Supporting Information

Ruthenium (II) Catalysed Highly Chemo- and Regioselective Oxidative C6 Alkenylation of Indole-7-carboxamides

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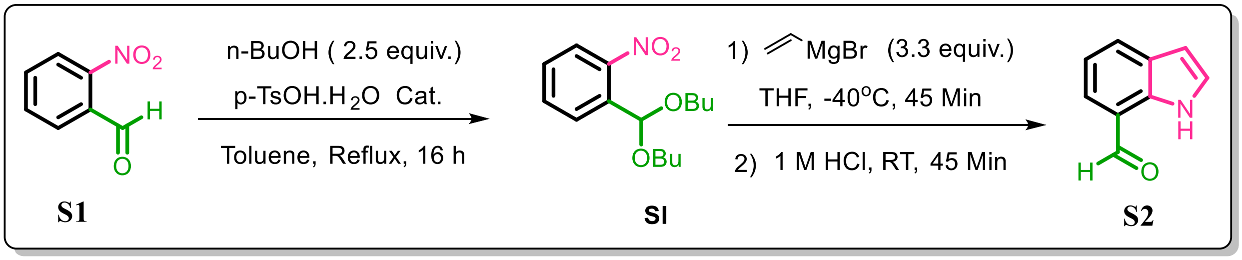
Contents

1. General Method

All the reactions were performed in oven-dried glassware under nitrogen atmosphere. Solvents were dried using standard methods. Chloroform, dichloromethane, 1,2-dichloroethane and toluene were distilled over calcium hydride. Unless otherwise stated, all the commercial reagents, acrylates, styrenes were used as received from Sigma Aldrich, Alfa Aesar, and Spectrochem. Progress of the reaction was monitored by thin layer chromatography (Merck Silica gel 60 F-254, pre-coated plates on alumina). Column chromatographic purifications were performed on Merck silica gel (100-200 mesh). For heating reaction, an oil bath was used as heat source. Melting points were recorded on a digital melting point apparatus and are uncorrected. Spectroscopic characterizations were carried at the Central Instrumentation Facility (CIF), Institute of Chemical Technology Mumbai. ^{1}H-NMR spectra were recorded at 500 MHz and 400MHz Agilent FT-NMR spectrometers. ^{13}C-NMR spectra were recorded at 101 MHz, 126 MHz. ^{1}H-NMR chemical shifts are reported in ppm relative to the TMS (= 0) and are abbreviated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). ^{13}C-NMR chemical shifts are reported in ppm relative to the residual $CDCl_3$ signal (= 77.16). IR spectra were recorded on a Shimadzu FT-IR spectrometer. HRMS data was obtained on a Bruker microTOF-QII or Agilent 5975C high resolution mass spectrometers. Single crystal X-ray data was recorded on diffractometer Bruker D8Venture.

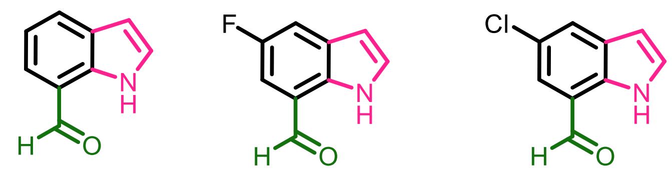
2 General procedures for synthesis of starting materials

2.1 Procedure for indole-7-carbaldehydes[1]:



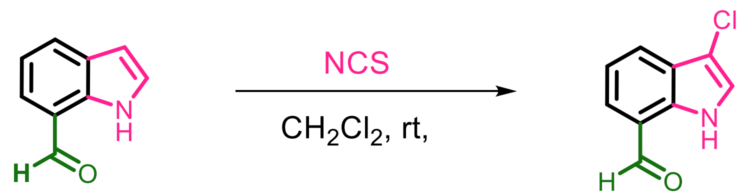
Step-1: To a stirred solution of 2-nitrobenzaldehyde (3.02 g, 20 mmol, 1 equiv) in toluene in a 250 ml round bottom flask fitted with a Dean-Stark apparatus added butan-1-ol (4.58 mL, 50 mmol, 2.5 equiv), *p*-TsOH.H_2O (10.32 mg, 0.06 mmol, 0.003 equiv). The reaction mixture was refluxed for 16 h and cooled to room temperature. To this added saturated solution of $NaHCO_3$ and then extracted with ethyl acetate (3x50 mL). The organic layers were dried over anhydrous Na_2SO_4 and solvents were removed under reduced pressure. The crude product was purified by silica gel flash column chromatography to obtain acetal **SI** as a viscous oil.

Step-2: Vinyl- magnesium bromide (1M solution in THF, 60 ml, 60 mmol, 3.3 equiv.) was added drop wise to a solution of acetal **SI** (18 mmol, 5 g, 1 equiv.) in dry THF at -40 °C under nitrogen atmosphere. The reaction mixture was stirred for 45 minutes at -40 °C and was then warmed to room temperature. To this added aqueous 1M HCl and the resulting mixture was stirred for 45 minutes. To this added saturated solution of $NaHCO_3$ and the resulting solution was extracted with ethyl acetate (3 x 30 mL). The organic layers were dried over anhydrous Na_2SO_4 and the solvents were removed under reduced pressure. The crude product was purified by using silica gel column chromatography to obtain indole-7-carbaldehyde **S2** as a white solid in 65% (1.7 g) yield. The indole-7-carbaldehyde **S2-S4** were prepared by following procedure **2.1**



S2, 65% **S3, 62 %** **S4, 61%**

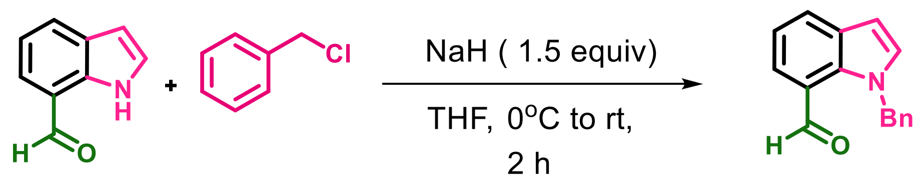
2.2 Procedure for C3 chlorination of indole-7-carbaldehydes[2]:



S5

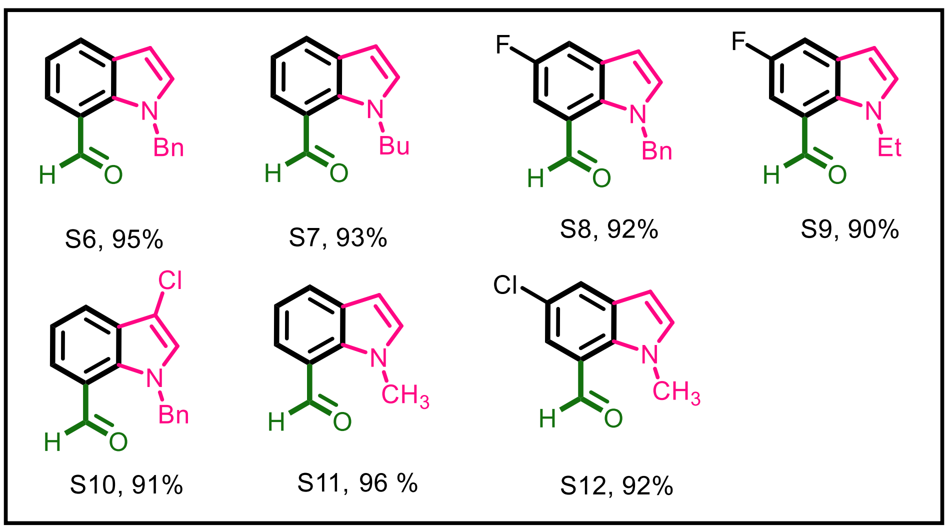
To a stirred solution of indole-7-carbaldehyde (1 g, 6.8 mmol, 1.0 equiv) in dry CH_2Cl_2 (10 mL) under nitrogen atmosphere added *N*-chlorosuccinimide (0.904 g, 6.8 mmol, 1.0 equiv). The reaction mixture was stirred for 3-4 h at room temperature. After the completion of the reaction (monitored by TLC) added 2M aqueous NaOH solution (20 ml). The product was extracted using CH_2Cl_2 (3 x 20 mL) and was dried over anhydrous Na_2SO_4. The organic layer was then concentrated under reduced pressure to obtain the crude product which was further purified by column chromatography (using 10% ethyl acetate/hexane) to give **S5** as a white solid in 80 % (0.980 mg) yield.

2.3 General procedure for preparation of *N*-protected indole-7-carbaldehydes[3]:

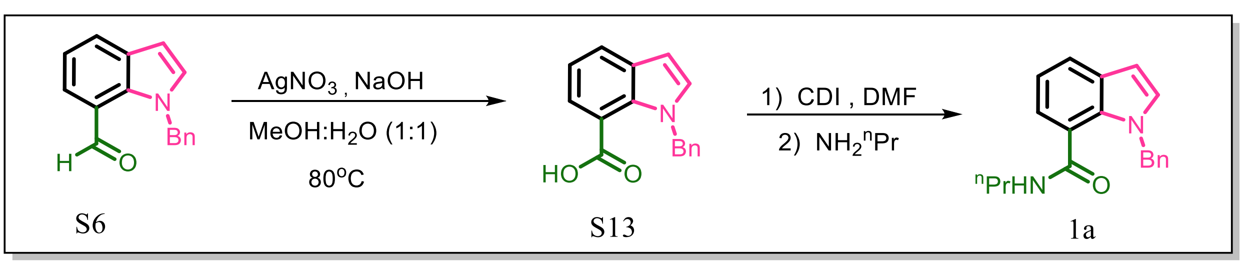


S2 **S6**

To a stirred solution of sodium hydride (60% in mineral oil, 18 mmol, 1.5 equiv) in THF (15 mL) added indole-7-carbaldehyde (1.75 g, 12 mmol, 1.0 equiv) at 0 ºC and stirred for 30 minutes. To this added benzyl chloride (1.76 g. 14 mmol, 1.2 equiv) drop wise. The reaction mixture was allowed to warm to room temperature and stirred. After completion of reaction added saturated NH_4Cl solution and the resulting solution was extracted with diethyl ether (3 x 30 mL), washed with water, brine, and dried over anhydrous Na_2SO_4. The mixture was concentrated under vacuum to obtain the crude product which was purified by column chromatography (using 10% ethyl acetate/hexane) to afford **S6** as a white solid. The *N*-alkylated indole-7-carbaldehydes **S6-S12** were prepared by using procedure **2.3**



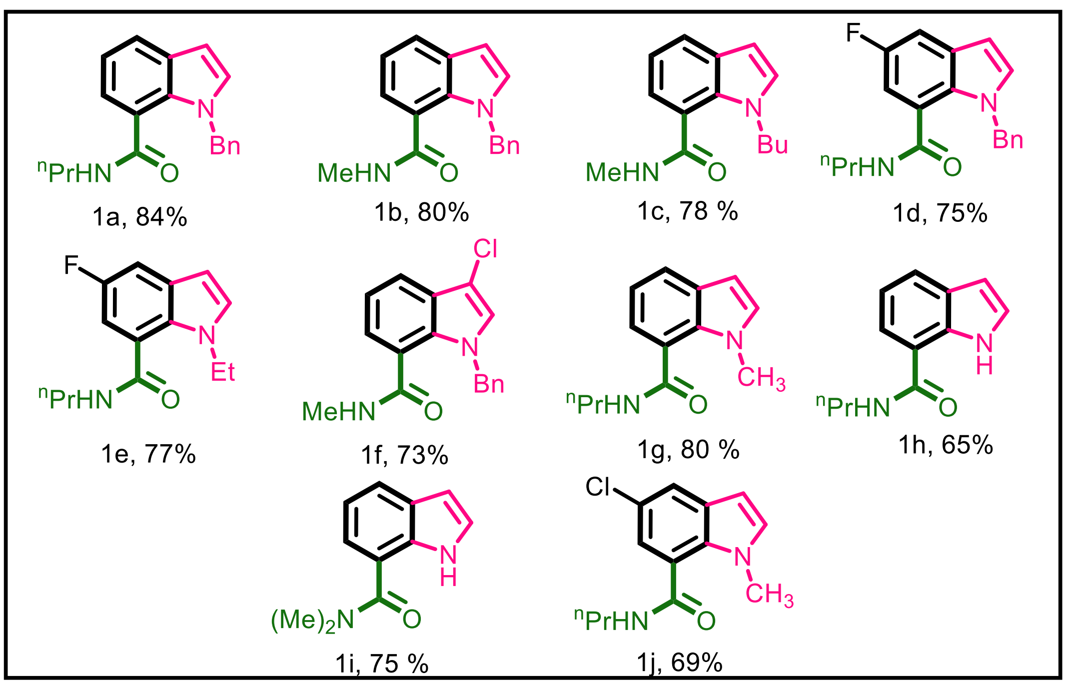
2.4 Procedure for preparation of indole-7-carboxamide (1a-1j):

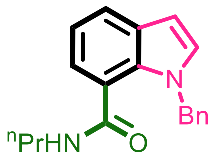


Step-1: To a solution of $AgNO_3$ (2.53 g. 15 mmol, 1.5 equiv.) in water added solution of NaOH (5 mmol) (MeOH/H_2O 1:1). To the above solution added 1-benzyl indole-7-carbaldehyde (2.35g, 10 mmol, 1 equiv.) and the reaction was stirred at 80 °C for 10-12 h. Then the reaction mixture was cooled to room temperature and filtered through celite. The filtrate was acidified to pH =3 by 2N HCl. The resulting solid was collected by filtration and washed with distilled water.

Step-2: In a 100 ml round-bottomed flask containing a solution of 1-benzyl-indole-7-carboxylic acid **S13** (1.55 g, 6.17 mmol, 1 equiv.) in anhydrous DMF (15 ml) fitted with a reflux condenser and drying tube added 1,1'-carbonyldiimidazole (CDI) (1.50 g, 9.2 mmol 1.5 equiv.) and stirred at 40-50°C for 30 min. The mixture was allowed to cool to room temperature and n-propylamine (0.547 g, 9.2 mmol, 1.5 equiv) was added, and the resulting mixture was stirred at room temperature. After completion of reaction saturated solution of NaCl was added and the reaction mixture was extracted with dichloromethane. The combined organic solution was washed with water, brine and dried over anhydrous Na_2SO_4. Solvents were evaporated under vacuum and the crude residue was purified by flash chromatography to afford products 1.52 g of **1a** as white solid. By following this method indole-7-carboxamide **1a-1h** were prepared.

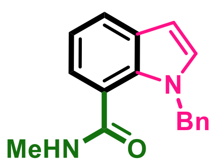
The characterization data for 1a-1j is as follows;





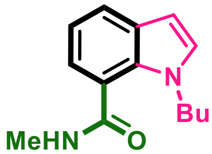
1a

1-benzyl-*N*-propyl-1H-indole-7-carboxamide (1a): White solid, Yield = 84%, (1.52 g); m. p. = 106-108 °C; R_f = 0.5 (Ethyl Acetate/Hexane:30/70); **^{1}H NMR (400 MHz, CDCl$_3$)** δ = 7.71 (d, *J*=6.0, 1H), 7.25 – 7.10 (m, 5H), 7.07 – 7.04 (m, 1H), 6.87 (d, *J*=2.2, 2H), 6.61 (s, *J*=2.4, 1H), 5.56 (m, 3H), 3.20 – 3.04 (t, 2H), 1.45 – 1.27 (m, 2H), 0.82 (t, *J*=3.8, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ = 169.5, 139.0, 131.7, 131.4, 131.3, 128.6, 127.2, 126.4, 123.4, 122.4, 121.4, 118.8, 102.1, 52.1, 41.9, 22.5, 11.5; **IR (neat):** 3310, 2962, 2856, 1729, 1648, 1630, 1531, 1280, 1176 cm^{-1}; **HRMS-ESI** (*m/z*)**:** Calculated for: $C_{19}H_{20}N_2NaO$ [M+Na]: 315.1473; found: 315.1479.



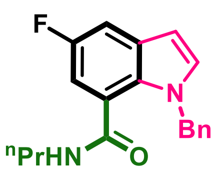
1b

1-benzyl-*N*-methyl-1H-indole-7-carboxamide (1b): White solid, Yield = 80%, (1.01 g); m. p.= 108-110 °C; R_f = 0.5 (Ethyl Acetate/Hexane : 30/70); **^{1}H NMR (400 MHz, CDCl$_3$)** δ = 7.71 (d, *J*=7.7, 1H), 7.15 (m, 5H), 7.05 (t, *J*=7.8, 1H), 6.87 (d, *J*=5.9, 2H), 6.61 (d, *J*=2.5, 1H), 5.54 (s, 2H), 5.42 (s, 1H), 2.69 (d, *J*=4.7, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ = 170.2, 138.9, 131.6, 131.4, 131.3, 128.5, 127.2, 126.4, 123.4, 122.2, 121.3, 118.9, 102.0, 52.2, 26.9; **IR (neat):** 3229, 2924, 2857, 1638, 1531, 1495, 1313, 1219 cm^{-1}; **HRMS-ESI** (*m/z*)**:** Calculated for: $C_{17}H_{16}N_2NaO$ [M+Na]: 287.1160; found: 287.1155.



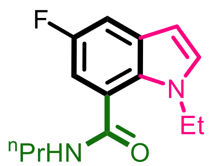
1c

1-butyl-*N*-methyl-1H-indole-7-carboxamide (1c): White solid, Yield = 78% (1.23 g); m.p.= 156-158 °C; R_f = 0.5 (Ethyl Acetate/Hexane : 30/70); **^{1}H NMR (400 MHz, CDCl$_3$)** δ = 7.67 (d, *J* = 7.8 Hz, 1H), 7.18 (d, *J* = 6.9 Hz, 1H), 7.10 (d,*J* = 3.2 Hz, 1H), 7.03 (t, *J* = 7.2 Hz, 1H), 6.51 (d, J = 2.8 Hz, 1H), 6.03 (s, 1H), 4.26 (t, *J* = 7.2 Hz, 2H), 3.03 (d, *J* = 4.7 Hz, 3H), 1.70-1.56 (m, 2H), 1.26 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ = 170.5, 131.5, 131.0, 130.6, 123.3, 121.7, 121.1, 118.5, 101.5, 48.9, 33.2, 27.0, 20.1, 13.9; **IR (neat):** 3332, 2932, 2934, 2854, 1718, 1634, 1272 cm^{-1}; **HRMS-ESI** (*m/z*)**:** Calculated for: $C_{14}H_{18}N_2NaO$ [M+Na]: 253.1317; found: 253.1314.



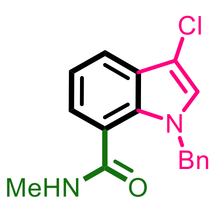
1d

1-benzyl-5-fluoro-*N*-propyl-1H-indole-7-carboxamide (1d): White solid, Yield = 75%, (1.38 g); m.p. = 118-120 °C; R_f = 0.4 (Ethyl Acetate/Hexane : 20/80); **^{1}H NMR (400 MHz, CDCl$_3$)** δ = 7.36 (dd, *J* = 2.4, 2.4 Hz, 1H), 7.26 – 7.11 (m, 4H), 6.91 (dd, *J* = 2 Hz, 2 Hz 1H), 6.84 (d, *J* = 6.8 Hz, 2 H) 6.56 (d, *J* = 3.2 Hz, 1H), 5.49 (s, 3H), 3.09 (t, *J* = 7.2, 6.9 Hz, 2H), 1.41-1.25 (dt, *J* = 7.7 Hz 2H), 0.85 (t,*J* = 7.6 Hz, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ = 168.1, 157.7, 155.3, 138.7, 133.1, 131.9 (d, *J*=9.7), 128.6, 127.3, 126.3, 122.7 (d, *J*=7.5), 109.7 (d, *J*=27.1), 108.00 (d, *J*=22.5), 102.2 (d, *J*=4.7), 52.8, 42.0, 22.5, 11.5; **IR (neat):** 3222, 2932, 2854 1631, 1547, 1530, 1420, 1255, 772 cm^{-1}; **HRMS-ESI** (*m/z*)**:** Calculated for: $C_{19}H_{19}FN_2NaO$ [M+Na]: 333.1380; found: 333.1374.



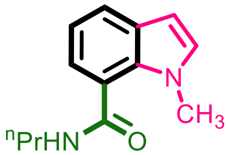
1e

1-ethyl-5-fluoro-*N*-propyl-1H-indole-7-carboxamide (1e): White solid, Yield = 77% (1.15 g); m.p.= 116-118 $^{\circ}$C; R_f = 0.4 (Ethyl Acetate/Hexane : 30/70); **^{1}H NMR (400 MHz, CDCl$_3$)** δ = 7.29 (d, *J* = 8.2 Hz, 1H), 7.16 (s, 1H), 6.95 (d, *J* = 9.2 Hz, 1H), 6.48 (s, 1H), 6.13 (s, 1H), 4.25 (dd, *J* = 6.8, 7.2 Hz, 2H), 3.42 (dd, *J* = 6.4, 6.8 Hz, 2H), 1.64 (t, 7.2 Hz, 2H), 1.30 (dd, *J* = 8.3, 7.2 Hz, 3H), 0.96 (t, *J* = 8.3 Hz, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ = 168.6, 157.5, 155.2, 131.5 (d, *J*=9.8), 128.9, 122.1 (d, *J*=7.7), 109.3 (d, *J*=27.1), 107.9 (d, *J*=22.4), 101.9, 43.4, 42.0, 22.9, 16.3, 11.5; **IR (neat):** 3241, 2958, 2924 1629, 1547, 1434, 1380, 1195, 772 cm^{-1}; **HRMS-ESI** (*m/z*)**:** Calculated for: $C_{14}H_{17}FN_2NaO$ [M+Na]: 271.1217; found: 271.1218.



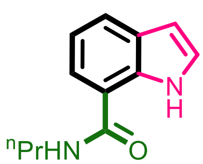
1f

1-benzyl-3-chloro-*N*-methyl-1H-indole-7-carboxamide (1f): White solid, Yield = 73% (0.650 g); m.p. = 138-140 $^{\circ}$C; R_f = 0.4 (Ethyl Acetate/Hexane : 20/80); **^{1}H NMR (400 MHz, DMSO-D$_6$)** δ = 8.29 (s, 1H), 7.61 (d, *J* = 4 Hz, 1H), 7.34-7.09 (m, 6H), 6.88 (d, *J* = 6.4 Hz, 2H), 5.62 (s, 2H), 2.58 (s, 3H); **^{13}C NMR (101 MHz, DMSO-D$_6$)** δ = 168.3, 137.7, 130.8, 128.9, 127.9, 127.0, 126.3, 125.8, 124.1, 123.5, 121.0, 119.8, 102.9, 48.5, 26.6; **IR (neat):** 3343, 2942, 2836, 1658, 1536, 1243, 730 cm^{-1}; **HRMS-ESI** (*m/z*)**:** Calculated for: $C_{17}H_{15}ClN_2NaO$ [M+Na]: 321.0765; found: 321.0762.



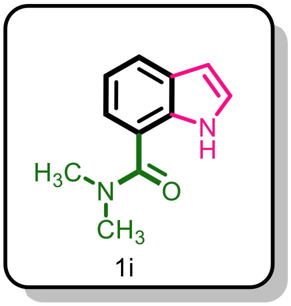
1g

1-methyl-*N*-propyl-1H-indole-7-carboxamide (1g): White solid, Yield = 80 %, (1.18 g); m.p. = 122-124 $^{\circ}$C; R_f = 0.5 (Ethyl Acetate/Hexane : 30/70); **^{1}H NMR (400 MHz, CDCl$_3$)** δ = 7.65 (dd, *J* = 2.02 Hz 1H), 7.15 (d, *J* = 5.3 Hz, 1H), 7.05-6.95 (m, 2H), 6.49 (t, *J*=3.0, 1H), 6.13 (s, 1H), 3.78 (d, *J* = 2.4 Hz, 3H), 3.46-3.35 (t, J= 7.2, 2H), 1.69 – 1.52 (m, 2H), 1.02 – 0.93 (t, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ = 169.6, 132.5, 131.3, 130.7, 123.1, 121.8, 121.0, 118.5, 101.4, 41.9, 35.9, 23.0, 11.5; **IR (neat):** 3318, 2962, 2962, 1712, 1629, 1515, 1290 cm^{-1}; **HRMS-ESI** (*m/z*)**:** Calculated for: $C_{13}H_{16}N_2NaO$ [M+Na]: 239.1155; found: 239.1146.

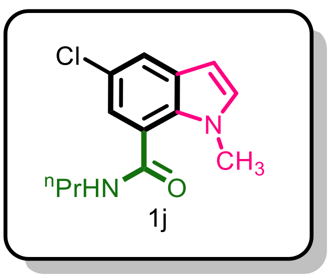


1h

***N*-propyl-1H-indole-7-carboxamide (1h):** White solid Yield = 65%, (0.610 g); m. p.= 110-112 $^{\circ}$C; R_f = 0.4 (Ethyl Acetate/Hexane : 30/70); **^{1}H NMR (500 MHz, CDCl$_3$)** δ = 10.32 (s, 1H), 7.78 (d, *J* = 8 Hz, 1H), 7.34 (d, *J* = 8 Hz, 1H), 7.29 (t, *J* = 3 Hz 1H), 7.08 (t, *J* = 3 Hz, 1H), 6.55 (dd, *J*=3.0, 2.4, 1H), 6.44 (s, 1H), 3.44 (t, *J* = 7.5 Hz, 2H), 1.72 – 1.56 (dt, *J* = 7.5 Hz, 2H), 0.99 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR (126 MHz, CDCl$_3$)** δ = 168.0, 135.6, 129.7, 125.7, 124.7, 118.8, 118.7, 116.3, 102.0, 41.5, 23.1, 11.6; **IR (neat):** 3424, 2942, 2825, 1694, 1636, 1523, 1268, 1134 cm^{-1}; **HRMS-ESI** (*m/z*)**:** Calculated for: $C_{12}H_{14}N_2NaO$ [M+Na]: 225.1000; found: 225.0994.



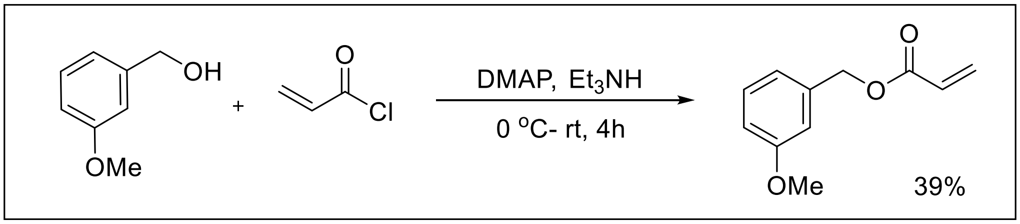
N, N-dimethyl-1H-indole-7-carboxamide (**1i**): White solid, Yield = 75%, (0.655 g); m.p. **=** 138-140 °C; R_f = 0.5 (Ethyl Acetate/Hexane : 30/70); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 9.37 (s, 1H), 7.70 (d, *J*=7.2, 1H), 7.26 – 7.22 (m, 2H), 7.12 – 7.04 (m, 1H), 6.54 (s, 1H), 3.17 (s, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 170.7, 135.0, 129.2, 125.3, 123.1, 121.6, 118.4, 117.4, 102.4, 37.7, 37.5; **IR (neat):** 3420, 2852, 1669, 1628, 1560, 1270, 1246, 759 cm^{-1}; **HRMS-ESI** (*m/z*)**:** Calculated for: $C_{11}H_{12}N_2NaO$: 211.0842 [M+Na]; found: 211.0836.



5-chloro-1-methyl-*N*-propyl-1H-indole-7-carboxamide (1j): White solid, Yield = 69%, (1.07 g); m.p. = 134-136 °C; R_f = 0.4 (Ethyl Acetate/Hexane:20/80); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.57 (s, 1H), 7.10 (s, 1H), 7.01 (d, *J* = 2.6 Hz, 1H), 6.41 (d, *J* = 3.0 Hz, 1H), 6.24 (s, 1H), 3.74 (s, 3H), 3.41 – 3.32 (t, J= 7.5, 2H), 1.68 – 1.54 (m, 2H), 0.97 (t, *J* = 6.0 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 168.2, 132.6, 131.7, 131.0, 124.0, 122.6, 122.1, 120.9, 101.1, 42.0, 35.9, 22.9, 11.5; **IR (neat):** 3357, 2964, 2928, 2874, 1634, 1549, 1269, 772 cm^{-1}; **HRMS-ESI** (*m/z*)**:** Calculated for: $C_{13}H_{15}ClN_2NaO$ [M+Na]: 273.0765; found: 273.0759.

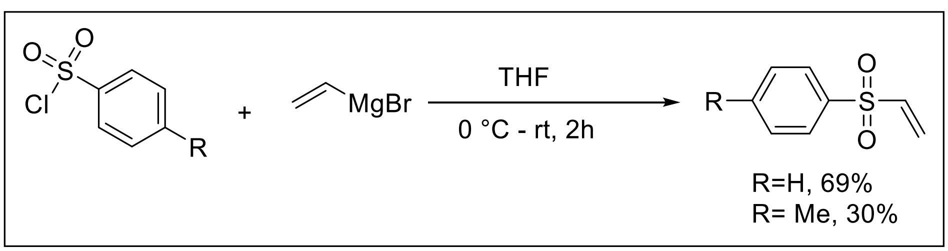
2.5 Preparation of acrylates and aryl vinyl sulfones (2):

2.5.1 Preparation of 3-methoxybenzyl acrylate: Prepared by following reported literature procedure[4].



In oven dried 100 ml round bottom flask the solution of 3-methoxybenzyl alcohol (5.0 mmol, 1.00 equiv) was dissolved in dry DCM (15 mL) and cooled to 0 ˚C. Then DMAP (30.5 mg, 0.250 mmol, 0.0500 equiv) and triethyl amine (5.0 mmol, 1.10 equiv) were added. Then acryloyl chloride (0.445 ml, 5 mmol, 1.10 equiv) was added drop wise and reaction mixture was warmed to room temperature followed by stirring for 4 h. Reaction mixture was quenched by adding water (5 mL) and then extracted with DCM (3x10 mL). The combined organic layers were washed with brine (3x10 mL). The organic layers were dried over anhydrous Na_2SO_4 and the solvents were removed under reduced pressure. The crude product was purified by using silica gel column chromatography to obtain as a colorless oil.

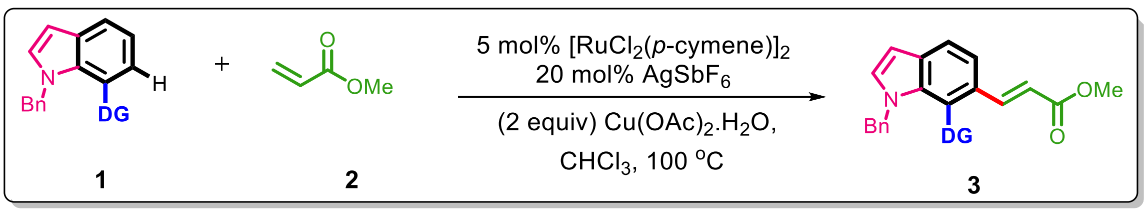
2.5.2 Preparation of aryl vinyl sulfones: Prepared by reported literature procedure.[5,6]



In oven dried 100 ml round bottom flask vinyl magnesium bromide (1M solution in THF, 6 ml, 1.2 equiv.) was added drop wise to a stirred solution of arylesulfonyl chloride (5.0 mmol) in dry THF (20 mL) under nitrogen atmosphere. The reaction mixture was stirred for 15 minutes at 0 °C and was then warmed to room temperature and stirred for 2 h. To this added aqueous 1M HCl and stirred for 45 minutes. Then the reaction mixture was quenched by adding saturated aqueous $NaHCO_3$ and the resulting solution extracted with ethyl acetate (3 x 20 mL). The organic layers were dried over anhydrous Na_2SO_4 and the solvents were removed under reduced pressure. The crude product was purified by using silica gel column chromatography.

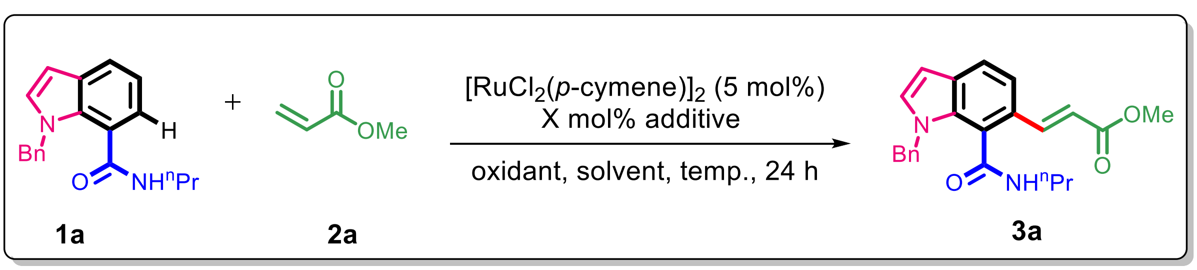
3. Detailed optimization C6 alkenylation of indole-7-carboxamides:

3.1 Optimization for C6 alkenylation of indoles using different directing groups:



Directing Groups (DGs)	Observations (yield)
-CHO	No reaction
-COOH	No reaction
-COOMe	No reaction
-CONH^{n}Pr	**45 %**

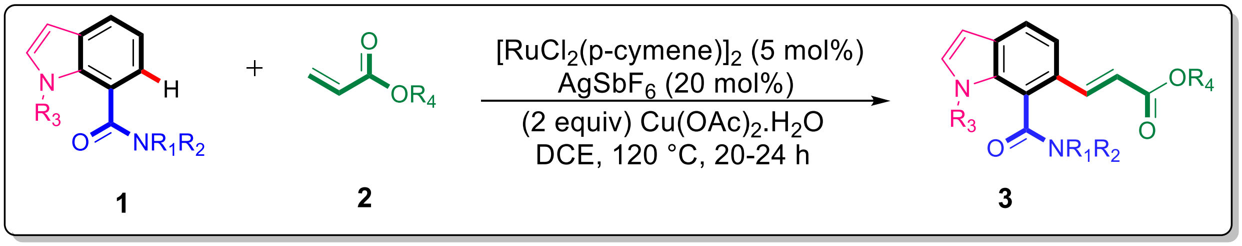
3.2 Optimization for C6 alkenylation of indole-7-carboxamide (3a):



entry	solvent	[a]Conditions	Yield[b] (%)
1	$CHCl_3$	$AgSbF_6$/ $Cu(OAc)_2.H_2O$ /100 °C	45
2	$CHCl_3$	$AgSbF_6$/ $Cu(OAc)_2.H_2O$ / 120 °C	68
3	dioxane	$AgSbF_6$/ $Cu(OAc)_2.H_2O$ / 120 °C	62
4	THF	$AgSbF_6$/ $Cu(OAc)_2.H_2O$ / 120 °C	56
5	toluene	$AgSbF_6$/ $Cu(OAc)_2.H_2O$ / 120 °C	65
6	**DCE**	**$AgSbF_6$/ $Cu(OAc)_2.H_2O$/ 120 °C**	**90**
7	EtOH	$AgSbF_6$/ $Cu(OAc)_2.H_2O$ / 120 °C	30
8	DMF	$AgSbF_6$/ $Cu(OAc)_2.H_2O$ / 120 °C	15
9	DCE	AgOTf/ $Cu(OAc)_2.H_2O$ / 120 °C	trace
10	DCE	NaOAc/ $Cu(OAc)_2.H_2O$ / 120 °C	34
11	DCE	KPF_6/ $Cu(OAc)_2.H_2O$ / 120 °C	25
12	DCE	$AgBF_4$/ $Cu(OAc)_2.H_2O$ / 120 °C	40
13	DCE	$AgSbF_6$/ Ag_2CO_3 / 120 °C	trace
14	DCE	$AgSbF_6$/ Ag_2O / 120 °C	trace
15	DCE	$AgSbF_6$/ $Na_2S_2O_8$ / 120 °C	nr
16	DCE	$AgSbF_6$/ $PhI(OAc)_2$ / 120 °C	nr

[a]Reaction conditions: indole-7-carboxamide **1a** (0.2 mmol), acrylate **2a** (0.3 mmol), $[RuCl_2(pcymene)]_2$ (5.0 mol%), additive (20 mol%), $Cu(OAc)_2{\cdot}H_2O$ (2.0 equiv), solvent (2.0 mL), The experiments were carried out at mentioned temperatures. [b]Isolated yield.

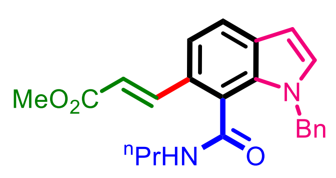
4.1 General procedure for C6 alkenylation of indole-7-carboxamide:



A oven-dried screw cap reaction tube equipped with stir bar was charged with [Ru(*p*-cymene)Cl_2]$_2$ (0.01 mmol), indole-7-carboxamide **1** (0.20 mmol), acrylate **2** (0.30 mmol), $AgSbF_6$ (0.04 mmol) and $Cu(OAc)_2{\cdot}H_2O$ (0.40 mmol). The reaction tube was evacuated and purged with nitrogen followed by the addition of 2 mL 1, 2-dichloroethane. The reaction tube then placed in an oil bath and reaction mixture allowed to stir at 120 °C for 20-24 hrs. The reaction mixture was diluted with ethyl acetate and filtered through a celite pad. The filtrate was concentrated under reduced pressure and the crude product was purified by silica gel column chromatography to obtain **3a-3z** as white solids.

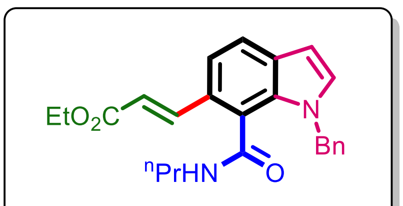
4.2 Synthetic procedure for 1 mmol scale synthesis of methyl (*E*)-3-(1-benzyl-7-(propylcarba-moyl)-1H-indol-6-yl)acrylate (3a): A oven-dried screw cap reaction tube equipped with stir bar was charged with [Ru(*p*-cymene)Cl_2]$_2$ (30 mg, 0.05 mmol), indole-7-carboxamide **1** (292 mg, 1.0 mmol), acrylate **2** (135 µL, 1.5 mmol), $AgSbF_6$ (69 mg, 0.2 mmol) and $Cu(OAc)_2{\cdot}H_2O$ (400 mg, 2 mmol). The reaction tube was evacuated and purged with nitrogen followed by the addition of 10 mL DCE. The reaction tube then placed in an oil bath and reaction mixture allowed to stir at 120 °C for 24 hrs. The reaction mixture was diluted with ethyl acetate and filtered through a celite pad. The filtrate was concentrated under reduced pressure and the crude product was purified by silica gel column chromatography to obtain 335 mg of **3a** as a white solid.

5. Characterization data for C6-alkenyl indole-7-carboxamides:



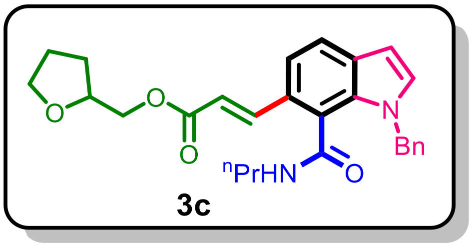
3a

methyl (*E*)-3-(1-benzyl-7-(propylcarbamoyl)-1H-indol-6-yl)acrylate (3a): White solid, Yield = 90%, (67 mg); m.p. = 144-146 °C; R_f = 0.3 (Ethyl Acetate/Hexane : 40/60); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.84 (d, *J*=15.7, 1H), 7.64 (d, *J*=8.3, 1H), 7.37 (d, *J*=8.3, 1H), 7.27 – 7.19 (m, 3H), 7.13 (d, *J*=2.3, 1H), 6.87 (d, *J* = 6.5, 2H), 6.60 (d, *J*=2.2, 1H), 6.37 (d, *J*=15.8, 1H), 5.60 (s, 1H), 5.43 (s, 2H), 3.72 (s, 3H), 2.99 (t, *J*=7.4, 2H), 1.34 (dd, *J*=8.4, 7.1, 2H), 0.82 (t, *J*= 7.2, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 167.8, 167.3, 142.7, 138.7, 132.7, 132.0, 131.5, 128.8, 127.5, 125.8, 125.5, 123.0, 122.3, 118.0, 117.5, 102.8, 51.6, 50.9, 42.1, 22.2, 11.5; **IR (neat):** 3285, 2959, 2925, 2854, 1725, 1627, 1548, 1453, 1275 cm^{-1}; **HRMS-ESI** (*m/z*)**:** Calculated for: $C_{23}H_{24}N_2NaO_3$ $[M+Na]^+$: 399.1685; found: 399.1681; **(CCDC 1990507)**.

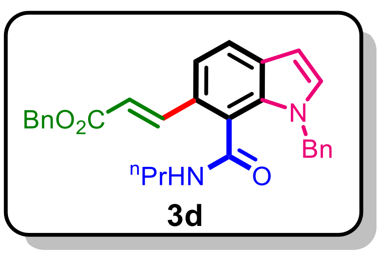


3b

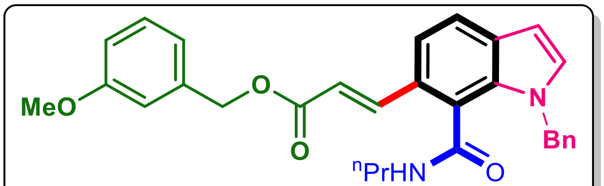
ethyl (*E*)-3-(1-benzyl-7-(propylcarbamoyl)-1H-indol-6-yl)acrylate (3b): White solid, Yield = 95% (73 mg); m. p.= 152-154 °C; R_f = 0.4 (Ethyl Acetate/Hexane : 40/60); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.83 (d, *J* =15.8, 1H), 7.64 (d, *J*=5.1, 1H), 7.39 (d, *J*=7.1, 1H), 7.26 – 7.11 (m, 4H), 6.87 (d, *J*=3.3, 2H), 6.60 (s, 1H), 6.37 (d, *J*=15.7, 1H), 5.52-5.41 (m, 3H), 4.20 – 4.15 (m, 2H), 3.31 – 2.80 (t, *J* = 7.8 2H), 1.44 – 1.15 (m, 5H), 0.89 – 0.76 (t, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 167.8, 166.9, 142.4, 138.8, 132.7, 131.9, 131.5, 128.8, 127.4, 125.8, 125.7, 122.9, 122.4, 118.6, 117.5, 102.8, 60.4, 51.0, 42.2, 22.3, 14.4, 11.5; **IR (neat):** 3339, 2925, 2855, 1724, 1626, 1534, 1495, 1275, 1174 cm^{-1}; **HRMS-ESI** (*m/z*)**:** Calculated for: $C_{24}H_{26}N_2NaO_3$ $[M+Na]^+$: 413.1836; found: 413.1827.



(tetrahydrofuran-2-yl)methyl(*E*)-3-(1-benzyl-7-(propylcarbamoyl)-1H-indol-6-yl)acrylate (3c): White solid, Yield = 83% (73 mg); m.p. = 138-140 °C; R_f = 0.3 (Ethyl Acetate/Hexane : 20/80); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.89 (d, *J*=15.5, 1H), 7.66 (d, *J*=8.1, 1H), 7.41 (d, *J*=8.1, 1H), 7.35 – 7.03 (m, 4H), 6.89 (d, *J*=6.4, 2H), 6.61 (s, 1H), 6.47 (d, *J*=15.7, 1H), 5.51 – 5.42 (m, 3H), 4.28 – 4.06 (m, 3H), 3.90 (d, *J*=6.7, 1H), 3.79 (d, *J*=6.9, 1H), 3.15 – 2.95 (m, 1H), 2.06 – 1.87 (m, 3H), 1.73 – 1.55 (t , 2H), 1.42 – 1.29 (m, 2H), 0.83 (t, *J*= 6.5, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 167.8, 166.9, 143.0, 138.8, 132.7, 132.0, 131.6, 128.8, 127.5, 125.8, 125.7, 123.0, 122.4, 118.2, 117.6, 102.9, 76.7, 68.6, 66.5, 51.0, 42.3, 28.9, 25.8, 22.3, 11.5; **IR (neat):** 3283, 2963, 2873, 1702, 1629, 1536, 1430, 1285, 1245, 1158 cm^{-1}; **HRMS-ESI** (*m/z*)**:** Calculated for: $C_{27}H_{30}N_2NaO_4$ $[M+Na]^+$: 469.2098; found: 469.2099.

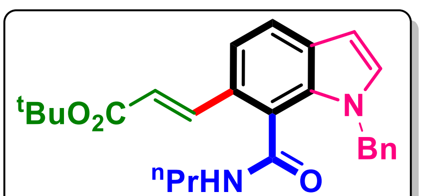


benzyl (*E*)-3-(1-benzyl-7-(propylcarbamoyl)-1H-indol-6-yl)acrylate (3d): (*E/Z* mixture 1:0.2), White solid, Yield =85% (76 mg) ; m.p.= 158-160 °C; R_f = 0.3 (Ethyl Acetate/Hexane : 30/70): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.89 (d, *J* = 15.6 Hz, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.43 – 7.13 (m, 10 H), 6.87 (d, *J* = 6.0 Hz, 2H), 6.60 (s, 1H), 6.44 (d, J = 16 Hz, 1H), 5.45 (s, 3H), 5.19 (s, 2H), 2.89 (t, *J*=7.6 2H), 1.31 – 1.20 (dt, *J*=7.2, *J*=8.2, 2H), 0.72 (t, *J*=7.2, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 167.7, 166.5, 142.9, 138.6, 132.6, 131.9, 128.7, 128.6, 128.5, 128.4, 128.2, 128.1, 128.0, 127.3, 127.2, 125.6, 122.3, 118.1, 117.5, 102.7, 66.2, 50.9, 42.1, 22.1, 11.3; **IR (neat):** 3300, 2923, 2853, 1708, 1633, 1531, 1454, 1268, 1158 cm^{-1}; **HRMS-ESI** (*m/z*)**:** Calculated for: $C_{29}H_{29}N_2O_3$ $[M+H]^+$: 453.2173; found: 453.2171.



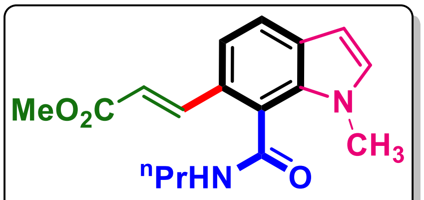
3e

3-methoxybenzyl (*E*)-3-(1-benzyl-7-(propylcarbamoyl)-1H-indol-6-yl)acrylate (3e): White solid, Yield = 88% (84 mg); m. p.= 124-128 °C; R_f = 0.4 (Ethyl Acetate/Hexane : 40/60) ; **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.91 (d, *J*=15.3, 1H), 7.65 (d, *J*=6.4, 1H), 7.40 (d, *J*=8.5, 1H), 7.26 – 7.13 (m, 5H), 6.98 – 6.83 (m, 5H), 6.61 (s, 1H), 6.46 (d, *J*=15.5, 1H), 5.60-5.25 (m, 3H), 5.17 (s, 2H), 3.80 (s, 3H), 2.96 (t, *J*=7.6, 2H), 1.33 – 1.22 (dt, *J*=7.5 , *J*=8.4 2H), 0.76 (t, *J*=8.2, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 167.8, 166.7, 159.9, 143.1, 138.8, 137.8, 132.9, 132.0, 131.8, 129.7, 128.8, 127.5, 125. 8, 125.7, 123.0, 122.4, 120.5, 118.2, 117.6, 113.9, 113.7, 102.9, 66.2, 55.4, 51.0, 42.2, 22.3, 11.5; **IR (neat):** 3319, 2925, 1694, 1651, 1626, 1545, 1269, 1175cm^{-1}; **HRMS-ESI** (*m/z*)**:** Calculated for: $C_{30}H_{30}N_2NaO_4$ $[M+Na]^+$: 505.2098; found: 505.2092.



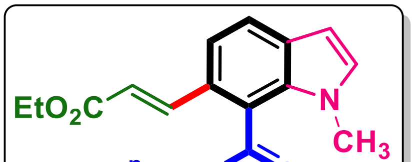
3f

tert-butyl (*E*)-3-(1-benzyl-7-(propylcarbamoyl)-1H-indol-6-yl)acrylate (3f): White solid, Yield =75% (62 mg); m.p.= 142-144 °C; R_f = 0.4 (Ethyl Acetate/Hexane : 30/70); **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 7.74 (d, *J*=15.7, 1H), 7.65 (d, *J*=8.4, 1H), 7.39 (d, *J*=8.4, 1H), 7.28 – 7.20 (m, 3H), 7.14 (d, *J*=2.9, 1H), 6.88 (d, *J*=6.9, 2H), 6.61 (d, *J*=2.9, 1H), 6.33 (d, *J*=15.7, 1H), 5.47 (s, 2H), 5.41 (s, 1H), 3.03 (t, *J*=7.2, 2H), 1.49 (s, 9H), 1.35 (dd, *J*=8.4, 7.3, 2H), 0.82 (t, *J*= 8.3, 3H); **^{13}C NMR (126 MHz, CDCl$_3$)** δ = 167.9, 166.2, 141.3, 138.9, 132.5, 131.7, 131.4, 128.8, 127.4, 126.1, 125.8, 122.9, 122.4, 121.0, 117.8, 102.8, 80.4, 51.1, 42.2, 28.3, 22.4, 11.6; **IR (neat):** 3427, 2921, 2836, 2816, 1692, 1639 1582, 1478, 1242 cm^{-1}; **HRMS-ESI** (*m/z*)**:** Calculated for: $C_{26}H_{30}N_2NaO_3$ [M+Na]$^+$: 441.2154; found: 441.2142.



3g

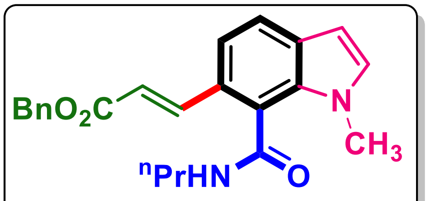
methyl (*E*)-3-(1-methyl-7-(propylcarbamoyl)-1H-indol-6-yl)acrylate (3g): White solid Yield = 85% (51 mg) ; m.p.= 156-158 ˚C; R$_f$ = 0.3 (Ethyl Acetate/Hexane : 40 /60); **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.88 (d, *J* = 16 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.5 Hz, 1H), 7.04 (d, *J* = 3 Hz, 1H), 6.47 (d, *J* = 3 Hz, 1H), 6.39 (d, *J* = 16 Hz, 1H), 6.16 (s, 1H), 3.78 (s, 3H), 3.75 (s, 3H), 3.50 (t, *J* = 7 Hz, 2H), 1.70 (dd, *J* = 7, 7.5 Hz, 2H), 1.01 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR (126 MHz, CDCl$_3$)** δ = 168.1, 167.5, 142.6, 132.9, 132.1, 131.6, 125.0, 122.9, 122.1, 117.9, 117.2, 101.8, 51.7, 42.1, 34.9, 22.8, 11.6; **IR (neat):** 3258, 2924, 1729, 1622, 1532, 1446, 1287, 1219cm^{-1}; **HRMS-ESI** (*m/z*)**:** Calculated for: $C_{17}H_{20}N_2NaO_3$ [M+Na]$^+$: 323.1372; found: 323.1368.



3h

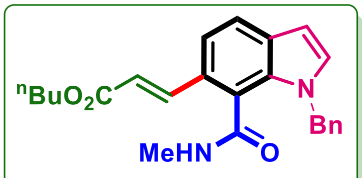
ethyl (*E*)-3-(1-methyl-7-(propylcarbamoyl)-1H-indol-6-yl)acrylate (3h): White solid, Yield = 90% (56 mg); m.p.= 140-132 ˚C; R$_f$ = 0.3 (Ethyl Acetate/Hexane : 30/70); **^{1}H NMR (400 MHz,**

CDCl₃) δ 7.86 (d, J = 15.8 Hz, 1H), 7.56 (d, J = 8.4 Hz, 1H), 7.33 (d, J = 8.4 Hz, 1H), 7.03 (d, J= 2.6 Hz, 1H), 6.47 (d, J = 2.8 Hz, 1H), 6.38 (d, J = 16.0 Hz, 1H), 6.19 (s, 1H), 4.19 (dd, J = 6.8, 6.8 Hz, 2H), 3.77 (s, 3H), 3.45 (t, J = 7.2 Hz, 2H), 1.77 – 1.63 (m, 2H), 1.30 (t, J = 6.8 Hz, 3H), 1.00 (t, J = 7.2 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 168.1, 167.0, 142.2, 132.9, 132.1, 131.6, 125.1, 122.8, 122.0, 118.4, 117.8, 101.7, 60.4, 42.1, 34.7, 22.8, 14.4, 11.7; **IR (neat):** 3221, 2867, 1625, 1636, 1610, 1520, 1220, 1137cm^{-1}; **HRMS-ESI** (*m/z*)**:** Calculated for: $C_{18}H_{22}N_2NaO_3$ $[M+Na]^+$: 337.1523; found : 337.1529.



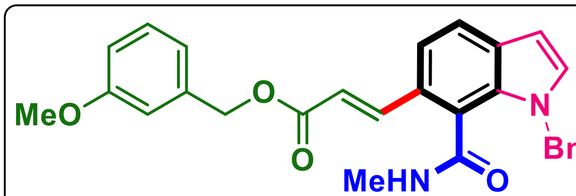
3i

benzyl (*E*)-3-(1-methyl-7-(propylcarbamoyl)-1H-indol-6-yl)acrylate (3i): White solid, Yield = 88% (68 mg); m.p.= 130-132 ˚C; R_f = 0.4 (Ethyl Acetate/Hexane : 40/60); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.89 (d, J = 15.8 Hz, 1H), 7.54 (d, J = 8.4 Hz, 1H), 7.41 – 7.22 (m, 6H), 7.00 (s, 1H), 6.52 – 6.32 (m, 2H), 6.19 (s, 1H), 5.20 (s, 2H), 3.73 (s, 3H), 3.40 (t, J = 7.4, 2H), 1.68 – 1.51 (m, 2H), 0.93 (t, J = 7.2 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 168.0, 166.8, 142.8, 136.2, 132.9, 132.0, 131.6, 128.6, 128.3, 128.2, 124.9, 122.9, 122.1, 117.9, 117.1, 101.7, 66.2, 42.0, 34.8, 22.7, 11.6; **IR (neat):** 3300, 3029, 2854, 2825, 1720, 1635, 1495, 1288, 1313 cm^{-1}; **HRMS-ESI** (*m/z*)**:** Calculated for: $C_{23}H_{24}N_2NaO_3$ $[M+Na]^+$: 399.1685; found: 399.1681.



