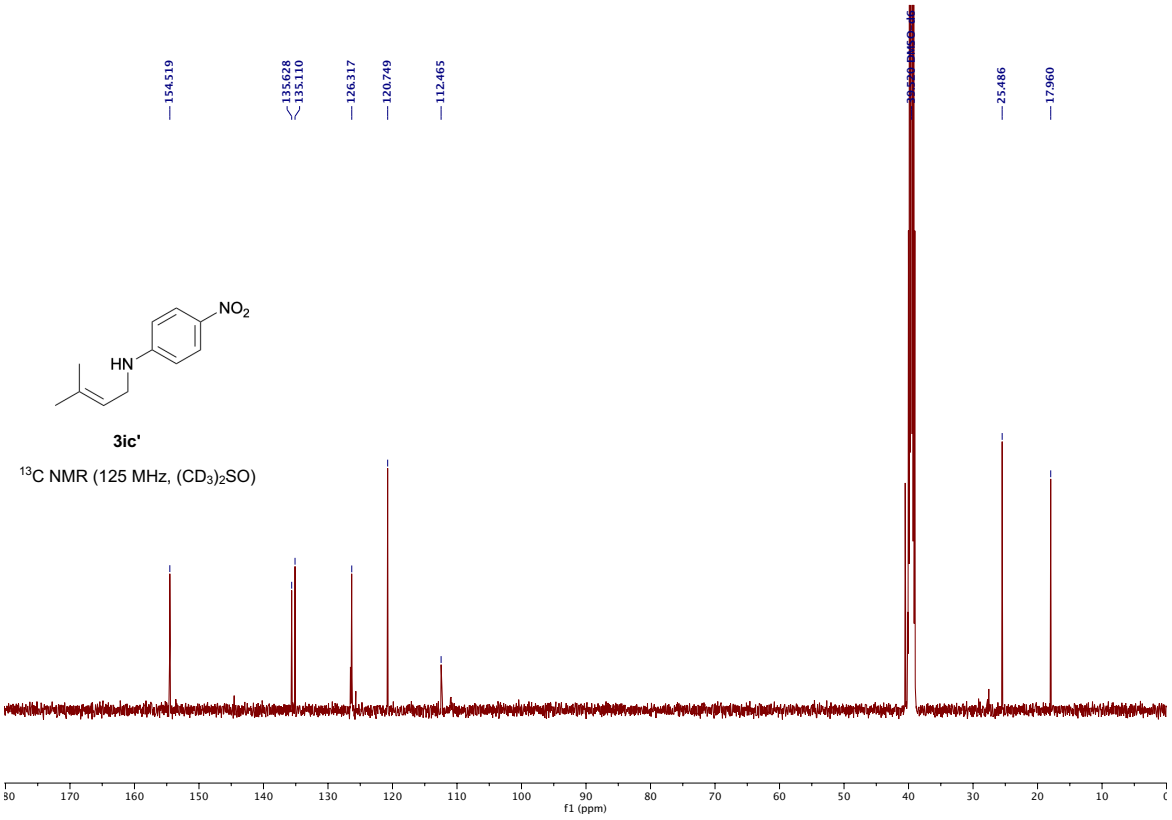
3hc

^{13}C NMR (125 MHz, $(CD_3)_2SO$)



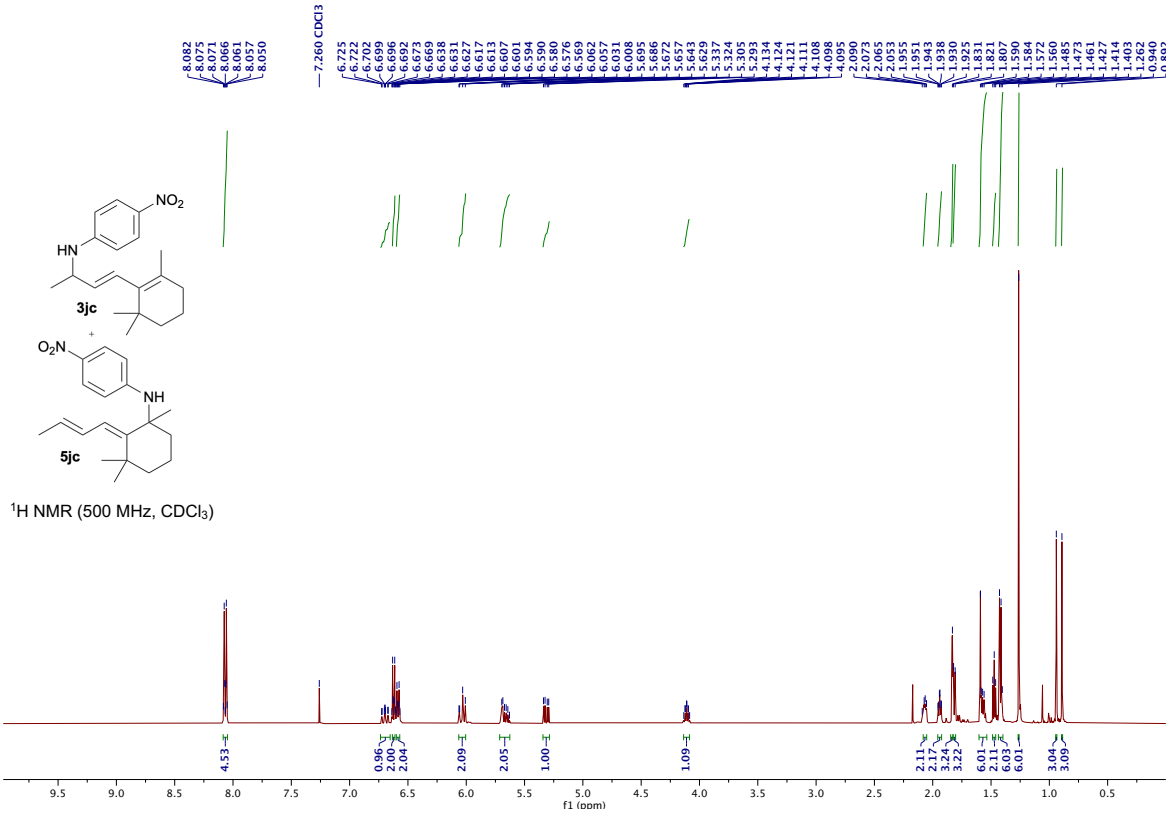
3ic'

