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Indole- and Pyrrole-BX: Bench-Stable Hypervalent Iodine Reagents for Heterocycle Umpolung

Paola Caramenti, Stefano Nicolai and Jerome Waser*

Abstract: The one-step synthesis of the bench-stable hypervalent iodine reagents IndoleBX and PyrroleBX using mild Lewis acid catalyzed conditions is reported. The new reagents are stable up to 150 °C and were applied in the C-H arylation of unactivated arenes using either rhodium or ruthenium catalysts. A broad range of heterocyclic systems of high interest for synthetic and medicinal chemistry was accessed in high yields. The developed C-H functionalization could not be achieved using reported reagents or methods, highlighting the unique reactivity of Indole- and Pyrrole-BX.

Pyrrole and indole heterocycles are omnipresent in natural and synthetic biologically active compounds and have found countless applications in the pharmaceutical and agrochemical industries.[1] Therefore, synthetic chemists have invested unceasing efforts towards their synthesis and functionalization.[2] As indoles and pyrroles are highly nucleophilic, the broad majority of functionalization methods is based on reactions with electrophiles, which limits the structural diversity of compounds in medicinal chemistry studies. In order to allow indoles and pyrroles to react with nucleophiles and discover new chemical space, an *Umpolung* of the innate reactivity of the heterocycles would be highly useful. However, accessing electrophilic indole and pyrrole synthons constitutes a formidable challenge. Most approaches rely on the substitution of the heterocycles with one or several electron-withdrawing groups or on reactive electrophilic indolyl intermediates generated *in situ*.[3] More stable halogenated indoles have been used only in cross-coupling reactions with activated partners.[4] Clearly, the development of better indole and pyrrole electrophilic synthons combining high reactivity with enhanced stability is needed.

In this context, hypervalent iodine reagents are recognized for their high reactivity, which can lead to the formal *Umpolung* of functional groups.[5] The introduction of reactive yet stable aryl iodonium salts (Scheme 1A) has led to the development of broadly applicable arylation reactions.[6] Nevertheless, there are only few reports on indole and pyrrole-based iodonium salts. Pioneering works by Neiland, Kost, Moriarty and co-workers required a multi-step procedure via a potentially explosive betaine intermediate to access NH unprotected indole iodonium salts.[7]

[a] Paola Caramenti, Dr. Stefano Nicolai and Prof. Dr. Jerome Waser
Laboratory of Catalysis and Organic Synthesis
Ecole Polytechnique Fédérale de Lausanne
EPFL SB ISIC LCSO, BCH 4306, 1015 Lausanne (CH)
Fax: (+)41 21 693 97 00
E-mail: jerome.waser@epfl.ch

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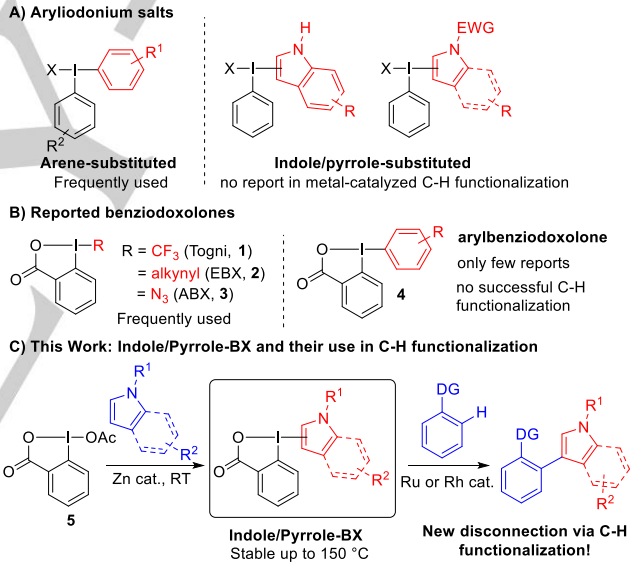
Recently, more stable indole and pyrrole iodonium salts were reported by Moriyama and co-workers[8] and Kita and co-workers[9] respectively, based on the introduction of an electron-withdrawing group on the nitrogen. The electrophilic character of these reagents was used for direct reactions with nucleophiles, such as alkyl lithium reagents,[7c] azides,[10a] amines[10b] and electron-rich arenes.[9] There is only one report on the use of indole iodonium salts involving a transition metal: the copper-catalyzed de-aromatization of indoles reported by You and co-workers.[11] This stands in stark contrast with the hundreds of transformations reported for other aryl iodonium salts,[6] and is probably due to the lower stability of indole and pyrrole iodonium salts in presence of metals and/or at higher temperature.



Scheme 1. Aryliodonium salts, benziodoxolones and Indole/Pyrrole-BX reagents.

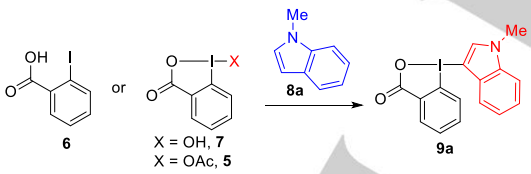
The enhanced stability of cyclic hypervalent iodine reagents, in particular those obtained from 2-iodobenzoic acid and its derivatives – the benzidoxol(on)es - has been established since several decades (Scheme 1B).[12] The use of reagents such as benziodoxolones **1**-**3** in group-transfer reactions (trifluoromethylation, alkynylation and azidation) has been investigated only more recently.[13] In the short time since their introduction, they have already had a strong impact in the fields of synthetic and medicinal chemistry. Aryl benziodoxolones **4** have also displayed enhanced stability and are easily accessible, but they have not found broad application in synthesis.[14] Indeed, in most reactions with nucleophiles, the benzoic acid group is transferred, limiting the scope of those transformations.[14c,15] There is no report on indole or pyrrole based benziodoxol(on)e

reagents, however, and the strongly acidic or oxidizing methods used for the introduction of other aryl groups cannot be used for these more sensitive heterocycles.

Herein, we report the first synthesis of pyrrole- and indole-based benziodoxolone reagents in one step from the heterocycles, based on a mild zinc-catalyzed direct iodonium transfer from acetoxy benziodoxolone (**5**) (Scheme 1C). The new reagents are air- moisture- and thermally stable. They were applied in the directed *ortho* C-H functionalization of arenes using rhodium and ruthenium catalysts, resulting in bond formations that could not be achieved using reported methods and reagents.

To access the targeted Indole- and Pyrrole-BX reagents, we first applied recently reported methods for aryl benziodoxolone synthesis based on the oxidation of iodobenzoic acid (**6**) followed by reaction with N-methyl indole (**8a**) in presence of triflic or sulfuric acid (Table 1, entries 1-2).[14] However, only decomposition of the indole was observed. To avoid the use of oxidants, iodine(III) precursors were then examined. Starting from hydroxy benziodoxolone **7** with trimethylsilyl triflate (TMSOTf) as activating agent,[16] decomposition was still occurring (entry 3). If a lower amount of TMSOTf was used, no conversion was observed (entry 4). A promising result was obtained with acetoxy benziodoxolone **5** as precursor: the desired indole-BX could be obtained in 16% yield using 20 mol% of TMSOTf (entries 5 and 6).[17] This compound could be purified by silica gel column chromatography and was thermally stable up to 150 °C.[18] No conversion was observed in absence of TMSOTf (entry 7). Better results were obtained with $Zn(OTf)_2$ and $Cu(OTf)_2$ as Lewis acids (entries 8 and 9), giving **9a** in 36% yield. Changing to dichloromethane as solvent with $Zn(OTf)_2$ as catalyst, **9a** was obtained in 97% yield with complete C3 selectivity (entry 10). This synthesis could be easily scaled up to give **9a** in 87% yield on the 10 mmol scale (entry 11).

Table 1. Optimization of the synthesis of Indole-BX **9a**.



Entry	Iodine precursor	Reaction Conditions[a]	Yield[b] (%)
1	**6**	*m*CPBA, TfOH, CH_2Cl_2, then NH_3[14b]	<5[c]
2	**6**	Oxone, H_2SO_4, CH_2Cl_2, then $NaHCO_3$[14c]	<5[c]
3	**7**	1 equiv TMSOTf, CH_3CN, then pyridine	<5[c]
4	**7**	20 mol% TMSOTf, CH_3CN	<5[d]
5	**5**	1 equiv TMSOTf, Et_2O	<5[c]
6	**5**	20 mol% TMSOTf, Et_2O	16
7	**5**	Et_2O	<5[d]
8	**5**	20 mol% $Zn(OTf)_2$, Et_2O	36
9	**5**	20 mol% $Cu(OTf)_2$, Et_2O	36[c]
10	**5**	20 mol% $Zn(OTf)_2$, CH_2Cl_2	97
11	**5**	20 mol% $Zn(OTf)_2$, CH_2Cl_2	87[e]

[a] Reactions were performed on 0.10 mmol scale with 1.1 equiv of iodine precursor. [b] Isolated yield after purification by column chromatography. [c] Decomposition of N-methylindole (**8a**) was observed. [d] No conversion of **7** or **8a**. [e] Reaction performed on 10 mmol scale.

Free NH IndoleBX **9b** could be also synthesized in 78% yield starting from N-silylated indole (Figure 1). The hypervalent structure of this compound was confirmed by X-ray analysis.[18] Different alkyl groups on the nitrogen were well tolerated (**9c-e**). Reagent **9f** bearing a C2-substituted indole was also obtained in good yield, but no conversion was observed with C3-substitution. Arenes bearing ethers (**9g**), halogens (**9h-j**) and a sensitive boronic ester (**9k**) could also be used. Reagent **9l** derived from a less reactive azaindole was still isolated in 30% yield. PyrroleBX **9m-q** were also successfully synthesized. When starting from *N*-silylated pyrrole, a complete C3 regioselectivity was achieved (**9m**). When methyl-and benzyl-pyrrole where used as substrates, mixtures of separable C2:C3 functionalized reagents were obtained. The availability of both isomers in pure form opened the way for the selective synthesis of C2- or C3- functionalized pyrroles by reaction with nucleophiles. The synthesis of new pyrrole and indole electrophilic synthons is especially important, as none of the currently available reagents can be used in C-H functionalization reactions, in contrast to other classes of heterocycles. Nevertheless, the use of other electron-rich aromatic compounds could also be envisaged. Indeed, carbazole-BX **9r**, thiophene-BX **9s** and furan-BX **9t** were also obtained in low to moderate yields without further optimization.

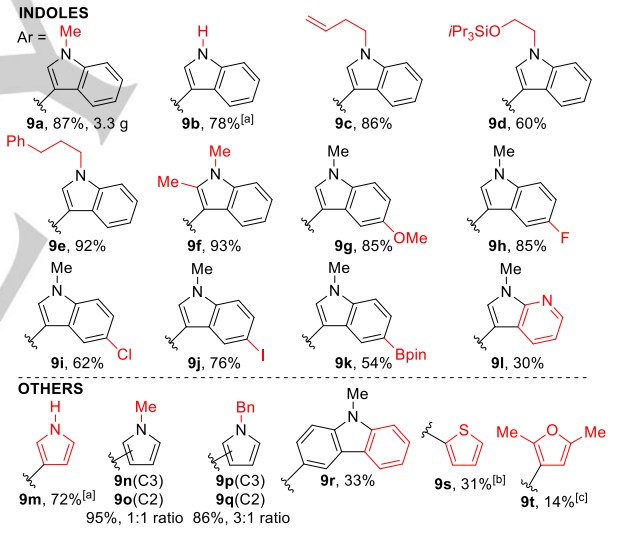
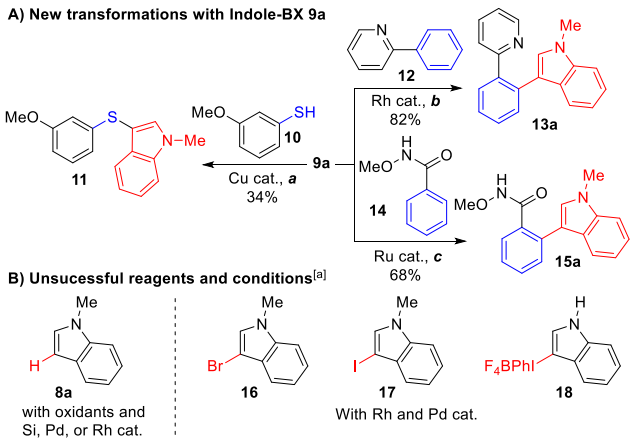


Figure 1. Scope of heteroaromatic benziodoxole reagents. Reaction conditions: 1.00 mmol heterocycle, 1.10 mmol **5**, 0.200 mmol $Zn(OTf)_2$, 0.05 M in DCM, RT, open air. Isolated yields. [a] $Sc(OTf)_3$ was used starting from N-TBS heterocycle. [b] $Sc(OTf)_3$ was used. [c] $In(OTf)_3$ was used.

Preliminary investigations showed that the reactivity of indole-BX **9a** differed from the one of both aryliodonium salts and EBX reagents (Scheme 2). The reaction of EBX reagents and aryliodonium salts with thiols, alcohols and stabilized carbon nucleophiles in presence of base is well established,[19] but no reaction occurred with **9a**. In the case of thiol **10**, a moderate yield of thiol indolation product **11** could be obtained in presence of a copper catalyst (Scheme 2A). Palladium-catalyzed C-H bond arylation,[6a,20] was also unsuccessful. In contrast, highly efficient C-H functionalizations could be developed using either rhodium-

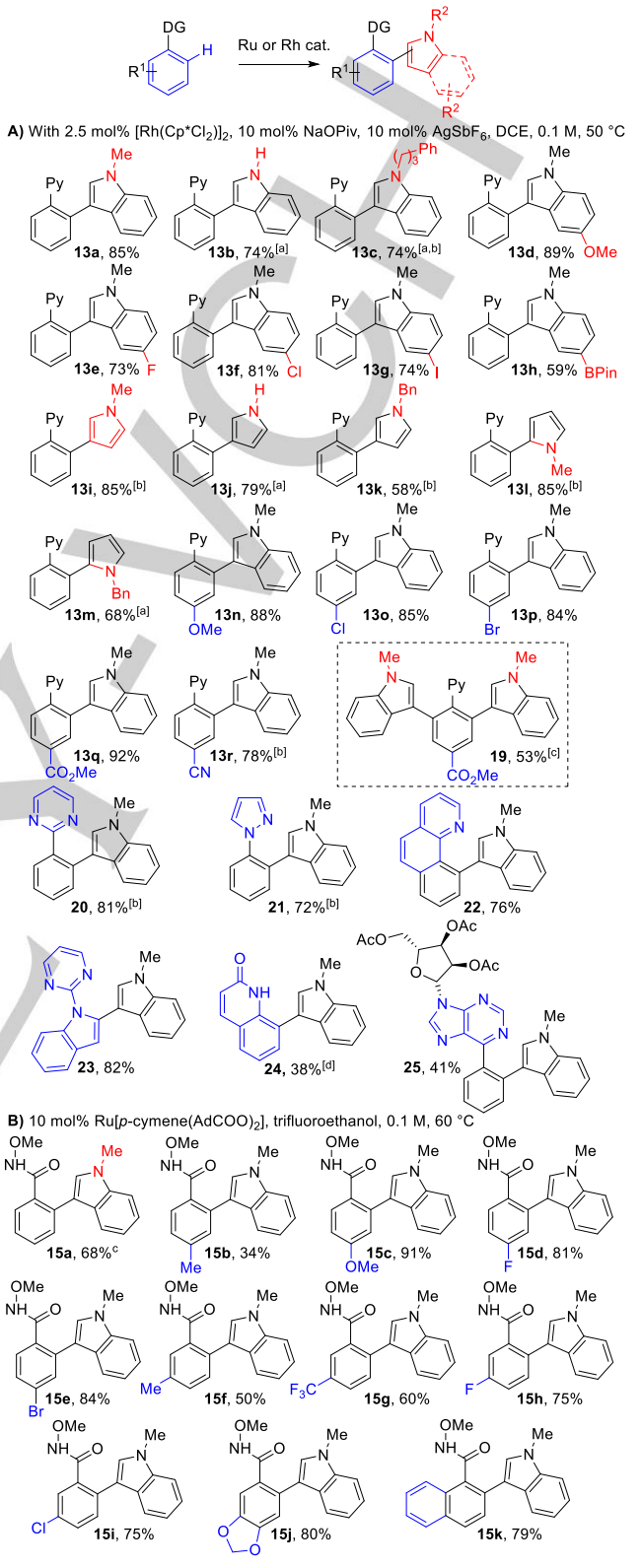
or ruthenium catalysts.[21] Importantly, complete and selective transfer of the indole was obtained to give **13a** and **15a**, with no coupling of benzoic acid.



Scheme 2. Preliminary studies of the reactivity of Indole-BX **9a**. Reaction conditions: a) **10**, 20 mol% CuOTf•C_6H_6, CH_2Cl_2, RT; b) **12**, 2.5 mol% $[Rh(Cp^*Cl_2)]_2$, 10 mol% NaOPiv, 10 mol% $AgSbF_6$, DCE, 0.1 M, 50 °C; c) **14**, 10 mol% Ru[*p*-cymene(AdCOO)$_2$],[22] trifluoroethanol, 0.1 M, 60 °C. [a] See supporting Information for detailed reaction conditions.

The latter results are especially interesting, as the introduction of an indole on a benzene C-H bond in *ortho* position to a pyridine or a benzamide has never been reported. This is surprising, as ortho C-H bond functionalization in arenes is now considered as a mature field.[23] When considering the high importance of indole and pyrrole heterocycles in synthetic and medicinal chemistry, realizing such a transformation would be an important breakthrough in the field. We wondered therefore if established methods for the introduction of indoles onto other types of C-H bonds could be used to access products **13a** and **15a**. However, when reported methods for C-H indolation based on oxidative C-H/C-H couplings[24-26] with indole **8a** or C-H functionalization with electrophilic indoles **16**, **17** and **18**,[18] were examined, compounds **13a** and **15a** could not be obtained (Scheme 2B). Therefore, the discovery of Indole-BX reagents allowed new C-H functionalizations which were not possible before.

The scope of the rhodium-catalyzed C-H functionalization was then examined (Scheme 3A). Indoles **13b** and **13c** bearing either a free NH group or an alkyl chain were obtained in good yield. Ethers, halogens and a sensitive boronic ester were well tolerated on the benzene ring of the indole reagent (**13d-h**). The regioselective synthesis of both C2 and C3 substituted pyrroles was possible (**13i-m**).[27] Methoxy, halogens, esters and cyanides functional groups could be present on the arene substrate (**13n-r**). Diarylation was also possible using an excess of reagent **8a** to give product **19**. Good results were also obtained with other heterocyclic directing groups such as pyrimidine (**20**) or pyrazole (**21**). Benzoquinoline **22** and pyrimidine-substituted indole **23** were also formed in good yield. When quinoline *N*-oxide was used as the starting material, quinolone **24** was obtained in 38% yield. The developed C-H arylation could also be applied to a purine-based nucleoside to give product **25**.



Scheme 3. Scope of the Rh- and Ru- catalyzed C-H Functionalizations. Reactions were performed on 0.30 mmol scale. [a] 0.1 M in DCE:MeOH (1:1 ratio). [b] at 80 °C. [c] Using 0.660 mmol **8a**. [d] at 100 °C.

The thermal stability of the developed reagents was essential to achieve a broad scope, as several substrates required higher temperature to reach useful conversion (80 °C for products **13c,k,l,r**, **20** and **21**, and 100 °C for compound **24**). Preliminary investigations of the scope of the ruthenium-catalyzed C-H functionalization were then conducted (Scheme 3B). The benzamide directing group is attractive, as it can be easily modified or removed. Alkyl groups, ethers, trifluoromethyl groups and halogens were all well tolerated both in *para* and *meta* position to the amide (**15a-i**). Tetrasubstituted arene **15j** and naphthyl derivatives **15k** were also obtained in good yields.

In conclusion, we have reported the first synthesis of indole- and pyrrole substituted benziodoxolone reagents. Indole- and Pyrrole-BX were synthesized in one-step from the heterocycles under mild Lewis acid catalyzed conditions and are thermally stable up to 150 °C. These new reagents can be used for the Rh- and Ru-ortho C-H functionalization of arenes using heterocyclic and benzamide directing groups, a transformation that could not be realized using previously reported methods. Many of the obtained products are new combinations of privileged (hetero)arenes, covering interesting chemical space for medicinal chemistry. The availability of stable electrophilic indole and pyrrole synthons is expected to lead to broad applications in synthetic and medicinal chemistry.

Acknowledgements

This work is supported by the Swiss National Science Foundation (No. 200021_159920), the European Research Council (ERC Starting Grant 334840) and the COST action CA15106 (C-H Activation in Organic Synthesis, CHAOS). We thank Dr R. Scopelliti and Dr F. F. Tirani from ISIC at EPFL for X-ray analysis, and Dr. Fides Benfatti and Ms. Marylene Stempien from Syngenta Crop Science for DSC experiments. Mr. Elliott Le Du from EPFL is thanked for performing the thiol indolation experiment.

Keywords: Indoles • Hypervalent Iodine • Umpolung • C-H Functionalization • Heterocycles

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[27] The rhodium-catalyzed C-H functionalization was not successful with reagents **9r-t**.

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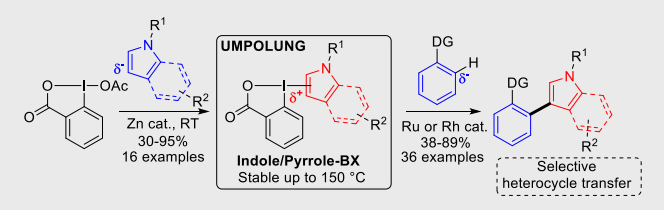

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Indole- and Pyrrole-BX: Bench-Stable Hypervalent Iodine Reagent for Heterocycle Umpolung

Electrophilic Indoles/Pyrroles: The first synthesis of indole and pyrrole-derived benziodoxole reagents in one step from the heterocycles is reported. The new Indole- and Pyrrole- BX reagents are stable up to 150 °C and can be used for selective heterocycle transfer onto the C-H bonds of arenes *ortho* to directing groups by using rhodium or ruthenium catalysts.

Supporting Information

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1. Materials and Methods.

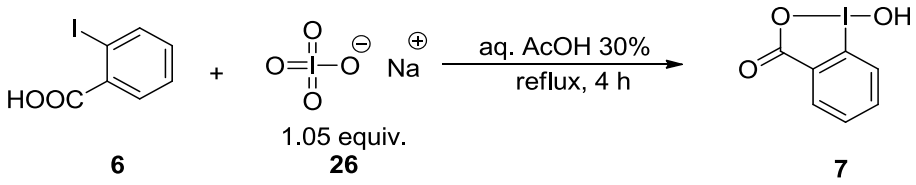
All reactions were carried out in oven dried glassware under an atmosphere of nitrogen, unless stated otherwise. For quantitative flash chromatography, technical grade solvents were used. For flash chromatography for analysis, HPLC grade solvents from Sigma-Aldrich were used. THF, Et_2O, CH_3CN, toluene, hexane and CH_2Cl_2 were dried by passage over activated alumina under nitrogen atmosphere (H_2O content < 10 ppm, *Karl-Fischer* titration). The solvents were degassed through Freeze-Pump-Thaw method when mentioned. All chemicals were purchased from Acros, Aldrich, Fluka, VWR, Aplichem, or Merck and used as such unless otherwise stated. Chromatographic purification was performed as flash chromatography using Macherey-Nagel silica 40-63, 60 Å, with the solvents indicated as eluent under 0.1-0.5 bar pressure. TLC was performed on Merck silica gel 60 F_{254} TLC glass plates or aluminium plates and visualized with UV light, permanganate stain, CAN stain, or Anisaldehyde stain. Melting points were measured on a Büchi B-540 melting point apparatus using open glass capillaries, the data is uncorrected. ^{1}H-NMR spectra were recorded on a Brucker DPX-400 400 MHz spectrometer in $CDCl_3$, DMSO-d_6 CD_3OD, C_6D_6 and CD_2Cl_2, all signals are reported in ppm with the internal chloroform signal at 7.26 ppm, the internal DMSO signal at 2.50 ppm the internal methanol signal at 3.30 ppm, the internal dichloromethane signal at 5.30 ppm as standard. The data is being reported as (s = singlet, d = doublet, t = triplet, q = quadruplet, qi = quintet, m = multiplet or unresolved, br = broad signal, app = apparent, coupling constant(s) in Hz, integration, interpretation).^{13}C-NMR spectra were recorded with ^{1}H-decoupling on a Brucker DPX-400 100 MHz spectrometer in $CDCl_3$, DMSO-d_6, CD_3OD or CD_2Cl_2, all signals are reported in ppm with the internal chloroform signal at 77.0 ppm, the internal DMSO signal at 39.5 ppm, the internal methanol signal at 49.0 ppm and the internal dichloromethane signal at 54.0 ppm as standard. Infrared spectra were recorded on a JASCO FT-IR B4100 spectrophotometer with an ATR PRO410-S and a ZnSe prisma and are reported as cm^{-1} (w = weak, m = medium, s = strong, br = broad). High resolution mass spectrometric measurements were performed by the mass spectrometry service of ISIC at the EPFL on a MICROMASS (ESI) Q-TOF Ultima API.

2. Preparation of PyrroleBXs and IndoleBXs.

The synthesis of the precursors for HeterocyclicBX reagents (**7** and **5**) **9a-9r** had been already described before. [1,2] The procedures here reported are taken from the cited publications to facilitate reproduction of the results by having all the data in the same file.

2.1 Preparation of Starting Materials for PyrroleBXs and IndoleBXs.

1-Hydroxy-1,2-benziodoxol-3-(1H)-one (27)

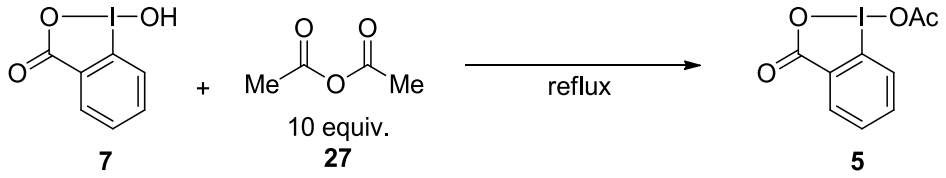


Following a reported procedure, $NaIO_4$ **26** (7.24 g, 33.8 mmol, 1.05 equiv) and 2-iodobenzoic acid **6** (8.00 g, 32.2 mmol, 1.00 equiv) were suspended in 30% (v/v) aq. AcOH (48 mL). The mixture was vigorously stirred and refluxed for 4 h. The reaction mixture was then diluted with cold water (180 mL) and allowed to cool to room temperature, protecting it from light. After 1 h, the crude product was collected by filtration, washed on the filter with ice water (3 x 20 mL) and acetone (3 x 20 mL), and air-dried in the dark to give the pure product **7** (8.30 g, 31.0 mmol, 98% yield) as a colorless solid. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.02 (dd, *J* = 7.7, 1.4 Hz, 1H, Ar*H*), 7.97 (m, 1H, Ar*H*), 7.85 (dd, *J* = 8.2, 0.7 Hz, 1H, Ar*H*), 7.71 (td, *J* = 7.6, 1.2 Hz, 1H, Ar*H*). **^{13}C NMR** (100 MHz, $(CD_3)_2SO$): δ 167.7, 134.5, 131.5, 131.1, 130.4, 126.3, 120.4. **IR** ν 3083 (w), 3060 (w), 2867 (w), 2402 (w), 1601 (m), 1585 (m), 1564 (m), 1440 (m), 1338 (s), 1302 (m), 1148 (m), 1018 (w), 834 (m), 798 (w), 740 (s), 694 (s), 674 (m), 649 (m). NMR values are in accordance with the data reported in literature.[1]

1-Acetoxy-1,2-benziodoxol-3-(1*H*)-one (**4**)

[1] D. P. Hari, J. Waser, *J. Am. Chem. Soc.* **2016**, *138*, 2190–2193.

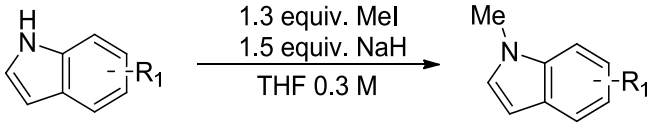
[2] G. L. Tolnai, S. Ganss, J. P. Brand, J. Waser, *Org. Lett.* **2013**, *15*, 112–115.



7 **27** **5**

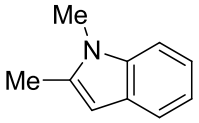
Following a reported procedure,[3] 1-hydroxy-1,2-benziodoxol-3-(1*H*)-one **7**, 10.3 g, 39.1 mmol, 1.00 equiv.) was suspended in acetic anhydride **27** (35 mL) and heated to reflux for 30 minutes. The resulting clear, slightly yellow solution was slowly let to warm up to room temperature and then cooled to 0 °C for 30 minutes. The white suspension was filtered and the filtrate was again cooled to 0 °C for 30 minutes. The suspension was once again filtered and the combined two batches of solid product were washed with hexane (2 x 20 mL) and dried *in vacuo* to afford 1-Acetoxy-1,2-benziodoxol-3-(1*H*)-one **5** (10.8 g, 35.3 mmol, 90%) as a white solid. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.24 (dd, *J* = 7.6, 1.6 Hz, 1H, Ar*H*), 8.00 (dd, *J* = 8.3, 1.0 Hz, 1H, Ar*H*), 7.92 (ddd, *J* = 8.4, 7.2, 1.6 Hz, 1H, Ar*H*), 7.71 (td, *J* = 7.3, 1.1 Hz, 1H, Ar*H*), 2.25 (s, 3 H, COCH_3). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 176.5, 168.2, 136.2, 133.3, 131.4, 129.4, 129.1, 118.4, 20.4. NMR values are in accordance with the data reported in literature.[4]

General Procedure GP1 for the N-Methylation of Indoles.

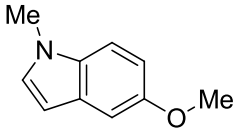


The corresponding indole (1.00 - 5.00 mmol, 1.00 equiv.) was dissolved in dry THF (0.3 M). Sodium hydride (60% suspension in mineral oil; 1.50 equiv.) was slowly added under N_2 flow at 0 °C. After being stirred at 0 °C for 15 min,the reaction mixture was allowed to warm to r.t for 1.5 h. It was then cooled back to 0 °C and methyl iodide (1.30 equiv.) was added. The mixture was warmed to r.t. and stirred overnight. After cooling again to 0° C, the reaction was quenched with water (10 mL), extracted with Et_2O (3 x 10 mL), the combined organic layers were dried over $MgSO_4$, and the solvent removed under reduced pressure. The resulting crude product was purified via flash column chromatography (Pentane:EtOAc 9:1-4:1), to give the desired N-methylated indole**.**

[3] A. T. Parsons, S. L. Buchwald, *Angew. Chem. Int. Ed.* **2011**, *50*, 9120–9123
[4] P. Eisenberger, S. Gischig, A. Togni, *Chem. – Eur. J.* **2006**, *12*, 2579–2586.



28



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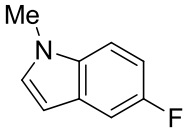
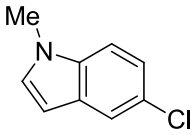
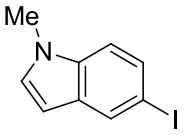


30

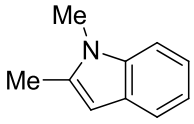


31



32

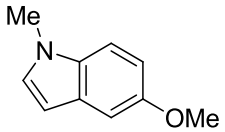
1,2-Dimethyl-1*H*-indole (28)



28

Starting from commercially available 2-methylindole (656 mg, 5.00 mmol), 1,2-dimethyl-1H-indole **28** (683 mg, 4.70 mmol, 94% yield) was obtained as an off-white solid. **^{1}H NMR** (400 MHz $CDCl_3$) δ 7.69 (d, *J* = 7.8 Hz, 1H, Ar*H*), 7.41 (dd, *J* = 8.1, 1.0 Hz, Ar*H*), 7.32 (m, 1H, Ar*H*), 7.24 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H, Ar*H*), 6.42 (s, 1H, NC(CH_3)C*H*), 3.79 (s, 3H, N*CH_3*), 2.57 (d, *J* = 1.0 Hz, 3H, NC*CH_3*). **^{13}C NMR** (125 MHz, $CDCl_3$) *δ* 138.1, 136.9, 128.1, 120.6, 119.8, 119.4, 108.8, 99.7, 29.5, 12.9. **IR** ν (neat) 3050 (w), 3020 (w), 2970 (m), 1610 (w), 1400 (s), 1340 (m), 1240 (m), 930 (m), 910 (w), 780 (m), 750 (m), 730 (s). ^{1}H NMR values are in accordance with the data reported in literature.[4]

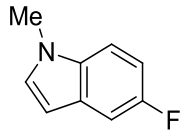
5-Methoxy-1-methyl-1*H*-indole (29)



29

Starting from commercially available 5-methoxy-1*H*-indole (736 mg, 5.00 mmol), 5-methoxy-1-methyl-1*H*-indole **29** (730 mg, 4.53 mmol, 91% yield) was obtained as a colorless crystalline solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ δ 7.30 (d, 1H, *J* = 8.5 Hz, Ar*H*) 7.13 (s, 1H, Ar*H*), 7.05 (s, 1 H, Ar*H*), 6.92 (d, 1H, *J* = 8.8 Hz, Ar*H*), 6.43 (d, 1H, *J* = 1.0 Hz, Ar*H*), 3.90 (s, 3H, N*Me*), 3.80 (s, 3H, O*Me*). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.0, 132.2, 129.3, 128.8, 111.9, 109.9, 102.5, 100.4, 55.9, 33.0. **IR** ν 2952 (w), 2918 (w), 2834 (w), 1622 (m), 1608 (w), 1577 (w), 1496 (s), 1459 (w), 1450 (m), 1449 (m), 1421 (s), 1347 (w), 1293 (w), 1243 (s), 1191 (m), 1152 (s), 1102 (w), 1026 (m), 942 (w), 855 (m), 845 (w), 805 (s).

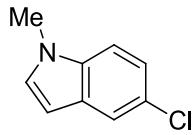
5-Fluoro-1-methyl-1*H*-indole (30)



30

Starting from commercially available 5-fluoro-1*H*-indole (676 mg, 5.00 mmol), 5-fluoro-1-methyl-1*H*-indole **30** (683 mg, 4.58 mmol, 92% yield) was obtained as a colorless solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 9.7, 2.4 Hz, 1H, Ar*H*), 7.26 (m, 1H, Ar*H*), 7.12 (d, *J* = 3.1 Hz, 1H, Ar*H*), 7.01 (dt, *J* = 9.1, 2 Hz, 1H, Ar*H*), 6.48 (dd, *J* = 3.1, 0.7 Hz, 1H, Ar*H*). 3.81 (s, 3H, N*CH₃*) **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.0 (d, *J*-F_6 = 232 Hz), 133.4, 130.4, 128.7 (d, *J*-F_6 = 10 Hz), 109.9 (d, *J*-F_6 = 15 Hz), 109.8, 105.5 (d, *J*-F_6 = 23 Hz), 100.8 (d, *J*-F_6 = 5.0 Hz), 33.1. **IR** 3104 (w), 2946 (w), 2922 (w), 2907 (w), 2887 (w), 2362 (w), 2343 (w), 1626 (w), 1576 (w), 1514 (m), 1492 (s), 1449 (m), 1423 (m), 1340 (m), 1283 (m), 1238 (s), 1228 (s), 1140 (m), 1129 (m), 1122 (m), 1100 (m), 1081 (m), 1013 (w), 949 (m), 859 (m), 811 (s).

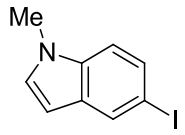
5-Chloro-1-methyl-1*H*-indole (31)



31

Starting from commercially available 5-chloro-1*H*-indole (758 mg, 5.00 mmol), 5-chloro-1-methyl-1*H*-indole **31** (800 mg, 4.83 mmol, 97% yield) was obtained as a colorless solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 2.1 Hz, 1H, Ar*H*), 7.30 – 7.19 (m, 2H, Ar*H*), 7.10 (d, *J* = 3.1 Hz, 1H, Ar*H*), 6.47 (dd, *J* = 3.1, 0.7 Hz, 1H, Ar*H*), 3.80 (s, 3H, N*CH₃*). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.1, 130.1, 130.1, 125.1, 121.8, 120.2, 110.2, 100.6, 33.1. **IR** ν 3102 (w), 2943 (w), 2913 (w), 2881 (w), 2817 (w), 1567 (w), 1513 (m), 1475 (s), 1441 (m), 1421 (s), 1379 (w), 1331 (m), 1278 (s), 1241 (s), 1199 (m), 1146 (m), 1106 (w), 1082 (m), 1063 (s), 1009 (m), 909 (m), 870 (m), 869 (m).

5-Iodo-1*H*-indole (32)

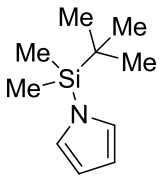


32

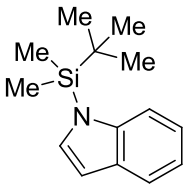
Starting from commercially available 5-iodo-1*H*-indole (257 mg, 1.00 mmol), 5-iodo-1-methyl-1*H*-indole **32** (380 mg, 0.755 mmol, 76% yield) was obtained as a colorless solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (s, 1 H, Ar*H*), 7.49 (d, *J* = 8.6 Hz, 1H, Ar*H*), 7.13 (d, *J* = 8.6 Hz, 1H, Ar*H*), 7.04 (s, 1H, Ar*H*), 6.43 (s, 1H, Ar*H*), 3.80 (s, 3H, N*CH₃*). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.8, 131.0, 129.8, 129.7, 129.6, 111.3, 100.3,

82.9, 33.0. **IR** ν 3093 (w), 3053 (w), 2940 (w), 2919 (w), 2886 (w), 2876 (w), 2856 (w), 1557 (m), 1510 (s), 1473 (s), 1432 (m), 1420 (s), 1379 (w), 1329 (m), 1277 (s), 1242 (s), 1193 (w), 1151 (w), 1103 (m), 1079 (m), 1045 (w), 1007 (m), 888 (s), 868 (m).

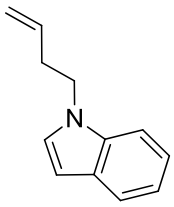
N-Functionalized Indoles



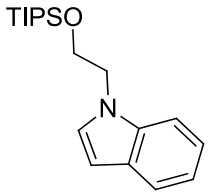
35



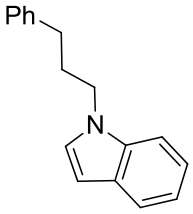
36



37

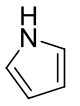


40

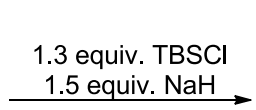


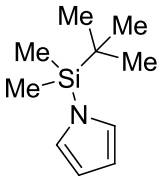
41

1-(*1-(tert*-Butyldimethylsilyl)-1*H*-pyrrole (35)



33





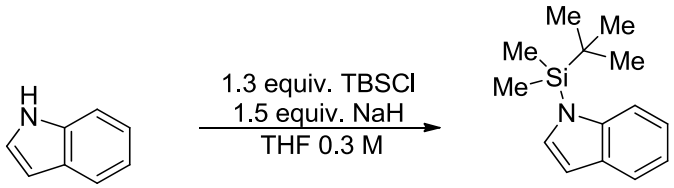
35

Following a reported procedure,[5] commercially available 1*H*-pyrrole **33** (700 µl, 10.0 mmol) was dissolved in dry THF (30 ml, 0.3 M). Sodium hydride (60% suspension in mineral oil; 600 mg, 15.0 mmol, 1.50 equiv.) was slowly added under N_2 flow at 0 °C. After being stirred at 0°C for 15

[5] A. F. G. Maier, S. Tussing, T. Schneider, U. Flörke, Z.-W. Qu, S. Grimme, J. Paradies, *Angew. Chem. Int. Ed.* **2016**, *55*, 12219–12223.

min, the reaction mixture was allowed to warm to r.t for 1.50 h. Then it was cooled back to 0°C and *tert*-butylchlorodimethylsilane (1.96 g, 13.0 mmol, 1.30 equiv.) was added. The mixture was warmed to r.t. and stirred overnight. The reaction was quenched by addition of water (10 mL) at 0°C. The aqueous layer was extracted with Et_2O (3 x 10 mL), the combined organic layers were dried over $MgSO_4$, and the solvent was removed under reduced pressure. The crude product was purified via flash column chromatography (Pentane:EtOAc 8:1), to give the desired 1-(*tert*-butyldimethylsilyl)-1*H*-pyrrole **35** (1.30 g, 7.17 mmol, 72% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.86 – 6.62 (m, 2H, Ar*H*), 6.39 – 6.21 (m, 2H, Ar*H*), 0.86 (s, 9H, SiC(*CH_3)$_3$*), 0.41 (s, 6H, Si*$(CH_3)_2$*). **IR** ν 3100 (w), 2956 (m), 2931 (m), 2858 (m), 1707 (w), 1473 (m), 1364 (w), 1259 (s), 1222 (w), 1190 (s), 1084 (s), 1048 (s), 1008 (w), 942 (w), 839 (s). ^{1}H NMR values are in accordance with the data reported in literature.[6]

1-(*tert*-Butyldimethylsilyl)-1*H*-Indole (36)



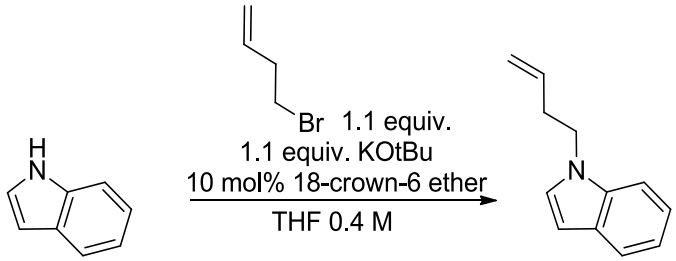
34 **36**

Following a reported procedure,[7] commercially available 1*H*-indole **34** (586 mg, 5.00 mmol) was dissolved in dry THF (10 mL, 0.5 M). Sodium hydride (60% suspension in mineral oil; 300 mg, 7.50 mmol, 1.50 equiv.) was slowly added under N_2 atmosphere at 0 °C. After being stirred at 0 °C for 15 min, the reaction mixture was allowed to warm to r.t for 1.5 h. Then it was cooled back to 0 °C and *tert*-butylchlorodimethylsilane (980 mg, 6.50 mmol, 1.30 equiv.) was added. The mixture was warmed to r.t. and stirred overnight. After cooling again to 0 °C, the reaction was quenched with water (10 mL), extracted with Et_2O (3 x 10 mL), the combined organic layers were dried over $MgSO_4$, and the solvent was removed under reduced pressure. The residue was purified via flash column chromatography (Pentane:EtOAc 4:1), to give the desired 1-(*tert*-butyldimethylsilyl)-1*H*-indole **36** (869 mg, 3.76 mmol, 75% yield). **^{1}H NMR** (400 MHz, $CDCl_3$)

[6] G. Simchen, M. W. Majchrzak, *Tetrahedron Lett.* **1985**, *26*, 5035–5036.
[7] S. Islam, I. Larrosa, *Chem. – Eur. J.* **2013**, *19*, 15093–15096

δ 7.79 (m, 1H, Ar*H*), 7.72 (dt, J = 8.2, 1.1 Hz, 1H, Ar*H*), 7.37 (d, *J* = 3.2 Hz, 1H, Ar*H*), 7.32 (ddd, *J* = 8.3, 7.0, 1.6 Hz, 1H, Ar*H*), 7.25 (m, 1H), 6.78 (dd, *J* = 3.3, 1.0 Hz, 1H, Ar*H*), 1.11 (s, 9H, SiC*CH₃*), 0.78 (s, 6H, Si*(CH₃)₂*). **IR** ν 3064.6 (w), 2950.5 (w), 2929.7 (m), 2855.9 (w), 1512.0 (s), 1427.6 (s), 1449.9 (m), 1284.3 (s), 1271.6 (s), 1255.8 (m), 1158.9 (s), 1140.9 (s), 984.2 (w), 840.1 (m). ^{1}H NMR values are in accordance with the data reported in literature.[8]

1-(But-3-en-1-yl)-1*H*-Indole (37)



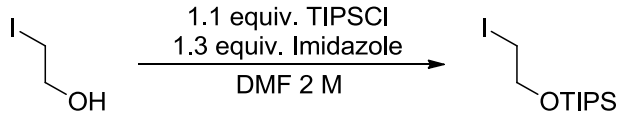
34 **37**

Following a reported procedure,[9] potassium *tert*butoxide (1.24 mg, 11.0 mmol, 1.10 equiv.) was added to a solution of 18-crown-6 ether (26.4 mg, 0.100 mmol, 10 mol%.) in dry THF (25 mL, 0.4 M) under a nitrogen atmosphere. Then, commercially available 1*H*-indole **34** (1.17 g, 10.0 mmol, 1.00 equiv.) was added under vigorous stirring. The reaction was cooled to 0°C in an ice bath. A solution of 4-bromobut-1-ene (1.20 mL, 11.0 mmol, 1.10 equiv.) in THF (5 mL) was added dropwise to the reaction mixture and the latter was stirred overnight. After cooling again to 0 °C, the reaction was quenched with water (20 mL), extracted with Et_2O (3 x 20 mL), the combined organic layers were dried over $MgSO_4$, and the solvent was removed under reduced pressure. The residue was purified via flash column chromatography (Pentane:EtOAc 9:1) to give the desired 1-(but-3-en-1-yl)-1*H*-indole **37** (280 mg, 1.64 mmol, 17% yield) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.52 (d, *J* = 8.2 Hz, 1H, Ar*H*), 7.41 (t, *J* = 7.6 Hz, 1H, Ar*H*), 7.31 (t, *J* = 7.4 Hz, 1H, Ar*H*), 7.23 (d, *J* = 3.2 Hz, 1H, Ar*H*), 6.68 (d, *J* = 3.2 Hz, 1H, Ar*H*), 5.94 (ddt, *J* = 17.1, 10.2, 6.8 Hz, 1H, Ar*H*), 5.32 – 5.12 (m, 2H, NCH_2CH_2CH=*CH_2*), 4.31 – 4.27 (m, 2H, *CH_2*), 2.72 (q, *J* = 7.1 Hz, 2H, *CH_2*). **IR** ν 2936 (w), 1640 (s), 1612 (s), 1508 (m), 1458

[8] D. Saha, R. Ghosh, A. Sarkar, *Tetrahedron* **2013**, *69*, 3951–3960.
[9] W. C. Guida, D. J. Mathre, *J. Org. Chem.* **1980**, *45*, 3172–3176.

(s), 910 (m), 740 (m), 712 (m). ^{1}H NMR values are in accordance with the data reported in literature.[10]

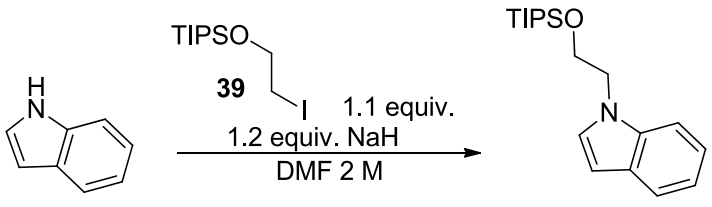
(2-Iodoethoxy)tri*iso*propylsilane (38)



38 **39**

Following a reported procedure,[11] commercially available 2-iodoethanol **38** (1.10 mL, 10.0 mmol, 1.00 equiv.) was added to a solution of imidazole (885 mg, 13.0 mmol, 1.30 equiv.) in DMF (5 mL, 2.0 M) under nitrogen atmosphere. chloro-tri*iso*propylsilane (2.80 mL, 13.0 mmol, 1.30 equiv.) was then added dropwise. After 1 h, the reaction turned into a thick suspension and a colorless solid precipitated. The mixture was allowed to warm to room temperature removed and was stirred for an additional hour. Water (5 mL) was added to dissolve the solid. The organic layer was separated and eluted through a SiO_2 plug with pentane (100 mL). The solvent was removed under reduced pressure to give (2-iodoethoxy)tri*iso*propylsilane **39** (3.15 g, 9.60 mmol, 96% yield) as a slightly yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.85 (t, *J* = 6.9 Hz, 2H, O*CH*$_2$), 3.15 (t, *J* = 7.0 Hz, 2H, I*CH*$_2$), 1.11-0.88 (m, 21H, *TIPS*). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 64.6, 18.0, 12.1, 6.9. **IR** ν 2958 (m), 2942 (m), 2891 (w), 2866 (m), 1464 (m), 1384 (w), 1275 (w), 1249 (w), 1190 (w), 1169 (w), 1123 (s), 1092 (s), 1069 (s), 1013 (w), 999 (m), 943 (w), 920 (w), 882 (s), 857 (w).

1-(2-((Tri*iso*propylsilyl)oxy)ethyl)- 1*H*-Indole (40)



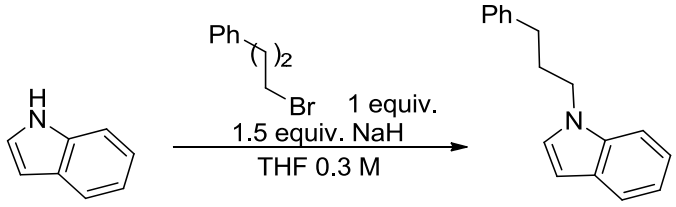
34 **40**

[10] H. A. Kerchner, J. Montgomery, *Org. Lett.* **2016**, *18*, 5760–5763.

[11] J. W. Bode, E. M. Carreira, *J. Org. Chem.* **2001**, *66*, 6410–6424.

Commercially available 1*H*-indole **34** (586 mg, 5.00 mmol) was dissolved in N,N-dimethylformamide (5 mL, 0.5 M *in total*). Sodium hydride (60% suspension in mineral oil; 144 mg, 6.00 mmol, 1.20 equiv.) was added at r.t. and the reaction mixture was stirred for one hour. N,N-Dimethylformamide (5 mL) was then added to dissolve the resulting colorless precipitate. The reaction was cooled to 0 °C and (2-iodoethoxy)tri*iso*propylsilane **39** (1.90 g, 5.50 mmol, 1.10 equiv.) was added dropwise. The reaction mixture was stirred overnight, allowing it to warm to r.t. The reaction was then quenched with water (20 mL) and the reaction mixture was extracted with EtOAc (3 x 25 mL). The combined organic layers were washed with water (10 mL), brine (3x10 mL), and dried over $MgSO_4$. The solvent was then removed under reduced pressure. Flash column chromatography (Pentane:EtOAc 9:1) afforded 1-(2-((tri*iso*propylsilyl)oxy)ethyl)- 1*H*-indole **40** (1.20 g, 3.78 mmol, 76% yield) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (m, 1 H, Ar*H*), 7.38 (dd, *J* = 8.2, 0.8 Hz, 1H, Ar*H*), 7.25 - 7.19 (m, 2H, Ar*H*), 7.13 (m, 1H, Ar*H*), 6.52 (dd, *J* = 3.1, 0.8 Hz, 1H, Ar*H*), 4.30 (t, *J* = 6.0 Hz, 2H, *CH_2*), 4.04 (t, *J* = 5.8 Hz, 2H, *CH_2*), 1.17 - 0.85 (m, 21H, *TIPS*). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.1, 128.7, 128.6, 121.3, 120.9, 119.2, 109.3, 101.0, 62.8, 48.8, 17.9, 11.9. **IR** ν 3056 (w), 2891 (m), 2865 (s), 1514 (w), 1464 (s), 1439 (w), 1387 (w), 1360 (w), 1334 (w), 1317 (m), 1115 (s), 1077 (m), 1013 (m), 923 (m), 819 (w).

1-(3-Phenylpropyl)-1*H*-indole (41)



34 **41**

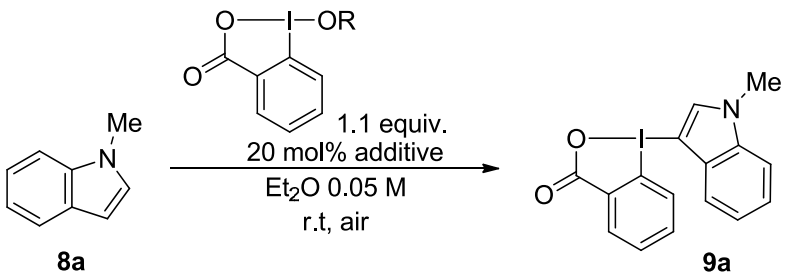
Following a reported procedure *(12)*, commercially available 1*H*-indole **34** (585 mg, 5.00 mmol, 1.00 equiv.) was dissolved in THF (15 mL). Sodium hydride (60% suspension in mineral oil; 300 mg, 7.50 mmol, 1.50 equiv.) was added at 0 °C and the reaction mixture was stirred for 30 min. (3-bromopropyl)benzene (760 µL, 5.00 mmol, 1.00 equiv.) was then added dropwise. After 15 min the ice bath was removed and the reaction mixture was stirred for 4 hours at r.t.. The reaction was cooled back to 0 °C, quenched with water, diluted with EtOAc (10 mL), extracted with water (2 x 10 mL), washed with brine (10 mL), and dried over $MgSO_4$. After filtration, the solvent was

[12] Y. R. Jorapur, J. M. Jeong, D. Y. Chi, *Tetrahedron Lett.* **2006**, *47*, 2435–2438.

removed under reduced pressure. Flash column chromatography (Pentane:EtOAc 20:1) afforded 1-(3-phenylpropyl)-1*H*-indole **41** (1.12 g, 4.76 mmol, 95% yield) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8 Hz, 1H, Ar*H*), 7.53-7.23 (m, 9H, Ar*H*), 6.72 (dd, *J* = 3.1, 0.8 Hz, 1H, Ar*H*), 4.26 (t, *J* = 7.1 Hz, 2H, NCH_2), 2.77 (t, *J* = 8 Hz, 2H, CH_2Ph), 2.34 (qi, *J* = 7.8 Hz, 2H, $CH_2CH_2CH_2$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.2, 136.2, 128.7, 128.7, 128.6, 128.0, 126.3, 121.6, 121.2, 119.5, 109.6, 101.3, 45.8, 33.2, 31.7 *(one aromatic Carbon signal not resolved)*. **IR** 3085 (w), 3057 (w), 3026 (w), 3004 (w), 2946 (w), 2945 (w), 2870 (w), 1780 (w), 1738 (s), 1717 (s), 1612 (w), 1603 (w), 1511 (m), 1497 (m), 1483 (m), 1464 (s), 1455 (s), 1400 (m), 1377 (s), 1354 (s), 1336 (s), 1315 (s), 1254 (s), 1207 (s), 1179 (m), 1166 (m), 1143 (m), 1143 (m), 1122 (m), 1114 (m), 1080 (m), 1031 (m), 1020 (m), 1004 (w), 952 (w), 928 (w), 909 (w), 885 (m), 855 (w), 838 (w), 821 (w), 811 (w), 802 (w).

2.2 Optimization in the synthesis of IndoleBX 9a.

Table S1: Screening of additives



8a **9a**

Entry	Reagent	Additive	Yield%[a]
1	HOBX **(7)**	TMSOTf	-[b]
2	HOBX **(7)**	$Zn(OTf)_2$	-[b]
3	AcOBX **(5)**	-	-[b]
4	AcOBX **(5)**	TMSOTf	16%
5	AcOBX **(5)**	**$Zn(OTf)_2$**	**36%[b]**
6	AcOBX **(5)**	$Cu(OTf)_2$	36%[c]
7	AcOBX **(5)**	$AgNTf_2$	-[c]
8	AcOBX **(5)**	AgF	-[c]
9	AcOBX **(5)**	CsF	-[c]
10	AcOBX **(5)**	TBAF	-[c]

a) Substrate **8a** (0.100 mmol), **reagents 7-5** (0.110 mmol), **additive** (20 mol%), and Et_2O (0.05 M) at 25 °C. Isolated yield after flash chromatography is given. b) No conversion: starting materials recovered. c) Complete decomposition of the hypervalent iodine reagents.

Table S2: Screening of solvents and additive loading

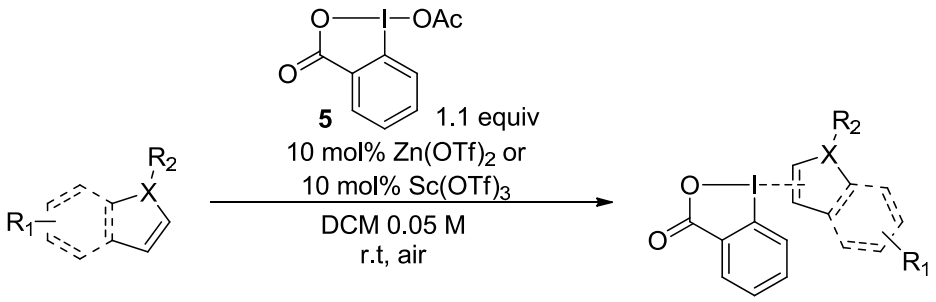
Entry	Solvent	X mol% $Zn(OTf)_3$	Yield%[a]
1	THF	10	-[b]
2	THF	20	-[b]
3	THF	1 equiv.	-[b]
4	DCM	10	Full conversion[c]

5	**DCM**	**20**	**97%**
6	DCM	1 equiv.	decomposition

a) Substrate **8a** (0.100 mmol), AcOBX **5** (0.110 mmol), $Zn(OTf)_2$ (**x** mol%), and **solvent** (0.05 M) at 25 °C. Isolated yield after flash chromatography is given. b) No conversion: starting materials recovered. c) 2 equiv. of OAcBX xx are needed.

2.3 Preparation of PyrroleBX and IndoleBX Reagents.

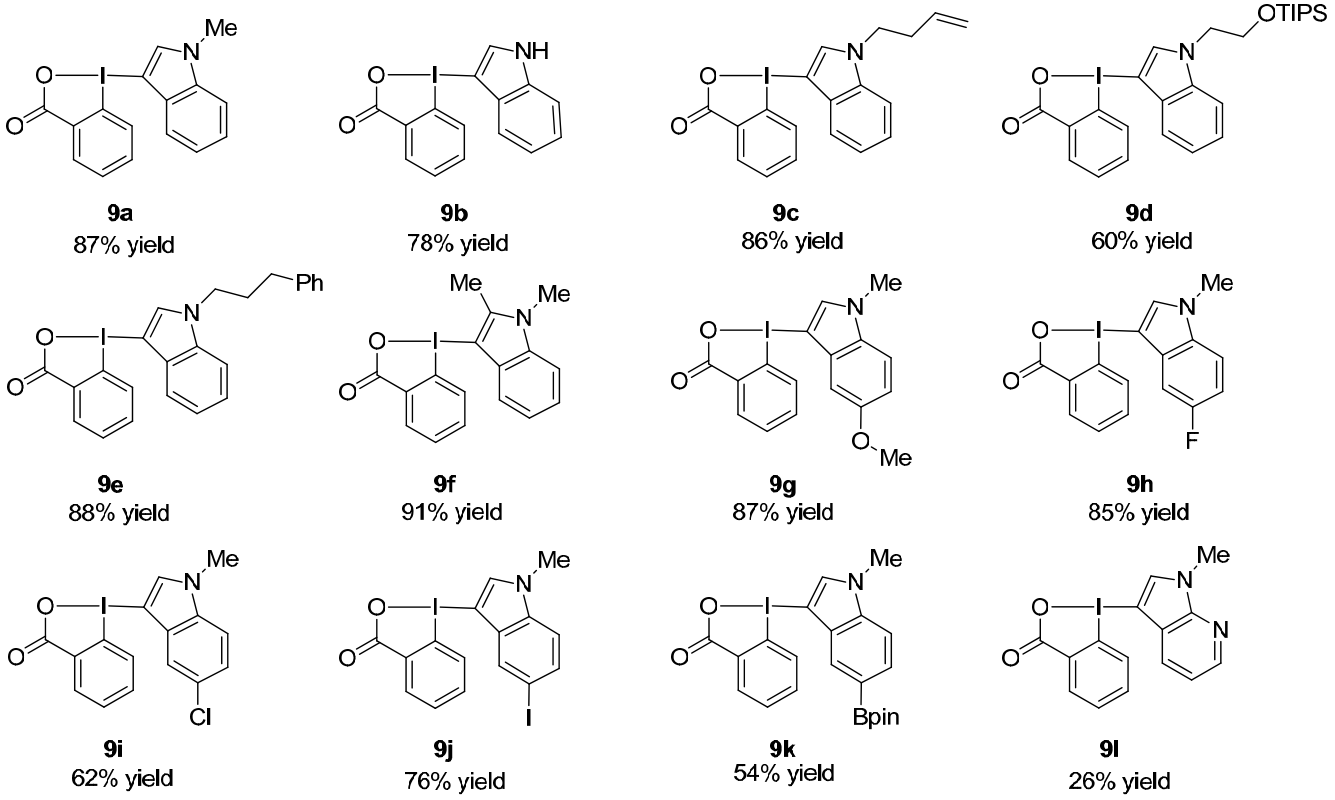
General Procedure GP2 for the Synthesis of Heterocyclic-BX Reagents



*Note: prior to the reaction, the glassware requires to be carefully cleaned with aqua regia to remove all metal traces; the commercially available heterocyclic starting material were purified through a short plug of silica prior to being used. Compound **5** can be prepared or purchased from commercial suppliers. Slow decomposition of **5** is observed at room temperature; for this reason, compound **5** should be stored at 3-5 °C and best results are obtained if it is prepared freshly.*

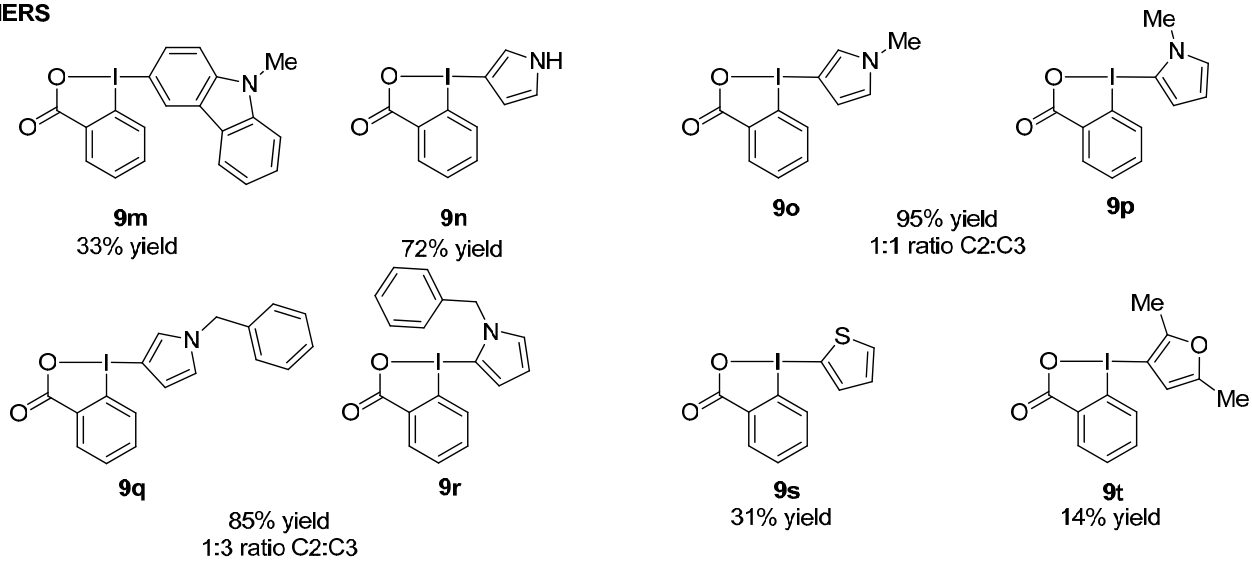
In an open air flask, the corresponding heterocycle (1.00 mmol, 1.00 equiv.), 1-acetoxy-1,2-benziodoxol-3-(1*H*)-one **5** (337 mg, 1.10 mmol, 1.10 equiv.) and zinc(II) trifluoromethanesulfonate (72.7 mg, 0.200 mmol, 20 mol%.) were dissolved in DCM (20 mL 0.05 M). The reaction was stirred while being monitored by TLC (Pentane:EtOAc 9:1 for the starting materials, DCM:MeOH 9:1 for the products). Upon consumption of the starting material, the crude was directly submitted to short-path flash chromatography (DCM:MeOH 10:1 or EtOAc:MeOH 10:1 for the separation of pyrrole-based reagents) to afford the desired Heterocyclic-BX compounds **9a-9r.*****The structure of compounds 9b and 9n was confirmed by X-Ray analysis (see par. 5 of the Supplementary Informations).***

INDOLES



9a 87% yield
9b 78% yield
9c 86% yield
9d 60% yield
9e 88% yield
9f 91% yield
9g 87% yield
9h 85% yield
9i 62% yield
9j 76% yield
9k 54% yield
9l 26% yield

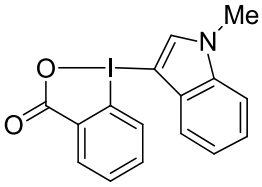
OTHERS



9m 33% yield
9n 72% yield
9o 95% yield 1:1 ratio C2:C3
9p
9q 85% yield 1:3 ratio C2:C3
9r
9s 31% yield
9t 14% yield

Figure S1: *Scope of Heterocyclic-BX reagents*

1-(3-1-Methyl-1*H*-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one (9a)

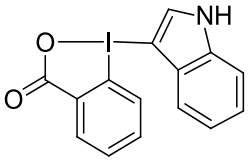


9a

The synthesis of 1-(3-1-methyl-1*H*-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one ***9a*** *was scaled up to 10 mmol without reoptimization of the protocol.*

Starting from commercially available 1-methyl-1-H-indole **8a** (1.35 g, 10.0 mmol), after 16 hours 1-(3-1-methyl-1*H*-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one **9a** (3.28 g, 8.70 mmol, 87% yield) was obtained as a brown foam. Rf: 0.4 (DCM:MeOH 9:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.40 (dd, *J* = 7.5, 1.7 Hz, 1H, Ar*H*), 7.82 (s, 1H, N*CH*Cl), 7.55 – 7.48 (m, 2H, Ar*H*), 7.39 – 7.35 (m, 2H, Ar*H*), 7.34 – 7.23 (m, 2H, Ar*H* + $CDCl_3$), 6.84 (d, *J* = 8.3 Hz, 1H, Ar*H*), 4.02 (s, 3H, N*CH*$_3$). **^{13}C NMR** (101 MHz, CDCl3) δ 166.8, 138.6, 137.6, 133.4, 133.3, 132.5, 130.5, 129.3, 125.2, 124.3, 122.6, 119.9, 116.1, 110.7, 78.9, 33.9. **IR** ν 3107 (w), 3059 (w), 2948 (w), 1599 (s), 1552 (m), 1506 (m), 1454 (w), 1392 (m), 1277 (s), 1245 (s), 1225 (s), 1166 (s), 1131 (m), 1031 (s), 1004 (w), 842 (w). **HRMS** (ESI) calcd for $C_{16}H_{13}INO_2^+$ $[M+H]^+$ 377.9986; found 377.9990. *The structure of the obtained regioisomer was assigned by NMR correlation to compound* ***9b****. DSC-analysis was performed on compound* ***9a****: see par.5 of Supplementary informations.*

1-(3-1*H*-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one (9b)

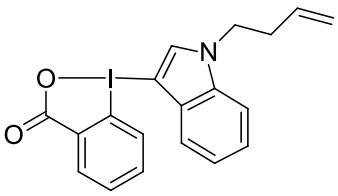


9b

Starting from 1-(*tert*-butyldimethylsilyl)-1*H*-indole **36** (231 mg, 1.00 mmol) and using $Sc(OTf)_3$ as the Lewis acid (20 mol %), after 16 hours 1-(3-1*H*-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one **9b** (294 mg, 8.10 mmol, 78% yield) was obtained as a brown solid. Rf: 0.4 (DCM:MeOH 9:1). **Mp:** 174.2°C (decomposition) **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.33 (s, 1H, N*H*), 8.21 (s, 1H, N*CH*Cl), 8.08 (dd, *J* = 7.3, 1.7 Hz, 1H, Ar*H*), 7.59 (d, *J* = 8.2 Hz, 1H, Ar*H*), 7.52 (t, *J* = 7.3 Hz, 1H, Ar*H*), 7.43 (d, *J* = 7.5 Hz, 1H, Ar*H*), 7.36 (ddd, *J* = 8.5, 7.3, 1.7 Hz, 1H, Ar*H*), 7.26 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H, Ar*H*), 7.15 (t, *J* = 7.5 Hz, 1H, Ar*H*), 6.72 (d, *J* = 8.5 Hz, 1H, Ar*H*). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 166.1, 136.6, 134.5, 133.3, 131.4, 130.2, 128.5, 126.3, 123.4, 122.3, 121.6, 119.2, 116.1, 112.9, 80.0. **IR** ν 3302 (w), 2975 (w), 2903 (w), 1722 (w), 1609 (m), 1584 (m), 1557 (w), 1490 (w), 1457 (w), 1385 (w), 1277 (s), 1258 (s), 1230 (m), 1174 (m), 1087 (w), 1036 (s), 880 (w), 841 (w). **HRMS** (ESI) calcd for $C_{15}H_{11}INO_2^+$ $[M+H]^+$ 363.9829;

found 363.9832. *The structure of the reagent was determined through X-Ray diffraction of a single crystal (CCDC number: **1540821**).*

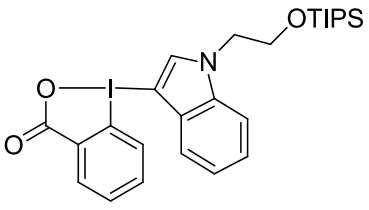
1-(3-1-(But-3-en-1-yl)-1H-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one (9c)



9c

Starting from 1-(but-3-en-1-yl)-1H-indole **37** (171 mg, 1.00 mmol), after 16 hours 1-(3-1-(but-3-en-1-yl)-1*H*-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one **9c** (359 mg, 0.860 mmol, 86% yield) was obtained, as a yellow amorphous solid. Rf: 0.44 (DCM:MeOH 9:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.35 (dd, *J* = 7.4, 1.7 Hz, 1H, Ar*H*), 7.91 (s, 1H, N*CH*Cl), 7.54 (m, 1H, Ar*H*), 7.49 (td, *J* = 7.3, 0.9 Hz, 1H, Ar*H*), 7.46 – 7.39 (m, 2H, Ar*H*), 7.32 – 7.19 (m, 2H, Ar*H*), 6.73 (dd, *J* = 8.3, 0.9 Hz, 1H, Ar*H*), 5.82 (ddt, *J* = 17.1, 10.3, 6.9 Hz, 1H, NCH_2CH_2CH=CH_2), 5.12 – 4.97 (m, 2H, NCH_2CH_2CH=CH_2), 4.41 (t, *J* = 6.9 Hz, 2H, NCH_2), 2.71 (m, 2H, CH_2). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.8, 137.9, 136.7, 133.6, 133.4, 133.2, 132.5, 130.5, 129.4, 125.2, 124.2, 122.5, 120.0, 118.6, 116.2, 110.9, 79.0, 46.9, 34.2. **IR** ν 3082 (w), 1607 (s), 1557 (m), 1500 (m), 1456 (w), 1437 (w), 1389 (w), 1358 (m), 1262 (w), 1160 (w), 1005 (w), 919 (w), 830 (w). **HRMS** (ESI) calcd for $C_{19}H_{17}INO_2^+$ $[M+H]^+$ 418.0299; found 418.0294. *The structure of the obtained regioisomer was assigned by NMR correlation to compound **9b**.*

1-(3-1-(2-((Tri*iso*propylsilyl)oxy)ethyl)-1*H*-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one (9d)

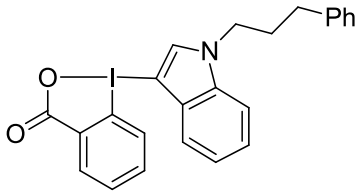


9d

Starting from 1-(2-((tri*iso*propylsilyl)oxy)ethyl)-1*H*-indole **40** (318 mg, 1.00 mmol), after 16 hours 1-(3-1-(2-((tri*iso*propylsilyl)oxy)ethyl)-1*H*-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one **9d** (873 mg, 0.929 mmol, 60% yield) was obtained as an orange oil. Rf: 0.40 (DCM:MeOH 9:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 7.5 Hz, 1H, Ar*H*), 7.99 (s, 1H, N*CH*Cl), 7.65 (d, *J* = 8.5 Hz, 1H, Ar*H*), 7.59 (t, *J* = 7.5 Hz, 1H, Ar*H*), 7.51 – 7.45 (m, 2H, Ar*H*), 7.35 (m, 2H, Ar*H*), 6.94 (d, *J* = 8.3 Hz, 1H, Ar*H*), 4.54 (t, *J* = 5.0 Hz, 2H, CH_2), 4.20 (t, *J* = 5.0 Hz, 2H, CH_2), 1.09 (dd, *J* = 8.7, 5.6 Hz, 3H, Si*CH*$(CH_3)_2$), 1.01 (d, *J* = 7.1 Hz, 18H, SiCH($CH_3)_2$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.0, 138.8,

137.1, 133.2, 133.2, 132.4, 130.4, 129.1, 125.3, 124.0, 122.4, 119.7, 115.8, 111.0, 78.3, 62.3, 49.8, 17.7, 11.6. **IR** ν 2942 (w), 2890 (w), 2865 (m), 1716 (w), 1604 (s), 1555 (w), 1500 (w), 1458 (w), 1358 (m), 1249 (m), 1169 (w), 1115 (w), 1015 (w), 883 (m), 831 (m). **HRMS (ESI)** calcd for $C_{26}H_{35}INO_3Si^+$ $[M+H]^+$ 564.1425; found 564.1431. *The structure of the obtained regioisomer was assigned by NMR correlation to compound **9b**.*

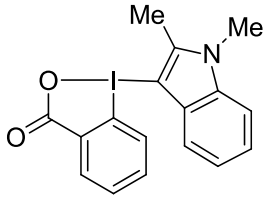
1-(3-1-(3-Phenylpropyl)-1*H*-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one (9e)



9e

Starting from 1-(3-phenylpropyl)--indole **41** (235 mg, 1.00 mmol), after 16 hours 1-(3-1-(3-phenylpropyl)-1*H*-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one **9e** (436 mg, 0.906 mmol, 91% yield) was obtained as an orange resin. Rf: 0.45 (DCM:MeOH 9:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.37 (dd, *J* = 7.5, 1.7 Hz, 1H, Ar*H*), 7.86 (s, 1H, N*CH*Cl), 7.54 – 7.36 (m, 4H, Ar*H*), 7.33 – 7.19 (m, 5H, Ar*H*), 7.18 – 7.14 (m, 2H, Ar*H*), 6.79 (dd, *J* = 8.3, 0.8 Hz, 1H, Ar*H*), 4.34 (t, *J* = 7.2 Hz, 2H, NC*H*$_2$), 2.73 (t, *J* = 7.5 Hz, 2H, C*H*$_2$Ph), 2.35 (m, 2H, CH_2-C*H*$_2$-CH_2). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.8, 140.0, 137.8, 136.8, 133.4, 133.2, 132.4, 130.4, 129.3, 128.6, 128.3, 126.4, 125.2, 124.1, 122.5, 120.0, 116.1, 110.9, 78.9, 46.7, 32.8, 31.1. **IR** ν 3060 (w), 3026 (w), 2939 (w), 1717 (w), 1601 (s), 1551 (m), 1498 (m), 1455 (w), 1364 (w), 1245 (w), 1165 (w), 1005 (w), 828 (m). **HRMS** (ESI) calcd for $C_{24}H_{21}INO_2^+$ $[M+H]^+$ 482.0612; found 482.0614. *The structure of the obtained regioisomer was assigned by NMR correlation to compound **9b**.*

1-(3-1,2-Dimethyl-1*H*-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one (9f)

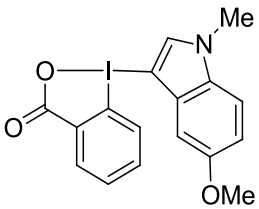


9f

Starting from 2-methyl-1-methyl-1*H*-indole **28** (145 mg, 1.00 mmol), after 16 hours 1-(3-1,2-dimethyl-1*H*-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one **9f** (364 mg, 0.930 mmol, 93% yield) was obtained as a dark violet foam. Rf: 0.43 (DCM:MeOH 9:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.42 (dd, *J* = 7.3, 1.7 Hz, 1H, Ar*H*), 7.52 (td, *J* = 7.3, 0.9 Hz, 1H, Ar*H*), 7.44 (d, *J* = 8.2 Hz, 1H, Ar*H*), 7.35 (m, 2H, Ar*H*), 7.28 (m, 1H, Ar*H*), 7.23 (ddd, *J* = 8.2, 6.9, 1.0 Hz, 1H, Ar*H*), 6.77 (m, 1H, Ar*H*), 3.91 (s, 3H, *CH*$_3$N), 2.65 (s, 3H, ICH=CH*CH*$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$)

