Ir(III)-catalyzed aryl C-H bond carbenoid functionalization cascade: access to 1,3-dihydroindole-2-ones

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Supporting Information

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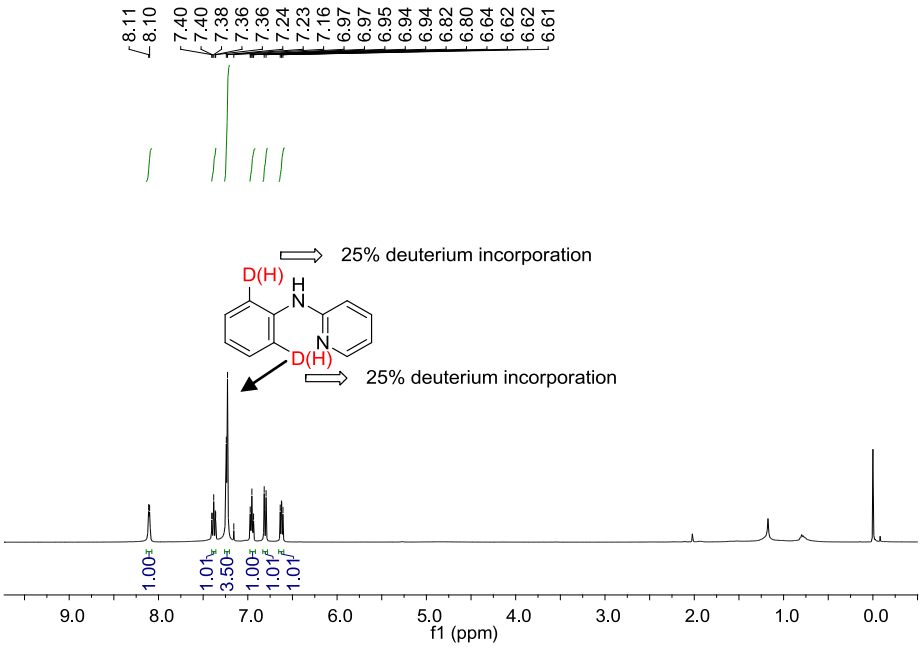
1. General Experimental Information

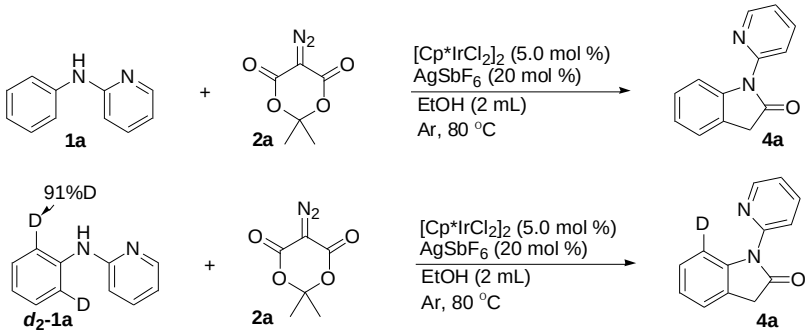
General Methods: All reactions were carried out in flame-dried sealed tubes with magnetic stirring. Unless otherwise noted, all experiments were performed under argon atmosphere. Solvents were treated with 4 Å molecular sieves or sodium and distilled prior to use. Flash chromatography was performed on silica gel (40~63 mm) by standard technique. ^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz NMR spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C). Splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q). Splitting patterns that could not be interpreted or easily visualized are designated as multiple (m). Low resolution mass spectra were recorded using HPLC Mass Spectrometer. High resolution exact mass measurements (HR-MS) were performed on a TOF spectrometer. Infrared spectra (IR) were reported as wavelength numbers (cm^{-1}). Infrared spectra were recorded by preparing a KBr pellet containing the title compound. Crystal data were obtained by employing graphite monochromated Mo - Kα radiation (λ = 1.54178 Å) at 293 (2) K and operating in the φ-ω scan mode. The structure was solved by direct methods SHELXS-97.

2. Control Experiments for the Mechanism Studies

The ^{1}H NMR spectrum ***d*-1a**



The crude ^{1}H NMR spectrum for the KIE values from 1a and d_2-1a



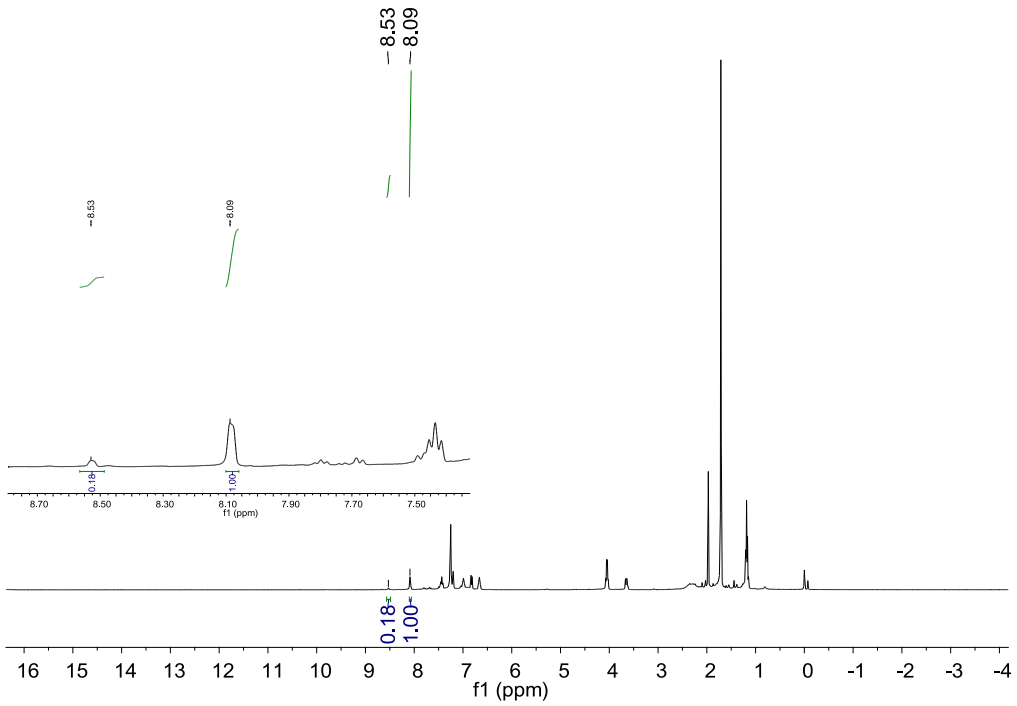


Figure S1. The conversion of **1a** after 3 min was monitored by ^{1}H NMR method

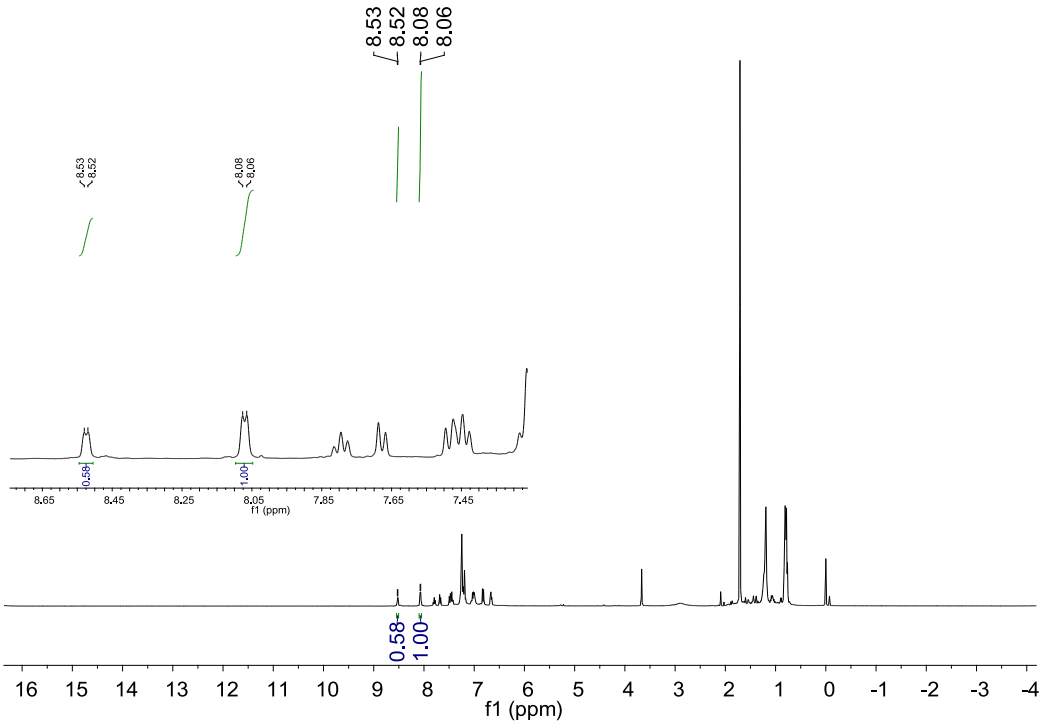


Figure S2. The conversion of **1a** after 6 min was monitored by ^{1}H NMR method

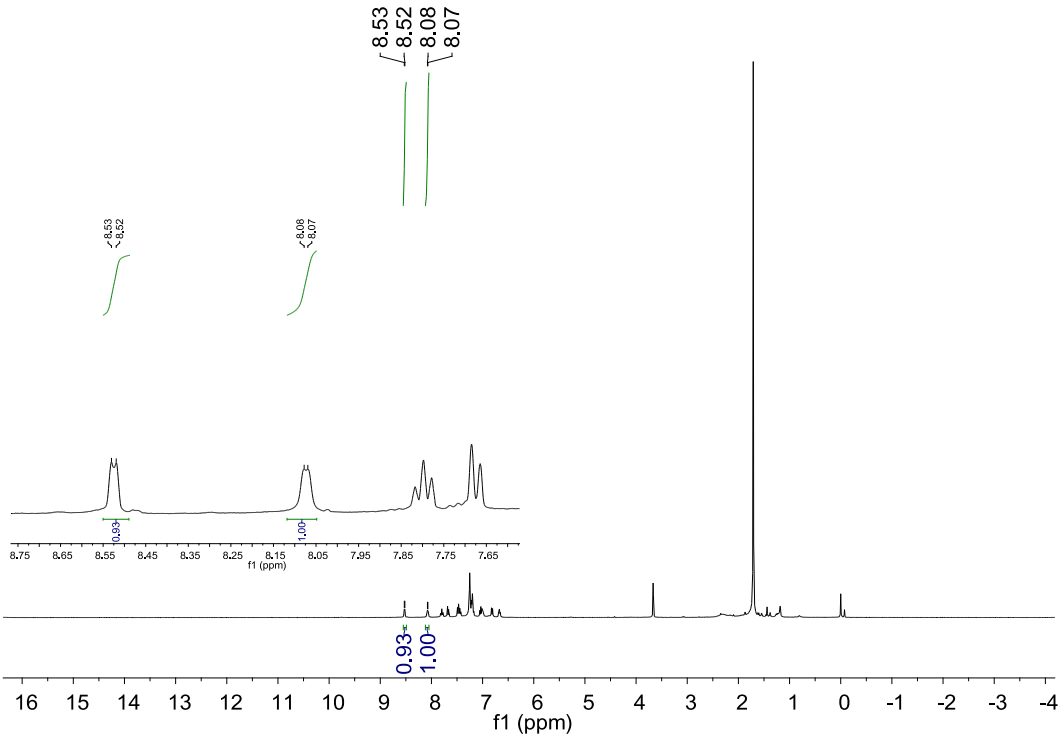


Figure S3. The conversion of **1a** after 9 min was monitored by ^{1}H NMR method

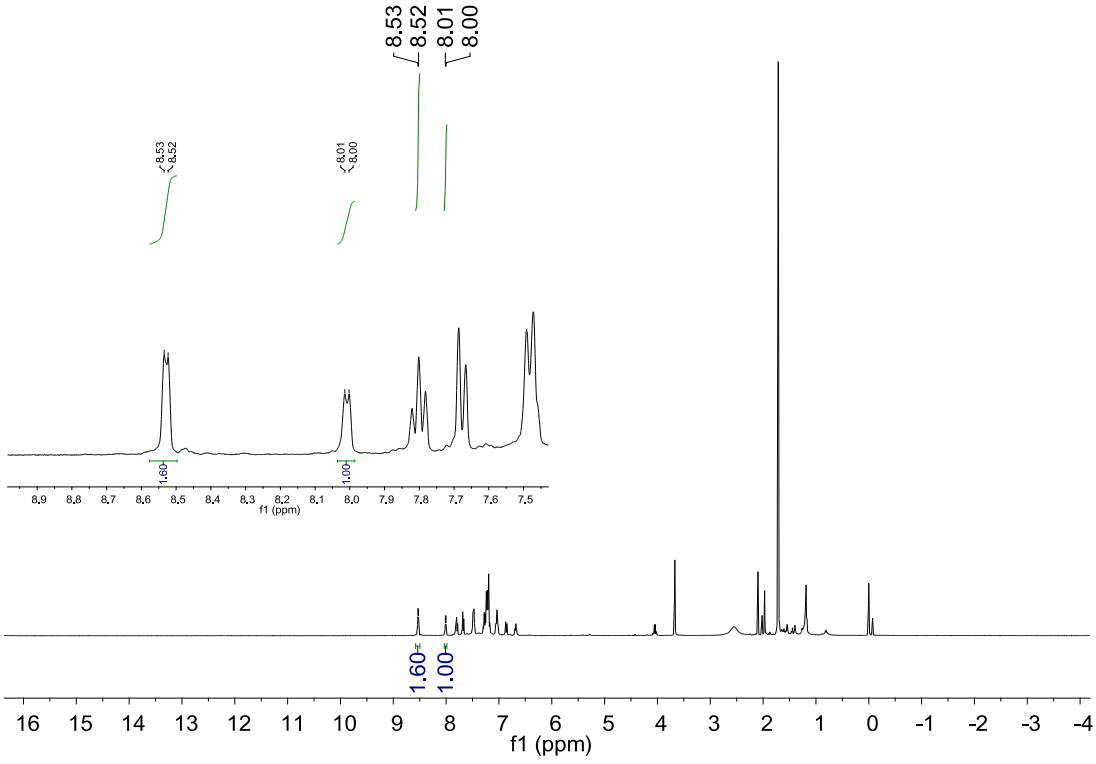


Figure S4. The conversion of **1a** after 12 min was monitored by ^{1}H NMR method