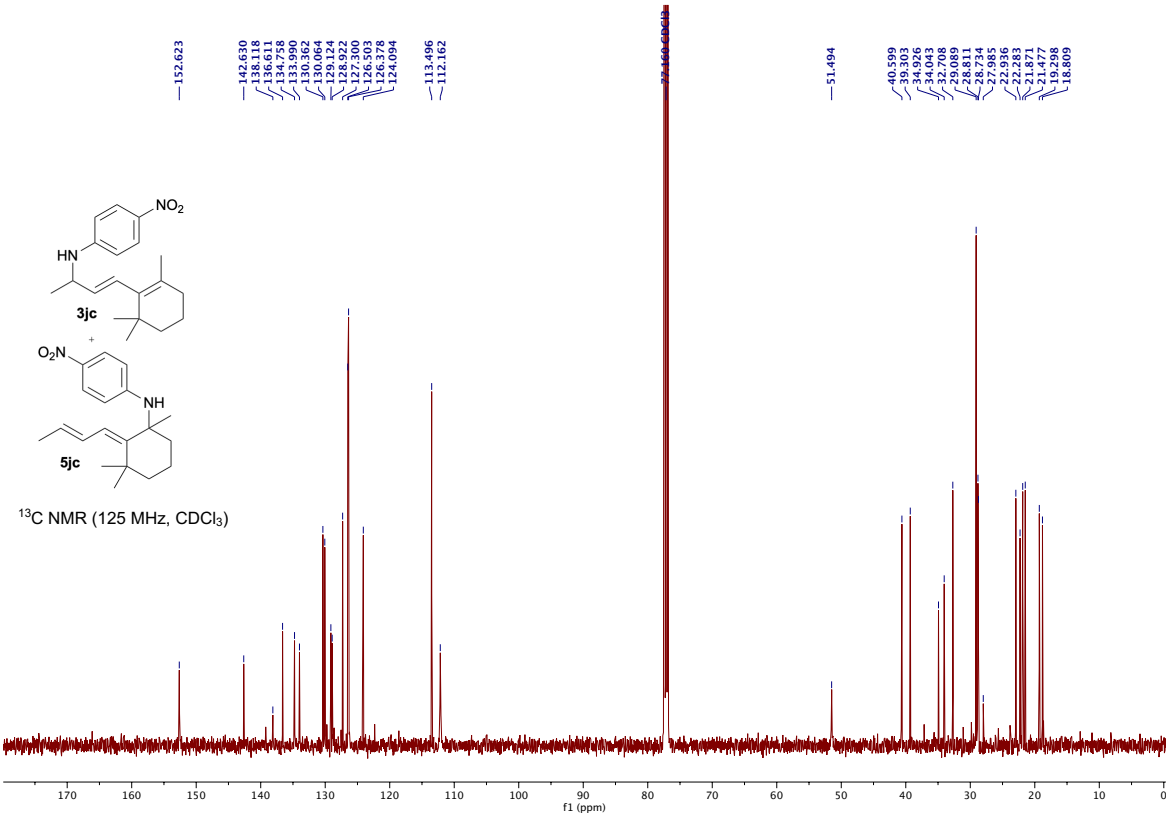
^{1}H NMR (500 MHz, $(CD_3)_2SO$)