δ 166.8, 145.3, 137.9, 133.7, 133.2, 132.7, 130.5, 128.9, 124.7, 123.6, 122.4, 119.2, 115.5, 110.4, 80.1, 31.1, 13.2. **IR** ν 3055 (w), 2987 (w), 2948 (w), 1717 (w), 1605 (s), 1584 (m), 1553 (m), 1516 (w), 1472 (w), 1437 (w), 1395 (m), 1378 (m), 1268 (m), 1154 (w), 1032 (w), 1011 (w), 829 (w). **HRMS** (ESI) calcd for $C_{17}H_{15}INO_2^+$ $[M+H]^+$ 392.0142; found 392.0146. *The structure of the obtained regioisomer was assigned by NMR correlation to compound **9b**.*

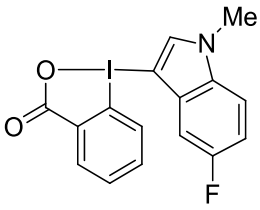
1-(3-5-Methoxy-1-methyl-1*H*-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one (9g)



9g

Starting from 5-methoxy-1-methyl- 1*H*-indole **29** (161 mg, 1.00 mmol), after 16 hours 1-(3-5-methoxy-1-methyl-1*H*-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one **9g** (346 mg, 0.850 mmol, 85% yield) was obtained as an orange resin. Rf: 0.42 (DCM:MeOH 9:1). ***NB: the reagent was isolated in presence of a small amount of the polymerized form of the heterocycles (4% of estimated impurity).*** **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.35 (dd, *J* = 7.5, 1.6 Hz, 1H, Ar*H*), 7.82 (s, 1H, N*CH*Cl), 7.48 (t, *J* = 7.3 Hz, 1H, Ar*H*), 7.40 (d, *J* = 9.0 Hz, 1H, Ar*H*), 7.27 (m, 1H, Ar*H*), 7.04 (dd, *J* = 9.0, 2.4 Hz, 1H, Ar*H*), 6.84 (d, *J* = 8.3 Hz, 1H, Ar*H*), 6.79 (d, *J* = 2.3 Hz, 1H, Ar*H*), 3.99 (s, 3H, *CH*$_3$N), 3.78 (s, 3H, O*CH*$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.1, 156.4, 138.9, 133.3, 132.5, 132.5, 130.5, 130.1, 125.2, 116.0, 114.8, 111.7, 100.8, 77.4, 55.8, 34.0 (*the signal for one aromatic C could not be resolved*). **IR** ν 3110 (w), 3062 (w), 3000 (w), 2944 (w), 2837 (w), 1719 (w), 1604 (m), 1584 (m), 1556 (w), 1504 (m), 1489 (m), 1439 (w), 1378 (w), 1249 (s), 1223 (s), 1158 (m), 1031 (s), 970 (w), 845 (m). **HRMS** (ESI) calcd for $C_{17}H_{15}INO_3^+$ $[M+H]^+$ 408.0091; found 408.0093. *The structure of the obtained regioisomer was assigned by NMR correlation to compound **9b**.*

1-(3-5-Fluoro-1-methyl-1*H*-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one (9h)

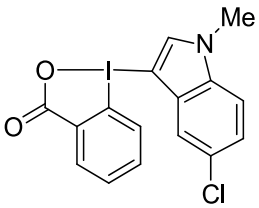


9h

Starting from 5-fluoro-1-methyl-1*H*-indole **30** (149 mg, 1.00 mmol), after 16 hours 1-(3-5-fluoro-1-methyl-1*H*-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one **9h** (336 mg, 0.850 mmol, 85% yield) was obtained as an yellow foam. Rf: 0.3 (DCM:MeOH 9:1). ***NB: the reagent was isolated in presence of a small amount of the polymerized form of the heterocycles (7% of***

estimated impurity). **^{1}H NMR** (400 MHz, CD_3OD) δ 8.1 (dd, *J* = 7.6, 1.7 Hz, 1H, Ar*H*), 8.01 (s, 1H, N*CH*Cl), 7.57 (ddd, *J* = 8.8, 4.2, 0.8 Hz, 1H, Ar*H*), 7.49 (td, *J* = 7.4, 1.0 Hz, 1H, Ar*H*), 7.30 (ddd, *J* = 8.3, 7.2, 1.7 Hz, 1H, Ar*H*), 7.14 – 7.03 (m, 2H, Ar*H*), 6.80 (dd, *J* = 8.3, 0.9 Hz, 1H, Ar*H*), 3.93 (s, 3H, *CH*$_3$N). **^{13}C NMR** (101 MHz, CD_3OD) δ 170.3, 160.91 (d, *J* = 238.2 Hz), 142.6, 135.9, 135.1, 134.4, 133.2, 131.7, 131.40 (d, *J* = 10.7 Hz), 127.7, 116.8, 113.71 (d, *J* = 9.8 Hz), 113.47 (d, *J* = 26.7 Hz), 105.67 (d, *J* = 25.3 Hz), 77.5, 34.3. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -119.8. **IR** ν 3083 (w), 2952 (w), 1717 (w), 1601 (s), 1557 (m), 1503 (m), 1485 (m), 1438 (w), 1338 (m), 1242 (m), 1193 (m), 1121 (m), 1032 (w), 1005 (w), 850 (m). **HRMS** (ESI) calcd for $C_{16}H_{12}FINO_2^+$ $[M+H]^+$ 395.9891; found 395.9894. *The structure of the obtained regioisomer was assigned by NMR correlation to compound* ***9b****.*

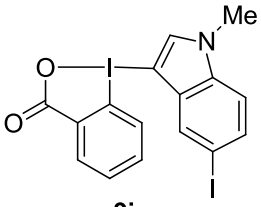
1-(3-5-Chloro-1-methyl-1*H*-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one (9i)



9i

Starting from 5-chloro-1-methyl-1*H*-indole **31** (166 mg, 1.00 mmol), after 16 hours 1-(3-5-chloro-1-methyl-1*H*-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one **9i** (256 mg, 0.622 mmol, 62% yield) was obtained as an orange amorphous solid. Rf: 0.4 (DCM:MeOH 9:1). **^{1}H NMR** (400 MHz, CD_2Cl_2) δ 8.20 (d, *J* = 7.4 Hz, 1H, Ar*H*), 7.78 (s, 1H, N*CH*Cl), 7.38 (d, *J* = 8.7 Hz, 1H, Ar*H*), 7.34 – 7.22 (m, 3H, Ar*H*), 7.17 (t, *J* = 7.7 Hz, 1H, Ar*H*), 6.68 (d, *J* = 8.2 Hz, 1H, Ar*H*), 3.87 (s, 3H, *CH*$_3$NCHCl). **^{13}C NMR** (101 MHz, CD_3OD) δ 170.3, 142.5, 137.8, 135.1, 134.4, 133.2, 131.7, 131.7, 129.6, 127.8, 125.4, 120.0, 116.8, 113.7, 77.5, 34.2. **IR** ν 3095 (w), 2953 (w), 1605 (s), 1556 (m), 1505 (m), 1438 (m), 1388 (m), 1370 (m), 1260 (s), 1226 (m), 1164 (m), 1144 (m), 1115 (w), 1070 (w), 1032 (s), 1004 (w), 837 (w). **HRMS** (ESI) calcd for $C_{16}H_{12}ClINO_2^+$ $[M+H]^+$ 411.9596; found 411.9603. *The structure of the obtained regioisomer was assigned by NMR correlation to compound* ***9b****.*

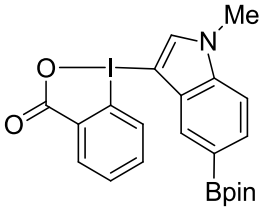
1-(3-5-Iodo-1-methyl-1*H*-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one (9j)



9j

Starting from 5-iodo-1-methyl-1*H*-indole **32** (257 mg, 1.00 mmol), after 16 hours 1-(3-5-iodo-1-methyl-1*H*-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one **9j** (380 mg, 0.755 mmol, 76% yield) was obtained as a yellow amorphous solid. Rf: 0.3 (DCM:MeOH 9:1). ***NB: the reagent is unstable in acidic deuterated solvents and it decompose in short time, we recommend the immediate use after the synthesis. The proton NMR presents about 21% of the open protonated form***. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.24 (m, 1H, Ar*H*), 7.83 (s, 1H, NCHCI), 7.58 – 7.47 (m, 2H, Ar*H*), 7.26 (m, 1H, Ar*H* + $CDCl_3$), 7.21 - 7.18 (m, 2H, Ar*H*), 6.67 (d, *J* = 8.1 Hz, 1H, Ar*H*), 3.87 (s, 3H, *CH*$_3$N). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.6, 140.5, 136.8, 133.7, 132.6, 132.3, 131.4, 130.3, 128.1, 126.0, 122.3, 119.1, 115.7, 112.9, 86.1, 34.0. **IR** ν 3092 (w), 3061 (w), 1600 (s), 1584 (m), 1557 (m), 1503 (m), 1436 (w), 1422 (w), 1371 (m), 1265 (s), 1245 (s), 1225 (m), 1163 (m), 1113 (w), 1031 (s), 1004 (w), 836 (w). **HRMS** (ESI) calcd for $C_{16}H_{12}I_2NO_2^+$ $[M+H]^+$ 503.8952; found 503.8952. *The structure of the obtained regioisomer was assigned by NMR correlation to compound **9b**.*

1-(3-1-Methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one (9k)

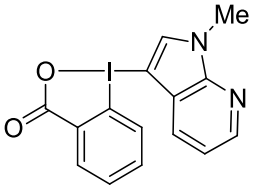


9k

Starting from commercially available 1-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (149 mg, 1.00 mmol), after 16 hours 1-(3-1-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one **9k** (276 mg, 0.549 mmol, 54% yield) was obtained as an orange amorphous solid. Rf: 0.46 (DCM:MeOH 9:1). **^{1}H NMR** (400 MHz, CD_2Cl_2) δ 8.32 (dd, *J* = 7.5, 1.7 Hz, 1H, Ar*H*), 7.93 (s, 1H, N*CH*Cl), 7.81 (dd, *J* = 8.4, 1.1 Hz, 1H, Ar*H*), 7.74 (s, 1H, C*CH*CBPin), 7.59 – 7.48 (m, 2H, Ar*H*), 7.31 (ddd, *J* = 8.6, 7.1, 1.7 Hz, 1H, Ar*H*), 6.85 (dd, *J* = 8.3, 0.9 Hz, 1H, Ar*H*), 3.99 (s, 3H, *CH*$_3$N), 1.30 (s, 12H, C*BPin*). **^{13}C NMR** (101 MHz, CD_2Cl_2) δ 167.0, 140.1, 139.6, 134.1, 133.8, 132.6, 131.0, 130.5, 129.5, 127.6, 126.0, 117.1, 110.7, 84.5, 80.3, 34.4, 25.2 *(one aromatic Carbon signal not resolved).* **IR** ν 3095 (w), 2979 (w), 1611 (s), 1558 (w), 1507 (w), 1436 (w), 1360 (s), 1303 (w), 1263 (w), 1142 (s), 1114 (w), 1074 (w), 970 (w), 861 (w). **HRMS** (ESI) calcd for

$C_{22}H_{24}BINO_4^+$ [M+H]$^+$ 504.0838; found 504.0835. *The structure of the obtained regioisomer was assigned by NMR correlation to compound* ***9b****.*

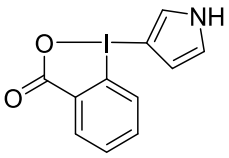
1-(3-1-Methyl-1H-pyrrolo[*2,3-b*]pyridine)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one (9l)



9l

Starting from commercially available 1-methyl-1*H*-pyrrolo[*2,3-b*]pyridine (132 mg, 1.00 mmol), after 16 hours 1-(3-1-methyl-1H-pyrrolo[*2,3-b*]pyridine)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one **9l** (114 mg, 0.301 mmol, 30% yield) was obtained as a brown amorphous solid. Rf: 0.2 (DCM:MeOH 9:1). **^{1}H NMR** (400 MHz, CD_2Cl_2) δ 8.37 (dd, *J* = 4.7, 1.6 Hz, 1H, Ar*H*), 8.06 (dd, *J* = 7.9, 1.2 Hz, 1H, Ar*H*), 7.96 (dd, *J* = 7.9, 1.7 Hz, 1H, Ar*H*), 7.92 (dd, *J* = 7.9, 1.7 Hz, 1H, Ar*H*), 7.46 (td, *J* = 7.7, 1.2 Hz, 1H, Ar*H*), 7.25 – 7.19 (m, 2H, Ar*H*), 7.14 (dd, *J* = 7.9, 4.7 Hz, 1H, Ar*H*), 3.86 (s, 3H, *CH*$_3$N). **^{13}C NMR** (101 MHz, CD_2Cl2) δ 168.6, 144.4, 142.3, 134.3, 133.8, 132.1, 128.7, 127.0, 126.3, 118.8, 116.5, 103.2, 94.9, 31.7 *(one Carbon signal not resolved).* **IR** ν 2925 (w), 2852 (w), 1719 (s), 1599 (m), 1585 (m), 1468 (m), 1408 (w), 1348 (w), 1289 (m), 1262 (s), 1136 (m), 1103 (w), 1042 (w), 1017 (m), 976 (w). **HRMS** (ESI) calcd for $C_{15}H_{12}IN_2O_2^+$ [M+H]$^+$ 378.9938; found 378.9945. *The structure of the obtained regioisomer was assigned by NMR correlation to compound* ***9b****.*

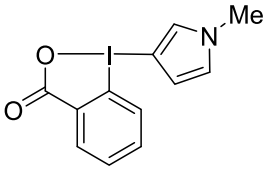
1-(3-1*H*-Pyrrole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one (9m)



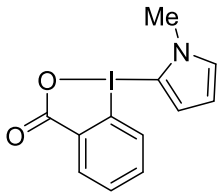
9m

Starting from 1-(*tert*-butyldimethylsilyl)-1*H*-pyrrole **35** (181 mg, 1.00 mmol) and using $Sc(OTf)_3$ as the Lewis Acid (20 mol%), after 16 hours 1-(3-1*H*-pyrrole)- 1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one **9m** (225 mg, 0.719 mmol, 72% yield) was obtained as a slightly brown solid. Rf: 0.5 (DCM:MeOH 9:1). **Mp**: 147°C (decomposition). **^{1}H NMR** (400 MHz, CD_3OD) δ 8.40 (dd, *J* = 7.5, 1.7 Hz, 1H, Ar*H*), 7.72 (d, *J* = 7.4 Hz, 1H, Ar*H*), 7.68 – 7.59 (m, 2H, Ar*H*), 7.23 (t, *J* = 2.4 Hz, 1H, Ar*H*), 7.14 (d, *J* = 8.2 Hz, 1H, Ar*H*), 6.74 (dd, *J* = 2.8, 1.5 Hz, 1H, Ar*H*) *(NH signal exchanges with CD$_3$OD).* **^{13}C NMR** (101 MHz, CD_3OD) δ 170.3, 135.0, 134.4, 132.9, 131.5, 130.4, 128.0, 123.7, 117.3, 115.9, 83.4. **IR** ν 3484 (w), 1607 (w), 1558 (w), 1439 (w), 1397 (w), 1260 (s), 1236 (s), 1174 (s), 1084 (w), 1050 (m), 1038 (m), 903 (w), 882 (w). **HRMS** (ESI) calcd for $C_{11}H_9INO_2^+$ [M+H]$^+$ 313.9673; found 313.9673. *The structure of the reagent was assigned based on X-Ray diffraction (CCDC number* ***1541174****).*

1-(3-1-Methyl-1*H*-pyrrole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one (9n) and 1-(2-1-methyl-1*H*-pyrrole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one (9o)

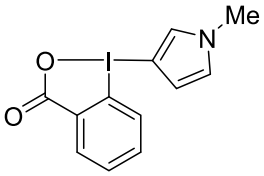


9n



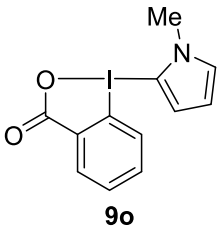
9o

Starting from commercially available 1-methyl-1*H*-pyrrole (0.890 ml, 1.00 mmol), after 12 hours 1-(3-1-methyl-1*H*-pyrrole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one **9n** and 1-(2-1-methyl-1*H*-pyrrole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one **9o** were obtained as a 1:1 mixture (overall yield 95%) as an off-white, sticky amorphous solid. Rf: 0.5 (DCM:MeOH 9:1). The two compounds were separated by slow flash column chromatography (EtOAc:MeOH 9:1). *The structure of the obtained regioisomers were assigned by NMR correlation to compound* **9m**.



9n

1-(3-1-methyl-1*H*-pyrrole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one **9n** (158 mg, 0.483 mmol, 48% yield; off-white, sticky amorphous solid). Rf: 0.25 (EtOAc:MeOH 9:1). **^{1}H NMR** (400 MHz, CD_3OD) δ 8.15 (dd, *J* = 7.5, 1.7 Hz, 1H, Ar*H*), 7.53 (td, *J* = 7.3, 1.1 Hz, 1H, Ar*H*), 7.49 – 7.40 (m, 2H, Ar*H*), 7.04 – 6.98 (m, 2H, Ar*H*), 6.58 (d, *J* = 1.2 Hz, 1H, Ar*H*), 3.85 (s, 3H, N*Me*). **^{13}C NMR** (101 MHz, CD_3OD) δ 170.0, 134.9, 134.2, 133.4, 132.8, 131.5, 127.9, 127.7, 117.4, 116.6, 82.8, 37.1. **IR** ν 3447 (w), 3106 (w), 2947 (w), 2863 (w), 1603 (s), 1591 (m), 1558 (m), 1512 (m), 1437 (w), 1354 (m), 1294 (w), 1110 (m), 1083 (w), 1007 (w), 829 (m). **HRMS** (ESI) calcd for $C_{12}H_{11}INO_2^+$ $[M+H]^+$ 327.9829; found 327.9831. *DSC-analysis was performed on compound* ***9n****: see par.5 of Supplementary informations.*

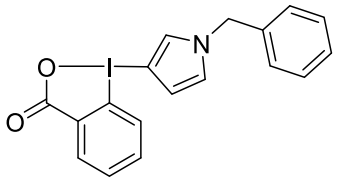


9o

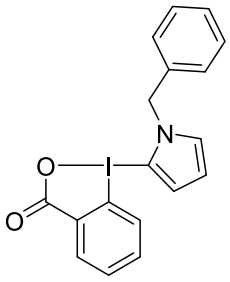
1-(2-1-methyl-1*H*-pyrrole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one **9o** (152 mg, 0.465 mmol, 47% yield; off-white, sticky amorphous solid) Rf: 0.3 (EtOAc:MeOH 9:1). **^{1}H NMR** (400 MHz, CD_3OD) δ 8.24 (dd, *J* = 7.5, 1.6 Hz, 1H, Ar*H*), 7.65 (td, *J* = 7.4, 1.0 Hz, 1H, Ar*H*), 7.55 (m, 1H, Ar*H*), 7.27 (t, *J* = 2.1 Hz, 1H, Ar*H*), 7.01 (dd, *J* = 3.9, 1.6 Hz, 1H, Ar*H*), 6.72 (dd, *J* = 8.3, 1.0 Hz, 1H, Ar*H*), 6.43 (dd, *J* = 3.9, 2.1 Hz, 1H, Ar*H*), 3.78 (s, 1H, N*CH$_3$*). **^{13}C NMR** (101 MHz, CD_3OD) δ 170.1, 135.5, 134.2, 133.2, 131.9, 131.4, 127.7, 126.6, 119.4, 112.9, 96.0, 37.4. **IR** ν

3415 (w), 3105 (w), 3049 (w), 2950 (w), 1604 (s), 1584 (m), 1558 (w), 1508 (w), 1437 (w), 1346 (m), 1288 (m), 1223 (w), 1149 (w), 1091 (w), 1047 (w), 1005 (w), 829 (m). **HRMS** (ESI) calcd for $C_{12}H_{11}INO_2^+$ $[M+H]^+$ 327.9829; found 327.9842. *DSC-analysis was performed on compound **9o**: see par.5 of Supplementary informations.*

1-(3-1-benzyl-1*H*-pyrrole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one (9p) and 1-(2-1-benzyl-1*H*-pyrrole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one (9q)

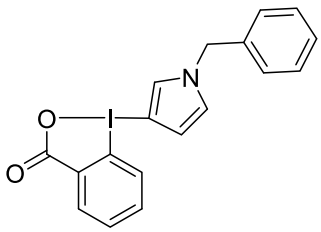


9p



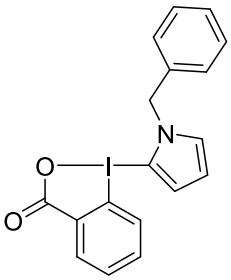
9q

Starting from commercially available 1-methyl-1*H*-pyrrole (0.890 ml, 1.00 mmol), after 12 hours 1-(3-1-benzyl-1*H*-pyrrole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one **9p** and 1-(2-1-benzyl-1*H*-pyrrole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one **9q** were obtained in 3:1 mixture (overall yield 86%), as a colorless amorphous solid. Rf: 0.7 (DCM:MeOH 9:1). The two compounds were separated by slow flash column chromatography (EtOAc:MeOH 9:1). *The structure of the obtained regioisomers were assigned by NMR correlation to compound* **9m**.



9p

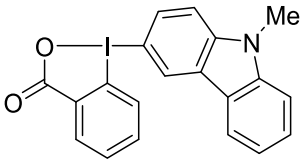
1-(3-1-benzyl-1*H*-pyrrole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one **9p** (260 mg, 0.645 mmol, 65% yield) as a colorless foam. Rf: 0.46 (EtOAc:MeOH 9:1). **^{1}H NMR** (400 MHz, *2:1 mixture CD_3OD:C_6D_6, refered to CD_3OD*) δ 8.29 (dd, *J* = 7.5, 1.7 Hz, 1H, Ar*H*), 7.36 (t, *J* = 7.3 Hz, 1H, Ar*H*), 7.30 – 7.20 (m, 3H Ar*H* + C_6D_6), 7.18 – 7.08 (m, 3H, Ar*H*), 6.97 (d, *J* = 2.0 Hz, 1H, Ar*H*), 6.83 – 6.78 (m, 2H, Ar*H*), 6.30 (dd, *J* = 3.0, 1.7 Hz, 1H, Ar*H*), 4.93 (s, 2H, N*CH*$_2$Ph). **^{13}C NMR** (101 MHz, *2:1 mixture CD_3OD:C_6D_6, refered to CD_3OD*) δ 168.7, 136.8, 133.5, 133.0, 131.8, 130.9, 130.3, 128.8, 128.1, 127.4, 126.2, 125.5, 116.3, 115.3, 82.4, 53.5. **IR** ν 3409 (w), 3114 (w), 2971 (w), 1609 (s), 1585 (m), 1558 (w), 1456 (w), 1438 (w), 1365 (m), 1277 (s), 1160 (w), 1079 (w), 1032 (m), 835 (w). **HRMS** (ESI) calcd for $C_{18}H_{15}INO_2^+$ $[M+H]^+$ 404.0142; found 404.0140.



9q

1-(2-1-benzyl-1*H*-pyrrole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one **9q** (85.0 mg, 0.211 mmol, 21% yield) as a colorless foam. Rf: 0.5 (EtOAc:MeOH 9:1). **^{1}H NMR** (400 MHz, *2:1 mixture CD_3OD:C_6D_6, referered to CD_3OD*) δ 8.18 (dd, *J* = 7.5, 1.6 Hz, 1H, Ar*H*), 7.28 (t, *J* = 7.4 Hz, 1H, Ar*H*), 7.10 (t, *J* = 2.2 Hz, 1H, Ar*H*), 6.92 (m, *J* = 7.6, 2.9 Hz, 6H, Ar*H* + C_6D_6), 6.71 (dd, *J* = 3.9, 1.7 Hz, 1H, Ar*H*), 6.35 (t, *J* = 3.4 Hz, 1H, Ar*H*), 6.23 (d, *J* = 8.3 Hz, 1H, Ar*H*), 4.90 (s, 2H, N*C*H_2Ph). **^{13}C NMR** (101 MHz, *2:1 mixture CD_3OD:C_6D_6, referered to CD_3OD*) δ 169.8, 136.9, 134.6, 132.7, 131.2, 131.1, 129.5, 129.0, 128.5, 127.2, 119.2, 112.9, 94.8, 54.7 *(two Carbon signals under the deuterated benzene*). **IR** ν 3109 (w), 3064 (w), 2968 (w), 2875 (w), 1609 (s), 1585 (m), 1558 (w), 1503 (w), 1456 (w), 1440 (w), 1357 (m), 1277 (w), 1103 (m), 1079 (w), 1032 (w), 1031 (w), 830 (w). **HRMS** (ESI) calcd for $C_{18}H_{15}INO_2^+$ $[M+H]^+$ 404.0142; found 404.0140.

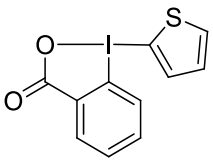
1-(3-9-Methyl-9*H*-carbazole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one (9r)



9r

Starting from commercially available 9-methyl-9*H*-carbazole (181 mg, 1.00 mmol), after 16 hours 1-(3-9-methyl-9*H*-carbazole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one **9r** (110 mg, 0.257 mmol, 33% yield) was obtained as a grey amorphous solid. Rf: 0.2 (DCM:MeOH 9:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 1.6 Hz, 1H, Ar*H*), 8.47 (dd, *J* = 7.5, 1.7 Hz, 1H, Ar*H*), 8.14 (d, *J* = 7.9 Hz, 1H, Ar*H*), 7.96 (dd, *J* = 8.5, 1.6 Hz, 1H, Ar*H*), 7.63 (ddd, *J* = 8.4, 7.1, 1.2 Hz, 1H, Ar*H*), 7.59 (d, *J* = 8.5 Hz, 1H, Ar*H*), 7.57 – 7.52 (m, 2H, Ar*H*), 7.37 (td, *J* = 7.5, 1.2 Hz, 1H, Ar*H*), 7.30 (ddd, *J* = 8.5, 7.1, 1.7 Hz, 1H, Ar*H*), 6.69 (dd, *J* = 8.5, 0.9 Hz, 1H, Ar*H*), 3.98 (s, 3H, N*C*H_3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.5, 142.4, 141.4, 133.4, 133.3, 132.7, 130.6, 130.0, 127.7, 125.8, 125.7, 121.4, 120.8, 120.7, 116.3, 112.0, 109.3, 101.8, 53.4, 29.5. **IR** ν 3082 (w), 2974 (w), 2924 (w), 2816 (w), 1652 (s), 1588 (w), 1570 (w), 1456 (w), 1440 (m), 1295 (m), 1245 (w), 1139 (w), 1017 (w), 982 (m), 831 (w). **HRMS** (ESI) calcd for $C_{20}H_{15}INO_2^+$ $[M+H]^+$ 428.0142; found 428.0147.

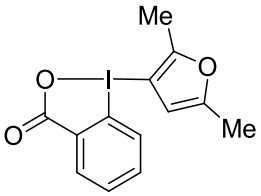
1-(2-1*H*-Thiophene)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one (9s)



9s

Starting from commercially available thiophene (80.0 µL, 1.00 mmol) and using $Sc(OTf)_3$ as the Lewis Acid (20 mol%), after 16 hours 1-(2-1*H*-thiophene)-1*H*-1λ3 -benzo[b]iodo-3(2*H*)-one (9s) (102 mg, 0.309 mmol, 31% yield) was obtained as a light yellow amorphous solid. Rf: 0.4 (DCM:MeOH 9:1). ***NB: the reagent is unstable in protic deuterated solvents and it decompose in short time, we recommend the immediate use after the synthesis. The proton NMR presents about 7% of the open protonated form.*** **^{1}H NMR** ^{1}H NMR (400 MHz, CD_3OD) δ 8.28 (dd, *J* = 7.5, 1.7 Hz, 1H, Ar*H*), 8.05 (dd, *J* = 5.2, 1.2 Hz, 1H, Ar*H*), 7.98 (dd, *J* = 3.7, 1.2 Hz, 1H, Ar*H*), 7.70 (td, *J* = 7.4, 0.9 Hz, 1H, Ar*H*), 7.61 (ddd, *J* = 8.7, 7.2, 1.7 Hz, 1H, Ar*H*), 7.37 (dd, *J* = 5.3, 3.6 Hz, 1H, Ar*H*), 6.92 (dd, *J* = 8.3, 0.9 Hz, 1H, Ar*H*). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.6, 141.5, 137.1, 134.1, 132.7, 131.0, 130.4, 125.2, 117.8, 104.2 *(one aromatic Carbon signal not resolved)*. **IR** ν 3080 (w), 2958 (w), 2925 (m), 2853 (w), 1716 (w), 1622 (s), 1603 (s), 1558 (m), 1438 (w), 1354 (w), 1341 (w), 1299 (w), 1223 (w), 1006 (w), 951 (w), 834 (w), 830 (w). **HRMS** (ESI) calcd for $C_{11}H_8IO_2S^+$ $[M+H]^+$ 330.9284; found 330.9291.

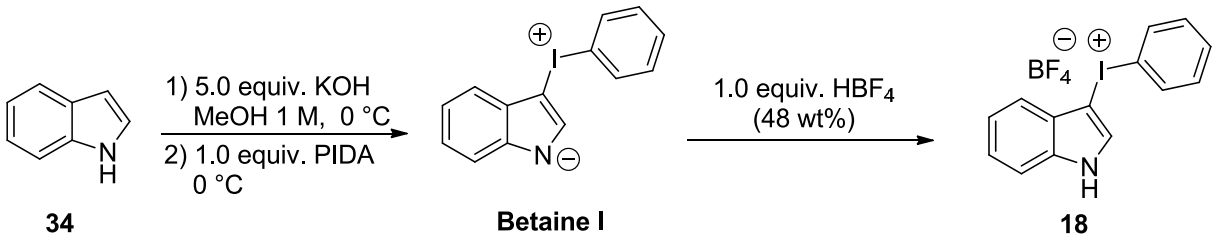
1-(3-1*H*-2,5-dimethylfuran)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one (9t)



9t

Starting from commercially available 2,5-dimethylfuran (107 µL, 1.00 mmol) and using $In(OTf)_3$ as the Lewis Acid (20 mol%), after 24 hours 1-(3-1*H*-2,5-dimethylfuran)-1*H*-1λ3 -benzo[b]iodo-3(2*H*)-one (9t) (47.0 mg, 0.137 mmol, 14% yield) was obtained as a brown resin. Rf: 0.3 (DCM:MeOH 9:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.28 (dd, *J* = 7.4, 1.8 Hz, 1H, Ar*H*), 7.50 (t, *J* = 7.3 Hz, 1H, Ar*H*), 7.43 (td, *J* = 7.7, 7.3, 1.8 Hz, 1H, Ar*H*), 7.00 (d, *J* = 8.1 Hz, 1H, Ar*H*), 6.21 (s, 1H, Ar*H*), 2.42 (s, 3H, *FuraneCH_3*), 2.31 (s, 3H, *FuraneCH_3*). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.9, 158.9, 154.2, 133.5, 133.1, 132.4, 130.4, 125.4, 115.0, 110.4, 88.0, 13.4, 13.2. **IR** ν 3430 (w), 3111 (w), 3065 (w), 2923 (w), 2854 (w), 1607 (s), 1559 (m), 1438 (m), 1348 (m), 1298 (w), 1229 (w), 1128 (w), 1039 (w), 1007 (w), 926 (w), 831 (m). **HRMS** (ESI) calcd for $C_{13}H_{12}IO_3^+$ $[M+H]^+$ 342.9826; found 342.9827.

2.3 Preparation of β-Phenyliodonioindole Tetrafluoroborate (18).



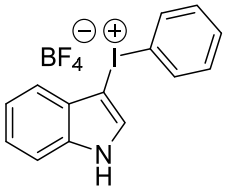
Following a reported procedure,[13] to a stirred solution of fine crushed KOH (5.61 g, 100 mmol, 5.00 equiv.) in MeOH (20.0 mL, 1.0 M), 1*H*-indole **34** (2.34 g, 20.0 mmol, 1.00 equiv.) was added in portions at 0 °C. The resulting mixture was left stirring at 0 °C until complete dissolution of the 1*H*-indole (1.5 h). Then PIDA (6.44 g, 20.0 mmol, 1.00 equiv.) was added portionwise and the reaction mixture left stirring at 0 °C for 1.5 h. **Betaine I** intermediate (dark yellow green solid in suspension) was then removed by filtration over a glass-synthered funnel, washed with cold MeOH and $CHCl_3$ and air dried in the dark at 0 °C. **Betaine I** intermediate (2.20 g, 6.89 mmol, 35% yield) was obtained as a dark yellow green amorphous solid.

Caution: Betaine I is a highly unstable intermediate, it is reported to detonate at room temperature; do NOT grind it, it may explode. The Betaine I intermediate decomposes at -20 °C, it is recommended to be used immediately after its preparation.

HBF_4 (450 µL, 6.89 mmol, 1.00 equiv., 48 wt.% solution in H_2O) was added to EtOH (10 mL) and the resulting solution cooled at -15 °C; then **Betaine I** intermediate (2.20 g, 6.89 mmol, 1.00 equiv.) was added portionwise under vigorous stirring at -15 °C. After all of **Betaine I** had been added, the dark brown resulting reaction mixture was diluted with Et_2O (50 mL) and stirred for 1.5 h at -15 °C. Then stirring was stopped and the reaction left at -15 °C for 30 min. The resulting precipitate was then removed by filtration over a glass-synthered funnel and dried at 0 °C to give β-Phenyliodonioindole Tetrafluoroborate **18** (2.10 g, 5.16 mmol, 75% yield) as a yellowish green amorphous solid.

[13] B. Y. Karele, L. é. Treigute, S. V. Kalnin', I. P. Grinberga, O. Y. Neiland, *Chem. Heterocycl. Compd.* **1974**, *10*, 189–192.

Caution: β-Phenyliodonioindole Tetrafluoroborate 18 is an unstable salt and it was immediately used after its preparation.



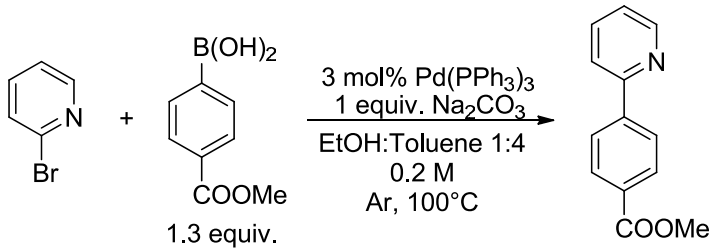
18

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.32 (brs, 1H, N*H*), 8.40 (d, J = 2.7 Hz, 1H, Ar*H*), 8.14 – 8.12 (m, 2H, Ar*H*), 7.74 (m, 1H, Ar*H*), 7.58 – 7.55 (m, 2H), 7.47 – 7.43 (m, 2H), 7.35 – 7.16 (m, 2H). *(presence of Et_2O residual solvent as the NMR analysis was performed on the slightly wet compound to prevent decomposition).* **^{13}C NMR** (101 MHz, DMSO-d_6) δ 135.8, 135.1, 134.0, 131.5, 127.1, 123.6, 121.9, 118.8, 117.3, 113.0, 78.0. *(one aromatic Carbon signal not resolved).* **IR** ν 3375 (s), 3132 (w), 1561 (m), 1491 (m), 1472 (s), 1411 (s), 1340 (m), 1328 (m), 1279 (s), 1244 (s). **HRMS** (ESI) calcd for $C_{14}H_{11}IN$ [M^+] 319.9931; found 319.9932.

3.1 Synthesis of Starting Materials.

All commercially available chemicals were purchased from the suppliers quoted in Paragraph 1.0 of Supplementary Informations: these chemicals were purified through a short plug of celite prior to their use in catalysis. The synthesis of non commercial available compounds is presented below.

Methyl 4-(pyridin-2-yl)benzoate (44)



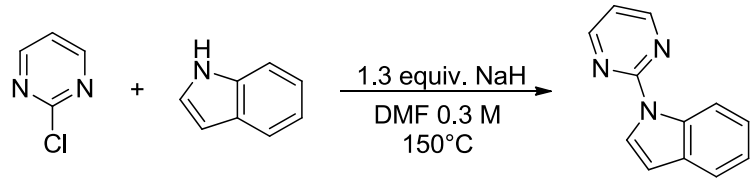
42 **43** **44**

Following a reported procedure,[14] to a solution of commercially available 2-bromopyridine **42** (100 µL, 1.00 mmol) in a mixture of 4/1 toluene/EtOH (5 mL, 0.2 M) was added Na_2CO_3 (106 mg, 1.00 mmol, 1.00 equiv.) followed by $Pd(PPh_3)_4$ (34.7 mg, 30.0 µmol, 3 mol %) and (4-(methoxycarbonyl)phenyl)boronic acid **43** (234 mg, 1.30 mmol, 1.30 equiv.) under argon atmosphere in a 50 mL two-necked flask. The reaction mixture was refluxed for 12 h, and then cooled to room temperature. To the reaction mixture was added sat. aqueous NH_4Cl (15 mL), then the mixture was extracted by EtOAc (3x5 ml). The combined organic extracts were dried over $MgSO_4$, filtered and and concentrated *in vacuo*. The resulting crude product was purified by flash chromatography (Pentane:EtOAc 4:1) to afford methyl 4-(pyridin-2-yl)benzoate **44** (181 mg, 0.849 mmol, 85% yield) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 4.7 Hz, 1H, Ar*H*), 8.06 (d, *J* = 8.4 Hz, 2H, Ar*H*), 7.98 (d, *J* = 8.3 Hz, 2H, Ar*H*), 7.73 – 7.63 (m, 2H, Ar*H*), 7.19 (q, *J* = 4.6 Hz, 1H, Ar*H*), 3.85 (s, 3H COO*Me*). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.8, 156.1, 149.8, 143.4, 136.8, 130.3, 130.0, 126.7, 122.8, 120.9, 52.1.**IR** ν 2944 (w), 2848 (w), 1708 (s), 1606 (w), 1586 (m), 1466 (w), 1435 (m), 1405 (w), 1319 (w), 1274 (s), 1194 (m), 1183 (m), 1153 (w), 1111 (s), 1014 (m), 965 (m), 868 (w), 830 (w), 797 (w), 754 (vs), 699 (m). NMR values are in accordance with the data reported in literature.[15]

[14] H. Mizuno, J. Takaya, N. Iwasawa, *J. Am. Chem. Soc.* **2011**, *133*, 1251–1253

[15] K. Muto, T. Hatakeyama, K. Itami, J. Yamaguchi, *Org. Lett.* **2016**, *18*, 5106–5109.

1-(Pyrimidin-2-yl)-1*H*-indole (46)

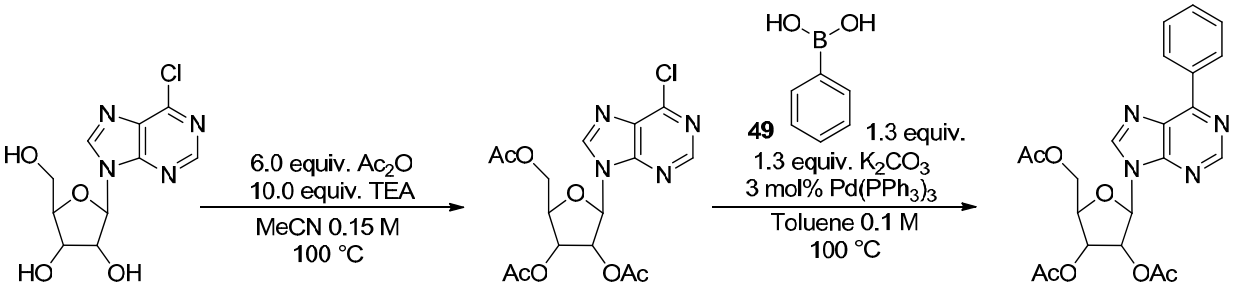


45 **34** **46**

Following a reported procedure,[16] commercially available 1*H*-indole **34** (586 mg, 5.00 mmol) was dissolved in N,N-dimethylformamide (15.0 mL, 0.3M) and sodium hydride (60% suspension in mineral oil, 300 mg, 7.50 mmol, 1.50 equiv.) was added at r.t. and the reaction mixture was stirred for one hour. Upon seizing of gas release, commercially available 2-chloropyrimidine **45** (573 mg, 5.00 mmol, 1.00 equiv.) was added portionwise. The reaction was heated up to 150 °C and stirred overnight. After 10 hours the reaction was allowed cooling to r.t. and was then quenched with water (20 mL). The majority of the solvent was removed under reduced pressure, then the crude was diluted with Et_2O (25 mL), the organic layer washed with brine (3x10 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. Flash column chromatography (Pentane:EtOAc 4:1) afforded 1-(pyrimidin-2-yl)-1*H*-indole **46** (926 mg, 4.74 mmol, 95% yield) as a light brown oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.94 (d, *J* = 8.4 Hz, 1H, Ar*H*), 8.75 (d, *J* = 4.8 Hz, 2H, Ar*H*), 8.40 (d, *J* = 3.7 Hz, 1H, Ar*H*), 7.75 (d, *J* = 7.8 Hz, 1H, Ar*H*), 7.51 – 7.43 (m, 1H, Ar*H*), 7.37 (t, *J* = 7.5 Hz, 1H, Ar*H*), 7.07 (t, *J* = 4.8 Hz, 1H, Ar*H*), 6.83 (d, *J* = 3.6 Hz, 1H, Ar*H*). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.7, 157.4, 135.1, 131.1, 125.6, 123.4, 121.9, 120.6, 116.2, 115.8, 106.6. **IR** ν 3138 (w), 3108 (w), 1575 (s), 1525 (m), 1456 (s), 1309 (m), 1204 (s), 1080 (m), 970 (s), 776 (m), 750 (w), 731 (w). NMR values are in accordance with the data reported in literature.[17]

(2*R*,3*R*,4*R*,5*R*)-2-(Acetoxymethyl)-5-(6-phenyl-9*H*-purin-9-yl)tetrahydrofuran-3,4-diyl diacetate (50)

[16] M. Nishino, K. Hirano, T. Satoh, M. Miura, *Angew. Chem. Int. Ed.* **2012**, *51*, 6993–6997.
[17] L. Ackermann, A. V. Lygin, *Org. Lett.* **2011**, *13*, 3332–3335.



47 **48** **50**

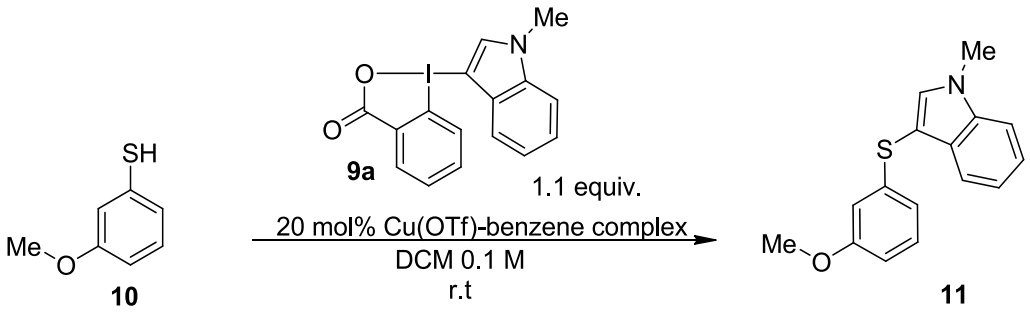
Following a reported procedure,[18] commercially available (2*R*,3*R*,4*S*,5*R*)-2-(6-chloro-9*H*-purin-9-yl)-5-(hydroxymethyl)tetrahydrofuran-3,4-diol **47** (573 mg, 2.00 mmol, 1.00 equiv.) was suspended in MeCN (12.5 mL, 0.15 M). Then Triethylamine (2.90 mL, 20.0 mmol, 10.0 equiv.) and Acetic Anhydride (1.10 mL µl, 12.00 mmol, 6.00 equiv.) were added at 0° C. After stirring for 1h at room temperature, the mixture was refluxed for 5 hours. The resulting solution was evaporated to dryness and EtOAc (30 mL) and water (30 mL) were added. The organic layer was separated, dried over Na_2SO_4, filtered and concentrated under reduced pressure to give a light brown oil, which was recrystallized from EtOAc/Ether to give (2*R*,3*R*,4*R*,5*R*)-2-(acetoxymethyl)-5-(6-chloro-9*H*-purin-9-yl)tetrahydrofuran-3,4-diyl diacetate **48** (693 mg, 1.68 mmol, 84 % yield)

Subsequently, to a solution of (2*R*,3*R*,4*R*,5*R*)-2-(acetoxymethyl)-5-(6-chloro-9*H*-purin-9-yl)tetrahydrofuran-3,4-diyl diacetate **48** (500 mg, 1.21 mmol) in a mixture of 4/1 toluene (12 mL, 0.1 M) was added K_2CO_3 (218 mg, 1.58 mmol, 1.30 equiv.) followed by $Pd(PPh_3)_4$ (42.0 mg, 30.0 µmol, 3 mol %) and phenylboronic acid **49** (192 mg, 1.58 mmol, 1.30 equiv.) under argon atmosphere in a 20 mL two-necked flask. The reaction mixture was refluxed for 12 h, and then cooled to room temperature. To the reaction mixture was added sat. aqueous NH_4Cl (15 mL), then the mixture was extracted by EtOAc (3x5 mL). The combined organic extracts were dried over $MgSO_4$, filtered and and concentrated *in vacuo*. The resulting crude product was purified by flash chromatography (Pentane:EtOAc 4:1) to afford (2*R*,3*R*,4*R*,5*R*)-2-(acetoxymethyl)-5-(6-phenyl-9*H*-purin-9-yl)tetrahydrofuran-3,4-diyl diacetate **50** (523 mg, 1.15 mmol, 95% yield) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.95 (s, 1H, Ar*H*), 8.68 (dd, *J* = 8.0, 1.8 Hz, Ar*H*), 8.21 (s, 1H, Ar*H*), 7.52 – 7.43 (m, 3H, Ar*H*), 6.22 (d, *J* = 5.3 Hz, 1H, *CH*), 5.95 (t, *J* = 5.4 Hz, 1H, *CH*),

[18] M. A. Ali, X. Yao, H. Sun, H. Lu, *Org. Lett.* **2015**, *17*, 1513–1516.

5.64 (m, 1H, *CH*), 4.45 – 4.24 (m, 3H, *CH* + *CH*$_2$), 2.08 (s, 3H, *CH*$_3$), 2.05 (s, 3H, *CH*$_3$), 2.00 (s, 3H, *CH*$_3$. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.9, 169.2, 169.0, 154.7, 152.1, 151.6, 142.5, 135.0, 131.2, 130.7, 129.4, 128.2, 86.1, 79.9, 72.7, 70.2, 62.7, 20.3, 20.1, 20.0. **IR** ν 2926 (m), 1749 (s), 1583 (s), 1566 (s), 1439 (m), 1220 (s), 1101 (m), 766 (m), 693 (m). NMR values are in accordance with the data reported in literature.[18]

3.2 Procedure for Thio-indolization *via* Lewis-acid activated IndoleBX



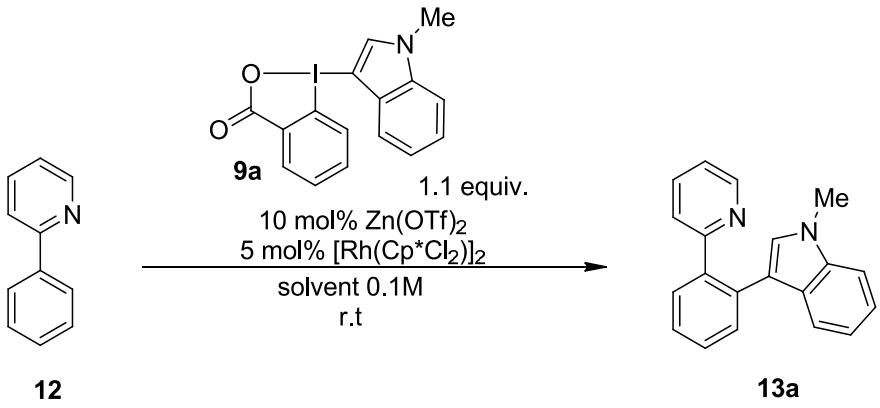
Commercially available 3-methoxybenzenethiol **10** (25.0 μL, 0.200 mmol, 1.00 equiv.) was dissolved in dry DCM (2.0 mL, 0.1 M) under nitrogen atmosphere. Then IndoleBX **9a** (75.0 mg, 0.200 mmol, 1.00 equiv.) and the reaction left stirring at r.t. overnite. The majority of the solvent was removed under reduced pressure, then the crude was diluted with EtOAc (25 mL), the organic layer washed with brine (3x10 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. Flash column chromatography (Pentane:EtOAc 4:1) afforded 3-((3-methoxyphenyl)thio)-1-methyl-1H-indole **11** (18.1 mg, 67.0 μmol, 34% yield) as a light yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.9 Hz, 1H, Ar*H*), 7.38 (d, *J* = 8.1 Hz, 1H, Ar*H*), 7.34 (s, 1H, Ar*H*), 7.30 (m, 1H, Ar*H*), 7.16 (ddd, *J* = 7.9, 6.8, 0.9 Hz, 1H, Ar*H*), 7.06 (t, *J* = 8.0 Hz, 1H, Ar*H*), 6.71 – 6.63 (m, 2H, Ar*H*), 6.59 (dd, *J* = 8.1, 2.5 Hz, 1H, Ar*H*), 3.85 (s, 3H, N*Me*), 3.68 (s, 3H, O*Me*). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.0, 141.4, 137.7, 135.3, 129.7, 129.6, 122.7, 120.7, 119.9, 118.3, 111.6, 110.3, 109.8, 100.4, 55.4, 33.4. NMR values are in accordance with the data reported in literature.[19]

[19] H. Qi, T. Zhang, K. Wan, M. Luo, *J. Org. Chem.* **2016**, *81*, 4262–4268.

3.3 Optimization of the Rh-Catalyzed Indolization of Arenes *via* C-H activation.

In a vial, 2-phenylpyridine **12** (14.0 µl, 0.100 mmol), 1-(3-1-methyl-1*H*-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one **9a** (1.10 equiv.), the catalyst system (1.25-5 mol%) and the relative additive (2.5-20 mol%) were dissolved in the appropriate dry solvent (0.1 M) under nitrogen. The reaction mixture was degassed (freeze-thaw-pump) and then stirred at the reported T in °C overnight. The reaction mixture was then allowed to cool to r.t., the organic layer was washed with sat. aqueous $NaHCO_3$ (2 mL), and the solvent was removed under reduced pressure. Flash column chromatography (Pentane:EtOAc 4:1) afforded the desired product **13a** (*see compound **13a**'s characterization for all the chemical data*).

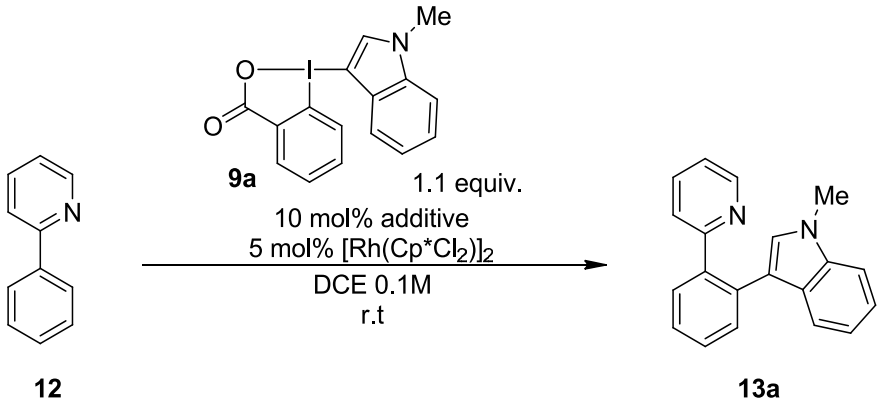
Table S3: Screening of solvents



Entry	Solvent	Yield%[a]
1	DCM	25%
2	DCE	55%
3	MeOH	-
4	EtOH	-
5	TFE	16%
6	Chlorobenzene	-
7	1,2-Chlorobenzene	-
8	Toluene	-
9	DMF (110°C)	66%

a) Substrate **12** (0.100 mmol), IndoleBX **9a** (0.110 mmol), $[Rh(Cp^*Cl_2)]_2$ (5 mol%), $Zn(OTf)_2$ (10 mol%) and solvent (0.1 M) at 25 °C. Isolated yield after flash chromatography is given.

Table S4: Screening of additives

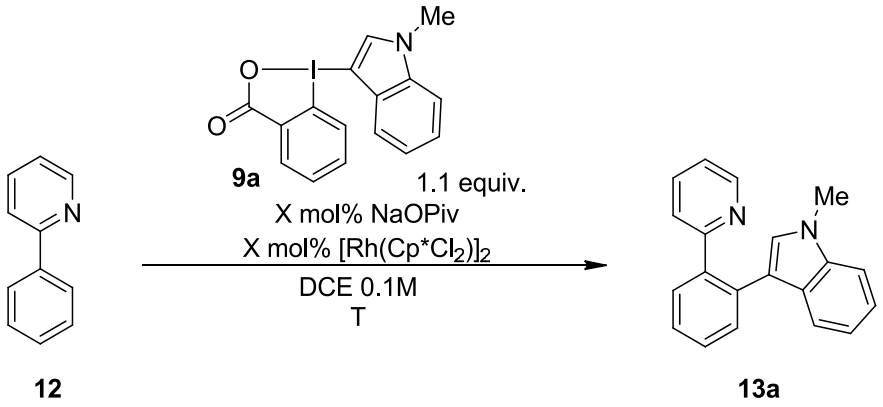


12 **13a**

Entry	Additive	Yield%[a]
1	-	-
2	$Zn(OTf)_2$	55%[b]
3	$Sc(OTf)_3$	56%[c]
4	K_2CO_3	28%
5	$Zn(NTf_2)_2$	56%
6	$AgNTf_2$	-
7	$AgSbF_6$[d]	17%
8	NaOAc	69%
9	KOAc	37%
10	**NaOPiv**	**72%**
11	KOPiv	49%
12	CsOPiv	36%

a) Substrate **12** (0.100 mmol), IndoleBX **9a** (0.110 mmol), $[Rh(Cp^*Cl_2)]_2$ (5 mol%), **additive** (10 mol%) and DCE (0.1 M) at 25 °C. Isolated yield after flash chromatography is given. b) incomplete conversion, remaining starting material completely recovered. c) decomposition observed. d) T of the reaction is 50°C.

Table S5: Screening of the catalyst:additive ratio at different T°C.



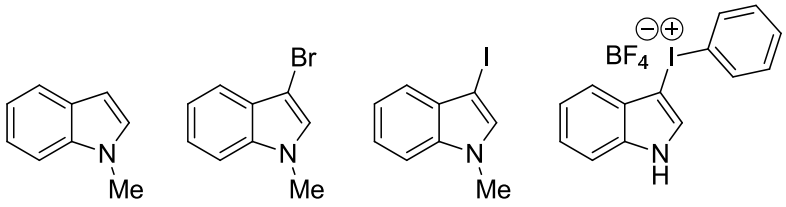
12 **13a**

Entry	Catalyst (mol%)	Additive (mol%)	T°C	Yield%[a]
1	$[Rh(Cp^*Cl_2)_2]$ (1.25)/$AgSbF_6$ (2.5)	NaOPiv (2.5)	r.t.	traces[b]
2	$[Rh(Cp^*Cl_2)_2]$ (1.25)/$AgSbF_6$ (10)	NaOPiv (10)	r.t.	traces[b]
3	$[Rh(Cp^*Cl_2)_2]$ (1.25)/$AgSbF_6$ (10)	NaOPiv (10)	40°C	traces[b]
4	$[Rh(Cp^*Cl_2)_2]$ (1.25)/$AgSbF_6$ (10)	NaOPiv (10)	50°C	37%[b]
5	$[Rh(Cp^*Cl_2)_2]$ (2.5)/$AgSbF_6$ (5)	NaOPiv (5)	r.t.	traces[c]
6	$[Rh(Cp^*Cl_2)_2]$ (2.5)/$AgSbF_6$ (10)	NaOPiv (10)	r.t.	78%
7	$[Rh(Cp^*Cl_2)_2]$ (2.5)/$AgSbF_6$ (10)	NaOPiv (10)	50°C	82%
8	**$[Rh(Cp^*Cl_2)_2]$ (2.5)/$AgSbF_6$ (10)**	**NaOPiv (10)**	**80°C**	**85%**
9	$[Rh(Cp^*Cl_2)_2]$ (5)/$AgSbF_6$ (10)	NaOPiv (10)	r.t.	90%

a)Substrate **12** (0.100 mmol), IndoleBX **9a** (0.110 mmol), $[Rh(Cp^*Cl_2)]_2$ (**X** mol%), NaOPiv (**X** mol%) and DCE (0.1 M) at 25 °C. Isolated yield after flash chromatography is given. b) the reaction time was 48 hours, hypervalent iodine decomposition was observed.

3.4 Control experiments for the Indolization of Arenes via C-H activation.

In order to assess the superiority of our reagents in catalysis compared to other indole-transfer reagents already known in cross-coupling reactions, we tested the latter under different sets of conditions. Substrates **8a**, **16** and **17** are commercially available, while compound **18** needed to be prepared and immediately used in the catalytic process.



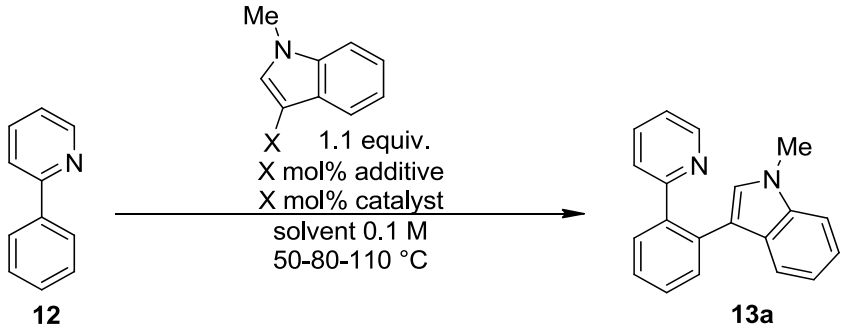
8a **16** **17** **18**

Substrates **8a**, **16** and **17** were tested under our optimized conditions (*table S6, entries 1-3*) at different temperatures (r.t.-50-60-110 °C): no conversion was observed. The hypervalent indolinium salt **18** was also tested in presence of $NaSbF_6$ (*table S6, entry 4*) as an alternative salt to promote the exchange of BF_4^- counteranion with SbF_6^-, but no conversion was observed. Substrates **16** and **17** were then tested under established conditions for Pd-catalyzed cross couplings of C*3*-halogenated indoles. 3- Bromo-N-methylindole **16** was tested under Hartwig Pd-catalyzed amination conditions[20] (*table S6, entry 5*), carbonylative Sonogashira conditions[21] (*table S6, entry 6*) and Heck conditions[22] (*table S6, entry 7*): the desired product was never observed. Furthermore, when 3-Iodo-*N*-methylindole **17** was tested under Suzuki and Sonogashira cross coupling conditions[23] (*table S6, entries 8-9*) no product was detected.

In *Table S7* oxidative methods were examined (*table S7, entries 1,4*),[24] Shi conditions (*table S7, entries 2,5*),[25] and Fagnou conditions (*table S7, entries 3,6*);[26] the desired compound was never observed.

[20] M. W. Hooper, M. Utsunomiya, J. F. Hartwig, *J. Org. Chem.* **2003**, *68*, 2861–2873.
[21] K. T. Neumann, S. R. Laursen, A. T. Lindhardt, B. Bang-Andersen, T. Skrydstrup, *Org. Lett.* **2014**, *16*, 2216–2219.
[22] D. S. G. Spinella, A. Izzo, *Synlett* **2006**, 1319–1322.
[23] B. Witulski, J. R. Azcon, C. Alayrac, A. Arnautu, V. Collot, S. Rault, *Synlett* **2005**, 771–780.
[24] J. Wencel-Delord, C. Nimphius, H. Wang, F. Glorius, *Angew. Chem. Int. Ed.* **2012**, *51*, 13001–13005.
[25] B.-J. Li, S.-L. Tian, Z. Fang, Z.-J. Shi, *Angew. Chem. Int. Ed.* **2008**, *47*, 1115–1118.
[26] D. R. Stuart, E. Villemure, K. Fagnou, *J. Am. Chem. Soc.* **2007**, *129*, 12072–12073.

Table S6: Control experiments (I)

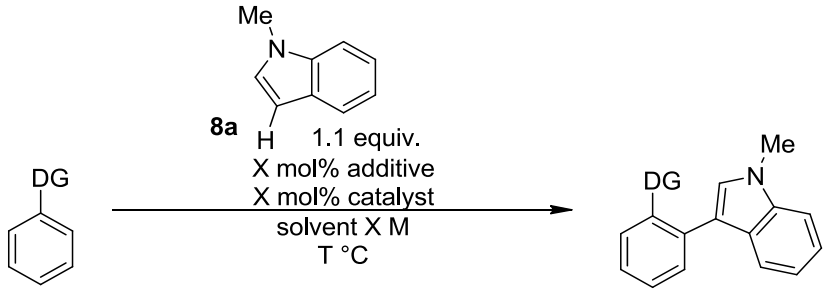


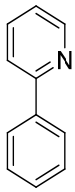
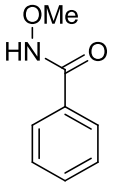
12 **13a**

Entry	X	Catalyst (mol%)	Additive (mol%)	Solvent (M)	Yield%[a]
1	H **(8a)**	$[Rh(Cp^*Cl_2)_2]$ (2.5)/$AgSbF_6$ (10)	NaOPiv (10)	DCE (0.1 M)	-
2	I **(17)**	$[Rh(Cp^*Cl_2)_2]$ (2.5)/$AgSbF_6$ (10)	NaOPiv (10)	DCE (0.1 M)	-
3	$I^{(III)}$ **(18)**	$[Rh(Cp^*Cl_2)_2]$ (2.5)/$NaSbF_6$ (10)	NaOPiv (10)	DCE (0.1 M)	-
4	$I^{(III)}$ **(18)**	$[Rh(Cp^*Cl_2)_2]$ (2.5)/$AgSbF_6$ (10)	NaOPiv (10)	DCE (0.1 M)	-
5	Br **(16)**	$Pd(dba)_2$ (5)/ PPh_3 (5)	-	Toluene (0.2 M)	-
6	Br **(16)**	$PdCl_2$ (5)/ XanthPhos (5)	TEA (3 equiv.)	Dioxane (0.2 M)	-
7	Br **(16)**	$Pd(OAc)_2$(20)/ P(*o*-Tol)$_3$ (20)	TEA (3 equiv.)	Toluene (0.2 M)	-
8	I **(17)**	$PdCl_2PPh_3$ (5)	CuI (10)/ TEA (3 equiv.)	DMF (0.1 M)	-
9	I **(17)**	$Pd(PPh_3)_3$ (2.5)	Na_2CO_3 (1 equiv.)	DMF (0.1 M)	-

a)Substrate (0.100 mmol), Indole source (0.110 mmol), Catalyst (**X** mol%), Additive (**X** mol%) and Solvent (0.1 M) at 50°-80°-110°C.T

Table S7: Control experiments (II)

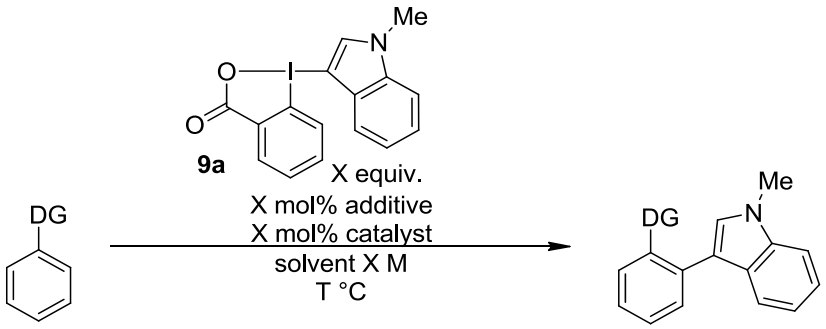


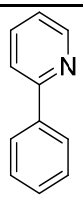
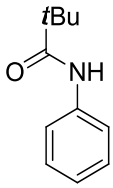
Entry	Substrate	Equiv.	Equiv. 8a	Catalyst (mol%)	Additive (mol%)	Solvent (M)/ T °C	Yield%[a]
1	 **12**	1	20	$[Rh(Cp^*Cl_2)_2]$ (2.5)/CsOPiv(20)	PivOH (50) 2.0 equiv. C_6Br_6/2.2 equiv. $Cu(OAc)_2$	2Cl-*p*-xylene (0.33 M)/140 °C	-
2		1	6.0	$Pd(OAc)_2$(10)	$Cu(OTf)_2$ (20) O_2 1 atm.	EtCOOH (0.2 M)/120°C	-
3		60	1	$Pd(TFA)_2$(5)	3.0 equiv. $Cu(OAc)_2$/6.0 equiv. PivOH	neat in arene (0.15 M)	-
4	 **14**	1	20	$[Rh(Cp^*Cl_2)_2]$ (2.5)/CsOPiv(20)	PivOH (50) 2.0 equiv. C_6Br_6/2.2 equiv. $Cu(OAc)_2$	2Cl-*p*-xylene (0.33 M)/140 °C	-
5		1	6.0	$Pd(OAc)_2$(10)	$Cu(OTf)_2$ (20) O_2 1 atm.	EtCOOH (0.2 M)/120 °C	-
6		60	1	$Pd(TFA)_2$(5)	3.0 equiv. $Cu(OAc)_2$/6.0 equiv. PivOH	neat in arene (0.15 M)/110 °C	-

a)Reaction performed on 0.1 mmol of the limiting reagent; substrate (**X** mmol), Indole **8a** (**X** mmol), Catalyst (**X** mol%), Additive (**X** mol%) and Solvent (**X** M) at T °C.

Finally, in *Table S8* are reported control experiments employing conditions suitable for hypervalent iodine reagents such as Kita conditions (*table S8, entry 1*),[27] Sanford conditions (*table S8, entry 2*),[28] and Daugulis conditions (*table S8, entry 3*);[29] the desired compounds was not observed also in this case; All conditions screened in *Tables S6, S7* and *S8* failed to afford the desired product, thus demonstrating the unique reactivity of our reagents.

Table S8: Control experiments (III)



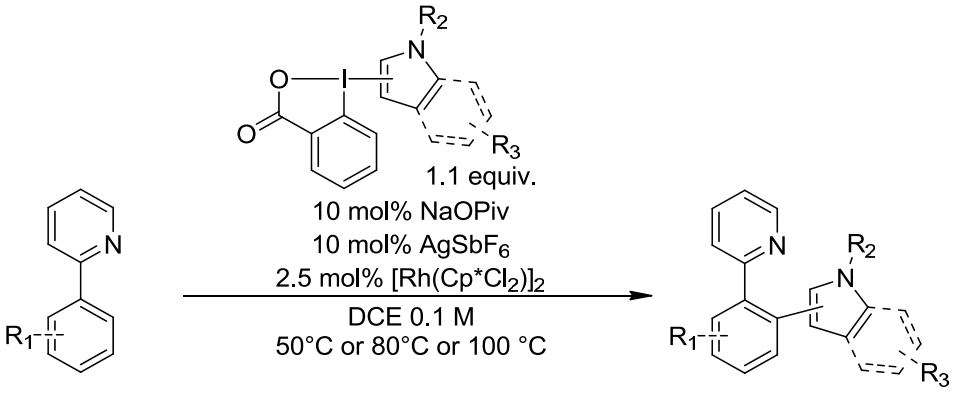
Entry	Substrate	Equiv.	Equiv. 13a	Catalyst (mol%)	Additive (mol%)	Solvent (M)/ T °C	Yield%[a]
1	 **12**	1.5	1	-	2.0 equiv. TMSBr	HFIP (0.1 M)	-
2		1	1.5	$Pd(OAc)_2$ (5)	-	MeCOOH (0.1 M)/110 °C	-
3	 **13**	1	5	$Pd(OAc)_2$ (5)	-	MeCOOH (1.5 M)/90 °C	-

a)Reaction performed on 0.1 mmol of the limiting reagent; substrate (**X** mmol), Indole source **19a** (**X** mmol), Catalyst (**X** mol%), Additive (**X** mol%) and Solvent (**X** M) at T °C.

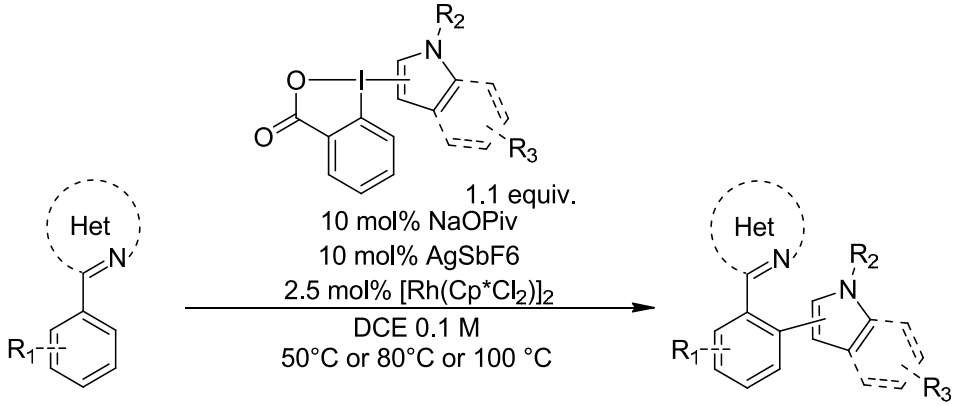
[27] Y. Kita, K. Morimoto, M. Ito, C. Ogawa, A. Goto, T. Dohi, *J. Am. Chem. Soc.* **2009**, *131*, 1668–1669.
[28] D. Kalyani, N. R. Deprez, L. V. Desai, M. S. Sanford, *J. Am. Chem. Soc.* **2005**, *127*, 7330–7331.
[29] O. Daugulis, V. G. Zaitsev, *Angew. Chem. Int. Ed.* **2005**, *44*, 4046–4048.

3.5 Scope of the Rh-Catalyzed Indolization *via* C-H activation.

General Procedures GP3-GP4 for Rh-Catalyzed Hetero-arylation *via* C-H activation



GP3: In a vial, the corresponding aryl-pyridine (0.300 mmol, 1 .00 equiv.), the relative heterocyclic hypervalent iodine reagent **9a-9r** (0.330 mmol, 1.10 equiv.), $[Rh(Cp^*Cl_2)]_2$ (4.60 mg, 7.50 µmol, 2.5 mol%), $AgSbF_6$ (10.3 mg, 30.0 µmol, 10 mol%) and NaOPiv (3.70 mg, 30.0 µmol, 10 mol%) were dissolved in dry 1,2-DCE (3 ml, 0.1 M) under nitrogen. the reaction mixture was degassed (freeze-thaw-pump) and stirred at the reported T in °C overnight. The reaction mixture was then allowed to cool to r.t., the organic layer was washed with sat. aquoeus $NaHCO_3$ (2ml), and the solvent was removed under reduced pressure. Flash column chromatography (Pentane:EtOAc) afforded the desired products **13a-13r.**



GP4: In a screw capped vial, the corresponding heterocycle (0.300 mmol, 1.00 equiv.), the relative heterocyclic hypervalent iodine reagent **9a** (0.330 mmol, 1.10 equiv.), $[Rh(Cp^*Cl_2)]_2$ (4.60 mg, 7.50 µmol, 2.5 mol%), $AgSbF_6$ (10.3 mg, 30.0 µmol, 10 mol%) and NaOPiv (3.70 mg, 30.0 µmol, 10 mol%) were dissolved in dry 1,2-DCE (3 ml, 0.1M) under nitrogen. the reaction mixture was

degassed (freeze-thaw-pump) and stirred at the reported T in °C overnight. The reaction mixture was then allowed to cool to r.t., the organic layer was washed with sat. aqueous $NaHCO_3$ (2 mL), and the solvent was removed under reduced pressure. Flash column chromatography (Pentane:EtOAc) afforded the desired products **19-25**.

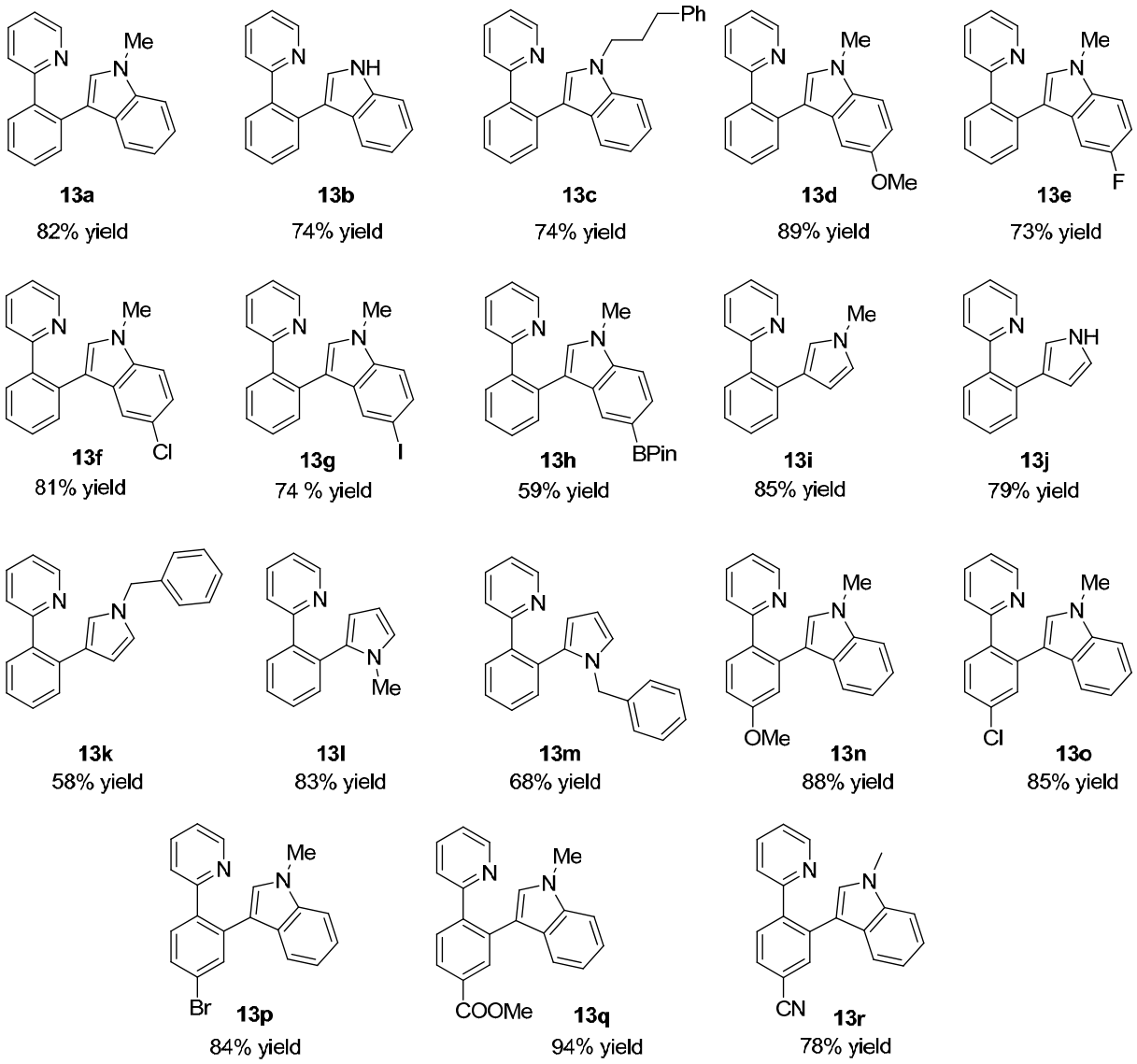
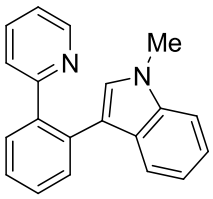


Figure S2: *Scope with Aryl-pyridines.*

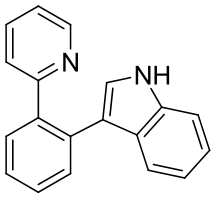
1-Methyl-3-(2-(pyridin-2-yl)phenyl)-1*H*-indole (13a)



13a

Starting from commercially available 2-phenylpyridine **12** (43.0 µl, 0.300 mmol, 1.00 equiv.) and with 1-(3-1-methyl-1H-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one **9a** (124 mg, 0.330 mmol, 1.10 equiv.) at 50 °C, 2-(2-(1-methyl-1H-pyrrol-2-yl)phenyl)pyridine **9a** (60.0 mg, 0.256 mmol, 85% yield) was obtained as a pale yellow oil. Rf: 0.48 (Pentane:EtOAc 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.65 (m, 1H, Ar*H*), 7.73 (dd, *J* = 7.4, 1.7 Hz, 1H, Ar*H*), 7.59 (m, 1H, Ar*H*), 7.52 – 7.38 (m, 3H, Ar*H*), 7.35 – 7.22 (m, 2H, Ar*H*), 7.19 (ddd, *J* = 8.2, 7.0, 1.1 Hz, 1H, Ar*H*), 7.11 – 6.94 (m, 3H, Ar*H*), 6.71 (s, 1H, N*CH*C), 3.70 (s, 3H, N*CH*$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.9, 149.3, 139.8, 136.8, 135.1, 133.3, 131.0, 130.5, 128.4, 128.2, 127.0, 126.7, 124.9, 121.6, 121.2, 119.9, 119.5, 115.4, 109.1, 32.7. **IR** ν 3057 (w), 2934 (w), 1725 (w), 1586 (s), 1545 (m), 1461 (s), 1425 (s), 1377 (s), 1330 (m), 1219 (m), 1162 (w), 1091 (w), 1024 (w), 942 (w), 910 (w). **HRMS** (ESI) calcd for $C_{20}H_{17}N_2^+$ $[M+H]^+$ 285.1386; found 285.1388.

