Palladium Catalyzed Decarboxylative Rearrangement of *N*-Alloc Indoles: Supplementary Information

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General Methods

All reactions were carried out under an atmosphere of argon in oven-dried glassware with magnetic stirring bar. All reactions were monitored by thin layer chromatography (TLC) using Merck TLC silica gel 60 sheets, which were visualised with ultraviolet light and then developed with basic potassium permanganate solution. Flash chromatography was performed on Sigma-Aldrich silica gel 60 or Fluorochem silica gel as the stationary phase and the solvents employed were of analytical grade. ^{1}H NMR spectra were recorded on a Bruker AVX400 (400 MHz) or Bruker AVX300 (75 MHz) or a Bruker DPX300 (75 MHz) spectrometer at ambient temperature. Data are reported as follows: chemical shift in parts per million (ppm) from deuterated chloroform ($CDCl_3$) taken as 7.26 ppm, integration, multiplicity (s = singlet; d = doublet; t = triplet; dd = double doublets, dt = double triplets, dq = double quartets, qt = quarter triplets, ddd = double double doublets, ddt = double double triplets, dddd = double double double doublets, m = multiplet, br = broad), and coupling constant (Hz). ^{13}C NMR spectra were recorded on either a Bruker AVX400 (100 MHz) spectrometer or Bruker AVX300 (75 MHz) or a Bruker DPX300 (75 MHz) spectrometer. Chemical shifts are reported in ppm from $CDCl_3$ taken as 77.0 ppm. Infrared spectra were recorded on a Perkin Elmer RX I FT-IR spectrometer as liquid films or as dilute solutions between two KBr discs. Mass spectra were recorded on either a Micromass GCT Premier or a Waters Micromass LCT Premier spectrometer using electron ionisation (EI) at 70 eV or electrospray (ES) techniques, respectively. Chiral HPLC spectra were recorded on Agilent Technologies 1260 Infinity high-performance liquid chromatography (HPLC). HPLC were preformed on Daicel Chemical Industries, LTD CHIRALCEL® OJ-H, AD-H, AS-H, OB-H, OD-H, OC-H Chiral columns. Unless stated otherwise, all commercially available reagents were used as received. When necessary, commonly used organic solvents were dried prior to use according to standard laboratory practices.

General procedure for synthesis of 1-N-alloc indole (A)

To an oven dried round bottomed flask equipped with a reflux condenser and magnetic

stirrer bar and purged with argon was added a solution of indole (1 eq) and sodium hydride (60 %) (1.5 eq) in DMF and stirred under 0^{o}C for 30 mins. Allyl chloroformate (1.5 eq) was injected into the mixture under 0 ^{o}C and the reaction was stirred at room temperature for 16 hours. The mixture was quenched by water and stirred for 30 mins, extracted with ether 3 times and washed with water again. After drying over $MgSO_4$, the organic layer was concentrated in vacuo to obtain the crude product. The residue was subjected to a flash chromatography to afford the pure alloc indole.

General procedure for Synthesis of 3-Allyl indole (B)

To an oven dried round bottomed flask equipped with a reflux condenser and magnetic stirrer bar and purged with argon was added, $Pd(PPh_3)_4$ (1 mol%) and alloc indole (1 eq) in dry DCM (2 mL). Then Et_3B (1 eq) was injected into flask slowly via syringe and the reaction was stirred at 50 ^{o}C for 16 hours. The mixture was diluted with EtOAc and washed by $NaHCO_3$ and brine. The organic layer was dried over $MgSO_4$ and filtered. After evaporation of the solvent, the residue was purified by chromatography.

General procedure for Synthesis of 3-Allyl indole (B2)

To an oven dried round bottomed flask equipped with a reflux condenser and magnetic stirrer bar and purged with argon was added, $Pd(PPh_3)_4$ (1 mol%) and alloc indole (1 eq) in dry DCM (2 mL). Then Et_3B (1 eq) was injected into flask slowly via syringe and the reaction was stirred at 50^{o}C for 16 hours. The mixture was diluted with EtOAc and washed by $NaHCO_3$ and brine. The organic layers was dried over $NaSO_4$ and filtered. After evaporation of the solvent, the residue was dissolved in MeOH (1 mL) and added $NaBCNH_3$ (1.5 eq) and the reaction was stirred for an hour. The mixture was diluted in Et_2O (3 mL) and $NaHCO_3$ was added. The organic layer was separated, dried ($MgSO_4$), and filtered. After elimination of the solvent, the residue was purified by chromatograph.

General procedure for Synthesis of 3-Allyl indole (B3)

To an oven dried round bottomed flask equipped with a reflux condenser and magnetic

stirrer bar and purged with argon was added, $Pd(PPh_3)_4$ (5 mol%) and alloc indole (1 eq) in dry DCM (2 mL). Then Et_3B (1 eq) and BSA (1 eq) was injected into flask slowly via syringe and the reaction was stirred at 50°C for 40 hours. The mixture was diluted with EtOAc and washed by $NaHCO_3$ and brine. The organic layers was dried over $MgSO_4$ and filtered. After evaporation of the solvent, the residue was purified by chromatograph.

General procedure for Asymmetric *C*-3 indole allylation (B4)

To an oven dried round bottomed flask equipped with a reflux condenser and magnetic stirrer bar and purged with argon was added, $[Pd_2(dba)_3.CHCl_3]$ (2.5 mol%), (*S*,*S*)-ANDEN-Trost ligand (7.5 mol%) and alloc indole (1eq) in dry DCM (2 mL). Then Et_3B (1 eq) was injected into flask slowly via syringe and the reaction was stirred at 50°C for 16 hours. The mixture was diluted with EtOAc and washed by $NaHCO_3$ and brine. The organic layers was dried over Na_2SO_4 and filtered. After evaporation of the solvent, the residue was purified by chromatograph.

General procedure for Asymmetric *C*-3 indole allylation (B5)

To an oven dried round bottomed flask equipped with a reflux condenser and magnetic stirrer bar and purged with argon was added, $[Pd_2(dba)_3.CHCl_3]$ (2.5 mol%), (*S*,*S*)-ANDEN-Trost ligand (7.5 mol%) and indole (1 eq) in dry DCM (2 mL). The mixture was allowed to stir for 15 min, then, Et_3B (1 eq) and allyl alcohol (3 eq) were injected into flask slowly via syringe and the reaction was stirred at 50°C for 16 hours. The mixture was diluted with EtOAc and washed by $NaHCO_3$ and brine. The organic layers was dried over Na_2SO_4 and filtered. After evaporation of the solvent, the residue was purified by chromatograph.

General procedure for alloc indole rearrangement and suzuki reaction in one pot (C)

To an oven dried round bottomed flask equipped with a reflux condenser and magnetic stirrer bar and purged with argon was added alloc protected 5-bromoindole (100mg, 0.3

mmol) and $Pd(PPh_3)_4$ (17.3 mg, 0.015 mg) in anhydrous DCM (1 mL). Then Et_3B (1 eq) was injected into flask slowly via syringe and the reaction was stirred at 50°C for 16 hours. Following the successive addition of 1 mL 2M Na_2CO_3 solution, Boronic acid (1.5 eq) in 1 mL absolute EtOH and anhydrous toluene (1 mL) were added respectively. The mixture was reflexed at 100°C. After the reaction is completed by TLC analysis, the water layer was extracted by EtOAc. The organic layers were washed by $NaHCO_3$ and brine. The solvent was dired over anhydrous Na_2SO_4 and evaporated to dryness to give crude product, which was purified by flash column chromatography.[71]

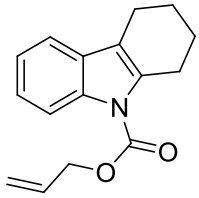
Preparation of Imidazole Carbamates (D)

1,1'-Carbonyldiimidazole (1.5 eq) was dissolved in DCM (20 mL) and the resulting solution was stirred with cooling to 0 °C. Alcohol (1 eq) was then added dropwise. The reaction mixture was stirred at 0 °C for 1 h, and then at room temperature for 16 h. The homogeneous mixture was then diluted with DCM (20 mL), washed with water (2 x 20 mL), dried over MgSO4, and concentrated in vacuo to afford crude product. If necessary the crude product was purified by flash chromatography.

Indole Acylation: Representative Procedure (E)

Indole (1.00 mmol) was dissolved in anhydrous acetonitrile (3 mL) and then 1*H*-imidazole-1-carboxylate (1.10 mmol) was added at room temperature, followed by DBU (0.2 mmol). The mixture was stirred for 16 hours. The reaction was quenched by addition of 1 M HCl (5 mL) and then the mixture was extracted with EtOAc (3 x 30 mL). The pooled organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo* to afford the crude product. Then the mixture was purified by flash chromatography using a mixture of EtOAc and hexanes as eluent.

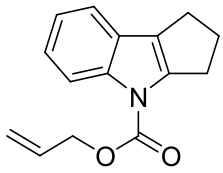
Allyl 3,4-dihydro-1H-carbazole-9(2H)-carboxylate (1a)



The title compound was prepared according to general procedure **A**, from 2,3,4,9-tetrahydro-1H-carbazole (2.00 g, 11.7 mmol), allyl chloroformate (2.12 g, 17.5m mol), NaH (60 %)(0.7 g, 17.5 mmol). The crude product was purified by silica column (Ethyl acetate-Hexane 1:6) to afford the **1a**(1.83 g, 62 %).

Rf (Ethyl acetate-Hexane 1:3) =0.68; IR: $_{max}$ (thin film) / cm^{-1} 2924, 2860, 1731, 1459, 1382, 1213, 1142, 745 ; ^{1}H-NMR (400MHz, $CDCl_3$): δ= 1.81-1.94 (m, 4H), 2.66 (tt, 2H, *J*= 2.0, 6.0 Hz), 3.03 (tt, 2H, *J*= 2.0, 6.3 Hz), 4.92 (dt, 2H, *J*=1.5, 5.5 Hz), 5.36 (dq, 1H, *J*= 1.3, 10.3 Hz), 5.48 (dq, 1H, *J*= 1.5, 17.3 Hz), 6.10 (ddt, 1H, *J*=17.3, 10.5, 5.8 Hz), 7.21- 7.29 (m, 2H), 7.39-7.42 (m, 1H), 8.13-8.16 (m, 1H). ^{13}C-NMR (100MHz, $CDCl_3$): δ= 21.1, 22.2, 23.5, 25.7, 67.1, 115.5, 117.3, 117.5, 119.2, 122.7, 123.6, 130.1, 131.8, 135.6, 136.7, 151.8.; HRMS(EST) called for $C_{16}H_{18}NO_2$ $(M+H)^+$ 256..1338 Found 256.1322.

Allyl 2,3-dihydrocyclopenta[b]indole-4(1H)-carboxylate (1b)

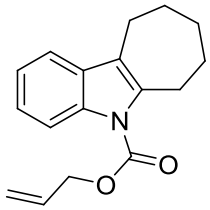


The title compound was prepared according to general procedure **A**, from 1,2,3,4-tetrahydrocyclopenta[b]indole (471 mg, 3 mmol), allyl chloroformate (542 mg, 4.5 mmol), NaH (60 %)(180 mg, 4.5 mmol). The crude product was purified by silica column (Ethyl acetate-Hexane 1:10) to afford the **1b** (570 mg, 79 %) as a white solid.

Rf (Ethyl acetate-Hexane 1:3) =0.88; IR: $_{max}$ (thin film) / cm^{-1} 2905, 2852, 1727, 1454, 1386, 1217, 1117, 914, 737; ^{1}H-NMR (400MHz, $CDCl_3$): δ= 2.53(dt, 2H, *J*= 7.0,

14.3Hz), 2.81 (t, 2H, *J*= 7.3 Hz), 3.14 (t, 2H, *J*= 7.5 Hz), 4.92 (d, 2H, *J*=5.8 Hz), 5.38 (dd, 1H, *J*= 1.3, 10.5 Hz), 5.49 (dd, 1H, *J*= 1.3, 17.1 Hz), 6.10 (ddt, 1H, *J*=17.1, 10.5, 5.8 Hz), 7.23- 7.30 (m, 2H), 7.39-7.42 (m, 1H), 8.21-8.22 (d, 1H). ^{13}C-NMR (100MHz, $CDCl_3$): δ= 24.1, 27.4, 28.9, 67.1, 115.8, 118.6, 119.0, 122.9, 123.1, 125.3, 127.0, 131.7, 151.0; HRMS(EST) called for $C_{15}H_{16}NO_2$ $(M+H)^+$ 242.1181 Found 242.1189.

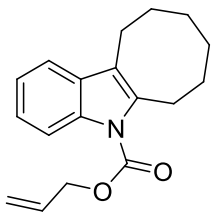
allyl 7,8,9,10-tetrahydrocyclohepta[b]indole-5(6H)-carboxylate (1c)



The title compound was prepared according to general procedure **A,** from 5,6,7,8,9,10-hexahydrocyclohepta[b]indole (2.00 g, 10.8 mmol), allyl chloroformate (1.96 g, 16.22 mmol), NaH (60 %)(0.65 g, 16.22 mmol). The crude product was purified by silica column (Ethyl acetate-Hexane 1:15) to afford the **1c** (1.87 g, 64 %) as a colourless oil.

Rf (Ethyl acetate-Hexane 1:6)=0.75 IR: $_{max}$ (thin film) / cm^{-1} 2924, 2853,1731, 1458 , 1377, 1316, 1221,742; ^{1}H-NMR (400MHz, $CDCl_3$): δ= 1.77-1.93 (m, 6H), 2.75-2.79 (m, 2H), 3.26-3.30 (m, 2H), 4.93(dt, 2h, *J*= 1.3,6.0 Hz), 5.37(dq, 1H, *J*=1.0, 10.3 Hz), 5.49(dq, 1H, *J*=1.5, 17.32 Hz), 6.10 (ddt, 1H, *J*= 17.1, 10.3, 6.0 Hz), 7.20-7.26 (m, 2H), 7.41-7.45 (m, 1H), 8.02-8.06 (m,1H) ; ^{13}C-NMR (100MHz, $CDCl_3$): δ= 23.0, 26.2, 26.8, 27.8, 30.2, 67.3,115.4, 117.5, 119.3, 122.5, 123.3, 130.4, 131.6, 135.3, 139.4, 152.0; HRMS(EST) called for $C_{17}H_{20}NO_2$ $(M+H)^+$ 270.1494 Found 270.1483.

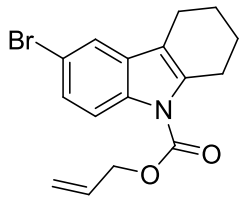
allyl 6,7,8,9,10,11-hexahydro-5H-cycloocta[b]indole-5-carboxylate (1d)



The title compound was prepared according to general procedure **A**, from 6,7,8,9,10,11-hexahydro-5H-cycloocta[b]indole (2.00 g, 10 mmol), allyl chloroformate (1.81 g, 15 mmol), NaH (60 %)(0. 60 g, 15 mmol). The crude product was purified by silica column (Ethyl acetate-Hexane 1:10) to afford the **1d** (2.15 g, 76 %) as a yellow solid.

Rf (Ethyl acetate-Hexane 1:6)=0.56 IR: $_{max}$ (thin film) / cm^{-1} 2924, 2853,1732, 1458 , 1379, 1317, 1216, 743; ^{1}H-NMR (400MHz, $CDCl_3$): δ= 1.32-1.38 (m, 2H), 1.50-1.57 (m, 2H), 1.67-1.73 (m, 2H), 1.76-1.83 (m, 2H), 2.79 (t, 2H, *J*= 6Hz), 3.21(t, 2H, *J*= 6.3Hz), 4.94(dt, 2h, *J*= 1.0, 5.8 Hz), 5.38(dd, 1H, *J*=1.0, 10.5 Hz), 5.49(dd, 1H, *J*=1.2, 17.1 Hz), 6.12(ddt, 1H, *J*=17.0,10.3, 6.0 Hz), 7.23-7.29 (m, 2H), 7.44-7.48 (m, 1H), 8.10-8.16 (m,1H) ; ^{13}C-NMR (100MHz, $CDCl_3$): δ= 23.1, 24.5, 25.7, 26.8, 29.2, 30.3 67.3, 115.7, 117.5, 119.4, 120.4, 122.6, 123.4, 129.8, 131.7, 135.9, 136.8, 151.8); HRMS(EST) called for $C_{18}H_{22}NO_2$ $(M+H)^+$ 284.1651 Found 284.1657.

allyl 6-bromo-3,4-dihydro-1H-carbazole-9(2H)-carboxylate (1e)

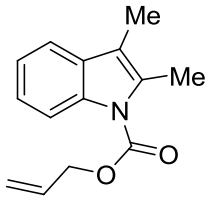


The title compound was prepared according to general procedure **A**, from 6-bromo-2,3,4,9-tetrahydro-1H-carbazole (1.70 g, 6.8mmol), allyl chloroformate (1.2 g, 10.2 mmol), NaH (60 %)(0.40 g, 10.2mmol). The crude product was purified by silica column (Ethyl acetate-Hexane 1:6) to afford the **1e** (1.80 g, 82 %) as a pale yellow solid.

Rf (Ethyl acetate-Hexane 1:3)=0.74; IR: $_{max}$ (thin film) / cm^{-1} 2937, 2853,1725, 1461 , 1388, 1212, 806, 579; ^{1}H-NMR (400MHz, $CDCl_3$): δ= 1.80-1.93 (m, 4H), 2.60 (tt, 2H, *J*= 2.0 , 6.0 Hz), 3.01(t, 2H, *J*= 2.0, 6.3Hz), 4.91(dt, 2h, *J*= 1.2, 6.0 Hz), 5.36(dq, 1H, *J*=1.2, 10.5 Hz), 5.47(dd, 1H, *J*=1.2, 17.0 Hz), 6.12(ddt, 1H, *J*=17.0 ,10.3, 6.0 Hz),

7.34 (dd, 1H, *J*= 2.0, 8.8 Hz), 7.51 (d, 1H, *J*= 2.0 Hz), 8.00 (d,1H, *J*= 9.0 Hz) ; ^{13}C-NMR (100MHz, $CDCl_3$): δ= 20.9, 22.0, 23.3, 25.6, 67.3, 116.0, 116.6, 116.8, 119.5, 120.8, 126.1, 131.5, 131.8, 134.4, 136.9, 151.4; HRMS(EST) called for $C_{16}H_{17}NO_2Br$ $(M+H)^+$ 334.0443 Found 334.0431.

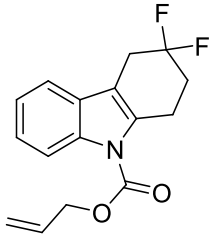
Allyl 2,3-dimethyl-1H-indole-1-carboxylate (1f)



The title compound was prepared according to general procedure **A**, from 2,3-dimethylindole (250 mg, 1.72mmol), allyl chloroformate (270.0 mg, 2.24mmol), NaH (60 %)(89.5 mg, 2.24 mmol). The crude product was purified by silica column (Ethyl acetate-Hexane 1:10) to afford the **1f** (221 mg, 56 %) as a white solid.

Rf (Ethyl acetate-Hexane 1:4) =0.66; IR: $_{max}$ (thin film) / cm^{-1} 2926, 1733, 1460, 1381, 1327, 1216, 1140, 755 ; ^{1}H-NMR (400MHz, $CDCl_3$): δ= 2.22 (s, 3H), 2.57 (s, 3H), 4.95 (dt, 2H, *J*=1.5, 6.0 Hz), 5.38 (d, 1H, *J*=10.3 Hz), 5.48 (dd, 1H, *J*=17.1 Hz), 6.13 (ddt, 1H, *J*=17.1, 10.2, 6.5 Hz), 7.23- 7.30 (m, 2H), 7.42-7.46 (m, 1H), 8.10-8.15 (m, 1H). ^{13}C-NMR (100MHz, $CDCl_3$): δ=8.7, 13.6, 67.2, 114.4, 115.4, 117.8, 119.2, 122.6, 123.5, 131.0, 131.7, 132.8, 135.5, 152.0. HRMS(EST) called for $C_{14}H_{16}NO_2$ $(M+H)^+$230.1181 Found 230.1175

allyl 3,3-difluoro-3,4-dihydro-1H-carbazole-9(2H)-carboxylate (1g)

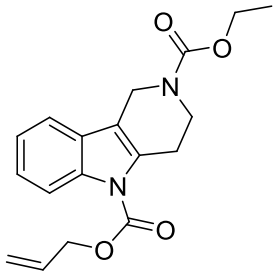


The title compound was prepared according to general procedure **A**, from 3,3-difluoro-2,3,4,9-tetrahydro-1H-carbazole (460 mg, 2.2 mmol), allyl chloroformate

(405 mg, 3.4 mmol), NaH (60 %)(134 mg, 3.4 mmol). The crude product was purified by silica column (Ethyl acetate-Hexane 1:6) to afford the **1g** (513 mg, 80 %) as a pale yellow solid.

Rf (Ethyl acetate-Hexane 1:3) = 0.67; IR: $_{max}$ (thin film) / cm^{-1} 2944, 2915, 1733, 1459, 1398, 1330, 1217, 1105, 755; ^{1}H-NMR (400MHz, $CDCl_3$): δ= 2.21-2.31(m, 2H), 3.10 (t, 2H, *J*= 13.6 Hz), 3.22(tt, 2H, *J*= 1.8, 6.8Hz), 4.88 (dt, 2H, *J*= 1.3, 6.0 Hz), 5.34(dq, 1H, *J*=1.0, 10.5 Hz), 5.45(dq, 1H, *J*=1.5, 17.3 Hz), 6.06(ddt, 1H, *J*= 17.3 ,10.5, 5.8 Hz), 7.19-7.31(m, 3H), 8.10(dt, 1H, *J*= 0.8, 8.3Hz); ^{19}F-NMR (376MHz, $CDCl_3$): δ= -97.3 ^{13}C-NMR (100MHz, $CDCl_3$): δ= 22.8 (t, J_{C-F} =5.5Hz), 31.0 (t, J_{C-F} =24.9 Hz), 31.1 (t, J_{C-F} =27.9 Hz), 67.4, 112.9 (t, J_{C-F} =6.2Hz), 115.6, 117.4, 119.6, 120.5, 122.9, 123.0, 124.3, 125.3, 128.6 (t, J_{C-F} =1.5Hz), 131.4, 132.9, 136.2, 151.4. HRMS(EST) called for $C_{16}H_{16}NO_2F_2$ $(M+H)^+$ 292.1149 Found 292.1147

5-allyl 2-ethyl 3,4-dihydro-1H-pyrido[4,3-b]indole-2,5-dicarboxylate (1h)

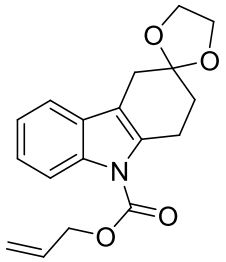


The title compound was prepared according to general procedure **A**, from 3,4-dihydro-1H-pyrido[4,3-b]indole-2(5H)-carboxylate (700 mg, 2.9 mmol), allyl chloroformate (550 mg, 4.5mmol), NaH (60 %)(180 mg, 4.5 mmol). The crude product was purified by silica column (Ethyl acetate-Hexane 1:10) to afford the **1h** (370 mg, 40 %) as a yellow solid.

Rf (Ethyl acetate-Hexane 1:6)=0.22; IR: $_{max}$ (thin film) / cm^{-1} 2923, 2852,1735, 1700, 1459 , 1382, 1217, 1107, 753; ^{1}H-NMR (400MHz, $CDCl_3$): δ= 1.32 (t, 3H, *J*= 7Hz), 3.18 (br, 2H), 3.81 (br, 2H), 4.22 (q, 2H, *J*=7Hz), 4.62 (br, 2H), 4.92(dt, 2h, *J*= 1.2, 5.8 Hz), 5.38(dq, 1H, *J*=1.3, 10.6 Hz), 5.47(dq, 1H, *J*=1.2, 17.0 Hz), 6.08 (ddt, 1H,

J=17.0,10.5, 6.0 Hz), 7.23-7.32 (m, 2H), 7.33-7.40 (m, 1H), 8.16 (d,1H, *J*=7.3 Hz) ; ^{13}C-NMR (100MHz, $CDCl_3$): δ= 14.7, 25.9 (br, rotameric), 40.7, 41.3 (br, rotameric), 61.5, 67.4, 115.6, 117.6, 119.5, 123.0, 124.2, 127.4, 131.4, 135.8, 151.4, 155.7; HRMS(EST) called for $C_{18}H_{21}N_2O_4$ $(M+H)^+$ 329.1501 Found329.1500.

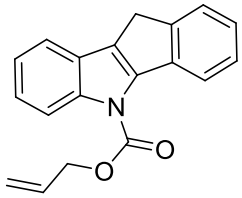
Allyl 1,2-dihydrospiro[carbazole-3,2'-[1,3]dioxolane]-9(4H)-carboxylate (1i)



The title compound was prepared according to general procedure **A**, from 1,2,4,9-tetrahydrospiro[carbazole-3,2'-[1,3]dioxolane] (500 mg, 2.2mmol), allyl chloroformate (393 mg, 3.3 mmol), NaH (60 %)(130 mg, 3.3 mmol). The crude product was purified by silica column (Ethyl acetate-Hexane 10:1) to afford the **1i** (442 mg, 64 %) as an orange solid.

Rf (Ethyl acetate-Hexane 1:2) =0.63; IR: $_{max}$ (thin film) / cm^{-1} 2954, 2924, 1732, 1459 , 1382, 1331, 1213, 1110, 1062, 945, 866, 754, 591; ^{1}H-NMR (300MHz, $CDCl_3$): δ= 2.07 (t, 2H, *J*=6.6 Hz), 2.92 (s, 1H), 3.25 (t, 2H, *J*= 6.6 Hz), 4.02-4.12 (m, 4H), 4.92 (dt, 2H, *J*=1.3, 5.8 Hz), 5.36 (dq, 1H, *J*= 1.1, 10.4 Hz), 5.46 (dq, 1H, *J*=1.5, 17.1 Hz), 6.08 (ddt, 1H, *J*=17.1, 10.4, 5.8 Hz), 7.20-7.30 (m, 1H), 7.35-7.38 (m, 1H), 8.12 (dd, 1H, *J*=1.3, 7.0Hz) ; ^{13}C-NMR (75MHz, $CDCl_3$): δ= 24.0, 31.9, 32.0, 64.7, 67.3, 108.2, 115.3, 115.6, 117.5, 119.4, 122.8, 123.9, 129.5, 131.6, 134.0, 136.4, 151.6; HRMS(EST) called for $C_{18}H_{20}NO_4$ $(M+H)^+$ 314.1392 Found 314.1392.

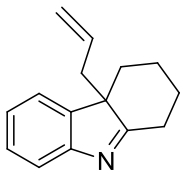
allyl indeno[1,2-b]indole-5(10H)-carboxylate (1j)



The title compound was prepared according to general procedure **A**, from5,10-dihydroindeno[1,2-b]indole (512 mg, 2.5 mmol), allyl chloroformate (452 mg, 3.75 mmol), NaH (60 %)(150 mg, 3.75 mmol). The crude product was purified by silica column (Ethyl acetate-Hexane 1:16) to afford the **1j** (550 mg, 76 %) as a pale yellow solid.

Rf (Ethyl acetate-Hexane 1:3) = 0.79; IR: $_{max}$ (thin film) / cm^{-1} 3052, 2894, 1737, 1606, 1453, 1376, 1226, 1144, 994, 742; ^{1}H-NMR (400MHz, $CDCl_3$): δ= 3.66 (s, 2H), 5.05 (dt, 2H, *J*= 1.3, 6.0Hz), 5.41 (dd, 1H, *J*= 1.0, 10.3 Hz), 5.53 (dd, 1H, *J*= 1.3, 17.3Hz), 6.18 (ddt, 1H, *J*=17.1, 10.3, 6.0 Hz), 7.22-7.36 (m, 4H), 7.51 (d, 1H, *J*= 7.3 Hz), 7.53-7.58 (m, 1H), 8.20-8.25 (m, 2H); ^{13}C-NMR (100MHz, $CDCl_3$): δ= 29.9, 67.8, 116.6, 118.9, 120.0, 122.2, 123.4, 124.2, 125.0, 125.2, 126.4, 126.8, 128.3, 131.5, 135.4, 140.1, 143.1, 147.2, 151.3 HRMS(EST) called for $C_{19}H_{16}NO_2$ $(M+H)^+$ 290.1181 Found 290.1178

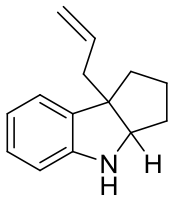
4a-allyl-2,3,4,4a-tetrahydro-1H-carbazole (2a)



The title compound was prepared according to general procedure **B**, from Allyl 3,4-dihydro-1H-carbazole-9(2H)-carboxylate (**1a)** (102 mg, 0.4 mmol), $Pd(PPh_3)_4$ (4.62 mg, 0.004 mmol), BEt_3 (1.0M in hexane)(0.4 mL, 0.4 mmol). The crude product was purified by silica column (Ethyl acetate-Hexane 1:10) to afford the **2a** (76 mg, 90 %) as a pink crystal solid.

Rf (Ethyl acetate-Hexane 1:5) = 0.15; IR: $_{max}$ (thin film) / cm^{-1} 2931, 2860, 1582, 1454, 752; ^{1}H-NMR (400MHz, $CDCl_3$): δ= 1.15 (dt, 1H, *J*=4.2, 13.5Hz), 1.42 (qt, 1H, *J*= 4.5, 13.3Hz,), 1.64-1.71 (m, 1H), 1.86 (qt, 1H, *J*=3.8, 13.3Hz), 2.15-2.23 (m, 1H), 2.35 (dq, 1H, *J*=2.5, 13.6Hz), 2.50-2.65(m, 3H), 2.92 (ddt , 1H, *J*=1.8, 4.3, 13.1Hz), 4.85 (ddt, 1H, *J*= 1.0, 2.0, 10.0 Hz), 4.94 (ddt, 1H, *J*=1.2, 2.0, 16.8Hz), 5.26 (ddt, 1H, *J*=17.0, 9.0, 7.5 Hz), 7.17 (dd, 1H, *J*= 1.0, 7.5Hz), 7.27-7.33(m, 2H), 7.52-7.67(dt, 1H, *J*=1.0, 7.5 Hz) .^{13}C-NMR (100MHz, $CDCl_3$): δ= 21.0, 28.7, 30.1, 36.9, 37.5, 57.6, 117.8, 120.0, 121.8, 124.5, 127.5, 132.1, 144.5, 154.8, 188.7; HRMS(EST) called for $C_{15}H_{18}N$ $(M+H)^+$ 212.1439 Found 212.1437

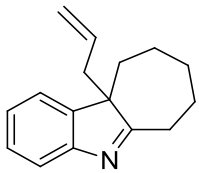
8b-allyl-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indole (2b)



The title compound was prepared according to general procedure **B2**, from Allyl 2,3-dihydrocyclopenta[b]indole-4(1H)-carboxylate(**1b**) (96 mg, 0.4 mmol), $Pd(PPh_3)_4$ (4.62 mg, 0.004 mmol), BEt_3 (1.0M in hexane) (0.4 mL, 0.4 mmol), $NaCNBH_3$ (37.7 mg, 0.6 mmol). The crude product was purified by silica column (Hexane: DCM 1:1) to afford the **2b** (63 mg, 79 %) as a brown oil.

Rf (Hexane: DCM 1:1) = 0.28; IR: $_{max}$ (thin film) / cm^{-1}3395, 2948, 2886, 1605, 1484, 1265, 912, 740; ^{1}H-NMR (400MHz, $CDCl_3$): δ= 1.48-1.60 (m, 1H), 1.62-1.69 (m, 2H), 1.76-1.87 (m, 2H), 1.90-1.95 (m, 1H), 2.41 (dd, 1H, *J*= 8.0, 14.1 Hz), 2.57 (dd, 1H, *J*= 6.5, 13.8 Hz), 3.76 (br, 1H), 3.97 (d, 1H, *J*= 6.5Hz), 5.04 (d, 1H, *J*= 9.0, 16.1Hz), 5.68-5.78 (m, 1H), 6.55 (d, 1H, *J*= 7.5Hz), 6.71 (t, 1H, *J*= 7.3Hz), 7.00-7.04 (m, 2H); ^{13}C-NMR (100MHz, $CDCl_3$): δ= 24.8, 37.1, 40.7, 44.9, 57.6, 67.3, 108.5, 117.3, 118.3, 123.5, 127.5, 135.4, 135.7, 151.2. HRMS(EST) called for $C_{14}H_{18}N$ $(M+H)^+$ 200.1439 Found 200.1435.

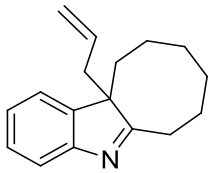
10a-allyl-6,7,8,9,10,10a-hexahydrocyclohepta[b]indole (2c)



The title compound was prepared according to general procedure **B**, from allyl 7,8,9,10-tetrahydrocyclohepta[b]indole-5(6H)-carboxylate **(1c)** (108.5 mg, 0.4 mmol), $Pd(PPh_3)_4$ (4.64 mg, 0.004 mmol), BEt_3 (1.0M in hexane)(0.4 mL, 0.4 mmol). The crude product was purified by silica column (Ethyl acetate-Hexane 1:9) to afford the **2c** (69 mg, 77 %) as yellow oil.

Rf (Ethyl acetate-Hexane 1:3) = 0.29; IR: $_{max}$ (thin film) / cm^{-1} 3075, 2926, 2851, 1691, 1571, 1466, 1346, 1076, 915, 773; ^{1}H-NMR (400MHz, $CDCl_3$): δ= 0.73 (q, 1H, *J*= 10.5Hz), 1.41-1.52 (m, 1H), 1.54-1.65 (m, 2H), 1.71-1.82 (m, 2H), 2.00-2.10 (m, 2H), 2.45 (dd, 1H, *J*=7.8, 13.6Hz), 2.57-2.64 (m, 2Hz), 2.92 (ddd, 1H, *J*=4.0, 6.0, 13.3Hz), 4.85 (d, 1H, *J*=10.0Hz), 4.91 (d, 1H, *J*= 16.6Hz), 5.21 (ddt, 1H, *J*=17.1, 9.8, 7.5 Hz), 7.17(t, 1H, *J*=7.28Hz), 7.23 (d, 1H, *J*= 7.3Hz), 7.29 (t, 1H, *J*= 8.3Hz), 7.50 (d, 1H, *J*= 7.5Hz).^{13}C-NMR (100MHz, $CDCl_3$): δ= 24.5, 28.5, 30.4, 31.4, 35.0, 41.5, 62.1, 117.9, 119.6, 121.8, 124.8, 127.6, 132.3, 143.6, 154.9, 190.5. HRMS(EST) called for $C_{16}H_{20}N$ $(M+H)^+$ 226.1596 Found 226.1603.

11a-allyl-7,8,9,10,11,11a-hexahydro-6H-cycloocta[b]indole (2d)

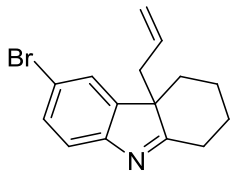


The title compound was prepared according to general procedure **B**, from allyl 6,7,8,9,10,11-hexahydro-5H-cycloocta[b]indole-5-carboxylate **(1d)** (113.2 mg, 0.4 mmol), $Pd(PPh_3)_4$ (4.64 mg, 0.004 mmol), BEt_3 (1.0M in hexane)(0.4 mL, 0.4 mmol).

The crude product was purified by silica column (Ethyl acetate-Hexane 1:9) to afford the **2d** (75 mg, 78 %) as yellow oil.

Rf (Ethyl acetate-Hexane 1:6) = 0.22; IR: $_{max}$ (thin film) / cm^{-1} 2917, 2849, 1640, 1567, 1457, 1270, 1217, 994, 915, 759; ^{1}H-NMR (400MHz, $CDCl_3$): δ= 0.83-0.94 (m, 2H), 0.96-1.05 (m, 1H), 1.26-1.39 (m, 2H), 1.41-1.50 (m, 1H), 1.59-1.69 (m, 1H), 1.86-1.96 (m,1H), 2.03-2.10 (m, 1H), 2.14 (ddd, 1H, *J*=3.3, 5.0, 14.3Hz), 2.25(ddd, 1H, *J*= 3.0, 11.5, 14.8Hz), 2.34 (ddt, 1H, *J*=1.0, 7.5, 13.6Hz), 2.54 (ddt, 1H, *J*=1.2, 6.6, 13.6Hz), 2.61 (dq, 1H, *J*=4.6, 13.3Hz), 2.81 (ddd, 1H, *J*=5.0, 6.5, 13.3Hz), 4.79-4.88 (m,1H), 5.11 (ddt, 1H, *J*=17.2, 10.0, 7.3 Hz), 7.16-7.22 (m, 1H), 7.31 (ddd, 1H, *J*= 2.3, 6.8, 8.8 Hz), 7.54 (dt, 1H, *J*=1.0, 7.5Hz).^{13}C-NMR (100MHz, $CDCl_3$): δ= 23.7, 25.2, 25.6, 29.9, 30.4, 31.7, 42.4, 61.8, 117.9, 119.9, 121.9, 124.7, 127.6, 132.2, 141.5, 155.0, 192.3. HRMS(EST) called for $C_{17}H_{22}N$ $(M+H)^+$ 240.1752 Found 240.1741.

4a-allyl-6-bromo-2,3,4,4a-tetrahydro-1H-carbazole (2e)

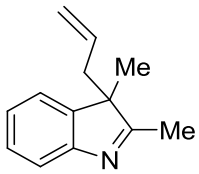


The title compound was prepared according to general procedure **B**, allyl 6-bromo-3,4-dihydro-1H-carbazole-9(2H)-carboxylate **(1e)** (100 mg, 0.3 mmol), $Pd(PPh_3)_4$ (3.47 mg, 0.003 mmol), BEt_3 (1.0M in hexane)(0.3 mL, 0.3 mmol). The crude product was purified by silica column (Ethyl acetate-Hexane 1:6) to afford the **2e**(74 mg, 85 %) as yellow oil.

Rf (Ethyl acetate-Hexane 1:3) = 0.23; IR: $_{max}$ (thin film) / cm^{-1} 3076, 2936, 1580, 1444, 1416, 1187, 1051, 994, 919, 821, 715, 668; ^{1}H-NMR (400MHz, $CDCl_3$): δ= 1.16 (dt, 1H, *J*=4.3, 13.6Hz), 1.42 (qt, 1H, *J*= 4.3, 13.3Hz,), 1.65-1.73 (m, 1H), 1.81 (qt, 1H, *J*=3.8, 14.0Hz), 2.16-2.24 (m, 1H), 2.42 (dq, 1H, *J*=2.5, 13.5Hz), 2.50-2.63(m, 3H), 2.87 (dt, 1H, *J*=2.0, 13.3Hz), 4.91 (ddt, 1H, *J*= 0.8, 2.0, 9.8 Hz), 5.00 (ddt, 1H, *J*=1.2,

1.8, 16.8Hz), 5.26 (ddt, 1H, *J*=17.6, 10.0, 7.0 Hz), 7.41-7.44 (m, 3H).^{13}C-NMR (100MHz, $CDCl_3$): δ= 21.0, 28.7, 30.1, 36.8, 37.5, 58.2, 118.4, 118.5, 121.4, 125.3, 130.7, 131.5, 146.8, 154.9, 189.3. HRMS(EST) called for $C_{15}H_{17}NBr$ $(M+H)^+$290.0544 Found 290.0534.

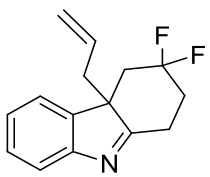
3-allyl-2,3-dimethyl-3H-indole (2f)



The title compound was prepared according to general procedure **B**, from Allyl 2,3-dimethyl-1H-indole-1-carboxylate **(1f)** (92 mg, 0.4 mmol), $Pd(PPh_3)_4$ (4.62 mg, 0.004 mmol), BEt_3 (1.0M in hexane)(0.4 ml, 0.4 mmol). The crude product was purified by silica column (Ethyl acetate-Hexane 1:10) to afford the **2f** (58 mg, 79 %) as a brown oil.

