Photoredox-Mediated α-Vinylation of α-Amino Acids and *N*-Aryl Amines

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Supporting Information

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1) General Information

Commercial reagents were purified prior to use following the guidelines of Perrin and Armarego.[1] When commercial, *N*-aryl amines were distilled prior to use. Commercial photocatalysts were used without purification. $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ was prepared according to the procedure of Malliaras and Bernhard.[2] All solvents were purified according to the method of Grubbs.[3] Non-aqueous reagents were transferred under nitrogen or argon via syringe or cannula. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator using a water bath. Chromatographic purification of products was accomplished using forced-flow chromatography on ICN 60 32-64 mesh silica gel 63 or Davisil Grade 643 silica gel according to the method of Still.[4] Thin-layer chromatography (TLC) was performed on Silicycle 0.25 mm silica gel F-254 plates. Visualization of the developed chromatogram was performed by fluorescence quenching or $KMnO_4$ stain. ^1H NMR spectra were recorded on a Brüker UltraShield Plus 500 MHz unless otherwise noted and are internally referenced to residual protio solvent signals. Data for ^1H NMR are reported as follows: chemical shift (δ ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, br = broad), coupling constant (Hz), and assignment. ^{13}C NMR spectra were recorded on a Brüker UltraShield Plus 500 MHz and data are reported in terms of chemical shift relative to $CDCl_3$ (77.0 ppm). IR spectra were recorded on a Perkin Elmer Spectrum 100 FTIR spectrometer and are reported in wavenumbers (cm^{-1}). High Resolution Mass Spectra were obtained from the Princeton University Mass Spectral Facility.

2) Preparation of *N*-Aryl Amines

General Procedure for N-Arylpyrrolidine Synthesis:
To a suspension of K_2CO_3 (3.80 g, 27.5 mmol, 1.1 equiv.) in DMF (25 mL) was added the appropriate aniline (25 mmol, 1.0 equiv.). The reaction was degassed by sparging with nitrogen for 15 min before the addition of 1,4-dibromobutane (3.26 mL, 27.5 mmol, 1.1 equiv.). The reaction was heated to 80 °C for 10 h before being allowed to cool and diluted with EtOAc (200 mL) and H_2O (200 mL). The layers were separated and the organic layer was extracted with 1 M HCl (3 x 50 mL). The acid layer were combined and adjusted to pH 8 with 1 M NaOH and then extracted with EtOAc (3 x 100 mL). The organic layers were washed with brine (50 mL), dried over Na_2SO_4, filtered, concentrated *in vacuo*, and purified by flash column chromatography.

***N*-(4-Methoxyphenyl)pyrrolidine**. The reaction of 4-methoxyaniline (3.08 g, 25.0 mmol) with 1,4-dibromobutane as outlined in the general procedure provided the title compound (3.48 g, 79%). ^1H NMR (500 MHz, $CDCl_3$) δ 1.99–2.02 (4H, m, $NCH_2C\mathbf{H_2}$), 3.24–3.27 (4H, m, $NC\mathbf{H_2}$), 3.78 (3H, s, $OC\mathbf{H_3}$), 6.54–6.58 (2H, m, Ar**H**), 6.85–6.89 (2H, m, Ar**H**). All spectroscopic data is in agreement with those previously reported.[5]

Methyl (4-pyrrolidin-1-yl)benzoate. The reaction of methyl-4-aminobenzoate (1.40 g, 9.26 mmol) with 1,4-dibromobutane as outlined in the general procedure provided the title compound (536 mg, 28%). ^1H NMR (500 MHz, $CDCl_3$) δ 2.02–2.05 (4H, m, $NCH_2C\mathbf{H_2}$), 3.34–3.37 (4H, m, $NC\mathbf{H_2}$), 3.86 (3H, s, $OC\mathbf{H_3}$), 6.49–6.52 (2H, m, Ar**H**), 7.89–7.92 (2H, m, Ar**H**). All spectroscopic data is in agreement with those previously reported.[5]

***N*-(4-Fluorophenyl)pyrrolidine**. The reaction of 4-fluoroaniline (2.78 g, 25.0 mmol) with 1,4-dibromobutane as outlined in the general procedure provided the title compound (3.50 g, 85%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.96–2.07 (4H, m, NCH_2CH_2), 3.20–3.30 (4H, m, NCH_2), 6.45–6.52 (2H, m, Ar**H**), 6.90–6.99 (2H, m, Ar**H**). All spectroscopic data is in agreement with those previously reported.[6]

***N*-(4-Bromophenyl)pyrrolidine**.[7] The reaction of 4-bromoaniline (4.30 g, 25.0 mmol) with 1,4-dibromobutane as outlined in the general procedure provided the title compound (4.14 g, 73%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.97–2.06 (4H, m, NCH_2CH_2), 3.21–3.29 (4H, m, NCH_2), 6.40–6.46 (2H, m, Ar**H**), 7.26–7.31 (2H, m, Ar**H**).

***N*-(2-Bromophenyl)pyrrolidine**. The reaction of 2-bromoaniline (3.44 g, 20.0 mmol) with 1,4-dibromobutane as outlined in the general procedure provided the title compound (1.32 g, 29%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.91–2.02 (4H, m, NCH_2CH_2), 3.33–3.43 (4H, m, NCH_2CH_2), 6.75 (1H, t, J = 7.5, Ar**H**), 6.93 (1H, d, J = 8.2, Ar**H**), 7.20 (1H, t, J = 7.7, Ar**H**), 7.52 (1H, d, J = 7.9, Ar**H**). All spectroscopic data is in agreement with those previously reported.[8]

***tert*-Butyl-(*E*)-4-phenyl-3-styrylpiperazine-1-carboxylate**. To a stirred mixture of *N*-phenylpiperazine (1.62 g, 10.0 mmol, 1.00 equiv.) and Boc_2O (2.18 g, 10.0 mmol, 1.00 equiv.) was added iodine (254 mg, 1.00 mmol, 10.0 mol%). The mixture was stirred at rt for 1 h before the addition of Et_2O (20 mL). The organic phase was washed with 10% sodium thiosulfate, sat. $NaHCO_3$, dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification by flash column chromatography (0-25% EtOAc/hexanes) provided the title compound (2.12 g, 81%) and a colorless solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.49 (9H, s, $C(CH_3)_3$), 3.11–3.17 (4H, m, NCH_2), 3.57–3.61 (4H, m, NCH_2), 6.90 (1H, t, J = 7.3, Ar**H**), 6.94 (1H, d, J = 7.9, Ar**H**), 7.27–7.31 (2H, m, Ar**H**). All spectroscopic data is in agreement with those previously reported.[9]

***N*-Phenylazepane**. To a solution of *N*-phenyl-ε-caprolactam[10] (1.67 g, 8.82 mmol) in THF (44 mL) at rt was added dropwise BH_3.THF (1 M in THF, 17.7 mL, 2.00 equiv.). The mixture was heated to reflux for 2 h before being allowed to cool and quenched by the slow addition of 1 M HCl until no further gas evolution occurred. The mixture was basified to pH 8 by the addition of saturated aq. $NaHCO_3$ and the product extracted into EtOAc (3 x 50 mL), washed with brine (50 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The product was purified by flash column chromatography (5-20% EtAOc/hexanes) to give the title compound (1.46 g, 94%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.53–1.60 (4H, m, $NCH_2CH_2CH_2$), 1.76–1.84 (4H, m, NCH_2CH_2), 3.46 (4H, t, J = 6.0, NCH_2), 6.64 (1H, t, J = 7.1, Ar**H**), 6.70 (2H, d, J = 8.2, Ar**H**), 7.22 (2H, t, J = 7.7, Ar**H**). All spectroscopic data is in agreement with those previously reported.[11]

***N*-Benzyl-1,2,3,4-tetrahydroquinoline**. A mixture of the 1,2,3,4-tetrahydroquinoline (20 mmol, 1.0 equiv.), K_2CO_2 (23.0 mmol, 1.15 equiv.), and BnCl (22.0 mmol, 1.10 equiv.) in MeOH (20 mL) was refluxed for 5 hours. The reaction was allowed to cool before being filtered through Celite® and concentrated *in vacuo*. The residue was taken up in Et_2O and washed with water, dried (Na_2SO_4), and concentrated *in vacuo*. Purification by flash column chromatography provided the title compound (2.86 g, 80%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.01–2.06 (2H, m,

C**H**$_2$CH$_2$Ar), 2.84 (2H, t, *J* = 6.3, CH$_2$C**H**$_2$Ar), 3.37–3.40 (2H, m, NC**H**$_2$CH$_2$CH$_2$Ar), 4.50 (2H, s, NC**H**$_2$Ph), 6.51 (1H, d, *J* = 8.2, Ar**H**), 6.59 (1H, td, *J* = 7.3, 1.1, Ar**H**), 6.97–7.01 (2H, m, Ar**H**), 7.23–7.42 (5H, m, Ar**H**). All spectroscopic data is in agreement with those previously reported.[12]

***N*-Benzylindoline**. The reaction of indoline with benzyl chloride, using the method described for the synthesis 1,2,3,4-tetrahydroquinoline, provided the title compound (3.46 g, 83%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 2.99 (2H, t, *J* = 8.3, NCH$_2$C**H**$_2$Ar), 3.33 (2H, t, *J* = 8.3, NC**H**$_2$CH$_2$Ar), 4.27 (2H, s, NC**H**$_2$Ph), 6.54 (1H, d, *J* = 7.7, Ar**H**), 6.69 (1H, t, *J* = 7.3, Ar**H**), 7.07 (1H, t, *J* = 7.6, Ar**H**), 7.11 (1H, d, *J* = 7.2, Ar**H**), 7.27–7.41 (5H, m, Ar**H**). All spectroscopic data is in agreement with those previously reported.[12]

3) Preparation of Vinyl Sulfones

General Procedures for the Synthesis of Vinyl Sulfones:

Vinyl Sulfone Synthesis, General Procedure A.[13] To a suspension of benzenesulfinic acid sodium salt (4.92 g, 30.0 mmol, 3.00 equiv.) and NaOAc (1.23 g, 15.0 mmol, 1.50 equiv.) in MeCN (40 mL) was added styrene (1.16 mL, 10.0 mmol, 1.00 equiv.) followed by iodine (3.81 g, 15.0 mmol, 1.50 equiv.). The mixture was heated to reflux for 1 h before being allowed to cool and the excess iodine quenched with 10% aq. sodium thiosulfate. Sat. aq. NaHCO$_3$ was added and the product extracted into EtOAc (3 x 20 mL). The combined organic phases were washed with H$_2$O (20 mL), brine (20 mL), dried (MgSO$_4$), filtered, and concentrated *in vacuo*. The crude product was purified by flash column chromatography and recrystallized from *i*-PrOH/hexanes.

Vinyl Sulfone Synthesis, General Procedure B.[14] To an oven-dried flask charged with LiBr (1.04 g, 12.0 mmol) was added a solution of diethyl ((phenylsulfonyl)methyl)phosphonate in MeCN (20 mL) and Et$_3$N (1.53 mL, 11.0 mmol). The resulting suspension was stirred for until it became homogeneous before being cooled to 0 °C. A solution of the aldehyde (10.0 mmol) in MeCN (4.0 mL) was added dropwise over 5 min. The mixture was then allowed to warm to rt in the ice bath overnight. The reaction was quenched by the addition of 0.1 M aq. HCl (40 mL) and the product extracted into EtOAc (2 x 20 mL). The combined organic extracts were washed with brine (20 mL), dried (MgSO$_4$), filtered, and concentrated *in vacuo*. The crude product was purified by flash column chromatography or recrystallization from MeOH.

Vinyl Sulfone Synthesis, General Procedure C.[15] To a solution of methylphenylsulfone (781 mg, 5.00 mmol, 1.00 equiv.) in THF (30 mL) at 0 °C was added dropwise *n*-BuLi (2.5 M in hexanes, 4.40 mL, 11.0 mmol, 2.20 equiv.). The yellow suspension was stirred at this temperature for 10 min before the addition of diethyl chlorophosphate (0.867 mL, 6.00 mmol, 1.20 equiv.). The resultant yellow solution was stirred at 0 °C for 10 min before being cooled to –78 °C. Aldehyde (5.00 mmol, 1.00 equiv.) was added and the reaction was allowed to warm to rt in the dry ice bath overnight. The reaction was quenched by the addition of sat. aq. NH$_4$Cl and the product was extracted into Et$_2$O (3 x 20 mL), washed with brine (20 mL), dried (MgSO$_4$), filtered, and concentrated *in vacuo*. The crude product was purified by flash column chromatography and recrystallized from *i*-PrOH/hexanes.

(*E*)-(2-(Phenylsulfonyl)vinyl)benzene (9). The reaction of styrene (1.16 mL, 10.0 mmol) as outlined in general procedure A provided the title compound (2.21 g, 90%, >98:2 *E*:*Z*). ^{1}H NMR

(500 MHz, $CDCl_3$) δ 6.87 (1H, d, *J* = 15.4, C**H**Ph), 7.39–7.45 (3H, m, Ar**H**), 7.50 (2H, dd, *J* = 7.7, 1.8, Ar**H**), 7.55–7.59 (2H, m, Ar**H**), 7.62–7.66 (1H, m, Ar**H**), 7.70 (1H, d, *J* = 15.4, C**H**SO_2Ph), 7.95–7.97 (2H, m, Ar**H**). All spectroscopic data is in agreement with those previously reported.[13]

(*E*)-1-Methyl-4-(2-(phenylsulfonyl)vinyl)benzene. The reaction of *p*-methylstyrene (0.659 mL, 5.00 mmol) as outlined in general procedure A provided the title compound (1.13 g, 87%, >98:2 *E*:*Z*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.38 (3H, s, C$\mathbf{H_3}$), 6.82 (1H, d, *J* = 15.5, C**H**Ar), 7.20 (2H, d, *J* = 7.9, Ar**H**), 7.39 (2H, d, *J* = 8.2, Ar**H**), 7.53–7.57 (2H, m, Ar**H**), 7.60–7.64 (1H, m, Ar**H**), 7.67 (1H, d, *J* = 15.4, C**H**SO_2Ph), 7.94–7.97 (2H, m, Ar**H**). All spectroscopic data is in agreement with those previously reported.[16]

(*E*)-1-Chloro-4-(2-(phenylsulfonyl)vinyl)benzene. The reaction of *p*-chlorostyrene (0.600 mL, 5.00 mmol) as outlined in general procedure A provided the title compound (986 mg, 71%, >98:2 *E*:*Z*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.86 (1H, d, *J* = 15.4), 7.37 (2H, d, *J* = 8.5), 7.42 (2H, d, *J* = 8.5), 7.57 (2H, t, *J* = 7.6), 7.64 (1H, d, *J* = 7.1), 7.65 (1H, d, *J* = 15.5), 7.95 (2H, d, *J* = 7.5). All spectroscopic data is in agreement with those previously reported.[13,16]

(*E*)-Methyl 4-(2-(phenylsulfonyl)vinyl)benzoate. The reaction of 4-formylbenzoate (1.64 g, 10.0 mmol) as outlined in general procedure B provided the title compound (2.70 g, 89%, >98:2 *E*:*Z*) as a white solid. IR (film) ν_{max} 3053–2952, 1716, 1609, 1446, 1434, 1307, 1279, 1193, 1144, 1109, 1084 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.94 (3H, s), 6.96 (1H, d, *J* = 15.4), 7.54–7.60 (4H, m), 7.64–7.68 (H, m), 7.72 (1H, d, *J* = 15.4), 7.96–7.98 (2H, m), 8.06 (2H, d, *J* = 8.3); ^{13}C NMR (126 MHz, $CDCl_3$) δ 52.4, 127.8, 128.5, 129.5, 129.7, 130.2, 132.2, 133.7, 136.5, 140.2, 140.9, 166.2; HRMS (ESI-TOF) *m*/*z* calcd. for $C_{16}H_{15}O_4S$ ($[M+H]^+$) 303.06856, found 303.06855.

(*E*)-1-Methoxy-4-(2-(phenylsulfonyl)vinyl)benzene. The reaction of 4-anisaldehyde (1.2 mL, 10.0 mmol) as outlined in general procedure B provided the title compound (2.06 g, 75%, >98:2 *E*:*Z*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.82 (3H, s), 6.72 (1H, d, *J* = 15.4), 6.88–6.91 (2H, m), 7.41–7.45 (2H, m), 7.51–7.56 (2H, m), 7.58–7.62 (1H, m), 7.63 (1H, d, *J* = 15.3), 7.92–7.96 (2H, m). All spectroscopic data is in agreement with those previously reported.[16]

(*E*)-1-Fluoro-2-(2-(phenylsulfonyl)vinyl)benzene. The reaction of 2-fluorobenzaldehyde (0.527 mL, 5.00 mmol) as outlined in general procedure C provided the title compound (764 mg, 58%, >98:2 *E*:*Z*) as an off-white solid. IR (film) ν_{max} 3059, 1612, 1485, 1449, 1308, 1290, 1146, 1085 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.03 (1H, d, *J* = 15.6), 7.12 (1H, ddd, *J* = 10.9, 8.3, 1.1), 7.19 (1H, td, *J* = 7.6, 1.1), 7.39–7.43 (1H, m), 7.48 (1H, td, *J* = 7.6, 1.7), 7.55–7.59 (2H, m), 7.63–7.66 (1H, m), 7.78 (1H, d, *J* = 15.6), 7.96–7.98 (2H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ 116.4 (1C, d, *J* = 21.7), 120.6 (1C, d, *J* = 11.5), 124.7 (1C, d, *J* = 3.7), 127.8, 129.4, 130.1 (1C, d, *J* = 8.6), 130.4 (1C, d, *J* = 2.6), 132.8 (1C, d, *J* = 8.9), 133.5, 135.6 (1C, d, *J* = 2.2), 140.5, 161.6 (1C, d, *J* = 255.4); HRMS (ESI-TOF) *m*/*z* calcd. for $C_{14}H_{12}FO_2S$ ($[M+H]^+$) 263.05365, found 263.05341.

(*E*)-1-(2-(Phenylsulfonyl)vinyl)-3-(trifluoromethyl)benzene. The reaction of 3-trifluoromethylbenzaldehyde (0.669 mL, 5.00 mmol) as outlined in general procedure C

provided the title compound (701 mg, 45%, >98:2 *E*:*Z*) as a white solid. IR (film) ν_{max} 3062, 1710, 1620, 1447, 1330, 1305, 1167, 1144, 1120, 1097, 1084, 1070 cm^{-1}; ^1H NMR (501 MHz, $CDCl_3$) δ 6.96 (1H, d, *J* = 15.4), 7.54–7.61 (3H, m), 7.64–7.69 (3H, m), 7.72 (1H, d, *J* = 15.6), 7.74 (1H, s), 7.96–7.99 (2H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ 123.6 (1C, q, *J* = 272.5), 125.0 (1C, q, *J* = 3.8), 127.6 (1C, q, *J* = 3.7), 127.8, 129.5, 129.5, 129.7, 131.7 (1C, q, *J* = 16.4), 131.7, 133.2, 133.7, 140.2, 140.5; HRMS (ESI-TOF) *m*/*z* calcd. for $C_{15}H_{12}F_3O_2S$ ($[M+H]^+$) 313.05046, found 313.05040.

((*E*)-1-(2-(Phenylsulfonyl)vinyl)naphthalene. The reaction of 1-naphthaldehyde (1.36 mL, 10.0 mmol) as outlined in general procedure B provided the title compound (2.75 g, 93%, >98:2 *E*:*Z*) as a white solid. ^1H NMR (500 MHz, $CDCl_3$) δ 6.98 (1H, d, *J* = 15.2), 7.48 (1H, t, *J* = 7.7), 7.55–7.61 (3H, m), 7.62–7.67 (2H, m), 7.69 (1H, d, *J* = 7.2), 7.90 (1H, d, *J* = 8.1), 7.94 (1H, d, *J* = 8.2), 8.01–8.03 (2H, m), 8.19 (1H, d, *J* = 8.4), 8.55 (1H, d, *J* = 15.2). All spectroscopic data is in agreement with those previously reported.[17]

(*E*)-4-(2-(Phenylsulfonyl)vinyl)pyridine. The reaction of 4-vinylpyridine (0.539 mL, 5.00 mmol) as outlined in general procedure A provided the title compound (411 mg, 34%, >98:2 *E*:*Z*) as a pale yellow solid. IR (film) ν_{max} 3052, 1594, 1446, 1414, 1308, 1291, 1145, 1085 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.06 (1H, d, *J* = 15.4), 7.33–7.35 (2H, m), 7.57–7.61 (2H, m), 7.63 (1H, d, *J* = 15.7), 7.66–7.70 (1H, m), 7.95–7.98 (2H, m), 8.67–8.69 (2H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ 122.1, 128.0, 129.6, 132.3, 134.0, 139.3, 139.7, 139.7, 150.7; HRMS (ESI-TOF) *m*/*z* calcd. for $C_{13}H_{12}NO_2S$ ($[M+H]^+$) 246.05833, found 246.05803.

(*E*)-1-Methyl-3-(2-(phenylsulfonyl)vinyl)-1*H*-indole. The reaction of 3-formyl-1-methylindole (796 mg, 5.00 mmol) as outlined in general procedure C provided the title compound (1.05 g, 70%, >98:2 *E*:*Z*) as a pale yellow solid. IR (film) ν_{max} 3107–2826, 1606, 1575, 1528, 1375, 1304, 1285, 1141, 1084, 1075 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.78 (1H, d, *J* = 15.3), 7.24–7.27 (1H, m), 7.31–7.38 (1H, m), 7.40 (1H, s), 7.51–7.55 (2H, m), 7.56–7.60 (1H, m), 7.78 (1H, d, *J* = 8.0), 7.88 (1H, d, *J* = 15.3), 7.96–7.99 (2H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ 33.4, 110.0, 110.2, 120.3, 120.4, 121.8, 123.4, 125.6, 127.3, 129.2, 132.7, 134.5, 136.3, 138.1, 142.2; HRMS (ESI-TOF) *m*/*z* calcd. for $C_{17}H_{16}NO_2S$ ($[M+H]^+$) 298.08963, found 298.09009.

(*E*)-2-(2-(Phenylsulfonyl)vinyl)furan. The reaction of furfural (0.828 mL, 10.0 mmol) as outlined in general procedure C provided the title compound (1.94 g, 83%, >98:2 *E*:*Z*) as a pale yellow solid. IR (film) ν_{max} 3129–3058, 1622, 1306, 1288, 1278, 1268, 1142, 1085 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.49 (1H, dd, *J* = 3.4, 1.8), 6.72 (1H, d, *J* = 3.5), 6.75 (1H, d, *J* = 15.0), 7.45 (1H, d, *J* = 15.0), 7.49 (1H, d, *J* = 1.8), 7.53–7.57 (2H, m), 7.60–7.64 (1H, m), 7.93–7.95 (2H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ 112.6, 117.0, 124.7, 127.6, 128.9, 129.3, 133.3, 140.9, 145.7, 148.7; HRMS (ESI-TOF) *m*/*z* calcd. for $C_{12}H_{11}O_3S$ ($[M+H]^+$) 235.04234, found 235.04260.

(*E*)-((4-Methylpenta-1,3-dien-1-yl)sulfonyl)benzene. The reaction of 3-methyl-2-butenal (0.965 mL, 10.0 mmol) as outlined in general procedure C provided the title compound (1.77 g, 80%, >98:2 *E*:*Z*) as a white solid. IR (film) ν_{max} 3049–2911, 1636, 1445, 1304, 1284, 1236, 1139, 1082 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.90 (3H, s), 1.94 (3H, s), 5.93 (1H, d, *J* = 11.6), 6.22 (1H, d, *J* = 14.6), 7.52–7.56 (3H, m), 7.58–7.62 (1H, m), 7.89–7.91 (2H, m); ^{13}C NMR (126

MHz, $CDCl_3$) δ 19.2, 26.7, 121.5, 126.8, 127.4, 129.2, 133.0, 138.8, 141.3, 149.8; HRMS (ESI-TOF) *m/z* calcd. for $C_{12}H_{15}O_2S$ ($[M+H]^+$) 223.07873, found 223.07844.

(*E*)-((2-Phenylprop-1-en-1-yl)sulfonyl)benzene. The reaction of methylphenylsulfone (1.56 g, 10.0 mmol) and acetophenone (1.28 mL, 11.0 mmol) according to the procedure of Carretero *et al*.[18] gave the title compound (1.88 g, 73%, >98:2 *E*:*Z*) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.54 (3H, d, *J* = 1.3), 6.62 (1H, d, *J* = 1.4), 7.35–7.42 (5H, m), 7.55–7.59 (2H, m), 7.62–7.66 (1H, m), 7.98–8.00 (2H, m,). All spectroscopic data is in agreement with those previously reported.[13,18]

(2-(Phenylsulfonyl)ethene-1,1-diyl)dibenzene. The reaction of 1,1-diphenylethylene (0.883 mL, 5.00 mmol) as outlined in general procedure A provided the title compound (675 mg, 42%) as a white solid. IR (film) ν_{max} 3058, 1588, 1568, 1445, 1302, 1136, 1082 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.04 (1H, s), 7.07–7.10 (2H, m), 7.21–7.24 (2H, m), 7.28–7.40 (8H, m), 7.48–7.51 (1H, m), 7.57–7.60 (2H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ 127.7, 127.9, 128.2, 128.6, 128.7, 128.8, 128.9, 129.8, 130.4, 132.9, 135.5, 139.1, 141.4, 155.2; HRMS (ESI-TOF) *m/z* calcd. for $C_{20}H_{17}O_2S$ ($[M+H]^+$) 321.09438, found 321.09394.

(*Z*)-2-(1-Phenyl-2-(phenylsulfonyl)vinyl)isoindole-1,3-dione. The title compound was prepared in three steps from phenylacetylene. The first step involved the reaction of phenylacetylene (1.10 mL, 10.0 mmol) as outlined in general procedure A to provide (*E*)-(1-iodo-2-(phenylsulfonyl)vinyl)benzene[19] (3.02 g, 82%). To a solution of (*E*)-(1-iodo-2-(phenylsulfonyl)vinyl)benzene (2.06 g, 5.56 mmol) in dry benzene (5.43 mL) was added Et_3N (5.43 mL, 39.0 mmol). The reaction was stirred at rt for 20 h during which time a white precipitate formed. The reaction was diluted with Et_2O, filtered through Celite® and concentrated *in vacuo*. Purification by recrystallization from MeOH gave ((phenylethynyl)sulfonyl)benzene[19] (1.20 g, 89%). To a solution of ((phenylethynyl)sulfonyl)benzene (507 mg, 2.09 mmol) in MeCN (15 mL) at rt was added phthalimide (616 mg, 4.18 mmol) followed by KOH (12 mg, 0.21 mmol). The mixture was stirred at rt for 16 h before removal of the solvent *in vacuo*. The residue was purified by flash column chromatography (5-20% EtOAc/hexanes) followed by recrystallization from *i*-PrOH/hexanes to give the title compound (347 mg, 43%) as a white solid. IR (film) ν_{max} 3061, 1735, 1718, 1374, 1321, 1152, 1085 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.00 (1H, s), 7.37–7.41 (2H, m), 7.44–7.47 (3H, m), 7.55–7.59 (2H, m), 7.64–7.67 (1H, m), 7.84 (2H, dd, *J* = 5.5, 3.1), 7.96–7.98 (2H, m), 8.01 (2H, dd, *J* = 5.5, 3.1); ^{13}C NMR (126 MHz, $CDCl_3$) δ 124.3, 126.7, 126.9, 128.0, 129.2, 129.4, 131.6, 132.2, 133.7, 134.0, 134.6, 140.1, 140.4, 166.4; HRMS (ESI-TOF) *m/z* calcd. for $C_{22}H_{16}NO_4S$ ($[M+H]^+$) 390.07946, found 390.07881.

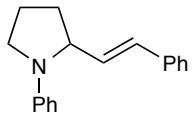
(*E*)-5-(2-(phenylsulfonyl)vinyl)benzo[*d*][1,3]dioxole. The reaction of piperonal (1.50 g, 10.0 mmol) as outlined in general procedure C provided the title compound (2.05 g, 71%, >98:2 *E*:*Z*) as a white solid. IR (film) ν_{max} 3055–2784, 1708, 1596, 1502, 1490, 1446, 1357, 1301, 1252, 1220, 1141, 1082, 1033 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.02 (2H, s), 6.68 (1H, d, *J* = 15.3), 6.83 (1H, d, *J* = 8.0), 6.95 (1H, s), 7.01 (1H, d, *J* = 8.0), 7.53–7.64 (4H, m), 7.95 (2H, d, *J* = 8.2); ^{13}C NMR (126 MHz, $CDCl_3$) δ 101.8, 106.8, 108.7, 124.9, 125.4, 126.6, 127.6, 129.3, 133.3, 141.0, 142.3, 148.5, 150.4; HRMS (ESI-TOF) *m/z* calcd. for $C_{15}H_{13}O_4S$ ($[M+H]^+$) 289.05291, found 289.05242.

(*E*)-2-(Methoxymethoxy)-5-(2-(phenylsulfonyl)vinyl)phenol. The reaction of 3-hydroxy-4-(methoxymethoxy)benzaldehyde (2.24 g, 11.4 mmol) as outlined in general procedure C provided the title compound (3.50 g, 92%, >98:2 *E*:*Z*) as a colorless solid. IR (film) ν_{max} 3055–2830, 1613, 1598, 1581, 1511, 1446, 1422, 1305, 1268, 1242, 1144, 1083 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.50 (3H, s, OC**H**$_3$), 3.90 (3H, s, OC**H**$_3$), 5.27 (2H, s, OC**H**$_2$O), 6.74 (1H, d, *J* = 15.3, C**H**=CHSO$_2$Ph), 7.00 (1H, d, *J* = 2.0, Ar**H**), 7.07 (1H, dd, *J* = 8.4, 2.0, Ar**H**), 7.16 (1H, d, *J* = 8.4, Ar**H**), 7.56 (2H, t, *J* = 7.5, Ar**H**), 7.61–7.64 (1H, m, Ar**H**). 7.63 (1H, d, *J* = 15.3, CH=C**H**SO$_2$Ph), 7.95–7.97 (2H, m, Ar**H**); ^{13}C NMR (126 MHz, $CDCl_3$) δ 56.0, 56.4, 95.1, 110.7, 115.7, 123.0, 125.2, 126.5, 127.6, 129.3, 133.3, 141.0, 142.4, 149.3, 149.9; HRMS (ESI-TOF) *m*/*z* calcd. for $C_{16}H_{17}O_5S$ ($[M+H]^+$) 335.09477, found 355.09503.

4) General C–H Vinylation Procedure

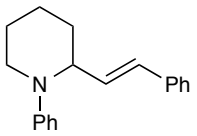
General procedure for the C–H vinylation of N-aryl amines:
To a dry 8 mL vial equipped with a stir bar was added Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (5.6 mg, 5.0 μmol, 0.010 equiv.), the vinyl sulfone (0.50 mmol, 1.0 equiv.), and the *N*-aryl amine (if solid, 1.25 mmol, 2.50 equiv.). The vial was sealed and triple evacuated/N_2 filled before being transferred into a glovebox. CsOAc (288 mg, 1.50 mmol, 3.0 equiv.) was added to the vial before transferring out of the glovebox and placing under an atmosphere of N_2. DCE (5.0 mL) was added to the vial, followed by the *N*-aryl amine (if liquid, 1.25 mmol, 2.50 equiv.). The reaction mixture was degassed by sparging with N_2 for 15 min. The reaction was then stirred vigorously and irradiated with two compact fluorescent light (CFL) bulbs until complete consumption (12–61h) of the vinyl sulfone, as determined by TLC analysis. The reaction mixture was diluted with sat. aq. $NaHCO_3$ (20 mL) and the layers separated. The aqueous phase was further extracted with DCM (2 x 10 mL) and the combined organic extracts were dried (Na_2SO_4), filtered, and concentrated *in vacuo*. Purification by removal of excess *N*-aryl amine by distillation and subsequent flash column chromatography or preparative TLC afforded the vinylation product.

5) Experimental Data for C–H Vinylation Products



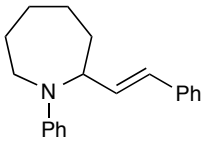
(*E*)-1-Phenyl-2-styrylpyrrolidine (10)
Prepared following the general procedure outlined above using (*E*)-(2-(phenylsulfonyl)vinyl)benzene (122 mg, 0.500 mmol, 1.00 equiv.), *N*-phenylpyrrolidine (181 μL, 2.50 equiv.), Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (5.6 mg, 0.010 equiv.), CsOAc (288 mg, 3.00 equiv.) and DCE (5.00 mL). After 12 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by removal of excess *N*-phenyl-pyrrolidine by heating to 100 °C under vaccum (~0.5 torr) followed by preparative TLC using 95:4:1 hexanes:acetone:Et_3N provided the title compound (105 mg, 84%, >98:2 *E*:*Z*) as a colorless oil. IR (film) ν_{max} 3058–2835, 1596, 1503, 1362, 1343, 1182, 1156 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$)

δ 1.91–2.22 (4H, m, $NCH_2(CH_2)_2$), 3.30 (1H, td, *J* = 9.0, 7.1, NCH_2), 3.53–3.61 (1H, m, NCH_2), 4.31–4.36 (1H, m, NCHCH=CHPh), 6.24 (1H, dd, *J* = 15.9, 5.3, CH=CHPh), 6.47 (1H, d, *J* = 15.9 Hz, CHPh), 6.64–6.72 (3H, m, ArH), 7.20–7.24 (3H, m, ArH), 7.30 (2H, t, *J* = 7.6, ArH), 7.36 (2H, d, *J* = 7.4, ArH); ^{13}C NMR (126 MHz, $CDCl_3$) δ 23.40, 33.0, 48.8, 60.8, 112.2, 115.7, 115.7, 115.7, 126.4, 127.2, 128.5, 129.0, 129.4, 131.6, 137.0, 147.5; HRMS (ESI-TOF) *m/z* calcd. for $C_{18}H_{20}N$ ($[M+H]^+$) 250.15903, found 250.15889.



(*E*)-1-Phenyl-2-styrylpiperidine (12)

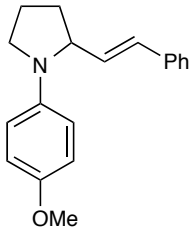
Prepared following the general procedure outlined above using (*E*)-(2-(phenylsulfonyl)vinyl)benzene (122 mg, 0.500 mmol, 1.00 equiv.), *N*-phenylpiperidine (201 μL, 2.50 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 0.010 equiv.), CsOAc (288 mg, 3.00 equiv.) and DCE (5.00 mL). After 16 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by removal of excess *N*-phenylpiperidine by heating to 100 °C under vaccum (~0.5 torr) followed by preparative TLC using 95:4:1 hexanes:acetone:Et_3N provided the title compound (110 mg, 84%, 97:3 *E*:*Z*) as a colorless oil. IR (film) ν_{max} 3082–2854, 1596, 1498, 1448, 1247 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ (*E*-isomer) 1.60–1.81 (4H, m, $NCH_2(CH_2)_3$), 1.87–1.92 (1H, m, $NCH_2(CH_2)_3$), 1.94–2.00 (1H, m, $NCH_2(CH_2)_3$), 3.19–3.24 (1H, m, NCH_2), 3.39 (1H, dt, *J* = 12.7, 4.1, NCH_2), 4.44 (1H, dt, *J* = 5.0, 5.0, NCHCH=CHPh), 6.25 (1H, dd, *J* = 16.2, 5.9, CH=CHPh), 6.42 (1H, d, *J* = 15.6, CH=CHPh), 6.80 (1H, t, *J* = 7.3, ArH), 6.97 (2H, d, *J* = 8.1, ArH), 7.17–7.30 (7H, m, ArH); ^{1}H NMR (500 MHz, $CDCl_3$) δ (*Z*-isomer) 4.51–4.56 (1H, m, NCHCH=CHPh), 5.76 (1H, dd, *J* = 11.9, 9.4, CH=CHPh), 6.71 (2H, d, *J* = 8.1, ArH), the remaining signals could not be determined; *m/z* calcd. for $C_{19}H_{22}N$ ($[M+H]^+$) 264.17468, found 264.17458.



(*E*)-1-Phenyl-2-styrylazepane (13)

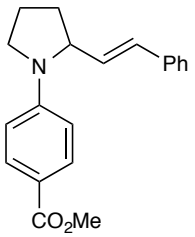
Prepared following the general procedure outlined above using (*E*)-(2-(phenylsulfonyl)vinyl)benzene (122 mg, 0.500 mmol, 1.00 equiv.), *N*-phenylazepane (219 mg, 2.50 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 0.010 equiv.), CsOAc (288 mg, 3.00 equiv.) and DCE (5.00 mL). After 16 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by removal of excess *N*-phenylazepane by heating to 100 °C under vaccum (~0.5 torr) followed by preparative TLC using 95:4:1 hexanes:acetone:Et_3N provided the title compound (136 mg, 98%, >98:2 *E*:*Z*) as a pale yellow oil. IR (film) ν_{max} 3080–2851, 1595, 1503, 1390 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.30–1.43 (2H, m, $NCH_2(CH_2)_3$), 1.61–1.68 (1H, m, $NCH_2(CH_2)_3$), 1.74–1.79 (2H, m, $NCH_2(CH_2)_3$), 1.85–1.90 (2H, m, $NCH_2(CH_2)_3$), 2.30 (1H, ddd, *J* = 14.7, 8.8, 5.6, $NCH_2(CH_2)_3$), 3.28–3.38 (1H, m, NCH_2), 3.63–3.67 (1H, m, NCH_2), 4.23–4.28 (1H, m, NCHCH=CHPh), 6.24 (1H, dd, *J* = 16.0, 4.0, CH=CHPh), 6.34 (1H, d, *J* = 16.2, CH=CHPh), 6.66 (1H, t, *J* = 7.2, ArH), 6.76 (2H, d, *J* = 8.3, ArH), 7.19–7.24 (3H, m, ArH), 7.29 (2H, t, *J* = 7.6, ArH), 7.36 (2H, d, *J* = 7.5, ArH); ^{13}C

NMR (126 MHz, $CDCl_3$) δ 25.7, 27.8, 29.9, 36.1, 44.2, 59.9, 111.1, 115.2, 126.3, 127.2, 128.3, 128.5, 129.2, 129.9, 137.1, 149.1; *m/z* calcd. for $C_{20}H_{24}N$ ($[M+H]^+$) 278.19033, found 278.19038.



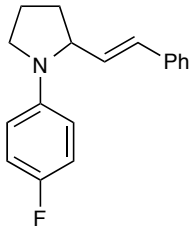
(*E*)-1-(4-Methoxyphenyl)-2-styrylpyrrolidine (14)

Prepared following the general procedure outlined above using (*E*)-(2-(phenylsulfonyl)vinyl)benzene (122 mg, 0.500 mmol, 1.00 equiv.), *N*-(4-methoxyphenyl)pyrrolidine (222 mg, 2.50 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 0.010 equiv.), CsOAc (288 mg, 3.00 equiv.) and DCE (5.00 mL). After 45 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by preparative TLC using 90:8:2 pentane:acetone:Et_3N provided the title compound (94 mg, 67%, >98:2 *E*:*Z*) as a colorless oil. IR (film) ν_{max} 3024–2830, 1511, 1364, 1239, 1179 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.91 (1H, ddt, *J* = 11.7, 5.8, 2.7, $NCH_2(CH_2)_2$), 1.95–2.11 (2H, m, $NCH_2(CH_2)_2$), 2.14–2.22 (1H, m, $NCH_2(CH_2)_2$), 3.24 (1H, td, *J* = 9.0, 6.7, NCH_2), 3.54–3.58 (1H, m, NCH_2), 3.75 (3H, s, OCH_3), 4.22–4.25 (1H, m, NCHCH=CHPh), 6.25 (1H, dd, *J* = 15.8, 5.5, CH=CHPh), 6.49 (1H, d, *J* = 15.9, CH=CHPh), 6.60–6.64 (2H, m, ArH), 6.82–6.85 (2H, m, ArH), 7.21 (1H, t, *J* = 7.3, ArH), 7.30 (2H, t, *J* = 7.6, ArH), 7.36 (2H, d, *J* = 7.3, ArH); ^{13}C NMR (126 MHz, $CDCl_3$) δ 23.6, 33.1, 49.4, 56.0, 61.3, 112.9, 114.8, 126.3, 127.2, 128.5, 129.3, 132.3, 137.1, 142.6, 150.8; *m/z* calcd. for $C_{19}H_{22}NO$ ($[M+H]^+$) 280.16959, found 280.16972.



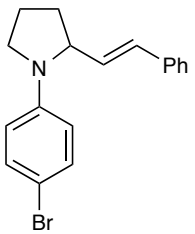
Methyl (*E*)-4-(2-styrylpyrrolidin-1-yl)benzoate (15)

Prepared following the general procedure outlined above using (*E*)-(2-(phenylsulfonyl)vinyl)benzene (122 mg, 0.500 mmol, 1.00 equiv.), methyl (4-pyrrolidin-1-yl)benzoate (257 mg, 2.50 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 0.010 equiv.), CsOAc (288 mg, 3.00 equiv.) and DCE (5.00 mL). After 13 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by preparative TLC using 80:16:4 pentane:acetone:Et_3N provided the title compound (116 mg, 75%, >98:2 *E*:*Z*) as a colorless oil. IR (film) ν_{max} 3082–2844, 1702, 1604, 1522, 1435, 1378, 1280, 1179, 1108 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.97 (1H, ddd, *J* = 11.7, 5.7, 2.8, $NCH_2(CH_2)_2$), 2.00–2.17 (2H, m, $NCH_2(CH_2)_2$), 2.18–2.25 (1H, m, $NCH_2(CH_2)_2$), 3.38 (1H, td, *J* = 9.3, 6.9, NCH_2), 3.61 (1H, ddd, *J* = 10.0, 7.7, 2.6, NCH_2), 3.85 (3H, s, OCH_3), 4.43–4.46 (1H, m, NCHCH=CHPh), 6.19 (1H, dd, *J* = 15.8, 5.3, CH=CHPh), 6.39 (1H, d, *J* = 15.9, CH=CHPh), 6.60–6.63 (2H, m, ArH), 7.20–7.24 (1H, m, ArH), 7.28–7.34 (4H, m, ArH), 7.87–7.90 (2H, m, ArH); ^{13}C NMR (126 MHz, $CDCl_3$) δ 23.2, 32.8, 48.6, 51.5, 60.6, 111.5, 116.9, 126.4, 127.5, 128.5, 129.9, 130.1, 131.2, 136.6, 150.5, 167.5; *m/z* calcd. for $C_{20}H_{22}NO_2$ ($[M+H]^+$) 308.16451, found 308.16451.



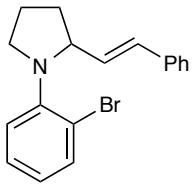
(*E*)-1-(4-Fluorophenyl)-2-styrylpyrrolidine (16)

Prepared following the general procedure outlined above using (*E*)-(2-(phenylsulfonyl)vinyl)benzene (122 mg, 0.500 mmol, 1.00 equiv.), *N*-(4-fluorophenyl)-pyrrolidine (207 mg, 2.50 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 0.010 equiv.), CsOAc (288 mg, 3.00 equiv.) and DCE (5.00 mL). After 13 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by removal of excess *N*-(4-fluorophenyl)-pyrrolidine by heating to 100 °C under vaccum (~0.5 torr) followed by preparative TLC using 95:4:1 hexanes:acetone:Et_3N provided the title compound (101 mg, 76%, >98:2 *E*:*Z*) as a colorless oil. IR (film) ν_{max} 3081–2839, 1515, 1365, 1223 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.90–1.94 (1H, m, $NCH_2(CH_2)_2$), 1.97–2.12 (2H, m, $NCH_2(CH_2)_2$), 2.15–2.23 (1H, m, $NCH_2(CH_2)_2$), 3.25 (1H, td, *J* = 9.0, 6.8, NCH_2), 3.54 (1H, ddd, *J* = 9.4, 7.7, 2.6, NCH_2), 4.24–4.27 (1H, m, NCHCH=CHPh), 6.22 (1H, dd, *J* = 15.8, 5.4, CH=CHPh), 6.45 (1H, d, *J* = 15.8, CH=CHPh), 6.54–6.58 (2H, m, Ar**H**), 6.89–6.94 (2H, m, Ar**H**), 7.20–7.23 (1H, m, Ar**H**), 7.30 (2H, t, *J* = 7.6, Ar**H**), 7.35–7.36 (2H, m, Ar**H**); ^{13}C NMR (126 MHz, $CDCl_3$) δ 23.5, 33.1, 49.3, 61.2, 112.6 (2C, d, *J* = 7.1), 115.4 (2C, d, *J* = 21.9), 126.3, 127.3, 128.5, 129.5, 131.6, 136.9, 144.2, 154.9 (1C, d, *J* = 233.7); ^{19}F NMR (282 MHz, $CDCl_3$) δ –130.6 (1F, m); *m*/*z* calcd. for $C_{18}H_{19}FN$ ($[M+H]^+$) 268.14960, found 268.14976.



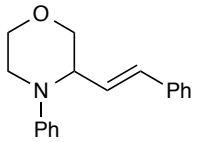
(*E*)-1-(4-Bromophenyl)-2-styrylpyrrolidine (17)

Prepared following the general procedure outlined above using (*E*)-(2-(phenylsulfonyl)vinyl)benzene (122 mg, 0.500 mmol, 1.00 equiv.), *N*-(4-bromophenyl)pyrrolidine (222 mg, 2.50 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 0.010 equiv.), CsOAc (288 mg, 3.00 equiv.) and DCE (5.00 mL). After 13 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by preparative TLC using 90:8:2 hexanes:acetone:Et_3N provided the title compound (123 mg, 75%, >98:2 *E*:*Z*) as a colorless oil. IR (film) ν_{max} 3058–2841, 1592, 1493, 1365, 1182 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.91–1.95 (1H, m, $NCH_2(CH_2)_2$) 1.98–2.12 (2H, m, $NCH_2(CH_2)_2$), 2.15–2.23 (1H, m, $NCH_2(CH_2)_2$), 3.26 (1H, td, *J* = 9.1, 6.8, NCH_2), 3.53 (1H, ddd, *J* = 10.1, 7.7, 2.6, NCH_2), 4.27–4.30 (1H, m, NCHCH=CHPh), 6.19 (1H, dd, *J* = 15.8, 5.3, CH=CHPh), 6.41 (1H, d, *J* = 15.9, CH=CHPh), 6.51 (2H, d, *J* = 8.9, Ar**H**), 7.21–7.24 (1H, m, Ar**H**), 7.25–7.31 (4H, m, Ar**H**), 7.34–7.35 (2H, m, Ar**H**); ^{13}C NMR (126 MHz, $CDCl_3$) δ 23.4, 33.0, 48.8, 60.8, 107.6, 113.8, 126.4, 127.4, 128.6, 129.7, 130.8, 131.6, 136.7, 146.3; *m*/*z* calcd. for $C_{18}H_{19}BrN$ ($[M+H]^+$) 328.06954, found 328.06974.



(*E*)-1-(2-Bromophenyl)-2-styrylpyrrolidine (18)

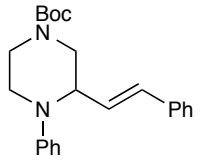
Prepared following the general procedure outlined above using (*E*)-(2-(phenylsulfonyl)vinyl)benzene (122 mg, 0.500 mmol, 1.00 equiv.), *N*-(2-bromophenyl)pyrrolidine (283 mg, 2.50 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 0.010 equiv.), CsOAc (288 mg, 3.00 equiv.) and DCE (5.00 mL). After 38 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by preparative TLC using 90:8:2 hexanes:acetone:Et_3N provided the title compound (106 mg, 65%, >98:2 *E*:*Z*) as a colorless oil. IR (film) ν_{max} 3058–2823, 1585, 1474, 1310, 1022 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.84–1.94 (2H, m, $NCH_2(C\mathbf{H}_2)_2$), 2.01–2.08 (1H, m, $NCH_2(C\mathbf{H}_2)_2$), 2.24–2.30 (1H, m, $NCH_2(C\mathbf{H}_2)_2$), 2.97 (1H, td, *J* = 9.2, 3.7, $NC\mathbf{H}_2$), 4.06–4.11 (1H, m, $NC\mathbf{H}_2$), 4.42 (1H, ddd, *J* = 7.5, 7.5, 7.5, N**C**HCH=CHPh), 6.03 (1H, dd, *J* = 15.9, 7.6, C**H**=CHPh), 6.53 (1H, d, *J* = 15.9, CH=C**H**Ph), 6.77 (1H, t, *J* = 7.5, Ar**H**), 7.01 (1H, d, *J* = 8.0, Ar**H**), 7.15–7.19 (2H, m, Ar**H**), 7.24–7.30 (4H, m, Ar**H**), 7.50 (1H, dd, *J* = 7.9, 1.5, Ar**H**); ^{13}C NMR (126 MHz, $CDCl_3$) δ 24.2, 33.5, 53.4, 62.4, 116.9, 120.5, 122.4, 126.3, 127.3, 127.5, 128.4, 131.0, 131.5, 134.1, 137.0, 147.9; *m*/*z* calcd. for $C_{18}H_{19}BrN$ ($[M+H]^+$) 328.06954, found 328.06947.



(*E*)-4-Phenyl-3-styrylmorpholine (19)

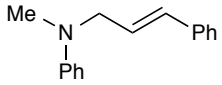
Prepared following the general procedure outlined above using (*E*)-(2-(phenylsulfonyl)vinyl)benzene (122 mg, 0.500 mmol, 1.00 equiv.), *N*-phenyl-morpholine (204 mg, 2.50 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 0.010 equiv.), CsOAc (288 mg, 3.00 equiv.) and DCE (5.00 mL). After 17 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by removal of excess *N*-phenyl-morpholine by heating to 100 °C under vaccum (~0.5 torr) followed by preparative TLC using 80:16:4 hexanes:acetone:Et_3N provided the title compound (105 mg, 79%, 94:6 *E*:*Z*) as a colorless oil. IR (film) ν_{max} 3059–2852, 1598, 1496, 1448, 1258, 1222, 1120 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ (*E*-isomer) 3.19 (1H, ddd, *J* = 12.3, 4.7, 3.3, $NC\mathbf{H}_2$), 3.37 (1H, ddd, *J* = 12.3, 8.6, 3.3, $NC\mathbf{H}_2$), 3.85 (1H, ddd, *J* = 11.5, 8.6, 3.3, $OC\mathbf{H}_2$), 3.93 (1H, dd, *J* = 11.3, 4.2, $OC\mathbf{H}_2$), 3.98 (1H, dd, *J* = 11.3, 3.3, $OC\mathbf{H}_2$), 4.00–4.04 (1H, m, $OC\mathbf{H}_2$), 4.21 (1H, dt, *J* = 7.4, 3.7, N**C**HCH=CH), 6.26 (1H, dd, *J* = 16.2, 7.4, C**H**=CHPh), 6.53 (1H, d, *J* = 16.2, CH=C**H**Ph), 6.88 (1H, t, *J* = 7.3, Ar**H**), 6.97 (2H, d, *J* = 7.9, Ar**H**), 7.18–7.21 (1H, m, Ar**H**), 7.24–7.31 (6H, m, Ar**H**); ^1H NMR (500 MHz, $CDCl_3$) δ (*Z*-isomer) 3.12 (1H, ddd, *J* = 12.4, 6.0, 3.2, $NC\mathbf{H}_2$), 3.29–3.33 (1H, m, $NC\mathbf{H}_2$), 4.43 (1H, dt, *J* = 9.5, 4.4, N**C**HCH=CH), 5.69 (1H, dd, *J* = 11.9, 9.5, C**H**=CHPh), 6.59 (1H, d, *J* = 11.9, CH=C**H**Ph), 6.68 (2H, d, *J* = 8.0, Ar**H**), the remaining signals could not be determined.^{13}C NMR (126 MHz, $CDCl_3$) δ (*E*-isomer) 46.8, 58.4, 67.3, 71.4, 117.8, 120.4, 126.2, 126.4, 127.6, 128.5, 129.1, 133.0, 136.7, 150.1; δ (*Z*-isomer) 48.4, 53.8, 67.4, 71.1,

118.7, 120.9, 127.3, 128.4, 128.6, 128.8, 132.3, the remaining signals could not be determined; HRMS (ESI-TOF) *m/z* calcd. for $C_{18}H_{20}NO$ ($[M+H]^+$) 266.15400, found 266.15394.



