

Supporting Information

Palladium-Catalyzed Selective *N*-Allylation of Indoles assisted by PEG-Water System

Bai-Jing Peng , Yi-Ting Huang , Ferenc Fülöp, I-Ling Lin and Shyh-Chyun Yang *

School of Pharmacy, College of Pharmacy, Kaohsiung Medical University, Kaohsiung 807, Taiwan,

Email: scyang@kmu.edu.tw

Table of Contents

1. General consideration.....	S2
2. General procedure	S2
3. Characterization data of compound.....	S3
4. ¹ H and ¹³ C NMR spectra 3a , 4a , 3b , 4b , 3c , 4c , 3d , 3e , 3f , 3g , 3h , 3i and 3j	S9
5. Reference.....	S22

General consideration

Reagents were obtained from Acros Organics (Geel, Belgium), Tokyo Chemical Industry (Tokyo, Japan), Sigma-Aldrich (St. Louis, USA), and Alfa-Aesar (Ward Hill, MA, USA), and used without further purification. All reactions were carried out under a nitrogen atmosphere. Solvents were dried and distilled by known methods. Column chromatography was performed on silica gel. IR absorption spectra were recorded on Shimadzu IR-27G and Perkin-Elmer System 2000FT-IR spectrophotometers. Proton nuclear magnetic resonance ($^1\text{H-NMR}$, 400 MHz) and carbon-13 NMR spectra were measured with Varian Unity-400 spectrometers. Carbon multiplicities were obtained from DEPT experiments. Chemical shifts (δ) and coupling constants (Hz) were measured with respect to TMS or chloroform- d_1 . Mass and high-resolution mass spectra (HRMS) were taken on a Hewlett-Packard 5989A or JEOL JMS D-100 instrument, with a direct inlet system.

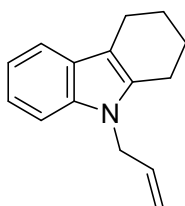
General procedure

A mixture of 1,2,3,4-tetrahydrocarbazole (**1a**, 1 mmol), allyl acetate (**2a**, 2 mmol), PEG-6000 (1 g), $\text{Pd}(\text{OAc})_2$ (9.7 mg, 0.025 mmol), and $(2\text{-Furyl})_3\text{P}$ (36.5 mg, 0.05 mmol) in distilled water (5 mL) were refluxed for 2 h. After cooling, the solvent was distilled under reduced pressure. Column chromatography (*n*-hexane/EtOAc = 4:1) of the residue only afforded 143 mg (68%) of **3a** and 40 mg (19%) of **4a**, respectively.

Products **3a**¹, **4a**¹, **3b**¹, **4b**¹, **3c**¹, **4c**¹, **3d**², **3e**³, **3f**¹, **3g**¹, **3h**⁴, **3i**⁴ and **3j**¹ are known.

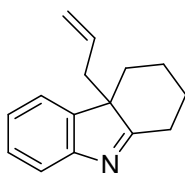
Characterization data of compound

3a: *N*-allyl-1,2,3,4-tetrahydrocarbazole



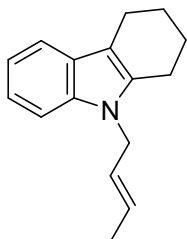
Yellow oil. IR (KBr): ν 1644, 1613, 1464 cm^{-1} . $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.47 (d, $J = 7.6$ Hz, 1H, ArH), 7.22 (d, $J = 8.4$ Hz, 1H, ArH), 7.12 (ddd, $J = 8.4, 6.8, 0.8$ Hz, 1H, ArH), 7.06 (ddd, $J = 8.4, 6.8, 0.8$ Hz, 1H, ArH), 5.90 (ddt, $J = 17.2, 10.4, 4.8$ Hz, 1H, vinyl H), 5.09 (ddt, $J = 10.4, 1.6, 1.6$ Hz, 1H, vinyl H), 4.88 (ddt, $J = 17.2, 1.6, 1.6$ Hz, 1H, vinyl H), 4.62 (dt, $J = 4.8, 1.6$ Hz, 2H, NCH_2), 2.73 (tt, $J = 6.0, 1.6$ Hz, 2H, CH_2), 2.67 (tt, $J = 6.0, 1.6$ Hz, 2H, CH_2), 1.82-1.96 (m, 4H, $\text{CH}_2 \times 2$); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 136.2 (C), 135.4 (C), 133.8 (CH), 127.4 (C), 120.5 (CH), 118.7 (CH), 117.7 (CH), 116.0 (CH_2), 109.5 (C), 108.8 (CH), 45.0 (CH_2), 23.2 (CH_2), 23.2 (CH_2), 22.0 (CH_2), 21.1 (CH_2). EI-MS: m/z 211 (M^+), 196, 183, 168, 154, 142, 128, 115, 89, 77, 63, 51. EI-HRMS calcd for $\text{C}_{15}\text{H}_{17}\text{N}$: 211.1361. Found: 211.1363.

4a: *N*-allyl-1,2,3,4-tetrahydrocarbazole



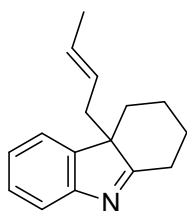
Yellow oil. IR (KBr): ν 1711, 1641, 1617, 1451 cm^{-1} . $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.58 (d, $J = 7.6$ Hz, 1H, ArH), 7.31 (ddd, $J = 7.6, 7.2, 1.2$ Hz, 1H, ArH), 7.30 (dd, $J = 7.6, 1.2$ Hz, 1H, ArH), 7.17 (ddd, $J = 7.6, 7.2, 1.2$ Hz, 1H, ArH), 5.17 (ddt, $J = 17.2, 10.0, 6.8$ Hz, 1H, vinyl H), 4.94 (ddt, $J = 17.2, 2.0, 1.2$ Hz, 1H, vinyl H), 4.86 (ddt, $J = 10.0, 2.0, 1.2$ Hz, 1H, vinyl H), 2.85-2.91 (m, 1H, CH), 2.62 (dt, $J = 13.2, 6.4$ Hz, 1H, CH), 2.54-2.59 (m, 1H, CH), 2.54 (dt, $J = 13.2, 5.6$ Hz, 1H, CH), 2.36 (ddt, $J = 13.2, 3.2, 2.8$ Hz, 1H, CH), 2.18-2.24 (m, 1H, CH), 1.83 (tq, $J = 13.6, 4.0$ Hz, 1H, CH), 1.66-1.72 (m, 1H, CH), 1.43 (tq, $J = 13.6, 4.0$ Hz, 1H, CH), 1.16 (dt, $J = 13.6, 4.0$ Hz, 1H, CH); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 188.9 (C), 154.8 (C), 144.6 (C), 132.1 (CH), 127.6 (CH), 124.7 (CH), 121.9 (CH), 120.1 (CH), 118.0 (CH_2), 57.6 (C), 37.6 (CH_2), 37.0 (CH_2), 30.1 (CH_2), 28.8 (CH_2), 21.1 (CH_2). EI-MS: m/z 211 (M^+), 196, 183, 170, 168, 154, 142, 128, 115, 89, 77, 63, 51. EI-HRMS calcd for $\text{C}_{15}\text{H}_{17}\text{N}$: 211.1361. Found: 211.1358.

3b: *N*-(But-2-en-1-yl)-1, 2, 3, 4-tetrahydrocarbazole



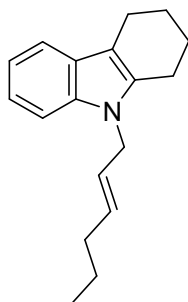
Yellow oil. IR (KBr): ν 1653, 1611, 1462 cm^{-1} . $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.46 (dd, $J = 8.0, 1.2$ Hz, 1H, ArH), 7.24 (dd, $J = 8.0, 1.2$ Hz, 1H, ArH), 7.12 (ddd, $J = 8.0, 7.2, 1.2$ Hz, 1H, ArH), 7.05 (ddd, $J = 8.0, 7.2, 1.2$ Hz, 1H, ArH), 5.40-5.61 (m, 2H, vinyl H), 4.53-4.55 (m, 2H, NCH_2), 2.73 (tt, $J = 6.0, 1.6$ Hz, 2H, CH_2), 2.68 (tt, $J = 6.0, 1.6$ Hz, 2H, CH_2), 1.80-1.95 (m, 4H, $\text{CH}_2 \times 2$), 1.63 (dd, $J = 6.4, 1.2$ Hz, 3H, CH_3); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 136.0 (C), 135.3 (C), 127.3 (C), 126.7 (CH), 120.4 (CH), 118.6 (CH), 117.7 (CH), 109.3 (C), 108.9 (CH), 44.4 (CH_2), 23.3 (CH_2), 23.2 (CH_2), 22.1 (CH_2), 21.1 (CH_2), 17.5 (CH_3). EI-MS: m/z 225 (M^+), 210, 197, 182, 168, 154, 143, 128, 115, 89, 77, 63, 51. EI-HRMS calcd for $\text{C}_{16}\text{H}_{19}\text{N}$: 225.1517. Found: 225.1517.

4b: 4a-(But-2-en-1-yl)-2,3,4,4a-tetrahydro-1*H*-carbazole



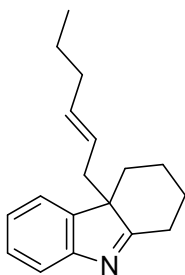
Yellow oil. IR (KBr): ν 1711, 1616, 1584, 1450 cm^{-1} . $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.57 (d, $J = 7.6$ Hz, 1H, ArH), 7.26-7.34 (m, 2H, ArH), 7.17 (t, $J = 7.6$ Hz, 1H, ArH), 5.37 (dq, $J = 13.6, 6.4$ Hz, 1H, vinyl H), 4.83 (tq, $J = 13.6, 6.4$ Hz, 1H, vinyl H), 2.84-2.89 (m, 1H, CH), 2.55-2.61 (m, 1H, CH), 2.54 (dt, $J = 13.6, 5.6$ Hz, 1H, CH), 2.44 (dd, $J = 13.6, 7.6$ Hz, 1H, CH), 2.34 (dq, $J = 13.6, 2.8$ Hz, 1H, CH), 2.15-2.24 (m, 1H, CH), 1.81 (tq, $J = 13.6, 4.0$ Hz, 1H, CH), 1.64-1.69 (m, 1H, CH), 1.48 (dd, $J = 6.4, 0.8$ Hz, 3H, CH_3), 1.41 (tq, $J = 13.6, 4.0$ Hz, 1H, CH), 1.12 (dt, $J = 13.6, 4.0$ Hz, 1H, CH); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 189.2 (C), 154.8 (C), 144.9 (C), 128.6 (CH), 127.4 (CH), 124.5 (CH), 124.4 (CH), 121.9 (CH), 120.0 (CH), 57.8 (C), 36.7 (CH_2), 36.4 (CH_2), 30.1 (CH_2), 28.8 (CH_2), 21.0 (CH_2), 17.7 (CH_3). EI-MS: m/z 225 (M^+), 210, 196, 182, 168, 154, 143, 128, 115, 89, 77, 63. EI-HRMS calcd for $\text{C}_{16}\text{H}_{19}\text{N}$: 225.1517. Found: 225.1518.

