

Divergent and Orthogonal Approach to Carbazoles and Pyridoindoles from Oxindoles via Indole Intermediates

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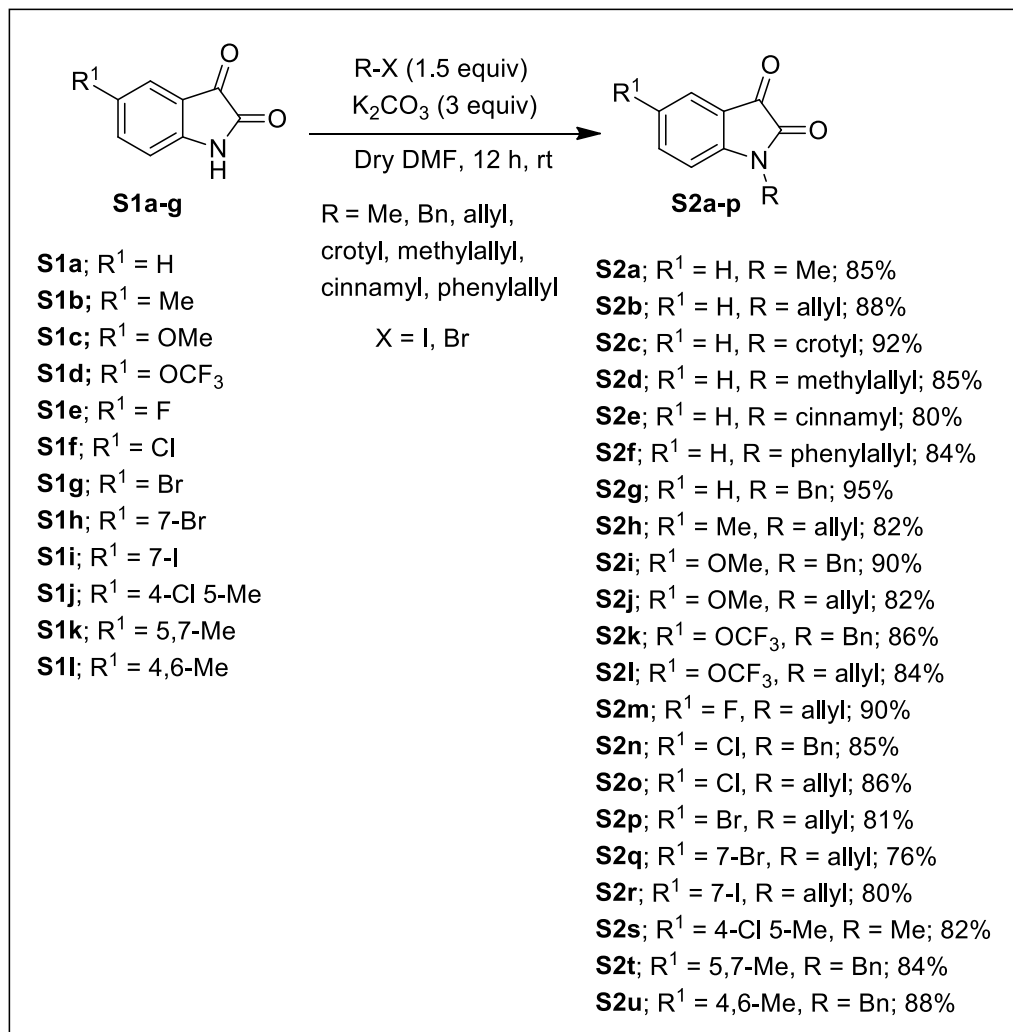
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1.0 General Information

All experiments were carried out under an inert atmosphere of argon in flame-dried flasks. Solvents were dried using standard procedures reported in Perrin, D. D.; Armarego, W. L. F., *Purification of Laboratory Chemicals*, 3rd edition, Pergamon Press, Oxford, 1988. All starting materials were obtained from commercial suppliers and used as received. All the reactions were monitored by thin layer chromatography (TLC) analysis on silica gel 60 F254. Products were purified by flash chromatography on silica gel (100-200 mesh, Merck). Unless otherwise stated, yields refer to analytical pure samples. NMR spectra were recorded in CDCl₃ unless otherwise stated. **¹H NMR** spectra were recorded at 500 MHz using Brüker AVANCE 500 MHz and JEOL 400 MHz instruments at 298K. Signals are quoted as δ values in ppm using residual protonated solvent signals as internal standard (CDCl₃: δ 7.26 ppm). Data is reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, br = broad, m = multiplet), and coupling constants (Hz). **¹³C NMR** spectra were recorded on either a JEOL-400 (100 MHz), or a Brüker AVANCE 500 MHz (125 MHz) with complete proton decoupling. Chemical shifts (δ) are reported in ppm downfield from tetramethylsilane with the solvent as the internal reference (CDCl₃: δ 77.16 ppm). **HRMS** analyses were performed with Q-TOF YA263 high resolution (Water Corporation) instruments by +ve mode electrospray ionization.

2.0 Synthesis of *N*-protected isatins **S2**:

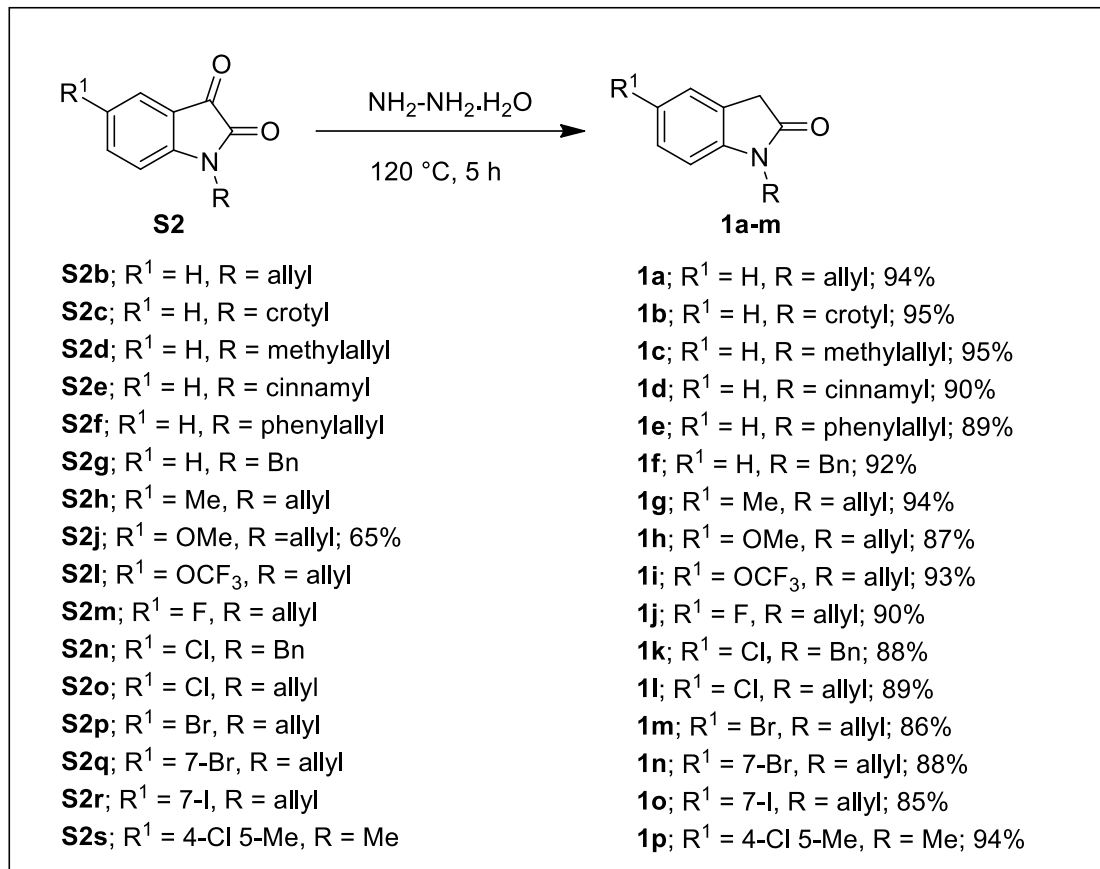
N-alkylated isatin derivatives **S2** were prepared using reported procedures¹⁻³ from commercially available isatins **S1** with different alkyl halides in the presence of K₂CO₃ in DMF at room temperature for 8 h (Scheme S1).



Scheme S1. Synthesis of *N*-protected isatins **S2**.

3.0 Synthesis of 2-oxindoles **1**:

N-protected 2-oxindoles **1** were prepared from *N*-protected isatins **S2** using reported procedure⁴ in presence of $\text{NH}_2\text{-NH}_2\cdot\text{H}_2\text{O}$ at 120 °C for 5 h (Scheme S2).

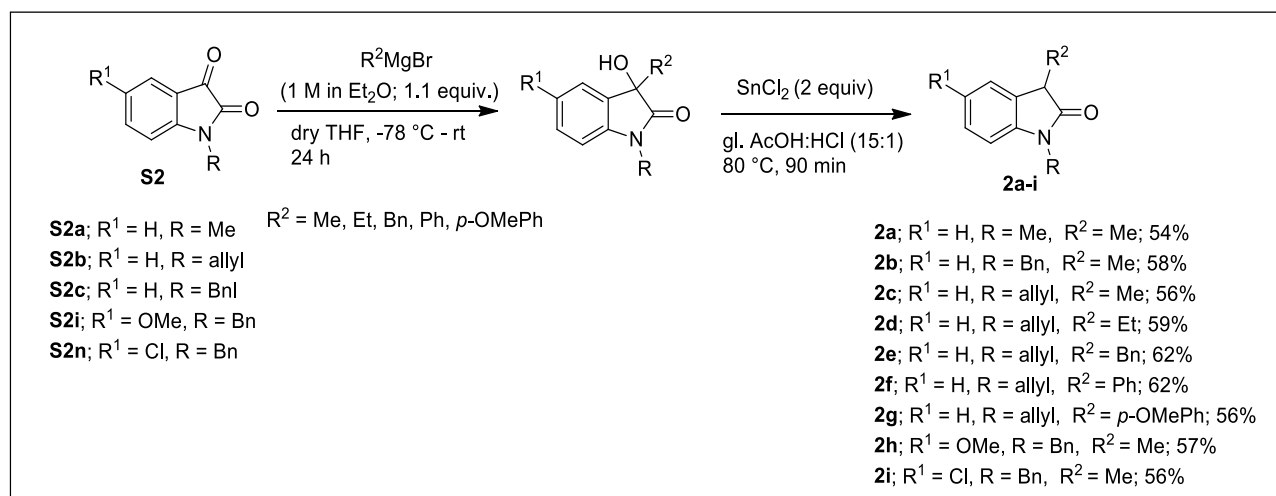


Scheme S2. Synthesis of 2-oxindoles **1** from isatins **S2**.

4.0 Synthesis of 3-substituted 2-oxindoles 2:

4.0.1 Synthesis of 3-alkyl/aryl 2-oxindoles 2a-i:

N-protected 3-alkyl/aryl 2-oxindoles **2a-i** were prepared from *N*-protected isatins **S2** using reported procedure⁵ on reaction with appropriate Grignard reagent (1.0 M solution in Et₂O; 1.1 equiv) followed by dehydroxylation using SnCl₂ in presence of AcOH/HCl (Scheme S3).

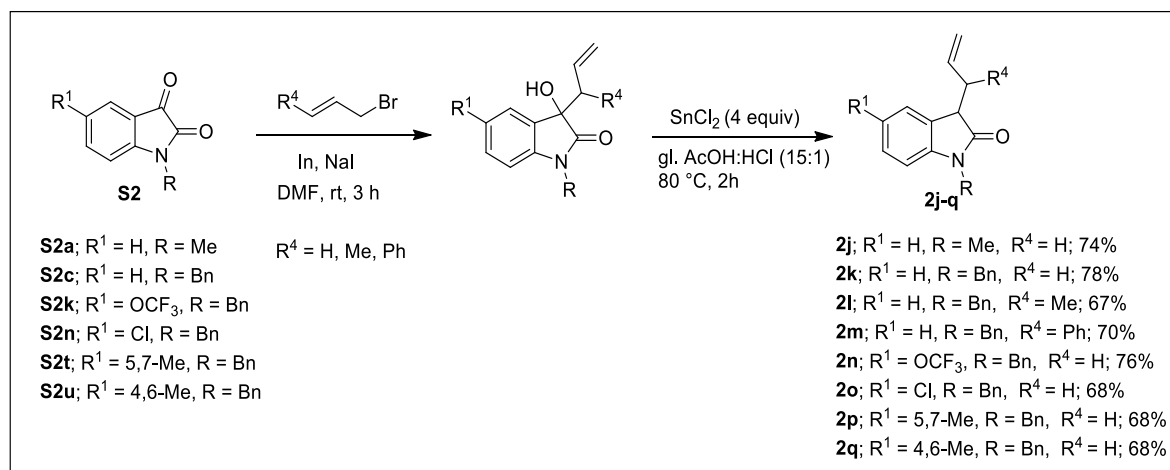


Scheme S3. Synthesis of 3-alkyl/aryl oxindoles **2a-i** from isatins **S2**.

4.0.2 General procedure for the synthesis of 3-allyl 2-oxindoles 2j-p (GP-1):

A mixture of indium metal (1.0 mmol, cut into small pieces), alkenyl bromide (1.6 mmol), *N*-substituted isatins **S2** (0.8 mmol) and NaI (1.6 mmol) was stirred in DMF (6 mL) at room temperature until the consumption of starting isatin (confirmed by TLC). It was then quenched with a few drops of 1 N HCl and extracted with Et₂O (3 × 15 mL). The combined organic extracts were washed with aq sat. NaHCO₃ solution (15 mL), brine (15 mL), and dried (Na₂SO₄), and concentrated in vacuo to provide crude 3-allyl 3-hydroxy 2-oxindoles.

The crude product was dissolved in 40 mL AcOH/HCl (15/1), and then SnCl₂ (4 equiv) was added. The reaction mixture was stirred at 80 °C for 2 h and then cooled to room temperature and diluted with water. The product was extracted with Et₂O (3 X 10 mL). The combined organic extracts were washed with aqs. NaOH, dried with MgSO₄, and then concentrated to afford crude oxindoles. Purification by column chromatography using ethylacetate-hexane (10/90 to 20/80) furnished compounds **2j-p** (Scheme S4).



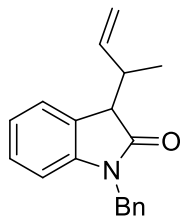
Scheme S4. Synthesis of 3-allyl oxindoles **2j-q** from isatins **S2**.

3-Allyl-1-methylindolin-2-one (2j)⁶: Using the general procedure **GP-1**, indium metal (1.7 g, 14.8 mmol), allyl bromide (2.1 mL, 24.8 mmol), compound **S2a** (2.0 g, 12.4 mmol,) and NaI (3.72 g, 24.8 mmol) provided the intermediate, which was then treated with SnCl₂ (9.4 g, 49.6 mmol) to furnish compound **2j** (1.74 g, 74%) as a colorless liquid; ¹H-NMR (500 MHz, CDCl₃): 7.28 (2H, t, *J* = 7.9 Hz), 7.04 (1H, t, *J* = 7.6 Hz), 6.82 (1H, d, *J* = 7.5 Hz), 5.78-5.71 (1H, m), 5.12-5.03 (2H, m), 3.49 (1H, t, *J* = 6.7 Hz), 3.21 (3H, s), 2.86-2.81 (1H, m), 2.58-2.52 (1H, m); ¹³C-NMR (100 MHz, CDCl₃) δ 177.3, 144.5, 134.3, 128.8, 128.1, 124.3, 122.4, 118.0, 108.0, 45.3, 35.1, 26.3; HRMS (ESI) calcd for C₁₂H₁₄NO [M+H]⁺: 188.1075; Found: 188.1066.

3-Allyl-1-benzylindolin-2-one (2k)⁷: Using the general procedure **GP-1**, indium metal (1.2 g, 10.1 mmol), allyl bromide (1.5 mL, 16.86 mmol), compound **S2c** (2.0 g, 8.43 mmol,) and NaI (2.53 g, 16.86 mmol) provided the intermediate, which was then treated with SnCl₂ (6.4 g, 33.7 mmol) to furnish compound **2k** (1.76 g, 78%) as a colorless liquid; ¹H-NMR (400 MHz, CDCl₃): 7.30-7.22 (6H, m), 7.14 (1H, t, *J* = 7.8 Hz), 6.98 (1H, t, *J* = 7.4 Hz), 6.69 (1H, d, *J* = 7.8 Hz), 5.79-5.69 (1H, m), 5.15-4.96 (3H, m), 4.81 (1H, d, *J* = 15.6 Hz), 3.59 (1H, t, *J* = 5.9 Hz), 2.91-

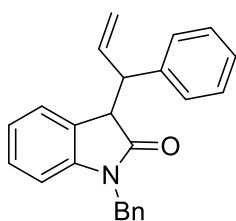
2.84 (1H, m), 2.68-2.61 (1H, m); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): 177.3, 143.6, 136.0, 134.0, 128.8, 128.7, 127.9, 127.6, 127.4, 124.3, 122.3, 118.2, 109.1, 45.3, 43.8, 35.0; HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{18}\text{NO}$ $[\text{M}+\text{H}]^+$: 264.1338; Found: 264.1319.

1-Benzyl-3-(but-3-en-2-yl)indolin-2-one (2l): Using the general procedure **GP-1**, indium metal (1.2 g, 10.1 mmol), crotyl bromide (1.74 mL, 16.86 mmol), compound **S2a** (2.0 g, 8.43 mmol)



and NaI (2.53 g, 16.86 mmol) provided the intermediate, which was then treated with SnCl_2 (6.4 g, 33.7 mmol) to furnish compound **2l** (1.56 g, 67%) containing 1:2 mixture of two diastereomer (confirmed by ^1H NMR analysis) as a colorless liquid; $^1\text{H-NMR}$ (500 MHz, CDCl_3): 7.31-7.21 (18H, m), 7.14 (3H, t, $J = 7.6$ Hz), 7.0-6.94 (3H, m), 6.71-6.67 (3H, m), 6.06-5.99 (2H, m), 5.67-5.60 (1H, m), 5.14-5.09 (5H, m), 5.05-5.00 (3H, m), 4.93 (1H, d, $J = 10.1$ Hz), 4.79 (2H, d, $J = 15.2$ Hz), 4.72 (1H, d, $J = 15.8$ Hz), 3.61 (2H, d, $J = 3.2$ Hz), 3.53 (1H, d, $J = 3.8$ Hz), 3.21-3.15 (2H, m), 3.12-3.06 (1H, m), 1.27 (3H, d, $J = 7.6$ Hz), 0.93 (6H, d, $J = 6.9$ Hz); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): 176.9, 176.8, 143.9, 140.8, 139.3, 136.2, 136.1, 128.8, 128.7, 128.0, 127.9, 127.7, 127.6, 127.5, 127.4, 127.3, 127.1, 124.7, 124.6, 122.2, 115.8, 115.2, 109.0, 108.9, 51.2, 50.3, 43.8, 43.7, 40.4, 38.7, 18.0, 14.0; HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{20}\text{NO}$ $[\text{M}+\text{H}]^+$: 278.1545; Found: 278.1531.

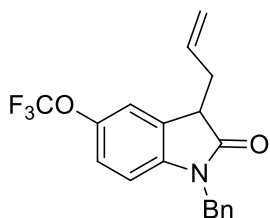
1-Benzyl-3-(1-phenylallyl)indolin-2-one (2m): Using the general procedure **GP-1**, indium metal (1.2 g, 10.1 mmol), cinnamyl bromide (2.5 mL, 16.86 mmol), compound **S2a** (2.0 g, 8.43 mmol)



and NaI (2.53 g, 16.86 mmol) provided the intermediate, which was then treated with SnCl_2 (6.4 g, 33.7 mmol) to furnish compound **2m** (2 g, 70%) containing 1:1 mixture of two diastereomer (confirmed by ^1H NMR analysis) as a colorless liquid; $^1\text{H-NMR}$ (500 MHz, CDCl_3): 7.41-7.07 (21H, m), 7.0-6.97 (2H, m), 6.85 (1H, t, $J = 7.6$ Hz), 6.71 (1H, d, $J = 7.6$ Hz), 6.60 (2H, d, $J = 8.4$ Hz), 6.49-6.43 (2H, m), 5.94-5.86 (1H, m), 5.33-5.23 (3H, m), 5.16 (1H, d, $J = 9.2$ Hz), 5.07 (2H, t, $J = 15.1$ Hz), 4.63 (1H, d, $J = 15.1$ Hz), 4.38-4.31 (3H, m), 3.99 (2H, t, $J = 4.2$ Hz); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): 176.3, 176.1, 143.9, 141.1, 139.2, 138.7, 135.7, 135.4, 135.3, 129.2, 128.7, 128.6, 128.3, 128.2, 128.1, 127.6, 127.4, 127.2, 127.1, 126.9,

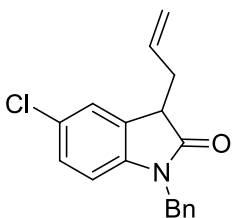
126.7, 126.5, 125.2, 124.9, 122.1, 118.9, 116.9, 109.3, 109.1, 51.5, 51.2, 50.9, 50.1, 43.8, 43.5; HRMS (ESI) calcd for C₂₄H₂₂NO [M+H]⁺: 340.1701; Found: 340.1711.

3-Allyl-1-benzyl-5-(trifluoromethoxy)indolin-2-one (2n): Using the general procedure **GP-1**,



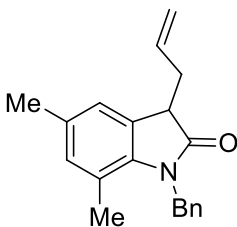
indium metal (851 mg, 7.5 mmol), allyl bromide (1.01 mL, 12.44 mmol), compound **S2k** (2.0 g, 6.22 mmol) and NaI (1.9 g, 12.44 mmol) provided the intermediate, which was then treated with SnCl₂ (4.72 g, 24.9 mmol) to furnish compound **2n** (1.65 g, 76%) as a colorless liquid; ¹H-NMR (400 MHz, CDCl₃): 7.34-7.24 (5H, m), 7.18 (1H, s), 7.02 (1H, d, *J* = 8.5 Hz), 6.66 (1H, d, *J* = 9.1 Hz), 5.78-5.68 (1H, m), 5.16-5.08 (2H, m), 4.97 (1H, d, *J* = 15.2 Hz), 4.82 (1H, d, *J* = 15.8 Hz) 3.61 (1H, t, *J* = 4.9 Hz), 2.92-2.86 (1H, m), 2.67-2.59 (1H, m); ¹³C-NMR (100 MHz, CDCl₃): 177.0, 144.6, 142.2, 135.6, 133.4, 130.1, 128.9, 127.9, 127.4, 121.1, 118.9, 118.4, 109.4, 45.4, 44.0, 34.9; HRMS (ESI) calcd for C₁₉H₁₇F₃NO₂ [M+H]⁺: 348.1211; Found: 348.1219.

3-Allyl-1-benzyl-5-chloroindolin-2-one (2o): Using the general procedure **GP-1**, indium metal



(1.0 g, 8.83 mmol), allyl bromide (1.3 mL, 14.7 mmol), compound **S2n** (2.0 g, 7.36 mmol) and NaI (2.21 g, 14.7 mmol) provided the intermediate, which was then treated with SnCl₂ (5.6 g, 29.44 mmol) to furnish compound **2o** (1.48 g, 68%) as a yellow liquid; ¹H-NMR (400 MHz, CDCl₃): 7.32-7.24 (6H, m), 7.11 (1H, dd, *J* = 1.8, 6.7 Hz), 6.59 (1H, d, *J* = 8.6 Hz), 5.76-5.67 (1H, m), 5.17-5.07 (2H, m), 4.96 (1H, d, *J* = 15.3 Hz), 4.79 (1H, d, *J* = 15.3 Hz), 3.59 (1H, t, *J* = 4.9 Hz), 2.90-2.83 (1H, m), 2.68-2.61 (1H, m); ¹³C-NMR (100 MHz, CDCl₃): 176.8, 142.1, 135.6, 133.5, 130.3, 128.9, 127.9, 127.8, 127.3, 124.8, 118.8, 109.9, 45.3, 43.9, 34.9; HRMS (ESI) calcd for C₁₈H₁₇ClNO [M+H]⁺: 298.0999; Found: 298.1007.

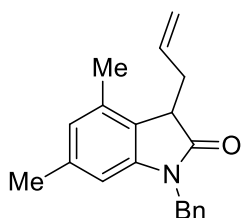
3-allyl-1-benzyl-5,7-dimethylindolin-2-one (2p): Using the general procedure **GP-1**, indium metal



(515 mg, 4.5 mmol), allyl bromide (0.5 mL, 5.7 mmol), compound **S2t** (1.0 g, 3.77 mmol) and NaI (1.1 g, 7.54 mmol) provided the

intermediate, which was then treated with SnCl_2 (2.9 g, 15.1 mmol) to furnish compound **2p** (681 mg, 62%) as a yellow liquid; $^1\text{H-NMR}$ (500 MHz, CDCl_3): 7.27 (2H, q, $J = 7.6$ Hz), 7.22 (1H, t, $J = 7.6$ Hz), 7.14 (1H, d, $J = 7.7$ Hz), 6.99 (1H, s), 6.74 (1H, s), 5.81-5.73 (1H, m), 5.24-5.01 (4H, m), 3.58 (1H, t, $J = 5.9$ Hz), 2.88-2.83 (1H, m), 2.73-2.67 (1H, m), 2.27 (3H, s), 2.21 (3H, s); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): 178.3, 139.3, 137.9, 134.3, 132.4, 131.9, 129.5, 128.9, 127.2, 125.9, 122.9, 119.5, 118.3, 45.1, 35.4, 20.9, 18.7; HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{22}\text{NO}$ $[\text{M}+\text{H}]^+$: 292.1701; Found: 298.1709.

3-allyl-1-benzyl-4,6-dimethylindolin-2-one (2q): Using the general procedure **GP-1**, indium



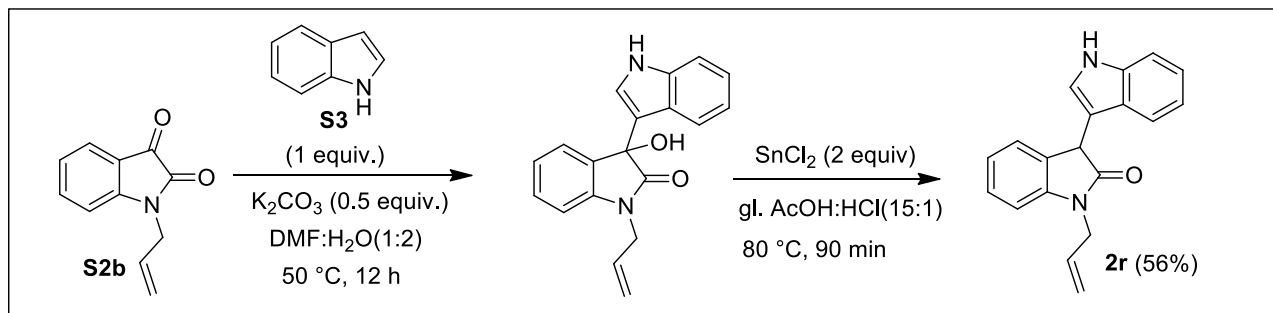
metal (515 mg, 4.5 mmol), allyl bromide (0.5 mL, 5.7 mmol), compound **S2u** (1.0 g, 3.8 mmol,) and NaI (1.1 g, 7.5 mmol) provided the intermediate, which was then treated with SnCl_2 (2.9 g, 15.1 mmol) to furnish compound **2q** (659 mg, 60%) as a yellow liquid; $^1\text{H-NMR}$ (500 MHz, CDCl_3): 7.29-7.19 (5H, m), 6.62 (1H, s), 6.35 (1H, s), 5.49-5.41 (1H, m), 5.09-5.05 (1H, m), 5.01 (1H, d, $J = 15.8$ Hz), 4.90 (1H, dd, $J = 1.3, 8.9$ Hz), 4.71 (1H, d, $J = 15.8$ Hz), 3.59 (1H, t, $J = 5.0$ Hz), 2.96-2.83 (2H, m), 2.29 (3H, s), 2.22 (3H, s); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): 177.7, 143.9, 137.9, 136.3, 134.1, 133.0, 128.7, 127.5, 127.3, 124.9, 123.0, 118.1, 107.5, 45.2, 43.7, 33.4, 21.7, 18.7; HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{22}\text{NO}$ $[\text{M}+\text{H}]^+$: 292.1701; Found: 292.1712.

4.0.3 Synthesis of 3-indolyl 2-oxindole 2r (GP-2):

To a stirring solution of isatin **S2b** (1 equiv.) and indole **S3** (1 equiv.) in $\text{DMF:H}_2\text{O}$ (1:2) was added K_2CO_3 (0.5 equiv.) portion wise and the resulting reaction mixture was heated at 50 °C for 12 h. After completion of reaction (TLC monitoring), the reaction mixture was cooled down to room temperature and quenched with water and extracted with ethyl acetate (3 X 20 mL). The combined organic extracts were washed with brine (15 mL) and dried on (Na_2SO_4), and concentrated in vacuo to provide crude 3-indolyl hydroxyl 2-oxindole.

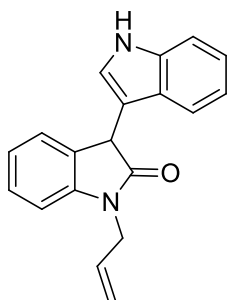
The crude product was dissolved in 40 mL AcOH/HCl (15/1) and then SnCl_2 (4 equiv) was added. The reaction mixture was stirred at 80 °C for 2 h, then cooled to room temperature and diluted with water. The product was extracted with Et_2O . The combined organic extracts

were washed with aq NaOH, dried with MgSO₄, and then concentrated. Purification by column chromatography using ethyl acetate-hexane (20/80 to 30/70) furnished compounds **2r** (Scheme S5).



Scheme S5. Synthesis of 3-indolyl oxindole **2r** from isatin **S2b**.

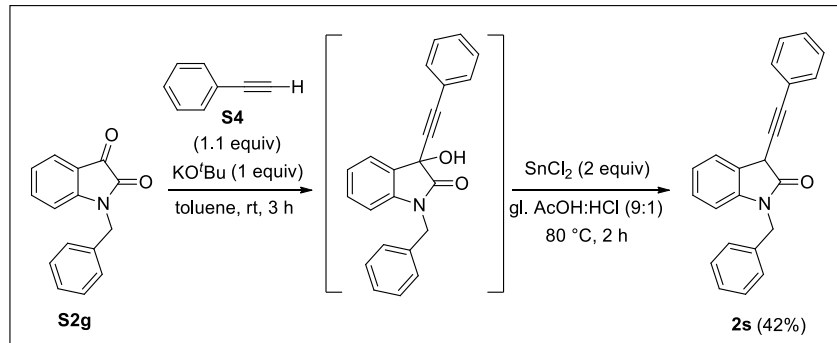
1-Allyl-3-(1H-indol-3-yl)indolin-2-one (2r): Using the general procedure **GP-2**, compound **S2b** (2 g, 10.7 mmol), indole **S3** (1.2 g, 10.7 mmol) and K₂CO₃ (730 mg, 5.32 mmol) provided the



intermediate, which upon treatment with SnCl₂ (4.18 g, 21.4 mmol) provided compound **2r** (1.78 g, 56%) as a deep purple colored gummy mass; ¹H-NMR (500 MHz, CDCl₃): 8.67 (1H, br s), 7.27 (1H, t, *J* = 7.6 Hz), 7.21 (1H, d, *J* = 8.2 Hz), 7.12 (1H, dd, *J* = 7.6, 5.1 Hz), 7.08 (1H, t, *J* = 7.6 Hz), 6.99-6.92 (3H, m), 6.75 (1H, s), 5.93-5.85 (1H, m), 5.26 (1H, dd, *J* = 12.9, 4.0 Hz), 4.86 (1H, s), 4.48-4.39 (1H, m); ¹³C-NMR (125

MHz, CDCl₃): 176.8, 143.3, 136.8, 131.6, 129.4, 128.1, 126.2, 125.0, 124.0, 122.9, 122.2, 119.6, 119.0, 117.9, 117.7, 110.1, 109.1, 44.8, 42.7; HRMS (ESI) calcd for C₁₉H₁₇N₂O [M+H]⁺: 289.1341; Found: 289.1363.

4.0.4 Synthesis of 1-benzyl-3-(phenylethynyl)indolin-2-one **2s**:



Scheme S6. Synthesis of 3-phenylethynyl- oxindole **2s** from isatin **S2g**.

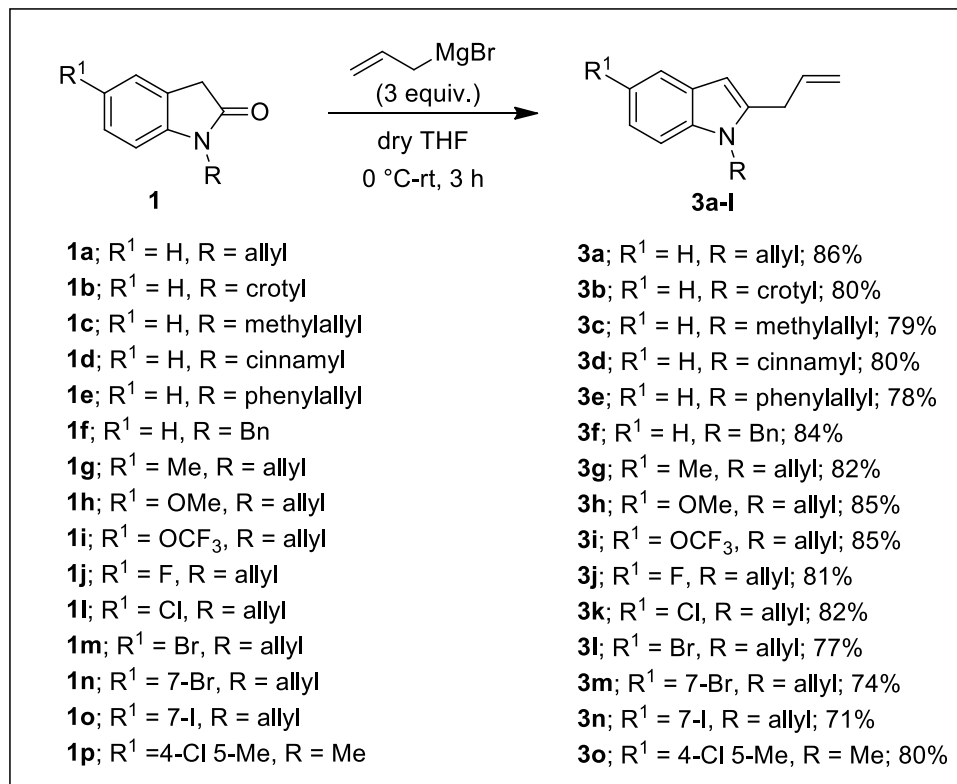
To a solution of phenylacetylene **S4** (1.2 mL, 1.1 equiv) in anhydrous toluene (3 mL) under an argon atmosphere, KO^tBu (473 mg, 1.0 equiv) was added, and the mixture was stirred for 10–15 min. Then, **S2g** (1.0 g, 1.0 equiv) was added to the reaction mixture, which was stirred for 3 h until all the isatin was consumed (confirmed by TLC).⁸ The reaction was quenched with a few drops of 1 N HCl and the resulting mixture was extracted with CH₂Cl₂ (2 × 15 mL). The combined organic phases were washed with a saturated aqueous solution of sodium chloride, dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure.

The crude product was dissolved in 40 mL AcOH/HCl (15/1), and then SnCl₂ (1.6 g, 2 equiv) was added. The reaction mixture was stirred at 80 °C for 2 h and then cooled to room temperature and diluted with water. The product was extracted with Et₂O (3 X 10 mL). The combined organic extracts were washed with aq. NaOH, dried with MgSO₄, and then concentrated to afford crude oxindole. Purification by column chromatography using ethylacetate-hexane (10/90 to 20/80) furnished compound **2s** (600 mg, 42%) as a brown solid (Scheme S6). ¹H-NMR (400 MHz, CDCl₃): 7.65 (2H, d, *J* = 7.8 Hz), 7.40 (2H, t, *J* = 7.3 Hz), 7.35-7.25 (5H, m), 7.19-7.14 (2H, m), 6.99 (2H, t, *J* = 5.9 Hz), 6.73 (1H, d, *J* = 7.8 Hz), 4.94 (2H, s), 4.79 (1H, d, *J* = 9.3 Hz); ¹³C-NMR (100 MHz, CDCl₃): 176.4, 143.4, 136.3, 136.0, 135.1, 128.9, 128.8, 128.4, 128.0, 127.8, 127.7, 127.5, 125.0, 124.8, 122.8, 122.3, 109.2, 79.0, 46.1, 44.2; HRMS (ESI) calcd for C₂₃H₁₈NO [M+H]⁺: 324.1388; Found: 323.1387.

5.0 Synthesis of 2-substituted indoles 3:

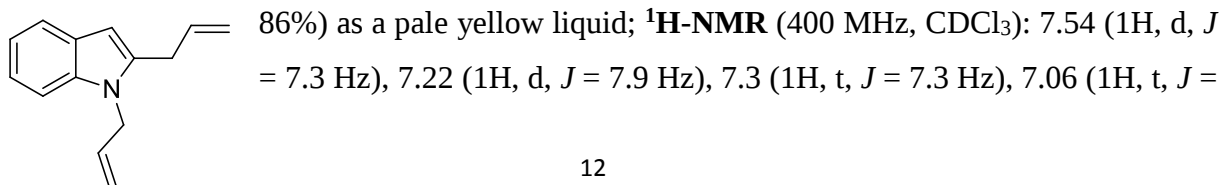
5.0.1 General procedure for the synthesis of 2-allyl indoles 3a-o (GP-3):

To a stirring solution of *N*-substituted 2-oxindoles **1** (2.1 mmol, 1 equiv.) in dry THF, allylmagnesium bromide solution (3 equiv., 1M in Et₂O) was added dropwise at room temperature. The reaction mixture was then stirred at room temperature for 3 h. After completion of reaction as monitored by the TLC, the reaction mixture was quenched with saturated aqueous NH₄Cl solution followed by extraction with EtOAc (3 x 20 mL). The combined organic phases were washed with brine, dried over anhydrous Na₂SO₄, filtered and concentrated in vacuo. The crude residue was then purified by column chromatography on silica gel with ethylacetate–hexane (5/95 to 10/80) to give compounds **3a-o** (Scheme S6).



Scheme S8. Synthesis of 2-allyl indoles **3** from oxindoles **1**.

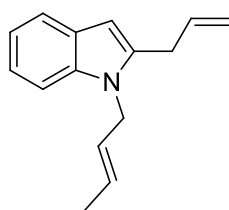
1,2-Diallyl-1H-indole (3a): Using the general procedure **GP-3**, compound **1a** (500 mg, 2.89 mmol) and allylmagnesium bromide (8.66 mL, 8.66 mmol) provided compound **3a** (482 mg,



7.3 Hz), 6.30 (1H, s), 6.04-5.87 (2H, m), 5.16-5.09 (3H, m), 4.83 (1H, d, $J = 17.7$ Hz), 4.68-4.66 (2H, m), 3.48 (2H, d, $J = 6.7$ Hz); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): 138.5, 137.2, 135.0, 133.7, 128.2, 120.9, 120.1, 119.6, 116.9, 116.3, 109.4, 100.5, 45.5, 31.4; HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{16}\text{N}$ $[\text{M}+\text{H}]^+$: 198.1283; Found: 198.1267.

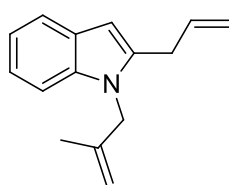
(E)-2-allyl-1-(but-2-en-1-yl)-1H-indole (3b): Using the general procedure **GP-3**, compound **1b** (500 mg, 2.67 mmol) and allylmagnesiumbromide (8.01 mL, 8.01 mmol) provided compound **3b**

(451 mg, 80%) as a colorless liquid; $^1\text{H-NMR}$ (400 MHz, CDCl_3): 7.53 (1H, d, $J = 7.3$ Hz), 7.25 (1H, d, $J = 7.9$ Hz), 7.13 (1H, t, $J = 7.9$ Hz), 7.06 (1H, t, $J = 7.9$ Hz), 6.23 (1H, s), 6.06-5.96 (1H, m), 5.56-5.49 (1H, m), 5.42-5.34 (1H, m), 5.16-5.09 (2H, m), 4.61-4.59 (2H, m), 3.48 (2H, d, $J = 2.5$ Hz), 1.62 (3H, dd, $J = 4.9, 1.8$ Hz); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): 138.4, 137.1, 135.1, 128.1, 127.6, 126.6, 120.8, 120.1, 119.4, 116.9, 109.4, 100.3, 44.9, 31.5, 17.6; HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{18}\text{N}$ $[\text{M}+\text{H}]^+$: 212.1439; Found: 212.1436.

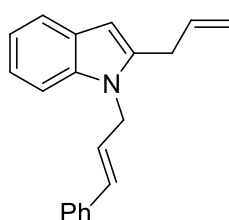


2-Allyl-1-(2-methylallyl)-1H-indole (3c): Using the general procedure **GP-3**, compound **1c** (500 mg, 2.67 mmol) and allylmagnesium bromide (8.01 mL, 8.01 mmol) provided compound **3c**

(448 mg, 79%) as a colorless liquid; $^1\text{H-NMR}$ (500 MHz, CDCl_3): 7.54 (1H, d, $J = 6.7$ Hz), 7.21 (1H, d, $J = 8.4$ Hz), 7.12 (1H, t, $J = 7.6$ Hz), 7.07-7.04 (1H, m), 6.30 (1H, s), 6.03-5.99 (1H, m), 5.15-5.09 (2H, m), 4.80 (1H, s), 4.55 (2H, s), 4.35 (1H, s), 3.45 (2H, d, $J = 5.9$ Hz), 1.69 (3H, s); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): 141.1, 138.7, 137.5, 134.9, 128.1, 120.9, 120.1, 119.5, 116.9, 111.3, 109.4, 100.4, 48.8, 31.5, 20.1; HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{18}\text{N}$ $[\text{M}+\text{H}]^+$: 212.1439; Found: 212.1426.



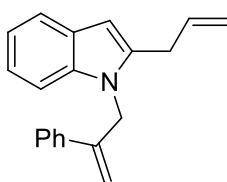
2-Allyl-1-cinnamyl-1H-indole (3d): Using the general procedure **GP-3**, compound **1d** (500 mg, 2.01 mmol) and allylmagnesium bromide (6.02 mL, 6.02 mmol) provided compound **3d** (439



mg, 80%) as a colorless liquid; $^1\text{H-NMR}$ (400 MHz, CDCl_3): 7.54 (1H, d, $J = 15.3$ Hz), 7.22-7.04 (8H, m), 6.29 (1H, s), 6.12 (2H, s), 6.01-5.91 (1H,

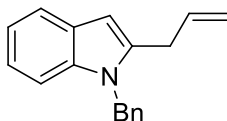
m), 5.11-5.04 (2H, m), 4.65 (2H, d, $J = 3.0$ Hz), 3.42 (2H, d, $J = 6.1$ Hz); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): 138.1, 137.1, 136.3, 134.9, 131.1, 128.5, 128.1, 127.7, 126.4, 125.2, 121.0, 120.1, 119.6, 116.9, 109.4, 100.6, 44.9, 31.4; HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{20}\text{N}$ $[\text{M}+\text{H}]^+$: 274.1596; Found: 274.1591.

2-Allyl-1-(2-phenylallyl)-1H-indole (3e): Using the general procedure **GP-3**, compound **1e** (500 mg, 2.01 mmol) and allylmagnesium bromide (6.02 mL, 6.02 mmol) provided compound **3e**

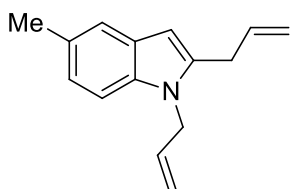


(434 mg, 78%) as a colorless liquid; $^1\text{H-NMR}$ (400 MHz, CDCl_3): 7.58 (1H, d, $J = 7.9$ Hz), 7.47 (2H, d, $J = 6.7$ Hz), 7.42-7.36 (3H, m), 7.23 (1H, d, $J = 7.9$ Hz), 7.16-7.07 (2H, m), 6.36 (1H, s), 6.08-5.98 (1H, m), 5.31 (1H, s), 5.16-5.10 (2H, m), 5.05 (2H, s), 4.27 (1H, s), 3.49 (2H, d, $J = 6.7$ Hz); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): 143.4, 139.2, 138.7, 137.4, 134.9, 128.8, 128.3, 126.0, 121.2, 120.2, 119.7, 117.0, 112.5, 109.4, 100.7, 46.5, 31.5; HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{20}\text{N}$ $[\text{M}+\text{H}]^+$: 274.1596; Found: 274.1603.

2-Allyl-1-benzyl-1H-indole (3f): Using the general procedure **GP-3**, compound **1f** (500 mg, 2.24 mmol) and allylmagnesium bromide (6.72 mL, 6.72 mmol) provided compound **3f** (420 mg, 84%) as a colorless liquid; $^1\text{H-NMR}$ (500 MHz, CDCl_3): 7.58 (1H, d, $J = 8.4$ Hz), 7.26-7.18 (4H, m), 7.11-7.08 (2H, m), 6.93 (2H, d, $J = 6.7$ Hz), 6.36 (1H, s), 6.01-5.93 (1H, m), 5.30 (2H, s), 5.09 (2H, t, $J = 12.6$ Hz), 3.42 (2H, d, $J = 5.9$ Hz); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): 138.7, 138.1, 137.6, 134.9, 128.9, 128.2, 127.4, 126.1, 121.2, 120.2, 119.7, 117.1, 109.5, 100.8, 46.6, 31.6; HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{18}\text{N}$ $[\text{M}+\text{H}]^+$: 248.1439; Found: 248.1451.

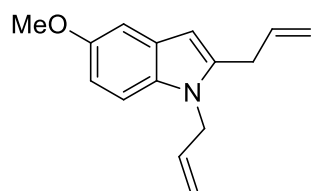


1,2-Diallyl-5-methyl-1H-indole (3g): Using the general procedure **GP-3**, compound **1g** (500 mg, 2.67 mmol) and allylmagnesium bromide (8.01 mL, 8.01 mmol) provided compound **3g** (458 mg, 82%) as a white gummy mass; $^1\text{H-NMR}$ (400 MHz, CDCl_3): 7.33 (1H, s), 7.11 (1H, d, $J = 8.8$ Hz), 6.95 (1H, d, $J = 7.9$ Hz), 6.21 (1H, s), 6.04-5.86 (2H, m), 5.15-5.08 (3H, m), 4.82 (1H, d, $J = 15.9$ Hz),



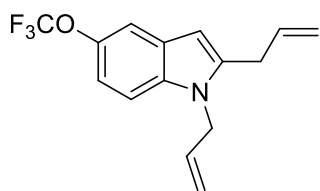
4.66-4.64 (2H, m), 3.47 (2H, d, J = 6.1 Hz), 2.43 (3H, s); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): 138.5, 135.2, 133.8, 128.7, 128.4, 122.5, 119.9, 116.8, 116.2, 109.0, 99.9, 45.5, 31.5, 21.5; HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{18}\text{N}$ $[\text{M}+\text{H}]^+$: 212.1439; Found: 212.1457.

1,2-Diallyl-5-methoxy-1H-indole (3h): Using the general procedure **GP-3**, compound **1h** (500 mg, 2.46 mmol) and allylmagnesium bromide (7.38 mL, 7.38 mmol) provided compound **3h**



(474 mg, 85%) as a colorless liquid; $^1\text{H-NMR}$ (400 MHz, CDCl_3): 7.11 (1H, d, J = 8.6 Hz), 7.03 (2H, d, J = 2.4 Hz), 6.79 (1H, dd, J = 6.1, 2.4 Hz), 6.22 (1H, s), 6.05-5.84 (2H, m), 5.15-5.09 (3H, m), 4.82 (1H, d, J = 17.7 Hz), 4.63 (2H, dd, J = 2.4, 1.9 Hz), 3.83 (3H, s), 3.46 (2H, d, J = 6.7 Hz); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): 154.2, 139.1, 135.0, 133.7, 132.5, 128.5, 116.9, 116.3, 110.9, 110.0, 102.4, 101.2, 56.0, 45.6, 31.5; HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{18}\text{NO}$ $[\text{M}+\text{H}]^+$: 228.1388; Found: 228.1385.

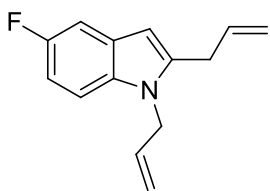
1,2-Diallyl-5-(trifluoromethoxy)-1H-indole (3i): Using the general procedure **GP-3**, compound **1i** (500 mg, 1.94 mmol) and allylmagnesium bromide (5.83 mL, 5.83 mmol) provided compound



3i (464 mg, 85%) as a colorless liquid; $^1\text{H-NMR}$ (400 MHz, CDCl_3): 7.39 (1H, s), 7.16 (1H, dd, J = 8.6, 2.5 Hz), 6.99 (1H, d, J = 7.8 Hz), 6.30 (1H, s), 5.99-5.84 (2H, m), 5.17-5.09 (3H, m), 4.80 (1H, d, J = 17.1 Hz), 4.64 (2H, d, J = 1.4 Hz), 3.46 (2H, s); $^{13}\text{C-NMR}$ (100

MHz, CDCl_3): 143.1, 140.5, 135.5, 134.5, 133.2, 128.2, 122.3, 119.8, 117.3, 116.6, 114.8, 112.5, 109.8, 100.7, 45.7, 31.6; HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{15}\text{F}_3\text{NO}$ $[\text{M}+\text{H}]^+$: 282.1106; Found: 282.1115.

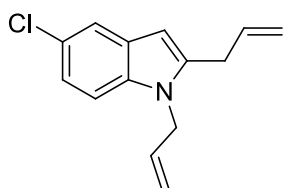
1,2-Diallyl-5-fluoro-1H-indole (3j): Using the general procedure **GP-3**, compound **1j** (500 mg, 2.62 mmol) and allylmagnesium bromide (7.85 mL, 7.85 mmol) provided compound **3j** (456 mg,



81%) as a colorless liquid; $^1\text{H-NMR}$ (400 MHz, CDCl_3): 7.18 (1H, d, J = 9.8 Hz), 7.11 (1H, dd, J = 4.4 Hz), 6.87 (1H, t, J = 9.3 Hz), 6.26 (1H, s), 6.03-5.85 (2H, m), 5.14 (3H, t, J = 11.2 Hz), 4.81 (1H, d, J = 17.1 Hz), 4.65 (2H, d, J = 2.4 Hz), 3.47 (2H, d, J = 6.4 Hz); $^{13}\text{C-NMR}$ (100

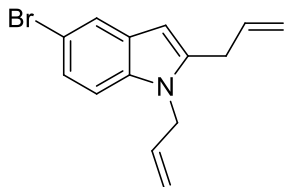
MHz, CDCl₃): 159.3, 156.9, 140.2, 134.7, 133.8, 133.4, 128.4, 128.3, 117.2, 116.5, 109.9, 109.8, 109.2, 108.9, 105.1, 104.9, 100.5, 100.4, 45.7, 31.5; HRMS (ESI) calcd for C₁₄H₁₅FN [M+H]⁺: 216.1189; Found: 216.1195.

1,2-Diallyl-5-chloro-1H-indole (3k): Using the general procedure **GP-3**, compound **1l** (500 mg, 2.41 mmol) and allylmagnesium bromide (7.22 mL, 7.22 mmol) provided compound **3k** (452



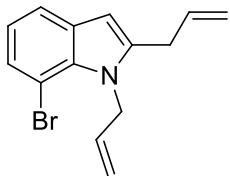
mg, 82%) as a pale yellowish liquid; ¹H-NMR (400 MHz, CDCl₃): 7.51 (1H, d, *J* = 1.8 Hz), 7.16-7.08 (2H, m), 6.25 (1H, s), 6.04-5.87 (2H, m), 5.19-5.10 (3H, m), 4.80 (1H, d, *J* = 17.1 Hz), 4.67 (2H, t, *J* = 2.4 Hz), 3.48 (2H, d, *J* = 6.1 Hz); ¹³C-NMR(100 MHz, CDCl₃): 139.9, 135.5, 134.6, 133.2, 130.5, 125.3, 121.2, 119.5, 117.3, 116.5, 110.3, 100.2, 45.6, 31.4; HRMS (ESI) calcd for C₁₄H₁₅ClN [M+H]⁺: 232.0893; Found: 232.0881.

1,2-Diallyl-5-bromo-1H-indole (3l): Using the general procedure **GP-3**, compound **1m** (500 mg, 1.98 mmol) and allylmagnesium bromide (5.95 mL, 5.95 mmol) provided compound **3l** (422 mg,



77%) as a colorless liquid; ¹H-NMR (500 MHz, CDCl₃): 7.64 (1H, s), 7.21 (1H, t, *J* = 8.4 Hz), 7.07 (1H, d, *J* = 8.4 Hz), 6.23 (1H, s), 6.01-5.84 (2H, m), 5.17-5.09 (3H, m), 4.77 (1H, d, *J* = 17.6 Hz), 4.63 (2H, t, *J* = 2.5 Hz), 3.45 (2H, d, *J* = 6.7 Hz); ¹³C-NMR (125 MHz, CDCl₃): 139.8, 135.8, 134.5, 133.2, 129.8, 123.7, 122.6, 117.3, 116.5, 112.8, 110.8, 100.1, 45.5, 31.4; HRMS (ESI) calcd for C₁₄H₁₅NBr [M+H]⁺: 276.0388; Found: 276.0390.

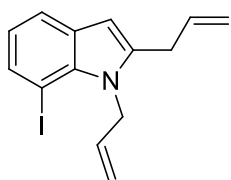
1,2-Diallyl-7-bromo-1H-indole (3m): Using the general procedure **GP-3**, compound **1n** (500 mg, 1.98 mmol) and allylmagnesium bromide (5.95 mL, 5.95 mmol) provided compound **3m**



(404 mg, 74%) as a colorless liquid; ¹H-NMR (500 MHz, CDCl₃): 7.49-7.46 (1H, m), 7.32-7.30 (1H, m), 6.92-6.88 (1H, m), 6.29 (1H, s), 6.06-6.01 (2H, m), 5.21-5.15 (4H, m), 4.41-4.38 (2H, m), 3.49 (2H, dd, *J* = 10.8, 16.4 Hz); ¹³C-NMR (100 MHz, CDCl₃): 140.8, 140.4, 135.3, 134.7, 131.5,

126.6, 120.5, 119.5, 119.4, 117.3, 115.5, 103.4, 101.3, 46.1, 31.8; HRMS (ESI) calcd for $C_{14}H_{15}NBr$ $[M+H]^+$: 276.0388; Found: 276.0397.

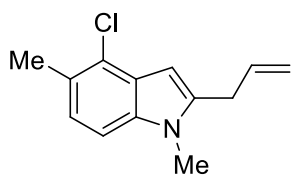
1,2-Diallyl-7-iodo-1H-indole (3n): Using the general procedure **GP-3**, compound **1o** (500 mg, 1.67 mmol) and allylmagnesium bromide (5.0 mL, 5.01 mmol) provided compound **3n** (383 mg,



71%) as a colorless liquid; 1H -NMR (500 MHz, $CDCl_3$): 7.54 (1H, d, J = 7.6 Hz), 7.15-7.12 (1H, m), 7.08-7.05 (1H, m), 6.30 (1H, s), 6.05-5.97 (1H, m), 5.95-5.87 (1H, m), 5.16-5.09 (3H, m), 4.86-4.82 (1H, m), 4.68-4.67 (2H, m), 3.48 (2H, d, J = 5.1 Hz); ^{13}C -NMR (100 MHz, $CDCl_3$): 138.5,

137.2, 135.0, 133.7, 129.2, 121.0, 120.8, 120.1, 119.6, 116.9, 116.3, 109.4, 100.5, 97.9, 45.5, 31.5; HRMS (ESI) calcd for $C_{14}H_{15}NI$ $[M+H]^+$: 324.0249; Found: 324.0241.

2-Allyl-4-chloro-1,5-dimethyl-1H-indole (3o): Using the general procedure **GP-3**, compound **1p** (200 mg, 1.02 mmol) and allylmagnesium bromide (3.1 mL, 3.07 mmol) provided compound **3o**

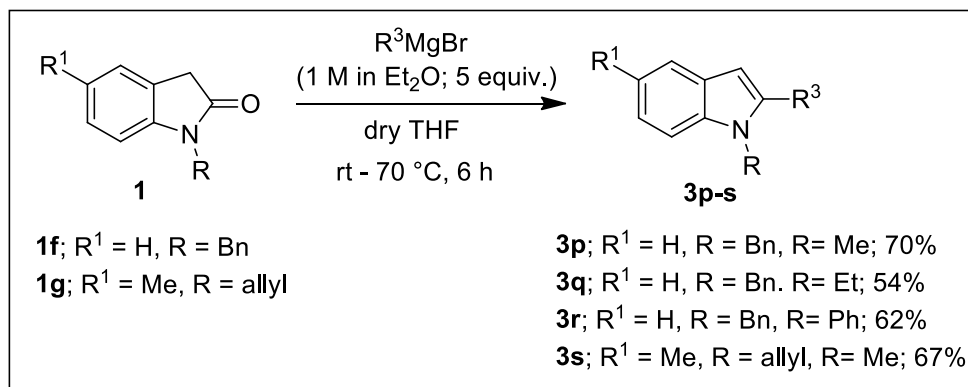


(179 mg, 80%) as a colorless liquid; 1H -NMR (500 MHz, $CDCl_3$): 7.14 (1H, d, J = 8.6 Hz), 7.08 (1H, d, J = 8.2 Hz), 6.43 (1H, s), 6.13-6.05 (1H, m), 5.25 (1H, d, J = 1.5, 17.0 Hz), 3.69 (3H, s), 3.59 (2H, d, J = 6.3 Hz), 2.54 (3H, s); ^{13}C -NMR (100 MHz, $CDCl_3$): 139.3, 136.9,

134.6, 127.2, 125.9, 123.6, 117.8, 107.3, 98.7, 31.6, 29.9, 19.4; HRMS (ESI) calcd for $C_{13}H_{15}NCl$ $[M+H]^+$: 220.0893; Found: 220.0899.

5.0.2 General procedure for the synthesis of 2-alkyl or 2-aryl indoles 3p-s (GP-4):

To a stirring solution of *N*-substituted 2-oxindoles **1** (1 equiv.) in dry THF, alkyl or aryl magnesium bromide reagent (5 equiv, 1M in Et_2O) was added dropwise at room temperature. The resulting reaction mixture was then heated at 70 °C for 6 h. After completion of reaction, as monitored by the TLC, the mixture was quenched with saturated aqueous NH_4Cl solution and extracted with $EtOAc$ (3 x 20 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4 , filtered and concentrated in vacuo. The crude residue was then purified by column chromatography on silica gel with $EtOAc$ –hexane (5/95 to 10/80) to give compounds **3p-s** (Scheme S7).

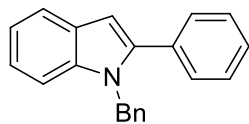


Scheme S9. Synthesis of 2-alkyl/aryl indoles **3p-s** from oxindoles **1**.

1-Benzyl-2-methyl-1H-indole (3p): Using the general procedure **GP-4**, compound **1f** (200 mg, 0.89 mmol) and methylmagnesium bromide (4.48 mL, 4.48 mmol) provided compound **3p** (138 mg, 70%) as a colorless liquid; **¹H-NMR** (400 MHz, CDCl₃): 7.55 (1H, d, *J* = 8.3 Hz), 7.27-7.19 (4H, m), 7.09-7.07 (2H, m), 6.97 (2H, d, *J* = 7.3 Hz), 6.33 (1H, s), 5.31 (2H, s), 2.37 (3H, s); **¹³C-NMR** (100 MHz, CDCl₃): 138.1, 137.4, 136.8, 128.9, 128.3, 127.4, 126.2, 120.9, 119.9, 119.8, 109.3, 100.7, 46.6, 12.9; HRMS (ESI) calcd for C₁₆H₁₆N [M+H]⁺: 222.1283; Found: 222.1268.

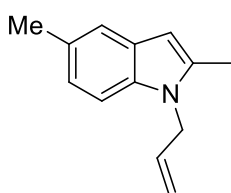
1-Benzyl-2-ethyl-1H-indole (3q): Using the general procedure **GP-4**, compound **1f** (200 mg, 0.89 mmol) and ethylmagnesium bromide (4.48 mL, 4.48 mmol) provided compound **3q** (112 mg, 54%) as a colorless liquid; **¹H-NMR** (400 MHz, CDCl₃): 7.58 (1H, dd, *J* = 3.4, 2.9 Hz), 7.27-7.18 (4H, m), 7.10-7.07 (2H, m), 6.95 (2H, d, *J* = 6.8 Hz), 6.35 (1H, s), 5.32 (2H, s), 2.68 (2H, q, *J* = 6.8 Hz), 1.32 (3H, t, *J* = 7.8 Hz); **¹³C-NMR** (100 MHz, CDCl₃): 143.0, 138.1, 137.4, 128.9, 128.3, 127.3, 128.1, 120.9, 120.0, 119.6, 109.3, 98.7, 96.5, 20.2, 12.7; HRMS (ESI) calcd for C₁₇H₁₈N [M+H]⁺: 236.1439; Found: 236.1455.

1-Benzyl-2-phenyl-1H-indole (3r): Using the general procedure **GP-4**, compound **1f** (200 mg, 0.89 mmol) and phenylmagnesium bromide (4.48 mL, 4.48 mmol)



provided compound **3r** (156 mg, 62%) as a colorless liquid; **¹H-NMR** (500 MHz, CDCl₃): 7.52 (2H, d, *J* = 7.6 Hz), 7.37 (3H, t, *J* = 6.9 Hz), 7.31-7.26 (3H, m), 7.20 (1H, s), 7.19-7.16 (1H, m), 7.08-7.06 (2H, m), 6.95 (2H, d, *J* = 7.6 Hz), 6.58 (1H, s), 5.30 (1H, s); **¹³C-NMR** (100 MHz, CDCl₃): 138.4, 138.2, 132.9, 129.4, 128.9, 128.7, 128.5, 128.2, 127.4, 127.3, 126.1, 122.1, 120.7, 120.3, 110.8, 102.5, 47.9; HRMS (ESI) calcd for C₂₁H₁₈N [M+H]⁺: 284.1439; Found: 284.1423.

1-Allyl-2,5-dimethyl-1H-indole (3s): Using the general procedure **GP-4**, compound **1g** (200 mg,

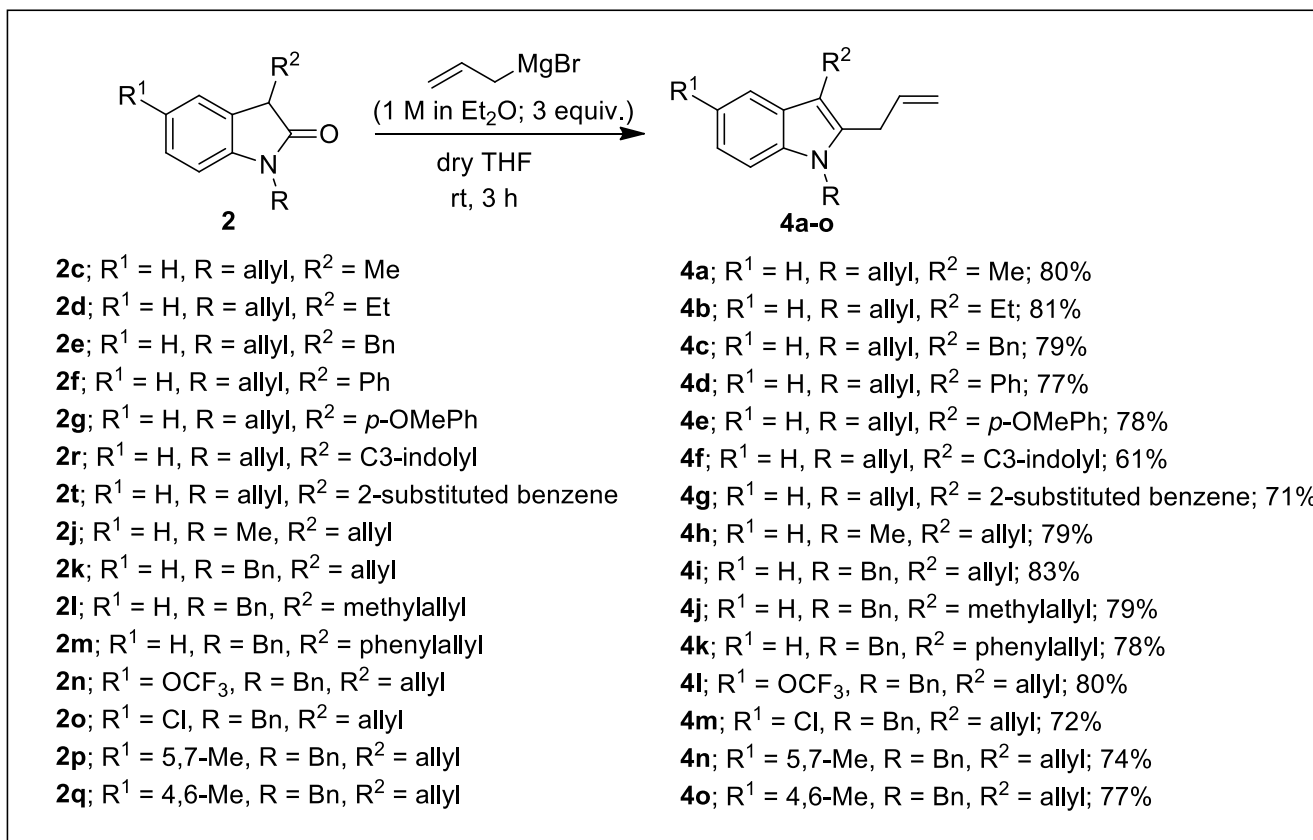


1.07 mmol) and methylmagnesium bromide (5.34 mL, 5.34 mmol) provided compound **3s** (133 mg, 67%) as a straw yellow colored liquid; **¹H-NMR** (400 MHz, CDCl₃): 7.31 (1H, s), 7.10 (1H, d, *J* = 8.6 Hz), 6.94 (1H, d, *J* = 7.9 Hz), 6.18 (1H, s), 5.95-5.88 (1H, m), 5.09 (1H, dd, *J* = 9.2, 1.2 Hz), 4.79 (1H, dd, *J* = 15.3, 1.8 Hz), 4.66-4.64 (2H, m), 2.42 (3H, s), 2.37 (3H, s); **¹³C-NMR** (100 MHz, CDCl₃): 136.7, 135.3, 133.6, 128.6, 128.5, 122.1, 119.6, 116.1, 108.8, 99.8, 45.4, 21.5, 12.6; HRMS (ESI) calcd for C₁₃H₁₆N [M+H]⁺: 186.1283; Found: 186.1274.

6.0 General procedure for the synthesis of 2,3-disubstituted indoles 4:

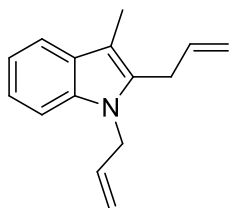
6.0.1 General procedure for the synthesis of C2 allyl 2,3-disubstituted indoles 4a-o (GP-5):

To a stirring solution of *N*- and 3-substituted 2-oxindoles **2** (1 equiv.) in dry THF, allylmagnesium bromide reagent (3 equiv, 1M in Et₂O) was added dropwise at room temperature. The resulting reaction mixture was then stirred at room temperature for 3 h. After completion of reaction as monitored by TLC, the mixture was quenched with saturated aqueous NH₄Cl solution and extracted with EtOAc (3 x 20 mL). The combined organic phases were washed with brine, dried over anhydrous Na₂SO₄, filtered and concentrated in vacuo. The crude residue was then purified by column chromatography on silica gel with EtOAc–hexane (5/95 to 20/80) to give compounds **4a-o** (Scheme S8).



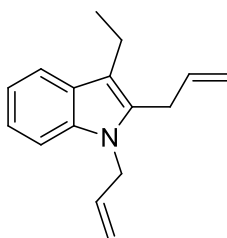
Scheme S10. Allyl Grignard addition to 3-substituted 2-oxindoles **2**.

1,2-Diallyl-3-methyl-1H-indole (4a): Using the general procedure **GP-5**, compound **2c** (500 mg,



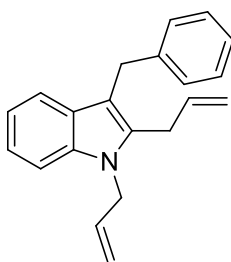
2.67 mmol) and allylmagnesium bromide (8 mL, 8.0 mmol) provided compound **4a** (455 mg, 80%) as a colorless liquid; **¹H-NMR** (500 MHz, CDCl₃): 7.51 (1H, d, *J* = 8.2 Hz), 7.19 (1H, d, *J* = 8.2 Hz), 7.15-7.12 (1H, m), 7.08 (1H, t, *J* = 7.6 Hz), 5.90-5.85 (2H, m), 5.08-5.03 (2H, m), 4.94 (1H, dd, *J* = 15.4, 1.3 Hz), 4.83 (1H, dd, *J* = 15.4, 1.9 Hz), 4.64-4.63 (2H, m), 3.48-3.47 (2H, m), 2.25 (3H, s); **¹³C-NMR** (100 MHz, CDCl₃): 136.4, 135.2, 134.2, 133.5, 128.7, 121.0, 118.9, 118.4, 116.1, 116.0, 109.2, 107.9, 45.6, 28.8, 8.8; HRMS (ESI) calcd for C₁₅H₁₈N [M+H]⁺: 212.1439; Found: 212.1424.

1,2-Diallyl-3-ethyl-1H-indole (4b): Using the general procedure **GP-5**, compound **2d** (500 mg, 2.48 mmol) and allylmagnesium bromide (7.5 mL, 7.5 mmol) provided compound **4b** (454 mg,



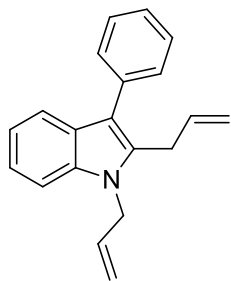
81%) as a pale yellow liquid; ¹H-NMR (500 MHz, CDCl₃): 7.56 (1H, d, *J* = 8.2 Hz), 7.21 (1H, d, *J* = 8.1 Hz), 7.15-7.12 (1H, m), 7.07 (1H, t, *J* = 6.9 Hz), 5.91-5.86 (2H, m), 5.08-5.04 (2H, m), 4.95 (1H, dd, *J* = 1.3, 15.2 Hz), 4.83 (1H, dd, *J* = 15.3, 1.3 Hz), 4.63 (2H, q, *J* = 1.9 Hz), 3.47-3.45 (2H, m), 2.73 (2H, q, *J* = 7.6 Hz), 1.21 (3H, t, *J* = 7.6 Hz); ¹³C-NMR (100 MHz, CDCl₃): 136.5, 135.8, 134.2, 132.9, 127.8, 121.0, 118.9, 118.5, 116.1, 114.8, 109.3, 45.6, 28.7, 17.8, 16.1; HRMS (ESI) calcd for C₁₆H₂₀N [M+H]⁺: 226.1596; Found: 226.1597.

1,2-Diallyl-3-benzyl-1H-indole (4c): Using the general procedure **GP-5**, compound **2e** (500 mg, 1.90 mmol) and allylmagnesium bromide (5.70 mL, 5.70 mmol) provided compound **4c** (426



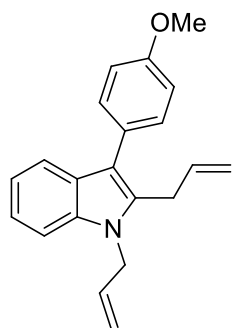
mg, 79%) as a white gummy mass; ¹H-NMR (400 MHz, CDCl₃): 7.47 (1H, d, *J* = 7.8 Hz), 7.30-7.25 (5H, m), 7.19 (2H, t, *J* = 6.4 Hz), 7.08 (1H, t, *J* = 7.8 Hz), 6.05-6.84 (2H, m), 5.11 (2H, dd, *J* = 16.6, 9.8 Hz), 5.01 (1H, d, *J* = 17.1 Hz), 4.89 (1H, d, *J* = 17.6 Hz), 4.78-4.74 (2H, m), 4.15 (2H, s), 3.56 (2H, d, *J* = 5.4 Hz); ¹³C-NMR (100 MHz, CDCl₃): 141.8, 136.6, 135.2, 134.5, 134.0, 133.8, 131.7, 128.5, 128.4, 128.3, 125.8, 121.8, 121.2, 119.9, 119.4, 119.2, 118.9, 116.3, 116.2, 111.2, 109.3, 45.7, 30.4, 28.9; HRMS (ESI) calcd for C₂₁H₂₂N [M+H]⁺: 288.1752; Found: 288.1750.

1,2-Diallyl-3-phenyl-1H-indole (4d): Using the general procedure **GP-5**, compound **2f** (500 mg, 2.01 mmol) and allylmagnesium bromide (6.02 mL, 6.02 mmol) provided



compound **4d** (422 mg, 77%) as a colorless liquid; ¹H-NMR (500 MHz, CDCl₃): 7.69 (1H, d, *J* = 7.5 Hz), 7.50 (2H, d, *J* = 7.2 Hz), 7.43 (2H, t, *J* = 7.6 Hz), 7.29 (2H, t, *J* = 7.6 Hz), 7.20 (1H, t, *J* = 7.6 Hz), 7.12 (1H, t, *J* = 7.5 Hz), 6.06-6.02 (1H, m), 5.91-5.96 (1H, m), 5.13 (2H, q, *J* = 9.2 Hz), 4.99 (1H, dd, *J* = 15.3, 1.7 Hz), 4.90 (1H, d, *J* = 16.8 Hz), 4.73 (2H, t, *J* = 2.5 Hz), 3.56 (2H, d, *J* = 5.1 Hz); ¹³C-NMR (100 MHz, CDCl₃): 136.6, 135.9, 135.6, 133.9, 133.8, 129.7, 128.6, 127.4, 126.1, 121.7, 119.9, 119.3, 116.7, 116.5, 115.7, 109.6, 45.8, 29.2; HRMS (ESI) calcd for C₂₀H₂₀N [M+H]⁺: 274.1596; Found: 274.1567.

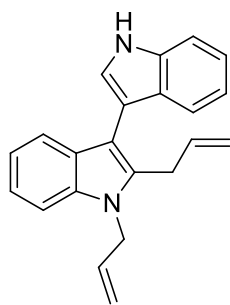
1,2-Diallyl-3-(4-methoxyphenyl)-1H-indole (4e): Using the general procedure **GP-5**, compound



2g (500 mg, 1.79 mmol) and allylmagnesium bromide (5.35 mL, 5.35 mmol) provided compound **4e** (421 mg, 78%) as a pale yellowish liquid; ¹H-NMR (400 MHz, CDCl₃): 7.56 (1H, d, *J* = 8.6 Hz), 7.36-7.32 (2H, m), 7.21 (1H, d, *J* = 7.9 Hz), 7.11 (1H, t, *J* = 7.9 Hz), 7.03 (1H, t, *J* = 7.3 Hz), 6.90 (1H, d, *J* = 9.2 Hz), 5.98-5.82 (2H, m), 5.05 (2H, ddd, *J* = 1.2 Hz), 4.91 (1H, dd, *J* = 1.8, 15.3 Hz), 4.83 (1H, dd, *J* = 1.2, 15.8 Hz), 4.64 (2H, t, *J* = 1.8 Hz), 3.76 (3H, s), 3.46 (2H, q, *J* = 1.8 Hz); ¹³C-NMR (100 MHz, CDCl₃): 158.2,

136.5, 136.0, 133.8, 133.6, 130.7, 127.9, 127.6, 121.5, 119.8, 119.3, 116.6, 16.4, 115.2, 114.1, 109.5, 55.4, 45.8, 29.2; HRMS (ESI) calcd for C₂₁H₂₂NO [M+H]⁺: 304.1701; Found: 304.1704.

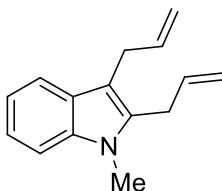
1,2-Diallyl-1H,1'H-3,3'-biindole (4f): Using the general procedure **GP-5**, compound **2r** (500 mg, 1.73 mmol) and allylmagnesium bromide (5.02 mL, 5.02 mmol) provided compound **4f** (331



mg, 61%) as a colorless liquid; ¹H-NMR (500 MHz, CDCl₃): 8.22 (1H, br s), 7.56 (2H, dd, *J* = 7.6, 5.7 Hz), 7.45 (1H, d, *J* = 8.2 Hz), 7.33 (1H, d, *J* = 8.2 Hz), 7.24-7.19 (3H, m), 7.12-7.06 (2H, m), 5.16-5.09 (2H, m), 5.02-4.94 (2H, m), 4.79 (2H, d, *J* = 4.4 Hz) 3.57 (2H, d, *J* = 4.4 Hz); ¹³C-NMR (125 MHz, CDCl₃): 136.7, 136.5, 134.8, 134.0, 128.6, 128.1, 122.9, 122.2, 121.3, 120.9, 120.2, 119.7, 119.4, 116.4, 116.3, 111.2, 110.9, 109.4, 107.9, 46.0,

29.6; HRMS (ESI) calcd for C₂₂H₂₁N₂ [M+H]⁺: 313.1705; Found: 313.1706.

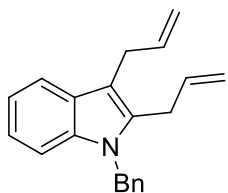
2,3-Diallyl-1-methyl-1H-indole (4h): Using the general procedure **GP-5**, compound **2j** (500 mg, 2.67 mmol) and allylmagnesium bromide (8 mL, 8 mmol) provided compound **4h** (450 mg,



79%) as a colorless liquid; ¹H-NMR (500 MHz, CDCl₃): 7.53 (1H, t, *J* = 8.0 Hz), 7.24 (1H, t, *J* = 8.1 Hz), 7.16 (1H, q, *J* = 7.0 Hz), 7.07 (1H, t, *J* = 8.1 Hz), 6.02-5.88 (2H, m), 5.08-4.93 (4H, m), 3.63 (3H, s), 3.49 (4H, dd, *J* = 6.0, 5.1 Hz); ¹³C-NMR (100 MHz, CDCl₃): 137.9, 137.0, 135.2, 134.4,

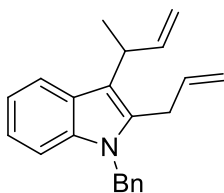
131.5, 127.8, 121.6, 121.0, 120.2, 118.9, 118.6, 116.3, 114.7, 114.5, 109.6, 108.8, 29.0, 28.9, 19.4; HRMS (ESI) calcd for C₁₅H₁₈N [M+H]⁺: 212.1439; Found: 212.1433.

2,3-Diallyl-1-benzyl-1H-indole (4i): Using the general procedure **GP-5**, compound **2k** (500 mg, 1.9 mmol) and allylmagnesium bromide (5.7 mL, 5.7 mmol) provided compound **4i** (457 mg,



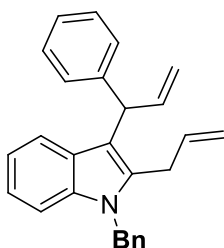
83%) as a colorless liquid; **¹H-NMR** (500 MHz, CDCl₃): 7.57 (1H, d, *J* = 8.6 Hz), 7.27-7.17 (4H, m), 7.12-7.07 (2H, m), 6.93 (2H, d, *J* = 7.1 Hz), 6.03-5.95 (1H, m), 5.87-5.79 (1H, m), 5.29 (2H, s), 5.09-4.93 (4H, m), 3.51 (2H, d, *J* = 6.0 Hz), 3.43 (2H, d, *J* = 5.1 Hz); **¹³C-NMR** (100 MHz, CDCl₃): 138.4, 137.8, 136.9, 135.2, 134.2, 128.8, 128.1, 127.3, 126.2, 126.1, 121.3, 119.2, 118.7, 116.3, 114.6, 110.4, 109.4, 46.7, 29.0, 28.9; HRMS (ESI) calcd for C₂₁H₂₂N [M+H]⁺: 288.1752; Found: 288.1762.

2-Allyl-1-benzyl-3-(but-3-en-2-yl)-1H-indole (4j): Using the general procedure **GP-5**, compound **2l** (500 mg, 1.80 mmol) and allylmagnesium bromide (5.41 mL, 5.41 mmol) provided



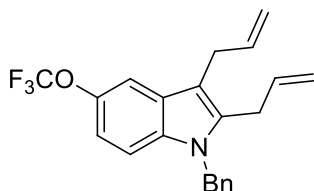
compound **4j** (430 mg, 79%) as a colorless liquid; **¹H-NMR** (500 MHz, CDCl₃): 7.67 (1H, d, *J* = 6.7 Hz), 7.22-7.16 (4H, m), 7.09-6.99 (2H, m), 6.92 (2H, d, *J* = 7.6 Hz), 6.27-6.21 (1H, m), 5.87-5.78 (1H, m), 5.27 (2H, d, *J* = 5.9 Hz), 5.13-4.89 (4H, m), 3.77-3.74 (1H, m), 3.45-3.41 (2H, m), 1.51 (3H, d, *J* = 6.7 Hz); **¹³C-NMR** (125 MHz, CDCl₃): 143.2, 138.5, 135.4, 133.2, 130.5, 128.8, 127.3, 126.8, 126.1, 124.9, 121.1, 119.9, 118.9, 116.3, 112.7, 109.5, 46.6, 34.6, 28.9, 20.2; HRMS (ESI) calcd for C₂₂H₂₄N [M+H]⁺: 302.1909; Found: 302.1914.

2-Allyl-1-benzyl-3-(1-phenylallyl)-1H-indole (4k): Using the general procedure **GP-5**, compound **2m** (500 mg, 1.47 mmol) and allylmagnesium bromide (4.42 mL, 4.42 mmol)



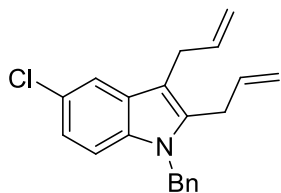
provided compound **4k** (415 mg, 78%) as a colorless liquid; **¹H-NMR** (400 MHz, CDCl₃): 7.38 (1H, d, *J* = 7.9 Hz), 7.32 (1H, d, *J* = 7.9 Hz), 7.27-7.15 (7H, m), 7.07 (1H, t, *J* = 7.9 Hz), 6.95 (3H, q, *J* = 7.9 Hz), 6.53-6.46 (1H, m), 5.82-5.72 (1H, m), 5.31 (2H, s), 5.19 (1H, d, *J* = 9.8 Hz), 5.08-4.90 (4H, m), 3.44 (2H, d, *J* = 5.5 Hz); **¹³C-NMR** (100 MHz, CDCl₃): 143.3, 140.3, 138.3, 137.2, 134.9, 134.5, 128.9, 128.4, 128.3, 127.3, 127.2, 126.1, 126.0, 121.3, 120.3, 119.2, 113.9, 109.5, 46.7, 29.2; HRMS (ESI) calcd for C₂₇H₂₆N [M+H]⁺: 364.2065; Found: 364.2068.

2,3-Diallyl-1-benzyl-5-(trifluoromethoxy)-1H-indole (4l): Using the general procedure **GP-5**, compound **2n** (500 mg, 1.44 mmol) and allylmagnesium bromide (4.32 mL, 4.32 mmol)



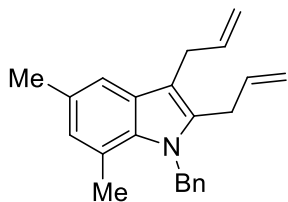
provided compound **4l** (431 mg, 80%) as a colorless liquid; ¹H-NMR (500 MHz, CDCl₃): 7.40 (1H, s), 7.30-7.21 (3H, m), 7.12 (1H, d, *J* = 9.2 Hz), 6.96 (1H, d, *J* = 9.2 Hz), 6.91 (2H, d, *J* = 6.7 Hz), 6.00-5.93 (1H, m), 5.87-5.79 (1H, m), 5.29 (2H, s), 5.09-4.94 (4H, m), 3.48 (2H, d, *J* = 6.7 Hz), 3.43 (2H, d, *J* = 5.0 Hz); ¹³C-NMR (100 MHz, CDCl₃): 142.9, 137.9, 137.2, 136.3, 135.2, 134.8, 128.9, 128.3, 127.6, 126.0, 116.6, 115.1, 115.0, 111.3, 110.9, 109.9, 46.9, 29.0, 28.9; HRMS (ESI) calcd for C₂₂H₂₁F₃NO [M+H]⁺: 372.1575; Found: 372.1574.

2,3-Diallyl-1-benzyl-5-chloro-1H-indole (4m): Using the general procedure **GP-5**, compound



2o (500 mg, 1.68 mmol) and allylmagnesium bromide (5.04 mL, 5.04 mmol) provided compound **4m** (390 mg, 72%) as a colorless liquid; ¹H-NMR (500 MHz, CDCl₃): 7.52 (1H, d, *J* = 1.7 Hz), 7.27-7.21 (3H, m), 7.08-7.03 (2H, m), 6.89 (2H, d, *J* = 6.7 Hz), 6.00-5.92 (1H, m), 5.86-5.79 (1H, m), 5.27 (2H, s), 5.07-4.92 (4H, m), 3.45 (2H, dd, *J* = 4.2, 1.7 Hz), 3.42 (2H, dd, *J* = 4.2, 1.7 Hz); ¹³C-NMR (100 MHz, CDCl₃): 137.9, 137.3, 135.8, 135.3, 134.8, 128.9, 127.5, 125.9, 125.0, 121.5, 118.3, 116.5, 114.9, 110.4, 110.2, 46.9, 29.0, 28.9; HRMS (ESI) calcd for C₂₁H₂₁ClN [M+H]⁺: 322.1363; Found: 322.1346.

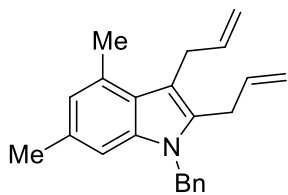
2,3-Diallyl-1-benzyl-5,7-dimethyl-1H-indole (4n): Using the general procedure **GP-5**,



compound **2p** (500 mg, 1.72 mmol) and allylmagnesium bromide (5.2 mL, 5.15 mmol) provided compound **4n** (401 mg, 74%) as a colorless liquid; ¹H-NMR (500 MHz, CDCl₃): 7.25-7.16 (4H, m), 6.88 (1H, d, *J* = 7.6 Hz), 6.79 (1H, d, *J* = 7.6 Hz), 6.67 (1H, s), 6.03-5.94 (1H, m), 5.87-5.79 (1H, m), 5.49 (1H, d, *J* = 10.2 Hz), 5.06-4.92 (4H, m), 3.46 (1H, d, *J* = 6.3 Hz), 3.35 (2H, d, *J* = 5.1 Hz), 2.43 (3H, d, *J* = 12.7 Hz), 2.38 (3H, d, *J* = 6.4 Hz); ¹³C-NMR (100 MHz, CDCl₃): 140.3, 137.9, 135.5, 134.8, 133.9, 132.3, 128.9, 128.5, 127.1, 126.4, 125.4, 125.2,

120.3, 120.0, 116.7, 116.4, 116.1, 114.5, 110.3, 48.2, 28.9, 28.8, 21.3, 19.7; HRMS (ESI) calcd for C₂₃H₂₆N [M+H]⁺: 316.2065; Found: 316.2078.

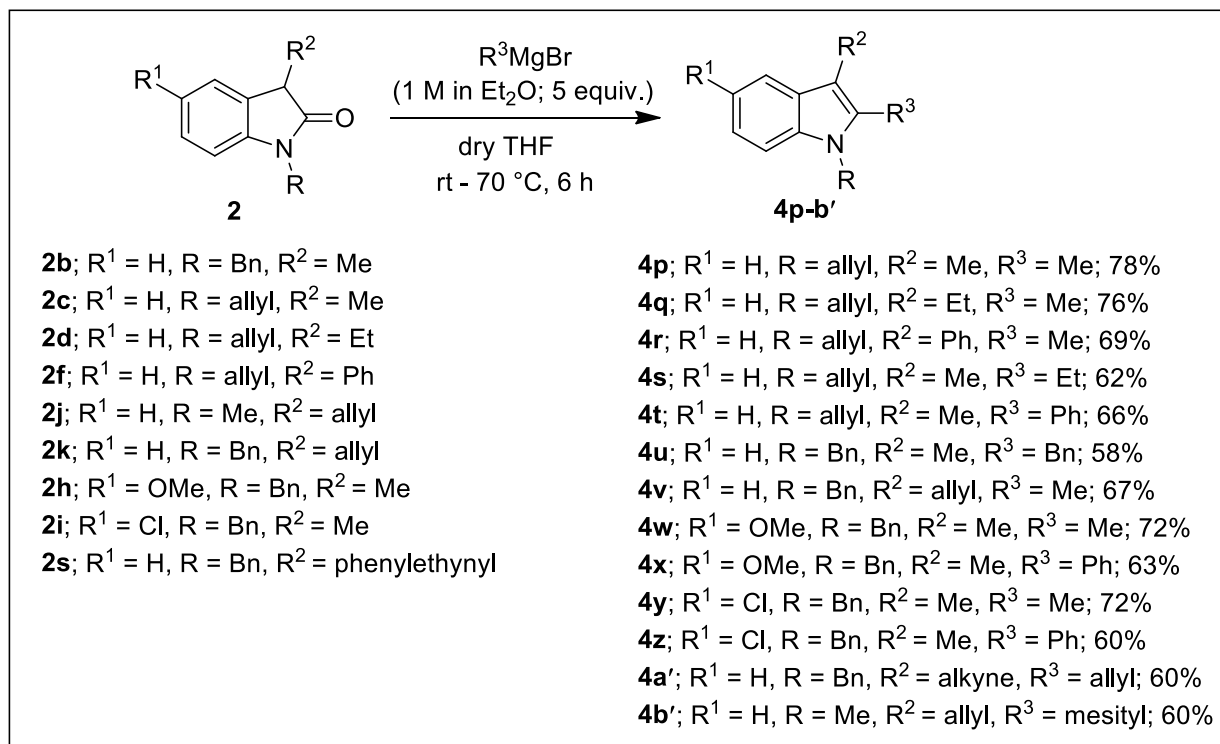
2,3-Diallyl-1-benzyl-4,6-dimethyl-1H-indole (4o): Using the general procedure **GP-5**,



compound **2q** (500 mg, 1.72 mmol) and allylmagnesium bromide (5.2 mL, 5.15 mmol) provided compound **4o** (418 mg, 77%) as a colorless liquid; ¹H-NMR (500 MHz, CDCl₃): 7.28-7.20 (3H, m), 7.01 (1H, d, *J* = 6.9 Hz), 6.91 (1H, d, *J* = 6.9 Hz), 6.80 (1H, d, *J* = 7.6 Hz), 6.66 (1H, d, *J* = 6.9 Hz), 6.18-6.02 (1H, m), 5.97-5.78 (1H, m), 5.27 (2H, d, *J* = 14.5 Hz), 5.08-4.85 (4H, m), 3.67-3.59 (3H, m), 3.37-3.35 (1H, m), 2.64 (3H, d, *J* = 3.2 Hz), 2.34 (2H, d, *J* = 5.1 Hz); ¹³C-NMR (100 MHz, CDCl₃): 139.6, 138.6, 137.7, 135.6, 133.8, 131.7, 130.6, 131.2, 130.2, 128.8, 127.2, 126.1, 123.3, 120.0, 116.0, 115.1, 114.7, 110.9, 107.4, 47.3, 30.4, 28.7, 21.8, 19.9; HRMS (ESI) calcd for C₂₃H₂₆N [M+H]⁺: 316.2065; Found: 316.2062.

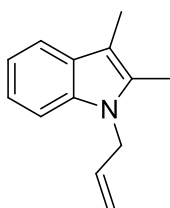
6.0.2 General procedure for the synthesis of 2,3-disubstituted indoles **4p-b'** (GP-6):

To a stirring solution of *N*-protected 3-substituted 2-oxindoles **2** (1 equiv) in dry THF, a calculated amount of alkyl or arylmagnesium bromide solution (5 equiv, 1M in Et₂O) was added dropwise at rt. The reaction mixture was then heated at 70 °C for 6 h. After completion of reaction as monitored by the TLC, the mixture was quenched with saturated aqueous NH₄Cl solution followed by extraction with EtOAc (3 x 20 mL). The combined organic phases were washed with brine, dried over anhydrous Na₂SO₄, filtered and concentrated in vacuo. The crude residue was then purified by column chromatography on silica gel with EtOAc–hexane (5/95 to 20/80) to give compounds **4p-b'** (Scheme S9).



Scheme S11. Alkyl or aryl Grignard addition to 3-substituted 2-oxindoles **2**.

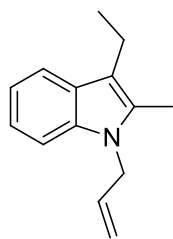
1-Allyl-2,3-dimethyl-1H-indole (4p): Using the general procedure **GP-6**, compound **2c** (200 mg,



1.07 mmol) and methylmagnesium bromide (5.34 mL, 5.34 mmol) provided compound **4p** (154 mg, 78%) as a colorless liquid; ¹H-NMR (400 MHz, CDCl₃): 7.48 (1H, d, *J* = 7.3 Hz), 7.18 (1H, d, *J* = 7.9 Hz), 7.14-7.05 (2H, m), 5.94-5.86 (1H, m), 5.07 (1H, d, *J* = 10.4 Hz), 4.80 (1H, dd, *J* = 15.8, 1.2 Hz), 4.63 (2H, t, *J* = 1.8 Hz), 2.29 (3H, s), 2.25 (3H, s); ¹³C-NMR (100 MHz, CDCl₃): 136.1, 133.9, 132.4, 128.7, 120.7, 118.8, 118.1, 116.1, 108.8, 106.8, 45.4, 10.0, 8.9;

HRMS (ESI) calcd for C₁₃H₁₆N [M+H]⁺: 186.1283; Found: 186.1274.

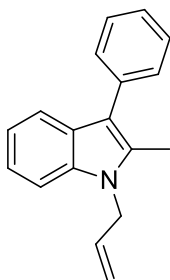
1-Allyl-3-ethyl-2-methyl-1H-indole (4q): Using the general procedure **GP-6**, compound **2d** (200



mg, 0.99 mmol) and methylmagnesium bromide (5 mL, 5 mmol) provided compound **4q** (150 mg, 76%) as a colorless liquid; ¹H-NMR (400 MHz, CDCl₃): 7.55 (1H, d, *J* = 7.9 Hz), 7.23 (1H, d, *J* = 7.9 Hz), 7.16-7.06 (2H, m), 5.99-5.89 (1H, m), 5.11 (1H, dd, *J* = 8.5, 1.8 Hz), 4.84 (1H, dd, *J* = 15.9, 1.2 Hz), 4.70-4.68 (2H, m), 2.76 (2H, q, *J* = 8.0 Hz), 2.34 (3H, s), 1.24 (3H, t, *J* = 7.9 Hz); ¹³C-

NMR (100 MHz, CDCl₃): 136.2, 133.9, 131.9, 127.8, 120.6, 118.8, 118.2, 116.1, 113.8, 108.9, 45.4, 17.8, 15.8, 9.9; HRMS (ESI) calcd for C₁₄H₁₈N [M+H]⁺: 200.1439; Found: 200.1438.

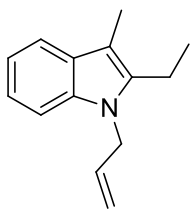
1-Allyl-2-methyl-3-phenyl-1H-indole (4r): Using the general procedure **GP-6**, compound **2f** (200 mg, 0.80 mmol) and methylmagnesium bromide (4 mL, 4 mmol) provided



compound **4r** (137 mg, 69%) as a colorless liquid; **¹H-NMR** (400 MHz, CDCl₃): 7.70 (1H, d, *J* = 7.9 Hz), 7.64 (1H, d, *J* = 7.3 Hz), 7.55-7.46 (3H, m), 7.32 (2H, d, *J* = 6.6 Hz), 7.22 (1H, t, *J* = 6.7 Hz), 7.14 (1H, t, *J* = 6.7 Hz), 6.06-5.97 (1H, m), 5.18 (1H, d, *J* = 12.8 Hz), 4.95 (1H, d, *J* = 17.8 Hz), 4.81-4.71 (2H, m), 2.53 (3H, s); **¹³C-NMR** (100 MHz, CDCl₃): 135.0, 134.5, 133.4,

133.1, 129.9, 129.2, 128.6, 128.2, 127.4, 125.9, 121.4, 119.9, 118.9, 116.5, 112.1, 109.2, 45.7, 10.9; HRMS (ESI) calcd for C₂₁H₂₃NO [M+H]⁺: 304.1439; Found: 304.1438.

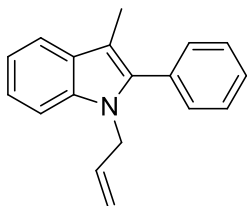
1-Allyl-2-ethyl-3-methyl-1H-indole (4s): Using the general procedure **GP-6**, compound **2c** (200 mg, 1.07 mmol) and ethylmagnesium bromide (5.34 mL, 5.34 mmol) provided



compound **4s** (132 mg, 62%) as a colorless liquid; **¹H-NMR** (400 MHz, CDCl₃): 7.50 (1H, d, *J* = 7.3 Hz), 7.20 (1H, d, *J* = 7.3 Hz), 7.15-7.06 (2H, m), 5.97-5.90 (1H, m), 5.10 (1H, dd, *J* = 9.1, 1.2 Hz), 4.86 (1H, dd, *J* = 15.8, 1.2 Hz), 4.69 (2H, t, *J* = 2.4 Hz), 2.74 (2H, q, *J* = 7.9 Hz), 2.28 (3H, s),

1.19 (3H, t, *J* = 7.9 Hz); **¹³C-NMR** (100 MHz, CDCl₃): 138.3, 136.2, 134.1, 128.9, 120.8, 118.9, 118.2, 116.2, 109.2, 106.3, 45.5, 17.8, 14.7, 8.8; HRMS (ESI) calcd for C₁₄H₁₈N [M+H]⁺: 200.1439; Found: 200.1442.

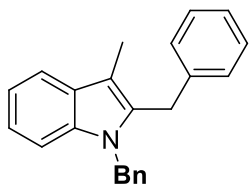
1-Allyl-3-methyl-2-phenyl-1H-indole (4t): Using the general procedure **GP-6**, compound **2c** (200 mg, 1.07 mmol) and phenylmagnesium bromide (5.34 mL, 5.34 mmol) provided



compound **4t** (174 mg, 66%) as a colorless liquid; **¹H-NMR** (400 MHz, CDCl₃): 7.60 (1H, dd, *J* = 4.3, 3.6 Hz), 7.46-7.34 (5H, m), 7.29 (1H, d, *J* = 7.9 Hz), 7.24-7.20 (1H, m), 7.17-7.13 (1H, m), 5.94-5.85 (1H, m), 5.11 (1H, dd, *J* = 9.2, 1.2 Hz), 4.91 (1H, dd, *J* = 15.9, 1.2 Hz), 4.60 (2H, t, *J* = 1.8

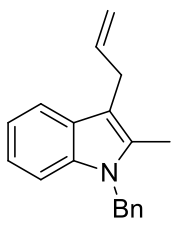
Hz), 2.28 (3H, s); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): 137.6, 136.9, 134.2, 132.3, 130.7, 128.9, 128.4, 127.4, 127.3, 121.9, 119.4, 118.9, 116.4, 110.1, 109.0, 46.6, 29.8, 9.5; HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{18}\text{N}$ $[\text{M}+\text{H}]^+$: 248.1439; Found: 248.1440.

1-Benzyl-3-methyl-2-benzyl-1H-indole (4u): Using the general procedure **GP-6**, compound **2b** (200 mg, 0.84 mmol) and phenylmagnesium bromide (4.2 mL, 4.20 mmol) provided compound



4u (174 mg, 58%) as a colorless liquid; $^1\text{H-NMR}$ (400 MHz, CDCl_3): 7.63 (1H, dd, $J = 3.0, 2.9$ Hz), 7.31-7.13 (9H, m), 7.07 (2H, d, $J = 7.3$ Hz), 6.88 (2H, d, $J = 8.0$ Hz), 5.13 (2H, s), 4.67 (2H, s), 2.39 (3H, s); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): 139.0, 138.4, 136.9, 134.5, 128.9, 128.7, 128.6, 128.5, 128.2, 127.3, 126.5, 126.1, 121.5, 119.1, 118.6, 118.6, 109.3, 109.0, 40.8, 30.6, 9.1; HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{22}\text{N}$ $[\text{M}+\text{H}]^+$: 312.1752; Found: 312.1756.

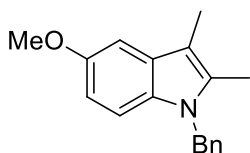
3-Allyl-1-benzyl-2-methyl-1H-indole (4v): Using the general procedure **GP-6**, compound **2k** (200 mg, 0.94 mmol) and methylmagnesium bromide (4.97 mL, 4.97 mmol)



provided compound **4v** (163mg, 67%) as a colorless liquid; $^1\text{H-NMR}$ (500 MHz, CDCl_3): 7.54 (1H, dd, $J = 3.7, 3.1$ Hz), 7.27-7.18 (4H, m), 7.12-7.05 (2H, m), 6.95 (2H, d, $J = 6.7$ Hz), 6.03-5.94 (1H, m), 5.29 (2H, s), 5.07-4.98 (2H, m), 3.50 (2H, d, $J = 6.1$ Hz), 2.27 (3H, s); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3):

138.3, 137.6, 136.7, 133.2, 128.8, 128.2, 127.3, 126.1, 120.9, 119.1, 118.3, 114.4, 109.4, 109.1, 46.7, 28.9, 10.3; HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{20}\text{N}$ $[\text{M}+\text{H}]^+$: 262.1596; Found: 262.1598.