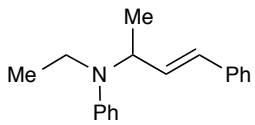
***tert*-Butyl-(*E*)-4-phenyl-3-styrylpiperazine-1-carboxylate (20)**

Prepared following the general procedure outlined above using (*E*)-(2-(phenylsulfonyl)vinyl)benzene (122 mg, 0.500 mmol, 1.00 equiv.), *tert*-butyl-(*E*)-4-phenyl-3-styrylpiperazine-1-carboxylate (328 mg, 2.50 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 0.010 equiv.), CsOAc (288 mg, 3.00 equiv.) and DCE (5.00 mL). After 15 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by preparative TLC using 90:8:2 toluene:acetone:Et_3N provided the title compound (135 mg, 74%, 94:6 *E*:*Z*) as a colorless oil. IR (film) ν_{max} 3059–2861, 1691, 1598, 1500, 1424, 1365, 1246, 1167, 1122 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ (*E*-isomer) 1.47 (9H, s, $OC(C\mathbf{H}_3)_3$), 3.24–3.47 (3H, br m, 2 x $N(Ph)C\mathbf{H}_2$ + 1 x $N(Boc)C\mathbf{H}_2$), 3.55 (1H, dd, *J* = 13.1, 3.7, $N(Boc)C\mathbf{H}_2$), 3.71–4.06 (2H, br m, $N(Boc)C\mathbf{H}_2$), 4.32 (1H, br s, NC**H**CH=CHPh), 6.12–6.18 (1H, m, C**H**=CHPh), 6.54 (d, *J* = 15.4, CH=C**H**Ph), 6.86 (1H, t, *J* = 7.3, Ar**H**), 6.93 (2H, d, *J* = 8.1, Ar**H**), 7.18–7.30 (2H, m, Ar**H**); ^1H NMR (500 MHz, $CDCl_3$) δ (*Z*-isomer) 5.58–5.67 (1H, m, C**H**=CHPh), the remaining signals could not be determined; ^{13}C NMR (126 MHz, $CDCl_3$) δ (*E*-isomer – mixture of rotamers) 28.5, 42.9, 44.0, 44.9, 45.0, 46.4, 48.2, 58.2, 58.5, 79.9, 117.0, 119.8, 126.3, 126.9, 127.1, 127.5, 128.5, 129.2, 132.5, 136.8, 150.0, 154.9; *m/z* calcd. for $C_{23}H_{29}N_2O_2$ ($[M+H]^+$) 365.22235, found 365.22204.



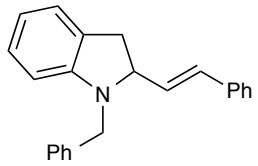
***N*-Cinnamyl-*N*-methylaniline (21)**

Prepared following the general procedure outlined above using (*E*)-(2-(phenylsulfonyl)vinyl)benzene (122 mg, 0.500 mmol, 1.00 equiv.), *N*,*N*-dimethylaniline (158 μL, 2.50 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 0.010 equiv.), CsOAc (288 mg, 3.00 equiv.) and DCE (5.00 mL). After 18 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by removal of excess *N*,*N*-dimethylaniline under vaccum (~0.5 torr) followed by preparative TLC using 90:8:2 hexanes:acetone:Et_3N provided the title compound (82 mg, 73%, >98:2 *E*:*Z*) as a colorless oil. IR (film) ν_{max} 3059–2819, 1598, 1505, 1448, 1354, 1206, 1118 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.00 (3H, s, $NC\mathbf{H_3}$), 4.11 (2H, dd, *J* = 5.4, 1.8, $NC\mathbf{H_2}$), 6.27 (1H, dt, *J* = 15.9, 5.4, C**H**=CHPh), 6.54 (1H, d, *J* = 15.9, CH=C**H**Ph), 6.75 (1H, t, *J* = 7.4, Ar**H**), 6.81 (2H, d, *J* = 8.1, Ar**H**), 7.22–7.27 (3H, m, Ar**H**), 7.32 (2H, t, *J* = 7.6, Ar**H**), 7.38 (2H, d, *J* = 7.2, Ar**H**); ^{13}C NMR (126 MHz, $CDCl_3$) δ 38.1, 54.9, 76.8, 77.1, 77.3, 112.6, 116.6, 125.7, 126.3, 127.4, 128.6, 129.2, 131.2, 136.9, 149.5; HRMS (ESI-TOF) *m/z* calcd. for $C_{16}H_{18}N$ ($[M+H]^+$) 224. 14338, found 224.14317.



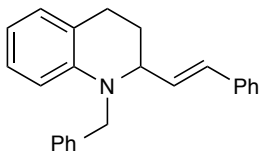
(*E*)-*N*-Ethyl-*N*-(4-phenylbut-3-en-2-yl)aniline (22)

Prepared following the general procedure outlined above using (*E*)-(2-(phenylsulfonyl)vinyl)benzene (122 mg, 0.500 mmol, 1.00 equiv.), *N*,*N*-diethylaniline (199 μL, 2.50 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 0.010 equiv.), CsOAc (288 mg, 3.00 equiv.) and DCE (5.00 mL). After 61 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by removal of excess *N*,*N*-diethylaniline by heating to 100 °C under vaccum (~0.5 torr) followed by preparative TLC using 95:4:1 pentane:acetone:Et_3N provided the title compound (100 mg, 80%, >98:2 *E*:*Z*) as a colorless oil. IR (film) ν_{max} 3083–2871, 1596, 1501, 1386, 1375, 1350, 1268, 1187 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.20 (3H, t, *J* = 7.0, NCH_2CH_3), 1.43 (3H, d, *J* = 6.8, $NCHCH_3$), 3.32 (2H, q, *J* = 7.0, NCH_2CH_3), 4.49–4.72 (1H, m, NCHCH=CH), 6.34 (1H, dd, *J* = 16.3, 4.6, CH=CHPh), 6.49 (1H, dd, *J* = 16.3, 1.9, CH=CHPh), 6.73 (1H, t, *J* = 7.2, ArH), 6.84 (2H, d, *J* = 8.2, ArH), 7.16–7.28 (3H, m, ArH), 7.33 (2H, t, *J* = 7.6, ArH), 7.39 (2H, d, *J* = 7.4, ArH); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.9, 17.3, 39.9, 54.6, 113.5, 116.4, 126.3, 127.4, 128.6, 129.2, 129.8, 131.7, 137.1, 148.3; HRMS (ESI-TOF) *m*/*z* calcd. for $C_{18}H_{22}N$ ($[M+H]^+$) 252.17468, found 252.17432.



(*E*)-1-Benzyl-2-styrylindoline (23)

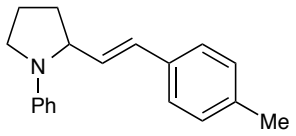
Prepared following the general procedure outlined above using (*E*)-(2-(phenylsulfonyl)vinyl)benzene (122 mg, 0.500 mmol, 1.00 equiv.), *N*-benzylindoline (262 mg, 2.50 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 0.010 equiv.), CsOAc (288 mg, 3.00 equiv.) and DCE (5.00 mL). After 60 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by preparative TLC using 1:1 hexanes:toluene provided the title compound (100 mg, 64%, >98:2 *E*:*Z*) as a colorless oil. IR (film) ν_{max} 3056–2844, 1605, 1493, 1482, 1461, 1452, 1352, 1268, 1248 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.96 (1H, dd, *J* = 15.6, 9.4, $NCHCH_2Ar$), 3.27 (1H, dd, *J* = 15.6, 8.7, $NCHCH_2Ar$), 4.16 (1H, d, *J* = 15.8, NCH_2Ph), 4.28 (1H, q, *J* = 8.9, NCHCH=CHPh), 4.46 (1H, d, *J* = 15.8, NCH_2Ph), 6.31 (1H, dd, *J* = 15.8, 8.6, CH=CHPh), 6.39 (1H, d, *J* = 7.8, ArH), 6.55 (1H, d, *J* = 15.8, CH=CHPh), 6.68 (1H, t, *J* = 7.3, ArH), 7.03 (1H, t, *J* = 7.6, ArH), 7.10 (1H, d, *J* = 7.1, ArH), 7.22–7.40 (10H, m, ArH); ^{13}C NMR (126 MHz, $CDCl_3$) δ 36.4, 50.6, 68.2, 107.3, 117.7, 124.2, 126.5, 126.9, 127.5, 127.6, 127.8, 128.5, 128.6, 128.7, 130.4, 132.9, 136.5, 138.8, 152.0; *m*/*z* calcd. for $C_{23}H_{22}N$ ($[M+H]^+$) 312.17468, found 312.17439.



(*E*)-1-Benzyl-2-styryl-1,2,3,4-tetrahydroquinoline (24)

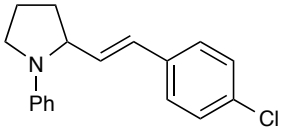
Prepared following the general procedure outlined above using (*E*)-(2-(phenylsulfonyl)vinyl)benzene (122 mg, 0.500 mmol, 1.00 equiv.), 1-benzyl-1,2,3,4-tetrahydroquinoline (279 mg, 2.50 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 0.010 equiv.), CsOAc (288 mg, 3.00 equiv.) and DCE (5.00 mL). After 37 h, the reaction mixture was

subjected to the workup protocol outlined in the general procedure. Purification by preparative TLC using 95:4:1 pentane:acetone:Et_3N provided the title compound (136 mg, 84%, >98:2 *E*:*Z*) as a colorless oil. IR (film) ν_{max} 3061–2855, 1601, 1496, 1464, 1450, 1349, 1244, 1207, 1173 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.05–2.11 (1H, m, $NCHCH_2C\mathbf{H}_2Ar$), 2.19 (1H, tt, *J* = 12.3, 4.7, $NCHCH_2C\mathbf{H}_2Ar$), 2.77 (1H, dt, *J* = 15.9, 4.3, $NCHC\mathbf{H}_2CH_2Ar$), 2.95 (1H, ddd, *J* = 16.4, 12.0, 4.7, $NCHC\mathbf{H}_2CH_2Ar$), 4.17 (1H, ddd, *J* = 6.9, 4.8, 3.4, $NC\mathbf{H}CH{=}CHPh$), 4.46 (1H, d, *J* = 17.5, $NC\mathbf{H}_2Ph$), 4.70 (1H, d, *J* = 17.4, $NC\mathbf{H}_2Ph$), 6.26 (1H, dd, *J* = 15.8, 6.9, $C\mathbf{H}{=}CHPh$), 6.45 (1H, d, *J* = 15.8, $CH{=}C\mathbf{H}Ph$), 6.52 (1H, d, *J* = 8.2, Ar**H**), 6.63 (1H, td, *J* = 7.4, 1.2, Ar**H**), 7.00–7.05 (2H, m, Ar**H**), 7.20–7.38 (10H, m, Ar**H**); ^{13}C NMR (126 MHz, $CDCl_3$) δ 24.4, 27.5, 52.6, 59.8, 111.0, 115.8, 122.0, 126.3, 126.4, 126.7, 127.3, 127.5, 128.6, 128.6, 128.8, 130.4, 131.0, 136.7, 138.9, 144.6; *m*/*z* calcd. for $C_{24}H_{24}N$ ($[M+H]^+$) 326.19033, found 326.19040.



(*E*)-2-(4-Methylstyryl)-1-phenylpyrrolidine (25)

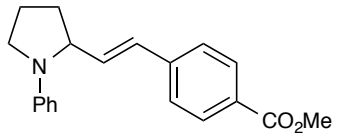
Prepared following the general procedure outlined above using (*E*)-1-methyl-4-(2-(phenylsulfonyl)vinyl)benzene (129 mg, 0.500 mmol, 1.00 equiv.), *N*-phenylpyrrolidine (181 μL, 2.50 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 0.010 equiv.), CsOAc (288 mg, 3.00 equiv.) and DCE (5.00 mL). After 22 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by removal of excess *N*-phenyl-pyrrolidine by heating to 100 °C under vaccum (~0.5 torr) followed by preparative TLC using 95:4:1 hexanes:acetone:Et_3N provided the title compound (105 mg, 80%, >98:2 *E*:*Z*) as a colorless oil. IR (film) ν_{max} 3088–2868, 1596, 1503, 1479, 1360, 1342, 1178, 1155 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.88–1.95 (1H, m, $NCH_2(C\mathbf{H}_2)_2$), 1.96–2.21 (3H, m, $NCH_2(C\mathbf{H}_2)_2$), 2.33 (3H, s, $ArC\mathbf{H}_3$), 3.29 (1H, td, *J* = 9.0, 6.6, $NC\mathbf{H}_2$), 3.56 (1H, td, *J* = 8.2, 7.4, 2.4, $NC\mathbf{H}_2$), 4.31 (1H, t, *J* = 6.5, $NC\mathbf{H}CH{=}CH$), 6.18 (1H, dd, *J* = 15.9, 5.4, $C\mathbf{H}{=}CHAr$), 6.43 (1H, d, *J* = 15.9, $CH{=}C\mathbf{H}Ar$), 6.65–6.68 (3H, m, Ar**H**), 7.10 (2H, d, *J* = 7.8, Ar**H**), 7.21 (2H, t, *J* = 7.9, Ar**H**), 7.25 (2H, d, *J* = 8.0, Ar**H**); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.2, 23.4, 33.1, 48.7, 60.8, 112.2, 115.6, 126.2, 129.0, 129.2, 129.2, 130.6, 134.2, 137.0, 147.6; HRMS (ESI-TOF) *m*/*z* calcd. for $C_{19}H_{22}N$ ($[M+H]^+$) 264.17468, found 264.17496.



(*E*)-2-(4-Chlorostyryl)-1-phenylpyrrolidine (26)

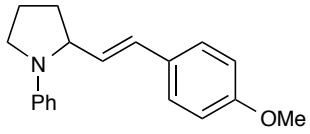
Prepared following the general procedure outlined above using (*E*)-1-chloro-4-(2-(phenylsulfonyl)vinyl)benzene (139 mg, 0.500 mmol, 1.00 equiv.), *N*-phenylpyrrolidine (181 μL, 2.50 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 0.010 equiv.), CsOAc (288 mg, 3.00 equiv.) and DCE (5.00 mL). After 19 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by removal of excess *N*-phenyl-pyrrolidine by heating to 100 °C under vaccum (~0.5 torr) followed by preparative TLC using 95:4:1 hexanes:acetone:Et_3N provided the title compound (113 mg, 80%, >98:2 *E*:*Z*) as a colorless oil. IR (film) ν_{max} 3088-2834, 1596, 1503, 1489, 1361, 1342, 1179, 1090 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.95–1.88 (1H, m, $NCH_2(C\mathbf{H}_2)_2$), 2.12–1.97 (2H, m, $NCH_2(C\mathbf{H}_2)_2$), 2.23–2.13 (1H, m,

$NCH_2(CH_2)_2$), 3.30 (1H, td, *J* = 9.1, 6.7, NCH_2), 3.57 (1H, ddd, *J* = 9.6, 7.5, 2.6, NCH_2), 4.30–4.33 (1H, m, NCHCH=CH), 6.21 (1H, dd, *J* = 15.8, 5.2, CH=CHAr), 6.41 (1H, dd, *J* = 15.8, 1.4, CH=CHAr), 6.64 (2H, d, *J* = 7.7, ArH), 6.69 (1H, t, *J* = 7.3, ArH), 7.31–7.17 (6H, m, ArH); ^{13}C NMR (126 MHz, $CDCl_3$) δ 23.4, 32.9, 48.8, 60.6, 112.2, 115.8, 127.6, 128.2, 128.6, 129.1, 132.3, 132.8, 135.5, 147.5; HRMS (ESI-TOF) *m/z* calcd. for $C_{18}H_{19}ClN$ ($[M+H]^+$) 284.12005, found 284.11993.



Methyl (*E*)-4-(2-(1-phenylpyrrolidin-2-yl)vinyl)benzoate (27)

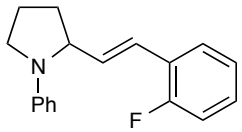
Prepared following the general procedure outlined above using methyl (*E*)-methyl 4-(2-(phenylsulfonyl)vinyl)benzoate (151 mg, 0.500 mmol, 1.00 equiv.), *N*-phenylpyrrolidine (181 µL, 2.50 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 0.010 equiv.), CsOAc (288 mg, 3.00 equiv.) and DCE (5.00 mL). After 12 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by removal of excess *N*-phenyl-pyrrolidine by heating to 100 °C under vaccum (~0.5 torr) followed by preparative TLC using 95:4:1 hexanes:acetone:Et_3N provided the title compound (113 mg, 74%, 93:7 *E*:*Z*) as a colorless oil. IR (film) ν_{max} 3089–2841, 1716, 1598, 1504, 1434, 1363, 1344, 1276, 1178, 1107 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ (*E*-isomer) 2.25–1.87 (4H, m, $NCH_2(CH_2)_2$), 3.31 (1H, td, *J* = 9.2, 6.7, NCH_2), 3.53–3.63 (1H, m, NCH_2), 3.91 (3H, s, CO_2CH_3), 4.32–4.39 (1H, m, NCHCH=CH), 6.37 (1H, dd, *J* = 15.9, 5.1, CH=CHAr), 6.50 (1H, d, *J* = 15.9, CH=CHAr), 6.65 (2H, d, *J* = 8.1, ArH), 6.69 (1H, t, *J* = 7.3, ArH), 7.19–7.27 (2H, m, ArH), 7.40 (2H, d, *J* = 8.4, ArH), 7.96 (2H, d, *J* = 8.4, ArH); ^{1}H NMR (500 MHz, $CDCl_3$) δ (*Z*-isomer) 3.95 (3H, s, CO_2CH_3), 4.61–4.54 (1H, m, NCHCH=CH), 5.77 (1H, dd, *J* = 11.8, 9.2, NCHCH=CH), 6.56 (1H, d, *J* = 11.8, NCHCH=CH), 7.10 (2H, t, *J* = 7.9, ArH), 8.08 (2H, d, *J* = 8.3, ArH), the remaining signals could not be determined; ^{13}C NMR (126 MHz, $CDCl_3$) δ (*E*-isomer) 23.4, 32.8, 48.8, 52.1, 60.7, 112.2, 115.9, 126.3, 128.6, 128.6, 129.1, 129.9, 134.5, 141.5, 147.4, 167.0; ^{13}C NMR (126 MHz, $CDCl_3$) δ (*Z*-isomer) 24.4, 33.7, 48.7, 52.2, 56.4, 128.9, 129.0, 129.7, 138.3, the remaining signals could not be determined; HRMS (ESI-TOF) *m/z* calcd. for $C_{20}H_{22}NO_2$ ($[M+H]^+$) 308.16451, found 308.16463.



(*E*)-2-(4-Methoxystyryl)-1-phenylpyrrolidine (28)

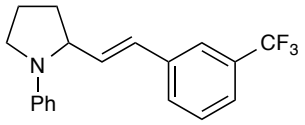
Prepared following the general procedure outlined above using (*E*)-1-methoxy-4-(2-(phenylsulfonyl)vinyl)benzene (137 mg, 0.500 mmol, 1.00 equiv.), *N*-phenylpyrrolidine (181 µL, 2.50 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 0.010 equiv.), CsOAc (288 mg, 3.00 equiv.) and DCE (5.00 mL). After 15 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by removal of excess *N*-phenyl-pyrrolidine by heating to 100 °C under vaccum (~0.5 torr) followed by preparative TLC using 90:8:2 hexanes:acetone:Et_3N provided the title compound (109 mg, 78%, 97:3 *E*:*Z*) as a colorless oil. IR (film) ν_{max} 3089–2834, 1597, 1504, 1362, 1343, 1246, 1174 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ (*E*-isomer) 1.91 (1H, ddd, *J* = 11.5, 6.0, 2.9, $NCH_2(CH_2)_2$), 1.94–2.22 (3H, m, $NCH_2(CH_2)_2$),

3.29 (1H, td, *J* = 9.0, 6.7, NC**H**$_2$), 3.56 (1H, ddd, *J* = 9.5, 7.5, 2.4, NC**H**$_2$), 3.80 (3H, s, OC**H**$_3$), 4.29–4.32 (1H, m, NC**H**CH=CHAr), 6.09 (1H, dd, *J* = 15.8, 5.4, C**H**=CHAr), 6.41 (1H, d, *J* = 15.8, CH=C**H**Ar), 6.65–6.68 (3H, m, Ar**H**), 6.82–6.85 (2H, m, Ar**H**), 7.20–7.23 (2H, m, Ar**H**), 7.28–7.30 (2H, m, Ar**H**); ^{1}H NMR (500 MHz, $CDCl_3$) δ (*Z*-isomer) 3.86 (3H, s, OC**H**$_3$), 4.59–4.63 (1H, m, NC**H**CH=CHAr), 5.57 (1H, dd, *J* = 11.7, 9.2, C**H**=CHAr), 6.47 (1H, d, *J* = 11.8, CH=C**H**Ar), 6.95 (2H, d, *J* = 8.7, Ar**H**), 7.11 (2H, dd, *J* = 8.7, 7.2, Ar**H**), the remaining signals could not be determined; ^{13}C NMR (126 MHz, $CDCl_3$) δ (*E*-isomer) 23.4, 33.1, 48.7, 55.3, 60.8, 112.2, 113.9, 115.6, 127.5, 128.8, 129.0, 129.4, 129.8, 147.6, 158.9; ^{13}C NMR (126 MHz, $CDCl_3$) δ (*Z*-isomer) 24.4, 33.8, 48.6, 56.4, 113.7, 128.9, 130.2, 134.5, the remaining signals could not be determined; HRMS (ESI-TOF) *m/z* calcd. for $C_{19}H_{22}NO$ ($[M+H]^+$) 280.16959, found 280.16946.



(*E*)-2-(2-Fluorostyryl)-1-phenylpyrrolidine (29)

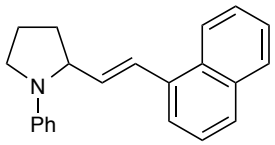
Prepared following the general procedure outlined above using (*E*)-1-fluoro-2-(2-(phenylsulfonyl)vinyl)benzene (131 mg, 0.500 mmol, 1.00 equiv.), *N*-phenylpyrrolidine (181 µL, 2.50 equiv.), Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (5.6 mg, 0.010 equiv.), CsOAc (288 mg, 3.00 equiv.) and DCE (5.00 mL). After 13 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by removal of excess *N*-phenyl-pyrrolidine by heating to 100 °C under vaccum (~0.5 torr) followed by preparative TLC using 95:4:1 hexanes:acetone:Et_3N provided the title compound (109 mg, 82%, >98:2 *E*:*Z*) as a colorless oil. IR (film) ν_{max} 3088–2839, 1597, 1504, 1486, 1455, 1363, 1343, 1228 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.90–2.25 (4H, m, $NCH_2(CH_2)_2$), 3.30 (1H, td, *J* = 9.0, 6.8, NC**H**$_2$), 3.59 (1H, td, *J* = 8.2, 7.6, 2.5, NC**H**$_2$), 4.33–4.36 (1H, m, NC**H**CH=CHAr), 6.33 (1H, dd, *J* = 16.0, 5.6, C**H**=CHAr), 6.63 (1H, d, *J* = 16.3, CH=C**H**Ar), 6.66–6.70 (3H, m, Ar**H**), 7.02 (1H, ddd, *J* = 11.1, 8.1, 1.3, Ar**H**), 7.07 (1H, t, *J* = 7.5, Ar**H**), 7.14–7.26 (3H, m, Ar**H**), 7.41 (1H, td, *J* = 7.7, 1.7, Ar**H**); ^{13}C NMR (126 MHz, $CDCl_3$) δ 23.4, 33.0, 48.8, 61.0, 112.2, 115.6, 115.8, 122.1 (1C, d, *J* = 3.2), 124.0 (1C, d, *J* = 3.5), 124.8 (1C, d, *J* = 12.2), 127.6 (1C, d, *J* = 3.9), 128.4 (1C, d, *J* = 8.4), 129.0, 134.6 (1C, d, *J* = 4.9), 147.5, 160.1 (1C, d, *J* = 249.0); ^{19}F NMR (282 MHz, $CDCl_3$) δ –117.8 (1F, m); HRMS (ESI-TOF) *m/z* calcd. for $C_{18}H_{19}FN$ ($[M+H]^+$) 268.14960, found 268.14949.



(*E*)-1-Phenyl-2-(3-(trifluoromethyl)styryl)pyrrolidine (30)

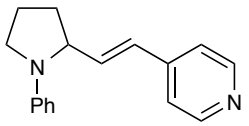
Prepared following the general procedure outlined above using (*E*)-1-(2-(phenylsulfonyl)vinyl)-3-(trifluoromethyl)benzene (156 mg, 0.500 mmol, 1.00 equiv.), *N*-phenylpyrrolidine (181 µL, 2.50 equiv.), Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (5.6 mg, 0.010 equiv.), CsOAc (288 mg, 3.00 equiv.) and DCE (5.00 mL). After 13 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by removal of excess *N*-phenyl-pyrrolidine by heating to 100 °C under vaccum (~0.5 torr) followed by preparative TLC using 95:4:1 hexanes:acetone:Et_3N provided the title compound (135 mg, 85%, >98:2 *E*:*Z*) as a pale yellow

oil. IR (film) ν_{max} 3059–2841, 1598, 1504, 1364, 1329, 1176, 1162, 1122, 1072 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.94 (1H, ddd, *J* = 11.8, 5.7, 2.7, $NCH_2(CH_2)_2$), 1.99–2.12 (2H, m, 1H, $NCH_2(CH_2)_2$), 2.19 (1H, tdd, *J* = 11.3, 8.4, 7.0, $NCH_2(CH_2)_2$), 3.31 (1H, td, *J* = 9.1, 6.8, NCH_2), 3.59 (1H, ddd, *J* = 9.5, 7.4, 2.6, NCH_2), 4.33–4.36 (1H, m, NCHCH=CHAr), 6.33 (1H, dd, *J* = 15.8, 5.1, CH=CHAr), 6.49 (1H, dd, *J* = 15.8, 1.4, CH=CHAr), 6.65 (2H, d, *J* = 7.9, ArH), 6.70 (1H, t, *J* = 7.3, ArH), 7.21–7.25 (2H, m, ArH), 7.40 (1H, t, *J* = 7.7, ArH), 7.46 (1H, d, *J* = 7.7, ArH), 7.51 (1H, d, *J* = 7.7, ArH), 7.60 (1H, s, ArH); ^{13}C NMR (126 MHz, $CDCl_3$) δ 23.4, 32.8, 48.8, 60.6, 112.1, 115.9, 123.0 (1C, q, *J* = 3.9), 123.8 (1C, q, *J* = 3.8), 124.1 (1C, q, *J* = 272.2), 128.2, 128.9, 129.1, 129.6, 130.8 (1C, q, *J* = 32.0), 133.5, 137.7, 147.4; ^{19}F NMR (282 MHz, $CDCl_3$) δ –62.8(1F, s); HRMS (ESI-TOF) *m/z* calcd. for $C_{19}H_{19}F_3N$ ($[M+H]^+$) 318.14641, found 318.14615.



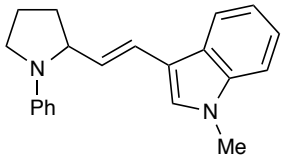
(*E*)-2-(2-(Naphthalen-1-yl)vinyl)-1-phenylpyrrolidine (31)

Prepared following the general procedure outlined above using (*E*)-1-(2-(phenylsulfonyl)vinyl)naphthalene (147 mg, 0.500 mmol, 1.00 equiv.), *N*-phenylpyrrolidine (181 µL, 2.50 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 0.010 equiv.), CsOAc (288 mg, 3.00 equiv.) and DCE (5.00 mL). After 12 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by removal of excess *N*-phenylpyrrolidine by heating to 100 °C under vaccum (~0.5 torr) followed by preparative TLC using 95:4:1 hexanes:acetone:Et_3N provided the title compound (116 mg, 77%, 92:8 *E*:*Z*) as a colorless oil. IR (film) ν_{max} 3058–2838, 1597, 1504, 1361, 1343 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ (*E*-isomer) 1.99–2.29 (4H, m, $NCH_2(CH_2)_2$), 3.37 (1H, td, *J* = 9.1, 6.6, NCH_2), 3.64 (1H, ddd, *J* = 9.6, 7.6, 2.4, NCH_2), 4.44–4.46 (1H, m, NCHCH=CHAr), 6.23 (1H, dd, *J* = 15.5, 5.2, CH=CHAr), 6.71 (1H, t, *J* = 7.3, ArH), 6.75 (2H, d, *J* = 8.3, ArH), 7.21 (1H, d, *J* = 15.6, CH=CHAr), 7.24–7.28 (2H, m, ArH), 7.41–7.48 (3H, m, ArH), 7.57 (1H, d, *J* = 7.1, ArH), 7.76 (1H, d, *J* = 8.2, ArH), 7.82–7.84 (1H, m, ArH), 7.96–7.98 (1H, m, ArH); ^1H NMR (500 MHz, $CDCl_3$) δ (*Z*-isomer) 3.25 (1H, dt, *J* = 9.0, 7.2, NCH_2), 3.54 (1H, td, *J* = 8.1, 4.4, NCH_2), 4.40–4.45 (1H, m, NCHCH=CHAr), 5.88 (1H, dd, *J* = 11.4, 9.5, CH=CHAr), 6.32 (2H, d, *J* = 8.1, ArH), 6.53 (1H, t, *J* = 7.3, ArH), 6.92 (2H, dd, *J* = 8.7, 7.2, ArH), 7.06 (1H, d, *J* = 11.6, CH=CHAr), 7.37 (1H, d, *J* = 6.9, ArH), 7.91–7.93 (1H, m, ArH), 8.09–8.11 (1H, m, ArH), the remaining signals could not be determined; ^{13}C NMR (126 MHz, $CDCl_3$) δ (*E*-isomer) 23.4, 33.0, 48.8, 60.9, 112.3, 115.8, 123.7, 124.0, 125.6, 125.7, 125.9, 127.1, 127.6, 128.4, 129.1, 131.1, 133.6, 134.7, 135.0, 147.5; ^{13}C NMR (126 MHz, $CDCl_3$) δ (*Z*-isomer) 24.3, 33.8, 48.6, 56.3, 112.4, 115.5, 125.1, 126.0, 126.1, 127.9, 128.0, 128.7, 136.6, the remaining signals could not be determined; HRMS (ESI-TOF) *m/z* calcd. for $C_{22}H_{22}N$ ($[M+H]^+$) 300.17468, found 300.17508.



(*E*)-4-(2-(1-Phenylpyrrolidin-2-yl)vinyl)pyridine (32)

Prepared following the general procedure outlined above using (*E*)-4-(2-(phenylsulfonyl)vinyl)pyridine (123 mg, 0.500 mmol, 1.00 equiv.), *N*-phenylpyrrolidine (181 µL, 2.50 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 0.010 equiv.), CsOAc (288 mg, 3.00 equiv.) and DCE (5.00 mL). After 21 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by flash column chromatography using 60:36:4 hexanes:acetone:Et_3N provided the title compound (98 mg, 78%, >98:2 *E*:*Z*) as a pale yellow oil. IR (film) ν_{max} 3059–2838, 1596, 1504, 1364, 1343 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.92–1.96 (1H , m, $NCH_2(CH_2)_2$), 2.01–2.08 (2H , m, $NCH_2(CH_2)_2$), 2.20 (1H , ddt, *J* = 11.8, 10.2, 8.3, $NCH_2(CH_2)_2$), 3.31 (1H, td, *J* = 8.9, 7.2, NCH_2), 3.57–3.61 (1H, m, NCH_2), 4.34–4.37 (1H, m, NCHCH=CHAr), 6.40 (1H, d, *J* = 16.2, CH=CHAr), 6.49 (1H, dd, *J* = 15.8, 4.8, CH=CHAr), 6.63 (2H, d, *J* = 7.6, ArH), 6.71 (1H, t, *J* = 7.3, ArH), 7.21–7.25 (4H, m, ArH), 8.51 (2H, d, *J* = 6.0, ArH); ^{13}C NMR (126 MHz, $CDCl_3$) δ 23.4, 32.6, 48.8, 60.5, 112.2, 116.1, 121.0, 127.3, 129.1, 136.7, 144.3, 147.3, 150.0; HRMS (ESI-TOF) *m*/*z* calcd. for $C_{17}H_{19}N_2$ ($[M+H]^+$) 251.15428, found 251.15433.



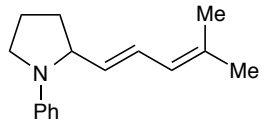
(*E*)-1-Methyl-3-(2-(1-phenylpyrrolidin-2-yl)vinyl)-1H-indole (33)

Prepared following the general procedure outlined above using (*E*)-1-methyl-3-(2-(phenylsulfonyl)vinyl)-1*H*-indole (149 mg, 0.500 mmol, 1.00 equiv.), *N*-phenylpyrrolidine (181 µL, 2.50 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 0.010 equiv.), CsOAc (288 mg, 3.00 equiv.) and DCE (5.00 mL). After 18 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by removal of excess *N*-phenylpyrrolidine by heating to 100 °C under vaccum (~0.5 torr) followed by flash column chromatography (5-25% EtOAc/hexanes) provided the title compound (103 mg, 68%, >98:2 *E*:*Z*) as a white solid (N.B. The crude reaction mixture showed an *E*:*Z* ratio of 82:18. Isomerization to >98:2 *E*:*Z* occurred during purification). IR (film) ν_{max} 3051–2869, 1598, 1505, 1475, 1361, 1344, 1332 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.92–2.04 (2H, m, $NCH_2(CH_2)_2$), 2.05–2.24 (2H, m, $NCH_2(CH_2)_2$), 3.30 (1H, td, *J* = 9.1, 6.5, NCH_2), 3.58 (1H, ddd, *J* = 9.6, 7.5, 2.3, NCH_2), 3.74 (3H, s, NCH_3), 4.33–4.36 (1H, m, NCHCH=CHAr), 6.19 (1H, dd, *J* = 16.0, 5.4, CH=CHAr), 6.61 (1H, dd, *J* = 16.0, 1.4, CH=CHAr), 6.66 (1H, t, *J* = 7.3, ArH), 6.71 (2H, d, *J* = 8.1, ArH), 7.04 (1H, s, ArH), 7.12–7.20 (1H, m, ArH), 7.17–7.28 (3H, m, ArH), 7.30 (1H, d, *J* = 8.2, ArH), 7.84 (1H, d, *J* = 8.0, ArH); ^{13}C NMR (126 MHz, $CDCl_3$) δ 23.4, 32.8, 33.5, 48.8, 61.3, 109.4, 112.2, 113.2, 115.4, 119.7, 120.3, 121.9, 122.0, 126.0, 127.5, 128.1, 129.0, 137.5, 147.8; HRMS (ESI-TOF) *m*/*z* calcd. for $C_{21}H_{23}N_2$ ($[M+H]^+$) 303.18558, found 303.18522.

(*E*)-2-(2-(Furan-2-yl)vinyl)-1-phenylpyrrolidine (34)

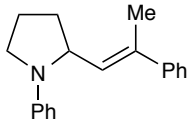
Prepared following the general procedure outlined above using (*E*)-2-(2-(phenylsulfonyl)vinyl)furan (117 mg, 0.500 mmol, 1.00 equiv.), *N*-phenylpyrrolidine (181 µL, 2.50 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 0.010 equiv.), CsOAc (288 mg, 3.00 equiv.) and DCE (5.00 mL). After 13 h, the reaction mixture was subjected to the workup protocol

outlined in the general procedure. Purification by removal of excess *N*-phenyl-pyrrolidine by heating to 100 °C under vaccum (~0.5 torr) followed by preparative TLC using 90:8:2 hexanes:acetone:Et_3N provided the title compound (99 mg, 83%, 93:7 *E*:*Z*) as a colorless oil. IR (film) ν_{max} 3027–2836, 1598, 1504, 1363, 1344 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ (*E*-isomer) 1.90–2.18 (4H, m, $NCH_2(CH_2)_2$), 3.28 (1H, td, *J* = 9.2, 6.6, NCH_2), 3.55 (1H, ddd, *J* = 9.3, 7.4, 2.2, NCH_2), 4.31 (1H, ddd, *J* = 7.9, 3.9, 1.6, NCHCH=CHAr), 6.14 (1H, d, *J* = 3.2, FurylH), 6.19 (1H, dd, *J* = 15.7, 4.5, CH=CHAr), 6.26 (1H, dd, *J* = 15.6, 1.3, CH=CHAr), 6.35 (1H, dd, *J* = 3.3, 1.9, FurylH), 6.63 (2H, d, *J* = 8.0, ArH), 6.68 (1H, t, *J* = 7.3, ArH), 7.20–7.24 (2H, m, ArH), 7.33 (1H, d, *J* = 1.8, FurylH), ^1H NMR (500 MHz, $CDCl_3$) δ (*Z*-isomer) 2.34–2.41 (1H, m, $NCH_2(CH_2)_2$), 4.92–4.97 (1H, m, NCHCH=CHAr), 5.58 (1H, dd, *J* = 12.0, 8.4, CH=CHAr), 6.47 (1H, dd, *J* = 3.3, 1.9, FurylH), 6.57 (2H, d, *J* = 8.1, ArH), 7.16–7.19 (2H, m, ArH), 7.48 (1H, d, *J* = 1.8, FurylH), the remaining signals could not be determined; ^{13}C NMR (126 MHz, $CDCl_3$) δ (*E*-isomer) 23.2, 32.7, 48.6, 60.3, 107.4, 111.3, 112.1, 115.7, 118.0, 129.1, 130.0, 141.6, 147.4, 152.7; ^{13}C NMR (126 MHz, $CDCl_3$) δ (*Z*-isomer) 24.4, 33.9, 57.6, 110.1, 111.3, 117.0, 135.1, 142.3, the remaining signals could not be determined; HRMS (ESI-TOF) *m*/*z* calcd. for $C_{16}H_{18}NO$ ($[M+H]^+$) 240.13829, found 240.13828.



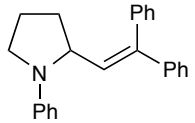
(*E*)-2-(4-Methylpenta-1,3-dien-1-yl)-1-phenylpyrrolidine (35)

Prepared following the general procedure outlined above using (*E*)-((4-methylpenta-1,3-dien-1-yl)sulfonyl)benzene (111 mg, 0.500 mmol, 1.00 equiv.), *N*-phenylpyrrolidine (181 μL, 2.50 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 0.010 equiv.), CsOAc (288 mg, 3.00 equiv.) and DCE (5.00 mL). After 15 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by removal of excess *N*-phenyl-pyrrolidine by heating to 100 °C under vaccum (~0.5 torr) followed by preparative TLC using 1:1 hexanes:toluene provided the title compound (68 mg, 60%, 93:7 *E*:*Z*) as a colorless oil. IR (film) ν_{max} 3090–2870, 1597, 1504, 1363, 1344 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ (*E*-isomer) 1.71 (3H, s, CH_3), 1.76 (3H, s, CH_3), 1.80–1.85 (1H, m, $NCH_2(CH_2)_2$), 1.92–2.15 (3H, m, $NCH_2(CH_2)_2$), 3.24 (1H, td, *J* = 8.9, 6.8, NCH_2), 3.51 (1H, ddd, *J* = 9.6, 7.6, 2.7, NCH_2), 4.18–4.21 (1H, m, NCHCH=CH), 5.55 (1H, dd, *J* = 15.1, 6.0, NCHCH=CH), 5.82 (1H, d, *J* = 10.9, $CH=CMe_2$), 6.33 (1H, dd, *J* = 15.0, 10.9, $CHCH=CMe_2$), 6.62 (2H, d, *J* = 8.3, ArH), 6.66 (1H, t, *J* = 7.3, ArH), 7.21 (2H, t, *J* = 7.9, ArH); ^1H NMR (500 MHz, $CDCl_3$) δ (*Z*-isomer) 1.69 (3H, s, CH_3), 1.74 (3H, s, CH_3), 4.41–4.44 (1H, m, NCHCH=CH), 5.48–5.53 (1H, m, NCHCH=CH), 5.78 (1H, d, *J* = 11.0, $CH=CMe_2$), 6.25–6.29 (1H, m, $CHCH=CMe_2$), 7.14 (2H, t, *J* = 7.9, ArH), the remaining signals could not be determined; ^{13}C NMR (126 MHz, $CDCl_3$) δ (*E*-isomer) 18.4, 23.4, 26.0, 33.4, 48.7, 60.7, 112.1, 115.5, 124.5, 126.3, 129.0, 132.9, 134.7, 147.6; ^{13}C NMR (126 MHz, $CDCl_3$) δ (*Z*-isomer) 18.1, 24.2, 26.6, 31.1, 34.3, 60.0, 112.2, 115.5, 124.6, 126.9, 129.0, 132.4, the remaining signals could not be determined; HRMS (ESI-TOF) *m*/*z* calcd. for $C_{16}H_{22}N$ ($[M+H]^+$) 228.17468, found 228.17451.



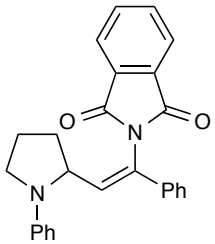
(*E*)-1-Phenyl-2-(2-phenylprop-1-en-1-yl)pyrrolidine (36)

Prepared following the general procedure outlined above using (*E*)-((2-phenylprop-1-en-1-yl)sulfonyl)benzene (129 mg, 0.500 mmol, 1.00 equiv.), *N*-phenylpyrrolidine (181 μL, 2.50 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 0.010 equiv.), CsOAc (288 mg, 3.00 equiv.) and DCE (5.00 mL). After 14 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by removal of excess *N*-phenyl-pyrrolidine by heating to 100 °C under vaccum (~0.5 torr) followed by preparative TLC using 95:4:1 pentane:acetone:Et_3N provided the title compound (110 mg, 84%, >98:2 *E*:*Z*) as a pale yellow oil. IR (film) ν_{max} 3058–2868, 1597, 1504, 1359, 1343 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.90 (1H, ddt, *J* = 11.6, 6.7, 4.3, $NCH_2(CH_2)_2$), 1.95–2.17 (2H, m, $NCH_2(CH_2)_2$), 2.24 (3H, d, *J* = 1.3, CH_3), 2.23–2.34 (1H, m, $NCH_2(CH_2)_2$), 3.32 (1H, dt, *J* = 9.1, 7.4, NCH_2), 3.57 (1H, ddd, *J* = 9.1, 7.6, 4.2, NCH_2), 4.50 (1H, td, *J* = 8.0, 3.9, NCHCH=C(Me)Ph), 5.85 (1H, dd, *J* = 8.1, 1.5, NCHCH=C(Me)Ph), 6.63 (2H, d, *J* = 8.0, Ar**H**), 6.68 (1H, t, *J* = 7.3, Ar**H**), 7.18–7.27 (3H, m, Ar**H**), 7.27–7.34 (2H, m, Ar**H**), 7.37–7.43 (2H, m, Ar**H**); ^{13}C NMR (126 MHz, $CDCl_3$) δ 16.1, 24.3, 33.8, 48.8, 57.8, 112.1, 115.6, 125.7, 126.9, 128.2, 129.1, 132.8, 134.6, 143.0, 147.7; HRMS (ESI-TOF) *m*/*z* calcd. for $C_{19}H_{22}N$ ($[M+H]^+$) 264.17468, found 264.17439.



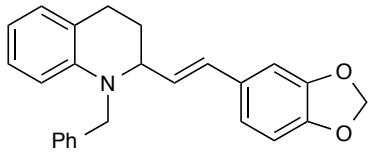
2-(2,2-Diphenylvinyl)-1-phenylpyrrolidine (37)

Prepared following the general procedure outlined above using (2-(phenylsulfonyl)ethene-1,1-diyl)dibenzene (160 mg, 0.500 mmol, 1.00 equiv.), *N*-phenylpyrrolidine (181 μL, 2.50 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 0.010 equiv.), CsOAc (288 mg, 3.00 equiv.) and DCE (5.00 mL). After 12 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by removal of excess *N*-phenyl-pyrrolidine by heating to 100 °C under vaccum (~0.5 torr) followed by preparative TLC using 95:4:1 hexanes:acetone:Et_3N provided the title compound (137 mg, 84%) as a pale yellow solid; IR (film) ν_{max} 3056–2867, 1597, 1504, 1357, 1344, 1177, 1157 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.95–2.09 (2H, m, $NCH_2(CH_2)_2$), 2.11–2.28 (2H, m, $NCH_2(CH_2)_2$), 3.26 (1H, dt, *J* = 8.8, 7.2, NCH_2), 3.57 (1H, ddd, *J* = 9.1, 7.4, 4.3, NCH_2), 4.17 (1H, ddd, *J* = 9.3, 7.8, 3.8, NCHCH=CPh_2), 6.07 (1H, d, *J* = 9.3, CH=CPh_2), 6.47 (2H, d, *J* = 7.6, Ar**H**), 6.63 (1H, t, *J* = 7.3, Ar**H**), 7.12–7.15 (2H, m, Ar**H**), 7.20–7.27 (5H, m, Ar**H**), 7.29–7.32 (2H, m, Ar**H**), 7.36–7.41 (1H, m, Ar**H**), 7.46 (2H, t, *J* = 7.4, Ar**H**); ^{13}C NMR (126 MHz, $CDCl_3$) δ 24.3, 34.3, 48.9, 57.7, 112.3, 115.6, 127.3, 127.5, 127.5, 128.1, 128.4, 128.9, 129.9, 132.7, 139.6, 141.8, 142.0, 147.5; HRMS (ESI-TOF) *m*/*z* calcd. for $C_{24}H_{24}N$ ($[M+H]^+$) 326.19033, found 326.19025.



(*Z*)-2-(1-Phenyl-2-(1-phenylpyrrolidin-2-yl)vinyl)isoindoline-1,3-dione (38)

Prepared following the general procedure outlined above using (*Z*)-2-(1-phenyl-2-(phenylsulfonyl)vinyl)isoindole-1,3-dione (196 mg, 0.500 mmol, 1.00 equiv.), *N*-phenylpyrrolidine (181 μL, 2.50 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 0.010 equiv.), CsOAc (288 mg, 3.00 equiv.) and DCE (5.00 mL). After 15 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by preparative TLC using 80:16:4 hexanes:acetone:Et_3N provided the title compound (155 mg, 79%, 15:85 *E*:*Z*) as a yellow solid. IR (film) ν_{max} 3060–2844, 1717, 1597, 1504, 1373 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ (*Z*-isomer) 1.94–2.01 (1H, m, $NCH_2(CH_2)_2$), 2.07–2.25 (3H, m, $NCH_2(CH_2)_2$), 3.25 (1H, dt, *J* = 8.8, 7.2, NCH_2), 3.54–3.58 (1H, m, NCH_2), 4.25 (1H, td, *J* = 8.1, 3.3, NCHCH=CNPh), 6.49 (1H, d, *J* = 8.2, CH=CNPh), 6.67–6.71 (3H, m, ArH), 7.20–7.24 (2H, m, ArH), 7.27–7.34 (5H, m, ArH), 7.82 (2H, dd, *J* = 5.5, 3.0, ArH), 7.95–8.00 (2H, m, ArH); ^1H NMR (500 MHz, $CDCl_3$) δ (*Z*-isomer) 2.29–2.38 (1H, m, $NCH_2(CH_2)_2$), 3.49–3.54 (1H, m, NCH_2), 4.40 (1H, td, *J* = 8.6, 3.3, NCHCH=CNPh), 5.94 (1H, d, *J* = 9.1, CH=CNPh), 6.56 (2H, d, *J* = 8.1, ArH), 7.17–7.20 (2H, m, ArH), 7.35–7.39 (1H, m, ArH), 7.41–7.44 (2H, m, ArH), 7.46–7.48 (2H, m, ArH), 7.72 (2H, dd, *J* = 5.5, 3.0, ArH), the remaining signals could not be determined; ^{13}C NMR (126 MHz, $CDCl_3$) δ (*Z*-isomer) 24.4, 33.3, 48.9, 57.6, 112.4, 116.3, 124.0, 125.2, 128.6, 128.7, 129.2, 130.1, 131.9, 131.9, 134.5, 134.6, 135.7, 136.8, 147.4, 166.8, 167.5; ^{13}C NMR (126 MHz, $CDCl_3$) δ (*E*-isomer) 24.3, 34.1, 48.9, 56.8, 112.6, 116.2, 123.6, 128.6, 128.7, 128.9, 129.7, 134.2, 135.4, 138.1, 147.2, 167.3, the remaining signals could not be determined; HRMS (ESI-TOF) *m*/*z* calcd. for $C_{26}H_{23}N_2O_2$ ($[M+H]^+$) 395.17540, found 395.17510.

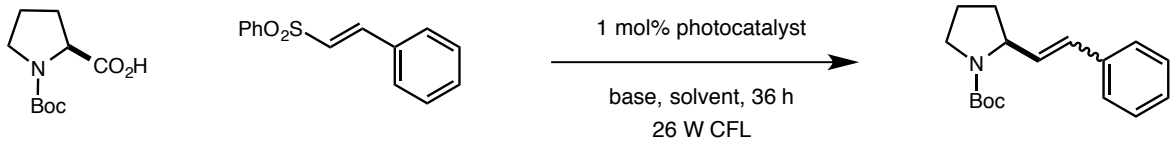


(*E*)-2-(2-(Benzo[*d*][1,3]dioxol-5-yl)vinyl)-1-benzyl-1,2,3,4-tetrahydroquinoline

Prepared following the general procedure outlined above using (*E*)-5-(2-(phenylsulfonyl)vinyl)benzo[*d*][1,3]dioxole (144 mg, 0.500 mmol, 1.00 equiv.), *N*-benzyl-1,2,3,4-tetrahydroquinoline (279 mg, 2.50 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 0.010 equiv.), CsOAc (288 mg, 3.00 equiv.) and DCE (5.00 mL). After 34 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by preparative TLC using 80:16:4 hexanes:acetone:Et_3N provided the title compound (158 mg, 86%, 87:13 *E*:*Z*) as a pale yellow oil. IR (film) ν_{max} 3063–2778, 1601, 1490, 1464, 1445, 1353, 1346, 1246, 1205, 1190, 1173, 1037 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ (*E*-isomer) 2.05–2.10 (1H, m, CH_2CH_2Ar), 2.14–2.23 (1H, m, CH_2CH_2Ar), 2.79 (1H, dt, *J* = 16.0, 4.5, CH_2CH_2Ar), 2.96 (1H, ddd, *J* = 16.3, 11.9, 4.7, CH_2CH_2Ar), 4.13–4.17 (1H, m, NCHCH=CHAr), 4.46 (1H, d, *J* = 17.4, NCH_2Ph), 4.70 (1H, d, *J* = 17.4, NCH_2Ph), 5.96 (2H, s, OCH_2O), 6.10 (1H, dd, *J* = 15.8, 7.1, CH=CHAr), 6.37 (1H, d, *J* = 15.8, CH=CHAr), 6.53 (1H, d, *J* = 8.2, ArH), 6.64 (1H, t, *J* = 7.2, ArH), 6.75–6.80 (2H, m, ArH), 6.90 (1H, d, *J* = 1.7, ArH), 7.01–7.06 (2H, m, ArH), 7.26–7.36 (5H, m, ArH); ^1H NMR (500 MHz, $CDCl_3$) δ (*Z*-isomer) 2.25–2.32 (1H, m, CH_2CH_2Ar), 2.87 (1H, dt, *J* = 16.1, 5.1, CH_2CH_2Ar), 3.00–3.06 (1H, m, CH_2CH_2Ar), 4.22 (1H, d, *J* = 17.0, NCH_2Ph), 4.52 (1H, d, *J* = 17.3, NCH_2Ph), 5.78 (1H, dd, *J* = 11.8, 9.7, CH=CHAr), 5.97 (2H, s, OCH_2O), 6.47 (1H, d, *J* = 7.8, ArH), 6.48 (1H, d, *J* = 11.8, CH=CHAr), 6.67–6.71 (2H, m, ArH), the remaining signals could not be determined; ^{13}C NMR (126 MHz, $CDCl_3$) δ (*E*-isomer) 24.5, 27.7, 52.6, 59.8, 101.1, 105.8, 108.3, 111.0, 115.8, 121.0, 122.0, 126.4, 126.7, 127.3, 128.6, 128.7, 128.8, 130.6, 131.3, 139.0, 144.7, 147.1, 148.0; ^{13}C NMR (126 MHz,

$CDCl_3$) δ (*Z*-isomer) 25.2, 28.3, 53.3, 55.1, 101.1, 108.2, 108.9, 111.8, 116.1, 122.1, 122.5, 126.5, 126.6, 127.3, 128.5, 128.9, 130.0, 130.8, 132.1, 139.3, 144.8, 146.6, 147.6; HRMS (ESI-TOF) *m/z* calcd. for $C_{25}H_{24}NO_2$ ([M+H]$^+$) 370.18016, found 370.18070.