3c: *N*-(Hex-2-en-1-yl)-1,2,3,4-tetrahydrocarbazole



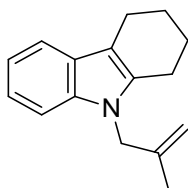
Yellow oil. IR (KBr): ν 1658, 1613, 1464 cm^{-1} . $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.54 (d, $J = 7.6$ Hz, 1H, ArH), 7.32 (d, $J = 8.0$ Hz, 1H, ArH), 7.20 (dt, $J = 8.0, 1.2$ Hz, 1H, ArH), 7.13 (dt, $J = 7.6, 1.2$ Hz, 1H, ArH), 5.47-5.61 (m, 2H, vinyl H), 4.63 (dd, $J = 4.8, 1.2$ Hz, 2H, NCH₂), 2.81 (t, $J = 6.0$ Hz, 2H, CH₂), 2.75 (t, $J = 6.0$ Hz, 2H, CH₂), 1.90-2.05 (m, 6H, CH₂ x 3), 1.41 (hext, $J = 7.6$ Hz, 2H, CH₂), 0.92 (t, $J = 7.6$ Hz, 3H, CH₃); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 136.1 (C), 135.3 (C), 132.6 (CH), 127.3 (C), 125.6 (CH), 120.4 (CH), 118.5 (CH), 117.6 (CH), 109.3 (C), 108.9 (CH), 44.6 (CH₂), 36.5 (CH₂), 23.3 (CH₂), 23.2 (CH₂), 22.2 (CH₂), 22.1 (CH₂), 21.1 (CH₂), 13.6 (CH₃). EI-MS: m/z 253 (M^+), 225, 210, 196, 182, 168, 154, 143, 128, 115, 89, 77, 63, 55. EI-HRMS calcd for $\text{C}_{18}\text{H}_{23}\text{N}$: 253.1830. Found: 253.1830.

4c: 4a-(Hex-2-en-1-yl)-2,3,4,4a-tetrahydro-1*H*-carbazole



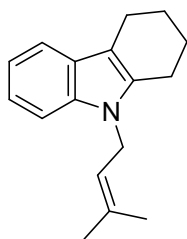
Yellow oil. IR (KBr): ν 1711, 1616, 1586, 1463 cm^{-1} . $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.57 (d, $J = 7.6$ Hz, 1H, ArH), 7.31 (dt, $J = 7.6, 1.2$ Hz, 1H, ArH), 7.28 (dd, $J = 7.6, 1.2$ Hz, 1H, ArH), 7.17 (dt, $J = 7.6, 1.2$ Hz, 1H, ArH), 5.33 (dt, $J = 15.2, 6.8$ Hz, 1H, vinyl H), 4.81 (dt, $J = 15.2, 6.8$ Hz, 1H, vinyl H), 2.85-2.90 (m, 1H, CH), 2.53-2.59 (m, 2H, CH₂), 2.49 (dt, $J = 13.6, 7.6$ Hz, 1H, CH), 2.35 (dq, $J = 13.6, 2.8$ Hz, 1H, CH), 2.16-2.23 (m, 1H, CH), 1.65-1.88 (m, 4H, CH x 4), 1.43 (tq, $J = 13.6, 4.4$ Hz, 1H, CH), 1.15-1.23 (m, 2H, CH₂), 1.14 (dt, $J = 13.6, 4.4$ Hz, 1H, CH), 0.73 (t, $J = 7.2$ Hz, 3H, CH₃); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 189.2 (C), 154.8 (C), 144.9 (C), 134.2 (CH), 127.4 (CH), 124.5 (CH), 123.3 (CH), 121.9 (CH), 120.0 (CH), 57.9 (C), 36.7 (CH₂), 36.4 (CH₂), 34.3 (CH₂), 30.1 (CH₂), 28.8 (CH₂), 22.4 (CH₂), 21.1 (CH₂), 13.4 (CH₃). EI-MS: m/z 253 (M^+), 225, 210, 196, 182, 168, 154, 143, 128, 115, 89, 77, 63, 55. EI-HRMS calcd for $\text{C}_{18}\text{H}_{23}\text{N}$: 253.1830. Found: 253.1832.

3d: *N*-(2-Methylallyl)-tetrahydrocarbazole



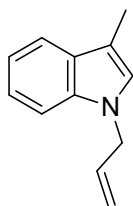
Deep brown oil. IR (KBr): ν 1656, 1614, 1465 cm^{-1} . $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.50 (d, $J = 7.2$ Hz, 1H, ArH), 7.24 (d, $J = 8.4$ Hz, 1H, ArH), 7.15 (ddd, $J = 8.4, 6.8, 1.2$ Hz, 1H, ArH), 7.09 (ddd, $J = 7.2, 6.8, 1.2$ Hz, 1H, ArH), 4.84 (dq, $J = 3.2, 0.8$ Hz, 1H, vinyl H), 4.54 (s, 2H, NCH_2), 4.50 (s, 1H, vinyl H), 2.76 (tt, $J = 6.0, 1.2$ Hz, 2H, CH_2), 2.68 (tt, $J = 6.0, 1.2$ Hz, 2H, CH_2) 1.81-1.96 (m, 4H, $\text{CH}_2 \times 2$), 1.72 (s, 3H, CH_3); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 141.4 (C), 136.5 (C), 135.6 (C), 127.3 (C), 120.5 (CH), 118.6 (CH), 117.6 (CH), 111.7 (CH), 111.2 (CH), 109.4 (C), 108.9 (CH), 48.5 (CH_2), 23.2 (CH_2), 23.2 (CH_2), 22.0 (CH_2), 21.1 (CH_2), 20.0 (CH_3). EI-MS: m/z 225 (M^+), 210, 197, 182, 168, 142, 115, 89, 77, 44. EI-HRMS calcd for $\text{C}_{16}\text{H}_{19}\text{N}$: 225.1517. Found: 225.1517.

3e: 9-(3-methylbut-2-en-1-yl)-2,3,4,9-tetrahydro-1H-carbazole



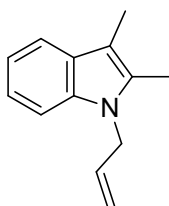
Deep brown oil. IR (KBr): ν 1678, 1654, 1612, 1463 cm^{-1} . $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.47 (d, $J = 7.6$ Hz, 1H, ArH), 7.24 (d, $J = 8.0$ Hz, 1H, ArH), 7.13 (dt, $J = 8.0, 1.2$ Hz, 1H, ArH), 7.06 (ddd, $J = 8.0, 7.6, 1.2$ Hz, 1H, ArH), 5.17-5.21 (m, 1H, vinyl H), 4.62 (d, $J = 6.8$ Hz, 2H, NCH_2), 2.73 (tt, $J = 6.4, 1.6$ Hz, 2H CH_2), 2.70 (tt, $J = 6.4, 1.6$ Hz, 2H CH_2), 1.85-1.97 (m, 4H, $\text{CH}_2 \times 2$), 1.84 (s, 3H, CH_3), 1.70 (s, 3H, CH_3); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 135.2 (C), 133.9 (C), 127.3 (C), 125.5 (C), 121.1 (CH), 120.3 (CH), 118.5 (CH), 117.7 (CH), 109.3 (C), 108.8 (CH), 40.9 (CH_2), 25.5 (CH_2), 23.3 (CH_2), 23.2 (CH_2), 22.2 (CH_2), 21.1 (CH_3), 18.0 (CH_3). EI-MS: m/z 239 (M^+), 211, 196, 183, 171, 168, 115, 89, 77. EI-HRMS calcd for $\text{C}_{17}\text{H}_{21}\text{N}$: 239.1674. Found: 239.1677.

3f: *N*-Allyl-3-methylindole



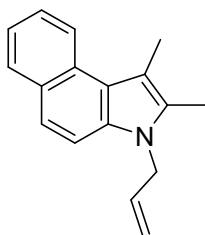
Yellow oil. IR (KBr): ν 1614, 1459 cm^{-1} . $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.57 (ddd, $J = 8.4, 1.2, 0.8$ Hz, 1H, ArH), 7.27 (ddd, $J = 8.0, 1.2, 0.8$ Hz, 1H, ArH), 7.18 (ddd, $J = 8.4, 6.8, 1.2$ Hz, 1H, ArH), 7.10 (ddd, $J = 8.0, 6.8, 0.8$ Hz, 1H, ArH), 6.86 (s, $J = 1$ Hz, ArH), 5.96 (ddt, $J = 17.2, 10.0, 5.2$ Hz, 1H, vinyl H), 5.16 (ddt, $J = 10.0, 1.6, 1.2$ Hz, 1H, vinyl H), 5.07 (ddt, $J = 17.2, 1.6, 1.2$ Hz, 1H, vinyl H), 4.65 (dt, $J = 5.2, 1.6$ Hz, 2H, NCH_2), 2.32 (s, 3H, CH_3); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 136.4 (C), 133.8 (CH), 128.9 (C), 125.4 (CH), 121.4 (CH), 119.0 (CH), 118.6 (CH), 117.0 (CH_2), 110.5 (C), 109.3 (CH), 48.5 (CH_2), 9.6 (CH_3). EI-MS: m/z 171 (M^+), 156, 144, 130, 129, 103, 89, 77, 51. EI-HRMS calcd for $\text{C}_{12}\text{H}_{13}\text{N}$: 171.1048. Found: 171.1051.

3g: *N*-Allyl-2,3-dimethylindole



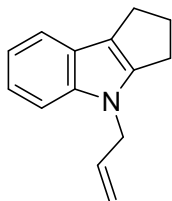
Yellow oil. IR (KBr): ν 1696, 1614, 1452 cm^{-1} . $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.49 (dd, $J = 7.6, 1.2$ Hz, 1H, ArH), 7.20 (dd, $J = 7.6, 1.2$ Hz, 1H, ArH), 7.12 (ddd, $J = 7.6, 7.2, 1.2$ Hz, 1H, ArH), 7.07 (ddd, $J = 7.6, 7.2, 1.2$ Hz, 1H, ArH), 5.92 (ddt, $J = 17.2, 10.4, 4.4$ Hz, 1H, vinyl H), 5.09 (ddt, $J = 10.4, 2.0, 1.2$ Hz, 1H, vinyl H), 4.82 (ddt, $J = 17.2, 2.0, 1.2$ Hz, 1H, vinyl H), 4.66 (dt, $J = 4.4, 2.0$ Hz, 2H, CH_2), 2.31 (s, 3H, CH_3), 2.26 (s, 3H, CH_3); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 136.0 (C), 133.7 (CH), 132.2 (C), 128.5 (C), 120.5 (CH), 118.7 (CH), 117.9 (CH), 115.9 (CH_2), 108.6 (CH), 106.7 (C), 45.3 (CH_2), 9.9 (CH_3), 8.8 (CH_3). EI-MS: m/z 185 (M^+), 170, 158, 144, 128, 115, 102, 88, 77, 51. EI-HRMS calcd for $\text{C}_{13}\text{H}_{15}\text{N}$: 185.1204. Found: 185.1202.

