De novo Synthesis of Multi-Substituted Aryl Amines using Alkene Cross Metathesis

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Electronic Supporting Information

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General methods

^{1}H nuclear magnetic resonance spectra (NMR) were recorded at 400 MHz, or 500 MHz. ^{13}C NMR spectra were recorded at 100 MHz or 126 MHz as stated. ^{19}F NMR spectra are recorded at 377 MHz and are externally calibrated to $CFCl_3$. Chemical shifts are reported relative to residual solvent peaks or tetramethylsilane internal standard with signal splittings recorded as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), sextet (sxt.) septet (sept.) and broad singlet (br. s). Coupling constants, *J*, are quoted to the nearest 0.1 Hz and to 1 Hz for ^{1}H NMR and ^{13}C NMR, respectively. ^{1}H and ^{13}C NMR spectra were recorded at room temperature.

Fourier transform infrared spectra (FTIR) were recorded as evaporated films. Absorption maxima are quoted in wavenumbers (cm^{-1}) for the range 3500-800 cm^{-1}. Mass spectra were recorded on a Fisons Platform II spectrometer under electrospray ionisation (ESI). Melting points (m.p.) were obtained from recrystallized samples using a Lecia VMTG heated-stage microscope and are uncorrected. The solvent systems used for recrystallization are quoted in parentheses. Optical rotations were recorded on a Perkin Elmer 241 Polarimeter (using the sodium D line, 589 nm) and $[\alpha]_D^{20}$ are given in units of deg $dm^{-1}cm^3g^{-1}$; concentrations given in brackets are in g $(100\ mL)^{-1}$.

Flash column chromatography was performed using silica gel (60 Å, 0.040-0.063 mm, VWR). TLC analyses were performed on Merck Kiesegel 60 F254 0.25 mm precoated silica plates. Petrol refers to petroleum ether in the boiling range 40-60 °C. Product spots were visualized under UV light (λmax = 254 nm) and/or by staining with potassium permanganate or vanillin solutions as deemed appropriate. Reagents obtained from Aldrich, Alfa and TCI suppliers were used directly as supplied. All anhydrous reactions were carried out in flame-dried glassware and under an inert atmosphere of argon. THF and CH_2Cl_2 were dried by purification through activated alumina purification columns.

Experimental Procedures and Data for the Synthesis of Aryl Amines

Procedure 1 for the cross-metathesis of homoallylic alcohols:
A resealable reaction tube, fitted with a magnetic follower, was charged with Zhan 1B catalyst (2 - 5 mol%). The tube was then sealed with a rubber septum and purged with argon. Argon sparged CH_2Cl_2 (0.10 M with respect to the homoallylic alcohol), the corresponding α,β-enone (500 mol%) and the corresponding homoallylic alcohol (100 mol%) were added sequentially *via* syringe. The rubber septum was then replaced with a screw cap and the tube was heated at 55 °C (oil bath temperature) for 24 to 48 h. After cooling to 0 ºC, the reaction mixture was diluted with CH_2Cl_2 (0.10 M with respect to the homoallylic alcohol), water (100 μL/mmol of homoallylic alcohol) and Dess-Martin periodinane (150 mol%) were added and the reaction was monitored by TLC until the cross-metathesis (CM) product was consumed. The reaction mixture was filtered through a cartridge of SiO_2 (eluting with Et_2O) and solvent was removed *in vacuo*. Purification of the residue by flash column chromatography, under the conditions noted, afforded the corresponding α,β-unsaturated 1,5-dicarbonyl.

Procedure 2 for the cross-metathesis of homoallylic alcohols:
A reaction tube, fitted with a magnetic follower, was charged with Zhan 1B catalyst (2 - 5 mol%). The tube was then sealed with a rubber septum and purged with argon. Argon sparged CH_2Cl_2 (0.10 M with respect to the homoallylic alcohol), methyl vinyl ketone (500 mol%) and the corresponding homoallylic alcohol (100 mol%) were added sequentially *via* syringe. The reaction mixture was heated at reflux under argon for 24 to 48 h. After cooling to room temperature the reaction mixture was filtered through a cartridge of SiO_2 (under the conditions noted). The fractions containing the target CM product were combined and concentrated *in vacuo*. The residue was dissolved in CH_2Cl_2 (0.10 M with respect to the homoallylic alcohol) and then cooled to 0 ºC. Water (100 μL/mmol of homoallylic alcohol) and Dess-Martin periodinane (200 - 300 mol%) were added sequentially and the reaction was monitored by TLC until the CM product was consumed. The reaction mixture was filtered through a cartridge of SiO_2 (eluting with Et_2O) and solvent was removed *in vacuo*. Purification of the residue by flash column chromatography, under the conditions noted, afforded the corresponding unsaturated 1,5-dicarbonyl.

Procedure 3 for the formation of Aryl Amines:
A microwave vial fitted with a magnetic follower was charged with the corresponding α,β-unsaturated 1,5-dicarbonyl (100 mol%), dissolved in CH_2Cl_2 (0.10 M with respect to α,β-unsaturated 1,5-dicarbonyl) and the corresponding amine (500 mol%) added. The reaction mixture was stirred at room temperature for 5-18 h. The crude mixture was concentrated and purified by flash column chromatography, under the conditions noted to afford the corresponding aryl amine.

Procedure 4 for the formation of Aryl Amines:
A microwave vial fitted with a magnetic follower was charged with the corresponding α,β-unsaturated 1,5-dicarbonyl (100 mol%), dissolved in CH_2Cl_2 (0.10 M with respect to α,β-unsaturated 1,5-dicarbonyl) and the corresponding amine (500 mol%) added. The reaction mixture was heated at 55 °C (oil bath temperature) for 18 h and then cooled to room temperature. The crude mixture was concentrated and purified by flash column chromatography, under the conditions noted to afford the corresponding aryl amine.

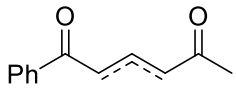
Procedure 5 for synthesis of allylic alcohols:
A solution of aldehyde (100 mol%) in THF (0.10 M with respect to aldehyde) was cooled to -78 °C and Grignard reagent (110 mol%.) added dropwise. The reaction was then monitored until full consumption of the aldehyde was observed by TLC. The reaction mixture was allowed to warm to room

temperature and then quenched by the addition a saturated aqueous solution of NH_4Cl (3 × 20 mL/mmol). The mixture was extracted with EtOAc (3 x 20 ml/mol). The organic layers were combined, dried ($MgSO_4$) and concentrated to give crude reaction mixture which was purified under the noted conditions.

Procedure 6 for synthesis of allylic alcohols:

To a mixture of the corresponding aldehyde (100 mol%) in THF (0.5 M with respect to aldehyde) and saturated aqueous NH_4Cl (0.25 M with respect to aldehyde) was added zinc powder (300 mol%) and the corresponding allylic halide (150 - 200 mol%) and the mixture was vigorously stirred at room temperature and monitored by TLC. After all of the aldehyde was consumed the reaction mixture was extracted with EtOAc (3 × 20 mL/mmol). The organic extracts were combined and extracted with brine (20 mL/mmol), dried (Na_2SO_4) and concentrated *in vacuo*. Purification of the residue by flash column was performed under the conditions noted, to afford the corresponding allyl alcohol.

(*E*)-1-Phenylhex-3-ene-1,5-dione (2a)



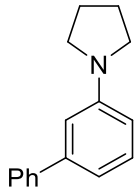
1-phenylbut-3-en-1-ol (100 mg, 0.746 mmol), Zhan 1B catalyst (5 mol%) and but-3-en-2-one were subjected to general procedure 1. The reaction mixture was heated for 36 h. Dess-Martin periodinane (200 mol%) was used for the oxidation step. The crude mixture was purified by flash column chromatography (petrol-EtOAc, 9:1 to 6:4) to afford unsaturated dicarbonyl **(2a)** (109 mg, 78%, 1:0.3 rr) as a red oil.

^{1}H NMR (400 MHz, *CHLOROFORM-d*) δ ppm 7.86 - 8.05 (2.6 H, m), 7.54 - 7.66 (1.3 H, m), 7.40 - 7.54 (2.6 H, m), 7.01 - 7.15 (1.3 H, m), 6.89 - 6.96 (0.3 H, m), 6.19 (1 H, dt, *J*=16.2, 1.4 Hz), 3.94 (2 H, dd, *J*=6.9, 1.4 Hz), 3.39 - 3.51 (0.6 H, m), 2.30 (3 H, s), 2.19 - 2.27 (0.9 H, m).

^{13}C NMR (100 MHz, *CHLOROFORM-d*) δ ppm 198.2, 196.1, 139.9, 136.1, 134.3, 133.7, 132.9, 129.3, 128.8, 128.6 (2C), 128.2, 47.0, 41.6, 30.0, 26.7 (only 16 signals observed).

Data were consistent with those previously reported.[1]

1-([1,1'-Biphenyl]-3-yl)pyrrolidine (3a)



Unsaturated 1,5-dicarbonyl **2a (**40 mg, 0.22 mmol) and pyrrolidine were subjected to general procedure 3. The reaction mixture was stirred for 2 h. In a modification to the general procedure the reaction was carried out at 0 °C. Purification by flash column chromatography (petrol-EtOAc, 19:1) afforded aryl amine **3a** (39 mg, 83%) as a colourless oil.

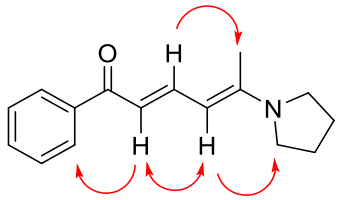
^{1}H NMR (400 MHz, *CHLOROFORM-d*) δ ppm 7.65 (2 H, d, *J*=7.1 Hz), 7.46 (2 H, t, *J*=7.5 Hz), 7.34 - 7.39 (1 H, m), 7.31 - 7.34 (1 H, m), 6.92 (1 H, d, *J*=7.6 Hz), 6.80 (1 H, t, *J*=2.0 Hz), 6.61 (1 H, dd, *J*=8.2, 2.1 Hz), 3.38 (4 H, t, *J*=6.6 Hz), 2.05 (4 H, t, *J*=6.6 Hz)

^{13}C NMR (100 MHz, *CHLOROFORM-d*) δ ppm 148.3, 142.4, 142.4, 129.5, 128.6, 127.4, 127.0, 114.7, 110.7, 110.5, 47.7, 25.5.

Data were consistent with those previously reported.[2]

[1] Donohoe, T. J.; Basutto, J. A.; Rathi, A. H.; Bower, J. F. *Org. Lett.* **2011**, *13*, 1036.
[2] Sezen, B.; Sames, D.; *J. Am. Chem. Soc.* **2006**, *128*, 3102.

(2*E*,4*E*)-1-Phenyl-5-(pyrrolidin-1-yl)hexa-2,4-dien-1-one (4)



To a solution of (*E*)-1-phenylhex-2-ene-1,5-dione **2a** (10 mg, 0.05 mmol) in CH_2Cl_2 (0.5 mL) in a round bottomed flask containing a magnetic follower was added pyrrolidine (5 µl, 0.05 mmol). The reaction mixture was stirred at room temperature for 24 h. The solvent was then removed *in vacuo* and purified by flash column chromatography (EtOAc) to give (2*E*,4*Z*)-1-phenyl-5-(pyrrolidin-1-yl)hexa-2,4-dien-1-one **4** (5 mg, 39 %) as an orange oil.

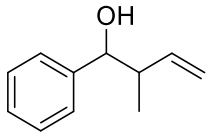
^{1}H NMR (500 MHz, *CHLOROFORM-d*) δ ppm 8.05 (1 H, dd, *J*=13.7, 12.5 Hz), 7.90 - 7.99 (2 H, m), 7.36 - 7.51 (3 H, m), 6.61 (1 H, d, *J*=13.9 Hz), 5.36 (1 H, d, *J*=12.6 Hz), 3.31 - 3.53 (4 H, m), 2.20 (3 H, s), 1.92 - 2.01 (4 H, m). *NOE enhancements associated with enamine **4** are represented by red arrows on the compound structure.*

^{13}C NMR (125 MHz, *CHLOROFORM-d*) δ ppm 189.1, 156.0, 146.0, 140.5, 130.9, 128.1, 127.8, 111.2, 98.0, 48.4, 25.1, 16.3.

FTIR 2967, 1721, 1678, 1597, 1448, 1264, 1100, 729 cm^{-1}.

HRMS m/z $[C_{16}H_{19}NO+H]^+$ cal.242.1539, found 242.1540.

2-Methyl-1-phenylbut-3-en-1-ol (1b)



Benzylaldehyde (0.930 g, 8.77 mmol, 0.894 mL) and crotyl bromide (2.37g, 17.5 mmol, 1.81 mL) were subjected to general procedure 6. The crude mixture was purified by flash column chromatography (petrol-EtOAc, 19:1) to afford allylic alcohol **1b** (1.42g, 95%, 1:1 dr) as an oil.

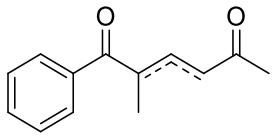
^{1}H NMR (400 MHz, *CHLOROFORM-d*) δ ppm 7.23 - 7.45 (10 H, m), 5.70 - 5.90 (2 H, m), 5.15 - 5.27 (2 H, m), 5.02 - 5.11 (2 H, m), 4.59 (1 H, d, *J*=5.6 Hz), 4.37 (1 H, d, *J*=7.8 Hz), 2.55 - 2.64 (1 H, m), 2.44 - 2.55 (1 H, m), 2.28 (2 H, br. s), 1.04 (3 H, d, *J*=6.8 Hz), 0.90 (3 H, d, *J*=6.8 Hz)

^{13}C NMR (100 MHz, *CHLOROFORM-d*) δ ppm 142.7, 142.5, 140.7, 140.4, 128.2, 128.1, 127.6, 127.3, 126.9, 126.6, 116.7, 115.5, 77.9, 76.8, 46.2, 44.7, 16.5, 14.1

Data were consistent with those previously reported.[3]

[3] Tan, K. T.; Chang, S. S.; Cheng, H. S.; Loh, T. P. *J. Am. Chem. Soc.* **2003**, *125*, 2958.

1-Phenyl-3-(phenylamino)hexane-1,5-dione (2b)



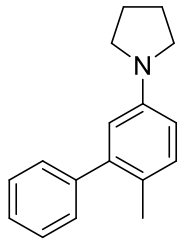
2-Methyl-1-phenylbut-3-en-1-ol (100 mg, 0.617 mmol), Zhan 1B catalyst (2 mol%) and but-3-en-2-one were subjected to general procedure 1. The reaction mixture was heated for 24 h. Dess-Martin periodinane (200 mol%) was used for the oxidation step. The crude mixture was purified by flash column chromatography (petrol-EtOAc 9:1 to 6:4) to afford unsaturated dicarbonyl **2b** (91 mg, 73%, 1:0.2 rr) as a red oil.

^{1}H NMR (400 MHz, *CHLOROFORM-d*) δ ppm 7.95 (0.4 H, d, *J*=7.3 Hz), 7.68 (2 H, d, *J*=7.1 Hz), 7.35 - 7.63 (3.4 H, m), 6.95 (0.2 H, dd, *J*=16.2, 7.8 Hz), 6.45 (1 H, td, *J*=7.0, 1.4 Hz), 6.15 (0.2 H, d, *J*=16.2 Hz), 4.33 (0.2 H, q, *J*=6.9 Hz), 3.43 (2 H, d, *J*=7.1 Hz), 2.24 (0.6 H, s), 2.20 (3 H, s), 1.95 (3 H, s), 1.40 (0.6 H, d, *J*=7.1 Hz).

^{13}C NMR (100 MHz, *CHLOROFORM-d*) δ ppm 204.3, 199.6, 198.3 (2C), 146.3, 138.7, 137.9, 135.9, 135.6, 133.6, 132.0, 131.8, 129.5, 128.8, 128.5, 128.2, 44.2, 43.4, 30.1, 26.9, 17.3, 13.1.

Data were consistent with those previously reported.[1]

1-(6-Methyl-[1,1'-biphenyl]-3-yl)pyrrolidine (3b)



Unsaturated 1,5-dicarbonyl **2b (**44 mg, 0.22 mmol) and pyrrolidine were subjected to general procedure 3. The reaction mixture was stirred for 18 h. Purification by flash column chromatography (petrol-EtOAc, 19:1) afforded aryl amine **3a** (39 mg, 75%) as a colourless oil.

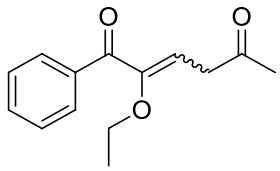
^{1}H NMR (400 MHz, *CHLOROFORM-d*) δ ppm 7.33 - 7.48 (5 H, m), 7.16 (1 H, d, *J*=8.2 Hz), 6.56 (1 H, d, *J*=7.8 Hz), 6.52 (1 H, br. s), 3.26 - 3.39 (4 H, m), 2.19 (3 H, s), 1.98 - 2.07 (4 H, m)

^{13}C NMR (100 MHz, *CHLOROFORM-d*) δ ppm 146.2, 143.0, 142.5, 131.0, 129.2, 128.0, 126.6, 122.0, 113.4, 110.9, 47.9, 25.5, 19.3.

FTIR 2965, 1613, 1562, 1509, 1488, 1460, 1420, 1369, 1282, 1180, 976, 847, 799, 773, 702, 630 cm^{-1}.

HRMS m/z $[C_{17}H_{19}N+H]^+$ cal.238.1590, found 238.1587.

2-Ethoxy-1-phenylhex-2-ene-1,5-dione (2c)



2-Ethoxy-1-phenylbut-3-en-1-ol[4] (82 mg, 0.43 mmol), Zhan 1B catalyst (5 mol%) and but-3-en-2-one were subjected to general procedure 2. The reaction mixture was heated for 48 h and then filtered using petrol-Et_2O (1:1). Dess-Martin periodinane (200 mol%) was used for the oxidation step. The crude mixture was purified by flash column chromatography (petrol-EtOAc, 9:1 to 6:4) to afford unsaturated dicarbonyl **2c** (44 mg, 45%, 1:0.5 dr) as a red oil.

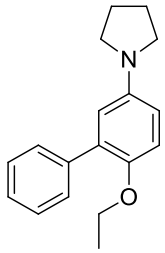
^{1}H NMR (400 MHz, *CHLOROFORM-d*) δ ppm 7.82 - 7.93 (3.0 H, m), 7.56 (1.5 H, t, *J*=7.5 Hz), 7.45 (3.0 H, t, *J*=7.7 Hz), 5.89 (1.0 H, t, *J*=7.1 Hz), 5.27-5.32 (0.5, t, *J*=6.8 Hz), 3.77 - 3.97 (3.0 H, m), 3.45 - 3.51 (2.0 H, m), 3.36 (1.0 H, d, *J*=7.3 Hz), 2.23 (3.0 H, s), 2.14 (1.5 H, s), 1.32 (1.5 H, t, *J*=6.9 Hz), 1.25 (3.0 H, t, *J*=6.9 Hz).

^{13}C NMR (*CHLOROFORM-d*) δ ppm 205.1, 192.2, 153.6, 137.2, 133.3, 132.8, 129.9, 129.5, 128.4, 128.3, 119.7, 100.0, 66.6, 63.7, 41.0, 40.4, 30.0, 15.5, 14.4.

FTIR 2979, 1716, 1657, 1597, 1448, 1359, 1253, 1160, 1047, 1017, 978, 717, 666 cm^{-1}.

HRMS m/z $[C_{14}H_{16}O_3+Na]^+$ cal. 255.0992, found 255.0989.

1-(6-Ethoxy-[1,1'-biphenyl]-3-yl)pyrrolidine (3c)



Unsaturated 1,5-dicarbonyl **2c (**24 mg, 0.10 mmol) and pyrrolidine were subjected to general procedure 3. The reaction mixture was stirred for 5 h. Purification by flash column chromatography (petrol-EtOAc, 19:1) afforded aryl amine **3c** (22 mg, 79%) as a colourless oil.

^{1}H NMR (500 MHz, *CHLOROFORM-d*) δ ppm 7.59 (2 H, m), 7.41 (2 H, t, *J*=7.6 Hz), 7.33 (1 H, m), 6.97 (1 H, d, *J*=8.8 Hz), 6.68 (2 H, m), 3.89 (2 H, q, *J*=6.9 Hz), 3.32 (4 H, m), 2.04 (4 H, m), 1.27 (3 H, t, J=6.9).

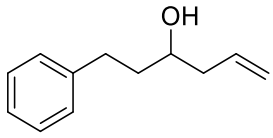
^{13}C NMR (125 MHz, *CHLOROFORM-d*) δ ppm 139.3, 132.6, 129.5, 129.3, 128.3, 127.9, 127.9, 126.8 (2C), 116.4, 65.9, 48.8, 25.4, 15.1.

FTIR 2973, 2873, 1613, 1508, 1487, 1420, 1390, 1369, 1230, 1050, 699 cm^{-1}.

HRMS m/z $[C_{18}H_{21}NO+H]^+$ cal. 268.1696, found 268.1697.

[4] Donohoe, T. J.; Fishlock, L. P.; Lacy, A. R.; Procopiou, P. A. *Org. Lett.* **2007**, *9*, 953.

1-Phenylhex-5-en-3-ol (1d)



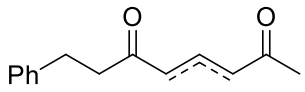
Propenyl aldehyde (5.00 g, 37.3 mmol, 4.91 mL) and allyl magnesium bromide (1.0 M in Et_2O, 41.0 mmol, 41.0 mL) was subjected to general procedure 5. The crude mixture was purified by flash column chromatography (petrol-EtOAc 9:1) to afford allylic alcohol **1d** (4.90 g, 75 %) as an oil.

^{1}H NMR (400 MHz, *CHLOROFORM-d*) δ ppm 7.15 - 7.40 (5 H, m), 5.72 - 5.97 (1 H, m), 5.17 (2 H, d, *J*=13.6 Hz), 3.70 (1 H, br. s), 2.79 - 2.91 (1 H, m), 2.62 - 2.78 (1 H, m), 2.33 - 2.37 (1 H, m), 2.15 - 2.29 (1 H, m), 1.66 - 1.90 (3 H, m).

^{13}C NMR (100 MHz, *CHLOROFORM-d*) δ ppm 142.1, 134.7, 128.5, 128.4, 125.8, 118.3, 69.9, 42.1, 38.5, 32.1.

Data were consistent with those previously reported. [5]

1-Phenylhex-5-en-3-one (2d)



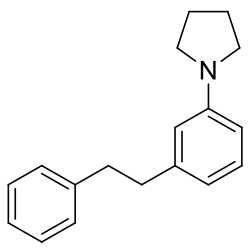
1-Phenylhex-5-en-3-one (97 mg, 0.46 mmol), Zhan 1B catalyst (2 mol%) and but-3-en-2-one were subjected to general procedure 2. The reaction mixture was heated for 48 h and then filtered using petrol-Et_2O (1:1). Dess-Martin periodinane (250 mol%) was used for the oxidation step. Purification by flash column chromatography (petrol-EtOAc, 9:1 to 6:4) afforded unsaturated dicarbonyl **2d** (77 mg, 61%, 1:1 rr) as an oil.

^{1}H NMR (400 MHz, *CHLOROFORM-d*) δ ppm 7.21 - 7.33 (4 H, m), 7.14 - 7.23 (6 H, m), 6.79 - 6.95 (2 H, m), 6.01 - 6.19 (2 H, m), 3.33 (4 H, m), 2.86 - 2.97 (6 H, m), 2.81 (2 H, d, *J*=7.3 Hz), 2.25 (3 H, s), 2.19 (3 H, s).

^{13}C NMR (100 MHz, *CHLOROFORM-d*) δ ppm 205.7, 204.4, 199.0, 198.1, 141.0, 140.5, 139.0, 138.2, 134.2, 133.3, 128.6, 128.5, 128.4, 128.3, 126.3, 126.1, 46.5, 45.9, 44.4, 41.5, 30.0, 29.9, 29.6, 26.7.

Data were consistent with those previously reported. [1]

1-(3-Phenethylphenyl)pyrrolidine (3d)



[5] Felpin, F. X.; Lebreton, J. *J. Org. Chem.* **2002**, *67*, 9192.

Unsaturated 1,5-dicarbonyl **2d (**50 mg, 0.23 mmol) and pyrrolidine were subjected to general procedure 3. The reaction mixture was stirred for 18 h. Purification by flash column chromatography (petrol-EtOAc, 19:1) afforded aryl amine **3d** (35 mg, 60%) as a colourless oil.

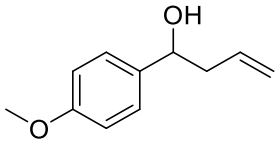
^{1}H NMR (400 MHz, *CHLOROFORM-d*) δ ppm 7.31 - 7.38 (2 H, m), 7.18 - 7.31 (4 H, m), 6.60 (1 H, d, *J*=7.3 Hz), 6.44 - 6.54 (2 H, m), 3.29 - 3.38 (4 H, m), 2.89 - 3.04 (4 H, m), 2.01 - 2.10 (4 H, m)

^{13}C NMR (100 MHz, *CHLOROFORM-d*) δ ppm 148.0, 142.9, 142.3, 129.2, 128.5, 128.3, 125.8, 115.8, 111.9, 109.6, 47.7, 38.5, 38.1, 25.5.

FTIR 2925, 1600, 1578, 1497, 1453, 1370, 1174, 1015, 908, 839, 770, 695 cm^{-1}.

HRMS m/z $[C_{18}H_{21}N+H]^+$ cal. 252.1747, found 252.1736.

1-(4-Methoxyphenyl)but-3-en-1-ol (1e)



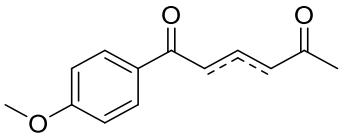
p-Anisaldehyde (1.00 g, 7.35mmol, 0.893 mL) and allyl magnesium chloride (2.0 M in THF, 8.09 mmol, 4.45 mL) were subjected to general procedure 5 to give alcohol **1e** (1.18 g, 90%).

^{1}H NMR (400 MHz, *CHLOROFORM-d*) δ ppm 7.29 (2 H, d, *J*=8.6 Hz), 6.89 (2 H, d, *J*=8.6 Hz), 5.68 - 5.90 (1 H, m), 5.05 - 5.21 (2 H, m), 4.69 (1 H, t, *J*=6.4 Hz), 3.81 (3 H, s), 2.50 (2 H, t, *J*=6.8 Hz), 2.07 (1 H, d, *J*=7.1 Hz).

^{13}C NMR (100 MHz, *CHLOROFORM-d*) δ ppm 159.0, 136.1, 134.7, 127.1, 118.2, 113.8, 73.0, 55.3, 43.8.

Data were consistent with those previously reported.[6]

(*E*)-1-(4-Methoxyphenyl)hex-3-ene-1,5-dione (2e)



1-(4-Methoxyphenyl)but-3-en-1-ol (100 mg, 0.56 mmol), Zhan 1B catalyst (5 mol%) and but-3-en-2-one were subjected to general procedure 2. The reaction mixture was heated for 48 h and then filtered using petrol-Et_2O (1:1). Dess-Martin periodinane (250 mol%) was used for the oxidation step. Purification by flash column chromatography (petrol-EtOAc, 9:1 to 6:4) afforded unsaturated dicarbonyl **2e** (77 mg, 62%, 1:0.2 rr) as an oil.

^{1}H NMR (400 MHz, *CHLOROFORM-d*) δ ppm 7.83 - 7.89 (2.4 H, m), 6.94 - 7.03 (1.2 H, m), 6.85 - 6.90 (2.6 H, m), 6.10 (1.0 H, d, *J*=16.1 Hz), 3.78 - 3.83 (5.6 H, m), 3.37 (0.4 H, d, *J*=7.1 Hz), 2.22 (3.0 H, s), 2.16 (0.6 H, s).

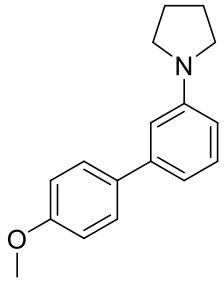
[6] Jang, D. O.; Lee, B. S. *Euro. J. Org. Chem.* **2013**, *15*, 3123.

^{13}C NMR (100 MHz, *CHLOROFORM-d*) δ ppm 203.6, 197.3, 193.6, 187.5, 162.9, 139.5, 137.8, 133.2, 130.0, 129.7, 129.6, 129.3, 128.1, 128.0, 113.0, 112.8, 54.5, 54.5, 46.0, 40.3, 29.0., 25.6.

FTIR 2963, 1671, 1598, 1511, 1511, 1421, 1314, 1258, 1171, 1026, 979, 839 cm^{-1}.

HRMS m/z $[C_{13}H_{14}O_3+Na]^+$ cal. 241.0829, found 241.0835.

1-(4'-Methoxy-[1,1'-biphenyl]-3-yl)pyrrolidine (3e)



Unsaturated 1,5-dicarbonyl **2e (**35 mg, 0.16 mmol) and pyrrolidine were subjected to general procedure 4. Purification by flash column chromatography (petrol-EtOAc to 19:1) afforded aryl amine **3e** (25 mg, 63%) as a colourless oil.

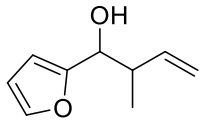
^{1}H NMR (400 MHz, *CHLOROFORM-d*) δ ppm 7.53 - 7.63 (2 H, m), 7.30 (1 H, t, *J*=7.8 Hz), 6.96 - 7.04 (2 H, m), 6.88 (1 H, d, *J*=7.6 Hz), 6.75 (1 H, s), 6.57 (1 H, dd, *J*=8.2, 2.1 Hz), 3.88 (3 H, s), 3.33 - 3.42 (4 H, m), 2.00 - 2.09 (4 H, m).

^{13}C NMR (100 MHz, *CHLOROFORM-d*) δ ppm 159.0, 148.3, 141.9, 134.9, 129.5, 128.3, 114.4, 114.0, 110.3, 110.2, 55.4, 47.7, 25.5.