6) Optimization Table for the Decarboxylative Vinylation Reaction



Boc-Pro-OH vinyl sulfone **9** allylic amine **(±)-39**

photocatalyst	solvent	concentration	temperature	base	yield	*E*:*Z*
Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)PF$_6$ (**1**)	DMF	0.10 M	30 °C	K_2HPO_4	35%	48:52
Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)PF$_6$ (**1**)	dioxane	0.10 M	30 °C	K_2HPO_4	80%	30:70
Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)PF$_6$ (**1**)	dioxane	0.10 M	30 °C	KOAc	85%	23:77
Ir(ppy)$_3$	dioxane	0.10 M	30 °C	KOAc	0%	-
Ir(ppy)$_2$(dtbbpy)PF$_6$ (**11**)	dioxane	0.10 M	30 °C	KOAc	66%	88:12
Ir(ppy)$_2$(dtbbpy)PF$_6$ (**11**)	dioxane	0.10 M	30 °C	$CsHCO_3$	59%	97:3
Ir(ppy)$_2$(dtbbpy)PF$_6$ (**11**)	dioxane	0.05 M	30 °C	$CsHCO_3$	66%	97:3
Ir(ppy)$_2$(dtbbpy)PF$_6$ (**11**)	dioxane	0.05 M	40 °C	$CsHCO_3$	72%	97:3
Ir(ppy)$_2$(dtbbpy)PF$_6$ (**11**)	dioxane	0.02 M	50 °C	$CsHCO_3$	***76%***	***96:4***

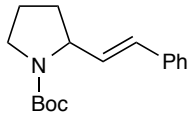
Optimization studies for the decarboxylative vinylation reaction were performed using vinyl sulfone **9** (1.0 equiv., 24 mg, 0.10 mmol), with Boc-Pro-OH (1.2 equiv., 26 mg, 0.15 mmol), and base (2.0 equiv.) in the appropriate solvent. The reactions were irradiated with 2 × CFL bulbs for 36 h. The reactions reached a temperature of approximately 28–30 °C as a result of the heat given off from the CFL bulb. Higher temperatures were achieved by heating in a shallow oil bath. Yields were determined by ^{1}H NMR analysis using an internal standard. *E*:*Z* ratios were determined by ^{1}H NMR analysis.

7) General Decarboxylative Vinylation Procedure

General procedure for the decarboxylative vinylation of N-Boc-α-amino acids:
To a dry 40 mL vial equipped with a stir bar was added Ir(ppy)$_2$(dtbbpy)PF$_6$ (2.2 mg, 2.5 μmol, 0.0050 equiv.), the vinyl sulfone (0.50 mmol, 1.0 equiv.), and the *N*-Boc-α-amino acid (0.60 mmol, 1.2 equiv.). The vial was sealed and triple evacuated/N_2 filled before being transferred into a glovebox. $CsHCO_3$ (194 mg, 1.00 mmol, 2.00 equiv.) was added to the vial before transferring out of the glovebox and placing under an atmosphere of N_2. Dioxane (30 mL) was added to the vial and the resulting mixture degassed by sparging with N_2 for 15 min. The vial

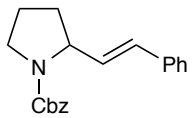
was then placed in a shallow oil bath, pre-set to 50 °C, and irradiated with 2 x CFL bulbs until complete consumption of the vinyl sulfone, as determined by TLC analysis (48–64h). The reaction mixture was diluted with Et_2O, filtered through a plug of silica, and the residue concentrated *in vacuo*. Purification by flash column chromatography or preparative TLC afforded the vinylation product.

8) Experimental Data for Decarboxylative Vinylation Products



***tert*-Butyl (*E*)-2-styrylpyrrolidine-1-carboxylate (39)**

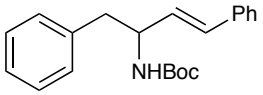
Prepared following the general procedure outlined above using (*E*)-(2-(phenylsulfonyl)vinyl)benzene (122 mg, 0.500 mmol, 1.00 equiv.), Boc-Pro-OH (129 mg, 1.20 equiv.), $Ir(ppy)_2(dtbbpy)PF_6$ (2.3 mg, 0.0050 equiv.), $CsHCO_3$ (194 mg, 2.00 equiv.) and 1,4-dioxane (30.0 mL). After 40 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by preparative TLC using 9:1 toluene:EtOAc provided the title compound (104 mg, 76%, 96:4 *E*:*Z*) as a colorless solid. IR (film) ν_{max} 3082–2875, 1686, 1449, 1389, 1364, 1251, 1159, 1113 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ (*Z*-isomer) 1.44 (9H, s, $OC(C\mathbf{H_3})_3$), 1.77–1.99 (3H, m, $NCH_2(C\mathbf{H_2})_2$), 2.06–2.14 (1H, m, $NCH_2(C\mathbf{H_2})_2$), 3.41–3.50 (2H, m, $NC\mathbf{H_2}$), 4.44 (1H, br. s, NC**H**CH=CHPh), 6.10 (1H, dd, *J* = 15.6, 6.5, C**H**=CHPh), 6.41 (1H, d, *J* = 15.9, CH=C**H**Ph), 7.22 (1H, t, *J* = 7.0, Ar**H**), 7.31 (2H, t, *J* = 7.4, Ar**H**), 7.36 (2H, d, *J* = 7.6, Ar**H**); ^1H NMR (500 MHz, $CDCl_3$) δ (*Z*-isomer) 1.34 (9H, s, $OC(C\mathbf{H_3})_3$), 2.18–2.23 (1H, m, $NCH_2(C\mathbf{H_2})_2$), 4.75 (1H, br. s, NC**H**CH=CHPh), 5.63 (1H, dd, *J* = 10.4, 10.4, C**H**=CHPh), the remaining signals could not be determined; ^{13}C NMR (126 MHz, $CDCl_3$) δ (*E*-isomer) 23.3, 28.5, 32.3, 46.4, 58.9, 79.2, 126.3, 127.3, 128.5, 129.4, 130.7, 137.1, 154.7; HRMS (ESI-TOF) *m*/*z* calcd. for $C_{17}H_{23}NO_2Na$ ($[M+Na]^+$) 296.16210, found 296.16179.



Benzyl (*E*)-2-styrylpyrrolidine-1-carboxylate (40)

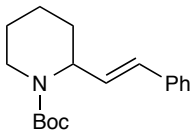
Prepared following the general procedure outlined above using (*E*)-(2-(phenylsulfonyl)vinyl)benzene (122 mg, 0.500 mmol, 1.00 equiv.), Cbz-Pro-OH (150 mg, 1.20 equiv.), $Ir(ppy)_2(dtbbpy)PF_6$ (2.3 mg, 0.0050 equiv.), $CsHCO_3$ (194 mg, 2.00 equiv.) and 1,4-dioxane (30.0 mL). After 64 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by preparative TLC using 9:1 toluene:EtOAc provided the title compound (116 mg, 75%, 92:8 *E*:*Z*) as a colorless oil. IR (film) ν_{max} 3083–2877, 1698, 1448, 1410, 1352, 1179, 1109 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ (*E*-isomer) 1.81–2.01 (3H, m, $NCH_2(C\mathbf{H_2})_2$), 2.06–2.15 (1H, m, $NCH_2(C\mathbf{H_2})_2$), 3.46–3.60 (2H, m, $NC\mathbf{H_2}$), 4.54–4.61 (1H, br. m, NC**H**CH=CHPh), 5.06–5.15 (1H, br. m, $OC\mathbf{H_2}Ph$), 5.20 (1H, d, *J* = 12.5, $OC\mathbf{H_2}Ph$), 6.08–6.17 (1H, m, C**H**=CHPh), 6.37 (rotamer A: 0.60H, d, *J* = 15.7, CH=C**H**Ph), 6.49 (rotamer B: 0.40H, d, *J* = 15.7, CH=C**H**Ph), 7.16–7.40 (10H, m, Ar**H**); ^1H NMR (500 MHz, $CDCl_3$) δ (*Z*-isomer) 4.84 (1H, br. d, *J* = 27.6, NC**H**CH=CHPh), 5.65 (1H, dd, *J* = 10.4, 10.4, C**H**=CHPh), the remaining signals could not be determined; ^{13}C NMR (126 MHz, $CDCl_3$) δ (*E*-

isomer) 23.0, 23.7, 31.6, 32.6, 46.4, 46.8, 58.9, 59.2, 66.7, 66.8, 126.4, 126.5, 127.4, 127.7, 127.8, 128.4, 128.4, 128.5, 129.7, 129.8, 130.2, 136.8, 154.8, 155.1; HRMS (ESI-TOF) *m*/*z* calcd. for $C_{20}H_{22}NO_2$ ([M+H]$^+$) 308.16451, found 308.16429.



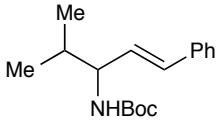
***tert*-Butyl (*E*)-(1,4-diphenylbut-3-en-2-yl)carbamate (41)**

Prepared following the general procedure outlined above using (*E*)-(2-(phenylsulfonyl)vinyl)benzene (122 mg, 0.500 mmol, 1.00 equiv.), Boc-Phe-OH (159 mg, 1.20 equiv.), $Ir(ppy)_2(dtbbpy)PF_6$ (2.3 mg, 0.0050 equiv.), $CsHCO_3$ (194 mg, 2.00 equiv.) and 1,4-dioxane (30.0 mL). After 33 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by preparative TLC using 9:1 toluene:EtOAc provided the title compound (124 mg, 77%, >98:2 *E*:*Z*) as a colorless solid. IR (film) ν_{max} 3341, 3061–2930, 1696, 1495, 1454, 1391, 1366, 1247, 1167 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.43 (9H, s, OC(C**H**$_3$)$_3$), 2.94 (2H, d, *J* = 5.4, C**H**$_2$Ph), 4.59 (2H, br. s, NHC**H** + N**H**), 6.14 (1H, dd, *J* = 16.0, 5.4, C**H**=CHPh), 6.46 (d, *J* = 15.9, CH=C**H**Ph), 7.22–7.34 (10H, m, Ar**H**); ^{13}C NMR (126 MHz, $CDCl_3$) δ 28.4, 42.0, 53.2, 79.5, 126.4, 126.5, 127.5, 128.4, 128.5, 129.6, 129.7, 130.2, 136.8, 137.3, 155.1; HRMS (ESI-TOF) *m*/*z* calcd. for $C_{21}H_{25}NO_2Na$ ([M+Na]$^+$) 346.17775, found 346.17813.



***tert*-Butyl (*E*)-2-styrylpiperidine-1-carboxylate (42)**

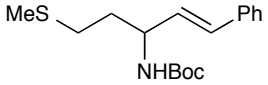
Prepared following the general procedure outlined above using (*E*)-(2-(phenylsulfonyl)vinyl)benzene (122 mg, 0.500 mmol, 1.00 equiv.), Boc-Pip-OH (138 mg, 1.20 equiv.), $Ir(ppy)_2(dtbbpy)PF_6$ (2.3 mg, 0.0050 equiv.), $CsHCO_3$ (194 mg, 2.00 equiv.) and 1,4-dioxane (30.0 mL). After 64 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by flash column chromatography (2–15% EtOAc/hexanes) provided the title compound (106 mg, 74%, >98:2 *E*:*Z*) as a colorless oil. IR (film) ν_{max} 3026–2858, 1689, 1408, 1365, 1270, 1251, 1163 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.48 (9H, s, OC(C**H**$_3$)$_3$), 1.48–1.65 (4H, m, NCH$_2$(C**H**$_2$)$_3$), 1.75–1.86 (2H, m, NCH$_2$(C**H**$_2$)$_3$), 2.92 (1H, t, *J* = 13.0, NC**H**$_2$), 4.01 (1H, d, *J* = 12.5, NC**H**$_2$), 4.97 (1H, br. s, NC**H**CH=CHPh), 6.19 (1H, dd, *J* = 16.2, 4.7, C**H**=CHPh), 6.40 (1H, d, *J* = 16.1, CH=C**H**Ph), 7.24 (1H, t, *J* = 7.1, Ar**H**), 7.32 (2H, t, *J* = 7.4, Ar**H**), 7.37 (2H, d, *J* = 7.5, Ar**H**); ^{13}C NMR (126 MHz, $CDCl_3$) δ 19.7, 25.6, 28.5, 29.5, 39.9, 52.2, 79.5, 126.2, 127.4, 128.6, 128.7, 130.7, 137.1, 155.4; HRMS (ESI-TOF) *m*/*z* calcd. for $C_{18}H_{25}NO_2Na$ ([M+Na]$^+$) 310.17775, found 310.17801.



***tert*-Butyl (*E*)-(4-methyl-1-phenylpent-1-en-3-yl)carbamate (43)**

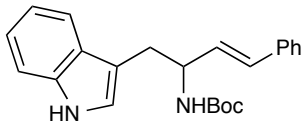
Prepared following the general procedure outlined above using (*E*)-(2-(phenylsulfonyl)vinyl)benzene (122 mg, 0.500 mmol, 1.00 equiv.), Boc-Val-OH (130 mg, 1.20

equiv.), $Ir(ppy)_2(dtbbpy)PF_6$ (2.3 mg, 0.0050 equiv.), $CsHCO_3$ (194 mg, 2.00 equiv.) and 1,4-dioxane (30.0 mL). After 64 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by preparative TLC using 9:1 toluene:EtOAc provided the title compound (101 mg, 73%, >98:2 *E*:*Z*) as a white solid. IR (film) ν_{max} 3342, 3082–2872, 1694, 1496, 1467, 1449, 1390, 1365, 1301, 1246, 1168 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.95 (3H, d, *J* = 6.0, CH(C**H**$_3$)$_2$), 0.97 (3H, d, *J* = 6.0, CH(C**H**$_3$)$_2$), 1.47 (9H, s, OC(C**H**$_3$)$_3$), 1.84–1.89 (1H, m, C**H**(CH$_3$)$_2$), 4.15 (1H, br. s,), 4.62 (1H, br. s,), 6.10 (1H, dd, *J* = 16.0, 6.6, C**H**=CHPh), 6.51 (1H, d, *J* = 15.9, CH=C**H**Ph), 7.23 (1H, t, *J* = 7.2, Ar**H**), 7.32 (1H, t, *J* = 7.4, Ar**H**), 7.37 (1H, d, *J* = 7.5, Ar**H**); ^{13}C NMR (126 MHz, $CDCl_3$) δ 18.3, 18.8, 28.4, 32.8, 57.8, 79.3, 126.4, 127.4, 128.5, 129.1, 130.7, 137.0, 155.5; HRMS (ESI-TOF) *m*/*z* calcd. for $C_{17}H_{25}NO_2Na$ ([M+Na]$^+$) 298.17775, found 298.17821.



***tert*-Butyl (*E*)-(5-(methylthio)-1-phenylpent-1-en-3-yl)carbamate (44)**

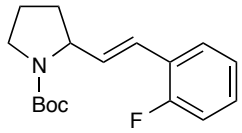
Prepared following the general procedure outlined above using (*E*)-(2-(phenylsulfonyl)vinyl)benzene (122 mg, 0.500 mmol, 1.00 equiv.), Boc-Met-OH (150 mg, 1.20 equiv.), $Ir(ppy)_2(dtbbpy)PF_6$ (2.3 mg, 0.0050 equiv.), $CsHCO_3$ (194 mg, 2.00 equiv.) and 1,4-dioxane (30.0 mL). After 24 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by preparative TLC using 9:1 toluene:EtOAc provided the title compound (107 mg, 70%, >98:2 *E*:*Z*) as a colorless solid. IR (film) ν_{max} 3332, 3060–2870, 1689, 1511, 1496, 1366, 1245, 1167 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.47 (9H, s, OC(C**H**$_3$)$_3$), 1.85–1.96 (2H, m, C**H**$_2$CH$_2$SMe), 2.13 (3H, s, SC**H**$_3$), 2.57 (2H, t, *J* = 7.6, C**H**$_2$SMe), 4.39 (1H, br. s, C**H**NH), 4.65 (1H, br. s, N**H**), 6.10 (1H, dd, *J* = 15.9, 6.4, C**H**=CHPh), 6.54 (1H, d, *J* = 15.9, CH=C**H**Ph), 7.25 (1H, t, *J* = 7.2, Ar**H**), 7.32 (2H, t, *J* = 7.6, Ar**H**), 7.37 (2H, d, *J* = 7.3, Ar**H**); ^{13}C NMR (126 MHz, $CDCl_3$) δ 15.6, 28.4, 30.6, 35.0, 52.0, 79.6, 126.4, 127.7, 128.6, 129.6, 130.6, 136.6, 155.2; HRMS (ESI-TOF) *m*/*z* calcd. for $C_{17}H_{25}NO_2SNa$ ([M+Na]$^+$) 330.14982, found 330.14980.



***tert*-Butyl (*E*)-(1-(1*H*-indol-3-yl)-4-phenylbut-3-en-2-yl)carbamate (45)**

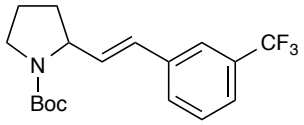
Prepared following the general procedure outlined above using (*E*)-(2-(phenylsulfonyl)vinyl)benzene (122 mg, 0.500 mmol, 1.00 equiv.), Boc-Trp-OH (183 mg, 1.20 equiv.), $Ir(ppy)_2(dtbbpy)PF_6$ (2.3 mg, 0.0050 equiv.), $CsHCO_3$ (194 mg, 2.00 equiv.) and 1,4-dioxane (30.0 mL). After 64 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by preparative TLC using 3:2 toluene:EtOAc provided the title compound (123 mg, 68%, >98:2 *E*:*Z*) as a white solid. IR (film) ν_{max} 3412, 3323, 3081–2848, 1686, 1494, 1456, 1391, 1365, 1246, 1233, 1163 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.43 (9H, s, OC(C**H**$_3$)$_3$), 3.08–3.15 (2H, br. s, C**H**$_2$Ar), 4.69 (2H, br. s, NC**H**CH$_2$Ar + N**H**Boc), 6.20 (1H, dd, *J* = 16.1, 4.8, C**H**=CHPh), 6.51 (1H, d, *J* = 15.9, CH=C**H**Ph), 7.07 (1H, s, Ar**H**), 7.14 (1H, t, *J* = 7.5, Ar**H**), 7.20–7.24 (2H, m, Ar**H**), 7.28–7.33 (4H, m, Ar**H**), 7.38 (1H, d, *J* = 8.1, Ar**H**), 7.65 (1H, d, *J* = 7.9, Ar**H**), 8.08 (1H, s, N**H**); ^{13}C NMR (126 MHz, $CDCl_3$) δ 28.4, 31.5, 52.8, 79.5, 111.1, 111.5, 119.2, 119.6, 122.1, 122.9, 126.4, 127.4, 127.9, 128.5, 129.9,

130.5, 136.2, 136.9, 155.4; HRMS (ESI-TOF) *m*/*z* calcd. for $C_{23}H_{27}N_2O_2$ ([M+H]$^+$) 363.20670, found 363.20613.



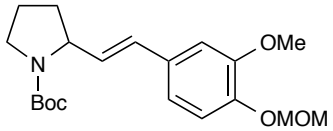
***tert*-Butyl (*E*)-2-(2-fluorostyryl)pyrrolidine-1-carboxylate (46)**

Prepared following the general procedure outlined above using (*E*)-1-fluoro-2-(2-(phenylsulfonyl)vinyl)benzene (131 mg, 0.500 mmol, 1.00 equiv.), Boc-Pro-OH (129 mg, 1.20 equiv.), $Ir(ppy)_2(dtbbpy)PF_6$ (2.3 mg, 0.0050 equiv.), $CsHCO_3$ (194 mg, 2.00 equiv.) and 1,4-dioxane (30.0 mL). After 50 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by preparative TLC using 9:1 toluene:EtOAc provided the title compound (122 mg, 84%, 94:6 *E*:*Z*) as a white solid. IR (film) ν_{max} 2974–2875, 1686, 1487, 1455, 1389, 1364, 1228, 1162, 1111, 1091 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ (*E*-isomer) 1.43 (9H, s, OC(C**H**$_3$)$_3$), 1.78–1.97 (2H, m, NCH$_2$(C**H**$_2$)$_2$), 2.11 (1H, br. s, NCH$_2$(C**H**$_2$)$_2$), 3.47 (2H, br. s, NC**H**$_2$), 4.38–4.57 (1H, br. m, NC**H**CH=CHAr), 6.13–6.29 (1H, m, C**H**=CHAr), 6.56 (1H, d, *J* = 15.9, CH=C**H**Ar), 7.01–7.20 (3H, m, Ar**H**), 7.42 (1H, t, *J* = 7.3, Ar**H**); ^{1}H NMR (500 MHz, $CDCl_3$) δ (*Z*-isomer) 5.72 (1H, t, *J* = 10.3, C**H**=CHAr), 6.44 (1H, d, *J* = 11.8, CH=C**H**Ar), the remaining signals could not be determined; ^{13}C NMR (126 MHz, $CDCl_3$) δ 23.1, 23.6, 28.5, 31.6, 32.6, 46.3, 46.6, 58.7, 59.3, 79.3, 115.7 (1C, d, *J* = 22.8), 121.4, 122.1, 124.0, 124.8 (1C, d, *J* = 12.2), 127.4, 128.5, 133.2, 133.4, 154.7, 160.2 (1C, d, *J* = 248.9); HRMS (ESI-TOF) *m*/*z* calcd. for $C_{17}H_{22}FNO_2Na$ ([M+Na]$^+$) 314.15268, found 314.15257.



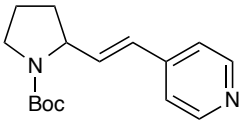
***tert*-Butyl (*E*)-2-(3-(trifluoromethyl)styryl)pyrrolidine-1-carboxylate (47)**

Prepared following the general procedure outlined above using (*E*)-1-(2-(phenylsulfonyl)vinyl)-3-(trifluoromethyl)benzene (156 mg, 0.500 mmol, 1.00 equiv.), Boc-Pro-OH (129 mg, 1.20 equiv.), $Ir(ppy)_2(dtbbpy)PF_6$ (2.3 mg, 0.0050 equiv.), $CsHCO_3$ (194 mg, 2.00 equiv.) and 1,4-dioxane (30.0 mL). After 50 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by preparative TLC using 9:1 toluene:EtOAc provided the title compound (135 mg, 79%, 94:6 *E*:*Z*) as a colorless oil. IR (film) ν_{max} 2976–2876, 1690, 1391, 1365, 1330, 1162, 1123, 1094, 1073 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ (*E*-isomer) 1.43 (9H, s, OC(C**H**$_3$)$_3$), 1.78–1.97 (3H, m, NCH$_2$(C**H**$_2$)$_2$), 2.12 (1H, br. s, NCH$_2$(C**H**$_2$)$_2$), 3.48 (2H, br. s, NC**H**$_2$), 4.41–4.54 (1H, br. m, NC**H**CH=CHAr), 6.19 (1H, br. s, C**H**=CHAr), 6.41–6.41 (1H, br. m, C**H**=CHAr), 7.39–7.52 (3H, m, Ar**H**), 7.60 (1H, s, Ar**H**); ^{1}H NMR (500 MHz, $CDCl_3$) δ (*Z*-isomer) 5.73 (d, *J* = 10.0 Hz, 1H), the remaining signals could not be determined; ^{13}C NMR (126 MHz, $CDCl_3$) δ (*E*-isomer) 23.1, 23.7, 28.5, 31.7, 32.5, 46.3, 46.7, 58.5, 58.9, 79.3, 122.8, 123.8, 124.14 (1C, q, *J* = 272.6), 128.1, 129.0, 129.5, 132.6, 132.9, 136.6, 137.8, 154.6; HRMS (ESI-TOF) *m*/*z* calcd. for $C_{18}H_{22}F_3NO_2Na$ ([M+Na]$^+$) 364.14948, found 364.14934.



***tert*-Butyl (*E*)-2-(3-methoxy-4-(methoxymethoxy)styryl)pyrrolidine-1-carboxylate (48)**

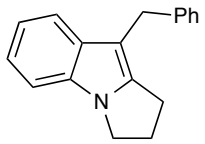
Prepared following the general procedure outlined above using (*E*)-2-methoxy-1-(methoxymethoxy)-4-(2-(phenylsulfonyl)vinyl)benzene (167 mg, 0.500 mmol, 1.00 equiv.), Boc-Pro-OH (129 mg, 1.20 equiv.), $Ir(ppy)_2(dtbbpy)PF_6$ (2.3 mg, 0.0050 equiv.), $CsHCO_3$ (194 mg, 2.00 equiv.) and 1,4-dioxane (30.0 mL). After 50 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by preparative TLC using 3:2 hexanes:EtOAc provided the title compound (125 mg, 69%, 97:3 *E*:*Z*) as a pale yellow oil. IR (film) ν_{max} 2971–2828, 1687, 1511, 1464, 1391, 1364, 1265, 1156, 1132, 1078 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ (*E*-isomer) 1.42 (9H, s, $OC(C\mathbf{H_3})_3$), 1.77–1.97 (3H, m, $NCH_2(C\mathbf{H_2})_2$), 2.09 (1H, br. s, $NCH_2(C\mathbf{H_2})_2$), 3.46 (2H, br. s, $NC\mathbf{H_2}$), 3.51 (3H, s, $OC\mathbf{H_3}$), 3.90 (3H, s, $OC\mathbf{H_3}$), 4.38–4.51 (1H, br. m, NC**H**CH=CHAr), 5.22 (2H, s, $OC\mathbf{H_2}O$), 5.98 (1H, br. s, C**H**=CHAr), 6.32 (1H, br. d, *J* = 15.8, CH=C**H**Ar), 6.87 (1H, d, *J* = 8.1, Ar**H**), 6.91 (1H, s, Ar**H**), 7.08 (1H, d, *J* = 8.1, Ar**H**); ^1H NMR (500 MHz, $CDCl_3$) δ (*Z*-isomer) 4.70 (1H, br. s,), 5.56 (1H, br. s,), the remaining signals could not be determined; ^{13}C NMR (126 MHz, $CDCl_3$) δ 23.1, 23.7, 28.5, 31.7, 32.6, 46.3, 46.6, 55.9, 56.2, 58.5, 59.0, 79.2, 95.5, 109.2, 109.5, 116.3, 119.3, 129.1, 129.4, 131.8, 145.9, 149.7, 154.7; HRMS (ESI-TOF) *m*/*z* calcd. for $C_{20}H_{29}NO_5Na$ ($[M+Na]^+$) 386.19379, found 386.19442.



***tert*-Butyl (*E*)-2-(2-(pyridin-4-yl)vinyl)pyrrolidine-1-carboxylate (49)**

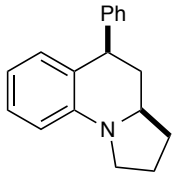
Prepared following the general procedure outlined above using (*E*)-4-(2-(phenylsulfonyl)vinyl)pyridine (123 mg, 0.500 mmol, 1.00 equiv.), Boc-Pro-OH (129 mg, 1.20 equiv.), $Ir(ppy)_2(dtbbpy)PF_6$ (2.3 mg, 0.0050 equiv.), $CsHCO_3$ (194 mg, 2.00 equiv.) and 1,4-dioxane (30.0 mL). After 50 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by preparative TLC using 50:45:5 EtOAc:hexanes:Et_3N provided the title compound (95 mg, 69%, 95:5 *E*:*Z*) as a pale yellow solid. IR (film) ν_{max} 3067–2875, 1687, 1597, 1390, 1364, 1162, 1110 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.38–1.48 (9H, m, $C(C\mathbf{H_3})_3$), 1.75–1.84 (1H, m, $NCH_2(C\mathbf{H_2})_2$), 1.84–1.97 (2H, m, $NCH_2(C\mathbf{H_2})_2$), 2.12 (1H, br. s, $NCH_2(C\mathbf{H_2})_2$), 3.39–3.49 (2H, br. m, $NC\mathbf{H_2}$), 4.40–4.53 (1H, br. m, NC**H**CH=CHAr), 6.31–6.39 (2H, br. m, C**H**=C**H**Ar), 7.22 (2H, s, Ar**H**), 8.52 (2H, br. s, Ar**H**); ^1H NMR (500 MHz, $CDCl_3$) δ (*Z*-isomer) 5.76–5.80 (1H, br. m, C**H**=CHAr), the remaining signals could not be determined; ^{13}C NMR (126 MHz, $CDCl_3$) δ (*E*-isomer) 23.1, 23.7, 28.5, 31.5, 32.4, 46.4, 46.7, 58.4, 58.8, 79.5, 120.9, 121.1, 127.1, 135.9, 136.0, 144.4, 149.7, 150.0, 154.5; HRMS (ESI-TOF) *m*/*z* calcd. for $C_{16}H_{23}N_2O_2$ ($[M+H]^+$) 275.17540, found 275.17578.

9) Experimental Data for Miscellaneous Compounds



9-Benzyl-2,3,-dihydro-1H-pyrrolo[1,2-a]indole (50)

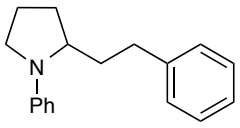
To an 8 mL vial containing (*E*)-1-(2-bromophenyl)-2-styrylpyrrolidine (**18**) (84 mg, 0.26 mmol) was added $Pd(PPh_3)_4$ (30 mg, 0.10 equiv.). The vial was triple evacuated/N_2 filled before the addition of MeCN (2.6 mL) followed by Et_3N (357 mL, 10.0 equiv.). The vial was sealed and the reaction heated to 100 °C with stirring for 18 hours. The reaction was allowed to cool to room temperature before being diluted with Et_2O and filtered through a plug of Celite®. After concentration *in vacuo* to removed excess Et_3N, the residue was diluted with toluene (5.0 mL), *p*-toluenesulfonic acid monohydrate (49 mg, 1.0 equiv.) was added and the mixture heated to 100 °C with stirring for 30 minutes to promote isomerization of the external olefin isomeric product to the desired product. The mixture was diluted with saturated aqueous $NaHCO_3$ and the product extracted into EtOAc, washed with brine, dried (Na_2SO_4), filtered, and concentrated *in vacuo*. Purification by flash column chromatography (2-10% EtOAc/hexanes) gave the title compound (55 mg, 87%) as a colorless oil. IR (film) ν_{max} 3083–2852, 1704, 1611, 1493, 1479, 1459, 1376, 1298, 1238 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.57 (2H, ddt, *J* = 7.2, 7.2, 7.2, NCH_2CH_2), 2.76 (2H, t, *J* = 7.3, $NCH_2CH_2CH_2$), 4.05 (2H, t, *J* = 7.0, NCH_2), 4.11 (2H, s, CH_2Ph), 7.05–7.09 (1H, m, Ar**H**), 7.12–7.16 (1H, m, Ar**H**), 7.18–7.22 (1H, m, Ar**H**), 7.24 (1H, d, *J* = 8.0, Ar**H**), 7.27–7.30 (4H, m, Ar**H**), 7.48–7.50 (1H, m, Ar**H**); ^{13}C NMR (126 MHz, $CDCl_3$) δ 23.3, 27.8, 31.1, 43.5, 104.7, 109.3, 118.7, 118.7, 120.2, 125.7, 128.3, 128.7, 132.5, 132.6, 141.8, 142.0; HRMS (ESI-TOF) *m/z* calcd. for $C_{18}H_{18}N$ ($[M+H]^+$) 248.14338, found 248.14337.



(3a*R,5*R**)-5-Phenyl-1,2,3,3a,4,5-hexahydropyrrolo[1,2-*a*]quinolone (51)**

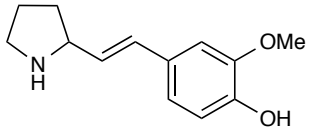
Prepared according to the literature procedure.[20] An 8 mL vial containing (*E*)-1-phenyl-2-styrylpyrrolidine (**10**) (74 mg, 0.30 mmol) was triple evacuated/N_2 filled before the addition of polyphosphoric acid (570 mg, 8.00 equiv.). The vial was then placed in a heating block pre-heated to 100 °C and stirred at this temperature for 15 minutes. The reaction was allowed to cool to room temperature before being neutralized with aqueous NH_4OH. The product was extracted into EtOAc (3 x 10 mL), dried (Na_2SO_4), filtered, and concentrated *in vacuo* to provide the crude product. Purification by preparative TLC using 85:15 hexanes:EtOAc gave the title compound (53 mg, 72%, 95:5 *cis*:*trans*) as a white solid. IR (film) ν_{max} 3061–2852, 1601, 1499, 1481, 1457, 1387, 1359, 1322, 1178 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ (*cis*-isomer) 1.56 (1H, ddd, *J* = 22.6, 11.5, 7.7, $NCH_2(CH_2)_2$), 1.80 (1H, dd, *J* = 12.1, 12.1, CH_2CHPh), 1.94–2.04 (1H, m, $NCH_2(CH_2)_2$), 2.11–2.20 (2H, m, $NCH_2(CH_2)_2$), 2.34 (1H, ddd, *J* = 12.5, 4.9, 2.8, CH_2CHPh), 3.33–3.41 (2H, m, NCH_2), 3.62–3.68 (1H, m, $NCHCH_2$), 4.14 (1H, dd, *J* = 12.6, 4.8, CHPh), 6.46–6.48 (2H, m, Ar**H**), 6.56 (1H, d, *J* = 7.7, Ar**H**), 7.10 (1H, t, *J* = 7.4, Ar**H**), 7.26–7.30 (3H, m, Ar**H**), 7.37 (2H, t, *J* = 7.5, Ar**H**); ^1H NMR (500 MHz, $CDCl_3$) δ (*trans*-isomer) 3.21–3.32 (2H, m, NCH_2), 3.47–3.50 (1H, m, $NCHCH_2$), 4.27 (1H, dd, *J* = 5.2, 2.3, CHPh), 6.62 (1H, t, *J* = 7.6, Ar**H**), 7.02 (1H, dd, *J* = 7.5, 1.7, Ar**H**), 7.18–7.22 (2H, m, Ar**H**), the remaining signals could

not be determined; ^{13}C NMR (126 MHz, $CDCl_3$) δ (*cis*-isomer) 23.8, 33.2, 37.4, 44.9, 47.1, 57.9, 110.0, 114.9, 125.1, 126.4, 127.4, 128.5, 128.8, 128.9, 145.0, 145.6; ^{13}C NMR (126 MHz, $CDCl_3$) δ (*trans*-isomer) 24.2, 33.1, 34.8, 43.2, 47.4, 52.5, 110.2, 114.8, 125.8, 127.9, 128.1, 128.4, 130.0, the remaining signals could not be determined; HRMS (ESI-TOF) *m*/*z* calcd. for $C_{18}H_{20}N$ ([M+H]$^+$) 250.15903, found 250.19884.



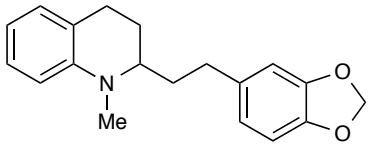
2-Phenethyl-1-phenylpyrrolidine (52)

A 25 mL flask containing a solution of (*E*)-1-phenyl-2-styrylpyrrolidine (**10**) (101 mg, 0.405 mmol) in EtOAc/MeOH (1:1, 8.1 mL) was carefully triple evacuated/N_2 filled before the addition of 10% palladium on carbon (22 mg, 0.050 equiv.). The flask was then triple evacuated/H_2 filled before being stirred under an atmosphere of H_2 at room temperature for 10 hours. The reaction was filtered through a plug of Celite®, eluting with EtOAc and MeOH, and the filtrate concentrated *in vacuo* to give the crude product. Purification by flash column chromatography (1-10% EtOAc/hexanes) gave the title compound (81 mg, 80%) as a colorless oil. IR (film) ν_{max} 3085–2864, 1596, 1503, 1454, 1363, 1344, 1186, 1157 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.59–1.67 (1H, m, C**H**$_2$CH$_2$Ph), 1.90–1.93 (1H, m, NCH$_2$(C**H**$_2$)$_2$), 1.98–2.11 (4H, m, 3 x , NCH$_2$(C**H**$_2$)$_2$ + 1 x C**H**$_2$CH$_2$Ph), 2.64–2.77 (2H, m, C**H**$_2$Ph), 3.14–3.19 (1H, m NC**H**$_2$), 3.45 (1H, ddd, *J* = 9.5, 7.4, 2.3, NC**H**$_2$), 3.69–3.72 (1H, m, NC**H**CH$_2$), 6.49 (2H, d, *J* = 8.0, Ar**H**), 6.65 (1H, t, *J* = 7.2, Ar**H**), 7.19–7.25 (5H, m, Ar**H**), 7.32 (2H, t, *J* = 7.5, Ar**H**); ^{13}C NMR (126 MHz, $CDCl_3$) δ 23.5, 30.2, 33.0, 34.6, 48.2, 57.9, 111.8, 115.2, 125.9, 128.4, 128.4, 129.2, 141.9, 147.2; HRMS (ESI-TOF) *m*/*z* calcd. for $C_{18}H_{22}N$ ([M+H]$^+$) 252.17468, found 252.17452.



(*E*)-2-Methoxy-4-(2-(pyrrolidin-2-yl)vinyl)phenol [(±)-Norruspoline] (53)

To a vial containing *tert*-butyl (*E*)-2-(3-methoxy-4-(methoxymethoxy)styryl)pyrrolidine-1-carboxylate (**48**) (98 mg, 0.27 mmol) at 0 °C was added trifluoroacetic acid (2.08 mL, 27.0 mmol, 100 equiv.). The mixture was stirred at 0 °C for 2 h before being diluted with MeOH (10 mL) and the mixture concentrated *in vacuo*. The residue was diluted with MeOH (10 mL) and sat. aq. $NaHCO_3$ was added to basify the mixture to pH ≥7 before removal of the MeOH and water under reduced pressure. MeOH was added to the residue and the $NaHCO_3$ removed by filtration before concentrating the filtrate *in vacuo* to yield the crude product. Purification by flash column chromatography (100:8:1, DCM:MeOH:NH_3) yielded the title compound (45 mg, 76%) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.52–1.60 (1H, m, NCH$_2$(C**H**$_2$)$_2$), 1.70–2.05 (3H, m, NCH$_2$(C**H**$_2$)$_2$), 2.93 (1H, m, NC**H**$_2$), 3.09 (1H, ddd, *J* = 10.0, 8.1, 5.9, NC**H**$_2$), 3.69 (1H, q, *J* = 7.7, NC**H**CH=CHAr), 3.84 (3H, s, OC**H**$_3$), 6.02 (1H, dd, *J* = 15.7, 7.5, C**H**=CHAr), 6.40 (1H, d, *J* = 15.9,CH=C**H**Ar), 6.80 (2H, s, Ar**H**), 6.87 (1H, s, Ar**H**). All spectroscopic data is in agreement with those previously reported.[21]

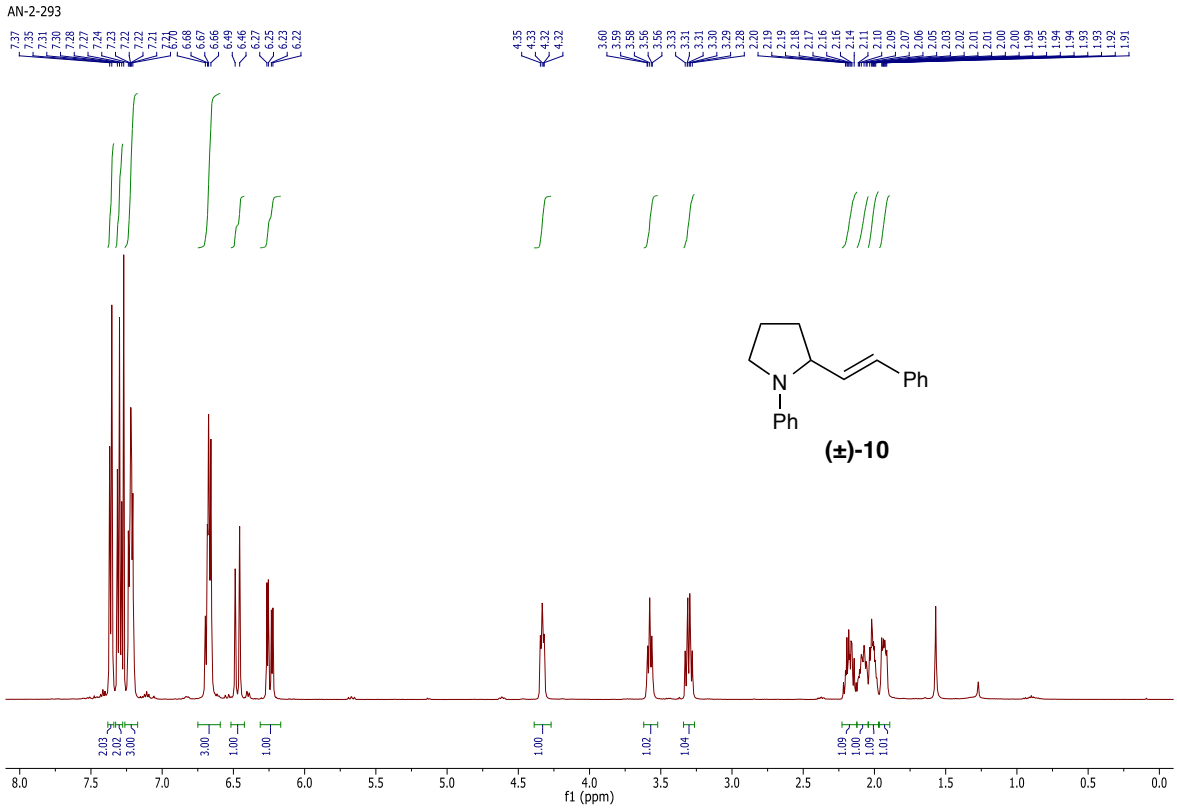


2-(2-(Benzo[*d*][1,3]dioxol-5-yl)ethyl)-1-methyl-1,2,3,4-tetrahydroquinoline [(±)-Galipinine] (54)

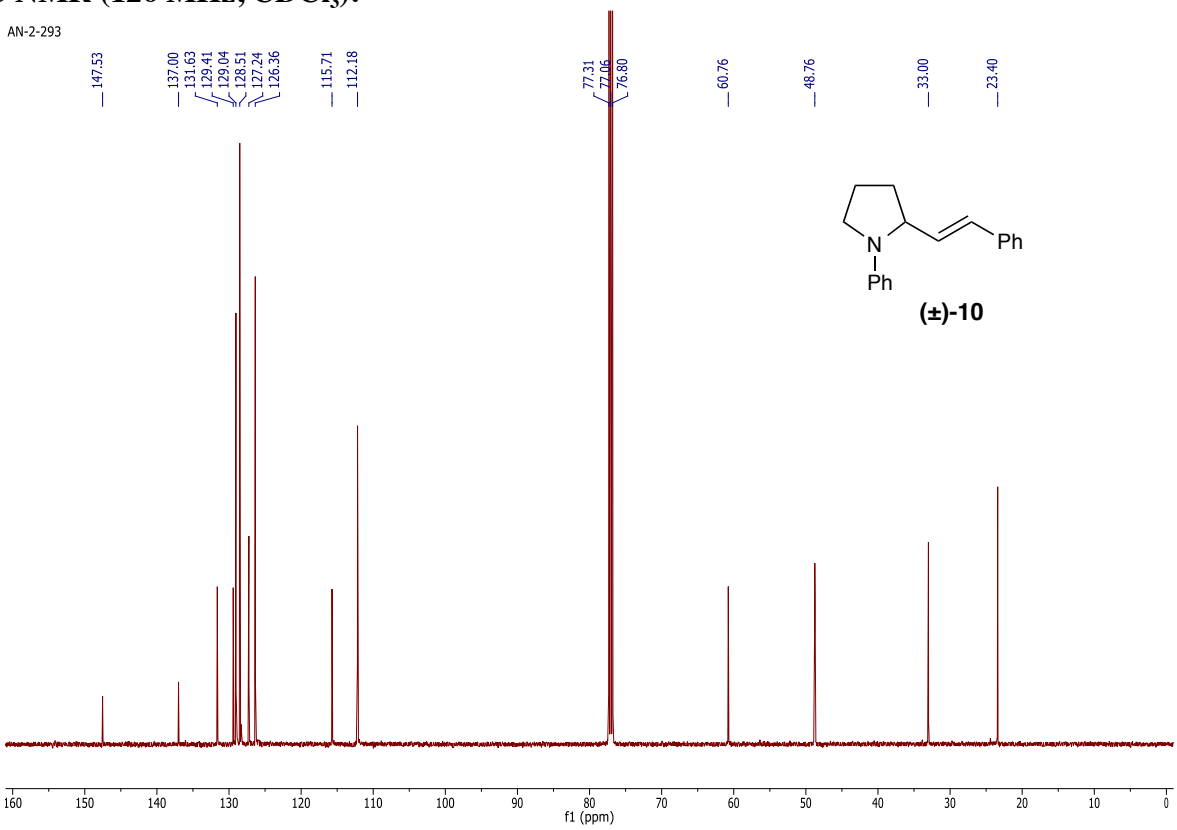
To an 8 mL vial containing (*E*)-2-(2-(benzo[*d*][1,3]dioxol-5-yl)vinyl)-1-benzyl-1,2,3,4-tetrahydroquinoline (72 mg, 0.20 mmol) was added 10% palladium on carbon. The vial was triple evacuated/N_2 filled before the addition of MeOH (3.90 mL) and formaldehyde (37% wt. in H_2O, 145 μL, 10.0 equiv.). The vial was triple evacuated/H_2 filled before being vigorously stirred under an atmosphere of H_2 at room temperature for 38 hours. The reaction was filtered through a plug of Celite®, eluting with EtOAc and MeOH, and the filtrate concentrated *in vacuo* to give the crude product. Purification by preparative TLC using 5:1 hexanes:EtOAc gave the title compound (54 mg, 94%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.67–1.75 (1H, m, C**H**$_2$CH$_2$Ar), 1.84–2.00 (3H, m, C**H**$_2$CH$_2$Ar), 2.51 (1H, ddd, *J* = 14.0, 9.9, 6.6, C**H**$_2$Ar), 2.61–2.73 (2H, m, C**H**$_2$Ar), 2.85 (1H, ddd, *J* = 16.7, 11.8, 6.3, C**H**$_2$Ar), 2.92 (3H, s, NC**H**$_3$), 3.26–3.30 (1H, m, NC**H**CH$_2$), 5.93 (2H, s, OC**H**$_2$O), 6.54 (1H, d, *J* = 8.2, Ar**H**), 6.60 (1H, t, *J* = 7.3, Ar**H**), 6.65 (1H, dd, *J* = 7.9, 1.7, Ar**H**), 6.70 (1H, d, *J* = 1.7, Ar**H**), 6.74 (1H, d, *J* = 7.9, Ar**H**), 6.99 (1H, d, *J* = 7.1, Ar**H**), 7.09 (1H, t, *J* = 7.6, Ar**H**). All spectroscopic data is in agreement with those previously reported.[22]

10) Spectral Data

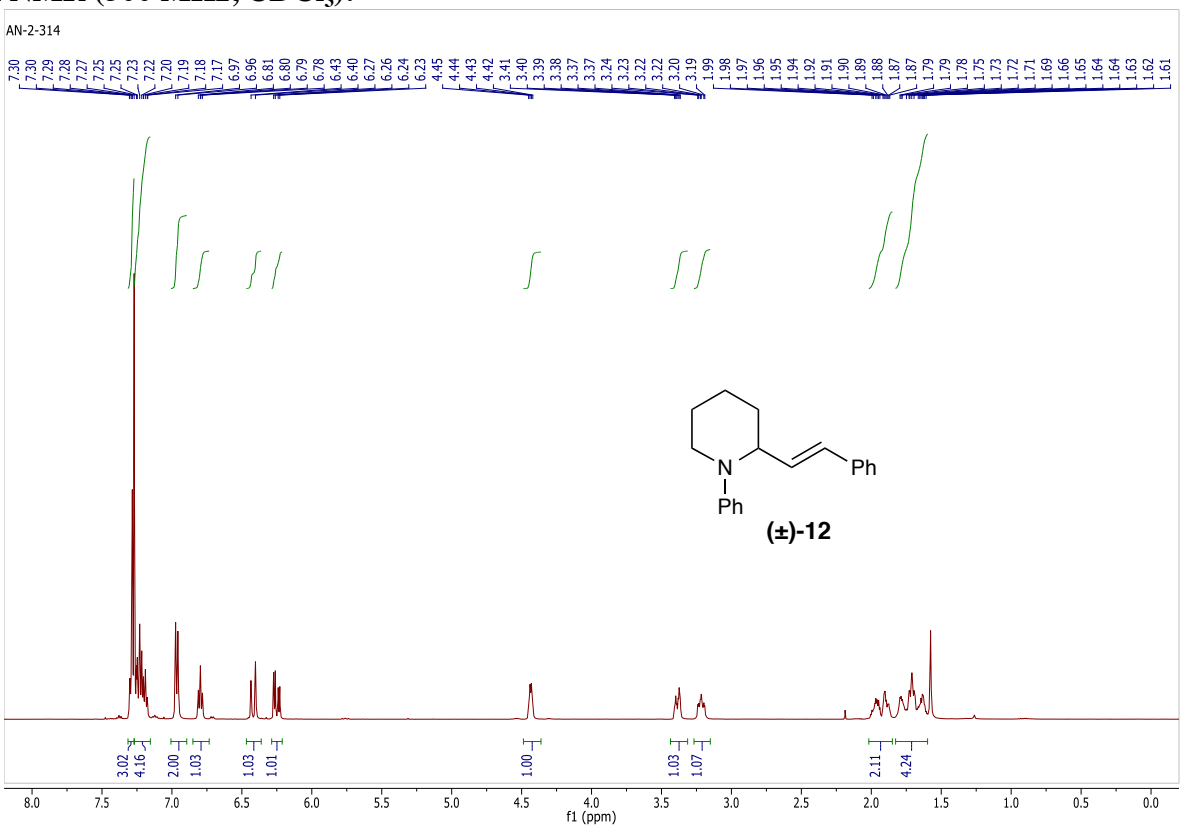
^{1}H NMR (500 MHz, $CDCl_3$):