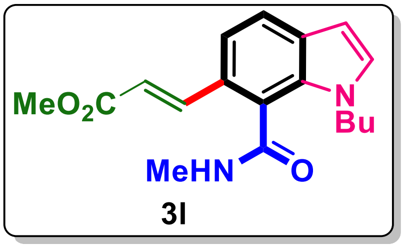
3j

butyl-3-(1-benzyl-7-(methylcarbamoyl)-1H-indol-6-yl)acrylate (3j): (mixture of *E/Z* isomer (1:0.2), White solid, Yield =86% (67 mg) ; m.p.= 142-144 ˚C; R_f = 0.3 (Ethyl Acetate/Hexane : 30/70) ; **^{1}H NMR (400 MHz, CDCl3)**δ = 7.75 (d, *J*= 15.8, 1H), 7.66 (d, *J*=8.4, 1H), 7.41 (d, *J*=8.5, 1H), 7.29 – 7.11 (m, 4H), 6.88 (d, *J*=6.2, 2H), 6.61 (d, *J*=2.6, 1H), 6.39 (d, *J*=15.7, 1H), 5.46 (s, 2H), 5.38 (s, 1H), 4.14 (t, *J*=6.2, 2H), 2.63 (d, *J*=4.6, 2H), 1.69 – 1.60 (m, 2H), 1.41 (dd, *J*=14.8, 7.5, 2H), 0.94 (t, *J*=7.3, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 168.5, 167.2, 142.4, 138.8, 132.7, 132.0, 128.8, 128.5, 127.5, 126.4, 125.7, 122.7, 122.5, 118.7, 117.7, 102.8, 64.4, 51.1, 30.9, 26.8, 19.3, 13.9; **IR (neat):** 3559, 2958, 2930, 2871, 1702, 1628 1452, 1282, 1164 cm^{-1}; **HRMS-ESI** (*m/z*)**:** Calculated for: $C_{24}H_{26}N_2NaO_3$ $[M+Na]^+$: 413.1836; found: 413.1841.

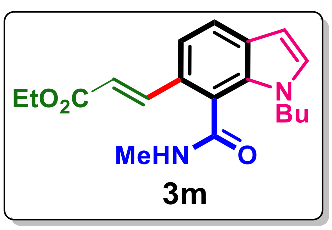


3k

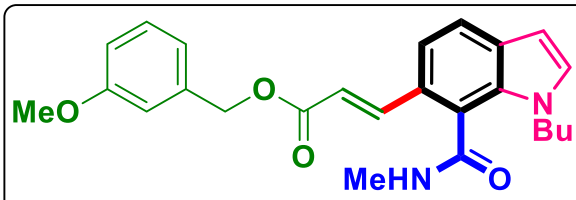
3-methoxybenzyl-3-(1-benzyl-7-(methylcarbamoyl)-1H-indol-6-yl)acrylate (3k): (mixture of *E/Z* isomer (1:0.2), White solid, Yield = 83% (76 mg); m.p.= 156-158 ˚C; R_f = 0.3 (Ethyl Acetate/Hexane : 30/70); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.84 (d, *J* = 16.0 Hz, 1H), 7.65 (d, *J* = 8.2 Hz, 1H), 7.40 (d, *J*= 8.2 Hz, 1H), 7.32 – 7.15 (m, 5H), 7.00 – 6.78 (m, 5H), 6.61 (d, *J* = 2.8 Hz, 1H), 6.44 (d, *J* = 14.8 Hz, 1H), 5.49-5.34 (m, 3H), 5.15 (s, 2H), 3.80 (s, 3H), 2.60 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 168.4, 166.8, 159.9, 143.1, 138.8, 137.8, 132.9, 132.1, 131.5, 129.7, 128.8, 127.5, 125.7, 125.6, 123.0, 122.4, 120.4, 118.1, 117.6, 113.8, 113.7, 102.8, 66.1, 55.4, 51.1, 26.8; **IR (neat):** 3287, 2926, 1705, 1627, 1587, 1265, 1246, 1151,774 cm^{-1}; **HRMS-ESI** (*m/z*)**:** Calculated for: $C_{28}H_{26}N_2NaO_4$ $[M+Na]^+$: 477.1785; found: 477.1788.



methyl (*E*)-3-(1-butyl-7-(methylcarbamoyl)-1H-indol-6-yl)acrylate (3l): White solid, Yield =78% (48 mg); m.p.= 120-124 °C; R_f = 0.3 (Ethyl Acetate/Hexane : 40/60) ; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.85 (d, *J* = 15.6 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 1H), 7.15 (d, *J* = 2.6 Hz, 1H), 6.51 (d, *J* = 2.6 Hz, 1H), 6.41 (d, *J* = 15.8 Hz, 1H), 6.02 (s, 1H), 4.12 (t, *J* = 6.8 Hz, 2H), 3.75 (s, 3H), 3.10 (d, *J* = 4.8 Hz, 3H), 1.80 – 1.68 (m, 2H), 1.33 (dd, J = 7.2, 7.6 Hz, 2H), 0.93 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 169.1, 167.6, 142.8, 131.8, 131.5, 125.3, 122.6, 122.3, 118.2, 118.1, 117.2, 102.2, 51.7, 47.8, 33.7, 27.0, 20.3, 13.9; **IR (neat):** 3280, 2930, 2874, 1710, 1625, 1505, 1432, 1282, 1164 cm^{-1}; **HRMS-ESI** (*m/z*)**:** Calculated for: $C_{18}H_{22}N_2NaO_3$ $[M+Na]^+$: 337.1519; found: 337.1523.

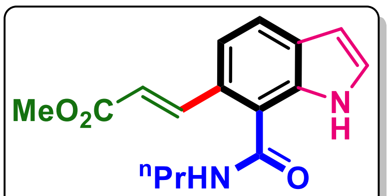


ethyl (*E*)-3-(1-butyl-7-(methylcarbamoyl)-1H-indol-6-yl)acrylate (3m): White solid, Yield =84% (55 mg); m.p.= 140-187 °C; R_f = 0.4 (Ethyl Acetate/Hexane : 40/60); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.81 (d, *J*=15.3, 1H), 7.57 (d, *J*=6.7, 1H), 7.34 (d, *J*=6.4, 1H), 7.12 (s, 1H), 6.49 (s, 1H), 6.36 (d, *J*=15.6, 1H), 6.14 (s, 1H), 4.20 – 4.02 (m, 4H), 3.07 (s, 3H), 1.81 – 1.65 (m, 2H), 1.44 – 1.16 (m, 5H), 0.91 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 169.1, 167.2, 142.5, 131.8, 131.7, 131.4, 125.3, 122.6, 122.2, 118.4, 117.2, 102.2, 60.4, 47.8, 33.7, 26.9, 20.3, 14.4, 13.9; **IR (neat):** 3284, 2961, 2941, 1705, 1626, 1547, 1431, 1281, 1176 cm^{-1}; **HRMS-ESI** (*m/z*)**:** Calculated for: $C_{19}H_{24}N_2NaO_3$ $[M+Na]^+$: 351.1680; found: 351.1678.



3n

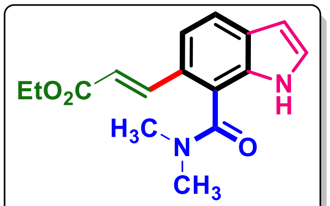
3-methoxybenzyl-3-(1-butyl-7-(methylcarbamoyl)-1H-indol-6-yl)acrylate (3n): (mixture of *E/Z* isomer (1:0.2), White solid, Yield = 79% (66 mg); m.p.= 156-158 ˚C; R_f = 0.3 (Ethyl Acetate/Hexane : 40/60); **^{1}H NMR (400 MHz, CDCl$_3$)** δ = 7.91 (d, *J*=14.4, 1H), 7.60 (s, 1H), 7.35 (d, *J*=21.2, 1H), 7.27 (d, *J*=7.3, 1H), 7.15 (s, 1H), 7.03 – 6.79 (m, 3H), 6.59-6.33 (m, 2H), 6.00 (s, 1H), 5.17 (s, 2H), 4.12 (t, *J*=13.2, 2H), 3.79 (s, 3H), 3.07 (s, 3H), 1.81 – 1.60 (m, 2H), 1.43 – 1.24 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ = 169.0, 166.9, 159.9, 143.2, 137.9, 132.0, 131.9, 131.46, 129.7, 125.3, 122.7, 122.3, 120.4, 118.0, 117.2, 113.8, 113.7, 102.3, 66.2, 55.4, 47.8, 33.7, 27.0, 20.3, 13.9; **IR (neat):** 3301, 2960, 2929, 2872, 1713, 1625, 1279, 1151 cm^{-1}; **HRMS-ESI** (*m/z*)**:** Calculated for: $C_{25}H_{28}N_2NaO_4$ $[M+Na]^+$: 443.1947; found: 443.1945.



3o

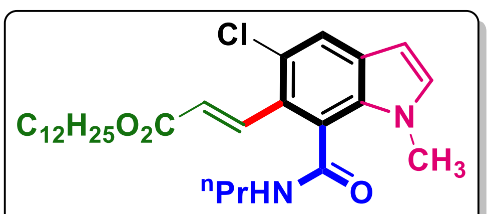
methyl (*E*)-3-(7-(propylcarbamoyl)-1H-indol-6-yl)acrylate (3o): White solid, Yield = 70% (40 mg); m.p.= 126-128 ˚C; R_f = 0.3 (Ethyl Acetate/Hexane : 30/70); **^{1}H NMR (400 MHz, CDCl$_3$)** δ 9.59 (s, 1H), 8.21 (d, *J* = 15.8 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.38-7.28 (m, 2H), 6.57 (d, *J* = 2.4 Hz, 1H), 6.45 (d, *J* = 15.8 Hz, 1H), 5.88 (s, 1H), 3.82 (s, 3H), 3.51 (t, *J* = 6.8 Hz, 2H), 1.73-

1.63 (m, 2H), 1.03 (t, J = 7.4 Hz, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ = 167.5, 167.2, 143.4, 135.1, 130.3, 127.3, 125.9, 123.3, 119.7, 119.4, 119.0, 103.0, 51.9, 42.2, 23.0, 11.6; **IR (neat):** 3421, 2822, 1668, 1628, 1512, 1241, 1157 cm^{-1}; **HRMS-ESI** (*m/z*)**:** Calculated for $C_{16}H_{18}N_2NaO_3$ $[M+Na]^+$: 309.1215; found : 309.1211.



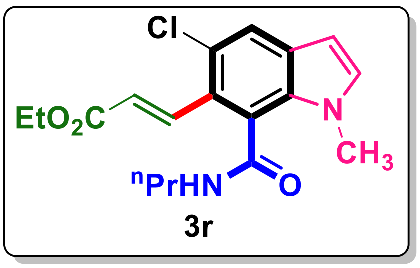
3p

ethyl (*E*)-3-(7-(dimethylcarbamoyl)-1H-indol-6-yl)acrylate (3p): White solid, Yield = 61% (35 mg); m.p.= 134-136 °C; R_f = 0.3 (Ethyl Acetate/Hexane : 40/60); **^{1}H NMR (400 MHz, CDCl$_3$)** δ = 9.01 (s, 1H), 7.78 (d, J = 16.4 Hz, 1H), 7.62 (d, J = 8.4 Hz, 1H), 7.41 (d, J = 8.8 Hz, 1H), 7.19 (d, J = 7.0 Hz 1H), 6.58 – 6.39 (m, 2H), 4.26 (dd, J = 6.8, 5.6 Hz, 2H), 3.25 (s, 3H), 2.83 (s, 3H), 1.34 (t, J = 6.8 Hz, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ = 168.9, 167.2, 142.6, 133.5, 130.2, 127.4, 124.7, 122.0, 120.5, 118.4, 117.9, 103.3, 60.6, 38.7, 35.7, 14.5; **IR (neat):** 3425, 2832, 1679, 1638, 1552, 1226, 1145 cm^{-1}; **HRMS-ESI** (*m/z*)**:** Calculated for $C_{16}H_{18}N_2NaO_3$ $[M+Na]^+$: 309.1215; found : 309.1212.

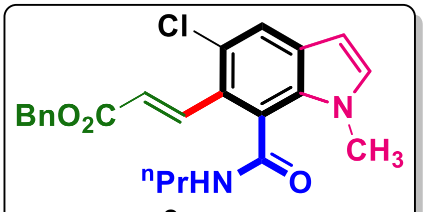


3q

dodecyl-3-(5-chloro-1-methyl-7-(propylcarbamoyl)-1H-indol-6-yl)acrylate (3q): (mixture of *E/Z* isomer (1:0.2), White solid Yield = 81% (80 mg); m.p.= 108-110 °C; R_f = 0.3 (Ethyl Acetate/Hexane : 30/60); **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.94 (d, J = 16.2 Hz, 1H), 7.59 (s, 1H), 7.07 – 6.93 (d, J = 3.0 Hz, 1H), 6.44 – 6.37 (m, 2H), 6.18 (s, J = 6.8 Hz 1H),4.15 (t, 2H) 3.76 (s, 3H), 3.46 – 3.28 (m, 2H), 1.66 (dd, J=14.8, 7.4, 2H), 1.59 (dd, J=14.8, 7.5, 2H), 1.43-1.12 (m, 14H), 1.04 – 0.80 (m, 10H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 167.7, 166.8, 140.47, 133.9, 132.7, 131.4, 131.0, 125.1, 123.4, 122.7, 120.9, 100.9, 64.9, 42.2, 34.9, 32.0, 29.9, 29.8, 29.72, 29.7, 29.5, 29.4, 28.8, 26.1, 22.8, 22.3, 14.2, 11.6; **IR (neat):** 3263, 2922, 2852, 1706, 1632, 1546, 1467, 1255, 1172, 771, 721 cm^{-1}; **HRMS-ESI** (*m/z*)**:** Calculated for: $C_{28}H_{41}ClN_2NaO_3$ $[M+Na]^+$: 511.2703; found: 511.2698

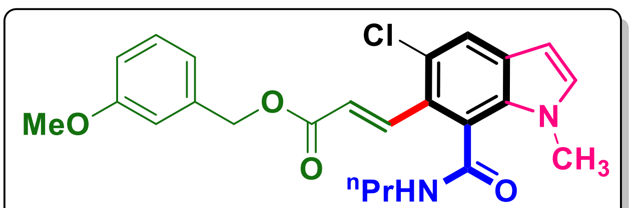


ethyl (*E*)-3-(5-chloro-1-methyl-7-(propylcarbamoyl)-1H-indol-6-yl)acrylate (3r): (mixture of *E/Z* isomer (1:0.2), White solid, Yield = 78% (54 mg); m.p. = 124-126 °C; R_f = 0.3 (Ethyl Acetate/Hexane : 30/70); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.95 (d, J=16.2, 1H), 7.62 (s, 1H), 7.05 (s, 1H), 6.47 – 6.34 (m, 2H), 6.07 (s, 1H), 4.23 (dd, J=13.8, 6.8, 2H), 3.78 (s, 3H), 3.3t (t, J =7.6, 2H), 1.71 – 1.49 (t, J=7.8, 2H), 1.46 – 1.17 (m, 3H), 0.94 (t, J=7.2, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 167.7, 166.7, 140.5, 133.9, 132.7, 131.4, 131.0, 125.0, 123.5, 122.3, 122.1, 100.9, 60.6, 42.2, 34.9, 22.3, 14.4, 11.6; **IR (neat):** 3262, 2963, 2926, 1714, 1628, 1505, 1444, 1263, 1176, 771cm^{-1}; **HRMS-ESI** (*m/z*)**:** Calculated for: $C_{18}H_{21}ClN_2NaO_3$ $[M+Na]^+$: 371.1133; found: 371.1138.



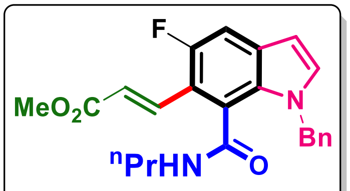
3s

benzyl (*E*)-3-(5-chloro-1-methyl-7-(propylcarbamoyl)-1H-indol-6-yl)acrylate (3s): White solid, Yield = 76% (62 mg); m.p.= 160-162 °C; R_f = 0.5 (Ethyl Acetate/Hexane: 50/50); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.98 (d, *J*=16.1, 1H), 7.59 (s, 1H), 7.49 – 7.26 (m, 5H), 7.02 (s, 1H), 6.44 (d, *J*=16.3, 1H), 6.38 (d, *J*= 5.6, 1H), 6.12 (s, 1H), 5.21 (s, 2H), 3.74 (s, 3H), 3.32 – 3.30 (t, *J* = 7.0, 2H), 1.52 (dd, *J*=14.1, 7.0, 2H), 0.86 (t, *J*=7.0, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 167.6, 166.5, 141.1, 136.2, 134.0, 131.5, 131.0, 128.7, 128.3, 128.2, 125.1, 123.3, 123.0, 122.3, 122.1, 100.9, 66.4, 42.2, 34.9, 22.3, 11.6; **IR (neat):** 3266, 2962, 1716, 1626, 1546, 1219, 1166, 772 cm^{-1}; **HRMS-ESI** (*m/z*)**:** Calculated for: $C_{23}H_{24}ClN_2O_3$ $[M+H]^+$: 411.1473; found: 411.1475.



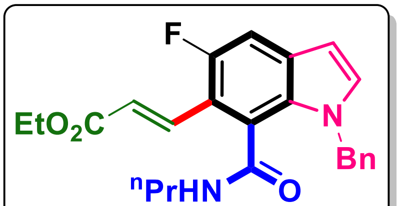
3t

3-methoxybenzyl (*E*)-3-(5-chloro-1-methyl-7-(propylcarbamoyl)-1H-indol-6-yl)acrylate (3t): White solid, Yield = 74% (65 mg); m.p.= 132-134 °C; R_f = 0.3 (Ethyl Acetate/Hexane : 30/70); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 8.02 (d, *J* = 16.2 Hz, 1H), 7.64 (s, 1H), 7.31 – 7.24 (m, 1H), 7.06 (d, *J* = 2.8 Hz, 1H), 7.02 – 6.91 (m, 2H), 6.87 (d, *J* = 8.0 Hz, 1H), 6.50 (d, *J* = 16.2 Hz, 1H), 6.40 (d, *J* = 2.8 Hz, 1H), 5.97 (s, 1H), 5.21 (s, 2H), 3.81 (d, *J* = 9.6 Hz, 6H), 3.35 (t, *J* = 5.6 Hz, 2H), 1.55 (dd, *J* = 6.8, 7.2 Hz, 2H), 0.88 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 167.6, 166.5, 159.9, 141.1, 137.7, 134.0, 131.6, 131.1, 129.7, 125.2, 123.5, 123.1, 122.4, 122.2, 120.5, 113.9, 113.7, 101.0, 66.3, 55.4, 42.3, 35.0, 22.3, 11.6; **IR (neat):** 3269, 3088, 2963, 2857 1714, 1625, 1568, 1508, 1264, 1168, 772 cm^{-1}; **HRMS-ESI** (*m/z*)**:** Calculated for: $C_{24}H_{25}ClN_2NaO_4$ $[M+H]^+$: 463.1401; found: 463.1397.



3u

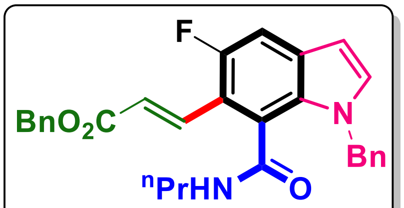
methyl (*E*)-3-(1-benzyl-5-fluoro-7-(propylcarbamoyl)-1H-indol-6-yl)acrylate (3u): (mixture of *E/Z* isomer (1:0.2), White solid, Yield = 75% (62 mg); m.p.= 122-124 ˚C; R_f = 0.3 (Ethyl Acetate/Hexane : 40/60); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.71 (d, *J* = 16.4 Hz, 1H), 7.36 (d, *J* = 12 Hz, 1H), 7.31-7.15 (m, 4H), 6.87 (d, *J* = 6.1 Hz, 2H), 6.62 (d, *J* = 16.2 Hz, 1H), 6.56 (s, 1H), 5.55-5.31 (m, 3H), 3.75 (s, 3H), 3.17- 2.93 (t, *J*=7.5, 2H), 1.31 (dd, *J*=7.7 *J*=7.4, 14.8, 2H), 0.81 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 167.6, 166.9, 157.6, 138.7, 137.2, 134.4, 131.7, 128.9, 128.4, 127.6, 125.7, 122.3 (d, *J*=14.5), 117.0, 115.0, 107.6 (d, *J*= 24.9), 102.6, 51.7, 51.1, 42.3, 22.2, 11.5; **IR (neat):** 3287, 2962, 1711, 1628, 1542, 1433, 1265, 1166,772 cm^{-1}; **HRMS-ESI** (*m/z*)**:** Calculated for: $C_{23}H_{23}FKN_2O_3$ $[M+K]^+$: 433.1324; found: 433.1310.



3v

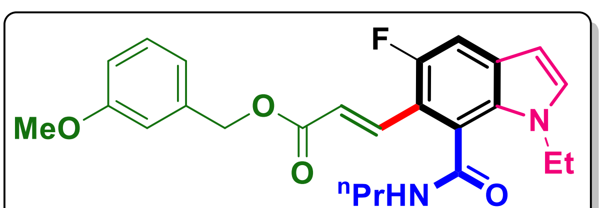
ethyl (*E*)-3-(1-benzyl-5-fluoro-7-(propylcarbamoyl)-1H-indol-6-yl)acrylate (3v): White solid, Yield = 72% (62 mg); m.p.= 128-130 ˚C; R_f = 0.3 (Ethyl Acetate/Hexane : 30/70); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.67 (d, *J* = 16.0 Hz, 1H), 7.34 (d, *J* = 11.6 Hz, 1H), 7.27 – 7.10 (m, 4H), 6.86 (d, *J* = 6.8 Hz, 2H), 6.64-6.48 (m, 2H), 5.60 (s, 1H), 5.42 (s, 2H), 4.18 (dd, *J* = 6.8, 6.8 Hz, 2H), 3.30-2.64 (t, *J*=7.2, 2H), 1.40 – 1.22 (dt, *J*=7.1, *J*=6.5 5H), 0.81 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR (101**

MHz, CDCl3) δ = 167.2, 166.9, 157.4, 138.6, 136.8, 134.3, 131.7, 128.9, 128.4, 127.5, 125.7, 123.2, 122.8, 115.0, 107.7, 102.6, 60.5, 51.0, 42.2, 22.2, 14.4, 11.5; **IR (neat):** 3291, 2929, 1705, 1604, 1538, 1264, 1166, 1035, 725 cm^{-1}; **HRMS-ESI** (*m/z*)**:** Calculated for: $C_{24}H_{25}FN_2NaO_3$ $[M+Na]^+$: 431.1742; found: 431.1738.



3w

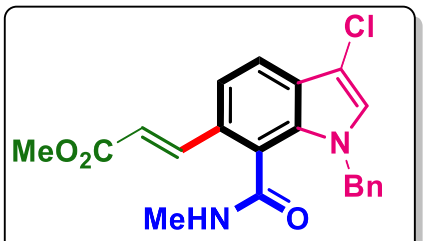
benzyl-3-(1-benzyl-5-fluoro-7-(propylcarbamoyl)-1H-indol-6-yl)acrylate (3w): (mixture of *E/Z* isomer (1:0.2), White solid, Yield 70% (69 mg); m.p.= 124-126 °C; R_f = 0.4 (Ethyl Acetate/Hexane : 40/60); **^{1}H NMR (400 MHz, CDCl3)** δ = 7.73 (d, *J* = 16.0 Hz, 1H), 7.38-7.15 (m, 10H), 6.85 (d, *J* = 6 Hz, 2H), 6.66 (d, *J* = 16.4 Hz, 1H), 6.55 (s, 1H), 5.57-5.34 (m , 3H), 5.19 (s, 2H), 3.28-2.61 (m, 2H), 1.33-1.15(m, 2H), 0.73 (t, *J* = 6.4 Hz, 3H); **^{13}C NMR (101 MHz, CDCl3)** δ = 167.0, 166.8, 157.4, 138.6, 137.4, 136.2, 134.4, 131.7 (d, *J*=10.5), 128.9, 128.8, 128.6, 128.4, 128.3, 128.2, 128.1, 127.5, 125.7, 122.9 (d, *J*=14.7), 107.6 (d, *J*=24.7), 102.6 (d, *J*=4.8), 66.3, 51.0, 42.3, 22.1, 11.5; **IR (neat):** 3228, 2966, 2925, 1687, 1651, 1530, 1425, 1298, 1249, 1164, 772 cm^{-1}; **HRMS-ESI** (*m/z*)**:** Calculated for: $C_{29}H_{27}FN_2NaO_3$ $[M+Na]^+$: 493.1903; found: 493.1898.



3x

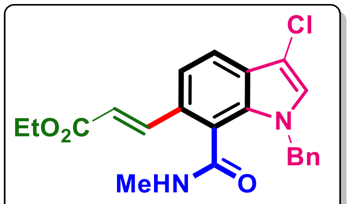
3-methoxybenzyl (*E*)-3-(1-ethyl-5-fluoro-7-(propylcarbamoyl)-1H-indol-6-yl)acrylate (3x):

White solid, Yield = 69% (63 mg); m.p.= 140-142 $^{\circ}$C; R_f = 0.3 (Ethyl Acetate/Hexane : 30/70); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.76 (d, *J* = 15.6 Hz, 1H), 7.33-7.22 (m, 2H), 7.19 (s, 1H), 7.03-6.90 (m, 2H), 6.87 (d, *J* = 5.6 Hz, 1H), 6.65 (d, *J* = 16 Hz, 1H), 6.46 (s, 1H), 6.28 (s, 1H), 5.16 (s, 2H), 4.25-4.05 (m, 2H), 3.82 (s, 3H), 3.42 (t, *J* = 6.4 Hz, 2H), 1.70-1.54 (m, 2H), 1.34 (t, *J* = 7.0 Hz, 3H), 0.95 (t, *J* = 6.4 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 167.4, 167.1, 159.8, 157.2, 154.8, 137.8, 137.6, 132.5, 131.5, 129.7, 128.1, 123.0, 121.8, 120.4, 114.2, 113.6, 107.2, 102.2, 66.2, 55.4, 42.4, 42.2, 22.5, 16.6, 11.6; **IR (neat):** 3259, 2959, 2933, 1698, 1633, 1587, 1263, 1158 cm^{-1}; **HRMS-ESI** (*m/z*)**:** Calculated for $C_{25}H_{28}FN_2O_4$ $[M+H]^+$: 439.2034; found : 439.2028.



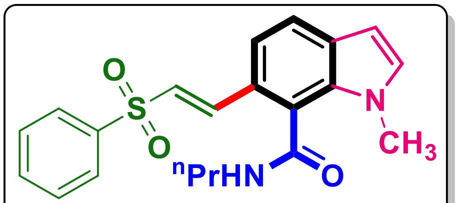
3y

methyl-3-(1-benzyl-3-chloro-7-(methylcarbamoyl)-1H-indol-6-yl)acrylate (3y): (mixture of *E/Z* isomer (1:0.3), White solid, Yield = 89% (69 mg); m.p.= 156-158 $^{\circ}$C; R_f = 0.4 (Ethyl Acetate/Hexane : 30/70); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.71(d, *J*=15.9, 1H), 7.62 (d, *J*=8.4, 1H), 7.46 (d, *J*=8.3, 1H), 7.29-7.22 (m, 5H), 6.83 (d, *J*=6.9, 2H), 6.38 (d, *J*=15.7, 1H), 5.56 (s, 2H), 5.39 (s, 1H), 3.73 (s, 3H), 2.55 (d, *J*=4.7, 3H); **^{13}C NMR (126 MHz, DMSO)** δ = 167.0, 166.6, 141.9, 137.3, 130.3, 129.0, 127.6, 126.7, 126.5, 126.4, 125.7, 124.7, 119.6, 118.9, 118.3, 103.4, 52.0, 48.9, 26.2; **IR (neat):** 3406, 2956, 2921, 2852, 1698, 1651, 1599, 1448, 1243, 1026 cm^{-1}; **HRMS-ESI** (*m/z*)**:** Calculated for: $C_{21}H_{19}ClN_2KO_3$ $[M+K]^+$: 421.0721; found: 421.0716.



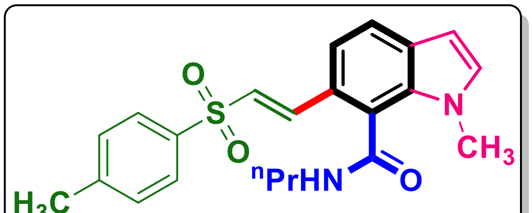
3z

ethyl-3-(1-benzyl-3-chloro-7-(methylcarbamoyl)-1H-indol-6-yl)acrylate (3z): (mixture of *E/Z* isomer (1:0.2), White solid, Yield = 85% (68 mg); m.p. = 146-148 °C; R_f = 0.4 (Ethyl Acetate/Hexane : 40/60); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.71 (d, *J*=15.8, 1H), 7.64 (d, *J*=7.5, 1H), 7.48 (d, *J*=7.5, 1H), 7.37 – 7.13 (m, 4H), 6.88 (d, *J*= 7.5, 2H), 6.39 (d, *J*=16.0, 1H), 5.57 (s, 2H), 5.42 (s, 1H), 4.25 – 4.13 (m, 2H), 2.56 (s, 3H), 1.31 (t, *J*= 7.0, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 167.5, 166.7, 141.6, 137.5, 129.9, 128.9, 127.5, 127.4, 127.3, 126.5, 124.9, 122.8, 119.8, 119.3, 119.0, 104.5, 60.6, 48.0, 26.8, 14.4; **IR (neat):** 3352, 2925, 1697, 1661, 1545, 1513, 1291, 1173, 772 cm^{-1}; **HRMS-ESI** (*m/z*)**:** Calculated for: $C_{22}H_{21}ClN_2NaO_3$ $[M+Na]^+$: 419.1138; found: 419.1131.



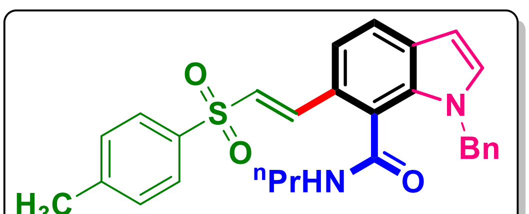
5a

1-methyl-6-(2-(phenylsulfonyl)vinyl)-*N*-propyl-1H-indole-7-carboxamide (5a): (mixture of *E/Z* isomer (1:0.2), White solid Yield = 77% (59 mg); m.p.= 130-132 °C; R_f = 0.3 (Ethyl Acetate/Hexane : 30/70); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.83 (d, *J*=15.4, 1H), 7.78 (d, *J*=7.8, 1H), 7.56 (d, *J*=8.6, 1H), 7.31 (d, *J*=7.8, 2H), 7.21 (d, *J*=8.4, 1H), 7.07 (d, *J*=17.8, 1H), 6.80 (d, *J*=15.2, 1H), 6.46 (d, *J*=23.0, 1H), 6.11 (s, 1H), 3.83 (s, 3H), 3.50 (t, *J*=6.7, 2H), 1.78 – 1.68 (dd, *J*=7.2, *J*=6.8, 2H), 1.04 (t, *J*=7.3, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 167.7, 141.1, 140.6, 133.6, 133.3, 132.3, 132.1, 129.4, 127.7, 127.1, 123.4, 122.9, 122.3, 117.7, 102.0, 42.3, 35.0, 22.8, 11.8; **IR (neat):** 3230, 2925, 1634, 1593, 1445, 1285, 1138 cm^{-1}; **HRMS-ESI** (*m/z*)**:** Calculated for: $C_{21}H_{22}N_2NaO_3S$ $[M+Na]^+$: 405.1249; found: 405.1239.



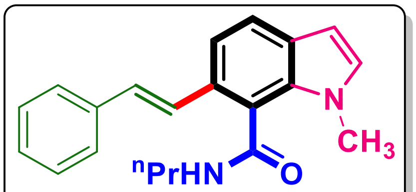
5b

1-methyl-*N*-propyl-6-(2-tosylvinyl)-1H-indole-7-carboxamide (5b): (mixture of *E/Z* isomer (1:0.2), White solid Yield = 81% (64 mg); m.p.= 138-140 ˚C; R_f = 0.3 (Ethyl Acetate/Hexane : 30/70); **^{1}H NMR (400 MHz, $CDCl_3$)** (major isomer) δ = 7.83 (d, *J*=15.4, 1H), 7.78 (d, *J*=7.8, 2H), 7.56 (d, *J*=8.6, 1H), 7.31 (d, *J*=7.8, 2H), 7.21 (d, *J*=8.4, 1H), 7.07 (d, *J*= 7.6, 1H), 6.80 (d, *J*=15.2, 1H), 6.46 (d, *J*= 7.6, 1H), 6.11 (s, 1H), 3.83 (s, 3H), 3.50 (t, *J*=7.7 , 2H), 2.42 (s, 3H), 1.78 – 1.68 (m, 2H), 1.04 (t, *J*= 7.3, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 167.7, 144.3, 140.1, 133.5, 132.2, 130.0, 129.8, 128.0, 127.8, 127.5, 123.1, 123.0, 122.1, 117.7, 101.9, 42.3, 35.0, 22.8, 21.7, 11.9; **IR (neat):** 3233, 2925, 2873, 1634, 1590, 1430, 1229, 1128 cm^{-1}; **HRMS-ESI** (*m/z*)**:** Calculated for: $C_{22}H_{25}N_2O_3S$ $[M+H]^+$: 397.1582; found: 397.1575.



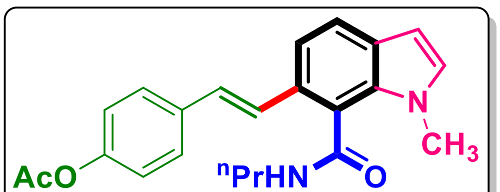
5c

1-benzyl-*N*-propyl-6-(2-tosylvinyl)-1H-indole-7-carboxamide (5c): (mixture of *E/Z* isomer), White solid, Yield = 75 % (71 mg); m.p.= 166-168 ˚C; R_f = 0.4 (Ethyl Acetate/Hexane : 40/60); **^{1}H NMR (400 MHz, $CDCl_3$)** (major isomer) δ = 7.83 – 7.70 (m, 3H), 7.63 (d, *J*=8.4, 1H), 7.31-7.21 (m, 6H), 7.17 (d, *J*=3.0, 1H), 6.87 (d, *J*=6.6, 2H), 6.80 (d, *J*=15.2, 1H), 6.60 (d, *J*=3.1, 1H), 5.53 – 5.43 (t, 3H), 2.47-2.28 (m, 2H), 2.41 (s, 3H), 1.36 (dd, *J*=14.8, 7.4, 2H), 0.85 (t, *J*=7.3, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 167.4, 144.3, 140.1, 138.6, 133.2, 131.5, 130.4, 130.0, 128.9, 128.2, 127.8, 127.7, 127.6, 125.8, 123.6, 123.4, 122.5, 118.0, 102.9, 51.1, 42.4, 22.3, 21.7, 11.7; **IR (neat):** 3247, 2929, 1633, 1504, 1399, 1288, 1142,1082 cm^{-1}; **HRMS-ESI** (*m/z*)**:** Calculated for: $C_{28}H_{29}N_2O_3S$ $[M+H]^+$: 473.1893; found: 473.1886.



5d

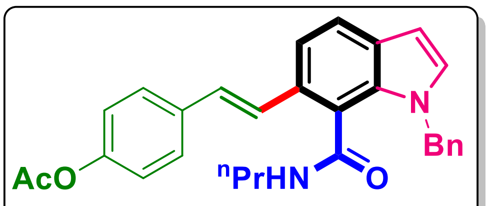
1-methyl-*N*-propyl-6-styryl-1H-indole-7-carboxamide (5d): (mixture of *E/Z* isomer 1:0.3), White solid, Yield = 56% (36 mg); m.p.= 156-158 °C; R_f = 0.3 (Ethyl Acetate/Hexane : 30/70); **^{1}H NMR (500 MHz, $CDCl_3$)** (major isomer) δ = 7.60 (d, *J*=15.4, 1H), 7.49 (d, *J*=7.5, 2H), 7.45 (d, *J*=8.4, 1H), 7.38 – 7.29 (m, 3H), 7.24 (d, *J*=6.9, 1H), 7.08 (t, *J*=3.5, 1H), 7.00 (d, *J*=3.0, 1H), 6.47 (d, *J*=3.0, 1H), 5.99 (s, 1H), 3.83 (s, 3H), 3.53 (t, *J*=7.2 2H),1.66-1.58 (dt, *J*=7.2, 8.1 2H), 0.98 (t, *J*= 7.9, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 169.3, 138.6, 137.8, 131.7, 129.7, 128.8, 127.6, 126.6, 126.4, 125.8, 124.0, 122.1, 116.9, 112.3, 101.6, 42.1, 34.9, 23.0, 11.7; **IR (neat):** 3258, 2927, 2832, 1675, 1610, 1536, 1236 cm^{-1}; **HRMS-ESI** (*m/z*)**:** Calculated for: $C_{21}H_{23}N_2O$ $[M+H]^+$: 319.1805; found: 319.1797.



5e

(*E*)-4-(2-(1-methyl-7-(propylcarbamoyl)-1H-indol-6-yl)vinyl)phenyl acetate (5e): White solid Yield = 68% (51 mg); m.p.= 150-152 °C; R_f = 0.3 (Ethyl Acetate/Hexane : 40/60); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.61 (d, *J*=8.4, 1H), 7.49 (d, *J*=8.5, 2H), 7.44 (d, *J*=8.4, 1H), 7.29 (s, *J*=8.7, 1H), 7.13 – 7.05 (m, 3H), 7.01 (d, *J*=2.9, 1H), 6.48 (d, *J*=3.0, 1H), 5.97 (s, 1H), 3.84 (s, 3H), 3.52

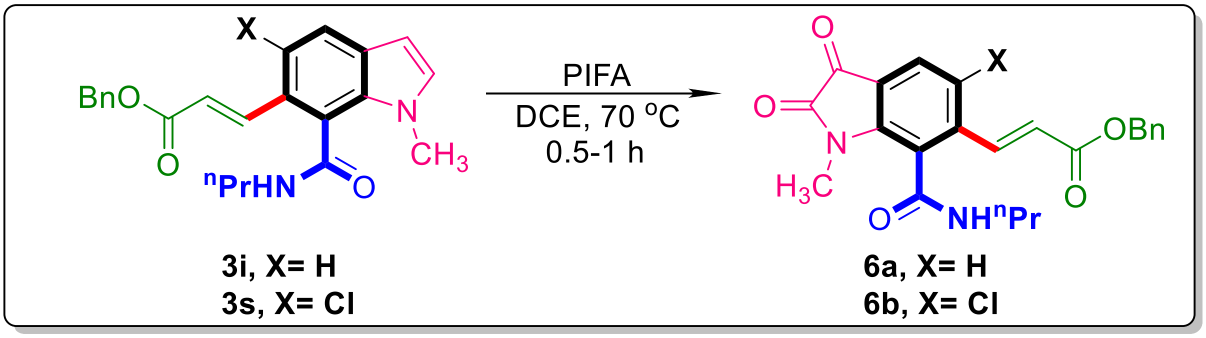
(dd, *J*=13.2, 6.8, 2H), 2.31 (s, 3H), 1.75 – 1.65 (m, 2H), 0.98 (t, *J*= 7.4, 3H); **^{13}C NMR (126 MHz, CDCl$_3$)** δ = 169.6, 169.9, 150.1, 135.6, 132.5, 131.7, 129.8, 128.6, 128.3, 127.5, 126.6, 122.1, 121.9, 120.8, 116.9, 101.6, 42.1, 34.9, 23.0, 21.3, 11.7; **IR (neat):** 3276, 2922, 2853, 1760, 1623, 1546, 1435, 1218, 1191cm^{-1}; **HRMS-ESI** (*m/z*)**:** Calculated for: $C_{23}H_{24}N_2NaO_3$ [M+Na]$^+$: 399.1685; found: 399.1681



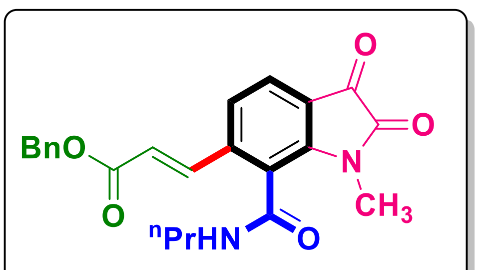
5f

4-(2-(1-benzyl-7-(propylcarbamoyl)-1H-indol-6-yl)vinyl)phenyl acetate (5f): (mixture of *E/Z* isomer 1:0.2), White solid, Yield = 56% (50 mg); m.p.= 148-150 °C; R$_f$ = 0.3 (Ethyl Acetate/Hexane : 40/60); **^{1}H NMR (400 MHz, CDCl$_3$)** δ = 7.66 (d, *J*=8.3, 1H), 7.49 – 7.42 (m, 2H), 7.25 – 7.16 (m, 5H), 7.12 – 7.01 (m, 4H), 6.90 (d, *J*=6.7, 2H), 6.60 (d, *J*=3.1, 1H), 5.48 (s, 2H), 5.43 (s, 1H), 3.13 – 3.01 (t, *J*= 7.2, 2H), 2.29 (s, 3H), 1.38 – 1.18 (m, 2H), 0.76 (t, *J*= 7.4, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ = 169.6, 168.8, 150.1, 139.2, 135.5, 131.8, 131.4, 130.1, 128.8, 128.7, 128.6, 127.4, 127.3, 126.7, 125.8, 122.3, 121.9, 121.0, 117.2, 102.6, 50.9, 42.1, 22.4, 21.3, 11.6; **IR (neat):** 3323, 2942, 2854, 1721, 1670, 1552, 1267, 1142cm^{-1}; **HRMS-ESI** (*m/z*)**:** Calculated for: $C_{29}H_{28}N_2NaO_3$ [M+Na]$^+$: 475.1994; found: 475.1987.

6. Preparation of isatin derivatives of alkenyl indole-7-carboxamides (6):

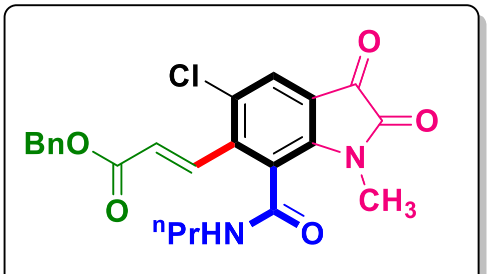


Compounds **3i** (75 mg, 0.2 mmol) was taken in a 10 mL oven dried Schlenk tube which was equipped with a magnetic stirrer in 1,2-dichloroethane (DCE) (2 mL). Then added (Bis(trifluroacetoxy)iodo) benzene (172 mg, 0.4 mmol). Then reaction mixture was stirred vigorously for 1 hour at 70 °C. After completion of reaction (monitored by TLC) the reaction mixture was filtered through Celite and the filtrate was concentrated. The crude product was purified by column chromatography (ethyl acetate/pet. ether 60%) to give the product **6a** as a yellow solid. Compound **6b** was also prepared by following similar procedure.



6a

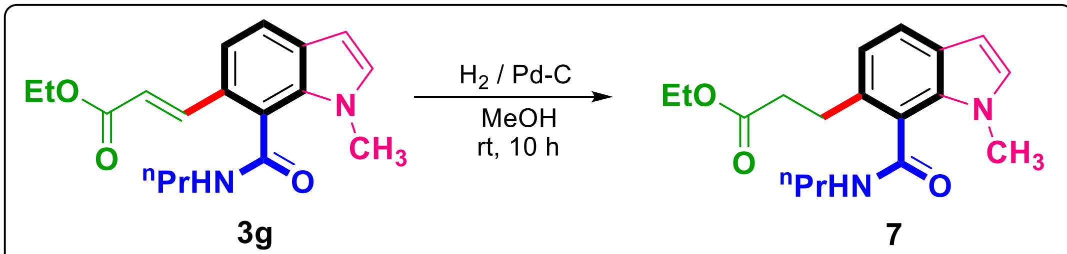
benzyl (*E*)-3-(1-methyl-2,3-dioxo-7-(propylcarbamoyl)indolin-6-yl)acrylate (6a): White solid, Yield = 68% (55 mg); m.p. =158-160 °C; R_f = 0.3 (Ethyl Acetate/Hexane: 50/50); **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 7.72 (d, *J*=15.9, 1H), 7.49 (d, *J*=7.9, 1H), 7.40 – 7.35 (m, 5H), 7.30 (d, *J*=7.9, 1H), 6.54 (d, *J*=15.9, 1H), 5.24 (s, 2H), 3.43 (t, *J*=7.3 Hz, 2H), 3.29 (s, 3H), 1.65 (dt, *J*=14.4, 7.2, 2H), 0.97 (t, *J*= 7.4, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 181.8, 165.4, 165.2, 158.6, 147.9, 142.1, 139.9, 135.6, 128.8, 128.6, 128.5, 125.6, 124.7, 122.6, 122.1, 118.1, 67.1, 42.3, 27.5, 22.6, 11.6; **IR (neat):** 3264, 2961, 2924, 2853, 1739, 1739, 1633, 1545, 1439, 1254, 1156, 754 cm^{-1}; **HRMS-ESI** (*m/z*)**:** Calculated for: $C_{23}H_{23}N_2O_5$ $[M+H]^+$: 407.1607; found: 407.1604.



6b

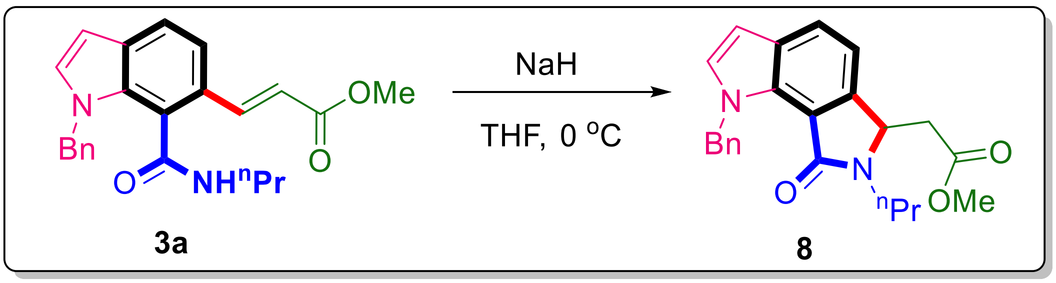
benzyl (*E*)-3-(5-chloro-1-methyl-2,3-dioxo-7-(propylcarbamoyl)indolin-6-yl)acrylate (6b): White solid, Yield =74% (65 mg); m.p. =138-140 °C; R_f = 0.3 (Ethyl Acetate/Hexane: 50/50); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.70 (d, *J*=16.3, 1H), 7.50 (s, 1H), 7.42 – 7.31 (m, 6H), 6.51 (d, *J*=16.1, 1H), 5.24 (s, 2H), 3.30-3.26 (t, *J*=7.3 2H), 3.26 (s, 3H), 1.54 (dt, *J*=8.3, 7.3, 2H), 0.88 (t, *J*=7.3, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 181.2, 165.3, 164.5, 158.1, 145.9, 140.5, 138.1, 135.6, 129.5, 128.8, 128.6, 128.5, 127.6, 126.3, 123.2, 118.5, 67.1, 42.3, 27.5, 22.1, 11.5; **IR (neat):** 3300, 3033, 2964, 2876, 1739, 1717, 1639, 1601, 1538, 1266, 1167, 779 cm^{-1}; **HRMS-ESI** (*m/z*)**:** Calculated for: $C_{23}H_{21}ClKN_2O_5$ $[M+K]^+$: 479.0771; found : 479.0774.

7. Preparation of ethyl 3-(1-methyl-7-(propylcarbamoyl)-1H-indol-6-yl) propanoate (7):



To a stirred solution **3g** (0.1 mmol) in methanol (4 mL) was added 10% Pd/C. Then hydrogen gas passed in the solution by using hydrogen balloon. Then reaction mixtures were stirred vigorously for 10 h at room temperature. After completion of reaction the reaction mixture was filtered through a Celite pad and the filtrate was concentrated. The crude product was purified by column chromatography (silica flash, ethyl acetate/pet. ether 20%) to obtain the product **7** as a white solid. Yield =84% (27 mg); m.p. = 96-98°C; R_f = 0.5 (Ethyl Acetate/Hexane: 20/80); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.53 (d, *J*=8.0, 1H), 7.00 – 6.87 (m, 2H), 6.64 (s, 1H), 6.42 (d, *J*= 3.0, 1H), 4.07 (dd, *J*=13.1, 6.3, 2H), 3.80 (s, 3H), 3.59 – 3.35 (m, 2H), 3.04 (t, *J*=10.9, 2H), 2.74 (t, *J*=7.1, 2H), 1.74 – 1.62 (m, 3H), 1.20 (t, *J*=7.0, 3H), 1.01 (t, *J*= 7.1, 3H); ^{13}C **NMR (126 MHz, $CDCl_3$)** δ = 173.5, 169.4, 132.5, 130.8, 130.4, 128.6, 121.9, 121.3, 120.0, 101.0, 60.6, 41.9, 36.2, 34.7, 27.7, 22.8, 14.3, 11.8; **IR (neat):** 3456, 2967, 1645, 1634, 1565, 1253, 1148 cm^{-1}; **HRMS-ESI** (*m/z*)**:** Calculated for: $C_{18}H_{24}N_2NaO_3$ $[M+Na]^+$: 339.1685; found: 339.1678.