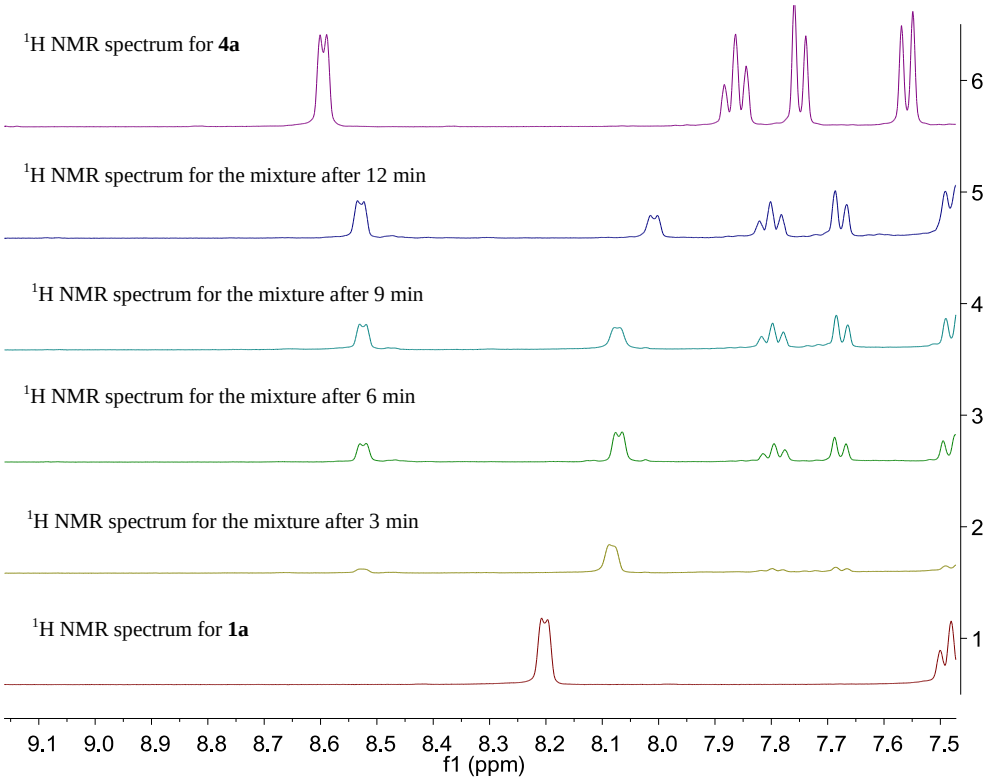


Figure S5. The combined crude [1]H NMR spectrum of the parallel experiments from the conversion of **1a** to ***d*-4a**

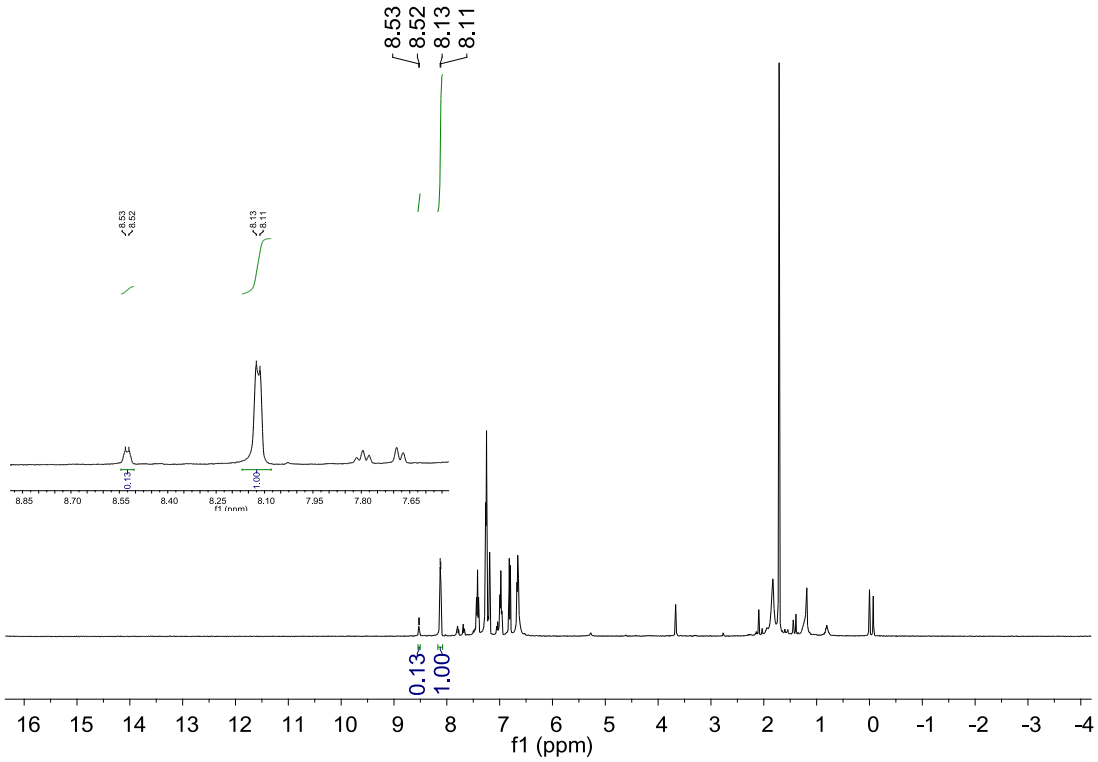


Figure S6. The conversion of d_2-**1a** after 3 min was monitored by [1]H NMR method

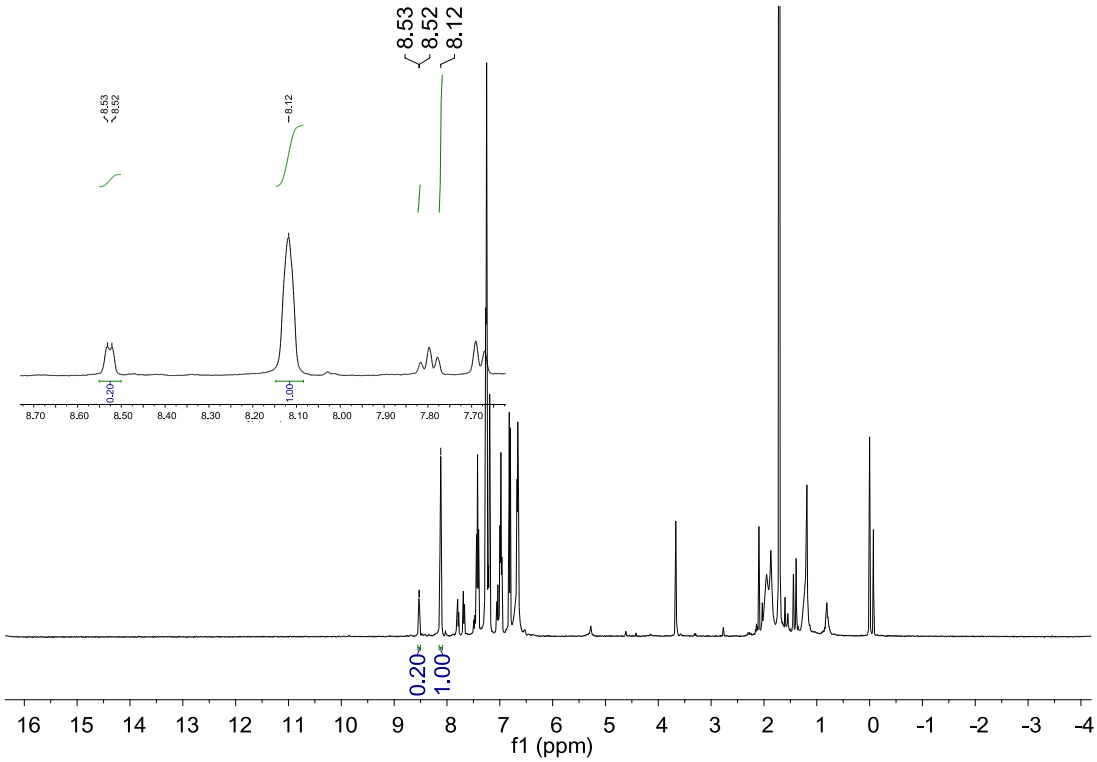


Figure S7. The conversion of d_2-**1a** after 6 min was monitored by ^{1}H NMR method

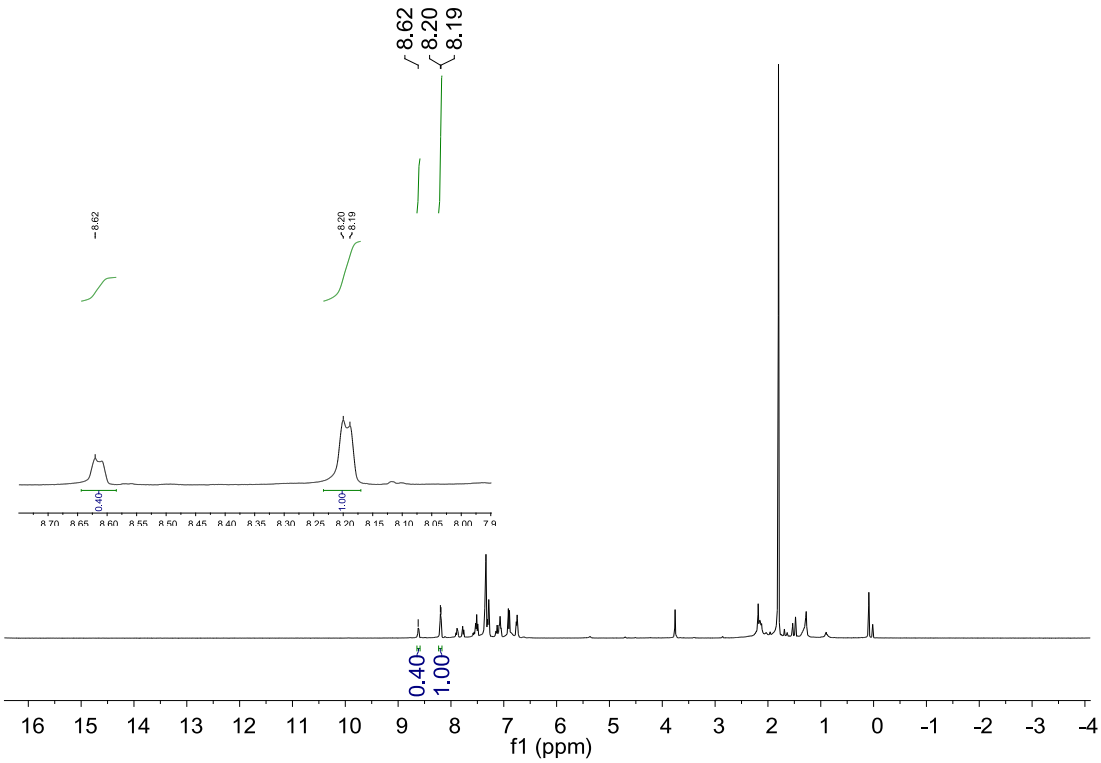


Figure S8. The conversion of d_2-**1a** after 9 min was monitored by ^{1}H NMR method

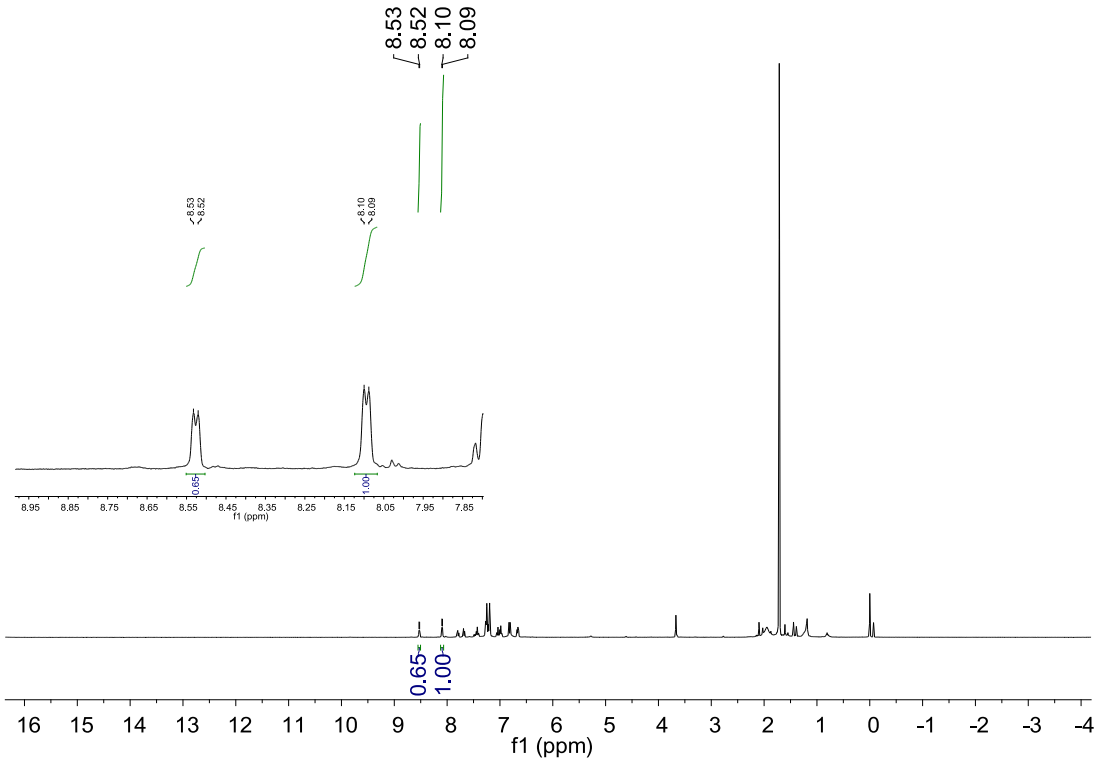


Figure S9. The conversion of ***d*$_2$-1a** after 12 min was monitored by ^{1}H NMR method