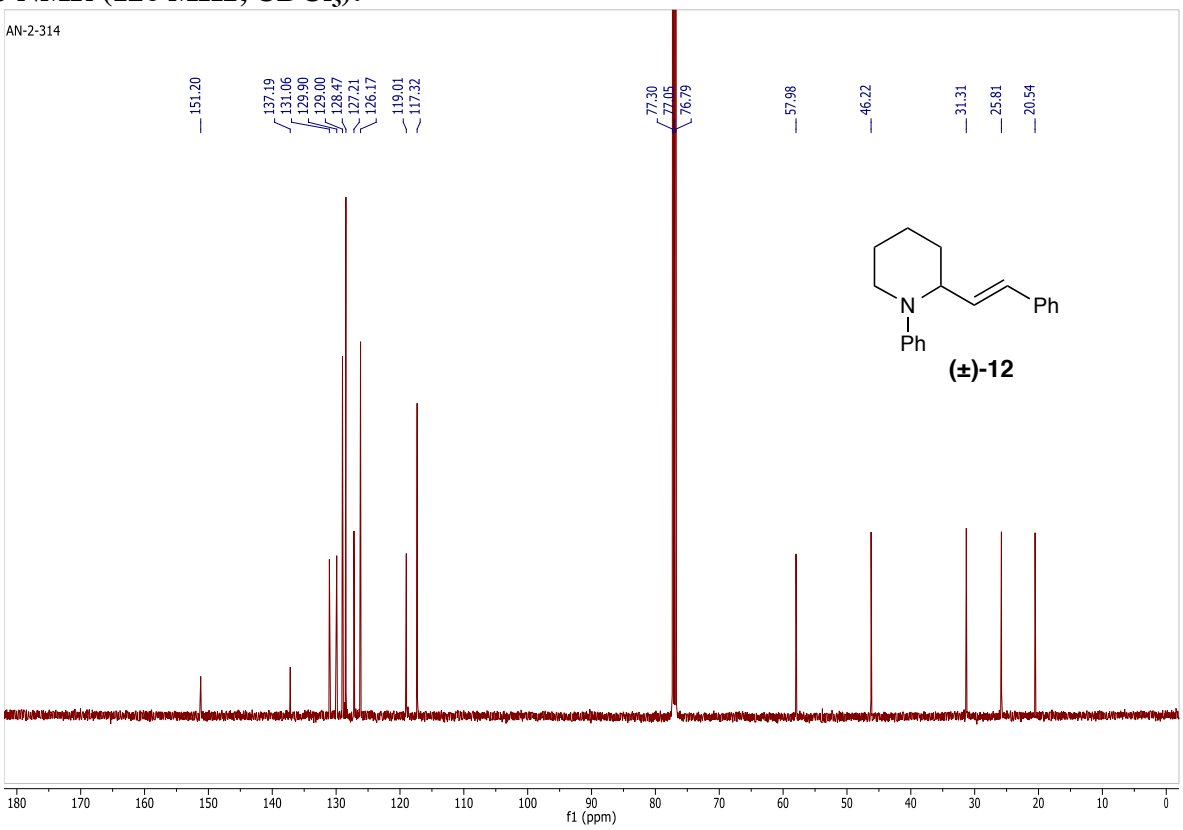
^{13}C NMR (126 MHz, $CDCl_3$):



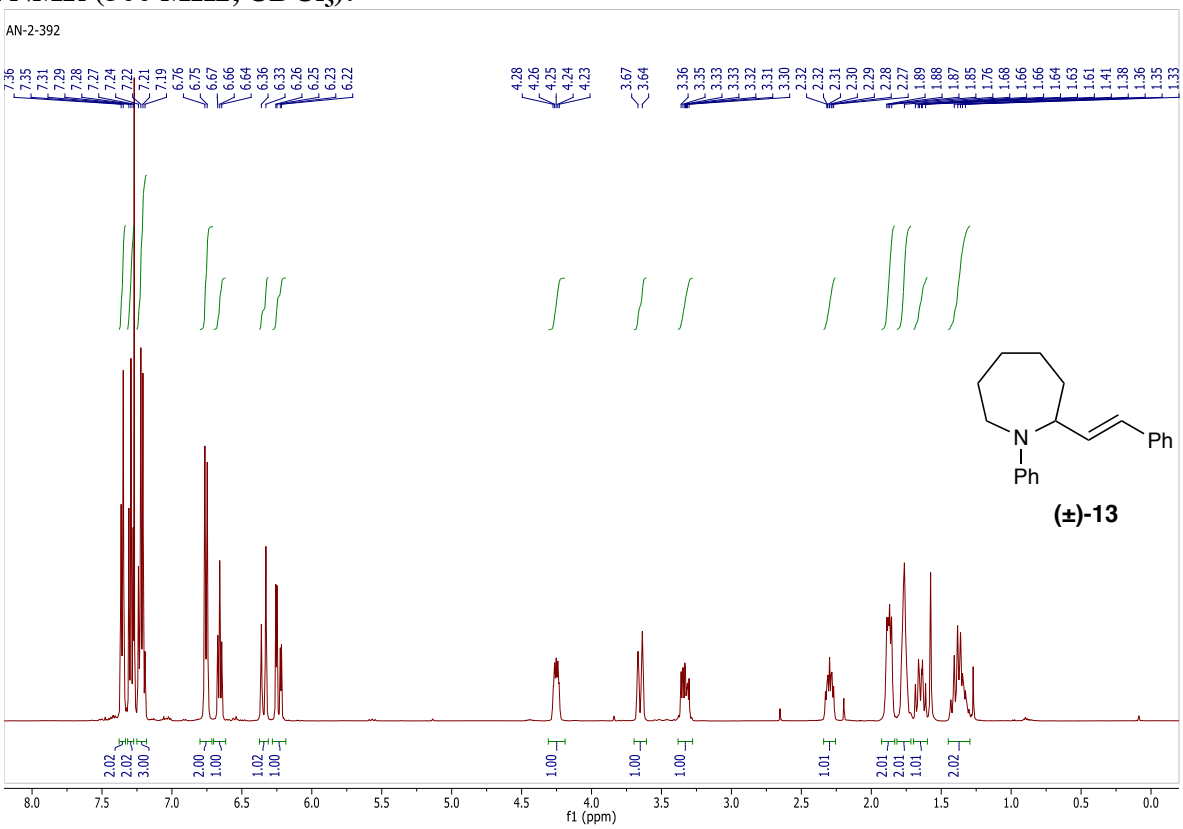
^{1}H NMR (500 MHz, $CDCl_3$):



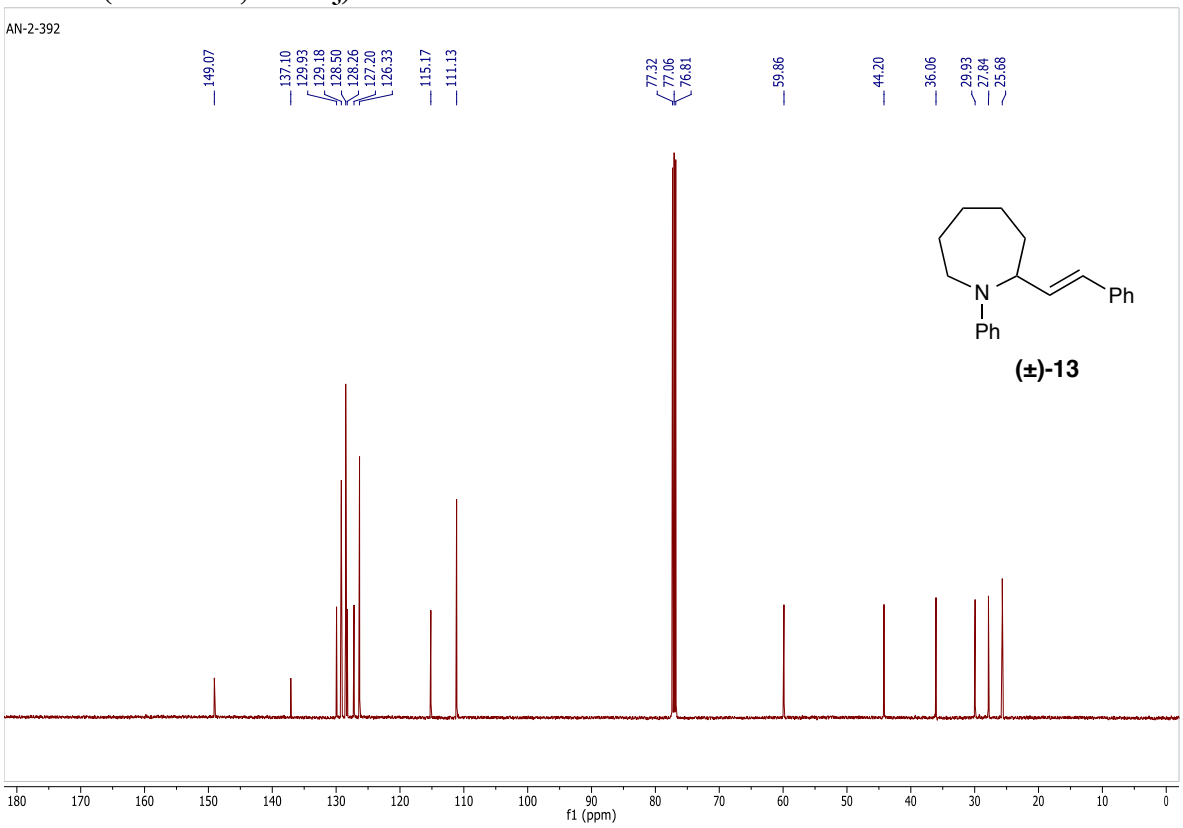
^{13}C NMR (126 MHz, $CDCl_3$):



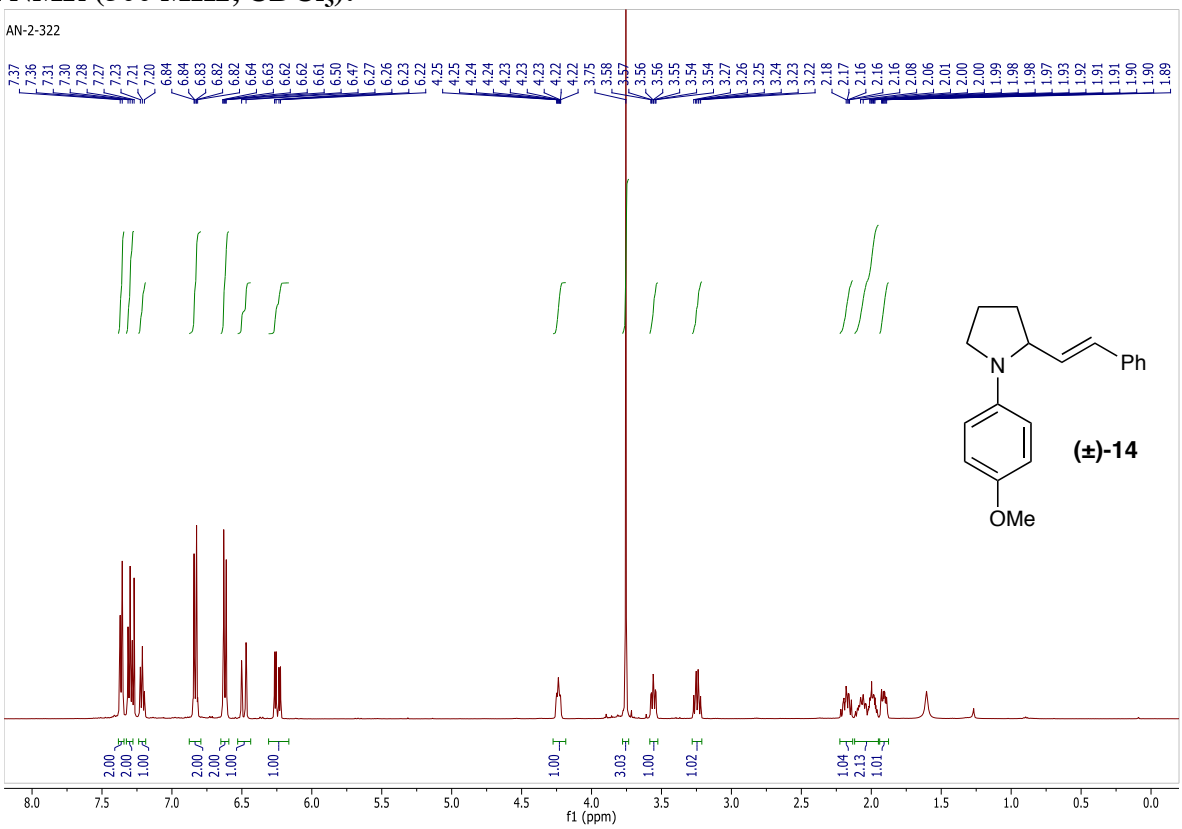
^{1}H NMR (500 MHz, $CDCl_3$):



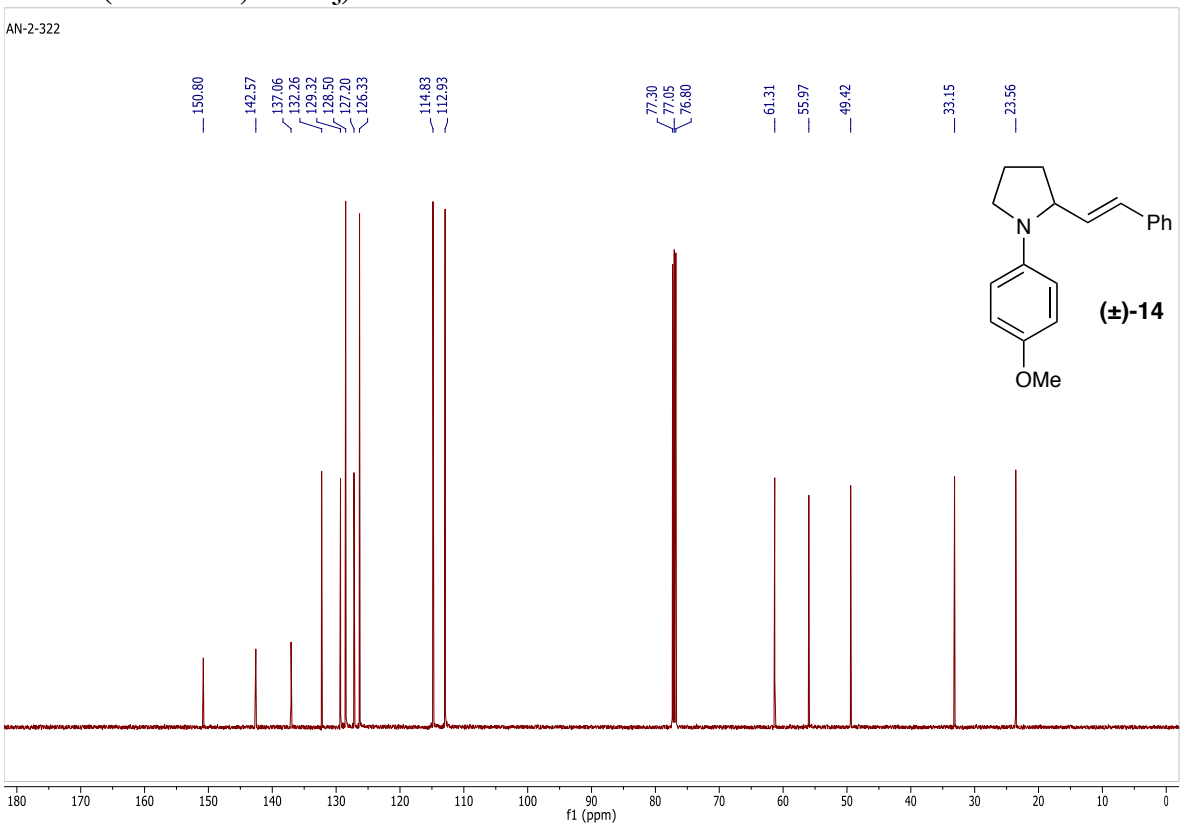
^{13}C NMR (126 MHz, $CDCl_3$):



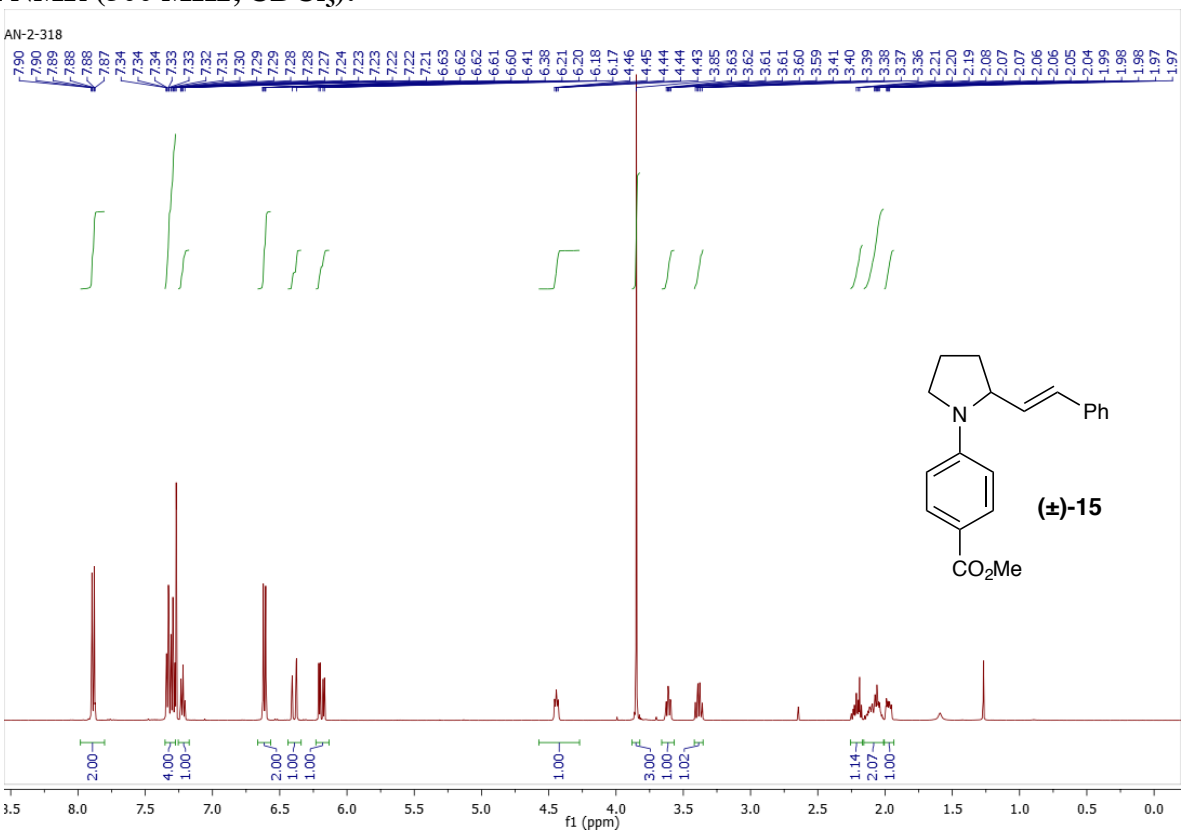
^{1}H NMR (500 MHz, $CDCl_3$):



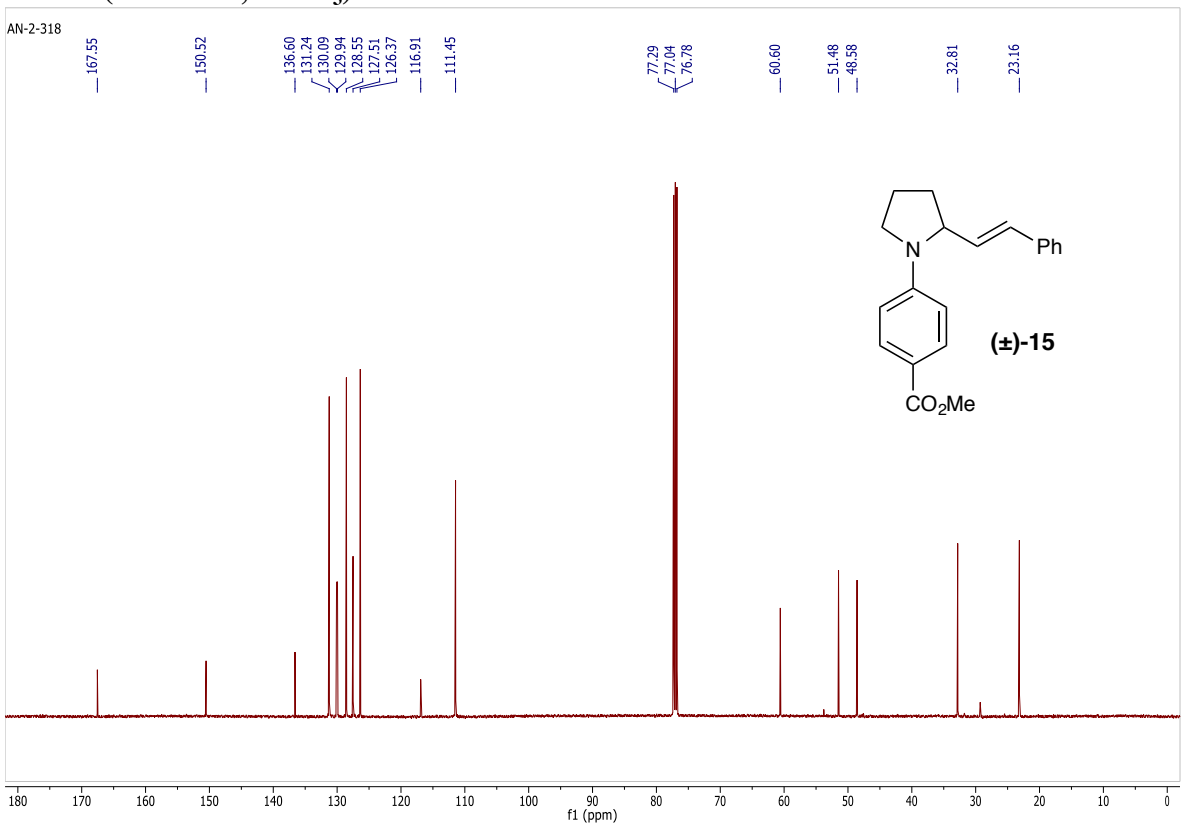
^{13}C NMR (126 MHz, $CDCl_3$):



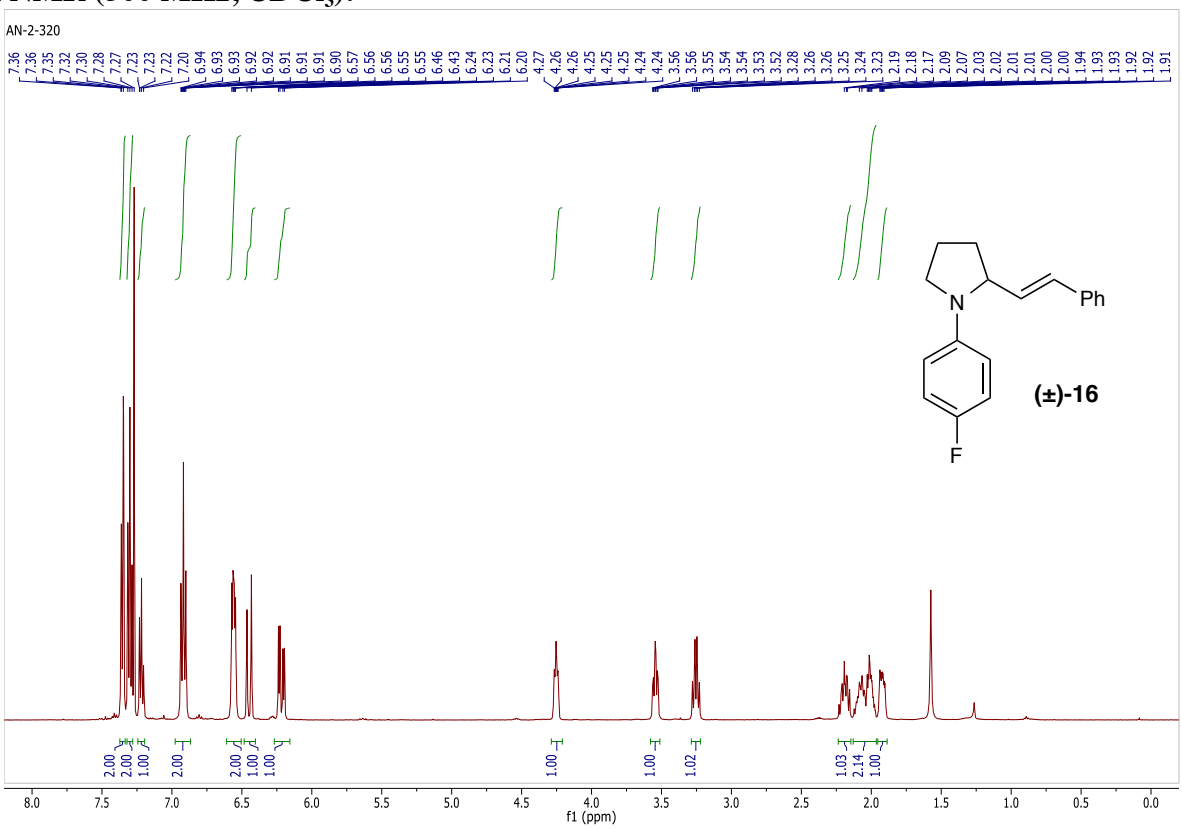
^{1}H NMR (500 MHz, $CDCl_3$):



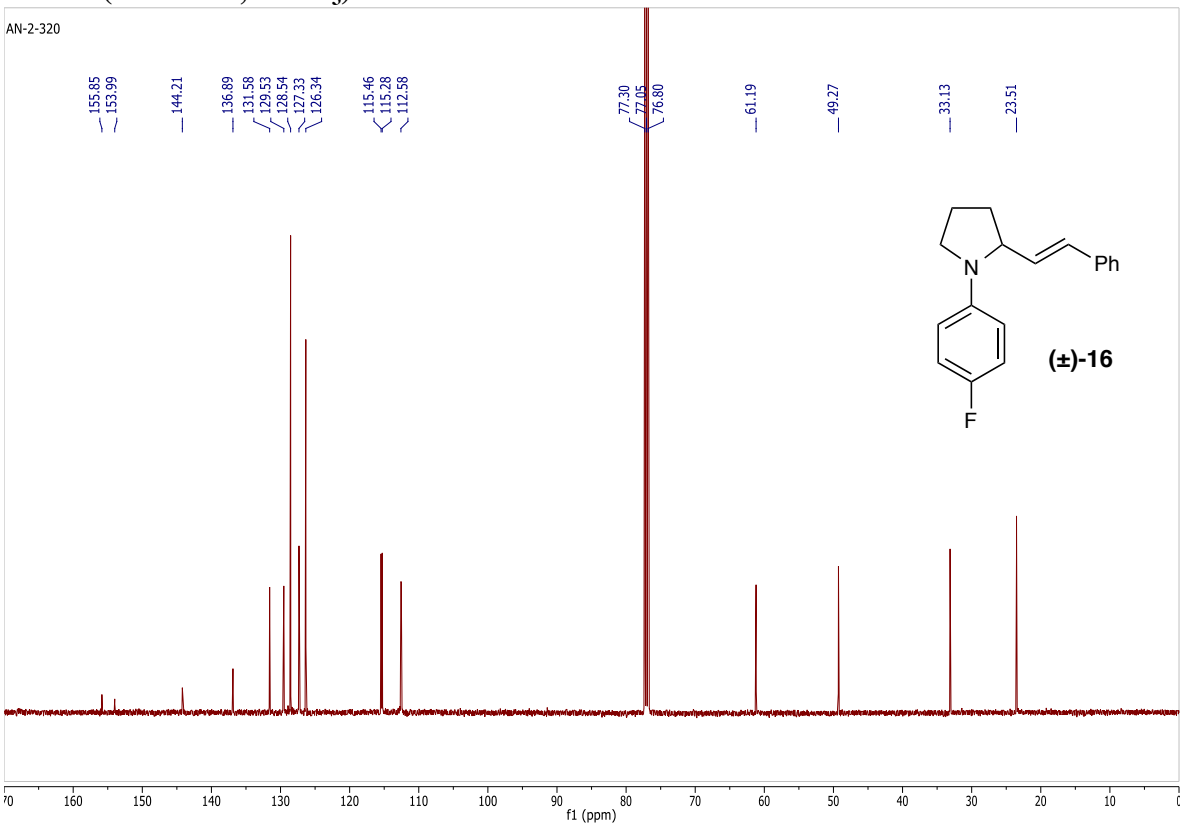
^{13}C NMR (126 MHz, $CDCl_3$):



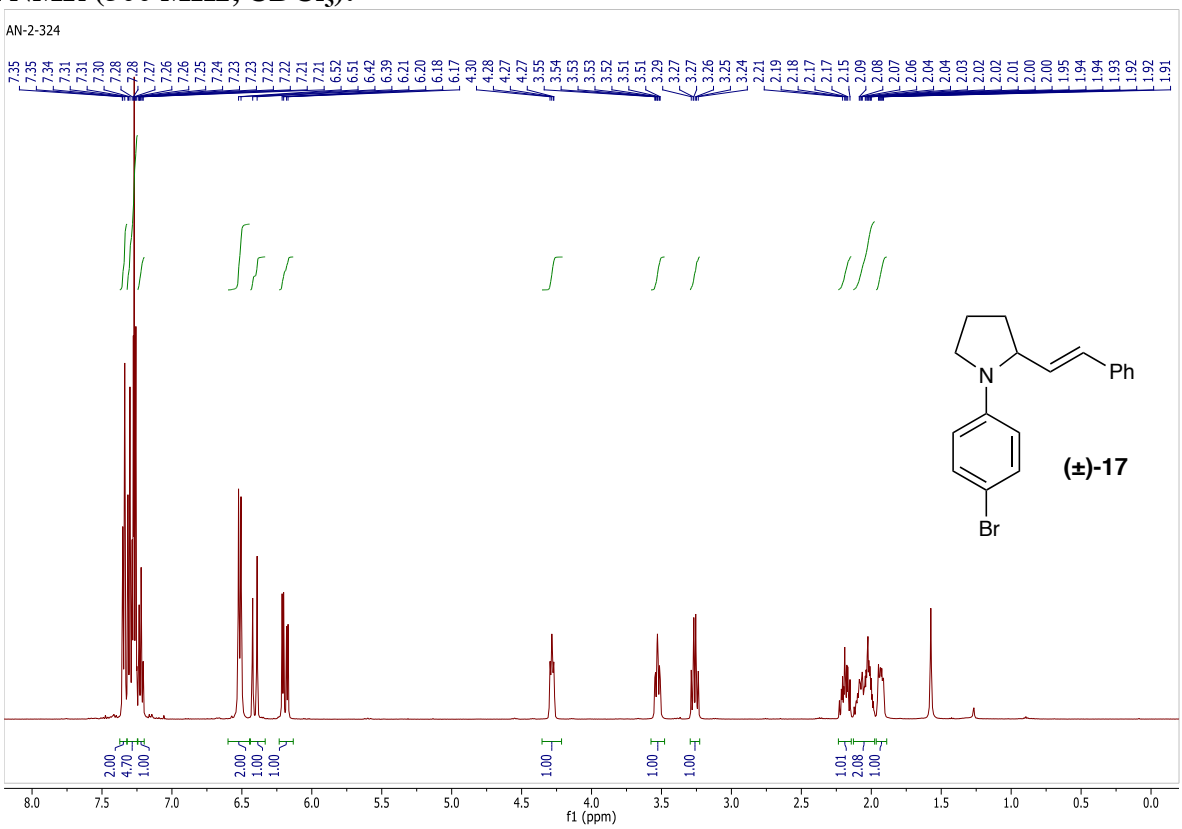
^{1}H NMR (500 MHz, $CDCl_3$):



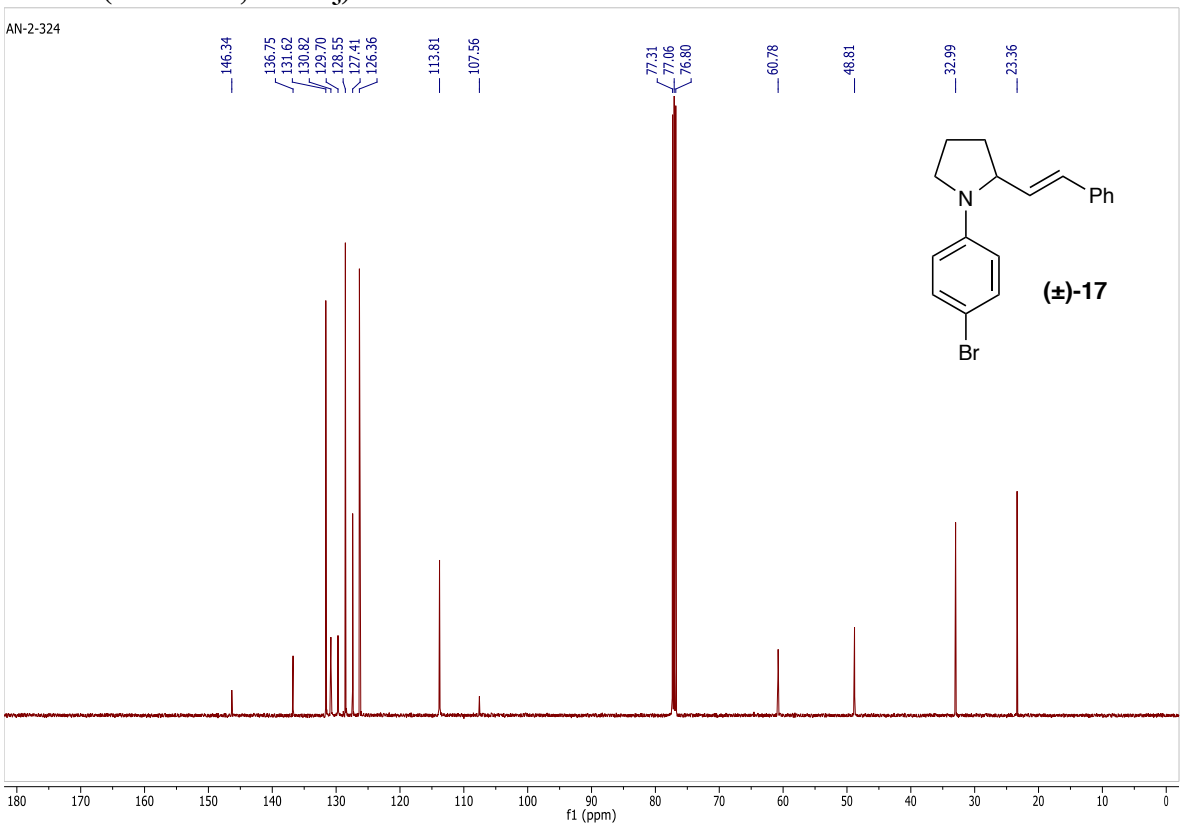
^{13}C NMR (126 MHz, $CDCl_3$):



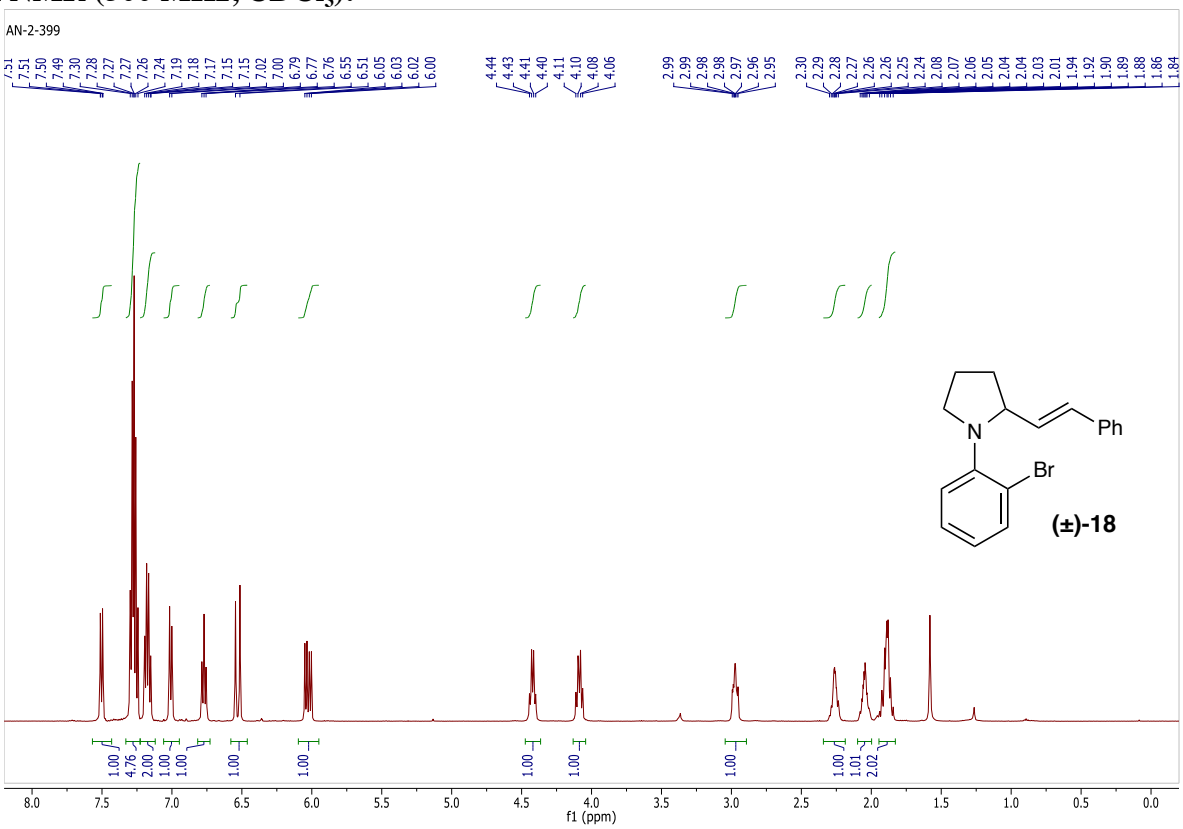
^{1}H NMR (500 MHz, $CDCl_3$):



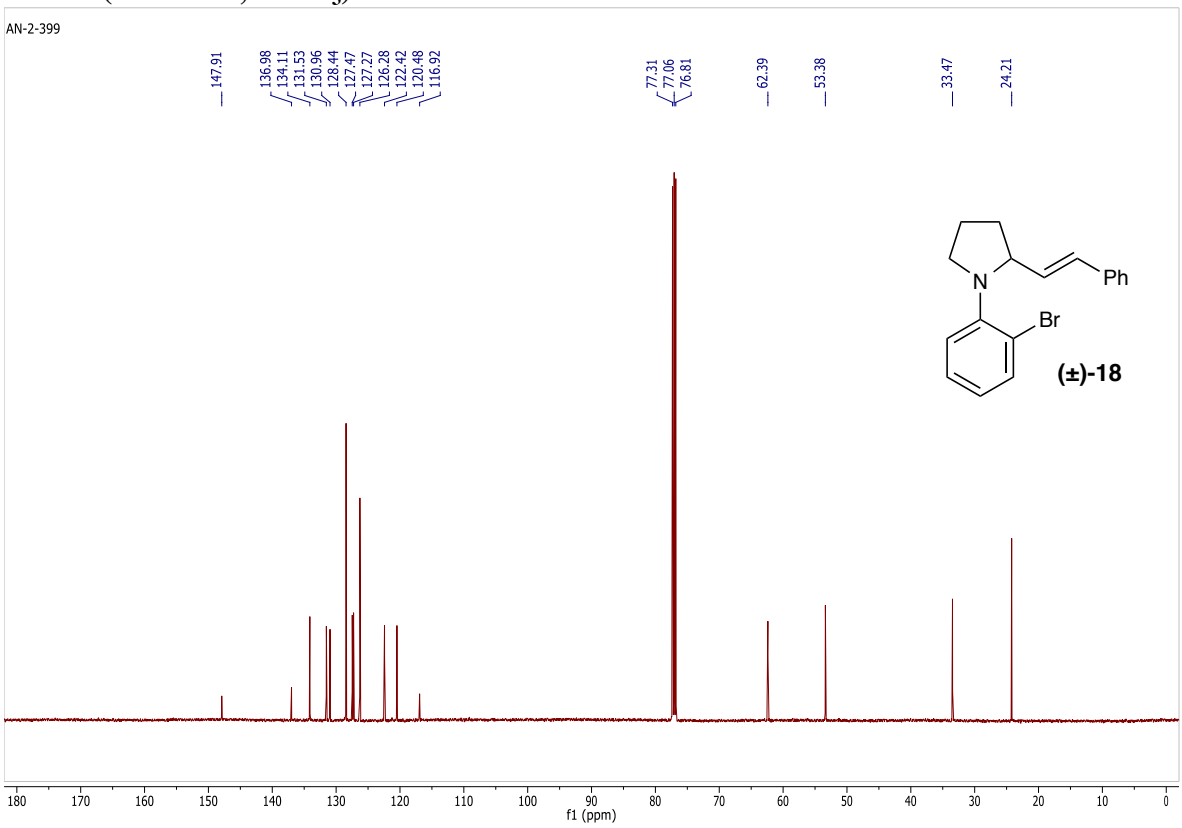
^{13}C NMR (126 MHz, $CDCl_3$):



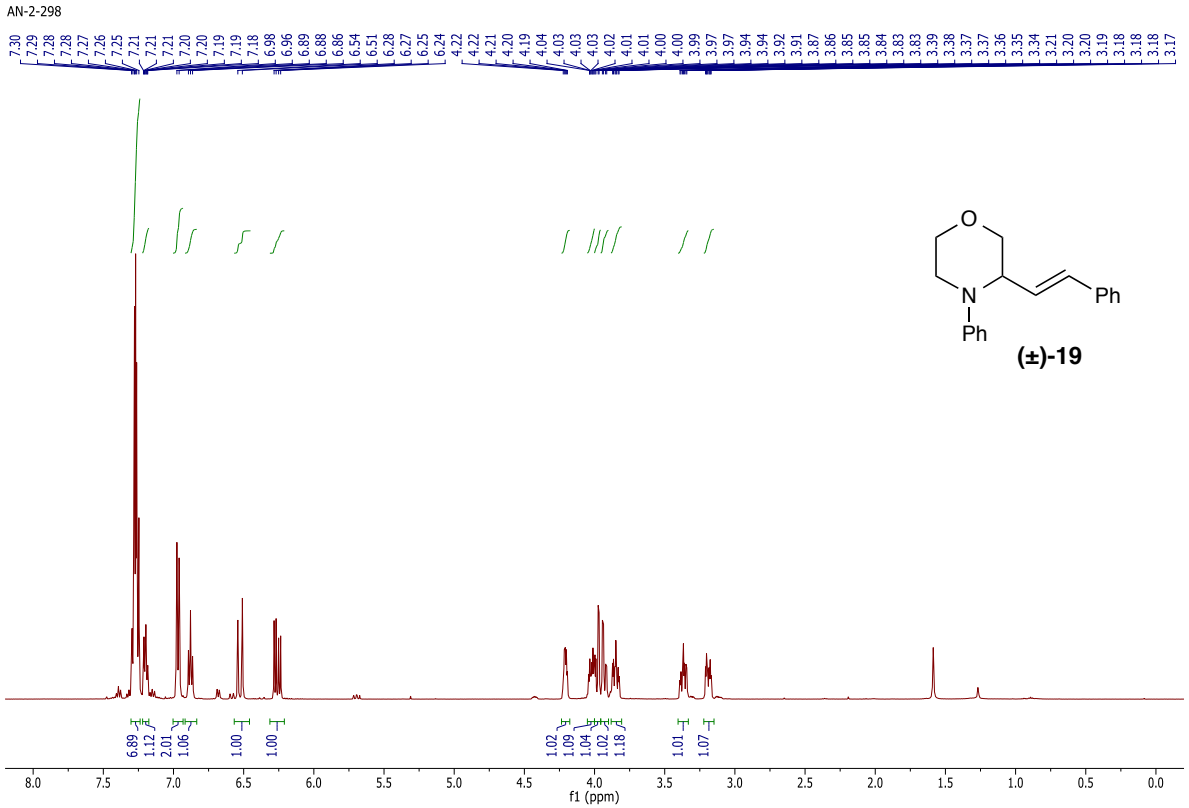
^{1}H NMR (500 MHz, $CDCl_3$):



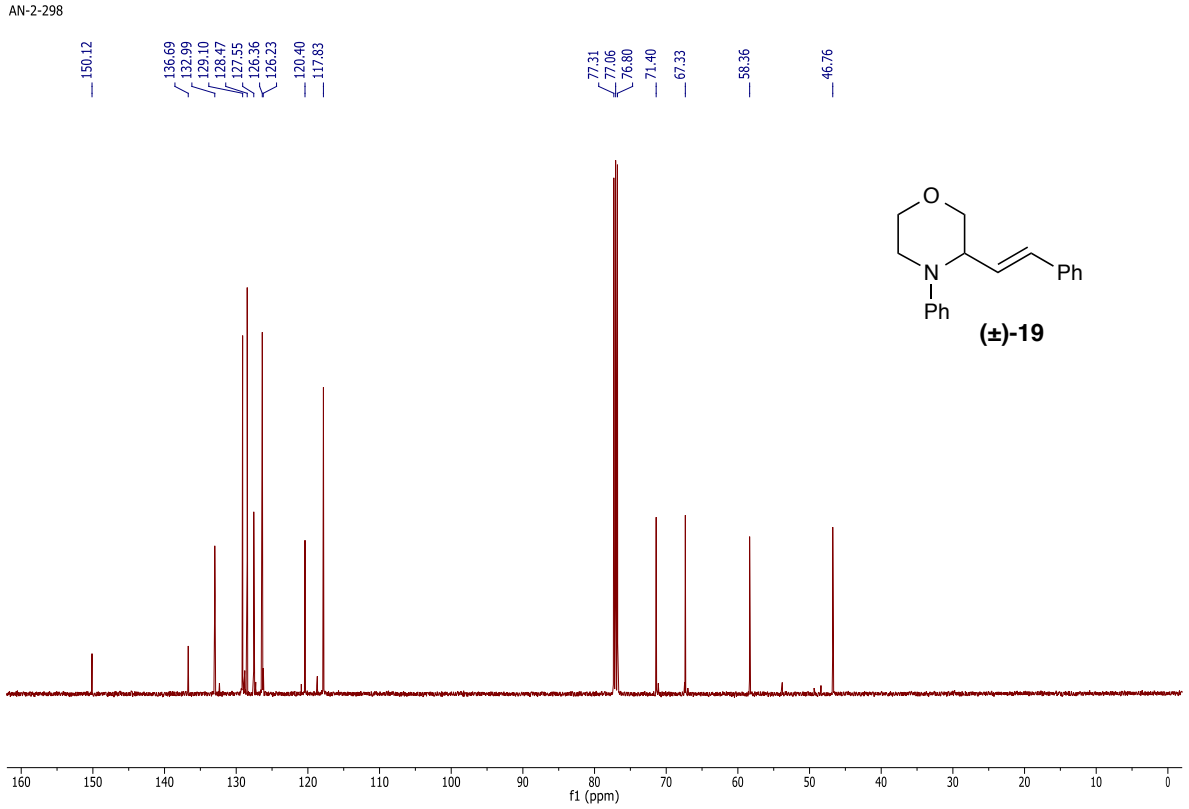
^{13}C NMR (126 MHz, $CDCl_3$):



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



^{13}C NMR (126 MHz, $CDCl_3$):



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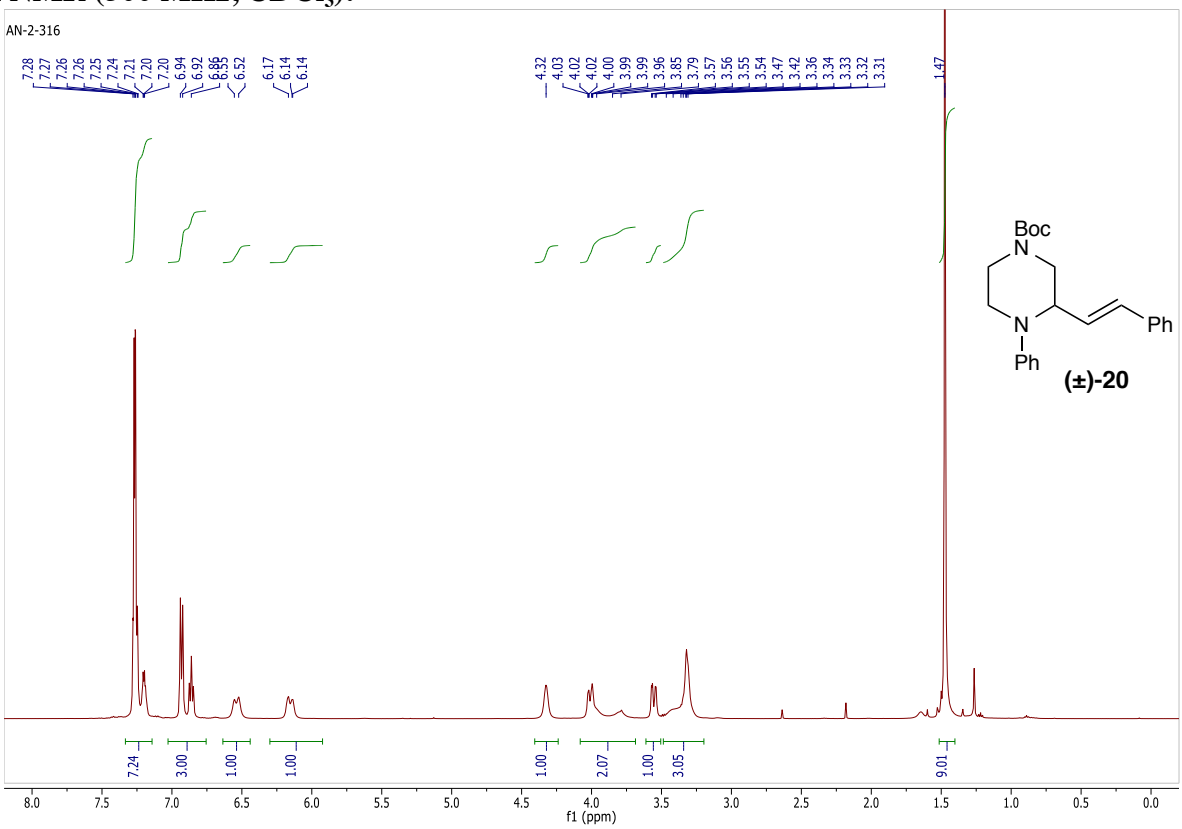
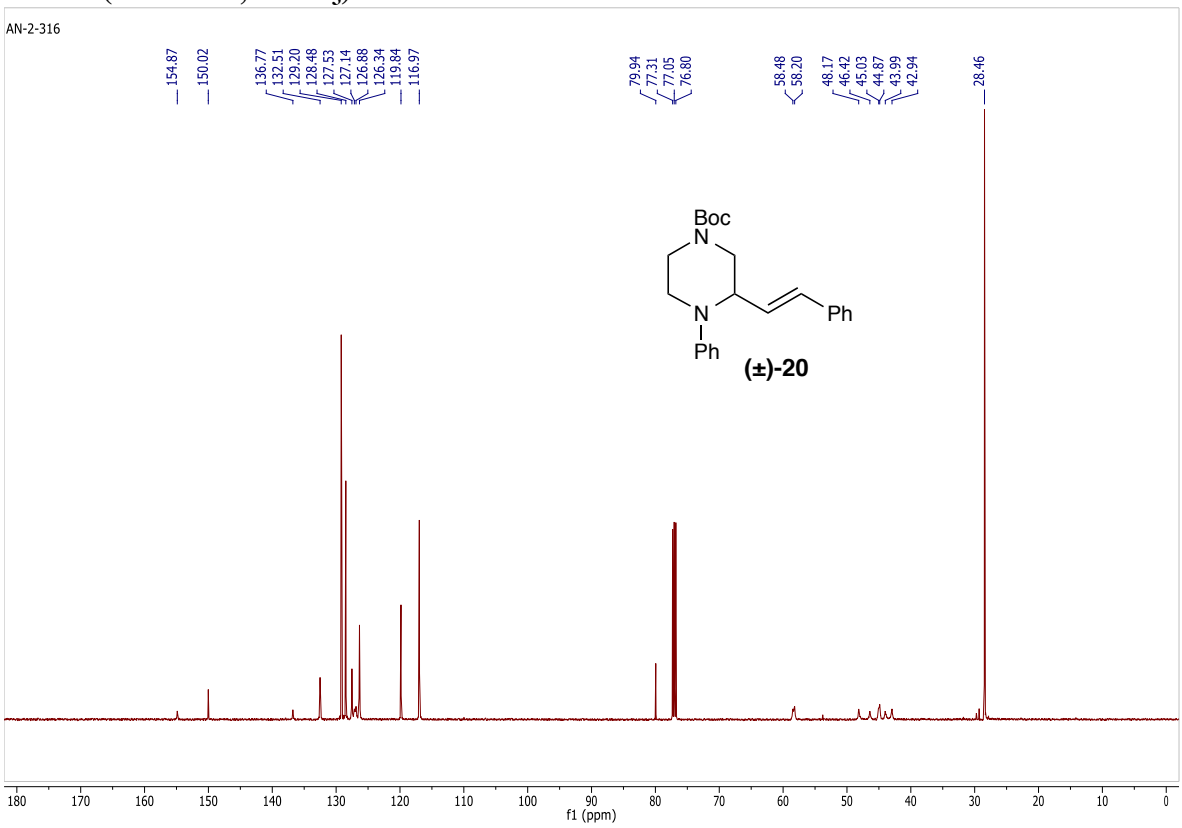