8. Preparation of methyl 2-(1-benzyl-8-oxo-7-propyl-1,6,7,8-tetrahydropyrrolo[3,4-g]indol-6-yl)acetate (8):



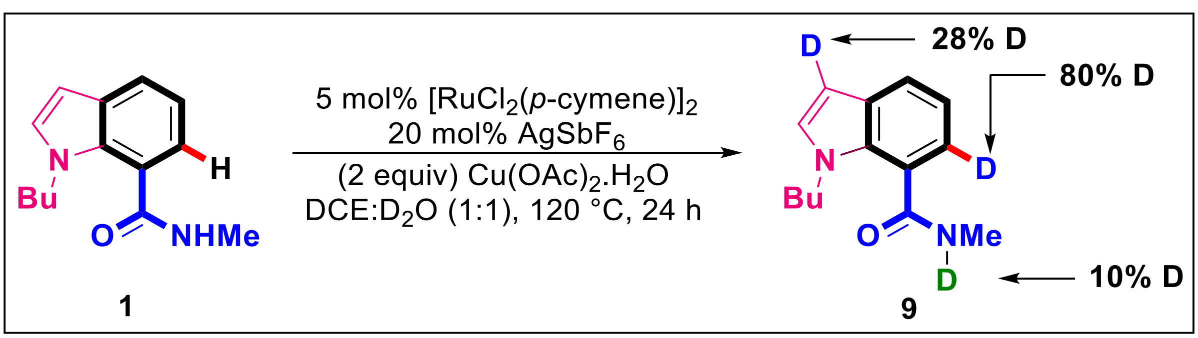
To a well stirred solution of Methyl (*E*)-3-(1-benzyl-7-(propylcarbamoyl)-1H-indol-6-yl)acrylate (38 mg, 1 equiv) in dry THF (2 mL) at 0 ºC was added sodium hydride (60% in mineral oil, 1.1 equiv) under N_2 atmosphere. Then reaction mixtures were stirred for 10-15 minutes at 0°C. After completion of reaction (Monitored by TLC), quenched with saturated aqueous NH_4Cl. The product was extracted with diethyl ether (3 x 5 mL) and dried over anhydrous Na_2SO_4. The organic phase was concentrated in vacuum to obtain the crude mixture which was further purified by column chromatography (using 10% ethyl acetate/hexane) giving a white solid with 72% (27 mg) yield**.** m.p. =120-122°C; R_f = 0.5 (Ethyl Acetate/Hexane: 20/80); **^{1}H NMR (400 MHz, $CDCl_3$) δ** = 7.77

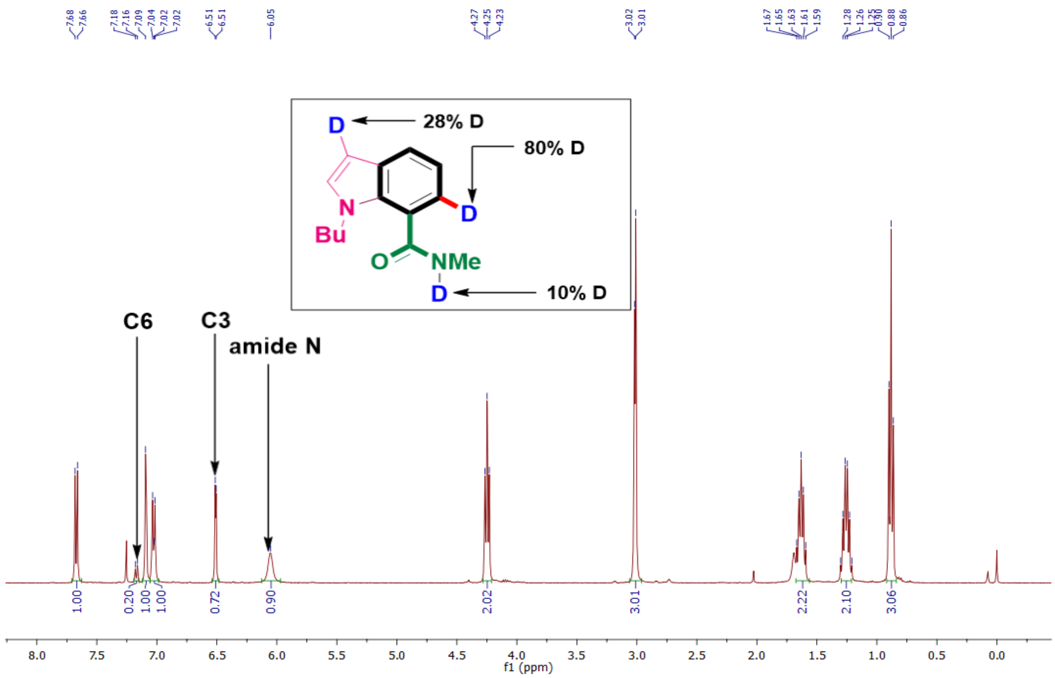
(d, J = 8.1 Hz, 1H), 7.32 – 7.01 (m, 7H), 6.62 (d, J = 3.2 Hz, 1H), 6.43 (d, J = 16 Hz, 1H), 6.22 (d, J = 8.1 Hz, 1H), 5.04 (t, J = 6.0 Hz, 1H), 3.92 (dt, J = 16.2, 8.1 Hz, 1H), 3.72 (s, 3H), 3.10 (ddd, J = 4.8, 4,8, 4.1 Hz, 1H), 2.85 (dd, J = 6.0, 5.6 Hz, 1H), 2.79 – 2.70 (dd, J = 6.0,6.0, 1H), 1.74 – 1.52 (m, 2H), 0.93 (t, J = 7.4 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 171.5, 168.2, 141.8, 139.7, 132.4, 130.2, 128.7, 128.6, 128.5, 127.2, 125.2, 116.4, 113.2, 103.7, 56.5, 53.6, 52.2, 42.2, 38.7, 21.8, 11.5; **IR (neat):** 1733, 1671, 1605, 1519, 1451, 1259, 1154 cm^{-1}; **HRMS-ESI** (*m/z*)**:** Calculated for: $C_{23}H_{24}N_2NaO_3$ $[M+Na]^+$: 399.1685; found: 399.1681

9. Mechanistic Studies:

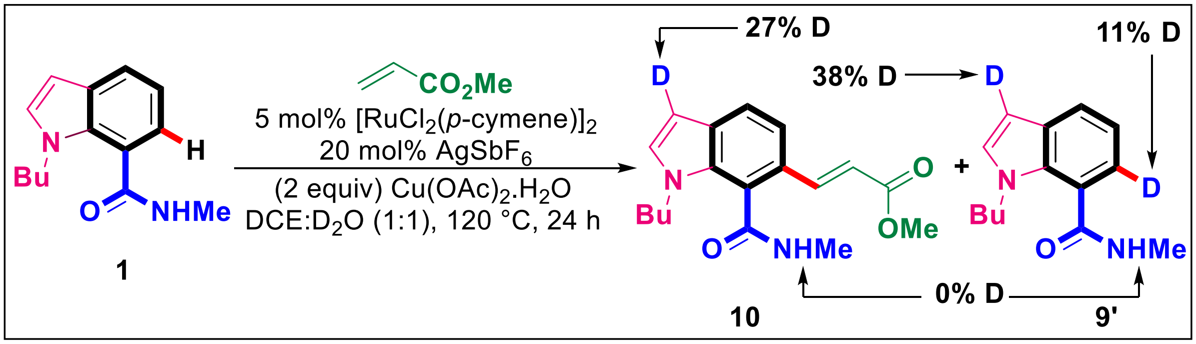
9.1 Deuterium labeling experiments:

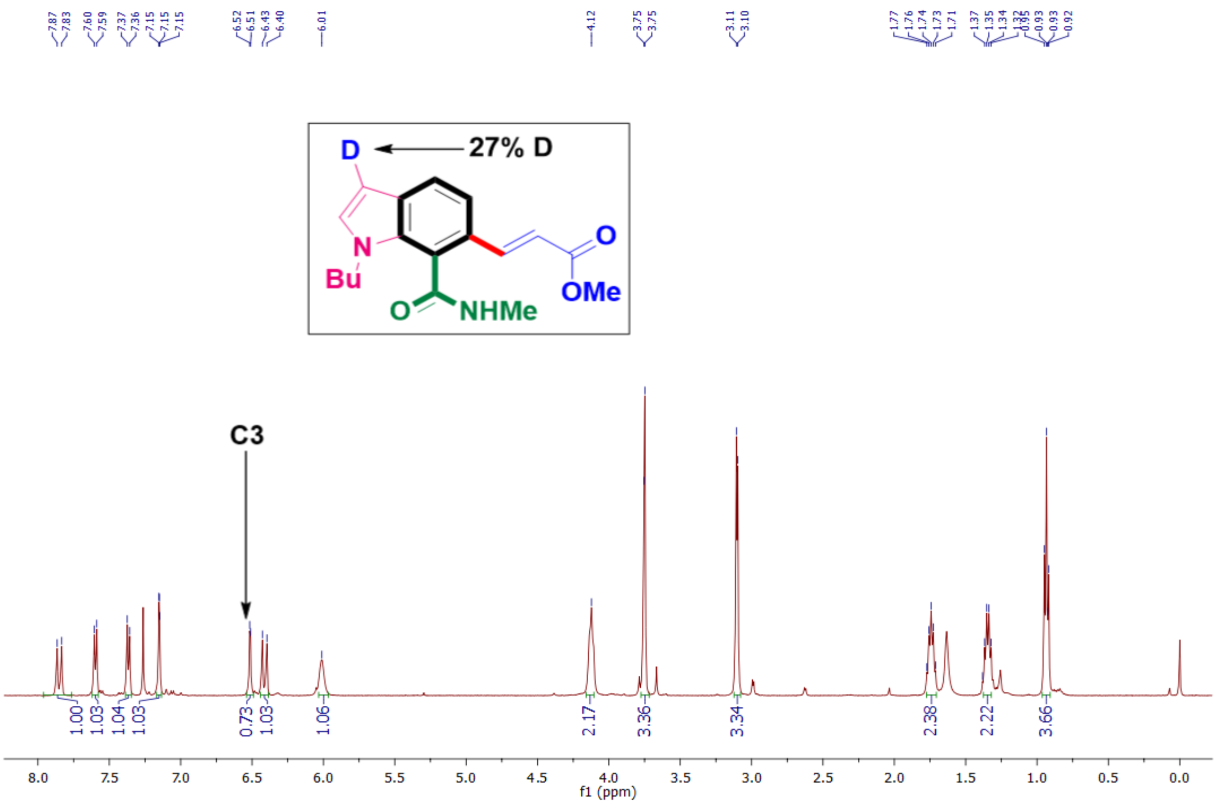
In an oven dried screw cap Schlenk tube equipped with stir bar was purged with nitrogen was charged with 1-butyl-N-methyl-1H-indole-7-carboxamide (0.1 mmol), $[RuCl_2(p\text{-cymene})]_2$ (5 mol%), $AgSbF_6$ (20 mol%), $Cu(OAc)_2{\cdot}H_2O$ (2 equiv). The tube was purged with nitrogen followed by addition of DCE and D_2O (1:1) 2 mL *via* syringe. The reaction mixture allowed to stir at 120 °C for 24 h. Then the reaction mixture was cooled to room temperature, and the solvents were removed under vacuum. The residue was purified by silica gel column chromatography using ethyl acetate: pet. ether as eluent to afford the deuteriated indole **9** in 88 % yield. Analysis of **9** by ^{1}H NMR shows that the C6, C3 positions of indole results in 80% and 28% of deuterium incorporation. The amide nitrogen also results in 10% deuterium incorporation.

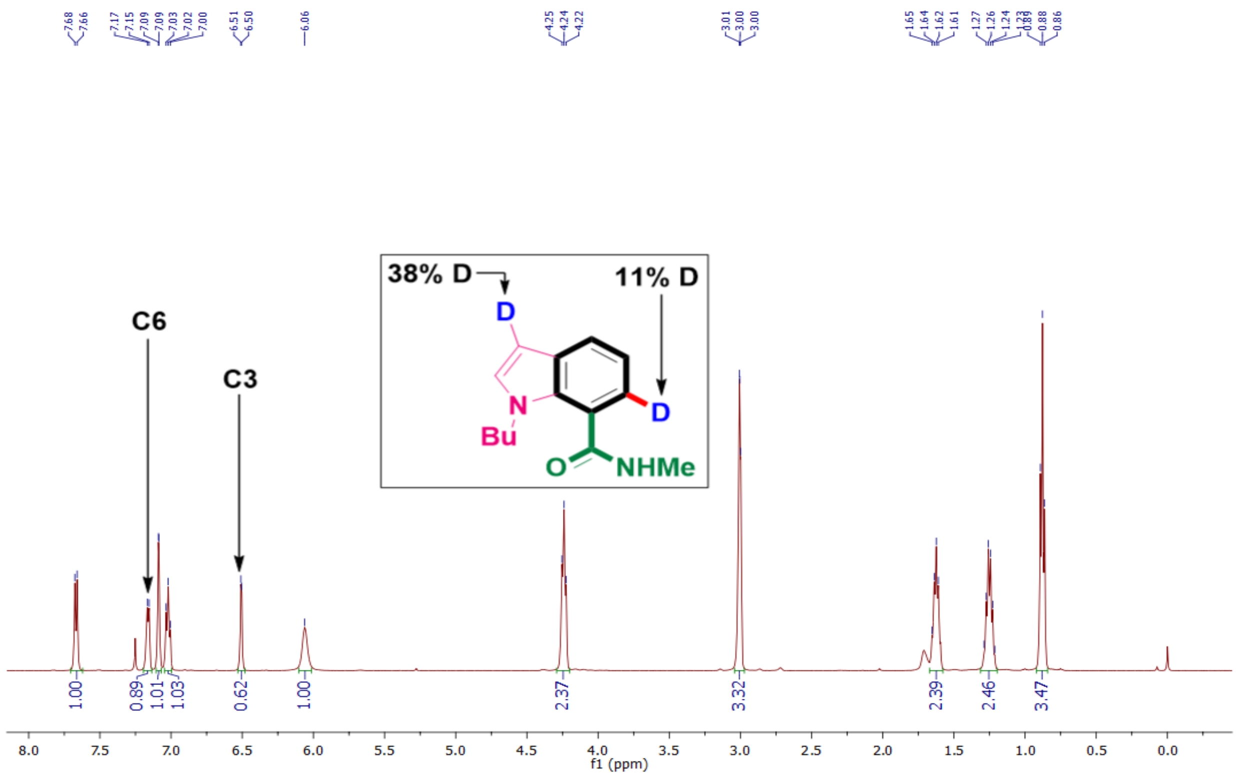




In an oven dried screw cap Schlenk tube equipped with stir bar was purged with nitrogen was charged with 1-butyl-N-methyl-1H-indole-7-carboxamide (0.1 mmol), methyl acrylate (0.15 mmol), $[RuCl_2(p\text{-cymene})]_2$ (5 mol%), $AgSbF_6$ (20 mol%), $Cu(OAc)_2{\cdot}H_2O$ (2 equiv). The tube was purged with nitrogen followed by addition of DCE and D_2O (1:1) 2 mL *via* syringe. The reaction mixture allowed to stir at 120°C for 24 h. The solution was then cooled to room temperature, and the solvents were removed under vacuum. The residue was purified by silica gel column chromatography using ethyl acetate: pet. ether as eluent to afford C6 alkenyl indole **10** and the non-alkenyl indole **9’** in 21% and 61% yield respectively. The compound **10** and **9’** were analyzed by ^{1}H NMR. The analysis shows that the C6 alkenyl indole contains 27% deuterium incorporation at C3-position while **9’** shows 11% and 38% deuterium incorporation at C6 and C3. However, in both **9’** and **10** no deuterium incorporation observed at amide nitrogen.


5 mol% [RuCl2(p-cymene)]2
20 mol% AgSbF6
(2 equiv) Cu(OAc)2.H2O
DCE:D2O (1:1), 120 °C, 24 h
1
10
9'
27% D
38% D
11% D
0% D


27% D
C3
f1 (ppm)



9.2 Identification of intermediates by HRMS analysis:

In an oven-dried 10-mL glass tube with a screw cap containing benzyl (*E*)-3-(1-benzyl-7-(propylcarbamoyl)-1H-indol-6-yl) **1a** (1.0 equiv), benzyl acrylate (1.5 equiv), was evacuated and purged with nitrogen gas. To the tube, were then added [Ru(*p*-cymene)Cl_2]$_2$ (1.0 equiv), $Cu(OAc)_2.H_2O$ (2.0 equiv), $AgSbF_6$ (1.0 equiv) and DCE (1.0 mL) via syringes and again the reaction mixture was evacuated and purged with nitrogen. Then, the reaction mixture was allowed to stir at 120°C. After 10 minute reaction mixture filtered through Celite and the filtrate was diluted with acetonitrile and subjected for LCMS analysis using maXis impact Bruker instrument without any further purification. The LC-MS graph obtained clearly indicates the formation of intermediate **ll, lll** and product **3d.**

Intermediates	**Formula**	**Calculated**	**Observed**
ll	$C_{29}H_{33}N_2ORu^+$	527.1631	527.1626
lll	$C_{39}H_{43}N_2O_3Ru^+$	689.2312	689.2266

3d (Product)	$C_{29}H_{29}N_2O_3$ $[M+H]^+$	453.2173	453.2154

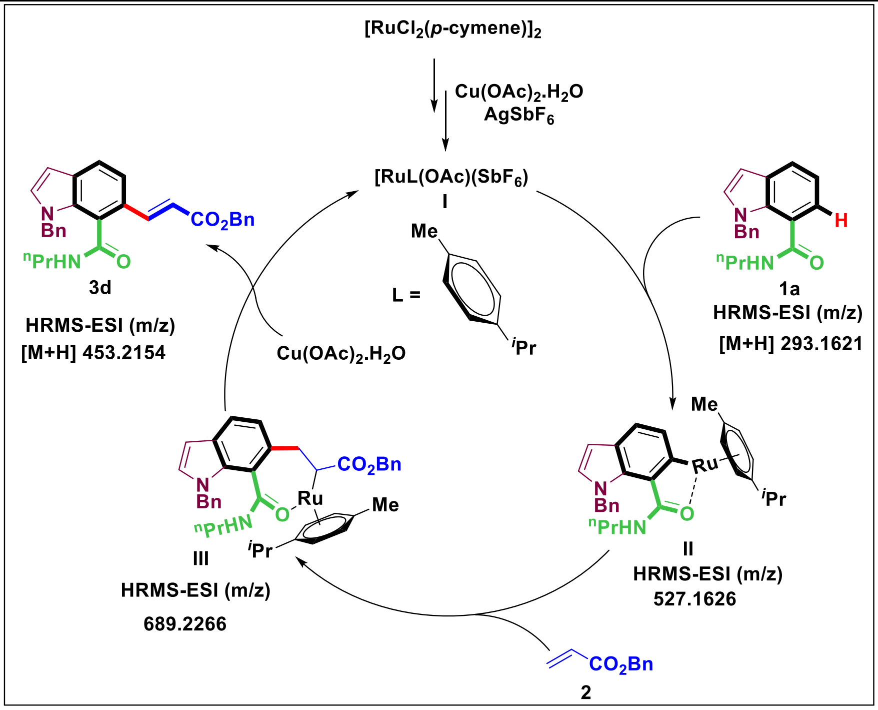
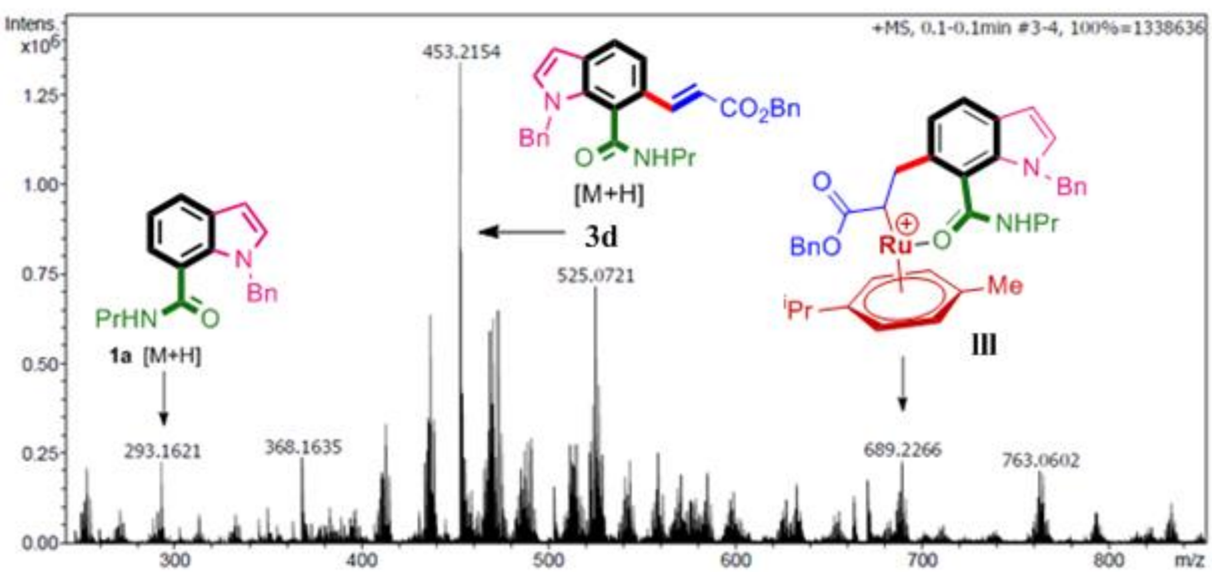
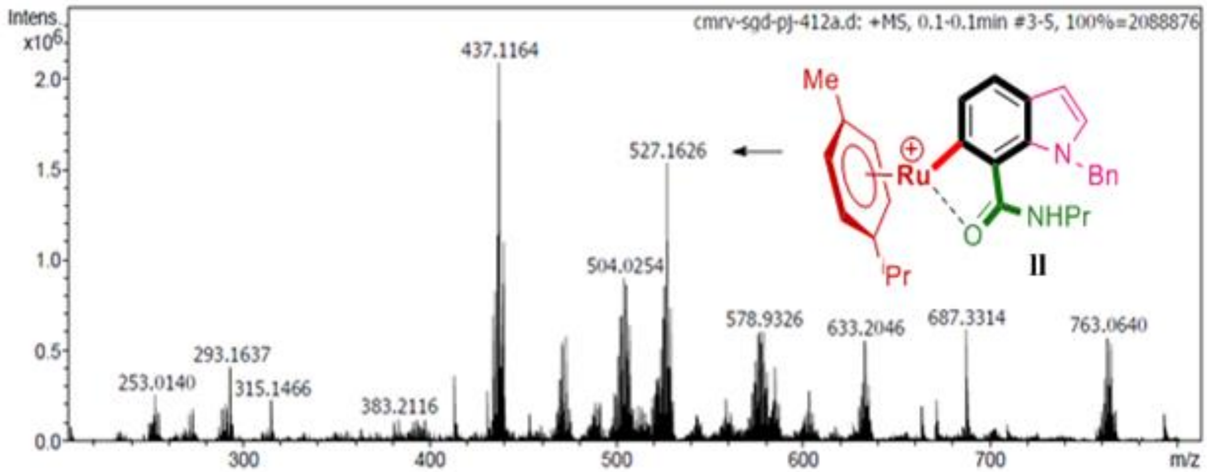
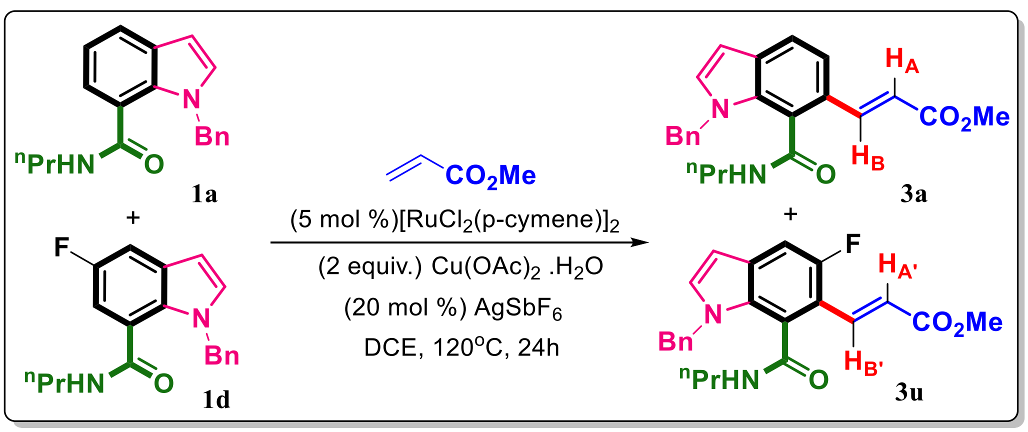


Fig: Plausible mechanism for Ru (II) catalysed C6 alkenylation of indole-7-carboxamide

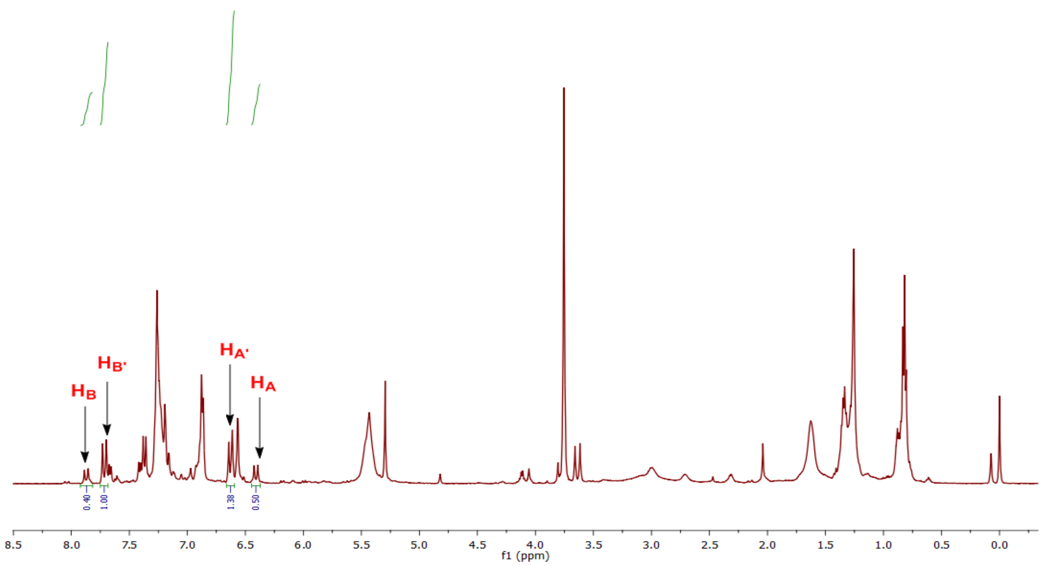




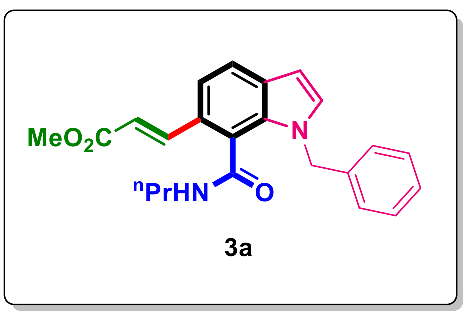
9.3. Intermolecular competition experiments between substituted indole-7-carboxamide

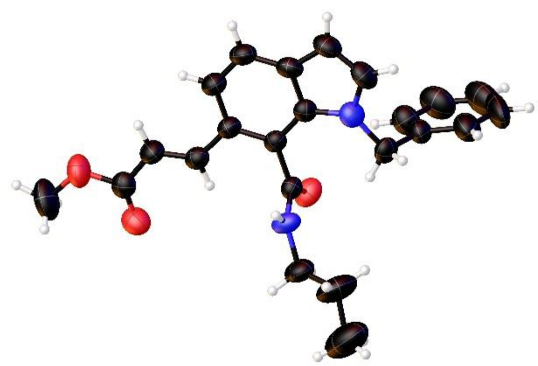


A oven-dried screw cap reaction tube equipped with stir bar was charged with mixture of 1-benzyl-*N*-propyl-1H-indole-7-carboxamide **1a** (73.25 mg, 0.25 mmol), 1-benzyl-5-fluoro-N-propyl-1H-indole-7-carboxamide **1d** (77.50 mg, 0.25 mmol), methyl acrylate **2a** (21.5 mg, 0.25 mmol), $[RuCl_2(p\text{-cymene})]_2$ (7.65 mg, 5.0 mol %) , AgSbF6 (17.18 mg, 20 mol %) and $Cu(OAc)_2{\cdot}H_2O$ (99.50 mg, 0.50 mmol) in DCE (2.0 mL) was stirred at 120 °C under nitrogen atmosphere for 24 h. After that reaction mixture was cooled to room temperature, then the filtered over silica gel pad and washed with DCM. The solvent was removed *under* reduced pressure. The ratio of products **3a:3u** (0.4:1.00) was determined by ^{1}H-NMR spectroscopy.



10. Crystallographic data of compound 3a:





(CCDC 1990507) ORTEP DIAGRAM

Data	**Compound (3a) (CCDC 1990507)**
Solvent system for crystal growth	Ethyl acetate-Pet. Ether
Crystal growth method	Solvent evaporation
Formula	$C_{23}H_{24}N_2O_3$
Formula Weight	376.4560
Wavelength	0.71073
Temperature(K)	273 K
Ellipsoid contour probability	50%
Space Group	P 21
a (Å)	6.3292(14)

b(Å)	15.250(3)
c(Å)	10.995(3)
α(°)	90
β(°)	104.076(9)
γ(°)	90
V(cm^3)	1029.4(4)
Z	2
Density(g cm^{-3})	1.214
μ(mm^{-1})	0.081
F (000)	400.0
θ (max)	25.500
$h_{min,max}$/ $k_{min,max}$/ $l_{min,max}$	7,18,13
No. unique ref./ obs. ref.	3825/ 3818
No. of parameters	259
R(reflections)	0.0711(2347
wR_2(reflections)	0.1829(3818)
Data completeness	1.92/1.00

11. References:

[1] Dalpozzo, R.; Bartoli, G. *Current Org. Chem.* **2005**, *9*, 163.

[2] Giardinetti, M.; Moreau, X.; Coeffard, V.; Greck, C. *Adv. Synth. Catal.* **2015**, *357*, 3501.

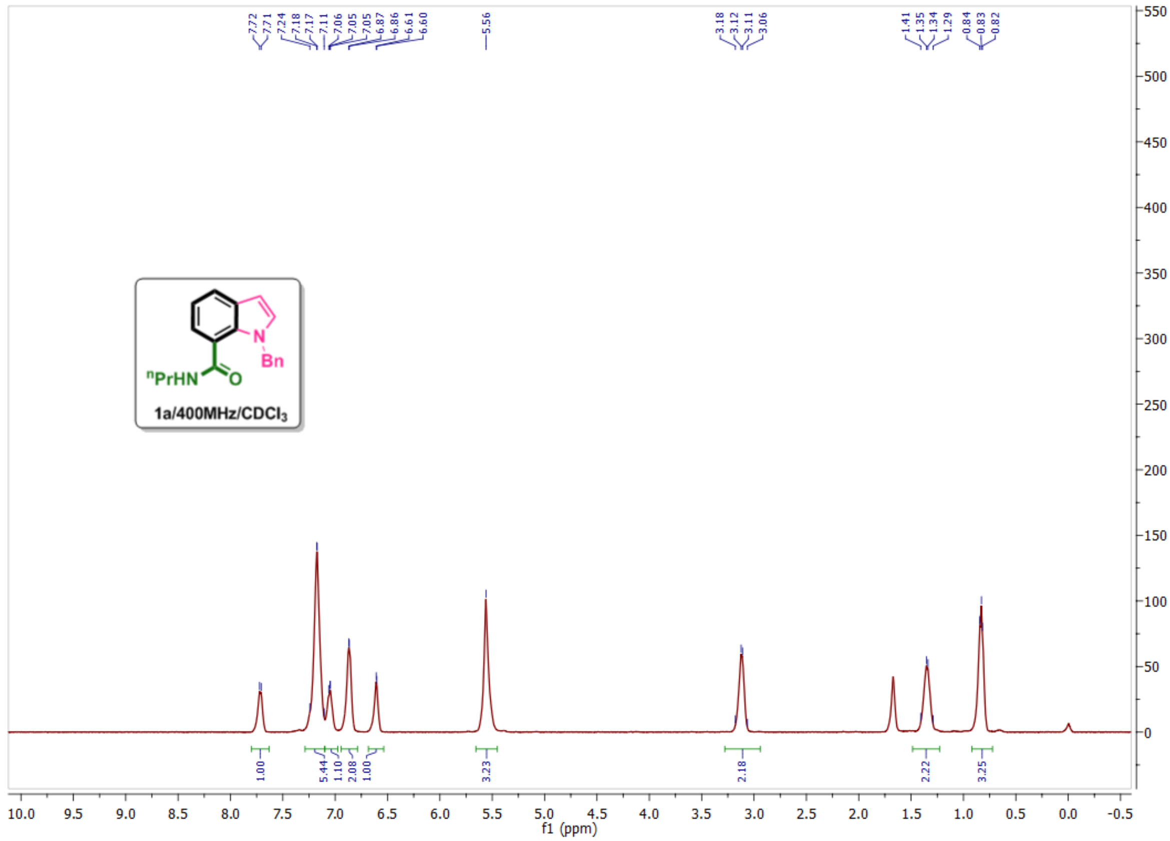
[3] Banjare, S. K.; Nanda, T.; Ravikumar, P. C. *Org. Lett.* **2019**, *21*, 8138.

[4] Yamamoto, E.; Hilton, M. J.; Orlandi, M.; Saini, V.; Toste, F. D.; Sigman, M. S. *J. Am.Chem. Soc*. **2016**, *138*, 15877.

[5] Kamata, K.; Hirano, T.; Mizuno, N. *Chem. Commun*. **2009**, 3958-3960.

[6] Roy, S.; Das, S. K.; Chattopadhyay, B. *Angew. Chem., Int. Ed*. **2018**, *57*, 2238.

12. NMR Spectra: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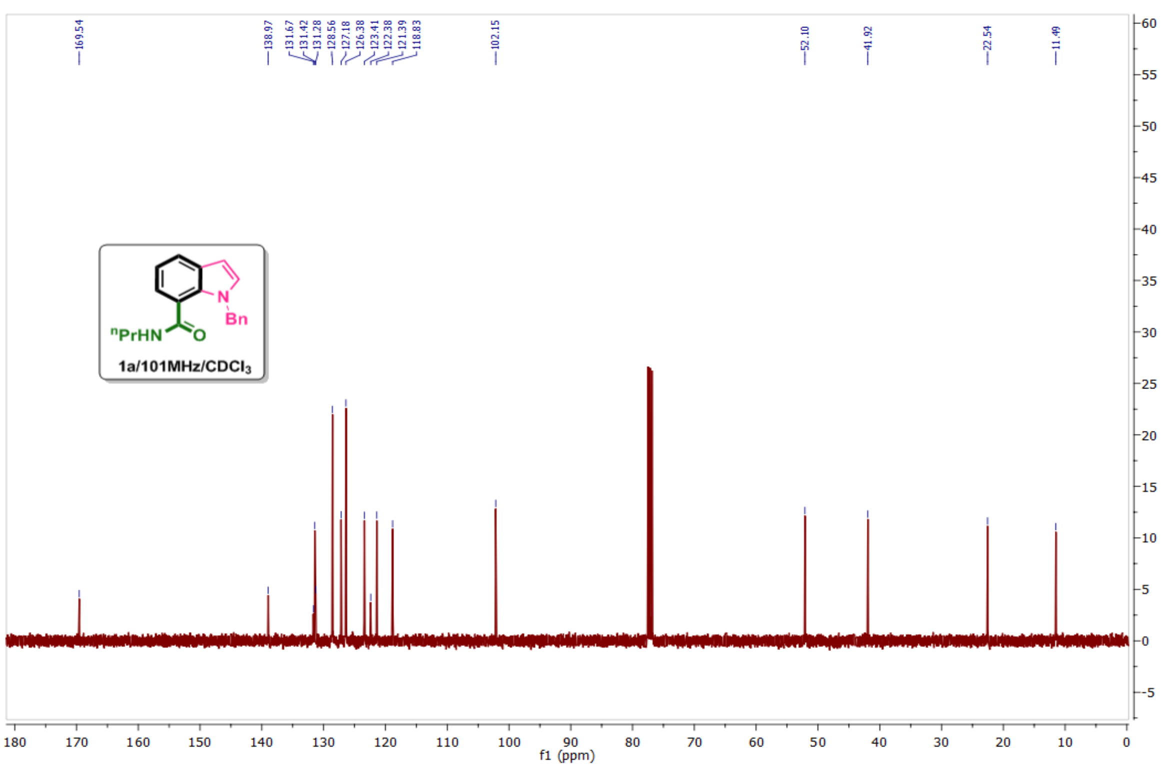
O
N
Bn
1a/400MHz/CDCl3
f1 (ppm)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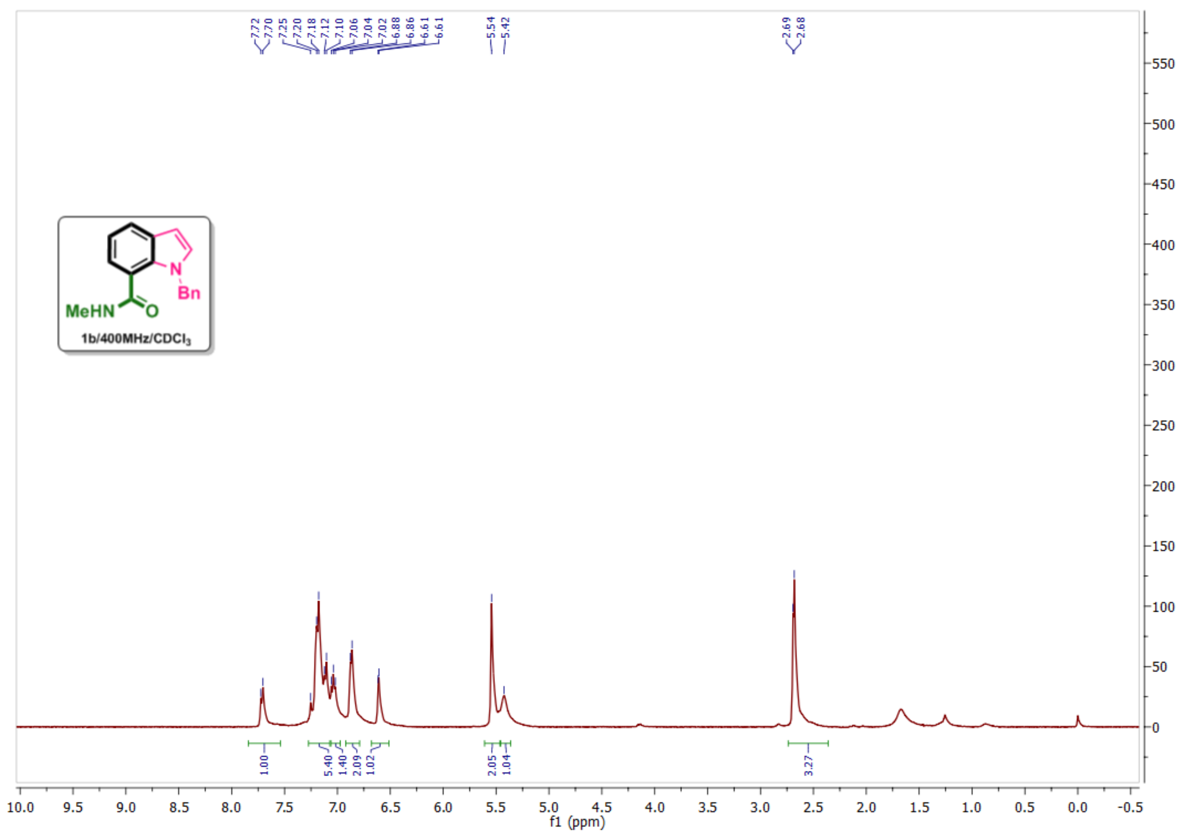
O
N
Bn
1a/101MHz/CDCl3
f1 (ppm)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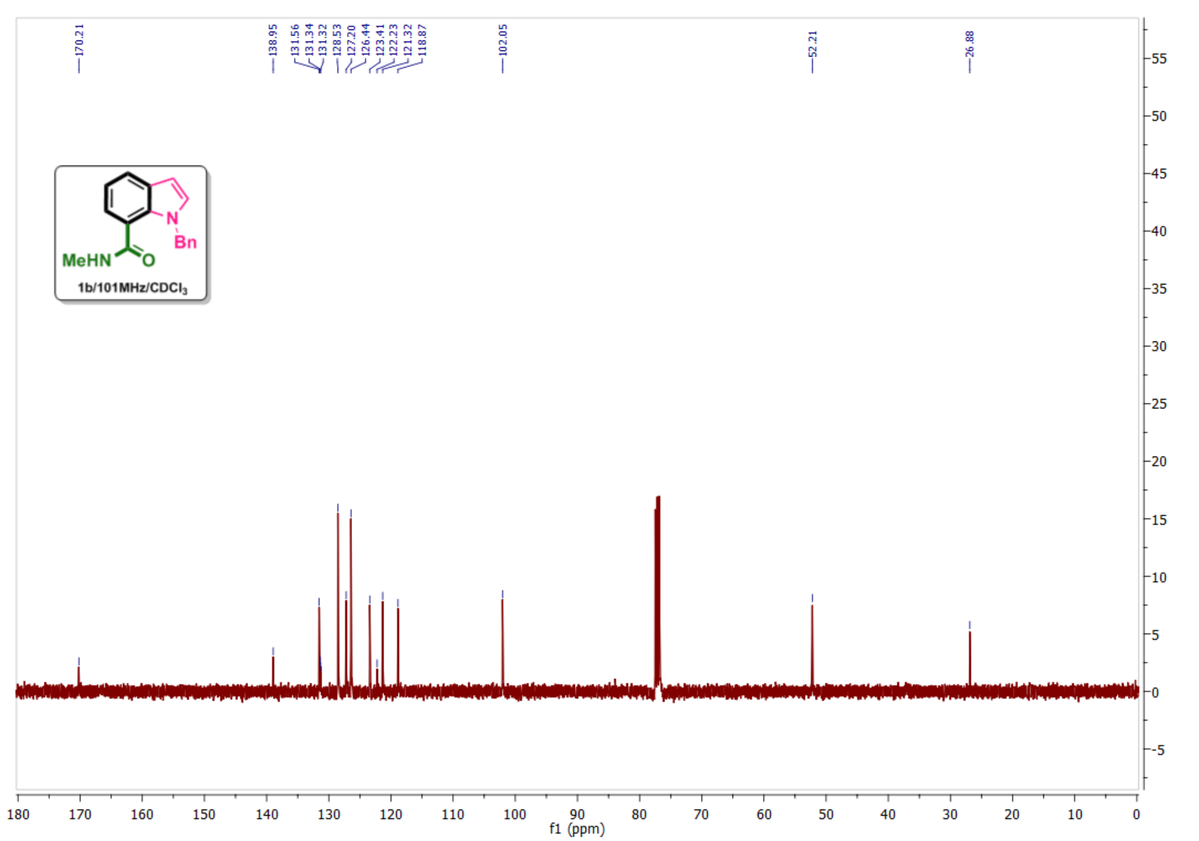
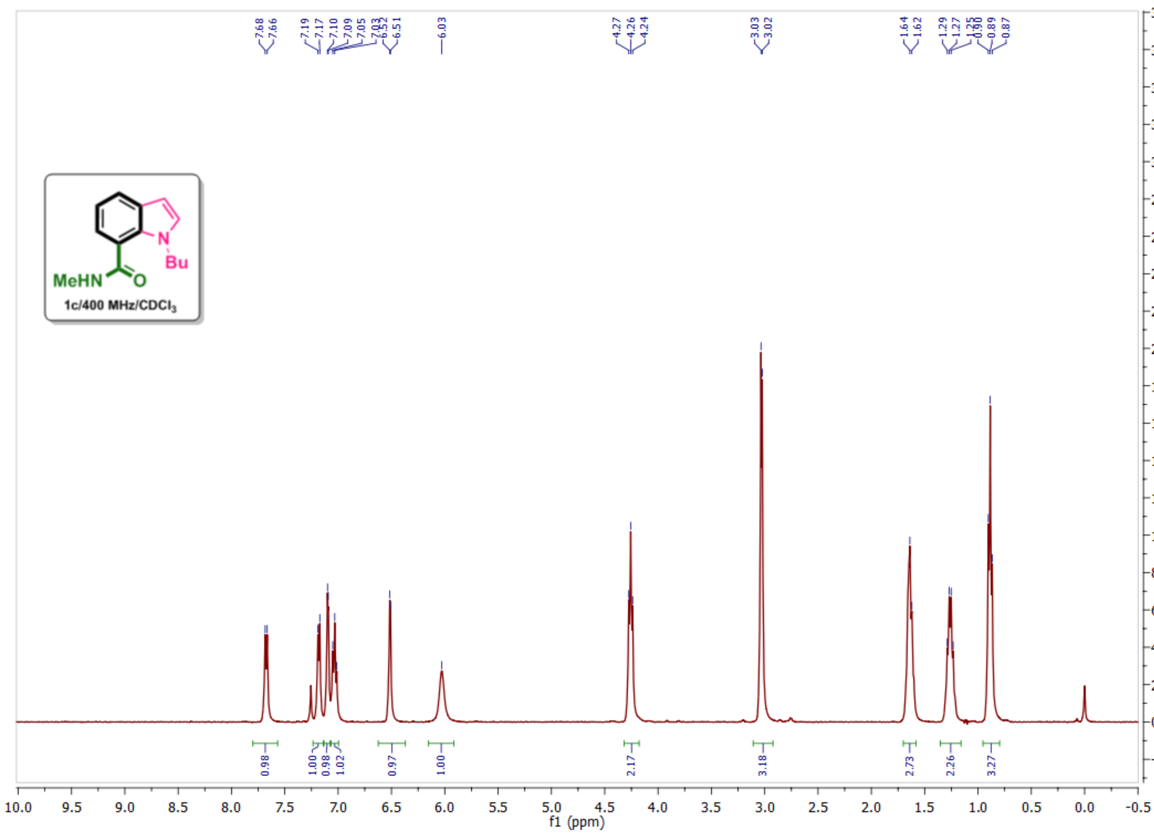
7.70
7.25
7.20
7.18
7.12
7.10
7.06
7.04
7.02
6.88
6.86
6.61
6.61
5.54
5.42
2.69
2.68
MeHN
O
N
Bn
1b/400MHz/CDCl3
1.00
5.40
1.40
2.09
1.02
2.05
1.04
3.27
f1 (ppm)


170.21
138.95
131.56
131.34
131.32
128.53
127.20
126.44
123.41
122.23
121.32
118.87
102.05
52.21
26.88
MeHN
O
N
Bn
1b/101MHz/CDCl3
f1 (ppm)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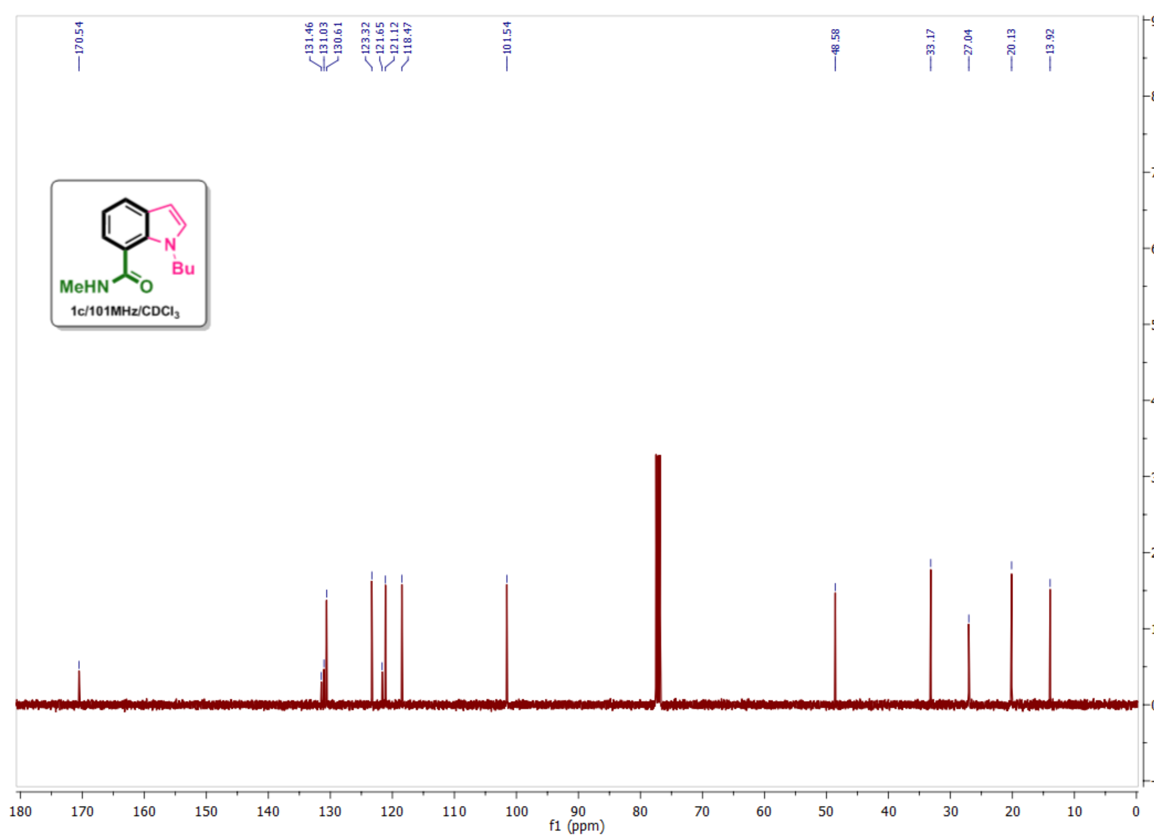
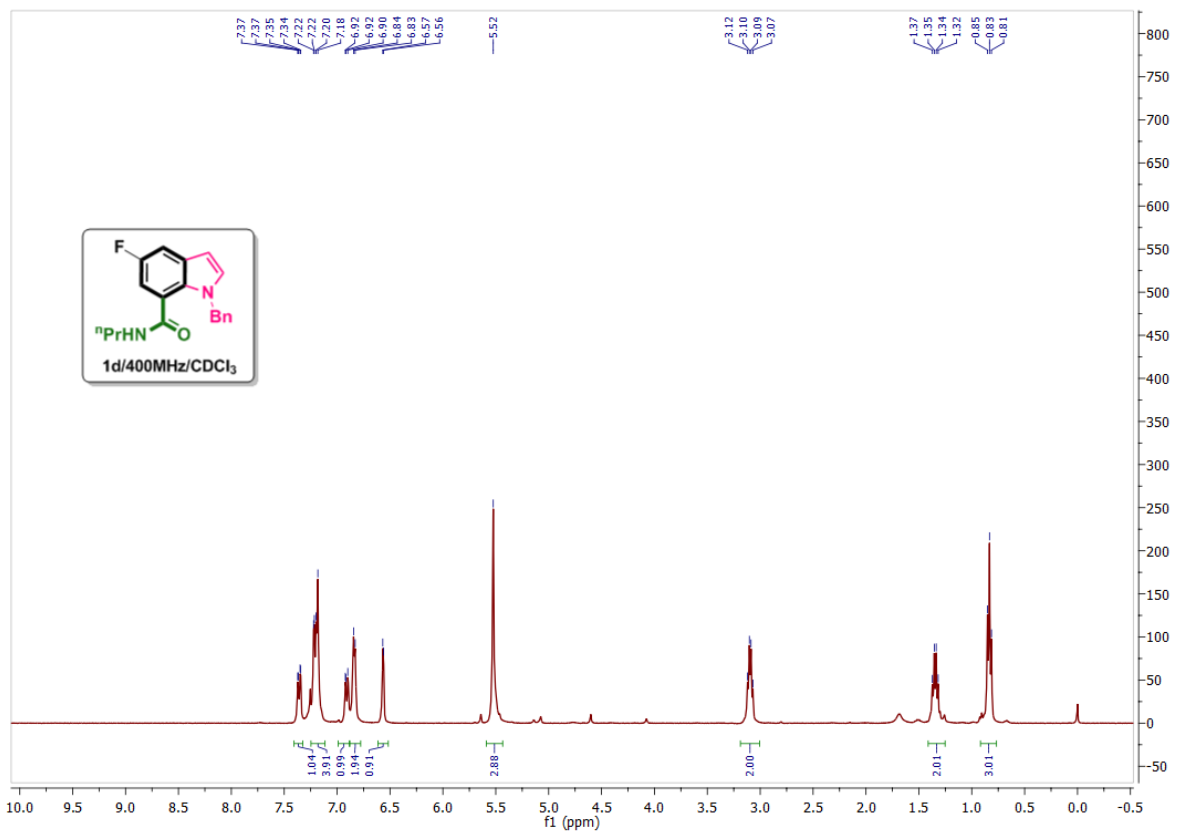
O
N
Bu
1c/400 MHz/CDCl3
f1 (ppm)


MeHN
O
N
Bu
1c/101MHz/CDCl3
f1 (ppm)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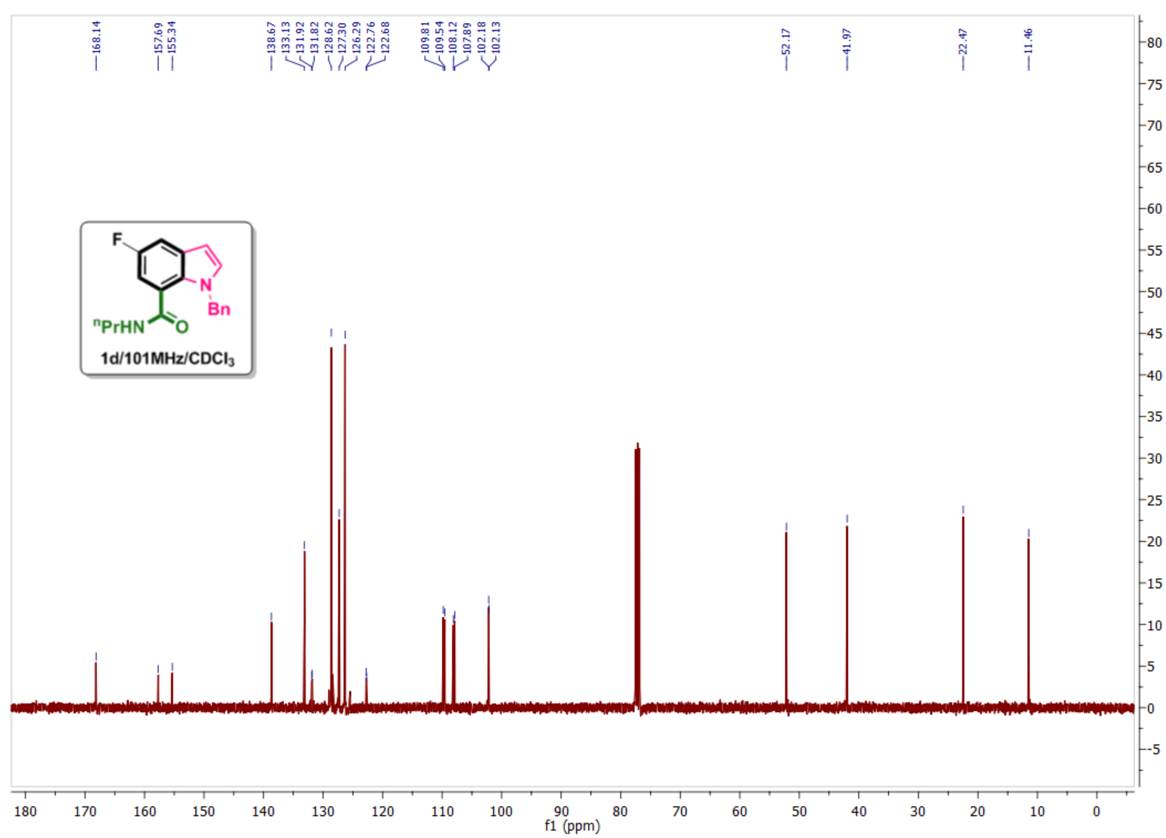
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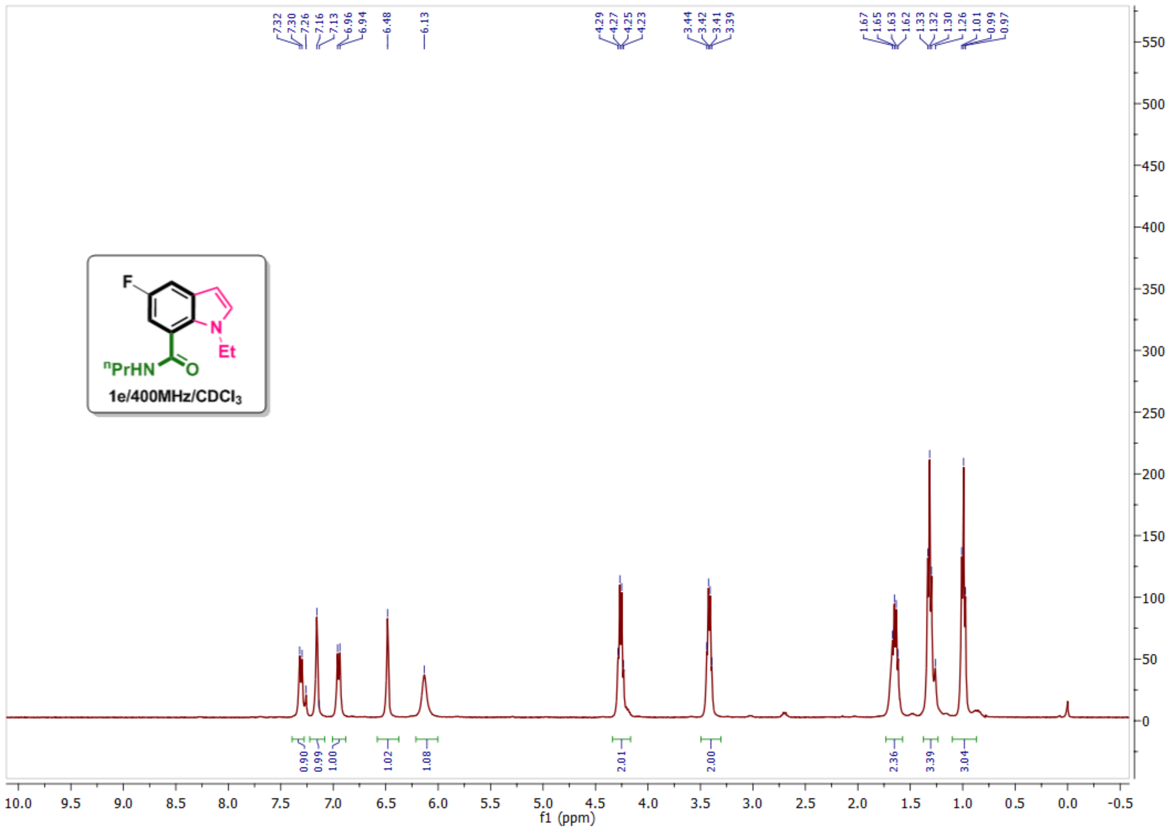
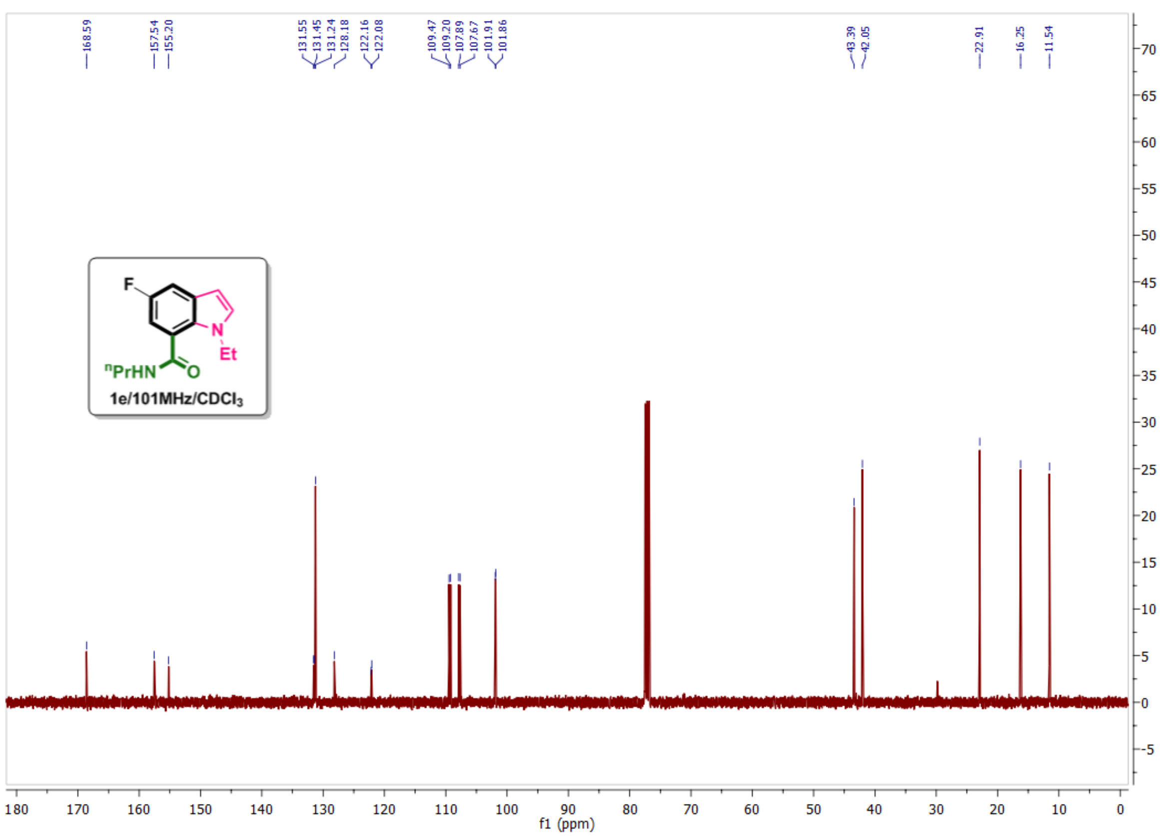
f1 (ppm)