FTIR 2967, 1597, 1573, 1508, 1423, 1381, 1359, 1328, 1304, 1250, 1196, 1163, 1111, 1017, 979, 909, 832, 728, 644 cm^{-1}.

HRMS m/z $[C_{17}H_{19}NO+H]^+$ cal. 254.1539, found 254.1541.

1-(Furan-2-yl)-2-methylbut-3-en-1-ol (1f)



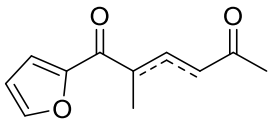
Furfural (1.00 g, 10.4 mmol, 0.862 mL) and 1-methyl-2-propenylmagnesium bromide (0.5 M in Et_2O, 11.4 mmol, 22.8 mL) were subjected to general procedure 5 to give alcohol **1f** (1.01 g, 78%, 1:1 dr).

^{1}H NMR (400 MHz, *CHLOROFORM-d*) δ ppm 7.35 - 7.45 (2 H, m), 6.36 (2 H, td, *J*=3.8, 2.0 Hz), 6.29 (1 H, d, *J*=2.9 Hz), 6.25 (1 H, d, *J*=2.9 Hz), 5.69 - 5.89 (2 H, m), 5.04 - 5.29 (4 H, m), 4.59 (1 H, t, *J*=5.6 Hz), 4.44 (1 H, dd, *J*=7.7, 3.5 Hz), 2.67 - 2.80 (2 H, m), 2.19 (1 H, br. s), 2.12 (1 H, br. s), 1.09 (3 H, d, *J*=6.8 Hz), 0.97 (3 H, d, *J*=6.8 Hz).

^{13}C NMR (100 MHz, *CHLOROFORM-d*) δ ppm 155.3, 155.0, 142.0, 141.8, 140.0, 139.6, 117.1, 116.0, 110.1, 110.1, 107.3, 106.9, 71.4, 71.4, 43.6, 43.1, 16.3, 15.1.

Data were consistent with those previously reported.[7]

(*E*)-1-(Furan-2-yl)-2-methylhex-2-ene-1,5-dione (2f)



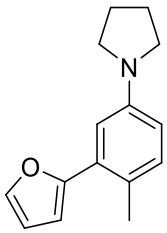
1-(Furan-2-yl)-2-methylbut-3-en-1-ol (150 mg, 0.99 mmol), Zhan 1B catalyst (5 mol%) and but-3-en-2-one were subjected to general procedure 2. The reaction mixture was heated for 24 h and then filtered using Petrol-Et_2O (1:1). Dess-Martin periodinane (200 mol%) was used for the oxidation step. Purification by flash column chromatography (petrol-EtOAc, 8:2 to 7:3) afforded unsaturated dicarbonyl **2f** (102 mg, 54%, 1:0.5 rr) as an oil.

^{1}H NMR (400 MHz, *CHLOROFORM-d*) δ ppm 7.53 - 7.60 (1.5 H, m), 7.20 (1.0 H, dd, *J*=3.7, 0.7 Hz), 7.12 (0.5 H, d, *J*=3.4 Hz), 6.84 (1.0 H, dd, *J*=16.1, 8.1 Hz), 6.69 - 6.76 (0.5 H, m), 6.48 - 6.54 (1.0 H, m), 6.43 - 6.48 (0.5 H, m), 6.12 (1.0 H, d, *J*=16.1 Hz), 3.97 - 4.15 (1.0 H, m), 3.39 (1.0 H, d, *J*=7.1 Hz), 2.14 - 2.23 (4.5 H, m), 1.87 (1.5 H, t, *J*=1.0 Hz), 1.33 (3.0 H, d, *J*=6.8 Hz).

^{13}C NMR (100 MHz, *CHLOROFORM-d*) δ ppm 204.7, 198.4, 188.3, 184.3, 151.7 (2 signals), 147.0 (2 signals), 145.6, 137.9, 133.2, 132.3, 120.1, 118.3, 112.6, 111.9, 44.9, 43.2, 30.1, 26.9, 16.6, 13.2.

Data were consistent with those previously reported.[1]

1-(3-(Furan-2-yl)-4-methylphenyl)pyrrolidine (3f)



Unsaturated 1,5-dicarbonyl **2f (**40 mg, 0.26 mmol) and pyrrolidine were subjected to general procedure 4. Purification by flash column chromatography (petrol-EtOAc, 19:1) afforded aryl amine **3f** (40 mg, 68%) as a colourless oil.

^{1}H NMR (400 MHz, *CHLOROFORM-d*) δ ppm 7.40 (1 H, dd, *J*=1.7, 0.7 Hz), 7.00 (1 H, d, *J*=8.6 Hz), 6.84 (1 H, d, *J*=2.7 Hz), 6.43 (1 H, dd, *J*=3.2, 0.7 Hz), 6.37 - 6.42 (2 H, m), 3.14 - 3.30 (4 H, m), 2.30 (3 H, s), 1.83 - 1.97 (4 H, m)

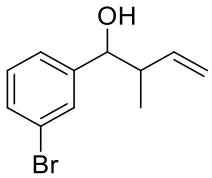
^{13}C NMR (100 MHz, *CHLOROFORM-d*) δ ppm 154.4, 146.4, 141.3, 131.8, 130.6, 121.6, 111.5, 111.2, 110.4, 108.2, 47.9, 25.5, 20.8.

FTIR 2966, 1615, 1511, 1487, 1461, 1366, 1284, 1245, 1211, 1156, 1037, 1016, 908, 849, 799, 734 cm^{-1}.

HRMS m/z $[C_{15}H_{17}NO+H]^+$ cal. 228.1383, found 228.1379.

[7] Fujita, K.; Yorimitsu, H.; Shinokubo, H.; Oshima, K. *J. Am. Chem. Soc*. **2004**, *126*, 6776.

1-(3-Bromophenyl)-2-methylbut-3-en-1-ol (1g)



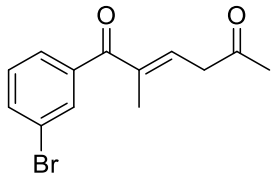
3-Bromo-benzylaldehyde (1.00 g, 5.41 mmol, 0.630 mL) and crotyl bromide (1.46 g, 10.8 mmol, 1.11 mL) were subjected to general procedure 6. The crude mixture was purified by flash column chromatography (petrol-EtOAc, 9:1) to afford allylic alcohol **1g** (1.10 g, 85%, 1:1 dr) as an oil.

^{1}H NMR (400 MHz, *CHLOROFORM-d*) δ ppm 7.34 - 7.58 (4 H, m), 7.12 - 7.30 (4 H, m), 5.66 - 5.87 (2 H, m), 5.16 - 5.25 (2 H, m), 5.02 - 5.14 (2 H, m), 4.54 - 4.68 (1 H, m), 4.34 (1 H, d, *J*=7.6 Hz), 2.51 - 2.60 (1 H, m), 2.39 - 2.51 (1 H, m), 2.18 - 2.25 (1 H, m), 2.01 (1 H, d, *J*=2.8 Hz), 0.99 (3 H, d, *J*=6.8 Hz), 0.90 (3 H, d, *J*=6.8 Hz).

^{13}C NMR (100 MHz, *CHLOROFORM-d*) δ ppm 144.9, 144.8, 140.0, 139.8, 130.7, 130.4, 129.9, 129.8, 129.6, 129.5, 125.6, 125.1, 122.5, 122.3, 117.5, 116.1, 77.1, 76.4, 46.3, 44.5, 16.5, 13.6.

Data were consistent with those previously reported. [8]

(*E*)-1-(3-Bromophenyl)-2-methylhex-2-ene-1,5-dione (2g)



1-Phenylhex-5-en-3-one (85 mg, 0.35 mmol), Zhan 1B catalyst (2 mol%) and but-3-en-2-one were subjected to general procedure 2. The reaction mixture was heated for 24 h and then filtered using petrol-Et_2O (1:1). Dess-Martin periodinane (200 mol%) was used for the oxidation step. Purification by flash column chromatography (petrol-EtOAc, 9:1 to 1:1) afforded unsaturated dicarbonyl **2g** (74 mg, 60%) as an oil.

^{1}H NMR (400 MHz, *CHLOROFORM-d*) δ ppm 7.78 (1 H, s), 7.61 (1 H, d, *J*=8.1 Hz), 7.57 (1 H, d, *J*=7.6 Hz), 7.28 (1 H, t, *J*=7.8 Hz), 6.44 (1 H, t, *J*=6.9 Hz), 3.44 (2 H, d, *J*=6.8 Hz), 2.20 (3 H, s), 1.92 (3 H, s).

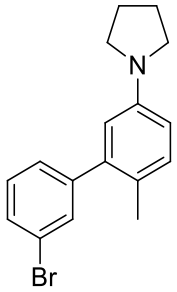
^{13}C NMR (100 MHz, *CHLOROFORM-d*) δ ppm 204.1, 196.6, 139.9, 137.8, 137.0, 134.7, 132.3, 129.8, 128.0, 122.4, 43.3, 30.1, 13.0.

FTIR 1717, 1681, 1651, 1562, 1416, 1359, 1254, 1162, 1070, 1027, 900, 737, 672 cm^{-1}.

HRMS m/z $[C_{13}H_{13}BrO_2+Na]^+$ cal.302.9991, found 302.9981.

[8] Bandini, M.; Cozzi, P. G.; Umani-Ronchi, A. *Tetrahedron*, **2001**, 57, 835.

1-(3'-Bromo-6-methyl-[1,1'-biphenyl]-3-yl)pyrrolidine (3g)



Unsaturated 1,5-dicarbonyl **2g (**50 mg, 0.18 mmol) and pyrrolidine were subjected to general procedure 3. The reaction mixture was heated for 8 h. Purification by flash column chromatography (petrol-EtOAc, 19:1) afforded aryl amine **3g** (46 mg, 82%) as a colourless oil.

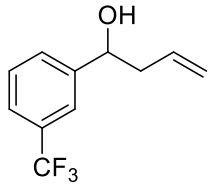
^{1}H NMR (400 MHz, *CHLOROFORM-d*) δ ppm 7.54 (1 H, s), 7.49 (1 H, d, *J*=6.8 Hz), 7.30 (2 H, m), 7.14 (1 H, d, *J*=8.3 Hz), 6.56 (1 H, d, *J*=8.2 Hz), 6.44 (1 H, m), 3.30 (4 H, m), 2.71 (3 H, s) 2.02 (4 H, m).

^{13}C NMR (100 MHz, *CHLOROFORM-d*) δ ppm 146.3, 145.1, 141.0, 132.1, 131.1, 129.6, 129.5, 127.9, 122.1, 121.7, 113.0, 111.4, 47.8, 25.5, 19.2.

FTIR 2966, 1614, 1592, 1557, 1510, 1473, 1403, 1370, 1282, 1160, 1073, 996, 846, 788, 753 cm^{-1}.

HRMS m/z $[C_{17}H_{18}BrN+H]^{+}$ cal. 316.0651, found 316.0655.

1-(3-(Trifluoromethyl)phenyl)but-3-en-1-ol (1h)



3-(Trifluoromethyl)benzaldehyde (500 mg, 2.87 mmol, 0.384 mL) and allyl magnesium bromide (2.0 M in THF, 3.16 mmol, 1.58 mL) were subjected to general procedure 5. The crude reaction mixture was purified by flash column chromatography (petrol-EtOAc, 9:1) to give alcohol **1h** (560 mg, 90%).

^{1}H NMR (400 MHz, *CHLOROFORM-d*) δ ppm 7.53 (1 H, s), 7.40 - 7.46 (2 H, m), 7.32 - 7.39 (1 H, m), 5.62 - 5.83 (1 H, m), 5.02 - 5.13 (2 H, m), 4.62 - 4.74 (1 H, m), 2.27 - 2.50 (3 H, m).

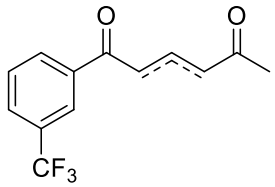
^{13}C NMR (100 MHz, *CHLOROFORM-d*) δ ppm 144.8, 133.7, 130.7 (q, *J*=31.8 Hz), 129.2, 128.8, 124.3 (q, *J*=4.0 Hz), 122.6 (q, *J*=4.0 Hz), 124.2 (q, *J*=273.4 Hz), 119.1, 72.6, 43.9.

^{19}F NMR (377 MHz, *CHLOROFORM-d*) δ ppm -62.6 (CF_3).

Data were consistent with those previously reported. [9]

[9] Doucet, H.; Santelli, M. *Tetrahedron Asymmetry* **2000**, 11, 4163.

(*E*)-1-(3-(Trifluoromethyl)phenyl)hex-3-ene-1,5-dione (2h)



1-(3-(Trifluoromethyl)phenyl)but-3-en-1-ol (150 mg, 0.694 mmol), Zhan 1B catalyst (5 mol%) and but-3-en-2-one were subjected to general procedure 2. The reaction mixture was heated for 24 h and then filtered using Petrol-Et_2O (1:1). Dess-Martin periodinane (300 mol%) was used for the oxidation step. Purification by flash column chromatography (petrol-EtOAc, 8:2 to 7:3) afforded unsaturated dicarbonyl **2g** (85 mg, 45%, 1:0.7 rr) as an oil.

^{1}H NMR (400 MHz, *CHLOROFORM-d*) δ ppm 8.06 - 8.28 (3.4 H, m), 7.84 (1.7 H, dd, *J*=17.5, 7.7 Hz), 7.54 - 7.71 (1.7 H, m), 7.00 - 7.21 (1.7 H, m), 6.92 (0.7 H, d, *J*=15.7 Hz), 6.21 (1.0 H, d, *J*=16.4 Hz), 3.98 (2 H, d, *J*=8.1 Hz), 3.50 (1.4 H, d, *J*=7.1 Hz), 2.31 (3.0 H, s), 2.26 (2.1 H, s).

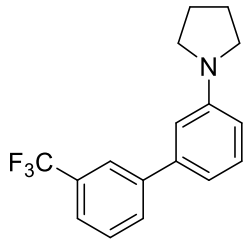
^{13}C NMR (125 MHz, *CHLOROFORM-d*) δ ppm 204.1, 198.0, 194.8, 188.9, 141.4, 138.9, 138.0, 136.6, 134.6, 131.7, 131.3, 131.5 (q, ^2J=33.4 Hz), 131.2 (q, ^2J=33.4 Hz), 130.1, 129.6, 129.3 (2C, m) 2 x C, 128.5, 125.4 (q, ^3J=3.8 Hz), 125.0 (q,^3J=3.8 Hz), 123.6 (q, ^1J=272.8 Hz), 123.5 (q, ^1J=272.8 Hz), 46.8, 41.5, 30.1, 26.8.

^{19}F NMR (377 MHz, *CHLOROFORM-d*) δ ppm -62.8 (CF_3).

FTIR 2360, 2342, 1674, 1331, 1168, 1127, 1073, 806, 695 cm^{-1}.

HRMS m/z $[C_{13}H_{11}F_3O_2+Na]^+$ cal. 279.0603, found 279.0607.

1-(3'-(Trifluoromethyl)-[1,1'-biphenyl]-3-yl)pyrrolidine (3h)



Unsaturated 1,5-dicarbonyl **2g (**35 mg, 0.14 mmol) and pyrrolidine were subjected to general procedure 3. The reaction mixture was heated for 5 h. In a modification to the general procedure the addition of amine took place at 0 °C then warmed to room temperature. Purification by flash column chromatography (petrol-EtOAc, 19:1) afforded aryl amine **3h** (30 mg, 72%) as a colourless oil.

^{1}H NMR (400 MHz, *CHLOROFORM-d*) δ ppm 7.87 (1 H, s), 7.80 (1 H, d, *J*=7.6 Hz), 7.51 - 7.64 (2 H, m), 7.34 (1 H, t, *J*=7.8 Hz), 6.89 (1 H, d, *J*=7.6 Hz), 6.75 (1 H, s), 6.63 (1 H, d, *J*=8.2 Hz), 3.38 (4 H, t, *J*=6.5 Hz), 1.99 - 2.13 (4 H, m).

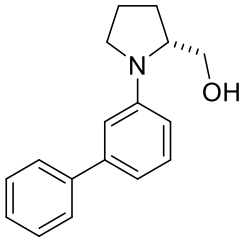
^{13}C NMR (126 MHz, *CHLOROFORM-d*) δ ppm 148.8, 143.6, 141.3, 131.0, 131.4 (q, ^2J=32.4 Hz), 130.1, 129.4, 124.5 (q, ^3J=3.7 Hz), 124.1 (q, ^3J=3.7 Hz), 124.8 (q, ^1J=272.8 Hz), 115.0, 111.9, 110.8, 48.2, 25.9.

^{19}F NMR (377 MHz, *CHLOROFORM-d*) δ ppm -62.5 (CF_3).

FTIR 2968, 1601, 1485, 1461, 1430, 1375, 1330, 1249, 1163, 1123, 1096, 1075, 997, 842, 803, 771, 700, 663 cm^{-1}.

HRMS m/z $[C_{17}H_{16}F_3N+H]^+$ cal. 292.1308, found 292.1315.

(1-([1,1'-Biphenyl]-3-yl)pyrrolidin-2-yl)methanol (3i)



Unsaturated 1,5-dicarbonyl **2a (**50 mg, 0.27 mmol) and D-prolinol were subjected to general procedure 3. In a modification to the general procedure $ZnCl_2$ (1.0 M in Et_2O, 0.27 mmol) was added. Purification by flash column chromatography (petrol-EtOAc, 19:1) afforded aryl amine **3i** (43 mg, 66%) as a colourless oil.

^{1}H NMR (400 MHz, *CHLOROFORM-d*) δ ppm 7.58 - 7.69 (2 H, m), 7.46 (2 H, t, *J*=7.6 Hz), 7.29 - 7.41 (2 H, m), 6.98 (1 H, d, *J*=7.6 Hz), 6.92 (1 H, br. s), 6.74 (1 H, d, *J*=8.1 Hz), 3.96 (1 H, d, *J*=4.0 Hz), 3.66 - 3.79 (2 H, m), 3.59 (1 H, t, *J*=7.6 Hz), 3.18 - 3.35 (1 H, m), 1.97 - 2.21 (4 H, m), 1.84 (1 H, br. s).

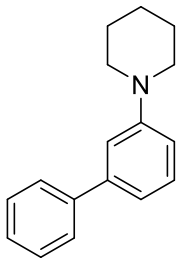
^{13}C NMR (100 MHz, *CHLOROFORM-d*) δ ppm 148.4, 142.5, 142.1, 129.6, 128.7, 127.4, 127.2, 115.7, 111.4, 111.3, 63.8, 60.2, 49.6, 28.8, 23.8.

FTIR 3373, 2952, 1597, 1569, 1487, 1427, 1365, 1261, 1174, 1037, 1174, 1037, 993, 908, 756, 732, 699 cm^{-1}.

HRMS m/z $[C_{17}H_{19}NO+H]^+$ cal.254.1539, found 254.1539.

Specific rotation $[\alpha]_D^{20}$ –18.5 (0.2 g/mL).

1-([1,1'-Biphenyl]-3-yl)piperidine (3j)



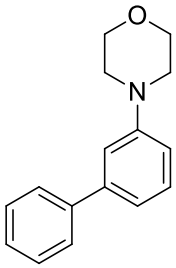
Unsaturated 1,5-dicarbonyl **2a (**40 mg, 0.21 mmol) and piperidine were subjected to general procedure 3. In a modification to the general procedure $ZnCl_2$ (1.0 M in Et_2O, 0.21 mmol) was added. Purification by flash column chromatography (petrol-EtOAc, 19:1) afforded aryl amine **3j** (36 mg, 72%) as a colourless oil.

^{1}H NMR (500 MHz, *CHLOROFORM-d*) δ ppm 7.60 (2 H, d, *J*=7.3 Hz), 7.39 - 7.47 (2 H, m), 7.28 - 7.39 (2 H, m), 7.18 (1 H, br. s), 7.07 (1 H, d, *J*=7.6 Hz), 6.97 (1 H, d, *J*=6.9 Hz), 3.17 - 3.31 (4 H, m), 1.76 (4 H, br. s), 1.54 - 1.65 (2 H, m).

^{13}C NMR (125 MHz, *CHLOROFORM-d*) δ ppm 152.7, 142.2, 141.9, 129.4, 128.6, 127.3, 127.1, 118.4, 115.7, 115.6, 50.9, 25.8, 24.3.

Data were consistent with those previously reported. [10]

4-([1,1'-Biphenyl]-3-yl)morpholine (3k)



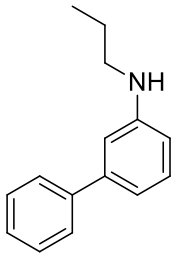
Unsaturated 1,5-dicarbonyl **2a (**30 mg, 0.16 mmol) and morpholine were subjected to general procedure 4. Purification by flash column chromatography (petrol-EtOAc, 19:1) afforded aryl amine **3k** (30 mg, 78%) as a colourless oil.

^{1}H NMR (500 MHz, *CHLOROFORM-d*) δ ppm 7.60 (2 H, d, J=6.9 Hz), 7.45 (2 H, t, J=7.3Hz), 7.34 – 7.40 (2 H, m), 7.11 - 7.18 (2 H, m), 6.94 (1 H, d, *J*=7.3 Hz), 3.91 (4 H, t, *J*=4.4 Hz), 3.25 (4 H, t, *J*=4.7 Hz).

^{13}C NMR (125 MHz, *CHLOROFORM-d*) δ ppm 152.1, 142.9, 142.1, 130.0, 129.1, 127.7 (2C), 119.7, 115.3, 115.2, 67.4, 50.0.

Data were consistent with those previously reported.[11]

***N*-Propyl-[1,1'-biphenyl]-3-amine (3l)**



Unsaturated 1,5-dicarbonyl **2a (**30 mg, 0.16 mmol) and propylamine were subjected to general procedure 4. Purification by flash column chromatography (petrol-EtOAc, 19:1) afforded aryl amine **3k** (24 mg, 71%) as a colourless oil.

[10] Girard, S. A.; Hu, X.; Knauber, T.; Zhou, F.; Simon, M.; Deng, G.; Li, C. *Org. Lett.*, **2012**, *14*, 5606.
[11] Zhang, L.; Wu, J. *J. Am. Chem. Soc.* **2008**, *130*, 12250.

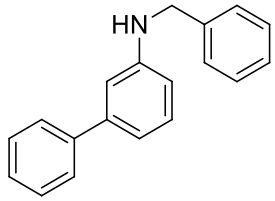
^{1}H NMR (400 MHz, *CHLOROFORM-d*) δ ppm 7.61 (2 H, d, *J*=7.6 Hz), 7.45 (2 H, t, *J*=7.6 Hz), 7.32 - 7.40 (1 H, m), 7.27 (1 H, t, *J*=7.8 Hz), 6.95 (1 H, d, *J*=7.6 Hz), 6.84 (1 H, s), 6.64 (1 H, d, *J*=8.1 Hz), 3.75 (1 H, br. s), 3.17 (2 H, t, *J*=7.1 Hz), 1.70 (2 H, sxt, *J*=7.3 Hz), 1.05 (3 H, t, *J*=7.5 Hz).

^{13}C NMR (100 MHz, *CHLOROFORM-d*) δ ppm 148.9, 142.4, 141.9, 129.6, 128.6, 127.2, 127.1, 116.3, 111.8, 111.5, 45.9, 22.8, 11.7.

FTIR 2961, 1601, 1573, 1488, 1330, 1229, 908, 756, 731, 698, 649 cm^{-1}.

HRMS m/z $[C_{15}H_{17}N]^+$ cal. 212.143, found 212.1434.

***N*-Benzyl-[1,1'-biphenyl]-3-amine (3m)**



Unsaturated 1,5-dicarbonyl **2a (**40 mg, 0.21 mmol) and benzylamine were subjected to general procedure 4. Purification by flash column chromatography (petrol-EtOAc, 19:1) afforded aryl amine **3m** (42 mg, 78%) as a colourless oil.

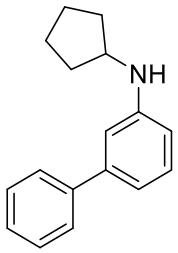
^{1}H NMR (400 MHz, *CHLOROFORM-d*) δ ppm 7.59 (2 H, d=7.6), 7.23 – 7.48 (9 H, m), 6.99 (1 H, d, *J*=7.8 Hz), 6.89 (1 H, t, *J*=2.0 Hz), 6.66 (1 H, d, *J*=8.0 Hz), 4.42 (2 H, s), 4.15 (1 H, br. s).

^{13}C NMR (100 MHz, *CHLOROFORM-d*) δ ppm 148.5, 142.4, 141.7, 139.4, 129.7, 128.7, 128.6, 127.6, 127.3, 127.2 (2C), 116.8, 111.9, 111.7, 48.4.

FTIR 2965, 1601, 182, 1394, 1355, 1322, 1183, 1134, 908, 821, 731, 703 cm^{-1}.

HRMS m/z $[C_{19}H_{17}N+H]^+$ cal. 260.1434, found 260.1431.

***N*-Cyclopentyl-[1,1'-biphenyl]-3-amine (3n)**



Unsaturated 1,5-dicarbonyl **2a (**35 mg, 0.19 mmol) and cyclopentanamine were subjected to general procedure 4. Purification by flash column chromatography (petrol-EtOAc, 19:1) afforded aryl amine **3n** (29 mg, 67%) as a colourless oil.

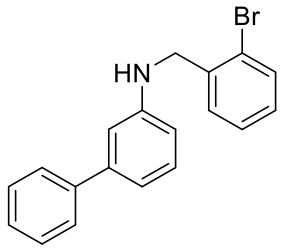
^{1}H NMR (400 MHz, *CHLOROFORM-d*) δ ppm 7.61 (2 H, d, *J*=6.3), 7.45 (2 H, t, *J*=7.3 Hz), 7.35 (1 H, t, *J*=7.3), 7.22 – 7.30 (1 H, m), 6.94 (1 H, d, *J*=8.8), 6.84 (1 H, s), 6.63 (1 H, d, *J*=9.3), 3.88 (1 H, quin, *J*=6.2 Hz), 3.77 (1 H, br. s), 2.03 – 2.16 (2 H, m), 1.60 – 1.85 (4 H, m), 1.48 – 1.59 (2 H, m).

^{13}C NMR (100 MHz, *CHLOROFORM-d*) δ ppm 148.4, 142.4, 141.9, 129.6, 128.6, 127.2, 127.1, 116.1, 112.2, 112.0, 54.7, 33.7, 24.1.

FTIR 2954, 1600, 1573, 1484, 1445, 1417, 1332, 1231, 991, 908, 855, 784, 755, 698, 615 cm^{-1}.

HRMS m/z $[C_{17}H_{19}N+H]^+$ cal. 238.1590, found 238.1584.

***N*-(2-Bromobenzyl)-[1,1'-biphenyl]-3-amine (3o)**



Unsaturated 1,5-dicarbonyl **2a (**35 mg, 0.19 mmol) and (2-bromophenyl)methanamine were subjected to general procedure 4. Purification by flash column chromatography (petrol-EtOAc, 19:1) afforded aryl amine **3o** (44 mg, 72%) as a colourless oil.

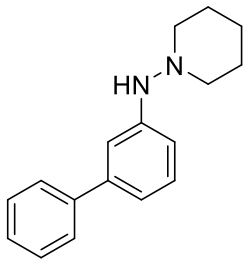
^{1}H NMR (400 MHz, *CHLOROFORM-d*) δ ppm 7.43 - 7.63 (3 H, m), 7.31 - 7.43 (3 H, m), 7.23 - 7.31 (1 H, m), 7.12 - 7.23 (2 H, m), 7.07 (1 H, t, *J*=8.6 Hz), 6.92 (1 H, d, *J*=7.8 Hz), 6.79 (1 H, t, *J*=1.9 Hz), 6.54 (1 H, d, *J*=8.1 Hz), 4.40 (2 H, br. s), 4.17 (1 H, br. s).

^{13}C NMR (100 MHz, *CHLOROFORM-d*) δ ppm 148.0, 142.4, 141.6, 138.1, 132.9, 129.7, 129.3, 128.8, 128.6, 127.6, 127.2, 127.2, 123.3, 117.0, 111.9, 111.9, 48.5.

FTIR 3423, 3058, 1601, 1573, 1516, 1486, 1441, 1328, 1231, 1025, 908, 755, 732, 699 cm^{-1}.

HRMS m/z $[C_{19}H_{16}BrN+H]^+$ cal.338.0539, found 338.0538.

***N*-([1,1'-Biphenyl]-3-yl)piperidin-1-amine (3p)**



Unsaturated 1,5-dicarbonyl **2a (**30 mg, 0.17 mmol) and piperidin-1-amine were subjected to general procedure 4. In a modification to the general procedure the reaction was heated to 85 °C. Purification by flash column chromatography (petrol-EtOAc, 19:1) afforded aryl amine **3o** (35 mg, 81%) as a colourless oil.

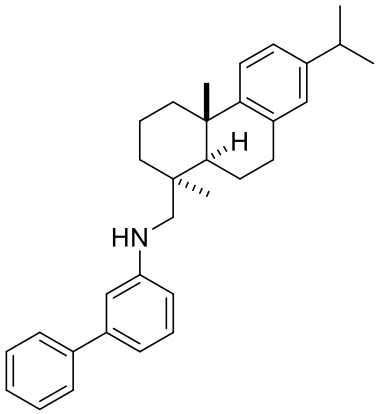
^{1}H NMR (400 MHz, *CHLOROFORM-d*) δ ppm 7.59 - 7.65 (2 H, m), 7.45 (2 H, t, *J*=7.6 Hz), 7.32 - 7.38 (1 H, m), 7.25 - 7.31 (1 H, m), 7.16 (1 H, t, *J*=1.8 Hz), 7.03 (1 H, d, *J*=7.6 Hz), 6.88 - 6.94 (1 H, m), 4.49 (1 H, br. s), 2.71 (4 H, br. s), 1.72 (4 H, quin, *J*=5.6 Hz), 1.46 (2 H, br. s)

^{13}C NMR (100 MHz, *CHLOROFORM-d*) δ ppm 148.2, 142.2, 141.8, 129.5, 128.6, 127.2, 127.1, 118.3, 112.7, 112.3, 57.4, 26.1, 23.7.