^{13}C NMR (126 MHz, $CDCl_3$):



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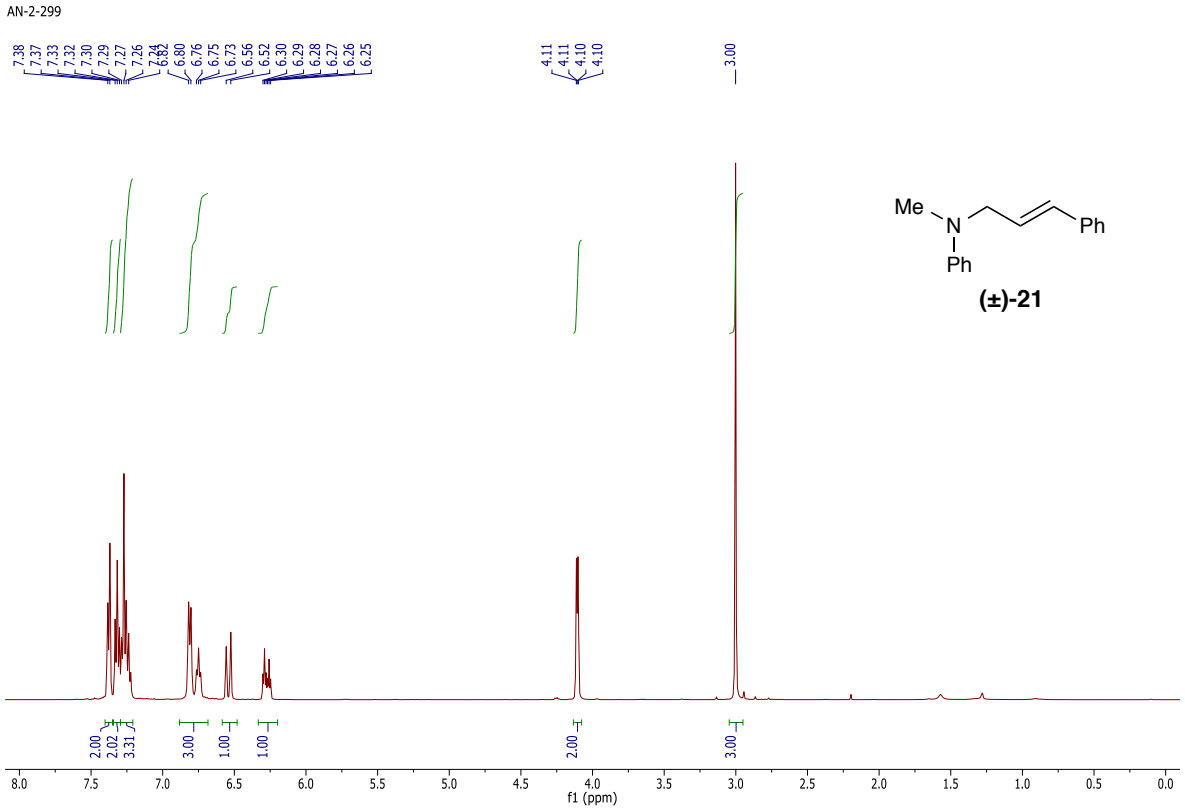

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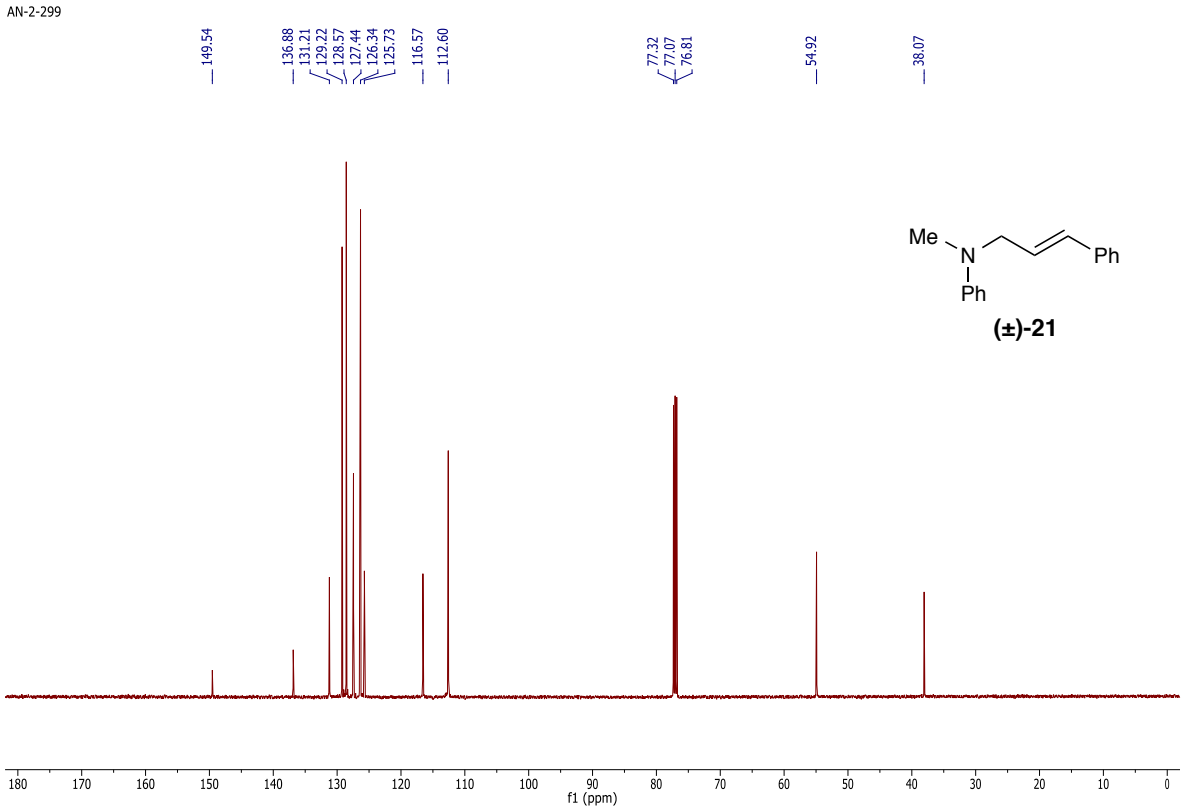

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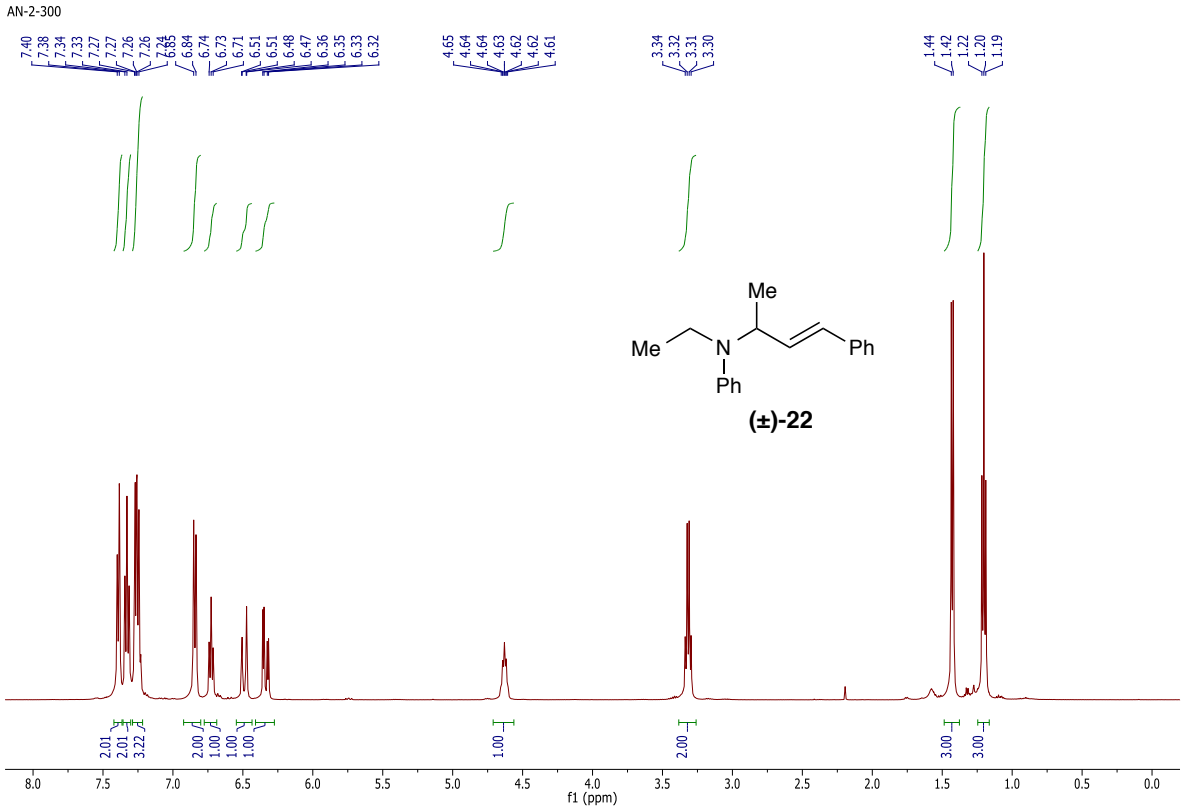

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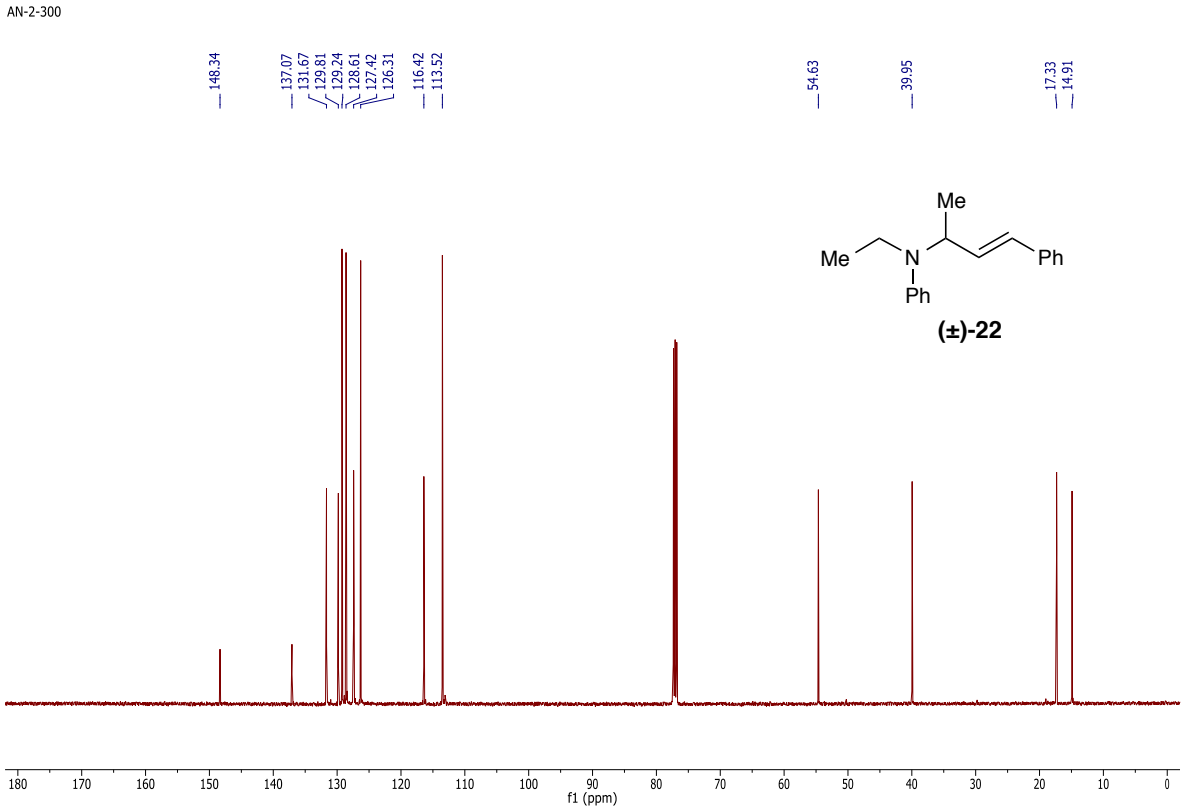

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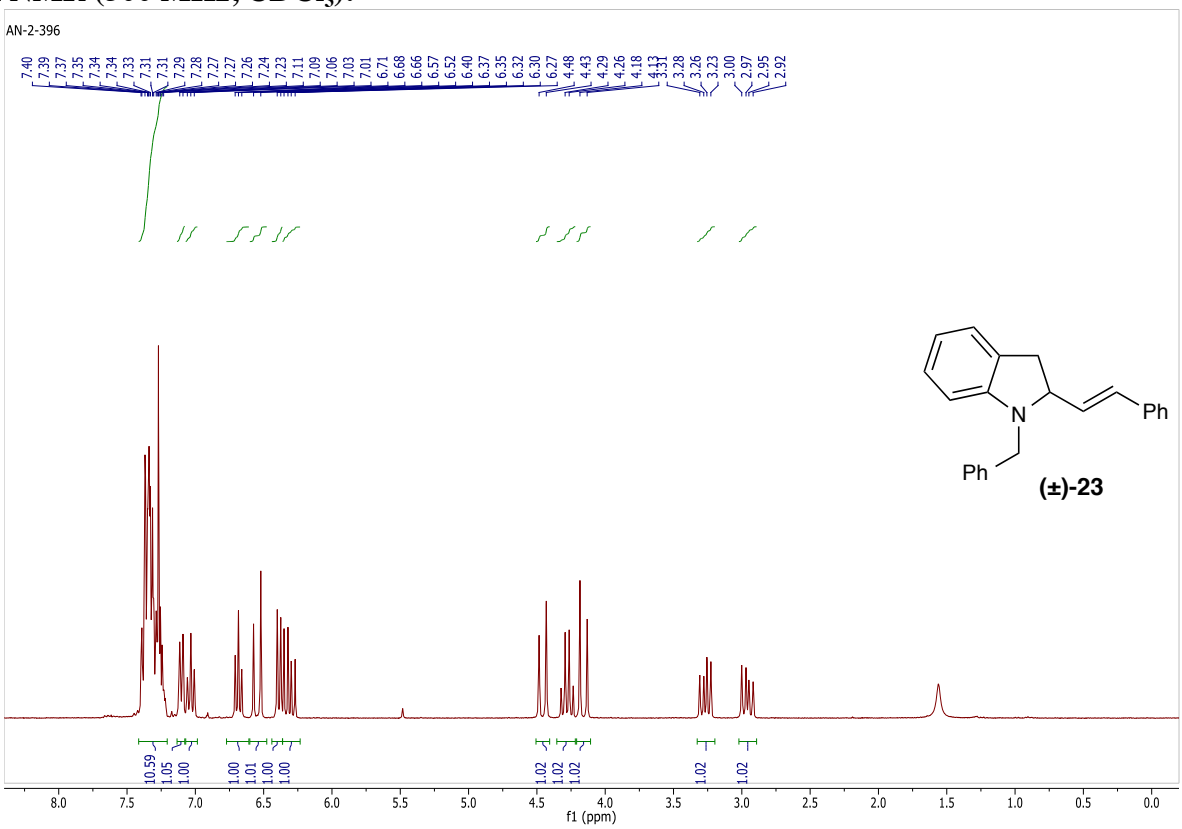

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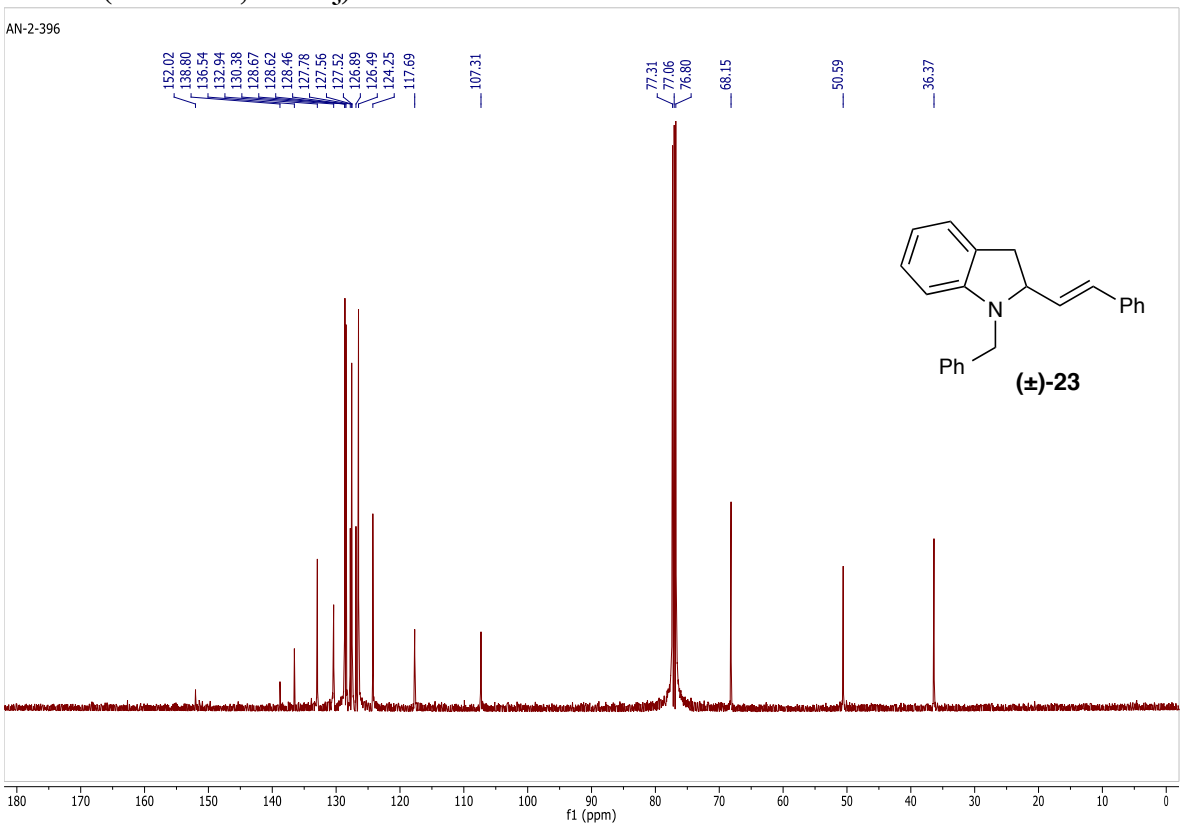

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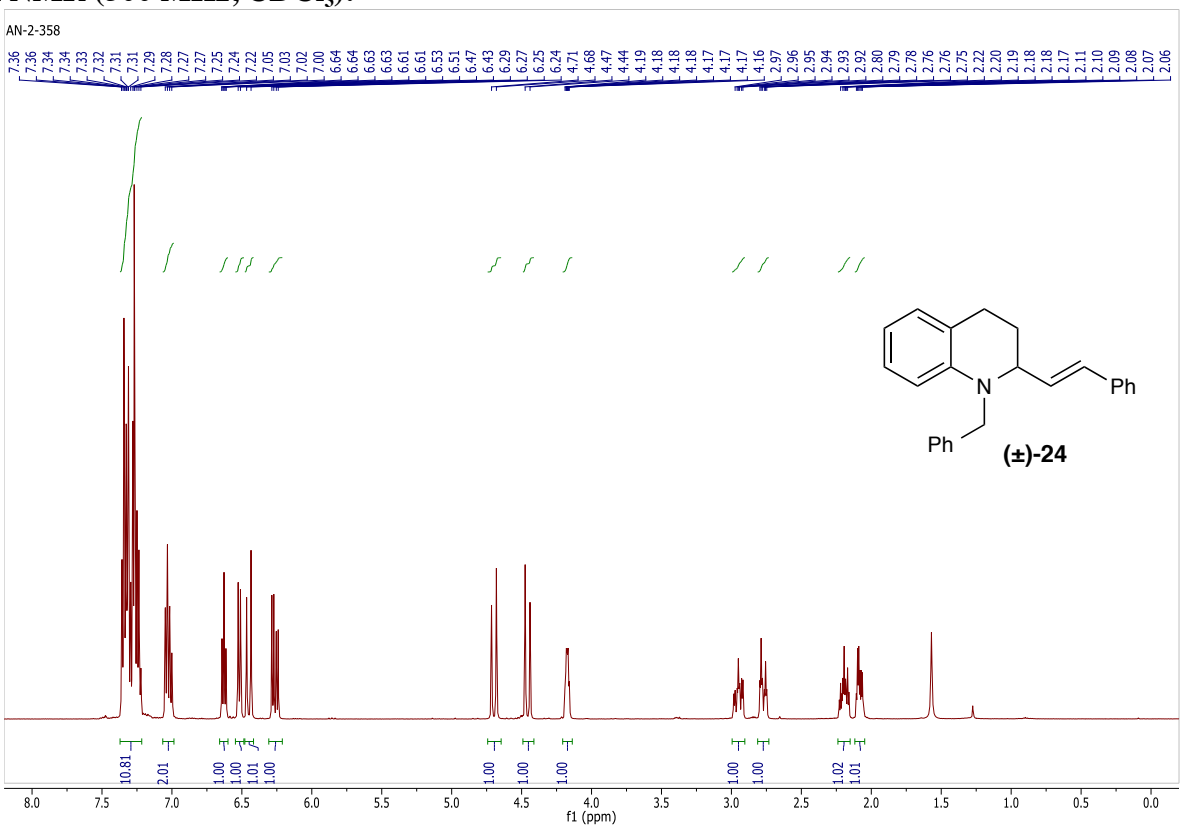

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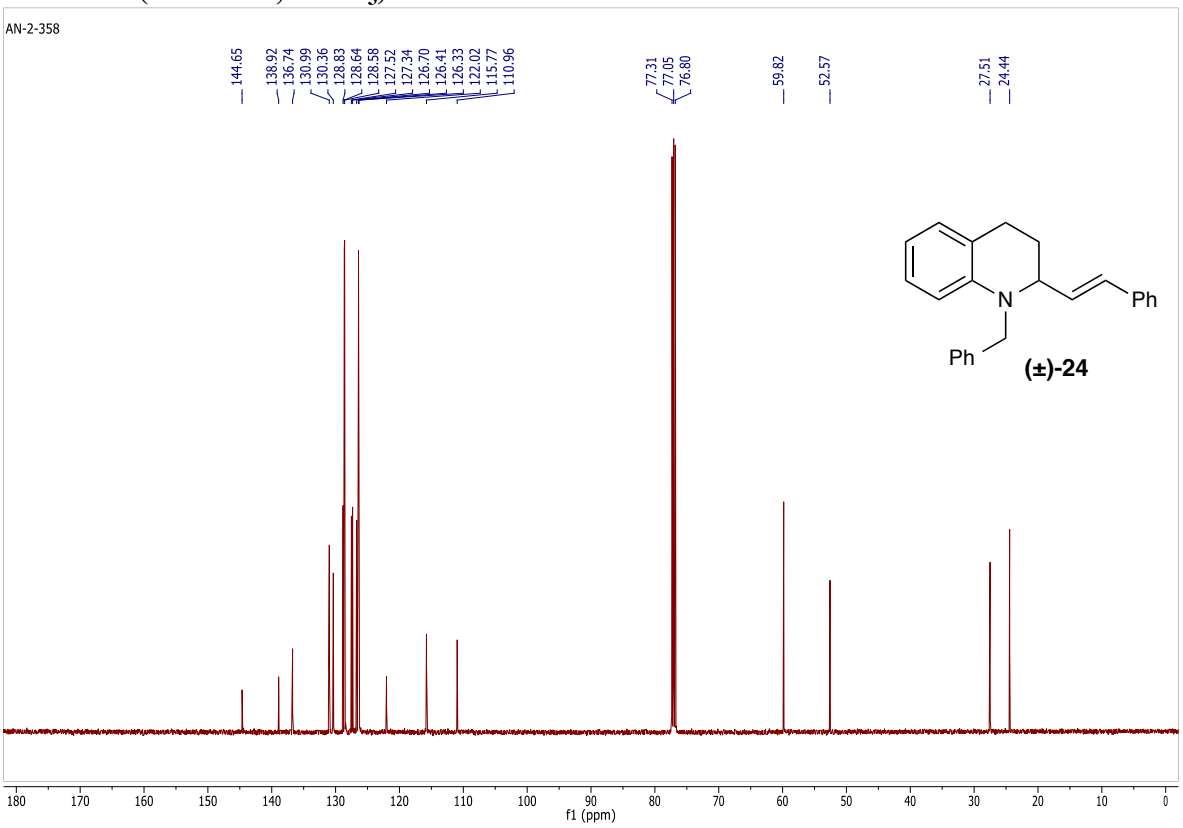

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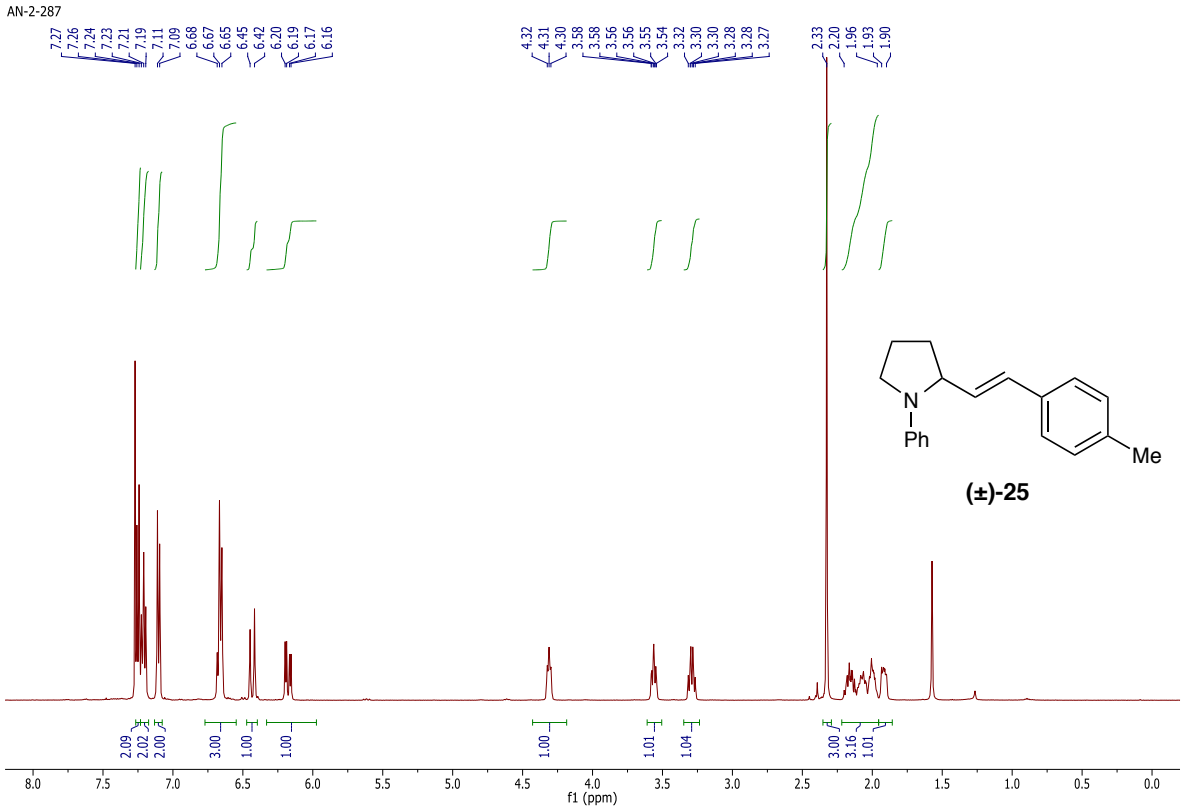

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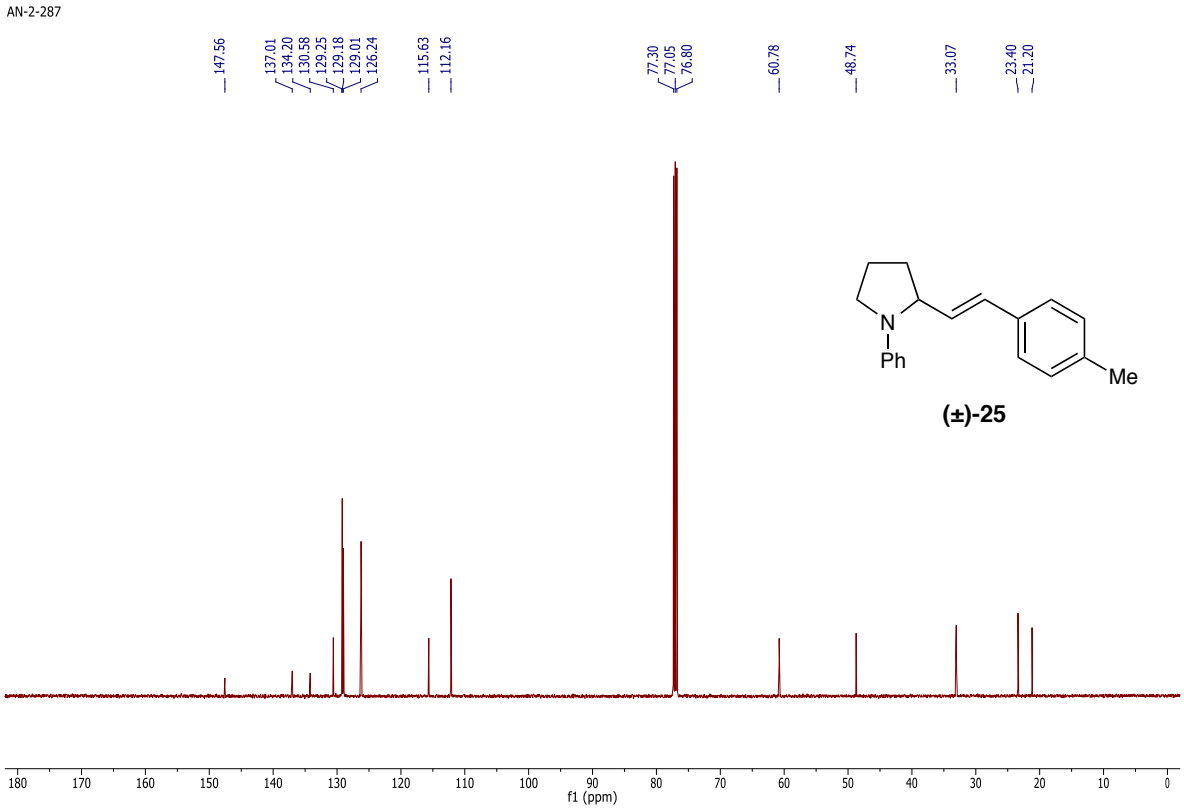

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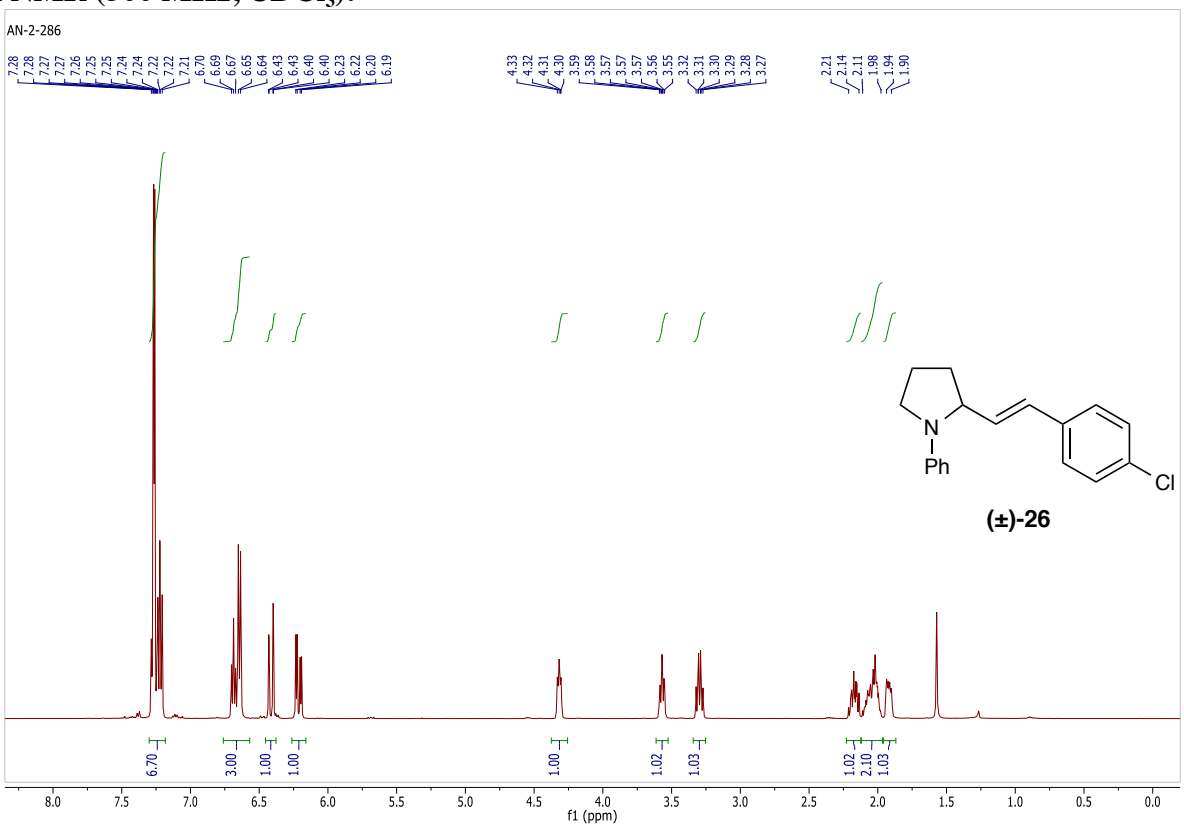

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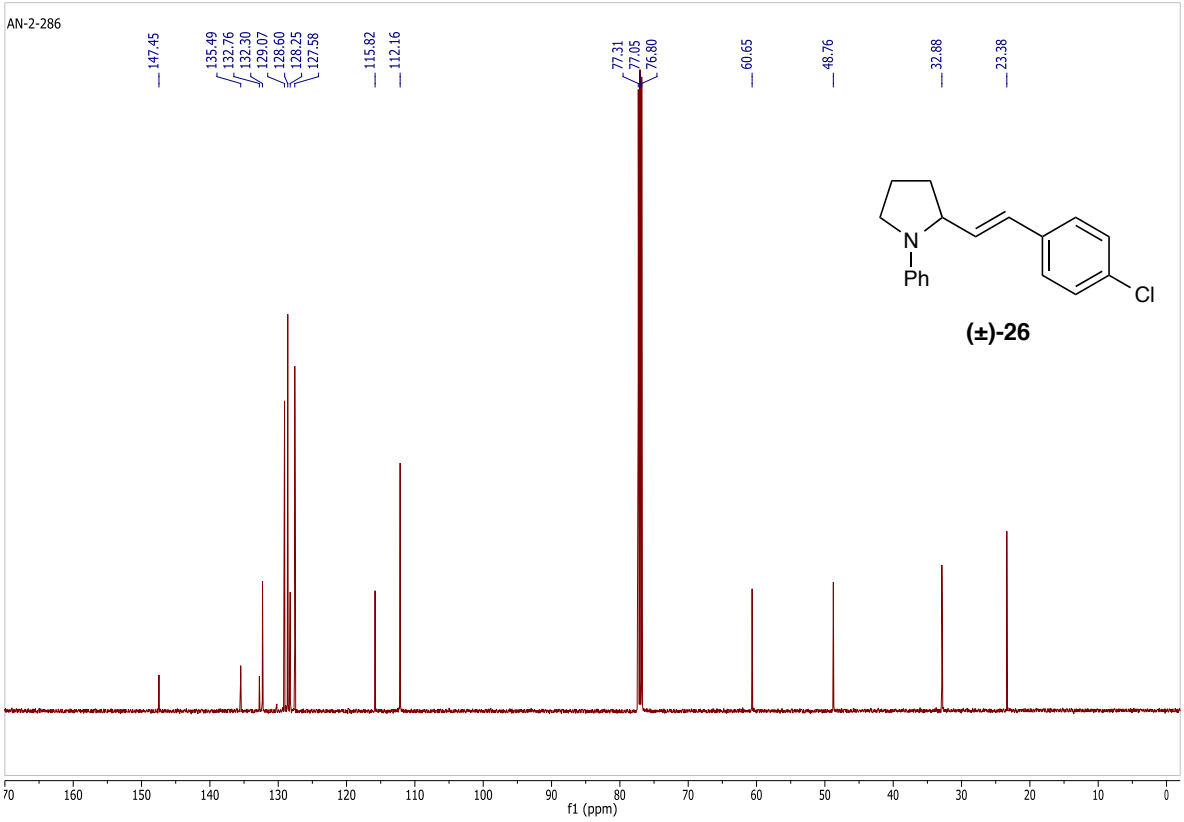

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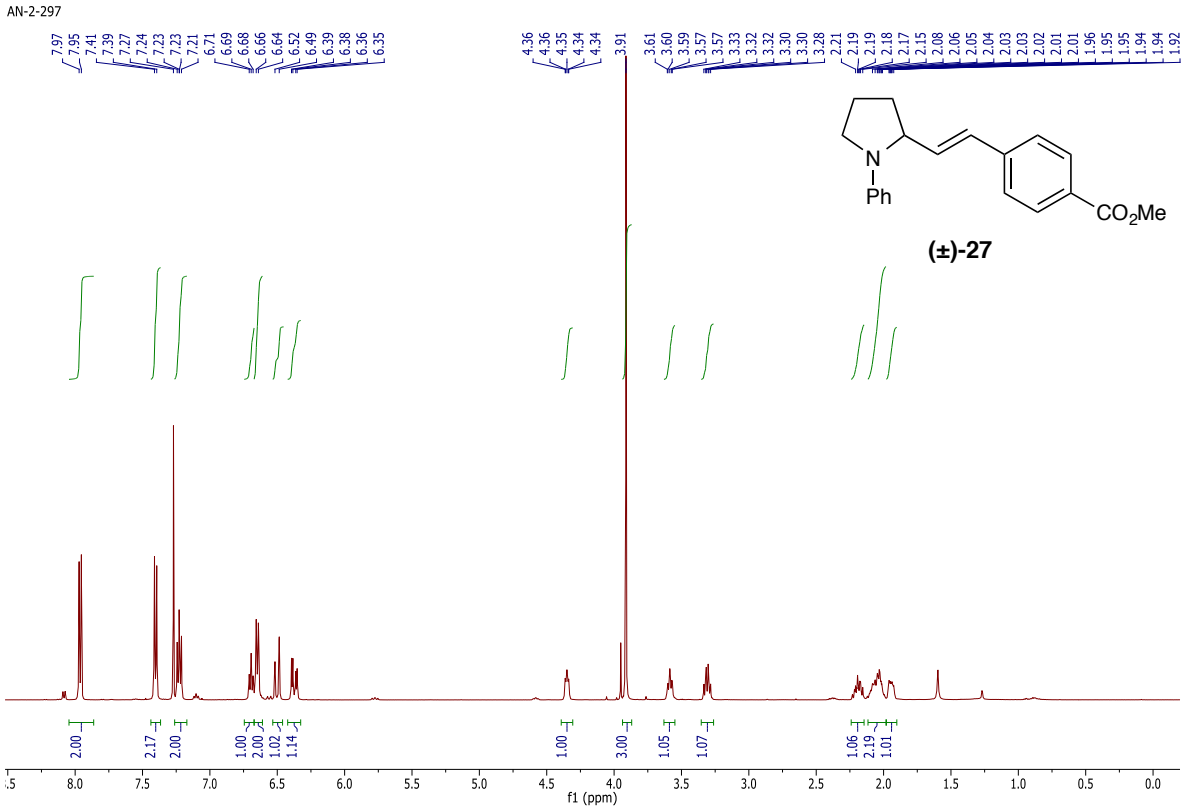

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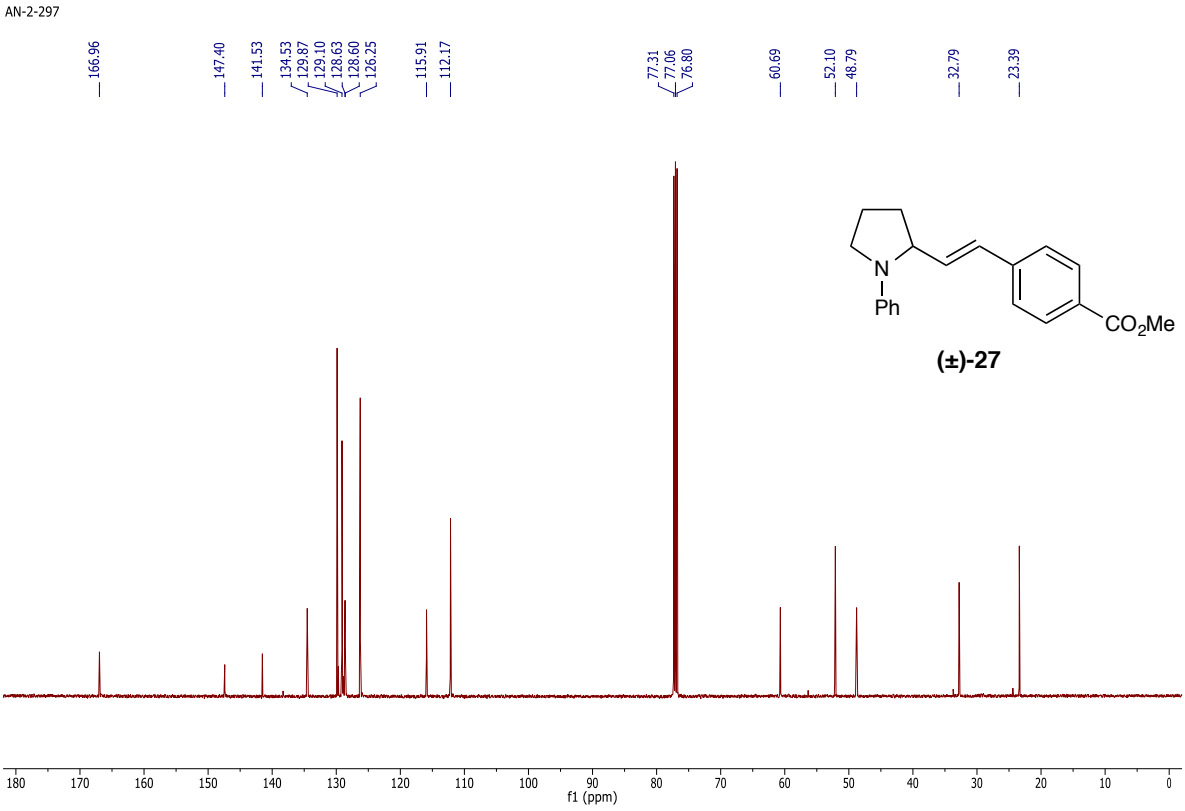

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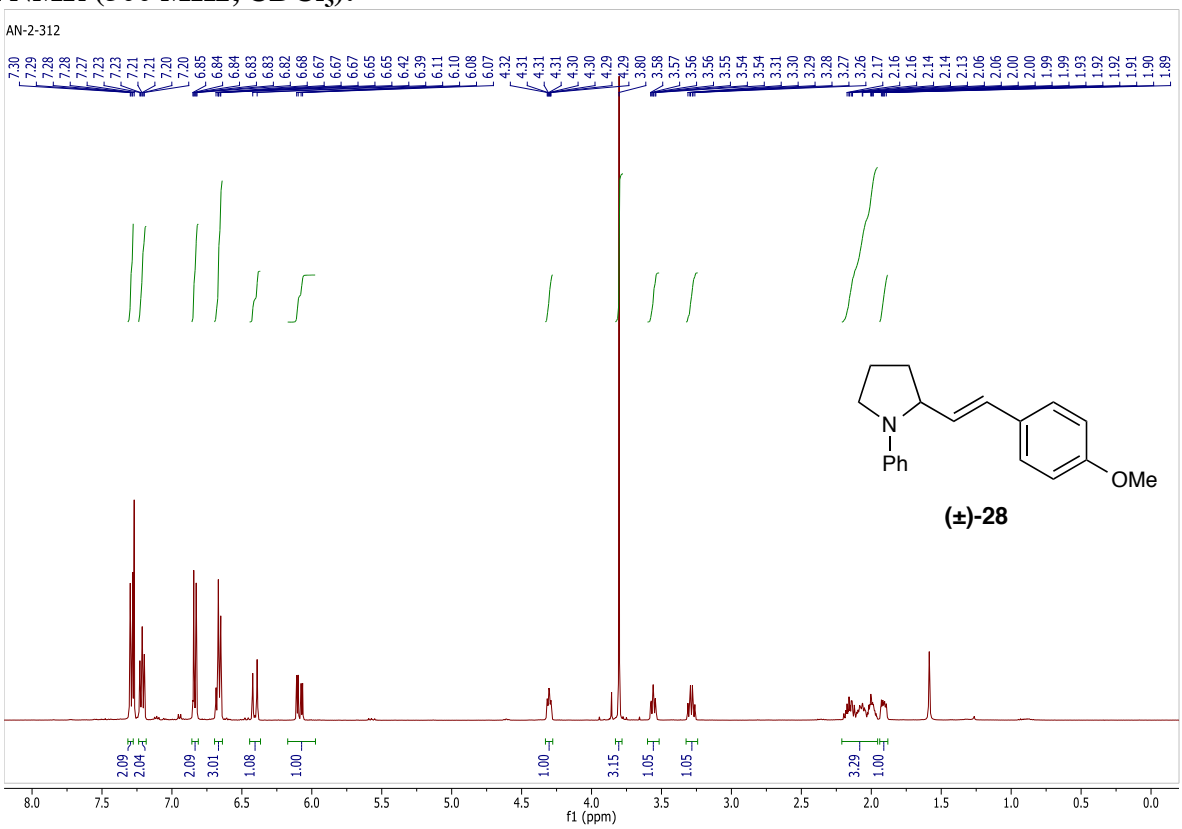

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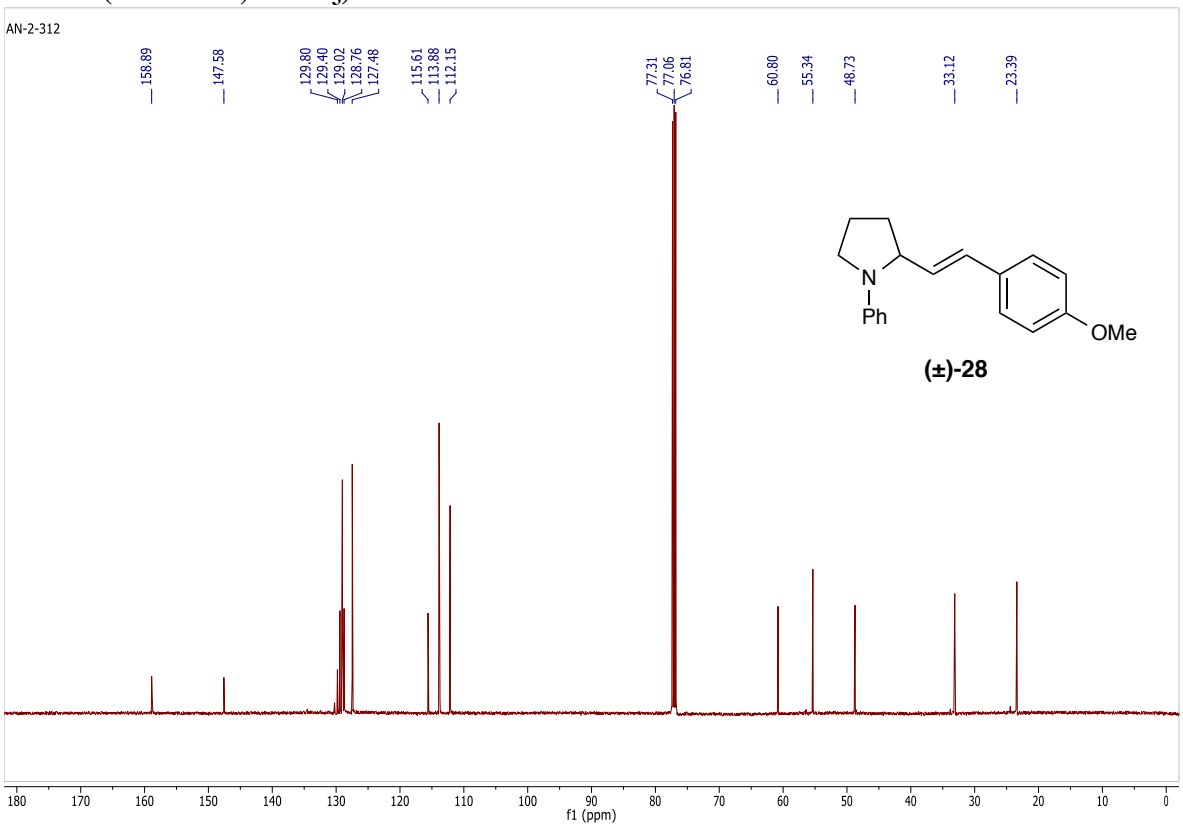