Rf (Ethyl acetate-Hexane 1:5) = 0.17; IR: $_{max}$ (thin film) / cm^{-1} 3076, 2975, 2912, 1640, 1578, 1451, 1270, 1198, 917, 715; ^{1}H-NMR (400MHz, $CDCl_3$): δ=1.31 (s, 3H), 2.26 (s, 3H), 2.41 (dd, 1H, *J*= 8.0, 13.8 Hz), 2.63 (dd, 1H, *J*= 6.3, 13.8 Hz), 4.86 (d, 1H, *J*= 10.0 Hz), 4.95 (d, 1H, *J*= 16.0 Hz), 5.16 (ddt, 1H, *J*=17.1, 10.0, 7.8 Hz), 7.19 (t, 1H, *J*= 7. 3 Hz), 7.26- 7.32 (m, 2H), 7.52 (d, 1H, *J*= 7.5 Hz). ^{13}C-NMR (100MHz, $CDCl_3$): δ=16.0, 21.8, 41.2, 57.5, 118.0, 119.8, 121.8, 125.0, 127.7, 132.5, 143.4, 154.3, 186.5; HRMS (EI) called for $C_{13}H_{16}N$ $(M+H)^+$ 186.1261 Found 186.1257.

4a-allyl-3,3-difluoro-2,3,4,4a-tetrahydro-1H-carbazole (2g)

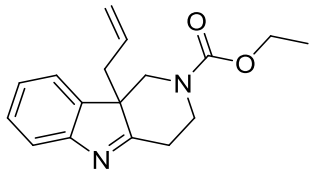


The title compound was prepared according to general procedure **B**, allyl 3,3-difluoro-3,4-dihydro-1H-carbazole-9(2H)-carboxylate **(1g)** (87.3 mg, 0.3 mmol),

$Pd(PPh_3)_4$ (3.47 mg, 0.003 mmol), BEt_3 (1.0M in hexane)(0.3 mL, 0.3 mmol). The crude product was purified by silica column (Ethyl acetate-Hexane 1:6) to afford the **2g** (64 mg, 87 %) as pale yellow solid.

Rf (Ethyl acetate-Hexane 1:3) = 0.27; IR: $_{max}$ (thin film) / cm^{-1} 3076, 3016, 2972, 2884, 1640, 1590, 1455, 1362, 1113, 960; ^{1}H-NMR (400MHz, $CDCl_3$): δ= 1.68 (dq, 1H, *J*=6.0, 34.9 Hz), 1.92-2.10 (m, 1H), 2.50-2.63 (m, 2H), 2.70-2.84 (m, 2H), 2.90-2.99 (m, 2H), 4.95 (ddt, 1H, *J*= 0.7, 2.0, 10.0 Hz), 5.01 (dq, 1H, *J*= 1.2, 16.8 Hz), 5.23 (m, 1H), 7.22 (dt, 1H, *J*= 1.0, 7.5 Hz), 7.27- 7.30 (m, 1H), 7.36 (dt, 1H, *J*= 1.5, 7.8Hz), 7.6 (dt, 1H, *J*= 0.8, 7.8 Hz).; ^{19}F-NMR (376MHz, $CDCl_3$): δ= -91.0 (d, *J*=249 Hz), -93.5 (d, *J*= 249 Hz); ^{13}C-NMR (100MHz, $CDCl_3$): δ= 25.0 (d, $J_{C\text{-}F}$ =10.3Hz), 34.5 (dd, $J_{C\text{-}F}$ = 25.0, 26.4 Hz), 38.6 (d, $J_{C\text{-}F}$= 5.9 Hz), 41.2 (dd, $J_{C\text{-}F}$= 23.5, 25.0 Hz), 56.0 (dd, $J_{C\text{-}F}$= 1.8, 11.0 Hz), 119.3, 120.7, 122.0, 122.7 (dd, $J_{C\text{-}F}$= 242.8, 243.6 Hz), 125.5, 128.3, 131.4, 143.2 (t, $J_{C\text{-}F}$= 1.1 Hz), 154.5, 184.8 (d, $J_{C\text{-}F}$= 2.2 Hz). ; HRMS(EST) called for $C_{15}H_{16}NF_2$ $(M+H)^+$248.1251 Found 248.1241.

Ethyl 9b-allyl-3,4-dihydro-1H-pyrido[4,3-b]indole-2(9bH)-carboxylate (2h)

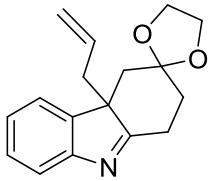


The title compound was prepared according to general procedure **B**, from 5-allyl 2-ethyl 3,4-dihydro-1H-pyrido[4,3-b]indole-2,5-dicarboxylate **(1h)** (98.4 mg, 0.3 mmol), $Pd(PPh_3)_4$ (3.47 mg, 0.003 mmol), BEt_3 (1.0M in hexane)(0.3 mL, 0.3 mmol). The crude product was purified by silica column (Ethyl acetate-Hexane 1:3) to afford the **2h** (60 mg, 71 %) as orange oil.

Rf (Ethyl acetate-Hexane 1:1) = 0.29; IR: $_{max}$ (thin film) / cm^{-1} 3269, 3077, 2980, 2925, 2854, 1699, 1472, 1432, 1234, 1009, 919, 754; ^{1}H-NMR (400MHz, DMSO-d_6): δ=

1.26 (t, 3H, *J*=7.3Hz), 2.19-2.36 (m, 1H), 2.42 (q, 1H, *J*=6.2Hz), 2.71-2.82 (m, 4H), 4.08-4.21 (m, 2H), 4.40-4.72(m, 2H), 4.78 (d, 1H, *J*=10.0Hz), 4.91 (d, 1H, *J*= 16.0 Hz), 5.00-5.14 (m, 1H), 7.22 (dt, 1H, $J_=$ 1.0, 7.5Hz), 7.32-7.37 (m, 1H), 7.50-7.55(m, 2H) .^{13}C-NMR (100MHz, DMSO-d_6): δ= 14.6, 29.9, 36.2, 45.0, 52.2, 58.8, 61.4, 118.3, 119.8, 123.1, 124.9, 128.2, 132.0, 140.6, 155.1, 184.7. HRMS(EST) called for $C_{17}H_{21}N_2O_2$ $(M+H)^+$ 285.1603 Found 285.1590.

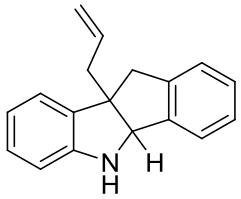
4a-allyl-1,2,4,4a-tetrahydrospiro[carbazole-3,4'-[1,2]dioxolane] (2i)



The title compound was prepared according to general procedure **B**, from Allyl 1,2-dihydrospiro[carbazole-3,2'-[1,3]dioxolane]-9(4H)-carboxylate (**1i)** (94 mg, 0.3 mmol), $Pd(PPh_3)_4$ (3.47 mg, 0.003 mmol), BEt_3 (1.0M in hexane)(0.3 mL, 0.3 mmol). The crude product was purified by silica column (Ethyl acetate-Hexane 1:5) to afford the **2i** (60.7 mg, 75 %) as yellow oil.

Rf (Ethyl acetate-Hexane 1:2) = 0.33; IR: $_{max}$ (thin film) / cm^{-1} 2920; 2854, 1585, 1455, 1112, 757; ^{1}H-NMR (400MHz, $CDCl_3$): δ= 1.52 (d, 1H, *J*= 13.8 Hz), 1.80 (dt, 1H, *J*=5.0, 13.6 Hz), 2.13-2.21 (m, 1H), 2.41 (dd, 1H, *J*=3.0, 13.8 Hz), 2.76 (dd, 1H, *J*= 6.5, 13.6 Hz), 2.82-2.87 (m, 2H), 2.95 (dt, 1H, *J*=5.0, 13.8 Hz), 3.91-4.01 (m, 2H), 4.06-4.17 (m, 2H), 4.89 (d, 1H, *J*= 10.0 Hz), 4.97 (d, 1H, *J*= 16.8 Hz), 5.23 (ddt, 1H, *J*=16.8, 10.0, 6.8 Hz), 7.18(t, 1H, *J*= 7.3 Hz), 7.25 (d, 1H, *J*= 7.3 Hz), 7.33(t, 1H, *J*= 7.8Hz), 7.58 (d, 1H, *J*=7.8 Hz). ^{13}C-NMR (100MHz, $CDCl_3$): δ= 26.5, 36.6, 38.6, 42.4, 57.3, 64.1, 65.0, 108.3, 118.3, 120.3, 121.9, 125.0, 127.8, 132.6, 144.4, 154.8, 187.6. ; HRMS(EST) called for $C_{17}H_{20}NO_2$ $(M+H)^+$ 270.1494 Found 270.1496.

9b-allyl-4b,5,9b,10-tetrahydroindeno[1,2-b]indole (2j)

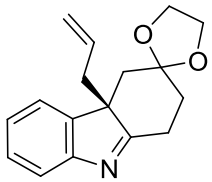


The title compound was prepared according to general procedure **B2**, from allyl indeno[1,2-b]indole-5(10H)-carboxylate **(1j)** (115.6 mg, 0.4 mmol), $Pd(PPh_3)_4$ (4.62 mg, 0.004 mmol), BEt_3 (1.0M in hexane)(0.4 mL, 0.4 mmol), $NaCNBH_3$ (37.7 mg, 0.6 mmol). The crude product was purified by silica column (Hexane: DCM 1:1) to afford the **2j** (53 mg, 55 %) as brown oil.

Rf (Hexane: DCM 1:1) = 0.47; IR: $_{max}$ (thin film) / cm^{-1} 3381, 3052, 2894, 1606, 1483, 1463, 1265, 993, 915, 734; ^{1}H-NMR (400MHz, $CDCl_3$): δ= 2.60 (ddd, 2H, *J*= 7.5, 13.6, 30.9 Hz), 3.31 (s, 2H), 4.24 (br, 1H), 4.92 (s, 1H), 5.06 (d, 1H, *J*= 10.0Hz), 5.10 (d, 1H, *J*= 16.8Hz), 5.78 (ddt, 1H, *J*=17.1, 9.8, 7.5 Hz), 6.60 (d, 1H, *J*= 7.8Hz), 6.74 (t, 1H, *J*= 7.3Hz), 7.00 (t, 1H, *J*= 7.8 Hz), 7.12-7.23 (m, 4H), 7.29 (d, 1H, *J*=6.5Hz); ^{13}C-NMR (100MHz, $CDCl_3$): δ= 44.2, 44.7, 57.0, 71.7, 110.4, 117.8, 119.2, 123.7, 128.9, 124.9, 127.1, 127.9, 128.0, 134.7, 135.6, 142.0, 144.1, 149.7. HRMS(EST) called for $C_{18}H_{18}N$ $(M+H)^+$248.1439 Found 248.1442.

Asymmetric *C*-3 indole allylation via Alloc indole rearrangement

(S)-4a-allyl-1,2,4,4a-tetrahydrospiro[carbazole-3,2'-[1,3]dioxolane] (2i)

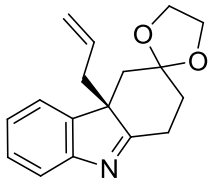


The title compound was prepared according to general procedure **B4**, from Allyl 1,2-dihydrospiro[carbazole-3,2'-[1,3]dioxolane]-9(4H)-carboxylate **(1i)** (62.6 mg, 0.2 mmol), (*S,S)*-ANDEN-Trost ligand (12.2 mg, 0.015 mmol), BEt_3 (1.0M in hexane)(0.2 mL, 0.2 mmol) and $[Pd_2(dba_3).CHCl_3]$ (5.2 mg, 0.005 mmol). The crude product was purified by silica column (Ethyl acetate-Hexane 1:4) to afford the **1i** (33.3 mg, 62 %) as

pale yellow solid. Enantiomeric excess was determined to be 63 % by chiral HPLC (Chiracel-OJ-H Column, 93:7, hexane: *i*PrOH, 1.0 mL/min, 7.54 min minor, 8.95 min major).

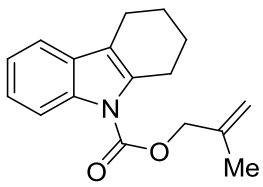
Asymmetric *C*-3 indole allylation via allylic alcohol addition

(S)-4a-allyl-1,2,4,4a-tetrahydrospiro[carbazole-3,2'-[1,3]dioxolane] (2i)



The title compound was prepared according to general procedure **B5**, from 1,2,4,9-tetrahydrospiro[carbazole-3,2'-[1,3]dioxolane] (62.6 mg, 0.2 mmol), (*S,S)*-ANDEN-Trost ligand (12.2 mg, 0.015 mmol), BEt_3 (1.0M in hexane)(0.2 mL, 0.2 mmol) , allyl alcohol (34.85 mg, 0.6 mmol) and [$Pd_2(dba_3).CHCl_3$] (5.2 mg, 0.005 mmol). The crude product was purified by silica column (Ethyl acetate-Hexane 1:4) to afford the **2i** (36.0 mg, 67 %) as pale yellow solid. Enantiomeric excess was determined to be 636 % by chiral HPLC (Chiracel-OJH Column, 93:7, hexane: *i*PrOH, 1.0 mL/min, 7.54 min minor, 8.95 min major).

2-methylallyl 3,4-dihydro-1H-carbazole-9(2H)-carboxylate (3)

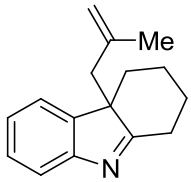


The title compound was prepared according to general procedure **E**, from 2,3,4,9-tetrahydro-1H-carbazole (171 mg, 1.0 mmol), 2-methylallyl 1H-imidazole-1-carboxylate(187 mg, 1.1mmol), DBU (30 mg, 0.2 mmol). The crude product was purified by silica column (Ethyl acetate-Hexane 1:20) to afford the **3** (165 mg, 62 %) as white solid.

Rf (Ethyl acetate-Hexane 1:3) = 0.84; IR: $_{max}$ (thin film) / cm^{-1} 2937, 2844, 1730, 1459,

1323, 1315, 1212, 1142, 1018, 908, 742; ^{1}H-NMR (400MHz, $CDCl_3$): δ= 1.77- 1.91 (m, 7H), 2.63 (m, 2H), 3.01 (m, 2H), 4.82 (s, 2H), 5,03 (s, 1H), 5.12 (s, 1H), 7.19- 7.27 (m, 2H), 7.37-7.39 (m, 1H), 8.13 (d, 1H, *J*= 7.3 Hz); ^{13}C-NMR (100MHz, $CDCl_3$): δ= 19.7, 21.0, 22.1, 23.5, 25.6, 69.9, 114.1, 115.4, 117.3, 117.5, 122.7, 123.6, 130.0, 135.6, 135.7, 139.4, 151.9. HRMS(EST) called for $C_{17}H_{20}NO_2$ $(M+H)^+$ 270.1494 Found 270.1479.

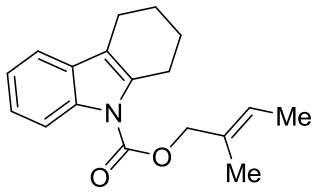
4a-(2-methylallyl)-2,3,4,4a-tetrahydro-1H-carbazole (4)



The title compound was prepared according to general procedure **B3**, from 2-methylallyl 3,4-dihydro-1H-carbazole-9(2H)-carboxylate **(3)** (80.7 mg, 0.3 mmol), $Pd(PPh_3)_4$ (17.4 mg, 0.015 mmol), BEt_3 (1.0M in hexane)(0.3 ml, 0.3 mmol), BSA (61.0 mg, 0.3 mmol). The crude product was purified by silica column (Ethyl acetate-Hexane 1:5) to afford the **4** (47 mg, 70 %) as white solid.

Rf (Ethyl acetate-Hexane 1:3) = 0.24; IR: $_{max}$ (thin film) / cm^{-1} 3074, 2936, 2860, 1646, 1579, 1453, 1013, 891, 773; ^{1}H-NMR (400MHz, $CDCl_3$): δ= 1.08-1.16 (m, 4H), 1.44 (qt, 1H, *J*= 4.3, 13..3 Hz), 1.64- 1.72 (m, 1H), 1.86 (qt, 1H, *J*= 3.8, 13.8 Hz), 2.18- 2.25 (m, 1H), 2.34 (dd, 1H, *J*= 2.3, 13.3 Hz), 2.59- 2.69 (m, 2H), 2.86- 2.95 (m, 2H), 4.48 (d, 2H, *J*= 21.1 Hz), 7.18 (t, 1H, *J*= 7.3 Hz), 7.27- 7.33 (m, 2H), 7.58 (d, 1H, *J*= 7.8 Hz) ; ^{13}C-NMR (100MHz, $CDCl_3$): δ= 21.3, 23.2 29.4, 30.7, 39.8, 41.7, 58.0, 113.6, 120.2, 122.0, 124.5, 127.5, 141.2, 144.9, 154.9, 189.3; HRMS(EST) called for $C_{16}H_{19}N$ $(M+H)^+$ 226.1596 Found 226.1604.

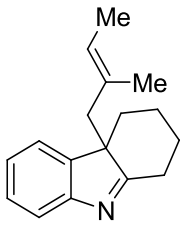
(E)-2-methylbut-2-enyl 3,4-dihydro-1H-carbazole-9(2H)-carboxylate (5)



The title compound was prepared according to general procedure **E**, from 2,3,4,9-tetrahydro-1H-carbazole (342 mg, 2.0 mmol), (E)-2-methylbut-2-enyl 1H-imidazole-1-carboxylate (396 mg, 2.2mmol), DBU (60 mg, 0.4 mmol). The crude product was purified by silica column (DCM-Hexane 1:10) to afford the **5** (230 mg, 41 %) as yellow solid.

Rf ((DCM-Hexane 2:1)) = 0.65; IR: $_{max}$ (thin film) / cm^{-1} 2939, 2842, 1730, 1459, 1322, 1312, 1213, 1142, 1017, 744; ^{1}H-NMR (400MHz, $CDCl_3$): δ= 1.68 (d, 3H, *J*= 6.8 Hz), 1.77 (s, 3H), 1.80- 1.92 (m, 4H), 2.62- 2.65 (m, 2H), 2.99- 3.02 (m, 2H), 4.79 (s, 2H), 5.70 (qq, 1H, *J*= 1.3, 6.8 Hz), 7.18-7.26 (m, 2H), 7.37- 7.39 (m, 1H), 8.12 (d, 1H, *J*= 7.0 Hz); ^{13}C-NMR (100MHz, $CDCl_3$): δ= 13.4, 14.0, 21.1, 22.2, 23.6, 25.7, 72.6, 115.5, 117.1, 117.5, 122.6, 123.5, 125.4, 130.0, 130.3, 135.7, 135.8, 152.1; HRMS(EST) called for $C_{18}H_{22}NO_2$ $(M+H)^+$ 284.1651 Found 284.1632.

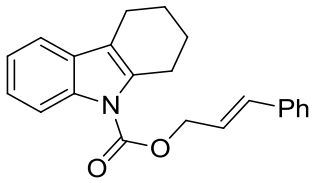
(E)-4a-(2-methylbut-2-enyl)-2,3,4,4a-tetrahydro-1H-carbazole (6)



The title compound was prepared according to general procedure **B3**, from (E)-2-methylbut-2-enyl 3,4-dihydro-1H-carbazole-9(2H)-carboxylate **(5)** (85 mg, 0.3 mmol), $Pd(PPh_3)_4$ (17.4 mg, 0.015 mmol), BEt_3 (1.0M in hexane)(0.3 mL, 0.3 mmol), BSA (61.0 mg, 0.3 mmol). The crude product was purified by silica column (Ethyl acetate-Hexane 1:5) to afford the **6** (52.1 mg, 73 %) as white solid.

Rf (Ethyl acetate-Hexane 1:3) = 0.35; IR: $_{max}$ (thin film) / cm^{-1} 2933, 2859, 1580, 1452, 1186, 1013, 861, 771, 749; ^{1}H-NMR (400MHz, $CDCl_3$): δ= 1.00 (s, 3H), 1.11 (dt, 1H, *J*= 4.0, 13.6 Hz), 1.34 (d, 3H, *J*= 6.8 Hz), 1.43 (qt, 1H, *J*= 4.3, 13.3 Hz), 1.64- 1.70 (m, 1H), 1.86 (qt, 1H, *J*= 3.8, 13.8 Hz), 2.16-2.24 (m, 1H), 2.33 (dq, 1H, *J*= 2.5, 13.3 Hz), 2.57 (d, 1H, *J*= 13.6 Hz), 2.66 (dt, 1H, *J*= 5.5, 13.1 Hz), 2.79 (d, 1H, 13.6 Hz), 2.90 (dt, 1H, *J*= 2.0, 12.8 Hz), 5.05 (q, 1H, *J*= 6.5, 13.3 Hz), 7.16 (t, 1H, *J*= 8.0 Hz), 7.25-7.32 (m, 2H), 7.55 (d, 1H, *J*= 7.5 Hz); ^{13}C-NMR (100MHz, $CDCl_3$): δ= 13.3, 16.5, 21.4, 29.3, 30.8, 39.3, 43.8, 58.4, 120.1, 122.21, 122.22, 124.3, 127.3, 131.5, 145.3, 155.0, 189.5; HRMS(EST) called for $C_{17}H_{21}N$ $(M+H)^+$ 240.1752 Found 240.1752.

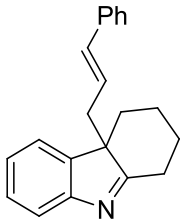
Cinnamyl 3,4-dihydro-1H-carbazole-9(2H)-carboxylate (7)



The title compound was prepared according to general procedure **E**, from 2,3,4,9-tetrahydro-1H-carbazole (171 mg, 1.0 mmol), cinnamyl 1H-imidazole-1-carboxylate (242 mg, 1.1mmol), DBU (30 mg, 0.2 mmol). The crude product was purified by silica column (Ethyl acetate-Hexane 1:20) to afford the **7** (145 mg, 44 %) as white solid.

Rf (Ethyl acetate-Hexane 1:3) = 0.82; IR: $_{max}$ (thin film) / cm^{-1} 2940, 2840, 1727, 1476, 1458, 1390, 1351, 1314, 1213, 1142, 964, 759; ^{1}H-NMR (400MHz, $CDCl_3$): δ= 1.81-1.94 (m, 4H), 2.64- 2.68 (m, 2H), 3.03- 3.06 (m, 2H), 5.08 (d, 2H, *J*= 6.5 Hz), 6.46 (dt, 1H, *J*= 6.5, 16.1 Hz), 6.81 (d, 1H, *J*= 15.8 Hz), 7.21-7.46 (m, 8H), 8.16 (d, 2H, *J*= 7.3 Hz); ^{13}C-NMR (100MHz, $CDCl_3$): δ= 21.1, 22.2, 23.5, 25.7, 67.1, 115.5, 117.3, 117.6, 122.6, 122.7, 123.6, 126.8, 128.3, 128.7, 130.1, 135.1, 135.6, 135.7, 136.0, 151.9; HRMS(EST) called for $C_{22}H_{22}NO_2$ $(M+H)^+$ 332.1651 Found 332.1649.

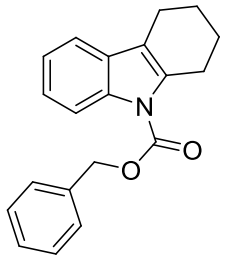
4a-cinnamyl-2,3,4,4a-tetrahydro-1H-carbazole (8)



The title compound was prepared according to general procedure **B3**, from cinnamyl 3,4-dihydro-1H-carbazole-9(2H)-carboxylate **(7)** (85 mg, 0.3 mmol), $Pd(PPh_3)_4$ (17.4 mg, 0.015 mmol), BEt_3 (1.0M in hexane)(0.3 mL, 0.3 mmol), BSA (61.0 mg, 0.3 mmol). The crude product was purified by silica column (Ethyl acetate-Hexane 1:5) to afford the **8** (61 mg, 71 %) as pale yellow solid.

Rf (Ethyl acetate-Hexane 1:3) = 0.22; IR: $_{max}$ (thin film) / cm^{-1} 2928, 2857, 1581, 1498, 1446, 1270, 964, 759; ^{1}H-NMR (400MHz, $CDCl_3$): δ= 1.20 (dt, 1H, *J*= 4.0, 13.6 Hz), 1.47 (qt, 1H, *J*= 4.3, 13.3 Hz), 1.70- 1.77 (m, 1H), 1.90 (qt, 1H, *J*= 3.5, 13.8 Hz), 2.21-2.29 (m, 1H), 2.45 (dq, 1H, *J*= 2.0, 13.3 Hz), 2.60-2.66 (m, 2H), 2.83 (dd, 1H, *J*= 8.0, 14.8 Hz), 2.92 (d, 1H, *J*= 13.5 Hz), 5.66 (dt, 1H, *J*= 7.3, 15.6 Hz), 6.34 (d, 1H, *J*= 15.6 Hz), 7.15-7.27 (m, 6H), 7.32-7.35 (m, 2H), 7.61 (d, 2H, *J*= 7.8 Hz); ^{13}C-NMR (100MHz, $CDCl_3$): δ= 21.1, 28.8, 30.2, 36.6, 57.8, 120.3, 122.0, 123.9, 124.7, 126.1, 127.2, 127.7, 128.4, 133.1, 137.0, 144.6, 154.9, 188.7; HRMS(EST) called for $C_{21}H_{22}N$ $(M+H)^+$ 288.1752 Found 288.1748.

Benzyl 3,4-dihydro-1H-carbazole-9(2H)-carboxylate (9)

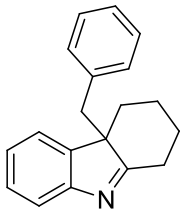


To an oven dried round bottomed flask equipped with a reflux condenser and magnetic stirrer bar and purged with argon was added a solution of 2,3,4,9-tetrahydro-1H-carbazole (514 mg, 3 mmol) and sodium hydride (60 %) (180

mg, 4.5 mmol) in DMF and stirred under 0°C for 30 mins. Benzyl chloroformate (767.7mg, 4.5 mmol) was injected into the mixture under 0°C and the reaction was stirred at room temperature for 16 hours. The mixture was quenched by water and stirred for 30 mins, extracted with ether 3 times and washed with water again. After dried over $MgSO_4$, the organic layer was concentrated in vacuo to obtain the crude product. The residue was subjected to a flash chromatograph (Ethyl acetate-Hexane: 1:15) to afford the pure **9** (830 mg, 90 %) as a white solid.

Rf (Ethyl acetate-Hexane 1:3) = 0.58; IR: $_{max}$ (thin film) / cm^{-1}2942, 2882, 1728, 1614, 1458, 1390, 1350, 1314, 1213, 1141, 1035, 745; ^{1}H-NMR (400MHz, $CDCl_3$): δ= 1.77-1.89 (m, 4H), 2.62 (t, 2H, *J*= 5.8 Hz), 2.98 (t, 2H, *J*= 6.0 Hz), 5.43 (s, 2H), 7.18-7.23 (m, 2H), 7.33-7.41 (m, 4H), 7.46-7.48 (d, 2H, *J*= 6.8Hz), 8.10-8.13 (m, 1H); ^{13}C-NMR (100MHz, $CDCl_3$): δ= 21.1, 22.1, 23.5, 25.7, 68.3, 115.5, 117.3, 117.5, 122.7, 123.6, 128.4, 128.5, 128.7, 130.1, 135.4, 135.6, 135.7, 151.9; HRMS(EST) called for $C_{20}H_{20}NO_2$ $(M+H)^+$ 306.1494 Found 306.1499.

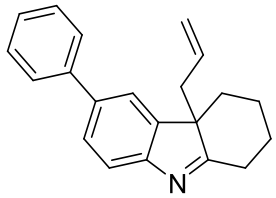
4a-benzyl-2,3,4,4a-tetrahydro-1H-carbazole (10)



To an oven dried round bottomed flask equipped with a reflux condenser and magnetic stirrer bar and purged with argon was added, $[Pd(allyl)Cl]_2$ (2.74 mg, 5mol%), Xantphos (9.6 mg, 11mol%) and Benzyl 3,4-dihydro-1H-carbazole-9(2H)- carboxylate **(9)** (46 mg, 0.15 mmol) in dry toluene (2 mL). Then BSA (36.6 mg, 0.18 mmol) and BEt_3 (0.17 mL, 0.17 mmol) (1.0M in hexane) was injected into flask slowly via syringe and the reaction was stirred at 100°C for 48 hours. The mixture was diluted with EtOAc and washed by $NaHCO_3$ and brine. The organic layers was dried over $NaSO_4$ and filtered. After evaporation of the solvent, the residue was purified by chromatograph (Ethyl acetate-Hexane: 1:10) to afford the pure **11** (28 mg, 72%) as yellow oil.

Rf (Ethyl acetate-Hexane 1:5) = 0.22; IR: $_{max}$ (thin film) / cm^{-1} 2929, 2861, 1580, 1492, 1453, 701; ^{1}H-NMR (400MHz, $CDCl_3$): δ= 1.18 (dt, 1H, *J*= 4.0, 13.6 Hz), 1.47 (qt, 1H, *J*= 4.0, 13.1 Hz), 1.79 (d, 1H, *J*= 14.1Hz), 2.02 (qt, 1H, *J*=3.5, 13.6 Hz), 2.24-2.32 (m, 1H), 2.46 (dq, 1H, *J*= 1.8, 13.3 Hz), 2.76 (dt, 1H, *J*=5.8, 13.3 Hz), 2.93 (dt, 1H, *J*= 1.8, 13.3 Hz), 2.99 (d, 1H, *J*=13.6), 3.22 (d, 1H, *J*= 13.6), 6.76-6.78 (m, 2H), 7.04-7.08 (m, 4H), 7.12 (t, 1H, $J_=$ 7.5 Hz), 7.26 (t, 1H, *J*= 7.0 Hz), 7.46 (d, 1H, *J*=7.5 Hz) ; ^{13}C-NMR (100MHz, $CDCl_3$): δ= 21.4, 29.1, 30.6, 25.7, 37.1, 39.1, 58.6, 120.1, 122.6, 124.2, 126.5, 127.6, 127.7, 129.4, 136.1, 144.2, 154.9, 188.4. HRMS(EST) called for $C_{19}H_{20}N$ $(M+H)^+$ 262.1596 Found 262.1597.

4a-allyl-6-phenyl-2,3,4,4a-tetrahydro-1H-carbazole (11a)

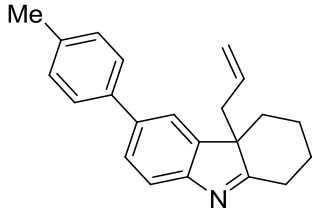


The title compound was prepared according to general procedure **C**, allyl 6-bromo-3,4-dihydro-1H-carbazole-9(2H)-carboxylate **(1e)** (100 mg, 0.3 mmol), $Pd(PPh_3)_4$ (3.47 mg, 0.003 mmol), BEt_3 (1.0M in hexane)(0.3 mL, 0.3 mmol), Phenyl boronic acid (54.9 mg, 0.45mmol). The crude product was purified by silica column (Ethyl acetate-Hexane 1:6) to afford the **11a** (60 mg, 70 %) as yellow oil.

Rf (Ethyl acetate-Hexane 1:3) = 0.23; IR: $_{max}$ (thin film) / cm^{-1} 3076, 3032, 2934, 2859, 1639, 1579, 1462, 917, 773; ^{1}H-NMR (400MHz, $CDCl_3$): δ= 1.24 (dt, 1H, *J*=4.0, 13.3Hz), 1.47 (qt, 1H, *J*= 4.3, 13.3Hz,), 1.69-1.76 (m, 1H), 1.86 (qt, 1H, *J*=3.8, 13.6Hz), 2.19-2.27 (m, 1H), 2.42 (dq, 1H, *J*=2.5, 13.6Hz), 2.55-2.72(m, 3H), 2.92 (dt, 1H, *J*=2.0, 13.1Hz), 4.91 (ddt, 1H, *J*= 0.8, 2.0, 10.0 Hz), 5.00 (ddt, 1H, *J*=1.3, 2.0, 17.1Hz), 5.26 (ddt, 1H, *J*=17.6, 10.0, 7.5Hz), 7.35 (tt, 1H, $J_=$ 1.3, 6.6Hz), 7.43-7.48 (m, 2H), 7.52-7.67(m, 5H) .^{13}C-NMR (100MHz, $CDCl_3$): δ= 21.0, 28.8, 30.2, 37.0, 37.7, 57.8,

118.1, 120.2, 120.7, 126.8, 127.0, 127.2, 128.7, 132.1, 138.0, 141.4, 145.2, 154.3, 189.2; HRMS(EST) called for $C_{21}H_{22}N$ $(M+H)^+$288.1752 Found 288.1735.

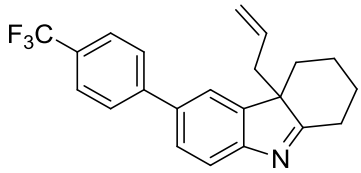
4a-allyl-6-p-tolyl-2,3,4,4a-tetrahydro-1H-carbazole (11b)



The title compound was prepared according to general procedure **C**, allyl 6-bromo-3,4-dihydro-1H-carbazole-9(2H)-carboxylate **(1g)** (100 mg, 0.3 mmol), $Pd(PPh_3)_4$ (3.47 mg, 0.003 mmol), BEt_3 (1.0M in hexane)(0.3 mL, 0.3 mmol), 3-Tolyl boronic acid (60.7 mg, 0.45mmol). The crude product was purified by silica column (Ethyl acetate-Hexane 1:6) to afford the **11b** (53 mg, 60%) as yellow oil.

Rf (Ethyl acetate-Hexane 1:3) = 0.23; IR: $_{max}$ (thin film) / cm^{-1} 3075, 3021, 2932, 2859, 1639, 1580, 1463, 916, 821; ^{1}H-NMR (400MHz, $CDCl_3$): δ= 1.24 (dt, 1H, *J*=4.2, 13.5Hz), 1.46 (qt, 1H, *J*= 4.5, 13.0Hz,), 1.69-1.76 (m, 1H), 1.86 (qt, 1H, *J*=3.8, 15.6Hz), 2.18-2.27 (m, 1H), 2.42 (m, 4H) , 2.55-2.72(m, 3H), 2.91 (dt, 1H, *J*=2.0, 13.1Hz), 4.91 (ddt, 1H, *J*= 1.0, 1.8, 10.0 Hz), 5.00 (ddt, 1H, *J*=1.3, 2.0, 17.1Hz), 5.26 (ddt, 1H, *J*=17.6, 9.0, 7.7 Hz), 7.25-7.28 (m, 2H), 7.50-7.56 (m, 4H), 7.62-7.64(m, 1H) .^{13}C-NMR (100MHz, $CDCl_3$): δ= 21.1, 28.8, 30.2, 37.0, 37.7, 57.7, 118.0, 120.1, 120.6, 126.5, 127.0, 129.4, 132.1, 136.7, 138.0, 138.6, 145.2, 154.1, 189.0. HRMS(EST) called for $C_{22}H_{24}N$ $(M+H)^+$302.1909 Found 302.1921.

4a-allyl-6-(4-(trifluoromethyl)phenyl)-2,3,4,4a-tetrahydro-1H-carbazole (11c)

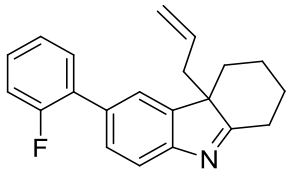


The title compound was prepared according to general procedure **C**, allyl

6-bromo-3,4-dihydro-1H-carbazole-9(2H)-carboxylate **(1e)** (100 mg, 0.3 mmol), $Pd(PPh_3)_4$ (3.47 mg, 0.003 mmol), BEt_3 (1.0M in hexane)(0.3 mL, 0.3 mmol), 4-(Trifluoromethyl)phenyl boronic acid (85.5 mg, 0.45 mmol). The crude product was purified by silica column (Ethyl acetate-Hexane 1:6) to afford the **11c** (47 mg, 45 %) as yellow solid.

Rf (Ethyl acetate-Hexane 1:3) = 0.19; IR: $_{max}$ (thin film) / cm^{-1} 3079, 3021, 2937, 2857, 1615, 1580, 1325, 1123, 919, 827; ^{1}H-NMR (400MHz, $CDCl_3$): δ= 1.24 (dt, 1H, *J*=4.3, 13.6 Hz), 1.47 (qt, 1H, *J*= 4.2, 13.3 Hz,), 1.69-1.77 (m, 1H), 1.84 (qt, 1H, *J*=3.8, 13.6 Hz), 2.20-2.28 (m, 1H), 2.35 (dq, 1H, *J*=2.8, 13.0Hz), 2.56-2.72(m, 3H), 2.93 (dt, 1H, *J*=2.0, 13.3 Hz), 4.91 (ddt, 1H, *J*= 1.0, 1.8, 10.0 Hz), 4.99 (dq, 1H, *J*=1.3, 16.8 Hz), 5.25 (ddt, 1H, *J*=17.6, 10.0, 7.5 Hz), 7.52 (d, 1H, *J*=1.5 Hz), 7.58 (dd, 1H, *J*=1.0, 8.0 Hz), 7.64-7.75 (m, 5H,) .^{19}F-NMR (376MHz, $CDCl_3$): δ= -62.3 ^{13}C-NMR (100MHz, $CDCl_3$): δ= 21.0, 28.8, 30.2, 37.0, 37.6, 57.9, 118.2, 120.4, 120.9, 123.0, 125.6 (q, J_{C-F} =3.7 Hz), 127.1, 127.5, 128.4, 129.1(q, J_{C-F} =32.1 Hz), 131.9, 136.5, 145.0 (q, J_{C-F} =1.1Hz) 145.5, 155.1, 189.9. HRMS(EST) called for $C_{22}H_{21}NF_3$ $(M+H)^+$356.1626 Found 356.1628

4a-allyl-6-(2-fluorophenyl)-2,3,4,4a-tetrahydro-1H-carbazole (11d)

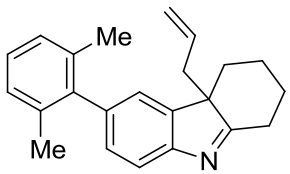


The title compound was prepared according to general procedure **C**, allyl 6-bromo-3,4-dihydro-1H-carbazole-9(2H)-carboxylate **(1e)** (100 mg, 0.3 mmol), $Pd(PPh_3)_4$ (3.47 mg, 0.003 mmol), BEt_3 (1.0M in hexane)(0.3 mL, 0.3 mmol), 2-fluorophenyl boronic acid (63 mg, 0.45 mmol). The crude product was purified by silica column (Ethyl acetate-Hexane 1:10) to afford the **11d** (28 mg, 31 %) as yellow solid.

Rf (Ethyl acetate-Hexane 1:3) = 0.22; IR: $_{max}$ (thin film) / cm^{-1} 3436, 2933, 2859, 1640,

1580, 1465, 1215, 918, 758; ^{1}H-NMR (400MHz, $CDCl_3$): δ= 1.24 (dt, 1H, *J*=4.2, 13.3 Hz), 1.47 (qt, 1H, *J*= 4.3, 13.3 Hz,), 1.68-1.76 (m, 1H), 1.86 (qt, 1H, *J*=3.8, 13.6 Hz), 2.20-2.28 (m, 1H), 2.41 (d, 1H, *J*= 13.0Hz), 2.56-2.71(m, 3H), 2.92 (d, 1H, *J*=2.2, 13.0 Hz), 4.91 (d, 1H, *J*= 10.0 Hz), 4.99 (dq, 1H, *J*= 17.0 Hz), 5.25 (ddt, 1H, *J*=16.8, 9.8, 7.6Hz), 7.14-7.24 (m, 2H), 7.29-7.34 (m, 1H), 7.44-7.52 (m, 3H), 7.66 (d, 1H, *J*= 8.0Hz) .; ^{19}F-NMR (376MHz, $CDCl_3$): δ= -117.8 ^{13}C-NMR (100MHz, $CDCl_3$): δ= 21.1, 28.9, 30.2, 36.9, 37.6, 57.8, 116.1(d, $J_{C\text{-}F}$ =23.0 Hz) , 118.2, 120.0, 122.8 (d, $J_{C\text{-}F}$ = 3.7 Hz), 124.3 (d, $J_{C\text{-}F}$ = 3.7Hz), 128.6 (d, $J_{C\text{-}F}$ =2.6 Hz), 128.7 (d, $J_{C\text{-}F}$ = 8.0 Hz), 129.3 (d, $J_{C\text{-}F}$ = 13.1Hz), 130.9 (d, $J_{C\text{-}F}$ = 3.3Hz), 132.1, 132,8 (d, $J_{C\text{-}F}$ = 1.5 Hz), 144.8, 154.5, 159.8 (d, $J_{C\text{-}F}$ = 245.7Hz), 189.6. ; HRMS(EST) called for $C_{21}H_{21}NF$ $(M+H)^{+}$306.1658 Found 306.1664.