FTIR 2935, 2853, 2728, 1602, 1573, 1479, 1443, 1265, 1216, 1153, 1036, 872, 790, 757, 699 cm^{-1}.

HRMS m/z $[C_{17}H_{20}N_2+H]^+$ cal. 253.1691, found 253.1699.

***N*-(((1*S*,4a*S*,10a*R*)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)-[1,1'-biphenyl]-3-amine (3q)**



Method A Unsaturated 1,5-dicarbonyl **2a (**40 mg, 0.21 mmol) and (+)-dehydroabietylamine were subjected to general procedure 4. In a modification to the general procedure $ZnCl_2$ (1.0 M in Et_2O, 0.216 mmol) was added. Purification by flash column chromatography (petrol-EtOAc, 19:1) afforded aryl amine **3q** (62 mg, 64%) as a colourless oil.

Method B (+)-Dehydroabietylamine (120 mg, 0.421 mmol) and $ZnCl_2$ (1.0 M in Et_2O, 0.053 mmol) were dissolved in DCE (1.0 mL) and heated to 55 °C. To this solution, unsaturated 1,5-dicarbonyl **2a** (50 mg, 0.28 mmol) was added dropwise over 12 h . The reaction mixture was stirred for 18 h, cooled and then concentrated. The crude product was purified by flash column chromatography (petrol - EtOAc, 98:2) to yield aryl amine **3q** (52 mg, 54%).

^{1}H NMR (400 MHz, *CHLOROFORM-d*) δ ppm 7.49 (2 H, d, *J*=7.3 Hz), 7.33 (2 H, t, *J*=7.5 Hz), 7.20 - 7.27 (1 H, m), 7.09 - 7.17 (2 H, m), 6.93 (1 H, d, *J*=7.1 Hz), 6.78 - 6.84 (2 H, m), 6.72 (1 H, s), 6.51 (1 H, dd, *J*=8.1, 1.7 Hz), 3.63 (1 H, br. s), 3.03 (1 H, d, *J*=12.2 Hz), 2.69 - 2.92 (4 H, m), 2.23 (1 H, d, *J*=13.0 Hz), 1.53 - 1.82 (6 H, m), 1.30 - 1.47 (4 H, m), 1.16 (6 H, d, *J*=4.6 Hz), 1.14 (3 H, s), 0.95 (3 H, s).

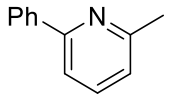
^{13}C NMR (100 MHz, *CHLOROFORM-d*) δ ppm 149.3, 147.4, 145.7, 142.5, 141.9, 134.7, 129.6, 128.6, 127.2, 127.1, 126.9, 124.3, 124.0, 116.1, 111.8, 111.4, 54.9, 53.4, 45.4, 38.4, 37.6, 37.6, 36.4, 33.5, 30.1, 25.4, 24.0, 19.4, 19.0, 18.8.

FTIR 2928, 1600, 1573, 1489, 1383, 1228, 908, 823, 755, 732, 698 cm^{-1}.

HRMS m/z $[C_{32}H_{39}N+H]^+$ cal.438.3155, found 438.3146.

Specific rotation $[\alpha]_D^{20}$ –18.5 (0.2 g/mL).

2-Methyl-6-phenylpyridine (5)



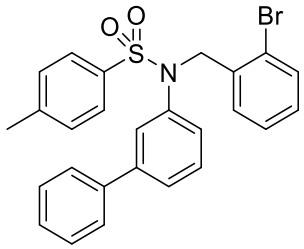
$NH_{3(g)}$ (0.5 mL) was condensed into a microwave vial cooled to -78°C. Unsaturated 1,5-dicarbonyl **2a** (20 mg, 0.11 mmol) in CH_2Cl_2 (2.0 mL) was then added and the solution allowed to warm to room temperature, then heated to 55 °C for 12 h. The reaction mixture was then concentrated and purified by flash column chromatography (petrol-EtOAc, 19:1 to 9:1) to give pyridine **5** (8 mg, 42%) as a colourless oil.

^{1}H NMR (400 MHz, *CHLOROFORM-d*) δ ppm 8.00 (d, *J*=7.6 Hz, 2 H), 7.64 (m, 1 H), 7.50 (m, 3 H), 7.41 (m, 1 H), 7.11 (d, *J*=7.6 Hz, 1 H), 2.65 (s, 3 H).

^{13}C NMR (100 MHz, *CHLOROFORM-d*) δ ppm 158.4, 157.0, 139.8, 136.9, 128.7 (2C), 127.0, 121.6, 117.7, 24.8.

Data were consistent with those previously reported.[12]

***N*-([1,1'-biphenyl]-3-yl)-*N*-(2-bromobenzyl)-4-methylbenzenesulfonamide (6)**



4-Toluenesulfonyl chloride (166 mg, 0.874 mmol) was added in one portion to *N*-(2-bromobenzyl)-[1,1'-biphenyl]-3-amine (98 mg, 0.29 mmol) in pyridine (3.0 mL) at room temperature. The resulting solution was stirred at 80 °C for 12 h. The reaction mixture was concentrated and the crude product purified by flash column chromatography (petrol-EtOAc, 1:0 to 8:2) to afford aryl amine **6** (143 mg, 90 %) as a tan foam.

^{1}H NMR (400 MHz, *CHLOROFORM-d*) δ ppm 7.63 (2 H, d, *J*=7.6 Hz), 7.58 (2 H, d, *J*=8.1 Hz), 7.34 - 7.44 (5 H, m), 7.21 - 7.34 (6 H, m), 6.95 - 7.10 (2 H, m), 4.92 (2 H, s), 2.42 (3 H, s).

^{13}C NMR (100 MHz, *CHLOROFORM-d*) δ ppm 143.7, 142.0, 140.1, 139.7, 135.4, 135.4, 132.6, 130.4, 129.6, 129.2, 129.0, 128.8, 127.9, 127.6, 127.6, 127.4, 127.4, 127.0, 126.6, 123.2, 54.2, 21.5.

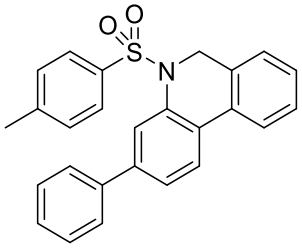
FTIR 3035, 1597, 1478, 1349, 1164, 1091, 1024, 880, 811, 756, 701, 658, 638 cm^{-1}.

HRMS m/z $[C_{26}H_{22}BrNO_2S+Na]^+$ cal. 514.0433, found 514.0447.

m.p. 117-119(CH_2Cl_2:petrol).

[12] Mee, S. P. H.; Lee, V.; Baldwin, J. E. *Chem. Eur. J.* **2005**, *11*, 3294.

3-phenyl-5-tosyl-5,6-dihydrophenanthridine (7)



Crushed potassium carbonate (56 mg, 0.41 mmol), 1-phenyl-5-tosyl-5,6-dihydrophenanthridine (80 mg, 96%), palladium acetate (2.0 mg, 0.10 mmol)and tricyclohexylphosphoniumtetrafluoroborate (7.0 mg, 0.02 mmol) were placed in a microwave vial equipped with a magnetic follower. The vial was purged with argon and degassed *N*,*N*-dimethylacetamide (1.0 mL) was added. The reaction was heated to 130 ºC for 18 h. The reaction mixture was then loaded directly onto silica and purified by flash column chromatography (petrol-EtOAc, 0:1 to 4:6) to give the desired product gave tricycle **7** (80 mg, 96 %) as a white dry film.

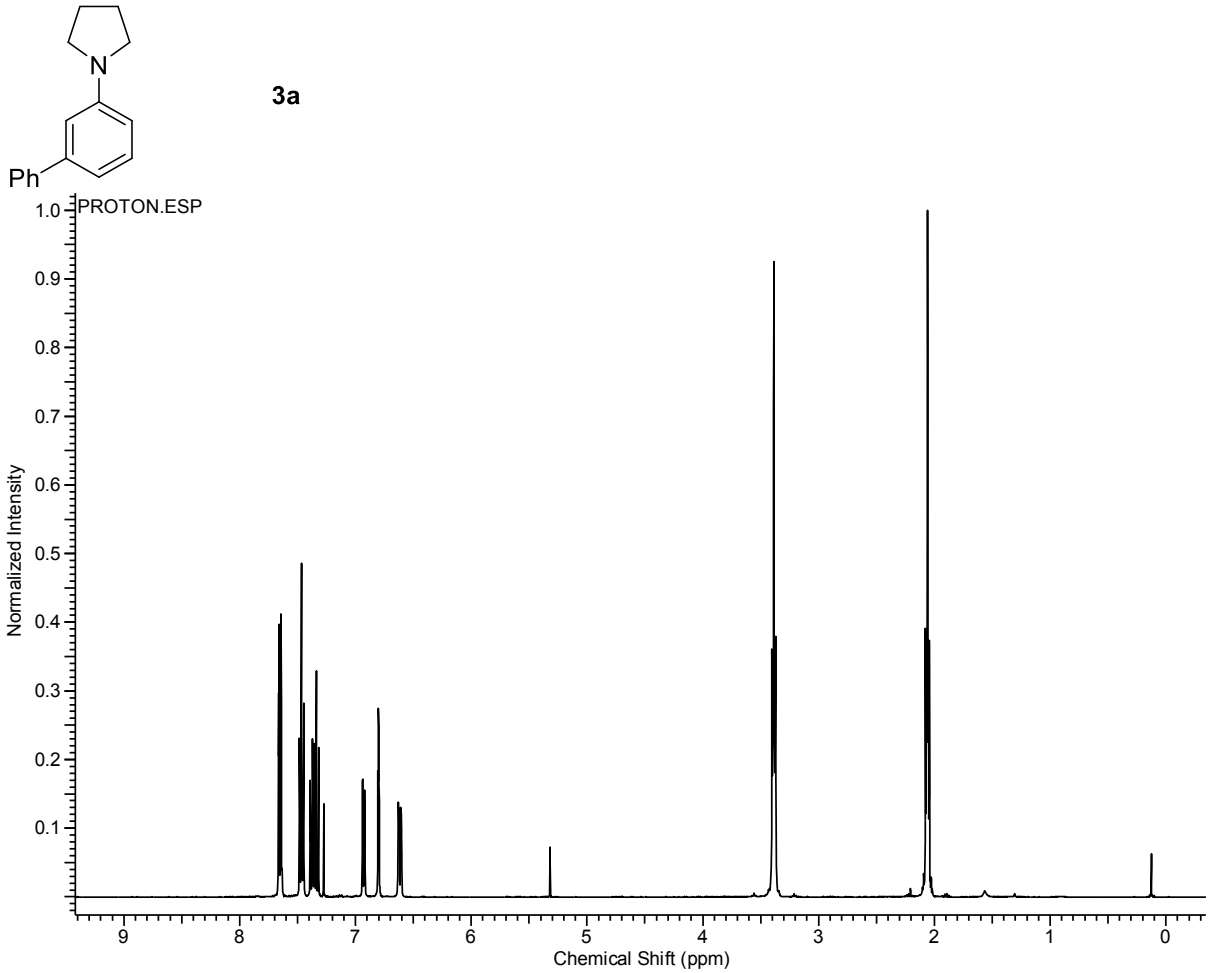
^{1}H NMR (400 MHz, *CHLOROFORM-d*) δ ppm 8.08 (1 H, d, *J*=1.8 Hz), 7.71 (2 H, d, *J*=7.1 Hz), 7.63 (1 H, d, *J*=8.1 Hz), 7.57 (1 H, dd, *J*=8.1, 1.8 Hz), 7.47 (2 H, t, *J*=7.6 Hz), 7.38 (1 H, t, *J*=7.6 Hz), 7.23 - 7.28 (1 H, m), 7.05 - 7.18 (3 H, m), 7.00 (2 H, d, *J*=8.1 Hz), 6.69 (2 H, d, *J*=8.1 Hz), 4.88 (2 H, s), 2.14 (3 H, s).

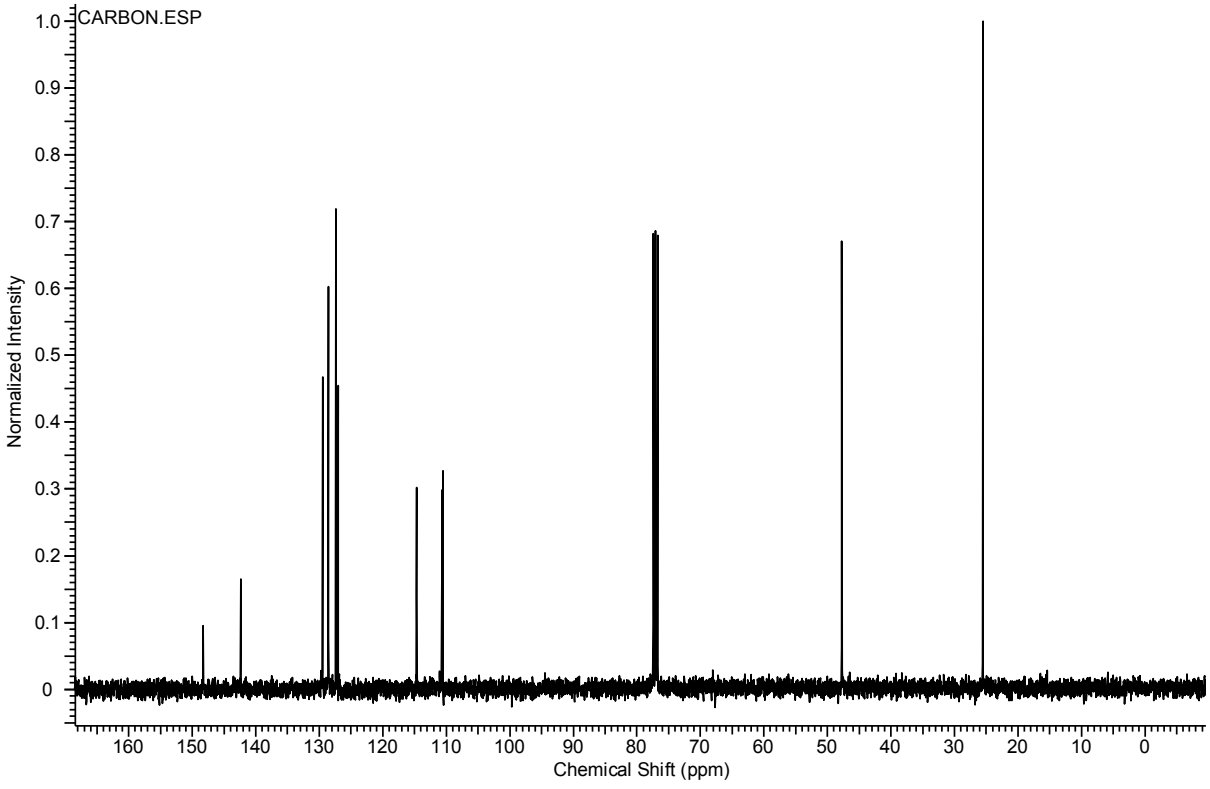
^{13}C NMR (100 MHz, *CHLOROFORM-d*) δ ppm 142.9, 141.2, 139.8, 136.5, 134.8, 131.3, 130.8, 129.4, 128.9, 128.4, 127.8, 127.8, 127.6, 127.1, 127.1, 126.5, 126.1, 125.9, 124.1, 122.8, 50.0, 21.2.

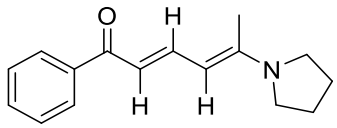
FTIR 1598, 1479, 1455, 1406, 1345, 1161, 1088, 1071, 1027, 899, 834, 812, 777, 760, 739, 689, 665, 629 cm^{-1}.

HRMS m/z $[C_{26}H_{21}NO_2S+Na]^+$ cal. 434.1179, found 434.1185.

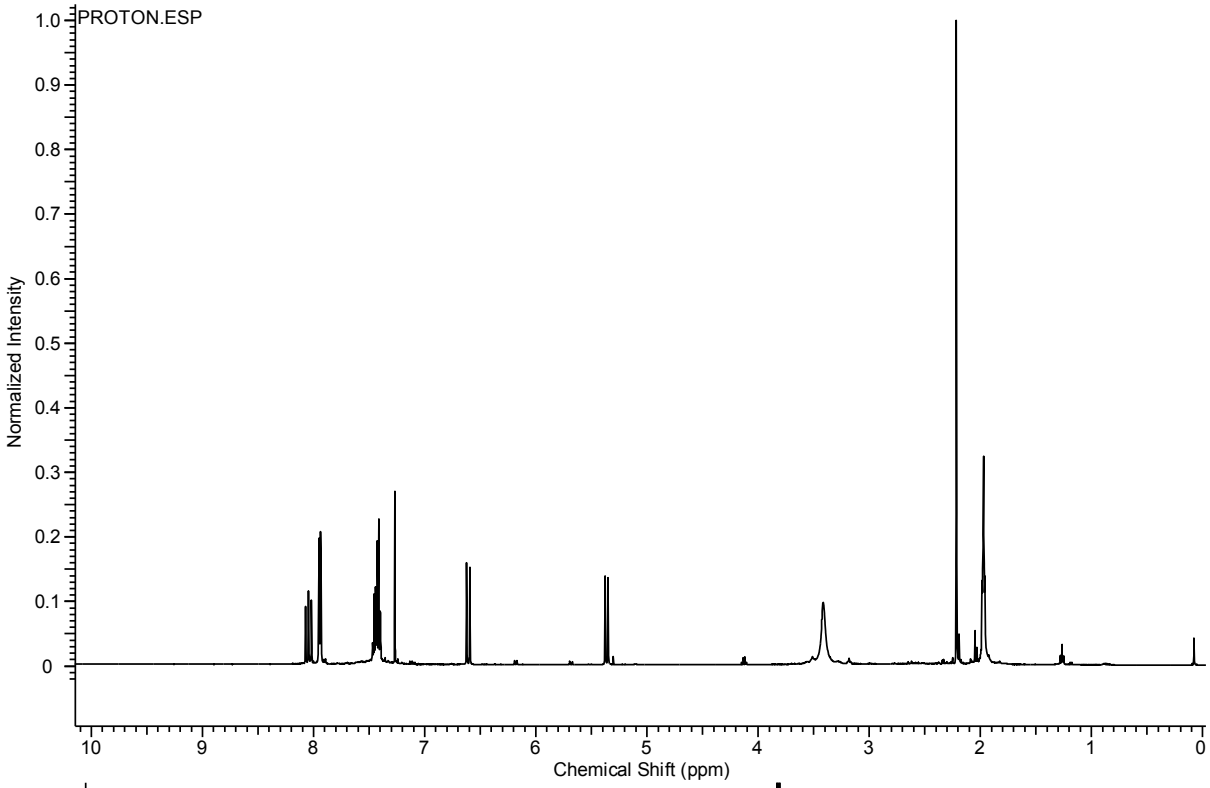
m.p. 158-160 °C (CH_2Cl_2:petrol).

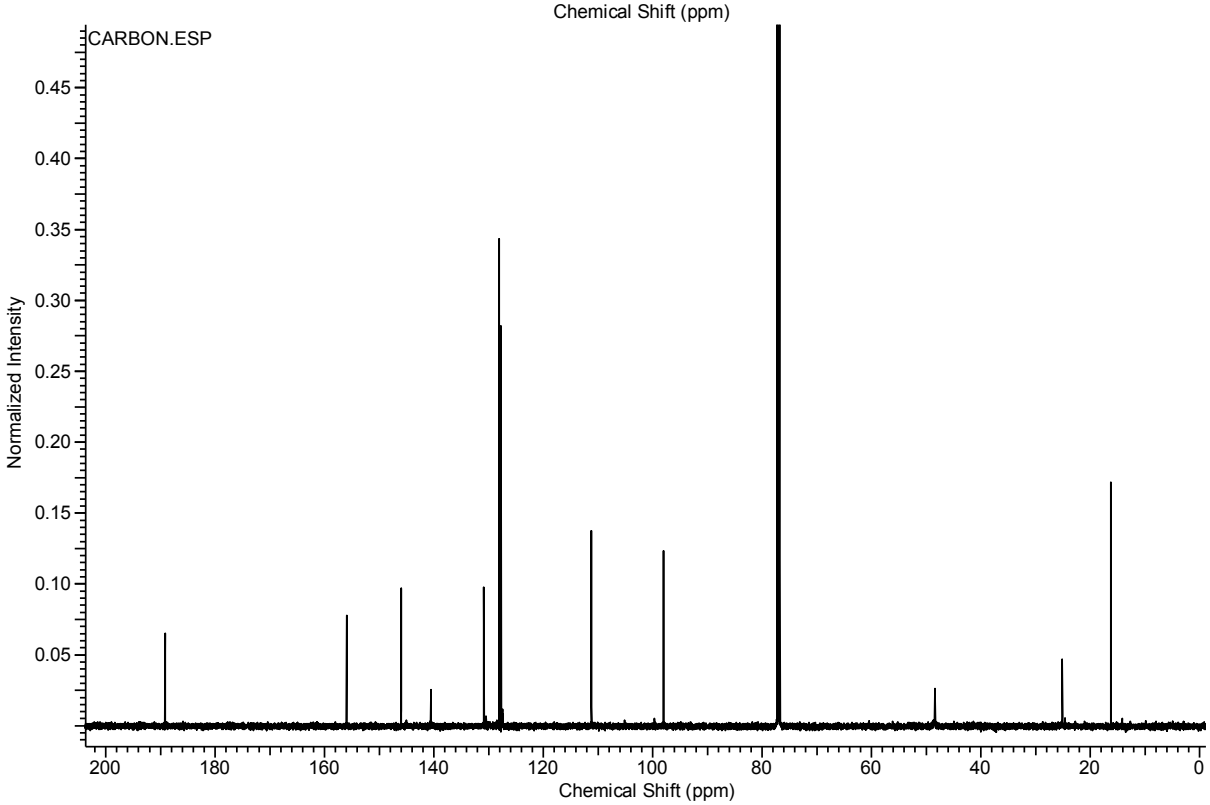

N
Ph
3a
PROTON.ESP
Normalized Intensity
Chemical Shift (ppm)

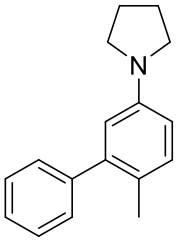

CARBON.ESP
Normalized Intensity
Chemical Shift (ppm)


O
H
N
H
H

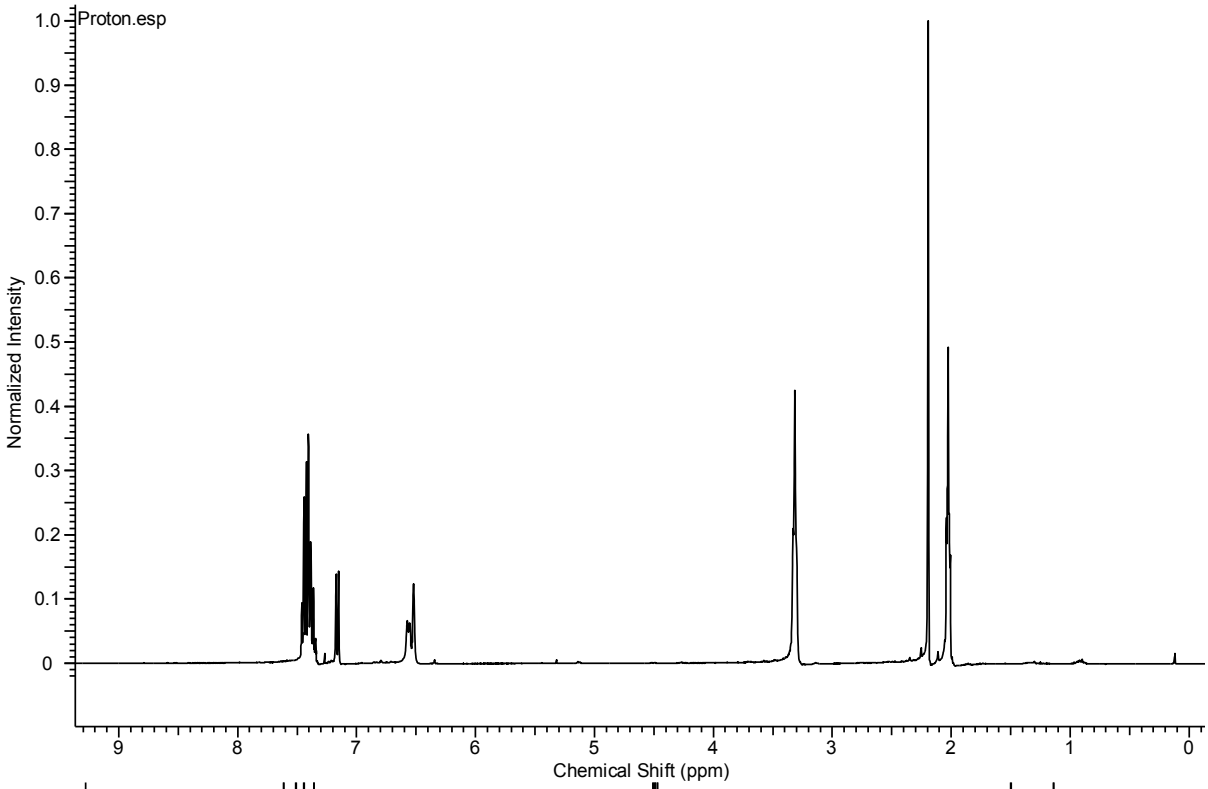
4


PROTON.ESP
Normalized Intensity
Chemical Shift (ppm)


CARBON.ESP
Normalized Intensity
Chemical Shift (ppm)