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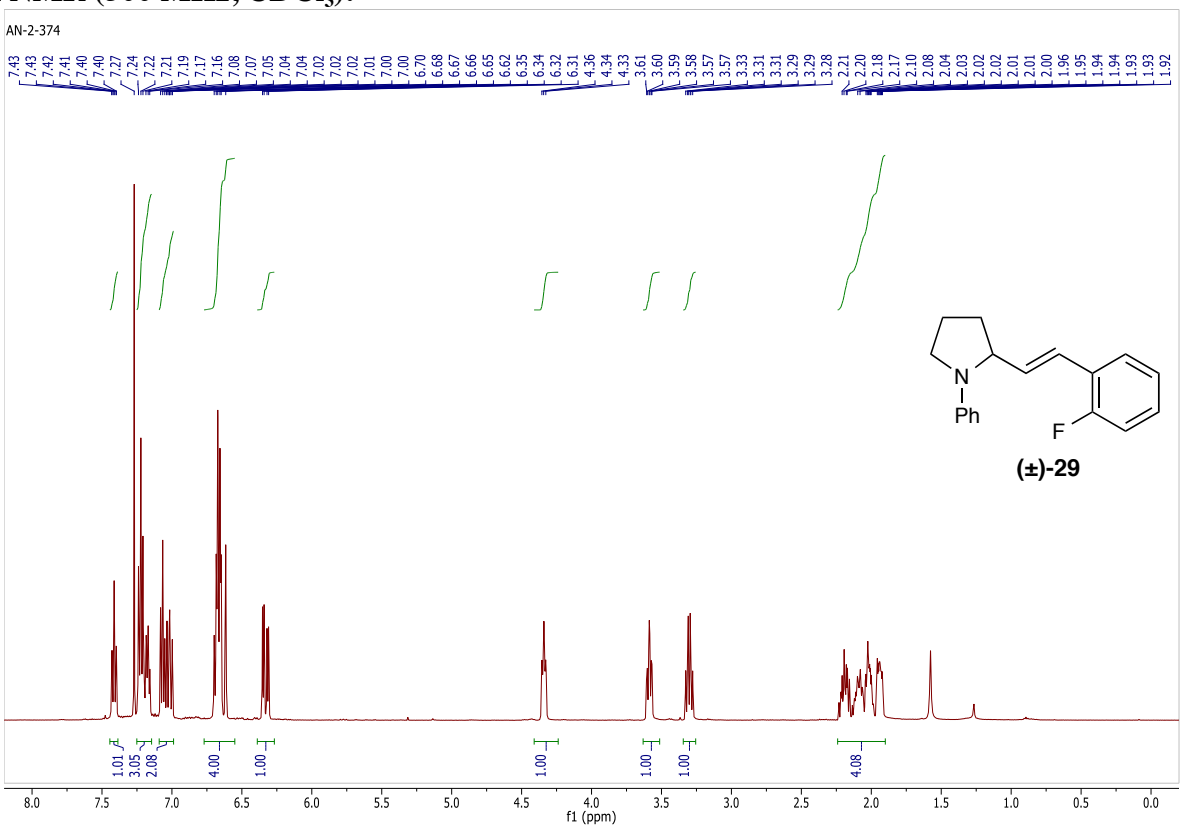

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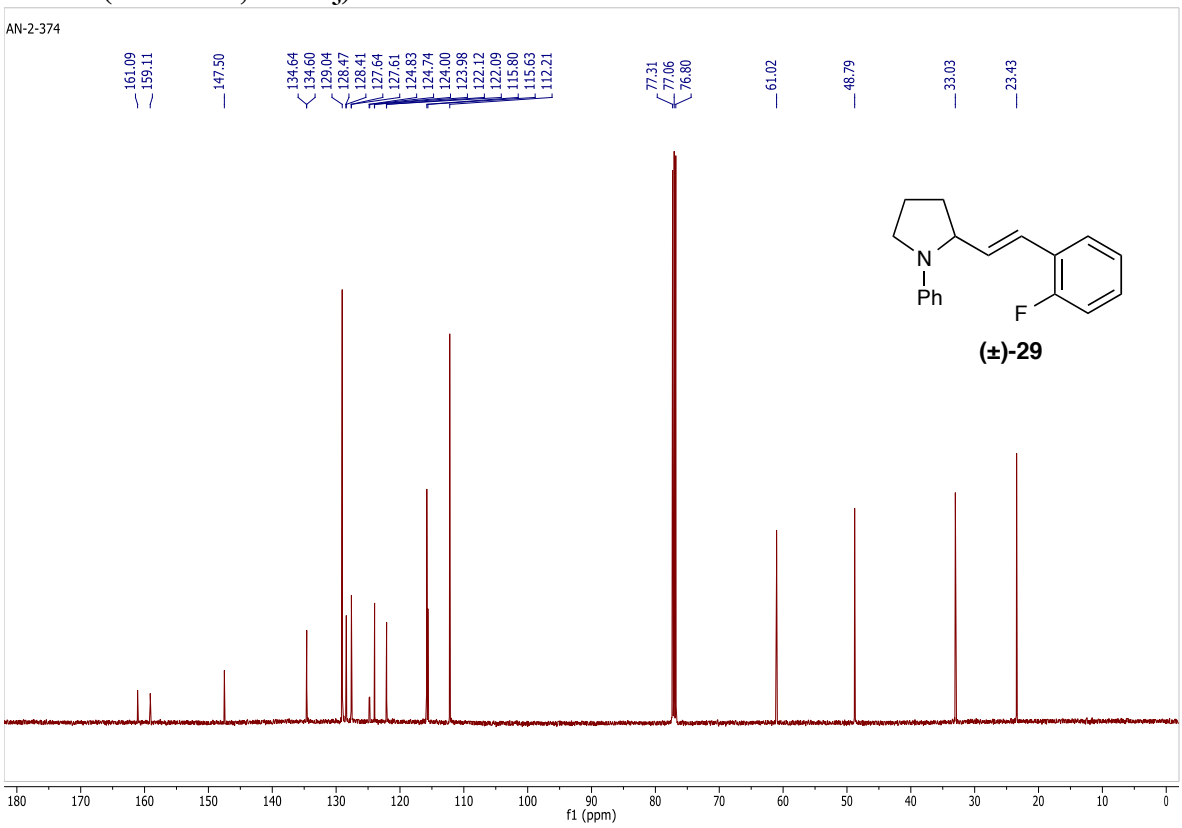

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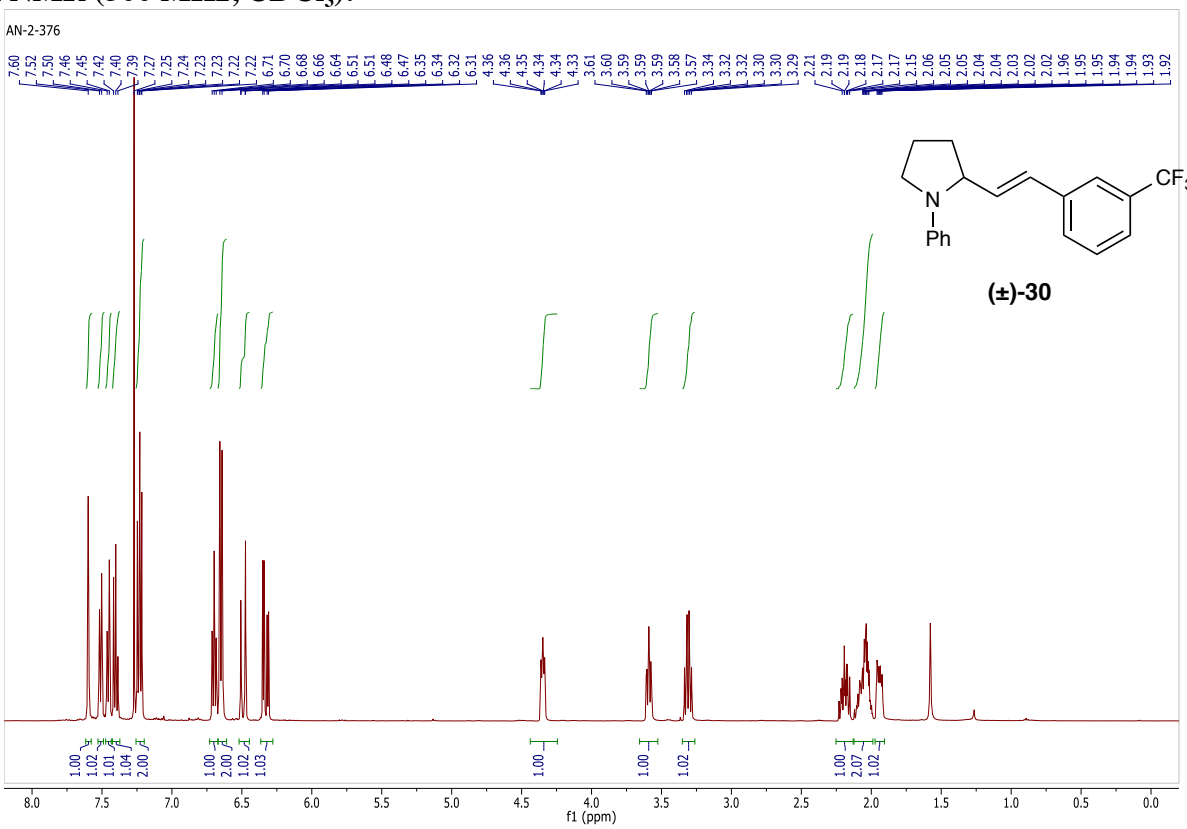

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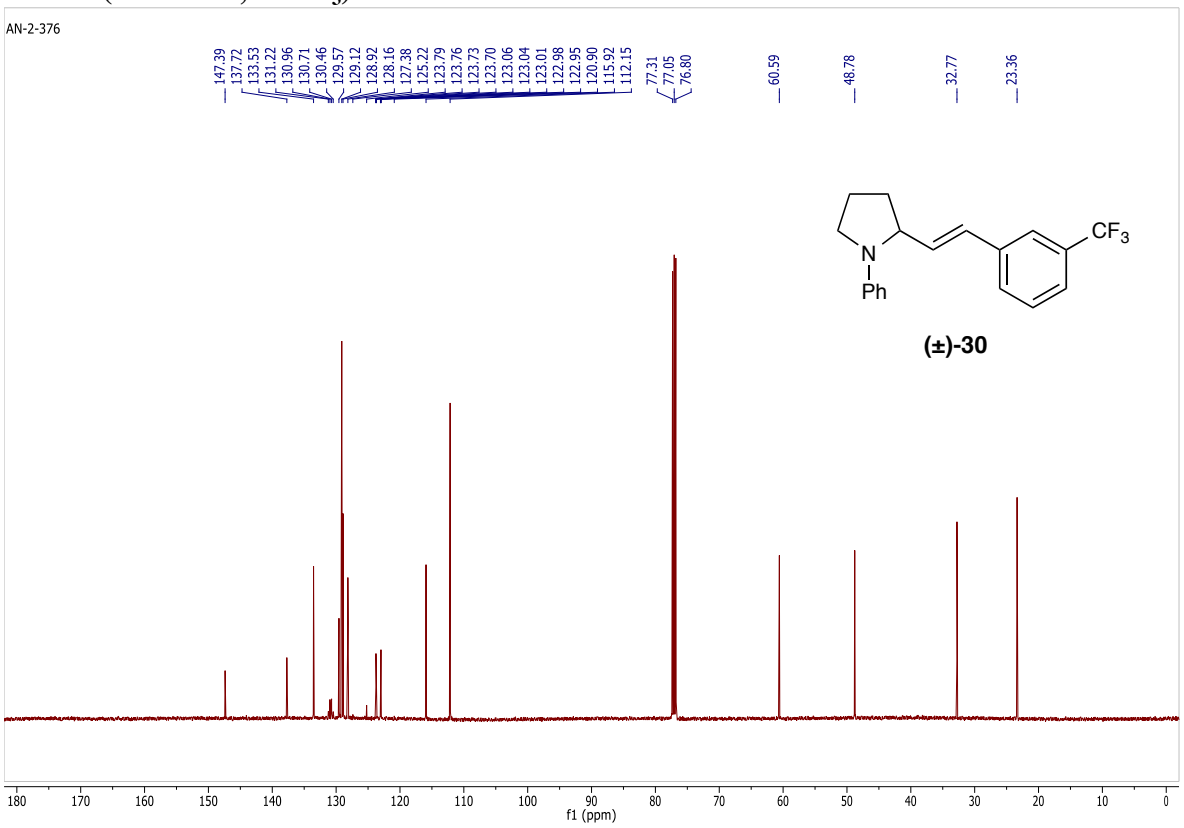

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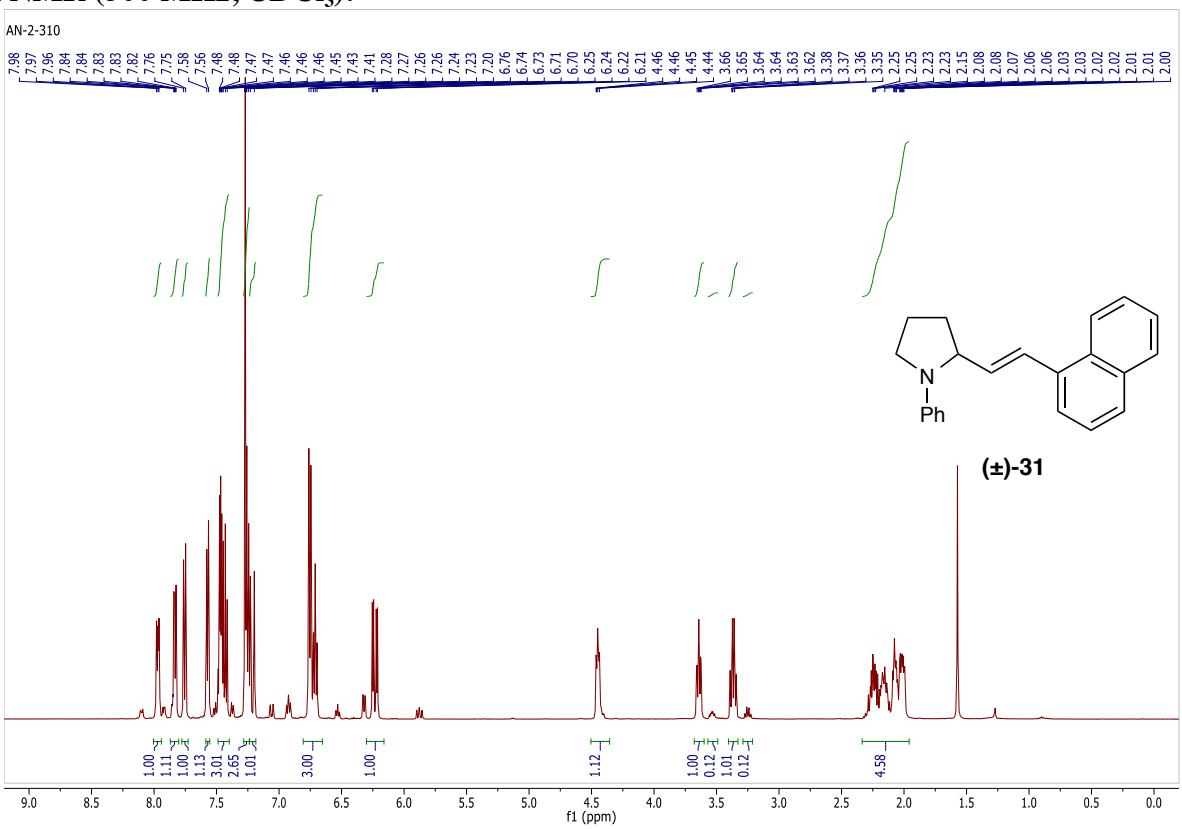

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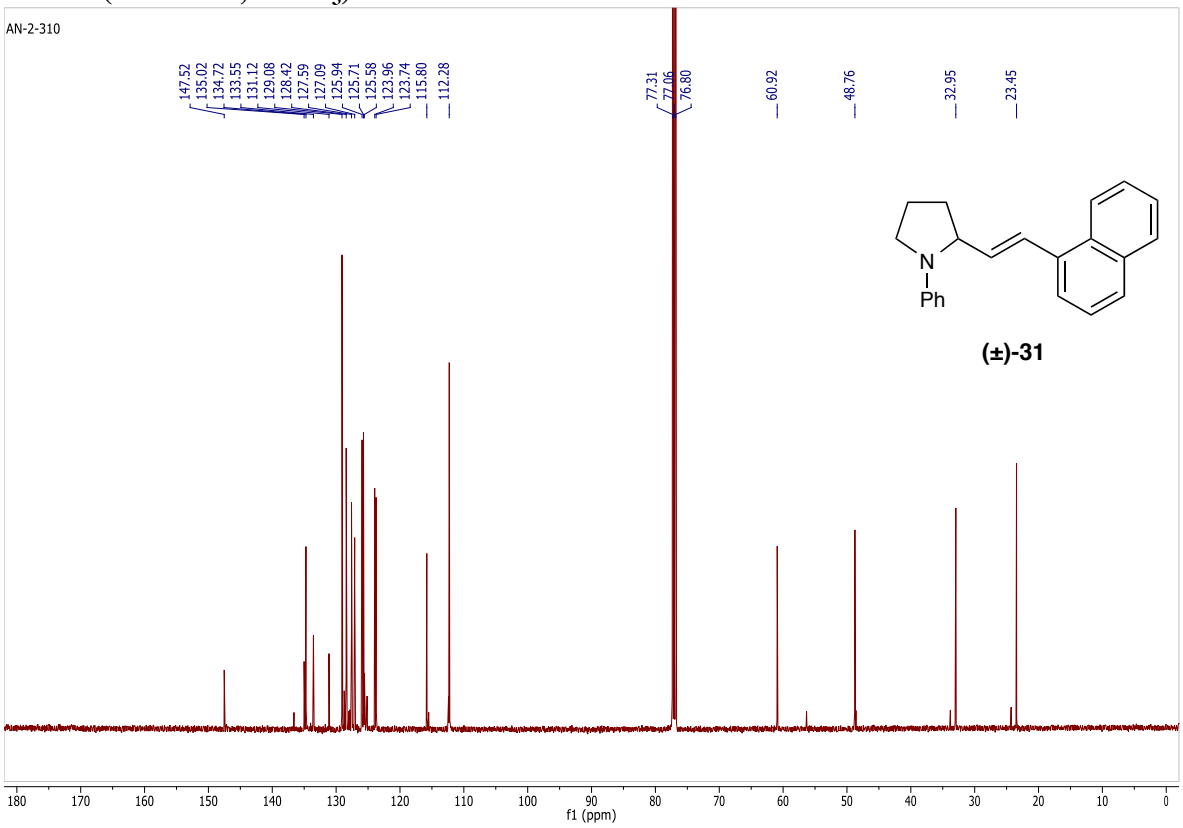

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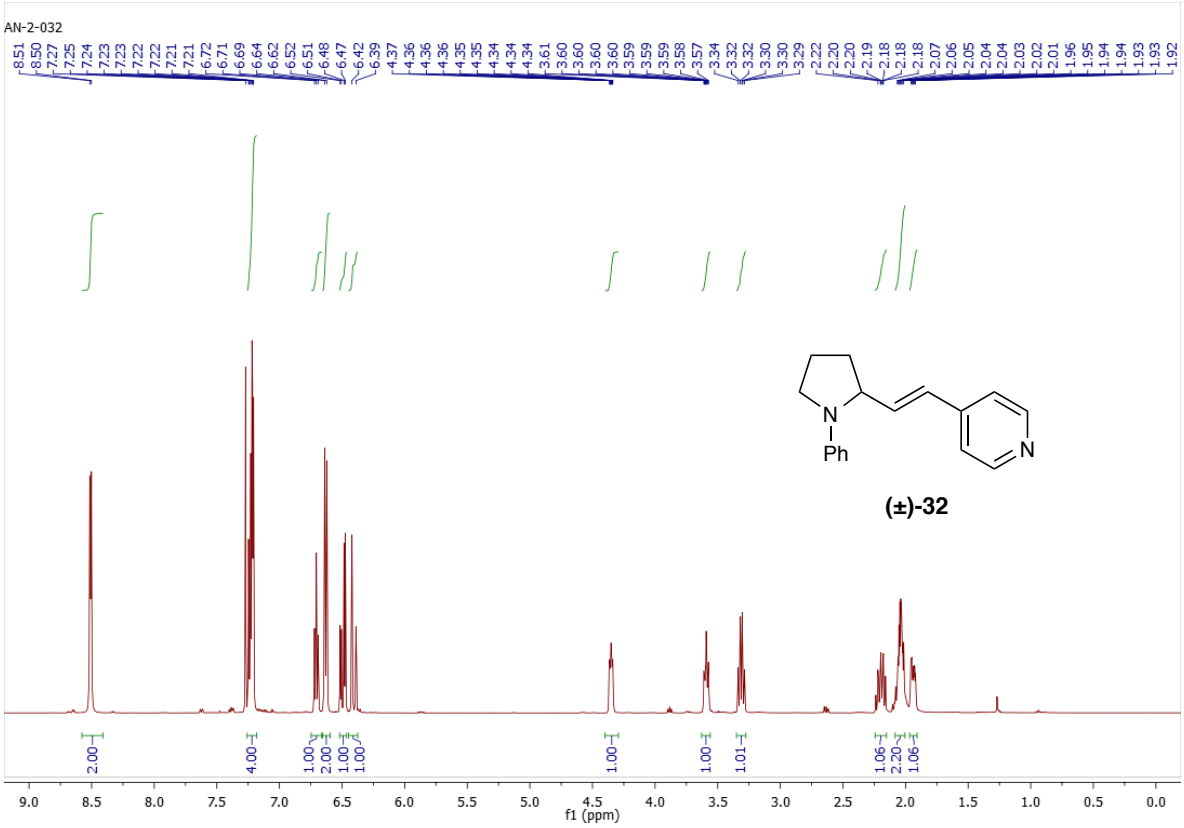

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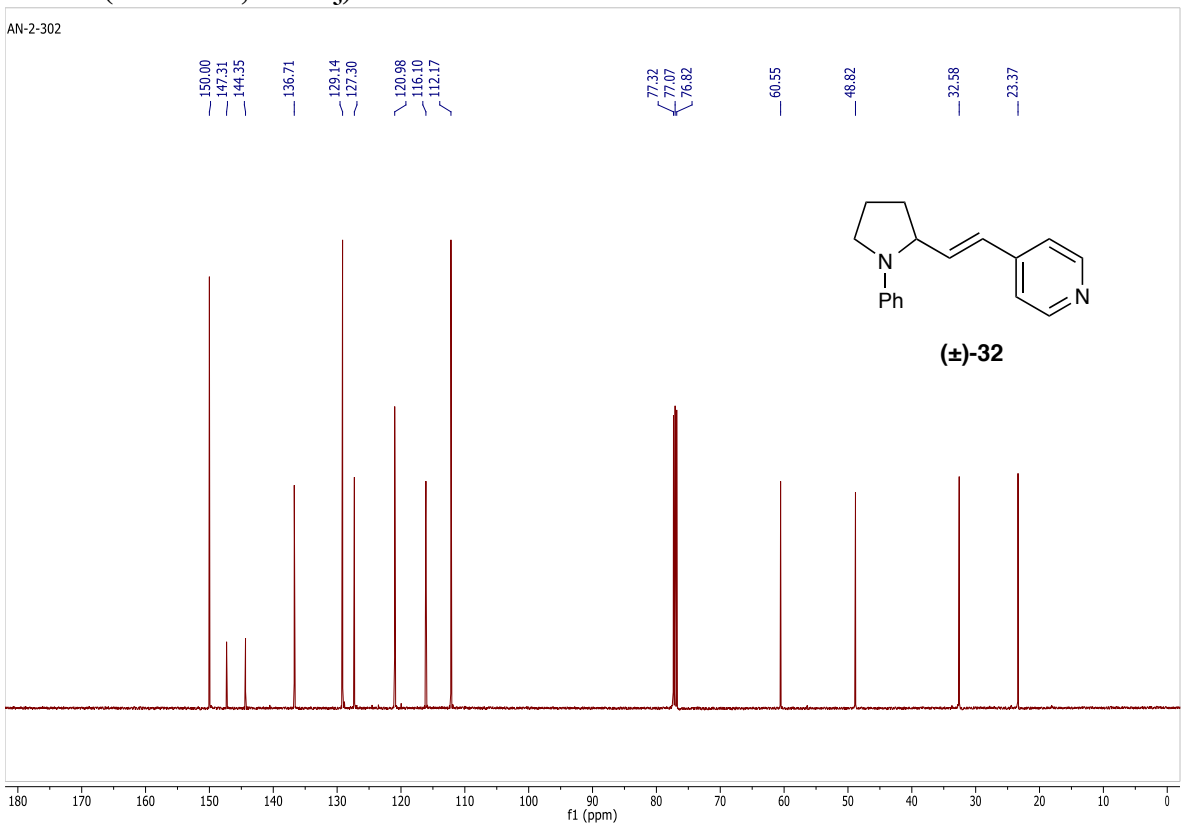

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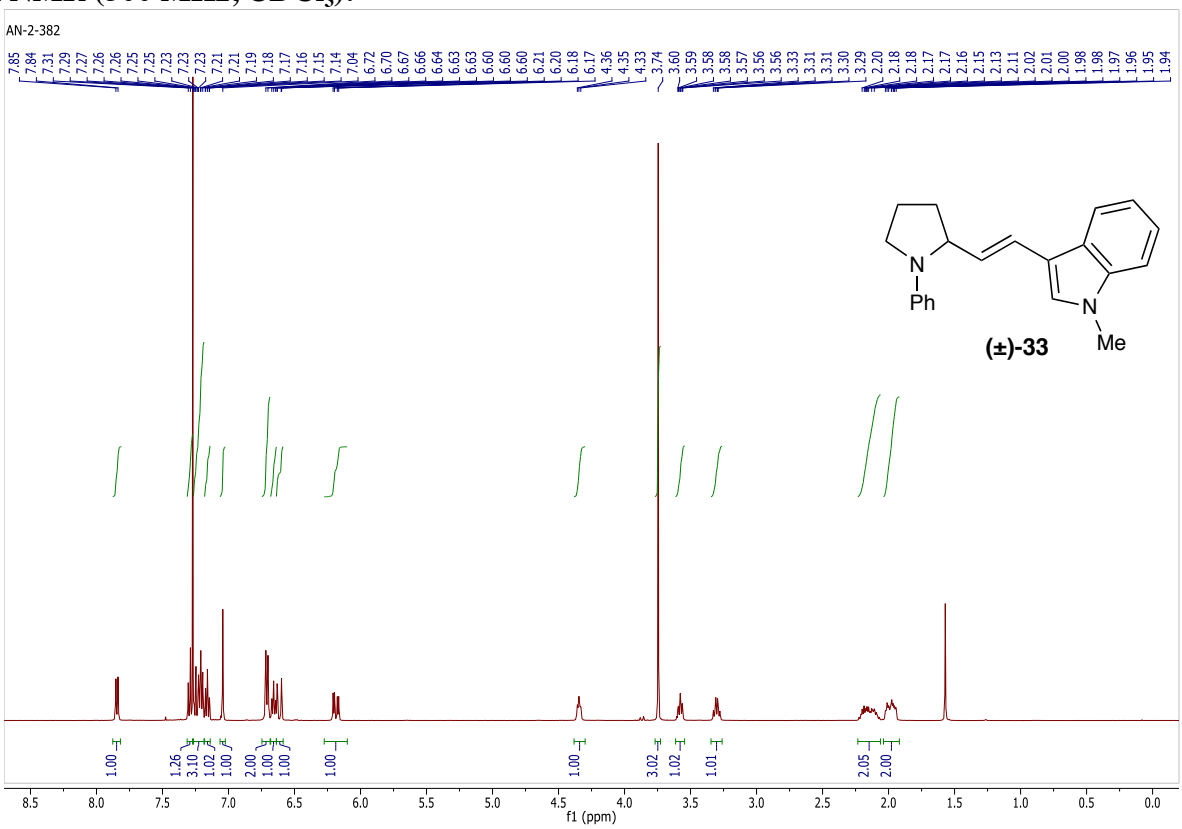

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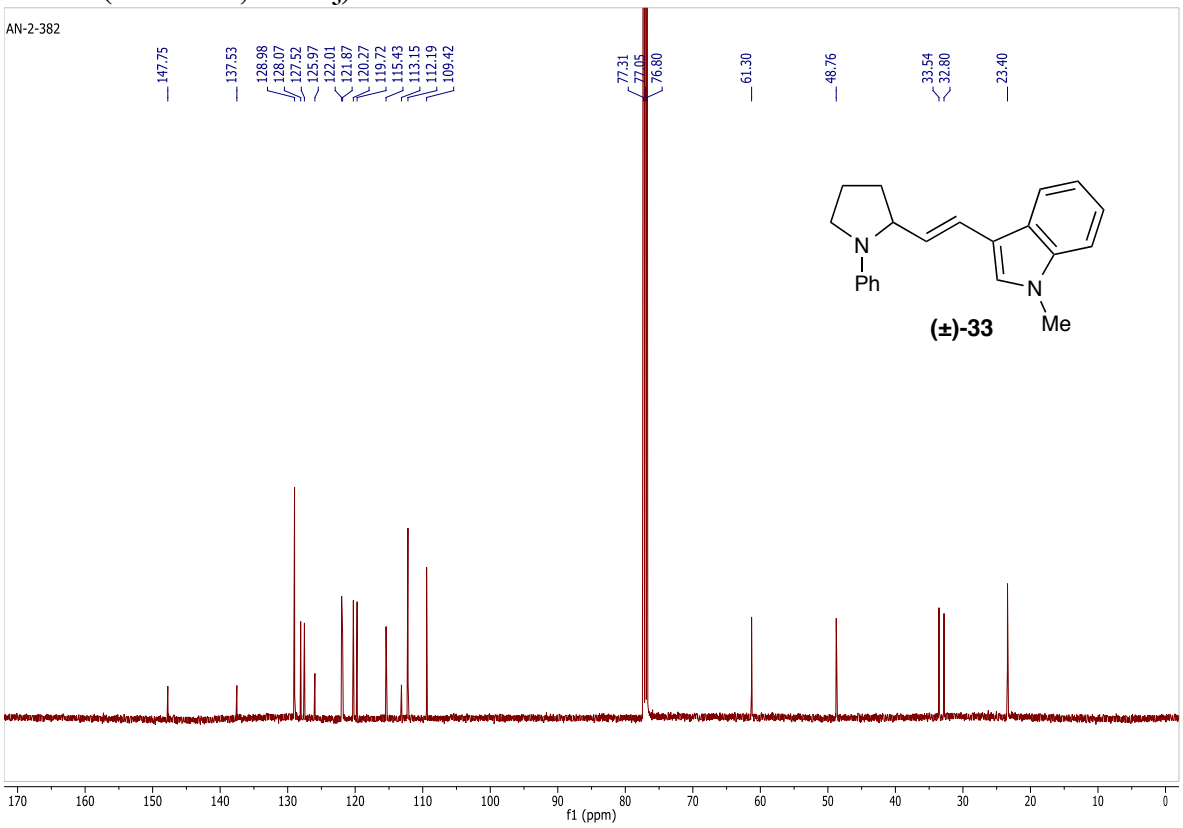

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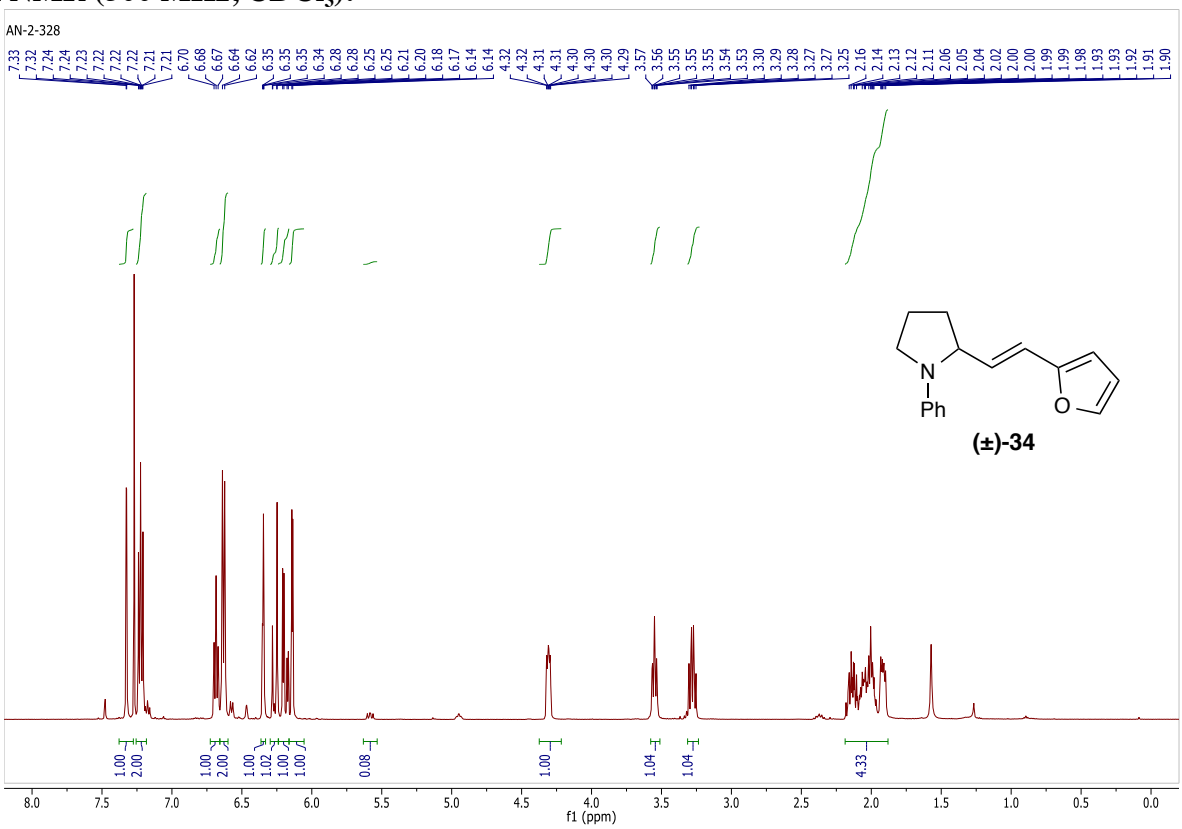

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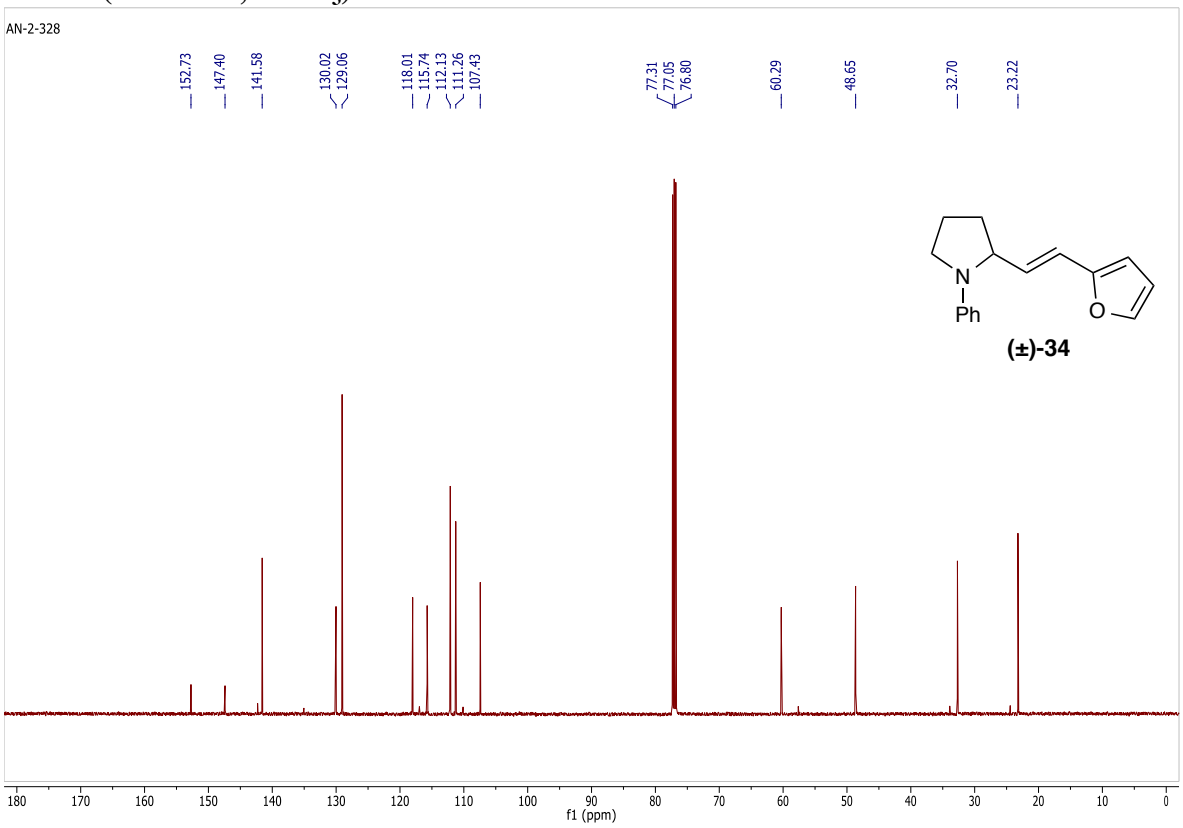

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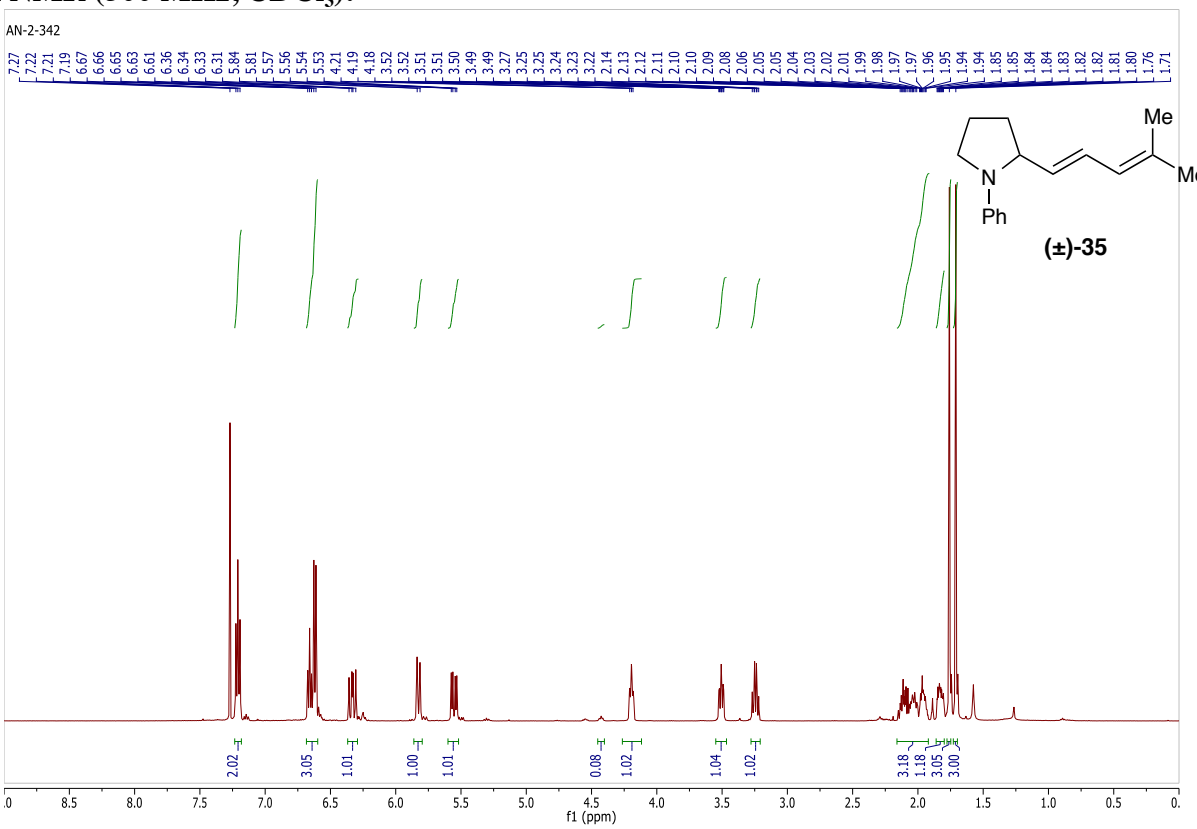

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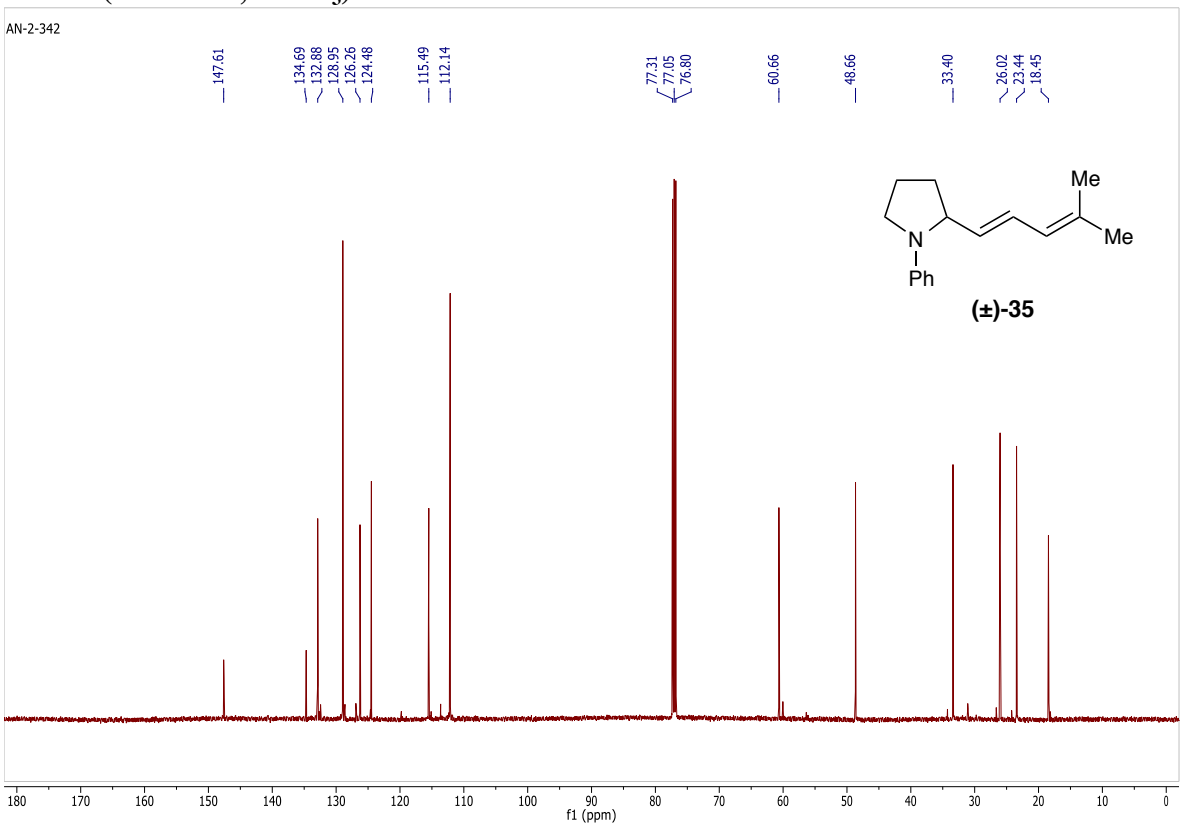

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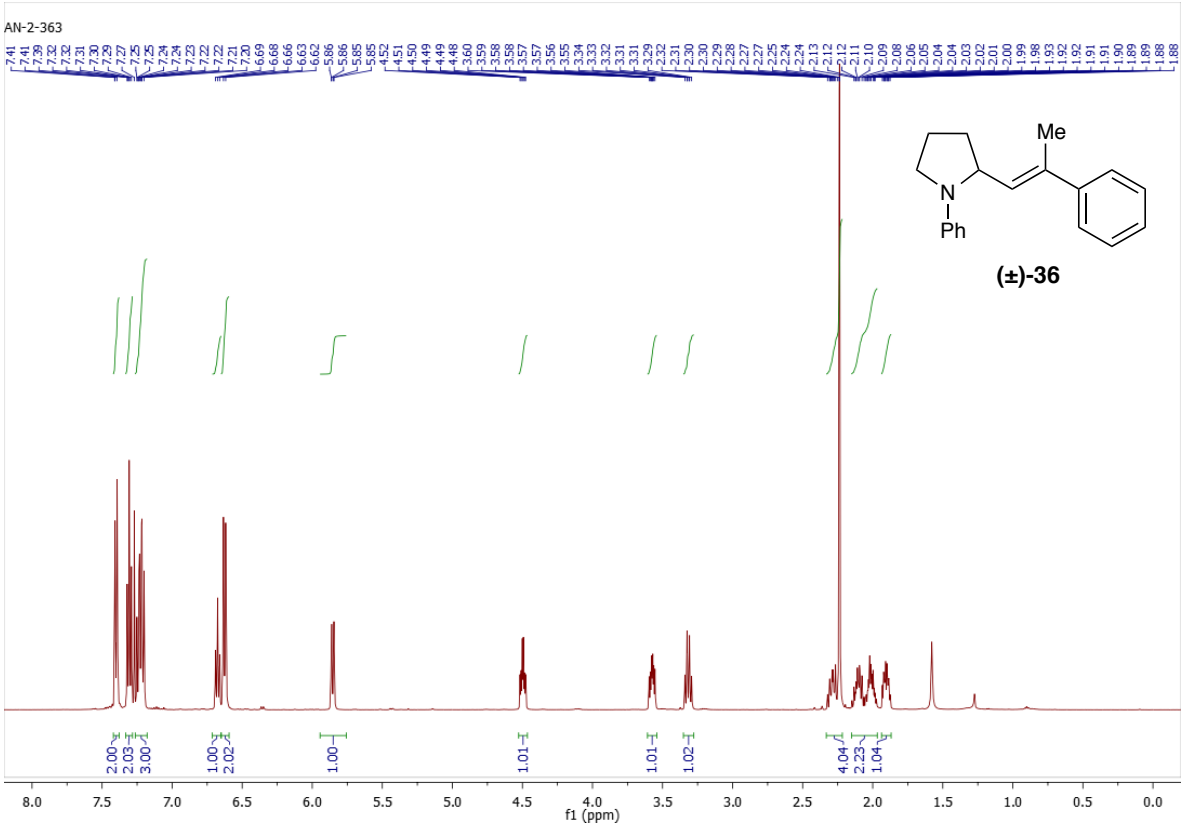

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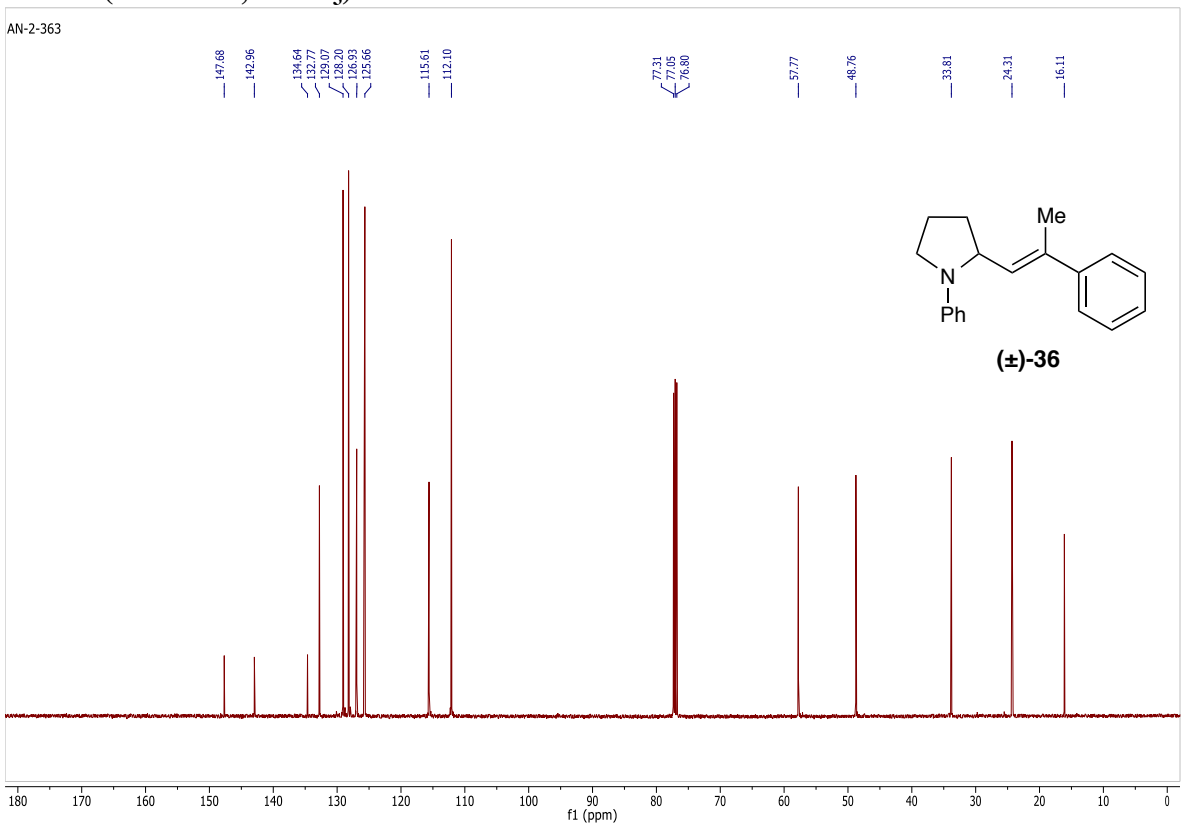

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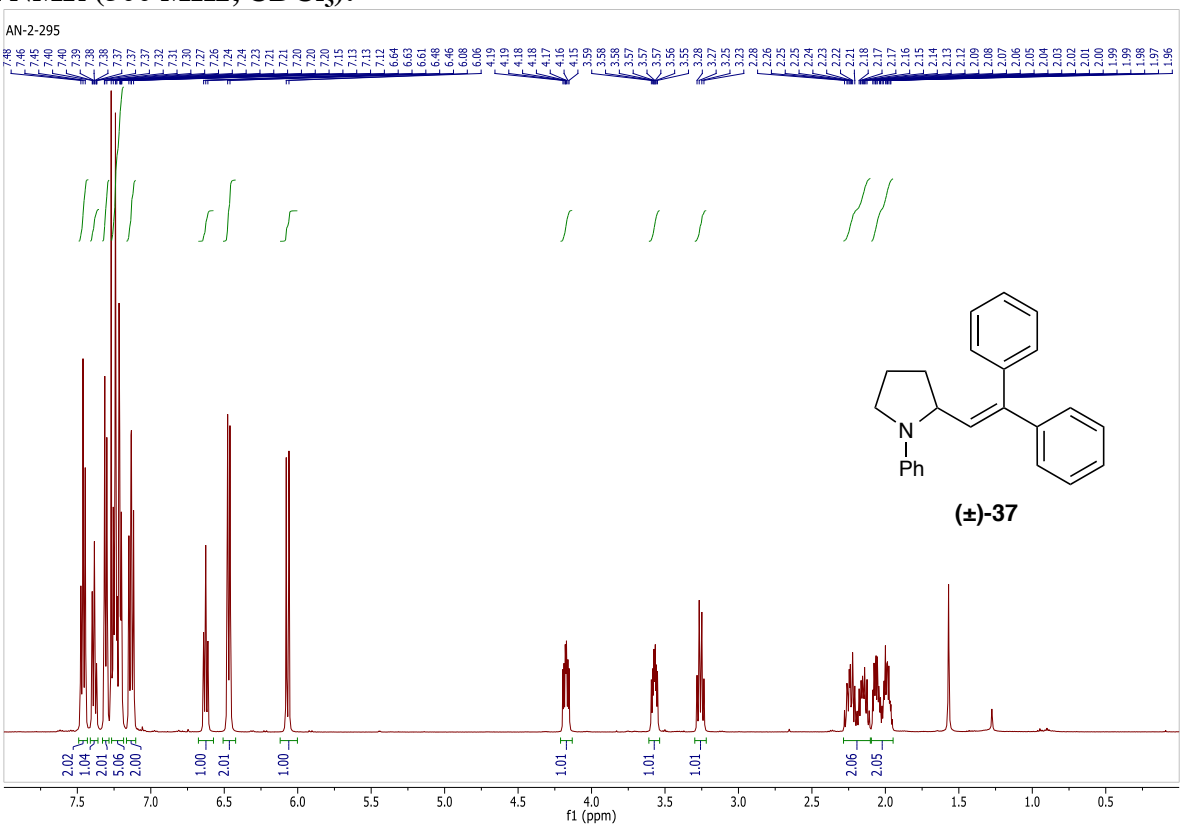

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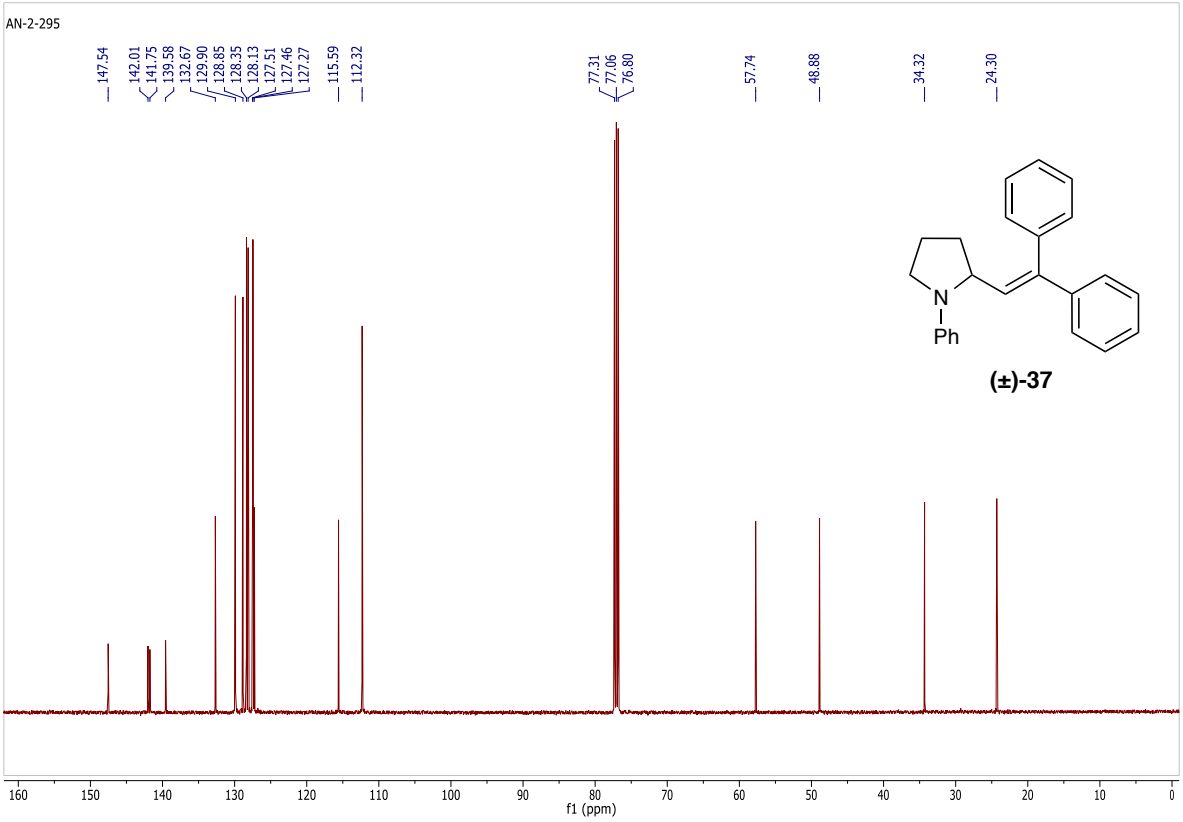

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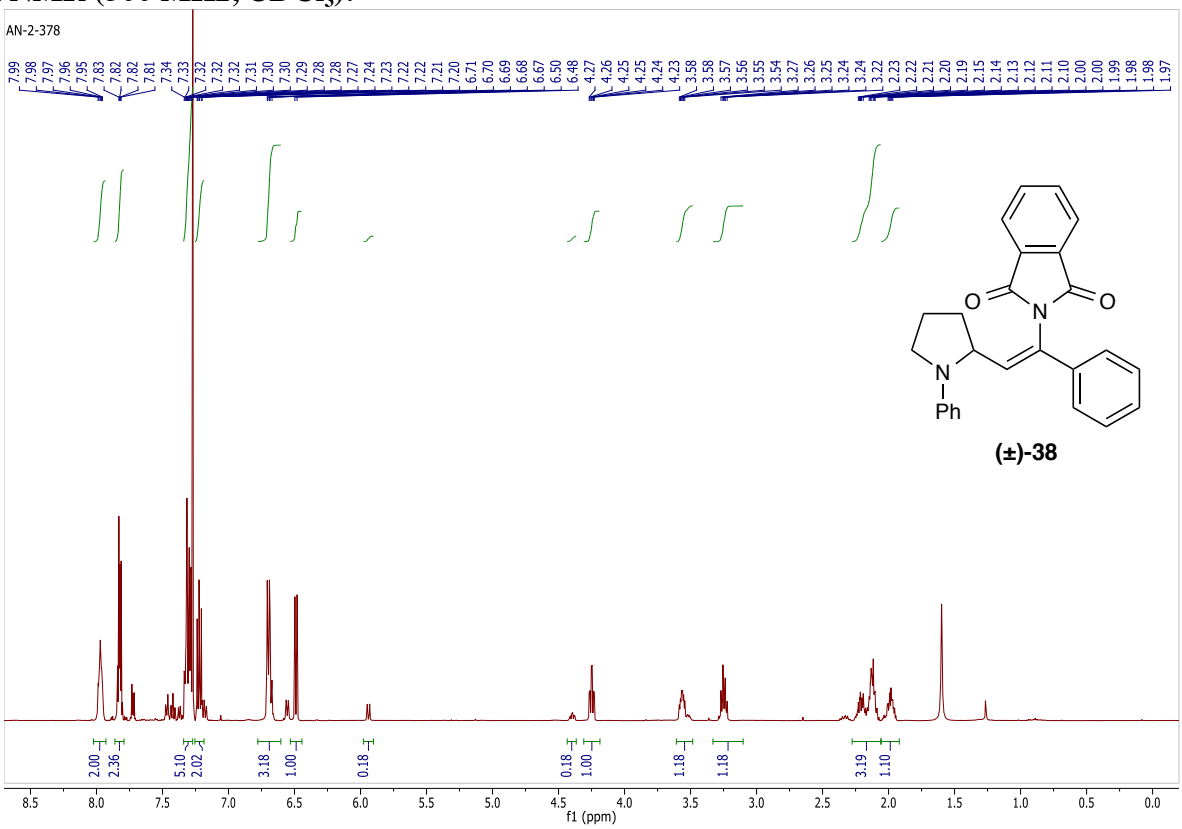

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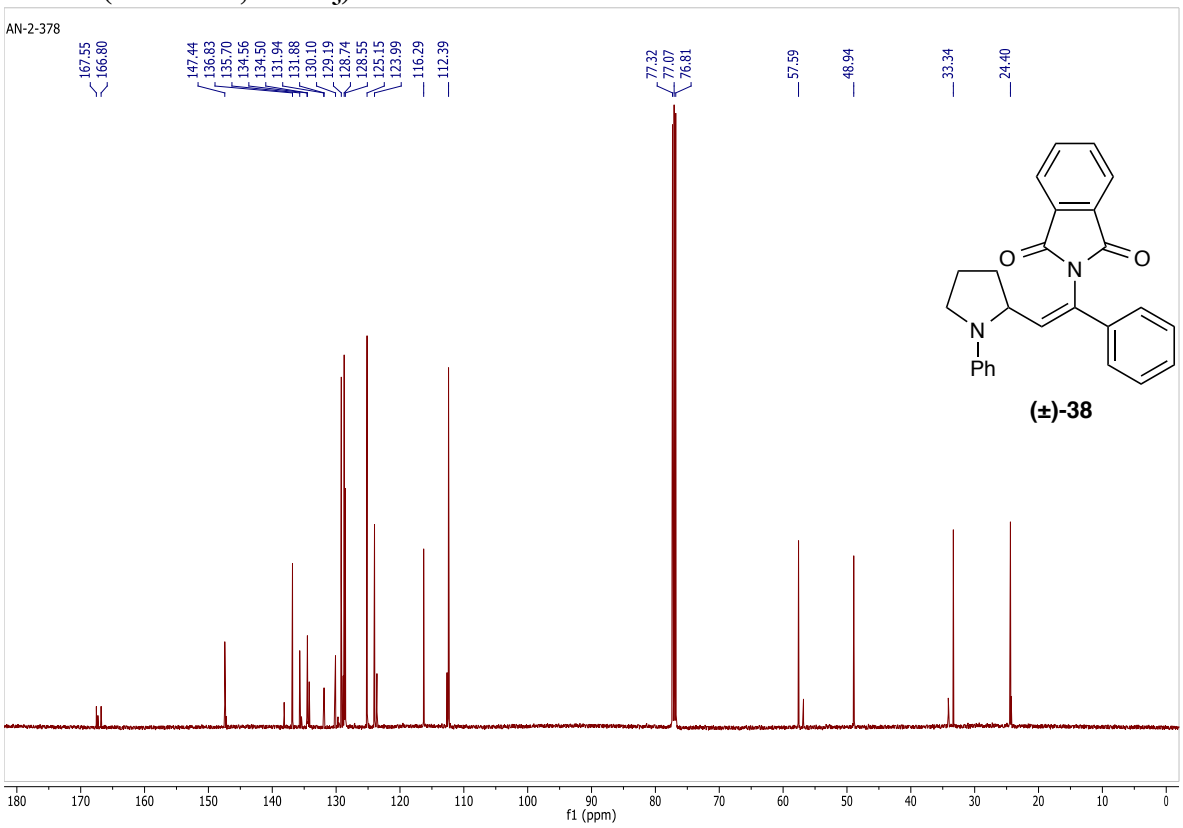

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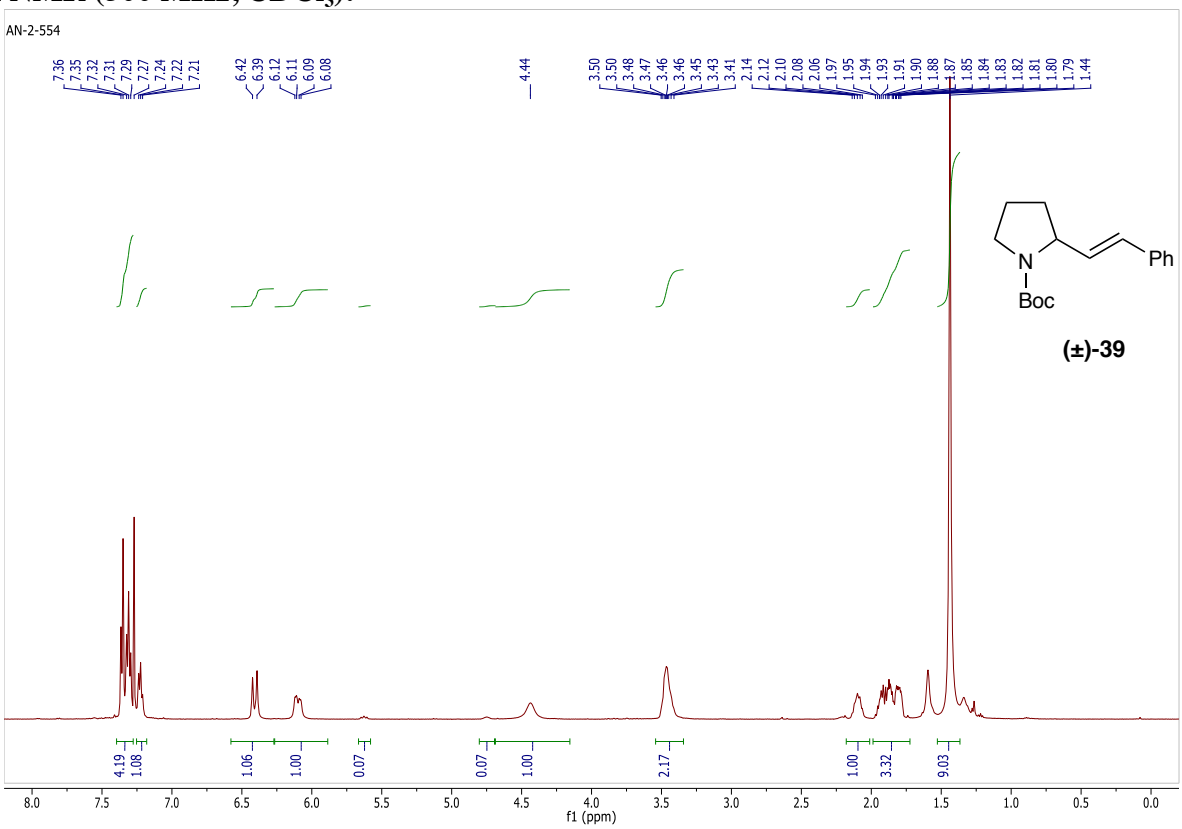

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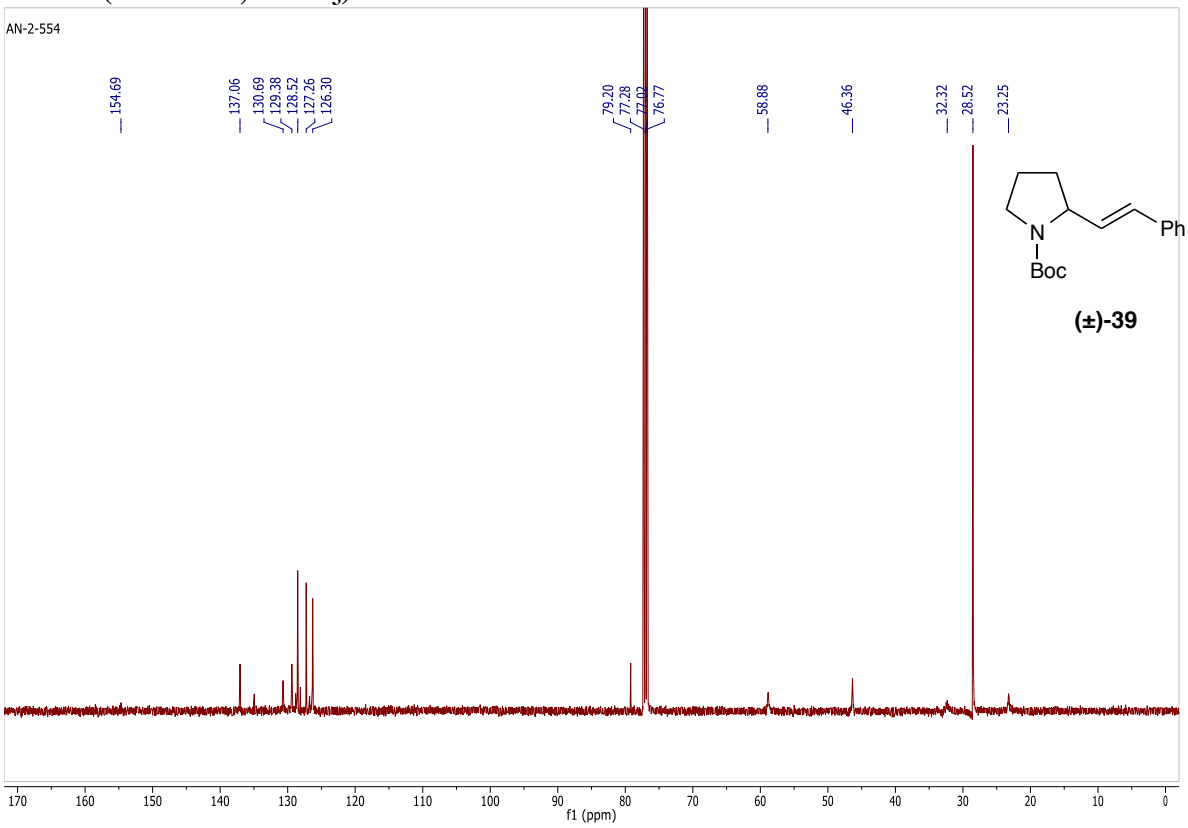

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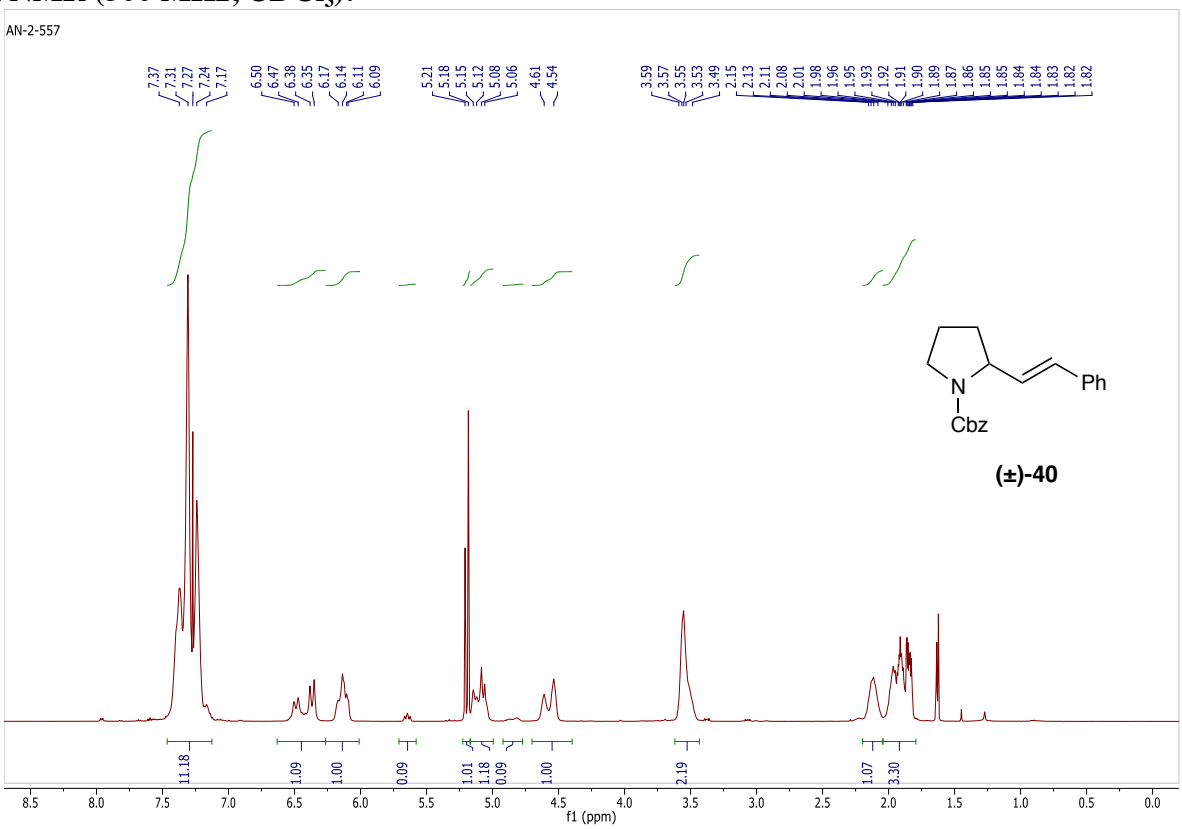

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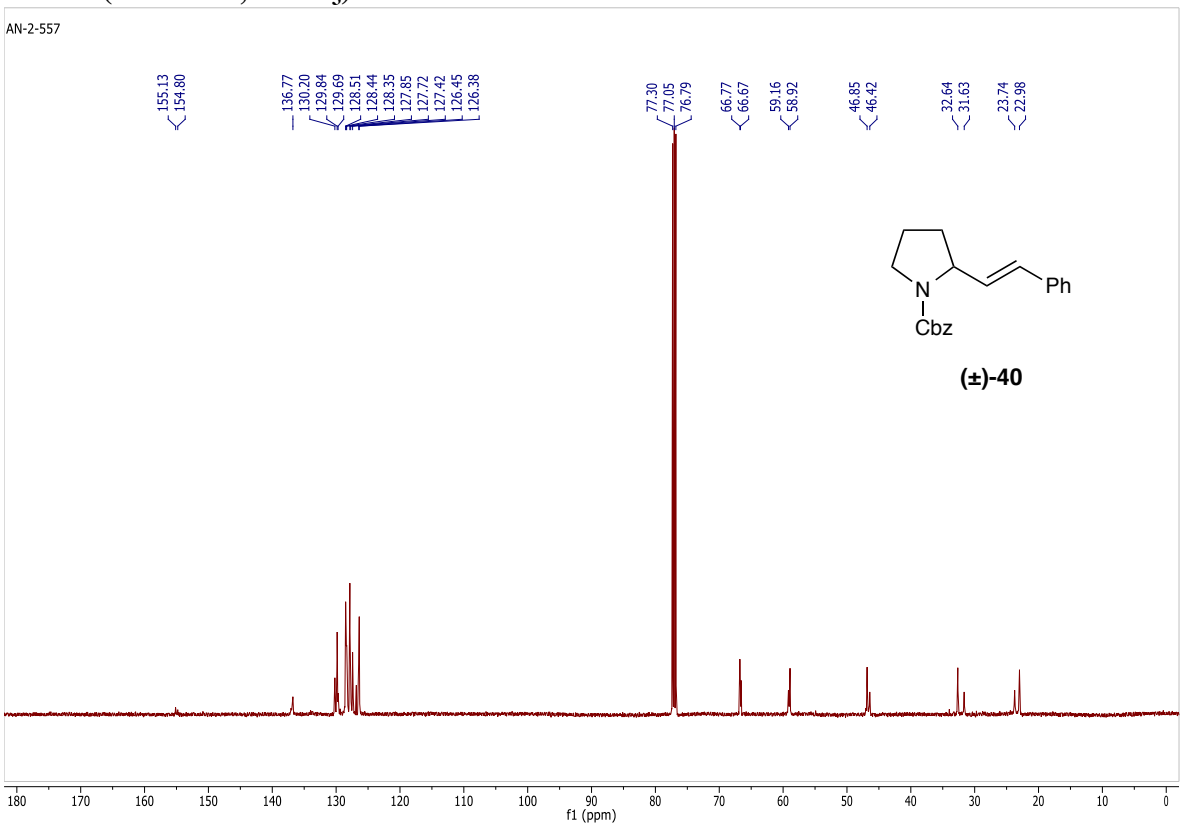

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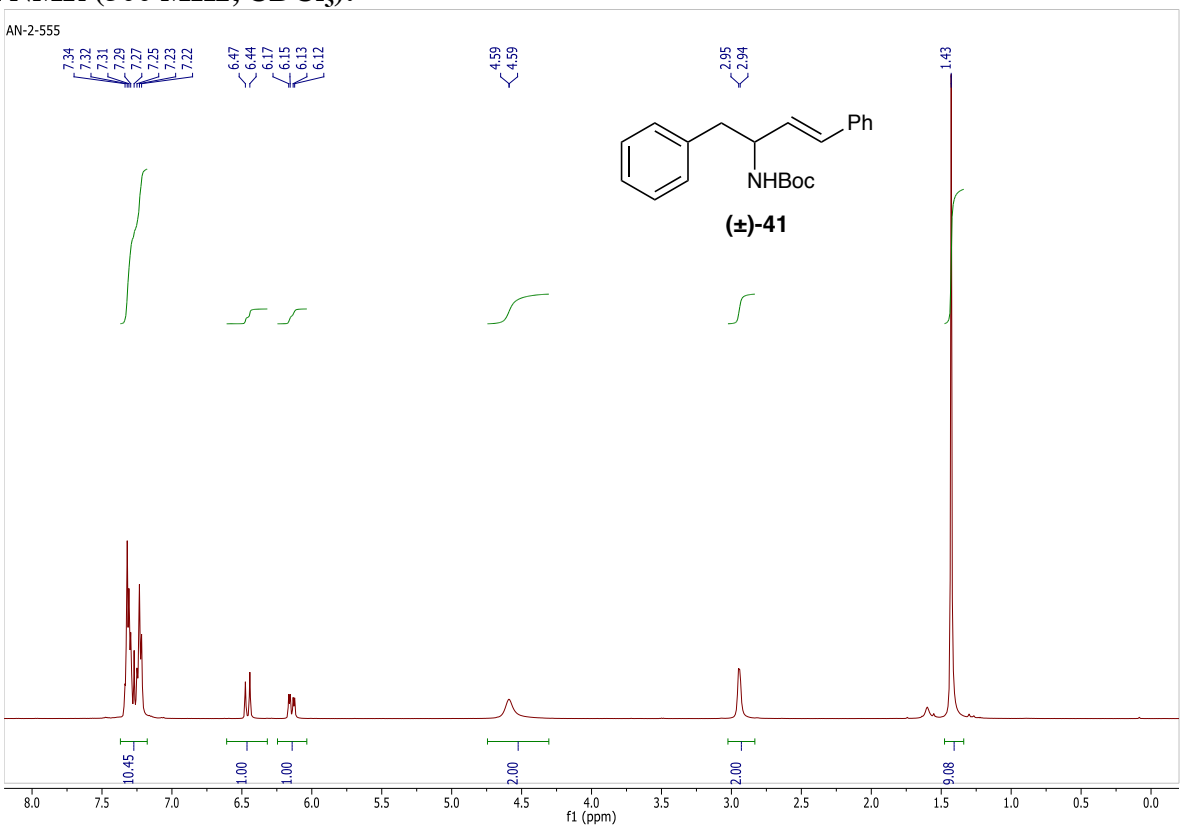

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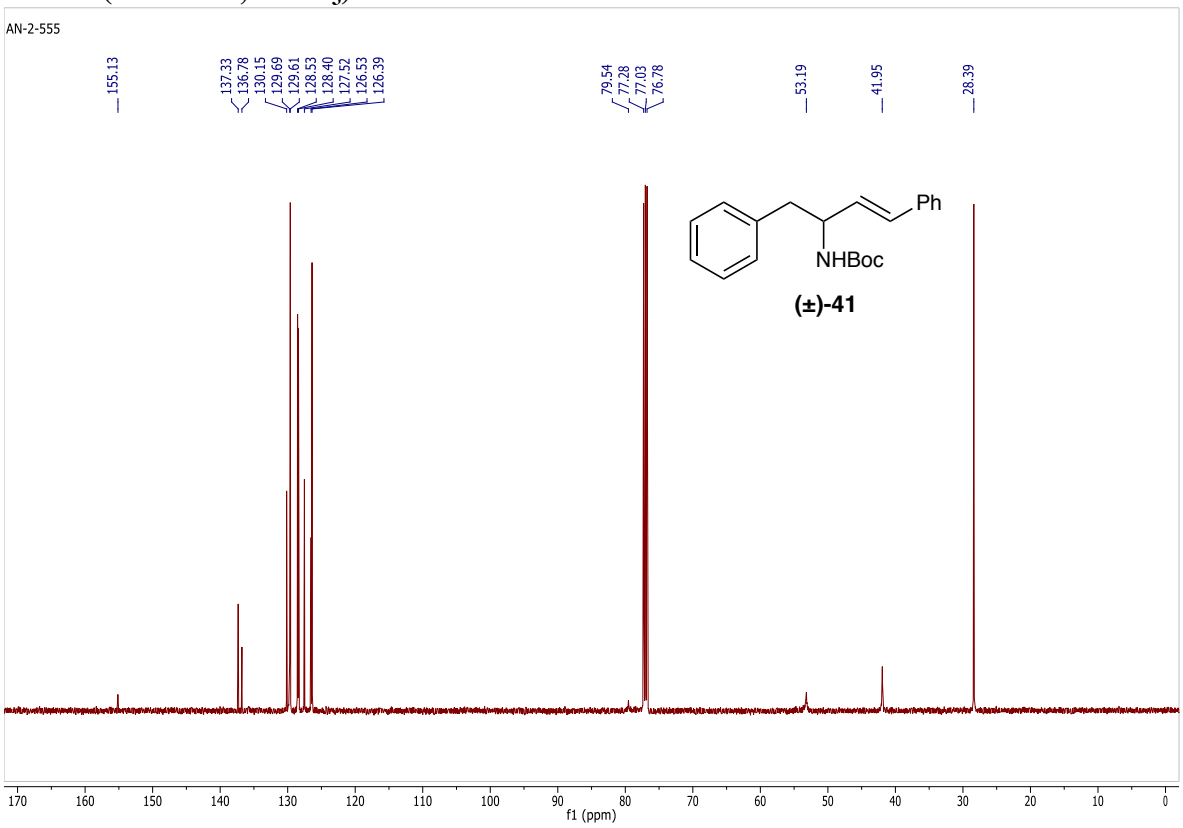

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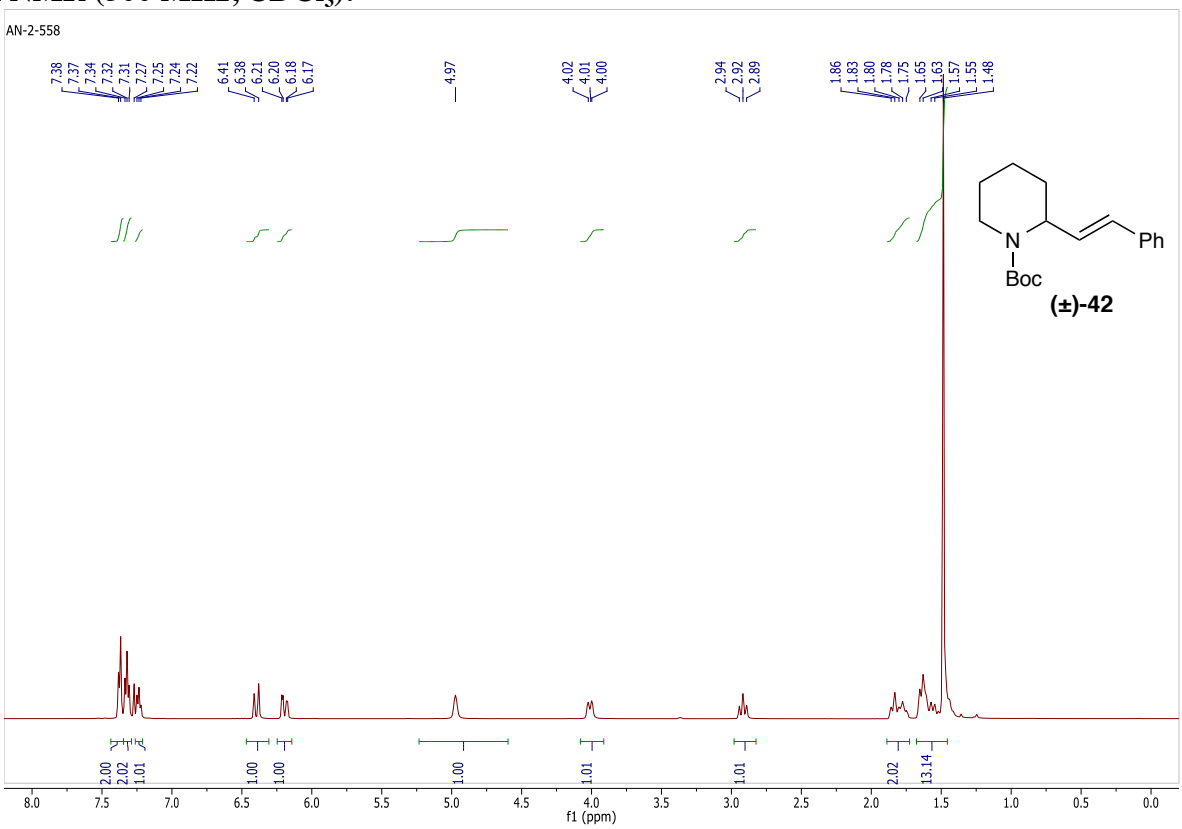

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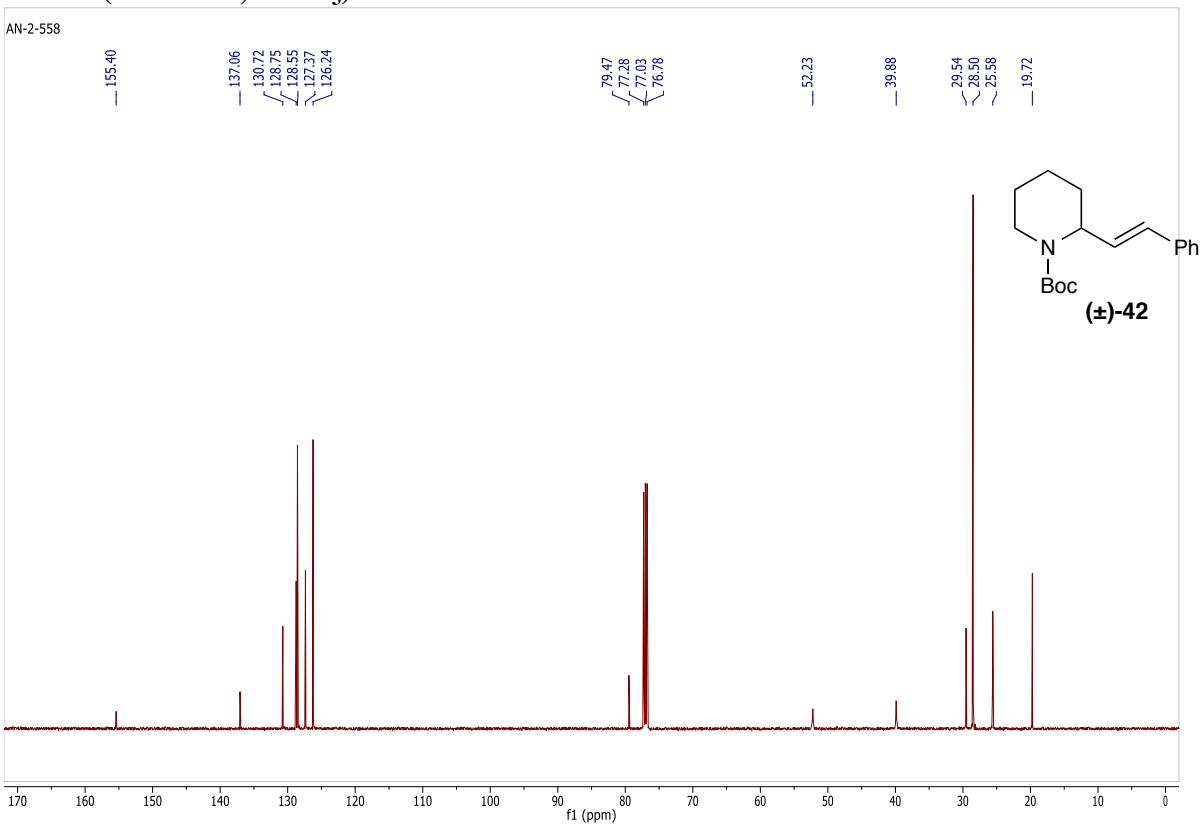

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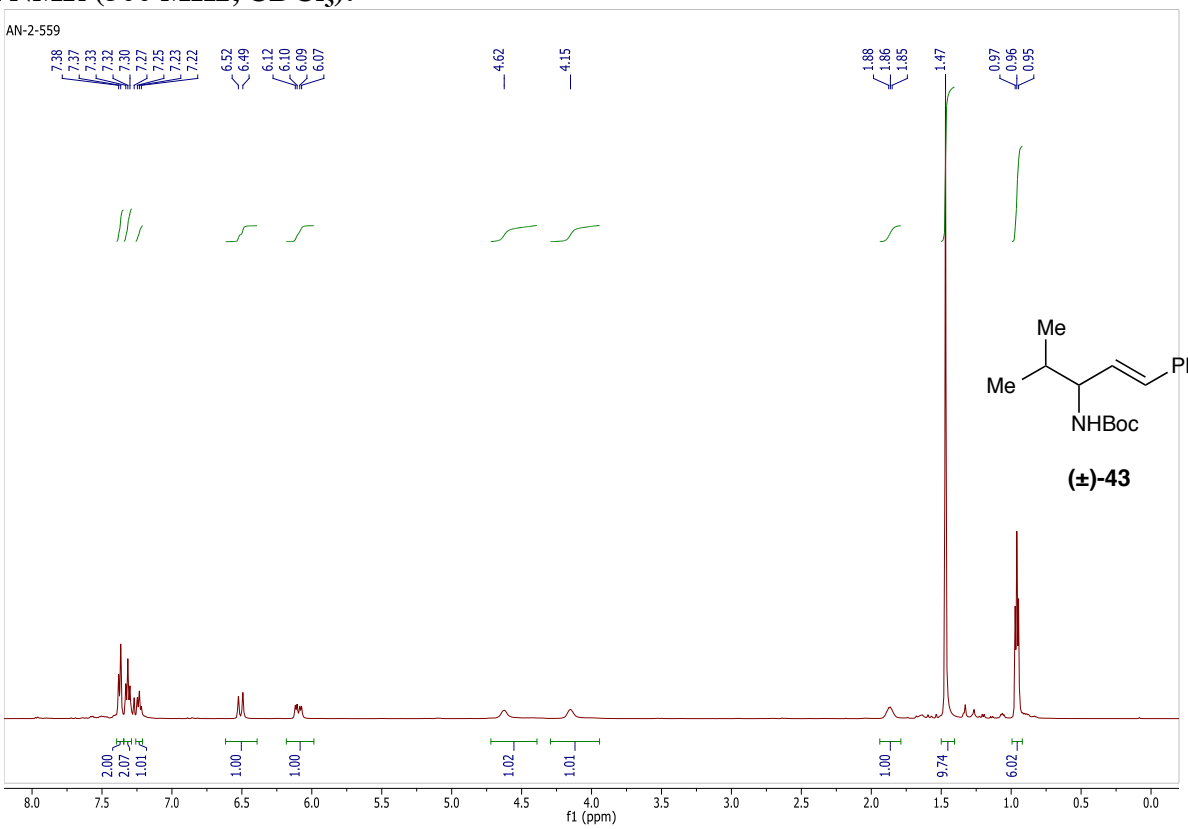

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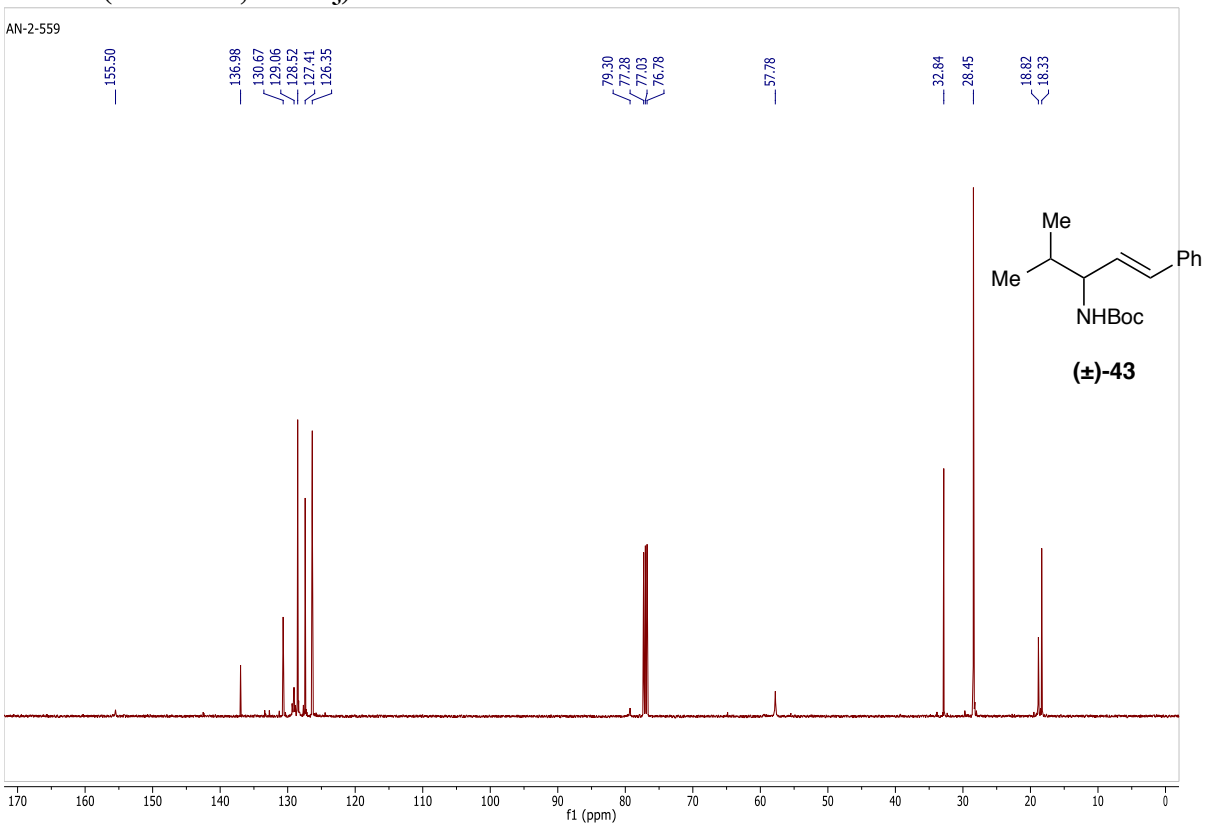

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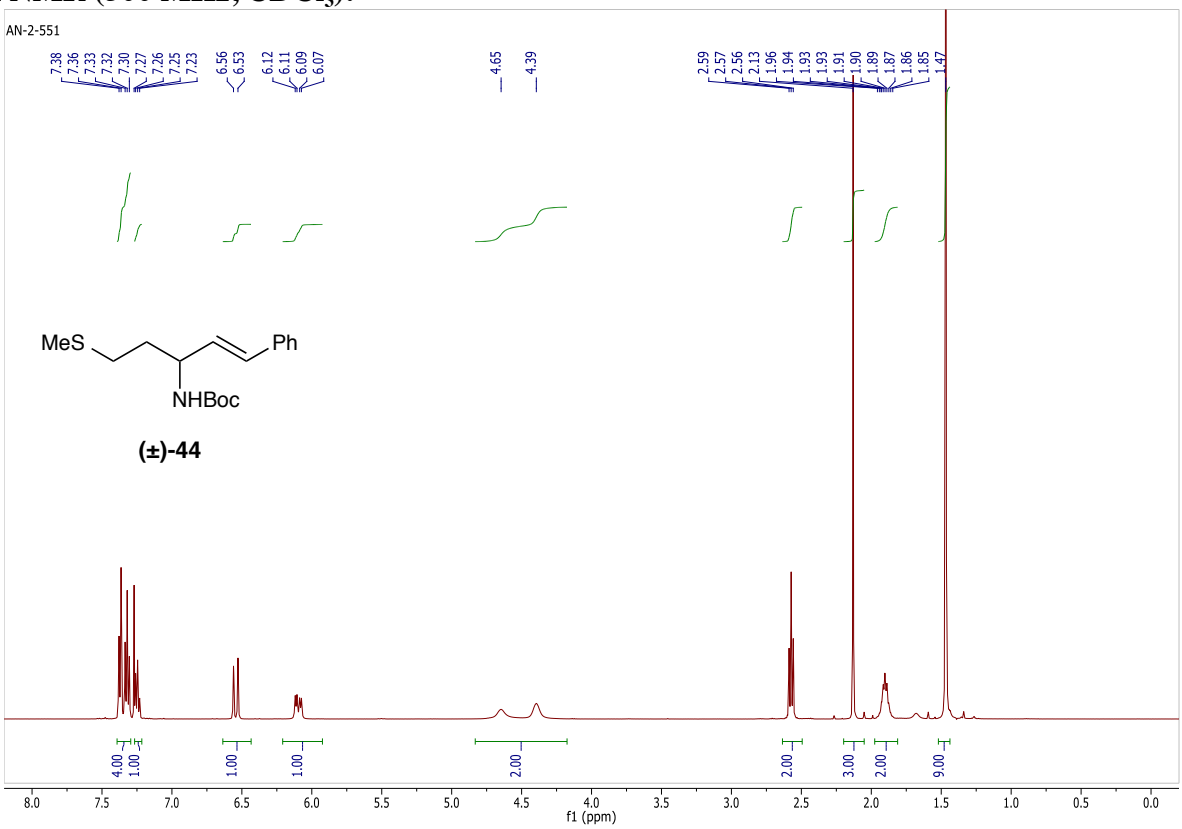

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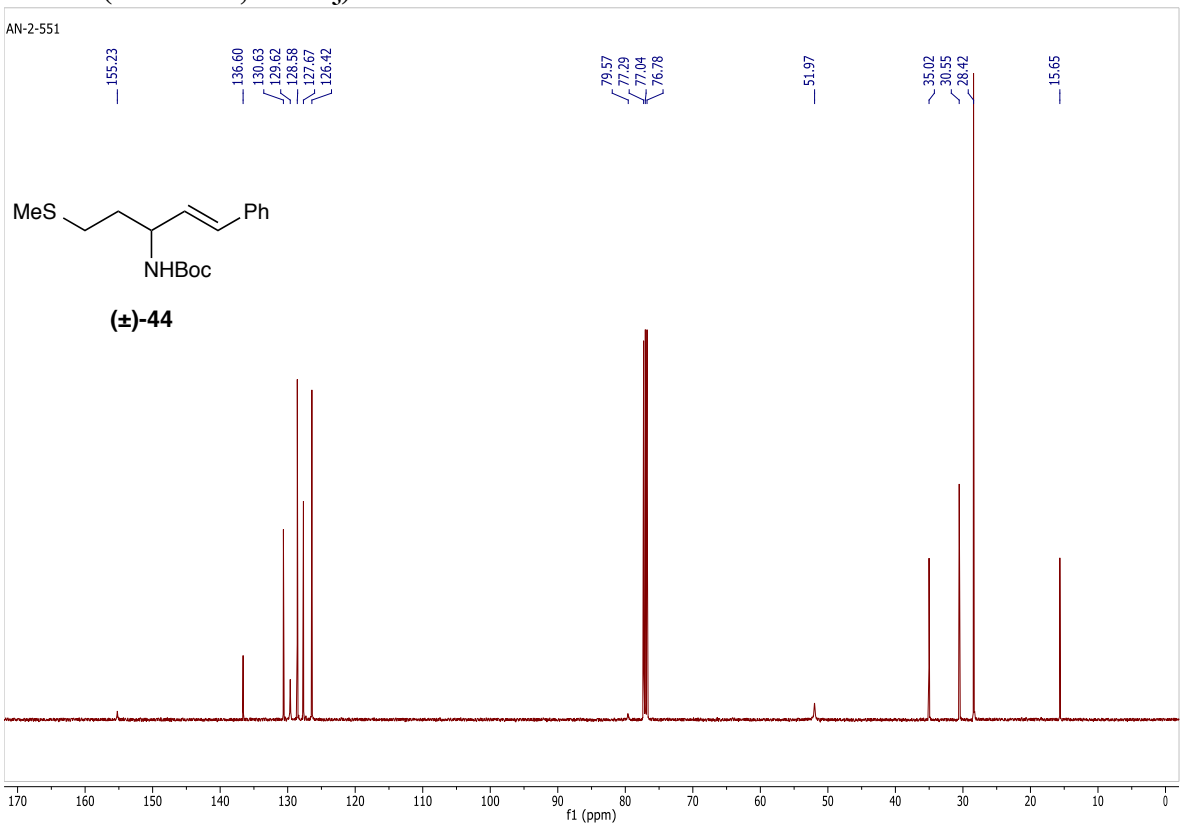
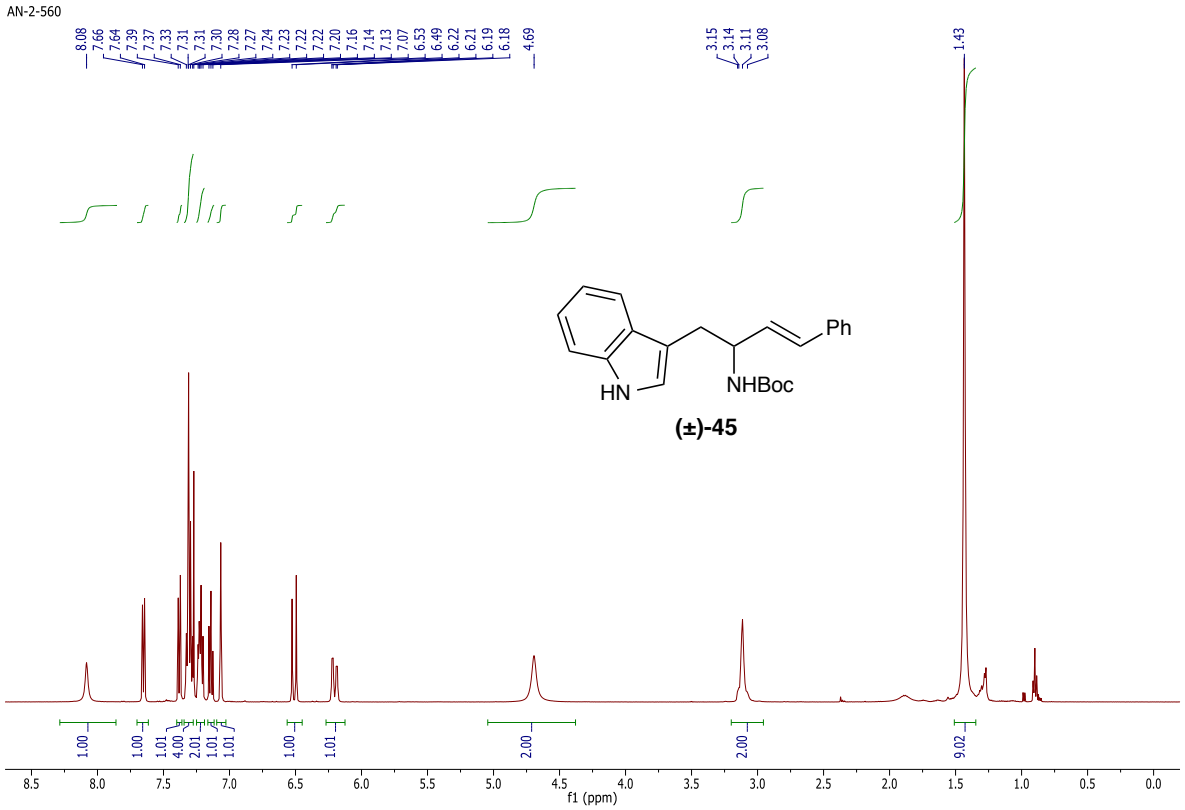
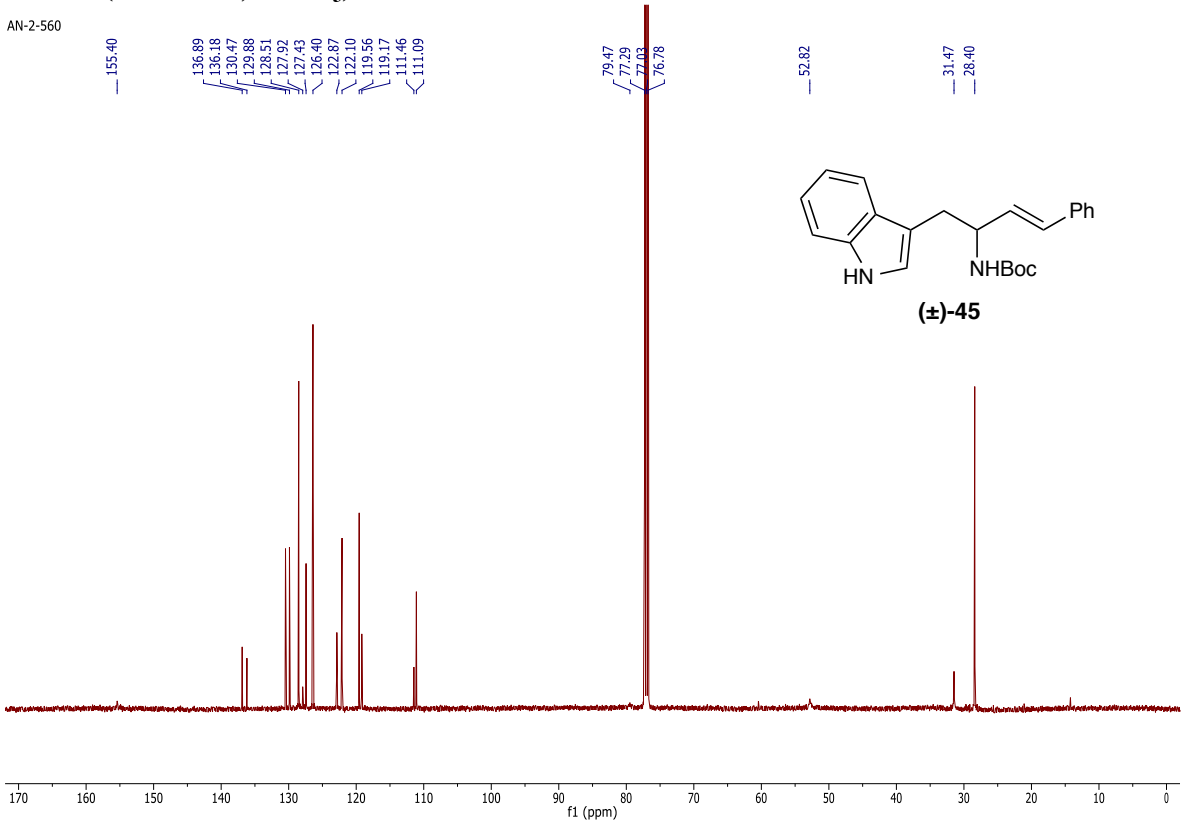