4a-allyl-6-(2,6-dimethylphenyl)-2,3,4,4a-tetrahydro-1H-carbazole (11e)

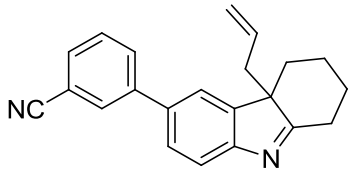


The title compound was prepared according to general procedure **C**, allyl 6-bromo-3,4-dihydro-1H-carbazole-9(2H)-carboxylate **(1e)** (100 mg, 0.3 mmol), $Pd(PPh_3)_4$ (3.47 mg, 0.003 mmol), BEt_3 (1.0M in hexane)(0.3 mL, 0.3 mmol), 2,6-dimethylphenyl boronic acid (67.5 mg, 0.45 mmol). The crude product was purified by silica column (Ethyl acetate-Hexane 1:6) to afford the **11e** (40 mg, 43 %) as yellow solid.

Rf (Ethyl acetate-Hexane 1:3) = 0.28; IR: $_{max}$ (thin film) / cm^{-1} 3057, 2931, 2859, 1640, 1580, 1461, 1265, 916, 740; ^{1}H-NMR (400MHz, $CDCl_3$): δ= 1.26 (dt, 1H, *J*=4.2, 13.6Hz), 1.47 (qt, 1H, *J*= 4.5, 13.3Hz,), 1.68-1.75 (m, 1H), 1.84 (qt, 1H, *J*=3.8, 13.5Hz), 2.04 (d, 6H, *J*=1.8Hz), 2.18-2.27 (m, 1H), 2.35 (dq, 1H, *J*=2.8, 13.0Hz), 2.54-2.66(m, 3H), 2.91 (dt, 1H, *J*=2.0, 13.3Hz), 4.86 (dt, 1H, *J*= 0.8, 10.0 Hz), 4.94 (dq, 1H, *J*=1.2, 17.1Hz), 5.22 (ddt, 1H, *J*=17.6, 10.0, 7.5 Hz), 7.08-7.20 (m, 5H), 7.62 (dd,1H, *J*= 1.0,

9.6Hz) .^{13}C-NMR (100MHz, $CDCl_3$): δ= 21.0, 28.8, 30.2, 37.0, 37.7, 57.8, 118.1, 120.2, 120.7, 126.8, 127.0, 127.2, 128.7, 132.1, 138.0, 141.4, 145.2, 154.3, 189.2. HRMS(EST) called for $C_{23}H_{26}N$ $(M+H)^+$316.2065 Found 316.2058.

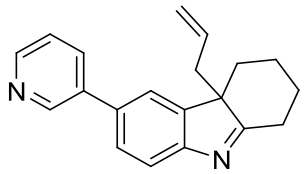
3-(4a-allyl-2,3,4,4a-tetrahydro-1H-carbazol-6-yl)benzonitrile (11f)



The title compound was prepared according to general procedure **C**, allyl 6-bromo-3,4-dihydro-1H-carbazole-9(2H)-carboxylate **(1e)** (100 mg, 0.3 mmol), $Pd(PPh_3)_4$ (3.47 mg, 0.003 mmol), BEt_3 (1.0M in hexane)(0.3 mL, 0.3 mmol), 3-Cyanophenyl boronic acid (66.1 mg, 0.45 mmol). The crude product was purified by silica column (Ethyl acetate-Hexane 1:6) to afford the **11f** (58 mg, 63 %) as yellow solid.

Rf (Ethyl acetate-Hexane 1:3) = 0.17; IR: $_{max}$ (thin film) / cm^{-1} 2935, 2860, 2228, 1579, 1464, 919, 797, 692; ^{1}H-NMR (400MHz, $CDCl_3$): δ= 1.23 (dt, 1H, *J*=4.3, 13.5 Hz), 1.47 (qt, 1H, *J*= 4.3, 13.3 Hz,), 1.70-1.77 (m, 1H), 1.87 (qt, 1H, *J*=3.8, 13.5 Hz), 2.20-2.28 (m, 1H), 2.43 (dq, 1H, *J*=2.5, 13.3Hz), 2.56-2.72(m, 3H), 2.92 (dt, 1H, *J*=2.0, 13.0 Hz), 4.91 (ddt, 1H, *J*= 1.0, 1.8, 10.0 Hz), 4.99 (dq, 1H, *J*=1.2, 17.1 Hz), 5.25 (ddt, 1H, *J*=16.1, 9.8, 7.8Hz), 7.48 (dd, 1H, *J*= 0.5, 2.0 Hz), 7.52-7.56 (m, 2H), 7.62 (dt,1H, *J*= 1.5, 7.8Hz), 7.67 (d, 1H, *J*= 8.0 Hz), 7.81-7.88 (m, 2H). ^{13}C-NMR (100MHz, $CDCl_3$): δ= 21.0, 28.8, 30.2, 37.0, 37.6, 58.0, 112.9, 118.3, 118.9, 120.5, 120.6, 126.9, 129.5, 130.3, 130.7, 131.5, 131.8, 135.5, 142.7, 145.7, 155.2, 190.1. HRMS(EST) called for $C_{22}H_{21}N_2$ $(M+H)^+$313.1705 Found 313.1693.

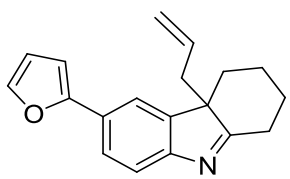
4a-allyl-6-(pyridin-3-yl)-2,3,4,4a-tetrahydro-1H-carbazole (11g)



The title compound was prepared according to general procedure **C**, allyl 6-bromo-3,4-dihydro-1H-carbazole-9(2H)-carboxylate **(1e)** (100 mg, 0.3 mmol), $Pd(PPh_3)_4$ (3.47 mg, 0.003 mmol), BEt_3 (1.0M in hexane)(0.3 mL, 0.3 mmol), 3-Pyridine boronic acid (55.3 mg, 0.45 mmol). The crude product was purified by silica column (Ethyl acetate-Hexane 1:9) and the mixture was purified by SCX-2 ion exchange resin column again to afford the **11g** (39 mg, 45 %) as yellow oil.

Rf (Ethyl acetate-Hexane 1:3) = 0.27; IR: $_{max}$ (thin film) / cm^{-1} 3053, 2934, 2859, 1718, 1679, 1461, 1264, 918, 804, 711; ^{1}H-NMR (400MHz, $CDCl_3$): δ= 1.23 (dt, 1H, *J*= 4.0, 13.3 Hz), 1.47 (qt, 1H, *J*= 4.3, 13.3 Hz), 1.69-1.77 (m, 1H), 1.87 (qt, 1H, *J*= 3.8, 13.6 Hz), 2.20-2.28 (m, 1H), 2.43 (dd, 1H, *J*= 2.5, 13.3 Hz), 2.56-2.72 (m, 3H), 2.92 (dt, 1H, *J*= 2.0, 13.1Hz), 4.91 (d, 1H, *J*= 10.0 Hz), 4.99 (d, 1H, *J*= 16.8 Hz), 5.25 (ddt, 1H, *J*=16.8, 10.0, 7.5 Hz), 7.37 (dd, 1H, *J*= 5.0, 8.0 Hz), 7.50 (d, 1H, *J*= 1.5 Hz), 7.55 (dd, 1H, *J*= 1.8, 8.0 Hz), 7.68 (d, 1H, *J*= 8.0 Hz), 7.89 (dt, 1H, *J*= 2.0, 8.0 Hz), 8.58 (dd, 1H, *J*= 1.5, 4.8 Hz), 8.86 (d, 1H, *J*= 2.3 Hz); ^{13}C-NMR (100MHz, $CDCl_3$): δ= 21.0, 28.8, 30.2, 37.0, 37.6, 57.9, 118.3, 120.6, 120.8, 123.5, 126.9, 131.9, 134.4, 134.5, 137.0, 145.6, 148.1, 148.3, 155.0. 189.9.; HRMS(EST) called for $C_{20}H_{21}N_2$ $(M+H)^+$ 289.1705 Found 289.1711.

4a-allyl-6-(furan-2-yl)-2,3,4,4a-tetrahydro-1H-carbazole (11h)

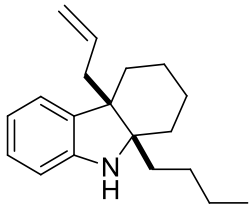


The title compound was prepared according to general procedure **C**, allyl 6-bromo-3,4-dihydro-1H-carbazole-9(2H)-carboxylate **(1e)** (100 mg, 0.3 mmol),

$Pd(PPh_3)_4$ (3.47 mg, 0.003 mmol), BEt_3 (1.0M in hexane)(0.3 mL, 0.3 mmol), 2-Furanyl boronic acid (50.4 mg, 0.45 mmol). The crude product was purified by silica column (Ethyl acetate-Hexane 1:9) to afford the **11h** (43 mg, 52 %) as yellow solid.

Rf (Ethyl acetate-Hexane 1:3) = 0.16; IR: $_{max}$ (thin film) / cm^{-1} 3016, 2976, 2941, 2891, 1657, 1578, 1456, 1410, 1235, 1011, 715; ^{1}H-NMR (400MHz, $CDCl_3$): δ= 1.21 (dt, 1H, *J*=4.0, 13.6 Hz), 1.45 (qt, 1H, *J*= 4.3, 13.3 Hz), 1.68-1.75 (m, 1H), 1.87 (qt, 1H, *J*=3.5, 13.6 Hz), 2.18-2.26 (m, 1H), 2.40 (dq, 1H, *J*= 2.0, 13.3Hz), 2.53-2.72(m, 3H), 2.89 (dt, 1H, *J*=1.5, 13.3 Hz), 4.88 (d, 1H, *J*= 10.0 Hz), 4.97 (d, 1H, *J*=16.8 Hz), 5.20 (ddt, 1H, *J*=16.8, 10.0, 7.5 Hz), 6.48 (dd,1H, *J*= 1.8, 3.3 Hz), 6.64 (d, 1H, *J*= 3.2 Hz) 7.47 (d, 1H, *J*= 1.0 Hz), 7.57-7.66 (m, 3H,) .; ^{13}C-NMR (100MHz, $CDCl_3$): δ= 21.1, 28.9, 30.2, 37.1, 37.7, 57.8, 104.5, 111.7, 117.4, 118.1, 120.2, 123.6, 127.6, 132.0, 141.2, 145.2, 154.3, 154.4, 189.9.; HRMS(EST) called for $C_{19}H_{20}NO$ $(M+H)^+$ 278.1545 Found 278.1532.

4a-allyl-9a-butyl-2,3,4,4a,9,9a-hexahydro-1H-carbazole (12a)

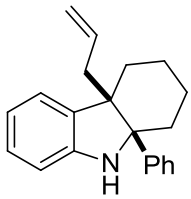


To a solution of 4a-allyl-2,3,4,4a-tetrahydro-1H-carbazole **(2a)** (50 mg, 0.22 mmol) in dry toluene (2 mL) at 0^{o}C and shielded from sunlight, was added the appropriate lithium reagent (0.12 mL, 0.28 mmol) (2.5M in hexane). The solution mixture was stirred at 0^{o}C for 4 hours and hydrolysed with Toluene:water 1:1 (2 mL). The organic layer was separated, extracted with DCM, dried with Na_2SO_4 and filtered. The solvent was evaporated and the residual oil, purified by column chromatography using Hexane/ EtOAc 6:1 as the eluent to afford the **12a** (48 mg, 82 %) as yellow oil. The product was obtained as a single diastereoisomer and tentatively assigned as the *syn*-diastereomer based on literature precedent.[1]

[1] Rodriguez, J. G.; Urrutia, A. *Tetrahedron* **1998**, *54*, 15613.

Rf (Ethyl acetate-Hexane 1:3) = 0.85 ; IR: $_{max}$ (thin film) / cm^{-1} 3361, 3074, 2929, 2856, 1637, 1607, 1480, 1461, 1319, 909, 806; ^{1}H-NMR (400MHz, $CDCl_3$): δ= 0.98 (t, 3H, *J*= 7.0 Hz), 1.13-1.49 (m, 9H), 1.66-1.80 (m, 3H), 2.04 (dd, 1H, *J*= 8.3, 13.3 Hz), 2.11-2.18 (m, 1H), 2.40 (dd, 1H, *J*=6.3, 13.1 Hz), 3.60 (br, 1H), 4.89 (d, 1H, *J*= 17.8Hz), 4.97 (d, 1H, *J*= 10.3Hz), 5.64 (dddd, 1H, *J*= 6.5, 8.3, 10.0, 16.8 Hz), 6.66 (d, 1H, *J*= 7.8Hz), 6.75 (t, 1H, *J*= 7.5Hz), 6.98 (d, 1H, *J*= 7.3Hz), 7.04 (dt, 1H, *J*= 1.0, 7.5 Hz).; ^{13}C-NMR (100MHz, $CDCl_3$): δ= 14.2, 22.2, 22.3, 23.6, 26.9, 30.0, 30.6, 32.4, 40.8, 50.2, 68.5, 110.6, 116.8, 118.1, 123.8, 127.0, 134.8, 135.6, 149.3.; HRMS(EST) called for $C_{19}H_{28}N$ $(M+H)^+$ 270.2222 Found 270.2216.

4a-allyl-9a-phenyl-2,3,4,4a,9,9a-hexahydro-1H-carbazole (12b)



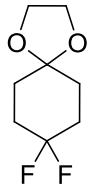
To an oven dried round bottomed flask equipped with a magnetic stirrer bar and purged with argon was added a solution of t-BuLi (0.47 mL, 0.8 mmol) and Bromobenzene (62.8 mg, 0.4 mmol) (1.7M in Pentane) in THF (0.5 ml) and stirred under -78^{o}C for 15 mins. A solution of 4a-allyl-2,3,4,4a-tetrahydro-1H-carbazole **(2a)** (42.3 mg, 0.2 mmol) in dry toluene (2 mL) was injected into the flask via a syringe at 0^{o}C and shielded from sunlight. The solution mixture was stirred at -0^{o}C for 6 hours and hydrolysed with Toluene:water 1:1 (2 mL). The organic layer was separated, extracted with DCM, dried with Na_2SO_4 and filtered. The solvent was evaporated and the residual oil, purified by column chromatography using Hexane/ EtOAc 6:1 as the eluent to afford the **12b** (34 mg, 61 %) as yellow oil. The product was obtained as a single diastereoisomer and tentatively assigned as the *syn*-diastereomer based on literature precedent.

Rf (Ethyl acetate-Hexane 1:3) = 0.87; IR: $_{max}$ (thin film) / cm^{-1}3345, 2934, 2864, 1606, 1483, 1463, 1321, 1131, 912, 700; ^{1}H-NMR (400MHz, $CDCl_3$): δ= 1.40-1.62 (m, 3H),

1.66-1.90 (m, 5H), 2.04 (dd, 1H, *J*= 6.5, 13.3Hz), 2.24 (dd, 1H, *J*= 4.5, 15.3 Hz), 3.87 (br, 1H), 4.62 (d, 1H, *J*= 16.8Hz), 4.82 (dd, 1H, *J*= 2.3, 10.3Hz), 5.45 (dddd, 1H, *J*=6.5, 8.5, 10.0, 16.8 Hz), 6.77 (dd, 2H, *J*= 7.5, 13.1Hz), 6.97 (d, 1H, *J*= 6.8Hz), 7.09 (dt, 1H, *J*= 1.3, 7.5Hz), 7.24-7.30 (m, 1H), 7.36 (t, 2H, *J*= 7.8Hz), 7.76 (d, 2H, *J*=7.5Hz); ^{13}C-NMR (100MHz, $CDCl_3$): δ= 21.4, 22.4 29.6, 39.3, 42.7, 50.5, 71.6, 110.4, 117.0, 118.3, 124.3, 126.5, 126.6, 127.4, 128.0, 133.3, 134.9, 144.8, 148.5. HRMS(EST) called for $C_{21}H_{23}N$ $(M+H)^+$ 290.1909 Found 290.1919.

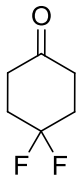
Synthesis of starting indoles

8,8-difluoro-1,4-dioxaspiro[4.5]decane



To a stirred suspension of XtalFluor-M (482 mg, 2.0 mmol) in DCM (2 mL) was added triethylamine trihydrofluoride (0.163 mL, 1.0 mmol) followed by 1,4-dioxaspiro[4.5] decam-8-one at r.t. After 24 hours, the reaction mixture wsa quenched with a 5% aqueous sodium bicarbonate solution, stirred for 15 min, and the resulting mixture was extracted twice with DCM. The organic phases were combined, dried over $MgSO_4$ and filtered through a pad of silica gel. Solvents were evaporated and the resulting crude material was purified by silica gel flash chromatography using hexane: EtOAc 9:1 to provide the title compound (130 mg, 74 %) as a white solid[1]; Rf (1:5 = ethyl acetate : hexane)= 0.48; ^{1}H-NMR (300MHz, $CDCl_3$): δ= 3.92 (s, 4H), 2.09-1.96 (m, 4H), 1.86-1.74 (m, 4H); ^{19}F-NMR (282MHz, $CDCl_3$): δ= -100.2.

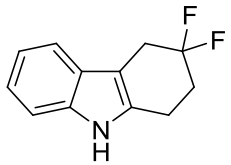
4,4-difluorocyclohexanone



The 8,8-difluoro-1,4-dioxaspiro[4.5]decane (0.9 g, 5.05 mol) was dissolved in acetone

10 ml and 3N HCl, and stirred until the reaction finished (1 hour). Then, the reaction mixture was extracted with DCM, washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The obtained residue was used in the next reaction without further purification. (0.53 g, 80 %); Rf (1:3 = ethyl acetate: hexane) = 0.47; ^{1}H-NMR (300MHz, $CDCl_3$): δ= 2.25-2.38 (m, 4H), 2.55 (t, 4H, *J*= 7.0Hz); ^{19}F-NMR (282MHz, $CDCl_3$): δ= -100.7

3,3-difluoro-2,3,4,9-tetrahydro-1H-carbazole



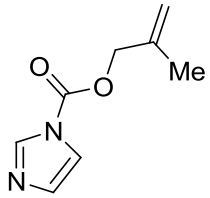
To a round bottom flask with a reflux condenser and magnetic stirrer bar was added with 4.4-difluorocyclohexanone (0.3 g, 2.24 mmol) and phenyl hydrazine.HCl (0.32 g, 2.24 mmol) in acetic acid. The solution was stirred at 140^{o}C over night. After acetic acid was partly evaporated, the residues was dissolved by EtOAc and washed with saturated $NaHCO_3$, water, dried over $MgSO_4$ and the solvent was evaporated. The crude product was eluted by silica gel column chromatography with EtOAc:Hexane (1:9). The solvent was removed under reduced pressure and pure product was achieved as a yellow solid (0.44 g, 95 %)

Rf (1:3 = ethyl acetate: hexane) = 0.56; IR: $_{max}$ (thin film) / cm^{-1} 3383, 2919, 1381, 1260, 1068, 746; ^{1}H-NMR (400MHz, $CDCl_3$): δ= 2.37 (tt, 2H, *J*= 6.8, 6.8 Hz), 2.97 (t, 2H, *J*= 6.8 Hz), 3.28 (t, 2H, *J*= 14.1 Hz), 7.17 (dt, 2H, *J*= 7.0, 23.1 Hz), 7.31 (d, 1H, *J*= 8.0 Hz), 7.46 (d, 1H, *J*= 7.5 Hz); ^{19}F-NMR (376MHz, $CDCl_3$): δ= -96.6 (dt, 2F, *J*= 13.6, 13.6 Hz); ^{13}C-NMR (100MHz, $CDCl_3$): δ= 20.5 (t, *J*= 5.5 Hz), 31.0 (t, *J*= 26.0 Hz), 31.5 (t, *J*= 27.1 Hz), 106.0 (t, *J*= 6.6 Hz), 110.7, 117.6, 119.7, 121.9, 123.8 (t, *J*= 242.1 Hz), 127,1 (t, *J*= 1.5 Hz), 131.2 (t, *J*= 1.5 Hz), 136.6; HRMS(EST) called for $C_{12}H_{10}NF_2$ (M-H$^+$) 206.0781 Found 206.0784.

General Propcedure D: Preparation of Imidazole Carbamates[2]

1,1'-Carbonyldiimidazole (1.5 eq) was dissolved in DCM (20 mL) and the resulting solution was stirred with cooling to 0 °C. Alcohol (1 eq) was then added dropwise. The reaction mixture was stirred at 0 °C for 1 h, and then at room temperature for 16 h. The homogeneous mixture was then diluted with DCM (20 mL), washed with water (2 x 20 mL), dried over MgSO4, and concentrated in vacuo to afford crude product. If necessary the crude product was purified by flash chromatography.

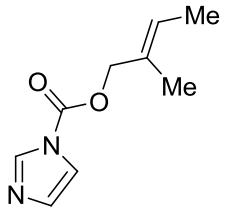
2-methylallyl 1H-imidazole-1-carboxylate



The title compound was prepared according to general procedure **D**, from 2-methylprop-2-en-1-ol (216 mg, 3 mmol), 1,1'-carbonyldiimidazole (0.57 g, 4.5 mmol), DCM 10ml. The crude product was purified by silica column (Ethyl acetate-Hexane 1:10) to afford the white solid (0.45 g, 88 %).

Rf (1:3 = ethyl acetate: hexane) = 0.13; ^{1}H-NMR (400MHz, $CDCl_3$): δ= 1.82 (s, 3H), 4.8 (s, 2H), 5.05 (s, 1H), 5.08 (s, 1H), 7.07 (s, 1H), 7.43 (d, 1H, *J*= 0.9 Hz), 8.15 (s, 1H); ^{13}C-NMR (100MHz, $CDCl_3$): δ= 19.5, 71.4, 115.1, 117.2, 130.8, 137.2, 138.4, 148.6.

(E)-2-methylbut-2-enyl 1H-imidazole-1-carboxylate



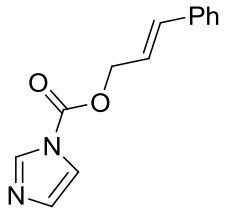
The title compound was prepared according to general procedure **D**, from (E)-2-methylbut-2-en-1-ol (516 mg, 6 mmol), 1,1'-carbonyldiimidazole (1.07 g, 9

[2] Heller, S. T.; Schultz, E. E.; Sarpong, R. *Angew. Chem. Int. Ed.* **2012**, *51*, 8304.

mmol), DCM 20 ml. The crude product was purified by silica column (Ethyl acetate-Hexane 1:10) to afford yellow oil (0.83 g, 76 %).

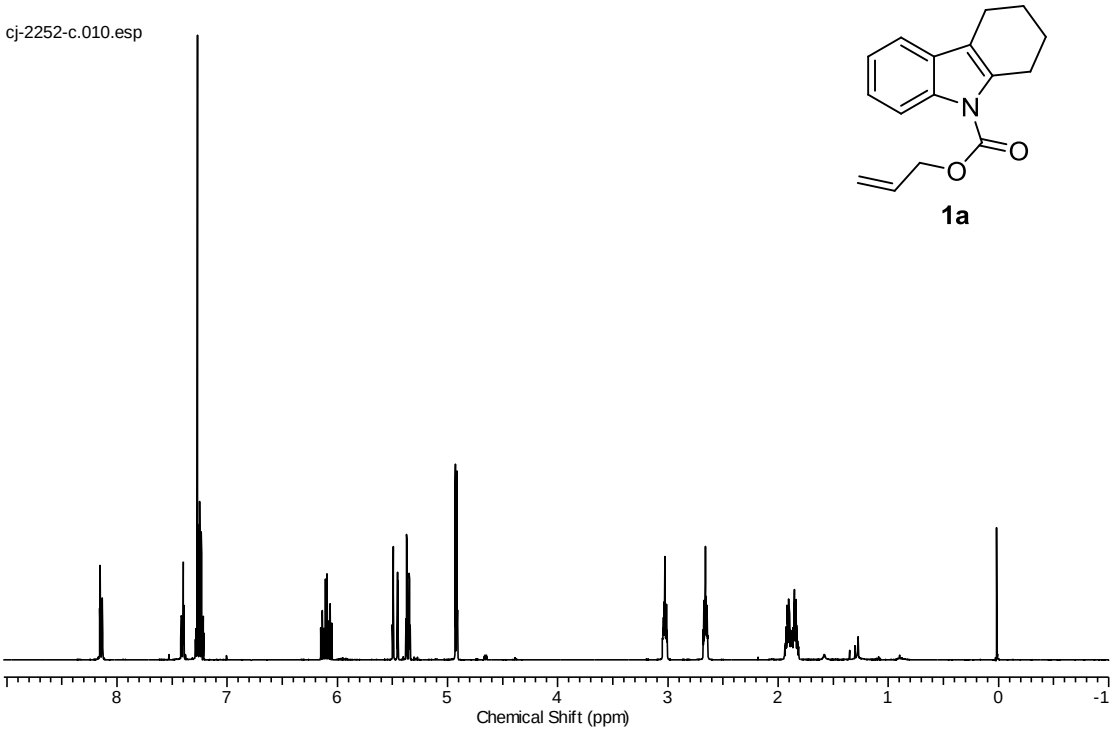
Rf (1:3 = ethyl acetate: hexane) = 0.23; IR: $_{max}$ (thin film) / cm^{-1} 3130, 2983, 1759, 1471, 1401, 1289, 1239, 1171, 1001. 760; ^{1}H-NMR (400MHz, $CDCl_3$): δ= 1.67 (d, 3H, *J*= 6.5 Hz), 1.72 (s, 3H), 4.78 (s, 2H), 5.69 (q, 1H, *J*= 6.5 Hz), 7.05 (s, 1H), 7.41 (s, 1H), 8.13 (s, 1H); ^{13}C-NMR (100MHz, $CDCl_3$): δ= 13.3, 13.6, 74.1, 117.1, 126.7, 129.3, 130.6, 137.1, 148.7.

cinnamyl 1H-imidazole-1-carboxylate



The title compound was prepared according to general procedure **D**, from cinnamyl alcohol (0.402 mg, 3 mmol), 1,1'-carbonyldiimidazole (0.57 g, 4.5 mmol), DCM 10 ml. The crude product was purified by silica column (Ethyl acetate-Hexane 1:10) to afford yellow oil (0.59 g, 89 %).

Rf (1:3 = ethyl acetate: hexane) = 0.19; IR: $_{max}$ (thin film) / cm^{-1} 2914, 2847, 1759, 1576, 1538, 1399, 1288, 1239, 1169, 1094, 999, 760; ^{1}H-NMR (400MHz, $CDCl_3$): δ= 5.04 (dd, 2H, *J*= 1.3, 6.8 Hz), 6.35 (dt, 2H, *J*= 6.8, 15.8 Hz), 6.78 (d, 1H, *J*= 15.8 Hz), 7.07 (t, 1H, *J*= 0.75 Hz), 7.26-7.45 (m, 6H), 8.16 (s, 1H); ^{13}C-NMR (100MHz, $CDCl_3$): δ= 68.7, 117.1, 120.9, 126.7, 128.6, 128.7, 130.6, 135.4, 136.5, 137.1, 148.6.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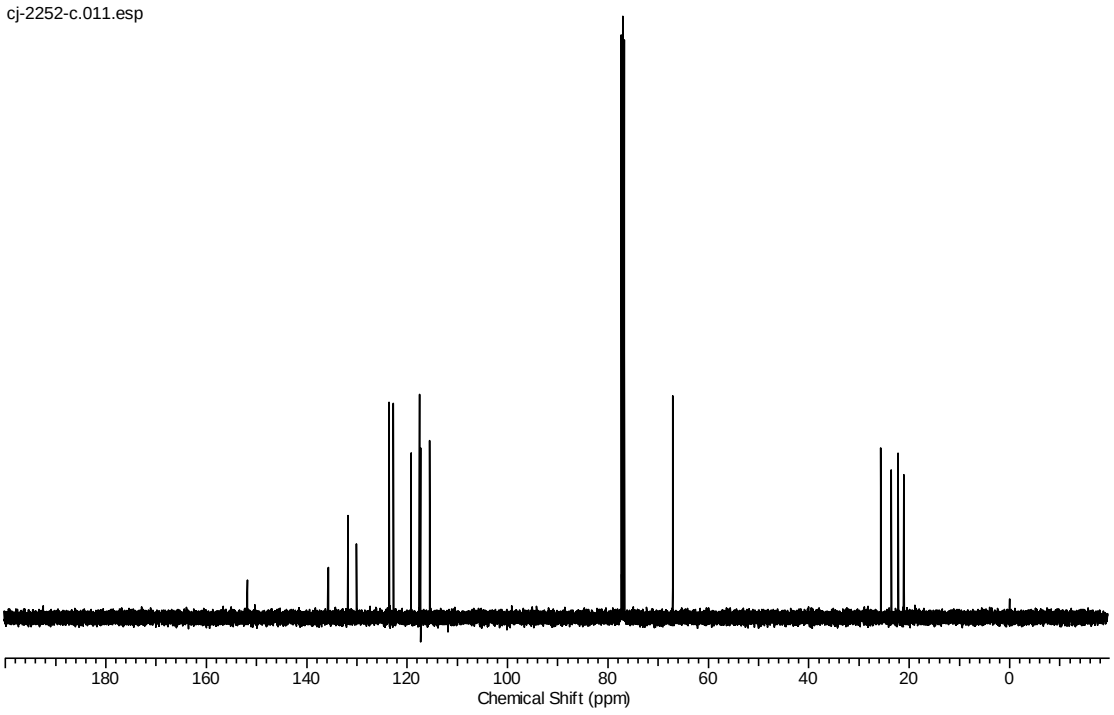
Chemical Shift (ppm)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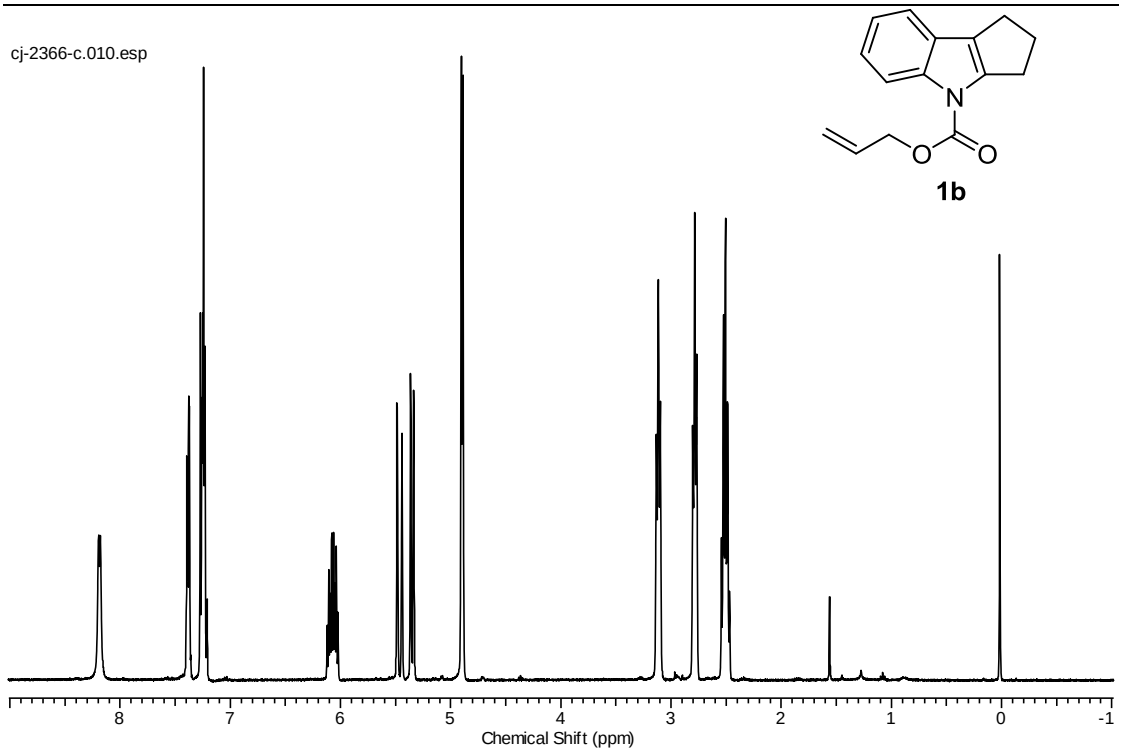
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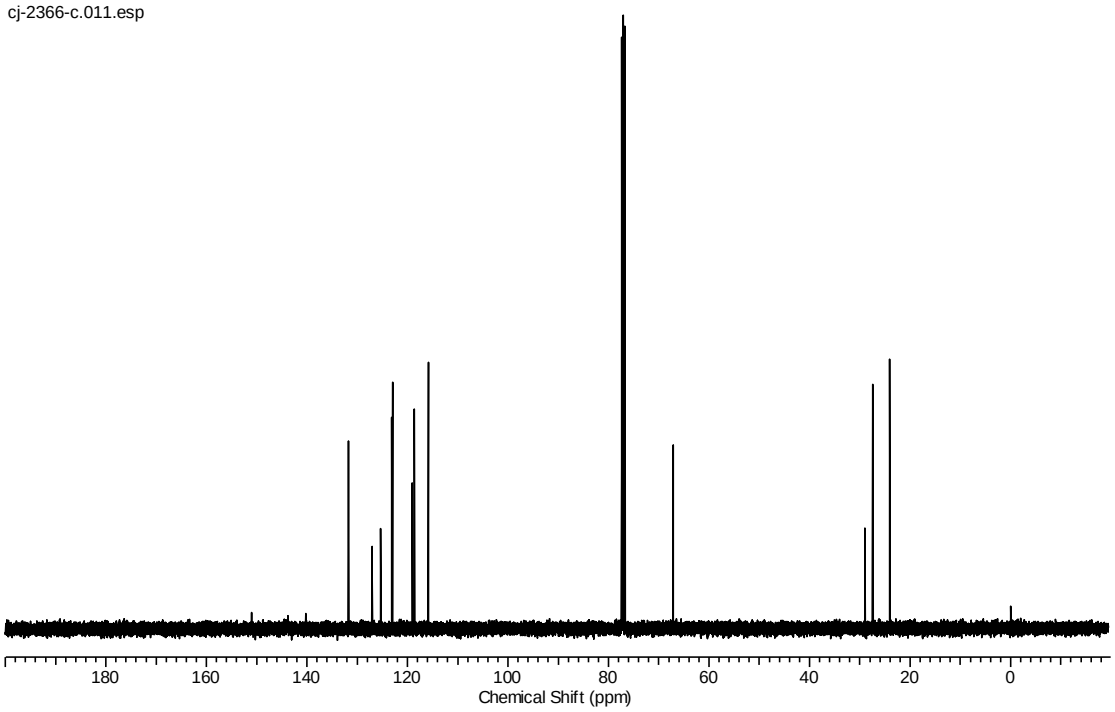
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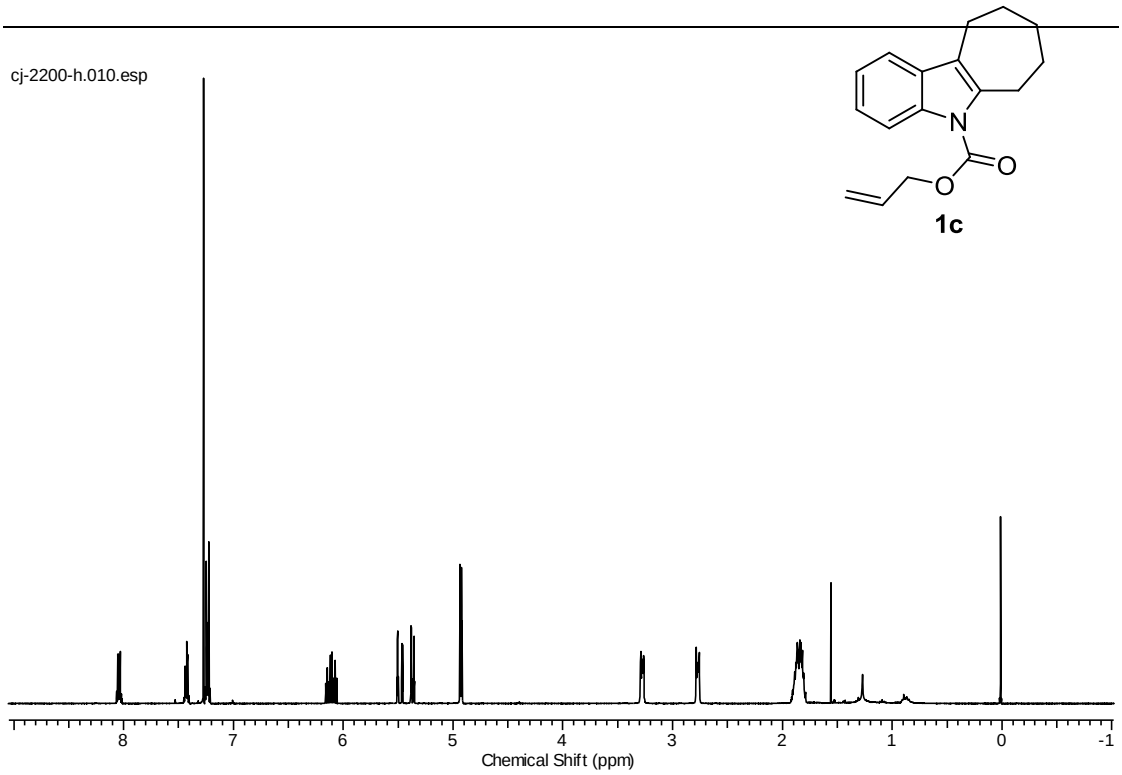
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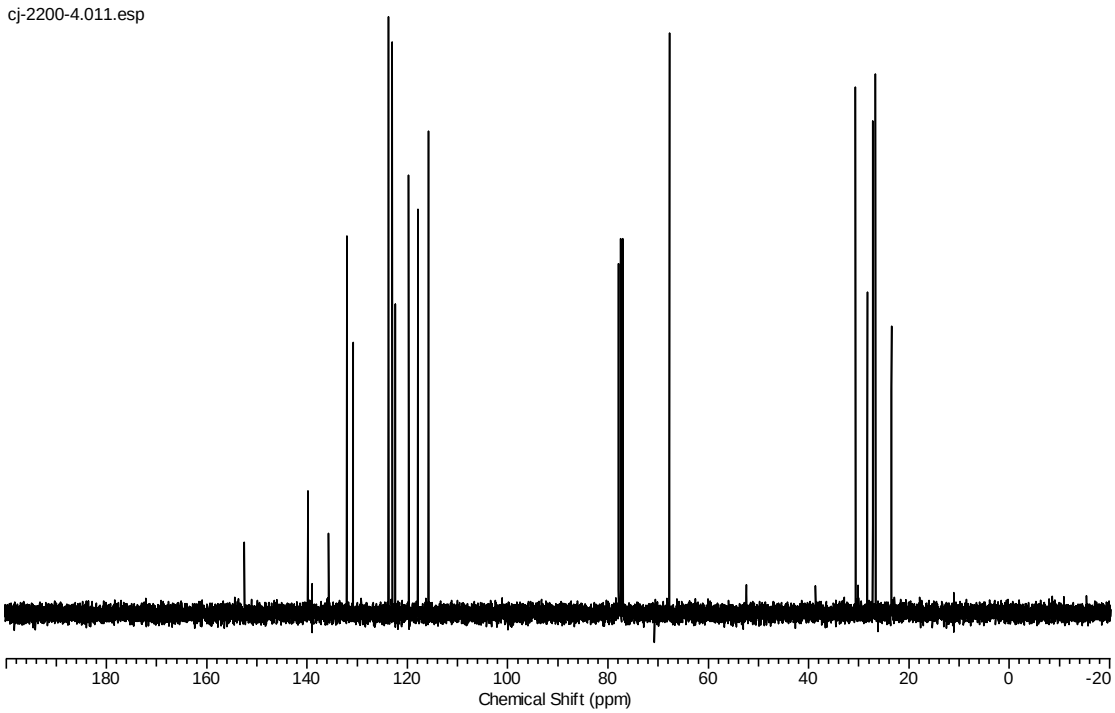
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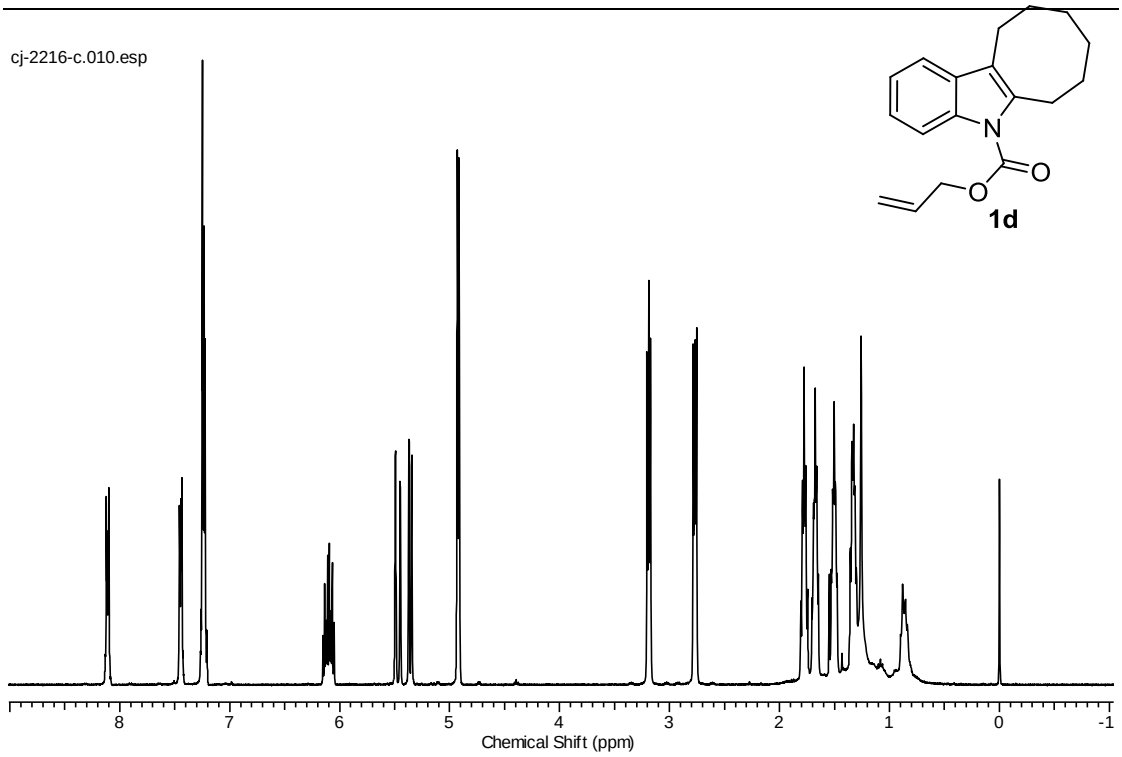
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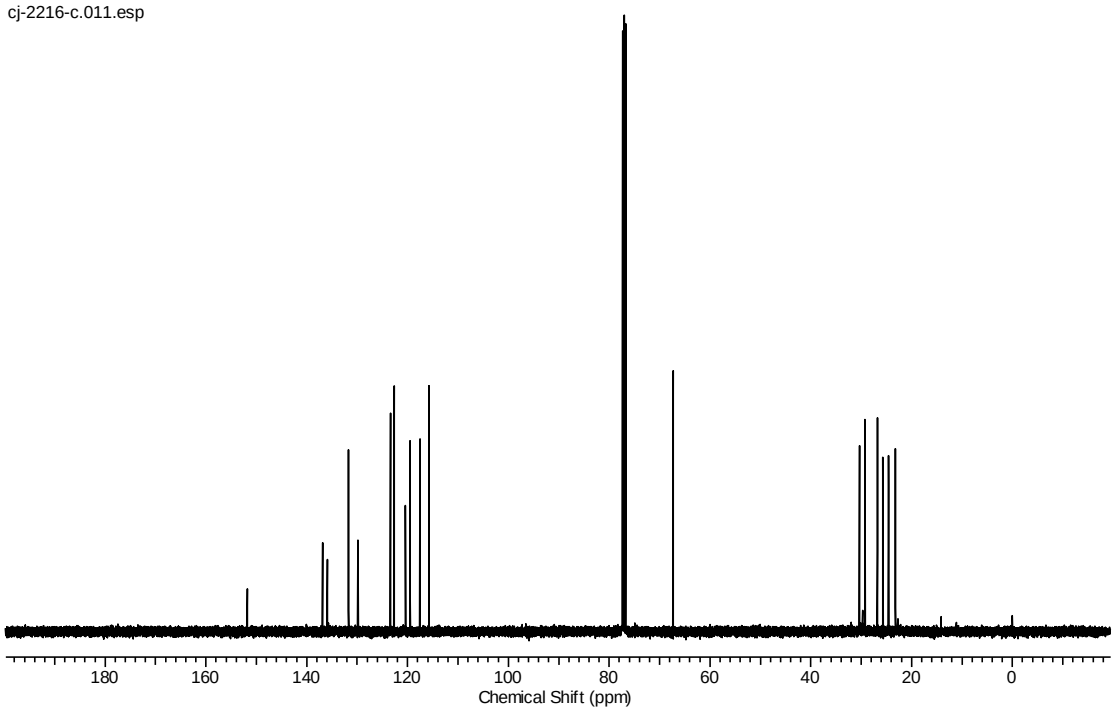
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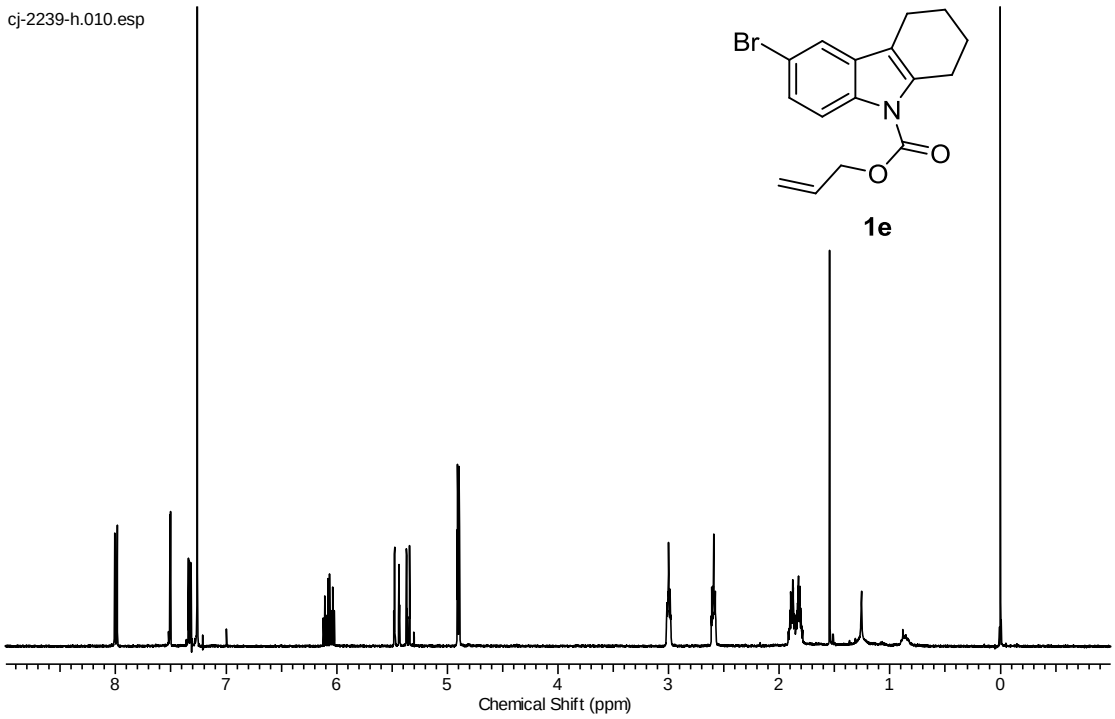
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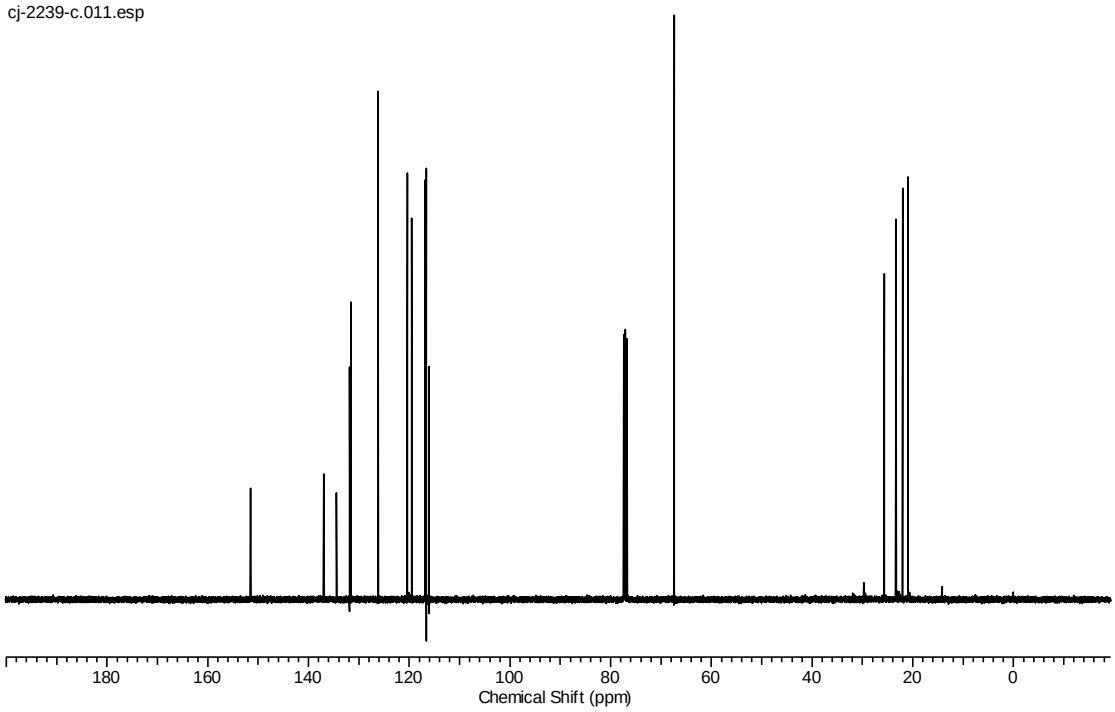
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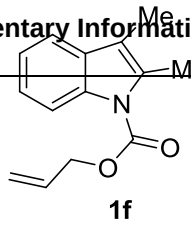