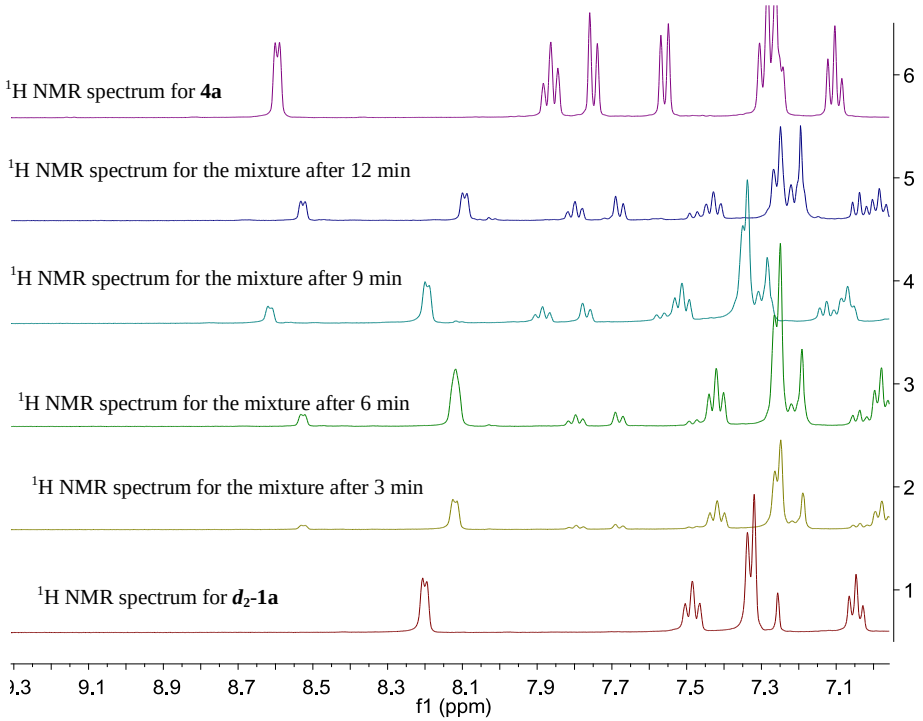


Figure S10. The combined crude ^{1}H NMR spectrum of the parallel experiments from the conversion of ***d*$_2$-1a** to ***d*-4** [a]

Time (min)	3	6	9	12
^{1}H NMR yield of **4a** from **1a** (%)	15	36	48	62
^{1}H NMR yield of d_1-**4a** from $\boldsymbol{d_2}$-**1a** (%)	11	17	29	39

Table S1. The relative yields (%) of **4a** and $\boldsymbol{d_1}$-**4a** were monitored by ^{1}H-NMR method

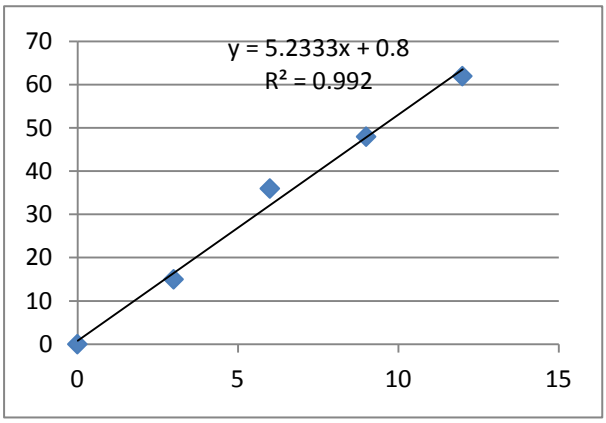


Figure S11. The plot of initial rates for the conversion of **1a**

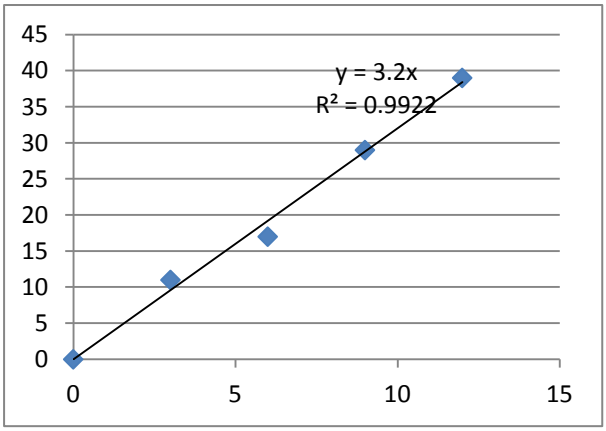
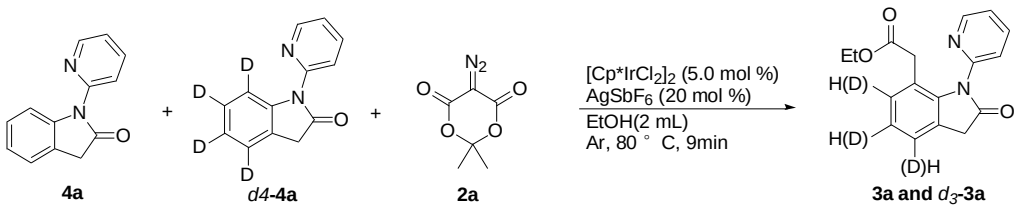


Figure S12. The plot of initial rates for the conversion of d_2-**1a**

The Competitive Kinetic Isotope Effect Derived from 4a and d_4-4a



4a + *d4*-**4a** + **2a** → **3a and d_3-3a**

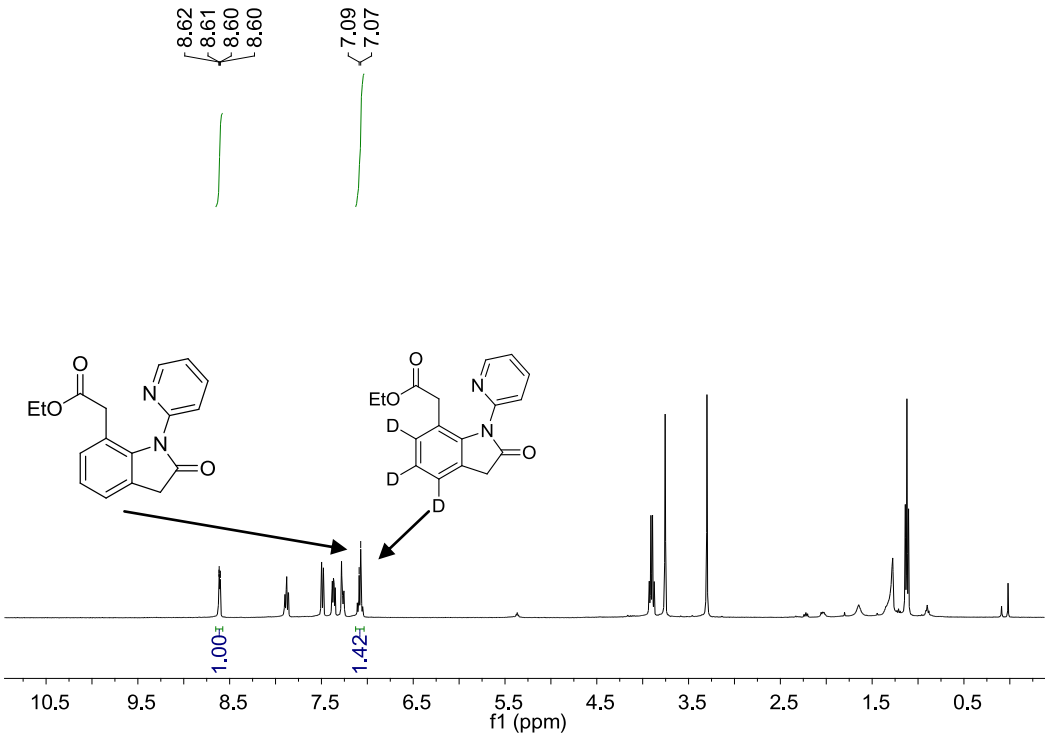
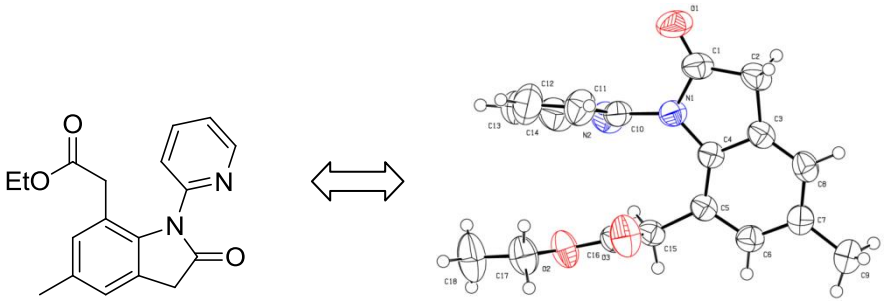


Figure S13. The conversion of **4a** and ***d*$_4$-4a** was monitored by ^{1}H-NMR method

3. Single crystal data about 3b



3b **Single crystal structure of 3b**

Fingure S14. The single crystal structure of **3b** (the ellipsoid contour probability level is 30%)

Table S2. Crystal data and structure refinement for **3b**.

Empirical formula	$C_{19}H_{19}NO_3$
Formula weight	309.35
Temperature	293(2) K
Wavelength	1.54184 A
Space group	P 21/c
a (Å)	13.8048(3)

b (Å)	15.2327(3)
c (Å)	15.2102(4)
α(°)	90
β(°)	90
γ(°)	90
V ($Å^3$)	3198.47
Z	8
Dc ($g\ cm^{-3}$)	1.285
Crystal size (mm)	0.25 x 0.20 x 0.18
Limiting indices	-14<=h<=15, -17<=k<=17, -17<=l<=12
Reflections collected / unique	7244 / 2439 [R(int) = 0.0221]
Completeness to theta = 62.65	94.8 %
Max. and min. transmission	0.8841 and 0.8441
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2439 / 0 / 210
Goodness-of-fit on F^2	1.089
Final R indices [I>2sigma(I)]	R1 = 0.0511, wR2 = 0.1399
R indices (all data)	R1 = 0.0571, wR2 = 0.1448
Largest diff. peak and hole	0.300 and -0.434 e.A^-3

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **3b**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	1669(1)	4560(1)	2138(1)	63(1)
C(2)	3404(1)	5054(1)	-208(1)	44(1)
O(3)	3250(1)	4393(1)	1896(1)	75(1)
C(4)	2435(1)	4403(1)	1632(1)	49(1)
N(5)	3283(1)	5932(1)	91(1)	50(1)
C(6)	1658(1)	6270(1)	333(1)	49(1)
O(7)	3915(1)	7287(1)	-243(1)	81(1)
C(8)	3218(2)	3525(1)	-391(1)	51(1)
C(9)	2923(1)	4291(1)	35(1)	44(1)
C(10)	4425(2)	4274(1)	-1224(1)	54(1)
C(11)	2545(2)	6275(1)	655(2)	51(1)
C(12)	3904(2)	6497(1)	-350(2)	57(1)
C(13)	4144(1)	5045(1)	-834(1)	47(1)
C(14)	3961(2)	3494(1)	-1007(1)	54(1)
C(15)	2121(1)	4238(1)	704(1)	47(1)
C(16)	4497(2)	5964(1)	-972(2)	57(1)
C(17)	4253(2)	2629(2)	-1414(2)	73(1)
C(18)	1850(2)	4740(2)	3060(2)	71(1)
C(19)	970(2)	6637(2)	825(2)	82(1)

C(20)	2784(2)	6625(2)	1449(2)	74(1)
C(21)	1145(3)	7013(2)	1622(2)	93(1)
C(22)	2061(3)	7005(2)	1938(2)	96(1)
C(23)	915(2)	5031(3)	3454(2)	97(1)

Table S4. Bond lengths [A] and angles [deg] for **3b**.

O(1)-C(4)	1.330(2)
O(1)-C(18)	1.450(3)
C(2)-C(9)	1.389(3)
C(2)-C(13)	1.397(3)
C(2)-N(5)	1.422(3)
O(3)-C(4)	1.194(2)
C(4)-C(15)	1.497(3)
N(5)-C(12)	1.388(3)
N(5)-C(11)	1.430(3)
C(6)-C(11)	1.318(3)
C(6)-C(19)	1.333(4)
C(6)-H(6)	0.9300
O(7)-C(12)	1.214(3)
C(8)-C(14)	1.391(3)
C(8)-C(9)	1.396(3)
C(8)-H(8)	0.9300
C(9)-C(15)	1.506(3)
C(10)-C(13)	1.371(3)
C(10)-C(14)	1.389(3)
C(10)-H(10)	0.9300
C(11)-C(20)	1.362(4)
C(12)-C(16)	1.491(3)
C(13)-C(16)	1.497(3)
C(14)-C(17)	1.510(3)
C(15)-H(15A)	0.9700
C(15)-H(15B)	0.9700
C(16)-H(16A)	0.9700
C(16)-H(16B)	0.9700
C(17)-H(17A)	0.9600
C(17)-H(17B)	0.9600
C(17)-H(17C)	0.9600
C(18)-C(23)	1.490(4)
C(18)-H(18A)	0.9700
C(18)-H(18B)	0.9700
C(19)-C(21)	1.362(5)
C(19)-H(19)	0.9300
C(20)-C(22)	1.372(4)

C(20)-H(20)	0.9300
C(21)-C(22)	1.352(5)
C(21)-H(21)	0.9300
C(22)-H(22)	0.9300
C(23)-H(23A)	0.9600
C(23)-H(23B)	0.9600
C(23)-H(23C)	0.9600

C(4)-O(1)-C(18)	117.20(17)
C(9)-C(2)-C(13)	121.48(19)
C(9)-C(2)-N(5)	130.24(17)
C(13)-C(2)-N(5)	108.27(16)
O(3)-C(4)-O(1)	123.8(2)
O(3)-C(4)-C(15)	126.04(19)
O(1)-C(4)-C(15)	110.18(16)
C(12)-N(5)-C(2)	110.84(17)
C(12)-N(5)-C(11)	120.26(17)
C(2)-N(5)-C(11)	128.17(16)
C(11)-C(6)-C(19)	116.8(2)
C(11)-C(6)-H(6)	121.6
C(19)-C(6)-H(6)	121.6
C(14)-C(8)-C(9)	123.84(19)
C(14)-C(8)-H(8)	118.1
C(9)-C(8)-H(8)	118.1
C(2)-C(9)-C(8)	115.89(18)
C(2)-C(9)-C(15)	125.20(18)
C(8)-C(9)-C(15)	118.91(17)
C(13)-C(10)-C(14)	119.92(19)
C(13)-C(10)-H(10)	120.0
C(14)-C(10)-H(10)	120.0
C(6)-C(11)-C(20)	123.8(2)
C(6)-C(11)-N(5)	115.9(2)
C(20)-C(11)-N(5)	120.1(2)
O(7)-C(12)-N(5)	123.8(2)
O(7)-C(12)-C(16)	128.2(2)
N(5)-C(12)-C(16)	107.95(18)
C(10)-C(13)-C(2)	120.74(19)
C(10)-C(13)-C(16)	130.39(18)
C(2)-C(13)-C(16)	108.87(18)
C(10)-C(14)-C(8)	118.1(2)
C(10)-C(14)-C(17)	121.7(2)
C(8)-C(14)-C(17)	120.1(2)
C(4)-C(15)-C(9)	114.48(16)
C(4)-C(15)-H(15A)	108.6

C(9)-C(15)-H(15A)	108.6
C(4)-C(15)-H(15B)	108.6
C(9)-C(15)-H(15B)	108.6
H(15A)-C(15)-H(15B)	107.6
C(12)-C(16)-C(13)	104.02(16)
C(12)-C(16)-H(16A)	111.0
C(13)-C(16)-H(16A)	111.0
C(12)-C(16)-H(16B)	111.0
C(13)-C(16)-H(16B)	111.0
H(16A)-C(16)-H(16B)	109.0
C(14)-C(17)-H(17A)	109.5
C(14)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(14)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
O(1)-C(18)-C(23)	107.23(19)
O(1)-C(18)-H(18A)	110.3
C(23)-C(18)-H(18A)	110.3
O(1)-C(18)-H(18B)	110.3
C(23)-C(18)-H(18B)	110.3
H(18A)-C(18)-H(18B)	108.5
C(6)-C(19)-C(21)	123.4(3)
C(6)-C(19)-H(19)	118.3
C(21)-C(19)-H(19)	118.3
C(11)-C(20)-C(22)	118.0(3)
C(11)-C(20)-H(20)	121.0
C(22)-C(20)-H(20)	121.0
C(22)-C(21)-C(19)	118.6(3)
C(22)-C(21)-H(21)	120.7
C(19)-C(21)-H(21)	120.7
C(21)-C(22)-C(20)	119.4(3)
C(21)-C(22)-H(22)	120.3
C(20)-C(22)-H(22)	120.3
C(18)-C(23)-H(23A)	109.5
C(18)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(18)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5

Table S5. Anisotropic displacement parameters (A^2 x 10^3) for **3b**.