3h: 3-Allyl-1,2-dimethyl-3*H*-benzo[*e*]indole



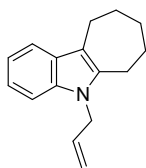
Yellow oil. IR (KBr): ν 1647, 1592, 1441 cm^{-1} . $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 8.59 (d, $J = 8.4$ Hz, 1H, ArH), 7.96 (d, $J = 8.0$ Hz, 1H, ArH), 7.58 (d, $J = 8.8$ Hz, 1H, ArH), 7.58 (ddd, $J = 8.4, 6.8, 1.2$ Hz, 1H, ArH), 7.45 (d, $J = 8.8$ Hz, 1H, ArH), 7.43 (ddd, $J = 8.0, 6.8, 1.2$ Hz, 1H, ArH), 5.99 (ddt, $J = 17.2, 10.4, 4.4$ Hz, 1H, vinyl H), 5.14 (ddt, $J = 10.4, 1.6, 1.2$ Hz, 1H, vinyl H), 4.80 (dt, $J = 4.4, 1.6$ Hz, 2H, NCH_2), 4.76 (ddt, $J = 17.2, 1.6, 1.2$ Hz, 2H, vinyl H), 2.73 (s, 3H, CH_3), 2.43 (s, 3H, CH_3); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 133.6 (CH), 132.3 (C), 130.6 (C), 129.2 (C), 128.6 (CH), 125.1 (CH), 123.2 (CH), 122.3 (CH), 121.4 (CH), 121.0 (C), 116.0 (CH_2), 110.8 (CH), 109.3 (C), 45.4 (CH_2), 12.8 (CH_3), 9.7 (CH_3). EI-MS: m/z 235 (M^+), 220, 194, 178, 152, 127, 108, 75. EI-HRMS calcd for $\text{C}_{17}\text{H}_{17}\text{N}$: 235.1361. Found: 235.1359

3i: 4-Allyl-1,2,3,4-tetrahydrocyclopenta[*b*]indole



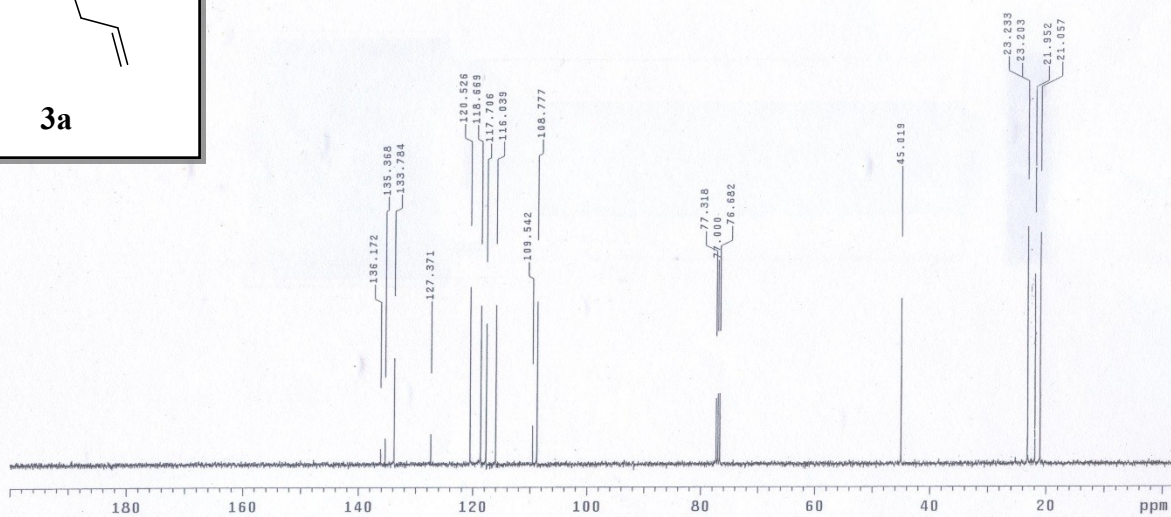
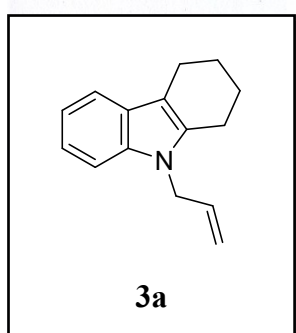
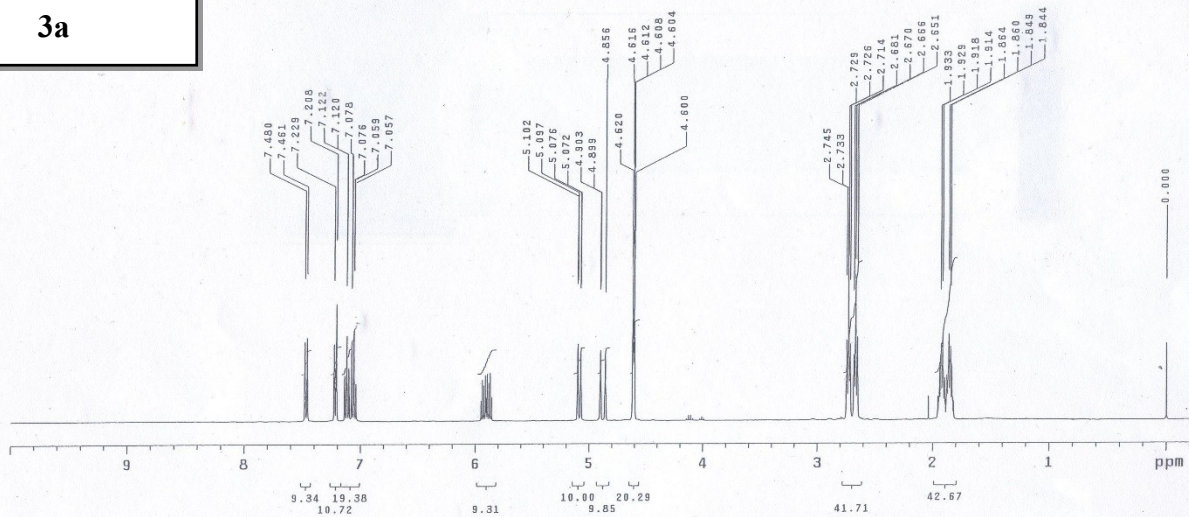
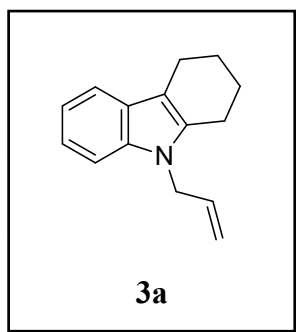
Yellow oil. IR (KBr): ν 1650, 1610, 1457 cm^{-1} . $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.47 (dd, $J = 7.2, 0.8$ Hz, 1H, ArH), 7.26 (dd, $J = 7.2, 1.6$ Hz, 1H, ArH), 7.13 (dt, $J = 7.2, 1.6$ Hz, 1H, ArH), 7.08 (dt, $J = 7.2, 0.8$ Hz, 1H, ArH), 5.97 (ddt, $J = 16.0, 10.4, 5.2$ Hz, 1H, vinyl H), 5.16 (ddt, $J = 10.4, 1.6, 1.6$ Hz, 1H, vinyl H), 5.03 (ddt, $J = 16.0, 1.6, 1.6$ Hz, 1H, vinyl H), 4.66 (dt, $J = 5.2, 1.6$ Hz, 2H, NCH_2), 2.89 (t, $J = 7.2$ Hz, 2H, CH_2), 2.85 (t, $J = 6.0$ Hz, 2H, CH_2), 2.56 (quin, $J = 6.8$ Hz, 2H, CH_2); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 146.1 (C), 140.8 (C), 133.7 (CH), 124.5 (C), 119.9 (CH), 119.0 (CH), 118.5 (CH), 118.0 (C), 116.4 (CH_2), 109.7 (CH), 47.1 (CH_2), 28.4 (CH_2), 25.0 (CH_2), 24.6 (CH_2). EI-MS: m/z 197 (M^+), 182, 168, 154, 143, 128, 115, 77. EI-HRMS calcd for $\text{C}_{14}\text{H}_{15}\text{N}$: 197.1204. Found: 197.1202.

3j: *N*-Allyl-6,7,8,9,10,10a-hexahydro-cyclohepta[*b*]indole

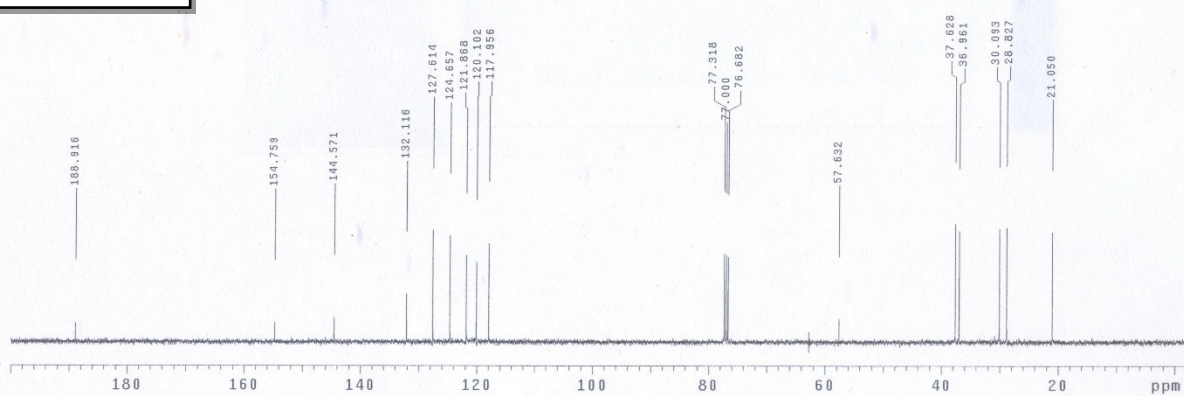
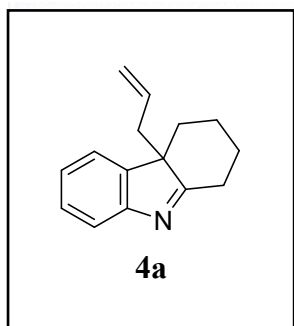
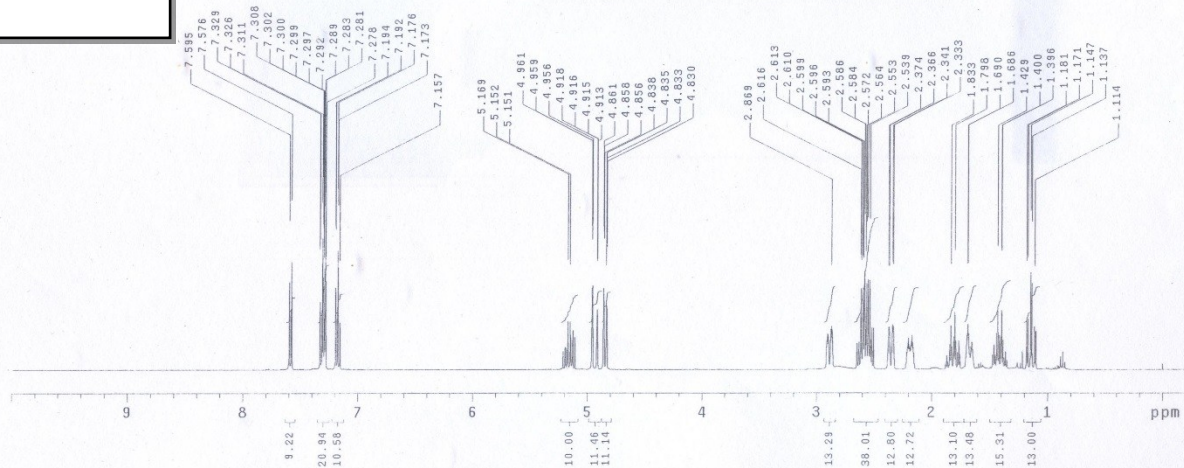
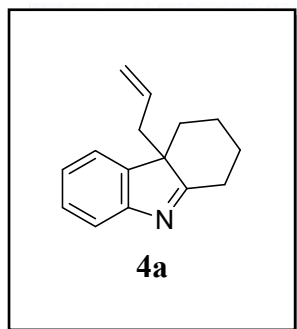


Yellow oil. IR (KBr): ν 1643, 1611, 1465 cm^{-1} . $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.56 (dd, $J = 7.6$ Hz, 1.2, 1H, ArH), 7.25 (dd, $J = 7.2, 1.2$ Hz, 1H, ArH), 7.17 (dt, $J = 7.2, 1.2$ Hz, 1H, ArH), 7.13 (dt, $J = 7.2, 1.2$ Hz, 1H, ArH), 5.97 (ddt, $J = 17.2, 10.4, 4.4$ Hz, 1H, vinyl H), 5.14 (ddt, $J = 10.4, 2.0, 1.2$ Hz, 1H, vinyl H), 4.88 (ddt, $J = 17.2, 2.0, 1.2$ Hz, 1H, vinyl H), 4.73 (dt, $J = 4.4, 2.0$ Hz, 2H, NCH_2), 2.84-2.93 (m, 4H, $\text{CH}_2 \times 2$), 1.80-1.98 (m, 6H, $\text{CH}_2 \times 3$); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 138.8 (C), 135.3 (C), 134.0 (CH), 127.9 (C), 120.3 (CH), 118.7 (CH), 117.6 (CH), 115.8 (CH_2), 113.9 (C), 108.8 (CH), 45.0 (CH_2), 31.7 (CH_2), 28.4 (CH_2), 27.2 (CH_2), 26.3 (CH_2), 24.4 (CH_2). EI-MS: m/z 225 (M^+), 209, 196, 182, 168, 156, 142, 128, 115, 89, 77, 63, 51. EI-HRMS calcd for $\text{C}_{16}\text{H}_{19}\text{N}$: 225.1517. Found: 225.1517.