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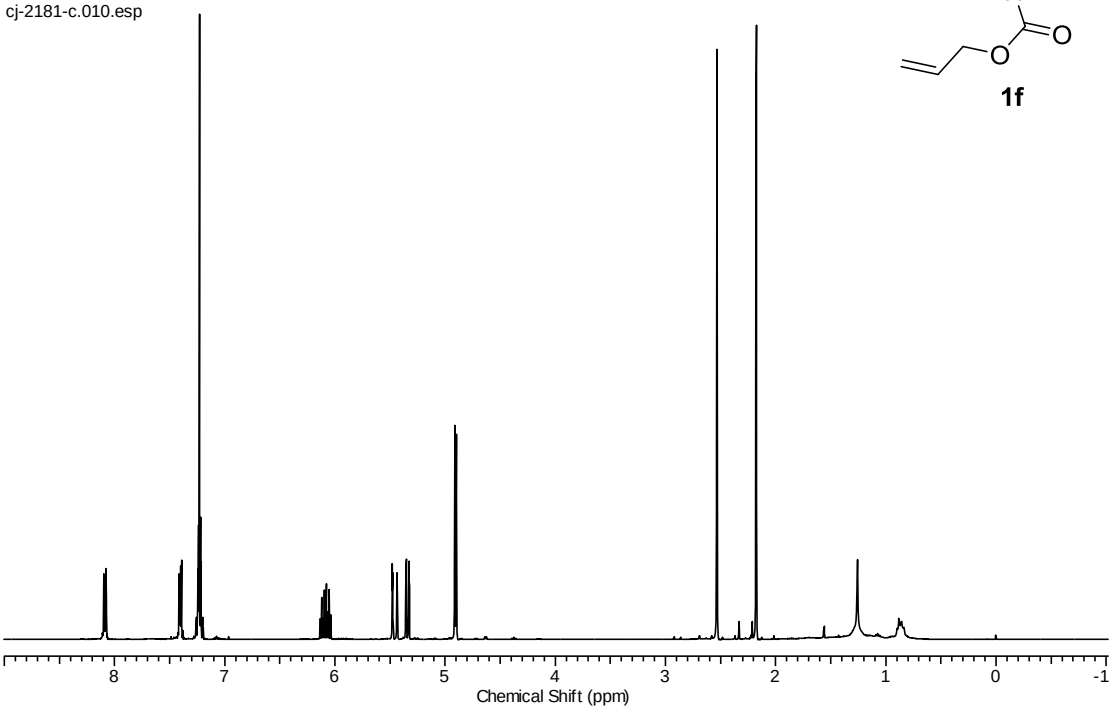

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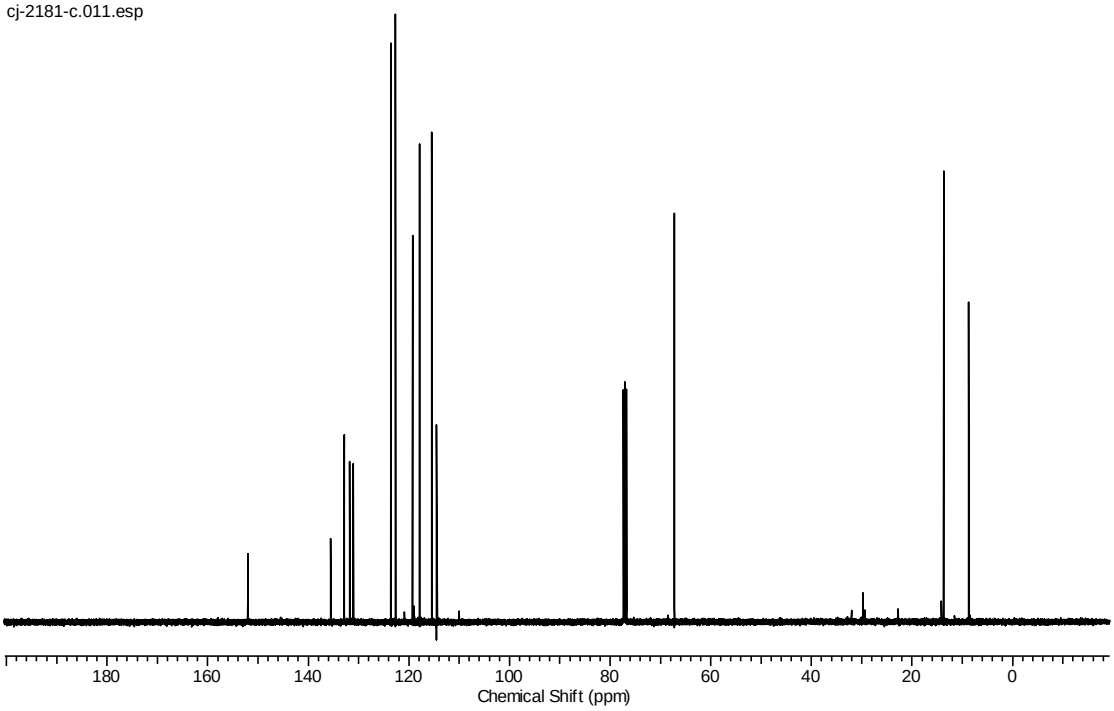

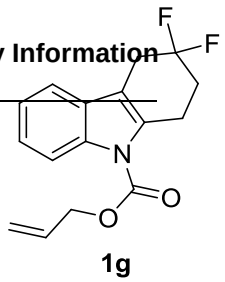

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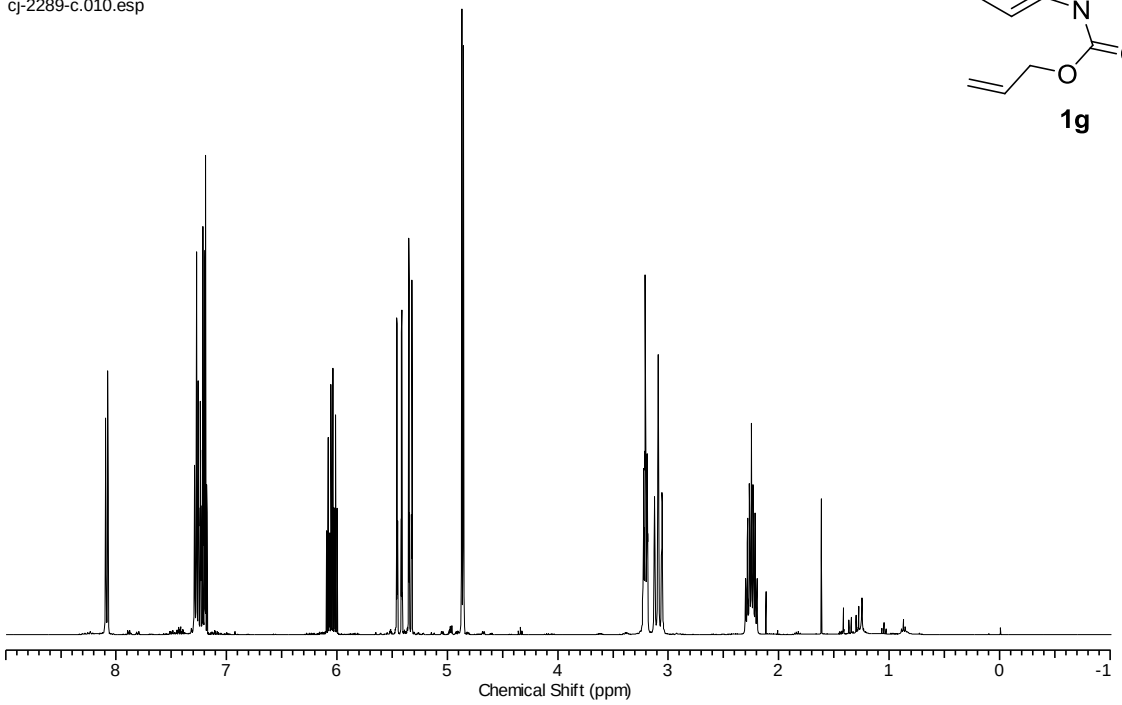

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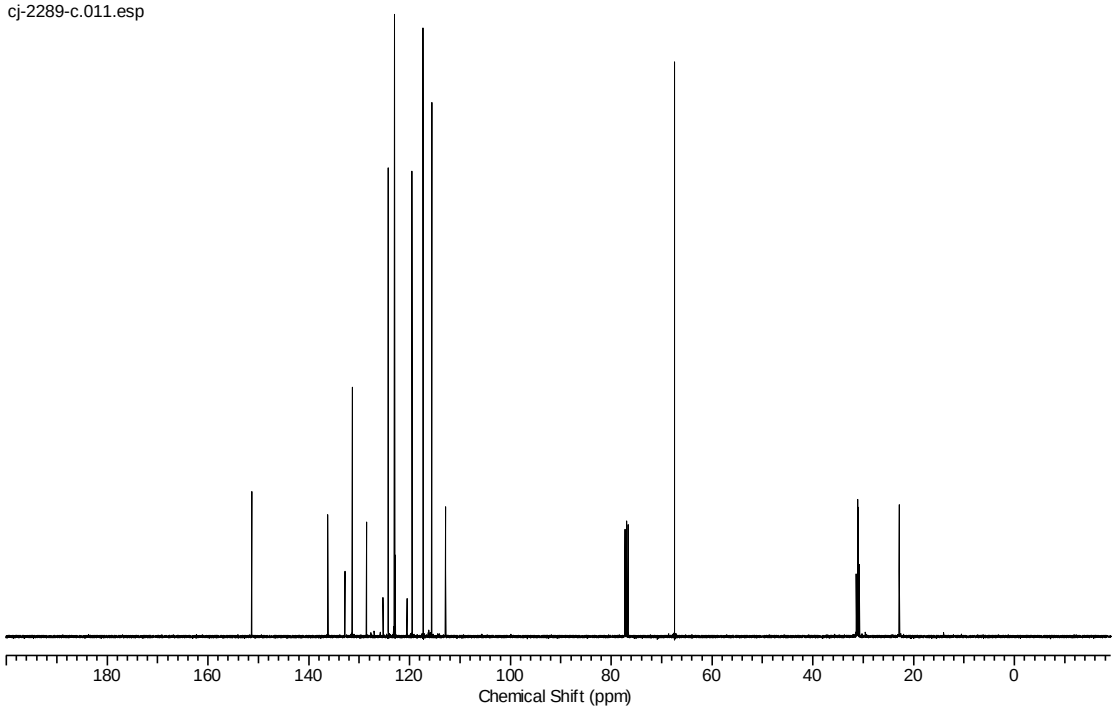

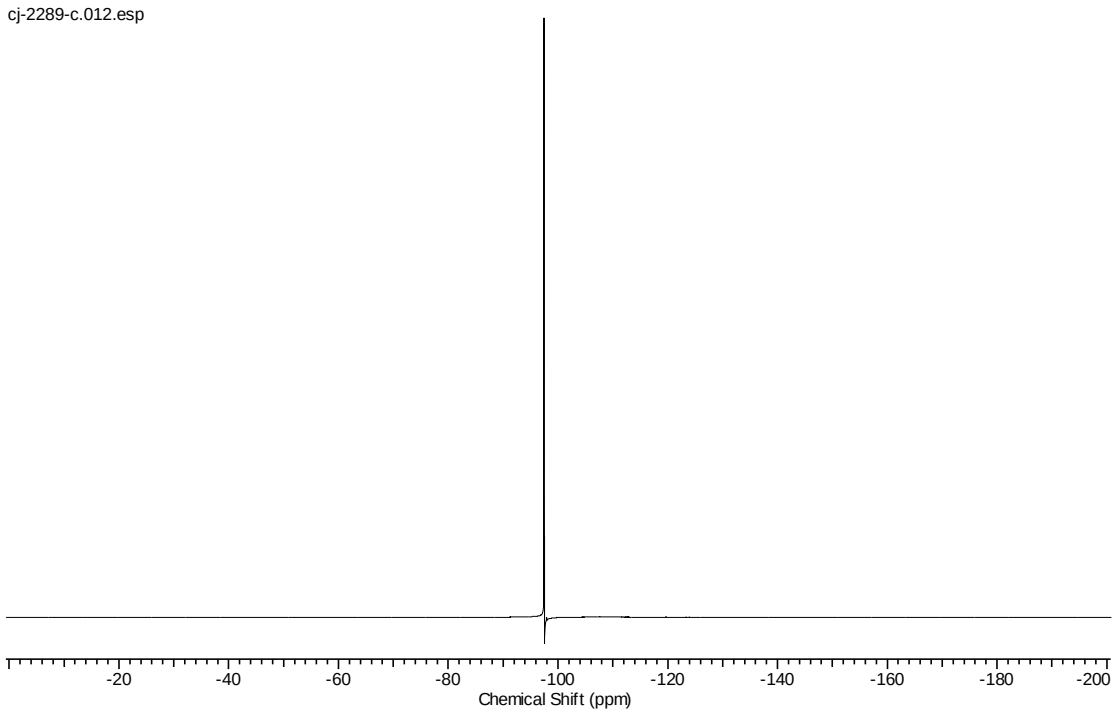
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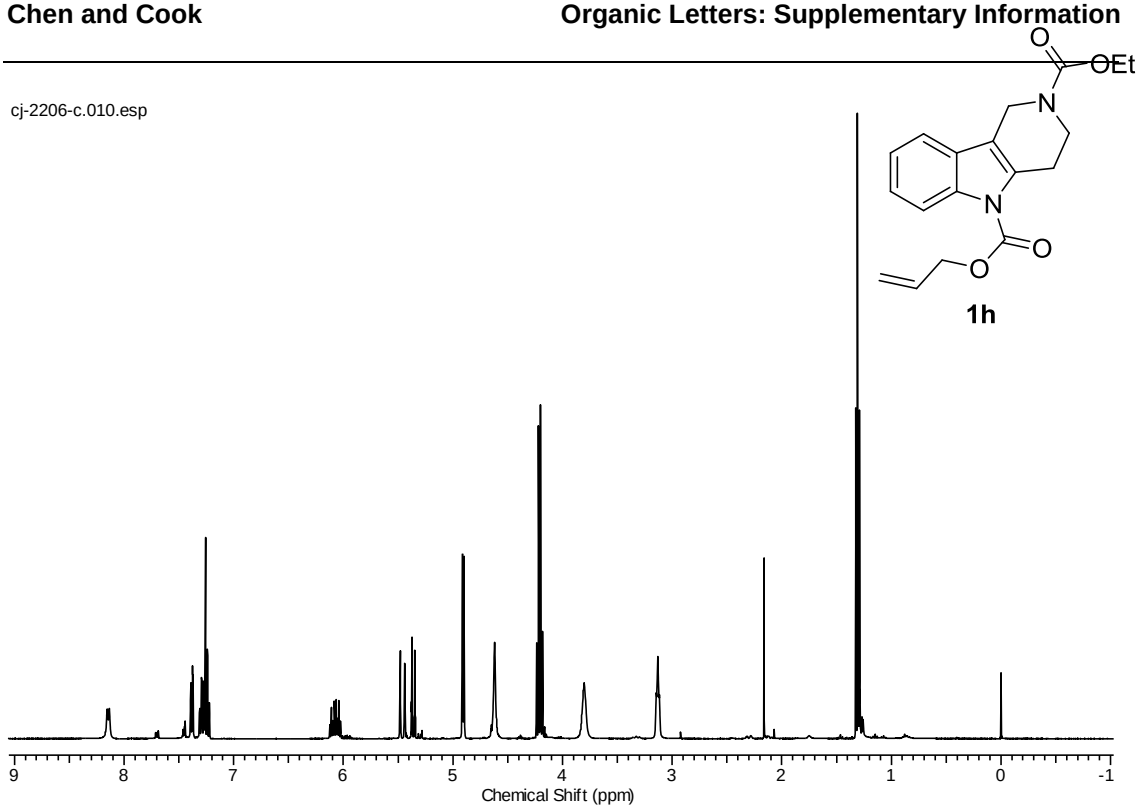

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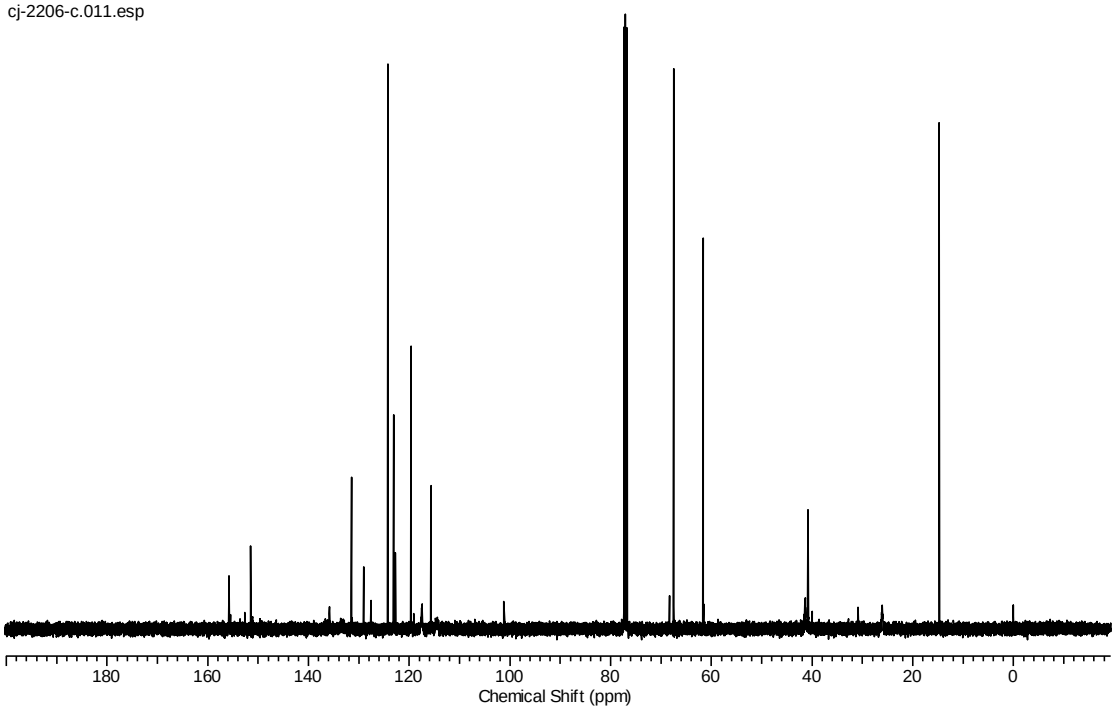

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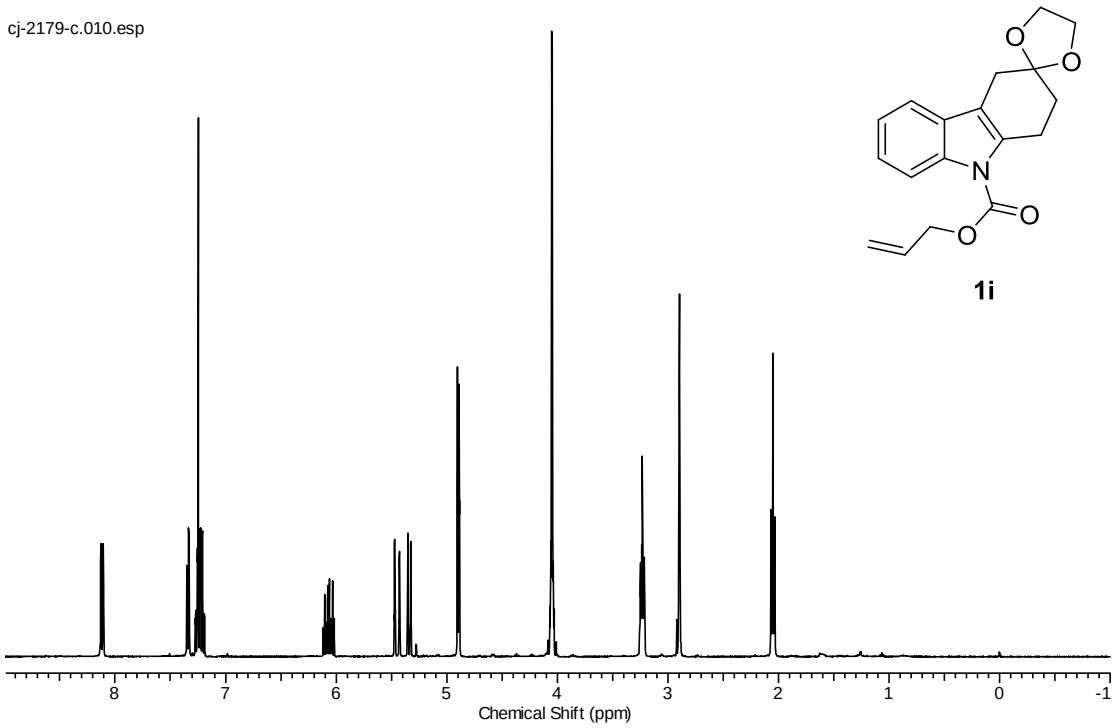

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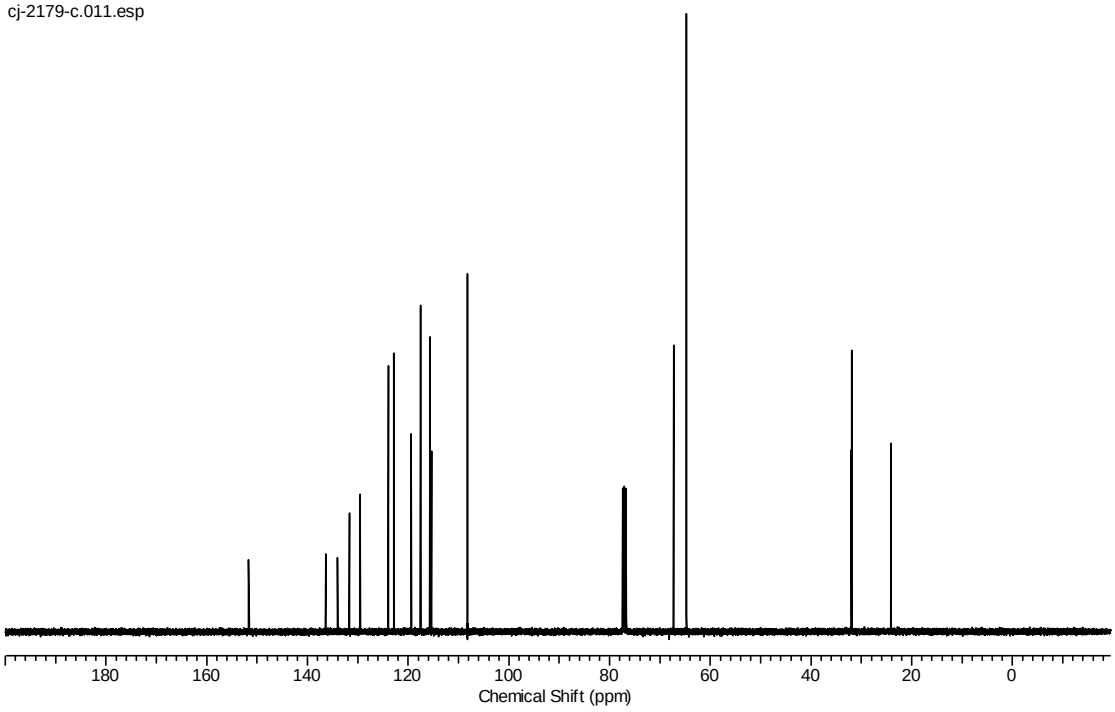

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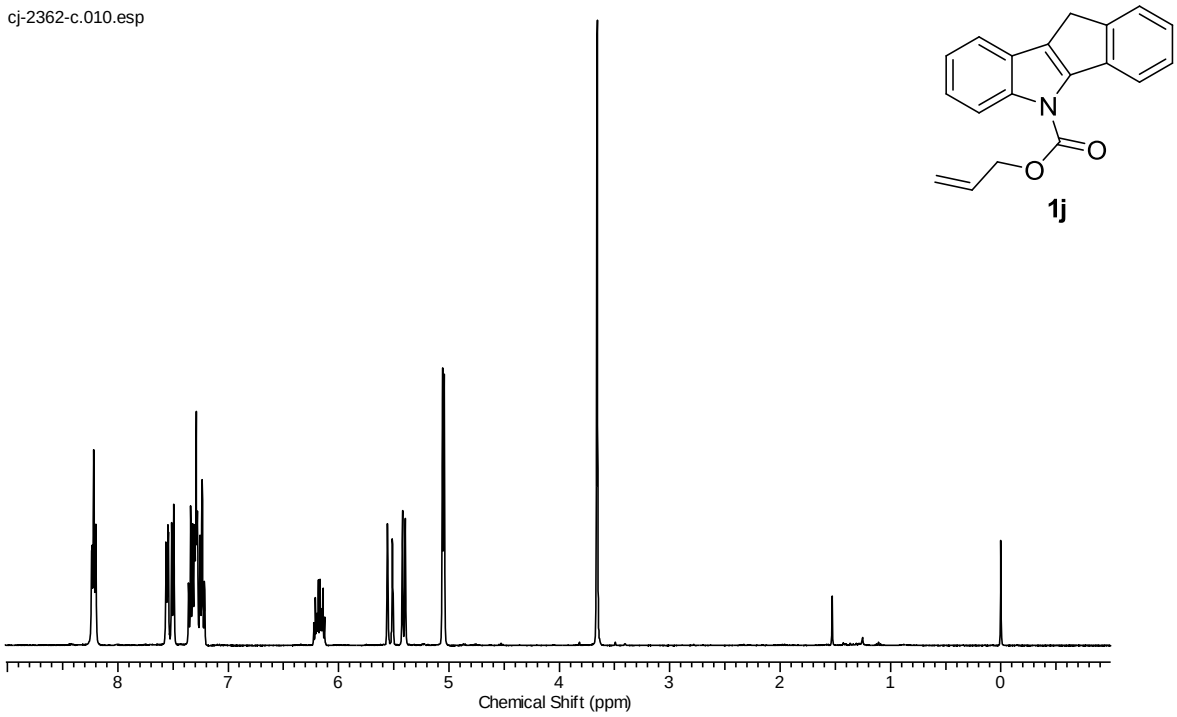
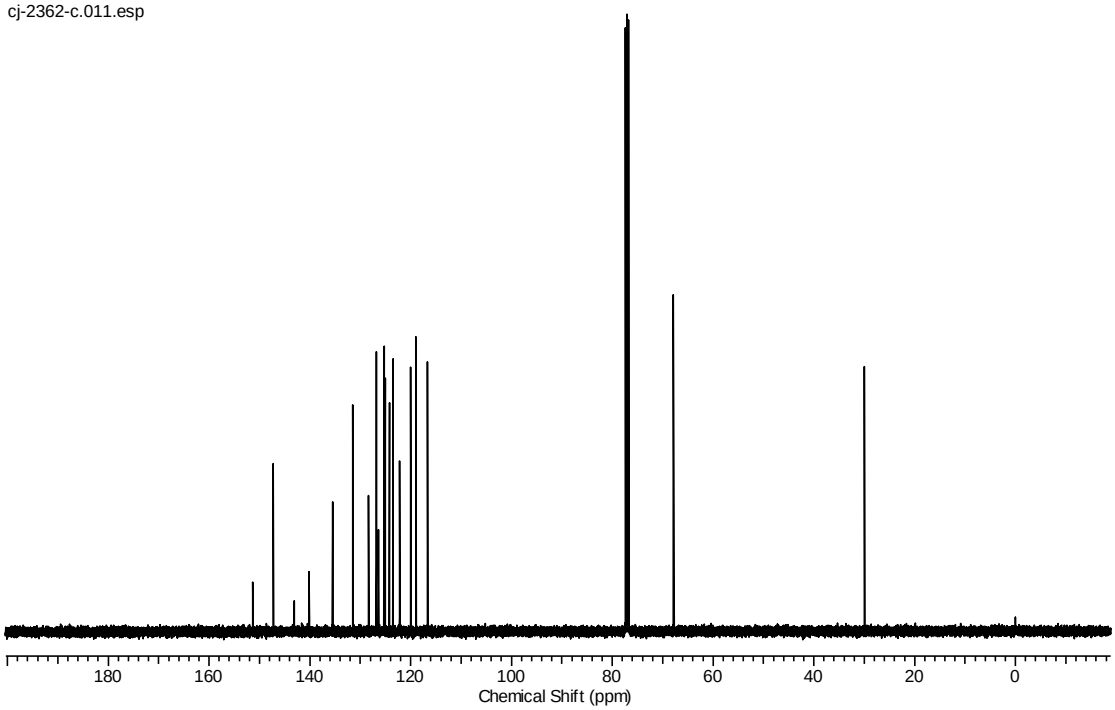
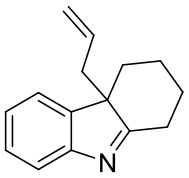


