Supporting Information

Rhodium-Catalyzed Cyclization of 2-Ethynylanilines in the Presence of Isocyanates: Approach toward Indole-3-Carboxamides

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1. General Comments

Melting points were measured with a Yanaco micro melting point apparatus and uncorrected. IR spectra were recorded on a SHIMADZU IRAffinity-1. ^{1}H-NMR spectra were recorded on a JEOL JNM-ECP400 (400 MHz) spectrometer. Chemical shifts (δ) are given from TMS (0 ppm) in $CDCl_3$ and coupling constants are expressed in herts (Hz). The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, sext = sextet, dd, = double doublet, m = multiplet, and br = broad signal. ^{13}C-NMR spectra were recorded on JEOL JNM-ECP400 (100 MHz) spectrometer. Chemical shifts (δ) are given from $^{13}CDCl_3$ (77.0 ppm). Mass spectra and high resolution mass spectra were measured on a JEOL JMS-700 instrument.

2. Materials

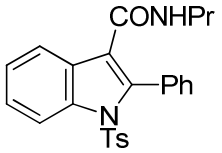
All commercially available materials including anhydrous 2-BuOH (Sigma–Aldrich Co., #294810, 99.5%) were purchased from Sigma–Aldrich Co., Tokyo Chemical Industry Co., and Wako Pure Chemical Industries, and were used as received. Starting materials **1a**–**k** were prepared according to the literature (Sonogashira coupling of the corresponding 2-iodoanilines followed by *N*-tosylation).[1]

3. Representative Procedure for the Synthesis of Indole 3-Carboxamides (Table 1, Entry 23)

Under an Ar atmosphere, a mixture of *N*-[2-(phenylethynyl)phenyl]-4-toluenesulfonamide (**1a**) (0.050 g, 0.14 mmol), propyl isocyanate (0.020 mL, 0.22 mmol), K_2CO_3 (0.024 g, 0.17 mmol), and $[RhCl(COD)_2]_2$ (3.6 mg, 0.0072 mmol) in 2-BuOH (4 mL) was stirred at room temperature for 2 h. 2 M HCl was added to the reaction mixture and extracted with AcOEt (30 mL × 3). The combined organic phase was washed with saturated aqueous NaCl (15 mL × 2) and dried over $MgSO_4$. The solvent was removed under a reduced pressure and the crude material was purified by silica gel column chromatography to give **2a** (0.051 g, 83%) as a colorless solid.

4. Spectroscopic and Analytical Data for 2a–k and 3a–c

2-Phenyl-*N*-propyl-1-tosyl-1*H*-indole-3-carboxamide (2a)



Yield: 83% (0.051 g).

Obtained as colorless scales (recrystallized from hexane/ethyl acetate, mp 140.2–141.5 °C).

IR (neat): 1647 cm^{-1}.

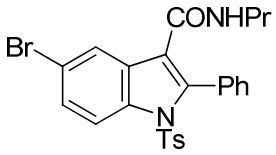
^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 0.62 (3H, t, *J* = 7.0 Hz), 1.13 (2H, sext, *J* = 7.0 Hz), 2.32 (3H, s), 3.05 (2H, q, *J* = 7.0 Hz), 5.01 (1H, br), 7.08 (2H, d, *J* = 8.0 Hz), 7.30–7.55 (9H, m), 8.14 (1H, d, *J* = 8.0 Hz), 8.33 (1H, d, *J* = 8.0 Hz).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 11.1, 21.5, 22.3, 40.9, 115.2, 118.7, 121.9, 124.6, 125.7, 126.8, 128.1, 128.4, 129.5, 129.9, 130.2, 131.4, 135.5, 136.5, 138.7, 145.2, 163.7.

LRMS (EI) *m/z*: 432 (M^+).

HRMS: Calcd. for $C_{25}H_{24}N_2O_3S$: 432.1508, found: 432.1504.

5-Bromo-2-phenyl-*N*-propyl-1-tosyl-1*H*-indole-3-carboxamide (2b)



Yield: 86% (0.063 g).

Obtained as colorless needles (recrystallized from hexane/ethyl acetate, mp 157.0–158.1 °C).

IR (neat): 1653 cm^{-1}.

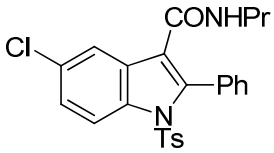
^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 0.61 (3H, t, *J* = 7.0 Hz), 1.12 (2H, sext, *J* = 7.0 Hz), 2.34 (3H, s), 3.04 (2H, q, *J* = 7.0 Hz), 4.96 (1H, br), 7.11 (2H, d, *J* = 8.2 Hz), 7.28 (2H, d, *J* = 8.2 Hz), 7.34 (2H, d, *J* = 7.6 Hz), 7.45–7.57 (4H, m), 8.20 (1H, d, *J* = 9.2 Hz), 8.36 (1H, d, *J* = 2.4 Hz).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 11.1, 21.6, 22.2, 40.9, 116.5, 117.6, 118.3, 124.9, 126.9, 128.3, 128.6, 129.7, 130.0, 130.3, 131.4, 135.2, 135.3, 139.7, 145.6, 163.2.

LRMS (EI) *m/z*: 510 (M^+), 512 (100).

HRMS: Calcd. for $C_{25}H_{23}{}^{79}BrN_2O_3S$: 510.0613, found: 510.0612.

5-Chloro-2-phenyl-*N*-propyl-1-tosyl-1*H*-indole-3-carboxamide (2c)



Yield: 75% (0.050 g).

Obtained as colorless scales (recrystallized from hexane/ethyl acetate, mp 142.9–144.6 °C).

IR (neat): 1647 cm^{-1}.

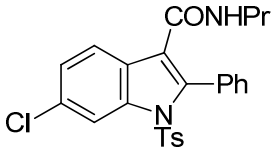
^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 0.62 (3H, t, *J* = 7.2 Hz), 1.13 (2H, sext, *J* = 7.2 Hz), 2.34 (3H, s), 3.05 (2H, q, *J* = 7.2 Hz), 4.96 (1H, br), 7.11 (2H, d, *J* = 8.2 Hz), 7.28 (2H, d, *J* = 8.2 Hz), 7.33–7.39 (3H, m), 7.47 (2H, t, *J* = 7.4 Hz), 7.55 (1H, t, *J* = 7.4 Hz), 8.20 (1H, d, *J* = 2.0 Hz), 8.26 (1H, d, *J* = 8.8 Hz).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 11.1, 21.6, 22.2, 41.0, 116.2, 117.8, 121.8, 126.0, 126.9, 128.3, 129.68 (2 signals), 129.75, 130.3, 130.6, 131.4, 134.8, 135.3, 139.9, 145.6, 163.2.

LRMS (EI) *m/z*: 466 (M^+).

HRMS: Calcd. for $C_{25}H_{23}{}^{35}ClN_2O_3S$: 466.1118, found: 466.1115.

6-Chloro-2-phenyl-*N*-propyl-1-tosyl-1*H*-indole-3-carboxamide (2d)



Yield: 77% (0.052 g).

Obtained as colorless prisms (recrystallized from hexane/ethyl acetate, mp 134.2–135.1 °C).

IR (neat): 1647 cm^{-1}.

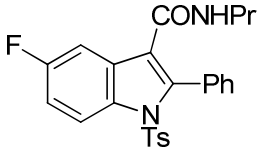
^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 0.61 (3H, t, *J* = 7.0 Hz), 1.12 (2H, sext, *J* = 7.0 Hz), 2.35 (3H, s), 3.04 (2H, q, *J* = 7.0 Hz), 4.98 (1H, br), 7.12 (2H, d, *J* = 8.0 Hz), 7.28–7.35 (5H, m), 7.46 (2H, t, *J* = 7.6 Hz), 7.55 (1H, t, *J* = 7.6 Hz), 8.11 (1H, d, *J* = 8.4 Hz), 8.38 (1H, d, *J* = 1.6 Hz).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 11.1, 21.6, 22.2, 40.9, 115.2, 118.0, 123.0, 125.2, 126.9 (2 signals), 128.3, 129.7 (2 signals), 130.2, 131.4, 131.7, 135.3, 136.7, 139.1, 145.6, 163.3.

LRMS (EI) *m/z*: 466 (M^+).

HRMS: Calcd. for $C_{25}H_{23}{}^{35}ClN_2O_3S$: 466.1118, found: 466.1117.

5-Fluoro-2-phenyl-*N*-propyl-1-tosyl-1*H*-indole-3-carboxamide (2e)



Yield: 68% (0.044 g).

Obtained as colorless needles (recrystallized from hexane/ethyl acetate, mp 129.7–130.8 °C).

IR (neat): 1647 cm^{-1}.

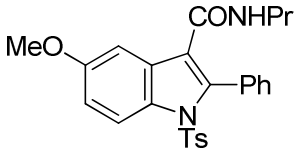
^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 0.62 (3H, t, *J* = 7.1 Hz), 1.12 (2H, sext, *J* = 7.1 Hz), 2.34 (3H, s), 3.05 (2H, q, *J* = 7.1 Hz), 4.96 (1H, br), 7.09–7.17 (3H, m), 7.28 (2H, d, *J* = 8.4 Hz), 7.35 (2H, d, *J* = 7.3 Hz), 7.47 (2H, t, *J* = 7.3 Hz), 7.55 (1H, t, *J* = 7.3 Hz), 7.87 (1H, dd, *J* = 9.1, 3.0 Hz), 8.28 (1H, dd, *J* = 9.1, 4.4 Hz).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 11.1, 21.5, 22.2, 40.9, 107.8 (d, *J* = 24.6 Hz), 113.7 (d, *J* = 25.4 Hz), 116.3 (d, *J* = 9.5 Hz), 118.2 (d, *J* = 4.0 Hz), 126.8, 128.3, 129.6, 129.7, 129.9, 130.2, 131.3, 132.7, 135.3, 140.2, 145.5, 160.3 (d, *J* = 240.0 Hz), 163.3.

LRMS (EI) *m/z*: 450 (M^+).

HRMS: Calcd. for $C_{25}H_{23}FN_2O_3S$: 450.1413, found: 450.1415.

5-Methoxy-2-phenyl-*N*-propyl-1-tosyl-1*H*-indole-3-carboxamide (2f)



Yield: 70% (0.047 g).

Obtained as colorless scales (recrystallized from hexane/ethyl acetate, mp 135.6–137.3 °C).

IR (neat): 1653 cm^{-1}.

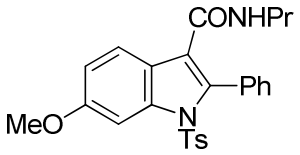
^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 0.62 (3H, t, *J* = 7.0 Hz), 1.13 (2H, sext, *J* = 7.0 Hz), 2.34 (3H, s), 3.05 (2H, q, *J* = 7.0 Hz), 3.86 (3H, s), 4.98 (1H, br), 7.02 (1H, dd, *J* = 9.2, 2.8 Hz), 7.08 (2H, d, *J* = 8.6 Hz), 7.28 (2H, d, *J* = 8.6 Hz), 7.36 (2H, d, *J* = 7.3 Hz), 7.46 (2H, t, *J* = 7.3 Hz), 7.53 (1H, t, *J* = 7.3 Hz), 7.64 (1H, d, *J* = 2.8 Hz), 8.21 (1H, d, *J* = 9.2 Hz).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 11.1, 21.5, 22.2, 40.9, 55.6, 103.3, 115.6, 116.2, 118.4, 126.8, 128.2, 129.5, 129.6, 130.0, 130.3, 131.0, 131.4, 135.4, 139.3, 145.2, 157.3, 163.9.

LRMS (EI) *m/z*: 462 (M^+).

HRMS: Calcd. for $C_{25}H_{26}N_2O_4S$: 462.1613, found: 462.1612.

6-Methoxy-2-phenyl-*N*-propyl-1-tosyl-1*H*-indole-3-carboxamide (2g)



Yield: 71% (0.047 g).

Obtained as colorless needles (recrystallized from hexane/ethyl acetate, mp 156.4–157.9 °C).

IR (neat): 1645 cm^{-1}.

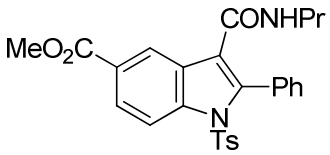
^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 0.61 (3H, t, *J* = 7.2 Hz), 1.12 (2H, sext, *J* = 7.2 Hz), 2.33 (3H, s), 3.05 (2H, q, *J* = 7.2 Hz), 3.93 (3H, s), 4.98 (1H, br), 6.99 (1H, dd, *J* = 8.8, 2.6 Hz), 7.10 (2H, d, *J* = 8.4 Hz), 7.30 (2H, d, *J* = 8.4 Hz), 7.34 (2H, d, *J* = 7.1 Hz), 7.45 (2H, t, *J* = 7.1 Hz), 7.51 (1H, t, *J* = 7.1 Hz), 7.88 (1H, d, *J* = 2.6 Hz), 8.02 (1H, d, *J* = 8.8 Hz).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 11.1, 21.5, 22.3, 40.9, 55.8, 99.5, 113.7, 118.5, 122.3, 122.6, 126.8, 128.1, 129.6, 129.8, 130.4, 131.5, 135.6, 137.4, 137.6, 145.2, 158.6, 163.8.

LRMS (EI) *m/z*: 462 (M^+).

HRMS: Calcd. for $C_{26}H_{26}N_2O_4S$: 462.1613, found: 462.1612.

5-Methoxycarbonyl-2-phenyl-*N*-propyl-1-tosyl-1*H*-indole-3-carboxamide (2h)



Yield: 67% (0.047 g).

Obtained as colorless needles (recrystallized from hexane/ethyl acetate, mp 160.1–161.2 °C).

IR (neat): 1721, 1647, 1225 cm^{-1}.

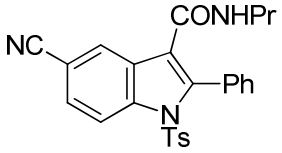
^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 0.62 (3H, t, *J* = 7.0 Hz), 1.14 (2H, sext, *J* = 7.0 Hz), 2.34 (3H, s), 3.07 (2H, q, *J* = 7.0 Hz), 3.92 (3H, s), 5.02 (1H, br), 7.10 (2H, d, *J* = 8.4 Hz), 7.30 (2H, d, *J* = 8.4 Hz), 7.36 (2H, d, *J* = 7.5 Hz), 7.48 (2H, t, *J* = 7.5 Hz), 7.56 (1H, t, *J* = 7.5 Hz), 8.12 (1H, dd, *J* = 9.0, 1.9 Hz), 8.38 (1H, d, *J* = 9.0 Hz), 8.86 (1H, d, *J* = 1.9 Hz).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 11.1, 21.5, 22.3, 41.0, 52.0, 114.9, 118.7, 124.2, 126.7, 126.9, 128.2 (2 signals), 128.3, 129.7, 130.2, 131.4 (2 signals), 135.3, 138.9, 139.8, 145.6, 163.2, 167.1.

LRMS (EI) *m/z*: 490 (M^+).

HRMS: Calcd. for $C_{27}H_{26}N_2O_5S$: 490.1562, found: 490.1562.

5-Cyano-2-phenyl-*N*-propyl-1-tosyl-1*H*-indole-3-carboxamide (2i)



Yield: 68% (0.045 g).

Obtained as colorless prisms (recrystallized from hexane/ethyl acetate, mp 167.8–169.5 °C).

IR (neat): 2223, 1647 cm^{-1}.

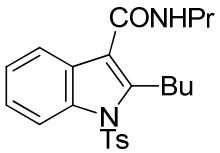
^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 0.61 (3H, t, *J* = 7.0 Hz), 1.13 (2H, sext, *J* = 7.0 Hz), 2.36 (3H, s), 3.05 (2H, q, *J* = 7.0 Hz), 4.99 (1H, br), 7.13 (2H, d, *J* = 8.2 Hz), 7.28 (2H, d, *J* = 8.2 Hz), 7.32 (2H, d, *J* = 7.3 Hz), 7.49 (2H, t, *J* = 7.3 Hz), 7.59 (1H, t, *J* = 7.3 Hz), 7.66 (1H, dd, *J* = 8.8, 1.2 Hz), 8.44 (1H, d, *J* = 8.8 Hz), 8.63 (1H, d, *J* = 1.2 Hz).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 11.1, 21.6, 22.2, 41.0, 108.2, 115.9, 117.5, 119.1, 127.0, 127.5, 128.4 (3 signals), 129.1, 129.8, 130.6, 131.3, 135.2, 138.0, 140.5, 146.0, 162.7.