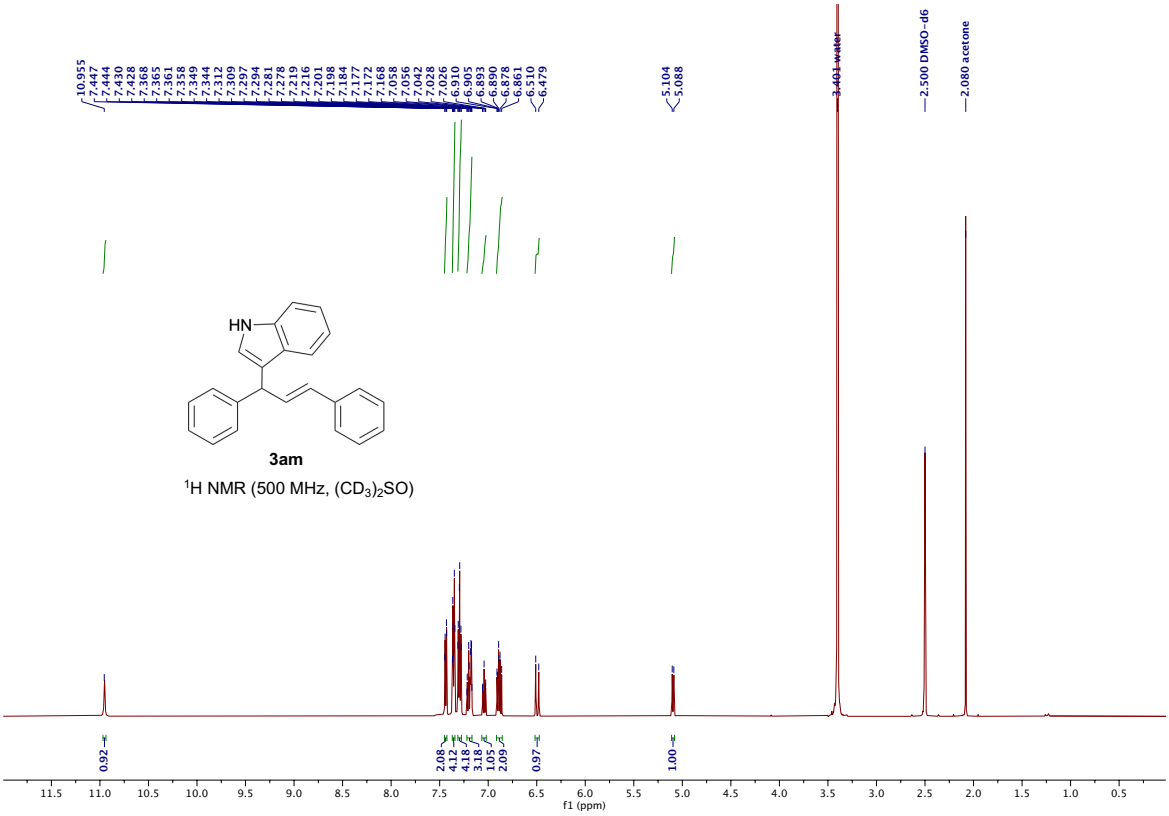


3ic'

^{13}C NMR (125 MHz, $(CD_3)_2SO$)