1j

cj-2362-c.011.esp

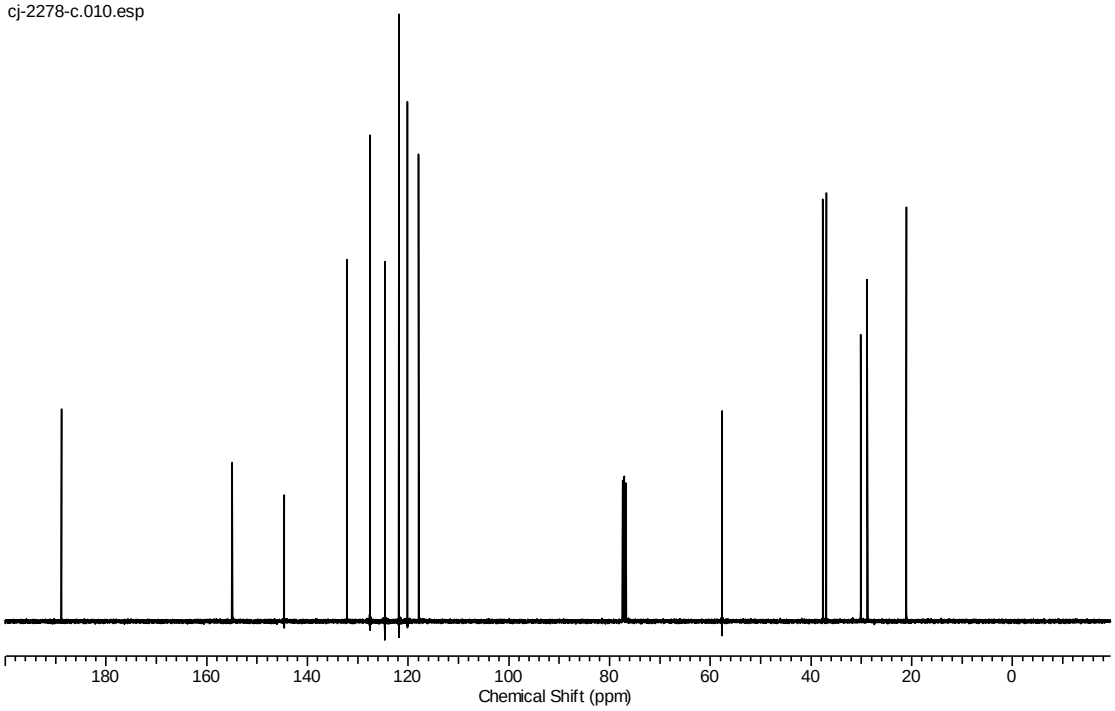


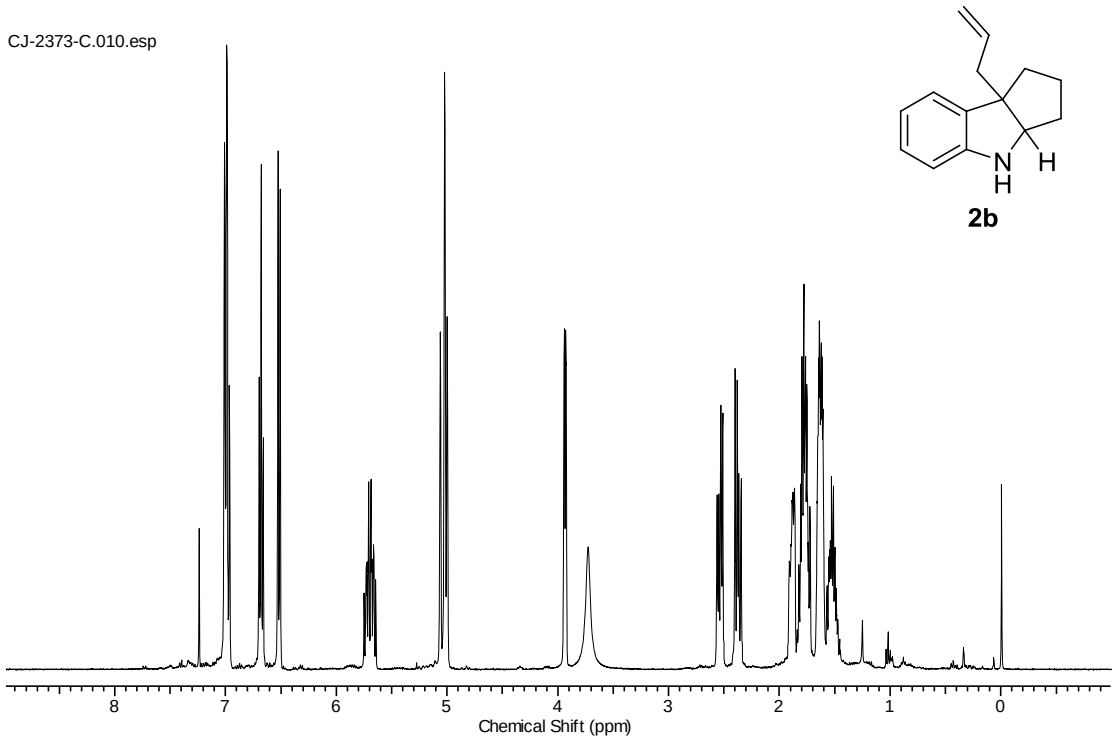
cj-2278-c.020.esp



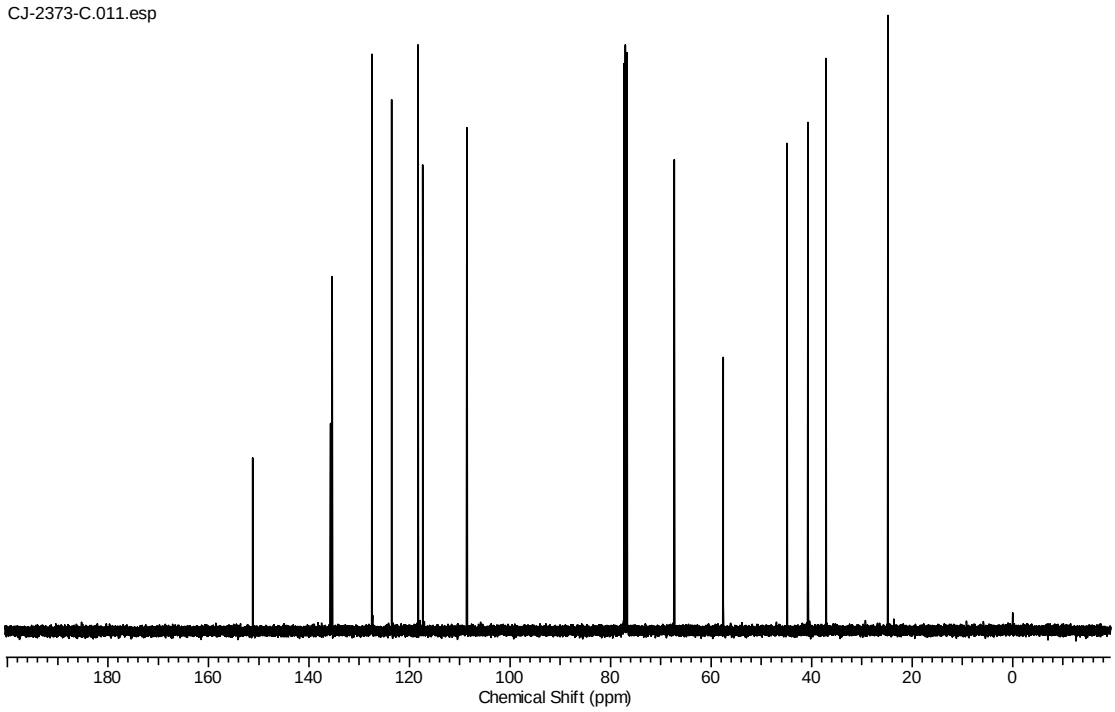
2a

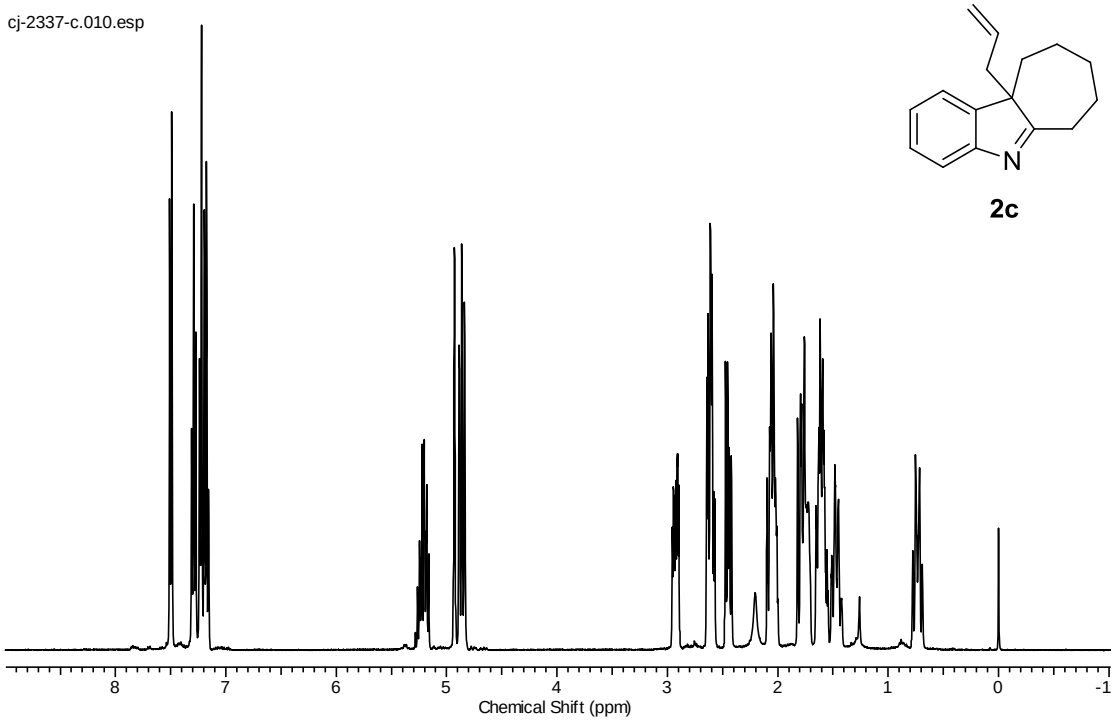
cj-2278-c.010.esp

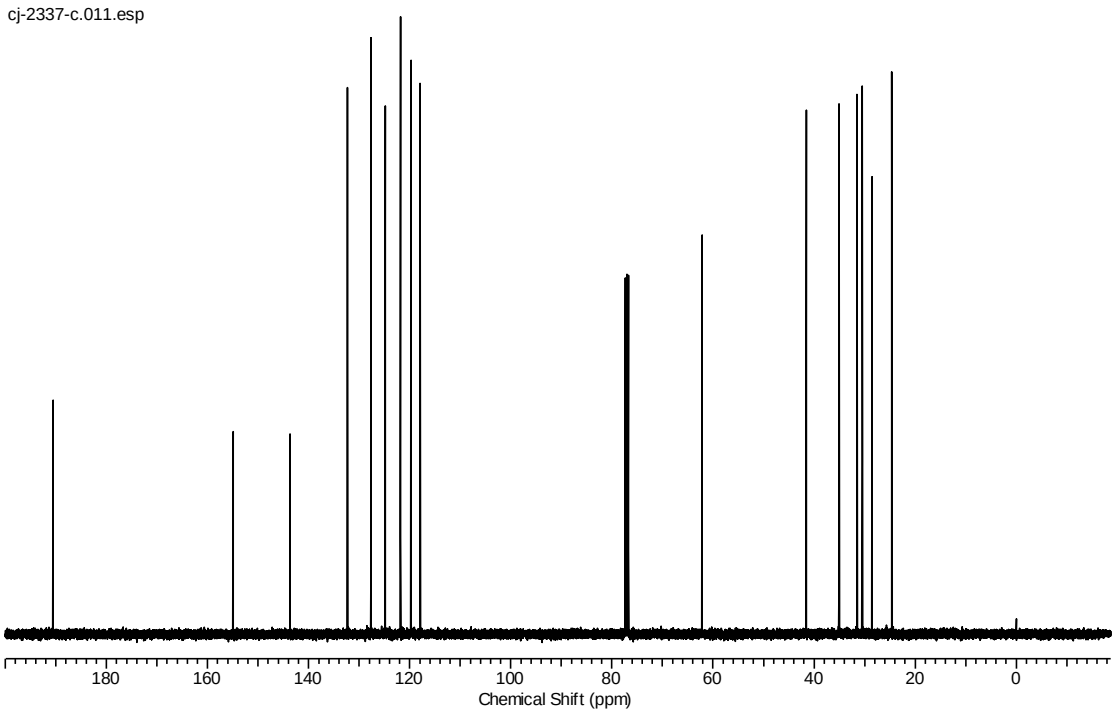



CJ-2373-C.010.esp
N
H
H
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

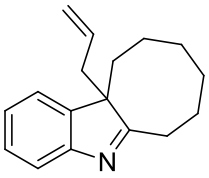
2b


CJ-2373-C.011.esp
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


cj-2337-c.010.esp
N
2c
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)

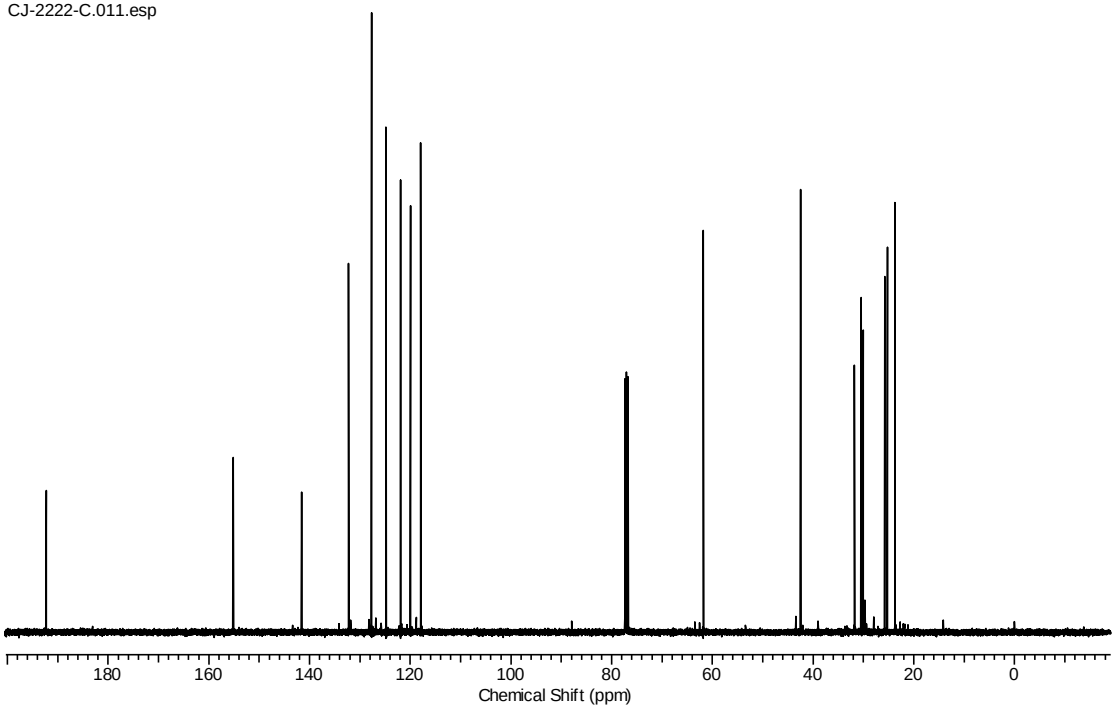

cj-2337-c.011.esp
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

CJ-2222-C.010.esp

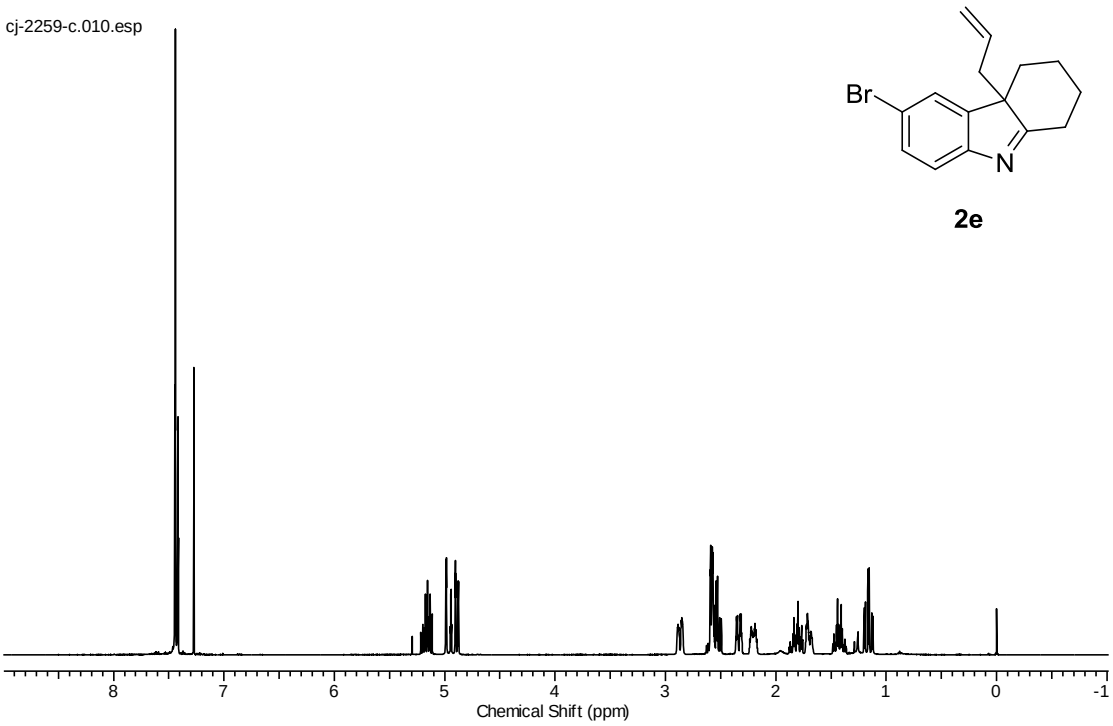


2d

CJ-2222-C.011.esp

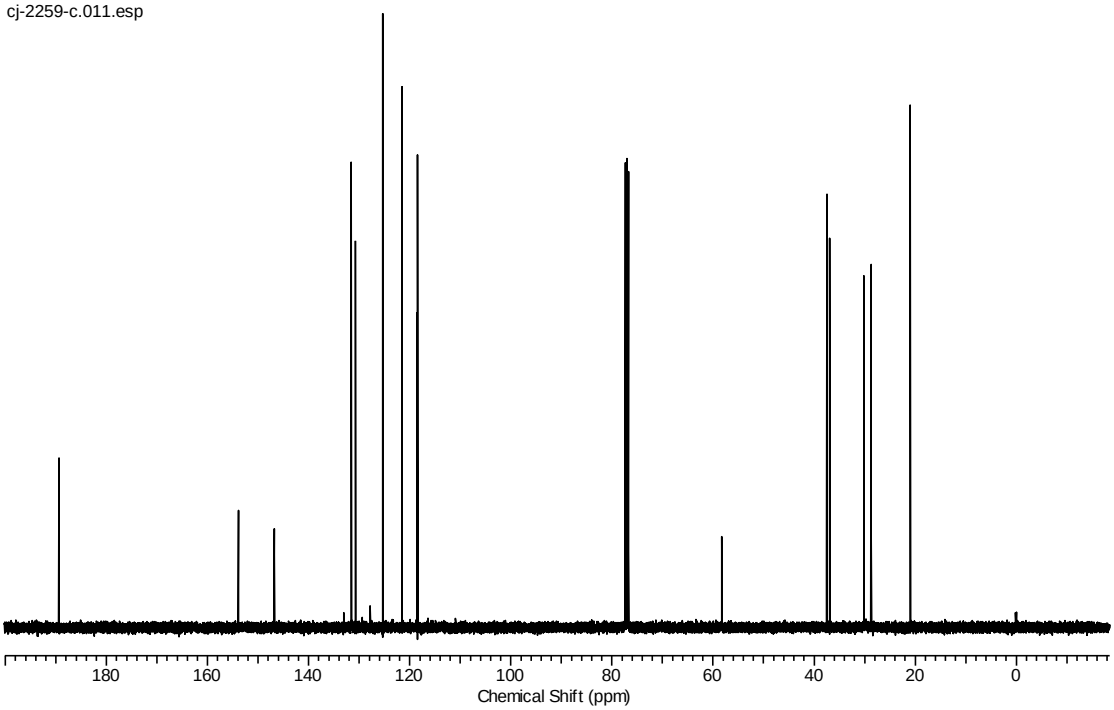


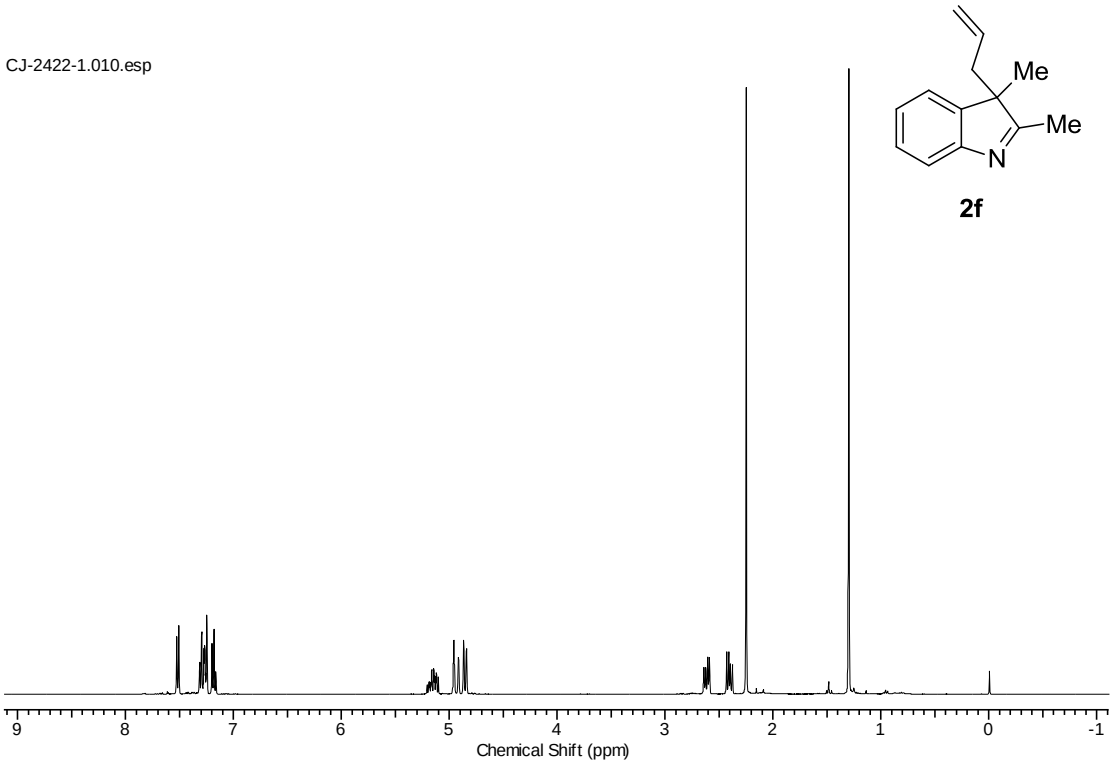
cj-2259-c.010.esp



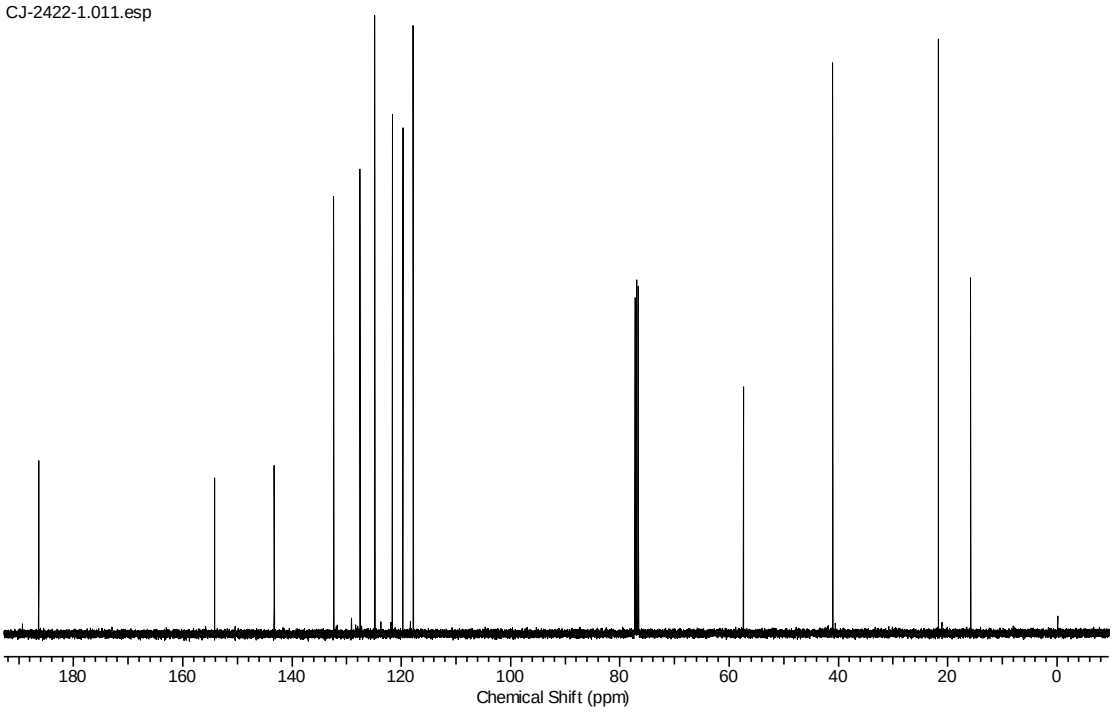
2e

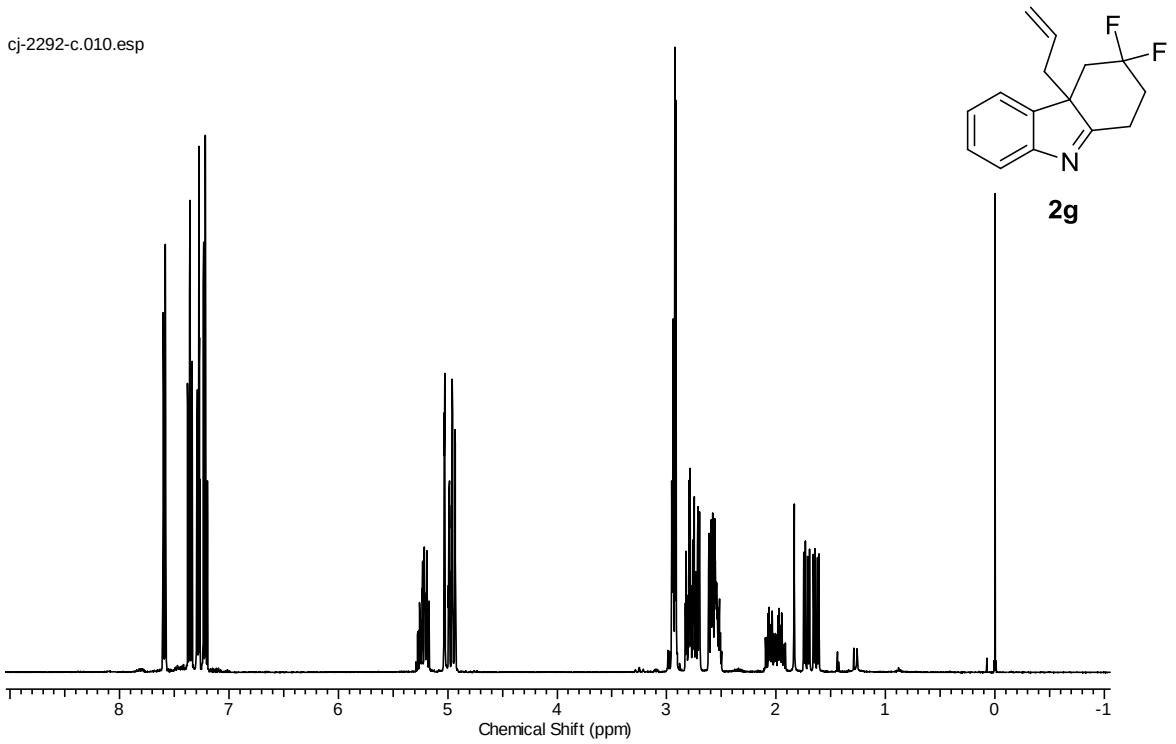
cj-2259-c.011.esp

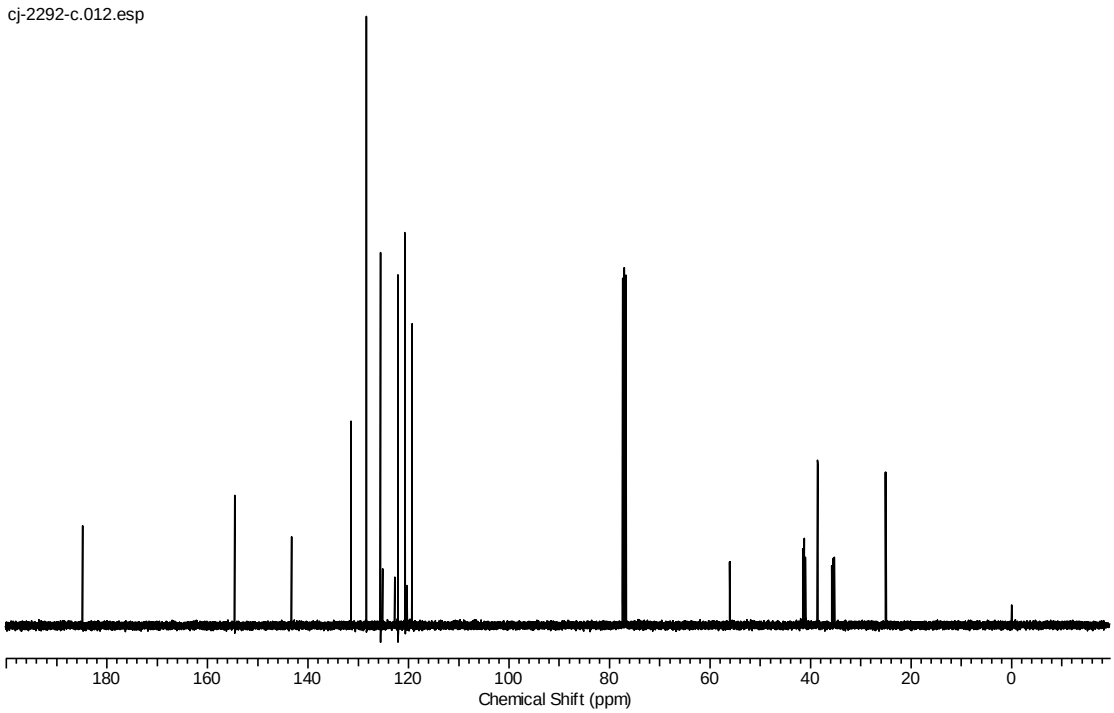


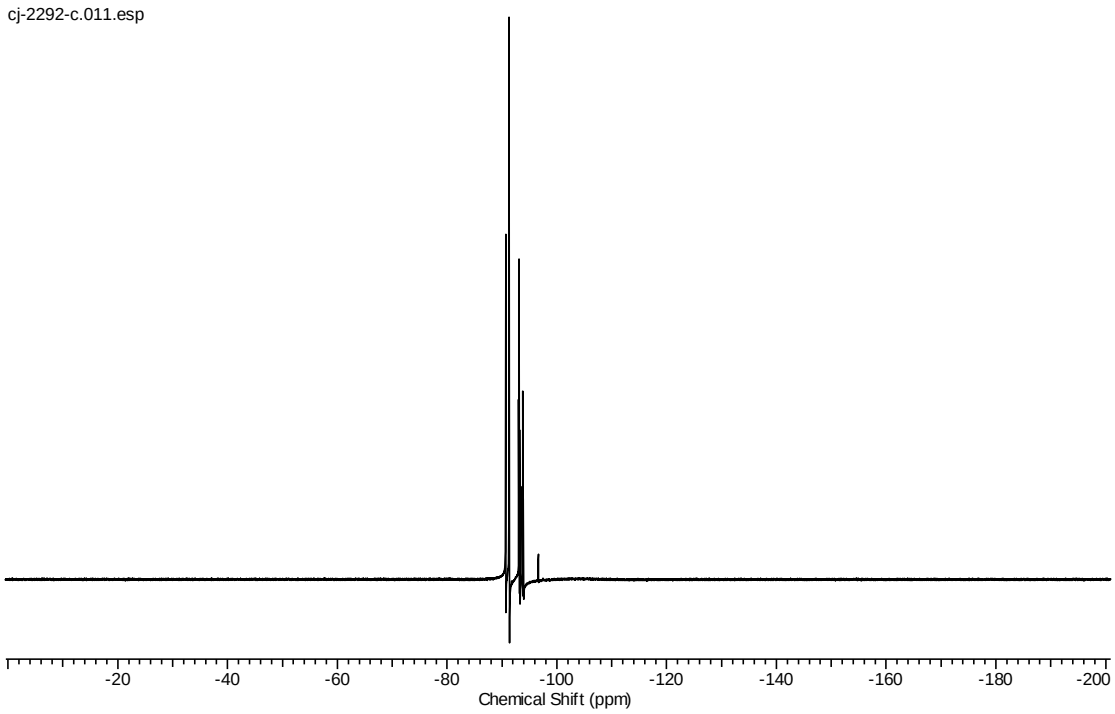

CJ-2422-1.010.esp
Me
Me
N
9
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)

2f

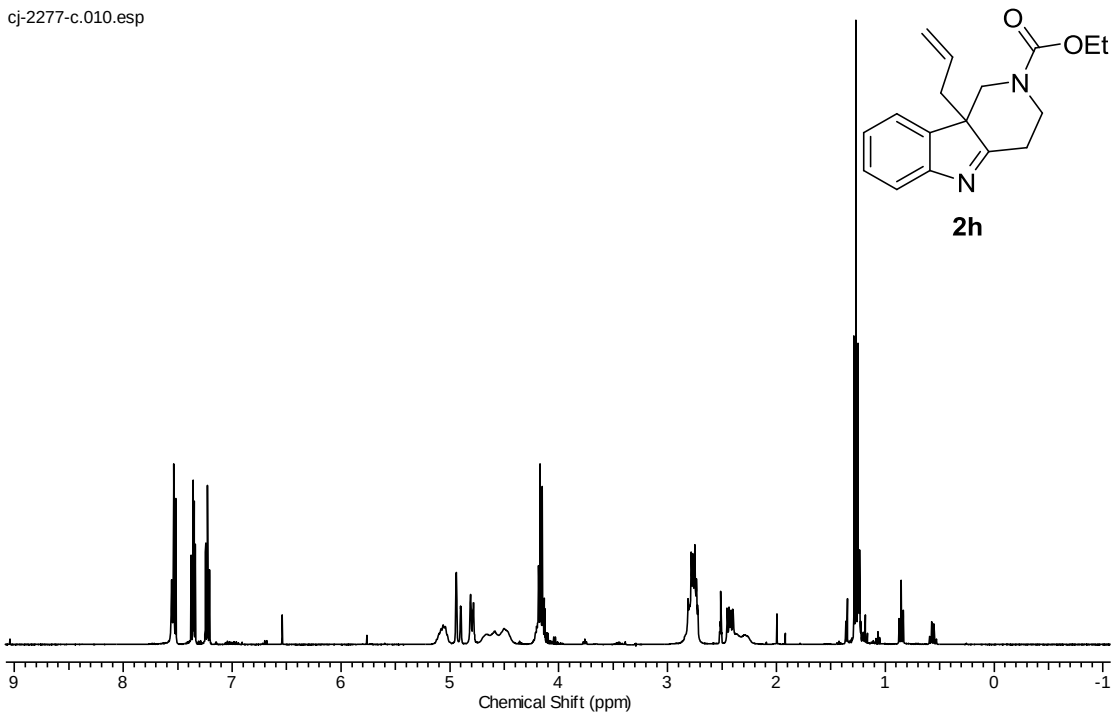

CJ-2422-1.011.esp
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


cj-2292-c.010.esp
F
F
N
2g
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)


cj-2292-c.012.esp
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

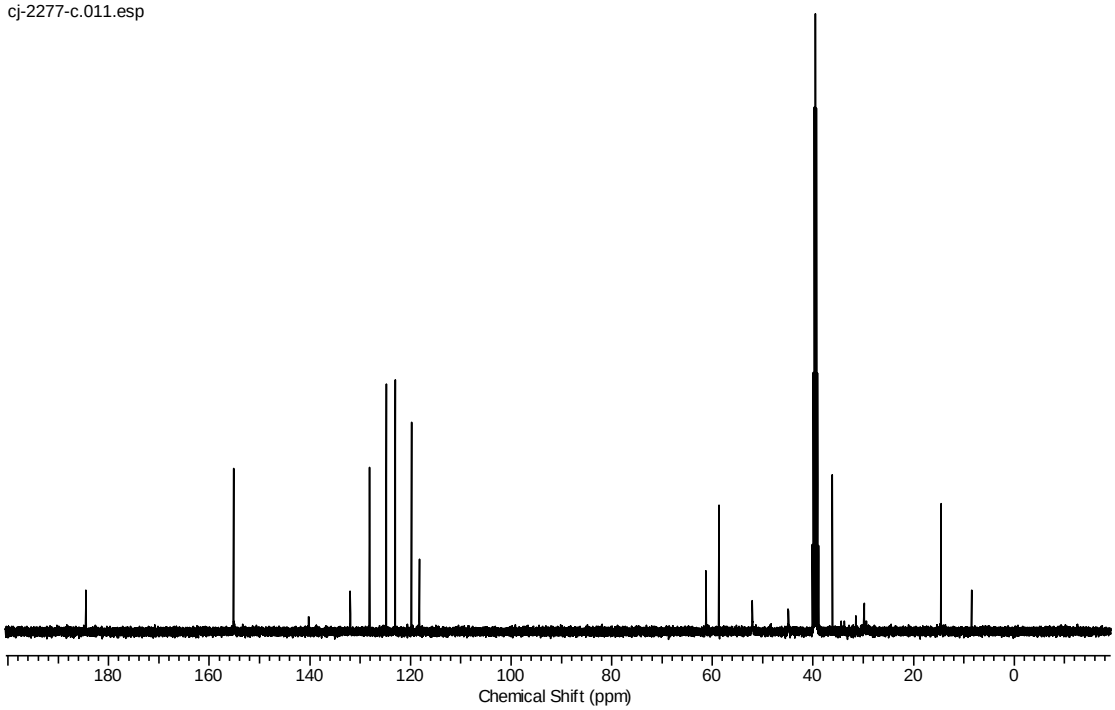

cj-2292-c.011.esp
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
Chemical Shift (ppm)