LRMS (EI) *m/z*: 457 (M^+).

HRMS: Calcd. for $C_{26}H_{23}N_3O_3S$: 457.1460, found: 457.1457.

2-Butyl-*N*-propyl-1-tosyl-1*H*-indole-3-carboxamide (2j)



Yield: 50% (0.030 g).

Obtained as brown oil.

IR (neat): 1643 cm^{-1}.

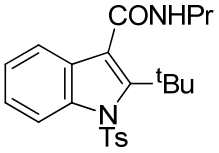
^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 0.93 (3H, t, *J* = 7.2 Hz), 1.00 (3H, t, *J* = 7.2 Hz), 1.43 (2H, sext, *J* = 7.2 Hz), 1.60–1.76 (4H, m), 2.32 (3H, s), 3.26 (2H, t, *J* = 7.2 Hz), 3.43 (2H, q, *J* = 7.2 Hz), 5.85 (1H, br), 7.19 (2H, d, *J* = 8.2 Hz), 7.24–7.32 (2H, m), 7.59 (1H, d, *J* = 7.6 Hz), 7.62 (2H, d, *J* = 8.2 Hz), 8.20 (1H, d, *J* = 7.6 Hz).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 11.5, 13.7, 21.5, 22.8, 23.0, 26.7, 33.4, 41.5, 115.2, 117.0, 119.0, 124.1, 124.6, 126.4, 127.3, 129.9, 136.09, 136.11, 144.2, 145.1, 164.5.

LRMS (EI) *m/z*: 412 (M^+).

HRMS: Calcd. for $C_{23}H_{28}N_2O_3S$: 412.1821, found: 412.1820.

2-*tert*-Butyl-*N*-propyl-1-tosyl-1*H*-indole-3-carboxamide (2k)



Yield: 56% (0.033 g).

Obtained as colorless prisms (recrystallized from hexane/ethyl acetate, mp 176.3–178.1 °C).

IR (neat): 1636 cm^{-1}.

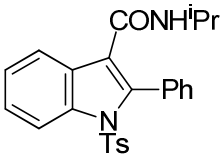
^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 0.98 (3H, t, *J* = 7.3 Hz), 1.61–1.70 (2H, m), 1.70 (9H, s), 2.26 (3H, s), 3.41 (2H, q, *J* = 7.2 Hz), 5.77 (1H, br), 7.05 (2H, d, *J* = 8.4 Hz), 7.12 (1H, t, *J* = 7.8 Hz), 7.19 (1H, t, *J* = 7.8 Hz), 7.27 (1H, d, *J* = 7.8 Hz), 7.38 (2H, d, *J* = 8.4 Hz), 7.96 (1H, d, *J* = 7.8 Hz).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 11.5, 21.4, 22.6, 31.5, 36.5, 41.8, 117.1, 119.0, 124.3, 124.4, 125.0, 126.2, 129.2, 129.6, 134.9, 138.4, 144.3, 149.7, 166.1.

LRMS (EI) *m/z*: 412 (M^+).

HRMS: Calcd. for $C_{23}H_{28}N_2O_3S$: 412.1821, found: 412.1820.

***N*-Isopropyl-2-phenyl-1-tosyl-1*H*-indole-3-carboxamide (3a)**



Yield: 94% (0.059 g).

Obtained as colorless prisms (recrystallized from hexane/ethyl acetate, mp 152.5–153.7 °C).

IR (neat): 1653 cm^{-1}.

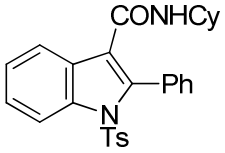
^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 0.79 (6H, d, *J* = 6.4 Hz), 2.32 (3H, s), 3.09–4.02 (1H, m), 4.76 (1H, d, *J* = 7.6 Hz), 7.09 (2H, d, *J* = 8.4 Hz), 7.32 (2H, d, *J* = 8.4 Hz), 7.35–7.49 (6H, m), 7.54 (1H, t, *J* = 7.5 Hz), 8.13 (1H, d, *J* = 7.5 Hz), 8.33 (1H, d, *J* = 8.4 Hz).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 21.5, 22.1, 40.9, 115.1, 118.9, 121.9, 124.6, 125.7, 126.8, 128.1, 128.4, 129.5, 129.9, 130.3, 131.4, 135.5, 136.4, 138.6, 145.2, 162.8.

LRMS (EI) *m/z*: 432 (M^+).

HRMS: Calcd. for $C_{25}H_{24}N_2O_3S$: 432.1508, found: 432.1508.

***N*-Cyclohexyl-2-phenyl-1-tosyl-1*H*-indole-3-carboxamide (3b)**



Yield: 94% (0.064 g).

Obtained as colorless prisms (recrystallized from hexane/ethyl acetate, mp 164.6–165.3 °C).

IR (neat): 1651 cm^{-1}.

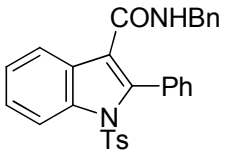
^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 0.62–0.72 (2H, m), 0.98–1.06 (1H, m), 1.17–1.27 (2H, m), 1.37–1.48 (3H, m), 1.56–1.60 (2H, m), 2.32 (3H, s), 3.66–3.74 (1H, m), 4.89 (1H, d, *J* = 8.0 Hz), 7.09 (2H, d, *J* = 8.0 Hz), 7.31–7.44 (6H, m), 7.47 (2H, t, *J* = 7.3 Hz), 7.54 (1H, t, *J* = 7.3 Hz), 8.14 (1H, d, *J* = 8.0 Hz), 8.33 (1H, d, *J* = 8.0 Hz).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 21.5, 24.2, 25.3, 32.3, 47.5, 115.1, 118.8, 122.0, 124.6, 125.7, 126.9, 128.2, 128.4, 129.5, 129.9, 130.3, 131.4, 135.5, 136.5, 138.6, 145.2, 162.7.

LRMS (EI) *m/z*: 472 (M^+).

HRMS: Calcd. for $C_{28}H_{28}N_2O_3S$: 472.1821, found: 472.1823.

***N*-Benzyl-2-phenyl-1-tosyl-1*H*-indole-3-carboxamide (3c)**



Yield: 75% (0.052 g).

Obtained as colorless scales (recrystallized from hexane/diethyl ether, mp 158.7–159.7 °C).

IR (neat): 1653 cm^{-1}.

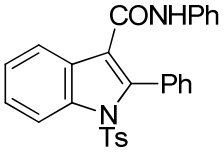
^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 2.32 (3H, s), 4.28 (2H, d, *J* = 6.0 Hz), 5.27 (1H, br), 6.86 (2H, dd, *J* = 6.6, 3.0 Hz), 7.08 (2H, d, *J* = 8.8 Hz), 7.17–7.20 (3H, m), 7.29–7.38 (7H, m), 7.41–7.45 (2H, m), 8.16 (1H, d, *J* = 8.0 Hz), 8.34 (1H, d, *J* = 8.0 Hz).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 21.5, 43.5, 115.2, 118.3, 121.9, 124.7, 125.7, 126.9, 127.3, 127.5, 128.2, 128.3, 128.5, 129.6, 129.9, 130.0, 131.3, 135.5, 136.5, 137.4, 139.0, 145.3, 163.6.

LRMS (EI) *m/z*: 480 (M^+).

HRMS: Calcd. for $C_{29}H_{24}N_2O_3S$: 480.1508, found: 480.1502.

2,*N*-Diphenyl-1-tosyl-1*H*-indole-3-carboxamide (3d)



Yield: 75% (0.050 g).

Obtained as colorless needles (recrystallized from hexane/ethyl acetate, mp 158.2–159.2 °C).

IR (neat): 1653 cm^{-1}.

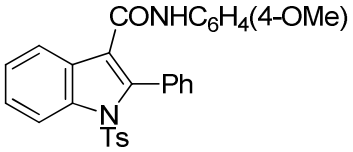
^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 2.32 (3H, s), 6.73 (1H, br), 6.97–7.03 (3H, m), 7.11 (2H, d, *J* = 7.9 Hz), 7.17 (2H, t, *J* = 7.9 Hz), 7.34–7.47 (6H, m), 7.53 (2H, t, *J* = 7.5 Hz), 7.61 (1H, t, *J* = 7.5 Hz), 8.30 (1H, d, *J* = 7.5 Hz), 8.37 (1H, d, *J* = 8.4 Hz).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 21.5, 115.1, 118.1, 119.4, 122.2, 124.1, 124.8, 125.9, 126.9, 128.3, 128.6, 128.8, 129.6, 130.0, 130.4, 131.6, 135.5, 136.5, 137.5, 139.2, 145.4, 161.6.

LRMS (EI) *m/z*: 466 (M^+).

HRMS: Calcd. for $C_{28}H_{22}N_2O_3S$: 466.1351, found: 466.1351.

***N*-(4-Methoxyphenyl)-2-phenyl-1-tosyl-1*H*-indole-3-carboxamide (3e)**



Yield: 86% (0.062 g).

Obtained as colorless scales (recrystallized from hexane/ethyl acetate, mp 209.0–211.6 °C).

IR (neat): 1653 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 2.33 (3H, s), 3.72 (3H, s), 6.61 (1H, br), 6.72 (2H, d, *J* = 9.0 Hz), 6.95 (2H, d, *J* = 9.0 Hz), 7.11 (2H, d, *J* = 8.0 Hz), 7.34–7.41 (3H, m), 7.43–7.47 (3H, m), 7.53 (2H, t, *J* = 7.5 Hz), 7.60 (1H, t, *J* = 7.5 Hz), 8.28 (1H, d, *J* = 7.5 Hz), 8.36 (1H, d, *J* = 8.4 Hz).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 21.5, 55.4, 114.0, 115.2, 118.3, 121.2, 122.2, 124.8, 125.9, 126.9, 128.4, 128.5, 129.6, 130.1, 130.3, 130.7, 131.6, 135.5, 136.5, 139.0, 145.4, 156.3, 161.4.

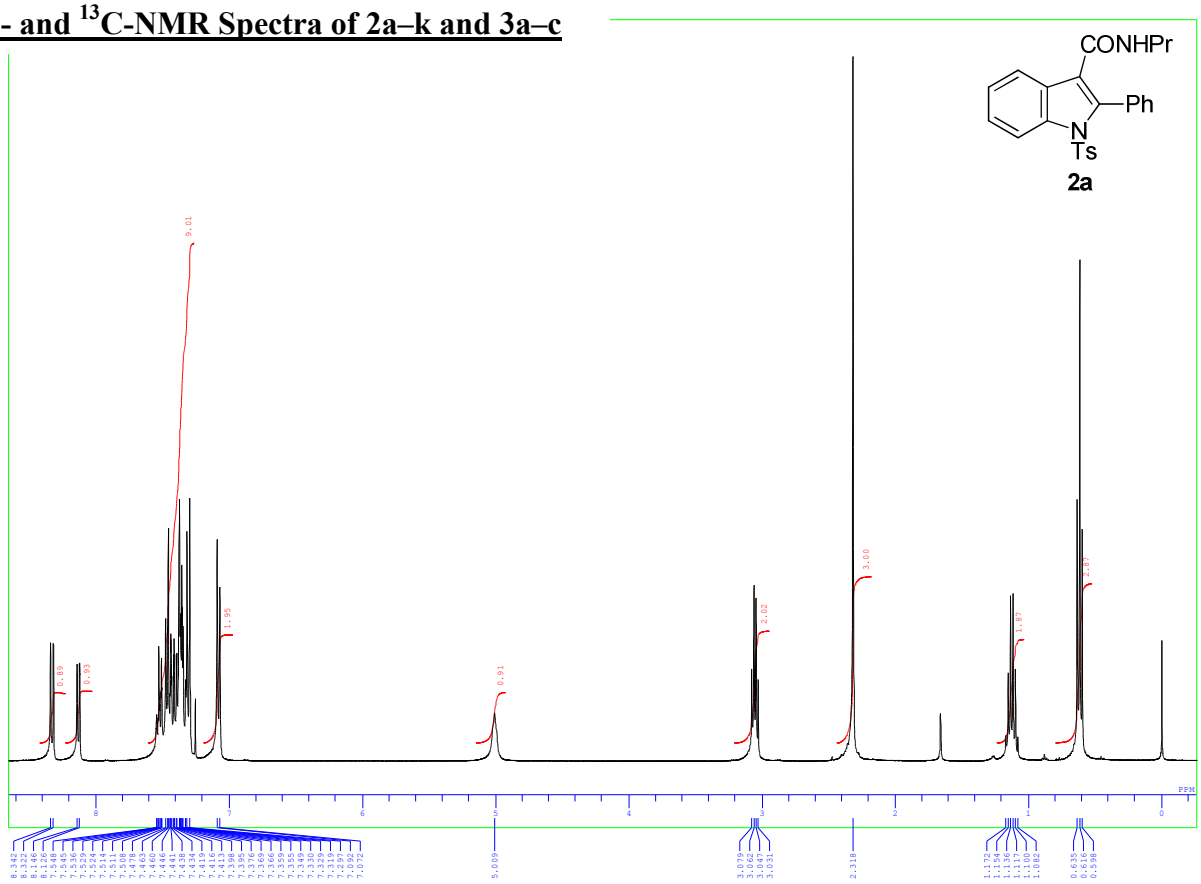
LRMS (EI) *m/z*: 496 (M^+).

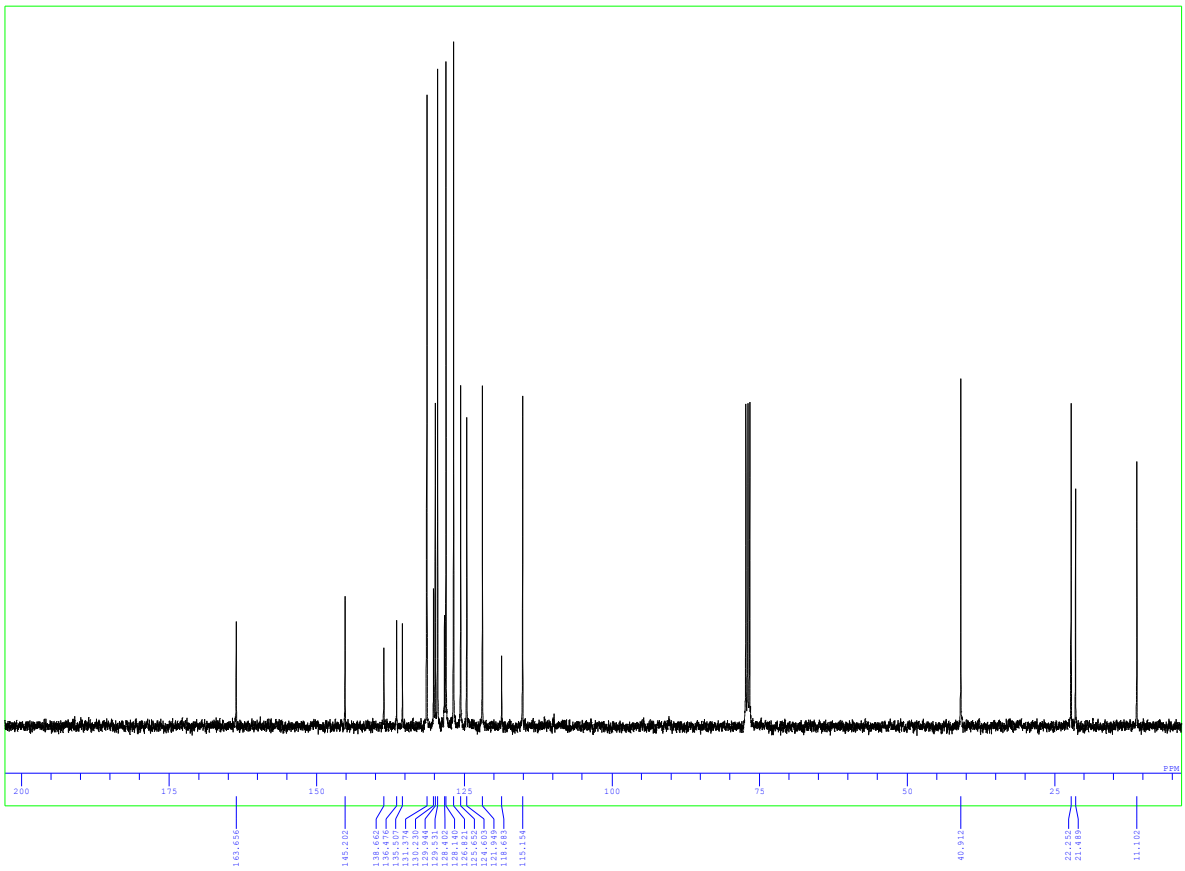
HRMS: Calcd. for $C_{29}H_{24}N_2O_4S$: 496.1457, found: 496.1458.