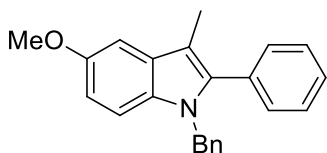
1-Benzyl-5-methoxy-2,3-dimethyl-1H-indole (4w): Using the general procedure **GP-6**, compound **2h** (200 mg, 0.75 mmol) and methylmagnesium bromide (3.74 mL, 3.74 mmol) provided compound **4w** (143 mg, 72%) as a colorless



liquid; $^1\text{H-NMR}$ (400 MHz, CDCl_3): 7.26-7.20 (3H, m), 7.54 (1H, d, $J = 9.2$ Hz), 6.98 (1H, d, $J = 2.5$ Hz), 6.94 (2H, d, $J = 6.7$ Hz), 6.74 (1H, dd, $J = 6.7, 2.4$ Hz), 5.24 (2H, s), 3.86 (3H, s), 2.25 (6H, d, $J = 2.44$ Hz); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): 153.9, 138.5,

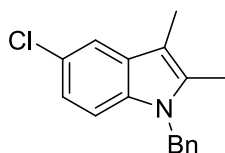
133.4, 131.9, 129.2, 128.4, 127.3, 126.1, 110.5, 109.6, 106.8, 100.7, 56.1, 46.8, 10.4, 9.1; HRMS (ESI) calcd for C₁₈H₂₀NO [M+H]⁺: 266.1545; Found: 266.1537.

1-Benzyl-5-methoxy-3-methyl-2-phenyl-1H-indole (4x): Using the general procedure **GP-6**,



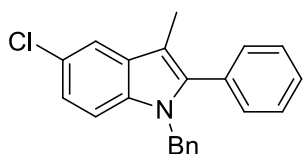
compound **2h** (200 mg, 0.75 mmol) and phenylmagnesium bromide (3.74 mL, 3.74 mmol) provided compound **4x** (154 mg, 63%) as a colorless liquid; ¹H-NMR (400 MHz, CDCl₃): 7.39-7.31 (4H, m), 7.20 (3H, t, *J* = 7.4 Hz), 7.07-7.02 (3H, m), 6.94 (2H, d, *J* = 5.8 Hz), 6.85-6.79 (1H, m), 5.19 (2H, s), 3.89 (3H, s), 2.28 (3H, s); ¹³C-NMR (100 MHz, CDCl₃): 154.3, 148.4, 138.8, 132.3, 132.2, 130.6, 129.2, 128.7, 128.4, 128.0, 127.4, 127.1, 126.2, 123.1, 121.9, 114.9, 112.1, 111.1, 108.9, 101.1, 56.1, 47.9, 9.6; HRMS (ESI) calcd for C₂₃H₂₂NO [M+H]⁺: 328.1701; Found: 328.1704.

1-Benzyl-5-chloro-2,3-dimethyl-1H-indole (4y): Using the general procedure **GP-6**, compound



2i (200 mg, 0.74 mmol) and methylmagnesium bromide (3.74 mL, 3.74 mmol) provided compound **4y** (144 mg, 72%) as a colorless liquid; ¹H-NMR (500 MHz, CDCl₃): 7.39 (1H, d, *J* = 1.7 Hz), 7.19-7.14 (3H, m), 7.00-6.94 (2H, m), 6.84 (2H, d, *J* = 7.6 Hz), 5.18 (2H, s), 2.19 (3H, s), 2.16 (3H, s); ¹³C-NMR (100 MHz, CDCl₃): 137.9, 134.9, 134.2, 129.9, 128.9, 127.5, 126.1, 124.8, 121.0, 117.7, 109.9, 107.3, 46.8, 10.4, 8.9; HRMS (ESI) calcd for C₁₇H₁₇NCl [M+H]⁺: 270.1050; Found: 270.1061.

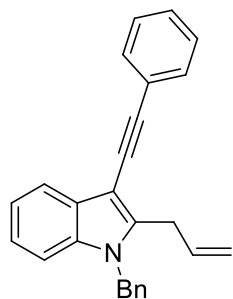
1-Benzyl-5-chloro-3-methyl-2-phenyl-1H-indole (4z): Using the general procedure **GP-6**,



compound **2i** (200 mg, 0.74 mmol) and phenylmagnesium bromide (3.74 mL, 3.74 mmol) provided compound **4z** (147 mg, 60%) as a colorless liquid; ¹H-NMR (500 MHz, CDCl₃): 7.53-7.50 (1H, m), 7.37-7.31 (3H, m), 7.23 (2H, dd, *J* = 2.5, 5.9 Hz), 7.17-7.12 (3H, m), 7.03-6.98 (2H, m), 6.83 (2H, d, *J* = 6.8 Hz), 5.13 (2H, s), 2.19 (3H, s); ¹³C-NMR (100 MHz, CDCl₃): 139.3, 138.2,

135.3, 131.7, 130.6, 130.1, 128.9, 128.8, 128.5, 128.4, 127.3, 126.1, 125.3, 122.2, 118.6, 11.4, 109.0, 47.9, 9.4; HRMS (ESI) calcd for C₂₂H₁₉NCl [M+H]⁺: 332.1206; Found: 332.1201.

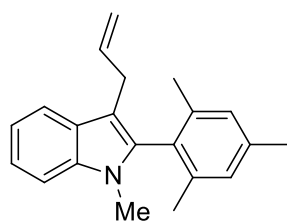
2-Allyl-1-benzyl-3-(phenylethynyl)-1H-indole (4a'): Using the general procedure **GP-6**,



compound **2s** (200 mg, 0.62 mmol) and allylmagnesium bromide (3.1 mL, 3.09 mmol) provided compound **4a'** (150 mg, 69%) as a colorless liquid; **¹H-NMR** (400 MHz, CDCl₃): 7.24-7.17 (5H, m), 7.13-7.07 (4H, m), 6.98-6.93 (3H, m), 6.68 (2H, dd, *J* = 6.3, 12.2 Hz), 5.73-5.63 (1H, m), 5.31 (2H, s), 4.98-4.89 (2H, m), 3.31 (2H, d, *J* = 5.8 Hz); **¹³C-NMR** (100 MHz, CDCl₃): 138.4, 138.1, 137.2, 135.3, 134.7, 130.5, 128.9, 128.8, 128.1, 127.4,

126.8, 126.0, 122.3, 121.6, 120.5, 116.3, 111.4, 109.4, 90.3, 79.3, 46.8, 29.8; HRMS (ESI) calcd for C₂₆H₂₂N [M+H]⁺: 348.1752; Found: 348.1743.

3-Allyl-2-mesityl-1-methyl-1H-indole (4b'): Using the general procedure **GP-6**, compound **2j**

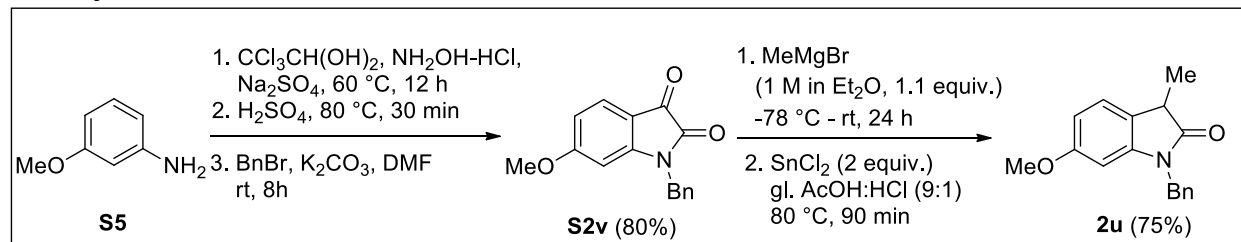


(200 mg, 1.07 mmol) and 2-mesitylmagnesium bromide (5.3 mL, 5.34 mmol) provided compound **4b'** (186 mg, 60%) as a colorless liquid; **¹H-NMR** (500 MHz, CDCl₃): 7.35 (1H, d, *J* = 9.8 Hz), 7.23-7.15 (2H, m), 7.04 (1H, t, *J* = 9.8 Hz), 6.98 (2H, s), 5.87-5.78 (1H, m), 5.05 (1H, dd, *J* = 1.8, 11.0 Hz), 4.97 (1H, dd, *J* = 1.9, 19.6 Hz), 3.76 (2H, s), 3.33 (2H, d, *J* = 6.7 Hz), 2.37 (3H, s), 1.99 (6H, s); **¹³C-NMR** (100 MHz, CDCl₃): 138.9, 138.3, 137.4,

136.5, 135.0, 134.4, 131.1, 129.3, 128.2, 128.0, 127.6, 121.6, 121.1, 120.2, 119.4, 119.2, 116.3, 112.9, 108.8, 30.2, 29.7, 21.2, 20.7; HRMS (ESI) calcd for C₂₁H₂₄N [M+H]⁺: 290.1909; Found: 290.1917.

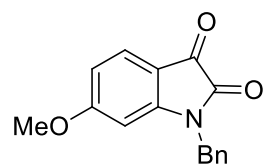
7.0 Synthesis of a 2,3-disubstituted indole microtubulin inhibitor 11:

7.0.1 Synthesis of oxindole 2u:



Scheme S12. Synthesis of oxindole **2u**.

Preparation of isatin S2v: Using Sandmayers method,⁹ to a solution of chloral hydrate (5.3 g, 32.3 mmol) in water (60 mL), sodium sulphate (19 g, 132 mmol) was added and the resulting solution was stirred at room temperature for 5 min. Then *m*-anisidine **S5** (4 g, 32.3mmol) was added portion-wise to the solution followed by hydroxylamine-hydrochloride (9 g in 10 mL

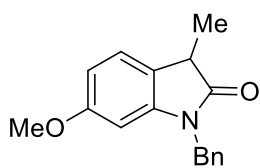


water). Subsequently, concentrated HCl 5 mL 1(N) was added and it was heated at $60\text{ }^\circ\text{C}$ overnight. The resulting precipitate was filtered off and dried under vacuo to give a straw yellow coloured intermediate. It was then dissolved in 20 mL conc. H_2SO_4 and heated at $80\text{ }^\circ\text{C}$ with stirring to

produce a dark solution. The reaction mixture was slowly cooled down to room temperature and the resulting solution was poured in a beaker containing ice cold water. It was kept for half an hour to give red precipitate, which was filtered to obtain the crude product of sufficient purity for the next step.

Using reported procedure¹, the crude 6-methoxy isatin **S1m** (1g, 5.64 mmol) and K_2CO_3 (2.3 g, 16.92 mmol) and benzyl bromide (1.01 mL, 8.46 mmol) provided compound **S2v** (1.6 g, 80 %) as a saffron colored solid; m.p. $104\text{--}106\text{ }^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3): 7.61 (1H, d, $J = 8.0$ Hz), 7.39–7.30 (5H, m), 6.54 (1H, dd, $J = 6.7, 1.8$ Hz), 6.26 (1H, d, $J = 1.8$ Hz), 4.91 (2H, s), 3.84 (3H, s); ^{13}C (100 MHz, CDCl_3): 180.7, 168.3, 159.9, 153.4, 134.9, 129.2, 128.3, 128.1, 127.6, 116.1, 108.1, 98.4, 56.2, 44.2; HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{13}\text{NO}_3$ $[\text{M}+\text{H}]^+$: 268.0974 ; Found: 268.0971.

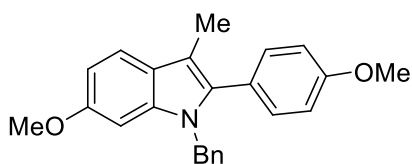
1-Benzyl-6-methoxy-3-methylindolin-2-one (2u): Using the reported procedure⁵, compound **S2v** (1 g, 3.74 mmol) and methylmagnesium bromide (3.74 mL, 3.74 mmol) provided the intermediate, which upon treatment with SnCl₂ (2.8 g, 14.9 mmol) furnished compound **2u** (748



mg, 75%) as a yellow oil; ¹H-NMR (400 MHz, CDCl₃): 7.22-7.17 (5H, m), 6.77 (1H, d, *J* = 1.5 Hz), 6.60-6.57 (1H, dd, *J* = 5.8, 3.9 Hz), 6.50 (1H, d, *J* = 8.8 Hz), 4.80 (2H, s), 3.67 (3H, s), 3.42 (1H, q, *J* = 7.4 Hz), 1.44 (3H, d, *J* = 7.8 Hz); ¹³C-NMR (100 MHz, CDCl₃): 178.5, 156.1, 136.7, 136.2, 136.2, 132.1, 128.8, 127.6, 127.4, 112.1, 111.4, 109.4, 55.9, 43.9, 41.1, 15.8; HRMS (ESI) calcd for C₁₇H₁₈NO₂ [M+H]⁺: 268.1338; Found: 268.1340.

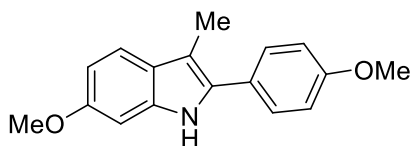
7.0.2 Synthesis of microtubulin inhibitor 11:

1-Benzyl-6-methoxy-2-(4-methoxyphenyl)-3-methyl-1H-indole (9): Using the general procedure **GP-6**, compound **2u** (500 mg, 1.87 mmol) and *p*-methoxyphenylmagnesium bromide (9.35 mL,



9.35 mmol) provided compound **9** (440 mg, 68%) as a colorless liquid; ¹H-NMR (400 MHz, CDCl₃): 7.40 (1H, d, *J* = 8.8 Hz), 7.18-7.11 (5H, m), 6.89 (2H, d, *J* = 6.8 Hz), 6.83 (2H, d, *J* = 8.8 Hz), 6.73 (1H, dd, *J* = 6.3, 2.0 Hz), 6.56 (1H, d, *J* = 2.0 Hz), 5.08 (2H, s), 3.75 (3H, s), 3.69 (3H, s), 2.19 (3H, s); ¹³C-NMR (100 MHz, CDCl₃): 159.3, 156.5, 138.7, 137.8, 136.7, 131.9, 128.7, 127.1, 126.2, 124.6, 123.6, 119.5, 113.9, 108.9, 94.4, 55.9, 55.4, 47.7, 9.6; HRMS (ESI) calcd for C₂₄H₂₄NO₂ [M+H]⁺: 358.1807; Found: 358.1804.

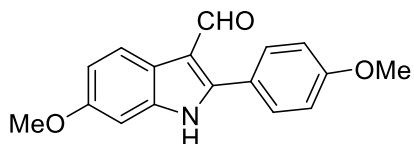
6-Methoxy-2-(4-methoxyphenyl)-3-methyl-1H-indole (10): To a solution of compound **9** (200 mg, 0.56 mmol) in dry DMSO was added potassium *tert* butoxide solution (1M in THF, 1.12



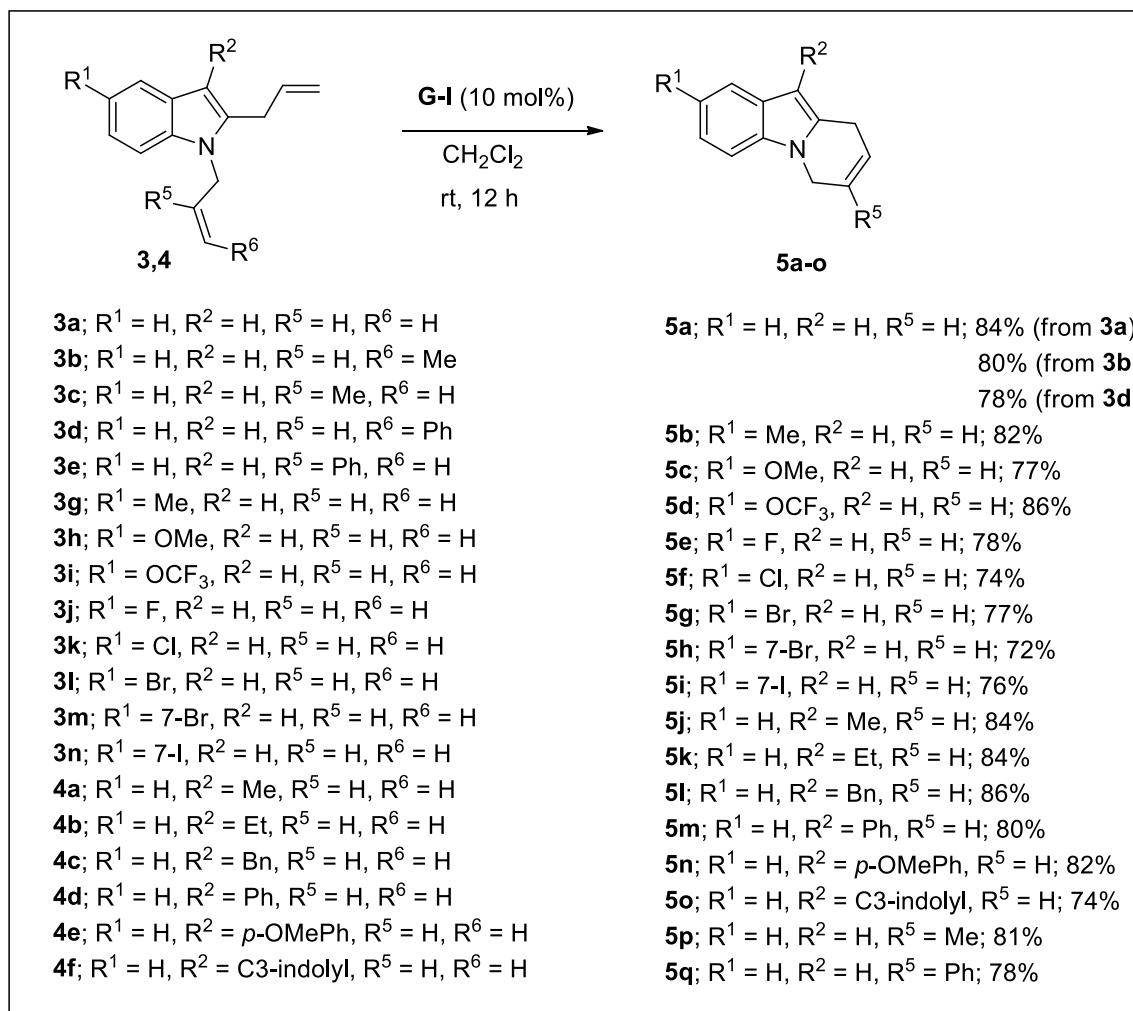
mL, 1.12 mmol) in the presence of O₂ and the reaction mixture was stirred at room temperature for an hour. After the completion of reaction (monitored by TLC), solvent was removed under vacuo and the crude product obtained was purified by column chromatography on silica gel with EtOAc–hexane (5/95 to 20/80) to provide compound **10** (132 mg, 88%) as a straw yellow colored solid; ¹H-NMR (400 MHz, CDCl₃): 7.85 (1H, br s), 7.49-7.46 (3H, m),

7.02-6.99 (2H, m), 6.86 (1H, t, $J = 2.0$ Hz), 6.83-6.79 (1H, m), 3.86 (6H, d, $J = 4.9$ Hz), 2.46 (3H, s); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): 162.4, 162.2, 134.8, 130.7, 128.1, 122.1, 114.4, 114.1, 111.5, 106.8, 94.2, 83.9, 55.9, 55.5, 9.6; HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{18}\text{NO}_2$ $[\text{M}+\text{H}]^+$: 268.1338; Found: 268.1332.

6-Methoxy-2-(4-methoxyphenyl)-1H-indole-3-carbaldehyde (11):¹⁰ To the solution of compound **10** (100 mg, 0.37 mmol) in THF:H₂O (9:1) was added DDQ (170 mg, 0.75 mmol) and the reaction mixture was stirred at room temperature for 12 h. After completion of the reaction (monitored by TLC), the reaction mixture was extracted with EtOAc (3 x 5 mL) and aq NaOH (2 N, 10 mL). The organic layer was evaporated under vacuo and the crude product obtained was purified by column chromatography on silica gel with EtOAc–hexane (5/95 to 20/80) to provide the target compound **11** (92 mg, 90%) as a pale yellow colored solid; $^1\text{H-NMR}$ (400 MHz, CDCl_3): 10.0 (1H, s), 8.40 (1H, br s), 8.28 (1H, d, $J = 9.1$ Hz), 7.56 (2H, d, $J = 8.6$ Hz), 7.06 (2H, d, $J = 8.6$ Hz), 6.96 (1H, dd, $J = 6.9, 1.8$ Hz), 6.90 (1H, d, $J = 1.8$ Hz), 3.88 (6H, d, $J = 8.6$ Hz); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): 186.7, 161.1, 157.7, 148.4, 136.3, 130.8, 127.3, 123.1, 122.5, 120.4, 114.7, 112.2, 95.1, 55.9, 55.6; HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{16}\text{NO}_3$ $[\text{M}+\text{H}]^+$: 282.1130; Found: 282.1144.

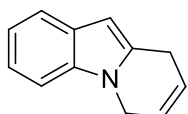


8.0 General procedure for the ring closing metathesis of 1,2-diallyl indoles (GP-7): To a solution of compound **3** or **4** (1 equiv.) in dry CH₂Cl₂ (4 mL) was added **G-I** (10 mol%) and stirred at room temperature for 8 h. The reaction mixture was then concentrated and purified on silica gel (EtOAc–hexane, 10/90 to 20/80) to give compounds **5** (Scheme S11) .



Scheme S13. RCM of 1,2-diallyl indolyl derivatives **3,4**.

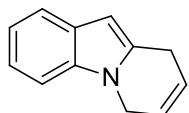
6,9-Dihydropyrido[1,2-*a*]indole (5a): Using the general procedure **GP-7**, compound **3a** (100



mg, 0.51 mmol) and **G-I** (41.7 mg, 0.05 mmol) provided compound **5a** (62 mg, 84%) as an ash colored solid; ¹H-NMR (500 MHz, CDCl₃): 7.56 (1H, d, *J* = 7.6 Hz), 7.29 (1H, d, *J* = 7.6 Hz), 7.17-7.09 (2H, m), 6.28 (1H, s),

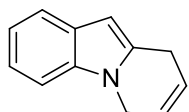
6.05-6.04 (2H, m), 4.60 (2H, d, $J = 1.3$ Hz), 3.62 (2H, t, $J = 1.3$ Hz); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): 135.8, 133.4, 128.5, 122.5, 120.5, 120.4, 120.0, 119.8, 108.9, 97.2, 41.9, 24.2; HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{12}\text{N}[\text{M}+\text{H}]^+$: 170.0970; Found: 170.0963.

6,9-Dihydropyrido[1,2-*a*]indole (5a): Using the general procedure **GP-7**, compound **3b** (100



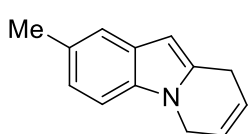
mg, 0.51 mmol) and **G-I** (41.7 mg, 0.05 mmol) provided compound **5a** (62 mg, 80 %) as an ash colored solid.

6,9-Dihydropyrido[1,2-*a*]indole (5a): Using the general procedure **GP-7**, compound **3d** (100



mg, 0.51 mmol) and **G-I** (41.7 mg, 0.05 mmol) provided compound **5a** (62 mg, 76%) as an ash colored solid.

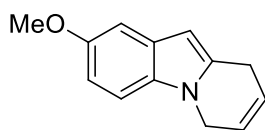
2-Methyl-6,9-dihydropyrido[1,2-*a*]indole (5b): Using the general procedure **GP-7**, compound



3g (100 mg, 0.47 mmol) and **G-I** (38.9 mg, 0.05 mmol) provided compound **5b** (62 mg, 82%) as a dark green solid; $^1\text{H-NMR}$ (500 MHz, CDCl_3): 7.39 (1H, s), 7.20 (1H, d, $J = 8.4$ Hz), 7.02 (1H, d, $J = 8.4$ Hz),

6.23 (1H, s), 6.09-6.03 (2H, m), 4.60 (2H, d, $J = 2.5$ Hz), 3.63 (2H, s), 2.49 (3H, s); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): 134.2, 133.4, 129.1, 128.7, 122.5, 121.9, 120.5, 119.6, 108.5, 96.6, 41.9, 24.2, 21.6; HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{14}\text{N}[\text{M}+\text{H}]^+$: 184.1126; Found: 184.1129.

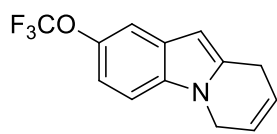
2-Methoxy-6,9-dihydropyrido[1,2-*a*]indole (5c): Using the general procedure **GP-7**, compound



3h (100 mg, 0.44 mmol) and **G-I** (36.21 mg, 0.04 mmol) provided compound **5c** (76 mg, 77 %) as a dark green solid; $^1\text{H-NMR}$ (500 MHz, CDCl_3): 7.17 (1H, d, $J = 8.4$ Hz), 7.05 (1H, d, $J = 1.7$ Hz), 6.81 (1H, dd, $J = 6.7, 2.5$ Hz), 6.20 (1H, s), 6.06-5.99 (2H, m), 4.56 (2H, s), 3.85 (2H, s), 3.59 (2H, s); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): 154.6, 134.1, 131.1, 128.8, 122.4, 120.5, 110.3, 109.5, 102.1, 96.9,

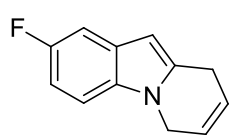
56.1, 41.9, 24.2; HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{14}\text{NO}[\text{M}+\text{H}]^+$: 200.1075; Found: 200.1081.

2-(Trifluoromethoxy)-6,9-dihydropyrido[1,2-a]indole (5d): Using the general procedure **GP-7**,



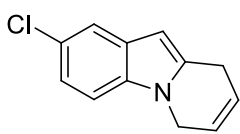
compound **3i** (100 mg, 0.36 mmol) and **G-I** (29.25 mg, 0.04 mmol) provided compound **5d** (76 mg, 86%) as a pale white solid; **¹H-NMR** (500 MHz, CDCl₃): 7.41 (1H, s), 7.22 (1H, d, *J* = 8.4 Hz), 7.02 (1H, d, *J* = 8.4 Hz), 6.28 (1H, s), 6.07-6.03 (2H, m), 4.58 (2H, d, *J* = 1.7 Hz), 3.62 (2H, s); **¹³C-NMR** (100 MHz, CDCl₃): 143.5, 135.5, 134.1, 128.5, 122.3, 120.2, 119.8, 114.2, 112.2, 109.3, 97.7, 42.0, 24.2; HRMS (ESI) calcd for C₁₃H₁₁NF₃O[M+H]⁺: 254.0793; Found: 254.0794.

2-Fluoro-6,9-dihydropyrido[1,2-a]indole (5e): Using the general procedure **GP-7**, compound **3j**



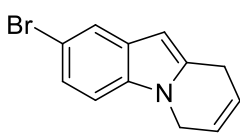
(100 mg, 0.51 mmol) and **G-I** (41.7 mg, 0.05 mmol) provided compound **5e** (62 mg, 78%) as an ash colored solid; **¹H-NMR** (500 MHz, CDCl₃): 7.23-7.18 (2H, m), 6.90 (1H, ddd, *J* = 6.3, 2.6, 2.5 Hz), 6.25 (1H, s), 6.09-6.02 (2H, m), 4.61-4.59 (2H, m), 3.62 (2H, s); **¹³C-NMR** (100 MHz, CDCl₃): 159.6, 157.3, 135.2, 132.4, 128.7, 128.6, 122.3, 120.3, 109.3, 109.2, 108.7, 108.4, 104.8, 104.6, 97.4, 94.3, 42.0, 24.2; HRMS (ESI) calcd for C₁₂H₁₁NF[M+H]⁺: 188.0876; Found: 188.0893.

2-Chloro-6,9-dihydropyrido[1,2-a]indole (5f): Using the general procedure **GP-7**, compound **3k** (100 mg, 0.43 mmol) and **G-I** (35.5 mg, 0.04 mmol) provided compound **5f** (57 mg, 74%) as



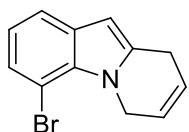
a white solid; **¹H-NMR** (500 MHz, CDCl₃): 7.52 (1H, d, *J* = 1.7 Hz), 7.18 (1H, d, *J* = 8.4 Hz), 7.10 (1H, dd, *J* = 6.7, 1.7 Hz), 6.22 (1H, s), 6.08-6.03 (2H, m), 4.59-4.57 (2H, m), 3.61 (2H, t, *J* = 1.7 Hz); **¹³C-NMR** (100 MHz, CDCl₃): 134.9, 134.2, 129.4, 125.7, 122.3, 120.6, 120.2, 119.2, 109.8, 97.4, 41.9, 24.4; HRMS (ESI) calcd for C₁₂H₁₁ClN[M+H]⁺: 204.0580; Found: 204.0569.

2-Bromo-6,9-dihydropyrido[1,2-a]indole (5g): Using the general procedure **GP-7**, compound **3l**



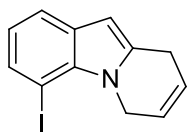
(100 mg, 0.36 mmol) and **G-I** (29.8 mg, 0.04 mmol) provided compound **5g** (69 mg, 77%) as a dark green solid; **¹H-NMR** (500 MHz, CDCl₃): 7.67 (1H, d, *J* = 1.7 Hz), 7.24-7.22 (1H, m), 7.14 (1H, d, *J* = 8.4 Hz), 6.22 (1H, s), 6.07-6.00 (2H, m), 4.58-4.56 (2H, m), 3.61 (2H, t, *J* = 1.7 Hz); **¹³C-NMR** (100 MHz, CDCl₃): 138.0, 136.8, 129.1, 128.8, 127.6, 126.9, 125.9, 121.7, 119.2, 118.9, 110.9, 109.6, 49.9, 9.8; HRMS (ESI) calcd for C₁₂H₁₁NBr [M+H]⁺: 248.0075; Found: 248.0056.

4-Bromo-6,9-dihydropyrido[1,2-*a*]indole (5h): Using the general procedure **GP-7**, compound



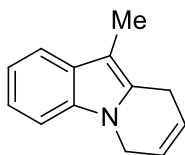
3m (100 mg, 0.36 mmol) and **G-I** (29.8 mg, 0.04 mmol) provided compound **5h** (65 mg, 72%) as a dark green solid; $^1\text{H-NMR}$ (400 MHz, CDCl_3): 7.47-7.44 (1H, m), 7.28-7.26 (1H, m), 6.91-6.85 (1H, m), 6.27 (1H, s), 5.99 (2H, s), 5.24 (2H, t, $J = 3.9$ Hz), 3.60 (2H, t, $J = 4.4$ Hz); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): 135.2, 134.7, 131.6, 125.7, 121.1, 119.2, 117.3, 103.7, 101.3, 98.7, 45.8, 24.7; HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{11}\text{NBr}$ $[\text{M}+\text{H}]^+$: 248.0075; Found: 248.0087.

4-Iodo-6,9-dihydropyrido[1,2-*a*]indole (5i): Using the general procedure **GP-7**, compound **3n**



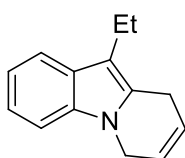
(100 mg, 0.31 mmol) and **G-I** (25.5 mg, 0.03 mmol) provided compound **5i** (69 mg, 76%) as a dark green solid; $^1\text{H-NMR}$ (400 MHz, CDCl_3): 7.58-7.53 (1H, m), 7.31-7.27 (1H, m), 7.18-7.11 (1H, m), 6.29 (1H, s), 6.05 (2H, s), 4.64-4.62 (2H, m), 3.65-3.62 (2H, m); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): 135.1, 133.7, 128.1, 122.5, 120.5, 120.4, 120.0, 119.8, 116.9, 108.9, 100.1, 97.2, 41.9, 24.2; HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{11}\text{NI}$ $[\text{M}+\text{H}]^+$: 295.9936; Found: 295.9941.

10-Methyl-6,9-dihydropyrido[1,2-*a*]indole (5j): Using the general procedure **GP-7**, compound



4a (100 mg, 0.47 mmol) and **G-I** (39 mg, 0.05 mmol) provided compound **5j** (62 mg, 84%) as a brown solid; $^1\text{H-NMR}$ (400 MHz, CDCl_3): 7.51 (1H, dd, $J = 5.2, 2.5$ Hz), 7.19 (1H, d, $J = 7.8$ Hz), 7.16-7.09 (2H, m), 6.03-5.92 (2H, m), 4.52-4.48 (2H, m), 3.43 (2H, s), 2.23 (3H, s); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): 135.4, 129.3, 128.6, 122.1, 120.6, 120.3, 119.2, 117.8, 108.6, 104.5, 41.8, 22.9, 8.3; HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{14}\text{N}$ $[\text{M}+\text{H}]^+$: 184.1126; Found: 184.1119.

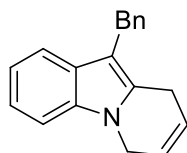
10-Ethyl-6,9-dihydropyrido[1,2-*a*]indole (5k): Using the general procedure **GP-7**, compound



4b (100 mg, 0.44 mmol) and **G-I** (41.7 mg, 0.044 mmol) provided compound **5k** (38.5 mg, 84%) as a brown solid; $^1\text{H-NMR}$ (500 MHz, CDCl_3): 7.58 (1H, d, $J = 7.6$ Hz), 7.26 (1H, d, $J = 8.2$ Hz), 7.17-7.09 (2H, m), 6.08-6.00 (2H, m), 4.60-4.57 (2H, m), 3.53-3.51 (2H, m), 2.73 (2H, q, $J = 7.6$ Hz), 1.24 (3H, t, $J = 7.6$ Hz); $^{13}\text{C-NMR}$

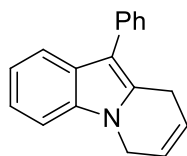
(100 MHz, CDCl₃): 135.6, 128.7, 127.7, 122.2, 120.6, 120.3, 119.3, 118.1, 111.5, 108.7, 41.9, 22.9, 17.5, 15.4; HRMS (ESI) calcd for C₁₄H₁₆N[M+H]⁺: 198.1283; Found: 198.1257.

10-Benzyl-6,9-dihydropyrido[1,2-a]indole (5l): Using the general procedure **GP-7**, compound



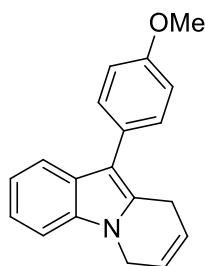
4c (100 mg, 0.35 mmol) and **G-I** (28.6 mg, 0.03 mmol) provided compound **5l** (78 mg, 86%) as a brownish gummy mass; ¹H-NMR (400 MHz, CDCl₃): 7.52 (1H, d, *J* = 7.4 Hz), 7.32 (1H, d, *J* = 8.1 Hz), 7.26 (4H, d, *J* = 4.4 Hz), 7.22-7.16 (2H, m), 7.13 (1H, t, *J* = 7.3 Hz), 6.06 (2H, t, *J* = 11.7 Hz), 4.65 (2H, t, *J* = 4.4 Hz), 4.14 (2H, s), 3.51 (2H, d, *J* = 5.9 Hz); ¹³C-NMR (100 MHz, CDCl₃): 141.7, 135.6, 130.2, 128.5, 128.4, 128.2, 125.8, 122.1, 120.6, 120.5, 119.6, 118.3, 108.7, 108.2, 41.9, 30.2, 23.1; HRMS (ESI) calcd for C₁₉H₁₈N[M+H]⁺: 260.1439; Found: 260.1447.

10-Phenyl-6,9-dihydropyrido[1,2-a]indole (5m): Using the general procedure **GP-7**, compound



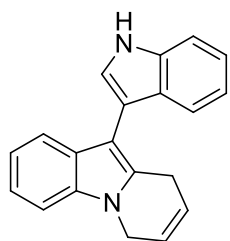
4d (100 mg, 0.36 mmol) and **G-I** (30.1 mg, 0.04 mmol) provided compound **5m** (62 mg, 80%) as a brownish gummy mass; ¹H-NMR (500 MHz, CDCl₃): 7.75 (1H, d, *J* = 7.6 Hz), 7.55 (2H, d, *J* = 7.6 Hz), 7.45 (2H, t, *J* = 7.6 Hz), 7.35 (1H, d, *J* = 8.2 Hz), 7.29-7.22 (2H, m), 7.16 (1H, t, *J* = 7.6 Hz), 6.12-6.06 (2H, m), 4.70 (2H, q, *J* = 1.9 Hz), 3.73 (1H, t, *J* = 3.2 Hz); ¹³C-NMR (100 MHz, CDCl₃): 135.9, 135.8, 130.1, 129.2, 128.7, 127.2, 125.7, 122.7, 121.2, 120.5, 118.9, 111.9, 108.9, 42.2, 24.1; HRMS (ESI) calcd for C₁₈H₁₆N[M+H]⁺: 246.1283; Found: 246.1282.

10-(4-Methoxy)phenyl-6,9-dihydropyrido[1,2-a]indole (5n): Using the general procedure **GP-7**,



compound **4e** (100 mg, 0.30 mmol) and **G-I** (29.6 mg, 0.03 mmol) provided compound **5n** (62 mg, 82%) as a deep greenish liquid; ¹H-NMR (500 MHz, CDCl₃): 7.71 (1H, d, *J* = 7.5 Hz), 7.46 (2H, d, *J* = 8.4 Hz), 7.34 (1H, d, *J* = 7.5 Hz), 7.22 (1H, t, *J* = 7.6 Hz), 7.16 (1H, t, *J* = 7.6 Hz), 7.01 (2H, d, *J* = 8.4 Hz), 6.08 (2H, s), 4.70 (2H, q, *J* = 6.7 Hz), 3.87 (3H, s), 3.69 (2H, t, *J* = 1.7 Hz); ¹³C-NMR (100 MHz, CDCl₃): 157.8, 135.7, 130.3, 129.7, 128.1, 127.4, 122.7, 121.0, 120.5, 120.3, 118.8, 114.2, 111.6, 108.9, 55.5, 42.2, 23.9; HRMS (ESI) calcd for C₁₉H₁₈NO[M+H]⁺: 276.1388; Found: 276.1391.

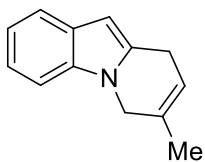
10-(1*H*-Indol-3-yl)-6,9-dihydropyrido[1,2-*a*]indole (5o): Using the general procedure **GP-7**, compound **4f** (100 mg, 0.2mmol) and **G-II** (8.5 mg, 0.01mmol) provided compound **5o** (58 mg,



74%) as a pale yellow solid; ¹H-NMR (400 MHz, CDCl₃): 8.20 (1H, br s), 7.50 (2H, t, *J* = 8.3 Hz), 7.39 (1H, d, *J* = 8.3 Hz), 7.20-7.14 (3H, m), 7.07-7.03 (2H, m), 6.00 (2H, s), 4.67 (2H, t, *J* = 3.9 Hz), 3.55 (2H, d, *J* = 3.9 Hz); ¹³C-NMR (100 MHz, CDCl₃): 144.9, 136.9, 135.9, 132.5, 131.4, 130.5, 129.2, 128.2, 122.9, 122.8, 120.8, 119.9, 119.7, 117.7, 111.6, 107.8, 100.3,

91.9, 42.3, 24.7; HRMS (ESI) calcd for C₂₀H₁₇N₂[M+H]⁺: 285.1392; Found: 285.1395.

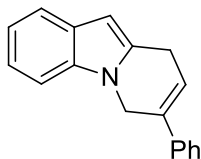
7-methyl-6,9-dihydropyrido[1,2-*a*]indole (5p): Using the general procedure **GP-7**, compound **3c** (100 mg, 0.47 mmol) and **G-I** (38.95 mg, 0.05 mmol) provided compound **5p** (62 mg, 81%)



as a green liquid; ¹H-NMR (400 MHz, CDCl₃): 7.58 (1H, d, *J* = 7.4 Hz), 7.32 (1H, d, *J* = 7.3 Hz), 7.19-7.11 (2H, m), 6.29 (1H, s), 5.76 (1H, d, *J* = 1.5 Hz), 4.47 (2H, s), 3.61 (2H, s), 1.94 (3H, s); ¹³C-NMR (100 MHz, CDCl₃): 135.5, 133.5, 128.7, 127.6, 120.3, 119.9, 119.8, 117.2, 108.9, 96.8, 45.6,

24.4, 20.9; HRMS (ESI) calcd for C₁₃H₁₄N[M+H]⁺: 184.1126; Found: 184.1128.

7-Phenyl-6,9-dihydropyrido[1,2-*a*]indole (5q): Using the general procedure **GP-7**, compound

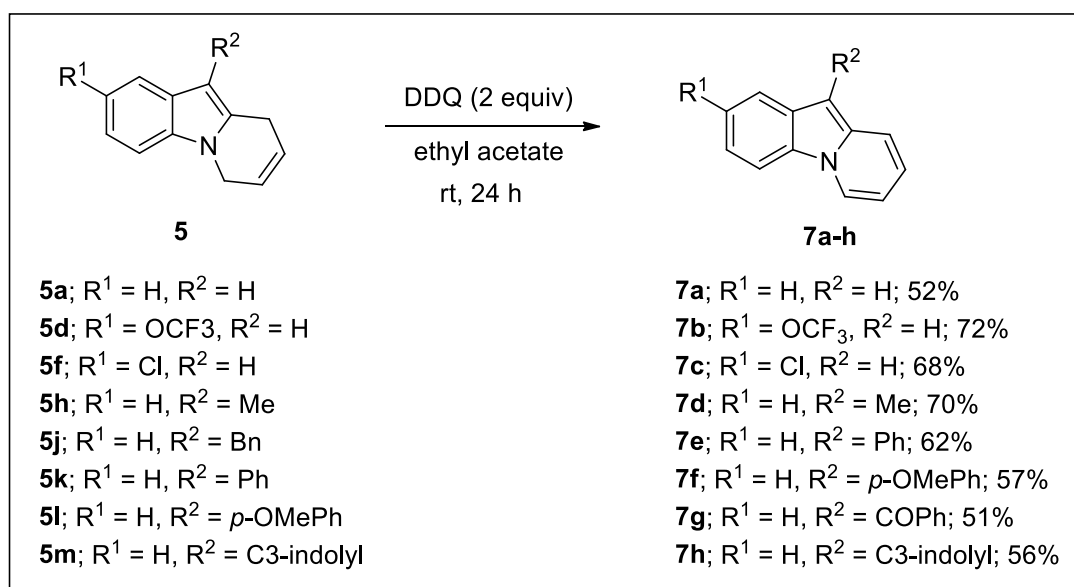


3e (100 mg, 0.36 mmol) and **G-I** (30.1 mg, 0.037 mmol) provided compound **5q** (62 mg, 78%) as a brown solid; ¹H-NMR (500 MHz, CDCl₃): 7.60 (1H, d, *J* = 7.3 Hz), 7.50 (2H, d, *J* = 7.4 Hz), 7.45-7.32 (4H,

m), 7.22-7.11 (2H, m), 6.40-6.38 (1H, m), 6.34 (1H, s), 5.00-4.96 (2H, m), 3.83 (2H, q, *J* = 3.7 Hz); ¹³C-NMR (100 MHz, CDCl₃): 139.2, 135.8, 132.9, 131.5, 128.9, 128.0, 125.5, 120.5, 120.2, 114.9, 108.9, 96.9, 43.7, 24.9; HRMS (ESI) calcd for C₁₈H₁₆N[M+H]⁺: 246.1283; Found: 246.1286.

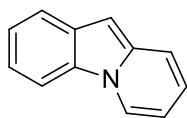
9.0 General procedure for the DDQ mediated aromatization to synthesize pyrido[1,2-*a*]indoles 7 (GP-8):

To a solution of dihydro-pyrido-indole derivatives **5** (1 equiv.) in ethyl acetate (4 mL) was added DDQ (2 equiv.) and the resulting mixture was allowed to stir at room temperature for 24 h. After completion of the reaction as monitored by TLC, the reaction mixture was extracted with aq NaOH (2 N, 10 mL) and ethyl acetate (3 x 10 mL). The combined organic fractions were concentrated in vacuo and purified by column chromatography (EtOAc–hexane, 5/95 to 1/99) on silica gel to give compounds **7a-h** (Scheme S12).



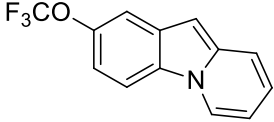
Scheme S14. Synthesis of pyrido[1,2-*a*]indoles **7**.

Pyrido[1,2-*a*]indole (7a): Using the general procedure **GP-8**, compound **5a** (50 mg, 0.30 mmol)

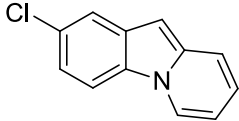


and DDQ (134.2 mg, 0.60 mmol) provided compound **7a** (26 mg, 52%) as a pale yellow oil; ¹H-NMR (500 MHz, CDCl₃): 8.39 (1H, t, *J* = 1.7 Hz), 7.66 (1H, d, *J* = 8.4 Hz), 7.56-7.52 (1H, m), 7.49 (1H, d, *J* = 8.4 Hz), 7.39 (1H, d, *J* = 7.6 Hz), 7.25 (1H, t, *J* = 5.0 Hz), 7.22-7.19 (1H, m), 7.13 (1H, t, *J* = 7.5 Hz), 6.57 (1H, s); ¹³C-NMR (100 MHz; CDCl₃): 142.4, 138.6, 135.9, 128.4, 127.9, 124.3, 122.7, 122.0, 120.8, 119.9, 111.2, 102.7; HRMS (ESI) calcd for C₁₂H₁₀N[M+H]⁺: 168.0813; Found: 168.0827.

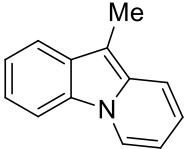
2-(Trifluoromethoxy)pyrido[1,2-*a*]indole (7b): Using the general procedure **GP-8**, compound

 **5d** (50 mg, 0.19 mmol) and DDQ (89.6 mg, 0.38 mmol) provided compound **7b** (34 mg, 72%) as a yellow oil; ¹H-NMR (400 MHz, CDCl₃): 8.27 (1H, d, *J* = 7.4 Hz), 7.85 (1H, d, *J* = 8.8 Hz), 7.63 (1H, s), 7.50 (1H, d, *J* = 9.3 Hz), 7.25 (1H, s), 7.17 (1H, d, *J* = 8.8 Hz), 7.03 (1H, t, *J* = 6.4 Hz), 6.57 (1H, t, *J* = 6.4 Hz); ¹³C-NMR (100 MHz; CDCl₃): 133.6, 126.7, 126.2, 124.4, 123.6, 119.6, 116.8, 114.5, 111.6, 109.9, 109.0, 93.9; HRMS (ESI) calcd for C₂₀H₁₅NOF₃ [M+H]⁺: 252.0636; Found: 252.0614.

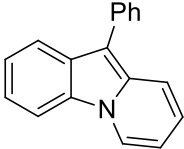
2-Chloropyrido[1,2-*a*]indole (7c): Using the general procedure **GP-8**, compound **5f** (50 mg,

 0.25 mmol) and DDQ (111.4 mg, 0.50 mmol) provided compound **7c** (34 mg, 68%) as a greenish yellow oil; ¹H-NMR (500 MHz, CDCl₃): 8.24 (1H, d, *J* = 7.5 Hz), 7.77 (2H, t, *J* = 6.7 Hz), 7.48 (1H, d, *J* = 9.2 Hz), 7.27-7.25 (2H, m), 7.0 (1H, dd, *J* = 5.9, 3.4 Hz), 6.54 (1H, t, *J* = 6.7 Hz); ¹³C-NMR (125 MHz; CDCl₃): 133.2, 129.6, 127.4, 124.3, 123.5, 121.0, 117.3, 116.8, 111.5, 108.8, 115.2; HRMS (ESI) calcd for C₁₂H₉ClN[M+H]⁺: 202.0424; Found: 202.0447.

10-Methylpyrido[1,2-*a*]indole (7d): Using the general procedure **GP-8**, compound **5h** (50 mg,

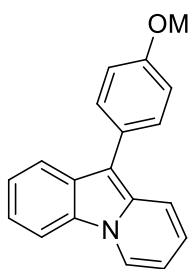
 0.27 mmol) and DDQ (122 mg, 0.54 mmol) provided compound **7d** (34 mg, 70%) as a yellow oil; ¹H-NMR (400 MHz, CDCl₃): 8.24 (1H, d, *J* = 7.6 Hz), 7.85 (1H, d, *J* = 7.6 Hz), 7.77 (1H, d, *J* = 7.6 Hz), 7.38 (2H, dd, *J* = 4.2, 3.4 Hz), 7.28 (1H, t, *J* = 6.7 Hz), 6.80 (1H, dd, *J* = 3.4, 5.9 Hz), 6.38 (1H, t, *J* = 5.9 Hz), 2.52 (3H, s); ¹³C-NMR (100 MHz; CDCl₃): 133.4, 129.2, 128.9, 124.4, 122.3, 120.8, 119.5, 118.8, 117.7, 110.1, 106.9, 98.9, 8.2; HRMS (ESI) calcd for C₁₃H₁₂N[M+H]⁺: 182.0970; Found: 182.0958.

10-Phenylpyrido[1,2-*a*]indole (7e): Using the general procedure **GP-8**, compound **5k** (50 mg,

 0.21 mmol) and DDQ (93 mg, 0.42 mmol) provided compound **7e** (32 mg, 62%) as a green oil; ¹H-NMR (400 MHz, CDCl₃): 8.36 (1H, d, *J* = 7.3 Hz), 8.03 (1H, d, *J* = 8.3 Hz), 7.92 (1H, d, *J* = 8.3 Hz), 7.71 (3H, t, *J* = 9.3 Hz), 7.51 (2H, t, *J* = 7.3 Hz), 7.42 (1H, t, *J* = 7.3 Hz), 7.36-7.29 (2H, m), 6.92

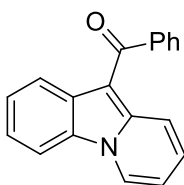
(1H, dd, $J = 6.4, 3.0$ Hz), 6.53 (1H, t, $J = 7.3$ Hz); $^{13}\text{C-NMR}$ (100 MHz; CDCl_3): 135.4, 133.5, 129.5, 129.3, 128.9, 127.8, 125.8, 124.5, 123.4, 122.9, 120.4, 119.5, 118.3, 114.3, 110.4, 108.5; HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{14}\text{N}[\text{M}+\text{H}]^+$: 244.1126; Found: 244.1119.

10-(4-Methoxyphenyl)pyrido[1,2-*a*]indole (7f): Using the general procedure **GP-8**, compound **5l**



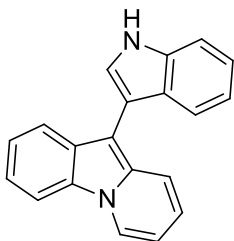
(50 mg, 0.18 mmol) and DDQ (82 mg, 0.36 mmol) provided compound **7f** (28 mg, 57%) as a yellow oil; $^1\text{H-NMR}$ (500 MHz, CDCl_3): 8.26 (1H, d, $J = 6.7$ Hz), 7.84 (1H, d, $J = 9.3$ Hz), 7.67 (1H, s), 7.55 (2H, d, $J = 9.3$ Hz), 7.49 (1H, d, $J = 9.2$ Hz), 7.17 (1H, d, $J = 8.4$ Hz), 7.02 (1H, dd, $J = 6.7, 2.5$ Hz), 6.68 (2H, d, $J = 9.3$ Hz), 6.56 (1H, t, $J = 7.5$ Hz), 3.77 (3H, s); $^{13}\text{C-NMR}$ (100 MHz; CDCl_3): 159.6, 145.7, 138.3, 133.5, 126.8, 126.2, 124.3, 123.6, 116.7, 116.5, 114.5, 111.6, 109.8, 108.9, 94.0, 82.9, 55.4; HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{16}\text{NO}[\text{M}+\text{H}]^+$: 274.1232; Found: 274.1224.

Phenyl(pyrido[1,2-*a*]indol-10-yl)methanone (7g): Using the general procedure **GP-8**, compound **5j** (50 mg, 0.19 mmol) and DDQ (85 mg, 0.39 mmol) provided compound **7g** (26 mg,



51%) as a green oil; $^1\text{H-NMR}$ (400 MHz, CDCl_3): 8.28 (1H, d, $J = 7.2$ Hz), 7.84 (1H, d, $J = 7.8$ Hz), 7.33 (2H, d, $J = 7.8$ Hz), 7.28-7.25 (4H, m), 7.23-7.13 (2H, m), 6.84 (1H, d, $J = 9.8$ Hz), 6.65-6.61 (1H, m), 6.37 (1H, t, $J = 13.2$ Hz); $^{13}\text{C-NMR}$ (100 MHz; CDCl_3): 188.0, 143.8, 133.8, 129.2, 128.9, 128.5, 126.4, 124.5, 122.6, 121.7, 119.9, 119.5, 118.2, 110.1, 107.3, 105.7; HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{14}\text{NO}[\text{M}+\text{H}]^+$: 272.1075; Found: 272.1078.

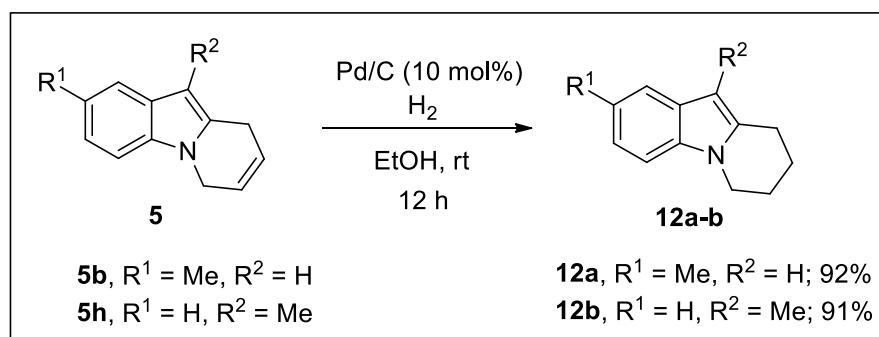
10-(1H-Indol-3-yl)pyrido[1,2-*a*]indole (7h): Using the general procedure **GP-8**, compound **5o** (50 mg, 0.18 mmol) and DDQ (80 mg, 0.36 mmol) provided compound **7h** (28 mg, 56%) as a



yellow oil; $^1\text{H-NMR}$ (400 MHz, CDCl_3): 8.94 (1H, d, $J = 3.7$ Hz), 8.16 (3H, t, $J = 7.3$ Hz), 7.83 (1H, d, $J = 8.1$ Hz), 7.74 (1H, t, $J = 7.4$ Hz), 7.62-7.55 (2H, m), 7.41 (1H, dd, $J = 4.4, 4.3$ Hz), 7.34 (1H, d, $J = 8.0$ Hz), 7.22-7.12 (2H, m), 6.97 (1H, s), 2.10 (1H, br s); $^{13}\text{C-NMR}$ (100 MHz; CDCl_3): 150.5, 148.4, 136.5, 136.2, 129.6, 129.5, 128.4, 127.9, 126.7,

121.9, 121.7, 121.2, 119.1, 118.9, 111.7, 111.1; HRMS (ESI) calcd for $C_{20}H_{14}N_2[M+H]^+$: 283.1235; Found: 283.1216.

10.0 General procedure for the synthesis of tetrahydropyrido[1,2-*a*]indole 12 (GP-9): To a solution of dihydropyrido[1,2-*a*]indole **5** (1 mmol) in EtOH (10 mL) was added Pd on charcoal (10 mol%) and the resulting mixture was stirred at room temperature in the presence of hydrogen gas for 12 h. After completion of the reaction (monitored by TLC), the reaction mixture was passed through celite bed and washed with ethyl acetate. The reaction mixture was then concentrated in vacuo and purified by column chromatography on silica gel with ethyl acetate-hexane (10/90 to 20/80) to provide the corresponding tetrahydropyrido[1,2-*a*]indoles **12** (Scheme S13).



Scheme S15. Synthesis of tetrahydro-pyrido-indole derivatives **12**.

2-Methyl-6,7,8,9-tetrahydropyrido[1,2-*a*]indole (12a): Using the general procedure **GP-9**, compound **5b** (50 mg, 0.27 mmol) and Pd/C (10 mol%, 3 mg,) provided compound **12a** (46 mg,

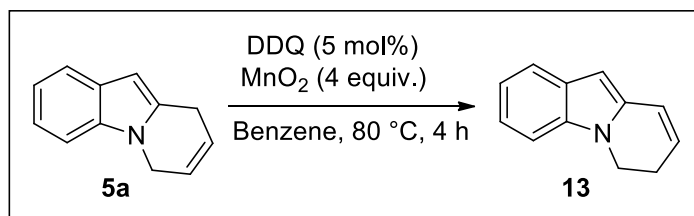
92%) as a colorless liquid; $^1\text{H-NMR}$ (500 MHz, CDCl_3): 7.32 (1H, s), 7.15 (1H, d, $J = 8.2$ Hz), 6.96 (1H, d, $J = 8.2$ Hz), 6.11 (1H, s), 4.02 (2H, t, $J = 6.3$ Hz), 2.96 (2H, t, $J = 6.3$ Hz), 2.45 (3H, s), 2.10-2.05 (2H, m), 1.91-1.86 (2H, m); $^{13}\text{C-NMR}$ (125 MHz; CDCl_3): 137.4, 134.9, 128.8, 128.6, 121.7, 119.5, 108.3, 97.1, 42.5, 24.4, 23.6, 21.6, 21.5; HRMS (ESI) calcd for $C_{13}H_{16}N[M+H]^+$: 186.1283; Found: 186.1296.

10-Methyl-6,7,8,9-tetrahydropyrido[1,2-*a*]indole (12b): Using the general procedure **GP-9**, compound **5h** (50 mg, 0.27 mmol) and Pd/C (10 mol%, 3 mg,) provided compound **12b** (45 mg,

91 %) as a colorless liquid; $^1\text{H-NMR}$ (500 MHz, CDCl_3): 7.47 (1H, d, $J = 7.6$

Hz), 7.18 (1H, d, $J = 8.2$ Hz), 7.12-7.05 (2H, m), 3.94 (2H, t, $J = 5.7$ Hz), 2.83 (2H, t, $J = 6.3$ Hz), 2.20 (3H, s), 2.01-1.96 (2H, m), 1.86-1.81 (2H, m); $^{13}\text{C-NMR}$ (125 MHz; CDCl_3): 136.0, 132.9, 128.7, 120.2, 118.9, 117.8, 108.4, 104.8, 42.4, 23.6, 22.5, 21.4, 8.2; HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{15}\text{N}[\text{M}+\text{H}]^+$: 186.1283; Found: 186.1262.

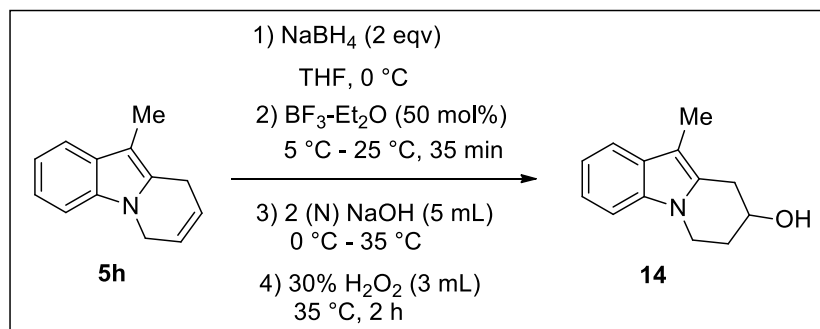
11.0 Synthesis of 6,7-dihydropyrido[1,2-*a*]indole **13**:



Scheme S16. Double bond isomerisation of dihydro-pyrido-indole **5a**.

To a solution of 6,9-dihydropyrido[1,2-*a*]indole **5a** (100 mg, 0.59 mmol) in benzene, MnO_2 (208.5 mg, 2.40 mmol) and DDQ (13.4 mg, 0.03 mmol) were added and the resulting reaction mixture was stirred at 80 °C for 4 h. After completion of reaction as monitored by TLC, solvent was removed under vacuo and the crude product was purified by using column chromatography (hexane/ethylacetate) to provide the double bond isomerized 6,7-dihydropyrido[1,2-*a*]indole **13** (98 mg, 98%) as a white solid. $^1\text{H-NMR}$ (500 MHz, CDCl_3): 7.58 (1H, d, $J = 7.6$ Hz), 7.29 (1H, d, $J = 4.4$ Hz), 7.21 (1H, t, $J = 7.0$ Hz), 7.01 (1H, t, $J = 8.2$ Hz), 6.62 (1H, d, $J = 10.1$ Hz), 6.37 (1H, s), 6.04-6.00 (1H, m), 4.13 (2H, t, $J = 7.0$ Hz), 2.69-2.66 (2H, m); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): 137.1, 135.1, 128.8, 124.2, 121.9, 120.8, 120.5, 119.7, 108.7, 99.4, 39.8, 24.4; HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{12}\text{N} [\text{M}+\text{H}]^+$: 170.0970; Found: 170.0977.

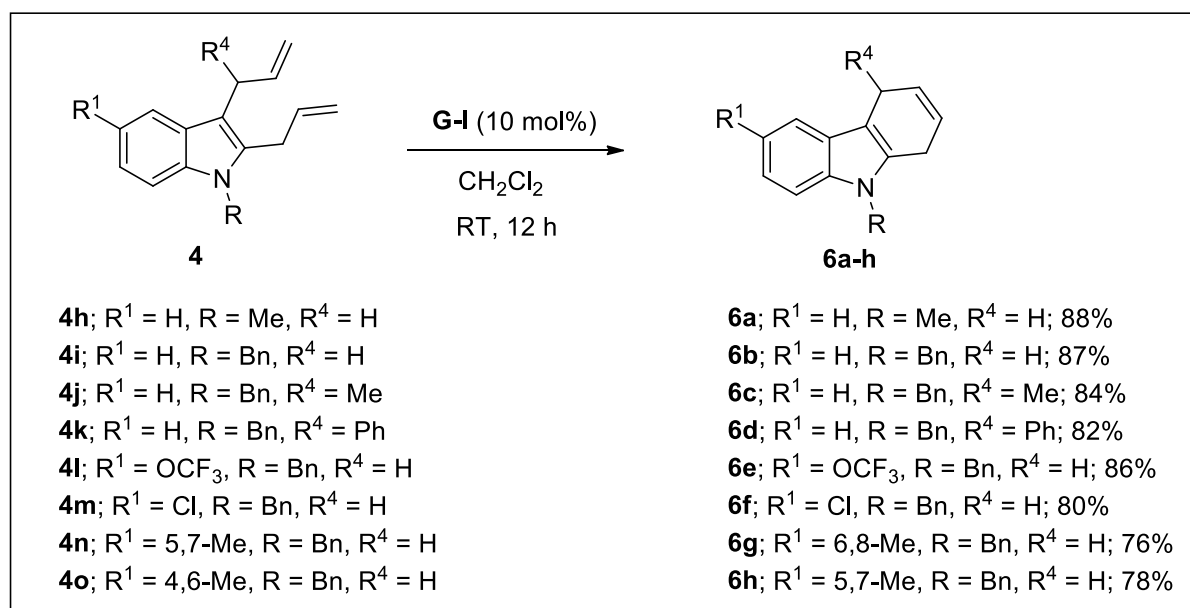
12.0 Synthesis of 10-methyl-6,7,8,9-tetrahydropyrido[1,2-*a*]indol-8-ol **14**:



Scheme S17. Selective hydroxylation of dihydro-pyrido-indole **5h**.

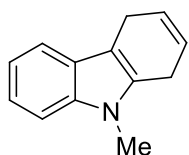
A suspension of **3h** (50 mg, 0.30 mmol) in anhydrous THF (5 mL) was taken in a round bottomed flask and cooled to 0 °C. Sodium borohydride (22.5 mg, 0.60 mmol) and boron trifluoride–ether complex (19 μL , 0.15 mmol) were added dropwise at 5–10 °C. The resulting mixture was stirred at 25 °C for 35 min and then cooled to 0 °C. Then aqueous solution of sodium hydroxide (2N, 5 mL) was added to it, and the mixture was heated to 35 °C. Subsequently, 30% hydrogen peroxide (3 mL) was added and the mixture was kept for 2 h at 35 °C. THF was distilled off, and the residue was dissolved in ethyl acetate. The solution was washed in succession with saturated solutions of NaCl, NaHCO_3 , and NaCl, dried over MgSO_4 , filtered, and evaporated. The crude product was purified by column chromatography to provide 10-methyl-6,7,8,9-tetrahydropyrido[1,2-*a*]indol-8-ol **14** (44 mg, 78%) as a brown solid. $^1\text{H-NMR}$ (400 MHz, CDCl_3): 7.48 (1H, d, $J = 7.7$ Hz), 7.22 (1H, t, $J = 7.8$ Hz), 7.16-7.08 (2H, m), 4.35 (1H, t, $J = 2.6$ Hz), 4.17 (1H, dd, $J = 7.7, 4.3$ Hz), 3.86 (1H, q, $J = 6.0$ Hz), 3.09-3.02 (1H, m), 2.89-2.82 (1H, m), 2.21 (3H, s), 2.11-2.04 (1H, m), 2.01-1.93 (2H, m); $^{13}\text{C-NMR}$ (100 MHz; CDCl_3): 136.1, 131.3, 129.2, 120.6, 119.3, 118.0, 108.5, 105.4, 65.8, 49.1, 29.2, 18.5, 8.3; HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{12}\text{N}$ $[\text{M}+\text{H}]^+$: 170.0970; Found: 170.0977.

13.0 General procedure for the ring closing metathesis of N-protected 2,3-diallyl indoles (GP-10): To a solution of the compound **4** (1 equiv.) in dry CH₂Cl₂ (4 mL) was added **G-I** (10 mol%) and the resulting mixture was stirred at room temperature for 8 h. The reaction mixture was then concentrated in vacuo and purified by using column chromatography on silica gel (EtOAc–hexane, 10/90 to 20/80) to give compounds **6a-h**.



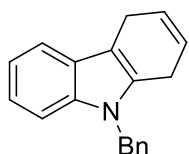
Scheme S18. RCM of 2,3-diallyl indolyl derivatives **4**.

9-Methyl-4,9-dihydro-1H-carbazole (6a): Using the general procedure **GP-10**, compound **4h**



(100 mg, 0.36 mmol) and **G-I** (17 mg, 0.04 mmol) provided compound **6a** (58 mg, 88%) as a white solid; ¹H-NMR (500 MHz, CDCl₃): 7.47 (1H, d, *J* = 7.6 Hz), 7.27 (1H, d, *J* = 8.4 Hz), 7.23-7.16 (1H, m), 7.08 (1H, t, *J* = 6.7 Hz), 6.05 (1H, d, *J* = 10.9 Hz), 5.92 (1H, d, *J* = 10.1 Hz), 3.64 (3H, s), 3.48-3.39 (4H, m); ¹³C-NMR (100 MHz, CDCl₃): 137.0, 132.9, 126.0, 125.8, 122.2, 120.9, 118.9, 118.0, 108.6, 106.3, 29.3, 23.7, 23.6; HRMS (ESI) calcd for C₁₃H₁₄N[M+H]⁺: 184.1126; Found: 184.1130.

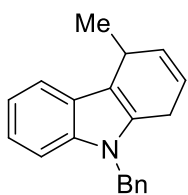
9-Benzyl-4,9-dihydro-1H-carbazole (6b): Using the general procedure **GP-10**, compound **4i**



(100 mg, 0.35 mmol) and **G-I** (14.9 mg, 0.035 mmol) provided compound **6b** (79 mg, 87%) as a white solid; ¹H-NMR (500 MHz, CDCl₃): 7.52 (1H,

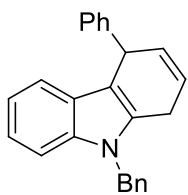
d, $J = 6.7$ Hz), 7.26-7.20 (4H, m), 7.14-7.08 (2H, m), 7.00 (2H, d, $J = 6.7$ Hz), 6.05 (1H, t, $J = 3.4$ Hz), 5.87 (1H, t, $J = 6.7$ Hz), 5.27 (2H, s), 3.51-3.47 (2H, m), 3.35-3.32 (2H, m); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): 138.3, 136.9, 132.8, 128.9, 127.4, 127.1, 126.3, 125.9, 122.4, 121.3, 119.2, 118.2, 109.2, 107.1, 46.6, 23.8, 23.7; HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{18}\text{N}[\text{M}+\text{H}]^+$: 260.1439; Found: 260.1440.

9-Benzyl-4-methyl-4,9-dihydro-1H-carbazole (6c): Using the general procedure **GP-10**,



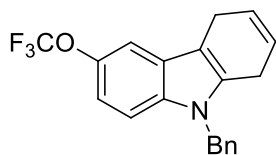
compound **4j** (100 mg, 0.33 mmol) and **G-I** (16.9 mg, 0.033 mmol) provided compound **6c** (76 mg, 84%) as a white solid; $^1\text{H-NMR}$ (400 MHz, CDCl_3): 7.62 (1H, dd, $J = 4.4, 2.4$ Hz), 7.52 (1H, dd, $J = 4.9, 1.9$ Hz), 7.27-7.19 (3H, m), 7.15-7.08 (2H, m), 7.00 (2H, d, $J = 7.3$ Hz), 5.94-5.86 (1H, m), 5.83-5.79 (1H, m), 5.27 (2H, d, $J = 3.0$ Hz), 3.51-3.47 (2H, m), 3.36-3.28 (2H, m), 1.46 (3H, d, $J = 7.3$ Hz); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): 138.3, 138.2, 137.0, 133.1, 132.4, 128.9, 127.4, 126.3, 125.9, 122.4, 121.3, 121.0, 120.6, 118.2, 112.6, 107.0, 46.6, 29.9, 23.8, 22.4; HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{20}\text{N}[\text{M}+\text{H}]^+$: 274.1596; Found: 274.1595.

9-Benzyl-4-phenyl-4,9-dihydro-1H-carbazole (6d): Using the general procedure **GP-10**,



compound **4k** (100 mg, 0.28 mmol) and **G-I** (16.9 mg, 0.03 mmol) provided compound **6d** (77 mg, 82%) as a pale yellow solid; $^1\text{H-NMR}$ (400 MHz, CDCl_3): 7.27-7.12 (10 H, m), 7.07-6.95 (3H, m), 6.94-6.87 (1H, m), 5.99-5.92 (1H, m), 5.86-5.81 (1H, m), 5.24 (2H, s), 4.87 (1H, d, $J = 2.4$ Hz), 3.45-3.27 (2H, m); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): 154.9, 138.1, 137.1, 133.2, 131.4, 128.9, 128.6, 128.4, 127.4, 126.6, 126.4, 126.2, 121.2, 120.6, 119.3, 119.2, 110.4, 109.1, 46.6, 42.1, 23.7; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{22}\text{N}[\text{M}+\text{H}]^+$: 336.1752; Found: 336.1744.

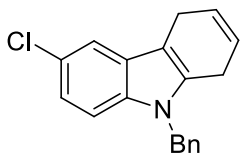
9-Benzyl-6-trifluoromethoxy-4,9-dihydro-1H-carbazole (6e): Using the general procedure **GP-10**, compound **4l** (100 mg, 0.27 mmol) and **G-I** (22.2 mg, 0.03 mmol) provided compound **6e**



(80 mg, 86%) as a colorless solid; $^1\text{H-NMR}$ (400 MHz, CDCl_3): 7.35 (1H, s), 7.29-7.20 (3H, m), 7.15 (1H, d, $J = 9.2$ Hz), 6.97 (3H, d, $J = 6.7$ Hz), 6.06-6.01 (1H, m), 5.89-5.85 (1H, m), 5.23 (2H, s), 3.47-3.42 (2H, m), 3.34-3.29 (2H, m); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): 142.9, 137.7,

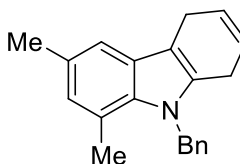
135.1, 134.9, 128.9, 127.6, 127.2, 126.2, 122.1, 119.8, 114.9, 110.7, 109.6, 107.5, 46.8, 23.8, 23.5; HRMS (ESI) calcd for $C_{20}H_{17}F_3NO[M+H]^+$: 344.1262; Found: 344.1266.

9-Benzyl-6-chloro-4,9-dihydro-1H-carbazole (6f): Using the general procedure **GP-10**, compound **4m** (100 mg, 0.30 mmol) and **G-I** (16.9 mg, 0.03 mmol) provided compound **6f** (71



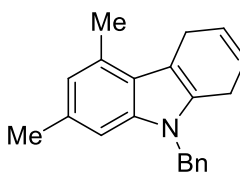
mg, 80%) as a white solid; 1H -NMR (400 MHz, $CDCl_3$): 7.47 (1H, d, $J = 1.9$ Hz), 7.29-7.20 (3H, m), 7.13-7.05 (2H, m), 6.96 (2H, d, $J = 6.8$ Hz), 6.06-6.01 (1H, m), 5.90-5.85 (1H, m), 5.25 (2H, s), 3.46-3.42 (2H, m), 3.34-3.30 (2H, m); ^{13}C -NMR (100 MHz, $CDCl_3$): 137.8, 135.3, 134.4, 128.9, 128.2, 127.6, 126.2, 125.7, 124.9, 122.2, 121.4, 117.8, 110.2, 106.9, 47.8, 23.8, 23.5; HRMS (ESI) calcd for $C_{19}H_{17}ClN[M+H]^+$: 294.1050; Found: 294.1059.

9-Benzyl-6,8-dimethyl-4,9-dihydro-1H-carbazole (6g): Using the general procedure **GP-10**, compound **4n** (100 mg, 0.32 mmol) and **G-I** (16.9 mg, 0.03 mmol) provided compound **6g** (69



mg, 76%) as a white solid; 1H -NMR (400 MHz, $CDCl_3$): 7.79 (1H, s), 7.27-7.16 (5H, m), 6.68 (1H, s), 6.06-6.02 (1H, m), 5.88-5.84 (1H, m), 5.48 (2H, s), 3.47-3.42 (2H, m), 3.29-3.24 (2H, m), 2.59 (3H, s), 2.41 (3H, s); ^{13}C -NMR (100 MHz, $CDCl_3$): 141.8, 139.1, 130.7, 129.0, 127.3, 125.6, 125.2, 124.1, 123.1, 120.1, 119.2, 115.9, 109.0, 48.3, 23.7, 21.2, 19.7; HRMS (ESI) calcd for $C_{21}H_{22}N[M+H]^+$: 288.1752; Found: 288.1746.

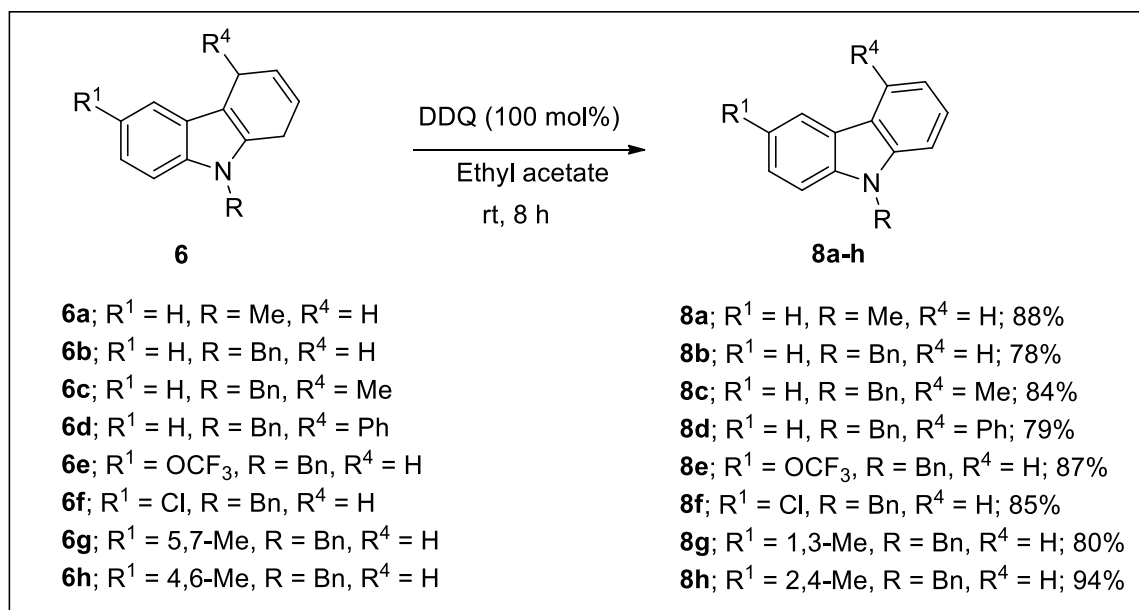
9-Benzyl-5,7-dimethyl-4,9-dihydro-1H-carbazole (6h): Using the general procedure **GP-10**, compound **4o** (100 mg, 0.32 mmol) and **G-I** (16.9 mg, 0.03 mmol) provided compound **6h** (71



mg, 78%) as a white solid; 1H -NMR (300 MHz, $CDCl_3$): 7.25-7.19 (4H, m), 7.11 (2H, d, $J = 6.8$ Hz), 6.66 (1H, s), 6.01-5.96 (1H, m), 5.87-5.79 (1H, m), 5.48 (2H, s), 3.80-3.73 (2H, m), 3.33-3.26 (2H, m), 2.86 (3H, s), 2.47 (3H, s); ^{13}C -NMR (100 MHz, $CDCl_3$): 141.5, 140.8, 138.5, 137.5, 135.9, 130.9, 128.9, 127.5, 126.5, 126.2, 124.8, 122.7, 122.4, 119.2, 108.7, 106.8, 46.6, 26.5, 23.8, 22.2, 20.8; HRMS (ESI) calcd for $C_{21}H_{22}N[M+H]^+$: 288.1752; Found: 288.1763.

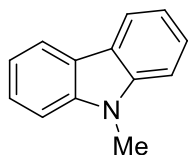
14.0 General procedure for the DDQ mediated aromatization to synthesize carbazoles **8** (GP-11):

To a solution of dihydrocarbazole compound **6** (1 equiv.) in ethyl acetate (4 mL) was added DDQ (100 mol %) and the resulting mixture was allowed to stir at room temperature for 8 h. The reaction mixture was then worked up with NaOH solution (2N) and extracted with ethyl acetate (2 x 5 mL). The combined organic fractions were concentrated in vacuo and purified by column chromatography (EtOAc–hexane, 5/95 to 10/90) on silica gel to provide compounds **8a-h**.



Scheme S19. Synthesis of carbazole derivatives **8a-h**.

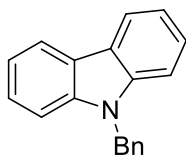
9-Methyl-9H-carbazole (8a): Using the general procedure **GP-11**, compound **6a** (50 mg, 0.27 mmol) and DDQ (61.9 mg, 0.27 mmol) provided compound **8a** (48 mg, 88%)



as a colorless solid; ¹H-NMR (500 MHz, CDCl₃): 8.02 (2H, d, *J* = 7.7 Hz), 7.39 (2H, t, *J* = 7.7 Hz), 7.31 (2H, d, *J* = 8.6 Hz), 7.15 (2H, t, *J* = 7.8 Hz), 3.75 (3H, s); ¹³C-NMR (125 MHz, CDCl₃): 141.2, 126.0, 123.0, 120.4, 119.0,

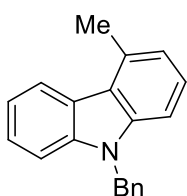
109.0, 30.0; HRMS (ESI) calcd for C₁₃H₁₂N [M+H]⁺: 182.0970; Found: 182.0964.

9-Benzyl-9H-carbazole (8b): Using the general procedure **GP-11**, compound **6b** (50 mg, 0.19 mmol) and DDQ (43.76 mg, 0.19 mmol) provided compound **8b** (40 mg, 78%)

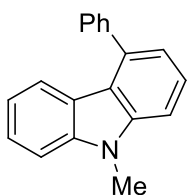


as a colorless solid; $^1\text{H-NMR}$ (500 MHz, CDCl_3): 8.14 (2H, ddd, $J = 7.8, 1.2, 0.7$ Hz), 7.43 (2H, ddd, $J = 8.2, 7.0, 1.2$ Hz), 7.37 (2H, t, $J = 8.2$ Hz), 7.28-7.22 (5H, m), 7.16-7.13 (2H, m), 5.53 (2H, s); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): 140.7, 137.2, 128.8, 127.4, 126.4, 125.8, 123.0, 120.4, 119.2, 108.9, 46.6; HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{16}\text{N}[\text{M}+\text{H}]^+$: 258.1283; Found: 258.1279.

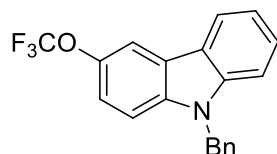
9-Benzyl-4-methyl-9H-carbazole (8c): Using the general procedure **GP-11**, compound **6c** (50 mg, 0.18 mmol) and DDQ (41.5 mg, 0.18 mmol) provided compound **8c** (41 mg, 84%) as a colorless solid; $^1\text{H-NMR}$ (400 MHz, CDCl_3): 8.22 (1H, d, $J = 8.0$ Hz), 8.11 (1H, d, $J = 7.9$ Hz), 7.43-7.29 (4H, m), 7.27-7.18 (3H, m), 7.13-7.09 (2H, m), 7.02 (1H, d, $J = 6.7$ Hz), 5.48 (2H, s), 2.90 (3H, s); $^{13}\text{C-NMR}$ (100 MHz; CDCl_3): 140.9, 140.8, 140.7, 137.4, 133.7, 128.9, 127.5, 126.5, 125.9, 125.8, 125.3, 123.8, 123.2, 122.8, 121.7, 121.0, 120.5, 119.4, 119.3, 106.6, 46.6, 20.9; HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{18}\text{N}[\text{M}+\text{H}]^+$: 272.1439; Found: 272.1432.



9-Methyl-4-phenyl-9H-carbazole (8d): Using the general procedure **GP-11**, compound **6d** (50 mg, 0.15 mmol) and DDQ (33.8 mg, 0.15 mmol) provided compound **8d** (40 mg, 79%) as a colorless solid; $^1\text{H-NMR}$ (500 MHz, CDCl_3): 7.67 (2H, dd, $J = 1.7, 5.1$ Hz), 7.56-7.46 (5H, m), 7.38 (3H, t, $J = 8.4$ Hz), 7.30-7.24 (3H, m), 7.19 (2H, d, $J = 6.7$ Hz), 7.14 (1H, d, $J = 7.6$ Hz), 7.02-6.99 (1H, m), 5.56 (2H, s); $^{13}\text{C-NMR}$ (100 MHz; CDCl_3): 141.5, 141.2, 141.1, 138.0, 137.3, 129.4, 128.9, 128.5, 127.7, 127.6, 126.6, 125.8, 124.7, 122.8, 122.6, 121.3, 120.6, 119.0, 108.8, 107.9, 46.8; HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{17}\text{N}[\text{M}+\text{H}]^+$: 258.1283; Found: 258.1271.

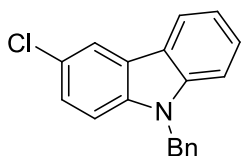


9-Benzyl-3-(trifluoromethoxy)-9H-carbazole (8e): Using the general procedure **GP-11**, compound **6e** (50 mg, 0.15 mmol) and DDQ (33.1 mg, 0.15 mmol) provided compound **8e** (59 mg, 87%) as a colorless solid; $^1\text{H-NMR}$ (500 MHz, CDCl_3): 8.02 (1H, d, $J = 7.8, 0.9$ Hz), 7.88 (1H, s), 7.39 (1H, t, $J = 8.6$ Hz), 7.31 (1H, d, $J = 8.2$ Hz), 7.25-7.16 (6H, m), 7.05 (2H, d, $J = 7.6$ Hz), 5.44 (2H, s); $^{13}\text{C-NMR}$



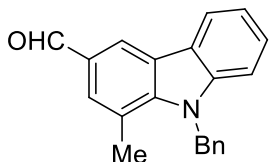
NMR (100 MHz; CDCl₃): 143.0, 142.0, 139.0, 137.0, 129.0, 128.0, 127.0, 126.4, 121.0, 120.0, 119.5, 113.3, 109.4, 109.3, 47.0; HRMS (ESI) calcd for C₂₀H₁₅NOF₃ [M+H]⁺: 342.1106; Found: 342.1128.

9-Benzyl-3-chloro-9H-carbazole (8f): Using the general procedure **GP-11**, compound **6f** (50 mg, 0.17 mmol) and DDQ (38.63 mg, 0.17 mmol) provided compound **8f** (42 mg, 85%) as a



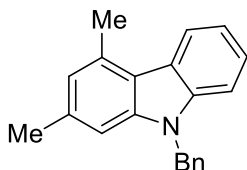
colorless solid; **¹H-NMR** (400 MHz, CDCl₃): 8.02-7.99 (2H, m), 7.41-7.35 (1H, m), 7.32-7.28 (2H, m), 7.20-7.16 (5H, m), 7.05-7.02 (2H, m), 5.42 (2H, s); **¹³C-NMR** (125 MHz, CDCl₃): 141.2, 139.0, 137.0, 129.0, 128.0, 127.0, 126.3, 126.0, 125.0, 121.0, 120.1, 120.0, 110.0, 109.2, 47.0; HRMS (ESI) calcd for C₁₉H₁₅NCl[M+H]⁺: 292.0893; Found: 292.0879.

9-benzyl-1-methyl-9H-carbazole-3-carbaldehyde (8g): Using the general procedure **GP-11**, compound **6g** (50 mg, 0.17 mmol) and DDQ (38.63 mg, 0.17 mmol) provided compound **8g** (41



mg, 80%) as a colorless solid; **¹H-NMR** (400 MHz, CDCl₃): 10.06 (1H, s), 8.50 (1H, s), 8.16 (1H, d, *J* = 7.9 Hz), 7.70 (1H, s), 7.47-7.43 (1H, m), 7.35-7.31 (2H, m), 7.29-7.23 (3H, m), 6.99 (2H, d, *J* = 6.7 Hz), 5.80 (2H, s), 2.69 (3H, s); **¹³C-NMR** (100 MHz, CDCl₃): 191.9, 143.2, 142.2, 138.1, 129.9, 129.2, 129.1, 127.7, 127.0, 125.5, 124.2, 123.4, 122.3, 121.0, 120.9, 120.5, 109.8, 48.5, 19.9; HRMS (ESI) calcd for C₂₁H₁₈NO[M+H]⁺: 300.1388; Found: 300.1379.

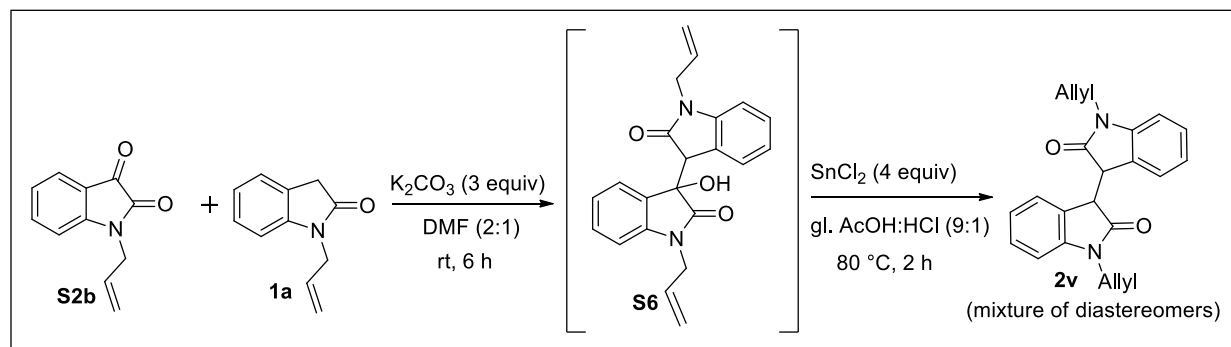
9-Benzyl-2,4-dimethyl-9H-carbazole (8h): Using the general procedure **GP-11**, compound **6h** (50 mg, 0.17 mmol) and DDQ (38.63 mg, 0.17 mmol) provided compound **8h** (46 mg, 94%) as a



colorless solid; **¹H-NMR** (300 MHz, CDCl₃): 8.17 (1H, d, *J* = 8.0 Hz), 7.40-7.30 (2H, m), 7.24-7.20 (4H, m), 7.11 (2H, d, *J* = 7.2 Hz), 7.02 (1H, s), 7.86 (1H, s), 5.47 (2H, s), 2.86 (3H, s), 2.47 (3H, s); **¹³C-NMR** (100 MHz, CDCl₃): 141.5, 140.8, 137.5, 136.0, 133.3, 128.9, 127.5, 126.5, 124.8, 123.9, 122.7, 122.4, 119.5, 119.2, 108.7, 106.7, 46.6, 22.2, 20.8; HRMS (ESI) calcd for C₂₁H₂₀N [M+H]⁺: 286.1596; Found: 286.1592.

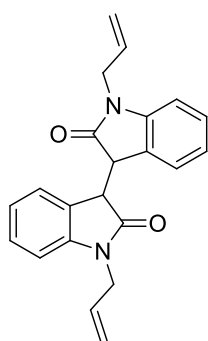
15.0 Synthesis of indole-fused dimeric heterocycles:

15.0.1. Synthesis of dimeric oxindole (2v):



Scheme S20. Synthesis of dimeric oxindole **2v**.

Synthesis of 1,1'-diallyl-[3,3'-biindoline]-2,2'-dione (2v): To a solution of 1-allyloxindole **1a** (1.0 g, 5.77 mmol) in dry DMF was added K_2CO_3 (2.5 g, 17.3 mmol) and stirred for 10 minutes.



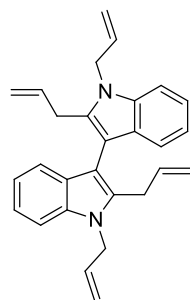
Then 1-allyl isatin **S2b** (1.1 g, 5.77 mmol) was added in the reaction mixture portionwise and allowed to stir at room temperature for 6 h. After completion of reaction as monitored by TLC, the reaction mixture was diluted with water and extracted with ethyl acetate (3 x 15 mL). The organic fractions were separated and dried over $MgSO_4$ and concentrated in vacuo. The crude **S6** was then directly used in next step.

In a mixture of gl. AcOH:HCl (20 mL, 9:1) in **S6** was added $SnCl_2$ (3.3 g, 17.3 mmol) portionwise and the resulting solution was heated at 80 °C for 2 h. After completion of reaction as monitored by TLC, the reaction mixture was cooled to room temperature and quenched with NaOH (2N, 10 mL) and extracted with diethyl ether (3 x 15 mL). The organic fractions were separated and dried over $MgSO_4$ and concentrated in vacuo. The crude residue was purified by column chromatography on silica gel using ethylacetate-hexane (10/90 to 30/70) to provide 1,1'-diallyl-[3,3'-biindoline]-2,2'-dione **2v** (1.2 g, 60%) containing a 1:5 mixture of two diastereomers of **7t** (confirmed by 1H NMR analysis) as a brown solid. 1H -NMR (400 MHz, $CDCl_3$): 7.24 (10 H, t, $J = 7.3$ Hz), 7.08 (2H, t, $J = 7.3$ Hz), 6.96 (2H, d, $J = 7.3$ Hz), 6.92 (10H, t, $J = 7.3$ Hz), 6.78 (12H, t, $J = 7.3$ Hz), 6.68 (2H, d, $J = 7.8$ Hz), 5.88-5.79 (2H, m), 5.70-5.60 (10H, m), 5.25 (2H, s), 5.22 (2H, d, $J = 5.4$ Hz), 5.11 (10H, d, $J = 1.5$ Hz), 5.08 (10H, d, $J = 2.9$ Hz), 4.50 (2H, dd, J

= 10.7, 5.9 Hz), 4.36-4.30 (12H, m), 4.22 (10H, s), 4.19-4.10 (12H, m); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): 175.7, 174.5, 144.4, 143.5, 131.4, 131.3, 128.8, 128.5, 125.9, 124.8, 124.1, 123.6, 122.4, 118.2, 117.5, 109.3, 109.1, 46.4, 46.2, 42.6, 42.5; HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{21}\text{N}_2\text{O}_2[\text{M}+\text{H}]^+$: 345.1603; Found: 345.1598.

15.0.2 Synthesis of dimeric pyrido-indole derivative 17:

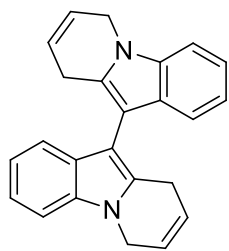
1,1',2,2'-Tetraallyl-1H,1'H-3,3'-biindole (15): Using the general procedure **GP-5**, compound **2v**



(500 mg, 1.45 mmol) and allylmagnesium bromide (8.7 mL, 8.71 mmol) provided compound **15** (436 mg, 76%) as a pale yellow liquid; $^1\text{H-NMR}$ (500 MHz, CDCl_3): 7.32 (2H, d, $J = 6.7$ Hz), 7.27 (2H, d, $J = 6.0$ Hz), 7.17 (2H, t, $J = 6.0$ Hz), 7.02 (2H, t, $J = 6.0$ Hz), 6.03-5.96 (2H, m), 5.84-5.77 (2H, m), 5.15 (2H, d, $J = 8.0$ Hz), 5.02-4.89 (6H, m), 4.80 (4H, d, $J = 2.0$ Hz), 3.42 (4H, d, $J = 3.2$ Hz); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): 136.8, 136.3, 135.9, 134.1, 121.1, 119.9, 119.3, 116.2, 116.0, 109.3, 107.1, 45.9, 29.8; HRMS (ESI) calcd for $\text{C}_{28}\text{H}_{29}\text{N}_2$

$[\text{M}+\text{H}]^+$: 393.2331; Found: 393.2327.

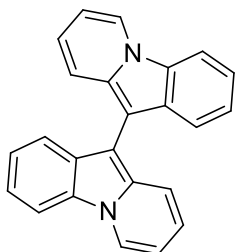
6,6',9,9'-Tetrahydro-10,10'-bipyrido[1,2-*a*]indole (16): Using the general procedure **GP-7**,



compound **15** (100 mg, 0.25 mmol) and **G-I** (24.4 mg, 0.03 mmol) provided compound **16** (72 mg, 84%) as a pale yellow solid; $^1\text{H-NMR}$ (500 MHz, CDCl_3): 7.40 (4H, dd, $J = 6.8, 8.4$ Hz), 7.24 (2H, t, $J = 8.4$ Hz), 7.12 (2H, t, $J = 7.6$ Hz), 6.12-6.04 (4H, m), 4.82-4.77 (4H, m), 3.56 (2H, dd, $J = 20.2, 1.7$ Hz), 3.36 (2H, dd, $J = 17.7, 3.4$ Hz); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3):

135.8, 131.3, 128.6, 122.8, 120.5, 120.4, 119.7, 119.5, 108.9, 103.9, 42.3, 24.1; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{21}\text{N}_2[\text{M}+\text{H}]^+$: 337.1705; Found: 337.1704.

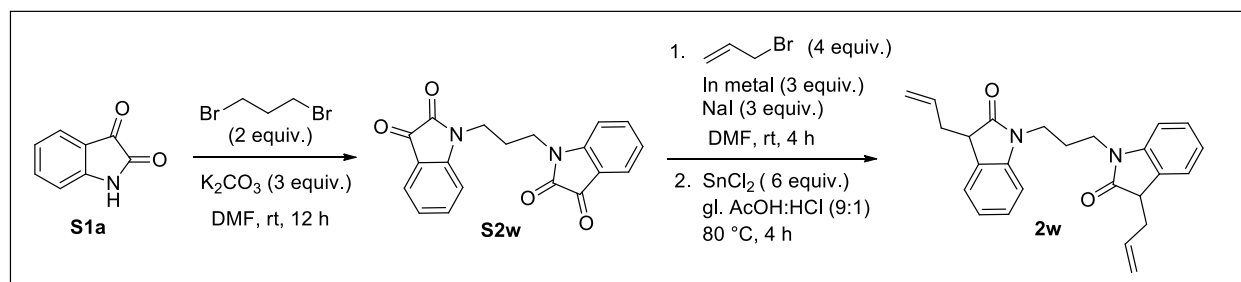
10,10'-Bipyrido[1,2-*a*]indole (17): Using the general procedure **GP-8**, compound **16** (50 mg,



0.15 mmol) and DDQ (68 mg, 0.30 mmol) provided compound **17** (32 mg, 65%) as a yellow oil; $^1\text{H-NMR}$ (400 MHz, CDCl_3): 8.26 (2H, d, $J = 7.6$ Hz), 7.86 (2H, d, $J = 7.6$ Hz), 7.78 (2H, d, $J = 7.5$ Hz), 7.40 (4H, dd, $J = 4.2, 3.4$ Hz), 7.29 (2H, t, $J = 6.7$ Hz), 6.82 (2H, dd, $J = 5.9, 3.4$

Hz), 6.39 (2H, t, $J = 5.9$ Hz); $^{13}\text{C-NMR}$ (100 MHz; CDCl_3): 133.4, 129.2, 128.9, 124.4, 122.3, 120.8, 119.5, 118.8, 117.7, 110.1, 106.9, 98.9; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{17}\text{N}_2[\text{M}+\text{H}]^+$: 333.1392; Found: 333.1394.

15.0.3. Synthesis of dimeric oxindole 2w:



Scheme S21. Synthesis of dimeric oxindole **2w**.

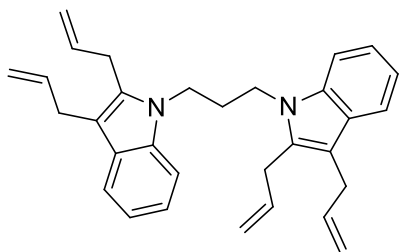
1-(2-Phenylallyl)indoline-2,3-dione (S2w): Using the reported procedure¹, isatin **S1a** (5.0 g, 34 mmol) and K_2CO_3 (11.7 g, 84.9 mmol) and 1,3-dibromopropane (5.2 mL, 50.97 mmol) provided compound **S2w** (8.9 g, 70%) as a red solid; $^1\text{H-NMR}$ (400 MHz, CDCl_3): 7.60-7.56 (4H, m), 7.14 (2H, t, $J = 7.3$ Hz), 6.89 (2H, d, $J = 7.8$ Hz), 3.86 (4H, t, $J = 6.8$ Hz), 2.23 (2H, t, $J = 6.9$ Hz); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): 182.9, 158.5, 150.3, 138.7, 125.8, 124.2, 117.8, 110.1, 38.3, 25.4; HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{15}\text{N}_2\text{O}_4$ $[\text{M}+\text{H}]^+$: 335.1032; Found: 335.1009.

1-Benzyl-3-(but-3-en-2-yl)indolin-2-one (2w): Using the general procedure **GP-1**, indium metal (1.2 g, 10.8 mmol), allyl bromide (1.1 mL, 13.5 mmol), compound **S2w** (3 g, 8.97 mmol) and NaI (2.7 g, 17.94 mmol) provided the intermediate, which was then treated with SnCl_2 (6.8 g, 35.88 mmol) to furnish compound **2w** (2.4 g, 68%) as a colorless oil; $^1\text{H-NMR}$ (400 MHz, CDCl_3): 7.21-7.13 (4H, m), 6.95 (2H, t, $J = 7.8$ Hz), 6.68 (2H, d, $J = 7.8$ Hz), 5.66-5.57 (2H, m), 4.97 (4H, dd, $J = 17.0, 14.7$ Hz), 3.65-3.38 (4H, m), 3.40 (2H, q, $J = 6.8$ Hz), 2.77-2.70 (2H, m), 2.54-2.47 (2H, m), 2.01-1.94 (2H, m); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): 177.2, 143.4, 133.9, 128.8,

128.1, 124.5, 122.4, 118.3, 108.2, 45.2, 37.9, 34.9, 25.7, 25.6; HRMS (ESI) calcd for $C_{25}H_{27}N_2O_2$ $[M+H]^+$: 387.2073; Found: 387.2069.

15.0.4 Synthesis of dimeric carbazole derivative 20:

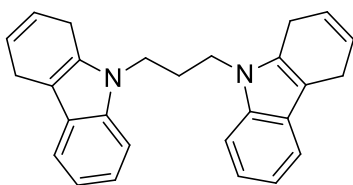
1,3-Bis(2,3-diallyl-1H-indol-1-yl)propane (18): Using the general procedure **GP-5**, compound **2w** (500 mg, 1.29 mmol) and allylmagnesium bromide (7.8 mL, 7.76 mmol) provided compound



18 (442 mg, 79%) as a colorless liquid; **1H -NMR** (400 MHz, $CDCl_3$): 7.53 (2H, d, J = 7.9 Hz), 7.12 (4H, d, J = 3.7 Hz), 7.09-7.04 (2H, m), 5.99-5.89 (2H, m), 5.83-5.73 (2H, m), 5.05 (1H, d, J = 1.8 Hz), 5.01 (1H, d, J = 1.2 Hz), 4.99-4.95 (4H, m), 4.81 (2H, dd, J = 15.8, 1.2 Hz), 4.1 (4H, t, J = 7.3 Hz),

3.45 (4H, d, J = 6.7 Hz), 3.39 (4H, d, J = 5.5 Hz), 2.19 (2H, t, J = 7.3 Hz); **^{13}C -NMR** (100 MHz, $CDCl_3$): 137.7, 136.2, 135.2, 133.6, 128.1, 121.2, 119.1, 118.9, 116.3, 114.5, 110.3, 108.9, 40.8, 31.0, 28.9, 28.8; HRMS (ESI) calcd for $C_{31}H_{35}N_2$ $[M+H]^+$: 435.2800; Found: 435.2804.