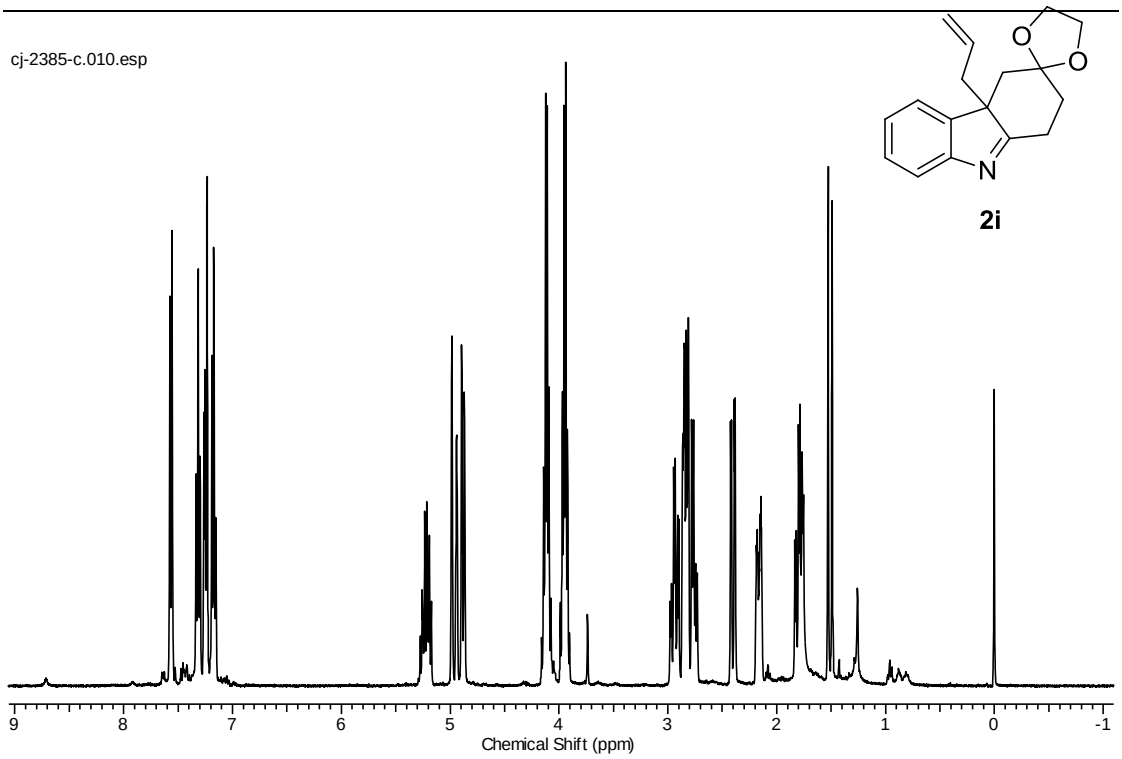
cj-2277-c.010.esp

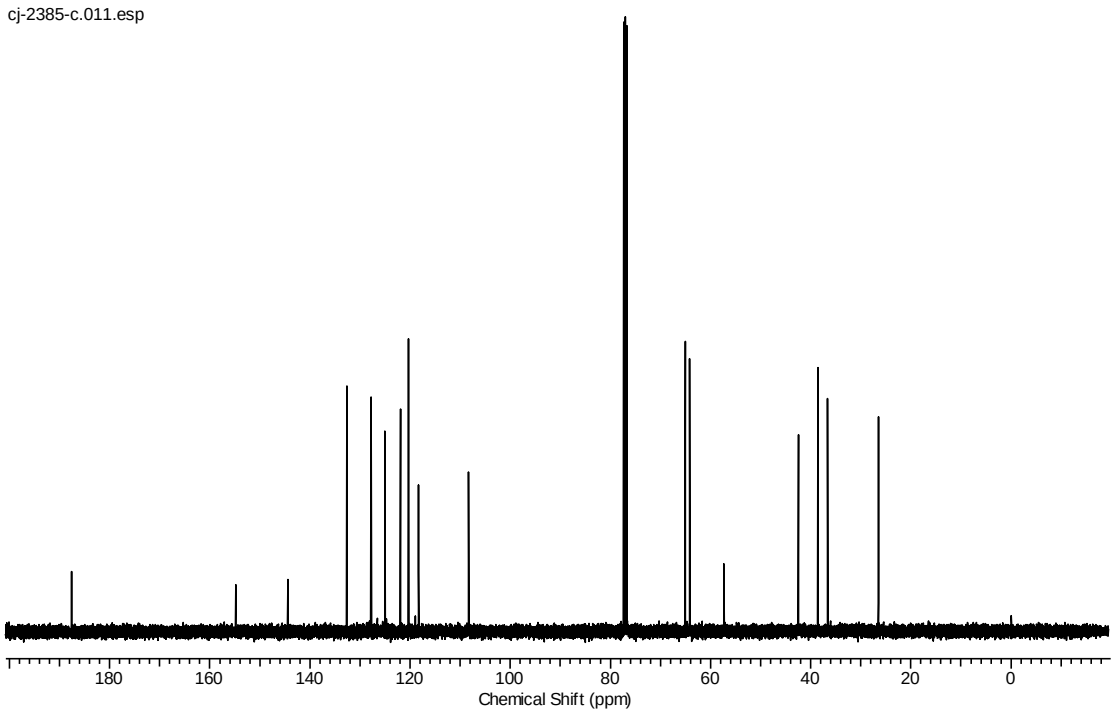


2h

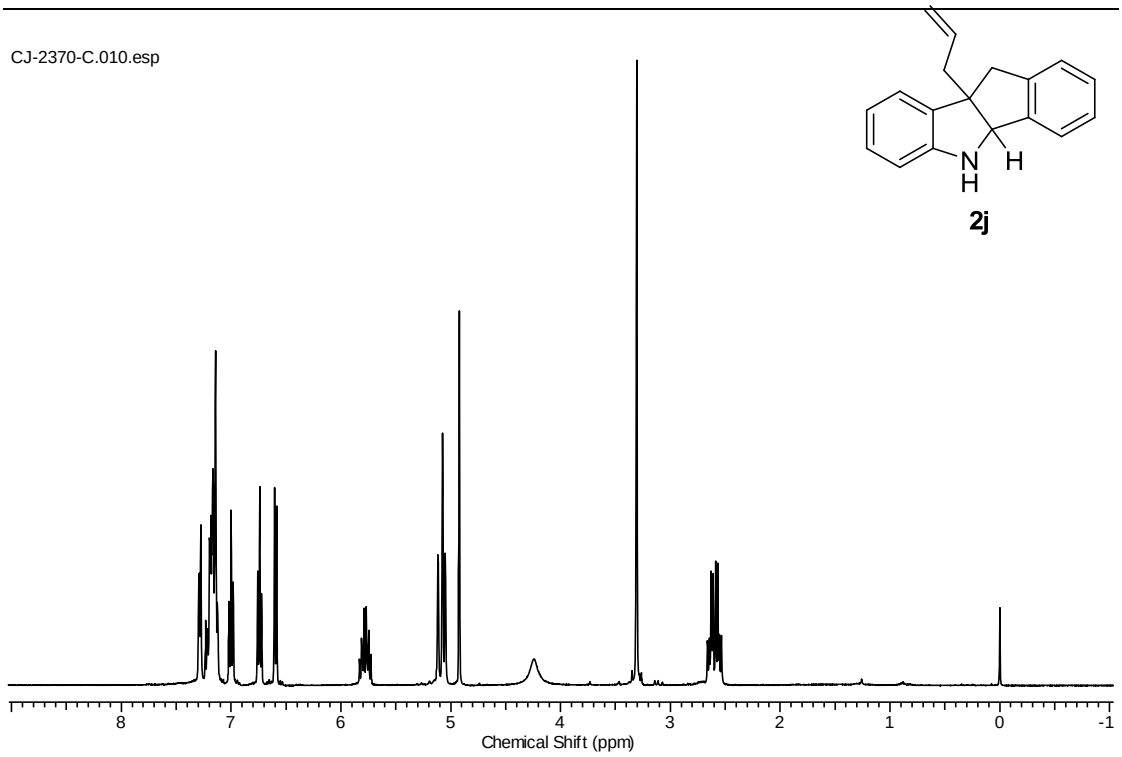
cj-2277-c.011.esp




cj-2385-c.010.esp
O
O
N
2i
9
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)

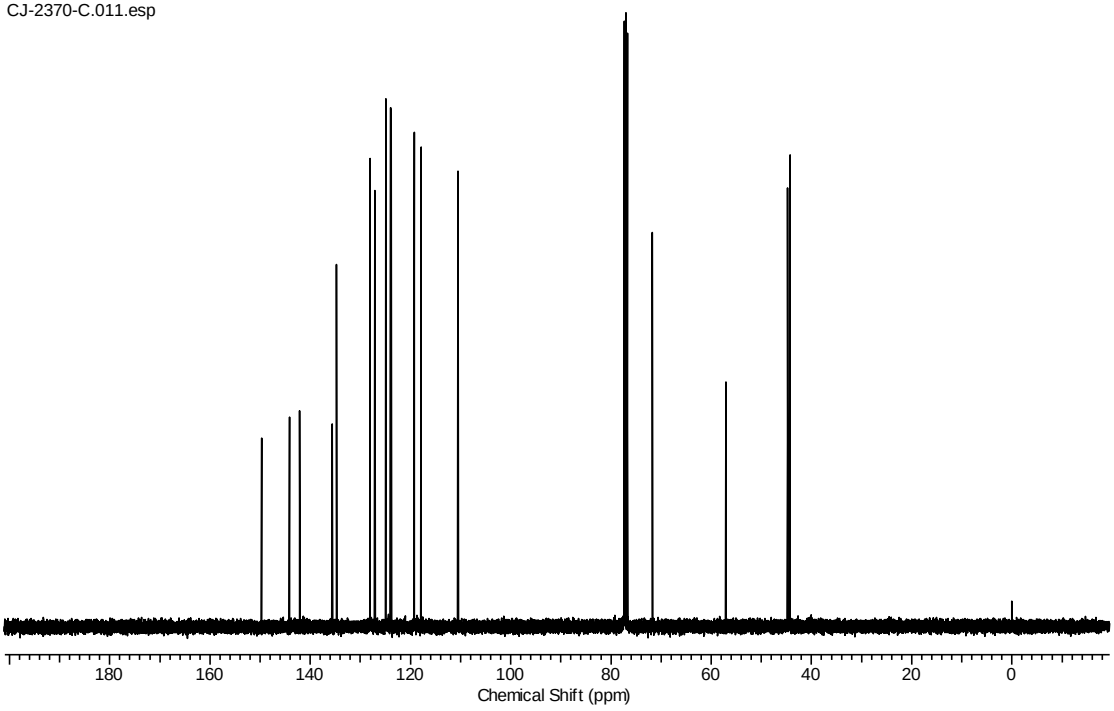

cj-2385-c.011.esp
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

CJ-2370-C.010.esp

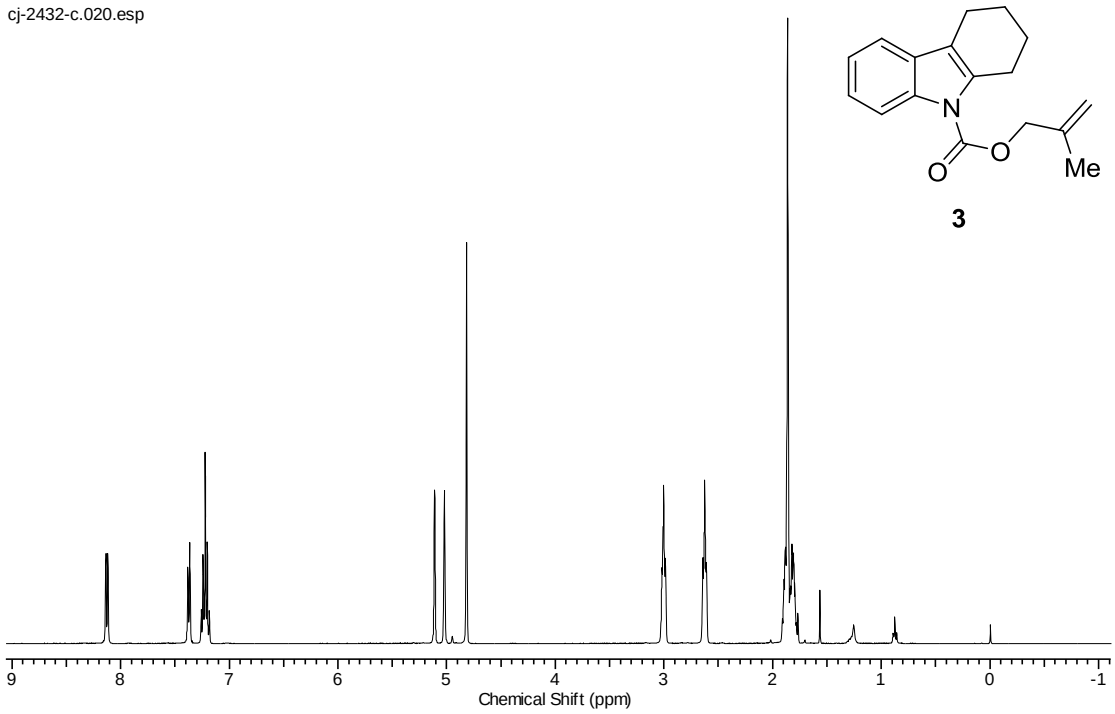


2j

CJ-2370-C.011.esp

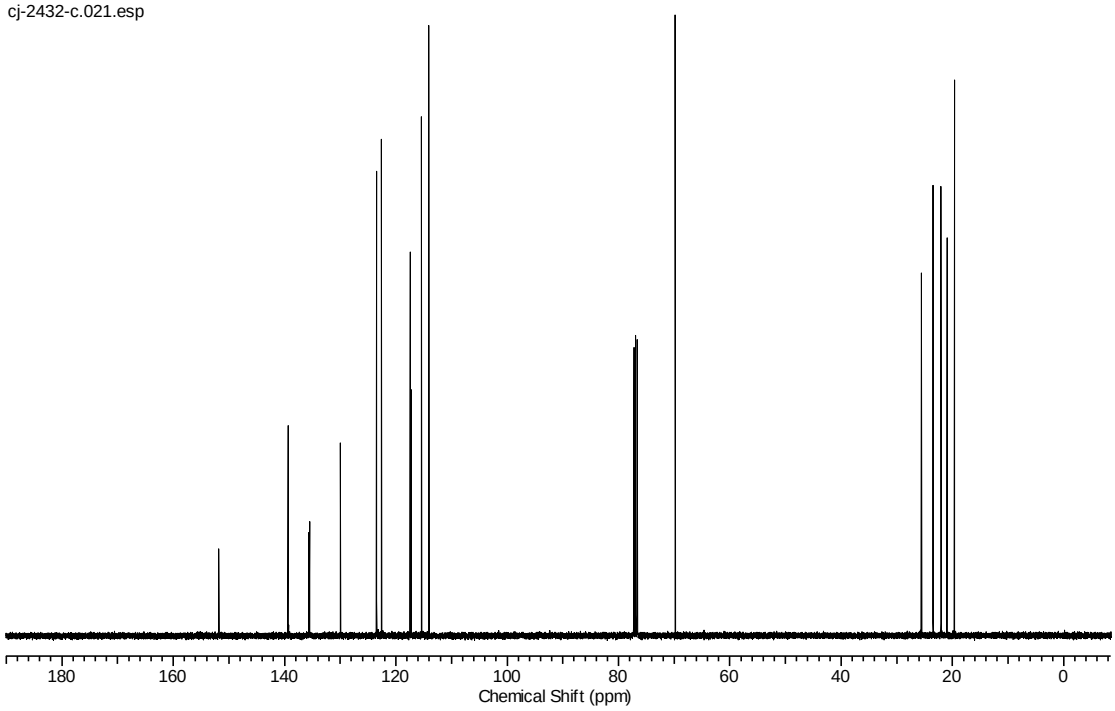


cj-2432-c.020.esp

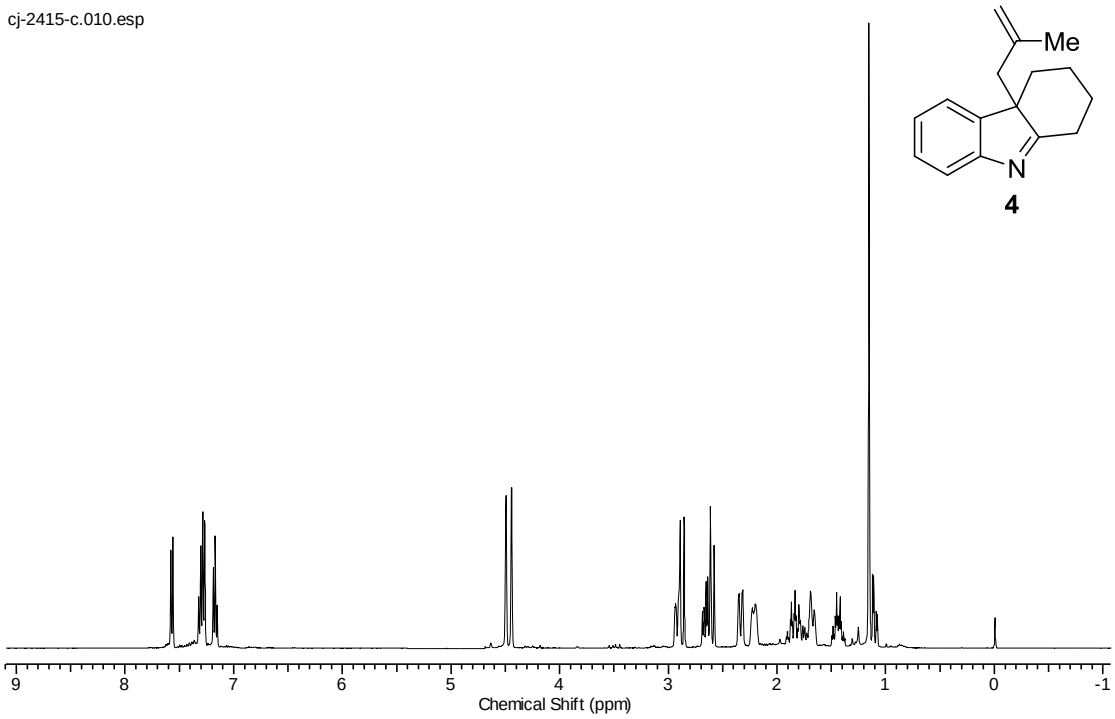


3

cj-2432-c.021.esp

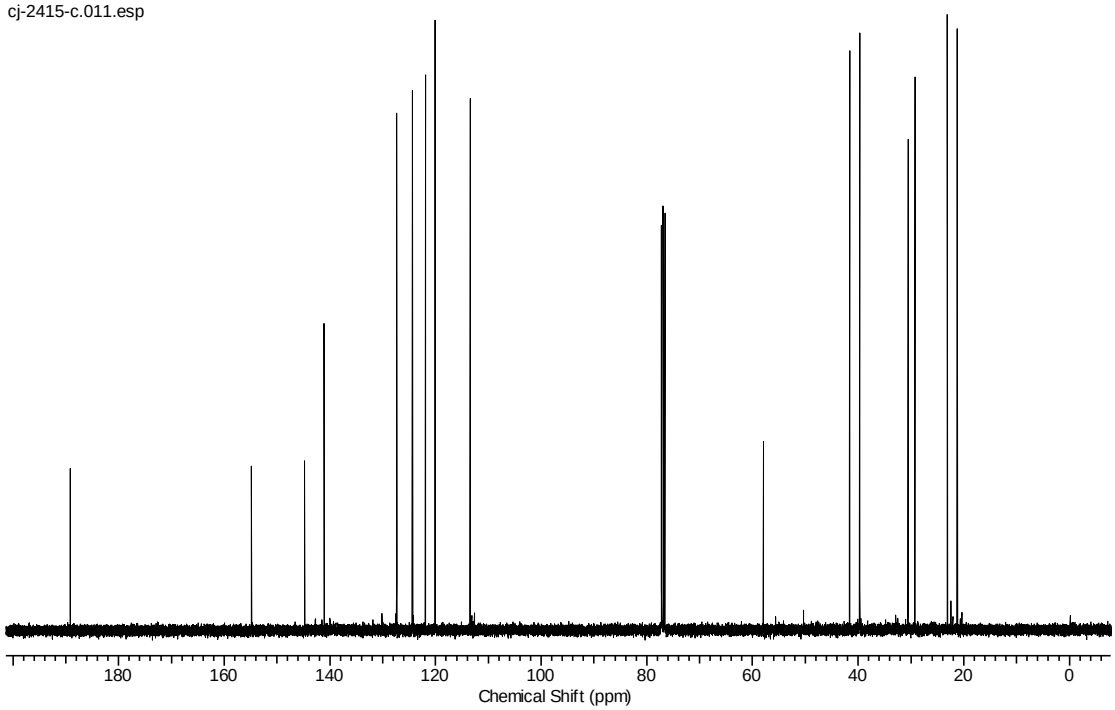


cj-2415-c.010.esp

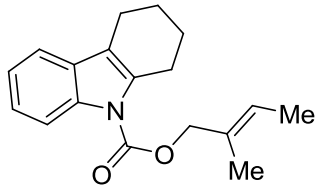


4

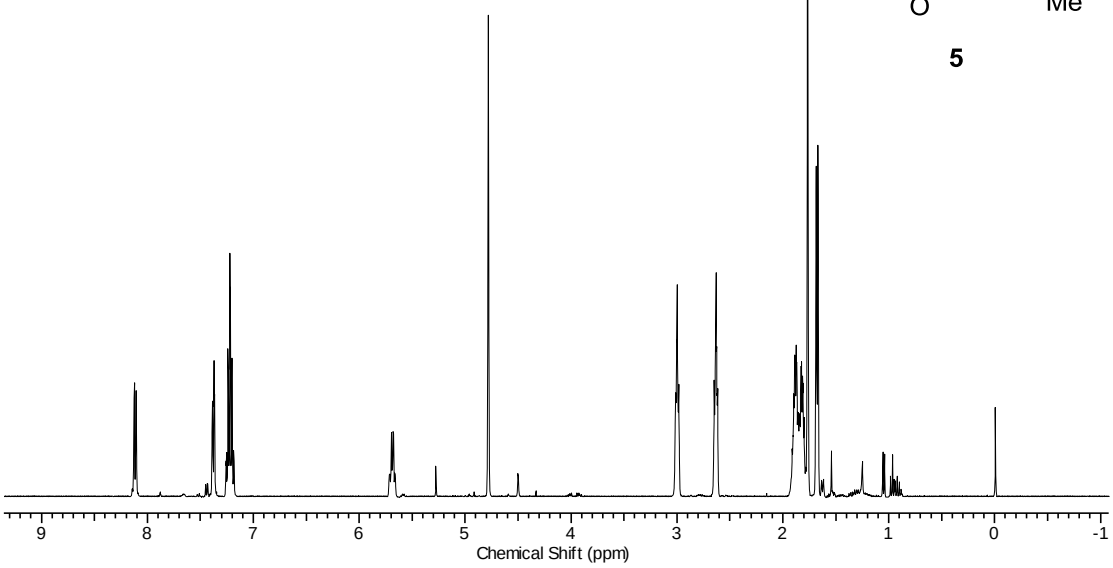
cj-2415-c.011.esp



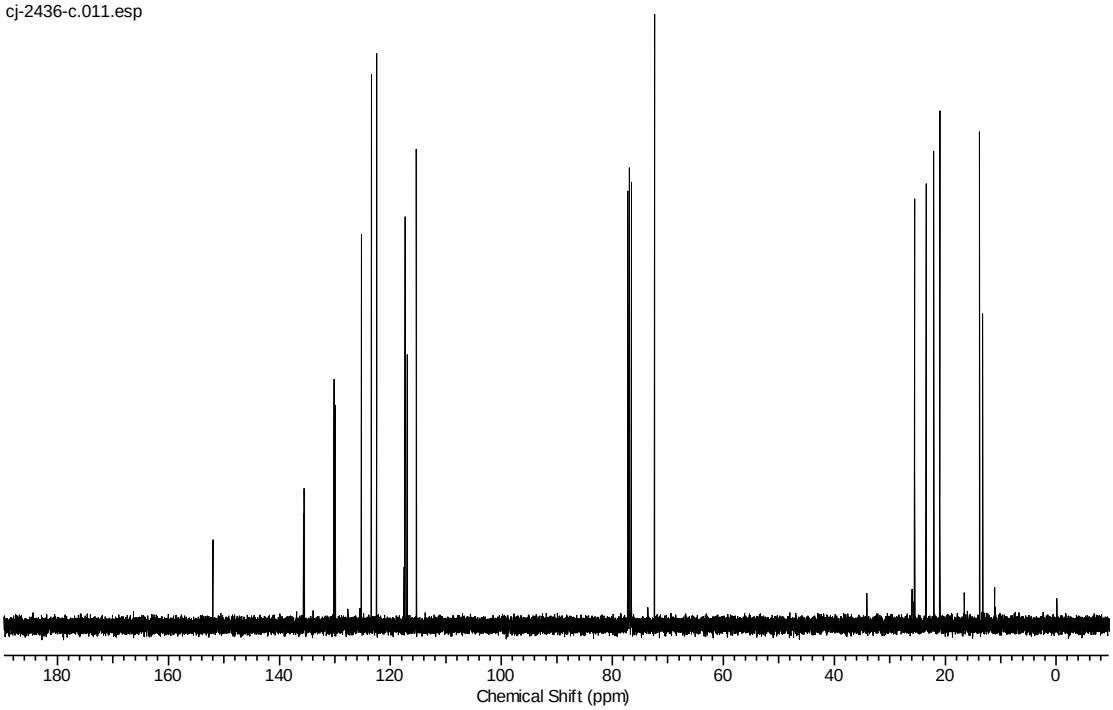
cj-2436-c.010.esp



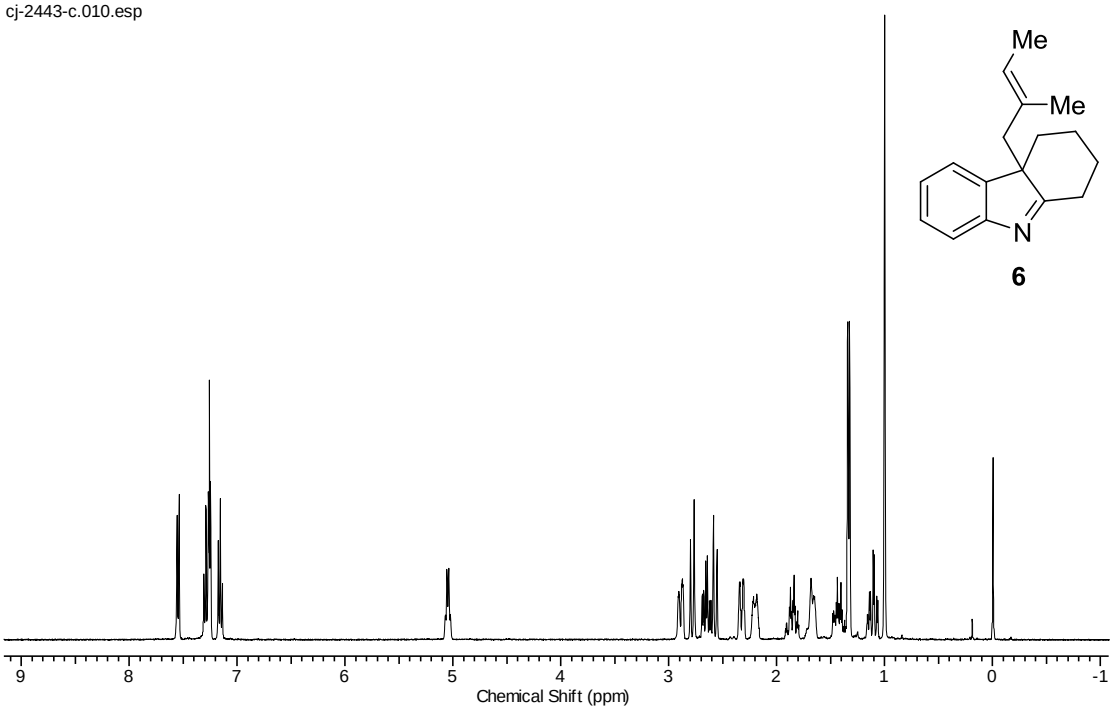
5



cj-2436-c.011.esp

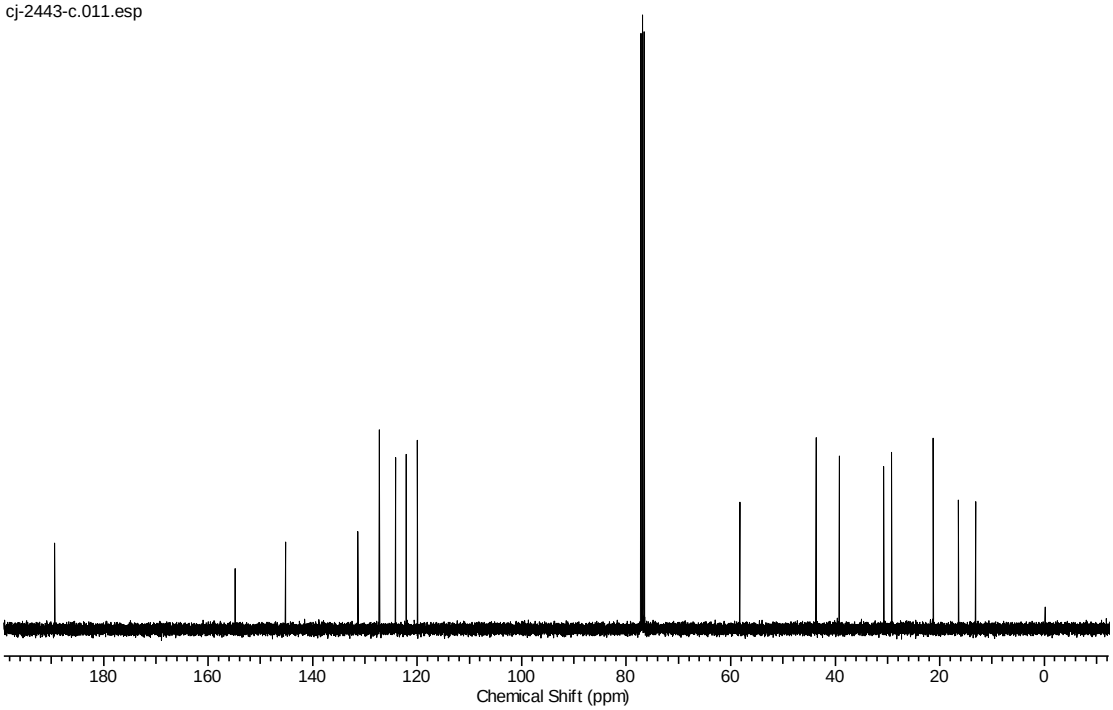


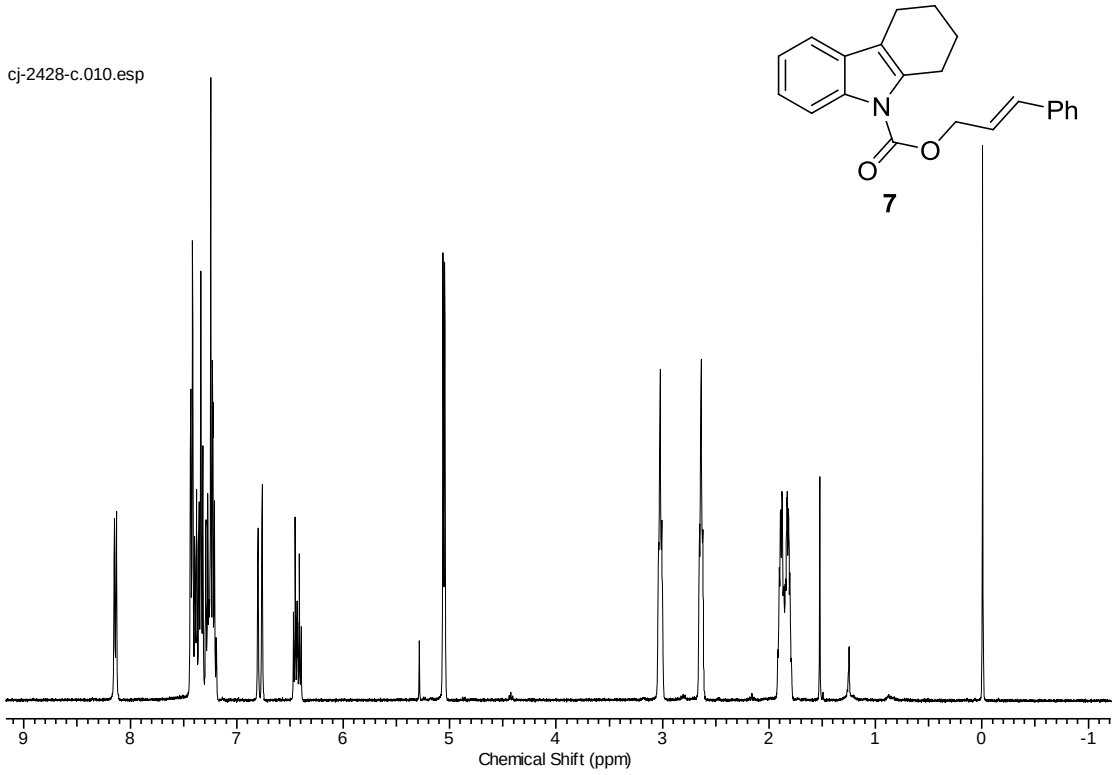
cj-2443-c.010.esp

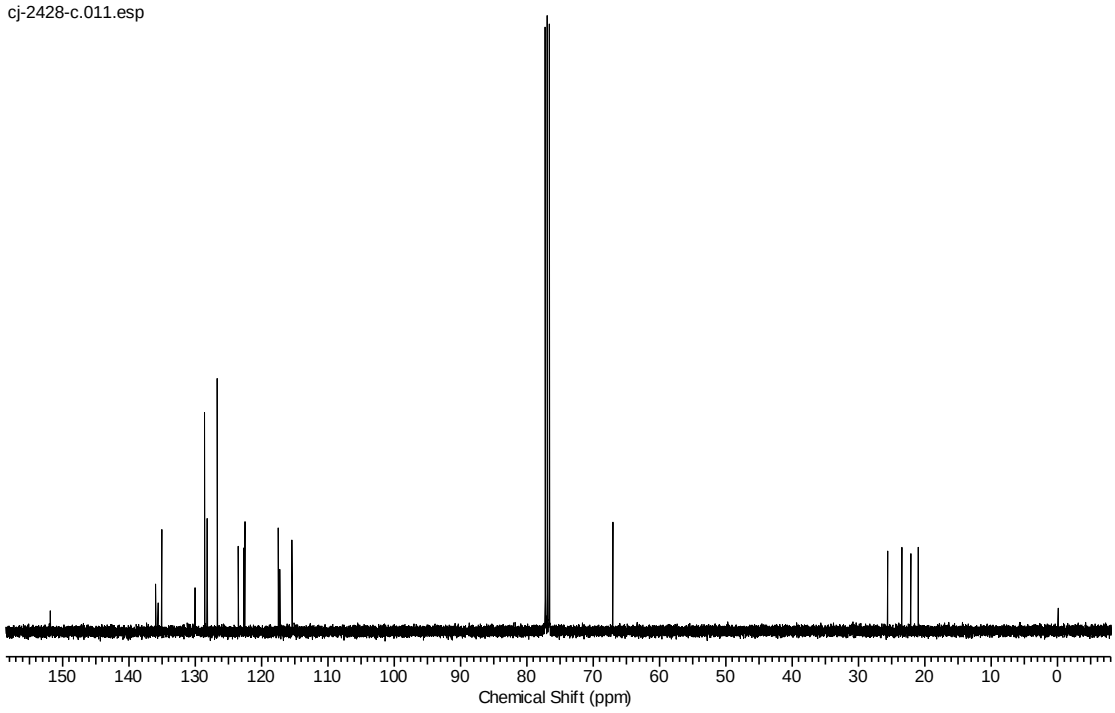


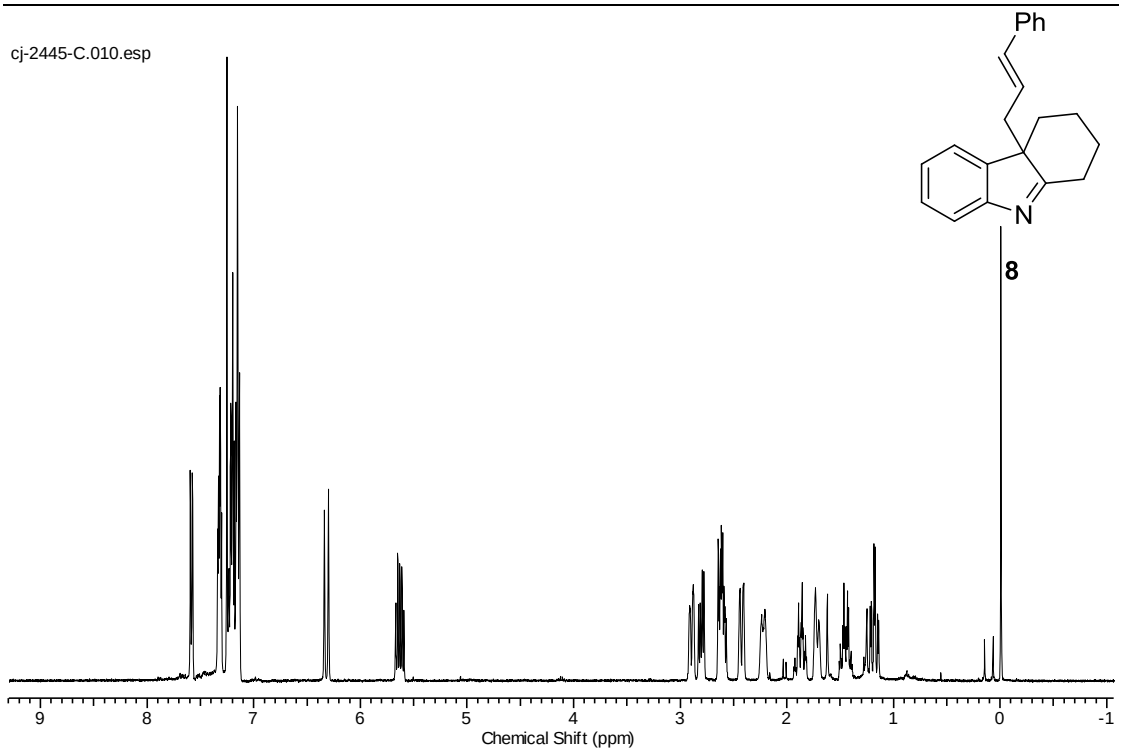
6

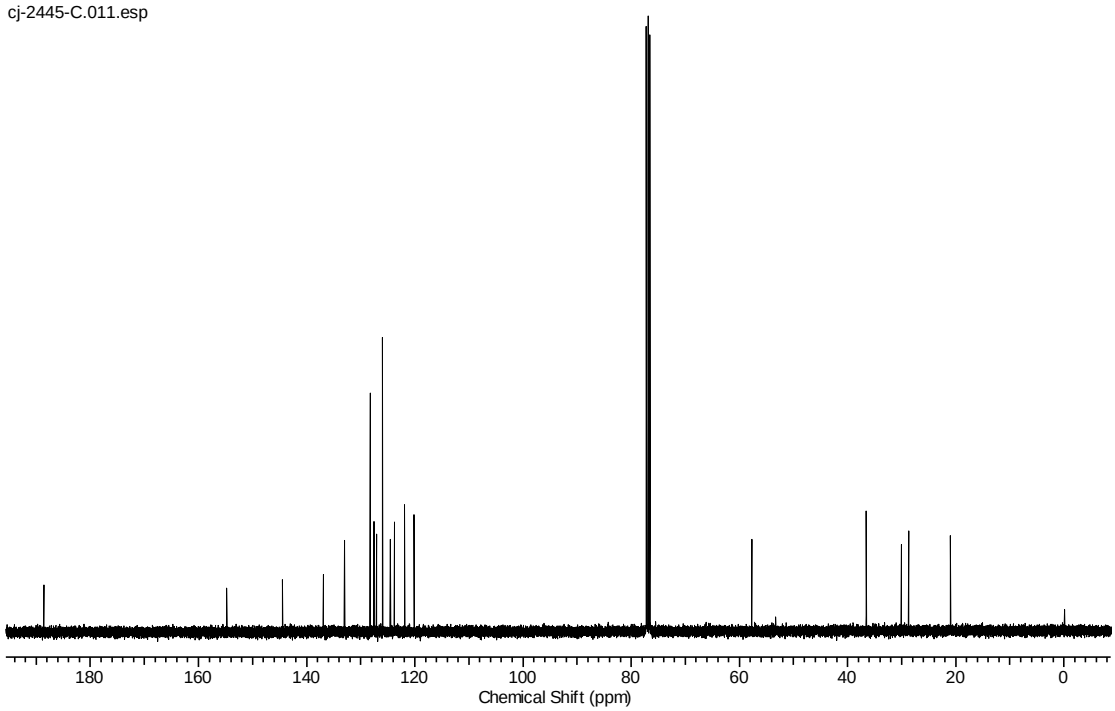
cj-2443-c.011.esp



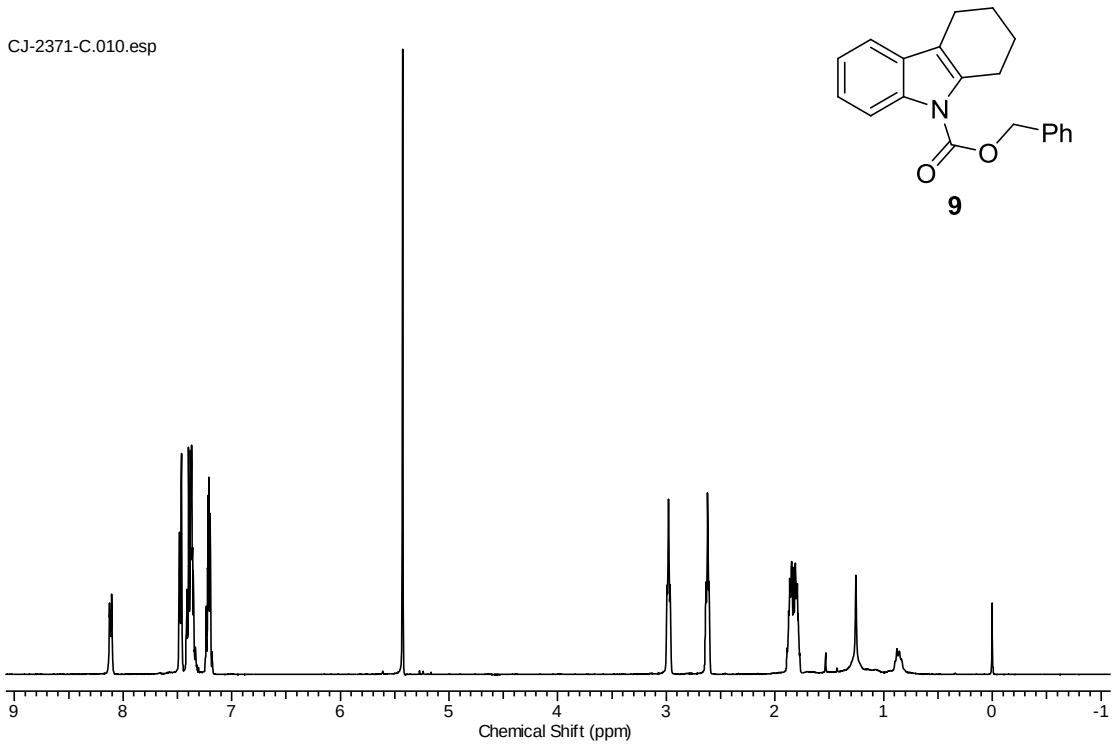

cj-2428-c.010.esp
N
O
O
Ph
7
9
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)


cj-2428-c.011.esp
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

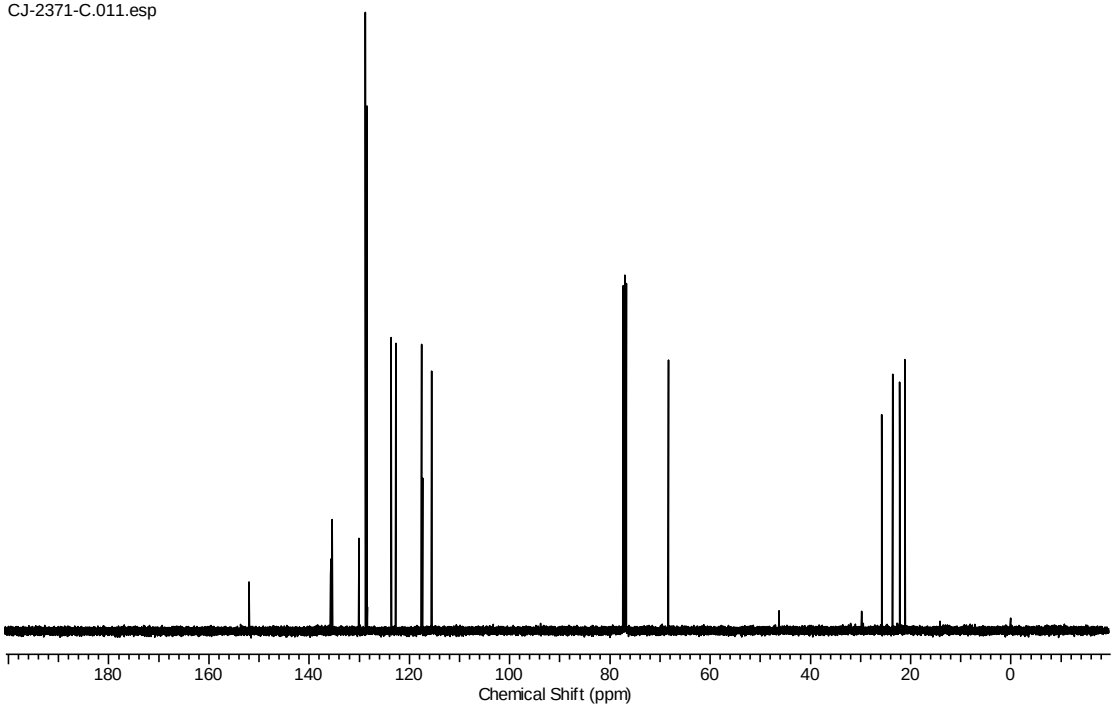

cj-2445-C.010.esp
Ph
N
8
9
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)


cj-2445-C.011.esp
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

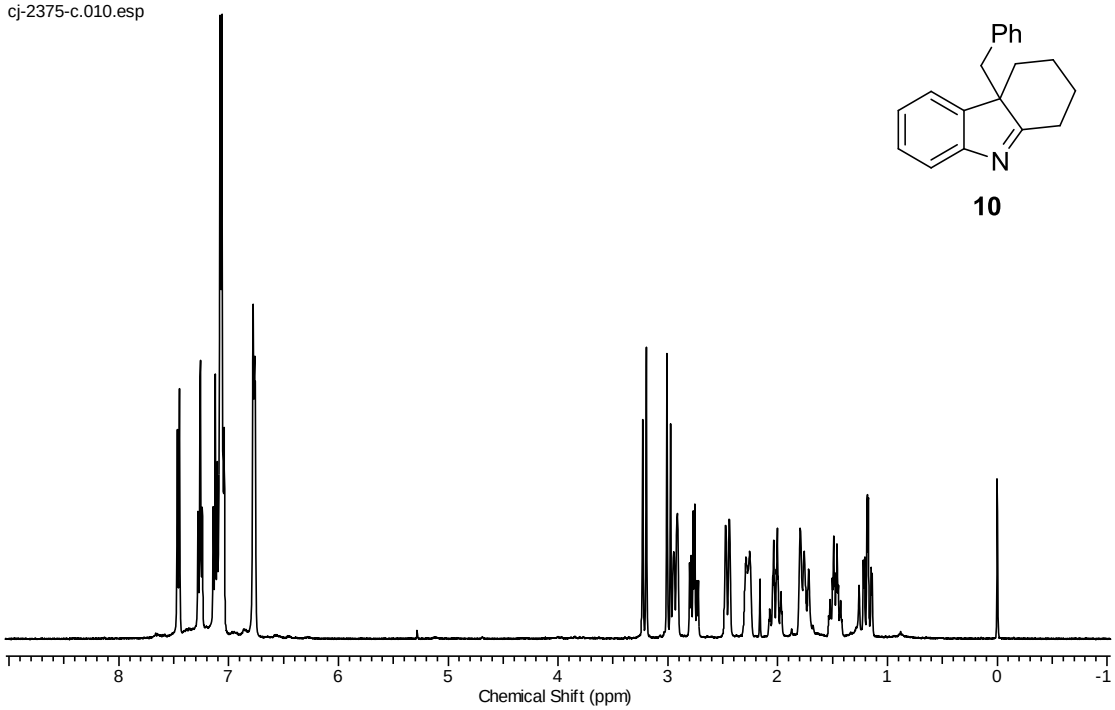
CJ-2371-C.010.esp



CJ-2371-C.011.esp

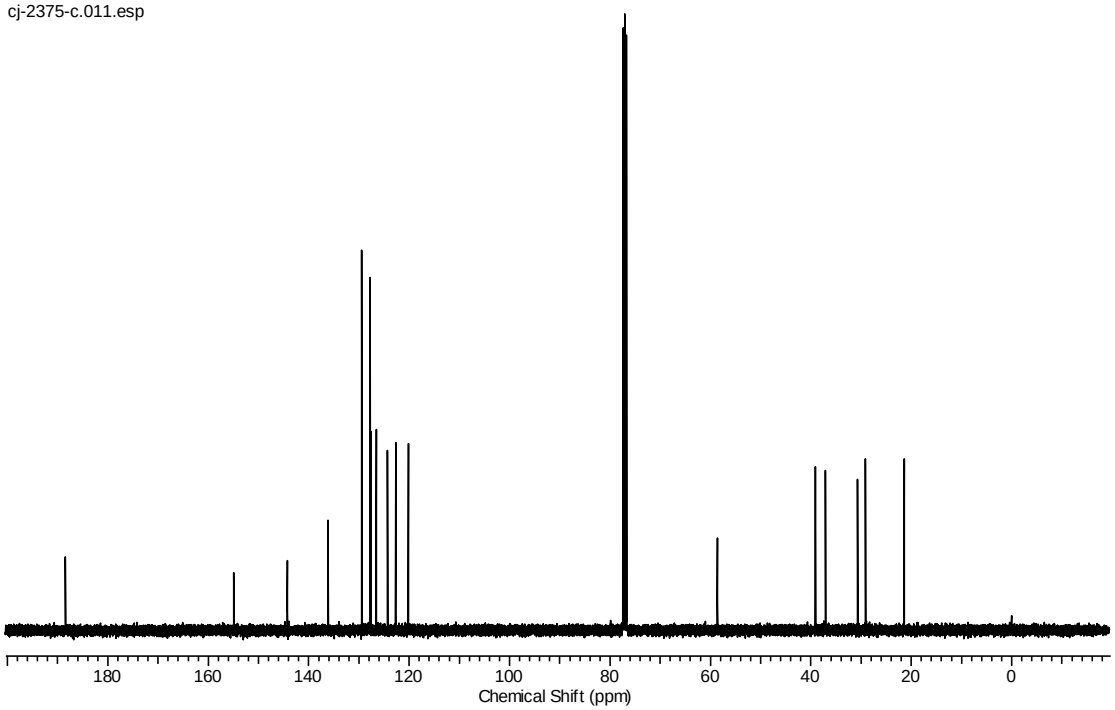


cj-2375-c.010.esp

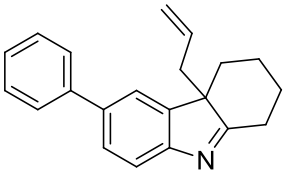


10

cj-2375-c.011.esp

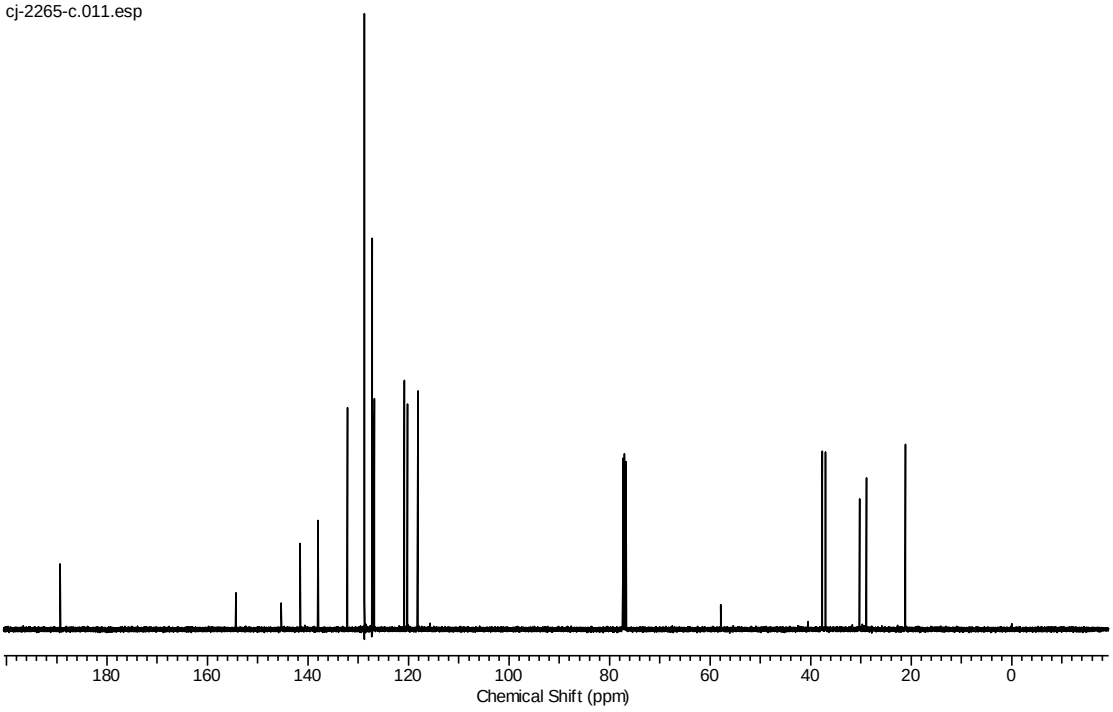


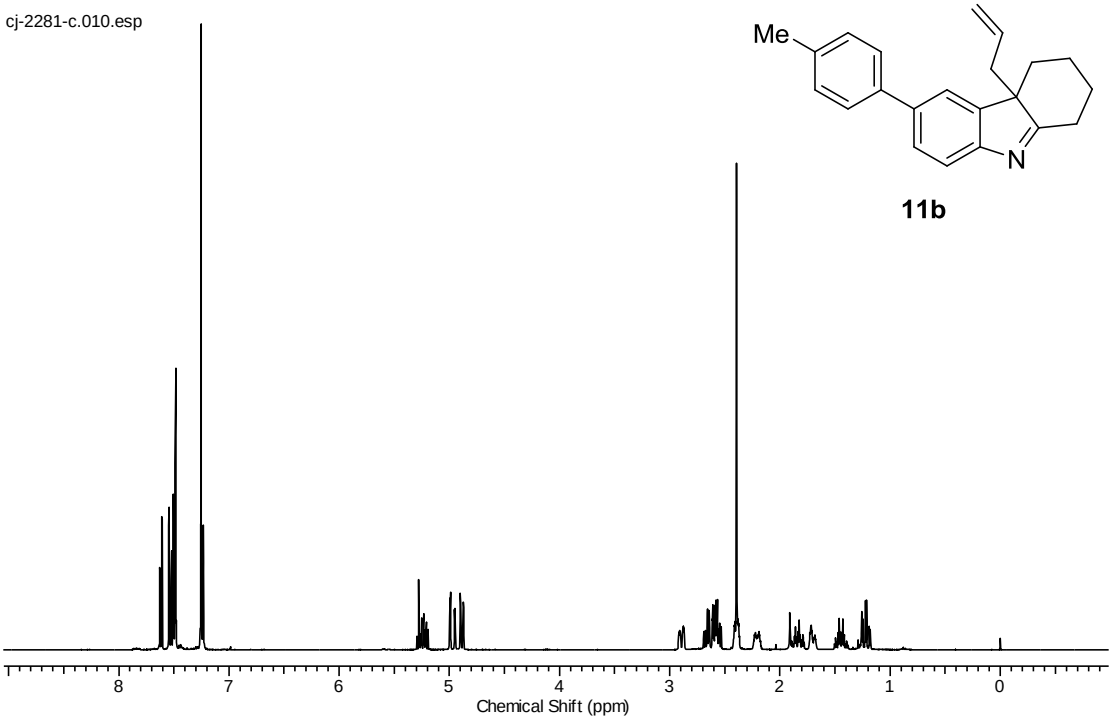
cj-2265-c.010.esp

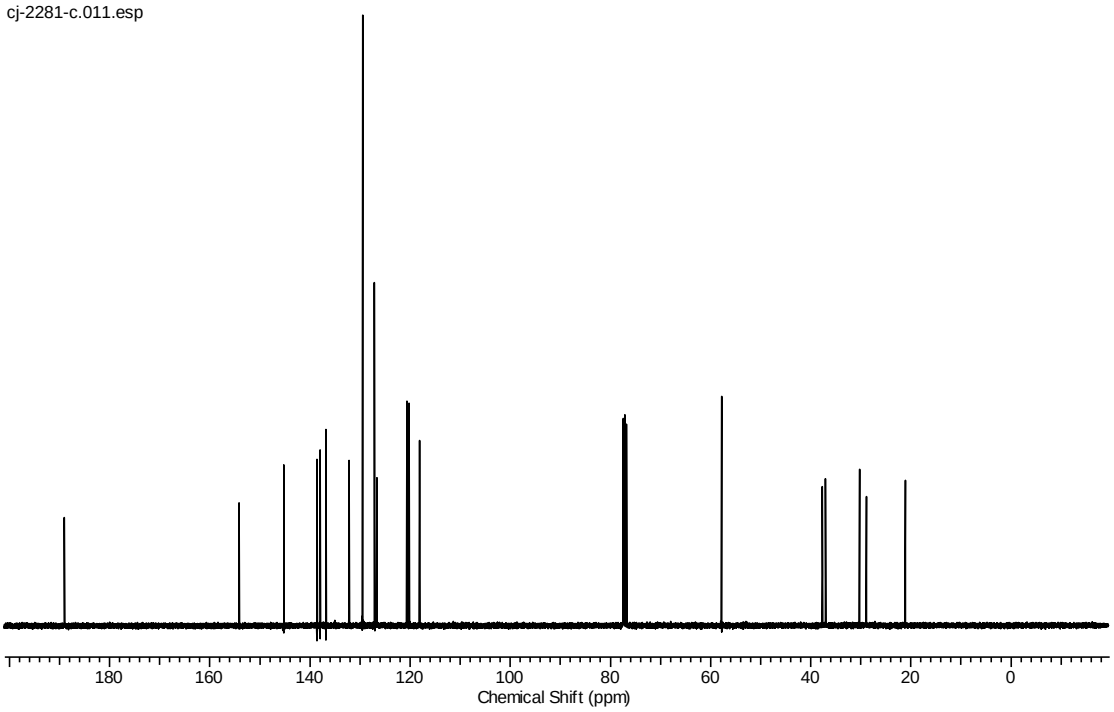


11a

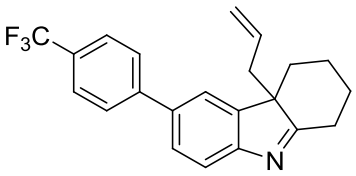
cj-2265-c.011.esp




cj-2281-c.010.esp
Me
N
11b
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

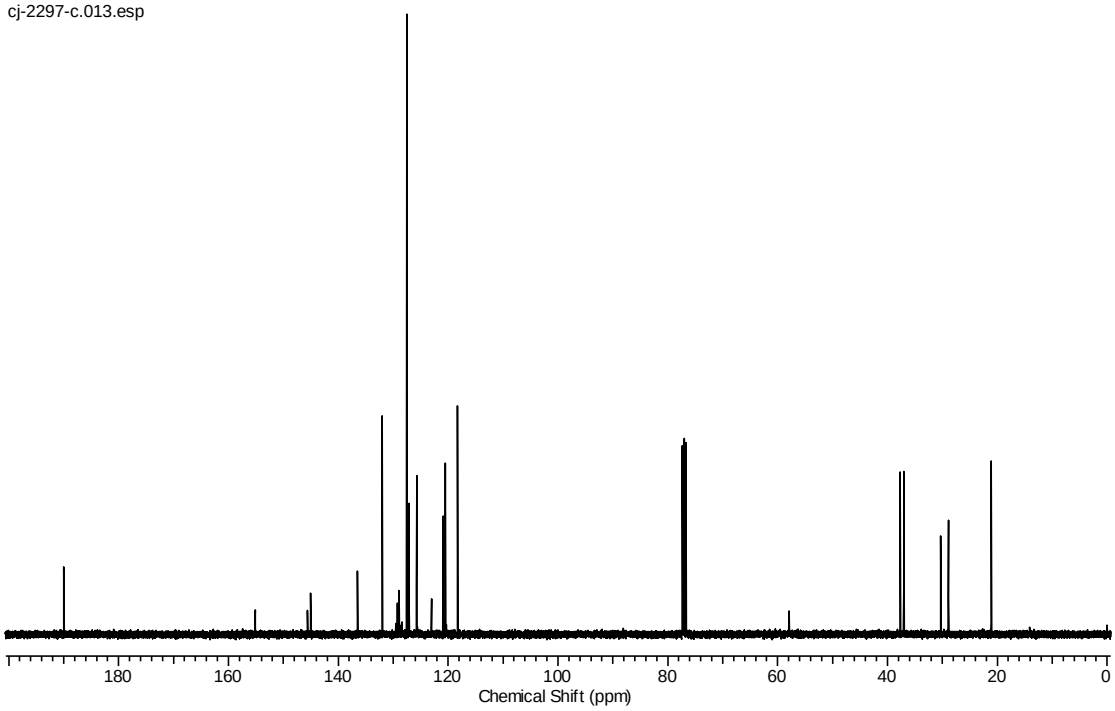

cj-2281-c.011.esp
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

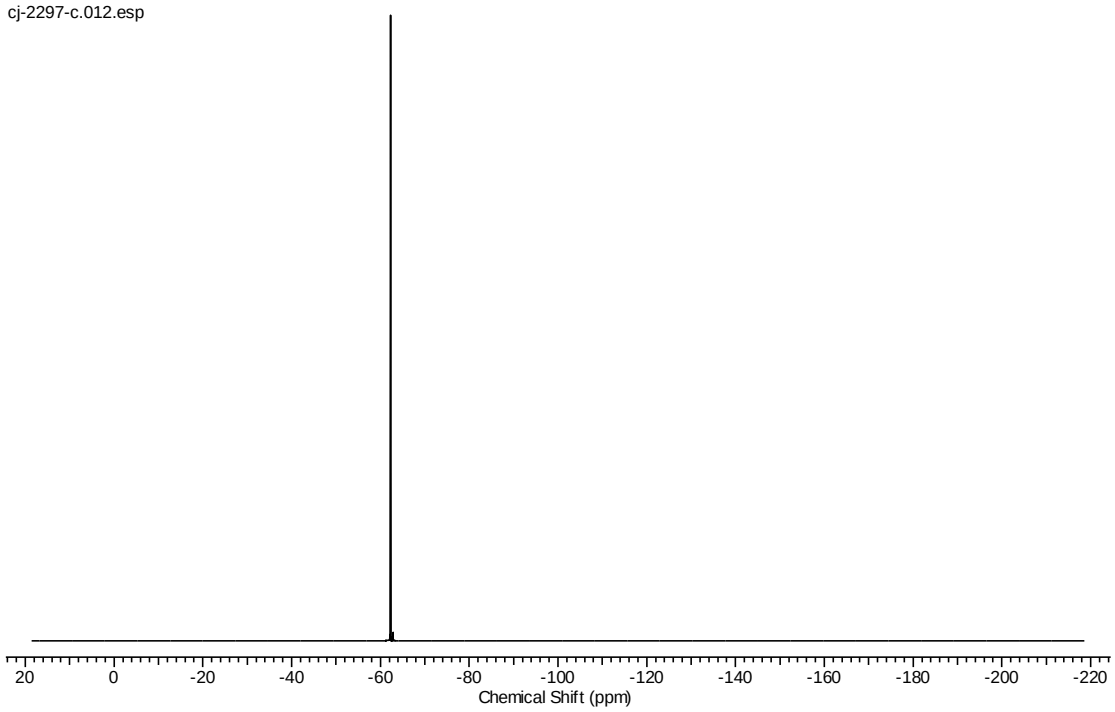
cj-2297-c.010.esp



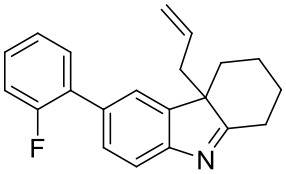
11c

cj-2297-c.013.esp



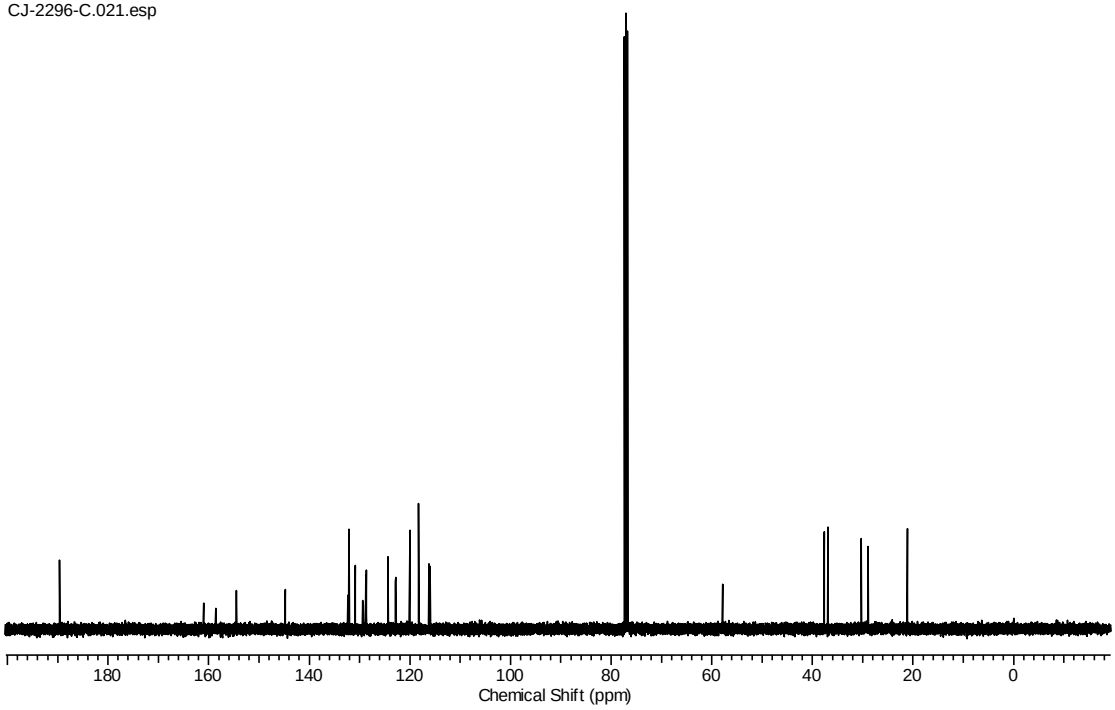

cj-2297-c.012.esp
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
Chemical Shift (ppm)

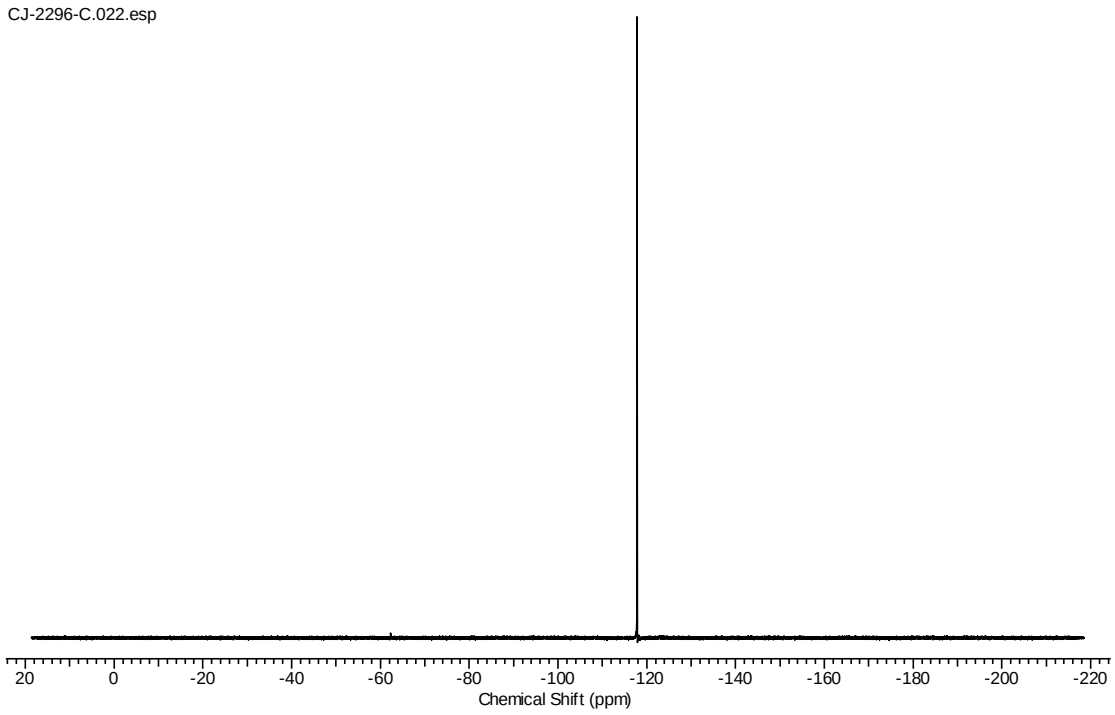
cj-2296-c-2.010.esp

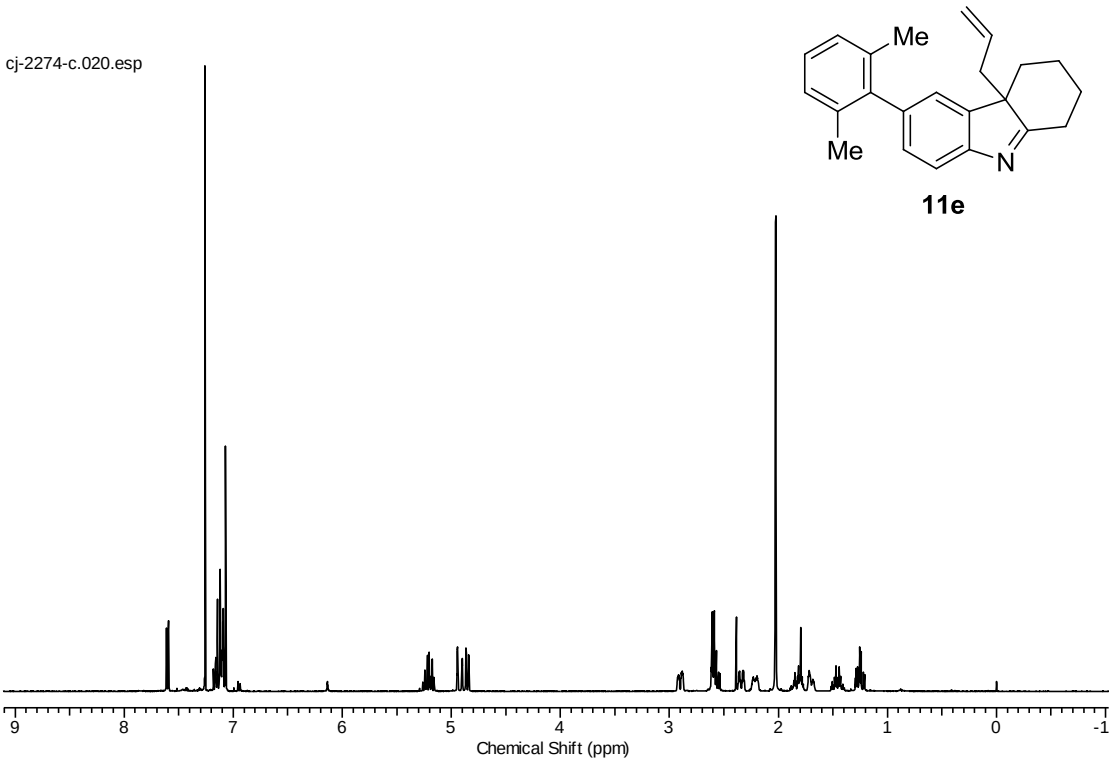


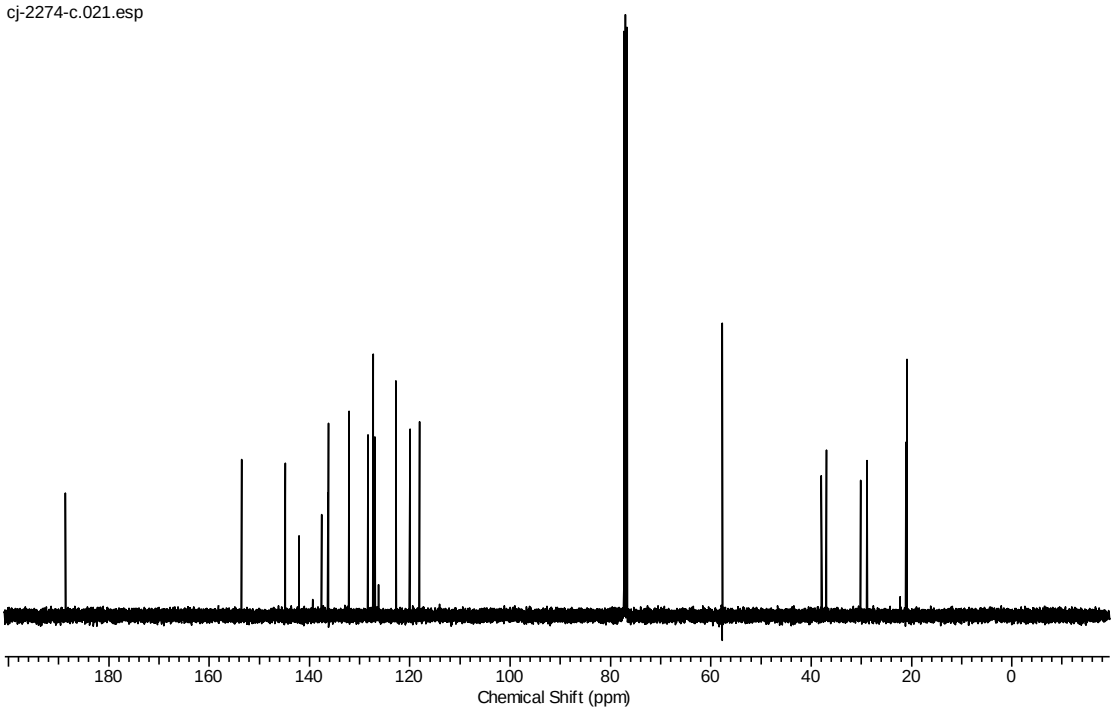
11d

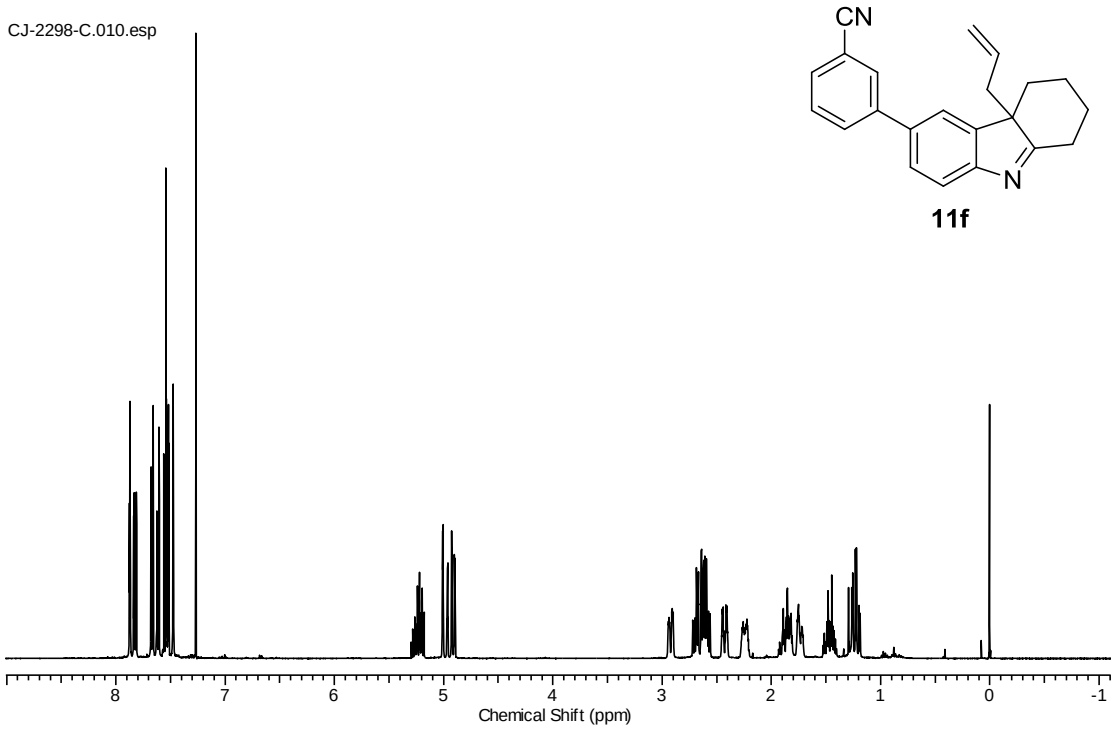
CJ-2296-C.021.esp

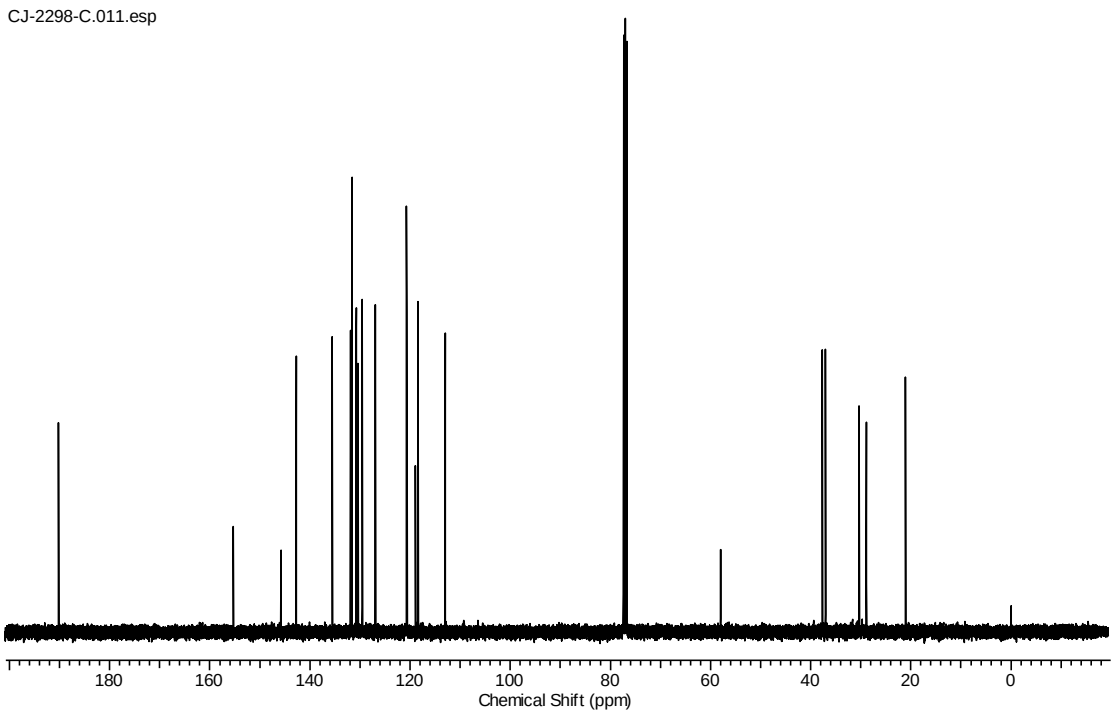


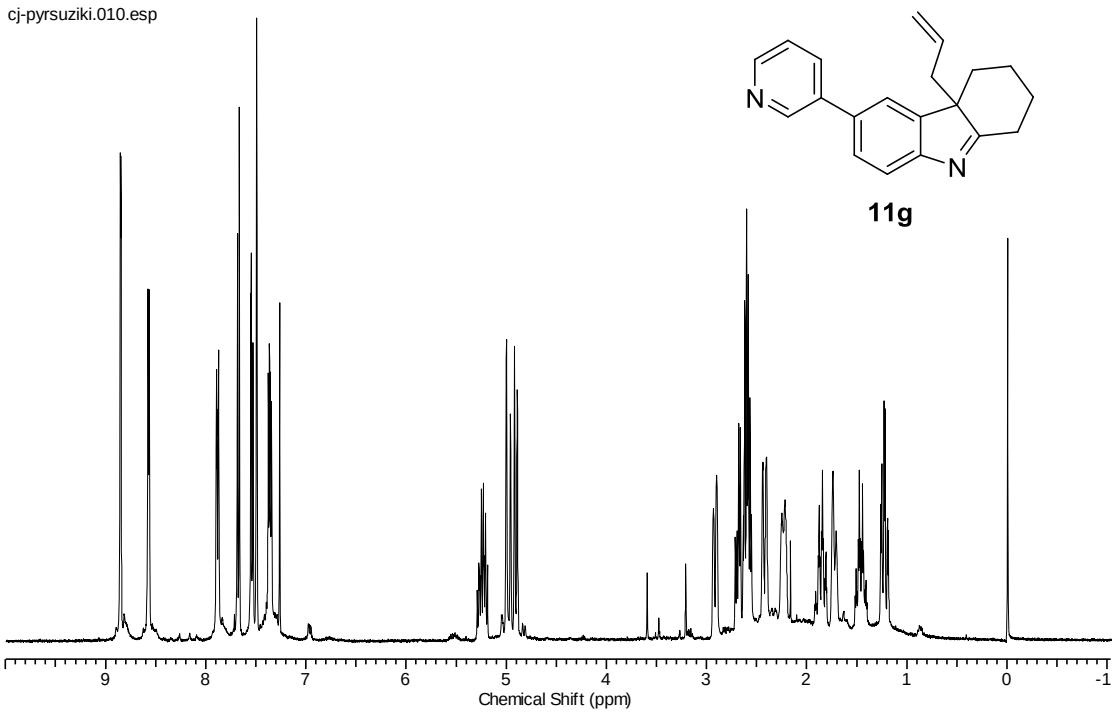

CJ-2296-C.022.esp
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
Chemical Shift (ppm)