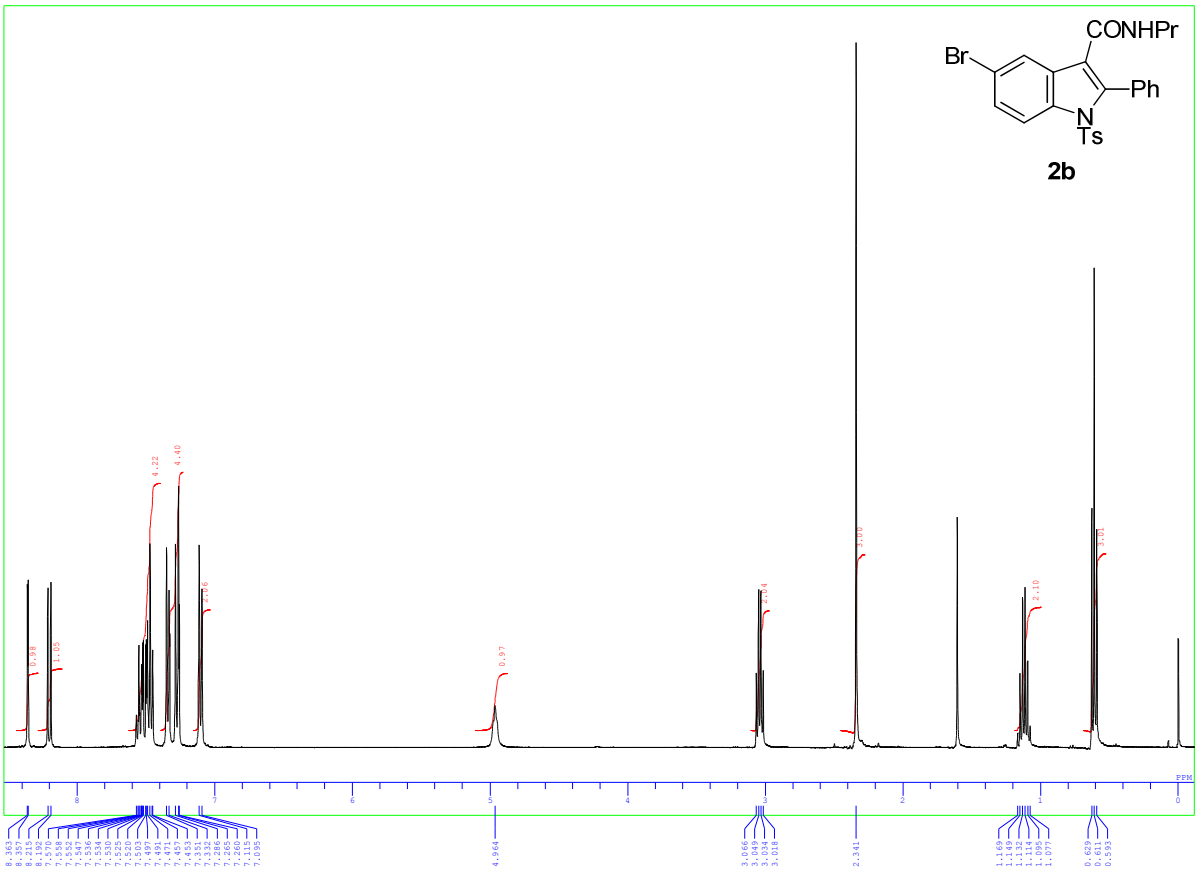
5. References

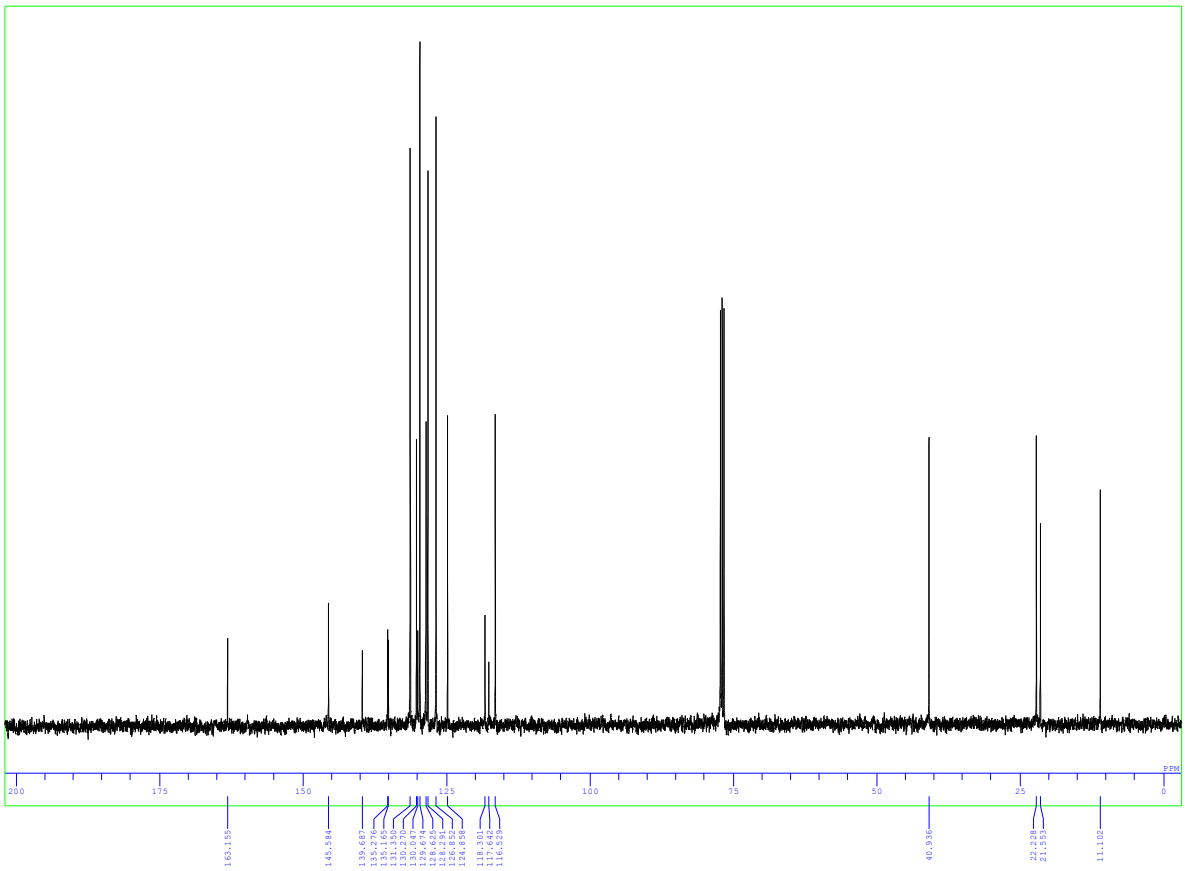
1) Inamoto, K.; Asano, N.; Nakamura, Y.; Yonemoto, M.; Kondo, Y. *Org. Lett.* **2012**, *14*, 2622.

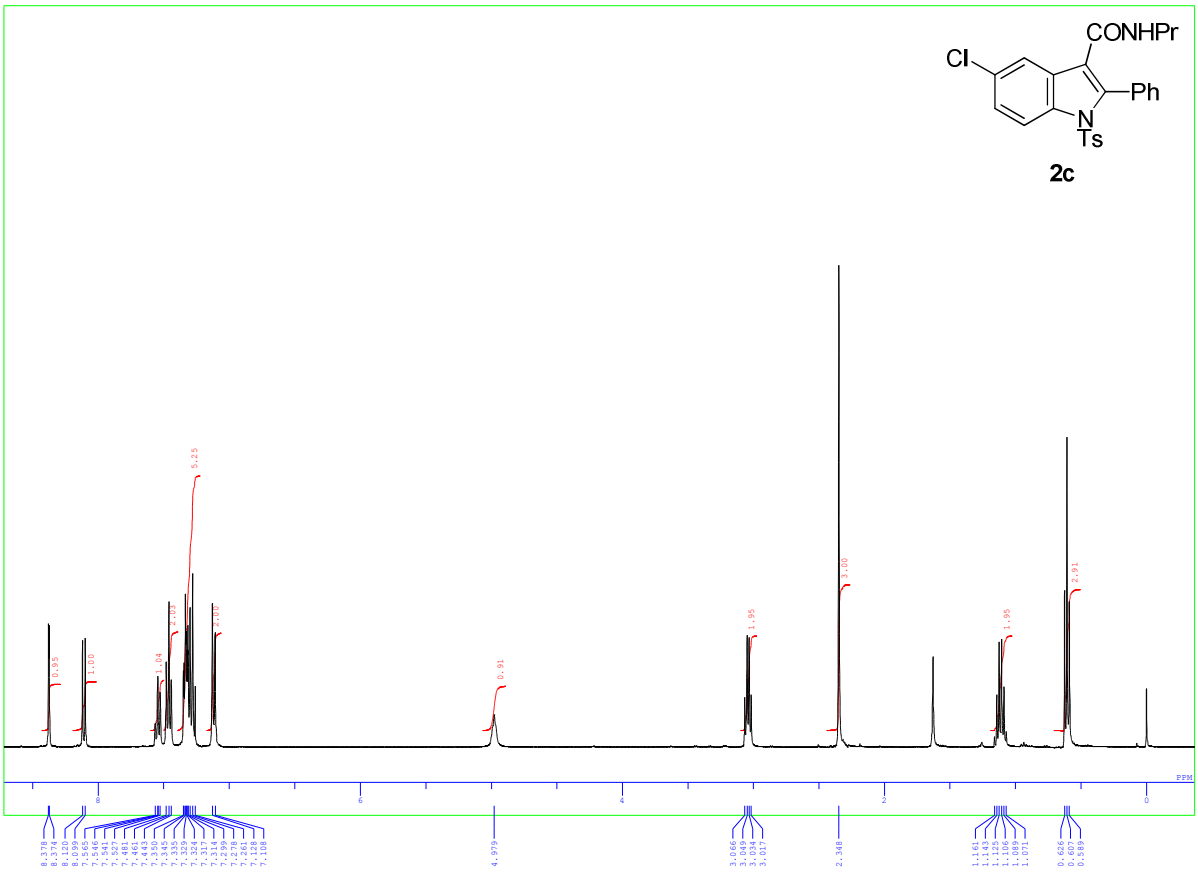
6. ^{1}H- and ^{13}C-NMR Spectra of 2a–k and 3a–c