3b


Proton.esp
Normalized Intensity
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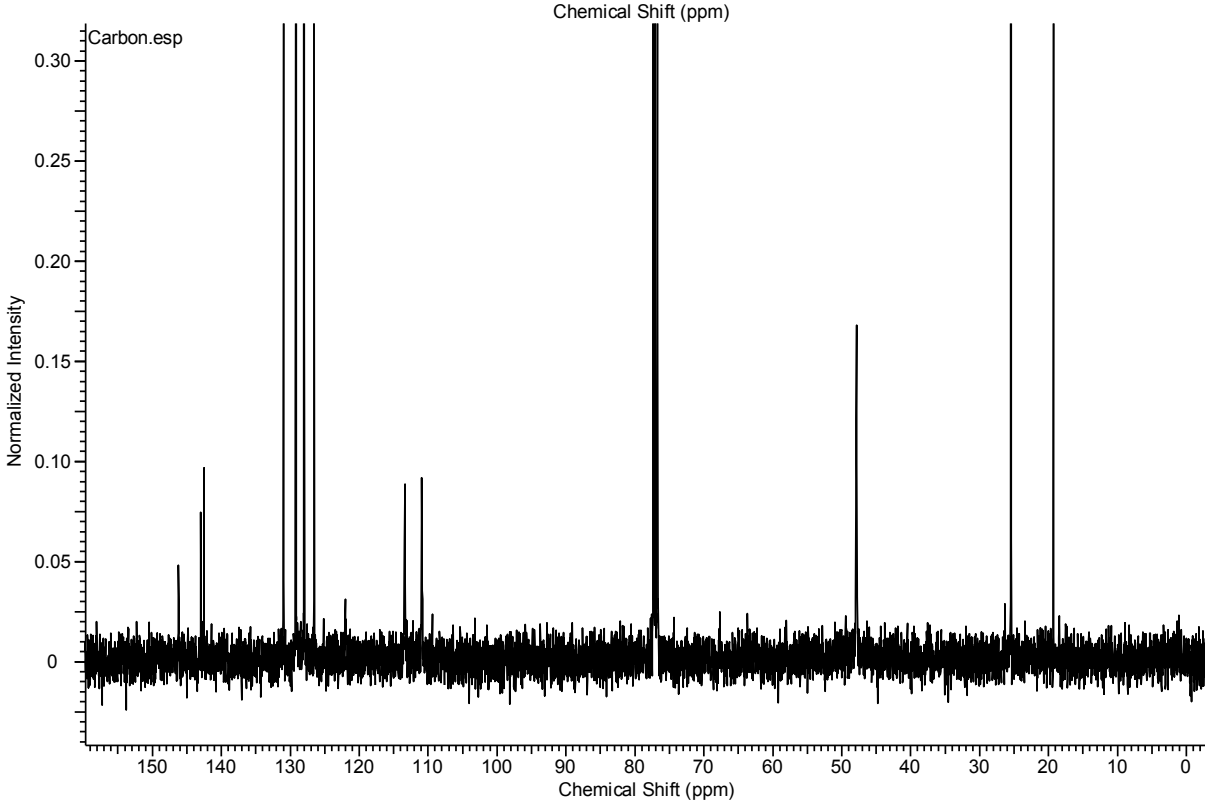
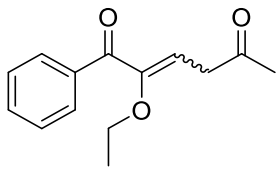
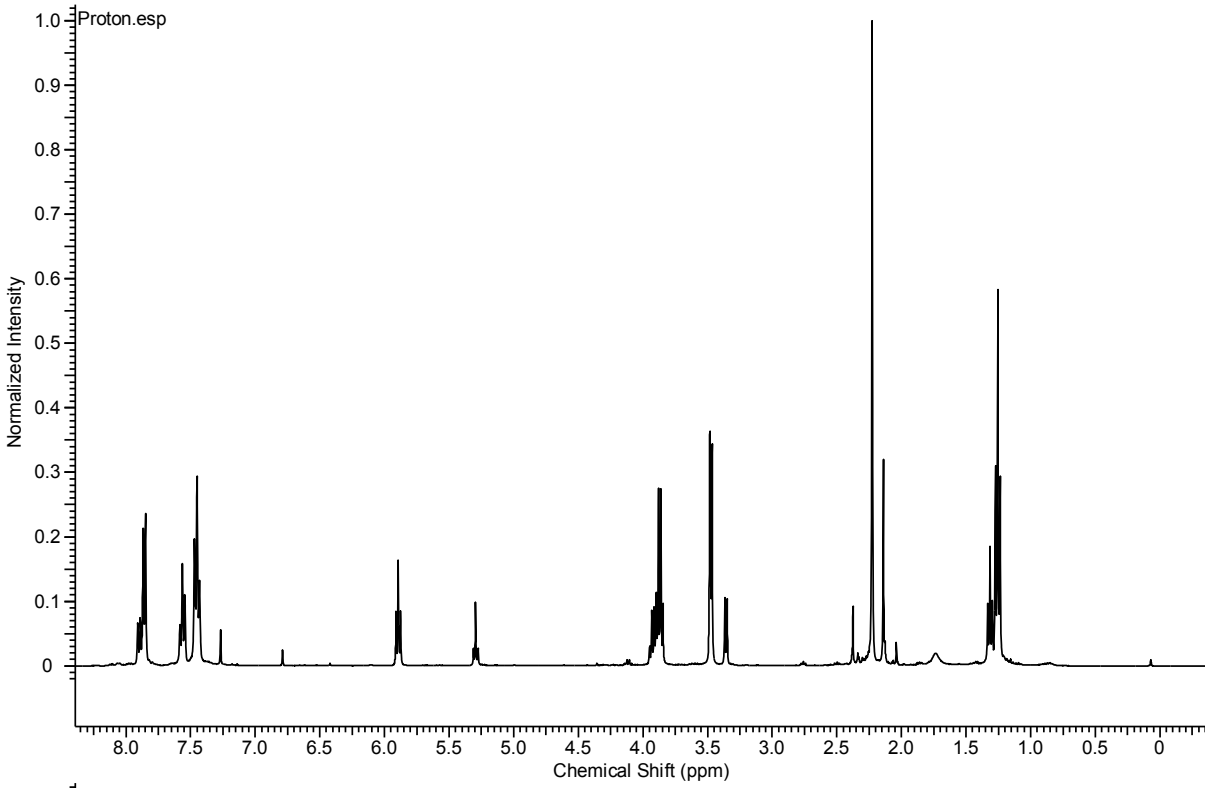
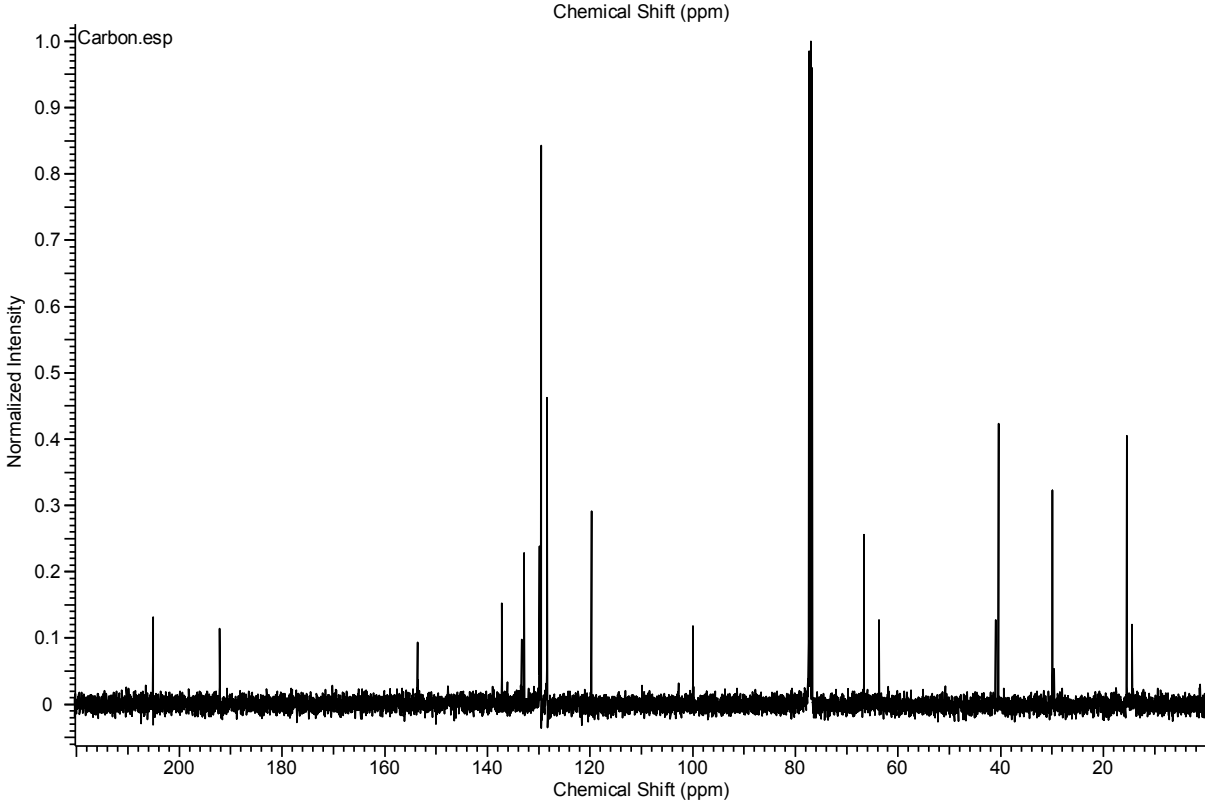
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

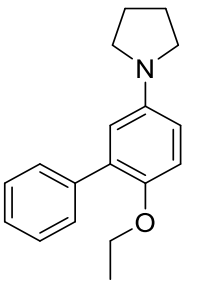

Carbon.esp
Normalized Intensity
0.30
0.25
0.20
0.15
0.10
0.05
0
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)



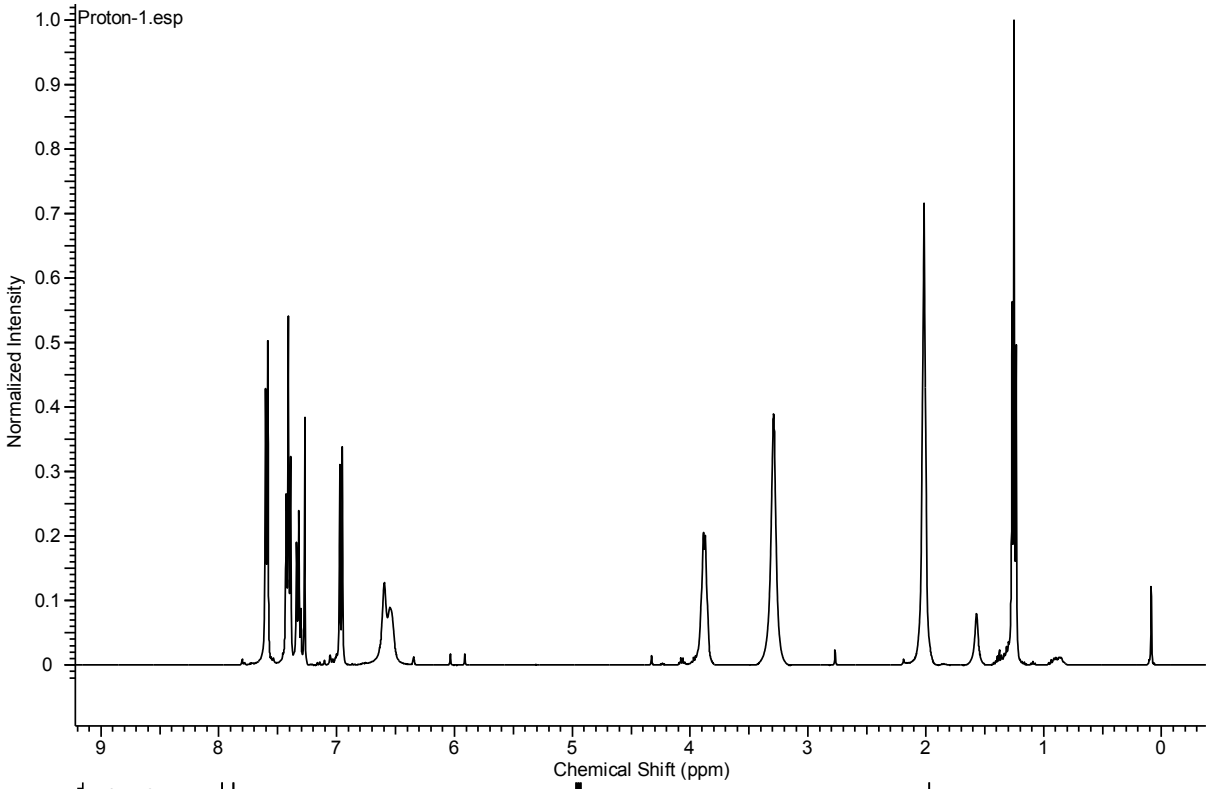
2c

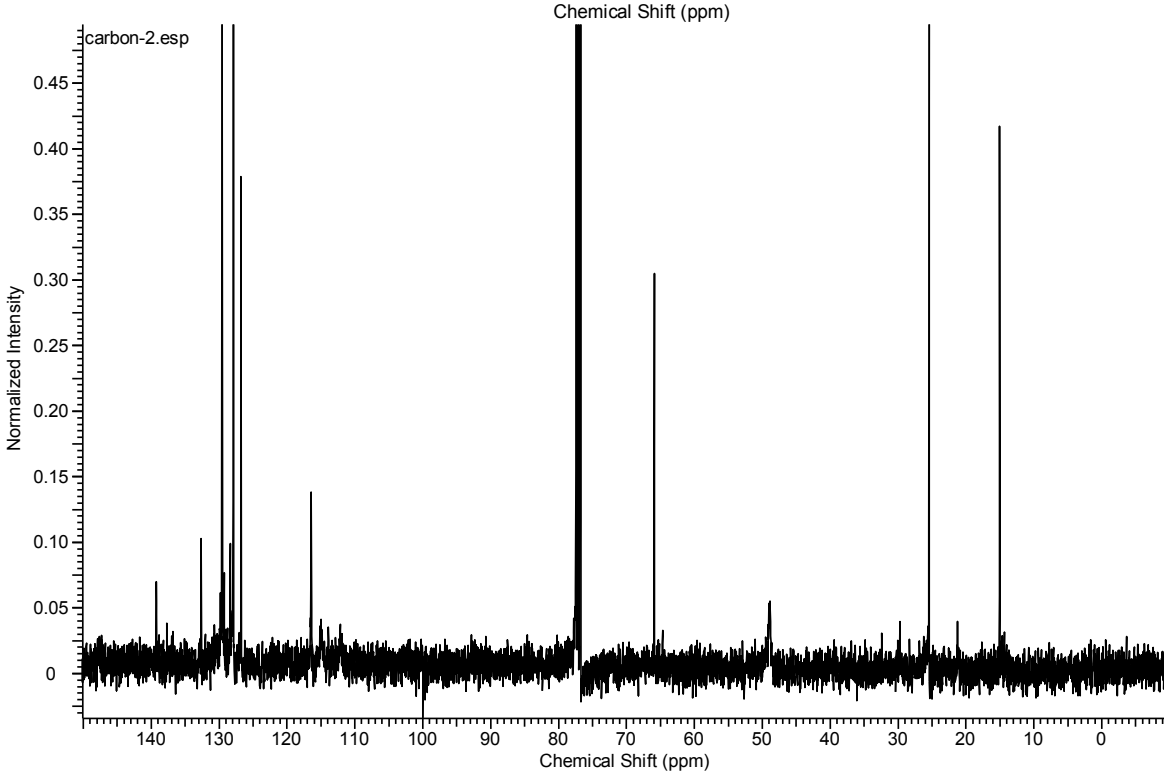

Proton.esp
Normalized Intensity
Chemical Shift (ppm)

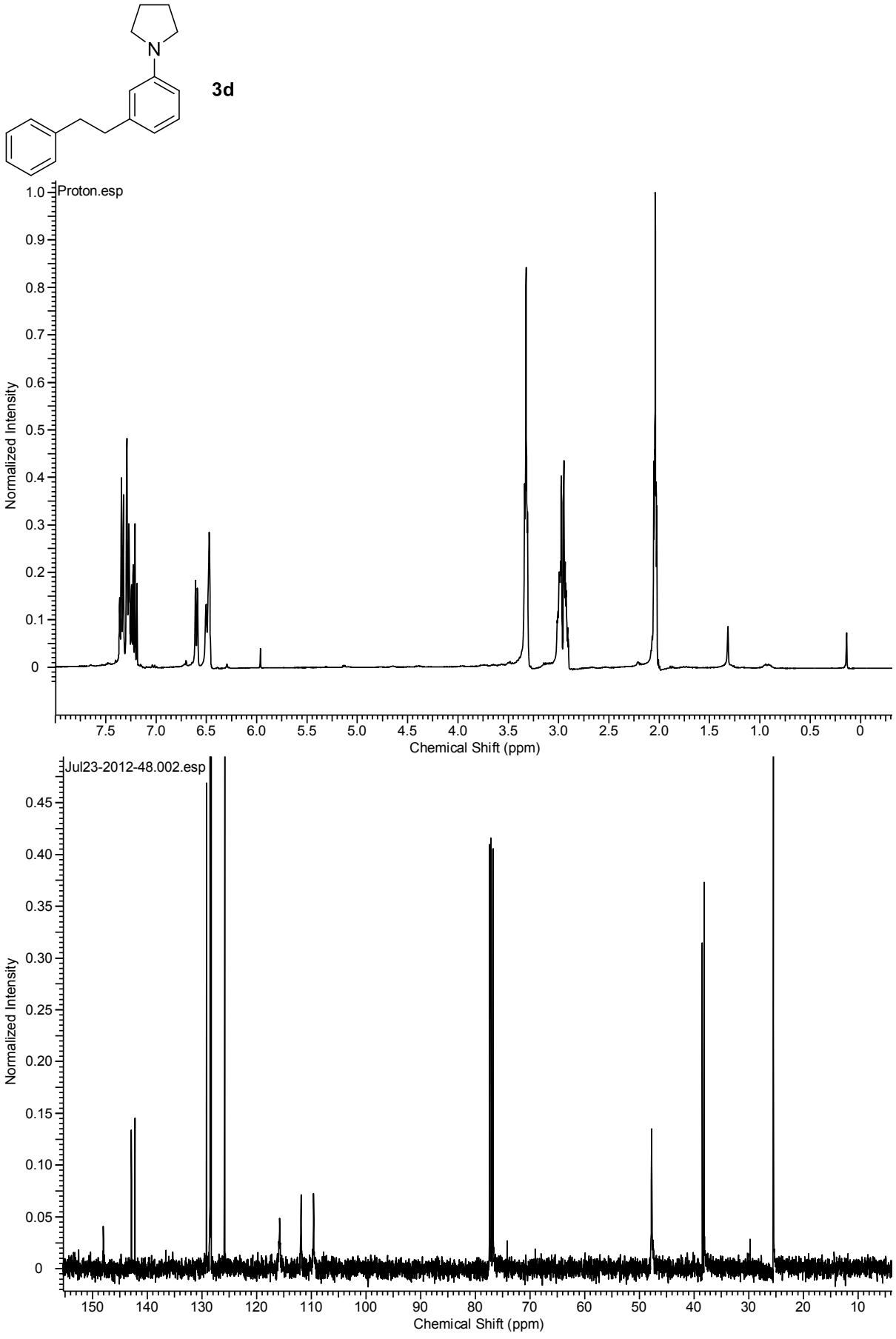

Carbon.esp
Normalized Intensity
Chemical Shift (ppm)

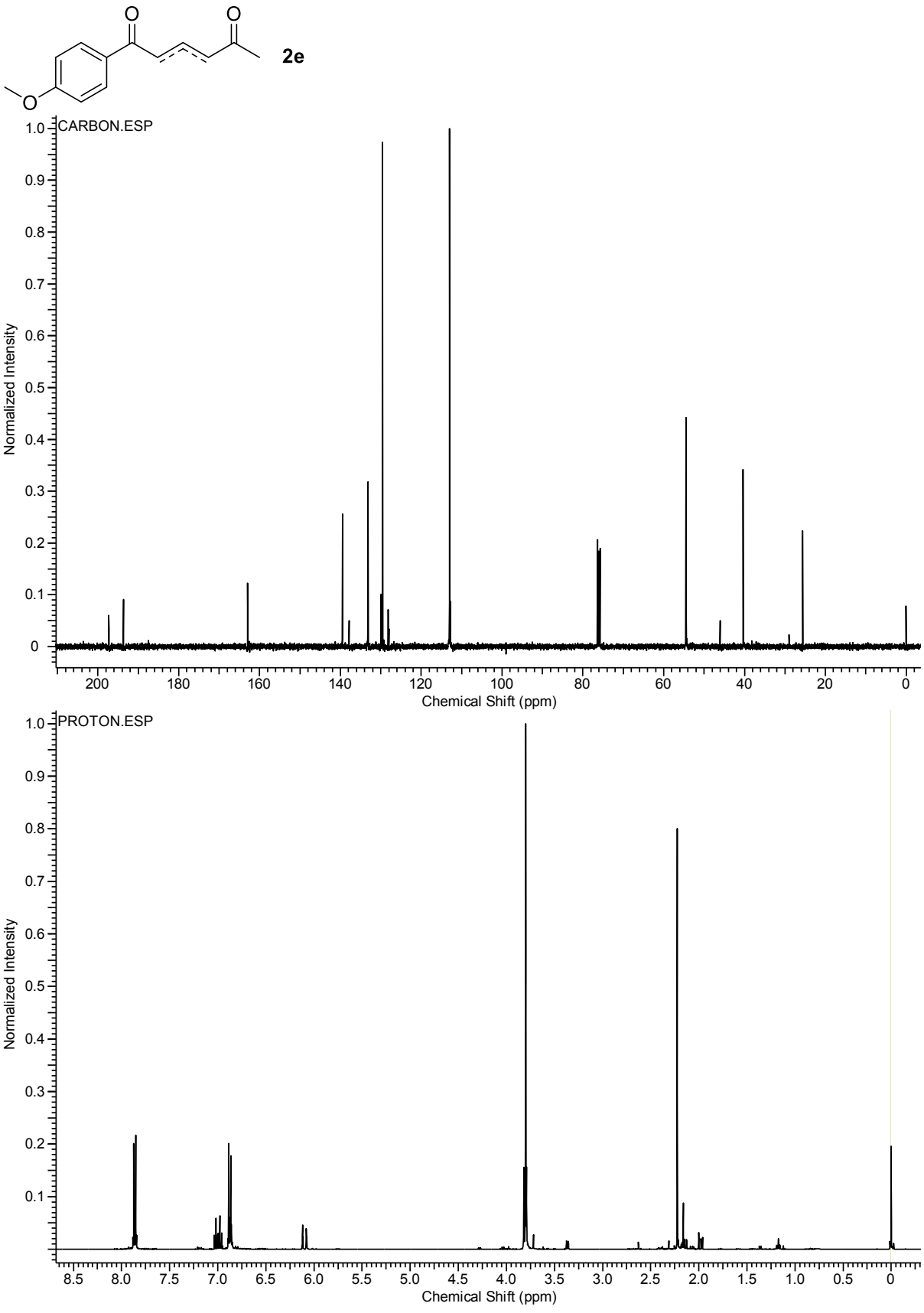

N
O

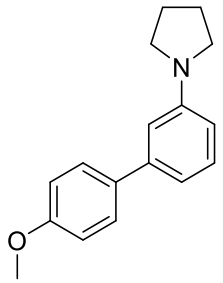
3c


Proton-1.esp
Normalized Intensity
Chemical Shift (ppm)

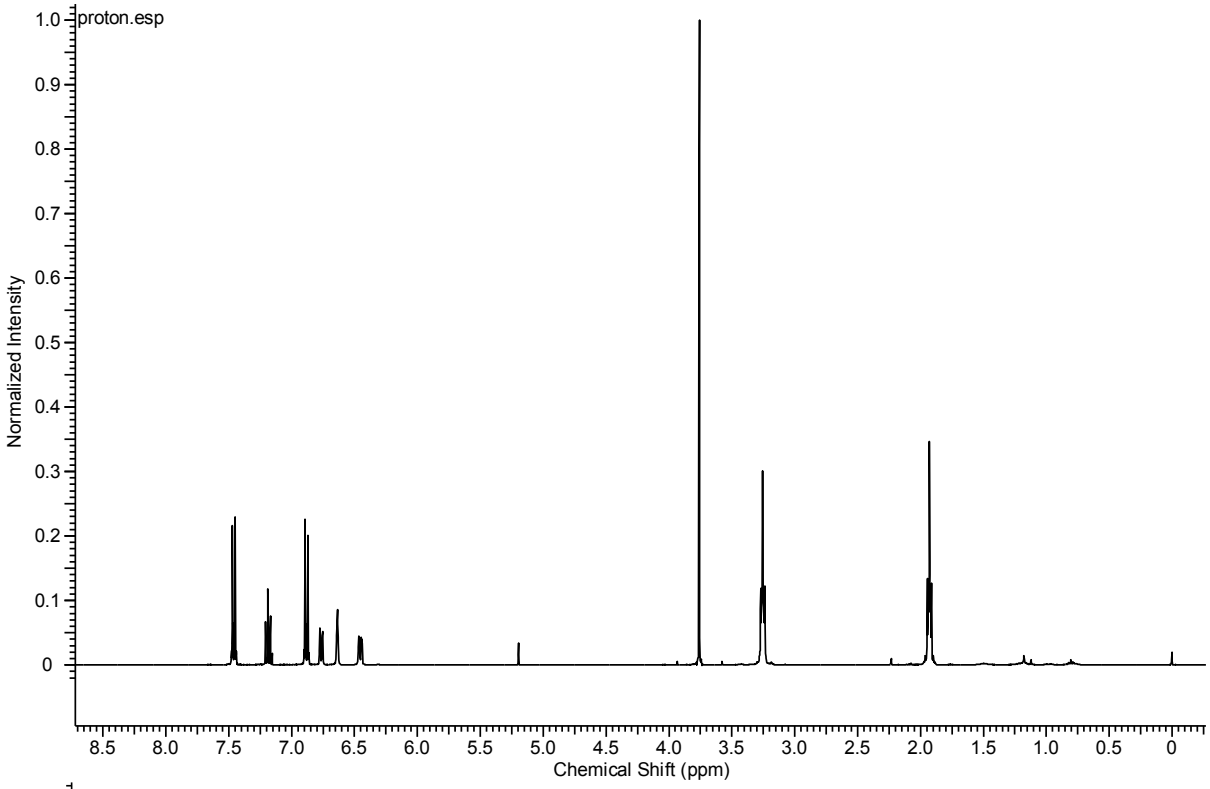

carbon-2.esp
Normalized Intensity
Chemical Shift (ppm)

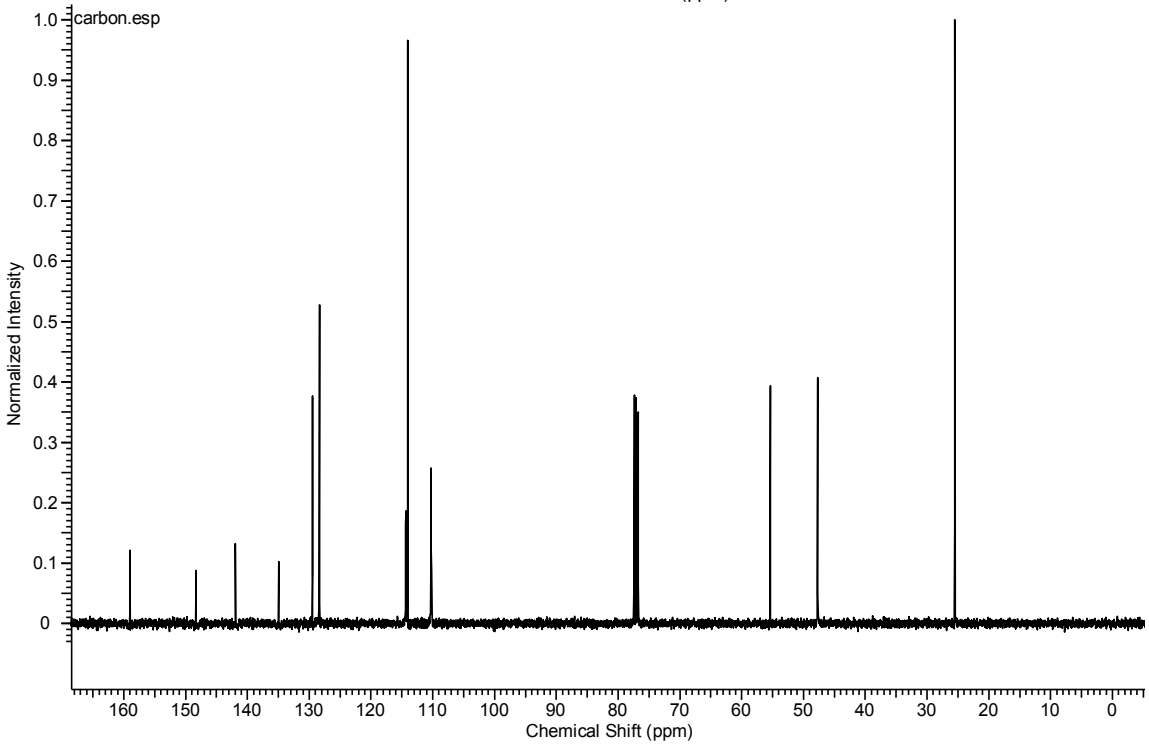

3d
Proton.esp
Normalized Intensity
Chemical Shift (ppm)
Jul23-2012-48.002.esp
Normalized Intensity
Chemical Shift (ppm)

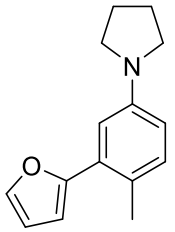

2e
CARBON.ESP
Normalized Intensity
Chemical Shift (ppm)
PROTON.ESP
Normalized Intensity
Chemical Shift (ppm)



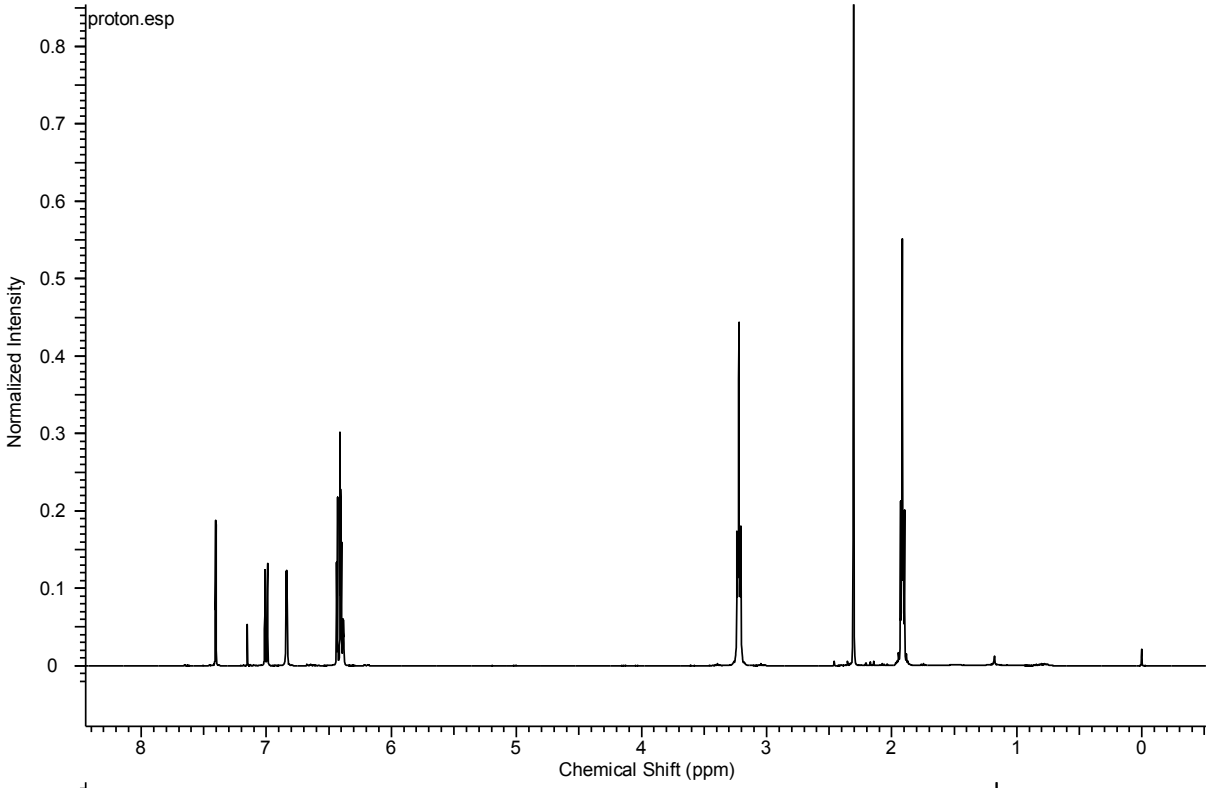
3e

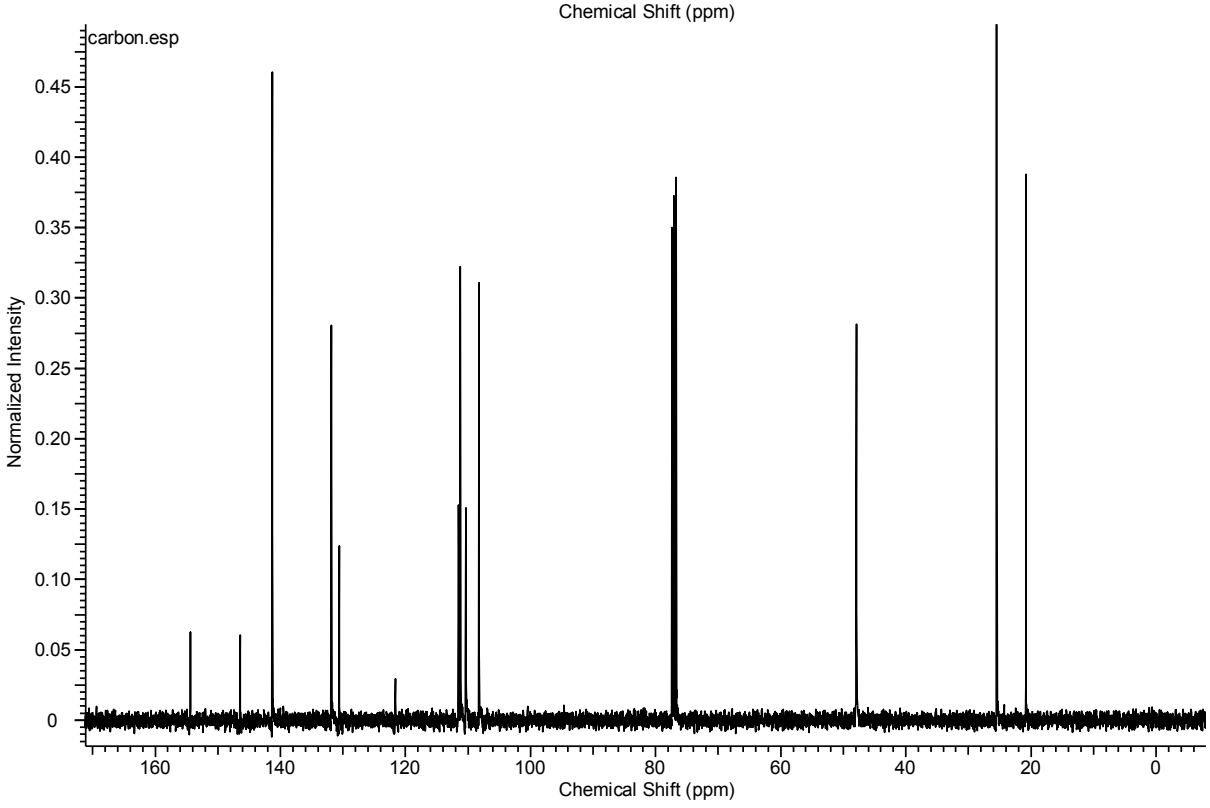

proton.esp
Normalized Intensity
Chemical Shift (ppm)