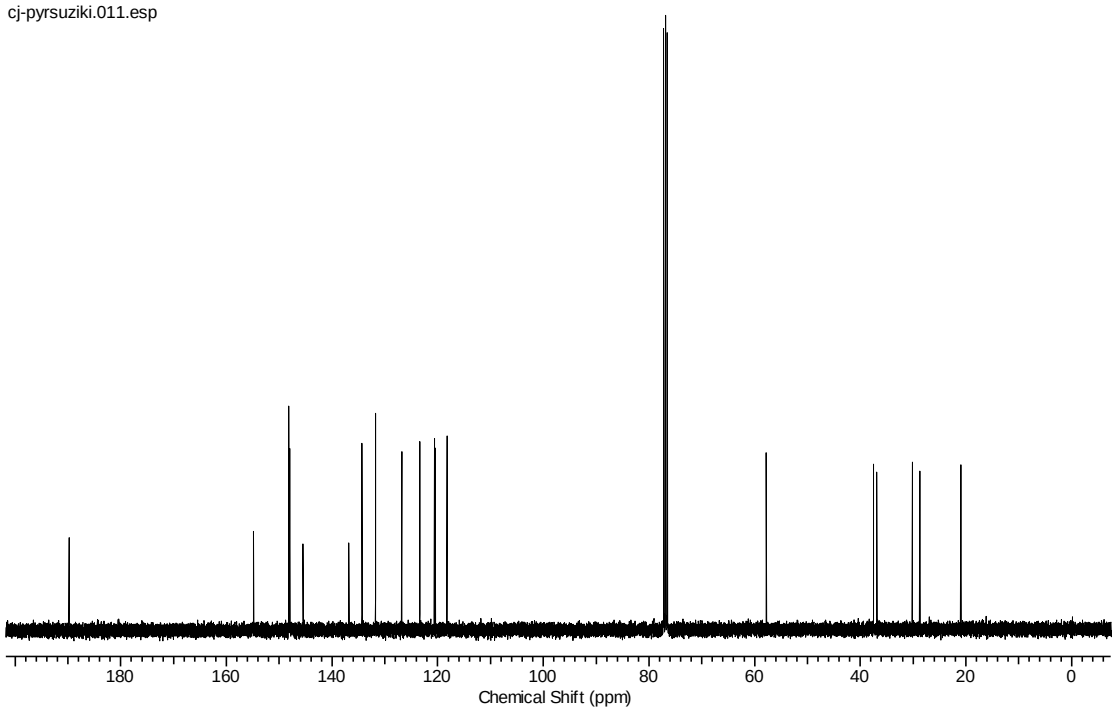

cj-2274-c.020.esp
Me
Me
N
11e
9
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)

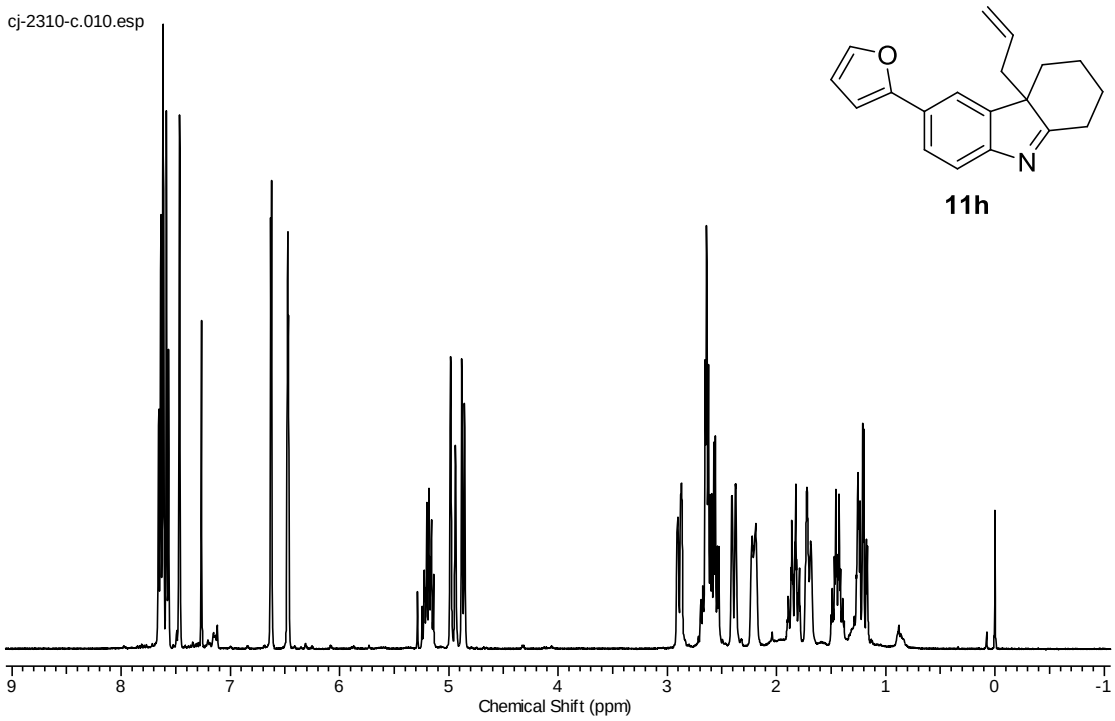

cj-2274-c.021.esp
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

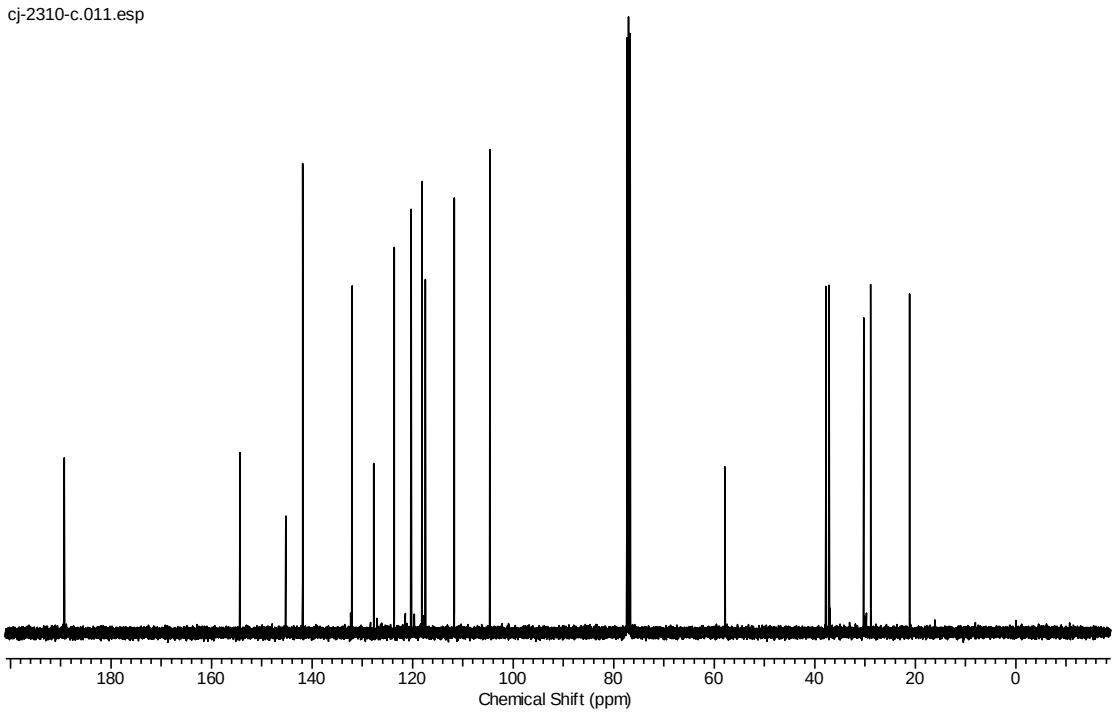

CJ-2298-C.010.esp
CN
N
11f
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)


CJ-2298-C.011.esp
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

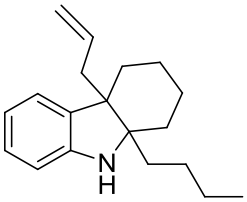

cj-pyrsuziki.010.esp
N
N
11g
9
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)


cj-pyrsuziki.011.esp
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

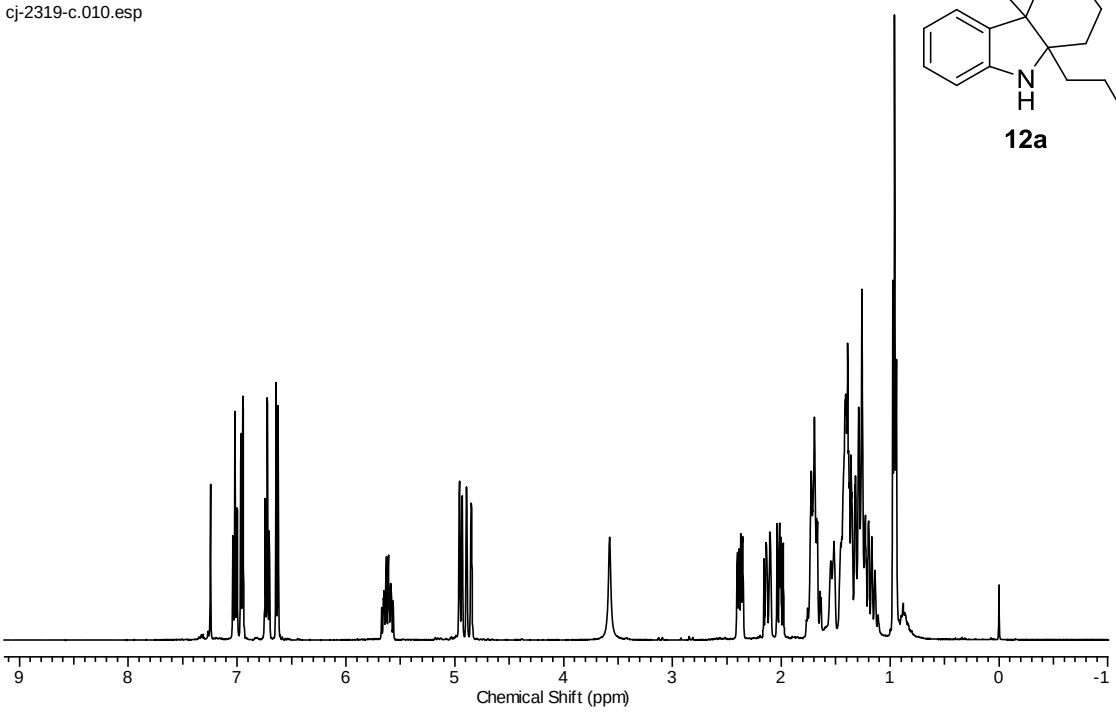

cj-2310-c.010.esp
O
N
11h
9
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)


cj-2310-c.011.esp
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

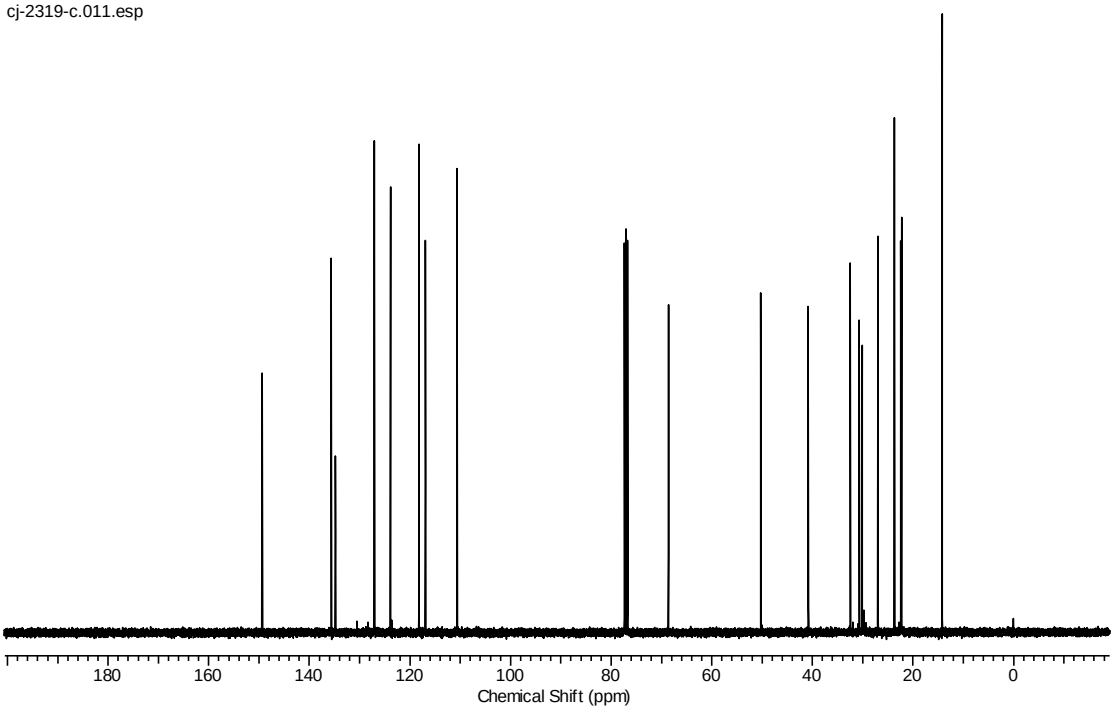
cj-2319-c.010.esp

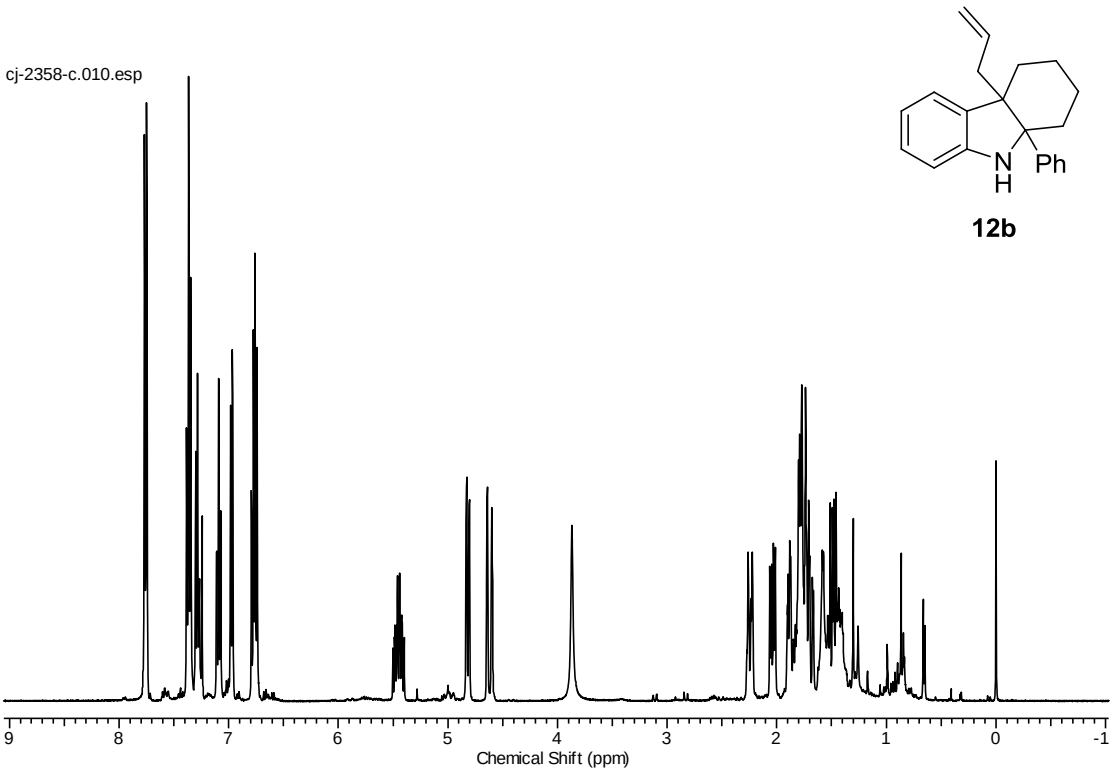


12a

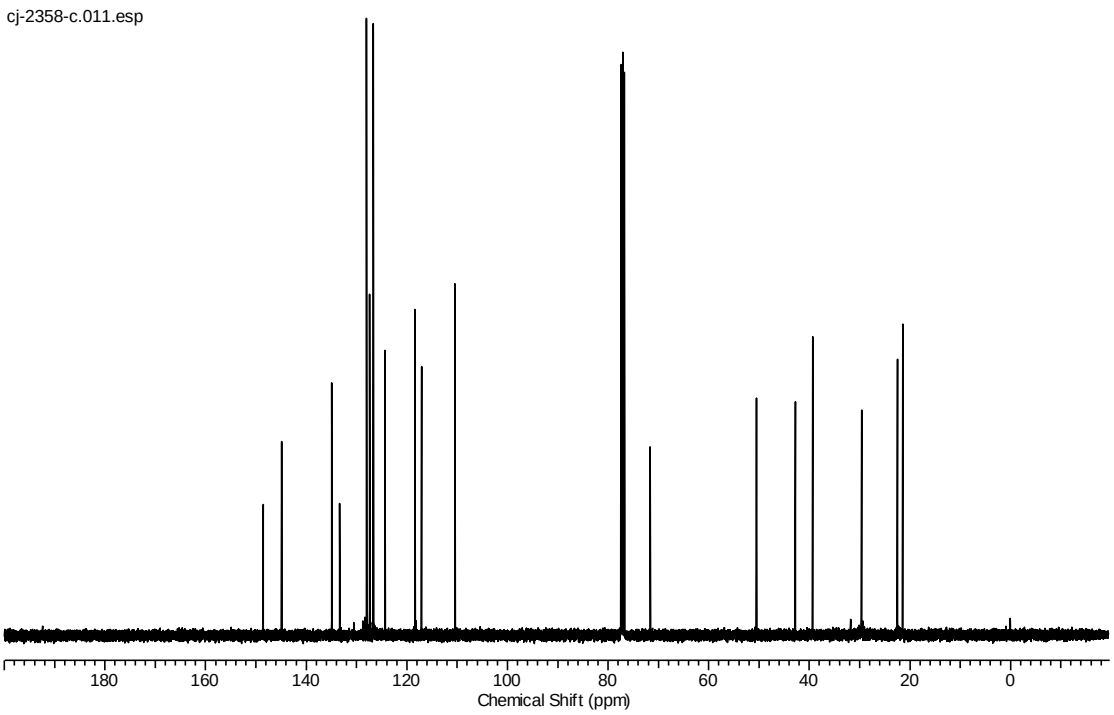


cj-2319-c.011.esp

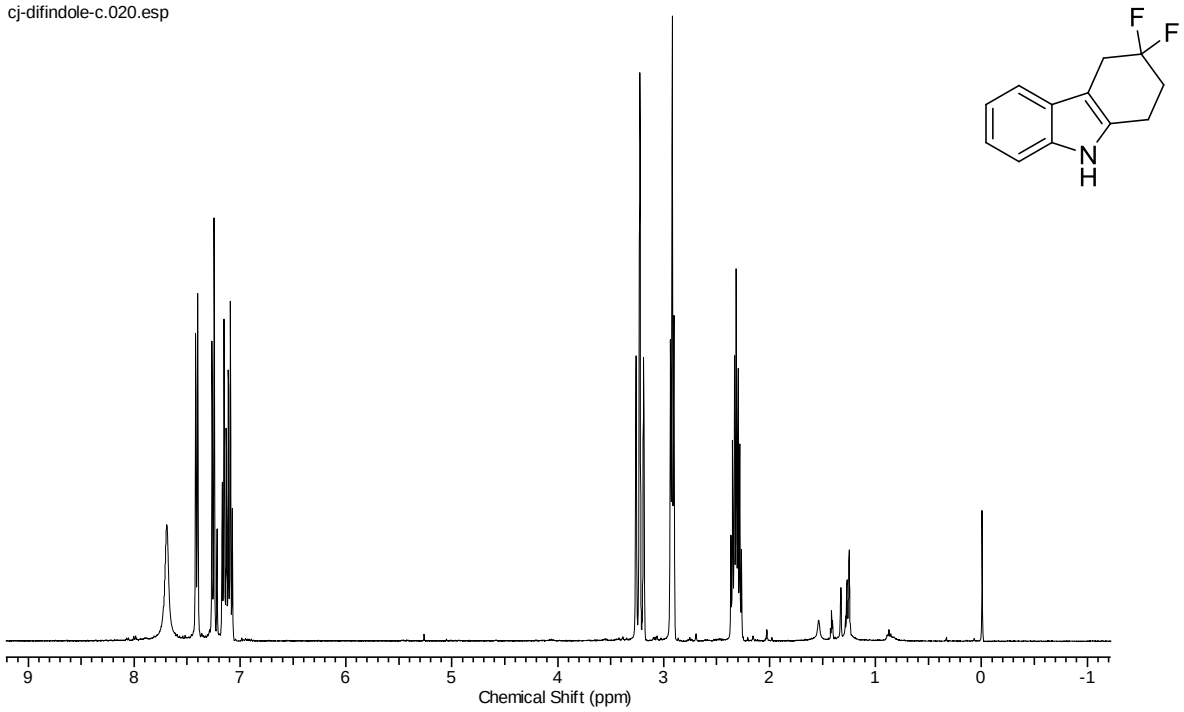



cj-2358-c.010.esp
N
H
Ph
9
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)

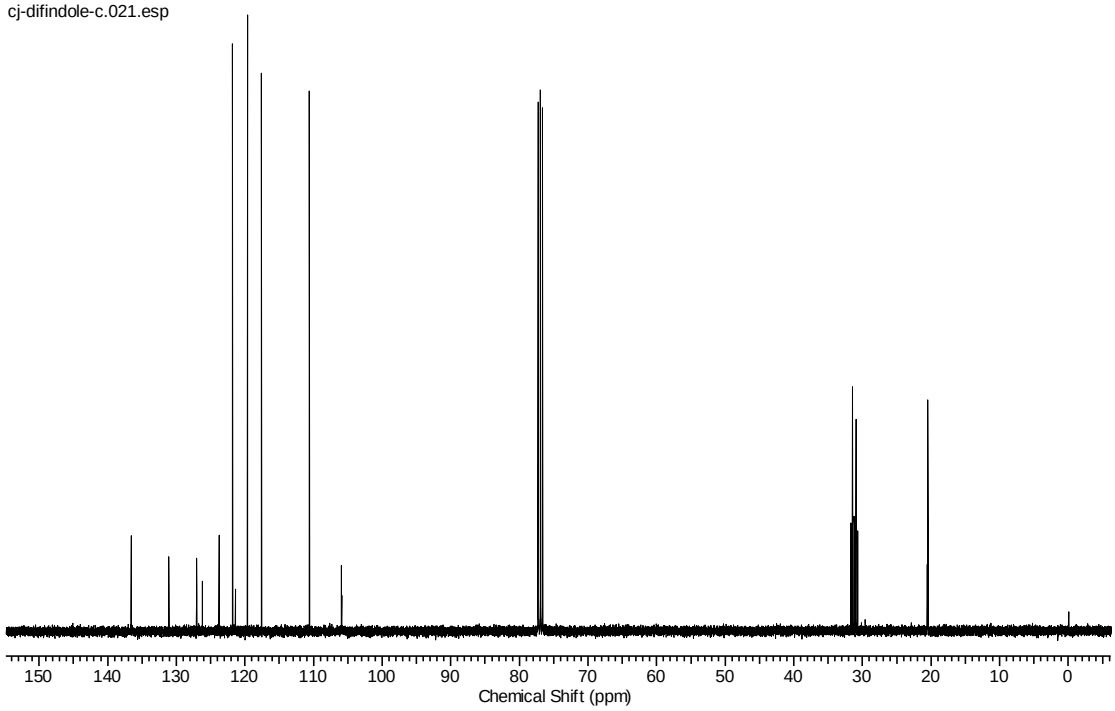
12b

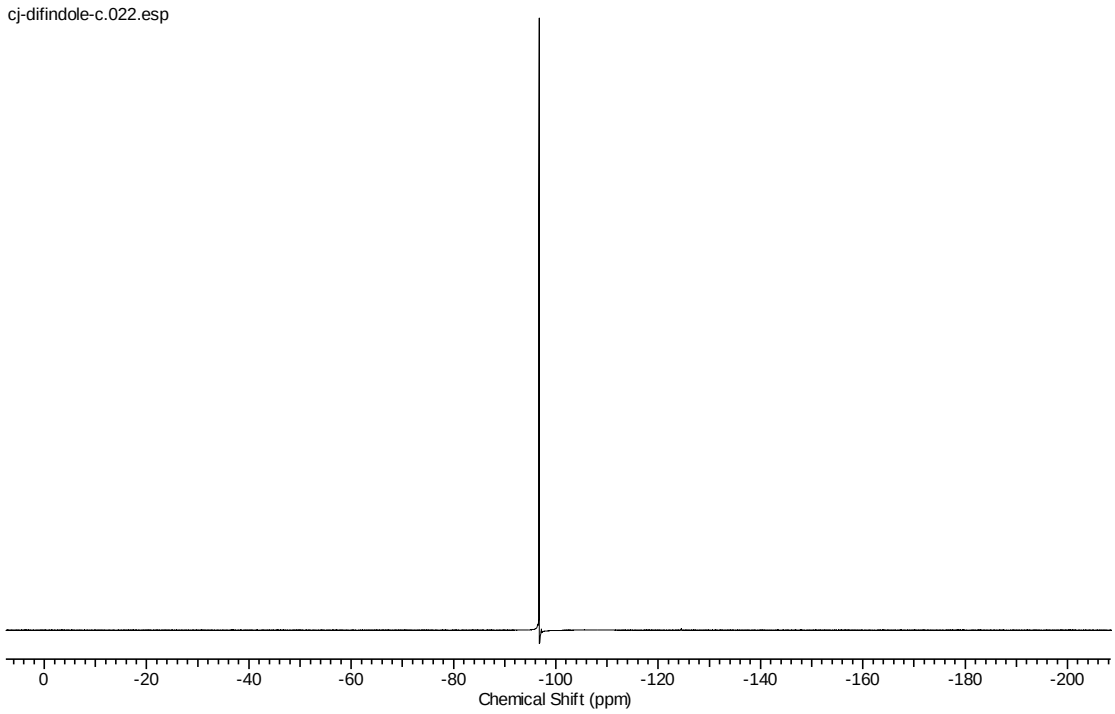

cj-2358-c.011.esp
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

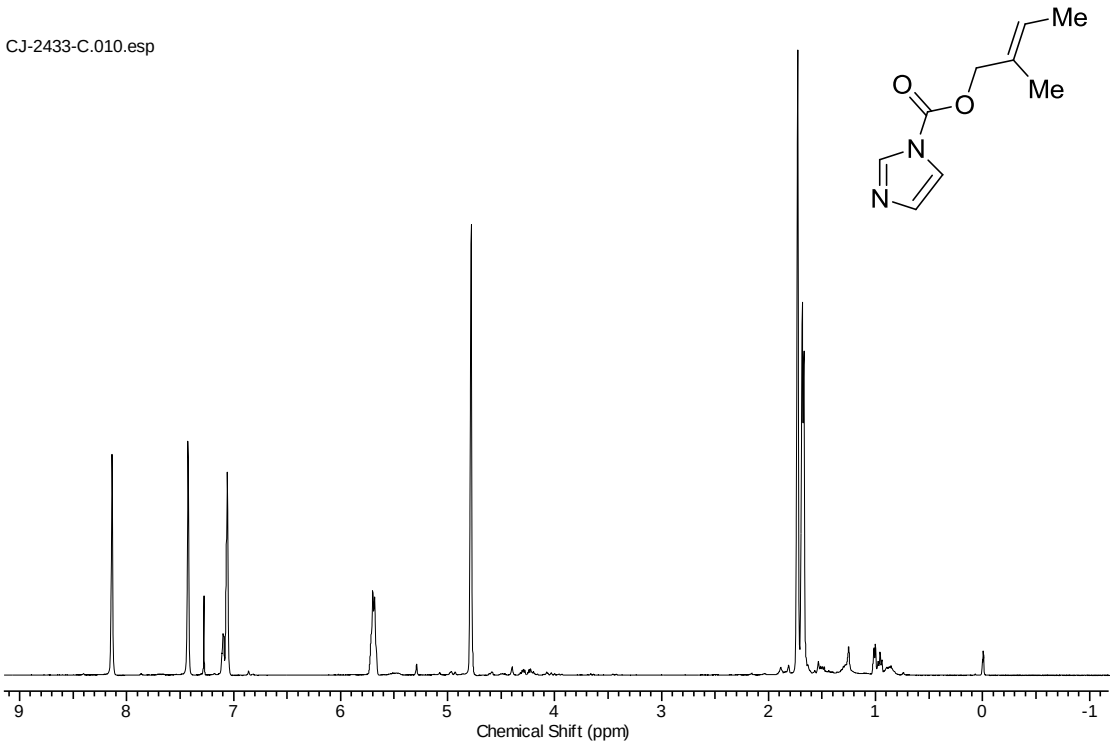
cj-difindole-c.020.esp

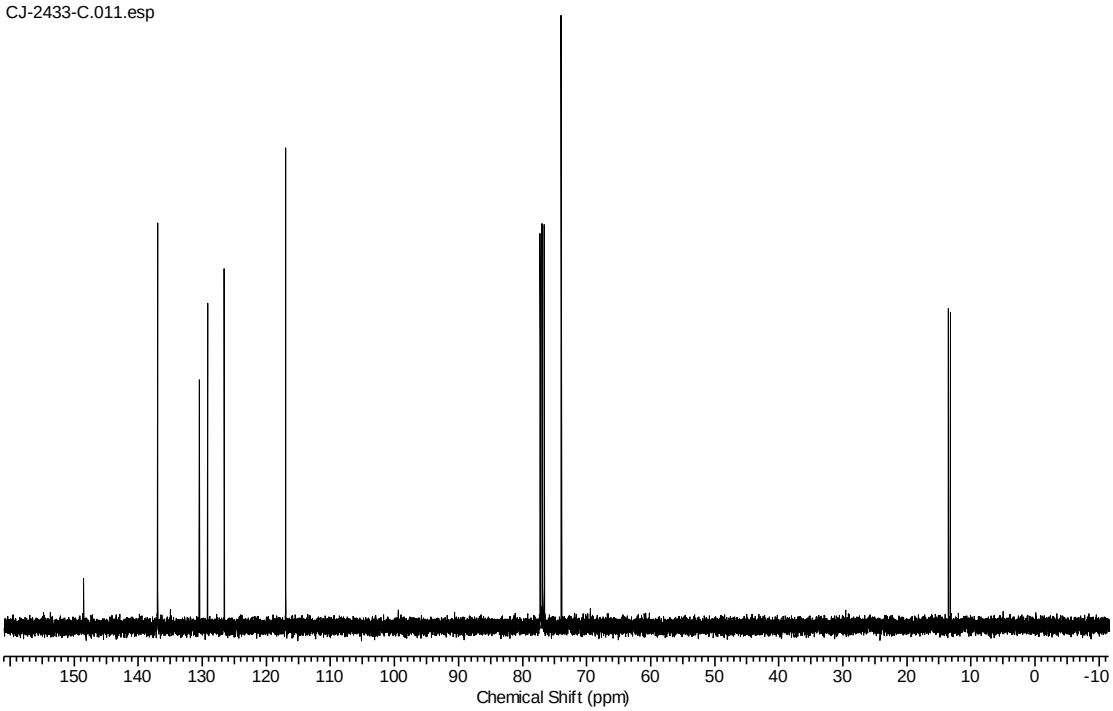


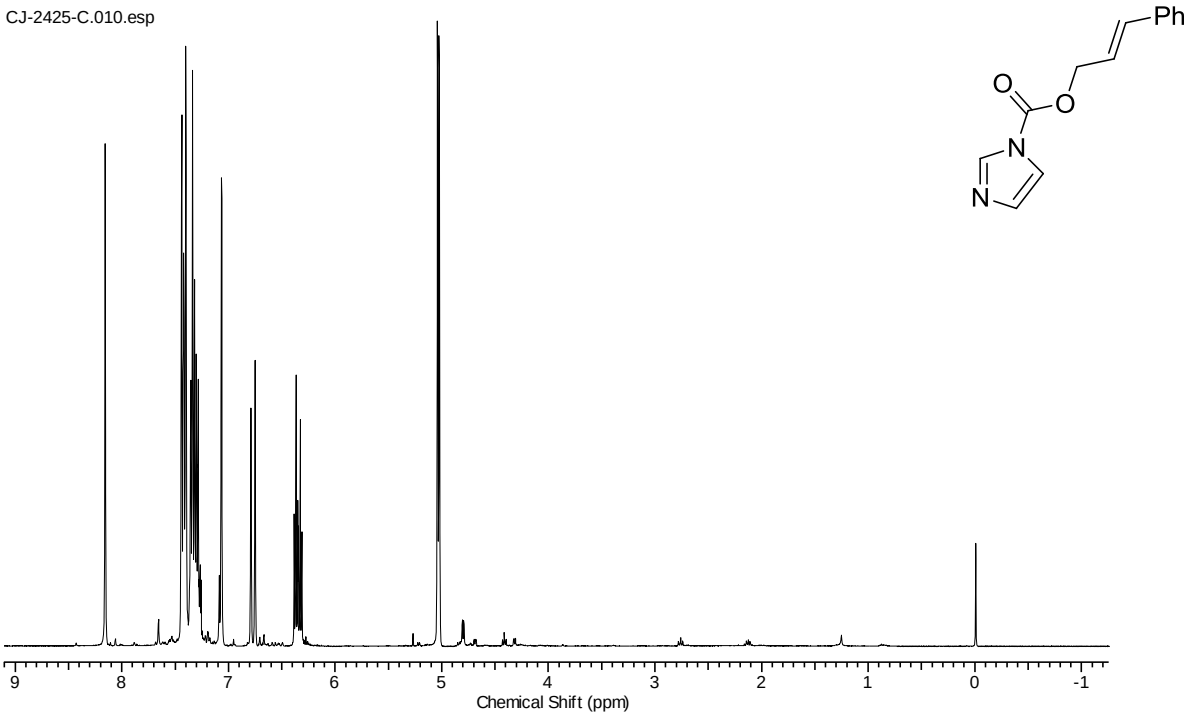
cj-difindole-c.021.esp

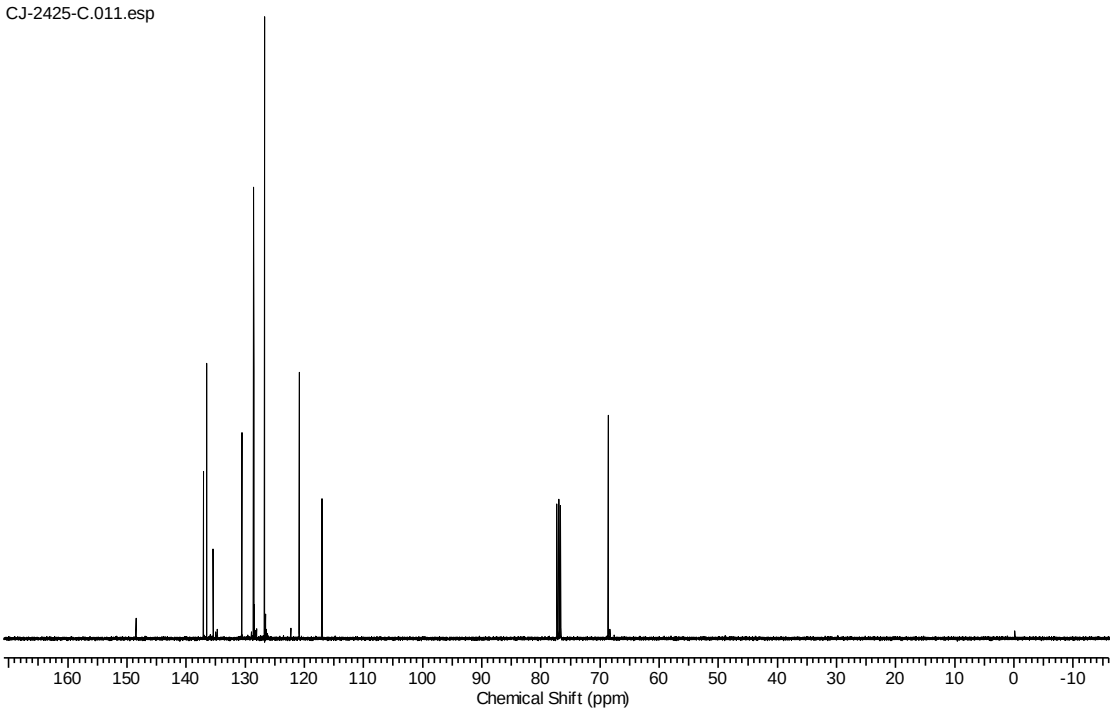



cj-difindole-c.022.esp
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
Chemical Shift (ppm)


CJ-2433-C.010.esp
Me
Me
O
O
N
N
9
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)


CJ-2433-C.011.esp
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
Chemical Shift (ppm)


CJ-2425-C.010.esp
Ph
O
O
N
N
9
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)


CJ-2425-C.011.esp
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
Chemical Shift (ppm)