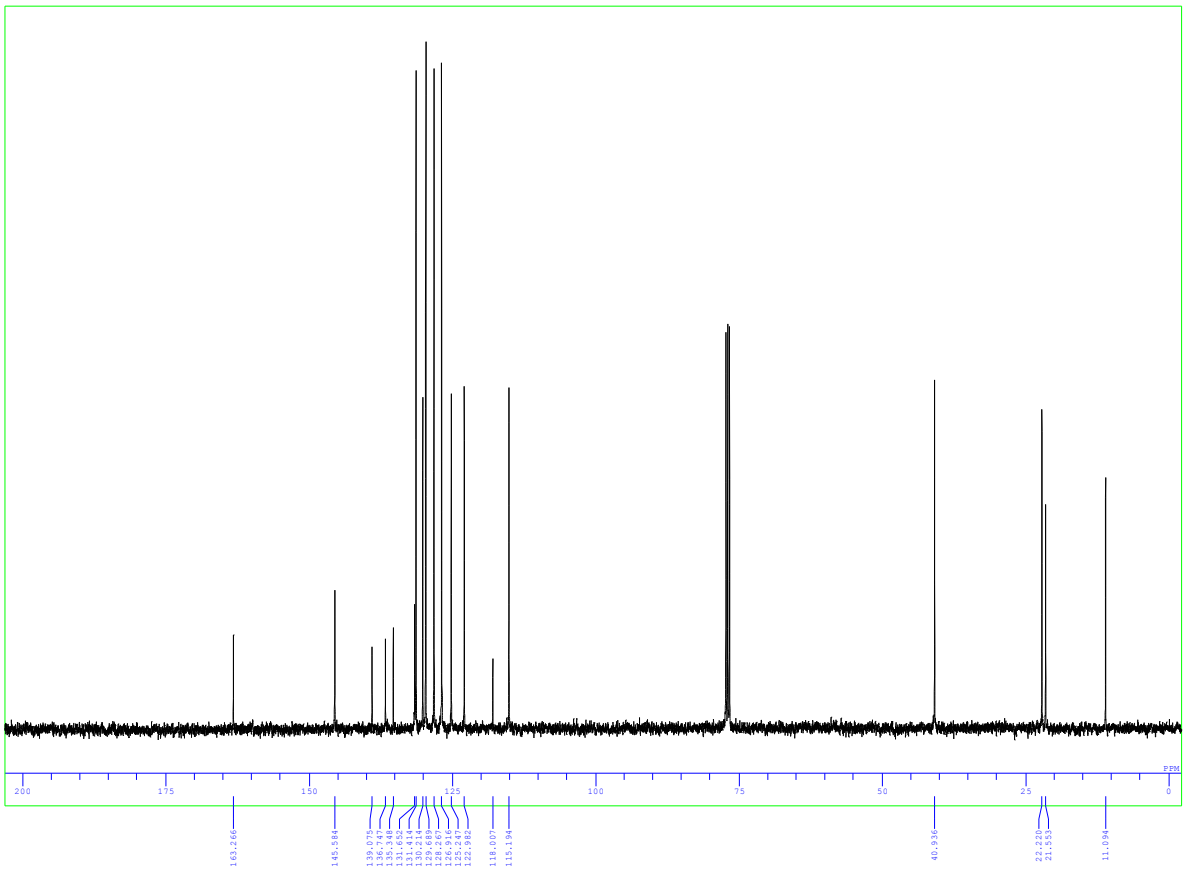


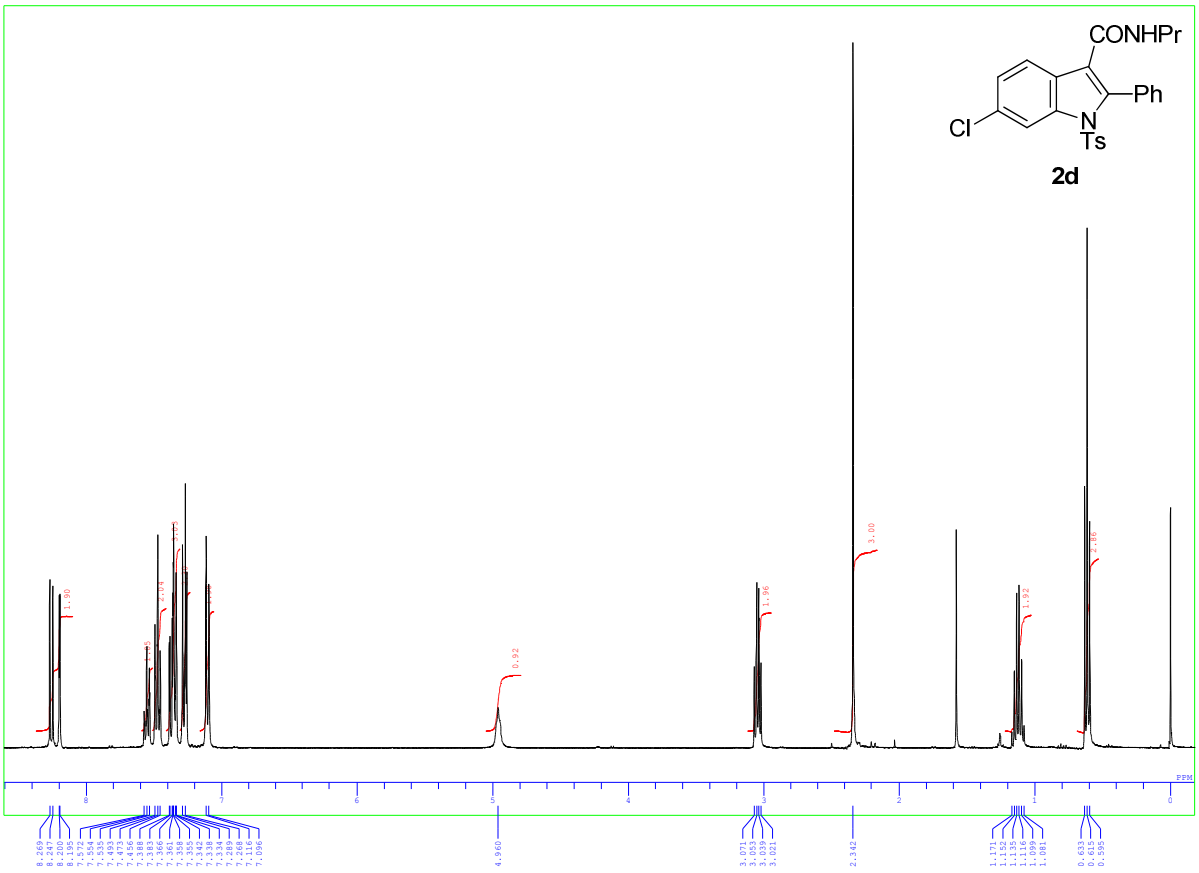


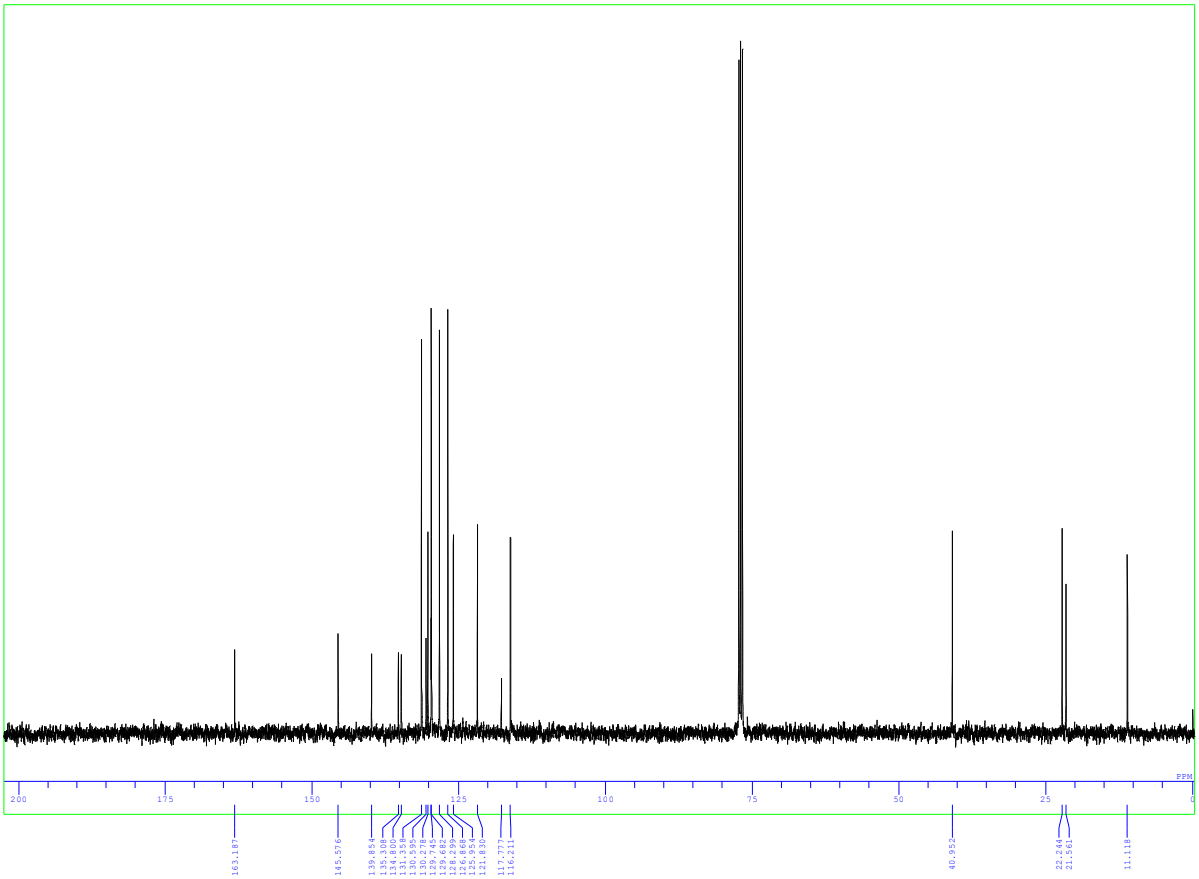

CONHPr
Br
Ph
N
Ts
2b

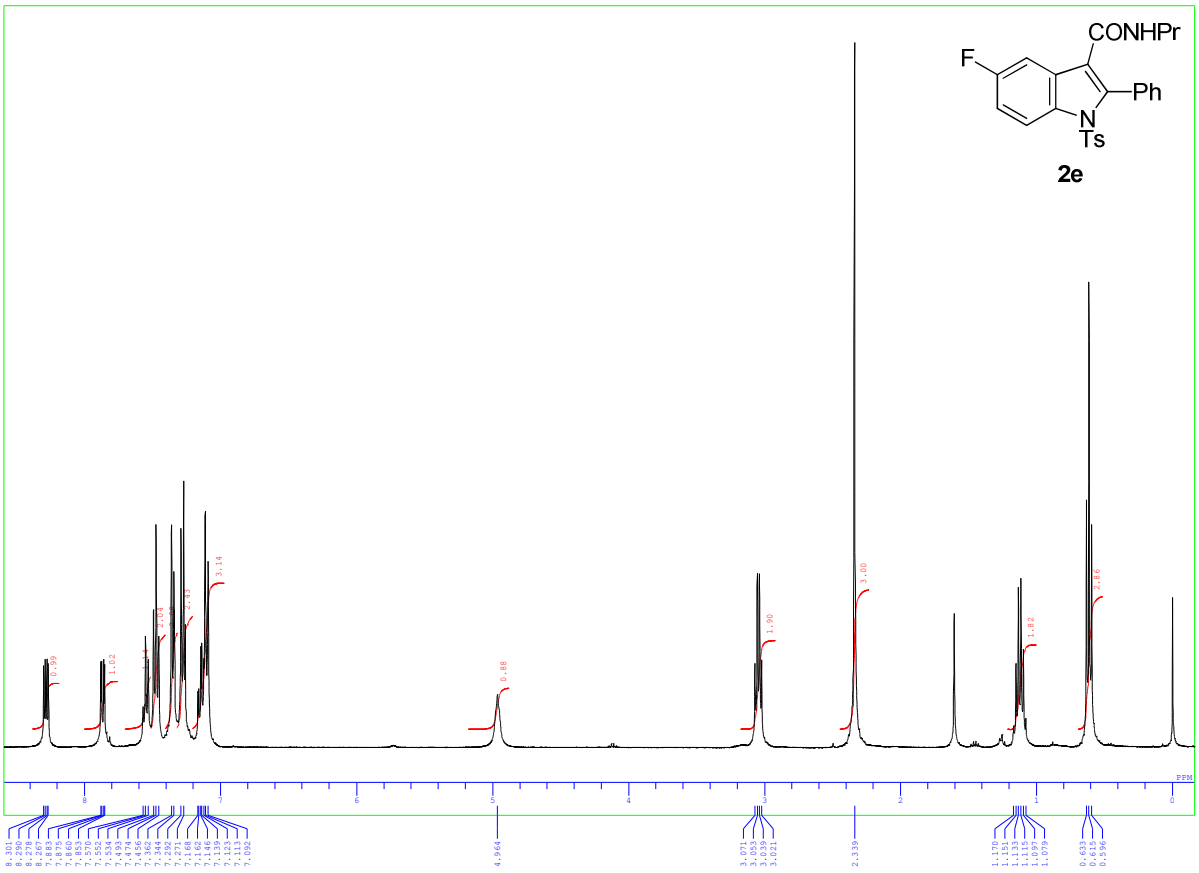


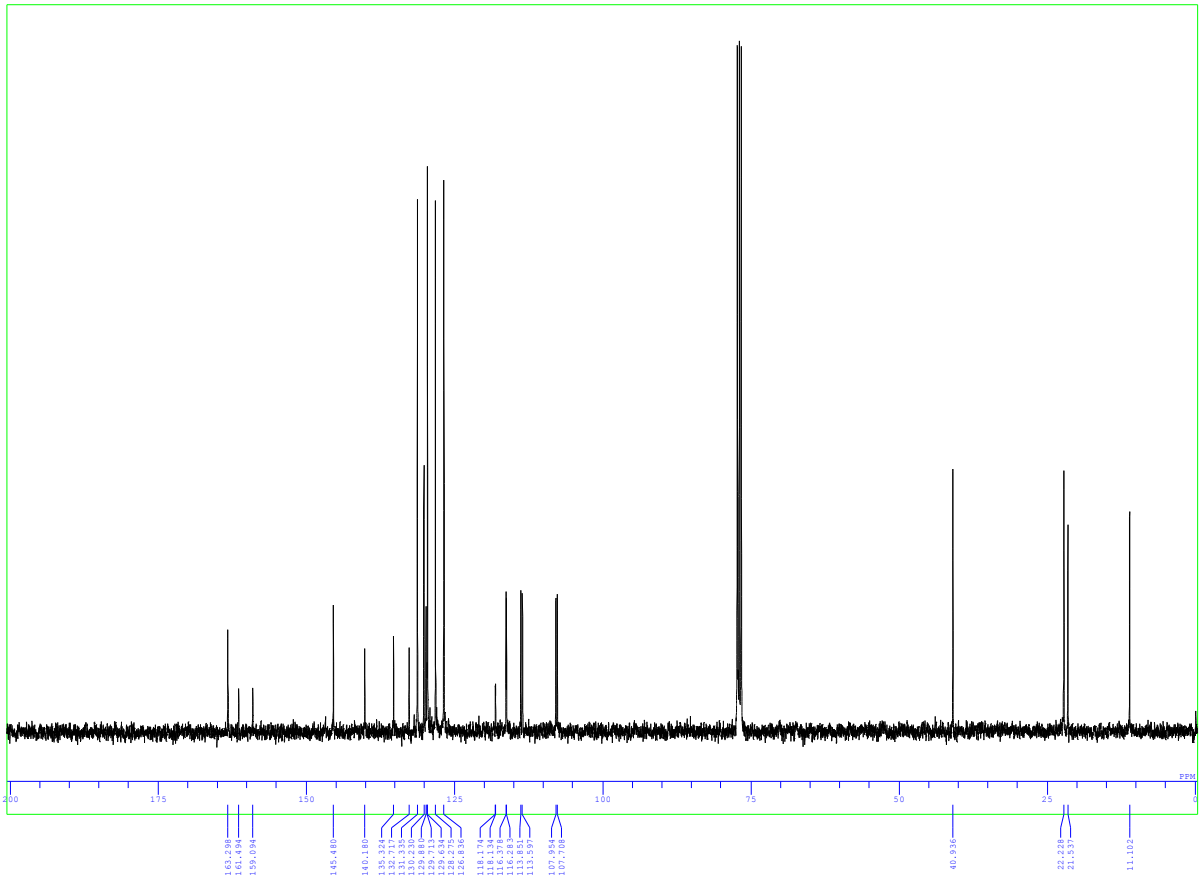

CONHPr
Cl
Ph
N
Ts
2c

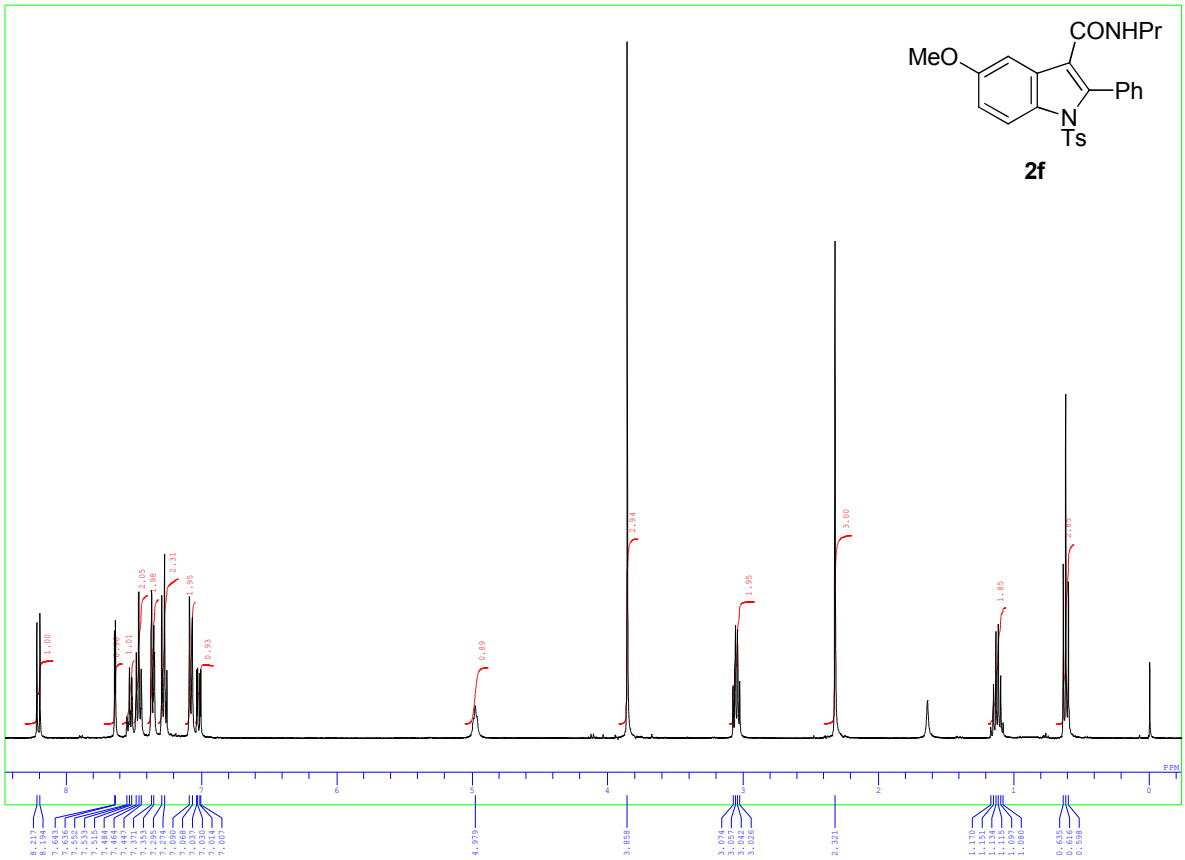


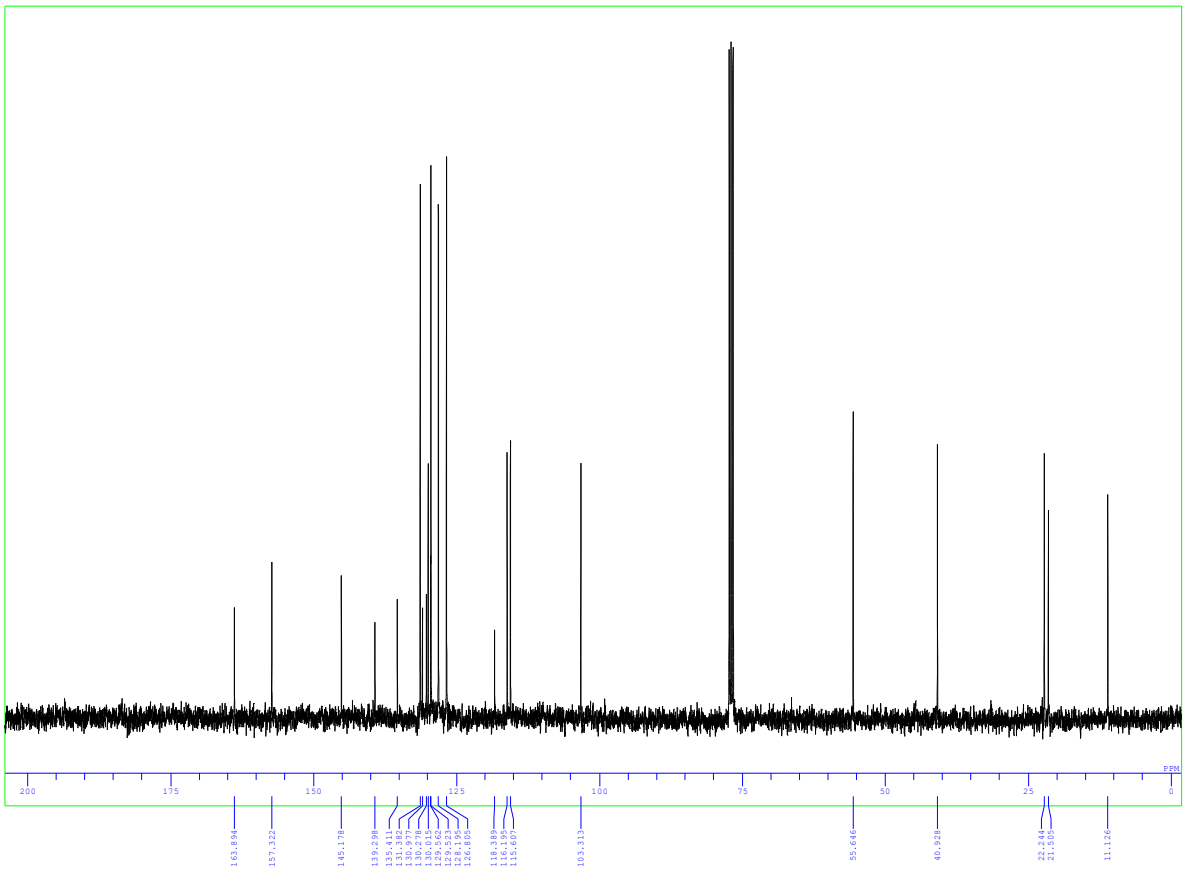

CONHPr
Ph
Cl
N
Ts
2d

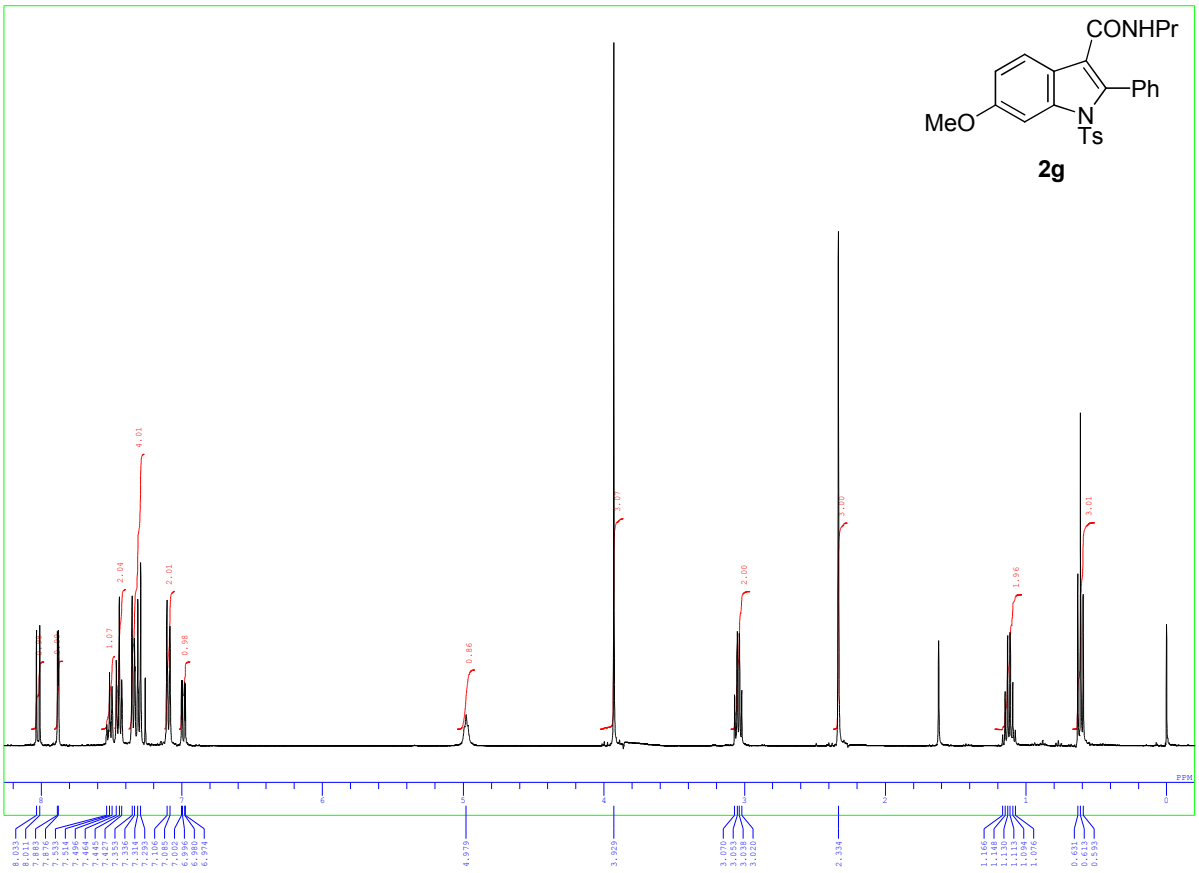


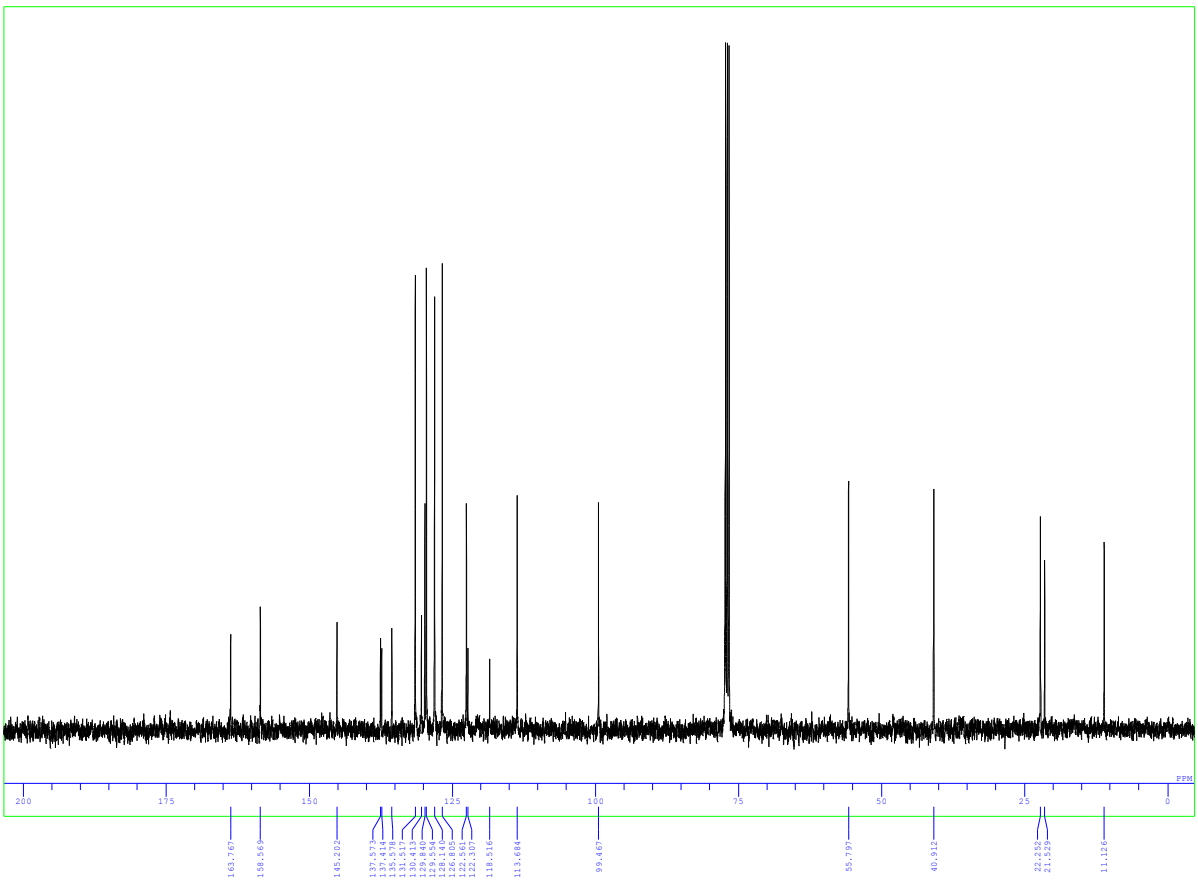

CONHPr
F
Ph
N
Ts
2e

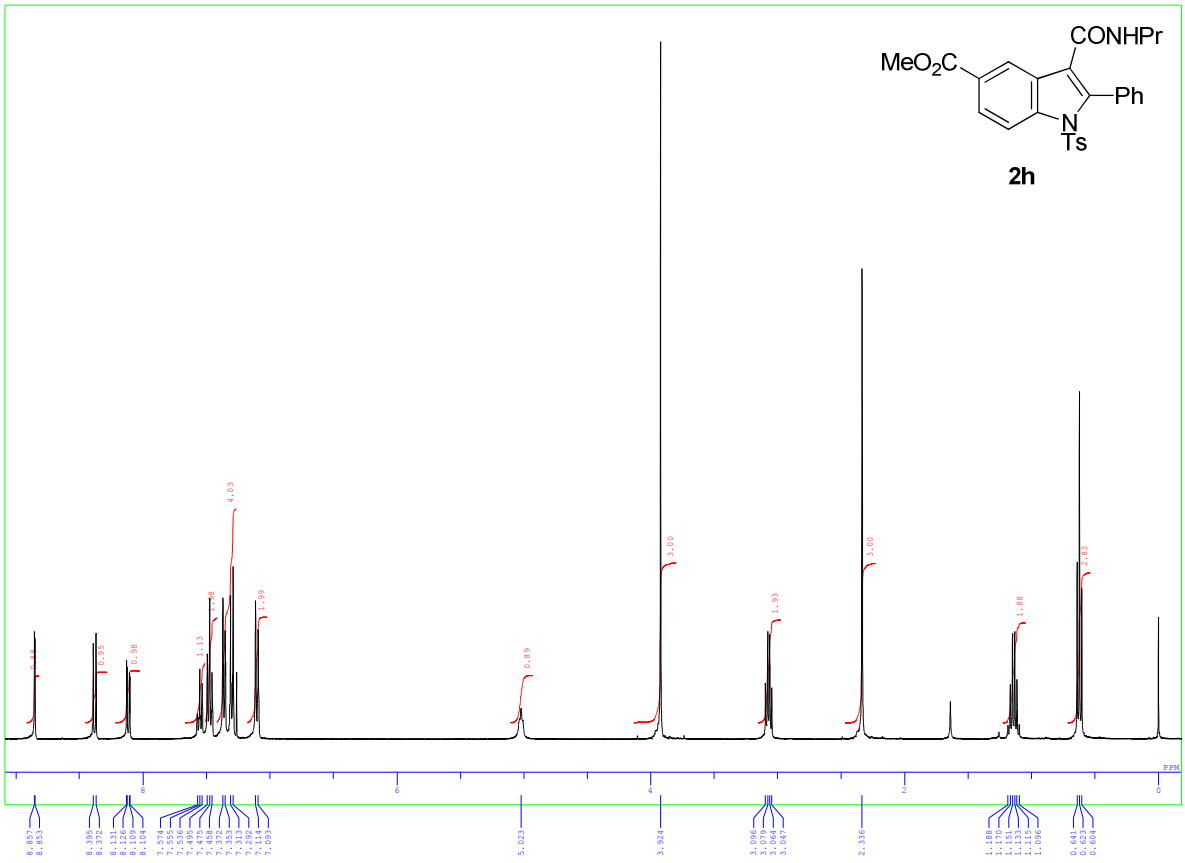


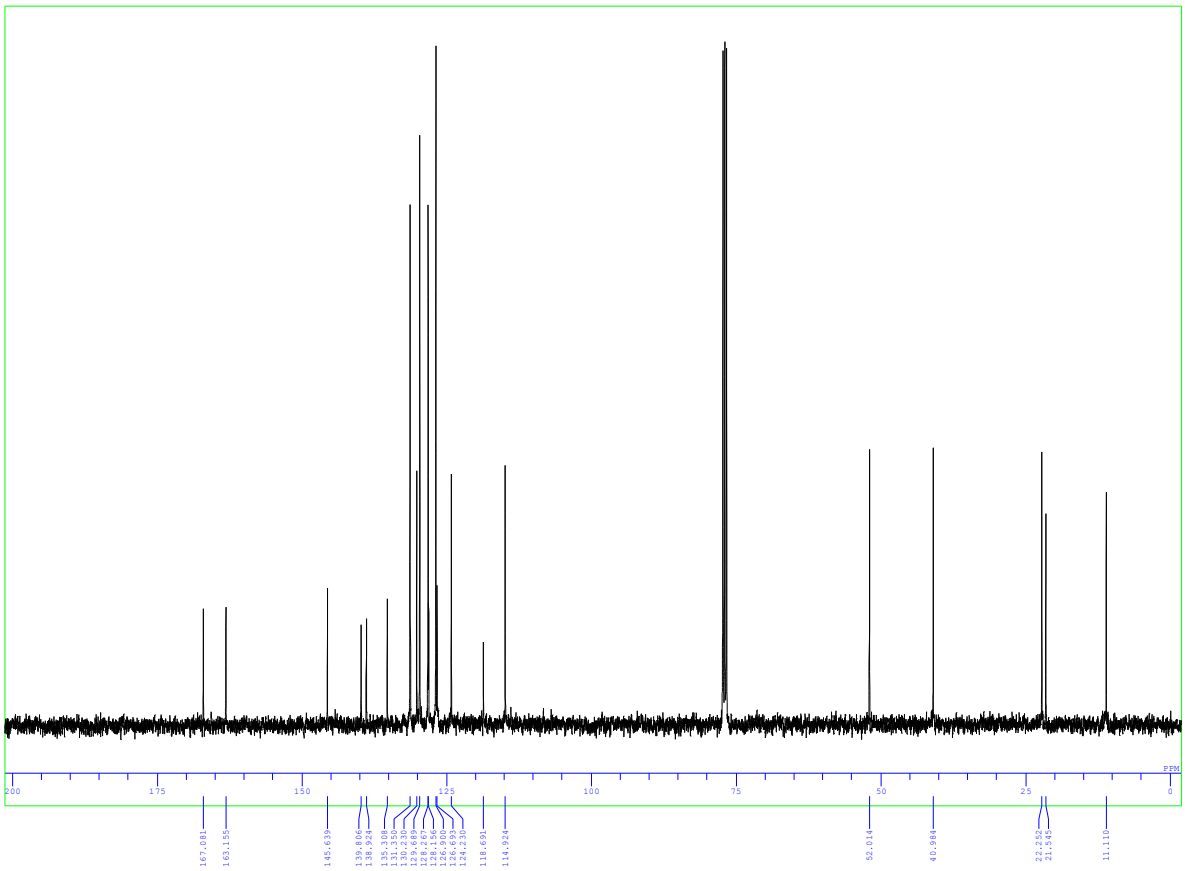

CONHPr
MeO
Ph
N
Ts
2f

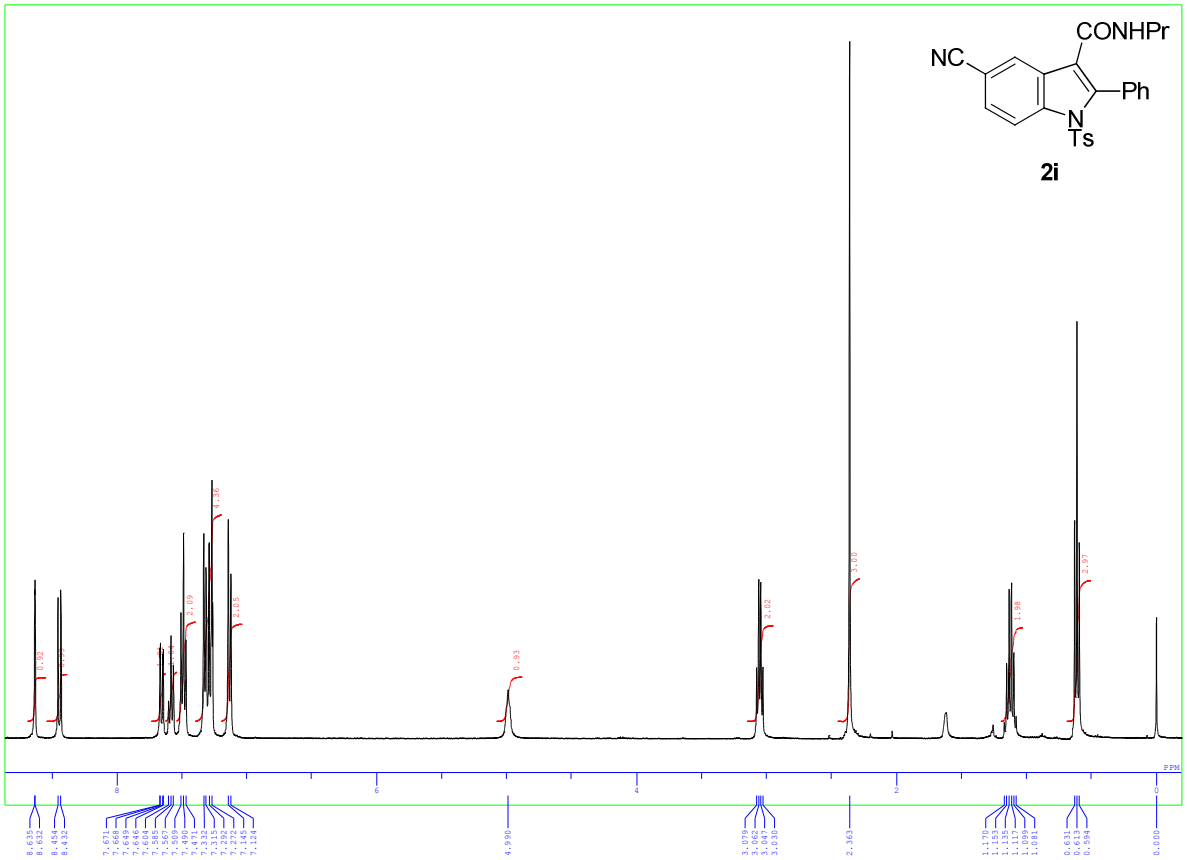


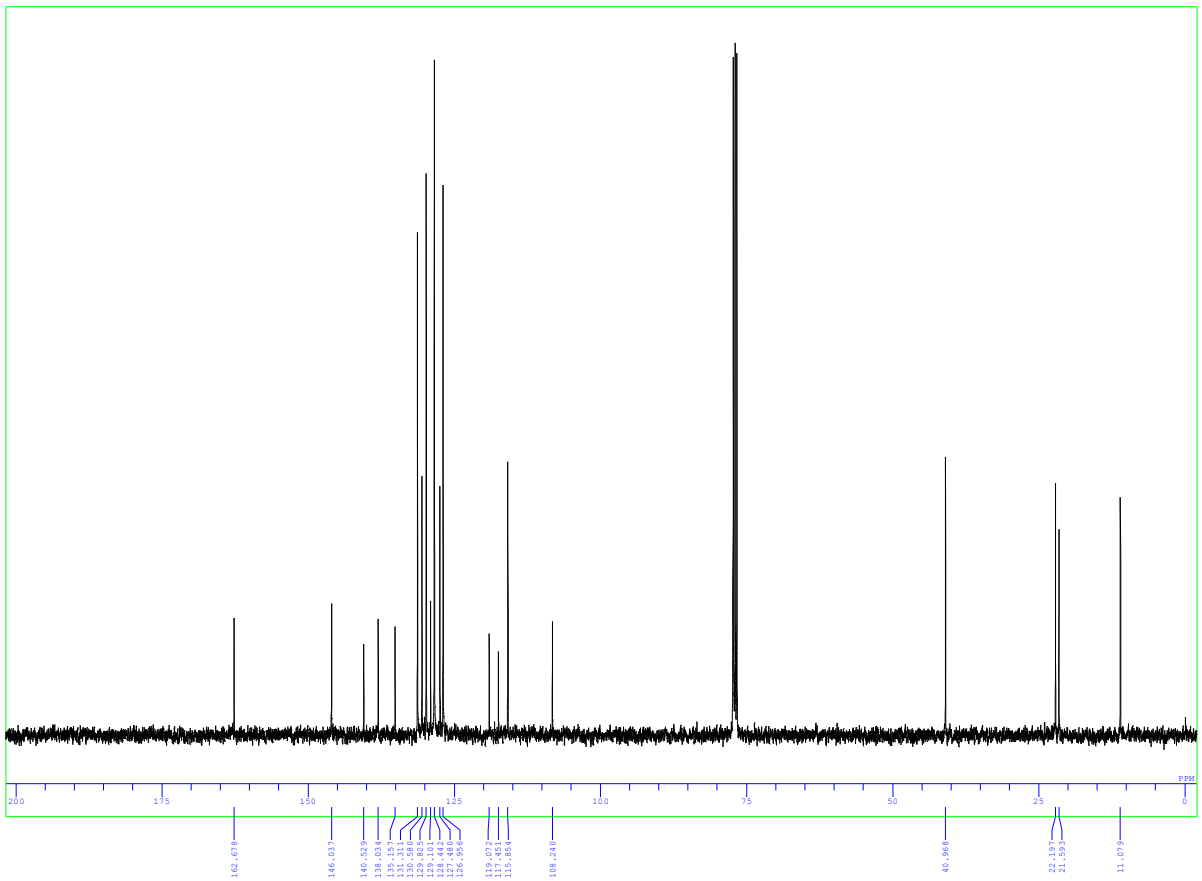

CONHPr
Ph
MeO
N
Ts
2g

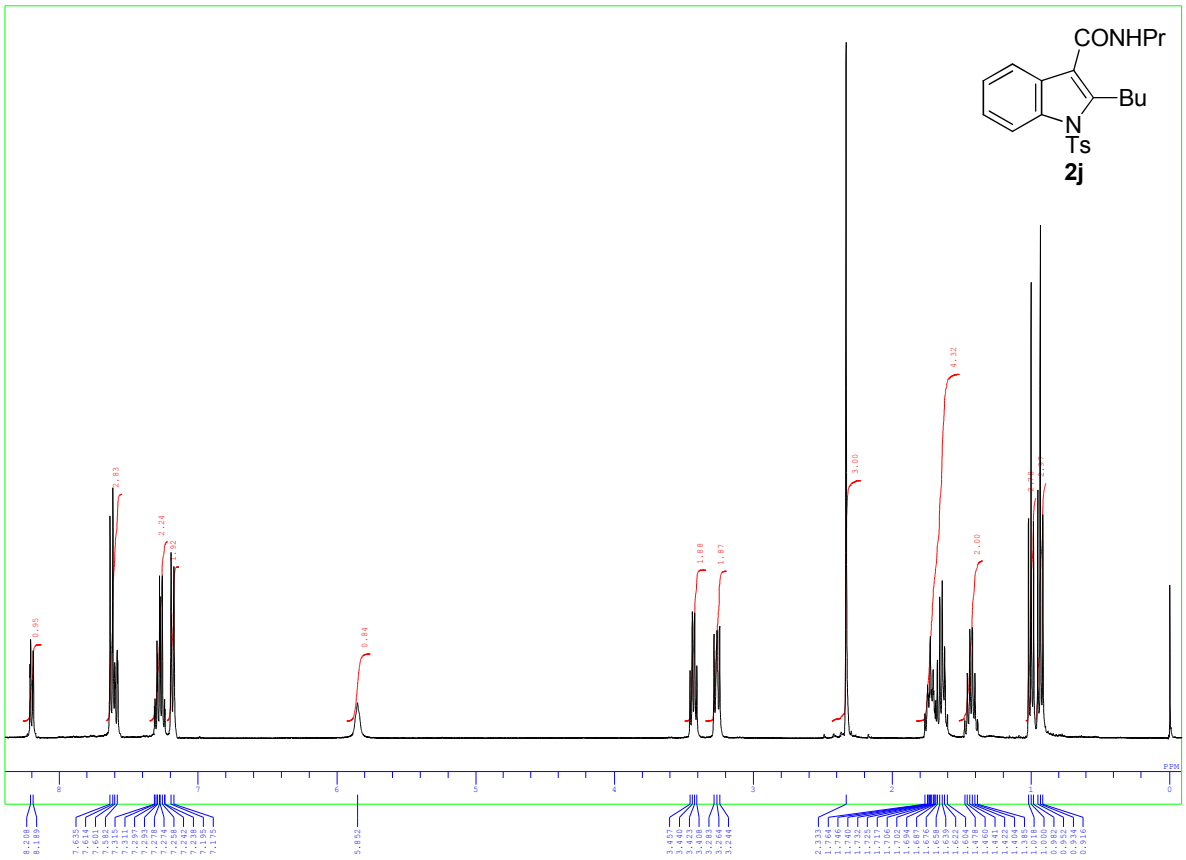


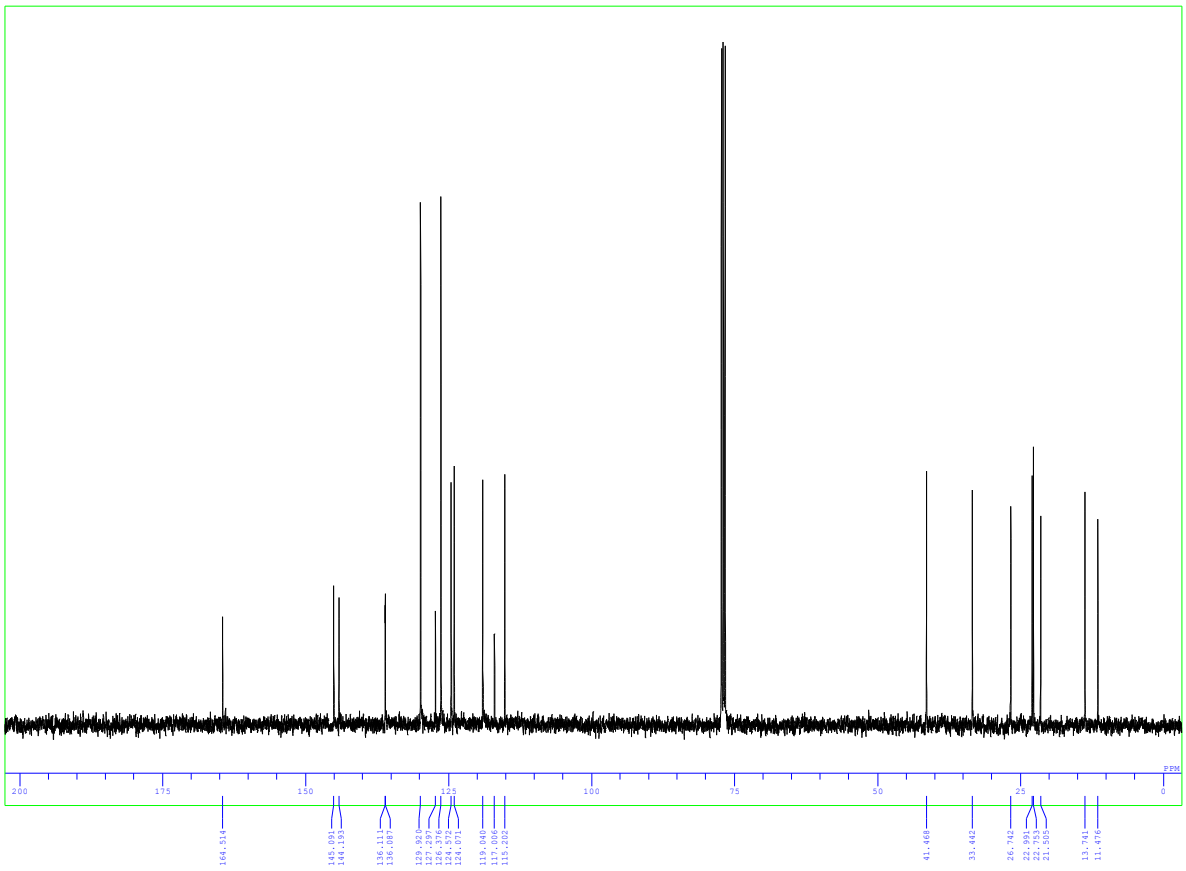

MeO2C
CONHPr
Ph
N
Ts
2h

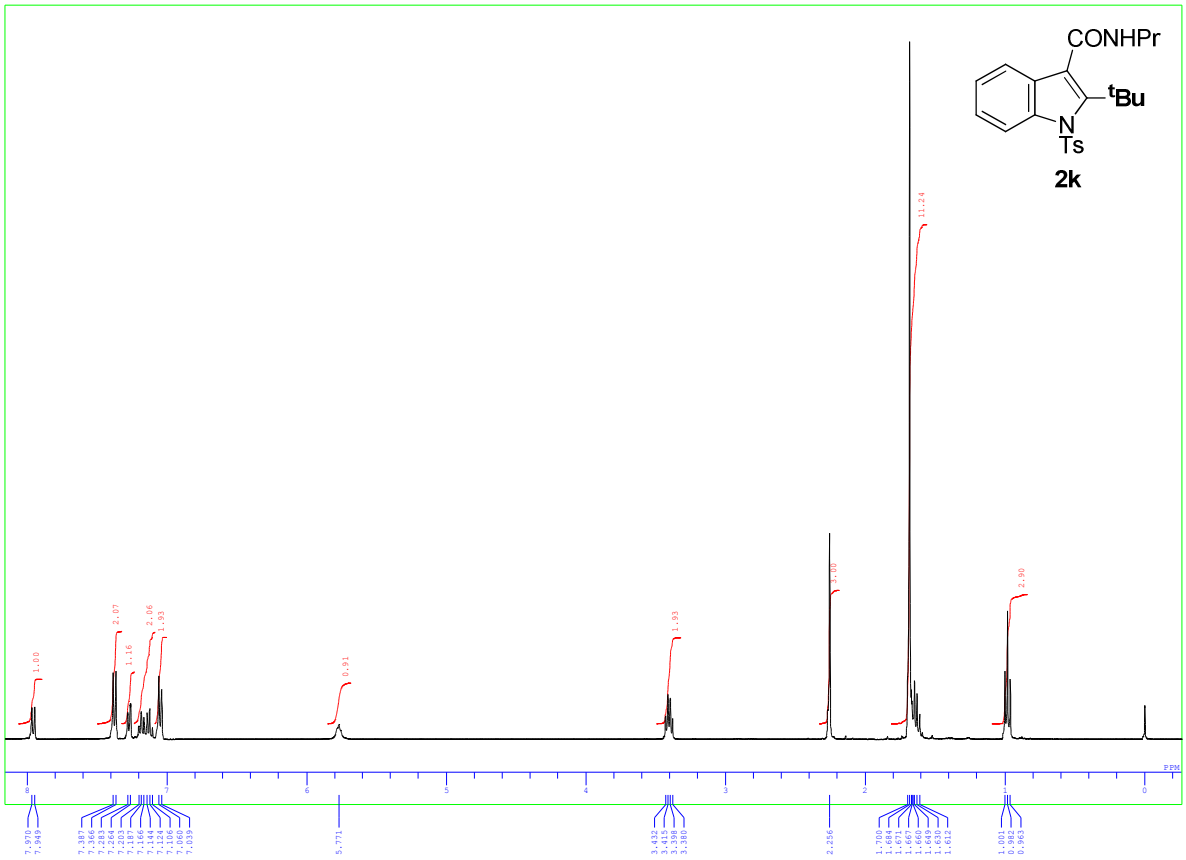


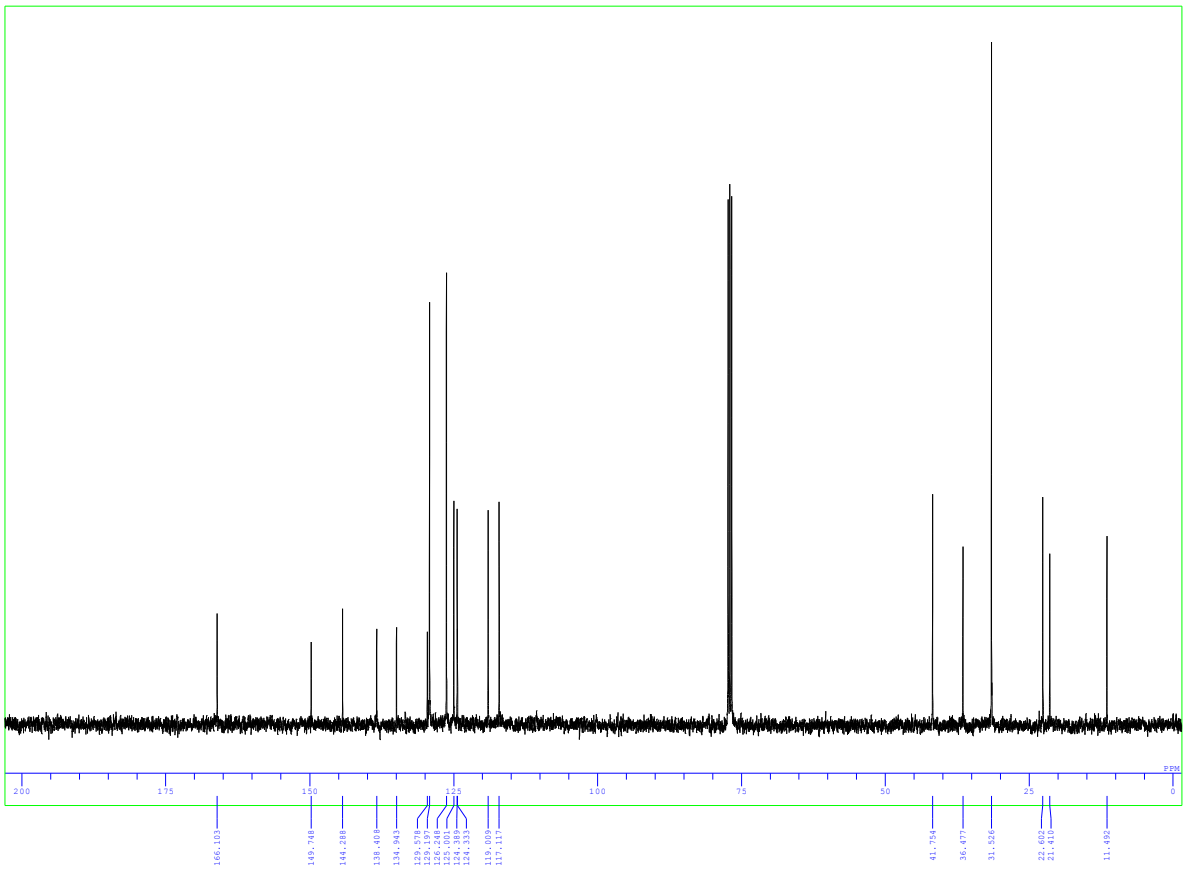

CONHPr
NC
Ph
N
Ts
2i

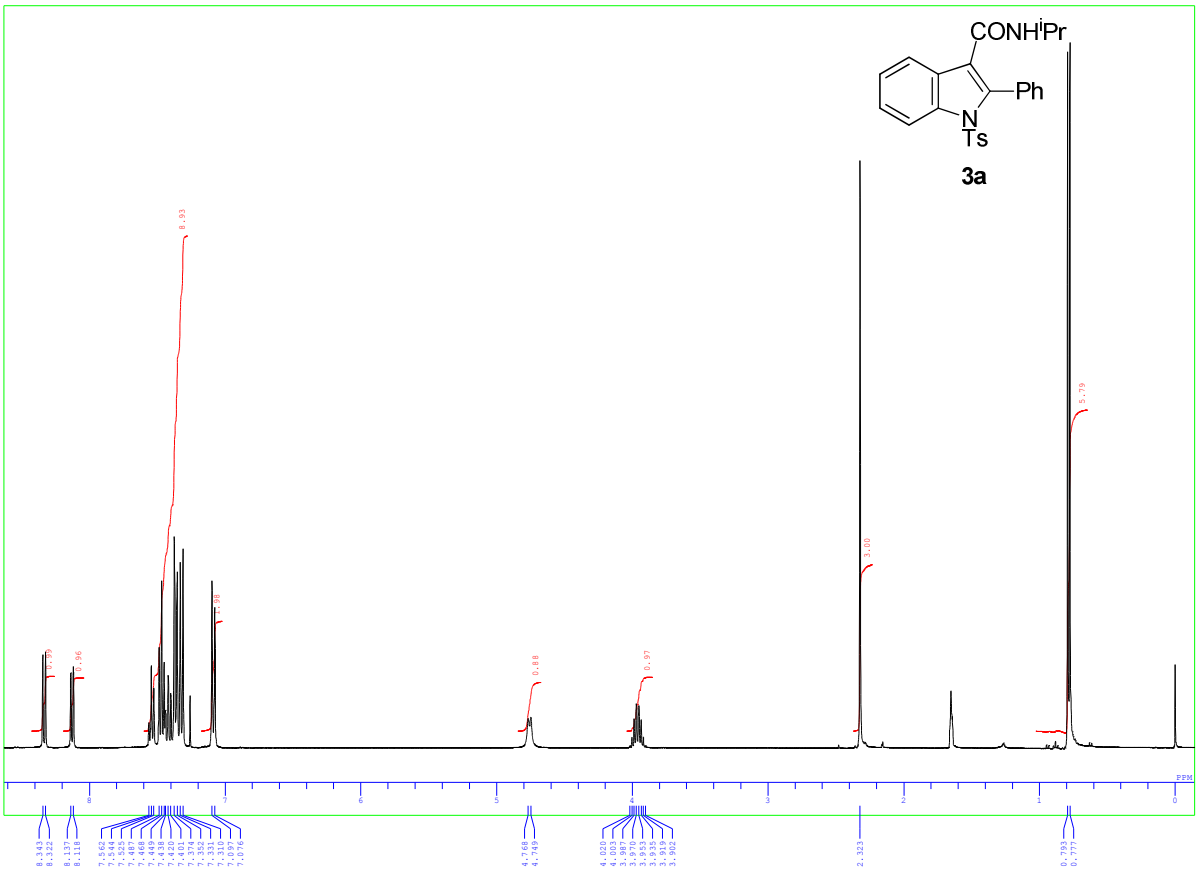


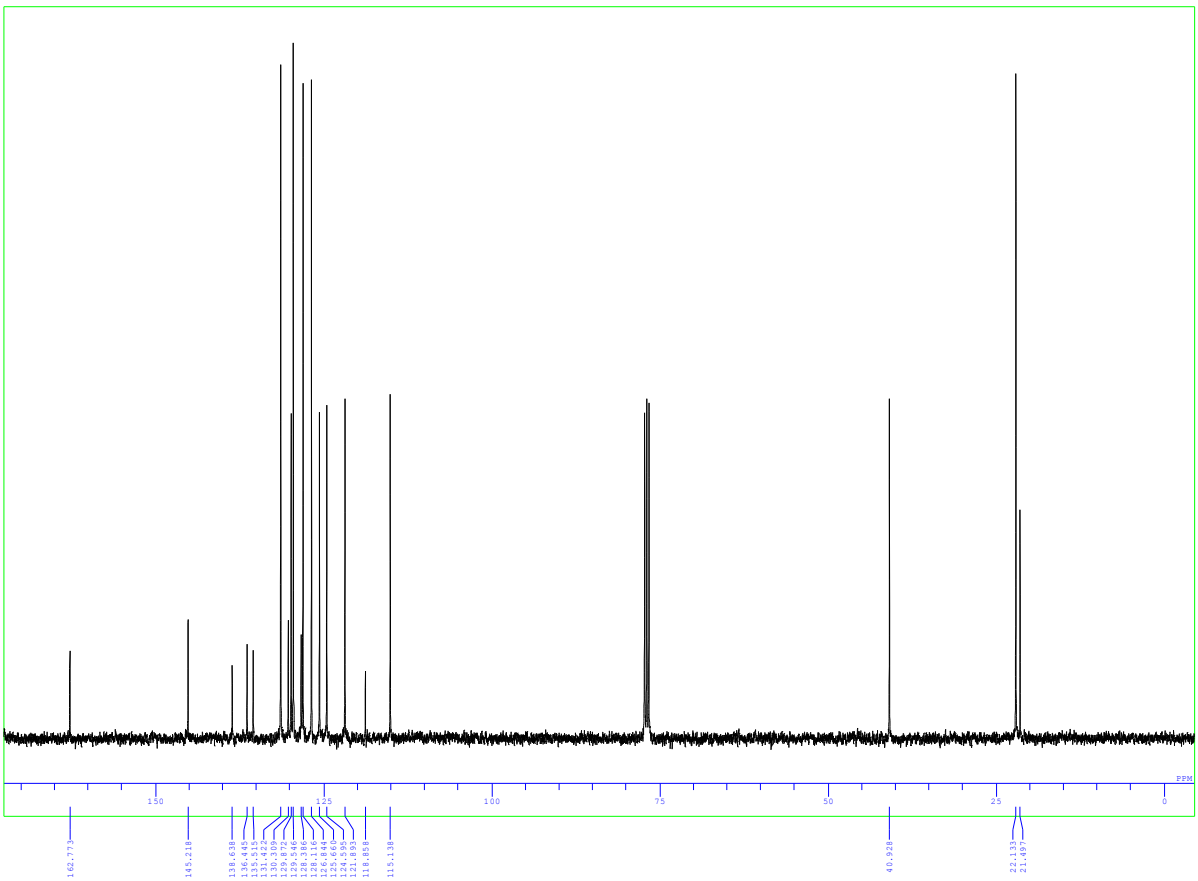

CONHPr
Bu
N
Ts
2j

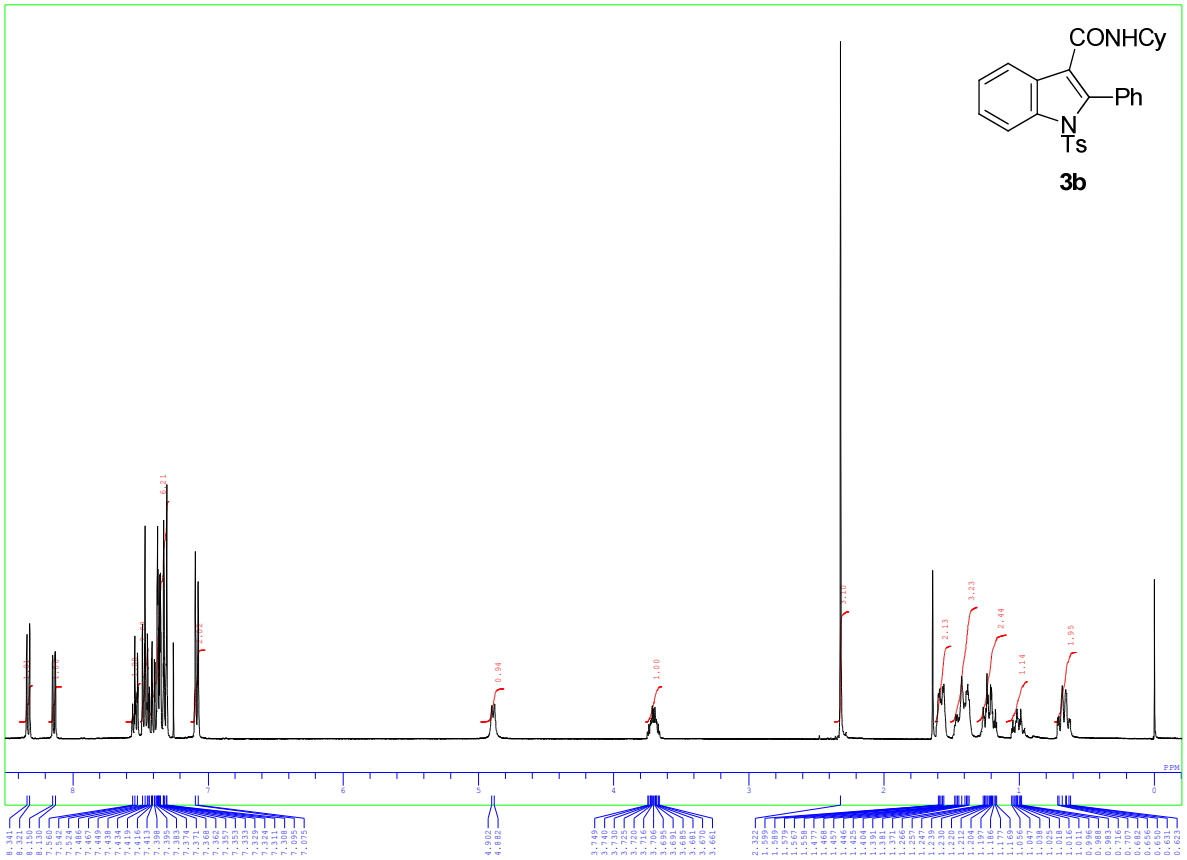


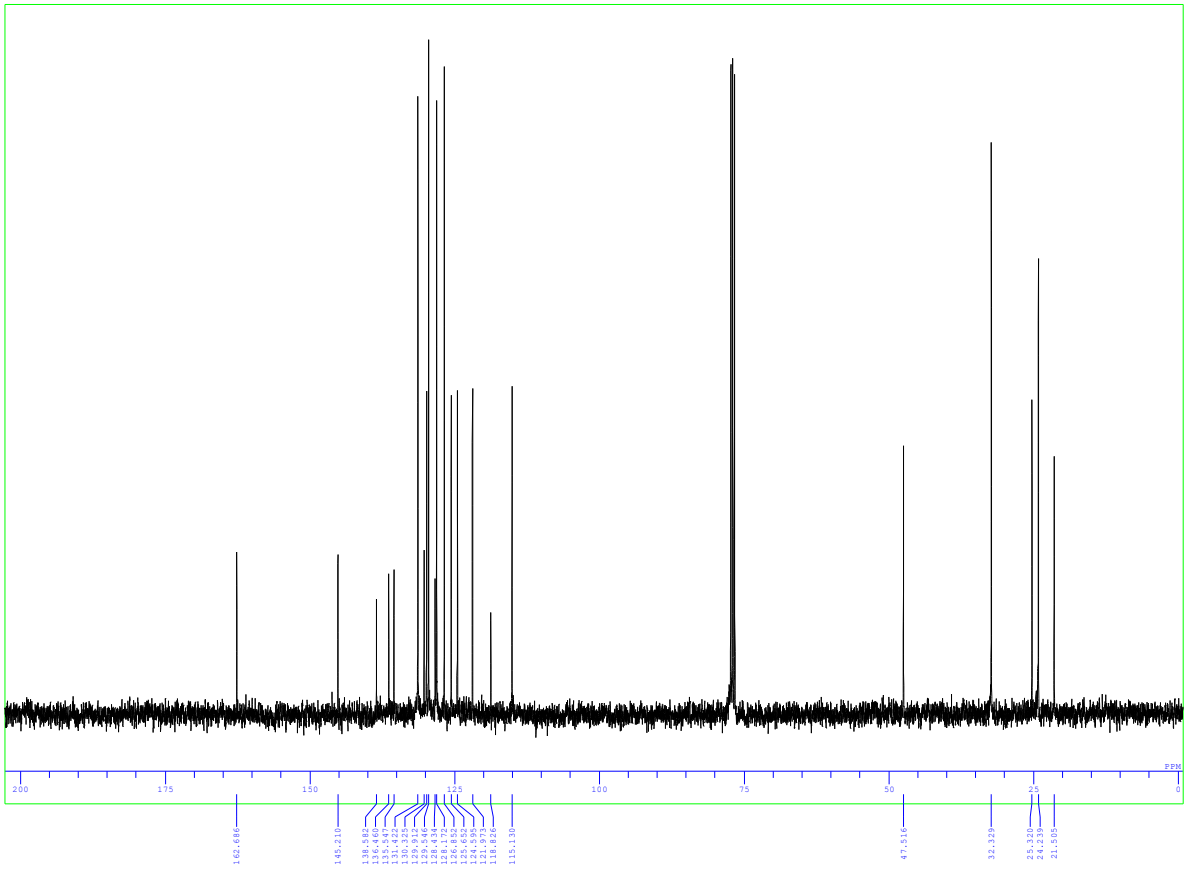

CONHPr
tBu
N
Ts
2k

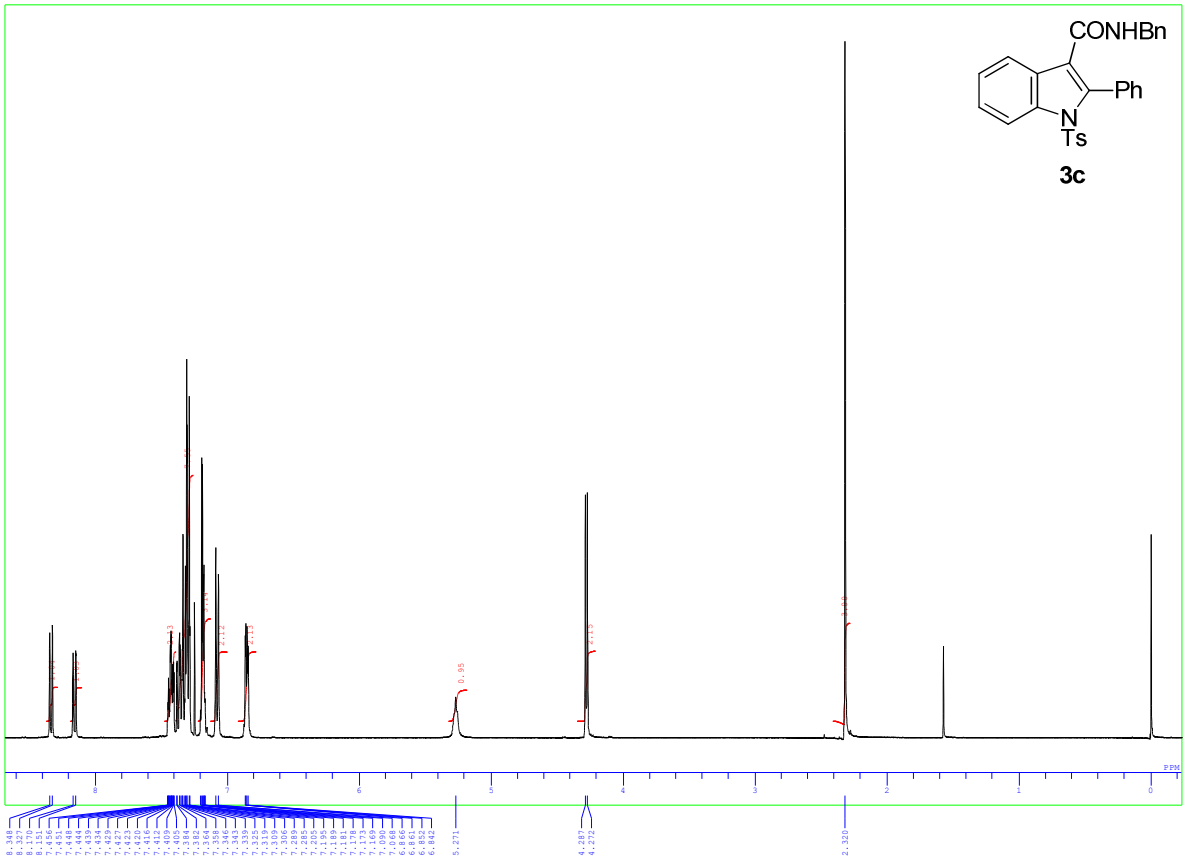