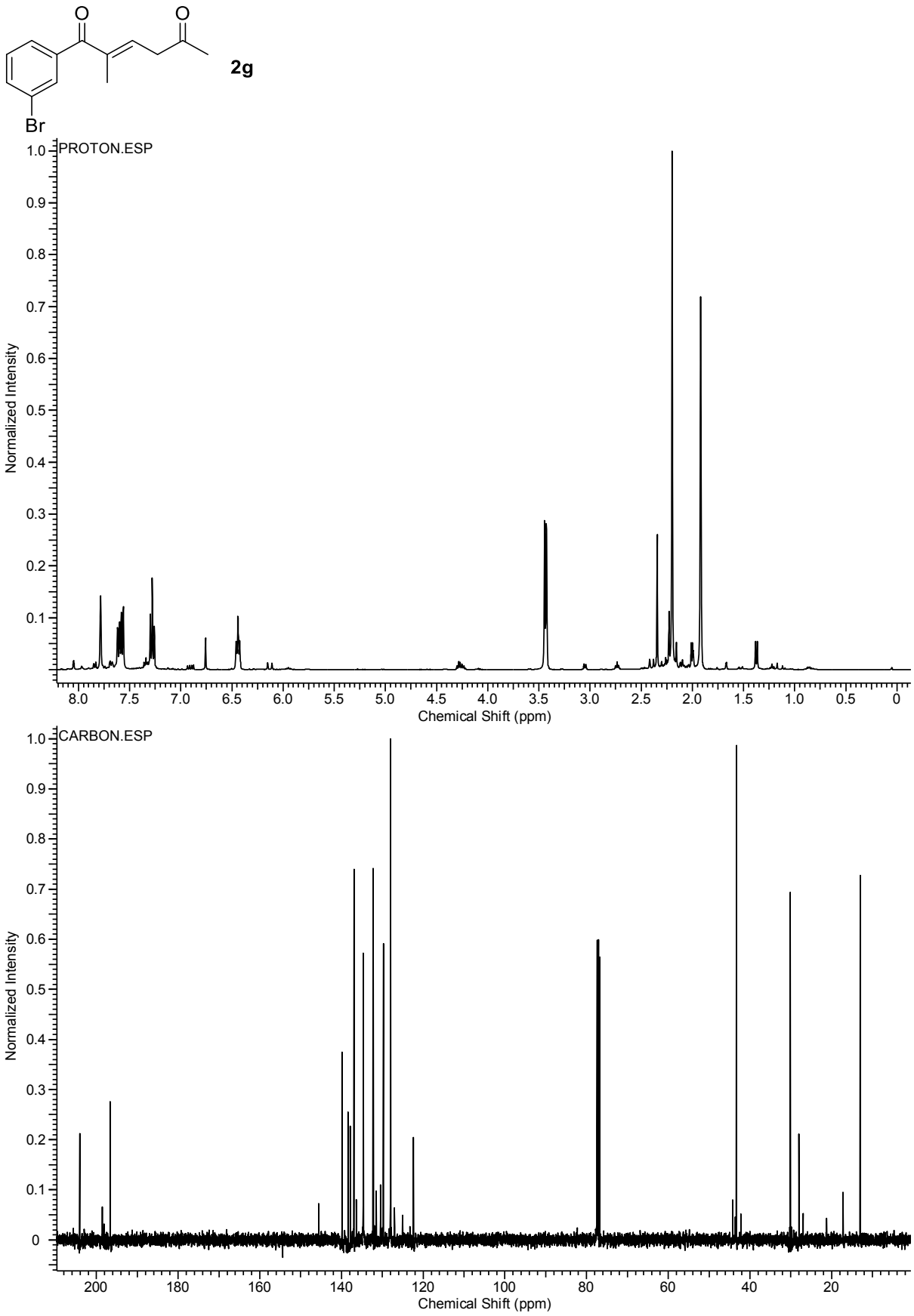

carbon.esp
Normalized Intensity
Chemical Shift (ppm)

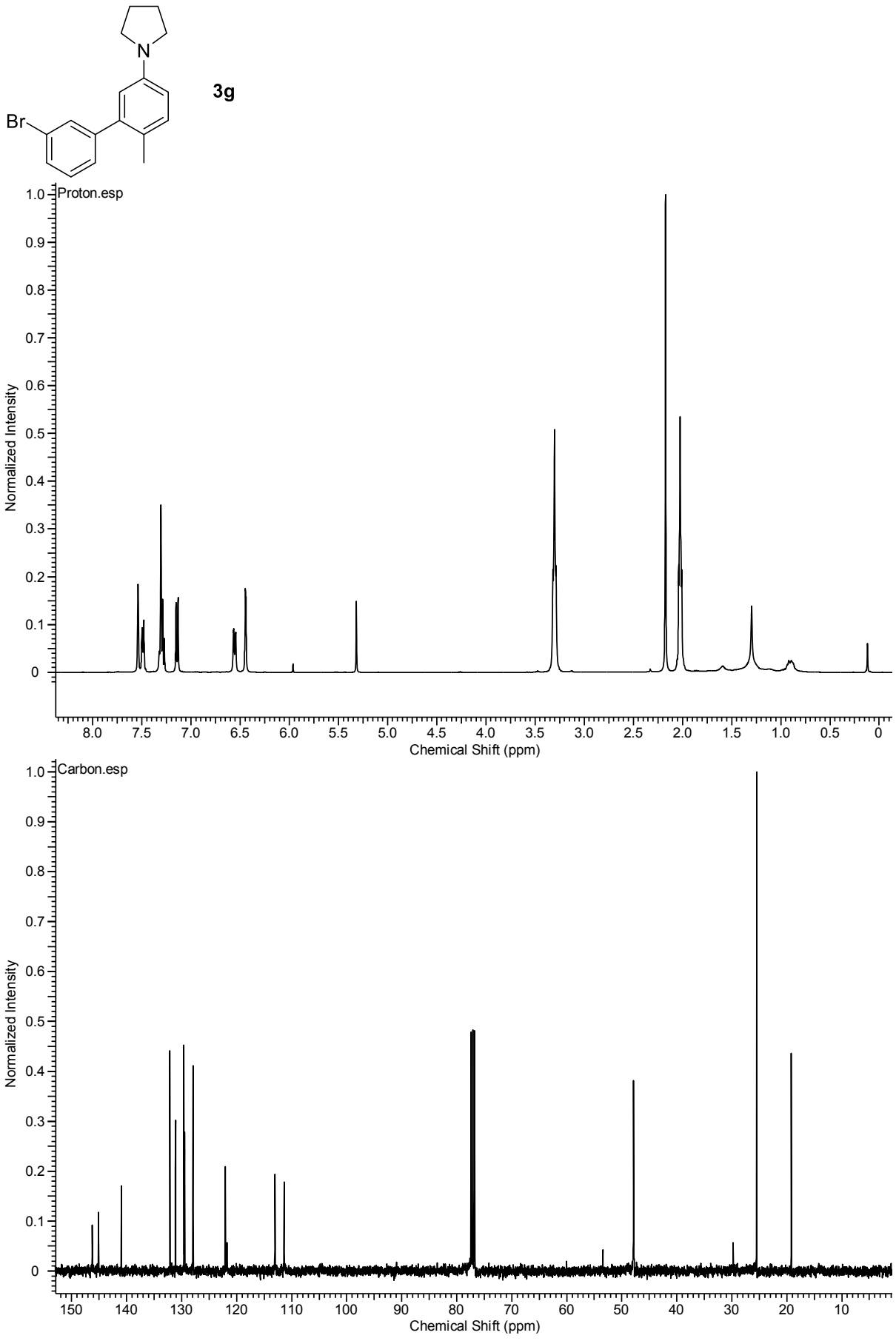

N
O

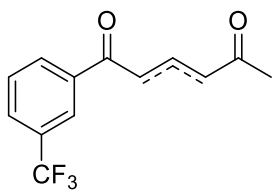
3f


proton.esp
Normalized Intensity
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

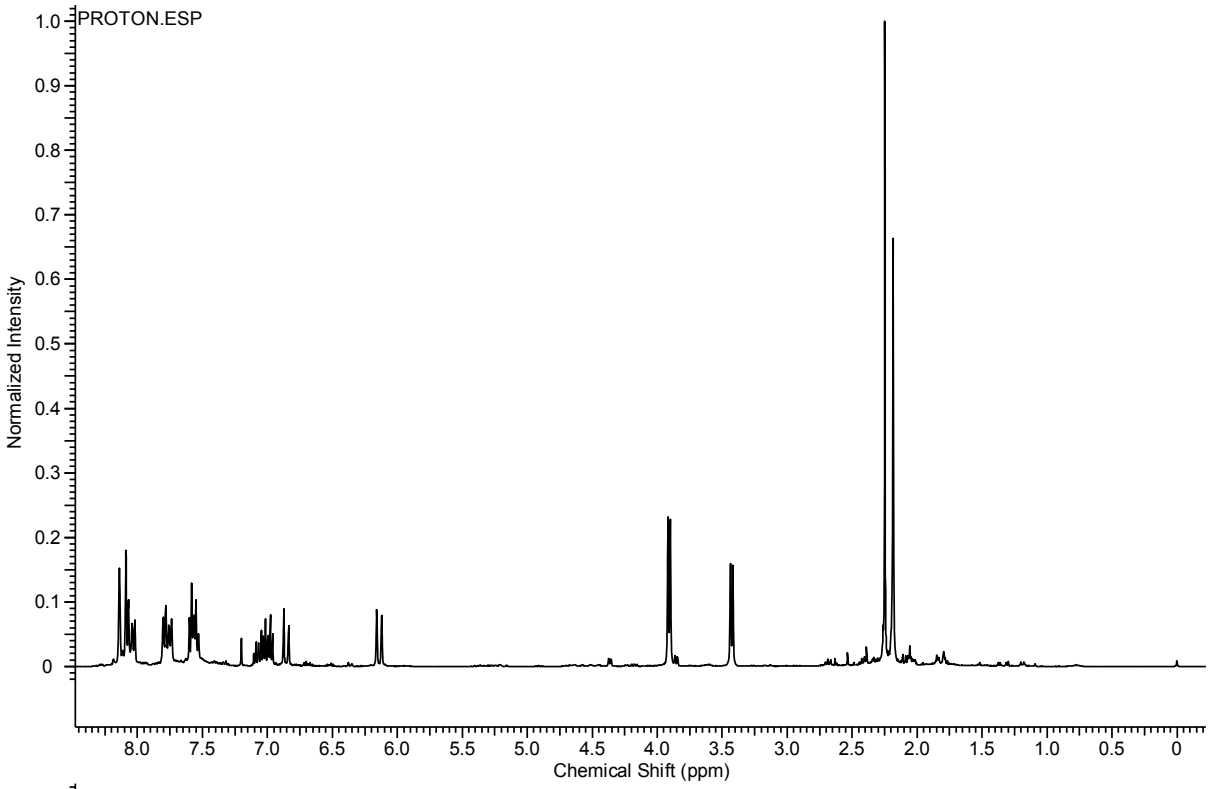

carbon.esp
Normalized Intensity
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

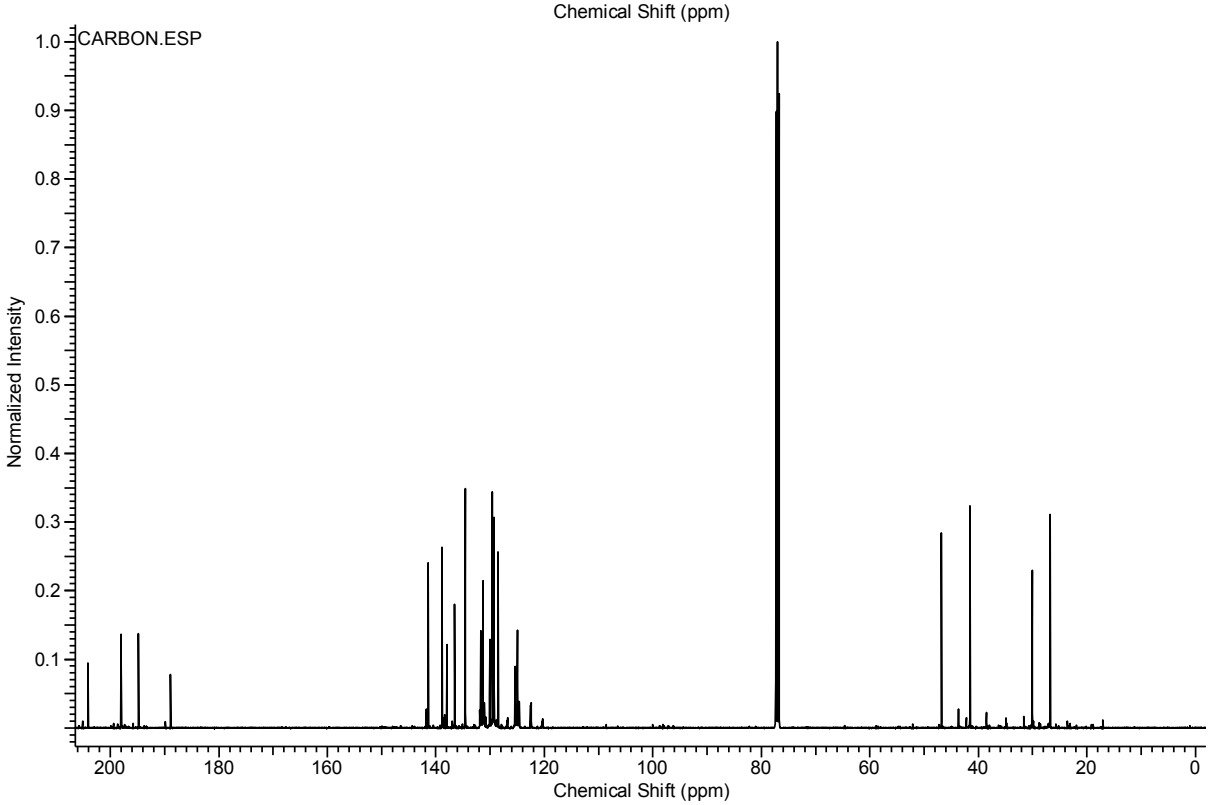

O
O
Br
2g
PROTON.ESP
Normalized Intensity
Chemical Shift (ppm)
CARBON.ESP
Normalized Intensity
Chemical Shift (ppm)

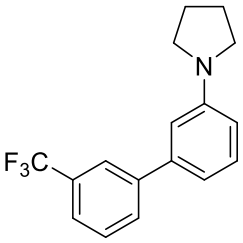

N
Br
3g
Proton.esp
Normalized Intensity
Chemical Shift (ppm)
Carbon.esp
Normalized Intensity
Chemical Shift (ppm)


O
O
CF3

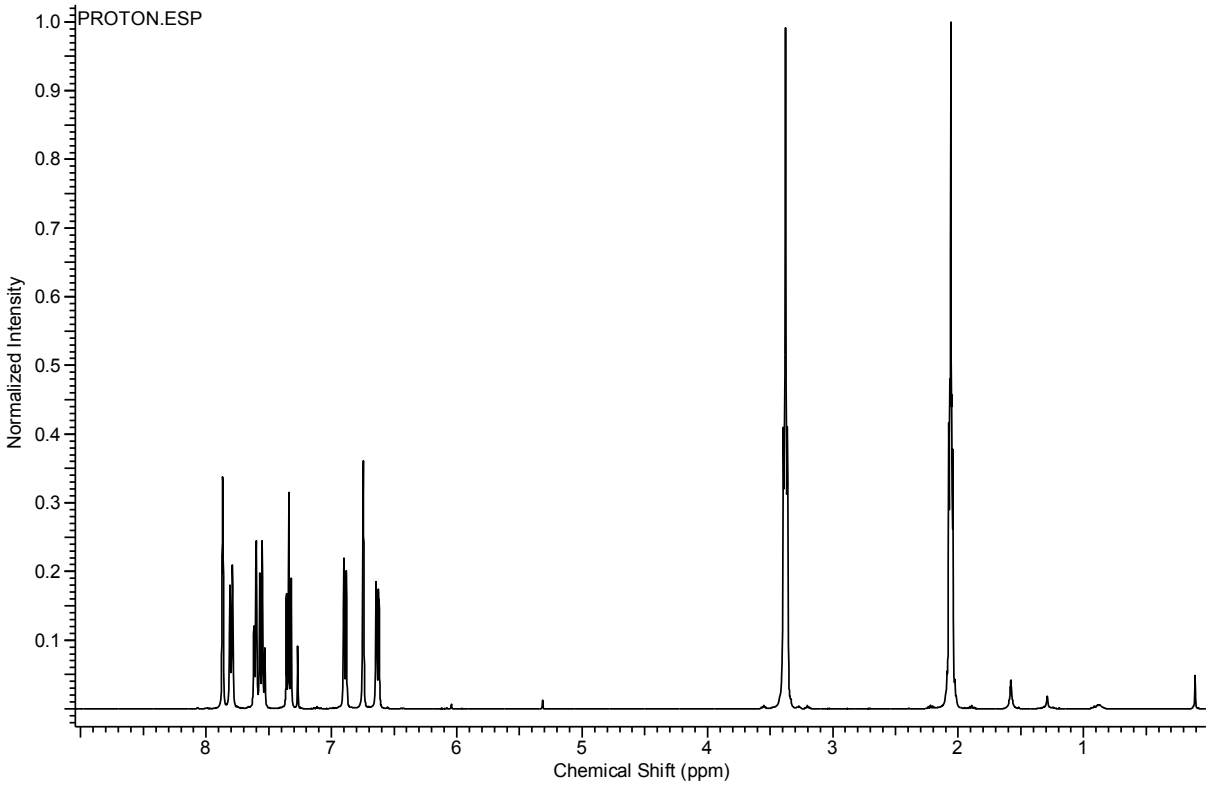
2h

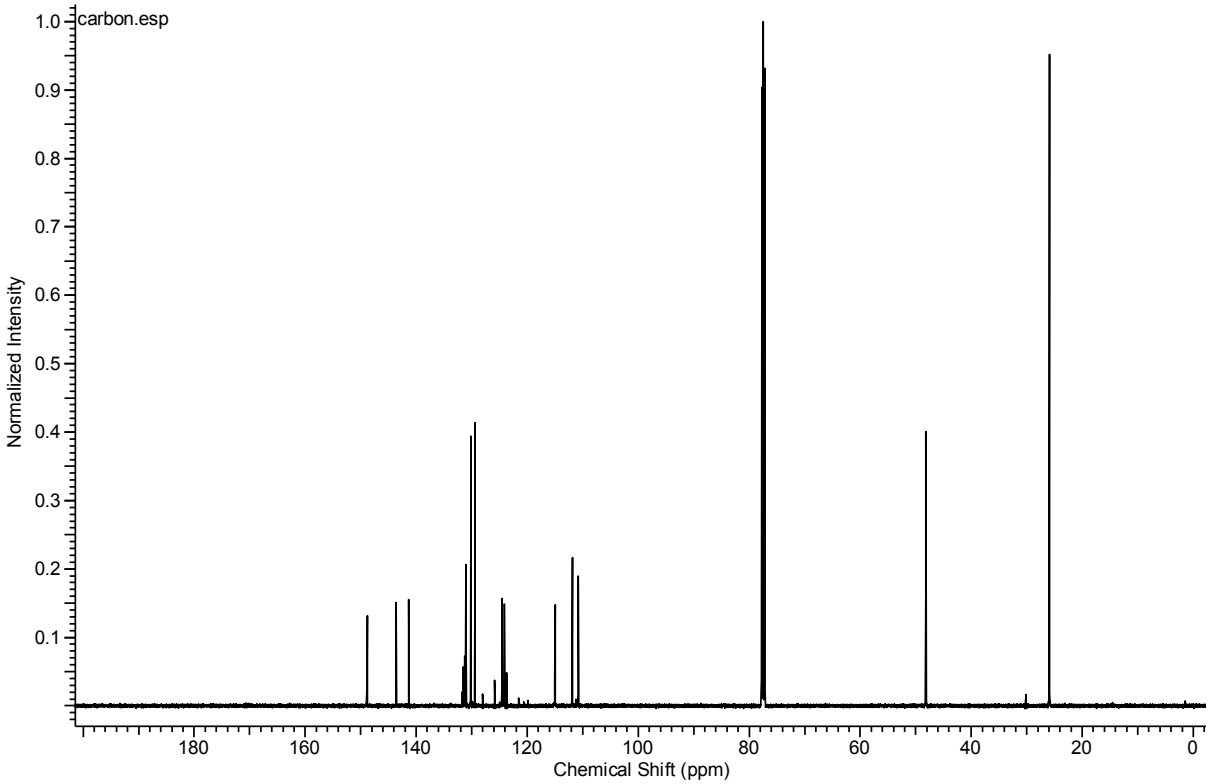

PROTON.ESP
Normalized Intensity
Chemical Shift (ppm)

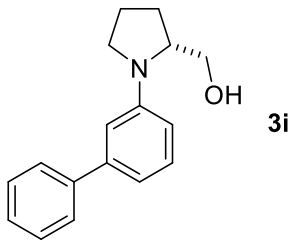

CARBON.ESP
Normalized Intensity
Chemical Shift (ppm)


N
F3C

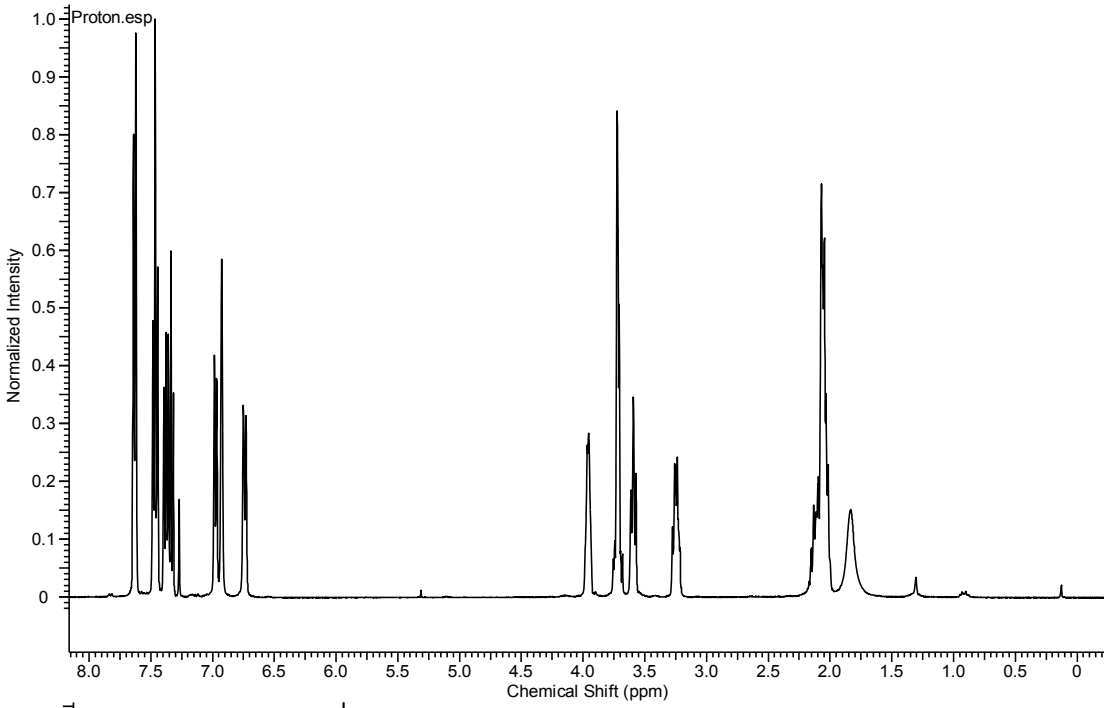
3h

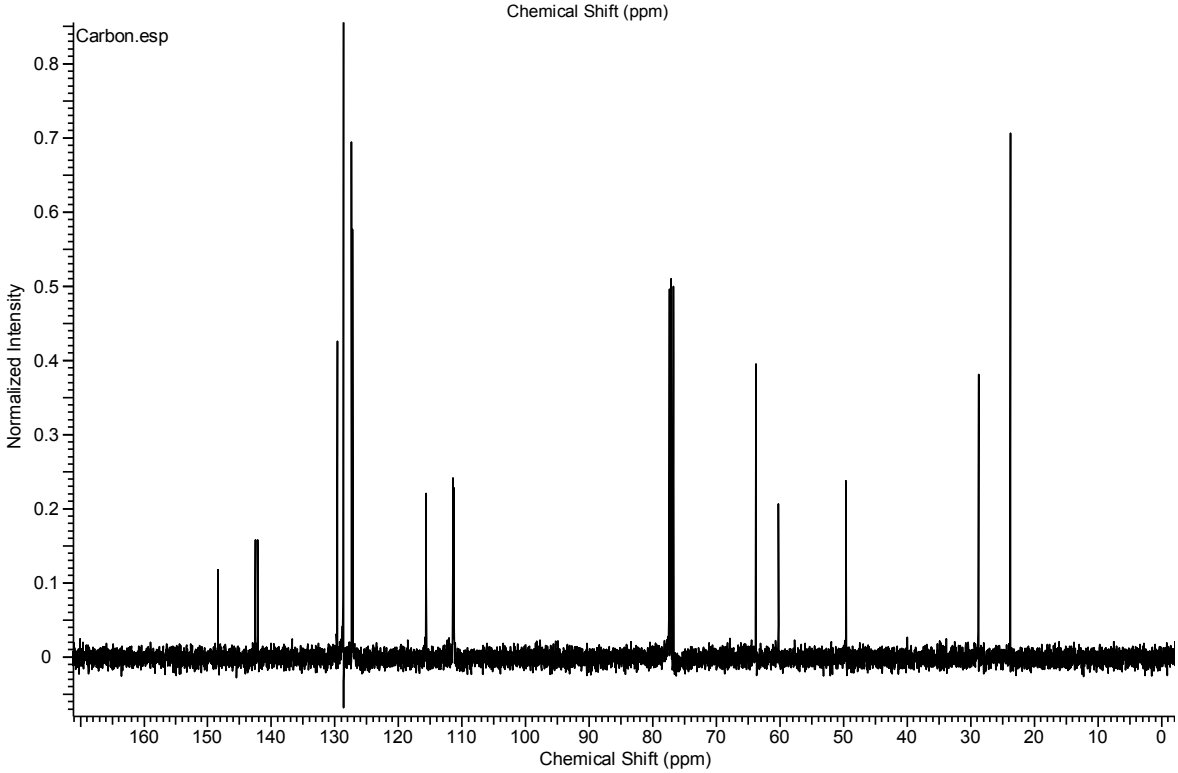

PROTON.ESP
Normalized Intensity
Chemical Shift (ppm)

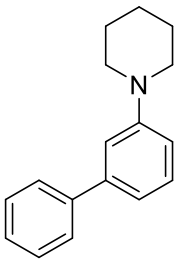

carbon.esp
Normalized Intensity
Chemical Shift (ppm)