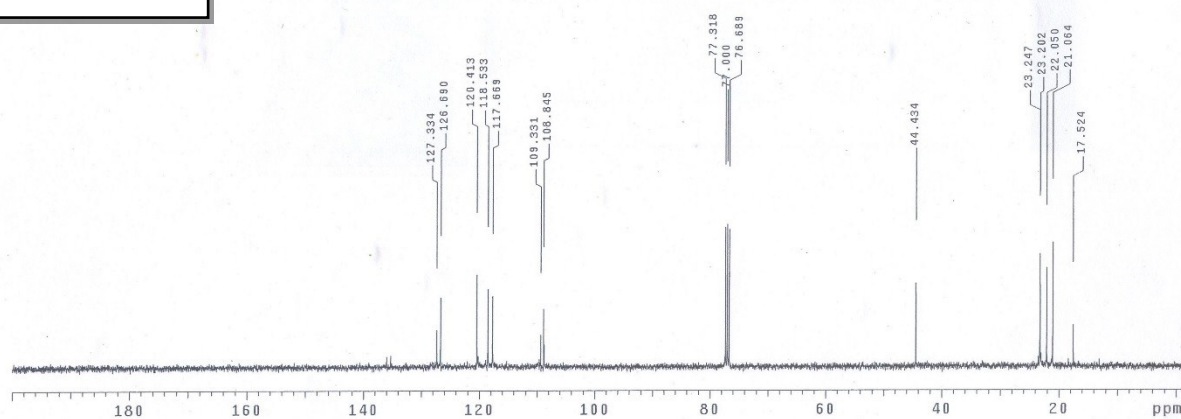
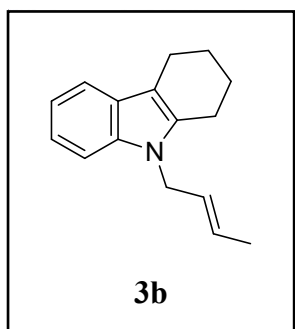
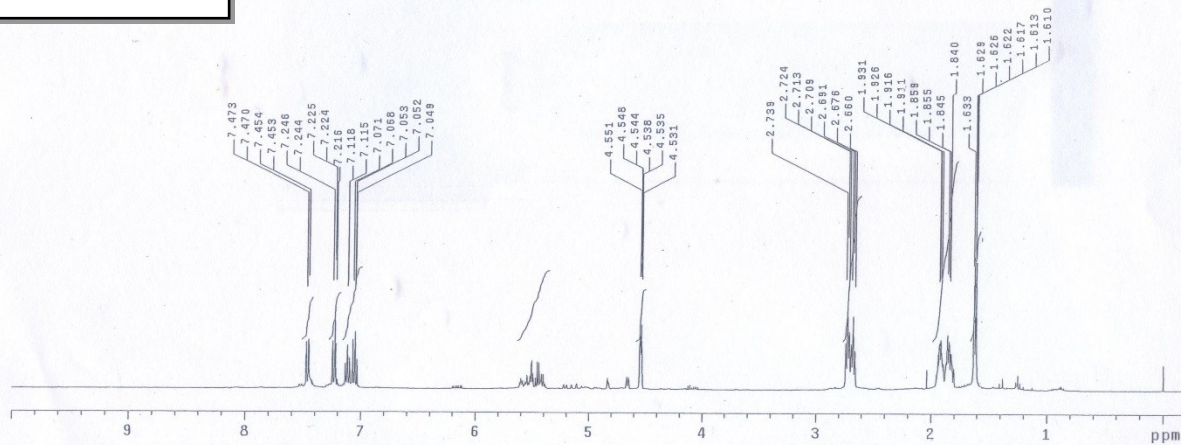
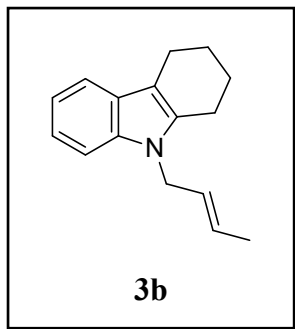
^1H and ^{13}C NMR spectra of **3a**



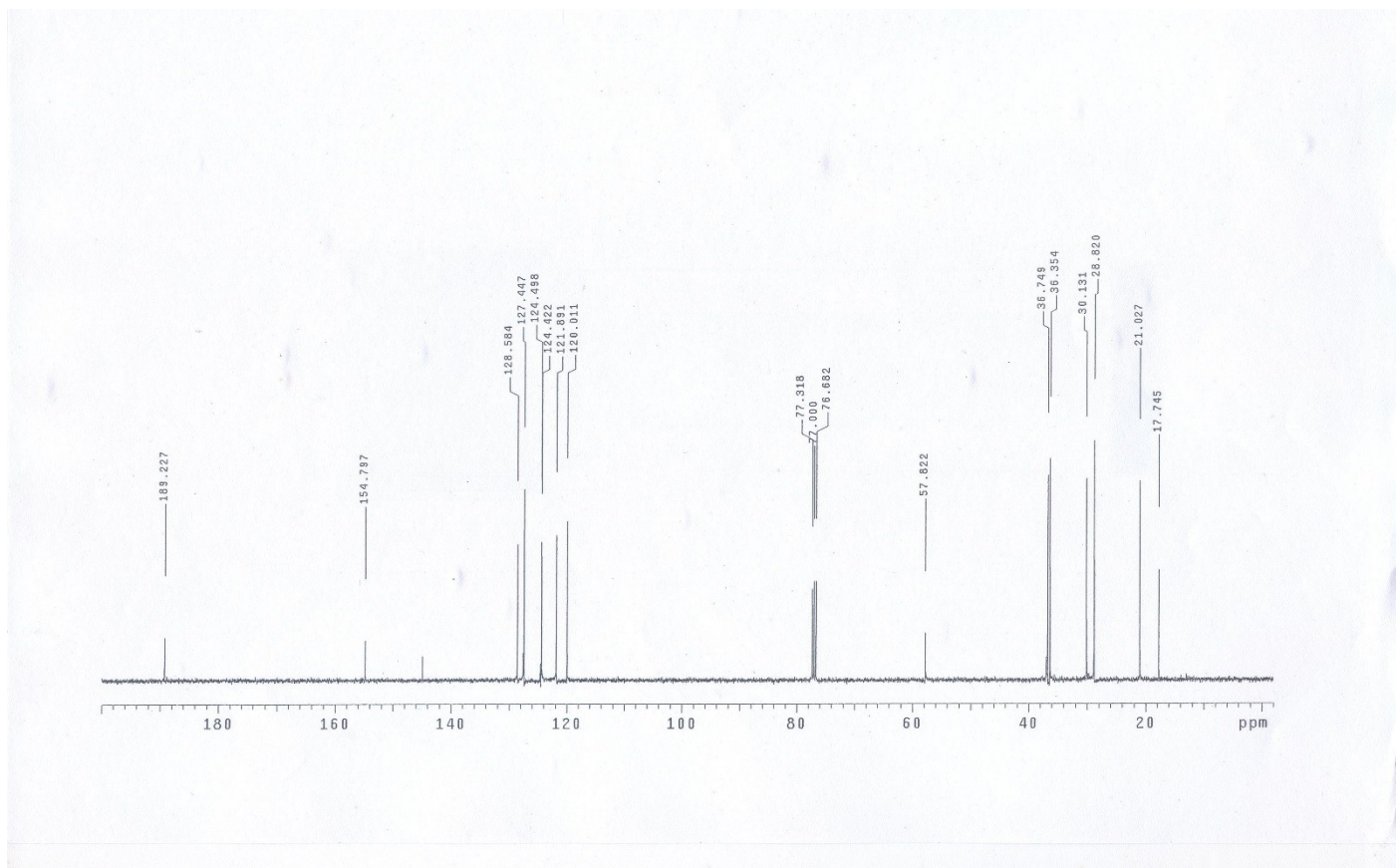
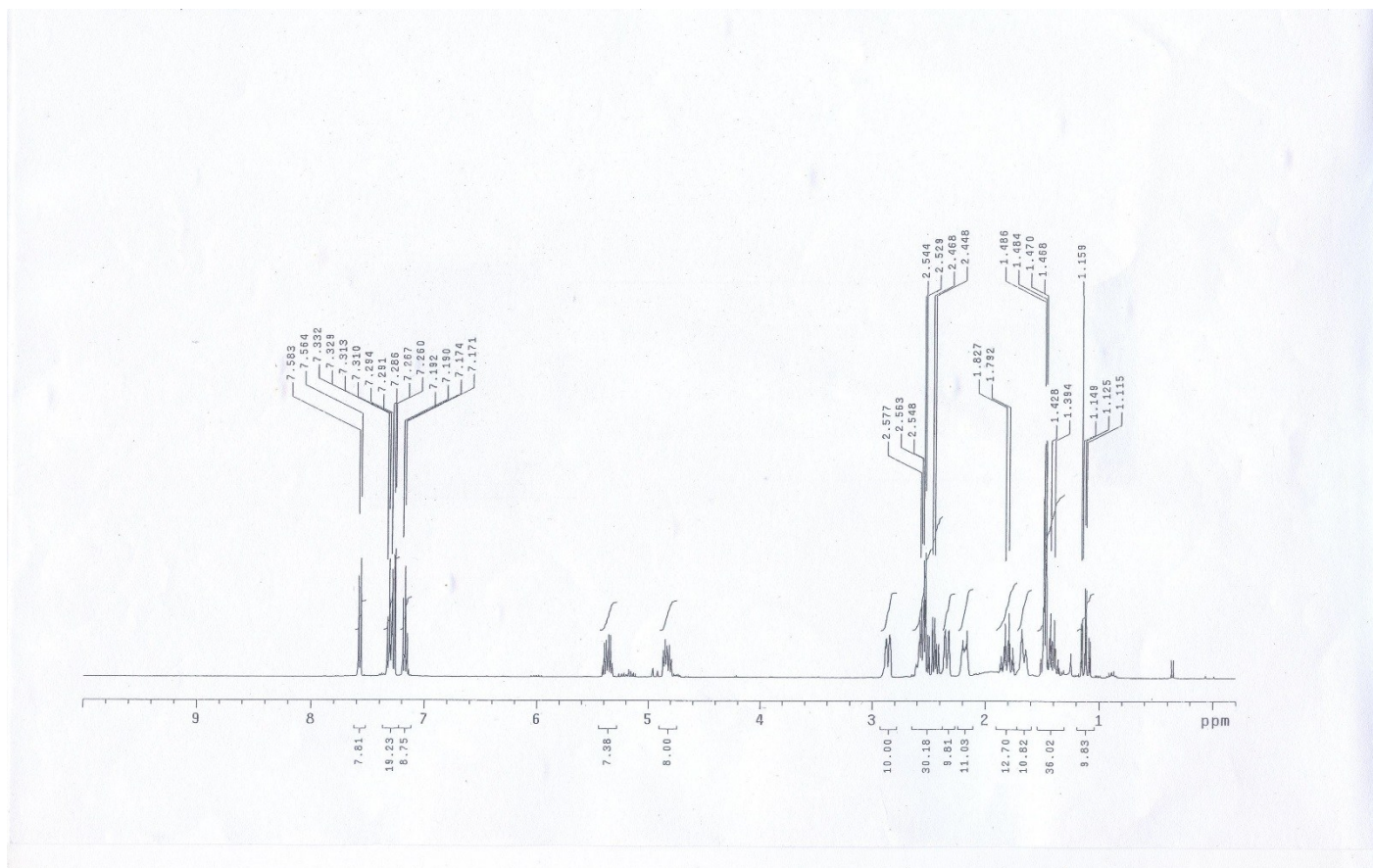
^1H and ^{13}C NMR spectra of **4a**