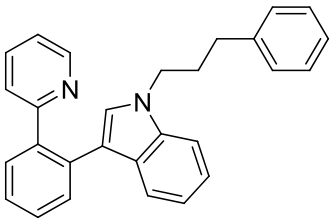
3-(2-(pyridin-2-yl)phenyl)-1*H*-indole (13b)



13b

Starting from commercially available 2-phenylpyridine **8** (43.0 µl, 0.300 mmol, 1.00 equiv.) and with 1-(3-1*H*-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one **9b** (120 mg, 0.330 mmol, 1.10 equiv.) at 50 °C, 2-(2-(1-methyl-1*H*-pyrrol-2-yl)phenyl)pyridine **13b** (60.3 mg, 0.223 mmol, 74% yield) was obtained as a slightly brown foam. Rf: 0.30 (Pentane:EtOAc 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.63 (m, 1H, Ar*H*), 8.40 (s, 1H, N*H*), 7.72 (dd, *J* = 7.3, 1.8 Hz, 1H, Ar*H*), 7.60 (dd, *J* = 7.3, 1.8 Hz, 1H, Ar*H*), 7.51 – 7.39 (m, 3H, Ar*H*), 7.33 – 7.22 (m, 2H, Ar*H*), 7.14 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H, Ar*H*), 7.02 (m, 3H, Ar*H*), 6.76 (d, *J* = 2.5 Hz, 1H, NHC*H*C). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.8, 149.0, 139.8, 135.9, 135.3, 133.3, 131.0, 130.5, 128.5, 126.9, 126.6, 125.0, 123.7, 122.0, 121.3, 119.9, 119.7, 116.7, 111.0. **IR** ν 3409 (w), 3170 (w), 3058 (w), 2921 (w), 1668 (w), 1600 (m), 1589 (s), 1544 (w), 1489 (w), 1464 (s), 1332 (w), 1245 (m), 1153 (w), 1098 (w), 910 (m). **HRMS** (ESI) calcd for $C_{19}H_{15}N_2^+$ $[M+H]^+$ 271.1230; found 271.1233.

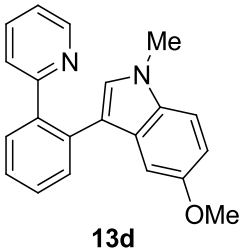
1-(3-Phenylpropyl)-3-(2-(pyridin-2-yl)phenyl)-1*H*-indole (13c)



13c

Starting from commercially available 2-phenylpyridine **12** (43.0 µl, 0.300 mmol) and with 1-(3-1-(3-phenylpropyl)-1*H*-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one **9e** (159 mg, 0.330 mmol, 1.10 equiv.) at 80 °C, 1-(3-phenylpropyl)-3-(2-(pyridin-2-yl)phenyl)-1*H*-indole **13c** (86.0 mg, 0.221 mmol, 74% yield) was obtained as an orange oil. Rf: 0.48 (Pentane:EtOAc 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.67 (m, 1H, Ar*H*), 7.76 (dd, *J* = 7.4, 1.7 Hz, 1H, Ar*H)*, 7.67 (dd, *J* = 7.4, 1.5 Hz, 1H, Ar*H*), 7.58 (d, *J* = 7.9 Hz, 1H, Ar*H*), 7.51 (td, *J* = 7.4, 1.7 Hz, 1H, Ar*H*), 7.47 (td, *J* = 7.4, 1.5 Hz, 1H, Ar*H*), 7.34 – 7.19 (m, 6H, Ar*H*), 7.09 (m, 3H, Ar*H*), 7.06 – 7.01 (m, 2H, Ar*H*), 6.71 (s, 1H, CH_2NCHC), 4.04 (t, *J* = 6.8 Hz, 2H, $PhCH_2CH_2CH_2N$), 2.48 (dd, *J* = 8.6, 6.7 Hz, 2H, $PhCH_2CH_2CH_2N$), 2.08 (dq, *J* = 9.0, 6.9 Hz, 2H, $PhCH_2CH_2CH_2N$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.0, 149.1, 140.8, 139.8, 136.0, 135.2, 133.3, 130.9, 130.5, 128.5, 128.3, 127.4, 127.3, 126.7, 126.1, 125.1, 121.6, 121.3, 119.9, 119.6, 115.2, 109.3, 45.4, 32.7, 31.3 (*one Carbon signal not resolved*). **IR** ν 3059 (w), 3027 (w), 2932 (w), 1602 (w), 1585 (m), 1547 (w), 1496 (w), 1462 (s), 1424 (w), 1392 (w), 1372 (w), 1334 (w), 1167 (w), 1024 (w), 911 (w). **HRMS** (ESI) calcd for $C_{28}H_{25}N_2^+$ $[M+H]^+$ 389.2012; found 389.2016.

5-Methoxy-1-methyl-3-(2-(pyridin-2-yl)phenyl)-1*H*-indole (13d)

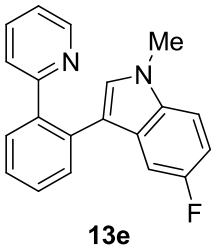


13d

Starting from commercially available 2-phenylpyridine **12** (43.0 µl, 0.300 mmol) and with 1-(3-5-methoxy-1-methyl-1*H*-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one **9g** (134 mg, 0.330 mmol, 1.10 equiv.) at 50 °C, 5-methoxy-1-methyl-3-(2-(pyridin-2-yl)phenyl)-1*H*-indole **13d** (84.0 mg, 0.267 mmol, 89% yield) was obtained as a yellow oil. Rf: 0.40 (Pentane:EtOAc 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.67 (dd, J = 4.9, 0.9 Hz, 1H, Ar*H*), 7.76 (dd, J = 7.2, 1.9 Hz, 1H, Ar*H*), 7.56 (dd, J = 7.2, 1.9 Hz, 1H, Ar*H*), 7.57 – 7.42 (m, 2H, Ar*H*), 7.26 (td, J = 7.7, 1.9 Hz, 1H, Ar*H*), 7.14 (d, J = 8.9 Hz, 1H, Ar*H*), 7.10 – 7.02 (m, 2H, Ar*H*), 6.84 (s, 1H, N*CH*C), 6.79 (dd, J = 8.9, 2.4 Hz, 1H, Ar*H*), 6.67 (d, J = 2.4 Hz, 1H, C*CH*COMe), 3.71 (s, 3H, NCH_3), 3.64 (s, 3H, OCH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.9, 153.9, 149.3, 139.4, 135.2, 133.4, 132.0, 131.0, 130.5, 128.5, 128.3, 126.9, 126.8, 124.9, 121.3, 115.3, 112.2, 109.8, 100.8, 55.6, 32.9. **IR** ν 3051 (w), 2946 (w), 1585 (m), 1489 (s), 1463 (m), 1424 (m), 1295 (w), 1266 (s),

1228 (m), 1210 (s), 1181 (w), 1136 (m), 1088 (w), 1031 (m), 866 (m). **HRMS** (ESI) calcd for $C_{21}H_{19}N_2O^+$ $[M+H]^+$ 315.1492; found 315.1493.

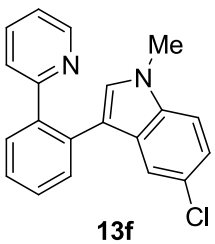
5-Fluoro-1-methyl-3-(2-(pyridin-2-yl)phenyl)-1*H*-indole (13e)



13e

Starting from commercially available 2-phenylpyridine **12** (43.0 µl, 0.300 mmol) and with 1-(3-5-fluoro-1-methyl-1*H*-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one **9h** (130 mg, 0.330 mmol, 1.10 equiv.) at 50 °C, 5-fluoro-1-methyl-3-(2-(pyridin-2-yl)phenyl)-1*H*-indole **13e** (66.0 mg, 0.218 mmol, 73% yield) was obtained as a yellow oil. Rf: 0.40 (Pentane:EtOAc 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.65 (d, *J* = 4.9 Hz, 1H, Ar*H*), 7.71 (d, *J* = 7.2 Hz, 1H, Ar*H*), 7.55 (d, *J* = 7.2 Hz, 1H, Ar*H*), 7.51 – 7.38 (m, 2H), 7.33 (t, *J* = 7.7 Hz, 1H, Ar*H*), 7.17 (dd, *J* = 9.0, 4.3 Hz, 1H, Ar*H*), 7.08 (t, *J* = 6.3 Hz, 1H, Ar*H*), 7.08 – 6.97 (m, 2H, Ar*H*), 6.91 (t, *J* = 9.0 Hz, 1H, Ar*H*), 6.77 (s, 1H, N*CH*C), 3.70 (s, 3H, N*CH*$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.8, 158.0 (d, *J* = 234.6 Hz), 149.3, 139.7, 135.2, 133.4, 132.9, 130.8, 130.6, 129.7, 128.5, 127.3 (d, *J* = 9.9 Hz), 126.9, 124.8, 121.3, 115.5 (d, *J* = 4.9 Hz), 110.0 (d, *J* = 26.5 Hz), 109.7 (d, *J* = 9.7 Hz), 104.7 (d, *J* = 24.2 Hz), 33.0. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -125.1. **IR** ν 3063 (w), 2930 (w), 1624 (m), 1585 (m), 1488 (s), 1464 (m), 1425 (m), 1292 (w), 1192 (s), 1123 (m), 1060 (w), 873 (s). **HRMS** (ESI) calcd for $C_{20}H_{16}FN_2^+$ $[M+H]^+$ 303.1292; found 303.1295

5-Chloro-1-methyl-3-(2-(pyridin-2-yl)phenyl)-1*H*-indole (13f)

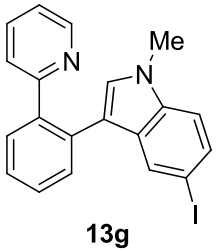


13f

Starting from commercially available 2-phenylpyridine **12** (43.0 µl, 0.300 mmol) and with 1-(3-5-chloro-1-methyl-1*H*-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one **9i** (136 mg, 0.330 mmol, 1.10 equiv.) at 50°C, 5-fluoro-1-methyl-3-(2-(pyridin-2-yl)phenyl)-1*H*-indole **13f** (77.0 mg, 0.242 mmol, 81% yield) was obtained as a yellow oil. Rf: 0.36 (Pentane:EtOAc 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.65 (m, 1H, Ar*H*), 7.72 (dd, *J* = 7.3, 1.8 Hz, 1H, Ar*H*), 7.55 (m, 1H, Ar*H*), 7.46 (pd, *J* = 7.3, 1.8 Hz, 2H, Ar*H*), 7.38 – 7.31 (m, 2H, Ar*H*), 7.17 (d, *J* = 8.6 Hz, 1H, Ar*H*), 7.14 – 7.07 (m, 2H, Ar*H*), 7.04 (m, 1H, Ar*H*), 6.75 (s, 1H, N*CH*C), 3.69 (s, 3H, N*CH*$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.6, 149.0, 139.5, 135.6, 135.2, 132.7, 131.0, 130.6, 129.4, 128.7, 128.0, 127.1, 125.5,

124.9, 121.9, 121.4, 119.3, 115.2, 110.2, 33.0. **IR** ν 3055 (w), 3014 (w), 2924 (w), 1586 (w), 1543 (w), 1477 (s), 1424 (m), 1374 (w), 1288 (w), 1218 (w), 1152 (w), 1096 (w), 1058 (w), 953 (w). **HRMS** (ESI) calcd for $C_{20}H_{16}ClN_2^+$ $[M+H]^+$ 319.0997; found 319.1006.

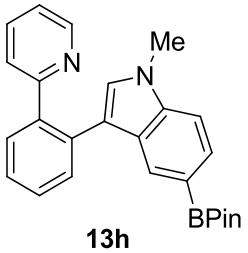
5-Iodo-1-methyl-3-(2-(pyridin-2-yl)phenyl)-1*H*-indole (13g)



13g

Starting from commercially available 2-phenylpyridine **12** (43.0 µl, 0.300 mmol) and with 1-(3-5-iodo-1-methyl-1*H*-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one **9j** (166 mg, 0.330 mmol, 1.10 equiv.) at 50 °C, 5-Iodo-1-methyl-3-(2-(pyridin-2-yl)phenyl)-1*H*-indole **13g** (91.0 mg, 0.222 mmol, 74% yield) was obtained as a yellow oil. Rf: 0.45 (Pentane:EtOAc 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.66 (dd, *J* = 5.0, 0.9 Hz, 1H, Ar*H*), 7.71 (m, 1H, Ar*H*), 7.65 (d, *J* = 1.6 Hz, 1H, Ar*H*), 7.53 (m, 1H, Ar*H*), 7.50 – 7.42 (m, 2H, Ar*H*), 7.39 (dd, *J* = 8.5, 1.6 Hz, 1H, Ar*H*), 7.32 (td, *J* = 7.7, 1.9 Hz, 1H, Ar*H*), 7.08 (ddd, *J* = 7.7, 5.0, 1.1 Hz, 1H, Ar*H*), 7.07 – 6.97 (m, 2H, Ar*H*), 6.70 (s, 1H, N*CH*C), 3.67 (s, 3H, N*CH*$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.7, 149.3, 139.8, 135.7, 135.2, 132.5, 130.9, 130.5, 129.8, 129.2, 128.7, 128.7, 128.5, 127.0, 124.7, 121.4, 114.9, 111.1, 83.2, 32.9. **IR** ν 3058 (w), 2920 (w), 1606 (w), 1585 (m), 1474 (s), 1422 (m), 1371 (w), 1287 (w), 1266 (w), 1217 (w), 1148 (w), 1092 (w), 1024 (w), 943 (w), 874 (w). **HRMS** (ESI) calcd for $C_{20}H_{16}IN_2^+$ $[M+H]^+$ 411.0353; found 411.0348.

1-Methyl-3-(2-(pyridin-2-yl)phenyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (13h)

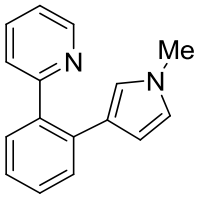


13h

Starting from commercially available 2-phenylpyridine **12** (43.0 µl, 0.300 mmol) and with 1-(3-1-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one **9k** (166 mg, 0.330 mmol, 1.10 equiv.) at 50 °C, 1-Methyl-3-(2-(pyridin-2-yl)phenyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole **13h** (73.0 mg, 0.178 mmol, 59% yield) was obtained as a yellow oil. Rf: 0.30 (Pentane:EtOAc 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 5.0 Hz, 1H, Ar*H*), 8.00 (s, 1H, Ar*H*), 7.71 (d, *J* = 7.5 Hz, 1H, Ar*H*), 7.64 (dd, *J* = 8.3, 1.1 Hz, 1H, Ar*H*), 7.61 (m, 1H, Ar*H*), 7.46 (td, *J* = 7.4, 1.7 Hz, 1H, Ar*H*), 7.41 (td, *J* = 7.4, 1.6 Hz, 1H, Ar*H*), 7.29 – 7.26 (m, 2H, Ar*H*), 7.00 (ddd, *J* = 7.5, 4.9, 1.2 Hz, 1H, Ar*H*), 6.95 (dt, *J* = 7.9, 1.0 Hz, 1H, Ar*H*), 6.62 (s, 1H, Ar*H*), 3.68 (s, 3H, N*CH*$_3$), 1.34 (s, 12H, B*Pin*). **^{13}C NMR**

(101 MHz, $CDCl_3$) δ 159.9, 149.1, 140.0, 138.6, 135.0, 133.1, 131.2, 130.3, 128.4, 128.2, 127.7, 127.7, 126.9, 126.7, 124.9, 121.1, 116.0, 108.5, 83.3, 32.6, 24.8 (*one aromatic Carbon signal not resolved*). **IR** ν 3063 (w), 2978 (w), 2940 (w), 2245 (w), 2214 (w), 1608 (m), 1605 (m), 1568 (w), 1463 (m), 1438 (m), 1383 (s), 1349 (s), 1311 (s), 1273 (m), 1142 (s), 1097 (m), 967 (m), 910 (s), 866 (m). **HRMS** (ESI) calcd for $C_{26}H_{28}BN_2O_2^+$ $[M+H]^+$ 411.2238; found 411.2248.

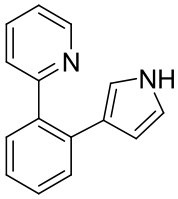
2-(2-(1-Methyl-1*H*-pyrrol-3-yl)phenyl)pyridine (13i)



13i

Starting from commercially available 2-phenylpyridine **12** (43.0 µl, 0.300 mmol, 1.00 equiv.) and with 1-(3-1-methyl-1*H*-pyrrole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one **9o** (108 mg, 0.330 mmol, 1.10 equiv.) at 80°C, 2-(2-(1-Methyl-1*H*-pyrrol-3-yl)phenyl)pyridine **13i** (60.0 mg, 0.256 mmol, 85% yield) was obtained as a yellow oil. Rf: 0.38 (Pentane:EtOAc 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 5.0 Hz, 1H, Ar*H*), 7.57 – 7.46 (m, 3H, Ar*H*), 7.37 (t, *J* = 7.5 Hz, 1H, Ar*H*), 7.31 (d, *J* = 7.5 Hz, 1H, Ar*H*), 7.22 (d, *J* = 7.9 Hz, 1H, Ar*H*), 7.18 (dd, *J* = 7.4, 5.1 Hz, 1H, Ar*H*), 6.43 (t, *J* = 2.5 Hz, 1H, Ar*H*), 6.30 (d, *J* = 1.6 Hz, 1H, Ar*H*), 5.80 (d, *J* = 1.6 Hz, 1H, Ar*H*), 3.54 (s, 3H, N*CH*$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.6, 149.1, 138.7, 135.2, 134.8, 130.2, 129.3, 128.3, 125.8, 125.2, 123.8, 121.5, 121.3, 120.6, 109.2, 36.1. **IR** ν 3056 (w), 3007 (w), 2943 (w), 1586 (s), 1551 (m), 1508 (m), 1463 (s), 1424 (s), 1361 (m), 1260 (w), 1202 (s), 1150 (w), 1087 (w), 1024 (w), 990 (w), 926 (w). **HRMS** (ESI) calcd for $C_{16}H_{15}N_2^+$ $[M+H]^+$ 235.1230; found 235.1230.

2-(2-(1*H*-Pyrrol-3-yl)phenyl)pyridine (13j)

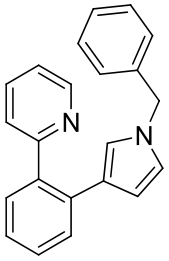


13j

Starting from commercially available 2-phenylpyridine **12** (43.0 µl, 0.300 mmol, 1.00 equiv.) and with 1-(3-1*H*-pyrrole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one **9n** (103 mg, 0.330 mmol, 1.10 equiv.) in a mixture of 1,2-DCE:MeOH (2:1, 0.1M) at 50 °C, 2-(2-(1*H*-pyrrol-3-yl)phenyl)pyridine **13j** (52.0 mg, 0.236 mmol, 79% yield) was obtained as a light brown foam. Rf: 0.42 (Pentane:EtOAc 4:1) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.67 (m, 1H, Ar*H*), 8.29 (m, 1H, N*H*), 7.57 – 7.47 (m, 3H, Ar*H*), 7.40 (dd, *J* = 8.2, 6.8 Hz, 1H, Ar*H*), 7.32 (t, *J* = 7.3 Hz, 1H, Ar*H*), 7.23 – 7.15 (m, 2H, Ar*H*), 6.62 (d, *J* = 2.6 Hz, 1H, Ar*H*), 6.43 (d, *J* = 2.6 Hz, 1H, Ar*H*), 5.95 (dd, *J* = 2.9, 1.6 Hz, 1H, Ar*H*). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.6, 149.2, 139.0, 135.2, 134.7, 130.2, 129.6, 128.4, 126.1, 125.2, 123.8, 121.4, 117.6, 116.8, 109.3. **IR** ν 3191 (m), 3054 (m), 2928 (w), 1601 (s), 1589 (s), 1562 (m), 1505 (m), 1464 (s),

1426 (s), 1267 (w), 1152 (w), 1078 (w), 1028 (m), 996 (w), 917 (w). **HRMS** (ESI) calcd for $C_{15}H_{13}N_2^+$ $[M+H]^+$ 221.1073; found 221.1077.

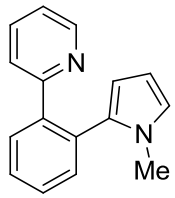
2-(2-(1-Benzyl-1*H*-pyrrol-3-yl)phenyl)pyridine (13k)



13k

Starting from commercially available 2-phenylpyridine **12** (43.0 µl, 0.300 mmol, 1.00 equiv.) and with 1-(3-1-benzyl-1*H*-pyrrole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one **9q** (133 mg, 0.330 mmol, 1.10 equiv.) at 80 °C, 2-(2-(1-Benzyl-1H-pyrrol-3-yl)phenyl)pyridine **13k** (54.0 mg, 0.174 mmol, 58% yield) was obtained as an pale yellow oil. Rf: 0.30 (Pentane:EtOAc 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.62 (m, 1H, Ar*H*), 7.51 – 7.45 (m, 3H, Ar*H*), 7.38 (td, *J* = 7.5, 1.6 Hz, 1H, Ar*H*), 7.34 – 7.26 (m, 4H, Ar*H*), 7.20 (d, *J* = 7.9 Hz, 1H, Ar*H*) 7.13 (ddd, *J* = 7.4, 4.9, 1.2 Hz, 1H, Ar*H*), 7.03 – 6.97 (m, 2H, Ar*H*), 6.54 (t, *J* = 2.5 Hz, 1H, Ar*H*), 6.25 (t, *J* = 1.8 Hz, 1H, Ar*H*), 5.99 (dd, *J* = 2.5, 1.8 Hz, 1H, Ar*H*), 4.92 (s, 2H, N*CH*$_2$Ph). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.5, 149.1, 138.8, 137.9, 135.2, 134.8, 130.1, 129.4, 128.6, 128.3, 127.6, 126.9, 126.0, 125.2, 123.9, 121.3, 121.0, 120.4, 109.4, 53.3. **IR** ν 3062 (m), 2925 (m), 2854 (w), 1708 (m), 1586 (s), 1562 (m), 1498 (s), 1463 (s), 1425 (s), 1355 (m), 1190 (m), 1082 (m), 1025 (m). **HRMS** (ESI) calcd for $C_{22}H_{19}N_2^+$ $[M+H]^+$ 311.1543; found 311.1545.

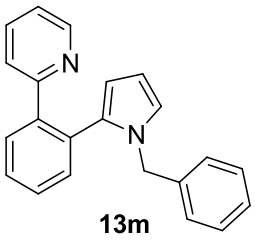
2-(2-(1-methyl-1*H*-pyrrol-2-yl)phenyl)pyridine (13l)



13l

Starting from commercially available 2-phenylpyridine **12** (43.0 µl, 0.300 mmol, 1.00 equiv.) and with 1-(2-1-methyl-1*H*-pyrrole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one **9p** (108 mg, 0.330 mmol, 1.10 equiv.) at 80 °C, 2-(2-(1-methyl-1*H*-pyrrol-2-yl)phenyl)pyridine **13l** (60.0 mg, 0.256 mmol, 85% yield) was obtained as a pale yellow oil. Rf: 0.42 (Pentane:EtOAc 4:1) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.67 (m, 1H, Ar*H*), 7.86 (d, *J* = 7.5 Hz, 1H, Ar*H*), 7.55 – 7.40 (m, 4H, Ar*H*), 7.14 (ddd, *J* = 7.5, 4.9, 1.1 Hz, 1H, Ar*H*), 6.80 (m, 1H, Ar*H*), 6.51 (t, *J* = 2.3 Hz, 1H, Ar*H*), 6.18 – 6.15 (m, 2H, Ar*H*), 2.90 (s, 3H, N*CH*$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.6, 149.5, 140.0, 135.7, 133.2, 131.8, 131.5, 130.1, 128.5, 128.4, 123.7, 122.2, 121.5, 109.2, 107.7, 33.8. **IR** ν 3098 (w), 3059 (w), 2926 (m), 2854 (w), 1707 (w), 1585 (s), 1473 (s), 1429 (s), 1310 (s), 1239 (w), 1090 (m), 1056 (m), 1024 (m). **HRMS** (ESI) calcd for $C_{16}H_{15}N_2^+$ $[M+H]^+$ 235.1230; found 235.1233.

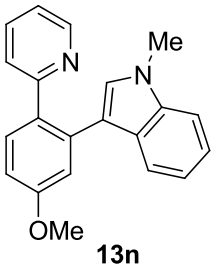
2-(2-(1-benzyl-1*H*-pyrrol-2-yl)phenyl)pyridine (13m)



13m

Starting from commercially available 2-phenylpyridine **12** (43.0 µl, 0.300 mmol, 1.00 equiv.) and with 1-(2-1-benzyl-1*H*-pyrrole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one **9r** (133 mg, 0.330 mmol, 1.10 equiv.) at 80 °C, 2-(2-(1-benzyl-1*H*-pyrrol-2-yl)phenyl)pyridine **13m** (63.0 mg, 0.203 mmol, 68% yield) as an pale yellow oil. Rf: 0.32 (Pentane:EtOAc 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 4.9 Hz, 1H, Ar*H*), 7.85 (m, 1H, Ar*H*), 7.53 – 7.42 (m, 2H, Ar*H*), 7.42 – 7.33 (m, 2H, Ar*H*), 7.17 – 7.13 (m, 4H, Ar*H*), 6.83 (d, *J* = 7.9 Hz, 1H, Ar*H*), 6.72 (dd, *J* = 6.6, 2.9 Hz, 2H, Ar*H*), 6.52 (m, 1H, Ar*H*), 6.24 – 6.13 (m, 2H, Ar*H*), 4.45 (s, 2H, N*CH*$_2$Ph). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.7, 149.5, 140.2, 138.1, 135.8, 133.2, 132.1, 131.7, 130.3, 128.6, 128.6, 128.4, 127.3, 127.2, 124.2, 121.7, 110.1, 108.3, 50.6. (*2 Cs overlapping at 121.7, shown by HSQC*) **IR** ν 3062 (m), 3029 (w), 2925 (w), 1585 (s), 1471 (s), 1427 (s), 1311 (m), 1298 (m), 1236 (m), 1153 (w), 1076 (m), 1024 (m), 989 (w). **HRMS** (ESI) calcd for $C_{22}H_{19}N_2^+$ $[M+H]^+$ 311.1543; found 311.1542.

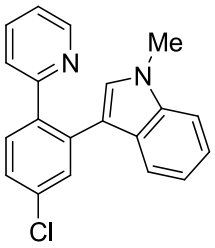
3-(5-Methoxy-2-(pyridin-2-yl)phenyl)-1-methyl-1*H*-indole (13n)



13n

Starting from commercially available 2-(4-methoxyphenyl)pyridine (55.6 mg, 0.300 mmol) and with 1-(3-1-methyl-1*H*-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one **9a** (124 mg, 0.330 mmol, 1.10 equiv.) at 50 °C, 3-(5-methoxy-2-(pyridin-2-yl)phenyl)-1-methyl-1*H*-indole **13n** (83.0 mg, 0.264 mmol, 88% yield) was obtained as a yellow oil. Rf: 0.38 (Pentane:EtOAc 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 5.0 Hz, 1H, Ar*H*), 7.70 (d, *J* = 8.5 Hz, 1H, Ar*H*), 7.45 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.31 – 7.23 (m, 2H, Ar*H*), 7.20 (t, *J* = 7.6 Hz, 1H, Ar*H*), 7.13 (d, *J* = 2.7 Hz, 1H, Ar*H*), 7.06 – 6.95 (m, 4H, Ar*H*), 6.73 (s, 1H, CH_3N*CH*C), 3.89 (s, 3H, N*CH*$_3$), 3.71 (s, 3H, O*CH*$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.6, 159.4, 148.9, 136.7, 135.2, 134.6, 132.3, 131.9, 128.2, 126.8, 125.0, 121.6, 120.8, 119.9, 119.5, 115.9, 115.3, 112.6, 109.1, 55.3, 32.8. **IR** ν 3049 (w), 2933 (w), 2834 (w), 1602 (s), 1568 (m), 1463 (s), 1426 (m), 1278 (s), 1232 (s), 1210 (m), 1062 (m), 1017 (m), 844 (w). **HRMS** (ESI) calcd for $C_{21}H_{19}N_2O^+$ $[M+H]^+$ 315.1492; found 315.1494.

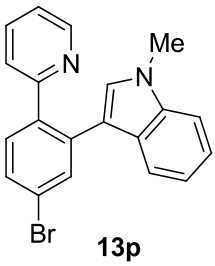
3-(5-Chloro-2-(pyridin-2-yl)phenyl)-1-methyl-1*H*-indole (13o)



13o

Starting from commercially available 2-(4-chlorophenyl)pyridine (57.0 mg, 0.300 mmol) and with 1-(3-1-methyl-1*H*-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one **9a** (124 mg, 0.330 mmol, 1.10 equiv.) at 50 °C, 3-(5-chloro-2-(pyridin-2-yl)phenyl)-1-methyl-1H-indole **13o** (81.2 mg, 0.255 mmol, 85% yield) was obtained as a yellow oil. Rf: 0.40 (Pentane:EtOAc 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.65 (m, 1H, Ar*H*), 7.68 (d, *J* = 8.3 Hz, 1H, Ar*H*), 7.59 (d, *J* = 2.2 Hz, 1H, Ar*H*), 7.40 (dd, *J* = 8.3, 2.2 Hz, 1H, Ar*H*), 7.37 (dd, *J* = 8.0, 1.0 Hz, 1H, Ar*H*), 7.30 (dd, *J* = 7.7, 1.7 Hz, 1H, Ar*H*), 7.27 (m, 1H, Ar*H*), 7.19 (ddd, *J* = 8.2, 7.0, 1.1 Hz, 1H, Ar*H*), 7.08 (ddd, *J* = 7.5, 4.9, 1.1 Hz, 1H, Ar*H*), 7.04 – 6.99 (m, 2H, Ar*H*), 6.75 (s, 1H, N*CH*C), 3.71 (s, 3H, N*CH*$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.7, 149.2, 137.9, 136.8, 135.4, 135.1, 134.3, 132.0, 130.7, 128.4, 126.7, 126.6, 124.9, 121.8, 121.5, 119.8, 119.7, 114.3, 109.2, 32.8. **IR** ν 3055 (w), 2926 (w), 1595 (s), 1566 (m), 1476 (m), 1461 (s), 1427 (w), 1329 (m), 1219 (w), 1163 (w), 1100 (m), 1026 (w), 913 (w), 830 (w). **HRMS** (ESI) calcd for $C_{20}H_{16}ClN_2^+$ $[M+H]^+$ 319.0997; found 319.0999.

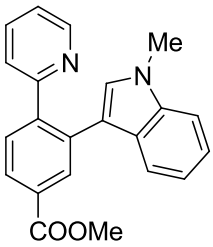
3-(5-Bromo-2-(pyridin-2-yl)phenyl)-1-methyl-1*H*-indole (13p)



13p

Starting from commercially available 2-(4-bromophenyl)pyridine (70.2 mg, 0.300 mmol) and with 1-(3-1-methyl-1H-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one **9a** (124 mg, 0.330 mmol, 1.10 equiv.) at 50 °C, 3-(5-methoxy-2-(pyridin-2-yl)phenyl)-1-methyl-1*H*-indole **13p** (91.0 mg, 0.251 mmol, 84% yield) was obtained as a yellow oil. Rf: 0.40 (Pentane:EtOAc 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.66 (m, 1H, Ar*H*), 7.75 (d, J = 2.0 Hz, 1H, Ar*H*), 7.63 (d, J = 8.3 Hz, 1H, Ar*H*), 7.56 (dd, J = 8.3, 2.0 Hz, 1H, Ar*H*), 7.36 – 7.31 (m, 2H, Ar*H*), 7.28 (dt, *J* = 8.2, 0.9 Hz, 1H, Ar*H*), 7.19 (ddd, J = 8.2, 6.9, 0.9 Hz, 1H, Ar*H*), 7.11 (t, J = 6.3 Hz, 1H, Ar*H*), 7.04 (d, J = 8.0 Hz, 1H, Ar*H*), 6.99 (m, 1H, Ar*H*), 6.77 (s, 1H, N*CH*C), 3.72 (s, 3H, N*CH*$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.7, 149.3, 138.5, 136.7, 135.4, 135.2, 133.5, 132.1, 129.6, 128.3, 126.5, 124.7, 122.4, 121.8, 121.5, 119.7, 119.6, 114.2, 109.2, 32.7. **IR** ν 2956 (w), 2929 (w), 2851 (w), 1678 (w), 1592 (m), 1510 (m), 1453 (m), 1453 (m), 1434 (s), 1399 (s), 1364 (s), 1264 (m), 1108 (m), 1031 (m), 956 (m). **HRMS** (ESI) calcd for $C_{20}H_{16}{}^{79}BrN_2^+$ $[M+H]^+$ 363.0491; found 363.0490

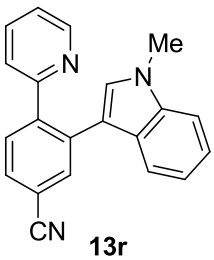
Methyl 3-(1-methyl-1*H*-indol-3-yl)-4-(pyridin-2-yl)benzoate (13q)



13q

Starting from methyl 4-(pyridin-2-yl)benzoate **44** (64.0 mg, 0.300 mmol) and with 1-(3-1-methyl-1H-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one **9a** (124 mg, 0.330 mmol, 1.10 equiv.) at 50°C, methyl 3-(1-methyl-1*H*-indol-3-yl)-4-(pyridin-2-yl)benzoate **13q** (94.0 mg, 0.275 mmol, 92% yield) was obtained as an orange oil. Rf: 0.33 (Pentane:EtOAc 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.61 (dd, *J* = 5.1, 1.6 Hz, 1H, Ar*H*), 8.20 (d, *J* = 1.7 Hz, 1H, Ar*H*), 7.99 (dd, *J* = 8.1, 1.8 Hz, 1H, Ar*H*), 7.72 (d, *J* = 8.1 Hz, 1H, Ar*H*), 7.26 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.24 – 7.16 (m, 2H, Ar*H*), 7.09 (t, *J* = 7.6 Hz, 1H, Ar*H*), 7.03 – 6.96 (m, 2H, Ar*H*), 6.90 (t, *J* = 7.5 Hz, 1H, Ar*H*), 6.71 (s, 1H, N*CH*C), 3.85 (s, 3H, COO*Me*), 3.61 (s, 3H, N*CH*$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.0, 158.8, 149.4, 143.8, 136.8, 135.3, 133.7, 132.3, 130.7, 129.9, 128.3, 127.6, 126.7, 124.7, 121.8, 121.7, 119.7, 114.7, 109.1, 52.1, 32.8 *(two aromatic Carbon signals overlapping at 119.7).* **IR** ν 3052 (w), 2950 (w), 2252 (w), 2218 (w), 1718 (s), 1587 (m), 1436 (m), 1365 (m), 1330 (m), 1286 (s), 1251 (s), 1162 (m), 1113 (m), 994 (w), 911 (s). **HRMS** (ESI) calcd for $C_{22}H_{19}N_2O_2^+$ $[M+H]^+$ 343.1441; found 343.1438.

3-(1-Methyl-1*H*-indol-3-yl)-4-(pyridin-2-yl)benzonitrile (13r)

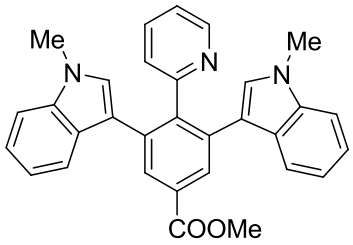


13r

Starting from commercially available 4-(pyridin-2-yl)benzonitrile (54.0 mg, 0.300 mmol) and with 1-(3-1-methyl-*1H*-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one **9a** (124 mg, 0.330 mmol, 1.10 equiv.) at 80 °C, 3-(1-methyl-1*H*-indol-3-yl)-4-(pyridin-2-yl)benzonitrile **13r** (72.0 mg, 0.233 mmol, 78% yield) was obtained as a yellow oil. Rf: 0.35 (Pentane:EtOAc 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.70 (m, 1H, Ar*H*), 7.88 (d, *J* = 1.7 Hz, 1H, Ar*H*), 7.83 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.69 (dd, *J* = 8.0, 1.7 Hz, 1H, Ar*H*), 7.36 – 7.27 (m, 3H, Ar*H*), 7.21 (ddd, *J* = 8.3, 7.0, 1.1 Hz, 1H, Ar*H*), 7.13 (ddd, *J* = 7.5, 4.9, 1.2 Hz, 1H, Ar*H*), 7.05 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.02 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H, Ar*H*), 6.77 (s, 1H, N*CH*C), 3.73 (s, 3H, N*CH*$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.9, 149.6, 143.6, 136.7, 135.6, 134.8, 134.5, 131.5, 129.8, 128.4, 126.3, 124.7, 122.2, 122.0, 120.1, 119.3, 118.9, 113.3, 112.1, 109.4, 32.9. **IR** ν 3053 (w), 2932 (w), 2230 (m),

1587 (m), 1558 (w), 1475 (m), 1463 (m), 1330 (w), 1266 (s), 1224 (w), 1160 (w), 1091 (w), 1026 (w), 902 (w), 839 (m). **HRMS** (ESI) calcd for $C_{21}H_{16}N_3^+$ $[M+H]^+$ 310.1339; found 310.1344.

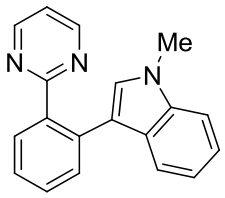
Methyl 3,5-bis(1-methyl-1H-indol-3-yl)-4-(pyridin-2-yl)benzoate (19)



19

Starting from methyl 4-(pyridin-2-yl)benzoate **44** (64.0 mg, 0.300 mmol) and with 1-(3-1-methyl-1H-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one **9a** (249 mg, 0.660 mmol, 2.20 equiv.) at 50 °C, methyl 3,5-bis(1-methyl-1H-indol-3-yl)-4-(pyridin-2-yl)benzoate **19** (75.0 mg, 0.159 mmol, 53% yield) was obtained as a yellow oil. Rf: 0.30 (Pentane:EtOAc 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.47 (m, 1H, Ar*H*), 8.32 (s, 2H, Ar*H*), 7.68 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.29 – 7.15 (m, 5H, Ar*H*), 7.08 (ddd, *J* = 8.2, 6.5, 1.5 Hz, 2H, Ar*H*), 6.99 – 6.93 (m, 2H, Ar*H*), 6.52 (s, 2H, Ar*H*), 3.94 (s, 3H, COO*Me*), 3.58 (s, 6H, N*Me*). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.2, 159.8, 147.9, 143.2, 136.4, 135.6, 135.4, 129.7, 128.9, 127.3, 125.7, 121.6, 121.5, 119.8, 119.5, 114.5, 109.0, 52.1, 32.6. **IR** ν 3056 (w), 2950 (w), 2247 (w), 1720 (m), 1571 (m), 1477 (m), 1427 (m), 1325 (m), 1293 (s), 1247 (s), 1161 (m), 1119 (m), 1004 (m), 908 (s). **HRMS** (ESI) calcd for $C_{31}H_{25}N_3O_2$ $[M+H]^+$ 472.1998; found 472.2021.

1-Methyl-3-(2-(pyrimidin-2-yl)phenyl)-1*H*-indole (20)

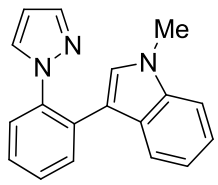


20

Starting from commercially available 2-phenylpyrimidine (47.0 mg, 0.300 mmol) and with 1-(3-1-methyl-1*H*-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one **9a** (124 mg, 0.330 mmol, 1.10 equiv.) at 80 °C, 1-methyl-3-(2-(pyrimidin-2-yl)phenyl)-1*H*-indole **20** (69.0 mg, 0.242 mmol, 81% yield) was obtained as a yellow oil. Rf: 0.40 (Pentane:EtOAc 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 4.9 Hz, 2H, Pyrimidine*H*), 7.84 (dd, *J* = 7.7, 1.5 Hz, 1H, Ar*H*), 7.59 (dd, *J* = 7.7, 1.5 Hz, 1H, Ar*H*), 7.51 (m, 1H, Ar*H*), 7.44 (td, *J* = 7.5, 1.5 Hz, 1H, Ar*H*), 7.24 (d, *J* = 8.2 Hz, 1H, Ar*H*), 7.10 (dd, *J* = 9.3, 7.5 Hz, 2H, Ar*H*), 7.03 (s, 1H, NC*H*Cl), 7.00 (t, *J* = 4.9 Hz, 1H, Ar*H*), 6.84 (t, *J* = 7.5 Hz, 1H, Ar*H*), 3.76 (s, 3H, N*CH*$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.5, 156.7, 138.1, 136.7, 134.1, 131.3, 130.7, 129.4, 127.5, 126.8, 126.5, 121.3, 119.3, 119.2, 118.2, 116.2, 109.0,

32.8 *(two aromatic Carbon signals overlapping at 156.7).* **IR** ν 3048 (w), 2932 (w), 1599 (w), 1568 (s), 1554 (m), 1473 (w), 1414 (s), 1377 (w), 1330 (w), 1268 (w), 1221 (w), 1162 (w), 1135 (w), 1015 (w), 943 (w), 822 (w). **HRMS** (ESI) calcd for $C_{19}H_{16}N_3^+$ $[M+H]^+$ 286.1339; found 286.1344.

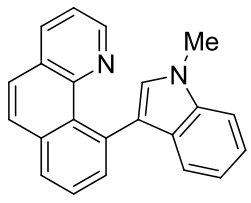
3-(2-(1H-Pyrazol-1-yl)phenyl)-1-methyl-1*H*-indole (21)



21

Starting from commercially available 1-phenyl-1*H*-pyrazole (43.0 mg, 0.300 mmol) and with 1-(3-1-methyl-1*H*-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one **9a** (124 mg, 0.330 mmol, 1.10 equiv.) at 80 °C, 3-(2-(1*H*-pyrazol-1-yl)phenyl)-1-methyl-1*H*-indole **21** (59.0 mg, 0.216 mmol, 72% yield) was obtained as a yellow oil. Rf: 0.40 (Pentane:EtOAc 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (dd, J = 7.8, 1.6 Hz, 1H, Ar*H*), 7.67 (d, J = 1.7 Hz, 1H, Ar*H*), 7.62 (dd, J = 7.8, 1.6 Hz, 1H, Ar*H*), 7.52 – 7.44 (m, 2H, Ar*H*), 7.40 (td, J = 7.8, 1.6 Hz, 1H, Ar*H*), 7.31 (d, J = 8.2 Hz, 1H, Ar*H*), 7.25 – 7.20 (m, 2H, Ar*H*), 7.07 (m, 1H, Ar*H*), 6.60 (s, 1H, N*CH*C), 6.15 (m, 1H, Ar*H*), 3.72 (s, 3H, N*CH$_3$*). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.9, 138.5, 136.7, 131.1, 131.0, 130.6, 128.2, 127.6, 127.0, 126.9, 126.6, 121.8, 119.9, 119.3, 112.0, 109.3, 106.2, 32.8. **IR** ν 3049 (w), 2926 (m), 2853 (w), 1680 (w), 1615 (w), 1604 (w), 1548 (m), 1518 (s), 1473 (s), 1423 (w), 1394 (s), 1378 (s), 1329 (s), 1264 (w), 1221 (m), 1089 (m), 1045 (s), 1019 (m), 936 (s). **HRMS** (ESI) calcd for $C_{18}H_{16}N_3^+$ $[M+H]^+$ 274.1339; found 274.1343.

10-(1-Methyl-1*H*-indol-3-yl)benzo[h]quinoline (22)

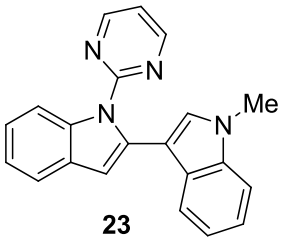


22

Starting from commercially available benzo[h]quinoline (54.0 mg, 0.300 mmol) and with 1-(3-1-methyl-1H-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one **9a** (124 mg, 0.330 mmol, 1.10 equiv.) at 50 °C, 10-(1-methyl-1*H*-indol-3-yl)benzo[h]quinoline **22** (70.0 mg, 0.227 mmol, 76% yield) was obtained as a light yellow oil. Rf: 0.40 (Pentane:EtOAc 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 2.4 Hz, 1H, Ar*H*), 8.10 (dd, *J* = 8.0, 1.9 Hz, 1H, Ar*H*), 7.93 – 7.90 (m, 1H, Ar*H*), 7.88 (d, *J* = 8.7 Hz, 1H, Ar*H*), 7.75 – 7.65 (m, 3H, Ar*H*), 7.37 (d, *J* = 8.2 Hz, 1H, Ar*H*), 7.29 (m, 1H, Ar*H*), 7.24 (m, 1H, Ar*H*), 7.16 (ddd, *J* = 8.2, 4.7, 3.5 Hz, 1H, Ar*H*), 6.79 (s, 1H, N*CH*C), 6.78 (t, *J* = 1.1 Hz, 1H, Ar*H*), 3.93 (s, 3H, N*CH$_3$*). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.0, 146.8,

137.0, 135.4, 135.3, 133.9, 132.8, 129.7, 128.5, 128.4, 127.8, 127.5, 127.4, 127.1, 126.2, 125.7, 121.0, 120.8, 120.7, 118.5, 108.9, 32.9. **IR** ν 3046 (m), 2929 (m), 1677 (w), 1615 (w), 1588 (m), 1569 (m), 1475 (s), 1418 (s), 1375 (s), 1323 (s), 1263 (w), 1230 (s), 1161 (w), 1129 (w), 1014 (w), 910 (m). **HRMS** (ESI) calcd for $C_{22}H_{17}N_2^+$ $[M+H]^+$ 309.1386; found 309.1398.

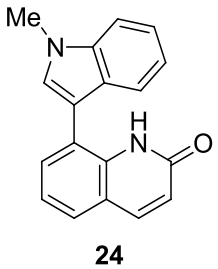
1'-Methyl-1-(pyrimidin-2-yl)-1*H*,1'*H*-2,3'-biindole (23)



23

Starting from 1-(pyrimidin-2-yl)-1*H*-indole **46** (59.0 mg, 0.300 mmol) and with 1-(3-1-methyl-1*H*-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one **9a** (124 mg, 0.330 mmol, 1.10 equiv.) at 50 °C, 1'-methyl-1-(pyrimidin-2-yl)-1*H*,1'*H*-2,3'-biindole **23** (80.0 mg, 0.247 mmol, 82% yield) was obtained as a yellow oil. Rf: 0.38 (Pentane:EtOAc 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 4.8 Hz, 2H, Ar*H*), 8.01 (m, 1H, Ar*H*), 7.56 (dd, *J* = 7.9, 1.3 Hz, 1H, Ar*H*), 7.22 – 7.14 (m, 3H, Ar*H*), 7.13 (s, 1H, Ar*H*), 7.06 (dd, *J* = 8.3, 6.9 Hz, 2H, Ar*H*), 6.93 (t, *J* = 4.8 Hz, 1H, Ar*H*), 6.82 (td, *J* = 7.4, 0.9 Hz, 1H, Ar*H*), 6.69 (s, 1H, CH_3NCHC), 3.71 (s, 3H, NCH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.2, 158.2, 137.5, 136.8, 134.6, 129.6, 127.8, 126.8, 122.6, 121.8, 121.7, 120.0, 119.8, 119.5, 117.5, 112.4, 109.3, 108.9, 106.5, 32.9. **IR** ν 3049 (w), 2931 (w), 1592 (w), 1563 (m), 1454 (m), 1423 (s), 1372 (w), 1350 (w), 1309 (m), 1258 (w), 1217 (w), 910 (w). **HRMS** (ESI) calcd for $C_{21}H_{17}N_4^+$ $[M+H]^+$ 325.1448; found 325.1452.

8-(1-Methyl-1*H*-indol-3-yl)quinolin-2(1*H*)-one (24)

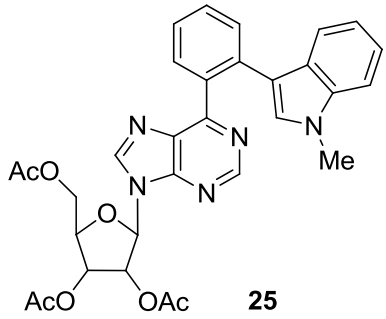


24

Starting from commercially available quinoline 1-oxide (44.0 mg, 0.300 mmol) and with 1-(3-1-methyl-1H-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one **9a** (124 mg, 0.330 mmol, 1.10 equiv.) at 100 °C, 8-(1-methyl-1*H*-indol-3-yl)quinolin-2(1*H*)-one **24** (31.0 mg, 0.113 mmol, 38% yield) was obtained as a yellow oil. Rf: 0.58 (EtOAc:MeOH 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.02 (s, 1H, N*H*CO), 7.83 (d, *J* = 9.5 Hz, 1H, Ar*H*), 7.61 – 7.54 (m, 2H, Ar*H*), 7.45 (dd, *J* = 8.3, 6.7 Hz, 2H, Ar*H*), 7.34 (m, 1H, Ar*H*), 7.30 (d, *J* = 7.6 Hz, 1H, Ar*H*), 7.23 (s, 1H, N*CH*C), 7.20 – 7.15 (m, 1H, Indole*H*), 6.66 (d, *J* = 9.3 Hz, 1H, Ar*H*), 3.91 (s, 3H, NCH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.4, 141.0, 136.3, 132.2, 127.8, 127.7, 126.9, 126.7, 122.9, 122.4, 121.9, 121.6,

120.6, 120.0, 119.4, 109.8, 109.4, 33.1. **IR** ν 3367 (w), 3053 (w), 2923 (m), 2853 (w), 1715 (w), 1651 (s), 1608 (m), 1541 (w), 1467 (m), 1372 (w), 1333 (w), 1234 (w), 1135 (w), 1014 (w), 840 (m). **HRMS** (ESI) calcd for $C_{18}H_{15}N_2O^+$ $[M+H]^+$ 275.1179; found 275.1185.

(2*R*,3*R*,4*R*,5*R*)-2-(Acetoxymethyl)-5-(6-(2-(1-methyl-1*H*-indol-3-yl)phenyl)-9*H*-purin-9-yl)tetrahydrofuran-3,4-diyl diacetate (25)



25

Starting from (2*R*,3*R*,4*R*,5*R*)-2-(acetoxymethyl)-5-(6-phenyl-9*H*-purin-9-yl)tetrahydrofuran-3,4-diyl diacetate **50** (136 mg, 0.300 mmol) and with 1-(3-1-methyl-1*H*-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one **9a** (124 mg, 0.330 mmol, 1.10 equiv.) at 50 °C, (2*R*,3*R*,4*R*,5*R*)-2-(Acetoxymethyl)-5-(6-(2-(1-methyl-1*H*-indol-3-yl)phenyl)-9*H*-purin-9-yl)tetrahydrofuran-3,4-diyl diacetate **25** (72 mg, 0.123 mmol, 41% yield)) was obtained as a yellow oil. Rf: 0.65 (EtOAc 100%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.81 (s, 1H, Ar*H*), 8.04 (s, 1H, Ar*H*), 7.76 (dd, *J* = 7.6, 1.4 Hz, 1H, Ar*H*), 7.70 (dd, *J* = 7.6, 1.3 Hz, 1H, Ar*H*), 7.56 (td, *J* = 7.6, 1.5 Hz, 1H, Ar*H*), 7.46 (td, *J* = 7.5, 1.3 Hz, 1H, Ar*H*), 7.30 – 7.23 (m, 1H, Ar*H* + *CDCl$_3$*), 7.18 (d, *J* = 8.3 Hz, 1H, Ar*H*), 7.08 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H, Ar*H*), 6.90 (s, 1H, Ar*H*), 6.86 (ddd, *J* = 8.0, 6.9, 1.0 Hz, 1H, Ar*H*), 6.18 (d, *J* = 5.1 Hz, 1H, C*H*), 5.89 (t, *J* = 5.3 Hz, 1H, C*H*), 5.65 (dd, *J* = 5.5, 4.5 Hz, 1H, C*H*), 4.47 – 4.40 (m, 2H, C*H* + C*H$_2$*), 4.34 (dd, *J* = 13.1, 5.2 Hz, 1H, C*H$_2$*), 3.67 (s, 3H, N*Me*), 2.14 (s, 3H, CO*CH$_3$*), 2.08 (s, 3H, CO*CH$_3$*), 2.06 (s, 3H, CO*CH$_3$*). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.3, 169.5, 169.2, 160.3, 152.3, 151.0, 142.4, 136.6, 134.7, 134.2, 132.9, 131.3, 131.0, 129.8, 128.2, 126.9, 126.2, 121.4, 119.5, 119.2, 115.4, 109.0, 86.3, 80.2, 73.0, 70.5, 62.9, 32.7, 20.7, 20.5, 20.4. **IR** ν 3056 (w), 2934 (w), 2825 (w), 2254 (w), 1749 (s), 1586 (m), 1505 (w), 1484 (w), 1435 (w), 1377 (m), 1332 (m), 1219 (s), 1101 (m), 1048 (m), 912 (m), 817 (w). **HRMS** (ESI) calcd for $C_{31}H_{30}N_5O_7^+$ $[M+H]^+$ 584.2140; found 584.2138.

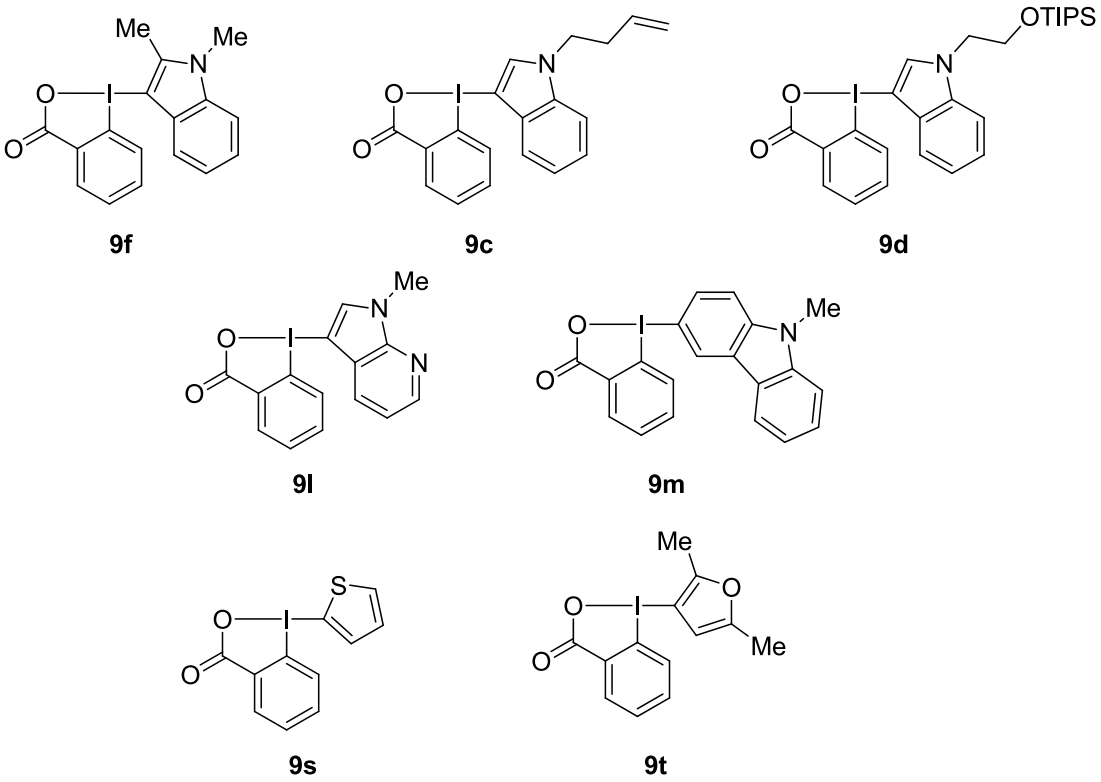
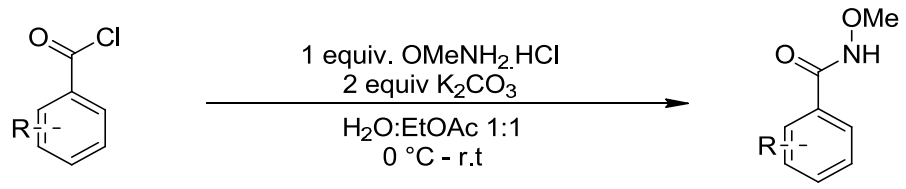


Figure S3: *Reagents found ineffective for Rh-catalyzed CH activation.*

4. Ru-Catalyzed C-H Indolization of Arenes *via* C-H activation.

4.1 Preparation of starting materials for Ru-Catalyzed C-H activation.



GP5: Following a reported procedure,[30] O-methylhydroxylamine hydrochloride (0.418 g, 5.00 mmol, 1.00 equiv.) was added to a solution of K_2CO_3 (1.38 g, 10.0 mmol, 2.00 equiv) in a mixture of EtOAc/H_2O (20 mL,1:1 0.25 M) under vigorous stirring. Then the reaction mixture was cooled to 0 °C and the corresponding (substituted) benzoyl chloride (5.00 mmol, 1.00 equiv) was added dropwise or portionwise. The reaction mixture was warmed to room temperature and stirred for additional 2 hours. The organic layer was separated and the aqueous layer was extracted with EtOAc (3x10 mL). The combined organic layers were dried over $MgSO_4$, filtered, and the solvent removed under reduced pressure. The crude product was purified by flash column chromatography (Pentane:EtOAc 2:1) to afford the desired N-methoxy benzamides **14-62.**

[30] Y. Fukui, P. Liu, Q. Liu, Z.-T. He, N.-Y. Wu, P. Tian, G.-Q. Lin, *J. Am. Chem. Soc.* **2014**, *136*, 15607–15614.

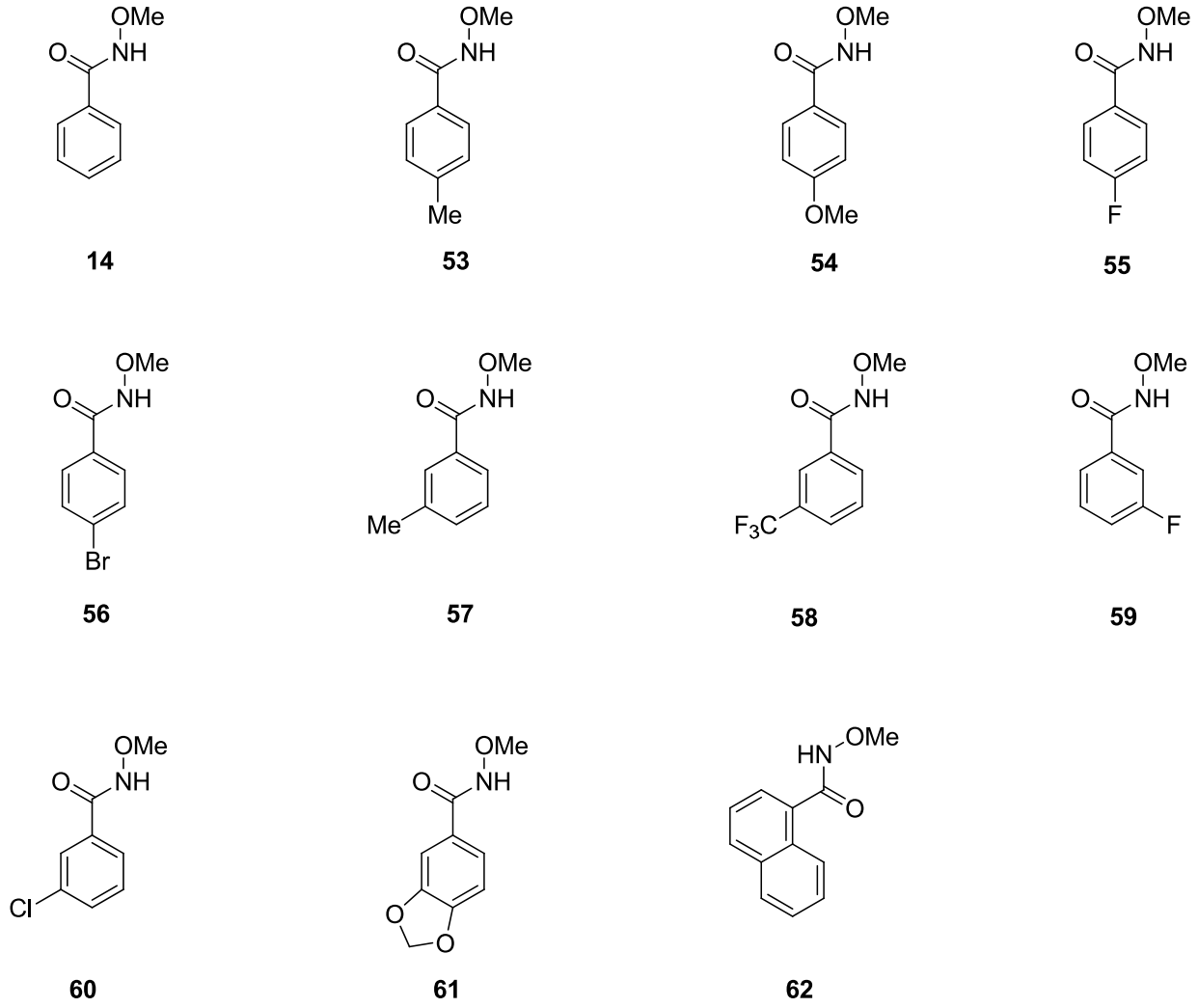
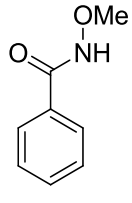


Figure S4: *Starting materials for Ru-catalyzed Indolization of Arenes via C-H activation..*

N-Methoxybenzamide (14)



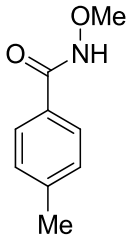
14

The synthesis of N-methoxybenzamide **14** *was scaled up to 10 mmol without reoptimization of the protocol.*

Starting from commercially available benzoyl chloride (1.15 mL, 10.0 mmol), N-methoxybenzamide **14** (1.20 g, 7.94 mmol, 79% yield) was obtained as a colorless solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.70 (s, 1H, N*H*OCH_3), 7.70 (dd, J = 8.3, 1.4 Hz, 2H, Ar*H*), 7.38 (m, 1H, Ar*H*), 7.26 (ddd, J = 8.3, 6.6, 1.3 Hz, 2H, Ar*H*), 3.69 (s, 3H, NHOCH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.2, 131.7, 128.3, 127.1, 63.9, 53.3. **IR** ν 3197 (w), 2980 (w),

2935 (w), 1646 (s), 1579 (m), 1516 (m), 1484 (m), 1310 (m), 1154 (w), 1045 (m), 1026 (m), 945 (w), 881 (s). NMR values are in accordance with the data reported in literature.[30]

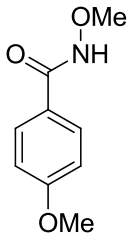
N-Methoxy-4-methylbenzamide (53)



53

Starting from commercially available 4-methylbenzoyl chloride (775 mg, 5.00 mmol), N-methoxy-4-methylbenzamide **53** (822 mg, 4.98 mmol, 100% yield) was obtained as a colorless solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.73 (brs, 1H, N*H*OCH_3), 7.67 (d, J = 8.2 Hz, 2H, Ar*H*), 7.10 (d, J = 8.0 Hz, 2H, Ar*H*), 3.74 (s, 3H, NHO*CH_3*), 2.30 (s, 3H, Ar*CH_3*). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 166.2, 142.1, 128.9, 127.1, 63.8, 21.2 *(2 aromatic Carbon signals overlapping at 128.9).* **IR** ν 3201 (w), 2975 (w), 2935 (w), 1646 (s), 1572 (w), 1494 (m), 1439 (w), 1308 (m), 1155 (w), 1043 (s), 1020 (m), 943 (w), 883 (s), 833 (m). NMR values are in accordance with the data reported in literature. [30]

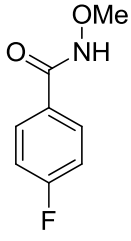
N,4-dimethoxybenzamide (54)



54

Starting from commercially available 4-methoxybenzoyl chloride (853 mg, 5.00 mmol), 4-fluoro- N,4-dimethoxybenzamide **54** (890 mg, 4.91 mmol, 98% yield) was obtained as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.67 (s, 1H, N*H*OMe), 7.77 (d, J = 8.9 Hz, 2H, Ar*H*), 6.81 (d, J = 8.4 Hz, 2H, Ar*H*), 3.77 (s, 3H, NH*OMe*), 3.76 (s, 3H, Ar*OMe*). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.2, 132.6, 128.9, 114.0, 113.5, 63.8, 55.1. **IR** ν 3205 (w), 2972 (w), 2938 (w), 1644 (m), 1606 (s), 1496 (m), 1255 (s), 1181 (m), 1159 (m), 1027 (s), 884 (m), 844 (m). NMR values are in accordance with the data reported in literature. [30]

4-Fluoro-N-methoxybenzamide (55)

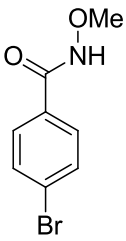


55

Starting from commercially available 4-fluorobenzoyl chloride (793 mg, 5.00 mmol), 4-fluoro-N-methoxybenzamide **55** (643 mg, 3.80 mmol, 76% yield) was obtained as a colorless solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.29 (s, 1H, N*H*OMe), 7.78 (m, 2H, Ar*H*), 6.96 (m, 2H, Ar*H*), 3.72 (s, 3H, NH*OMe*). **^{13}C NMR** (101 MHz, $CDCl_3$) 165.2, 164.7 (d, J = 252.5 Hz), 129.6 (d, J = 9.0 Hz), 127.6 (d, J = 3.3 Hz), 115.3 (d, J = 22.0

Hz), 63.7. **IR** ν 3210 (w), 2984 (w), 2941 (w), 1656 (s), 1592 (s), 1481 (s), 1439 (w), 1318 (w), 1154 (w), 1072 (s), 1012 (s), 944 (w), 879 (s), 841 (m). NMR data is corresponding to the reported values. [30]

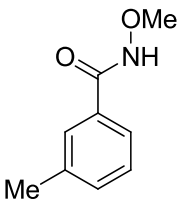
4-Bromo-N-methoxybenzamide (56)



56

Starting from commercially available 4-bromobenzoyl chloride (1.09 g, 5.00 mmol), 4-bromo-N-methoxybenzamide **56** (700 mg, 3.04 mmol, 61% yield) was obtained as a colorless solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.59 (brs, 1H, N*H*OCH_3), 7.56 (d, *J* = 8.5 Hz, 2H, Ar*H*), 7.41 (d, *J* = 8.6 Hz, 2H), 3.71 (s, 3H, NHO*CH_3*). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.4, 131.7, 130.4, 128.8, 126.7, 64.1. **IR** ν 3059 (w), 3006 (w), 1647 (s), 1604 (s), 1497 (s), 1267 (s), 1237 (s), 1158 (m), 1041 (m), 885 (m), 850 (s) ^{1}H NMR data is corresponding to the reported values. [30]

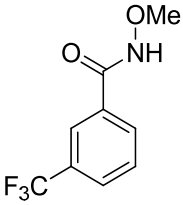
N-Methoxy-3-methylbenzamide (57)



57

Starting from commercially available 3-methylbenzoyl chloride (775 mg, 5.00 mmol), N-methoxy-3-methylbenzamide **57** (813 mg, 4.92 mmol, 98% yield) was obtained as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 11.09 (s, 1H, N*H*OCH_3), 8.37 (s, 1H, Ar*H*), 8.03 (dt, *J* = 7.8, 1.5 Hz, 1H), 7.98 (dt, *J* = 7.8, 1.5 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 1H), 3.78 (s, 6H, NHO*Me* + Ar*CH_3*). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.0, 132.4, 132.0, 131.6, 130.1, 128.5, 128.1, 63.9, 52.1. **IR** ν 3004 (w), 2953 (w), 1726 (s), 1650 (m), 1516 (w), 1439 (m), 1303 (m), 1264 (s), 1156 (m), 1109 (w), 982 (w), 826 (w). NMR values are in accordance with the data reported in literature. [30]

N-Methoxy-3-(trifluoromethyl)benzamide (58)

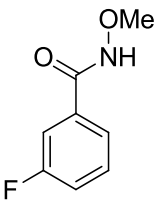


58

Starting from commercially available 3-(trifluoromethyl)benzoyl chloride (1.04 g, 5.00 mmol), N-methoxy-4-methylbenzamide **58** (822 mg, 3.75 mmol, 75% yield) was obtained as a colorless solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.60 (s, 1H, N*H*OCH_3), 8.02 (s, 1H, Ar*H*), 7.95 (d, J = 8.1 Hz, 1H, Ar*H*), 7.56 (t, J = 7.8 Hz, 1H, Ar*H*), 3.87 (s, 3H, NHO*CH_3*). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.3,

130.5, 129.3, 128.7, 128.6, 124.2, 124.2, 123.5 (q, J_F = 272.6 Hz), 64.6. **IR** ν 3190 (w), 2995 (w), 1656 (m), 1522 (w), 1440 (w), 1330 (s), 1283 (m), 1169 (s), 1125 (s), 1075 (m), 909 (w). NMR values are in accordance with the data reported in literature.[31]

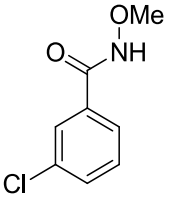
3-Fluoro-N-methoxybenzamide (59)



59

Starting from commercially available 3-fluorobenzoyl chloride (775 mg, 5.00 mmol), 3-fluoro-N-methoxybenzamide **59** (710 mg, 4.20 mmol, 84% yield) was obtained as a colorless solid. **Mp:** 67.9°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.76 (brs, 1H, N*H*OCH$_3$), 7.57 (m, 1H, Ar*H*), 7.50 (ddd, *J* = 9.4, 2.6, 1.6 Hz, 1H, Ar*H*), 7.30 – 7.21 (m, 1H, Ar*H*), 7.08 (t, *J* = 8.8 Hz, 1H, Ar*H*), 3.73 (s, 3H, NHO*CH$_3$*). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.0, 162.4 (d, *J* = 247.6 Hz), 133.7 (d, *J* = 6.9 Hz), 130.1 (d, *J* = 7.8 Hz), 122.8, 118.9 (d, *J* = 21.2 Hz), 114.4 (d, *J* = 23.3 Hz), 64.0. **IR** 2979 (w), 2940 (w), 1652 (s), 1587 (s), 1519 (m), 1483 (m), 1226 (s), 1046 (m), 937 (m), 816 (s). Mp and IR significative values are in accordance with the data reported in literature.[32]

3-Chloro-N-methoxybenzamide (60)

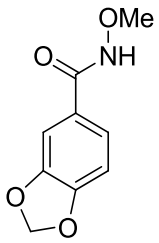


60

Starting from commercially available 3-chlorobenzoyl chloride (875 g, 5.00 mmol), 3-chloro-N-methoxybenzamide **60** (830 mg, 4.47 mmol, 89% yield) was obtained as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.90 (br s, 1H, N*H*OCH$_3$), 7.75 (s, 1H, Ar*H*), 7.64 (d, *J* = 7.8 Hz, 1H, Ar*H*), 7.45 (dd, *J* = 8.1, 2.1 Hz, 1H, Ar*H*), 7.32 (t, *J* = 7.9 Hz, 1H, Ar*H*), 3.83 (s, 3H, NHO*CH$_3$*). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 165.1, 134.7, 133.4, 132.0, 129.9, 127.5, 125.3, 64.4. **IR** ν 3187 (w), 3006 (w), 2937 (w), 1646 (s), 1572 (s), 1519 (m), 1471 (m), 1298 (m), 1162 (m), 1048 (m), 944 (m), 904 (m). NMR values are in accordance with the data reported in literature.[33]

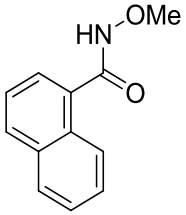
[31] N. Guimond, S. I. Gorelsky, K. Fagnou, *J. Am. Chem. Soc.* **2011**, *133*, 6449–6457.
[32] V.P. Semenov, O.B. Ratner, K.A. Ogloblin, *Zhurnal Organicheskoi Khimii* **1979**, *15*, 1870–1873. Compound **59** is purchaseable via Adlab Chemicals Building Blocks and Aurora Building Blocks.
[33] H. Zhong, D. Yang, S. Wang, J. Huang, *Chem. Commun.* **2012**, *48*, 3236–3238.

N-Methoxybenzo[d][1,3]dioxole-5-carboxamide (61)


61

Starting from commercially available benzo[d][1,3]dioxole-5-carbonyl chloride (923 mg, 5.00 mmol), N-methoxybenzo[d][1,3]dioxole-5-carboxamide **61** (865 mg, 4.43 mmol, 89% yield) was obtained as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.59 (br s, 1H, N*H*OCH$_3$), 7.31 (d, *J* = 8.2, 1.8 Hz, 1H, Ar*H*), 7.23 (s, 1H, Ar*H*), 6.69 (d, *J* = 8.1, Hz, 1H, Ar*H*), 5.92 (s, 2H, O*CH$_2$*O), 3.75 (s, 3H, NHO*CH$_3$*). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.7, 150.4, 147.6, 125.5, 122.1, 107.8, 107.5, 101.5, 63.9. **IR** ν 2982 (w), 2938 (w), 1650 (m), 1605 (m), 1478 (s), 1438 (m), 1300 (m), 1252 (s), 1093 (m), 1034 (s), 927 (s), 839 (m). **HRMS** (ESI) calcd for $C_9H_{10}NO_4^+$ $[M+H]^+$ 196.0604; found 196.0604.

N-Methoxy-1-naphthamide (62)


62

For this starting material the synthesis was performed on 1.00 mmol scale

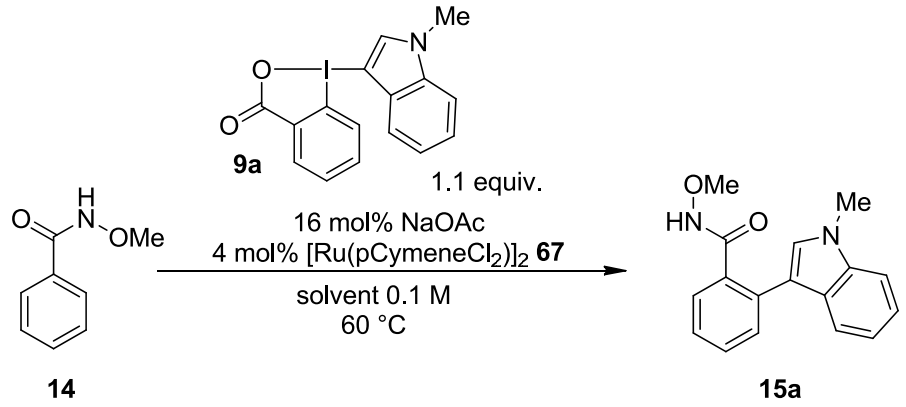
Starting from commercially available 1-naphthoyl chloride (191 mg, 1.00 mmol), N-methoxy-1-naphthamide **62** (183 mg, 0.909 mmol, 91% yield) was obtained as a white solid. **^{1}H NMR** (300 MHz, DMSO-*d$_6$*) δ 8.72 (br s, 1H, N*H*OCH$_3$), 8.28 (m, 1H, Ar*H*), 8.10–7.90 (m, 2H, Ar*H*), 7.71–7.41 (m, 4H, Ar*H*), 3.94 (s, 3H, NHO*CH$_3$*). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 167.3, 133.6, 131.4, 130.3, 129.6, 128.3, 127.4, 126.6, 125.6, 125.1, 124.5, 64.8. **IR** 2943 (w), 2907 (w), 2827 (w), 1631 (s), 1617 (s), 1591 (m), 1537 (w), 1318 (w), 1262 (w), 1063 (m), 958 (m), 889 (w). NMR values are in accordance with the data reported in literature.[34]

[34] S. Rakshit, C. Grohmann, T. Besset, F. Glorius, *J. Am. Chem. Soc.* **2011**, *133*, 2350–2353.

4.2 Optimization of the Ru-Catalyzed Indolization of Arenes via C-H activation.

GP5: In a vial, N-methoxybenzamide **14** (15.0 mg, 0.100 mmol), 1-(3-1-methyl-1*H*-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one **9a** (1.10 equiv.), $[RuCl_2(p\text{-cymene})]_2$ **67** (2.45 mg, 4.00 μmol, 4 mol%) and the relative additives (16 mol%) were dissolved in the specified dry solvent (0.1 M) under nitrogen. the reaction mixture was degassed (freeze-thaw-pump) and stirred at the reported T in °C overnight. Then the reaction was stopped, the organic layer washed with a saturated solution of $NaHCO_3$ (2 ml) and the solvent removed under reduced pressure. Flash column chromatography (Pentane:EtOAc 2:1) afforded the desired product **15a** (*see compound **15a**'s characterization for all the chemical data*).

Table S9: Screening of solvents

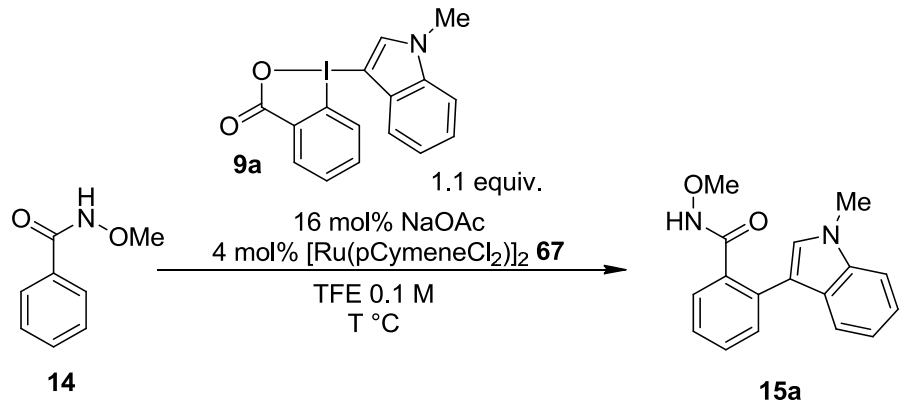


Entry	Solvent	Yield%[a]
1	DCM	-
2	DCE	-
3	**MeOH**	**43%**
4	EtOH	34%
5	*t*-BuOH	-
6	t-AmylOH	-
7	Toluene	-
8	Xylene	-
9	Dioxane	28%
10	MeCN	-

11	DMF	-
12	**2,2,2-Trifluoroethanol (TFE)**	**55%**
13	Hexafluoroisopropanol (HFIP)	30%
14	Nonafluoroisopropanol (NFIP):HFIP 1:9	-
15	HFIP:DCE 9:1	-
16	HFIP:DCE 8:2	35%
17	HFIP:DCE 1:1	-
18	Monofluoroethanol (MFE)	21%

a) Substrate **14** (0.100 mmol), IndoleBX **9a** (0.110 mmol), $[Ru(pCymeneCl_2)]_2$ **67** (4 mol%), NaOAc (16 mol%) and **solvent** (0.1 M) at 60 °C. Isolated yield after flash chromatography is given.

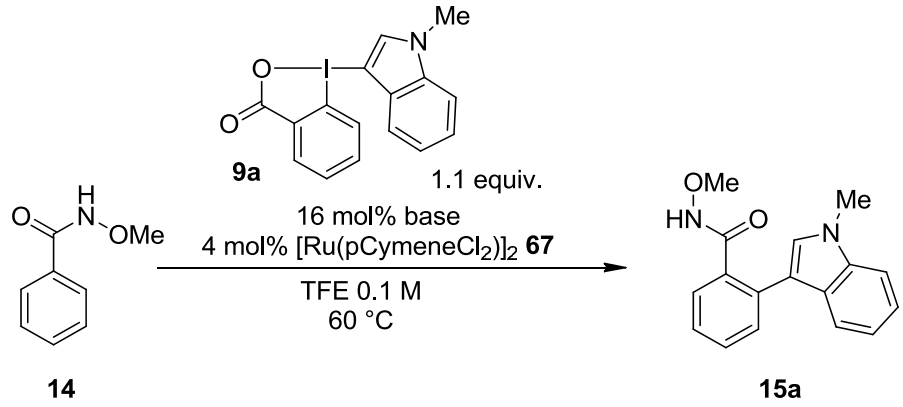
Table S10: Screening of the Temperature



Entry	T	Yield%[a]
1	r.t	-[b]
2	40	low conversion[b]
3	**60**	**55%**
4	80	low conversion[c]
5	120	-[c]

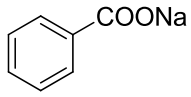
a) Substrate **14** (0.100 mmol), IndoleBX **9a** (0.110 mmol), $[Ru(pCymeneCl_2)]_2$ **67** (4 mol%), NaOAc (16 mol%) and TFE (0.1 M) at **T** °C. Isolated yield after flash chromatography is given. b) clean reaction, starting material recovered. c) decomposition occurred.

Table S11: Screening of the base

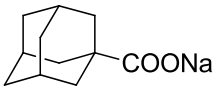


Entry	Base	Yield%[a]
1	LiOPiv	-
2	Li_2CO_3	-
3	LiMes	-[b]
4	NaOAc	55%
5	Na_2CO_3	-
6	NaOPiv	50%
7	NaMes	34%
8	63	-[b]
9	**64**	**68%**[c]
10	65	65%[b]
11	66	66%[b]
12	KOAc	-
13	KOPiv	-
14	KMes	26%[b]
15	CsOPiv	-
16	Cs_2CO_3	-

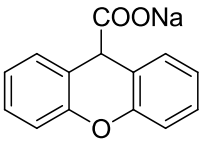
a) Substrate **14** (0.100 mmol), IndoleBX **9a** (0.110 mmol), [Ru(pCymeneCl2)]2 **67** (4 mol%), **base** (16 mol%) and TFE (0.1 M) at 60 °C. Isolated yield after flash chromatography is given. b) decomposition occurred. c)clean reaction, starting material recovered.



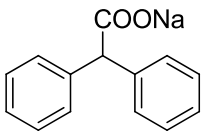
63



64



65



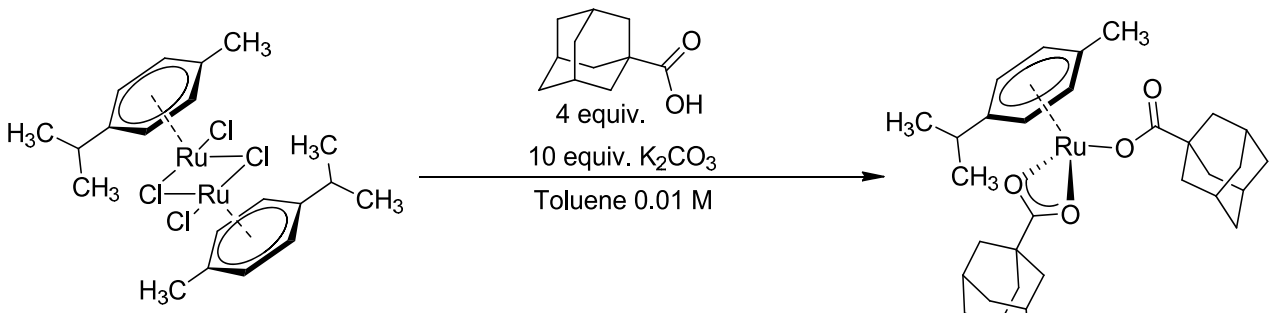
66

Table S12: Screening of the silver(I) additive

Entry	Solvent	Yield%[a]
1	none	68%[c]
2	$Ag(NTf_2)$	-[b]
3	$AgSbF_6$	-[c]
4	$AgPF_6$	-[b]
5	$AgBF_4$	-[b]
6	AgOTf	-[b]
7	AgOTs	-[b]
8	AgOAc	-[c]
9	AgBenzoate	-[b]
10	AgTFA	-[c]

a) Substrate **21** (0.100 mmol), IndoleBX **5a** (0.110 mmol), $[Ru(pCymeneCl_2)]_2$ **65** (4 mol%), NaCOOAd (16 mol%), **silver(I) additive** (16 mol%) and TFE (0.1 M) at 60 °C. Isolated yield after flash chromatography is given. b) decomposition occurred. c) clean reaction, starting material recovered.

4.3 Preparation of the Ruthenium Catalyst 68.

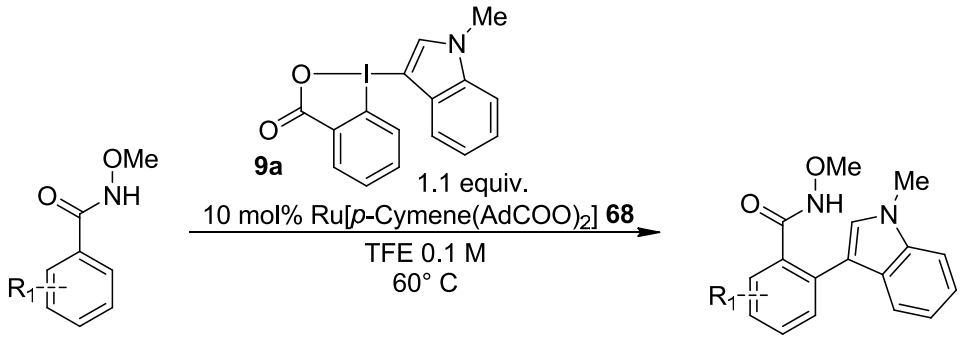


67 **68**

Following a reported procedure,[35] $[RuCl_2(p\text{-cymene})]_2$ **67** (105 mg, 0.163 mmol), adamantane-1-carboxylic acid (118 mg, 0.652 mmol, 4.00 equiv.) and K_2CO_3 (225 mg, 1.63 mmol, 10.0 equiv.) were suspended in toluene (16.0 mL, 0.01 M) under N_2. The resulting suspension was stirred for 3 hours at r.t.. The solvent was then removed *in vacuo* and the residue dissolved in dry CH_2Cl_2 (20 mL). The resulting suspension was filtered under N_2 through a short plug of celite. The solvent was removed *in vacuo* to yield (catalyst) complex **68** (90.0 mg, 0.156 mmol, 96% yield) as an orange solid. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 5.70 (d, *J* = 5.7 Hz, 2H, Ar*H*), 5.49 (d, *J* = 5.7 Hz, 2H, Ar*H*), 2.88 (hept, *J* = 7.1 Hz, 1H, *ArCH(*$CH_3)_2$), 2.23 (s, 3H, Ar*CH₃*), 1.92 (t, *J* = 3.3 Hz, 6H, ArCH*(CH₃)₂*), 1.78 (s, 12H, Ad*CH₂*), 1.63 (s, 12H, Ad*CH₂*), 1.33 (d, *J* = 6.9 Hz, 6H, Ad*CH*). ^{1}H-NMR values are in accordance with the data reported in literature.[35]

[35] L. Ackermann, P. Novák, R. Vicente, N. Hofmann, *Angew. Chem. Int. Ed.* **2009**, *48*, 6045–6048.

4.4 Scope of the Ru-Catalyzed Indolization via C-H activation.



GP6: In a vial, freshly synthetized benzamide **14-62** (50.0 mg, 0.300 mmol), 1-(3-1-methyl-1*H*-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one (0.330 mmol, 1.10 equiv.) and freshly synthetized Ruthenium complex **68** (18.2 mg, 30.0 µmol, 10 mol%), were dissolved in dry TFE (3 ml, 0.1 M) under nitrogen. the reaction mixture was degassed (freeze-thaw-pump) and stirred at 60 °C overnight. It was then allowed to cool down to r.t., washed with a saturated aqueous $NaHCO_3$ (2ml) and concentrated under reduced pressure. Flash column chromatography (Pentane:EtOAc) afforded the desired products **15a-15k**.

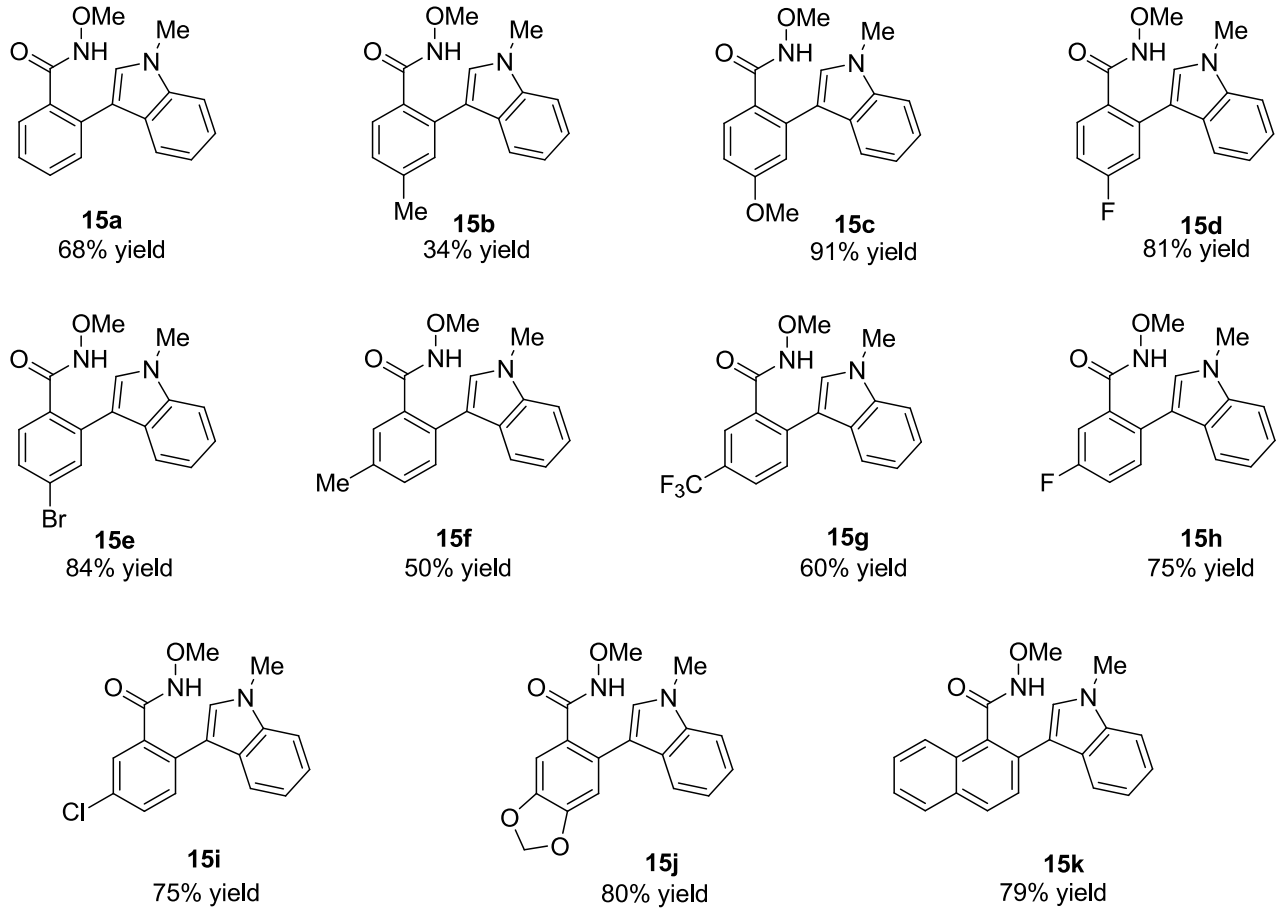
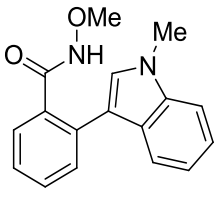


Figure S5: *Scope with Methoxy-amides.*

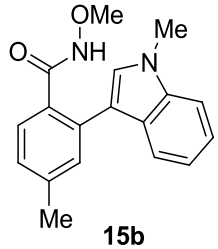
N-Methoxy-2-(1-methyl-1*H*-indol-3-yl)benzamide (15a)



Starting from N-methoxybenzamide **14** (45.3 mg, 0.300 mmol), N-methoxy-2-(1-methyl-1H-indol-3-yl)benzamide **15a** (57.0 mg, 0.203 mmol, 68% yield) was obtained as a yellow oil. Rf: 0.4 (Pentane:EtOAc 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (br s, 1H, N*H*OCH$_3$), 7.74 (dd, *J* = 7.5, 5.9 Hz, 1H, Ar*H*), 7.67 (d, *J* = 7.9 Hz, 1H, Indole*H*), 7.57 (dd, *J* = 7.8, 1.4 Hz, 1H, Ar*H*), 7.52 (td, *J* = 7.5, 1.4 Hz, 1H, Ar*H*), 7.38 (m, 2H, Ar*H* + Indole*H*), 7.30 (ddd, *J* = 8.2, 6.9, 1.1 Hz, 1H, Indole*H*), 7.24 (s, 1H, CH$_3$N*CH*C), 7.18 (ddd, *J* = 7.9, 6.9, 1.0 Hz, 1H, Indole*H*), 3.85 (s, 3H, N*CH$_3$*), 3.46 (s, 3H, NHO*CH$_3$*). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.4, 137.0, 132.5, 132.4, 130.8, 130.7, 129.5, 128.1, 126.8, 126.7, 122.5, 120.3, 119.5, 113.5, 109.6, 63.9, 33.0. **IR** ν 3209 (w), 3057 (w), 2968

(w), 2934 (m), 2816 (w), 1655 (s), 1599 (w), 1547 (w), 1482 (s), 1464 (m), 1378 (m), 1329 (m), 1223 (m), 1161 (w), 1034 (m), 944 (m), 885 (m). HRMS (ESI) calcd for $C_{17}H_{16}N_2NaO_2^+$ $[M+Na]^+$ 303.1104; found 303.1108

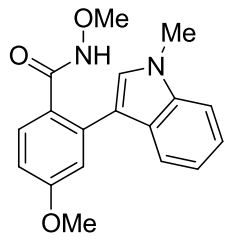
N-Methoxy-4-methyl-2-(1-methyl-1*H*-indol-3-yl)benzamide (15b)



15b

Starting from N-methoxy-4-methylbenzamide **53** (50.0 mg, 0.300 mmol), N-methoxy-4-methyl-2-(1-methyl-1*H*-indol-3-yl)benzamide **15b** (30.0 mg, 0.102 mmol, 34% yield) was obtained as a yellow oil. Rf: 0.44 (Pentane:EtOAc 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (br s, 1H, N*H*OCH$_3$), 7.71 – 7.64 (m, 2H, Ar*H*), 7.40 – 7.34 (m, 2H, Ar*H*), 7.30 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H, Ar*H*), 7.22 – 7.16 (m, 3H, Ar*H*), 3.85 (s, 3H, N*CH$_3$*), 3.44 (s, 3H, NHO*CH$_3$*), 2.42 (s, 3H, Ar*CH$_3$*). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.5, 141.1, 137.0, 132.4, 131.4, 129.7, 129.6, 128.0, 127.7, 126.8, 122.5, 120.4, 119.6, 113.8, 109.6, 63.8, 33.0, 21.5. **IR** ν 3200 (w), 3047 (w), 2936 (w), 1662 (s), 1615 (m), 1543 (w), 1482 (m), 1370 (w), 1331 (w), 1232 (w), 1160 (w), 1086 (w), 1040 (w), 1015 (w), 912 (w), 887 (w), 834 (w). **HRMS** (ESI) calcd for $C_{18}H_{18}N_2NaO_2^+$ $[M+Na]^+$ 317.1260; found 317.1264.

N,4-Dimethoxy-2-(1-methyl-1*H*-indol-3-yl)benzamide (15c)

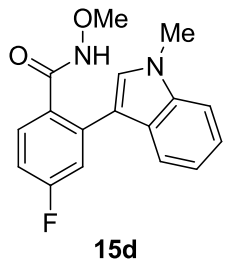


15c

Starting from N,4-dimethoxybenzamide **54** (54.5 mg, 0.300 mmol), N,4-dimethoxy-2-(1-methyl-1H-indol-3-yl)benzamide **15c** (85.0 mg, 0.274 mmol, 91% yield) was obtained as a yellow oil. Rf: 0.48 (Pentane:EtOAc 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (br s, 1H, N*H*OCH$_3$), 7.75 (d, *J* = 8.6 Hz, 1H, Ar*H*), 7.66 (dd, *J* = 8.0, 1.0 Hz, 1H, Ar*H*), 7.38 (d, *J* = 8.3 Hz, 1H, Ar*H*), 7.30 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H, Ar*H*), 7.22 (s, 1H, N*CH*C), 7.18 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H, Ar*H*), 7.03 (d, *J* = 2.6 Hz, 1H, Ar*H*), 6.92 (dd, *J* = 8.6, 2.6 Hz, 1H, Ar*H*), 3.85 (s, 3H, N*CH$_3$*), 3.85 (s, 3H, O*CH$_3$*), 3.43 (s, 3H, NHO*CH$_3$*). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.1, 161.3, 137.0, 134.3, 131.5, 128.0, 126.7, 124.8, 122.5, 120.4, 119.6, 115.7, 113.7, 112.5, 109.7, 63.8, 55.4, 33.0. **IR** ν 3203 (w), 2961 (w), 2936 (w), 2838 (w), 1661 (s), 1603 (s), 1467 (m), 1330

(m), 1279 (m), 1238 (m), 1214 (m), 1084 (m), 1030 (m), 886 (w). **HRMS** (ESI) calcd for $C_{18}H_{18}N_2NaO_3^+$ $[M+Na]^+$ 333.1210; found 333.1210.

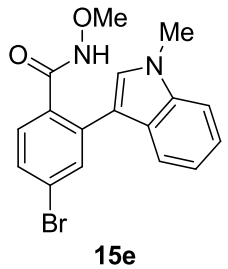
5-Fluoro-N-methoxy-2-(1-methyl-1*H*-indol-3-yl)benzamide (15d)



15d

Starting from 4-fluoro-N-methoxybenzamide **55** (50.7 mg, 0.300 mmol), 4-bromo-N-methoxy-2-(1-methyl-1H-indol-3-yl)benzamide **15d** (78.0 mg, 0.243 mmol, 81% yield) was obtained as a yellow oil. Rf: 0.40 (Pentane:EtOAc 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (s, 1H, N*H*OCH$_3$), 7.55 (d, *J* = 7.7 Hz, 1H, Ar*H*), 7.48 (m, 1H, Ar*H*), 7.42 – 7.35 (m, 2H, Ar*H*), 7.33 – 7.27 (m, 2H, Ar*H*), 7.23 (s, 1H, N*CH*C), 7.17 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H, Ar*H*), 3.84 (s, 3H, N*CH$_3$*), 3.31 (s, 3H, NHO*CH$_3$*). **^{13}C NMR** (101 MHz, $CDCl_3$; *two doublet were not resolved*) δ 166.6, 160.1 (d, *J* = 247.4 Hz), 136.8, 135.2, 129.2, 128.6 (d, *J* = 8.5 Hz), 127.1, 125.0, 122.5, 120.4, 119.9 (d, *J* = 2.2 Hz), 118.01 (d, *J* = 23.3 Hz), 109.6, 105.9, 63.6, 33.1. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -111.7. **IR** ν 3201 (w), 3055 (w), 2984 (w), 2938 (w), 1932 (w), 1663 (m), 1551 (w), 1481 (m), 1455 (m), 1374 (m), 1330 (m), 1266 (s), 1245 (m), 1224 (m), 1161 (w), 1052 (m), 943 (w), 829 (s). **HRMS** (ESI) calcd for $C_{17}H_{15}FN_2NaO_2^+$ $[M+Na]^+$ 321.1010; found 321.1008.

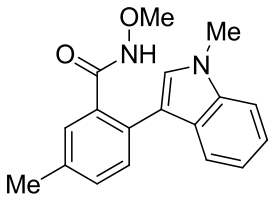
4-Bromo-N-methoxy-2-(1-methyl-1*H*-indol-3-yl)benzamide (15e)



15e

Starting from 4-bromo-N-methoxybenzamide **56** (69.0 mg, 0.300 mmol), 4-bromo-N-methoxy-2-(1-methyl-1*H*-indol-3-yl)benzamide **15e** (91.0 mg, 0.253 mmol, 84% yield) was obtained as an orange oil. Rf: 0.35 (Pentane:EtOAc 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (br s, 1H, N*H*OCH$_3$), 7.75 (m, 1H, Ar*H*), 7.67 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.39 (d, *J* = 8.2 Hz, 1H, Ar*H*), 7.33 (m, 1H, Ar*H*), 7.28 – 7.24 (m, 2H, Ar*H*), 7.21 (m, 1H, Ar*H*), 7.07 (td, *J* = 8.3, 2.6 Hz, 1H, Ar*H*), 3.85 (s, 3H, N*CH$_3$*), 3.46 (s, 3H, NHO*CH$_3$*). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.4, 137.0, 134.6, 133.3, 131.2, 129.8, 128.4, 126.4, 125.2, 122.8, 120.7, 119.3, 112.3, 109.8, 63.9, 33.1 *(one Carbon signal not resolved).* **IR** ν 3186 (w), 3063 (w), 2934 (w), 1656 (s), 1605 (s), 1580 (m), 1480 (s), 1364 (w), 1331 (m), 1265 (s), 1195 (m), 1082 (w), 1037 (m), 986 (w), 939 (w), 887 (m), 826 (m). **HRMS** (ESI) calcd for $C_{17}H_{15}{}^{79}BrN_2NaO_2^+$ $[M+Na]^+$ 381.0209; found 381.0204.

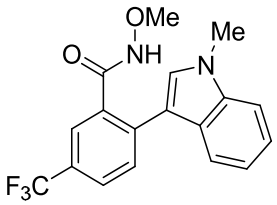
N-Methoxy-5-methyl-2-(1-methyl-1*H*-indol-3-yl)benzamide (15f)



15f

Starting from N-methoxy-3-methylbenzamide **57** (50.0 mg, 0.300 mmol), N-methoxy-5-methyl-2-(1-methyl-1H-indol-3-yl)benzamide **15f** (44.0 mg, 0.149 mmol, 50% yield) was obtained as a yellow oil. Rf: 0.40 (Pentane:EtOAc 2:1). **^{1}H NMR** (400 MHz, CD_2Cl_2) δ 8.27 (s, 1H, Ar*H*), 8.24 (s, 1H, N*H*OCH$_3$), 8.13 (dd, *J* = 8.1, 1.9 Hz, 1H, Ar*H*), 7.67 (dd, *J* = 9.9, 8.0 Hz, 2H, Ar*H*), 7.41 (dt, *J* = 8.3, 0.9 Hz, 1H, Ar*H*), 7.34 (s, 1H, Ar*H*), 7.29 (ddd, *J* = 8.2, 7.0, 1.1 Hz, 1H, Ar*H*), 7.18 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H, Ar*H*), 3.92 (s, 3H, N*CH$_3$*), 3.85 (s, 3H, *CH$_3$*), 3.49 (s, 3H, NHO*CH$_3$*). **^{13}C NMR** (101 MHz, CD_2Cl_2) δ 166.7, 138.2, 137.8, 133.1, 131.8, 131.2, 131.0, 129.5, 128.6, 127.0, 123.1, 121.0, 119.9, 113.3, 110.4, 64.3, 52.7, 33.6. **IR** ν 3181 (w), 2932 (w), 1713 (s), 1660 (s), 1606 (m), 1538 (w), 1466 (w), 1437 (w), 1289 (m), 1262 (s), 1248 (s), 1162 (w), 1128 (m), 1107 (m), 1038 (w). **HRMS** (ESI) calcd for $C_{18}H_{18}N_2NaO_2^+$ $[M+Na]^+$ 317.1260; found 317.1265.

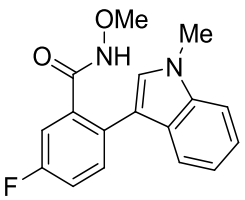
N-Methoxy-2-(1-methyl-1*H*-indol-3-yl)-5-(trifluoromethyl)benzamide (15g)



15g

Starting from N-methoxy-3-(trifluoromethyl)benzamide **58** (65.7 mg, 0.300 mmol), N-methoxy-2-(1-methyl-1H-indol-3-yl)-5-(trifluoromethyl)benzamide **15g** (63.0 mg, 0.181 mmol, 60% yield) was obtained as a colorless oil. Rf: 0.37 (Pentane:EtOAc 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (br s, 1H, N*H*OCH$_3$), 7.91 (s, 1H, Ar*H*), 7.70 – 7.62 (m, 2H, Ar*H*), 7.59 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.33 (m, 1H, Ar*H*), 7.27 (m, 1H, Ar*H*), 7.24 (s, 1H, N*CH*C), 7.14 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 1H, Ar*H*), 3.79 (s, 3H, N*CH$_3$*), 3.45 (s, 3H, NHO*CH$_3$*). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.1, 137.1, 136.4, 132.6, 130.9, 128.8, 128.7, 127.3, 126.7, 126.4, 123.80 (q, *J* = 272.1 Hz, *C*F$_3$), 122.8, 120.8, 119.2, 112.2, 109.9, 64.1, 33.1. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.5. **IR** ν 3187 (w), 2978 (w), 2935 (w), 1657 (m), 1617 (w), 1549 (w), 1469 (w), 1331 (s), 1274 (w), 1173 (m), 1159 (m), 1127 (s), 1092 (m), 947 (w), 911 (w), 849 (w). **HRMS** (ESI) calcd for $C_{18}H_{15}F_3N_2NaO_2^+$ $[M+Na]^+$ 371.0978; found 371.0979.

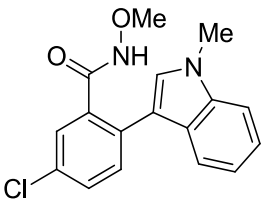
5-Fluoro-N-methoxy-2-(1-methyl-1*H*-indol-3-yl)benzamide (15h)



15h

Starting from 3-fluoro-N-methoxybenzamide **59** (50.7 mg, 0.300 mmol), 4-bromo-N-methoxy-2-(1-methyl-1*H*-indol-3-yl)benzamide **16h** (84.0 mg, 0.225 mmol, 75% yield) was obtained as a yellow oil. Rf: 0.38 (Pentane:EtOAc 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (br s, 1H, N*H*OCH$_3$), 7.72 (d, *J* = 2.0 Hz, 1H, Ar*H*), 7.64 (t, *J* = 9.1 Hz, 2H, Ar*H*), 7.52 (dd, *J* = 8.2, 2.0 Hz, 1H, Ar*H*), 7.40 (m, 1H, Ar*H*), 7.32 (dd, *J* = 7.0, 1.2 Hz, 1H, Ar*H*), 7.25 (s, 1H, N*CH*C), 7.21 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 1H, Ar*H*), 3.85 (s, 3H, N*CH$_3$*), 3.45 (s, 3H, NHO*CH$_3$*). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.6, 163.8 (d, *J* = 250.9 Hz), 137.0, 135.4, 135.3 (d, *J* = 9.4 Hz), 131.8 (d, *J* = 9.5 Hz), 128.4, 128.3, 126.4, 122.7, 120.7, 117.10 (d, *J* = 21.5 Hz), 113.79 (d, *J* = 21.9 Hz), 112.5, 109.8, 63.9, 33.1. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -109.3. **IR** ν 3179 (w), 3055 (w), 2932 (m), 2853 (w), 1662 (s), 1586 (m), 1550 (w), 1479 (s), 1329 (w), 1256 (w), 1222 (w), 1163 (w), 1089 (m), 1038 (m), 956 (w), 911 (m), 882 (m), 824 (w). **HRMS** (ESI) calcd for $C_{17}H_{15}FN_2NaO_2^+$ $[M+Na]^+$ 321.1010; found 321.1011.

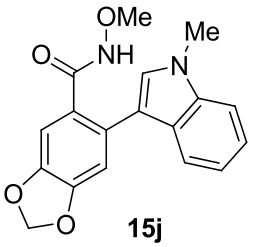
5-Chloro-N-methoxy-2-(1-methyl-1*H*-indol-3-yl)benzamide (15i)



15i

Starting from 3-chloro-N-methoxybenzamide **60** (55.7 mg, 0.300 mmol), N-methoxy-2-(1-methyl-1H-indol-3-yl)-5-(trifluoromethyl)benzamide **15i** (70.9 mg, 0.225 mmol, 75% yield) was obtained as a yellow oil. Rf: 0.35 (Pentane:EtOAc 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (br s, 1H, N*H*OCH$_3$), 7.64 (dd, *J* = 8.0, 1.3 Hz, 1H, Ar*H*), 7.60 (d, *J* = 7.7 Hz, 1H, Ar*H*), 7.45 – 7.37 (m, 2H, Ar*H*), 7.35 (d, *J* = 7.9 Hz, 1H, Ar*H*), 7.29 (m, 1H, Ar*H*), 7.19 (s, 1H, N*CH*C), 7.15 (t, *J* = 7.5 Hz, 1H, Ar*H*), 3.87 (s, 3H, N*CH$_3$*), 3.15 (s, 3H, NHO*CH$_3$*). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.9, 137.0, 133.6, 132.7, 132.0, 131.1, 130.9, 129.5, 128.2, 126.6, 122.7, 120.6, 119.3, 112.3, 109.8, 64.0, 33.1. **IR** ν 3185 (w), 3058 (w), 2931 (m), 2852 (w), 1656 (s), 1543 (w), 1482 (m), 1466 (m), 1374 (w), 1330 (w), 1256 (w), 1163 (w), 1100 (m), 1041 (w), 943 (m), 824 (w). **HRMS** (ESI) calcd for $C_{17}H_{15}ClN_2NaO_2^+$ $[M+Na]^+$ 337.0714; found 337.0720.

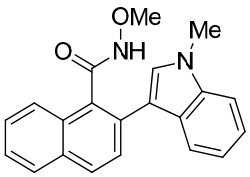
N-Methoxy-6-(1-methyl-1*H*-indol-3-yl)benzo[d][1,3]dioxole-5-carboxamide (15j)



15j

Starting from N-methoxybenzo[d][1,3]dioxole-5-carboxamide **61** (58.6 mg, 0.300 mmol), N-methoxy-6-(1-methyl-1H-indol-3-yl)benzo[d][1,3]dioxole-5-carboxamide **15j** (78.0 mg, 0.240 mmol, 80% yield) was obtained as a white oil. Rf: 0.48 (Pentane:EtOAc 2:1). **^{1}H NMR** (400 MHz, CD_2Cl_2) δ 7.49 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.40 (d, *J* = 8.3 Hz, 1H, Indole*H*), 7.33 – 7.25 (m, 3H, Indole*H*), 7.14 (ddd, *J* = 8.0, 6.9, 1.0 Hz, 1H, Ar*H*), 6.85 (d, *J* = 8.1 Hz, 1H, Indole*H*), 6.01 (s, 2H, O*CH*$_2$O), 3.84 (s, 3H, N*CH*$_3$), 3.35 (s, 3H, NHO*CH*$_3$). *(NHOMe proton present at 8.2 ppm)* **^{13}C NMR** (101 MHz, CD_2Cl_2; the signals of two aromatic carbons were not resolved) δ 166.8, 149.5, 146.1, 137.0, 129.4, 127.1, 126.9, 124.1, 122.4, 120.2, 115.2, 109.8, 107.0, 106.8, 101.7, 63.6, 33.1. **IR** ν 3191 (w), 2967 (w), 2934 (w), 2899 (w), 1656 (m), 1628 (m), 1480 (m), 1448 (s), 1374 (w), 1340 (m), 1250 (s), 1224 (w), 1132 (w), 1040 (s), 1017 (w), 929 (m), 833 (w). **HRMS** (ESI) calcd for $C_{18}H_{16}N_2NaO_4^+$ $[M+Na]^+$ 347.1002; found 347.1002.

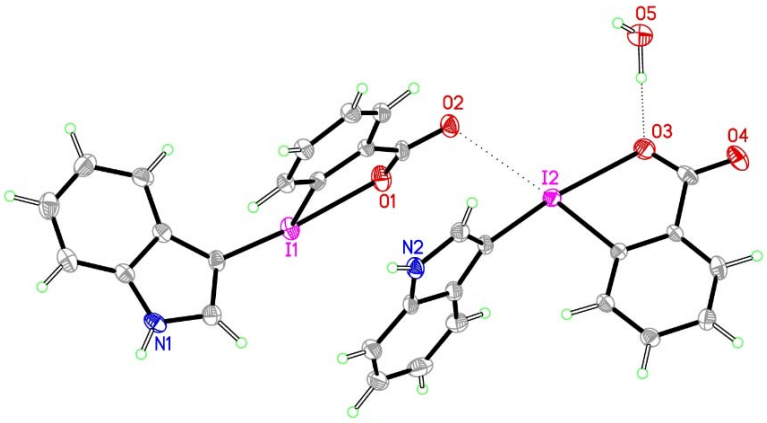
N-Methoxy-2-(1-methyl-1*H*-indol-3-yl)-1-naphthamide (15k)



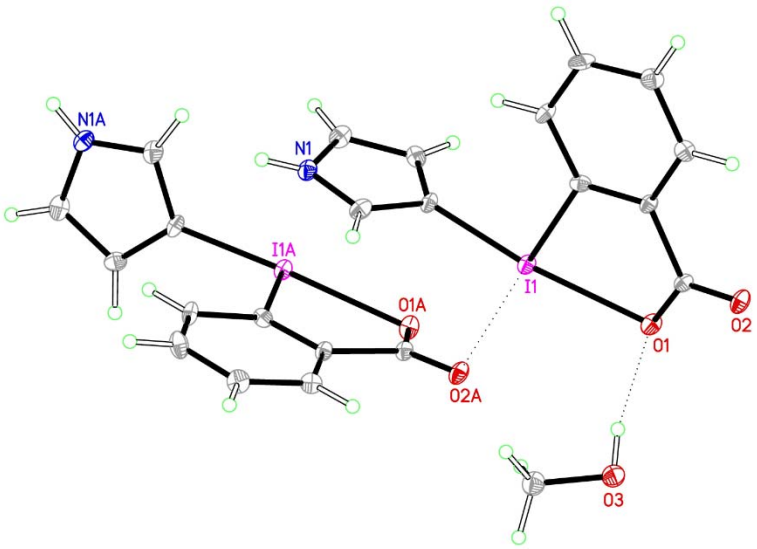
15k

Starting from N-methoxy-1-naphthamide **62** (60.4 mg, 0.300 mmol), N-methoxy-2-(1-methyl-1*H*-indol-3-yl)-1-naphthamide **15k** (78.0 mg, 0.236 mmol, 79% yield) was obtained as a colorless oil. Rf: 0.35 (Pentane:EtOAc 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.5 Hz, 1H, Ar*H*), 8.00 – 7.95 (m, 2H, Ar*H* + N*H*OCH$_3$), 7.89 (m, 1H, Ar*H*), 7.80 (t, *J* = 8.6 Hz, 2H, Ar*H*), 7.58 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H, Ar*H*), 7.52 (ddd, *J* = 8.1, 6.9, 1.3 Hz, 1H, Ar*H*), 7.41 (d, *J* = 9.7 Hz, 2H, Ar*H*), 7.32 (m, 1H, Ar*H*), 7.22 (m, 1H, Ar*H*), 3.86 (s, 3H, N*CH*$_3$), 3.66 (s, 3H, NHO*CH*$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.3, 137.1, 131.8, 131.3, 131.1, 130.0, 128.9, 128.5, 128.0, 127.6, 127.4, 126.9, 126.0, 124.8, 122.3, 120.2, 119.4, 113.1, 109.8, 64.0, 33.0. **IR** ν 3186 (w), 3056 (w), 2958 (w), 2929 (m), 2854 (w), 1651 (s), 1615 (m), 1545 (w), 1479 (m), 1384 (w), 1339 (w), 1264 (w), 1230 (w), 1134 (w), 1101 (w), 1074 (m), 1019 (m), 892 (w), 821 (s). **HRMS** (ESI) calcd for $C_{21}H_{18}N_2NaO_2^+$ $[M+Na]^+$ 353.1260; found 353.1256.

5. Crystal Structure and DSC Measurements.

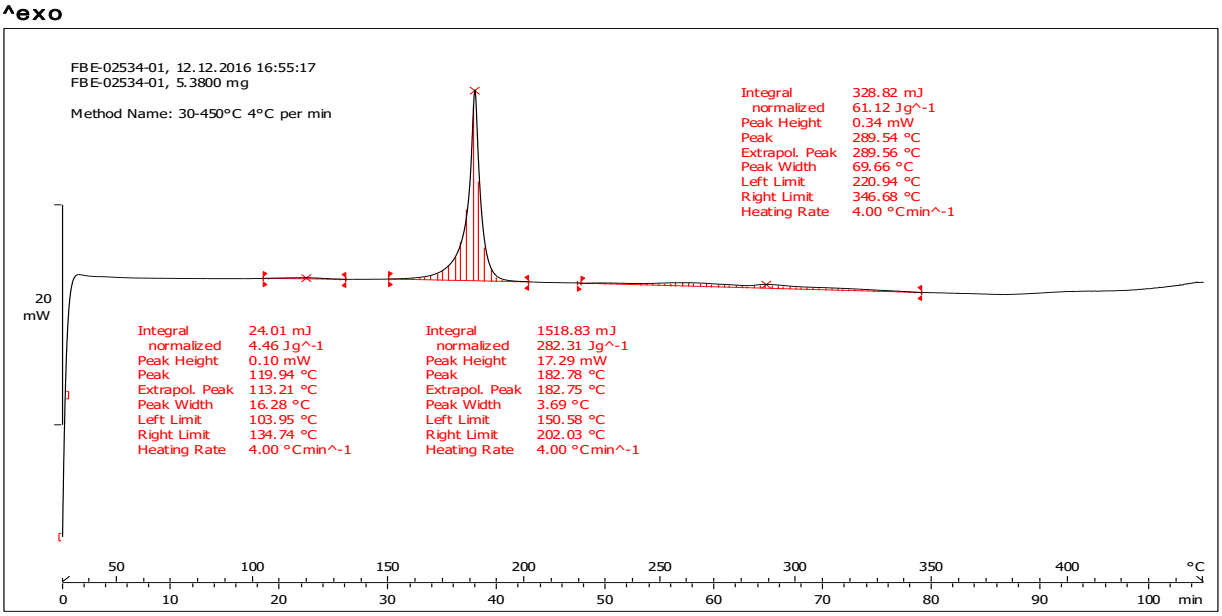


A single crystal was grown by slow diffusion of the solution of **9b** in MeOD/CCl_4 mixture. Supplementary crystallographic data for this compound have been deposited at Cambridge Crystallographic Data Centre (**1540821**) and can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

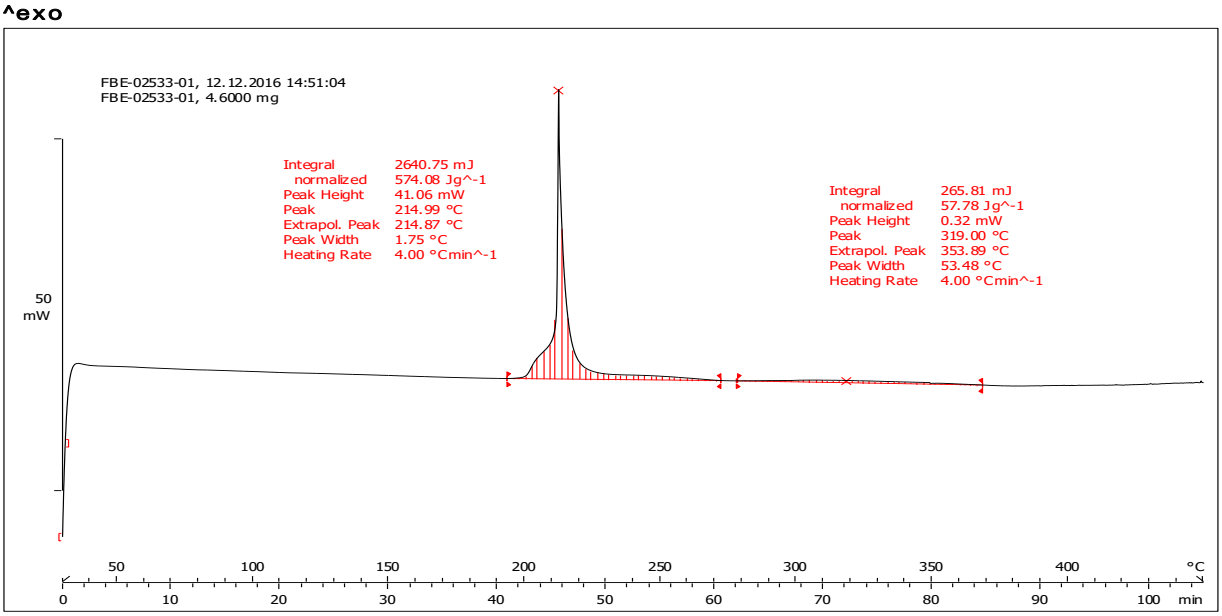


A single crystal was grown by slow diffusion of the solution of **9m** in MeOD/CCl_4 mixture. Supplementary crystallographic data for this compound have been deposited at Cambridge Crystallographic Data Centre (**1541174**) and can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

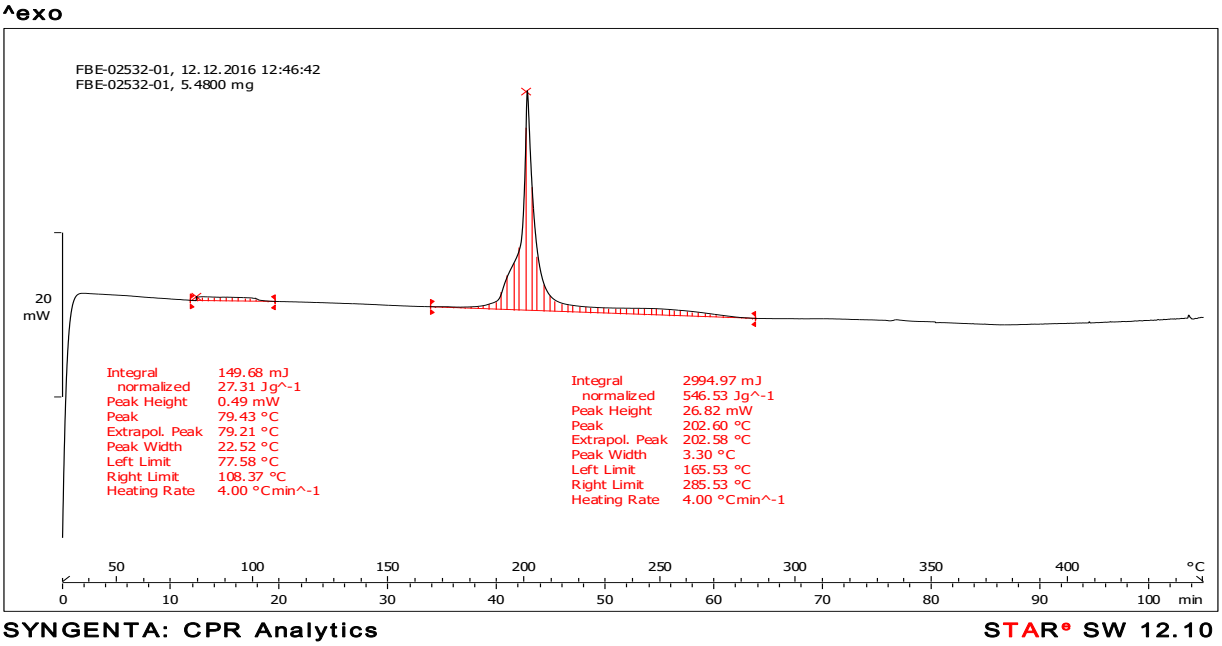
DSC measurements of compound 9a



DSC measurements of compound 9n

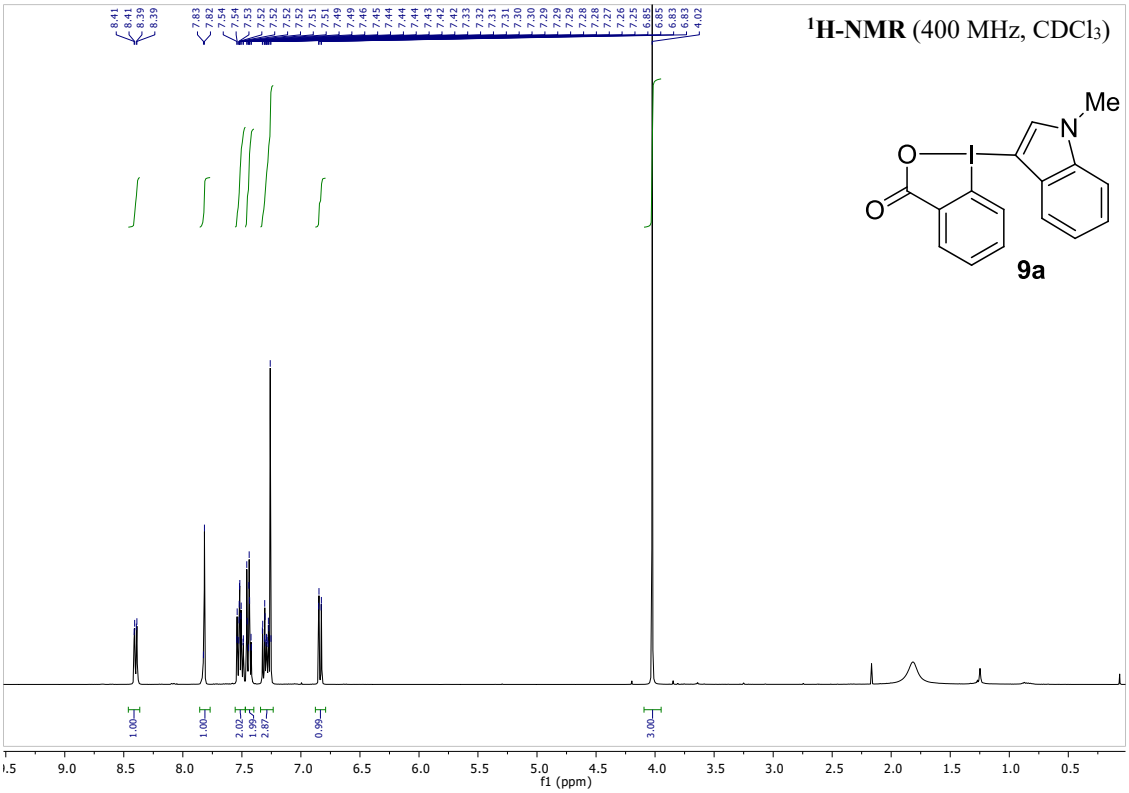


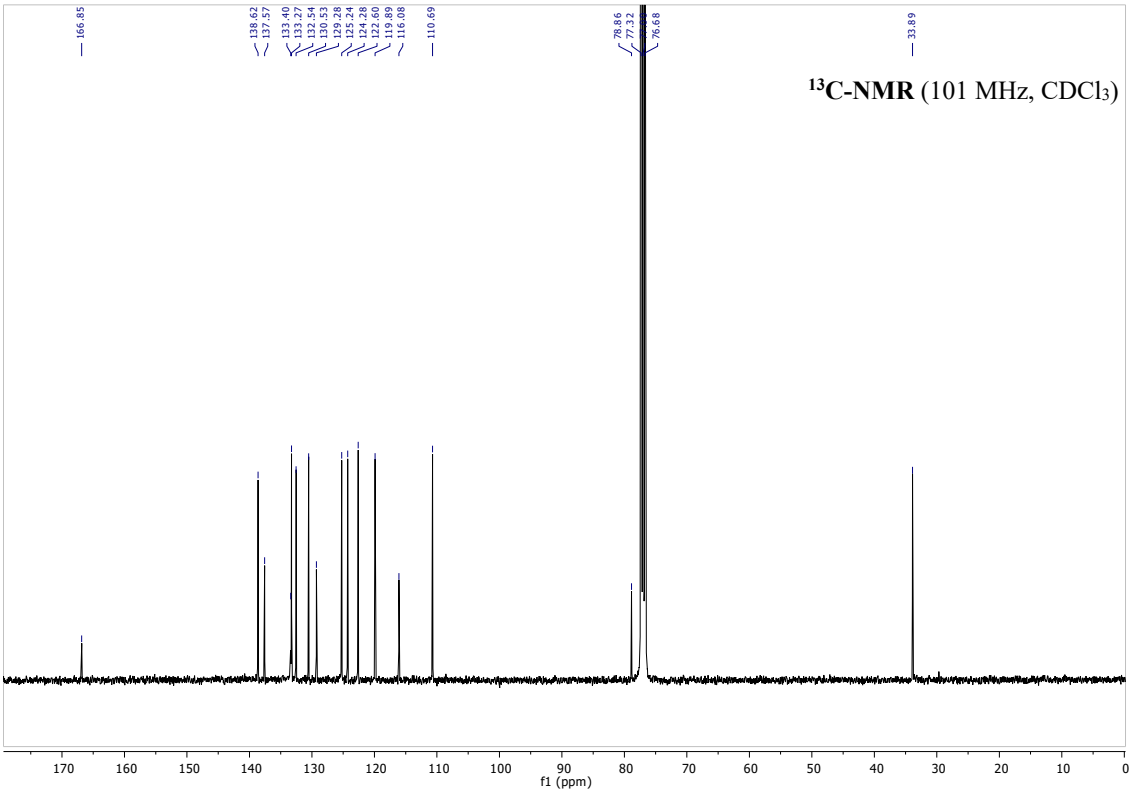
DSC measurements of compound 9o



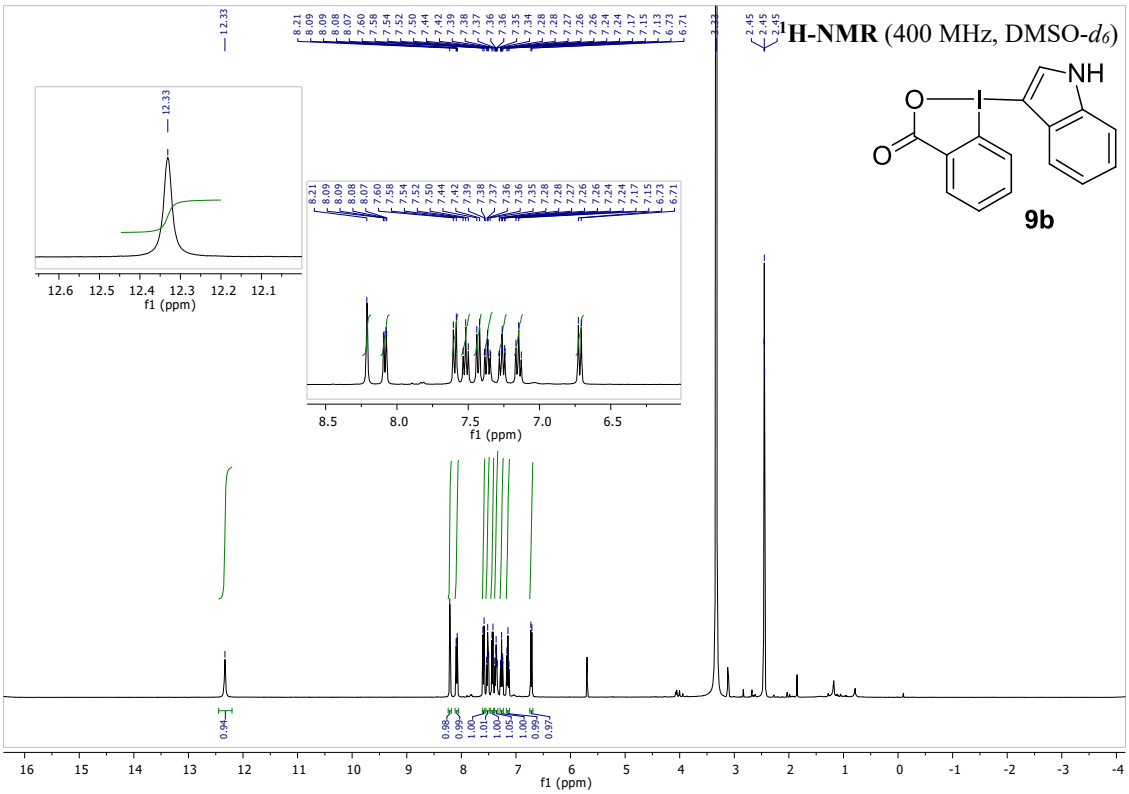
6. Spectra of new compounds

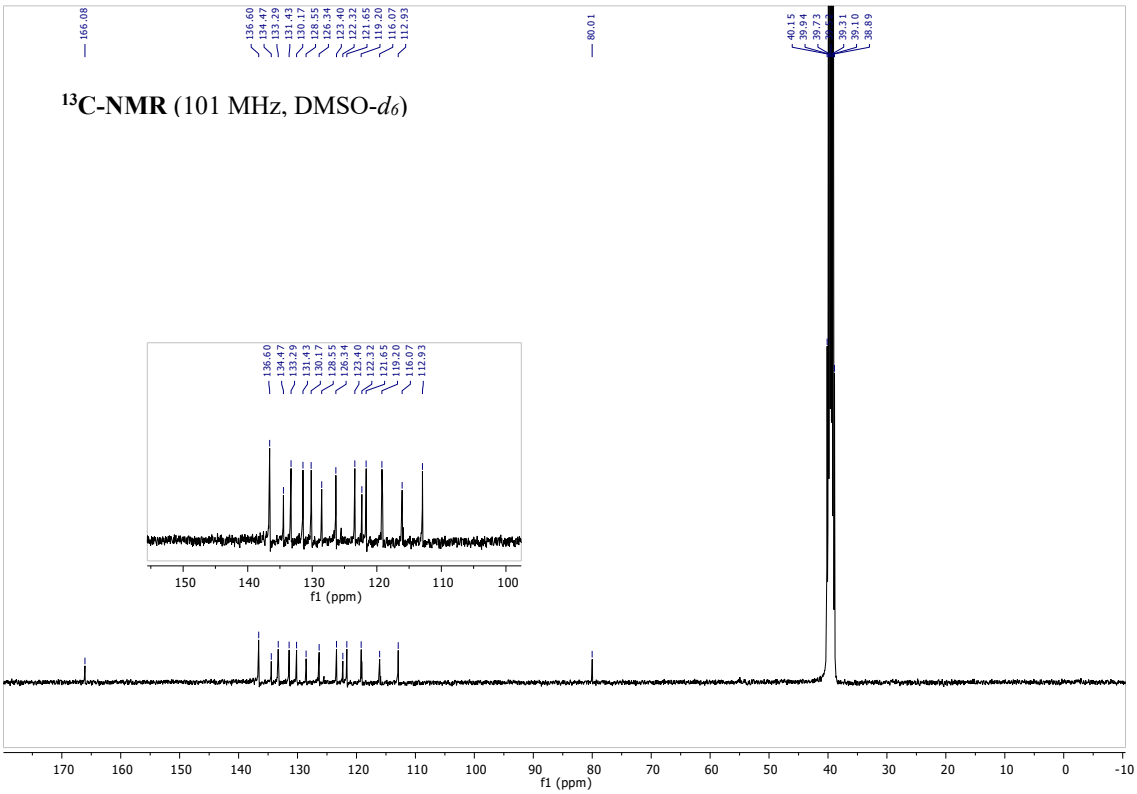
1-(3-1-Methyl-1*H*-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one (9a)



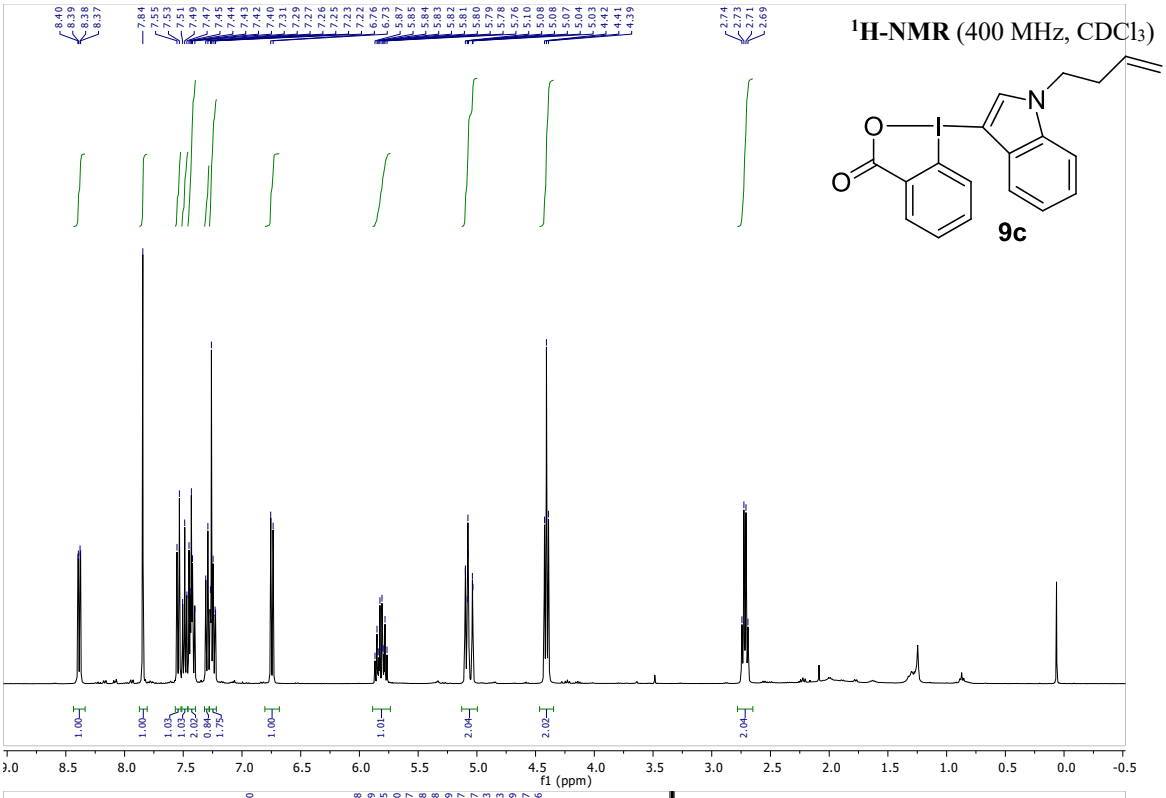


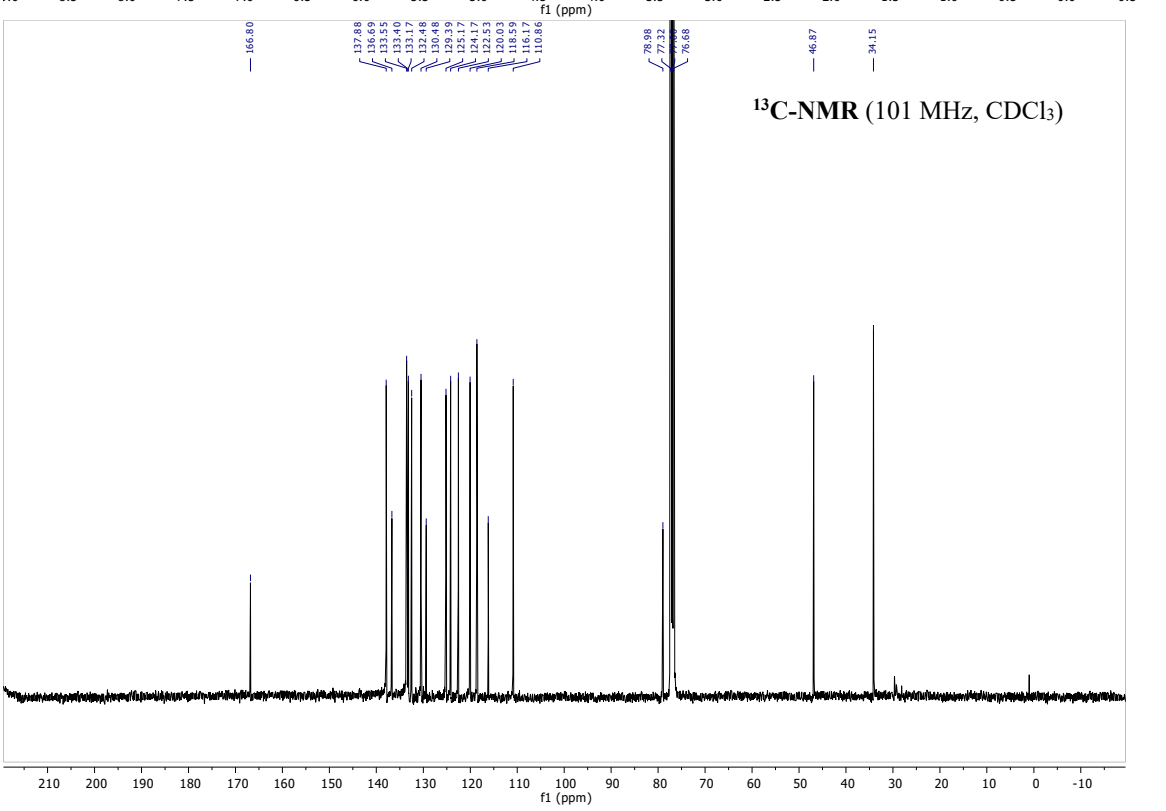
1-(3-1*H*-Indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one (9b)



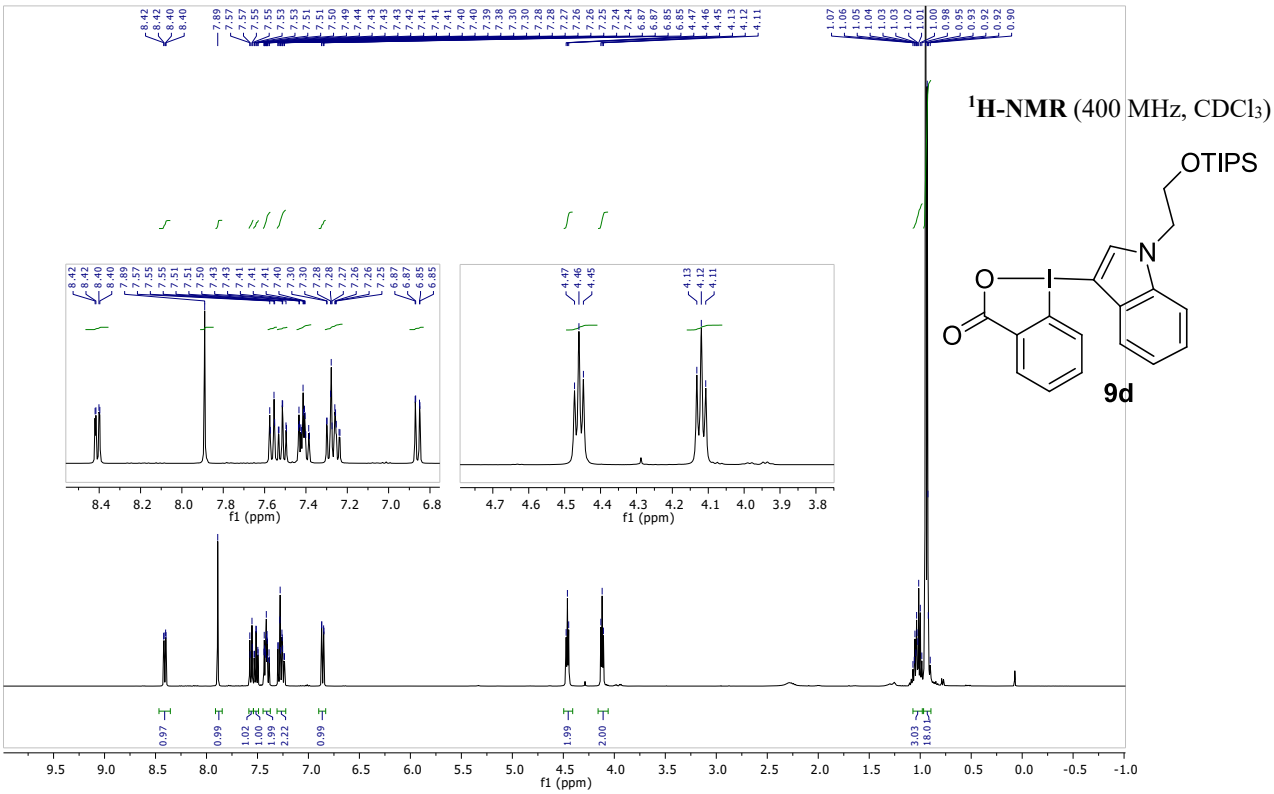


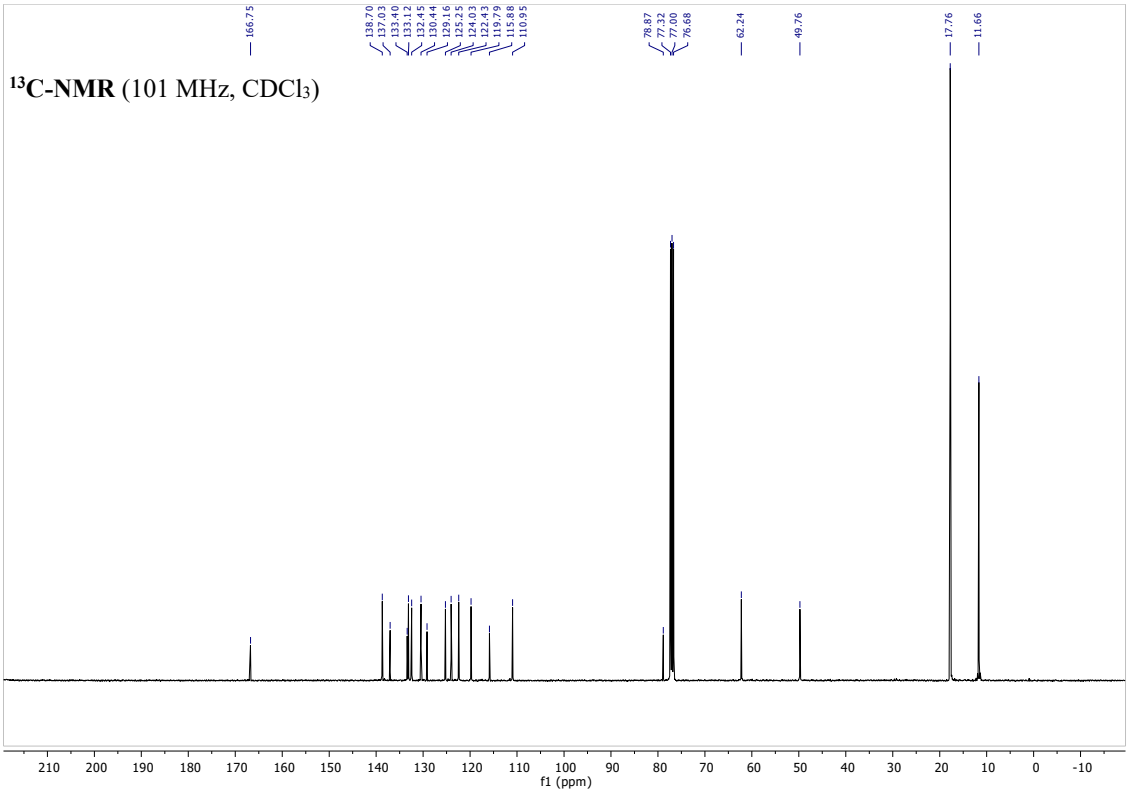
1-(3-1-(But-3-en-1-yl)-1*H*-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one (9c)



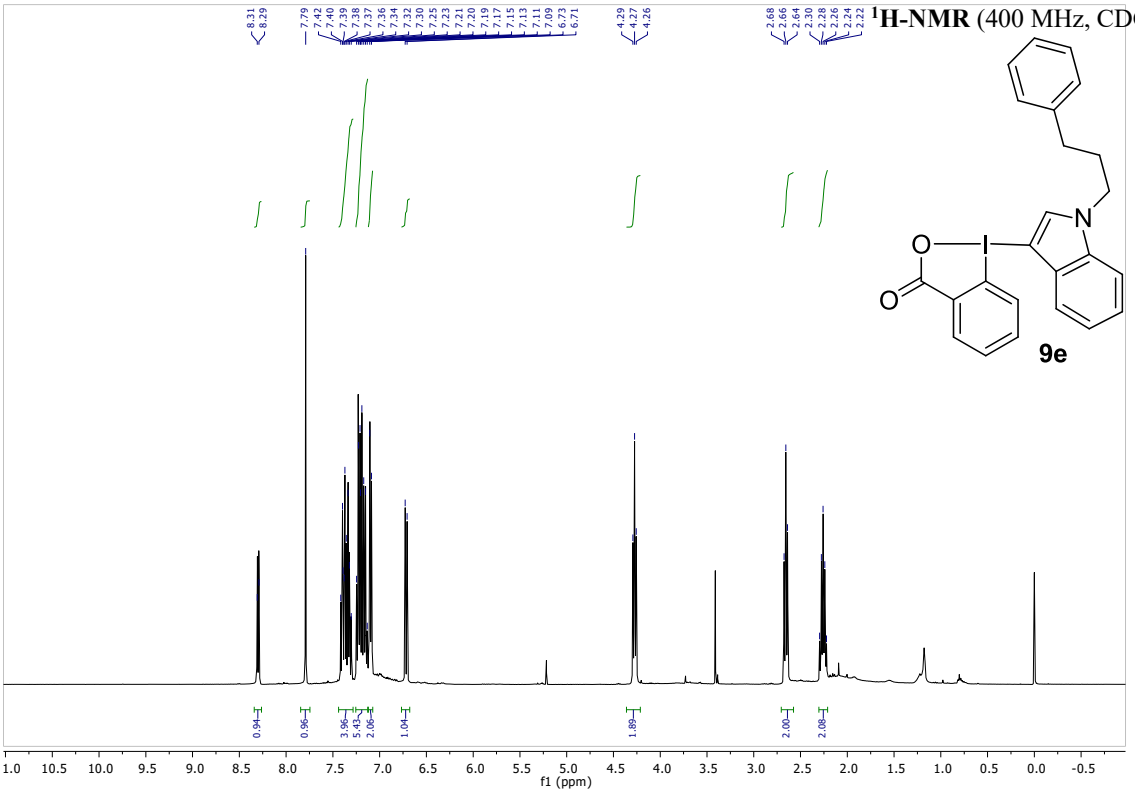


1-(3-1-(2-((Tri*iso*propylsilyl)oxy)ethyl)-1*H*-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one (9d)



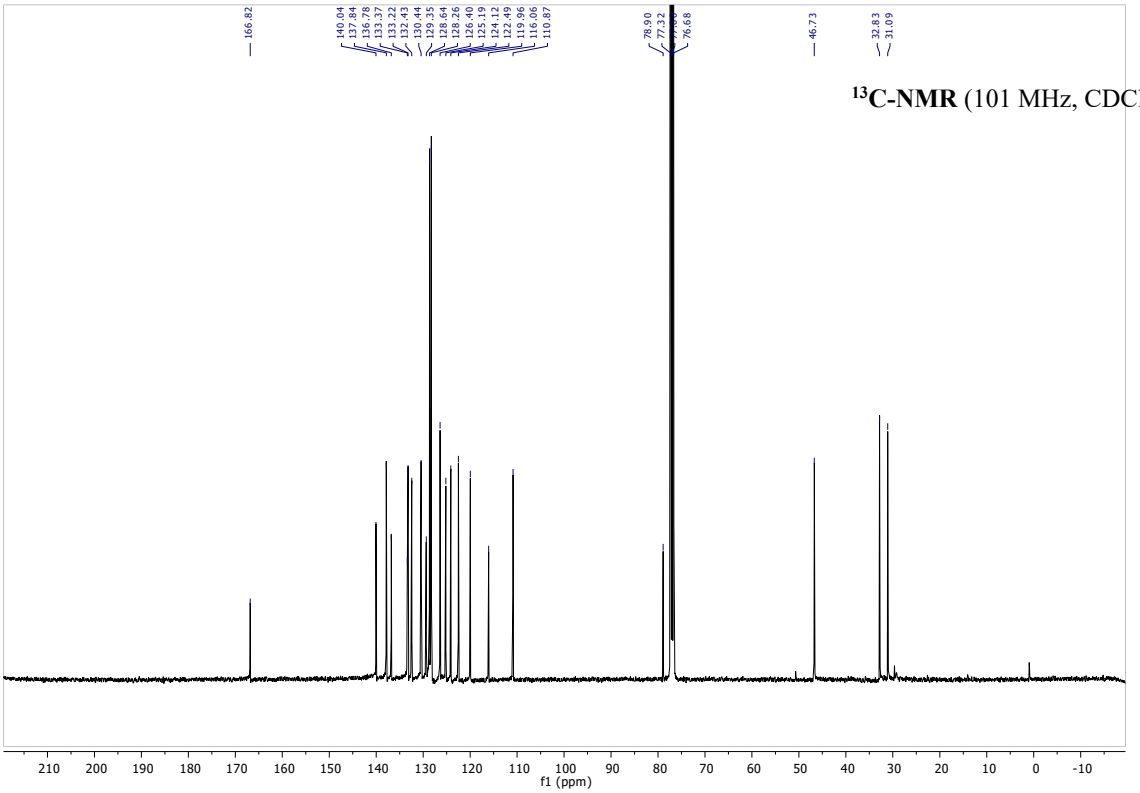


1-(3-1-(3-Phenylpropyl)-1*H*-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one (9e)



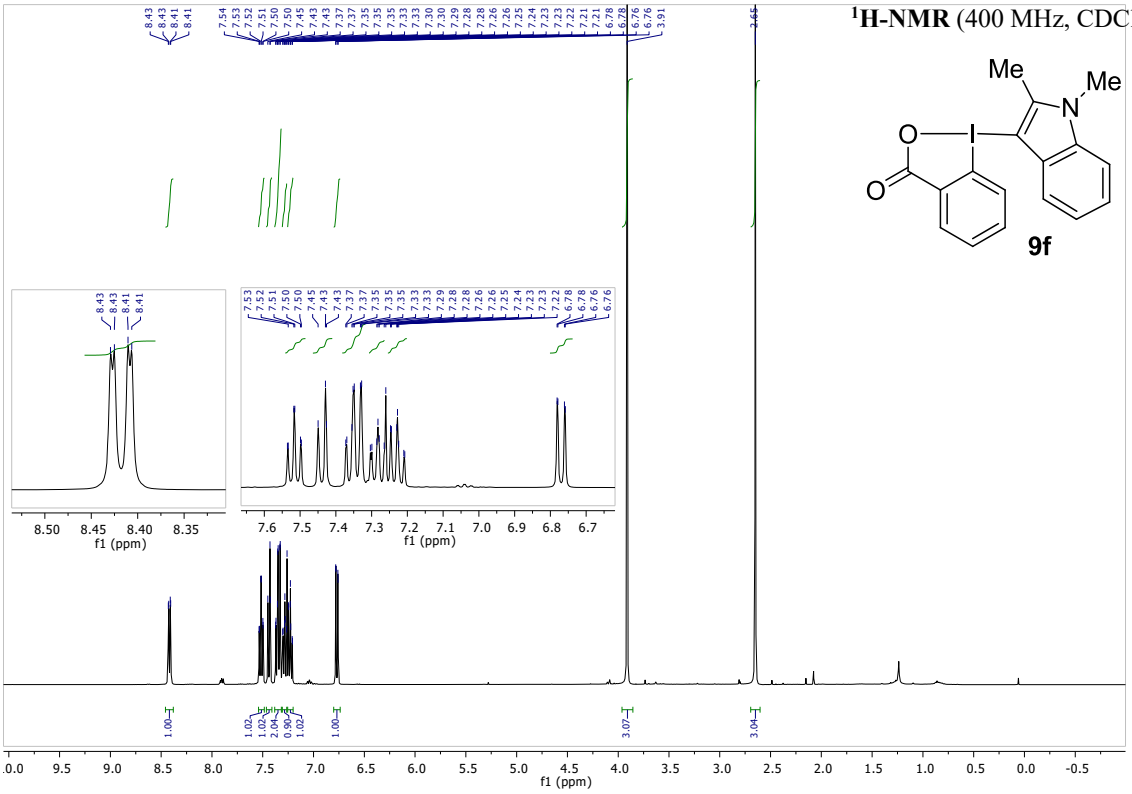
^{1}H-NMR (400 MHz, $CDCl_3$)

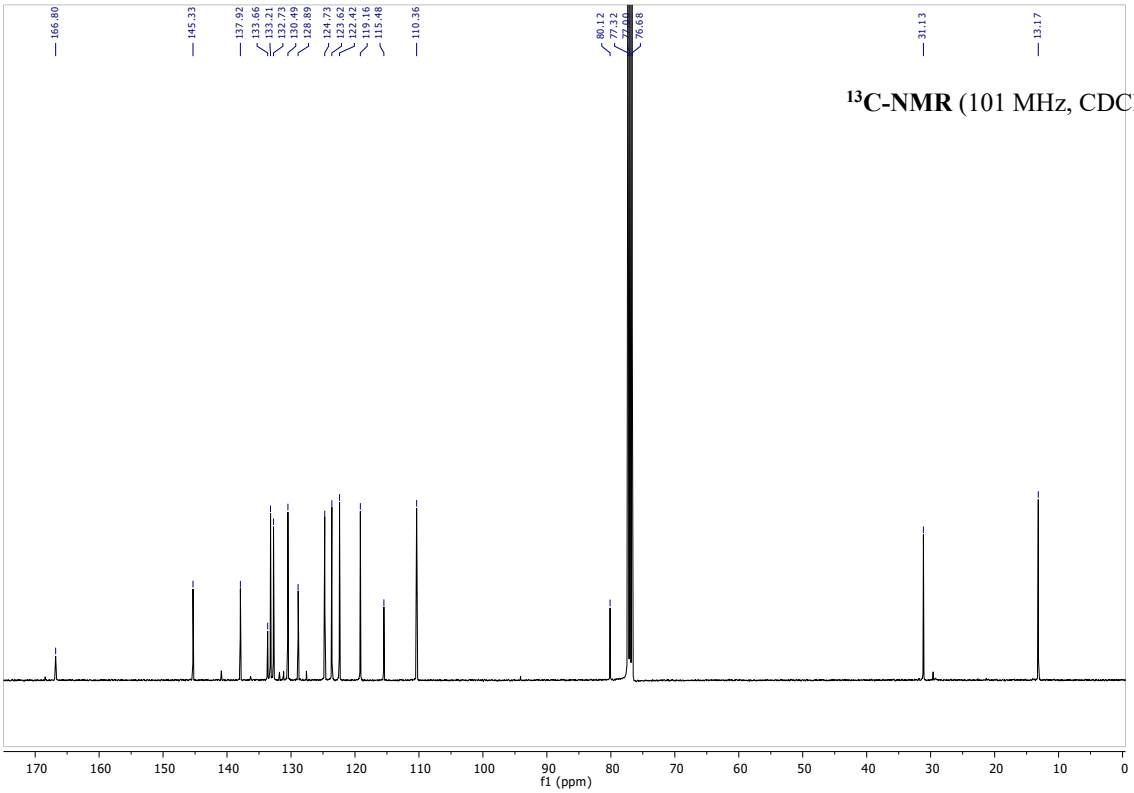
9e



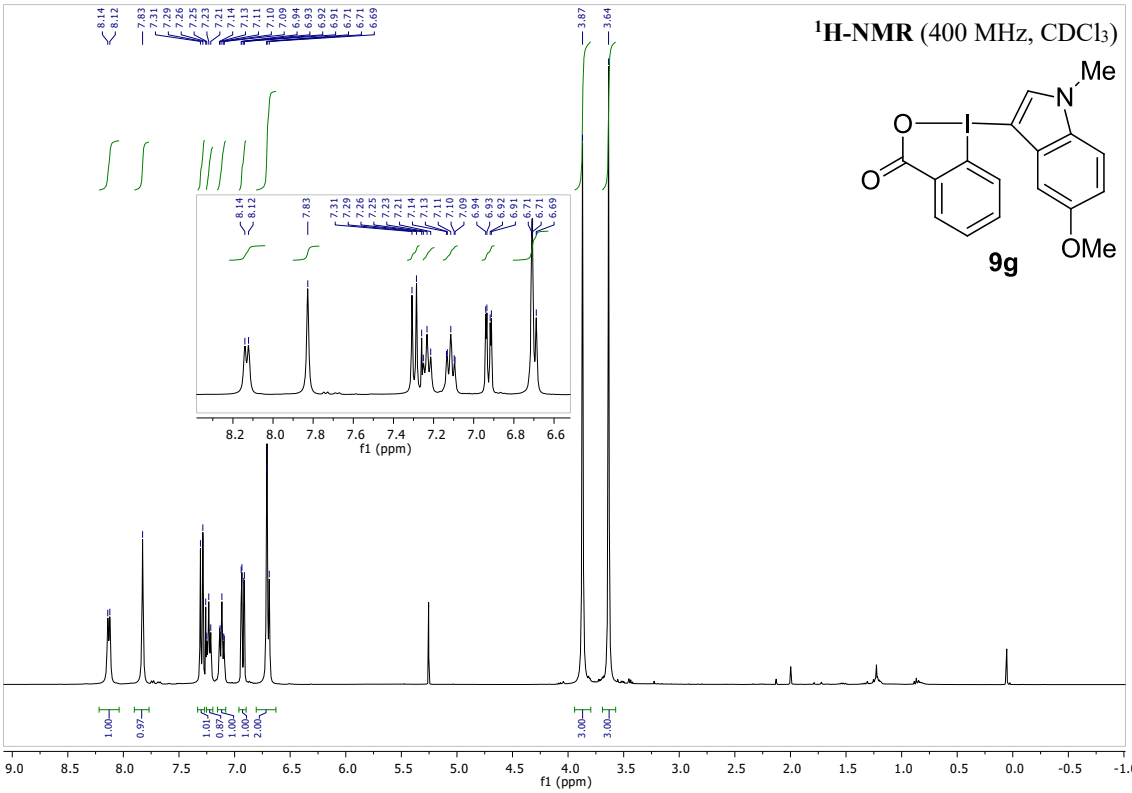
^{13}C-NMR (101 MHz, $CDCl_3$)

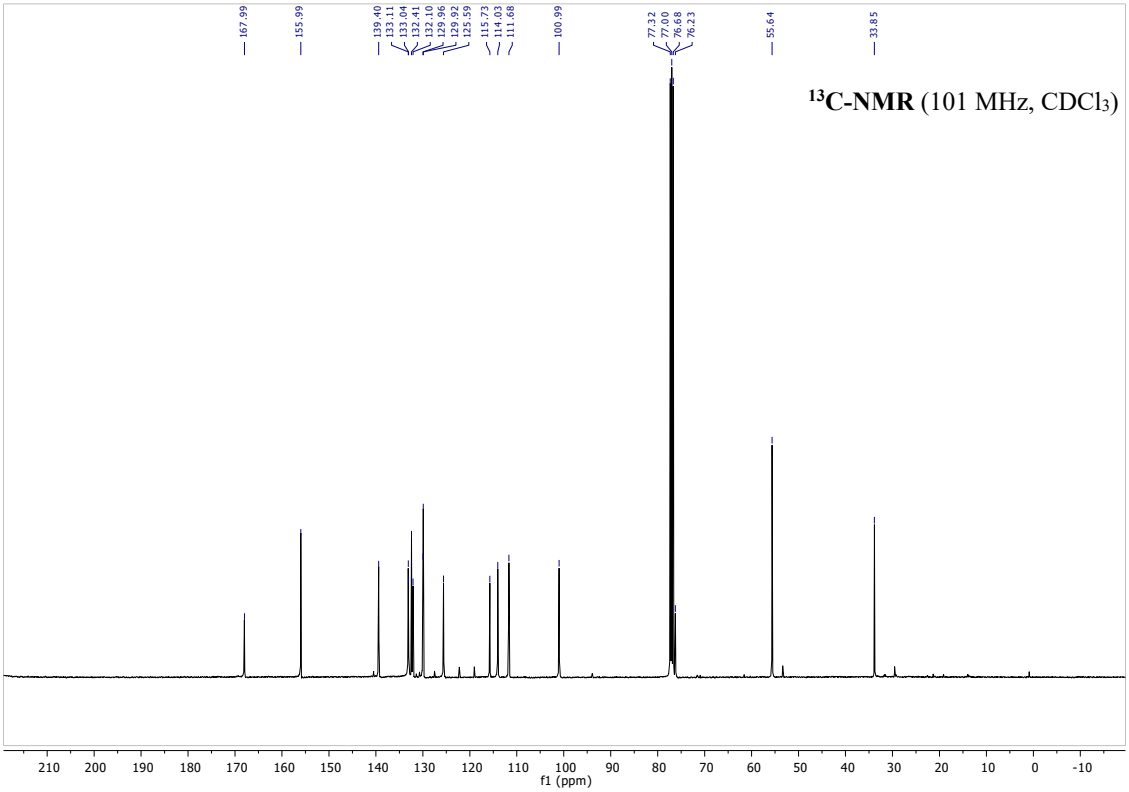
1-(3-1,2-Dimethyl-1*H*-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one (9f)



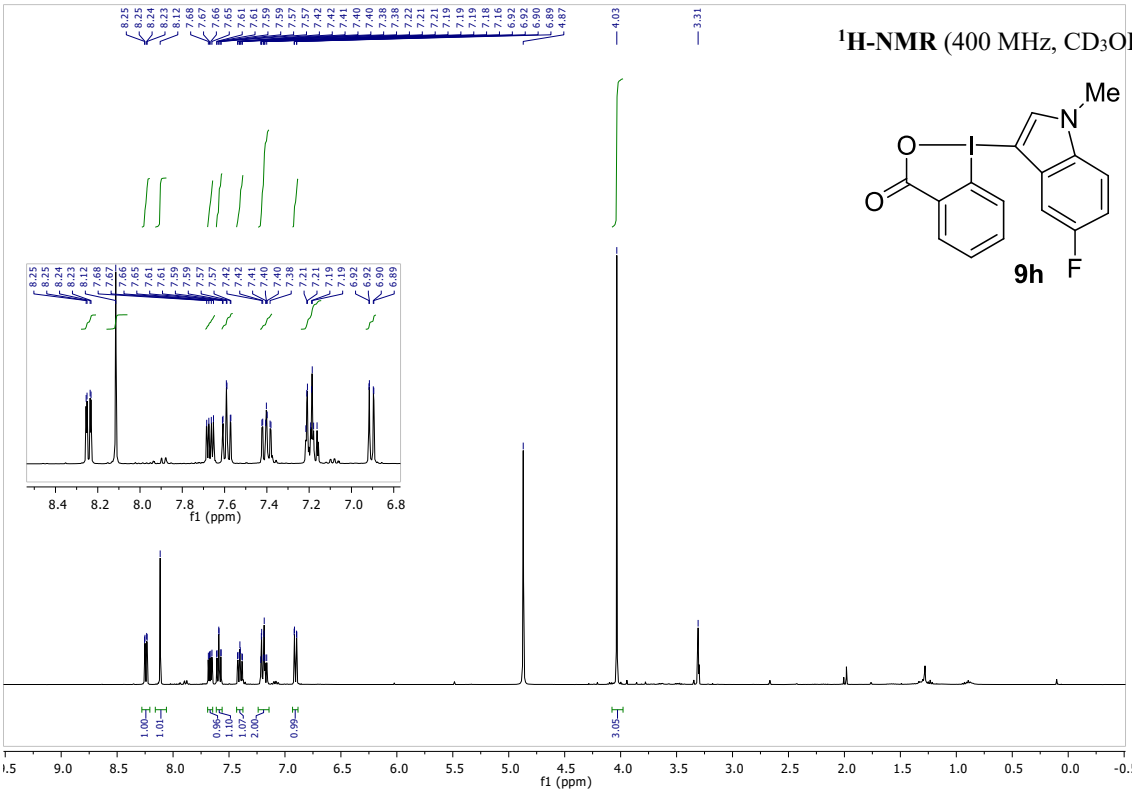


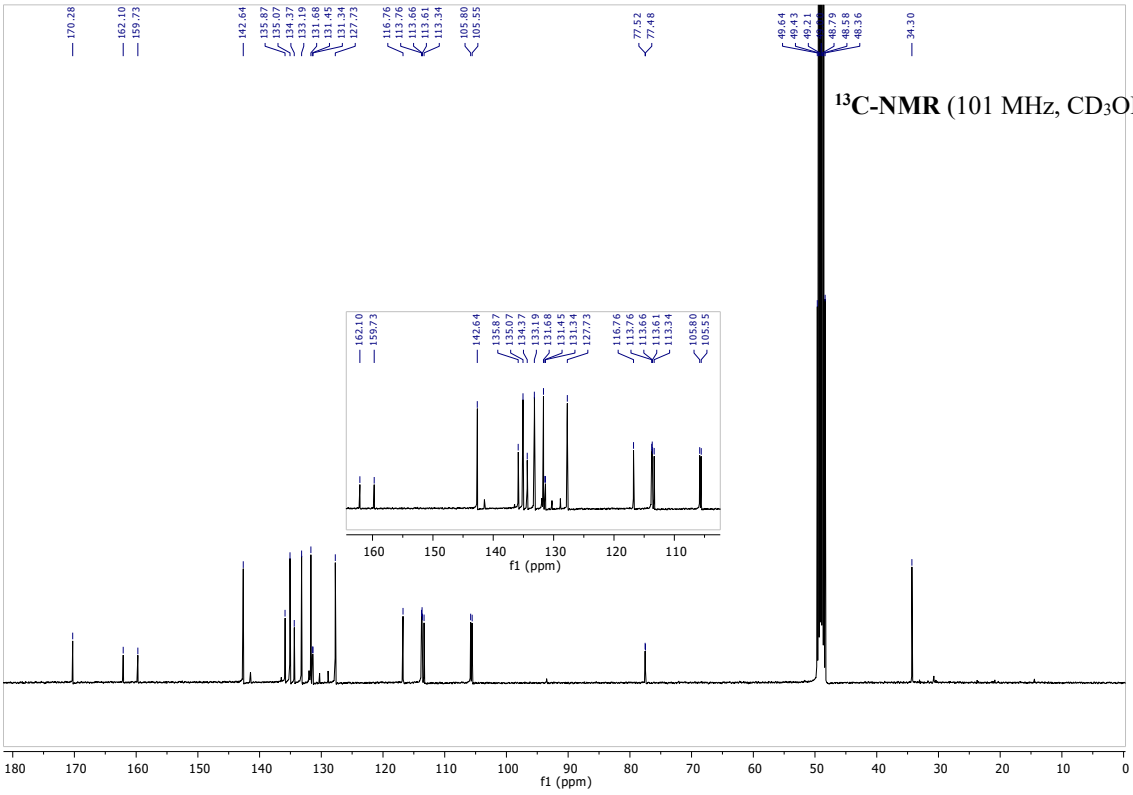
1-(3-5-Methoxy-1-methyl-1*H*-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one (9g)



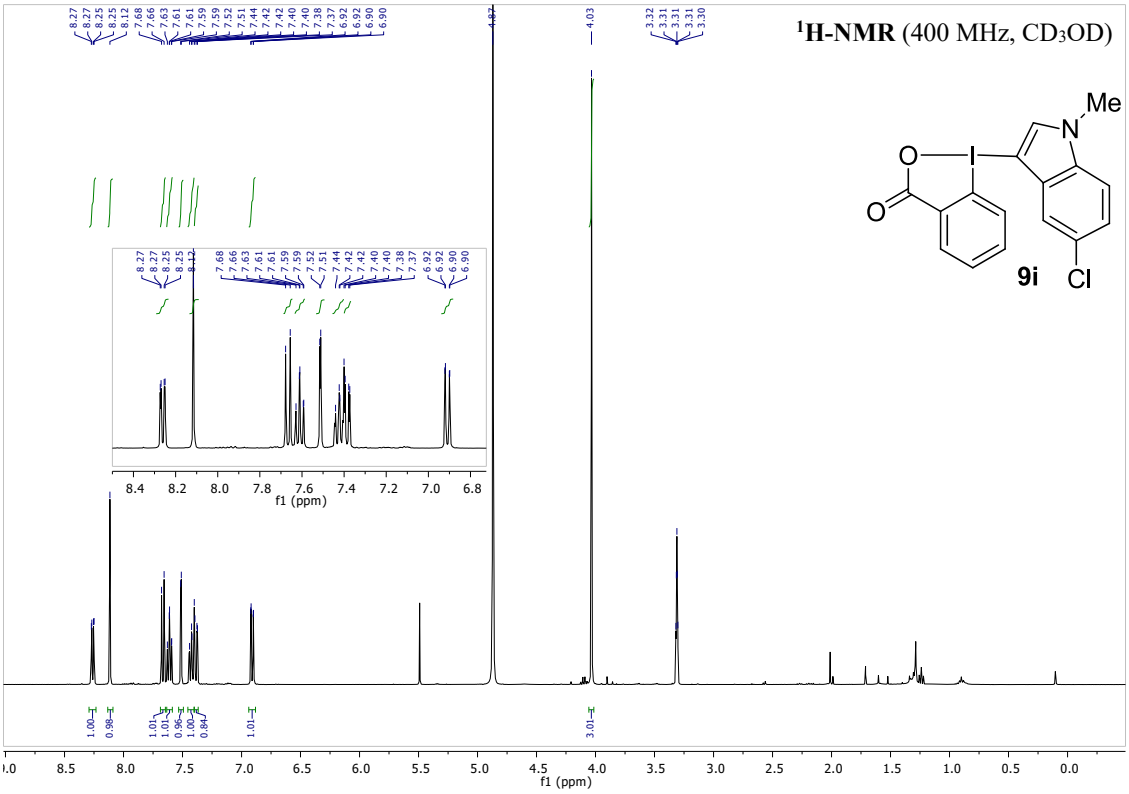


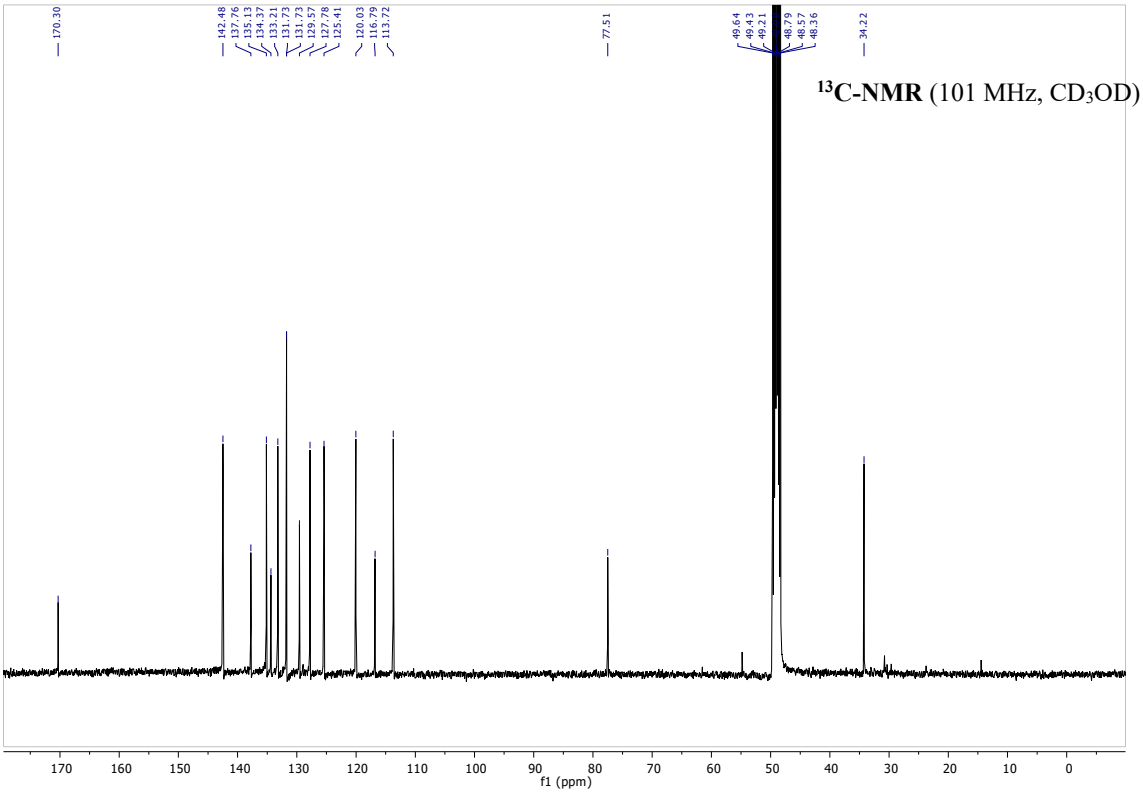
1-(3-5-fluoro-1-methyl-1*H*-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one (9h)



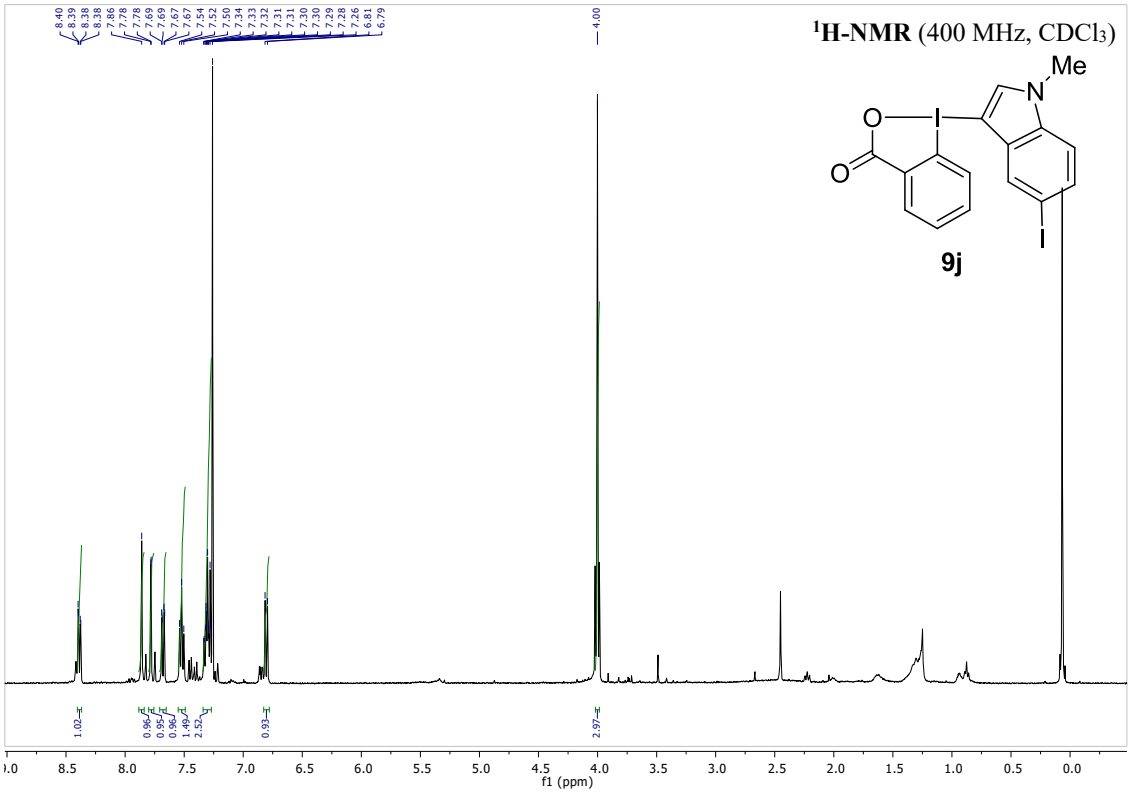


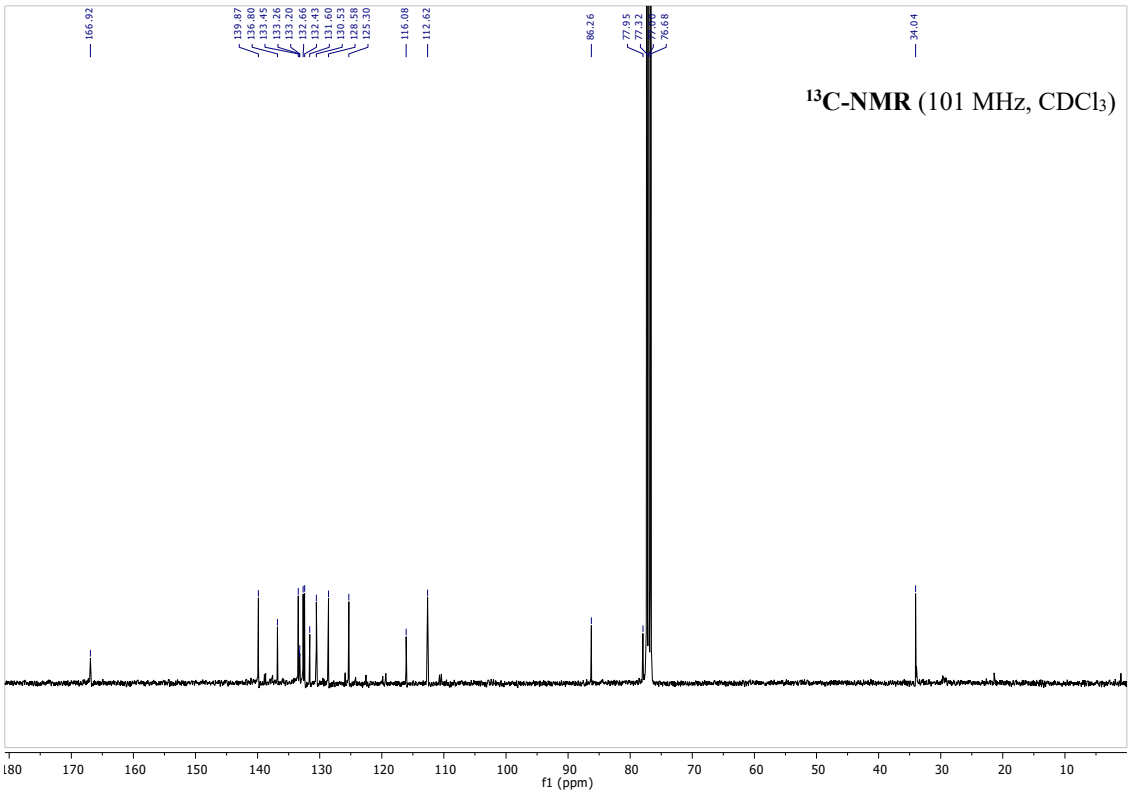
1-(3-5-Chloro-1-methyl-1*H*-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one (9i)



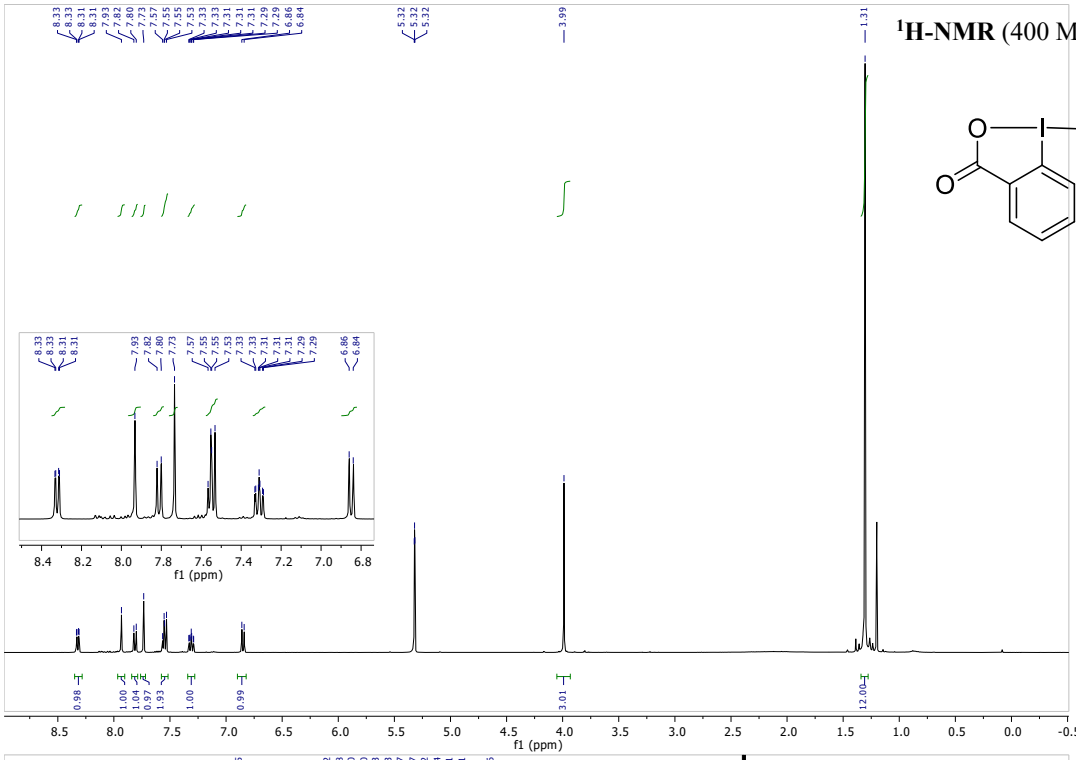


1-(3-5-Iodo-1-methyl-1*H*-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one (9j)



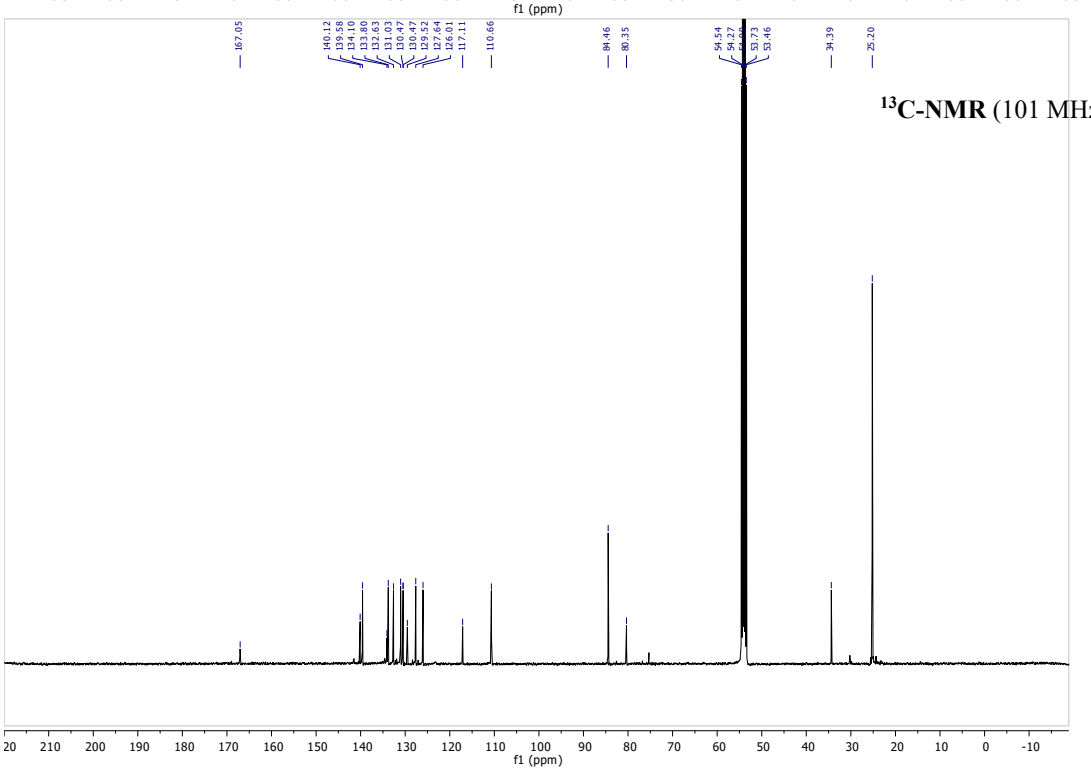


1-(3-1-Methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one (9k)



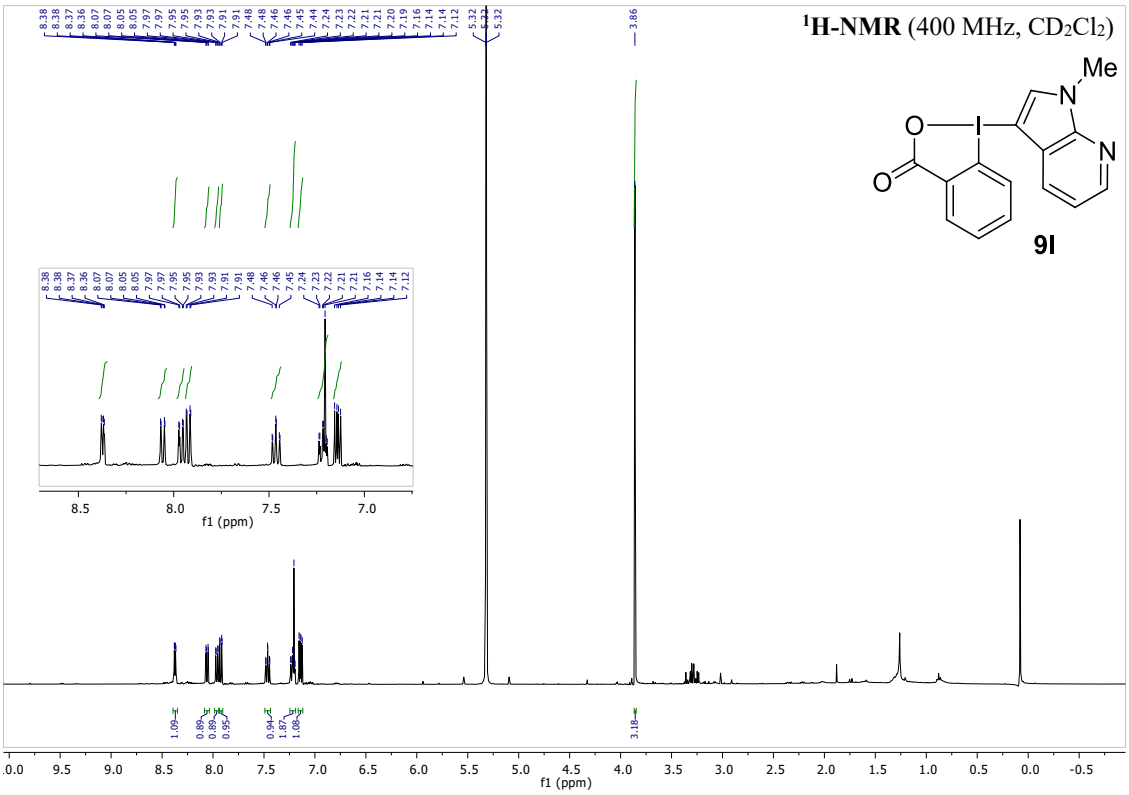
^{1}H-NMR (400 MHz, CD_2Cl_2)

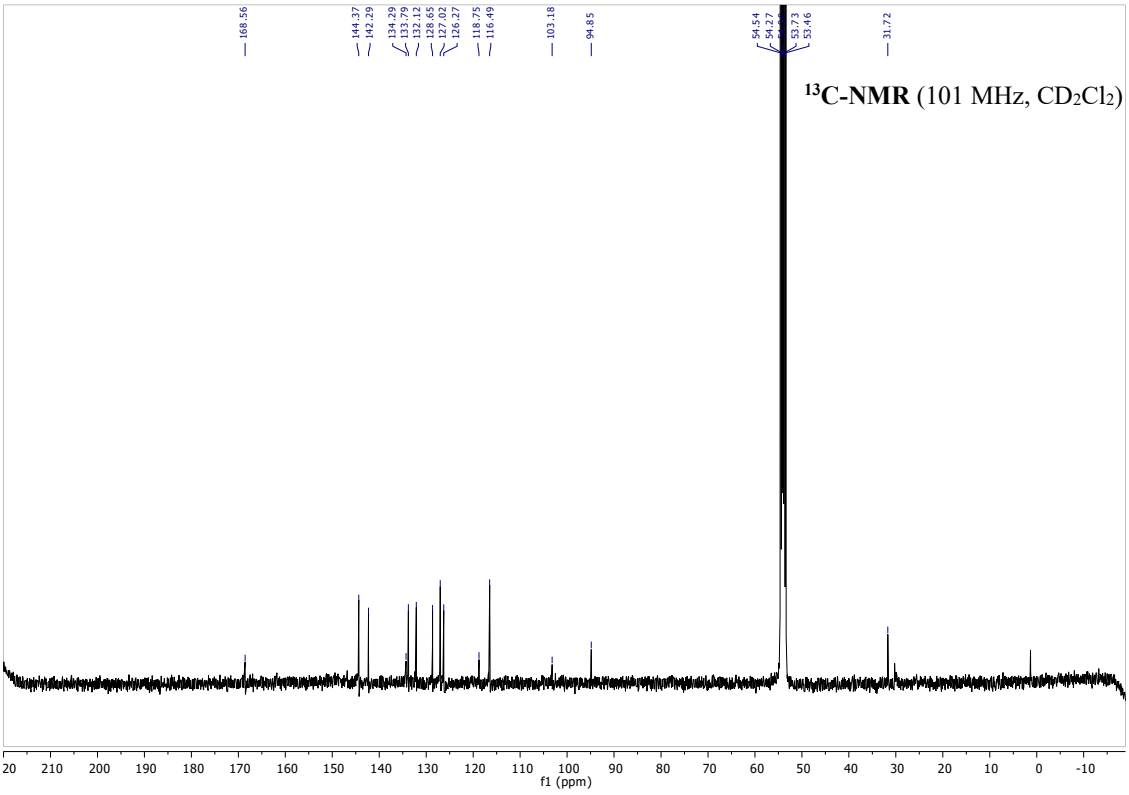
9k



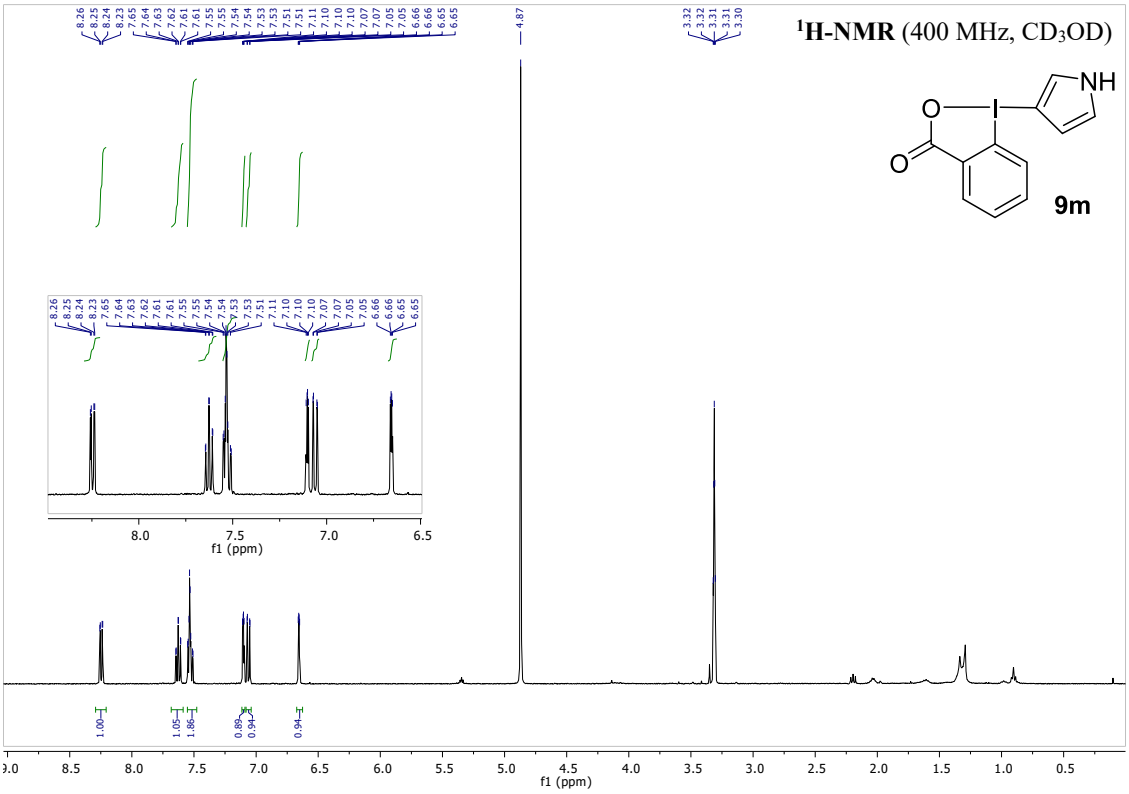
^{13}C-NMR (101 MHz, CD_2Cl_2)

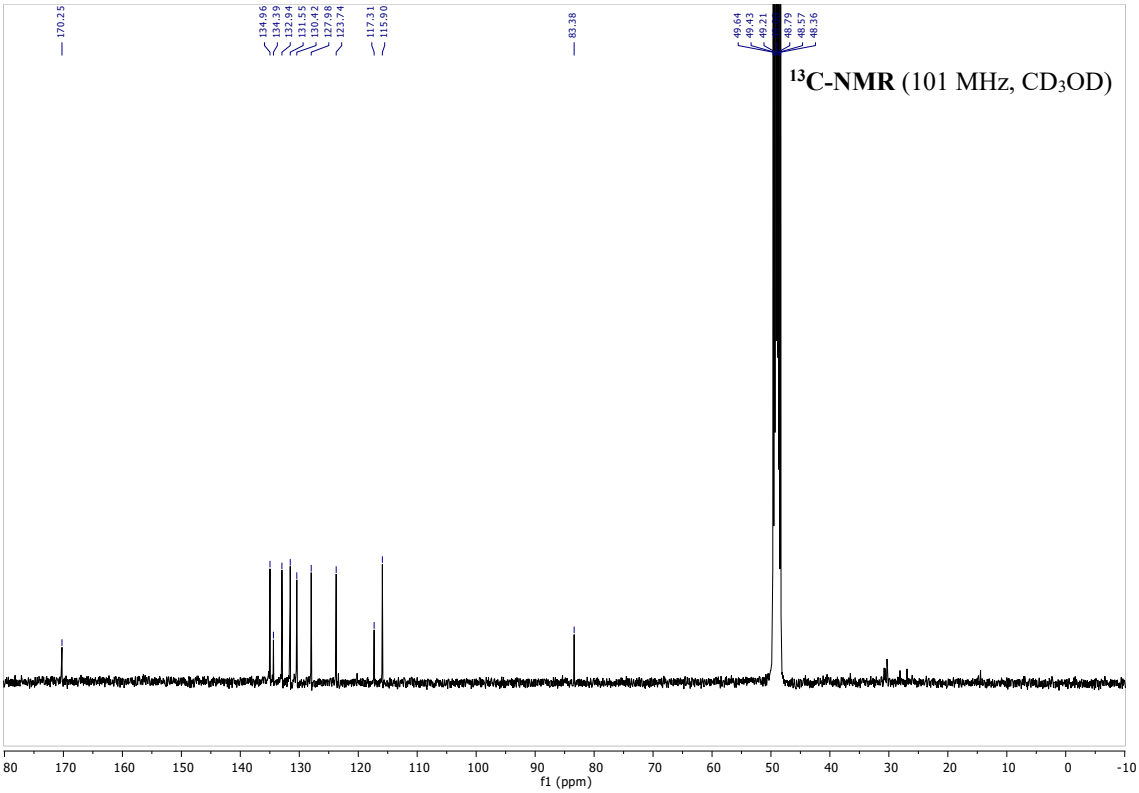
1-(3-1-Methyl-1*H*-pyrrolo[*2,3-b*]pyridine)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one (9l)



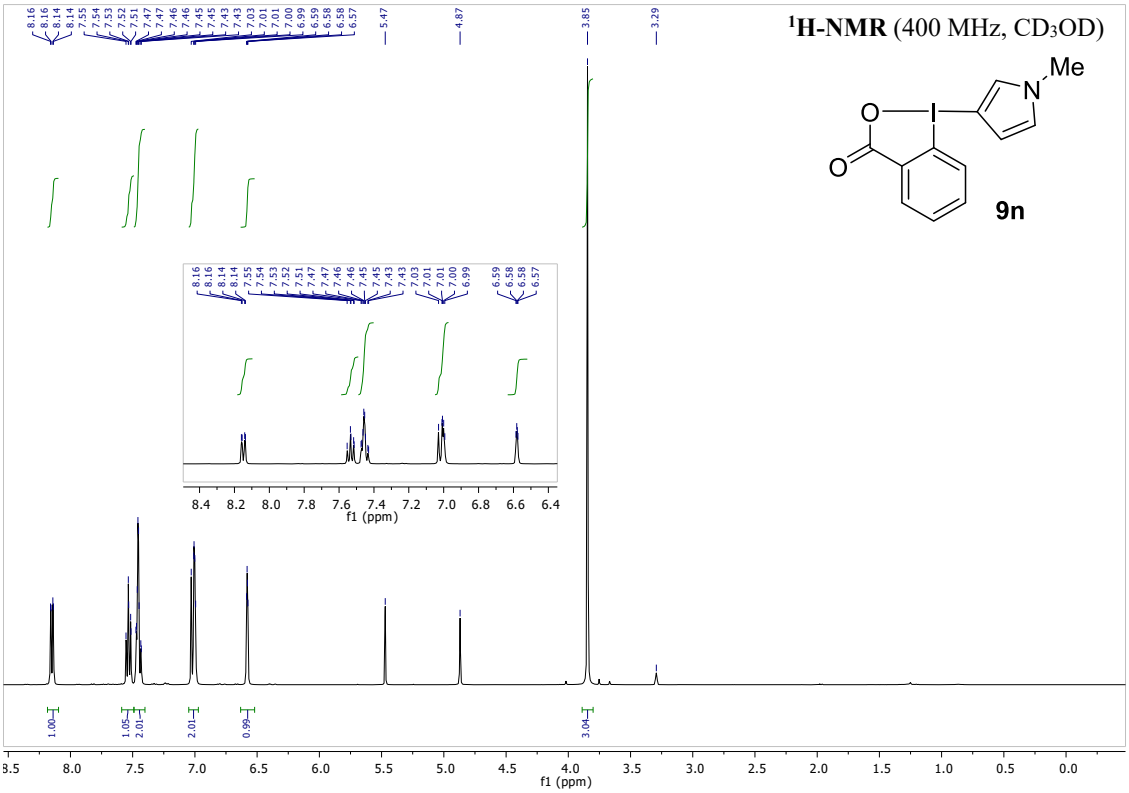


1-(3-1*H*-Pyrrole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one (9m)



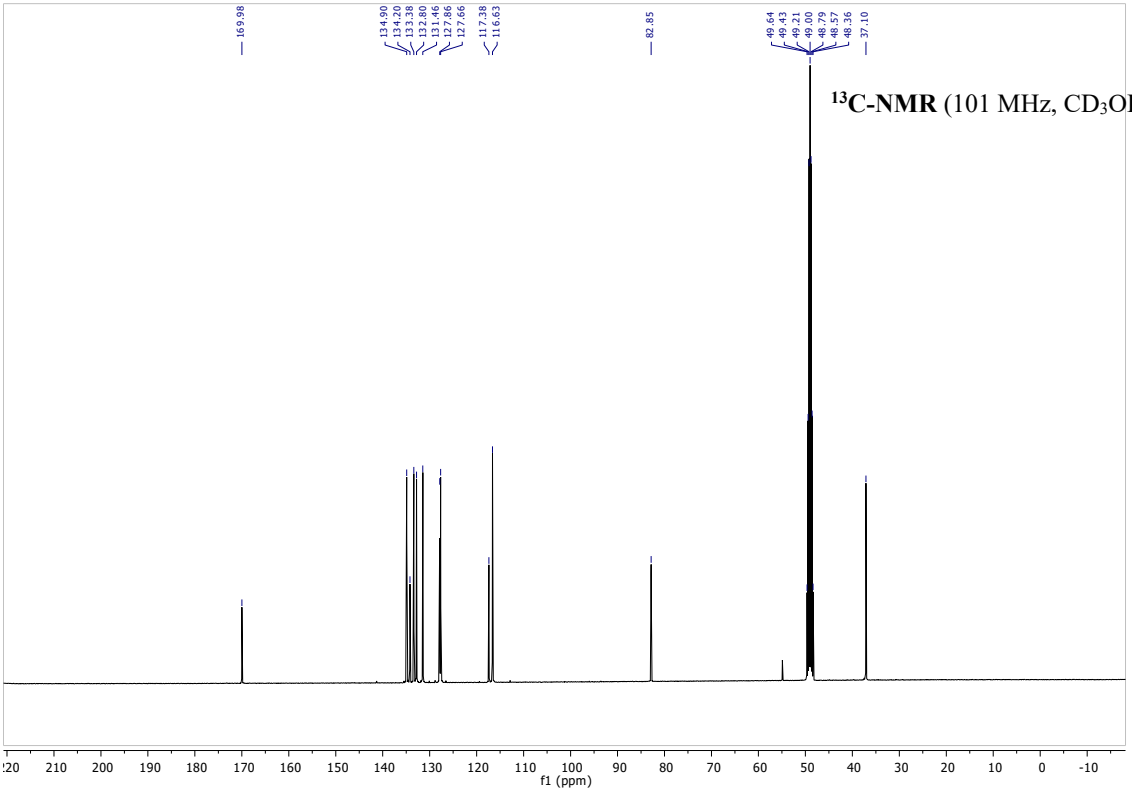


1-(3-1-Methyl-1*H*-pyrrole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one (9n)



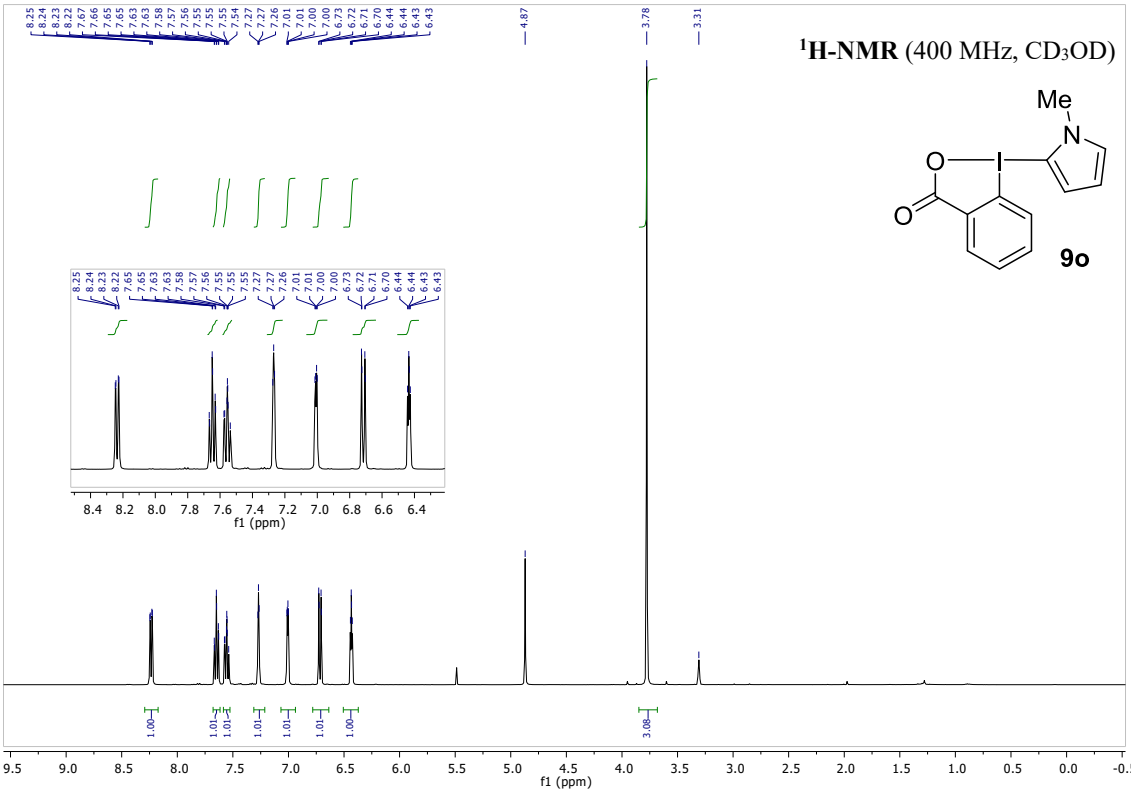
^{1}H-NMR (400 MHz, CD_3OD)

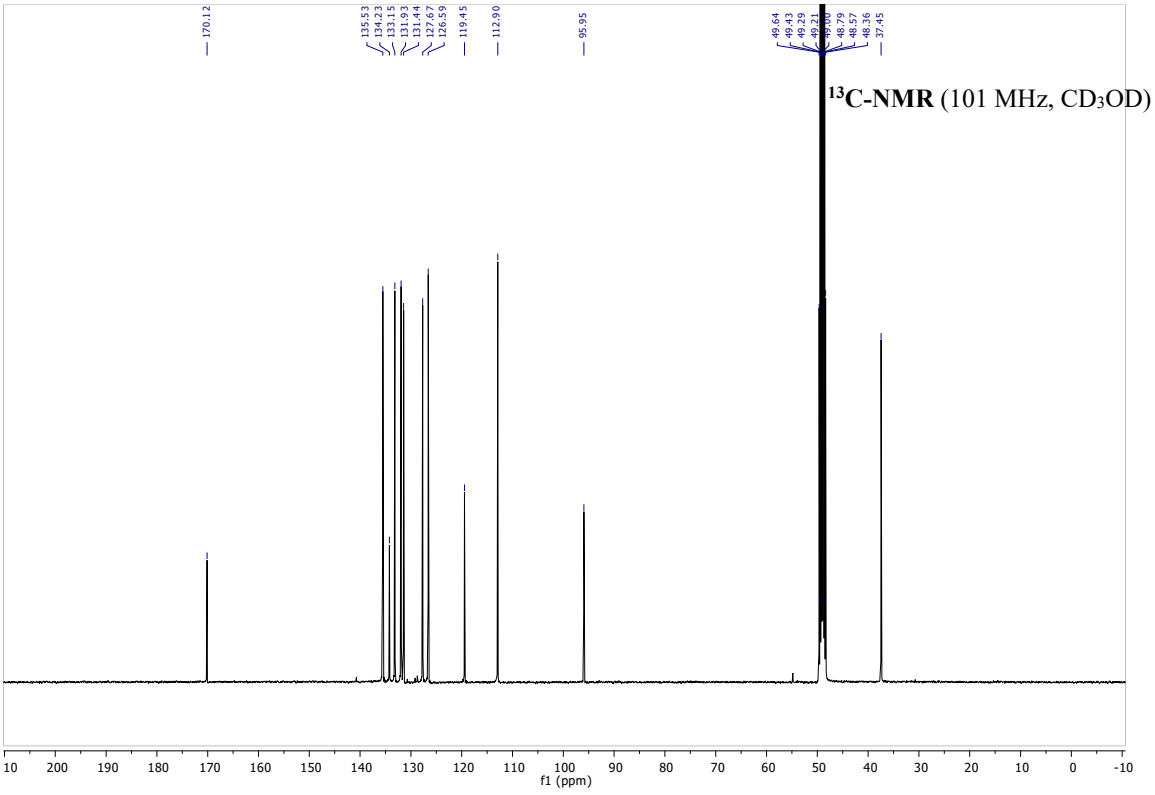
9n



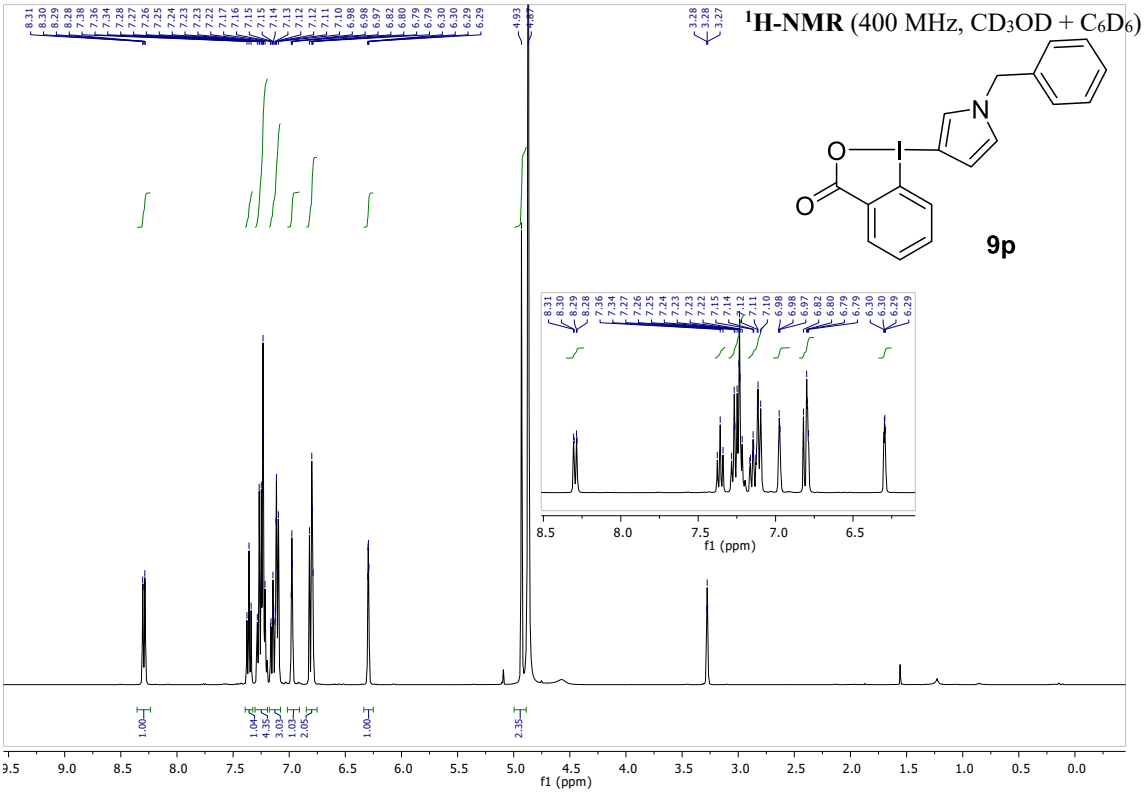
^{13}C-NMR (101 MHz, CD_3OD)

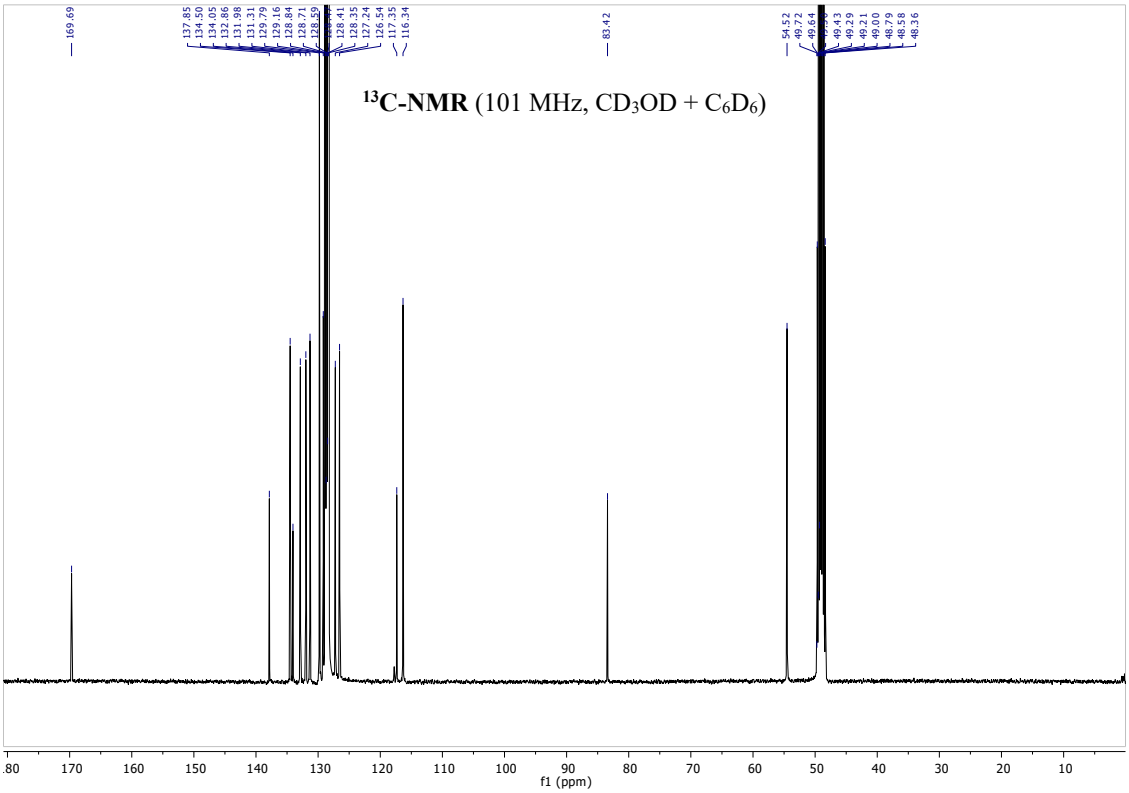
1-(2-1-Methyl-1*H*-pyrrole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one (9o)



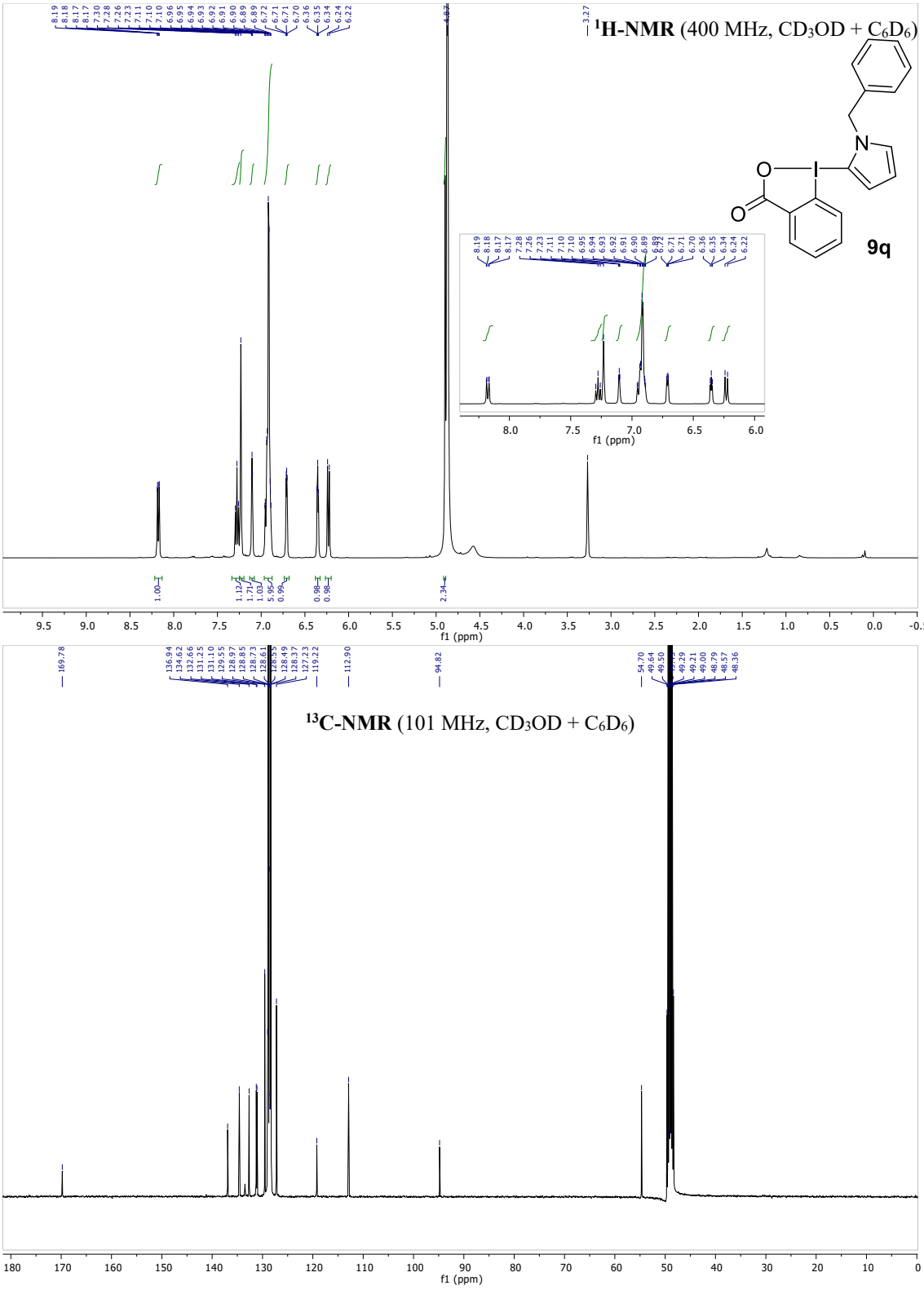


1-(3-1-Benzyl-1*H*-pyrrole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one (9p)

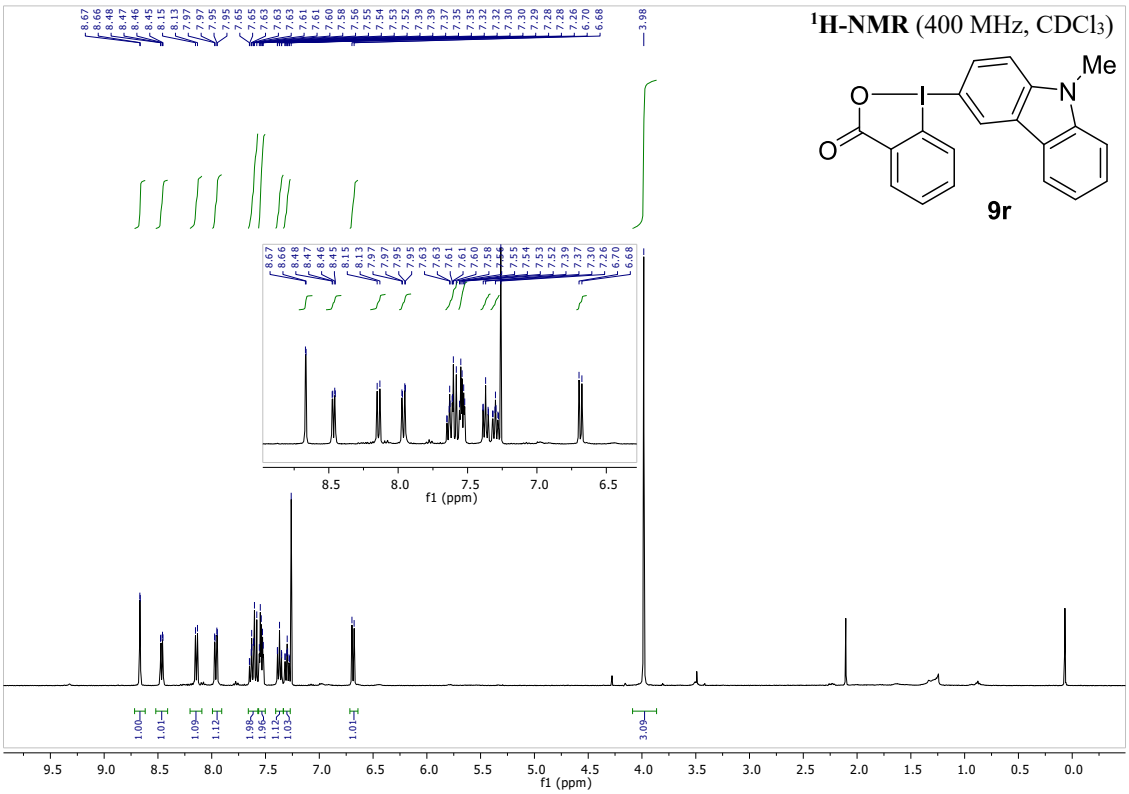


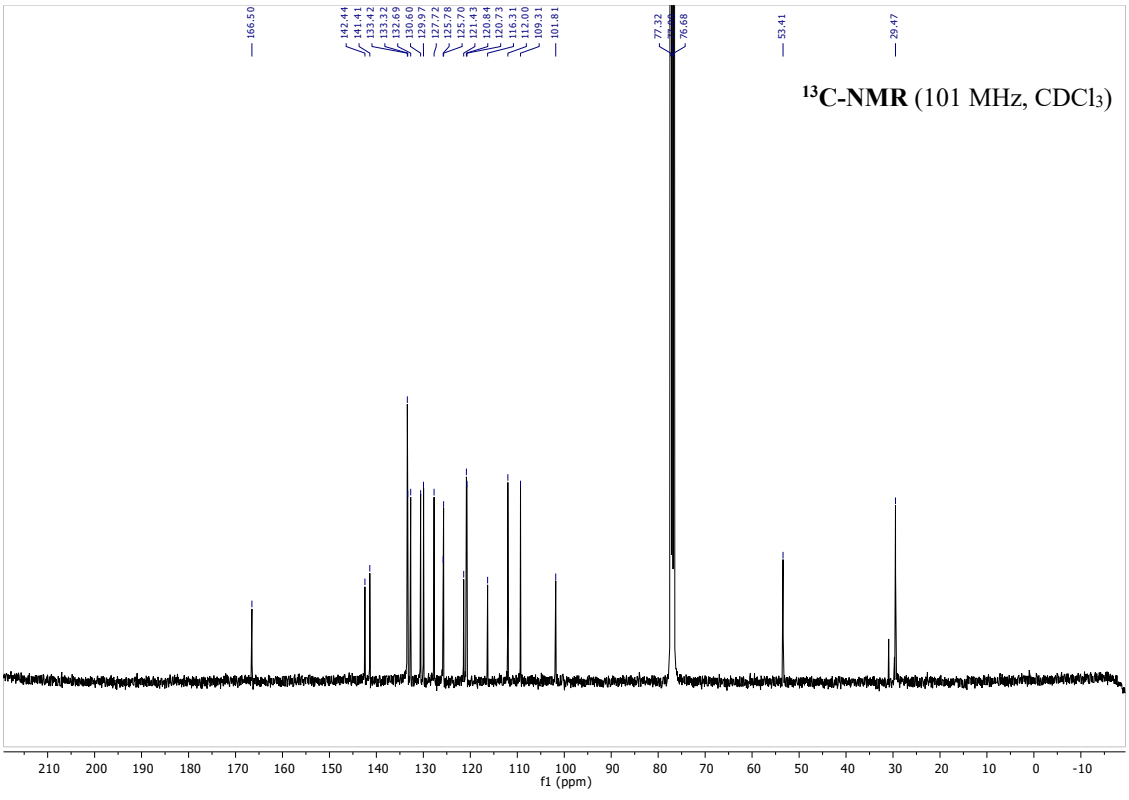


1-(2-1-Benzyl-1*H*-pyrrole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one (9q)

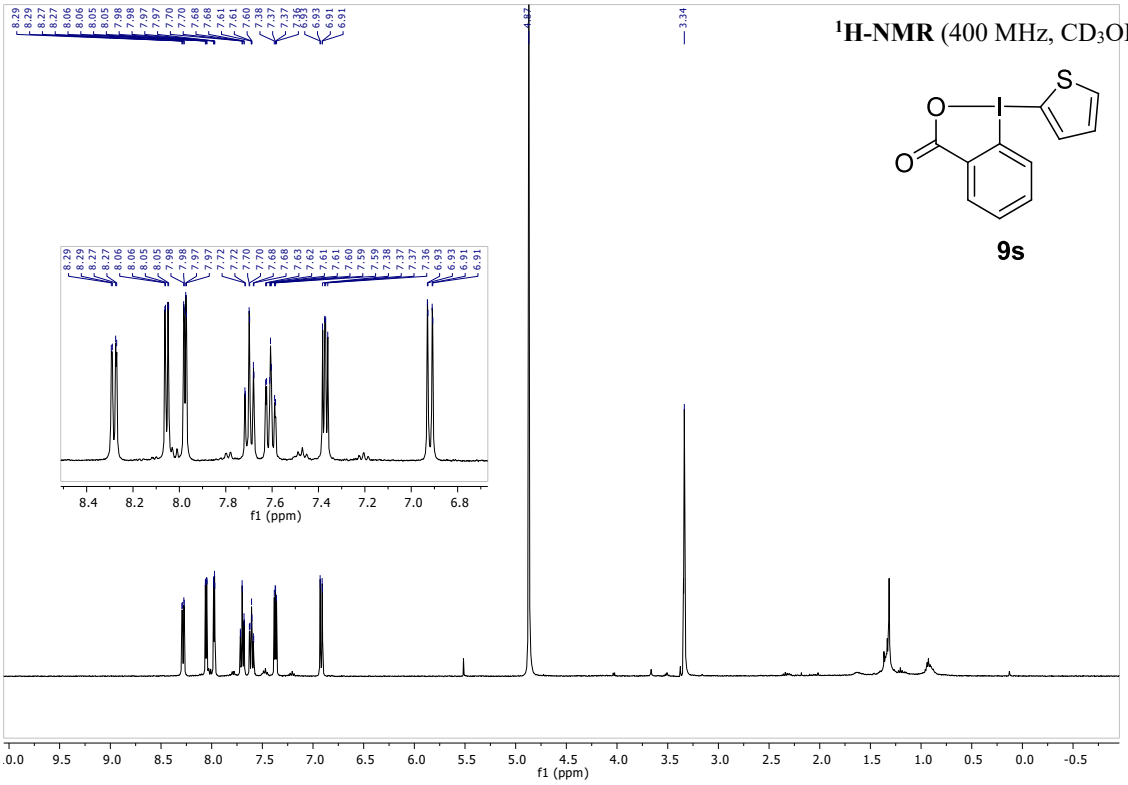


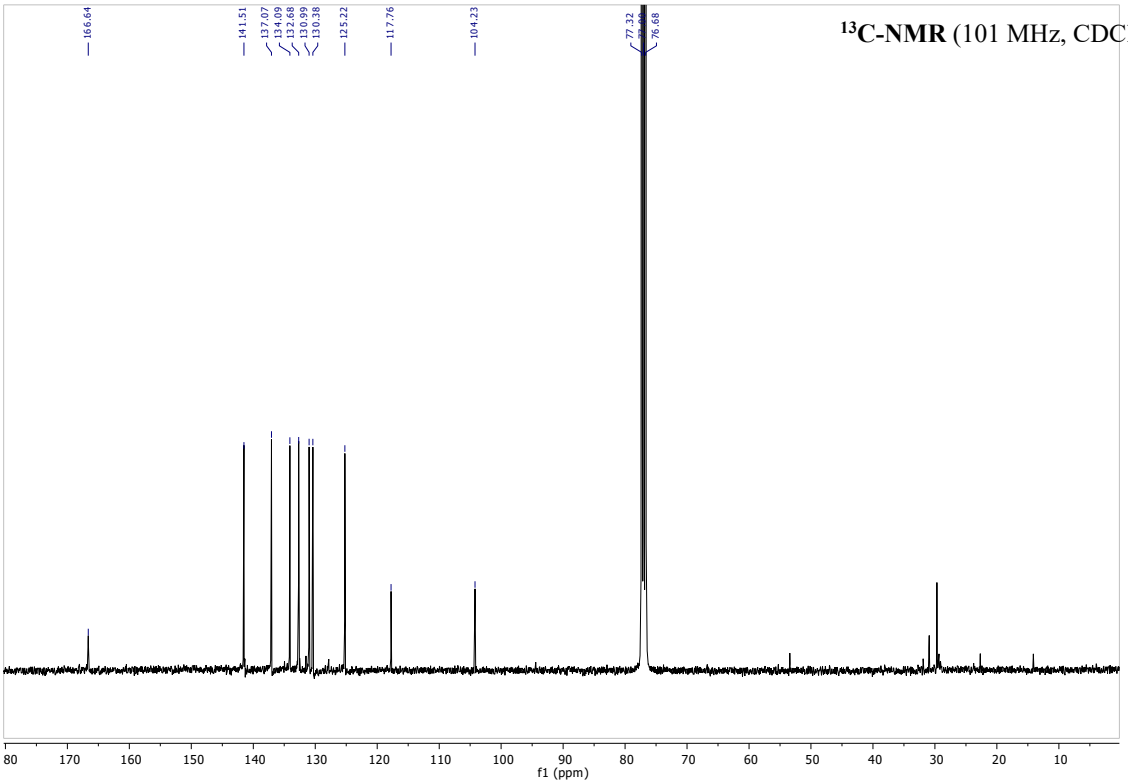
1-(3-9-Methyl-9*H*-carbazole)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one (9r)



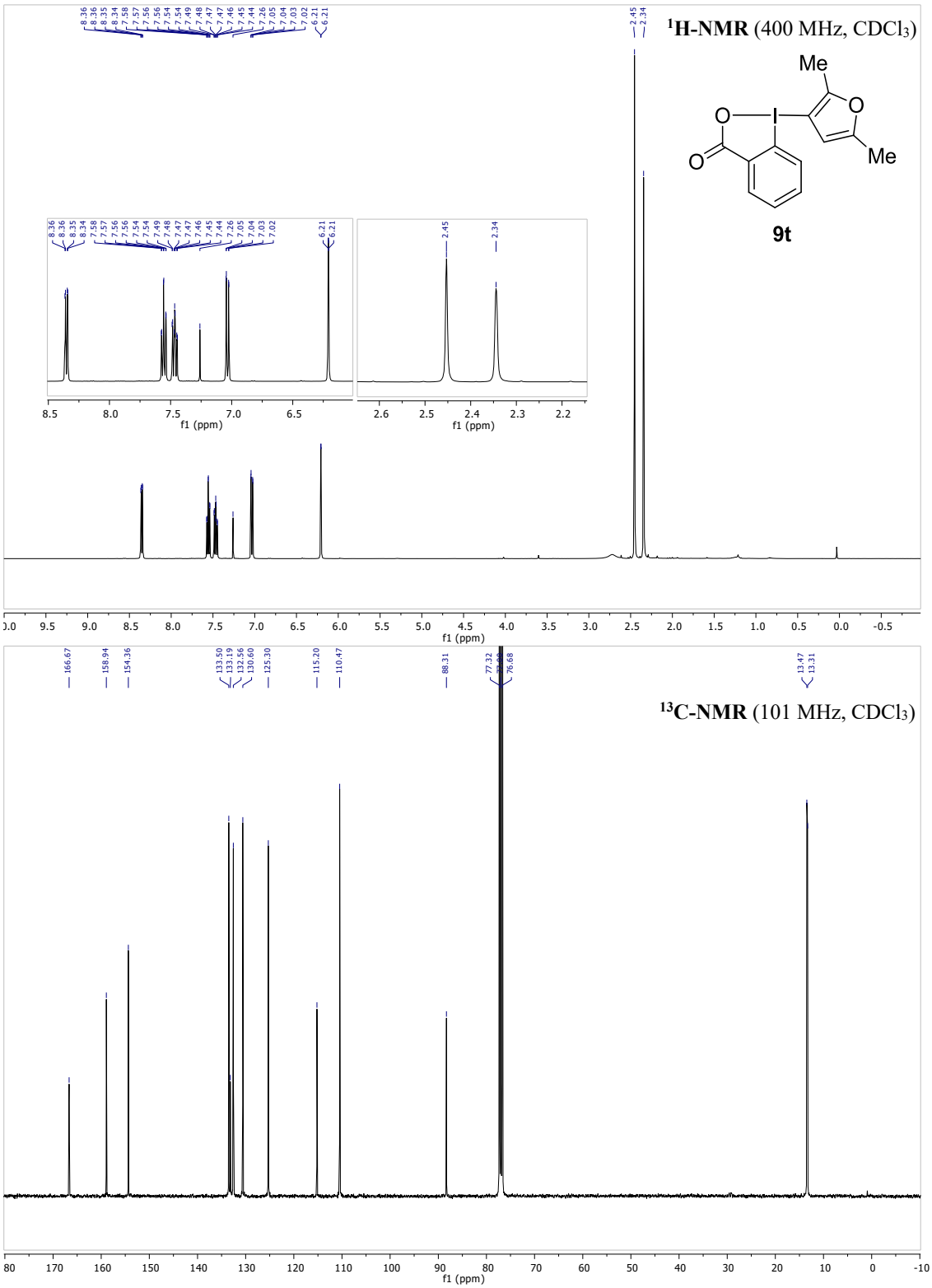


1-(2-1*H*-Thiophene)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one (9s)

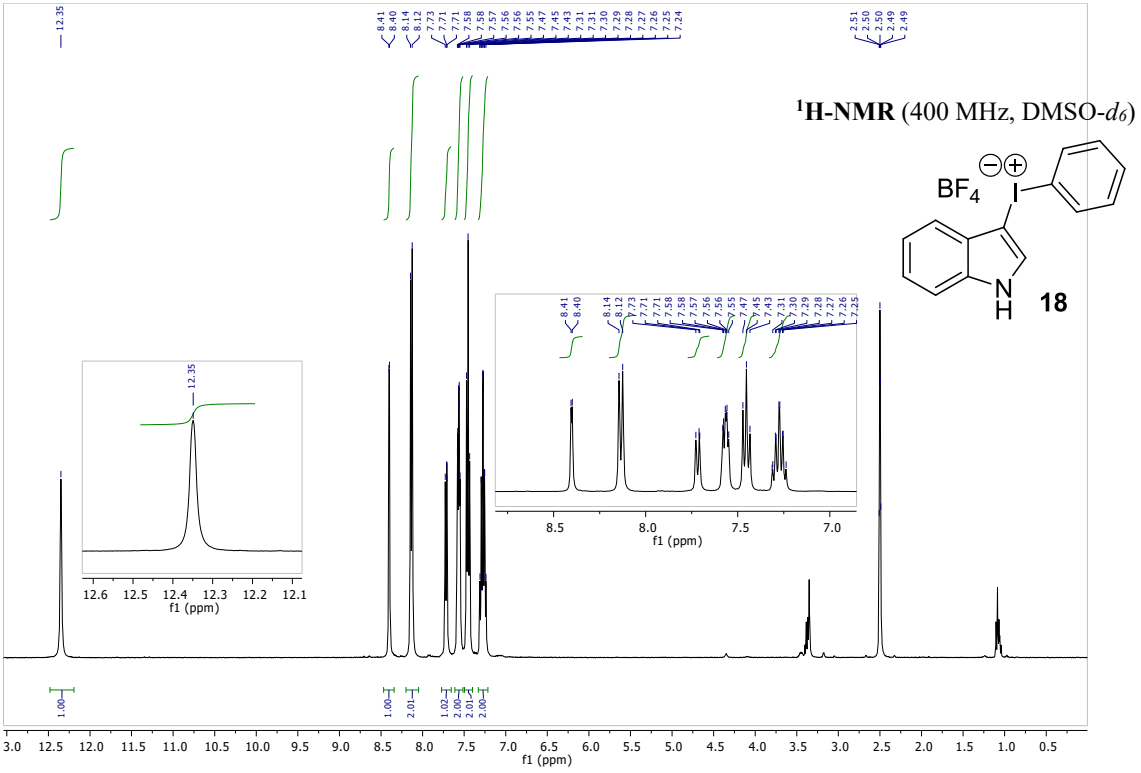


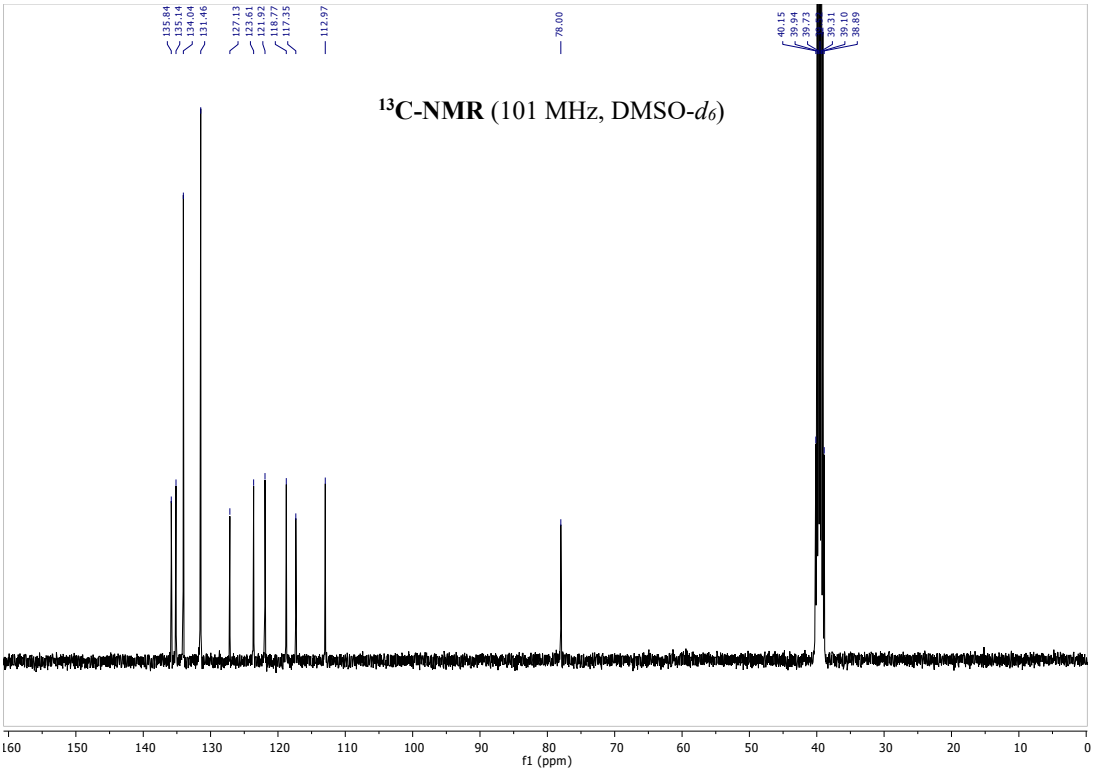


1-(3-1*H*-2,5-dimethylfuran)-1*H*-1λ_3 -benzo[*b*]iodo-3(2*H*)-one (9t)

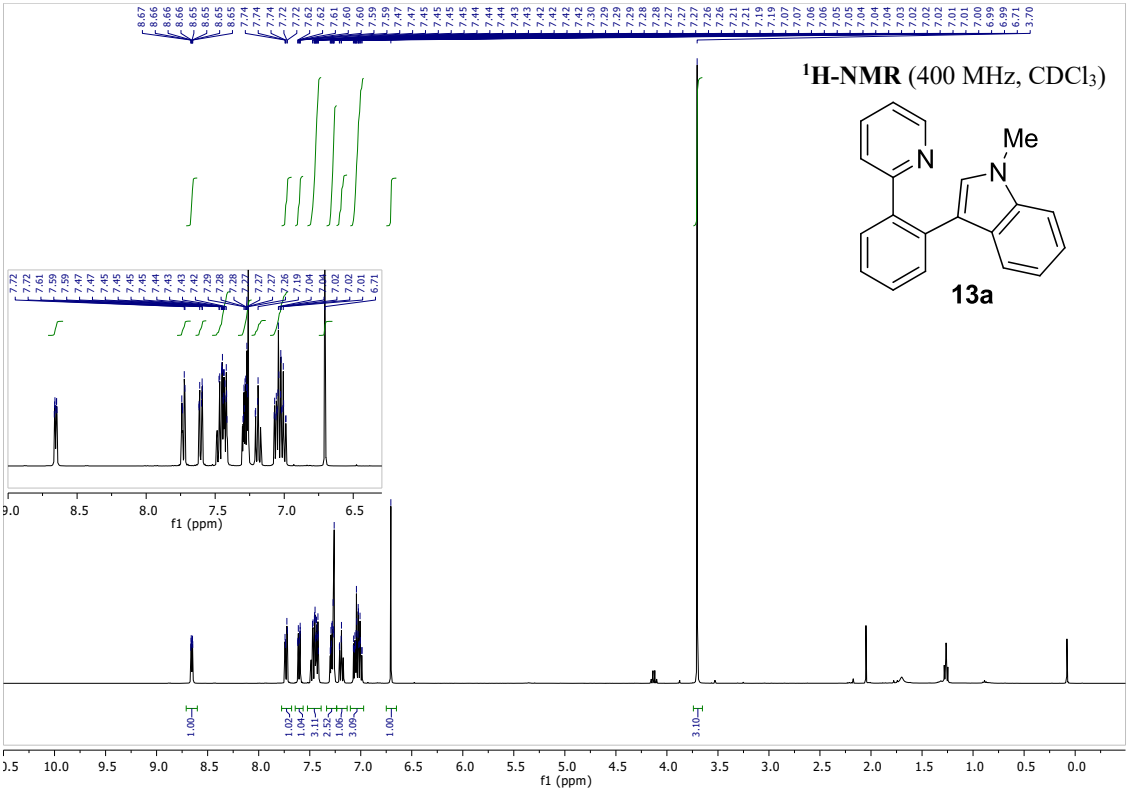


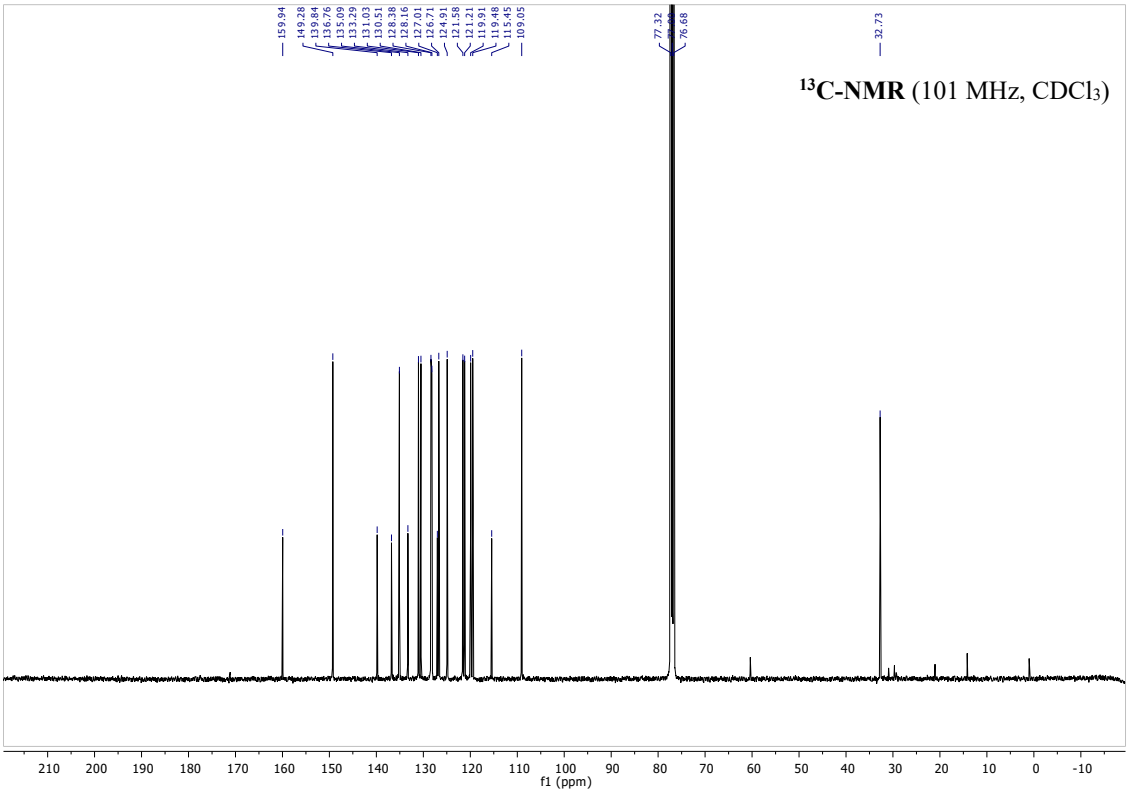
β-Phenyliodonioindole Tetrafluoroborate (18).



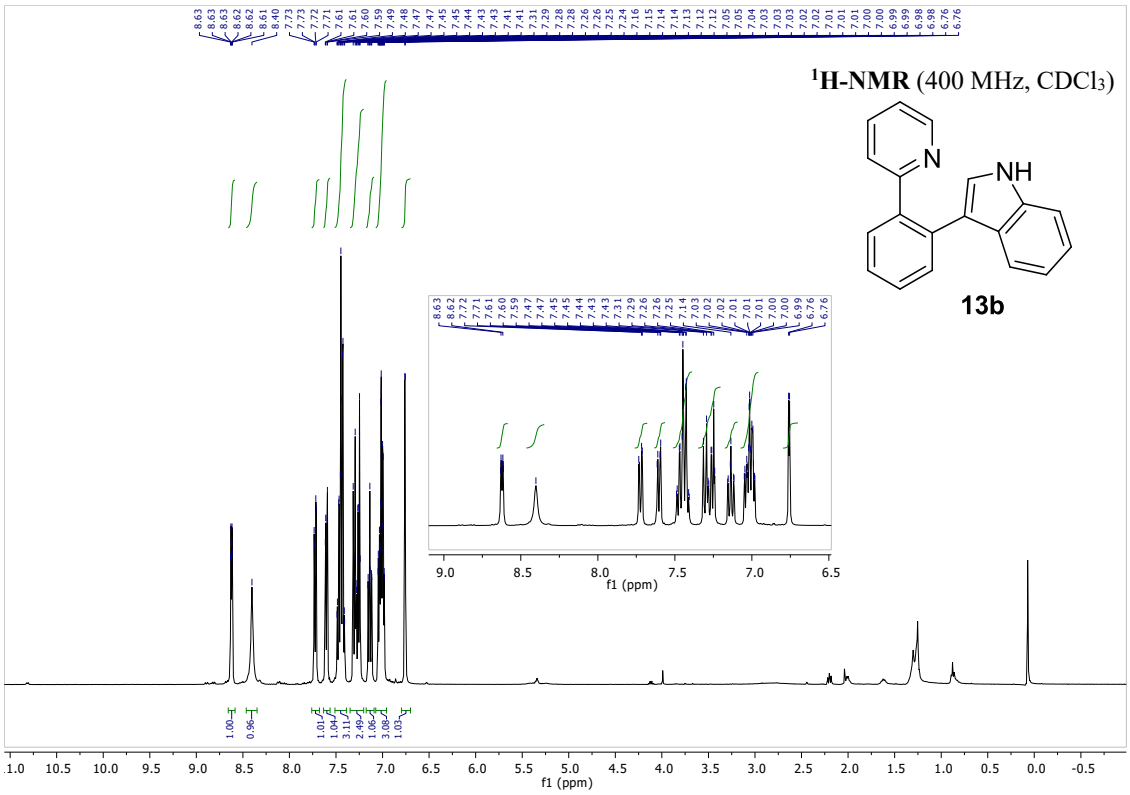


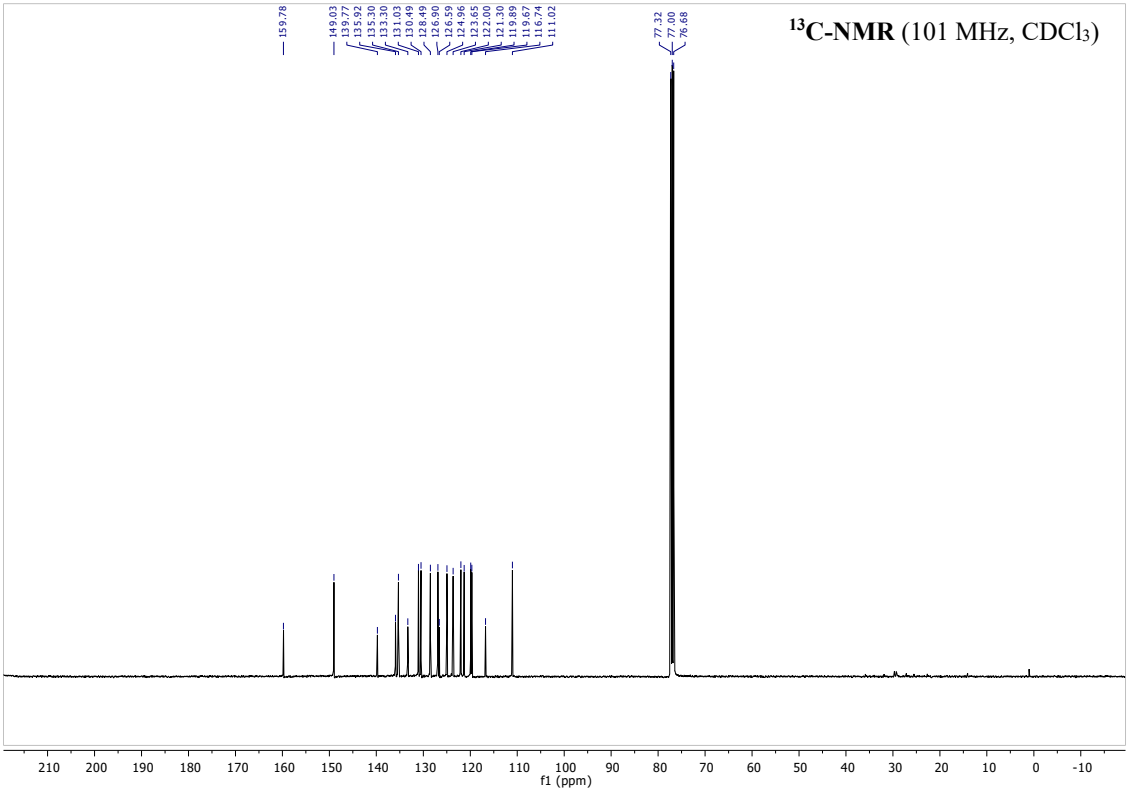
1-Methyl-3-(2-(pyridin-2-yl)phenyl)-1*H*-indole (13a)



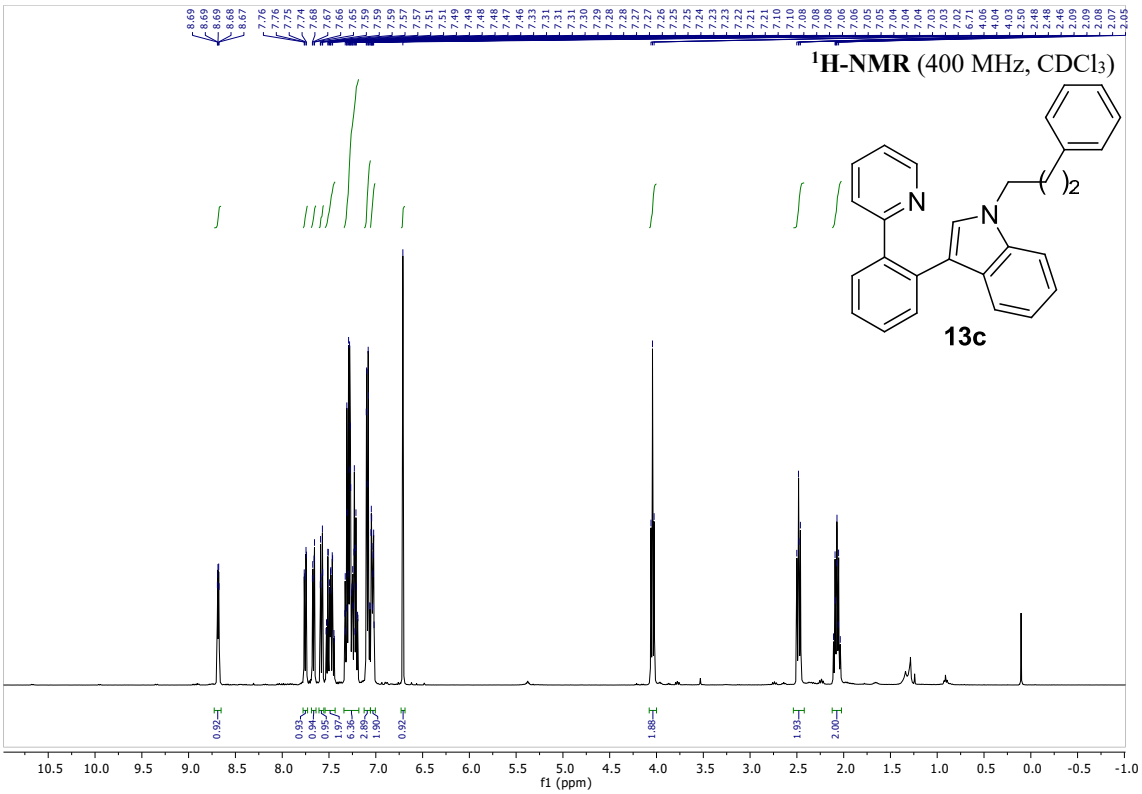


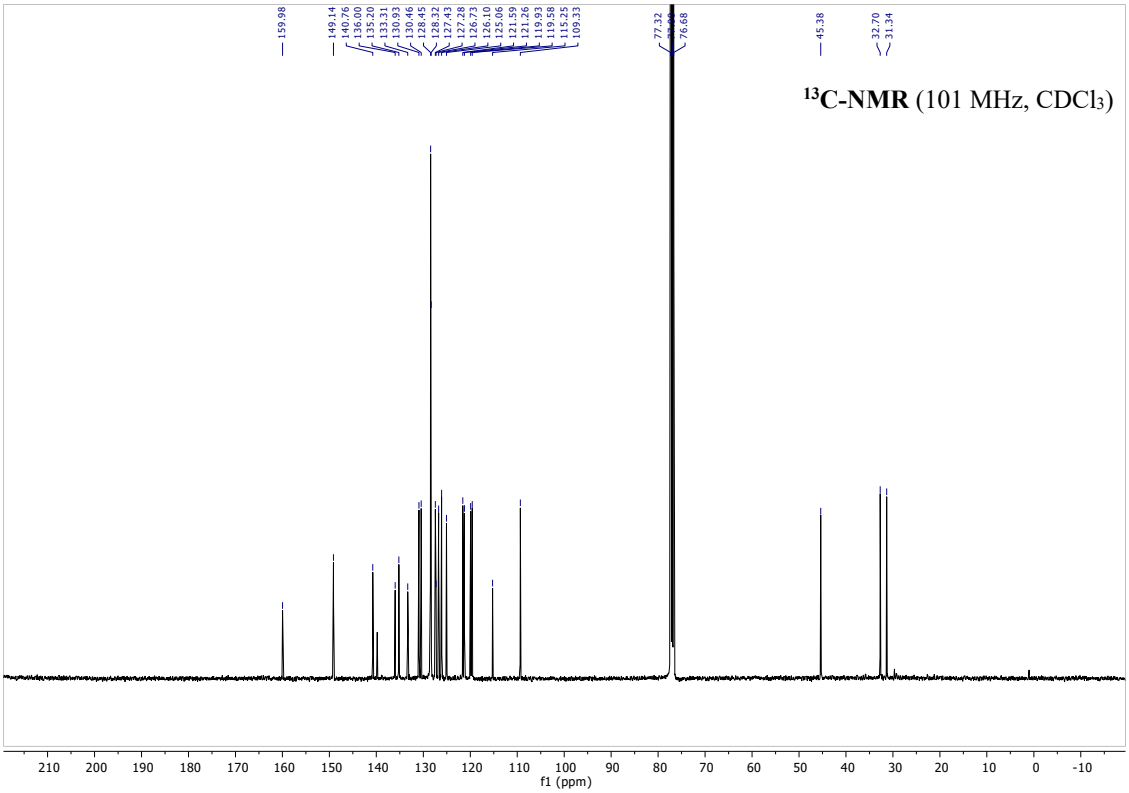
3-(2-(Pyridin-2-yl)phenyl)-1*H*-indole (13b)



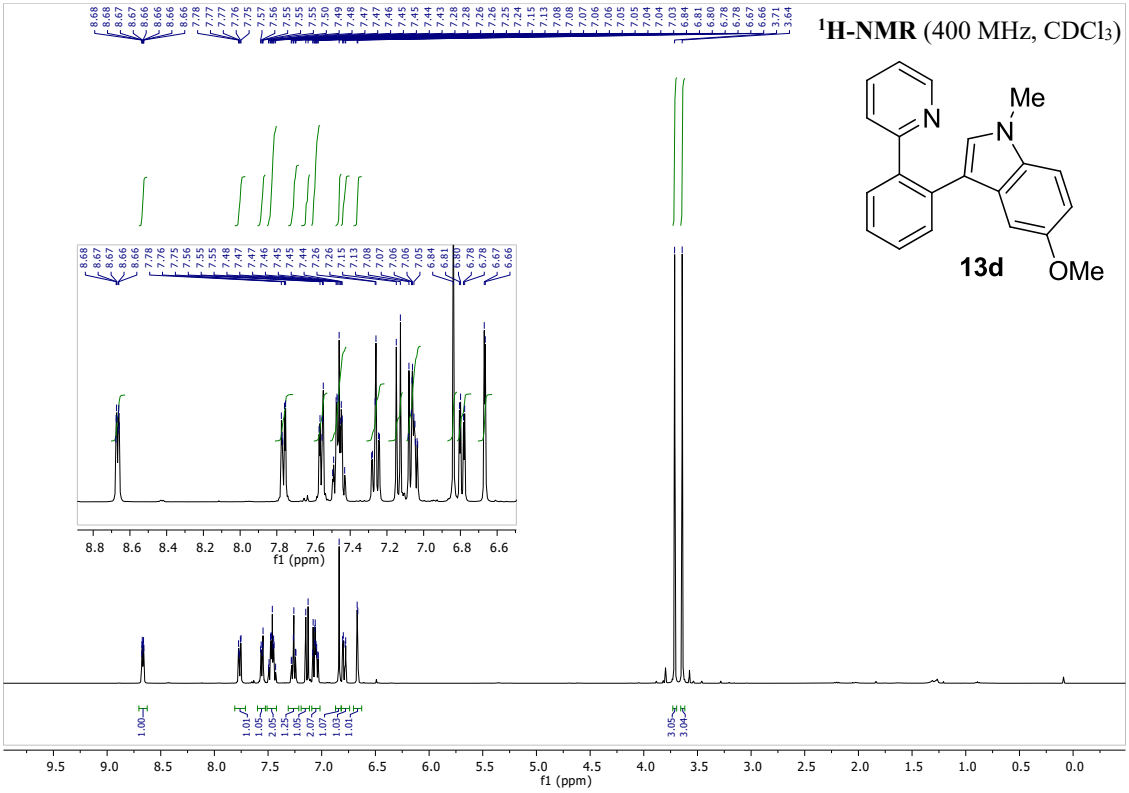


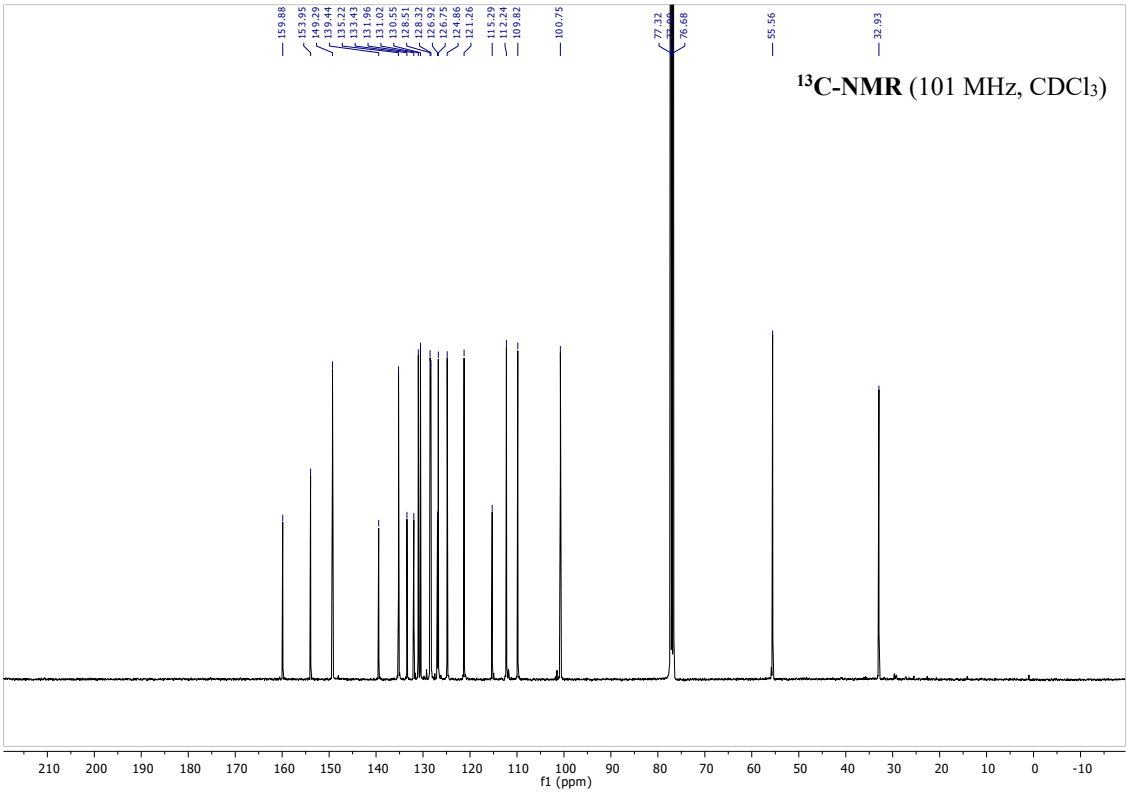
1-(3-Phenylpropyl)-3-(2-(pyridin-2-yl)phenyl)-1*H*-indole (13c)





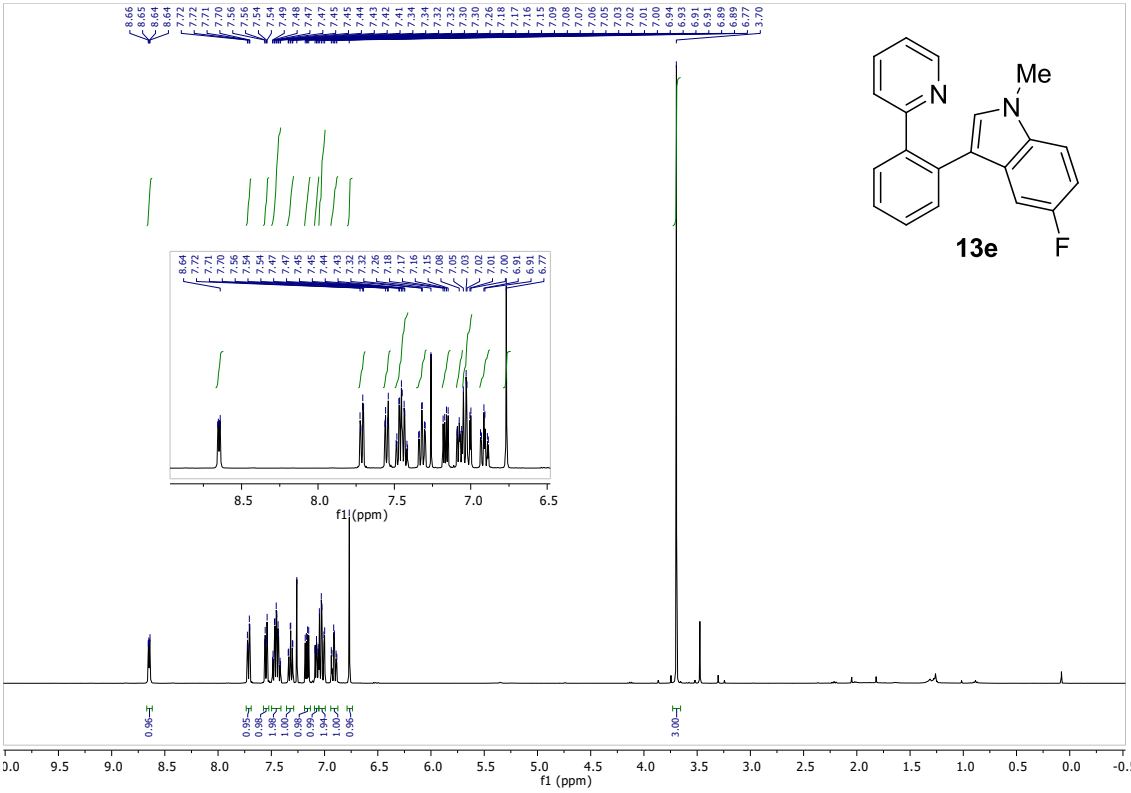
5-Methoxy-1-methyl-3-(2-(pyridin-2-yl)phenyl)-1*H*-indole (13d)

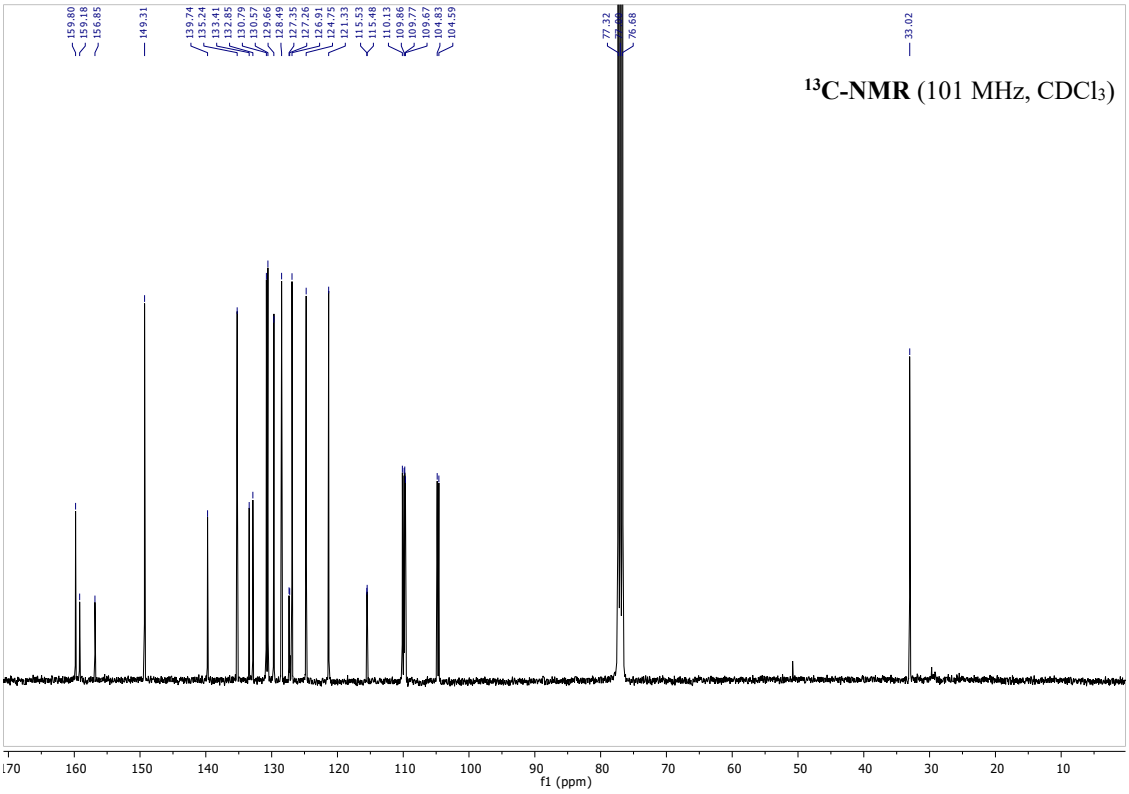




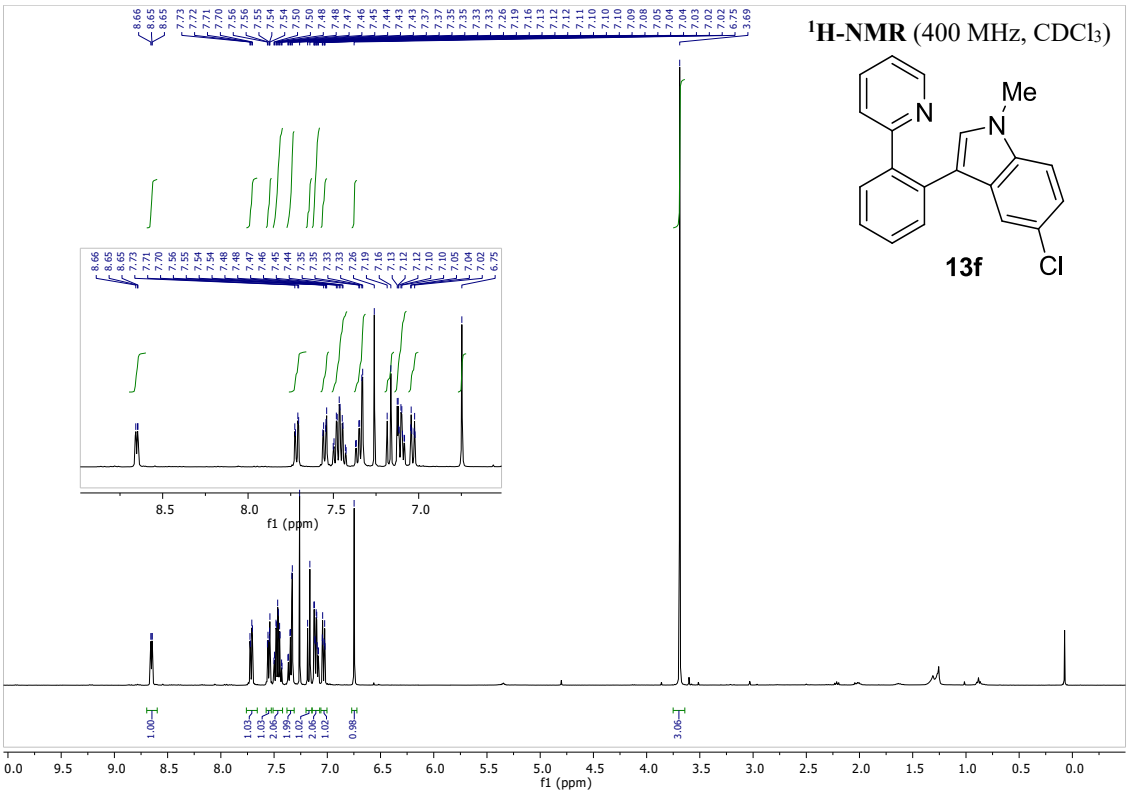
5-Fluoro-1-methyl-3-(2-(pyridin-2-yl)phenyl)-1*H*-indole (13e)

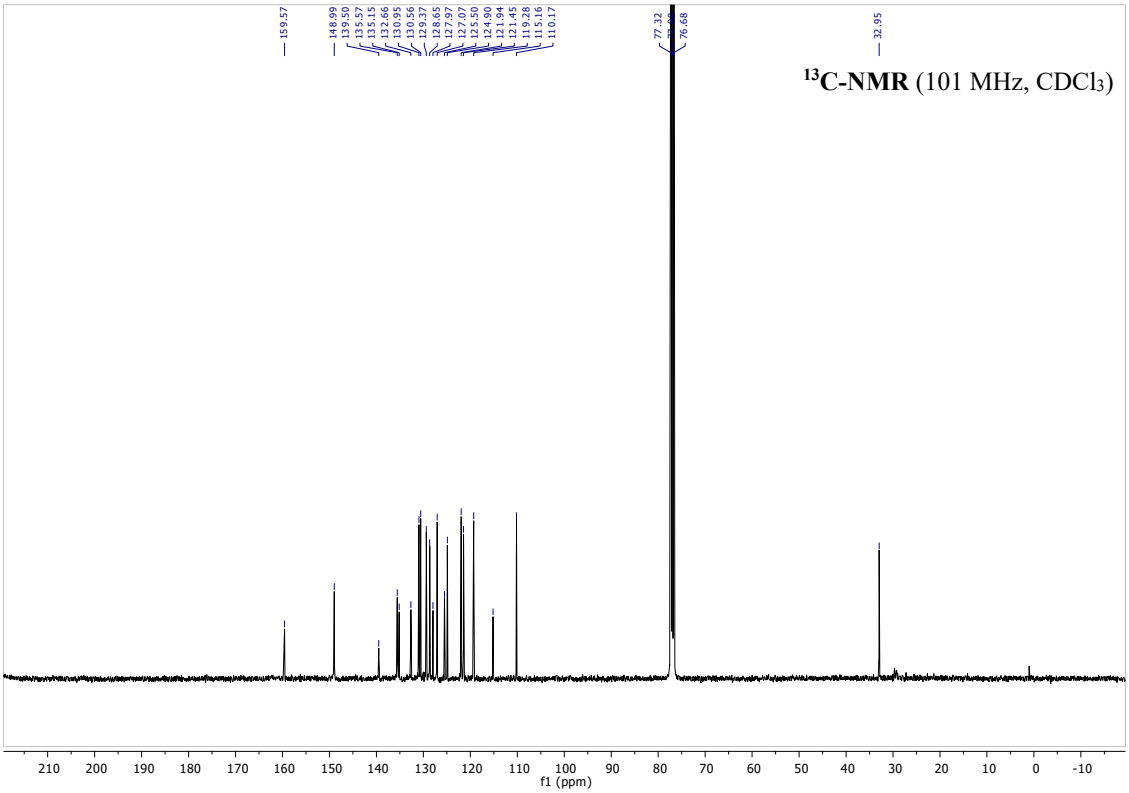
¹H-NMR (400 MHz, $CDCl_3$)



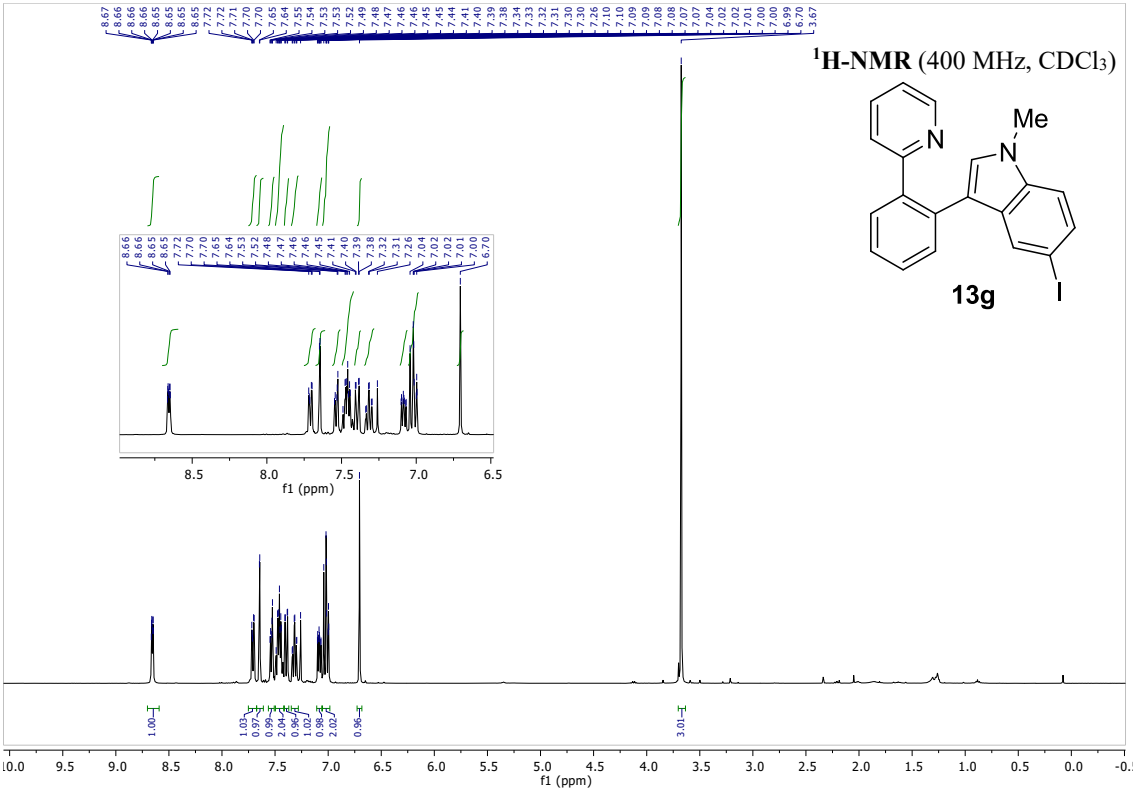


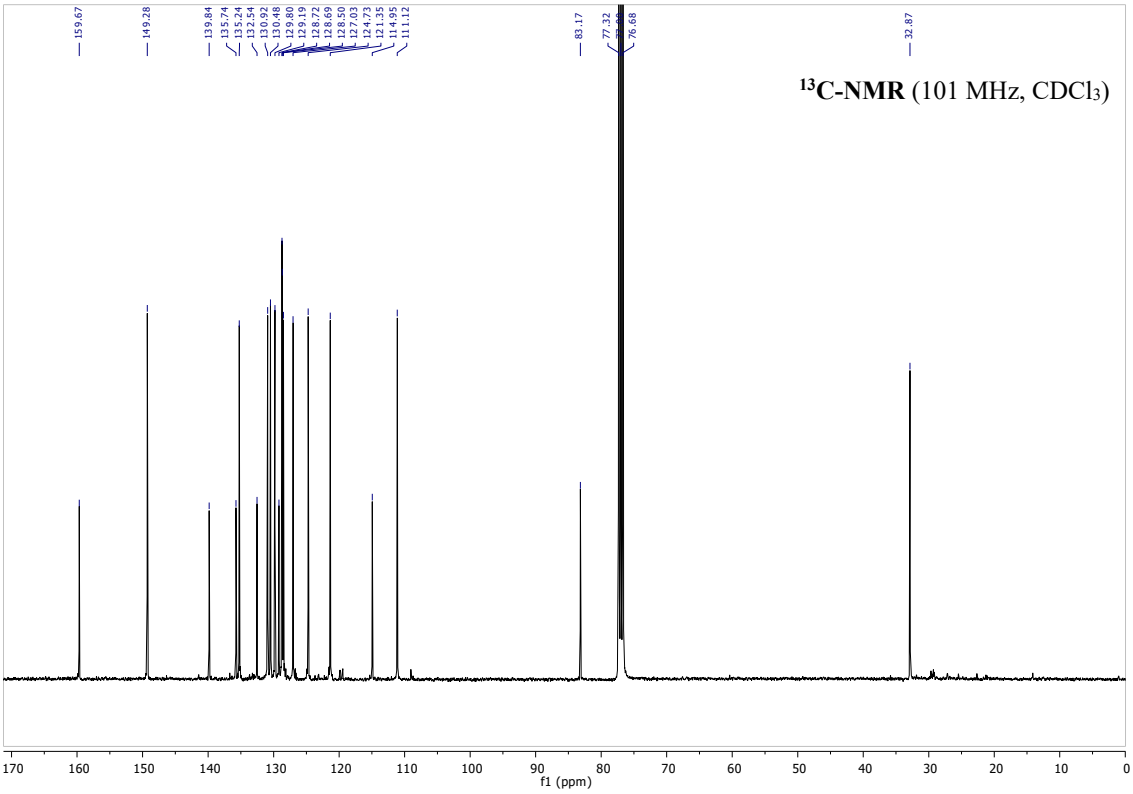
5-Chloro-1-methyl-3-(2-(pyridin-2-yl)phenyl)-1*H*-indole (13f)





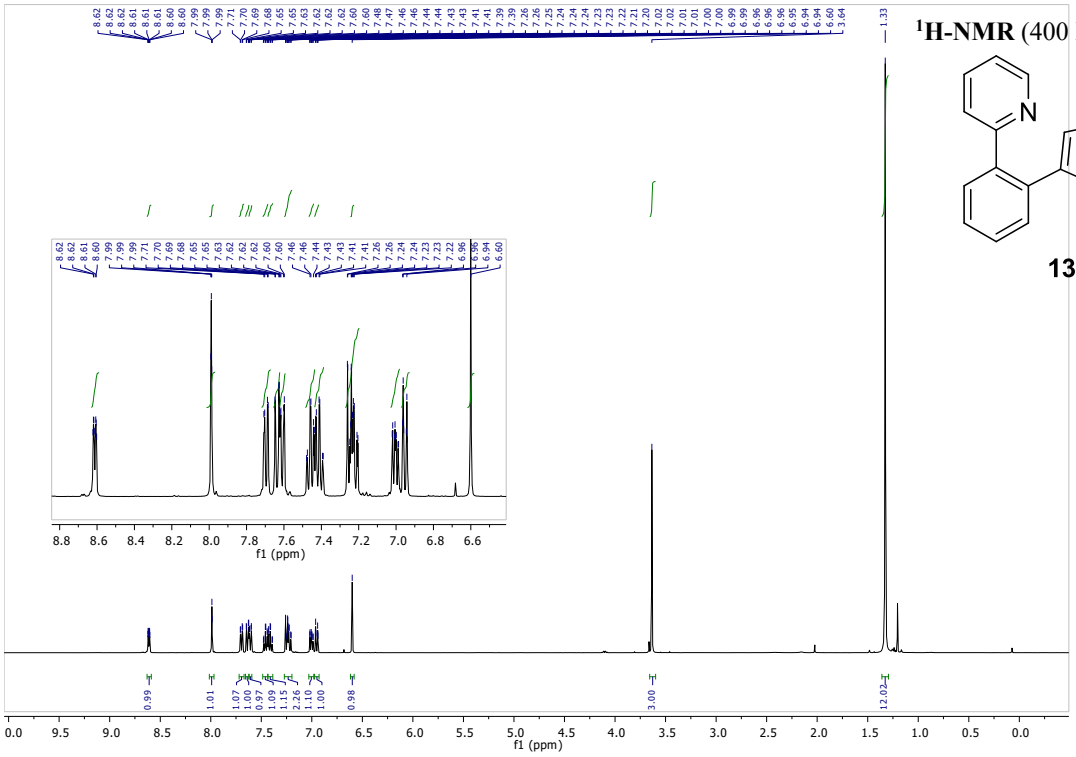
5-Iodo-1-methyl-3-(2-(pyridin-2-yl)phenyl)-1*H*-indole (13g)


1H-NMR (400 MHz, CDCl3)
Me
N
N
I
13g
f1 (ppm)

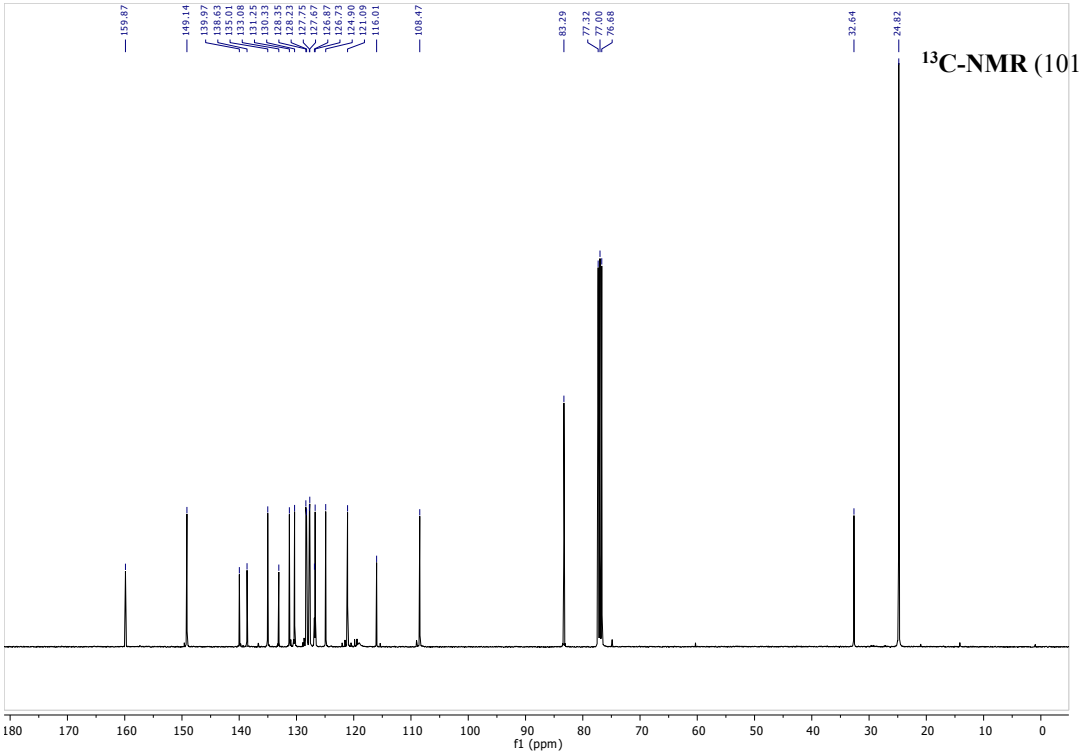

13C-NMR (101 MHz, CDCl3)
f1 (ppm)

1-Methyl-3-(2-(pyridin-2-yl)phenyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (13h)

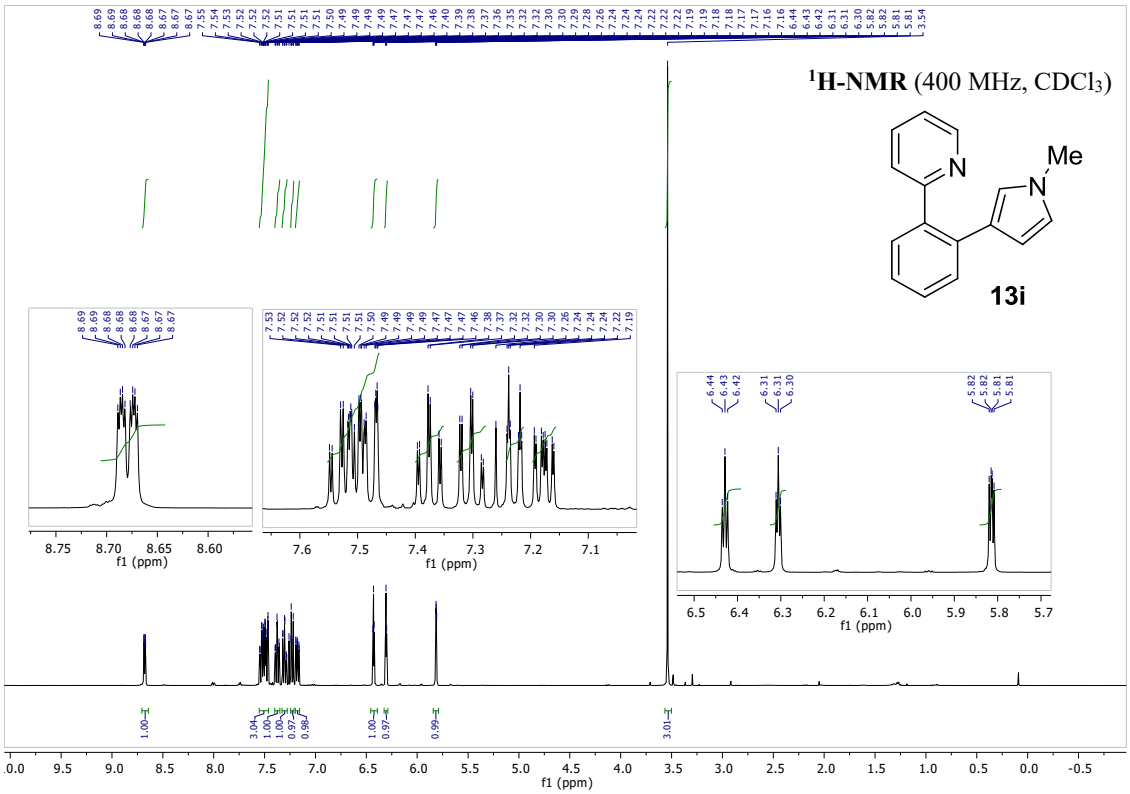
^{1}H-NMR (400 MHz, $CDCl_3$)

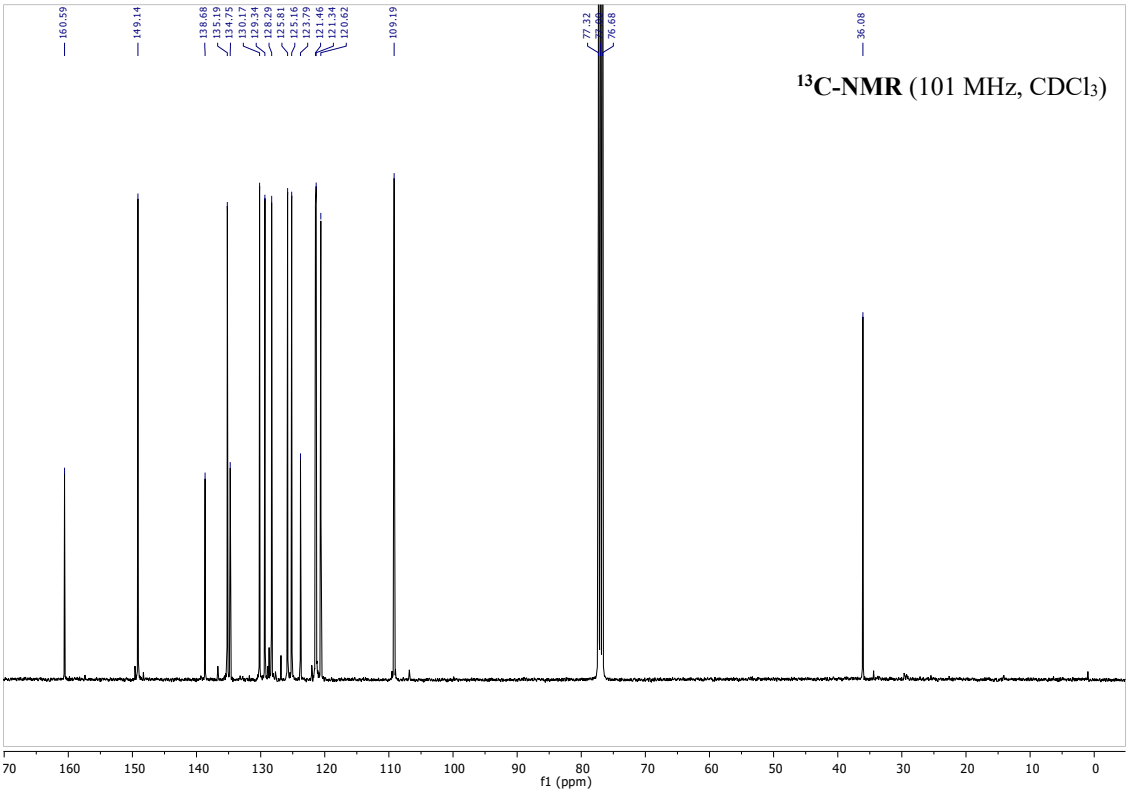


^{13}C-NMR (101 MHz, $CDCl_3$)

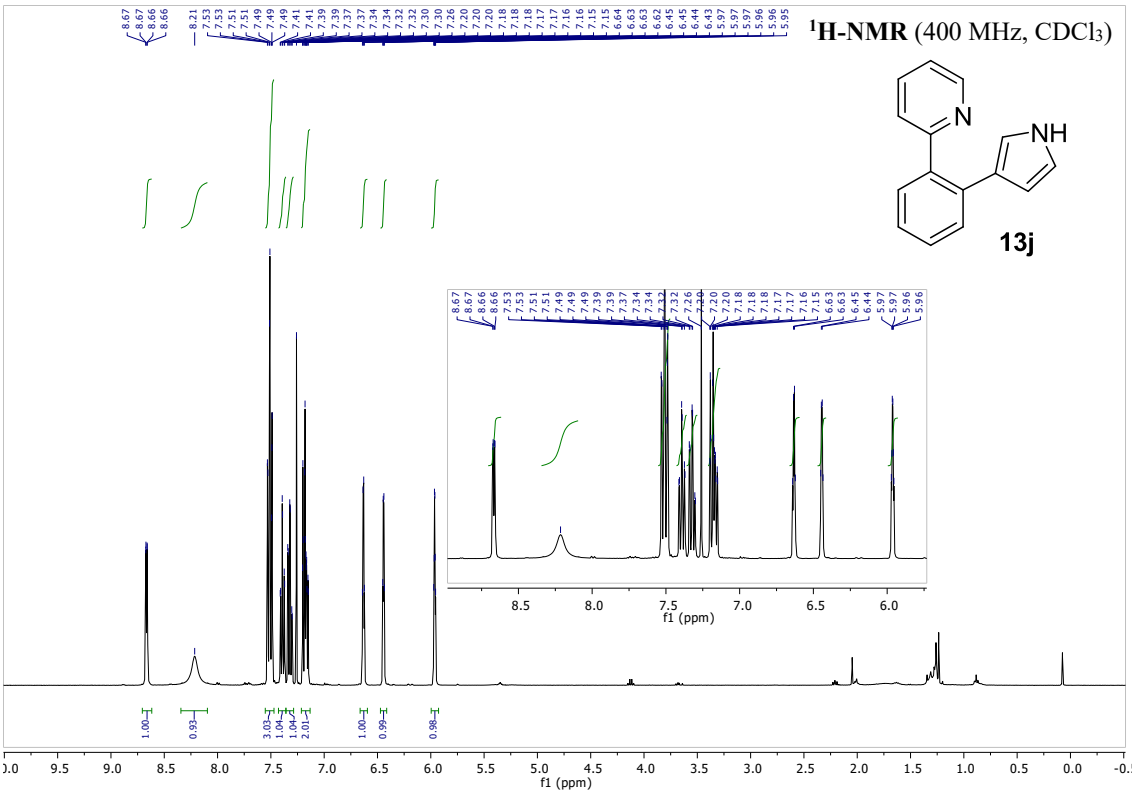


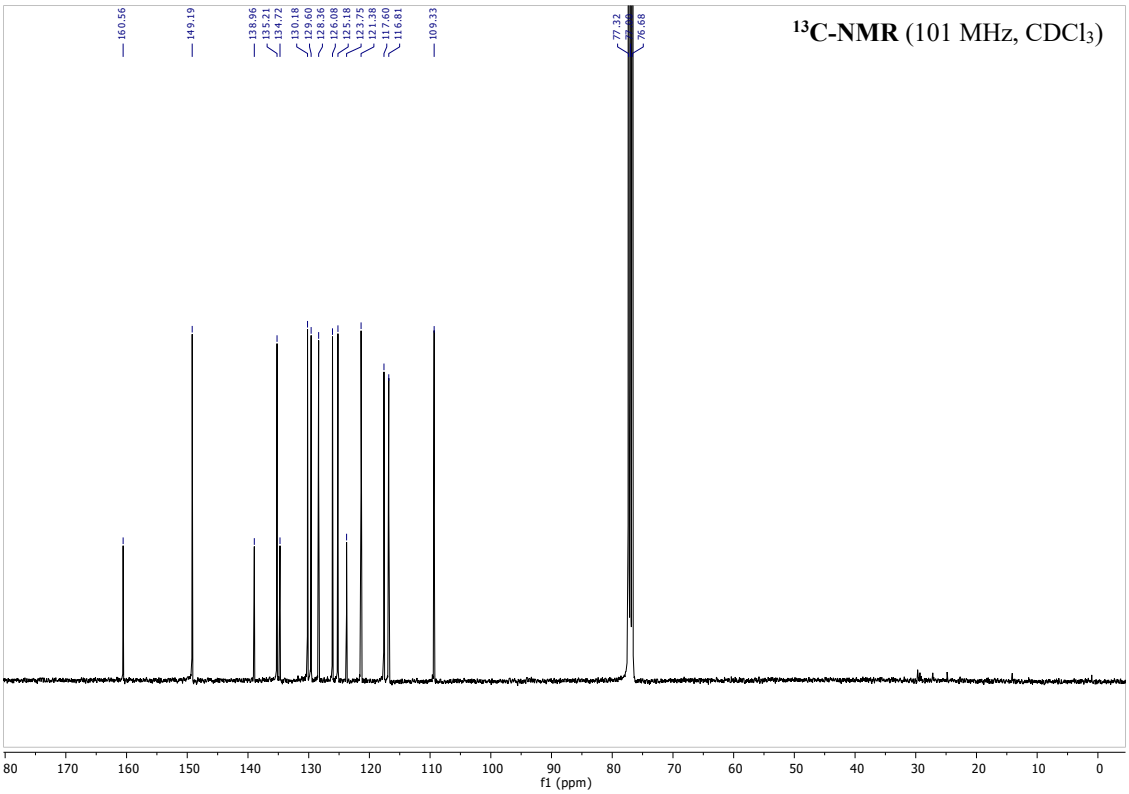
2-(2-(1-Methyl-1*H*-pyrrol-3-yl)phenyl)pyridine (13i)



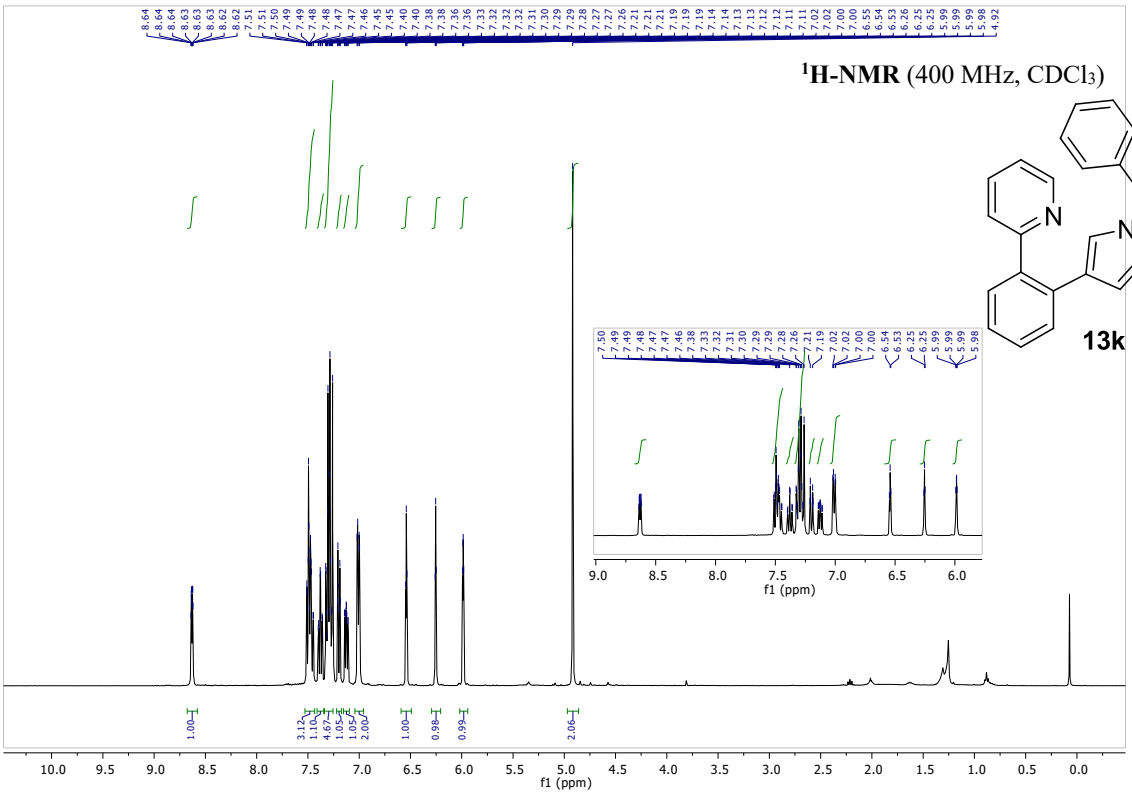


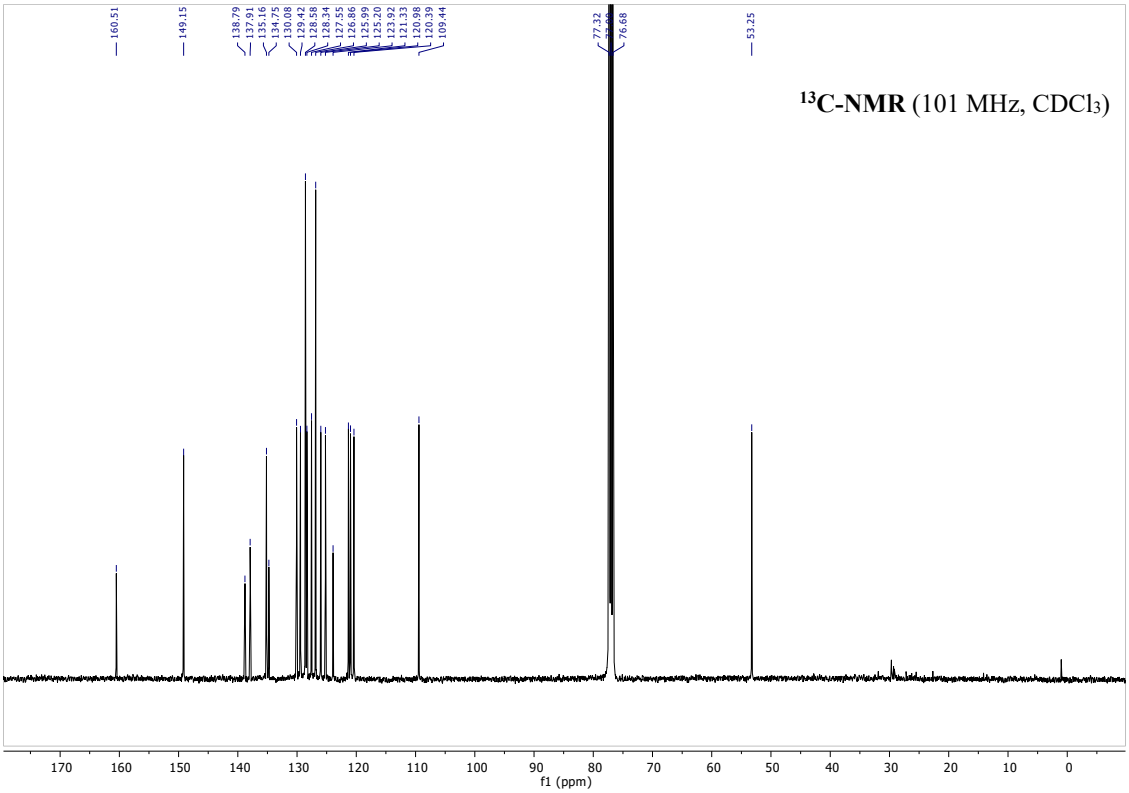
2-(2-(1*H*-Pyrrol-3-yl)phenyl)pyridine (13j)



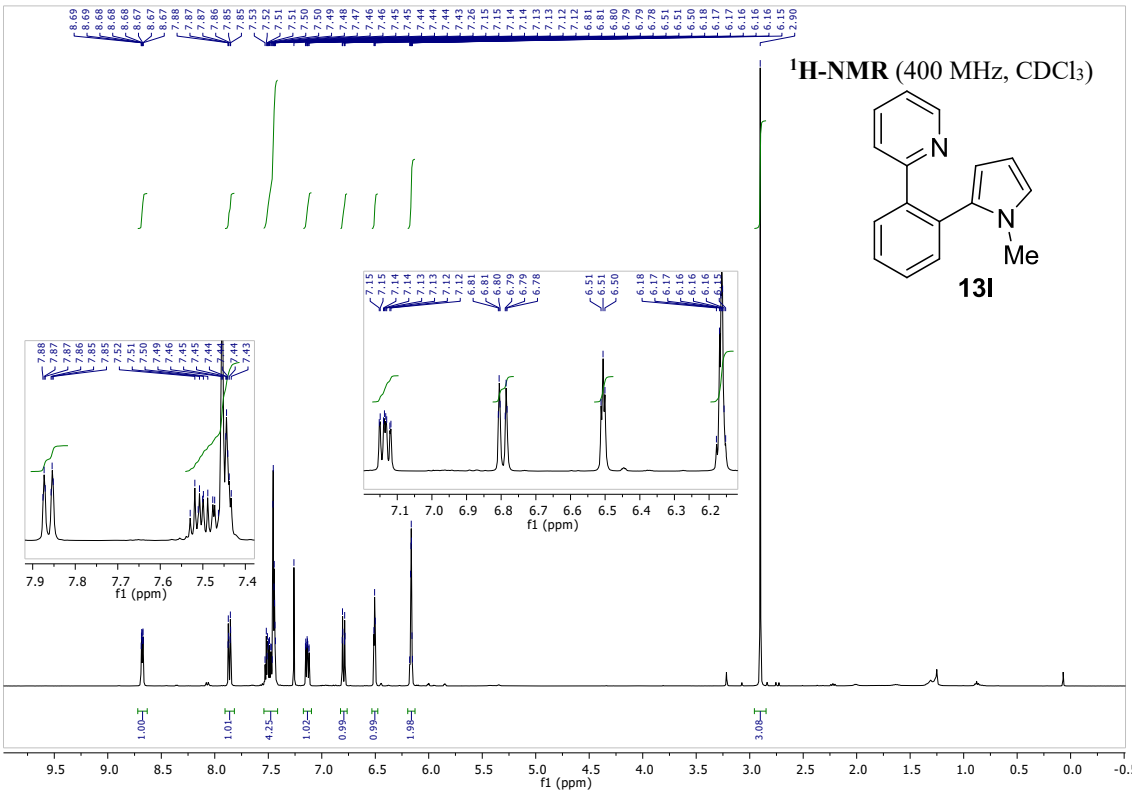


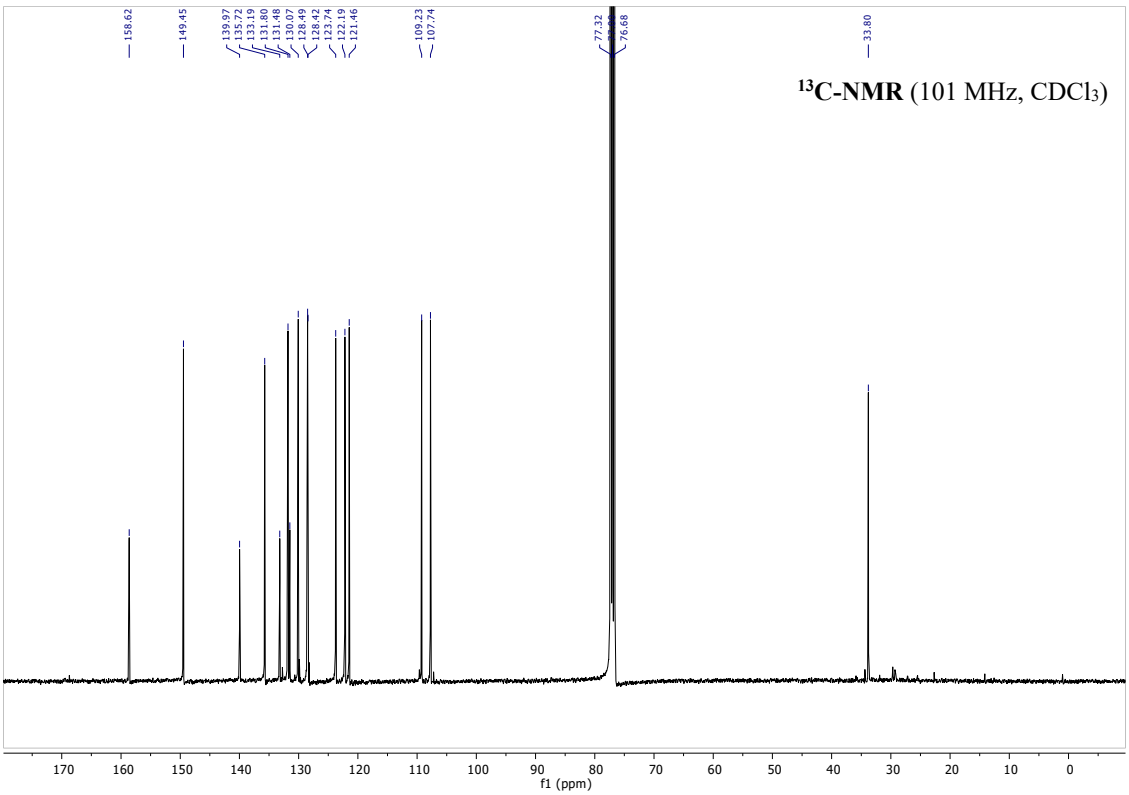
2-(2-(1-Benzyl-1*H*-pyrrol-3-yl)phenyl)pyridine (13k)



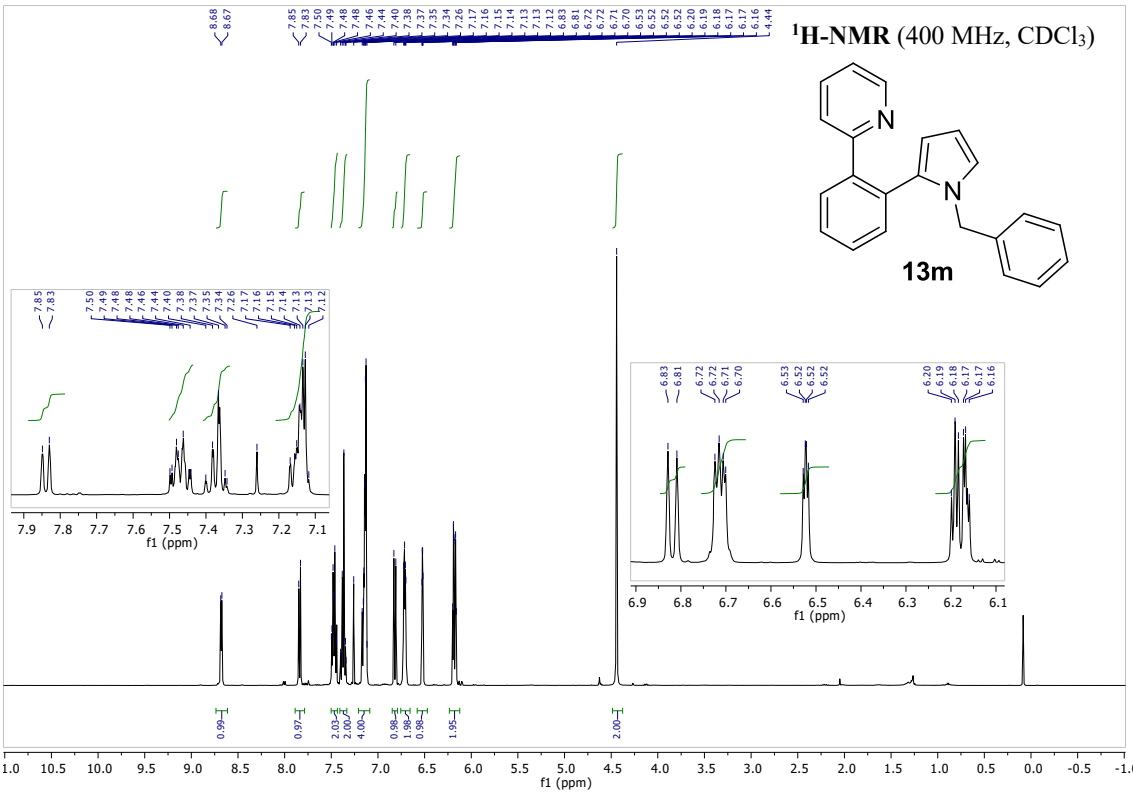


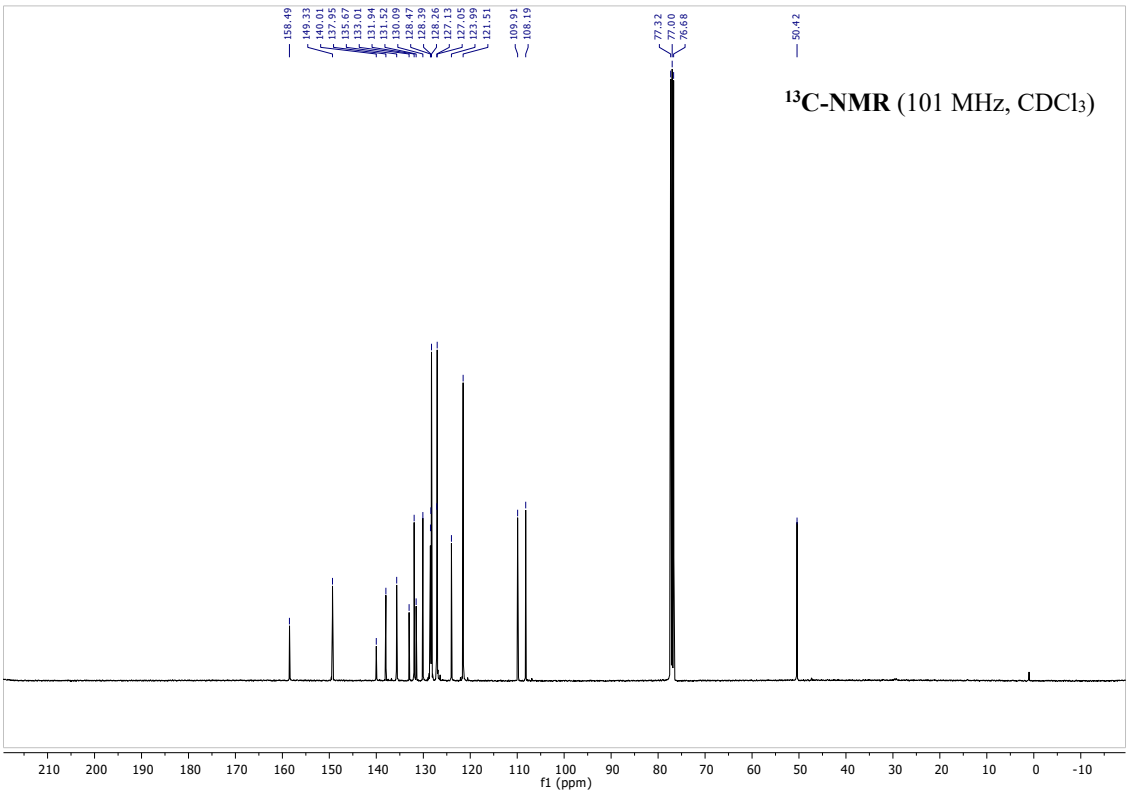
2-(2-(1-Methyl-1*H*-pyrrol-2-yl)phenyl)pyridine (13l)



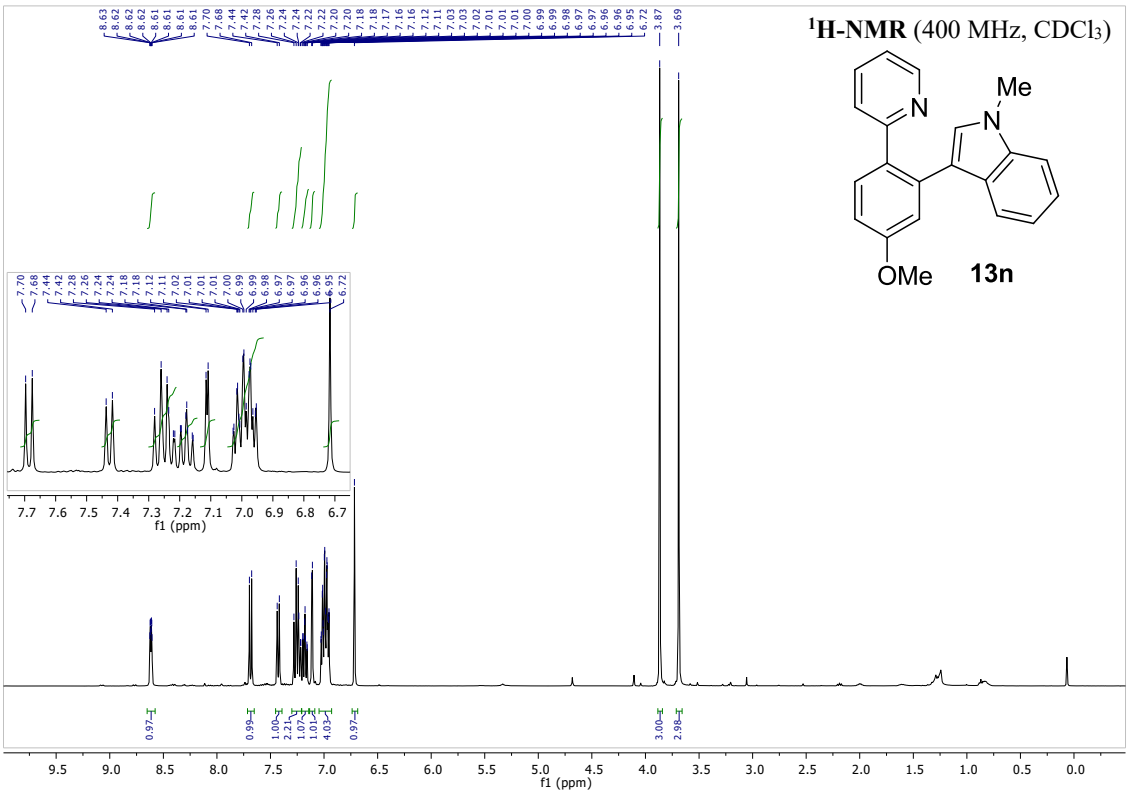


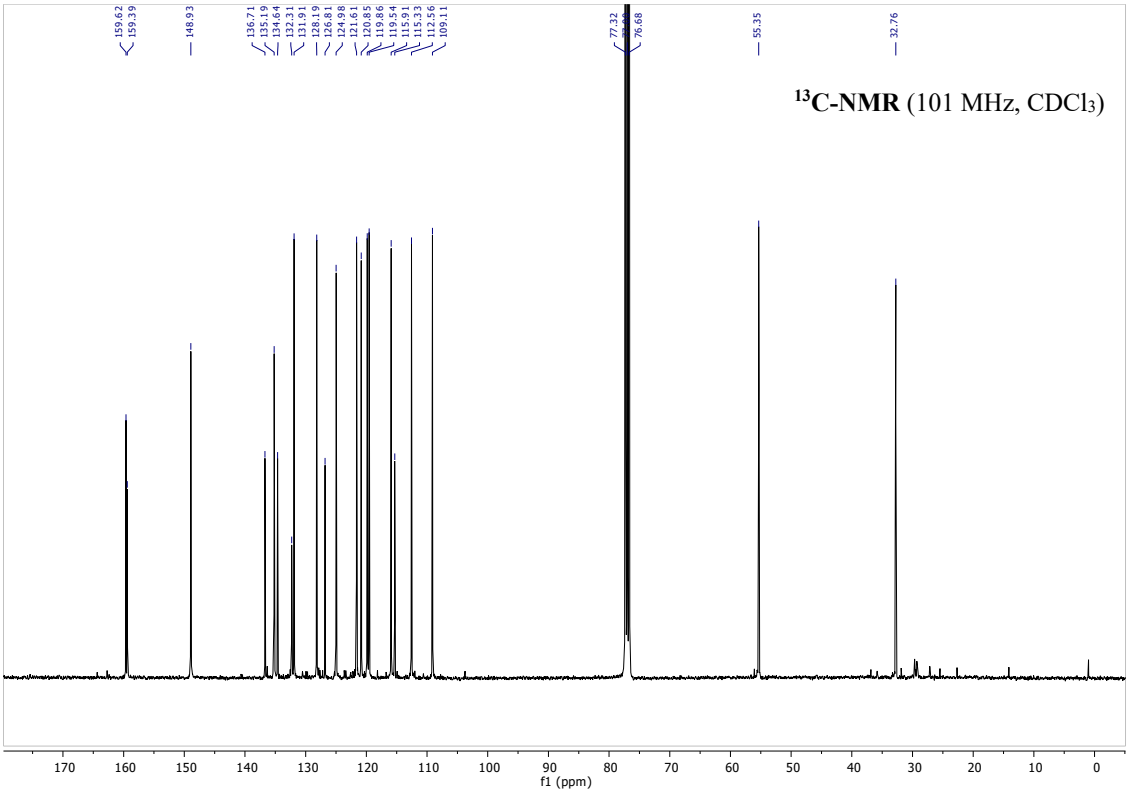
2-(2-(1-Benzyl-1*H*-pyrrol-2-yl)phenyl)pyridine (13m)



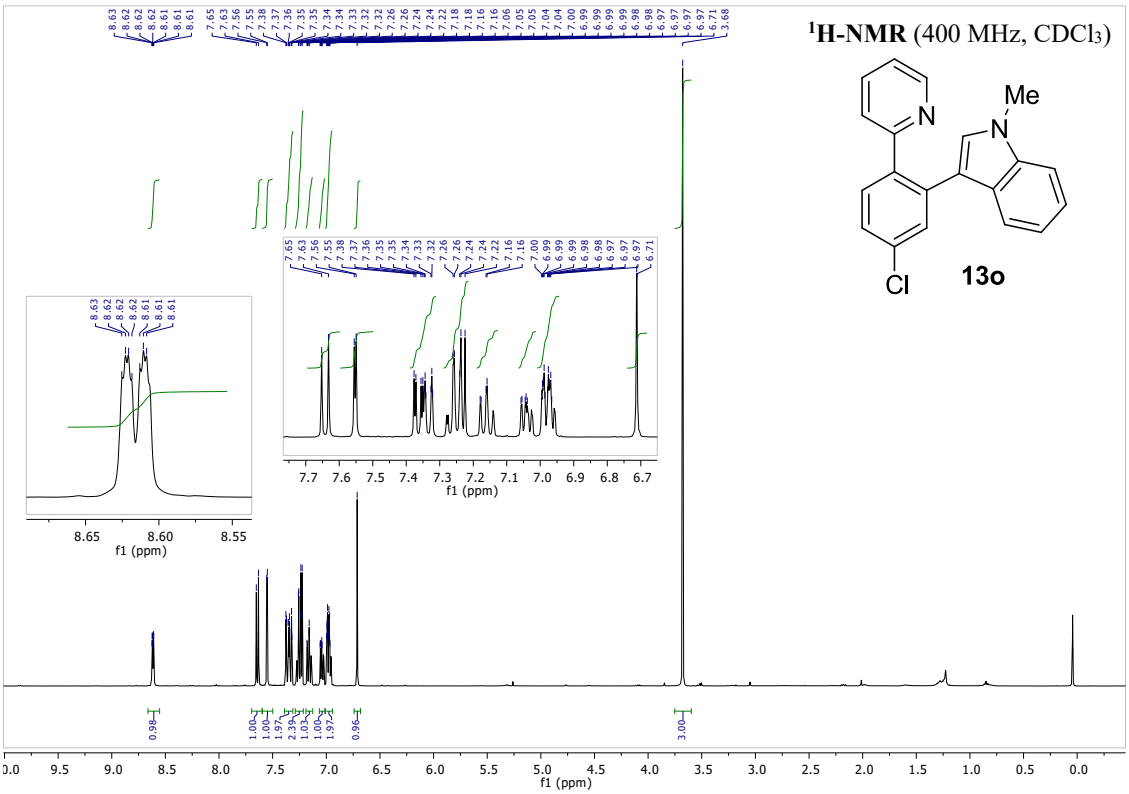


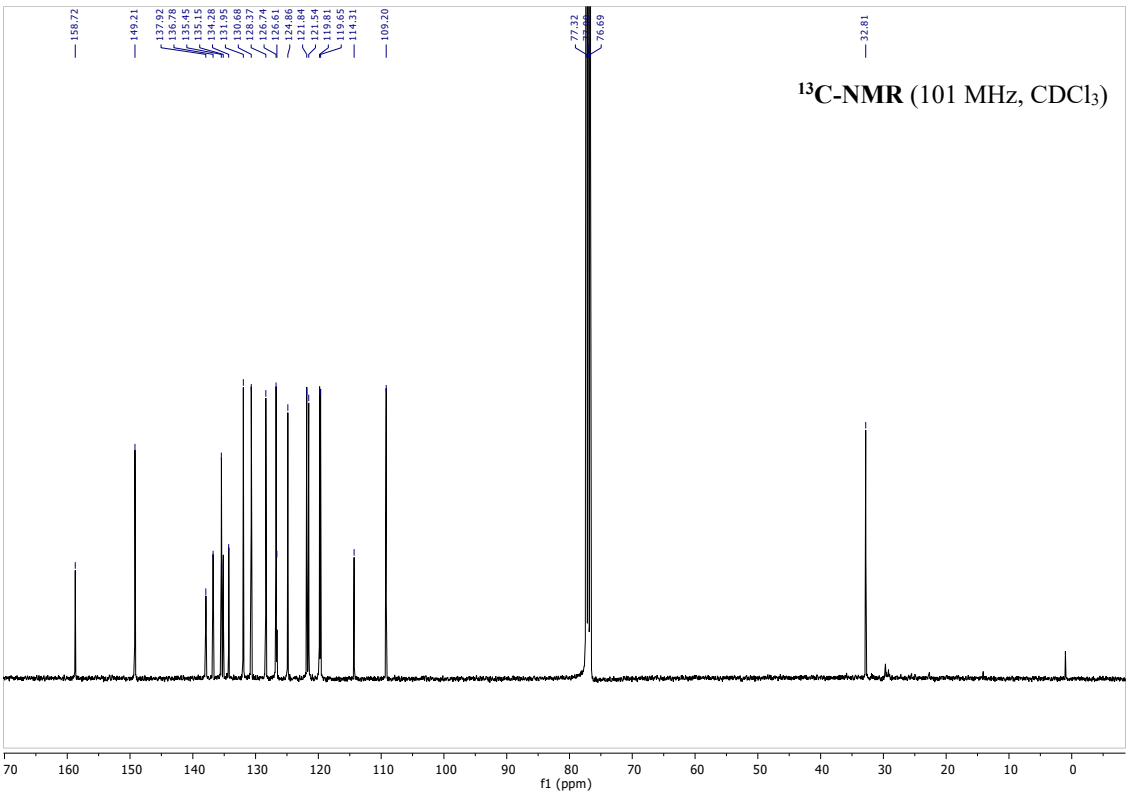
3-(5-Methoxy-2-(pyridin-2-yl)phenyl)-1-methyl-1*H*-indole (13n)



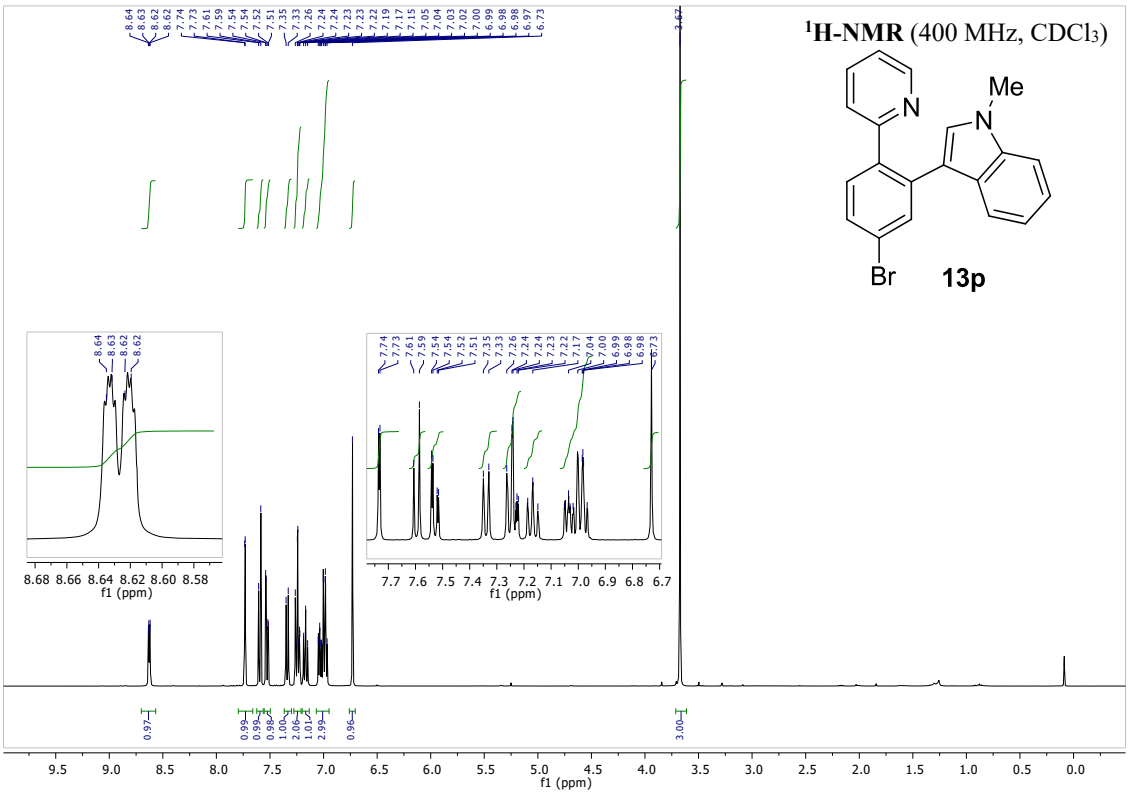


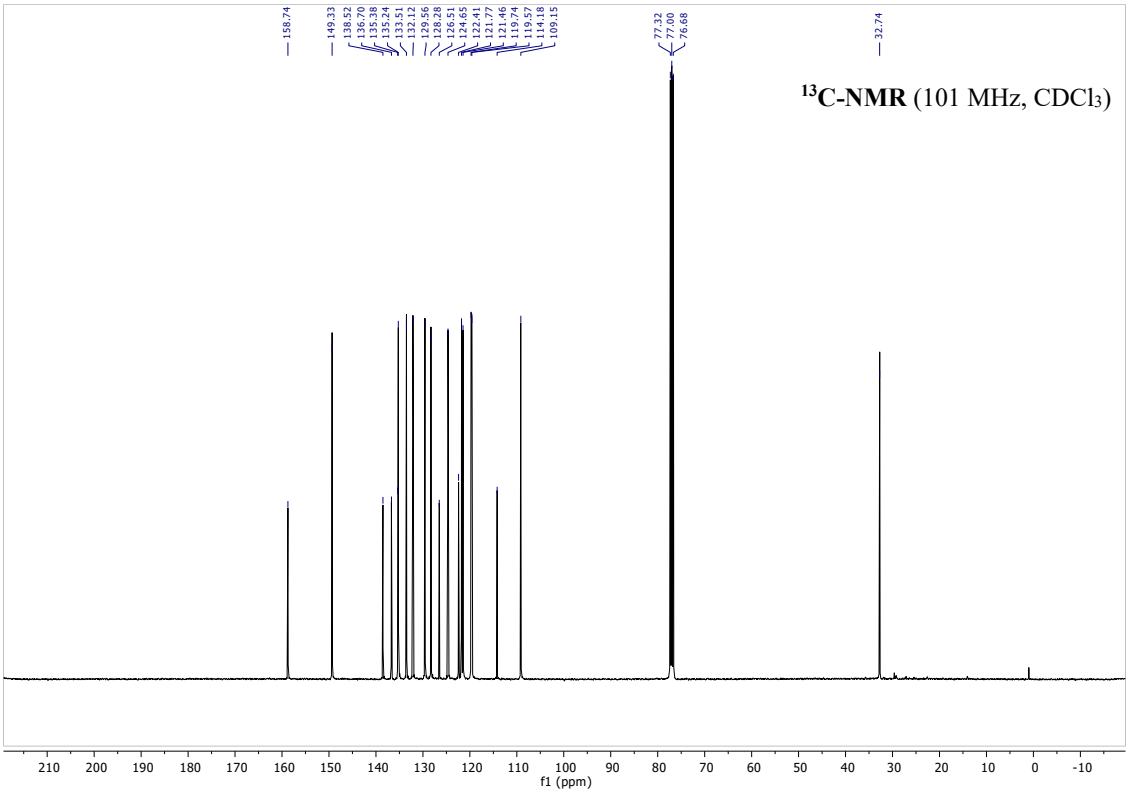
3-(5-Chloro-2-(pyridin-2-yl)phenyl)-1-methyl-1*H*-indole (13o)



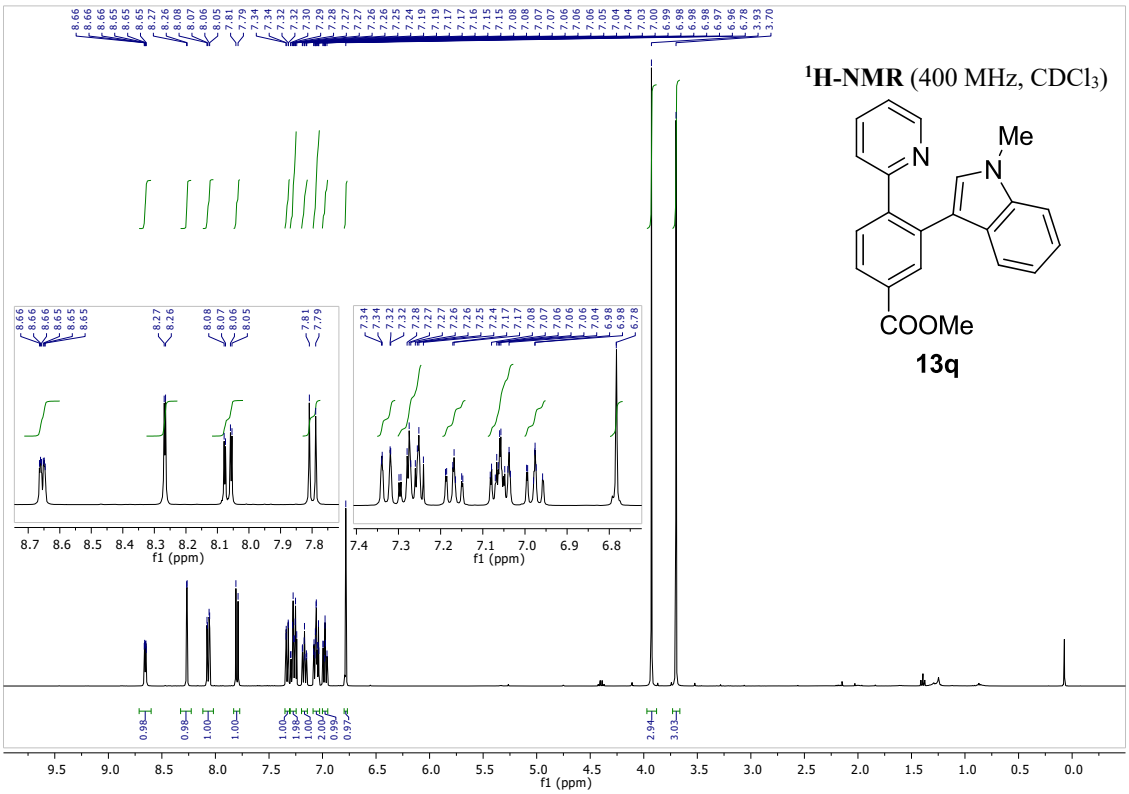


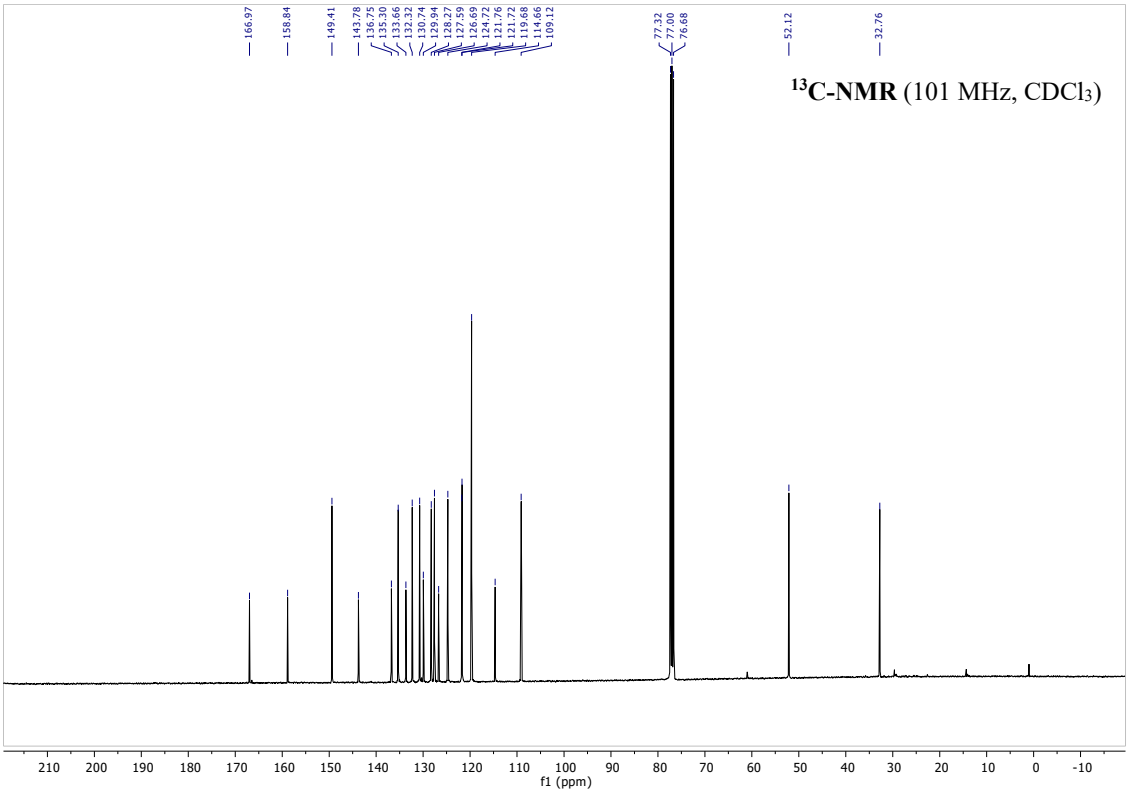
3-(5-Bromo-2-(pyridin-2-yl)phenyl)-1-methyl-1*H*-indole (13p)



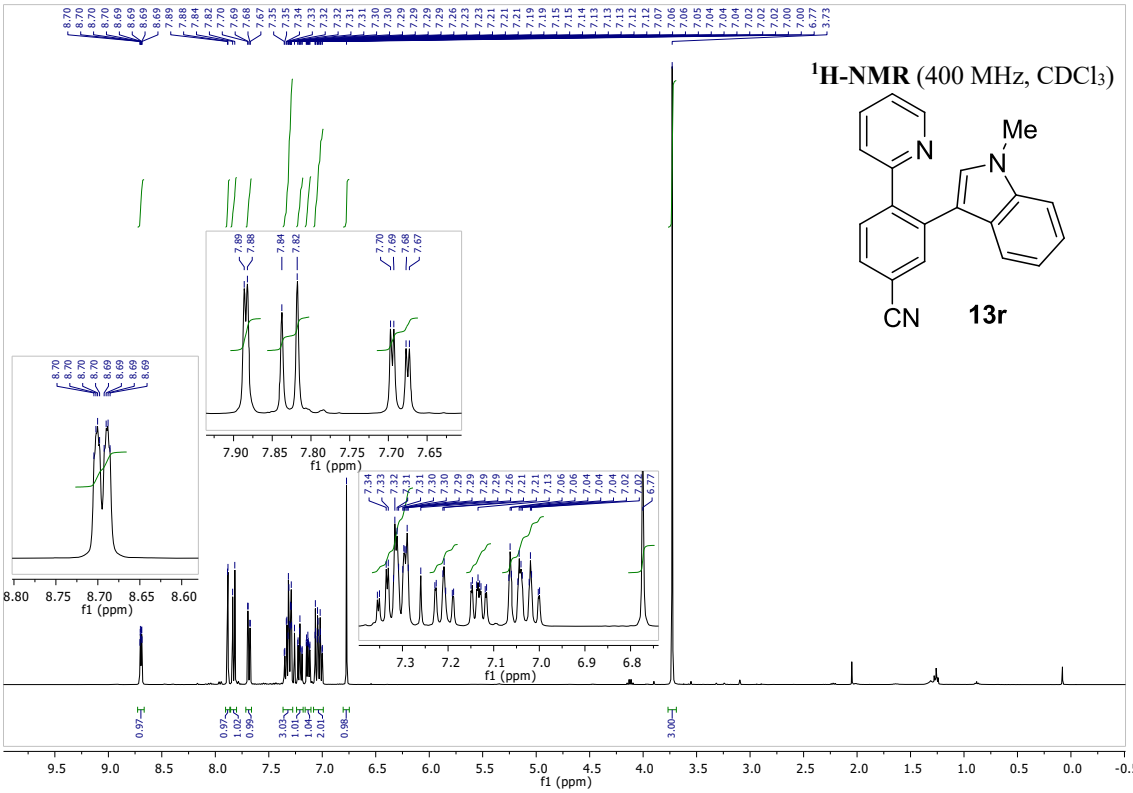


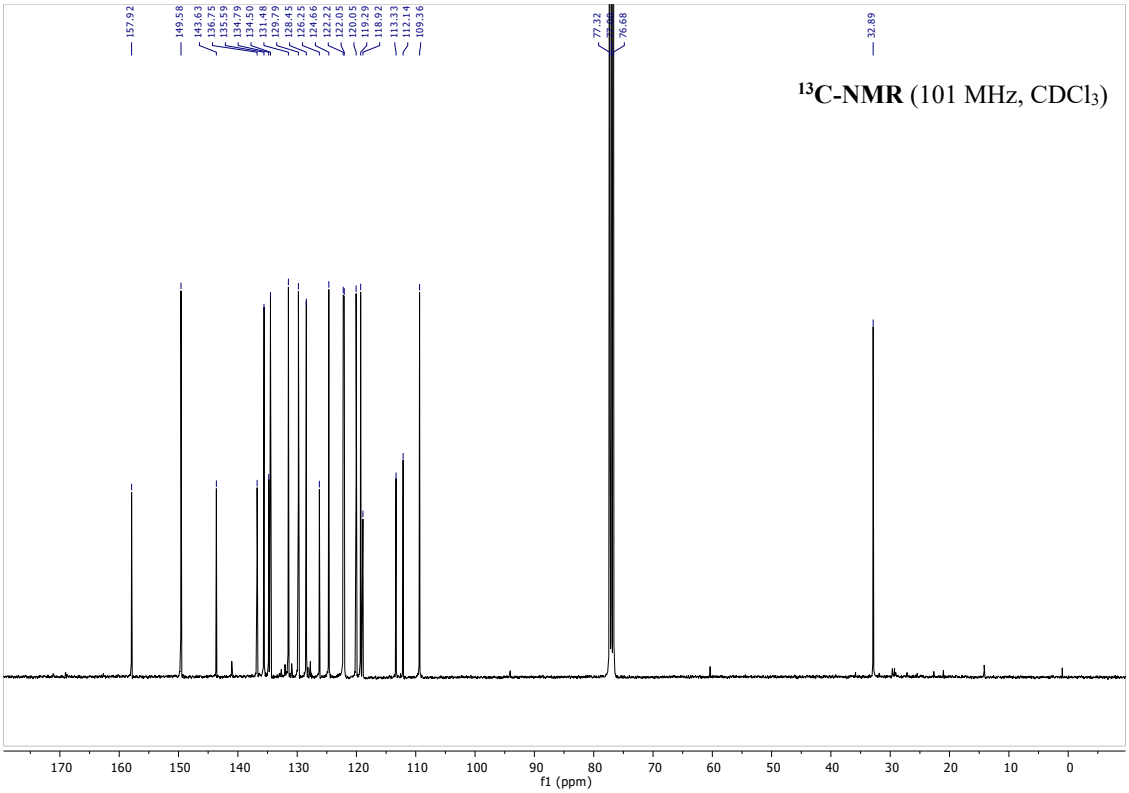
Methyl 3-(1-methyl-1*H*-indol-3-yl)-4-(pyridin-2-yl)benzoate (13q)



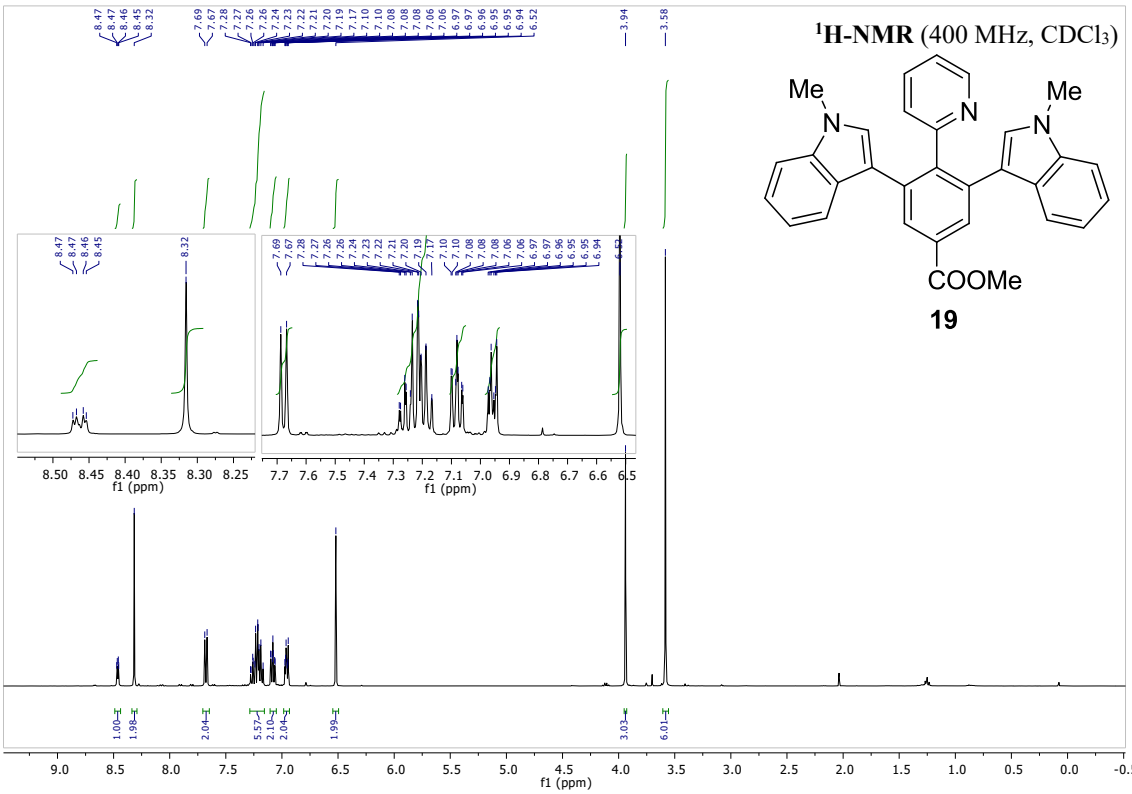


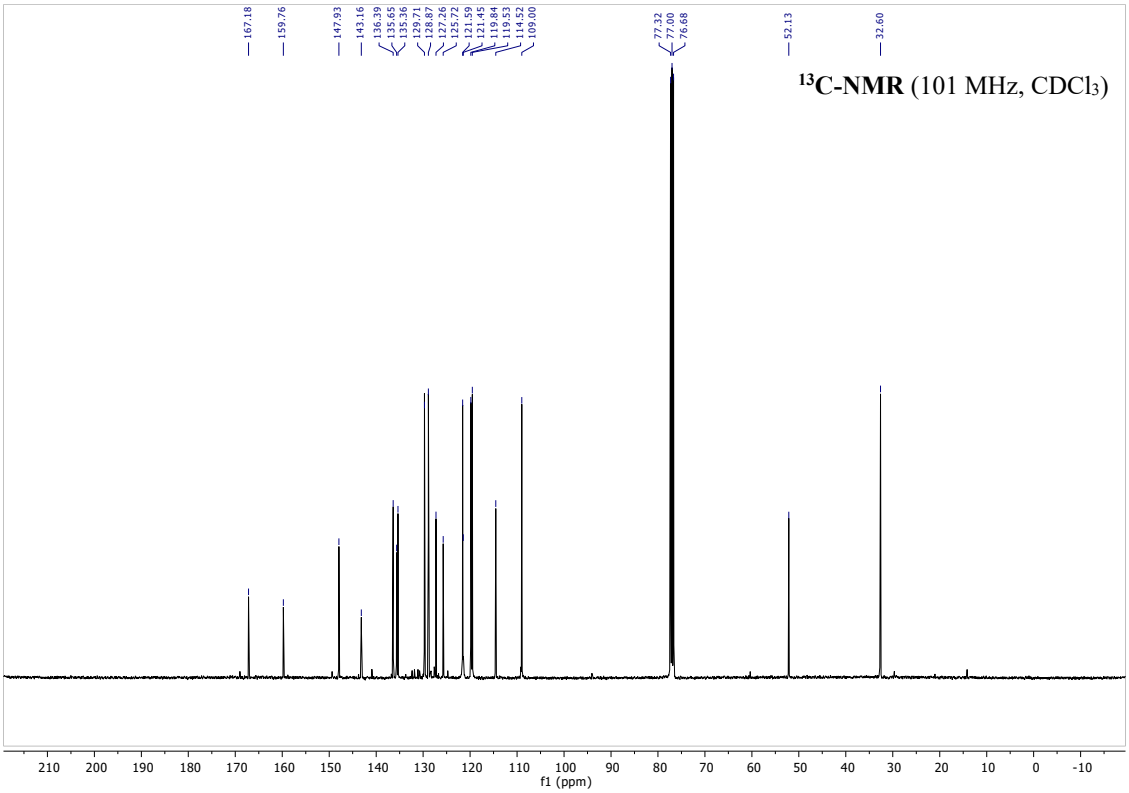
3-(1-Methyl-1*H*-indol-3-yl)-4-(pyridin-2-yl)benzonitrile (13r)



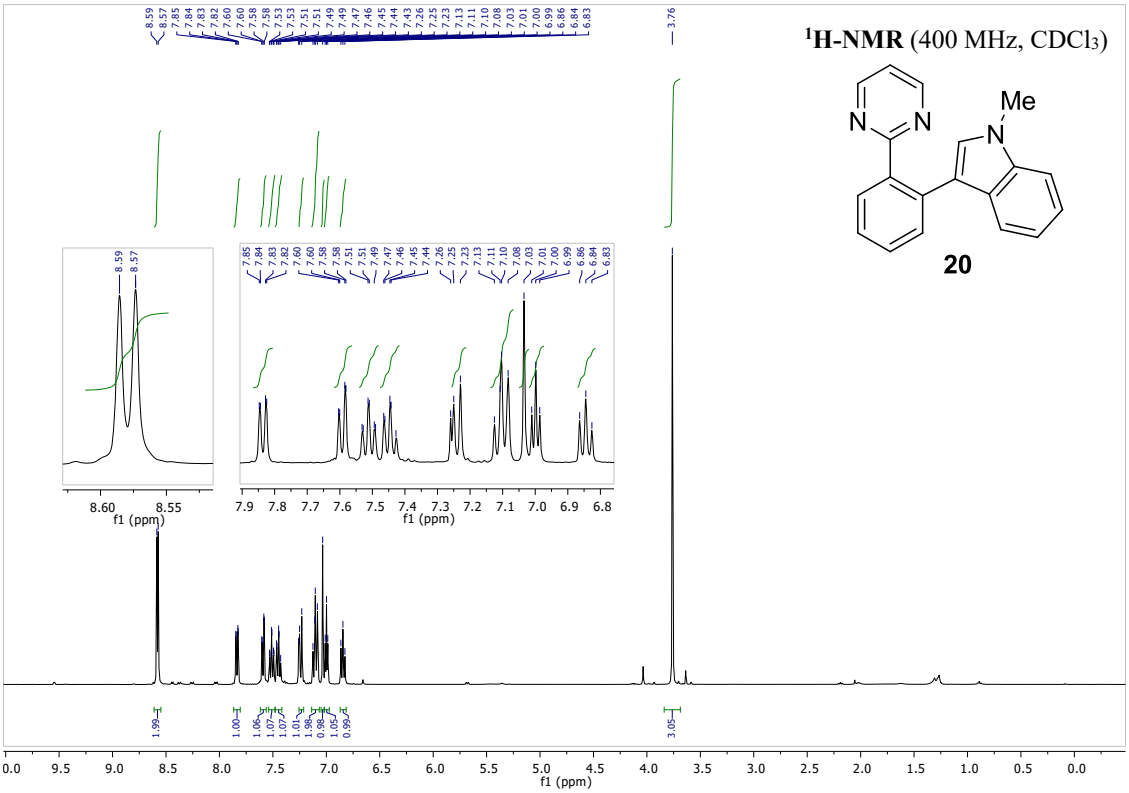


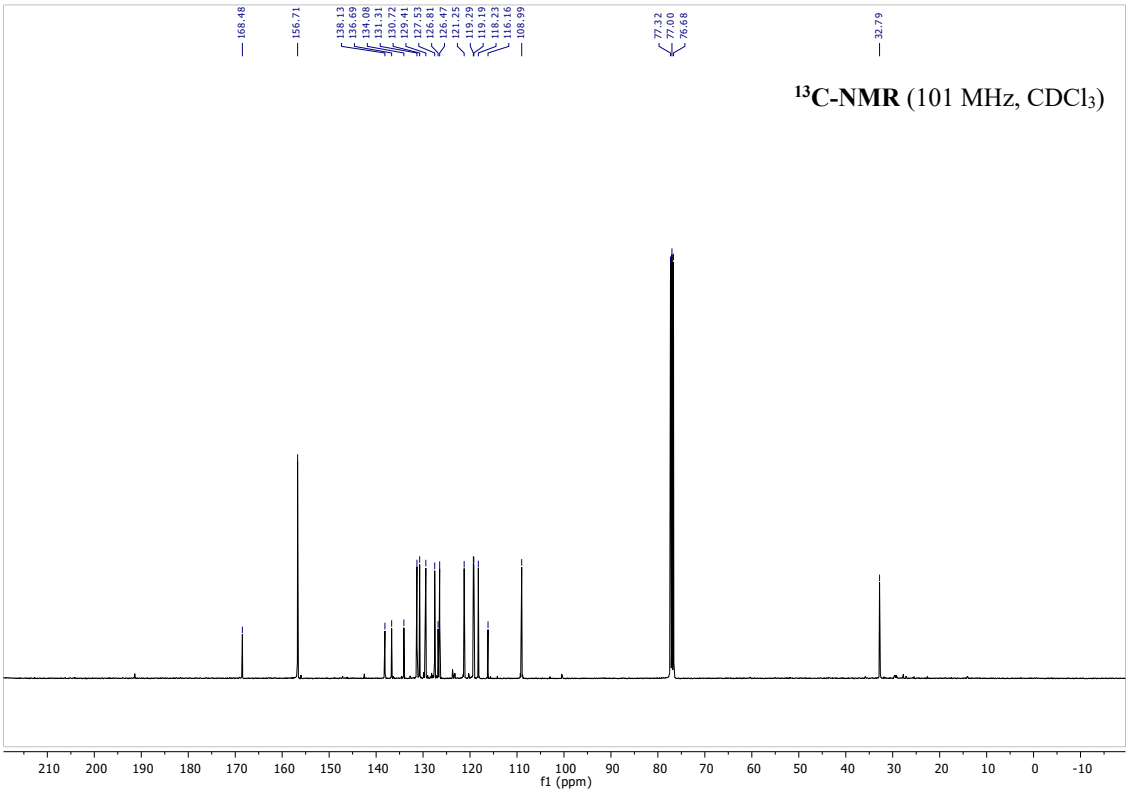
Methyl 3,5-bis(1-methyl-1*H*-indol-3-yl)-4-(pyridin-2-yl)benzoate (19)



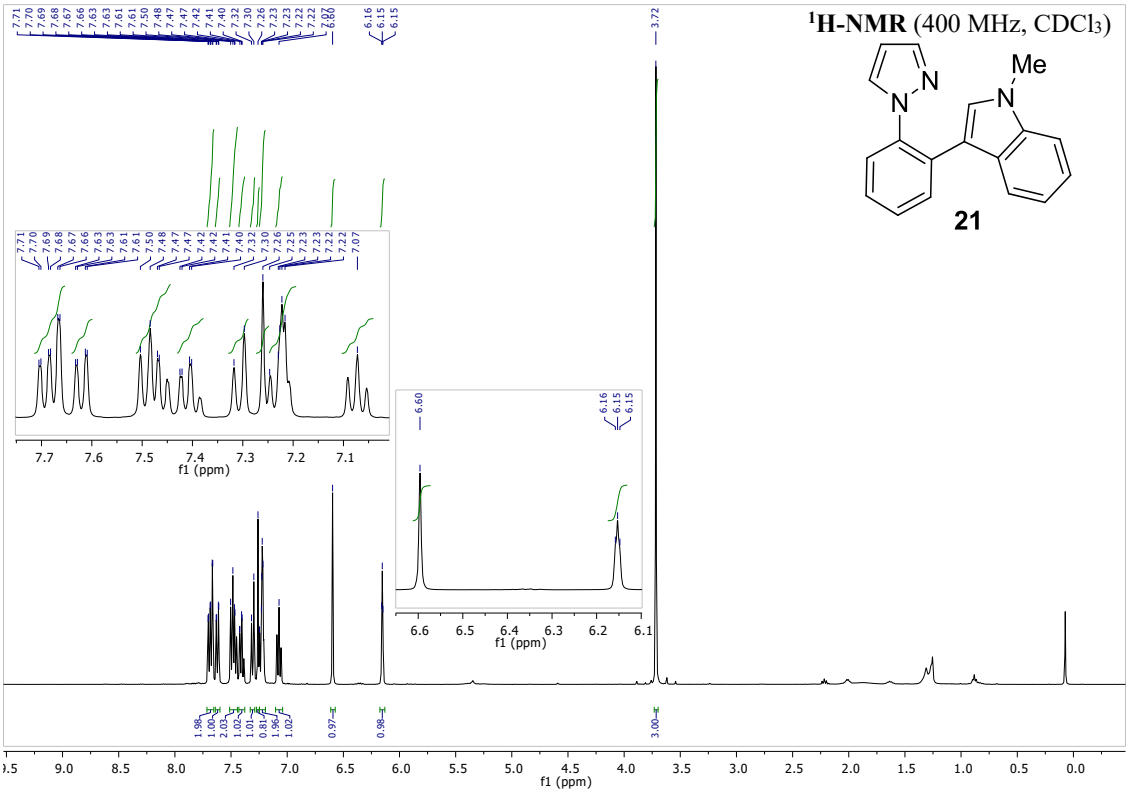


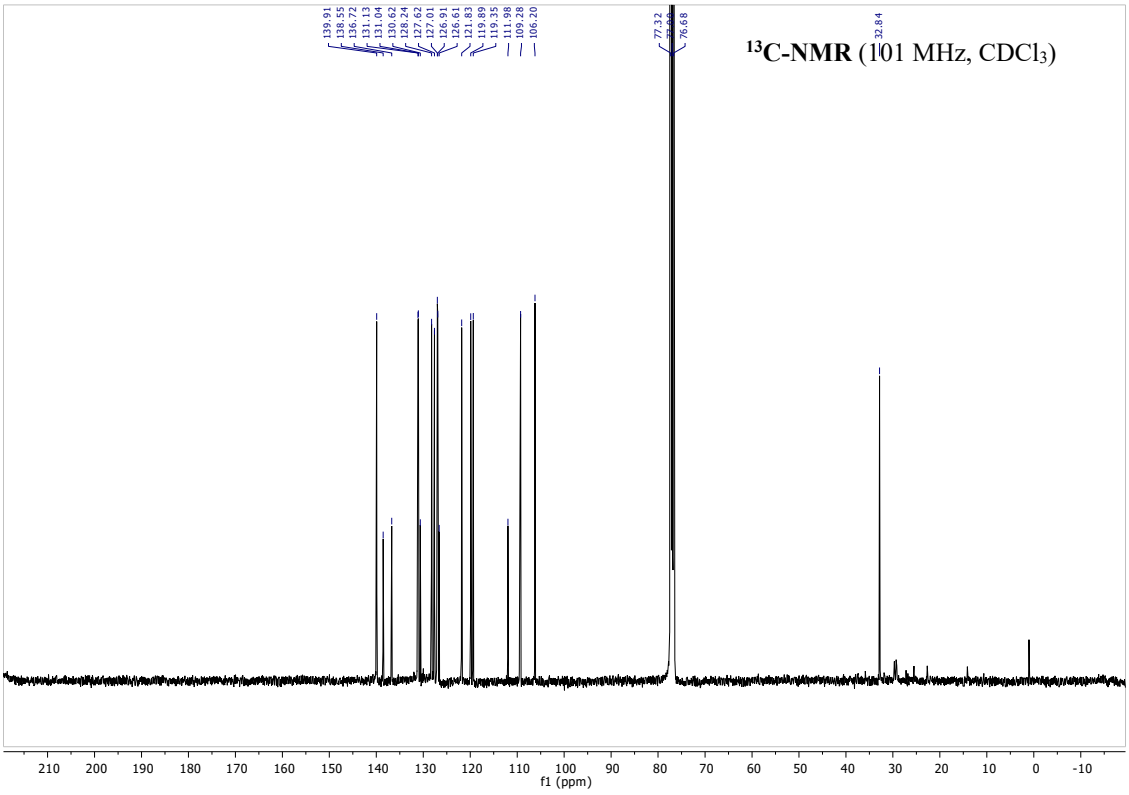
1-Methyl-3-(2-(pyrimidin-2-yl)phenyl)-1*H*-indole (20)



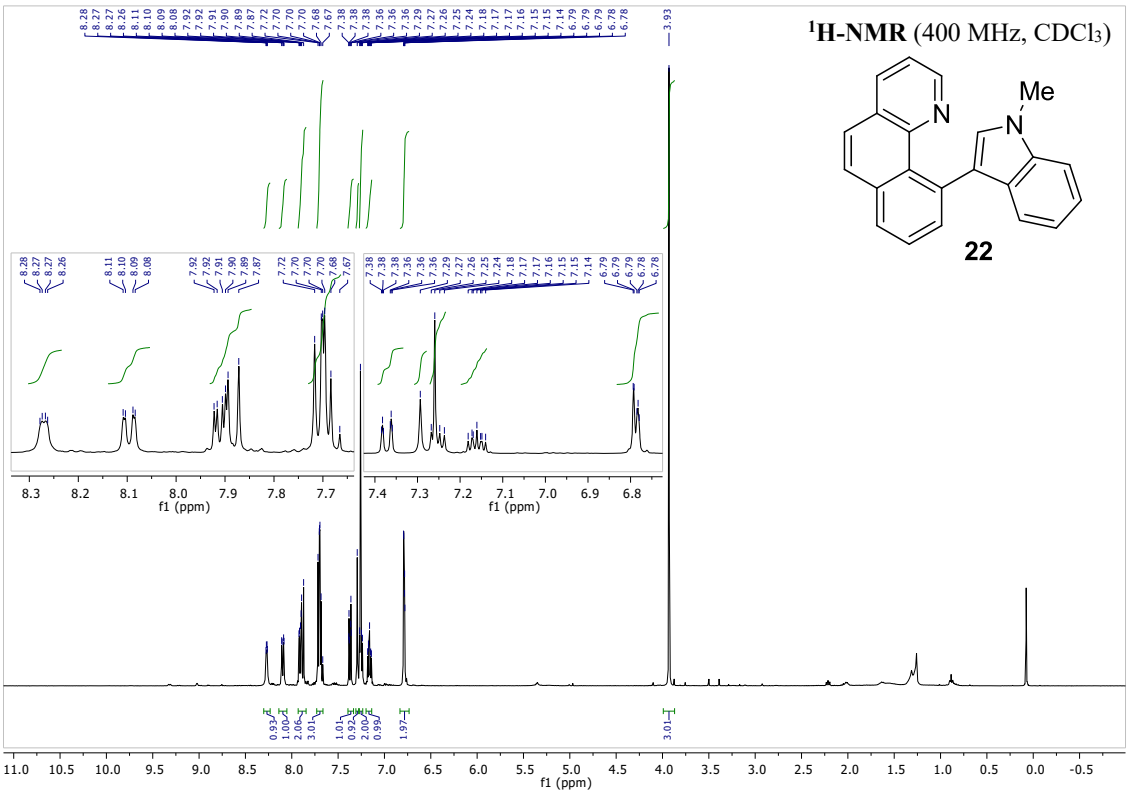


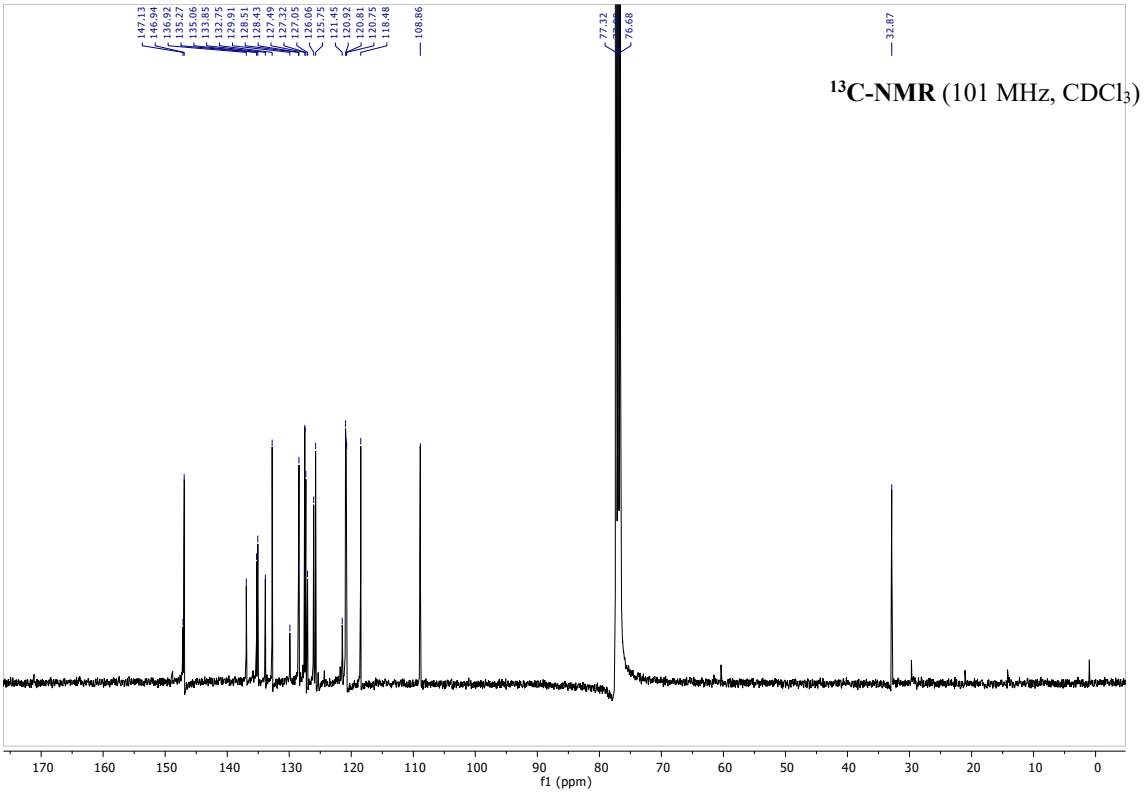
3-(2-(1H-Pyrazol-1-yl)phenyl)-1-methyl-1*H*-indole (21)



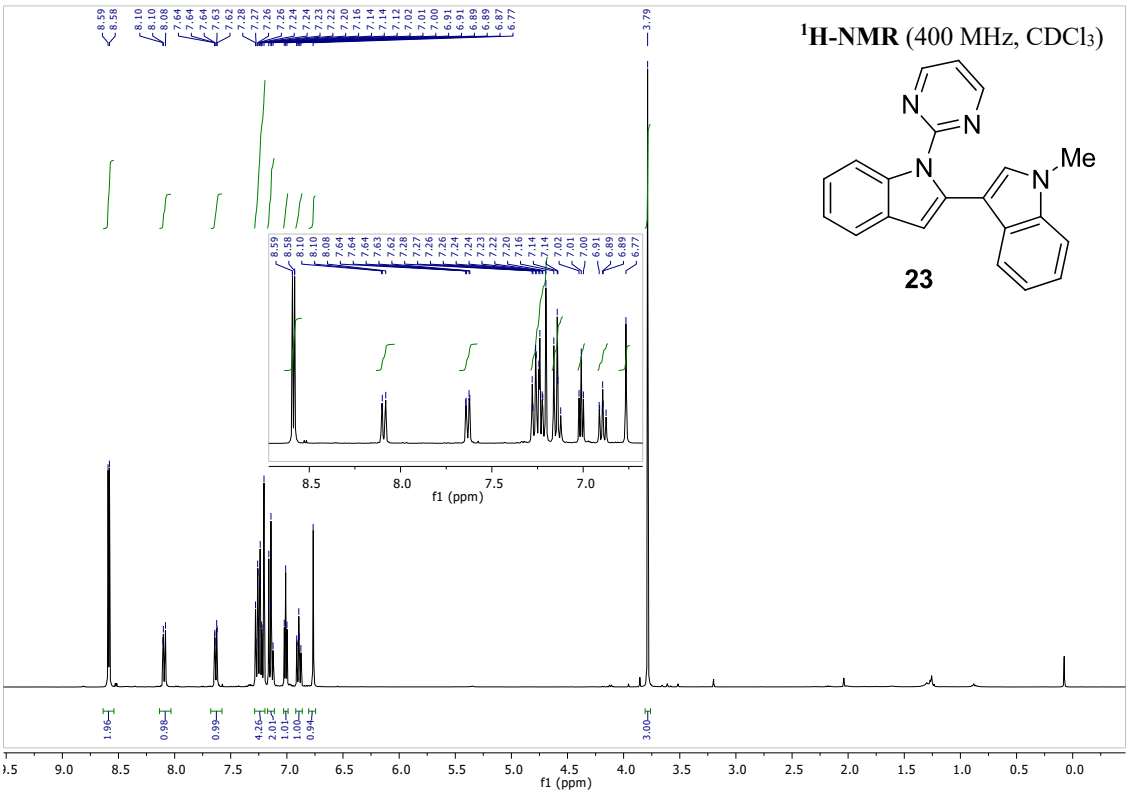


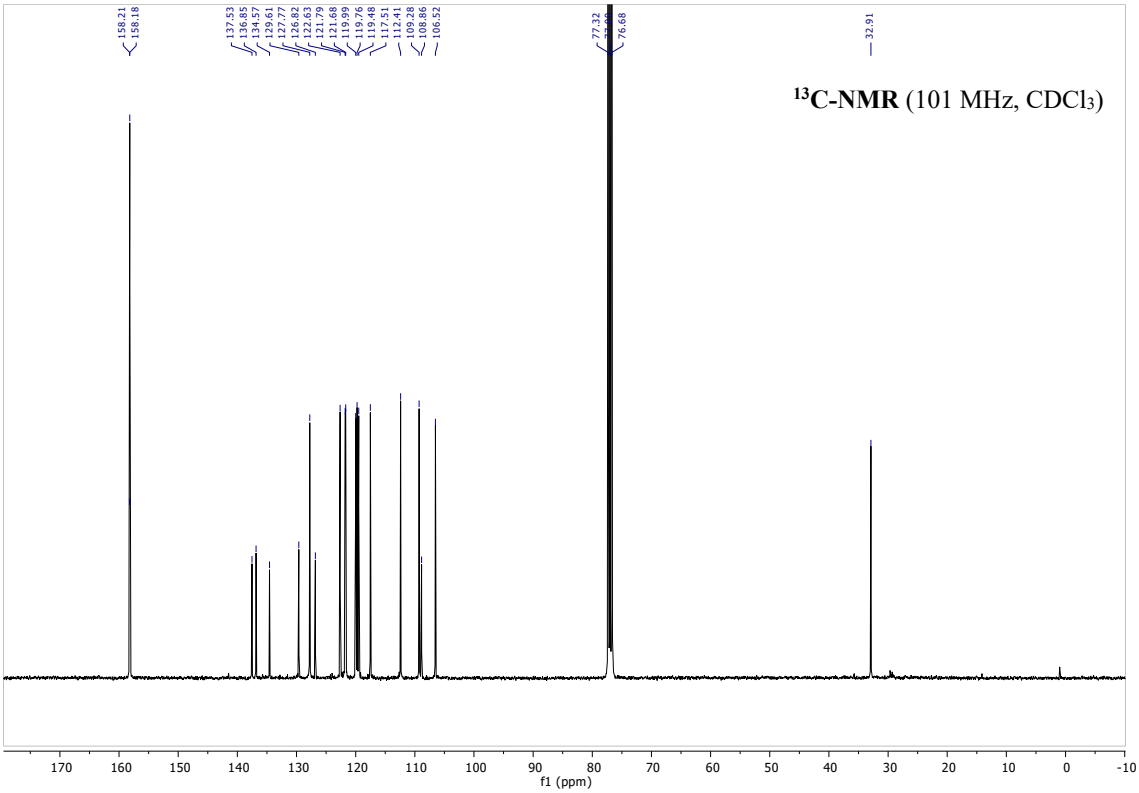
10-(1-Methyl-1*H*-indol-3-yl)benzo[h]quinoline (22)



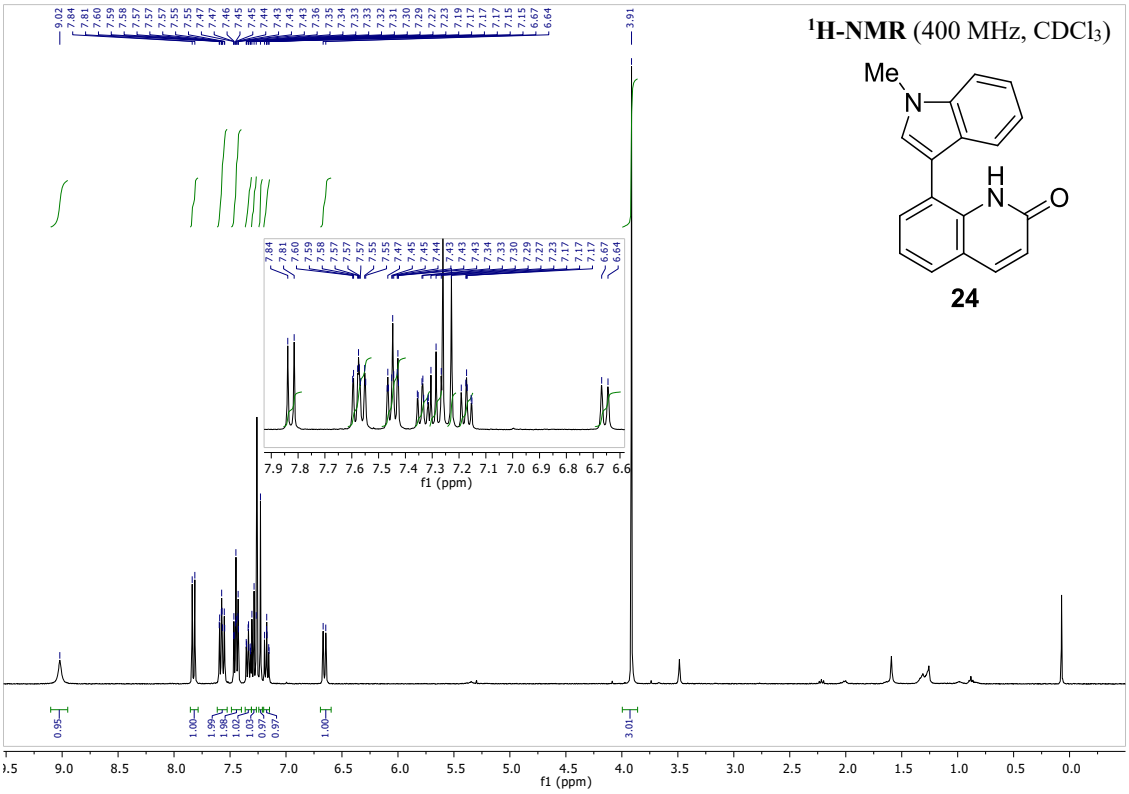


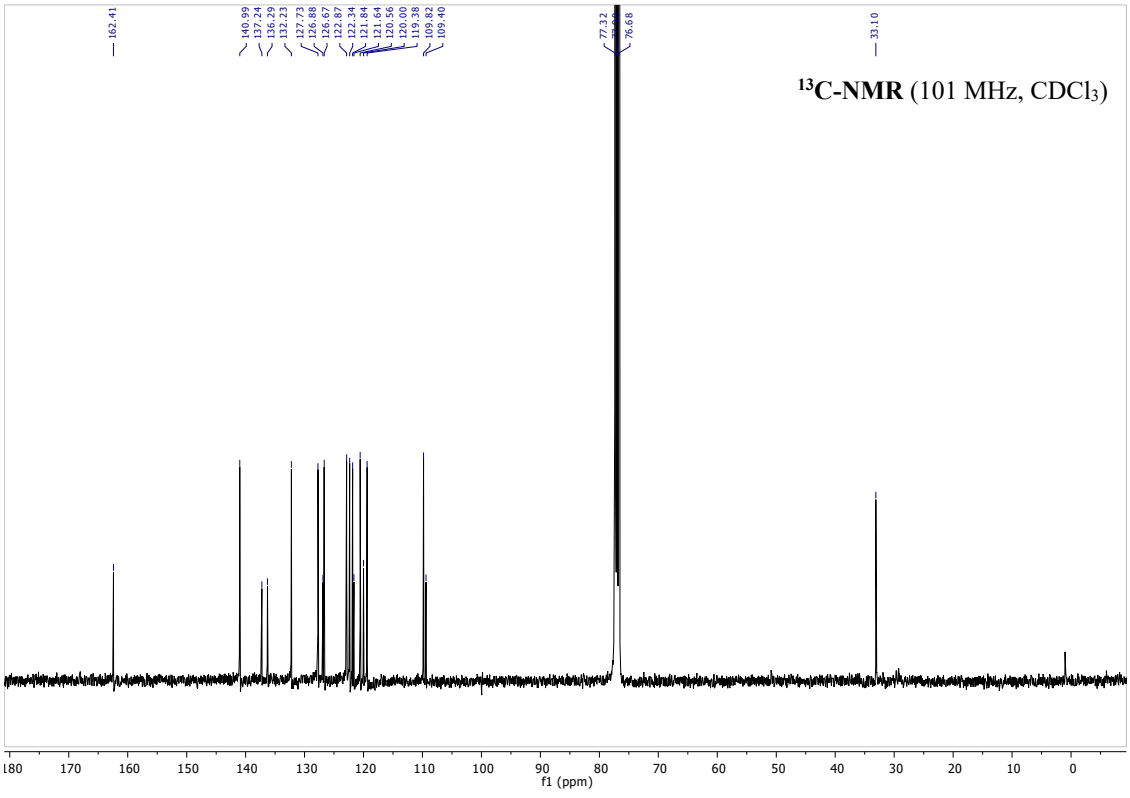
1'-Methyl-1-(pyrimidin-2-yl)-1*H*,1'*H*-2,3'-biindole (23)



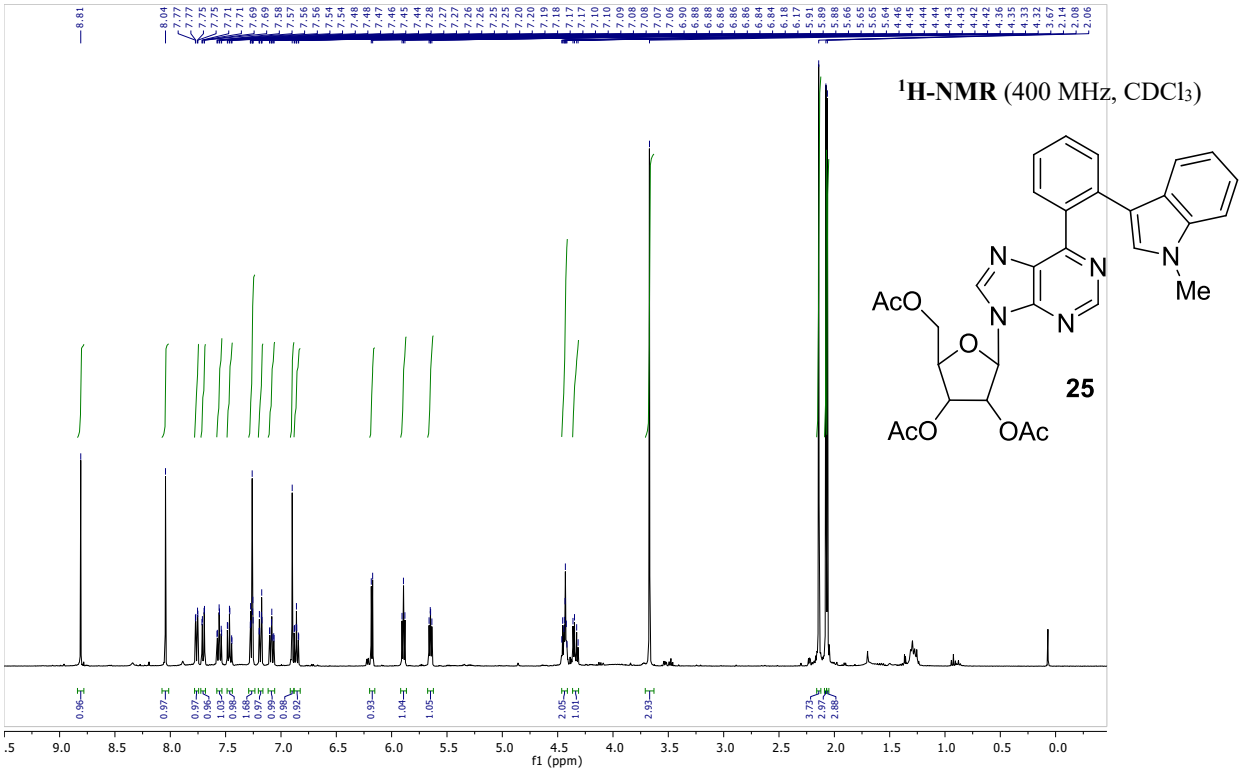


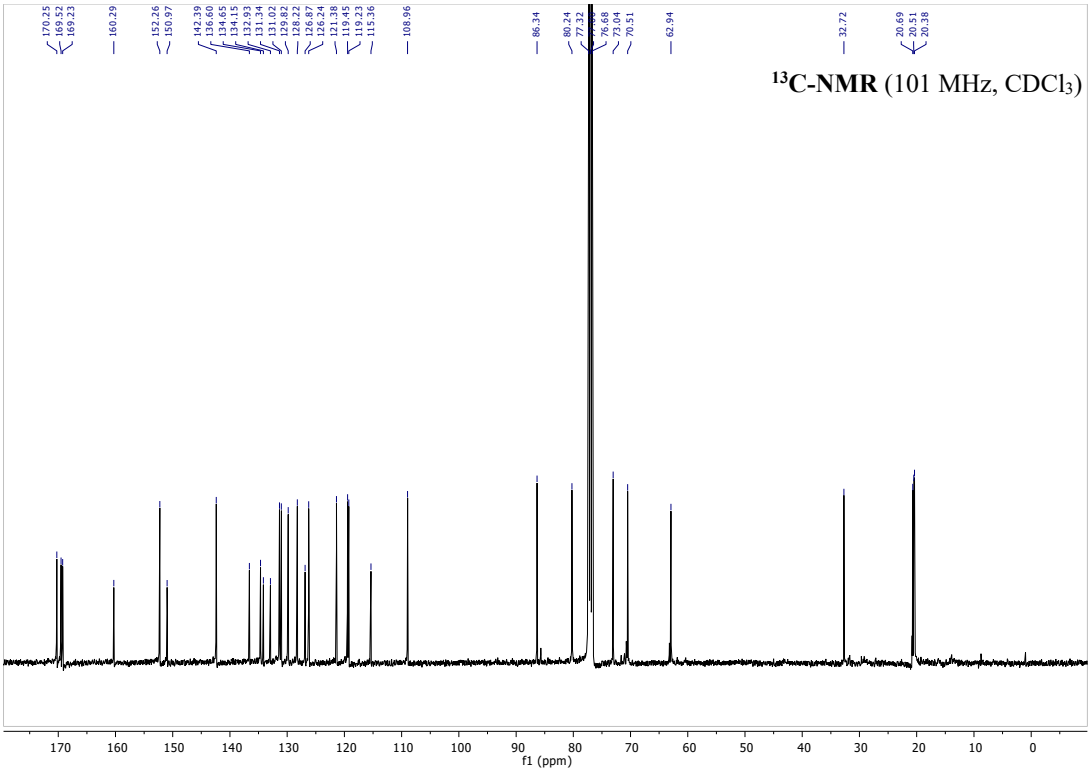
8-(1-Methyl-1*H*-indol-3-yl)quinolin-2(1*H*)-one (24)



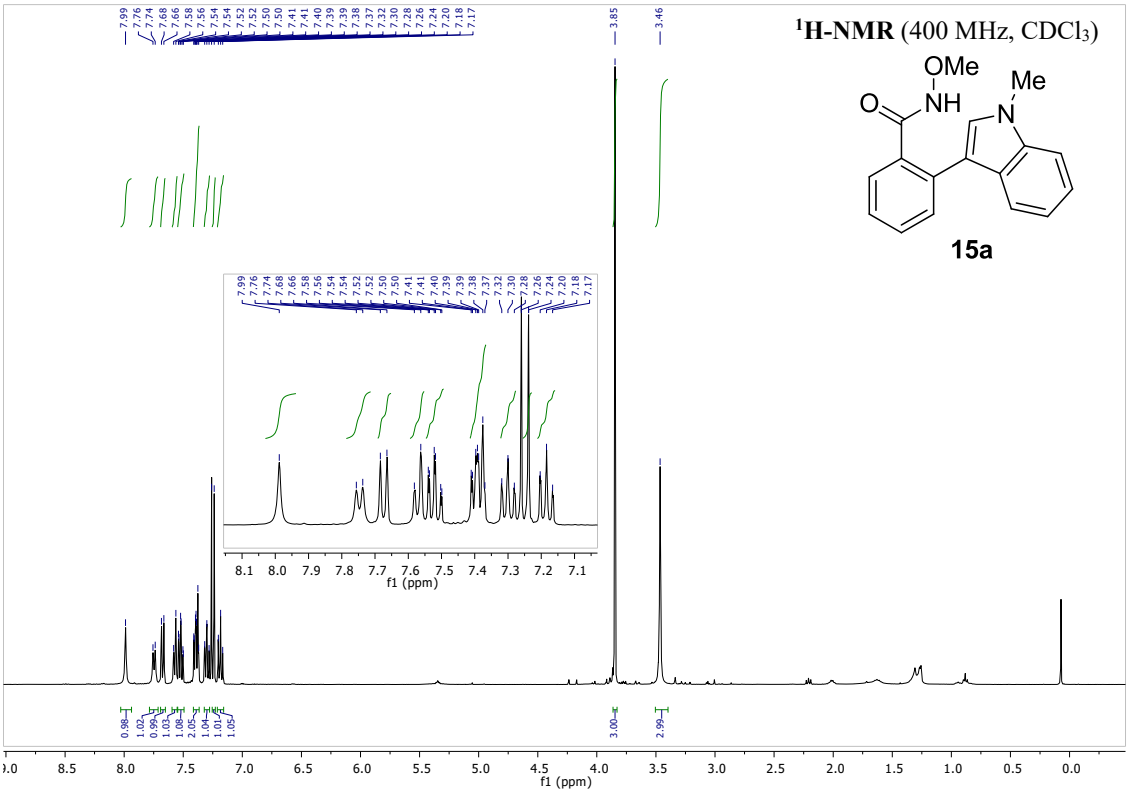


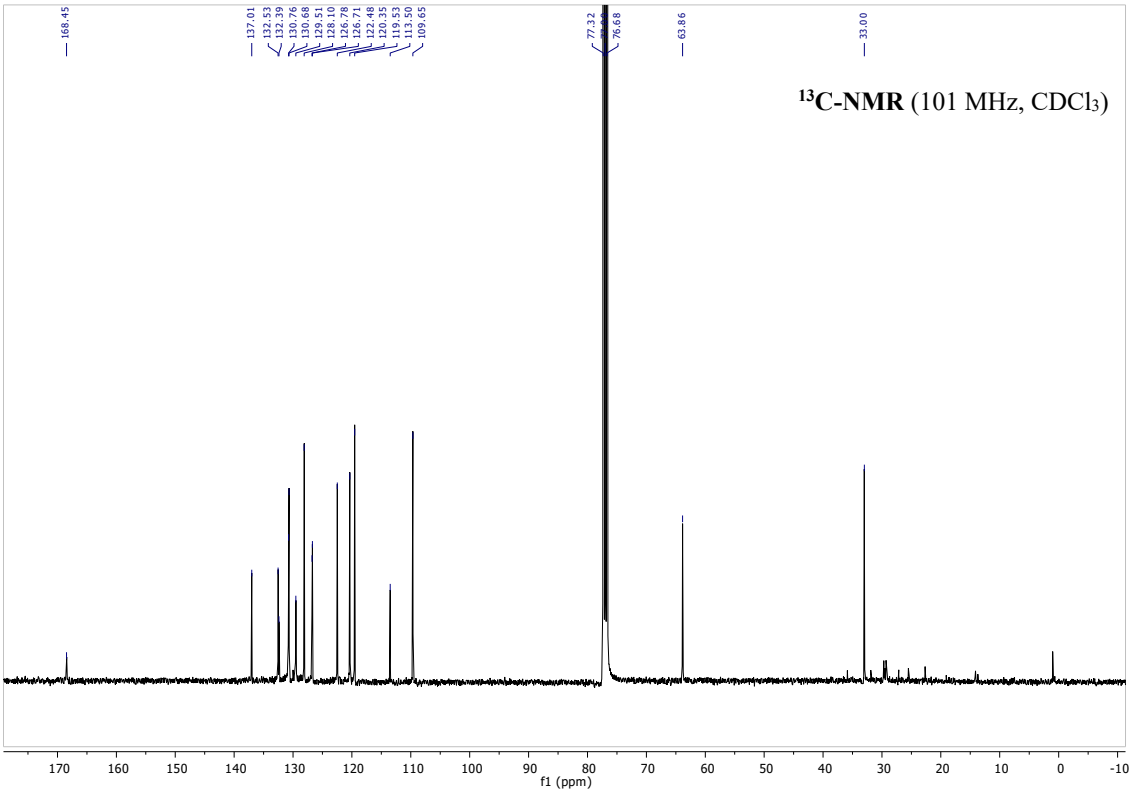
(2*R*,3*R*,4*R*,5*R*)-2-(Acetoxymethyl)-5-(6-(2-(1-methyl-1*H*-indol-3-yl)phenyl)-9*H*-purin-9-yl)tetrahydrofuran-3,4-diyl diacetate (25)



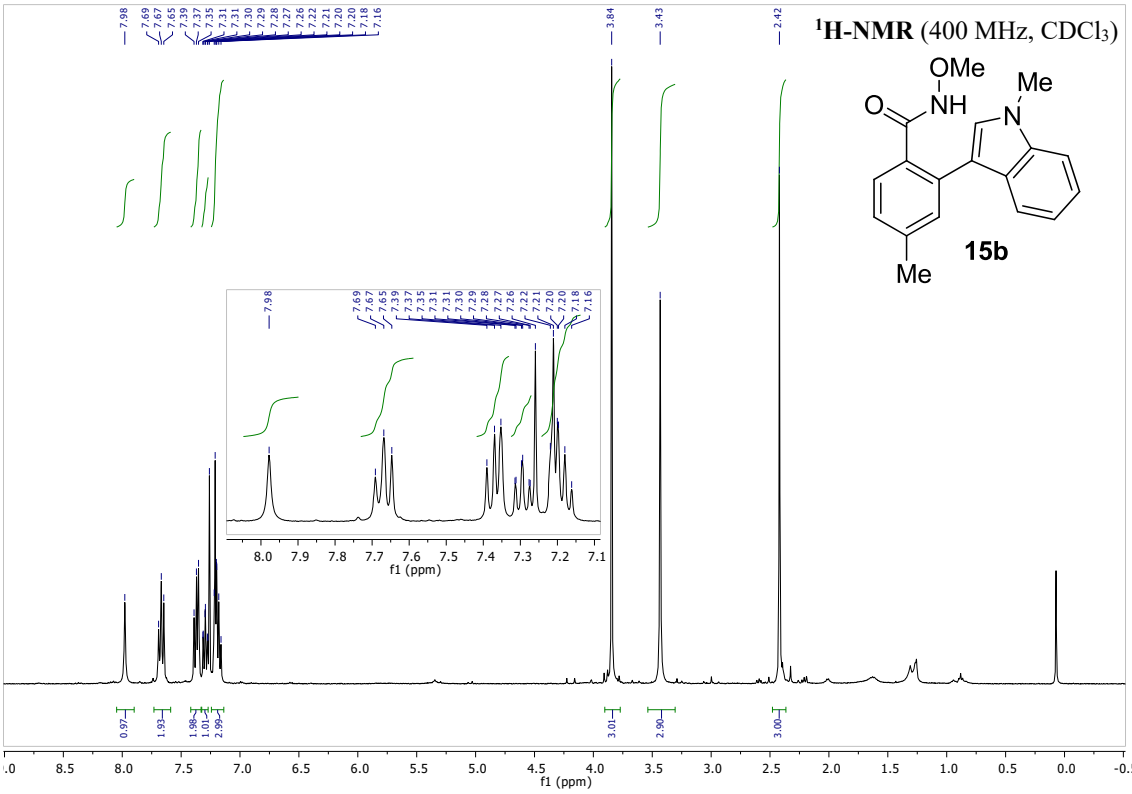


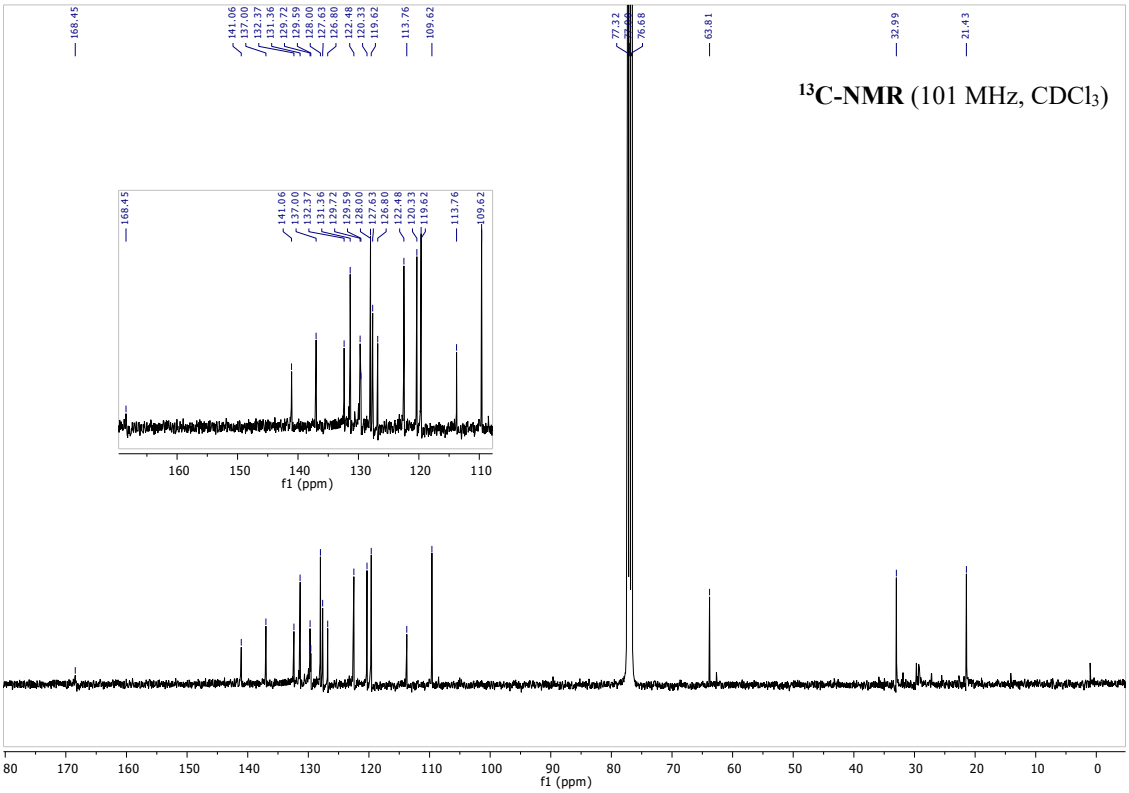
N-Methoxy-2-(1-methyl-1*H*-indol-3-yl)benzamide (15a)



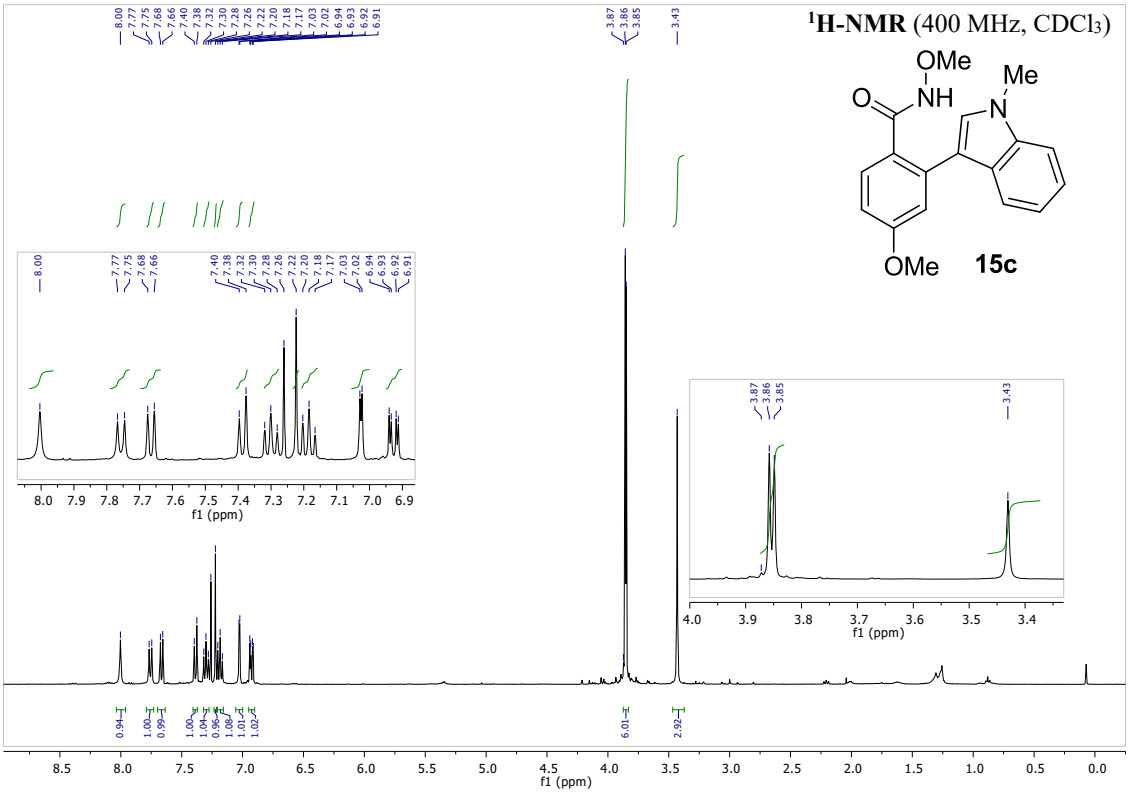


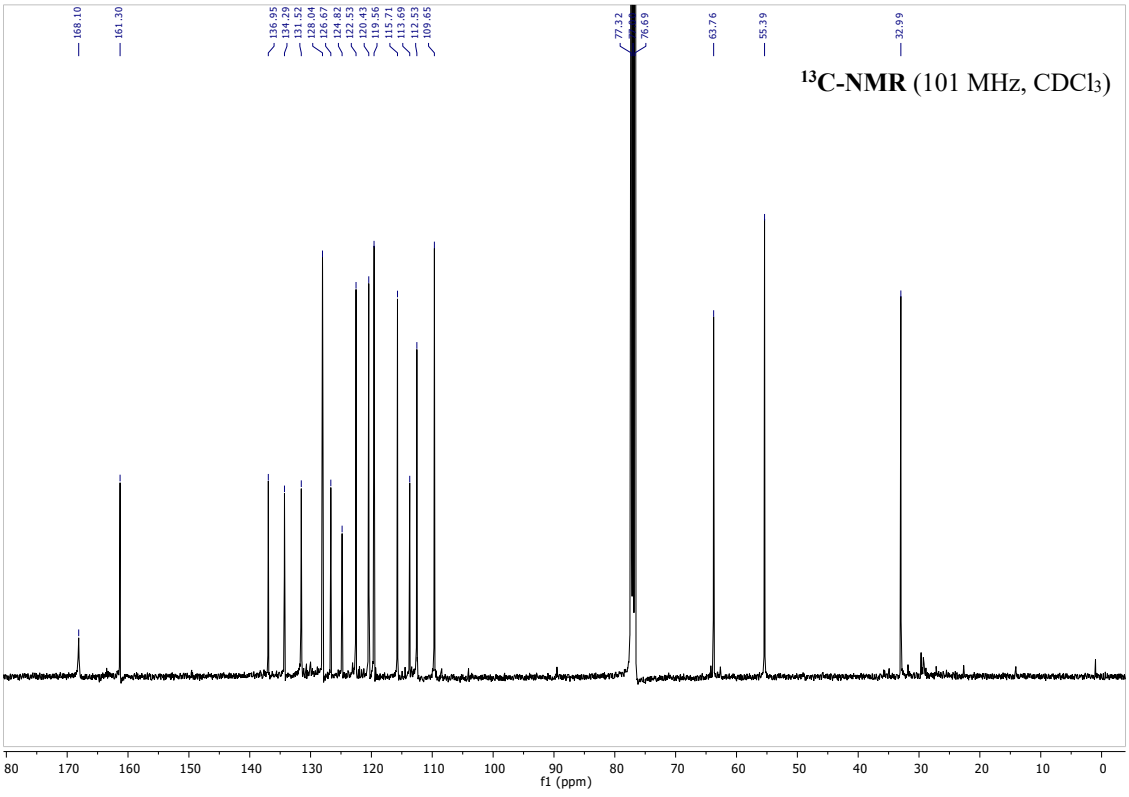
N-Methoxy-4-methyl-2-(1-methyl-1*H*-indol-3-yl)benzamide (15b)



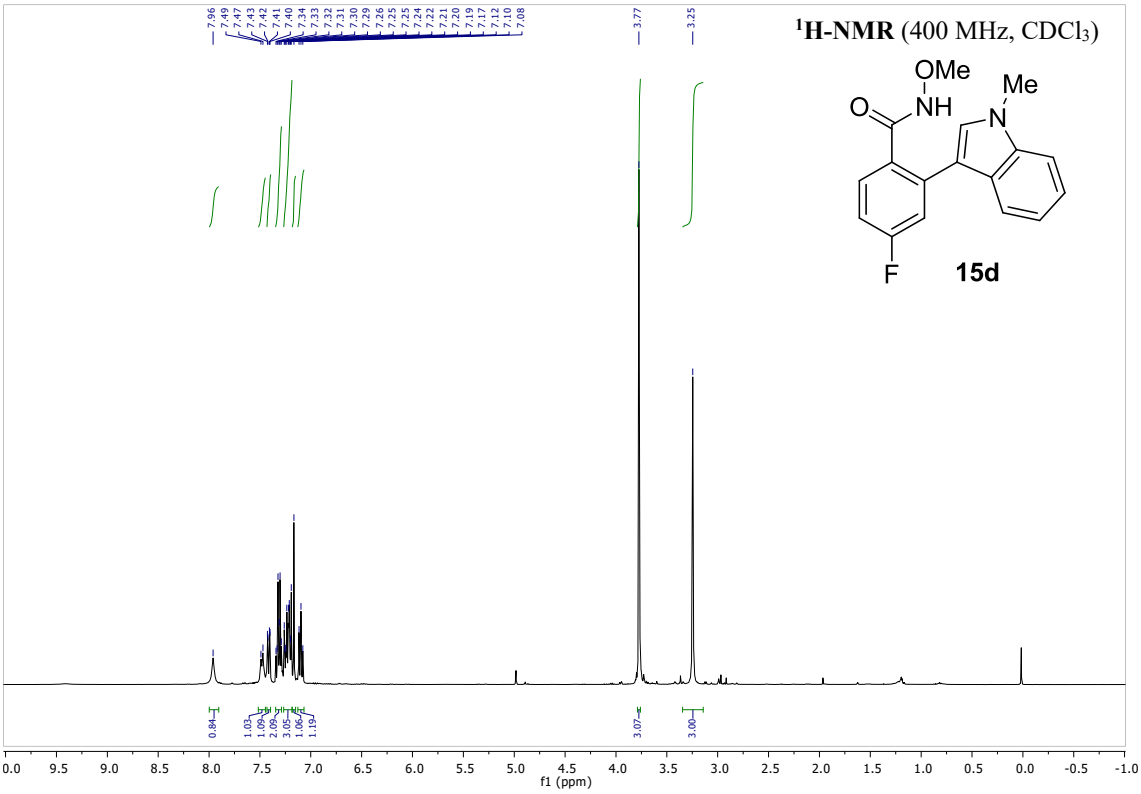


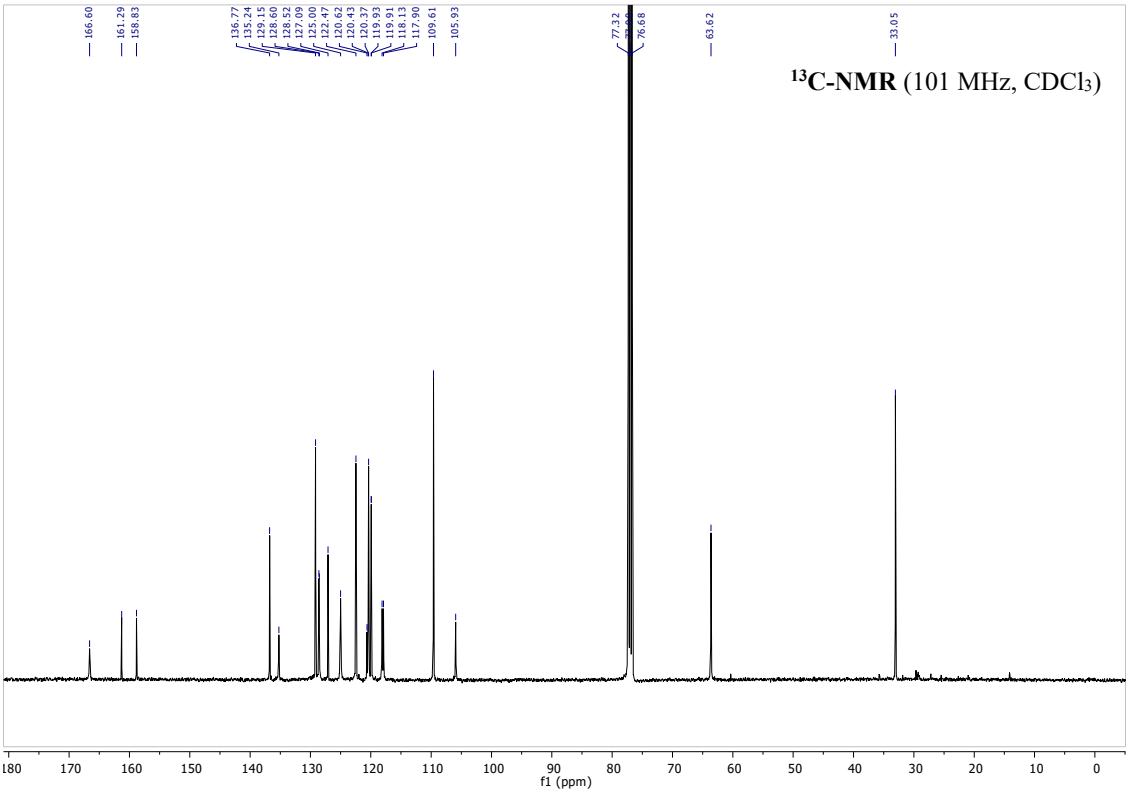
N,4-Dimethoxy-2-(1-methyl-1*H*-indol-3-yl)benzamide (15c)



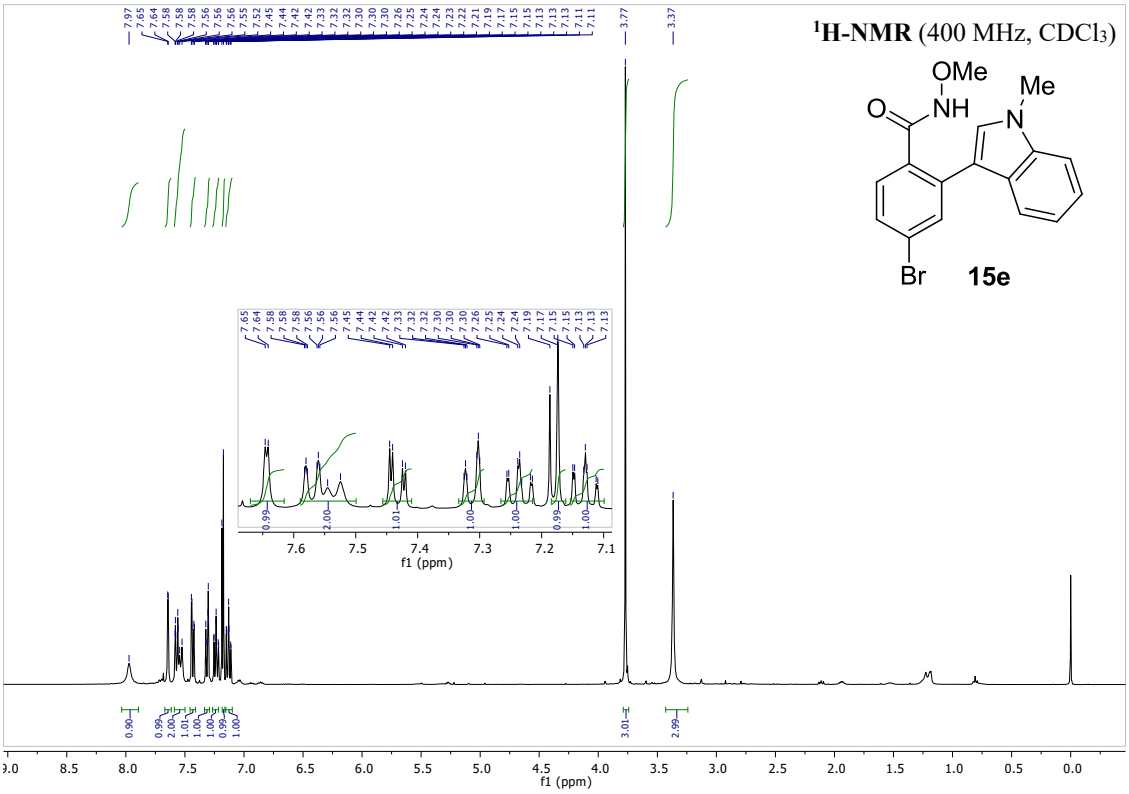


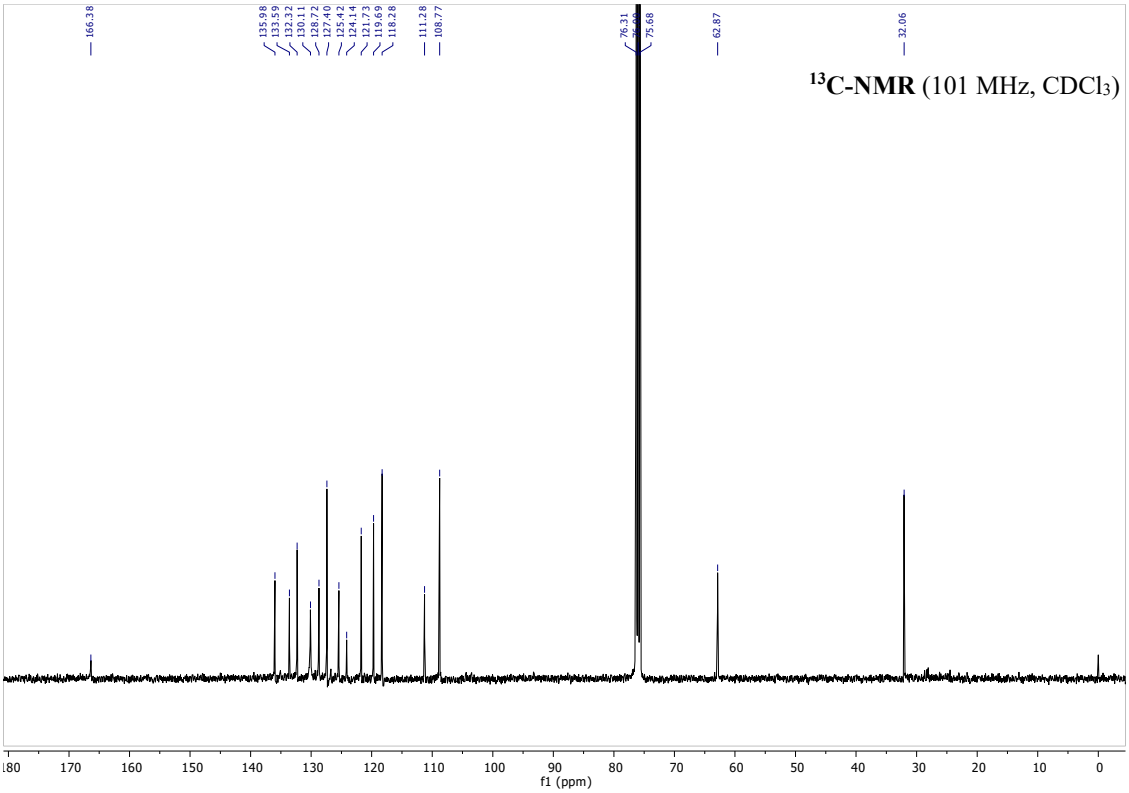
5-Fluoro-N-methoxy-2-(1-methyl-1*H*-indol-3-yl)benzamide (15d)



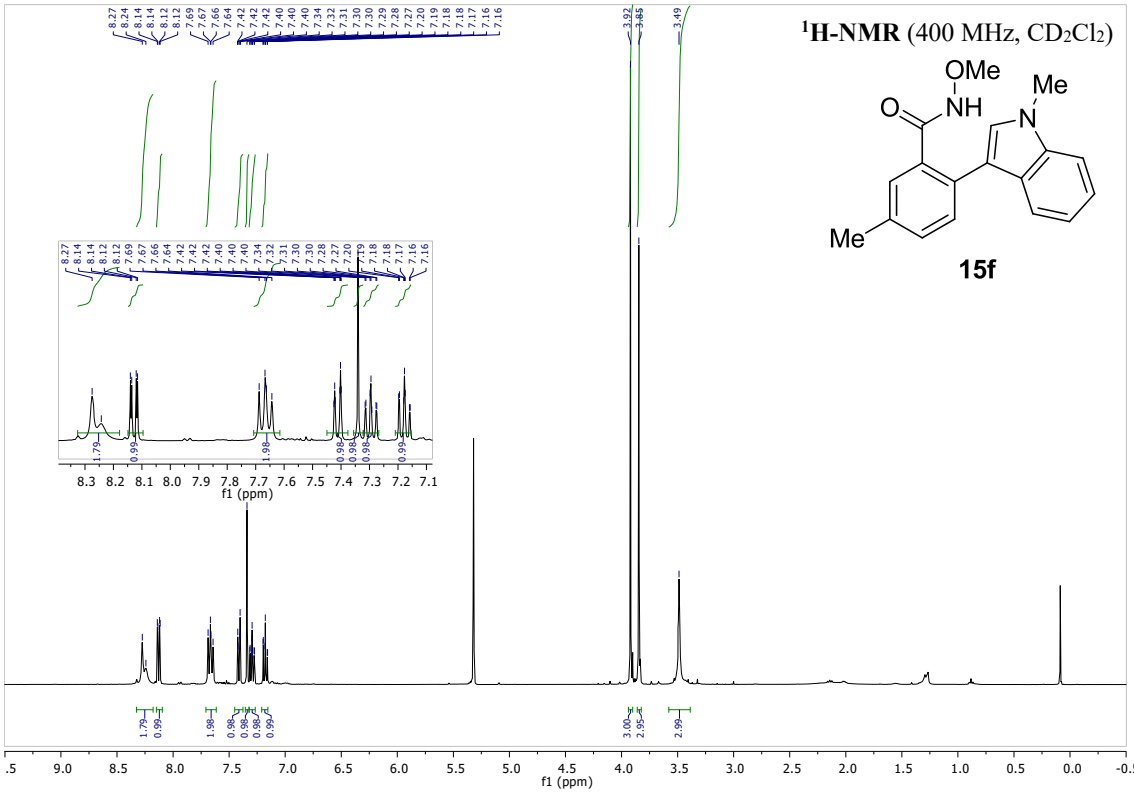


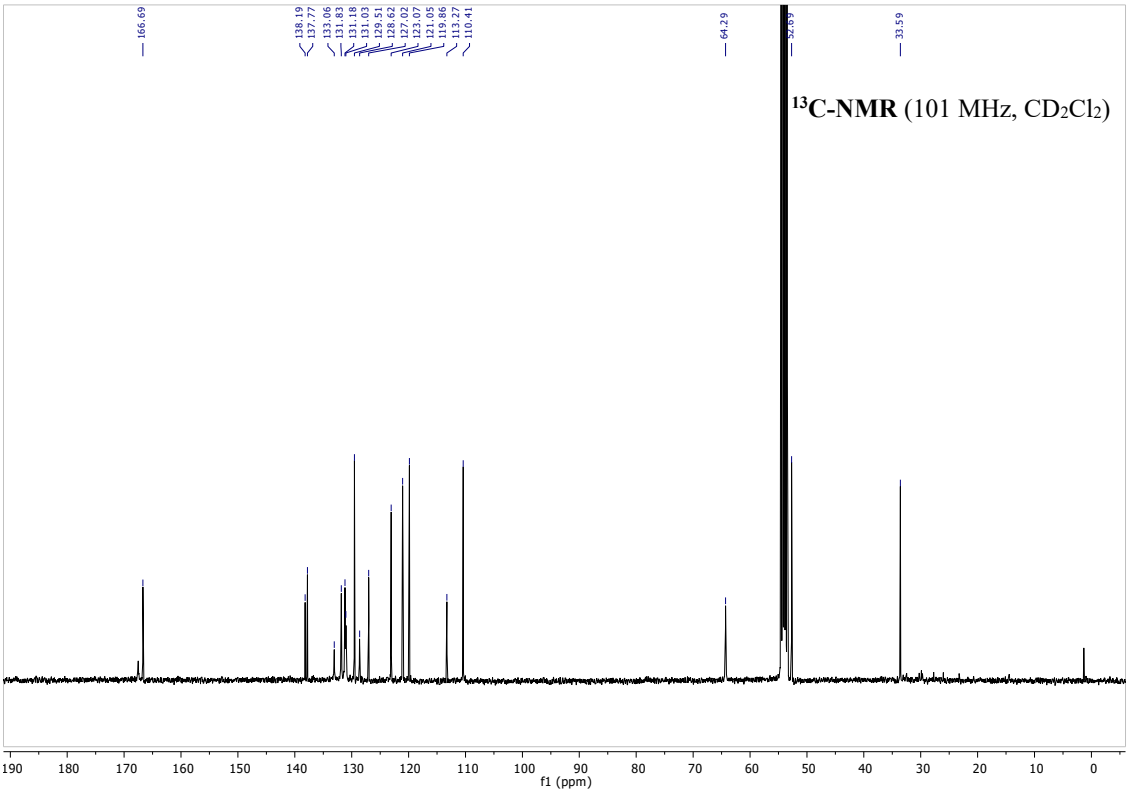
4-Bromo-N-methoxy-2-(1-methyl-1*H*-indol-3-yl)benzamide (15e)



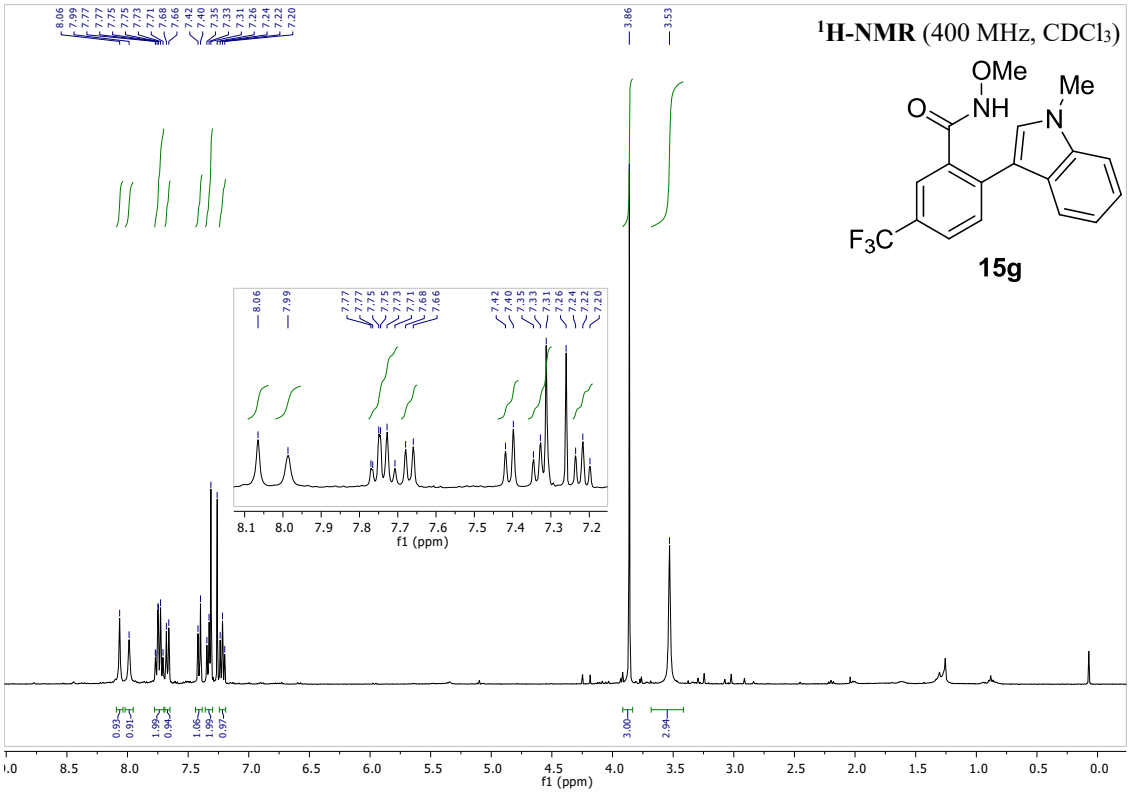


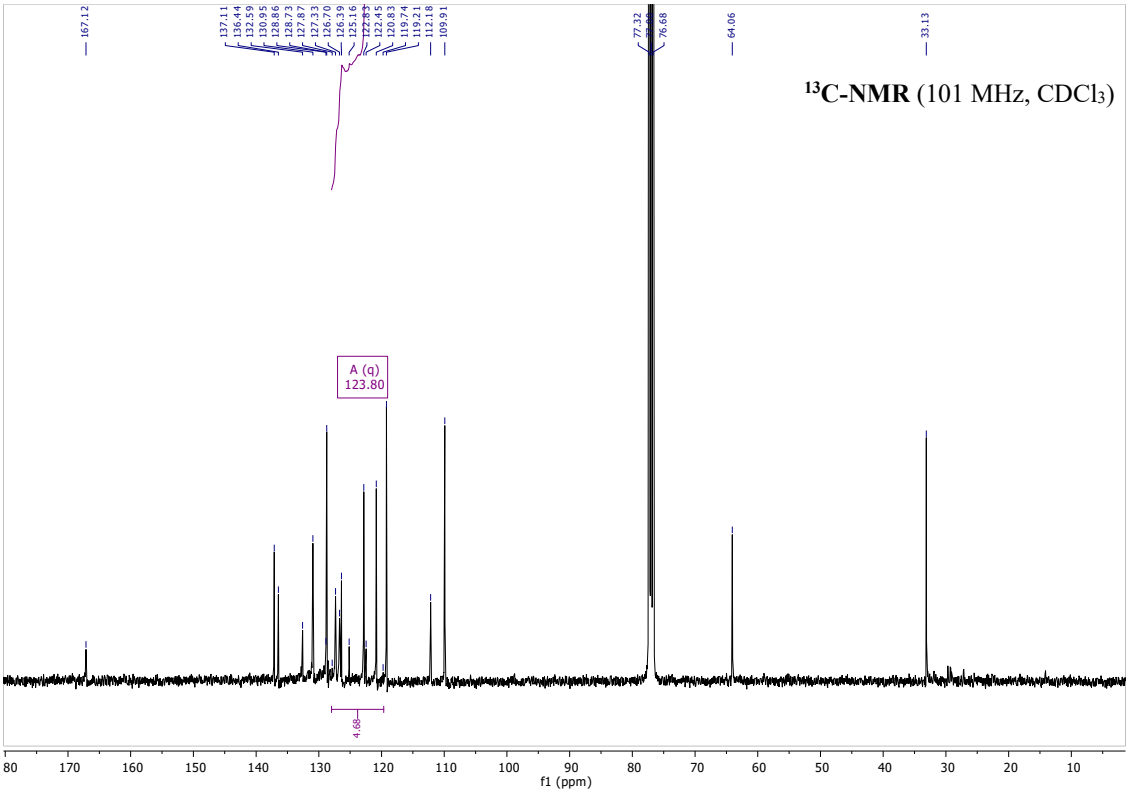
N-Methoxy-5-methyl-2-(1-methyl-1*H*-indol-3-yl)benzamide (15f)



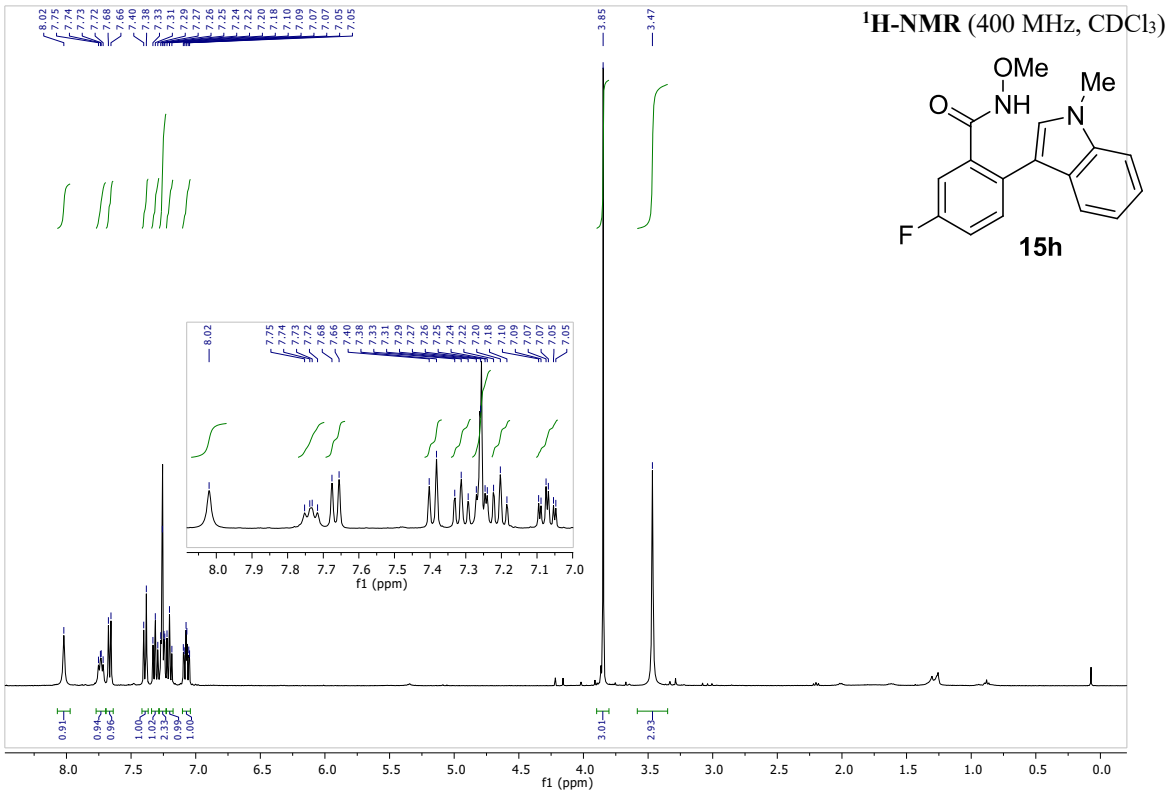


N-Methoxy-2-(1-methyl-1*H*-indol-3-yl)-5-(trifluoromethyl)benzamide (15g)

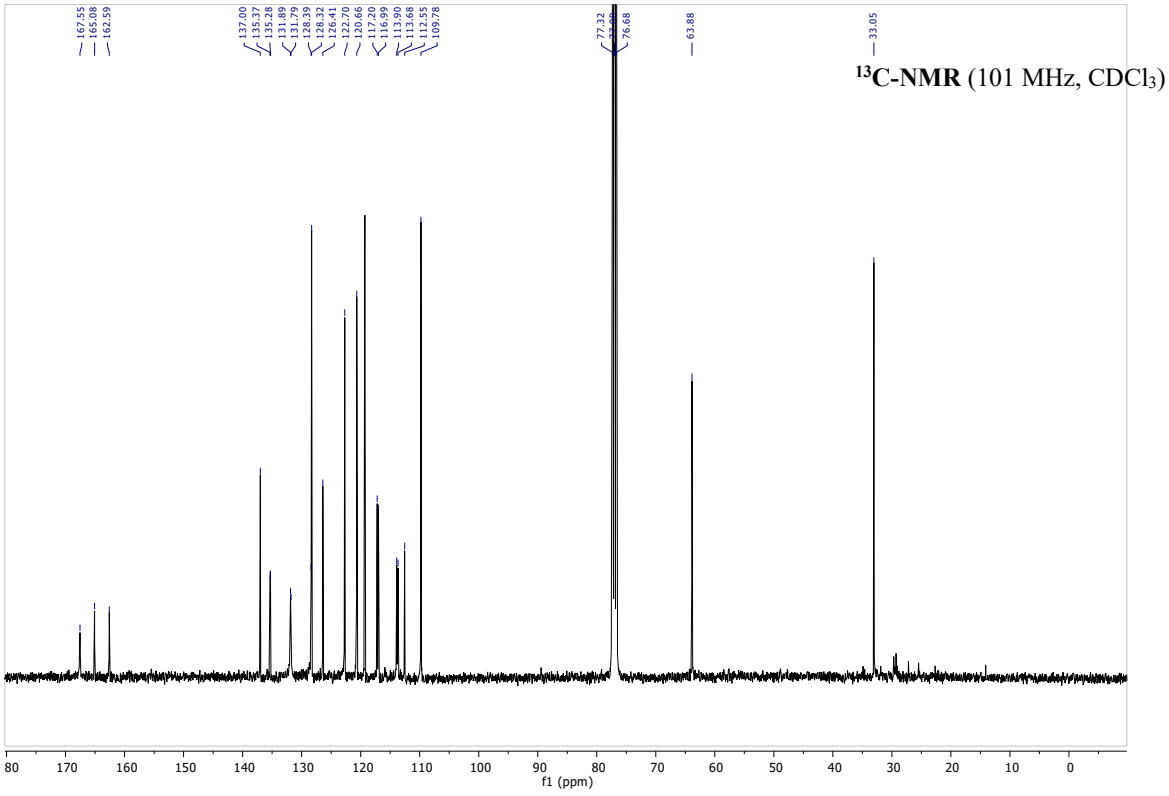




5-Fluoro-N-methoxy-2-(1-methyl-1*H*-indol-3-yl)benzamide (15h)

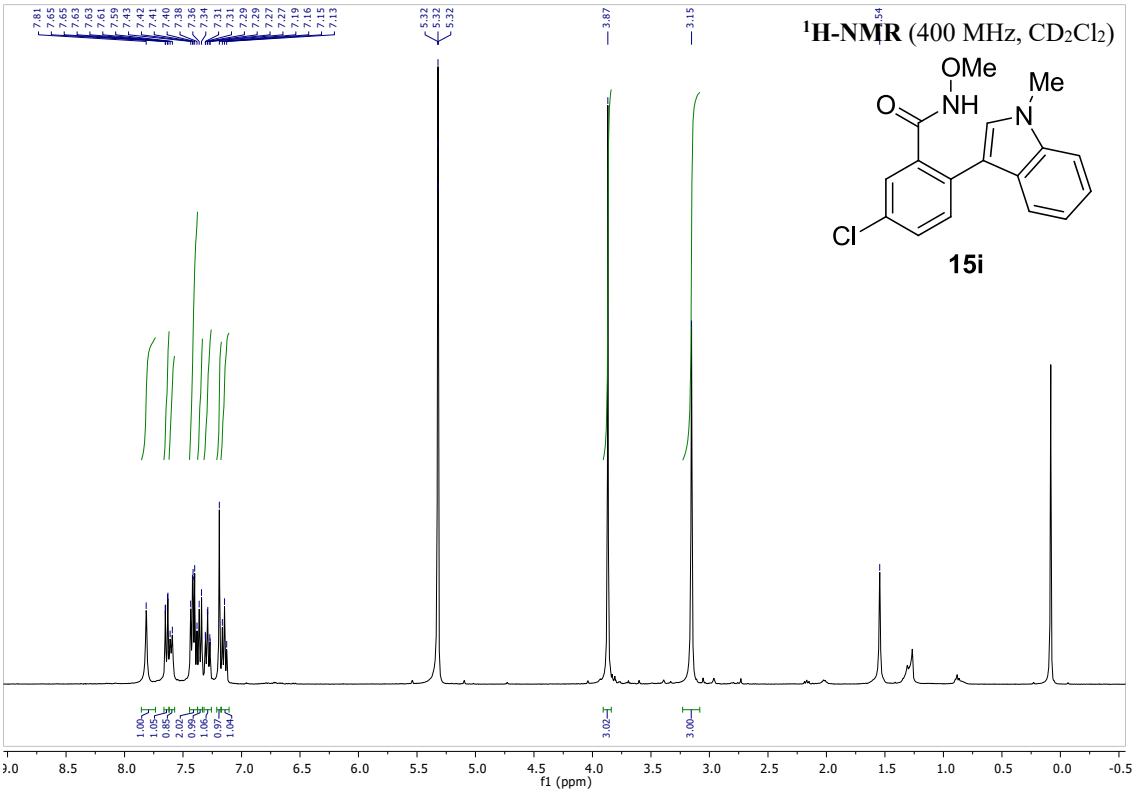


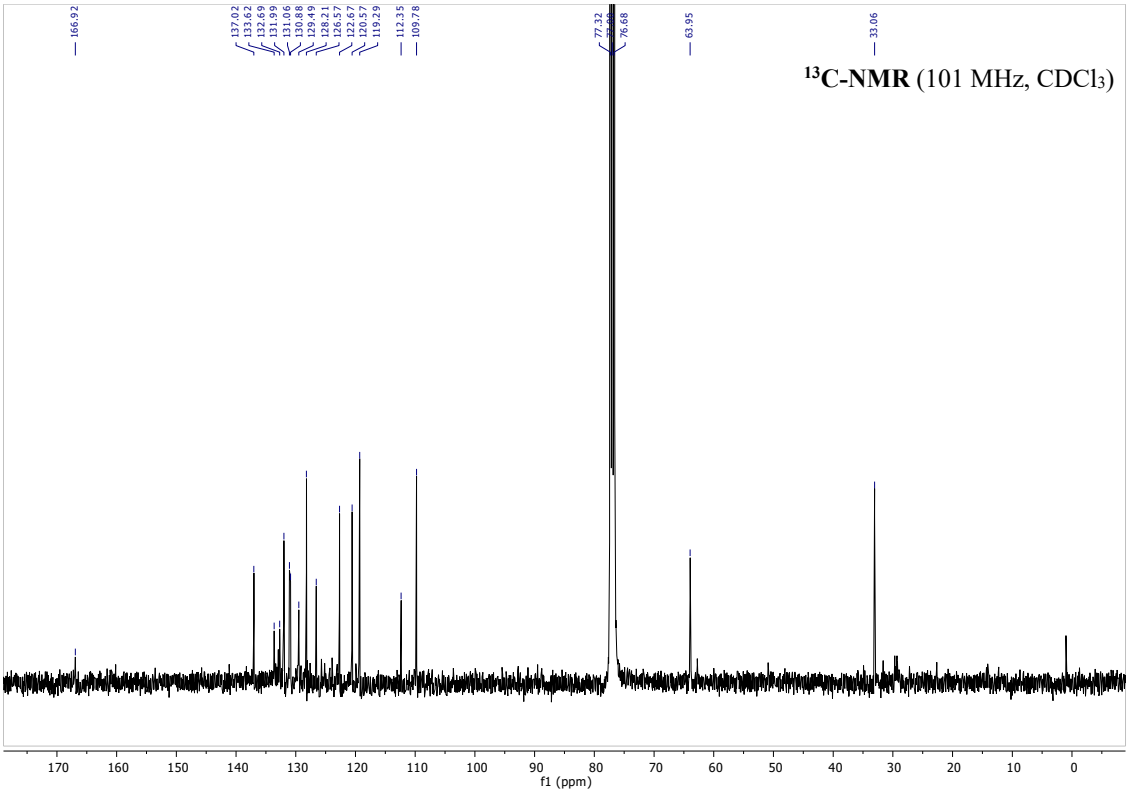
^{1}H-NMR (400 MHz, $CDCl_3$)



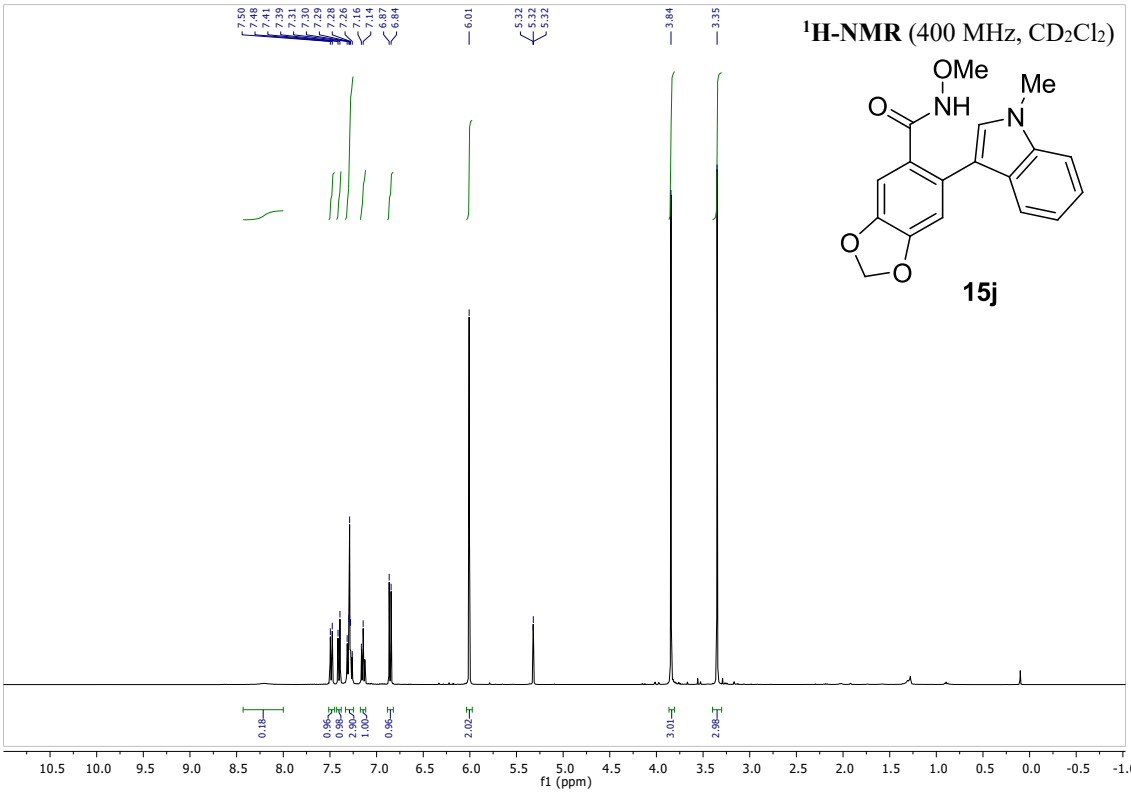
^{13}C-NMR (101 MHz, $CDCl_3$)

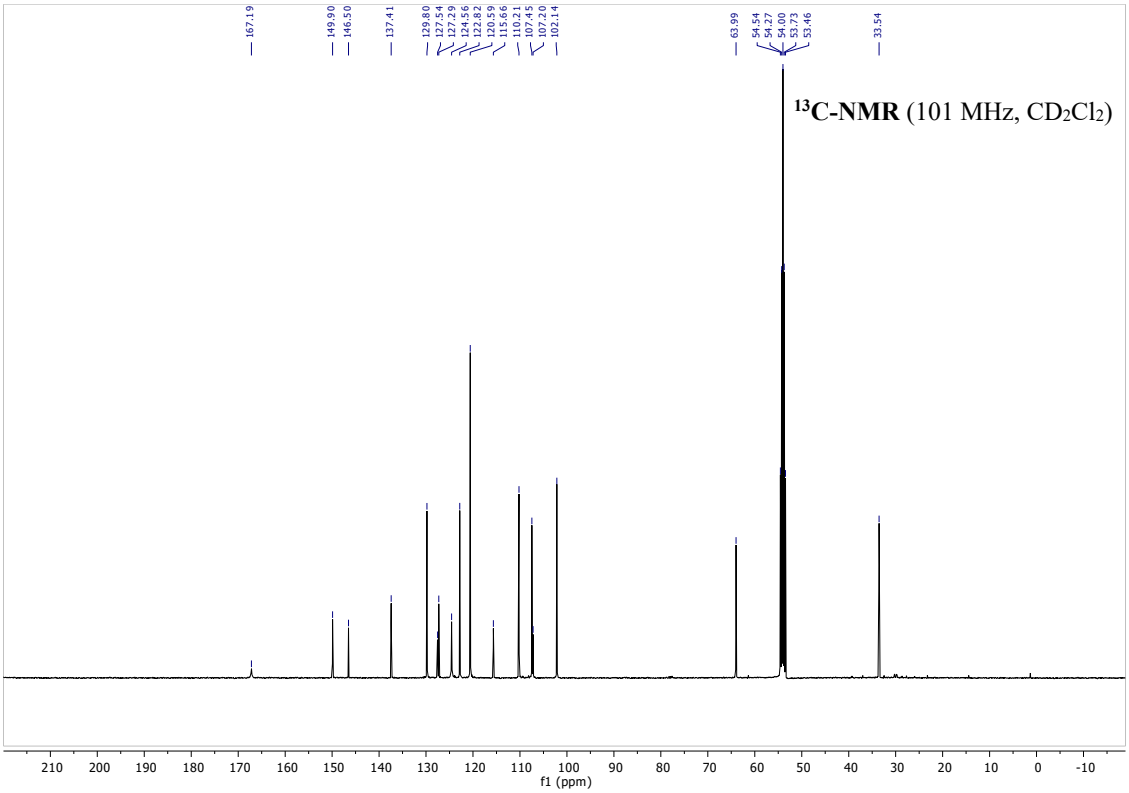
5-Chloro-*N*-methoxy-2-(1-methyl-1*H*-indol-3-yl)benzamide (15i)



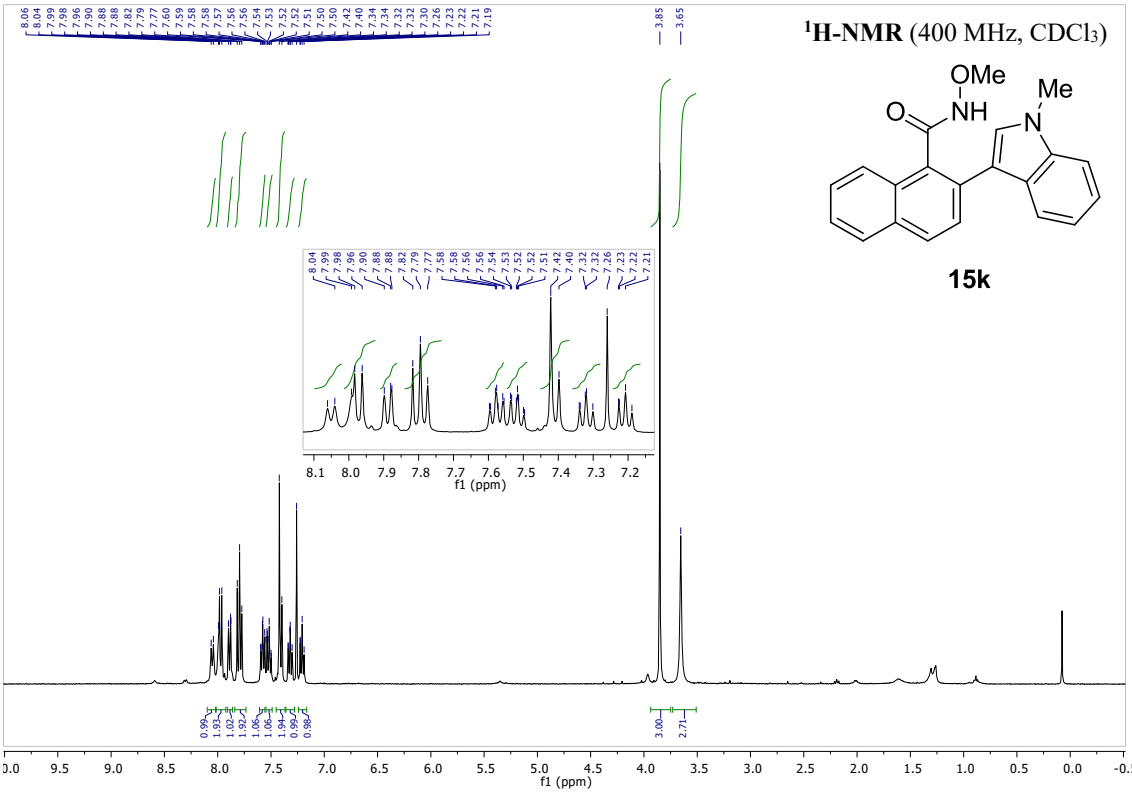


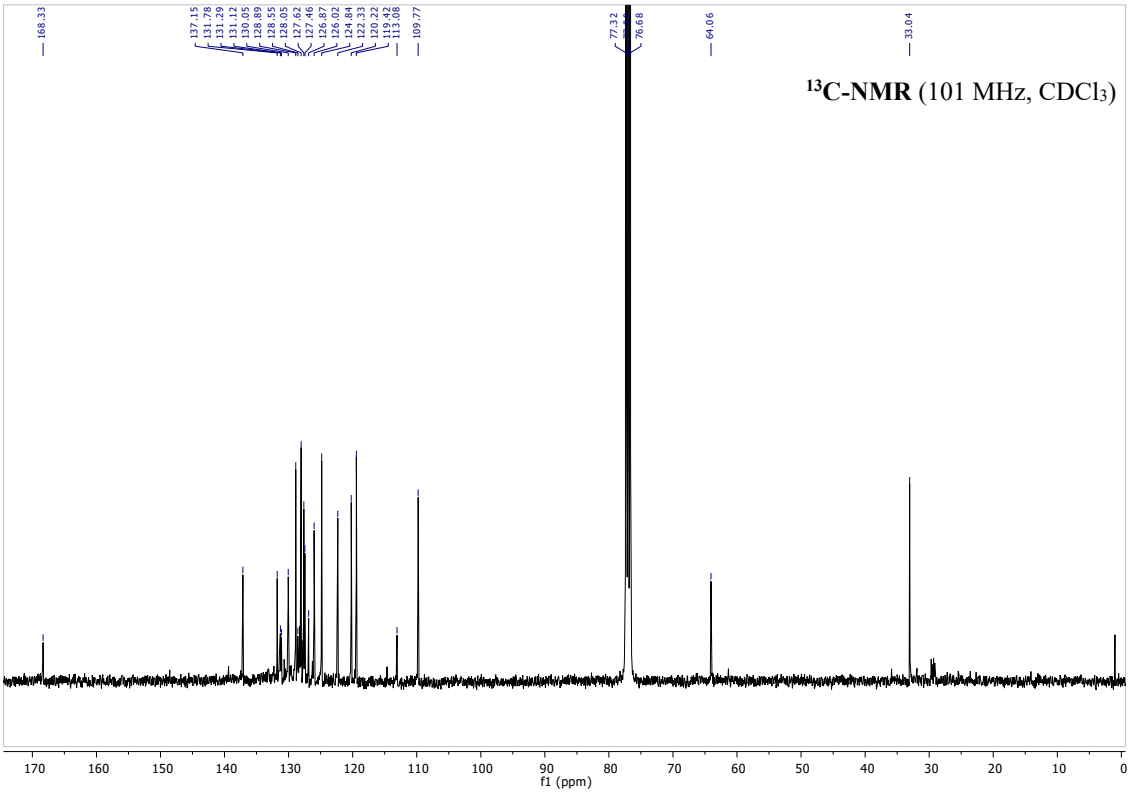
N-Methoxy-6-(1-methyl-1*H*-indol-3-yl)benzo[d][1,3]dioxole-5-carboxamide (15j)



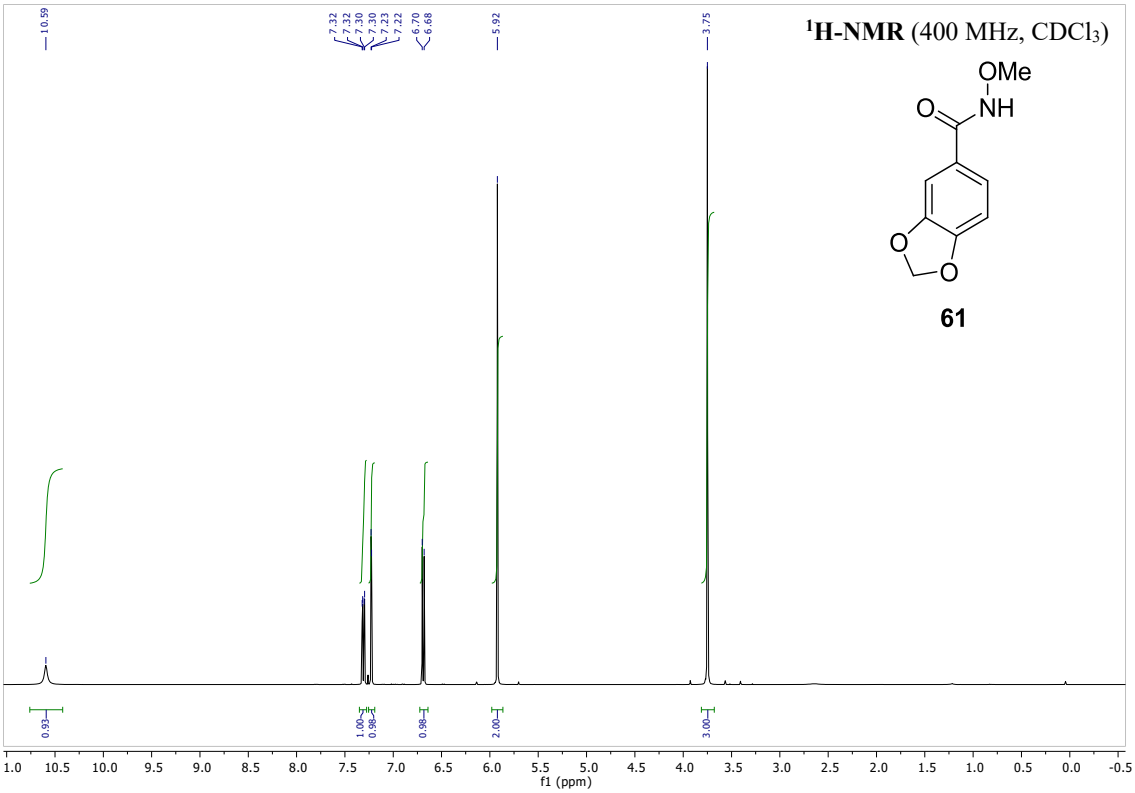


N-Methoxy-2-(1-methyl-1*H*-indol-3-yl)-1-naphthamide (15k)



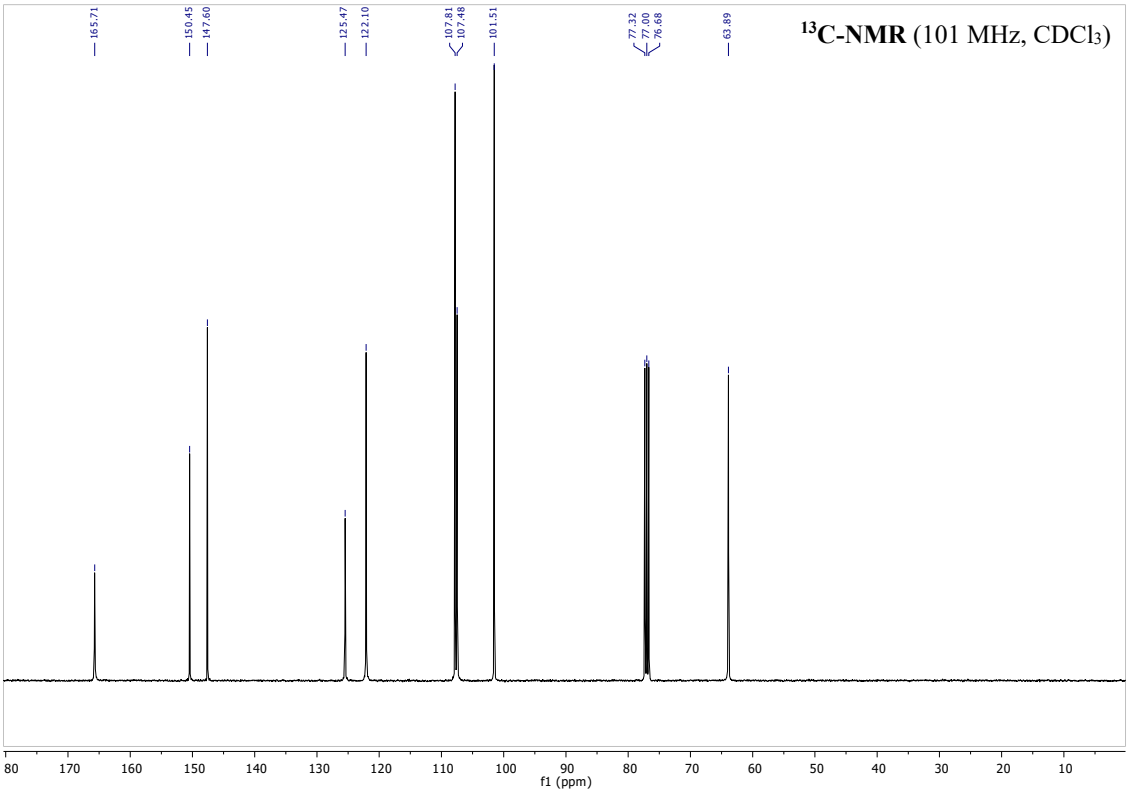


N-Methoxybenzo[d][1,3]dioxole-5-carboxamide (61)



^{1}H-NMR (400 MHz, $CDCl_3$)

61



^{13}C-NMR (101 MHz, $CDCl_3$)