N
OH

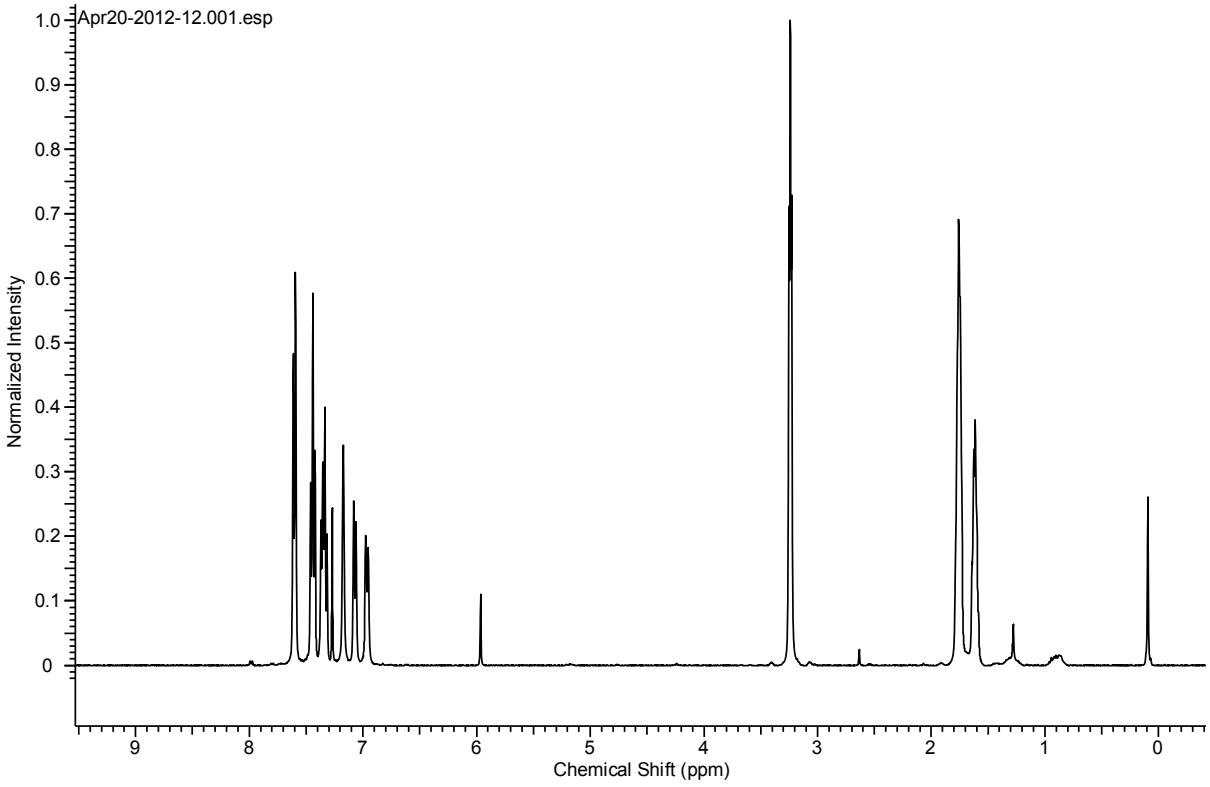
3i

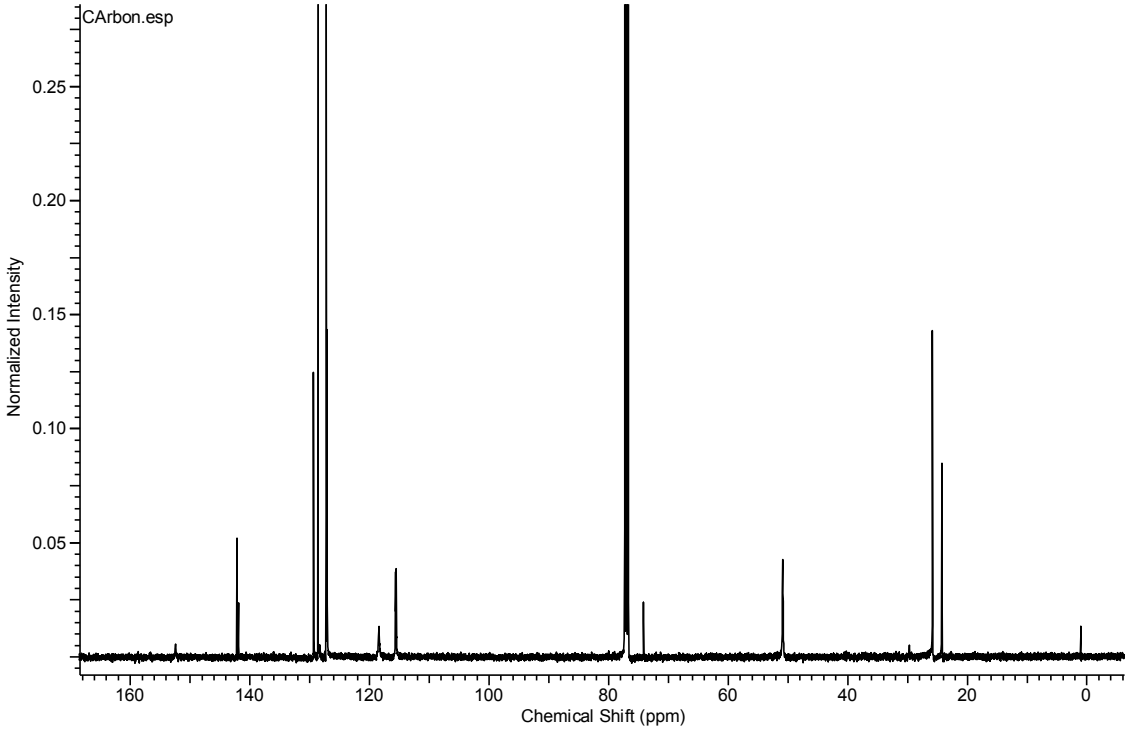

Proton.esp
Normalized Intensity
Chemical Shift (ppm)

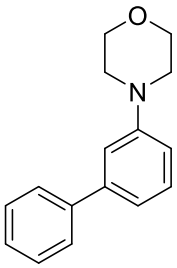

Carbon.esp
Normalized Intensity
Chemical Shift (ppm)



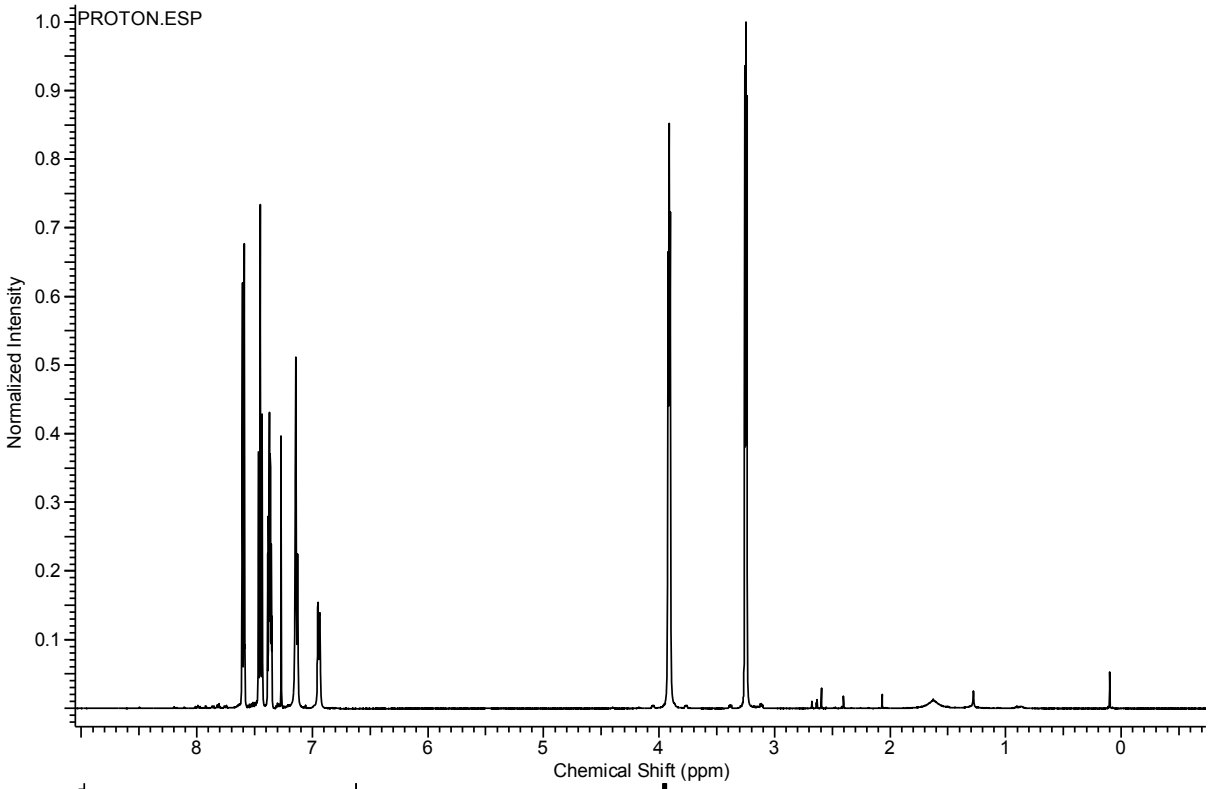
3j

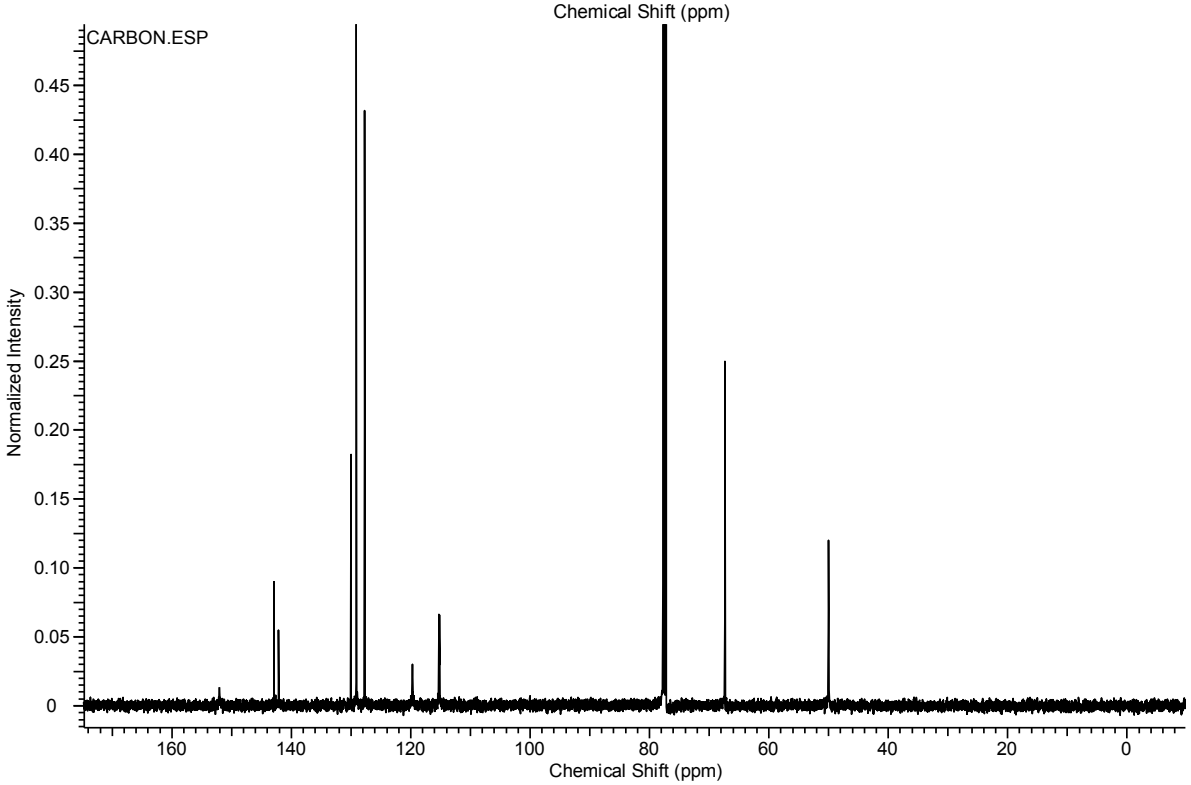

Apr20-2012-12.001.esp
Normalized Intensity
Chemical Shift (ppm)

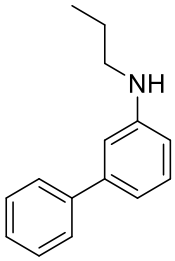

CArbon.esp
Normalized Intensity
Chemical Shift (ppm)


O
N

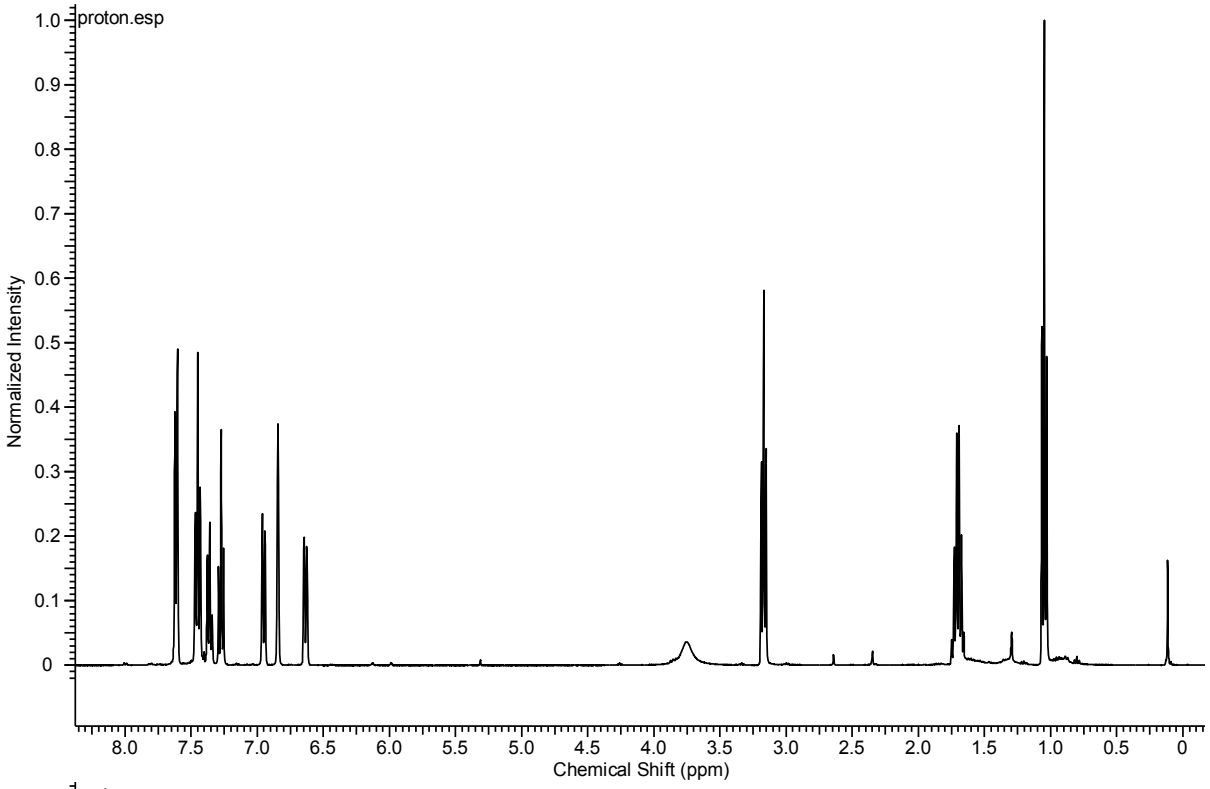
3k

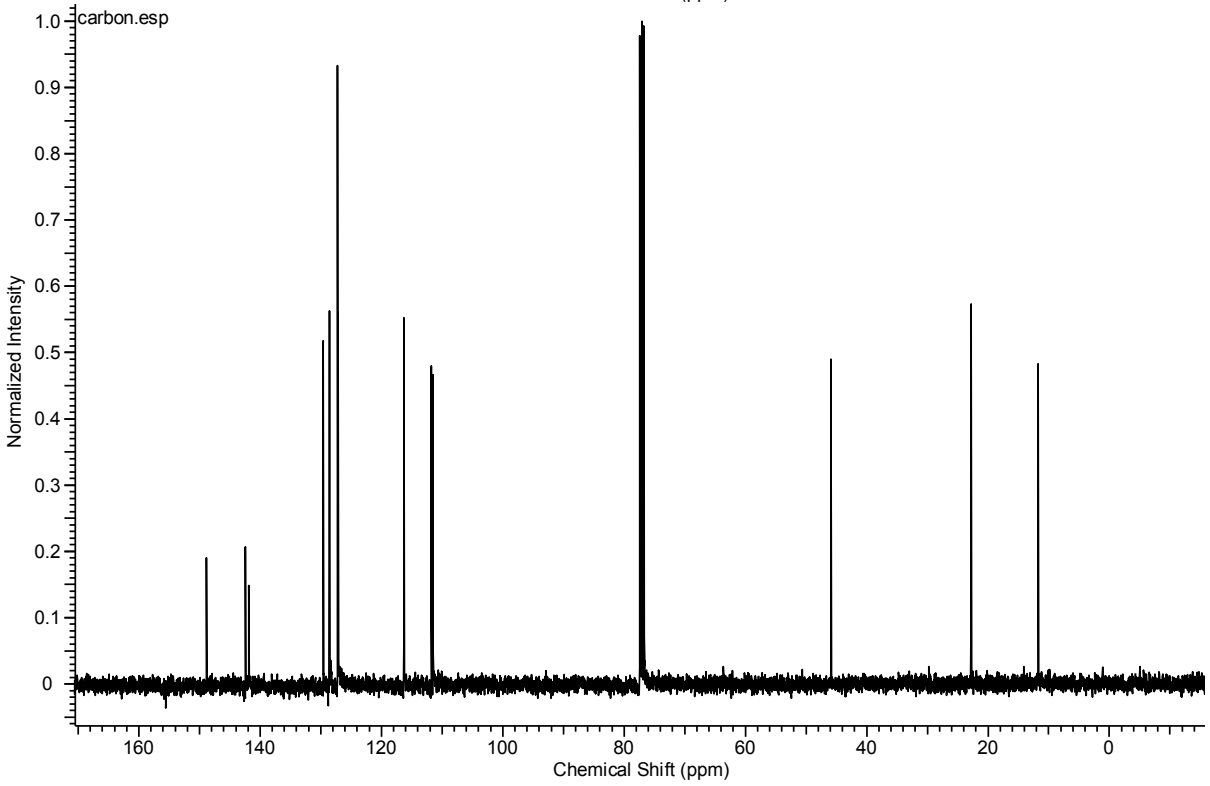

PROTON.ESP
Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

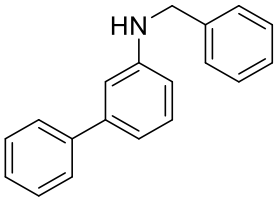

CARBON.ESP
Normalized Intensity
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


NH

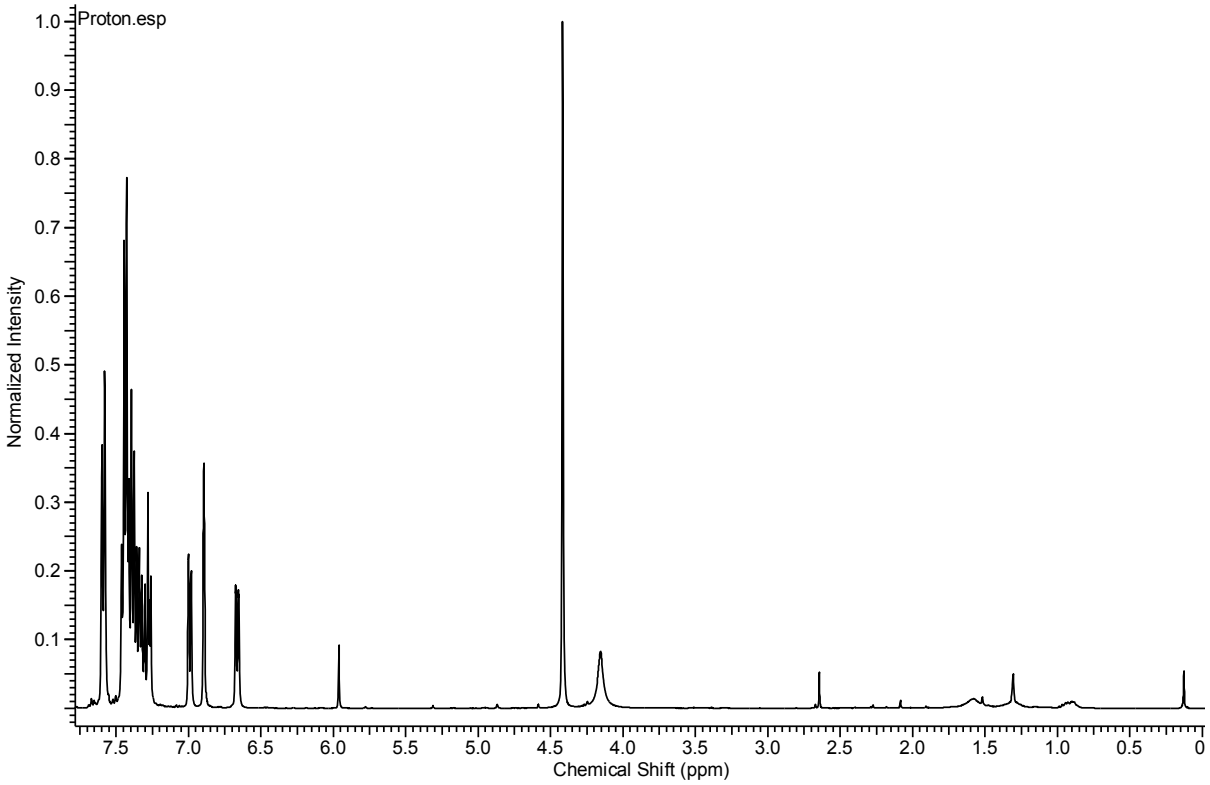
3l

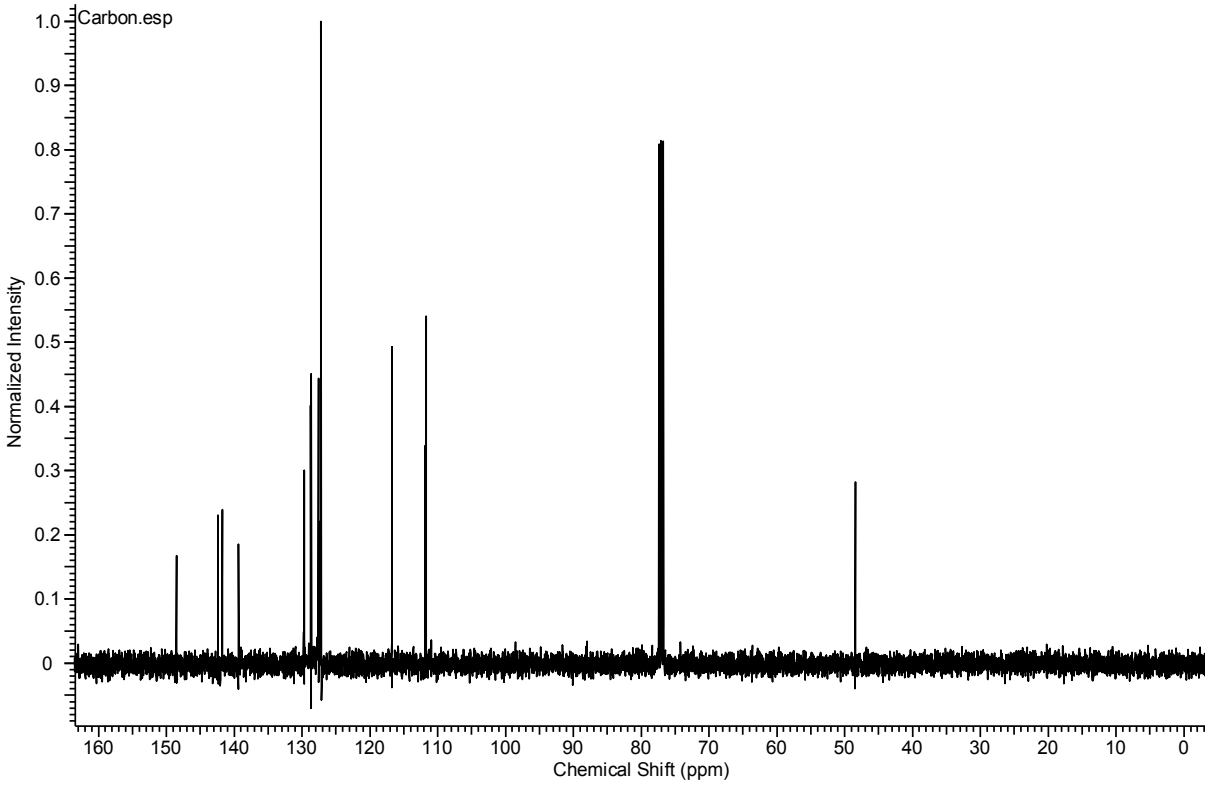

proton.esp
Normalized Intensity
Chemical Shift (ppm)

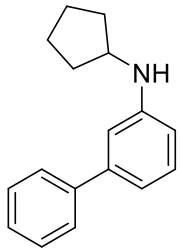

carbon.esp
Normalized Intensity
Chemical Shift (ppm)


HN

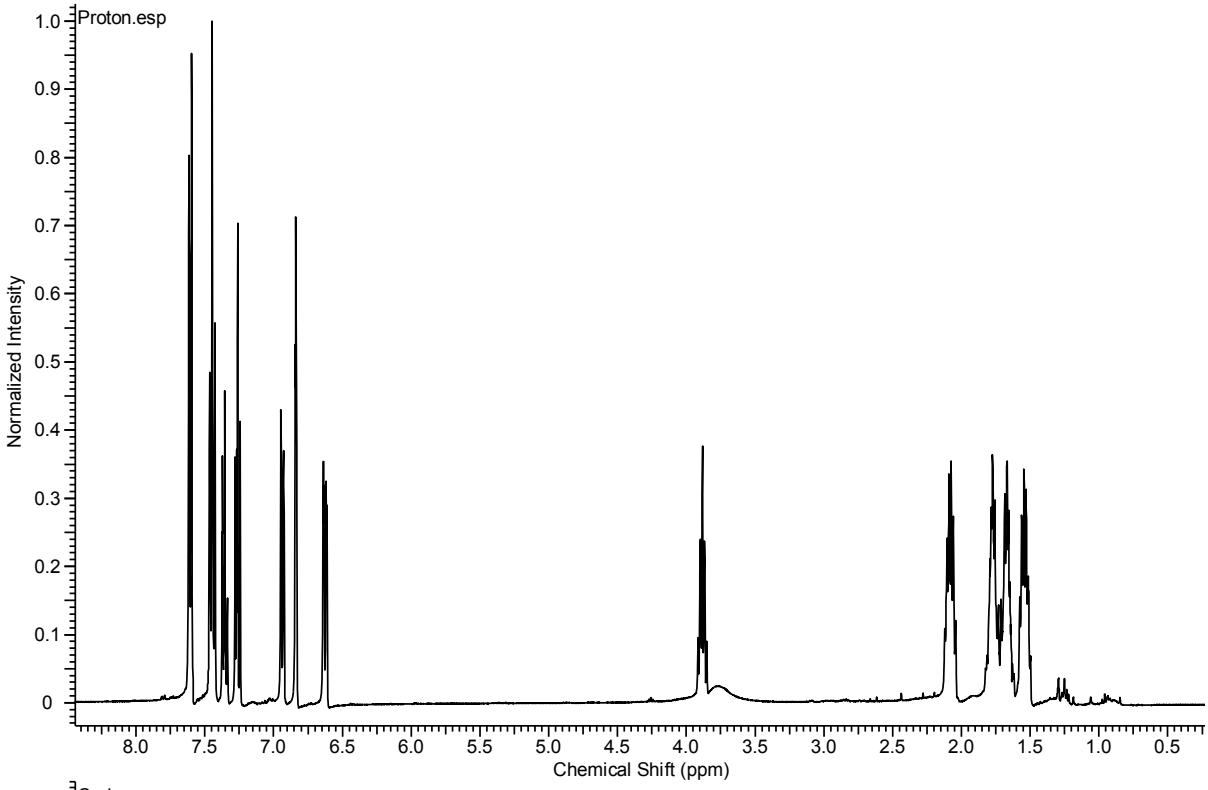
3m

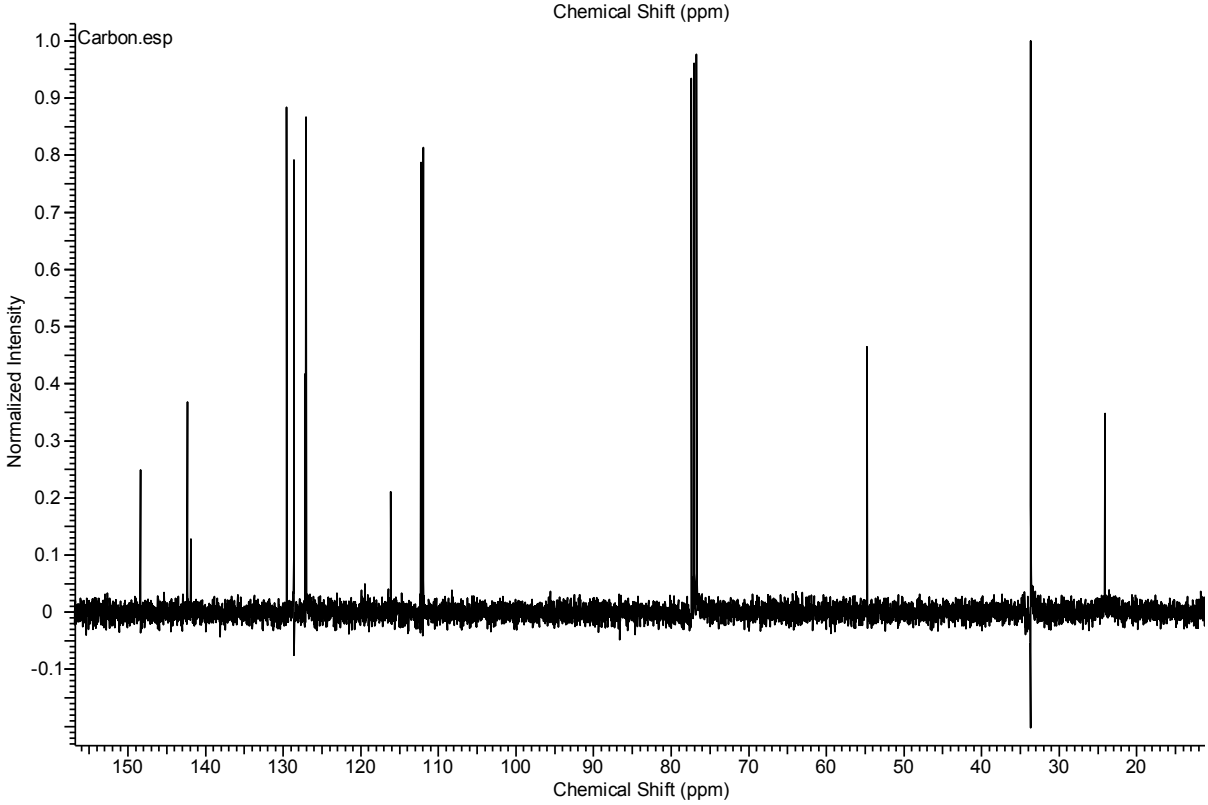

Proton.esp
Normalized Intensity
Chemical Shift (ppm)

