Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Platinum(II)-catalyzed dehydrative C3-benzylation of electron-deficient indoles with benzyl alcohols

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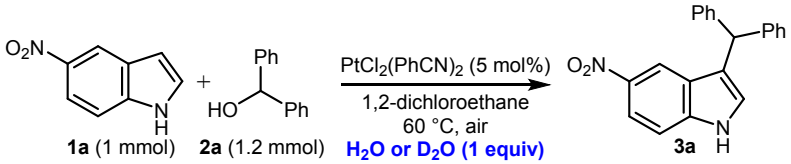
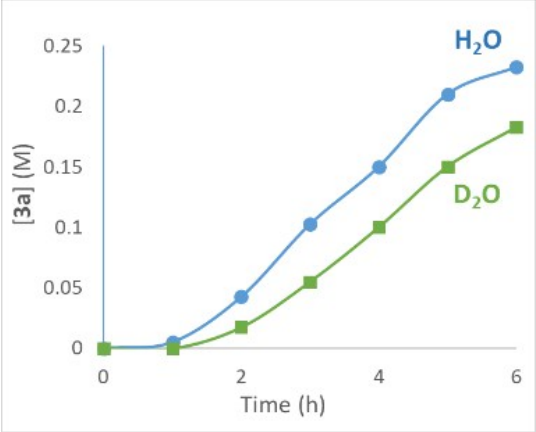
Scheme S1. Rates on the dehydrative coupling with stoichiometric amounts of water.

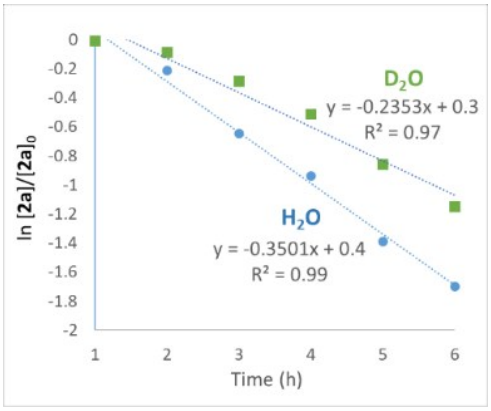


A mixture of 5-nitroindole **1a** (165 mg, 1 mmol), $PtCl_2(PhCN)_2$ (23 mg, 0.05 mmol), benzhydrole **2a** (221 mg, 1.2 mmol), and H_2O or D_2O (1 mmol) in 1,2-dichloroethane (4 mL) was heated at 60 °C under air. After the reaction mixture was cooled, 1,3,5-trimethoxybenzene (168 mg, 1 mmol, internal standard) was added to the reaction mixture, which was extracted with EtOAc. The organic layer was concentrated in vacuo. The residue was analyzed by ^{1}H-NMR spectroscopy.



Time (h)	[**3a**] (M)	
	H_2O	D_2O
0	0	0
1	0.005	0
2	0.0425	0.0175
3	0.1025	0.055
4	0.15	0.1
5	0.21	0.15
6	0.2325	0.1825

Figure S1. Comparison of reaction rates in the presence of H_2O and D_2O.

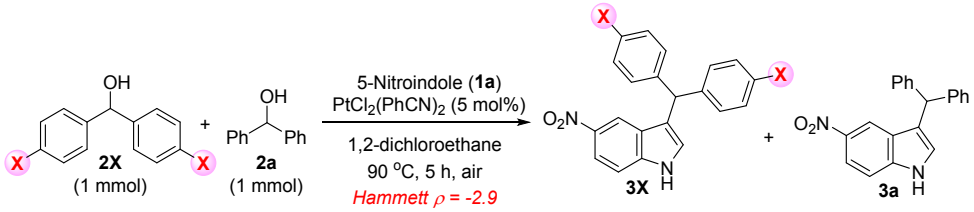


Time (h)	ln [**2a**]/[**2a**]$_0$		[**2a**]/[**2a**]$_0$	
	H_2O	D_2O	H_2O	D_2O
1	-0.00837	-0.00837	0.991667	0.99167
2	-0.21278	-0.08701	0.808333	0.91667
3	-0.64436	-0.2877	0.525	0.75
4	-0.93735	-0.51083	0.391666	0.6
5	-1.38629	-0.85567	0.25	0.425
6	-1.69647	-1.1499	0.18333	0.31667

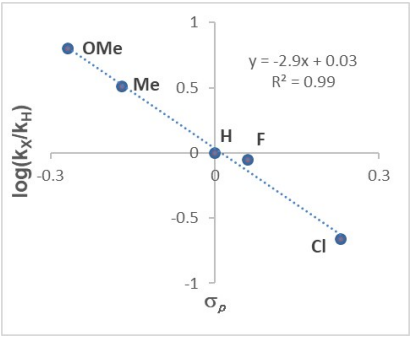
Figure S2. Isotope effect measured for the reactions.

KSIE (k_{H_2O}/k_{D_2O}) = 0.3501/0.2353 =1.5

Scheme S2. Hammett study [see: (a) Wang, D. *et al. Org. Chem. Front.* **2019**, *6*, 62-69. (b) Echavarren, A. M. *et al. ACS Catal.* **2018**, *8*, 2166-2172. (c) M. Szostak, *J. Org. Chem.* **2017**, *82*, 6528-6540. (d) Q. Song, *Org. Lett.* **2016**, *18*, 4088-4091.]

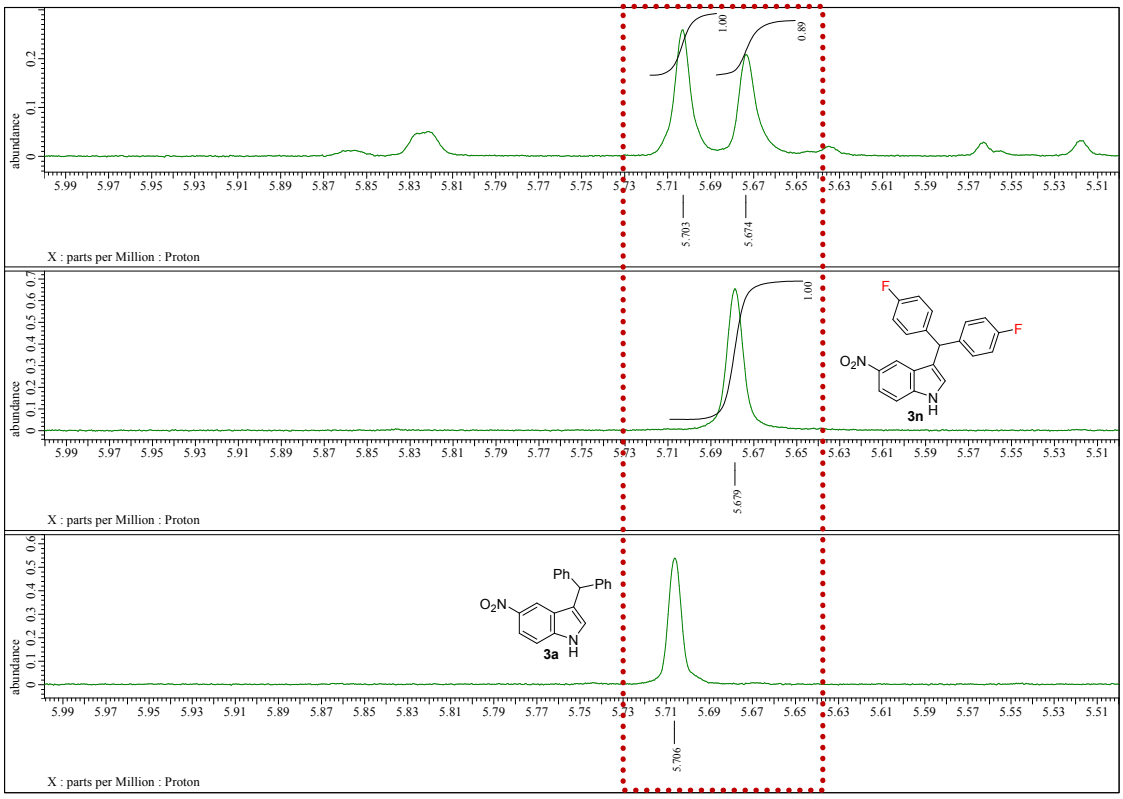


A mixture of benzhydryl alcohols **2X** (1 mmol), benzhydrol (**2a**) (186 mg, 1 mmol), 5-nitroindole (**1a**) (165 mg, 1 mmol), $PtCl_2(PhCN)_2$ (23.6 mg, 0.05 mmol) in 1,2-dichloroethane (4 mL) was heated at 90 °C for 5 h in a sealed tube under air. After cooling, the reaction mixture was poured into water and extracted with EtOAc. The organic layer was analyzed by ^{1}H-NMR spectroscopy.

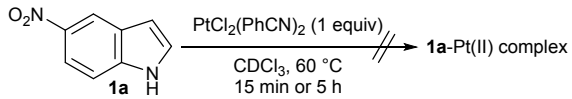


	σ_p	$\log(k_X/k_H)$
OMe	-0.27	0.8
Me	-0.17	0.51
H	0	0
F	0.06	-0.051
Cl	0.23	-0.66

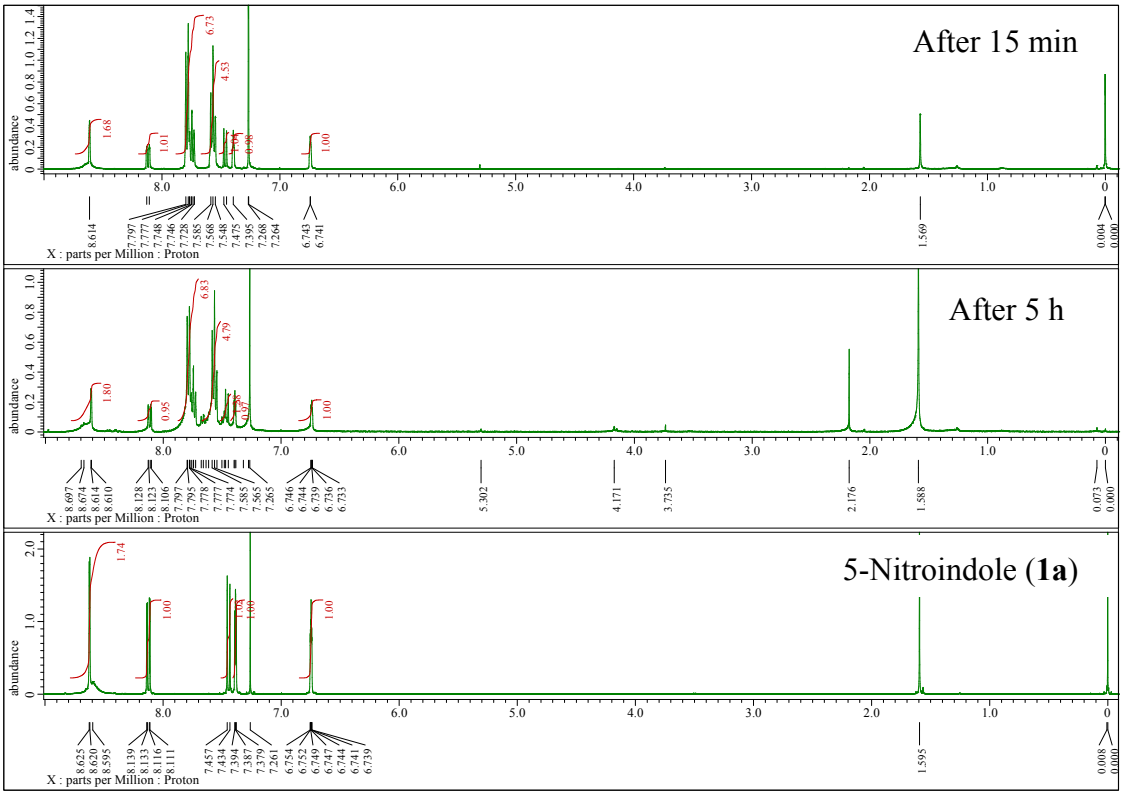
log(conversion X/conversion H) = log (0.89/1) = -0.051



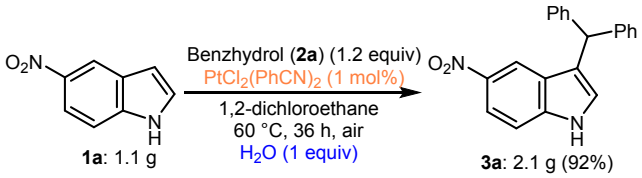
Scheme S3: a ^{1}H NMR study



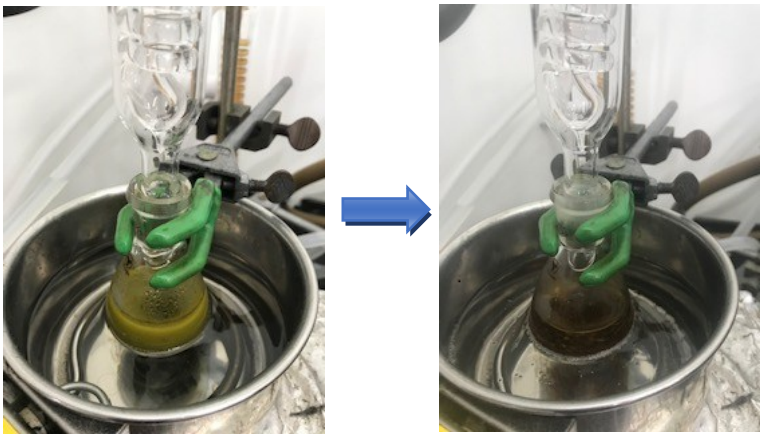
A mixture of 5-nitroindole **1a** (8.4 mg, 0.05 mmol), bis(benzonitrile)dichloroplatinum(II) (13.3 mg, 0.05 mmol) and $CDCl_3$ (4 mL) was heated at 60 °C under air. After cooling, the reaction mixture was analyzed by ^{1}H-NMR spectroscopy.



Scheme S4. Scale-up experiment.



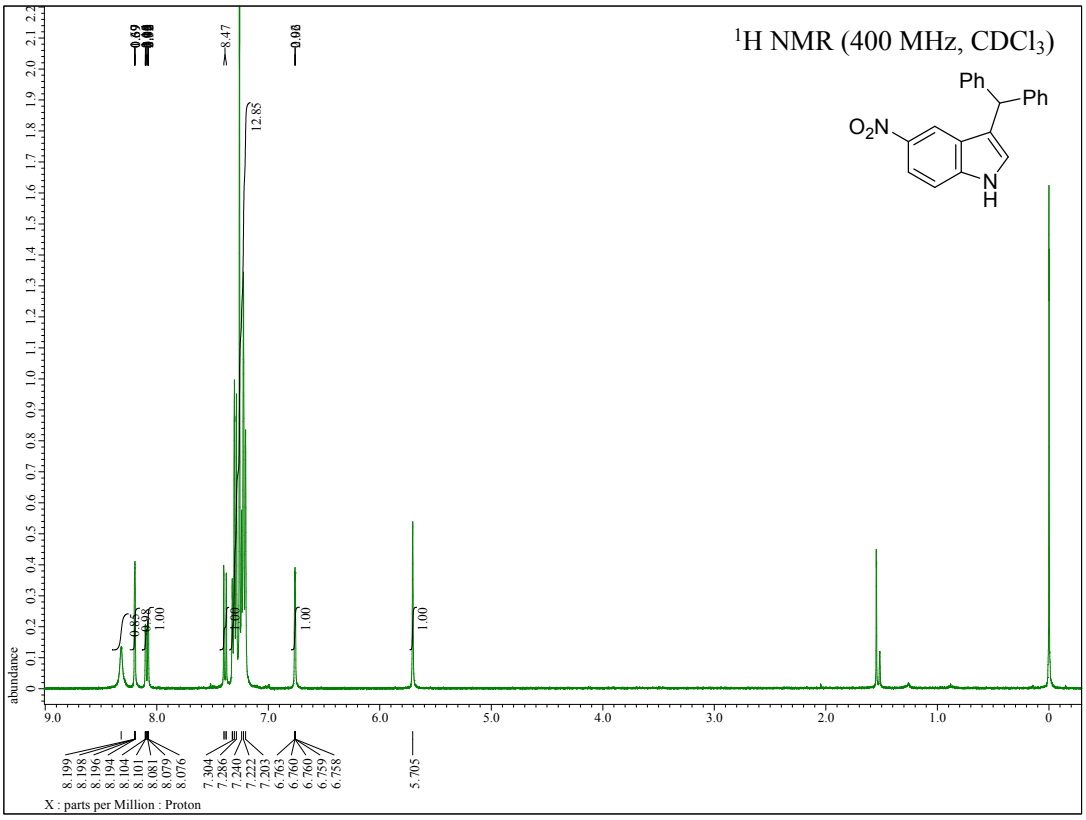
A mixture of 5-nitroindole **1a** (1.14 g, 7 mmol), bis(benzonitrile)dichloroplatinum(II) (33 mg, 0.07 mmol), benzhydrol **2a** (1.55 g, 8.4 mmol) and water (126 mg, 7 mmol) in 1,2-dichloroethane (28 mL) was heated at 60 °C for 36 h under air. After cooling, *n*-hexane was added to the reaction mixture. The precipitate was filtered to give desired product **3a** as yellow solid (2.12 g, 92%).

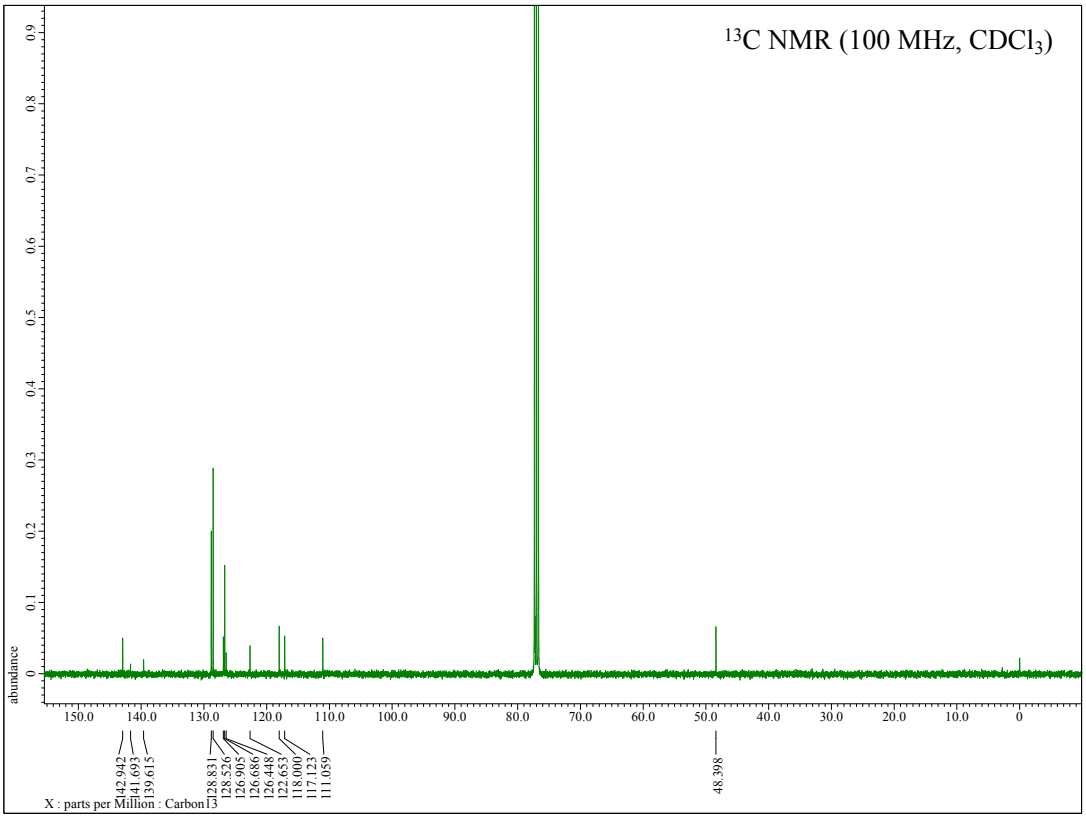


15 min

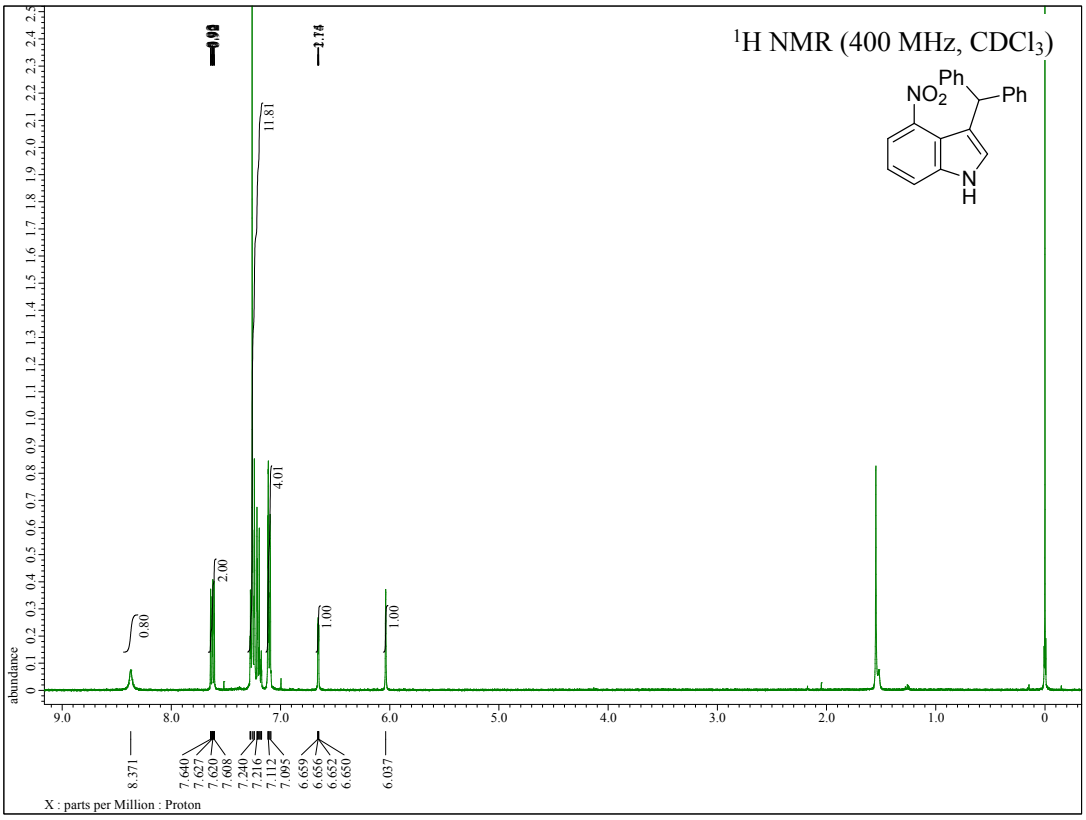
36 h

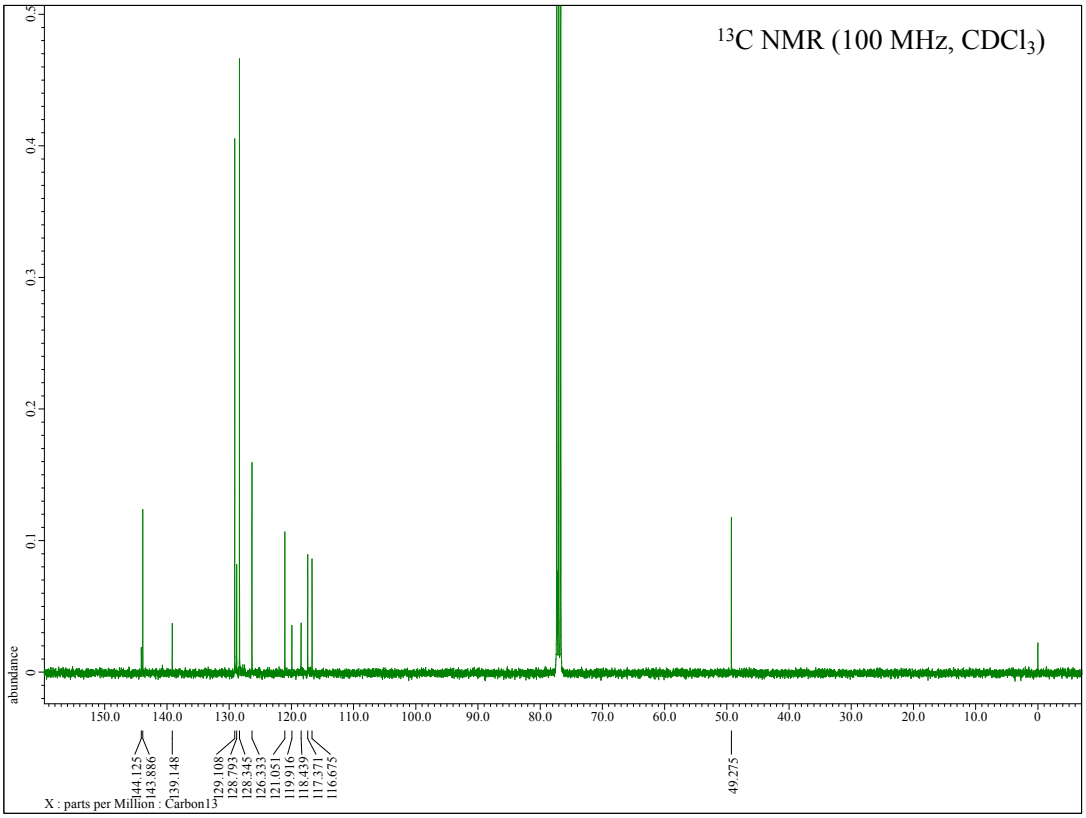
3-Benzhydryl-5-nitro-1*H*-indole **3a**



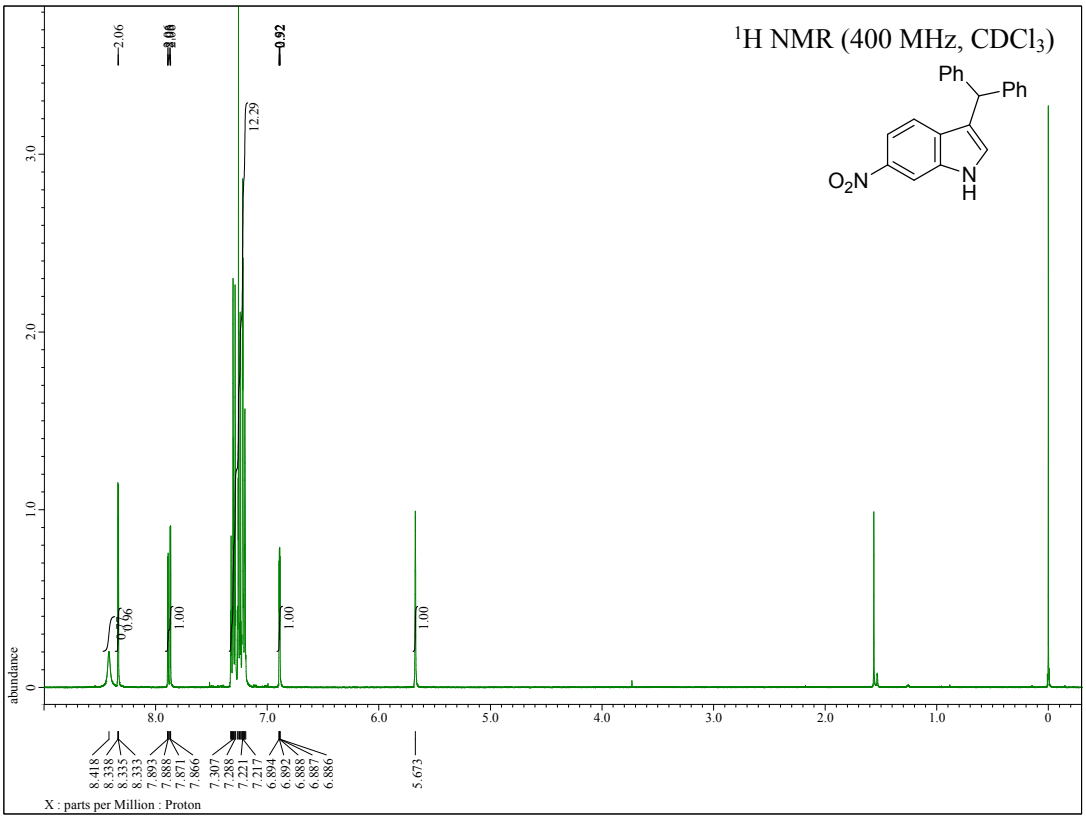


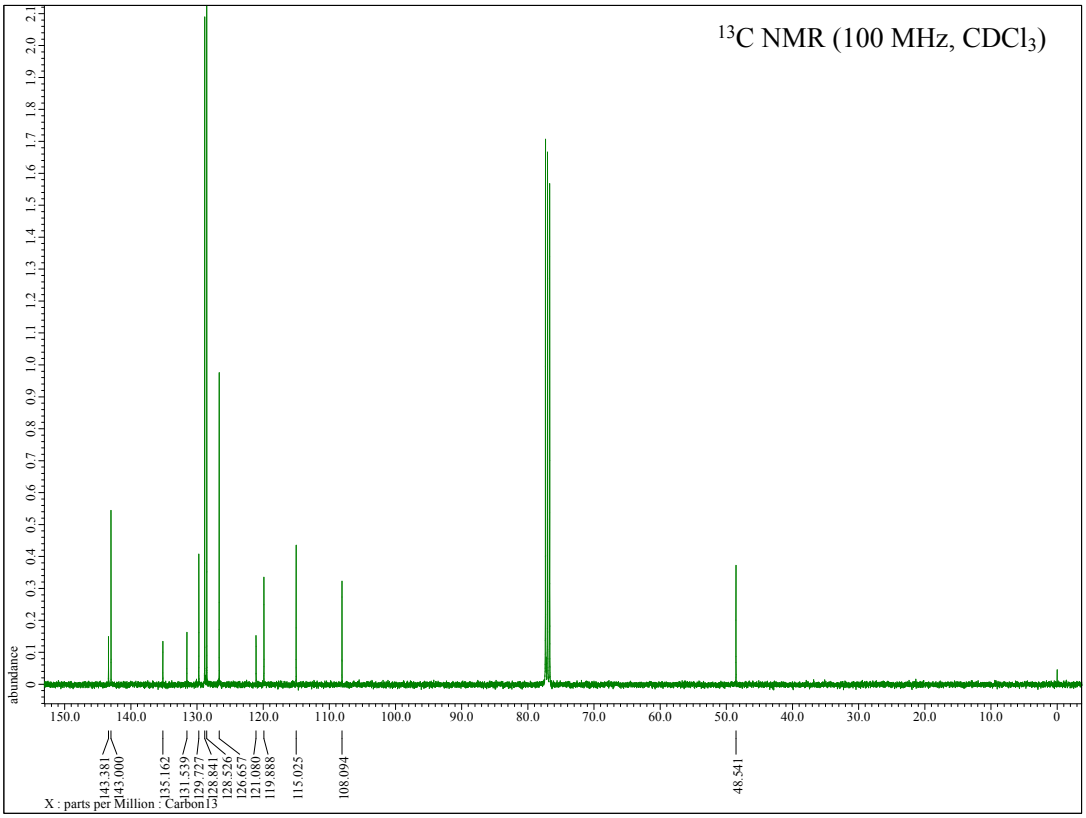
3-Benzhydryl-4-nitro-1*H*-indole **3b**



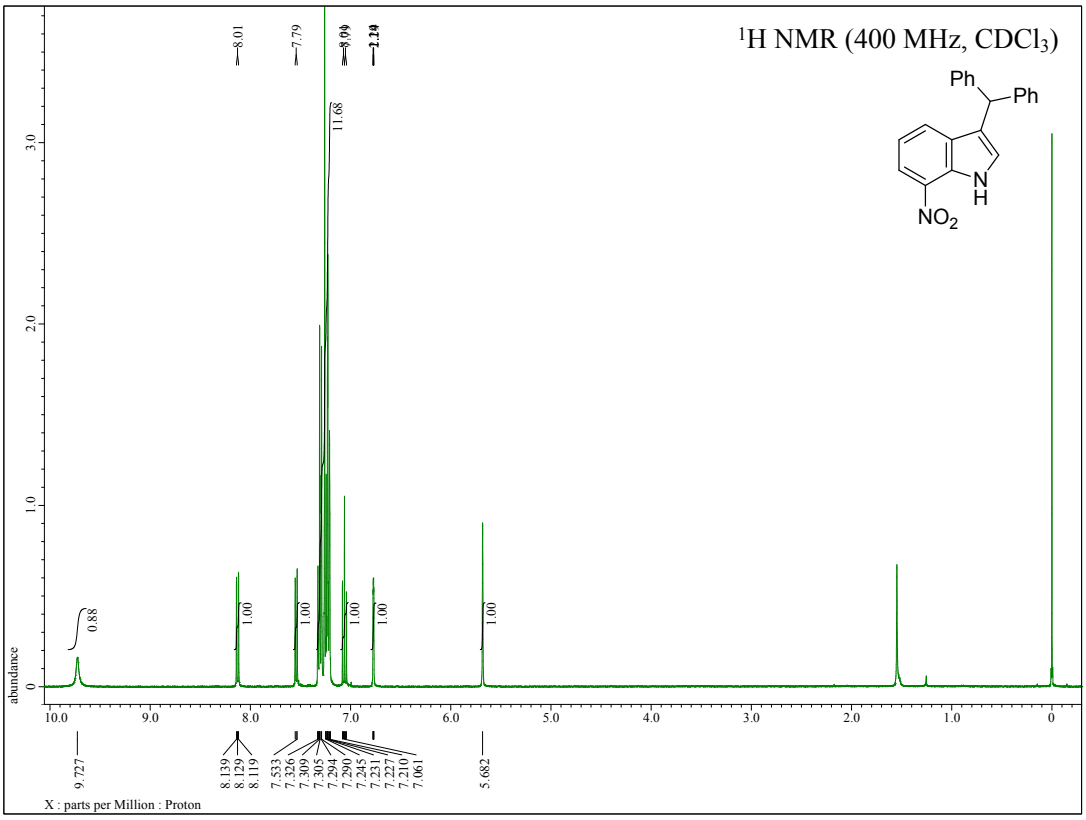


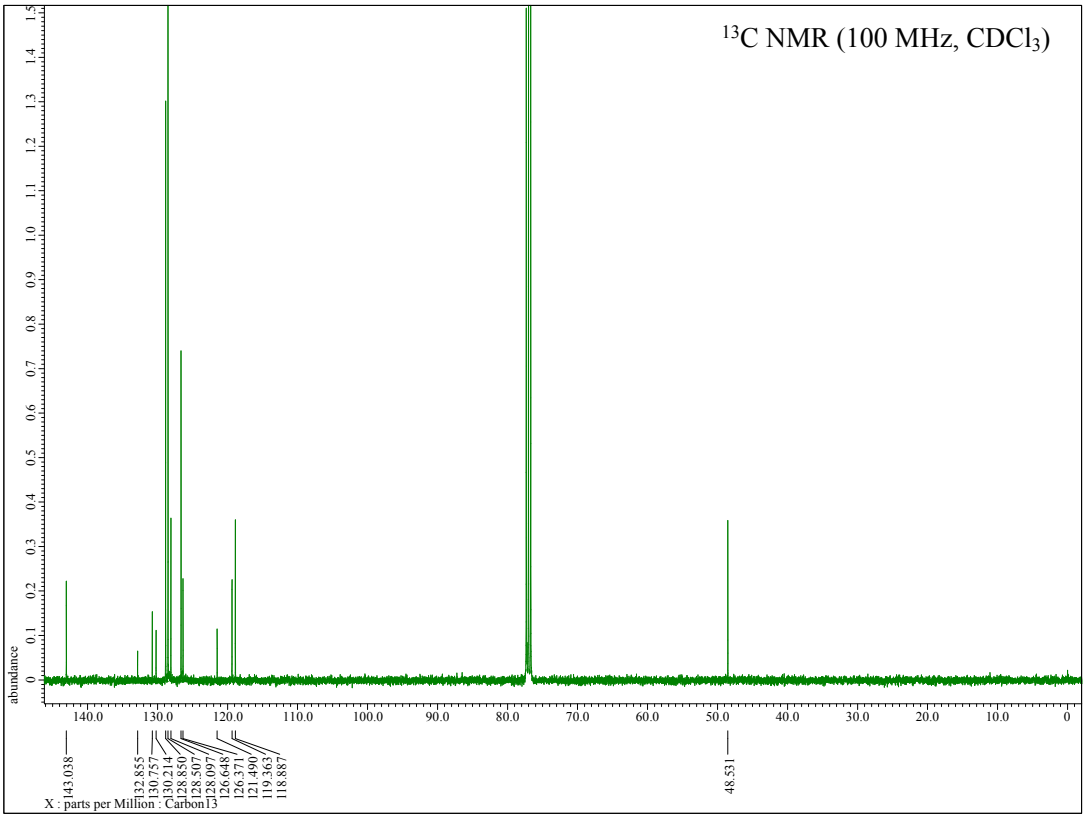
3-Benzhydryl-6-nitro-1*H*-indole **3c**



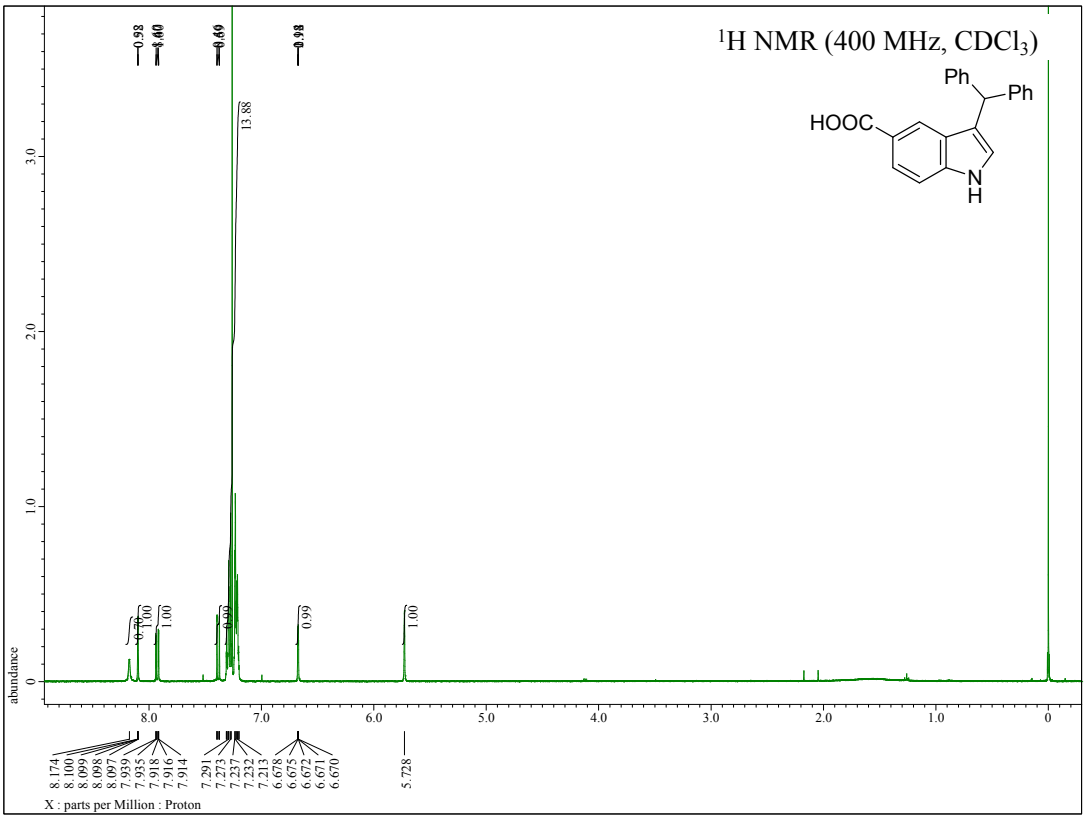


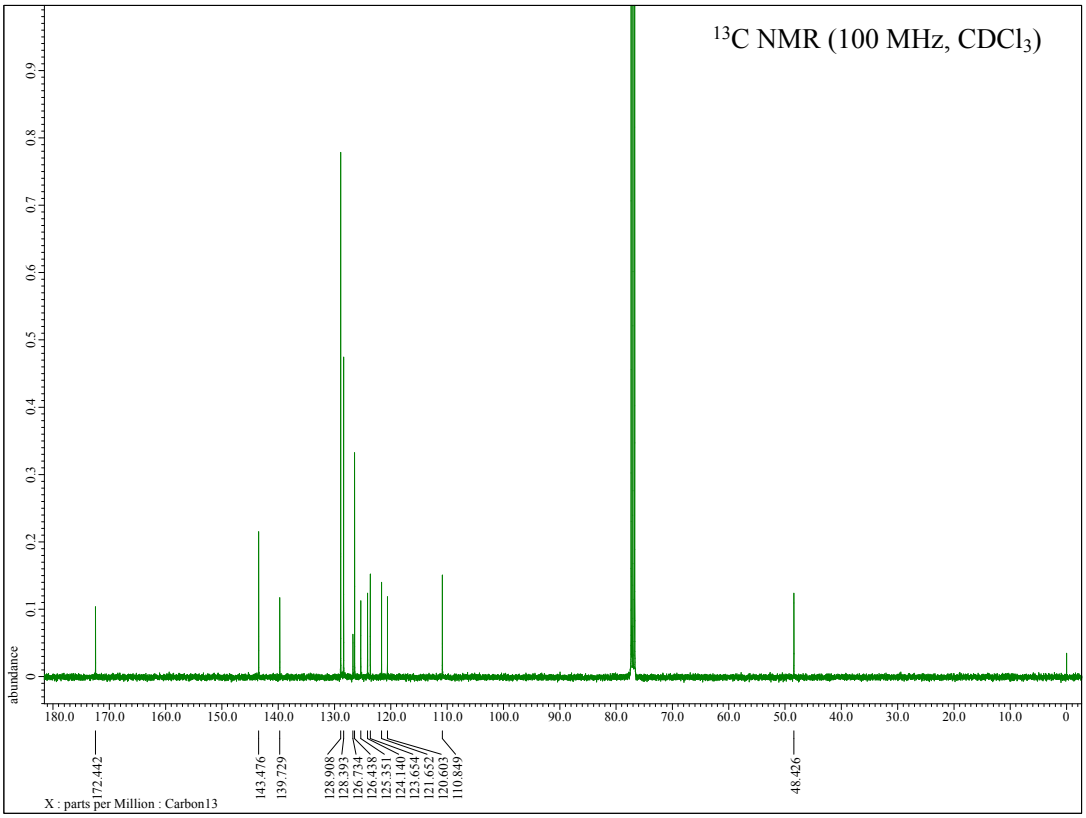
3-Benzhydryl-7-nitro-1*H*-indole **3d**



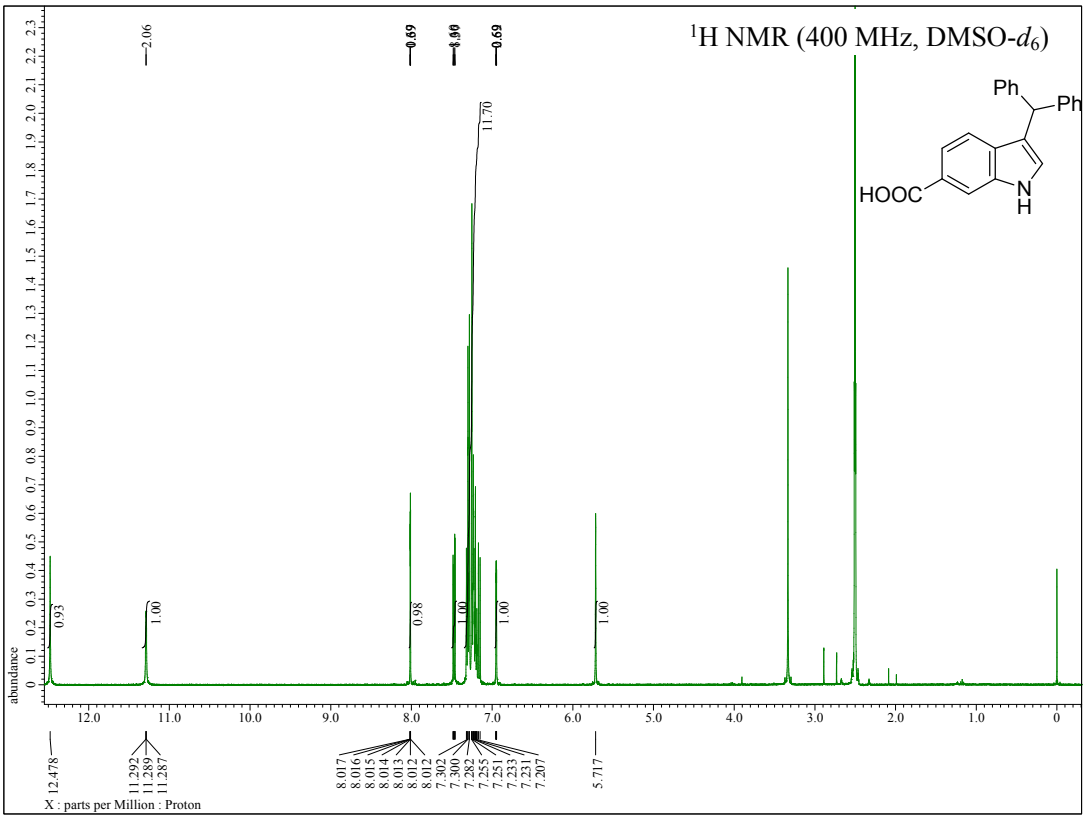


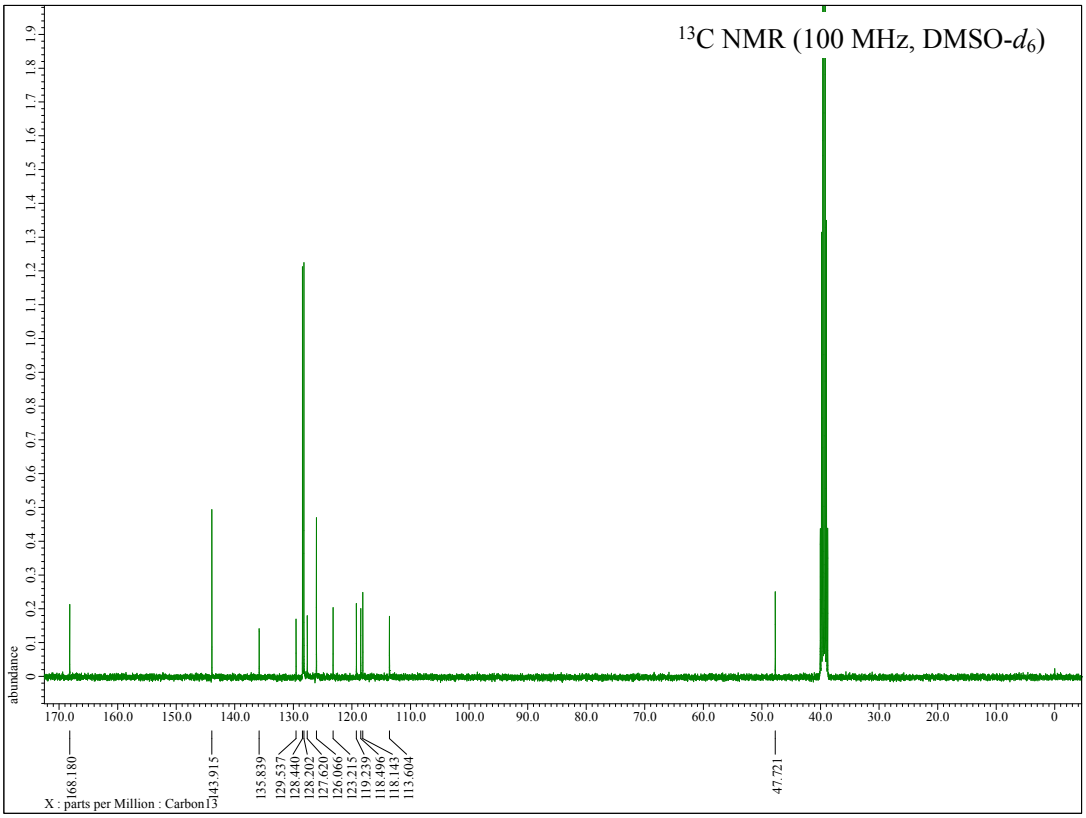
3-Benzhydryl-1*H*-indole-5-carboxylic acid **3e**



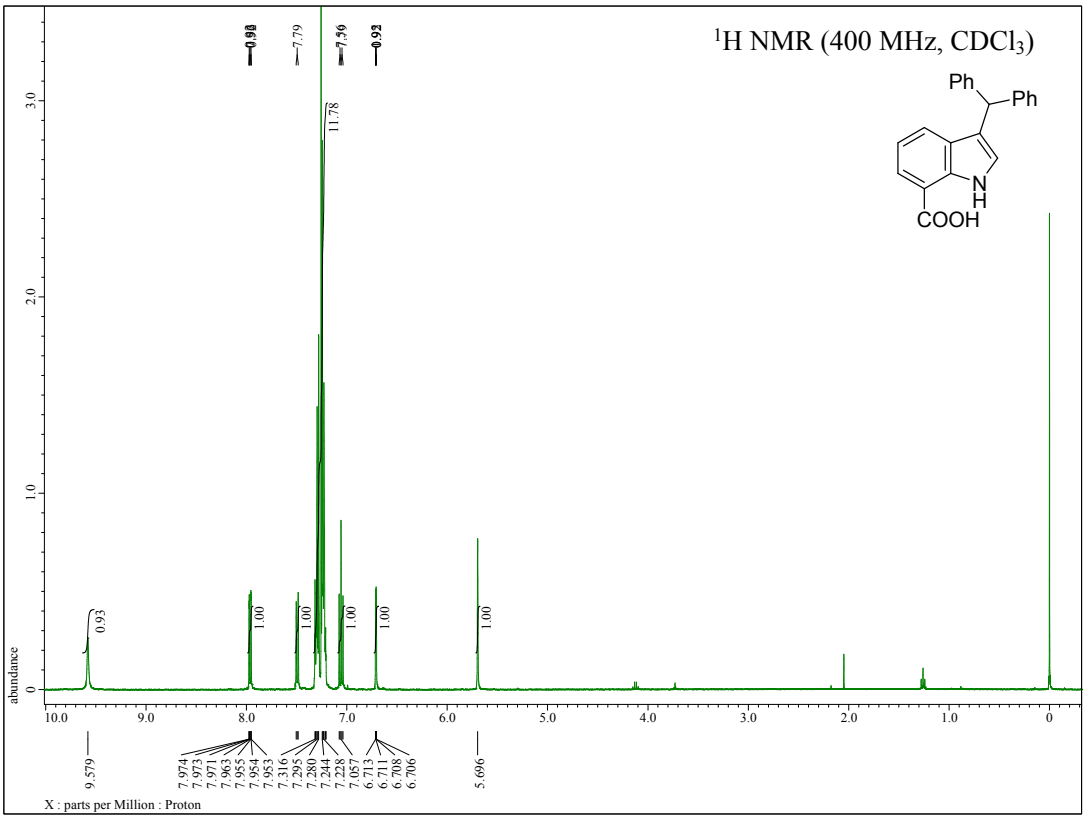


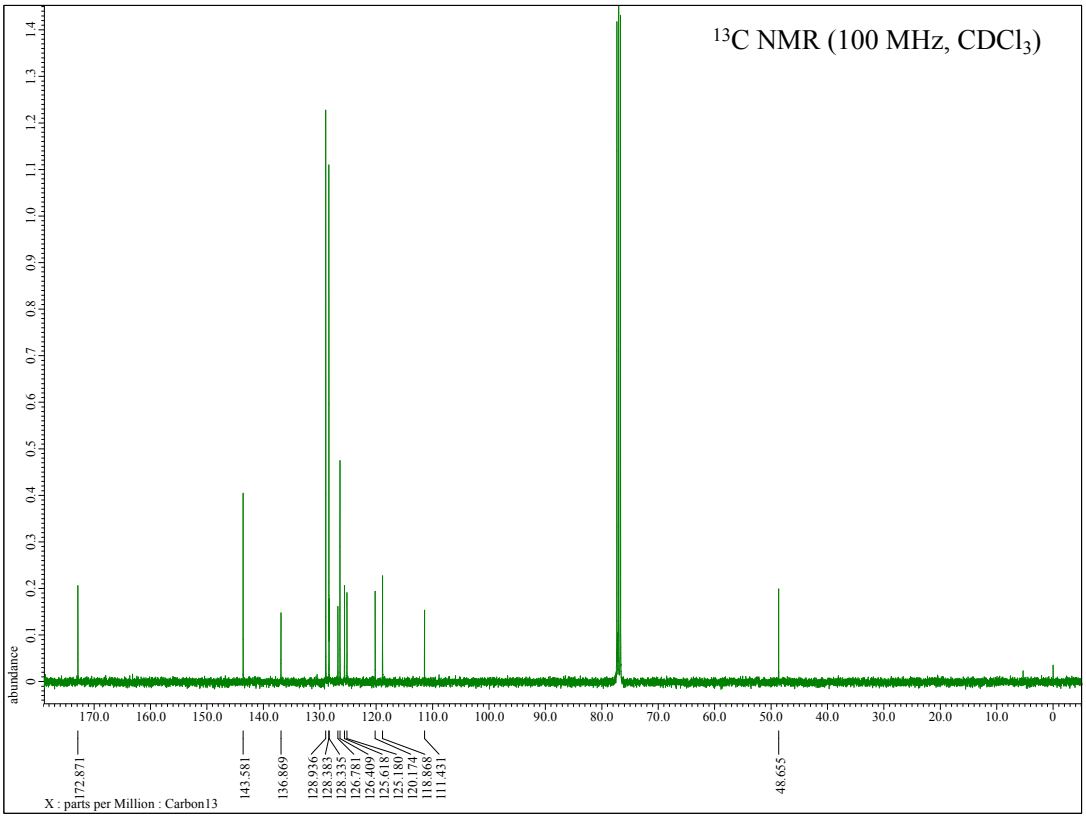
3-Benzhydryl-1*H*-indole-6-carboxylic acid **3f**



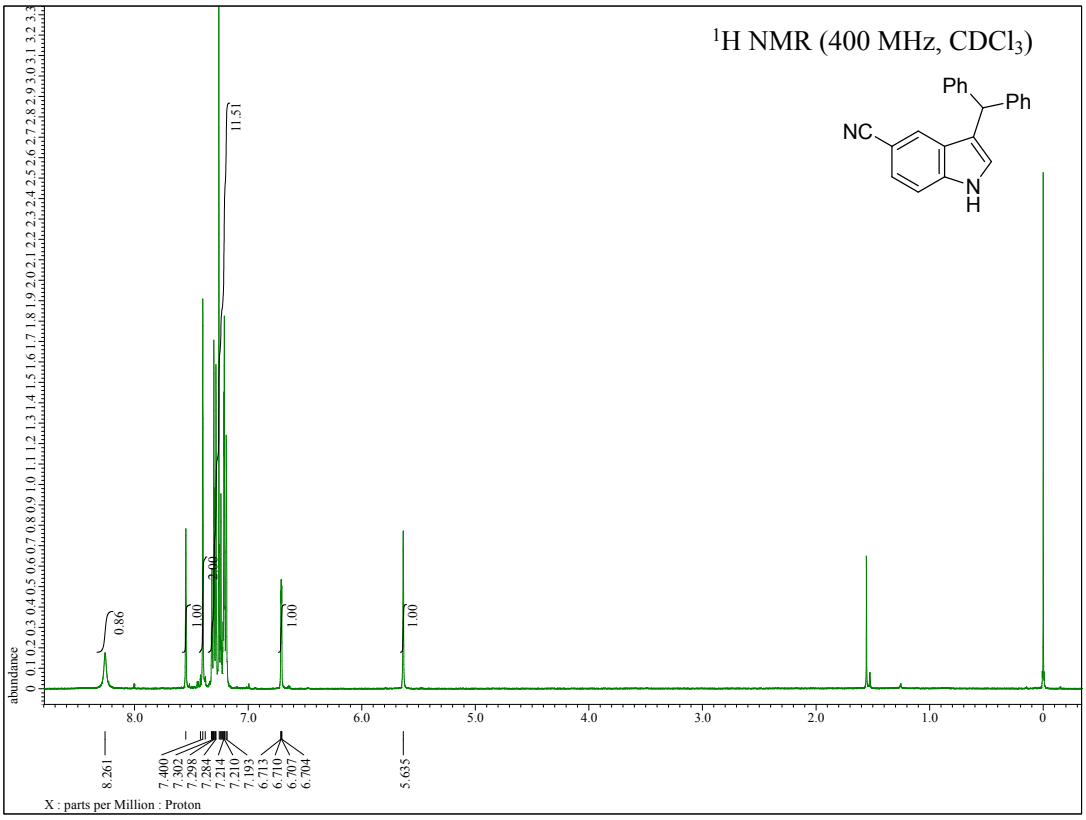


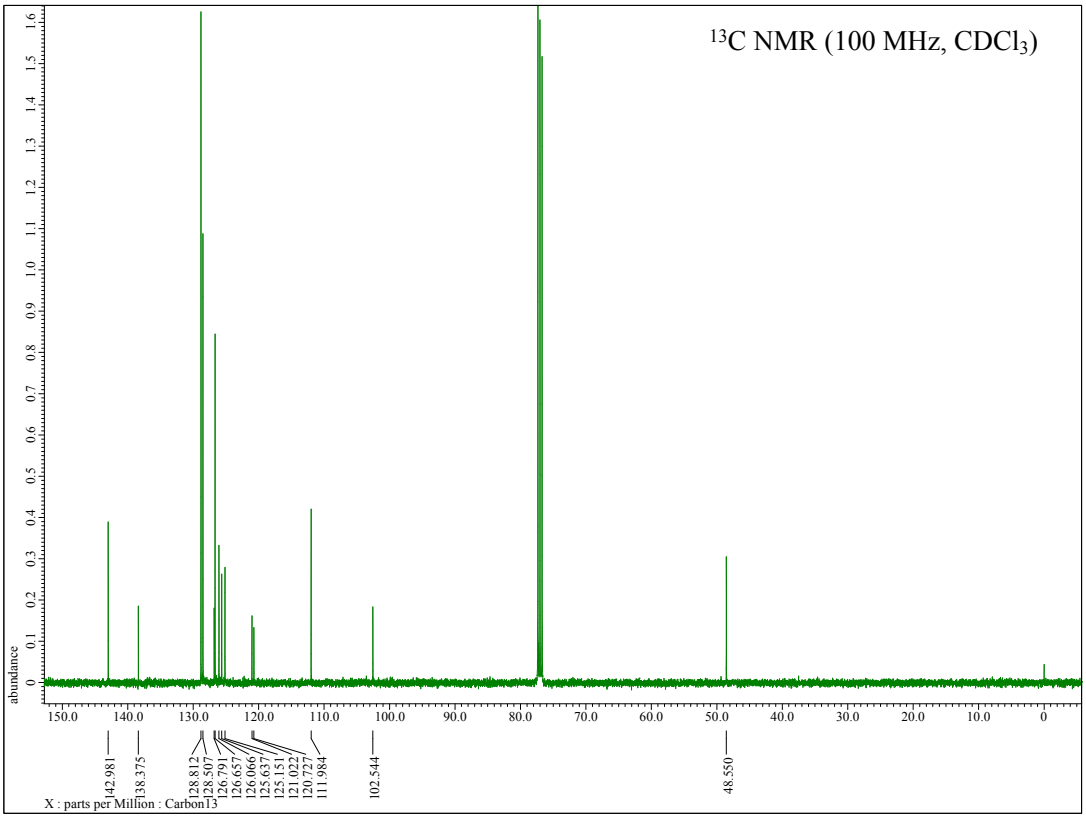
3-Benzhydryl-1*H*-indole-7-carboxylic aci **3g**



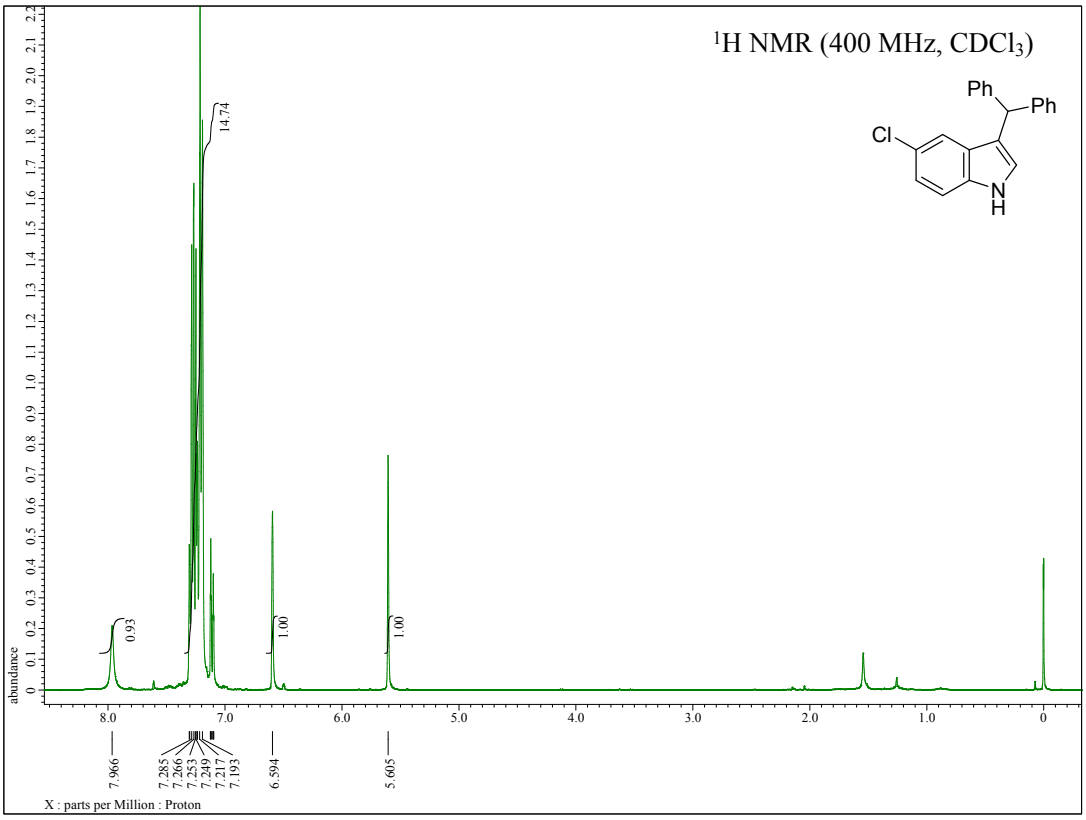


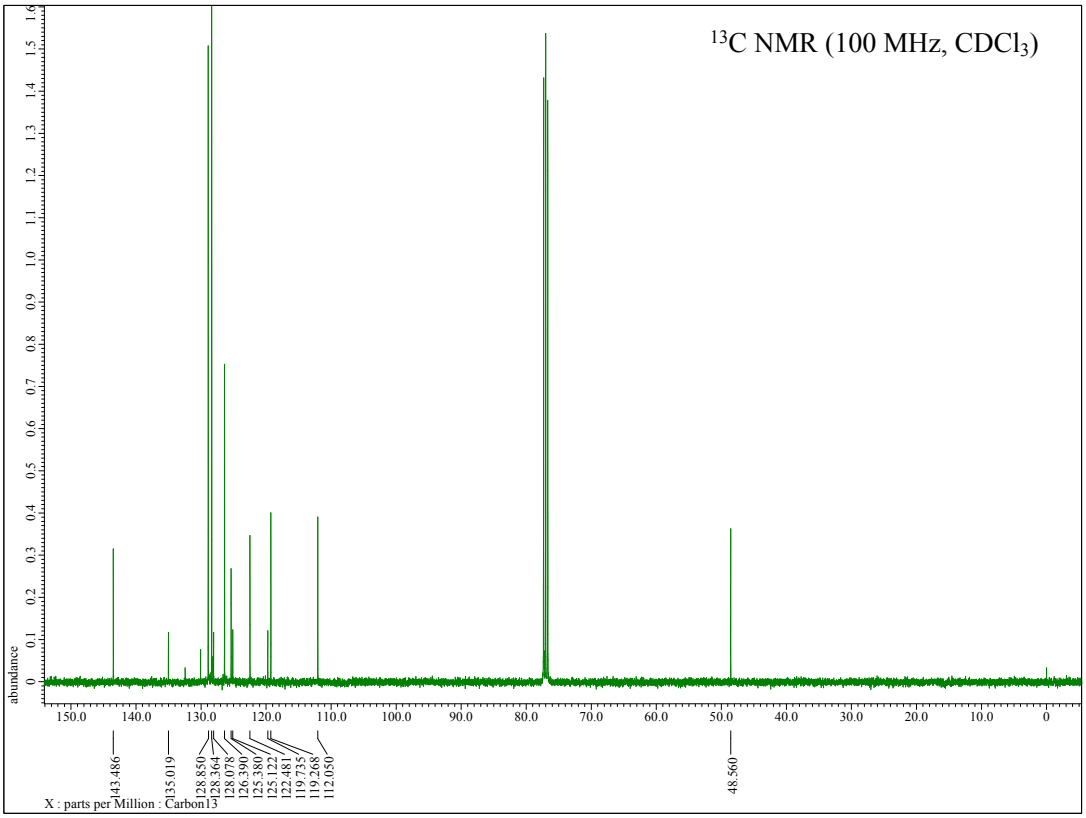
3-Benzhydryl-1*H*-indole-5-carbonitrile **3h**



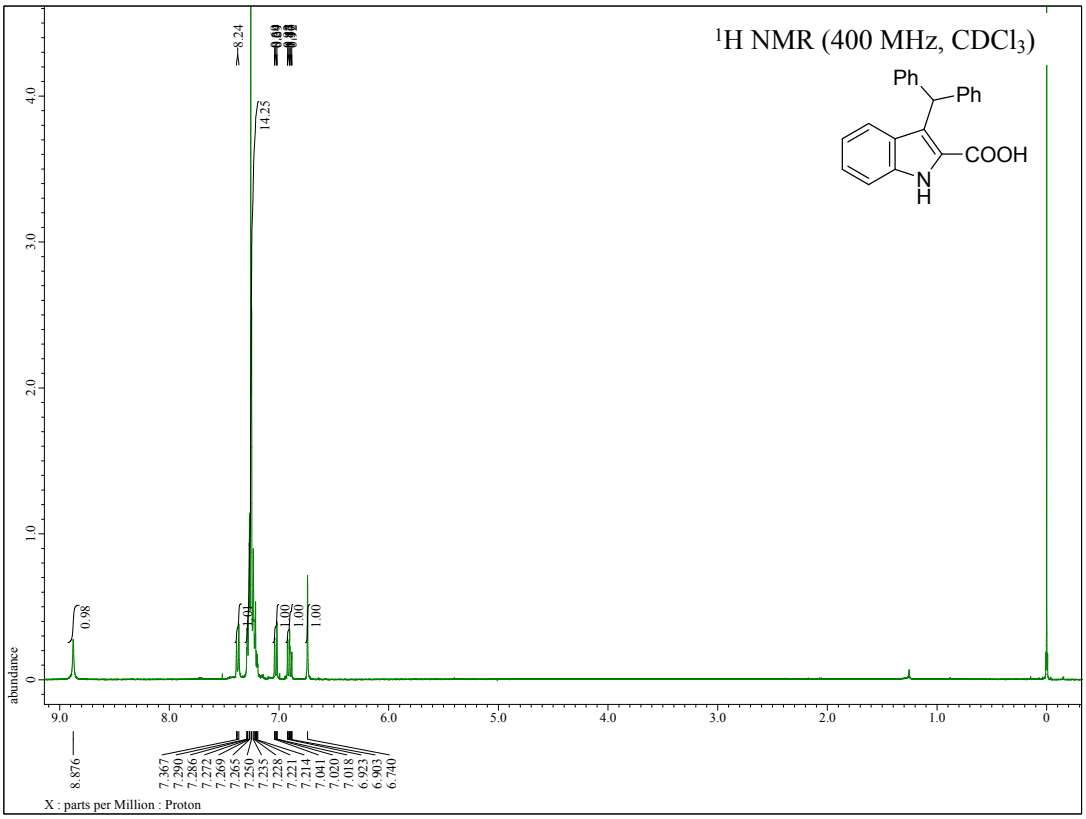


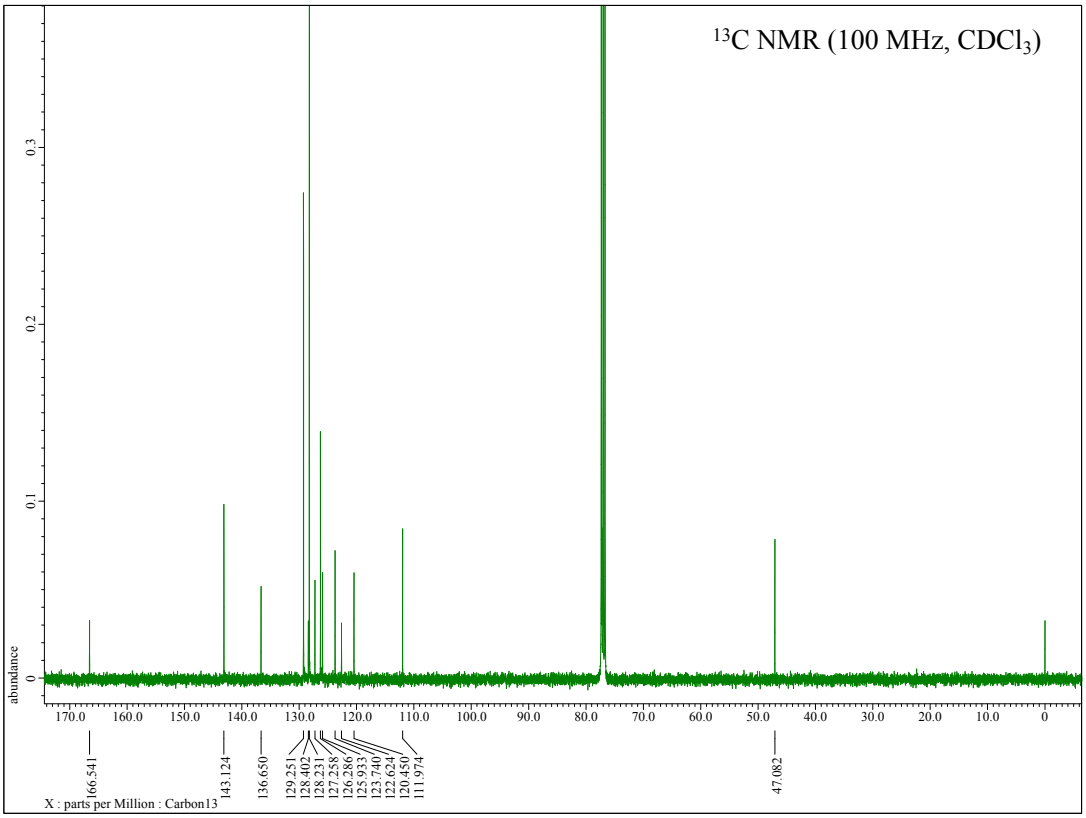
3-Benzhydryl-5-chloro-1*H*-indole **3i**



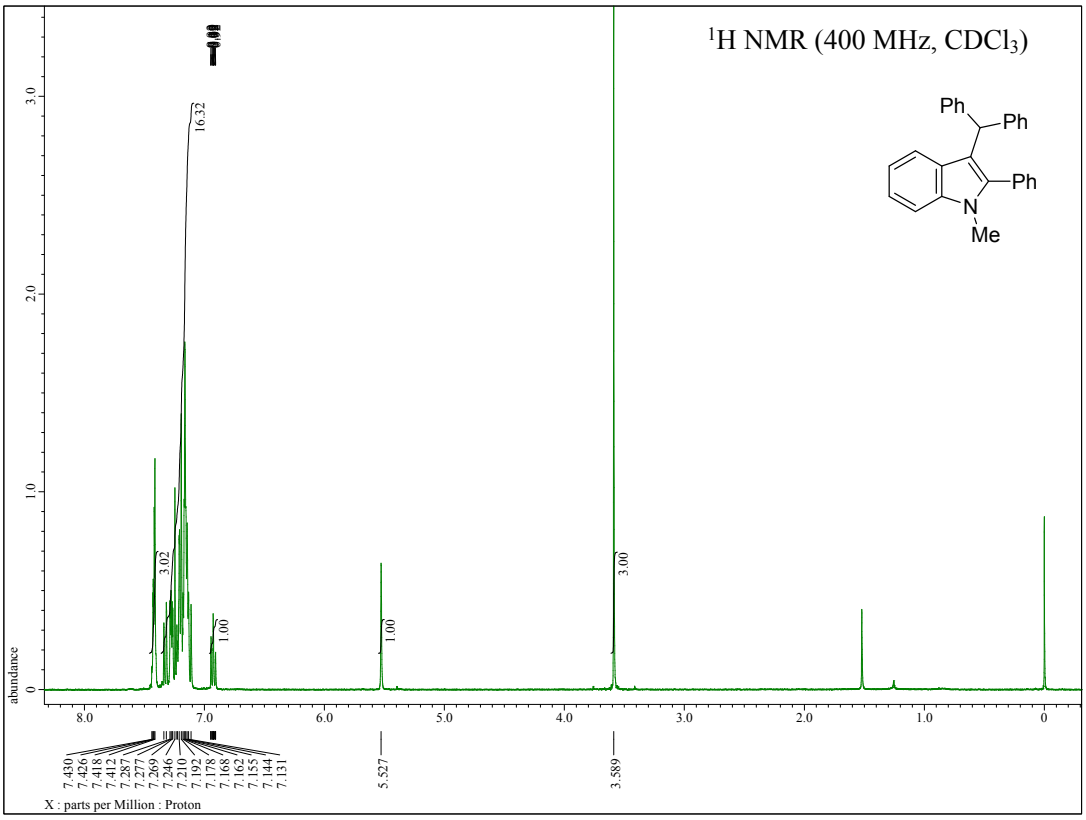


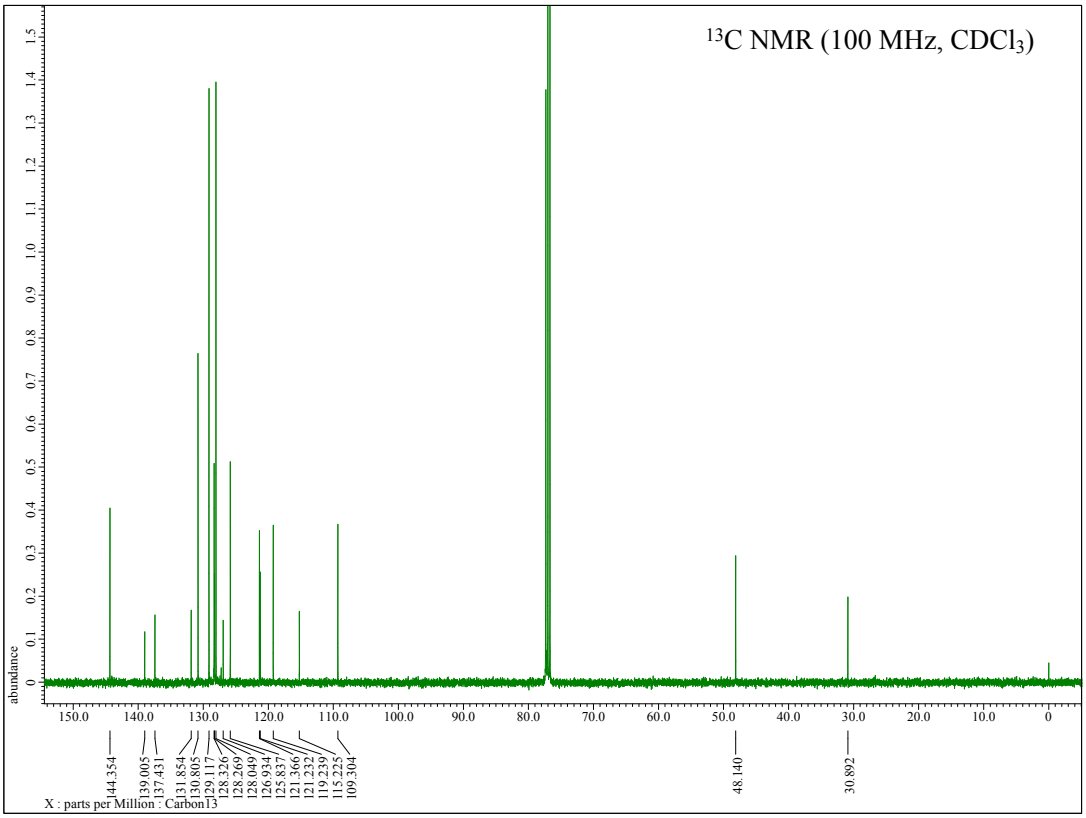
3-Benzhydryl-1*H*-indole-2-carboxylic acid **3j**



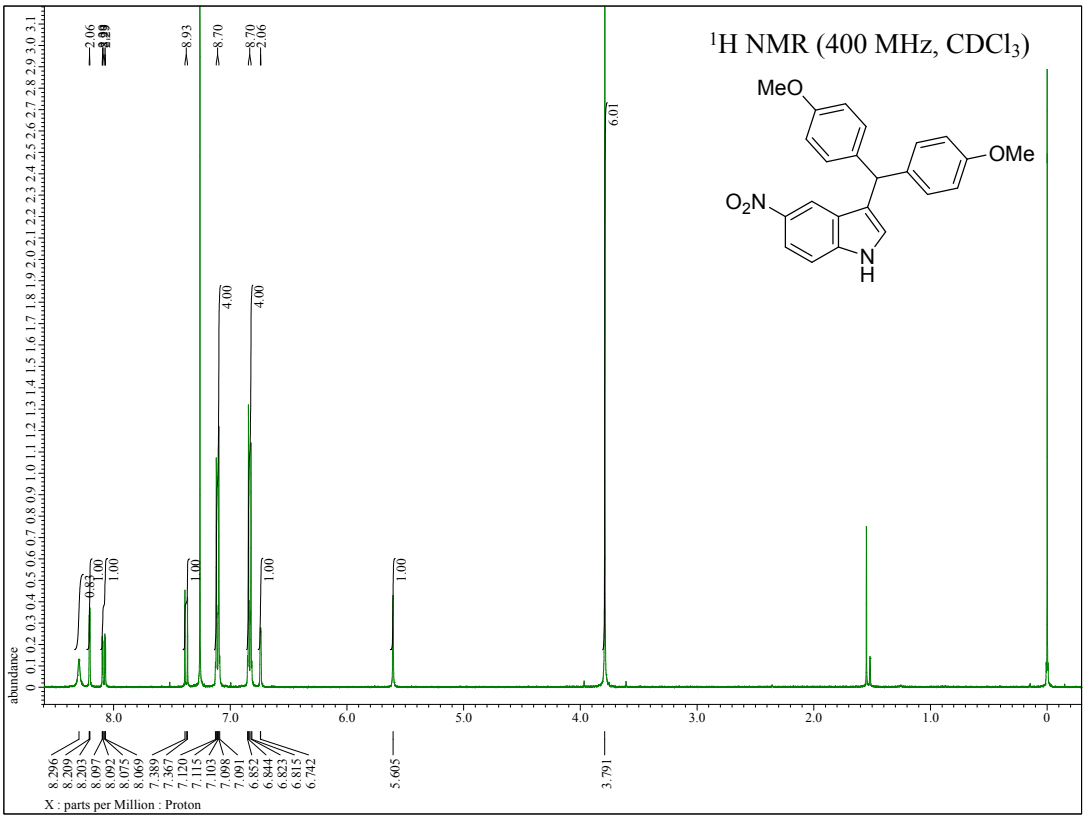


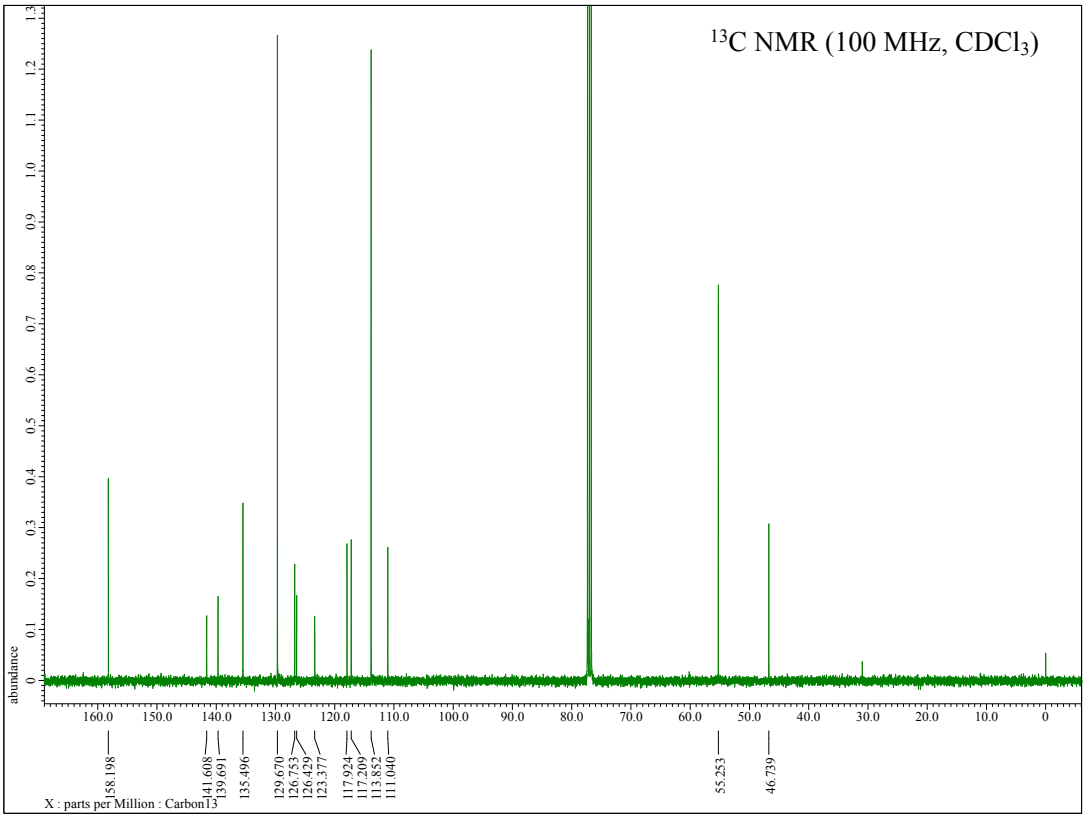
3-Benzhydryl-1-methyl-2-phenyl-1*H*-indole **3k**



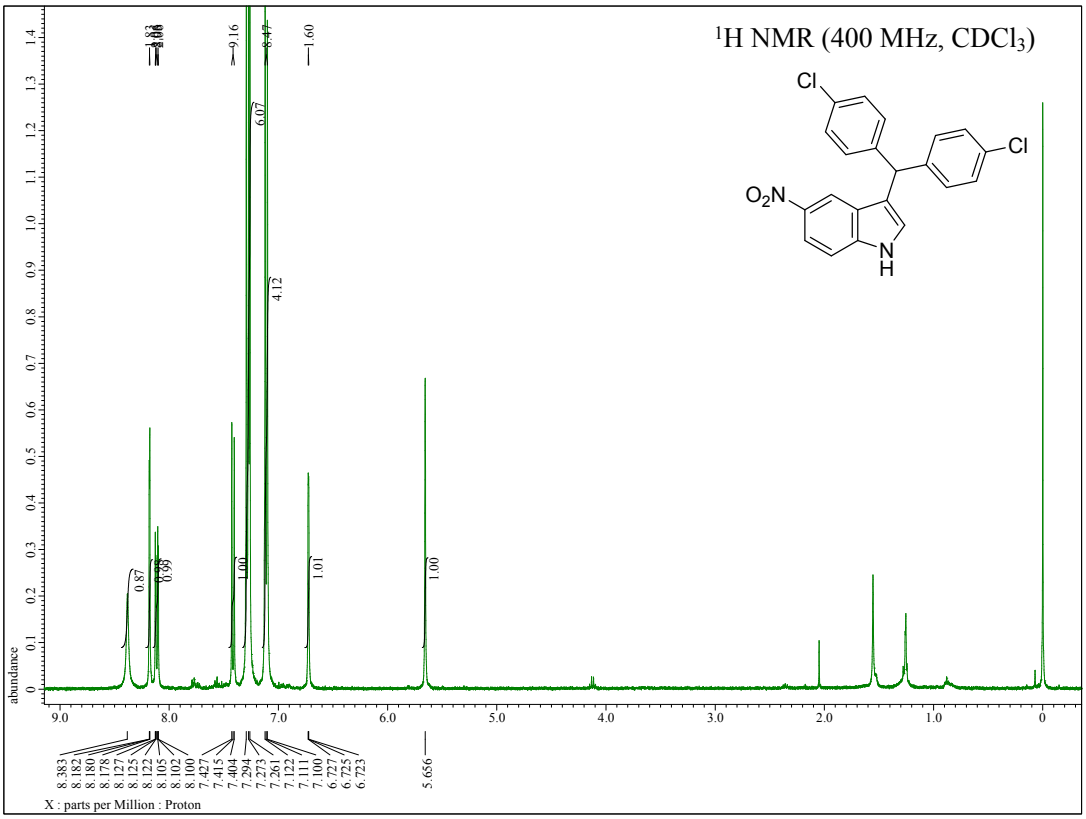


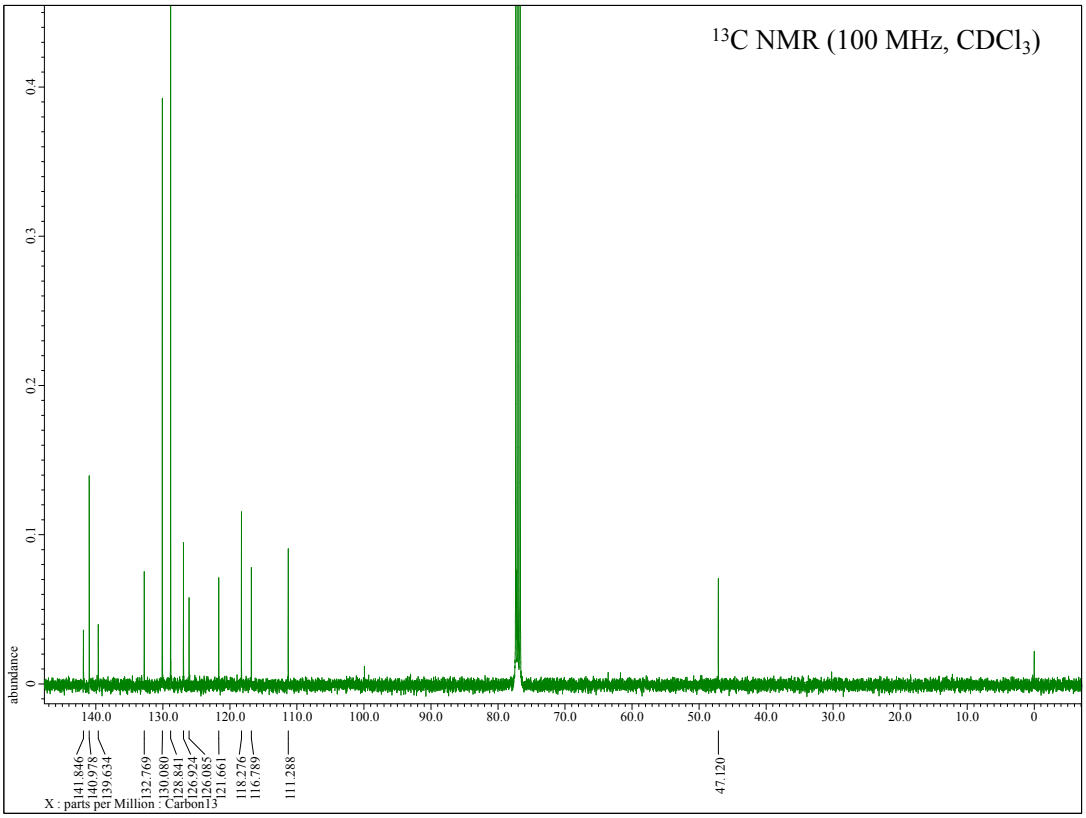
3-[Bis(4-methoxyphenyl)methyl]-5-nitro-1*H*-indole **3l**



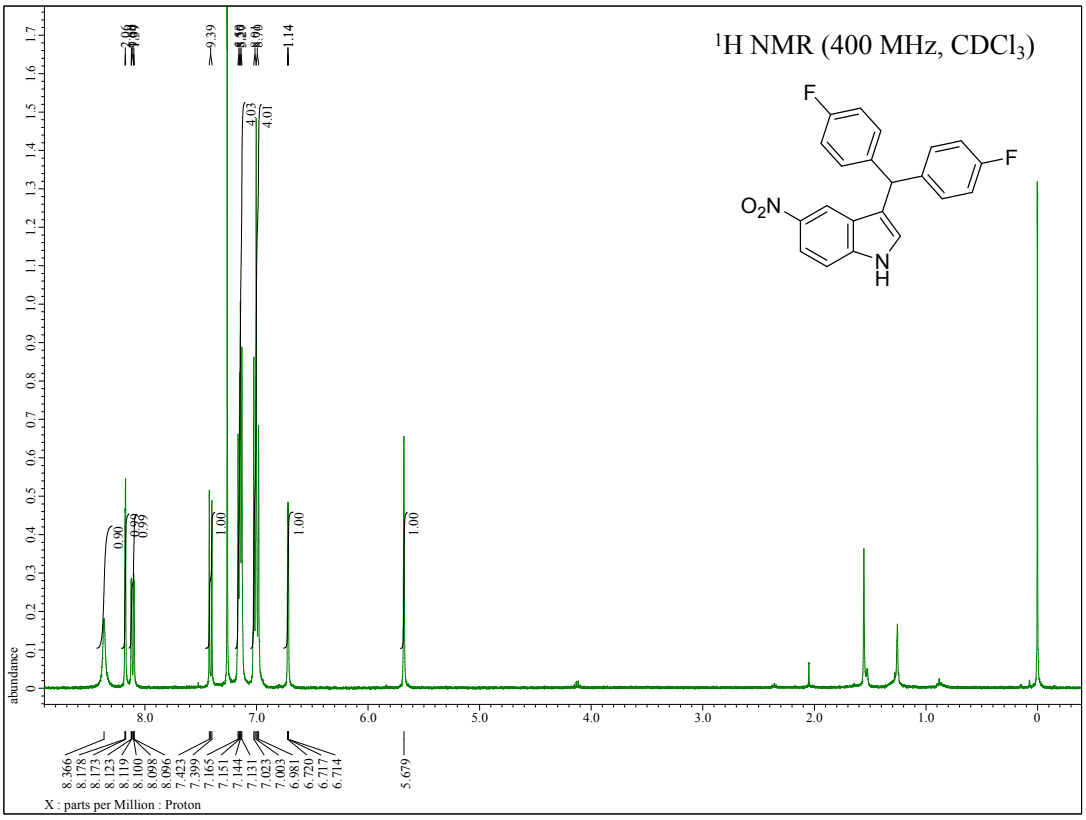


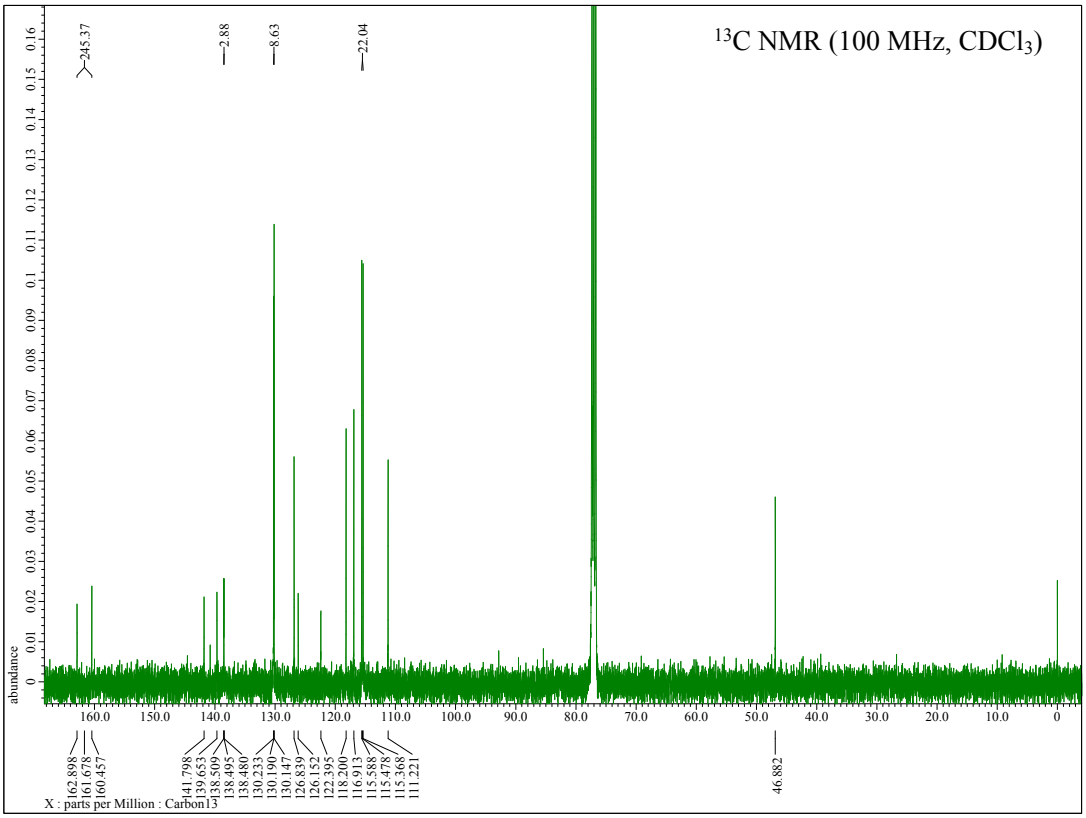
3-[Bis(4-chlorophenyl)methyl]-5-nitro-1*H*-indole **3m**



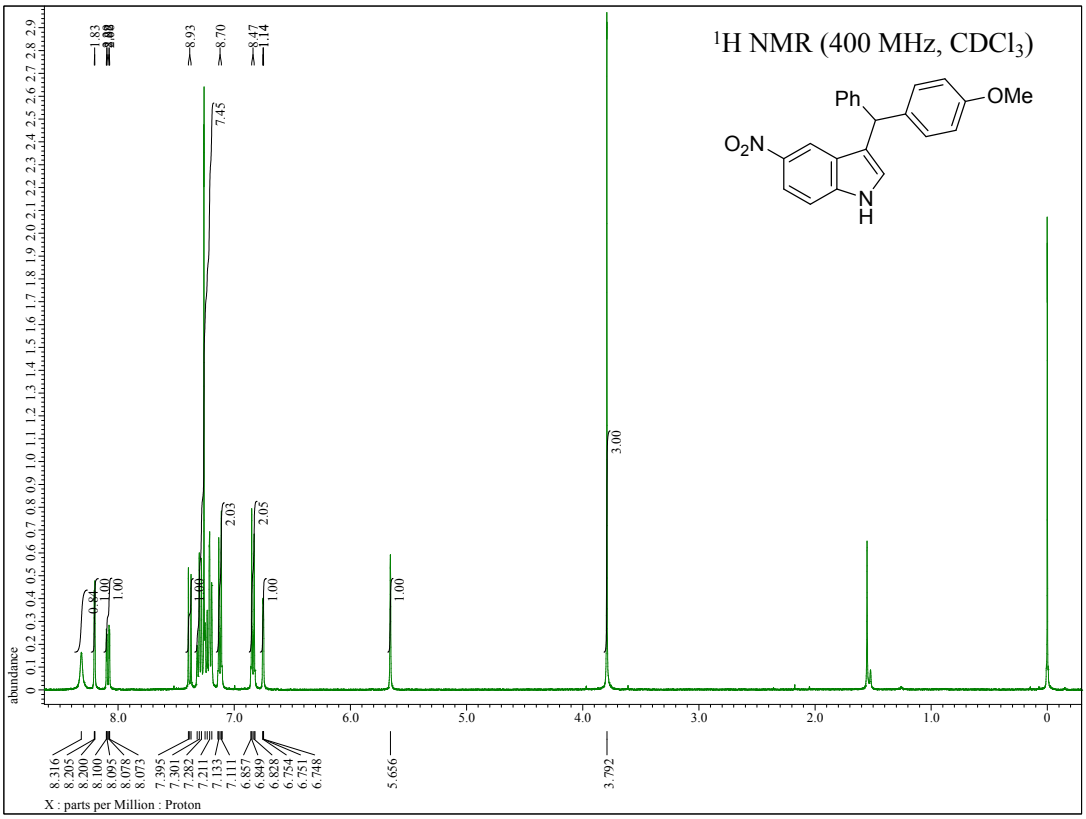


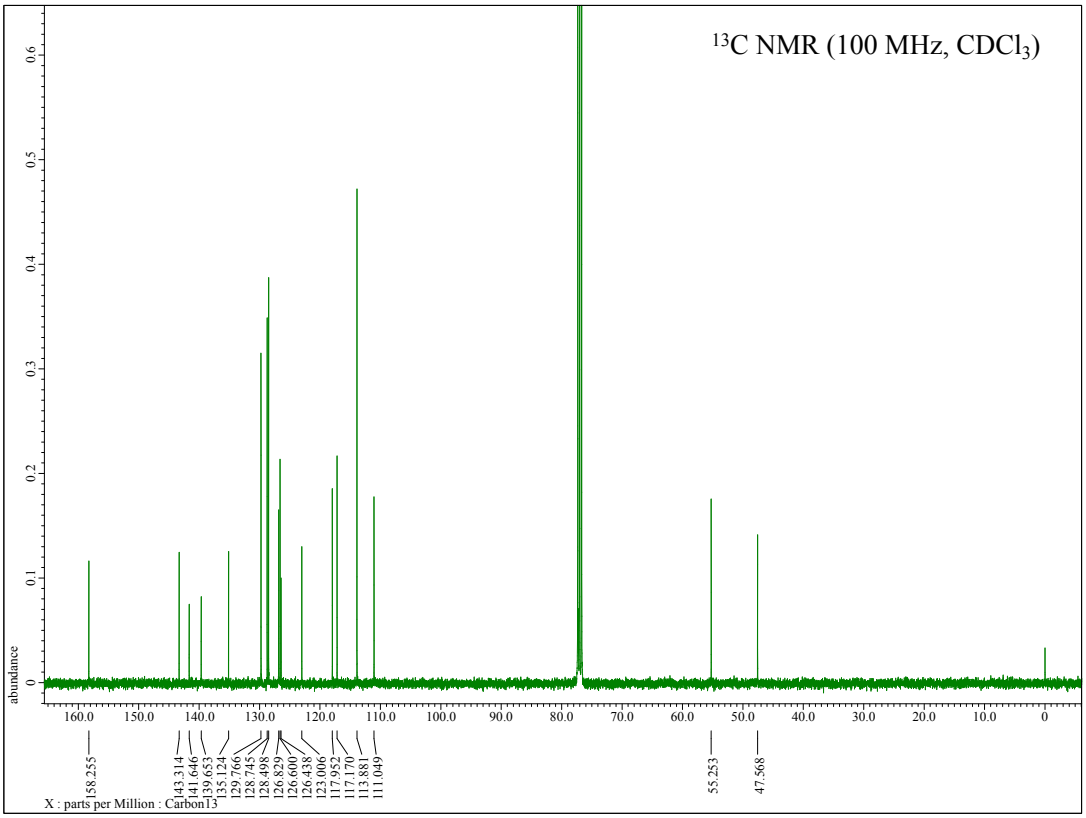
3-[Bis(4-fluorophenyl)methyl]-5-nitro-1*H*-indole **3n**



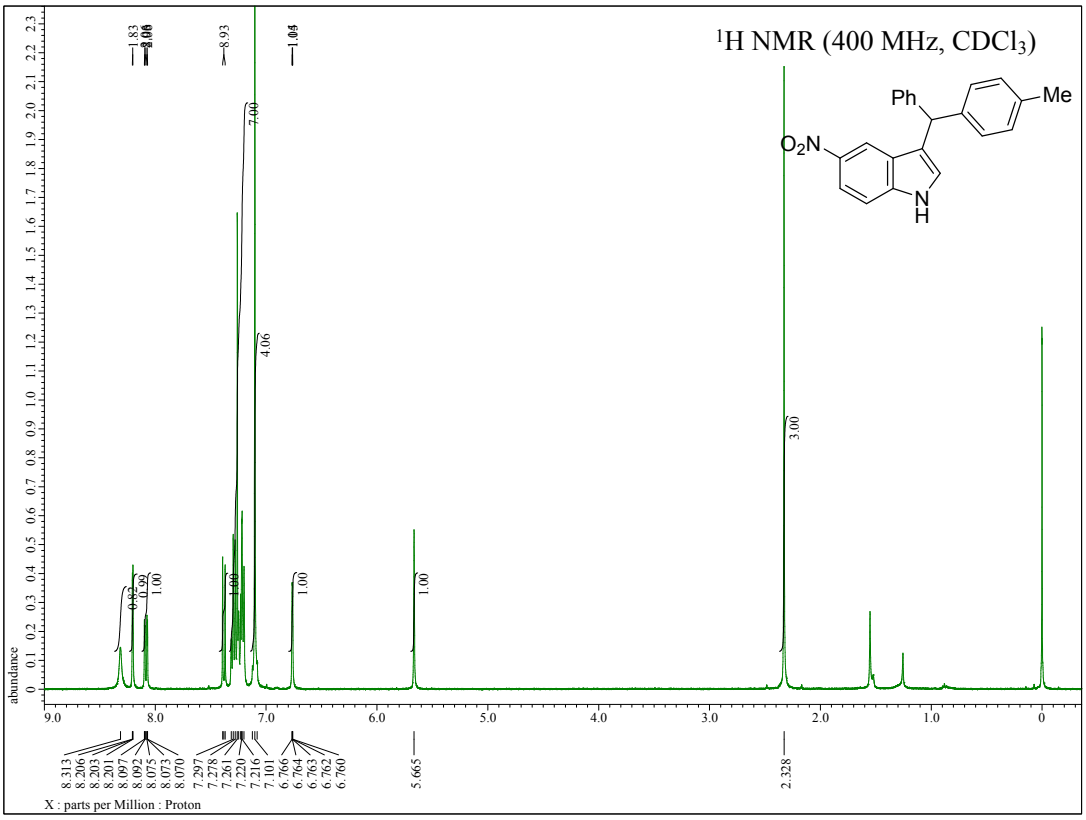


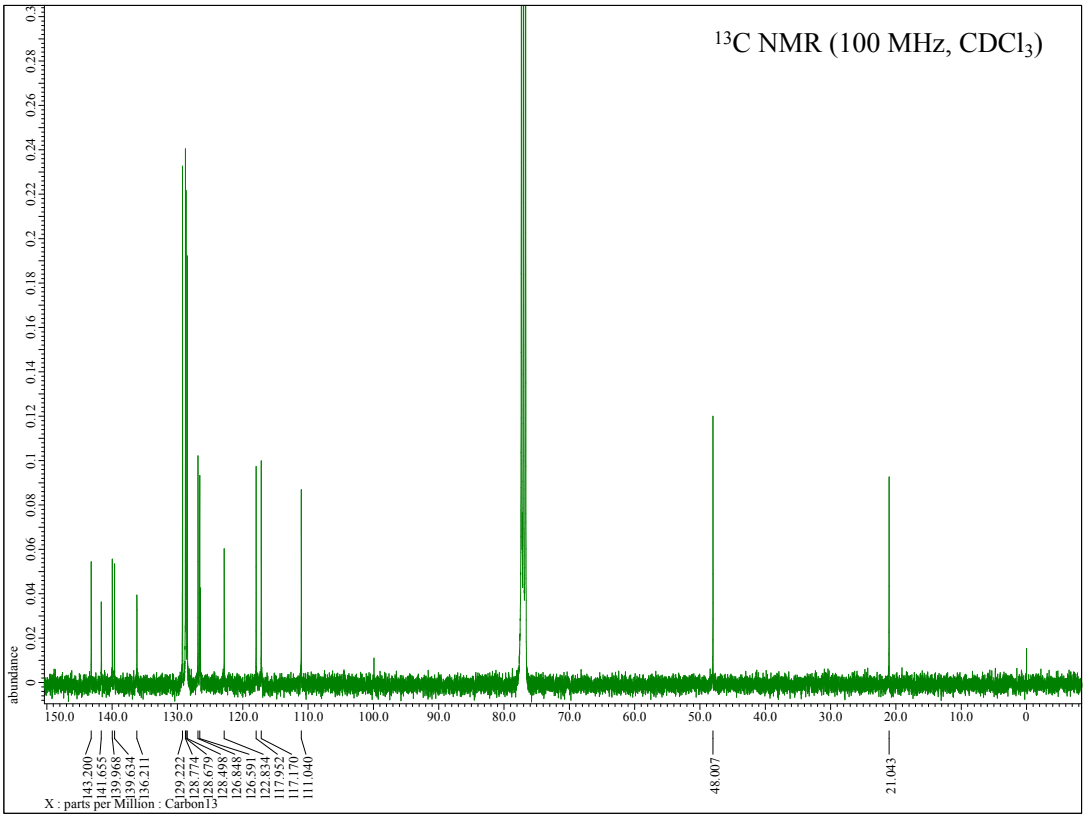
3-[(4-Methoxyphenyl)(phenyl)methyl]-5-nitro-1*H*-indole **3o**



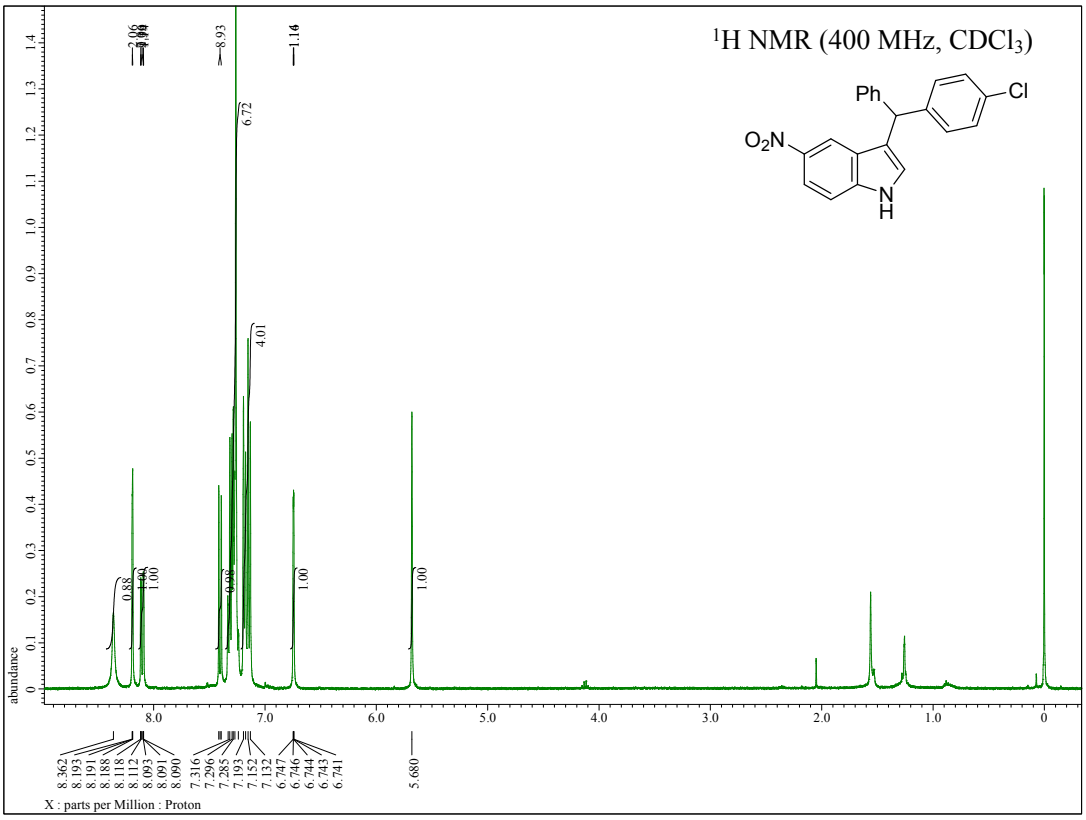


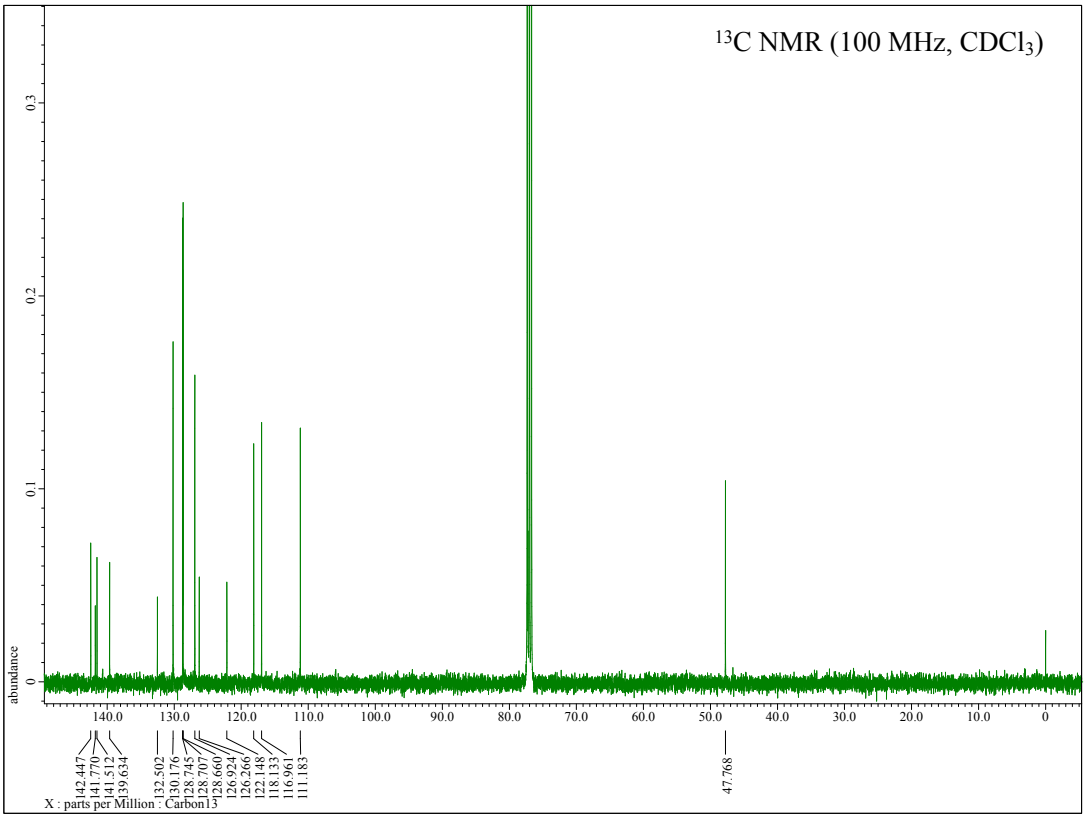
5-Nitro-3-[phenyl(*p*-tolyl)methyl]-1*H*-indole **3p**



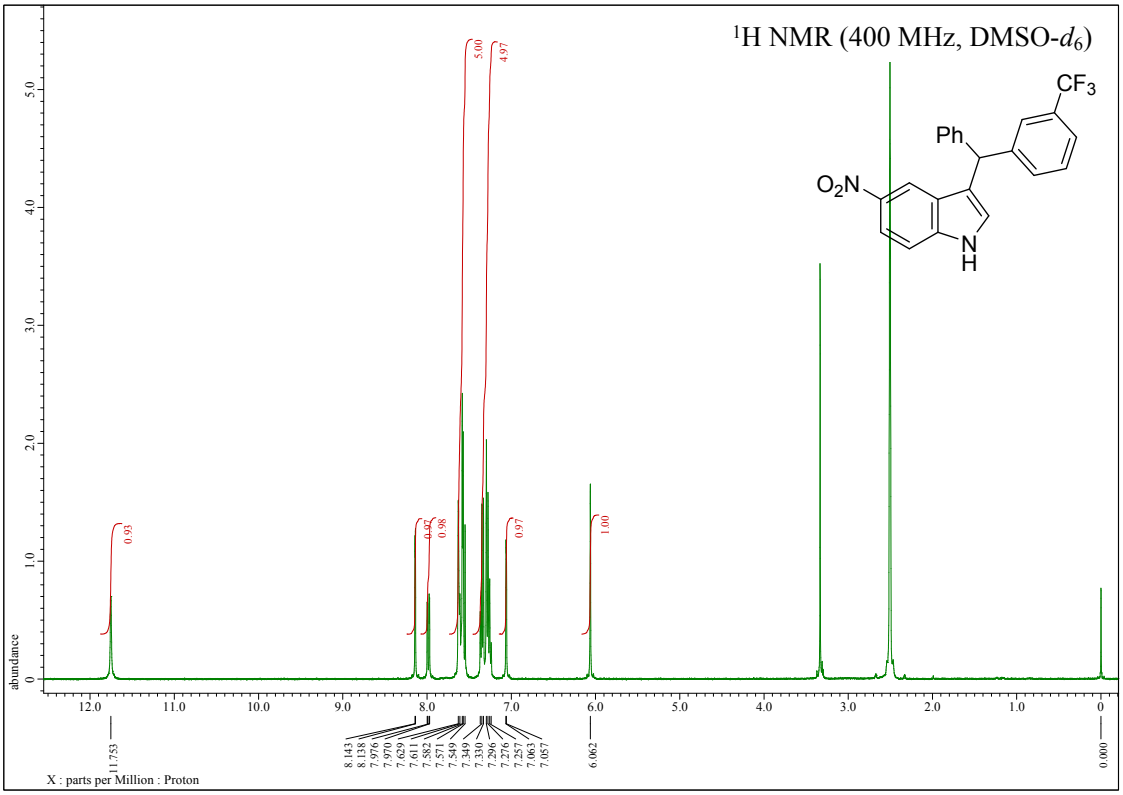


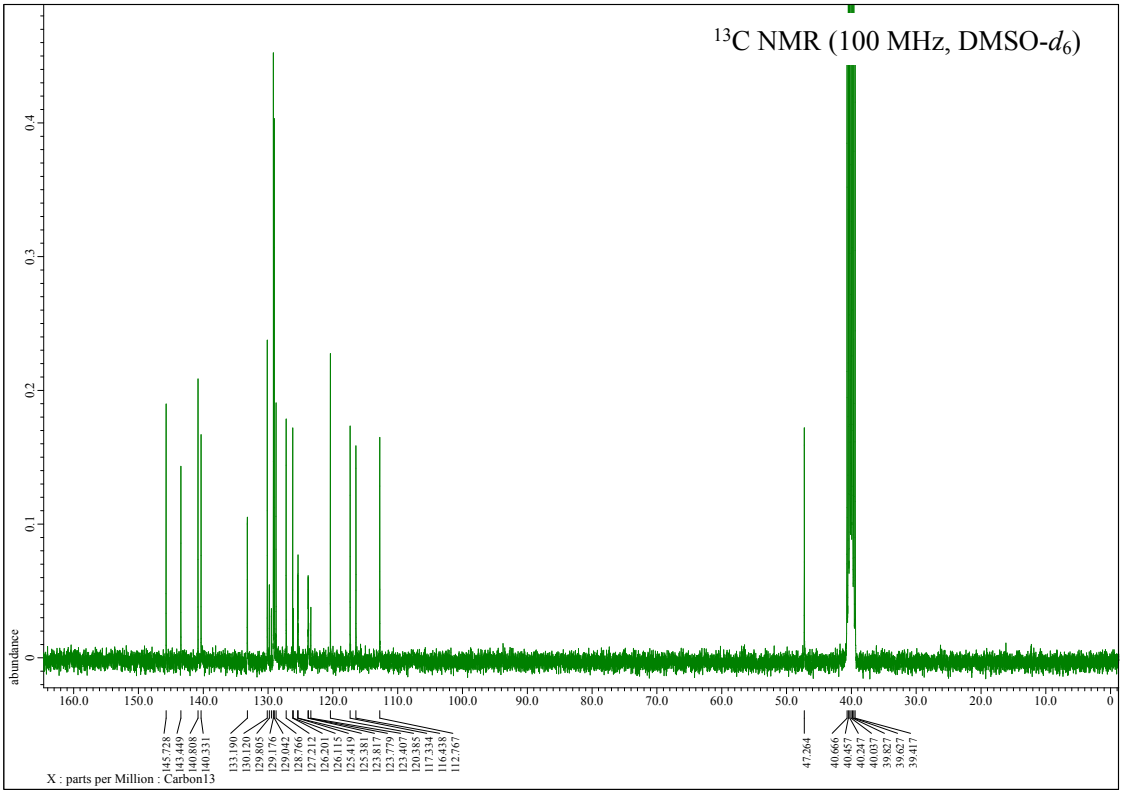
3-[(4-Chlorophenyl)(phenyl)methyl]-5-nitro-1*H*-indole **3q**



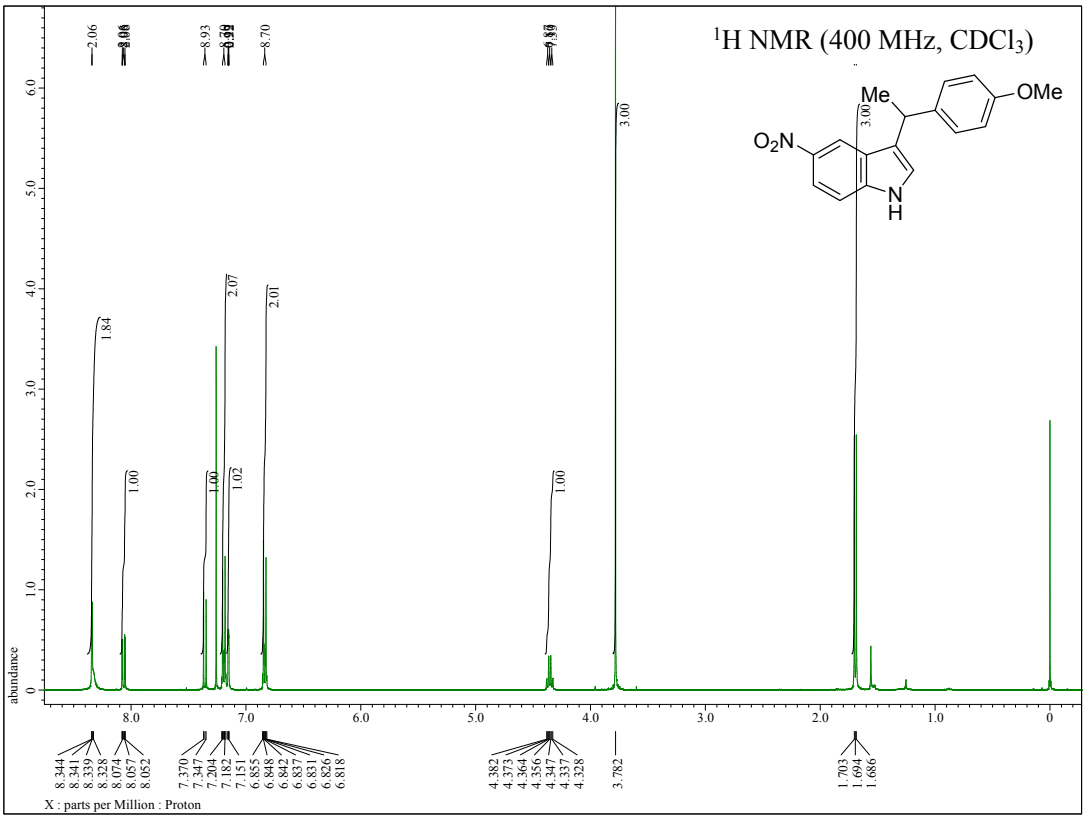


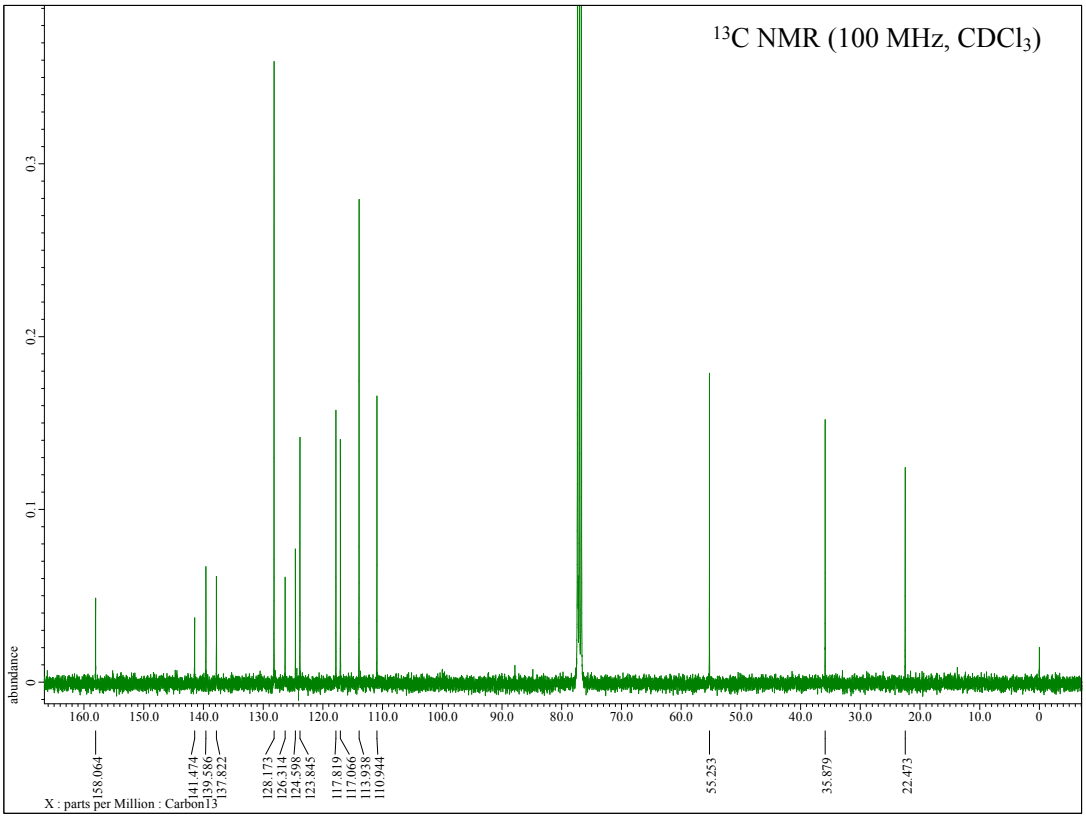
5-Nitro-3-{phenyl[3-(trifluoromethyl)phenyl]methyl}-1*H*-indole **3r**



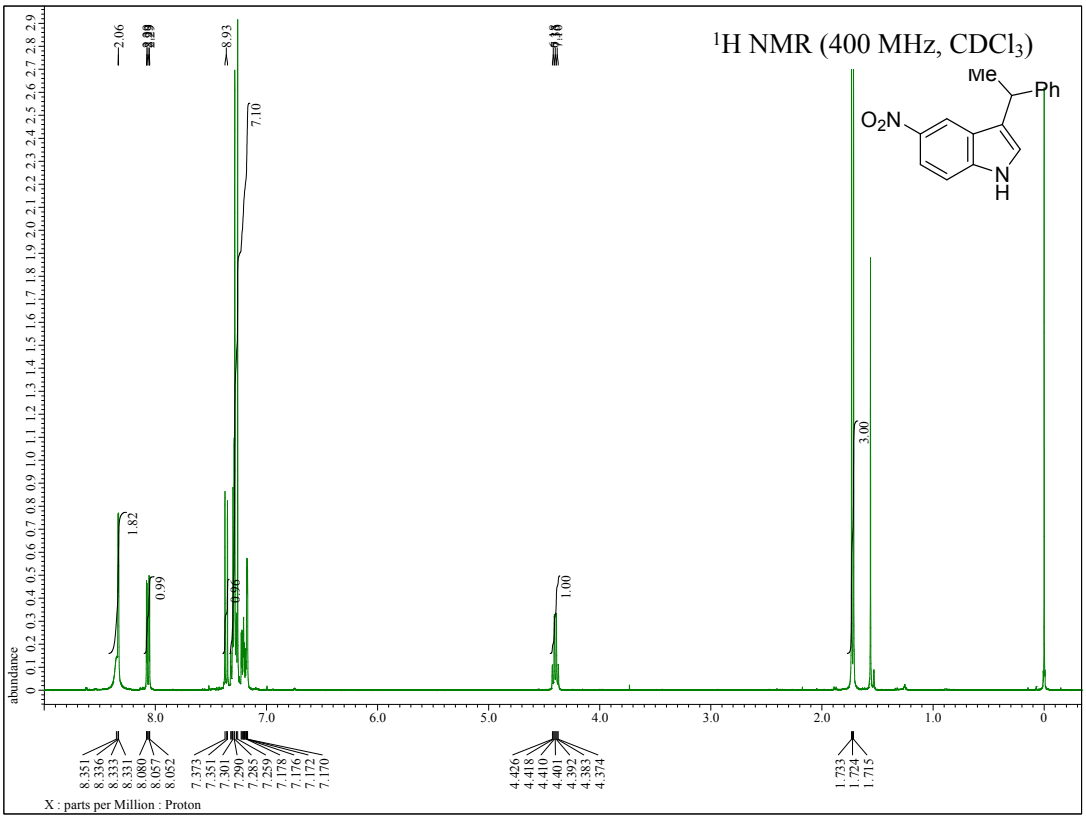


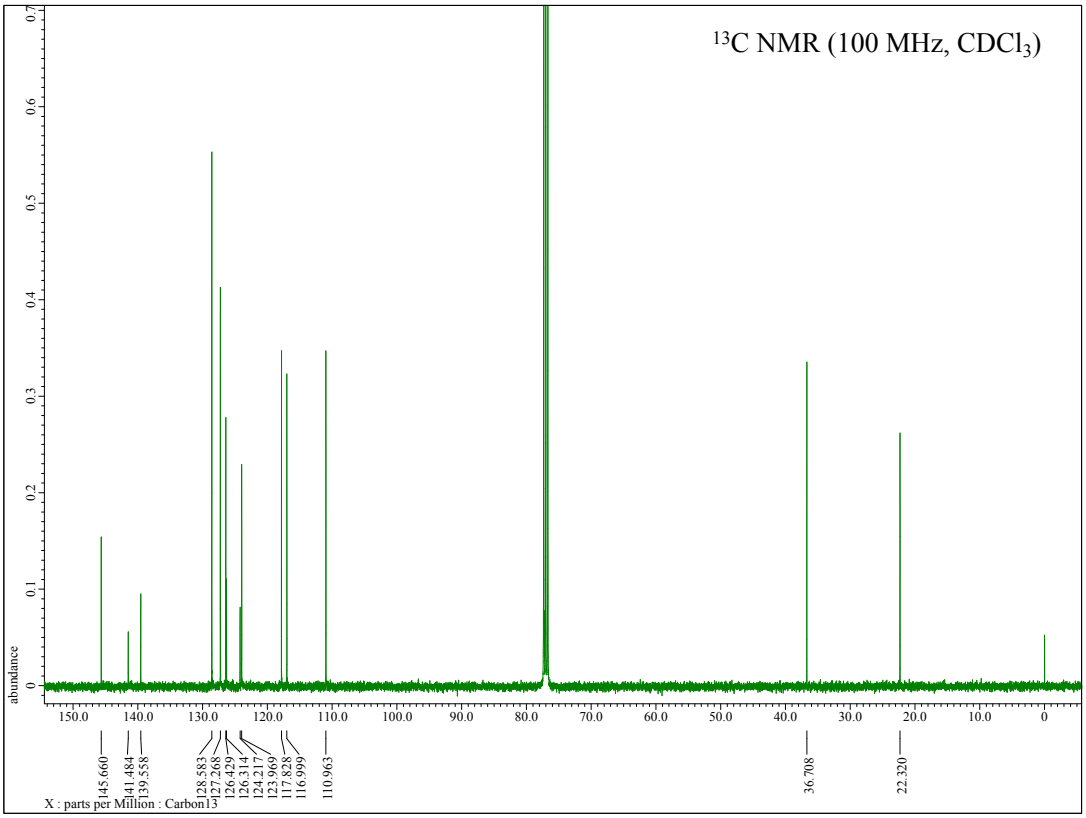
3-[1-(4-Methoxyphenyl)ethyl]-5-nitro-1*H*-indole **3s**



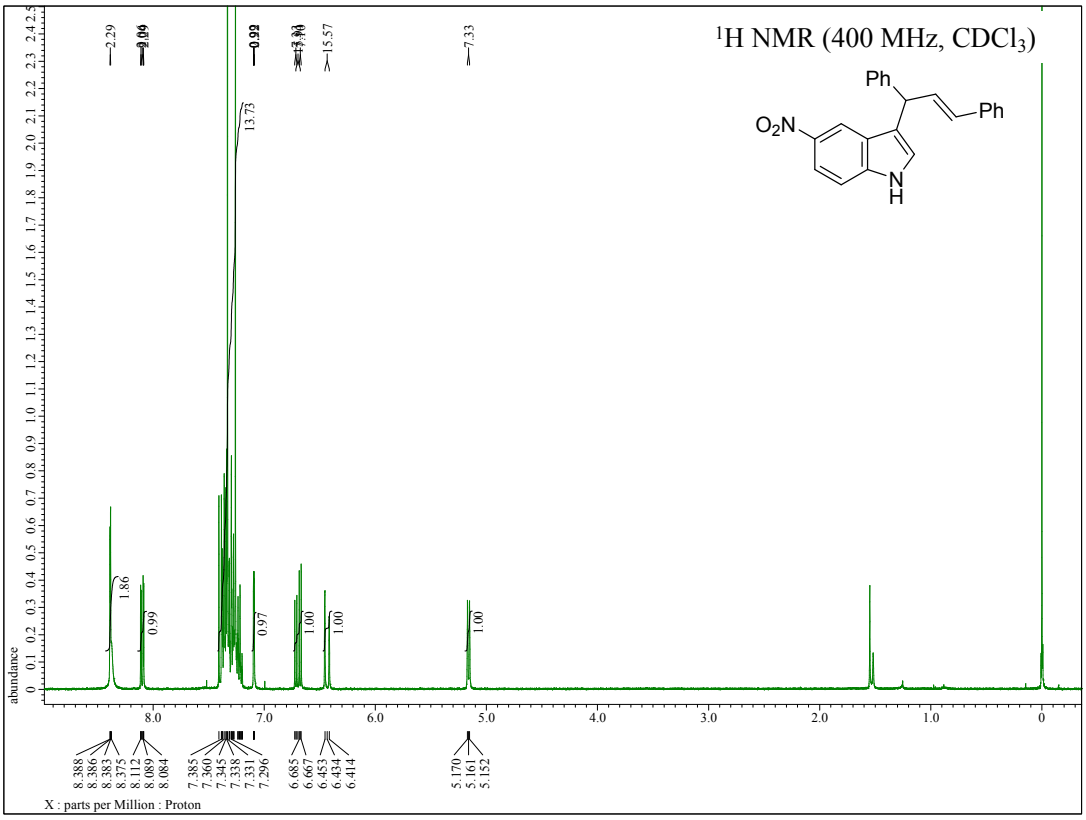


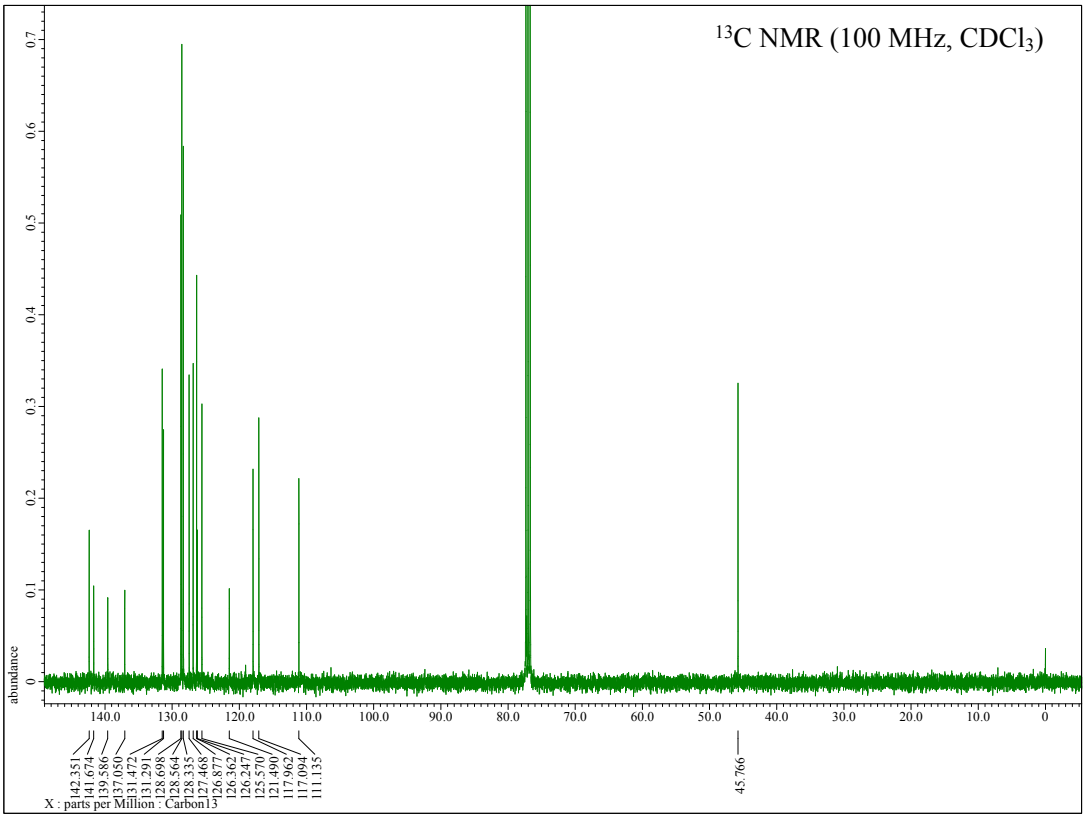
5-Nitro-3-(1-phenylethyl)-1*H*-indole **3t**





(*E*)-3-(1,3-Diphenylallyl)-5-nitro-1*H*-indole **3u**





5-Nitro-3-trityl-1*H*-indole **3v**