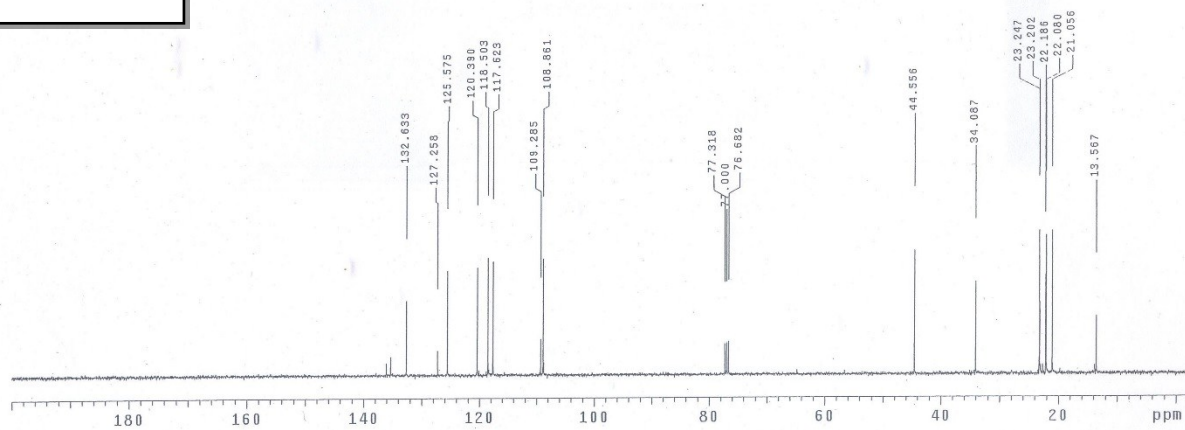
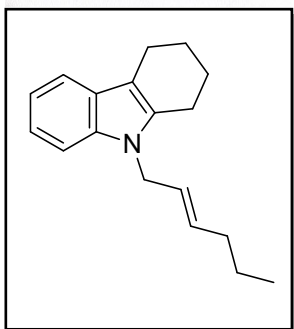
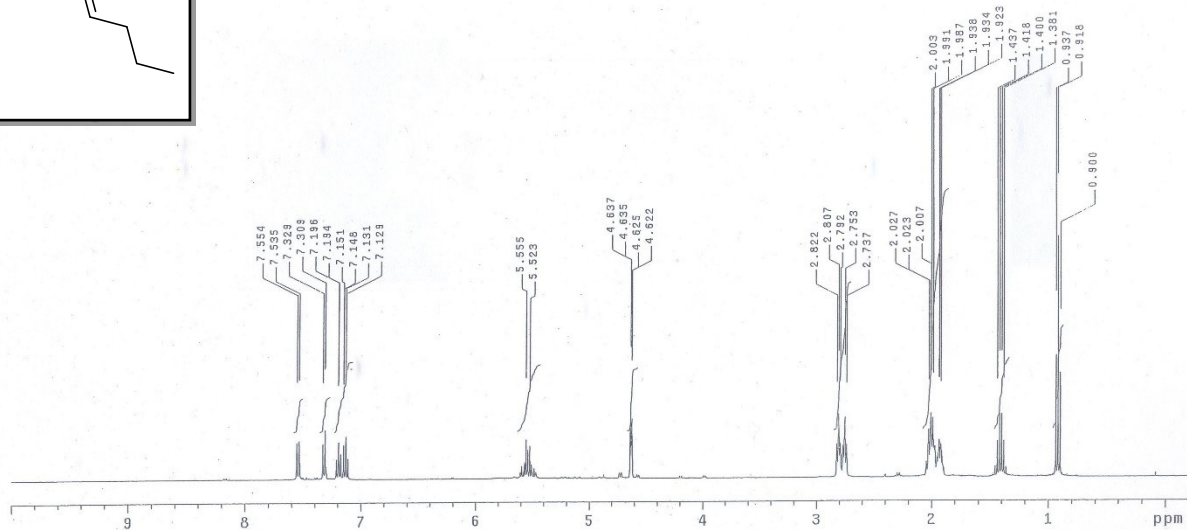
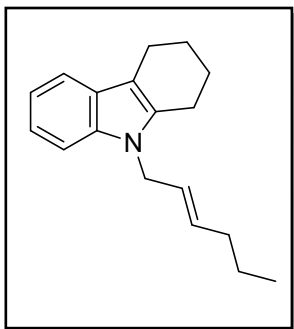
^1H and ^{13}C NMR spectra of **3b**



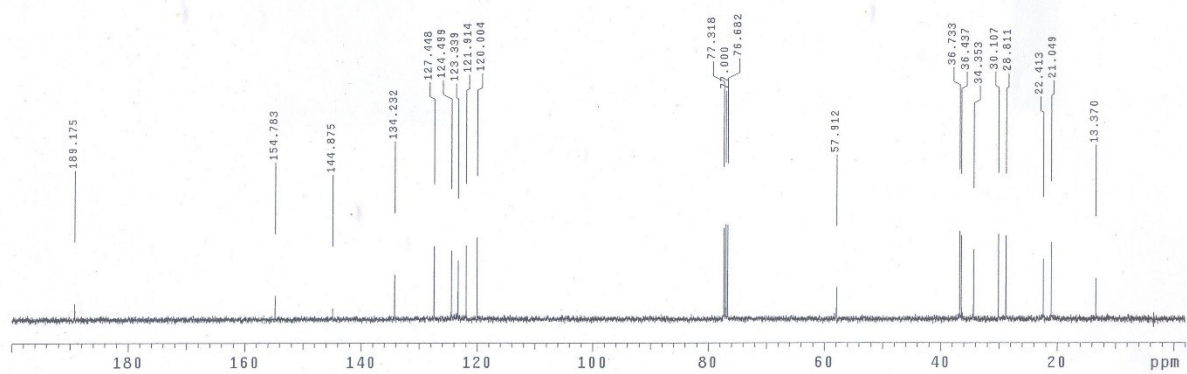
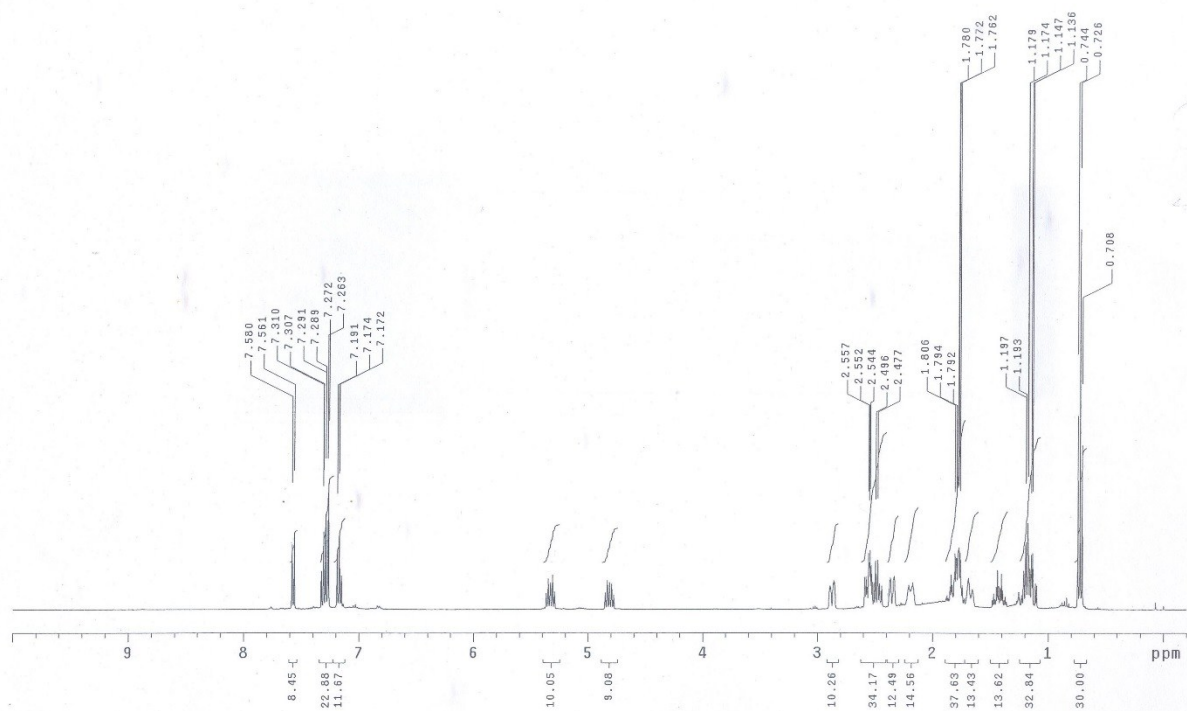
^1H and ^{13}C NMR spectra of **4b**



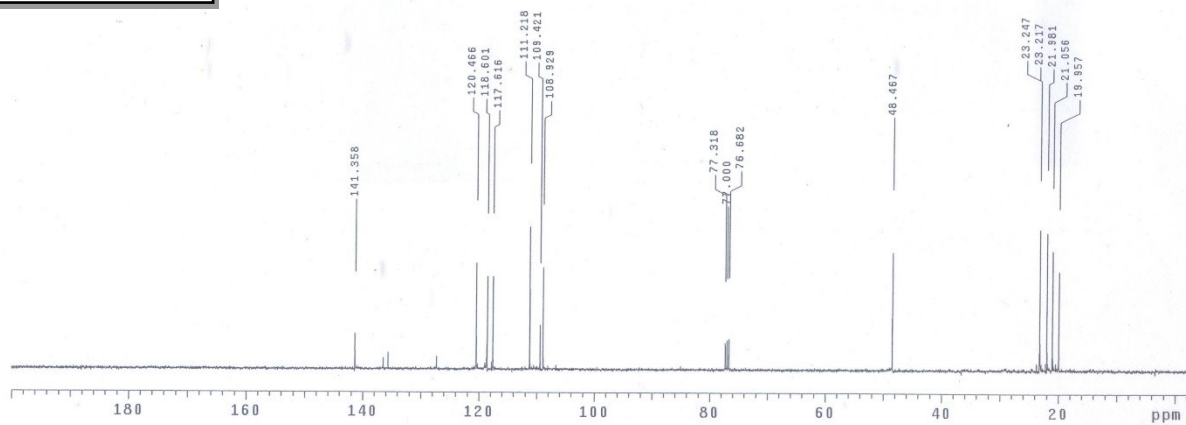
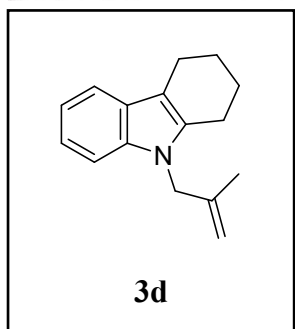
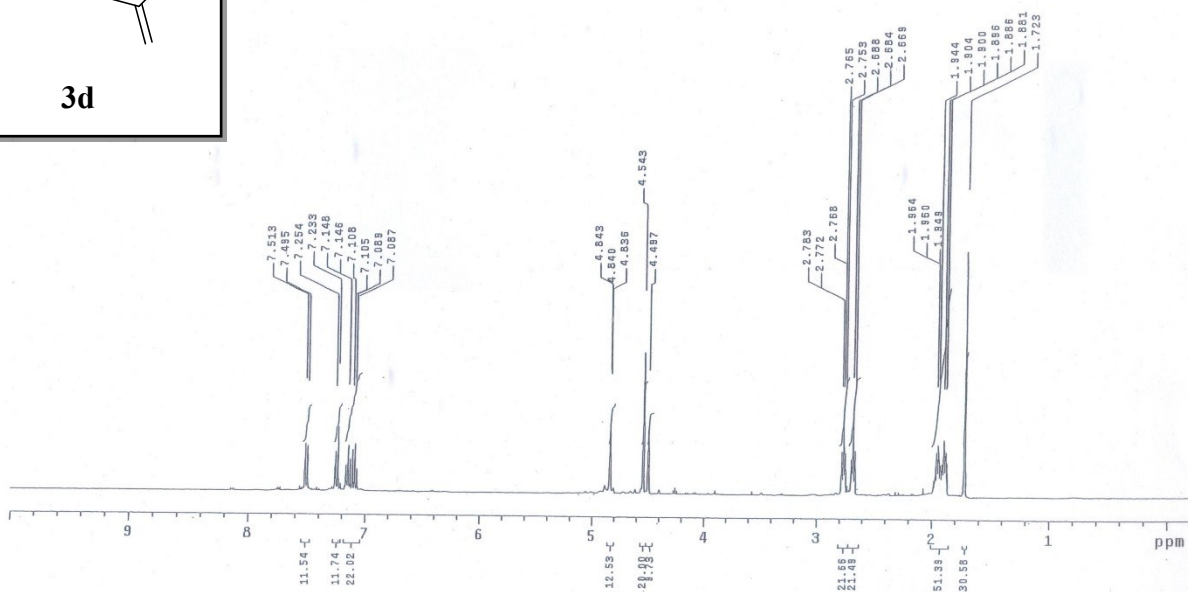
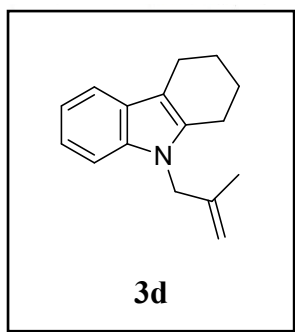
^1H and ^{13}C NMR spectra of **3c**



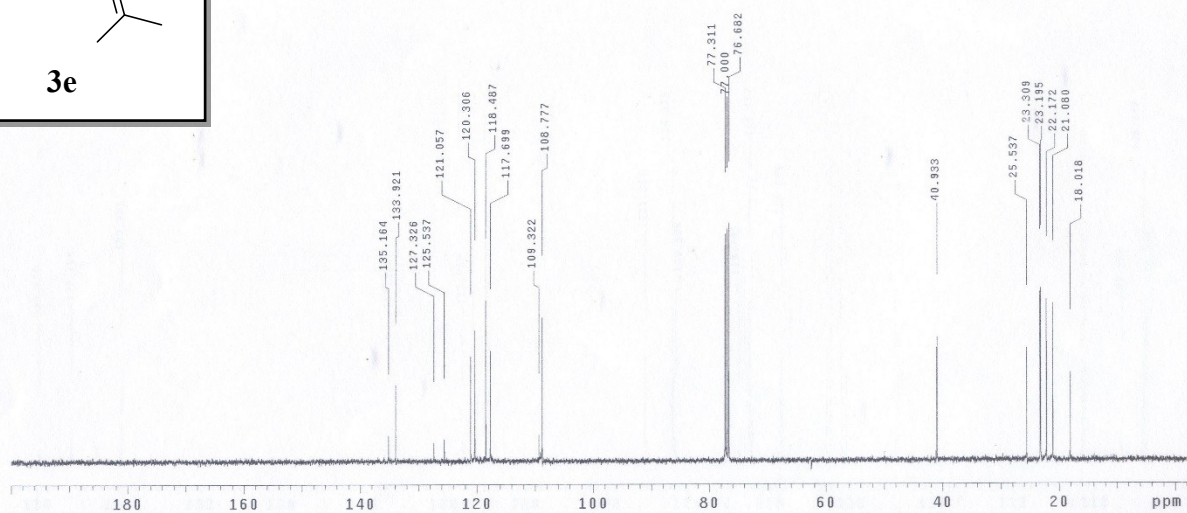
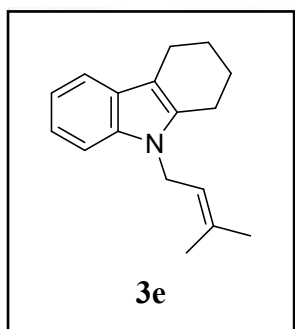
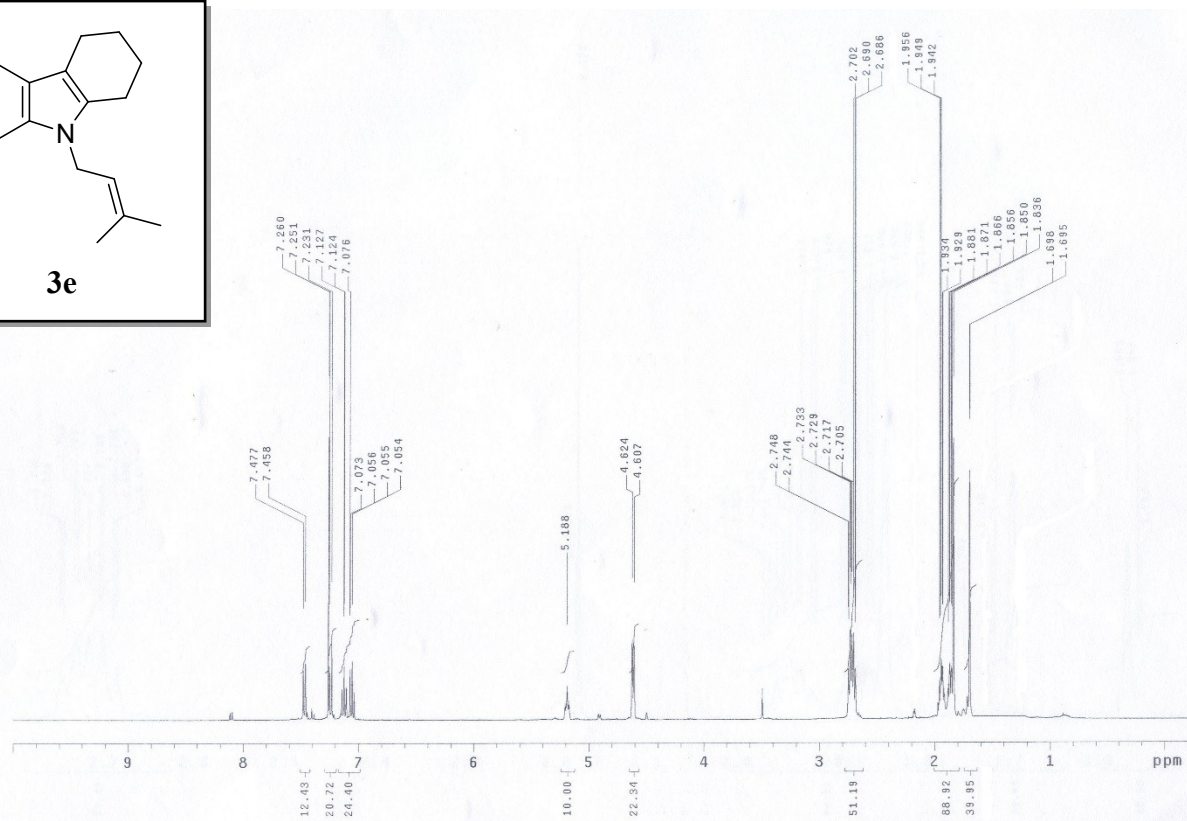
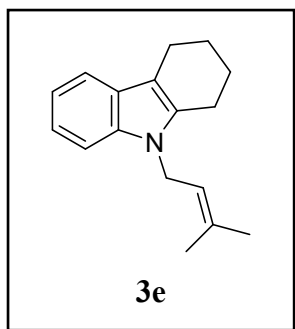
^1H and ^{13}C NMR spectra of **4c**



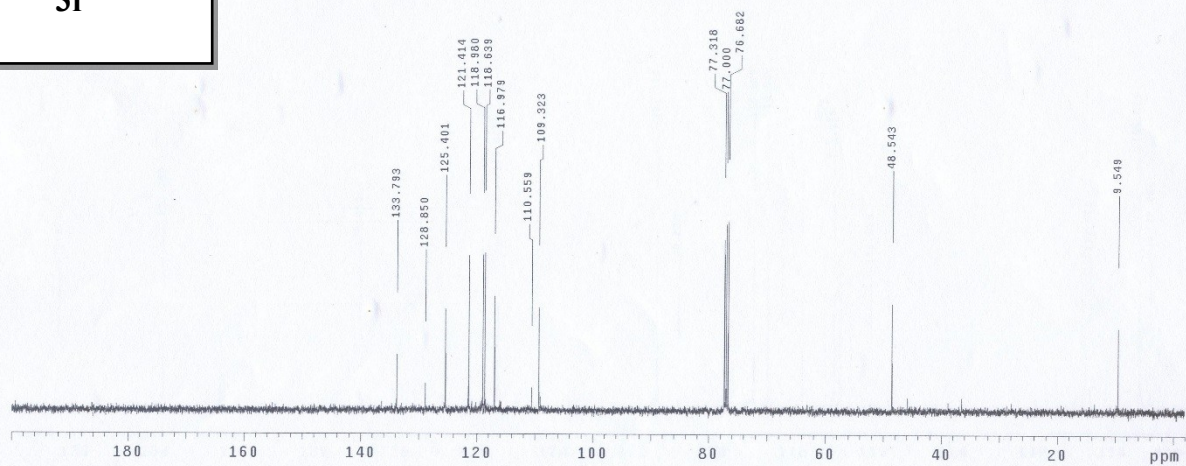
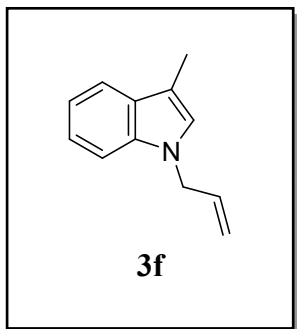
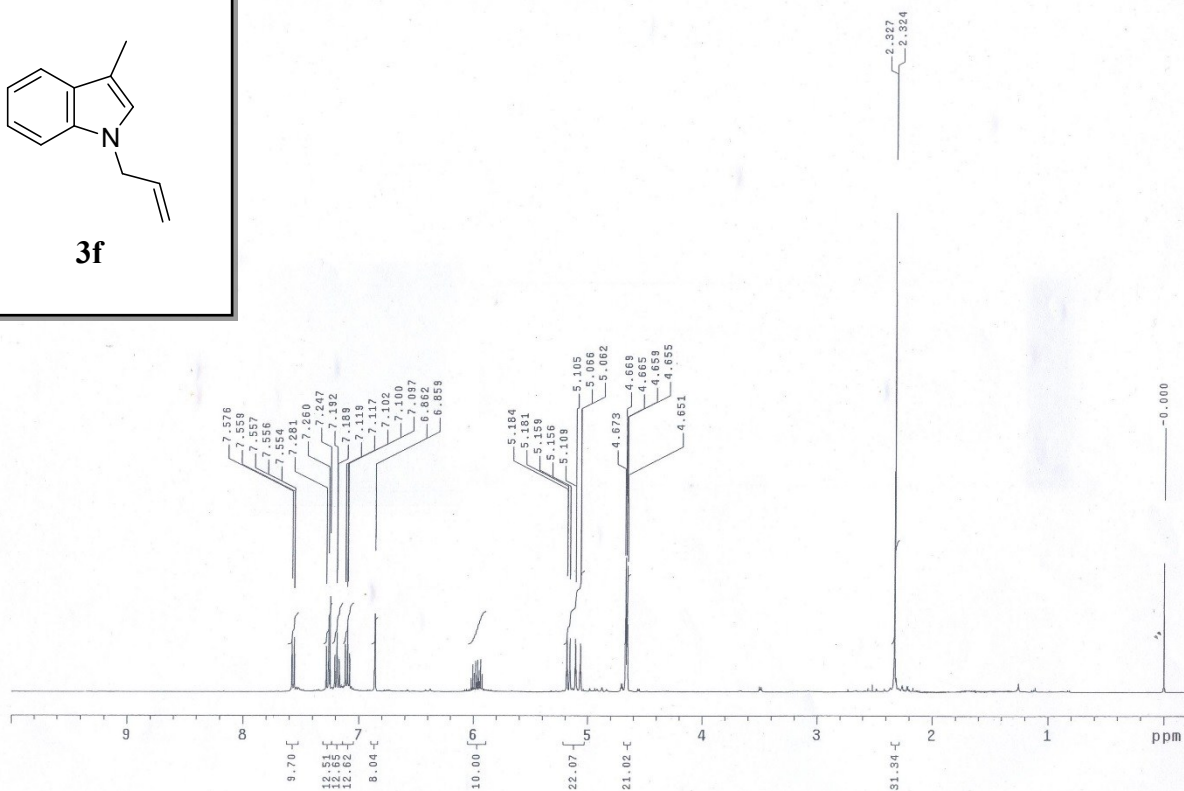
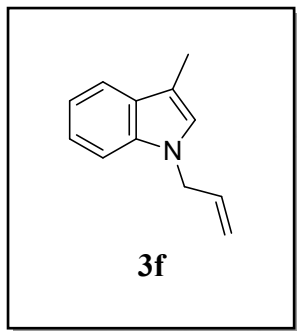
^1H and ^{13}C NMR spectra of **3d**



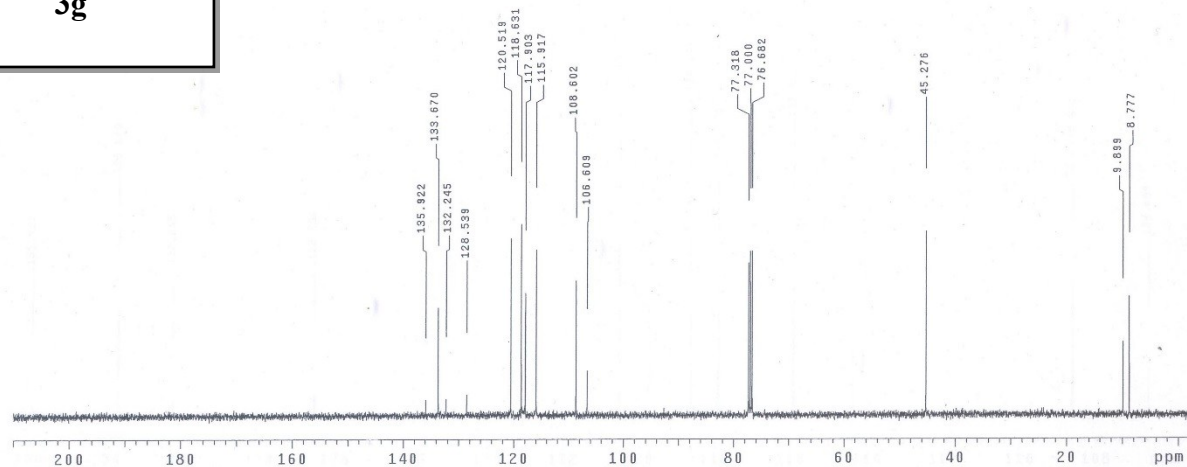
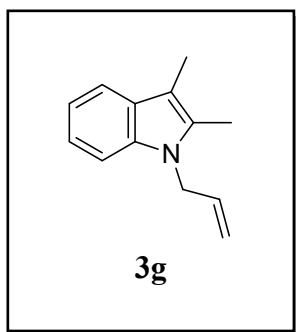
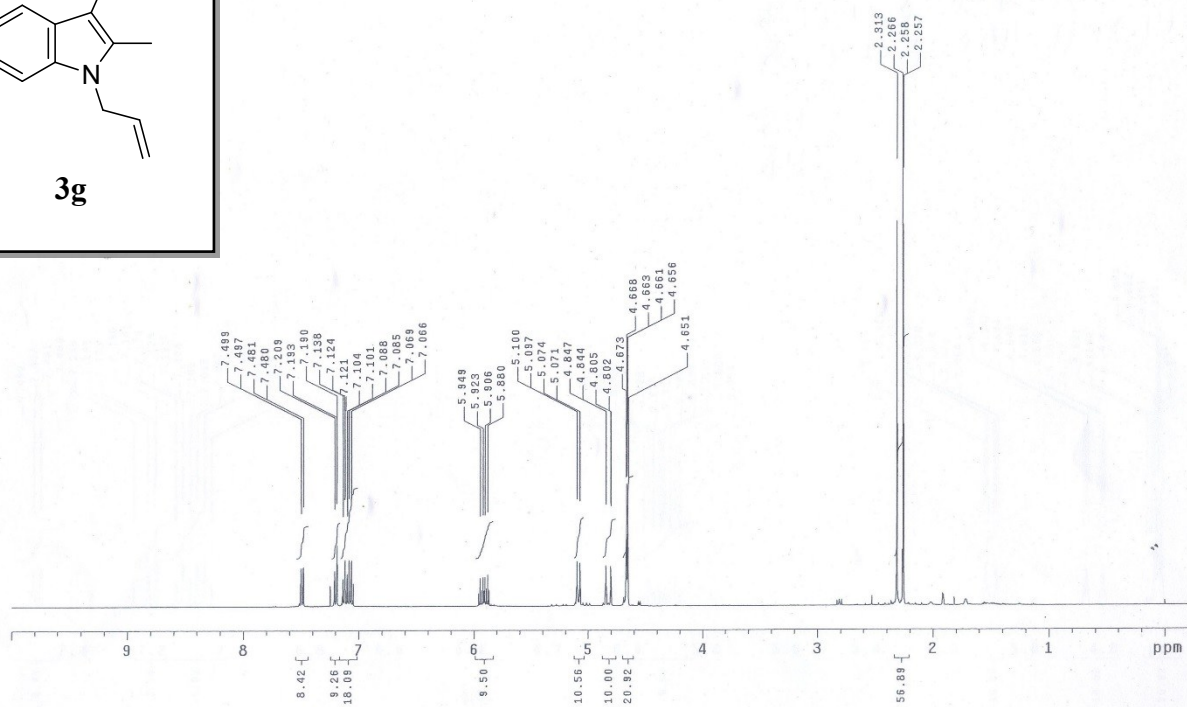
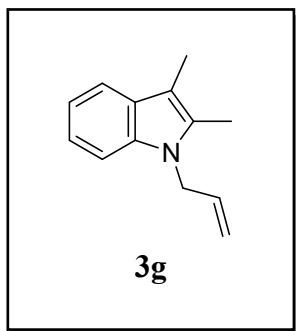
^1H and ^{13}C NMR spectra of **3e**



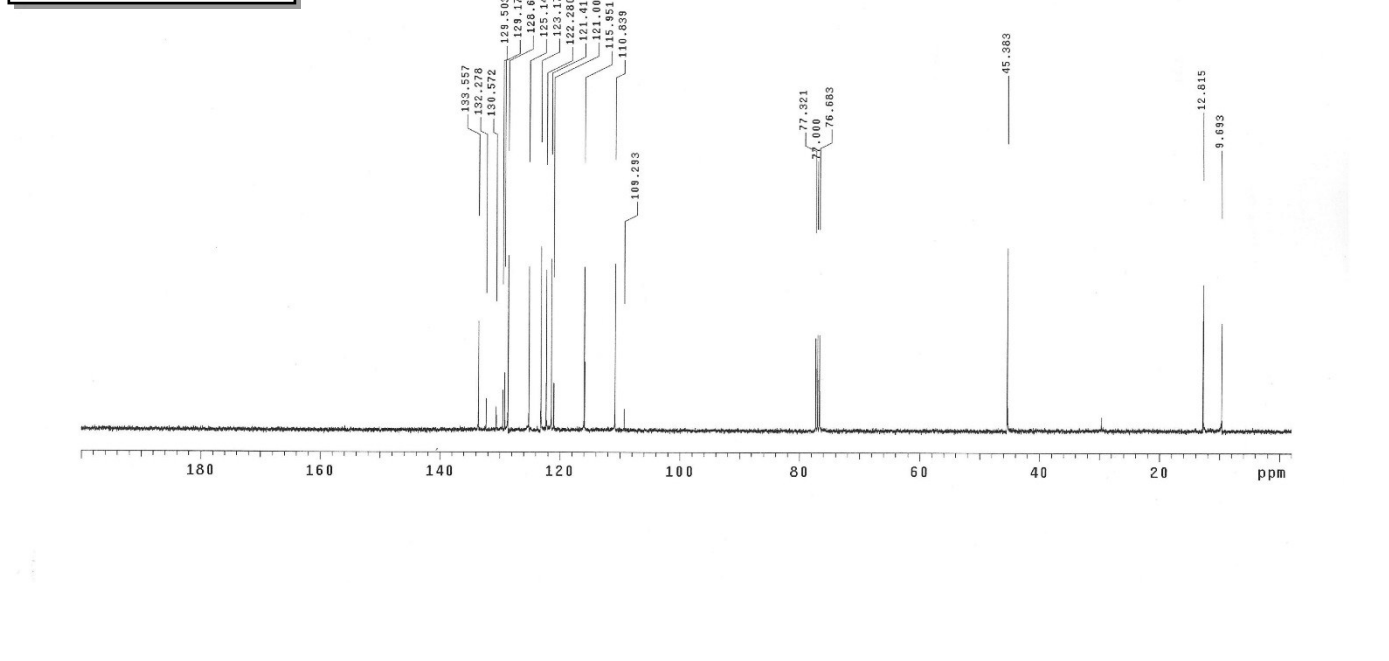
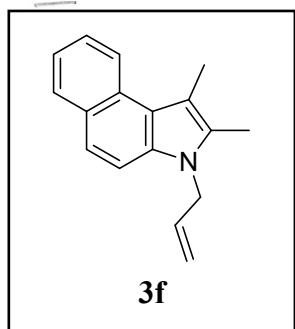
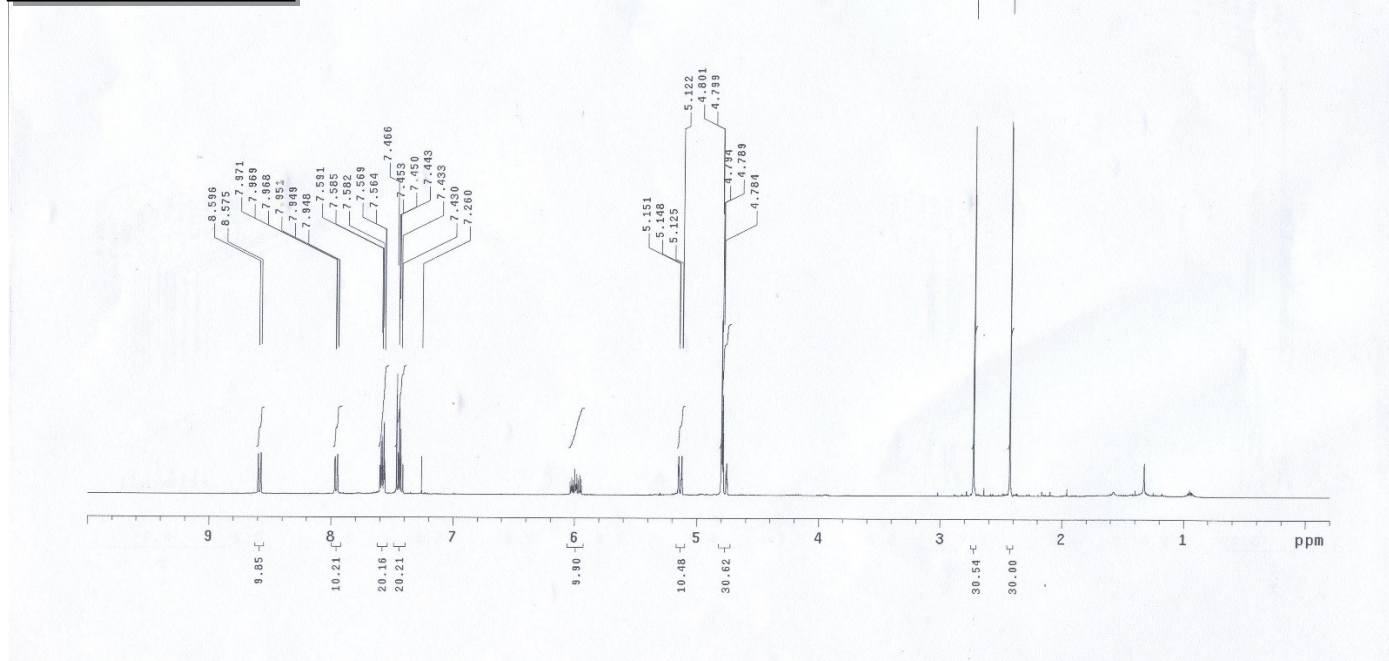
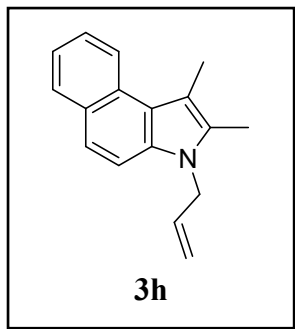
^1H and ^{13}C NMR spectra of **3f**



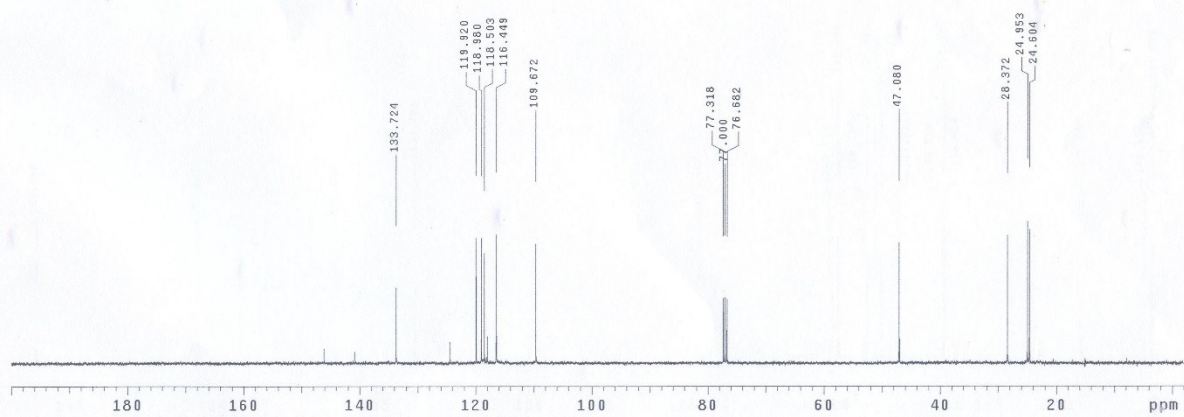
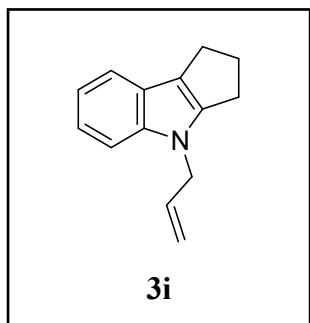
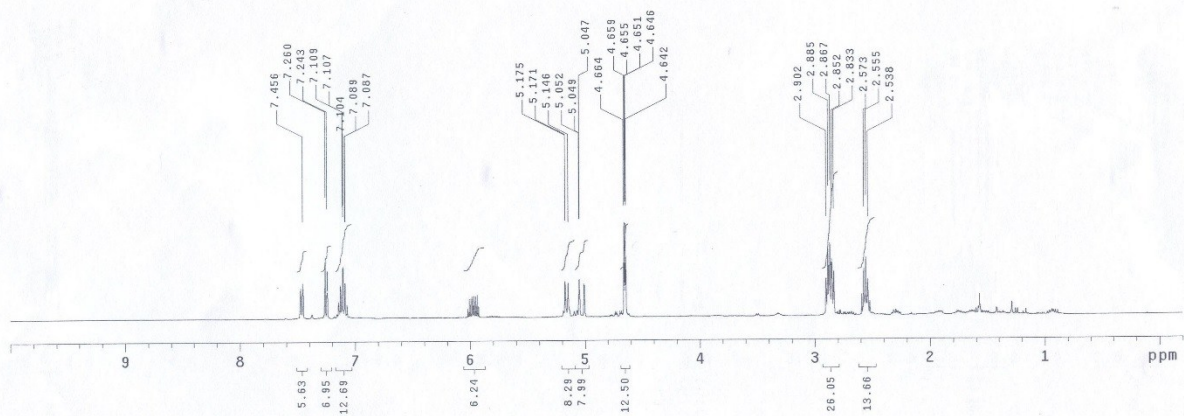
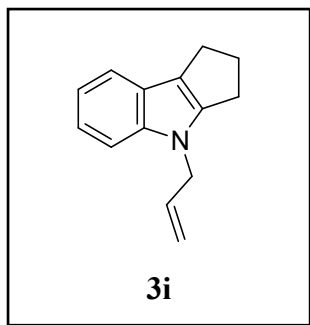
^1H and ^{13}C NMR spectra of **3g**



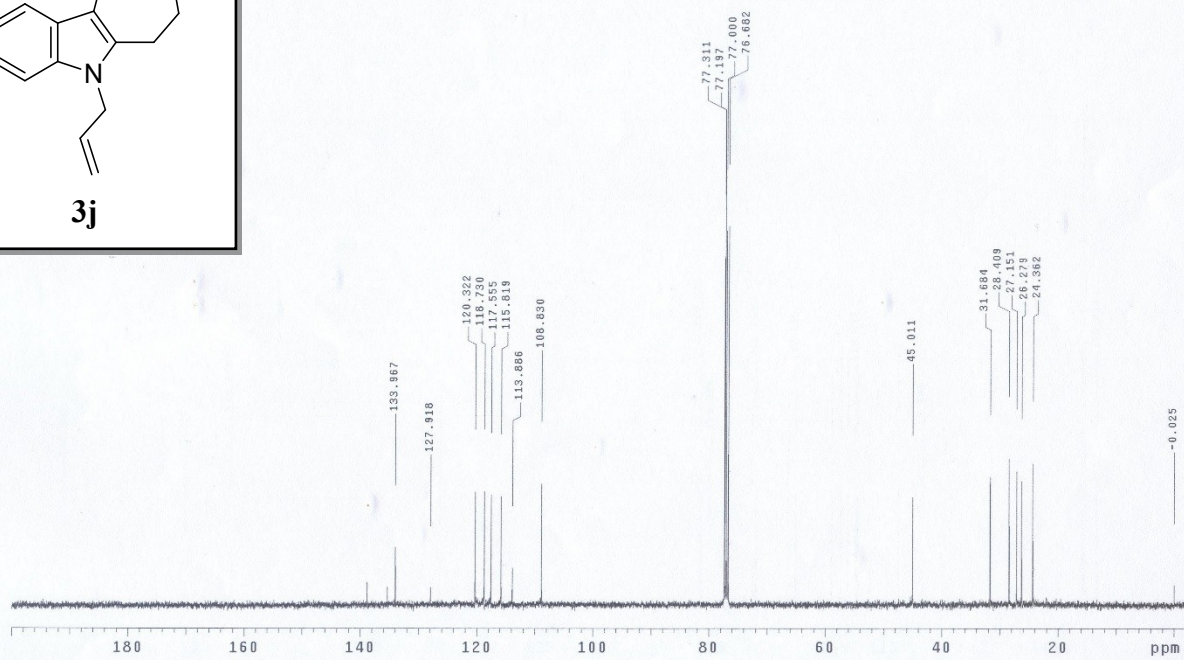
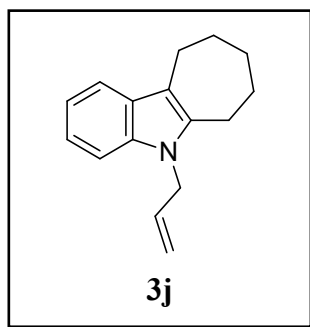
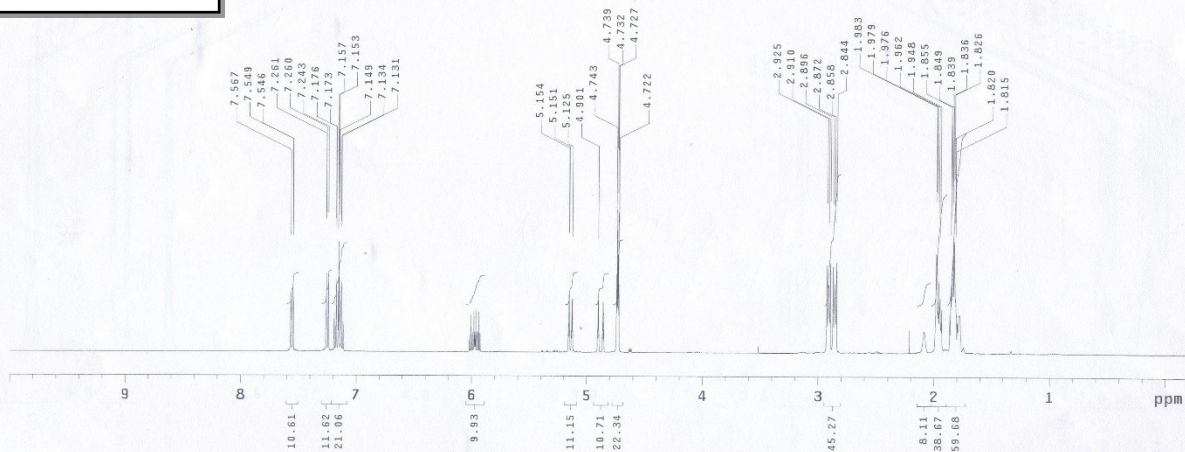
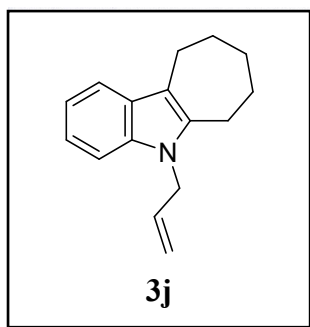
^1H and ^{13}C NMR spectra of **3h**



^1H and ^{13}C NMR spectra of **3i**



^1H and ^{13}C NMR spectra of **3j**



Reference

1. B.-J. Peng, W.-T. Wu and S.-C. Yang, *Molecules*, 2017, **22**, 2097.
2. C.-Y. Chang, Y.-H. Lin and Y.-K. Wu, *Chem. Commun.*, 2019, **55**, 1116-1119.
3. R. K. Bramely, J. Caldwell and R. Grigg, *J. Chem. Soc., Perkin Trans. 1*, 1973, 1913-1921.
4. B.-J. Peng, W.-T. Hsueh, F. Fülöp and S.-C. Yang, *New J. Chem.*, 2019, **43**, 58-62.