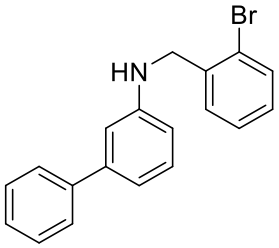

Carbon.esp
Normalized Intensity
Chemical Shift (ppm)


NH

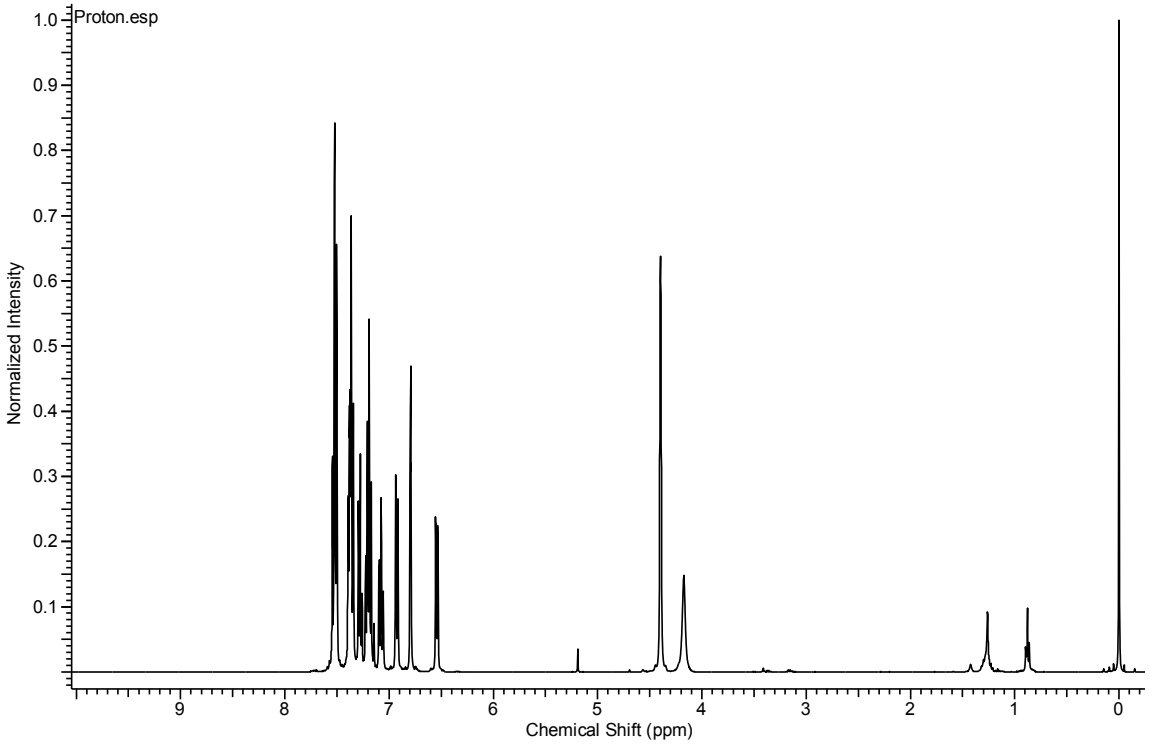
3n

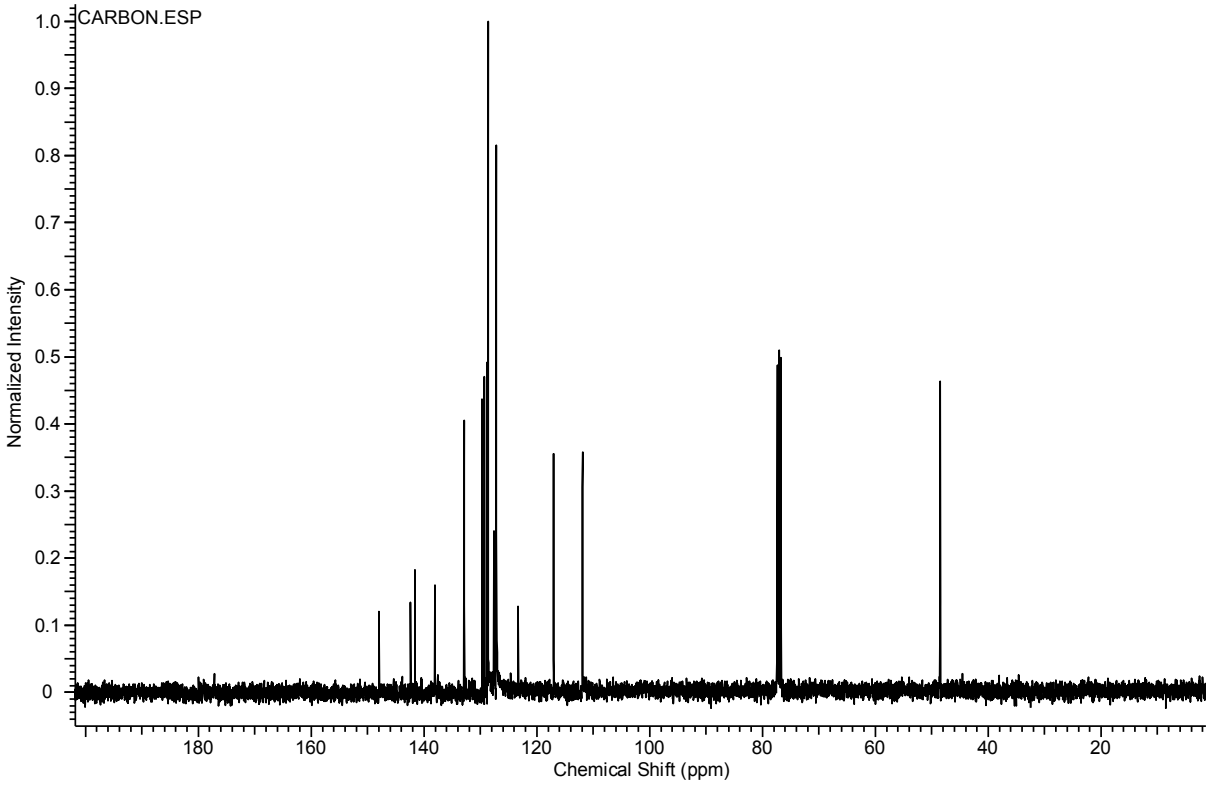

Proton.esp
Normalized Intensity
Chemical Shift (ppm)

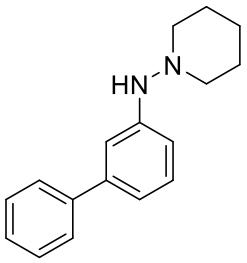

Carbon.esp
Normalized Intensity
Chemical Shift (ppm)


Br
HN

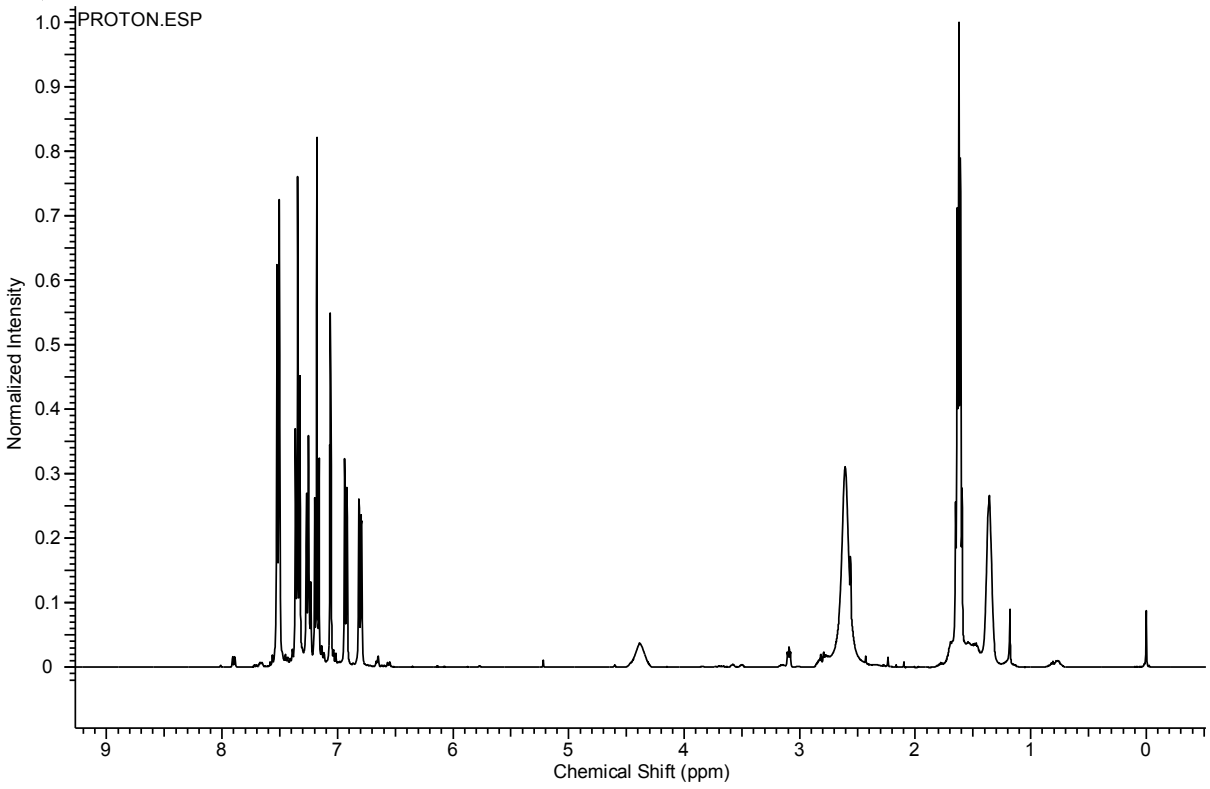
3o

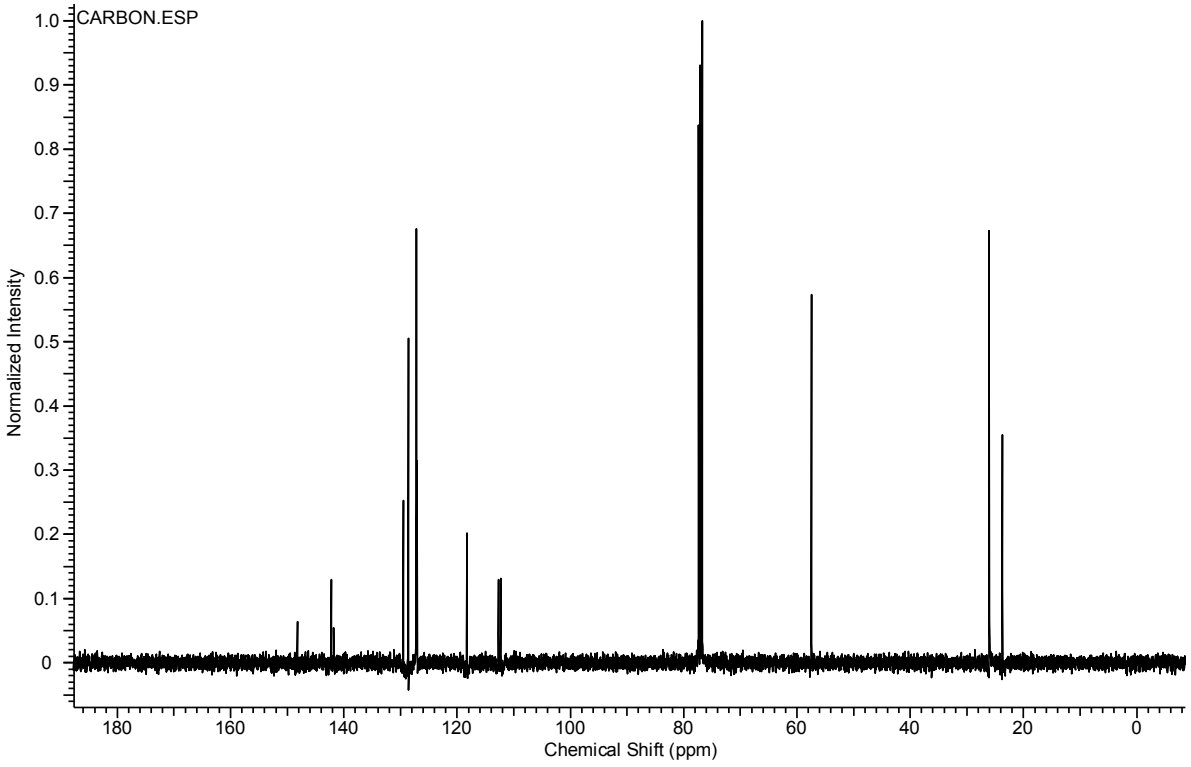

Proton.esp
Normalized Intensity
Chemical Shift (ppm)

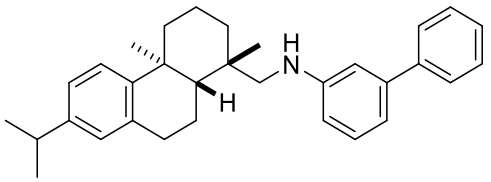

CARBON.ESP
Normalized Intensity
Chemical Shift (ppm)


HN
N

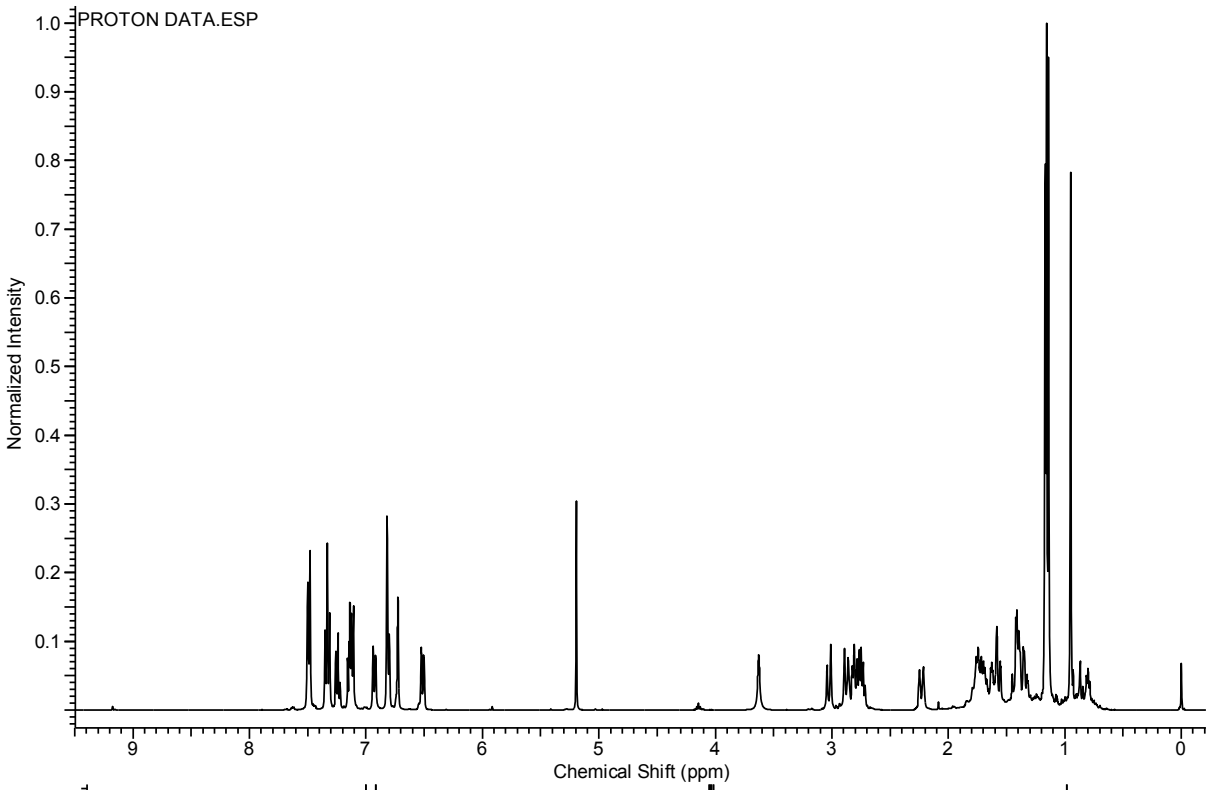
3p

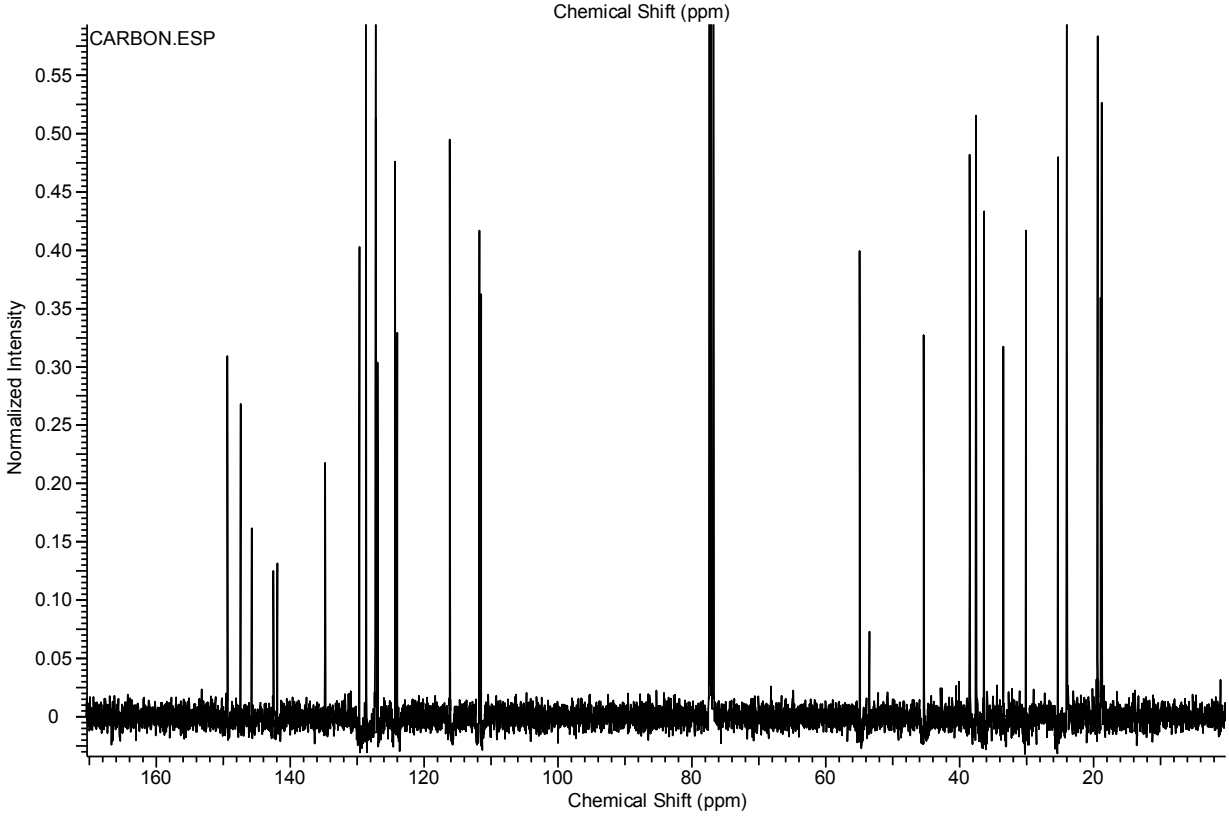

PROTON.ESP
Normalized Intensity
Chemical Shift (ppm)

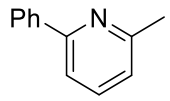

CARBON.ESP
Normalized Intensity
Chemical Shift (ppm)



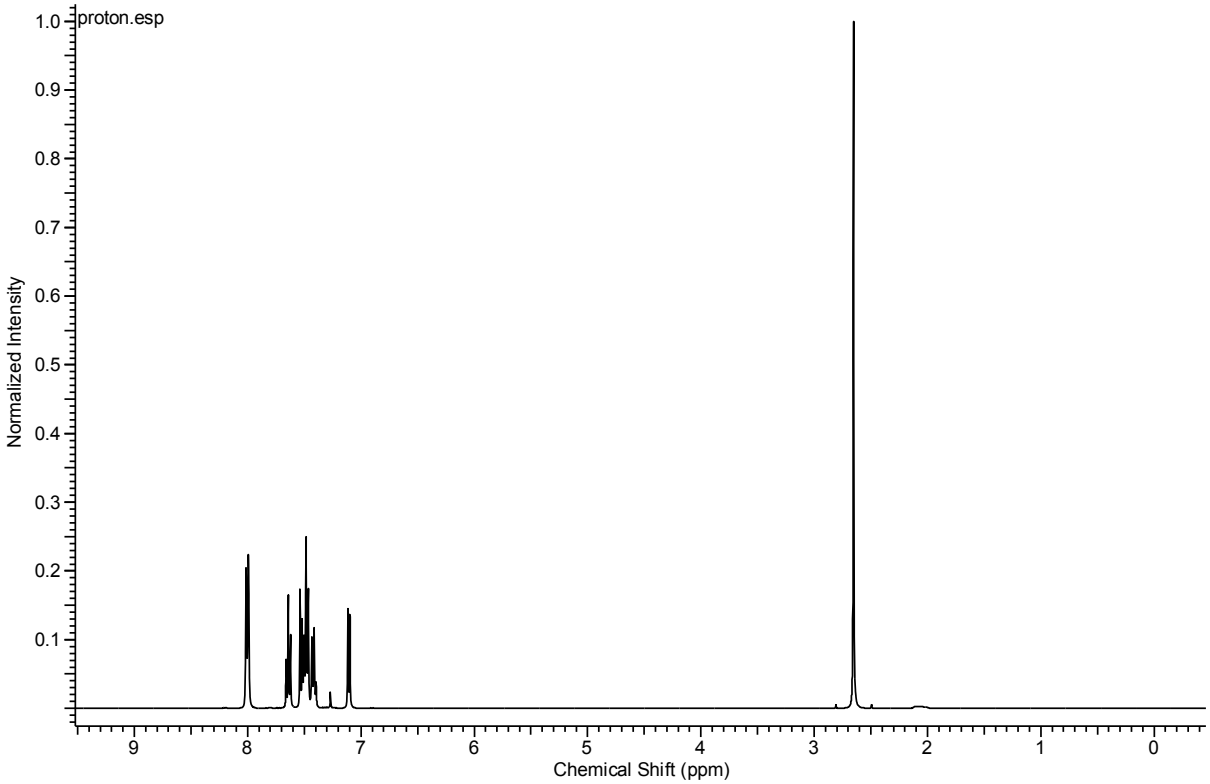
3q


PROTON DATA.ESP
Normalized Intensity
Chemical Shift (ppm)


CARBON.ESP
Normalized Intensity
Chemical Shift (ppm)


Ph
N

5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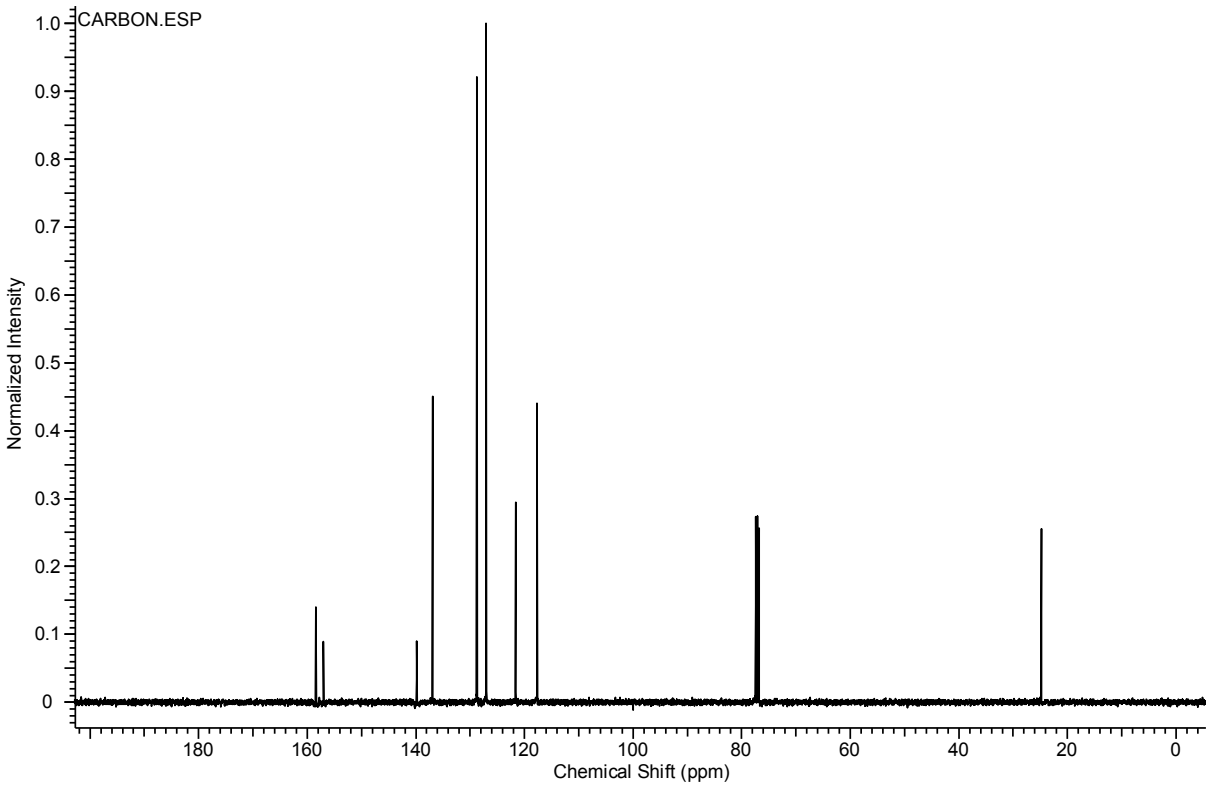
Normalized Intensity
Chemical Shift (ppm)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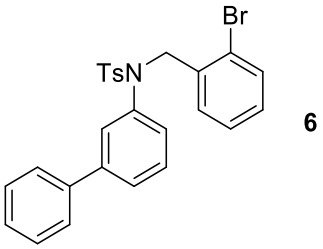
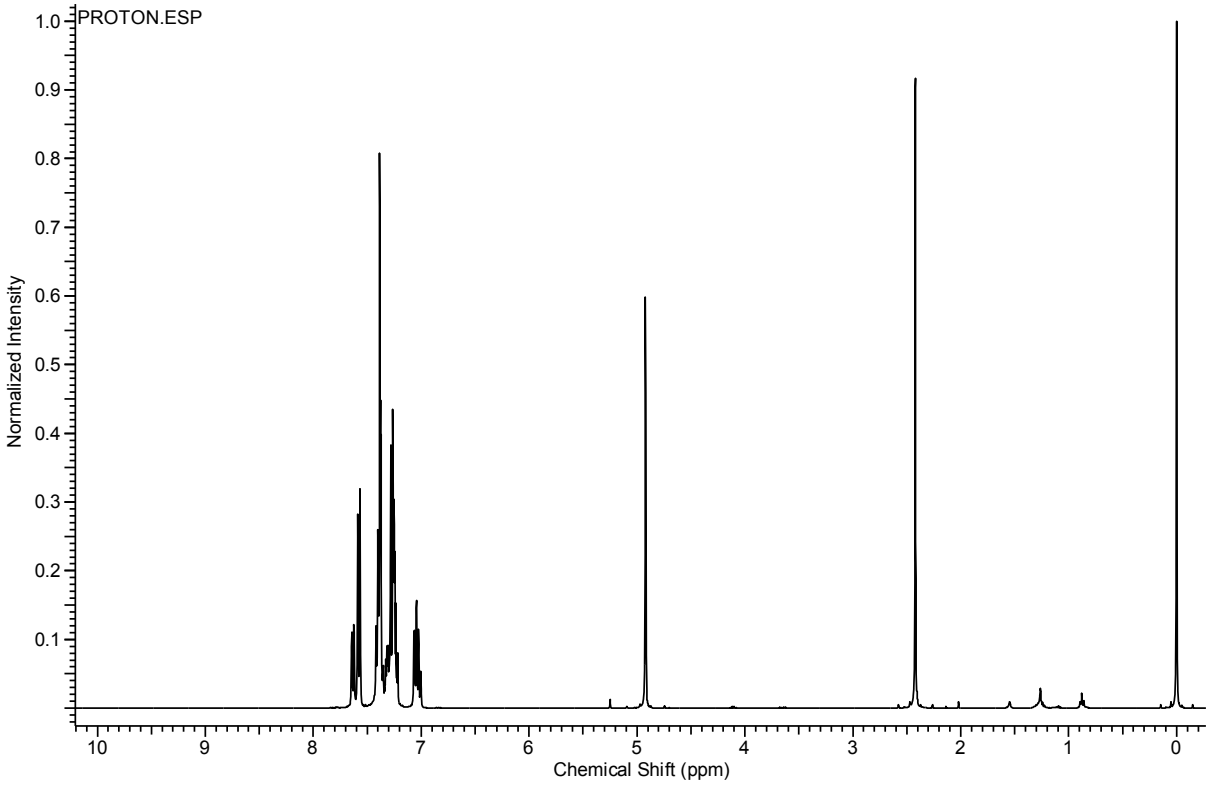