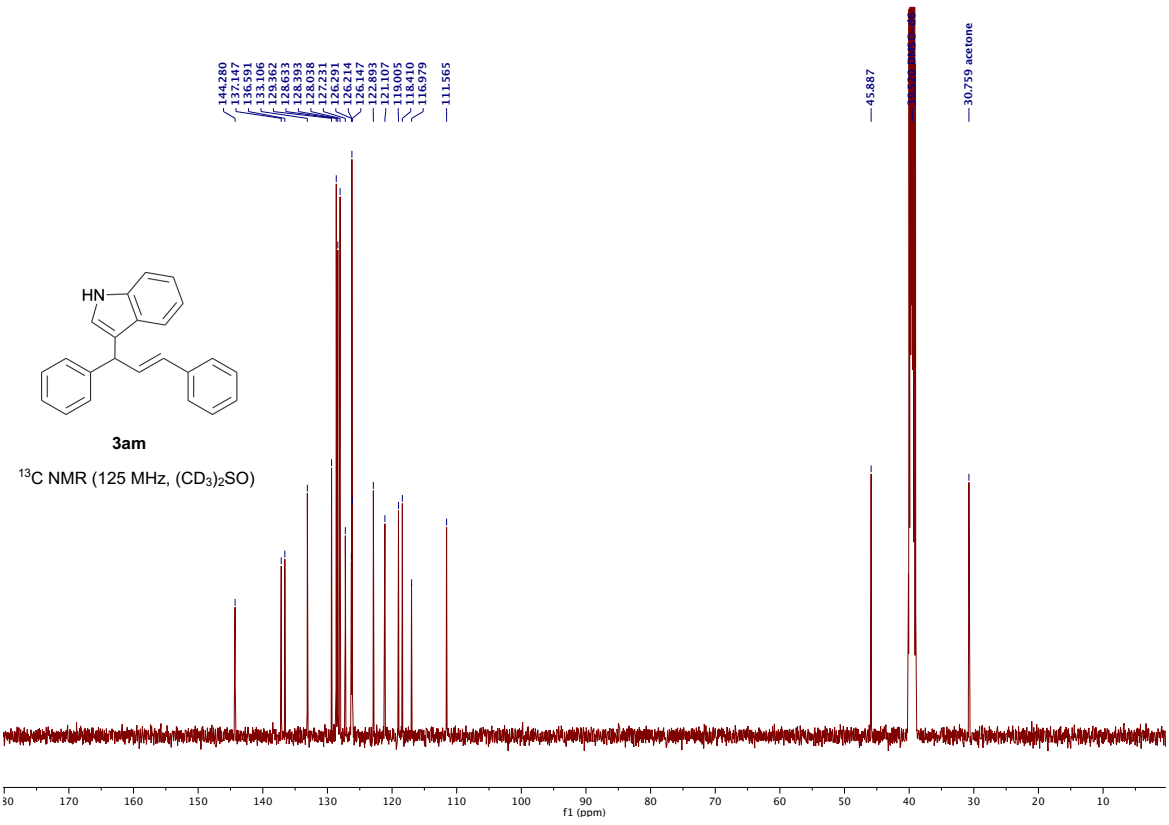

NO2
HN
3jc
O2N
NH
5jc
1H NMR (500 MHz, CDCl3)
f1 (ppm)


NO2
HN
3jc
O2N
NH
5jc
13C NMR (125 MHz, CDCl3)
f1 (ppm)



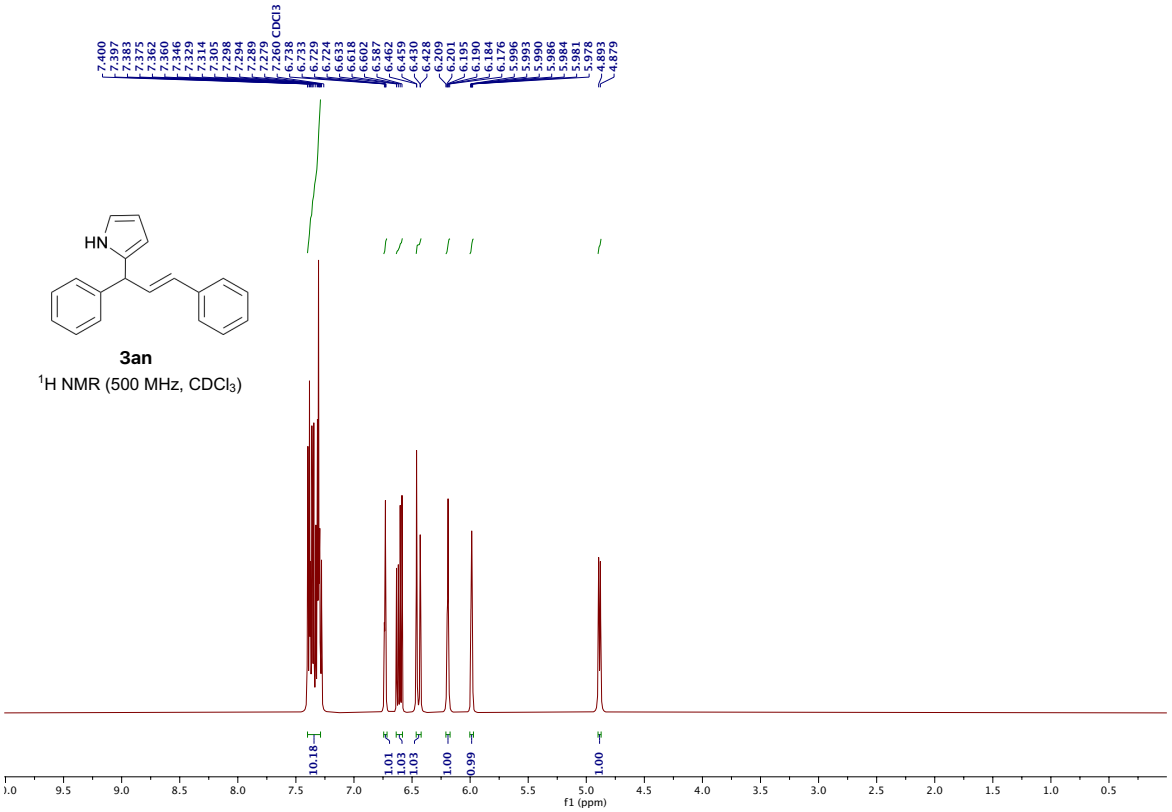
3am

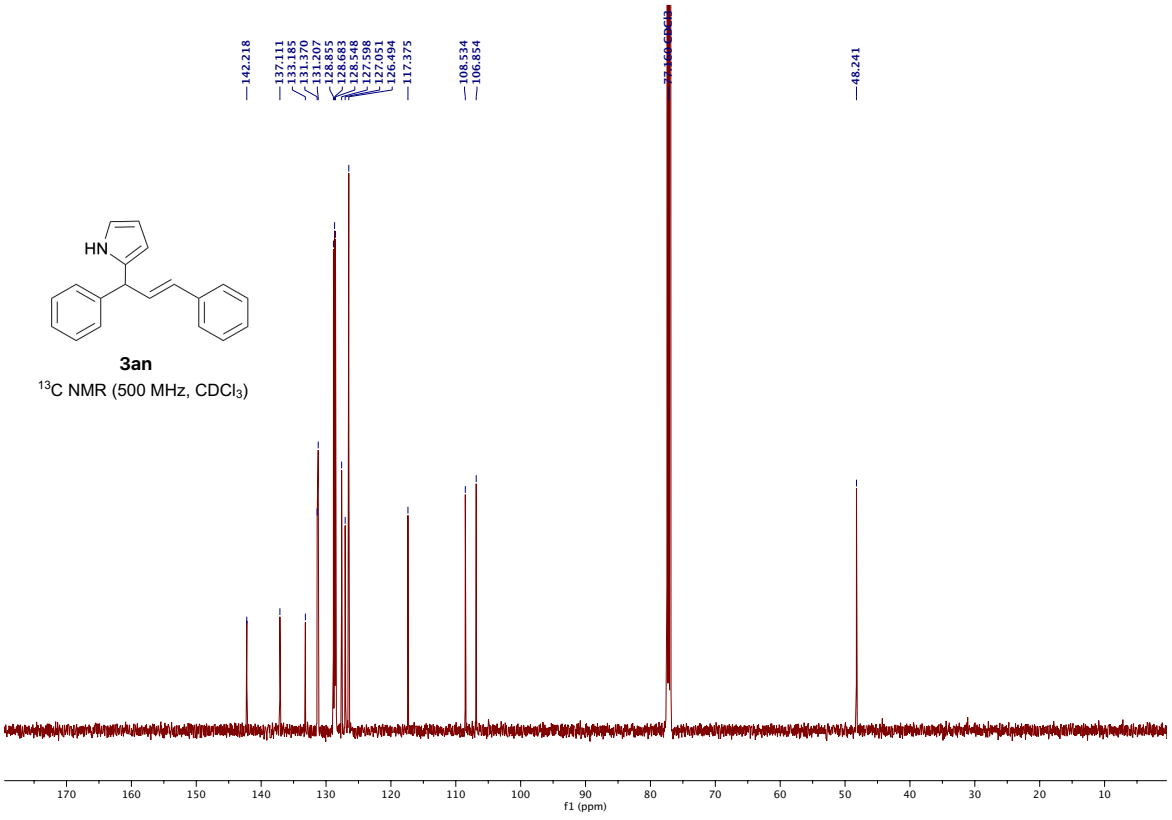
^{1}H NMR (500 MHz, $(CD_3)_2SO$)

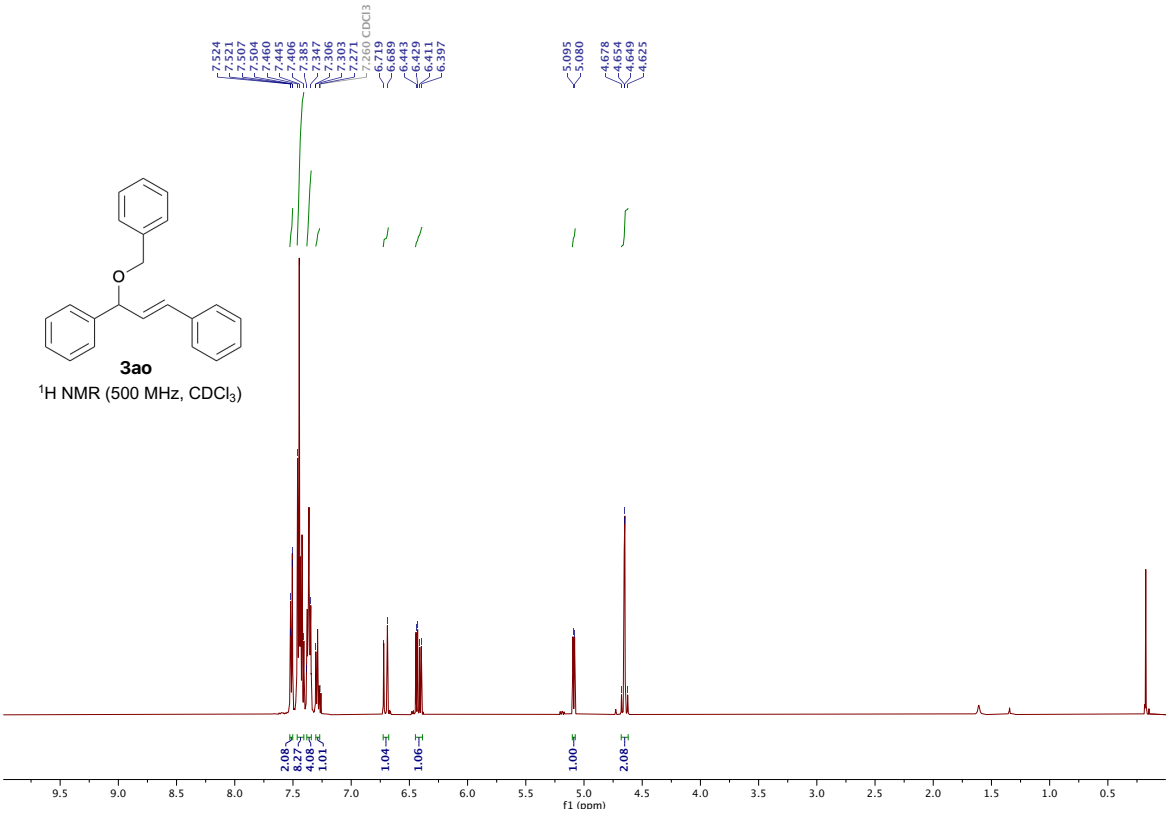


3am

^{13}C NMR (125 MHz, $(CD_3)_2SO$)

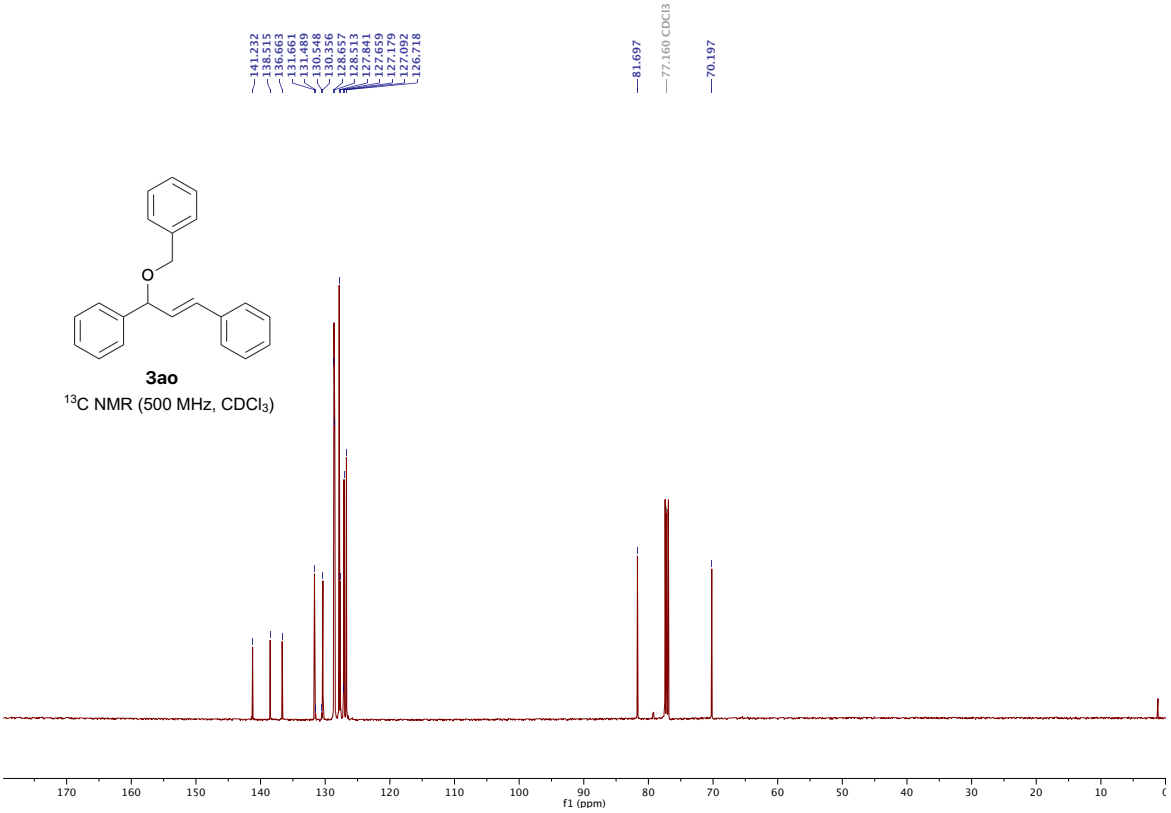

7.400
7.397
7.383
7.375
7.362
7.360
7.346
7.329
7.314
7.305
7.298
7.294
7.289
7.279
7.260 CDCl3
6.738
6.733
6.729
6.724
6.633
6.618
6.602
6.587
6.462
6.459
6.430
6.428
6.209
6.201
6.195
6.190
6.184
6.176
5.996
5.993
5.990
5.986
5.984
5.981
5.978
4.893
4.879
HN
3an
1H NMR (500 MHz, CDCl3)
10.18
1.01
1.03
1.03
1.00
0.99
1.00
f1 (ppm)


142.218
137.111
133.185
131.370
131.207
128.855
128.683
128.548
127.698
127.251
126.494
117.375
108.534
106.854
77.160 CDCl3
48.241
HN
3an
13C NMR (500 MHz, CDCl3)
f1 (ppm)



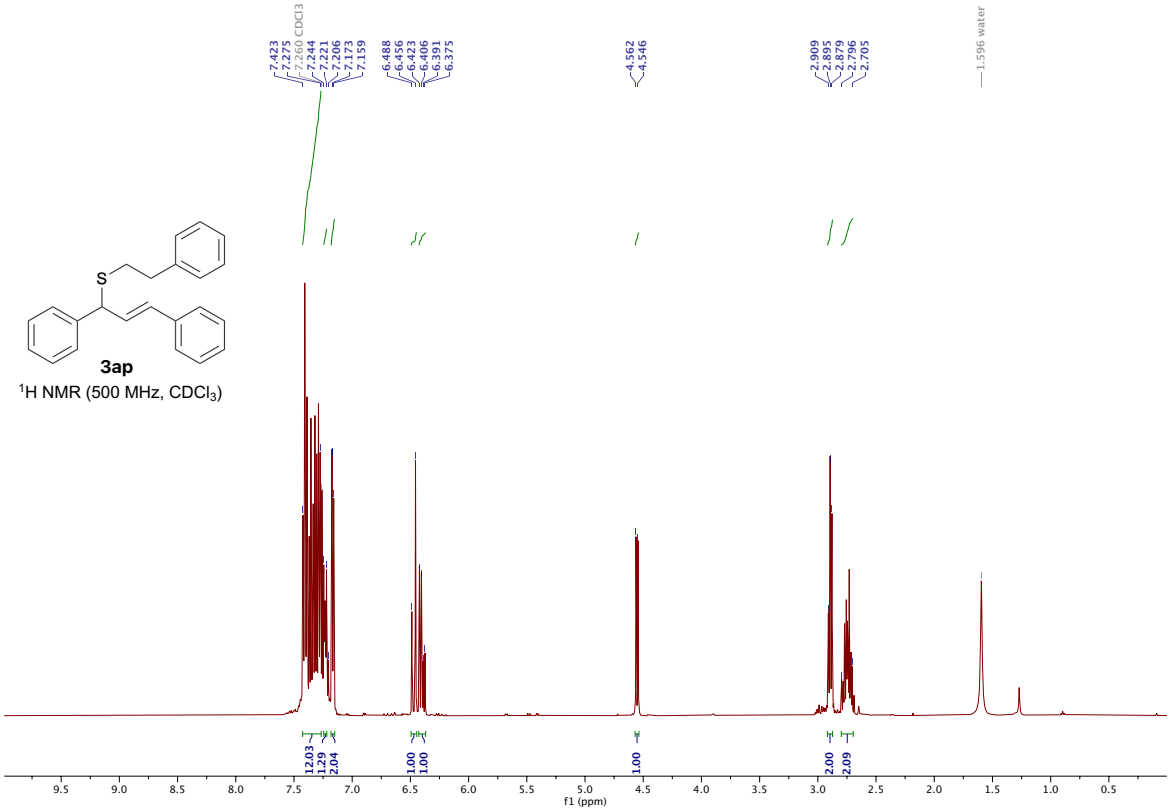
3ao

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



3ao

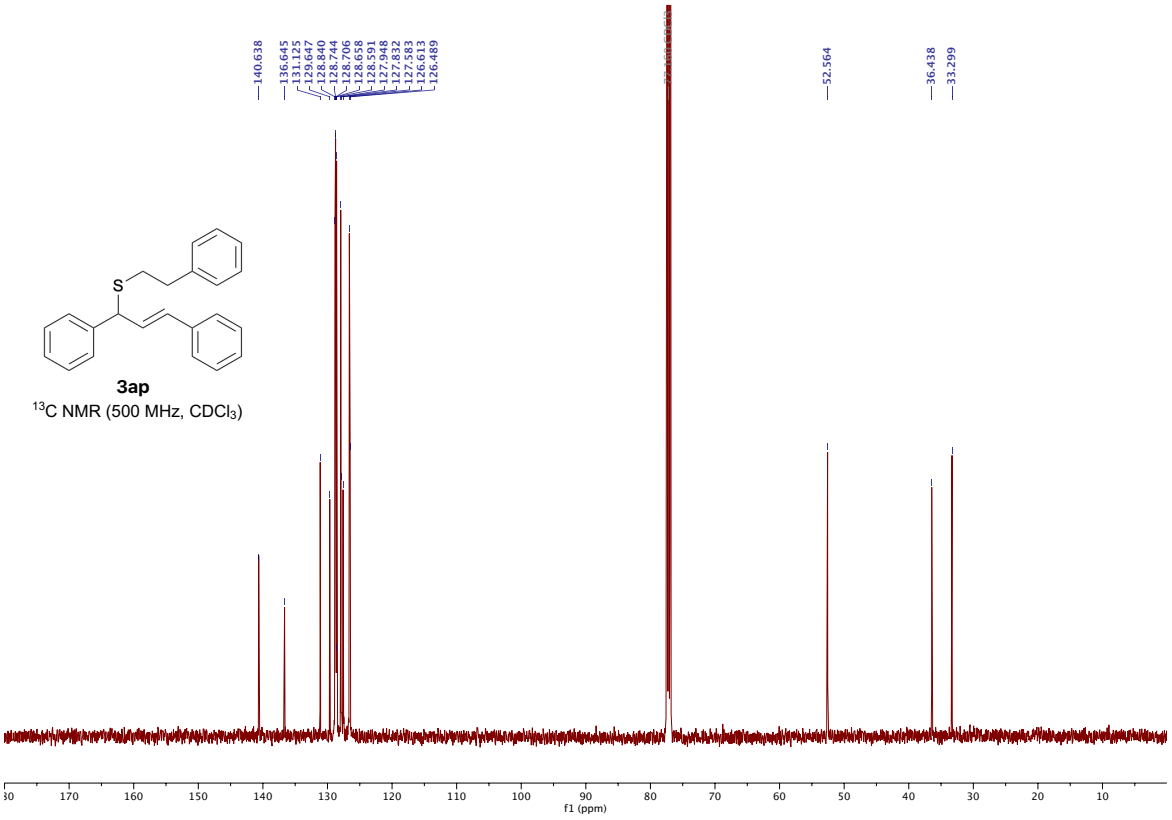
^{13}C NMR (500 MHz, $CDCl_3$)



S

3ap

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



S

3ap

^{13}C NMR (500 MHz, $CDCl_3$)

References

1. Y. C. Guo, K. W. Chiu and R. J. Chein, *J. Org. Chem.*, 2022**, 1**, 559–572.
2. C., Gomes, C. S. Vinagreiro, L. Damas, G. Aquino, J. Quaresma, C. Chaves, J. Pimenta, J. Campos, M. Pereira and M. Pineiro, *ACS omega,* 2020, **19**, 10868–10877.
3. F. Sonmez, S. Sevmezler, A. Atahan, M. Ceylan, D. Demir, N. Gencer, O. Arslan and M. Kucukislamoglu, *Bioorg. Med. Chem.*, 2011, **24**, 7479–7482.
4. N. Solin, L. Han, S. Che and O. Terasaki, *Catal. Commun.*, 2009, **10**, 1386–1389.
5. M. Al-Masum and K. Y. Liu, *Tetrahedron Lett.* 2011, **39**, 5090–5093.
6. J. Ma, W. Li, L. He and H. Lv, *ChemComm.*, 2022, **58,** 5841–5844.
7. P. Song, C. Lu, Z. Fei, B. Zhao and Y. Yao, *J. Org. Chem.*, 2018, **11**, 6093–6100.
8. D. Wang, D. Chen, J. X. Haberman and C. J. Li, *Tetrahedron*, 1998, **20**, 5129–5142.
9. S. Akai, R. Hanada, N. Fujiwara, Y. Kita and M. Egi, *Org. Lett.*, 2010, **21**, 4900–4903.
10. D. Titu and A. Chadha, *Tetrahedron: Asymmetry*, 2008, **19**, 1698**–**1701.
11. W. Yin, Y. Ma, J. Xu and Y. Zhao, *J. Org. Chem.*, 2006, **71**, 4312–4315.
12. M. Y. Chang., C. Y. Tsai and M. H. Wu, *Tetrahedron*, 2013, **69**, 6364–6370.
13. M. Albert-Soriano, L. Hernández-Martínez and I. M. Pastor, *ACS Sustain. Chem. Eng.*, 2018, **6**, 14063–14070.
14. R. Nallagonda, M. Rehan and P. Ghorai, *J. Org. Chem.,* 2014, **79**, 2934–2943.
15. K. Chen, Y. Li, S. A. Pullarkat and P.-H. Leung, *Adv. Synth. Catal.*, 2012, **354**, 83**–**87.
16. P. Trillo, A. Baeza and C. Nájera, *Eur. J. Org. Chem.*, 2012, **2012**, 2929–2934.
17. P. Trillo and I. M. Pastor, *Adv. Synth. Catal.*, 2016, **358**, 2929–2939.
18. P. Trillo, A. Baeza and C. Najera, *J. Org. Chem.*, 2012, **77**, 7344–7354.
19. Y. C. Hsu, K. H. Gan and S. C. Yang, *Chem. Pharm. Bull.,* 2005, **53**, 1266–1269.
20. A. N. Duncan and R. A. Widenhoefer, *Synlett*, 2010, **2010**, 419–422.
21. W. Rao and P. W. H. Chan, *Org. Biomol. Chem.*, 2008, **6**, 2426–2433.
22. H. Zhang, R. Liu and X. Zhou, *Sci. China Chem.*, 2014, **57**, 282–288.