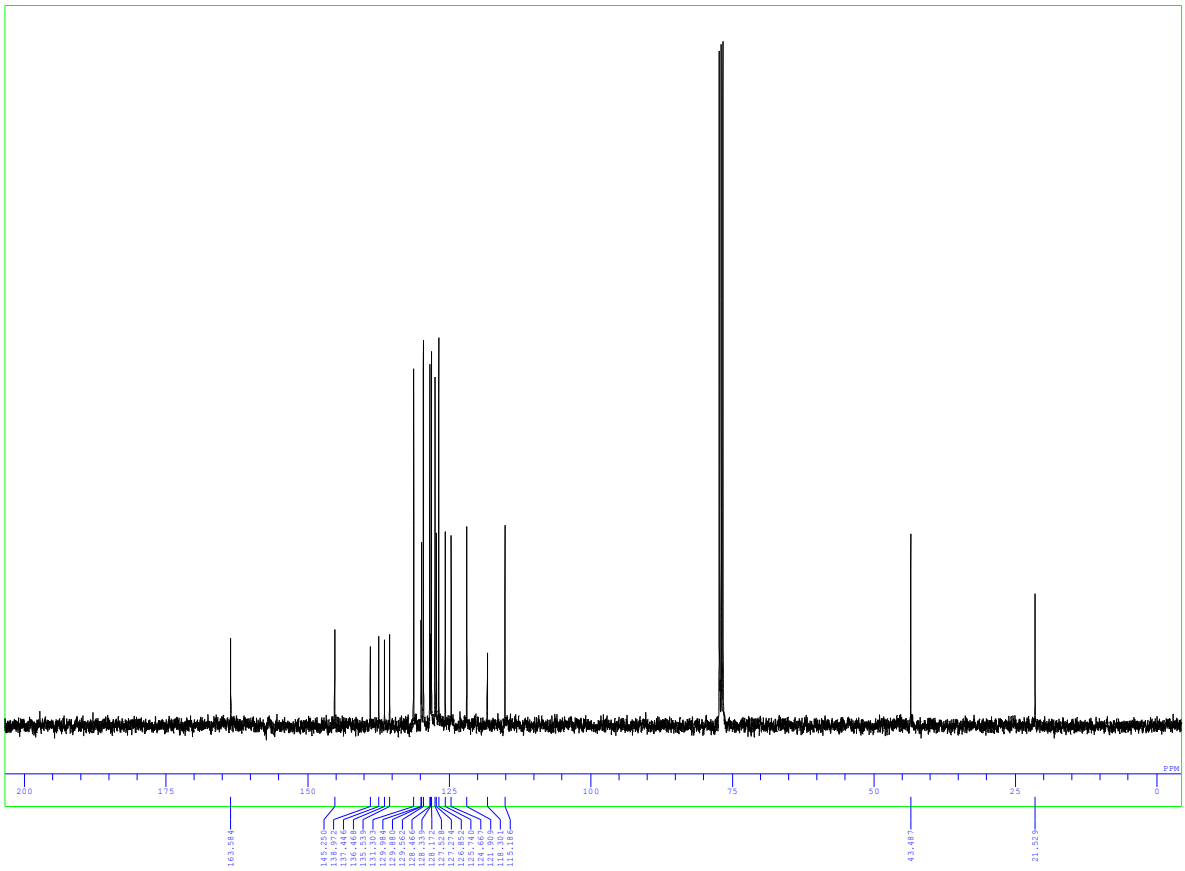

CONHiPr
Ph
N
Ts
3a

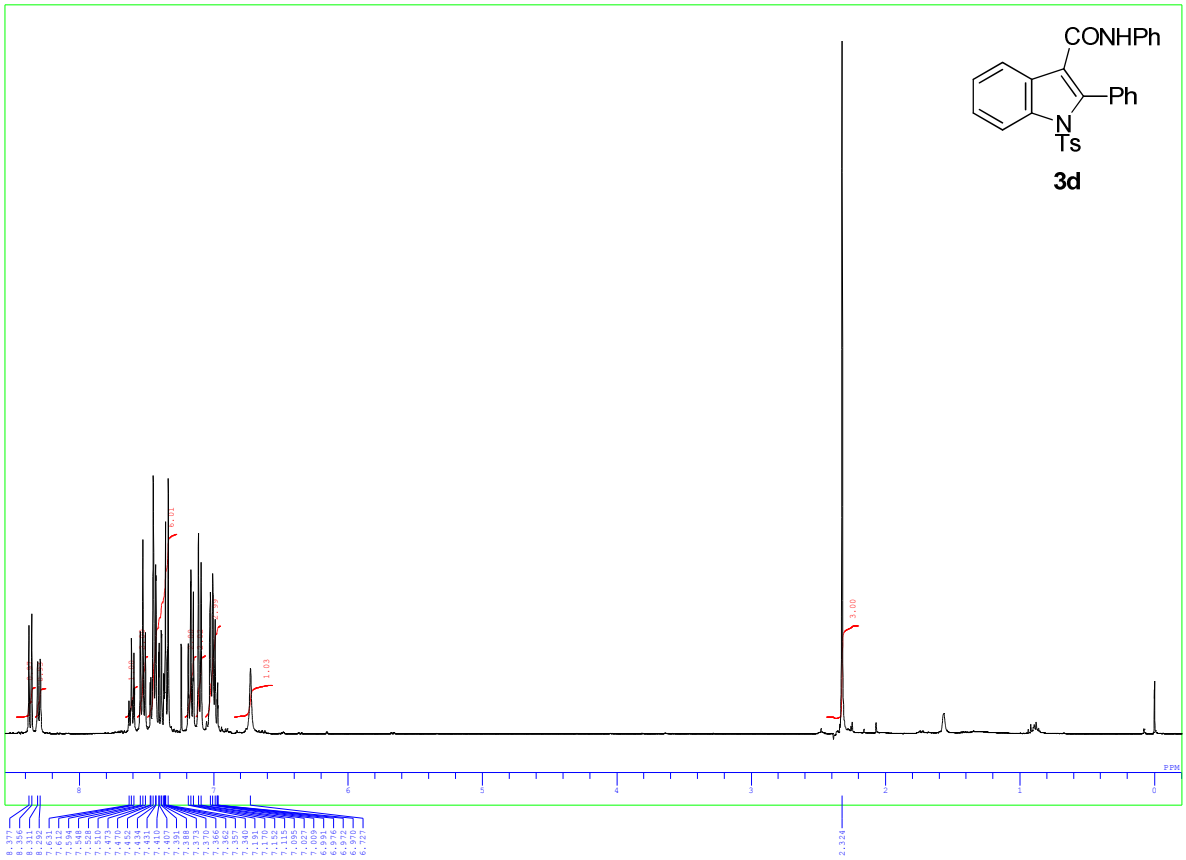


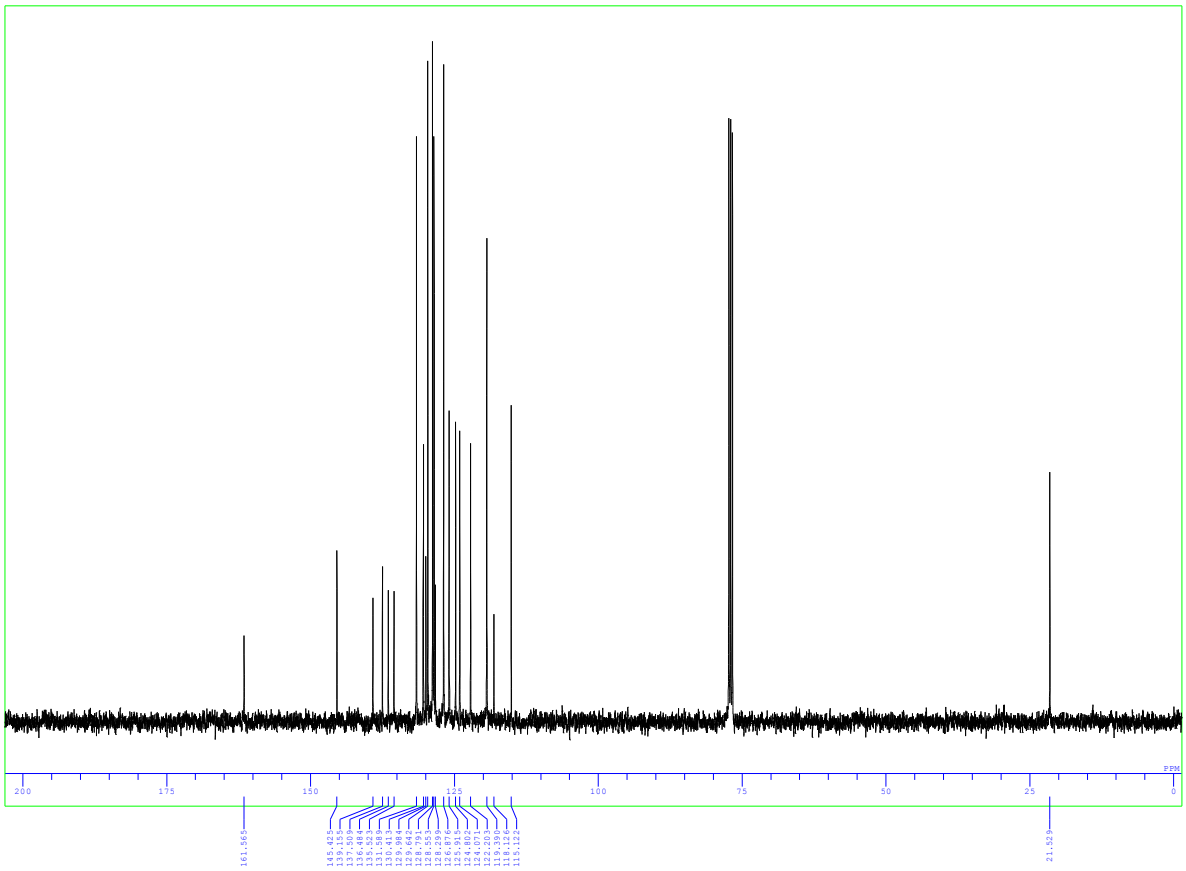

CONHCy
Ph
N
Ts
3b

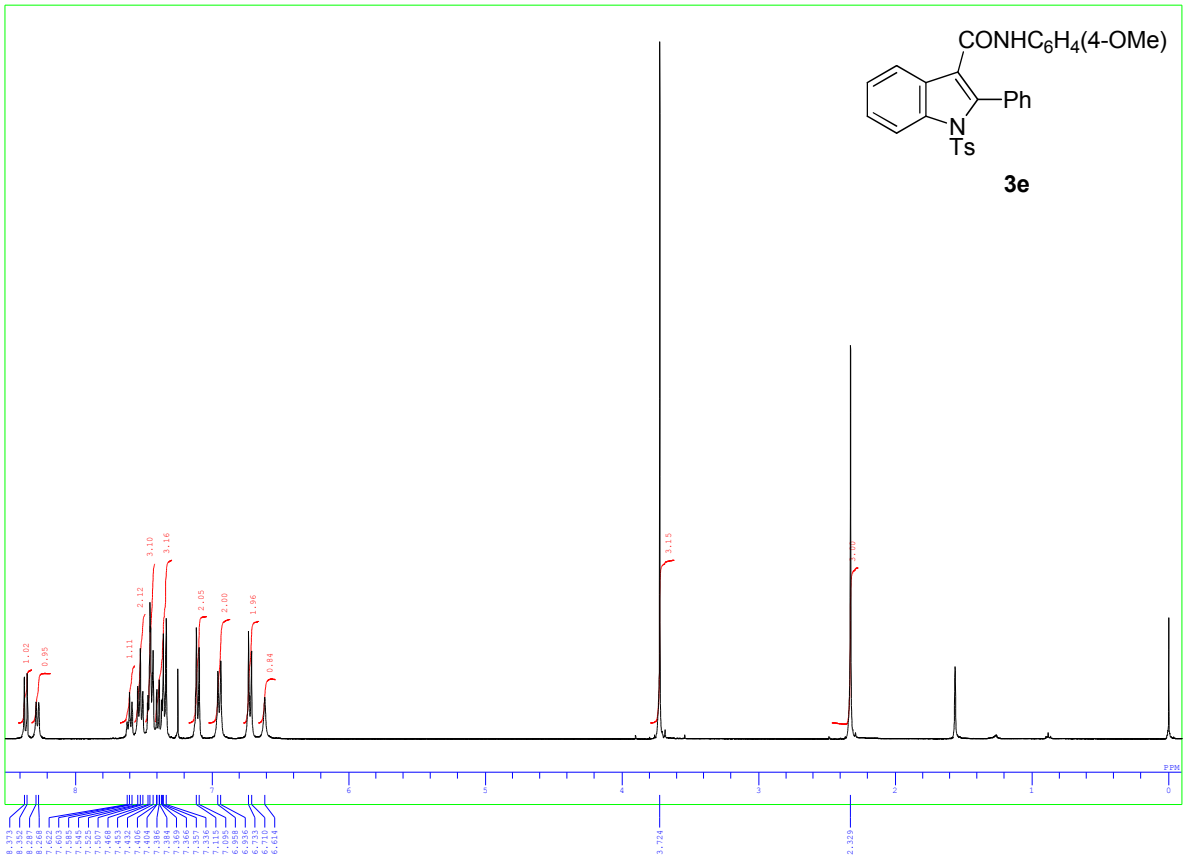



CONHBn
Ph
N
Ts
3c




CONHPh
Ph
N
Ts
3d




CONHC6H4(4-OMe)
Ph
N
Ts
3e