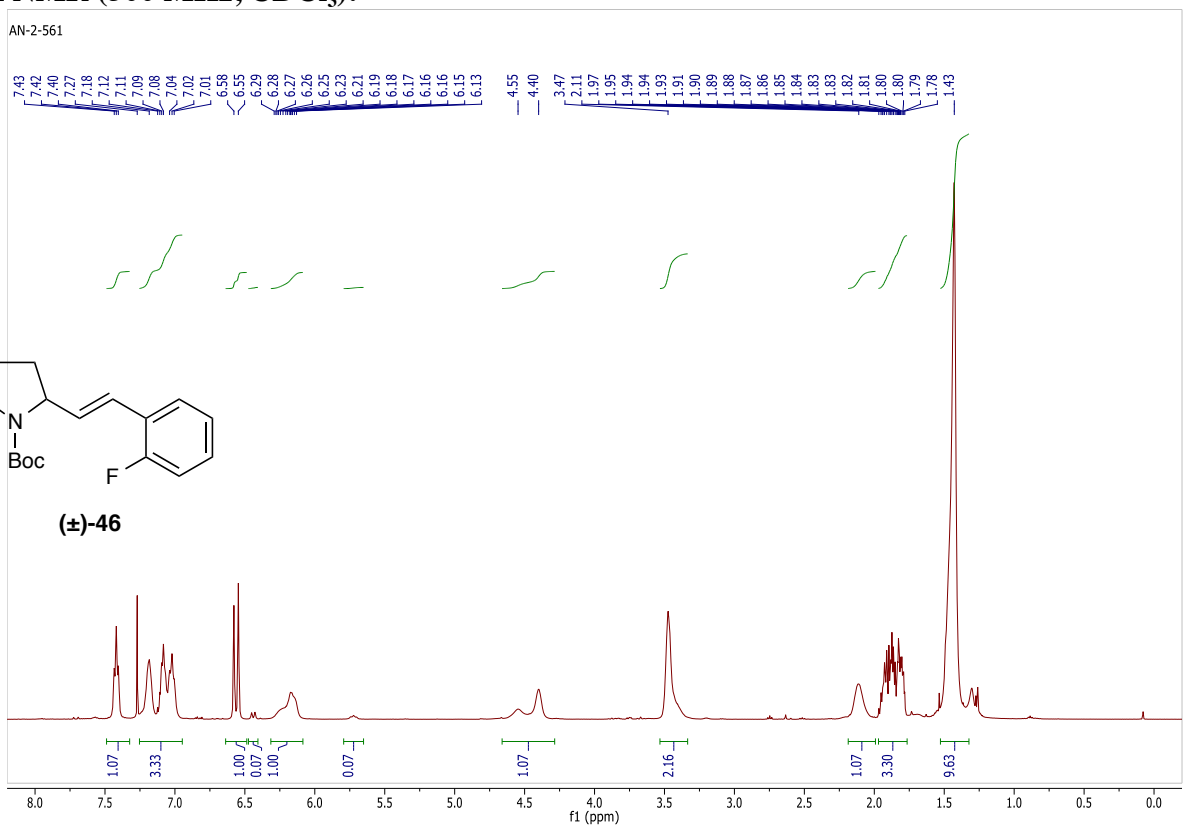
^{1}H NMR (500 MHz, $CDCl_3$):

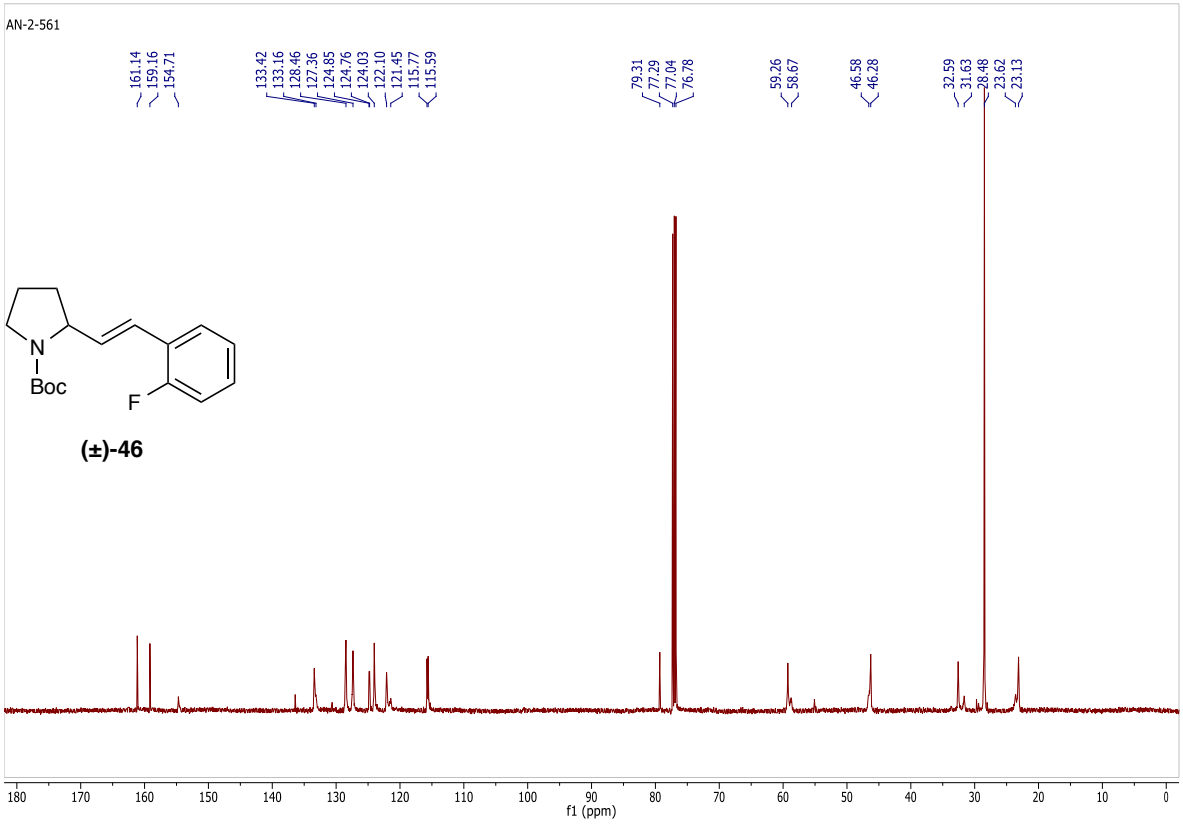


^{13}C NMR (126 MHz, $CDCl_3$):

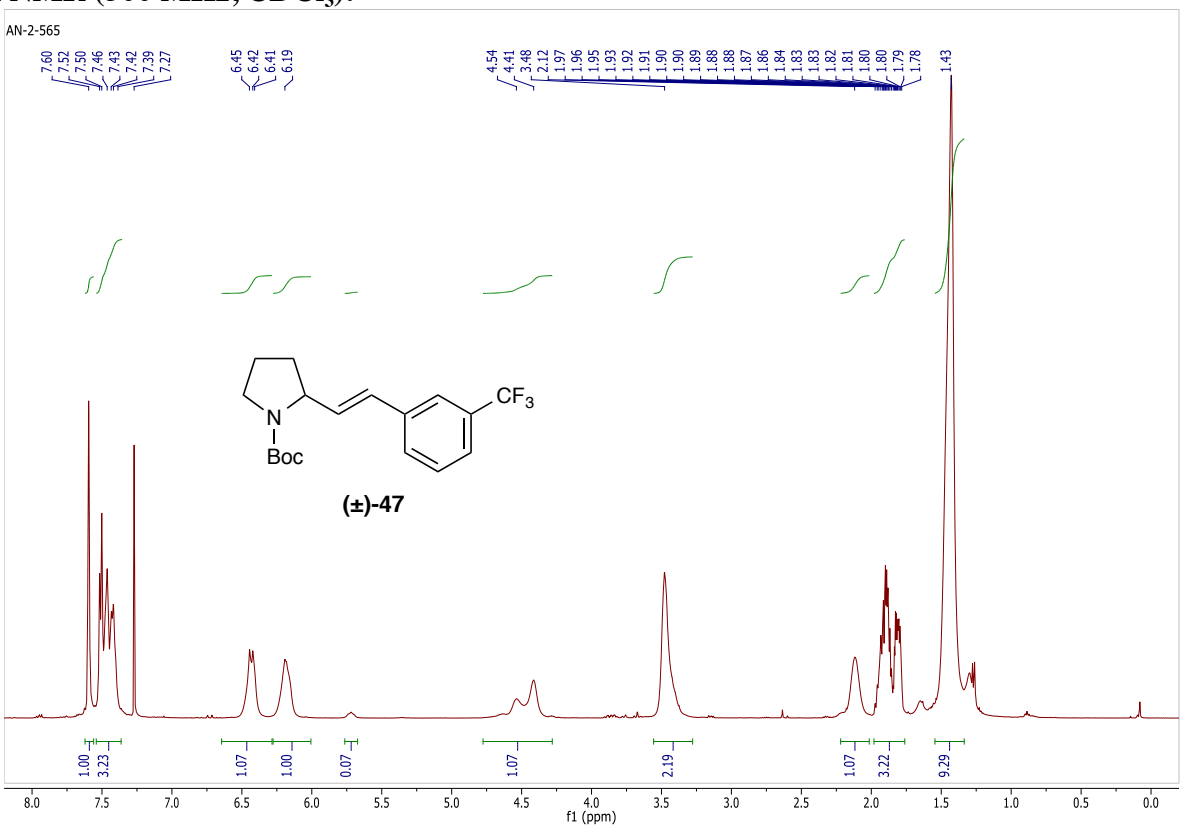


^{1}H NMR (500 MHz, $CDCl_3$):

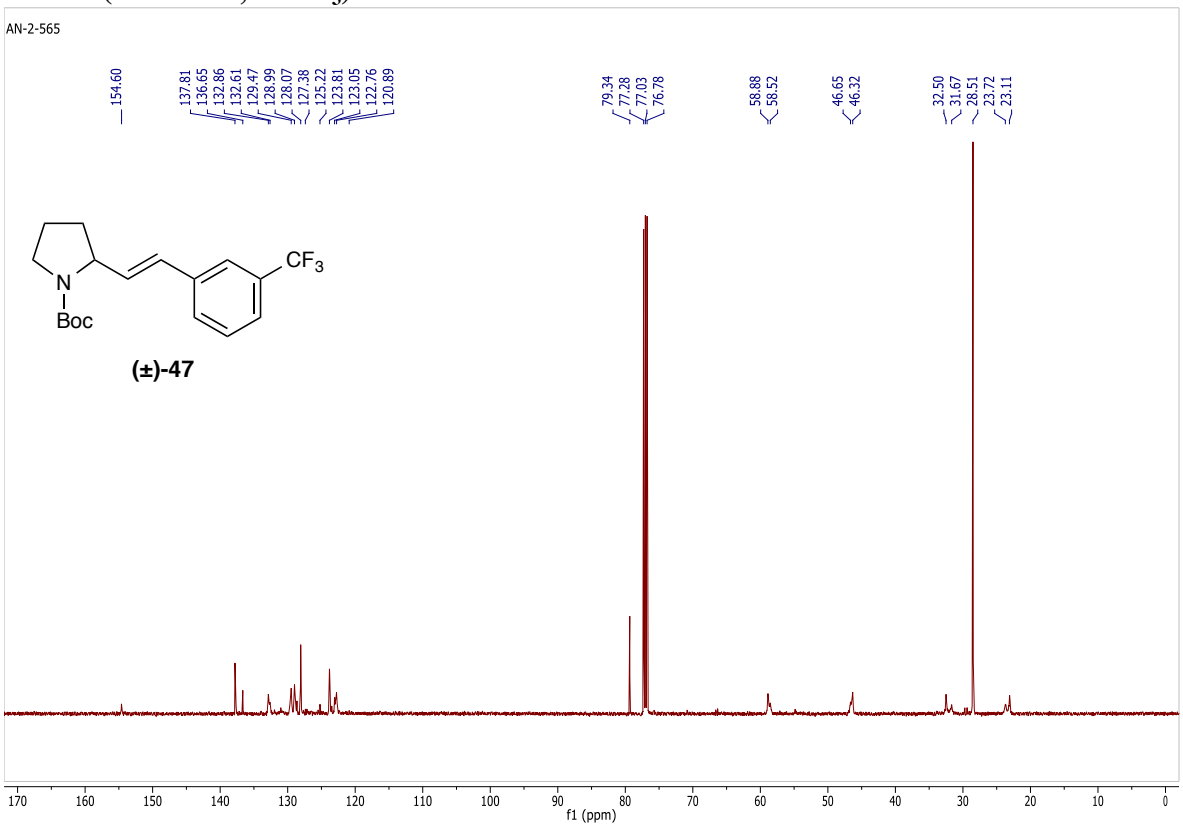




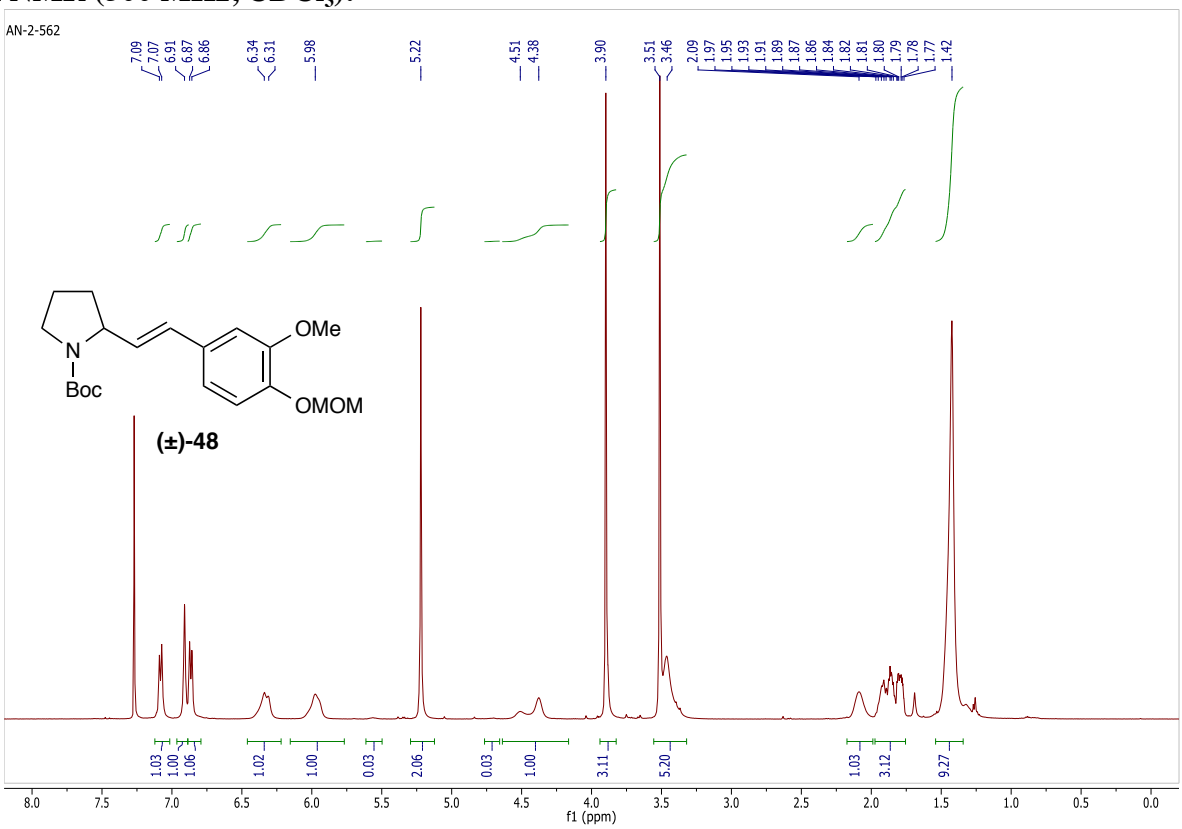
^{1}H NMR (500 MHz, $CDCl_3$):



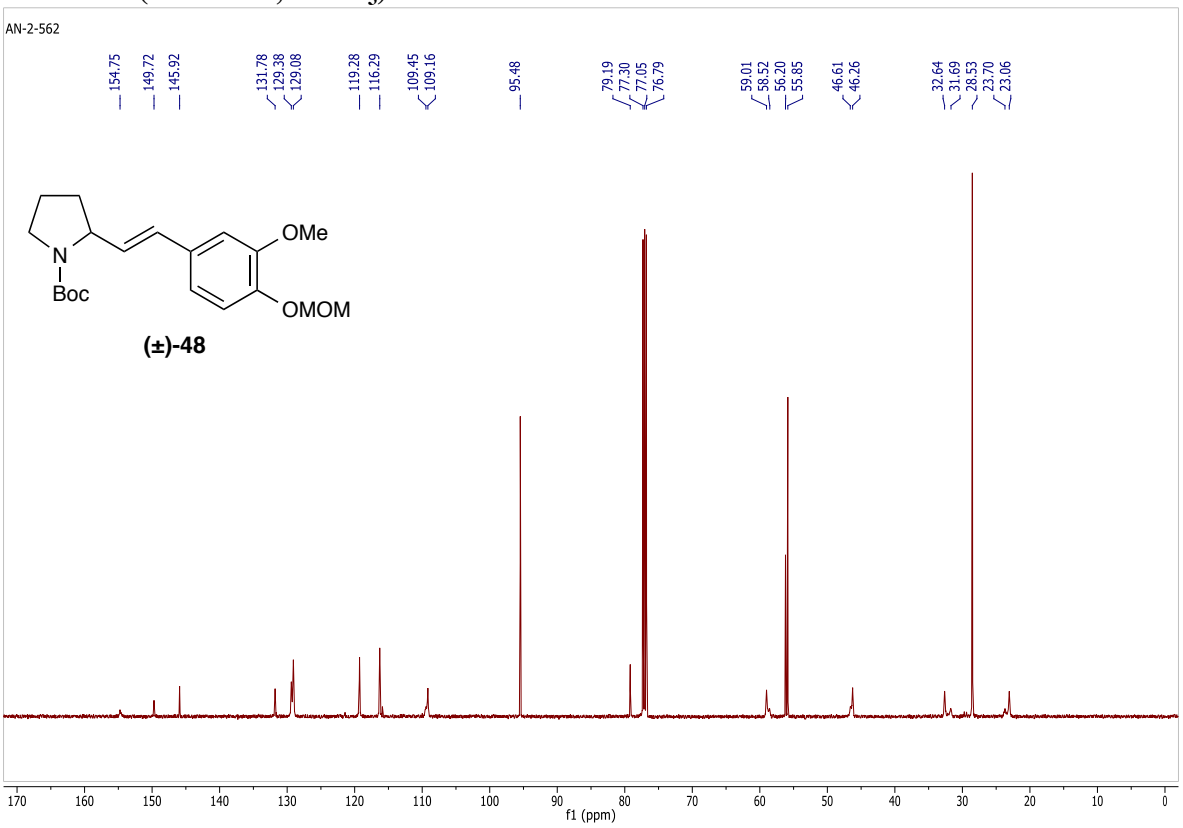
^{13}C NMR (126 MHz, $CDCl_3$):



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



^{13}C NMR (126 MHz, $CDCl_3$):



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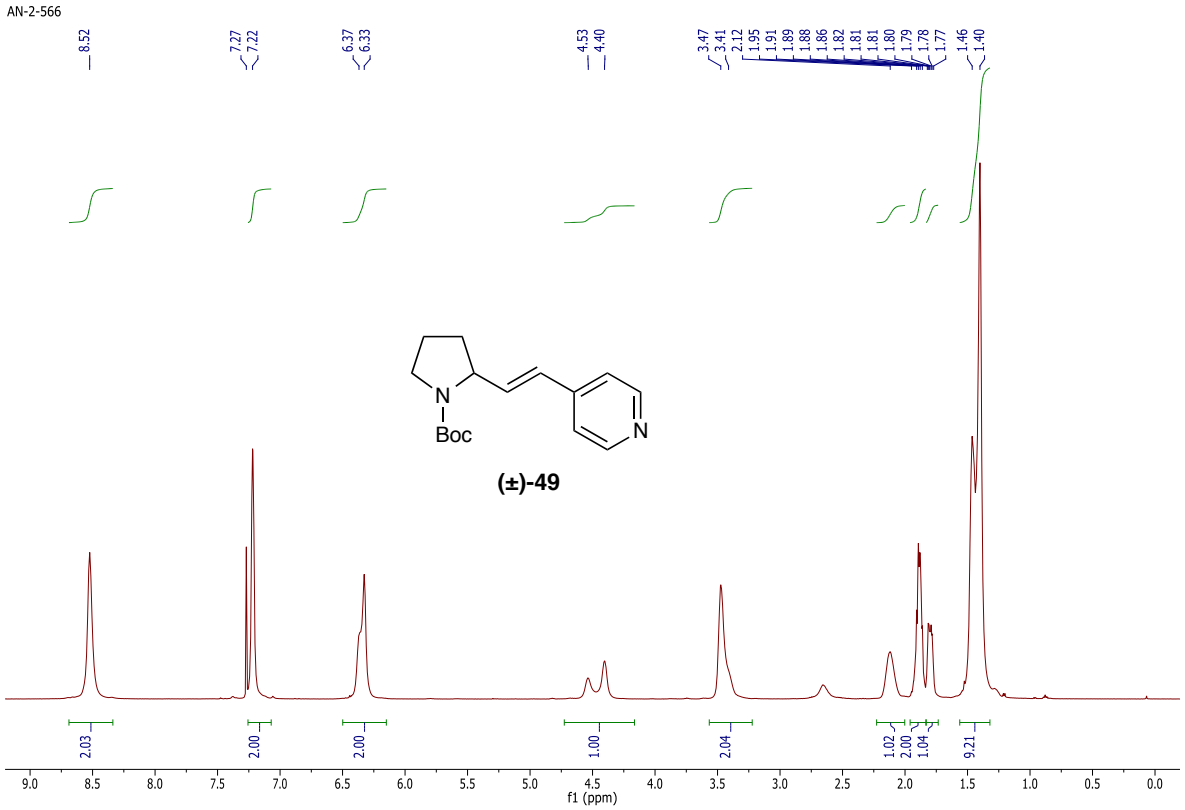

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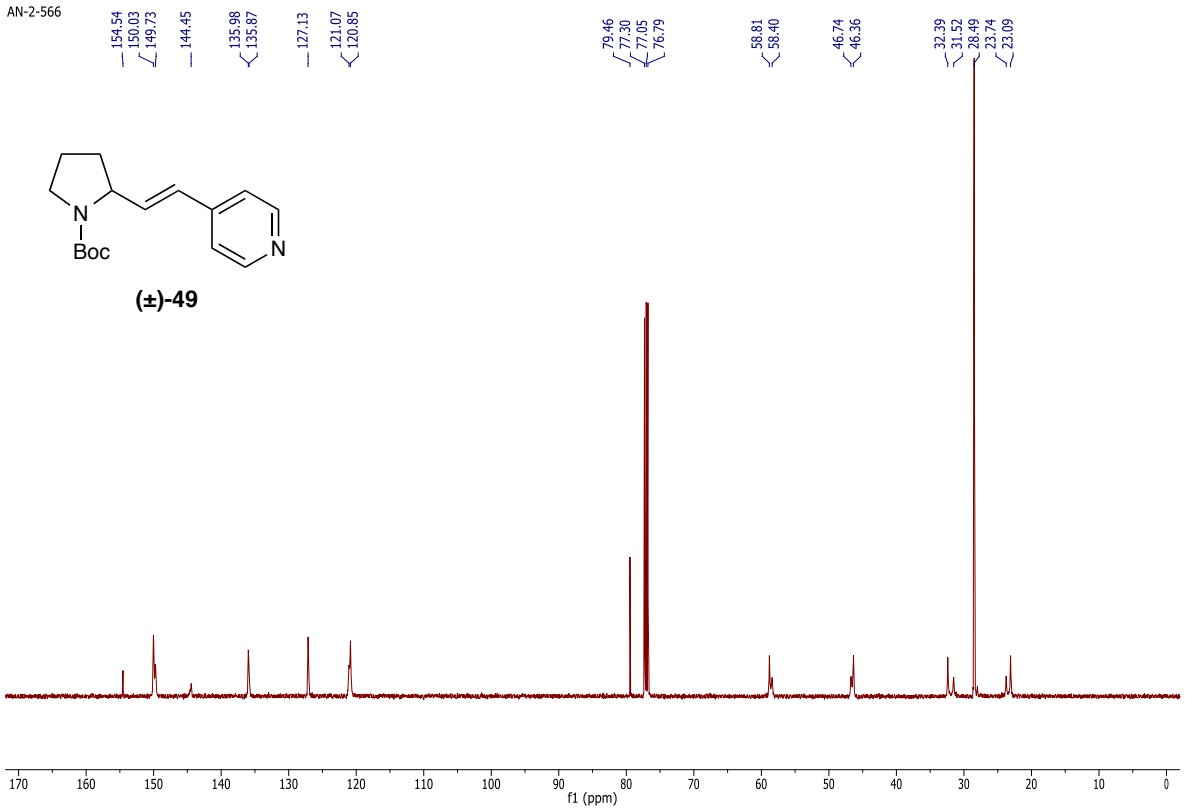

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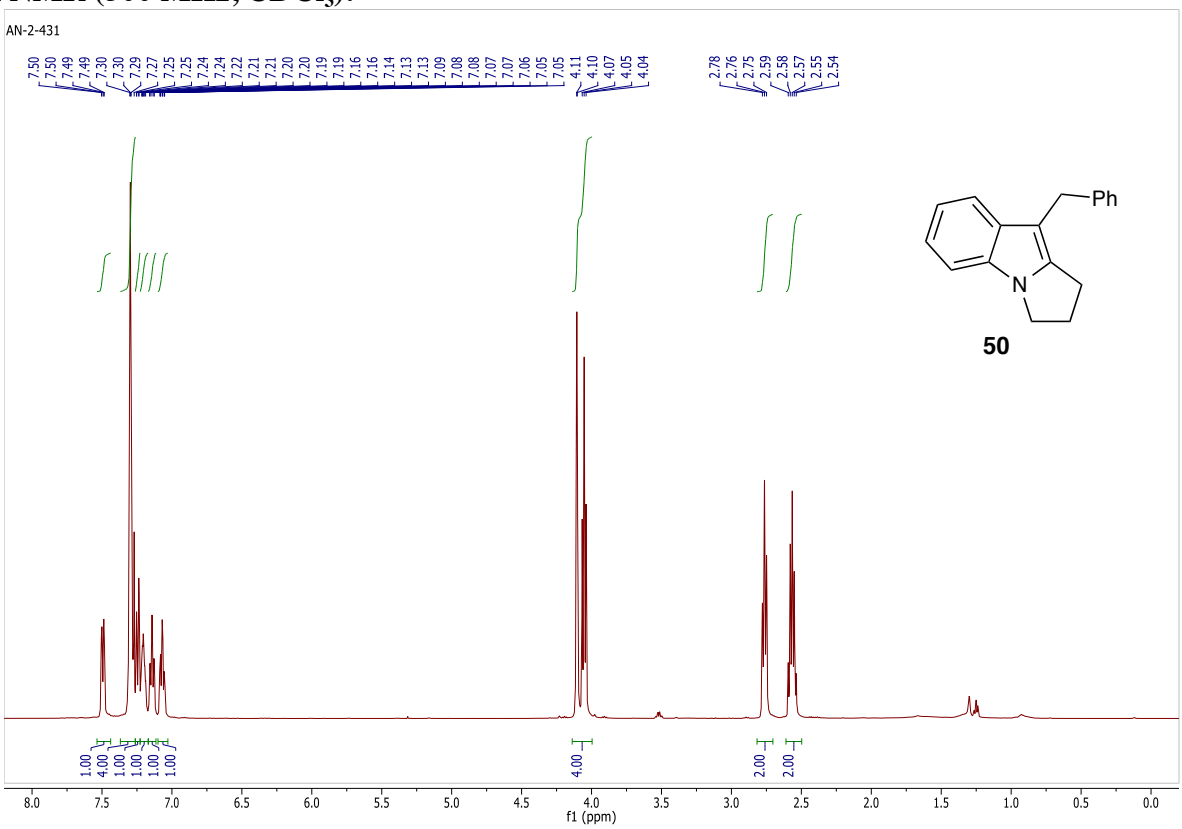

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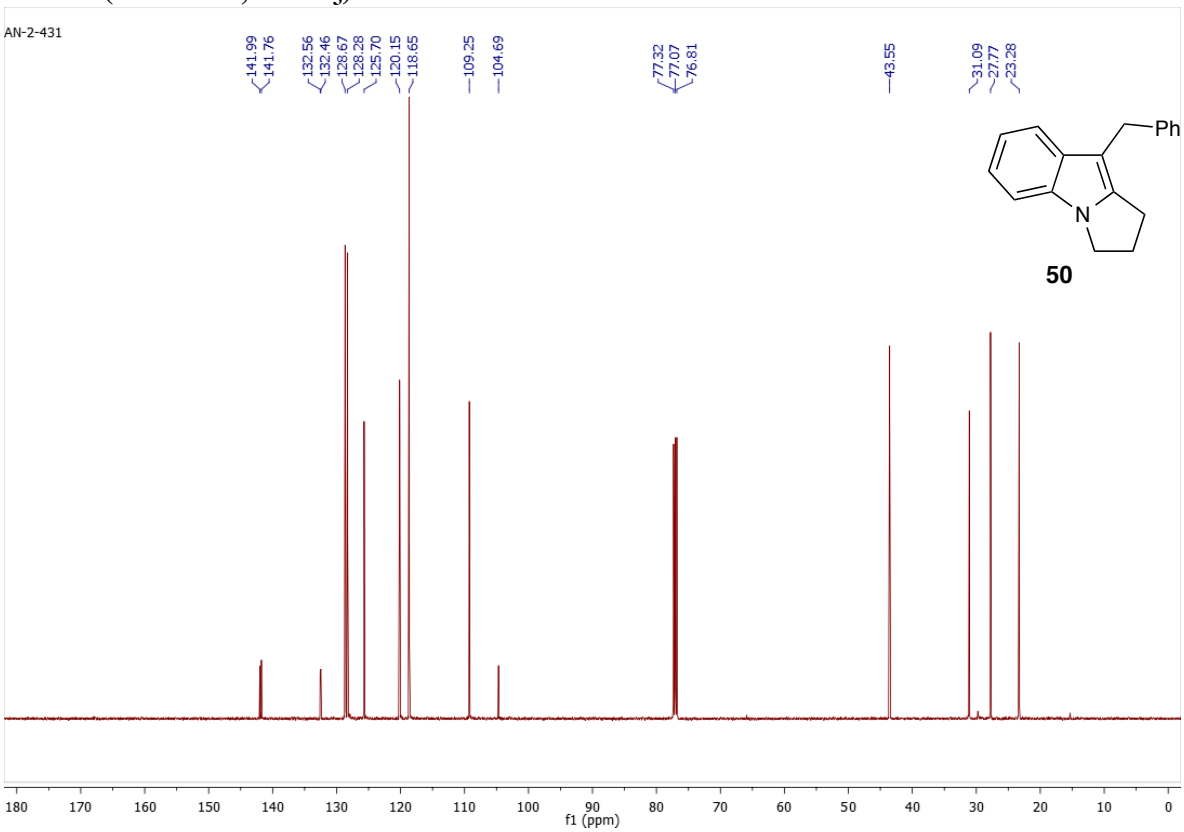

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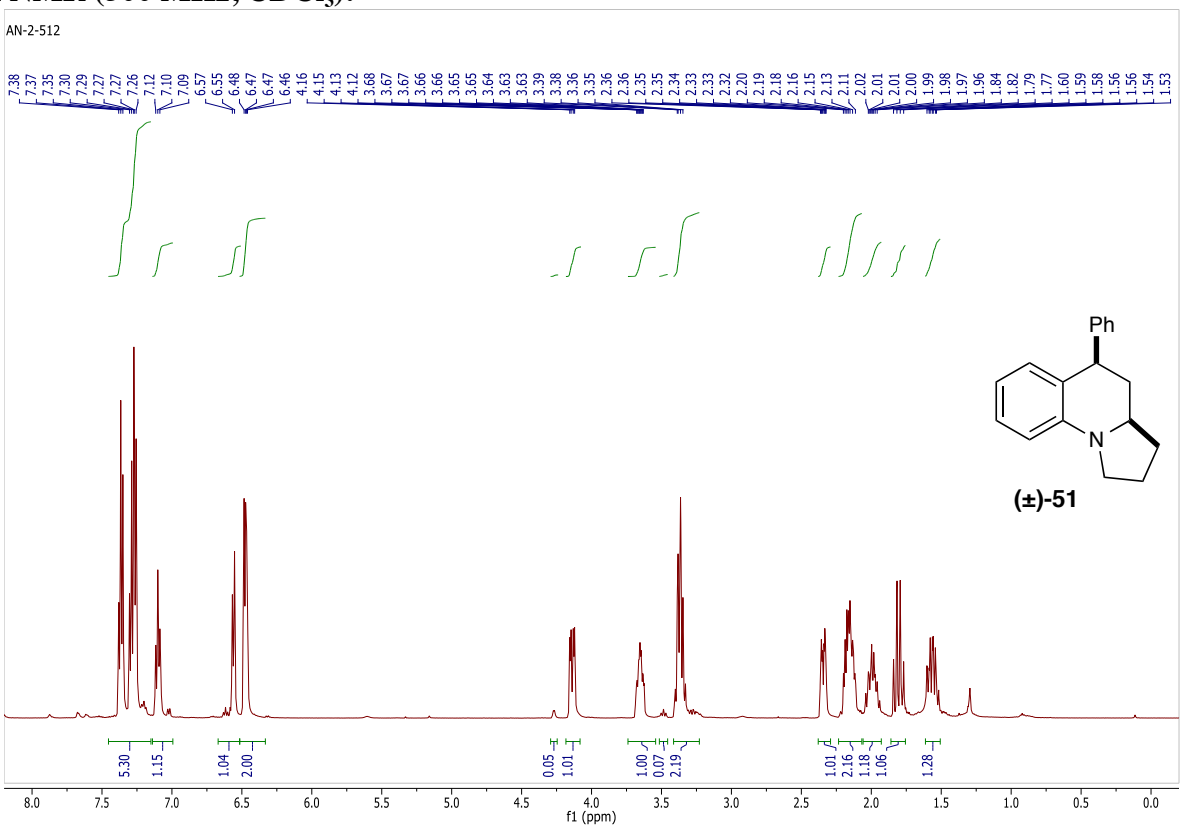

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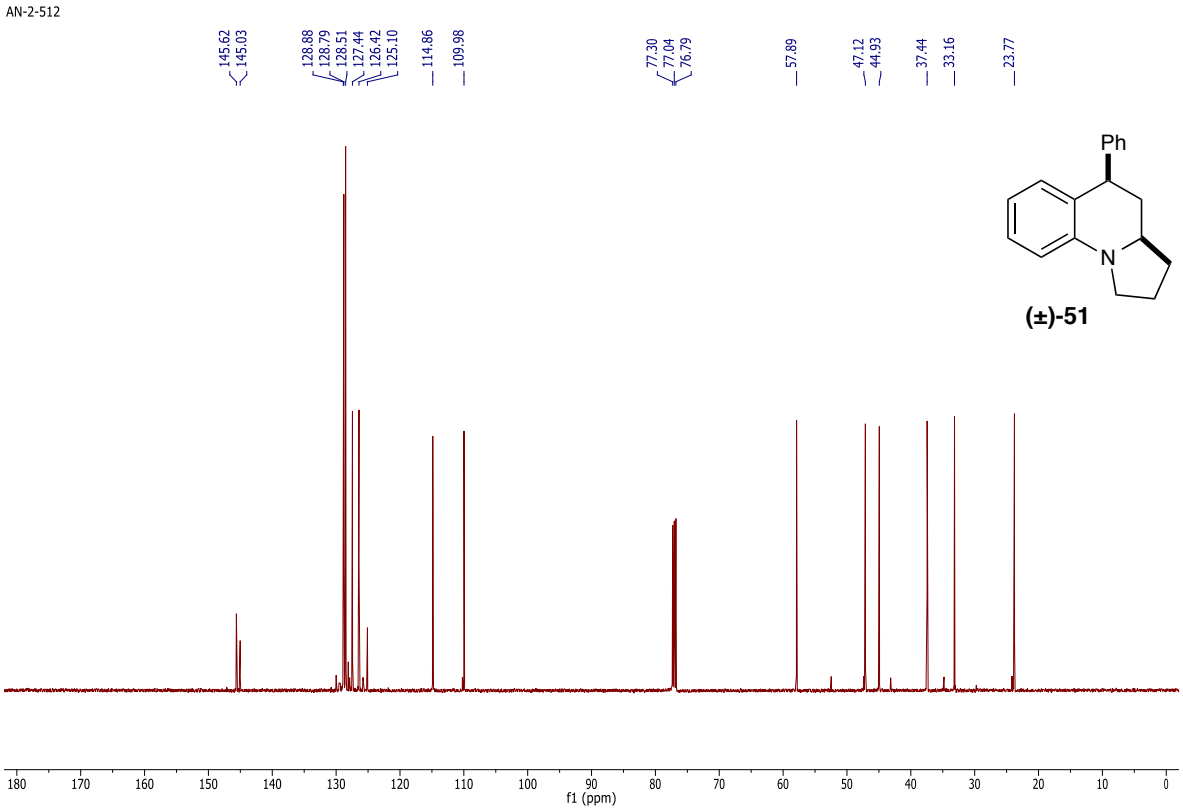

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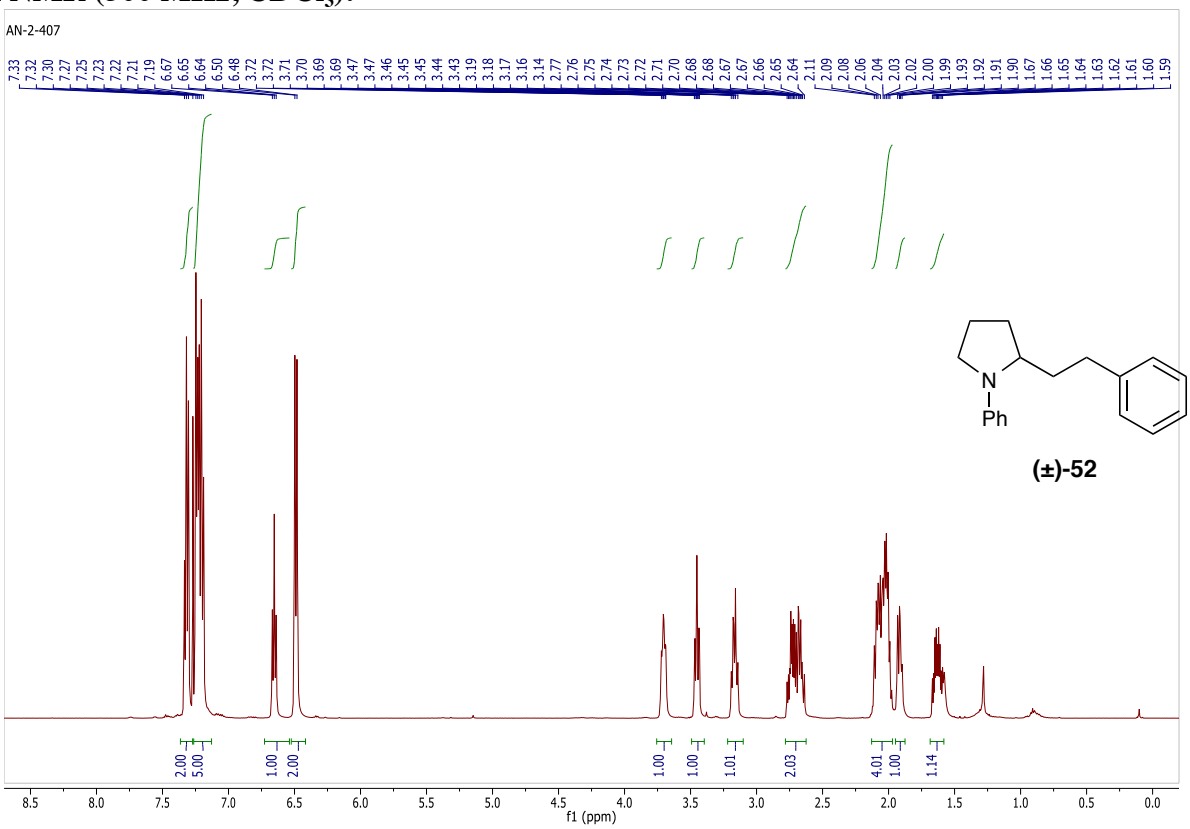
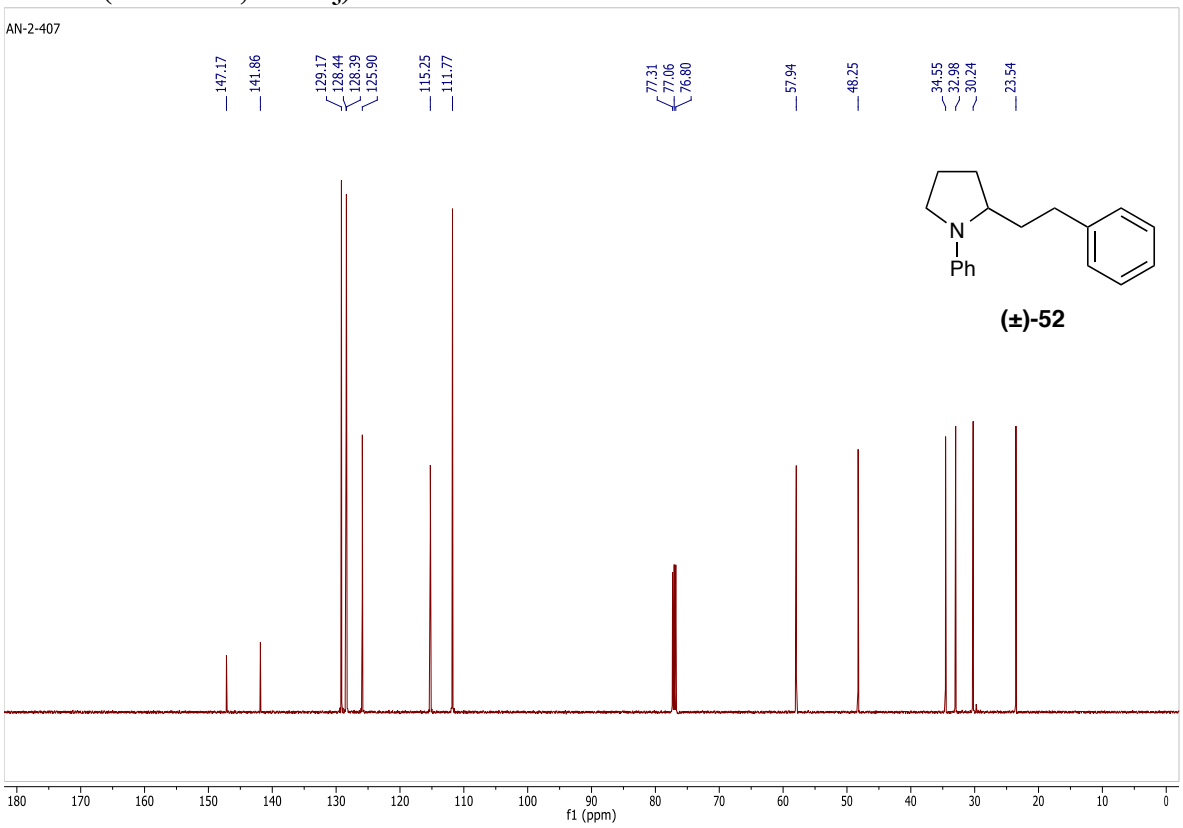


^{13}C NMR (126 MHz, $CDCl_3$):



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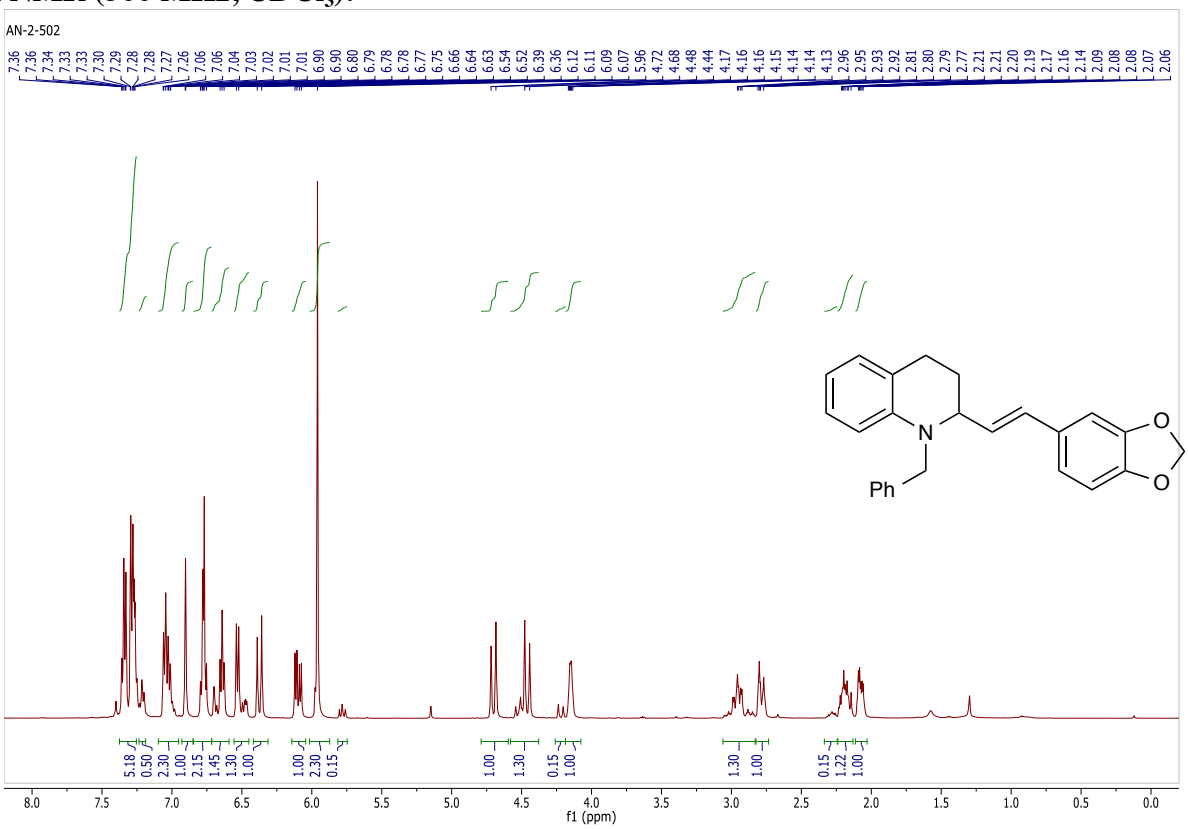

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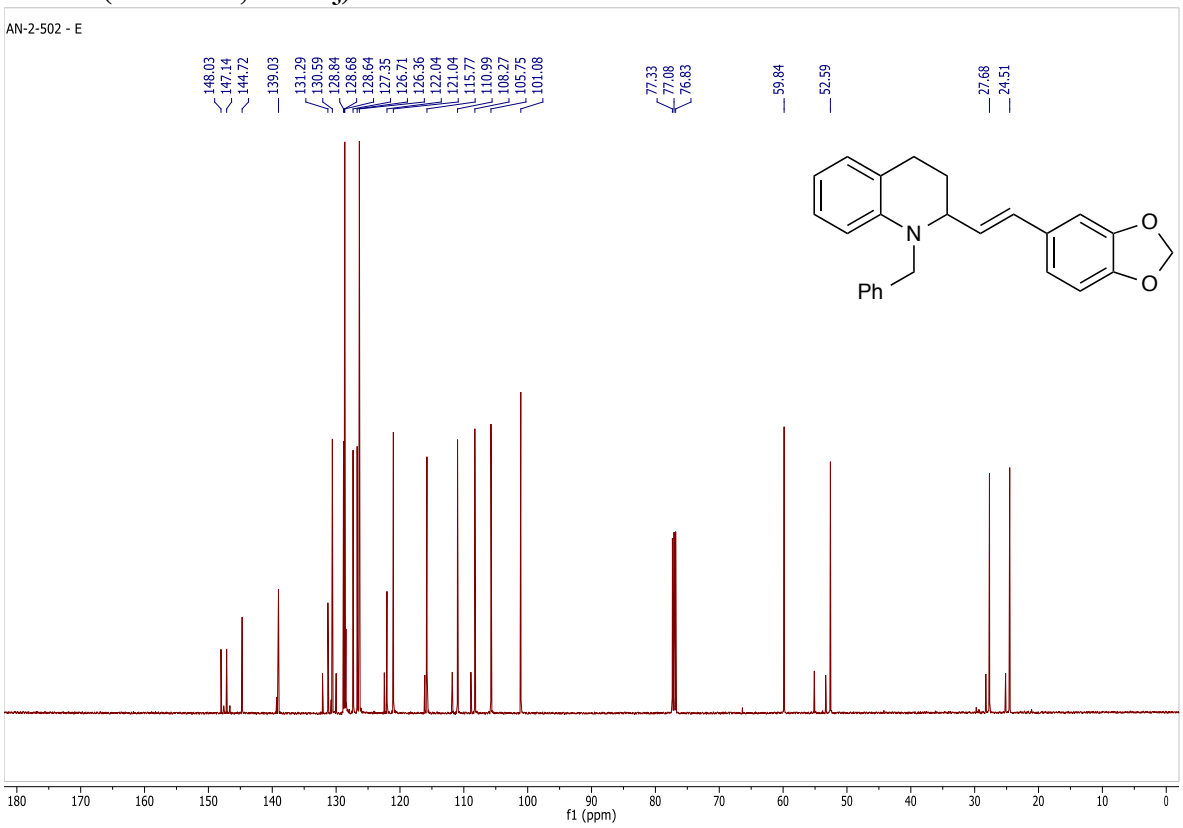

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