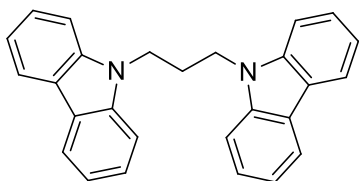
1,3-Di(1H-carbazol-9(4H)-yl)propane (19): Using the general procedure **GP-10**, compound **18** (100 mg, 0.23 mmol) and **G-I** (18.9 mg, 0.023 mmol) provided compound **19** (70 mg, 82%) as a



pale yellow solid; **1H -NMR** (500 MHz, $CDCl_3$): 7.48 (2H, d, J = 7.6 Hz), 7.12 (4H, d, J = 3.4 Hz), 7.11-7.10 (2H, m), 6.03 (2H, d, J = 10.0 Hz), 5.86 (2H, d, J = 10.1 Hz), 4.05 (4H, t, J = 7.6 Hz), 3.44 (4H, t, J = 7.6 Hz), 3.25 (4H, t, J = 6.7 Hz), 2.21 (2H,

t, J = 7.6 Hz); **^{13}C -NMR** (100 MHz, $CDCl_3$): 136.3, 132.2, 127.2, 125.9, 122.1, 121.2, 119.1, 118.3, 108.8, 107.0, 40.6, 31.0, 23.7, 23.6; HRMS (ESI) calcd for $C_{27}H_{27}N_2$ $[M+H]^+$: 379.2174; Found: 379.2178.

1,3-Di(9H-carbazol-9-yl)propane (20): Using the general procedure **GP-11**, compound **19** (50 mg, 0.13 mmol) and DDQ (90 mg, 0.39 mmol) provided

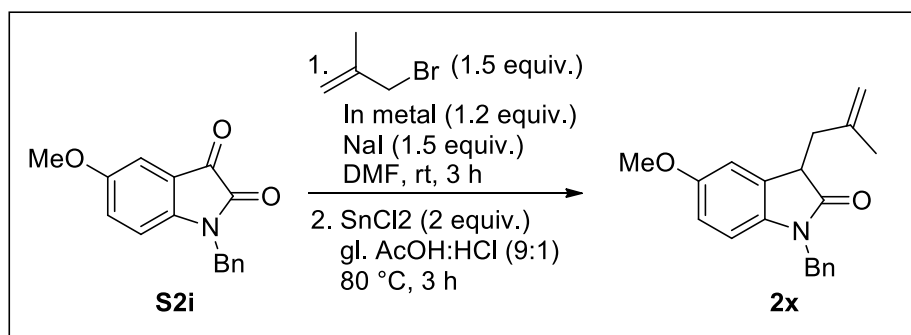


compound **20** (41 mg, 80%) as a colorless solid; **1H -NMR** (500 MHz, $CDCl_3$): 8.11 (4H, d, J = 7.6 Hz), 7.41 (4H, t, J = 8.4 Hz), 7.27-7.21 (8H, m), 4.38 (4H, t, J = 7.6 Hz), 2.52-2.46 (2H, m);

$^{13}\text{C-NMR}$ (125 MHz; CDCl_3): 140.3, 125.9, 123.2, 120.6, 119.3, 108.6, 40.7, 28.1; HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{23}\text{N}_2[\text{M}+\text{H}]^+$: 375.1863; Found: 375.1865.

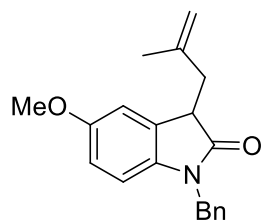
16.0 Synthesis of naturally occurring carbazole alkaloids:

16.0.1 Synthesis of oxindole 2x:



Scheme S22. Synthesis of oxindole 2x.

1-Benzyl-5-methoxy-3-(2-methylallyl)indolin-2-one (2x): Using the general procedure **GP-1**, indium metal (1.02 g, 8.98 mmol), methylallyl bromide (1.51 mL, 14.96 mmol), compound **S2i**



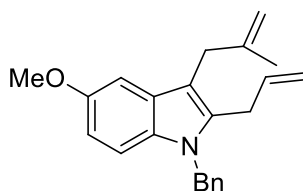
(2g, 7.48 mmol) and NaI (2.24 g, 14.96 mmol) provided the intermediate, which was then treated with SnCl_2 (5.67 g, 29.92 mmol) to furnish compound **2x** (1.5 g, 65%) as a colorless oil; $^1\text{H-NMR}$ (500 MHz, CDCl_3): 7.34-7.26 (5H, m), 6.80 (1H, d, $J = 1.9$ Hz), 6.69 (1H, dd, $J = 2.5$, 5.7 Hz), 6.60 (1H, d, $J = 8.2$ Hz), 5.12 (1H, d, $J = 8.8$ Hz), 4.90 (2H, d, $J = 5.1$ Hz), 4.42 (1H, d, $J = 8.8$ Hz), 3.76 (3H, s), 3.75 (1H, s), 1.94 (2H, s), 1.87 (3H, s); $^{13}\text{C-NMR}$

(125 MHz, CDCl_3): 176.3, 141.4, 136.3, 131.0, 128.8, 127.6, 127.5, 120.8, 118.7, 112.3, 111.9, 109.3, 95.7, 55.9, 46.7, 43.9, 25.8; HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{22}\text{NO}_2$ $[\text{M}+\text{H}]^+$: 308.1651; Found: 308.1654.

16.0.2 Synthesis of glycozoline and glycozolinol:

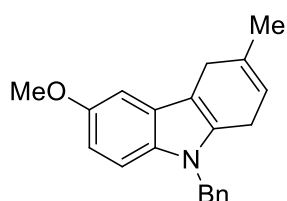
2-Allyl-1-benzyl-5-methoxy-3-(2-methylallyl)-1H-indole (21): Using the general procedure **GP-5**, compound **2x** (500 mg, 1.47 mmol) and allylmagnesium bromide (4.42 mL, 4.42 mmol)

provided compound **15** (419 mg, 78%) as a colorless liquid; $^1\text{H-NMR}$



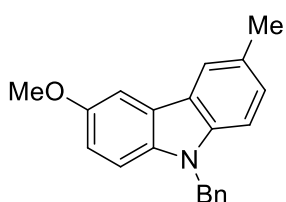
NMR (500 MHz, CDCl₃): 7.24-7.18 (3H, m), 7.04 (1H, d, *J* = 8.4 Hz), 6.90 (2H, dd, *J* = 5.6, 1.7 Hz), 6.76 (1H, dd, *J* = 6.7, 1.7 Hz), 6.20 (1H, s), 5.86-5.80 (1H, m), 5.30 (1H, d, *J* = 10.4 Hz), 5.26 (2H, s), 5.01-4.93 (2H, m), 4.76 (1H, d, *J* = 9.3 Hz), 3.82 (3H, s), 3.41-3.37 (2H, m), 1.96 (2H, s), 1.69 (3H, s); **¹³C-NMR** (125 MHz, CDCl₃): 154.2, 138.5, 136.7, 135.3, 135.2, 132.1, 128.8, 128.3, 127.3, 126.0, 125.9, 116.8, 116.1, 111.1, 102.1, 56.0, 46.9, 29.9, 25.8, 20.6; HRMS (ESI) calcd for C₂₃H₂₆NO [M+H]⁺: 332.2014; Found: 332.2008.

9-Benzyl-6-methoxy-3-methyl-4,9-dihydro-1H-carbazole (22): Using the general procedure **GP-**



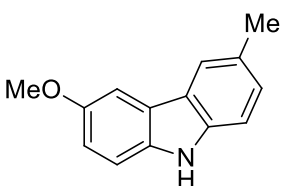
10, compound **15** (100 mg, 0.31 mmol) and **G-I** (16.9 mg, 0.03 mmol) provided compound **16** (84.8 mg, 81%) as a white solid; **¹H-NMR** (500 MHz, CDCl₃): 7.26-7.19 (4H, m), 7.09 (1H, d, *J* = 9.2 Hz), 6.99-6.96 (2H, m), 6.77 (1H, dd, *J* = 6.1, 2.4 Hz), 5.58 (1H, d, *J* = 1.2 Hz), 5.23 (2H, s), 3.86 (3H, s), 3.36-3.29 (4H, m), 1.90 (3H, s); **¹³C-NMR** (100 MHz, CDCl₃): 154.0, 138.4, 133.8, 133.1, 132.4, 128.9, 127.3, 126.2, 117.0, 110.6, 109.8, 107.1, 100.7, 56.1, 46.7, 28.5, 24.2, 23.8; HRMS (ESI) calcd for C₂₁H₂₂NO[M+H]⁺: 304.1701; Found: 304.1704.

9-Benzyl-3-methoxy-6-methyl-9H-carbazole (23): Using the general procedure **GP-11**, compound **16** (70 mg, 0.23 mmol) and DDQ (51.4 mg, 0.23 mmol) provided compound **23** (64.8



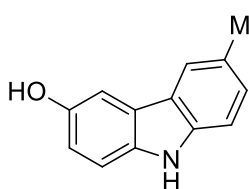
mg, 92 %) as a grey colored solid; **¹H-NMR** (400 MHz, CDCl₃): 7.87 (1H, s), 7.57 (1H, d, *J* = 2.4 Hz), 7.36 (2H, t, *J* = 2.4 Hz), 7.23-7.19 (4H, m), 7.09 (2H, dd, *J* = 6.1, 1.8 Hz), 7.02 (1H, dd, *J* = 6.7, 2.4 Hz), 5.43 (2H, s), 3.91 (3H, s), 2.52 (3H, s); **¹³C-NMR** (100 MHz, CDCl₃): 153.8, 139.7, 137.6, 136.1, 128.8, 128.2, 127.5, 127.3, 126.5, 123.3, 123.1, 120.4, 114.9, 109.7, 108.8, 103.6, 56.3, 46.8, 21.5; HRMS (ESI) calcd for C₂₁H₂₀NO[M+H]⁺: 302.1545; Found: 302.1539.

Synthesis of glycozoline (24):¹¹ To a stirred solution of **17** (50 mg, 0.17 mmol) in ethanol was added Pd/C (6 mg, 0.034 mmol) and the resulting mixture was allowed to stir overnight under pressure of hydrogen gas. After completion of the reaction, the reaction



mixture was passed through celite bed and the filtrate was concentrated in vacuum followed by column chromatography to afford glycozoline **24** (34 mg, 96%) as a brownish solid; **¹H-NMR** (500 MHz, CDCl₃): 7.83 (1H, s), 7.52 (1H, d, *J* = 2.6 Hz), 7.29 (2H, dd, *J* = 5.9, 3.4 Hz), 7.21 (1H, d, *J* = 7.6 Hz), 7.04 (1H, dd, *J* = 6.7, 1.7 Hz), 3.92 (3H, s), 2.52 (3H, s); **¹³C-NMR** (100 MHz, CDCl₃): 154.0, 138.8, 135.0, 128.5, 127.3, 123.9, 123.8, 120.3, 115.0, 111.4, 110.6, 103.4, 56.3, 21.4; HRMS (ESI) calcd for C₁₄H₁₄NO [M+H]⁺: 212.1075; Found: 212.1074.

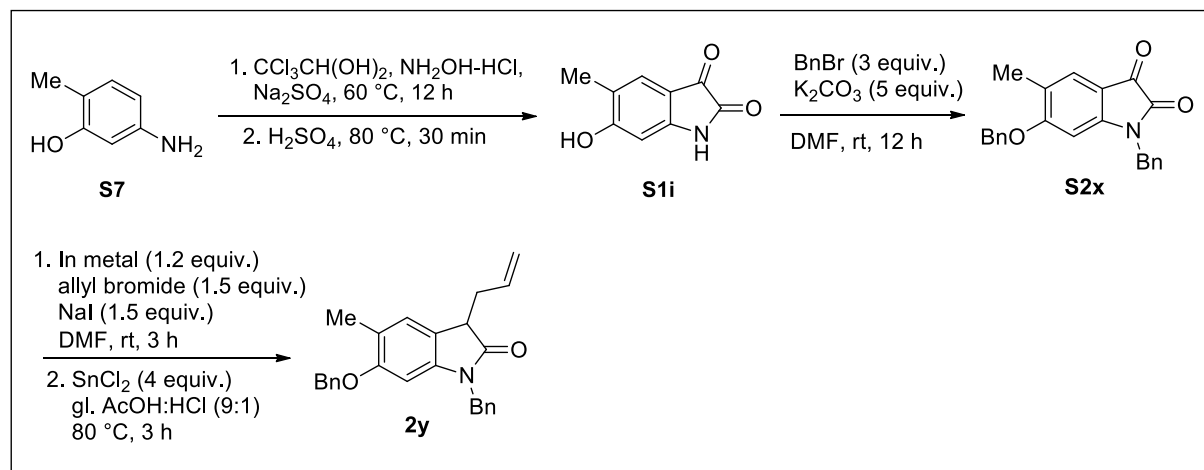
Synthesis of glycozolinol (25):¹² To a solution of **24** (20 mg, 0.09 mmol) in dry CH₂Cl₂ was added BBr₃ (19 μL, 0.19 mmol) and the resulting mixture was stirred overnight at room



temperature. After completion of the reaction as monitored by TLC, NaHCO₃ was added and the organic fraction was separated and concentrated in vacuo followed by column chromatography on silica gel with ethylacetate-hexane (5/95 to 10/90) to afford glycozolinol **25** (16

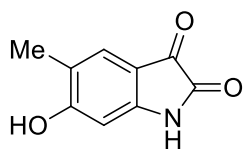
mg, 90%) as a brown solid; **¹H-NMR** (400 MHz, CDCl₃): 10.7 (1H, s), 8.88 (1H, s), 7.75 (1H, s), 7.37 (1H, d, *J* = 2.2 Hz), 7.26 (2H, dd, *J* = 8.1, 6.6 Hz), 7.12 (1H, t, *J* = 8.1 Hz), 6.86 (1H, dd, *J* = 6.6, 2.2 Hz), 2.42 (3H, s); **¹³C-NMR** (100 MHz, CDCl₃): 150.2, 138.7, 134.1, 126.6, 126.3, 122.9, 122.4, 119.8, 114.8, 111.2, 110.5, 104.7, 21.0; HRMS (ESI) calcd for C₁₃H₁₂NO [M+H]⁺: 198.0919; Found: 198.0908.

16.0.3 Synthesis of oxindole 2y:



Scheme S23. Synthesis of oxindole **2y**.

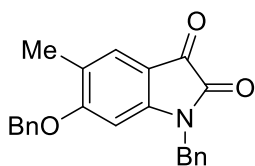
Preparation of isatin S1i¹: Using Sandmayers method,⁹ to a solution of chloral hydrate (5g, 30.3 mmol) in water (60 mL), sodium sulphate (25g, 142 mmol) was added and the resulting solution was stirred at room temperature for 5 min. Then 5-amino-2-methylphenol **S7** (3.5g,



30.3mmol) was added portion-wise to the solution followed by hydroxylamine-hydrochloride (8.0 g in 10 mL water). Subsequently, concentrated HCl 5 mL 1(N) was added and the reaction mixture was heated at 60 °C overnight. The resulting precipitate was filtered off and

dried under vacuo to give a brown coloured intermediate. The crude residue was then dissolved in 20 mL conc. H₂SO₄ and heated at 80 °C with stirring to produce a dark solution. After cooling to room temp, the dark solution was poured in a beaker containing ice cold water. The resulting mixture was kept for half an hour to provide red precipitate, which was filtered to obtain the crude product. The crude residue was then purified by column chromatography on silica gel with ethyl acetate-hexane (40/60 to 60/40) to provide compound **S1i** (2.0 g, 65%) as a red solid; ¹H-NMR (400 MHz, DMSO-d₆): 10.68 (1H , s_{br}), 7.27 (1H , s), 6.36 (1H , s), 2.03 (3H , s); ¹³C-NMR (125 MHz, DMSO-d₆): 181.7, 160.4, 152.1, 127.6, 119.1, 108.8, 98.5, 15.2; HRMS (ESI) calcd for C₉H₈NO₃ [M+H]⁺: 178.0504; Found: 178.0514.

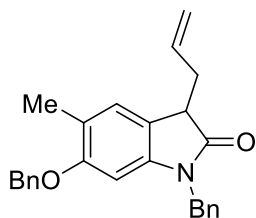
1-Benzyl-6-(benzyloxy)-5-methylindoline-2, 3-dione (S2x):¹ Using the reported procedure¹, 6-hydroxy-5-methylindoline-2,3-dione **S1i** (1g, 5.64 mmol) and K₂CO₃ (2.3 g, 16.92 mmol) and



benzyl bromide (1.01 mL, 8.46 mmol) provided compound **S2x** (1.8 g, 90 %) as a red solid; ¹H-NMR (500 MHz, CDCl₃): 7.31-7.16 (11H , m), 6.12 (1H , s), 4.94 (2H , s), 4.75 (2H , s), 2.07 (3H, s) ; ¹³C-NMR (125 MHz, CDCl₃): 180.7, 165.4, 159.7, 152.7, 135.6, 135.1, 129.2, 129.0,

128.6, 128.2, 127.8, 127.5, 127.1, 122.6, 110.4, 95.4, 70.7, 44.1, 16.0; HRMS (ESI) calcd for C₂₃H₂₀NO₃ [M+H]⁺: 358.1443; Found: 358.1445.

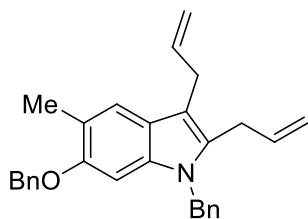
3-Allyl-1-benzyl-6-(benzyloxy)-5-methylindolin-2-one (2y): Using the general procedure **GP-1**,



compound **S2x** (1.5g, 4.0 mmol), indium metal (576 mg, 5.04 mmol), allyl bromide (0.5 ml, 6.3 mmol), NaI (1.3 g, 8.4 mmol) and SnCl₂ (3.2 g, 16.8 mmol) provided compound **2y** (1.1 g, 73%) as a colorless liquid; ¹H-NMR (500 MHz, CDCl₃): 7.34-7.21 (10H, m), 7.05 (1H, s), 6.27 (1H, s), 5.77-5.70 (1H, m), 5.08 (1H, dd, *J* = 19.0, 17.0 Hz), 4.96-4.87 (4H, m), 4.75 (1H, d, *J* = 16.0 Hz), 3.53-3.49 (1H, m), 2.88-2.80 (1H, m), 2.63-2.56 (1H, m), 2.21 (3H, s); ¹³C-NMR (400 MHz, CDCl₃): 174.8, 158.4, 137.3, 136.9, 136.2, 134.4, 129.5, 129.0, 128.9, 128.8, 128.7, 128.1, 128.0, 127.7, 127.4, 127.2, 126.4, 120.4, 119.9, 118.1, 95.2, 70.5, 45.1, 43.6, 35.3, 16.1 HRMS (ESI) calcd for C₂₆H₂₆NO₂ [M+H]⁺: 384.1964; Found: 384.1957.

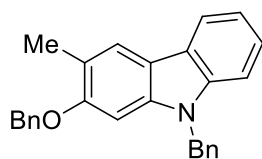
16.0.4 Synthesis of girinimbine, murrayacine and euchrestifoline:

2,3-Diallyl-1-benzyl-6-(benzyloxy)-5-methyl-1H-indole (26): Using the general procedure **GP-5**,



compound **2y** (1g, 2.61 mmol) and allylmagnesium bromide (7.8 mL, 7.8 mmol) provided compound **26** (820 mg, 76%) as a colorless liquid; ¹H-NMR (400 MHz, CDCl₃): 7.41 (2H, d, *J* = 7.3 Hz), 7.35-7.27 (6H, m), 7.23 (1H, d, *J* = 2.0 Hz), 6.93 (2H, d, *J* = 6.8 Hz), 6.68 (1H, s), 6.11-5.78 (2H, m), 5.22 (2H, s), 5.07 (2H, dd, *J* = 15.6, 1.5 Hz), 5.02-5.00 (1H, m), 4.99 (2H, s), 4.94 (1H, dd, *J* = 15.6, 1.5 Hz), 3.46 (2H, d, *J* = 5.8 Hz), 3.38 (2H, d, *J* = 5.9 Hz), 2.30 (3H, s); ¹³C-NMR (100 MHz, CDCl₃): 153.7, 138.5, 138.0, 135.9, 135.7, 132.5, 130.3, 128.8, 128.5, 127.7, 127.3, 127.2, 126.1, 122.0, 120.1, 119.9, 115.9, 114.5, 109.8, 93.4, 70.6, 46.8, 29.1, 29.0, 17.1; HRMS (ESI) calcd for C₂₉H₃₀NO [M+H]⁺: 408.232; Found: 408.2322.

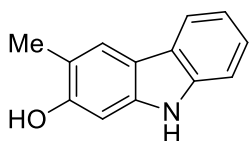
9-Benzyl-2-(benzyloxy)-3-methyl-9H-carbazole (27)¹: Using the general procedures **GP-10** and **GP-11**, compound **26** (400 mg, 1.05 mmol) was first treated with **G-I** (91 mg, 0.11 mmol) to



produce the corresponding dihydrocarbazole derivative, which was then treated with DDQ (240 mg, 1.05 mmol) to obtain compound **27** (380 mg, 95%) as a brown solid; ¹H-NMR (500 MHz, CDCl₃): 7.99 (1H, d, *J* = 7.7 Hz), 7.87 (1H, s), 7.45 (2H, d, *J* = 7.5 Hz), 7.39-7.18 (9H, m), 7.11 (2H, d,

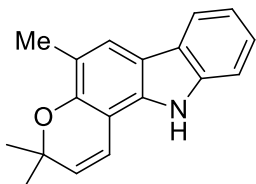
$J = 6.6$ Hz), 6.82 (1H, s), 5.44 (2H, s), 5.09 (2H, s), 2.44 (3H, s); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): 156.7, 140.7, 140.4, 137.5, 137.4, 128.9, 128.6, 127.9, 127.6, 127.3, 126.6, 124.3, 123.3, 121.9, 119.6, 119.6, 119.2, 108.7, 92.7, 70.4, 46.8, 16.9; HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{24}\text{NO}$ $[\text{M}+\text{H}]^+$: 378.1858; Found: 378.1856.

Synthesis of 1-Methyl-9H-carbazol-2-ol (28):¹ To a solution of compound **27** (350 mg, 0.93 mmol) in methanol (6 mL), Pd on charcoal (20 mol%, 20.4 mg, 0.19 mmol) was added and the resulting mixture was stirred at room temperature in the presence of hydrogen gas for 36 h. After



completion of the reaction, the reaction mixture was passed through celite bed and washed with ethyl acetate. The reaction mixture was then concentrated and purified by column chromatography on silica gel with ethyl acetate-hexane (30/70 to 40/60) to provide compound **28** (170 mg, 92%) as a brown solid; $^1\text{H-NMR}$ (500 MHz, CDCl_3): 7.94 (1H, d, $J = 7.5$ Hz), 7.87 (1H, br s), 7.78 (1H, s), 7.36 (1H, d, $J = 8.4$ Hz), 7.32 (1H, t, $J = 6.7$ Hz), 7.18 (1H, t, $J = 6.7$ Hz), 6.86 (1H, s), 4.90 (1H, br s), 2.41 (3H, s); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): 153.3, 139.8, 139.5, 124.6, 123.7, 121.9, 119.6, 119.5, 117.5, 116.5, 110.4, 96.7, 16.3; HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{12}\text{NO}$ $[\text{M}+\text{H}]^+$: 198.0919; Found: 198.0918.

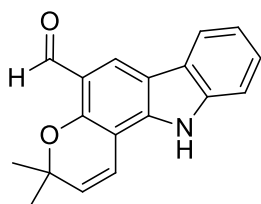
Synthesis of girinimbine (30):¹³ To a solution of compound **28** (100 mg, 0.51 mmol) in dry toluene (5 mL) was added 3-methyl 2-butenal **29** (74 μL , 0.77 mmol) at -78°C . To this stirring solution, titanium isopropoxide (0.5 mL, 1.5 mmol) was added dropwise and the temperature was



allowed to reach room temperature. Stirring was continued for 24 h. After completion of the reaction (TLC monitoring), the reaction mixture was treated with 1.5 (N) HCl and extracted with ethyl acetate (3 X 5 mL). The organic fractions were then concentrated and purified by column chromatography on silica gel with ethyl acetate-hexane (30/70 to 40/60) to provide compound **30** (98 mg, 74%) as a white solid; $^1\text{H-NMR}$ (400 MHz, CDCl_3): 7.91 (1H, d, $J = 7.8$ Hz), 7.88 (1H, br s), 7.67 (1H, s), 7.37 (1H, d, $J = 7.8$ Hz), 7.31 (1H, t, $J = 7.8$ Hz), 7.18 (1H, t, $J = 7.3$ Hz), 6.63 (1H, d, $J = 9.8$ Hz), 5.70 (1H, d, $J = 9.8$ Hz), 2.34 (3H, s), 1.49 (6H, s); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): 150.0, 139.7, 135.0, 129.6, 124.4, 124.1, 121.3, 119.7, 119.5, 118.8, 117.4, 117.0,

110.5, 104.6, 76.0, 27.8, 16.2; HRMS (ESI) calcd for $C_{18}H_{18}NO$ $[M+H]^+$: 264.1388; Found: 264.1381.

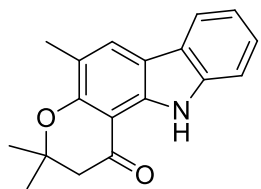
Synthesis of murrayacine (31):¹³ To a stirred solution of girinimbine **30** (40 mg, 0.15 mmol) in methanol (5 mL) was added DDQ (68 mg, 0.30 mmol) and the resulting mixture was allowed to



stir at room temperature for 30 min. After completion of the reaction (TLC monitoring), the reaction mixture was treated with aq NaOH (2 N, 5 mL) and extracted with ethyl acetate (3 x 5 mL). The organic fractions were then concentrated in vacuo and purified by column chromatography on silica gel with ethyl acetate-hexane (30/70 to 40/60) to provide

compound **25** (36 mg, 87%) as a white solid; 1H NMR (400 MHz, $CDCl_3$): 10.5 (s, 1H), 8.42 (s, 1H), 8.20 (br s, 1H), 7.98 (d, 1H, $J = 7.3$ Hz), 7.39-7.38 (m, 2H), 7.18-7.12 (m, 1H), 6.63 (d, 1H, $J = 10.2$ Hz), 5.80 (d, 1H, $J = 9.8$ Hz), 1.57 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): 189.4, 154.9, 140.4, 140.3, 130.3, 128.3, 126.1, 124.3, 121.1, 120.4, 120.0, 118.9, 116.3, 110.9, 104.3, 77.4, 27.8; HRMS (ESI) calcd for $C_{18}H_{16}NO_2$ $[M+H]^+$: 278.1181; Found: 278.1189.

Synthesis of euchrestifoline (32):¹⁴ A sealed tube containing girinimbine **31** (40 mg, 0.15 mmol) and $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) was evacuated and filled with dioxygen gas using an oxygen balloon. A mixture of DMSO: H_2O (4:1 mL) and TFA (1 mL) was added to it. The



reaction was then heated at 120 °C for 12 h. After completion of the reaction (TLC monitoring), it was treated with water (5 mL) and extracted with ethyl acetate (3 x mL). The organic fractions were then concentrated in vacuo and purified by column chromatography on silica gel with ethyl

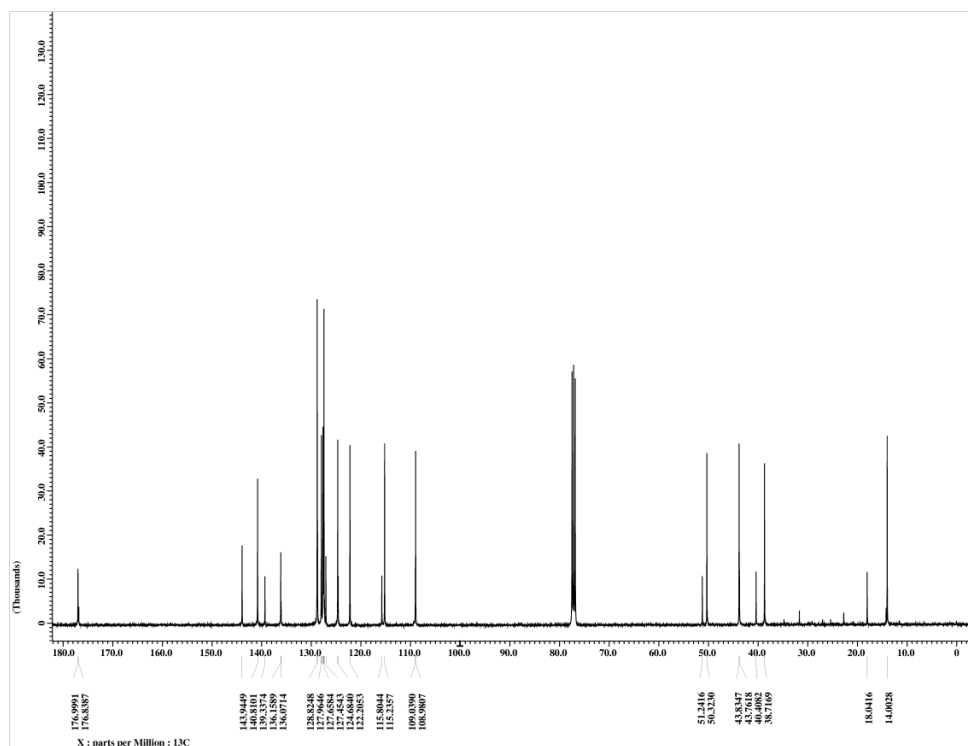
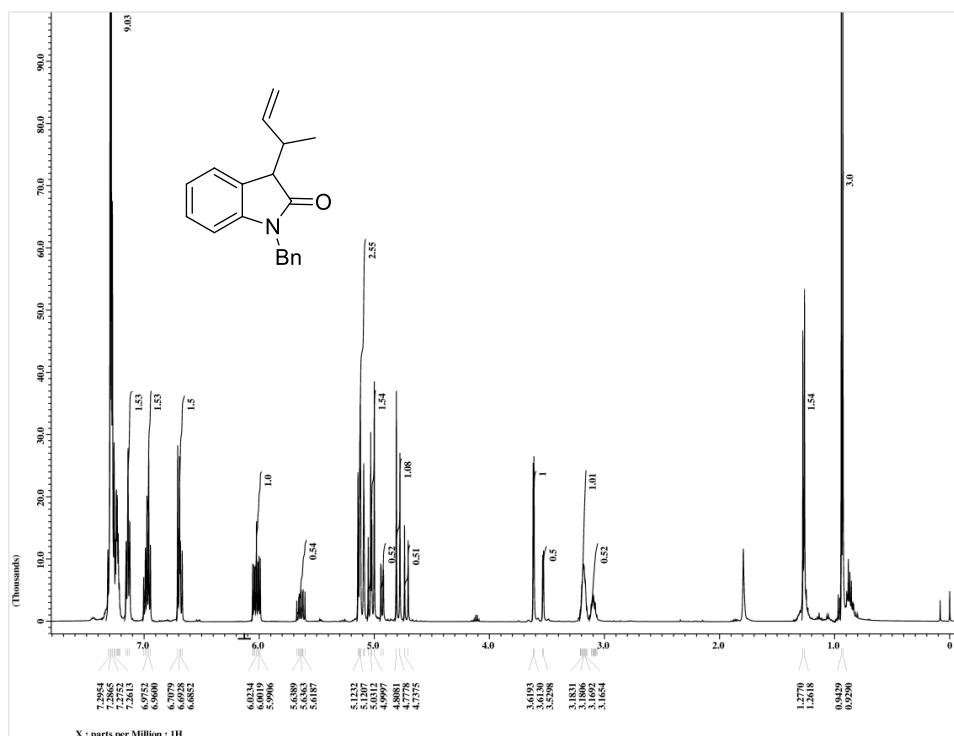
acetate-hexane (30/70 to 40/60) to provide compound **26** (28 mg, 67%) as a white solid; 1H -NMR (400 MHz, $CDCl_3$): 10.1 (1H, s), 8.01 (1H, s), 7.93 (1H, d, $J = 7.4$ Hz), 7.47 (1H, d, $J = 7.8$ Hz), 7.38-7.34 (1H, m), 2.82 (2H, s), 2.34 (3H, s), 1.54 (6H, s); ^{13}C -NMR (100 MHz, $CDCl_3$): 194.5, 157.9, 139.7, 137.2, 129.4, 124.8, 122.5, 120.2, 119.4, 117.9, 116.5, 111.3, 104.9, 79.7, 48.8, 27.0, 16.2; HRMS (ESI) calcd for $C_{18}H_{18}NO_2$ $[M+H]^+$: 280.1338; Found: 280.1336.

17.0 References.

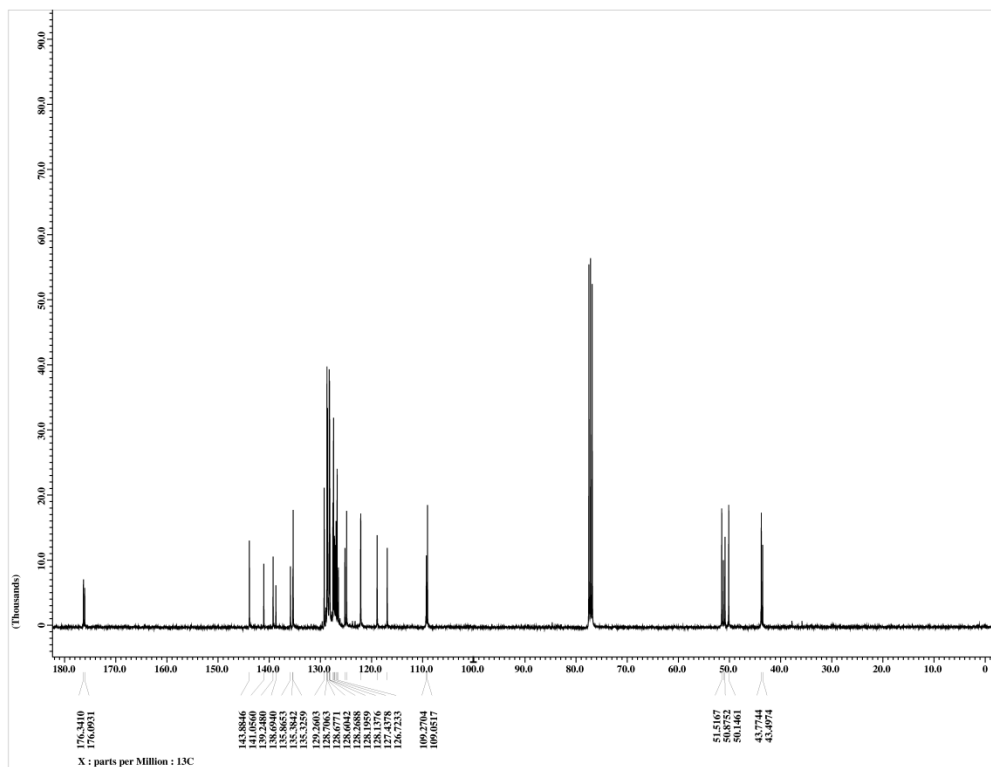
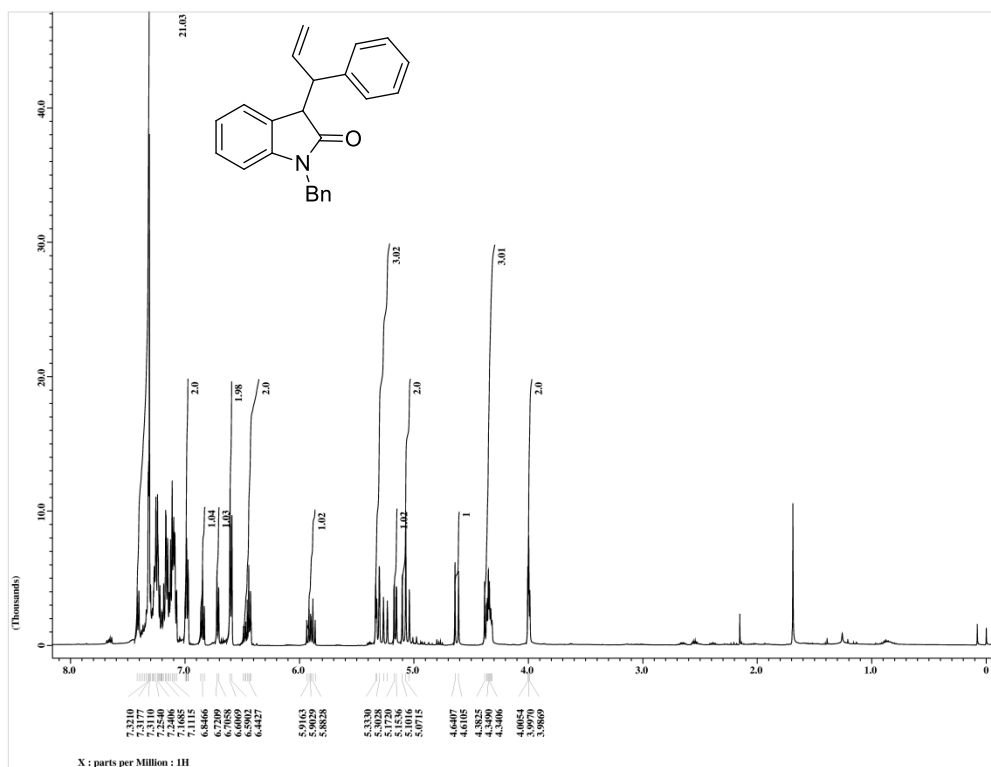
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18.0 NMR spectra of all compounds

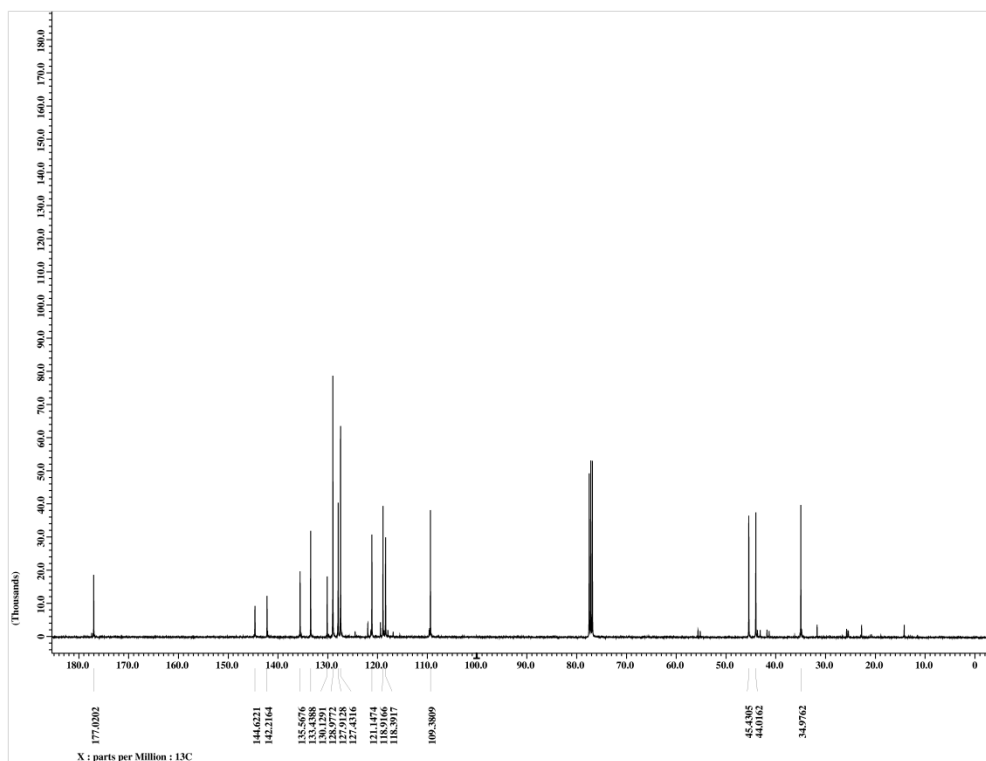
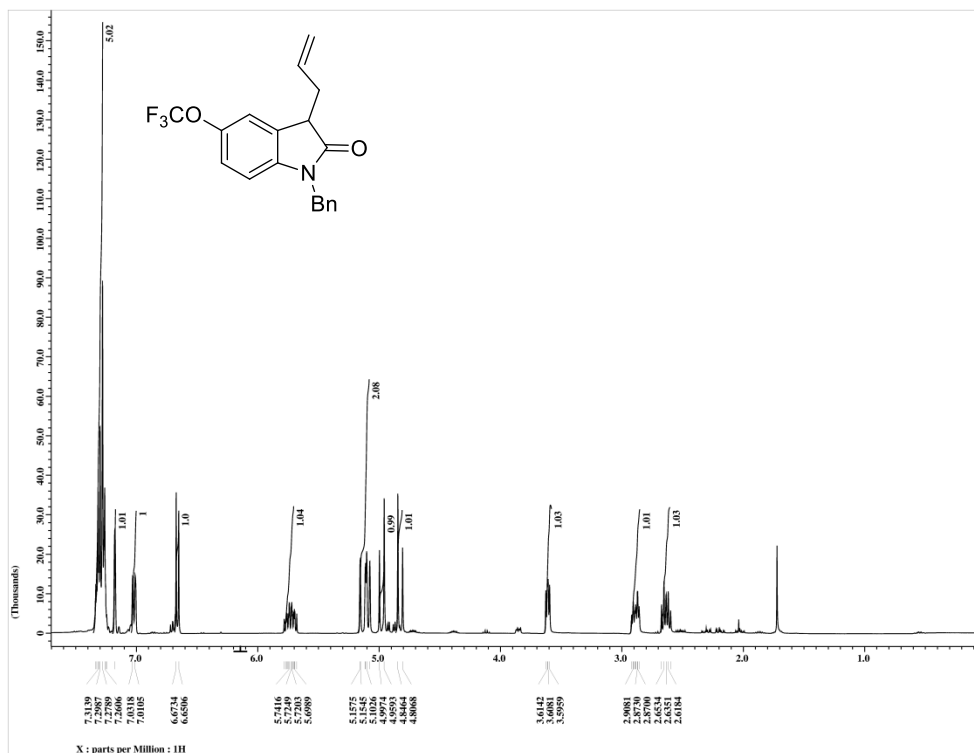
^1H and ^{13}C NMR of 2l:



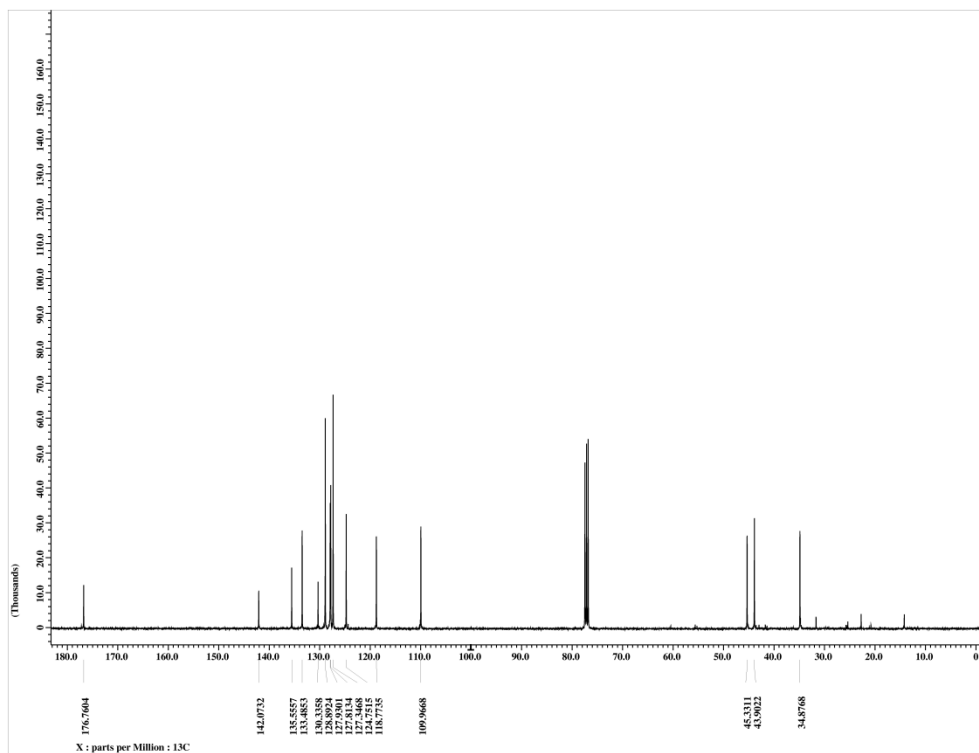
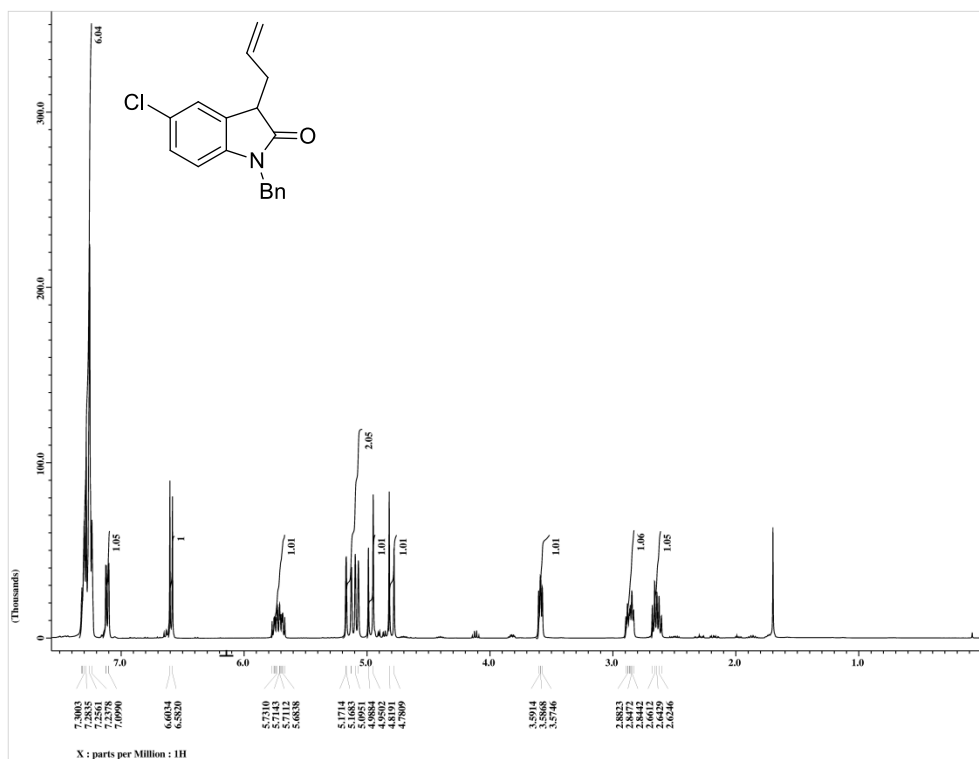
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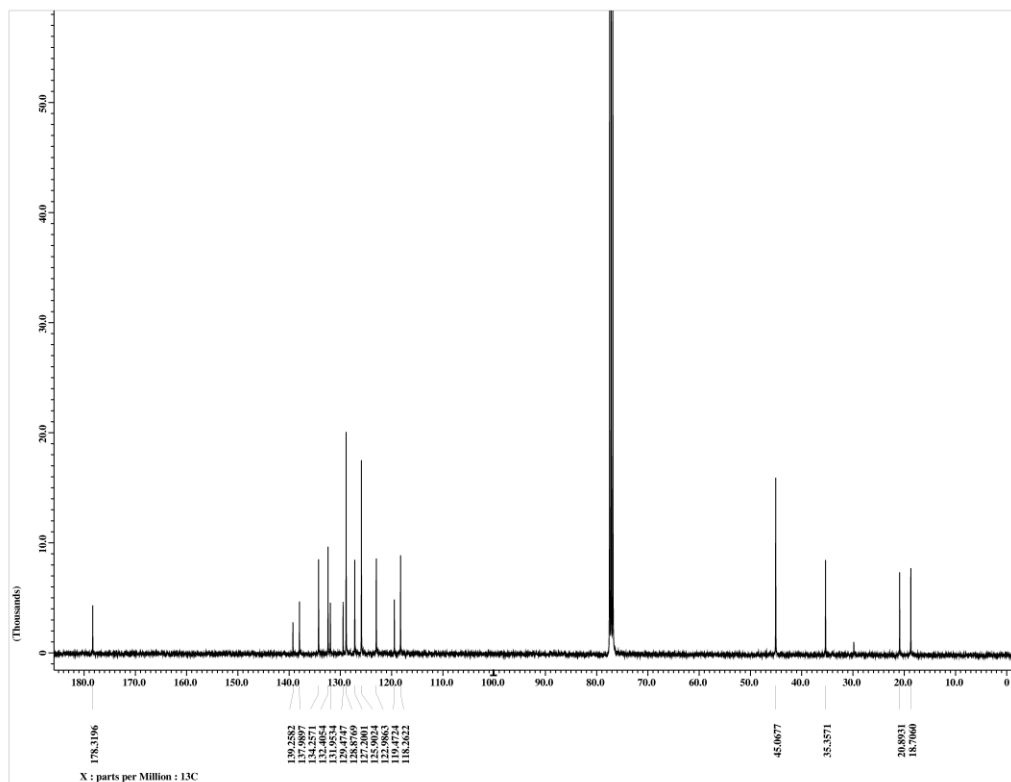
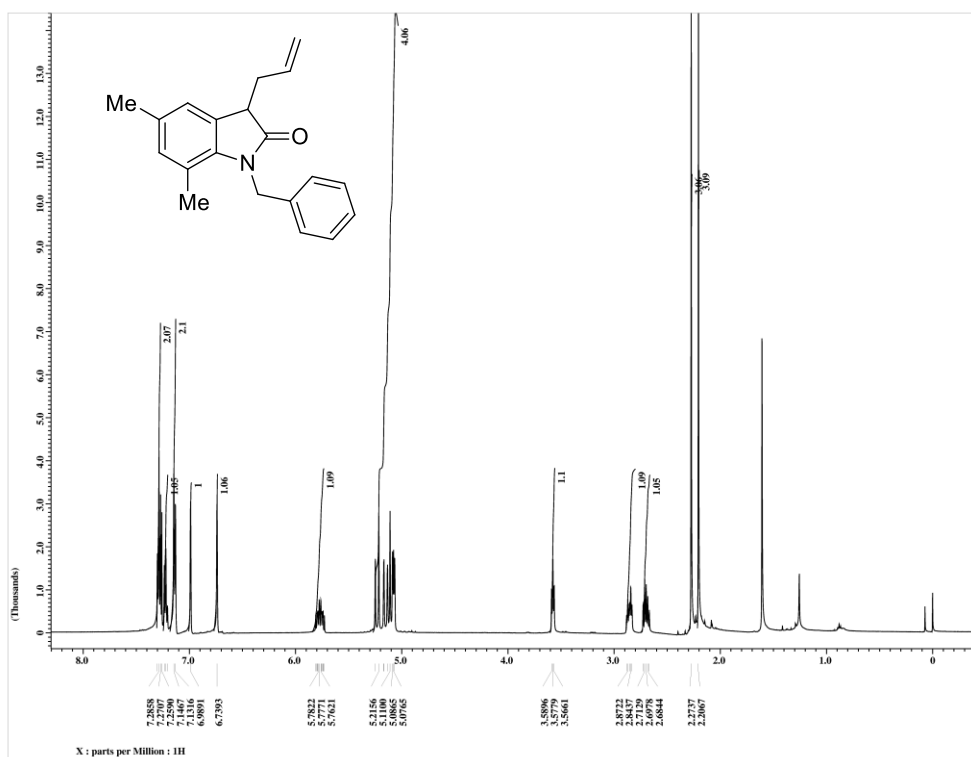
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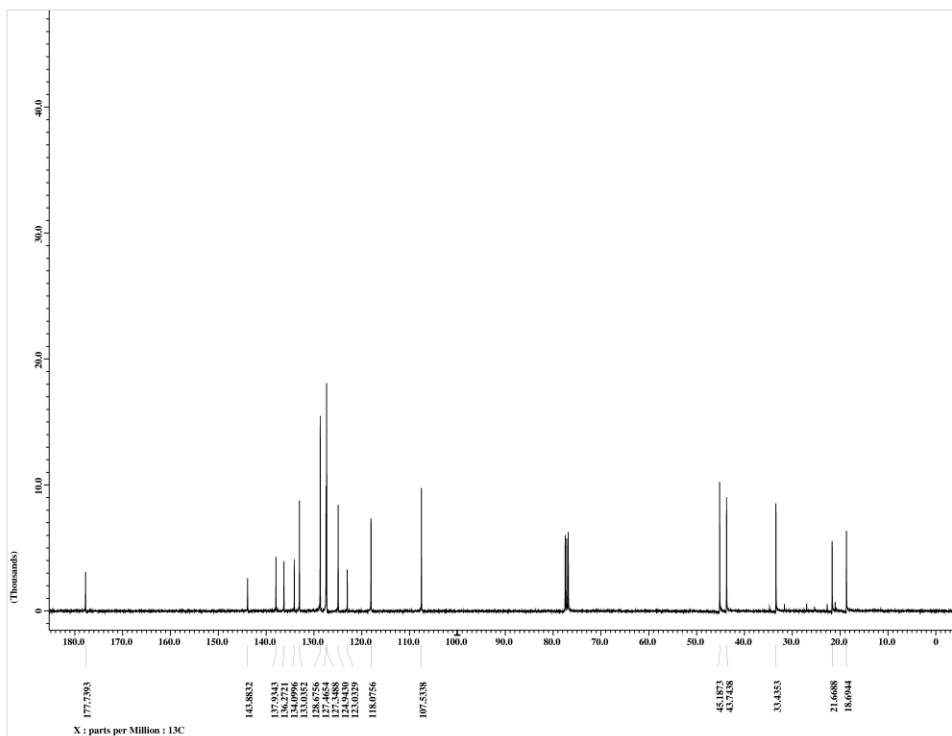
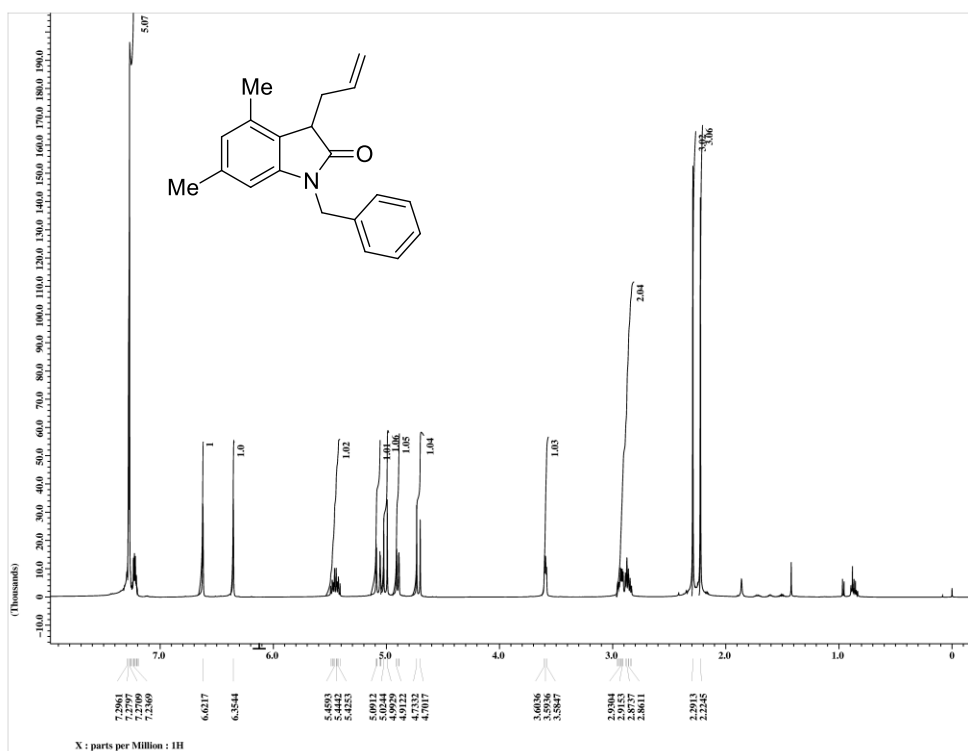
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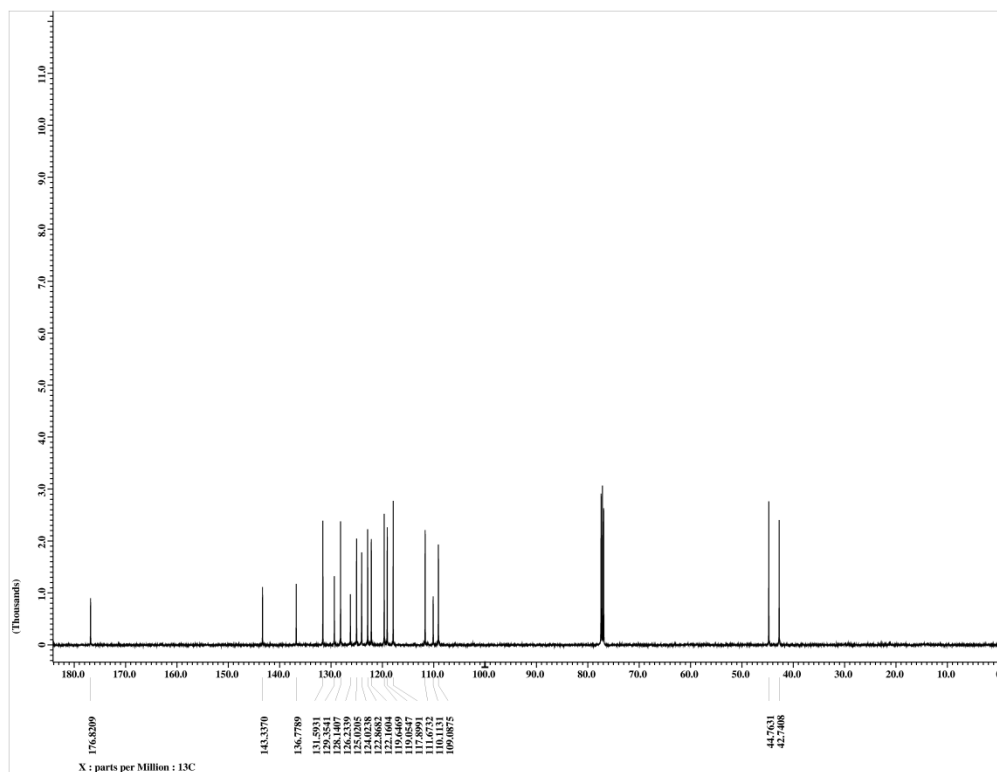
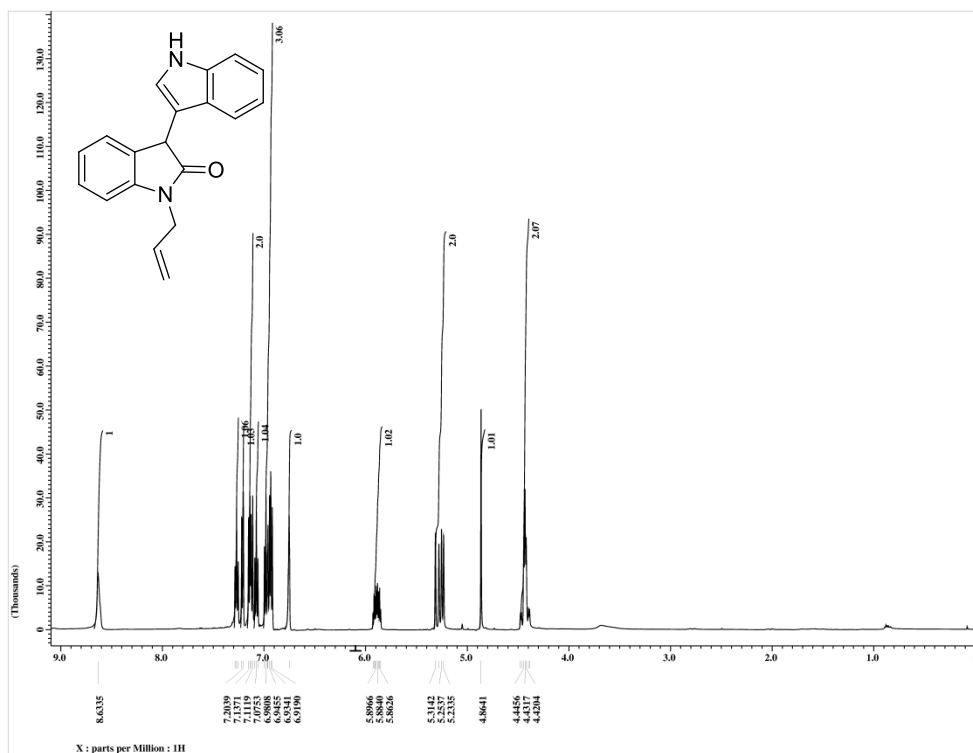
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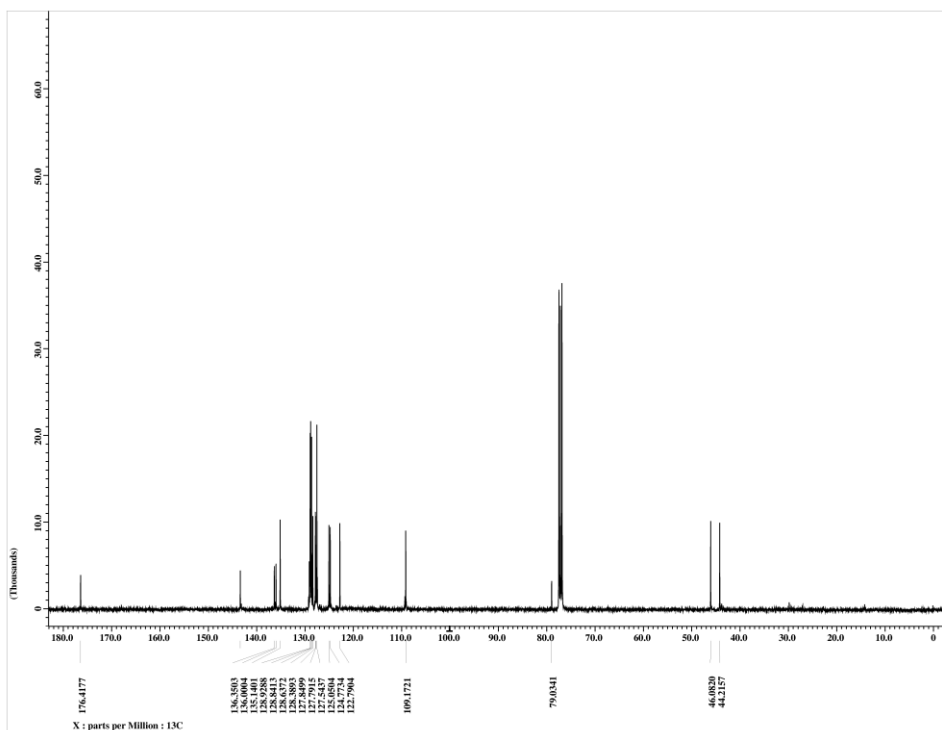
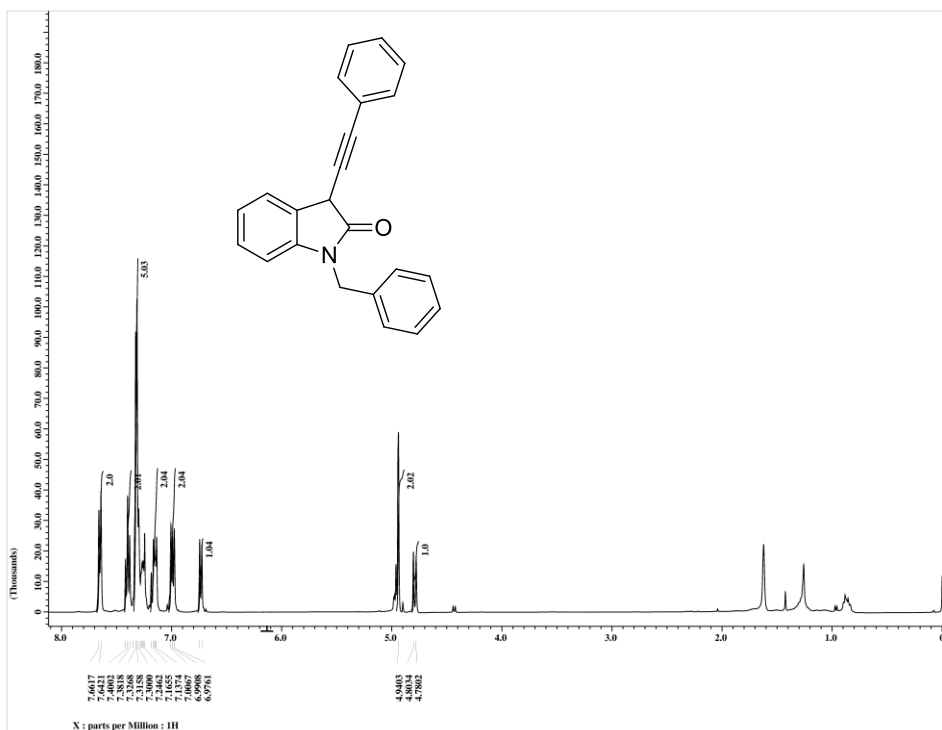
^1H and ^{13}C NMR of 2q:



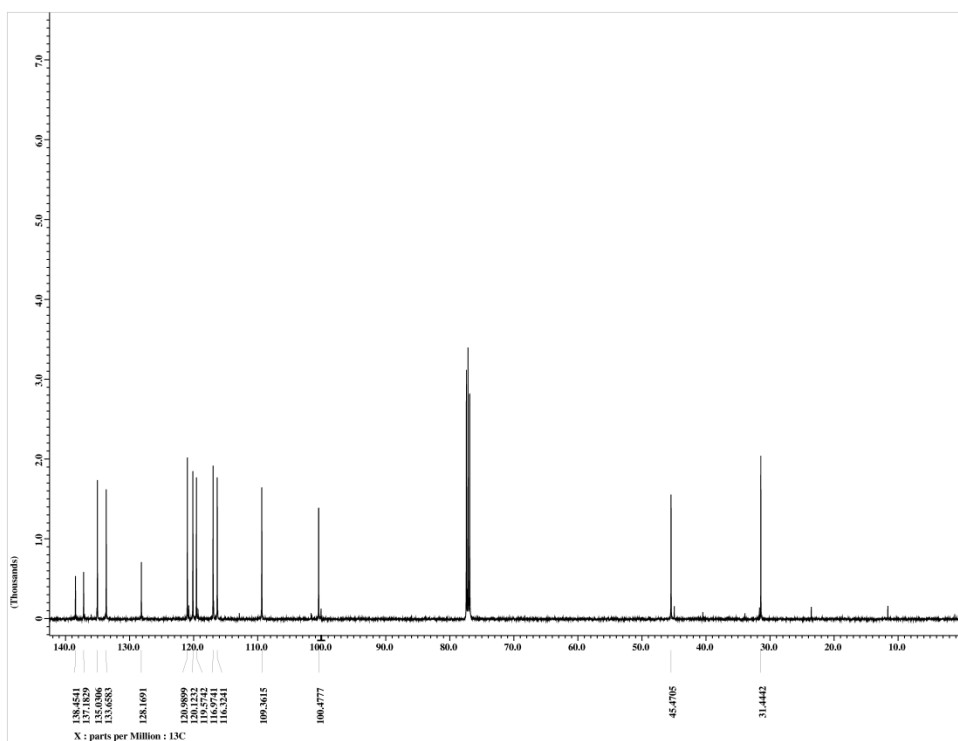
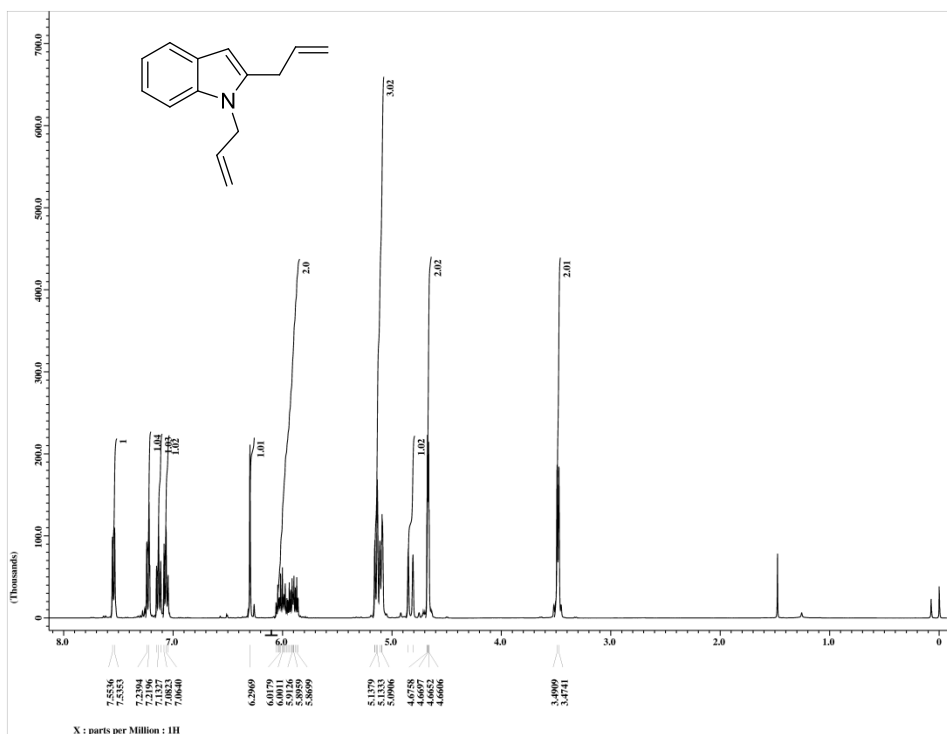
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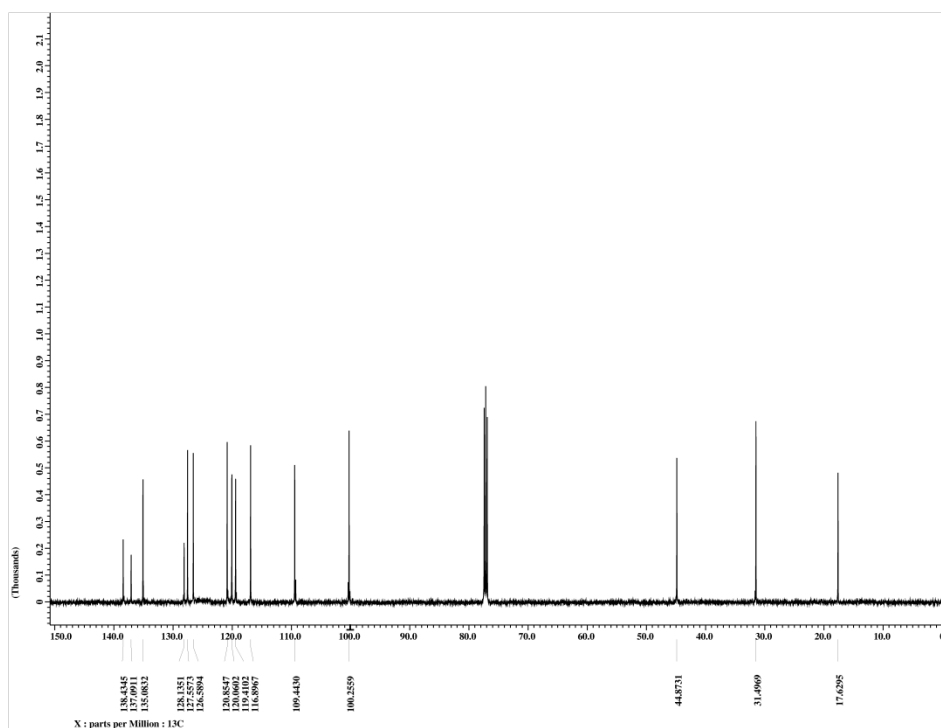
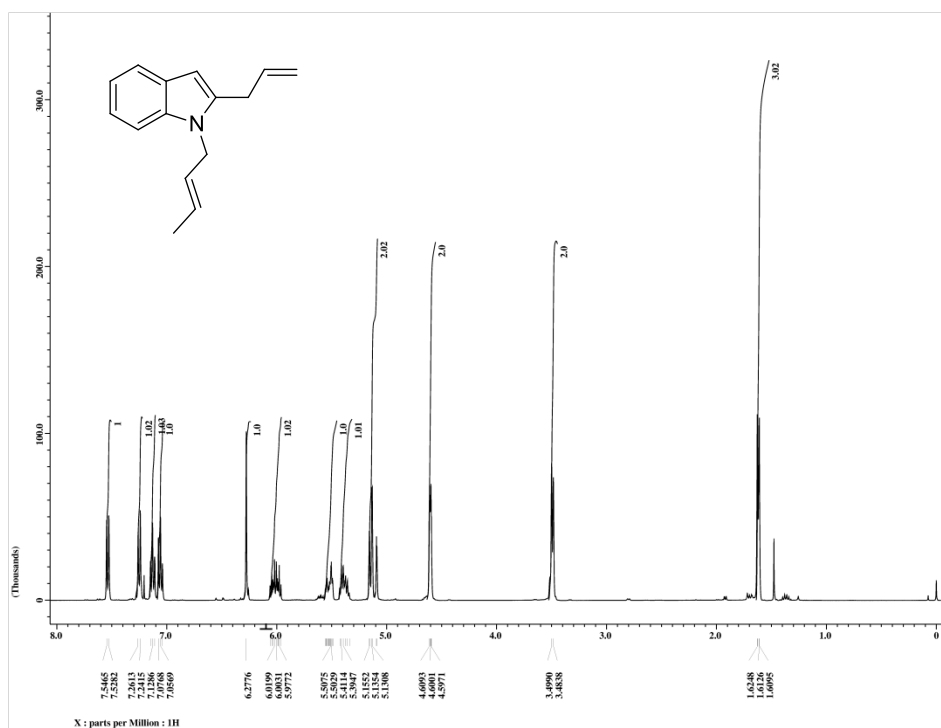
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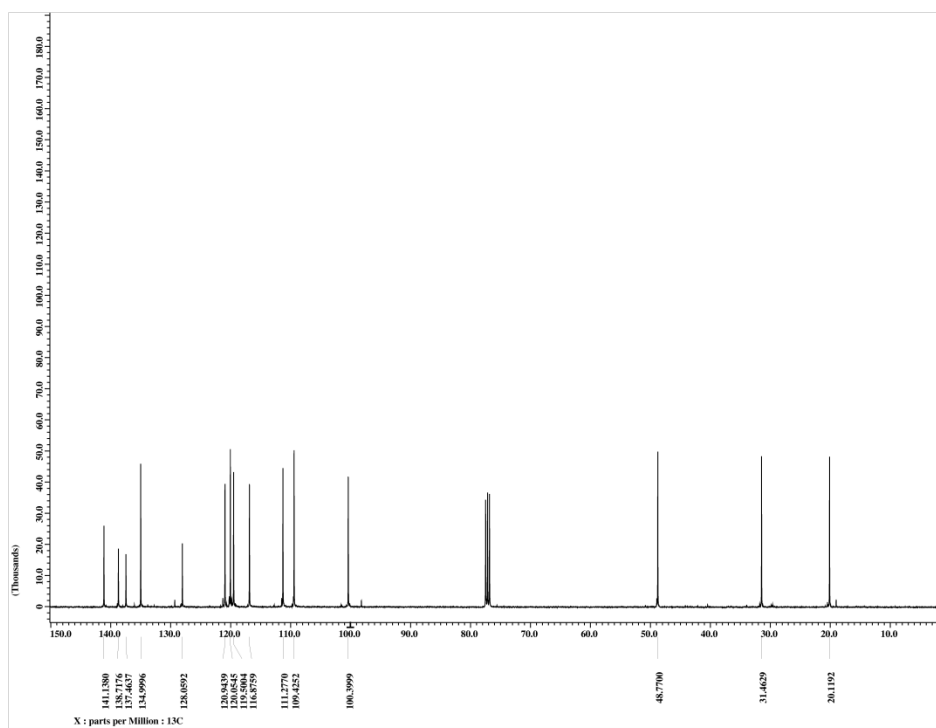
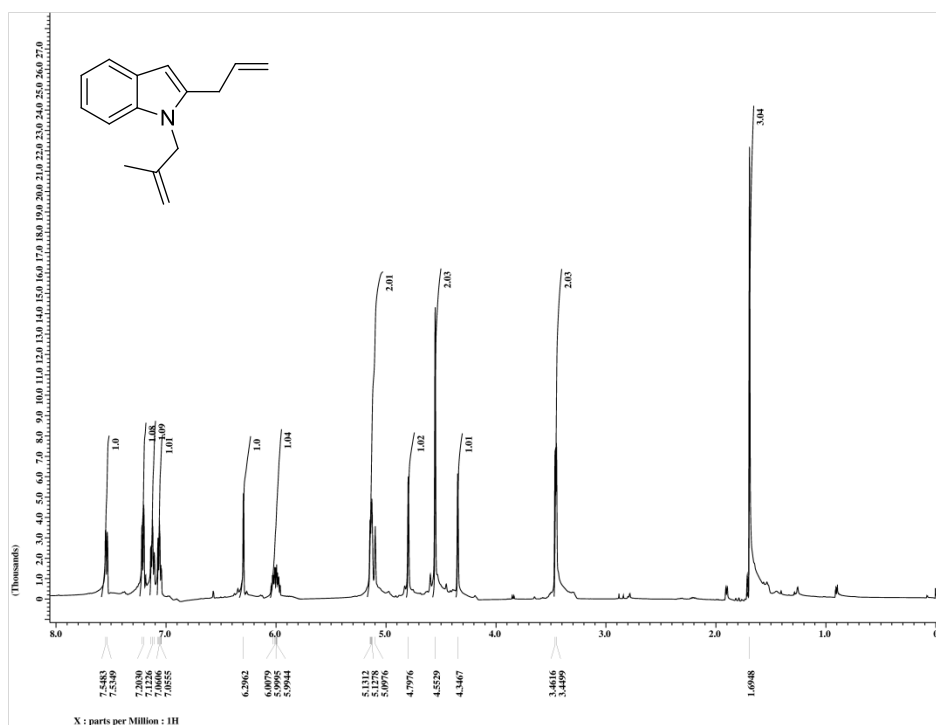
^1H and ^{13}C NMR of 3a:



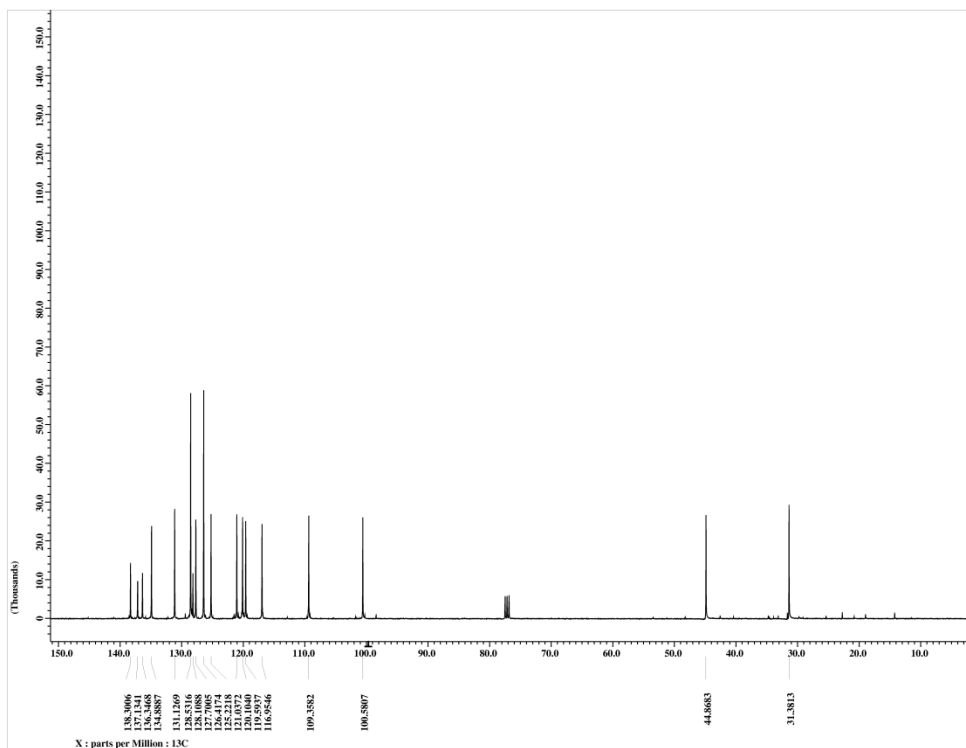
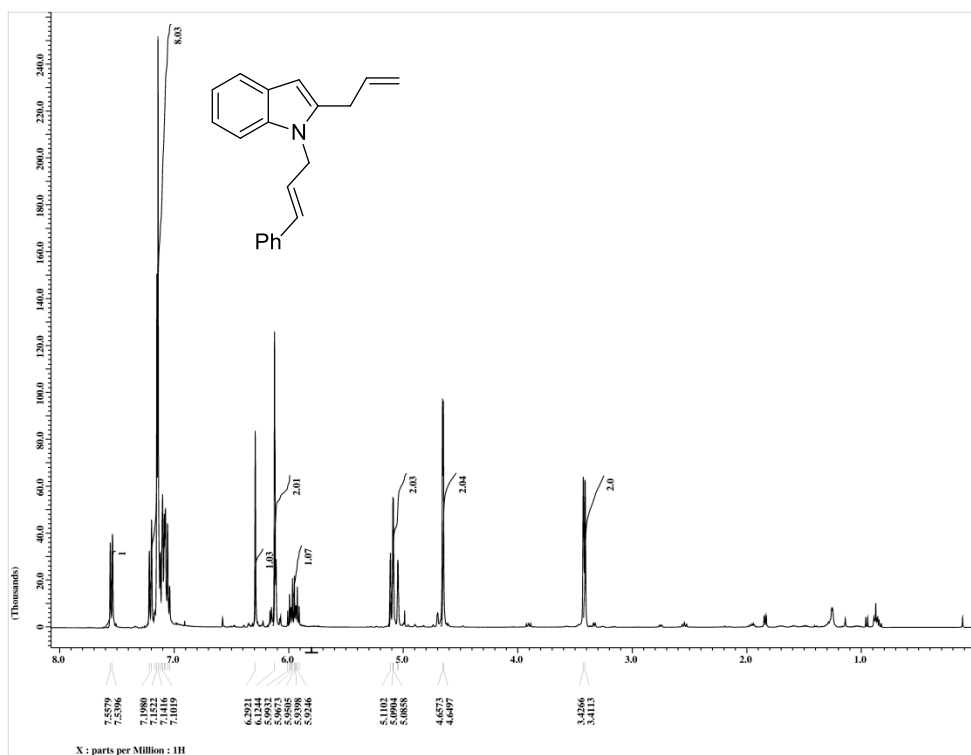
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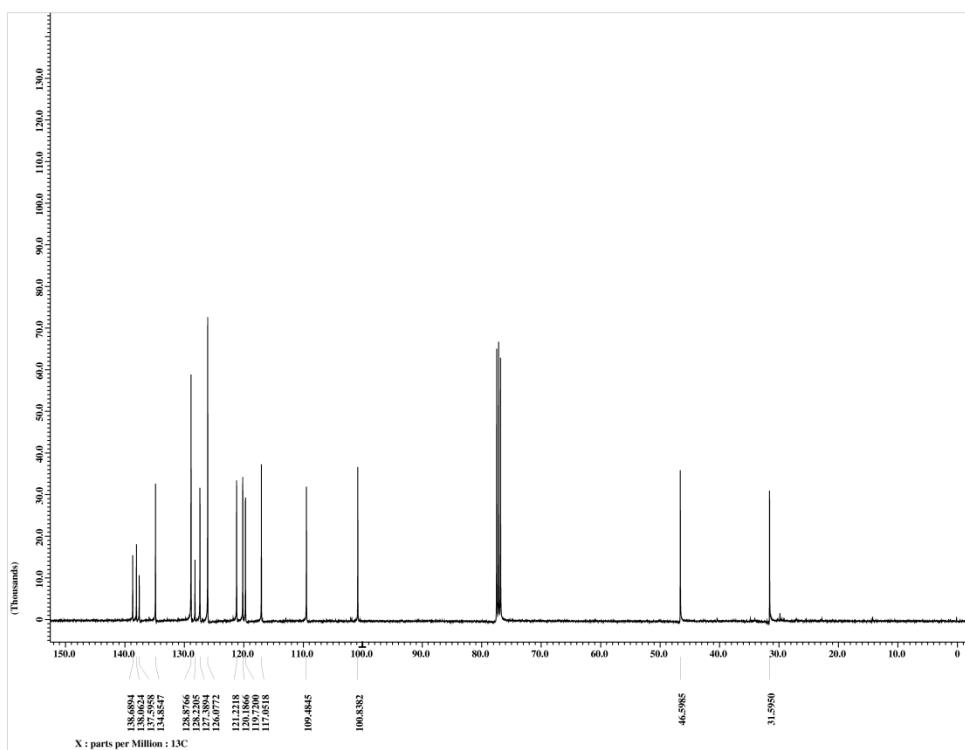
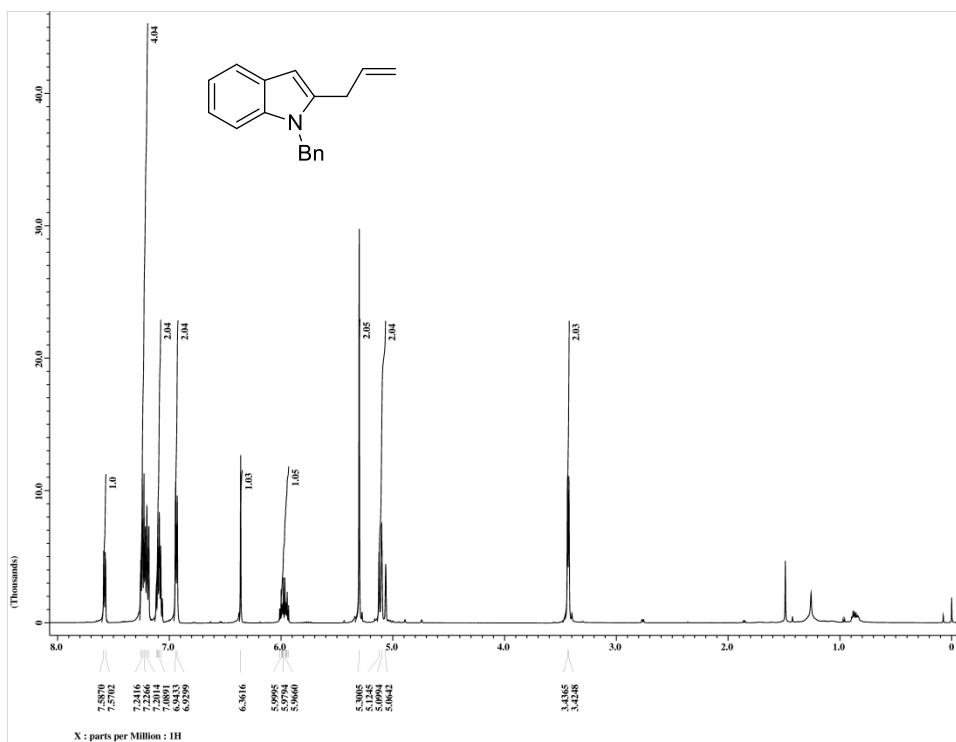
^1H and ^{13}C NMR of 3c:



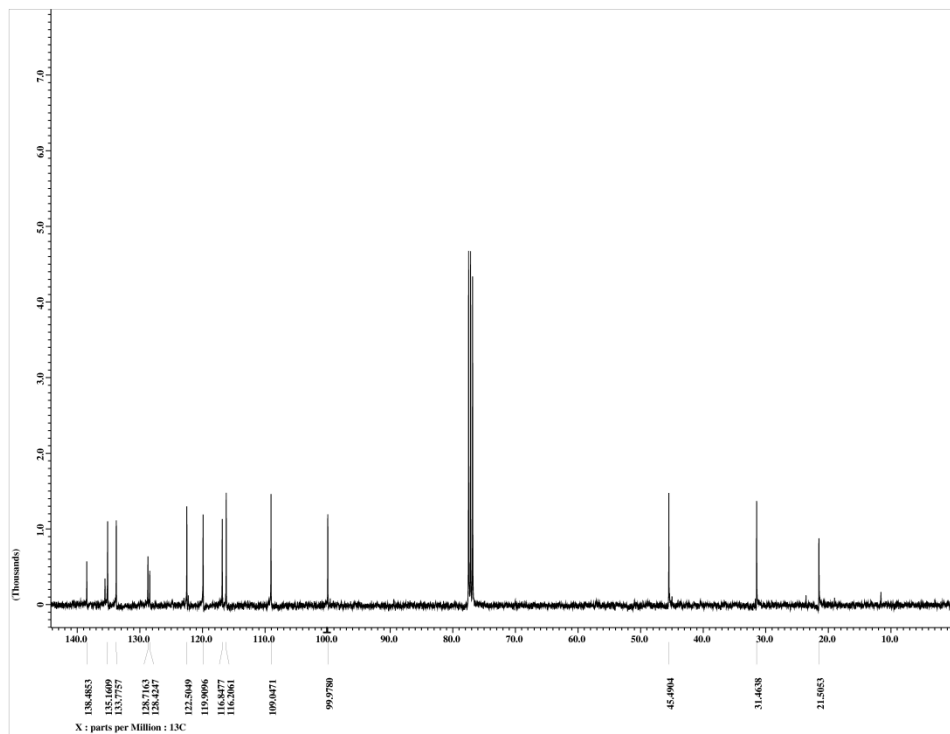
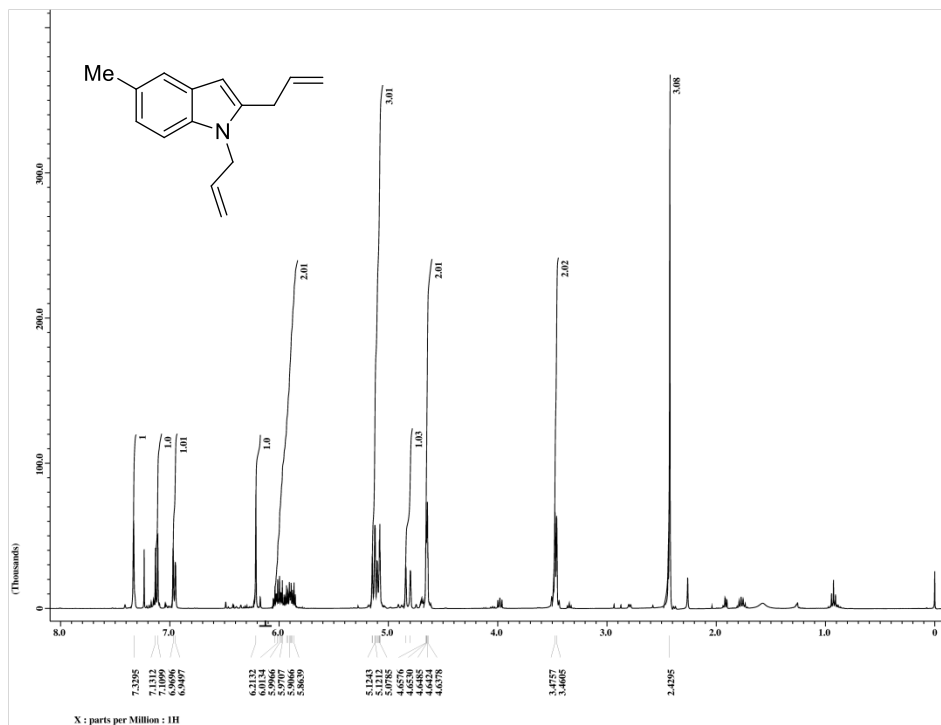
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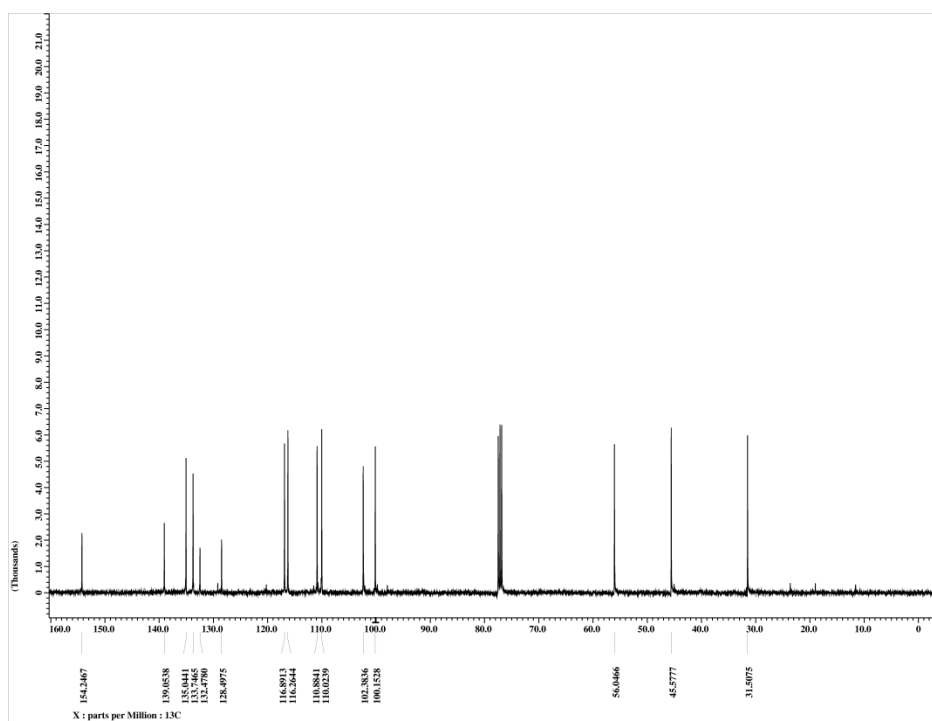
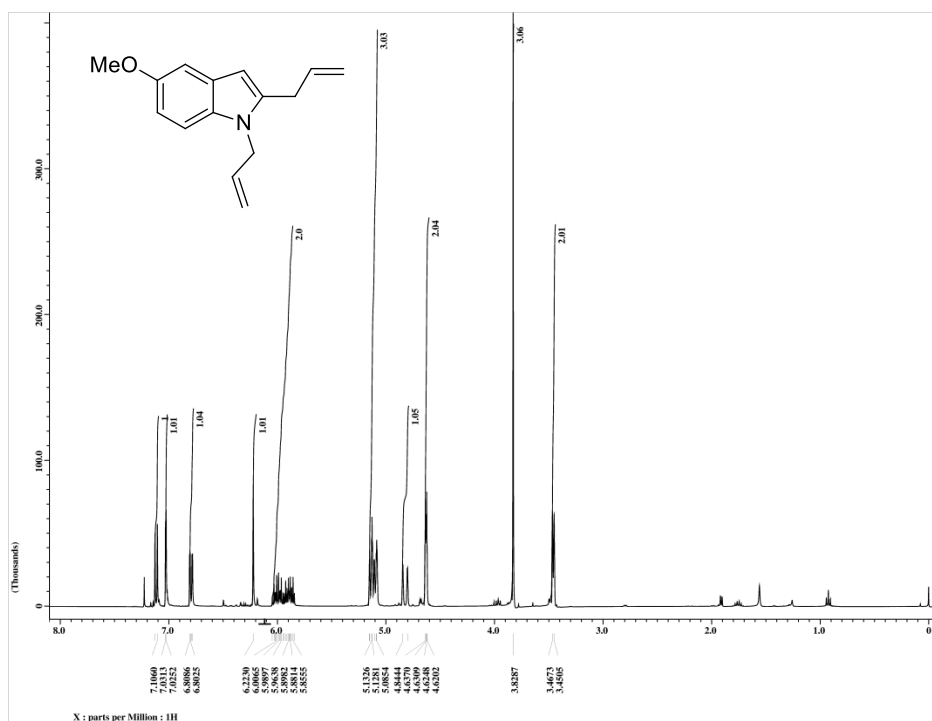
^1H and ^{13}C NMR of 3f:



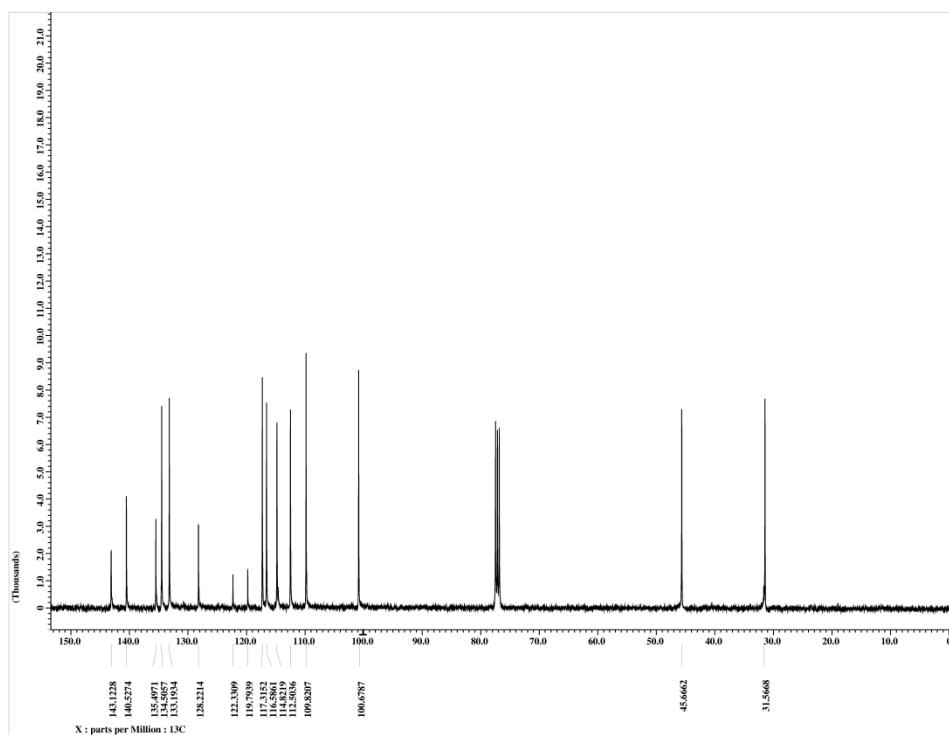
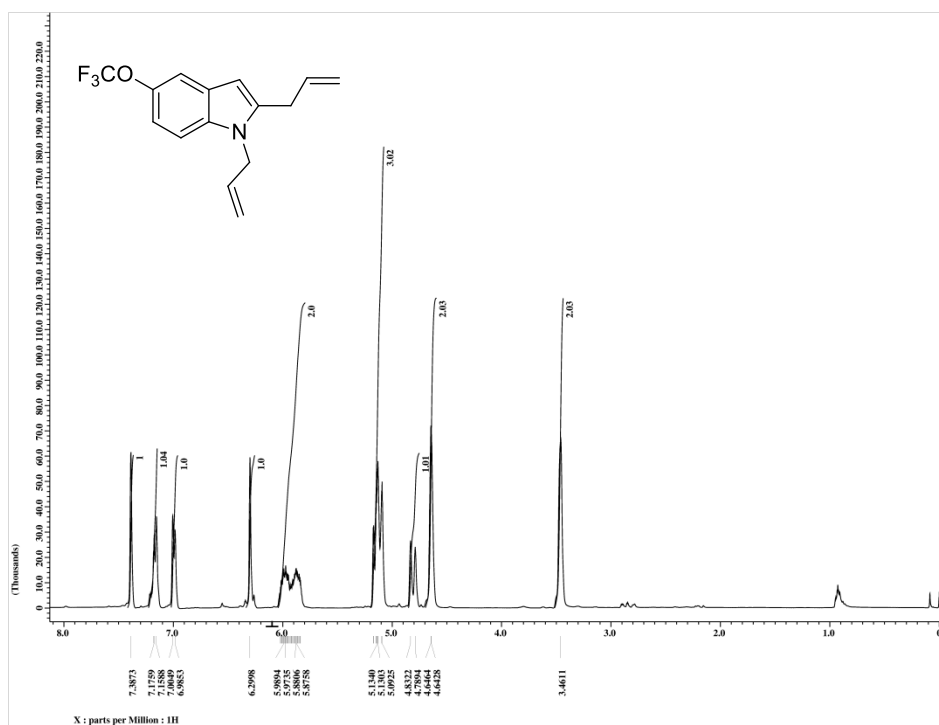
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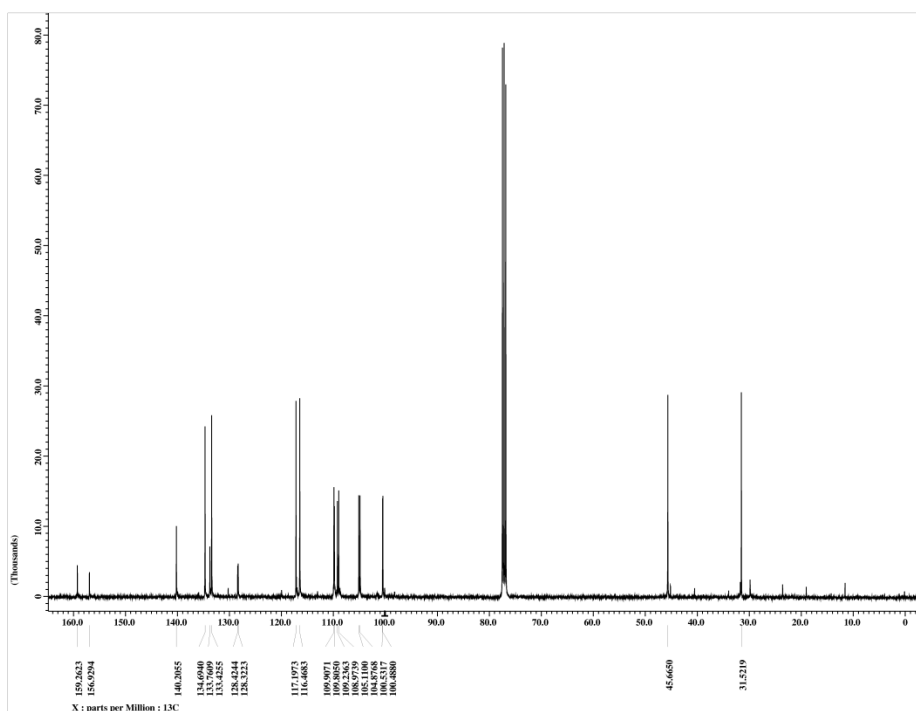
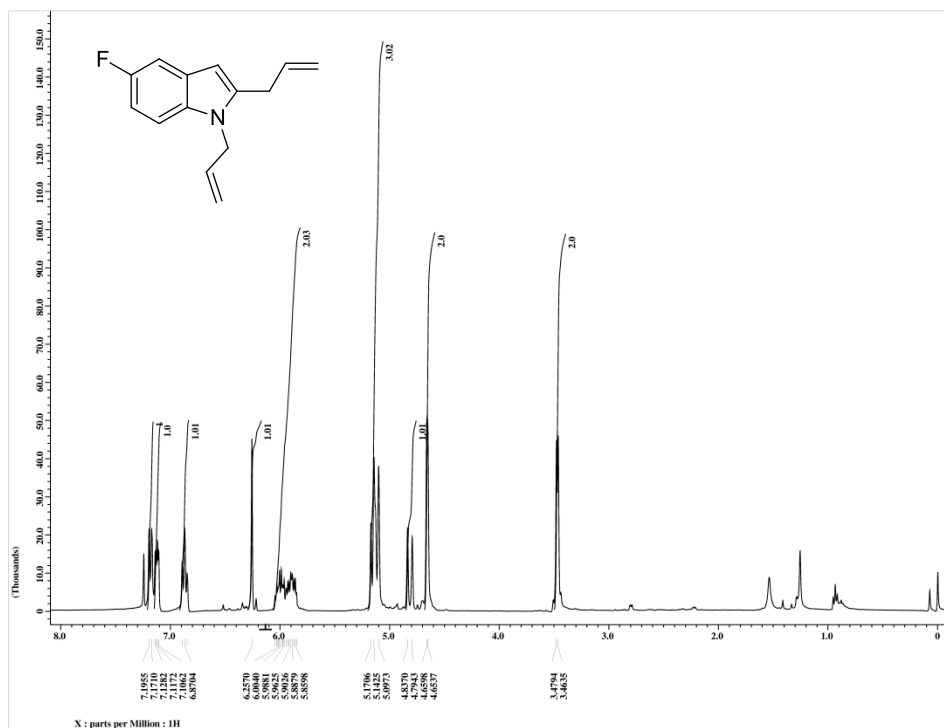
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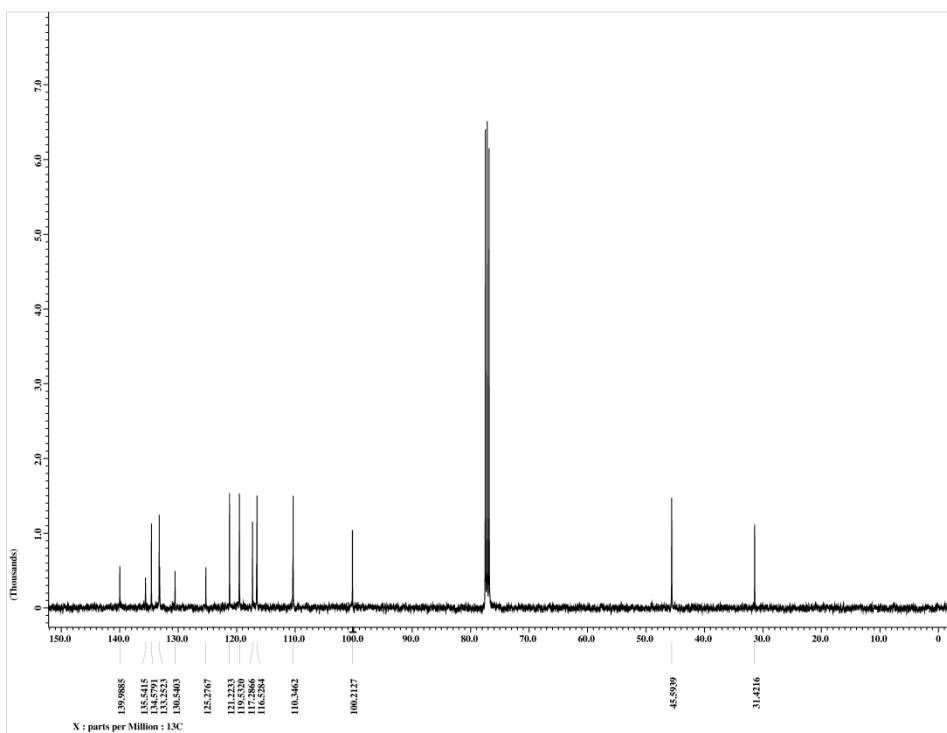
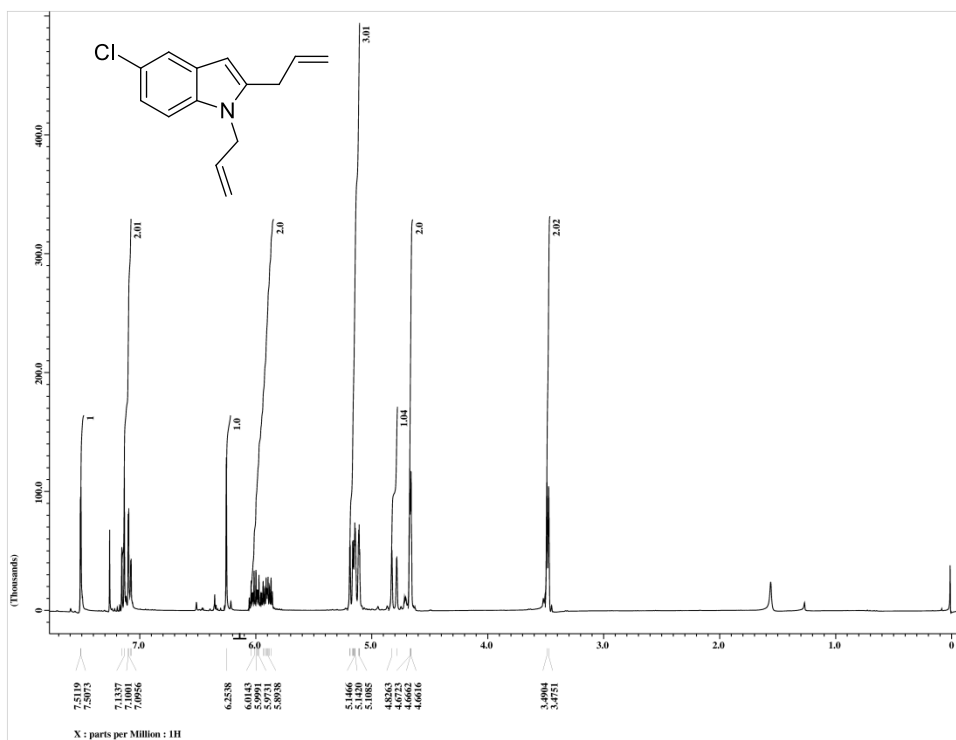
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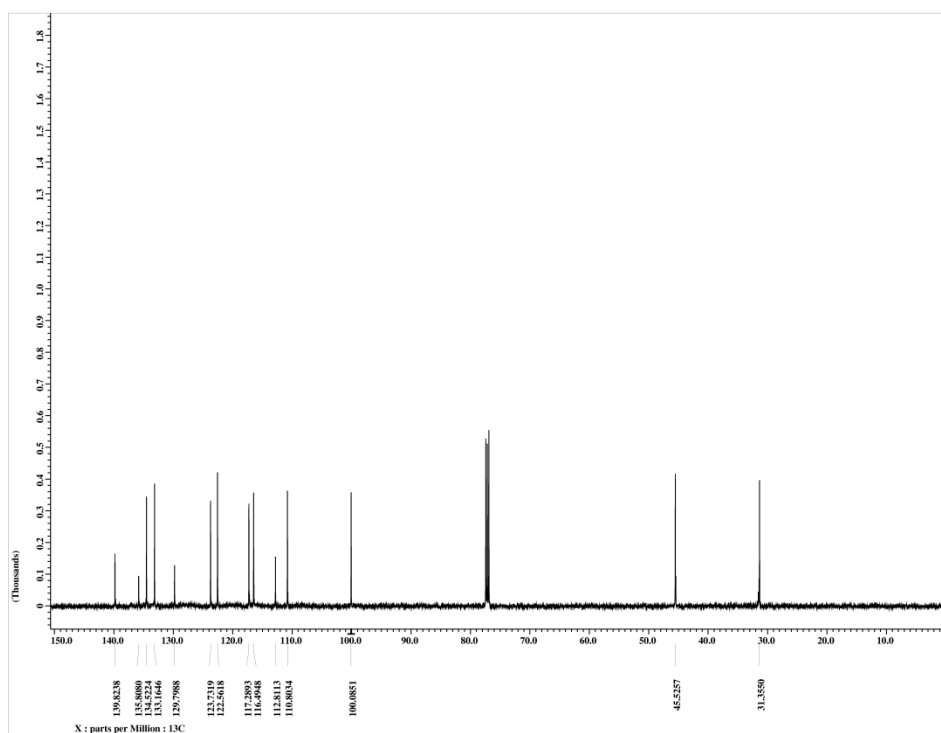
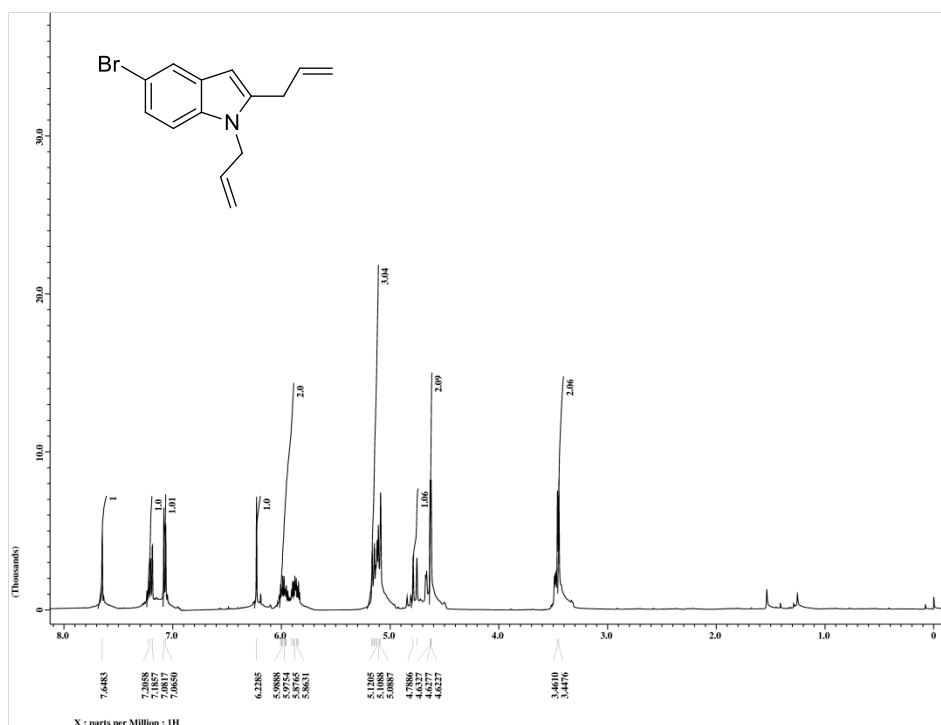
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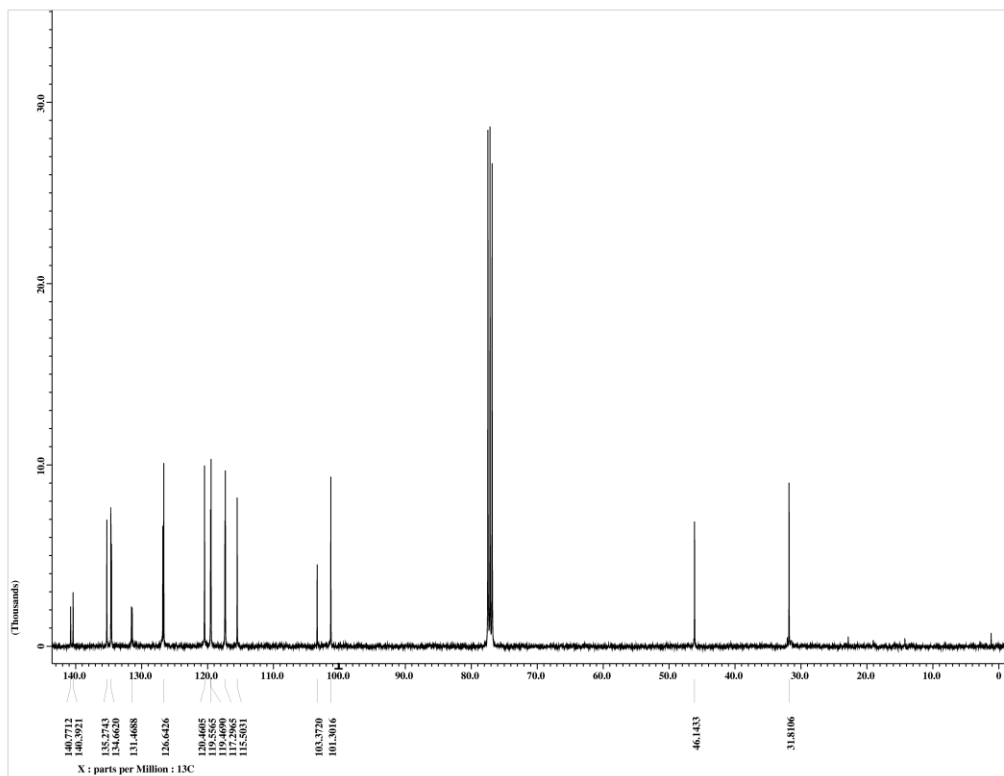
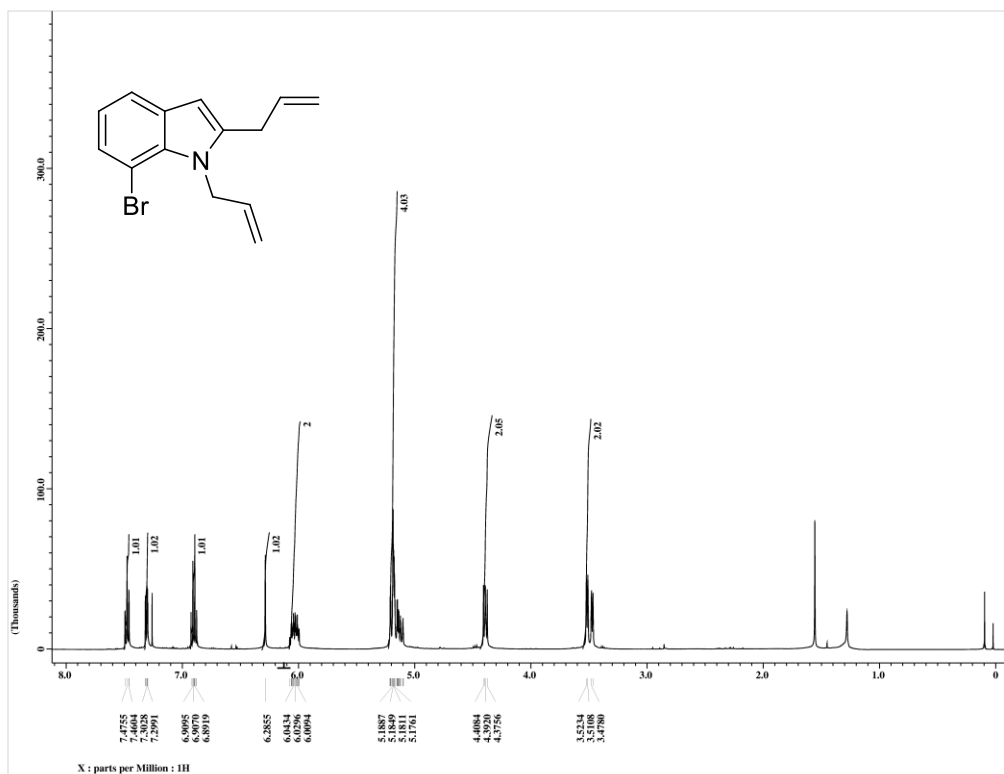
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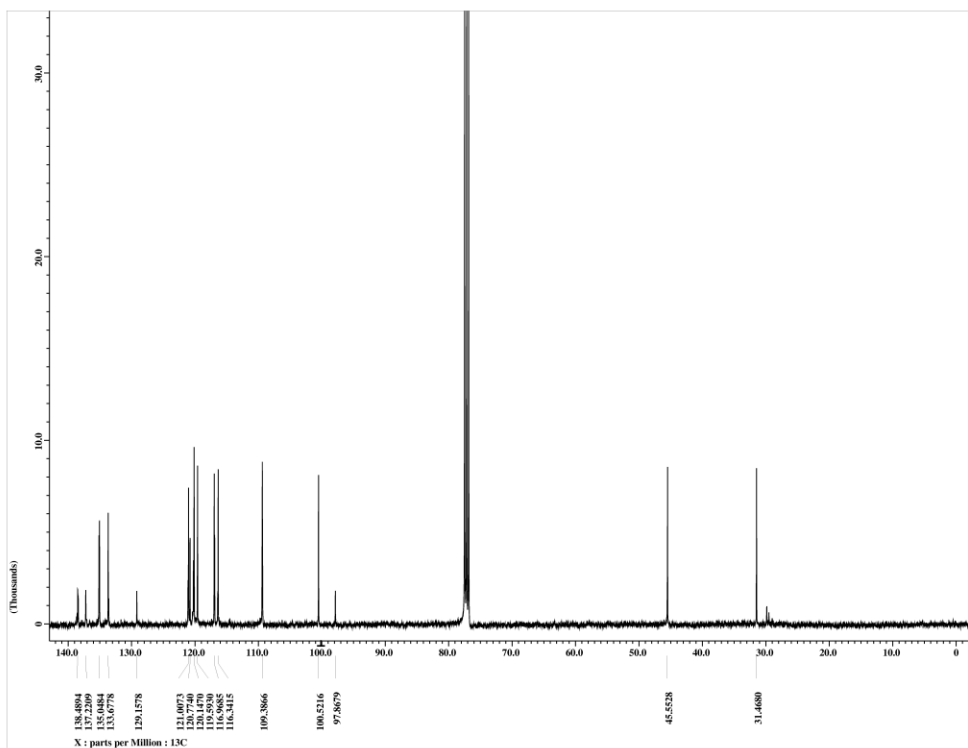
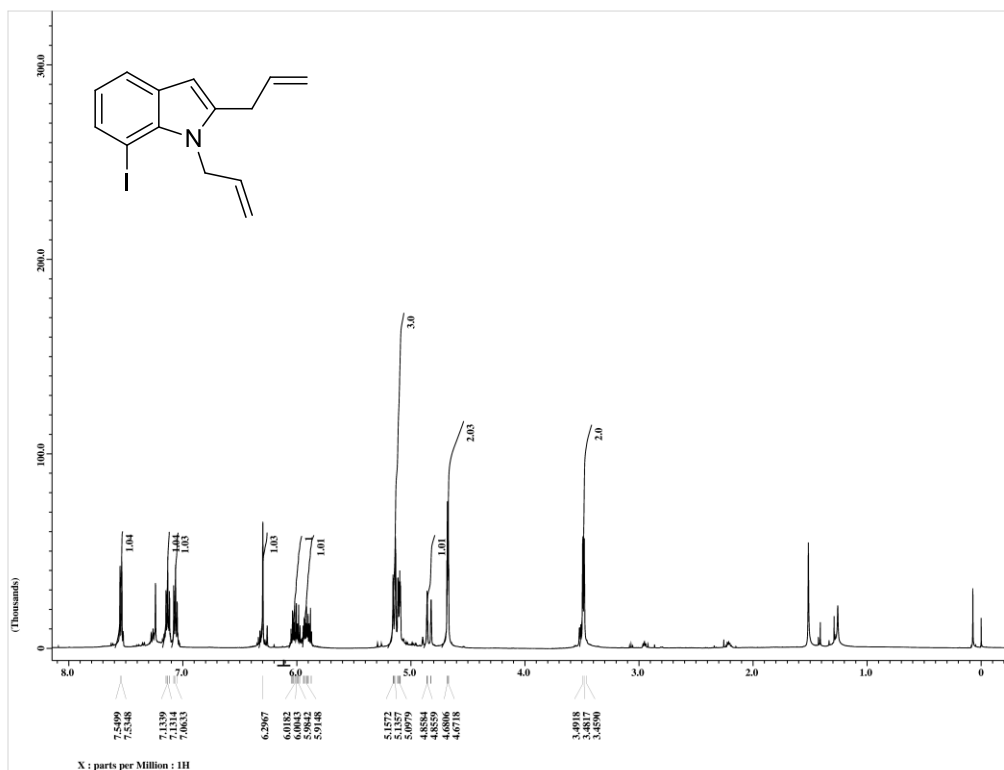
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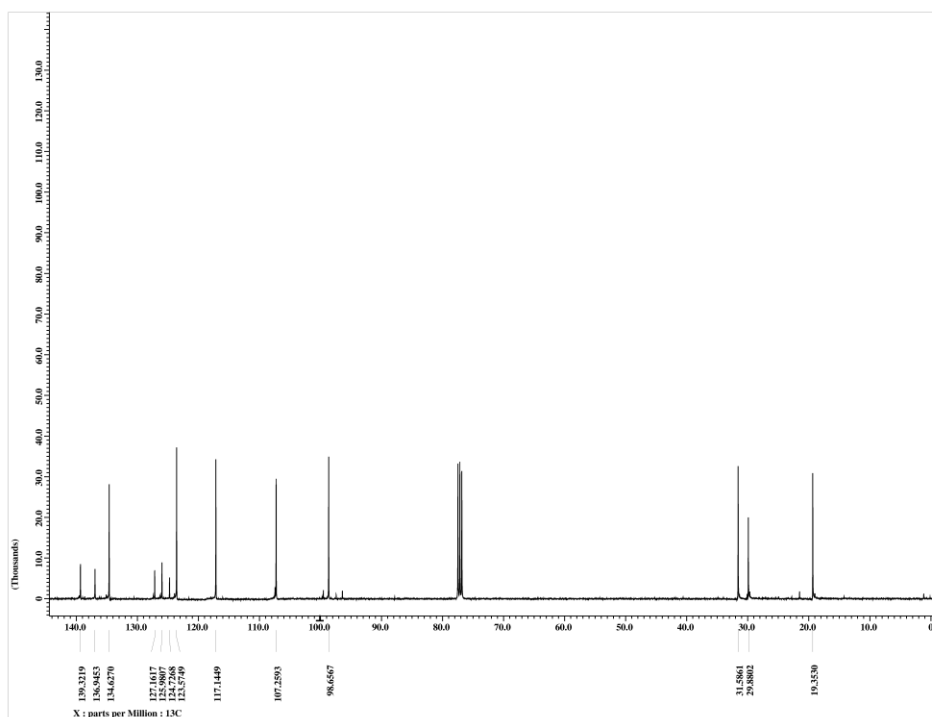
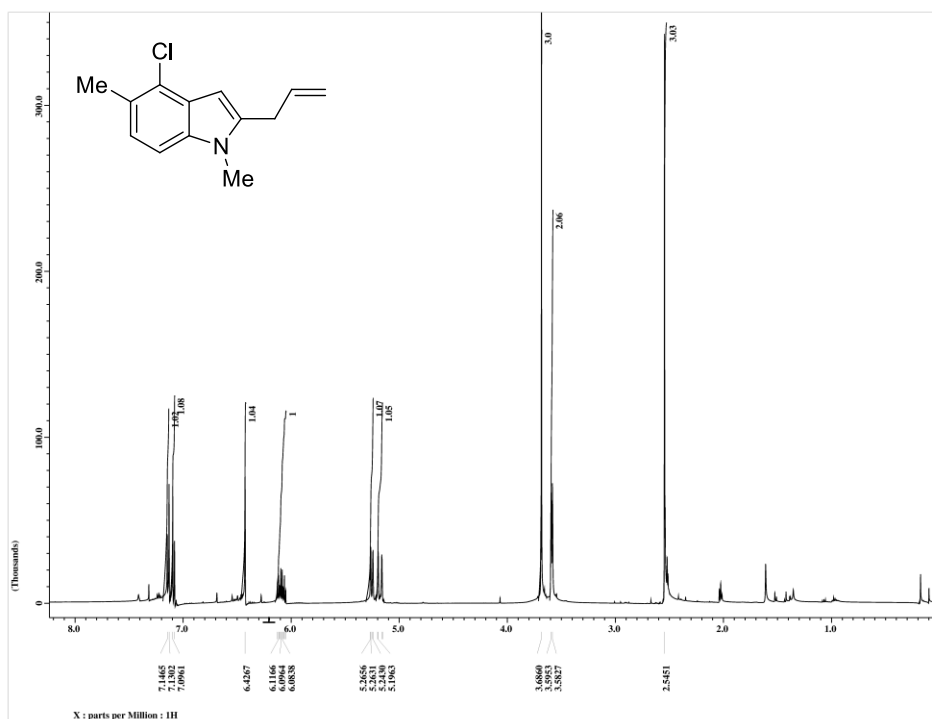
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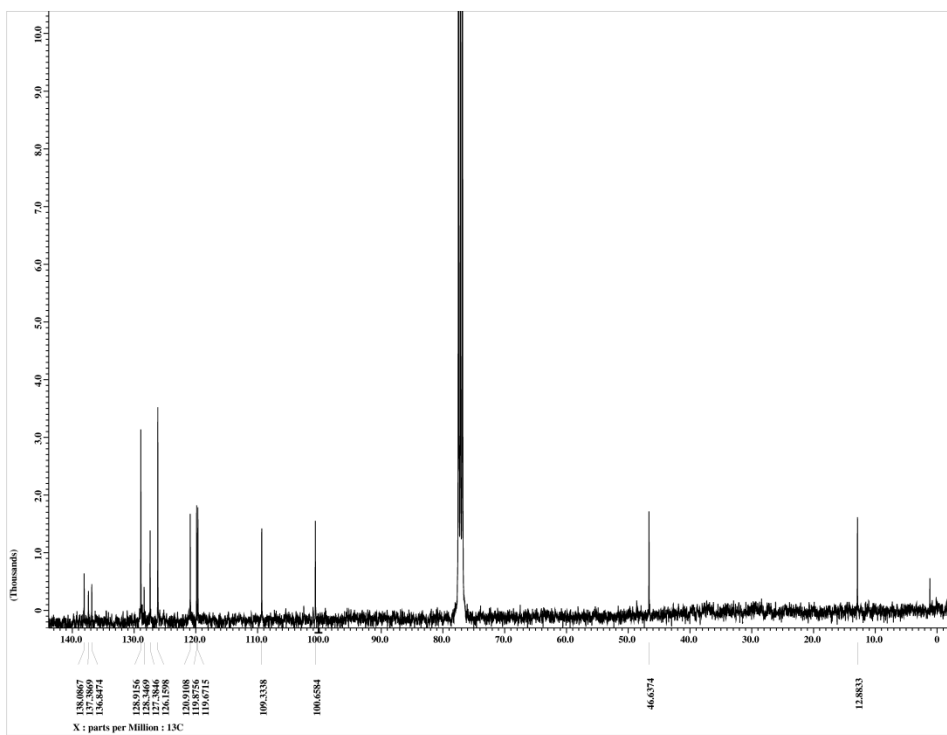
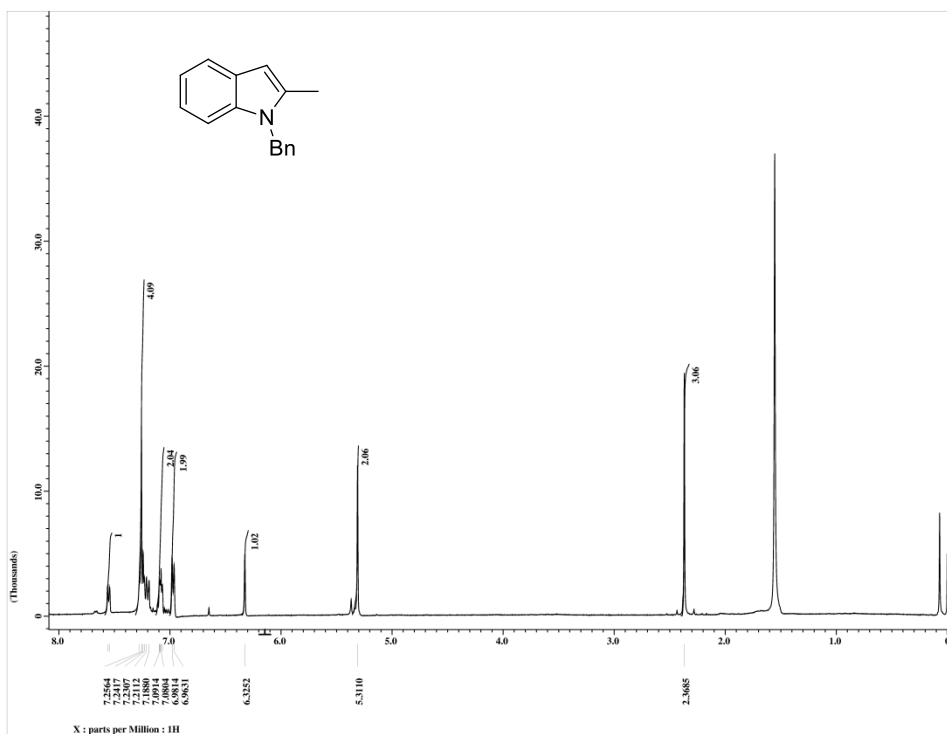
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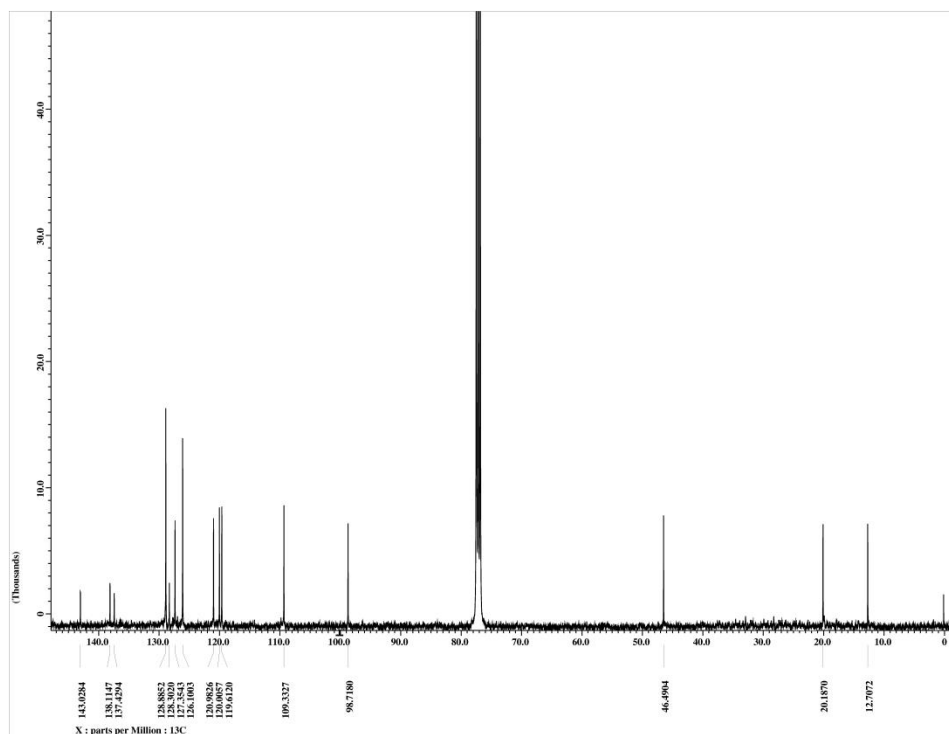
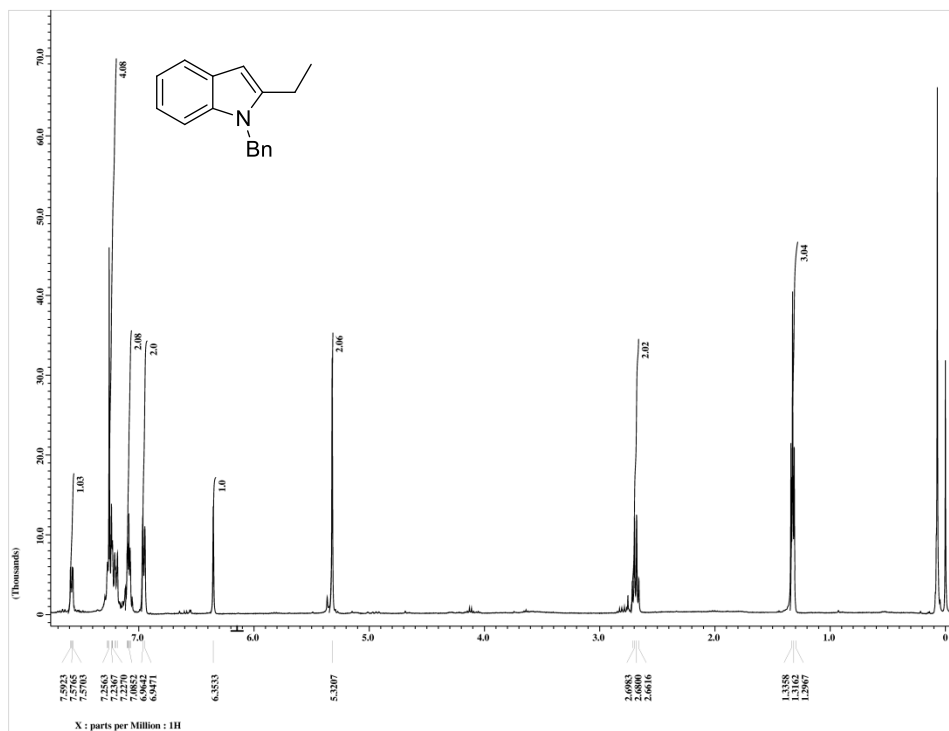
^1H and ^{13}C NMR of 3o:



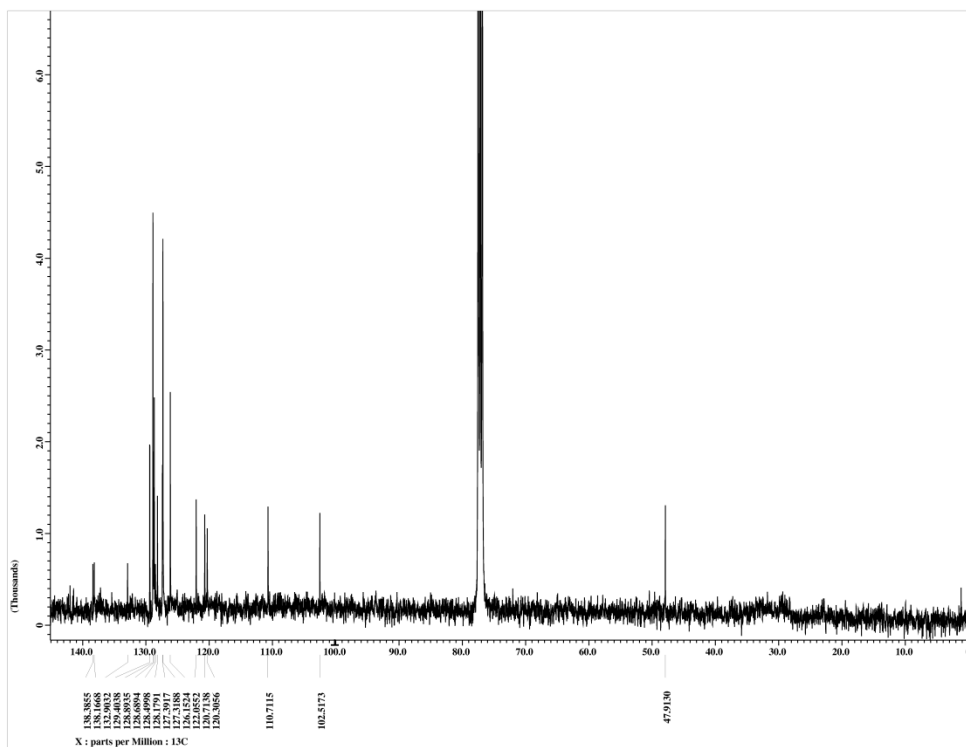
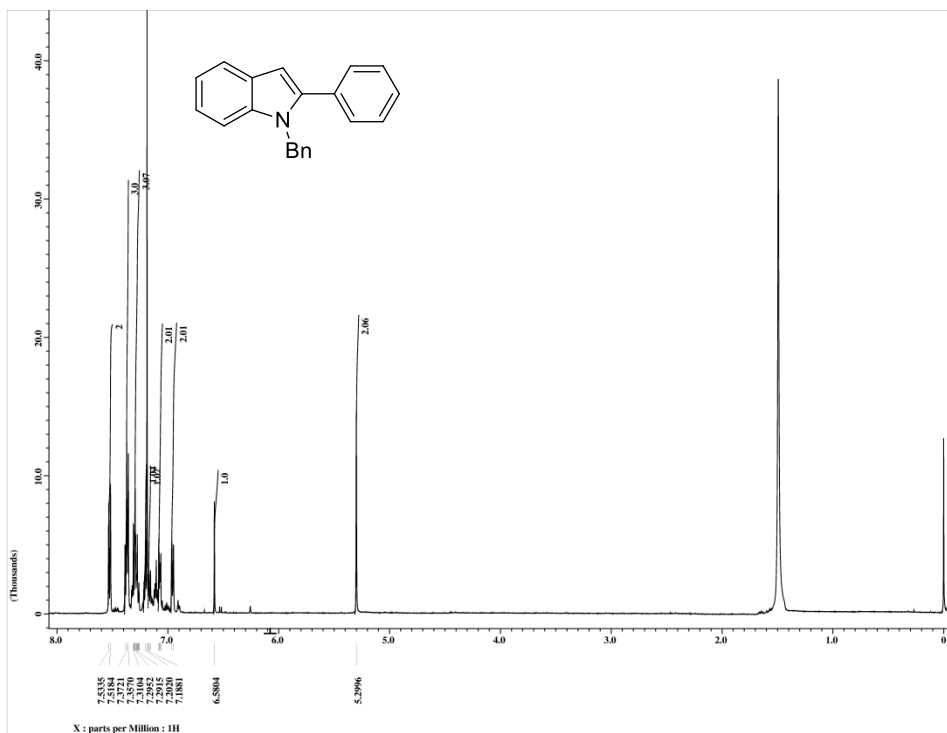
^1H and ^{13}C NMR of 3p:



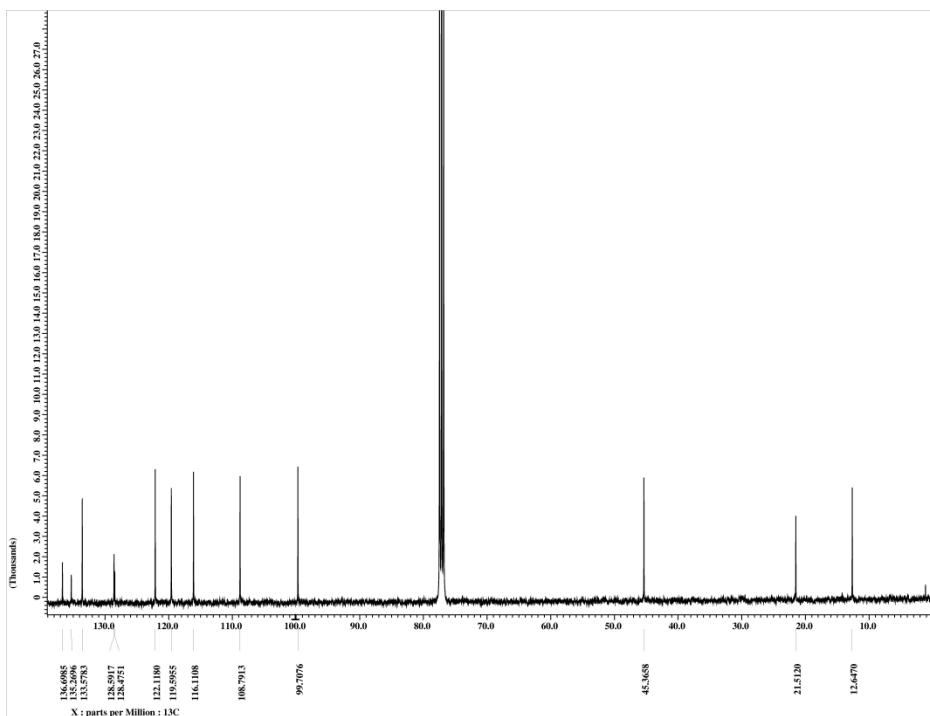
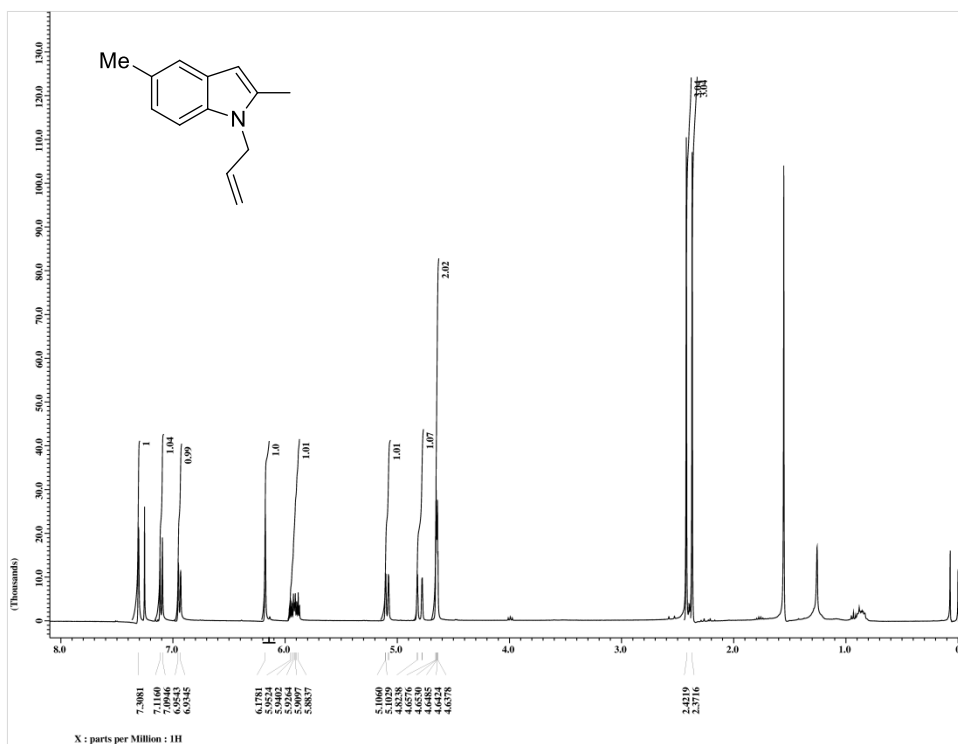
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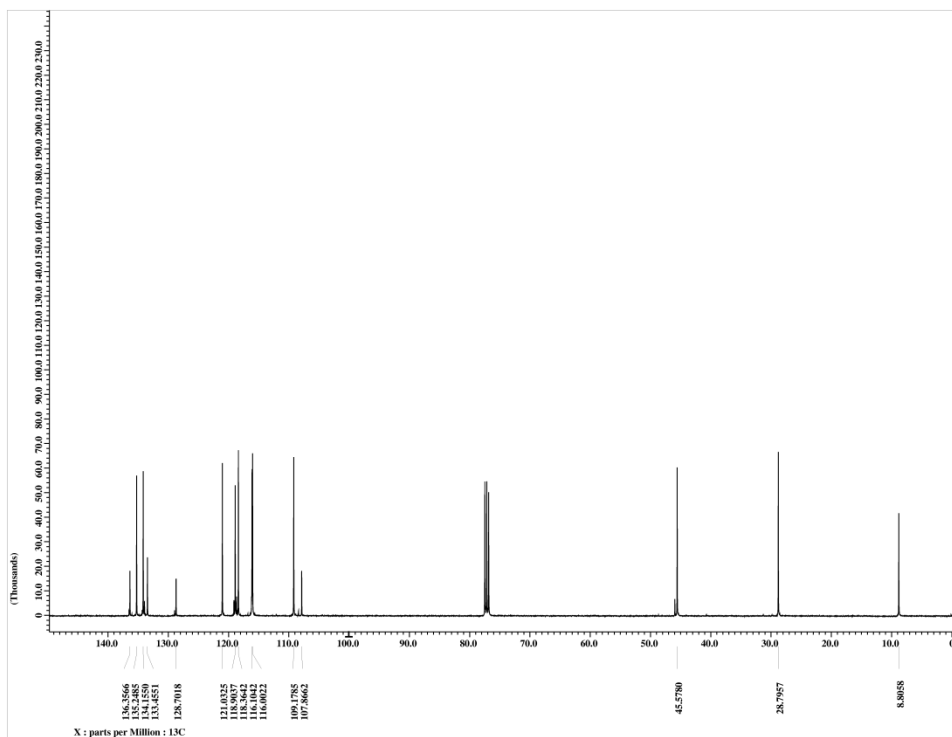
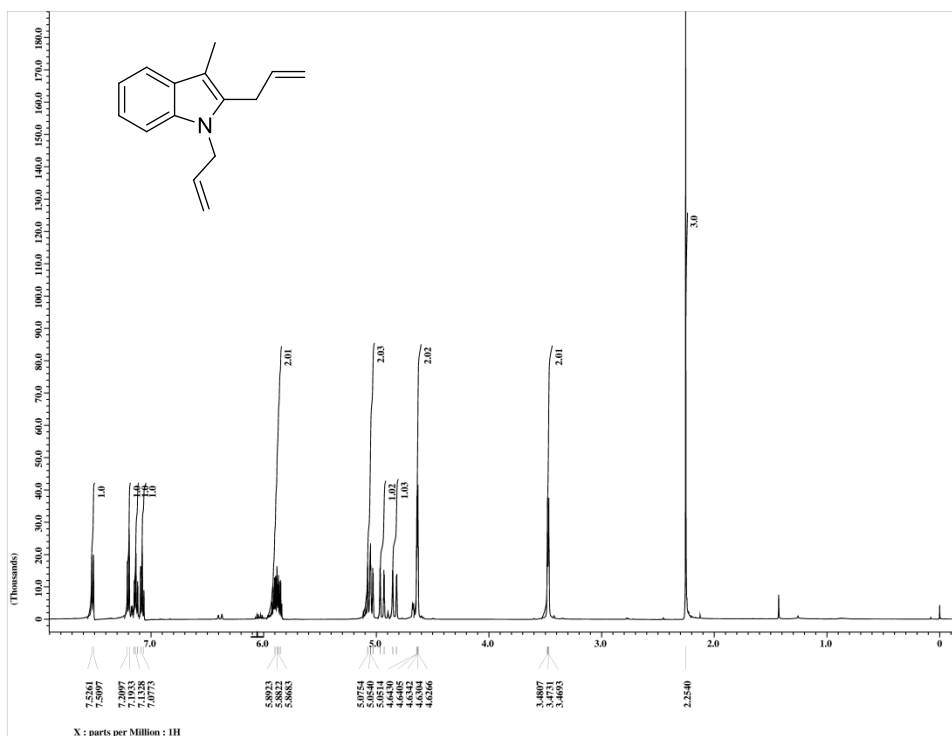
^1H and ^{13}C NMR of 3r:



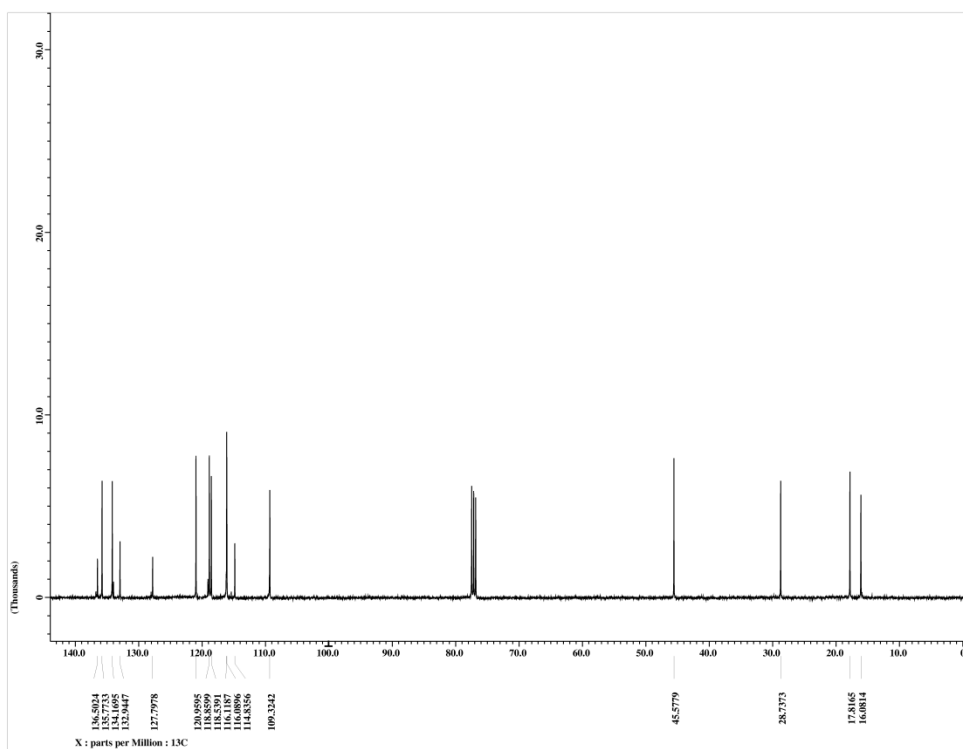
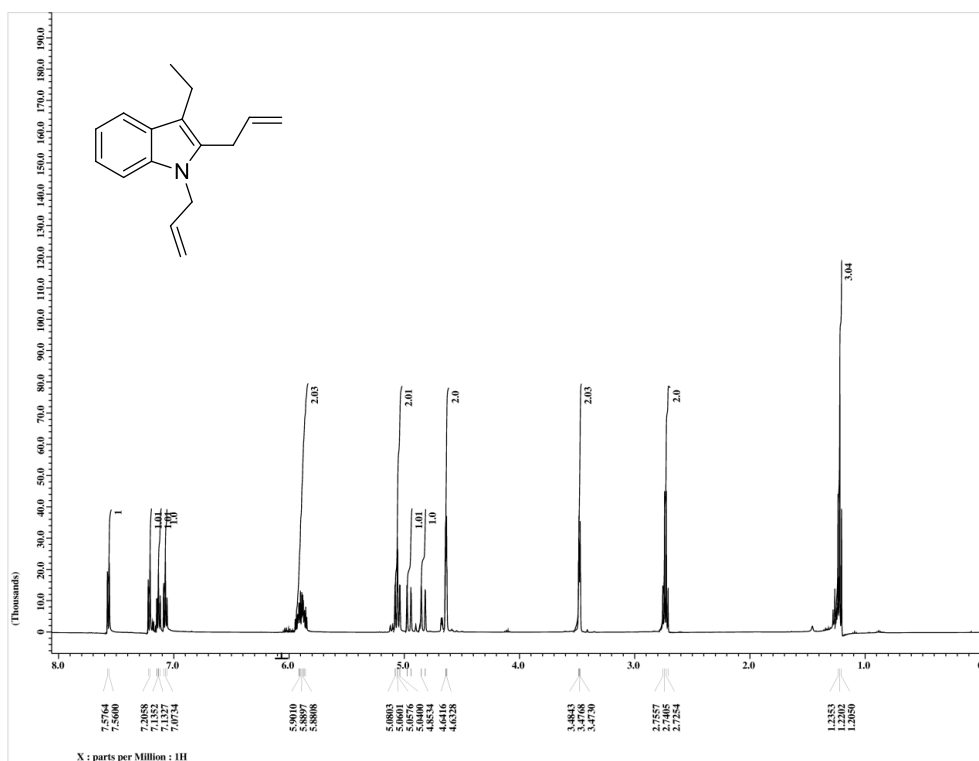
^1H and ^{13}C NMR of 3s:



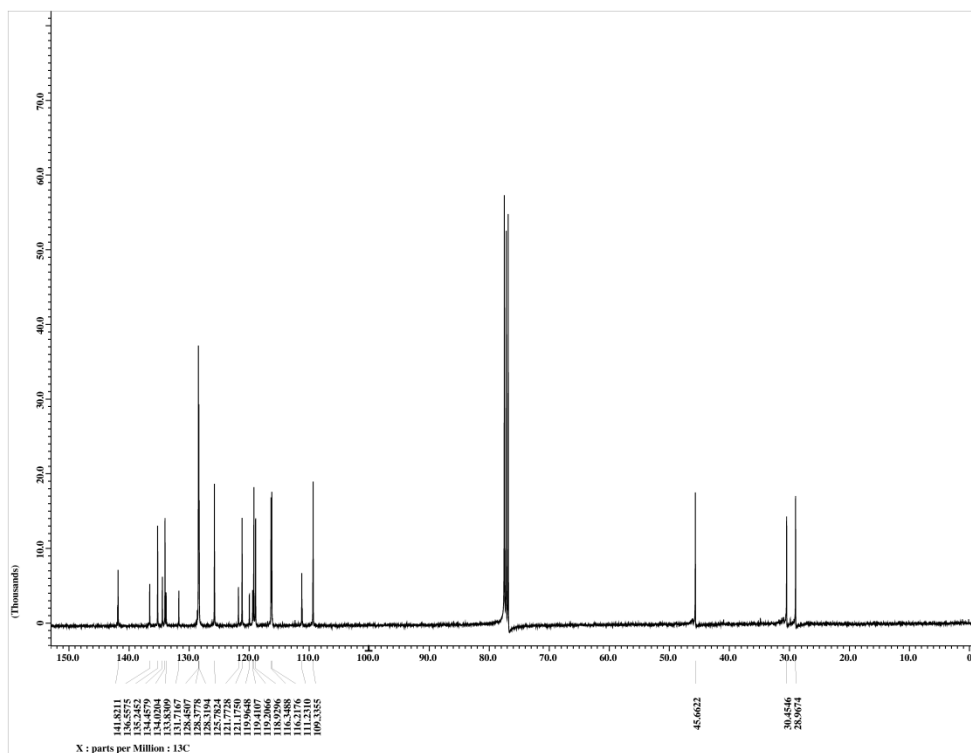
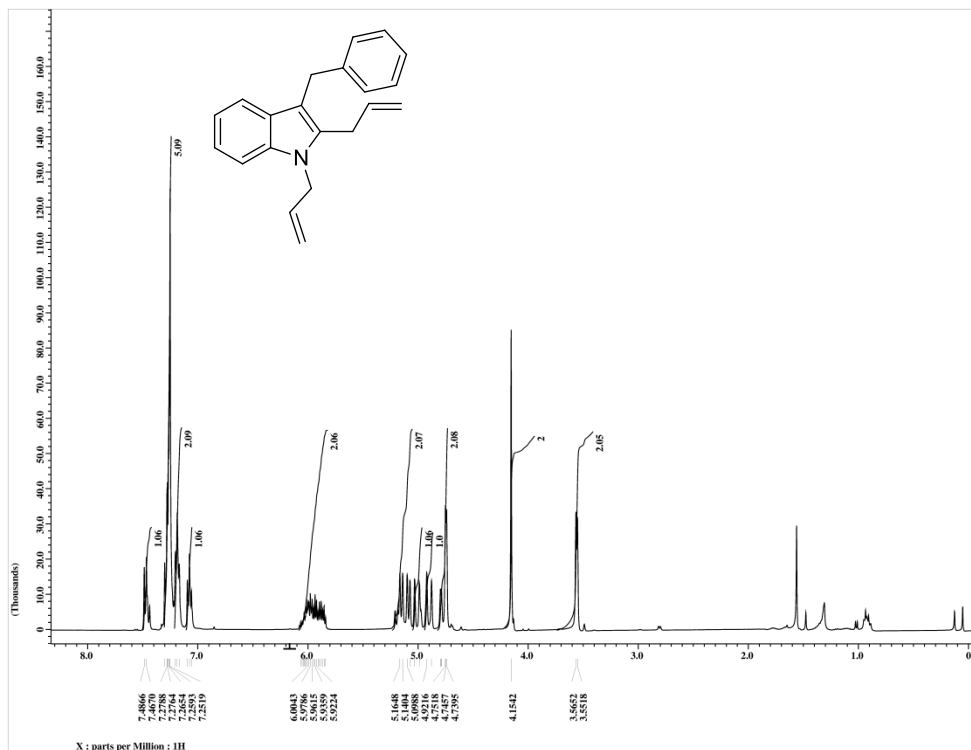
^1H and ^{13}C NMR of 4a:



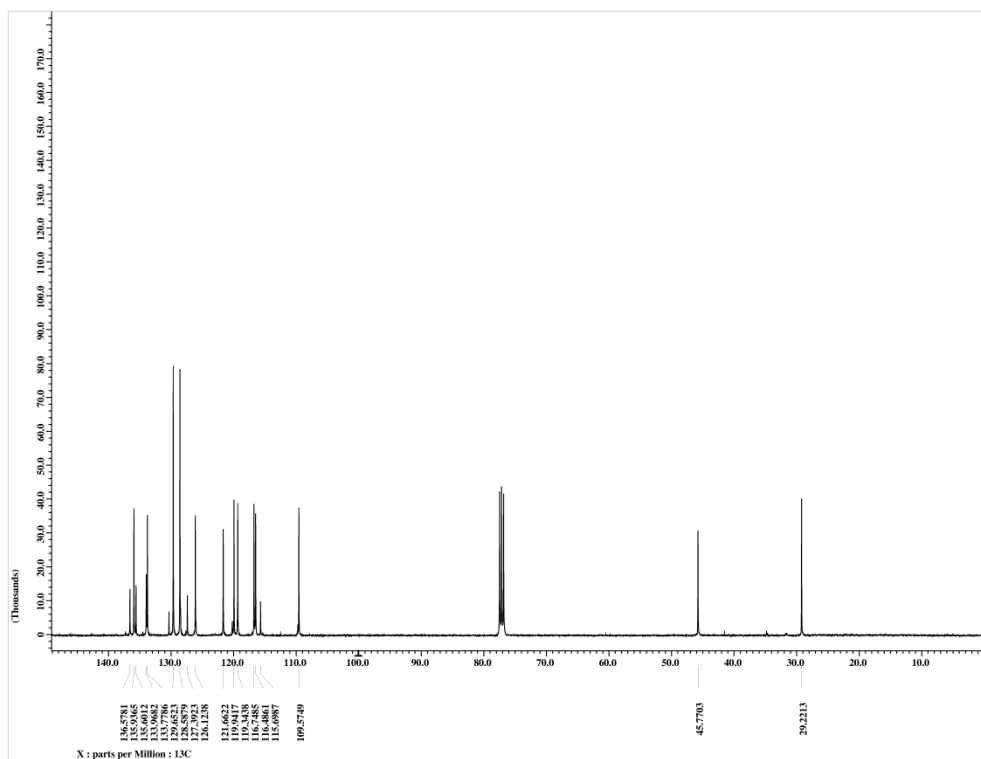
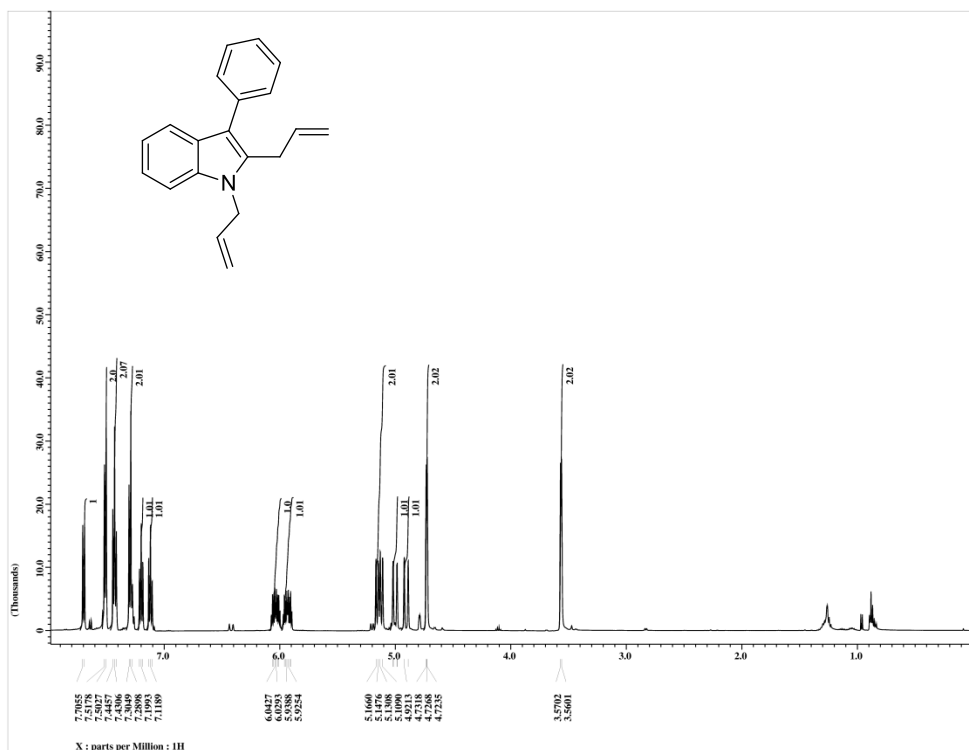
^1H and ^{13}C NMR of 4b:



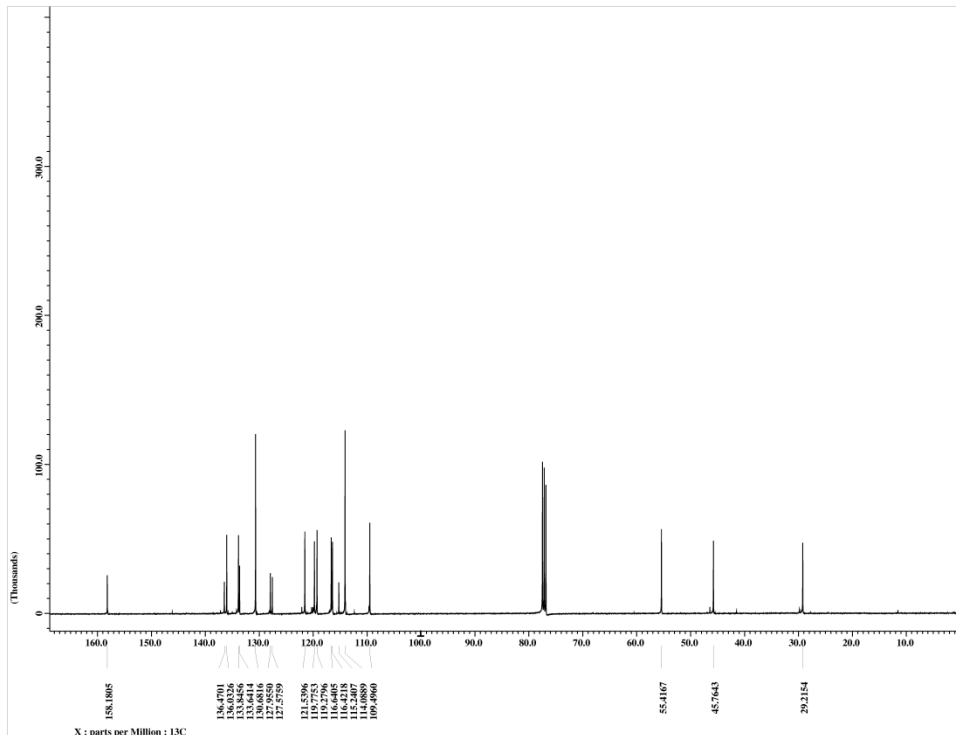
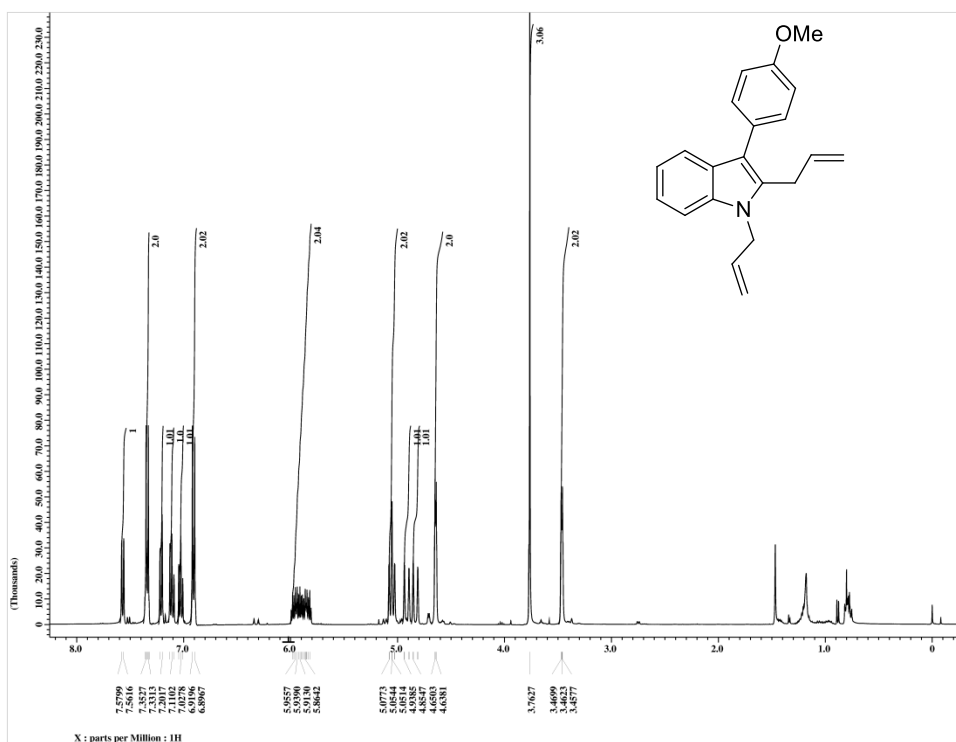
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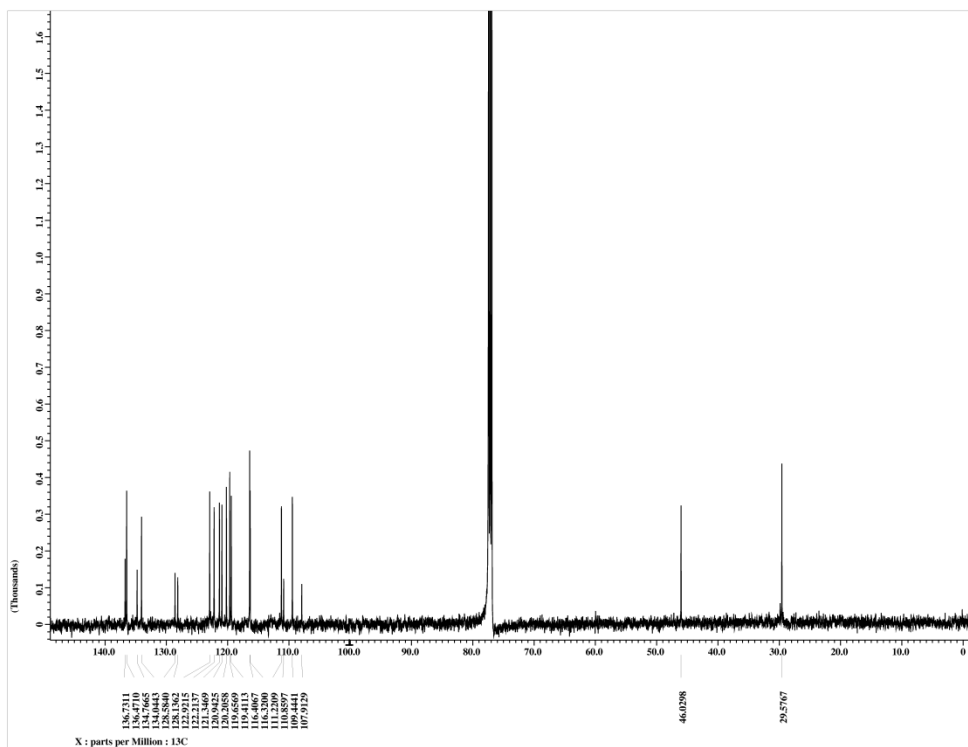
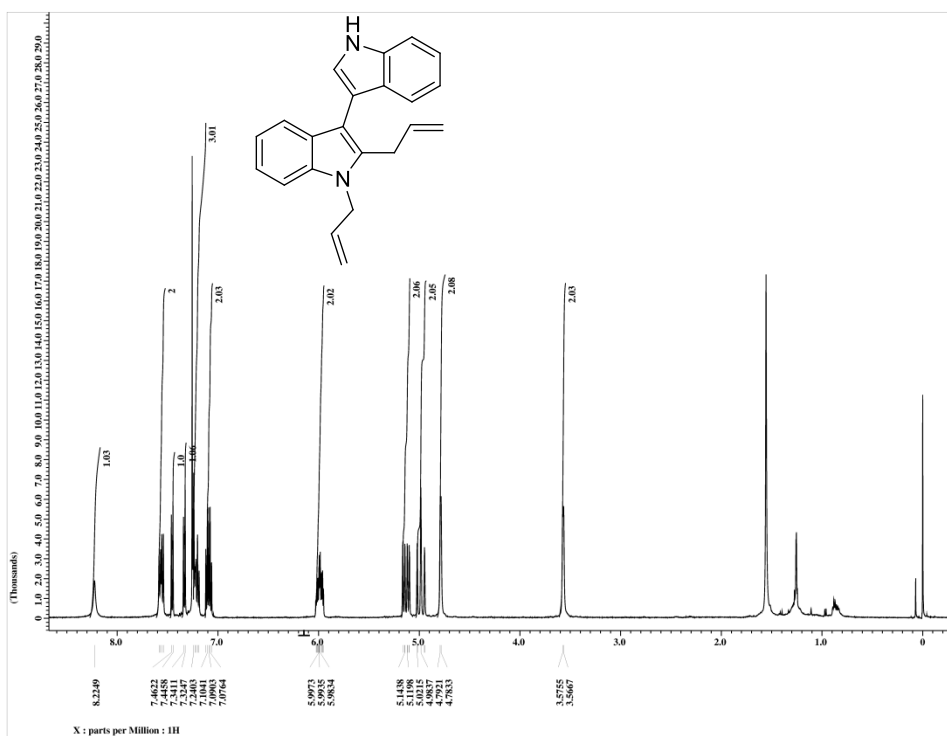
^1H and ^{13}C NMR of 4d:



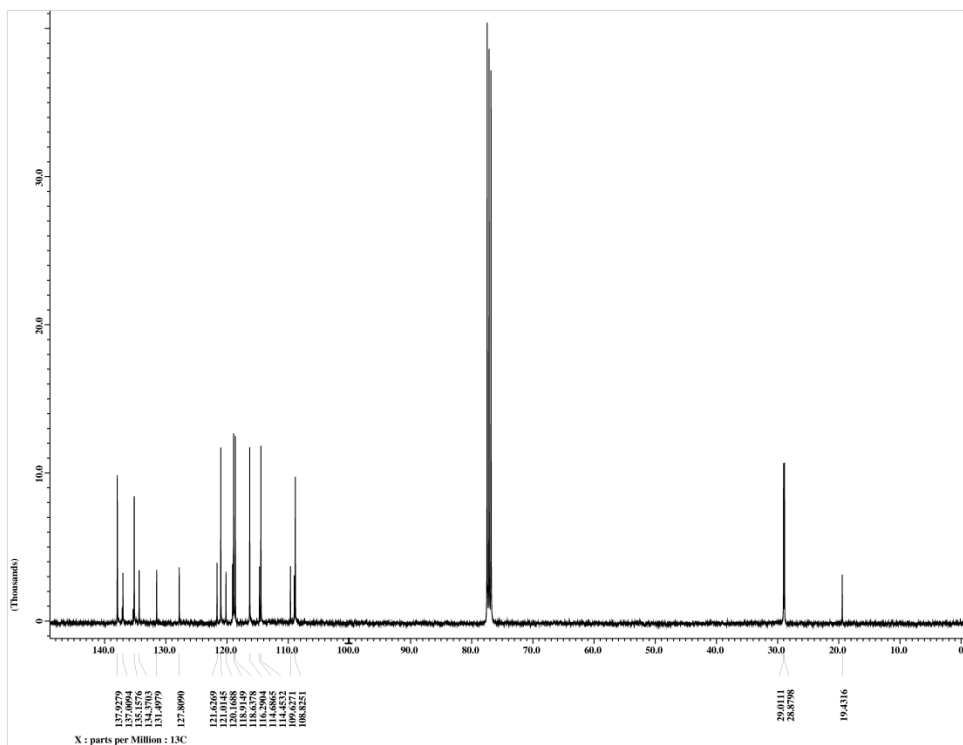
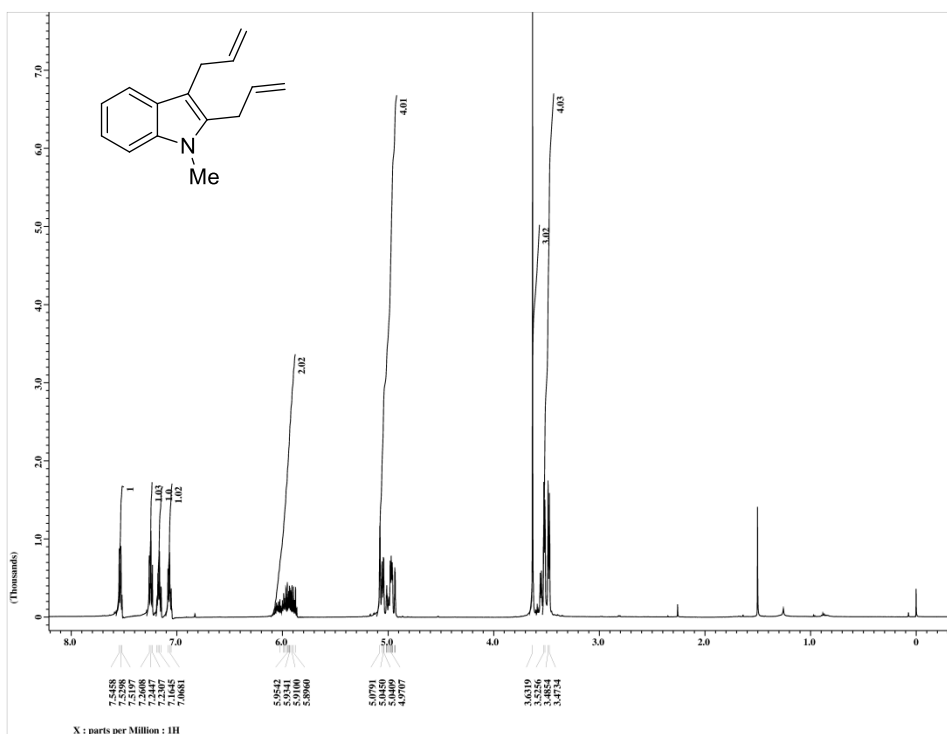
^1H and ^{13}C NMR of 4e:



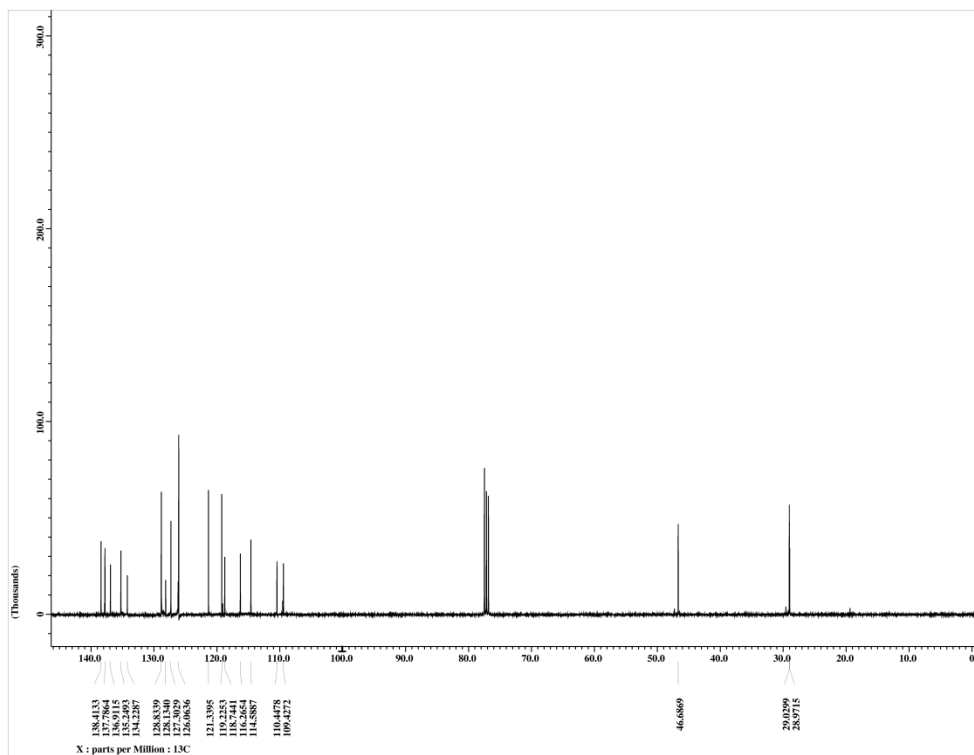
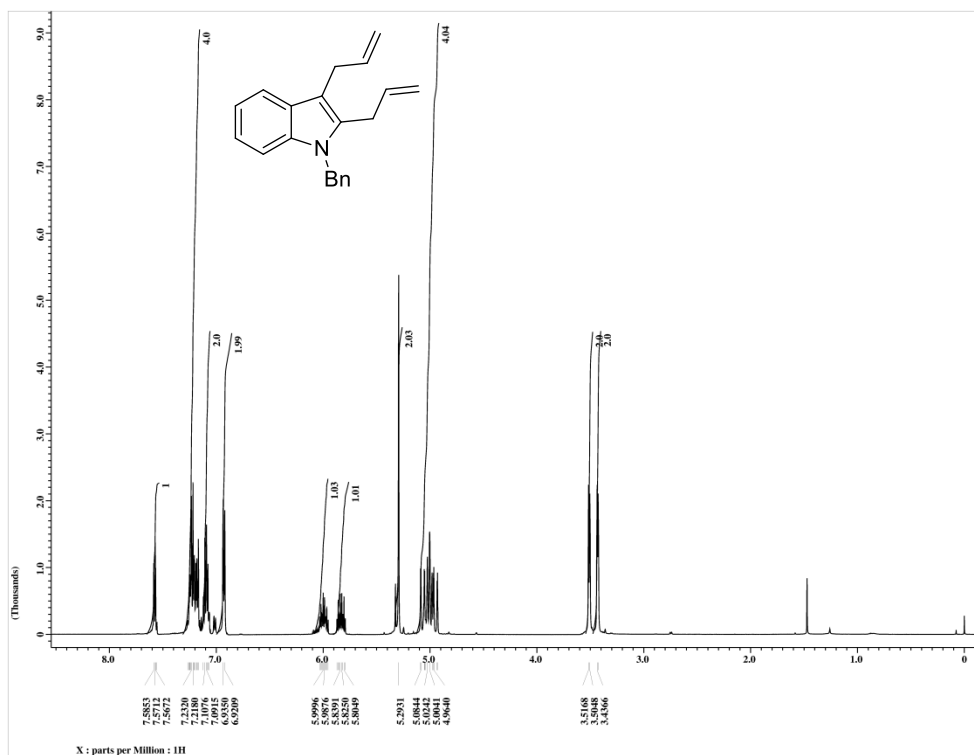
^1H and ^{13}C NMR of 4f:



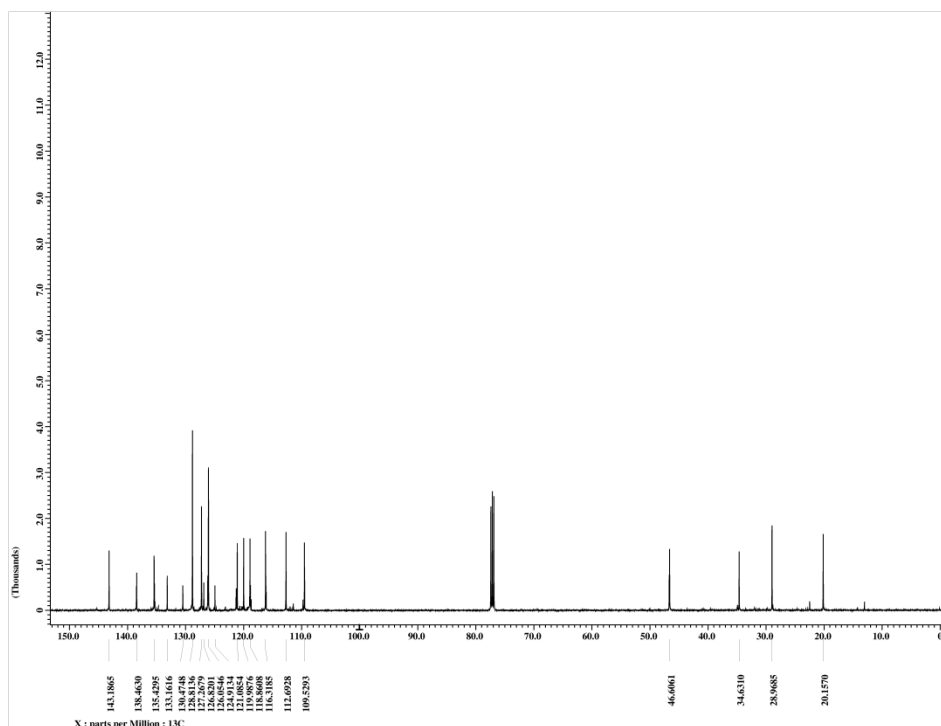
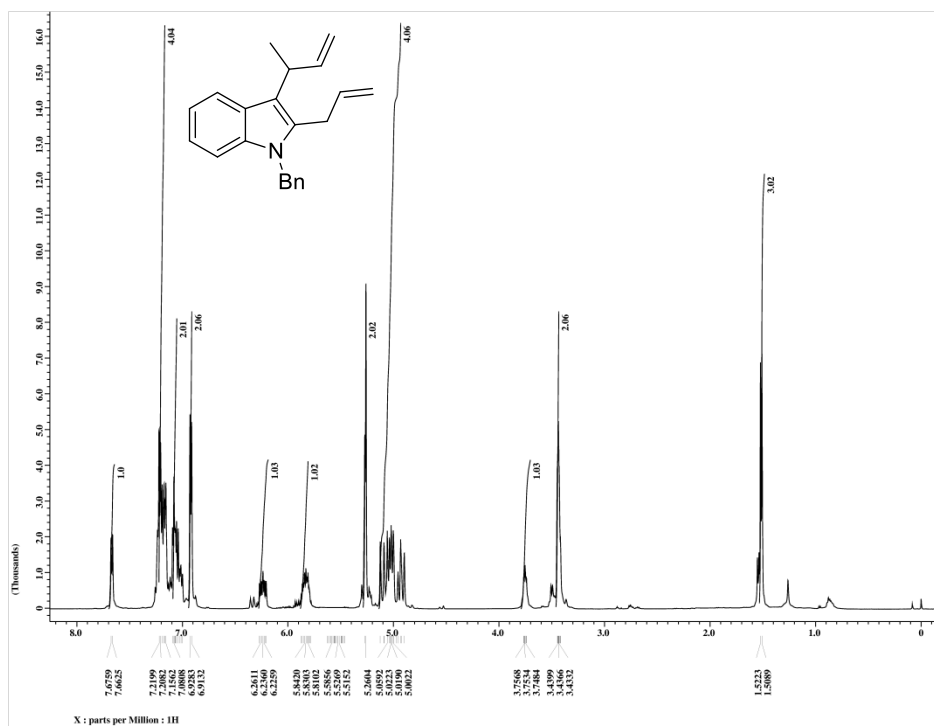
¹H and ¹³C NMR of 4h:



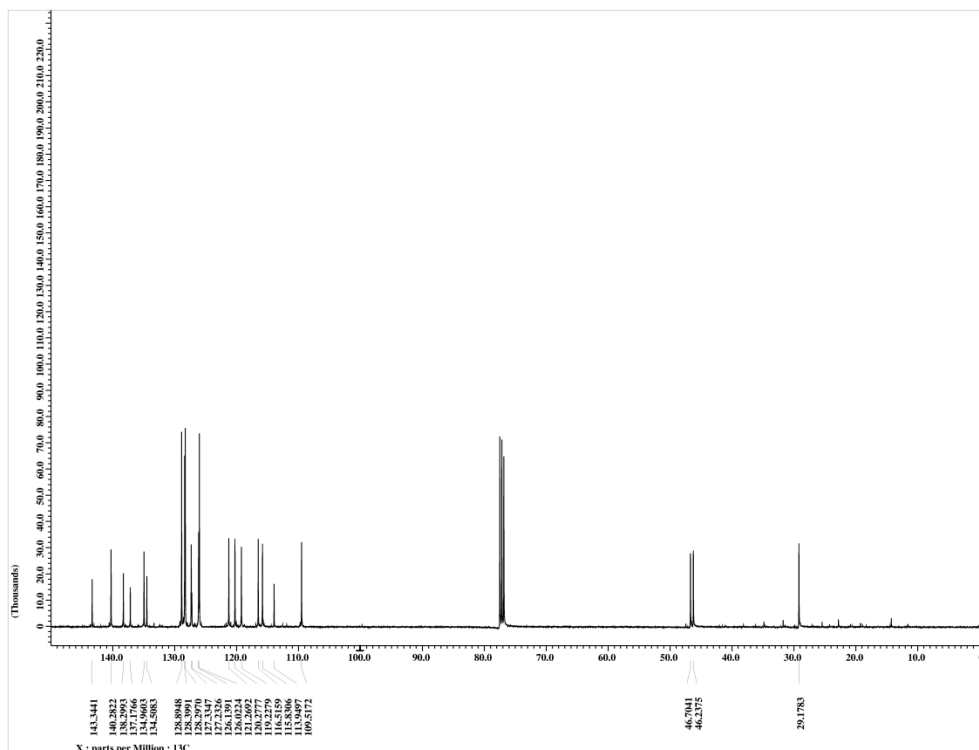
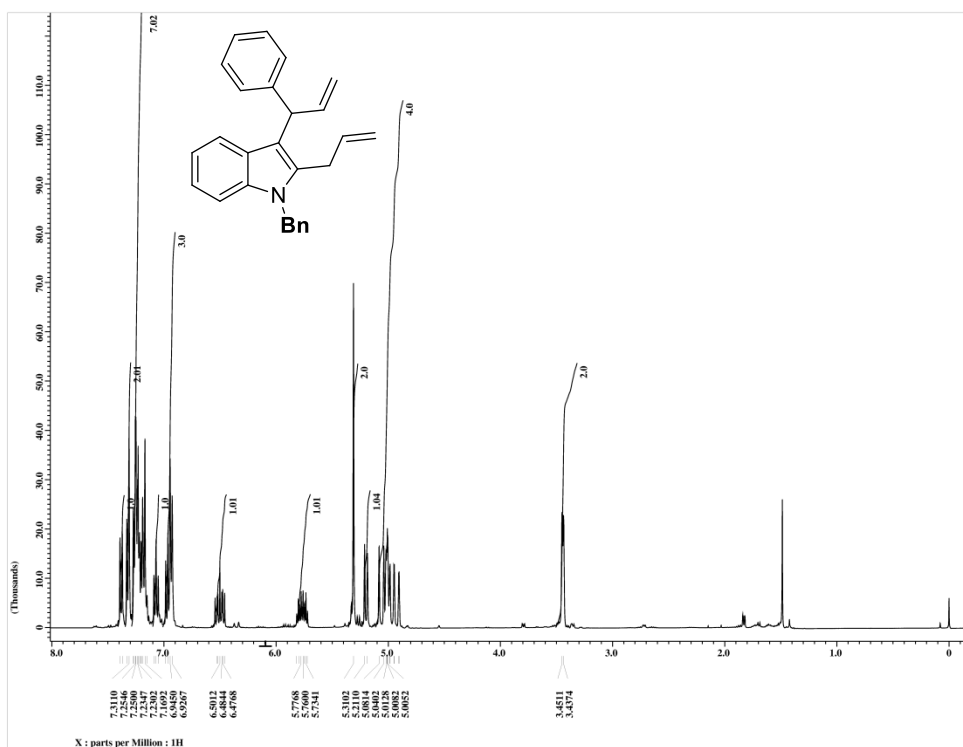
^1H and ^{13}C NMR of 4i:



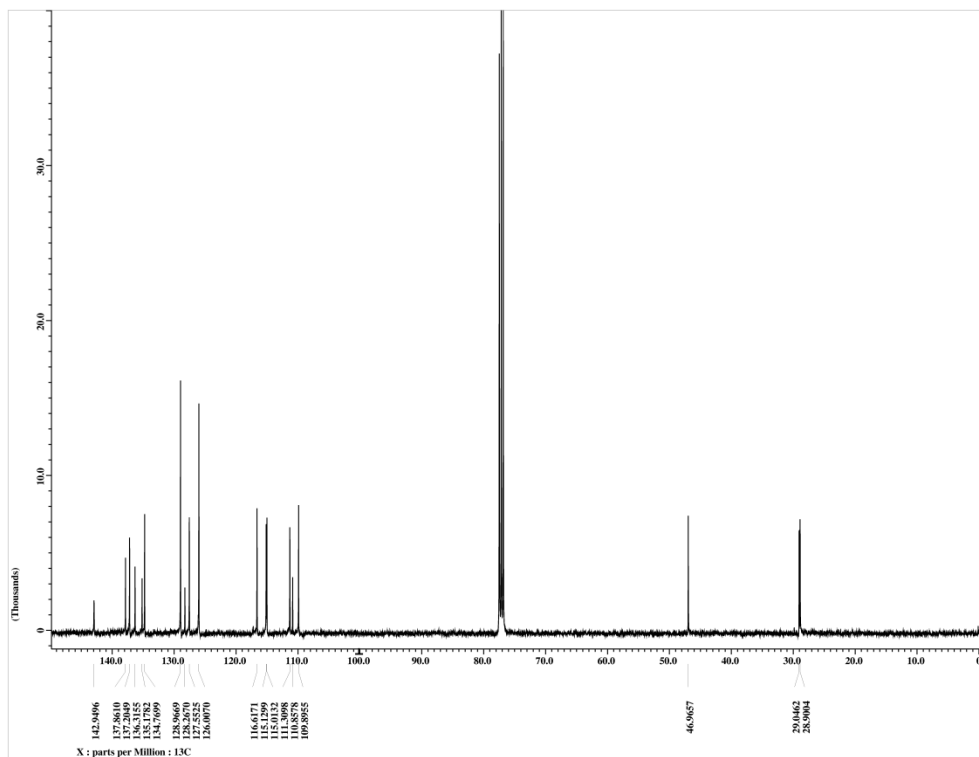
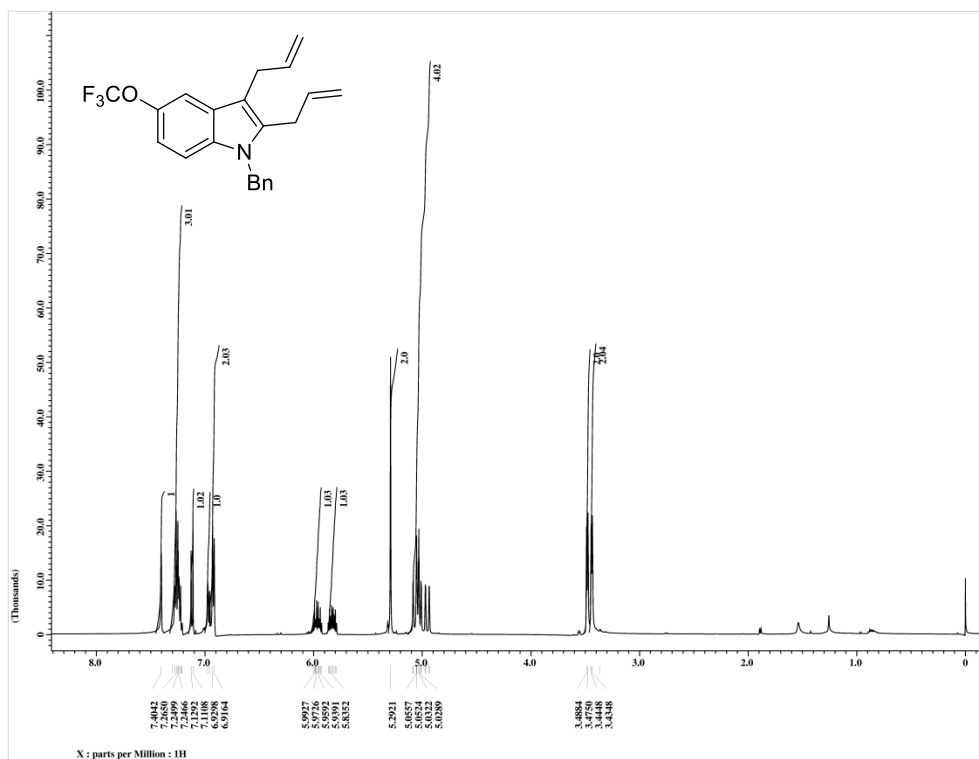
^1H and ^{13}C NMR of 4j:



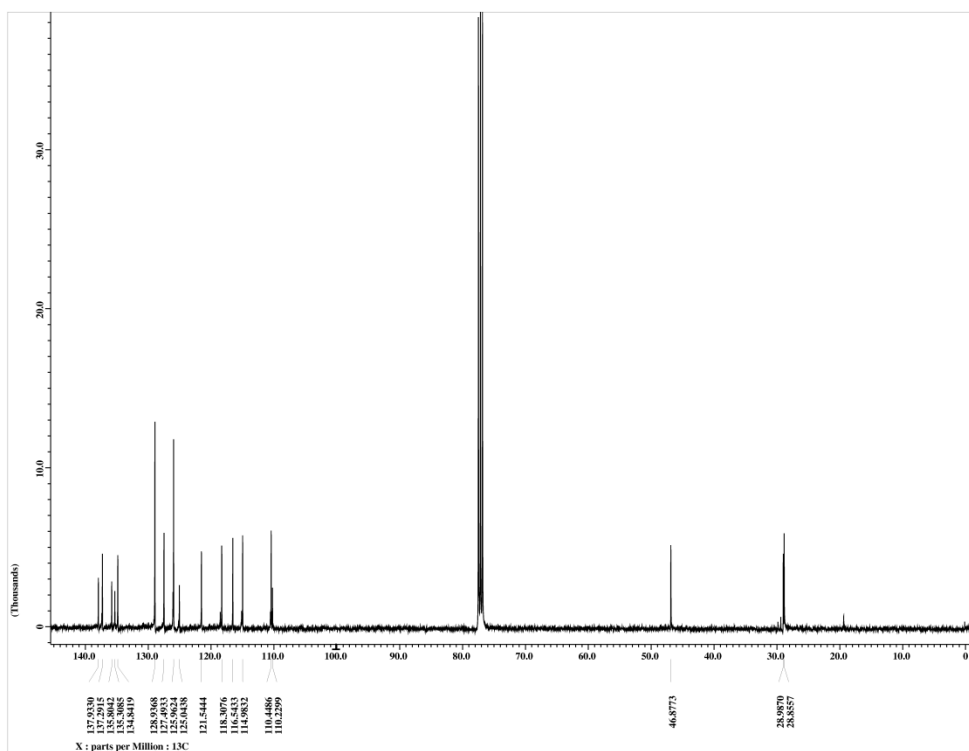
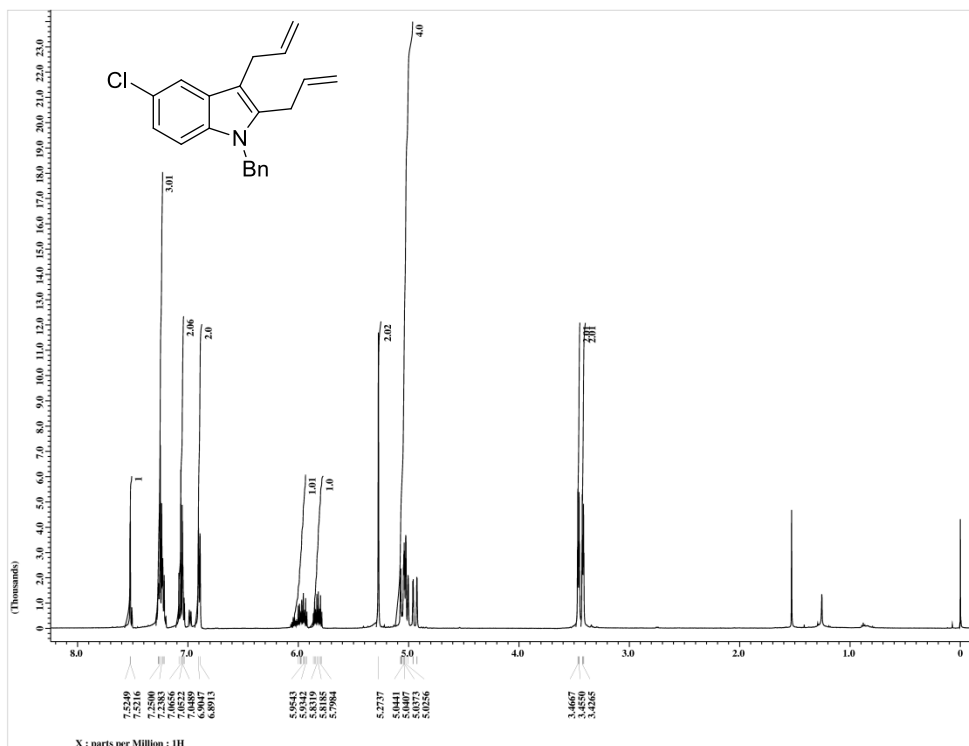
^1H and ^{13}C NMR of 4k:



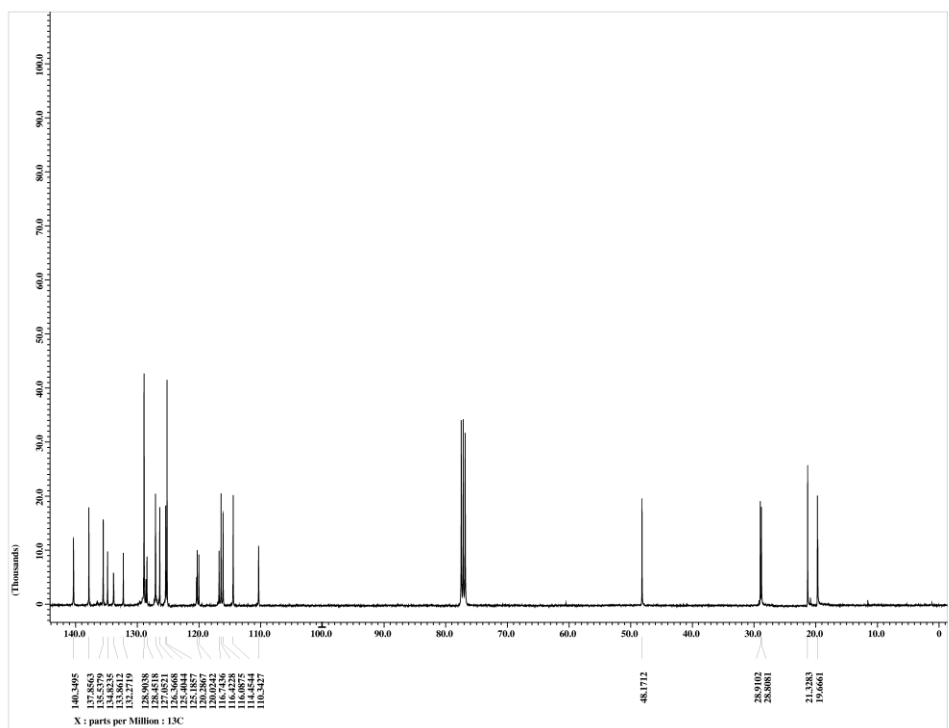
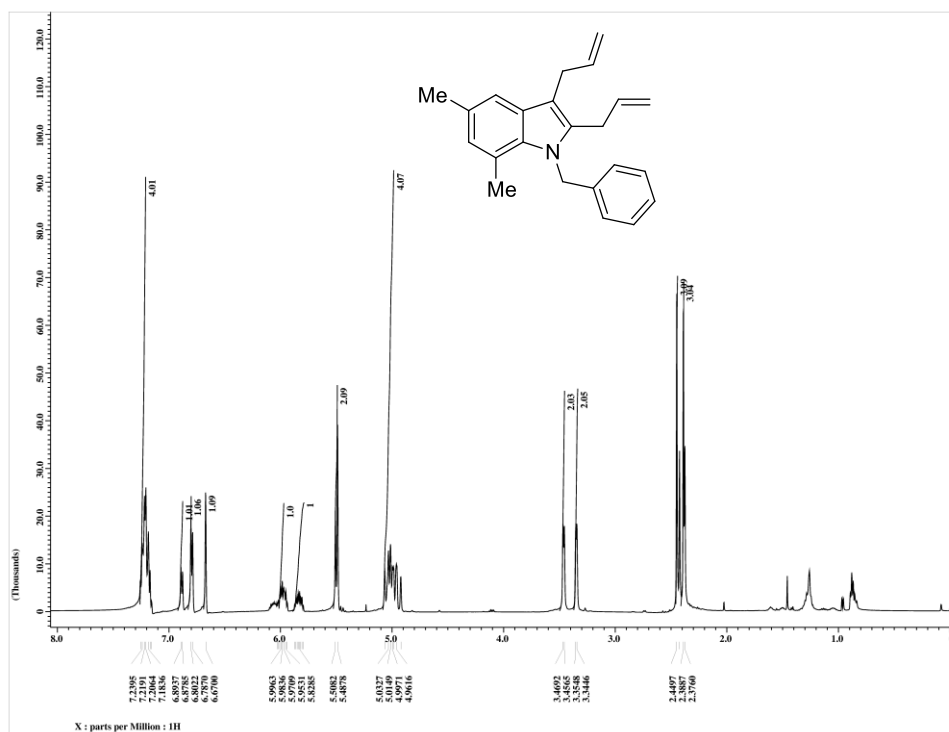
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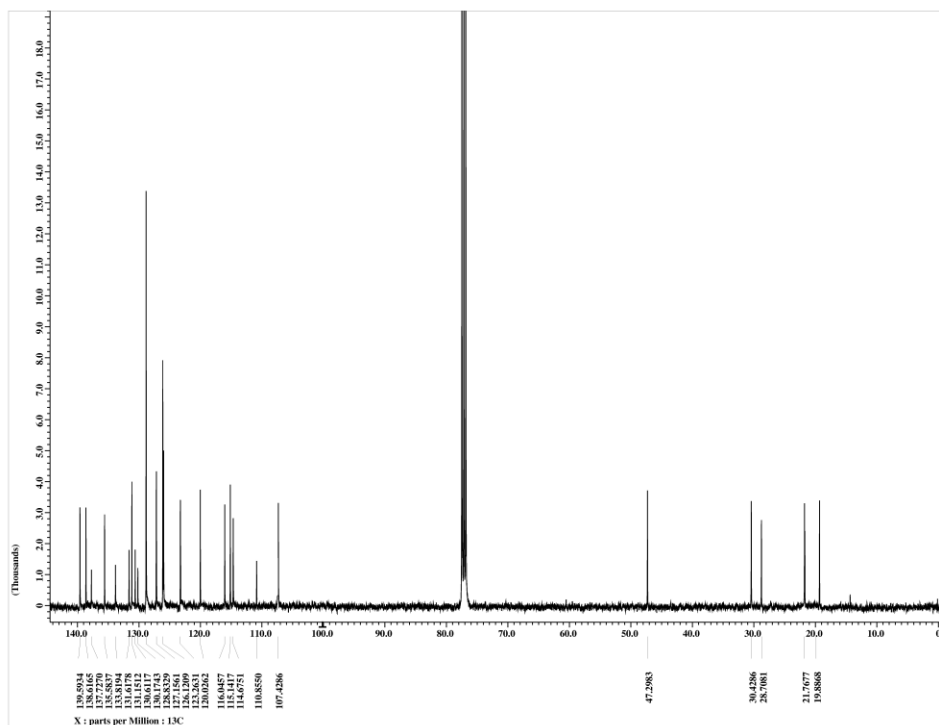
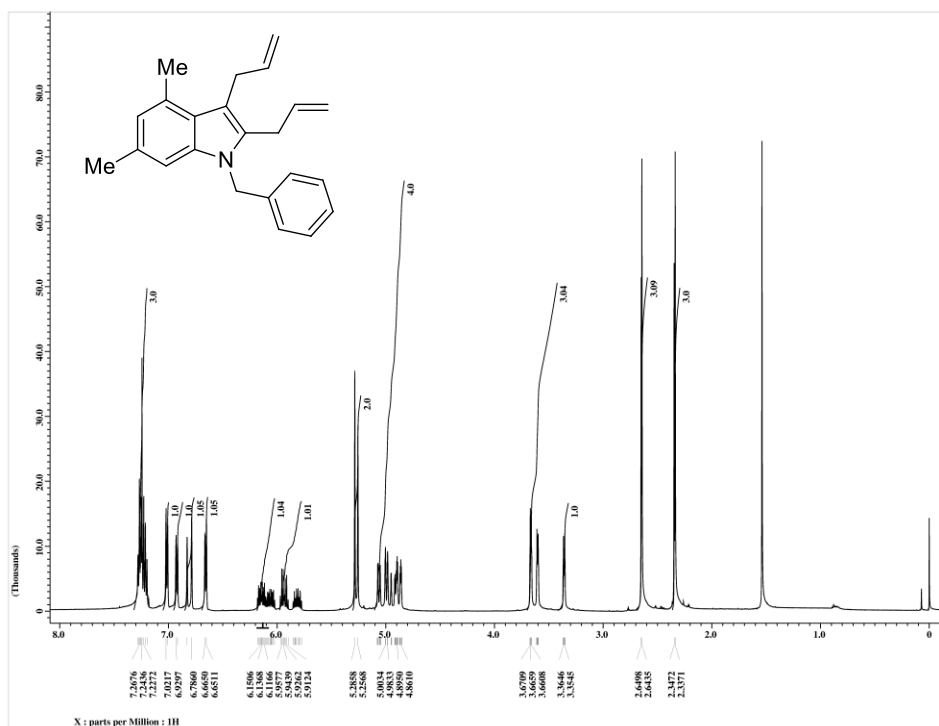
^1H and ^{13}C NMR of 4m:



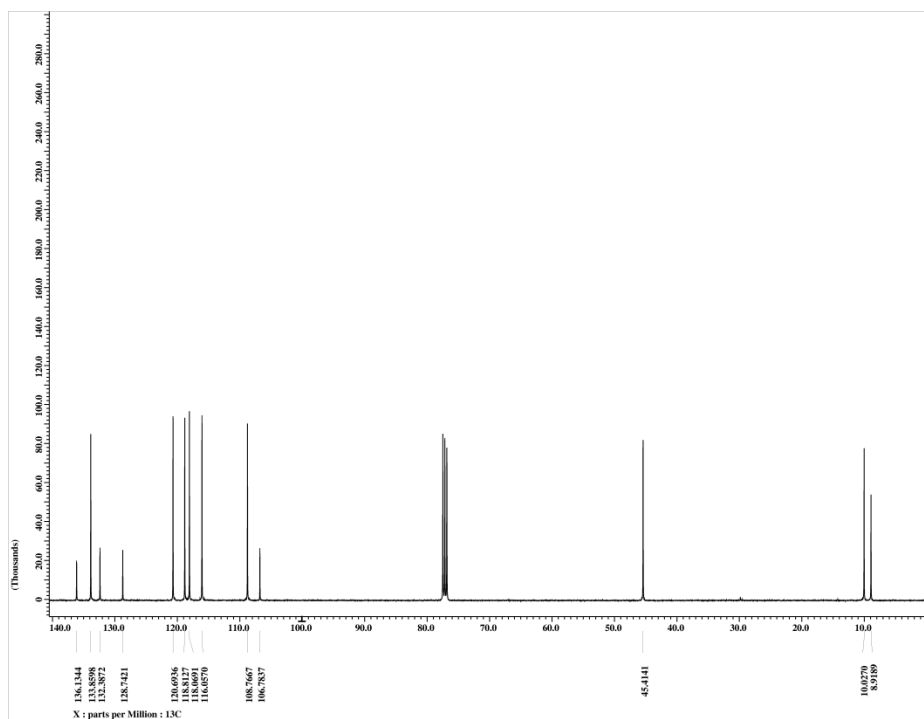
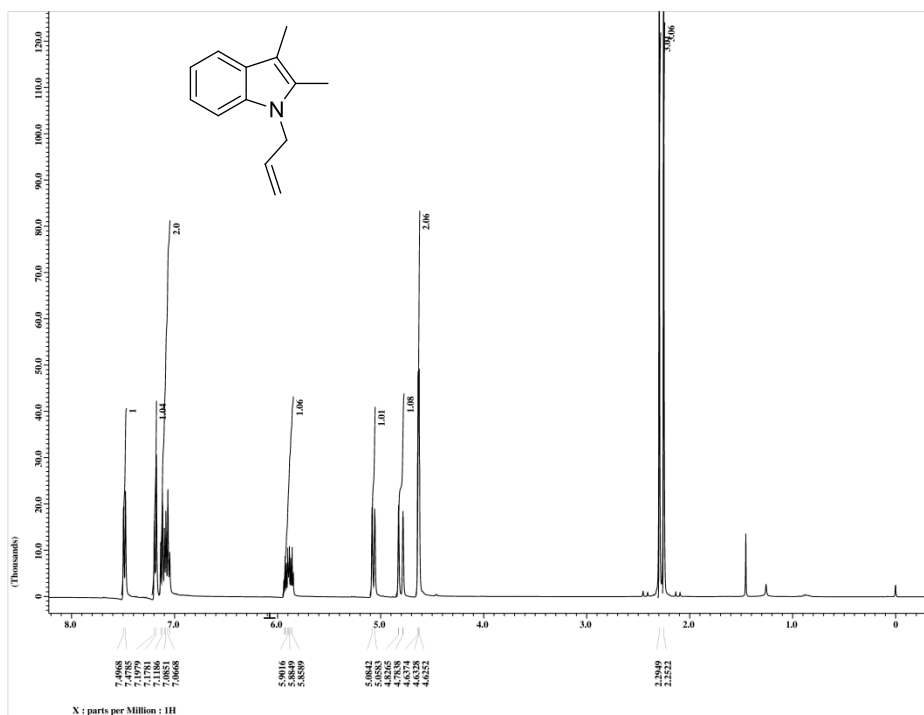
^1H and ^{13}C NMR of 4n:



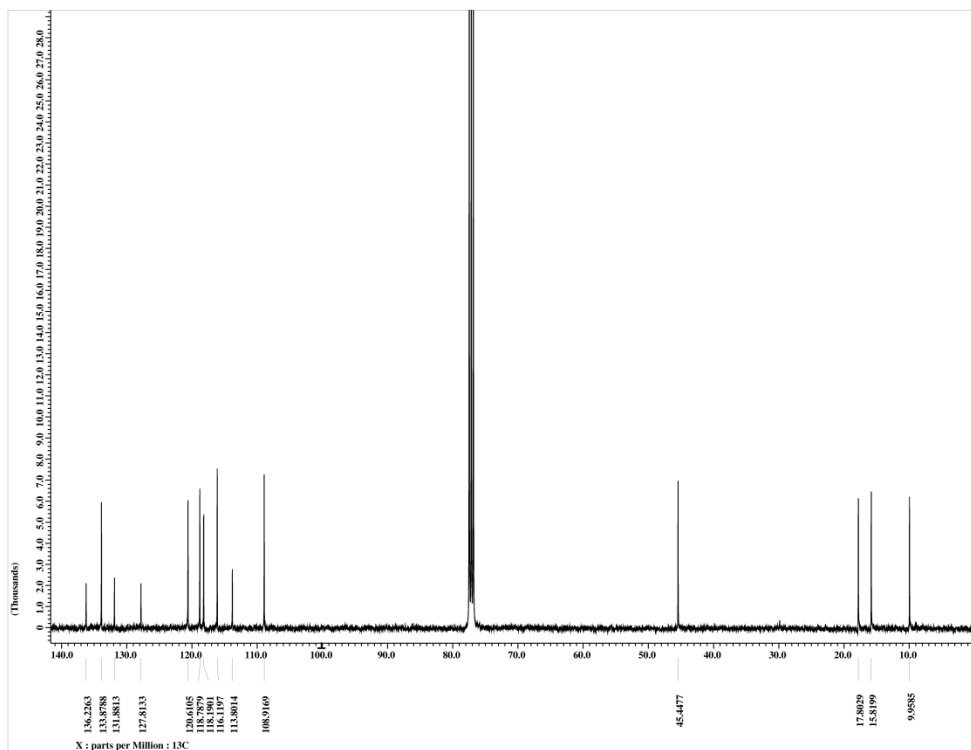
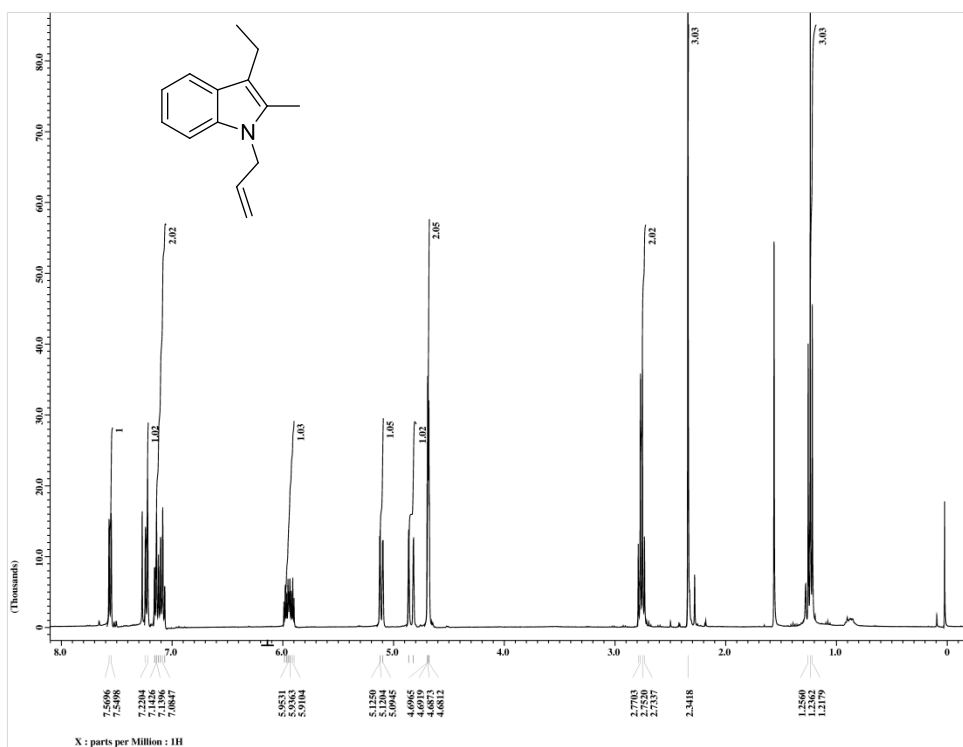
^1H and ^{13}C NMR of 4o:



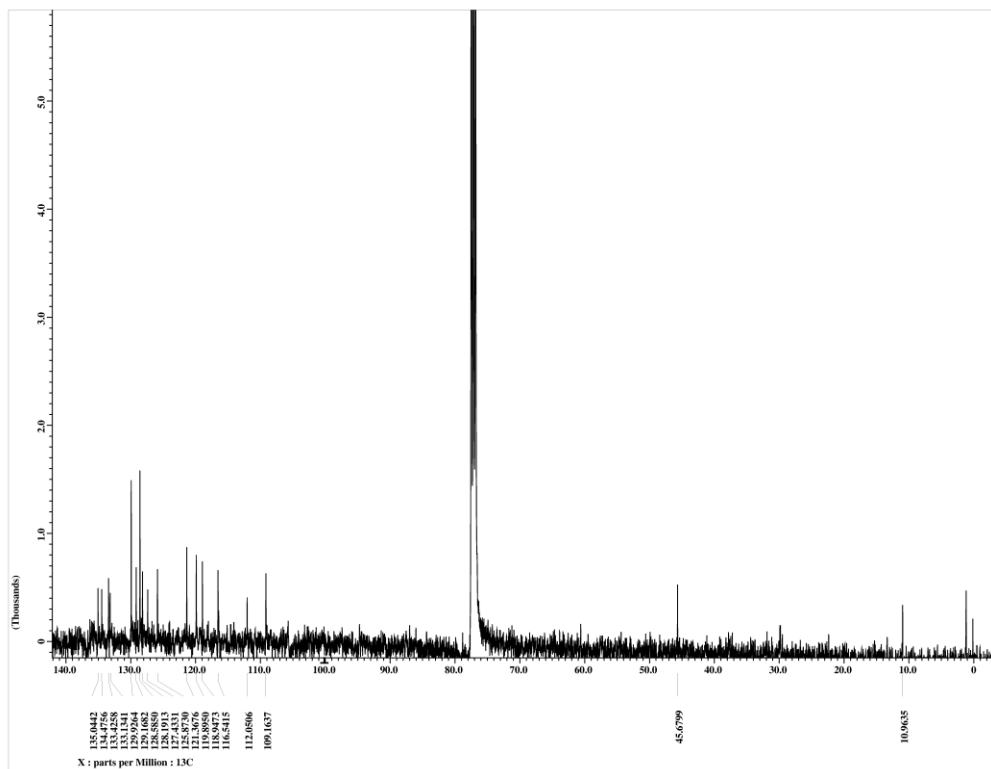
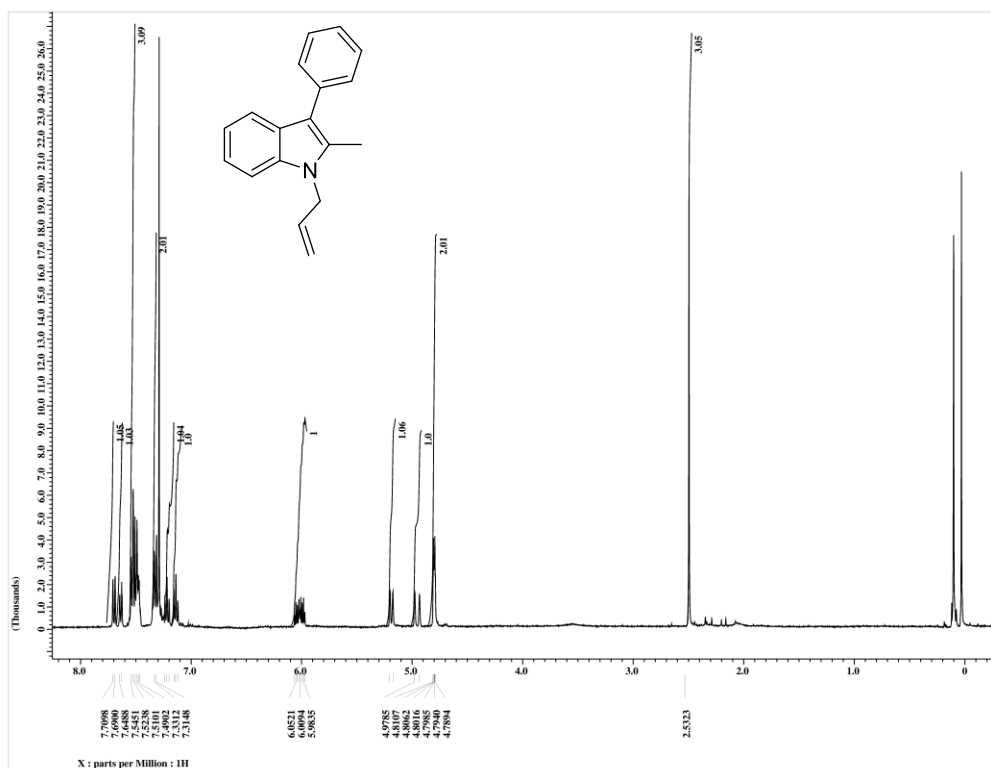
^1H and ^{13}C NMR of 4p:



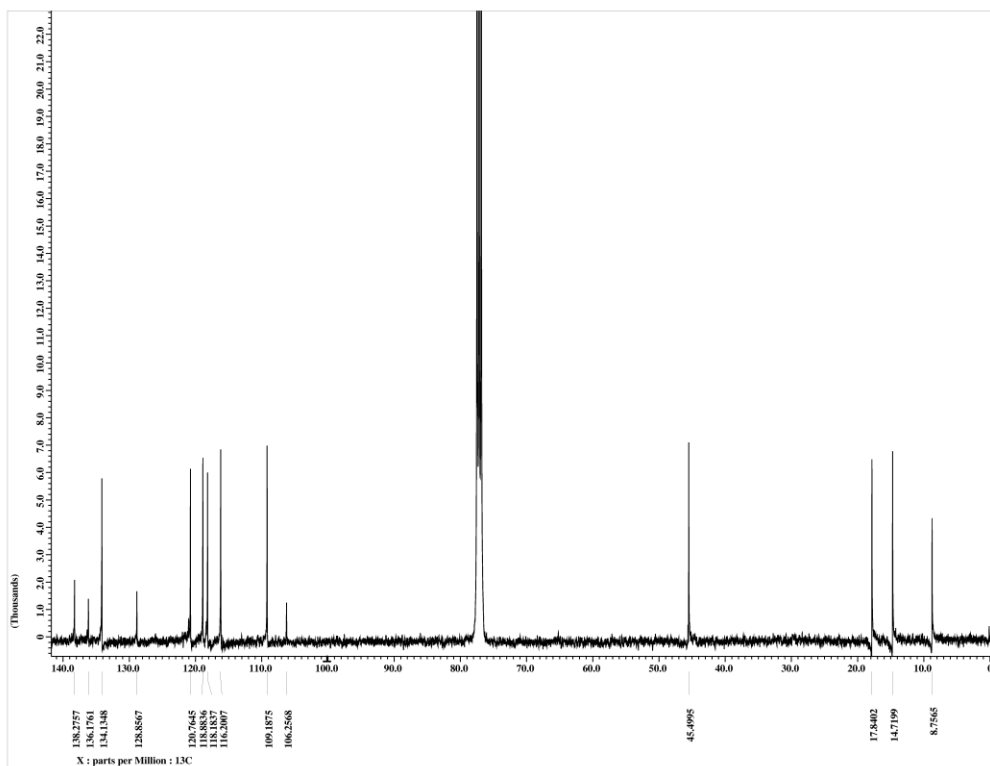
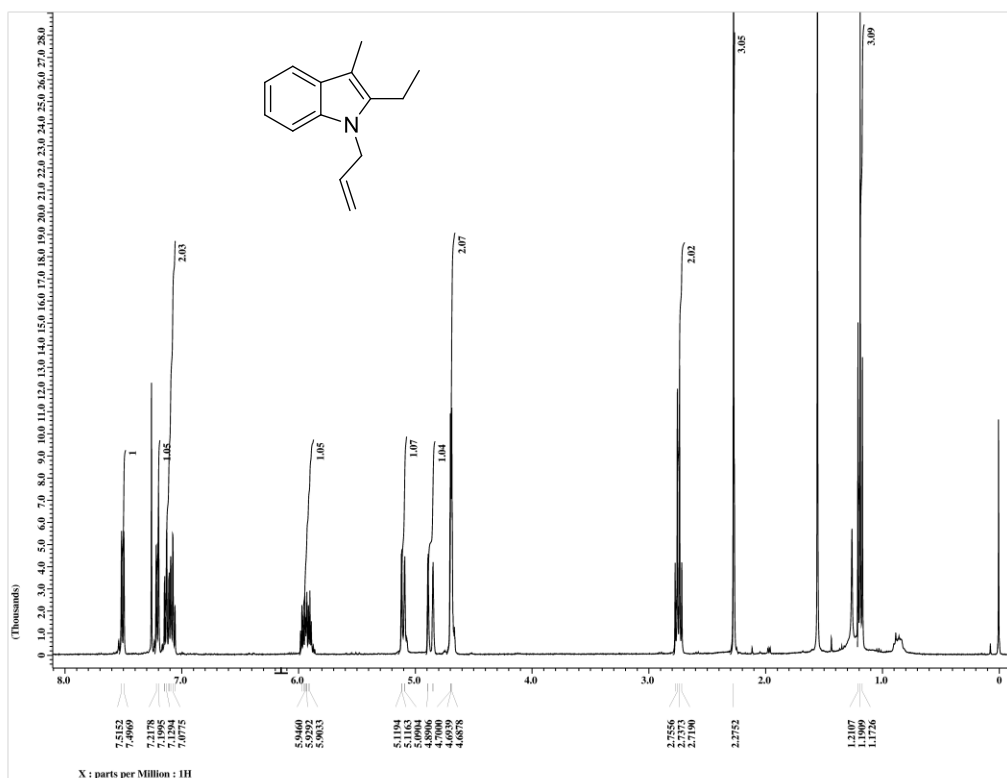
^1H and ^{13}C NMR of 4q:



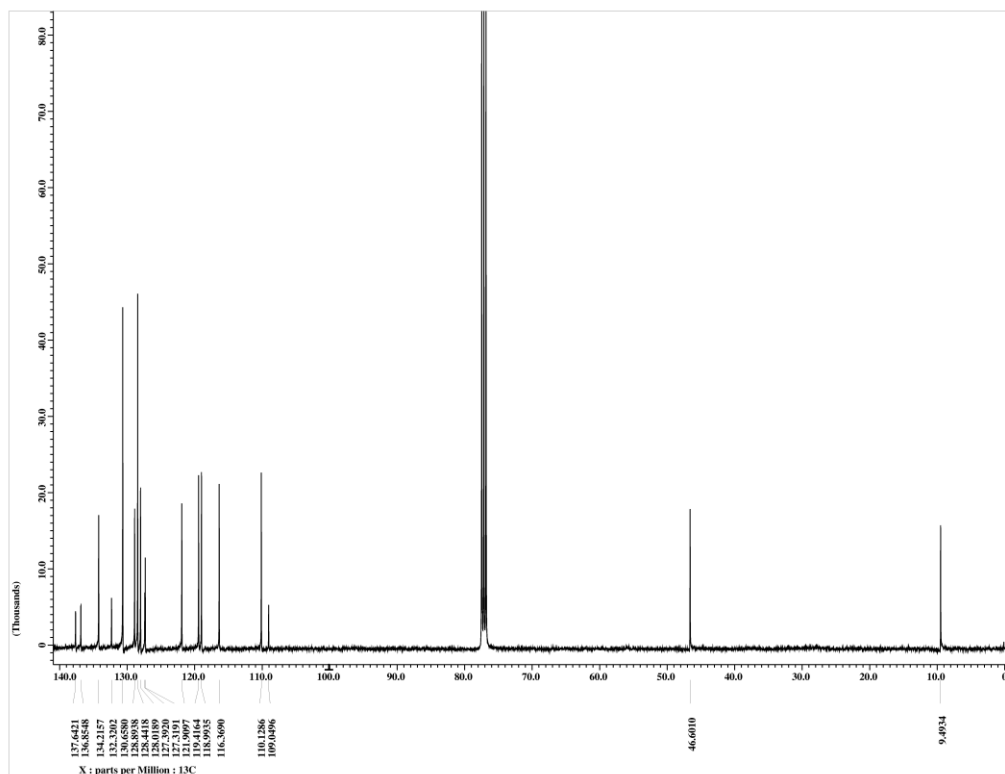
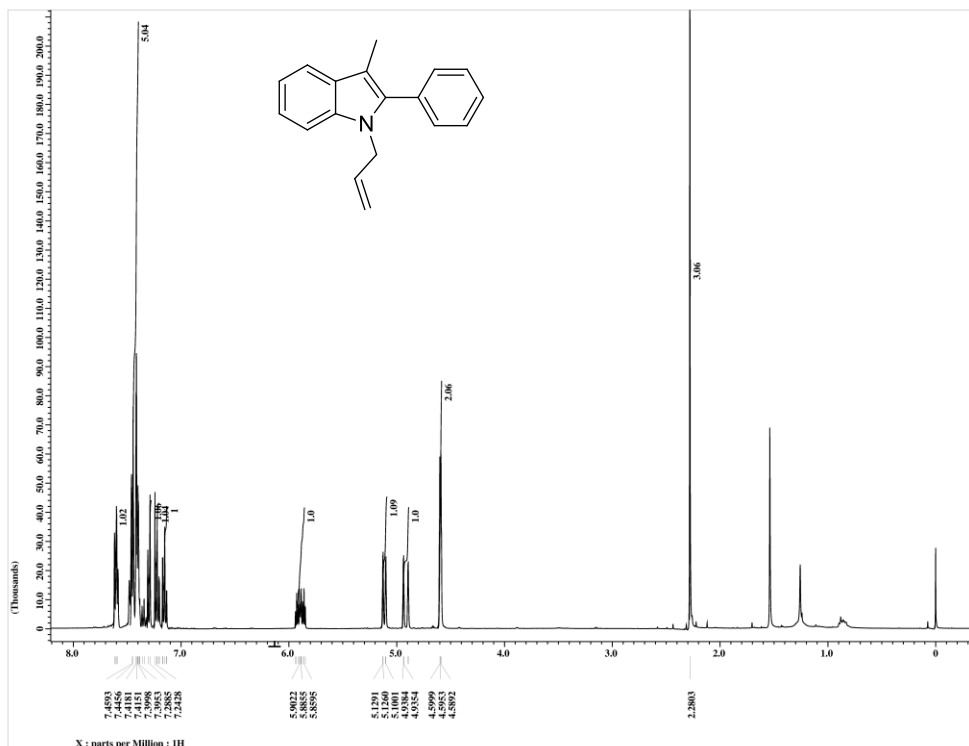
^1H and ^{13}C NMR of 4r:



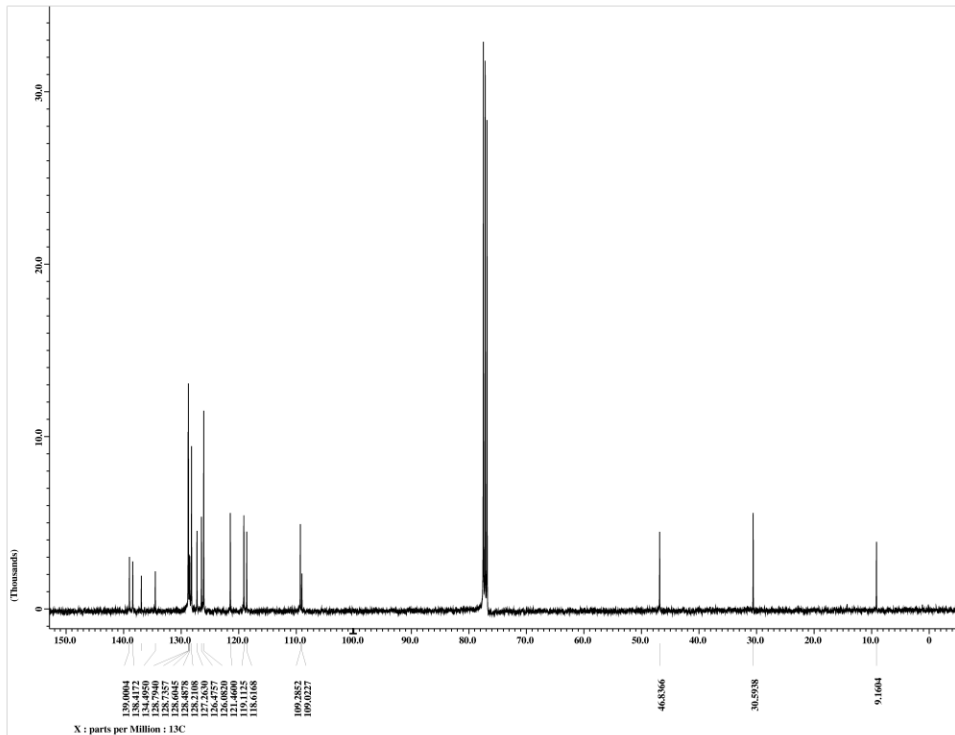
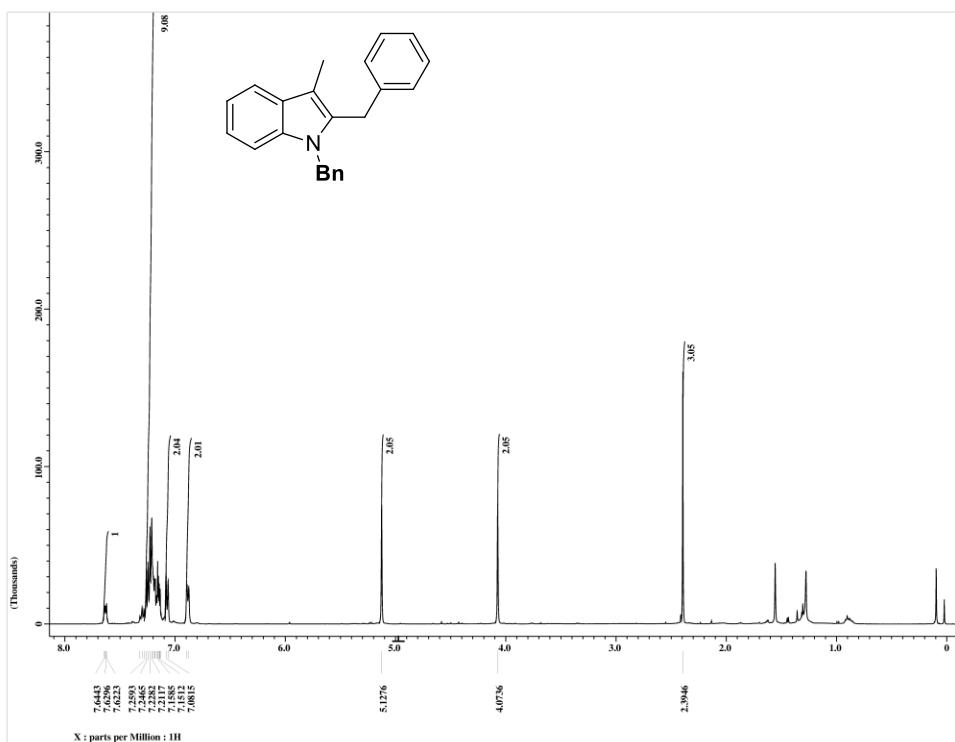
^1H and ^{13}C NMR of 4s:



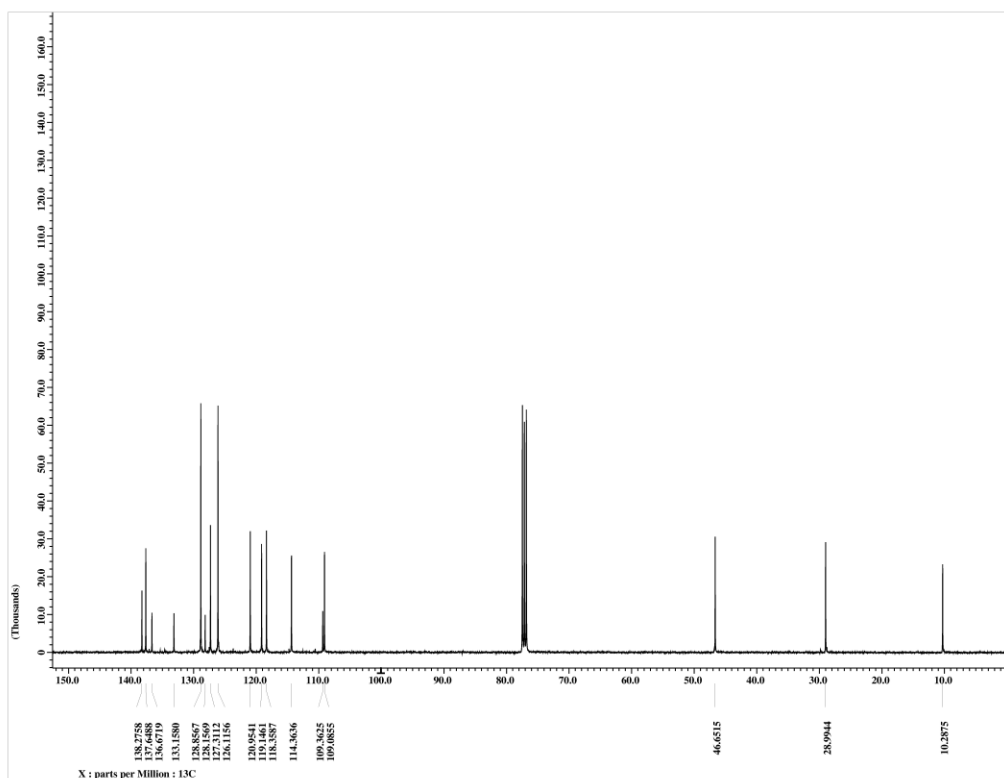
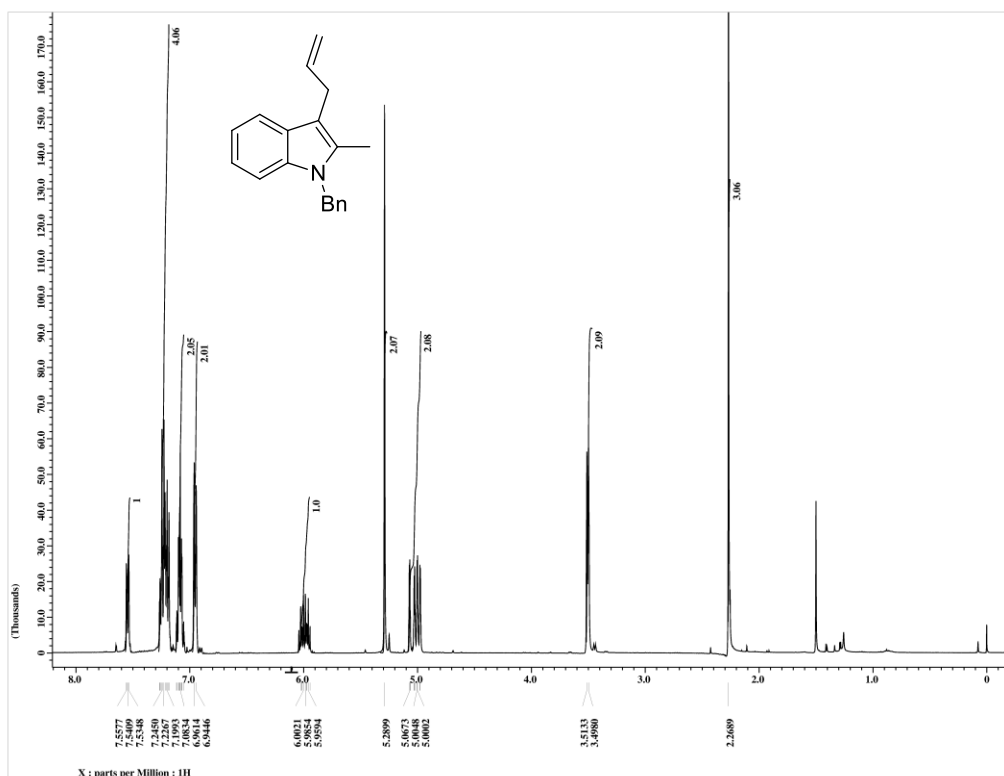
^1H and ^{13}C NMR of 4t:



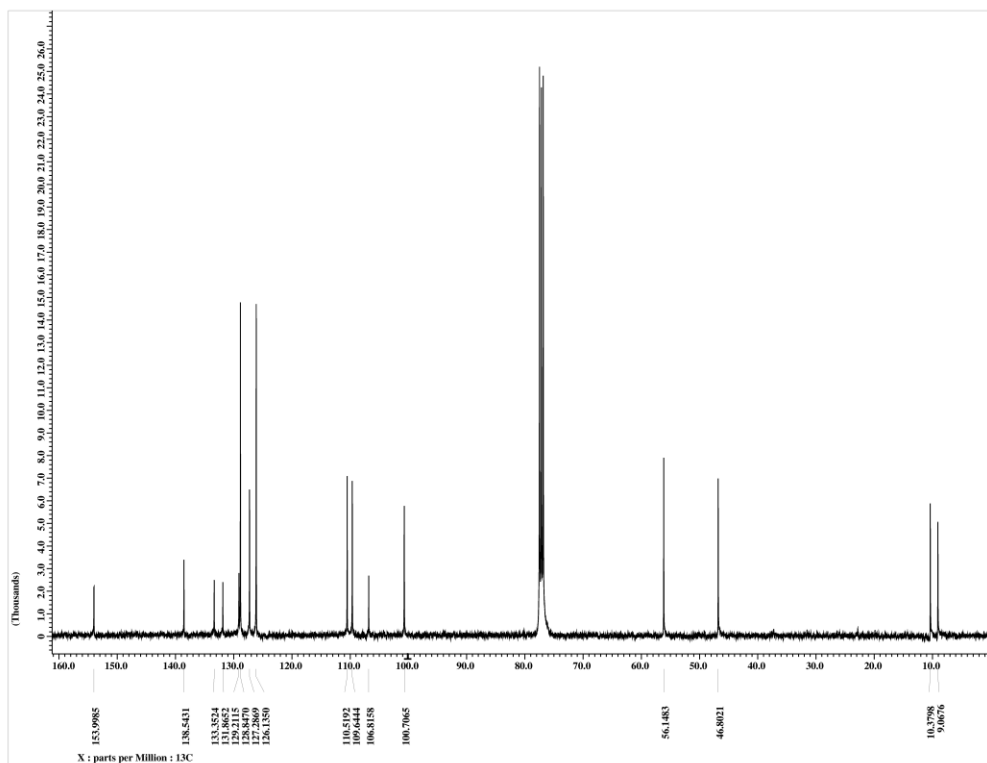
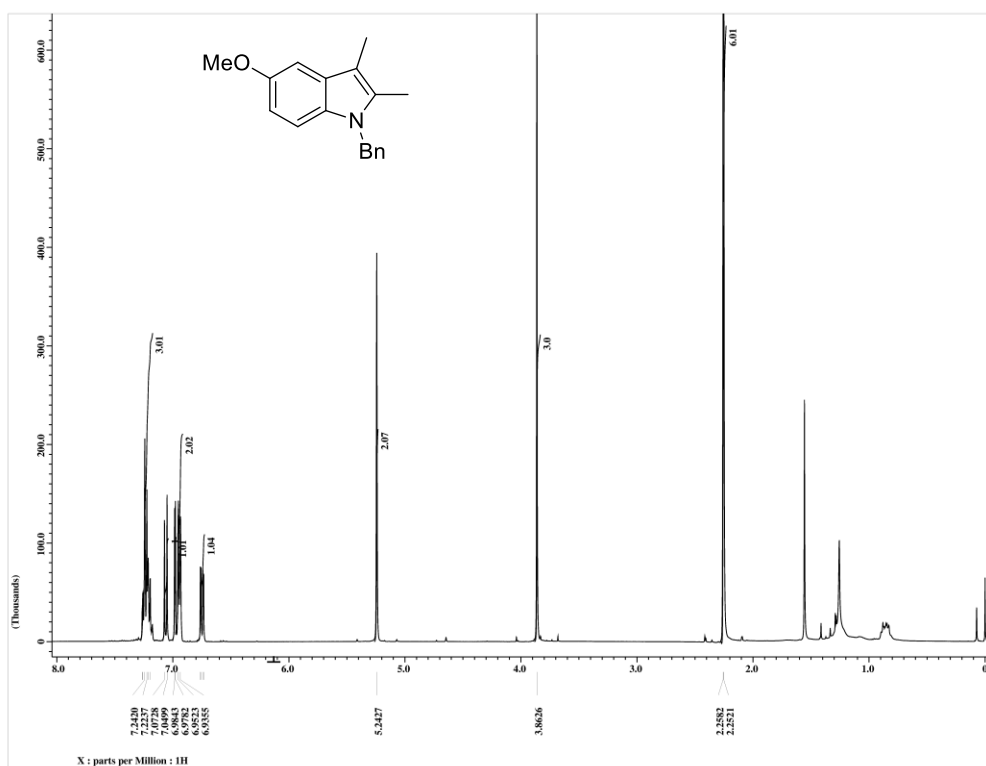
^1H and ^{13}C NMR of 4u:



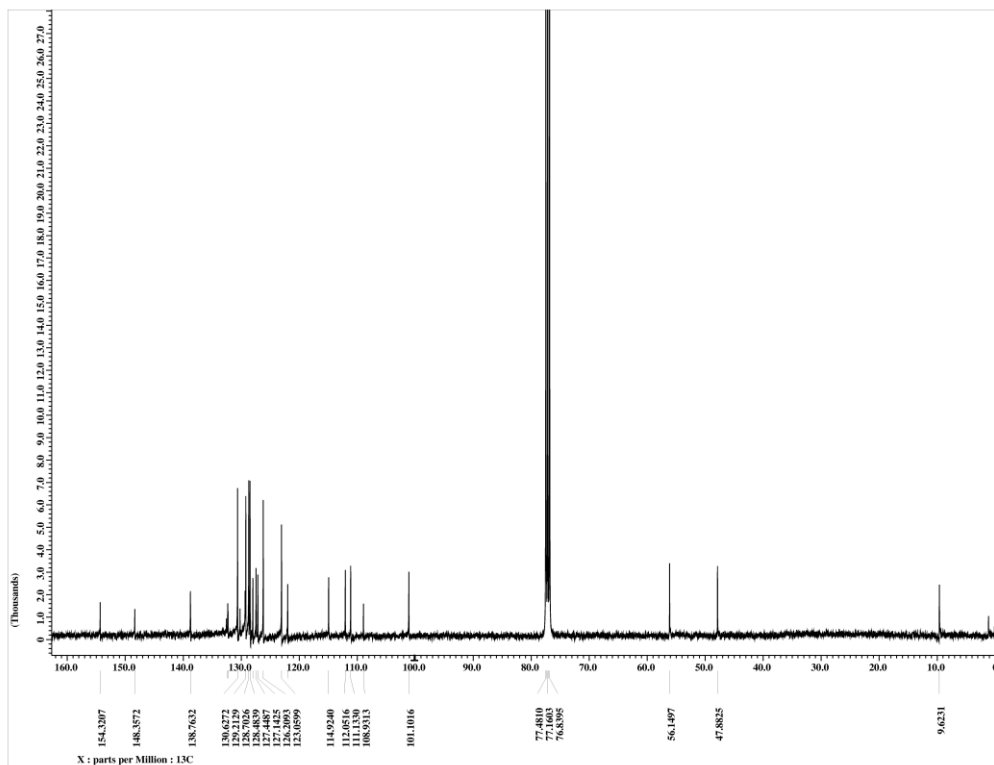
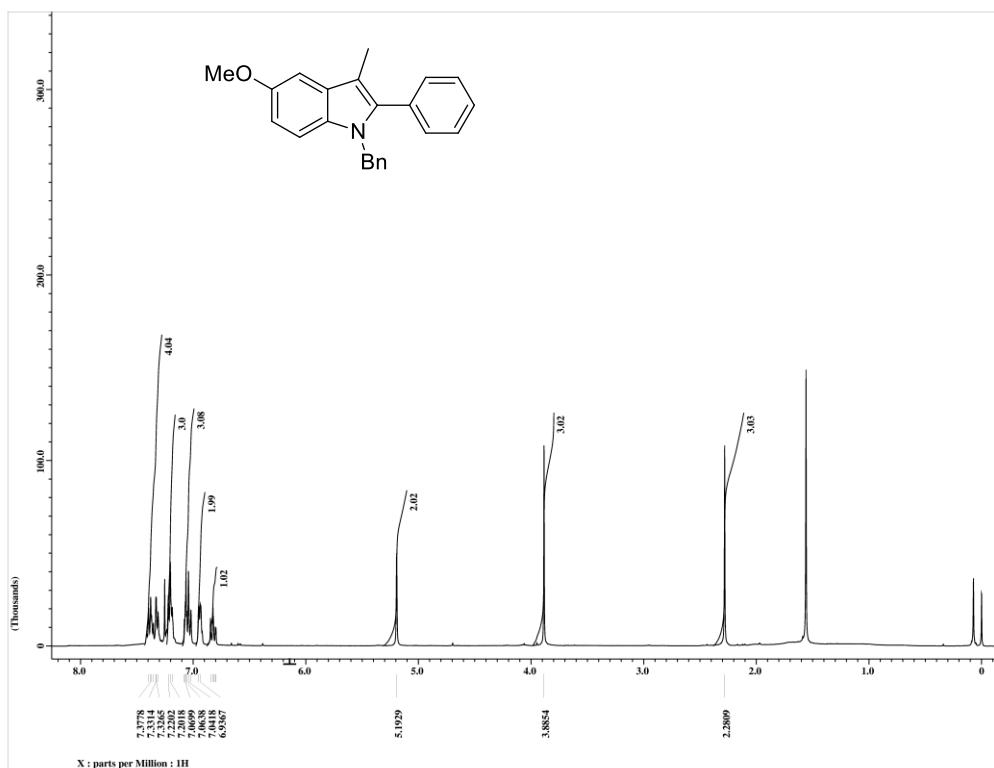
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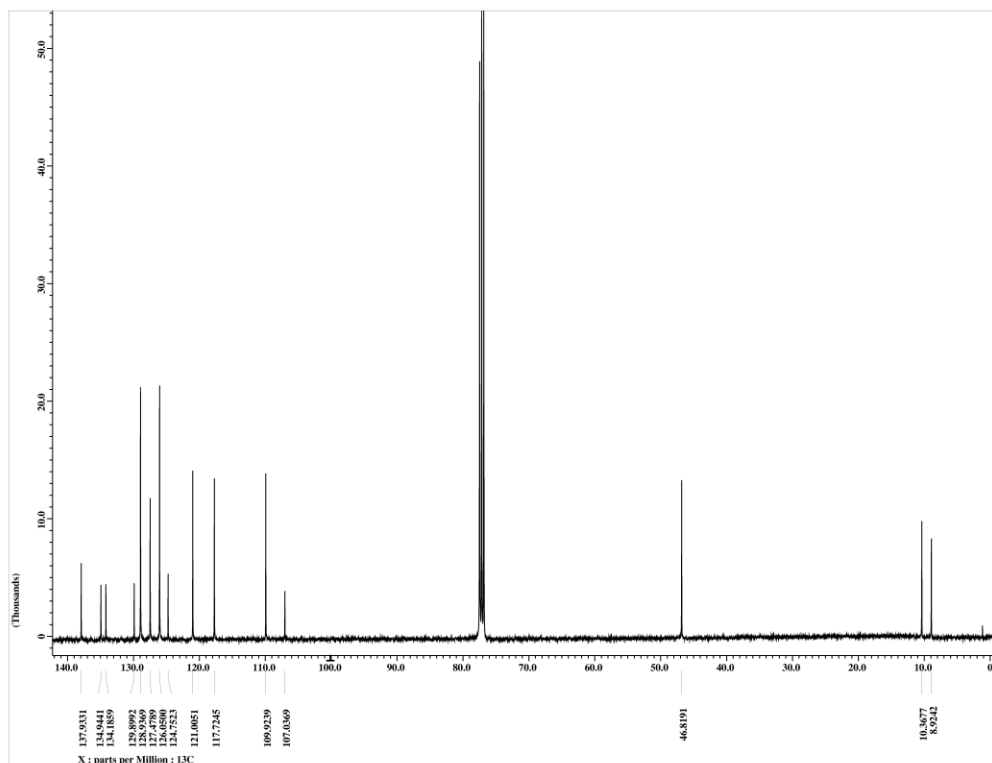
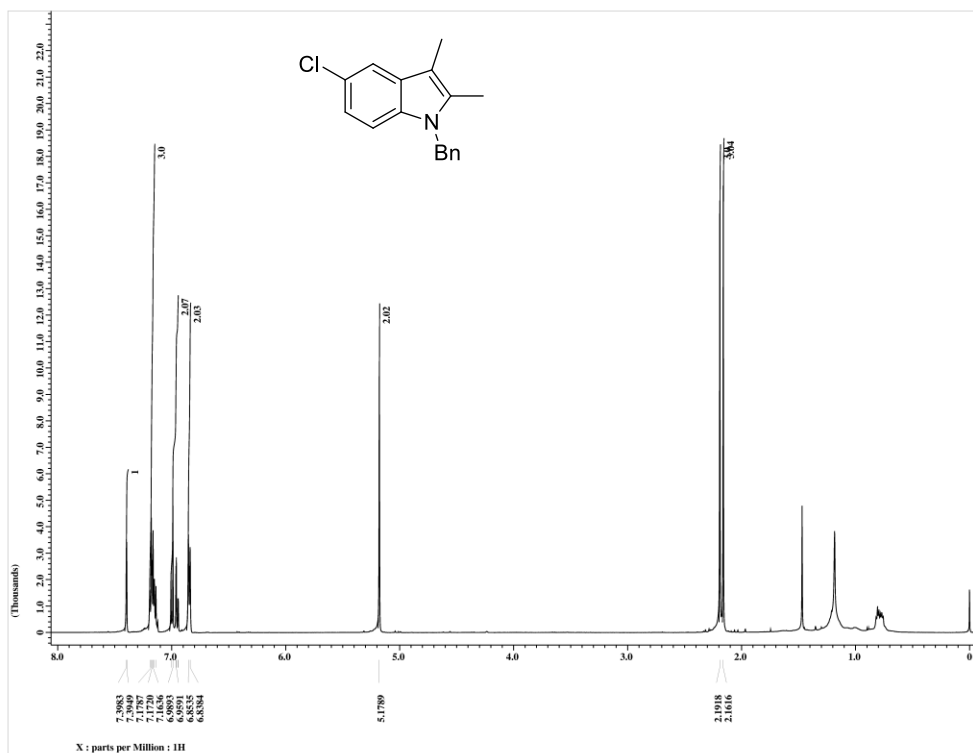
^1H and ^{13}C NMR of 4w:



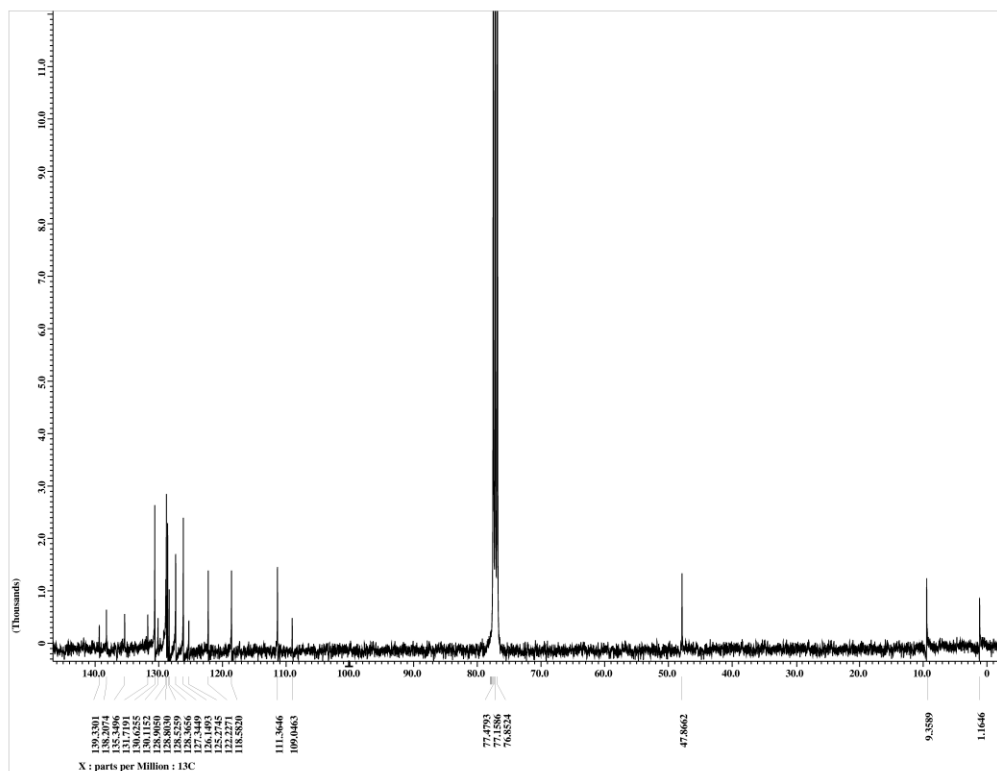
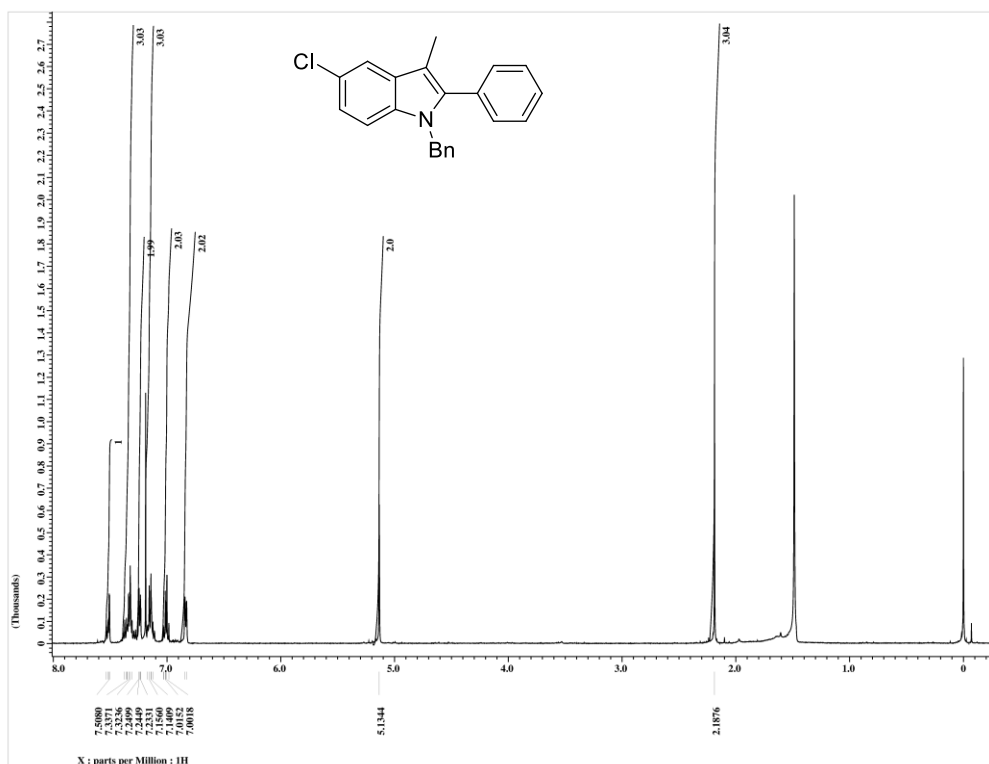
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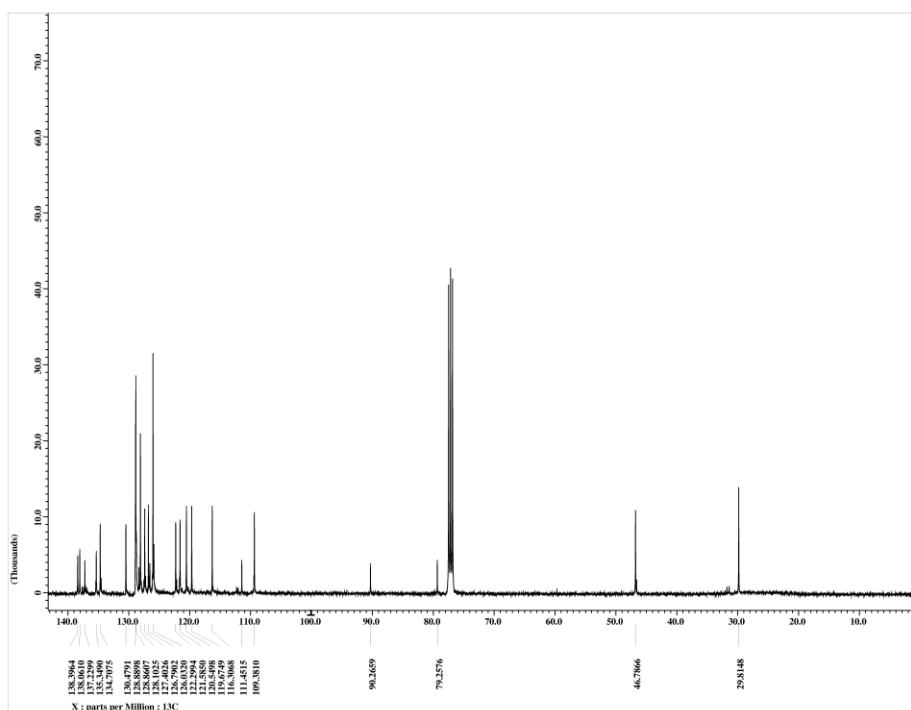
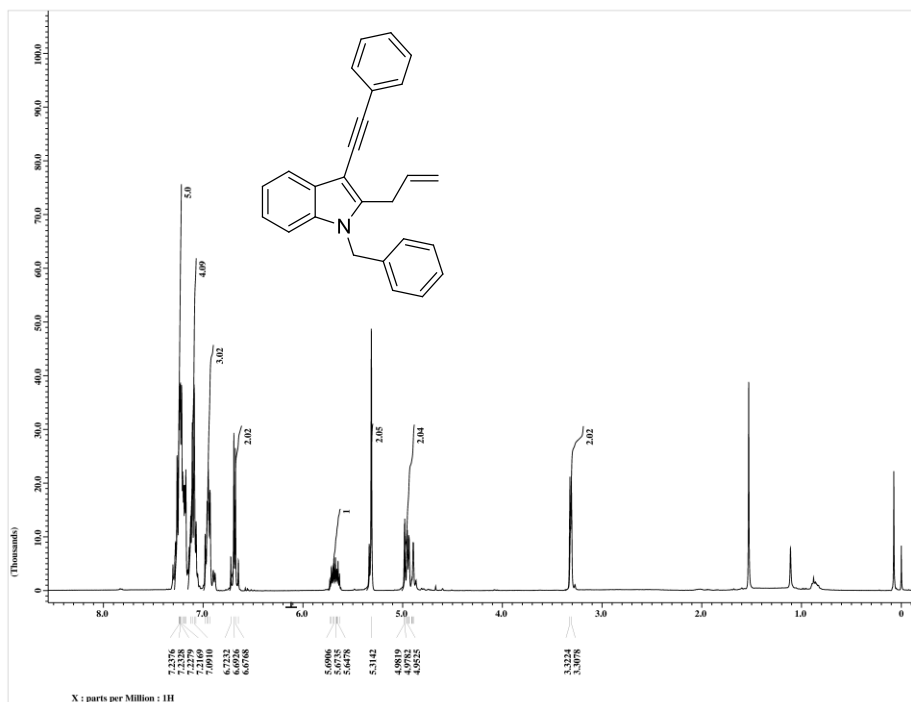
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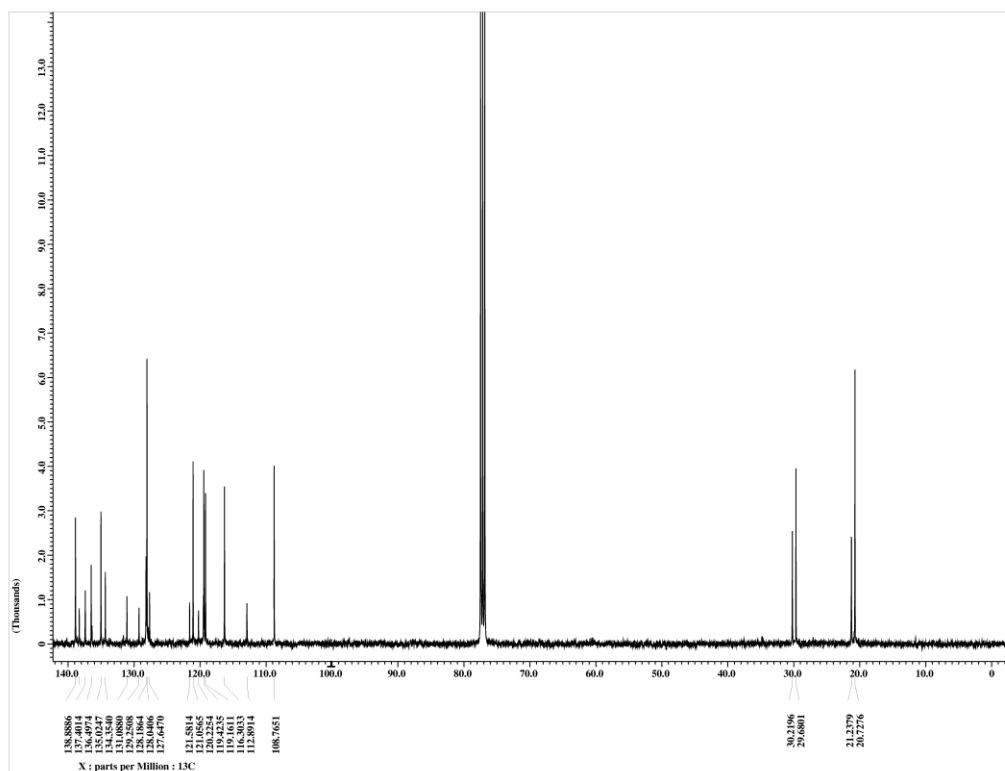
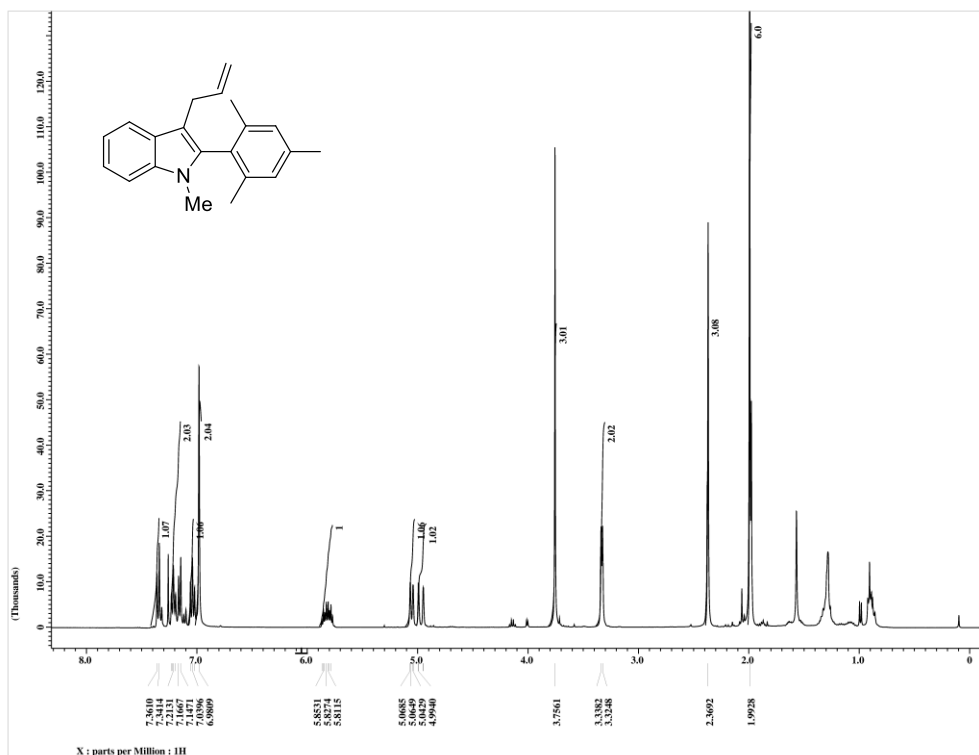
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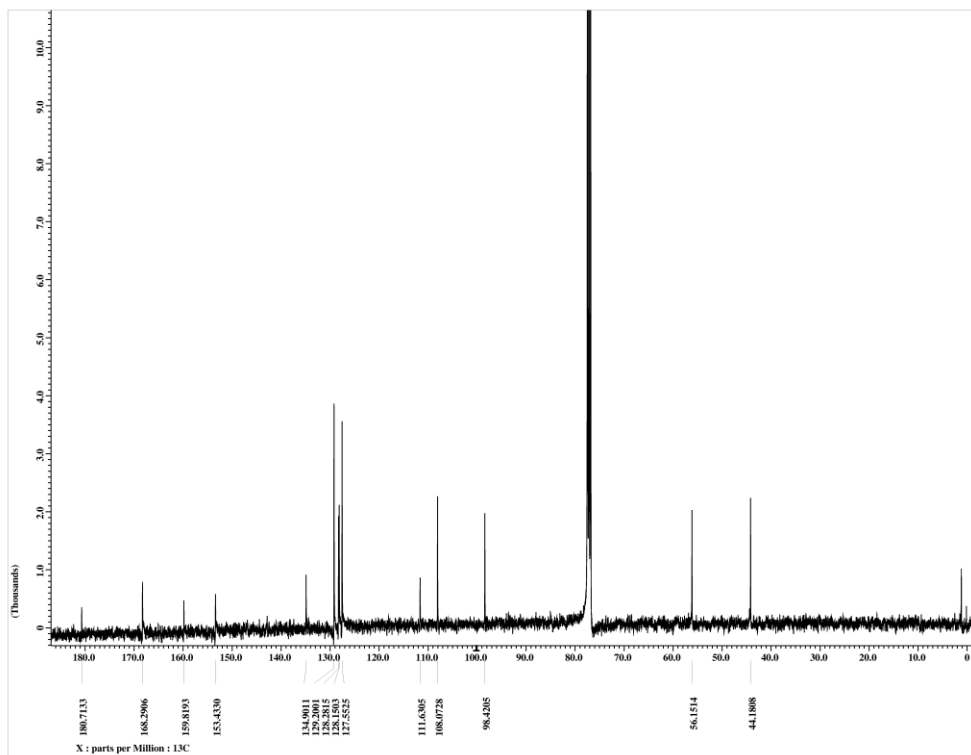
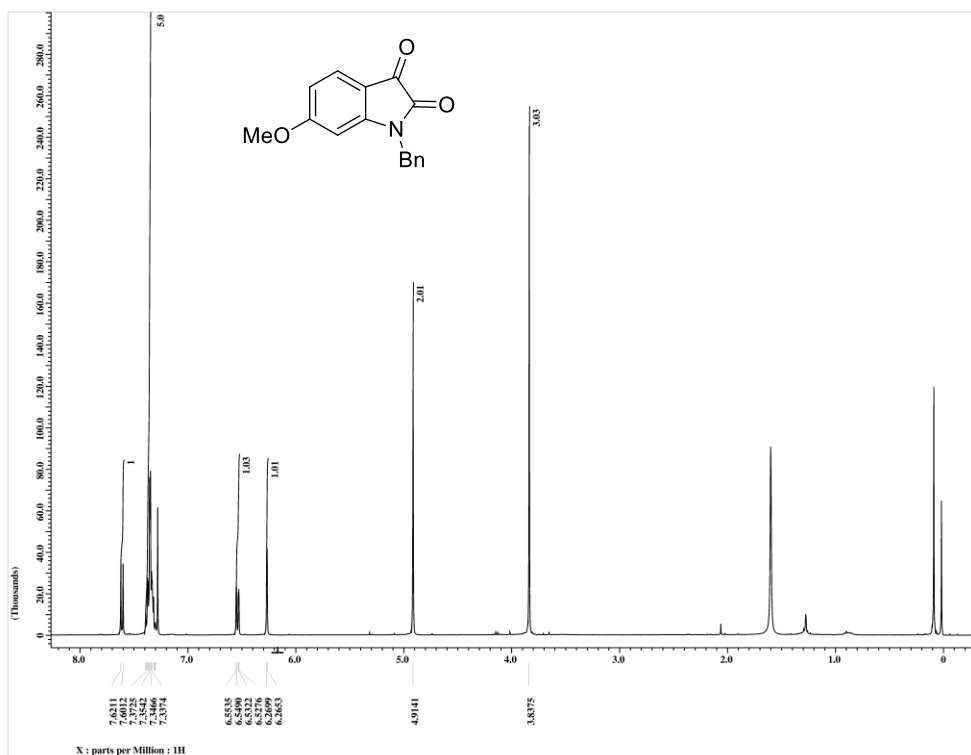
^1H and ^{13}C NMR of 4a':



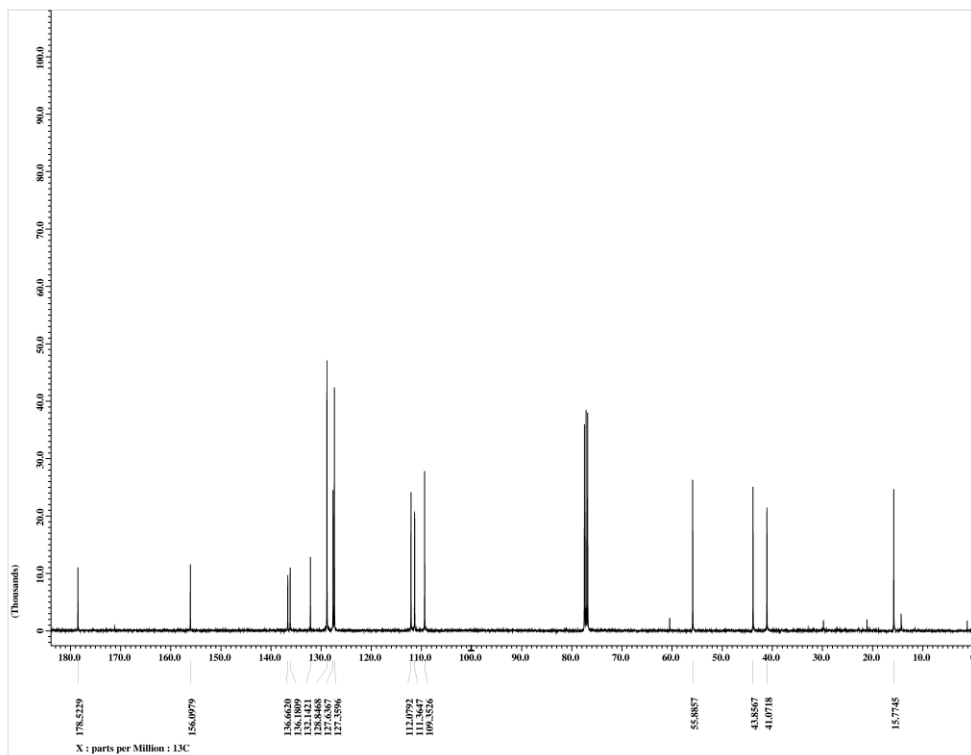
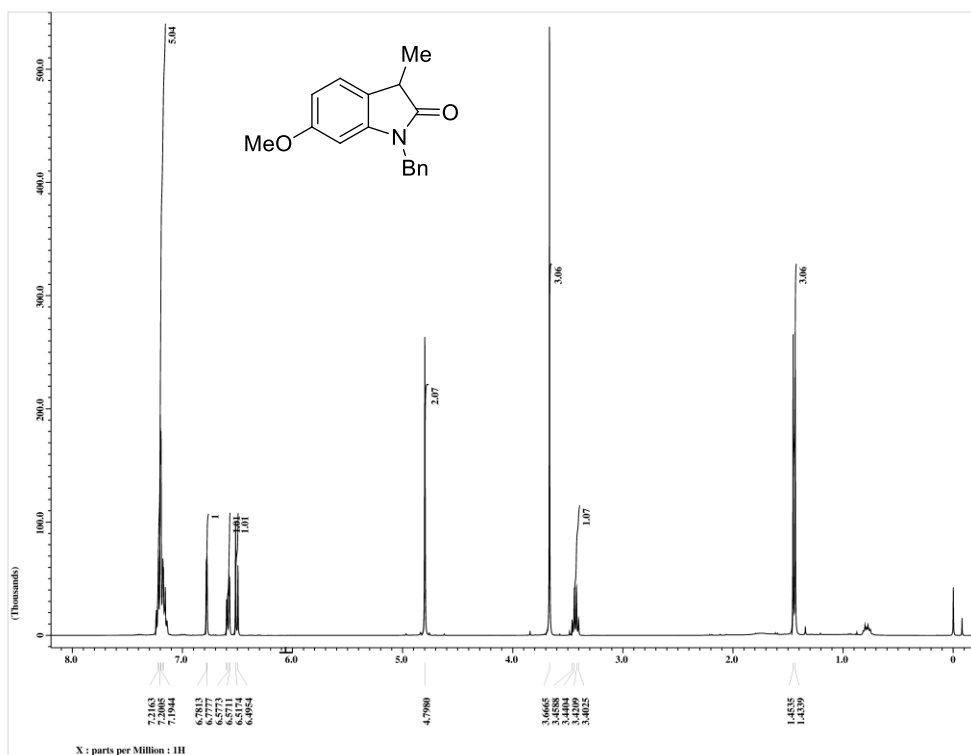
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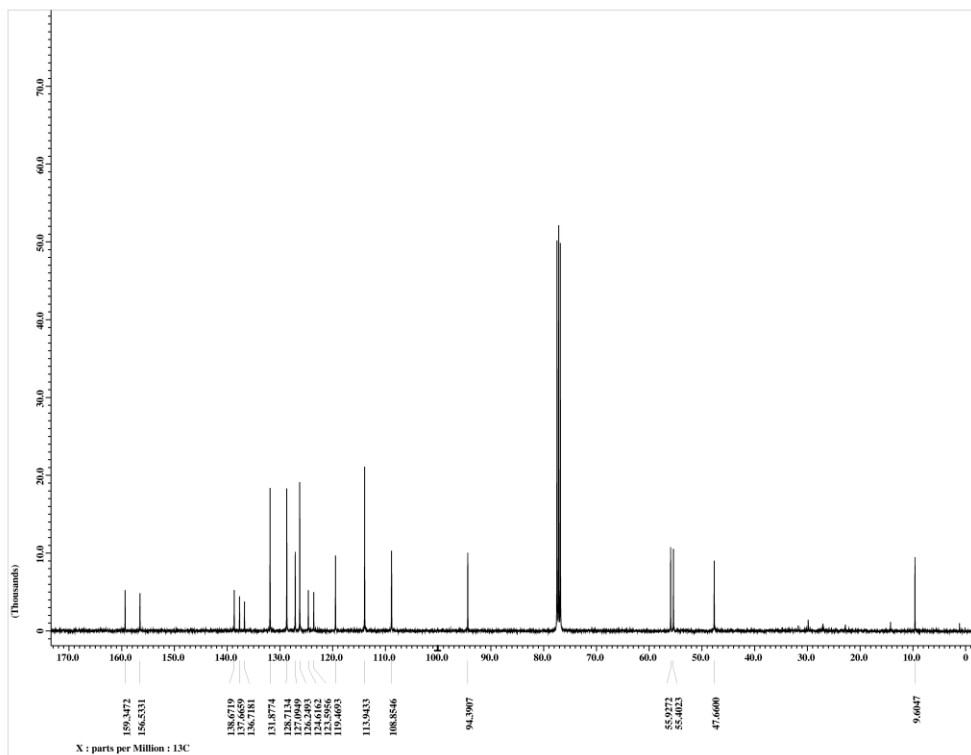
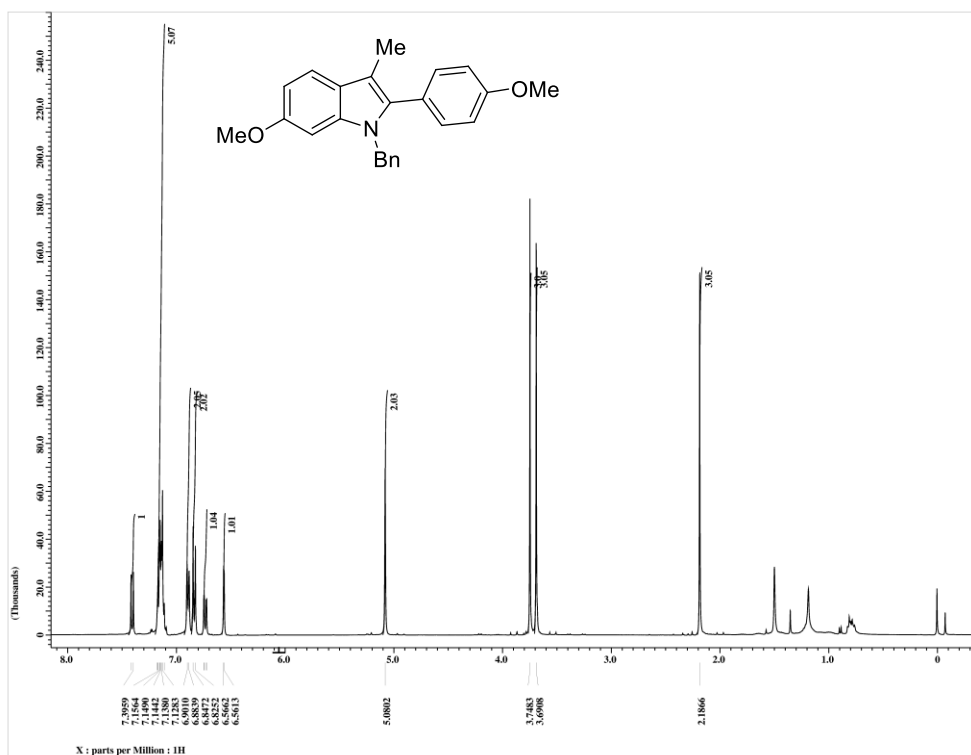
^1H and ^{13}C NMR of S2q:



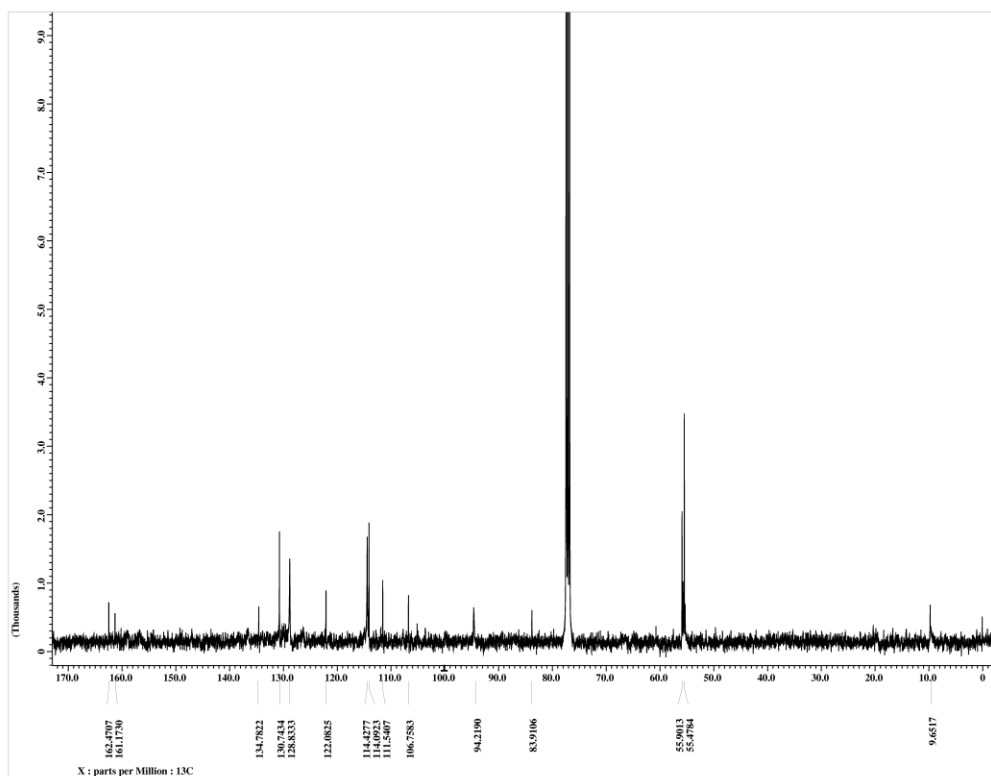
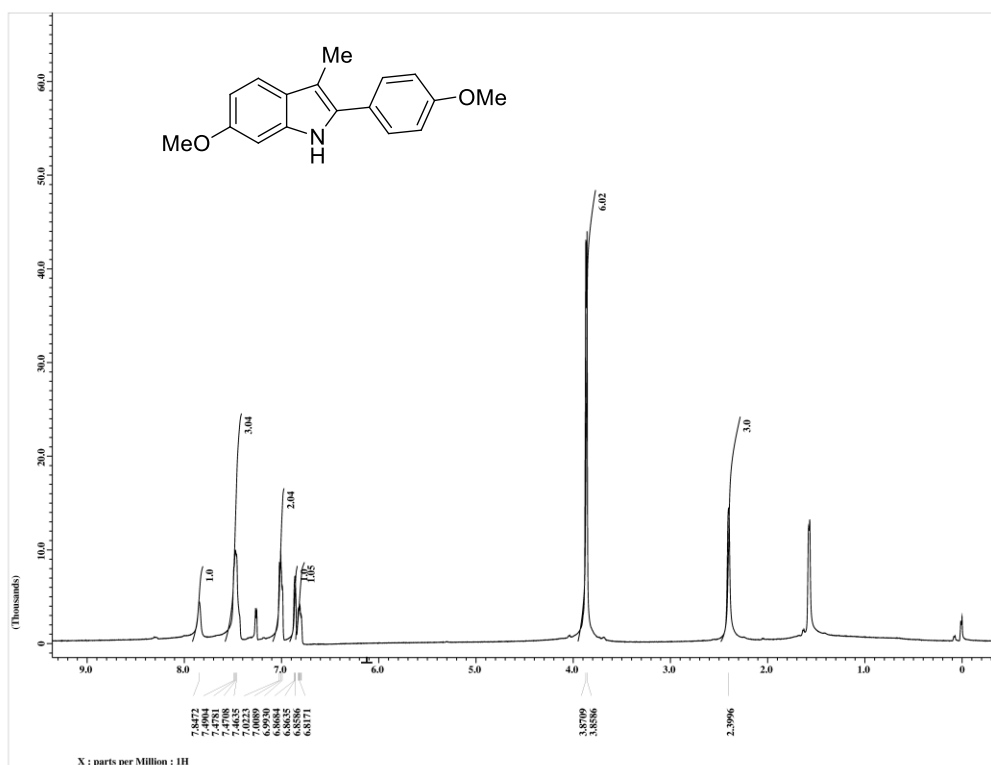
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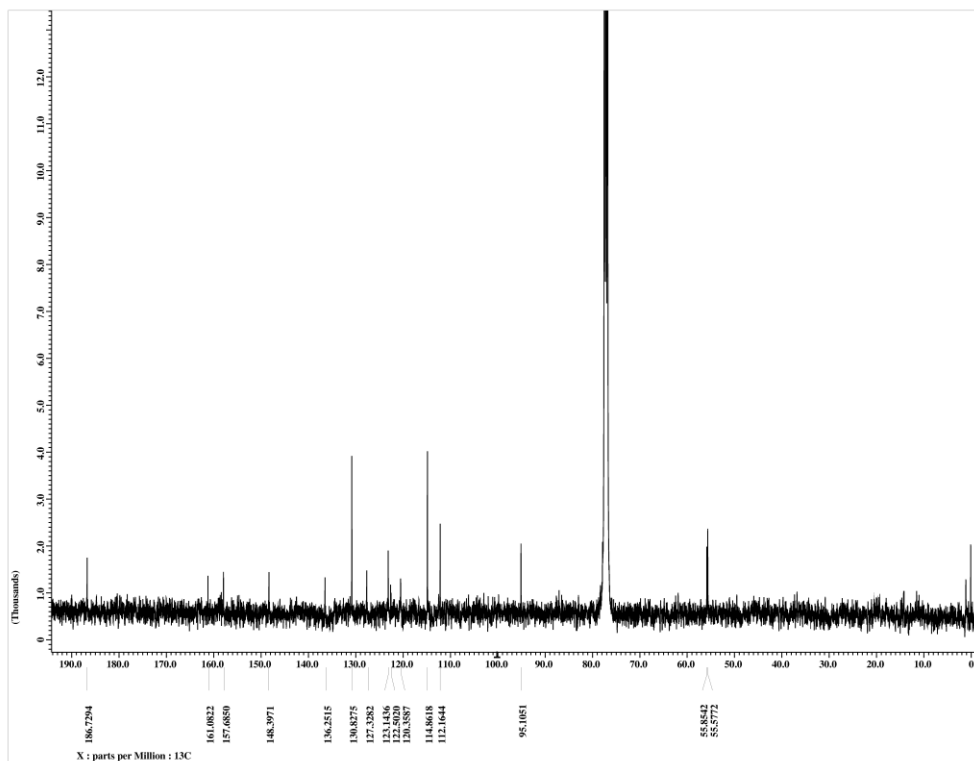
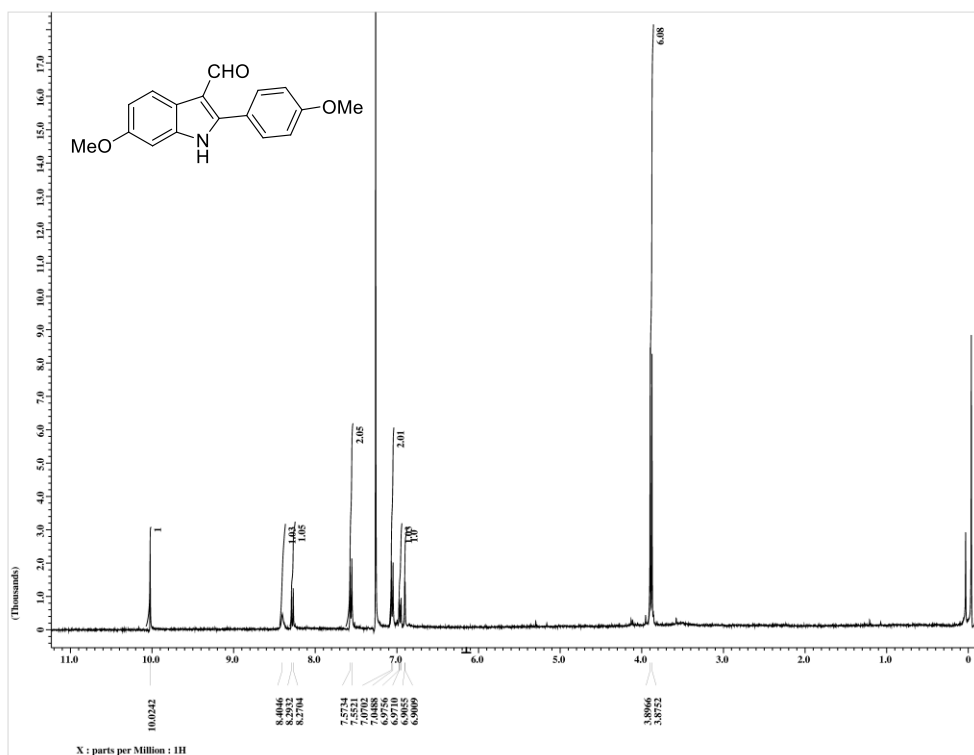
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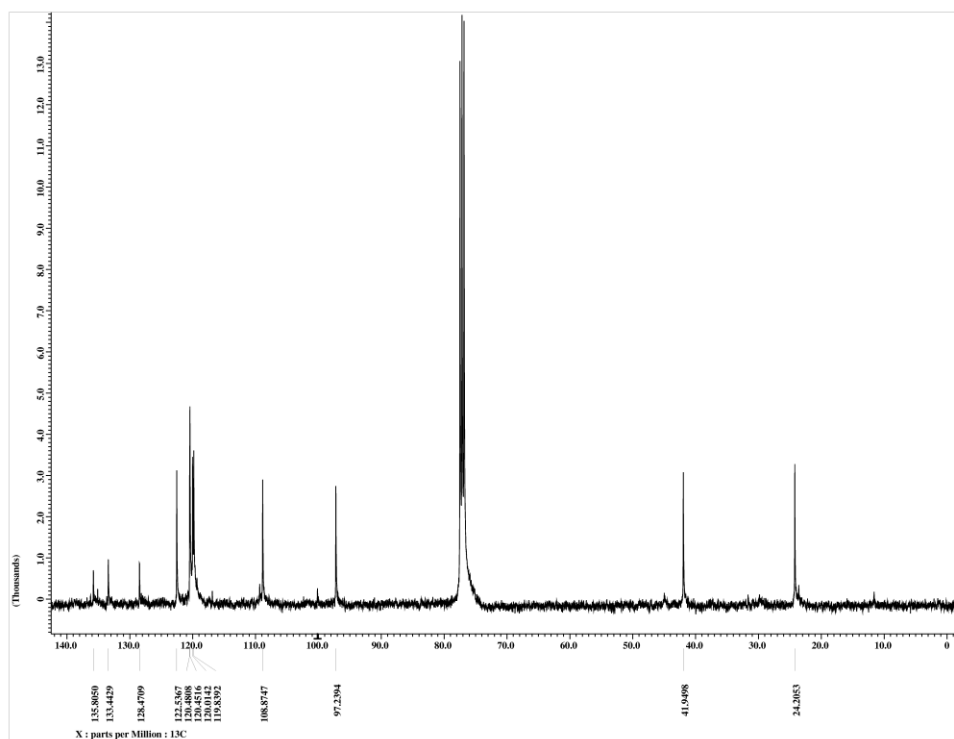
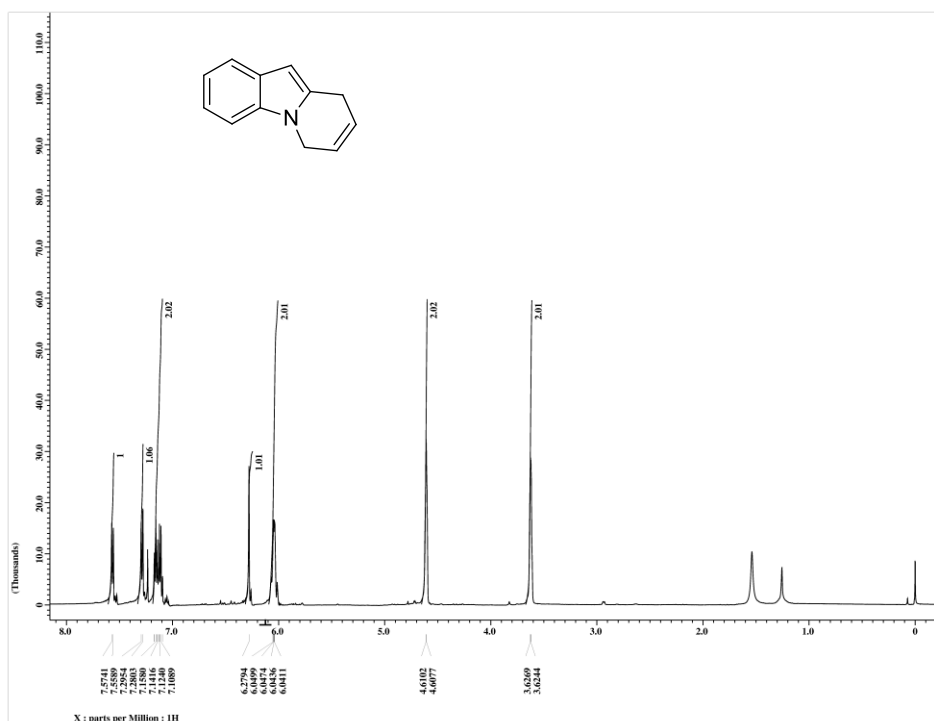
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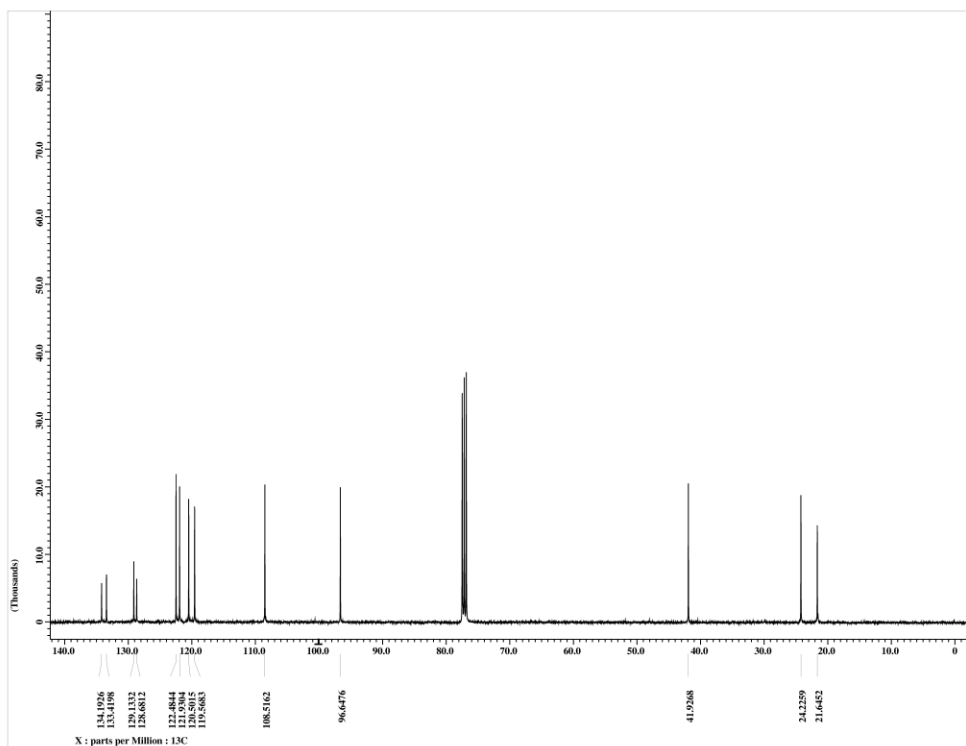
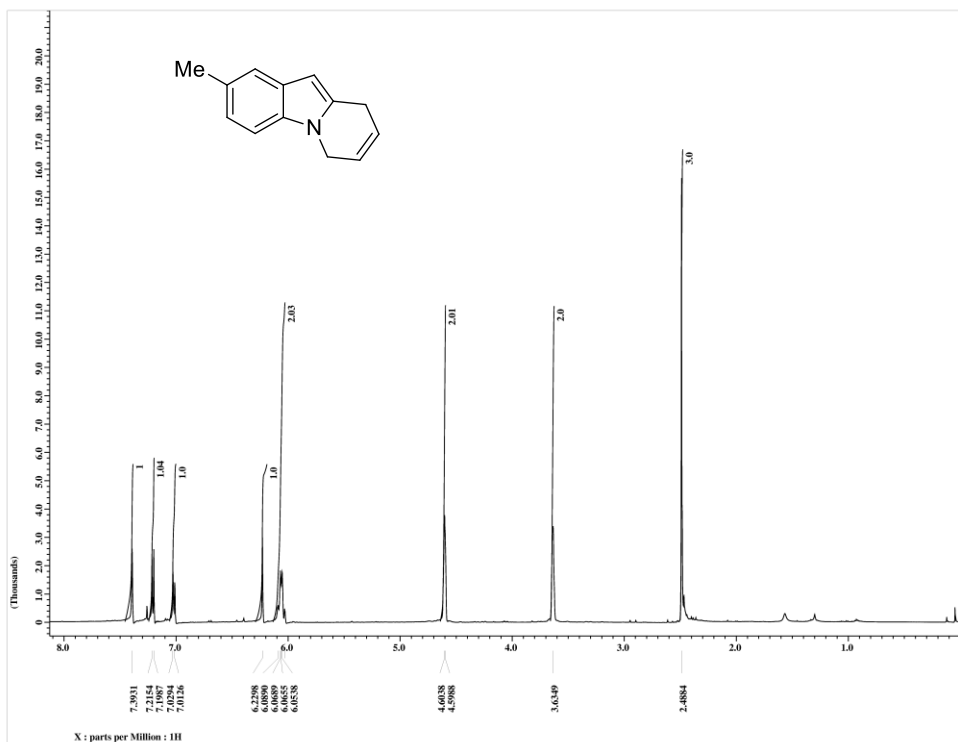
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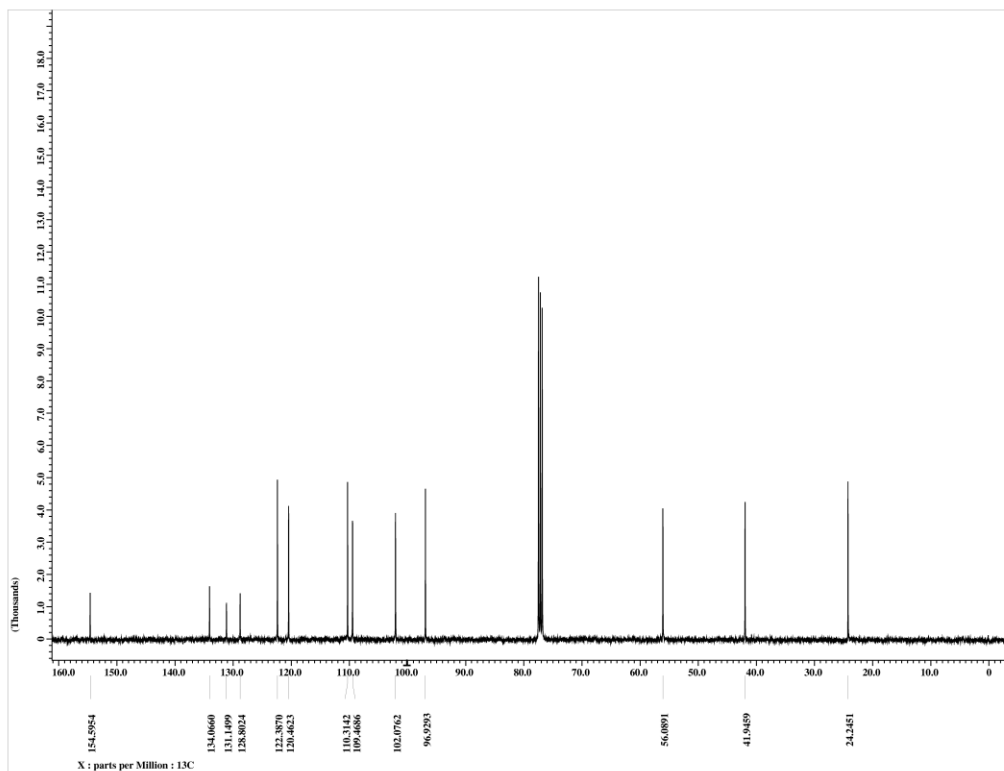
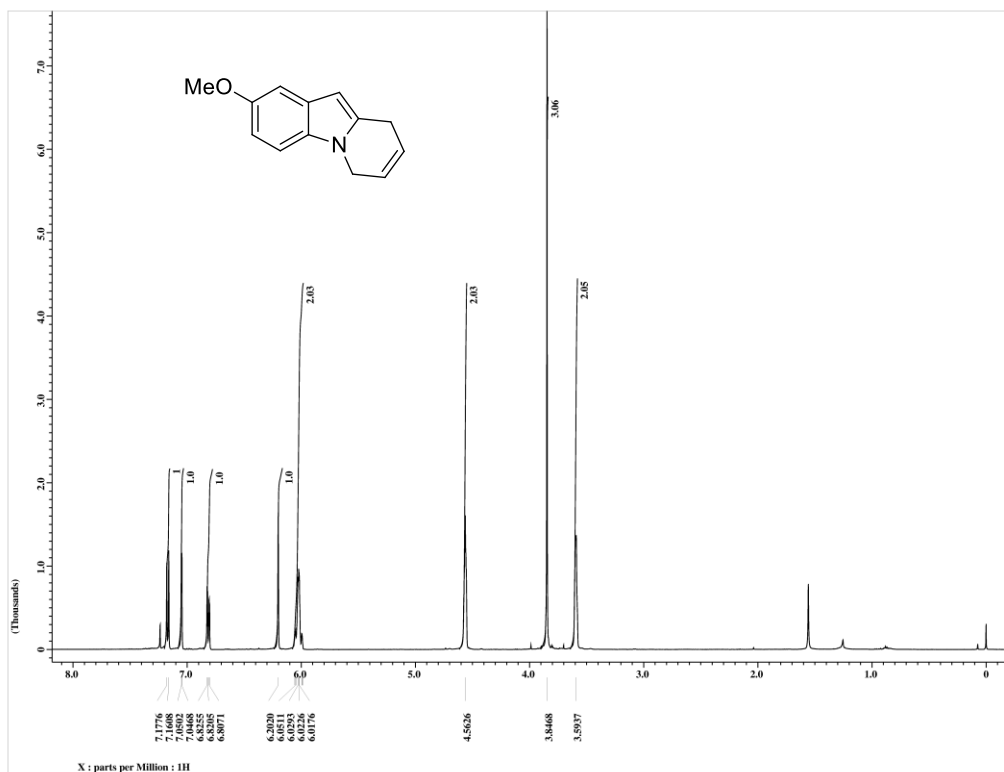
^1H and ^{13}C NMR of 5a:



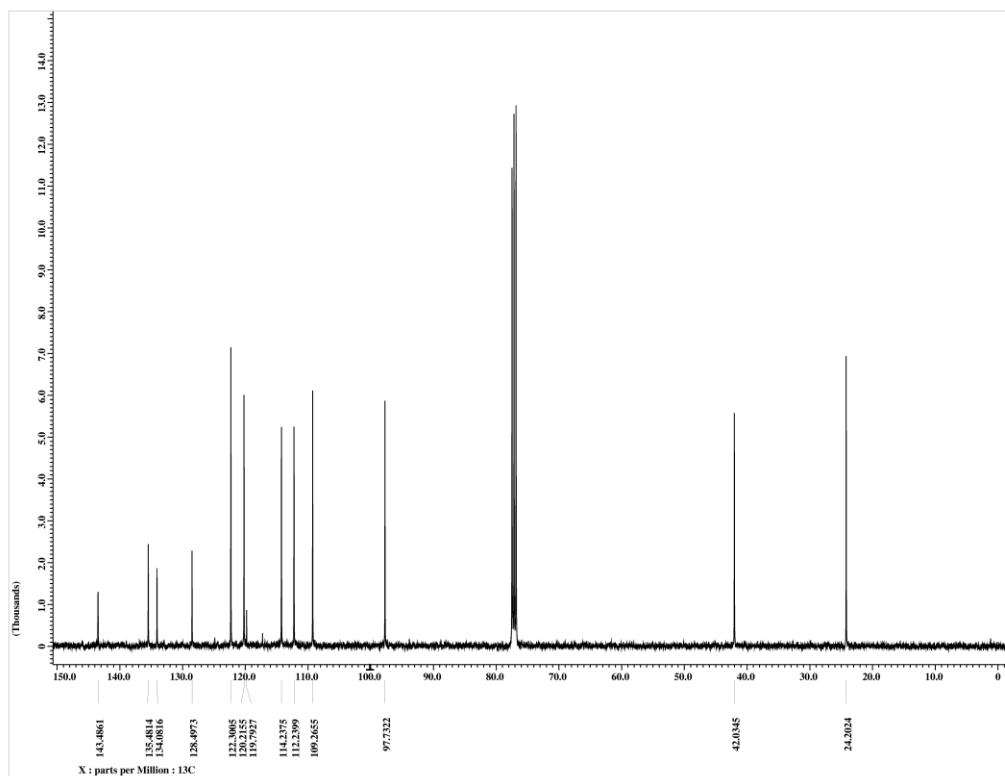
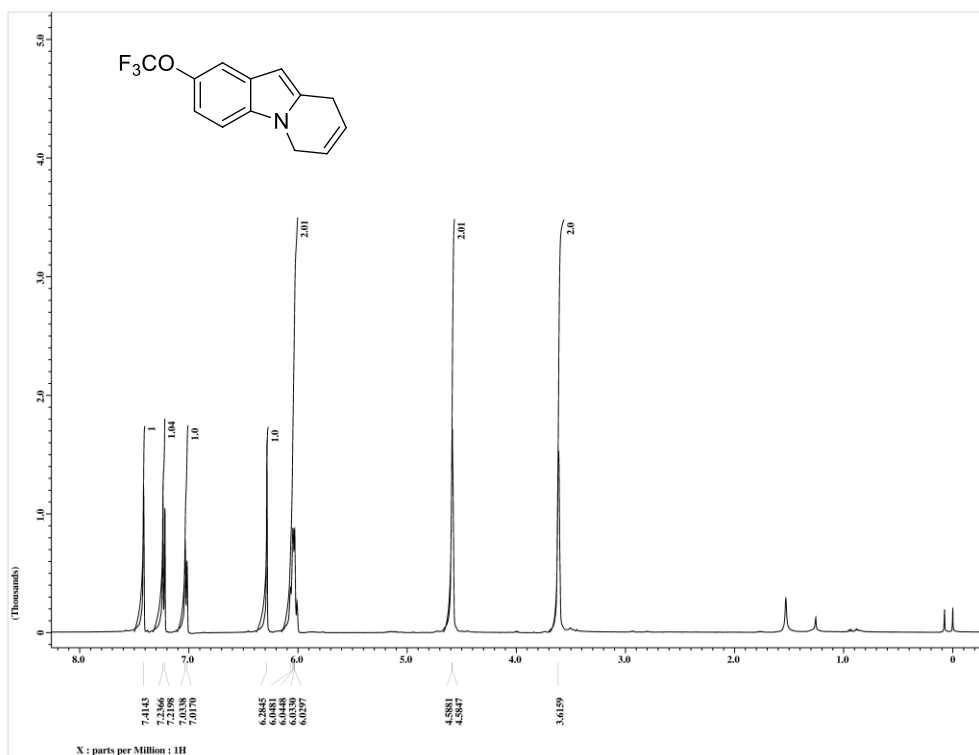
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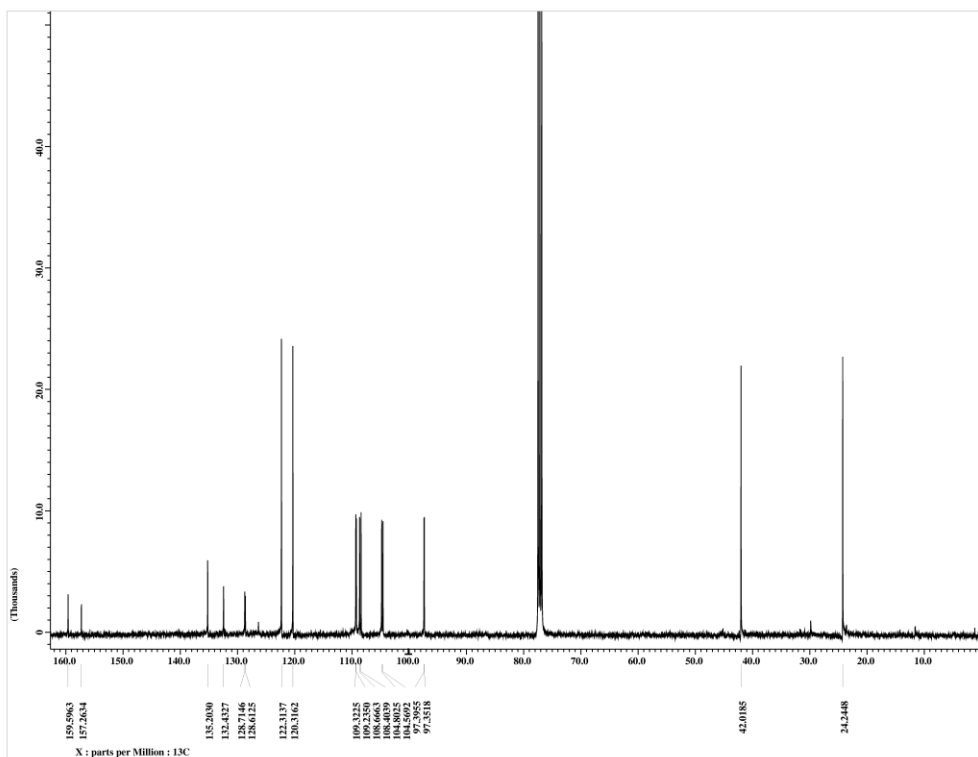
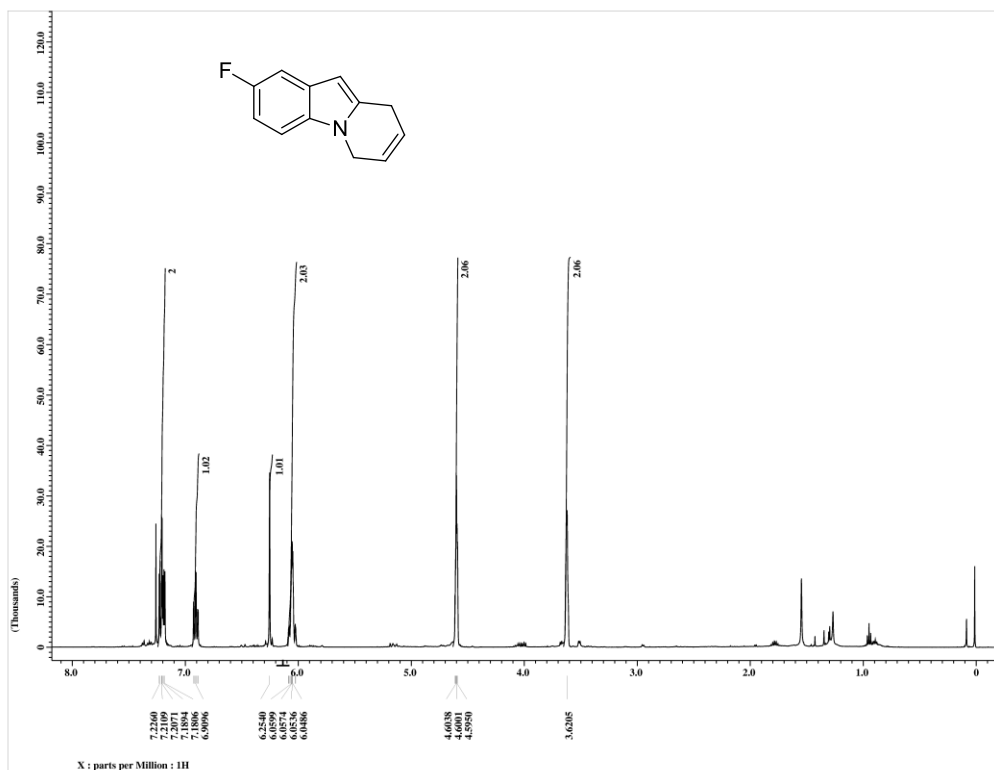
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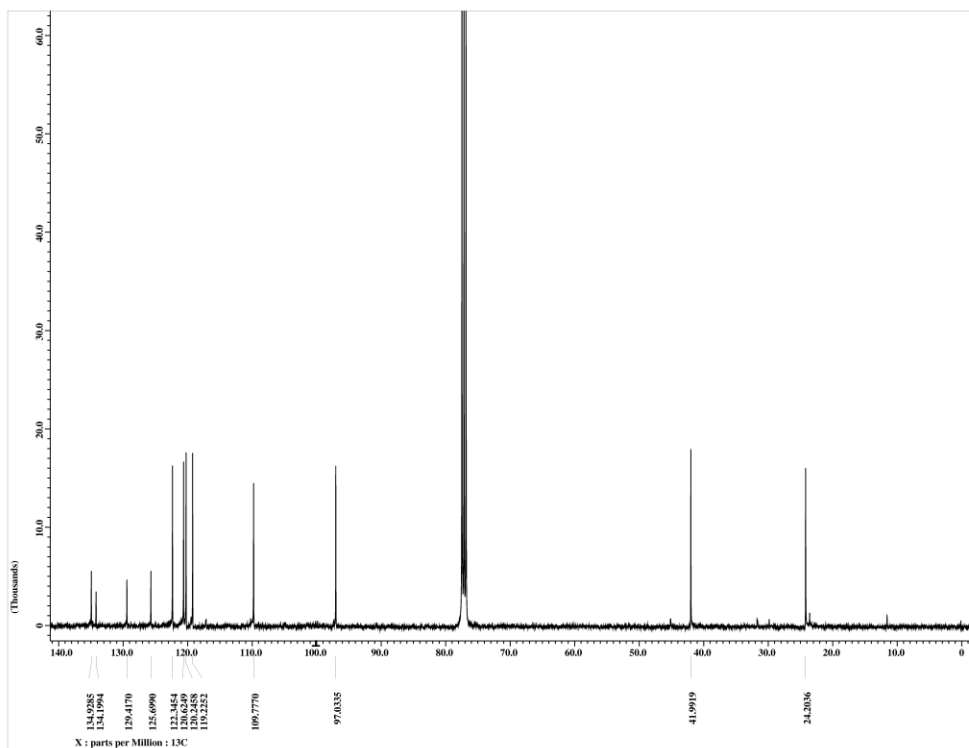
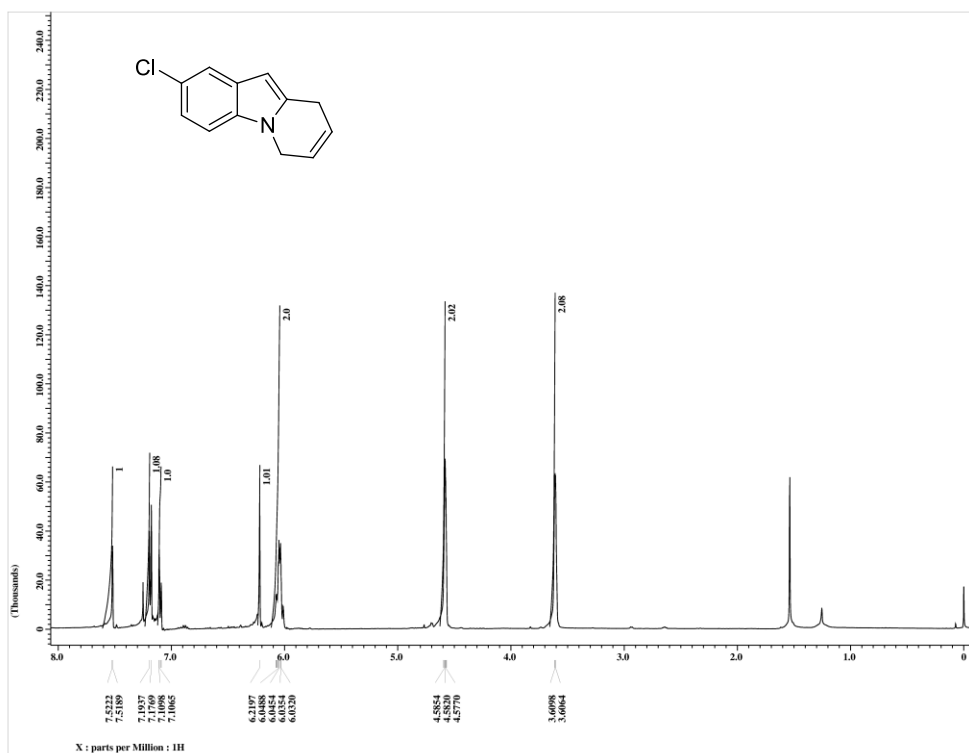
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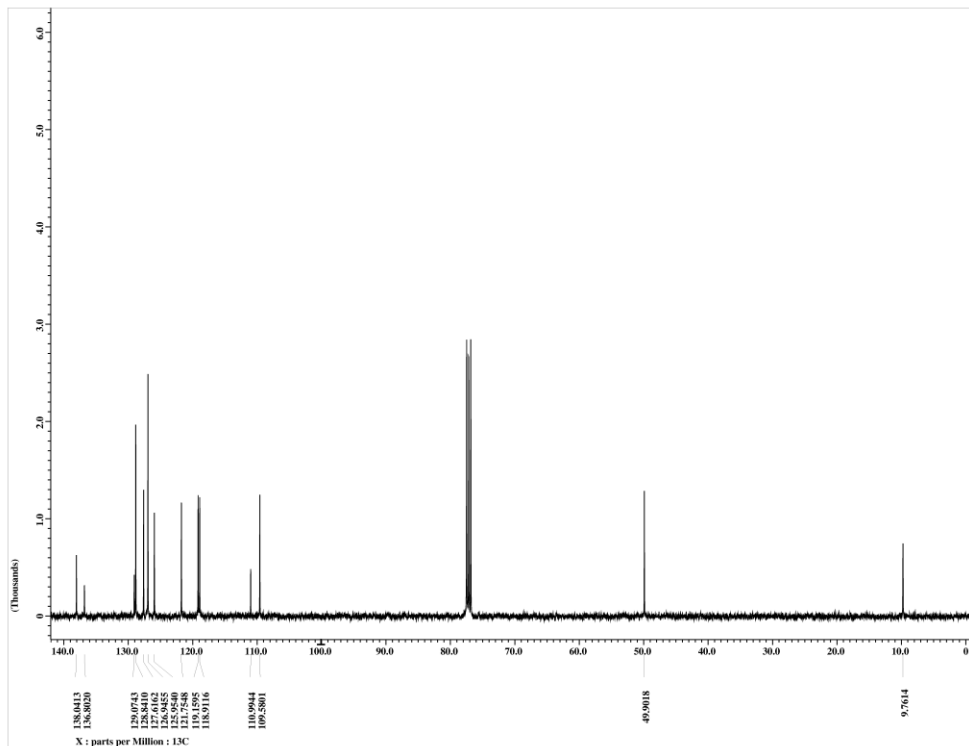
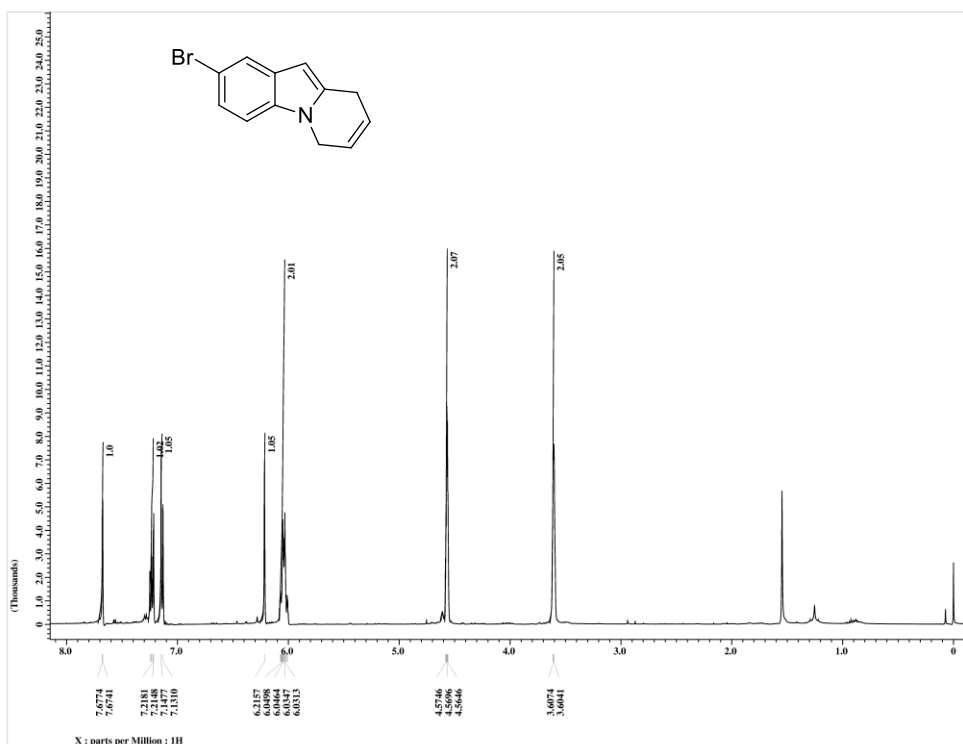
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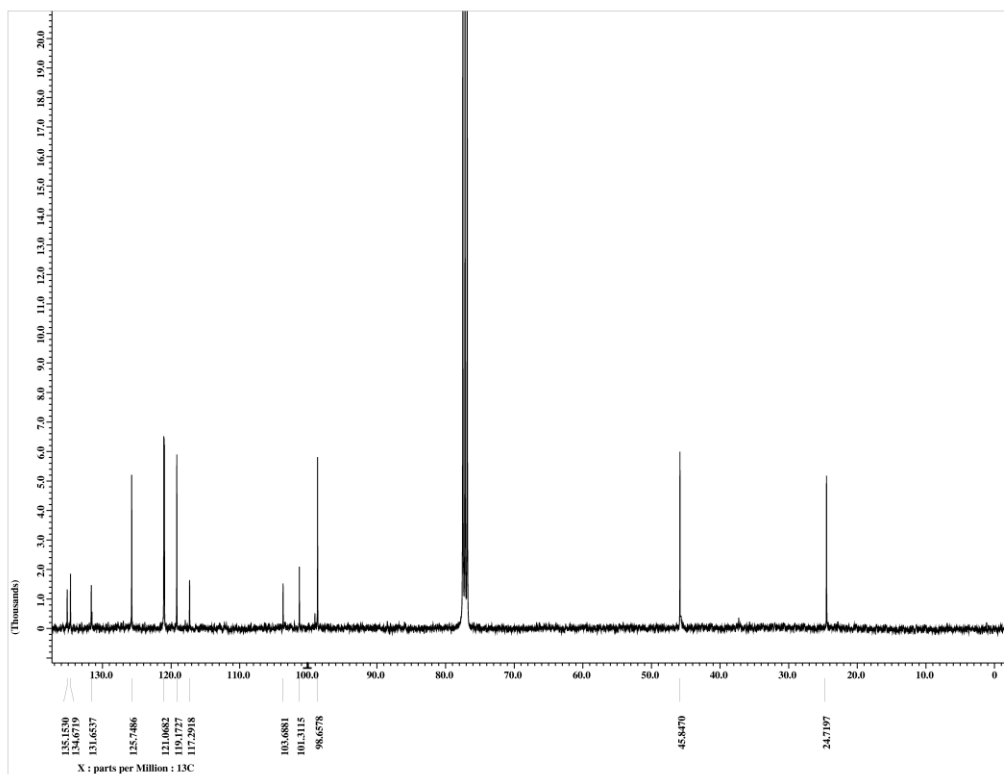
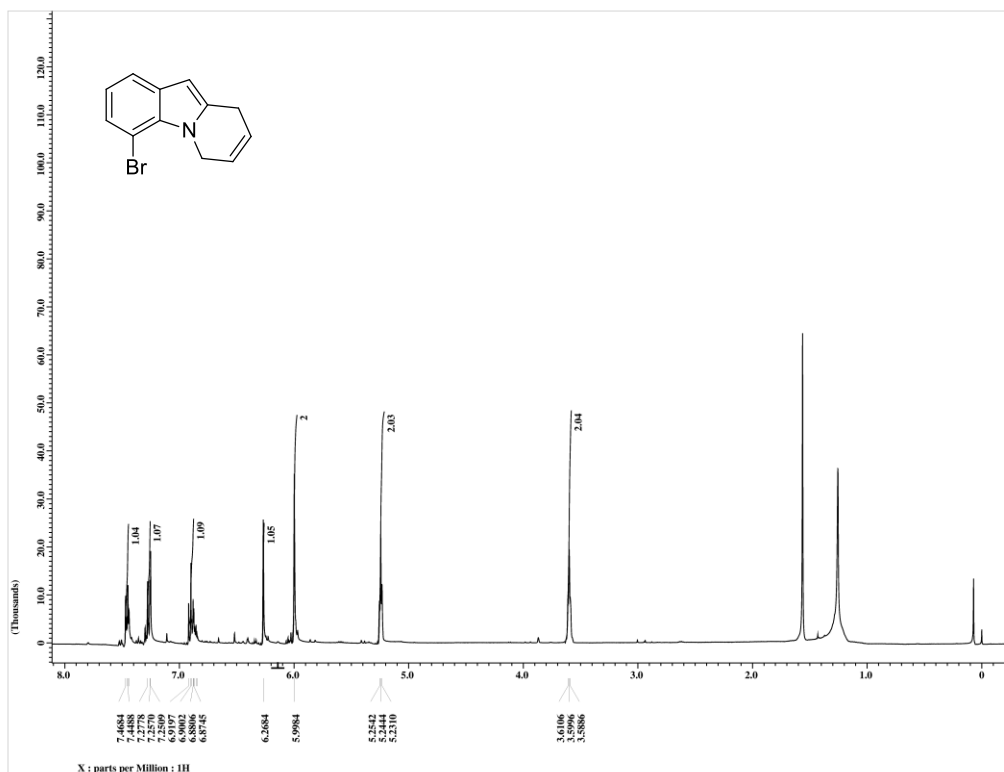
^1H and ^{13}C NMR of 5f:



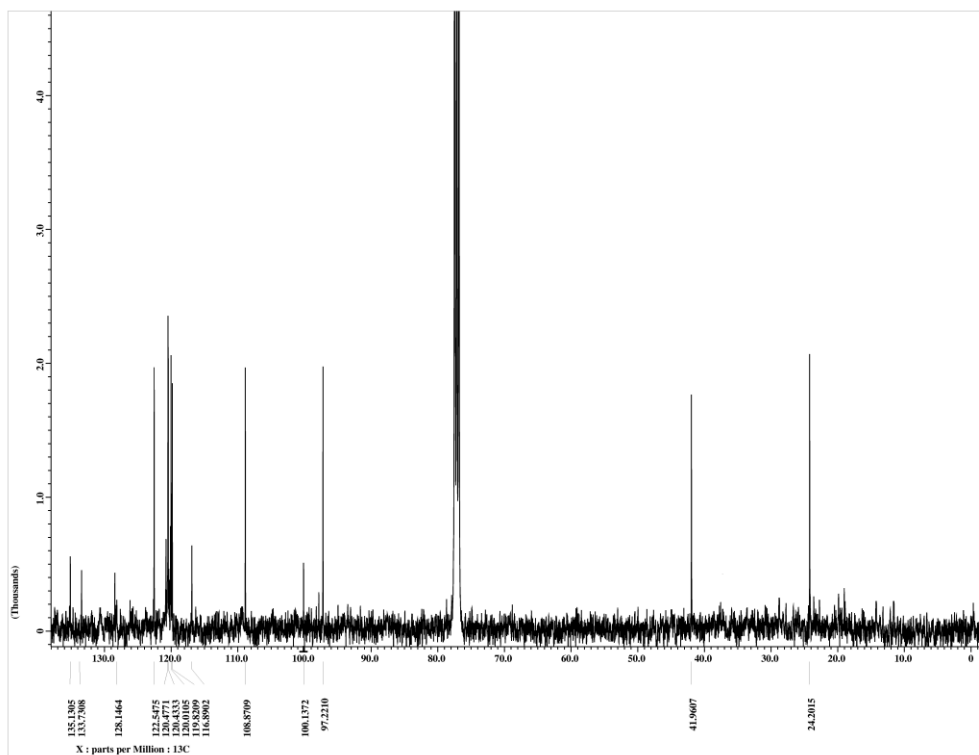
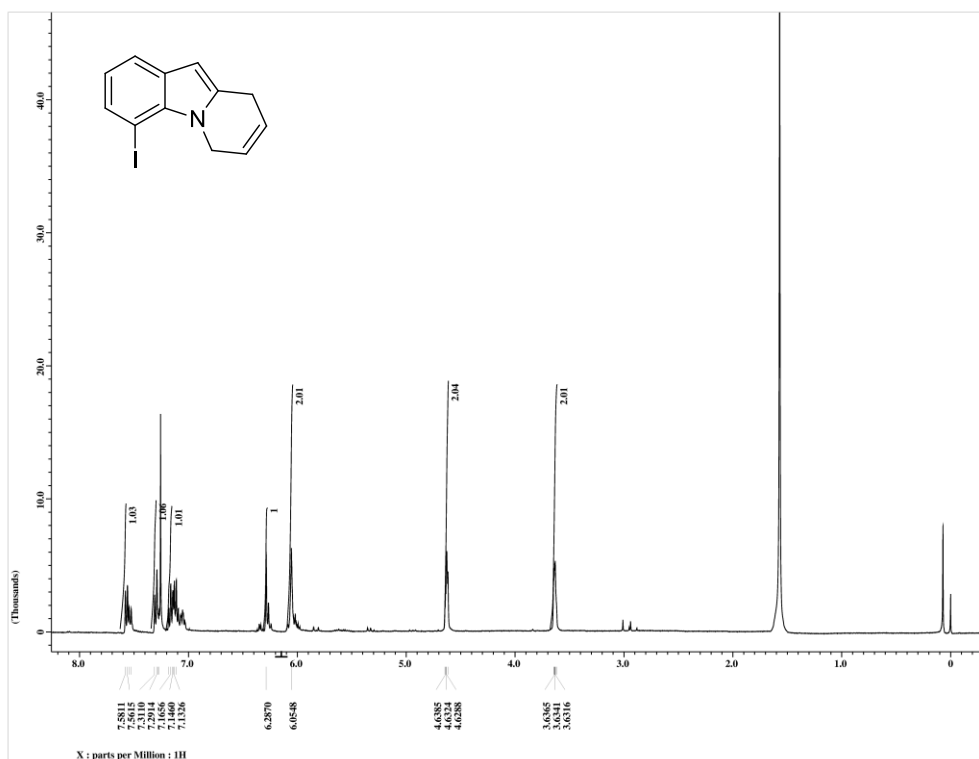
^1H and ^{13}C NMR of 5g:



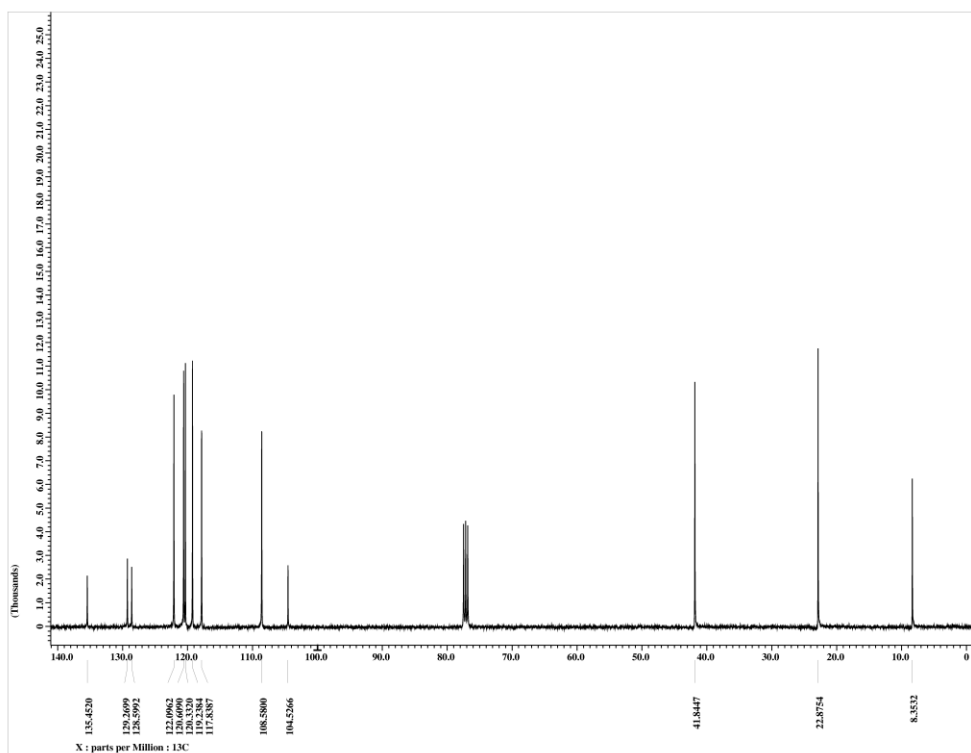
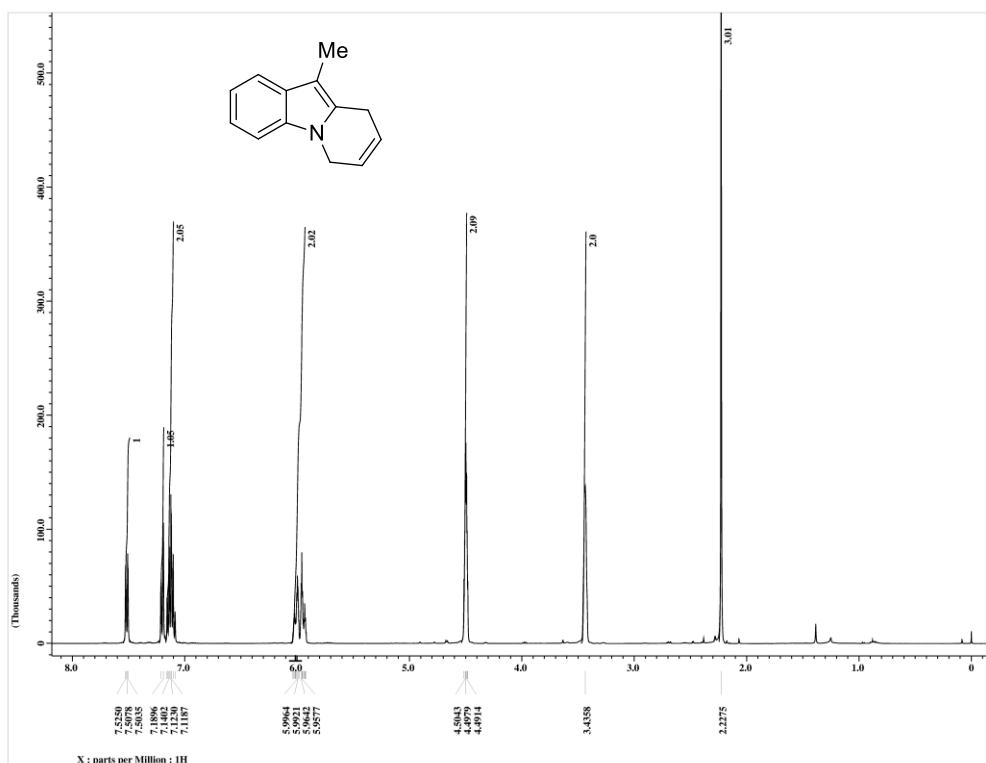
^1H and ^{13}C NMR of 5h:



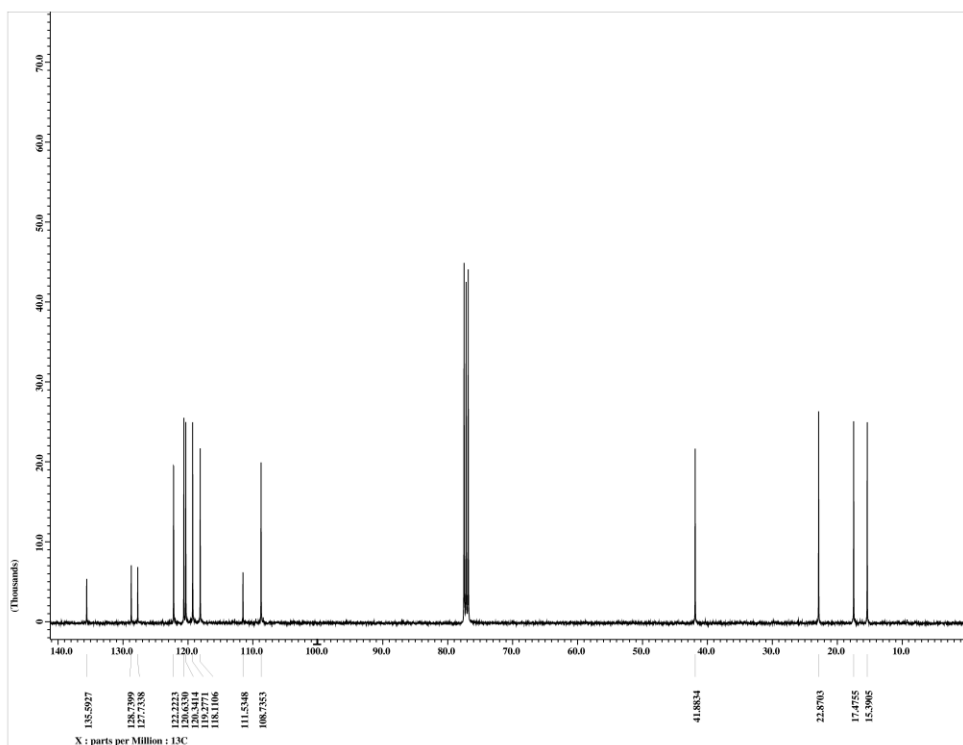
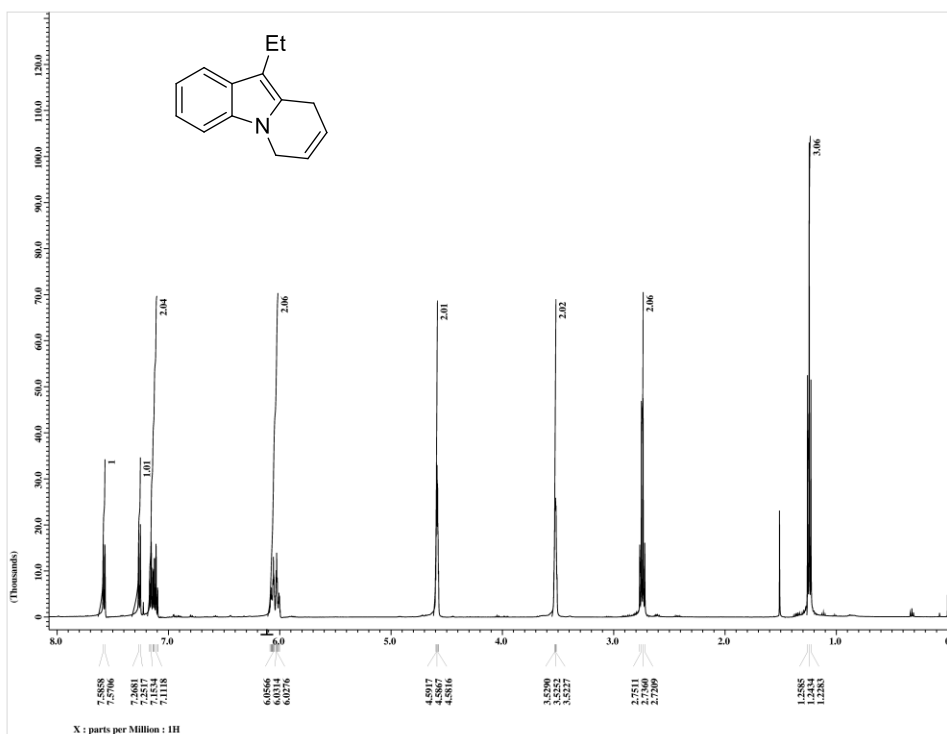
^1H and ^{13}C NMR of 5i:



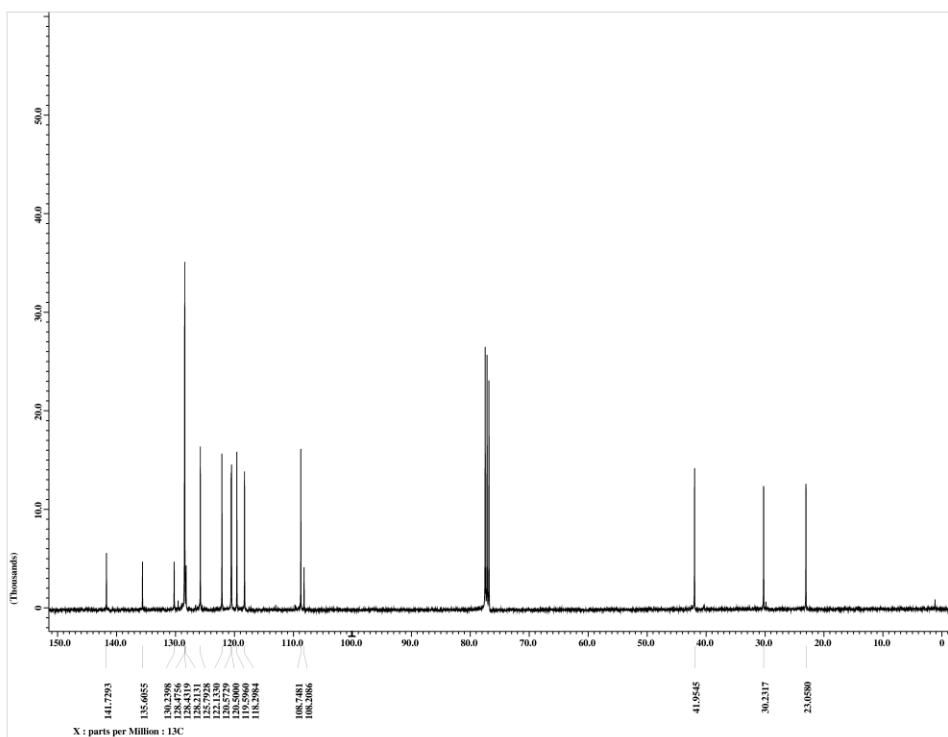
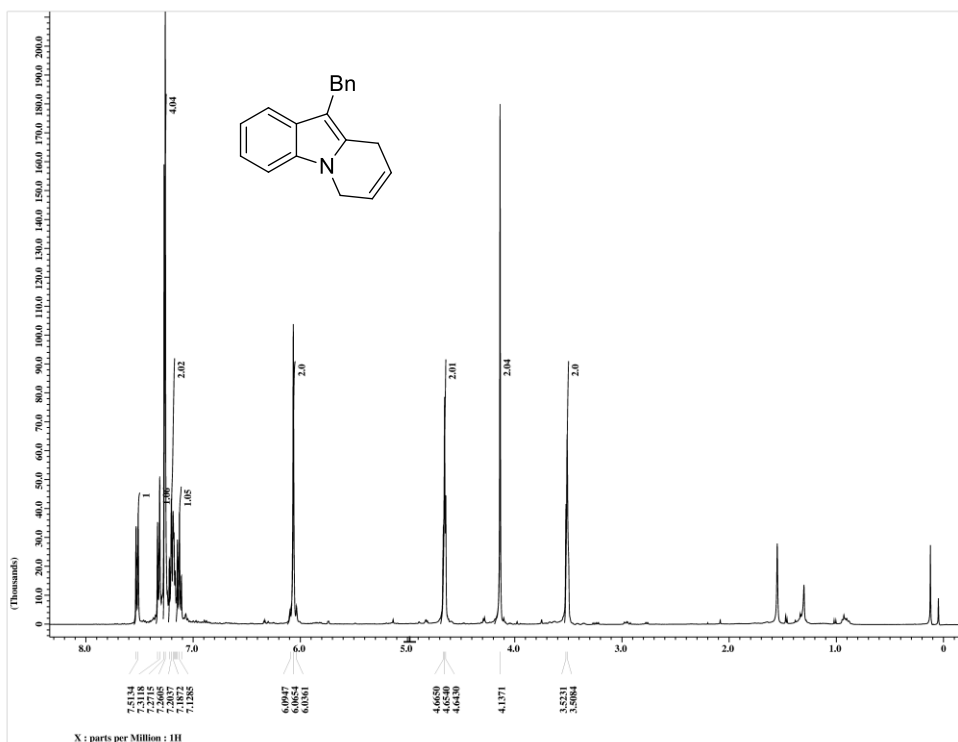
^1H and ^{13}C NMR of 5j:



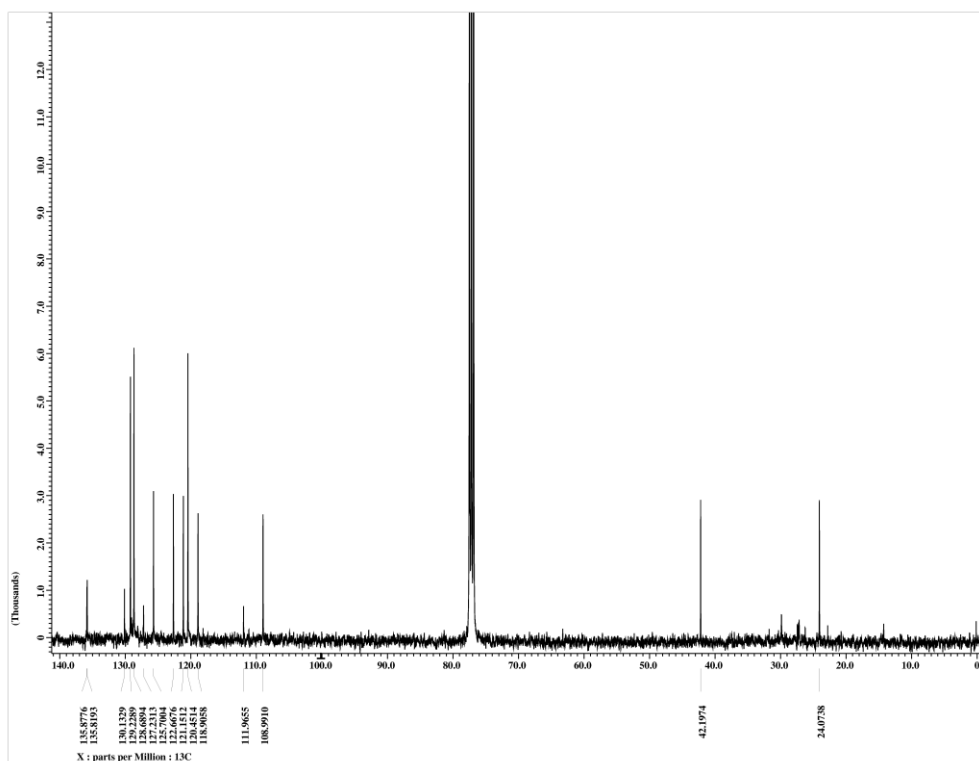
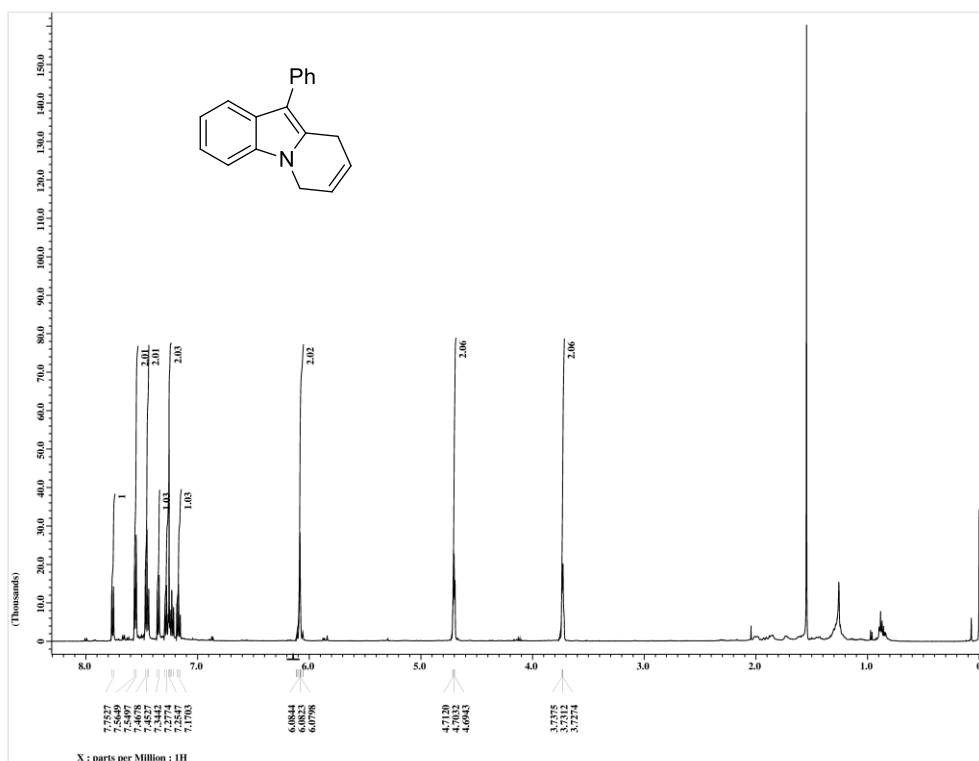
¹H and ¹³C NMR of 5k:



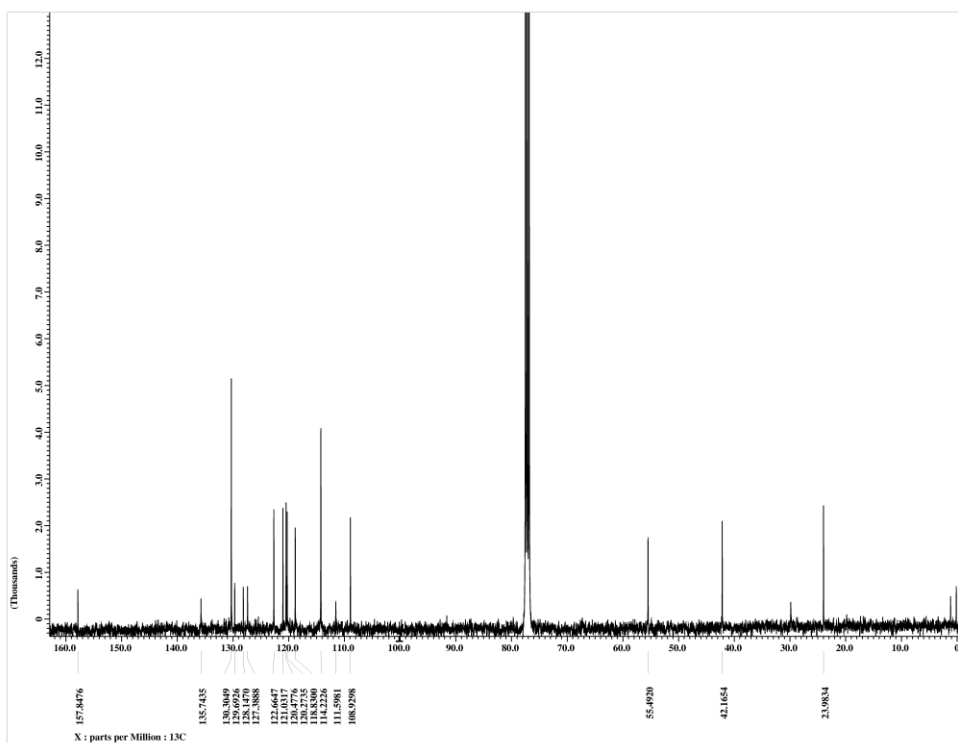
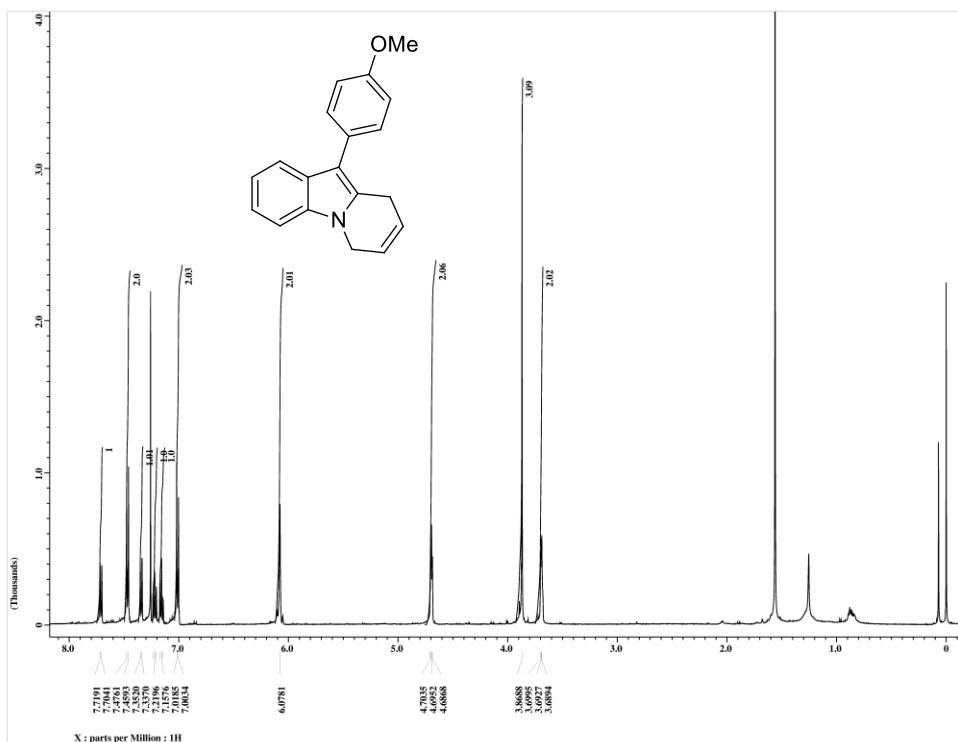
^1H and ^{13}C NMR of 5l:



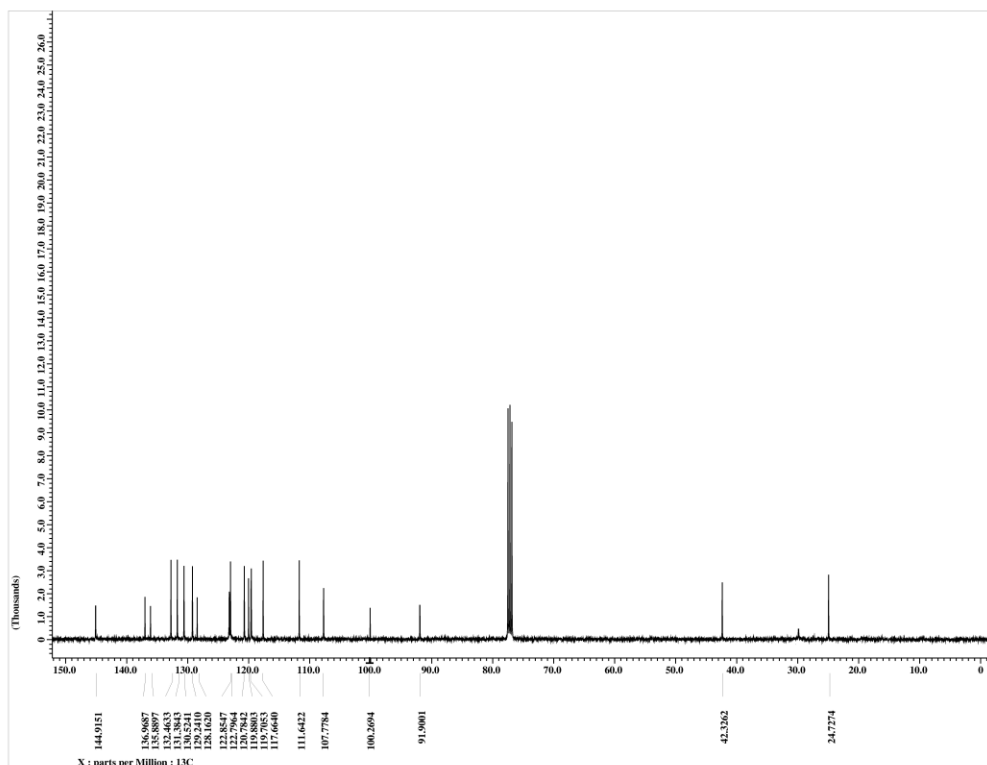
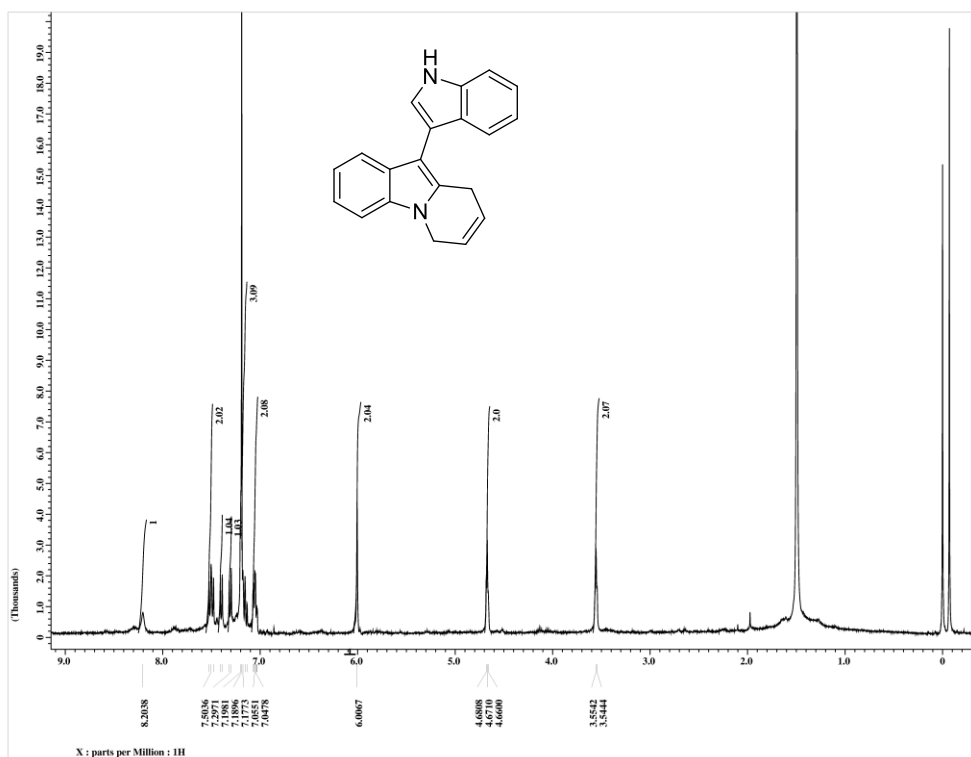
^1H and ^{13}C NMR of 5m:



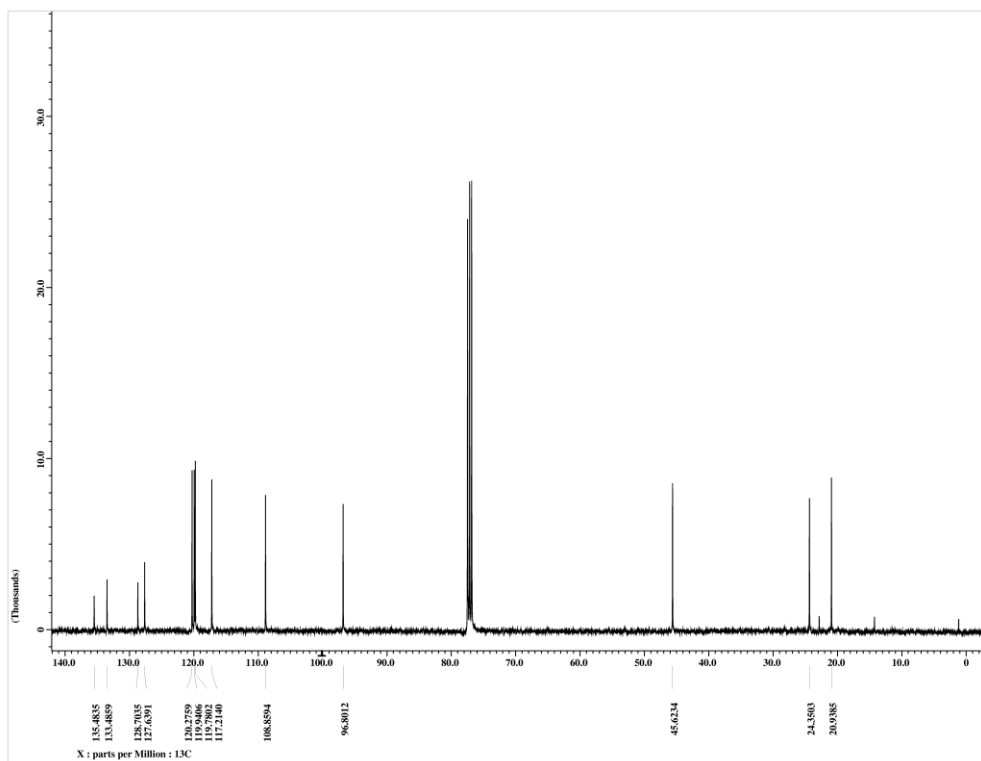
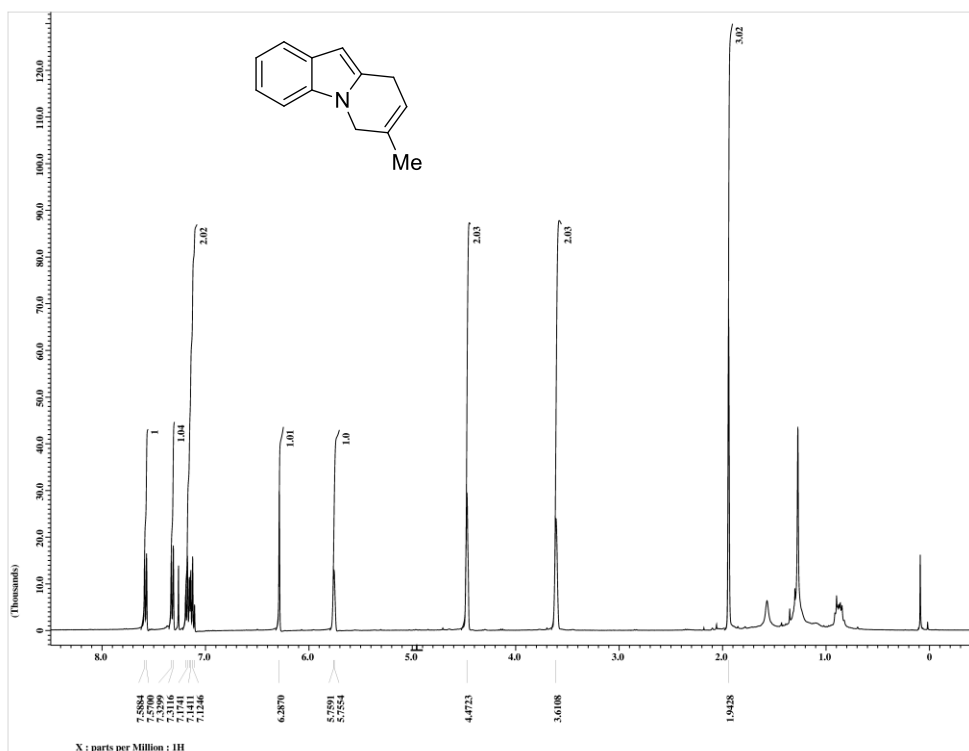
^1H and ^{13}C NMR of 5n:



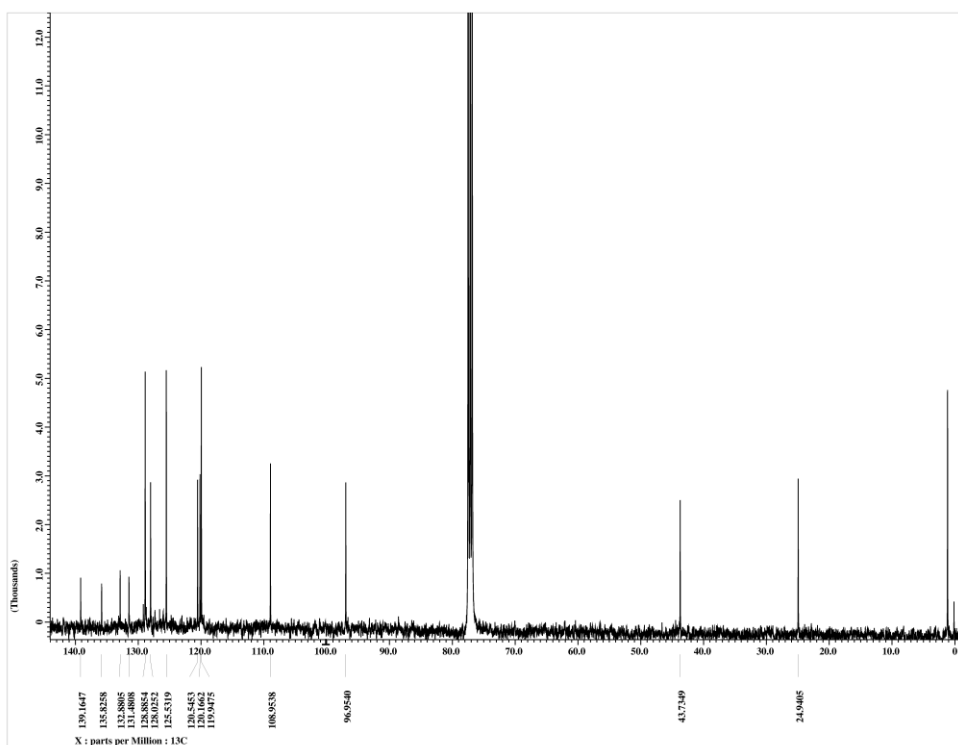
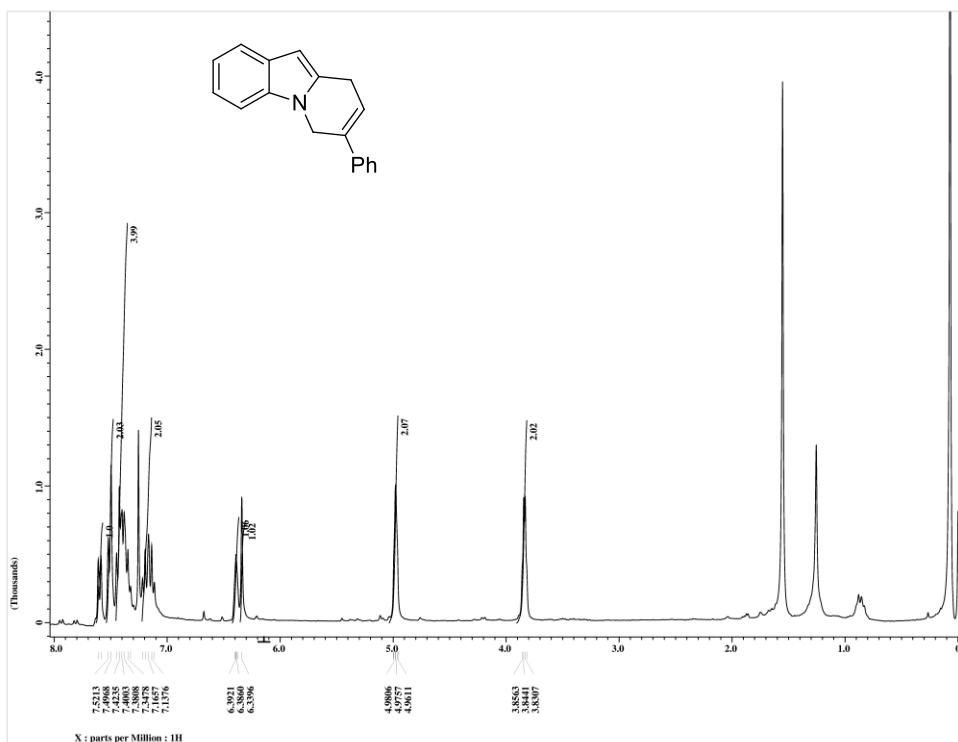
^1H and ^{13}C NMR of 5o:



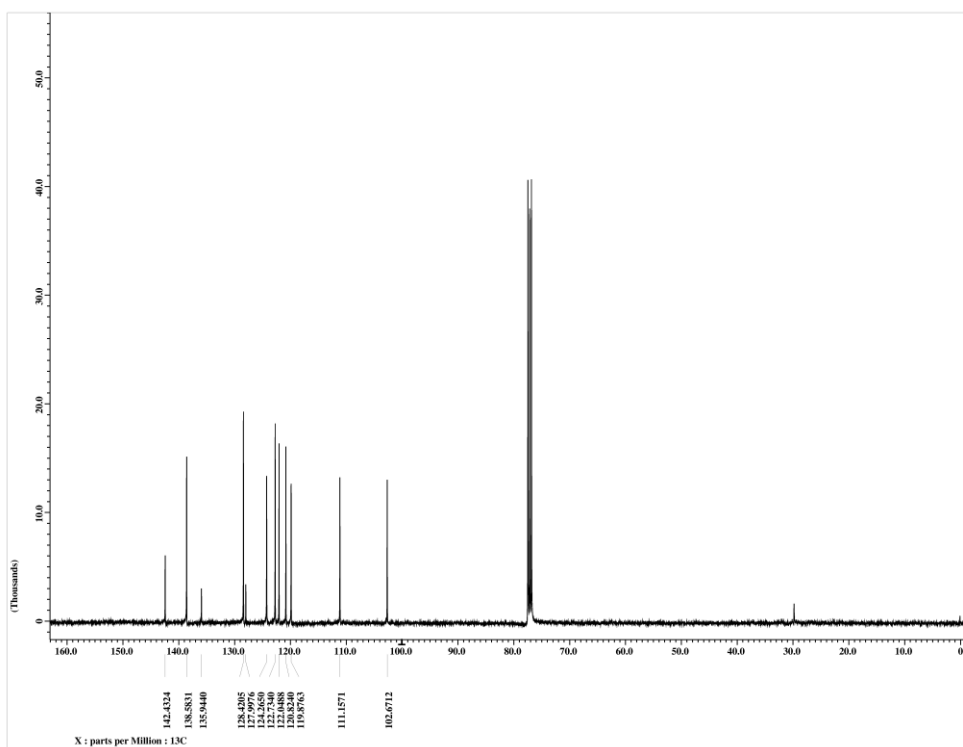
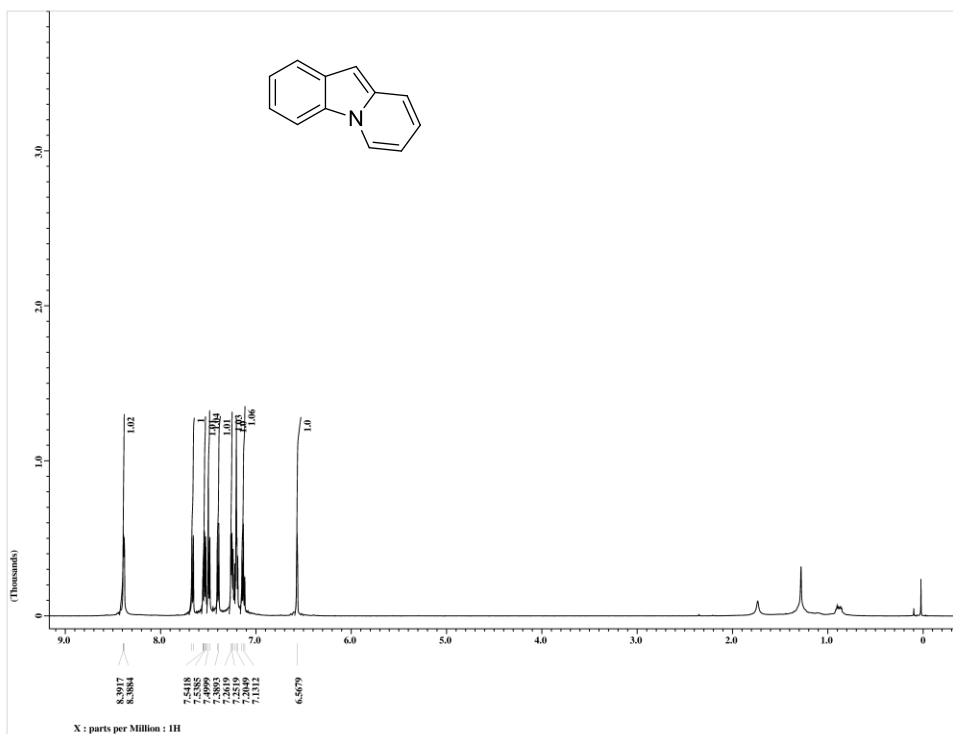
^1H and ^{13}C NMR of 5p:



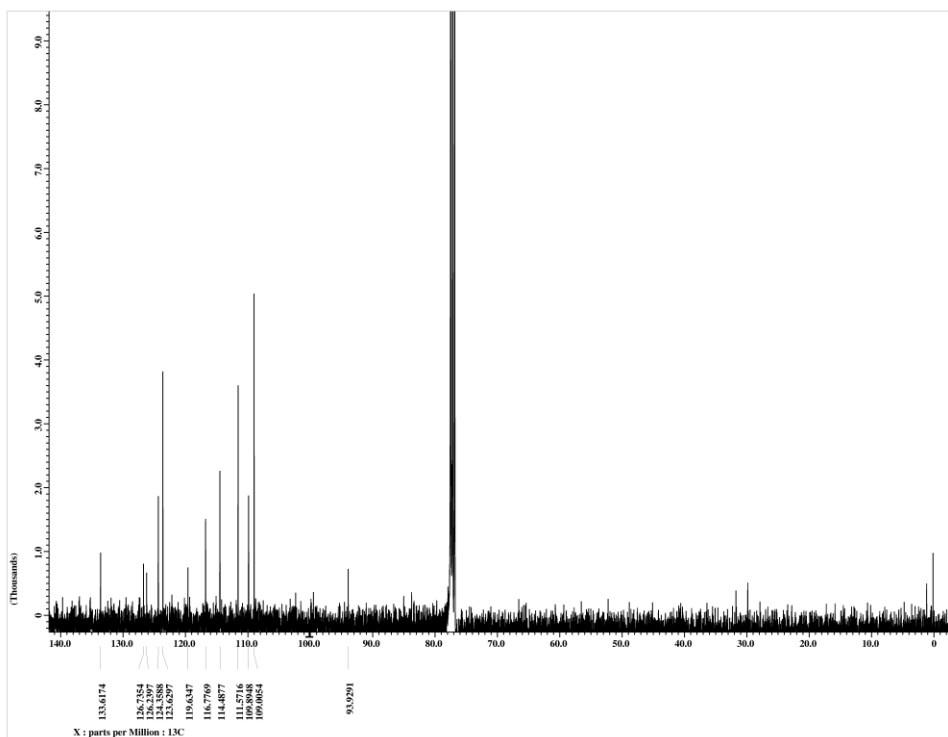
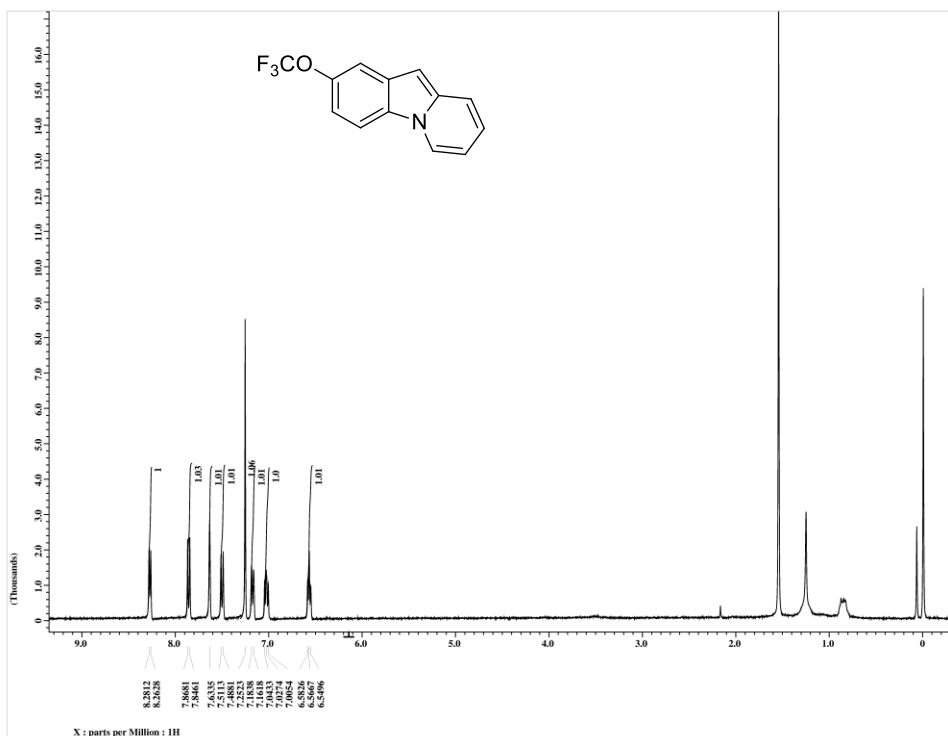
^1H and ^{13}C NMR of 5q:



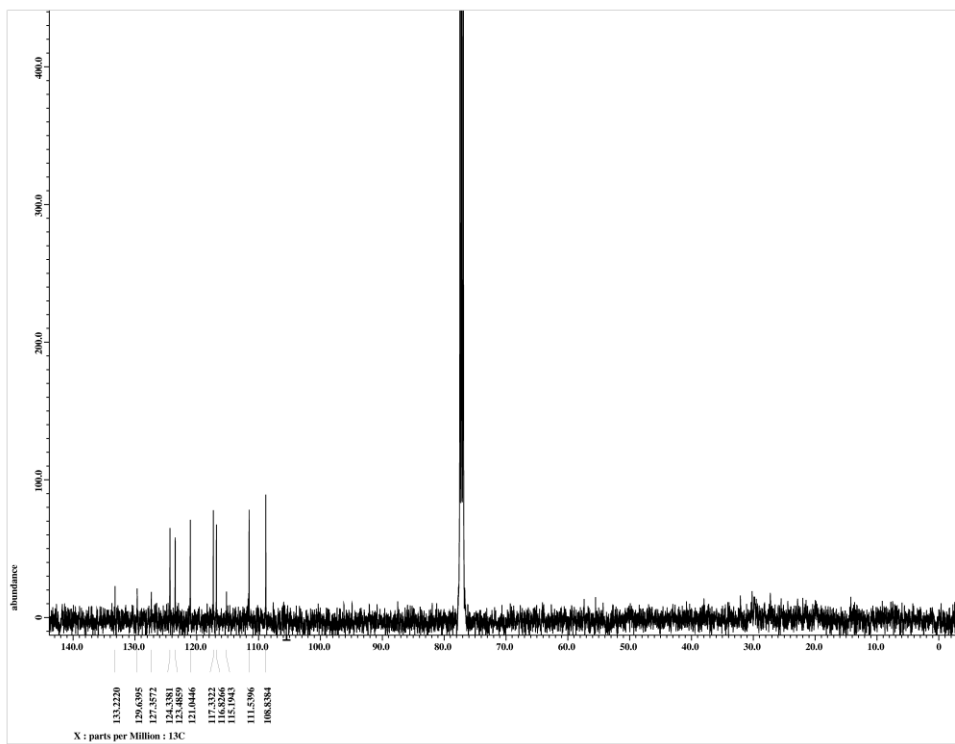
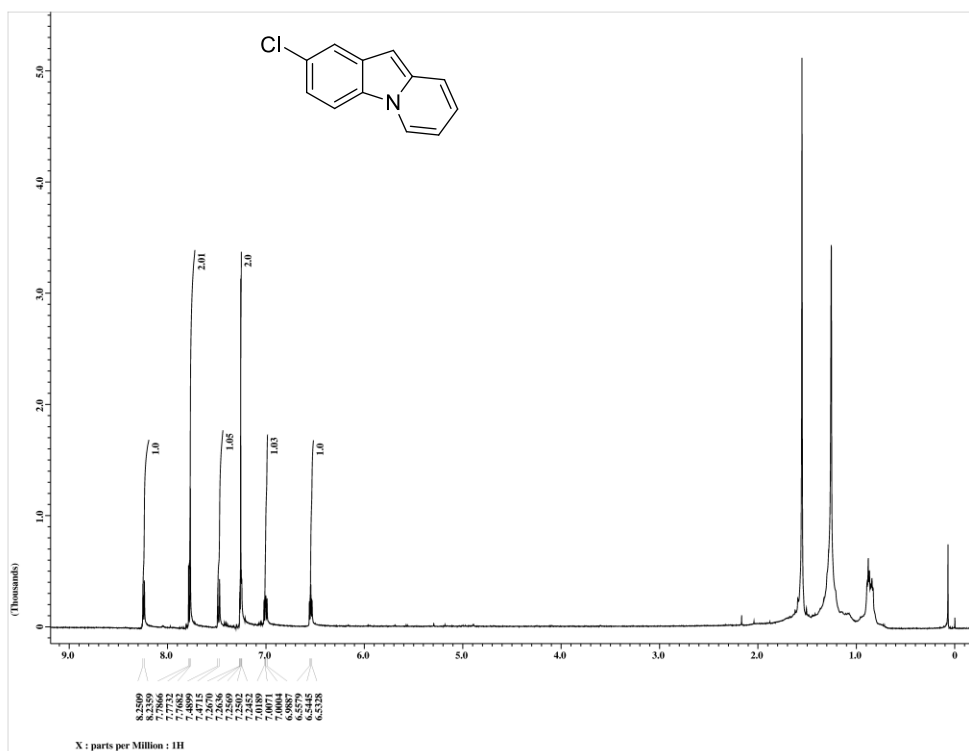
^1H and ^{13}C NMR of 7a:



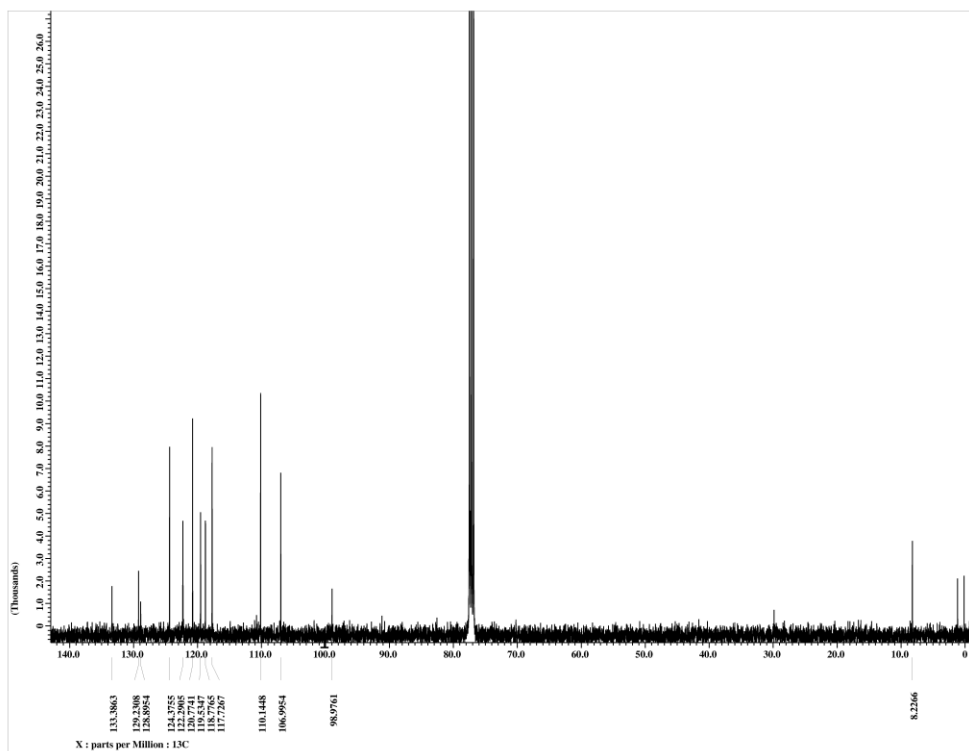
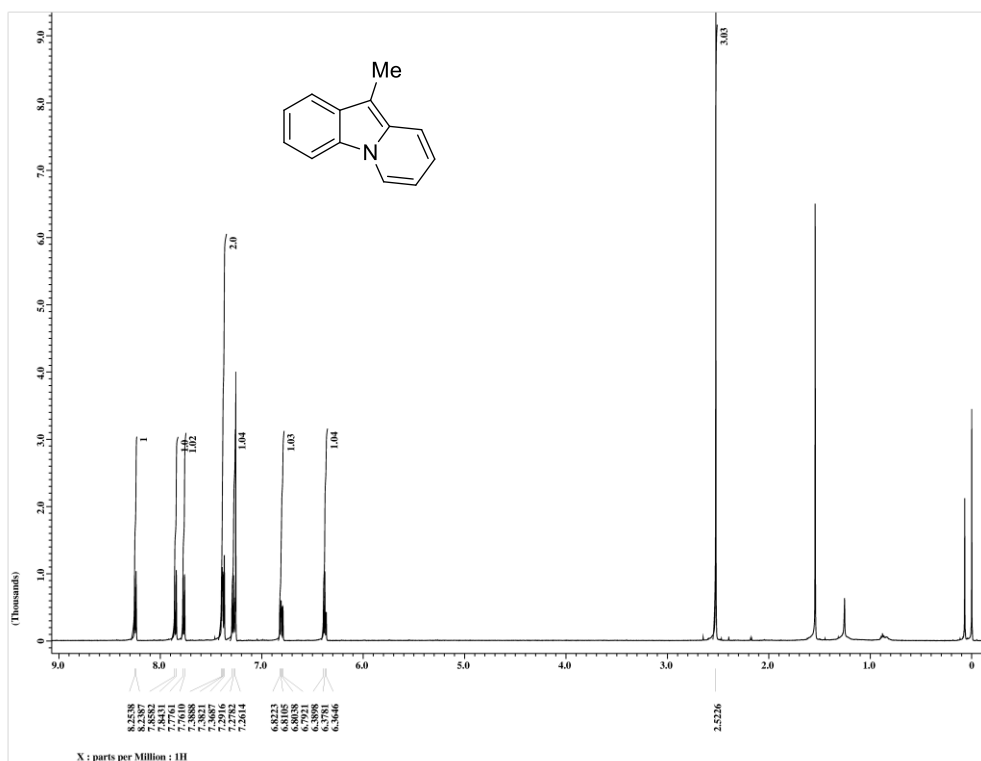
^1H and ^{13}C NMR of 7b:



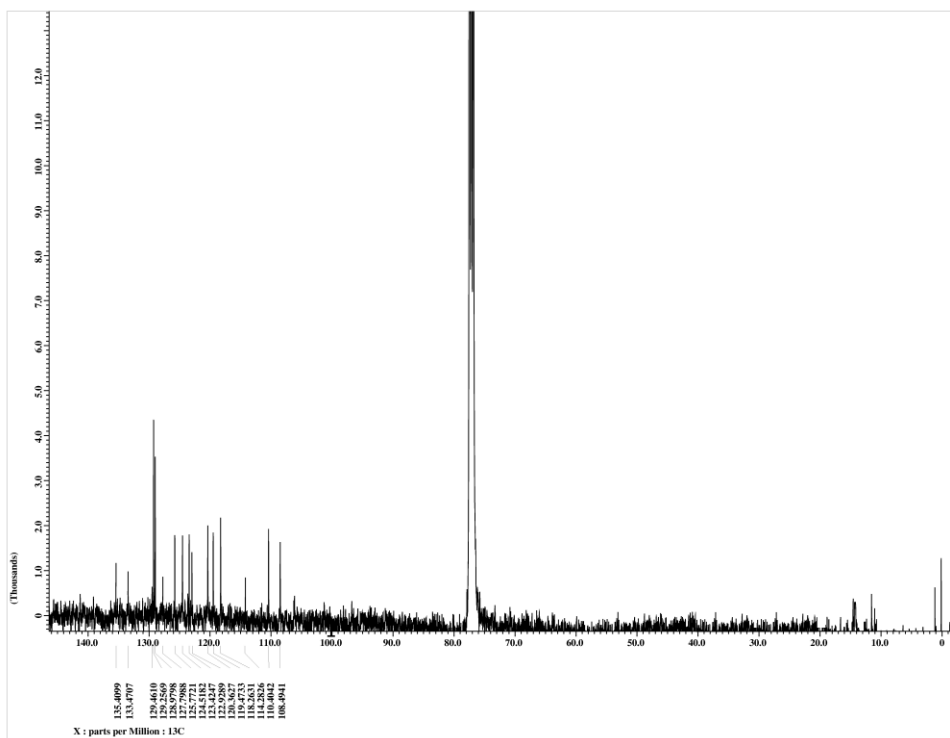
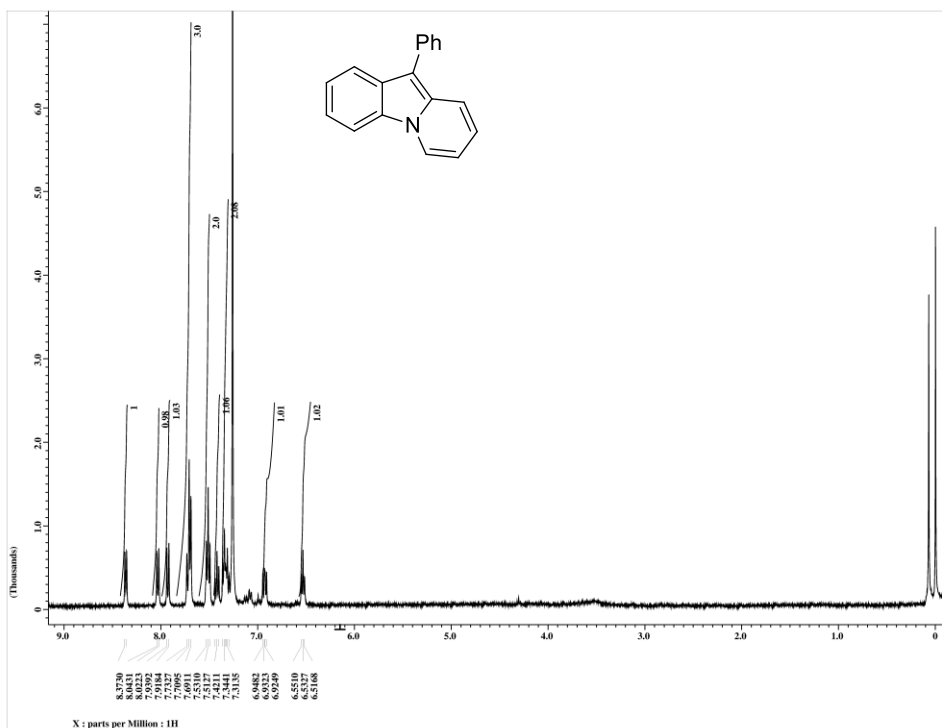
^1H and ^{13}C NMR of 7c:



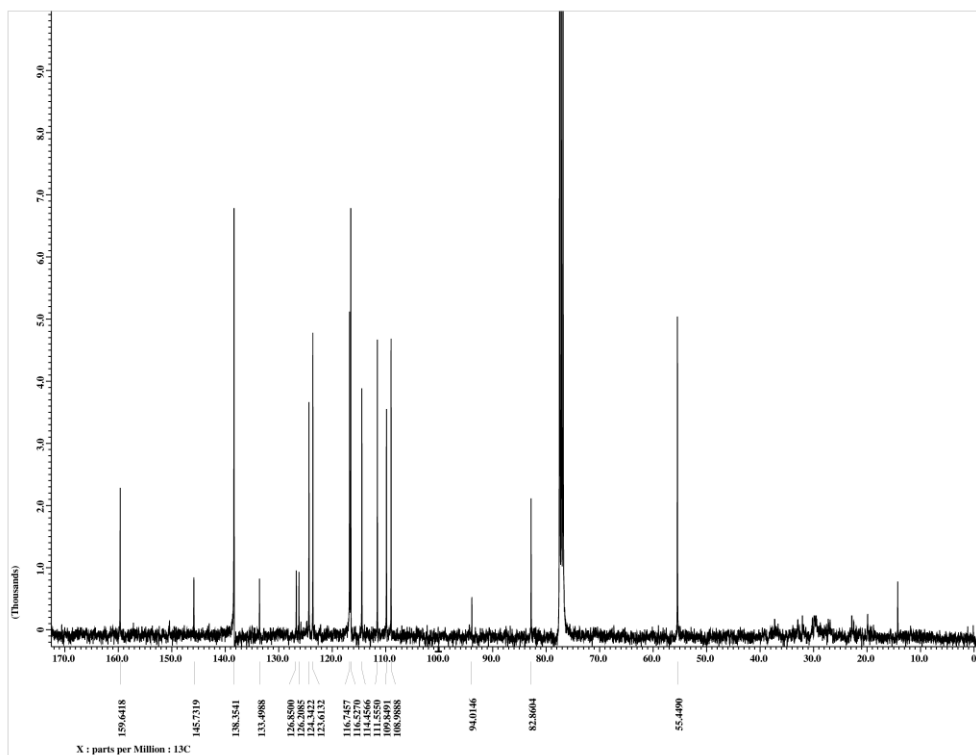
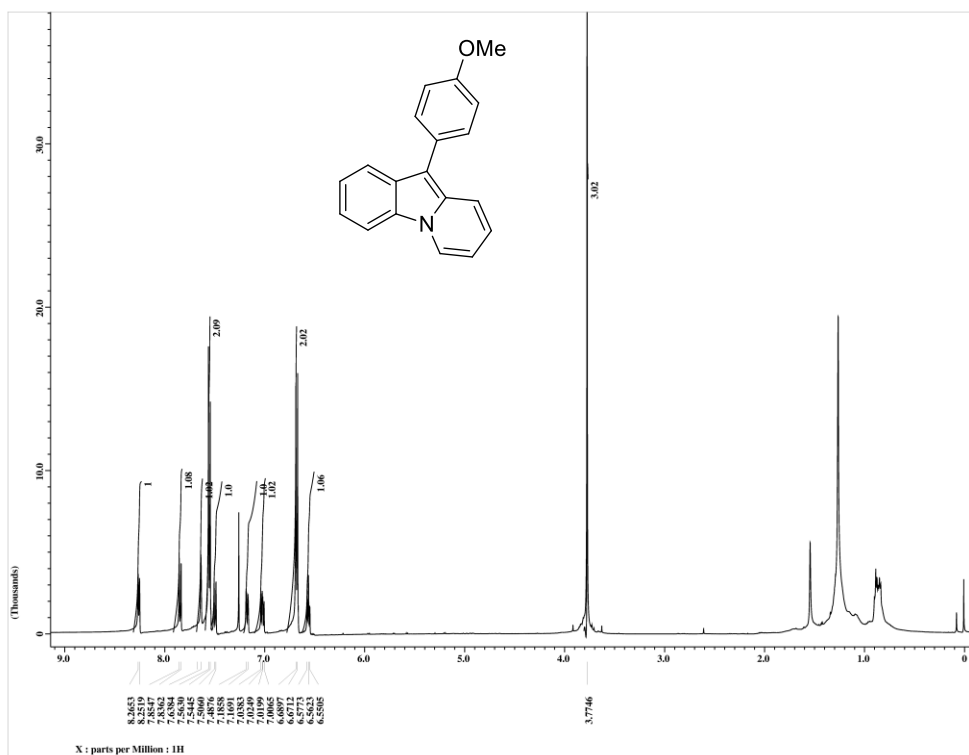
^1H and ^{13}C NMR of 7d:



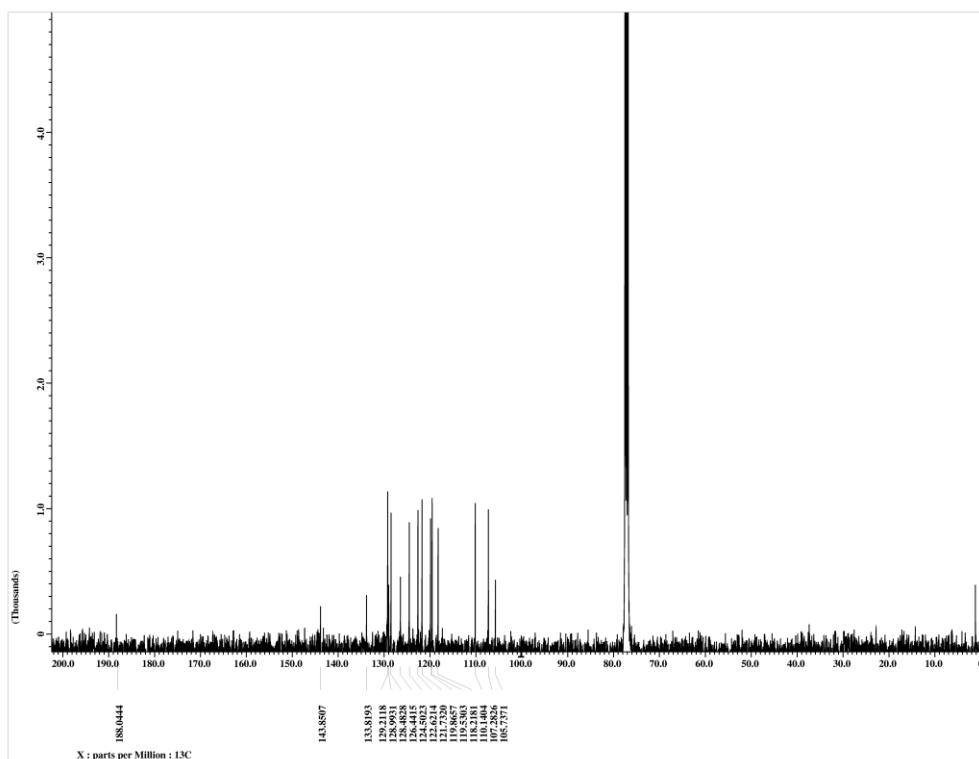
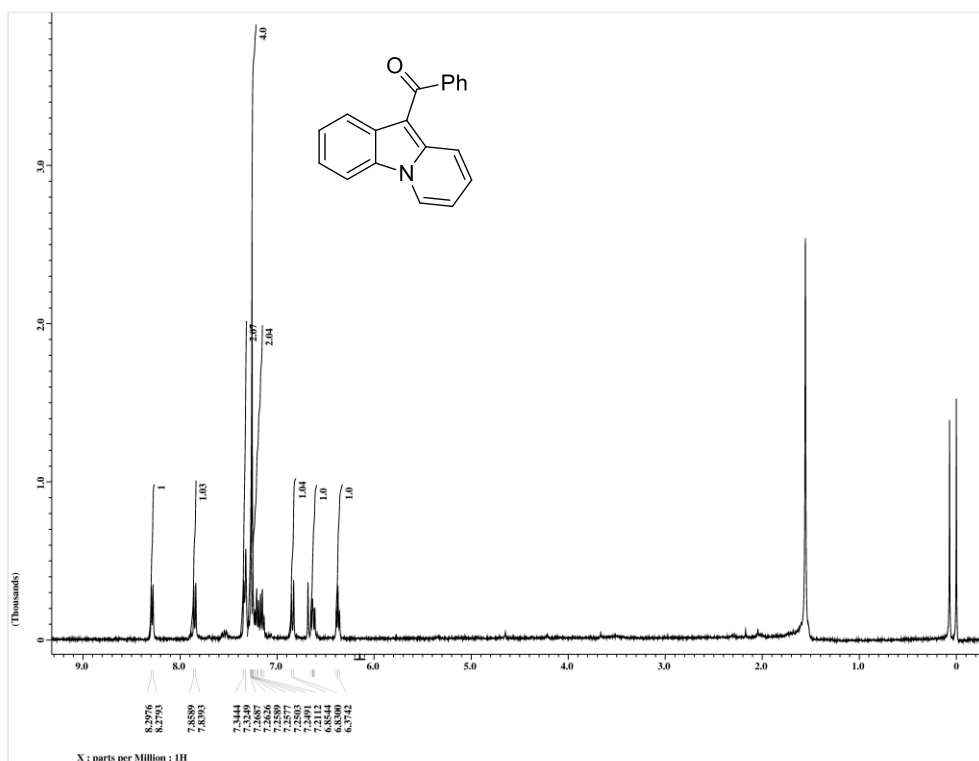
^1H and ^{13}C NMR of 7e:



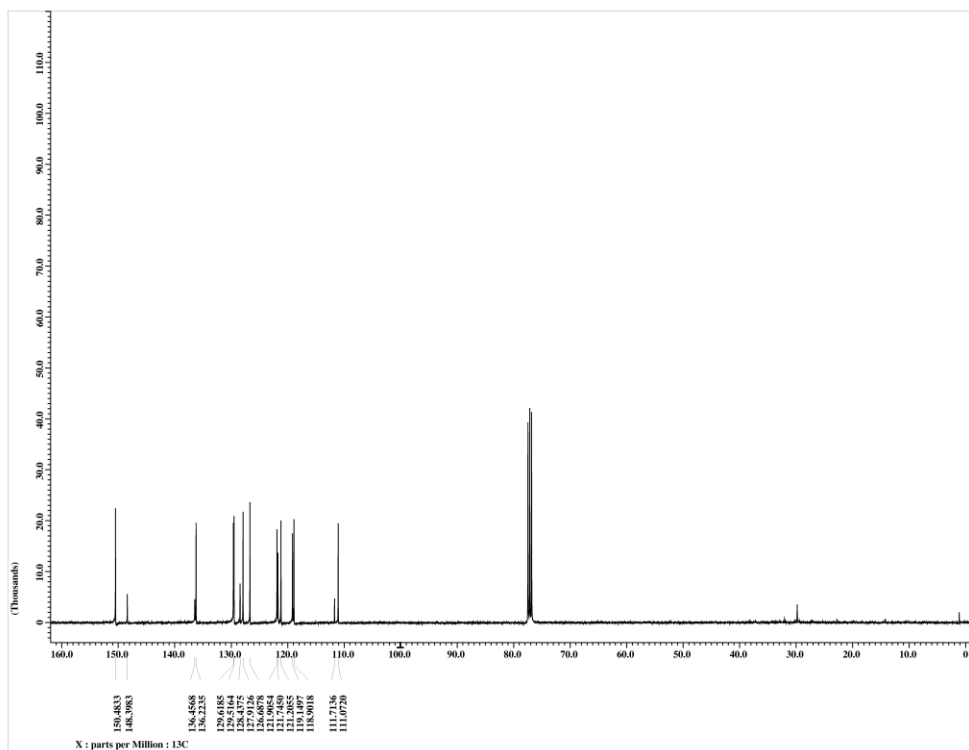
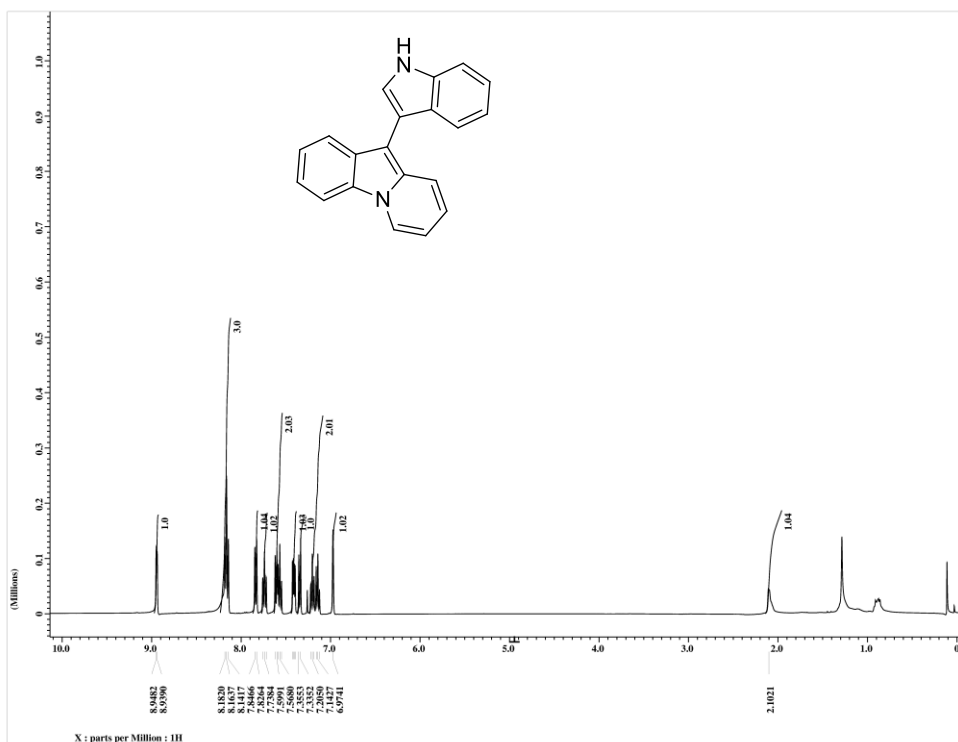
^1H and ^{13}C NMR of 7f:



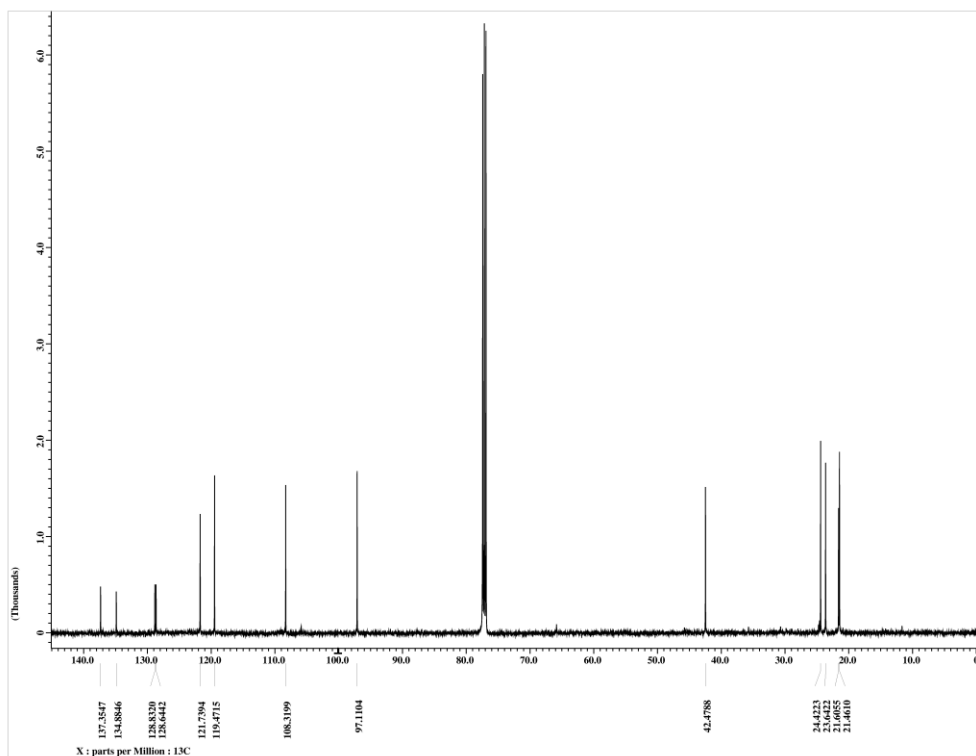
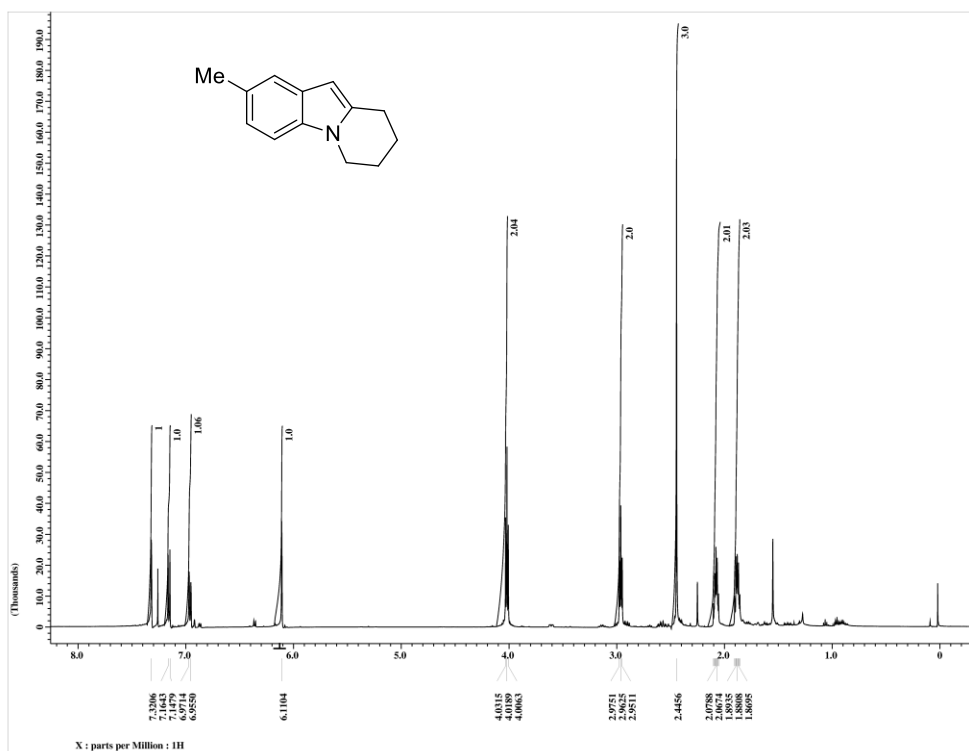
^1H and ^{13}C NMR of 7g:



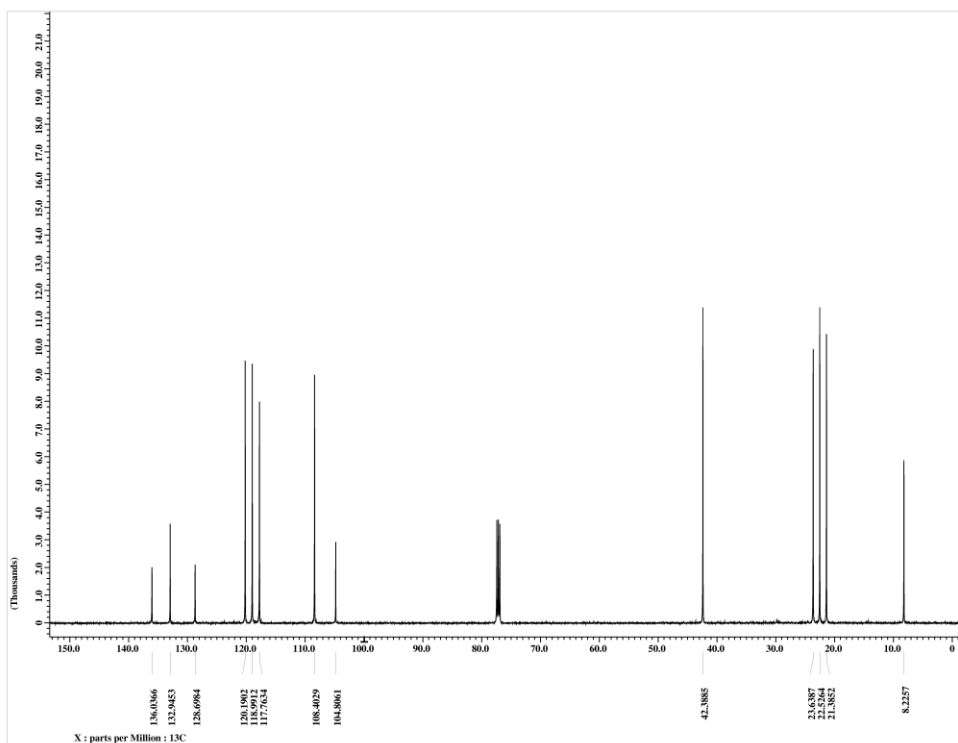
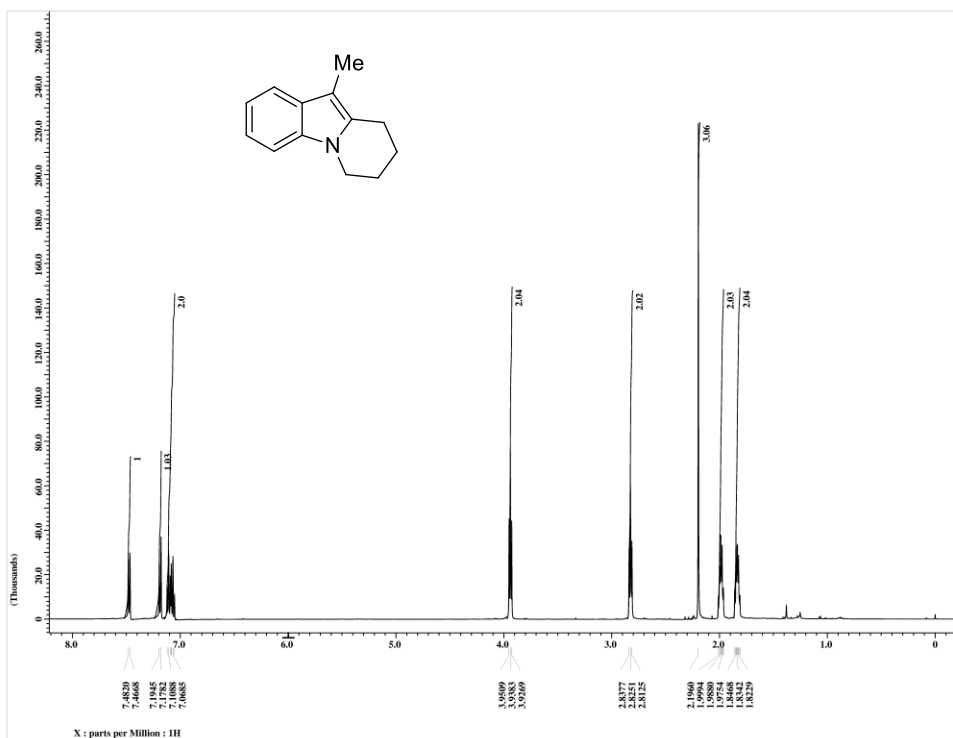
^1H and ^{13}C NMR of 7h:



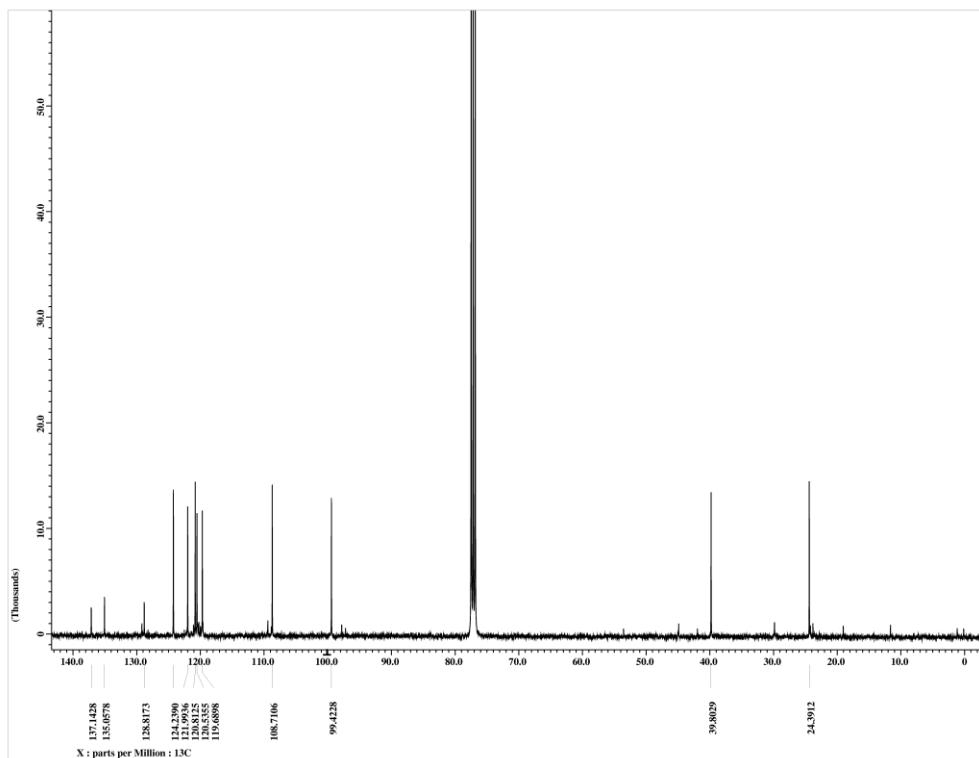
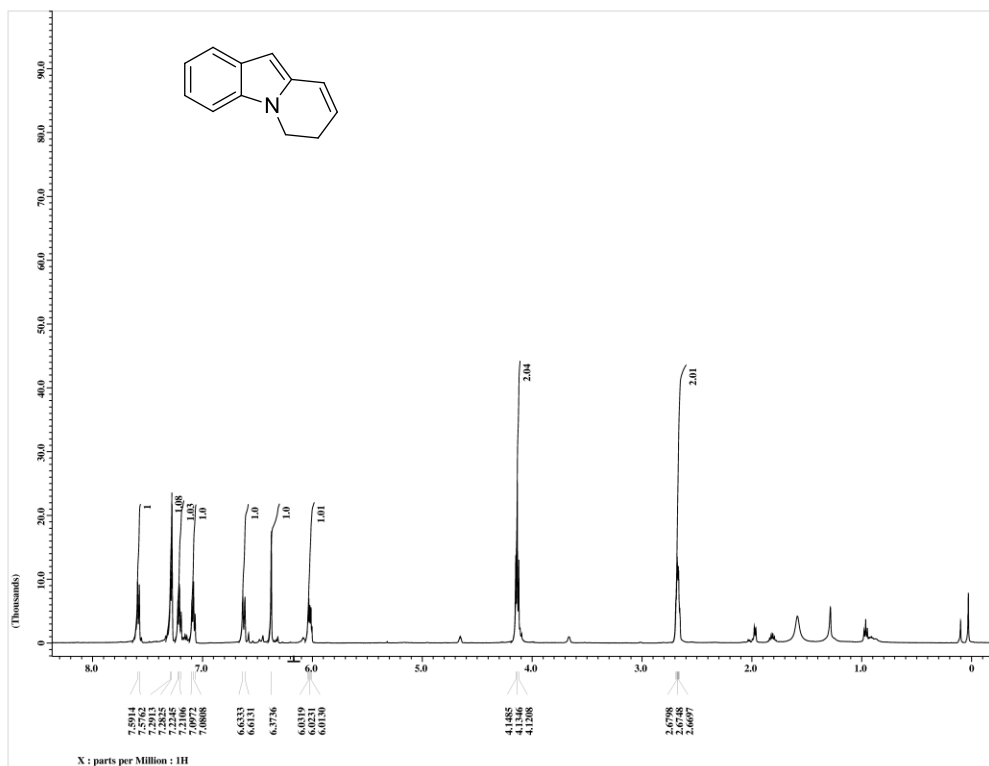
^1H and ^{13}C NMR of 12a:



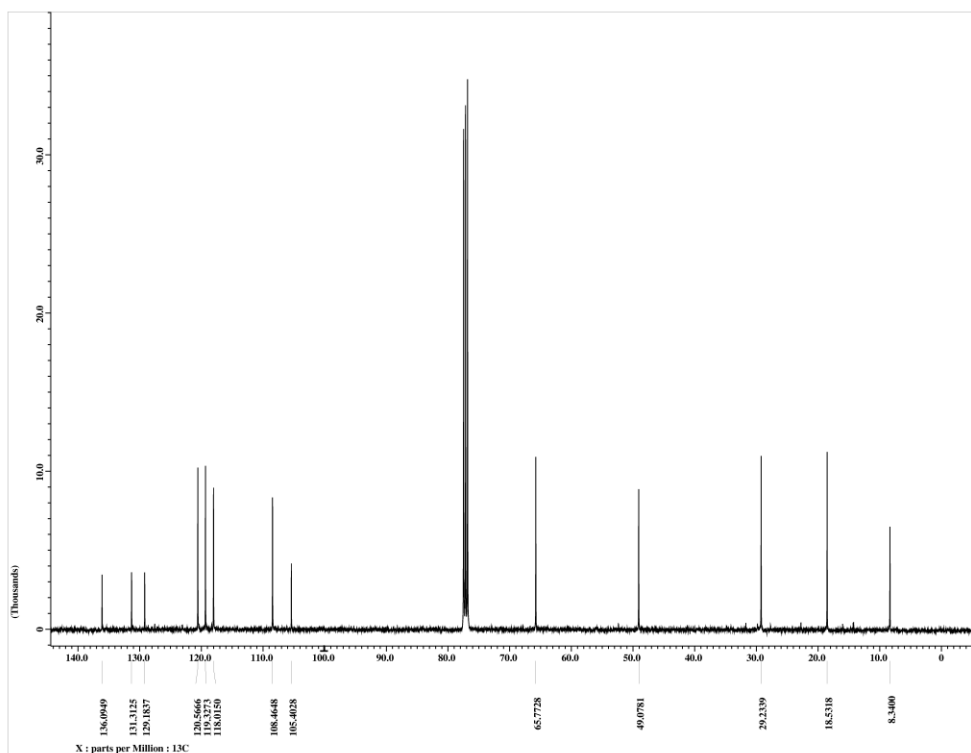
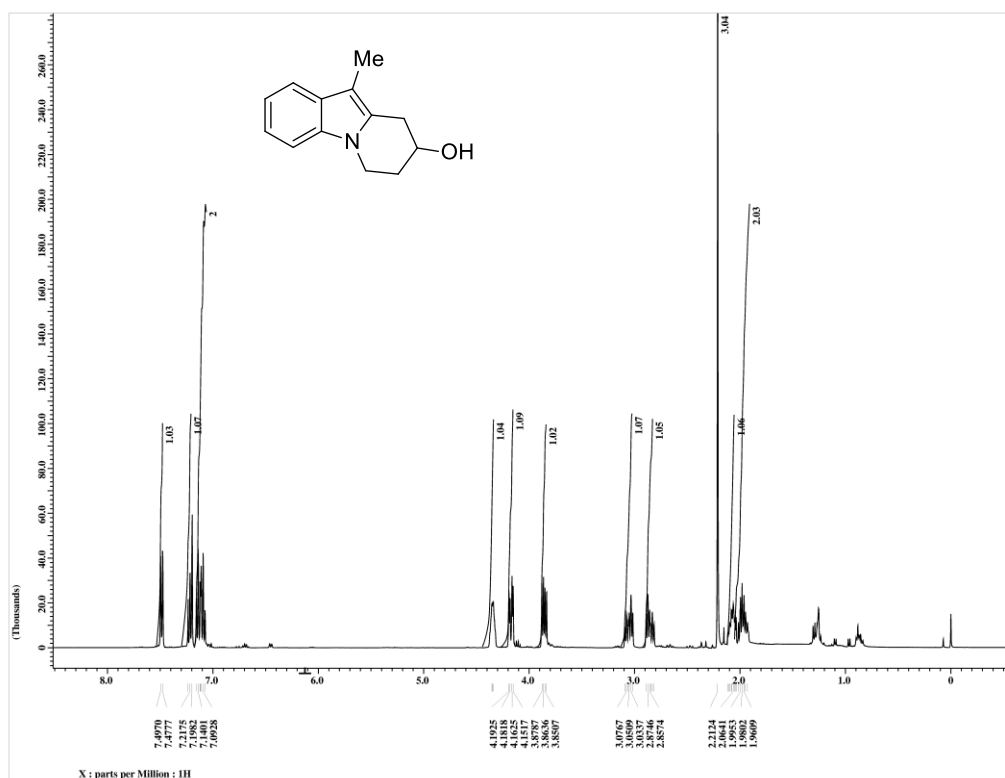
^1H and ^{13}C NMR of 12b:



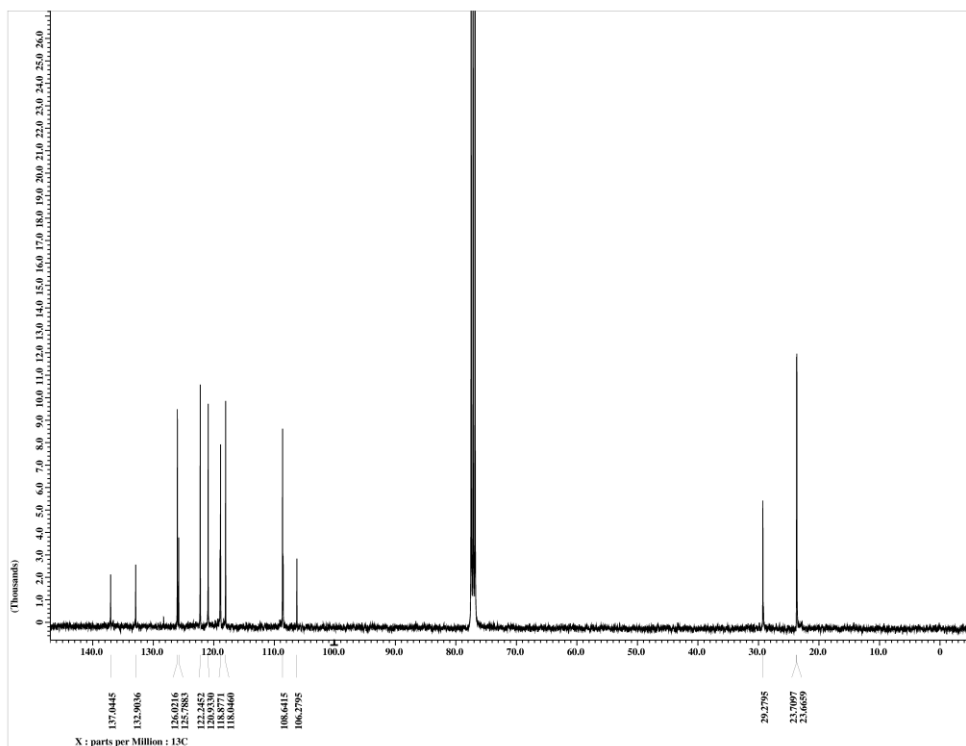
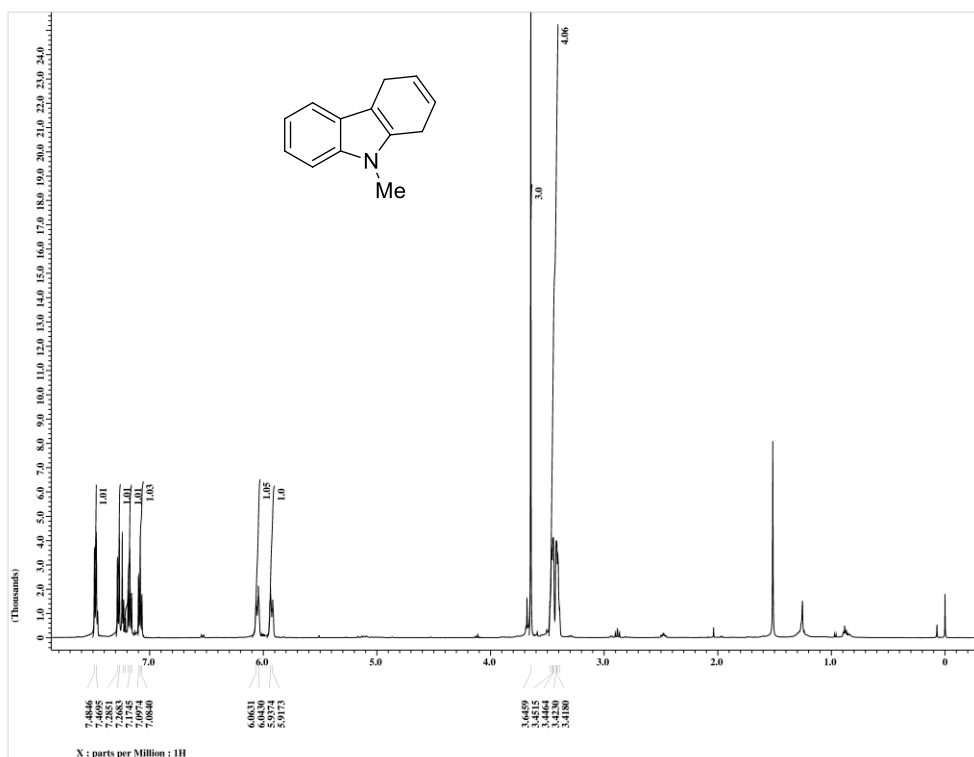
^1H and ^{13}C NMR of 13:



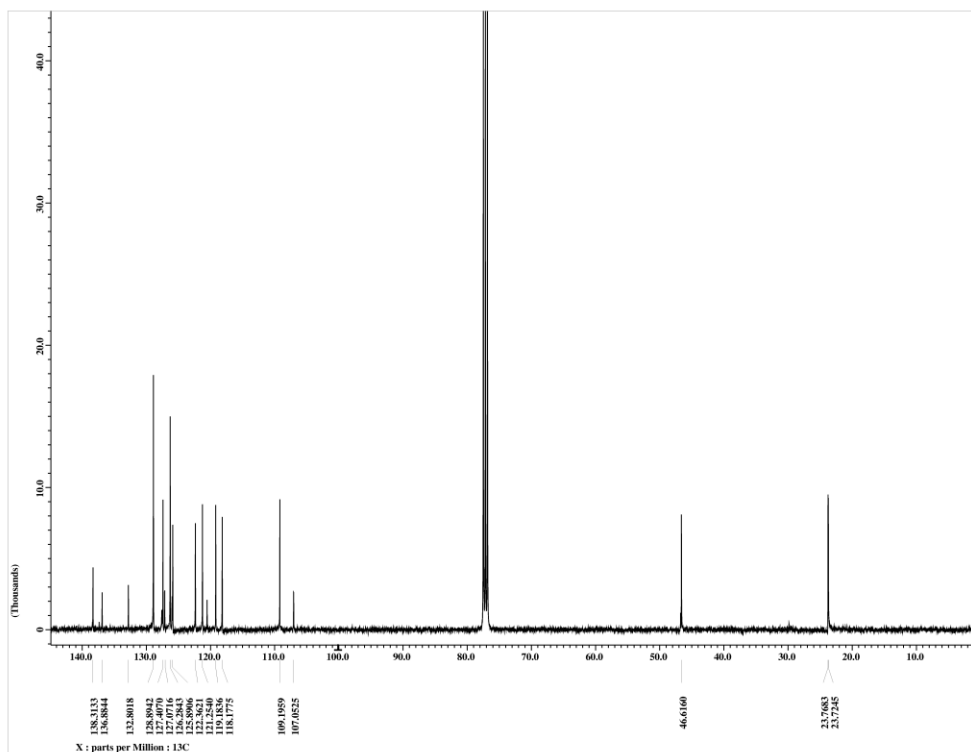
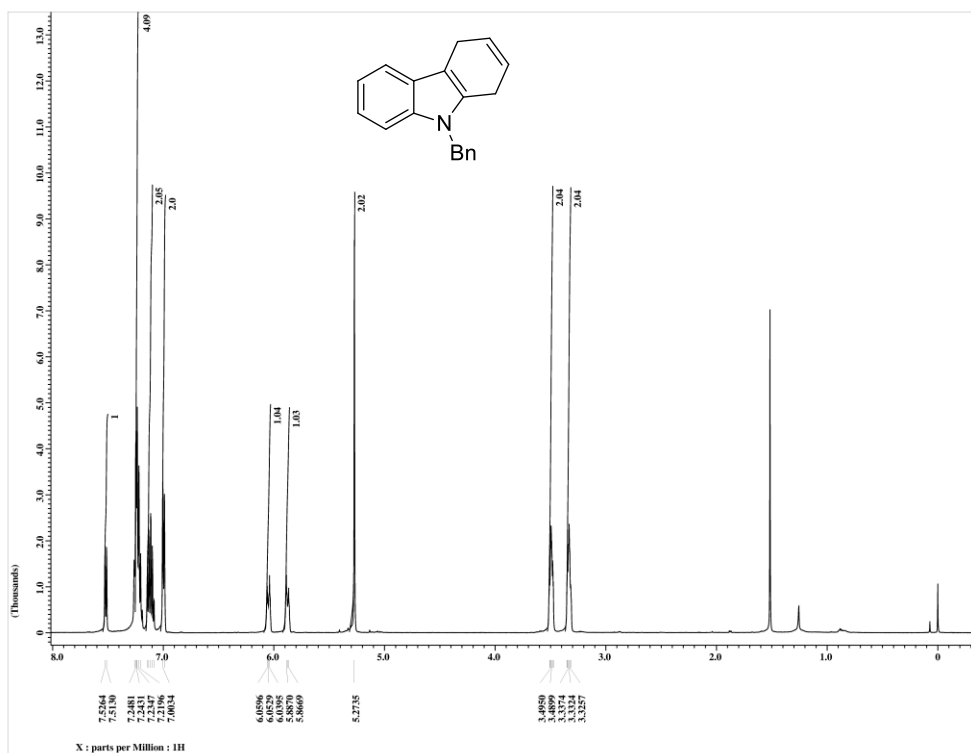
^1H and ^{13}C NMR of 14:



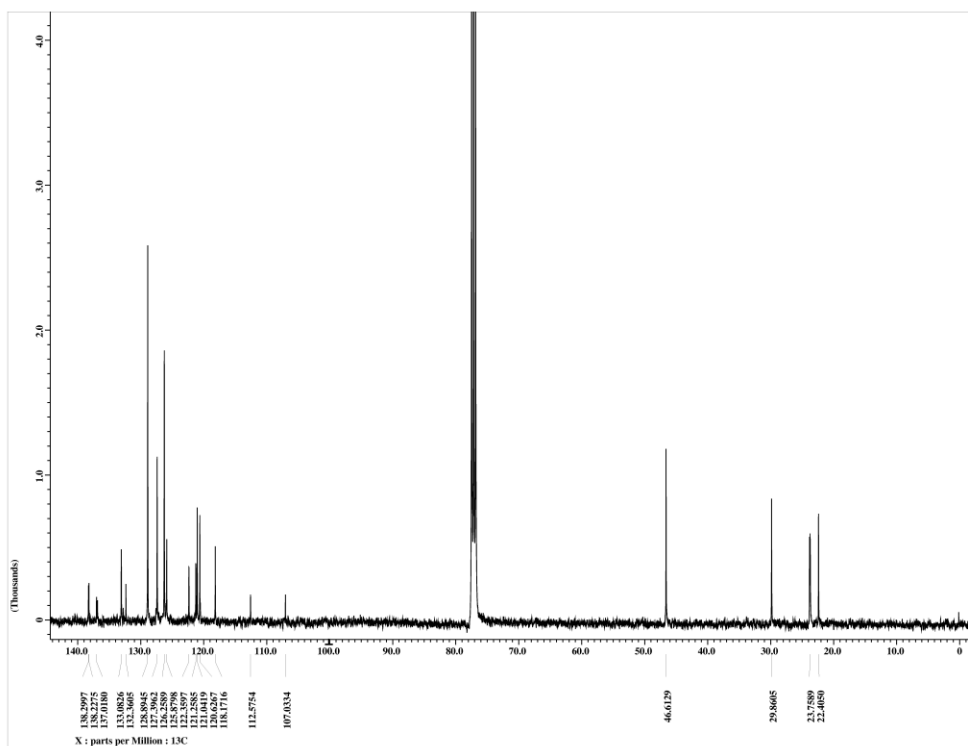
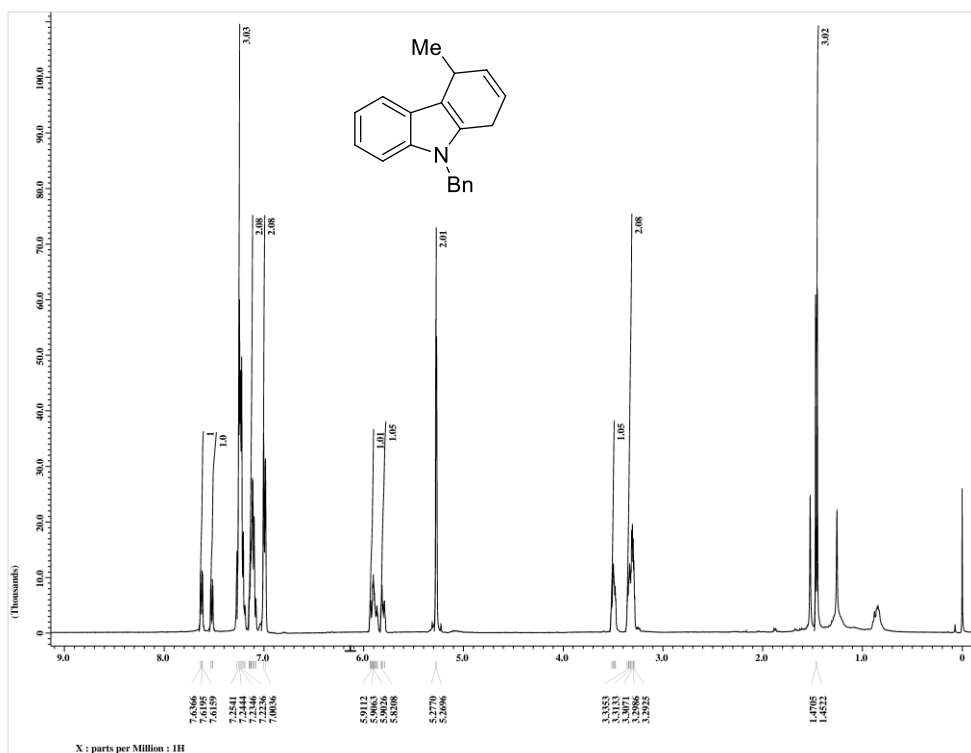
^1H and ^{13}C NMR of 6a:



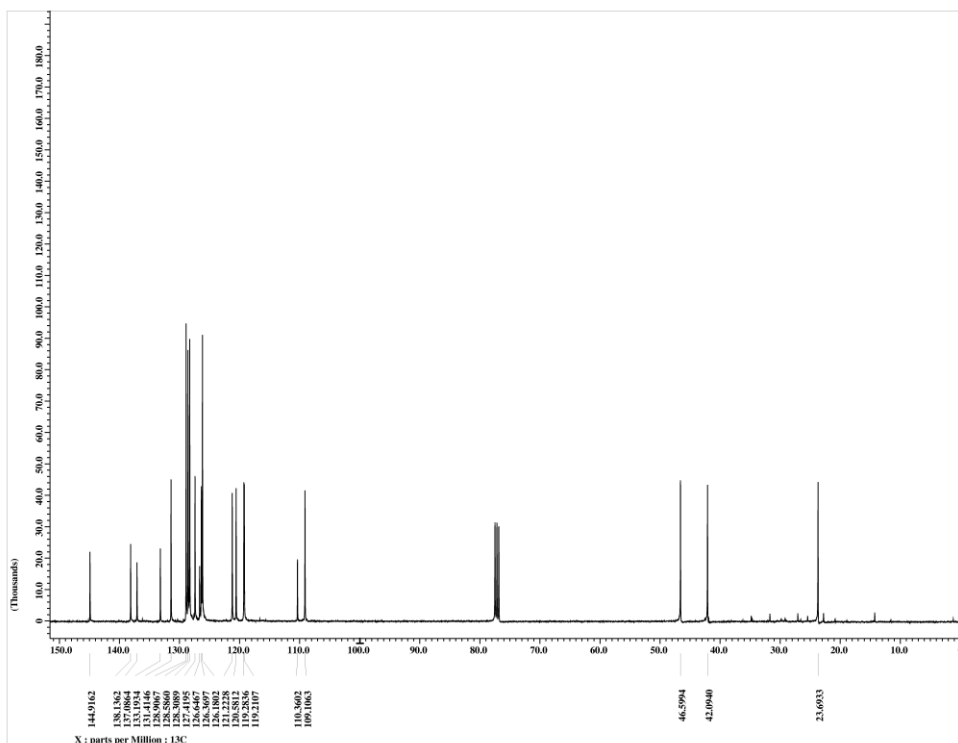
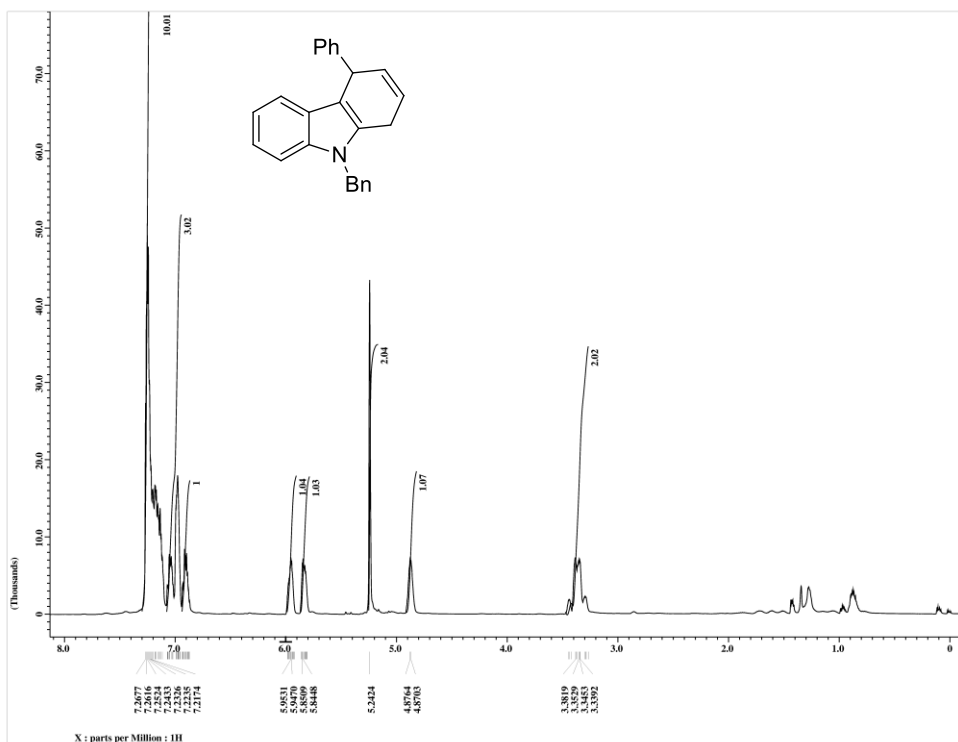
^1H and ^{13}C NMR of 6b:



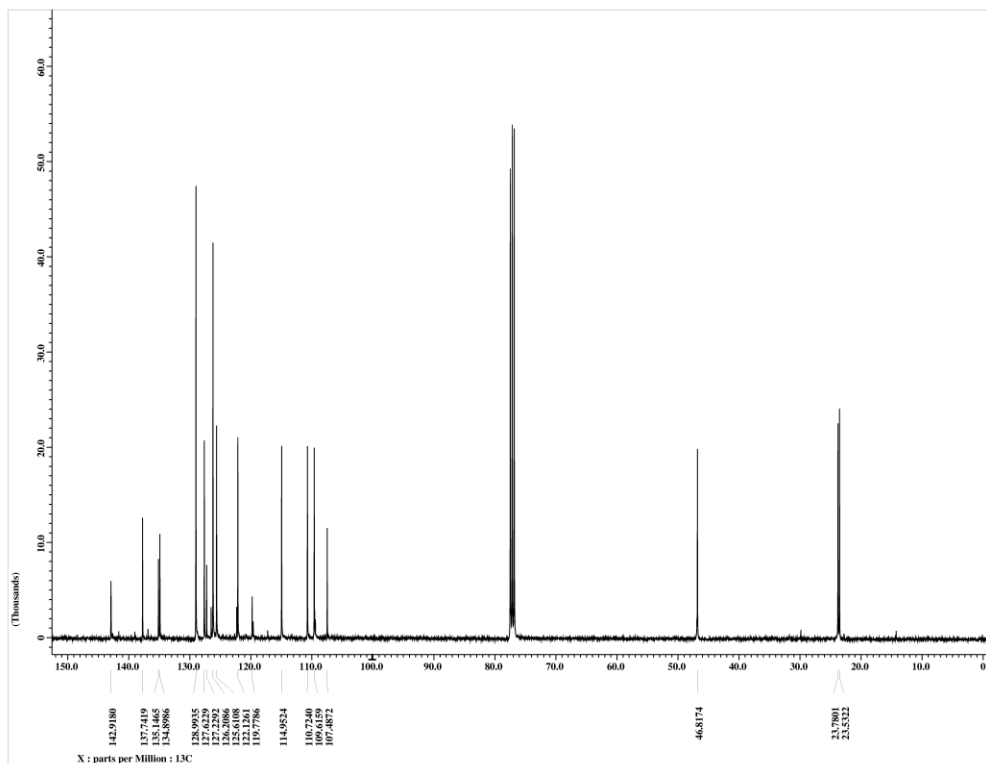
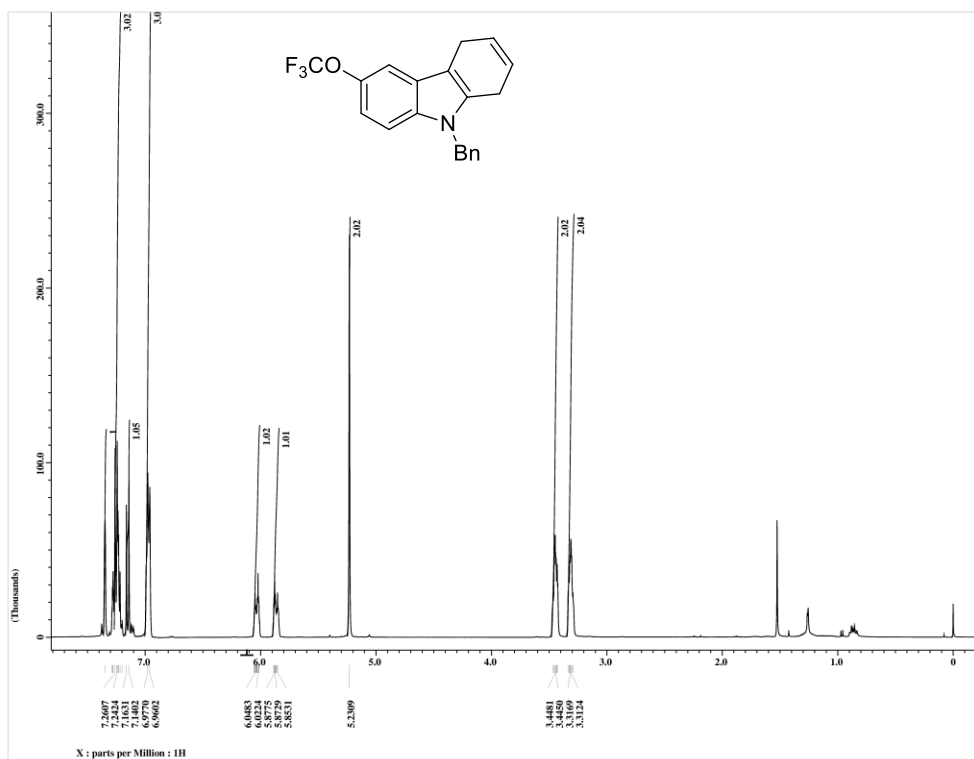
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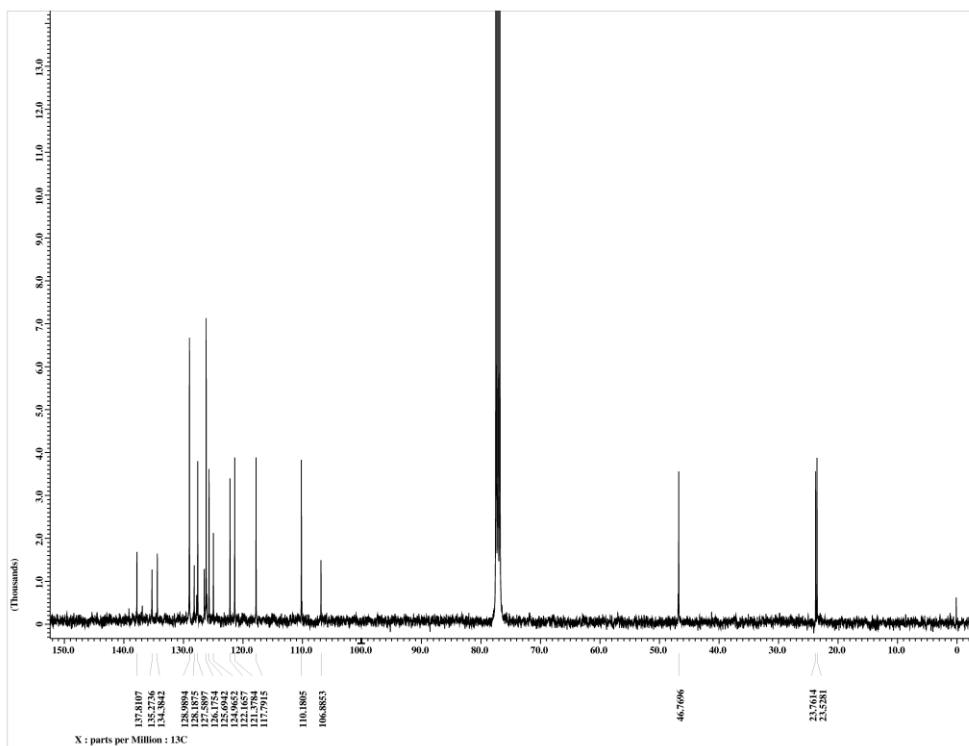
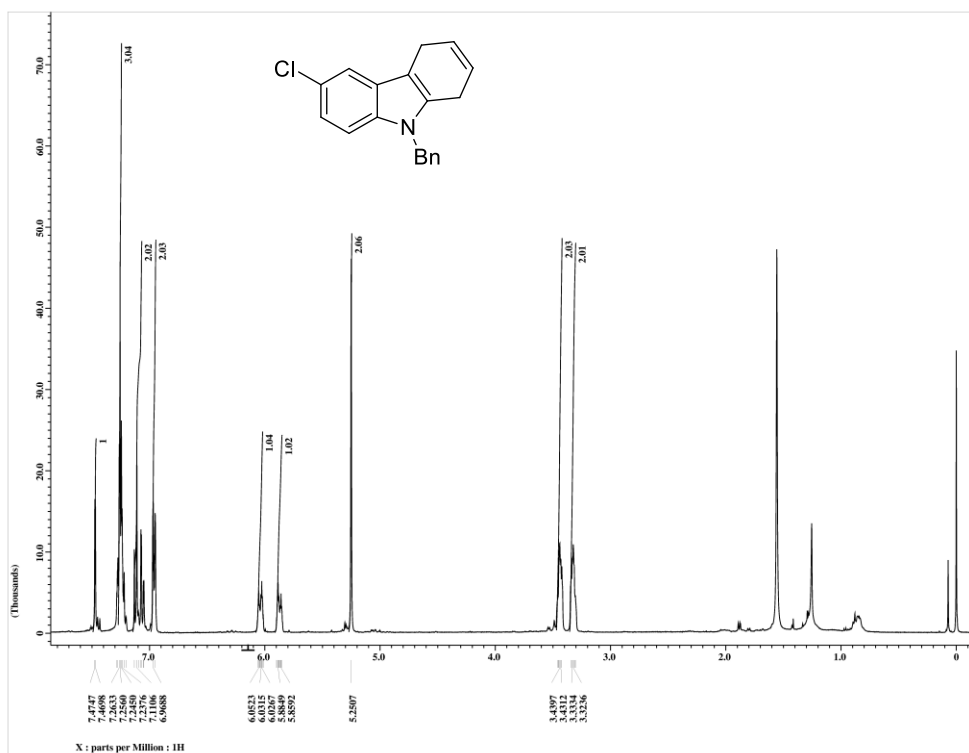
^1H and ^{13}C NMR of 6d:



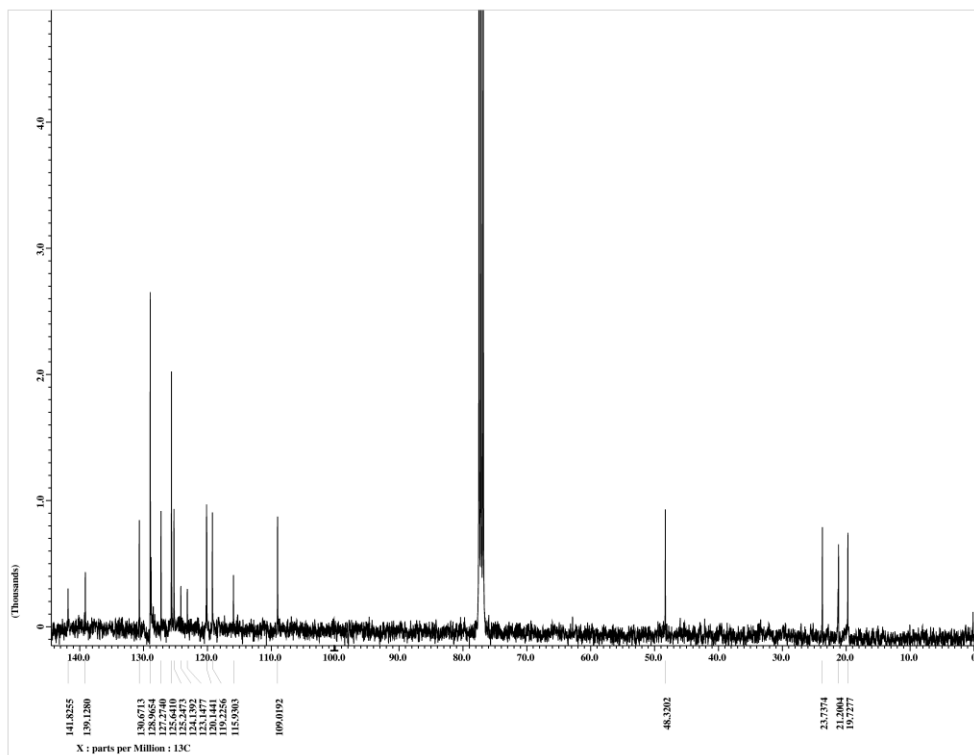
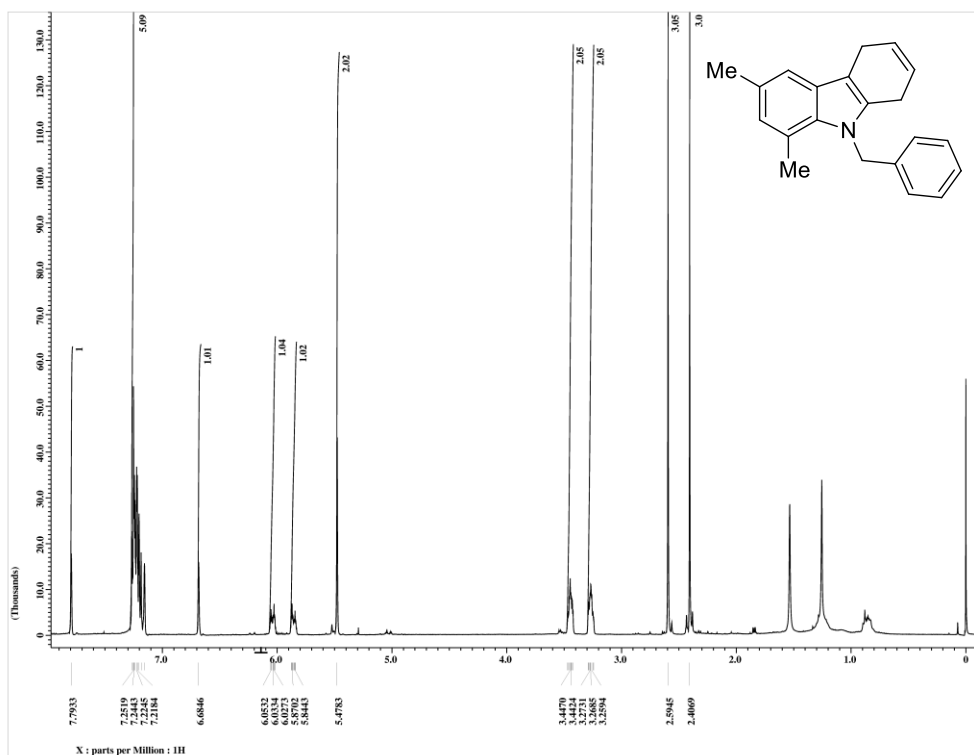
^1H and ^{13}C NMR of 6e:



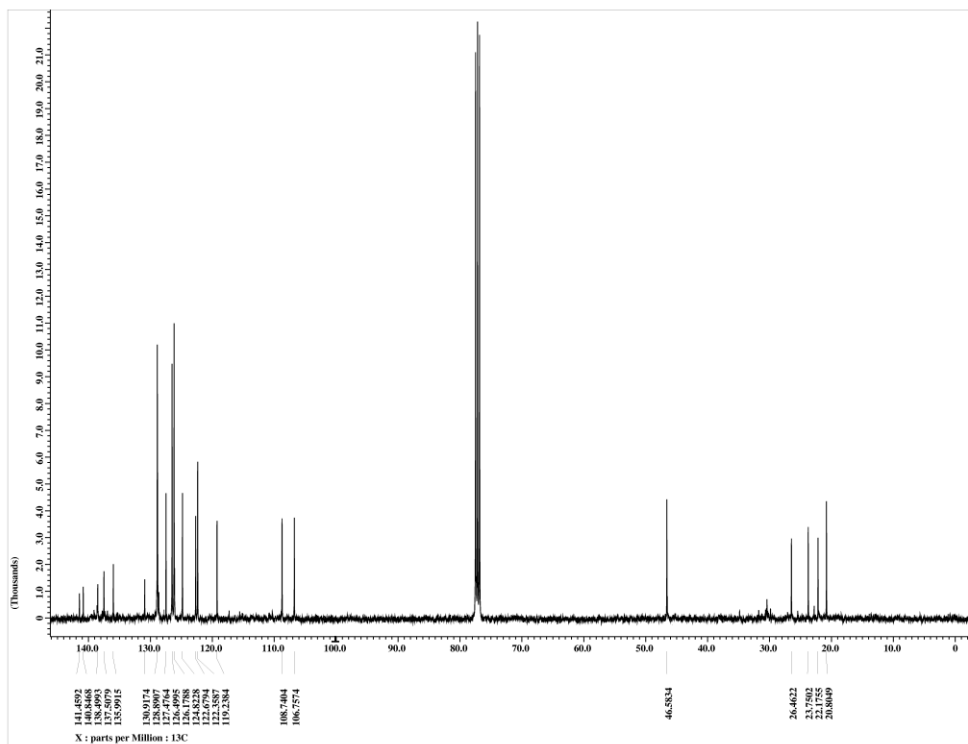
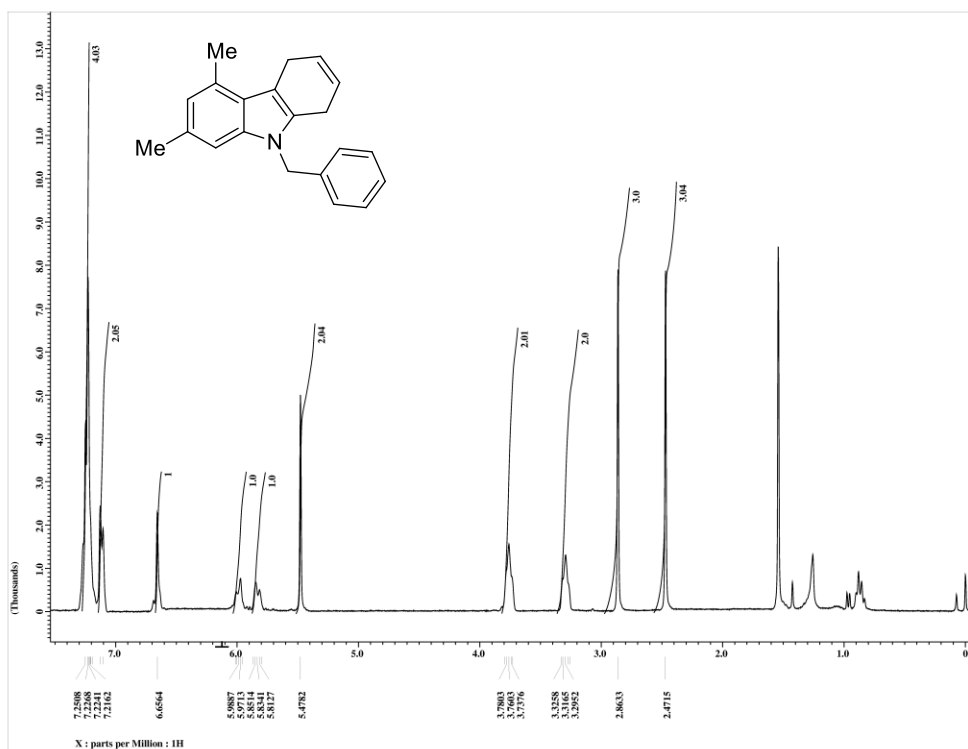
^1H and ^{13}C NMR of 6f:



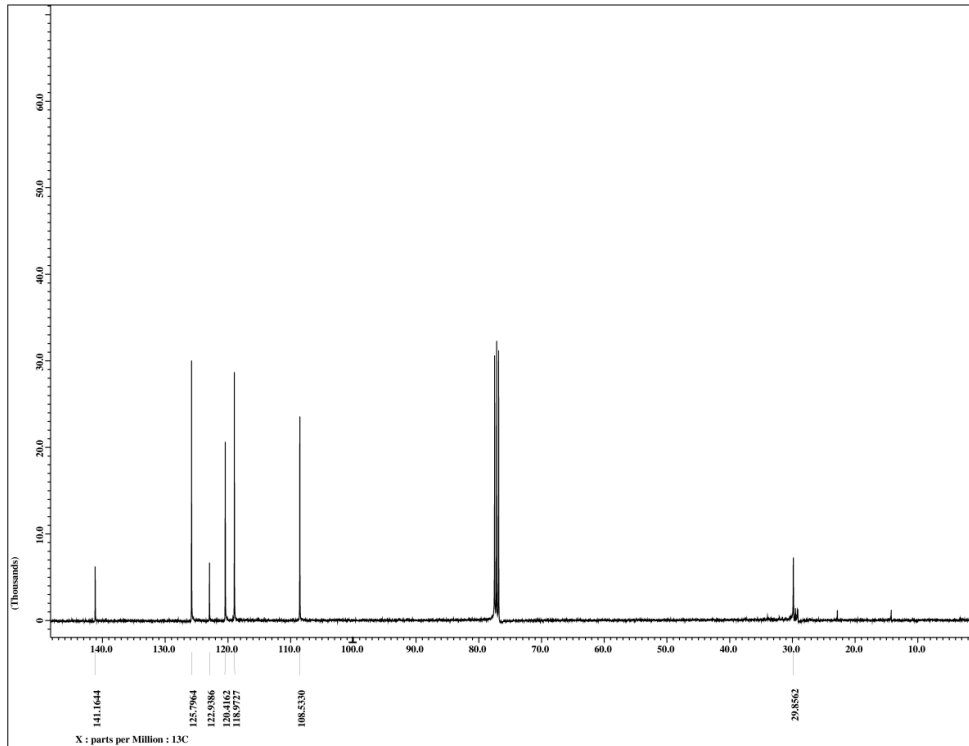
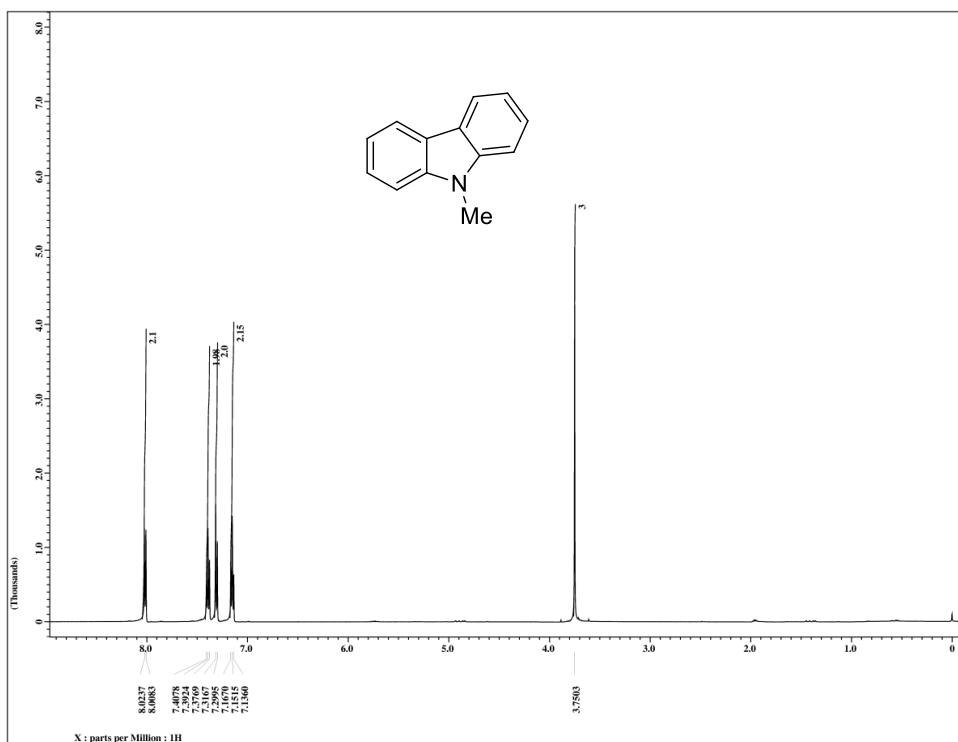
^1H and ^{13}C NMR of 6g:



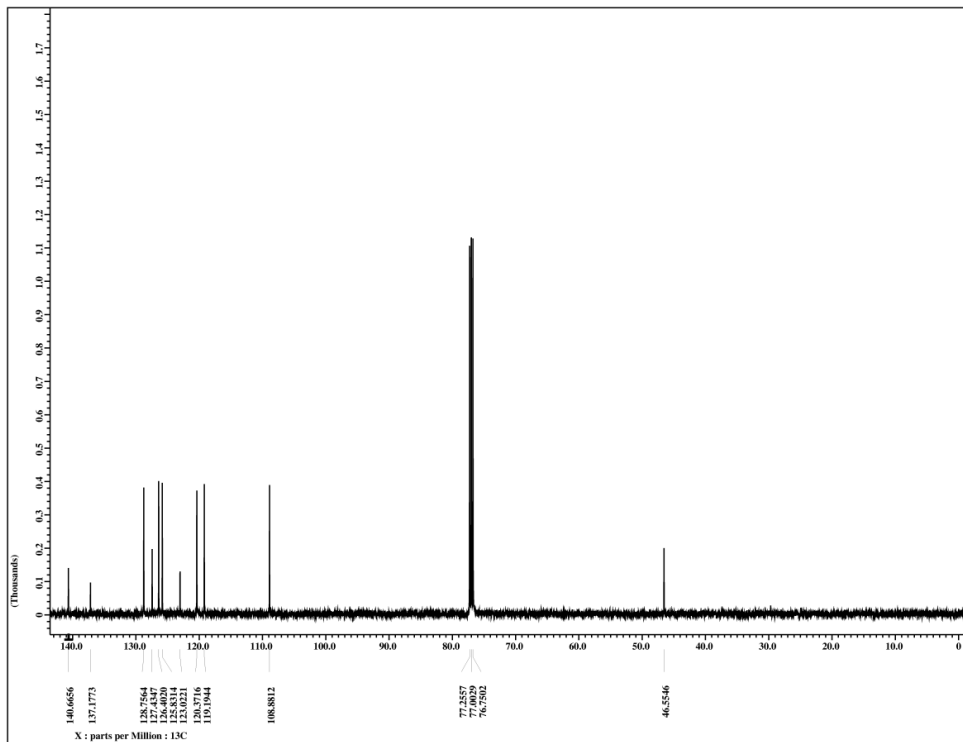
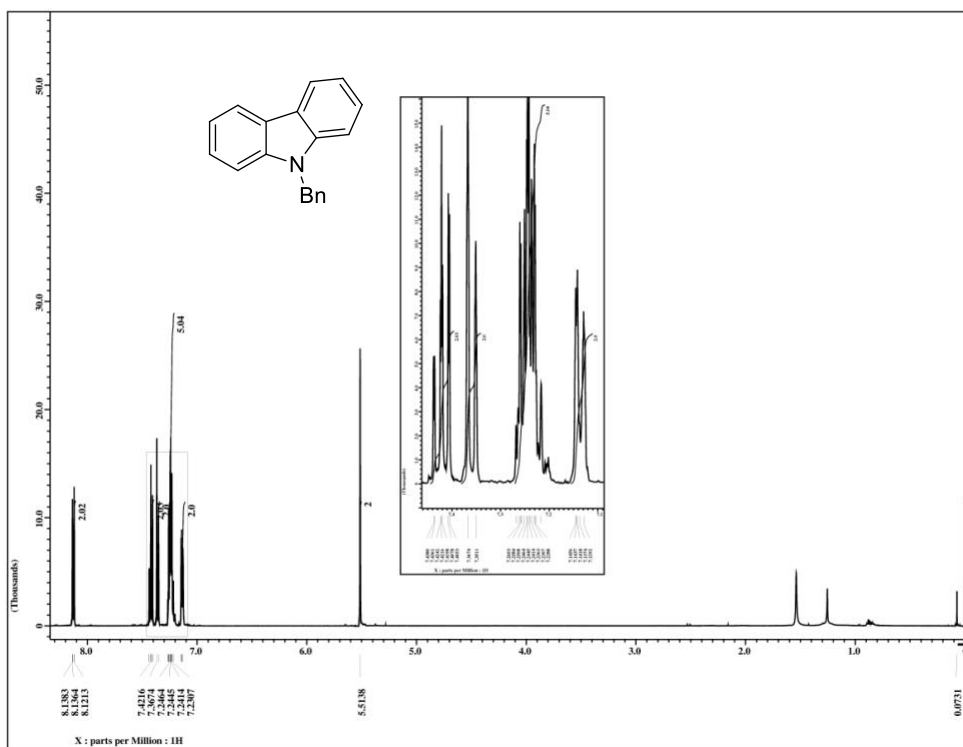
^1H and ^{13}C NMR of 6h:



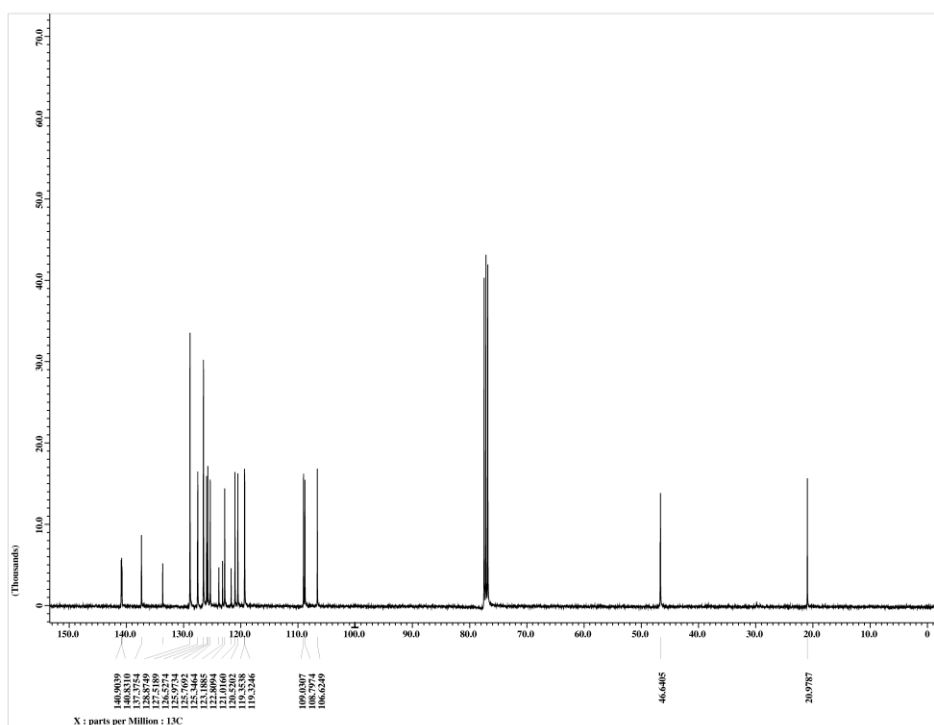
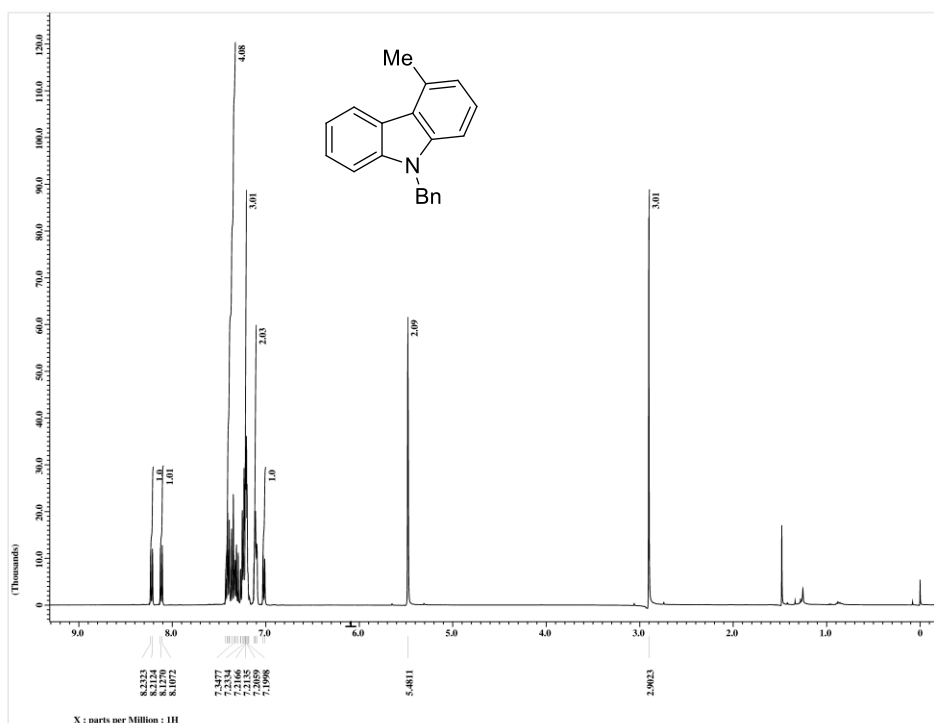
^1H and ^{13}C NMR of 8a:



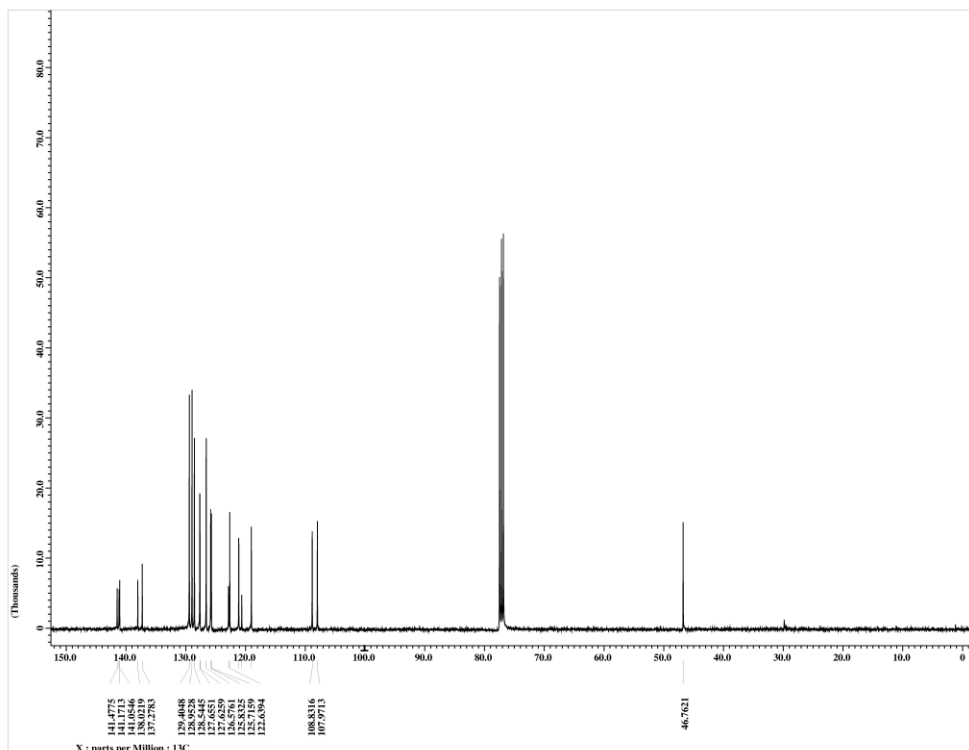
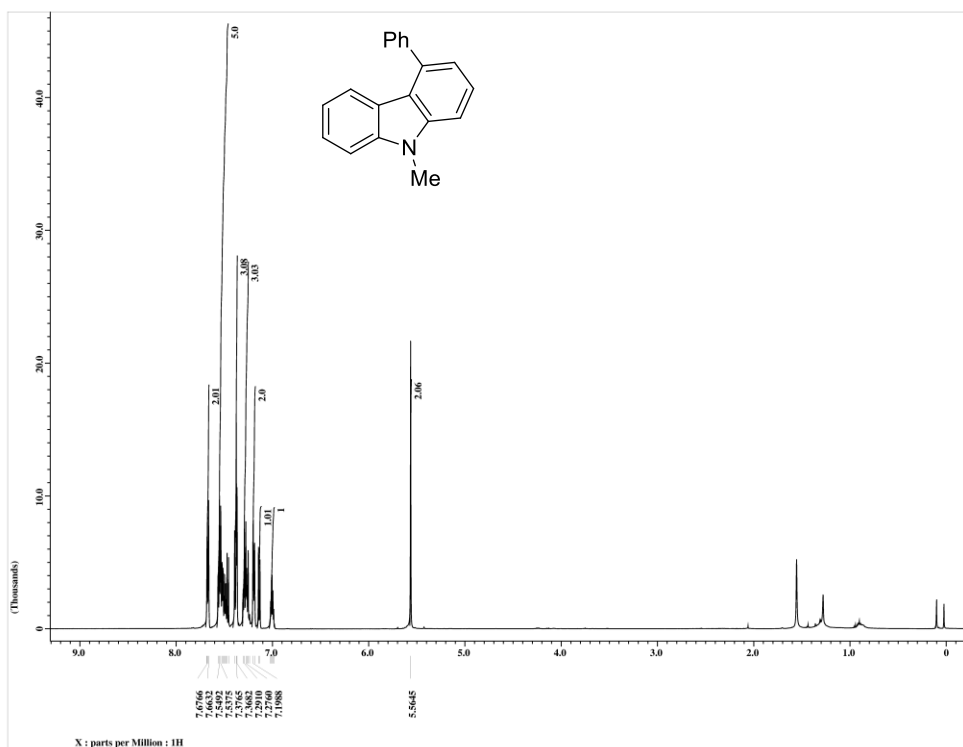
^1H and ^{13}C NMR of 8b:



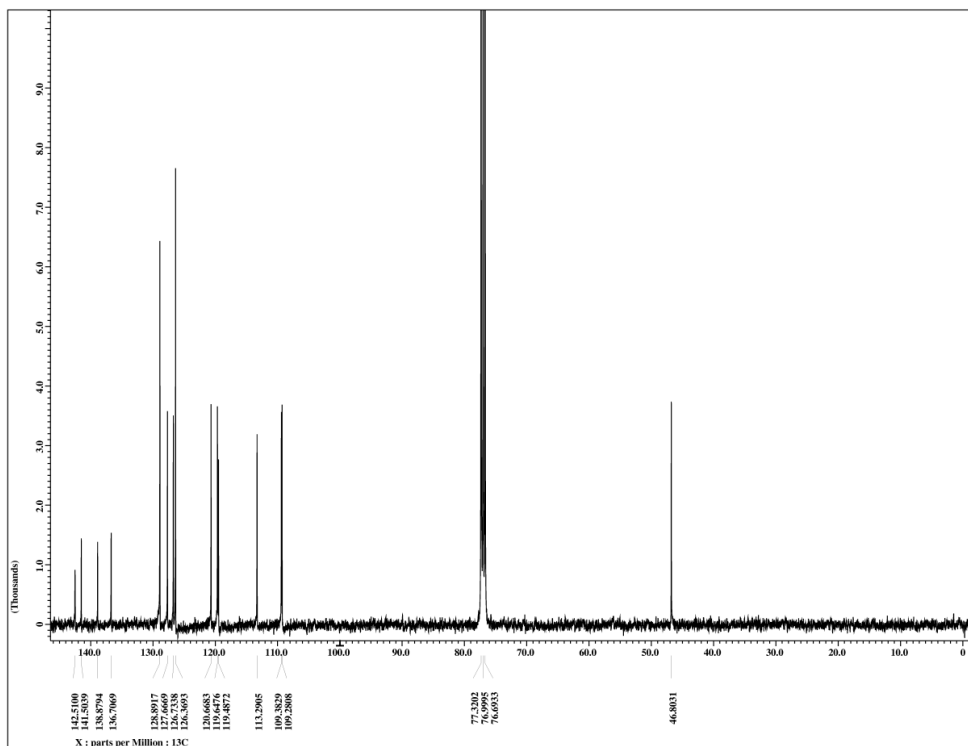
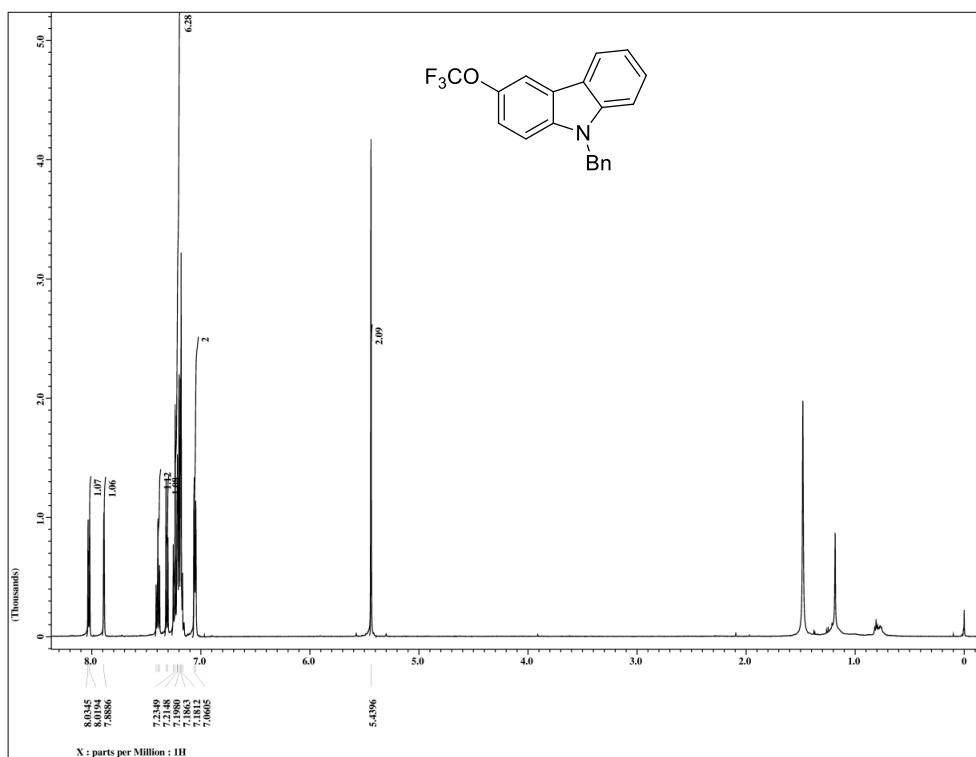
^1H and ^{13}C NMR of 8c:



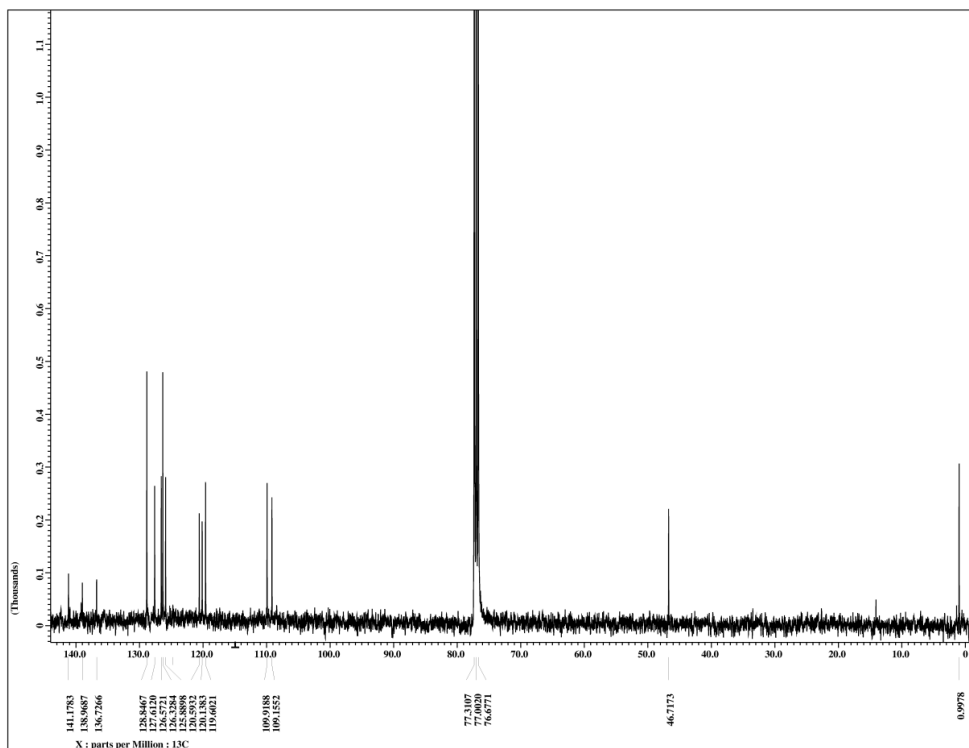
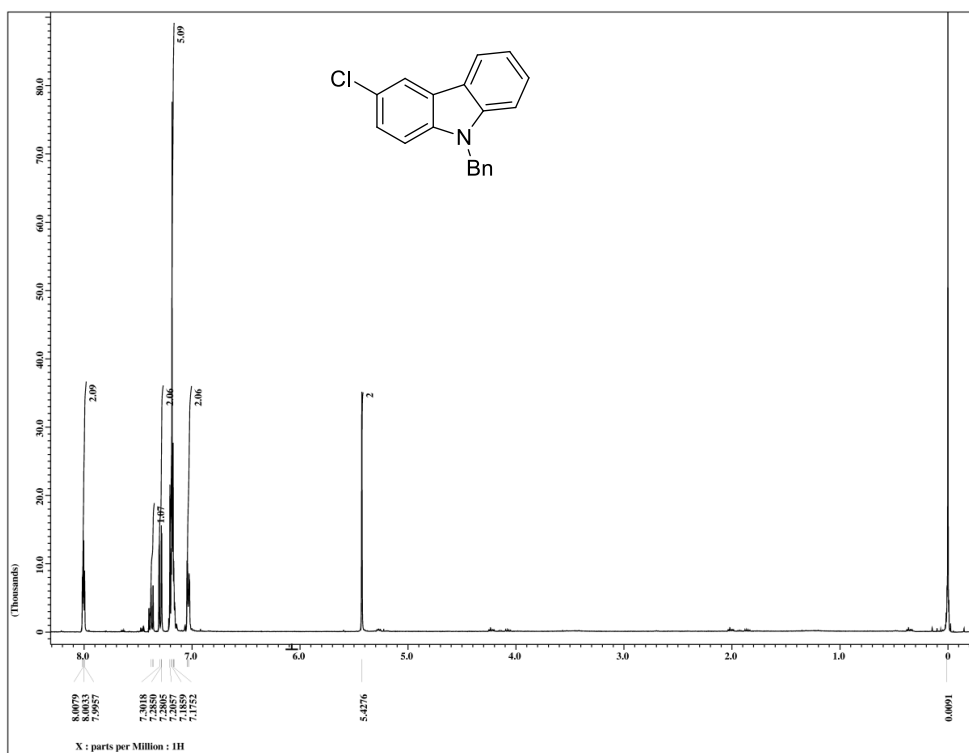
^1H and ^{13}C NMR of 8d:



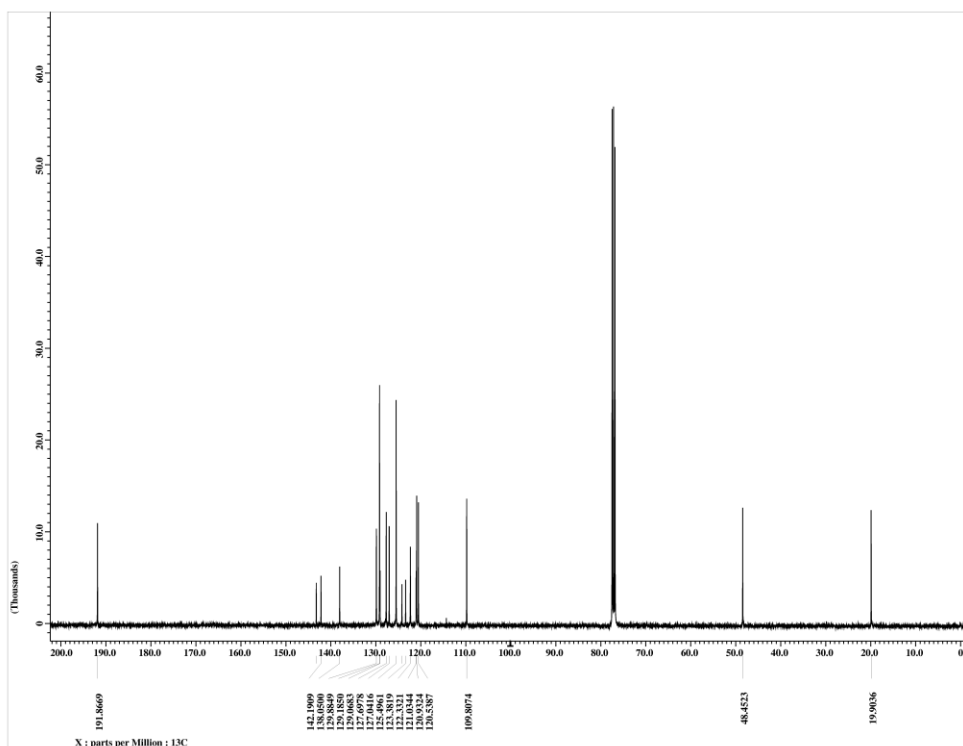
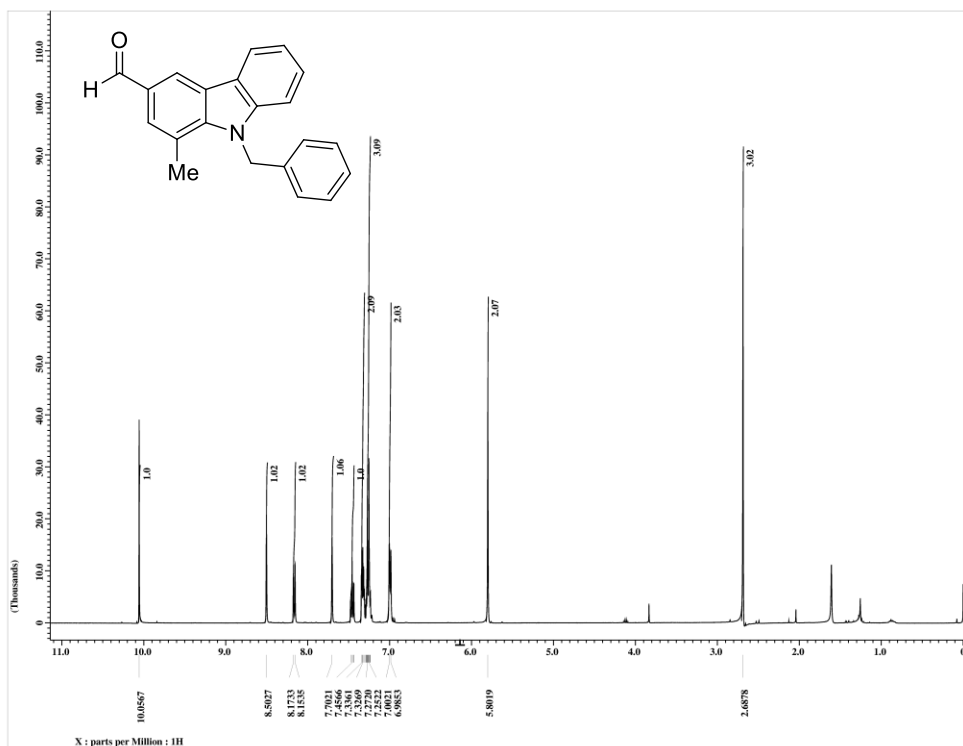
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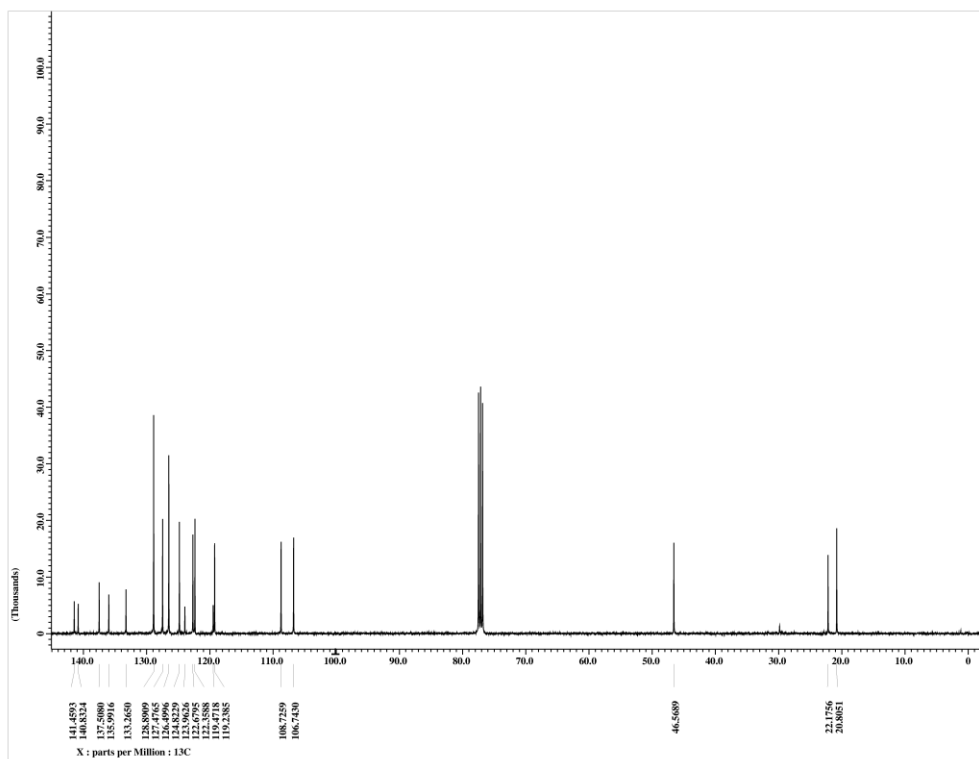
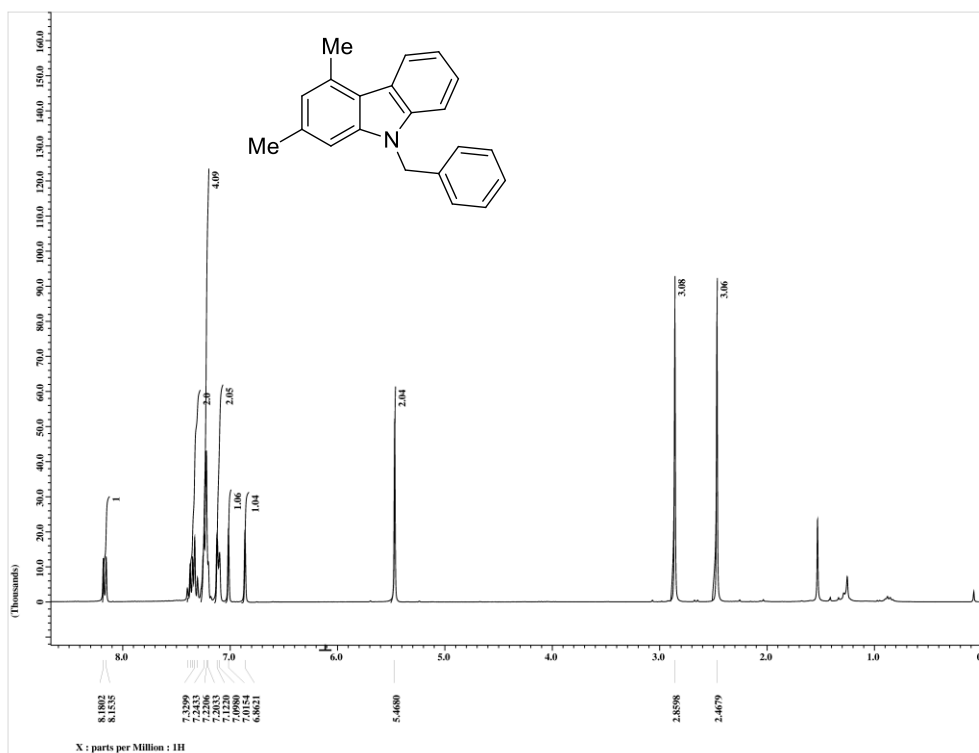
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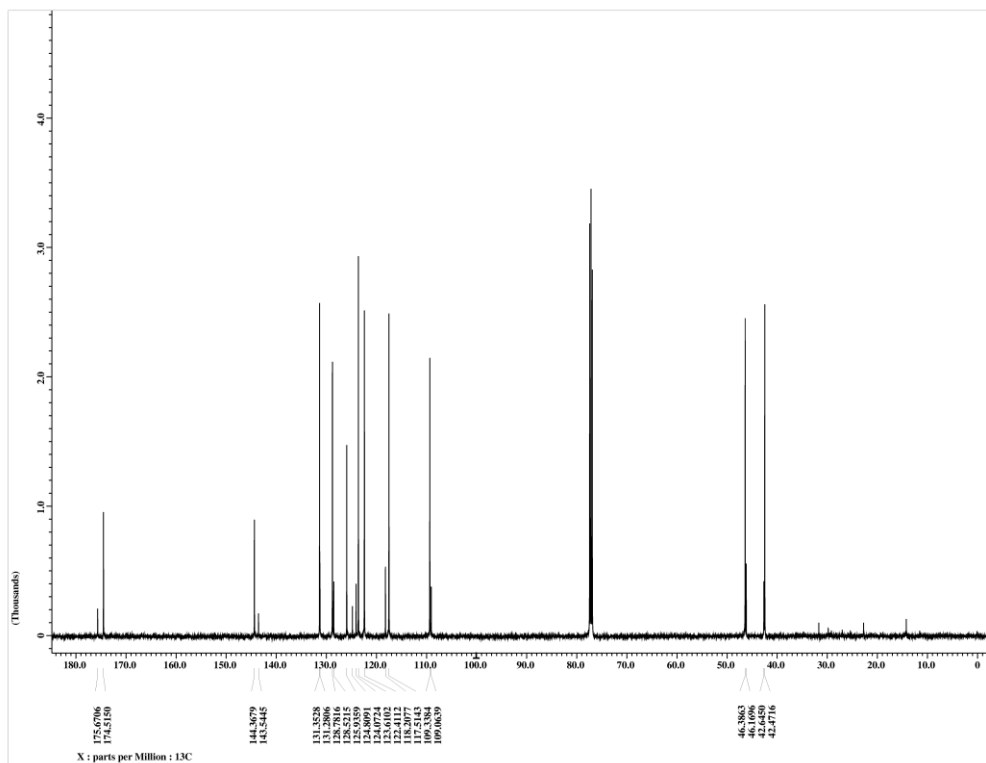
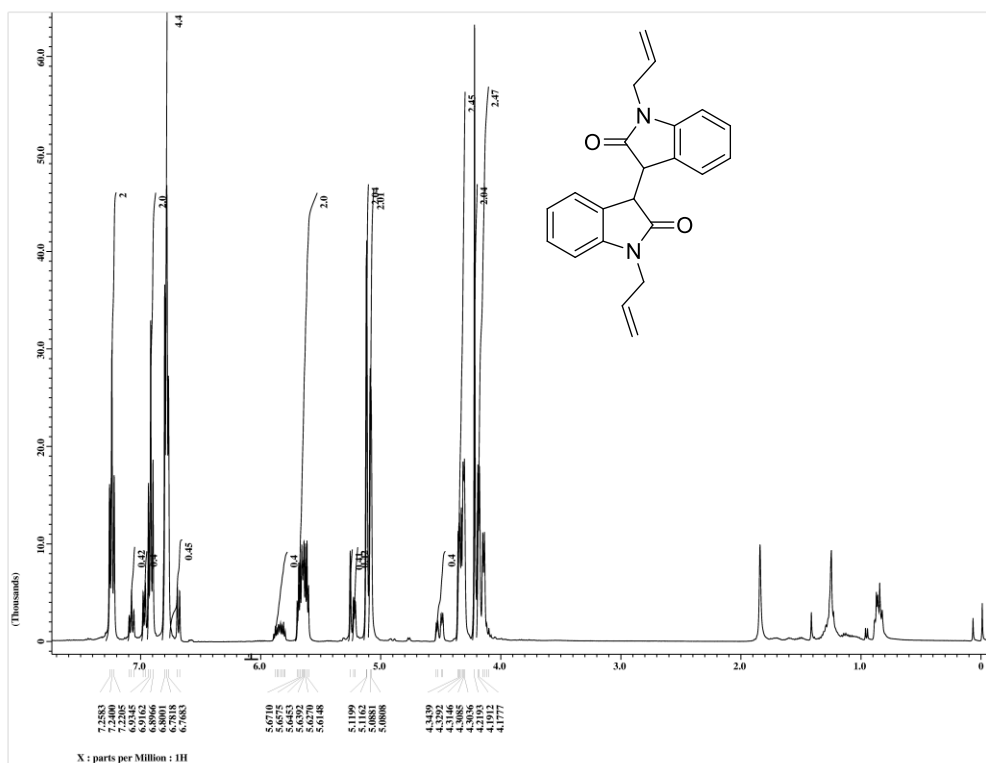
^1H and ^{13}C NMR of 8g:



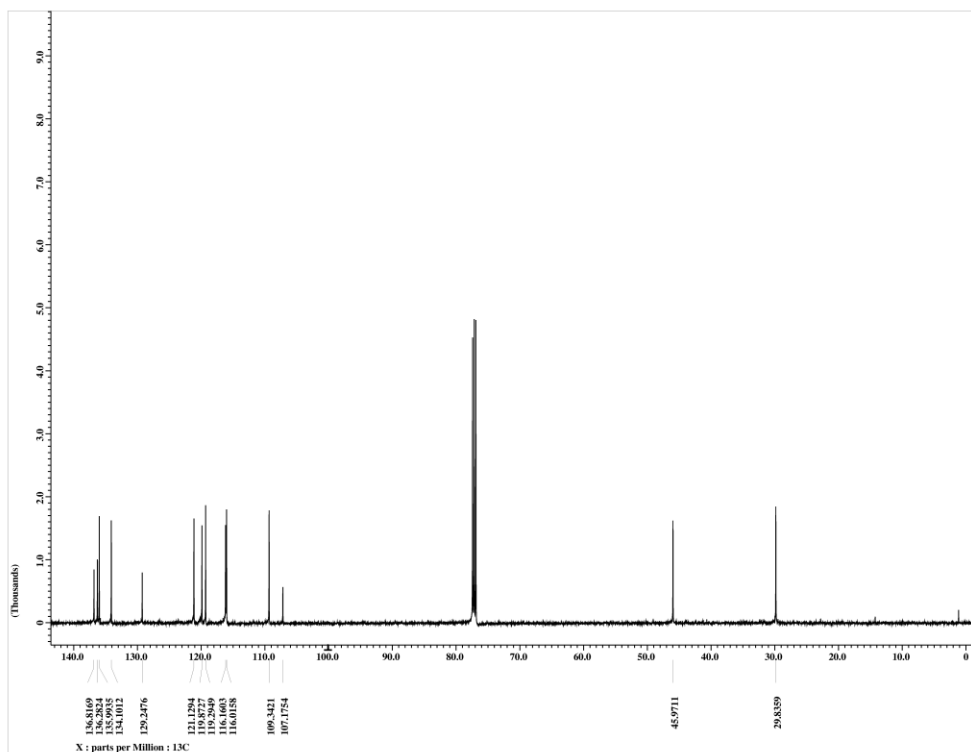
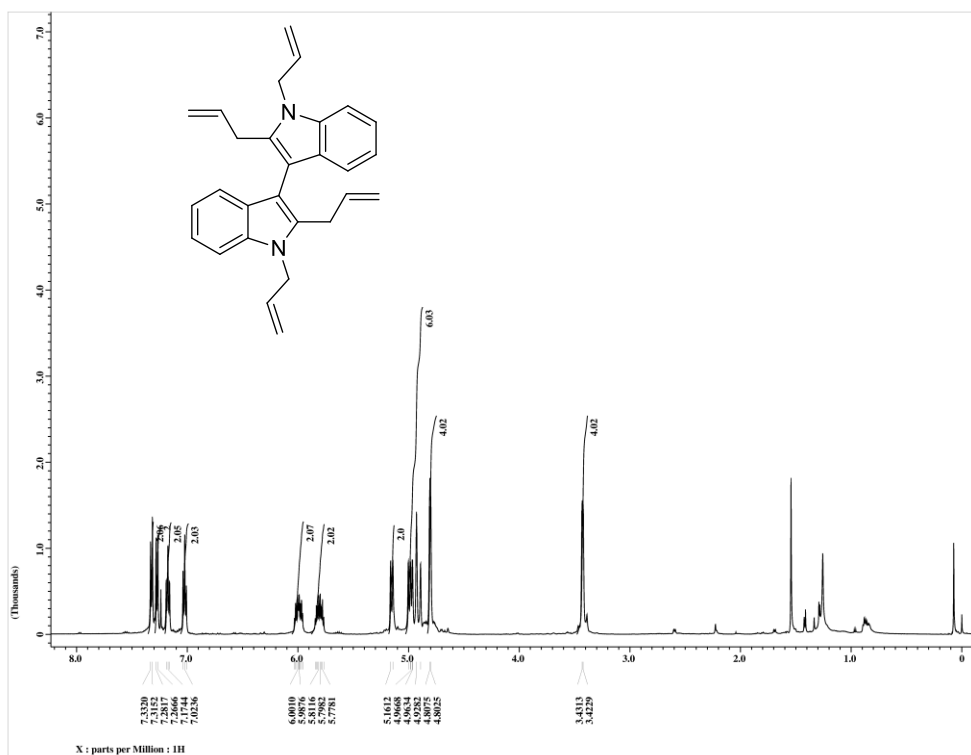
^1H and ^{13}C NMR of 8h:



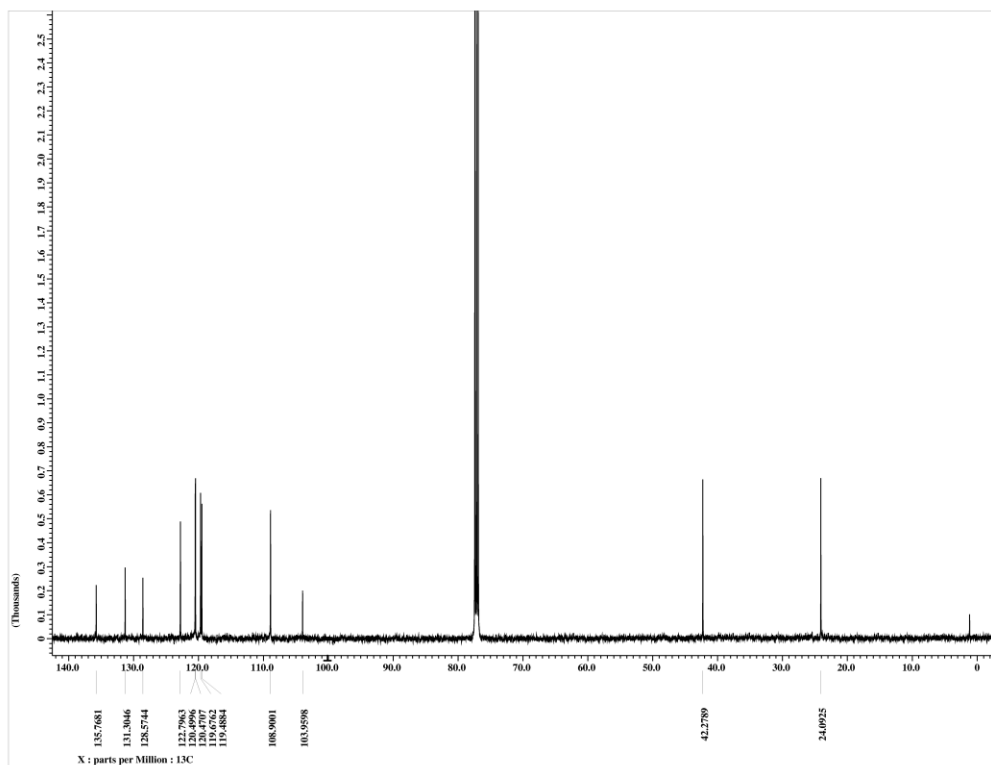
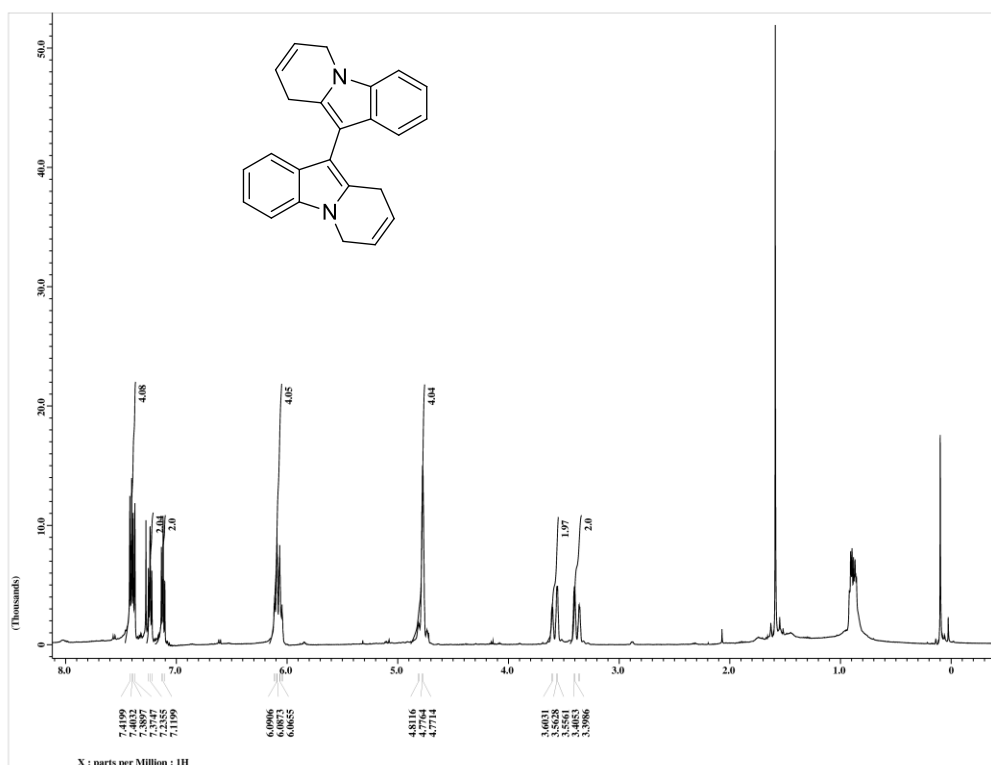
^1H and ^{13}C NMR of 2v:



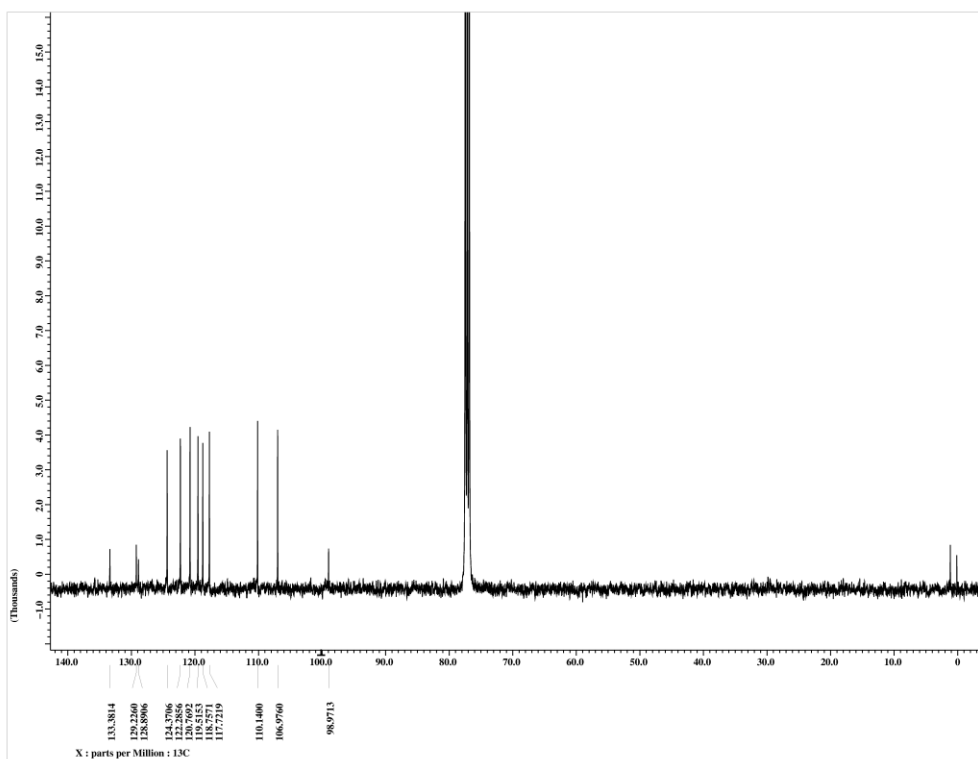
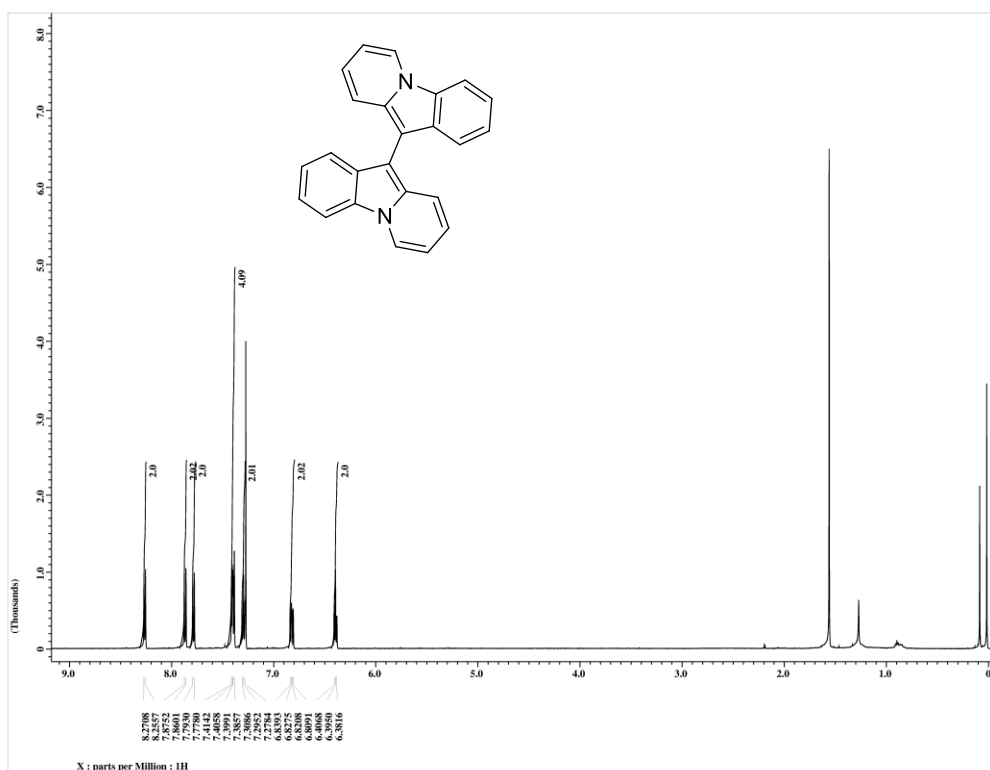
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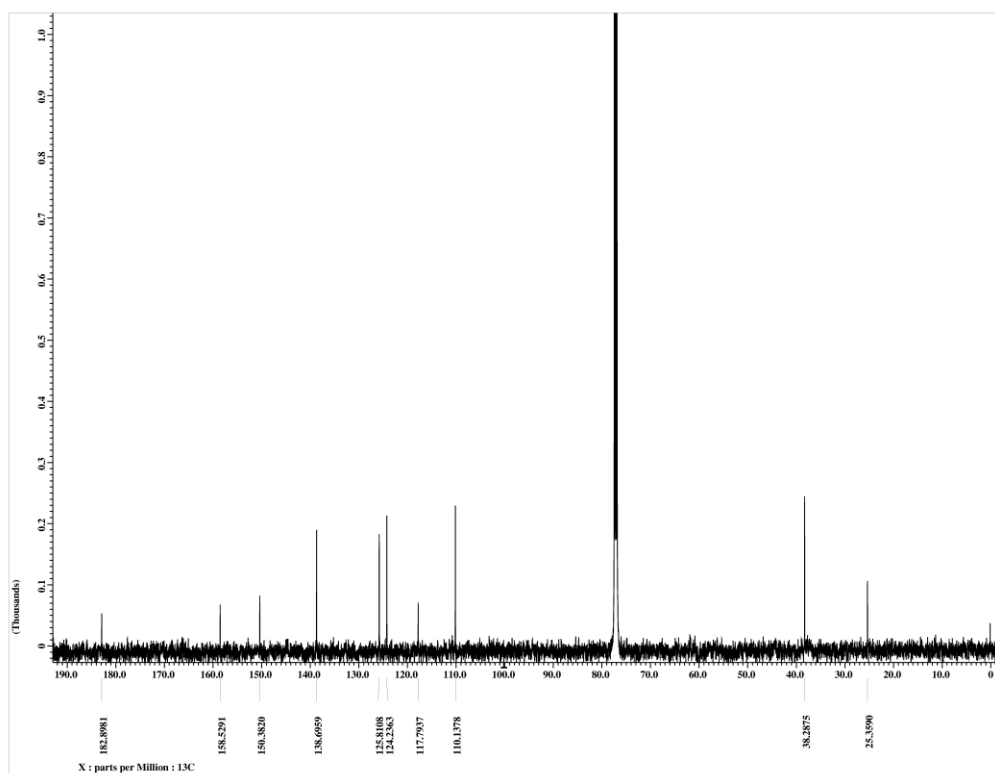
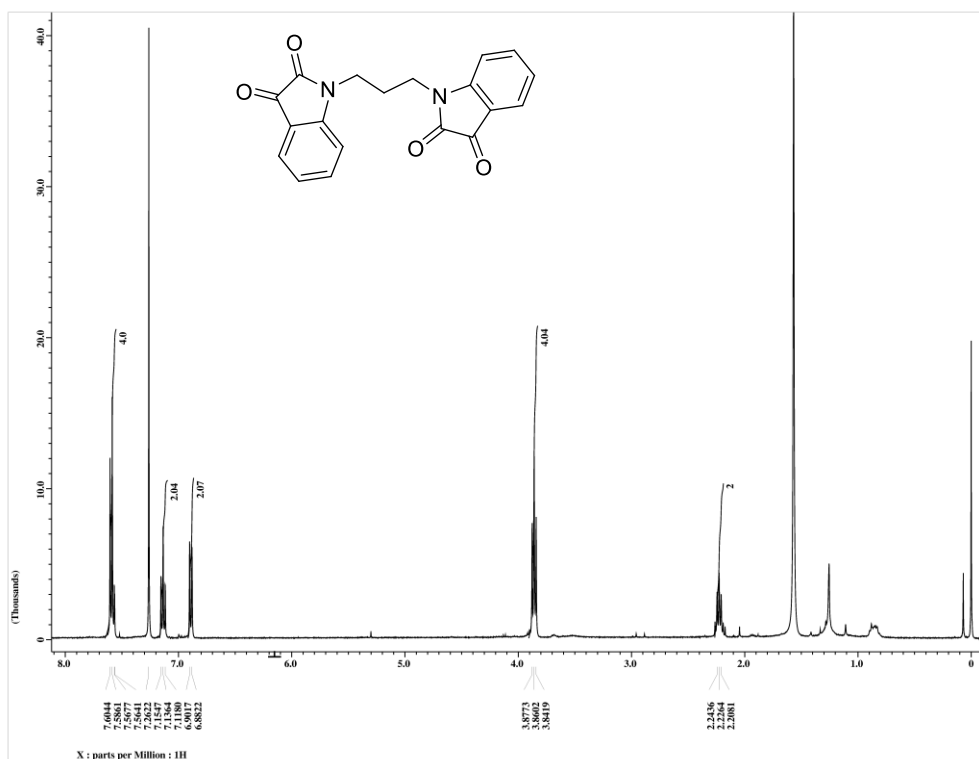
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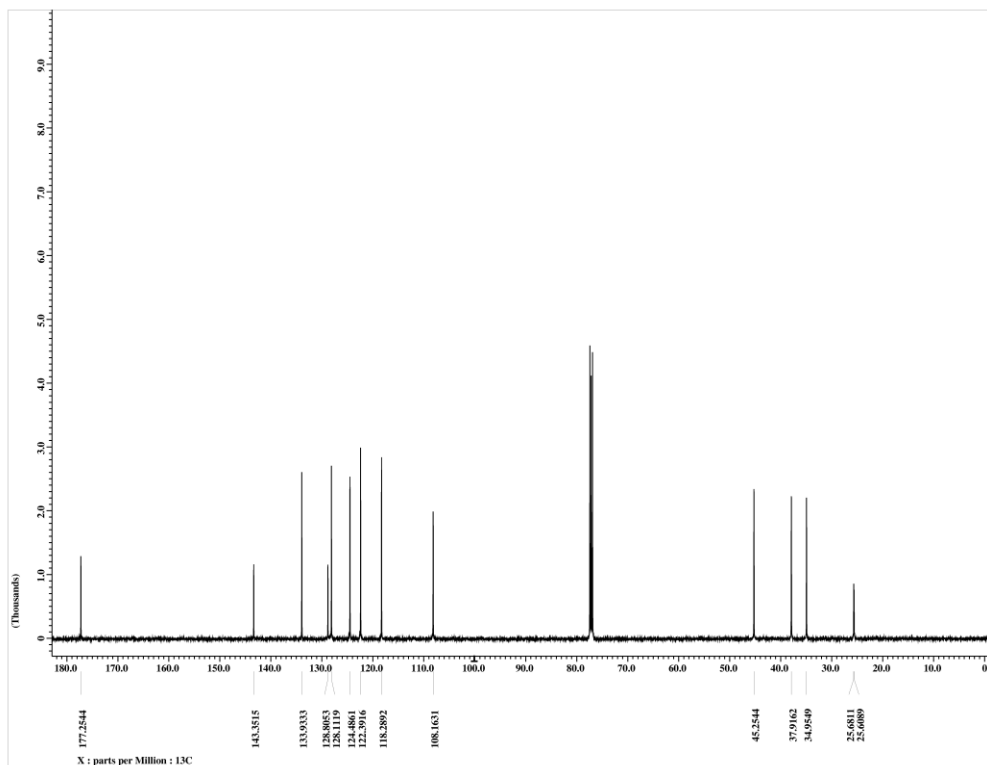
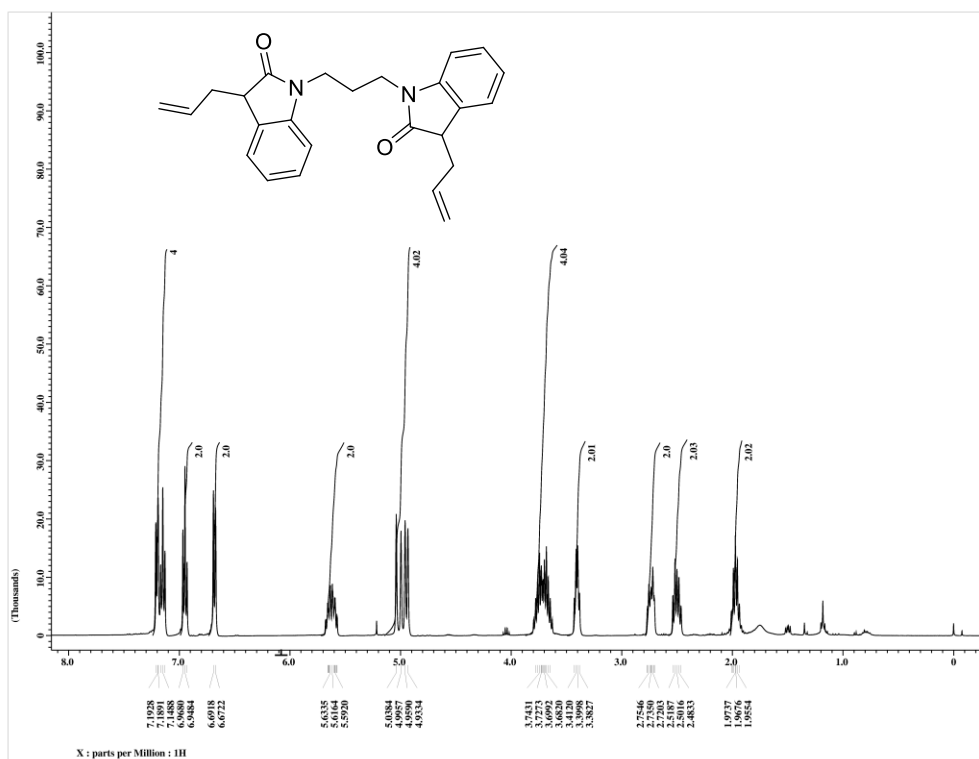
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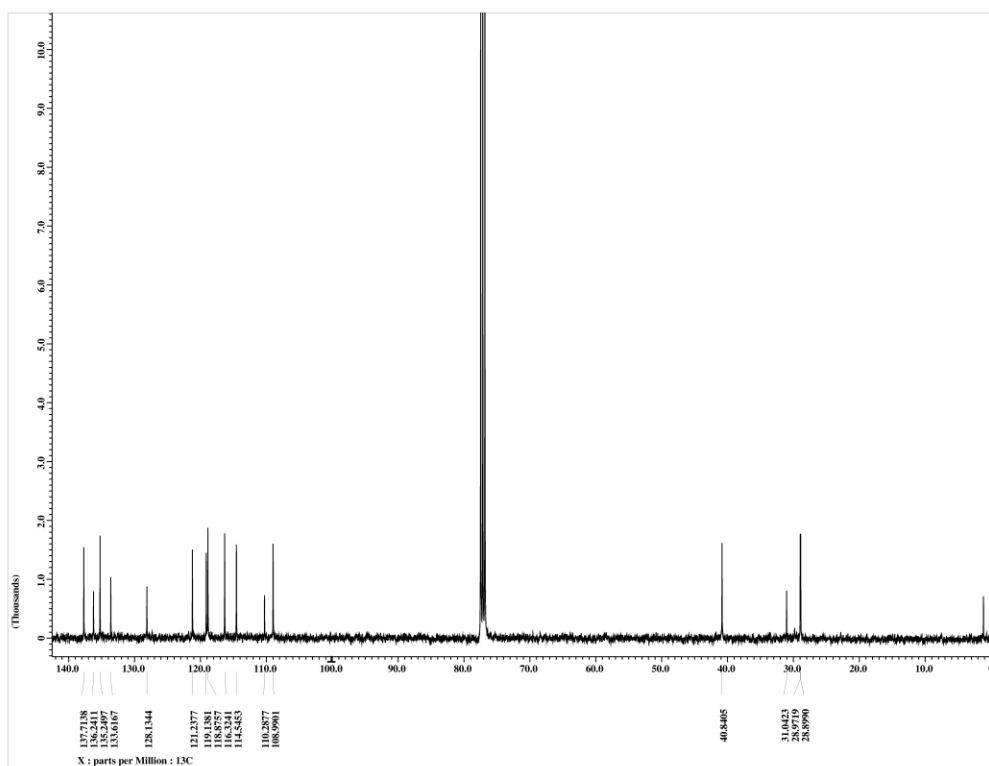
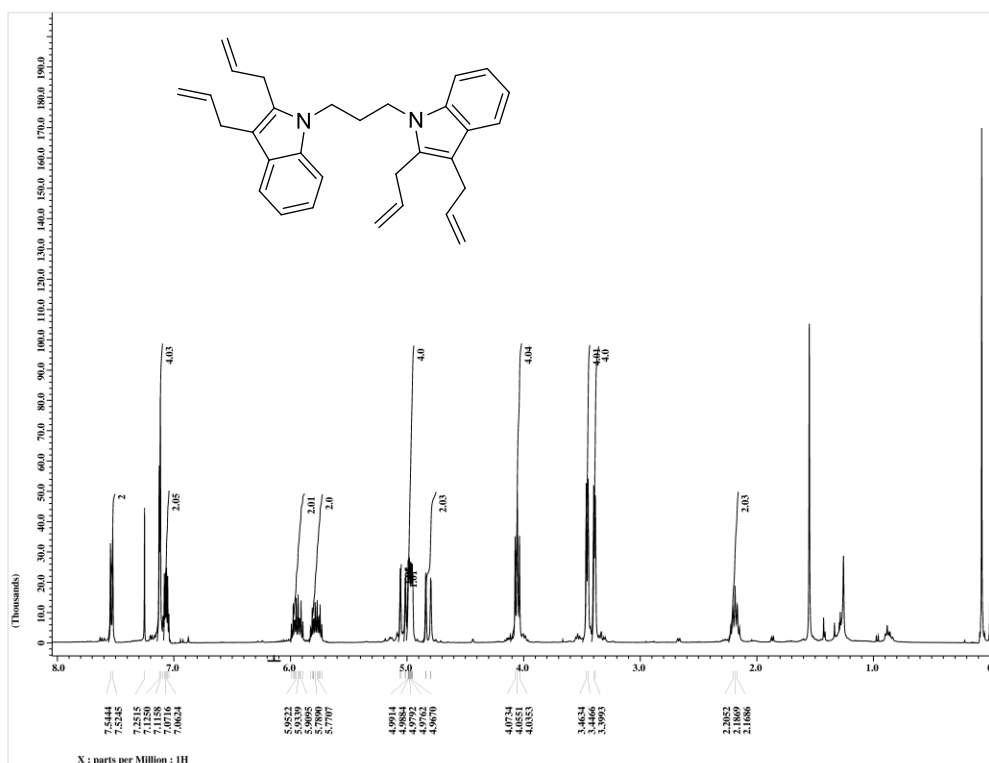
^1H and ^{13}C NMR of S2r:



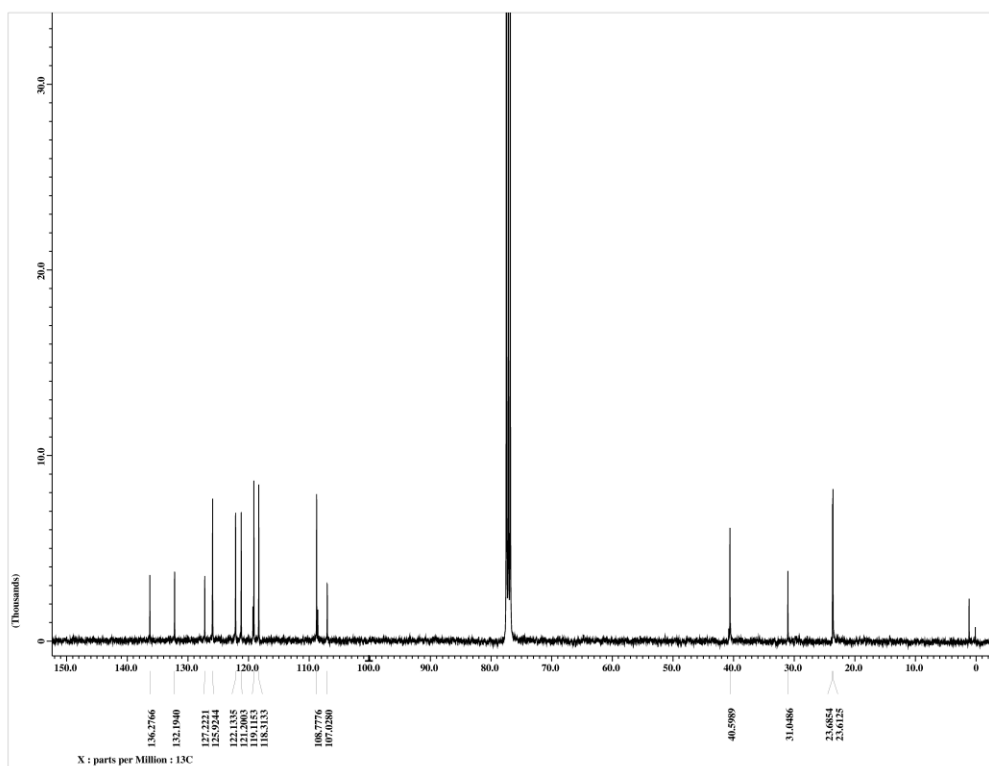
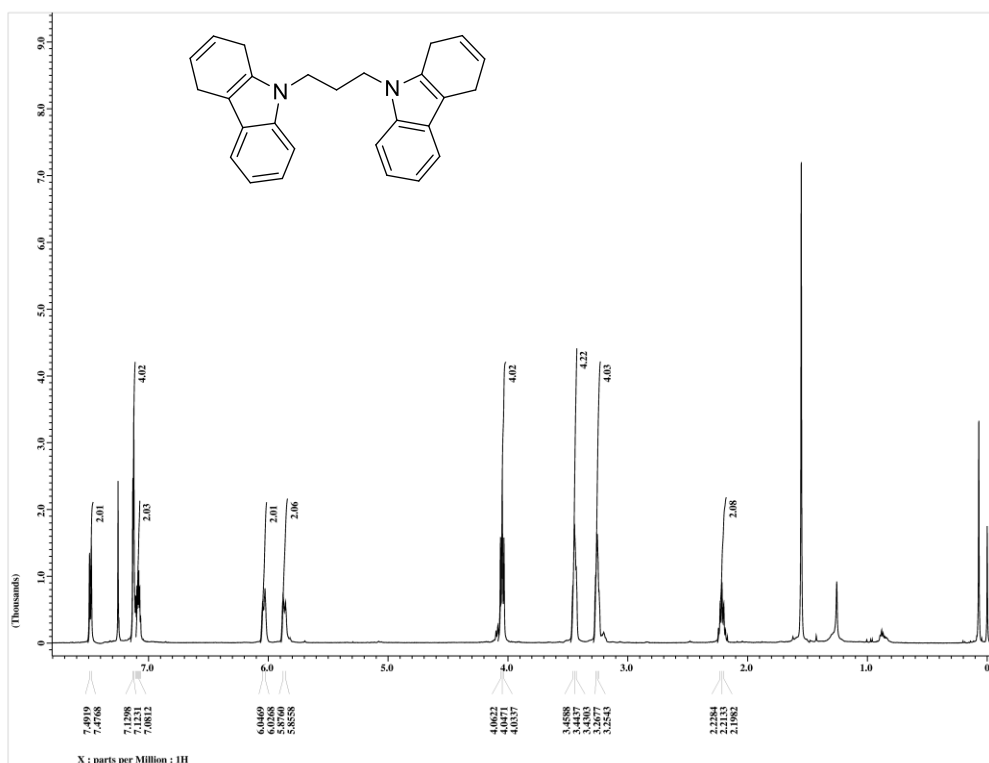
^1H and ^{13}C NMR of 2w:



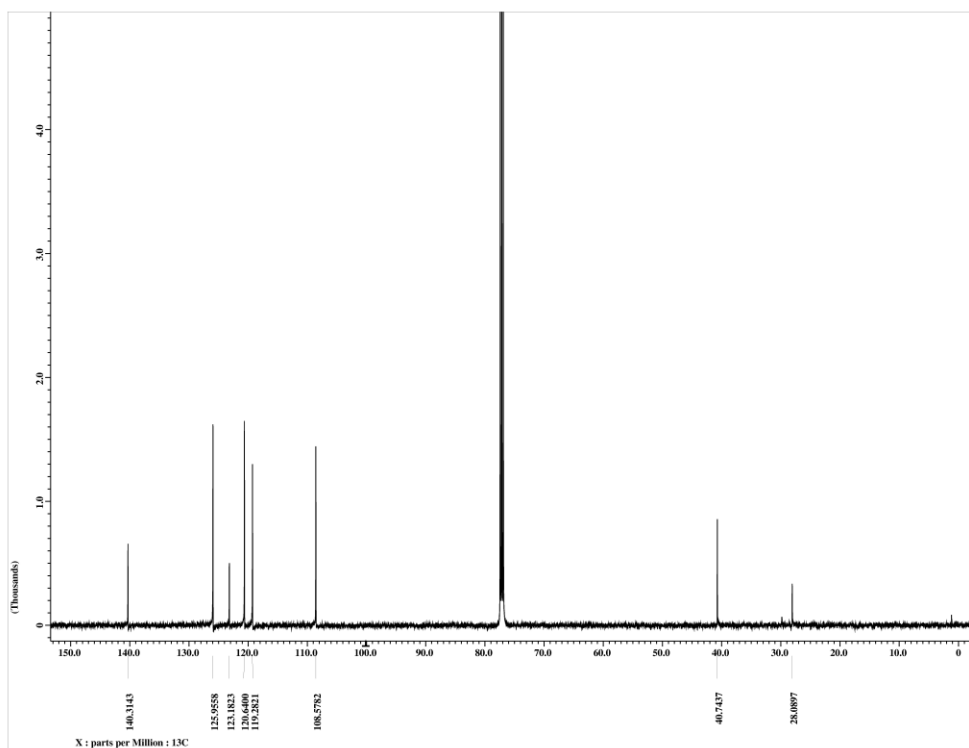
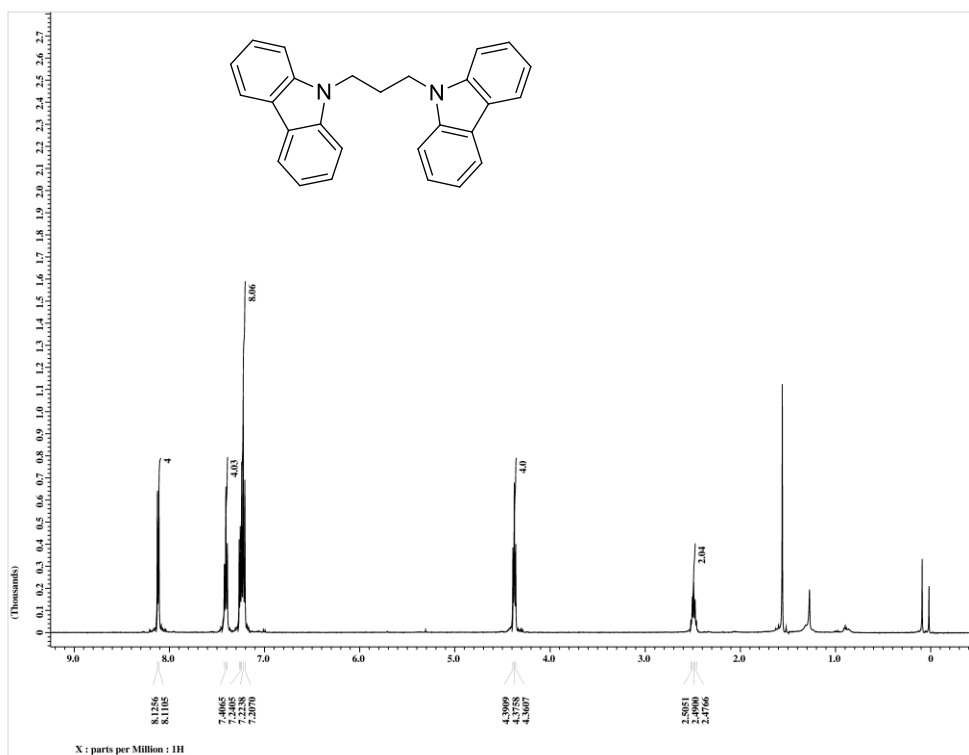
^1H and ^{13}C NMR of 18:



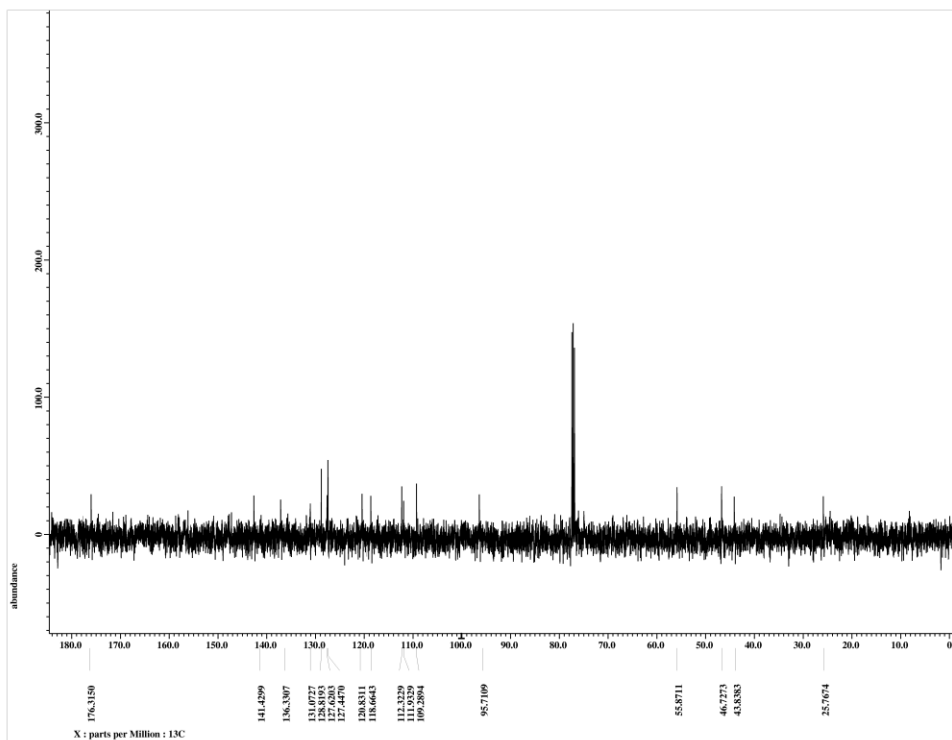
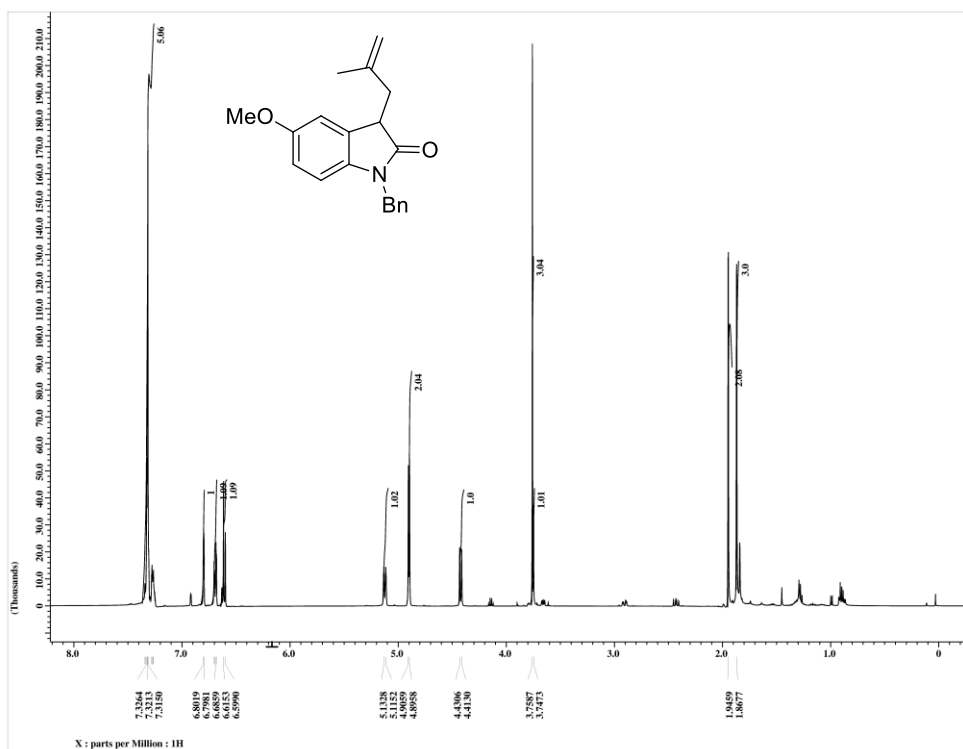
^1H and ^{13}C NMR of 19:



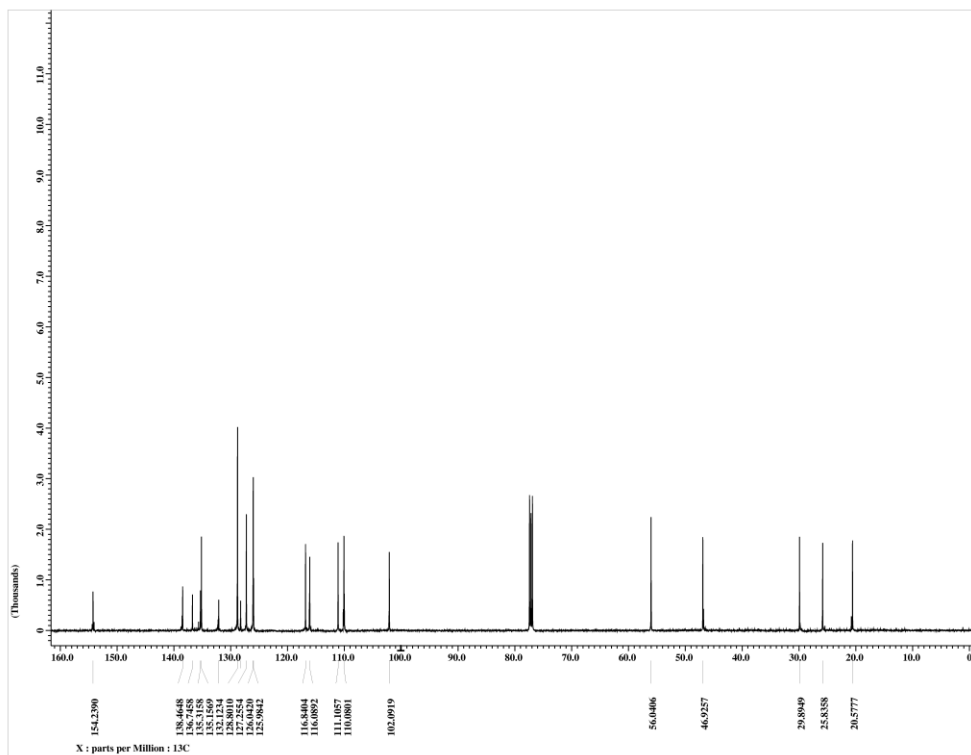
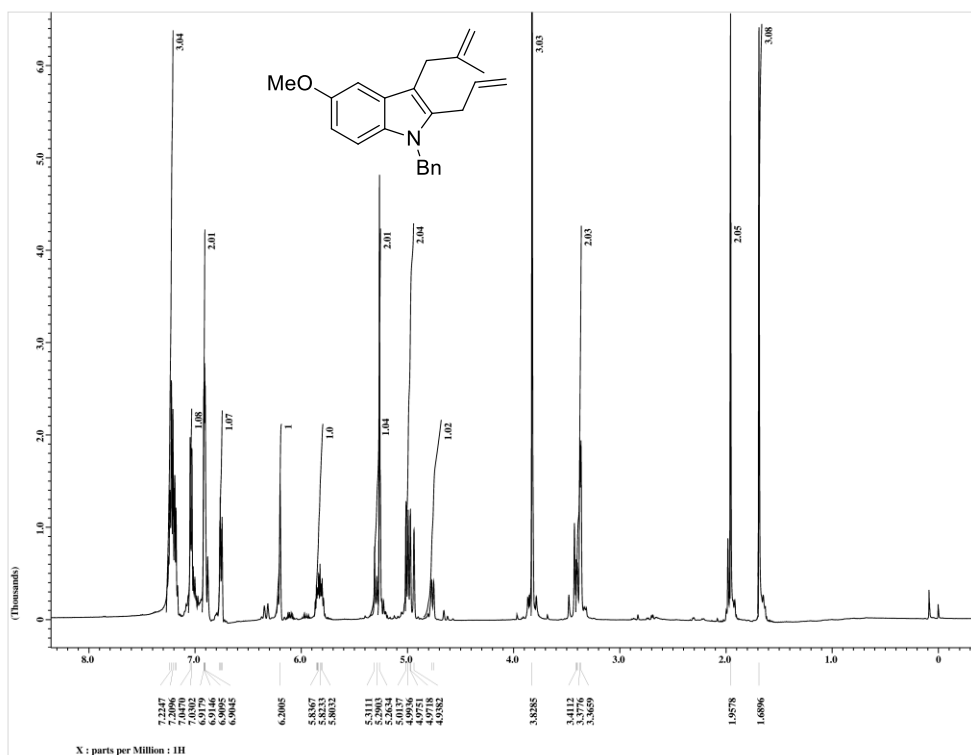
^1H and ^{13}C NMR of 20:



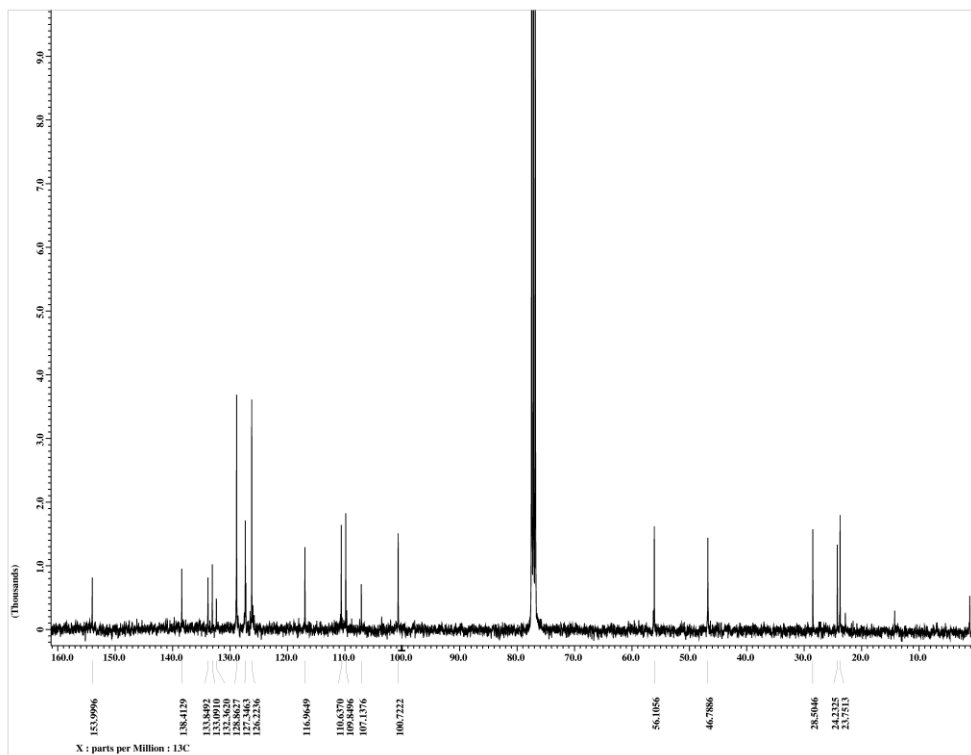
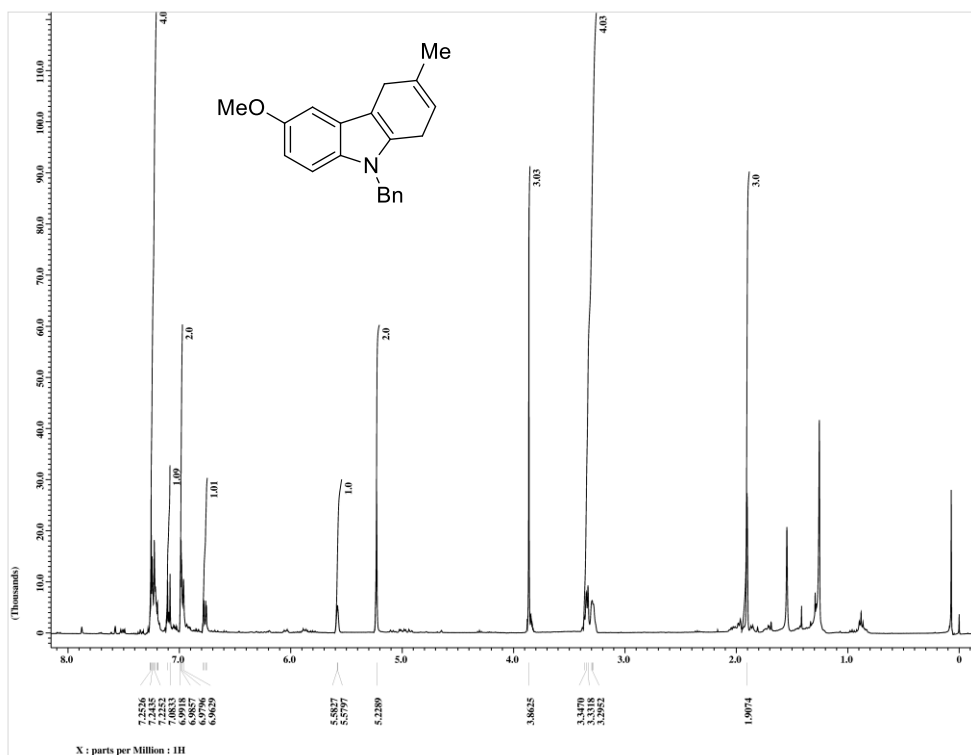
^1H and ^{13}C NMR of 2x:



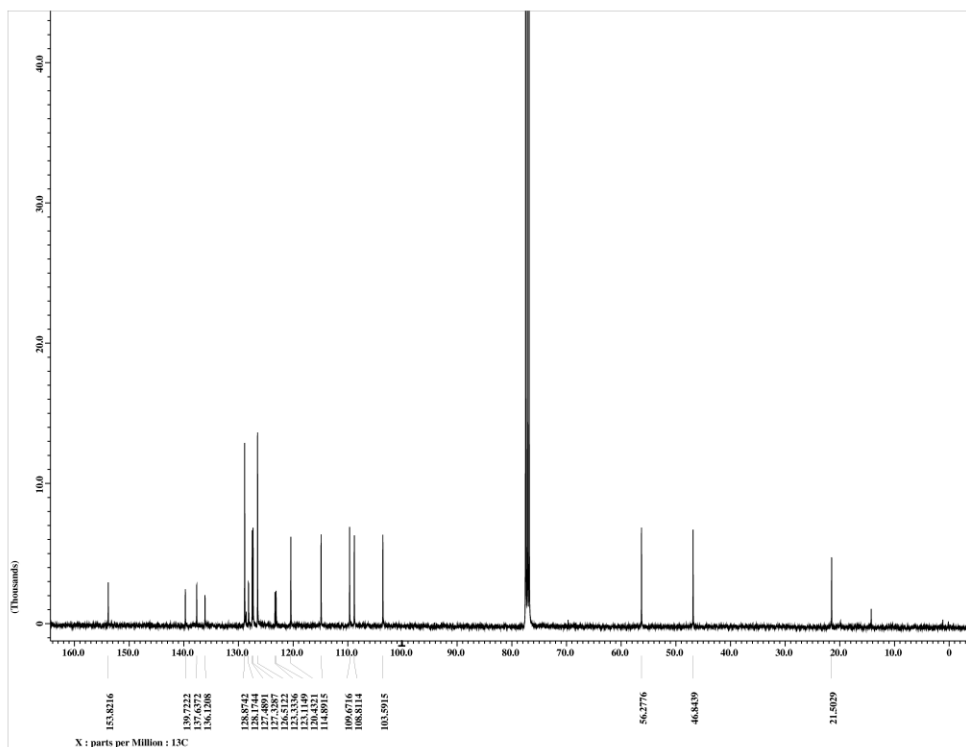
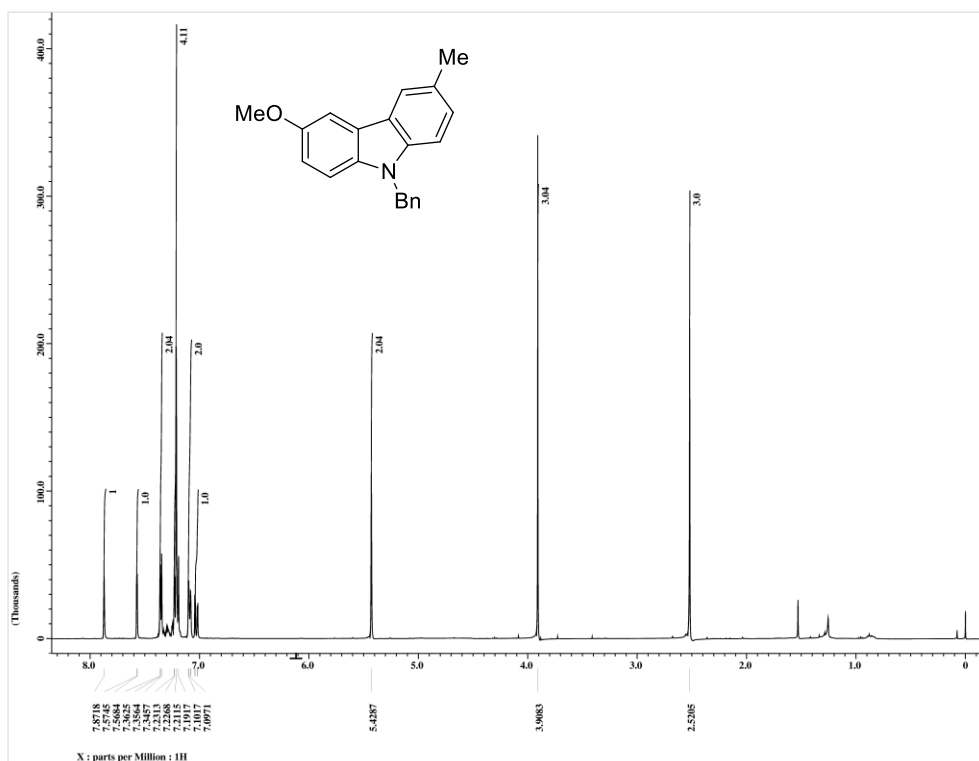
^1H and ^{13}C NMR of 21:



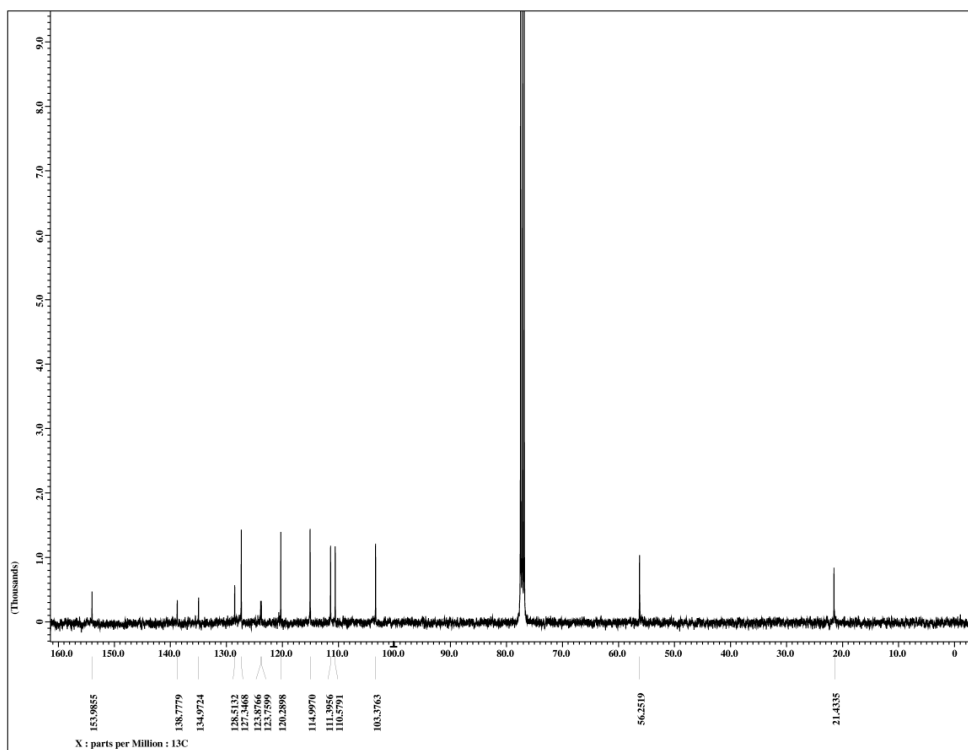
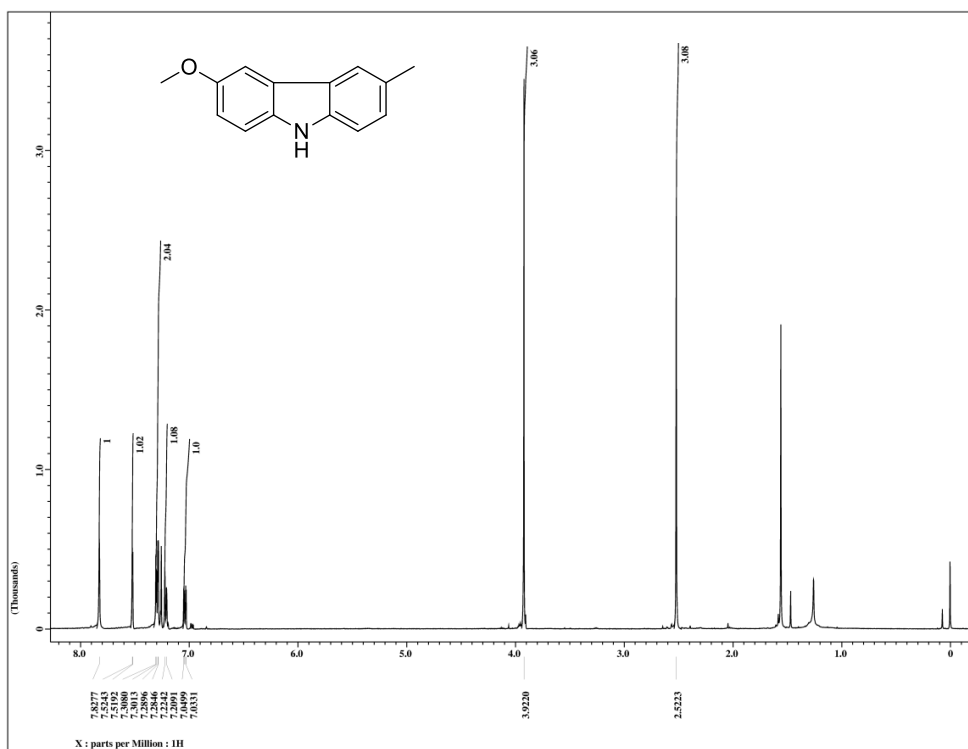
^1H and ^{13}C NMR of 22:



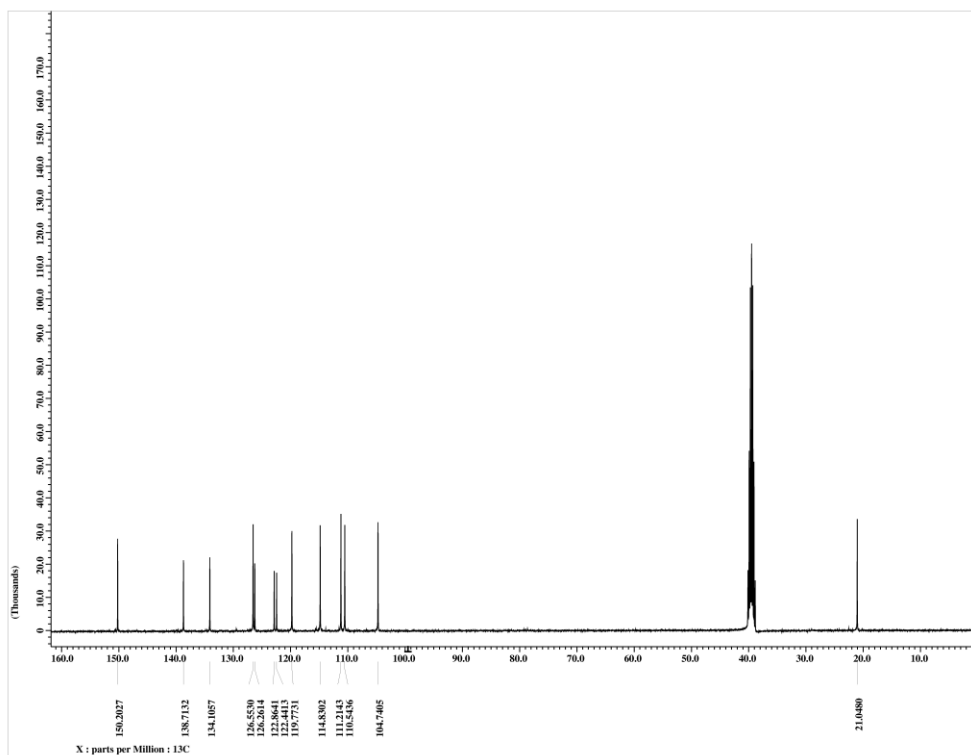
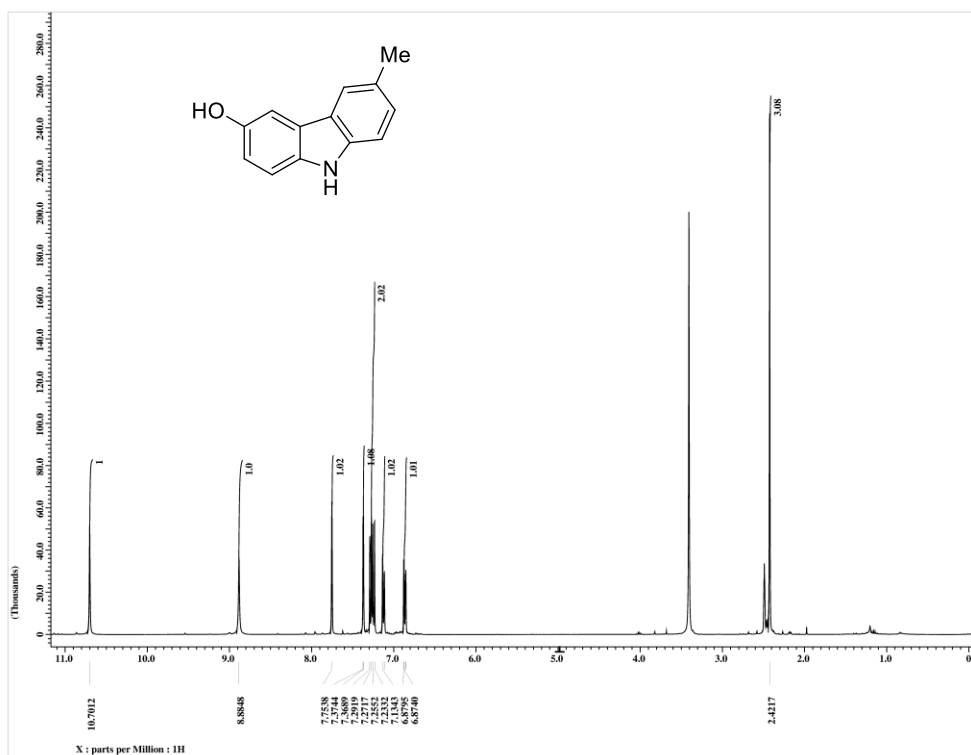
^1H and ^{13}C NMR of 23:



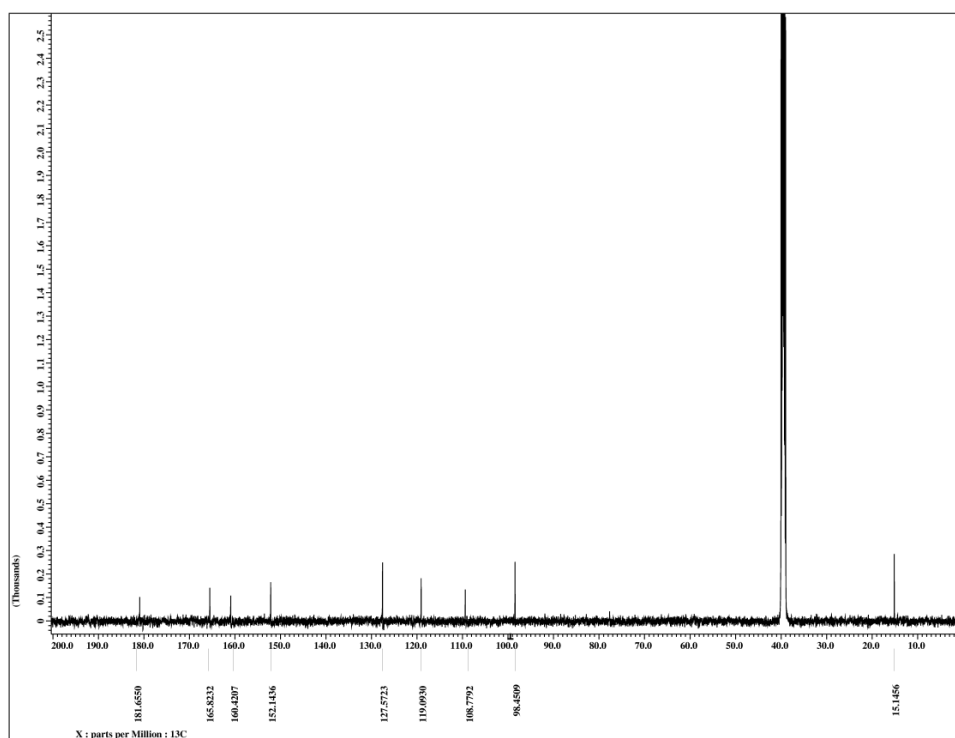
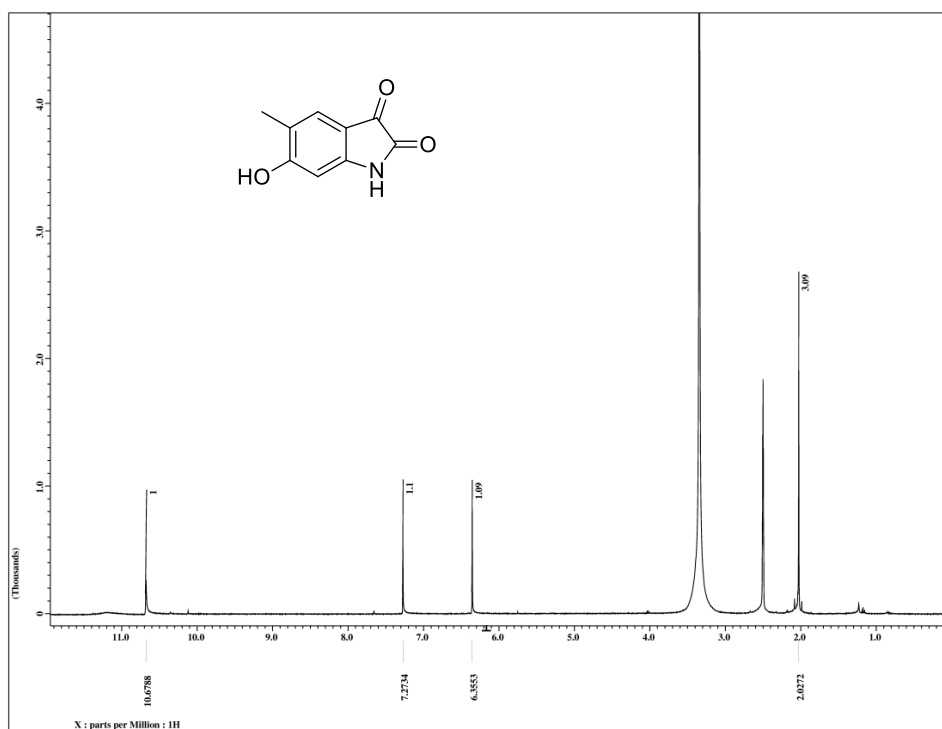
^1H and ^{13}C NMR of 24:



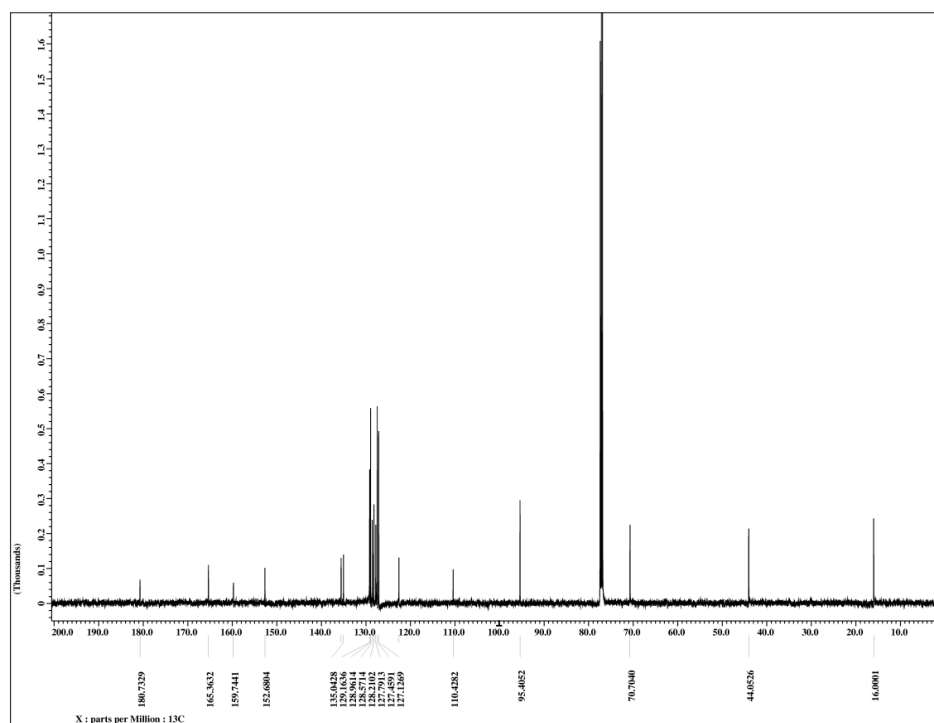
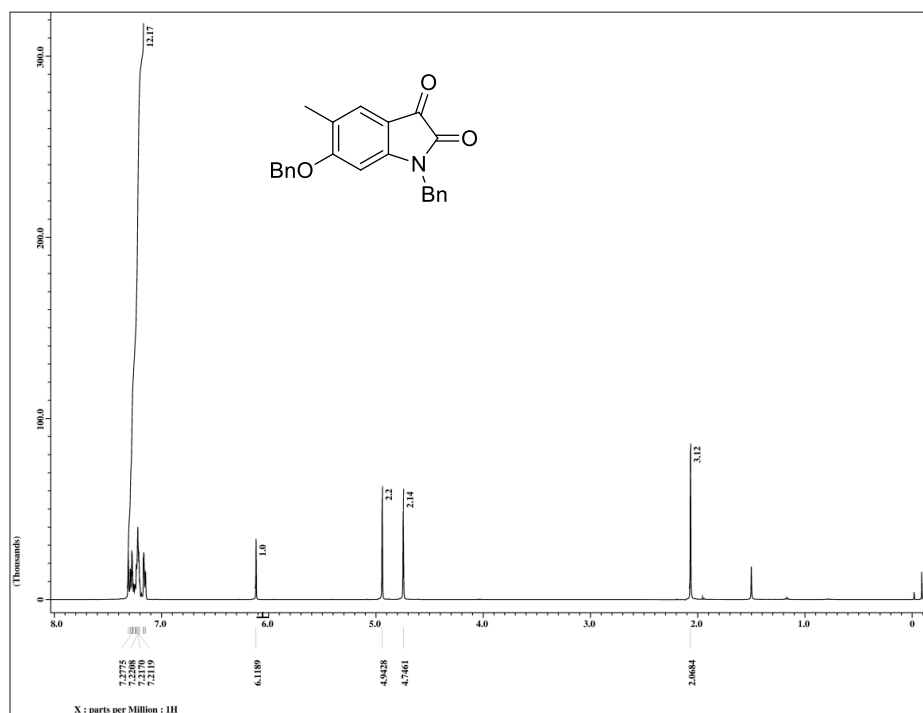
^1H and ^{13}C NMR of 25:



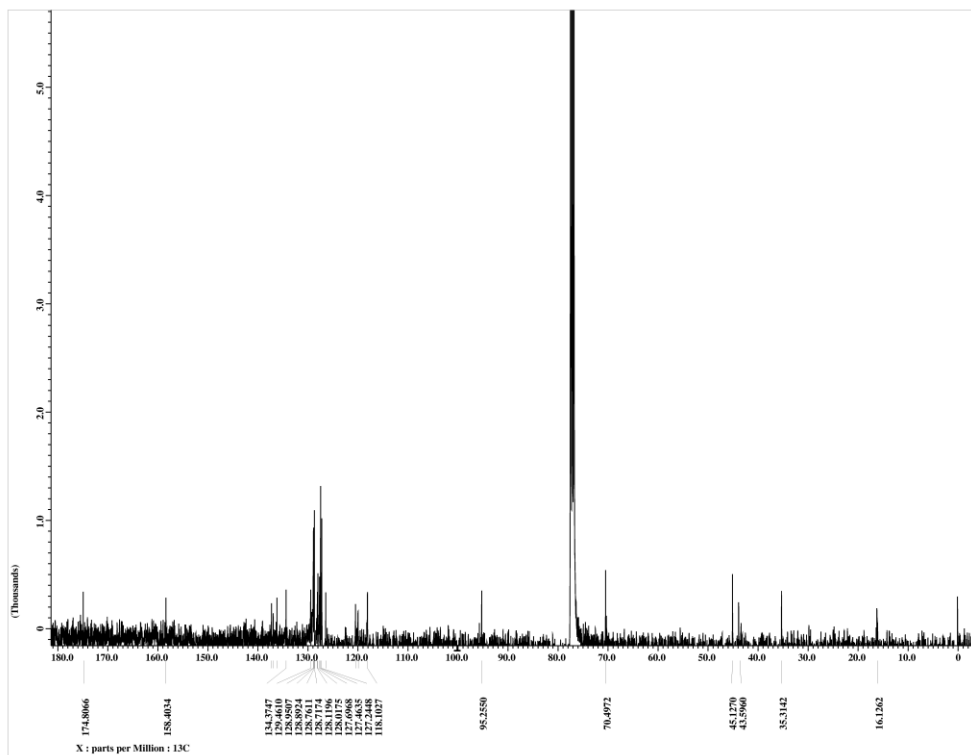
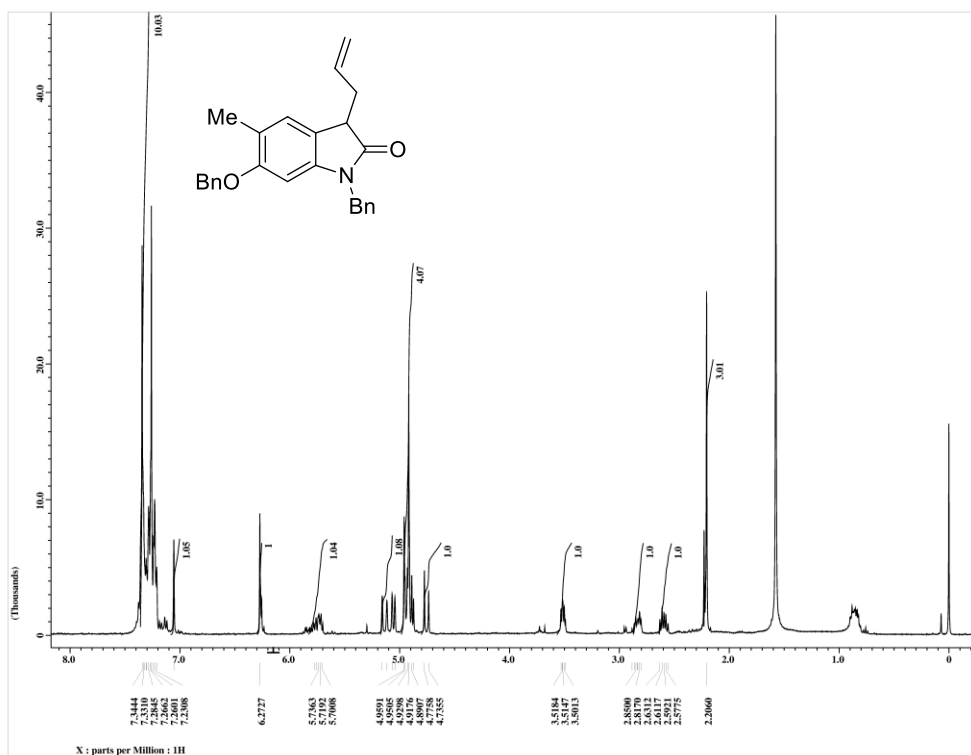
¹H and ¹³C NMR of S11:



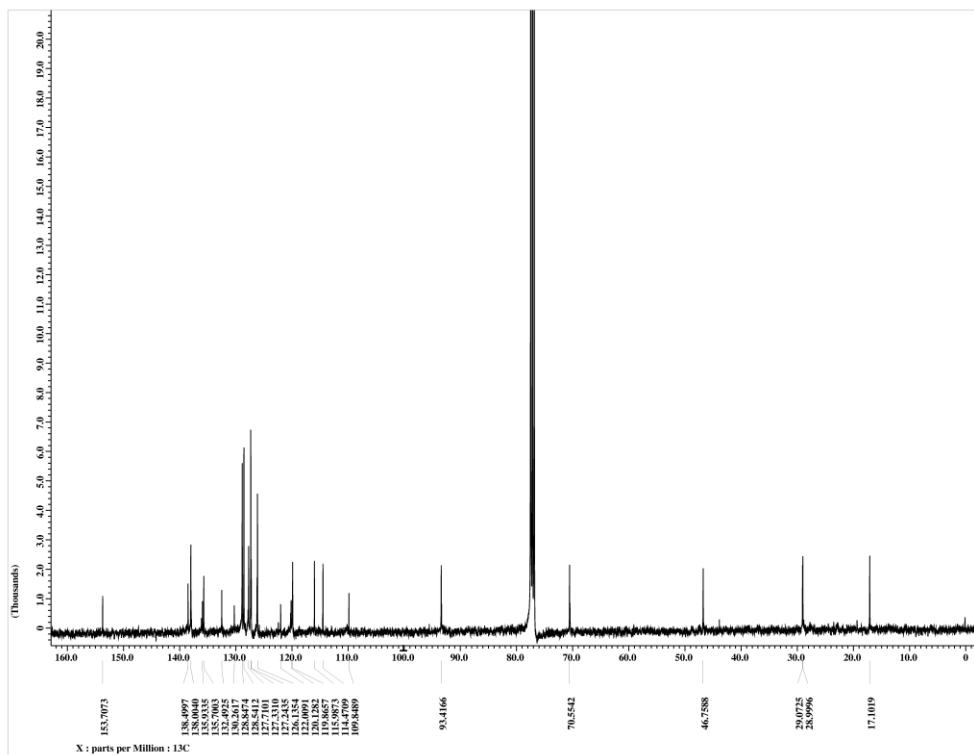
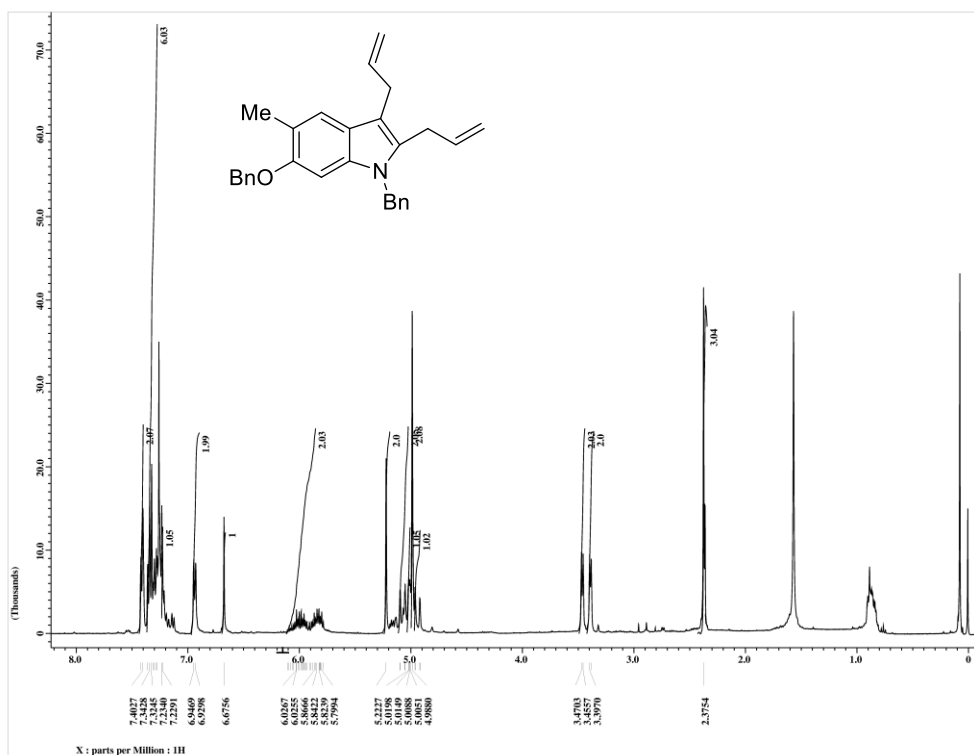
^1H and ^{13}C NMR of S2s:



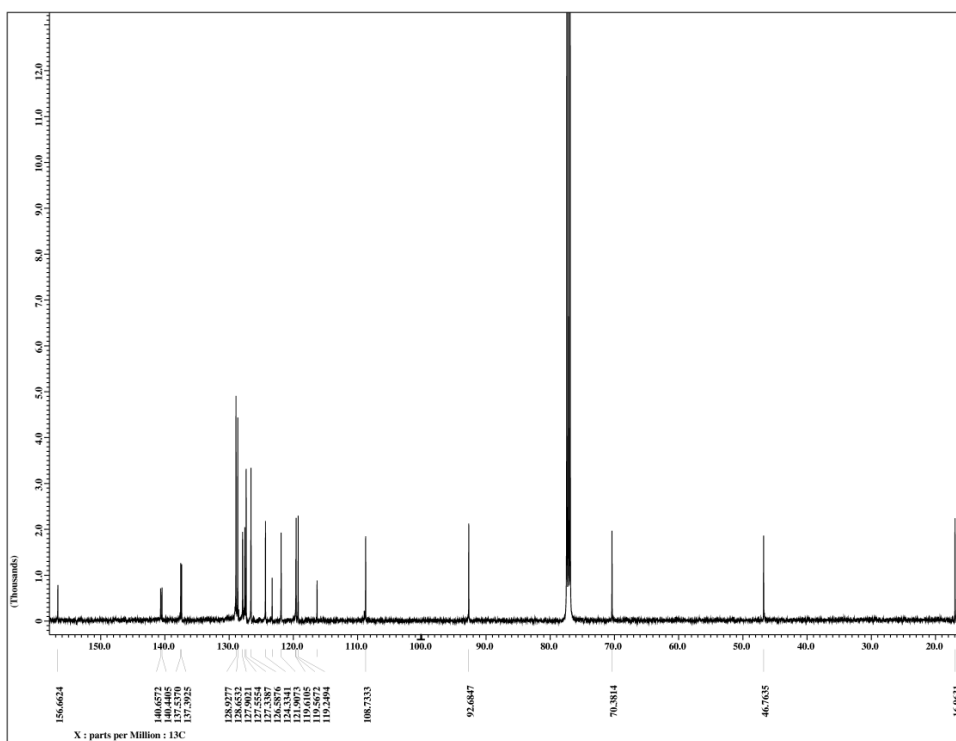
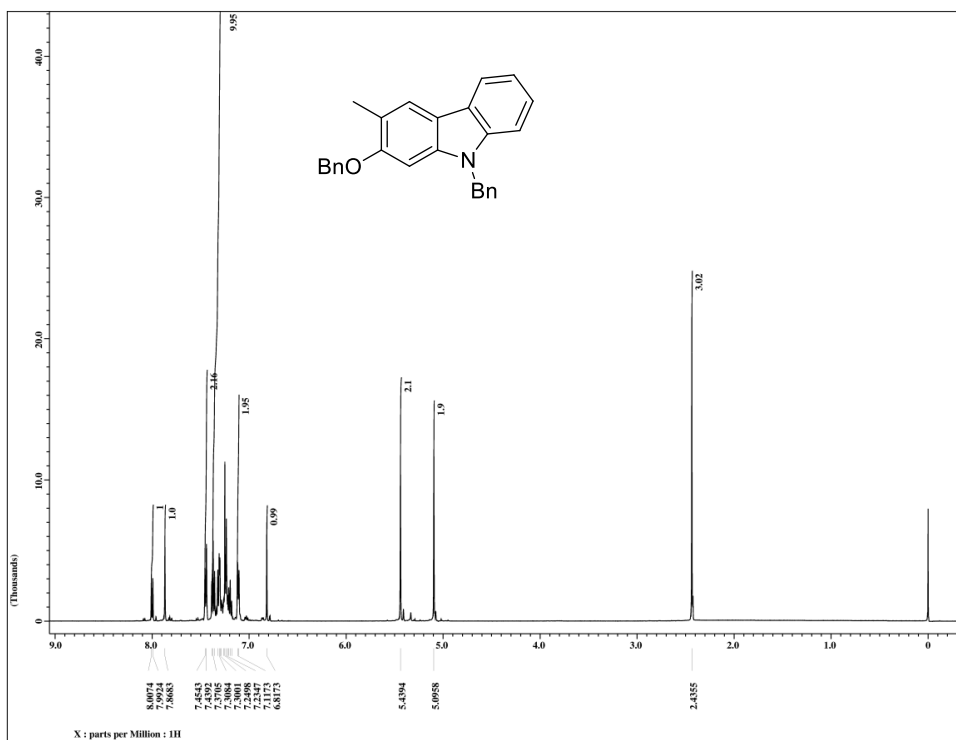
^1H and ^{13}C NMR of 2y:



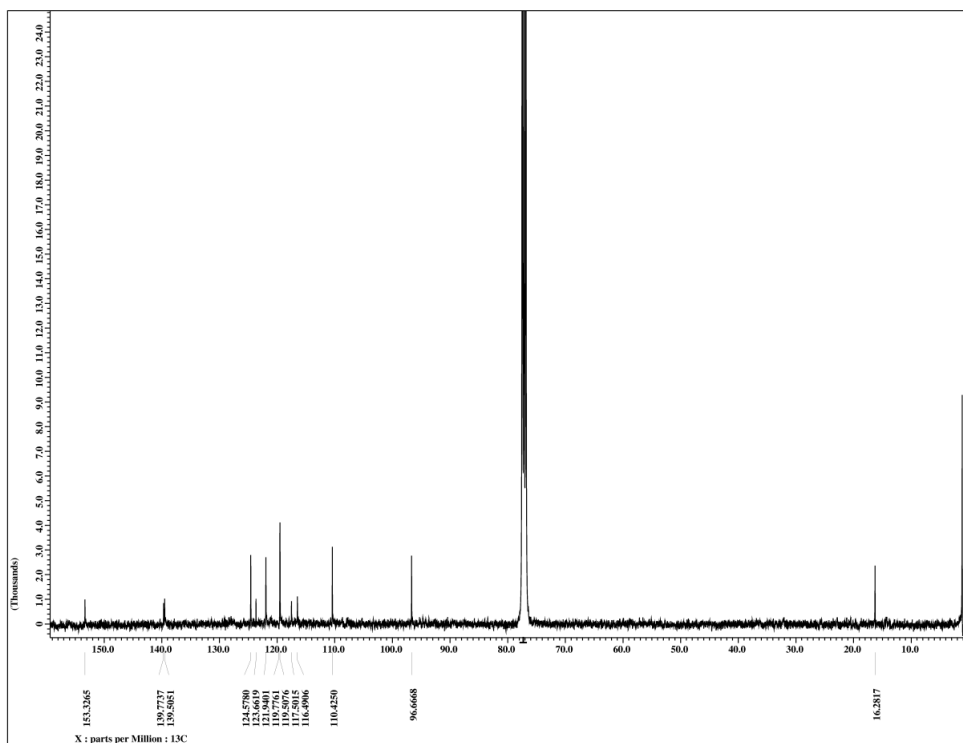
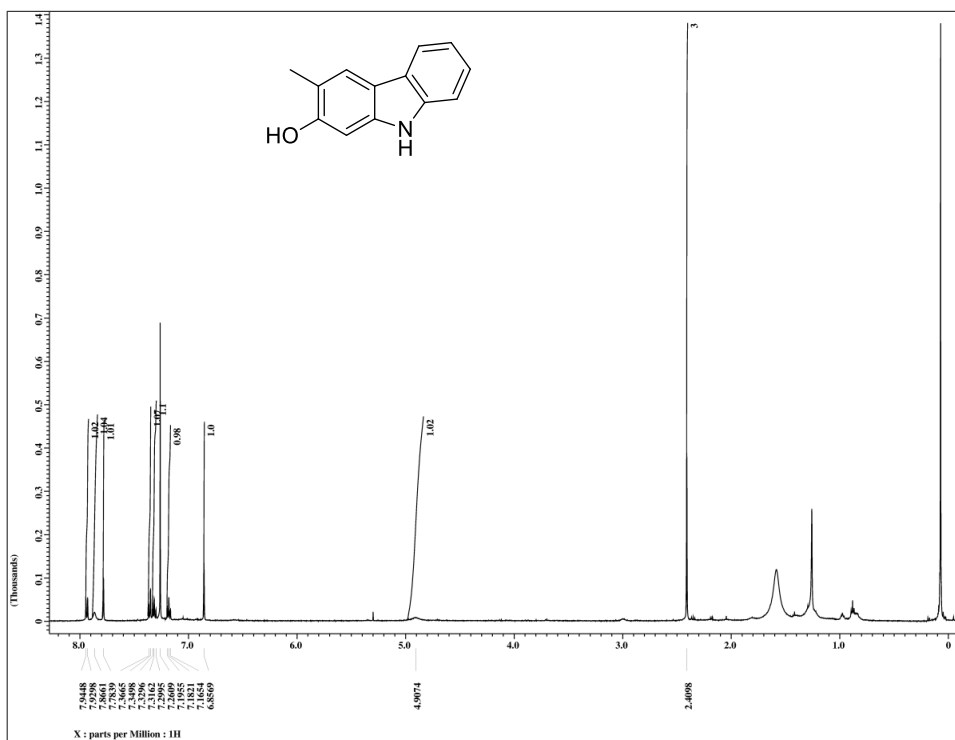
^1H and ^{13}C NMR of 26:



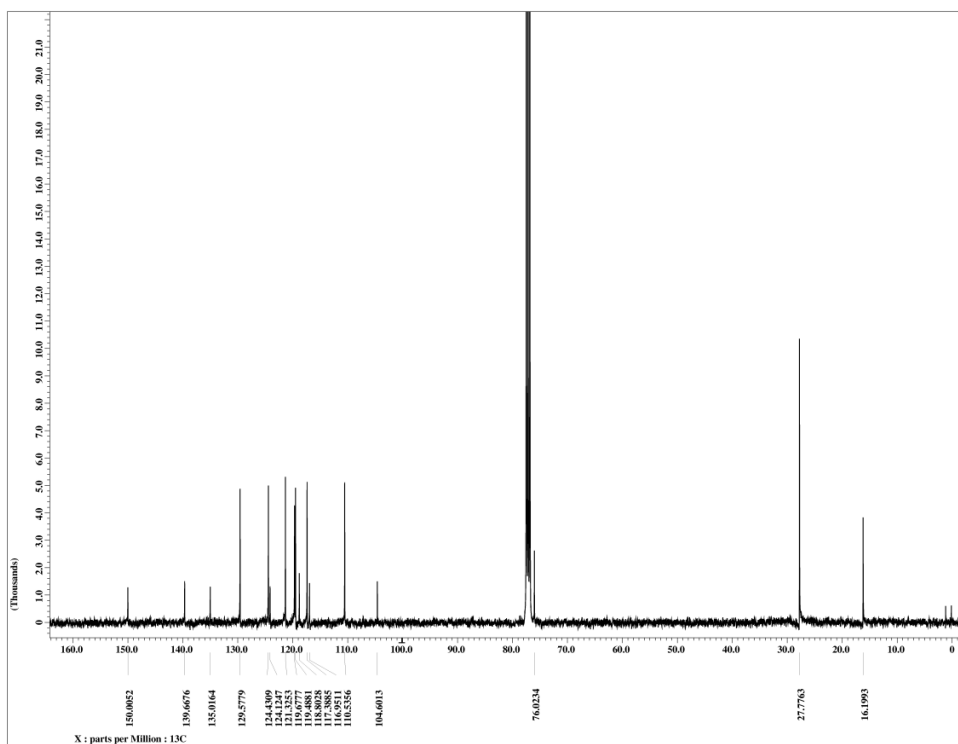
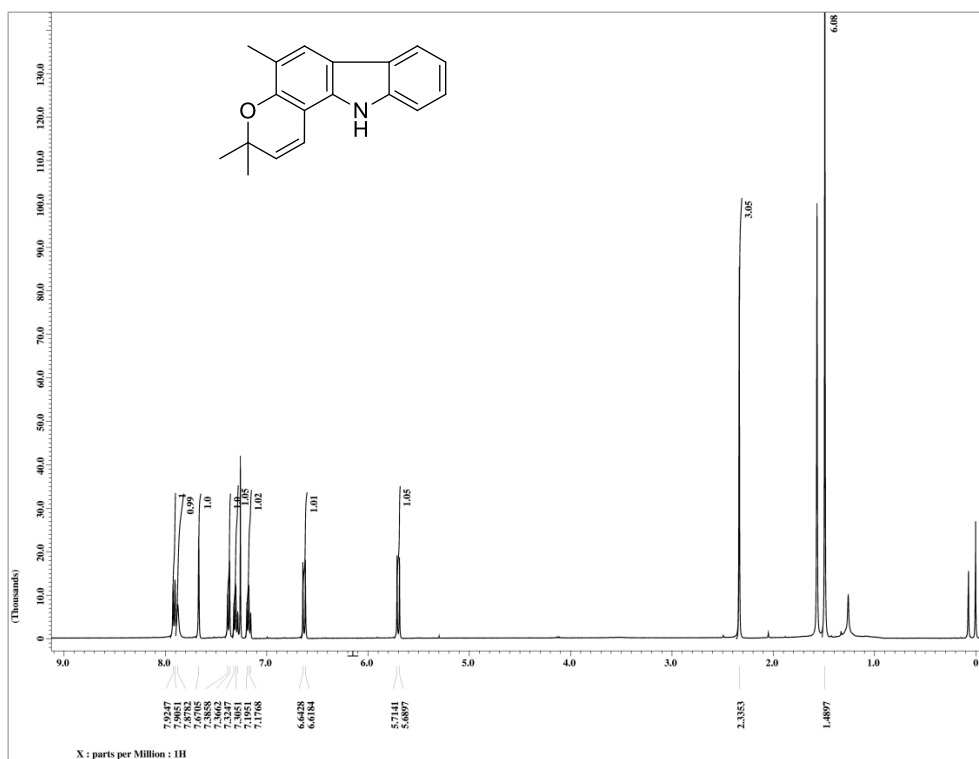
^1H and ^{13}C NMR of 27:



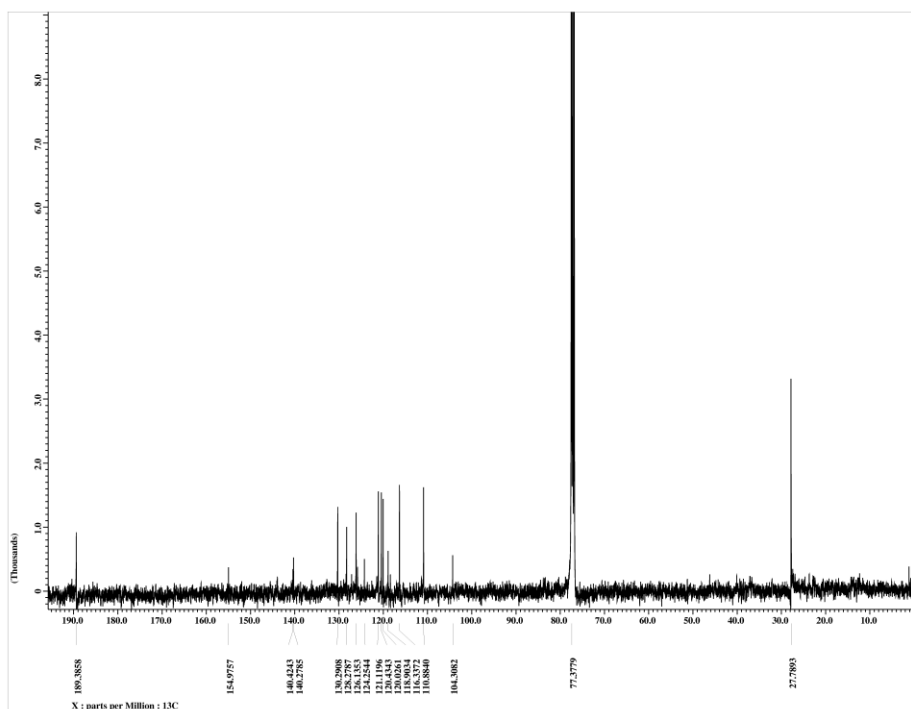
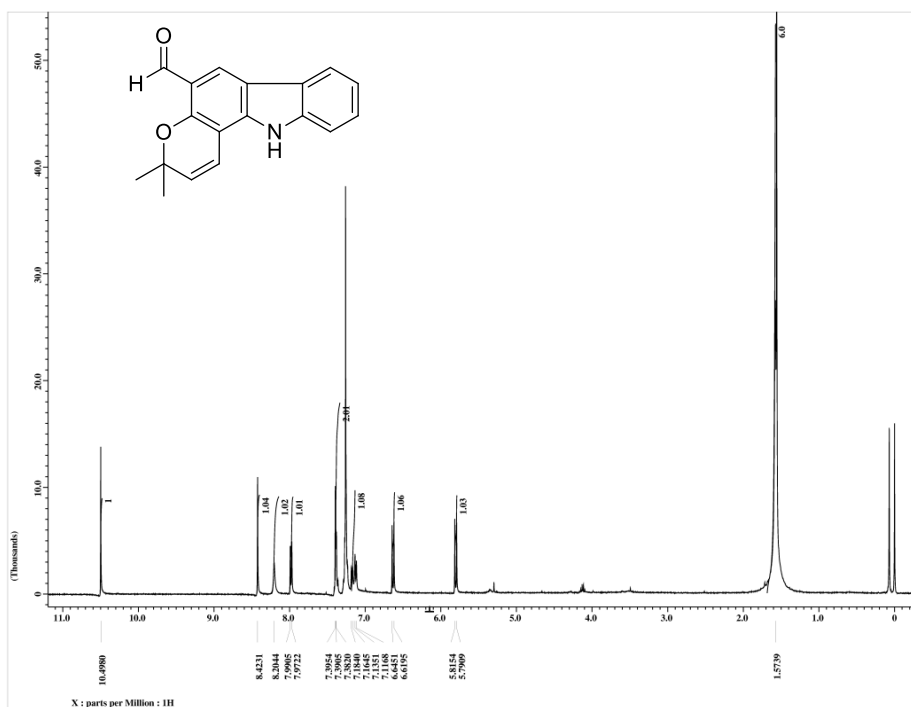
^1H and ^{13}C NMR of 28:



^1H and ^{13}C NMR of 30:



^1H and ^{13}C NMR of 31:



^1H and ^{13}C NMR of 32:

