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Pd-Catalyzed Suzuki-Type Cross-Coupling of 2-Pyridyl Carbamoyl Fluorides

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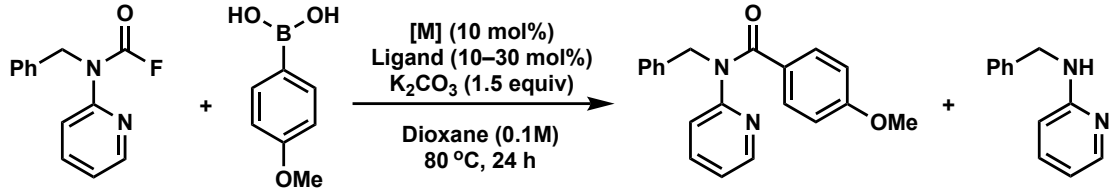
1 General Considerations

Commercial reagents were purchased from Acros-Organics, Alfa Aesar, Combi-Blocks, Fisher, Sigma-Aldrich, or TCI and used without further purification. Unless otherwise stated, all reactions were carried out under an inert atmosphere of nitrogen or argon using glassware that was oven- (175 °C) or flame-dried, whereas the work-up and isolation of the products were conducted on the benchtop using standard techniques. Solvents and solutions were transferred by a syringe or cannula. Anhydrous THF, toluene, DCM, MeCN and Et_2O were obtained from an MBraun MB-SPS 800 solvent drying system under a N_2 atmosphere and stored in a Strauss flask. The remaining anhydrous solvents were purchased directly from Milipore- Sigma (sure-seal bottle). Boronic acids were purchased from Combi-Blocks and used directly without further purification. Reactions were monitored by thin layer chromatography (TLC) using SiliaPlate glass-backed silica gel plates (hard layer) with F254 indicator. Visualization was accomplished using 250 nm UV light, followed by immersion in $KMnO_4$ stain. Unless otherwise stated, flash chromatography was performed using SiliaFlash P60 40−63 μm (230−400 mesh) 60 Å irregular silica gel. NMR characterization data were collected at 296 K on a Bruker 700 MHz spectrometer, Bruker DRX 600 MHz spectrometer, Bruker ARX 400 MHz spectrometer, or Bruker ARX 300 MHz spectrometer. For samples in $CDCl_3$, ^1H NMR spectra were internally referenced to the residual solvent signal (7.26 ppm) or TMS (0 ppm) and ^{13}C NMR spectra were internally referenced to the residual solvent signal (77.16 ppm) and are reported as observed. Data for ^1H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = double of doublets, dt = doublet of triplets, b = broad), coupling constant (Hz), and integration. Infrared (IR) spectra were recorded using Alpha-Platinum ATR Bruker, diamond crystal. High-resolution mass spectrometry (HRMS) spectra were recorded using Thermo Fisher Orbitrap Elite or JEOL AccuTOF Plus 4G mass spectrometers. NMR yields were obtained by analysis of the crude reaction mixtures by ^1H NMR spectroscopy using a 10 s relaxation delay and 1,3,5-trimethoxybenzene as the internal standard or by ^{19}F NMR spectroscopy using a 30 s relaxation delay and 2-fluoro-4-nitrotoluene as the internal standard.

2 General Procedure for Reaction Optimization

A 1 dram vial equipped with a stir bar was charged with *N*-Benzyl-*N*-(2-pyridyl)carbamoyl fluoride **1a** (0.023 g, 0.10 mmol, 1.0 equiv), 4-methoxyboronic acid **2a** (0.023 – 0.030 g, 0.15 – 0.20 mmol, 1.5 – 2.0 equiv), K_2CO_3 (0.020 – 0.027 g, 0.15 – 0.20 mmol, 1.5 – 2.0 equiv), and the metal complex (0.010 mmol, 10 mol%). The vial was evacuated and backfilled with N_2 (3x) and the indicated solvent (0.1 M, 1.0 mL) was added. The reaction was sealed with a Teflon-lined screwcap, submerged into an 80 °C oil bath and heated for 24 h. After cooling to RT, the reaction mixture was diluted with EtOAc or DCM, filtered through celite and concentrated under reduced pressure. A known amount of 1,3,5-trimethoxybenzene as an internal standard was added and the crude material was dissolved in $CDCl_3$ for quantitative ^1H NMR analysis.

Table S1. Catalyst Screen

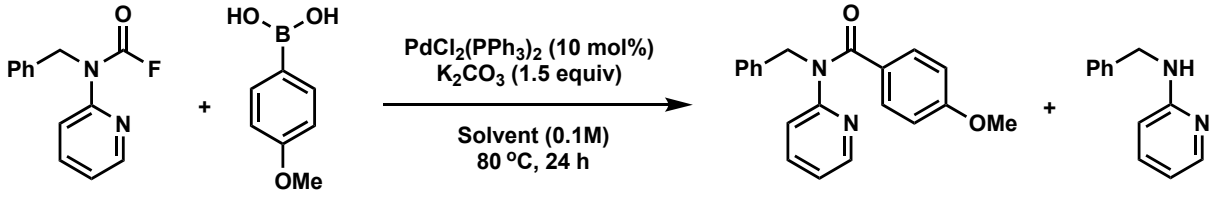


1a 2a, (1.5 equiv) 3a 4a

Catalyst	Ligand	Conversion of 1a (%)[a]	3a yield (%)[a]	4a yield (%)[a]
$Ni(COD)_2$	1,10-phenanthroline (10 mol%)	93	27	55
$Ni(COD)_2$	PPh_3 (20 mol%)	95	21	64
$Ni(COD)_2$	dtbbpy[b] (10 mol%)	92	30	51
$Ni(COD)_2$	BINAP[c] (10 mol%)	81	20	26
$Pd(OAc)_2$	PPh_3 (30 mol %)	84	13	28
Pd_2dba_3[d]	PPh_3 (30 mol%)	97	43	27
$Pd(PPh_3)_4$	-	97	10	72
$PdCl_2(PPh_3)_2$	**-**	**97**	**77**	**7**
$Pd(dppf)Cl_2$	-	96	28	16

[a]Conversions and yields acquired by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard; [b]dtbbpy = 4,4′-Di-tert-butyl-2,2′-dipyridyl. [c]BINAP = 2,2′-Bis(diphenylphosphino)-1,1′-binaphthalene [d]5 mol% of Pd_2dba_3.

Table S2. Solvent Screen



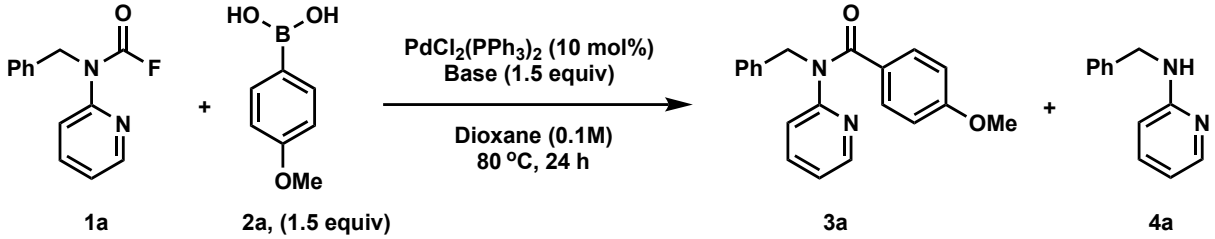
1a 2a, (1.5 equiv) 3a 4a

Solvent	Conversion of 1a (%)	3a yield (%)	4a yield (%)
THF	93	68	7
1,4-dioxane	**97**	**77**	**7**
DCE	100	72	13
1,4-dioxane/H_2O (4:1)	100	42	29

Toluene	98	34	18

Conversions and yields acquired by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.

Table S3. Base Screen

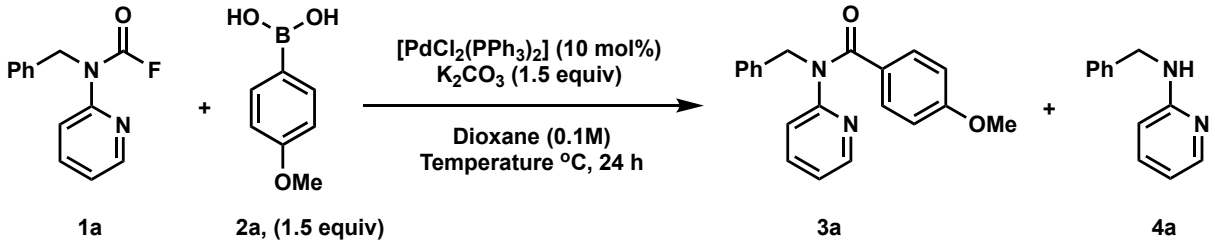


1a 2a, (1.5 equiv) 3a 4a

Base	Conversion of 1a (%)	3a yield (%)	4a yield (%)
K_2CO_3	**97**	**77**	**7**
K_3PO_4	85	60	8
KF	56	24	4
KOH	74	0	98
Na_2CO_3	76	4	4

Conversions and yields acquired by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.

Table S4. Temperature screen

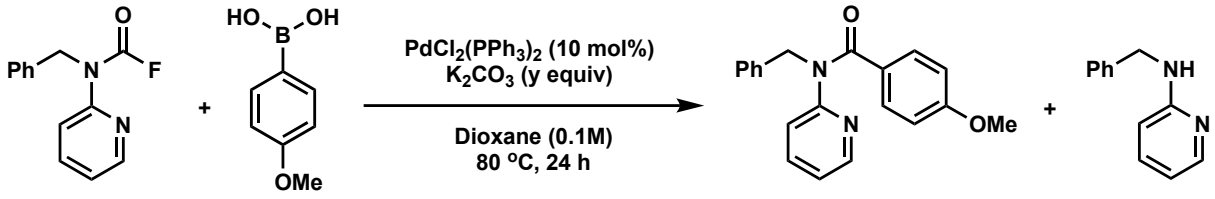


1a 2a, (1.5 equiv) 3a 4a

Temperature	Conversion of 1a (%)	3a yield (%)	4a yield (%)
70	93	71	7
80	**97**	**77**	**7**
90	100	79	14

Conversions and yields acquired by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.

Table S5. Equivalence screen

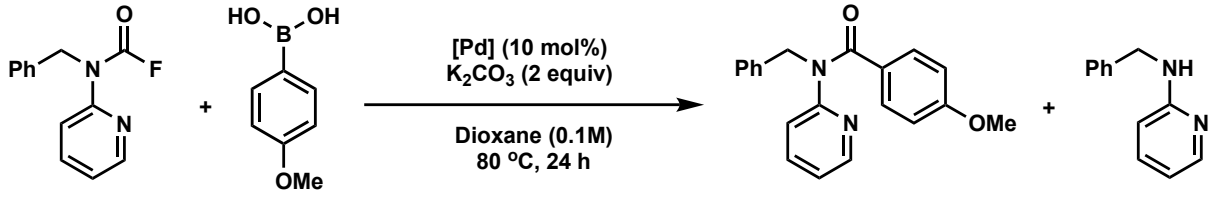


1a 2a, (x equiv) 3a 4a

x (equiv)	y (equiv)	Conversion of 1a (%)	3a yield (%)	4a yield (%)
1.5	1.5	97	77	7
1	1.5	93	66	13
2	**1.5**	**97**	**84**	**7**
2	1	93	75	6
2	**2**	**100**	**90**	**8**

Conversions and yields acquired by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.

Table S6. Effect of $Ph_3P=O$ on reaction yield

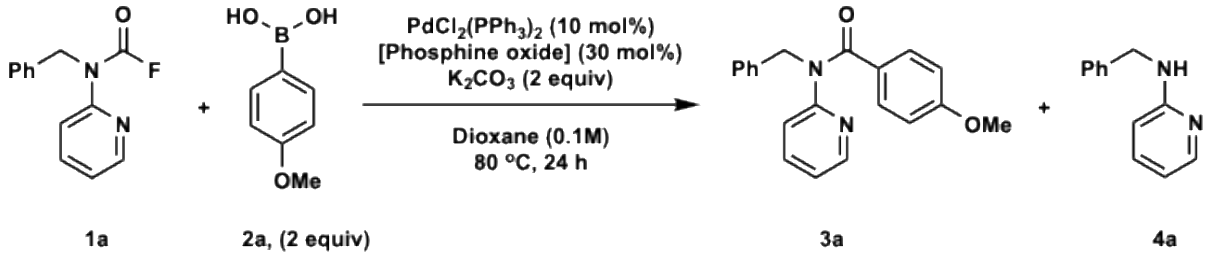


1a 2a, (2 equiv) 3a 4a

Catalyst	Conversion of 1a (%)[a]	3a yield (%)[a]	4a yield (%)[a]
$Pd(PPh_3)_4$[b]	97	10	72
$Pd(PPh_3)_4$[c]	100	84	7
$Pd(PPh_3)_4$[b] + $Ph_3P=O$ (30 mol%)	98	42	38
$PdCl_2(PPh_3)_2$+ $Ph_3P=O$ (30 mol%)	**100**	**95**	**4**

[a]Conversions and yields acquired by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. [b]Batch stored in Argon-filled glovebox at -35 °C (no $Ph_3P=O$ contamination); [c] Batch stored under N_2 at 4 °C [$Pd(PPh_3)_4$/$Ph_3P=O$ ratio = 1:1.7 by ^{1}H NMR].

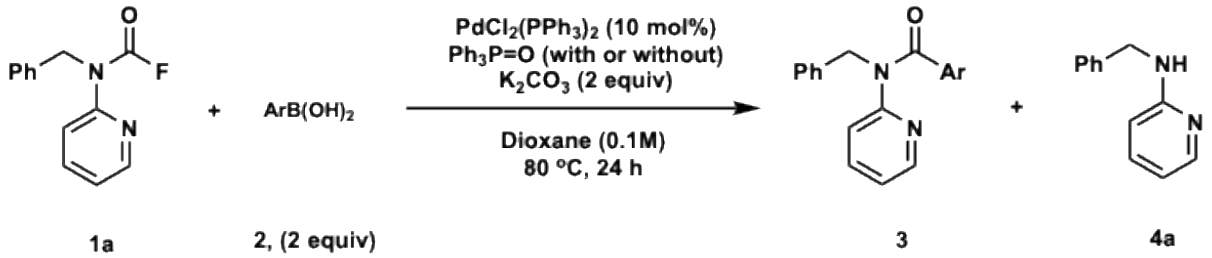
Table S7. The effect of different phosphine oxides in the reaction



Phosphine oxide	Conversion of 1a (%)	3a yield (%)	4a yield (%)
$Ph_3P=O$	**100**	**95**	**4**
$(o\text{-tol})_3P=O$	100	92	5
$Et_3P=O$	99	90	8

Conversions and yields acquired by ^1H NMR with 1,3,5-trimethoxybenzene as an internal standard

Table S8. The effect of $Ph_3P=O$ with different boronic acids in the reaction

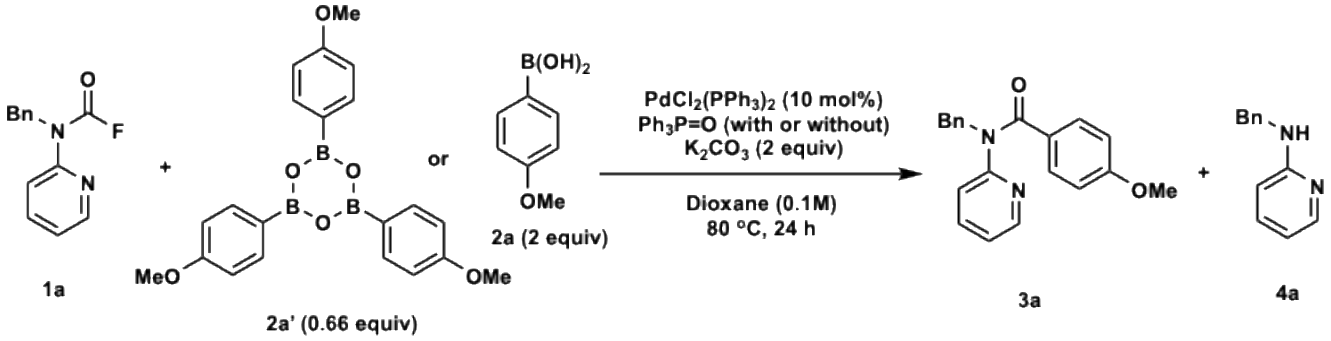


Boronic acid	$Ph_3P=O$	Conversion of 1a (%)[a]	3a yield (%)[a]	4a yield (%)[a]
4-methyphenyboronic acid **(2b)**	**30 mol%**	**99**	**78(76)**	**12**
4-methyphenyboronic acid **(2b)**	-	100	65	17
phenyboronic acid **(2c)**	**30 mol%**	**100**	**76(73)**	**23**
phenyboronic acid **(2c)**	-	99	50	37
4-fluorophenyboronic acid **(2d)**	**30 mol %**	**100**	**84(82)**	**9**
4-fluorophenyboronic acid **(2d)**	-	100	52	38
3-thiopheneboronic acid **(2f)**	**30 mol%**	**65**	**38 (32)**	**10**

3-thiopheneboronic acid **(2f)**	-	43	6	30
3-methoxyphenylboronic acid **(2g)**	**30 mol%**	**97**	**59 (53)**	**29**
3-methoxyphenylboronic acid **(2g)**	-	88	39	9
2-naphthylboronic acid **(2j)**	**30 mol %**	**100**	**70(62)**	**16**
2-naphthylboronic acid **(2j)**	-	99	40	36

[a]Conversions and yields acquired by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. Isolated yields shown in parentheses.

Table S9. Effect of Ph_3P=O with commercial boronic acid and pure boroxine

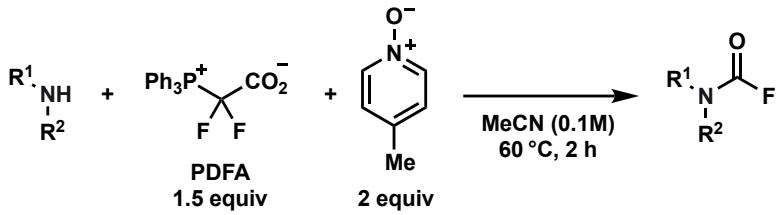


Boron compound	Ph_3P=O	Conversion of 1a (%)[a]	3a yield (%)[a]	4a yield (%)[a]
Commercial Boronic acid (**2a**)[b]	-	100	90	8
Commercial Boronic acid (**2a**)[b]	30 mol %	100	95	4
Boroxine (**2a′**)	-	94	67	22
Boroxine (**2a′**)	30 mol %	91	84	5

[a]Conversions and yields acquired by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. [b] boronic acid: boroxine = 1:1.3.

3 Synthesis of Starting Materials

3.1 Preparation of Carbamoyl Fluorides

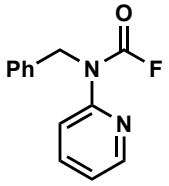


A round-bottom flask equipped with a stir bar was charged with the indicated secondary amine (1.0 equiv), 4-methylpyridine *N*-oxide (2.0 equiv) and PDFA (1.5 equiv). The flask was evacuated and backfilled with N_2 (3x) and MeCN (0.1 M, 50 mL) was added. The reaction vessel was submerged in a pre-heated 60 °C oil bath and heated for 2 h. The solvent was removed under reduced pressure and the crude material was purified by column chromatography using the indicated eluent.

3.2 Synthesis and Characterization Data for Carbamoyl Fluorides

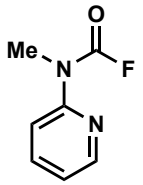
***Note**: In accordance with previous reports, carbamoyl fluorides show restricted rotation about the N-C_{acyl} bond, resulting in rotamers in solution.*[1–3] *Resonances for rotamers can be observed for unsymmetrically substituted carbamoyl fluorides (R' ≠ R) in all ^{19}F NMR spectra, but are generally not well resolved in the ^{13}C and ^{1}H NMR spectra. In the ^{13}C NMR spectra, the peaks for the major rotamer are listed.*

_N_-Benzyl-_N_-(2-pyridyl)carbamoyl fluoride (1a)



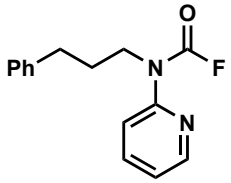
The title carbamoyl fluoride was synthesized from 2-benzylaminopyridine (0.921 g, 5.00 mmol, 1.0 equiv) and was isolated as a light-yellow oil (0.840 g, 3.65 mmol, 73%) after purification by flash column chromatography (10% EtOAc/hexanes). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.49 (dd, J = 4.8, 2.0 Hz, 1H), 7.93 – 7.85 (m, 1H), 7.67 (bs, 1H), 7.40 – 7.20 (m, 6H), 5.15 (bs, 2H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 151.5, 148.4, 145.5 (d, J = 290.9 Hz), 138.8, 136.5, 128.5, 127.4, 127.1, 122.2, 119.6 (b), 51.0 (b). **^{19}F NMR** (377 MHz, $CDCl_3$): δ − 6.92 (bs, major rotamer), −14.43 (bs, minor rotamer). **IR** (ATR, neat, cm^{-1}) 1789, 1588, 1471, 1434, 1389, 1302, 1271, 1222, 741, 699. **HRMS** (ESI) m/z: $[M+H]^+$ calc'd for $[C_{13}H_{12}FN_2O]$ 231.0928; found 231.0931. The spectral data are consistent with literature values.[1]

***N*-Methyl-*N*-(2-pyridyl)carbamoyl fluoride (1p)**



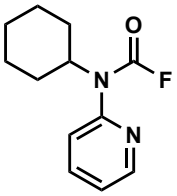
The title carbamoyl fluoride was synthesized from 2-(methylamino)pyridine (0.216 g, 2.00 mmol, 1.0 equiv) and was isolated as a colourless oil (0.163 g, 1.06 mmol, 53%) after purification by flash column chromatography (5% EtOAc/hexanes). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.48 (ddd, J = 4.8, 2.0, 0.9 Hz, 1H), 7.91 (ddd, J = 8.3, 7.4, 2.0 Hz, 1H), 7.66 (bd, 1H), 7.32 (dd, J = 7.4, 4.8 Hz, 1H), 3.39 (bd, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 152.9, 148.6, 145.9 (d, J = 290.9 Hz), 139.1, 122.3, 119.1 (b), 35.5. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -7.37 (bs, major rotamer), -14.99 (bs, minor rotamer). **IR** (ATR, neat, cm^{-1}) 3379, 1791, 1662, 1049, 1025, 1005, 774, 738. **HRMS** (ESI) m/z: $[M+H]^+$ calc'd for $[C_7H_8FN_2O]$ 155.0615; found 155.0613.

***N*-(3-phenylpropyl)-*N*-(2-pyridyl)carbamoyl fluoride (1q)**



The title carbamoyl fluoride was synthesized from *N*-(3-phenylpropyl)-*N*-2-aminopyridine (0.425 g, 2.00 mmol, 1.0 equiv) and was isolated as a light-yellow oil (0.336g, 1.30 mmol, 65%) after purification by flash column chromatography (10% EtOAc/hexanes). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.40 (d, J = 2.6 Hz, 1H), 7.81 (td, J = 7.8, 2.0 Hz, 1H), 7.51 (bd, J = 8.6 Hz, 1H), 7.24 (t, 1H), 7.15 (t, J = 7.7 Hz, 2H), 7.10 – 6.98 (m, 3H), 3.80 (t, J = 7.5 Hz, 2H), 2.50 (t, J = 7.5 Hz, 2H), 1.77 (p, J = 7.5 Hz, 2H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 151.7, 148.4, 145.2 (d, J = 290.9 Hz), 141.0, 138.7, 128.2, 128.1, 125.8, 122.3 (b), 120.1 (b), 47.9 (b), 32.0, 29.3 (b).**^{19}F NMR** (377 MHz, $CDCl_3$) δ -9.80 (bs, major rotamer), -13.63 (bs, minor rotamer). **IR** (ATR, neat, cm^{-1}) 1786, 1587, 1574, 1471, 1434, 1392, 741, 698. **HRMS** (ESI) m/z: $[M+H]^+$ calc'd for $[C_{15}H_{16}FN_2O]$ 259.1241; found 259.1253.

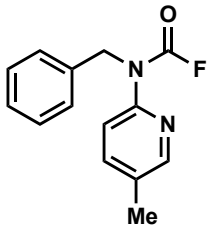
***N*-cyclohexyl-*N*-(2-pyridyl)carbamoyl fluoride (1r)**



The title carbamoyl fluoride was synthesized from 2-cyclohexylaminopyridine (0.176 g, 1.00 mmol, 1.0 equiv) and was isolated as a yellow liquid (0.158 g, 0.710 mmol, 71%) after purification by flash column chromatography (10% EtOAc/hexanes). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.59 (dd, J = 5.2, 2.4 Hz, 1H), 7.82 (td, J = 7.8, 2.1 Hz, 1H), 7.37 – 7.32 (m, 1H), 7.25 (d, 1H), 4.07 (tt, J = 12.1, 3.8 Hz, 1H), 2.05 (bd,

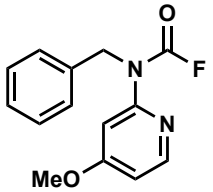
2H), 1.85 (bd, 2H), 1.67 (bd, 1H), 1.56 (apparent qd, J = 12.4, 3.5 Hz, 2H), 1.38 (apparent qt, J = 13.0, 3.5 Hz, 2H), 1.09 (apparent qt, J = 13.0, 3.5 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.4, 149.2, 145.8 (d, J = 291.9 Hz), 138.3, 123.3, 123.2 (d, J = 2.0 Hz), 59.9, 31.1, 25.9, 25.2. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -9.70 (bs). **IR** (ATR, neat, cm^{-1}) 2932, 2857, 1781, 1571, 1469, 1312, 1262, 989, 745. **HRMS** (ESI) m/z: $[M+H]^+$ calc'd for $[C_{12}H_{16}FN_2O]$ 223.1241; found 223.1239.

***N*-benzyl-*N*-(5-methyl-2-pyridyl)carbamoyl fluoride (1s)**



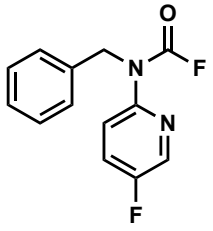
The title carbamoyl fluoride was synthesized from 2-(*N*-benzylamino)-5-methypyridine (0.198 g, 1.00 mmol, 1.0 equiv) and was isolated as a colourless oil (0.105 g, 0.430 mmol, 43%) after purification by flash column chromatography (5% EtOAc/hexanes). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.31 (bs, 1H), 7.71 (bd, 1H), 7.51 (bs, 1H), 7.34 – 7.23 (m, 5H), 5.09 (bs, 2H), 2.29 (bs, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 149.8, 148.7, 146.0 (d, J = 291.9 Hz), 139.6, 137.0, 132.3, 129.0, 127.9, 127.7, 119.8 (b), 51.6 (b), 17.7. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -8.32 (bs, major rotamer), -14.86 (bs, minor rotamer). **IR** (ATR, neat, cm^{-1}) 1789, 1480, 1396, 1379, 1225, 749. **HRMS** (ESI) m/z: $[M+H]^+$ calc'd for $[C_{14}H_{14}FN_2O]$ 245.1085; found 245.1089.

***N*-benzyl-*N*-(4-methoxy-2-pyridyl)carbamoyl fluoride (1t)**



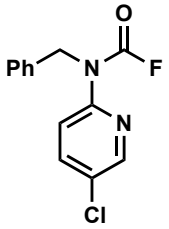
The title carbamoyl fluoride was synthesized from 2-(*N*-benzylamino)-4-methoxypyridine (0.223 g, 1.04 mmol, 1.0 equiv) and was isolated as a colourless oil (0.141 g, 0.540 mmol, 52%) after purification by flash column chromatography (2 →15% EtOAc/hexanes). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.29 (d, J = 5.8 Hz, 1H), 7.36 – 7.21 (m, 6H), 6.93 (dd, J = 5.9, 2.3 Hz, 1H), 5.12 (s, 2H), 3.83 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 166.9, 153.1, 149.4, 145.5 (d, J = 291.9 Hz), 136.6, 128.4, 127.4, 127.2, 108.8, 105.7 (b), 55.8, 51.1 (b). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -6.62 (bs, major rotamer), -14.17 (bs, minor rotamer). **IR** (ATR, neat, cm^{-1}) 1789, 1596, 1563, 1391, 1206, 1173, 1033, 752. **HRMS** (ESI) m/z: $[M+H]^+$ calc'd for $[C_{14}H_{14}FN_2O_2]$ 261.1034; found 261.1036.

***N*-benzyl-*N*-(5-fluoro-2-pyridyl)carbamoyl fluoride (1u)**



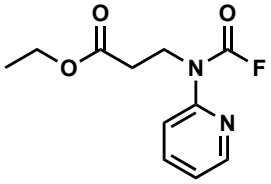
The title carbamoyl fluoride was synthesized from 2-(*N*-benzylamino)-5-fluoropyridine (0.081 g, 0.40 mmol, 1.0 equiv) and was isolated as a colourless oil (0.049 g, 0.200 mmol, 50%) after purification by flash column chromatography (5% EtOAc/hexanes). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.43 (t, J = 3.3 Hz, 1H), 7.86 – 7.75 (m, 1H), 7.67 (bs, 1H), 7.27 – 7.17 (m, 5H), 5.04 (s, 2H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 157.4 (d, J = 252.9 Hz), 147.8, 145.5 (d, J = 291.9 Hz), 136.2, 135.9, 128.5, 127.5. 127.2, 125.9 (d, J = 20.2 Hz), 121.6 (b), 51.5 (b).**^{19}F NMR** (377 MHz, $CDCl_3$) δ -8.57 (bs, major rotamer), -14.50 (bs, minor rotamer), -128.43 (bs, minor rotamer), -130.48 (bs, major rotamer). **IR** (ATR, neat, cm^{-1}) 1788, 1475, 1382, 1218, 745, 697, 569. **HRMS** (ESI) m/z: $[M+H]^+$ calc'd for $[C_{13}H_{11}F_2N_2O]$ 249.0834; found 249.0834.

***N*-benzyl-*N*-(5-chloro-2-pyridyl)carbamoyl fluoride (1v)**



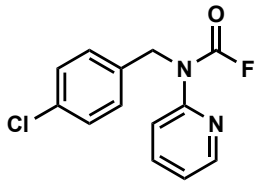
The title carbamoyl fluoride was synthesized from 2-(*N*-benzylamino)-5-chloropyridine (0.219 g, 1.00 mmol, 1.0 equiv) and was isolated as a colourless oil (0.085 g, 0.320 mmol, 32%) after purification by flash column chromatography (2% EtOAc/hexanes). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.55 (d, J = 2.6 Hz, 1H), 8.05 (dd, J = 8.8, 2.7 Hz, 1H), 7.75 (bd, 1H), 7.35 – 7.26 (m, 5H), 5.13 (s, 2H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 150.7, 147.2, 145.8 (d, J = 289.2 Hz; *doublet partially overlapping with peak at 147.2*), 139.0, 136.8, 133.8 (d, J = 19.2 Hz), 129.0, 128.0, 127.6, 121.2 (b), 51.5 (b). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -6.62 (bs, major rotamer), -14.05 (bs, minor rotamer). **IR** (ATR, neat, cm^{-1}) 1789, 1464, 1395, 1372, 1219, 1114, 746, 699. **HRMS** (ESI) m/z: $[M+H]^+$ calc'd for $[C_{13}H_{11}ClFN_2O]$ 265.0538; found 265.0538.

***N*-[(3-ethoxy-3-oxopropyl)]-*N*-(2-pyridyl)carbamoyl fluoride (1w)**



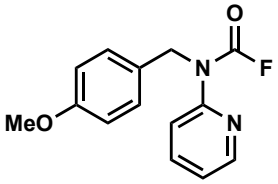
The title carbamoyl fluoride was synthesized from ethyl 3-(2-pyridylamino) propanoate (0.388 g, 2.00 mmol, 1.0 equiv) and was isolated as a light-yellow oil (0.335 g, 1.26 mmol, 70%) after purification by flash column chromatography (10→30% EtOAc/hexanes). **^{1}H NMR** (400 MHz, DMSO-d_6, major rotamer) δ 8.50 (dd, *J* = 4.9, 2.0 Hz, 1H), 7.93 (tt, *J* = 8.2, 2.0 Hz, 1H), 7.59 (bs, 1H), 7.38 – 7.33 (m, 1H), 4.12 (t, *J* = 7.0 Hz, 2H), 4.00 (q, *J* = 7.1 Hz, 2H), 2.68 (td, *J* = 7.0 Hz, 2H), 1.12 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 171.0, 151.9, 148.8, 145.5 (d, *J* = 290.9 Hz), 139.1 (d, *J* = 9.1 Hz), 122.7, 120.2 (b), 60.6, 44.5 (b), 33.2, 14.3. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -9.26 (bs, major rotamer), -13.89 (bs, minor rotamer). **IR** (ATR, neat, cm^{-1}) 1791, 1728, 1589, 1471, 1410, 1392, 1182, 1056, 775, 745. **HRMS** (ESI) m/z: $[M+H]^+$ calc'd for $[C_{11}H_{14}FN_2O_3]$ 241.0983; found 241.0987.

***N*-[(4-chlorophenyl)methyl]-*N*-(2-pyridyl)carbamoyl fluoride (1x)**



The title carbamoyl fluoride was synthesized from *N*-[(4-chlorophenyl)methyl]-2-pyridineamine (0.394 g, 1.80 mmol, 1.0 equiv) and was isolated as a light-yellow oil (0.335 g, 1.26 mmol, 70%) after purification by flash column chromatography (10% EtOAc/hexanes). **^{1}H NMR** (400 MHz, DMSO) δ 8.47 (dd, *J* = 4.9, 2.9 Hz, 1H), 7.91 (td, *J* = 7.9, 2.1 Hz, 1H), 7.67 (bs, 1H), 7.41 – 7.22 (m, 5H), 5.11 (s, 2H). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 4.9 Hz, 1H), 7.71 (td, *J* = 7.8, 2.0 Hz, 1H), 7.32 – 6.99 (m, 6H), 5.18 (s, 2H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 151.9, 148.9, 145.9 (d, *J* = 291.9 Hz), 139.3, 136.1, 132.6, 129.7, 128.9, 122.8, 120.1 (b), 51.0 (b). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -6.35 (bs, minor rotamer), -14.29 (bs, major rotamer). **IR** (ATR, neat, cm^{-1}) 1789, 1588, 1470, 1435, 1387, 1222, 781. **HRMS** (ESI) m/z: $[M+H]^+$ calc'd for $[C_{13}H_{11}ClFN_2O]$ 265.0538; found 265.0535.

***N*-[(4-methoxyphenyl)methyl]-*N*-(2-pyridyl)carbamoyl fluoride (1y)**

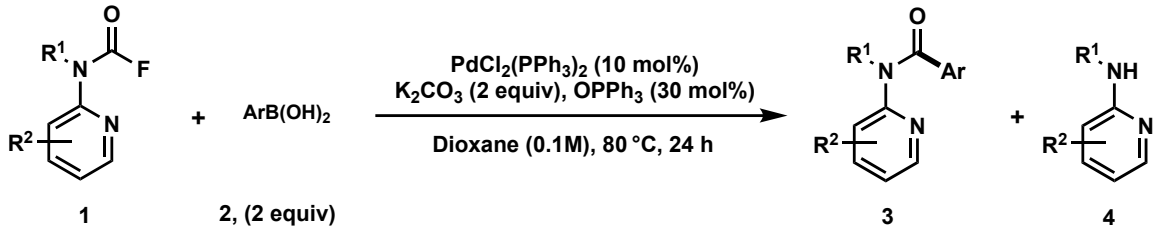


The title carbamoyl fluoride was synthesized from 2-(4-methoxybenzylamino)pyridine (0.225 g, 1.05 mmol, 1.0 equiv) and was isolated as a light-yellow oil (0.120 g, 0.460 mmol, 44%) after purification by flash column chromatography (10% EtOAc/hexanes). **^{1}H NMR** (400 MHz, DMSO-d_6, major rotamer) δ 8.50 (dd, *J* = 4.8, 2.1 Hz, 1H), 7.88 (qd, *J* = 7.6, 2.1 Hz, 1H), 7.60 (bs, 1H), 7.31 (m, 1H), 7.23 (dd, *J* = 8.7, 3.4 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 5.06 (s, 2H), 3.71 (bs, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 158.6, 151.5, 148.4, 145.5 (d, *J* = 290.9 Hz), 138.7, 128.9, 128.3, 122.3, 119.8, 113.9, 55.0 (b), 50.6 (b). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -7.34 (bs, major rotamer), -14.34 (bs, minor rotamer). **IR** (ATR, neat, cm^{-}

[1]) 1788, 1587, 1512, 1470, 1435, 1389, 1177, 1155, 1033, 742. **HRMS** (ESI) m/z: $[M+H]^+$ calc'd for $[C_{14}H_{14}FN_2O_2]$ 261.1034; found 261.1034.

4 General Procedures and Characterization Data for Amide Synthesis

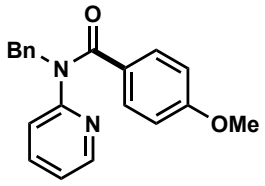
4.1 General Procedure for Synthesis of Amides



A 1 dram vial equipped with a stir bar was charged with carbamoyl fluoride **1a** (0.20 mmol, 1.0 equiv), arylboronic acid **2** (0.40 mmol, 2 equiv), K_2CO_3 (0.40 mmol, 2 equiv), $OPPh_3$ (0.017g, 0.06 mmol, 0.30 equiv), and $PdCl_2(PPh_3)_2$ (0.014g, 0.02 mmol, 10 mol%). The vial was evacuated and backfilled with N_2 (3x), then 1,4-dioxane (0.1 M, 2 mL) was added. The septum cap was quickly replaced with a Teflon-lined screwcap and the reaction vessel was submerged into an 80 °C oil bath and heated for 24 h. The reaction mixture was diluted with EtOAc or DCM, filtered through celite, and concentrated under reduced pressure. An established quantity of 1,3,5-trimethoxybenzene was introduced as an internal standard and the crude material was solved in $CDCl_3$ for quantitative ^1H NMR analysis. The crude material was purified by column chromatography (Et_2O/DCM).

4.2 Characterization Data for Products

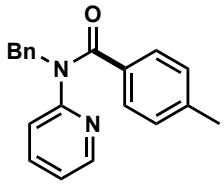
***N*-benzyl-4-methoxy-*N*-(2-pyridyl)benzamide (3a)**



The title compound was synthesized from *N*-benzyl-*N*-(2-pyridyl)carbamoyl fluoride **1a** (0.046 g, 0.20 mmol) and 4-methoxyphenyboronic acid **2a** (0.060 g, 0.40 mmol), and was isolated as a light yellow solid (0.0562 g, 0.176 mmol, 89%) after purification by flash column chromatography (10% Et_2O/DCM). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.46 (dd, *J* = 4.9, 1.3 Hz, 1H), 7.43 – 7.27 (m, 6H), 7.25 – 7.17 (m, 2H), 6.99 (ddd, *J* = 7.4, 4.9, 1.0 Hz, 1H), 6.72 (d, *J* = 8.9 Hz, 2H), 6.61 (d, *J* = 8.0 Hz, 1H), 5.36 (s, 2H), 3.76 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.3, 161.2, 156.4, 148.8, 137.9, 137.2, 130.9, 128.33, 128.29, 128.0, 127.1, 122.8, 120.8, 113.3, 55.3, 51.7. **IR** (ATR, neat, cm^{-1}) 1635, 1462, 1376, 1310, 1253, 1235, 1173, 846, 764, 710, 600. **HRMS** (ESI) m/z: $[M+H]^+$ calc'd for $[C_{12}H_{19}N_2O_2]$ 319.1441; found 319.1420. **mp** (°C) 112–114.

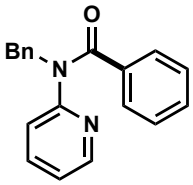
Scale-up: A flame-dried round bottom flask was added a stir bar and charged with **1a** (1.00 g, 4.30 mmol, 1 equiv), 4-methoxyphenyboronic acid **2a** (1.3 g, 8.60 mmol, 2 equiv), K_2CO_3 (1.16 g, 8.6 mmol, 2 equiv), $OPPh_3$ (0.360 g, 1.29 mmol, 0.30 equiv), and $PdCl_2(PPh_3)_2$ (0.302 g, 0.43 mmol, 10 mol%), followed by the addition of dioxane (0.1 M, 43 ml). The flask was capped with a suitable septum and the reaction was submerged into an 80 °C oil bath for 24 hours. The reaction vessel was taken out from the oil bath and concentrated by the rotary evaporator. The crude material was purified by column chromatography (10% Et_2O/DCM) and **3a** was collected as a light-yellow solid (1.012 g, 3.18 mmol, 74%).

***N*-benzyl-4-methyl-*N*-(2-pyridyl)benzamide (3b)**



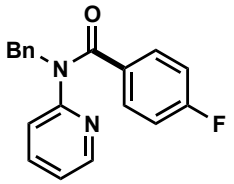
The title compound was synthesized from *N*-benzyl-*N*-(2-pyridyl)carbamoyl fluoride **1a** (0.044 g, 0.19 mmol) and 4-methyphenyboronic acid **2b** (0.052 g, 0.38 mmol), and was isolated as a yellow solid (0.044 g, 0.145 mmol, 76%) after purification by flash column chromatography (10% Et_2O/DCM). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.47 (dd, *J* = 4.9, 1.9 Hz, 1H), 7.43 – 7.27 (m, 7H), 7.24 – 7.18 (m, 1H), 7.05 – 6.98 (m, 3H), 6.61 (d, *J* = 8.0 Hz, 1H), 5.37 (s, 2H), 2.30 (s, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.7, 156.1, 148.8, 140.6, 137.9, 137.2, 133.0, 128.9, 128.7, 128.34, 128.29, 127.1, 122.8, 120.8, 51.6, 21.4. **IR** (ATR, neat, cm^{-1}) 1644, 1469, 1381, 1359, 1230, 829, 751, 729, 603. **HRMS** (ESI) m/z: $[M+H]^+$ calc'd for $[C_{20}H_{19}N_2O]$ 303.1492; found 303.1502. **mp** (°C) 120–122.

***N*-benzyl-*N*-(2-pyridyl)benzamide (3c)**



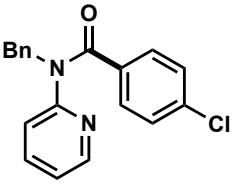
The title compound was synthesized from *N*-benzyl-*N*-(2-pyridyl)carbamoyl fluoride **1a** (0.046 g, 0.20 mmol) and phenyboronic acid **2c** (0.049 g, 0.40 mmol), and was isolated as a yellow solid (0.042 g, 0.147 mmol, 73%) after purification by flash column chromatography (10% Et_2O/DCM). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.46 (dd, *J* = 4.8, 1.9 Hz, 1H), 7.42 – 7.27 (m, 8H), 7.22 – 7.18 (m, 3H), 7.00 (dd, *J* = 7.3, 4.8 Hz, 1H), 6.62 (d, *J* = 8.0 Hz, 1H), 5.38 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.7, 155.9, 148.8, 137.8, 137.2, 136.0, 130.2, 128.8, 128.4, 128.3, 128.0, 127.2, 122.7, 121.0, 51.6. **IR** (ATR, neat, cm^{-1}) 1644, 1468, 1372, 1326, 1287, 1235, 738, 706, 690. **HRMS** (ESI) m/z: $[M+H]^+$ calc'd for $[C_{19}H_{17}N_2O]$ 289.1335; found 289.1339. **mp** (°C) 111–113. The spectral data are consistent with reported literature values.[4]

***N*-benzyl-4-fluoro-*N*-(2-pyridyl)benzamide (3d)**



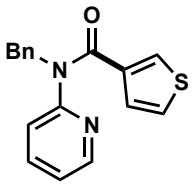
The title compound was synthesized from *N*-benzyl-*N*-(2-pyridyl)carbamoyl fluoride **1a** (0.041 g, 0.18 mmol) and 4-fluorophenyboronic acid **2d** (0.050 g, 0.36 mmol), and was isolated as a yellow solid (0.045 g, 0.147 mmol, 82%) after purification by flash column chromatography (10% Et_2O/DCM). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.47 (ddd, *J* = 4.9, 2.0, 0.8 Hz, 1H), 7.44 – 7.34 (m, 5H), 7.31 – 7.27 (m, 2H), 7.25 – 7.18 (m, 1H), 7.03 (ddd, *J* = 7.4, 4.9, 1.1 Hz, 1H), 6.97 – 6.85 (m, 2H), 6.61 (d, *J* = 8.0 Hz, 1H), 5.35 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.6, 163.6 (d, *J* = 251.3 Hz), 155.9, 149.0, 137.6, 137.4, 132.1 (d, *J* = 3.3 Hz), 131.1 (d, *J* = 8.7 Hz), 128.4 (d, *J* = 10.2 Hz), 127.3, 122.6, 121.2, 115.2, 115.0, 51.8. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -109.1 (s). **IR** (ATR, neat, cm^{-1}) 1643, 1586, 1467, 1374, 1324, 1235, 984, 851, 761, 712, 599. **HRMS** (ESI) m/z: $[M+H]^+$ calc'd for $[C_{19}H_{16}FN_2O]$ 307.1241; found 307.1243. **mp** (°C) 105–107.

***N*-benzyl-4-chloro-*N*-(2-pyridyl)benzamide (3e)**



The title compound was synthesized from *N*-benzyl-*N*-(2-pyridyl)carbamoyl fluoride **1a** (0.048 g, 0.21 mmol) and 4-chlorophenylboronic acid **2e** (0.065 g, 0.42 mmol), and was isolated as a yellow solid (0.036 g, 0.111 mmol, 53%) after purification by flash column chromatography (5% Et_2O/DCM). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.44 (ddd, *J* = 4.9, 1.9, 0.9 Hz, 1H), 7.40 – 7.27 (m, 6H), 7.25 – 7.15 (m, 4H), 7.02 (ddd, *J* = 7.4, 4.8, 1.0 Hz, 1H), 6.59 (d, *J* = 8.0 Hz, 1H), 5.31 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.6, 155.7, 149.0, 137.5, 137.5, 136.4, 134.4, 130.2, 128.4 (2C), 128.3, 127.3, 122.5, 121.3, 51.8. **IR** (ATR, neat, cm^{-1}) 1643, 1470, 1387, 1230, 838, 752, 729, 698, 575. **HRMS** (ESI) m/z: $[M+H]^+$ calc'd for $[C_{19}H_{16}ClN_2O]$ 323.0946; found 323.0950. **mp** (°C) 97–99.

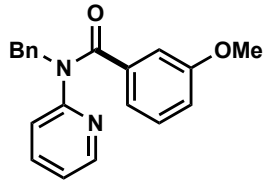
***N*-benzyl-*N*-(3-pyridyl)thiophene-3-carboxamide (3f)**



The title compound was synthesized from *N*-benzyl-*N*-(2-pyridyl)carbamoyl fluoride **1a** (0.044 g, 0.19 mmol) and 3-thienyl boronic acid **2f** (0.049 g, 0.38 mmol), and was isolated as an orange solid (0.018 g, 0.061 mmol, 32%) after purification by flash column chromatography (10% Et_2O/DCM). **^{1}H NMR** (400

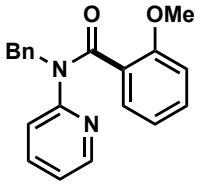
MHz, $CDCl_3$) δ 8.52 (dd, *J* = 5.2, 1.9 Hz, 1H), 7.45 (td, *J* = 7.8, 2.0 Hz, 1H), 7.39 (dd, *J* = 3.0, 1.3 Hz, 1H), 7.38 – 7.31 (m, 2H), 7.30 – 7.27 (m, 2H), 7.25 – 7.19 (m, 1H), 7.14 – 7.05 (m, 2H), 6.92 (dd, *J* = 5.1, 1.3 Hz, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 5.33 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.4, 155.9, 149.2, 137.7, 137.6, 137.3, 130.0, 128.5, 128.4, 128.0, 127.4, 125.2, 123.0, 121.7, 51.8. **IR** (ATR, neat, cm^{-1}) 1638, 1580, 1434, 1413, 1360, 1272, 1204, 733, 697, 551. **HRMS** (ESI) m/z: $[M+H]^+$ calc'd for $[C_{17}H_{15}N_2OS]$ 295.0900; found 295.0899. **mp** (°C) 114–116.

***N*-benzyl-3-methoxy-*N*-(2-pyridyl)benzamide (3g)**



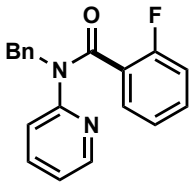
The title compound was synthesized from *N*-benzyl-*N*-(2-pyridyl)carbamoyl fluoride **1a** (0.046 g, 0.20 mmol) and 3-methoxyphenyboronic acid **2g** (0.06 g, 0.40 mmol), and was isolated as a yellow solid (0.034 g, 0.106 mmol, 53%) after purification by flash column chromatography (10% Et_2O/DCM). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.47 (ddd, *J* = 4.9, 2.0, 0.9 Hz, 1H), 7.41 – 7.34 (m, 3H), 7.30 – 7.27 (m, 2), 7.25 – 7.19 (m, 1H), 7.10 (t, *J* = 7.9 Hz, 1H), 7.02 (ddd, *J* = 7.4, 4.9, 1.0 Hz, 1H), 6.98 (dd, *J* = 2.6, 1.5 Hz, 1H), 6.91 (dt, *J* = 7.6, 1.3 Hz, 1H), 6.86 (ddd, *J* = 8.3, 2.6, 1.1 Hz, 1H), 6.66 (d, *J* = 8.0 Hz, 1H), 5.37 (s, 2H), 3.70 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.6, 159.3, 156.0, 148.9, 137.8, 137.4, 137.3, 129.1, 128.5, 128.4, 127.3, 122.9, 121.3, 121.2, 117.1, 113.5, 55.4, 51.7. **IR** (ATR, neat, cm^{-1}) 1649, 1583, 1467, 1433, 1376, 1321, 1286, 746. **HRMS** (ESI) m/z: $[M+H]^+$ calc'd for $[C_{20}H_{19}N_2O_2]$ 319.1441; found 319.1445. **mp** (°C) 110–112.

***N*-benzyl-2-methoxy-*N*-(2-pyridyl)benzamide (3h)**



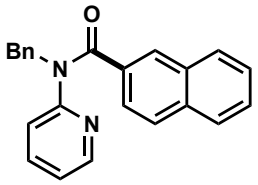
The title compound was synthesized from *N*-benzyl-*N*-(2-pyridyl)carbamoyl fluoride **1a** (0.041 g, 0.18 mmol) and 2-methoxyphenyboronic acid **2h** (0.055 g, 0.36 mmol), and was isolated as a yellow solid (0.011 g, 0.034 mmol, 19%) after purification by flash column chromatography (10% Et_2O/DCM). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.47 – 8.40 (m, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.65 (ddd, *J* = 8.4, 7.3, 2.0 Hz, 1H), 7.40 (d, *J* = 7.1 Hz, 2H), 7.33 – 7.27 (m, 2H), 7.27 – 7.24 (m, 1H), 7.21 (td, *J* = 7.8, 1.7 Hz, 1H), 7.08 (ddd, *J* = 7.3, 4.9, 1.0 Hz, 1H), 7.03 (dd, *J* = 7.8, 1.7 Hz, 1H), 6.99 (dd, *J* = 8.4, 1.4 Hz, 1H), 6.94 (td, *J* = 7.6, 1.4 Hz, 1H), 5.42 (s, 2H), 3.82 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.8, 153.5, 151.5, 147.8, 140.1, 138.4, 137.4, 128.2 (2C), 127.8, 127.0, 126.7, 123.1, 120.8, 120.3, 112.5, 55.9, 50.5. **IR** (ATR, neat, cm^{-1}) 1724, 1468, 1381, 1256, 1193, 1171, 769, 696. **HRMS** (ESI) m/z: $[M+H]^+$ calc'd for $[C_{20}H_{19}N_2O_2]$ 319.1441; found 319.1445. **mp** (°C) 107–109.

***N*-benzyl-2-fluoro-*N*-(2-pyridyl)benzamide (3i)**



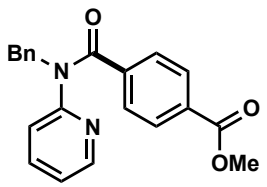
The title compound was synthesized from *N*-benzyl-*N*-(2-pyridyl)carbamoyl fluoride **1a** (0.046 g, 0.20 mmol) and 2-fluorophenylboronic acid **2i** (0.056 g, 0.40 mmol), and was isolated as a yellow solid (0.023, 0.075 mmol, 37%) after purification by flash column chromatography (5% Et_2O/DCM). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.46 (dt, *J* = 4.9, 1.6 Hz, 1H), 7.77 – 7.62 (m, 2H), 7.39 – 7.28 (m, 4H), 7.25 – 7.05 (m, 6H), 5.40 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.6 (d, *J* = 249.2 Hz), 153.5, 153.0, 148.1, 138.5 (d, *J* = 12.4 Hz), 138.1, 137.7, 128.5, 127.8, 127.3, 127.1 (d, *J* = 6.9 Hz), 124.5 (d, *J* = 4.0 Hz), 124.2, 120.9, 120.3, 116.8 (d, *J* = 18.5 Hz), 50.9. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -128.97 (s). **IR** (ATR, neat, cm^{-1}) 1645, 1468, 1223, 1181, 743, 696. **HRMS** (ESI) m/z: $[M+H]^+$ calc'd for $[C_{19}H_{16}FN_2O]$ 307.1241; found 307.1235. **mp** (°C) 93–95.

***N*-benzyl-*N*-(2-pyridyl)naphthalene-2-carboxamide (3j)**



The title compound was synthesized from *N*-benzyl-*N*-(2-pyridyl)carbamoyl fluoride **1a** (0.046 g, 0.20 mmol) and 2-naphthylboronic acid **2j** (0.068 g, 0.40 mmol), and was isolated as a yellow solid (0.042 g, 0.124 mmol, 62%) after purification by flash column chromatography (5% Et_2O/DCM). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.45 (dd, *J* = 4.8, 1.9 Hz, 1H), 7.95 (s, 1H), 7.78 – 7.68 (m, 2H), 7.63 (d, *J* = 8.5 Hz, 1H), 7.52 – 7.35 (m, 5H), 7.32 – 7.27 (m, 3H), 7.24 – 7.17 (m, 1H), 6.95 (dd, *J* = 7.4, 4.9 Hz, 1H), 6.61 (d, *J* = 8.0 Hz, 1H), 5.41 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.7, 155.9, 148.9, 137.8, 137.3, 134.9, 133.9, 133.3, 132.5, 129.5, 128.7, 128.4, 128.3, 127.6, 127.4, 127.2, 126.5, 125.3, 122.8, 121.0, 51.7. **IR** (ATR, neat, cm^{-1}) 1644, 1495, 1434, 1375, 1283, 1196, 697, 476. **HRMS** (ESI) m/z: $[M+H]^+$ calc'd for $[C_{23}H_{19}N_2O]$ 339.1492; found 339.1497. **mp** (°C) 110–112.

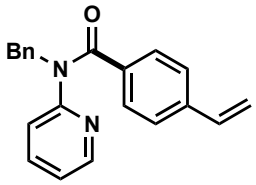
Methyl 4-[benzyl(2-pyridyl)carbamoyl]benzoate (3k)



The title compound was synthesized from *N*-benzyl-*N*-(2-pyridyl)carbamoyl fluoride **1a** (0.044 g, 0.19 mmol) and 4-methoxycarbonyl-phenylboronic acid **2k** (0.068 g, 0.38 mmol) using slightly modified conditions with 1 equiv $O{=}PPh_3$ (0.053 g, 0.19 mmol). The product was isolated as a white solid (0.028g,

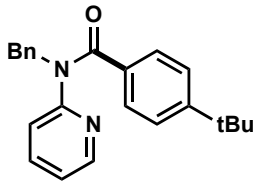
0.08 mmol, 42%) after purification by flash column chromatography: (5% Et_2O/DCM). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.42 (dd, *J* = 4.7, 1.0 Hz, 1H), 7.87 (d, *J* = 7.9 Hz, 2H), 7.41 (d, *J* = 7.9 Hz, 2H), 7.34 (d, *J* = 7.3 Hz, 3H), 7.30 – 7.26 (m, 1H), 7.24 – 7.17 (m, 2H), 7.01 (dd, *J* = 7.4, 4.8 Hz, 1H), 6.60 (d, *J* = 7.9 Hz, 1H), 5.33 (s, 2H), 3.88 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.8, 166.3, 155.4, 149.0, 140.3, 137.5, 137.3, 131.4, 129.3, 128.6, 128.4, 128.3, 127.4, 122.5, 121.4, 52.3, 51.7. **IR** (ATR, neat, cm^{-1}) 1647, 1605, 1467, 1376, 1283, 696. **HRMS** (ESI) m/z: $[M+H]^+$ calc'd for $[C_{21}H_{19}N_2O_3]$ 347.1390; found 347.1394. **mp** (°C) 111–113.

***N*-benzyl-*N*-(2-pyridyl)-4-vinyl-benzamide (3l)**



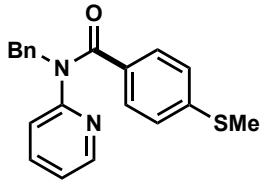
The title compound was synthesized from *N*-benzyl-*N*-(2-pyridyl)carbamoyl fluoride **1a** (0.044 g, 0.19 mmol) and 4-vinylphenylboronic acid **2l** (0.056 g, 0.38 mmol), and was isolated as a yellow solid (0.036 g, 0.11 mmol, 60%) after purification by flash column chromatography (10% Et_2O/DCM). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 5.0 Hz, 1H), 7.36 (t, *J* = 8.3 Hz, 5H), 7.32 – 7.27 (m, 3H), 7.27 – 7.18 (m, 2H), 7.02 (t, *J* = 6.2 Hz, 1H), 6.67 (d, *J* = 11.1 Hz, 1H), 6.63 (d, *J* = 9.0 Hz, 1H), 5.76 (d, *J* = 17.6 Hz, 1H), 5.37 (s, 2H), 5.30 (d, *J* = 11.0 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.5, 156.1, 149.0, 139.5, 137.9, 137.4, 136.1, 135.2, 129.3, 128.5, 128.4, 127.3, 125.9, 122.8, 121.1, 115.7, 51.8. **IR** (ATR, neat, cm^{-1}) 1644, 1606, 1467, 1435, 1375, 1320, 1282, 696. **HRMS** (ESI) m/z: $[M+H]^+$ calc'd for $[C_{21}H_{19}N_2O]$ 315.1492; found 315.1495. **mp** (°C) 90–92.

***N*-benzyl-4-tert-butyl-*N*-(2-pyridyl)benzamide (3m)**



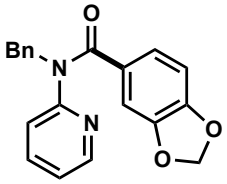
The title compound was synthesized from *N*-benzyl-*N*-(2-pyridyl)carbamoyl fluoride **1a** (0.044 g, 0.19 mmol) and 4-*tert*-Butylphenylboronic acid **2m** (0.068 g, 0.38 mmol), and was isolated as an orange solid (0.042 g, 0.12 mmol, 63%) after purification by flash column chromatography (20% Et_2O/DCM). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.45 (ddd, *J* = 4.9, 2.0, 0.9 Hz, 1H), 7.39 – 7.27 (m, 7H), 7.25 – 7.17 (m, 3H), 6.99 (ddd, *J* = 7.4, 4.9, 1.0 Hz, 1H), 6.63 (d, *J* = 8.1 Hz, 1H), 5.36 (s, 2H), 1.25 (s, 9H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.7, 156.1, 153.8, 148.7, 137.9, 137.1, 132.9, 128.7, 128.3, 128.2, 127.1, 125.0, 122.7, 120.9, 51.6, 34.8, 31.1. **IR** (ATR, neat, cm^{-1}) 1648, 1466, 1373, 1250, 980, 724, 709, 695. **HRMS** (ESI) m/z: $[M+H]^+$ calc'd for $[C_{23}H_{25}N_2O]$ 345.1961; found 345.1968. **mp** (°C) 110–112.

***N*-benzyl-4-methylsulfanyl-*N*-(2-pyridyl)benzamide (3n)**



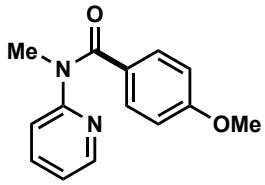
The title compound was synthesized from *N*-benzyl-*N*-(2-pyridyl)carbamoyl fluoride **1a** (0.044 g, 0.19 mmol) and 4-(methylthio)phenylboronic acid **2n** (0.064 g, 0.38 mmol), and was isolated as a yellow solid (0.042 g, 0.12 mmol, 64%) after purification by flash column chromatography (10% Et_2O/DCM). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.46 (dd, *J* = 5.3, 1.8 Hz, 1H), 7.45 – 7.27 (m, 7H), 7.24 – 7.17 (m, 1H), 7.08 – 6.98 (m, 3H), 6.61 (d, *J* = 8.1 Hz, 1H), 5.35 (s, 2H), 2.43 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.2, 156.0, 148.9, 142.1, 137.8, 137.3, 132.0, 129.4, 128.4, 128.3, 127.2, 124.9, 122.7, 121.0, 51.7, 14.9. **IR** (ATR, neat, cm^{-1}) 1646, 1585, 1469, 1370, 1324, 1234, 984, 752, 726, 695. **HRMS** (ESI) m/z: $[M+H]^+$ calc'd for $[C_{20}H_{19}N_2OS]$ 335.1213; found 335.1218. **mp** (°C) 108–110.

***N*-benzyl-*N*-(2-pyridyl)-1,3-benzodioxole-5-carboxamide (3o)**



The title compound was synthesized from *N*-benzyl-*N*-(2-pyridyl)carbamoyl fluoride **1a** (0.048 g, 0.21 mmol) and 3,4-methylenedioxyphenylboronic acid **2o** (0.070 g, 0.42 mmol), and was isolated as a yellow solid (0.054 g, 0.16 mmol, 77%) after purification by flash column chromatography (5% Et_2O/DCM). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.36 (dd, *J* = 4.9, 2.1 Hz, 1H), 7.31 – 7.27 (m, 2H), 7.20 – 7.07 (m, 4H), 6.91 (ddd, *J* = 7.4, 4.9, 1.1 Hz, 1H), 6.83 – 6.77 (m, 2H), 6.53 (d, *J* = 8.0 Hz, 1H), 6.50 (d, *J* = 8.1 Hz, 1H), 5.82 (s, 2H), 5.23 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.0, 156.3, 149.4, 149.0, 147.4, 137.9, 137.3, 129.8, 128.42, 128.37, 127.2, 124.2, 122.6, 121.0, 109.5, 107.8, 101.5, 51.8. **IR** (ATR, neat, cm^{-1}) 1645, 1434, 1239, 1033, 753, 696. **HRMS** (ESI) m/z: $[M+H]^+$ calc'd for $[C_{20}H_{17}N_2O_3]$ 333.1234; found 333.1245. **mp** (°C) 112–114.

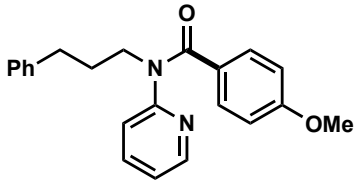
4-methoxy-*N*-methyl-*N*-(2-pyridyl)benzamide (3p)



The title compound was synthesized from *N*-methyl-*N*-(2-pyridyl)carbamoyl fluoride **1p** (0.030 g, 0.20 mmol) and 4-methoxyphenyboronic acid **2a** (0.061 g, 0.40 mmol), and was isolated as a colourless solid (0.038 g, 0.157 mmol, 78%) after purification by flash column chromatography (15% Et_2O/DCM). **^{1}H NMR** (400 MHz, $CDCl_3$) 8.49 (d, *J* = 2.8 Hz, 1H), 7.47 (td, *J* = 7.8, 1.9 Hz, 1H), 7.33 (d, *J* = 8.9 Hz, 2H),

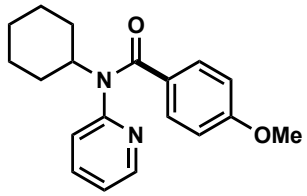
7.06 (dd, *J* = 6.4, 4.9 Hz, 1H), 6.80 (d, *J* = 8.3 Hz, 1H), 6.75 (d, *J* = 8.9 Hz, 2H), 3.80 (s, 3H), 3.61 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.7, 161.1, 157.3, 148.7, 137.3, 130.7, 128.1, 121.6, 120.6, 113.3, 55.2, 36.0. **IR** (ATR, neat, cm^{-1}) 1642, 1604, 1585, 1469, 1351, 1252, 1170, 763. **HRMS** (ESI) m/z: $[M+H]^+$ calc'd for $[C_{14}H_{15}N_2O_2]$ 243.1128; found 243.1133. **mp** (°C) 81–83. The spectral data are consistent with reported literature values.[5,6]

4-methoxy-*N*-(3-phenylpropyl)-*N*-(2-pyridyl)benzamide (3q)



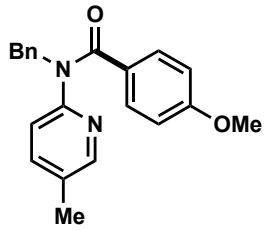
The title compound was synthesized from *N*-(3-phenylpropyl)-*N*-(2-pyridyl)carbamoyl fluoride **1q** (0.049 g, 0.19 mmol) and 4-methoxyphenyboronic acid **2a** (0.058 g, 0.38 mmol), and was isolated as a yellow solid (0.045 g, 0.13 mmol, 69%) after purification by flash column chromatography (5% Et_2O/DCM). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.50 – 8.44 (m, 1H), 7.41 (td, *J* = 7.6, 2.0 Hz, 1H), 7.29 (d, *J* = 9.0 Hz, 3H), 7.24 (s, 1H), 7.17 (d, *J* = 6.5 Hz, 3H), 7.03 (ddd, *J* = 7.5, 4.9, 1.0 Hz, 1H), 6.70 (d, *J* = 8.8 Hz, 2H), 6.67 (d, *J* = 8.0 Hz, 1H), 4.18 (t, 2H), 3.77 (s, 3H), 2.70 (t, 2H), 2.01 (p, *J* = 7.8 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.2, 161.0, 156.6, 148.9, 141.8, 137.2, 130.8, 128.4, 128.33, 128.29, 125.8, 122.6, 120.7, 113.3, 55.2, 48.3, 33.4, 29.9. **IR** (ATR, neat, cm^{-1}) 1643, 1604, 1467, 1251, 1171. 742. **HRMS** (ESI) m/z: $[M+H]^+$ calc'd for $[C_{22}H_{23}N_2O_2]$ 347.1754; found 347.1762. **mp** (°C) 85–87.

***N*-cyclohexyl-4-methoxy-*N*-(2-pyridyl)benzamide (3r)**



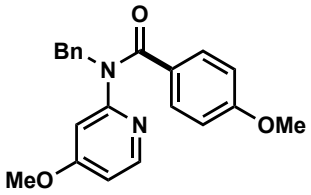
The title compound was synthesized from *N*-cyclohexyl-*N*-(2-pyridyl)carbamoyl fluoride **1r** (0.035 g, 0.16 mmol) and 4-methoxyphenyboronic acid **2a** (0.049 g, 0.32 mmol), and was isolated as a yellow solid (0.030 g, 0.096 mmol, 60%) after purification by flash column chromatography: 10% Et_2O in DCM. **^{1}H NMR** (400 MHz, $CDCl_3$) 8.56 (dd, *J* = 5.0, 1.7 Hz, 1H), 7.74 (td, *J* = 7.7, 2.0 Hz, 1H), 7.28 (s, 1H), 7.25 – 7.22 (m, 1H), 7.03 – 6.96 (m, 2H), 6.86 – 6.78 (m, 2H), 4.21 (tt, *J* = 12.0, 3.9 Hz, 1H), 3.77 (s, 3H), 2.03 (d, *J* = 11.8 Hz, 2H), 1.78 (d, *J* = 12.7 Hz, 2H), 1.59 (d, 1H), 1.46 – 1.32 (m, 4H), 1.02 (qt, *J* = 12.6, 3.5 Hz, 1H). **^{13}C NMR** (176 MHz, $CDCl_3$) δ 157.0, 153.9, 153.2, 149.0, 144.9, 137.8, 124.5, 122.63, 122.62, 114.3, 58.4, 55.8, 31.7, 26.1, 25.5. **IR** (ATR, neat, cm^{-1}) 2930, 2855, 1719, 1507, 1264, 1200, 733, 702. **HRMS** (ESI) m/z: $[M+H]^+$ calc'd for $[C_{19}H_{22}N_2O_2]$ 311.1754; found 311.1751. **mp** (°C) 72–74. The spectral data are consistent with reported literature values[7].

***N*-benzyl-4-methoxy-*N*-(5-methyl-2-pyridyl)benzamide (3s)**



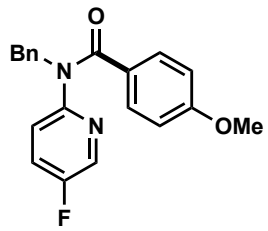
The title compound was synthesized from *N*-benzyl-*N*-(5-methyl-2-pyridyl)carbamoyl fluoride **1s** (0.046 g, 0.19 mmol) and 4-methoxyphenyboronic acid **2a** (0.058 g, 0.38 mmol), and was isolated as a yellow solid (0.053 g, 0.16 mmol, 85%) after purification by flash column chromatography (10% Et_2O/DCM). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (dt, *J* = 2.4, 0.8 Hz, 1H), 7.29 – 7.23 (m, 4H), 7.19 – 7.14 (m, 2H), 7.13 – 7.08 (m, 1H), 7.06 (ddd, *J* = 8.3, 2.5, 0.9 Hz, 1H), 6.62 (d, *J* = 8.9 Hz, 2H), 6.39 (d, *J* = 8.1 Hz, 1H), 5.23 (s, 2H), 3.67 (s, 3H), 2.15 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.2, 161.1, 153.9, 149.0, 138.0, 137.9, 130.9, 130.5, 128.34, 128.30, 128.2, 127.1, 122.3, 113.2, 55.2, 51.7, 17.9. **IR** (ATR, neat, cm^{-1}) 1642, 1601, 1478, 1248, 1172, 1027,839. **HRMS** (ESI) m/z: $[M+H]^+$ calc'd for $[C_{21}H_{21}N_2O_2]$ 333.1598; found 333.1611. **mp** (°C) 107–109.

***N*-benzyl-4-methoxy-*N*-(4-methoxy-2-pyridyl)benzamide (3t)**



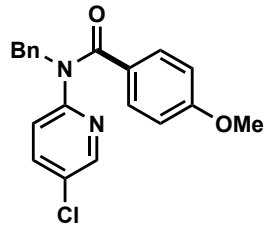
The title compound was synthesized from *N*-benzyl-*N*-(4-methoxy-2-pyridyl)carbamoyl fluoride **1t** (0.052 g, 0.20 mmol) and 4-methoxyphenyboronic acid **2a** (0.061 g, 0.40 mmol), and was isolated as a colourless solid (0.033 g, 0.095 mmol, 47%) after purification by flash column chromatography (10% Et_2O/DCM). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 5.8 Hz, 1H), 7.40 – 7.33 (m, 4H), 7.31 – 7.19 (m, 3H), 6.72 (d, *J* = 8.8 Hz, 2H), 6.54 (dd, *J* = 5.8, 2.3 Hz, 1H), 6.09 (d, *J* = 2.3 Hz, 1H), 5.30 (s, 2H), 3.76 (s, 3H), 3.52 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.3, 166.3, 161.2, 157.9, 149.5, 138.0, 130.7, 128.3, 128.29, 127.1, 113.3, 108.4, 108.0, 55.3, 55.2, 51.7 (2 signals overlapping in the aromatic region). **IR** (ATR, neat, cm^{-1}) 1592, 1562, 1250, 1169, 1025, 837. **HRMS** (ESI) m/z: $[M+H]^+$ calc'd for $[C_{21}H_{20}N_2O_3]$ 349.1547; found 349.1553. **mp** (°C) 95–97.

***N*-benzyl-*N*-(5-fluoro-2-pyridyl)-4-methoxy-benzamide (3u)**



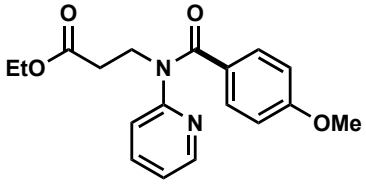
The title compound was synthesized from *N*-benzyl-*N*-(5-fluoro-2-pyridyl)carbamoyl fluoride **1u** (0.049 g, 0.20 mmol) and 4-methoxyphenyboronic acid **2a** (0.061, 0.40 mmol), and was isolated as a yellow solid (0.052 g, 0.156 mmol, 78%) after purification by flash column chromatography (10% Et_2O/DCM). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 3.0 Hz, 1H), 7.44 – 7.27 (m, 6H), 7.25 – 7.19 (m, 1H), 7.08 (td, *J* = 7.5, 3.1 Hz, 1H), 6.74 (d, *J* = 8.9 Hz, 2H), 6.60 (dd, *J* = 8.8, 3.8 Hz, 1H), 5.32 (s, 2H), 3.79 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.2, 161.3, 157.0 (d, *J* = 256.5 Hz), 152.2 (d, *J* = 3.0 Hz), 137.6, 136.5 (d, *J* = 26.2 Hz), 130.8, 128.4, 128.3, 127.8, 127.2, 124.3 (d, *J* = 20.2 Hz), 123.6 (d, *J* = 5.0 Hz), 113.4, 55.3, 51.8. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -130.32 (s). **IR** (ATR, neat, cm^{-1}) 1648, 1602, 1473, 1392, 1304, 1219, 847, 578. **HRMS** (ESI) m/z: $[M+H]^+$ calc'd for $[C_{20}H_{18}FN_2O_2]$ 337.1347; found 337.1351. **mp** (°C) 99–101.

_N_-benzyl-_N_-(5-chloro-2-pyridyl)-4-methoxy-benzamide (3v)



The title compound was synthesized from *N*-benzyl-*N*-(5-chloro-2-pyridyl)carbamoyl fluoride **1v** (0.050 g, 0.19 mmol) and 4-methoxyphenyboronic acid **2a** (0.058 g, 0.38 mmol), and was isolated as a yellow solid (0.042 g, 0.12mmol, 62%) after purification by flash column chromatography (5% Et_2O/DCM). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 2.6 Hz, 1H), 7.32 – 7.27 (m, 5H), 7.23 – 7.12 (m, 3H), 6.69 (d, *J* = 8.8 Hz, 2H), 6.50 (d, *J* = 8.5 Hz, 1H), 5.27 (s, 2H), 3.73 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.3, 161.4, 154.6, 147.4, 137.7, 136.8, 130.9, 128.4, 128.3, 128.2, 127.7, 127.2, 123.1, 113.5, 55.3, 51.6. **IR** (ATR, neat, cm^{-1}) 1647, 1496, 1461, 1252, 1238, 1171, 1112, 838, 697. **HRMS** (ESI) m/z: $[M+H]^+$ calc'd for $[C_{20}H_{18}ClN_2O_2]$ 353.1051; found 353.1054. **mp** (°C) 94–96.

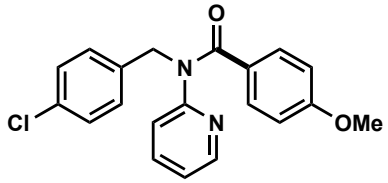
Ethyl 3-[(4-methoxybenzoyl)-(2-pyridyl)amino]propanoate (3w)



The title compound was synthesized from *N*-[(3-ethoxy-3-oxopropyl)]-*N*-(2-pyridyl)carbamoyl fluoride **1w** (0.048 g, 0.20 mmol) and 4-methoxyphenyboronic acid **2a** (0.061 g, 0.40 mmol), and was isolated as a yellow solid (0.043 g, 0.13 mmol, 65%) after purification by flash column chromatography (10% Et_2O/DCM). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 2.9 Hz, 1H), 7.41 (td, *J* = 7.6, 1.9 Hz, 1H), 7.31 – 7.27 (m, 2H), 7.03 (dd, *J* = 7.6, 4.9 Hz, 1H), 6.73 – 6.66 (m, 3H), 4.38 (t, *J* = 7.3 Hz, 2H), 4.06 (q, *J* = 7.1 Hz, 2H), 3.75 (s, 3H), 2.77 (t, *J* = 7.3 Hz, 2H), 1.20 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.9, 170.4, 161.3, 156.6, 149.0, 137.4, 130.9, 128.1, 122.6, 121.0, 113.4, 60.6, 55.4, 44.7, 33.5, 14.3.

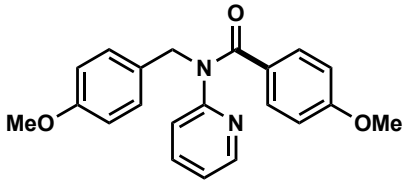
IR (ATR, neat, cm^{-1}) 1729, 1645, 1264, 737, 702. **HRMS** (ESI) m/z: $[M+H]^+$ calc'd for $[C_{18}H_{21}N_2O_4]$ 329.1496; found 329.1502. **mp** (°C) 80–82.

_N_-[(4-chlorophenyl)methyl]-4-methoxy-_N_-(2-pyridyl)benzamide (3x)



The title compound was synthesized from *N*-[(4-chlorophenyl)methyl]-*N*-(2-pyridyl)carbamoyl fluoride **1x** (0.053 g, 0.20 mmol) and 4-methoxyphenyboronic acid **2a** (0.061 g, 0.40 mmol), and was isolated as a yellow solid (0.061 g, 0.17 mmol, 87%) after purification by flash column chromatography (5% Et_2O/DCM). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.50 (dd, *J* = 4.9, 1.9 Hz, 1H), 7.41 – 7.35 (m, 5H), 7.24 (s, 1H), 7.04 (dd, *J* = 6.9, 5.3 Hz, 1H), 6.79 (s, 1H), 6.74 (d, *J* = 8.8 Hz, 2H), 6.60 (d, *J* = 8.0 Hz, 1H), 5.34 (s, 2H), 3.79 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.3, 161.4, 156.2, 148.9, 137.2, 136.5, 132.9, 131.0, 129.9, 128.5, 127.7, 122.7, 120.9, 113.4, 55.3, 51.0. **IR** (ATR, neat, cm^{-1}) 1646, 1603, 1467, 1250, 1219, 1172, 842. **HRMS** (ESI) m/z: $[M+H]^+$ calc'd for $[C_{20}H_{19}ClN_2O_2]$ 353.1051; found 353.1056. **mp** (°C) 104–106.

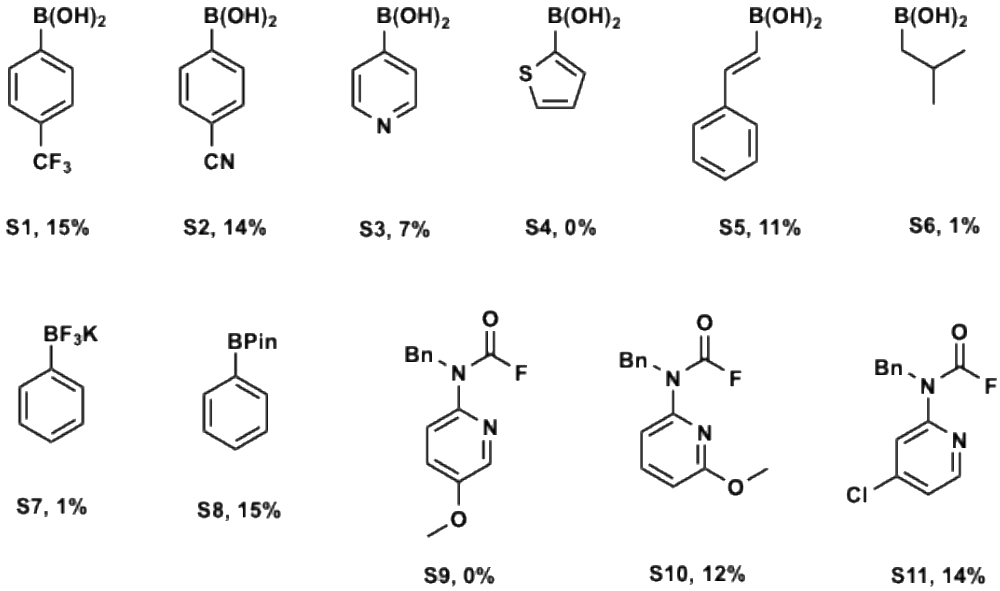
4-methoxy-_N_-[(4-methoxyphenyl)methyl]-_N_-(2-pyridyl)benzamide (3y)



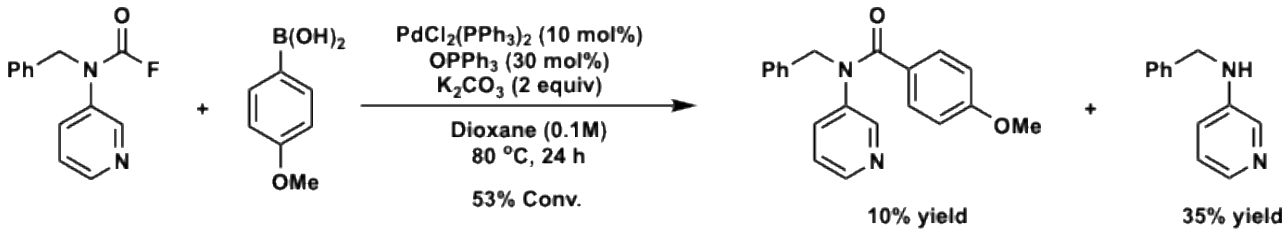
The title compound was synthesized from *N*-[(4-methoxyphenyl)methyl]-*N*-(2-pyridyl)carbamoyl fluoride **1y** (0.026 g, 0.10 mmol) and 4-methoxyphenyboronic acid **2a** (0.030 g, 0.20 mmol), and was isolated as a yellow solid (0.017 g, 0.048 mmol, 48%) after purification by flash column chromatography (5% Et_2O/DCM). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.44 – 8.38 (m, 1H), 7.30 – 7.20 (m, 5H), 6.94 (ddd, *J* = 7.4, 4.9, 1.1 Hz, 1H), 6.73 (d, *J* = 8.9 Hz, 2H), 6.64 (d, *J* = 9.0 Hz, 2H), 6.49 (dd, *J* = 8.1, 1.1 Hz, 1H), 5.22 (s, 2H), 3.70 (2 overlapping singlets, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.3, 161.3, 158.9, 156.5, 148.9, 137.3, 131.0, 130.2, 129.9, 128.2, 123.0, 120.9, 113.8, 113.4, 55.4, 55.3, 51.2. **IR** (ATR, neat, cm^{-1}) 1604, 1510, 1467,1247, 1150, 1030. **HRMS** (ESI) m/z: $[M+H]^+$ calc'd for $[C_{21}H_{21}N_2O_3]$ 349.1547; found 349.1537. **mp** (°C) 108–110.

4.3 Poorly Reactive Substrates

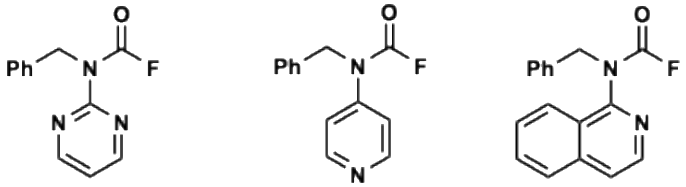
Substrates depicted below showed poor reactivity (<15% yield) under the optimized reaction conditions.



4.4 Use of Other *N*-directing Groups



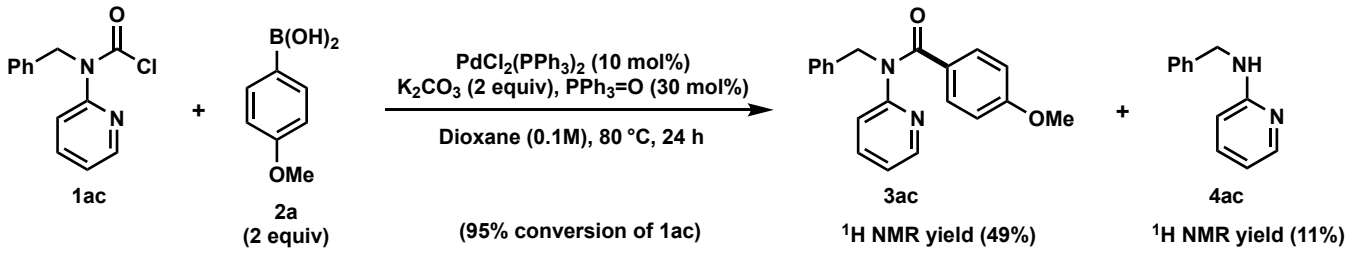
- The following carbamoyl fluorides were either challenging to synthesize and/or purify:



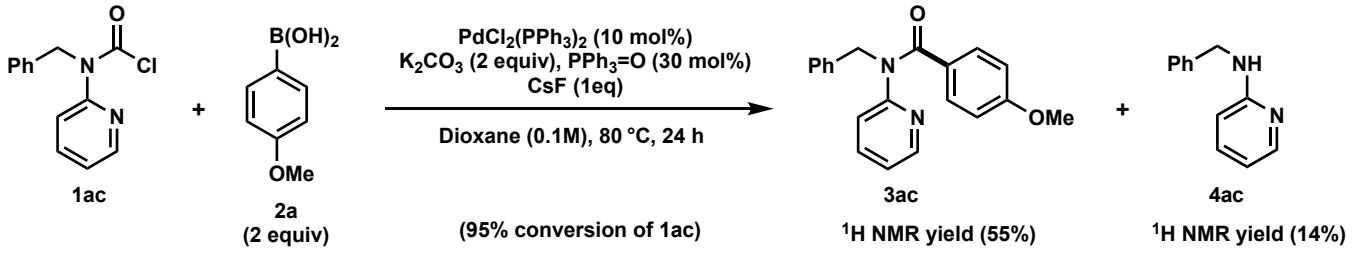
5 Control Experiments

Carbamoyl Chloride Reactivity

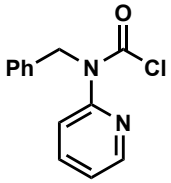
Without external fluoride source: To a 1-dram vial equipped with a stir bar, **1ac** (0.037 g, 0.15 mmol, 1equiv), 4-methoxyphenyboronic acid **2** (0.045 g, 0.30 mmol, 2 equiv), K_2CO_3 (0.041 g, 0.30 mmol, 2 equiv), $OPPh_3$ (0.012 g, 0.045 mmol, 0.30 equiv), and $PdCl_2(PPh_3)_2$ (0.010 g, 0.015 mmol, 10 mol%) were added. The vial was evacuated and backfilled with N_2 (3x), and 1,4-dioxane (0.1 M, 1 mL) was added to the vial. The reaction was sealed with a Teflon-lined screwcap, immersed in an 80 °C oil bath and heated for 24 h. The vial was removed from the oil bath, washed with EtOAc and filtered through celite. The crude mixture was diluted with EtOAc, filtered through celite, and concentrated under reduced pressure. A known amount of 1,3,5-trimethoxybenzene as an internal standard was added and the crude material was solved in $CDCl_3$ for quantitative ^1H NMR analysis.



With external fluoride source: To a 1-dram vial equipped with a stir bar, **1ac** (0.032 g, 0.13 mmol, 1 equiv), 4-methoxyphenyboronic acid **2** (0.039 g, 0.26 mmol, 2 equiv), K_2CO_3 (0.036 g, 0.26 mmol, 2 equiv), $OPPh_3$ (0.011 g, 0.04 mmol, 0.30 equiv), $PdCl_2(PPh_3)_2$ (0.009 g, 0.013 mmol, 10 mol%) and CsF (0.020 g, 0.13 mmol, 1 equiv) were added. The vial was evacuated and backfilled with N_2 (3x), and 1,4-dioxane (0.1 M, 1.3 mL) was then added. The reaction was sealed with a Teflon-lined screwcap, immersed in an 80 °C oil bath and heated for 24 h. the vial was removed from the oil bath, washed with EtOAc and filtered through celite. The crude mixture was diluted with EtOAc, filtered through celite, and concentrated under reduced pressure. A known amount of 1,3,5-trimethoxybenzene as an internal standard was added and the crude material was solved in $CDCl_3$ for quantitative ^1H NMR analysis.



***N*-Benzyl-*N*-(2-pyridyl)carbamoyl chloride (1ac)**

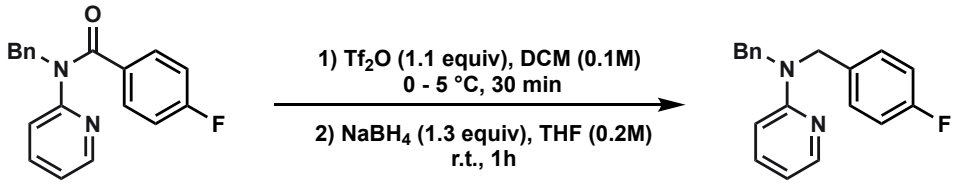


The title compound was synthesized according to the reported procedure using *N*-benzyl-2-pyridinamine (0.368 g, 2 mmol, 1eq).[8] The product was isolated as a colourless oil (0.064 g, 0.26 mmol, 13%) after purification by flash column chromatography (20% EtOAc/hexanes). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 2.9 Hz, 1H), 7.68 (td, *J* = 7.8, 2.0 Hz, 1H), 7.32 – 7.27 (m, 3H), 7.25 – 7.20 (m, 4H), 5.20 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.4, 149.1, 138.1, 135.9, 128.6, 128.1, 127.9, 123.0, 54.5 (Due to coincidental overlap, 2 signals are less in the aromatic region). **IR** (ATR, neat, cm^{-1}) 1732, 1586, 1468, 1455, 1372, 1236, 1194, 705. **HRMS** (ESI) m/z: $[M+H]^+$ calc'd for $[C_{13}H_{12}ClN_2O]$ 247.0633; found 247.0630.

6 Derivatization of Products

6.1 Synthesis of Tertiary Amine **3ab** from **3b**

***N*-benzyl-4-fluoro-benzyl-*N*-2-pyridinamine (3ba)**



3b **3ba, 47%**

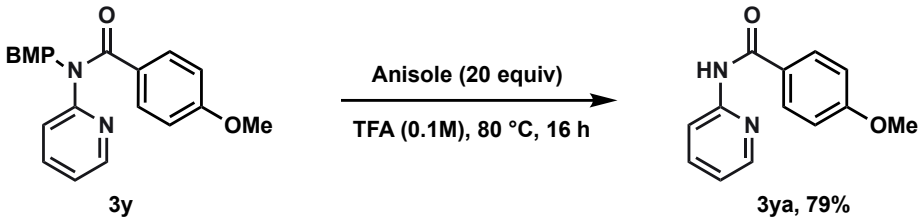
Following a literature procedure,[9] a 1-dram vial equipped with a stir bar was charged with *N*-benzyl-4-fluoro-*N*-(2-pyridyl)benzamide **3b** (0.030 g, 0.10 mmol, 1 equiv) and anhydrous CH_2Cl_2 (1mL, 0.1 M). To this solution, Tf_2O (18.5 µL, 0.11 mmol, 1.1 equiv) was added at 0 °C and the reaction was stirred for 30 minutes. $NaBH_4$ (0.005 g, 0.13 mmol, 1.3 equiv) was added in one portion, and then THF (0.5 mL) was added dropwise. After stirring for 1 h, the reaction was quenched by H_2O and the solution was brought to pH=11 using saturated sodium bicarbonate. The aqueous layer was extracted with Et_2O, and the combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The crude material was purified by column chromatography (10% EtOAc/hexanes) to give **3ba** as a white solid (0.014 g, 0.048 mmol, 48%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.35 – 7.30 (m, 1H), 7.24 – 7.11 (m, 7H), 6.92 (t, *J* = 8.7 Hz, 2H), 6.53 (dd, *J* = 7.5, 4.5 Hz, 1H), 6.39 (d, *J* = 8.5 Hz, 1H), 4.70 (d, *J* = 15.1 Hz, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.0 (d, *J* = 245.4 Hz), 158.5, 148.1, 138.2, 137.5, 134.2 (d, *J* = 3.0 Hz), 128.8 (d, *J* = 8.0 Hz), 128.6, 127.0, 127.0, 115.4 (d, *J* = 22.2 Hz), 112.4, 105.9, 50.9, 50.2. **^{19}F NMR** (377

MHz, $CDCl_3$) δ -116.14 (s, 1F). **IR** (ATR, neat, cm^{-1}) 2922, 2852, 1593, 1506, 1487, 1435, 1415, 1219, 1154, 768, 730, 697. **HRMS** (ESI) m/z: $[M+H]^+$ calc'd for $[C_{19}H_{17}FN_2]$ 293.1449; found 293.1447.

6.2 Synthesis of Secondary Amide **3ya** from **3y**

4-methoxy-*N*-(2-pyridyl)benzamide (3ya)



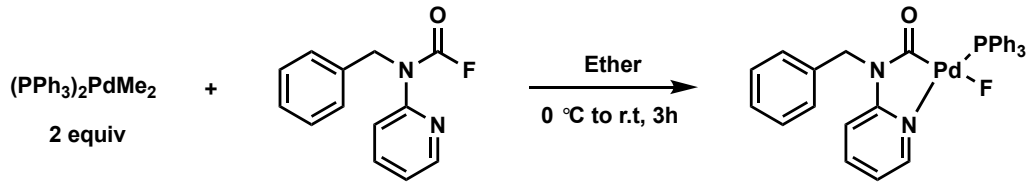
3y 3ya, 79%

Following the literature procedure,[10] a 1-dram vial equipped with a stir bar was charged with amide **3y** (0.035 g, 0.10 mmol, 1 equiv), TFA (0.1 M, 1 mL) and anisole (0.22 mL, 2 mmol, 20 equiv). The vial was submerged in an 80 °C oil bath and heated for 16 h. The reaction was quenched by NEt_3 to pH = 8, extracted by DCM (3x), and washed with water and brine. The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The crude material was purified by column chromatography (10→40% EtOAc/hexanes) to give **3ya** as a yellow solid (0.018 g, 0.079 mmol, 79%). The spectral data are consistent with reported literature values.[11]

7 Mechanistic Studies

7.1 Synthesis and Characterization Data for Carbamoyl Pd–F Complex **1ae**

Method A: Direct Synthesis of Carbamoyl Pd–F Complex

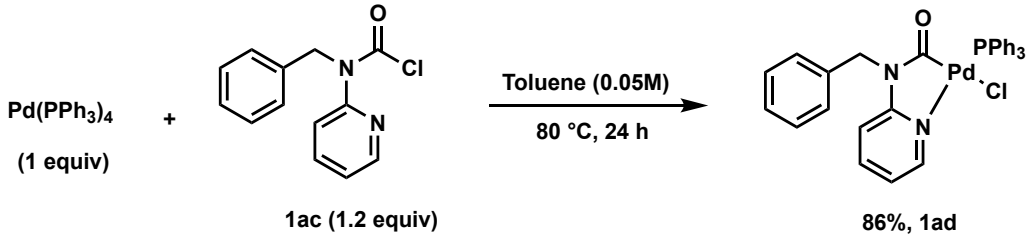


61%, 1ae

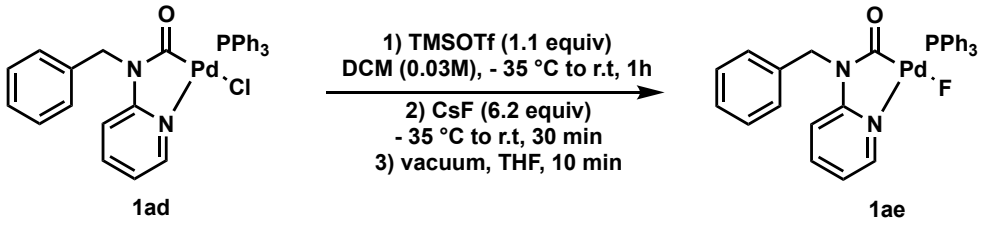
In a N_2-filled glovebox, $PdMe_2(PPh_3)_2$ (0.090 g, 0.137 mmol, 2.03 equiv) was added to a 20 mL vial equipped with a stir bar. A separate 20 mL vial was charged with carbamoyl fluoride **1a** (0.009 g, 0.040 mmol, 1.0 equiv) and Et_2O (0.01 M, 5 mL) was added. Both vials were cooled to -35 °C in the glovebox freezer. The solution of carbamoyl fluoride in ether was added to the solid $PdMe_2(PPh_3)_2$ resulting in a white suspension. The mixture was stirred for 3 hours and slowly came to room temperature, with periodic venting every hour to prevent gas build-up. With constant stirring, 10 mL of cold pentane was then added resulting in a brown precipitate. The supernatant was decanted, and the resulting solid was washed with ether until the washes became colourless. The resulting brown solid was then dried under reduced pressure

to yield **1ae** as a brown powder (0.025 mg, 0.041 mmol, 61%). The product was crystallized by cooling a saturated toluene solution to yield colourless crystals suitable for XRD analysis. Although this method was suitable to obtain **1ae**, we found that purification of the residual $Pd(PPh_3)_n$ species from the reaction mixture was challenging and the yields were not reproducible. Hence, we opted for a two-step approach starting from carbamoyl chloride **1ac** (see Method B below).

Method B: Synthesis of Carbamoyl Pd–F Complex via Cl-to-F Exchange



In a N_2-filled glovebox, $Pd(PPh_3)_4$ (0.762 g, 0.659 mmol, 1 equiv), carbamoyl chloride **1ac** (0.195 g, 0.792 mmol, 1.2 equiv) and toluene (0.05 M, 12 mL) were added to a 50 mL round bottom flask equipped with a stir bar. The vial was submerged in an 80 °C oil bath and heated for 24 h. The reaction mixture was cooled down to -10 °C, the precipitate was isolated by suction filtration, and washed with cold toluene and ether. Carbamoyl Pd–Cl complex **1ad** was isolated as a white solid (0.347 g, 0.564 mmol, 86%).
*Characterization data for **1ad**:* **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.33 (dd, 1H), 7.87 – 7.71 (m, 6H), 7.66 (ddd, *J* = 8.6, 7.3, 1.8 Hz, 1H), 7.49 – 7.33 (m, 9H), 7.32 – 7.21 (m, 3H), 7.14 – 7.07 (m, 2H), 6.95 (ddd, *J* = 7.1, 5.7, 1.2 Hz, 1H), 6.72 (d, *J* = 8.4 Hz, 1H), 4.75 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.9, 155.3, 148.6, 140.9, 135.8, 134.8, 134.7, 131.4, 130.9, 130.4, 130.3, 128.6, 128.0, 127.9, 127.3, 126.5, 116.5, 108.3, 44.2. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 37.95 (s, 1P). **HRMS** (ESI) m/z: $[M–Cl]^+$ calc'd for $[C_{31}H_{26}N_2OPPd^+]$ 579.0812 found 579.0824. Note: Ionization of **1ad** for HRMS analysis resulted in fragmentation (via loss of halide) and a very weak parent ion signal.

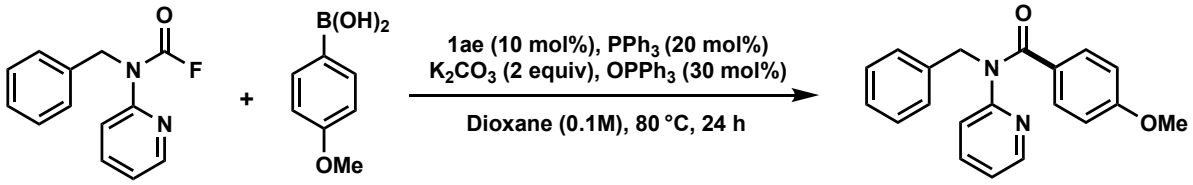


In a N_2-filled glovebox, a 20 mL vial equipped with a stir bar was charged with **1ad** (0.068 g, 0.110 mmol, 1 equiv) and DCM (0.04 M, 3 mL). To separate 1-dram vial, a solution of TMSOTf (0.027 g, 0.122 mmol, 1.1 equiv) in DCM (0.12 M, 1 mL) was prepared. Both vials were cooled in the glovebox freezer (-35 °C). After 30 minutes, both vials were removed from the glovebox freezer and the solution of TMSOTf in DCM was added dropwise to the vial containing **1ad** in DCM and stirred for 1 h at room temperature. CsF (0.104 g, 0.680 mmol, 5 equiv) was then added to the reaction mixture as a solid. After stirring for 15

minutes, DCM was removed under reduced pressure, THF (0.11 M, 1 mL) was added, and the solution was mixed for 10 minutes. The reaction was concentrated, washed with toluene, filtered through glass filter paper, and dried under reduced pressure to yield **1ae** as a white solid (0.042 g, 0.07 mmol, 64%).[12]

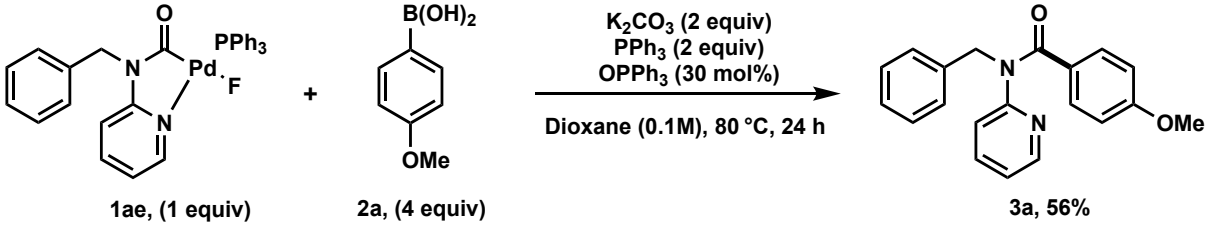
*Characterization data for **1ae*** (trans isomer): **^{1}H NMR** (700 MHz, $CDCl_3$) δ 8.85 (s, 1H), 7.72 (dd, *J* = 11.8, 7.4 Hz, 6H), 7.60 (t, *J* = 7.9 Hz, 1H), 7.42 – 7.38 (m, 3H), 7.37 – 7.32 (m, 6H), 7.23 (t, *J* = 7.5 Hz, 2H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.07 (d, *J* = 7.3 Hz, 2H), 6.90 (t, *J* = 6.5 Hz, 1H), 6.66 (d, *J* = 8.5 Hz, 1H), 4.69 (s, 2H). **^{13}C NMR** (176 MHz, $CDCl_3$) δ 175.8 (d, *J* = 80.96 Hz), 155.1, 146.2 (d, *J* = 8.8 Hz), 140.9, 136.0, 134.7 (d, *J* = 12.32 Hz), 130.6 (d, *J* = 1.76 Hz), 130.3, 128.7, 128.3 (d, *J* = 10.56 Hz), 127.3, 126.6, 116.2, 108.2, 44.0. **^{19}F NMR** (659 MHz, $CDCl_3$) δ -250.48 (s, 1F). **^{31}P NMR** (121 MHz, $CDCl_3$) δ 32.65 (s, 1P). **HRMS** (ESI) m/z: $[M–F]^+$calc'd for $[C_{31}H_{26}N_2OPPd^+]$ 579.0812 found 579.0822. Note: Ionization of **1ae** for HRMS analysis resulted in fragmentation (via loss of halide) and a very weak parent ion signal.

7.2 Catalytic Activity of Pd–F Complex **1ae** under Optimized Conditions



The reaction set-up was done in a N_2-filled glovebox. A 1-dram vial equipped with a stir bar was charged with carbamoyl fluoride **1a** (0.021 g, 0.092 mmol, 0.9 equiv), 4-methoxyphenyboronic acid **2** (0.031 g, 0.204 mmol, 2 equiv), K_2CO_3 (0.028 g, 0.204 mmol, 2 equiv), $OPPh_3$ (0.009 g, 0.031 mmol, 0.30 equiv), PPh_3 (0.005 g, 0.020 mmol, 0.2 equiv), and Pd complex **1ae** (0.006 g, 0.01 mmol, 10 mol%) 1,4-dioxane (0.1 M, 1 mL) was then added and the reaction was sealed with a Teflon-lined screwcap, immersed in an 80 °C oil bath and heated for 24 h. The vial was removed from the oil bath, washed with EtOAc and filtered through celite. The crude mixture was diluted with EtOAc, filtered through celite, and concentrated under reduced pressure. A known amount of 1,3,5-trimethoxybenzene as an internal standard was added and the crude material was solved in $CDCl_3$ for quantitative ^{1}H NMR analysis.

7.3 Stoichiometric Reactivity of Pd–F Complex **1ae**



The reaction set-up was done in a N_2-filled glovebox. A 1-dram vial equipped with a stir bar was charged with Pd complex **1ae** (0.024 g, 0.040 mmol, 1 equiv), 4-methoxyphenyboronic acid **2a** (0.024 g, 0.160 mmol, 4 equiv), K_2CO_3 (0.011 g, 0.080 mmol, 2 equiv), $OPPh_3$ (0.003 g, 0.012 mmol, 0.30 equiv), and PPh_3 (0.021 g, 0.080 mmol, 2 equiv). 1,4-dioxane (0.1 M, 0.4 mL) was then added and the reaction was sealed with a Teflon-lined screwcap, immersed in an 80 °C oil bath and heated for 24 h. The vial was removed from the oil bath, washed with EtOAc and filtered through celite. The crude mixture was diluted with EtOAc, filtered through celite, and concentrated under reduced pressure. A known amount of 1,3,5-trimethoxybenzene as an internal standard was added and the crude material was solved in $CDCl_3$ for quantitative ^1H NMR analysis.

8 Crystallographic Data

8.1 Crystal structure of Pd–Cl Complex **1ad**

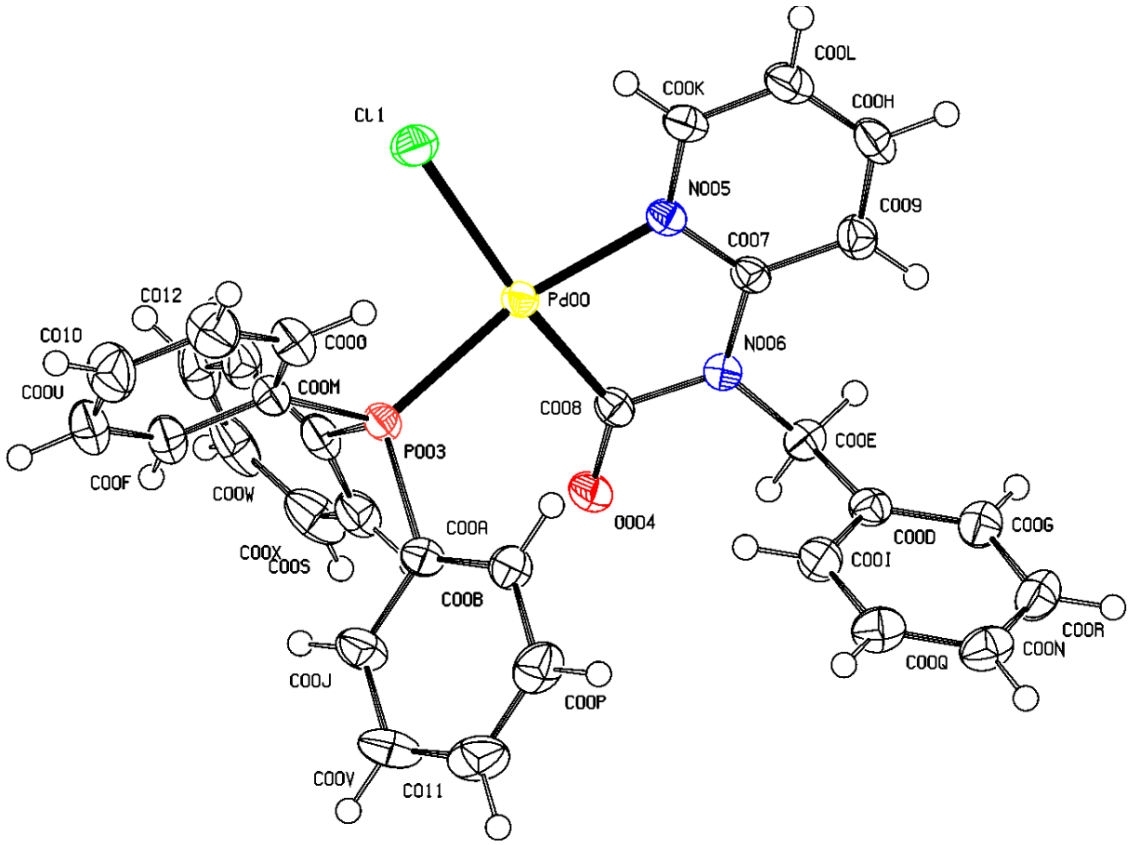


Table S8. Crystal data and structure refinement for **1ad**

Identification code	JJL694
Empirical formula	$C_{35}H_{34}ClN_2O_3PPd$
Formula weight	703.46
Temperature/K	173.00

Crystal system	monoclinic
Space group	P21/n
a/Å	11.0260(6)
b/Å	16.8504(11)
c/Å	17.4371(11)
α/°	90
β/°	99.551(2)
γ/°	90
Volume/Å^3	3194.8(3)
Z	4
ρ_{calc}g/cm^3	1.463
μ/mm^{-1}	0.752
F(000)	1440
Crystal size/mm^3	0.1 × 0.1 × 0.02
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.086 to 56.63
Index ranges	$-14 \leq h \leq 14$, $-22 \leq k \leq 22$, $-23 \leq l \leq 23$
Reflections collected	61357
Independent reflections	7953 [R_{int} = 0.0770, R_{sigma} = 0.0469]
Data/restraints/parameters	7953/0/334
Goodness-of-fit on F^2	1.048
Final R indexes [I>=2σ (I)]	R1 = 0.0480, wR2 = 0.1182
Final R indexes [all data]	R1 = 0.0760, wR2 = 0.1405
Largest diff. peak/hole / e Å^{-3}	1.76/-1.11

8.2 Crystal structure of Pd–F Complex **1ae**

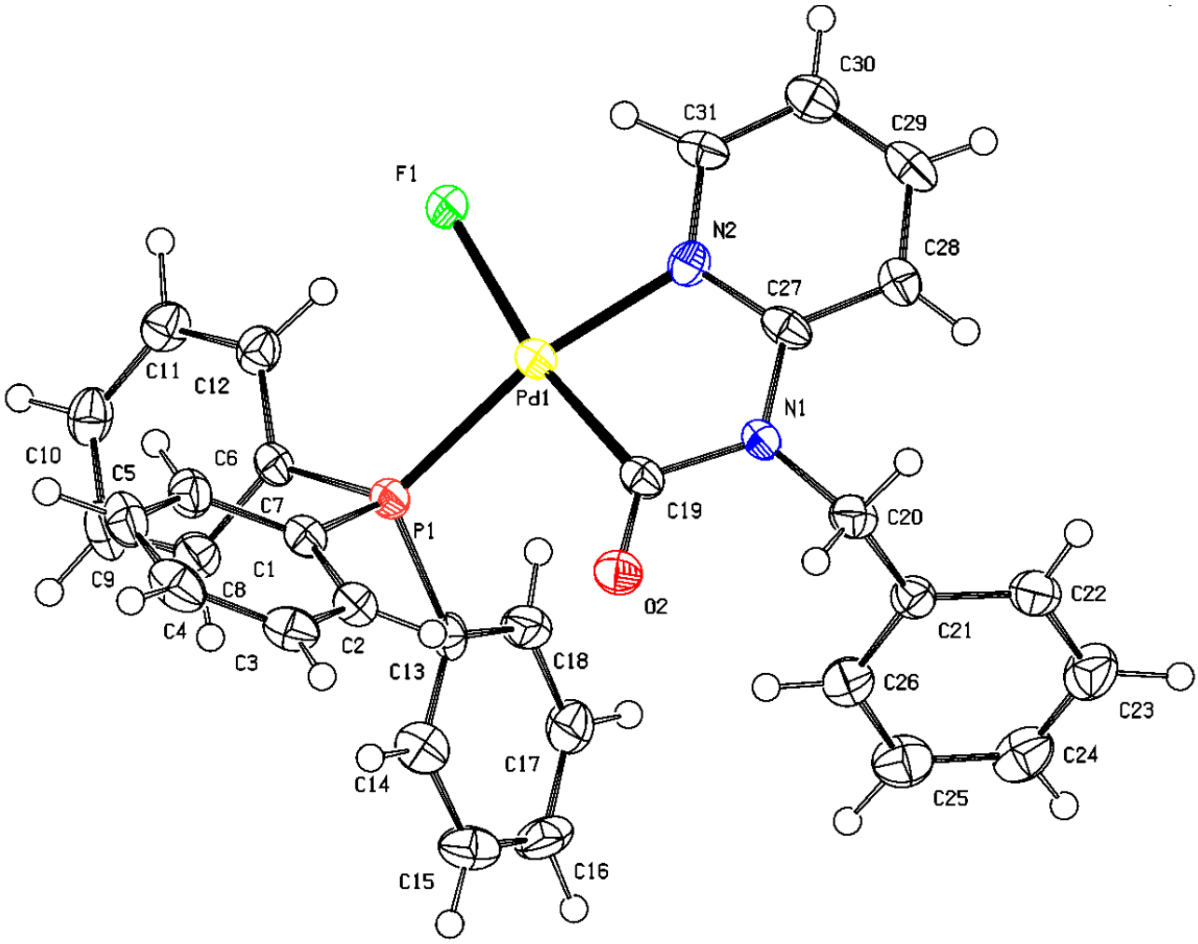


Table S9. Crystal data and structure refinement for **1ae**

Identification code	JJL724
Empirical formula	$C_{31}H_{26}FN_2OPPd$
Formula weight	598.91
Temperature/K	173(2)
Crystal system	triclinic
Space group	P-1
a/Å	9.6832(8)
b/Å	11.7011(9)
c/Å	13.0161(10)
α/°	73.358(3)
β/°	74.524(3)
γ/°	66.061(3)
Volume/Å^3	1272.21(18)
Z	2
ρ_{calc}g/cm^3	1.563

μ/mm^{-1}	0.828
F(000)	608.0
Crystal size/mm^3	0.04 × 0.02 × 0.02
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.572 to 52.316
Index ranges	$-12 \leq h \leq 12$, $-14 \leq k \leq 14$, $-16 \leq l \leq 16$
Reflections collected	36104
Independent reflections	5083 [R_{int} = 0.1798, R_{sigma} = 0.1170]
Data/restraints/parameters	5083/0/431
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0602, wR_2 = 0.0900
Final R indexes [all data]	R_1 = 0.1153, wR_2 = 0.1095
Largest diff. peak/hole / e $Å^{-3}$	0.80/-0.85

9 References

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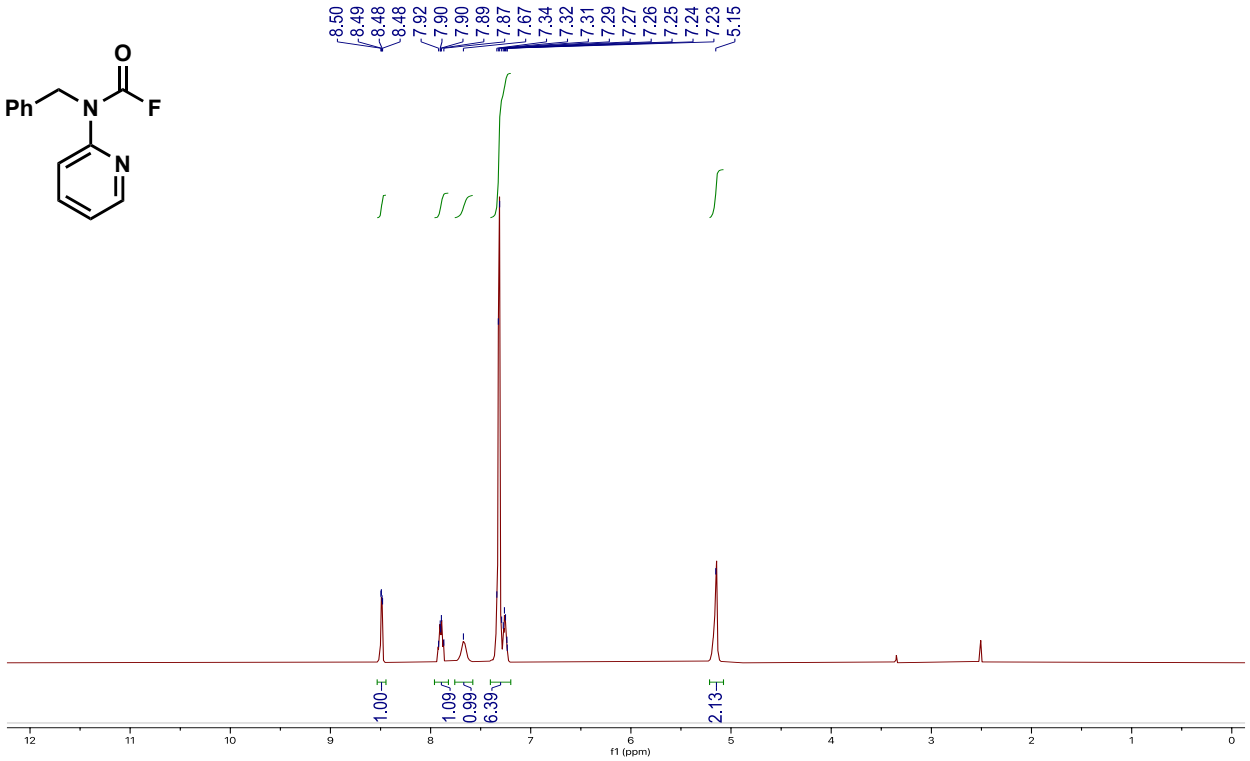
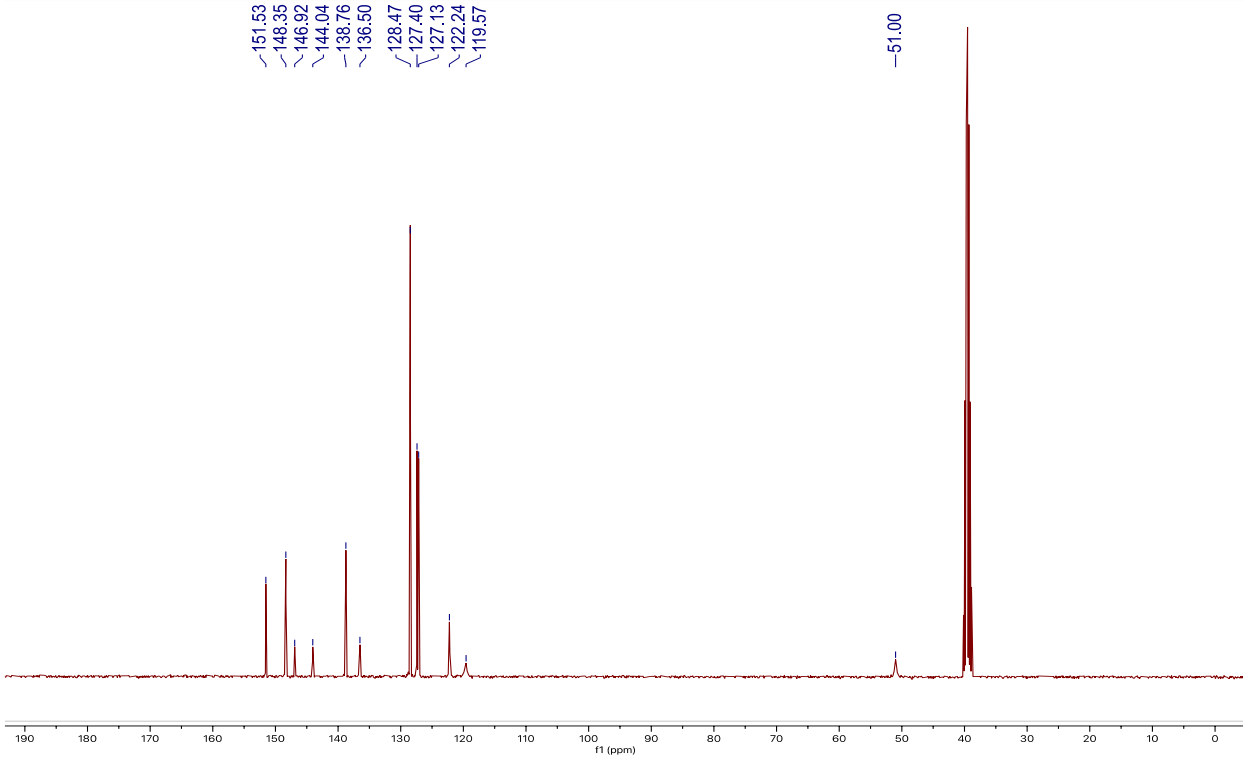
10 NMR Spectra

_N_-Benzyl-_N_-(2-pyridyl)carbamoyl fluoride (1a)

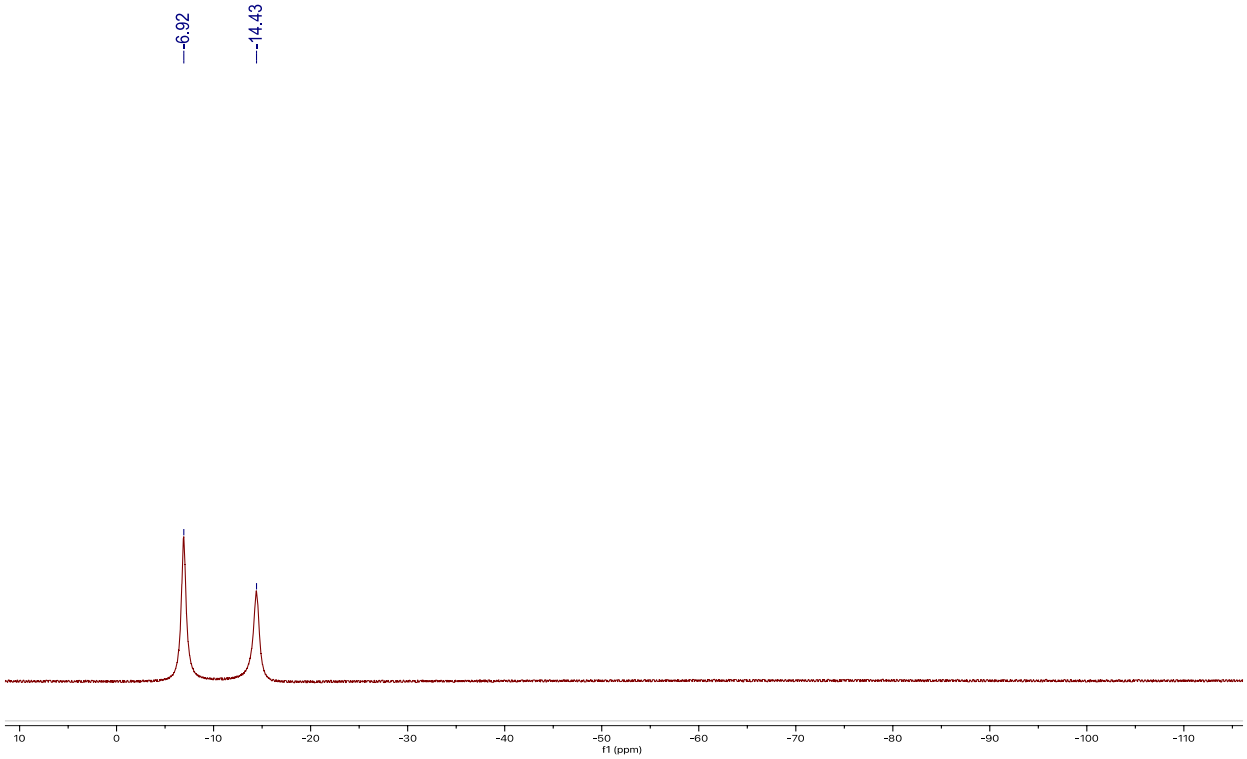
^{1}H NMR Spectrum DMSO (400 MHz)



^{13}C NMR Spectrum DMSO (101 MHz)

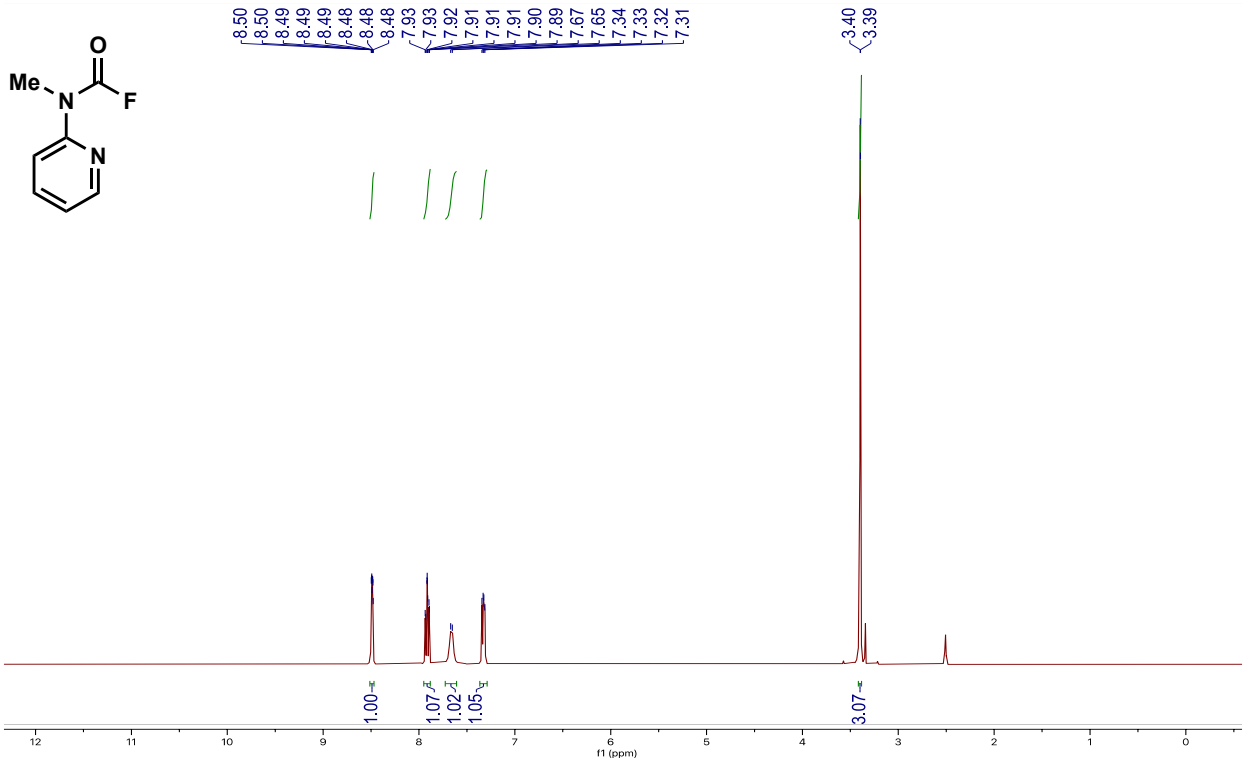


^{19}F NMR Spectrum $CDCl_3$ (377 MHz)

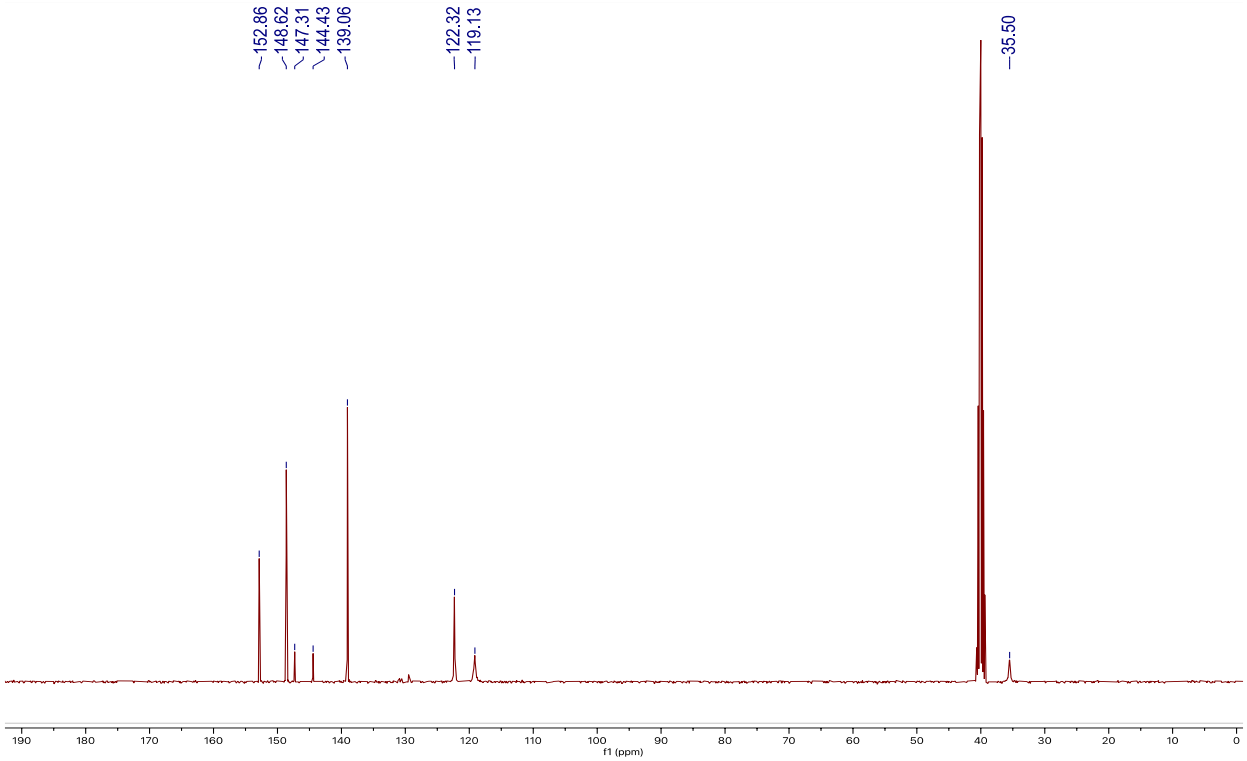


***N*-Methyl-*N*-(2-pyridyl)carbamoyl fluoride (1p)**

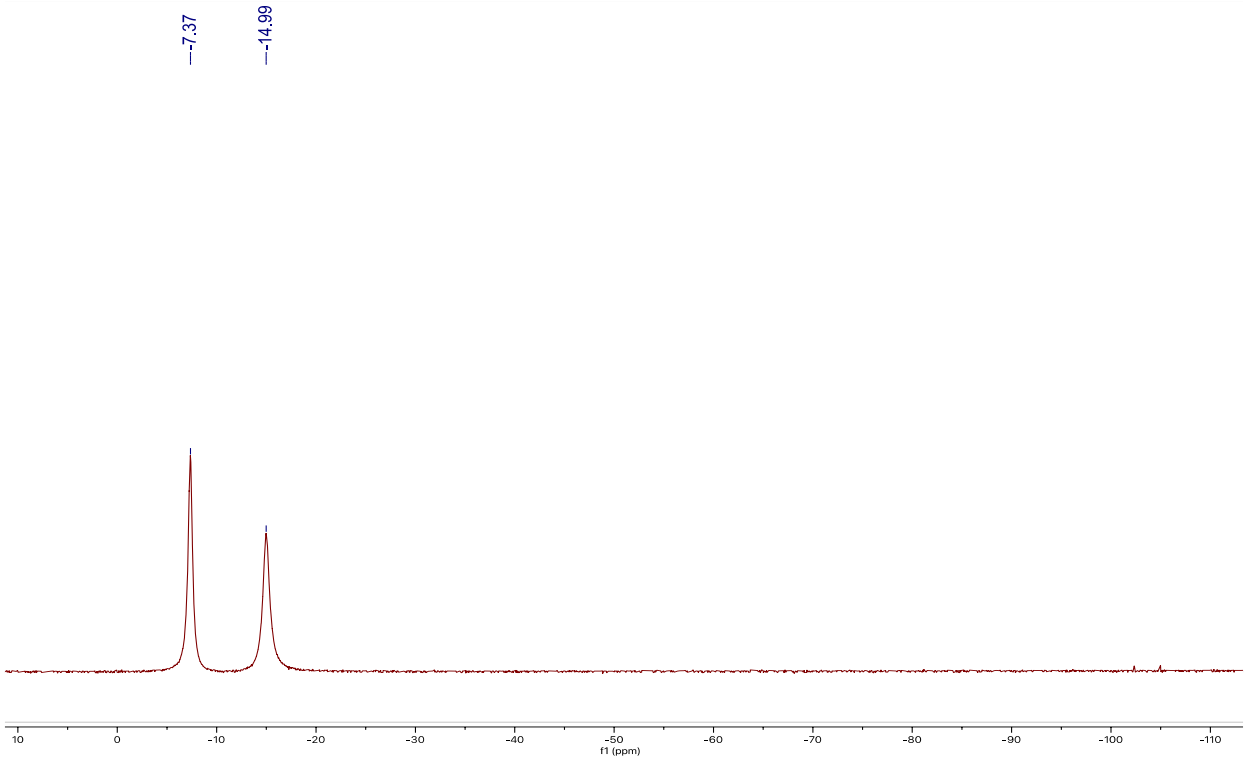
^{1}H NMR Spectrum DMSO (400 MHz)



^{13}C NMR Spectrum DMSO (101 MHz)

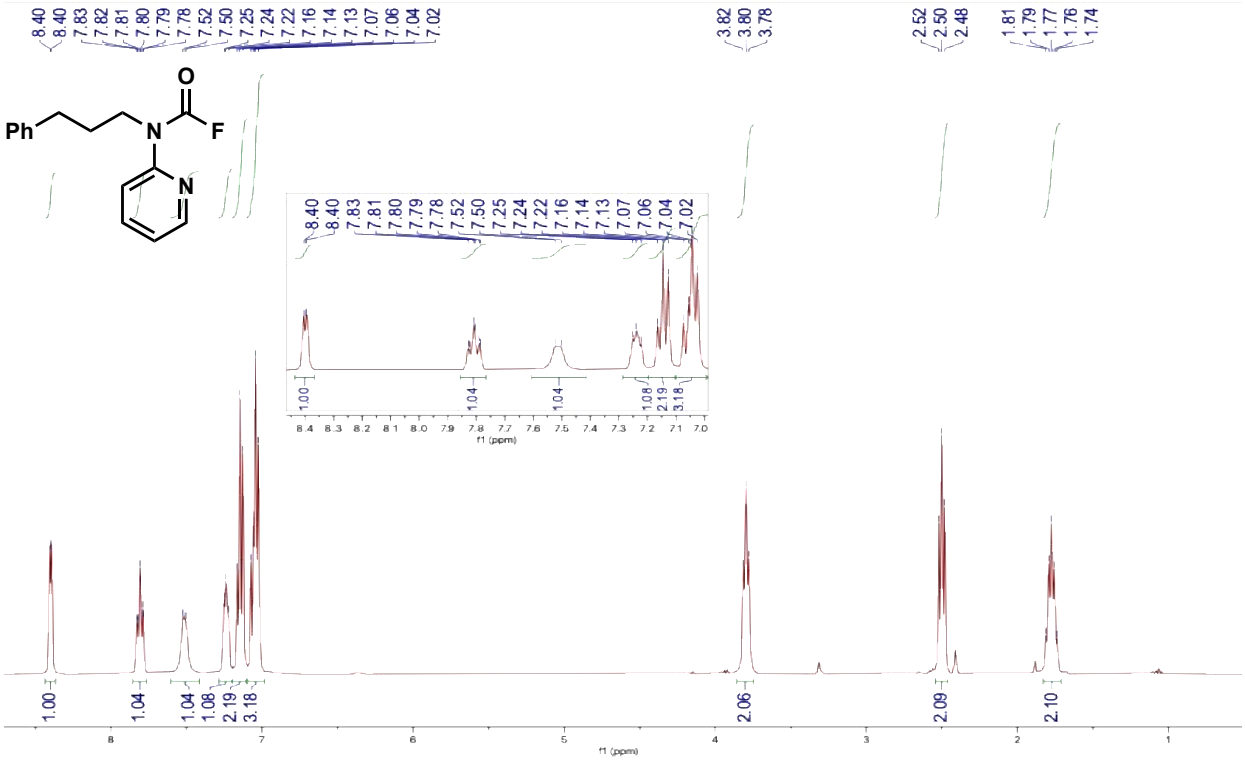


^{19}F NMR Spectrum $CDCl_3$ (377 MHz)

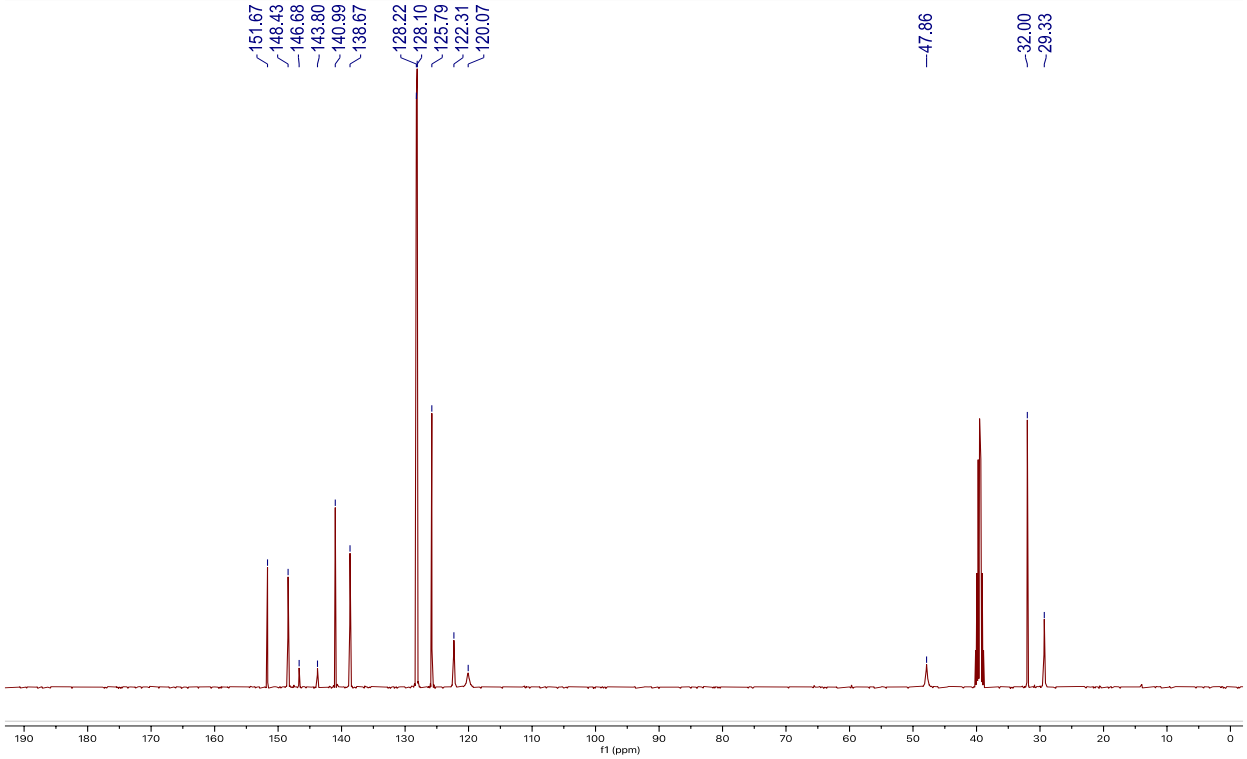


_N_-(3-phenylpropyl)-_N_-(2-pyridyl)carbamoyl fluoride (1q)

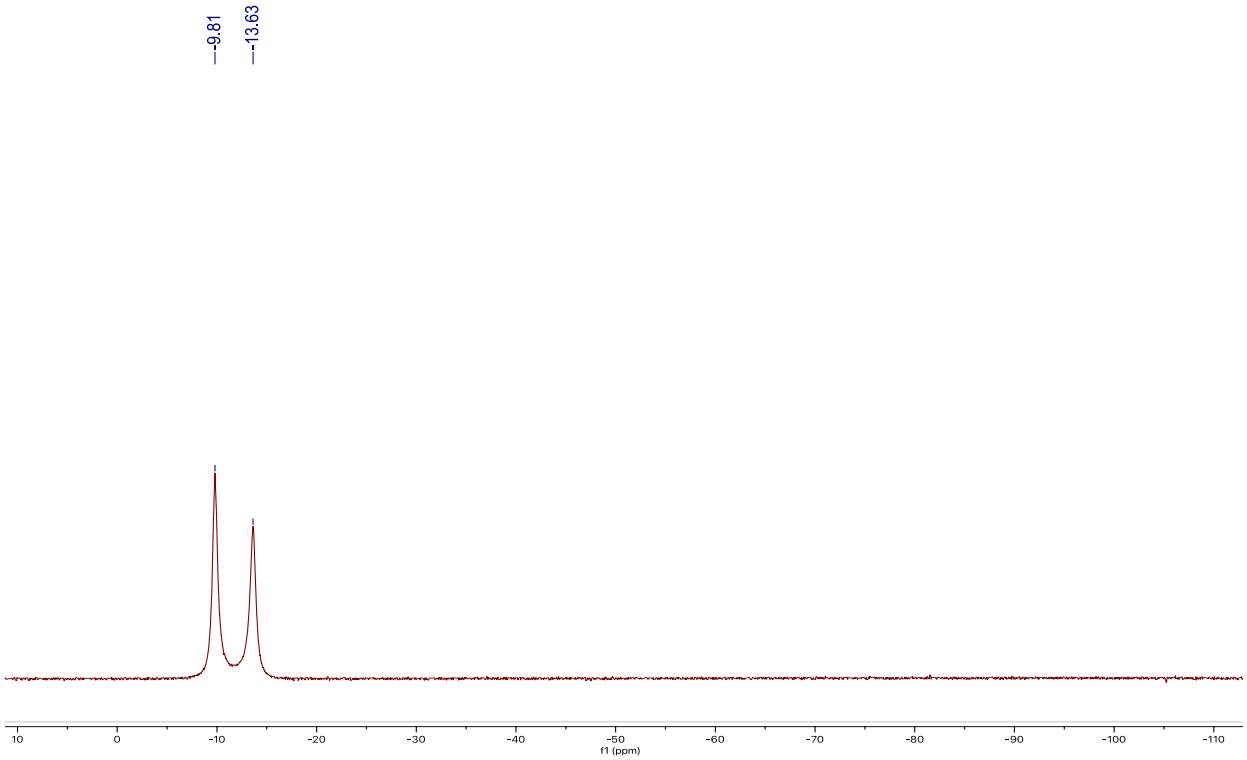
^{1}H NMR Spectrum DMSO (400 MHz)



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

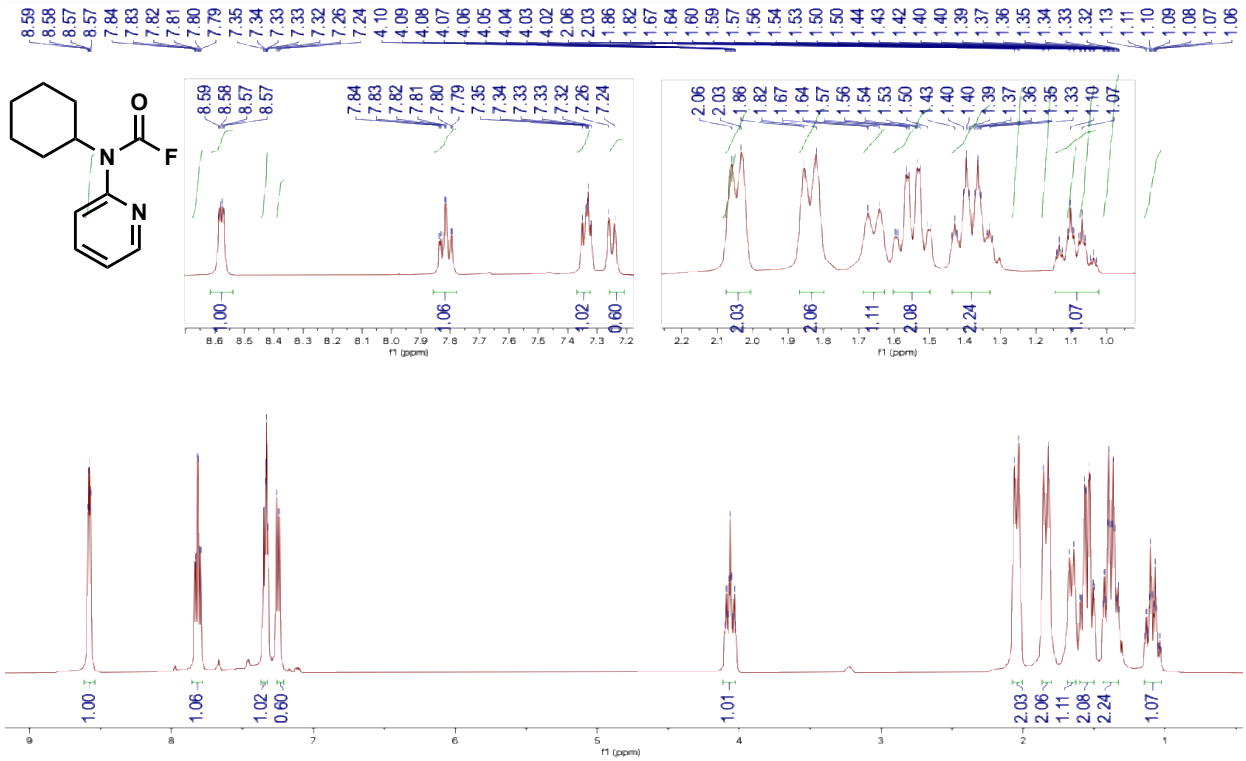


^{19}F NMR Spectrum $CDCl_3$ (377 MHz)

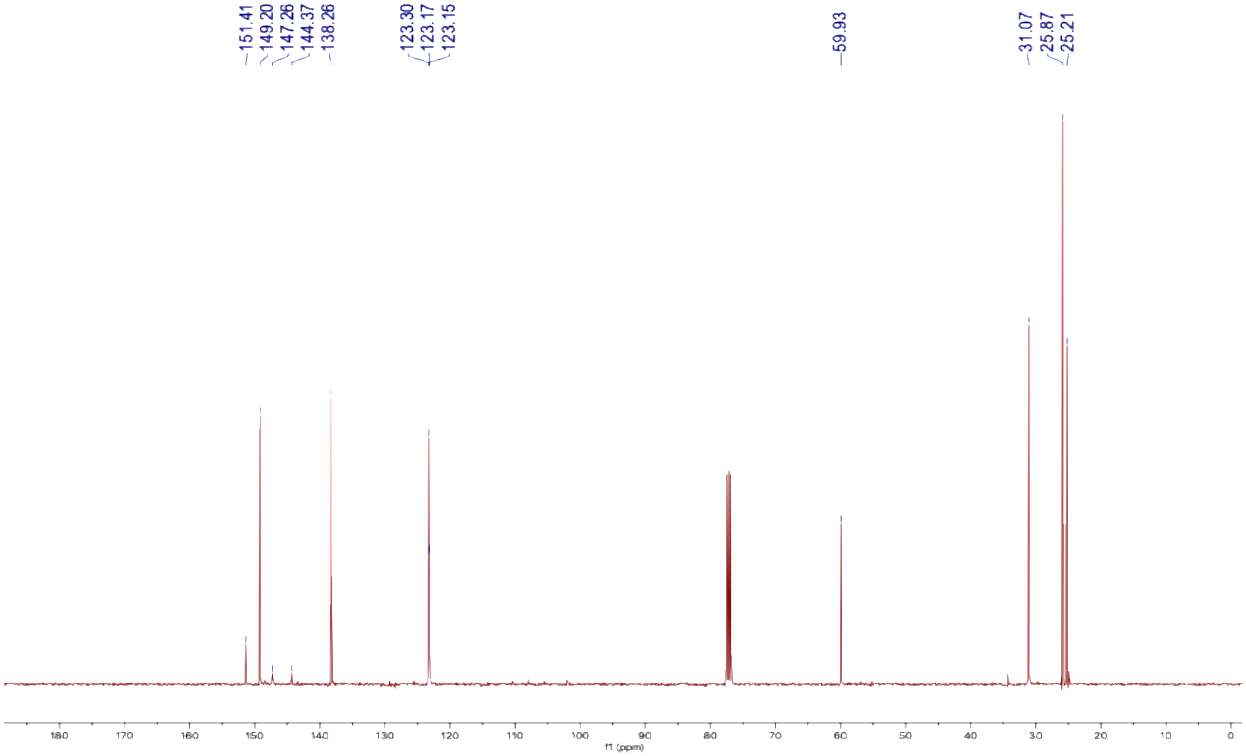


_N_-cyclohexyl-_N_-(2-pyridyl)carbamoyl fluoride (1r)

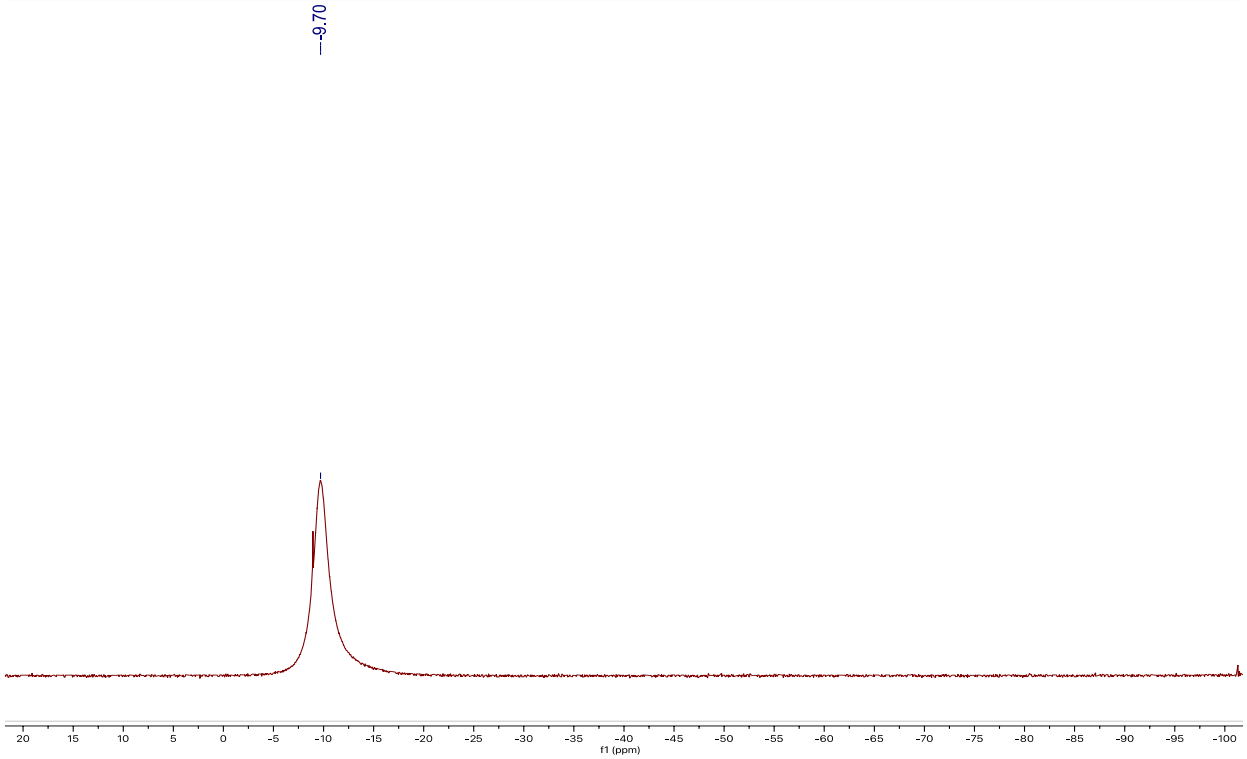
^{1}H NMR Spectrum $CDCl_3$ (400 MHz)



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

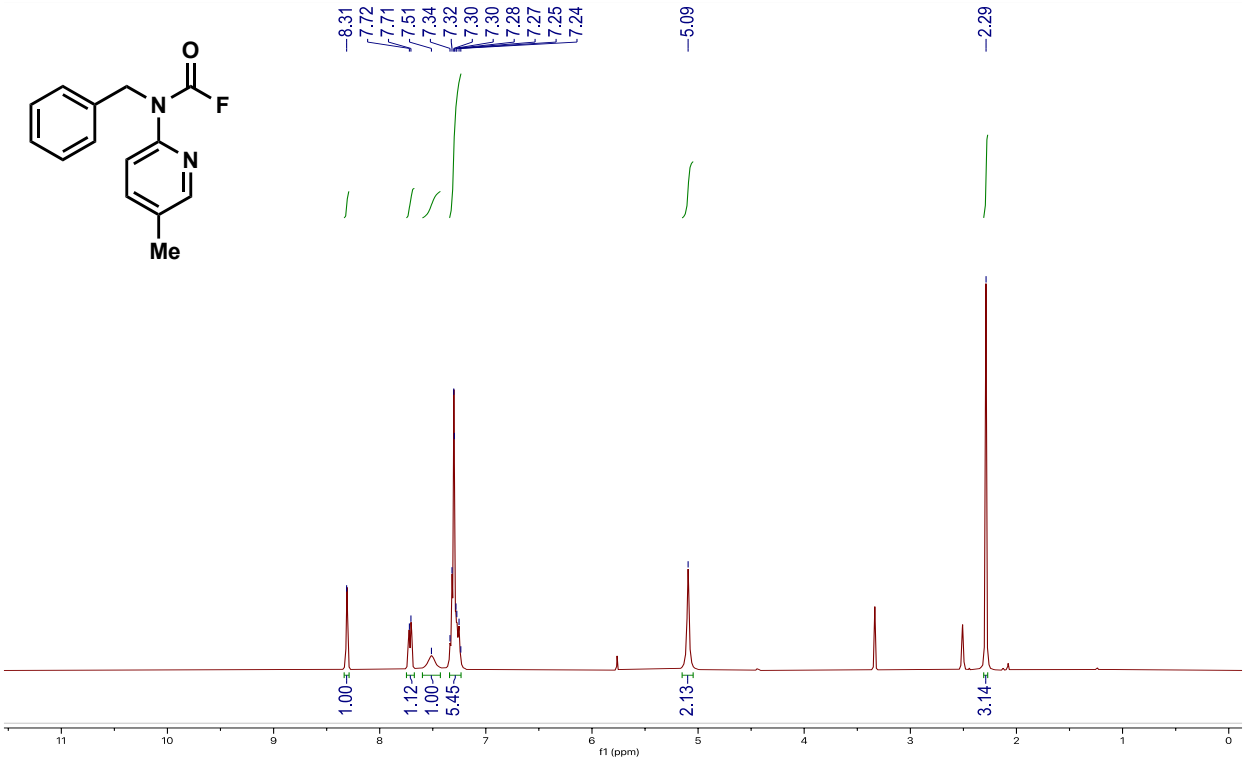


^{19}F NMR Spectrum $CDCl_3$ (377 MHz)

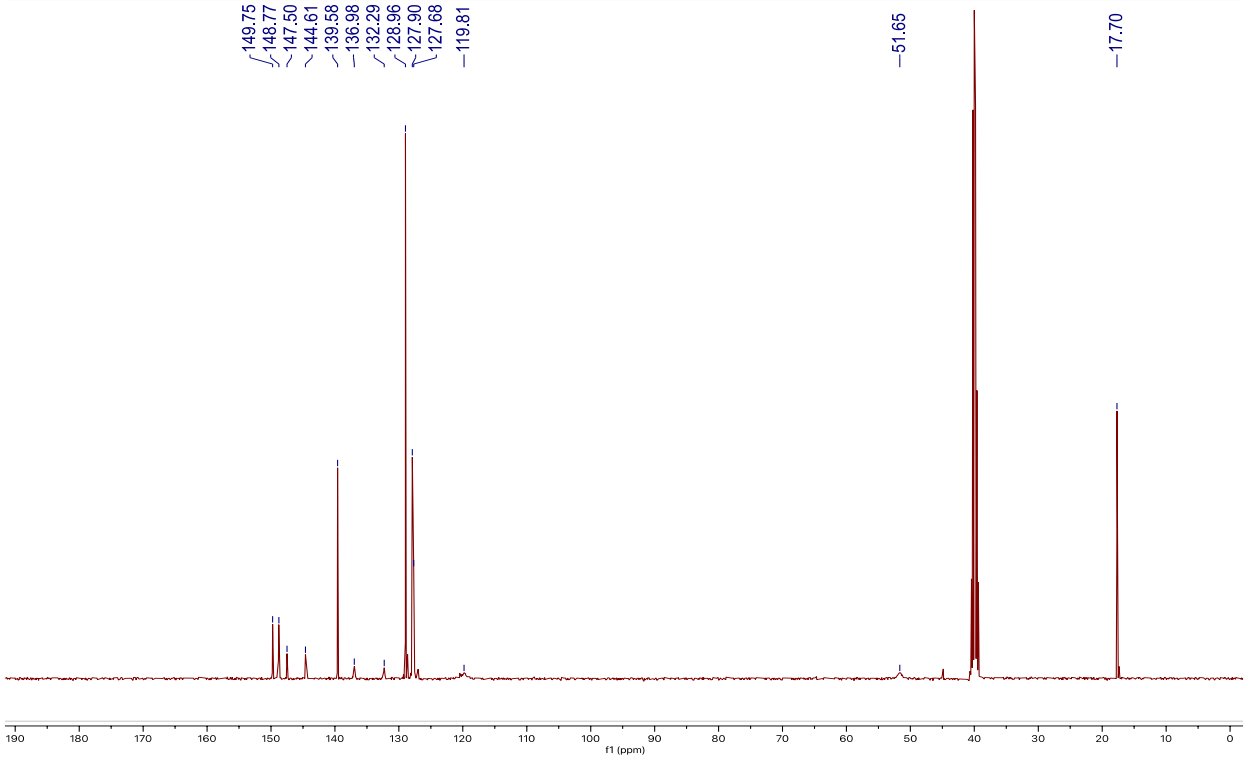


_N_-benzyl-_N_-(5-methyl-2-pyridyl)carbamoyl fluoride (1s)

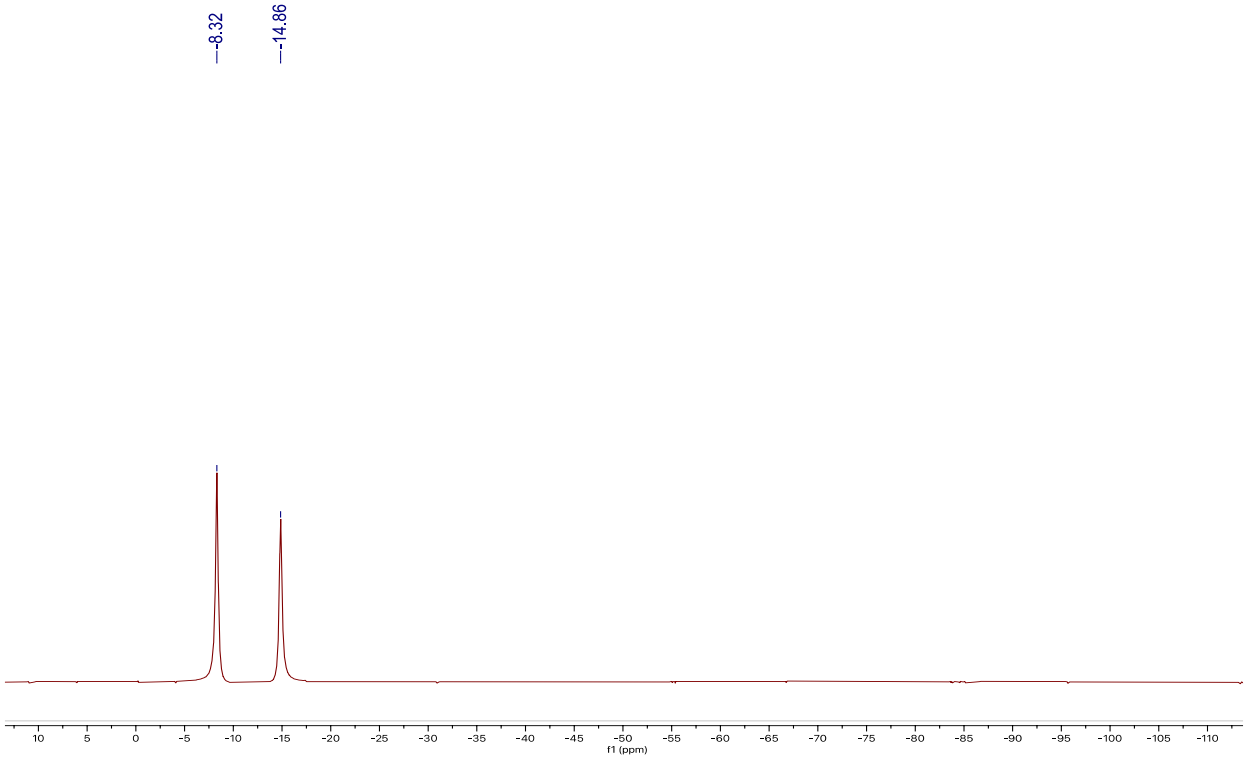
^{1}H NMR Spectrum DMSO (400 MHz)



^{13}C NMR Spectrum DMSO (101 MHz)

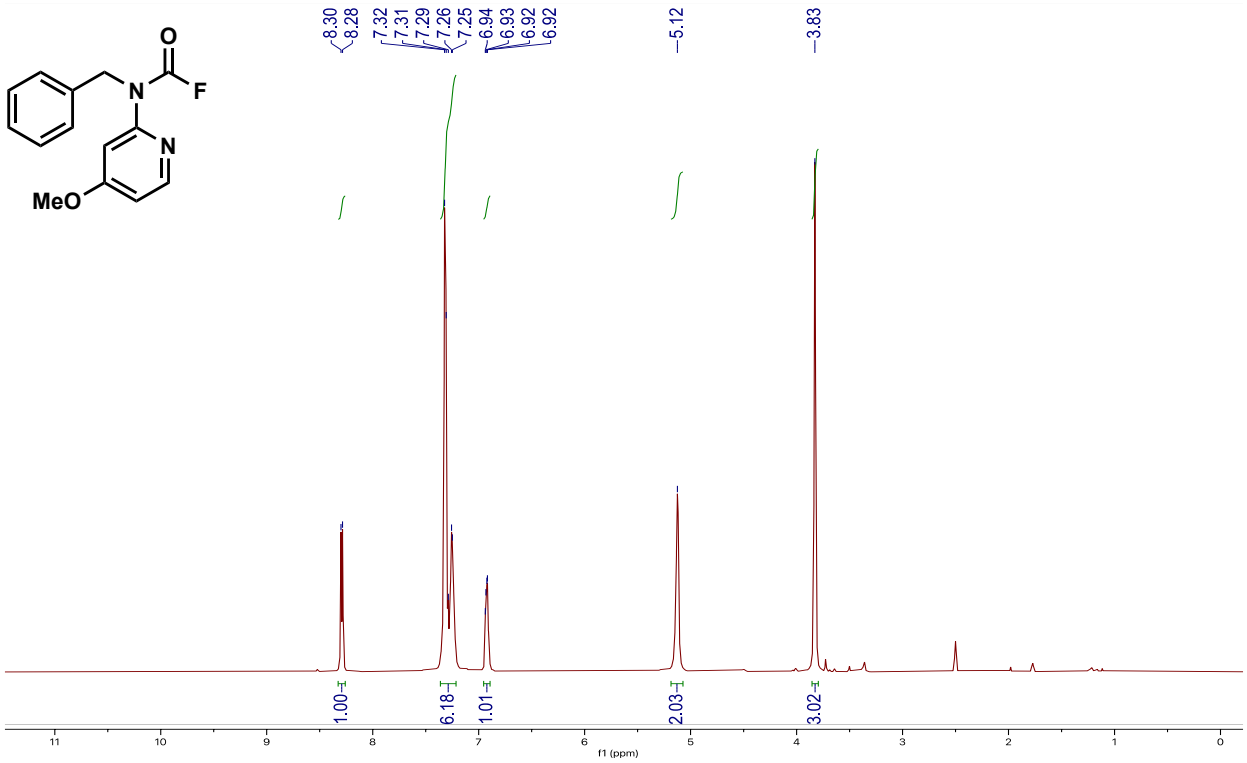


^{19}F NMR Spectrum $CDCl_3$ (377 MHz)

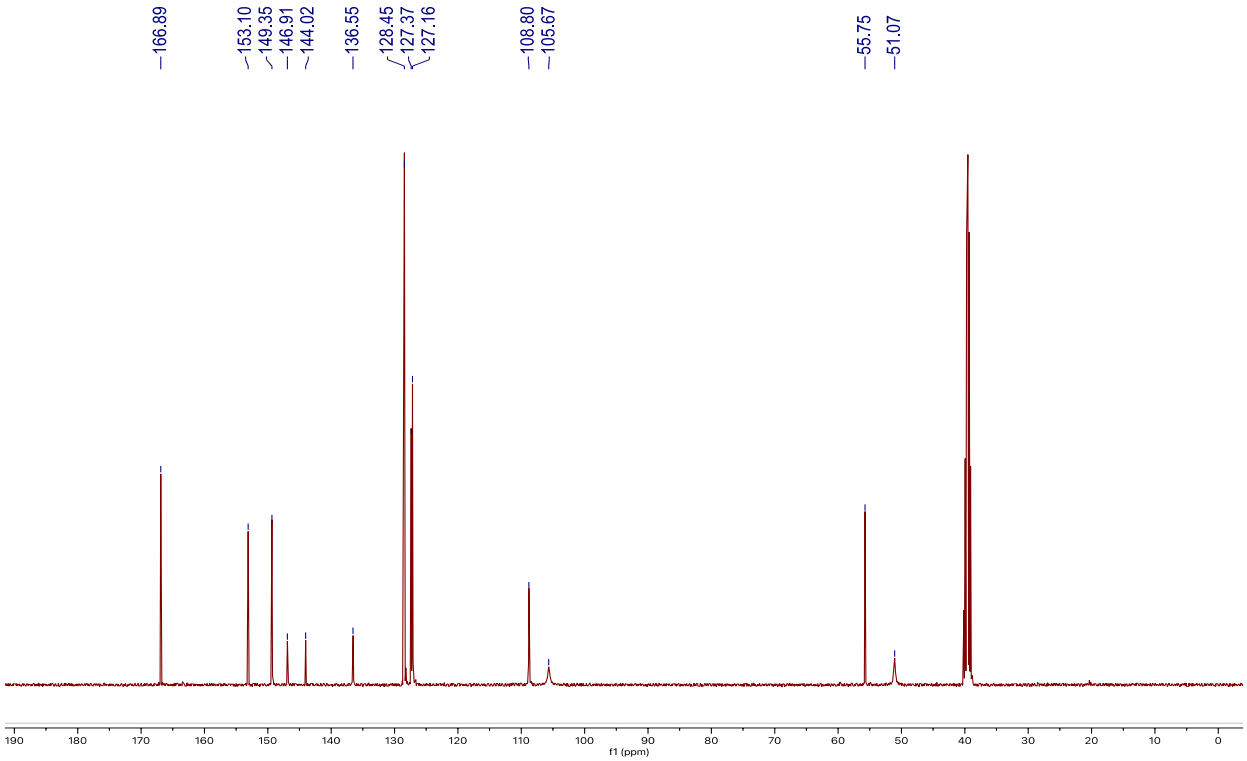


***N*-benzyl-*N*-(4-methoxy-2-pyridyl)carbamoyl fluoride (1t)**

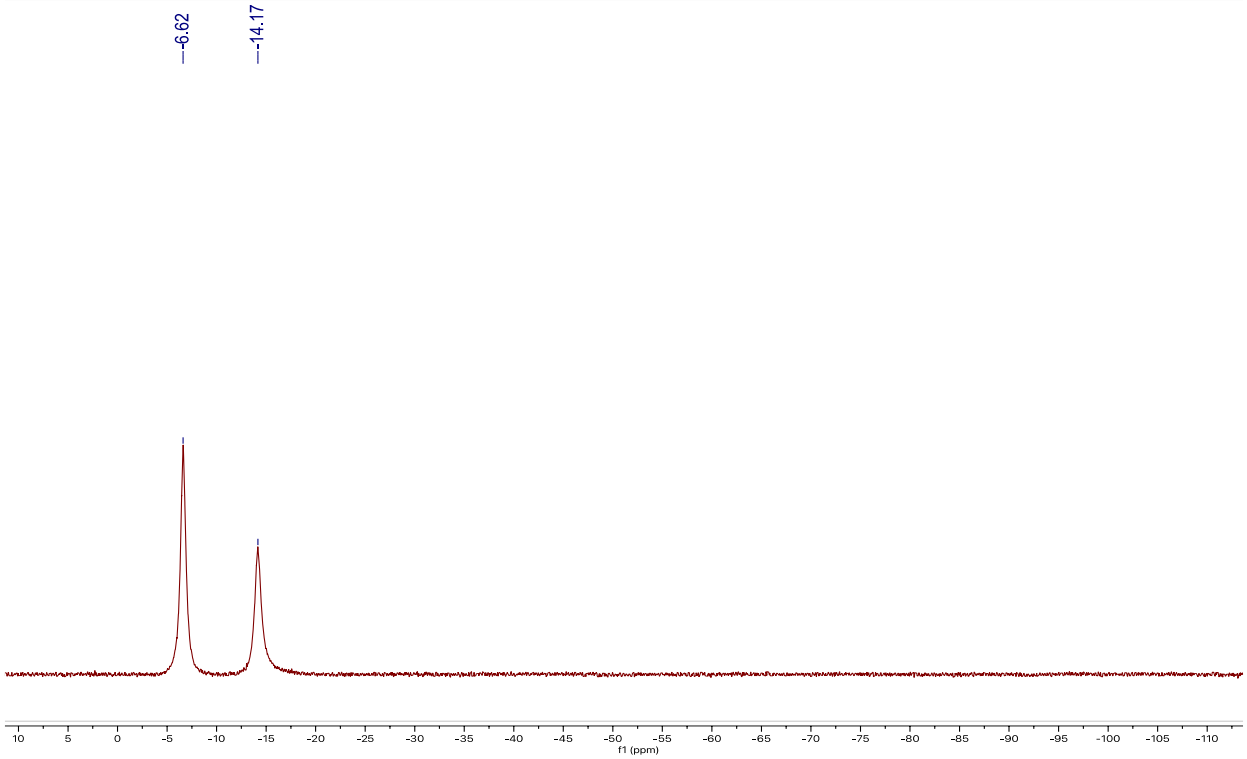
^{1}H NMR Spectrum DMSO (400 MHz)



^{13}C NMR Spectrum DMSO (101 MHz)

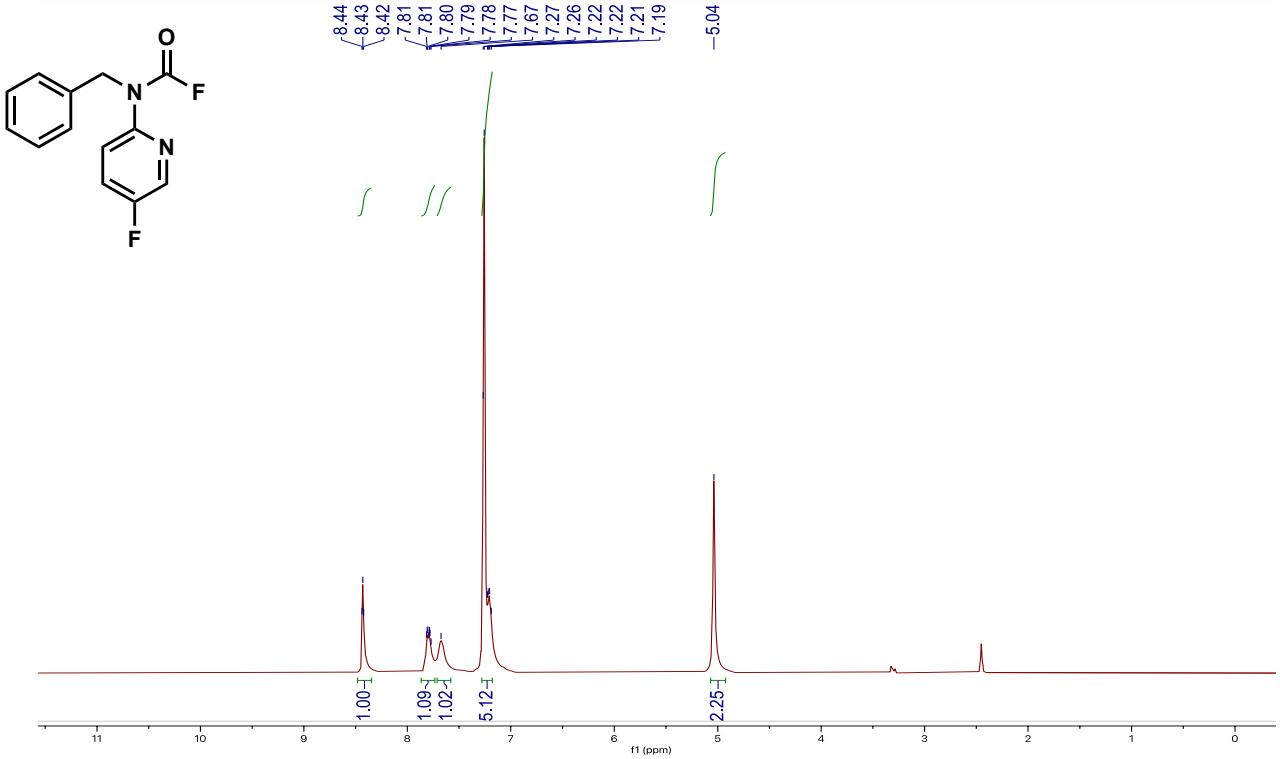


^{19}F NMR Spectrum $CDCl_3$ (377 MHz)

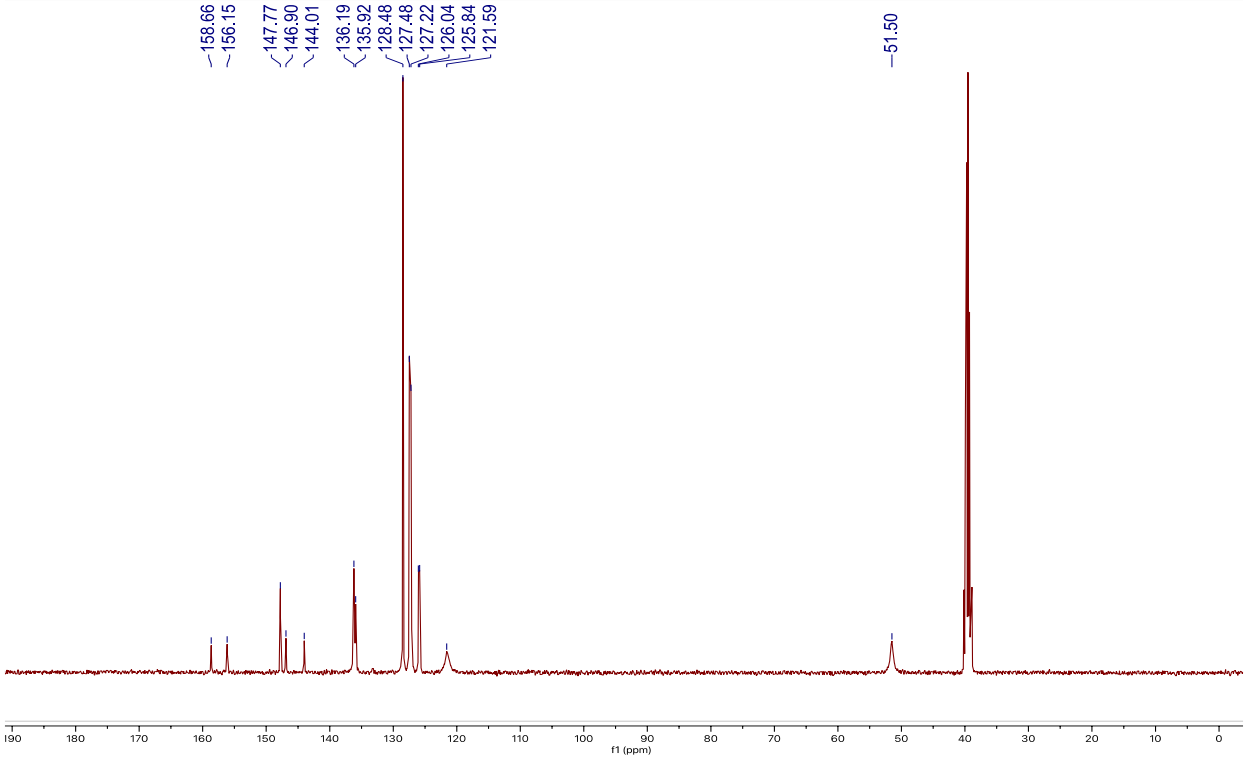


_N_-benzyl-_N_-(5-fluoro-2-pyridyl)carbamoyl fluoride (1u)

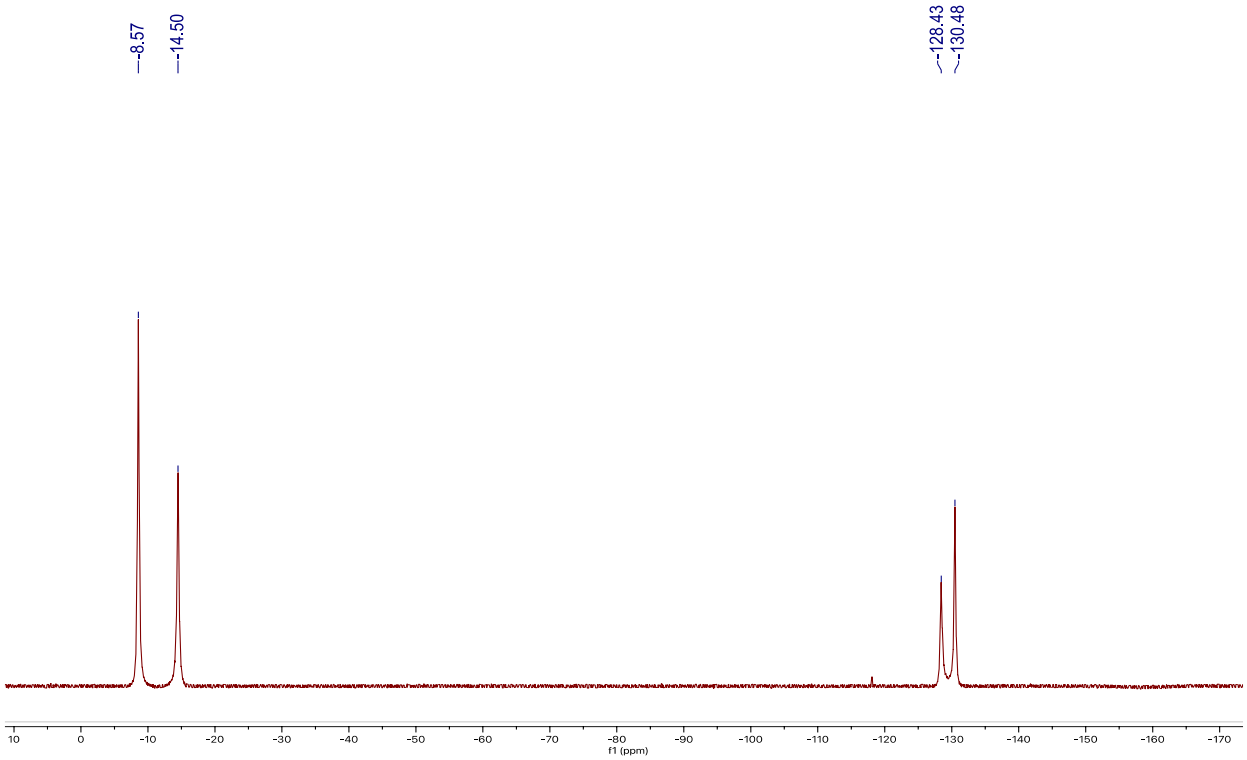
^{1}H NMR Spectrum DMSO (400 MHz)



^{13}C NMR Spectrum DMSO (101 MHz)

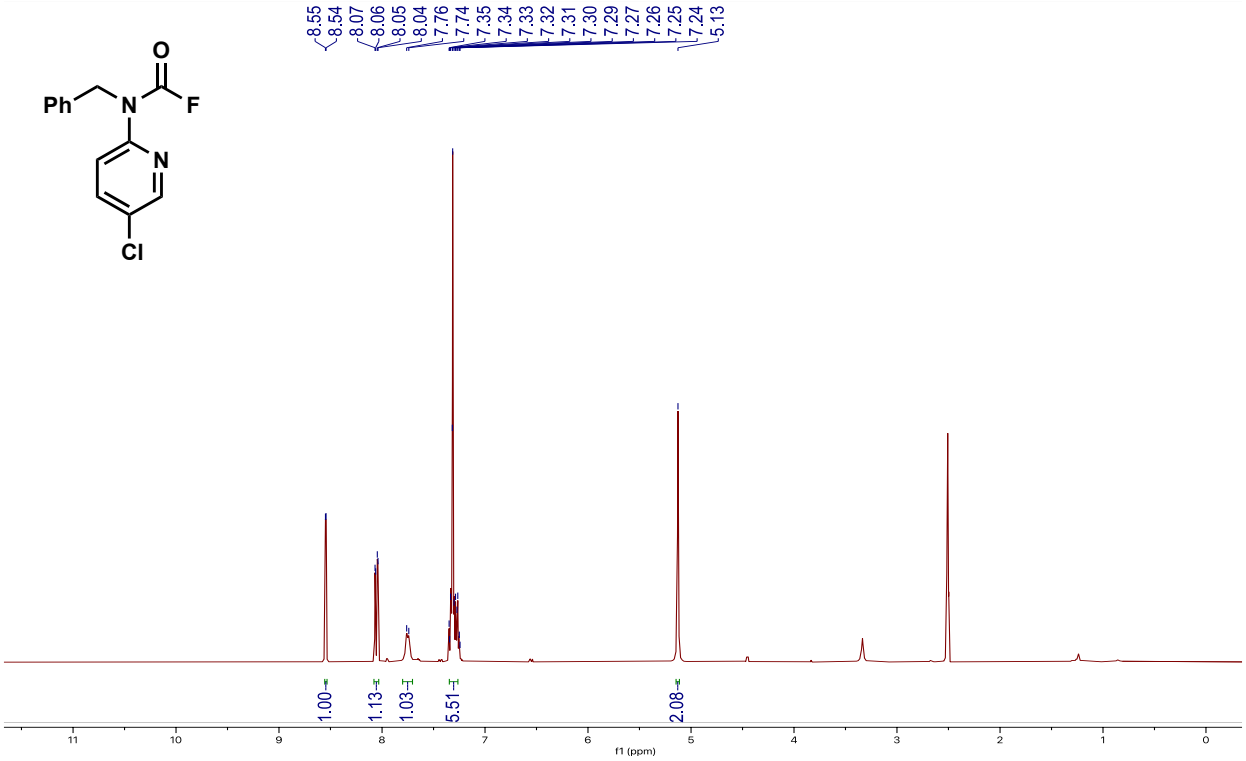


^{19}F NMR Spectrum $CDCl_3$ (377 MHz)

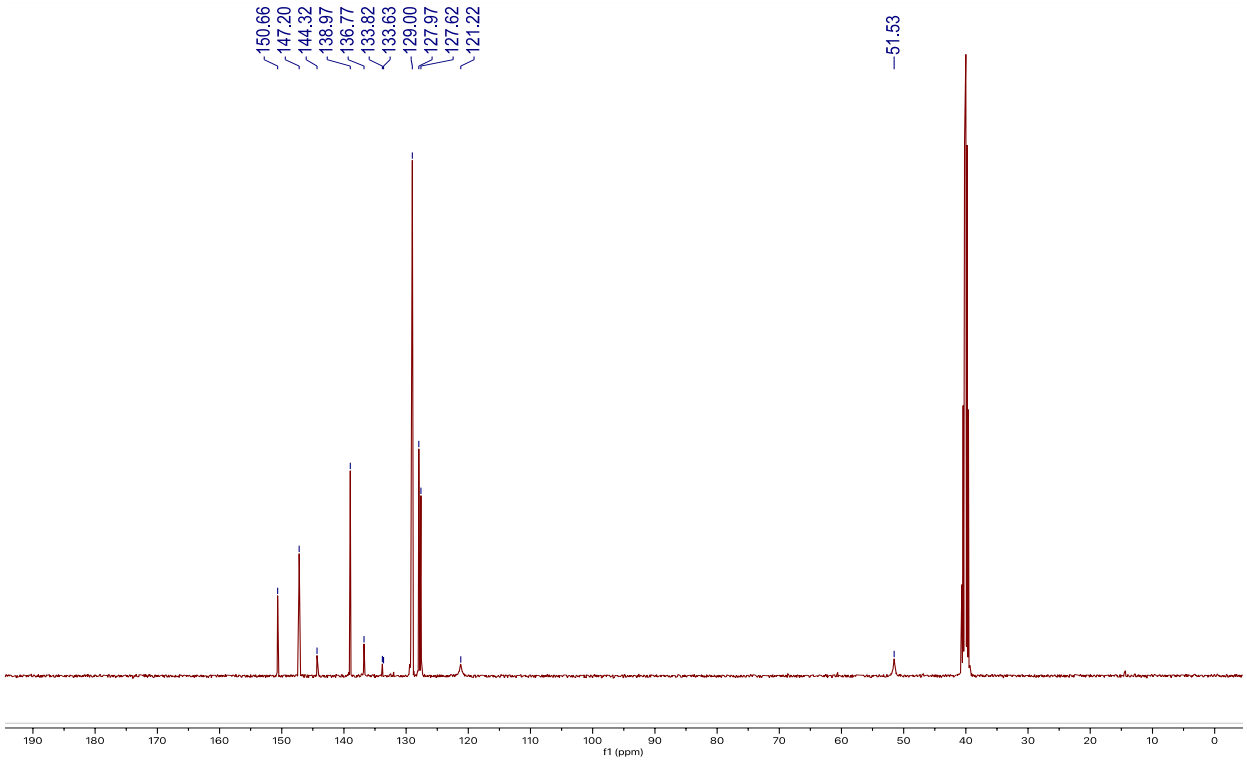


***N*-benzyl-*N*-(5-chloro-2-pyridyl)carbamoyl fluoride (1v)**

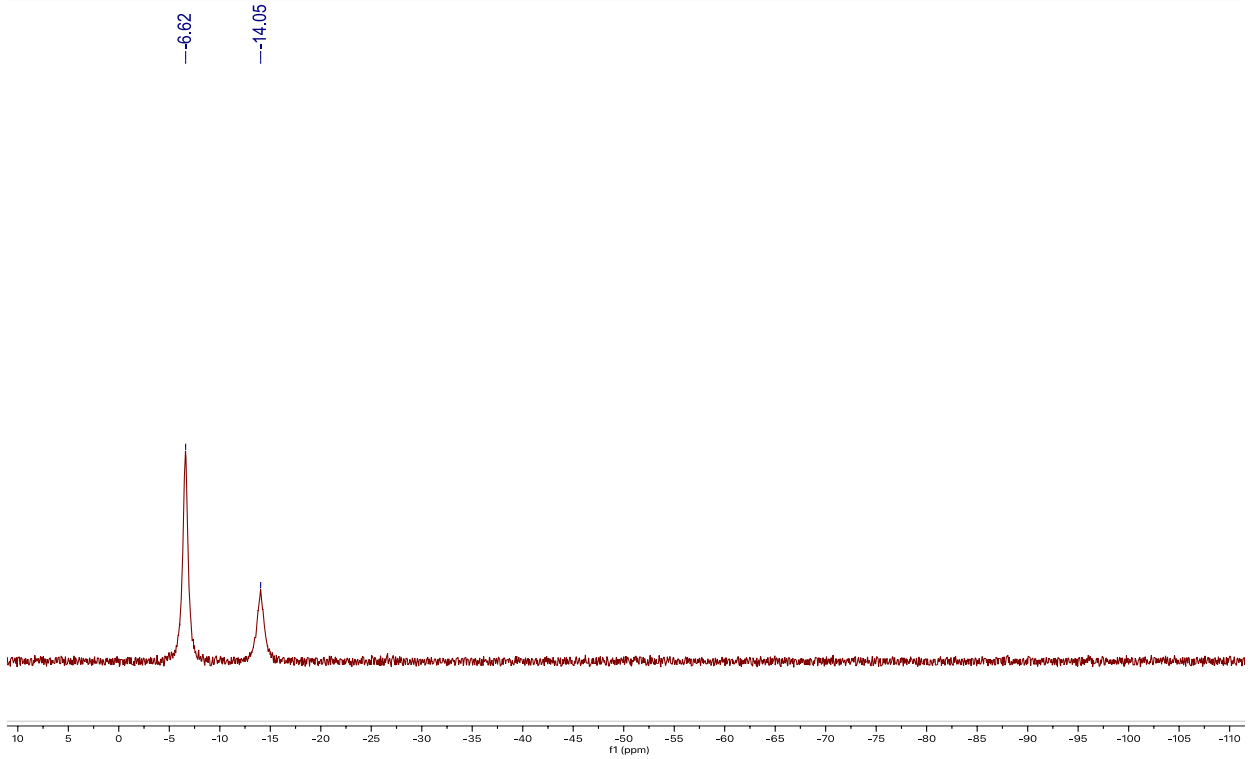
^{1}H NMR Spectrum DMSO (400 MHz)



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

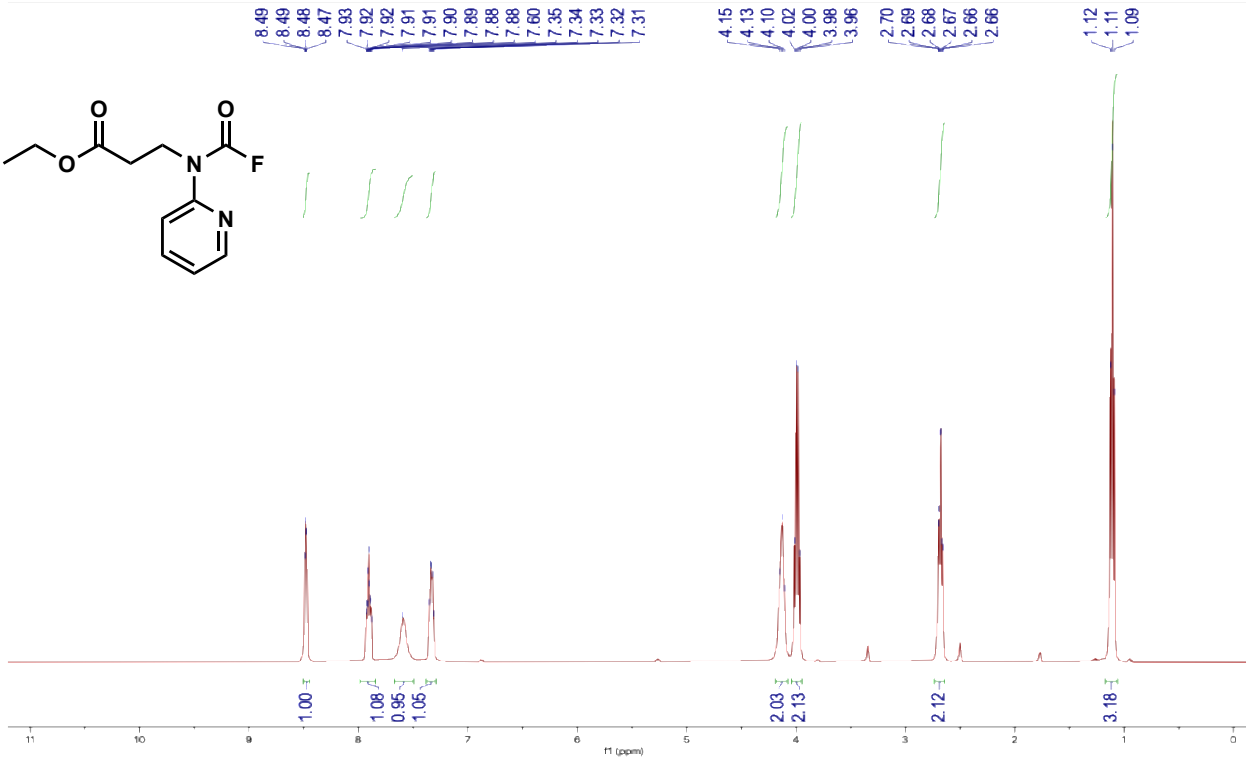


^{19}F NMR Spectrum $CDCl_3$ (377 MHz)

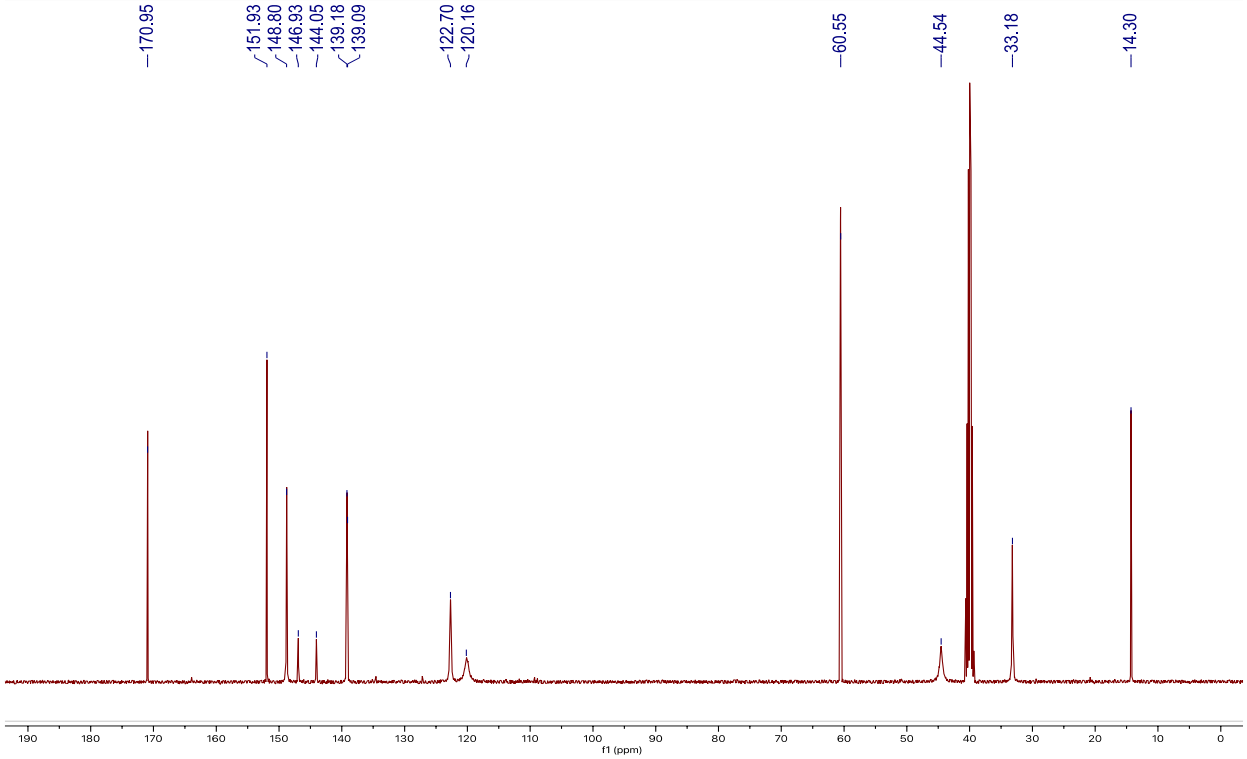


***N*-[(3-ethoxy-3-oxopropyl)]-*N*-(2-pyridyl)carbamoyl fluoride (1w)**

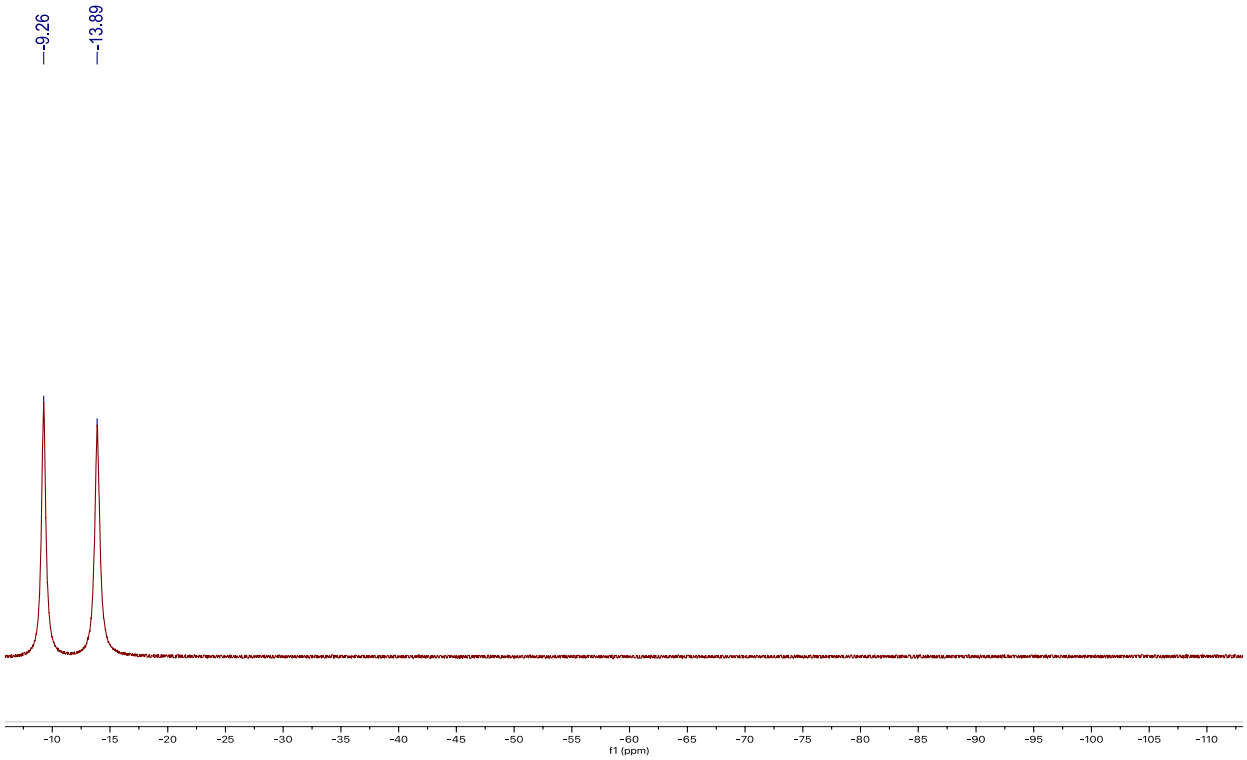
^{1}H NMR Spectrum DMSO (400 MHz)



^{13}C NMR Spectrum DMSO (101 MHz)

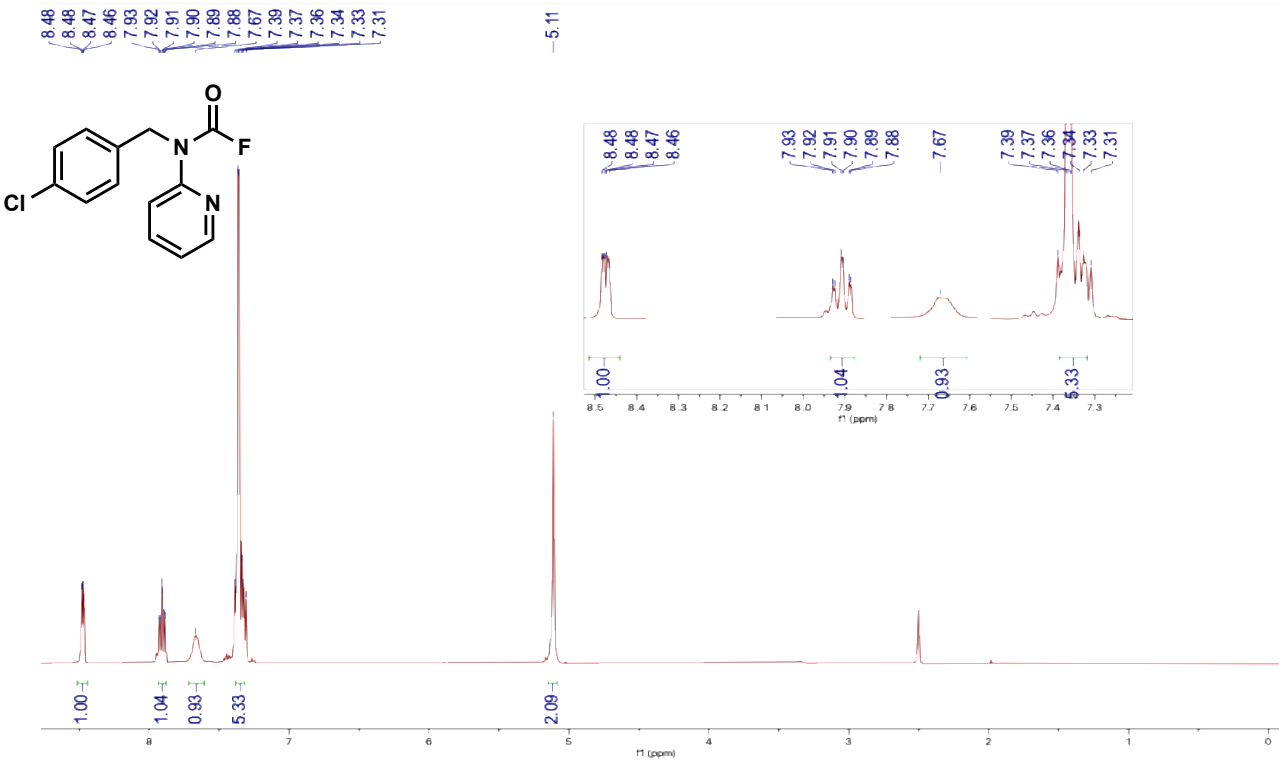


^{19}F NMR Spectrum $CDCl_3$ (377 MHz)

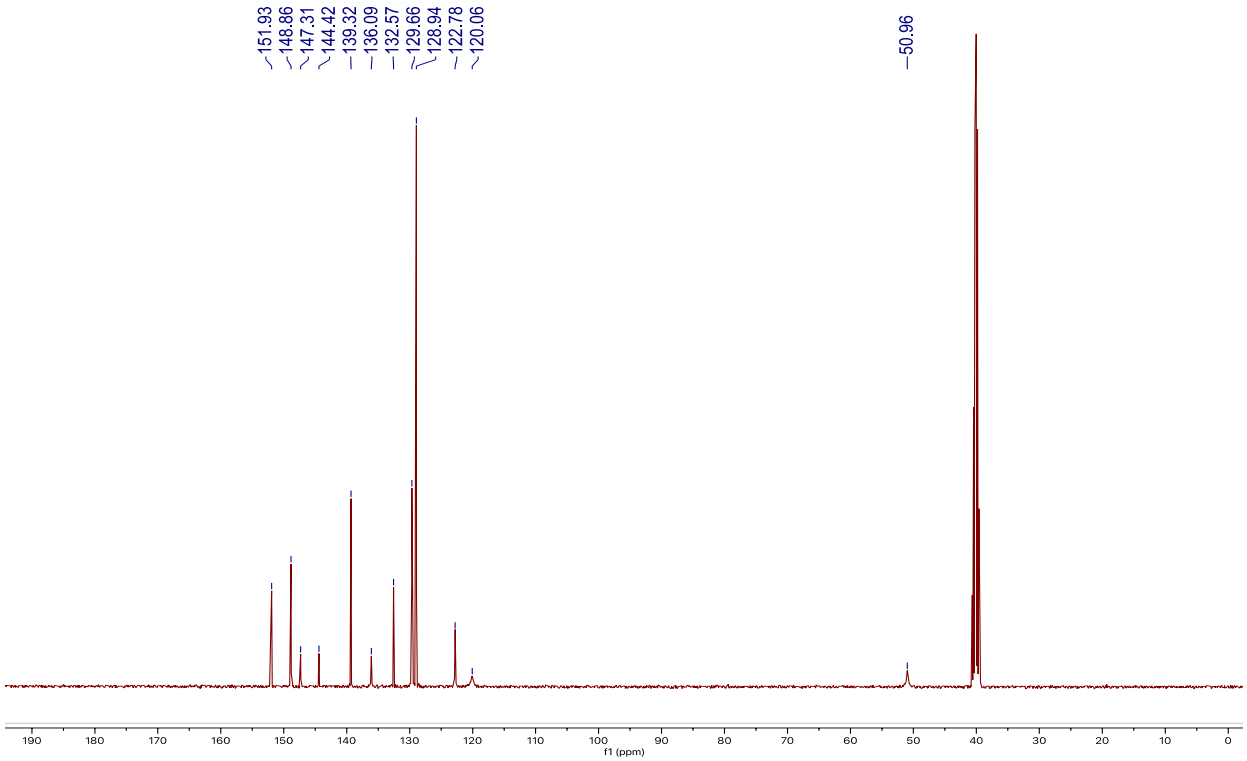


_N_-[(4-chlorophenyl)methyl]-_N_-(2-pyridyl)carbamoyl fluoride (1x)

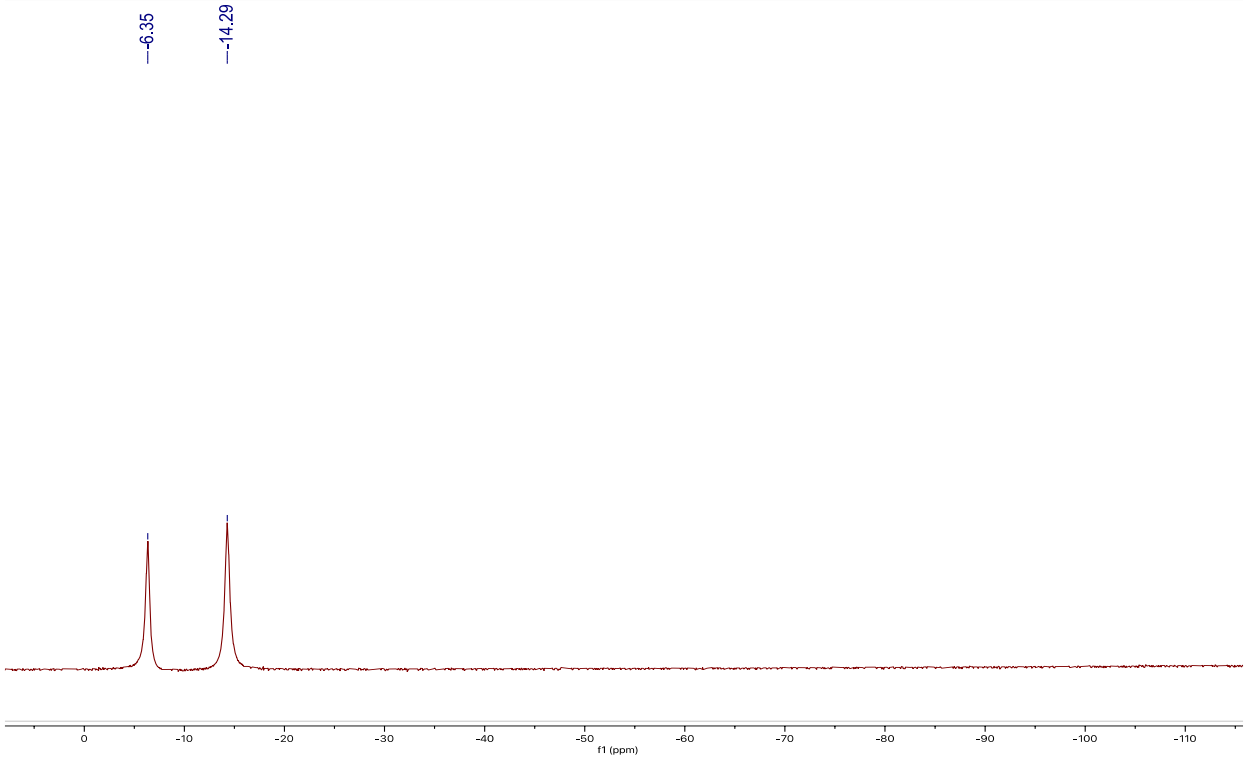
^{1}H NMR Spectrum DMSO (400 MHz)



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

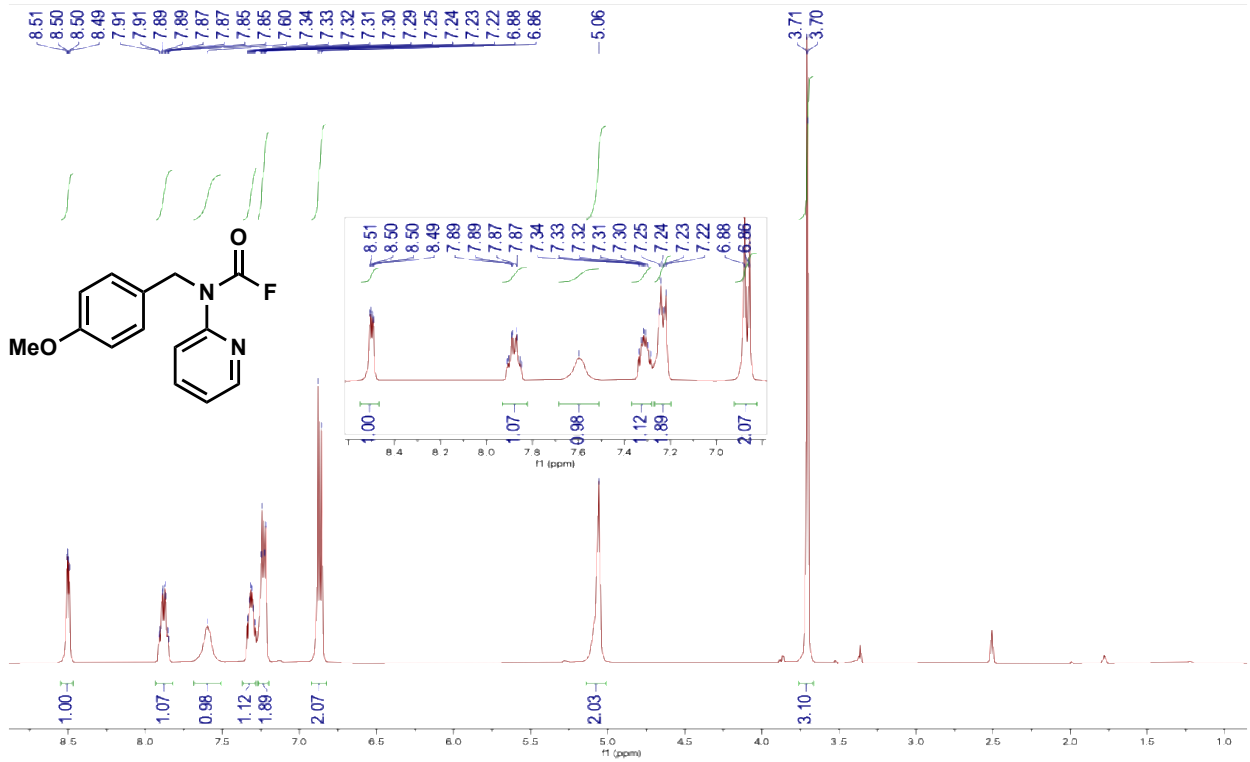


^{19}F NMR Spectrum $CDCl_3$ (377 MHz)

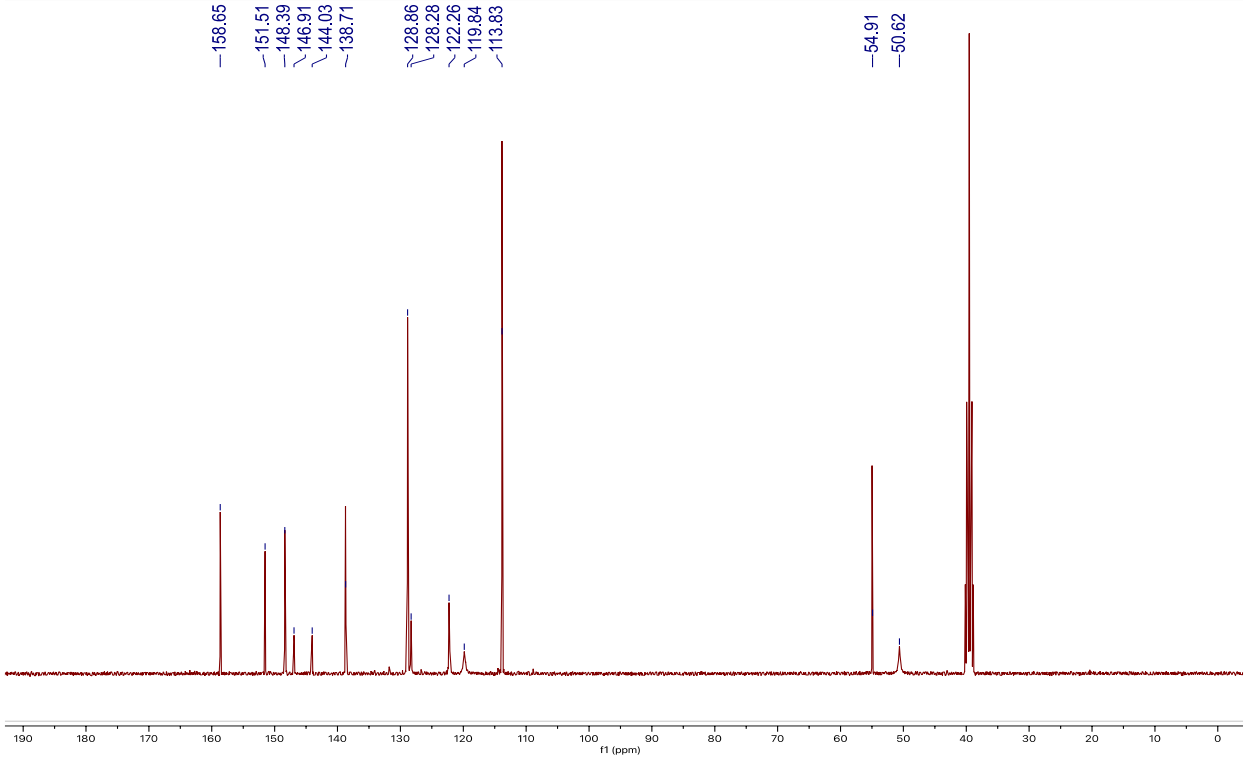


_N_-[(4-methoxyphenyl)methyl]-_N_-(2-pyridyl)carbamoyl fluoride (1y)

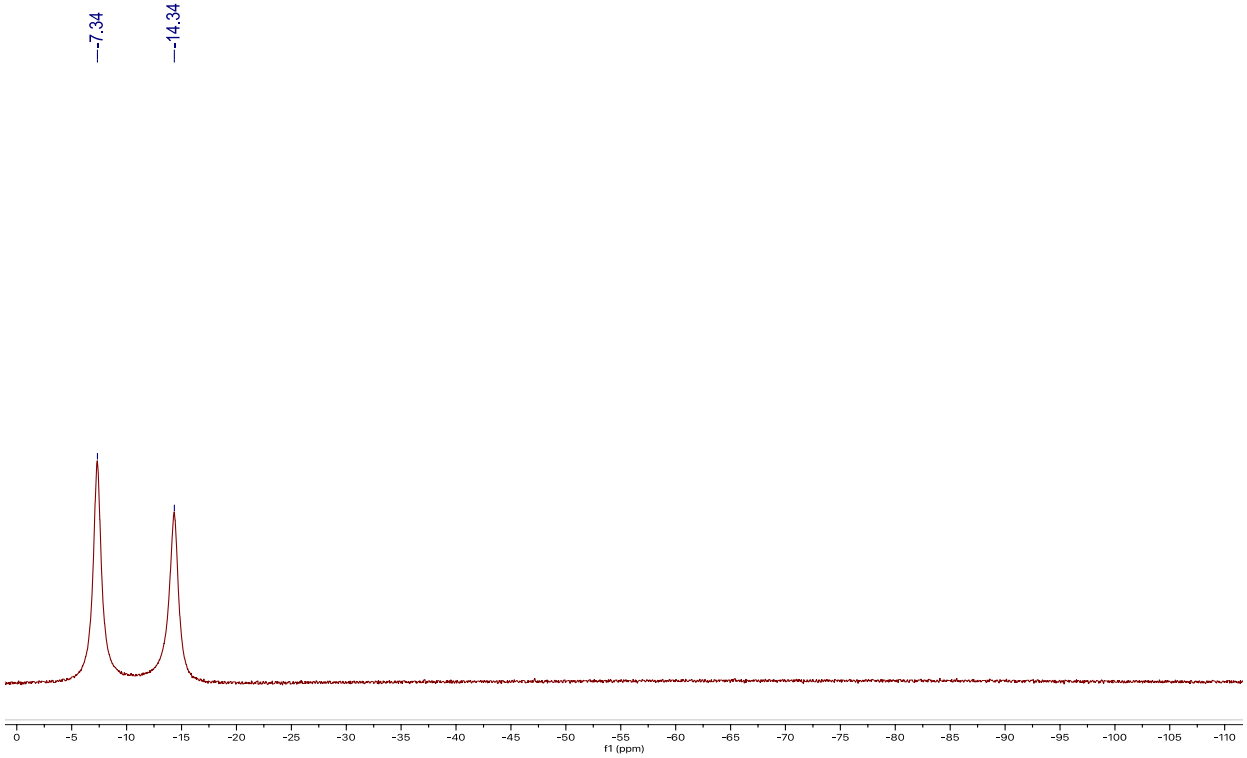
^{1}H NMR Spectrum DMSO (400 MHz)



^{13}C NMR Spectrum DMSO (101 MHz)

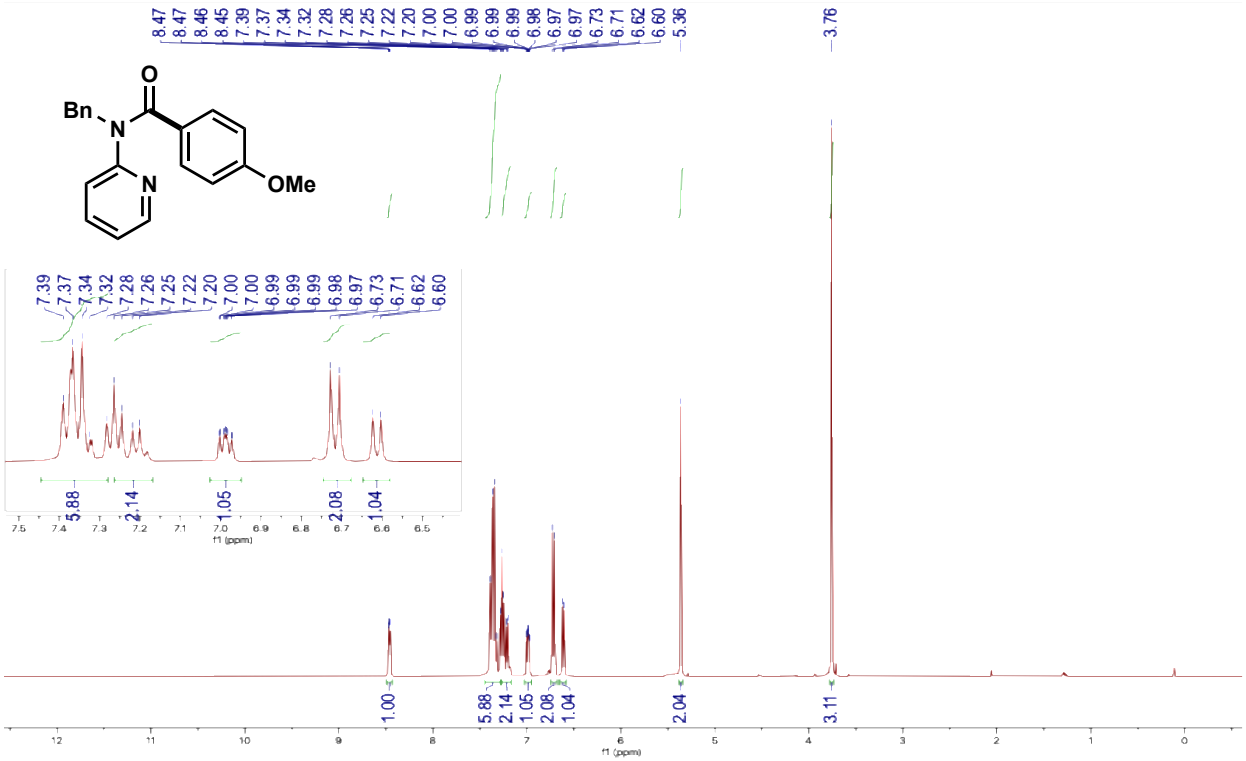


^{19}F NMR Spectrum $CDCl_3$ (377 MHz)

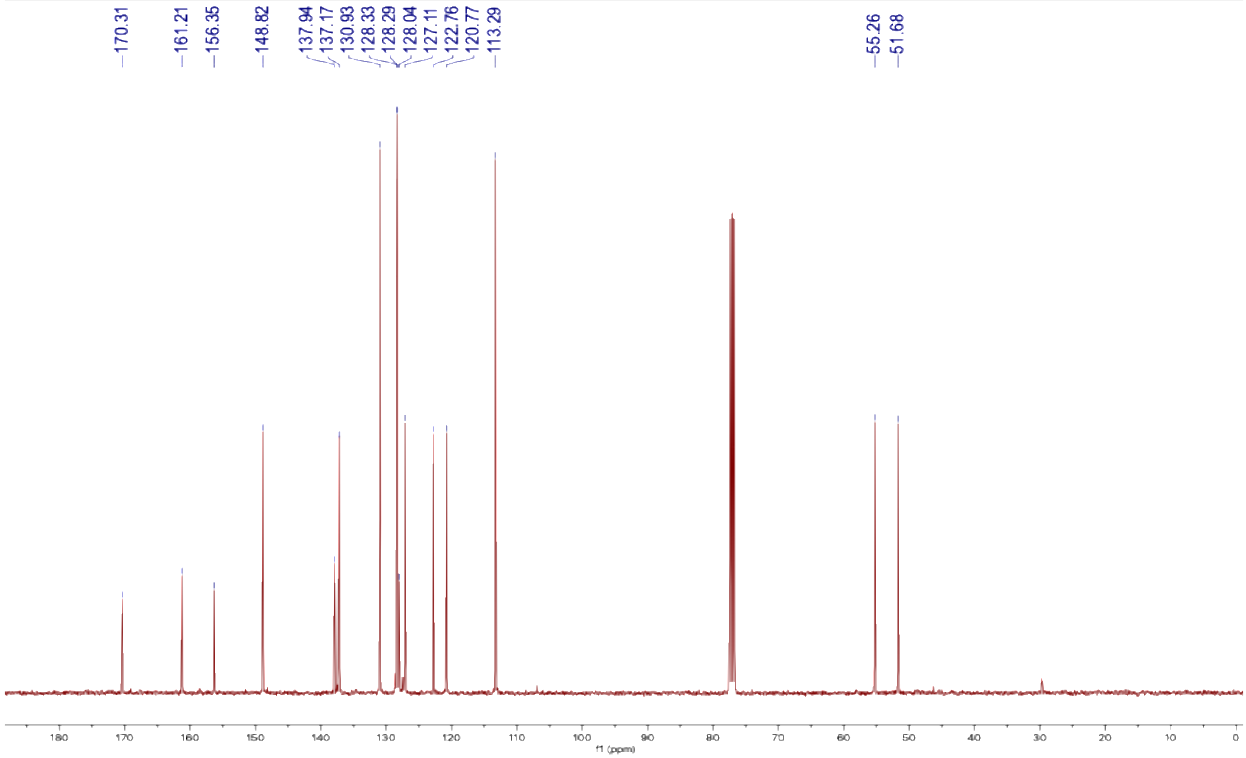


_N_-benzyl-4-methoxy-_N_-(2-pyridyl)benzamide (3a)

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

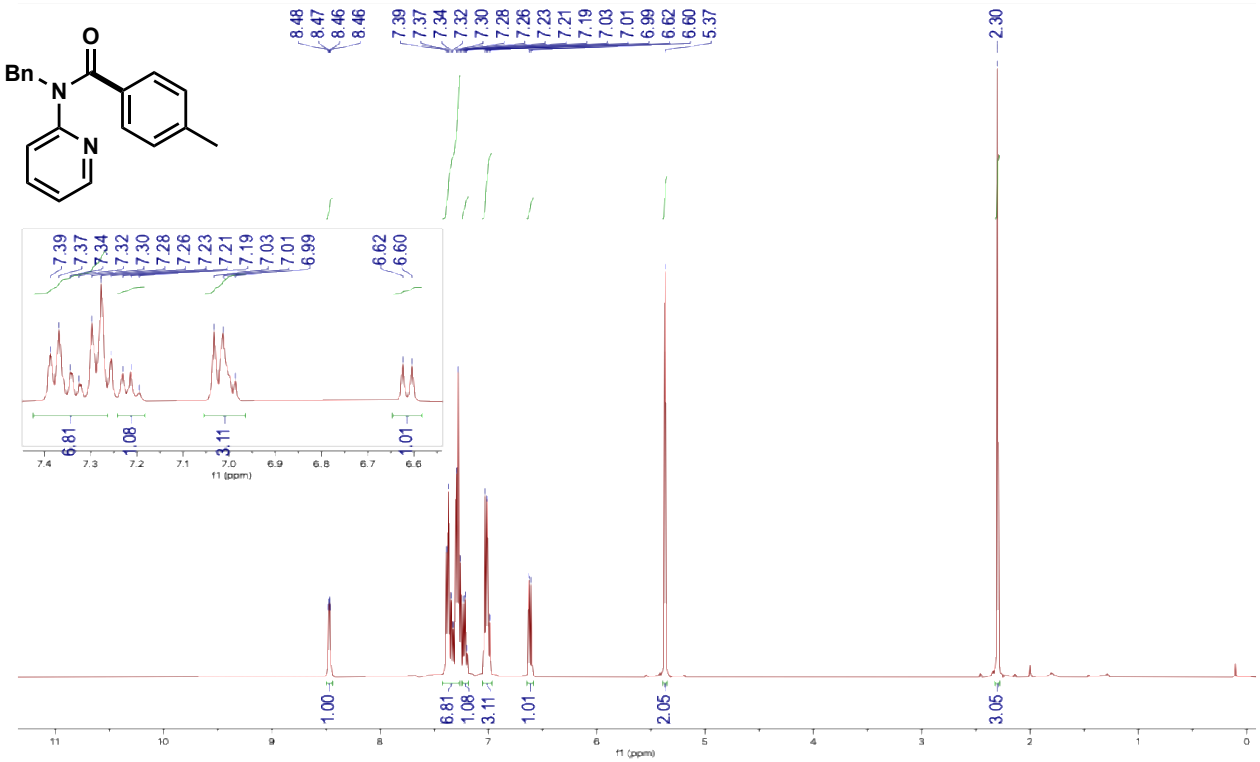


^{13}C NMR Spectrum $CDCl_3$ (101 MHz)

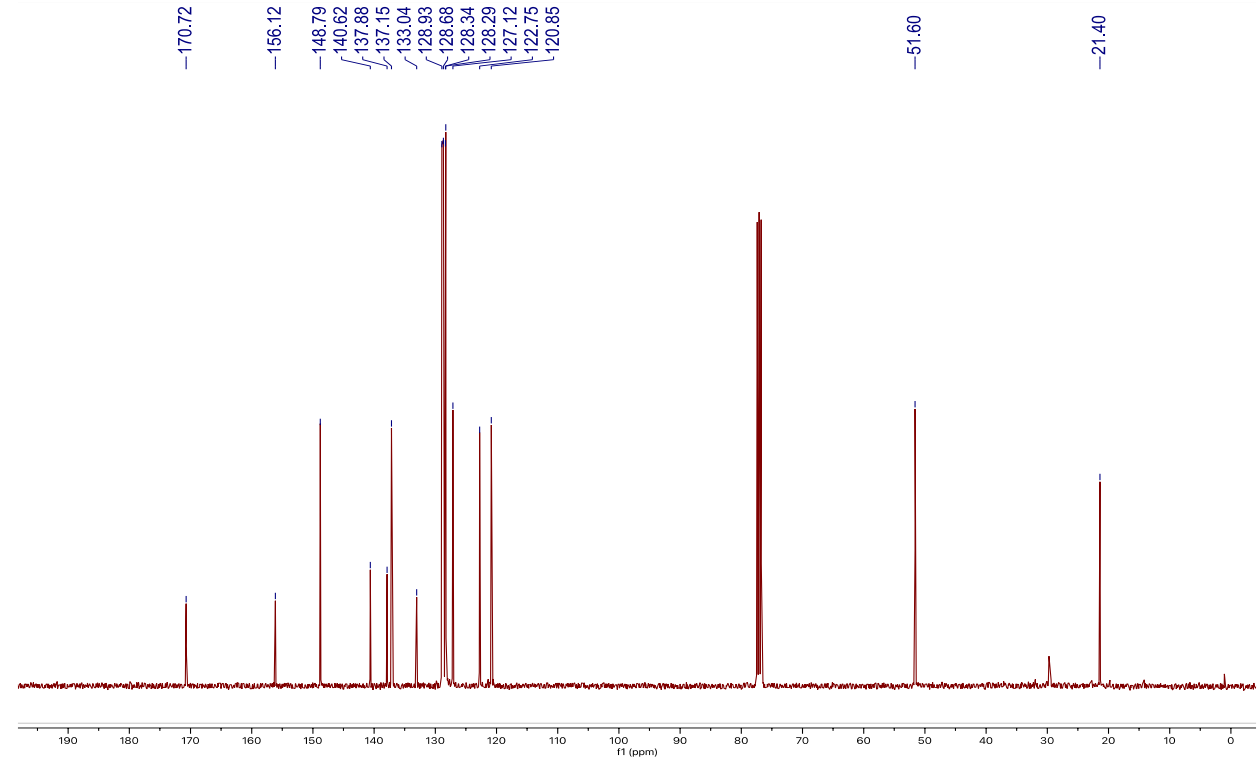


***N*-benzyl-4-methyl-*N*-(2-pyridyl)benzamide (3b)**

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

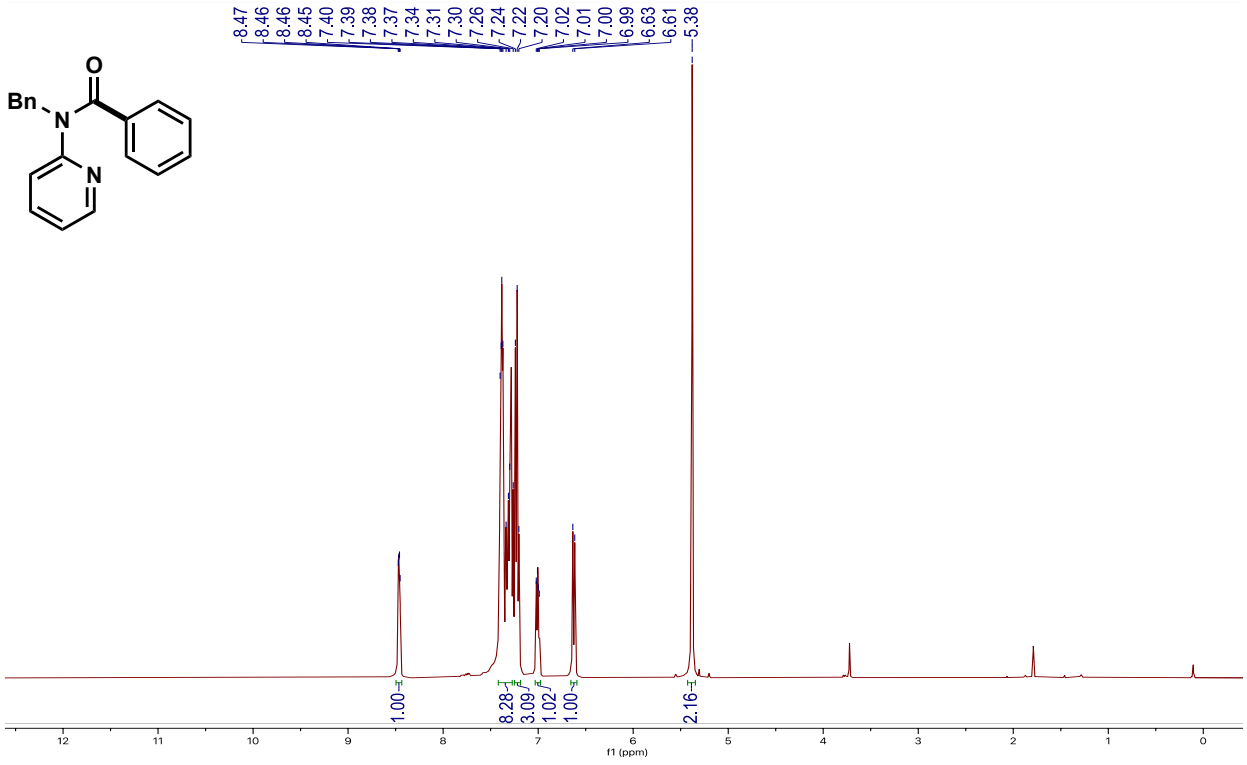


^{13}C NMR Spectrum $CDCl_3$ (101 MHz)

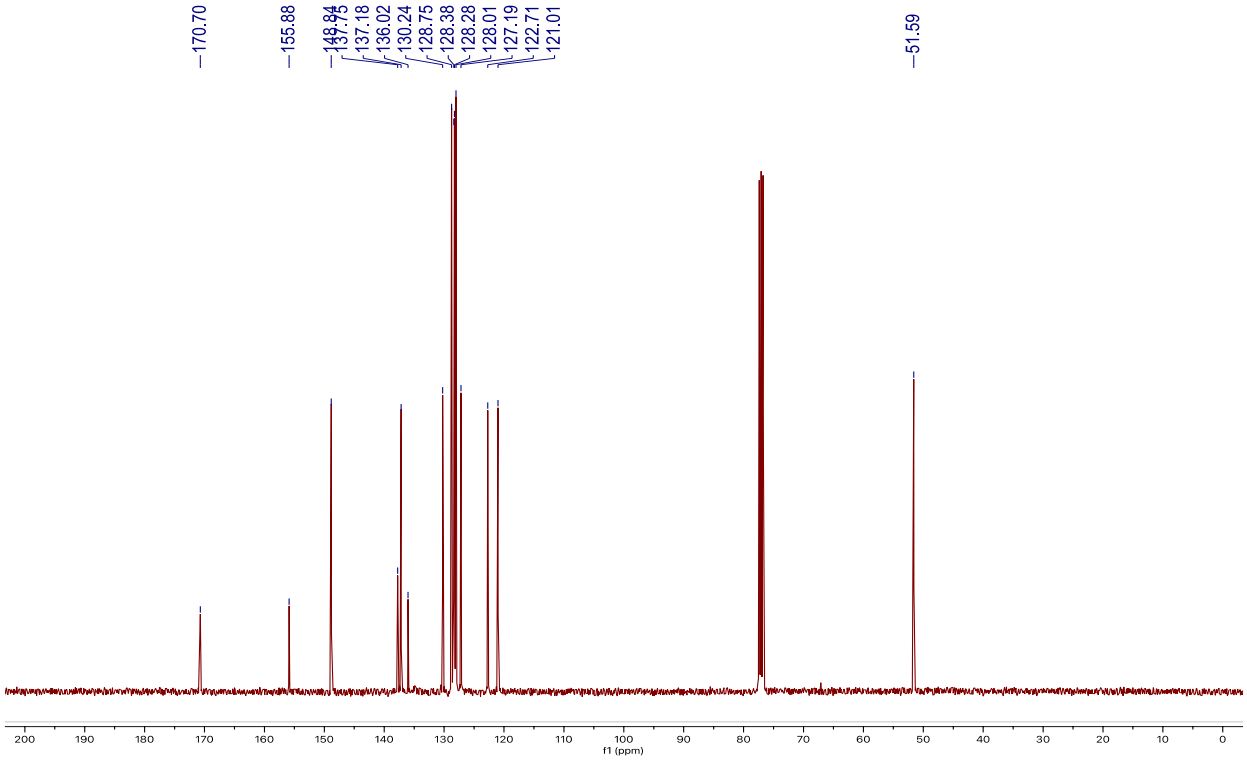


***N*-benzyl-*N*-(2-pyridyl)benzamide (3c)**

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

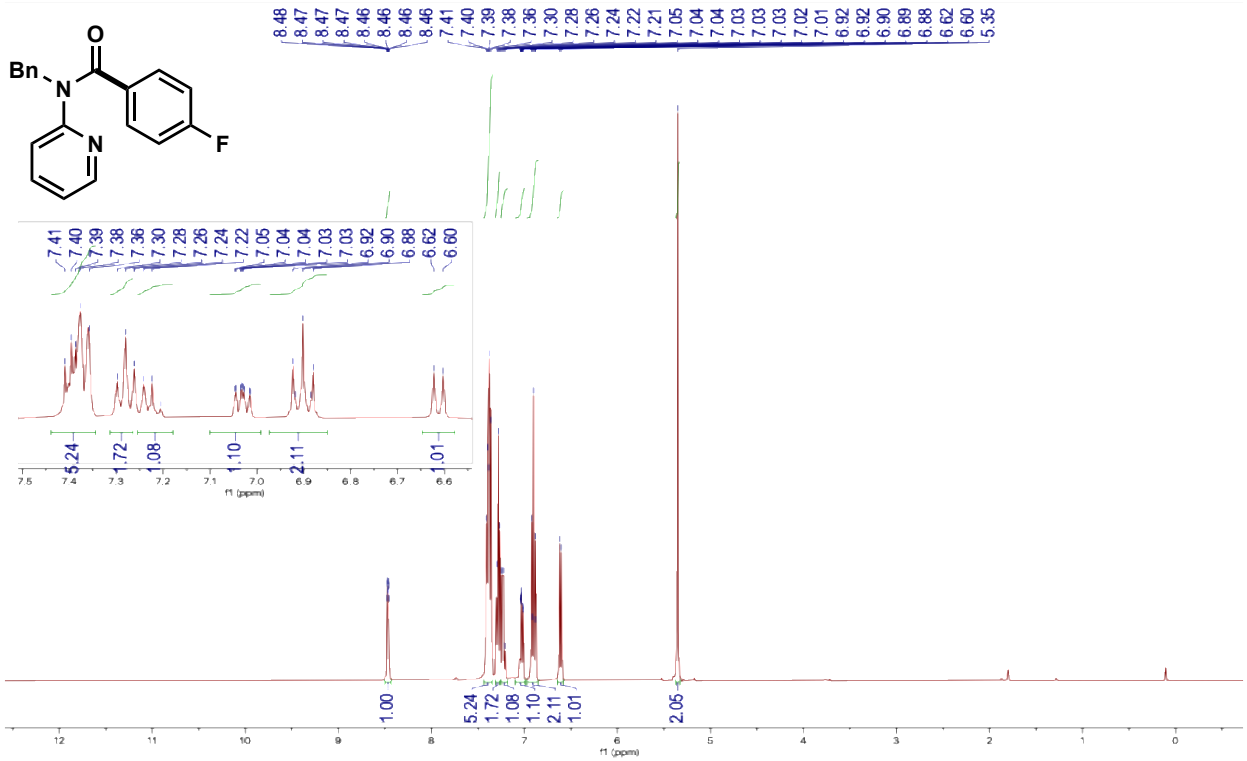


^{13}C NMR Spectrum $CDCl_3$ (101 MHz)

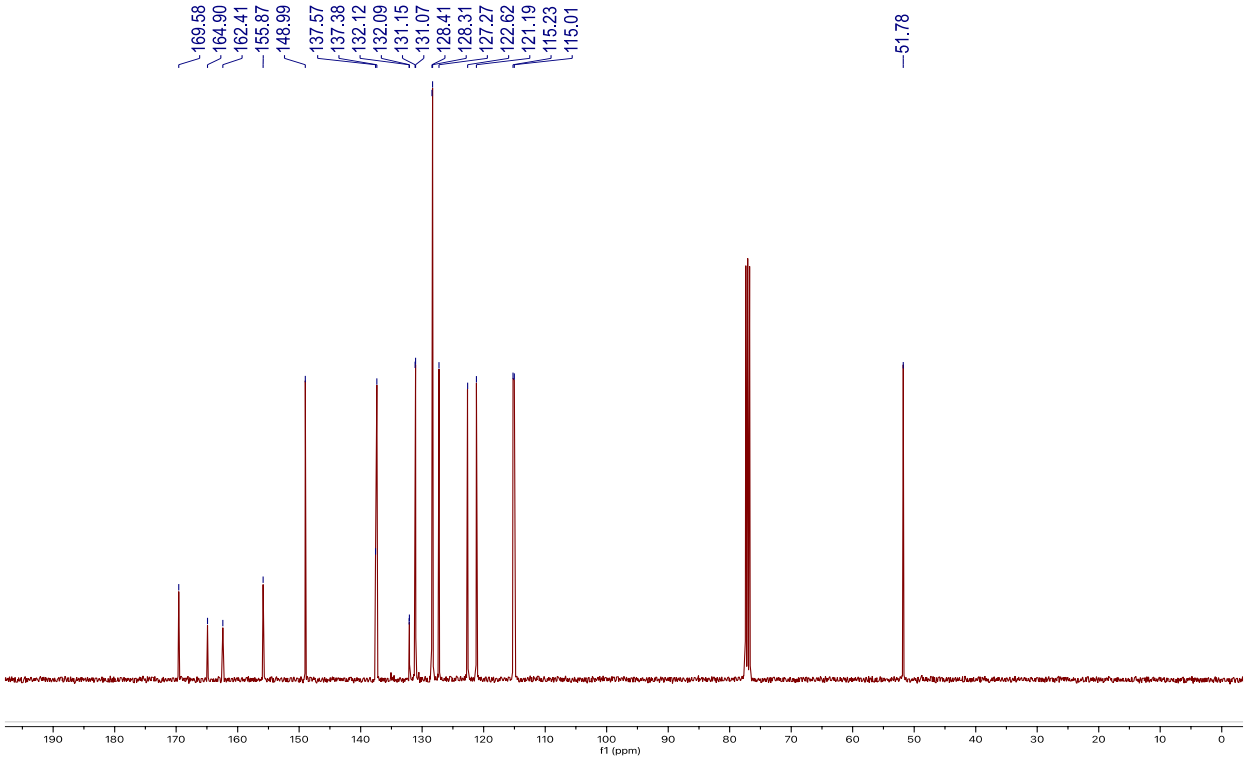


***N*-benzyl-4-fluoro-*N*-(2-pyridyl)benzamide (3d)**

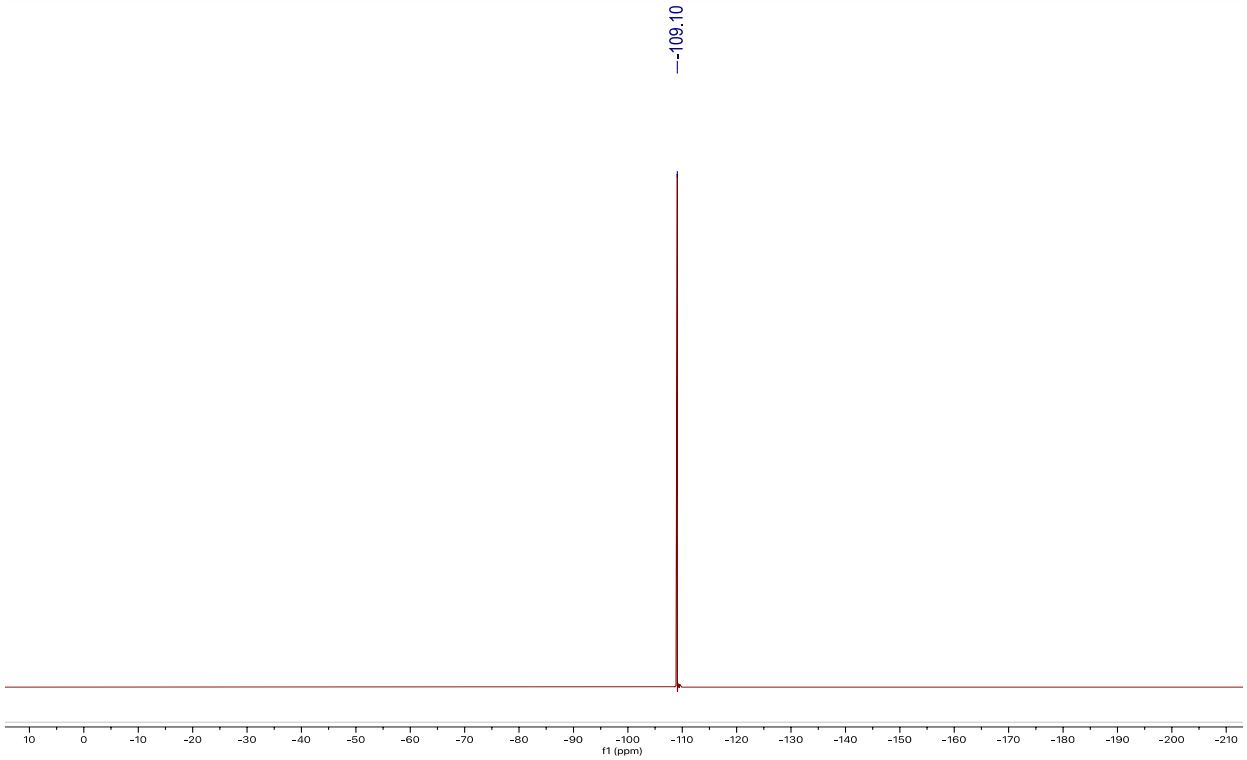
^{1}H NMR Spectrum $CDCl_3$ (400 MHz)



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

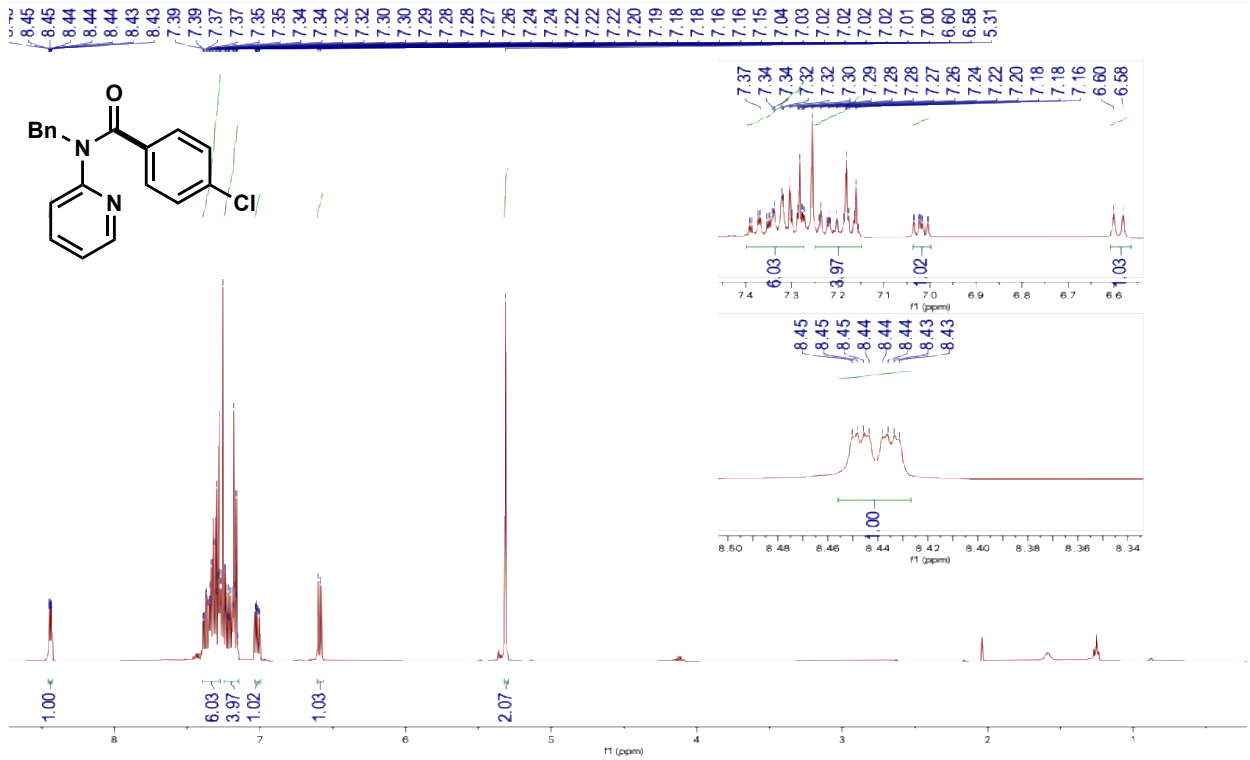


^{19}F NMR Spectrum $CDCl_3$ (377 MHz)

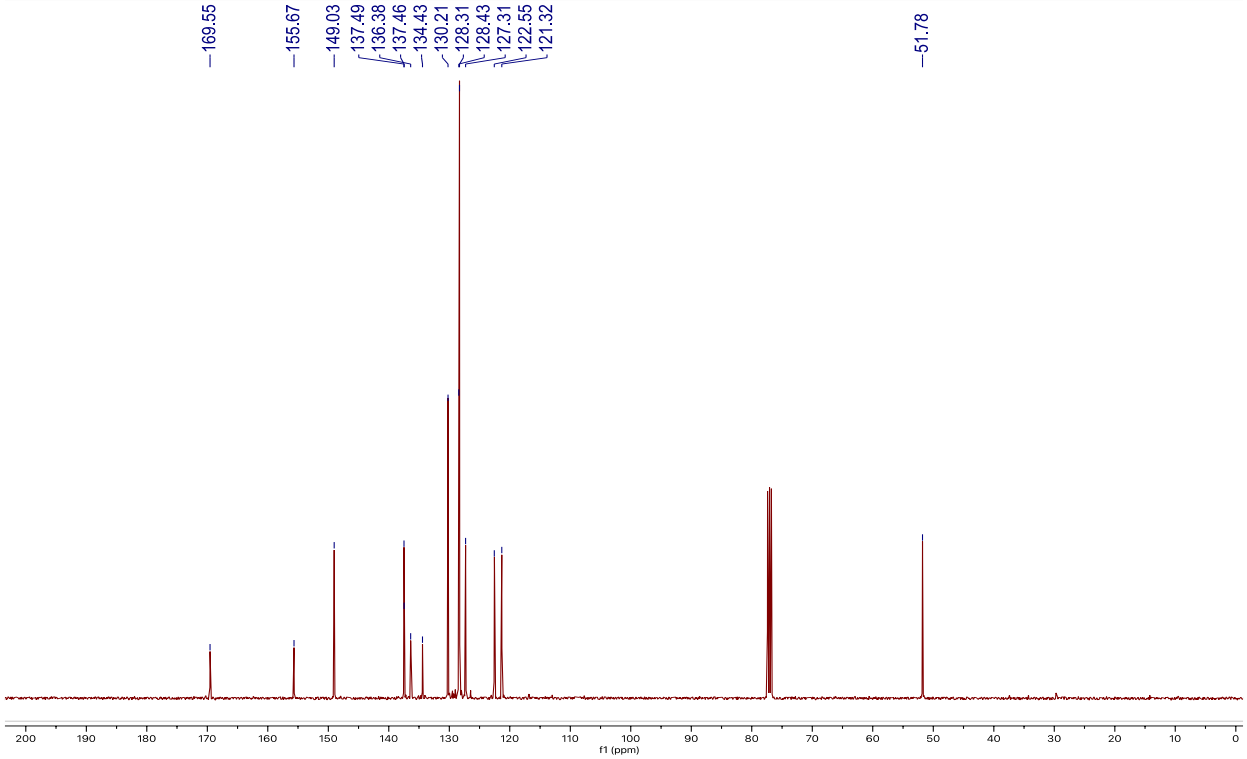


_N_-benzyl-4-chloro-_N_-(2-pyridyl)benzamide (3e)

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

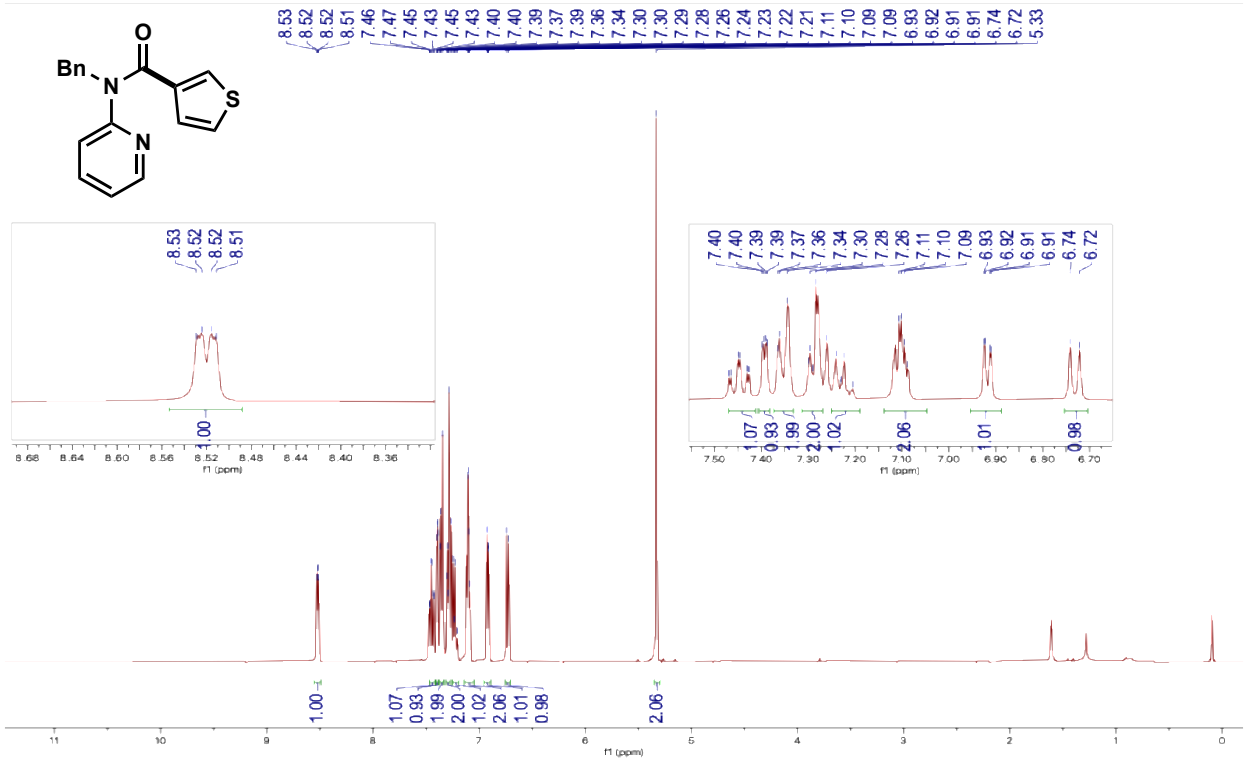


^{13}C NMR Spectrum $CDCl_3$ (101 MHz)

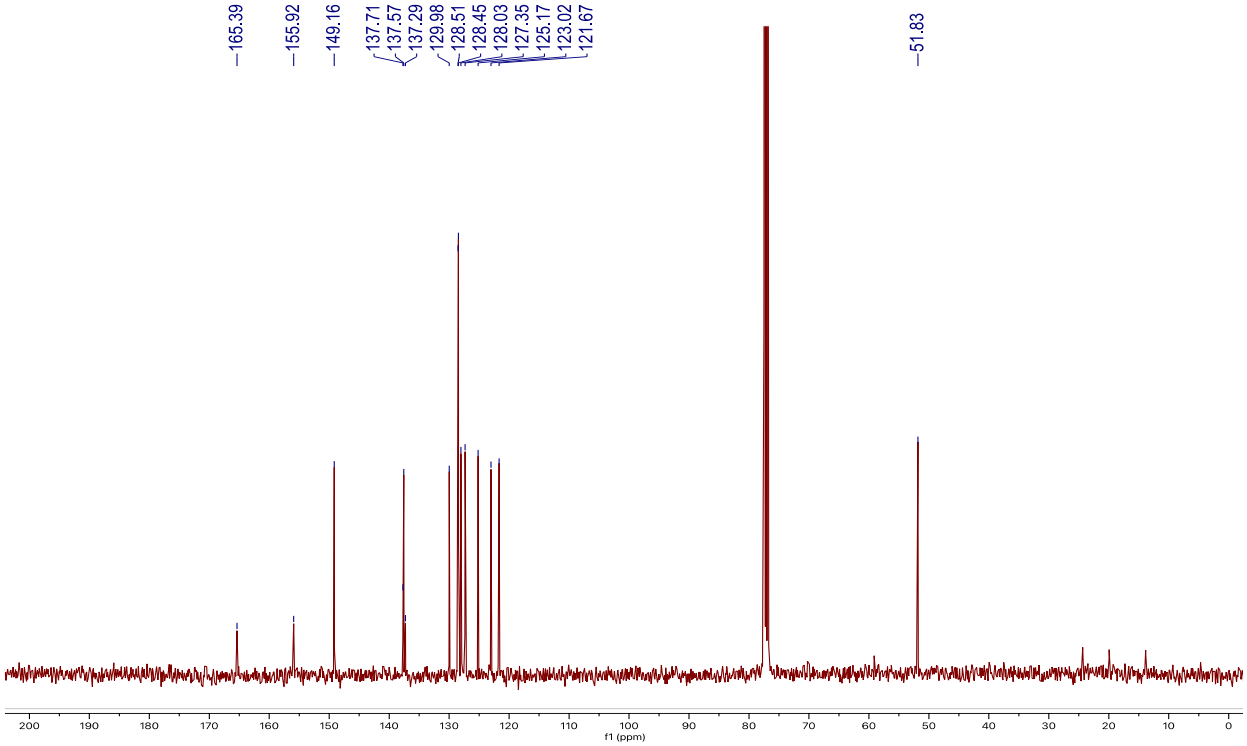


_N_-benzyl-_N_-(2-pyridyl)thiophene-3-carboxamide (3f)

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

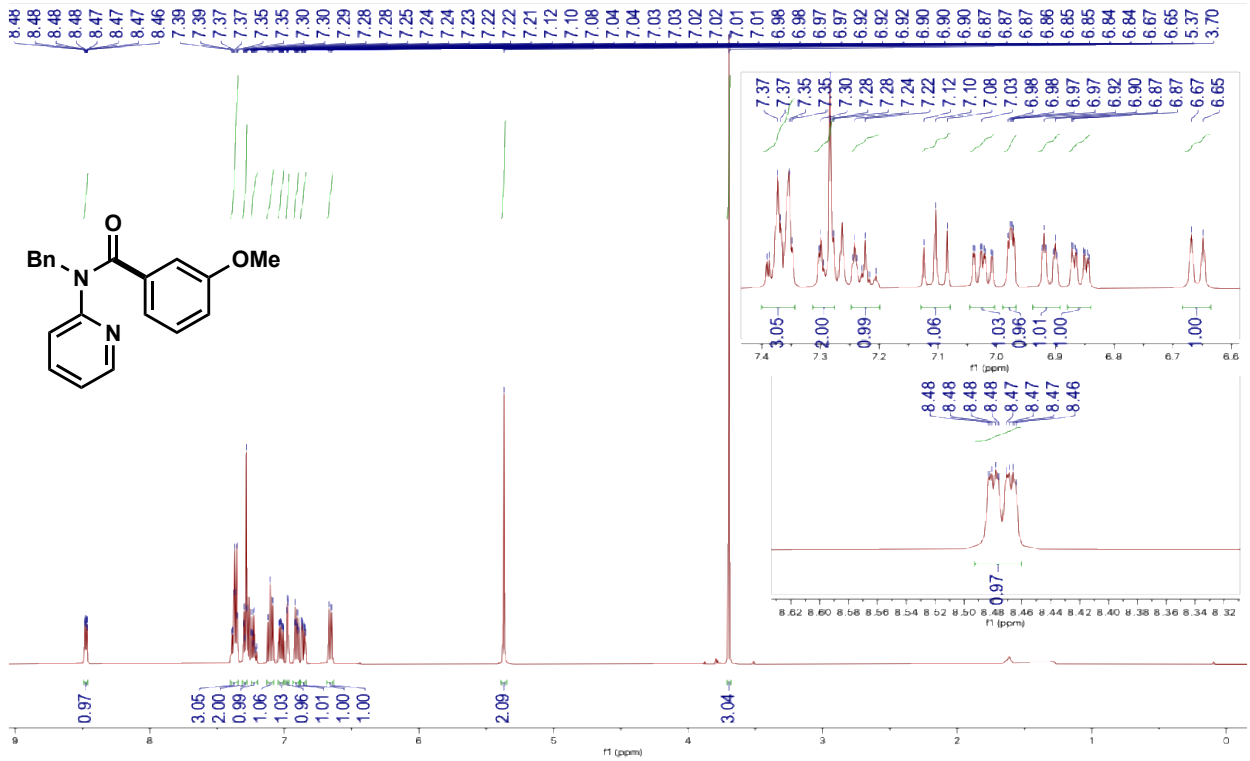


^{13}C NMR Spectrum $CDCl_3$ (101 MHz)

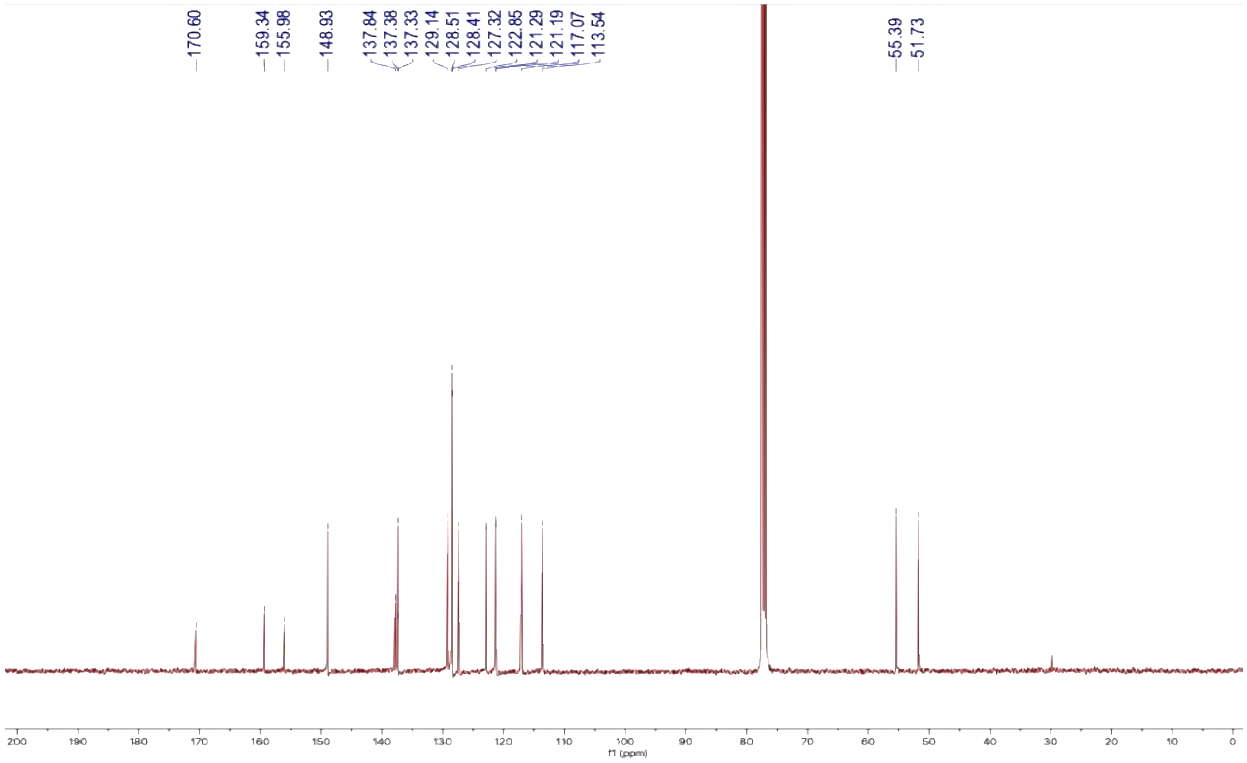


3-methoxy-*N*-methyl-*N*-(2-pyridyl)benzamide (3g)

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

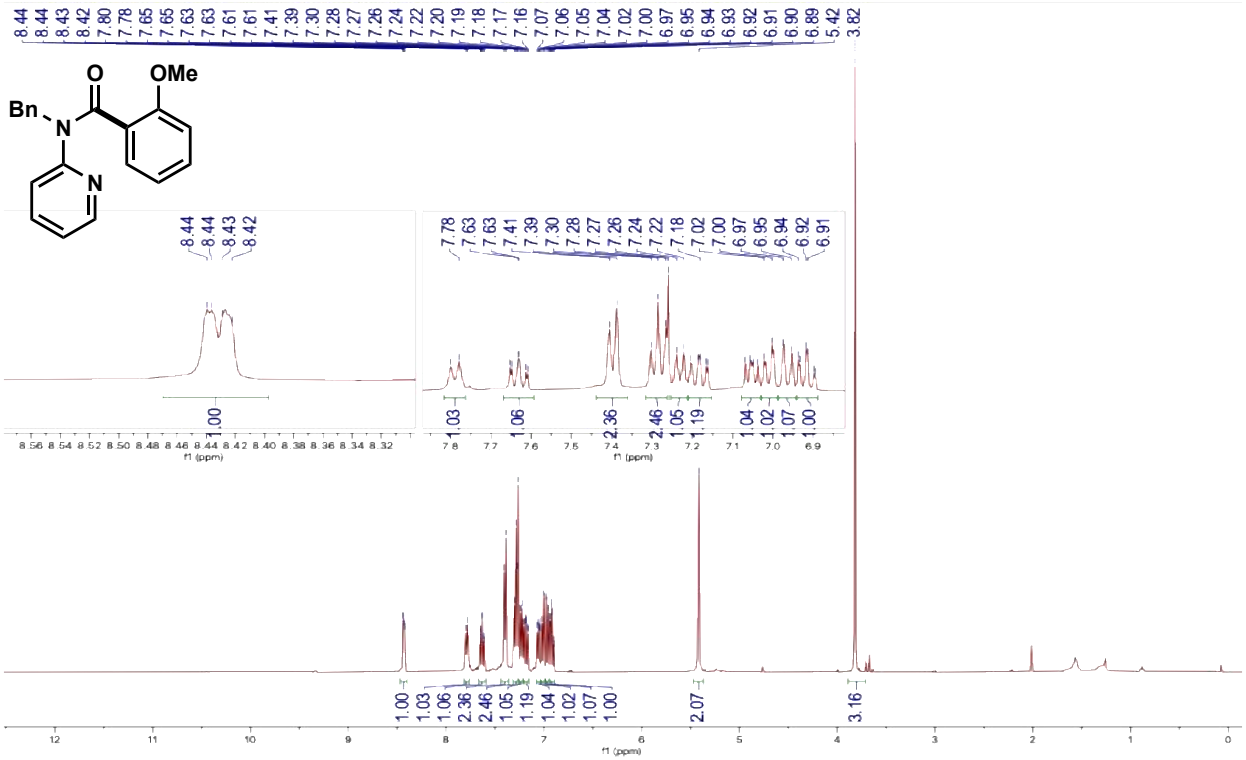


^{13}C NMR Spectrum $CDCl_3$ (101 MHz)

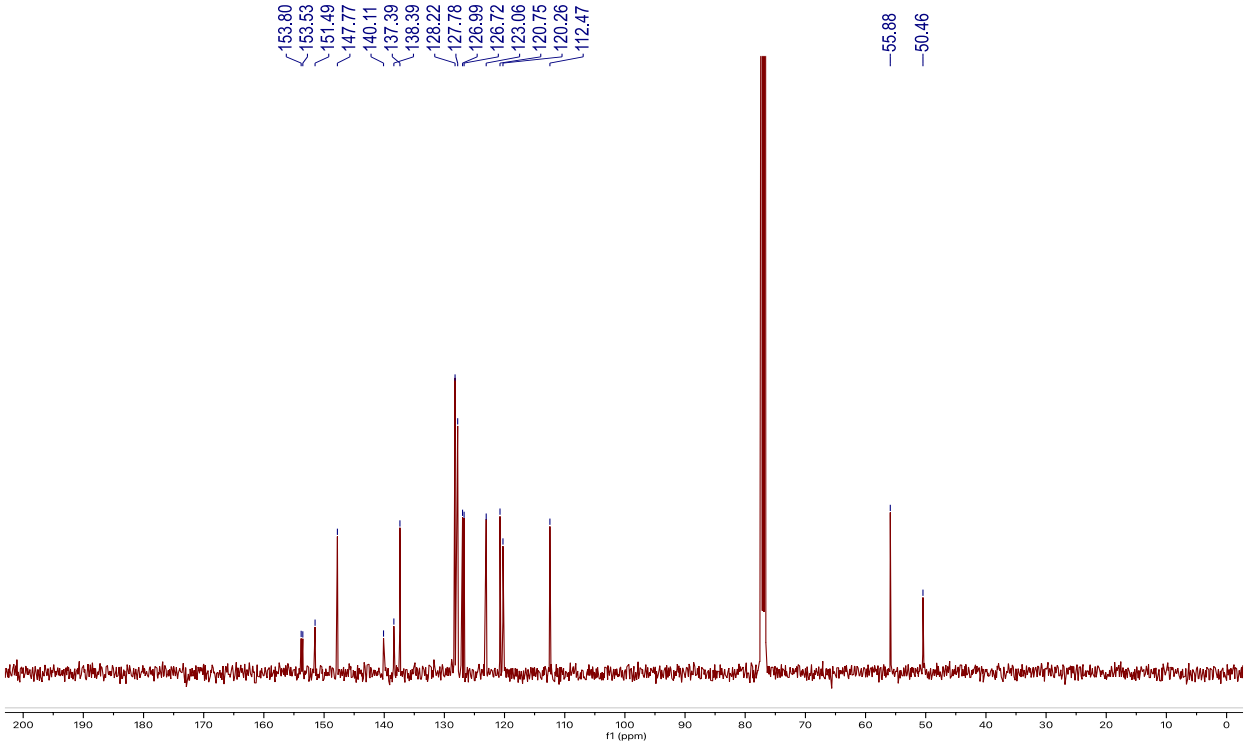


N-benzyl-2-methoxy-*N*-(2-pyridyl)benzamide (3h)

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

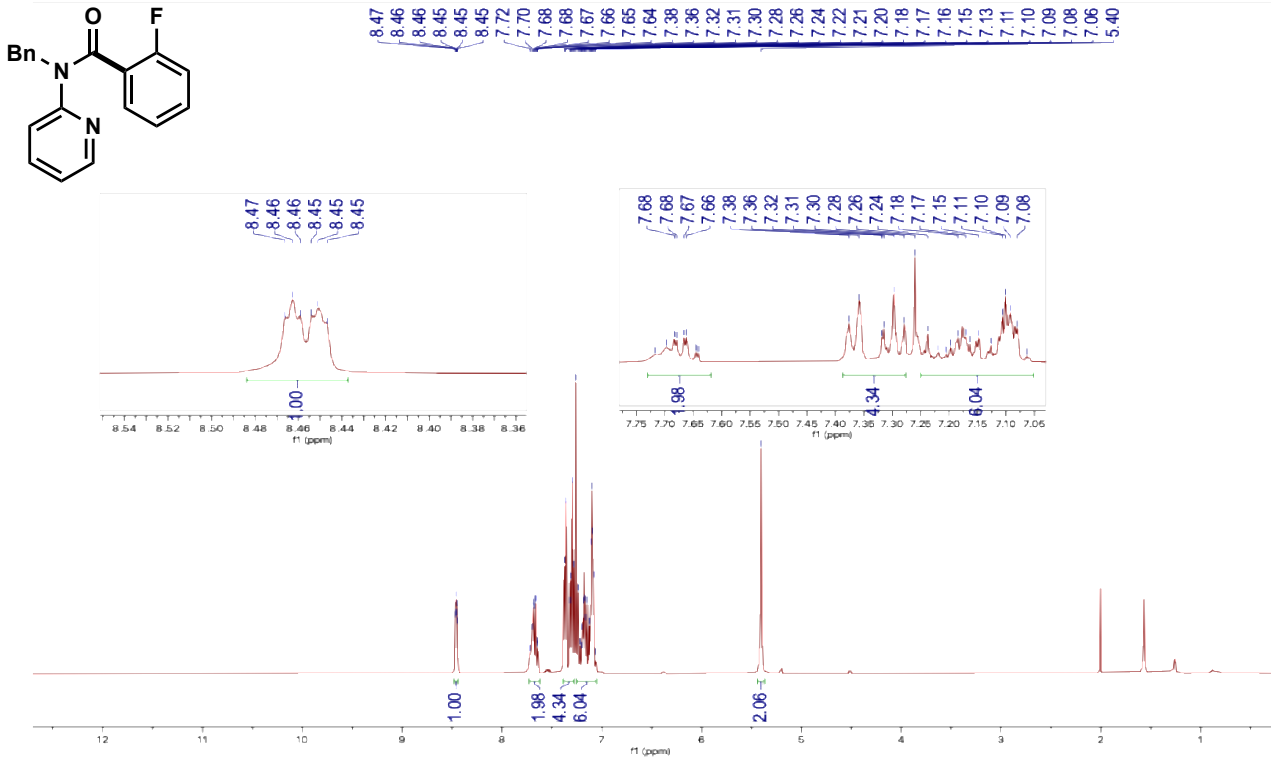


^{13}C NMR Spectrum $CDCl_3$ (101 MHz)

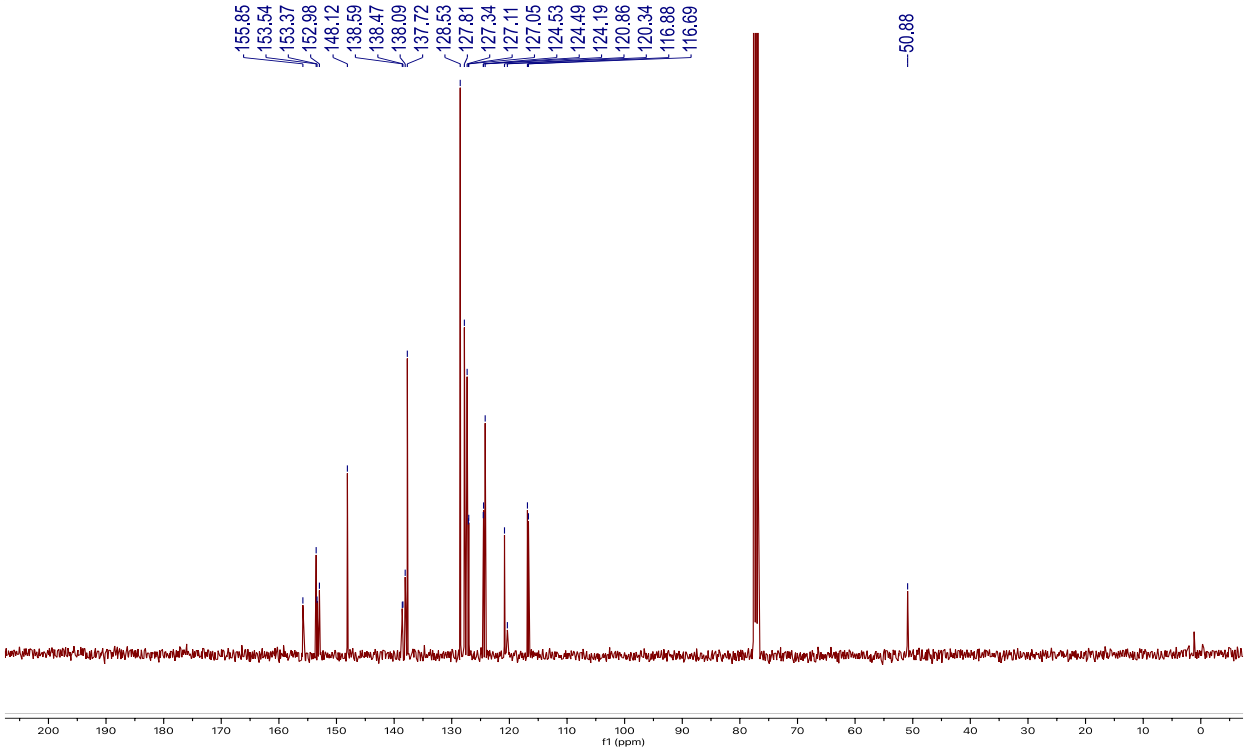


_N_-benzyl-2-fluoro-_N_-(2-pyridyl)benzamide (3i)

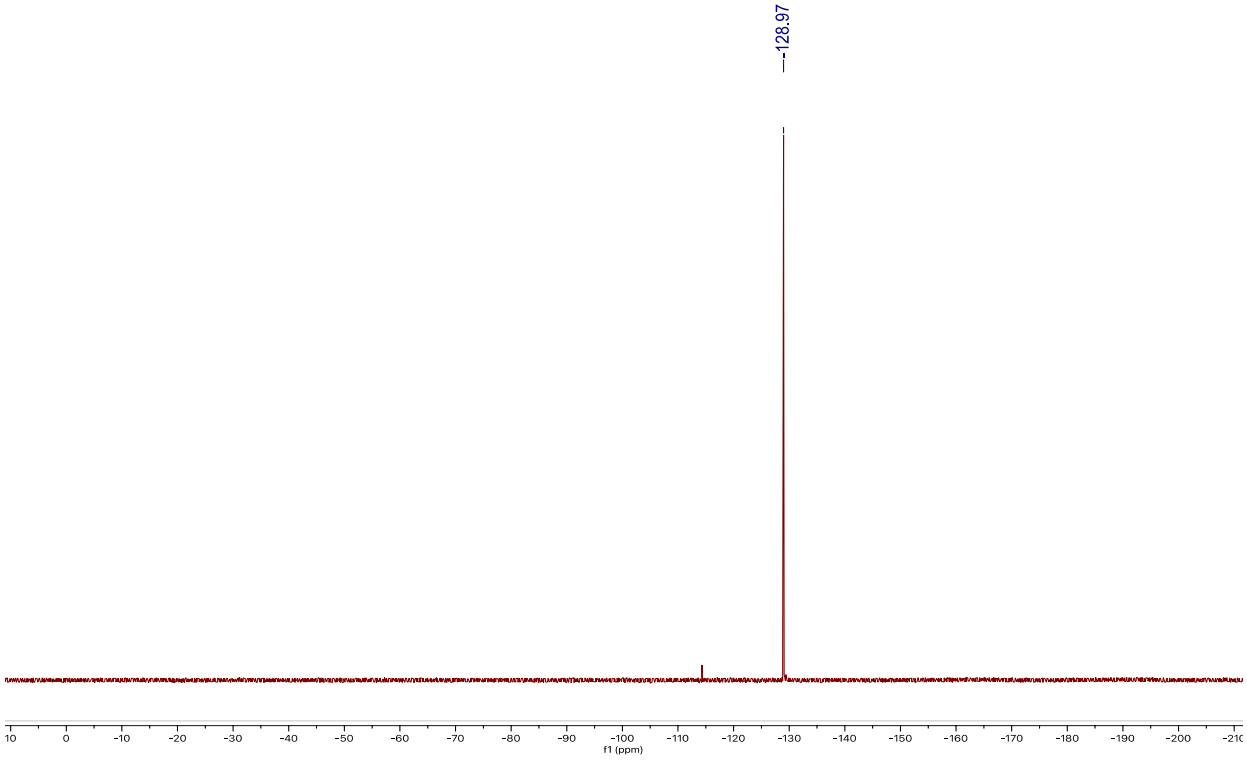
^{1}H NMR Spectrum $CDCl_3$ (400 MHz)



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

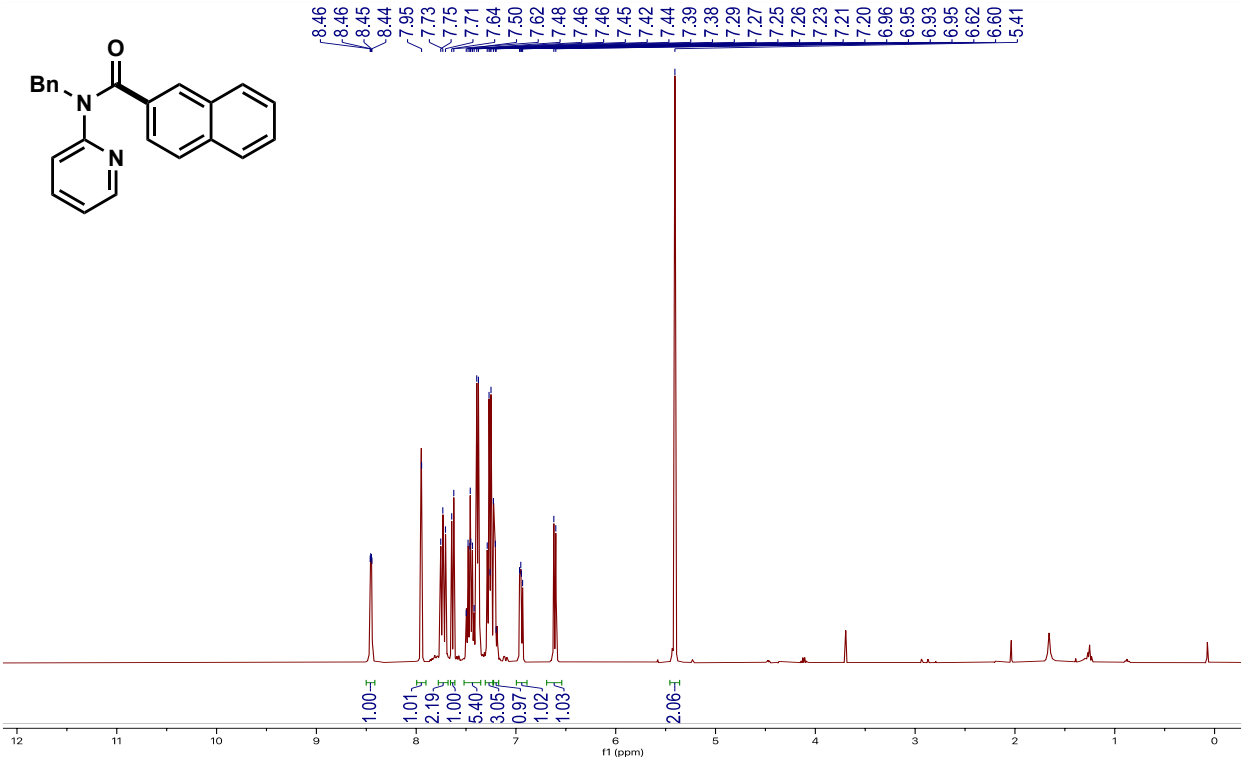


^{19}F NMR Spectrum $CDCl_3$ (377 MHz)

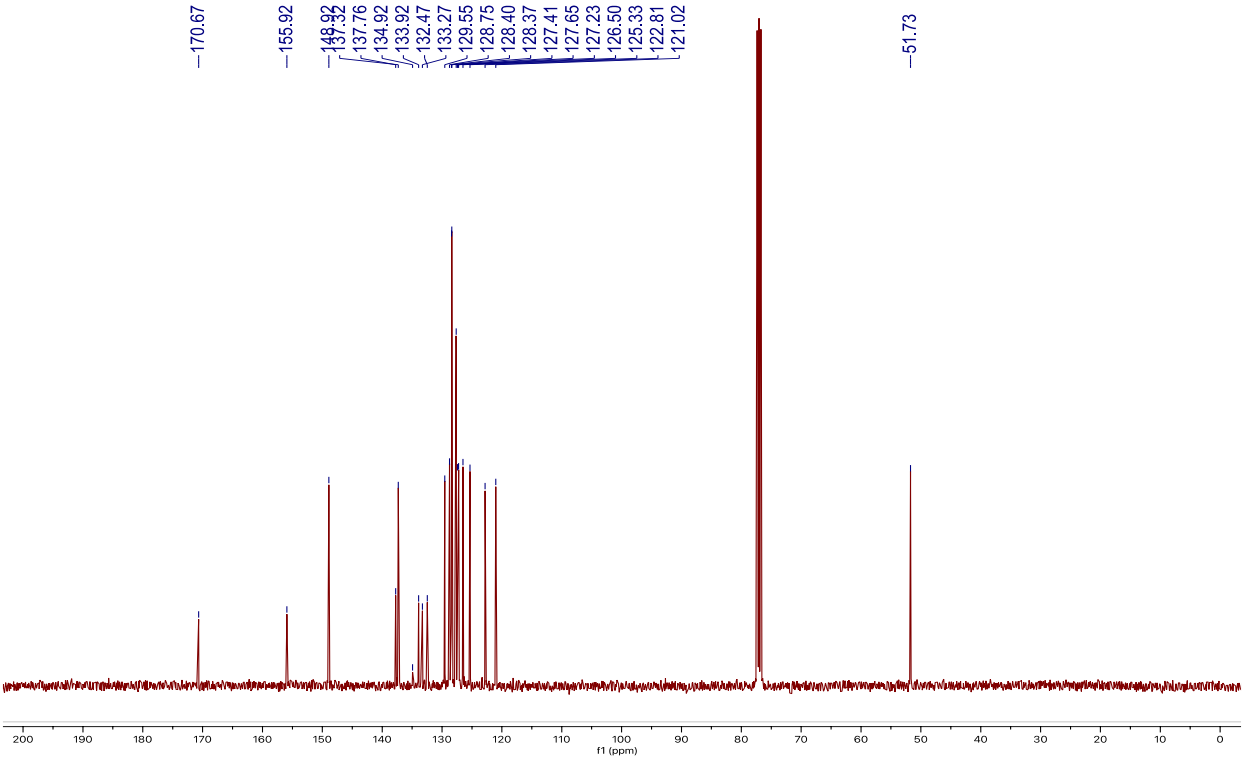


_N_-benzyl-_N_-(2-pyridyl)naphthalene-2-carboxamide (3j)

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

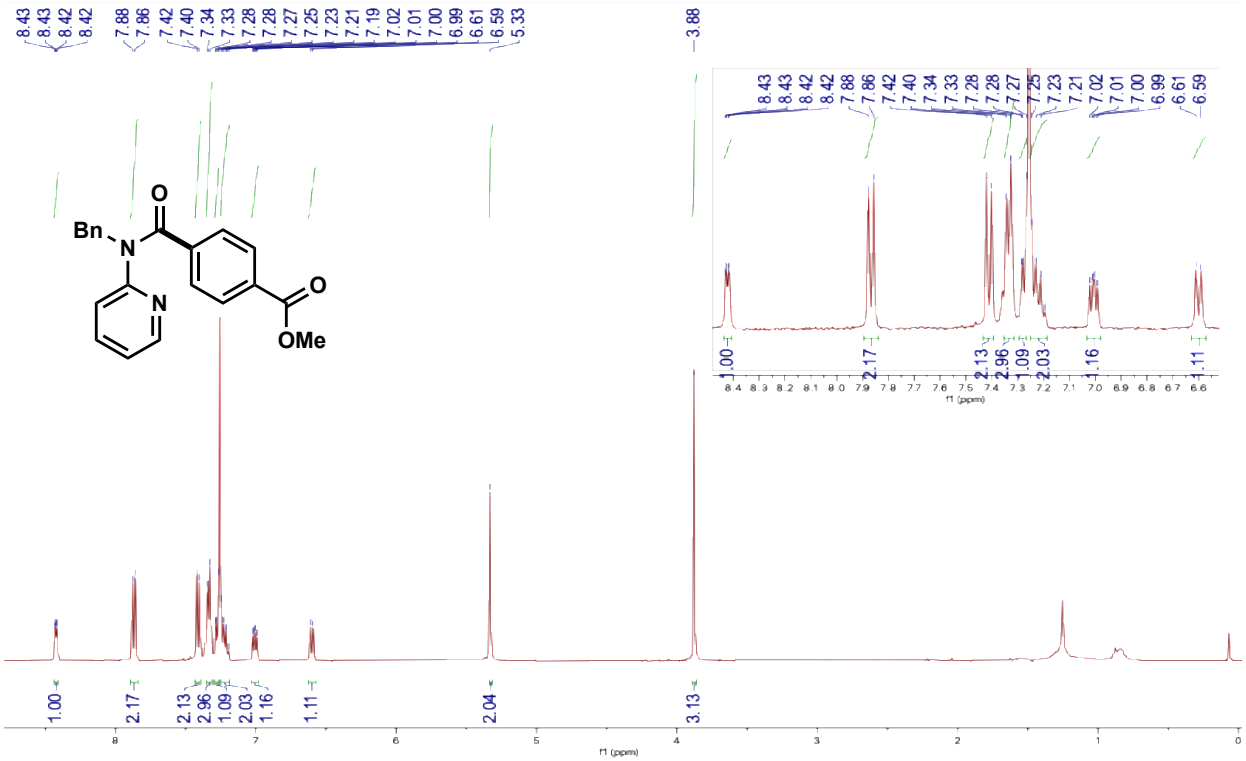


^{13}C NMR Spectrum $CDCl_3$ (101 MHz)

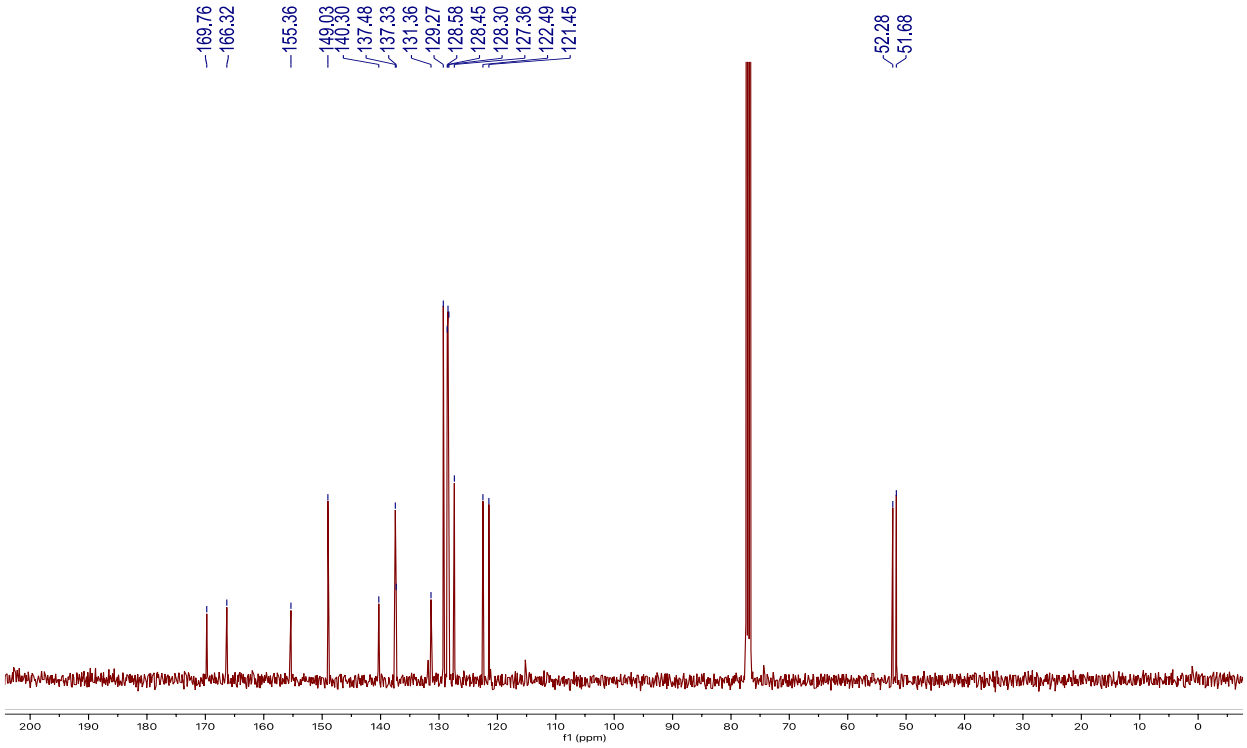


Methyl 4-[benzyl(2-pyridyl)carbamoyl]benzoate (3k)

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

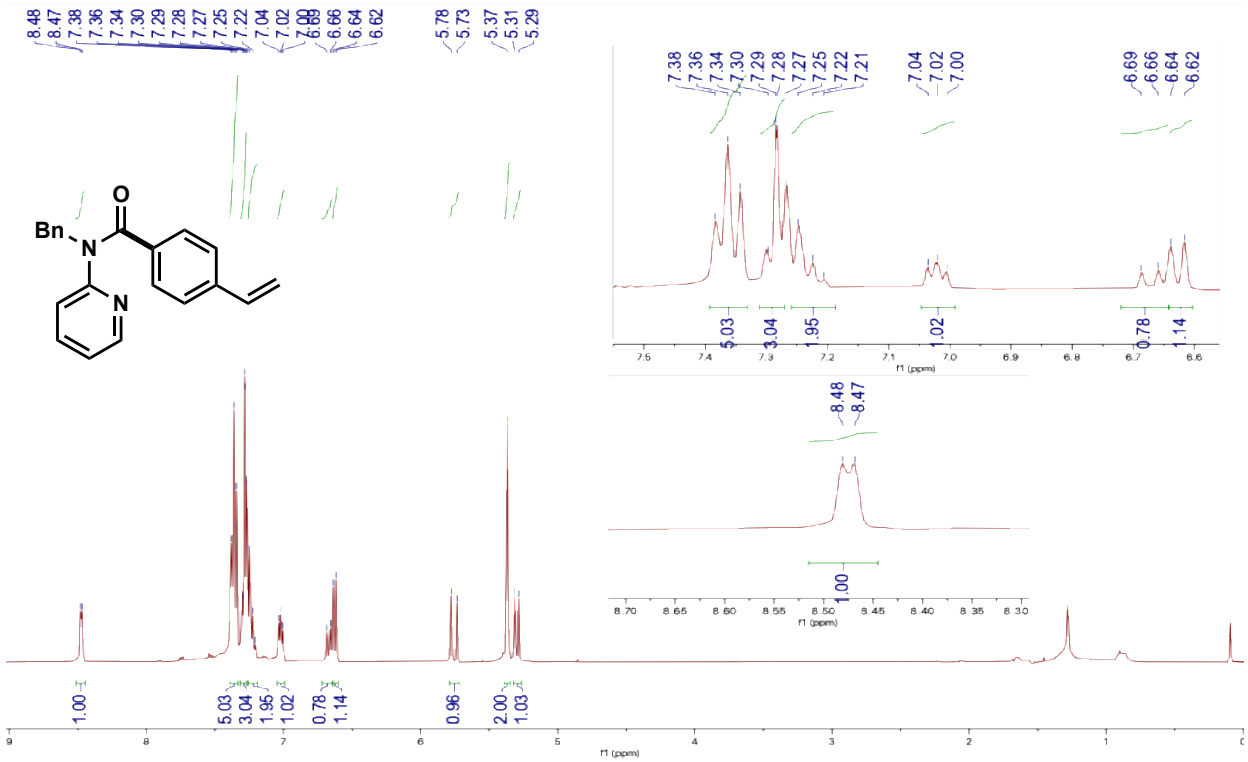


^{13}C NMR Spectrum $CDCl_3$ (101 MHz)

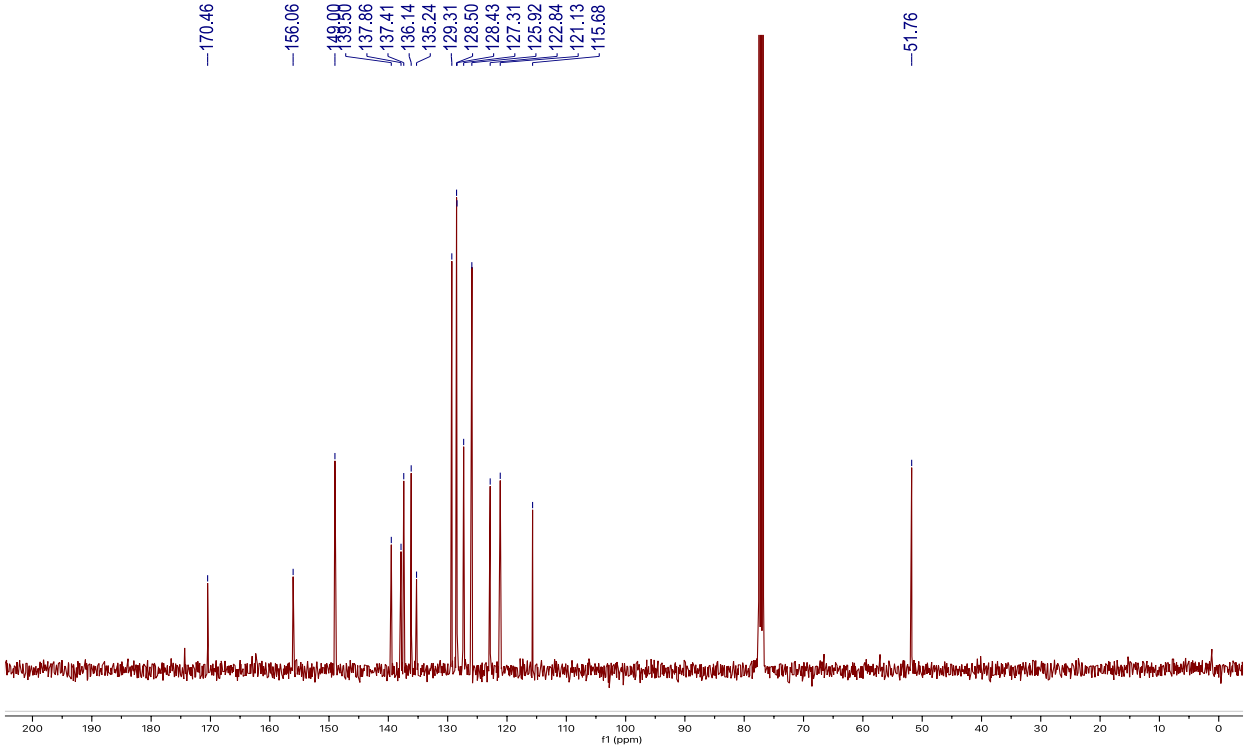


_N_-benzyl-_N_-(2-pyridyl)-4-vinyl-benzamide (3l)

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

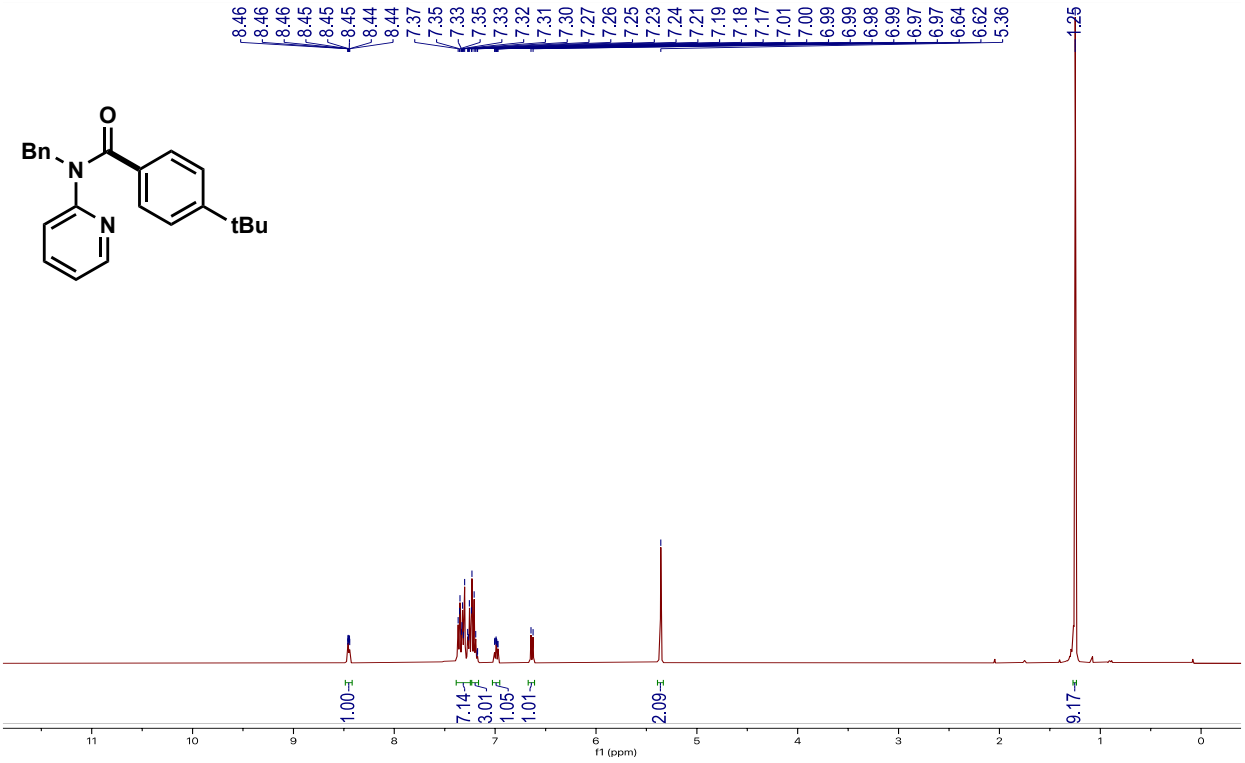


^{13}C NMR Spectrum $CDCl_3$ (101 MHz)

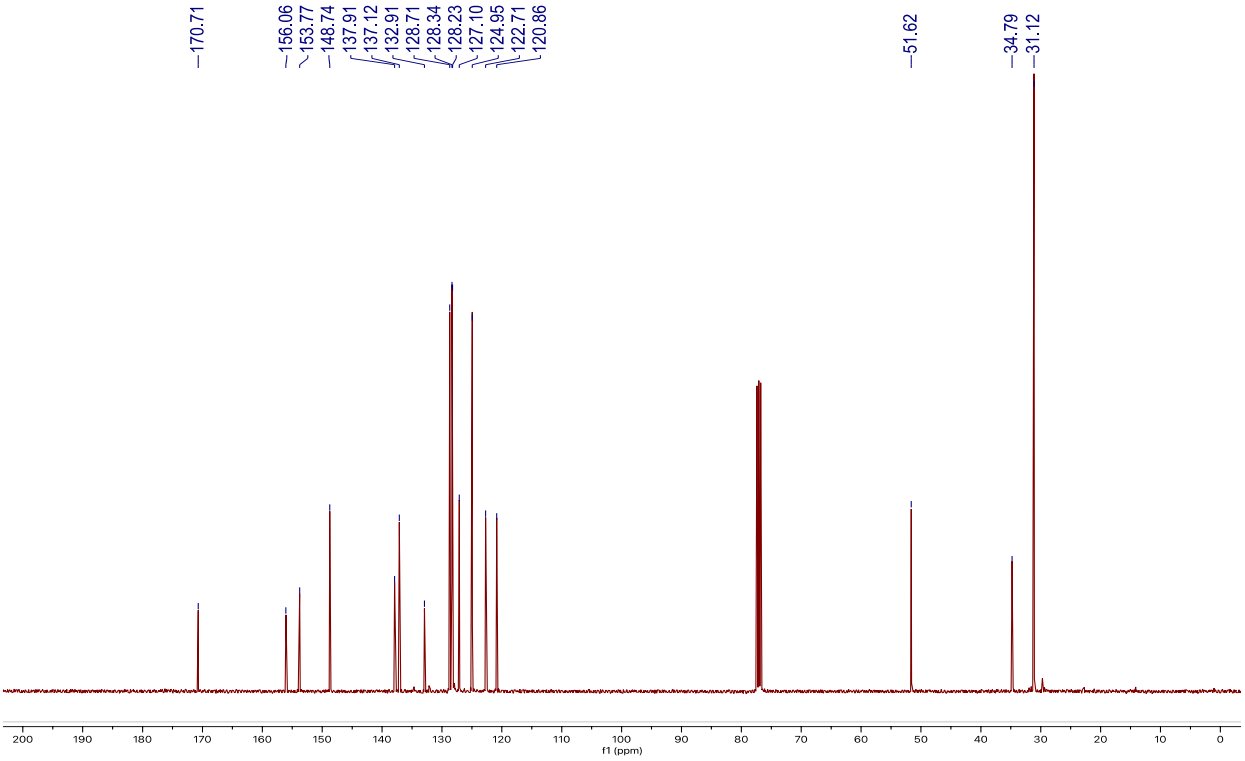


***N*-benzyl-4-tert-butyl-*N*-(2-pyridyl)benzamide (3m)**

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

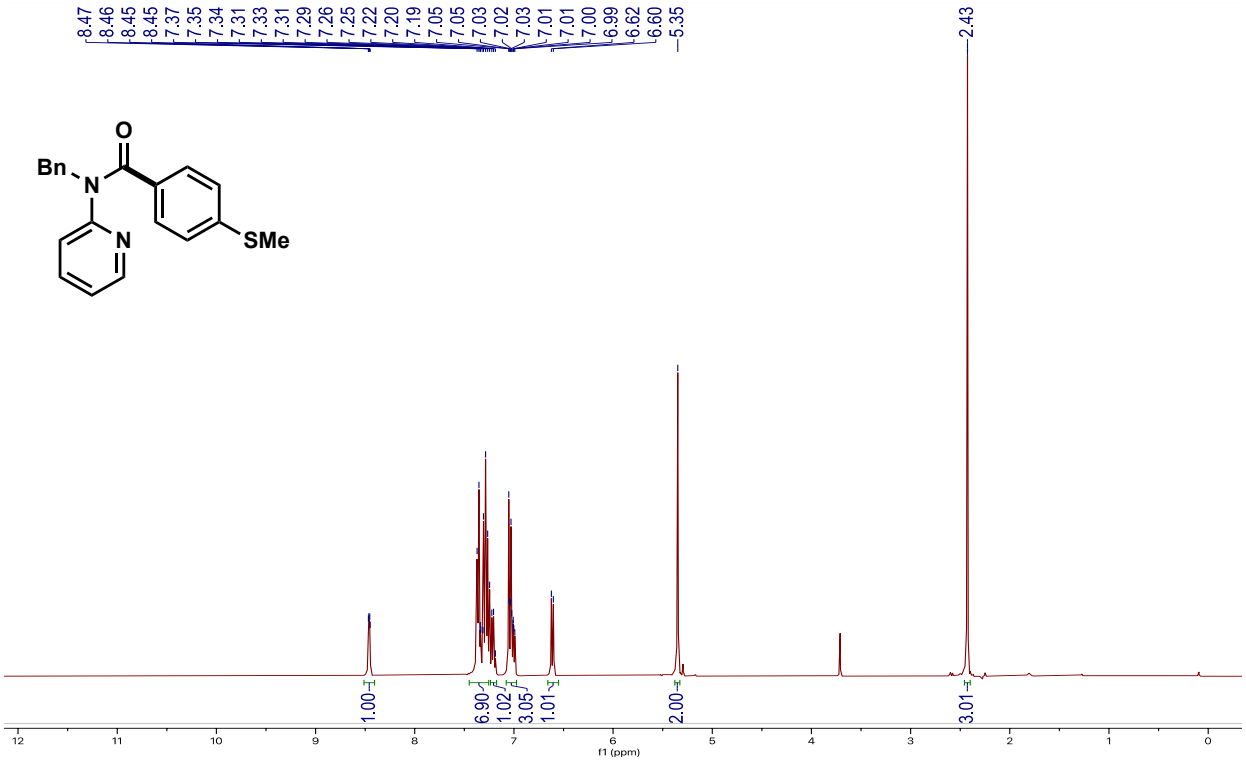


^{13}C NMR Spectrum $CDCl_3$ (101 MHz)

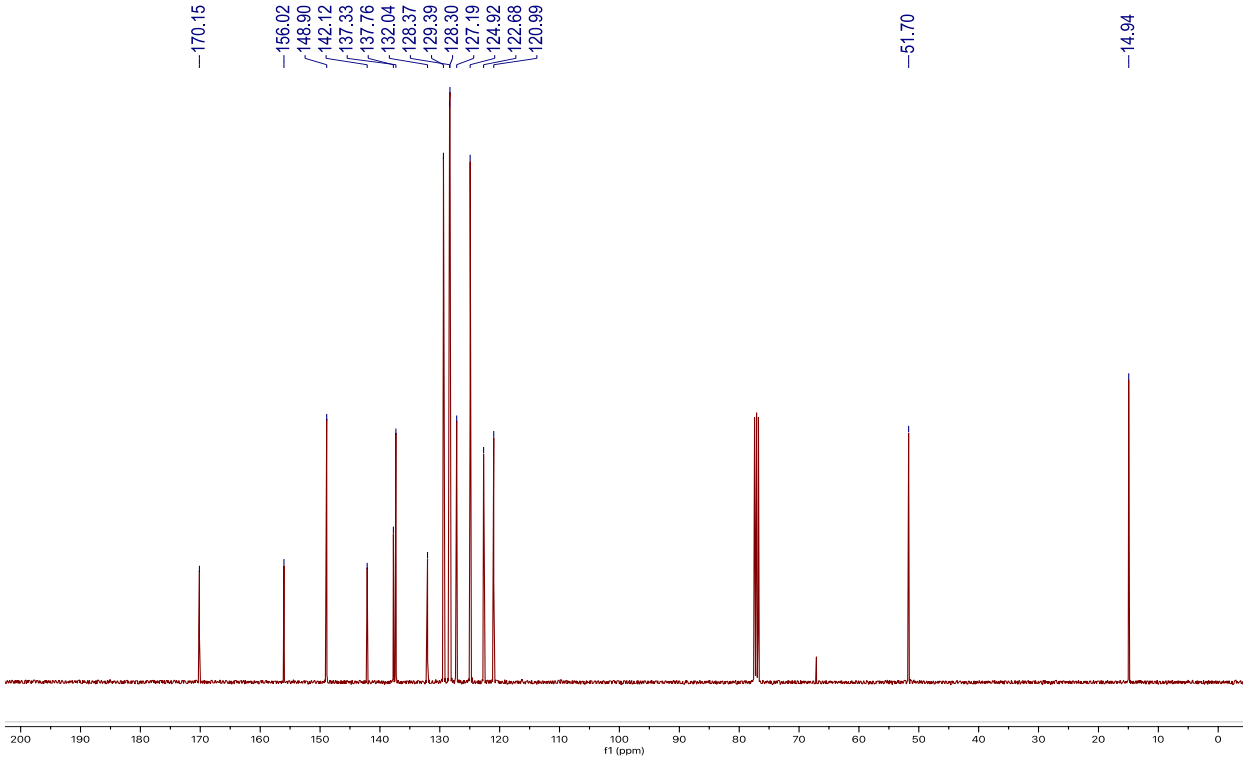


_N_-benzyl-4-methylsulfanyl-_N_-(2-pyridyl)benzamide (3n)

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

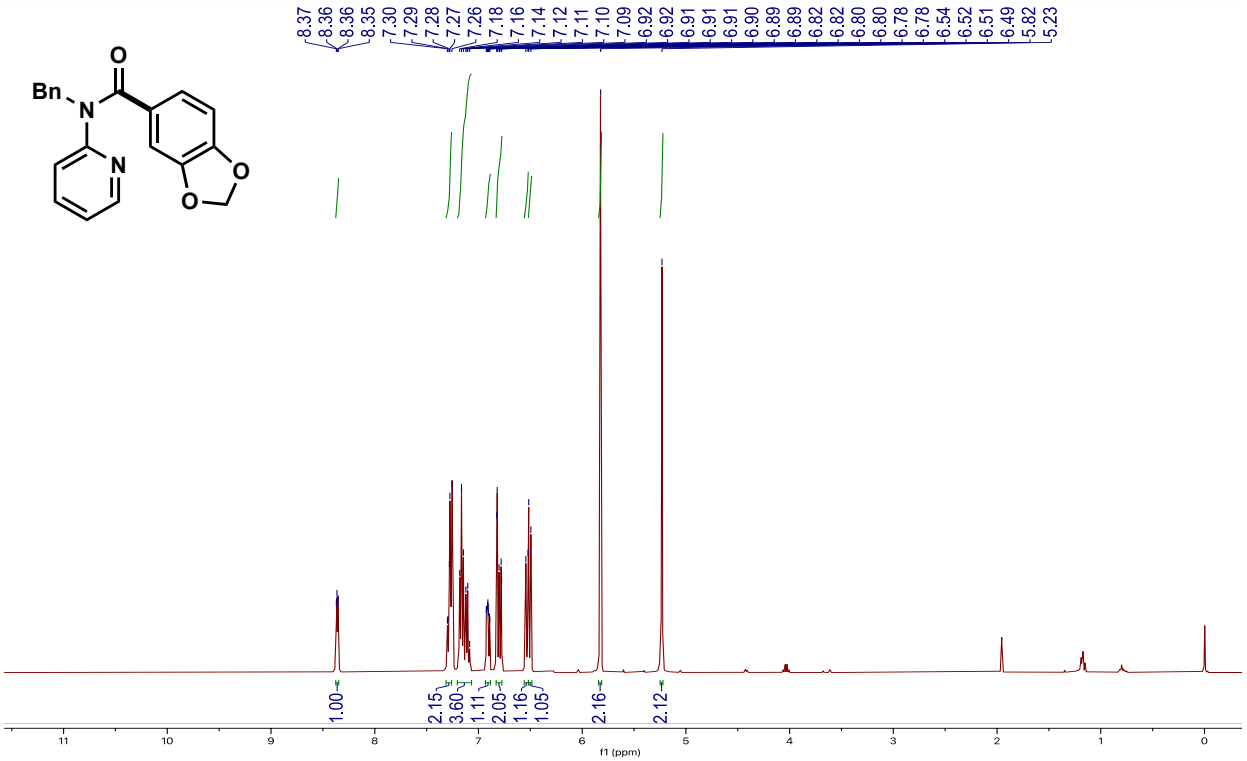


^{13}C NMR Spectrum $CDCl_3$ (101 MHz)

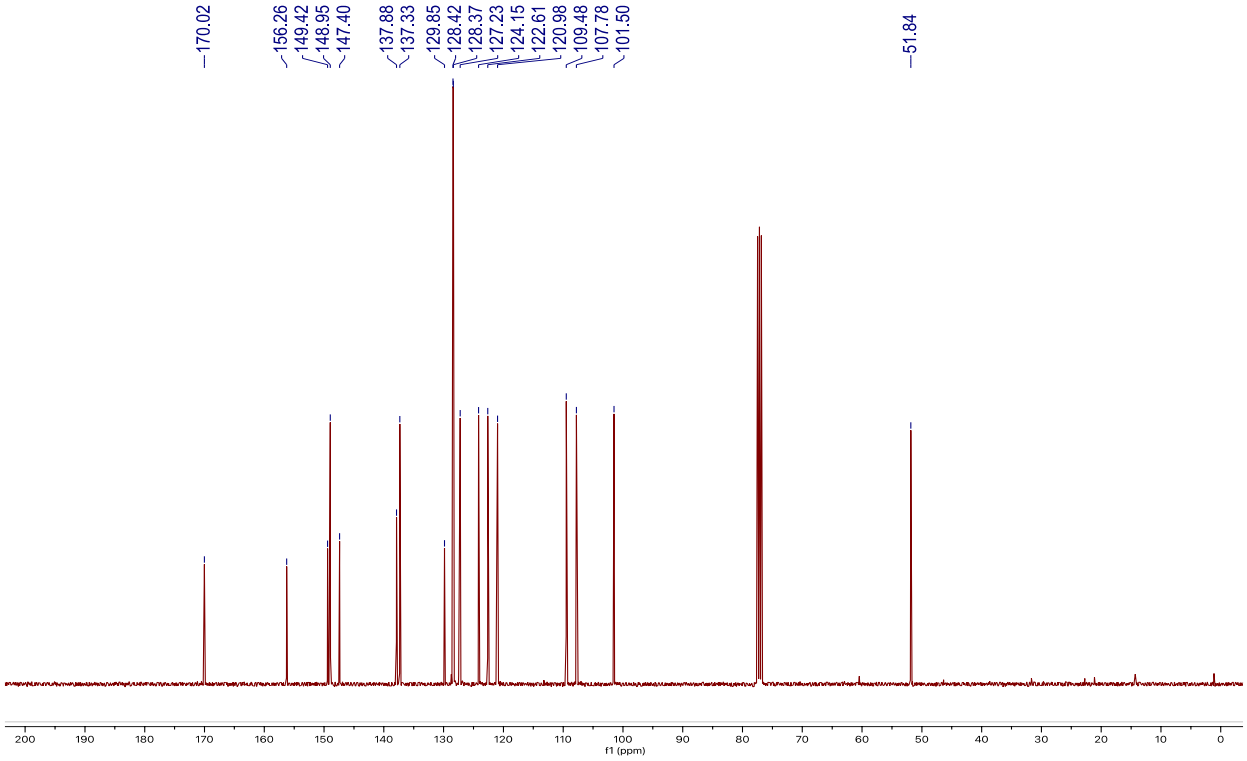


_N_-benzyl-_N_-(2-pyridyl)-1,3-benzodioxole-5-carboxamide (3o)

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

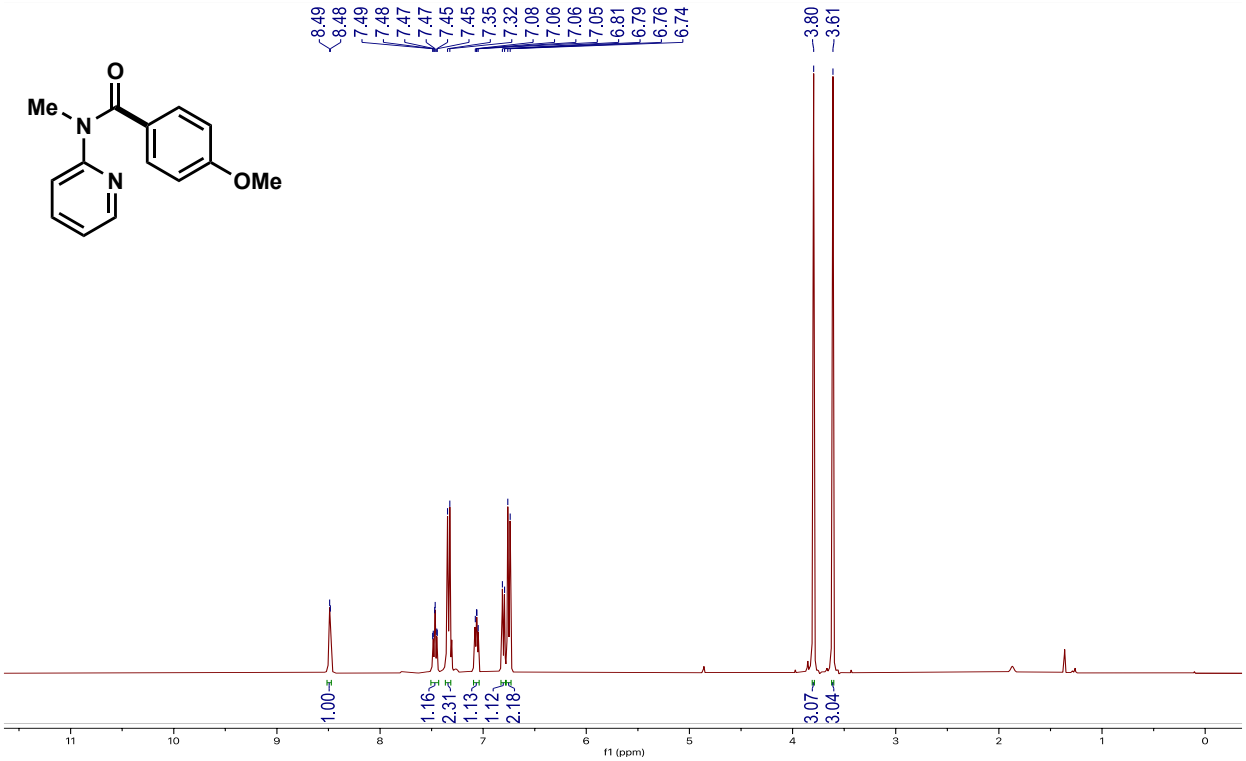


^{13}C NMR Spectrum $CDCl_3$ (101 MHz)

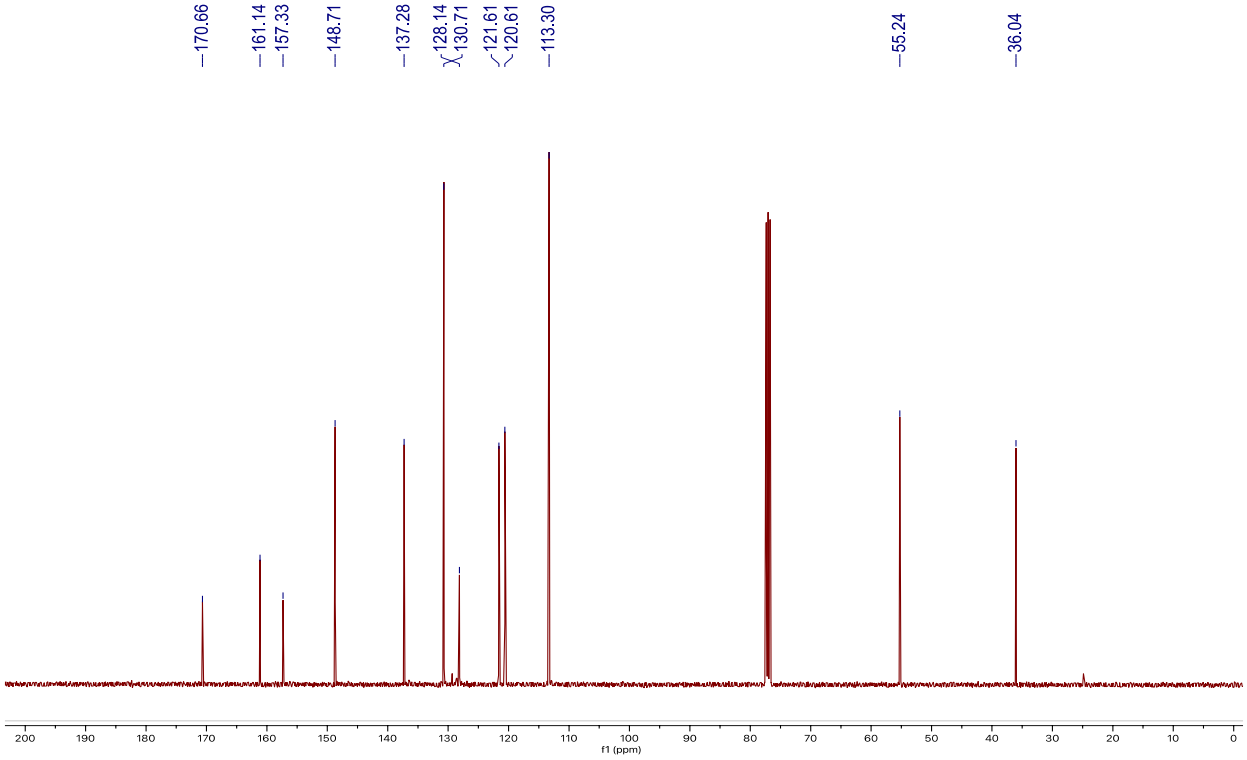


4-methoxy-*N*-methyl-*N*-(2-pyridyl)benzamide (3p)

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

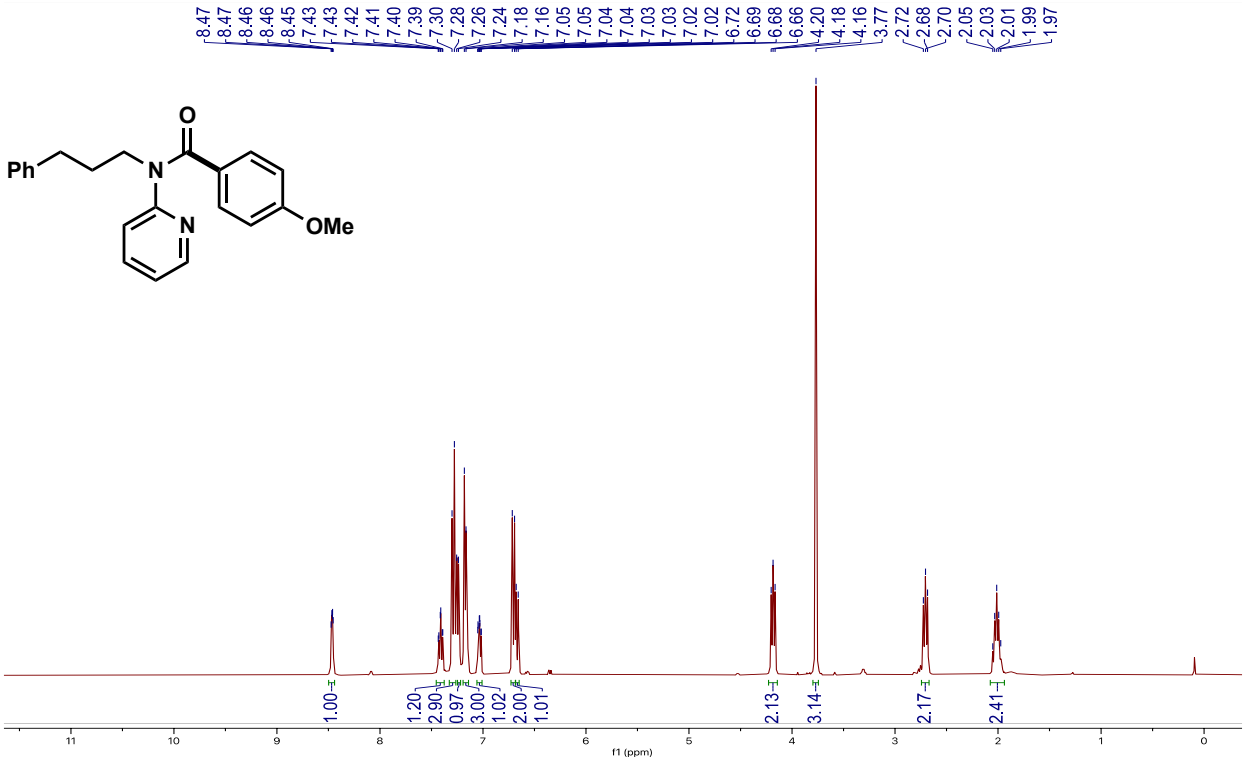


^{13}C NMR Spectrum $CDCl_3$ (101 MHz)

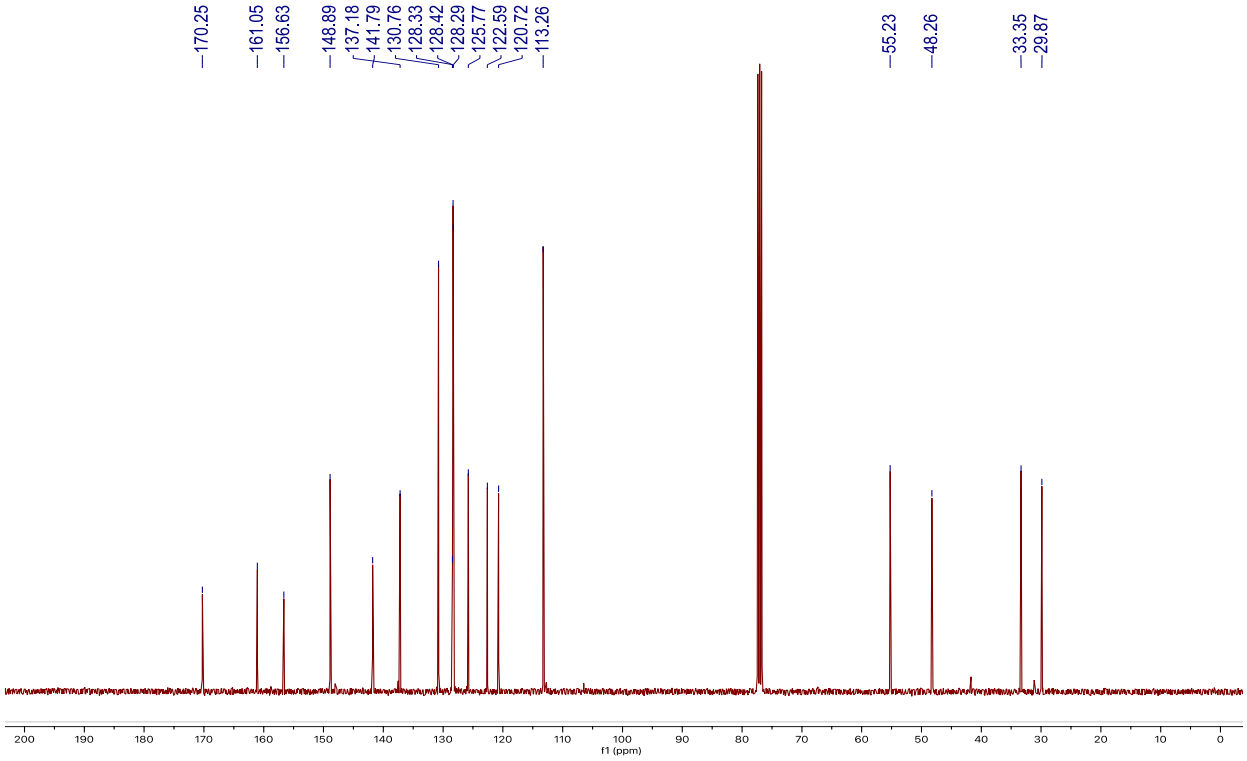


4-methoxy-*N*-(3-phenylpropyl)-*N*-(2-pyridyl)benzamide (3q)

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

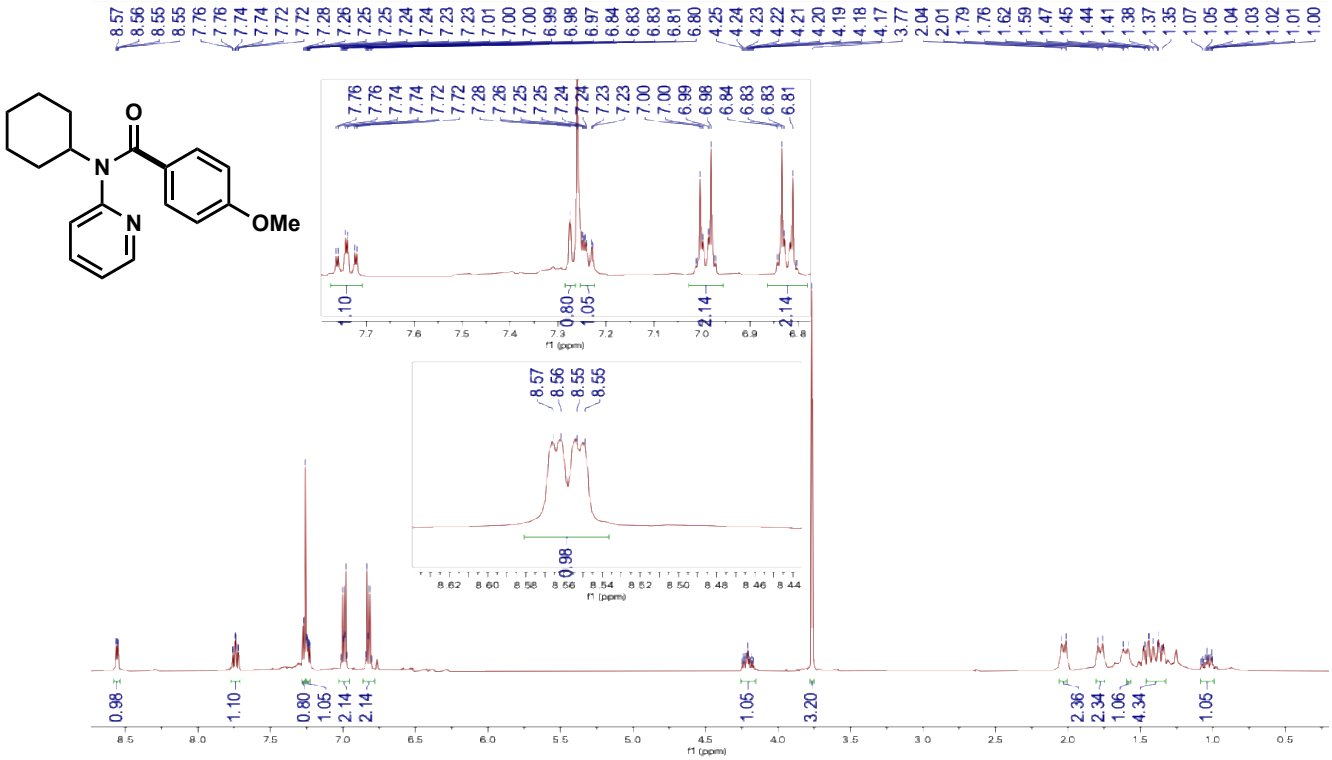


^{13}C NMR Spectrum $CDCl_3$ (101 MHz)

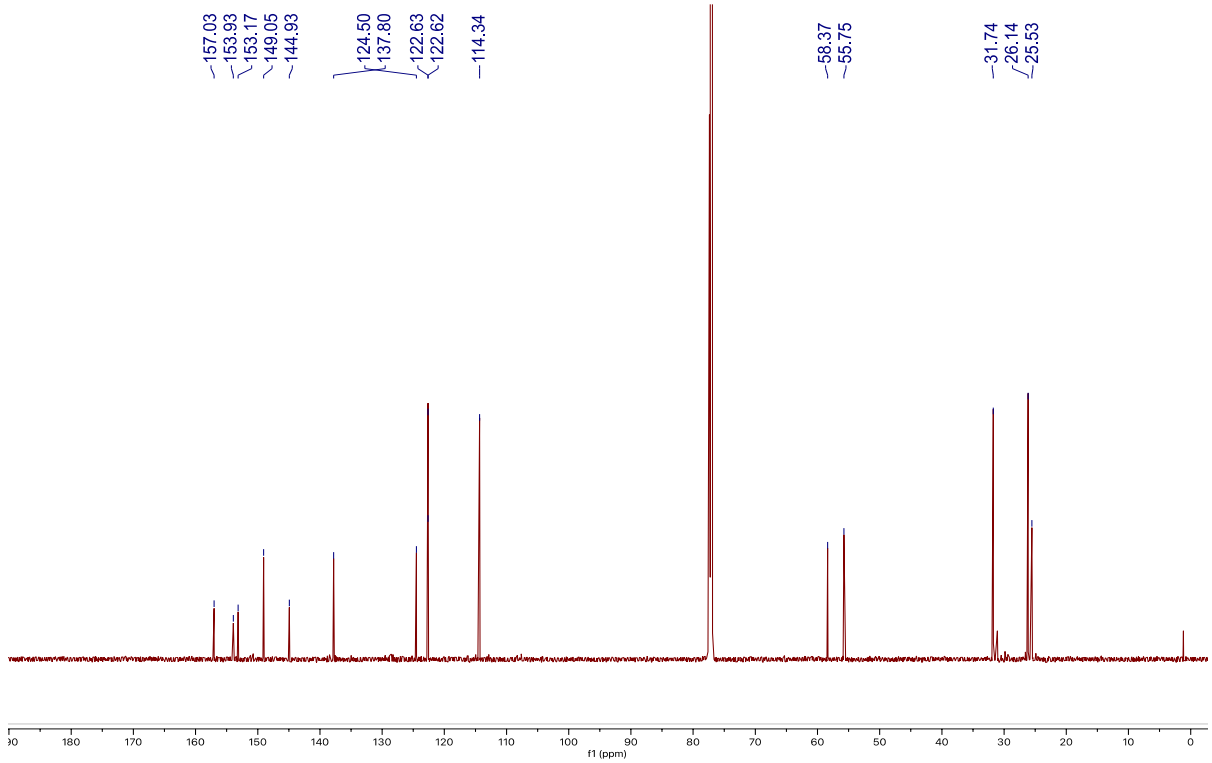


_N_-cyclohexyl-4-methoxy-_N_-(2-pyridyl)benzamide (3r)

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

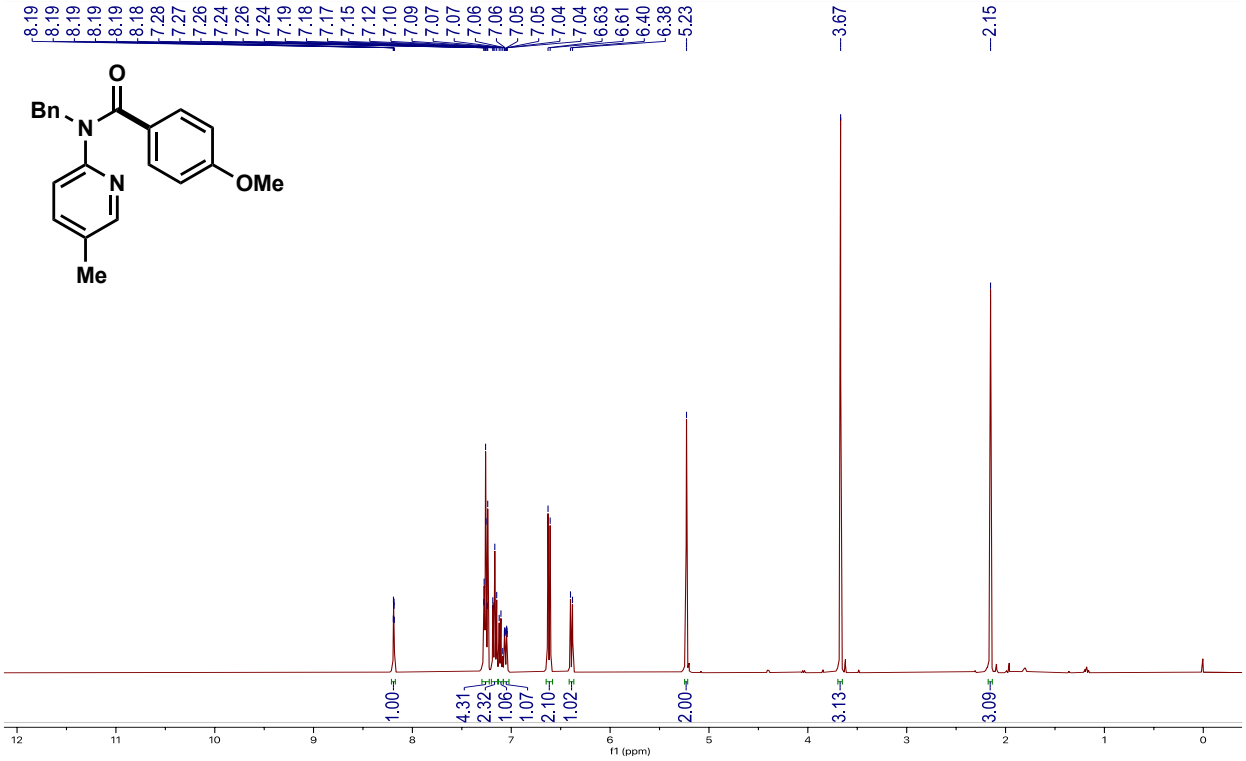


^{13}C NMR Spectrum $CDCl_3$ (101 MHz)

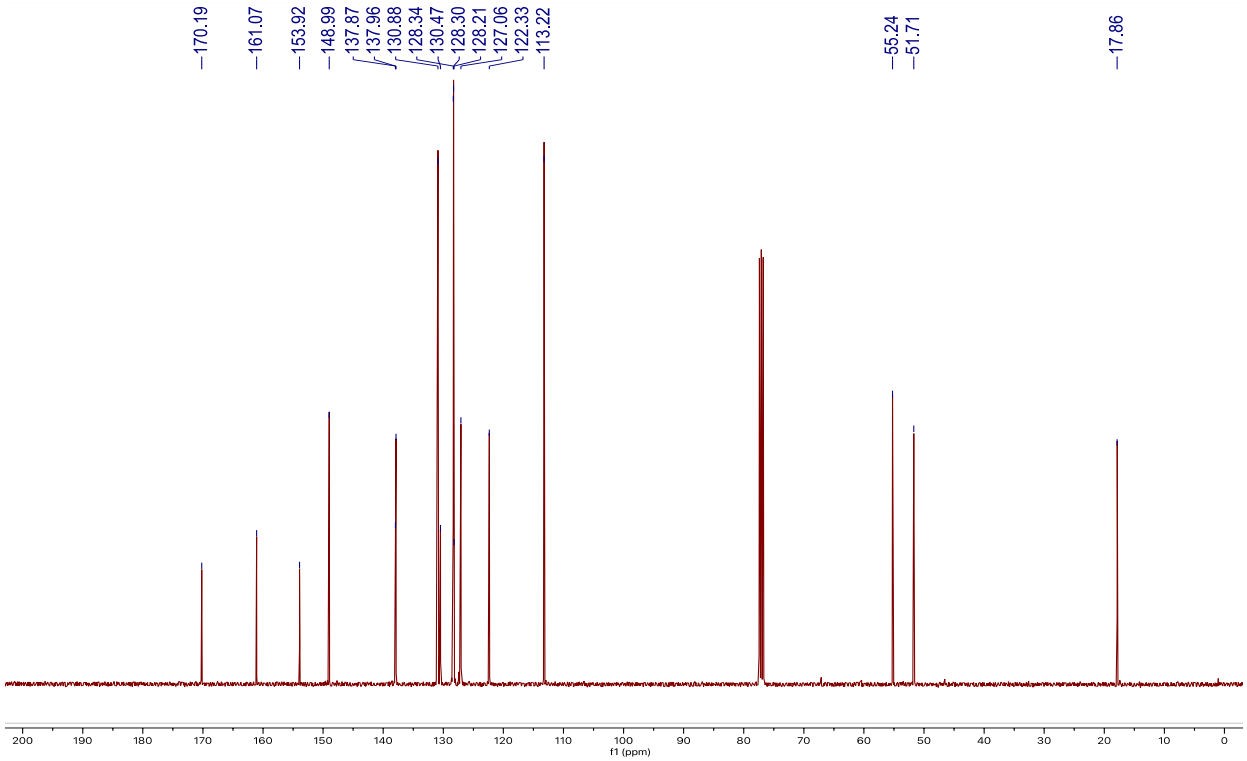


***N*-benzyl-4-methoxy-*N*-(5-methyl-2-pyridyl)benzamide (3s)**

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

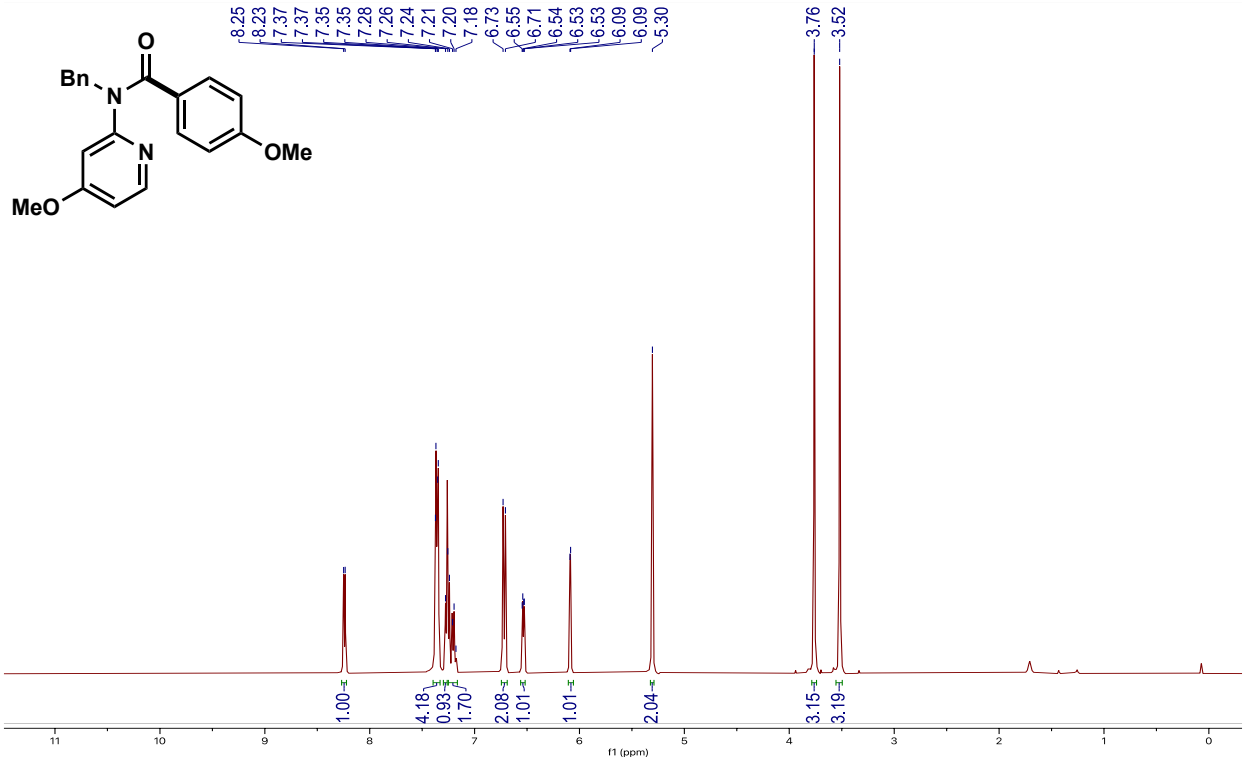


^{13}C NMR Spectrum $CDCl_3$ (101 MHz)

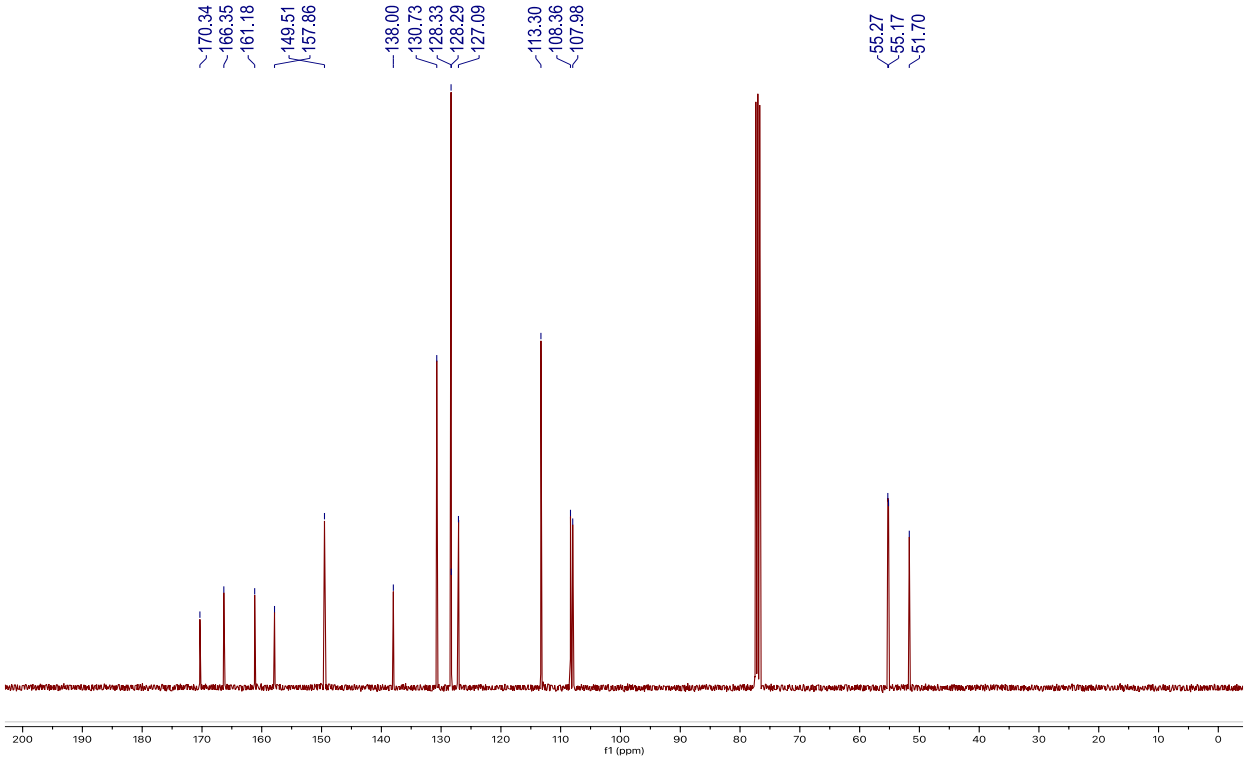


***N*-benzyl-4-methoxy-*N*-(4-methoxy-2-pyridyl)benzamide (3t)**

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

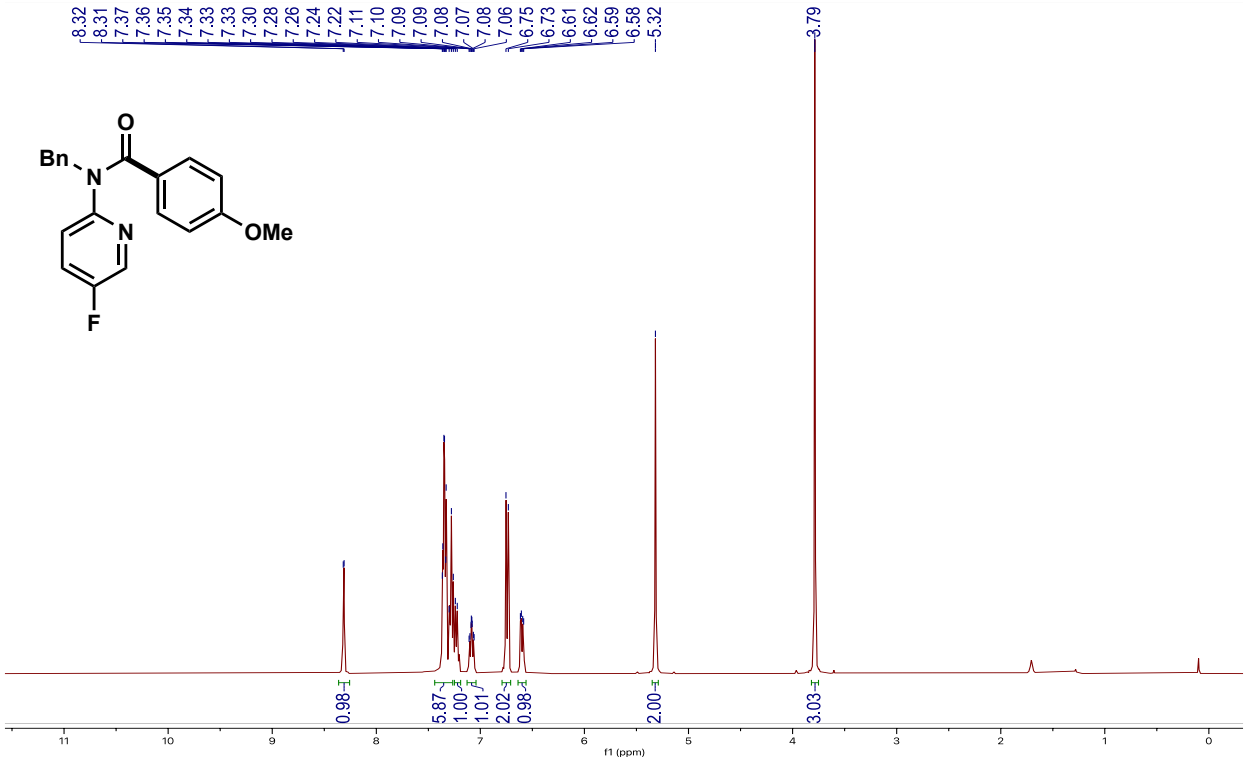


^{13}C NMR Spectrum $CDCl_3$ (101 MHz)

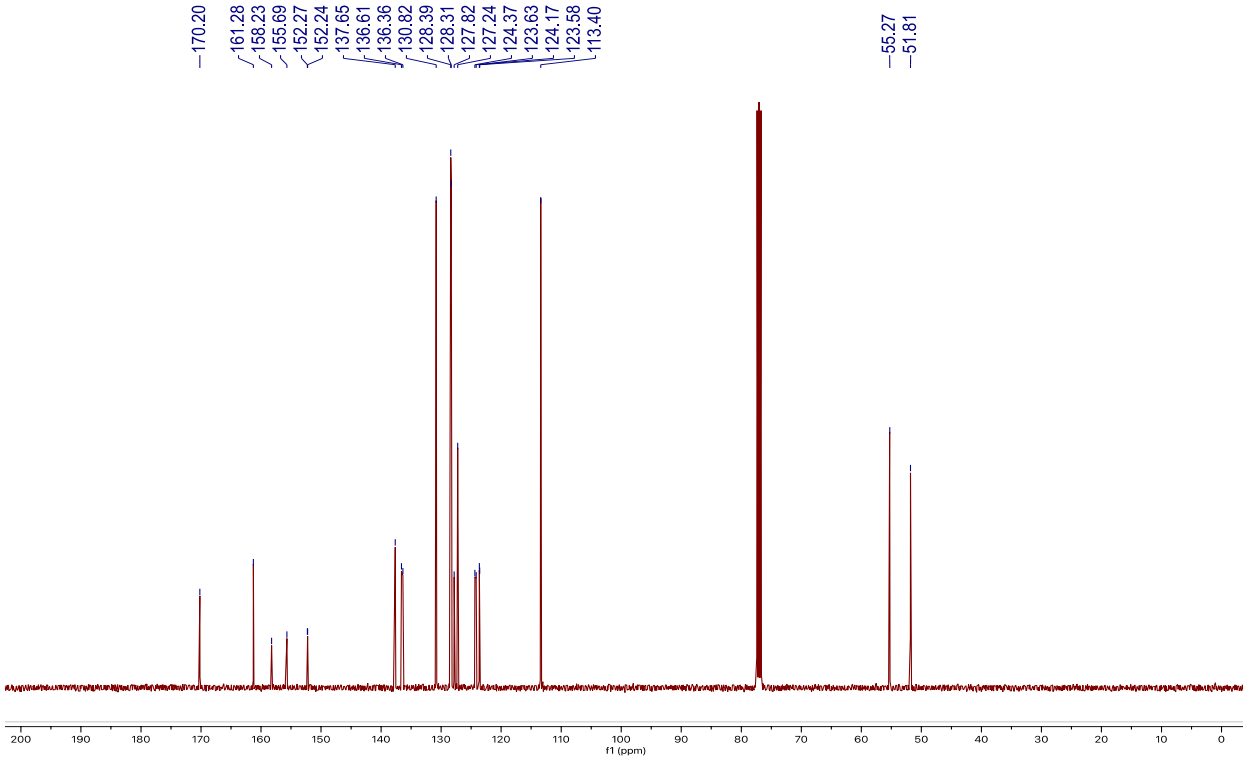


_N_-benzyl-_N_-(5-fluoro-2-pyridyl)-4-methoxy-benzamide (3u)

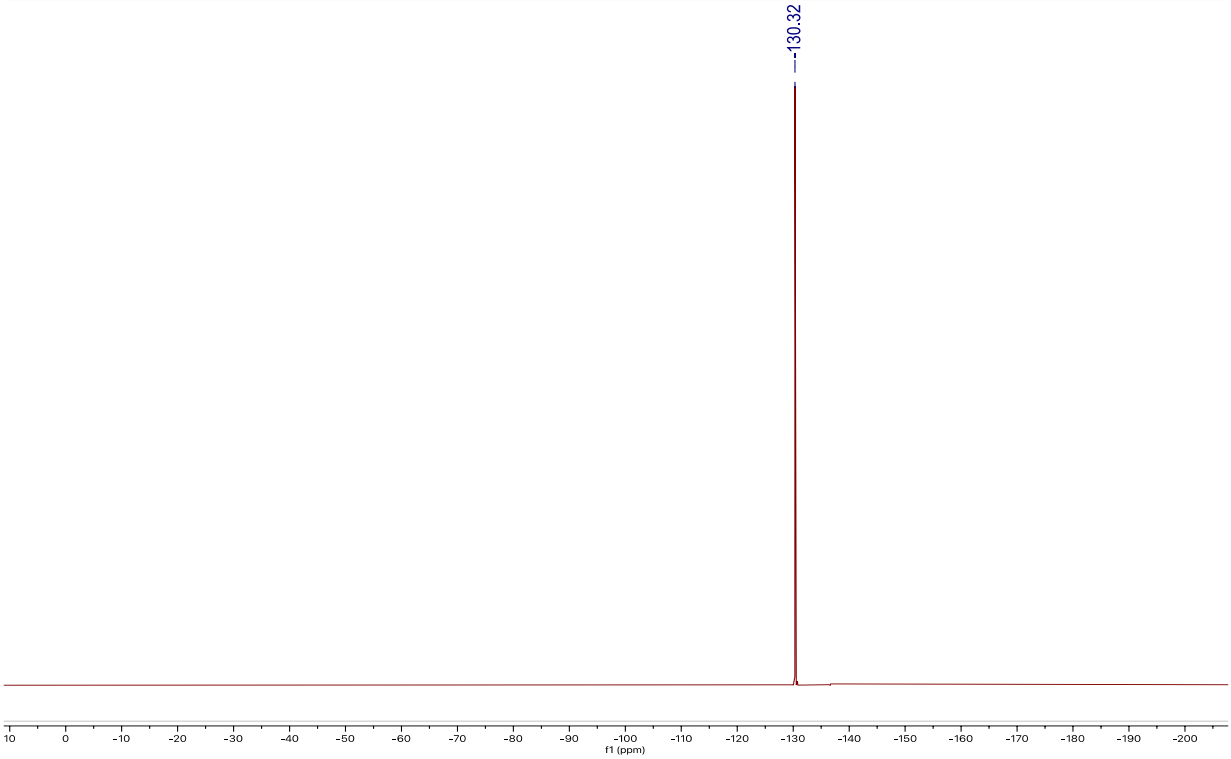
^{1}H NMR Spectrum $CDCl_3$ (400 MHz)



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

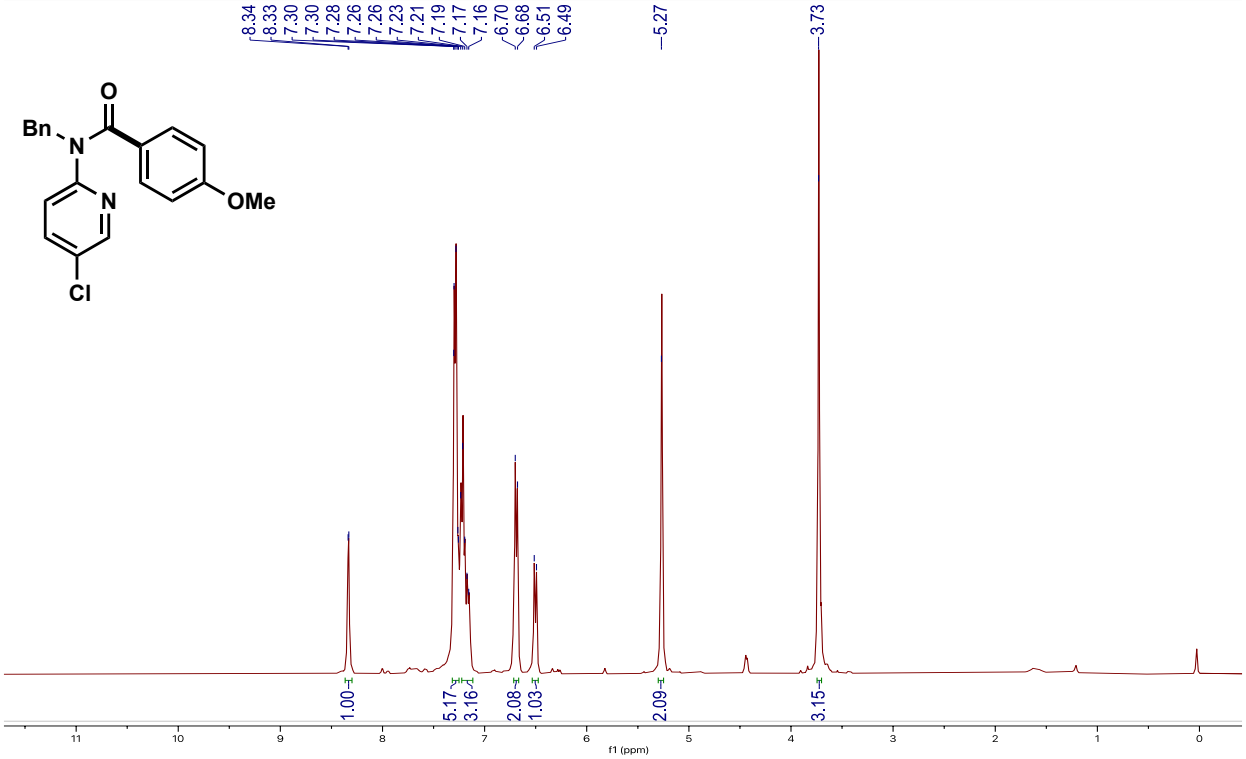


^{19}F NMR Spectrum $CDCl_3$ (377 MHz)

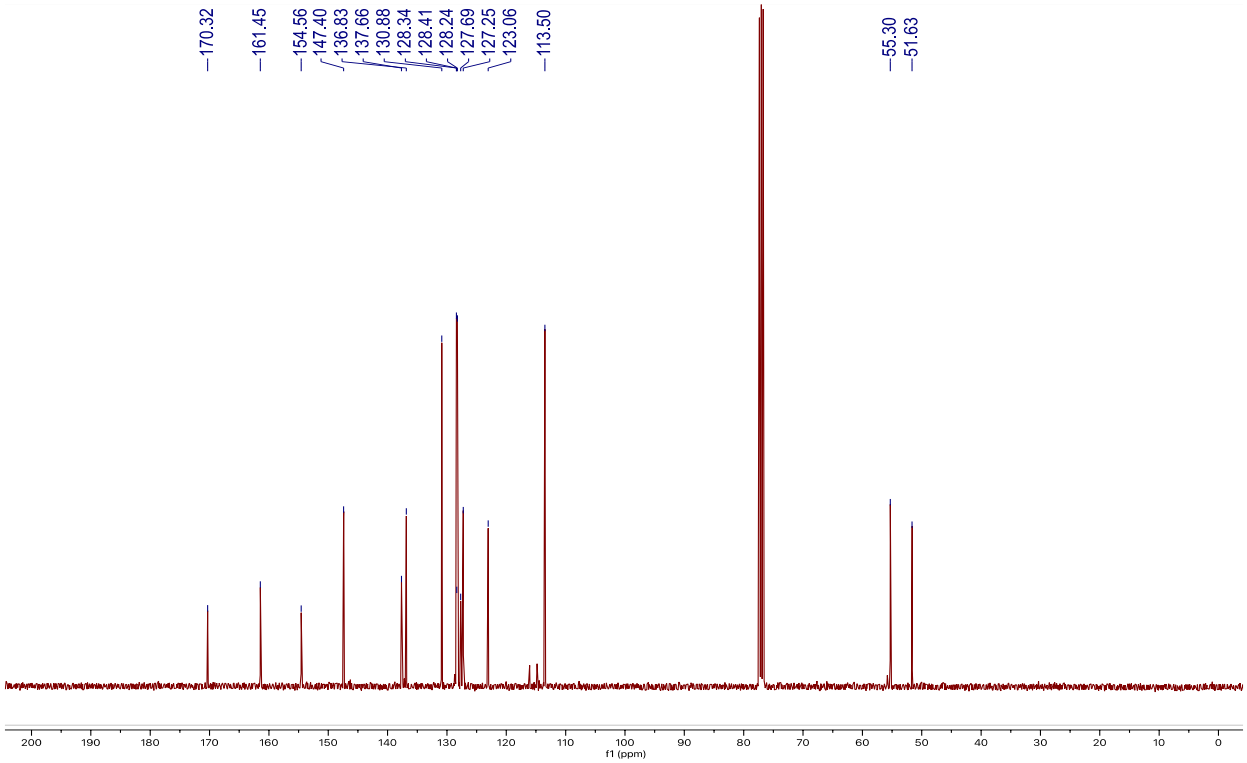


_N_-benzyl-_N_-(5-chloro-2-pyridyl)-4-methoxy-benzamide (3v)

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

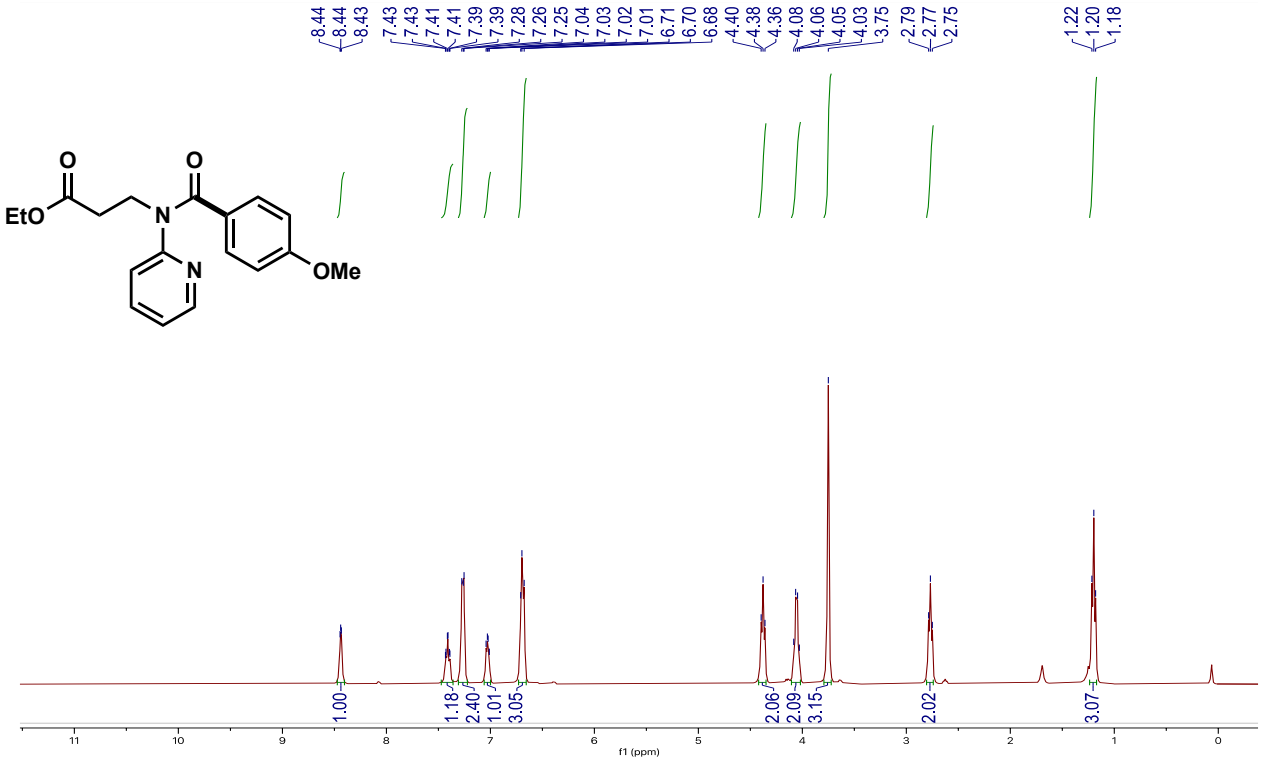


^{13}C NMR Spectrum $CDCl_3$ (101 MHz)

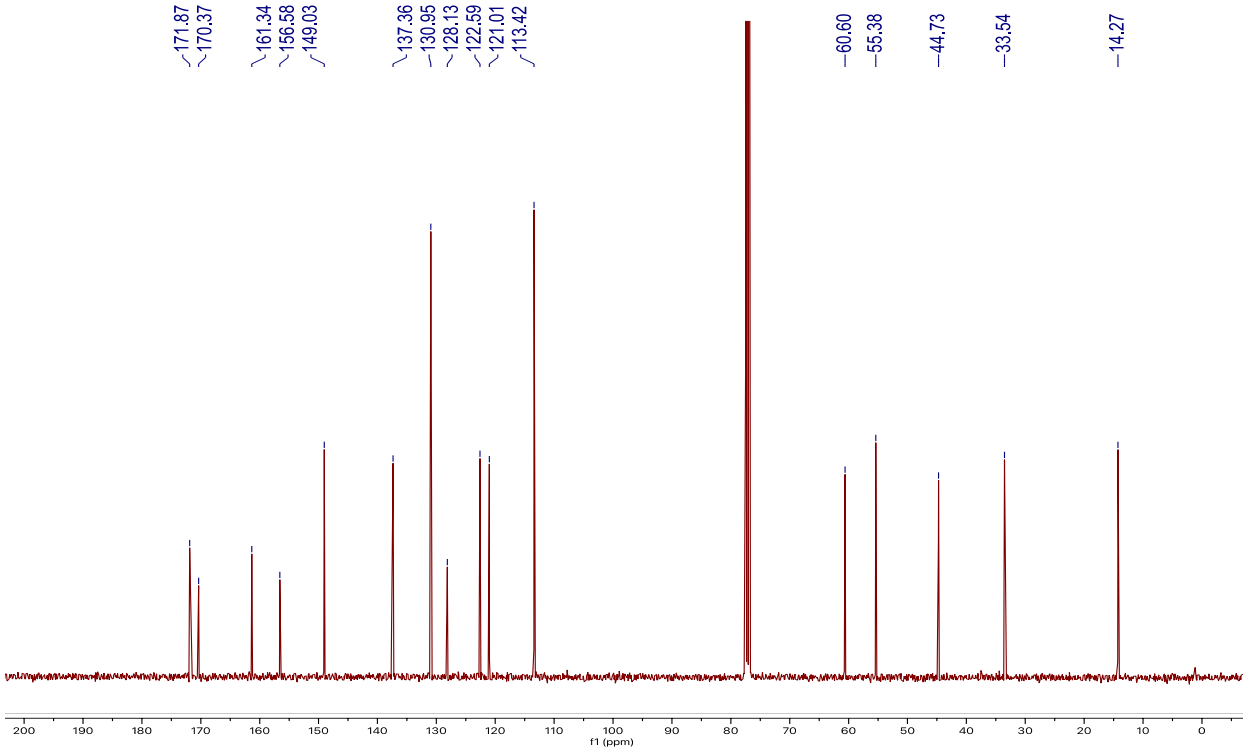


Ethyl 3-[(4-methoxybenzoyl)-(2-pyridyl)amino]propanoate (3w)

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

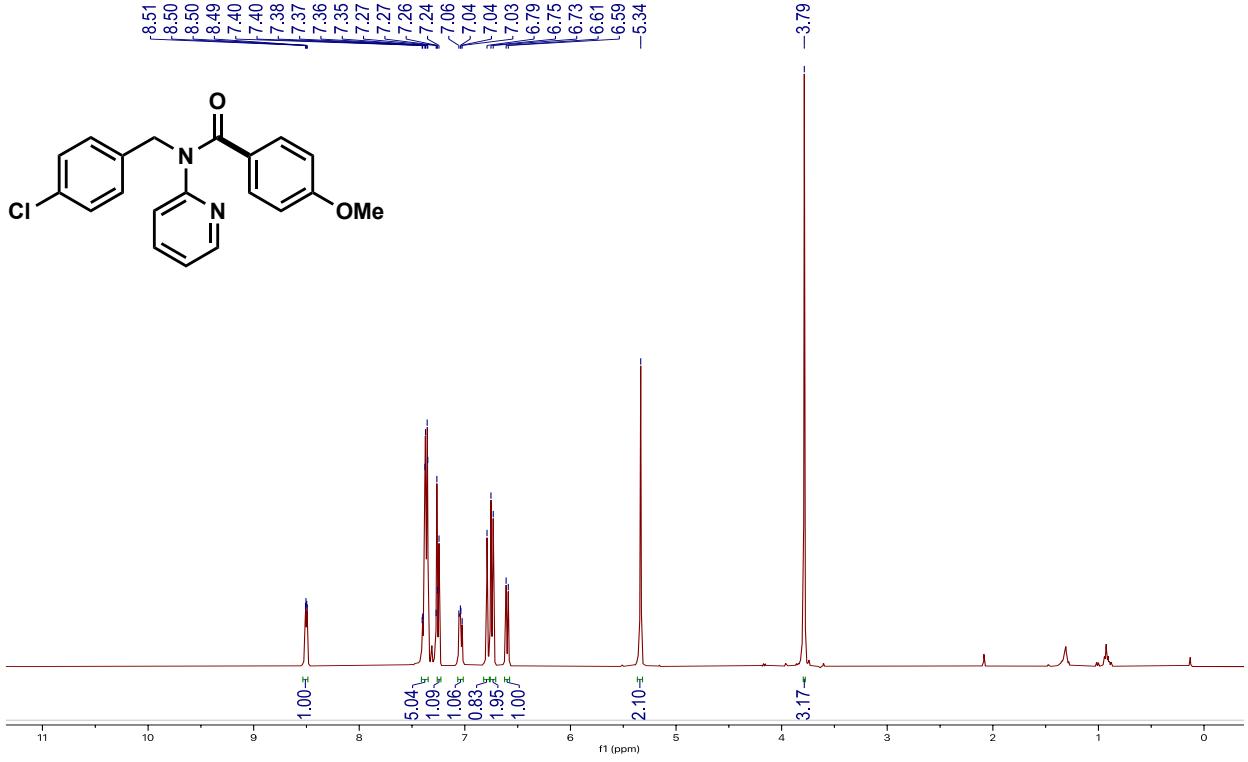


^{13}C NMR Spectrum $CDCl_3$ (101 MHz)

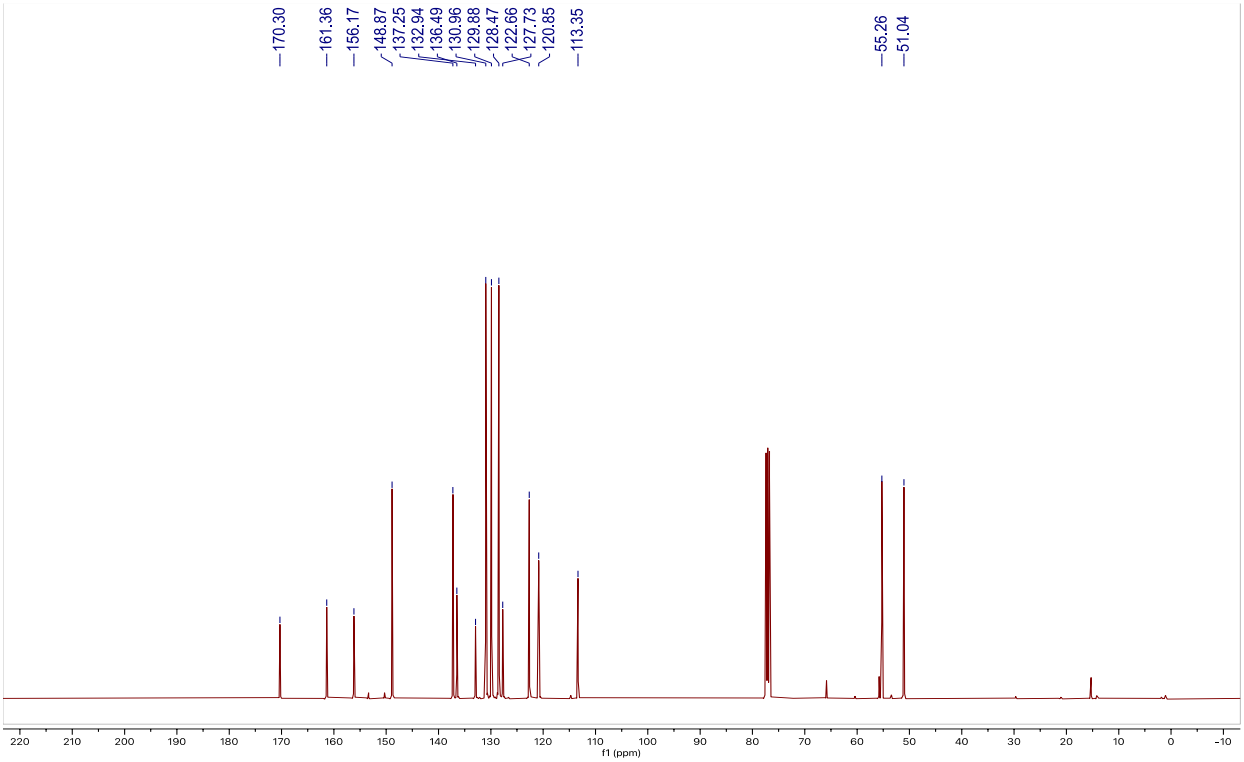


_N_-[(4-chlorophenyl)methyl]-4-methoxy-_N_-(2-pyridyl)benzamide (3x)

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

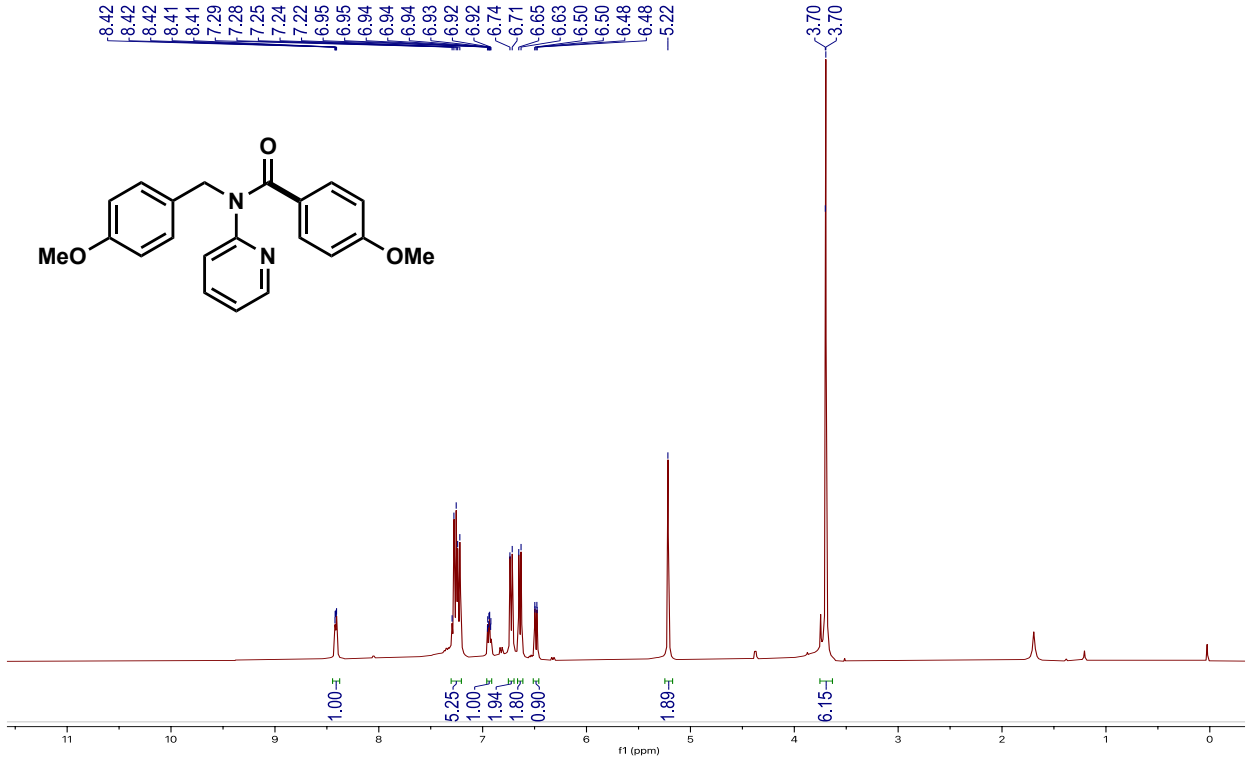


^{13}C NMR Spectrum $CDCl_3$ (101 MHz)

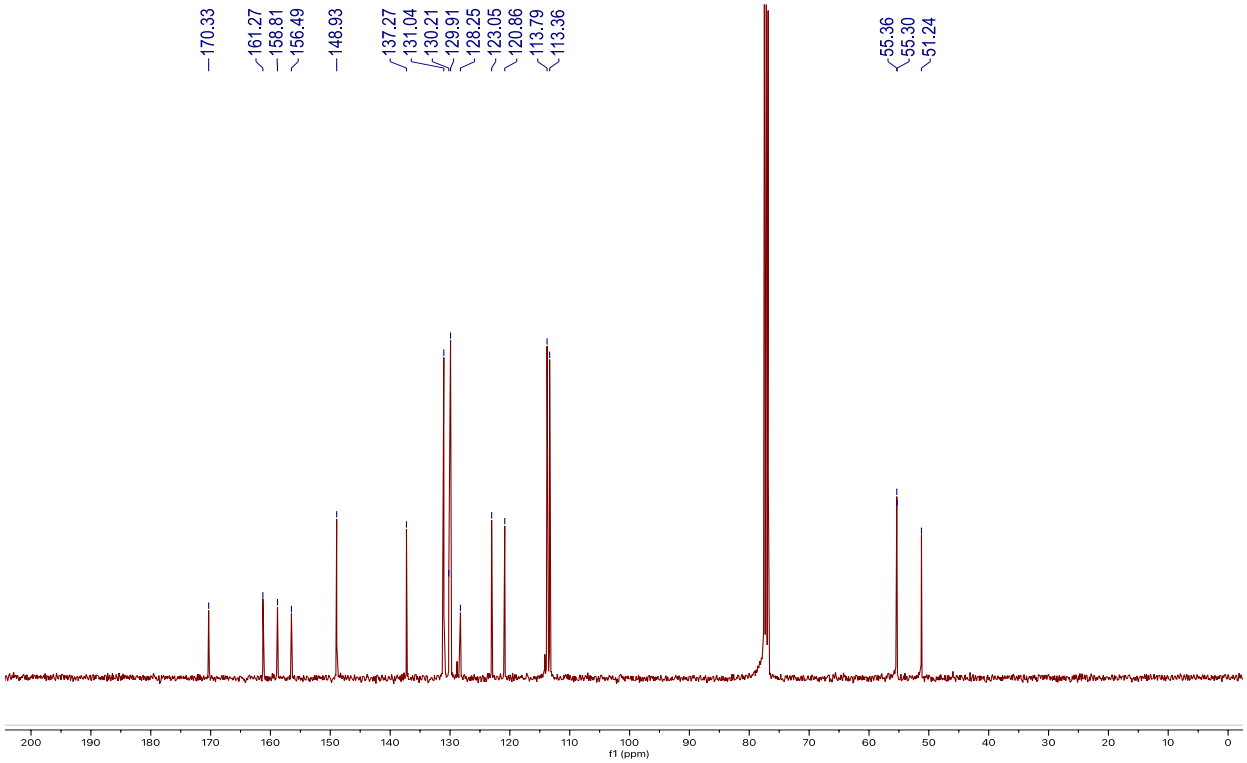


4-methoxy-*N*-[(4-methoxyphenyl)methyl]-*N*-(2-pyridyl)benzamide (3y)

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

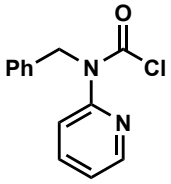


^{13}C NMR Spectrum $CDCl_3$ (101 MHz)

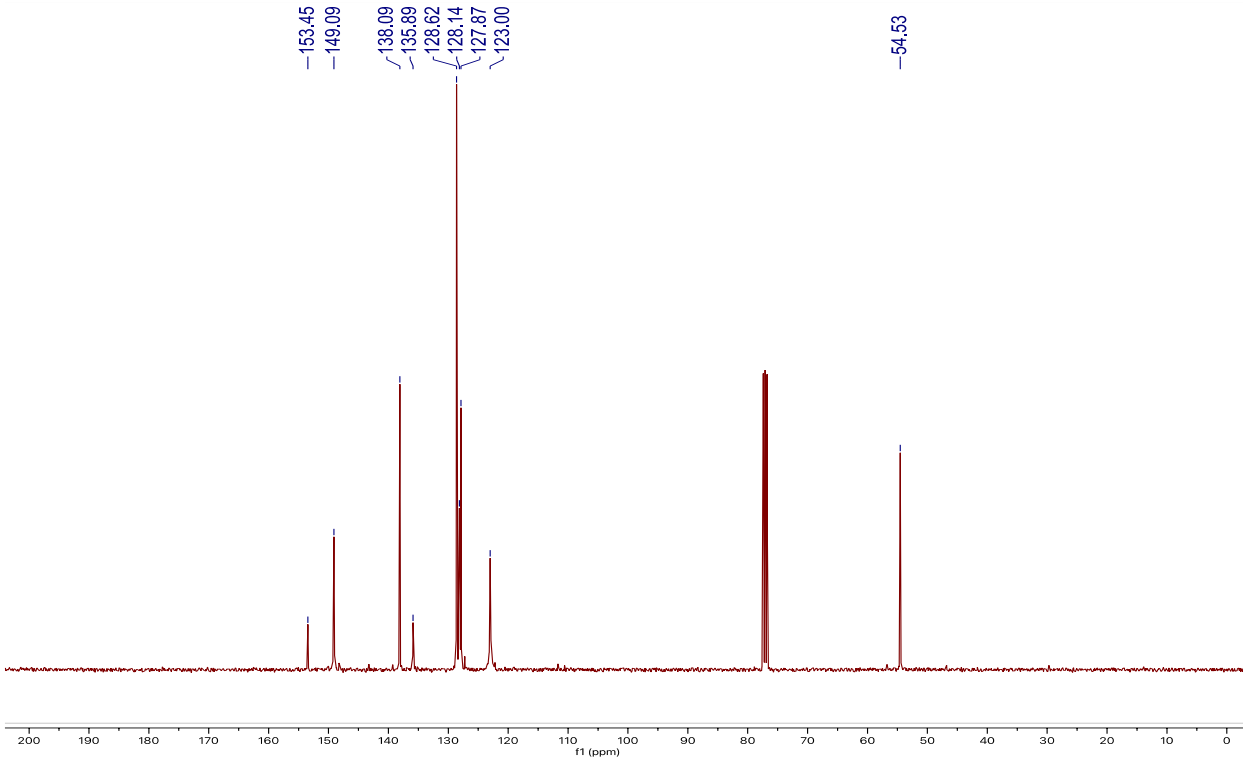


_N_-Benzyl-_N_-(2-pyridyl)carbamoyl chloride (1ac)

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

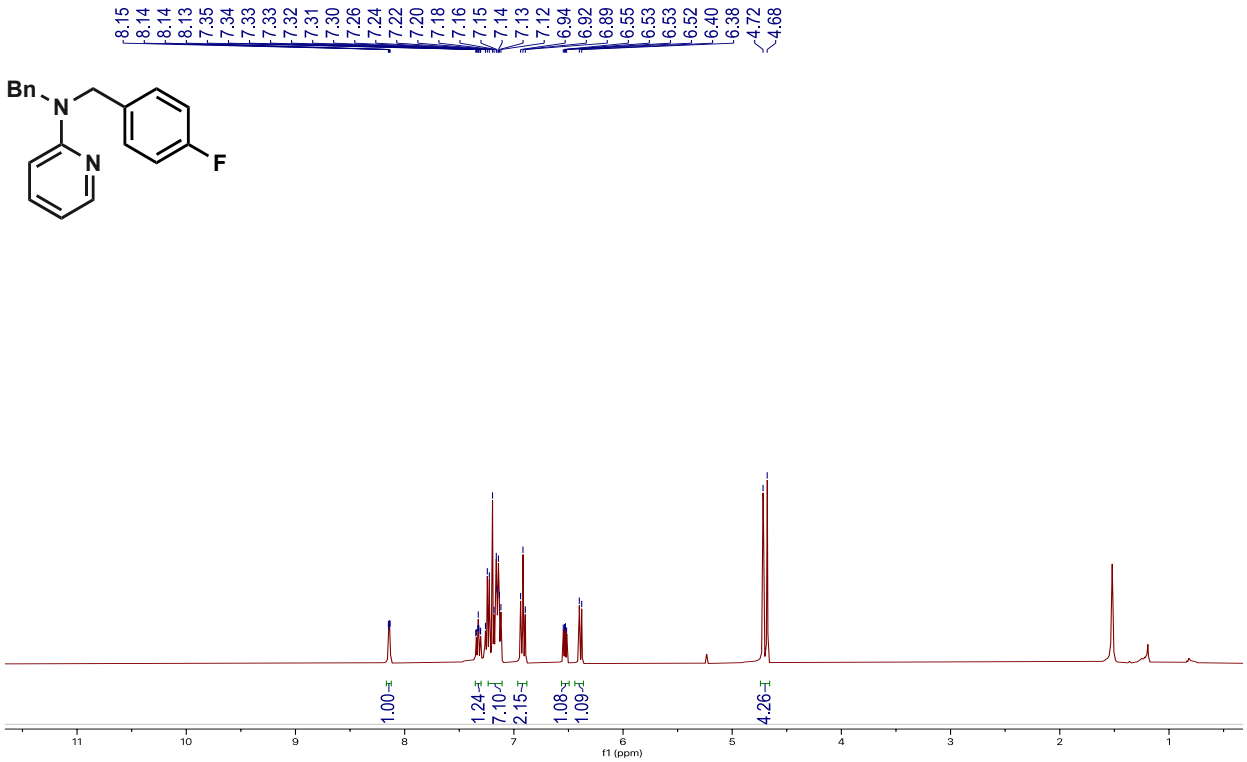


^{13}C NMR Spectrum $CDCl_3$ (101 MHz)

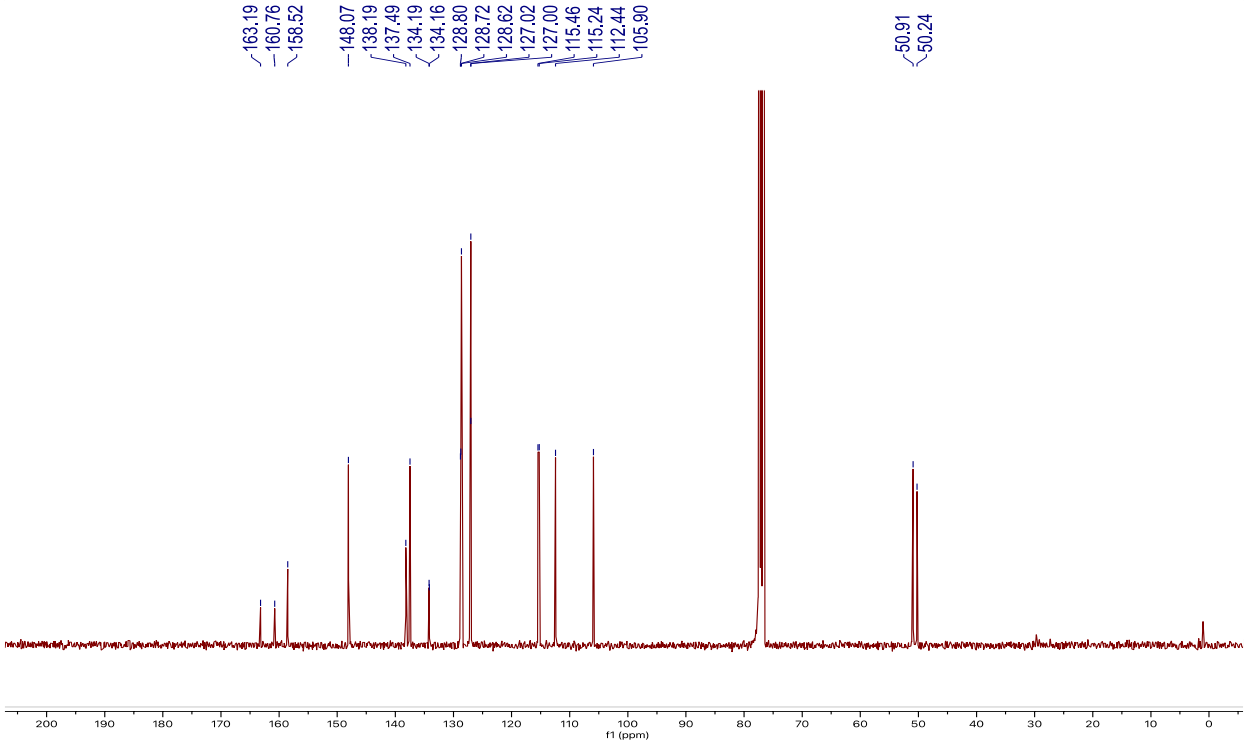


N-benzyl-4-fluoro-benzyl-*N*-2-pyridinamine (3ba)

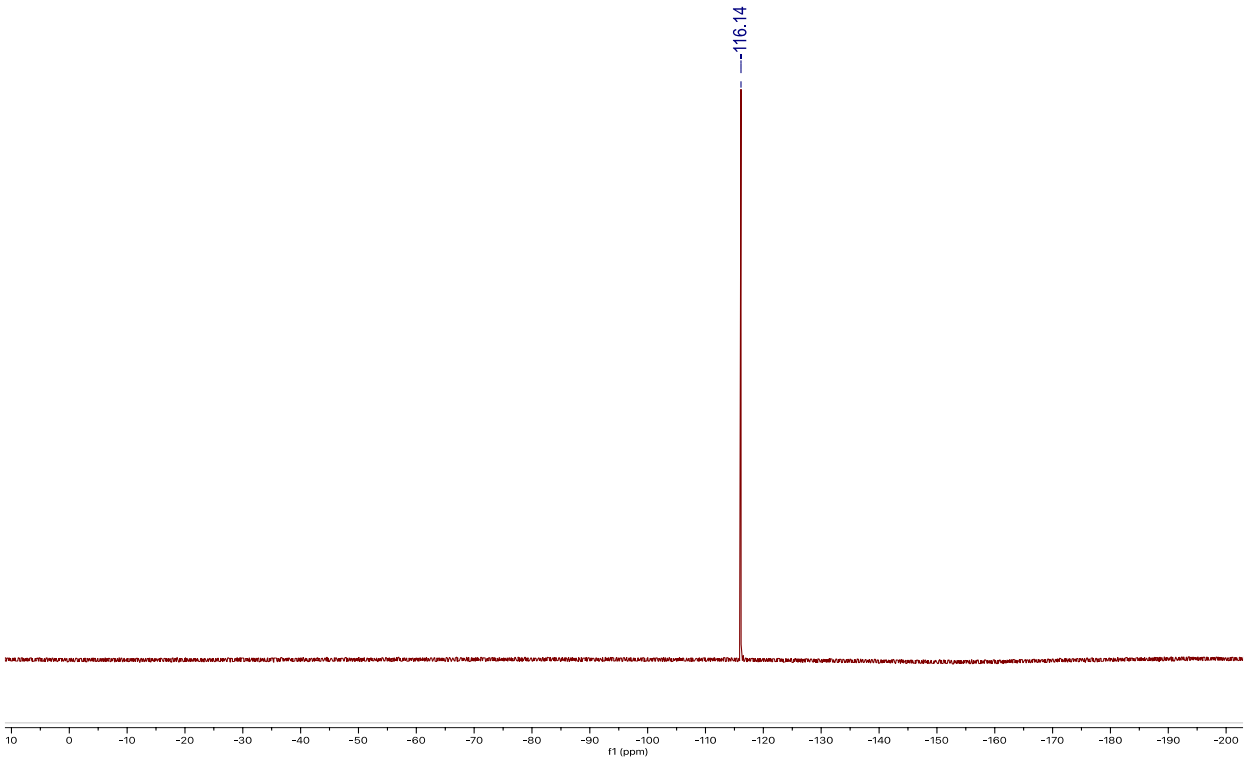
^{1}H NMR Spectrum $CDCl_3$ (400 MHz)



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

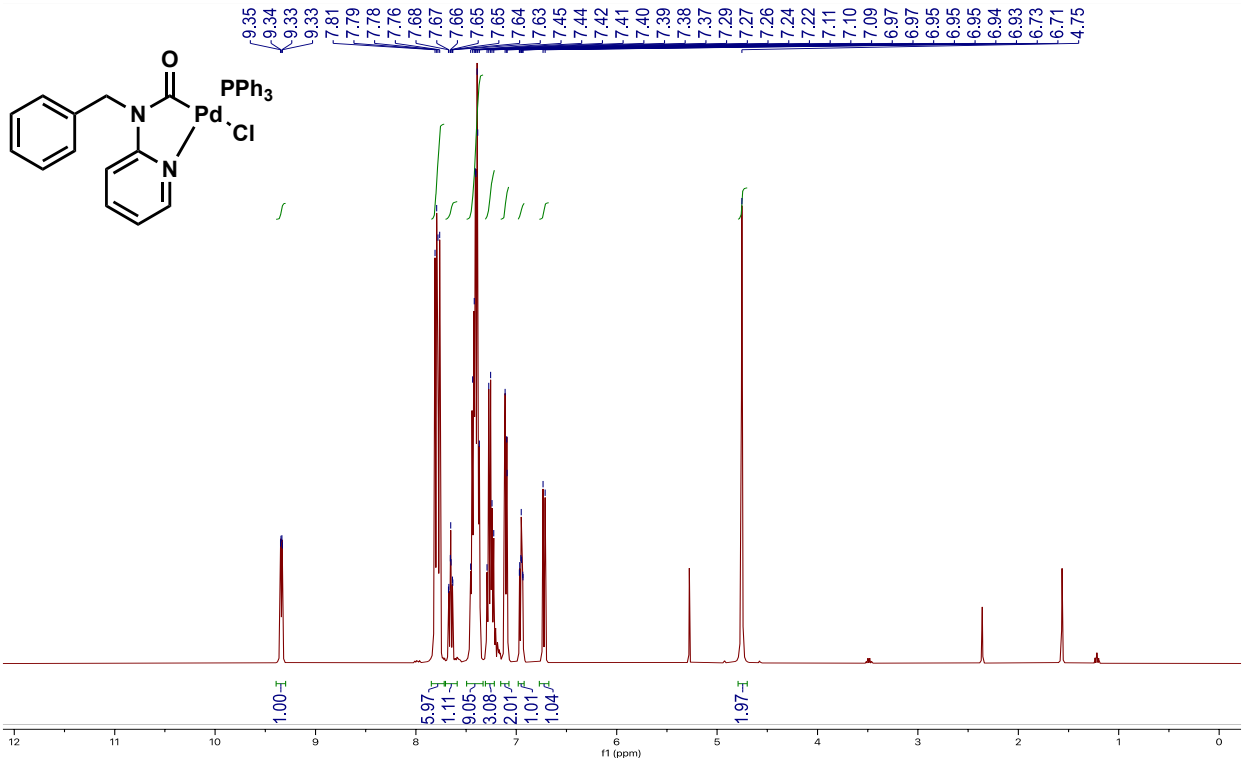


^{19}F NMR Spectrum $CDCl_3$ (377 MHz)

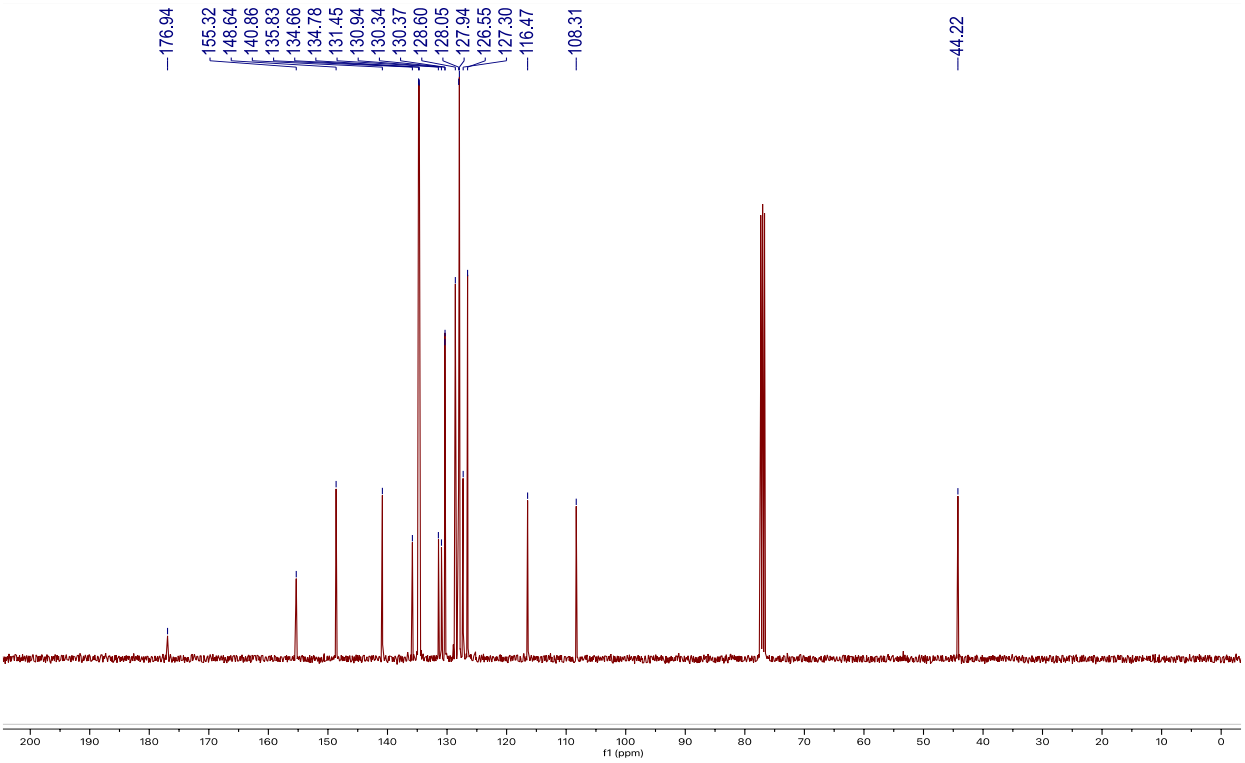


Pd-Cl complex (1ad)

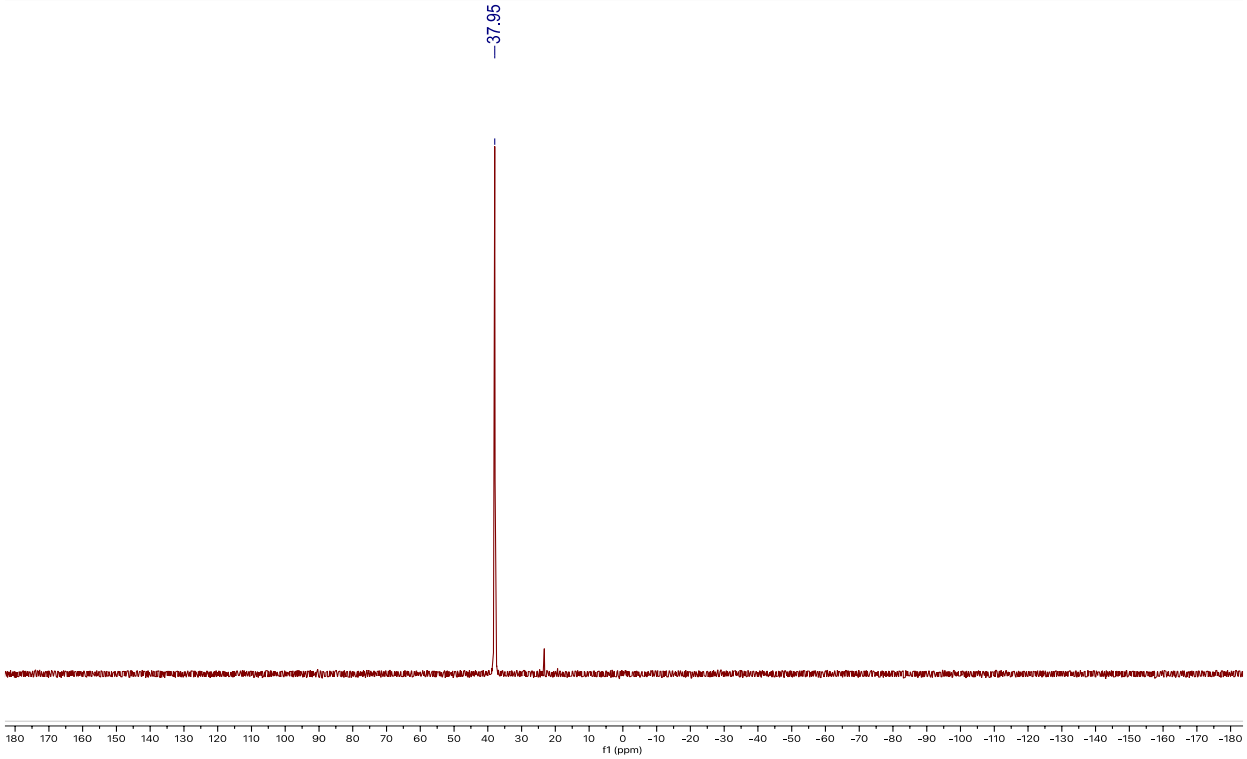
^{1}H NMR Spectrum $CDCl_3$ (400 MHz)



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

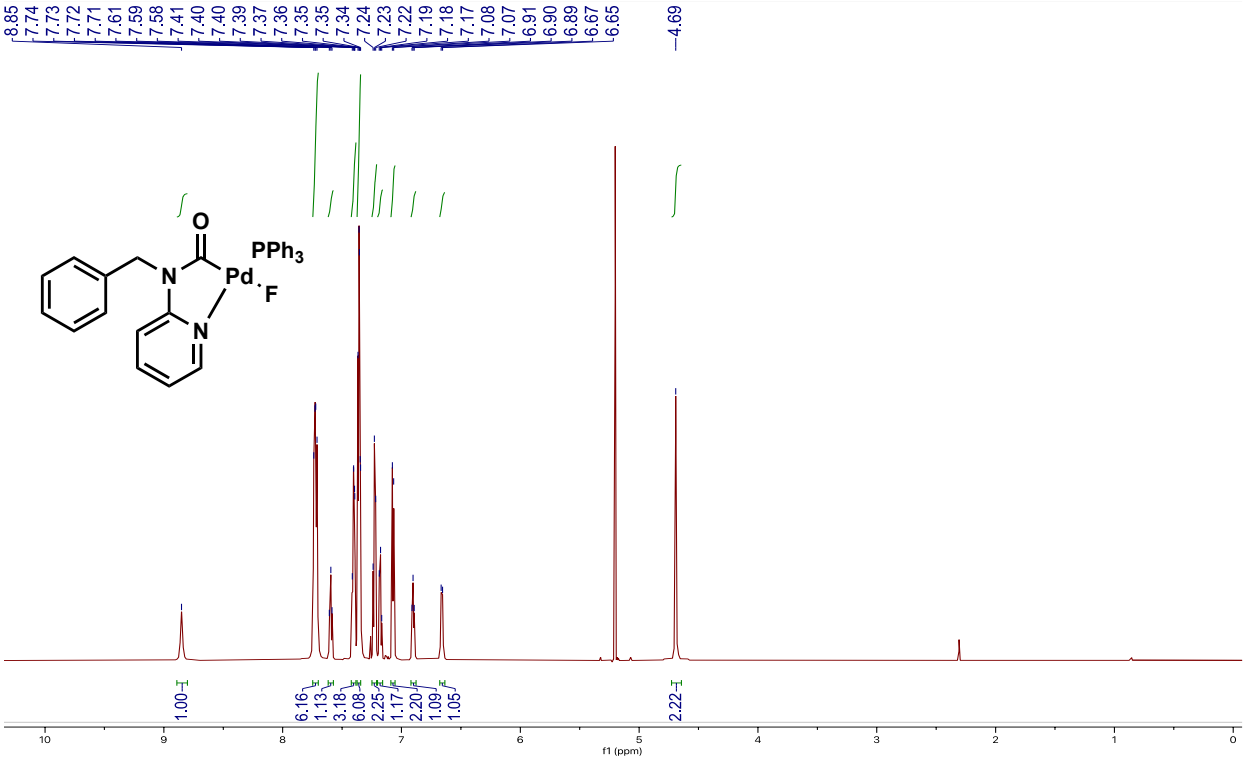


^{31}P NMR spectrum $CDCl_3$ (162 MHz)

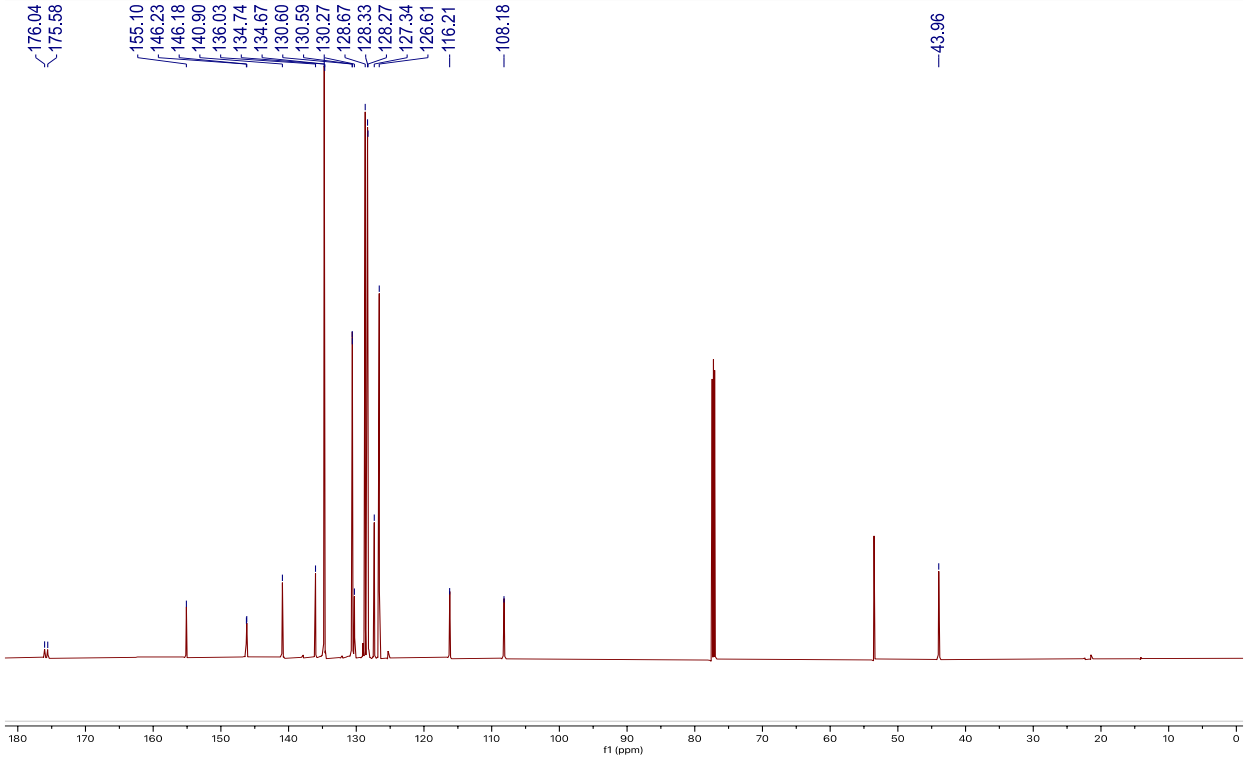


Pd-F Complex (1ae)

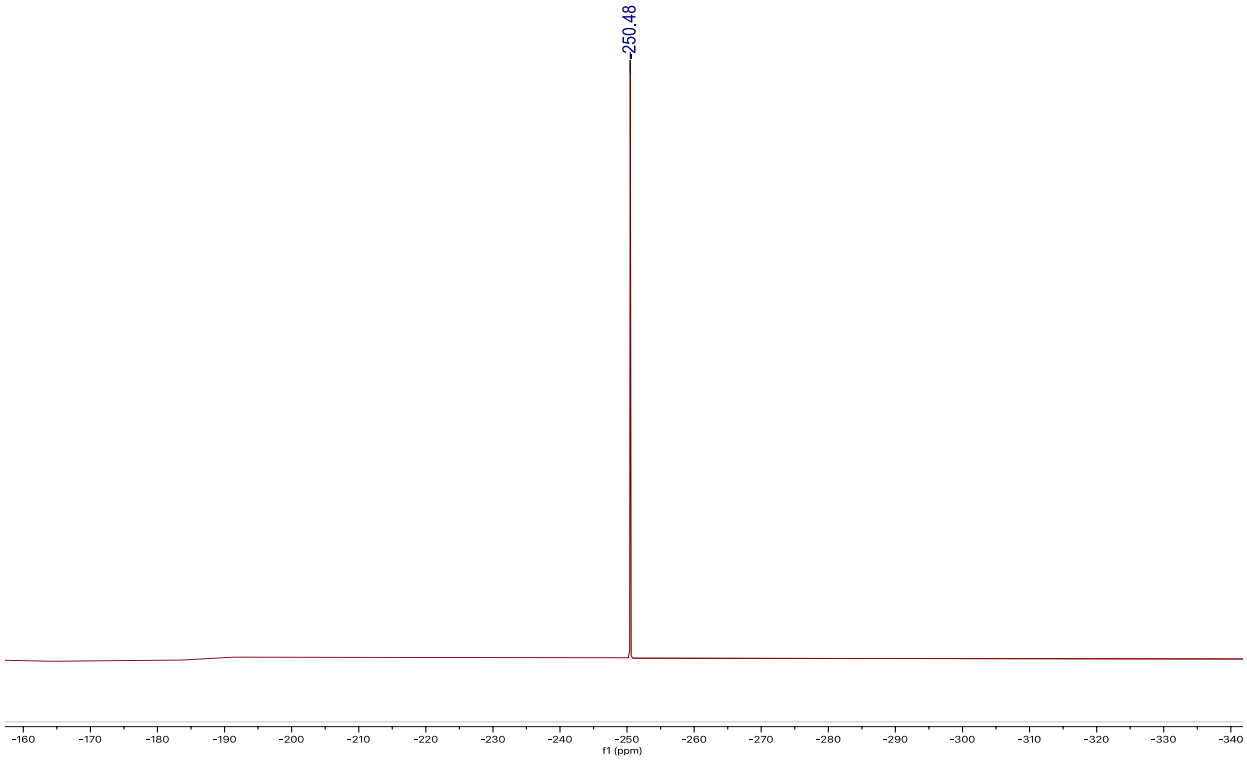
^{1}H NMR Spectrum $CDCl_3$ (400 MHz)



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



^{19}F NMR Spectrum $CDCl_3$ (377 MHz)



^{31}P NMR spectrum $CDCl_3$ (162 MHz)