Br
TsN

6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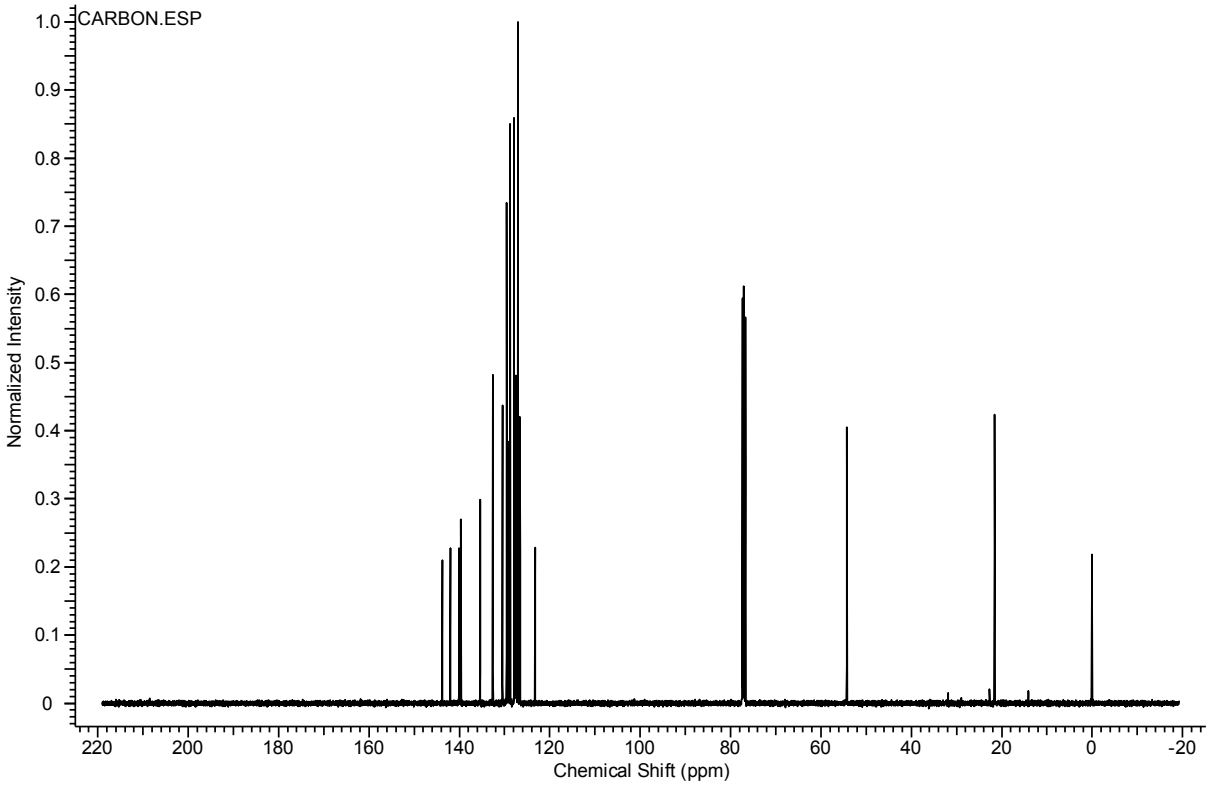
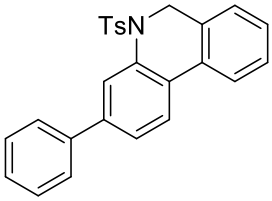
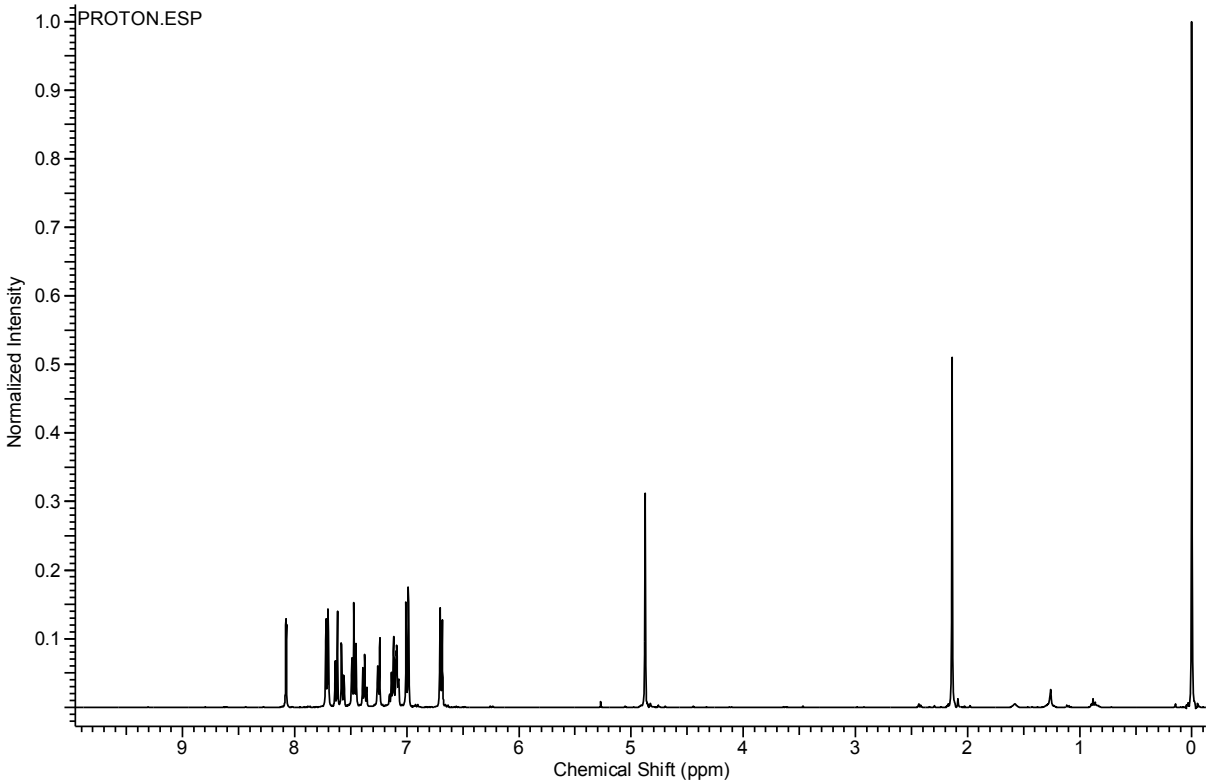
Chemical Shift (ppm)


CARBON.ESP
Normalized Intensity
Chemical Shift (ppm)


TsN

7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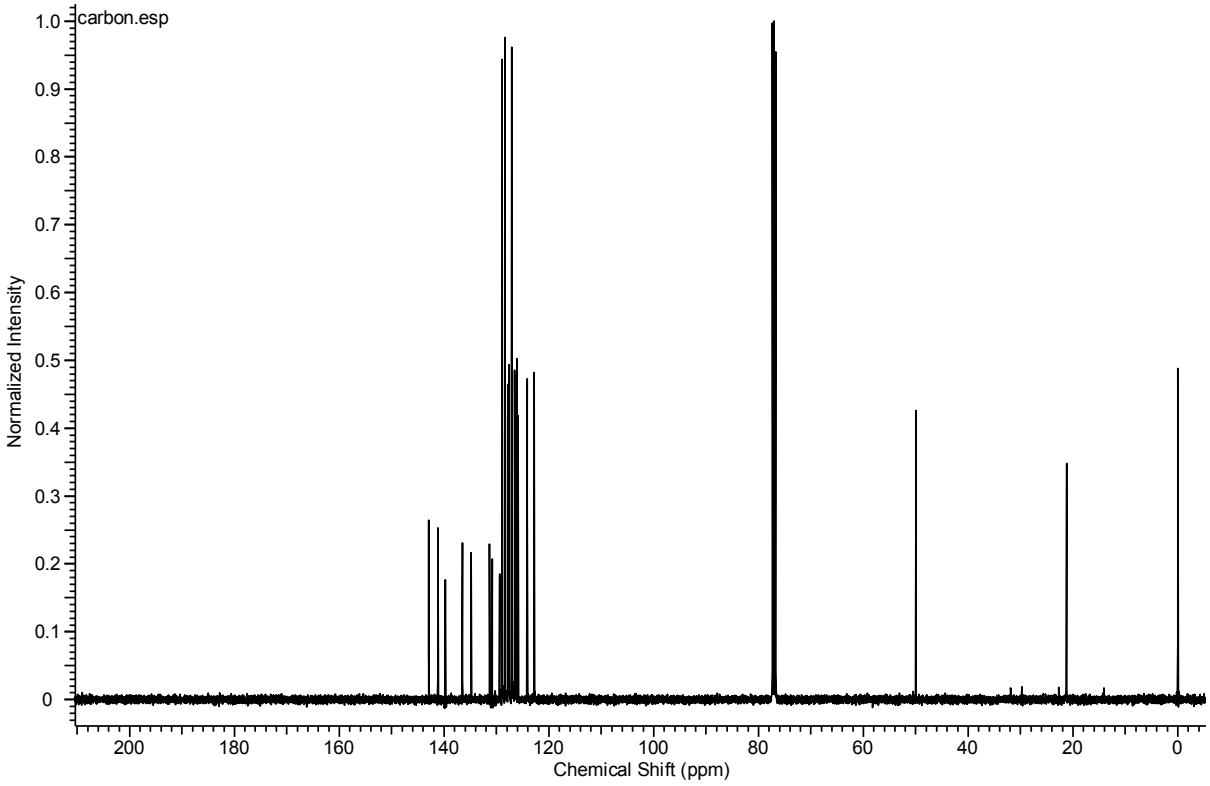
Normalized Intensity
Chemical Shift (ppm)


carbon.esp
Normalized Intensity
Chemical Shift (ppm)

Crystal Structure Determination by X-ray Diffraction

Preliminary studies indicated that the crystal underwent a phase transition between room temperature and 150 K, so a more in-depth study was carried out. Colourless block-like crystals were isolated from the mother liquor, and mounted on a glass fibre, secured with nail polish; data were collected using an Oxford Diffraction SuperNova diffractometer (λ(Mo K_α) = 0.71070Å). Initial frames were collected at 300 K to determine the unit cell. A hemisphere of data (plus a 240° φ-scan) was then collected at 300 K. The crystal was then cooled from 300 K in increments of 10 K to 120 K and at each temperature three ω-scans were collected which were indexed using the same orientation matrix giving a similar primitive cell in each case. The cell parameters were plotted as a function of temperature (Figures 1-3) and indicate that the transition took place between 200 K and 190 K on cooling. Examination with PASCal[13] showed that there was a small amount of 1D negative thermal expansion when the cell was orthogonalized (Figure 4-5).

At 120 K, the data collection was repeated and on completion, the crystal was warmed to 300 K at 120 K/h, where the unit cell was found to be consistent with that previously determined at 300 K, suggesting that the phase transition was reversible.

Cell parameter and intensity data for both datasets were determined using CrysAlisPro and the structure was solved at 300 K by charge-flipping using 'Superflip'.[14] The data collected at 120 K were solved from the 300 K structure using difference Fourier maps to generate the second molecule in the asymmetric unit. Both structures were refined by full-matrix least squares on F^2 using the CRYSTALS suite.[15] All non-hydrogen atoms were refined with anisotropic displacement parameters and the hydrogen atoms were initially refined with soft restraints, and then constrained using a riding model for the final refinement.[16]

The 300 K structure showed a small degree of librational disorder in the two terminal rings however attempts at modelling this demonstrated that there was a high degree of correlation and gave no improvement in the agreement factors.

From the cell parameter measurements, it was observed that there was a discontinuity between 200 K and 190 K on cooling. Associated with this, the crystal went through a change in symmetry from $P2_1/n$ to $P\bar{1}$ (as shown by the systematic absence violations given in Table 1).

Below the phase transition there are two molecules in the asymmetric unit; Fig. 7 shows the two molecules overlaid, highlighting the changes in conformation (the angle between the terminal benzene rings in each molecule is approximately 30°; there is also a small difference between the tolyl-rings). On cooling through the phase transition the crystal also underwent twinning by a 180° rotation about the *b* axis. Thus for the final refinement, the following twin law was applied[17] giving a 29.3(2)% minor component:

$$\begin{pmatrix} h' \\ k' \\ l' \end{pmatrix} = \begin{pmatrix} -1 & 0.042 & 0 \\ 0 & 1 & 0 \\ 0 & 0.086 & -1 \end{pmatrix} \begin{pmatrix} h \\ k \\ l \end{pmatrix}$$

[13] Cliffe, M.; Goodwin, A. *J. Appl. Cryst.* **2012**, *45*, 1321.
[14] Palatinus, L.; Chapuis, G. *J. Appl. Cryst.* **2007**, *40*, 786.
[15] Betteridge, P. W.; Carruthers, J. R.; Cooper, R. I.; Prout, K.; Watkin, D. J. *J. Appl. Cryst.* **2003**, *36*, 1487; Cooper R. I.; Thompson, A. L.; Watkin, D. J. *J. Appl. Cryst.* **2010**, *43*, 1100.
[16] Cooper, R. I.; Thompson, A. L.; Watkin, D. J. *J. Appl. Cryst.* **2010**, *43*, 1100.
[17] Cooper, R. I.; Gould, R. O.; Parsons, S.; Watkin, D. J. *J. Appl. Cryst.* **2002**, *35*, 168.

	2_1--	*b*--	*c*--	*n*--
N	33/35	619/590	603/575	608/581
N I>3σ(I)	**2/32**	466/486	459/462	466/431
[I]	**0.6/51.7**	83.9/90.1	118.5/111.7	104.5/100.2
I/s	**1.0/16.2**	20.1/18.5	22.1/19.4	20.8/18.9

	-2_1-	-*a*-	-*c*-	-*n*-
N	24/24	685/660	682/664	691/668
N I>3σ(I)	**6/15**	265/560	262/590	**3/574**
[I]	**1.7/22.9**	80.9/129.1	81.2/127.6	**0.0/49.1**
I/s	**1.8/8.9**	13.3/19.8	13.4/19.5	**0.0/13.8**

	--2_1	--*a*	--*b*	--*n*
N	23/24	606/595	607/598	603/599
N I>3σ(I)	**0/20**	423/506	434/503	419/493
[I]	**0.1/66.1**	45.2/64.8	55.4/75.5	56.9/66.7
I/s	**0.2/22.5**	13.9/14.2	14.8/15.0	15.0/14.4

Table 1 Systematic absences violations shown for the 300 K and 120 K data (left and right respectively); lost symmetry is highlighted in red.

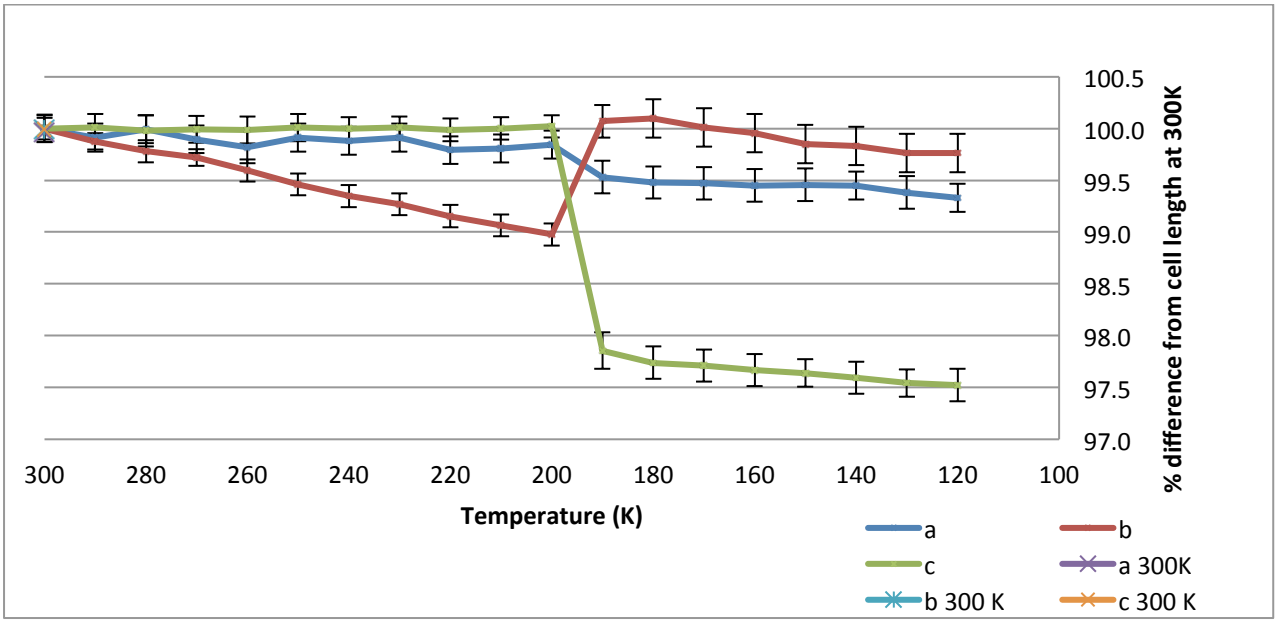


Figure 1 Percentage change in cell length as a function of temperature showing the discontinuity between 200 K and 190 K (error bars drawn at 3σ(I)).

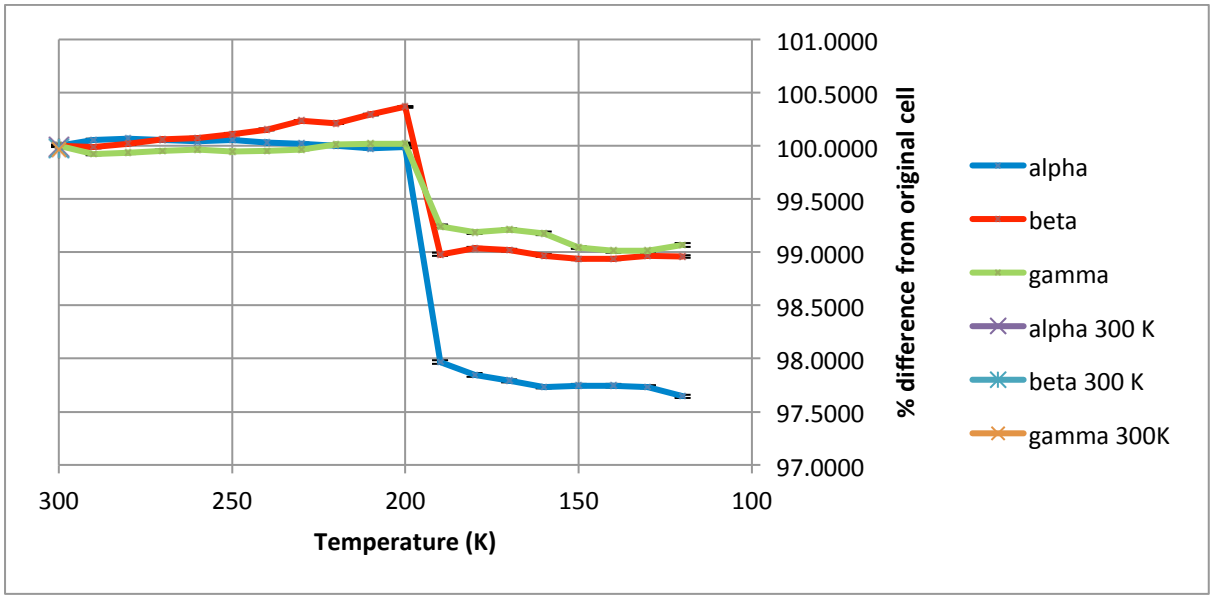


Figure 2 Percentage change in cell angles as a function of temperature showing the discontinuity between 200 K and 190 K (error bars drawn at 3σ(I))..

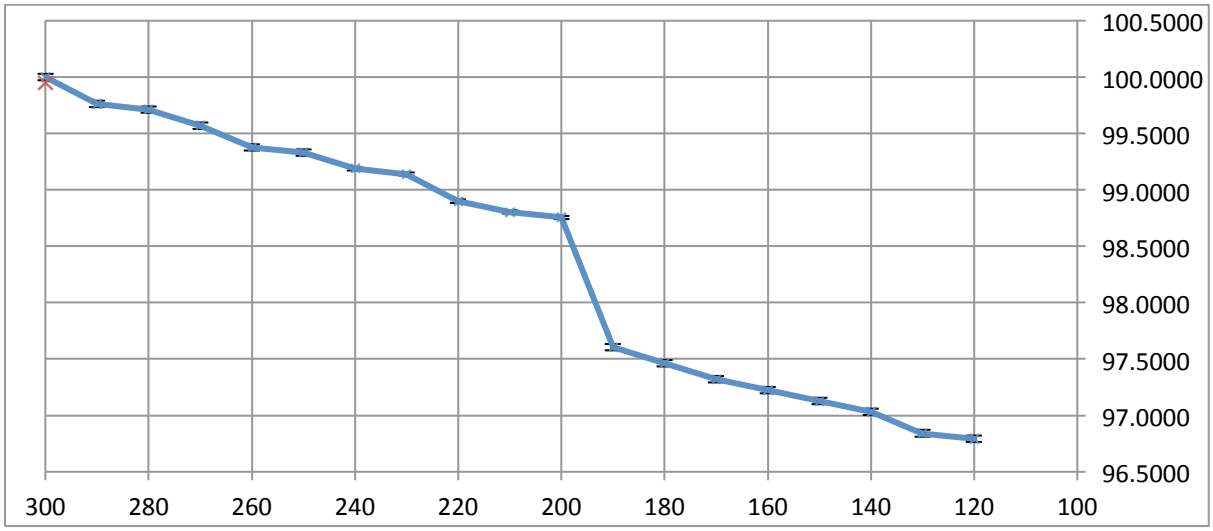


Figure 3 Percentage change in unit cell volume as a function of temperature showing the discontinuity between 200 K and 190 K (error bars drawn at 3σ(I)).

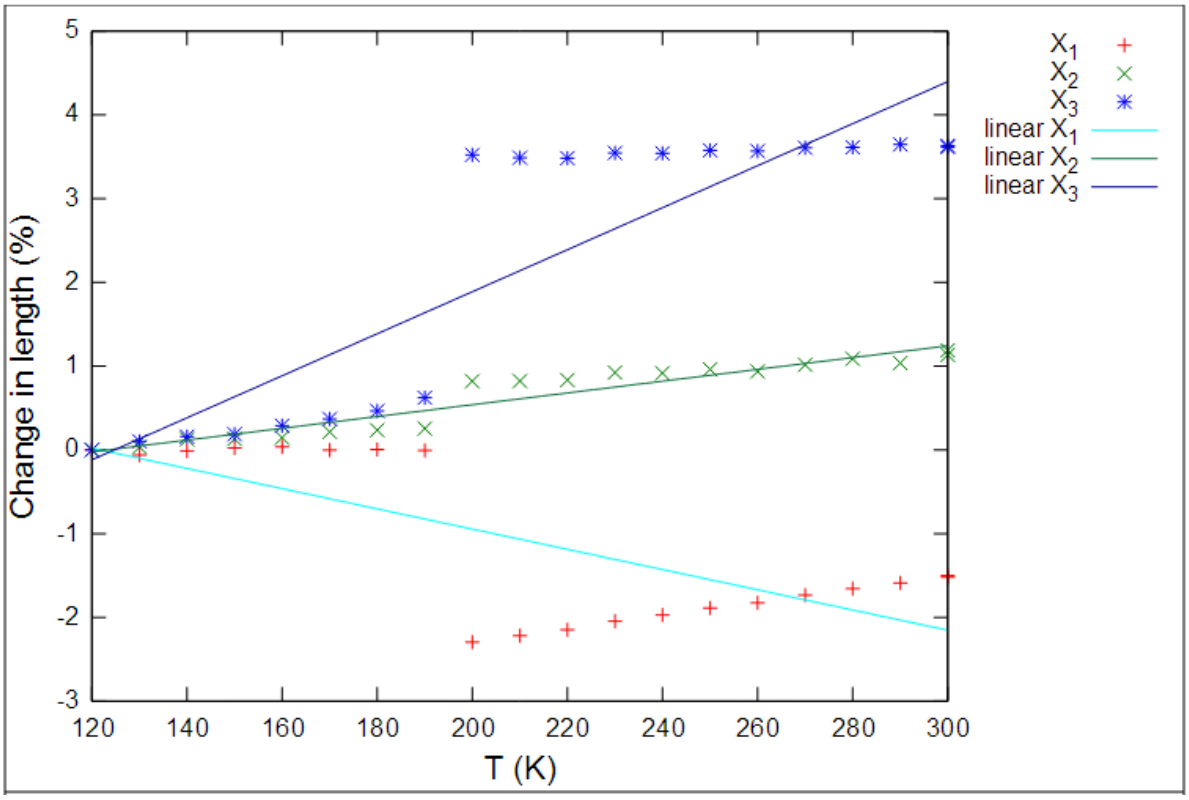


Figure 4 Percentage change in orthogonalized axes as a function of temperature showing the discontinuity between 200 K and 190 K.

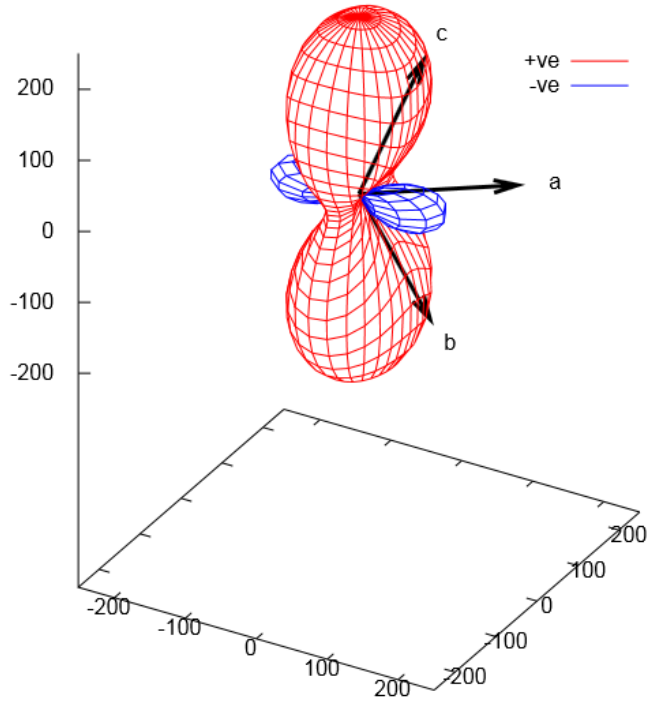


Figure 5 Expansivity indicatrix calculated using PASCal.[13]

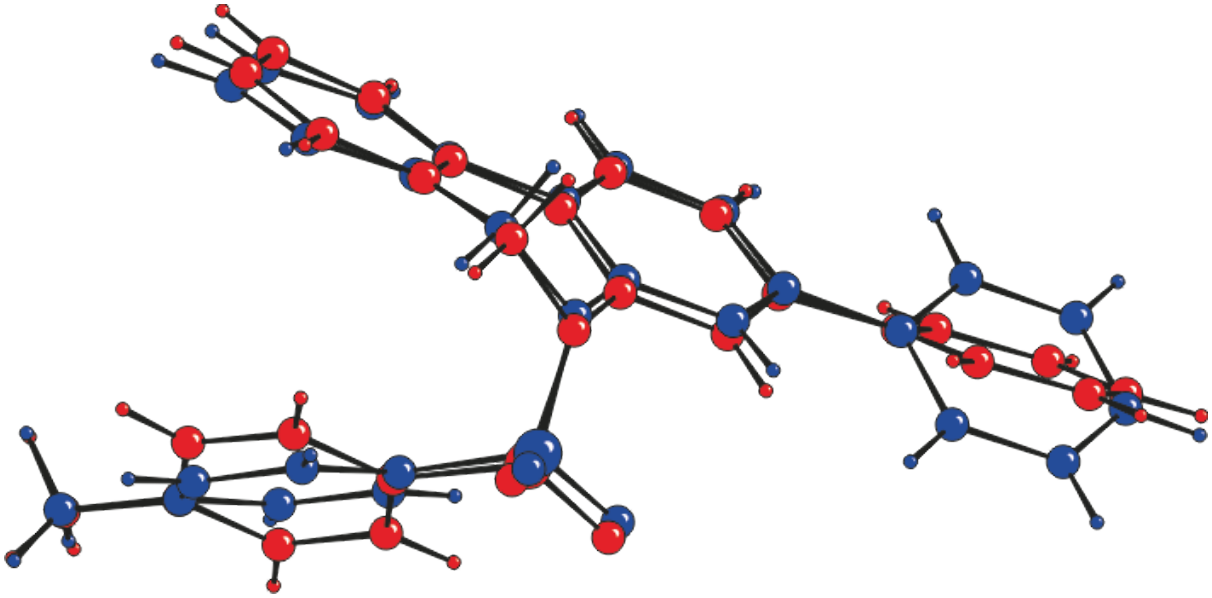


Figure 6 Overlay plots of two molecules in 120 K data.