1e/400MHz/CDCl3
f1 (ppm)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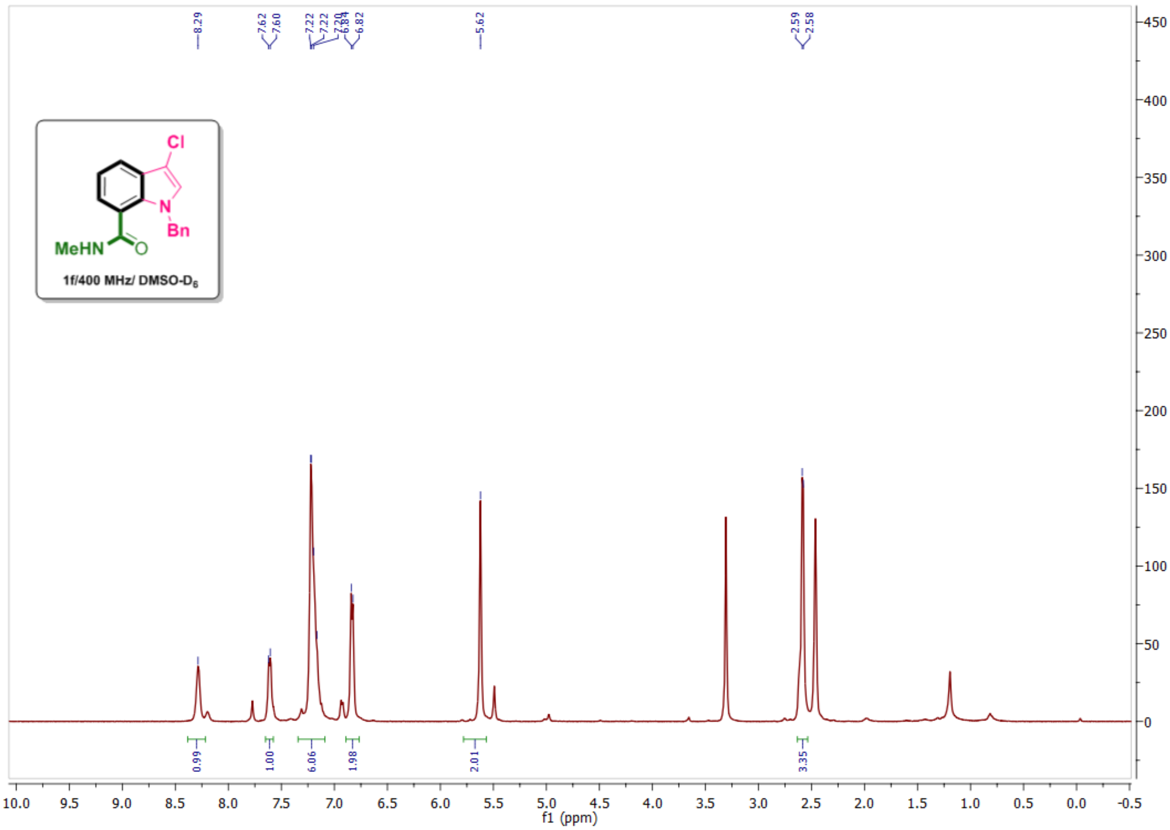
f1 (ppm)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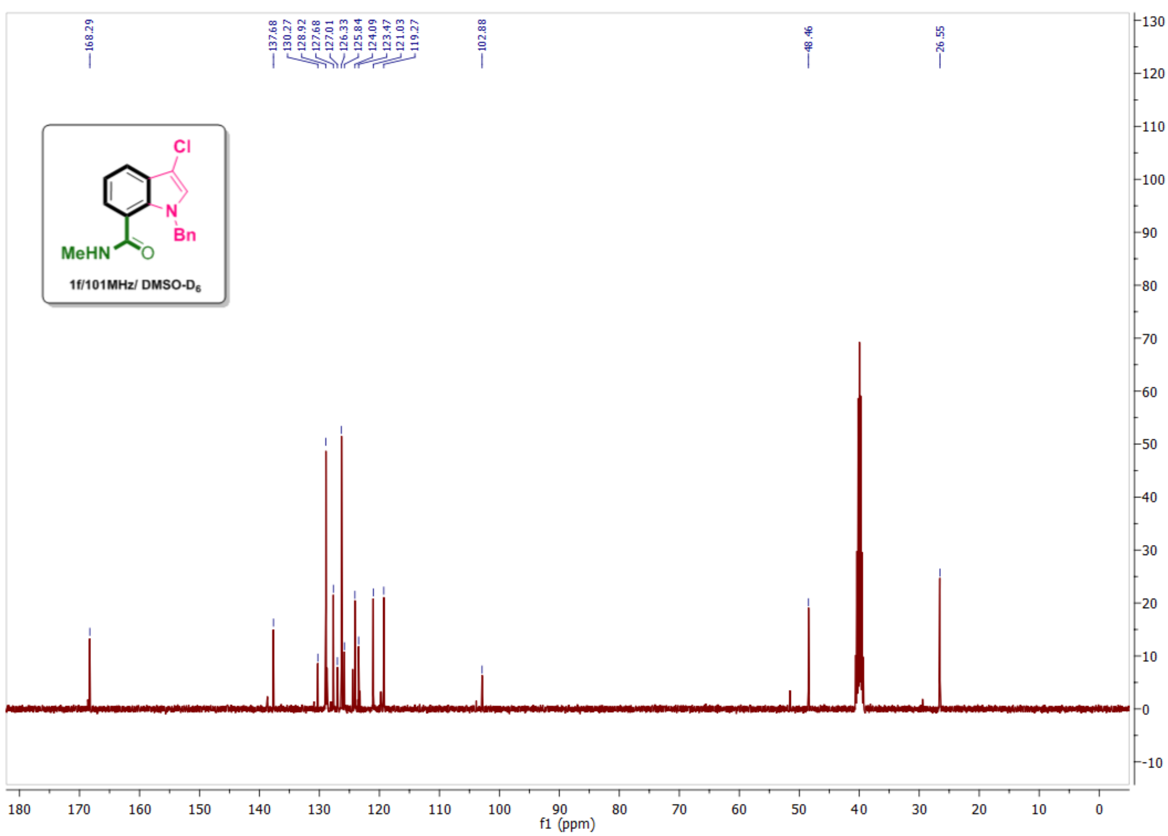
7.60
7.22
7.22
6.84
6.82
5.62
2.59
2.58
Cl
N
Bn
MeHN
O
1f/400 MHz/ DMSO-D6
0.99
1.00
6.06
1.98
2.01
3.35
f1 (ppm)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137.68
130.27
128.92
127.68
127.01
126.33
125.84
124.09
123.47
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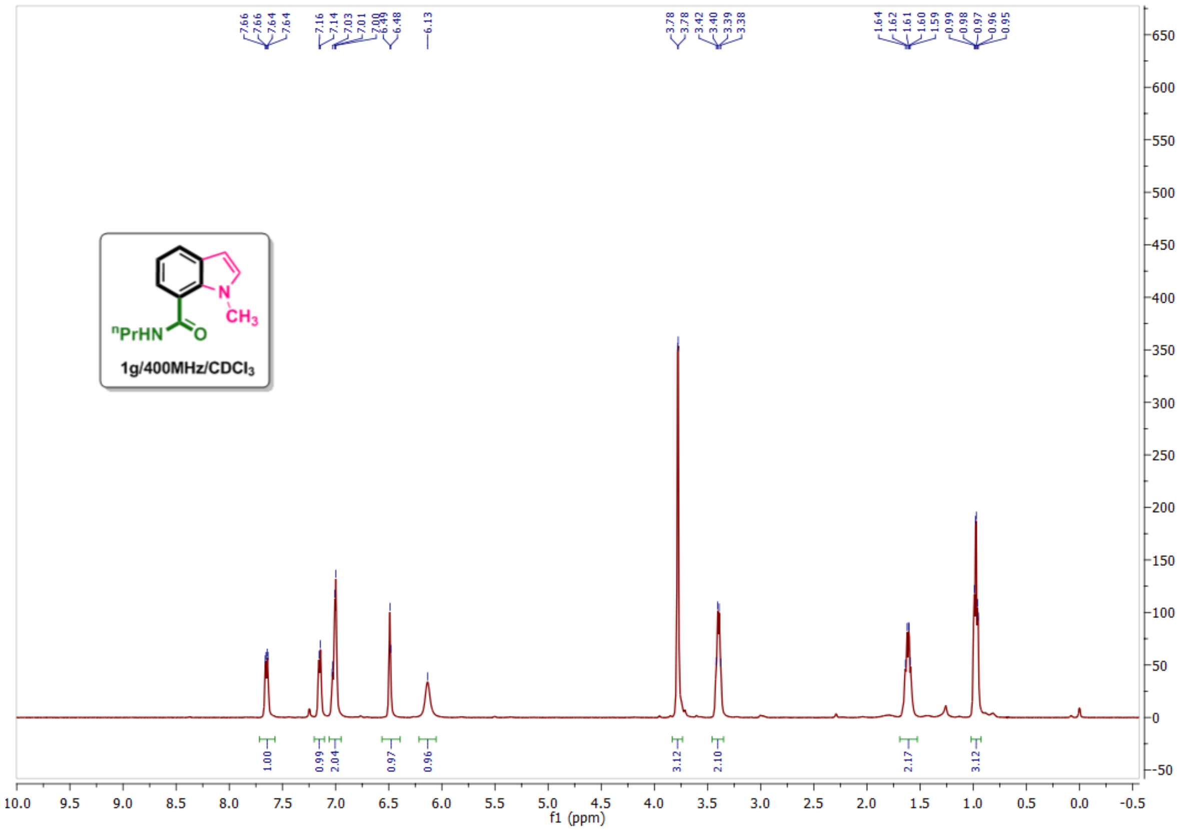
102.88
48.46
26.55
Cl
N
Bn
MeHN
O
1f/101MHz/ DMSO-D6
f1 (ppm)



1g/400MHz/CDCl3
"PrHN
O
N
CH3
7.66
7.66
7.64
7.64
7.16
7.14
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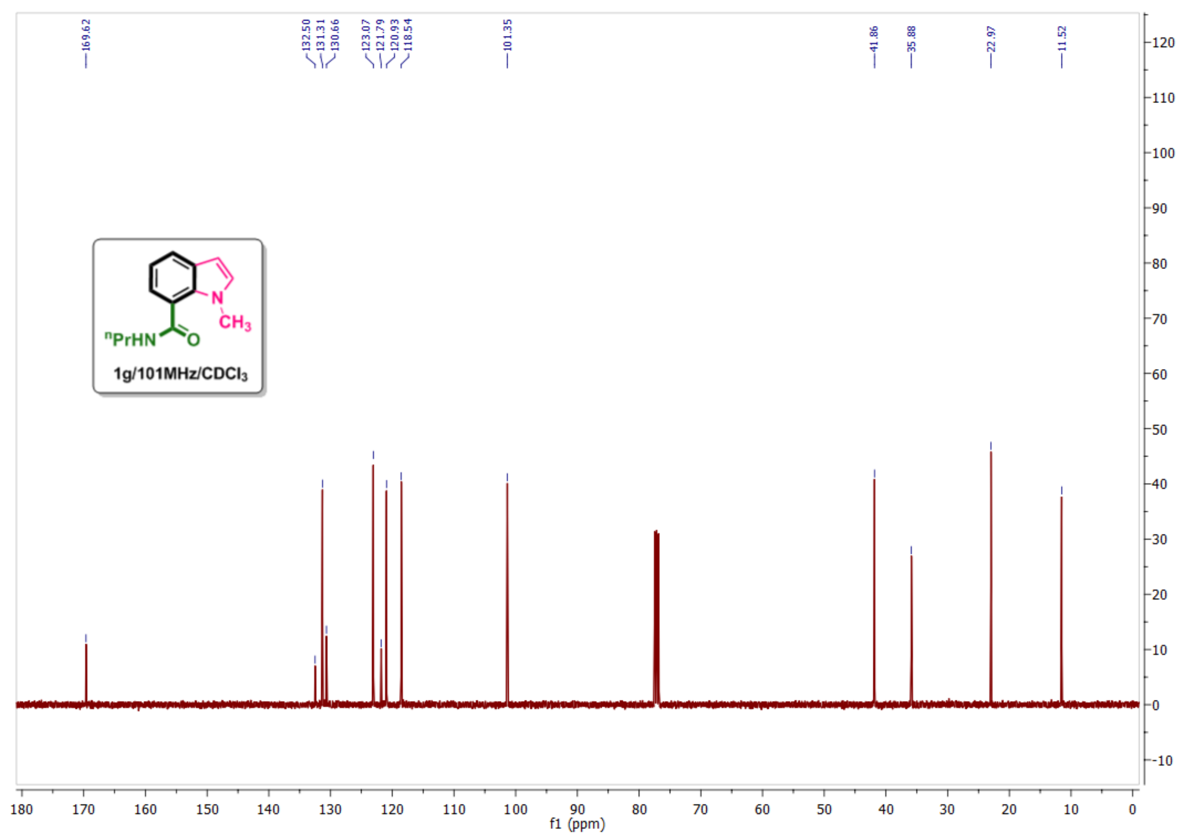
7.01
7.00
6.49
6.48
6.13
3.78
3.78
3.42
3.40
3.39
3.38
1.64
1.62
1.61
1.60
1.59
0.99
0.98
0.97
0.96
0.95
1.00
0.99
2.04
0.97
0.96
3.12
2.10
2.17
3.12
f1 (ppm)



1g/101MHz/CDCl3
"PrHN
O
N
CH3
169.62
132.50
131.31
130.66
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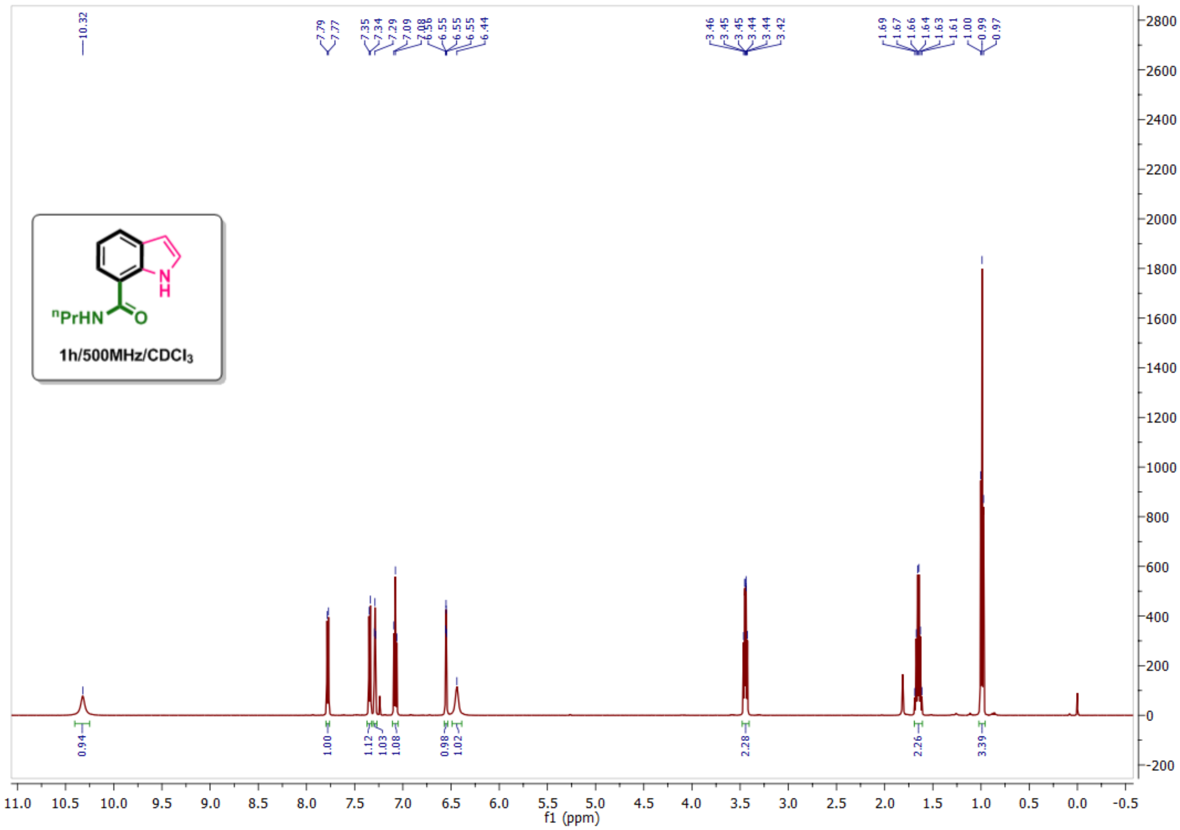
121.79
120.93
118.54
101.35
41.86
35.88
22.97
11.52
f1 (ppm)



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7.29
7.09
7.08
7.08
6.56
6.55
6.55
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6.44
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3.45
3.45
3.44
3.44
3.42
1.69
1.67
1.66
1.64
1.63
1.61
1.00
0.99
0.97
nPrHN
O
N
H
1h/500MHz/CDCl3
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1.12
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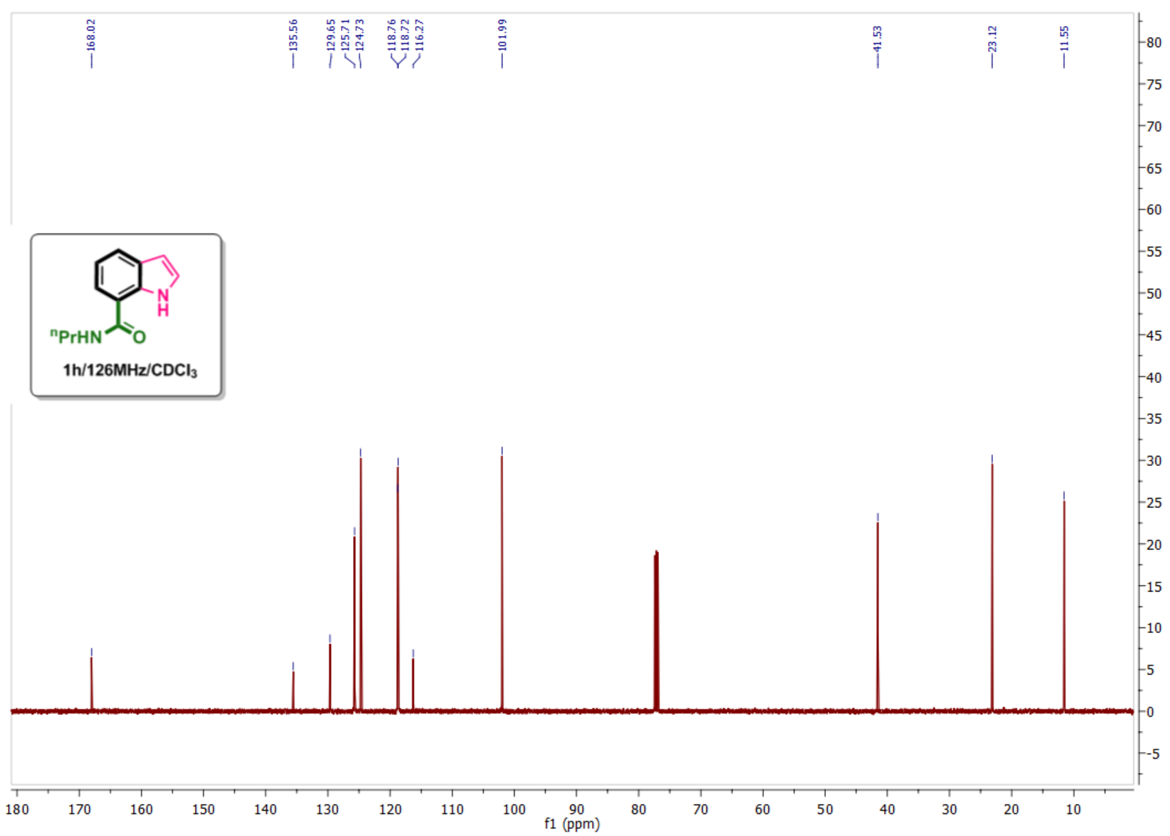
1.08
0.98
1.02
2.28
2.26
3.39
f1 (ppm)



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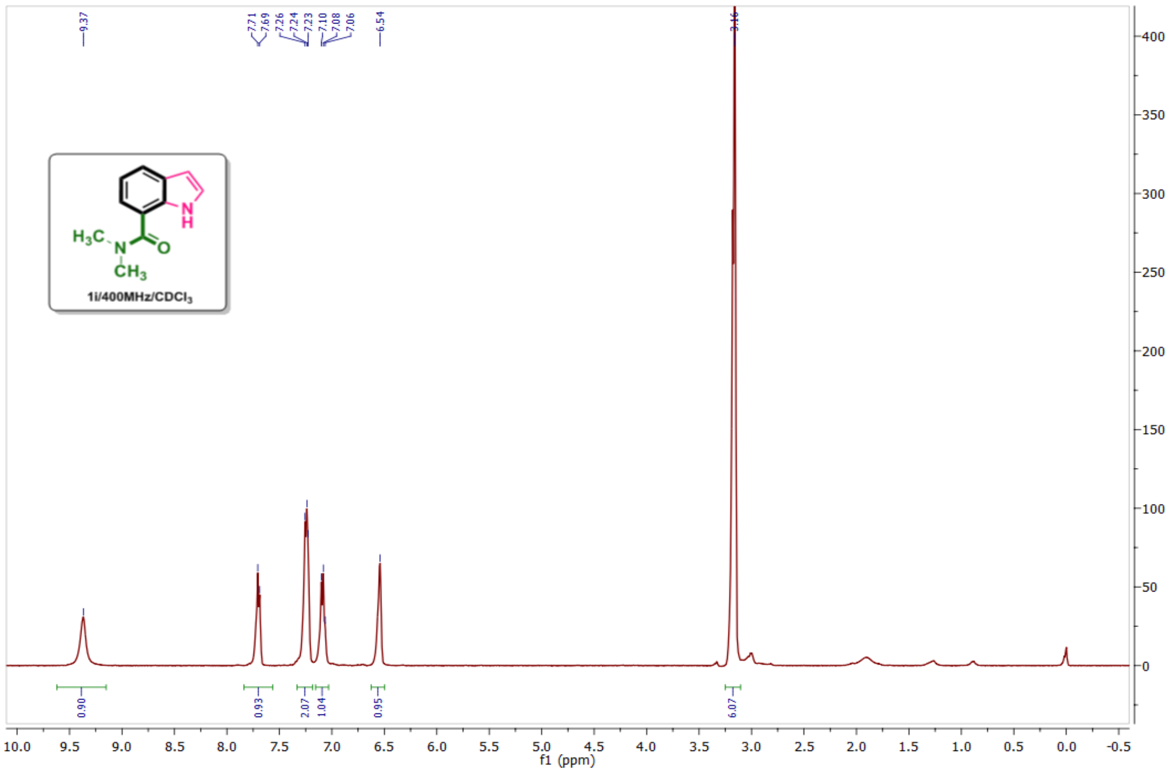
135.56
129.65
125.71
124.73
118.76
118.72
116.27
101.99
41.53
23.12
11.55
nPrHN
O
N
H
1h/126MHz/CDCl3
f1 (ppm)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7.26
7.24
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7.08
7.06
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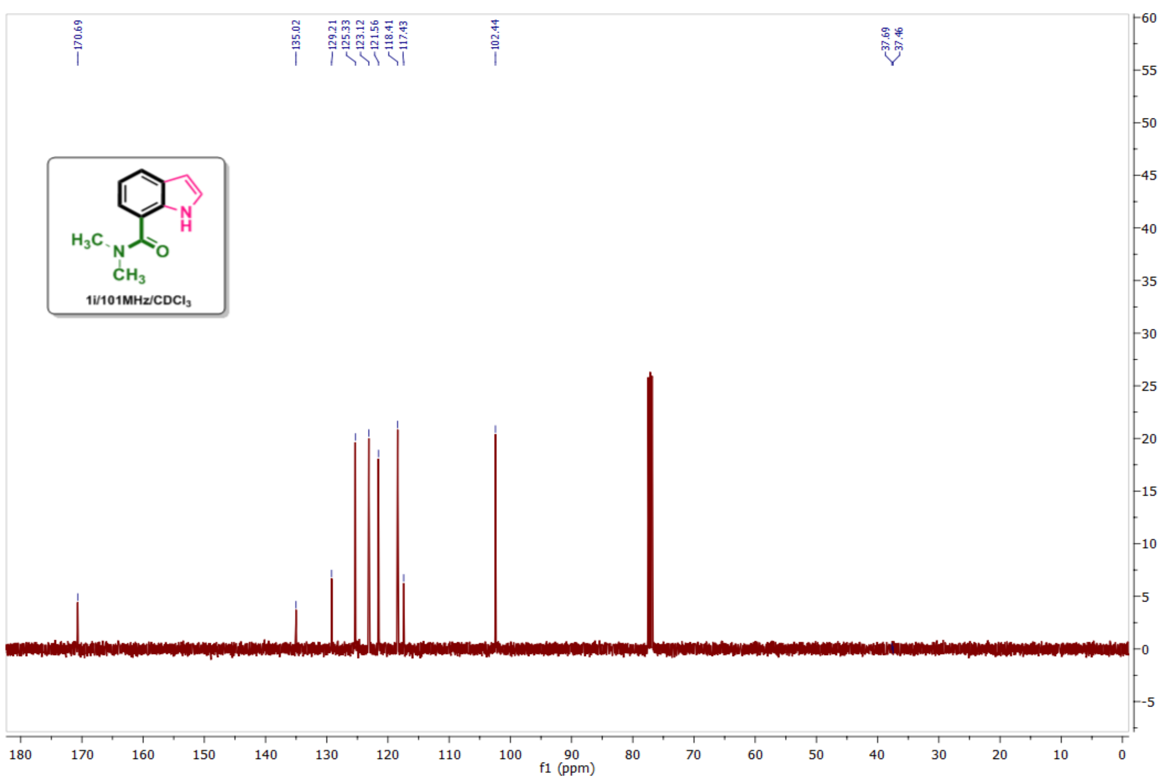
6.07
f1 (ppm)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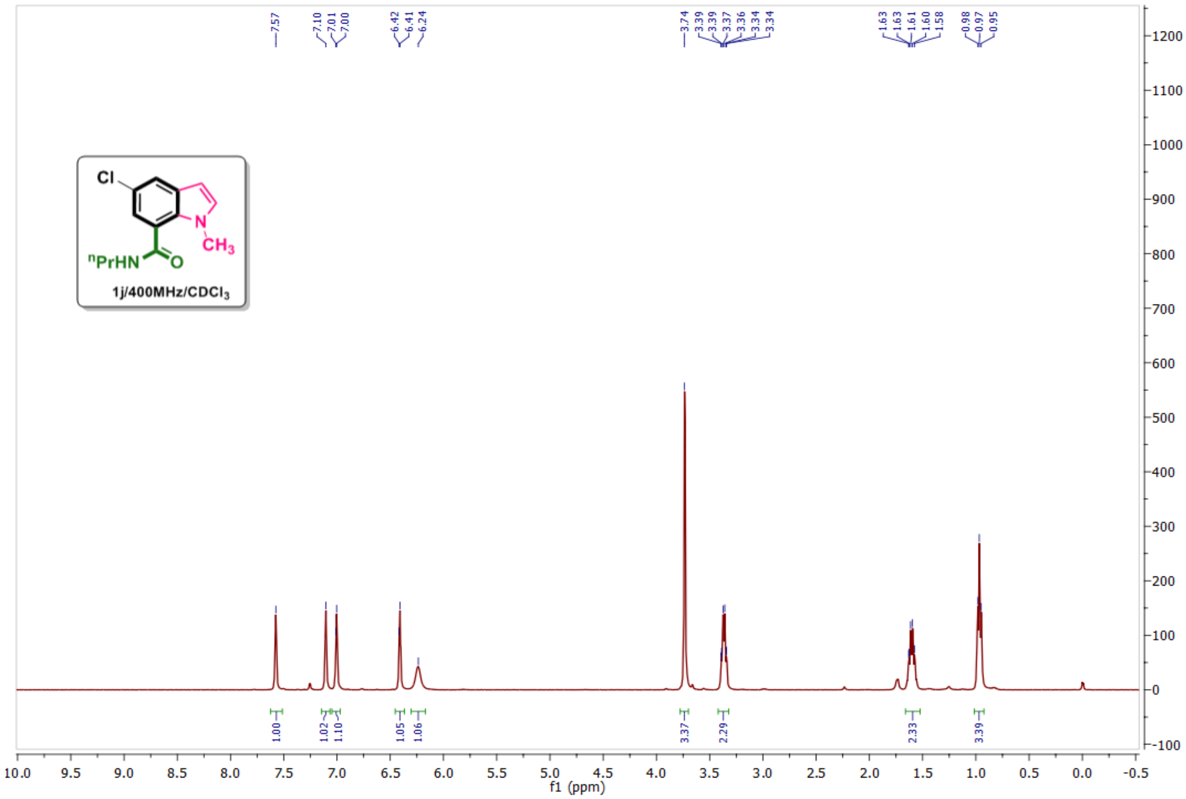
f1 (ppm)



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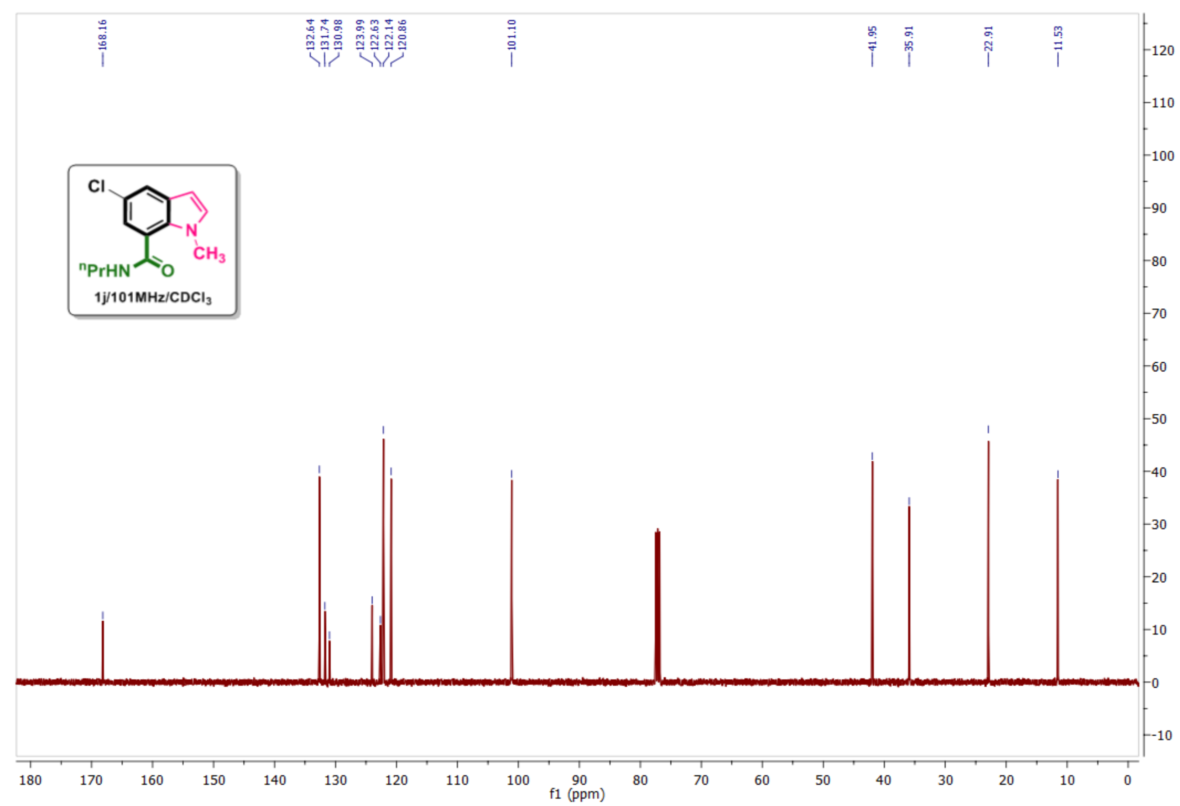
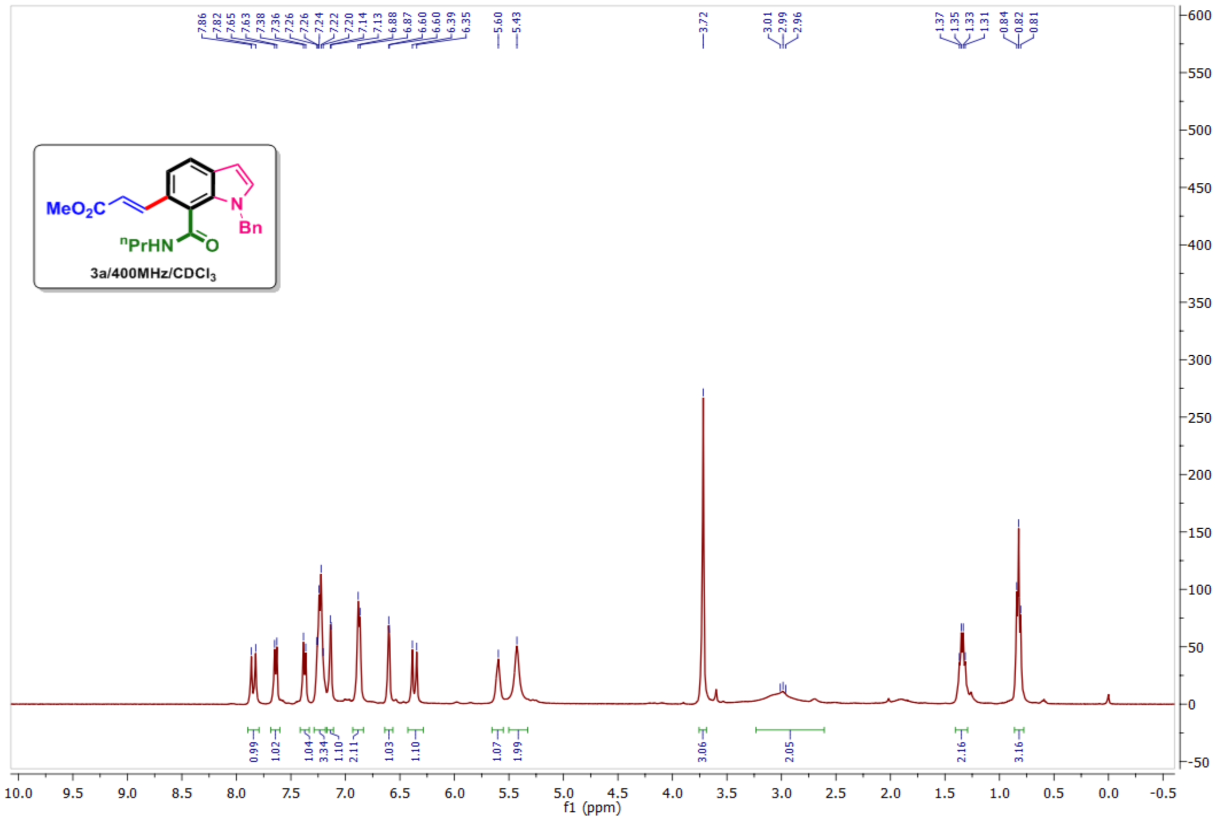


1j/101MHz/CDCl3
f1 (ppm)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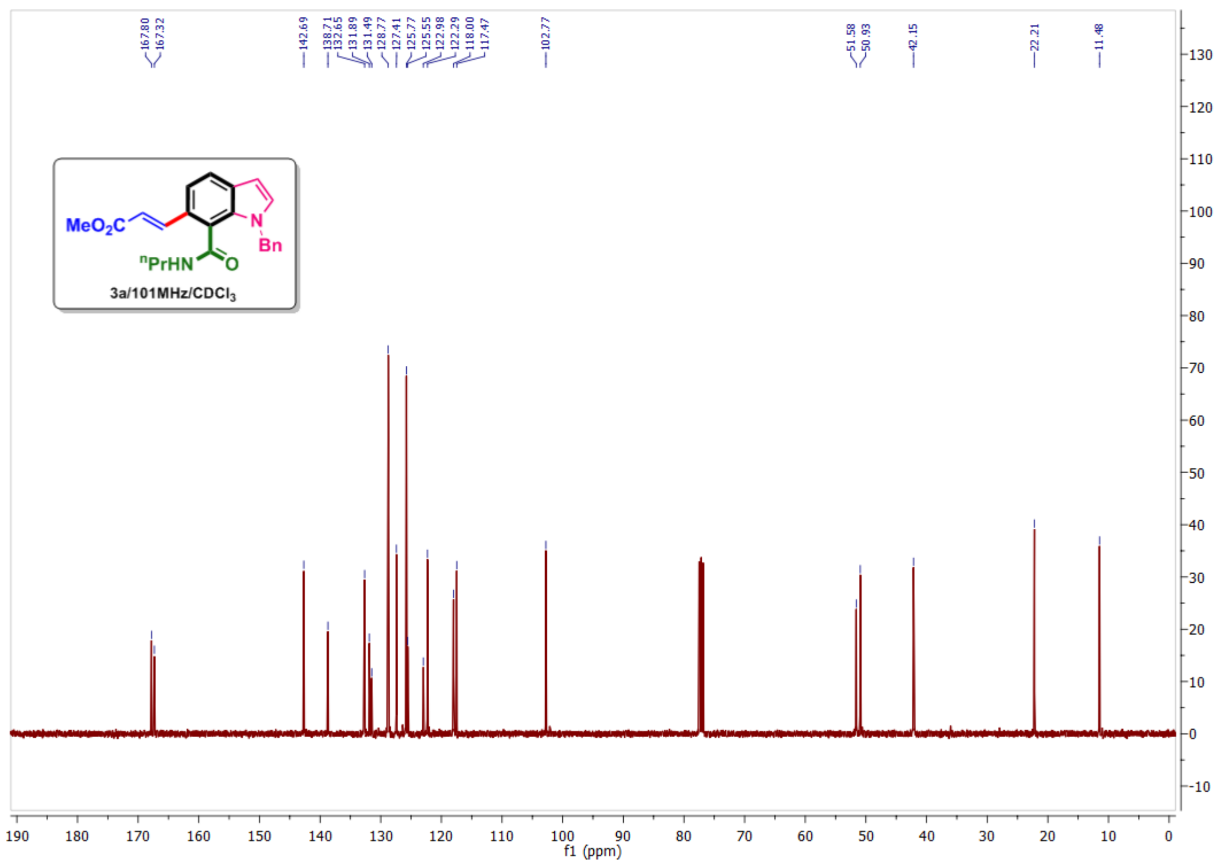
MeO$_2$C
N
Bn
^{n}PrHN
O
3a/400MHz/CDCl$_3$
0.99 1.02 1.04 3.34 1.10 2.11 1.03 1.10 1.07 1.99 3.06 2.05 2.16 3.16
f1 (ppm)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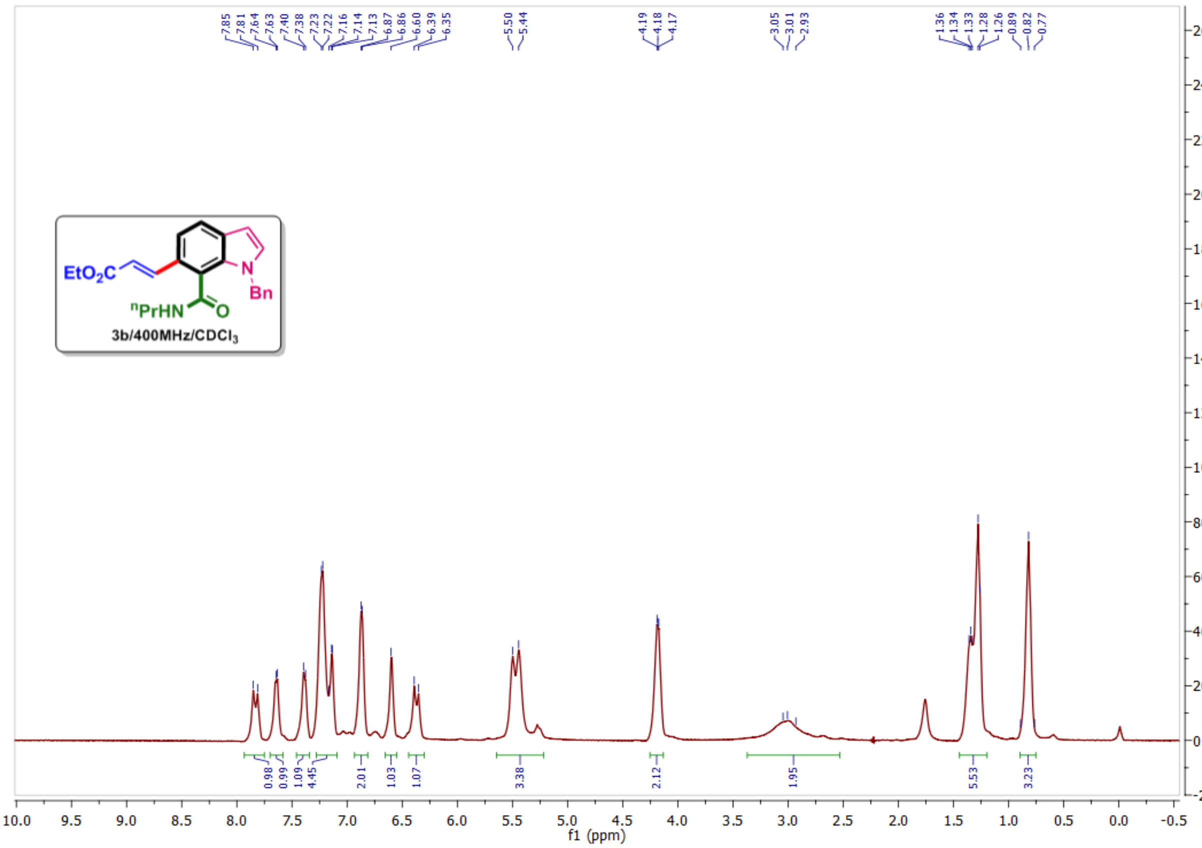
MeO$_2$C
N
Bn
^{n}PrHN
O
3a/101MHz/CDCl$_3$
f1 (ppm)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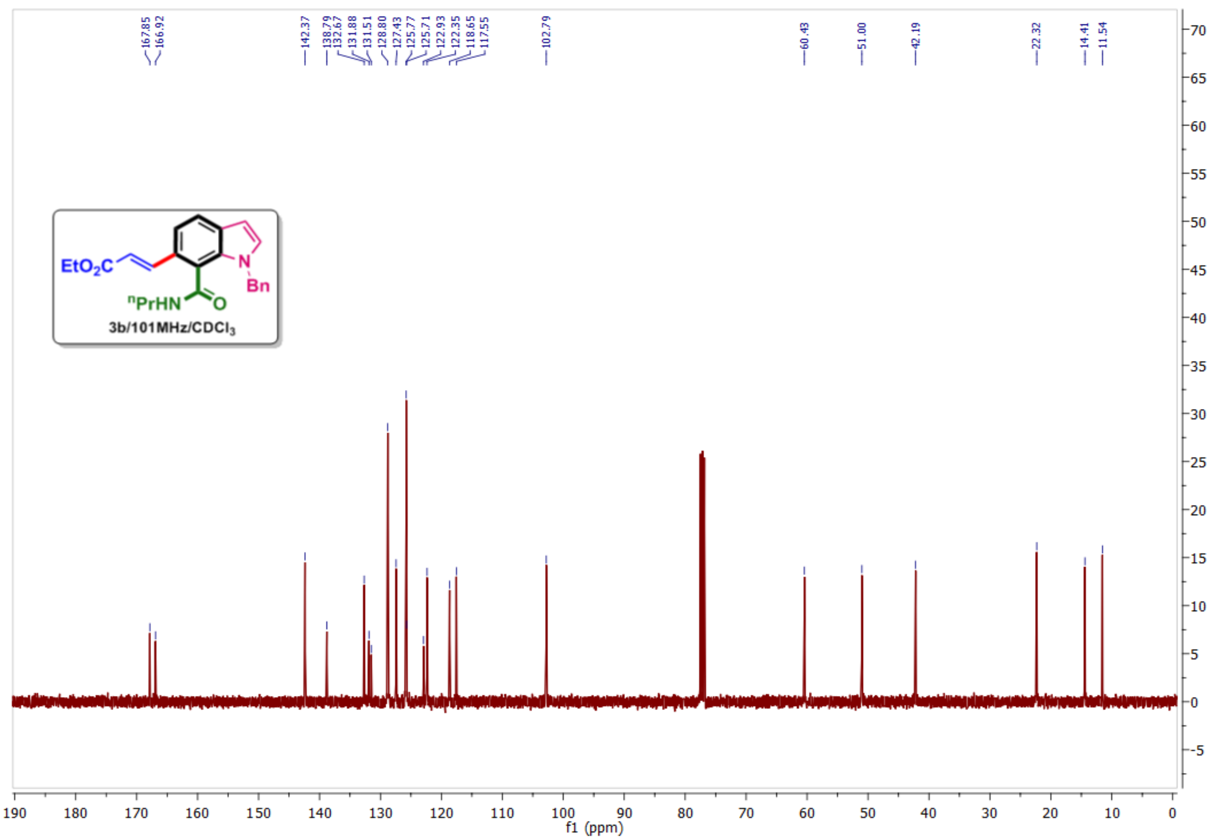
f1 (ppm)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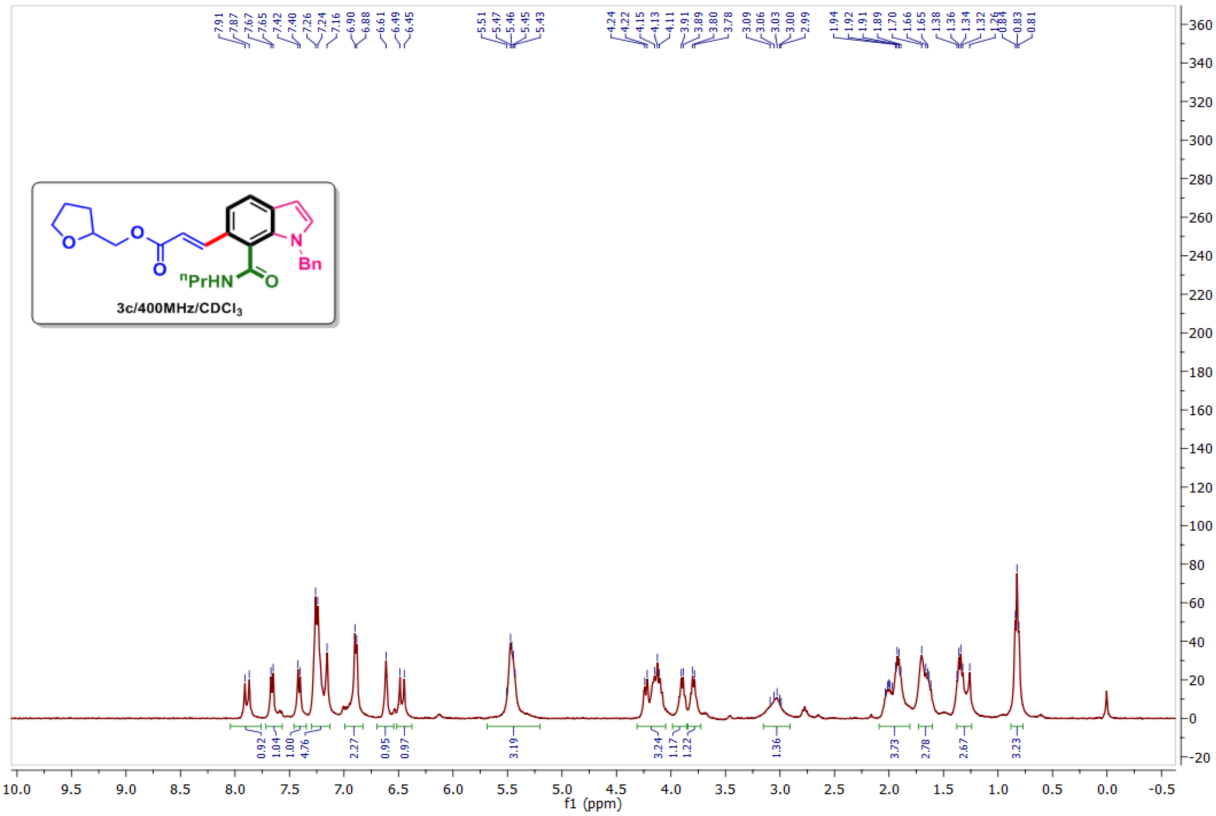
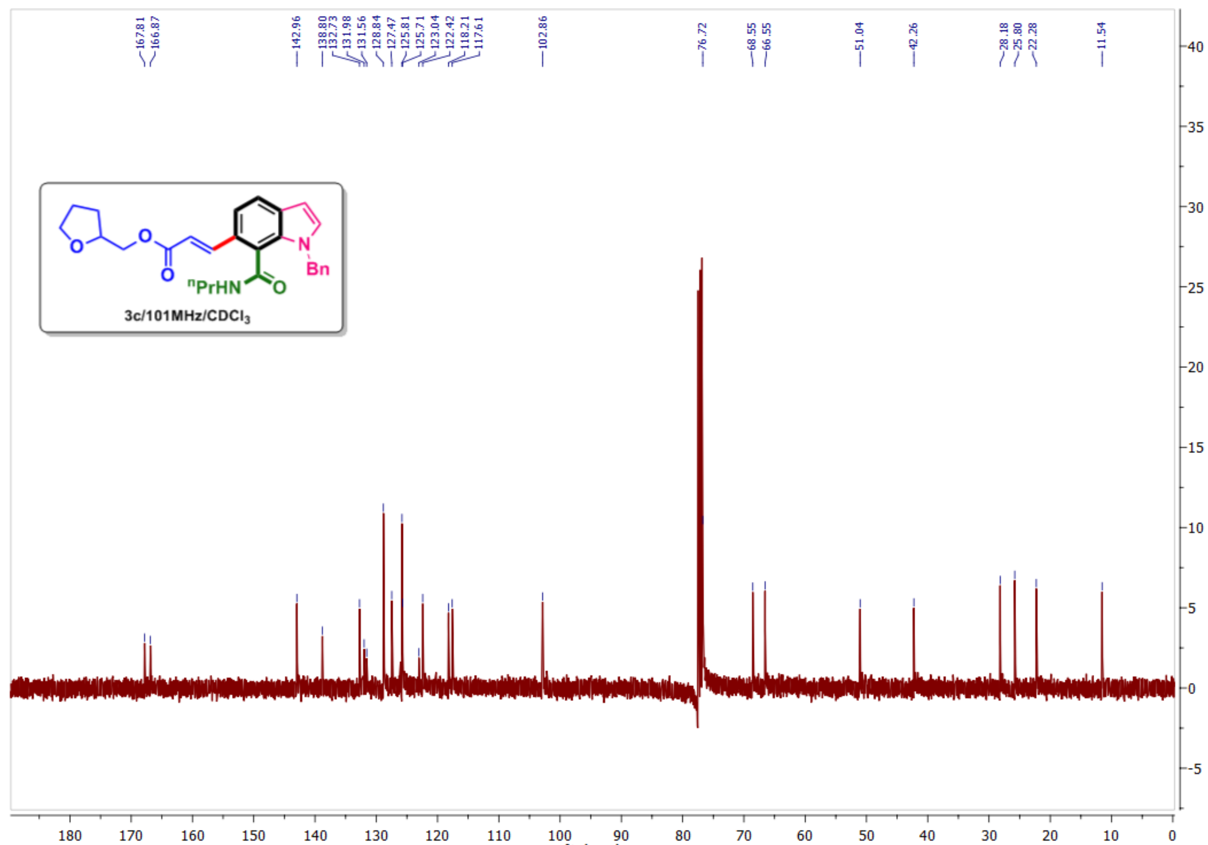
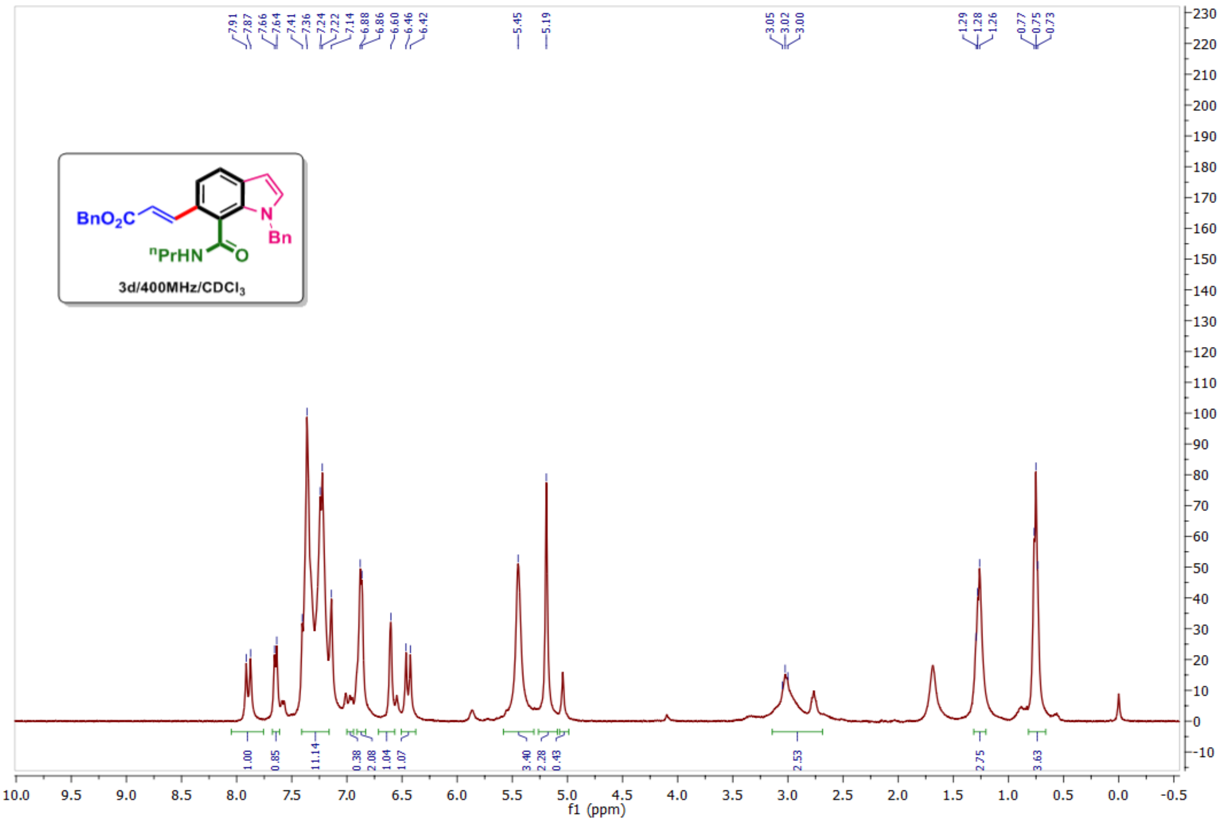
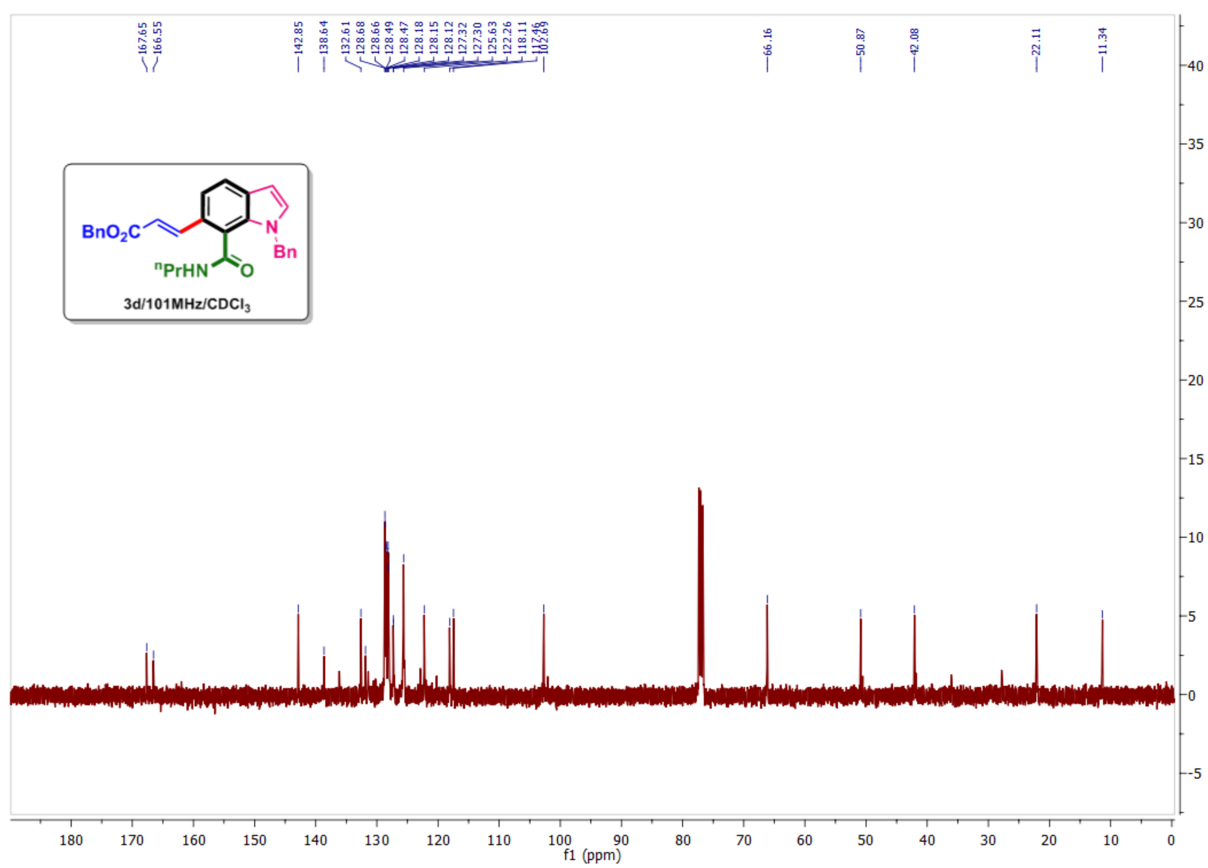


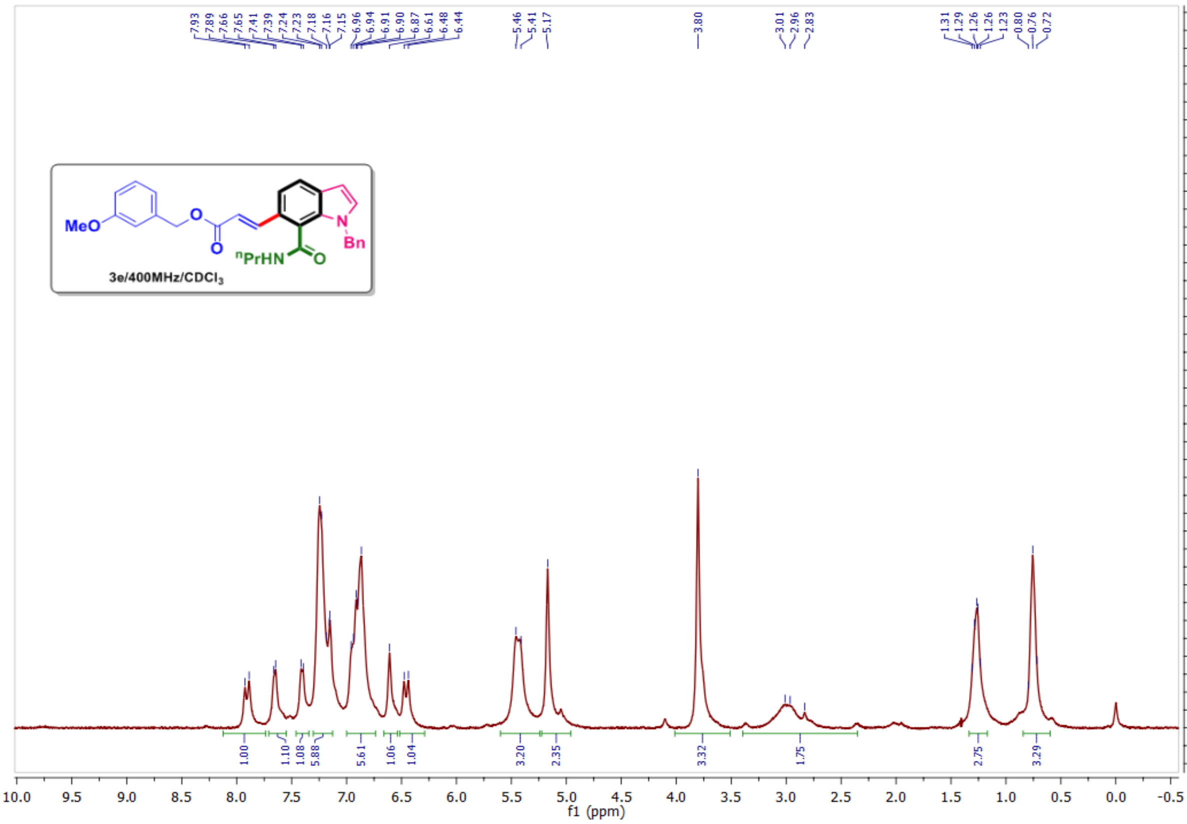


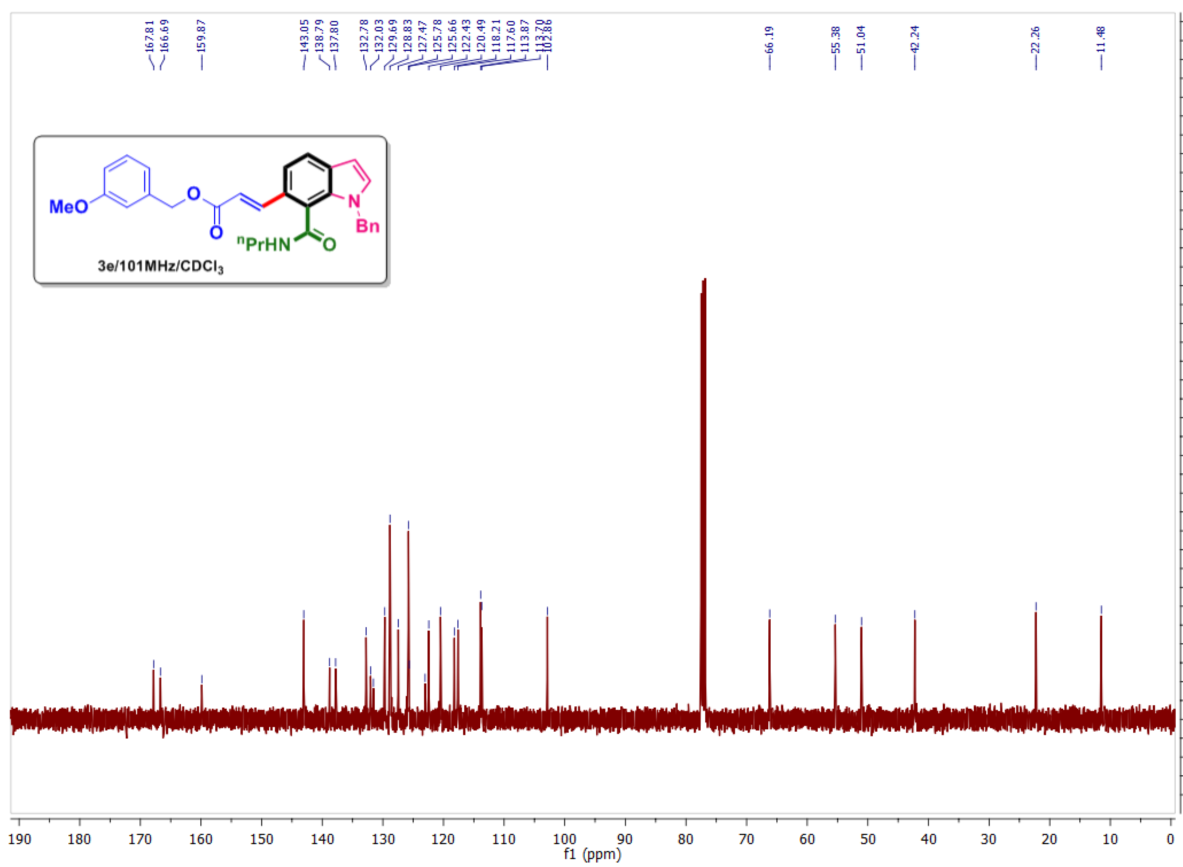


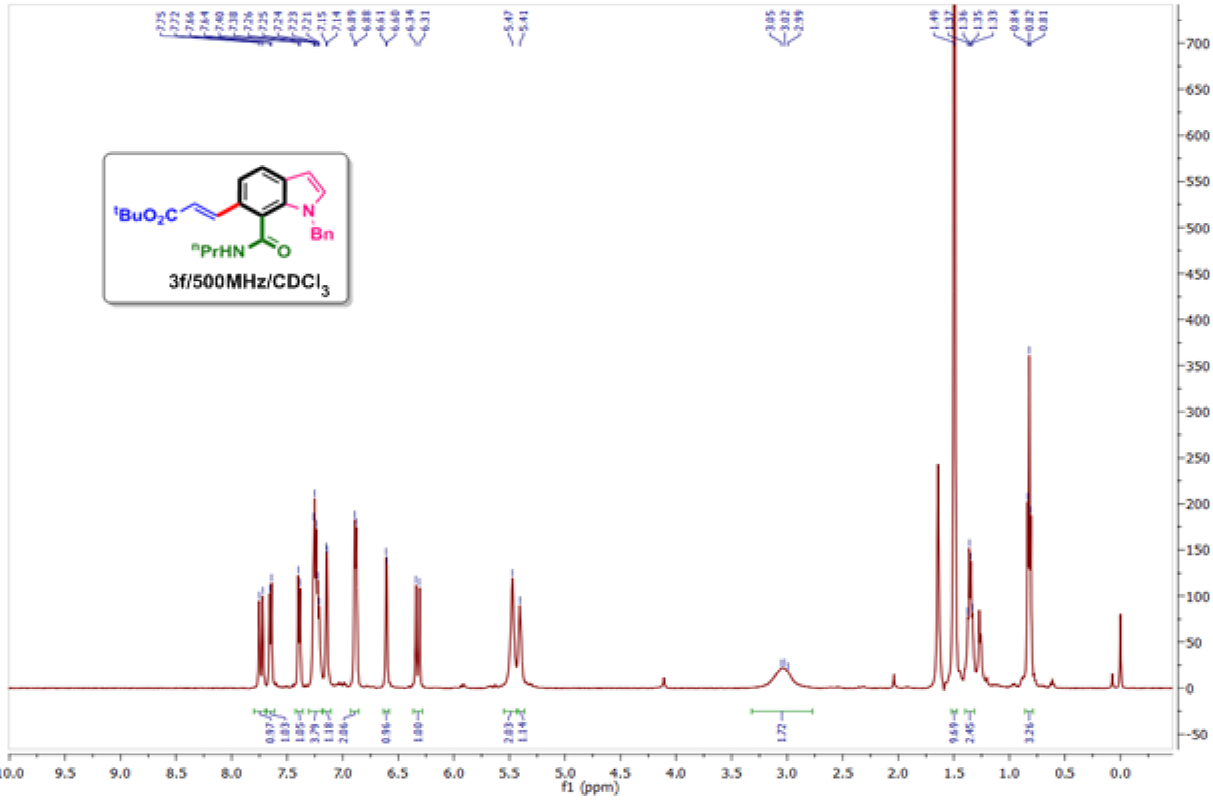
7.91
7.87
7.66
7.64
7.41
7.36
7.24
7.22
7.14
6.88
6.86
6.60
6.46
6.42
5.45
5.19
3.05
3.02
3.00
1.29
1.28
1.26
0.77
0.75
0.73
BnO$_2$C
N
Bn
^{n}PrHN
O
3d/400MHz/CDCl$_3$
1.00
0.85
11.14
0.38
2.08
1.04
1.07
3.40
2.28
0.43
2.53
2.75
3.63
f1 (ppm)



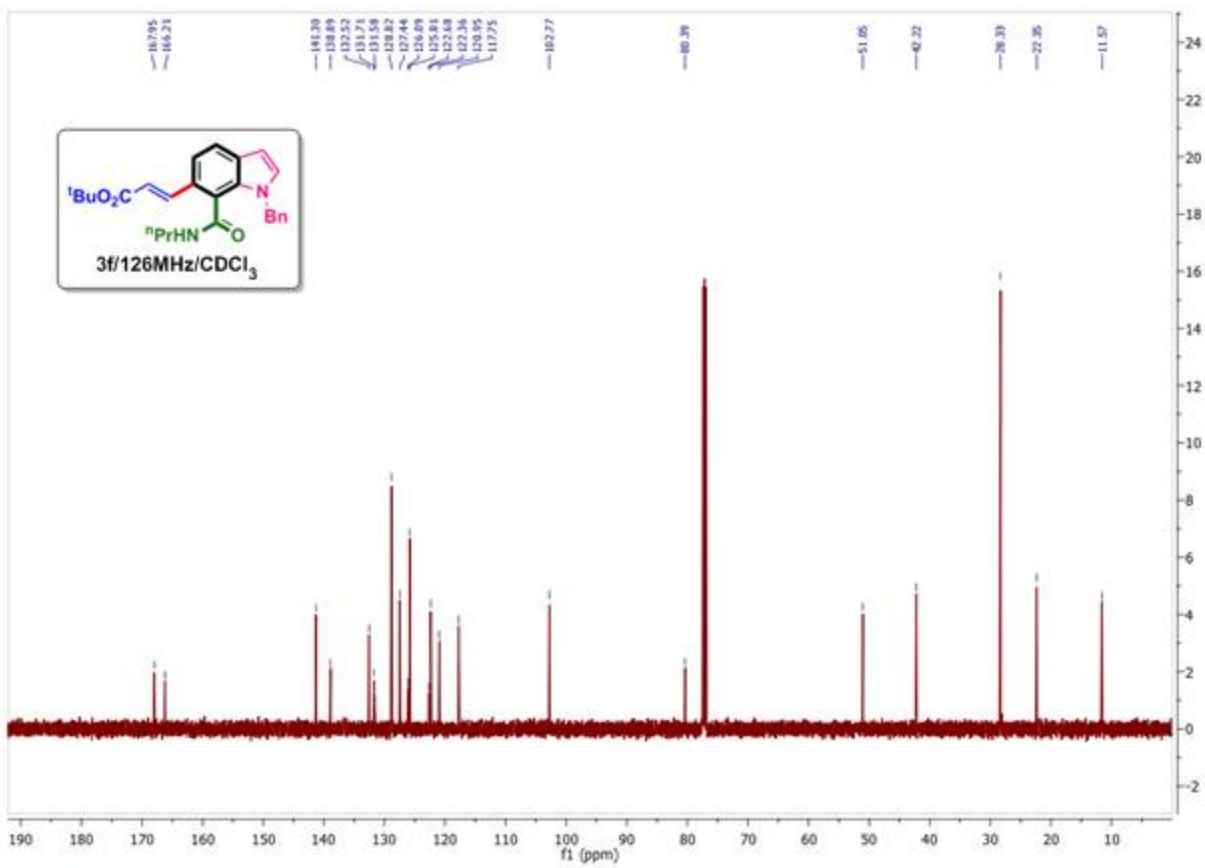
167.65
166.55
142.85
138.64
132.61
128.68
128.66
128.49
128.47
128.18
128.15
128.12
127.32
127.30
125.63
122.26
118.11
102.69
66.16
50.87
42.08
22.11
11.34
BnO$_2$C
N
Bn
^{n}PrHN
O
3d/101MHz/CDCl$_3$
f1 (ppm)


3e/400MHz/CDCl$_3$
f1 (ppm)

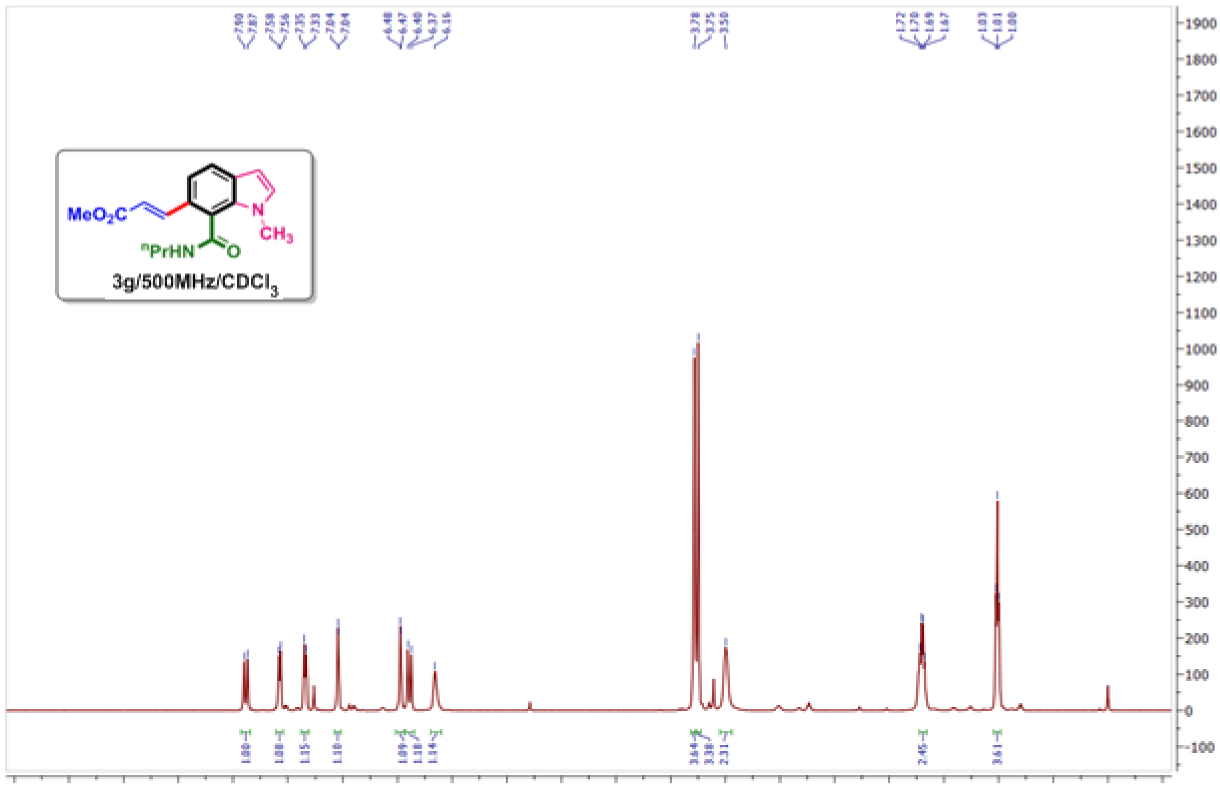

3e/101MHz/CDCl$_3$
f1 (ppm)

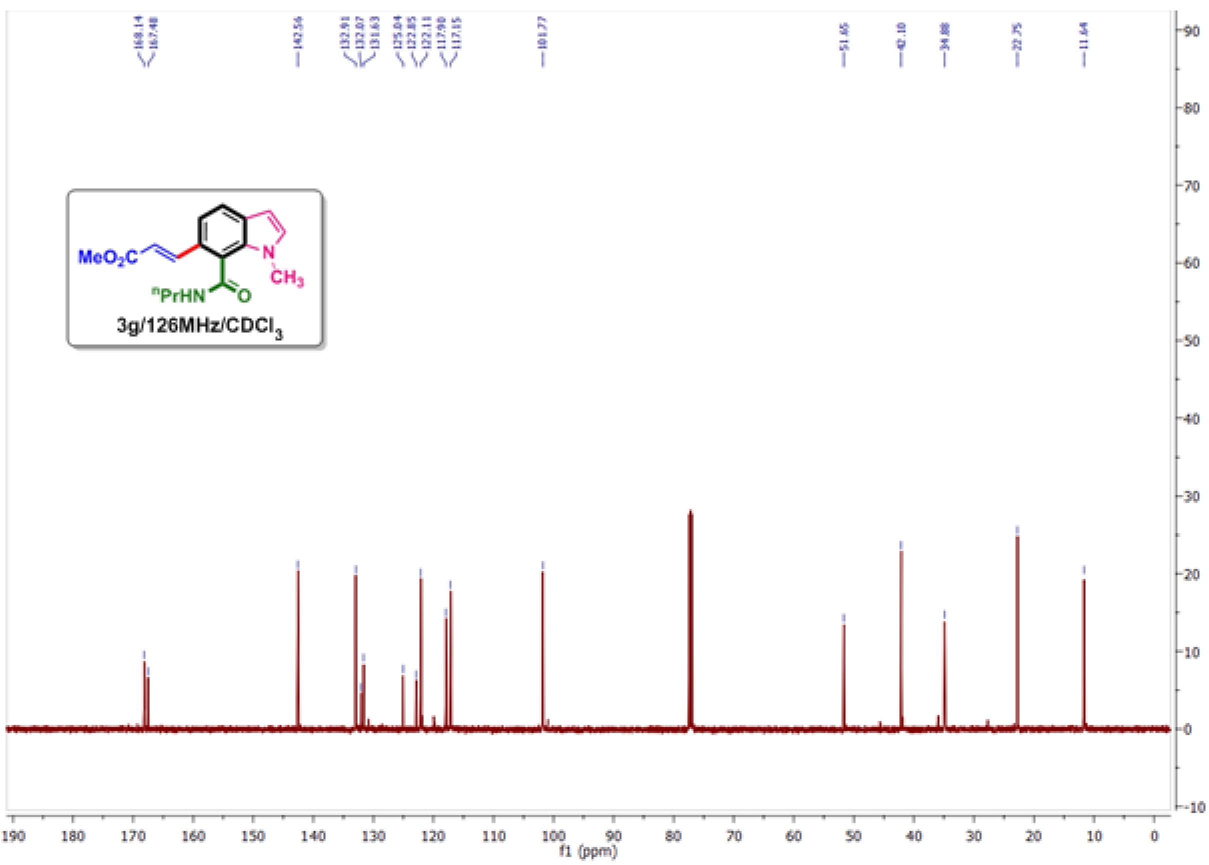


3f/500MHz/CDCl3
f1 (ppm)



3f/126MHz/CDCl3
f1 (ppm)


MeO2C
nPrHN
N
CH3
O
3g/500MHz/CDCl3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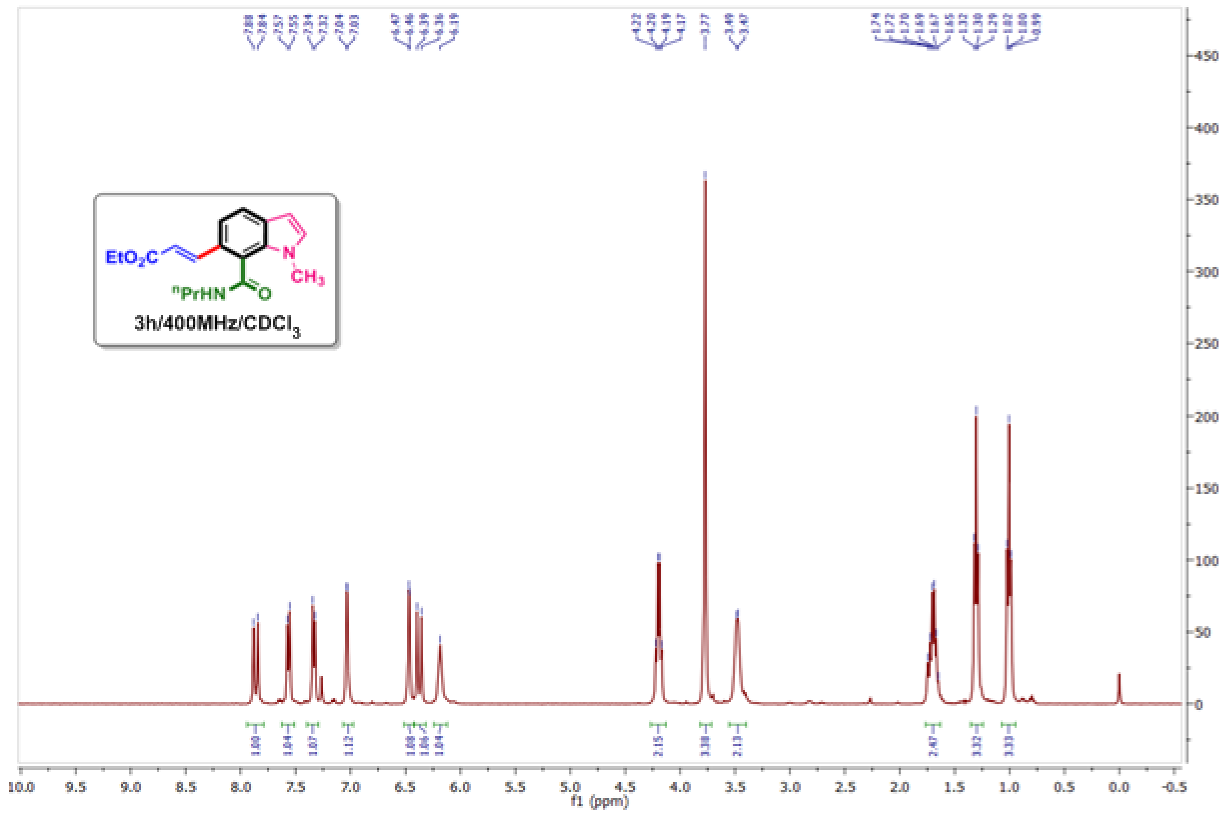
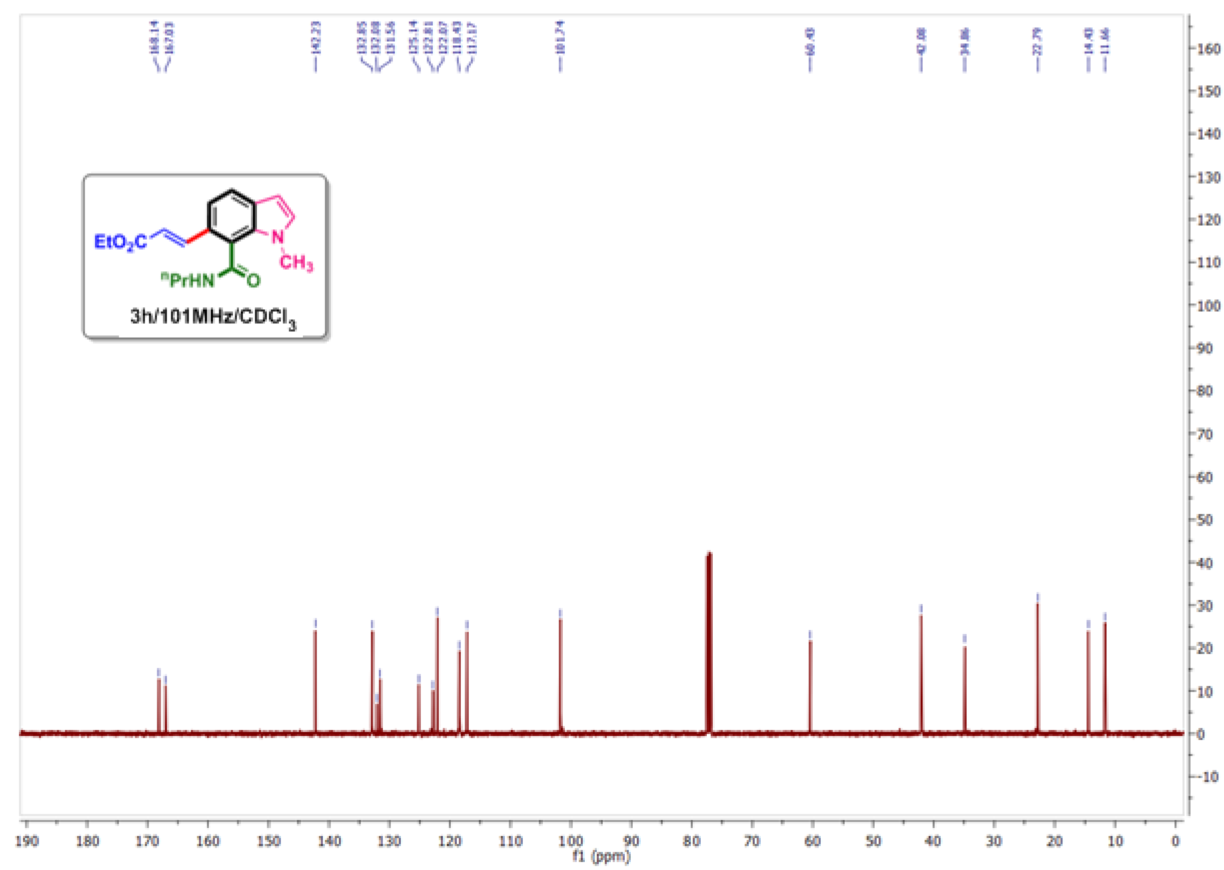
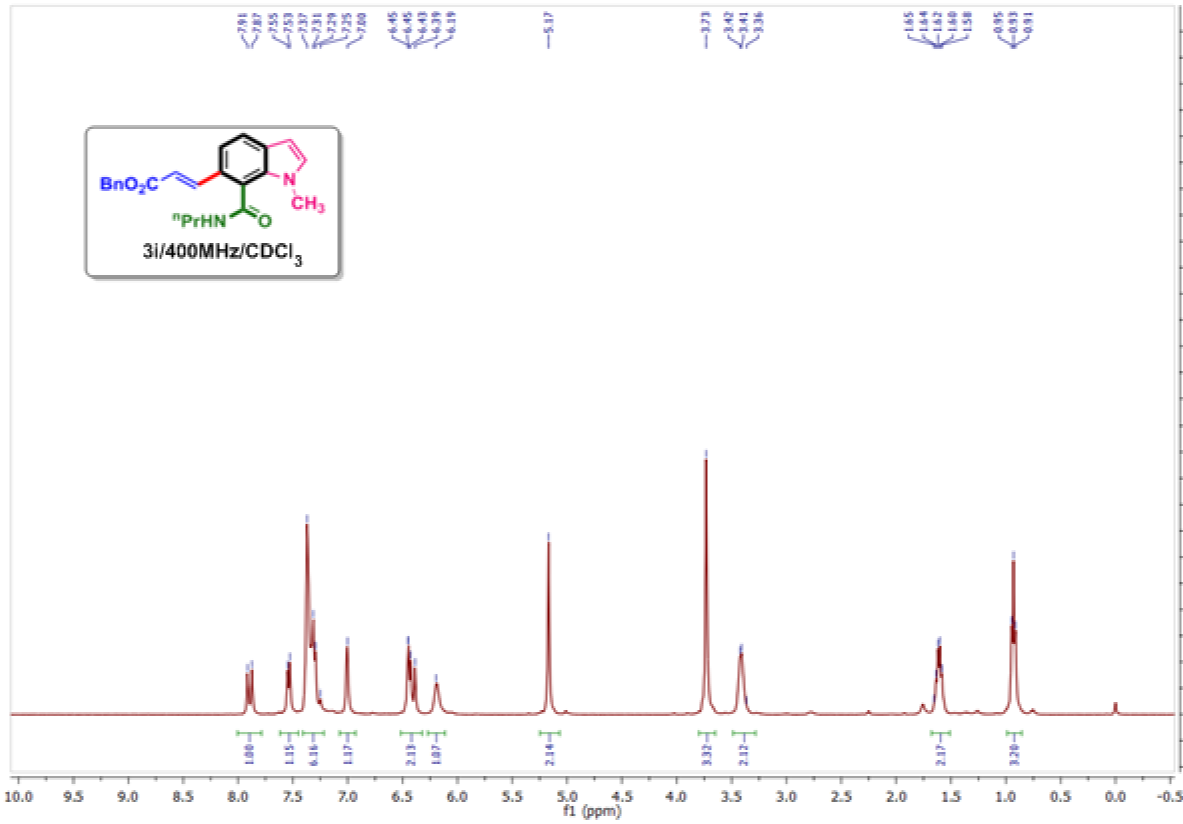
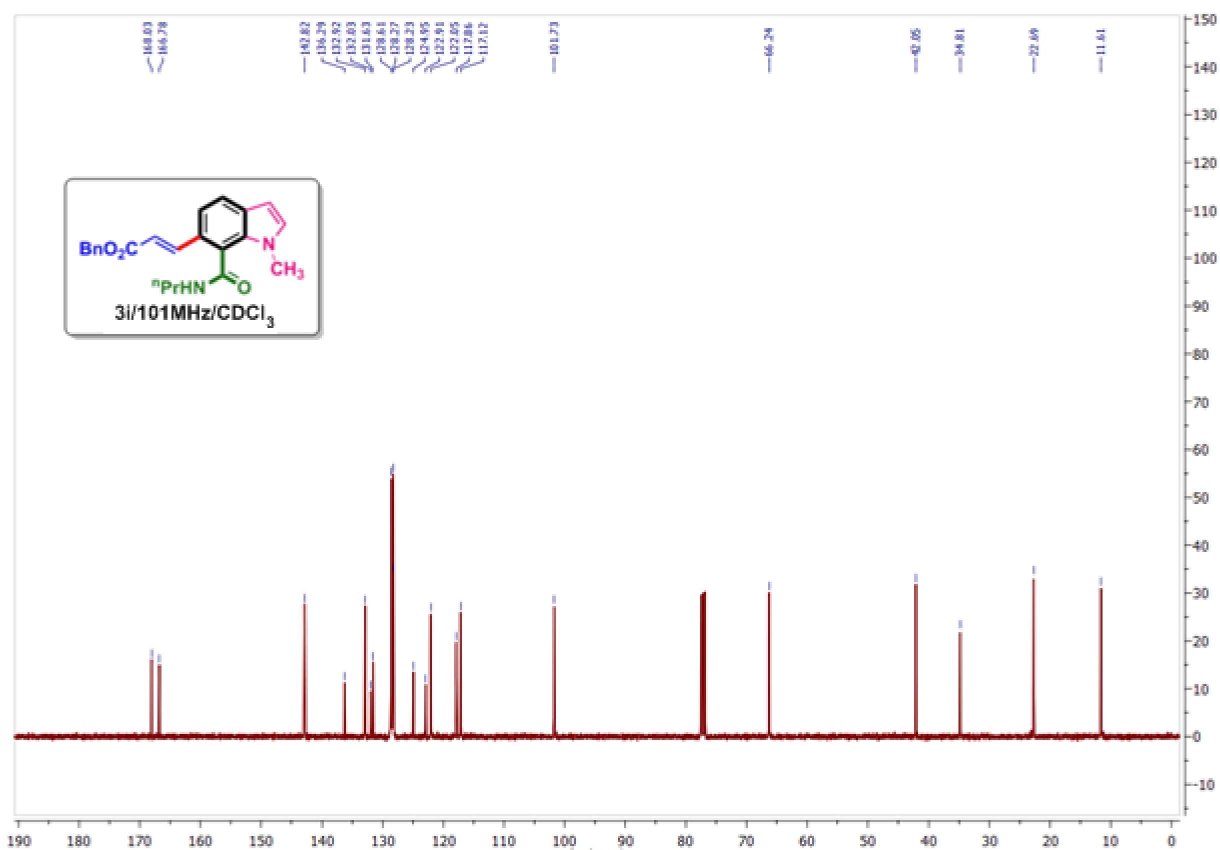
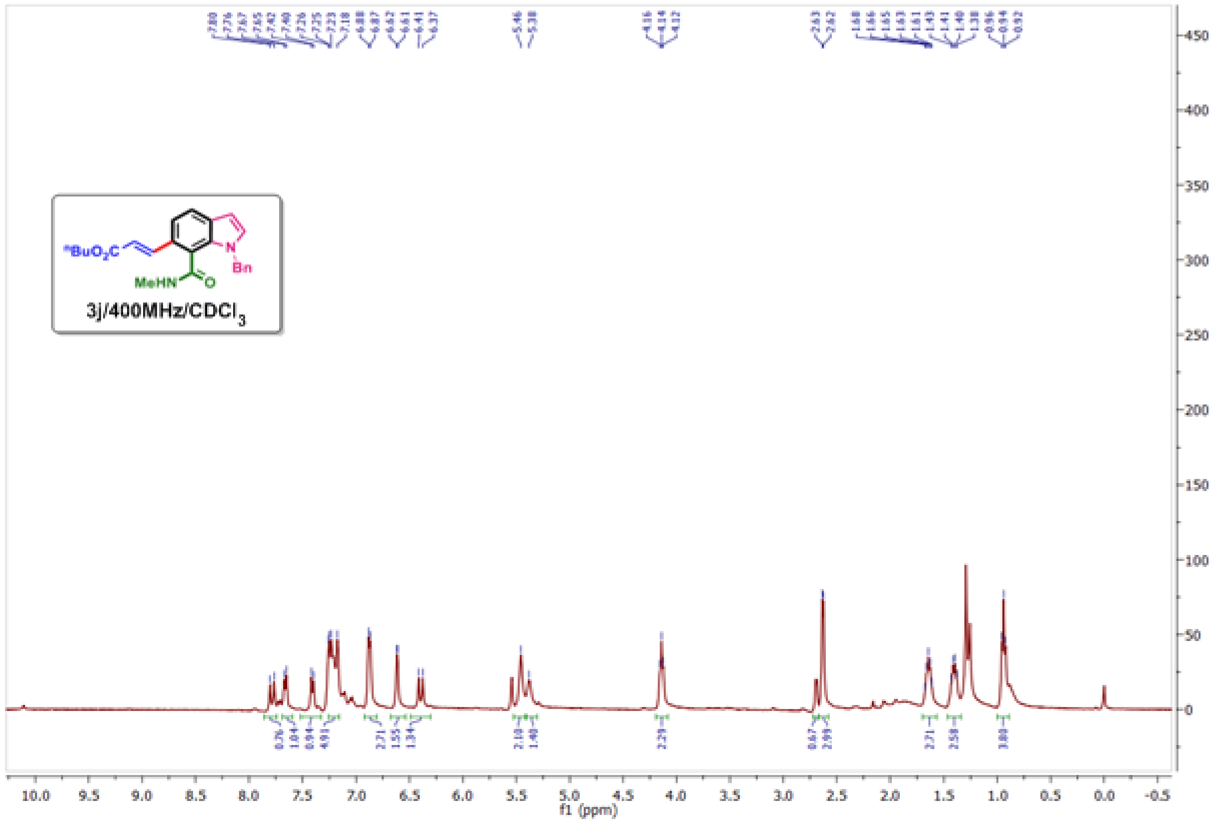
142.56
132.91
132.07
131.63
125.04
122.85
122.11
117.90
117.15
101.77
51.65
42.10
34.88
22.75
11.64
MeO2C
nPrHN
N
CH3
O
3g/126MHz/CDCl3
f1 (ppm)






BnO$_2$C
^{n}PrHN
N
CH$_3$
O
3i/400MHz/CDCl$_3$
f1 (ppm)


BnO$_2$C
^{n}PrHN
N
CH$_3$
O
3i/101MHz/CDCl$_3$
f1 (ppm)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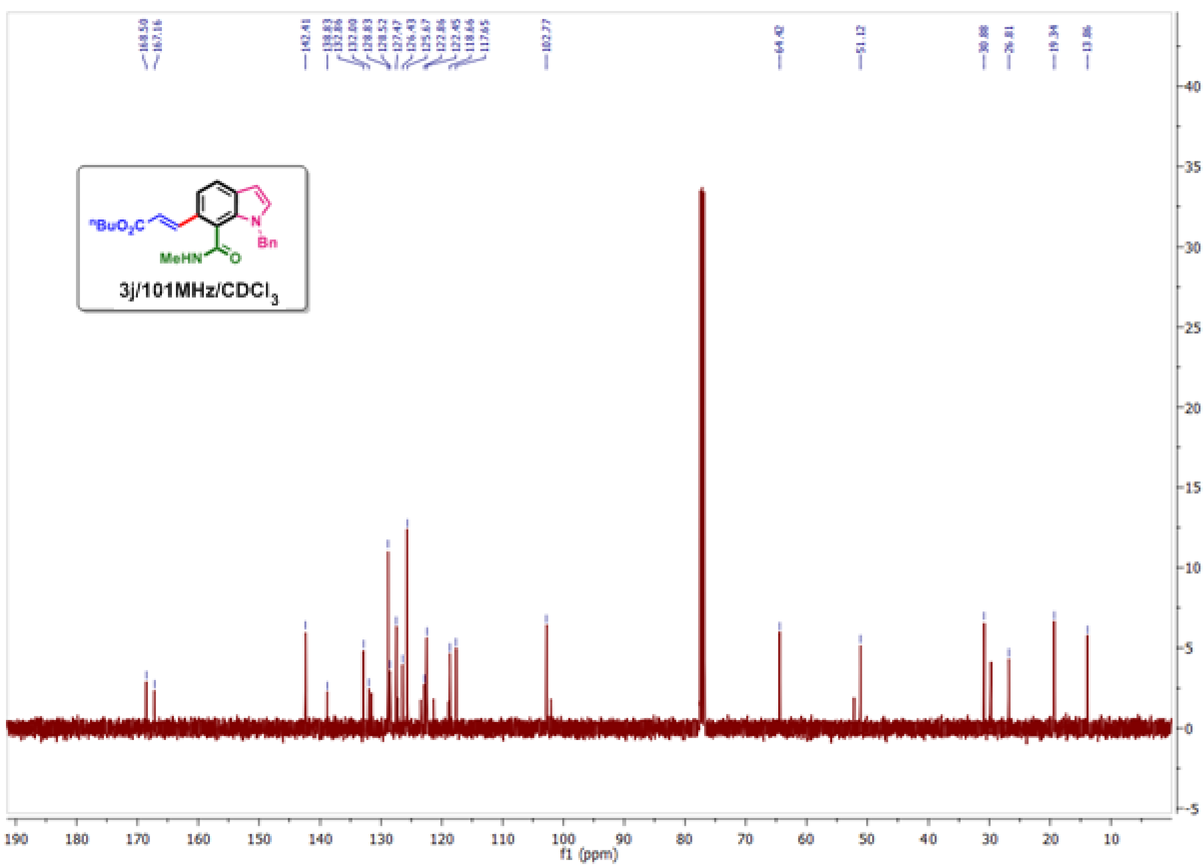
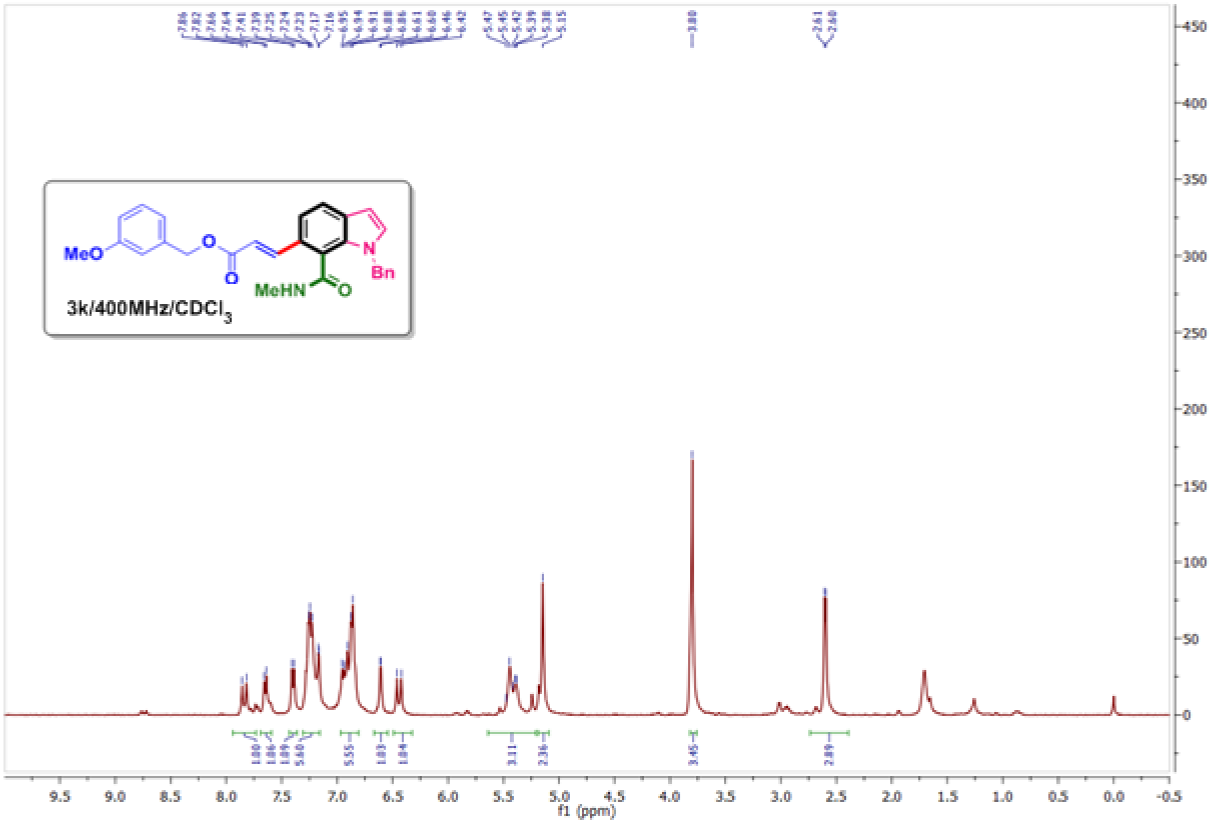
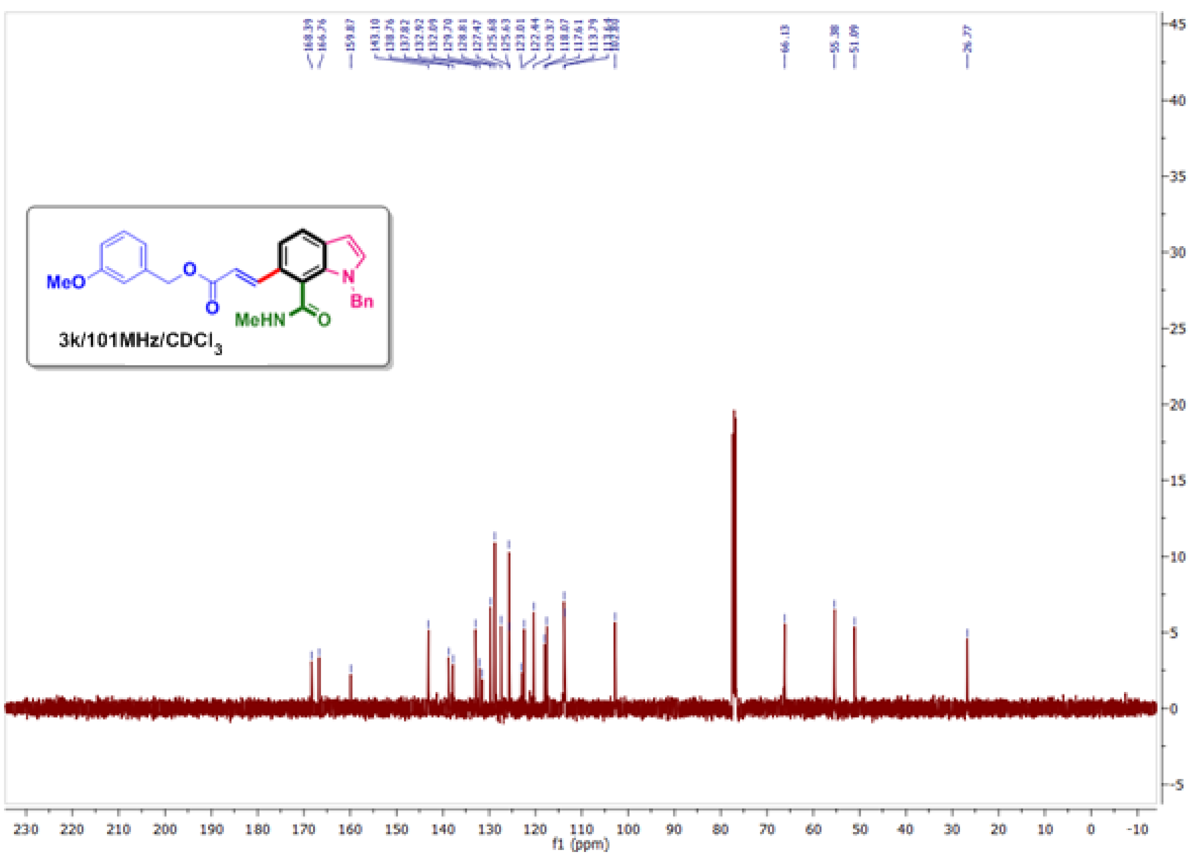
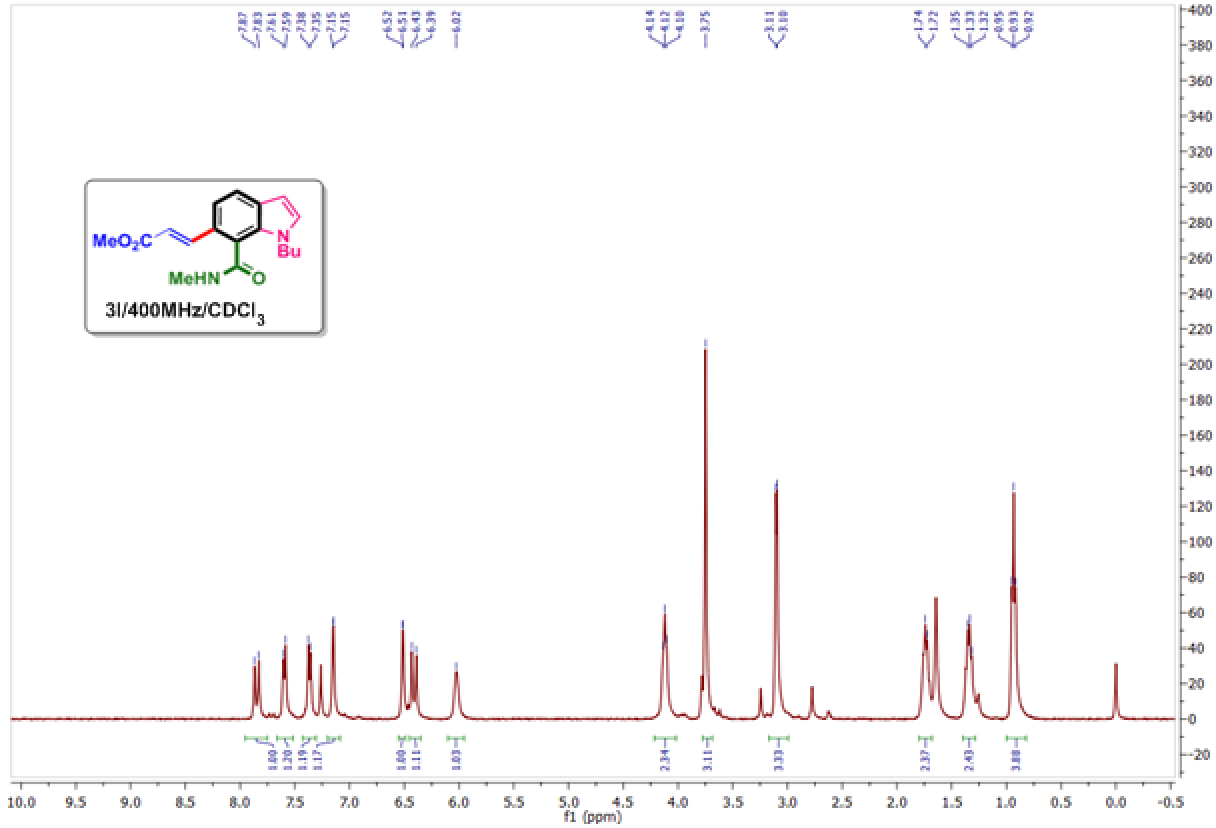
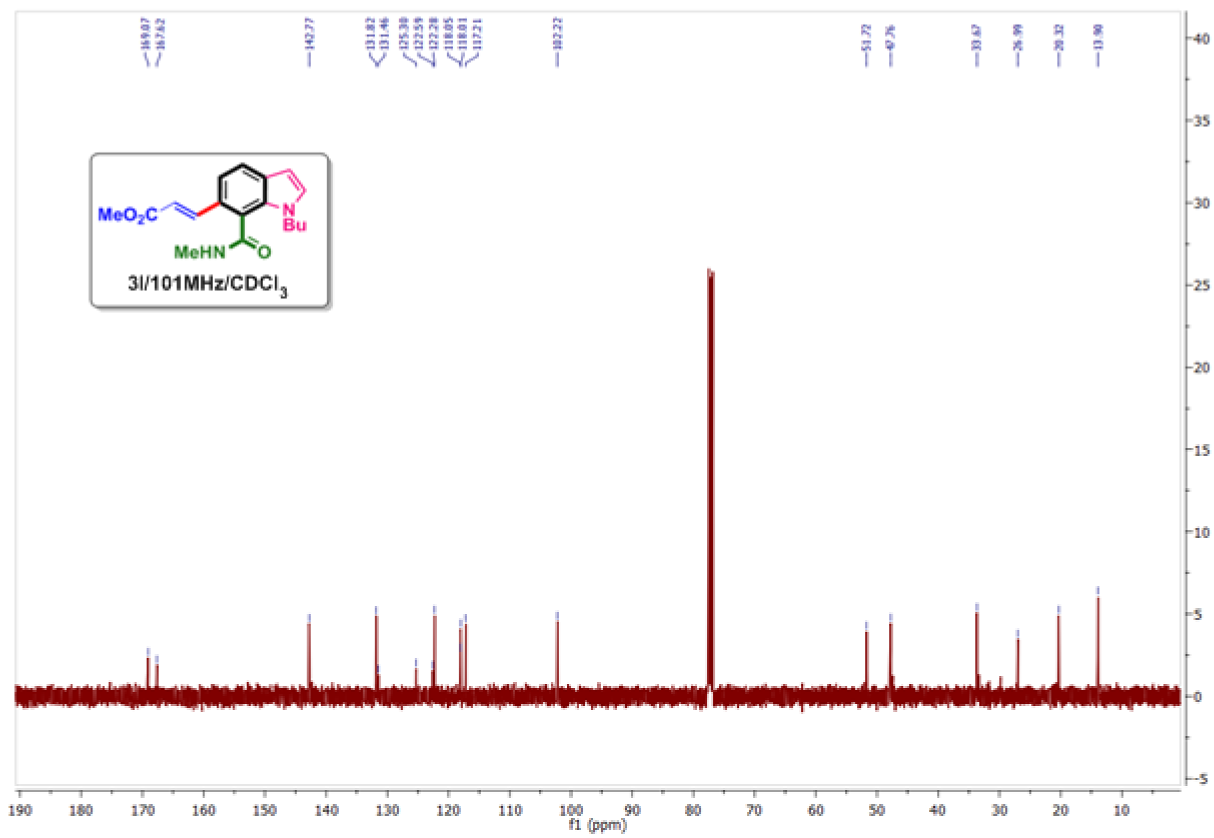
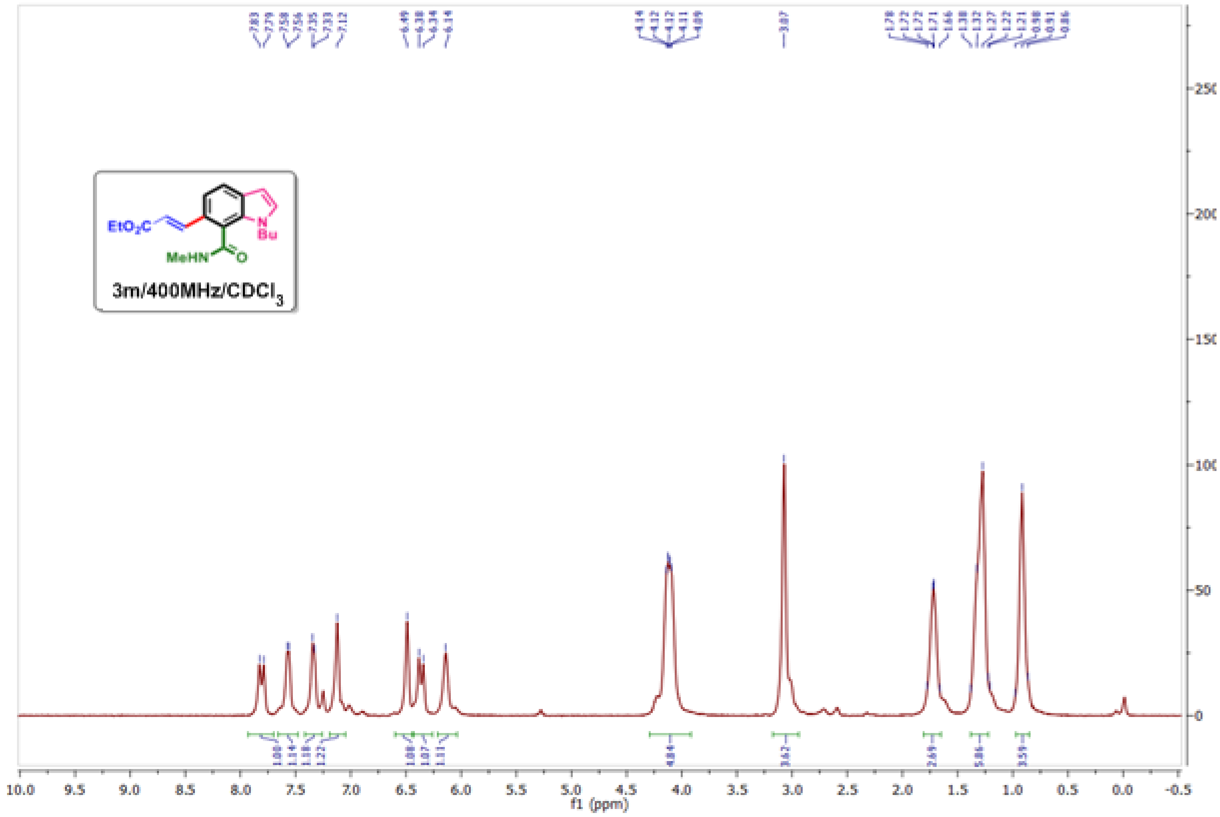

3j/101MHz/CDCl3


3k/400MHz/CDCl3
MeO
O
MeHN
N
Bn
f1 (ppm)


3k/101MHz/CDCl3
MeO
O
MeHN
N
Bn
f1 (ppm)


MeO2C
N
Bu
MeHN
O
3l/400MHz/CDCl3
f1 (ppm)


MeO2C
N
Bu
MeHN
O
3l/101MHz/CDCl3
f1 (ppm)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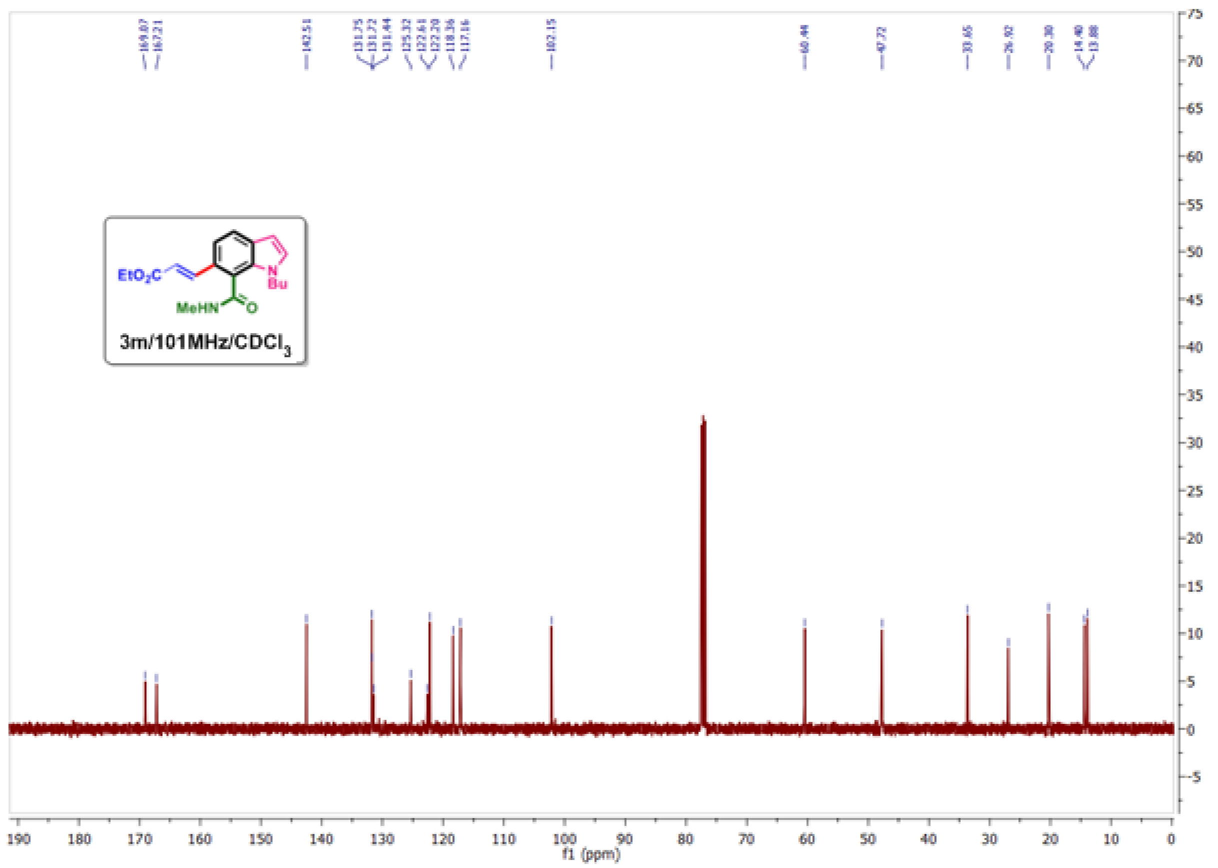
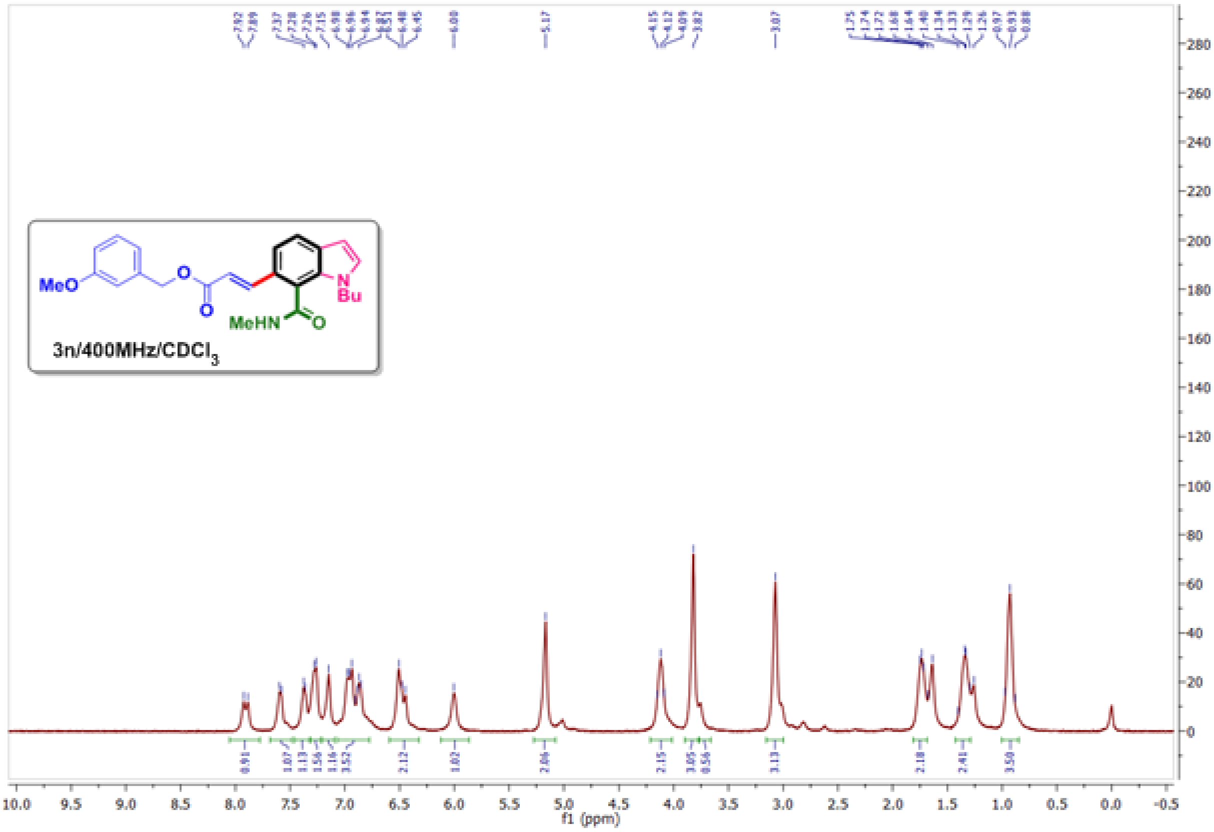
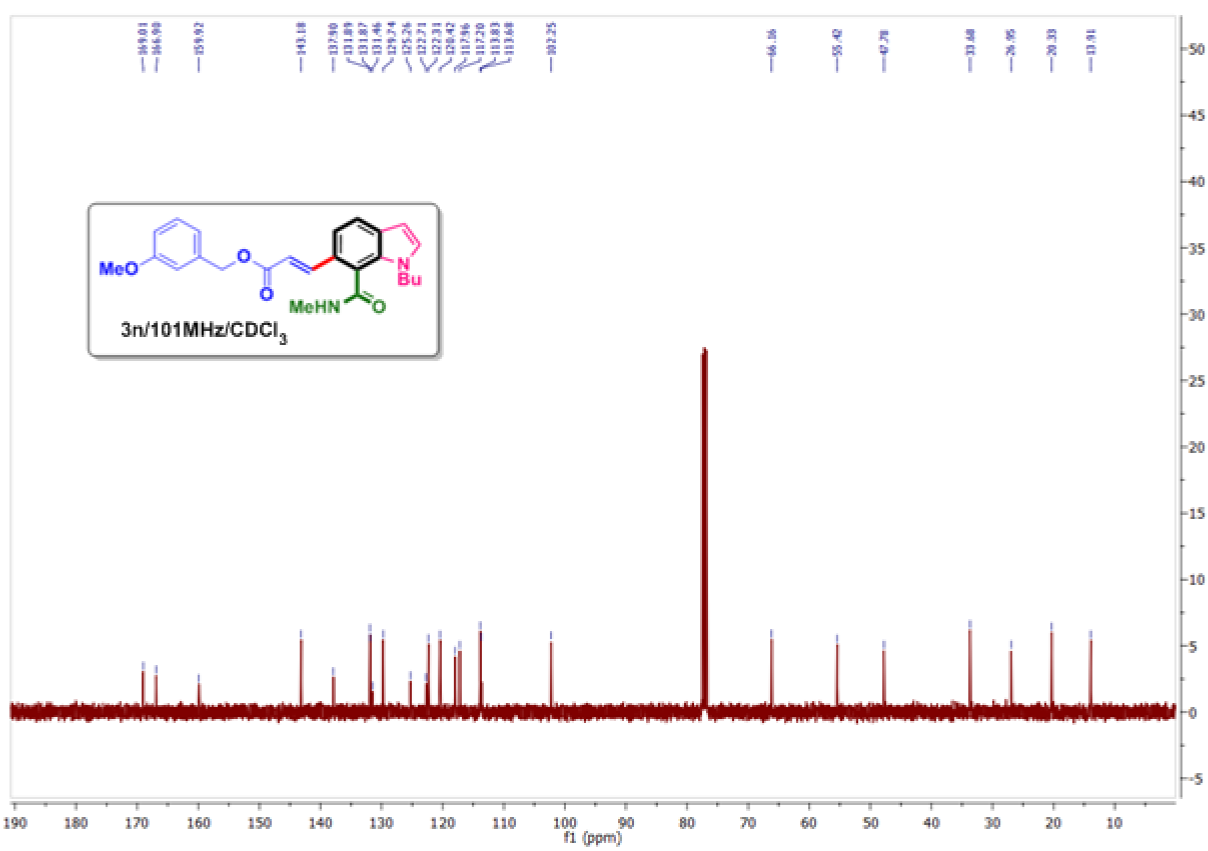
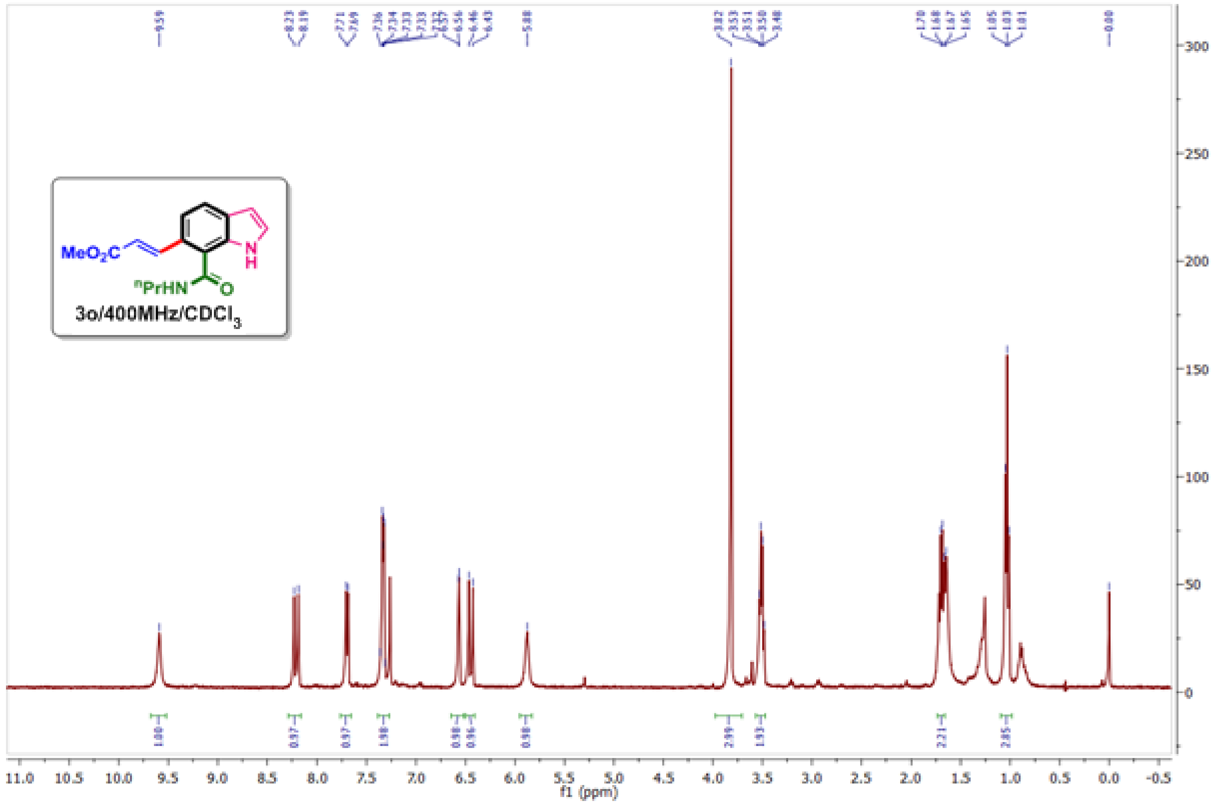
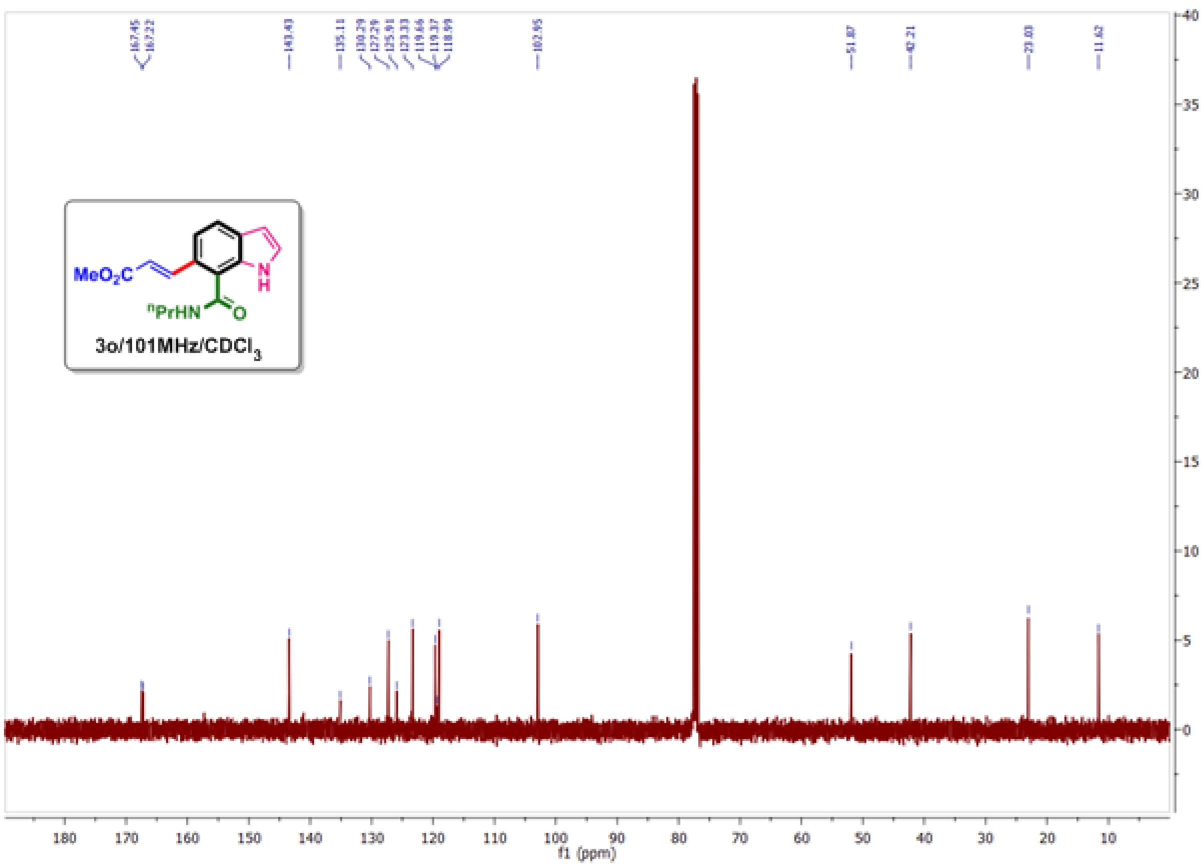
f1 (ppm)

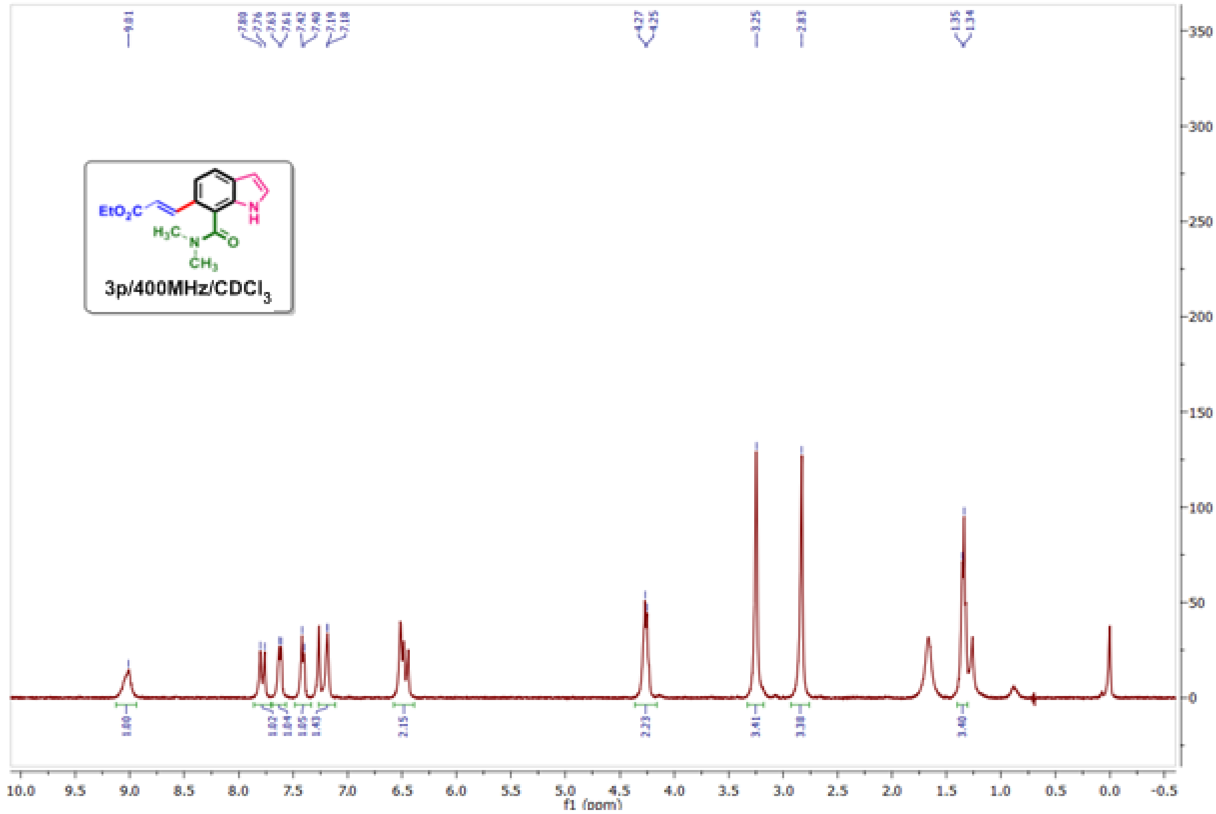

3m/101MHz/CDCl3
f1 (ppm)

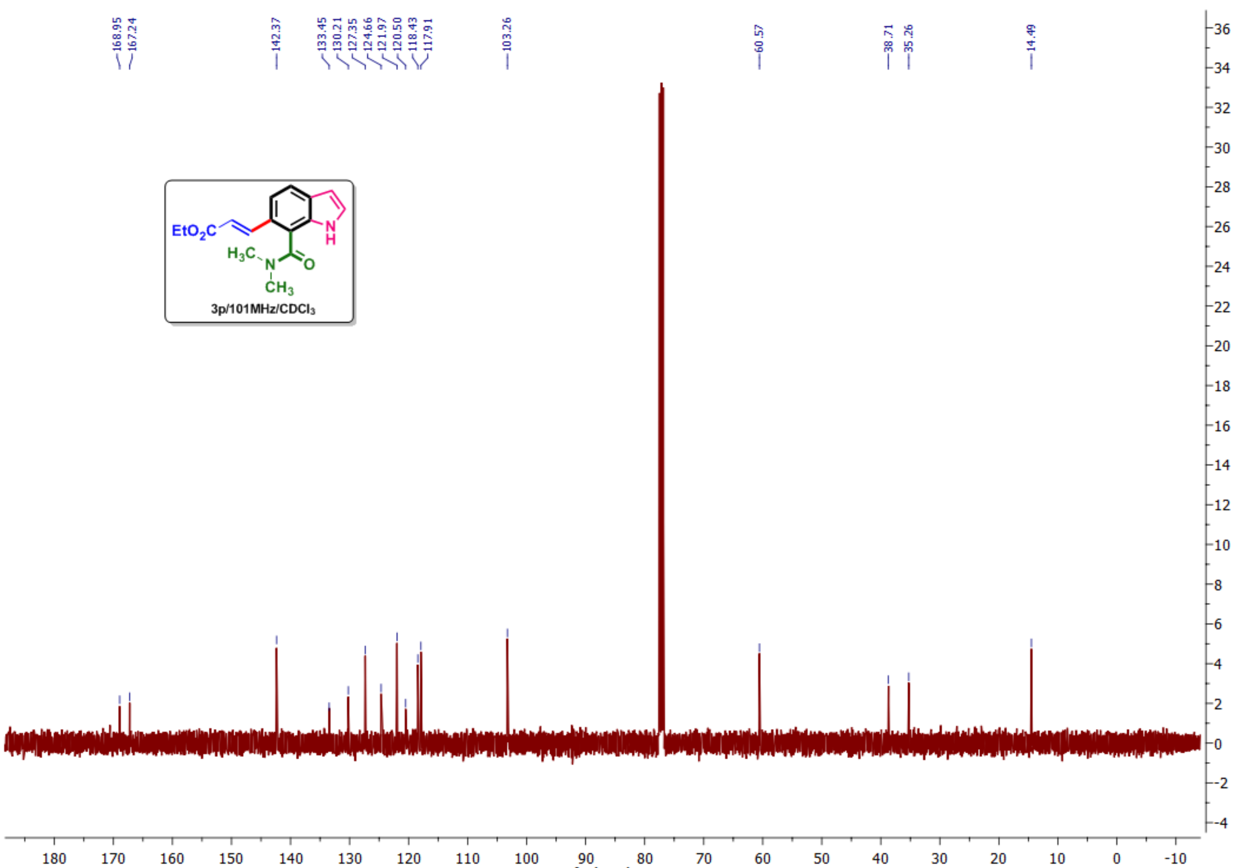

MeO
O
O
N
Bu
MeHN
O
3n/400MHz/CDCl3
f1 (ppm)


MeO
O
O
N
Bu
MeHN
O
3n/101MHz/CDCl3
f1 (ppm)


MeO2C
nPrHN
3o/400MHz/CDCl3
f1 (ppm)


MeO2C
nPrHN
3o/101MHz/CDCl3
f1 (ppm)


9.01
7.80
7.76
7.63
7.61
7.42
7.40
7.19
7.18
4.27
4.25
3.25
2.83
1.35
1.34
EtO$_2$C
H$_3$C
N
CH$_3$
O
NH
3p/400MHz/CDCl$_3$
f1 (ppm)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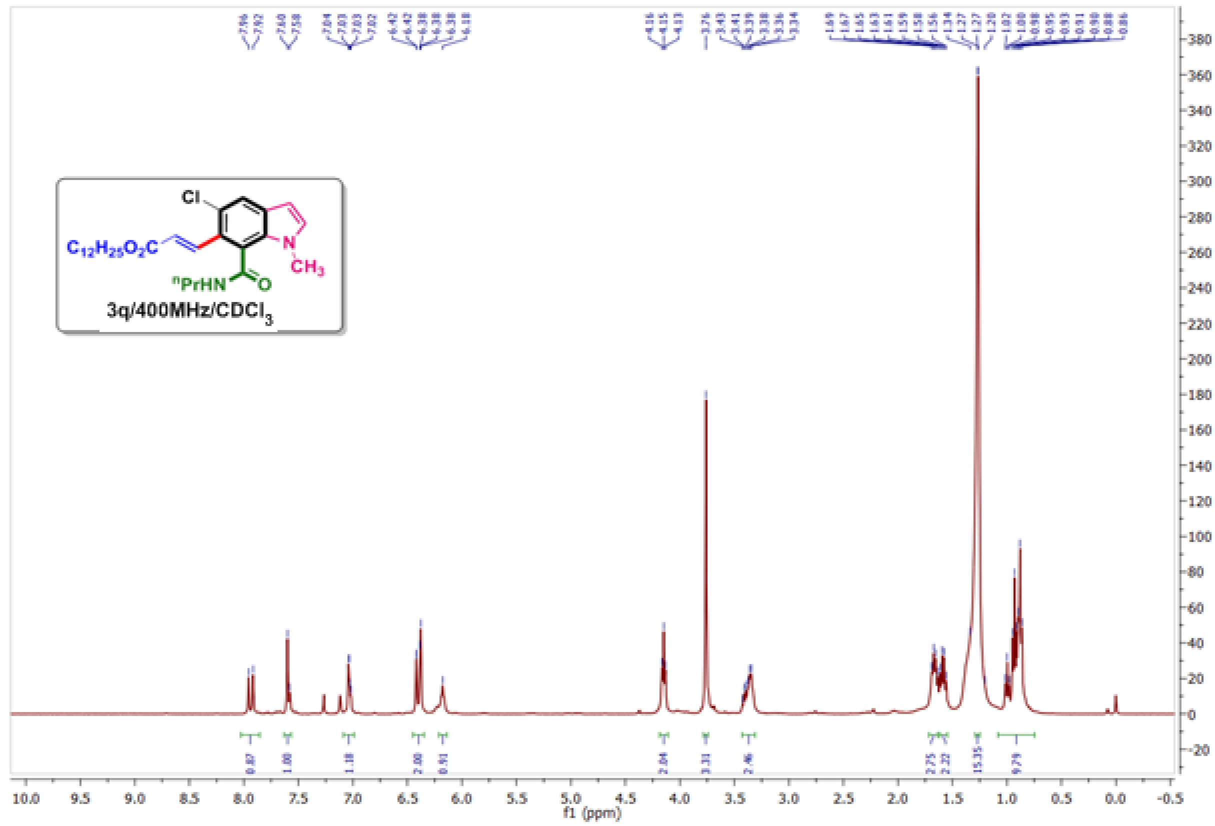
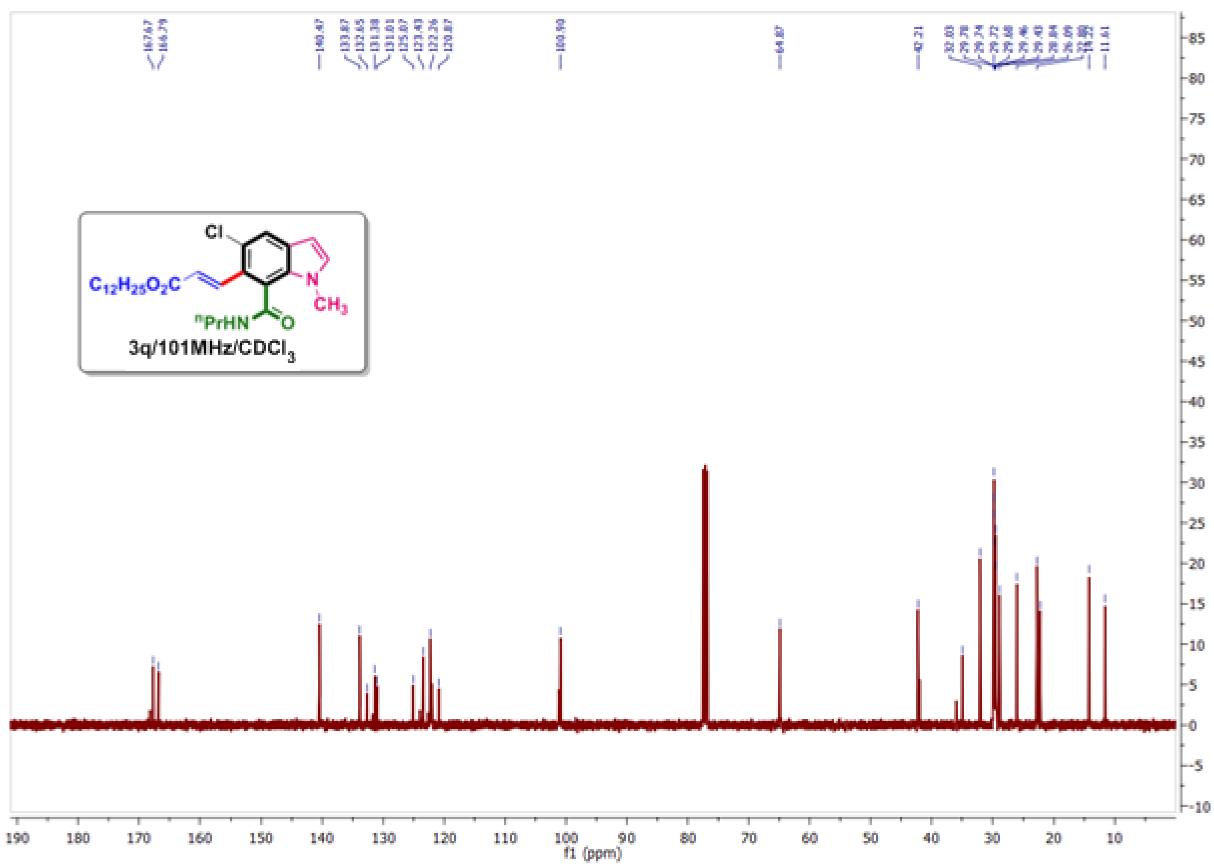
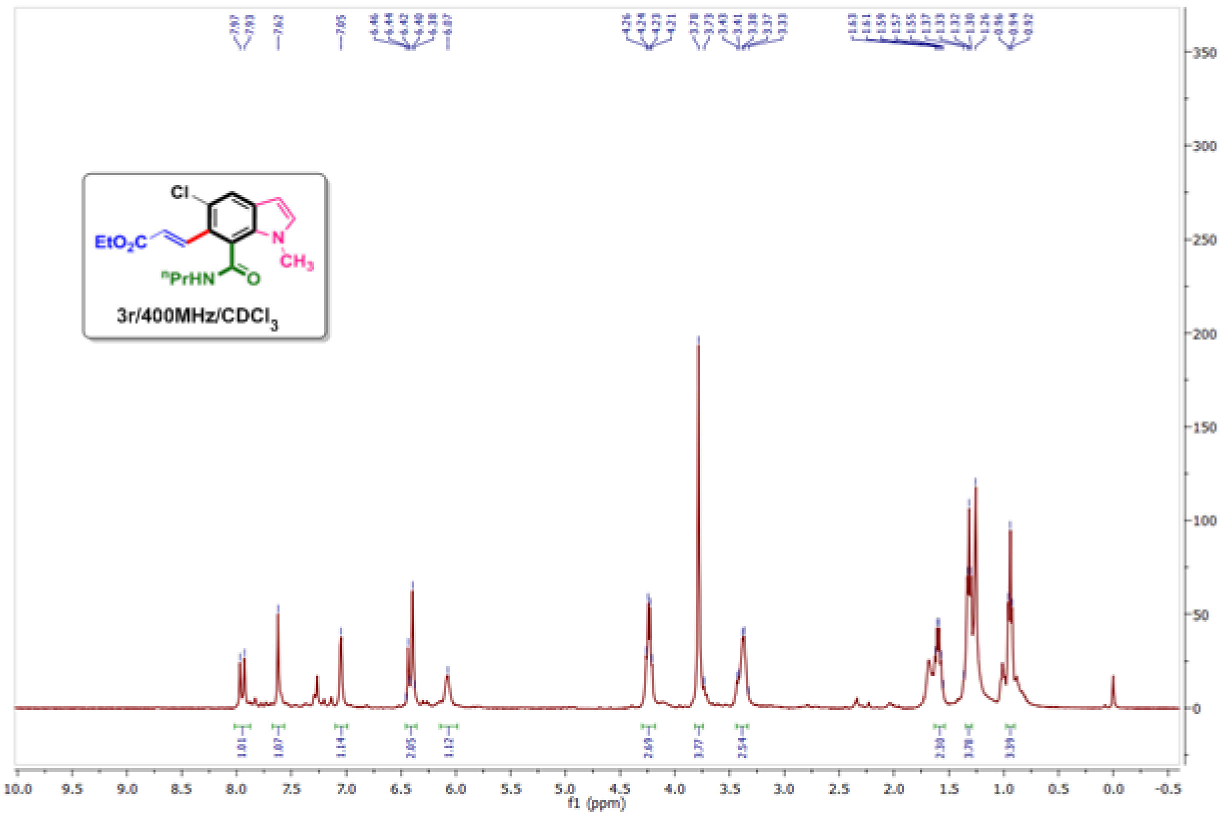
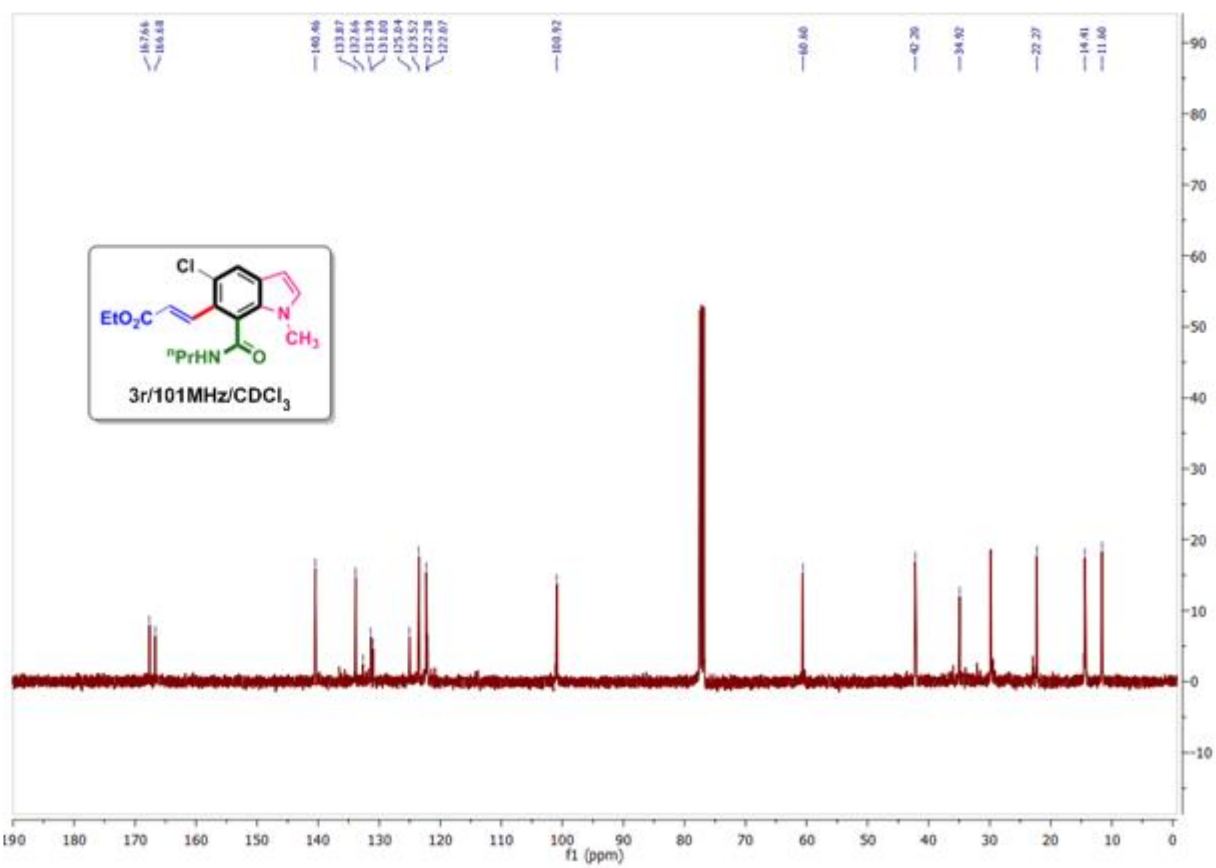
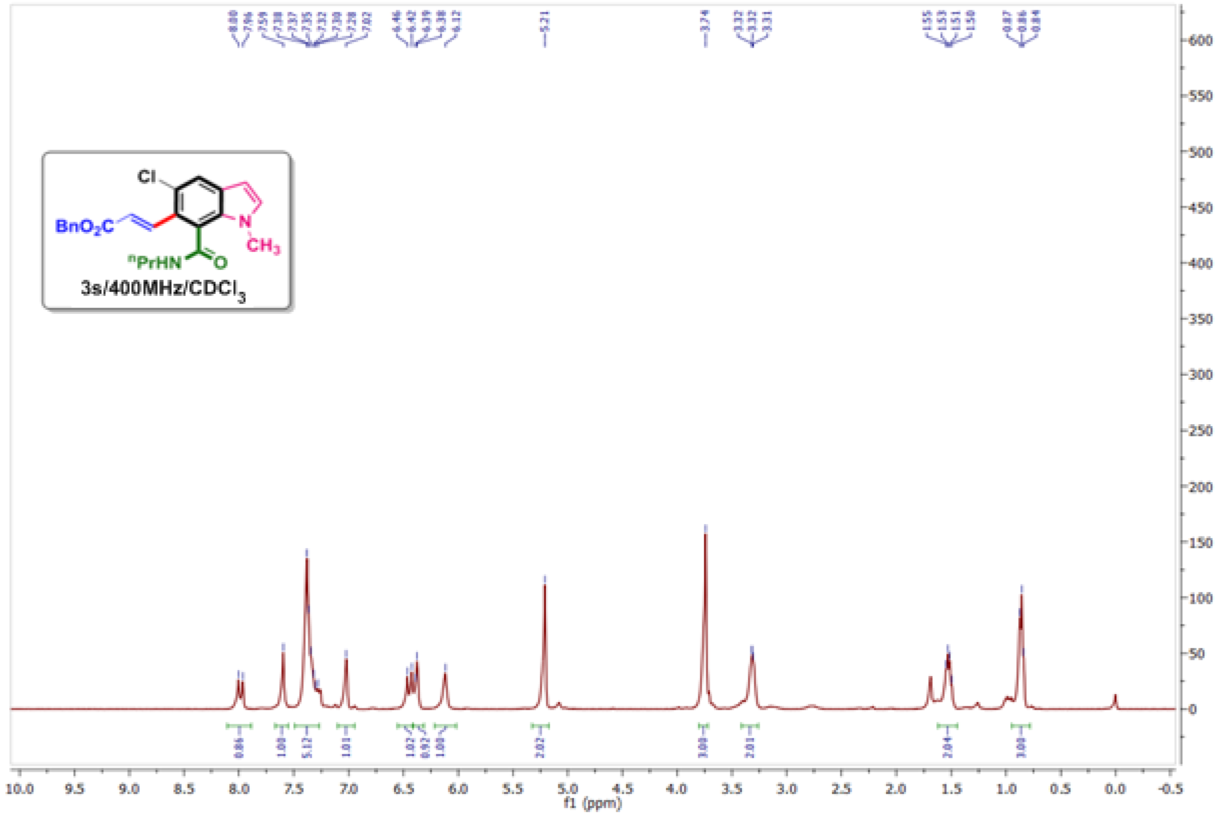
167.24
142.37
133.45
130.21
127.35
124.66
121.97
120.50
118.43
117.91
103.26
60.57
38.71
35.26
14.49
EtO$_2$C
H$_3$C
N
CH$_3$
O
NH
3p/101MHz/CDCl$_3$
f1 (ppm)


3q/400MHz/CDCl$_3$
f1 (ppm)


3q/101MHz/CDCl$_3$
f1 (ppm)


Cl
EtO_2C
N
CH_3
^nPrHN
O
3r/400MHz/$CDCl_3$
f1 (ppm)


Cl
EtO_2C
N
CH_3
^nPrHN
O
3r/101MHz/$CDCl_3$
f1 (ppm)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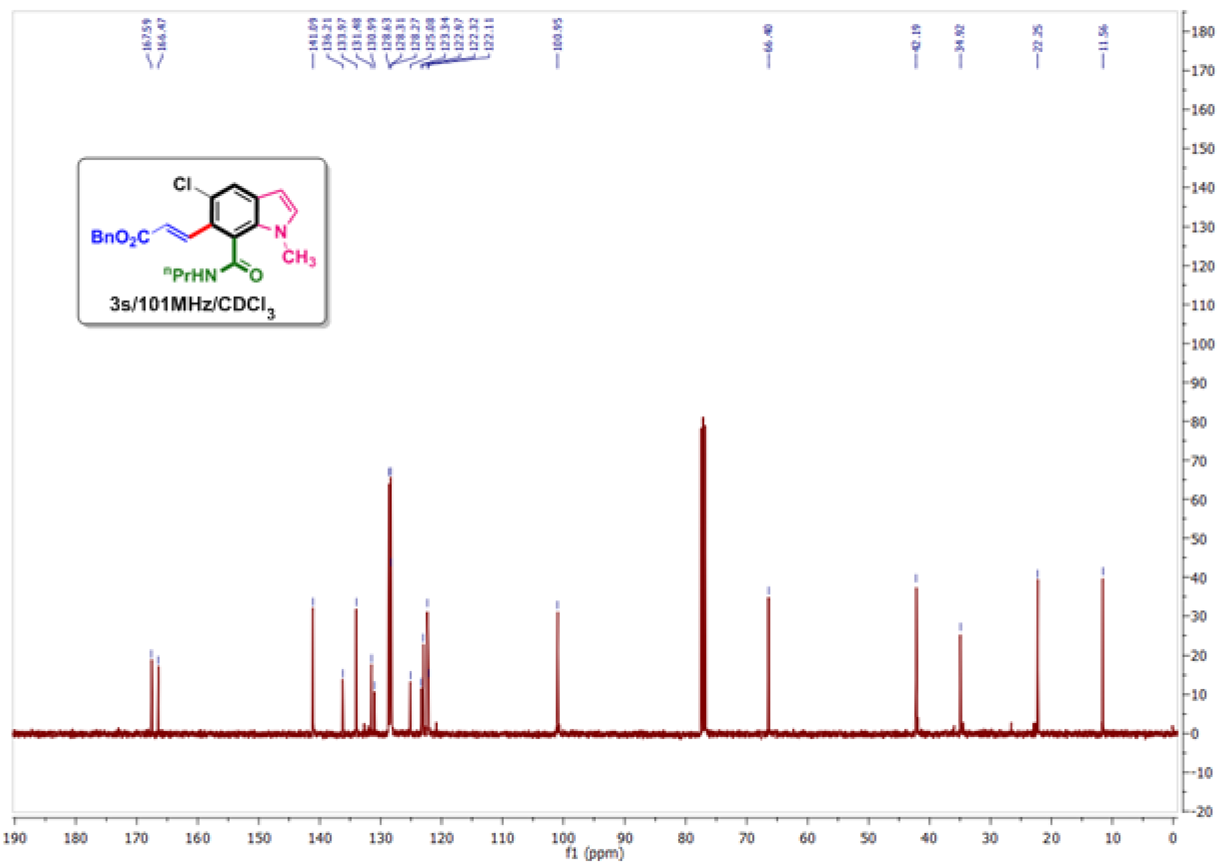
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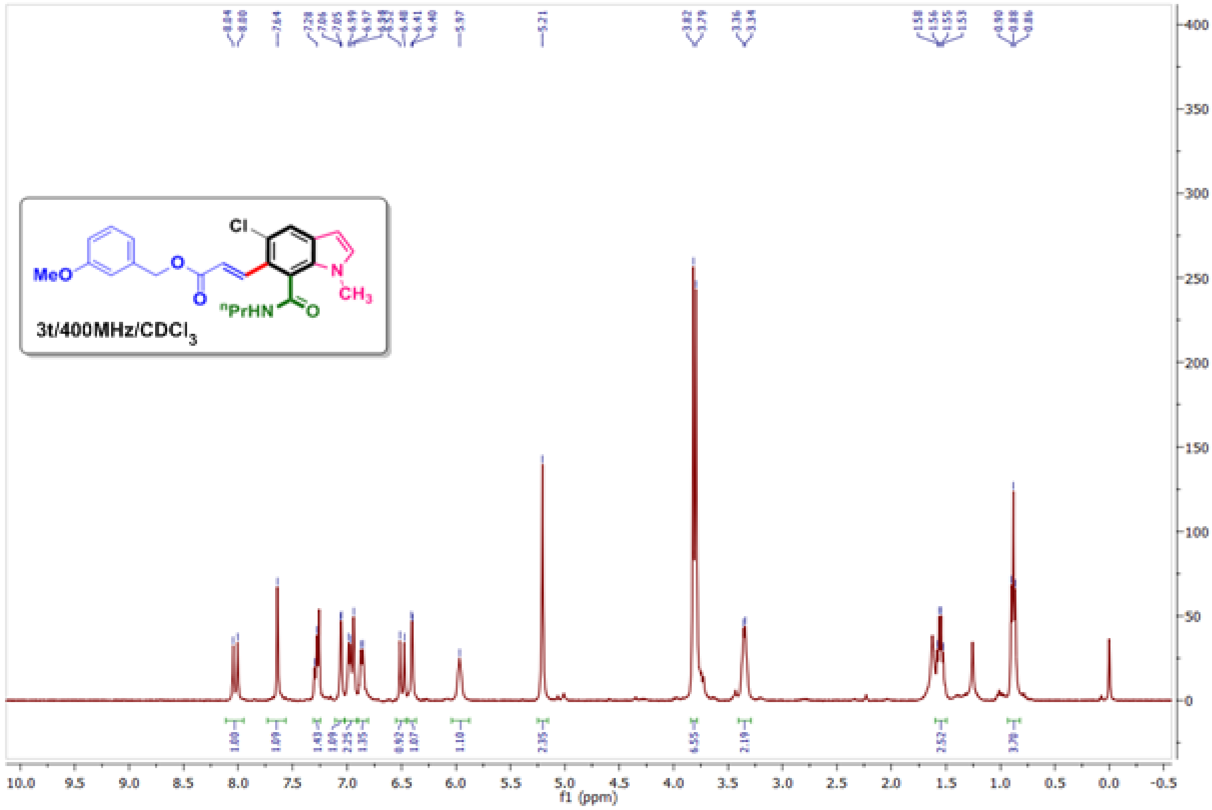
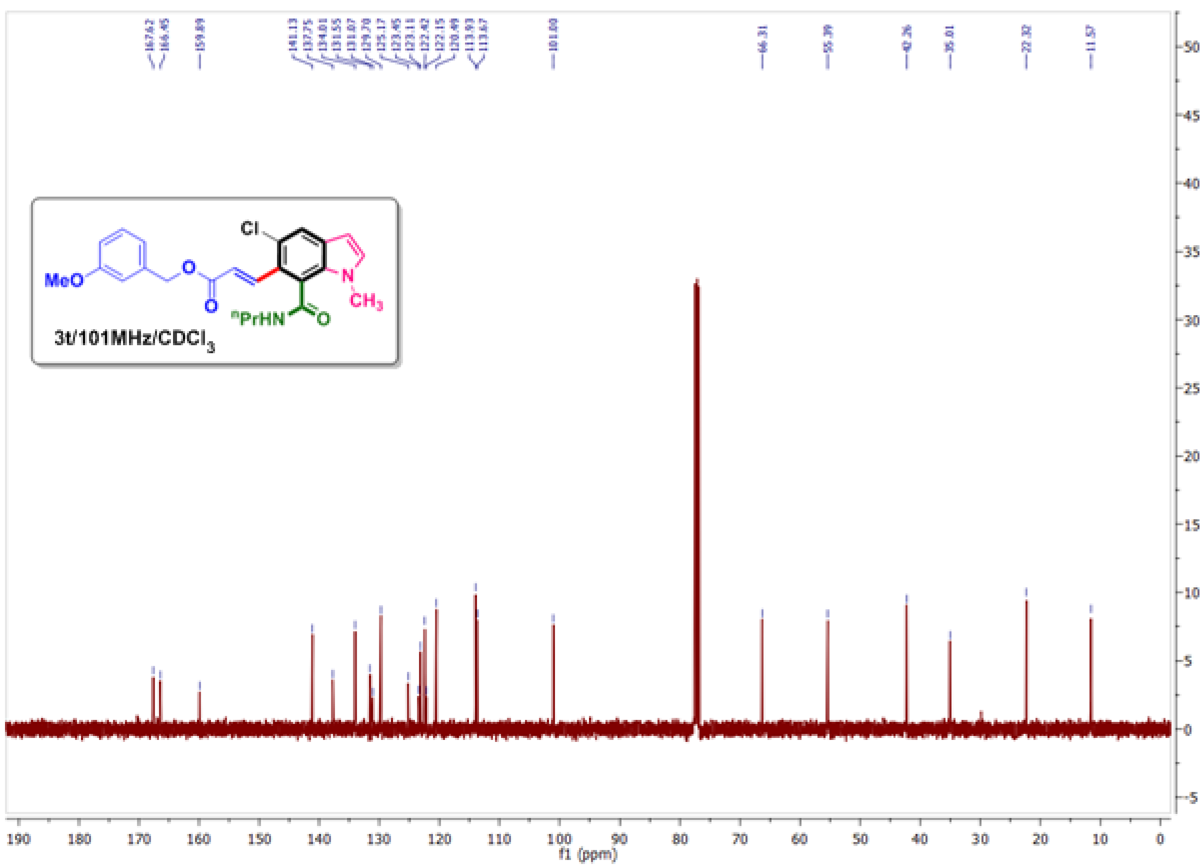
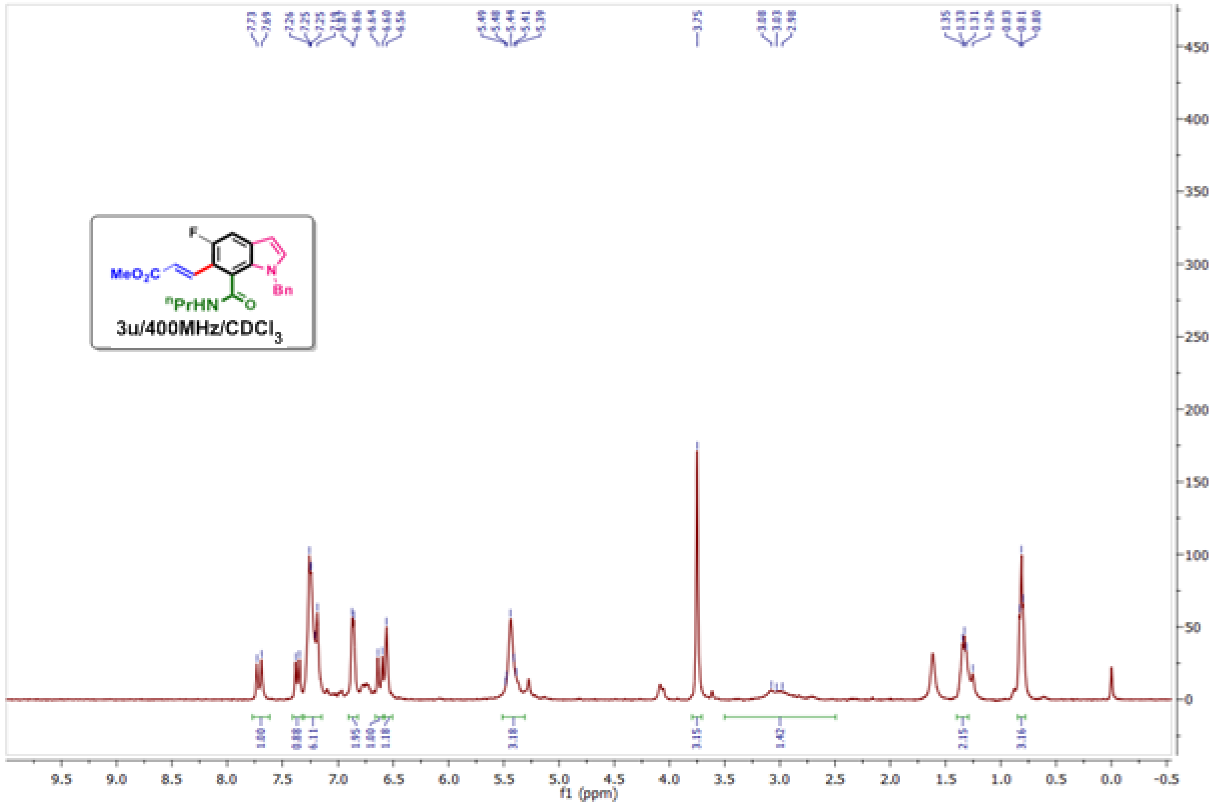
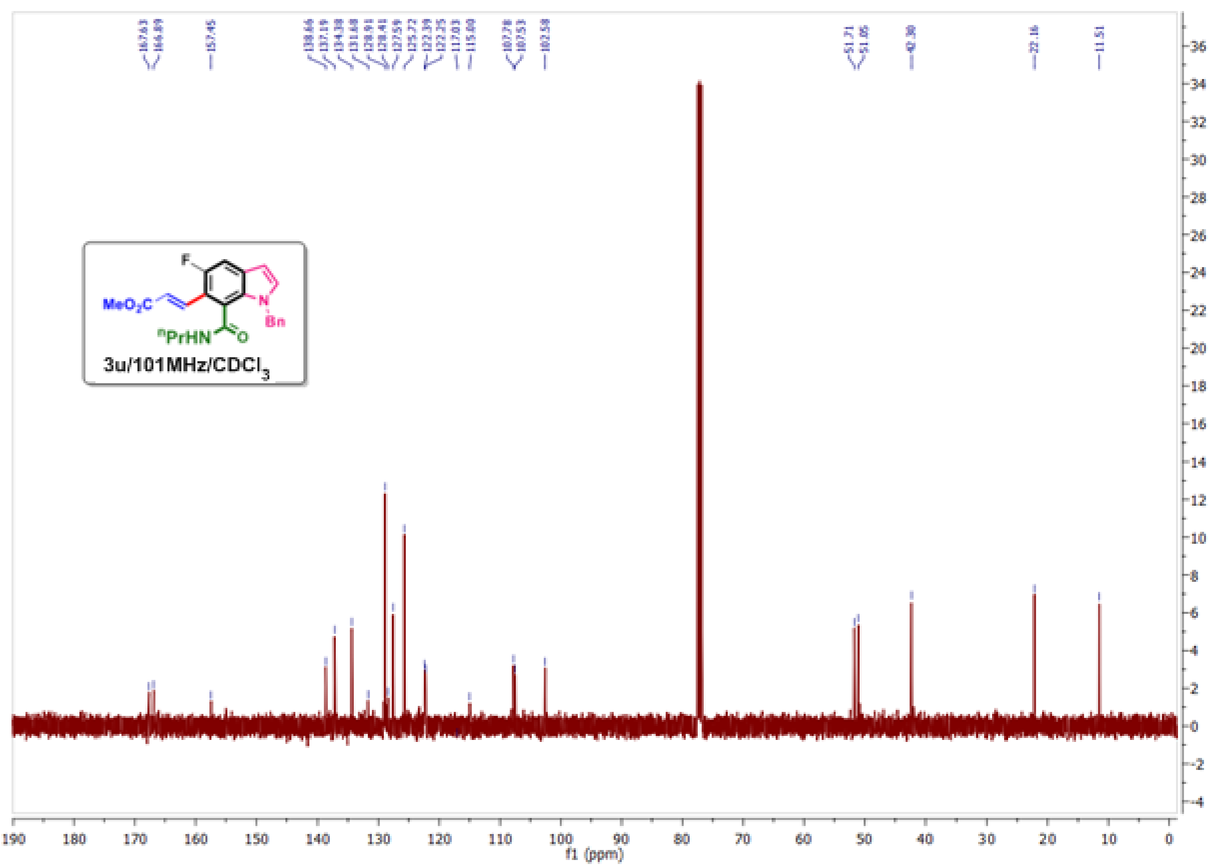

3t/400MHz/CDCl3
f1 (ppm)

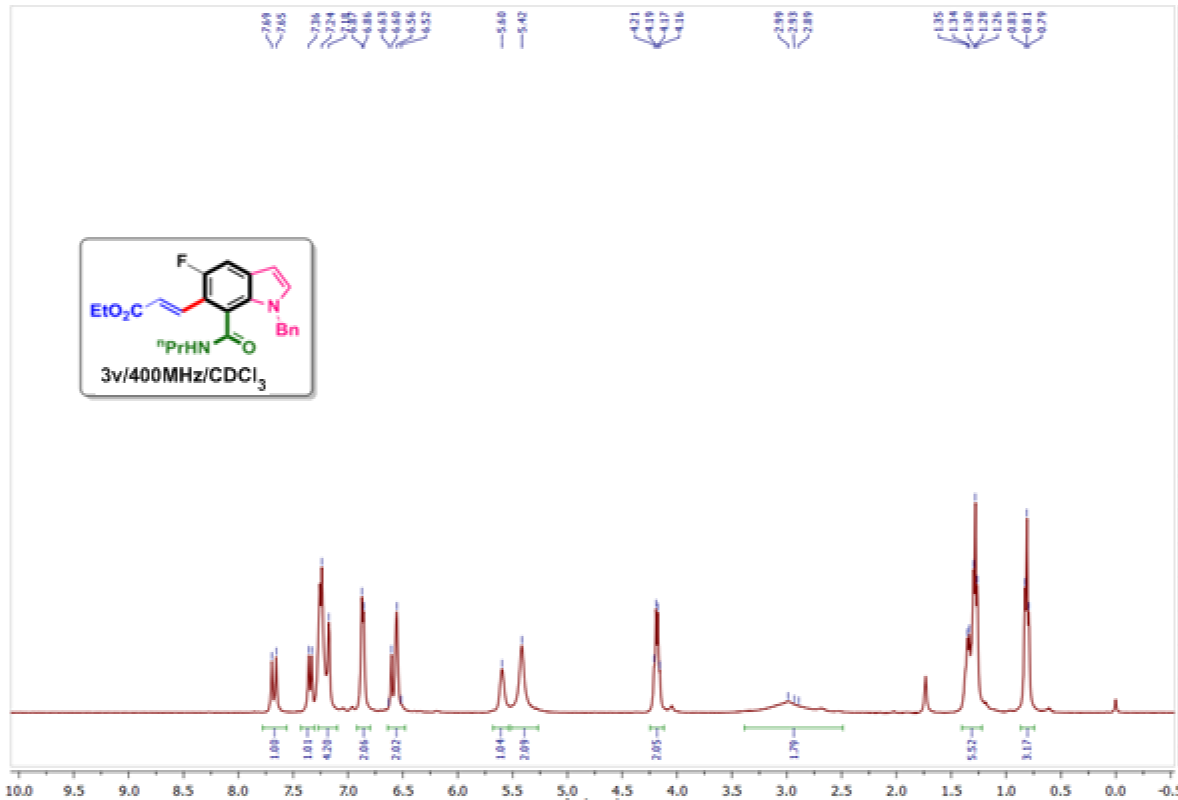

3t/101MHz/CDCl3
f1 (ppm)



F
MeO2C
N
Bn
nPrHN
O
3u/400MHz/CDCl3
f1 (ppm)



F
MeO2C
N
Bn
nPrHN
O
3u/101MHz/CDCl3
f1 (ppm)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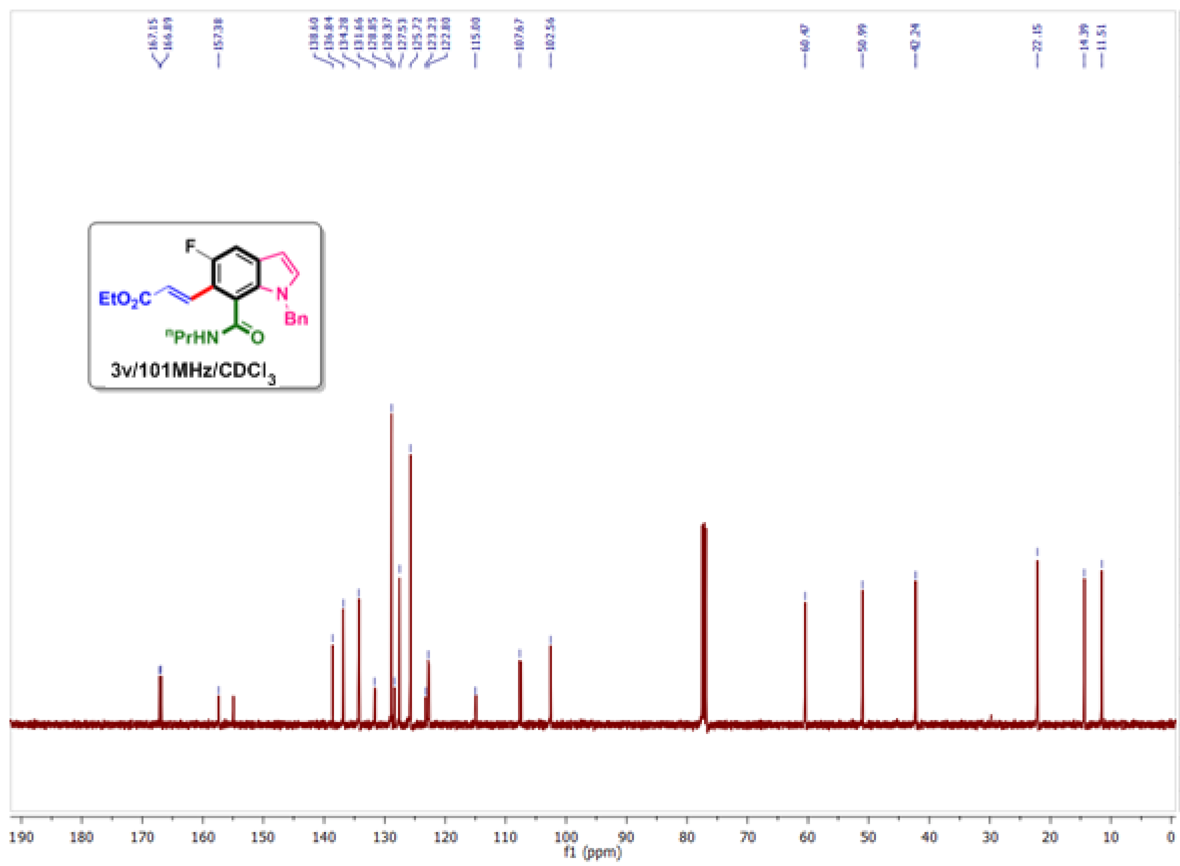
EtO2C
nPrHN
Bn
F
N
O


3v/101MHz/CDCl3
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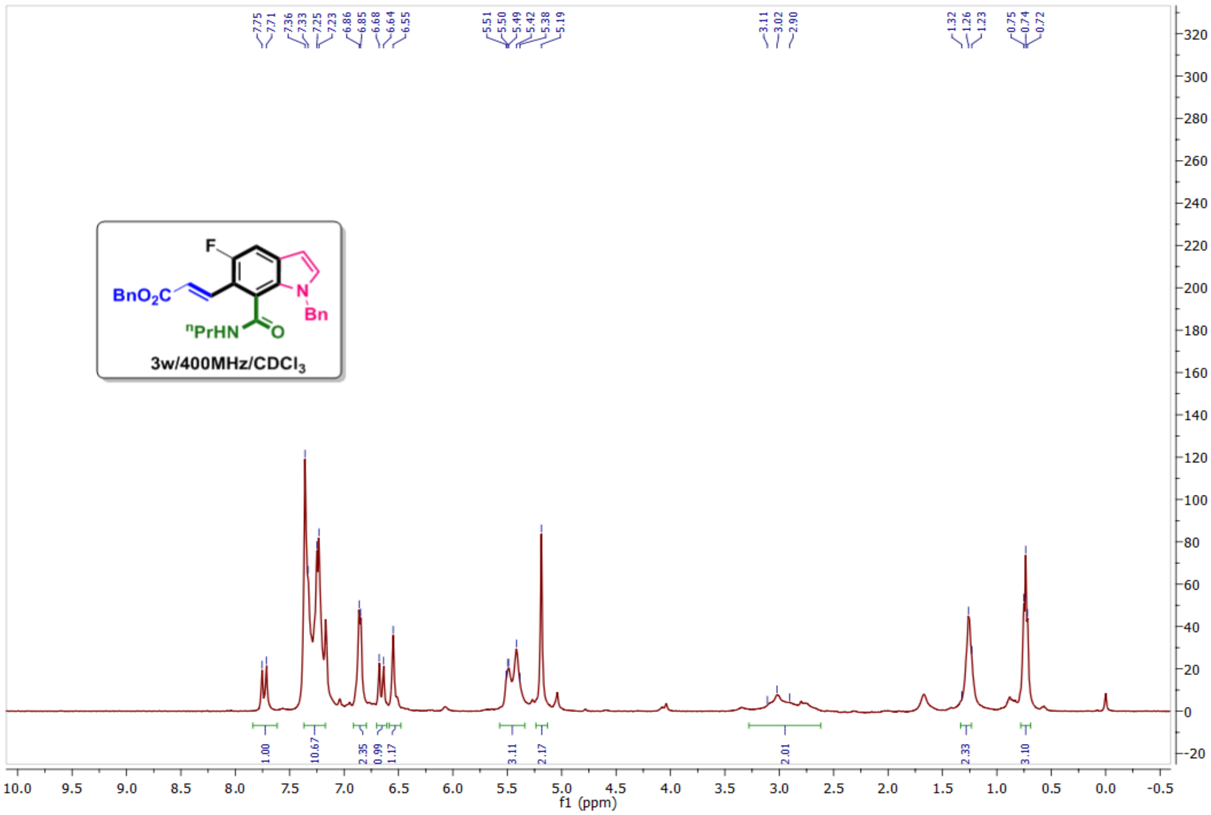
nPrHN
Bn
F
N
O
f1 (ppm)



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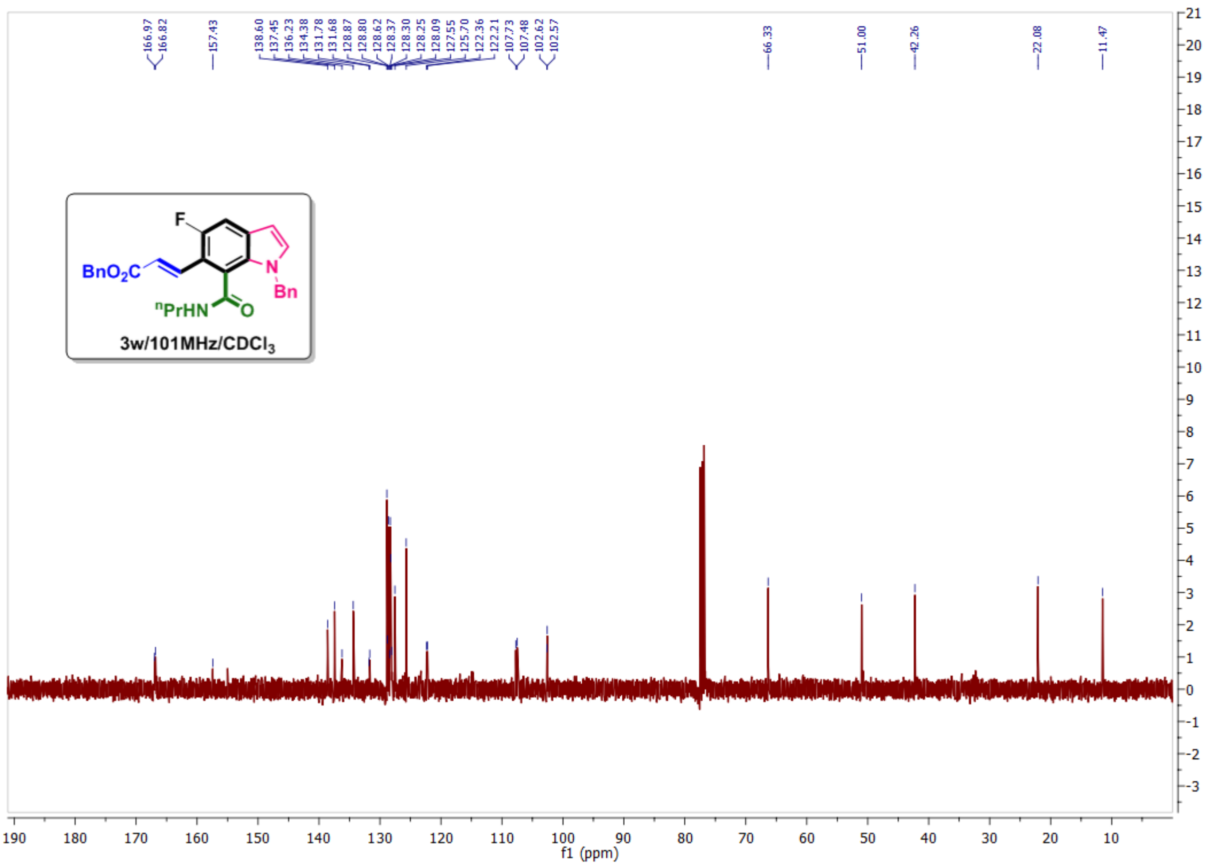
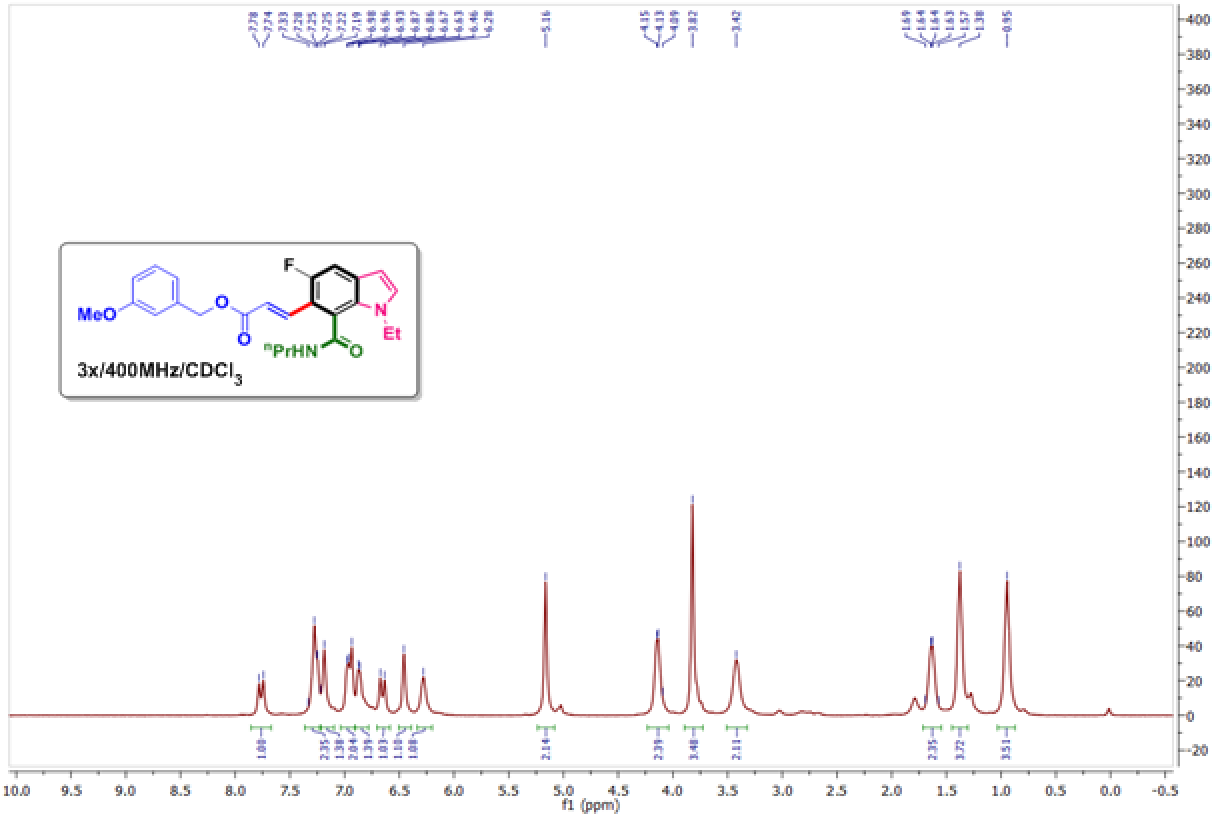
BnO2C
N
Bn
nPrHN
O
3w/400MHz/CDCl3
f1 (ppm)



F
BnO2C
N
Bn
nPrHN
O
3w/101MHz/CDCl3
f1 (ppm)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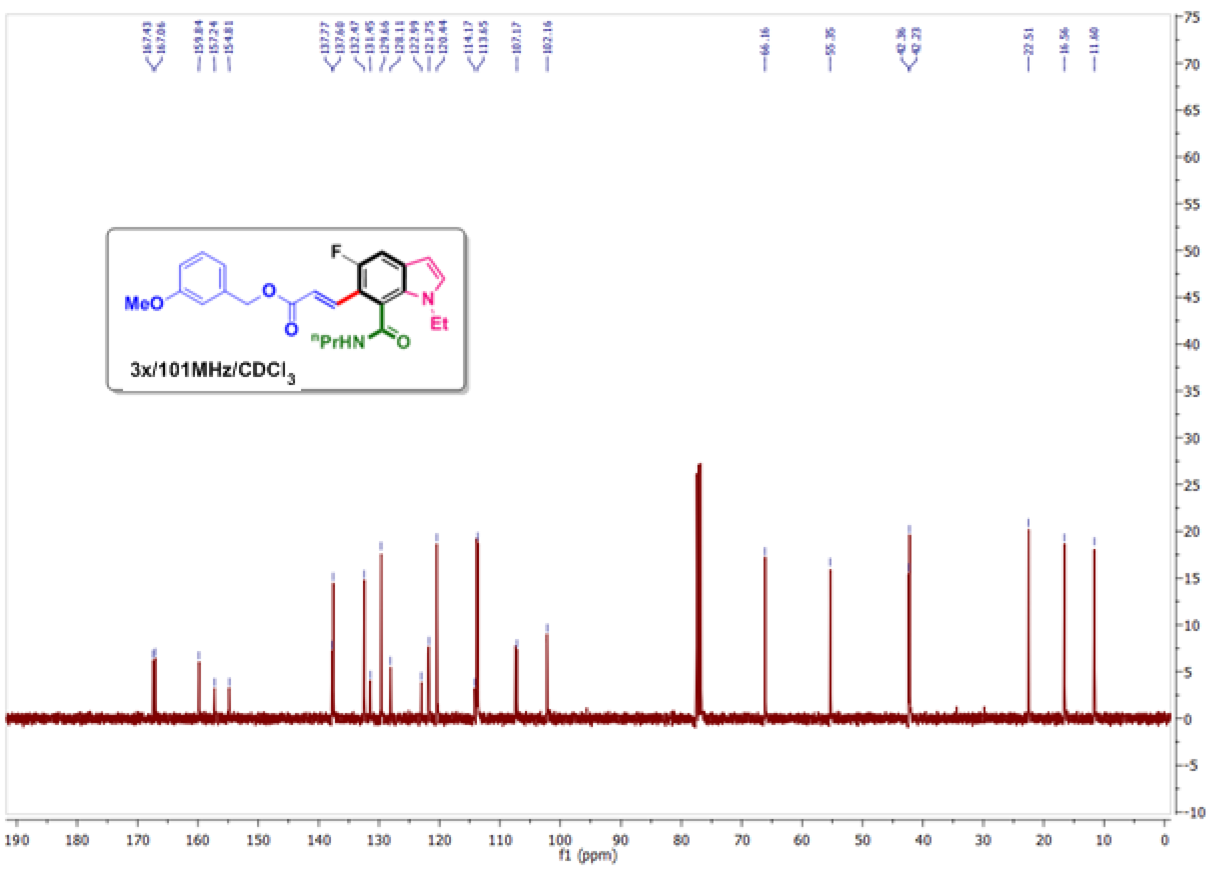
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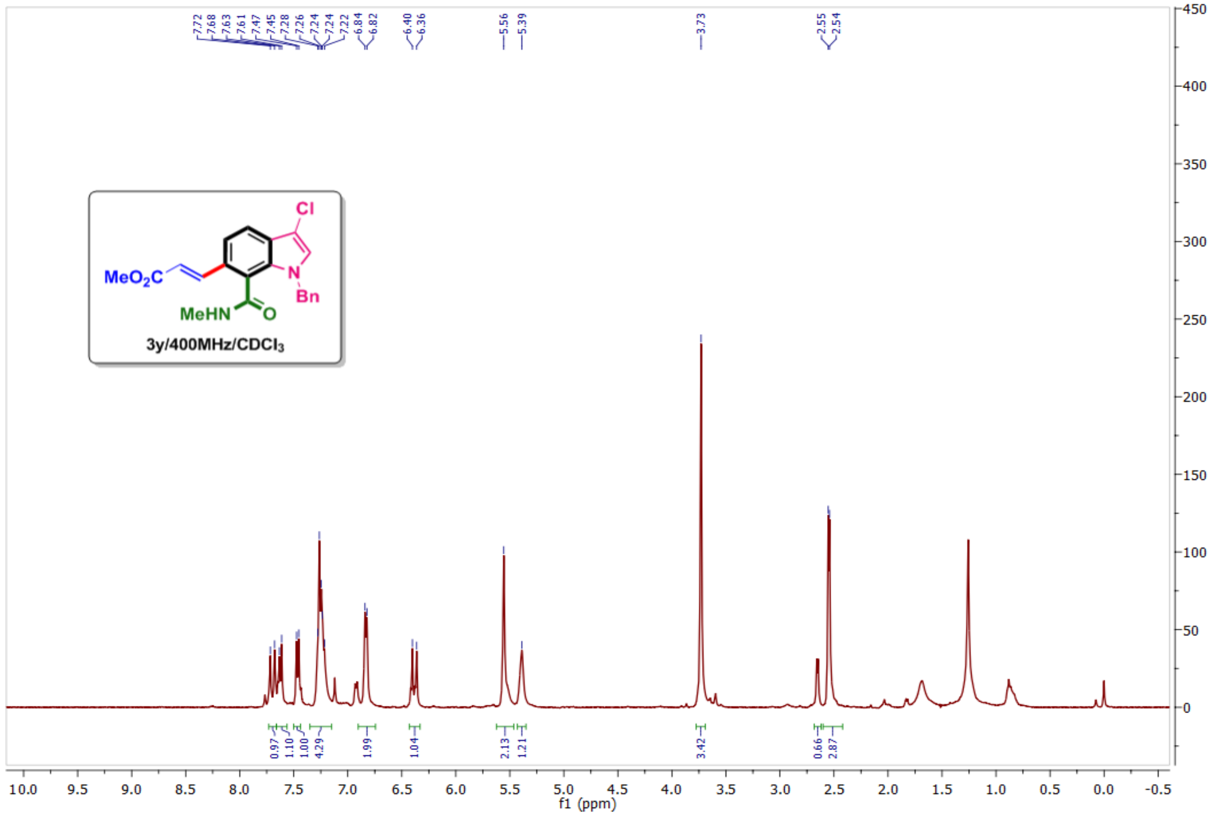
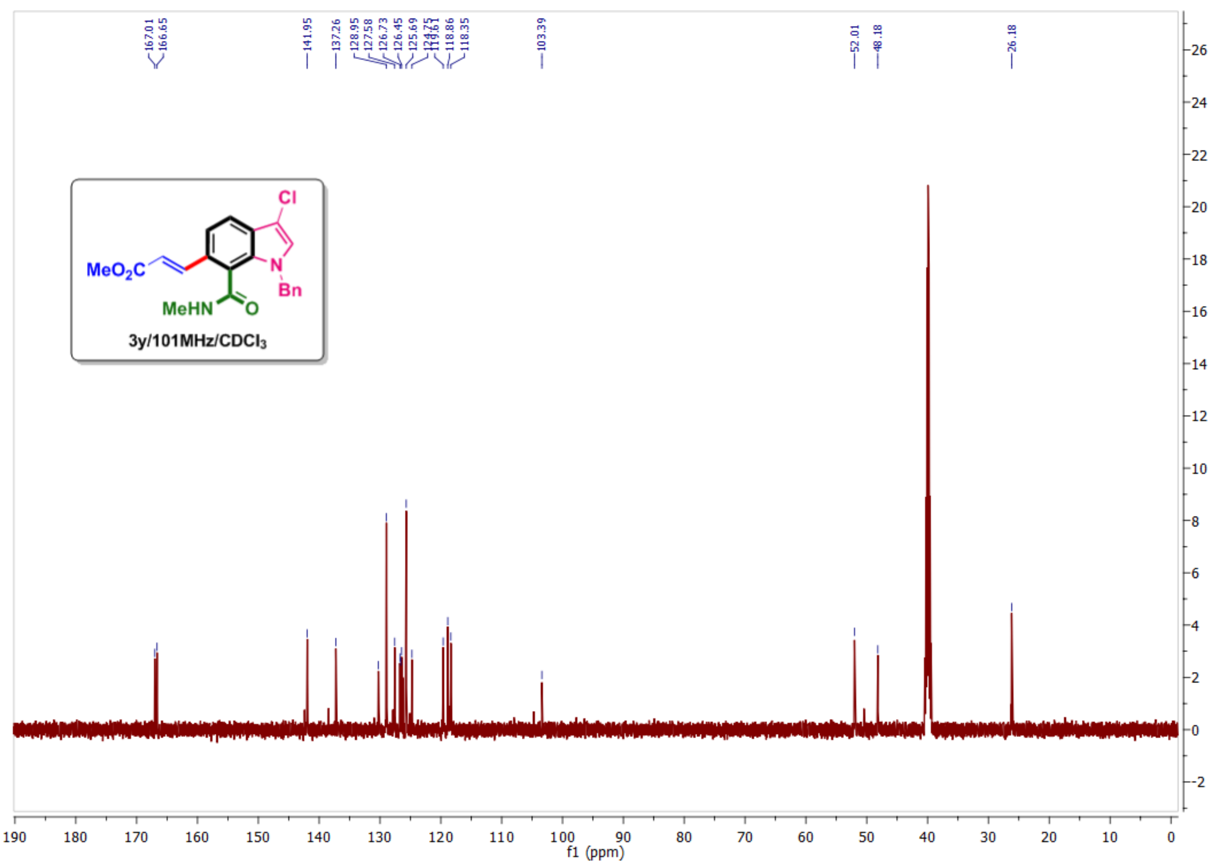
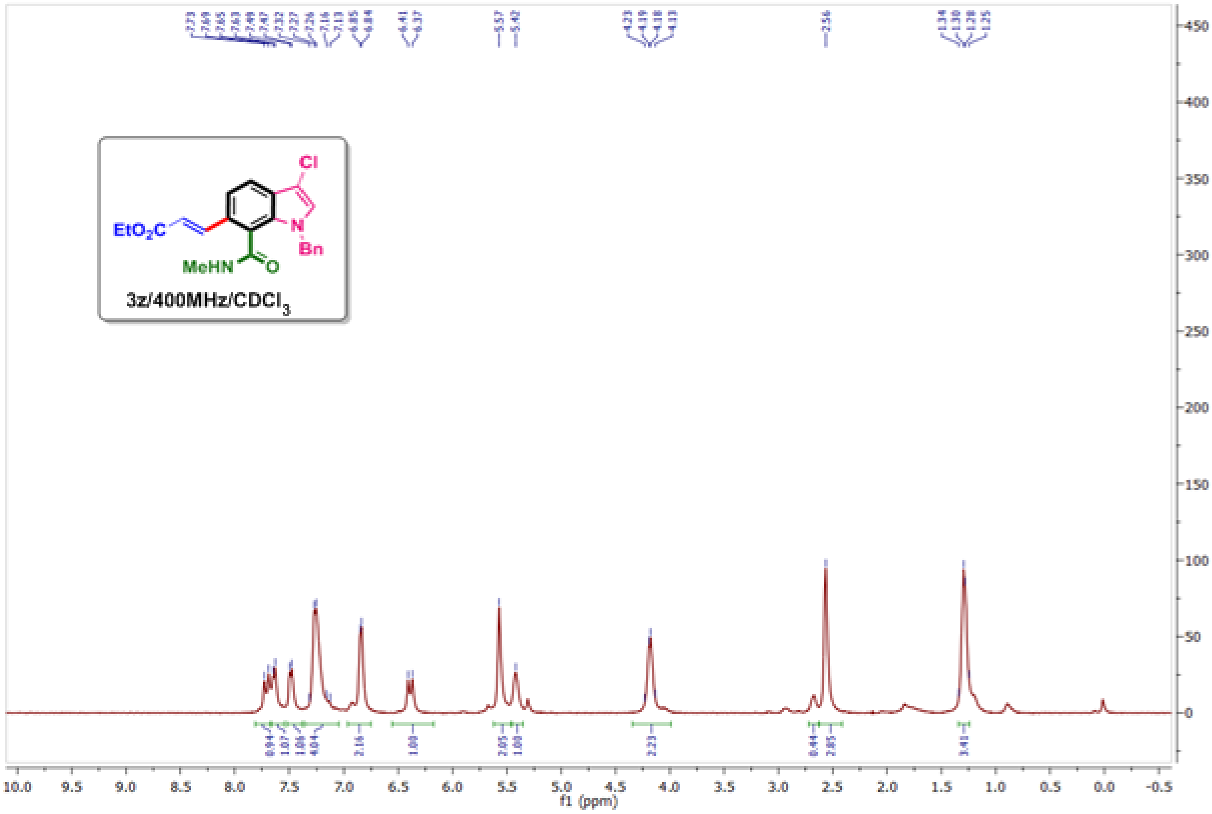
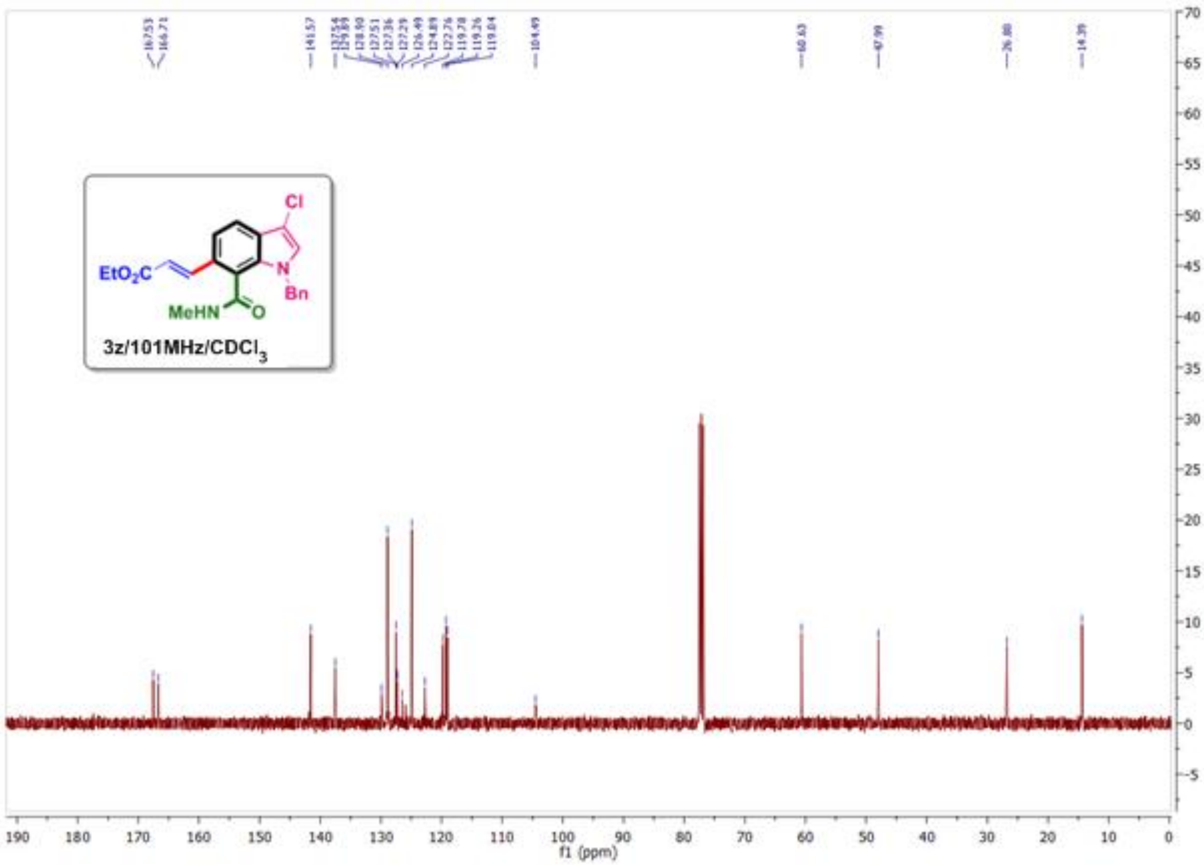
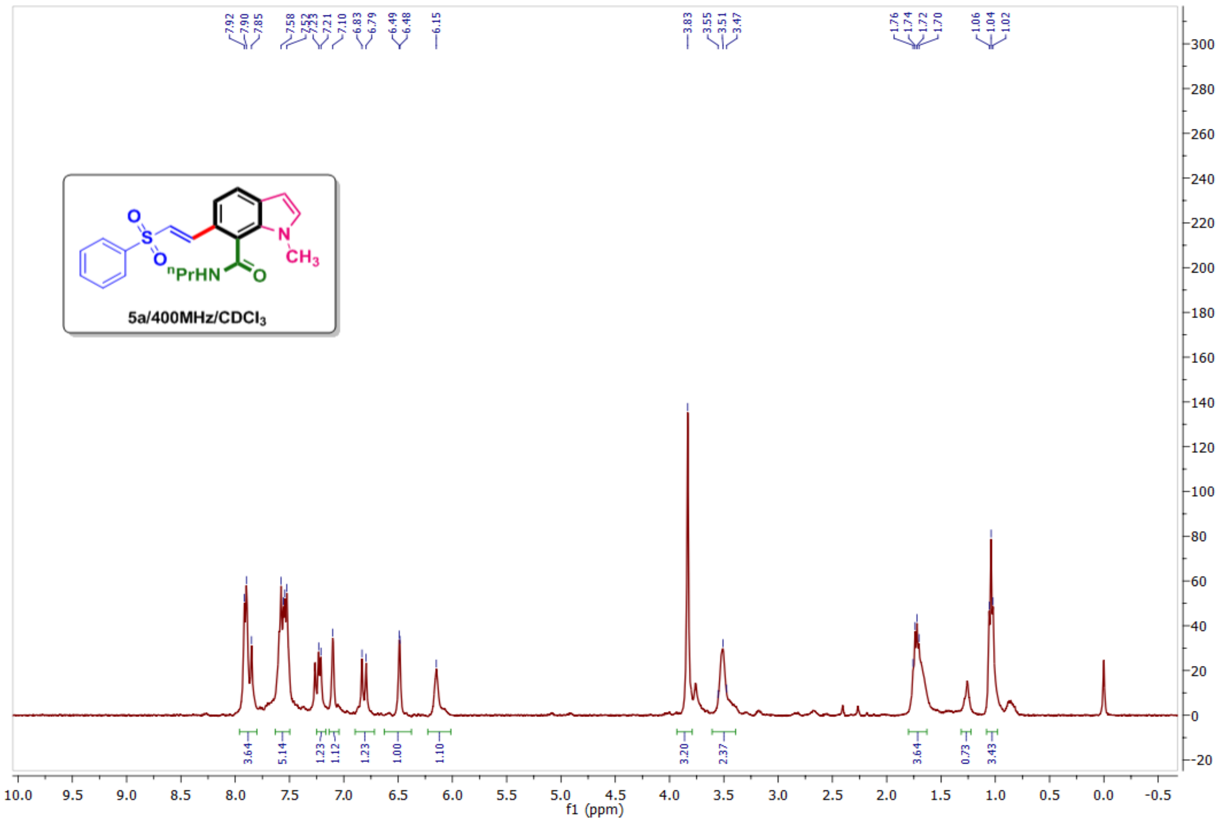
f1 (ppm)






Cl
EtO2C
N
Bn
MeHN
O
3z/400MHz/CDCl3
f1 (ppm)


Cl
EtO2C
N
Bn
MeHN
O
3z/101MHz/CDCl3
f1 (ppm)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3.55
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3.47
1.76
1.74
1.72
1.70
1.06
1.04
1.02
3.64
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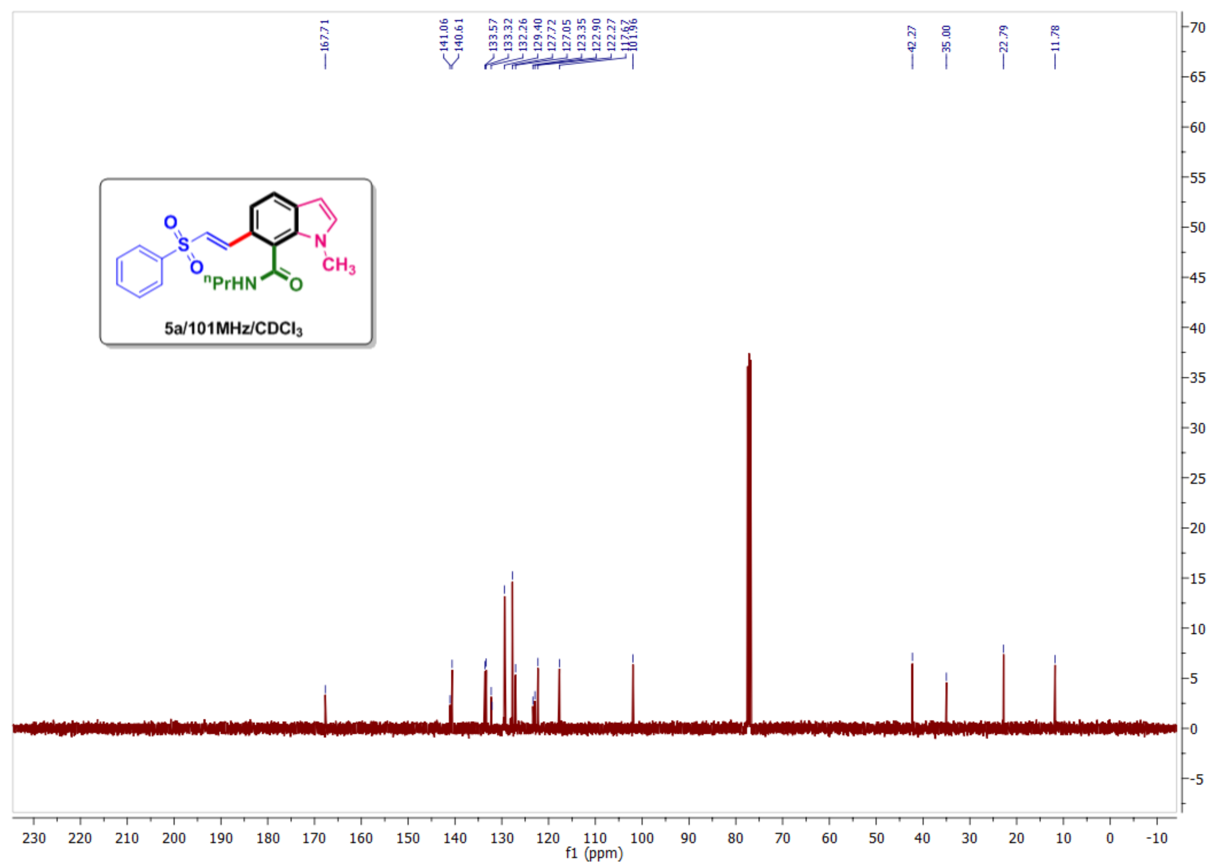
3.43
f1 (ppm)


5a/101MHz/CDCl3
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133.57
133.32
132.26
129.40
127.72
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122.90
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117.67
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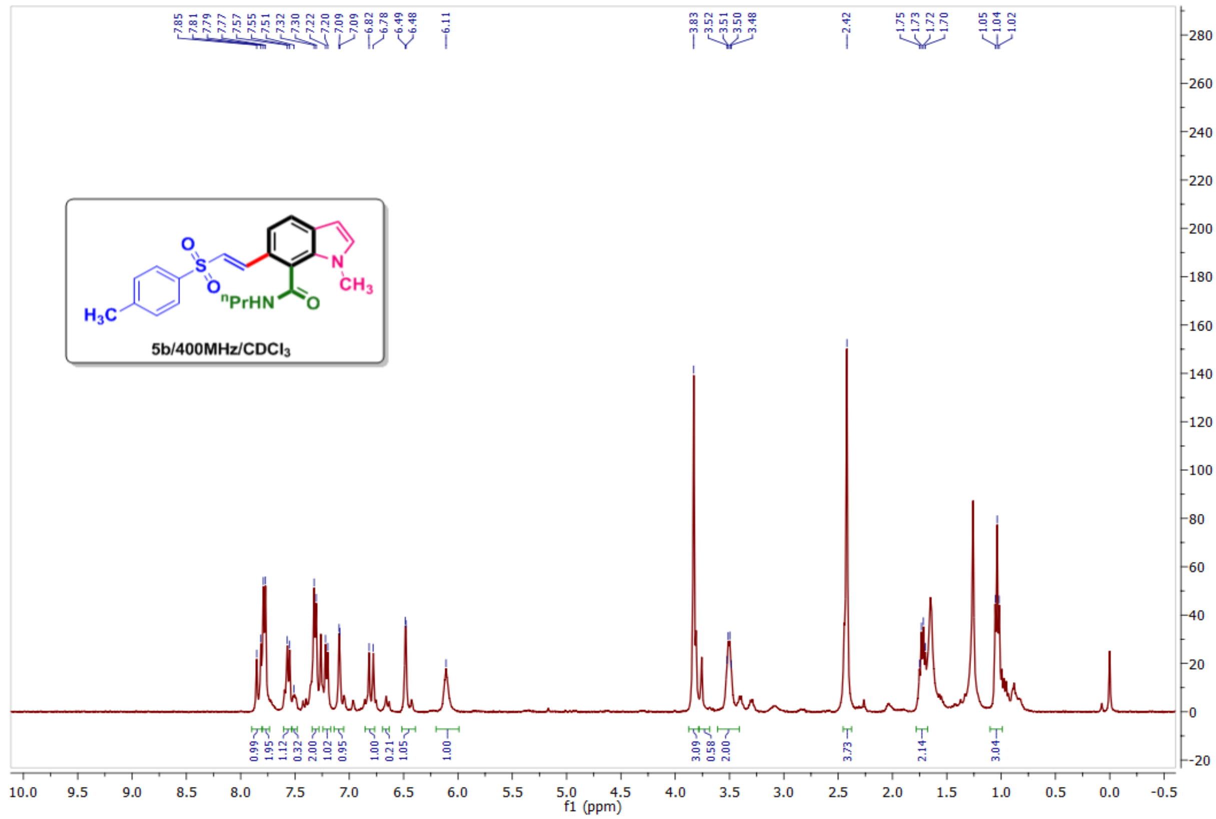
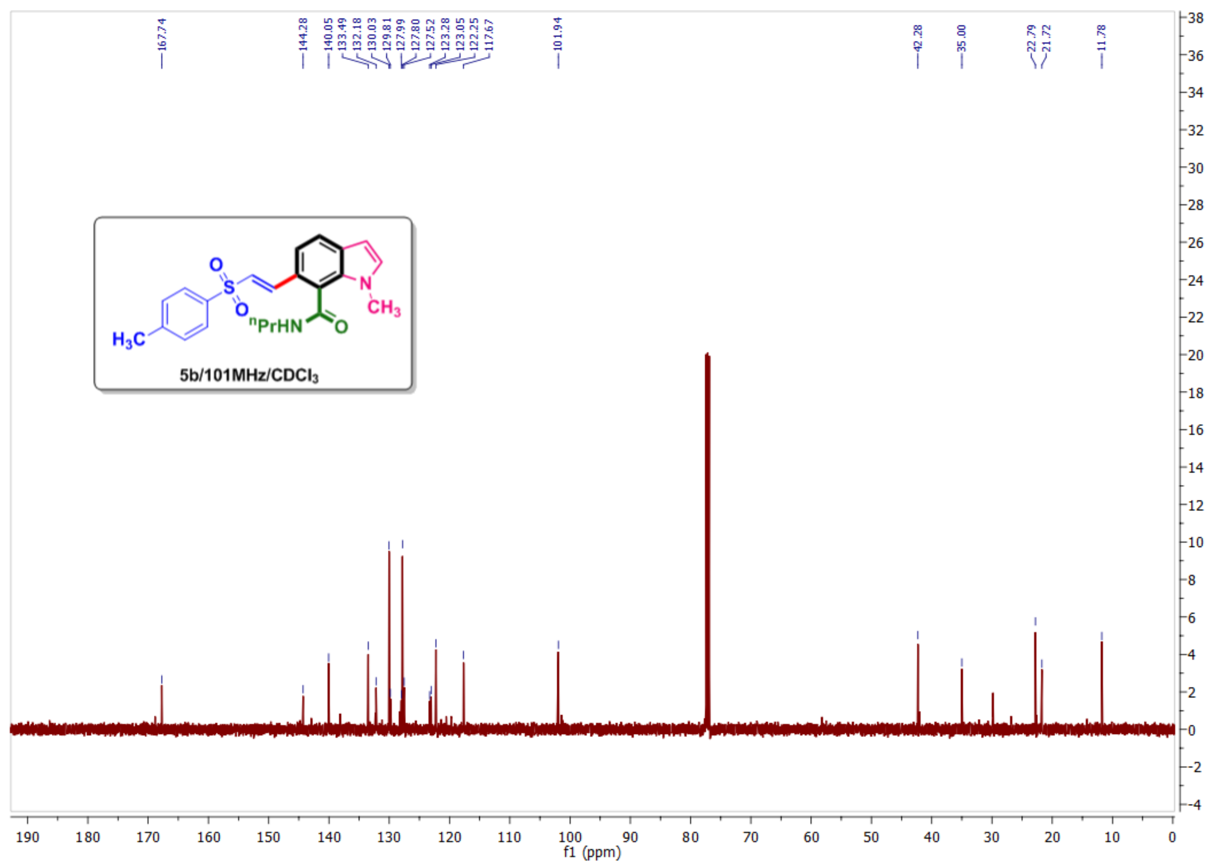
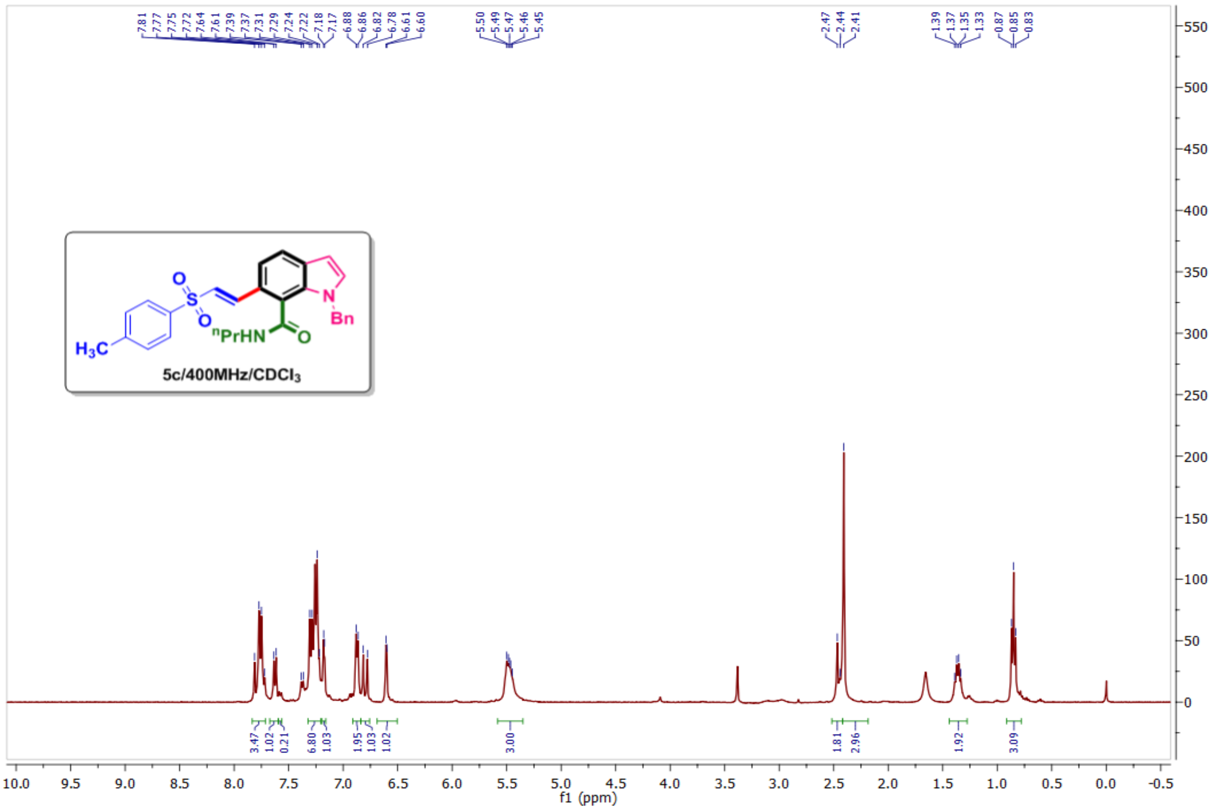
35.00
22.79
11.78
f1 (ppm)


5b/400MHz/CDCl3
nPrHN
H3C
f1 (ppm)


5b/101MHz/CDCl3
nPrHN
H3C
f1 (ppm)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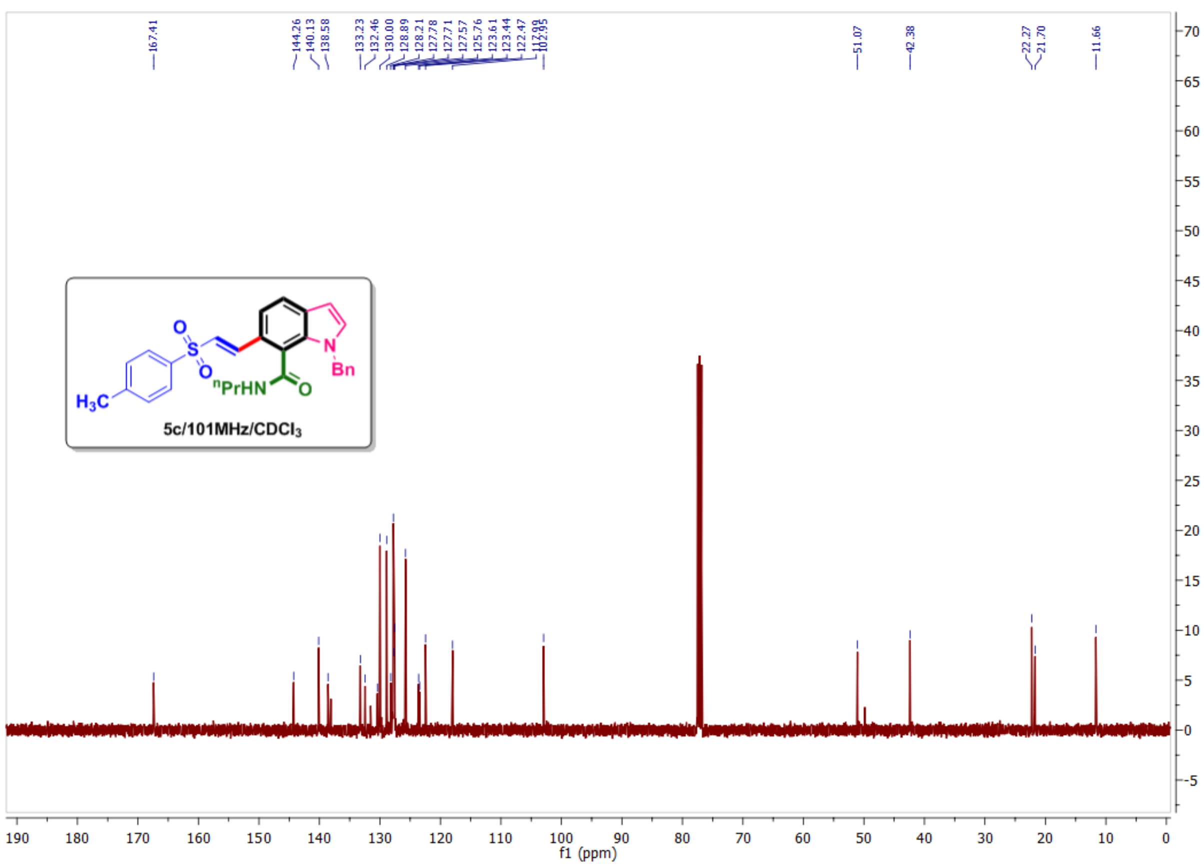
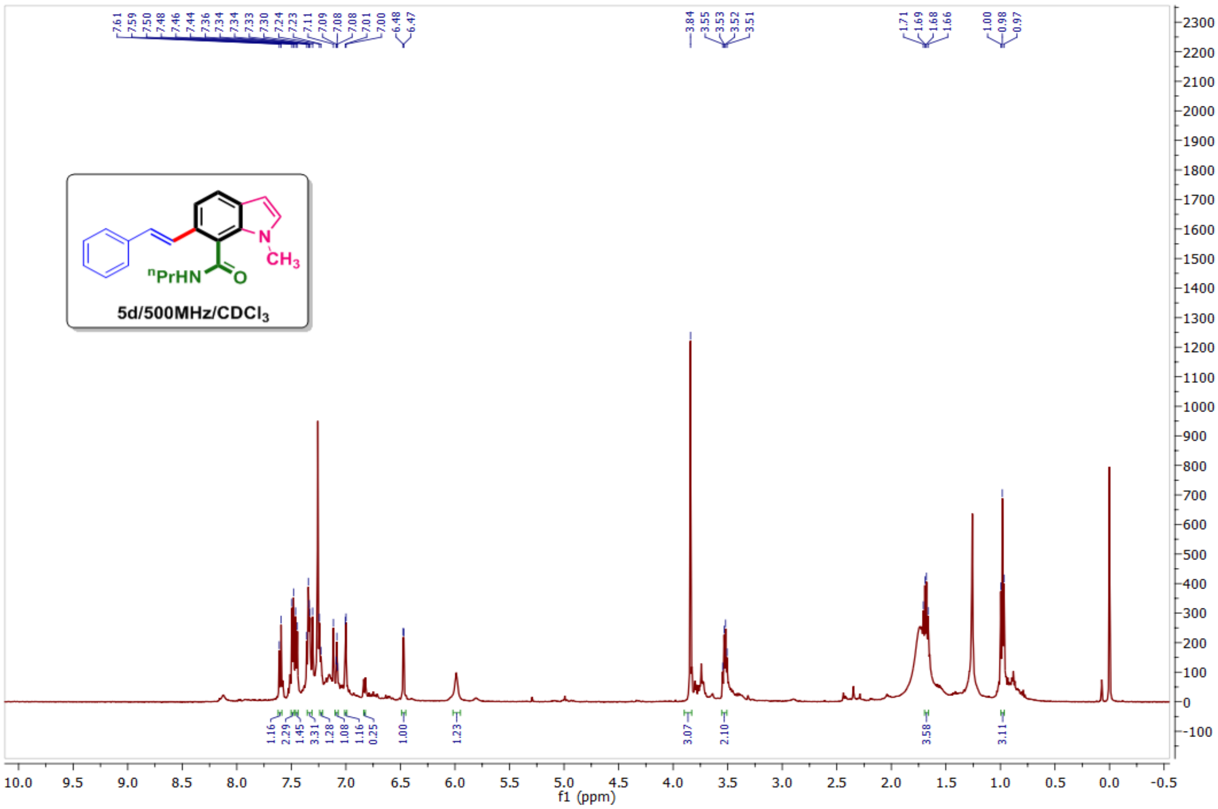
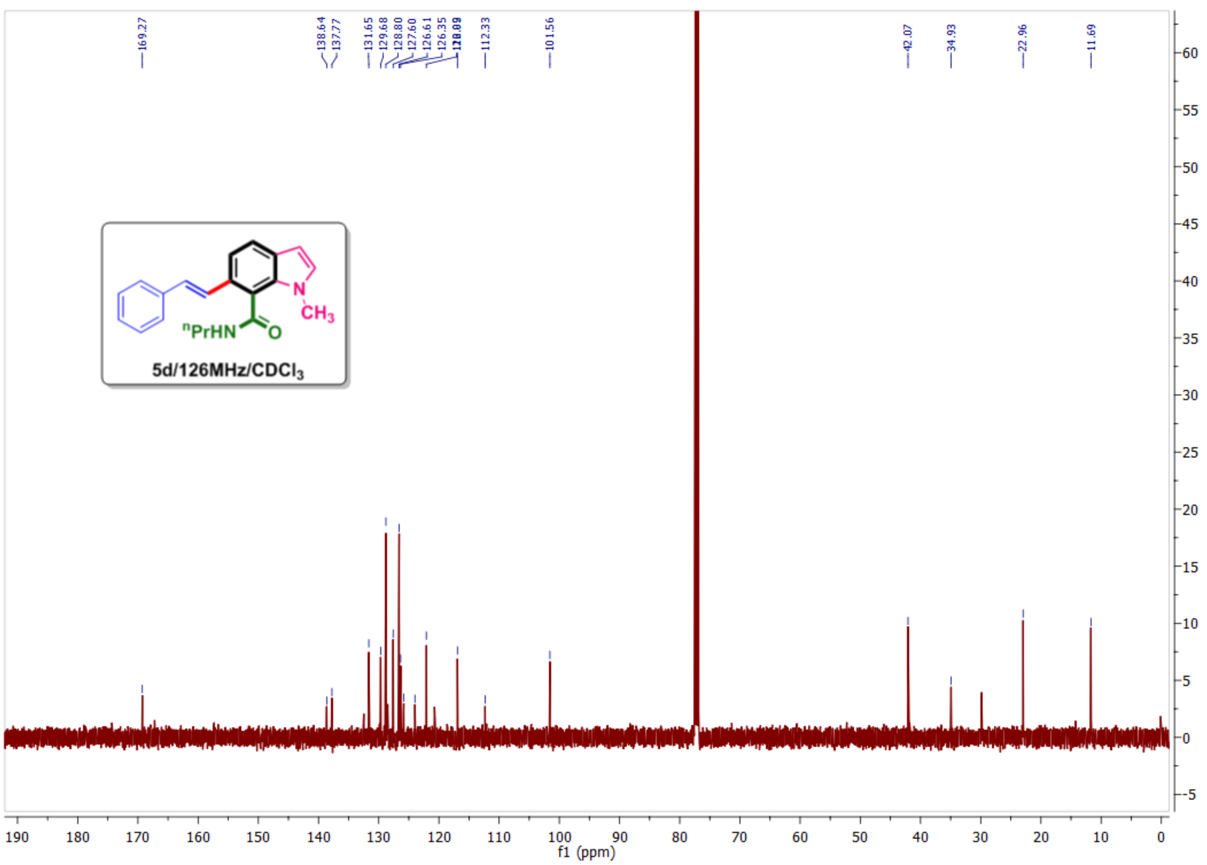
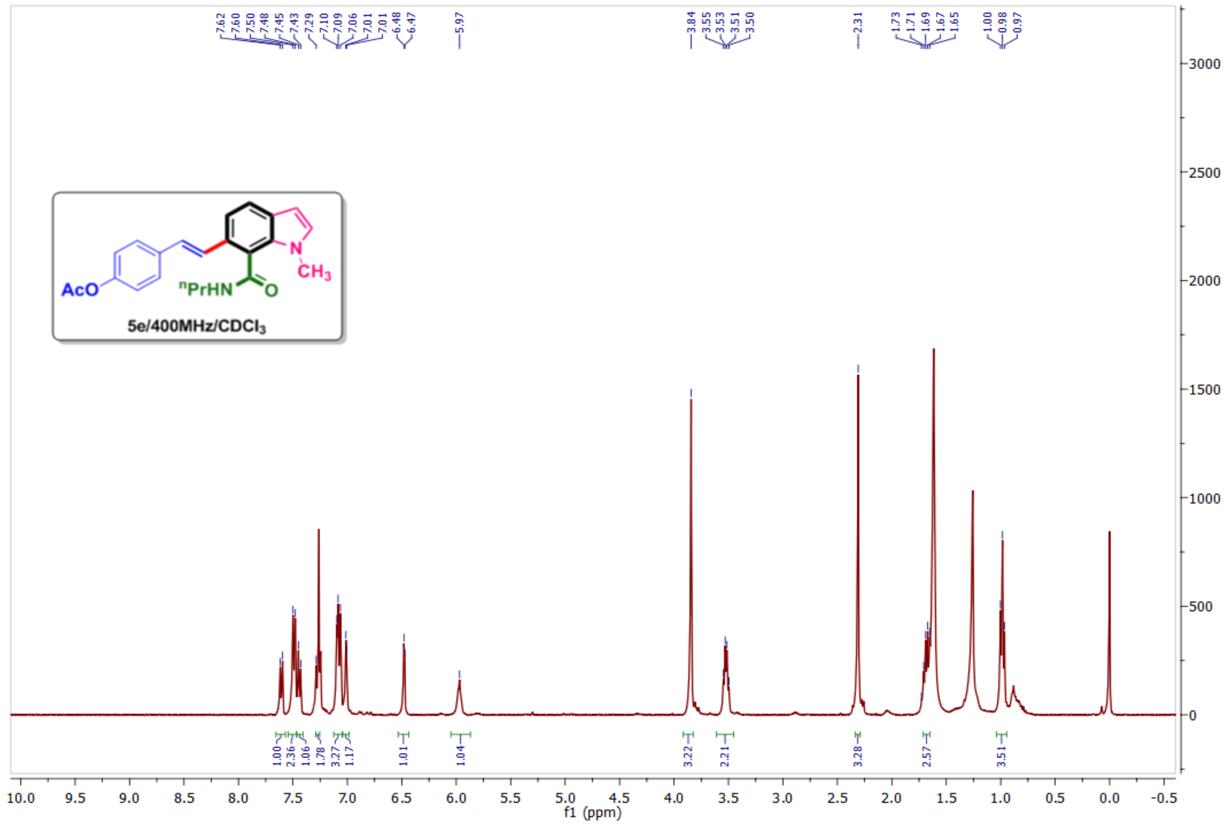
nPrHN
Bn
H3C
f1 (ppm)

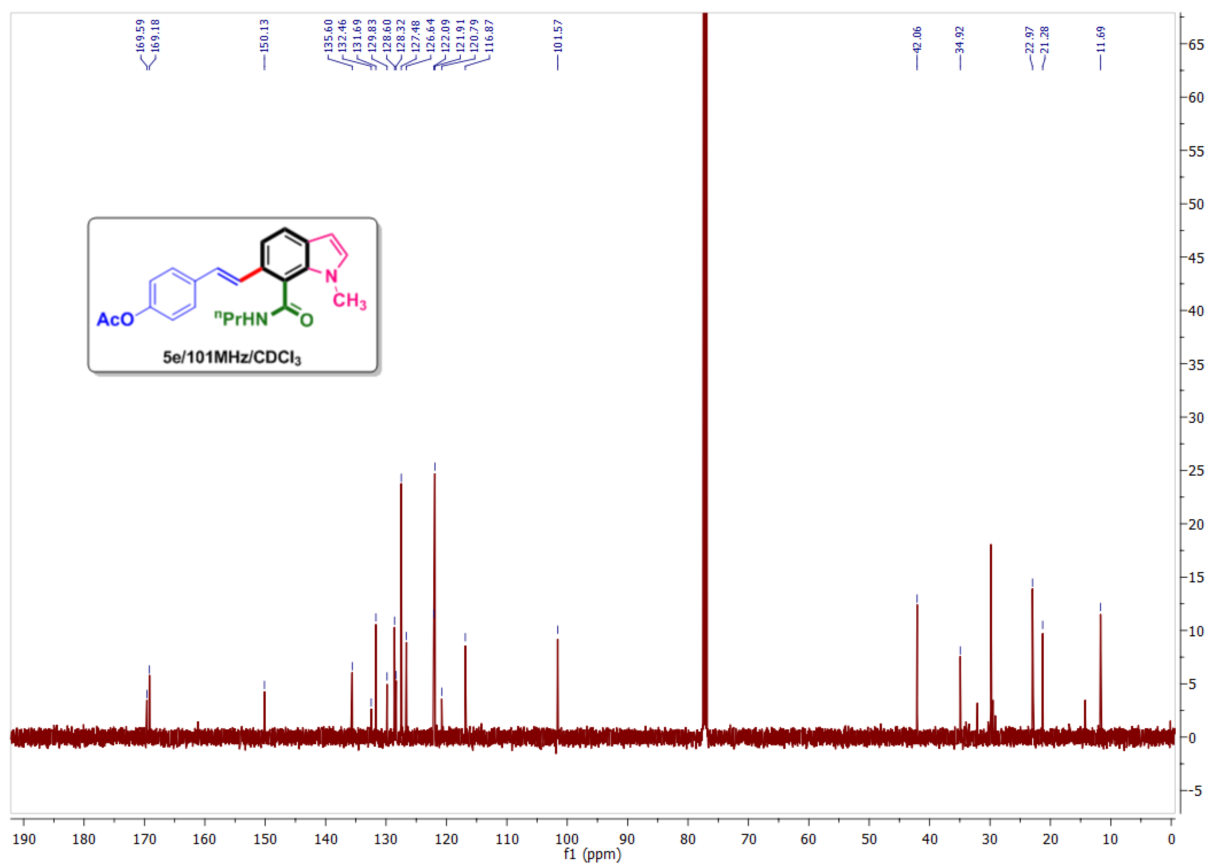

5c/101MHz/CDCl3
nPrHN
Bn
H3C
f1 (ppm)


ⁿPrHN
N
CH3
O
5d/500MHz/CDCl3
f1 (ppm)

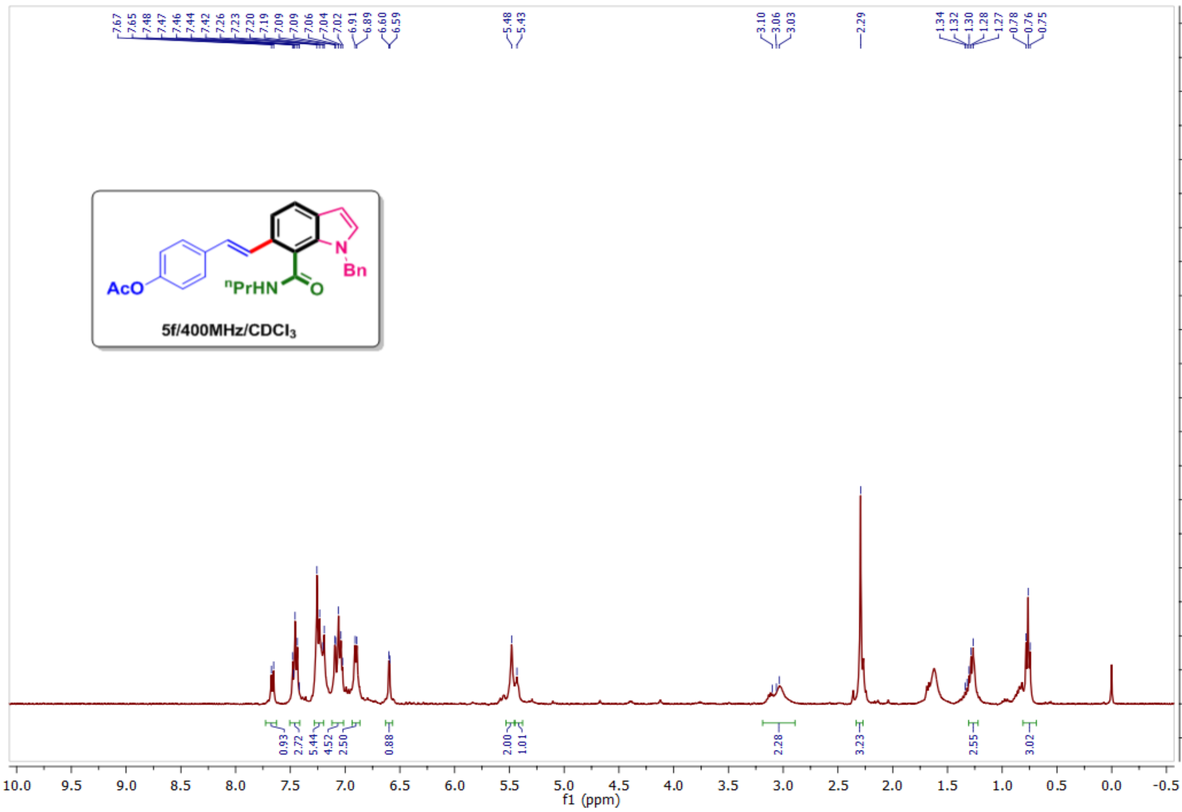

ⁿPrHN
N
CH3
O
5d/126MHz/CDCl3
f1 (ppm)

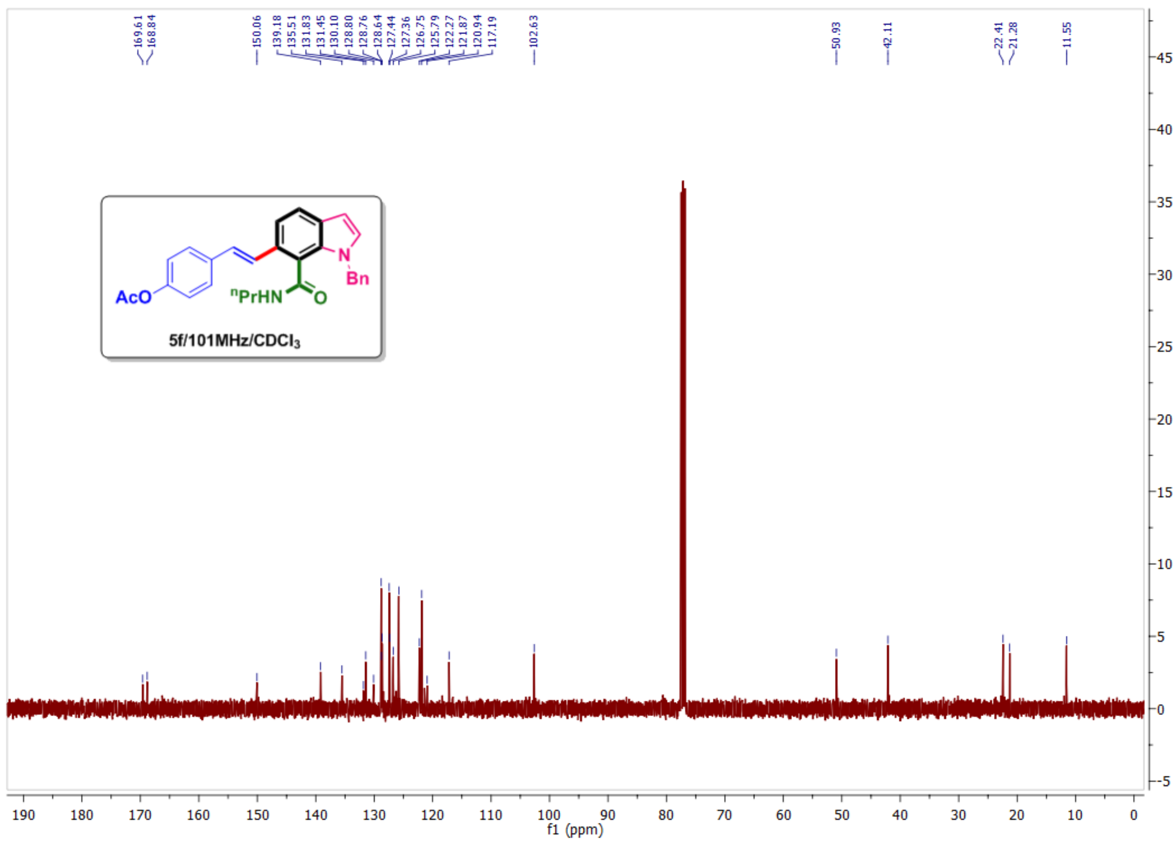


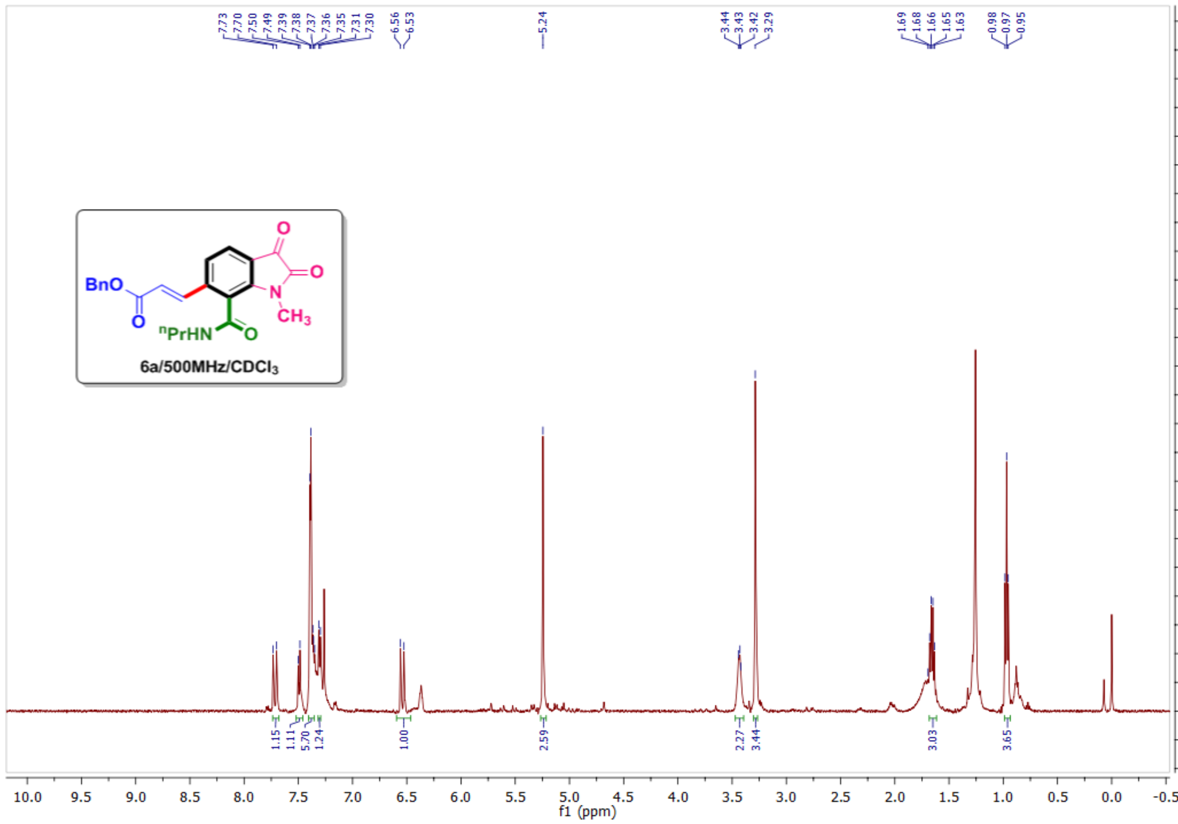
5e/400MHz/CDCl3
f1 (ppm)

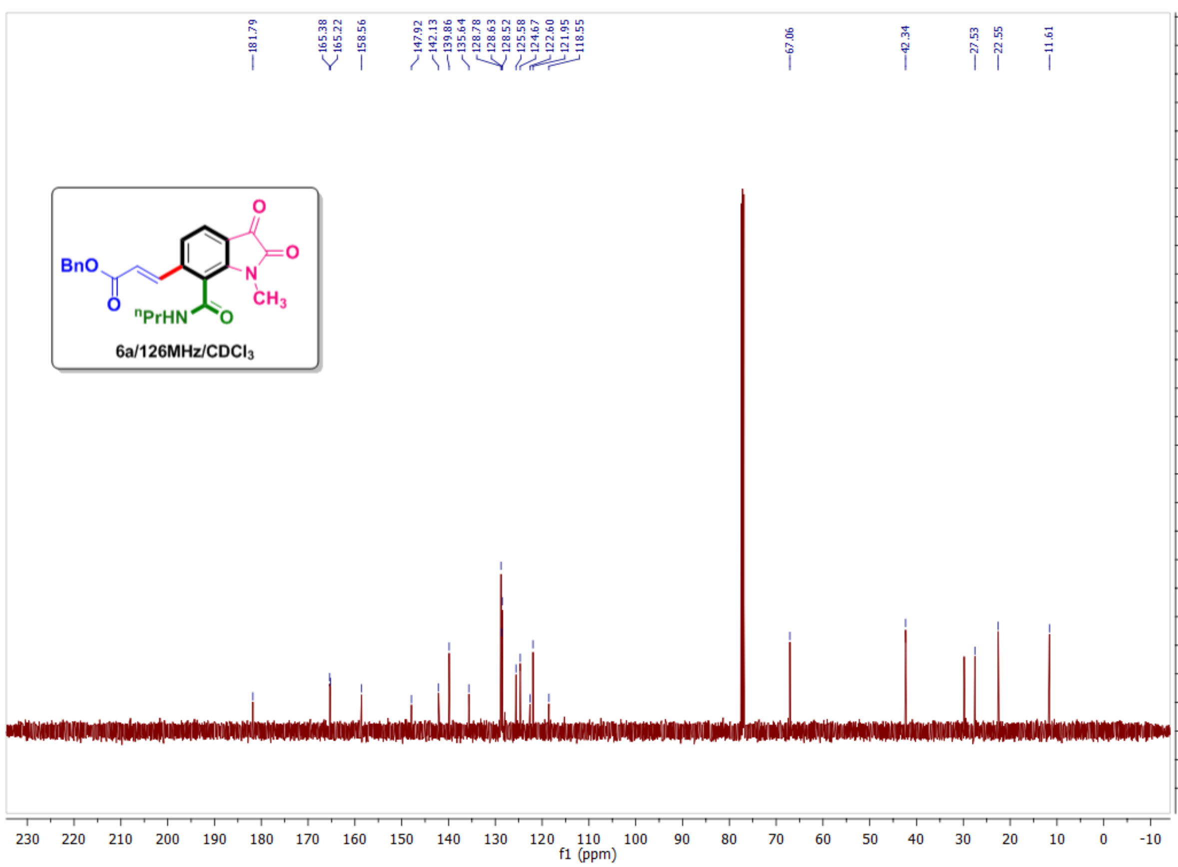


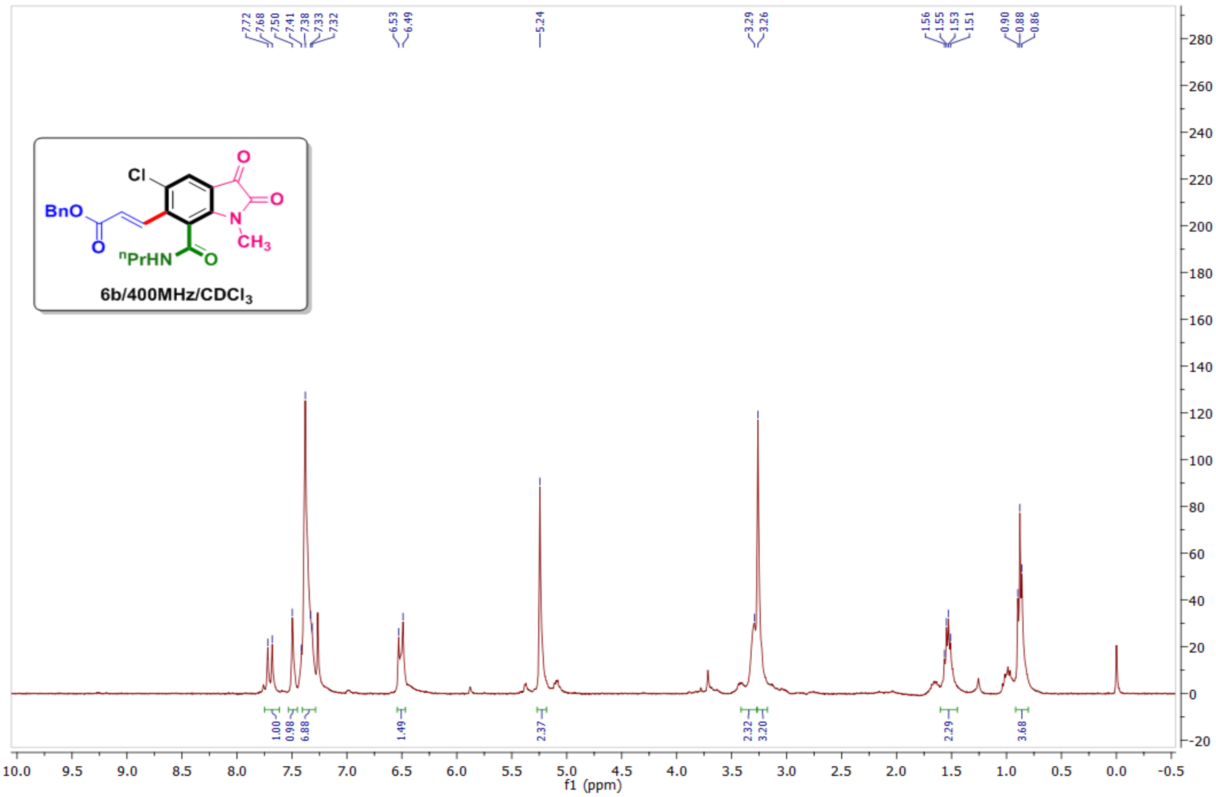
5e/101MHz/CDCl3
f1 (ppm)

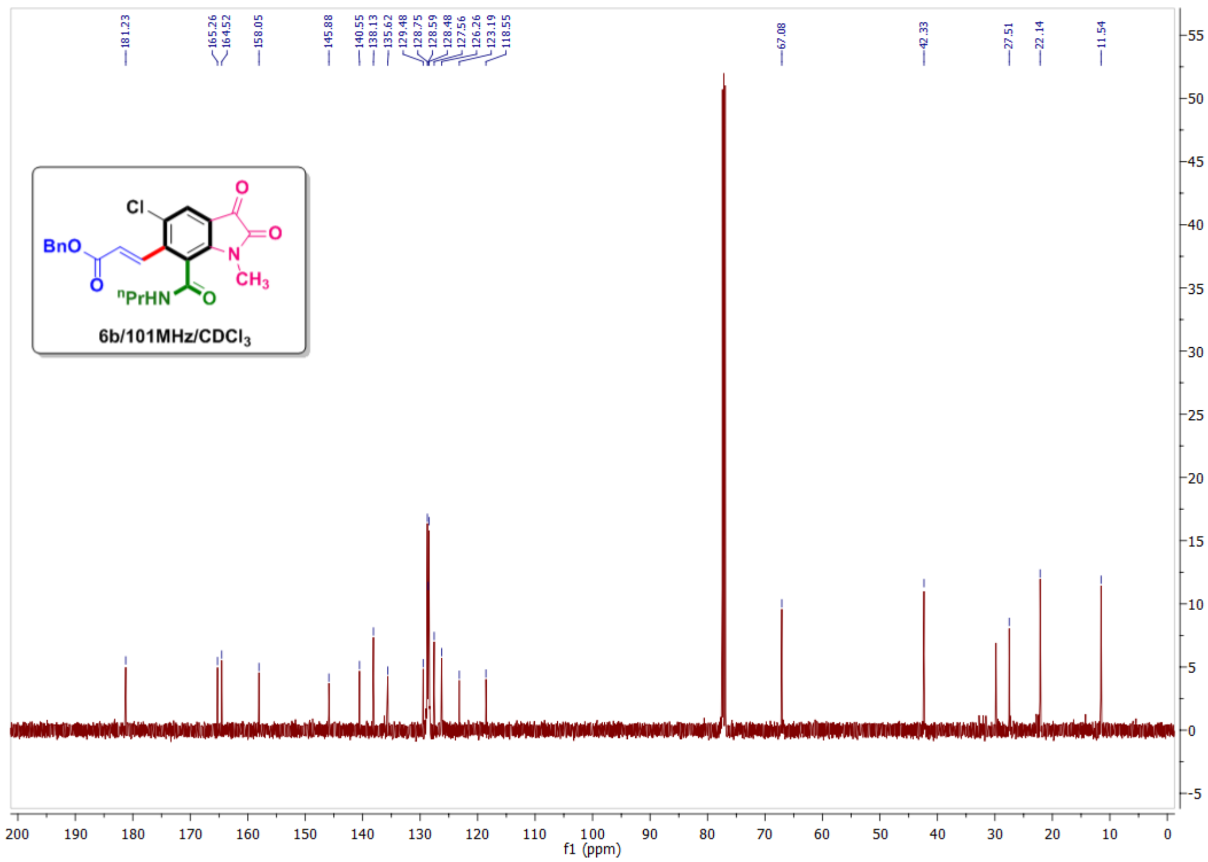

7.67 7.65 7.48 7.47 7.46 7.44 7.42 7.26 7.23 7.20 7.19 7.09 7.09 7.06 7.04 7.02 6.91 6.89 6.60 6.59
5.48 5.43
3.10 3.06 3.03
2.29
1.34 1.32 1.30 1.28 1.27 0.78 0.76 0.75
AcO
ⁿPrHN
O
N
Bn
5f/400MHz/CDCl3
0.93 2.72 5.44 4.52 2.50 0.88 2.00 1.01 2.28 3.23 2.55 3.02
f1 (ppm)

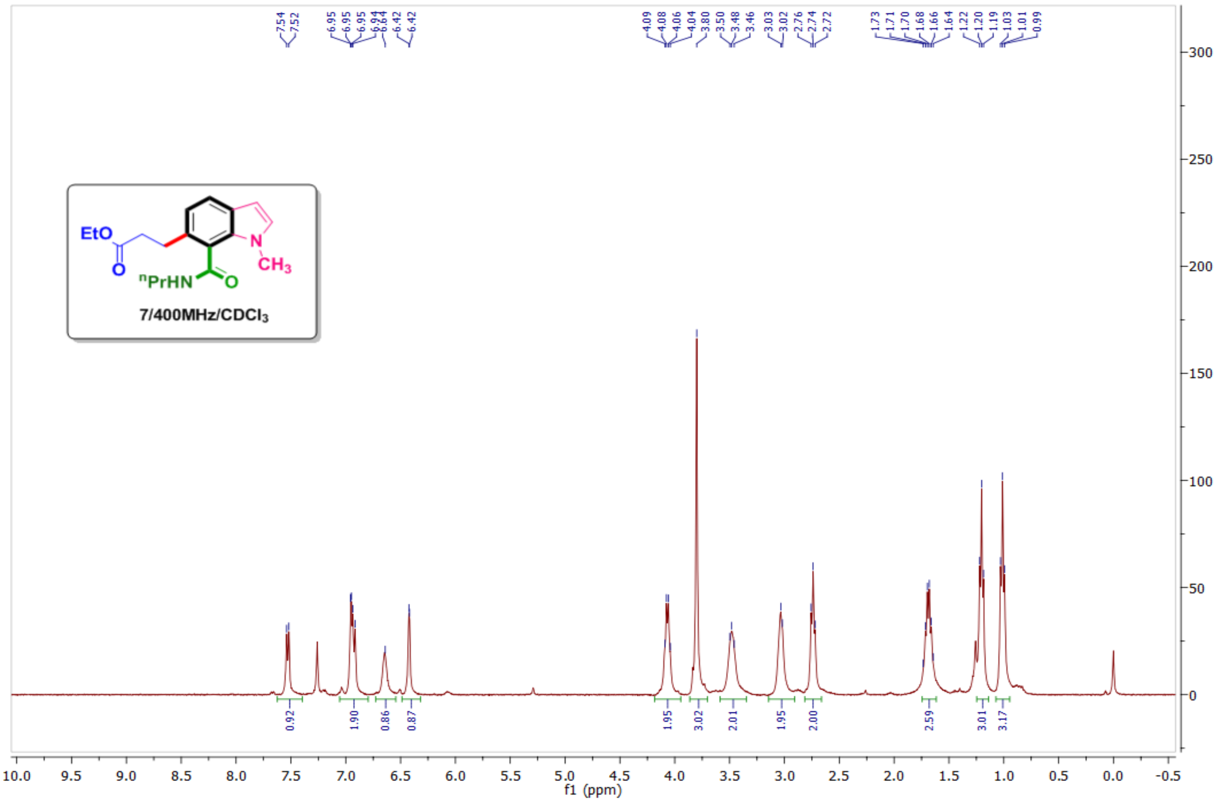

169.61 168.84
150.06 139.18 135.51 131.83 131.45 130.10 128.80 128.76 128.64 127.44 127.36 126.75 125.79 122.27 121.87 120.94 117.19
102.63
50.93
42.11
22.41 21.28
11.55
AcO
ⁿPrHN
O
N
Bn
5f/101MHz/CDCl3
f1 (ppm)

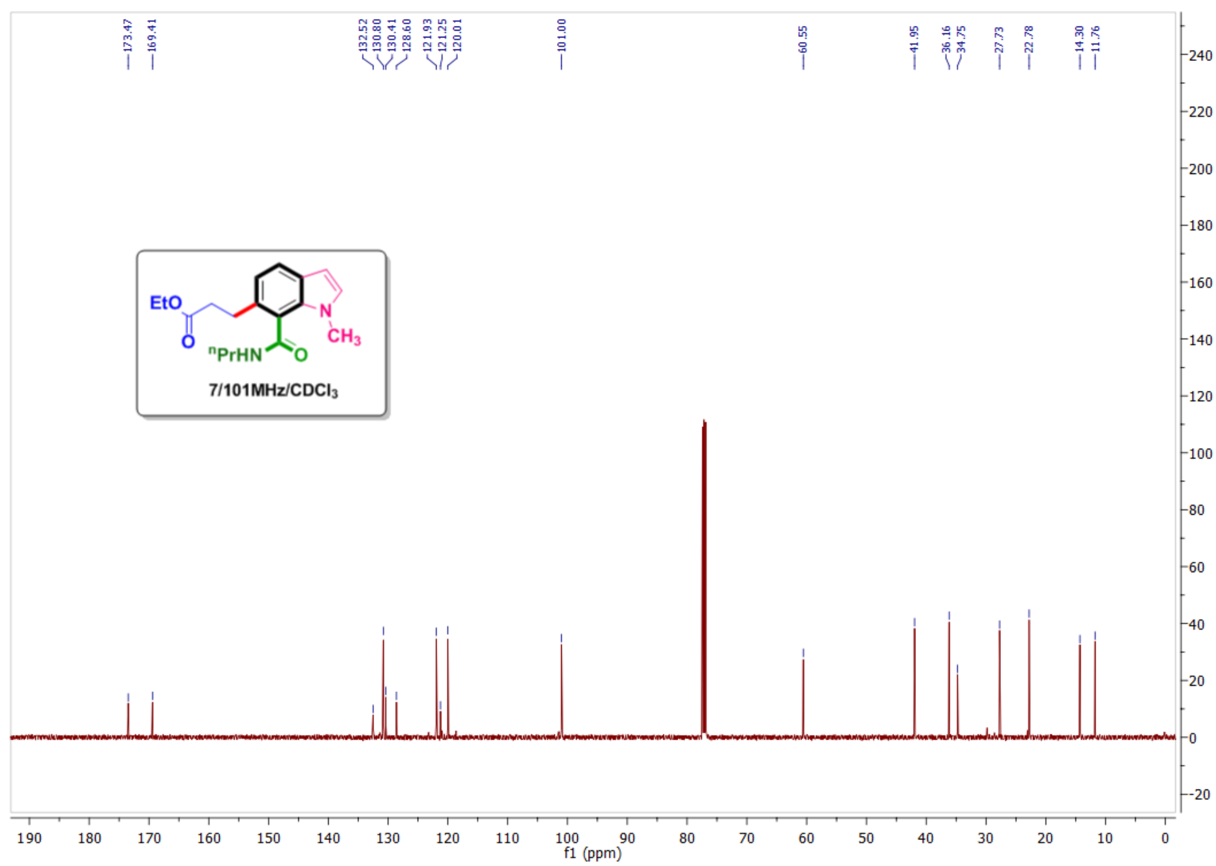


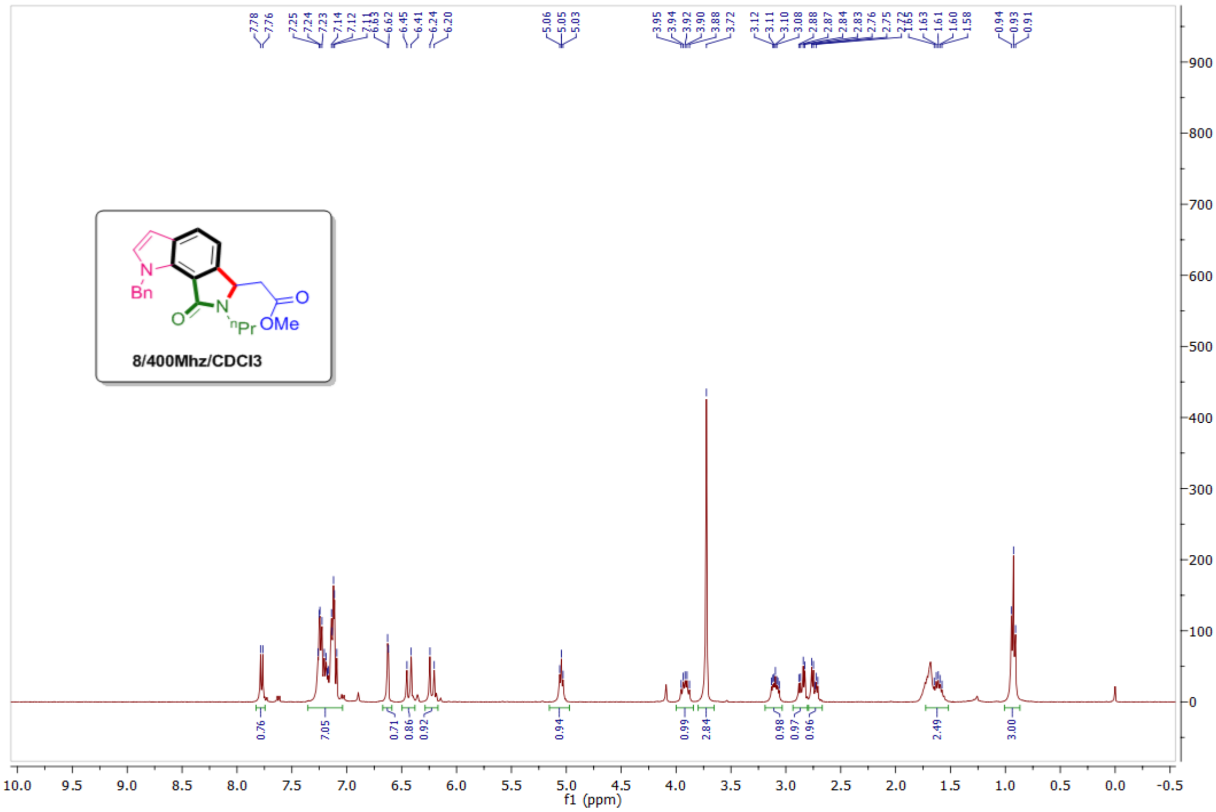


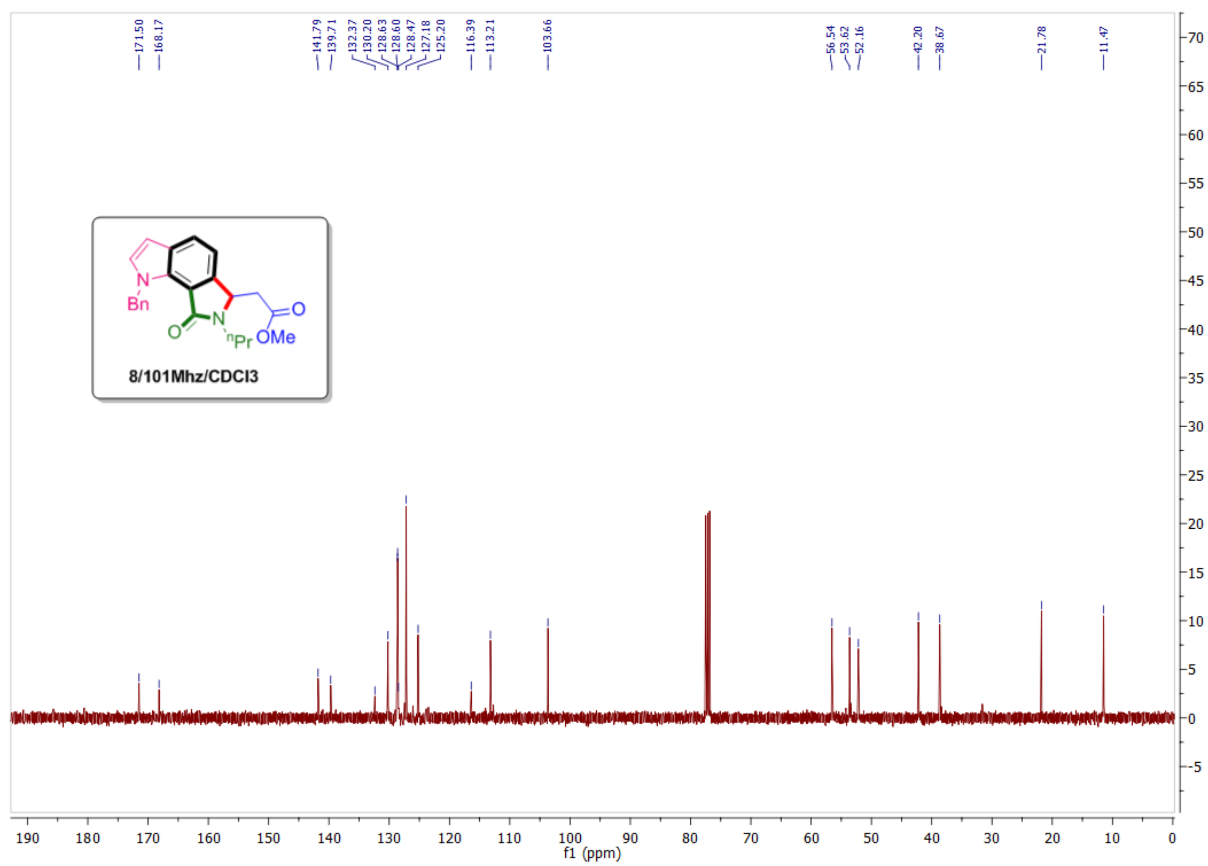

7.72
7.68
7.50
7.41
7.38
7.33
7.32
6.53
6.49
5.24
3.29
3.26
1.56
1.55
1.53
1.51
0.90
0.88
0.86
Cl
O
O
BnO
N
CH3
O
nPrHN
O
6b/400MHz/CDCl3
1.00
0.98
6.88
1.49
2.37
2.32
3.20
2.29
3.68
f1 (ppm)


181.23
165.26
164.52
158.05
145.88
140.55
138.13
135.62
129.48
128.75
128.59
128.48
127.56
126.26
123.19
118.55
67.08
42.33
27.51
22.14
11.54
Cl
O
O
BnO
N
CH3
O
nPrHN
O
6b/101MHz/CDCl3
f1 (ppm)


EtO
O
ⁿPrHN
O
N
CH3
7/400MHz/CDCl3


EtO
O
ⁿPrHN
O
N
CH3
7/101MHz/CDCl3


8/400Mhz/CDCl3
f1 (ppm)


8/101Mhz/CDCl3
f1 (ppm)