U11	U22	U33	U23	U13	U12

O(1)	44(1)	99(1)	47(1)	-4(1)	2(1)	1(1)
C(2)	34(1)	48(1)	50(1)	4(1)	-2(1)	2(1)
O(3)	42(1)	119(2)	65(1)	-8(1)	-6(1)	10(1)
C(4)	41(1)	52(1)	53(1)	5(1)	2(1)	0(1)
N(5)	35(1)	46(1)	69(1)	2(1)	6(1)	0(1)
C(6)	28(1)	58(1)	60(1)	9(1)	1(1)	6(1)
O(7)	58(1)	49(1)	135(2)	9(1)	24(1)	-5(1)
C(8)	49(1)	49(1)	56(1)	2(1)	-1(1)	-2(1)
C(9)	37(1)	50(1)	47(1)	3(1)	-1(1)	0(1)
C(10)	44(1)	69(1)	48(1)	5(1)	6(1)	7(1)
C(11)	43(1)	43(1)	68(1)	6(1)	7(1)	2(1)
C(12)	38(1)	50(1)	83(2)	10(1)	4(1)	-1(1)
C(13)	34(1)	56(1)	52(1)	8(1)	0(1)	2(1)
C(14)	54(1)	58(1)	51(1)	-3(1)	1(1)	5(1)
C(15)	40(1)	50(1)	51(1)	4(1)	2(1)	-4(1)
C(16)	39(1)	61(1)	71(1)	15(1)	7(1)	-1(1)
C(17)	80(2)	69(2)	71(2)	-12(1)	13(1)	8(1)
C(18)	60(1)	104(2)	48(1)	-3(1)	-5(1)	6(1)
C(19)	50(1)	84(2)	113(2)	28(2)	18(1)	14(1)
C(20)	61(2)	79(2)	84(2)	-16(1)	1(1)	0(1)
C(21)	89(2)	72(2)	119(3)	7(2)	51(2)	20(2)
C(22)	97(2)	94(2)	96(2)	-30(2)	20(2)	7(2)
C(23)	79(2)	158(3)	53(2)	-10(2)	3(1)	32(2)

Table S6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **3b**.

	x	y	z	U(eq)
H(6)	1520	6022	-212	58
H(8)	2898	3005	-255	61
H(10)	4926	4273	-1633	64
H(15A)	1625	4662	551	56
H(15B)	1830	3659	673	56
H(16A)	5181	6012	-835	68
H(16B)	4393	6151	-1574	68
H(17A)	4871	2453	-1186	110
H(17B)	4294	2694	-2041	110
H(17C)	3777	2191	-1273	110
H(18A)	2335	5197	3120	85
H(18B)	2083	4216	3354	85
H(19)	338	6636	614	99
H(20)	3418	6608	1655	89

H(21)	646	7269	1942	112
H(22)	2199	7255	2481	115
H(23A)	724	5580	3197	145
H(23B)	993	5102	4077	145
H(23C)	426	4597	3341	145

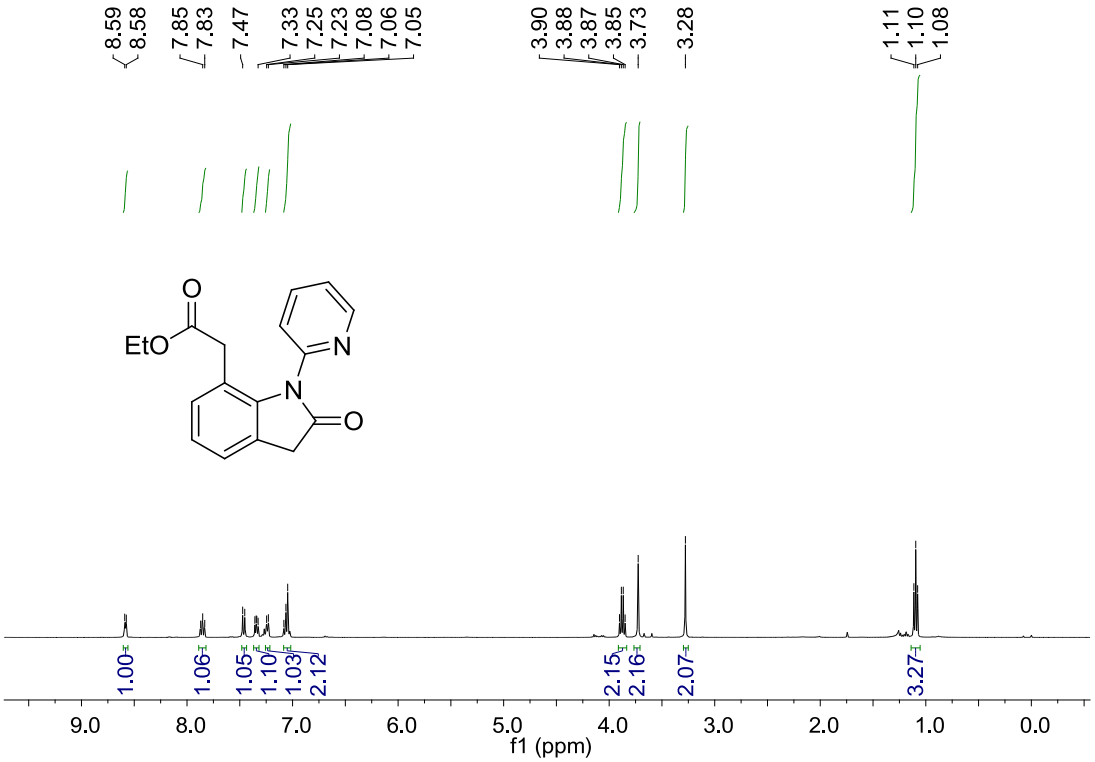
Table S7. Torsion angles [deg] for **3b**.

C(18)-O(1)-C(4)-O(3)	1.0(3)
C(18)-O(1)-C(4)-C(15)	-179.6(2)
C(9)-C(2)-N(5)-C(12)	-178.4(2)
C(13)-C(2)-N(5)-C(12)	2.2(2)
C(9)-C(2)-N(5)-C(11)	-8.3(3)
C(13)-C(2)-N(5)-C(11)	172.31(19)
C(13)-C(2)-C(9)-C(8)	-0.7(3)
N(5)-C(2)-C(9)-C(8)	179.92(19)
C(13)-C(2)-C(9)-C(15)	179.78(18)
N(5)-C(2)-C(9)-C(15)	0.4(3)
C(14)-C(8)-C(9)-C(2)	1.7(3)
C(14)-C(8)-C(9)-C(15)	-178.76(19)
C(19)-C(6)-C(11)-C(20)	0.4(3)
C(19)-C(6)-C(11)-N(5)	-175.9(2)
C(12)-N(5)-C(11)-C(6)	103.2(2)
C(2)-N(5)-C(11)-C(6)	-66.1(3)
C(12)-N(5)-C(11)-C(20)	-73.2(3)
C(2)-N(5)-C(11)-C(20)	117.5(3)
C(2)-N(5)-C(12)-O(7)	176.8(2)
C(11)-N(5)-C(12)-O(7)	5.8(3)
C(2)-N(5)-C(12)-C(16)	-1.4(2)
C(11)-N(5)-C(12)-C(16)	-172.41(18)
C(14)-C(10)-C(13)-C(2)	1.1(3)
C(14)-C(10)-C(13)-C(16)	-177.8(2)
C(9)-C(2)-C(13)-C(10)	-0.6(3)
N(5)-C(2)-C(13)-C(10)	178.87(18)
C(9)-C(2)-C(13)-C(16)	178.43(18)
N(5)-C(2)-C(13)-C(16)	-2.1(2)
C(13)-C(10)-C(14)-C(8)	-0.1(3)
C(13)-C(10)-C(14)-C(17)	-179.5(2)
C(9)-C(8)-C(14)-C(10)	-1.3(3)
C(9)-C(8)-C(14)-C(17)	178.0(2)
O(3)-C(4)-C(15)-C(9)	-16.0(3)
O(1)-C(4)-C(15)-C(9)	164.54(17)
C(2)-C(9)-C(15)-C(4)	-68.9(3)
C(8)-C(9)-C(15)-C(4)	111.6(2)

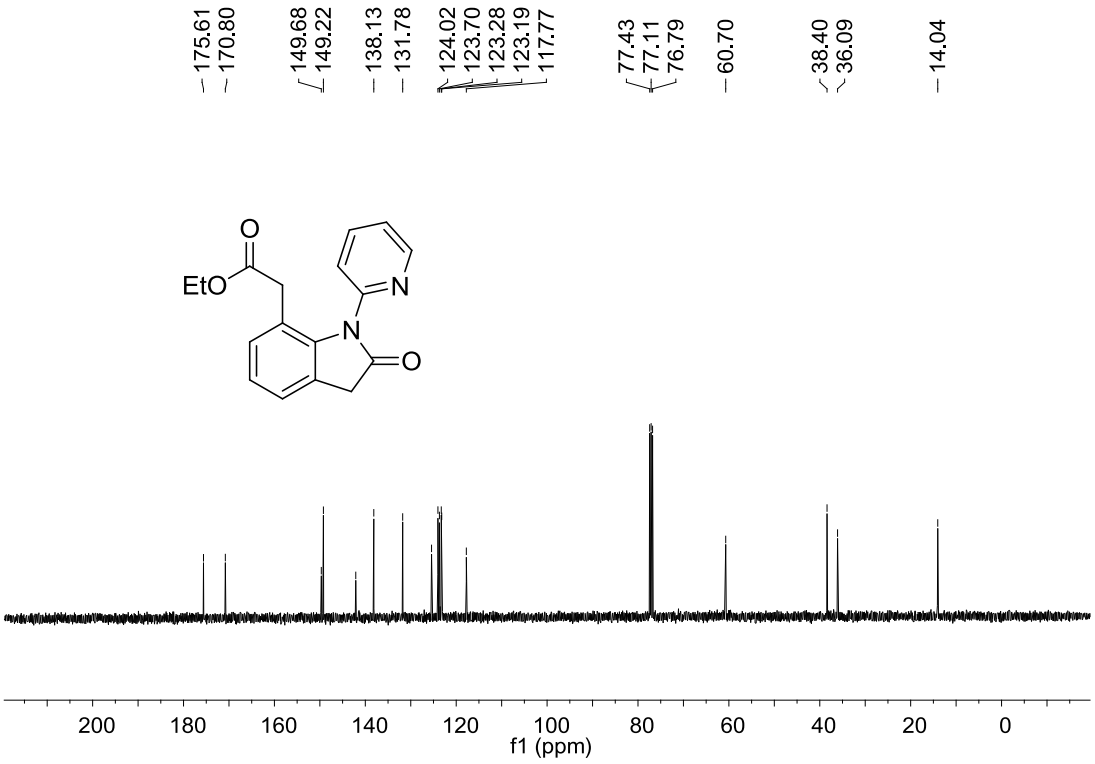
O(7)-C(12)-C(16)-C(13)	-177.9(2)
N(5)-C(12)-C(16)-C(13)	0.1(2)
C(10)-C(13)-C(16)-C(12)	-179.9(2)
C(2)-C(13)-C(16)-C(12)	1.2(2)
C(4)-O(1)-C(18)-C(23)	171.2(2)
C(11)-C(6)-C(19)-C(21)	0.6(4)
C(6)-C(11)-C(20)-C(22)	-0.9(4)
N(5)-C(11)-C(20)-C(22)	175.2(2)
C(6)-C(19)-C(21)-C(22)	-0.9(5)
C(19)-C(21)-C(22)-C(20)	0.3(5)
C(11)-C(20)-C(22)-C(21)	0.5(5)

4. ^{1}H NMR and ^{13}C NMR copies of all products

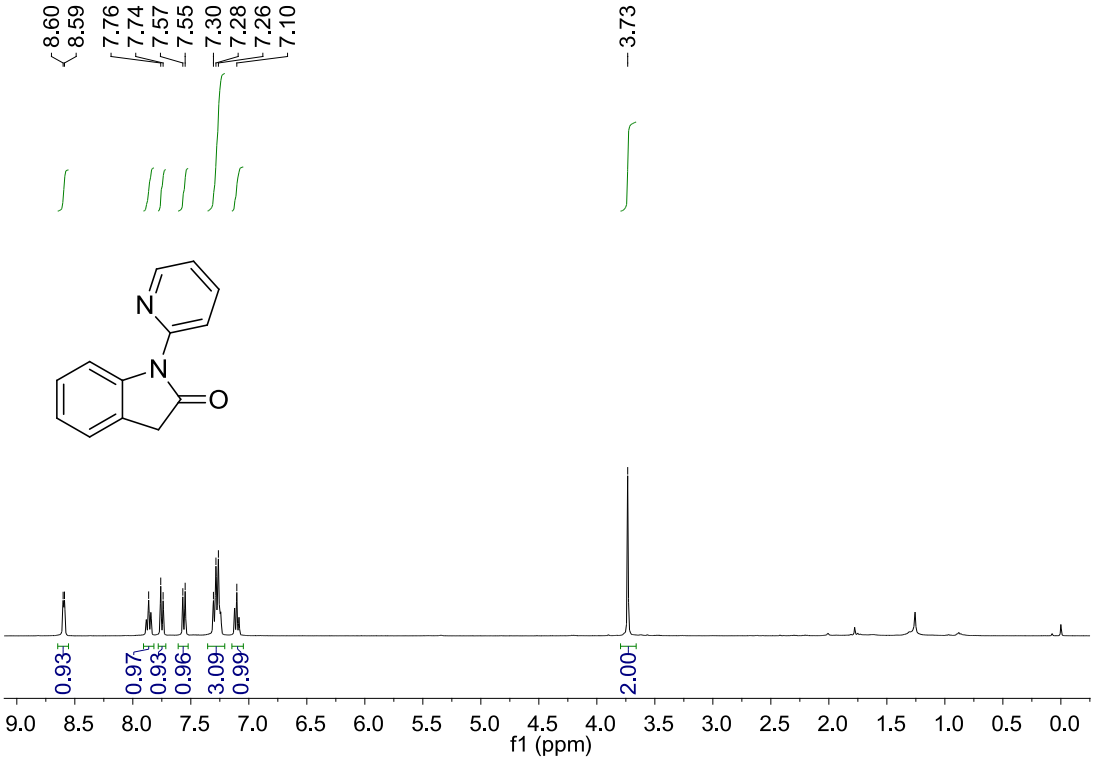
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3a**



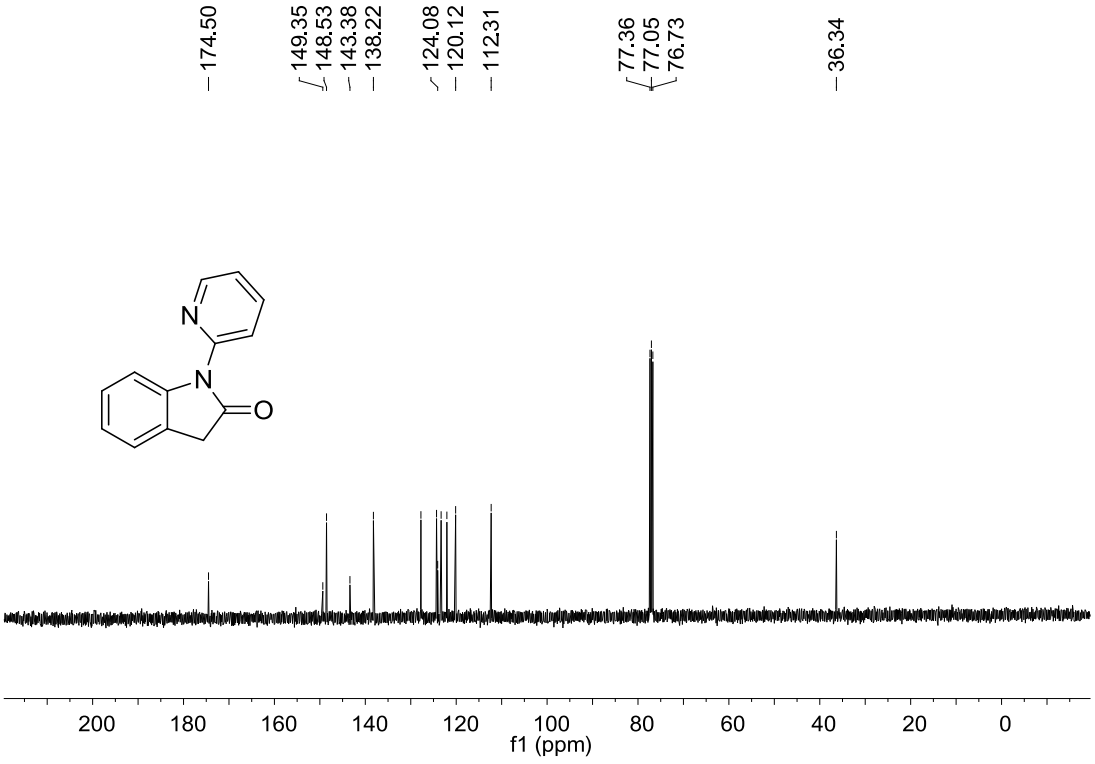
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **3a**



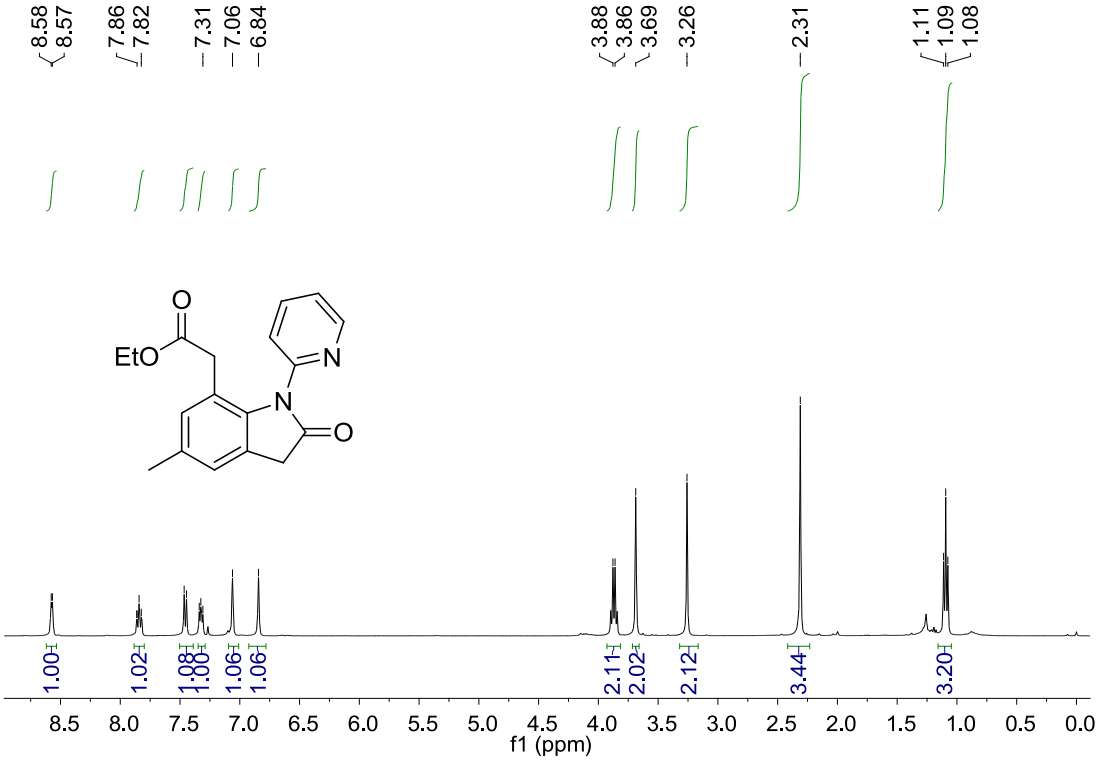
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4a**



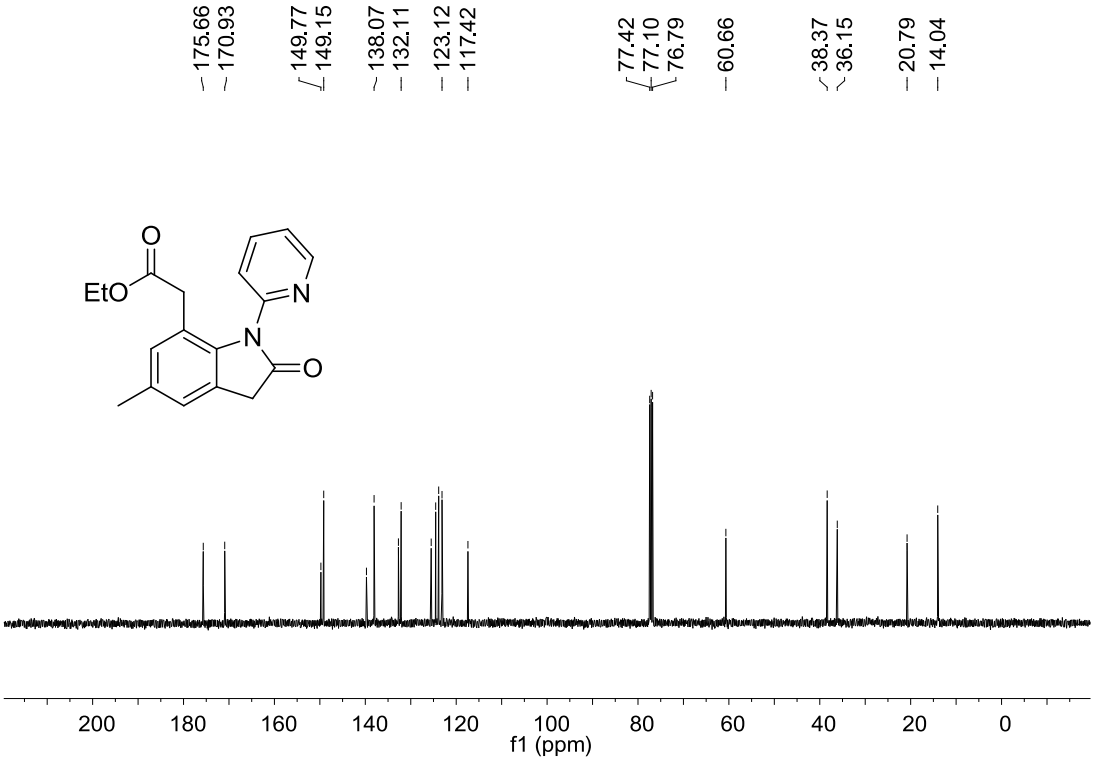
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **4a**



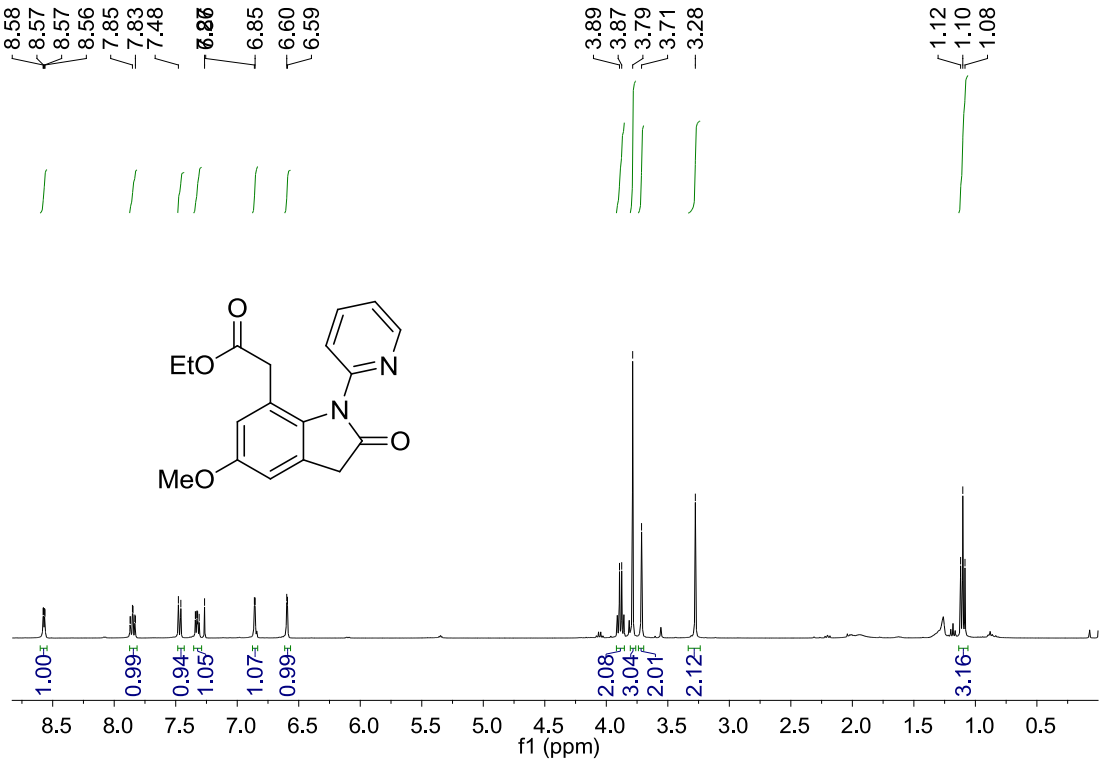
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3b**



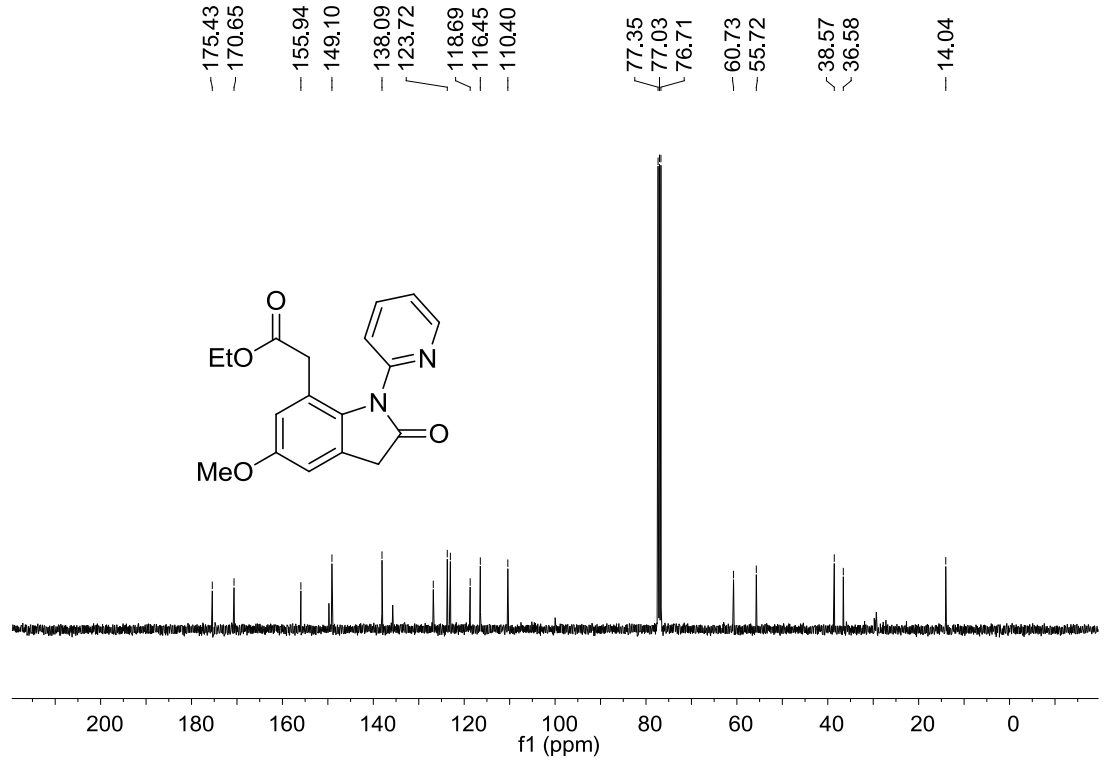
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **3b**



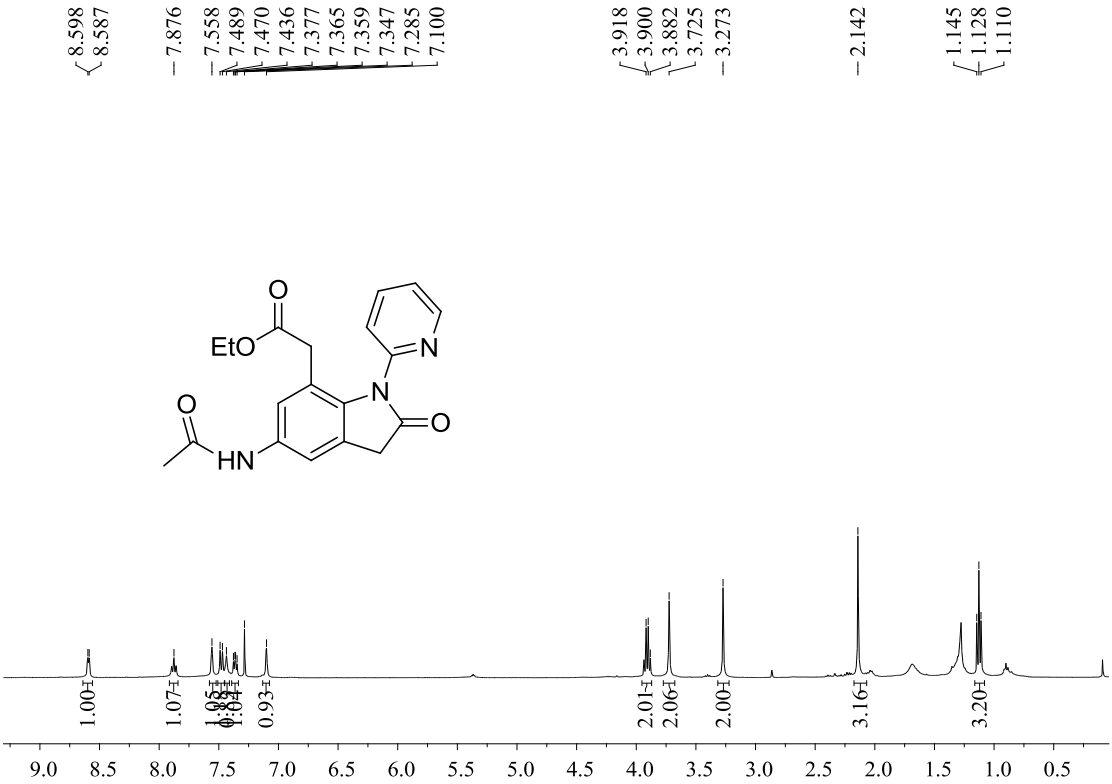
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3c**



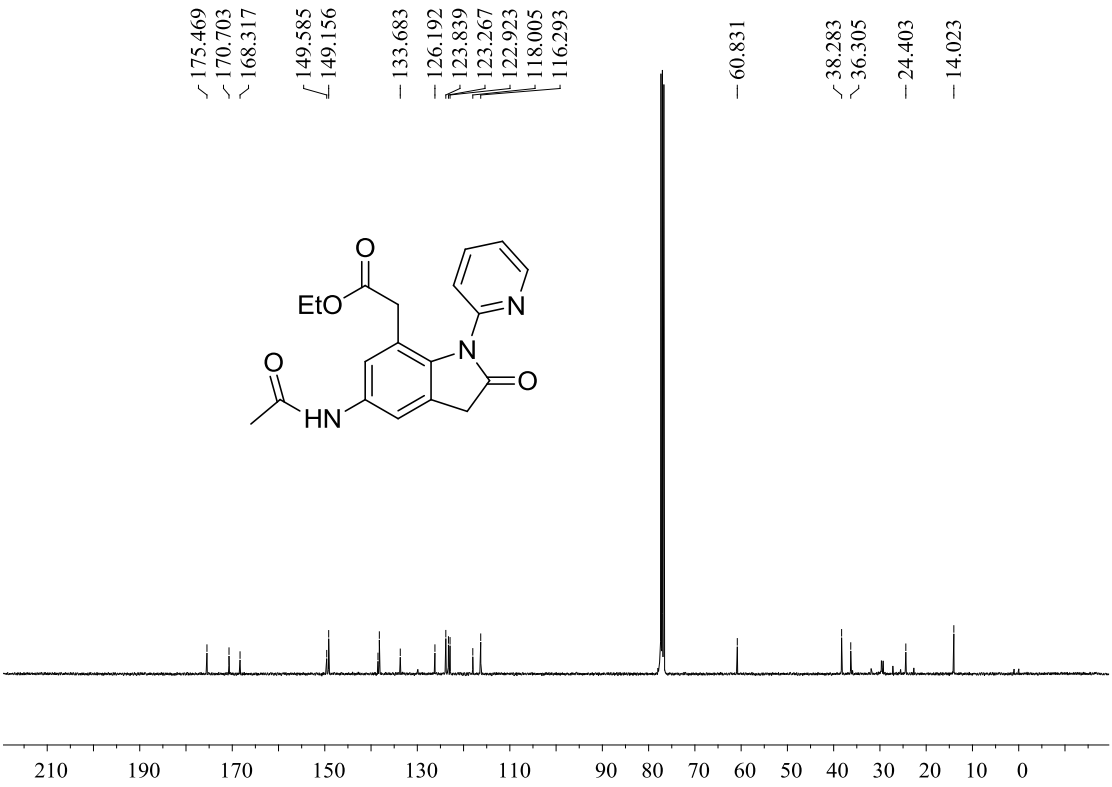
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **3c**



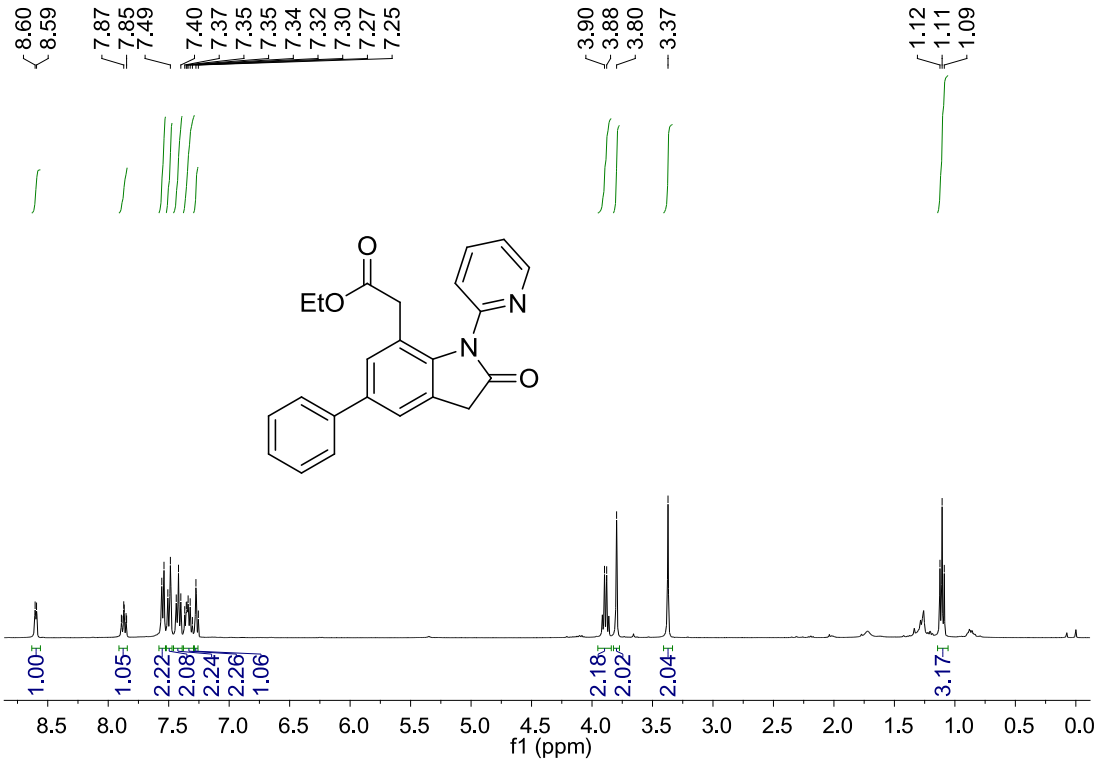
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3d**



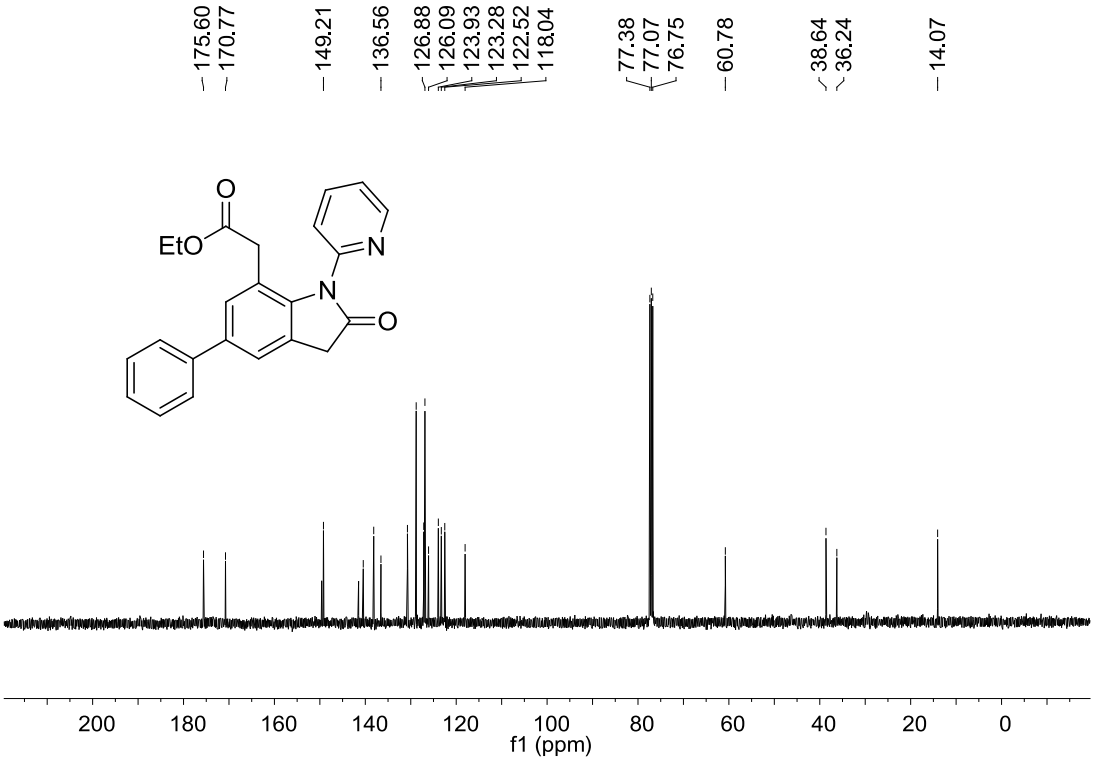
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **3d**



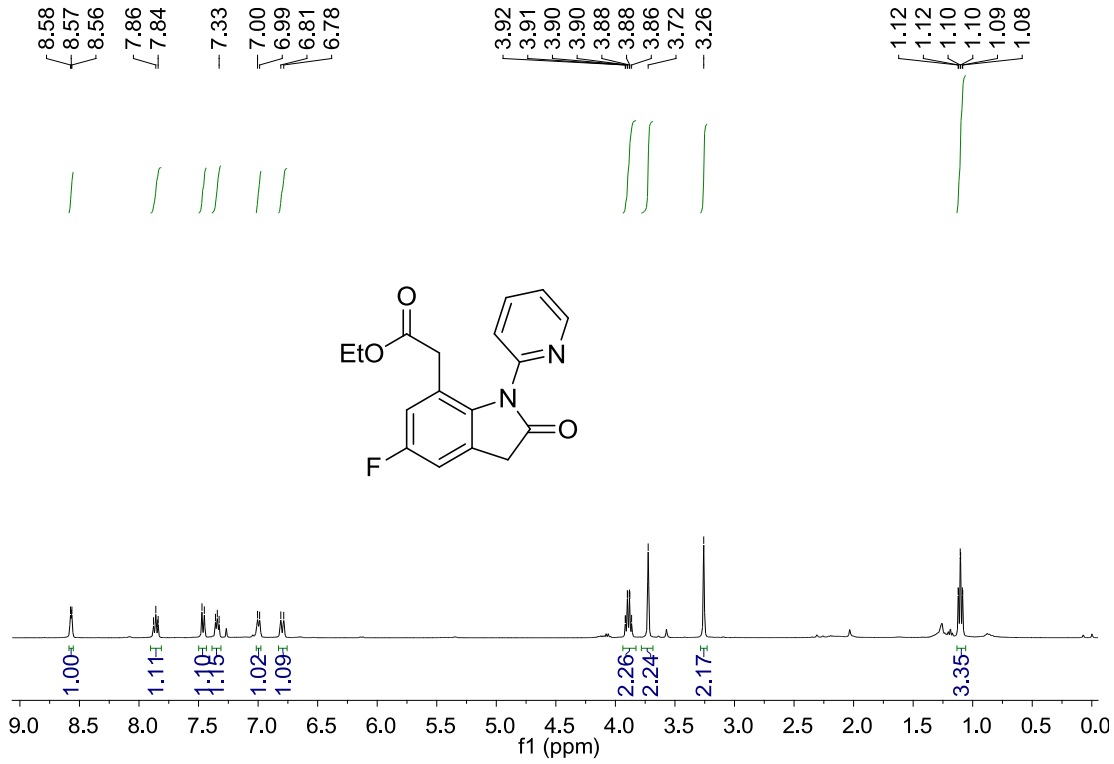
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3e**



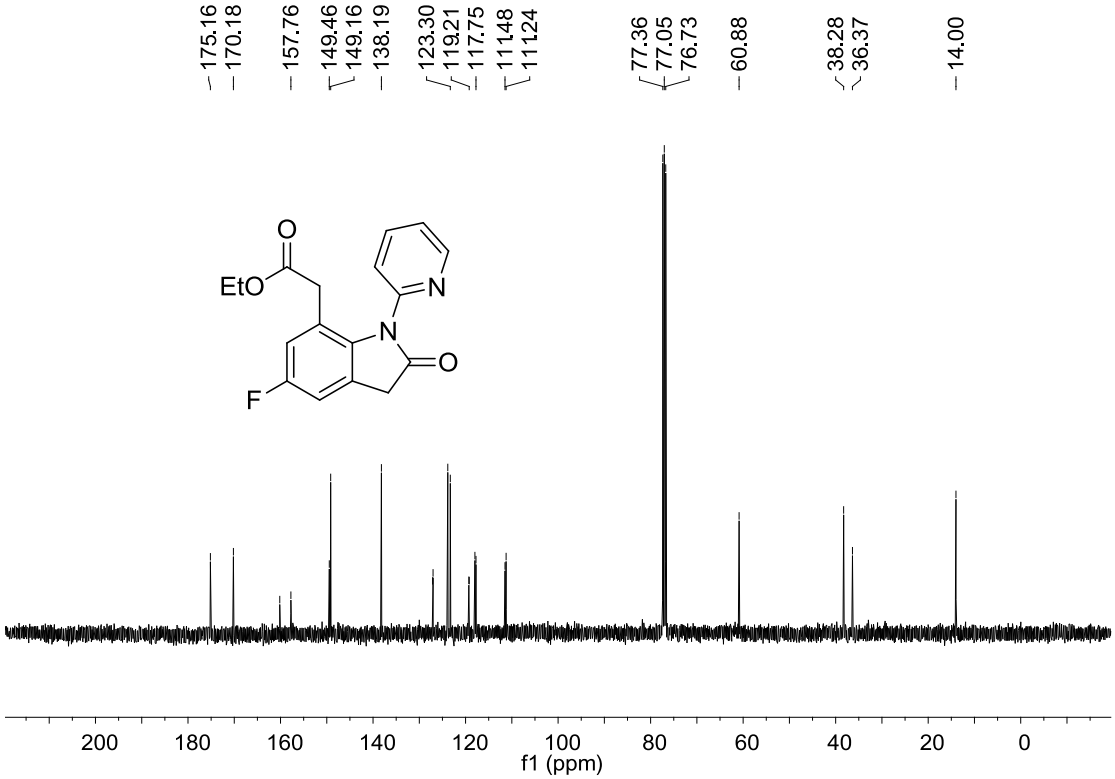
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **3e**



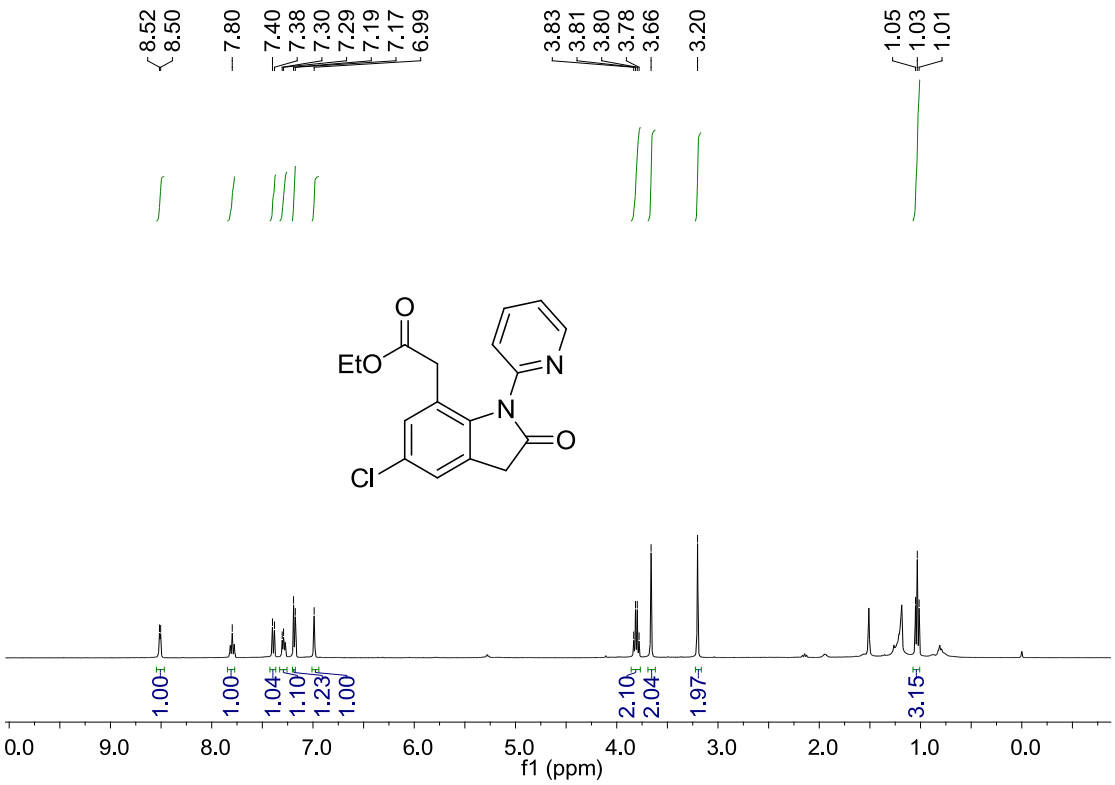
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3f**



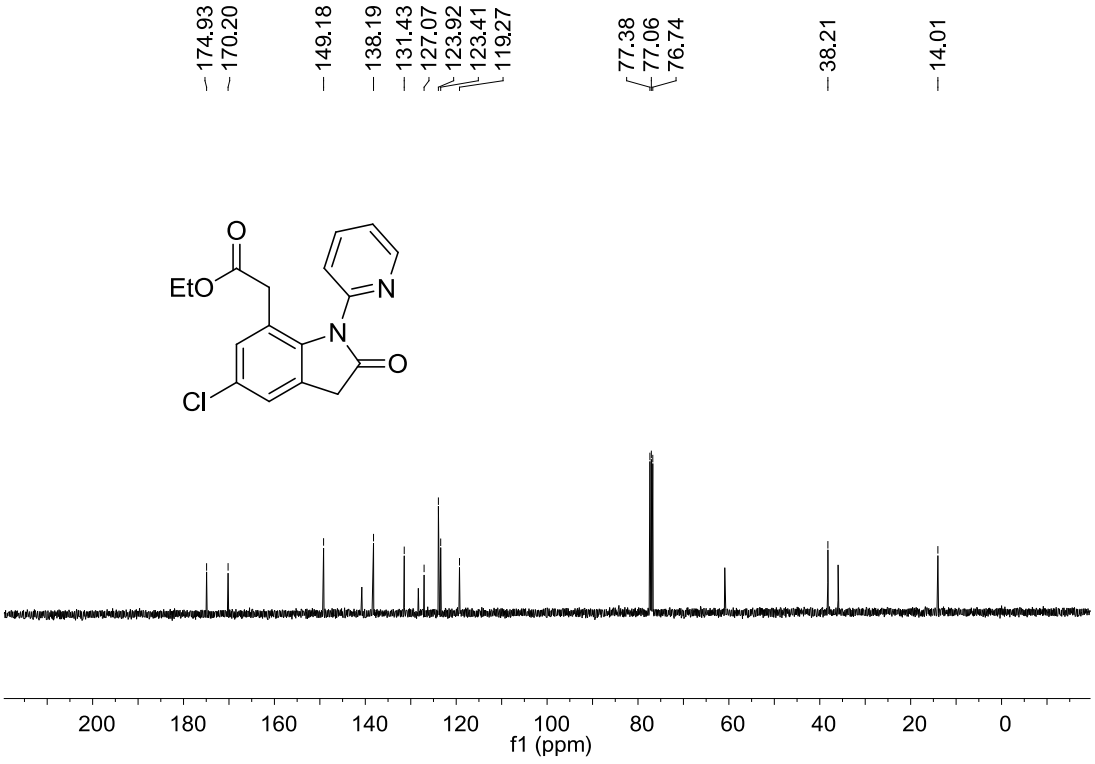
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **3f**



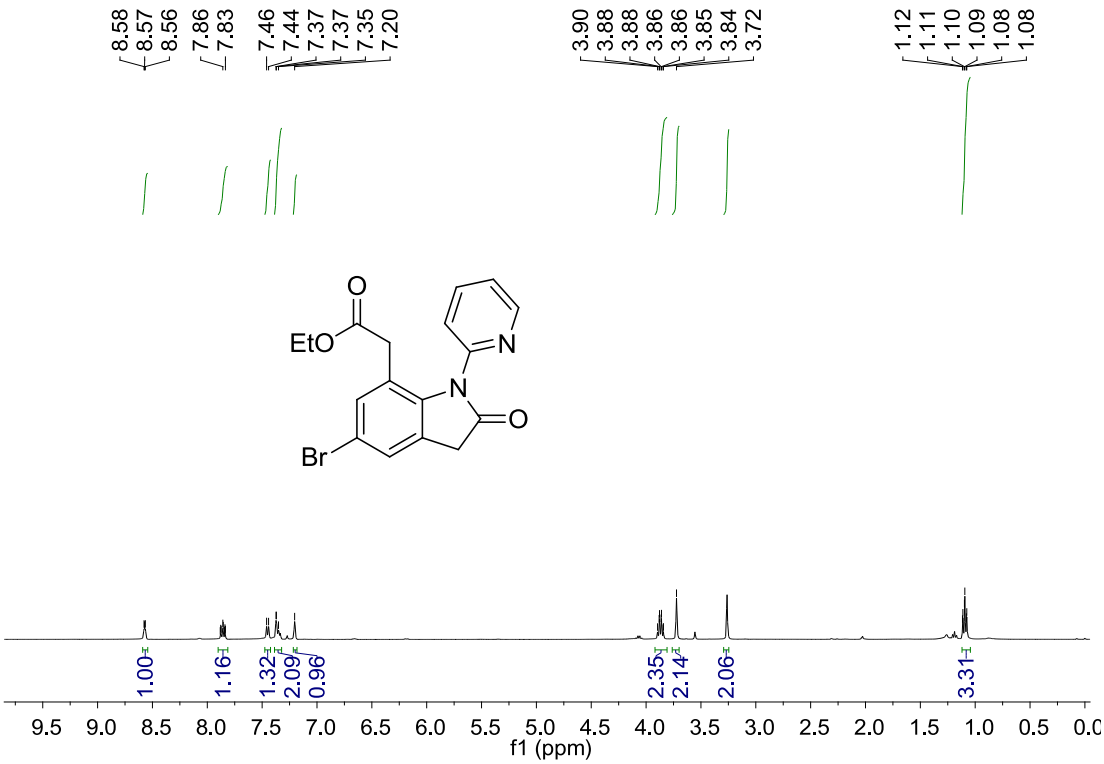
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3g**



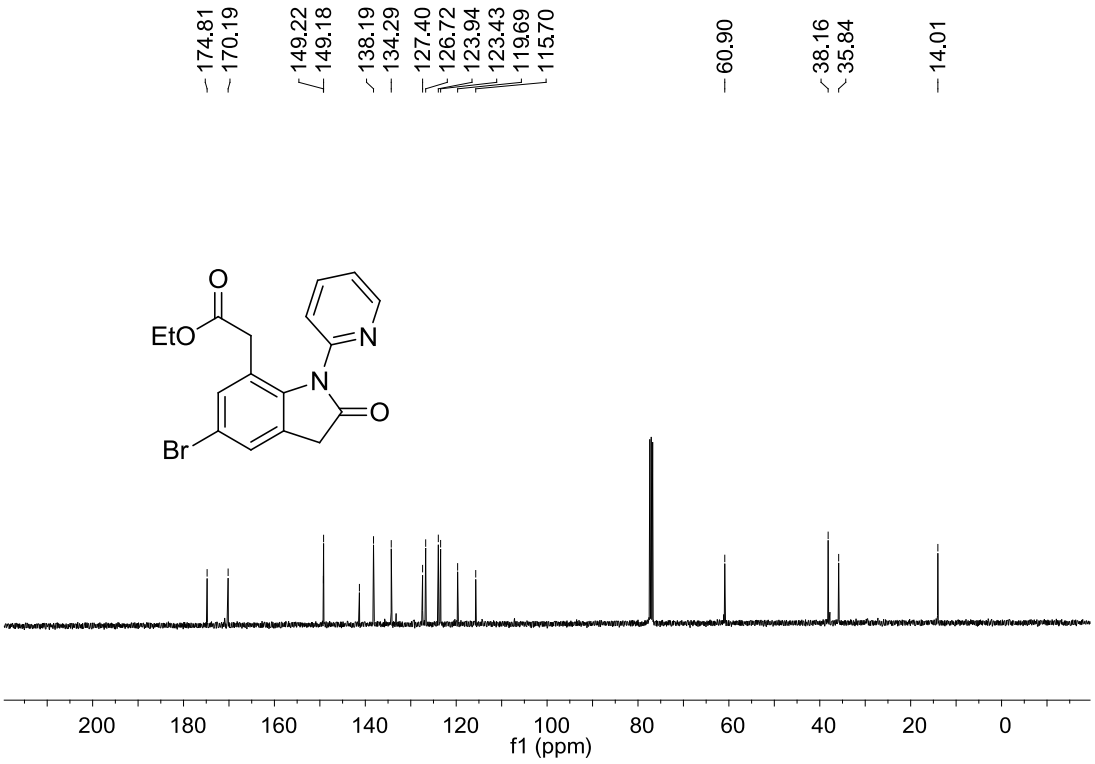
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **3g**



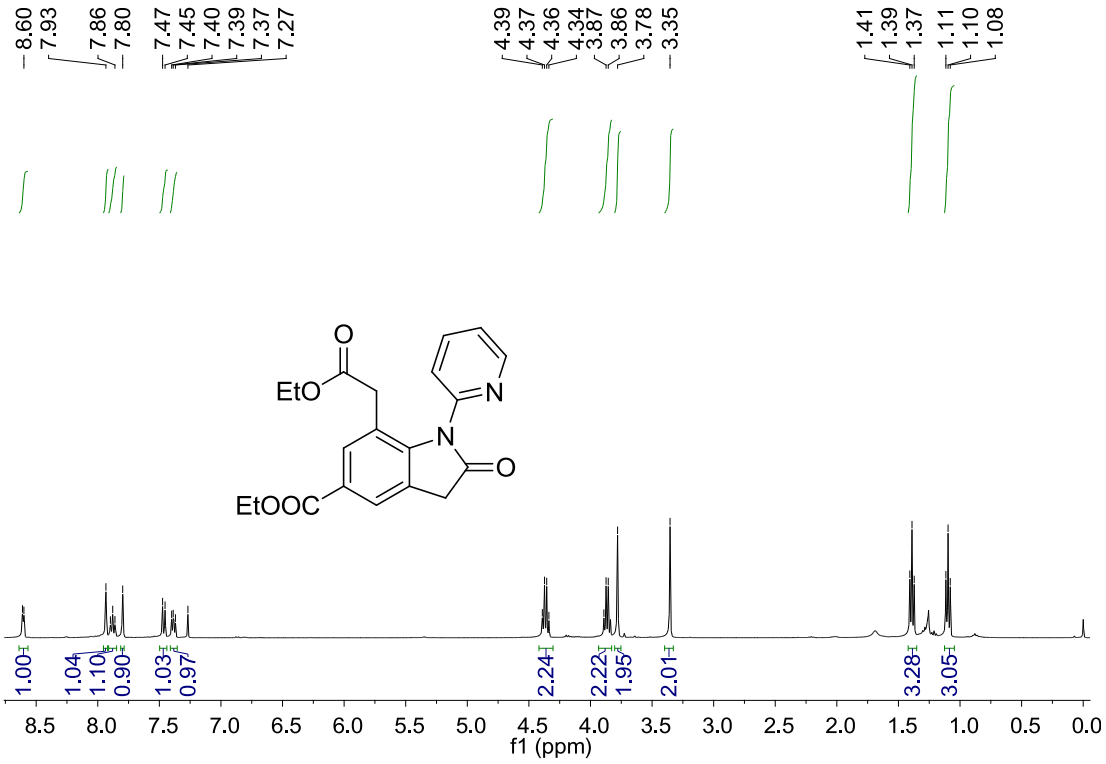
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3h**



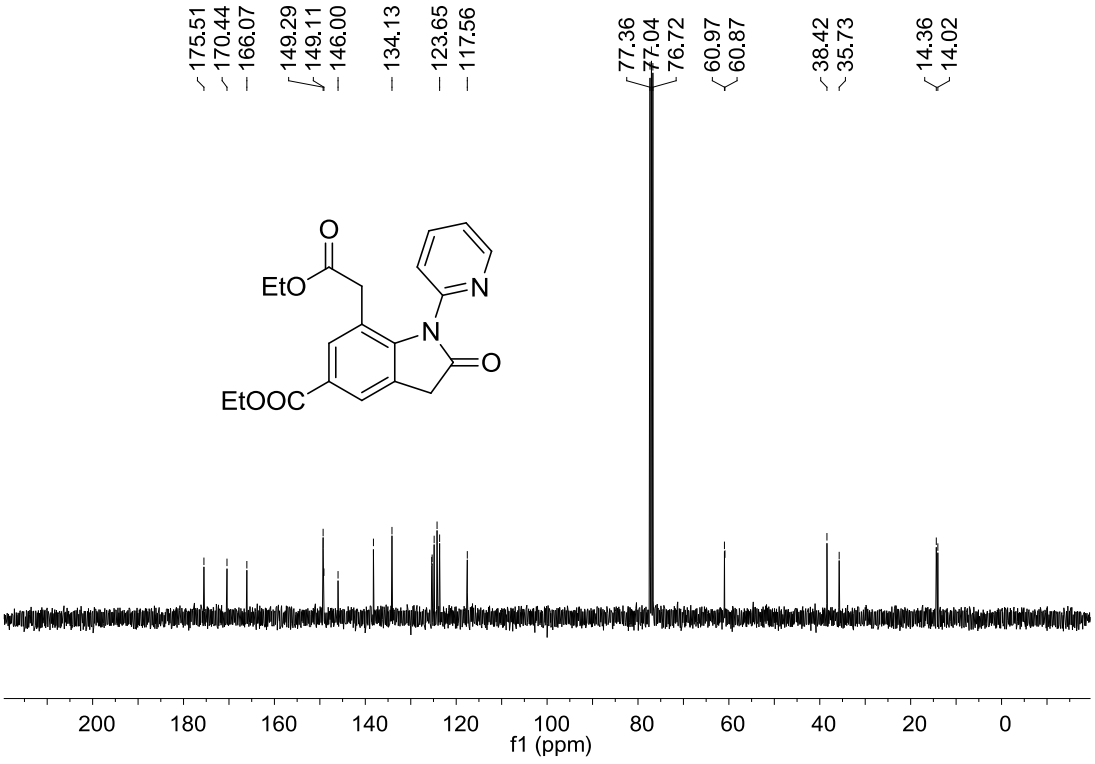
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **3h**



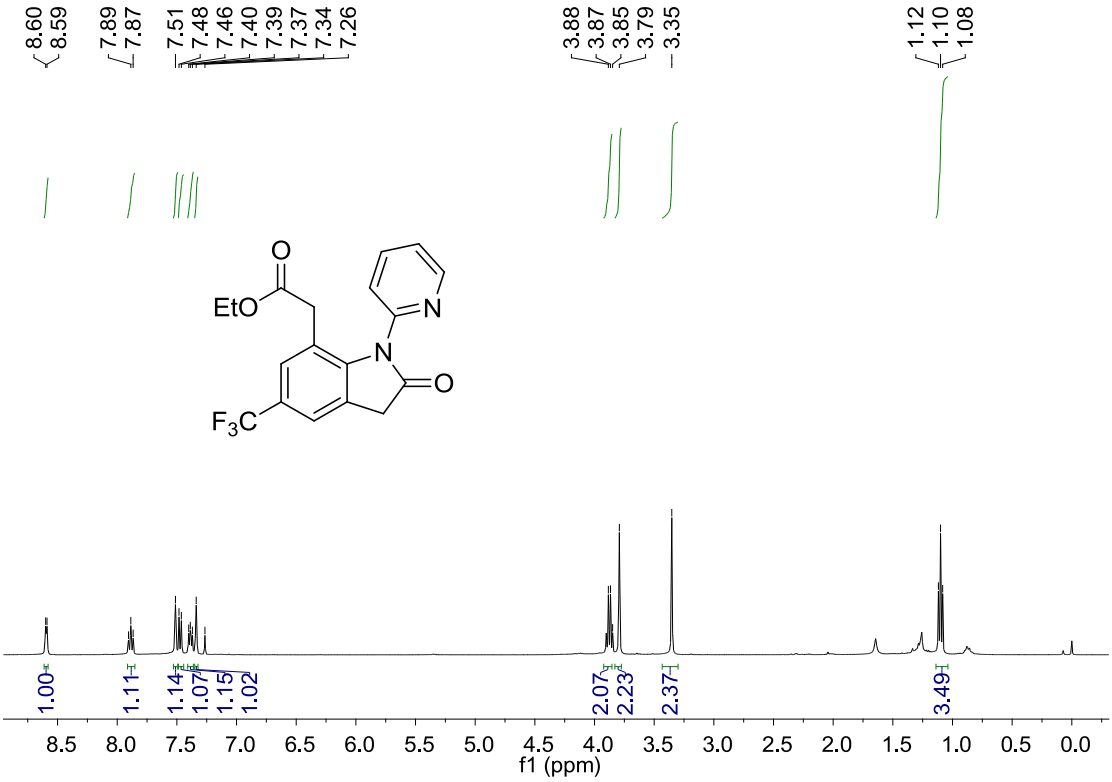
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3i**



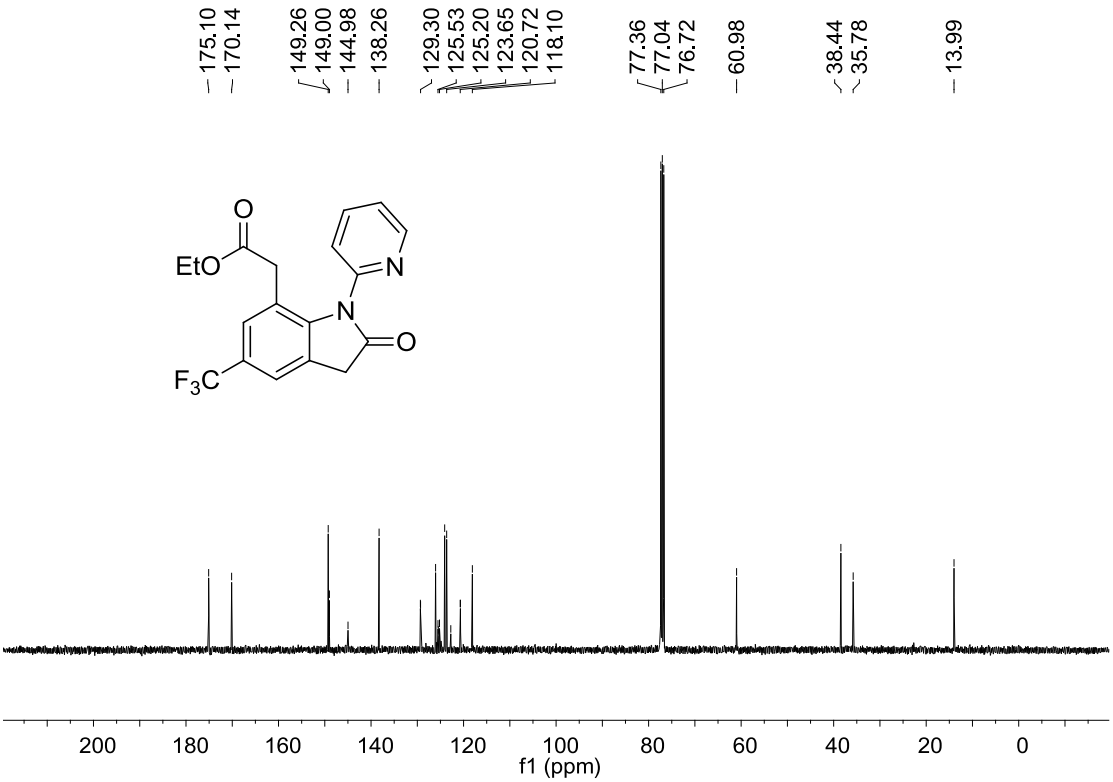
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **3i**



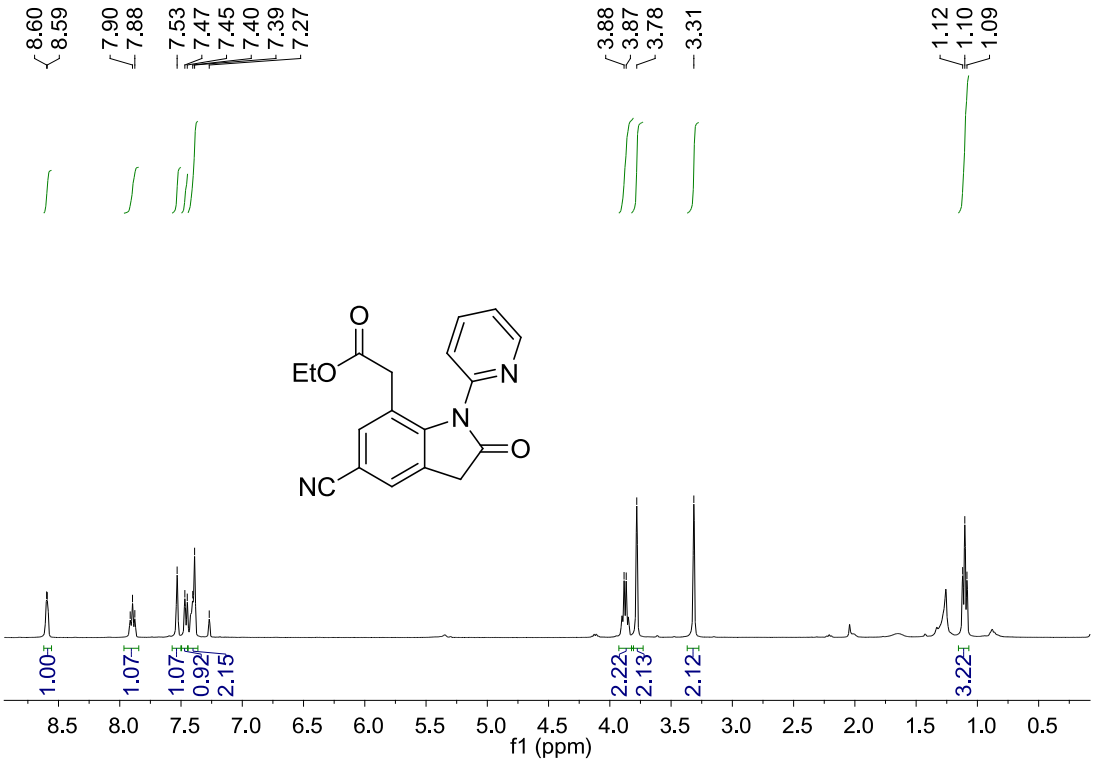
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3j**



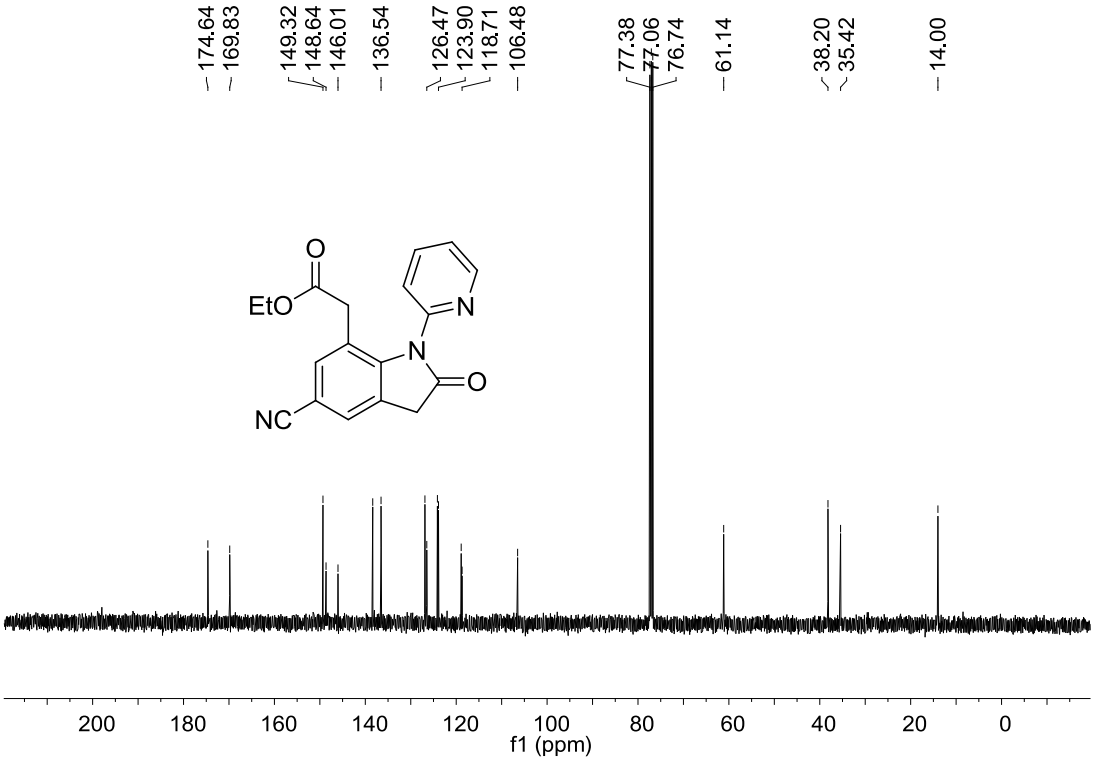
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **3j**



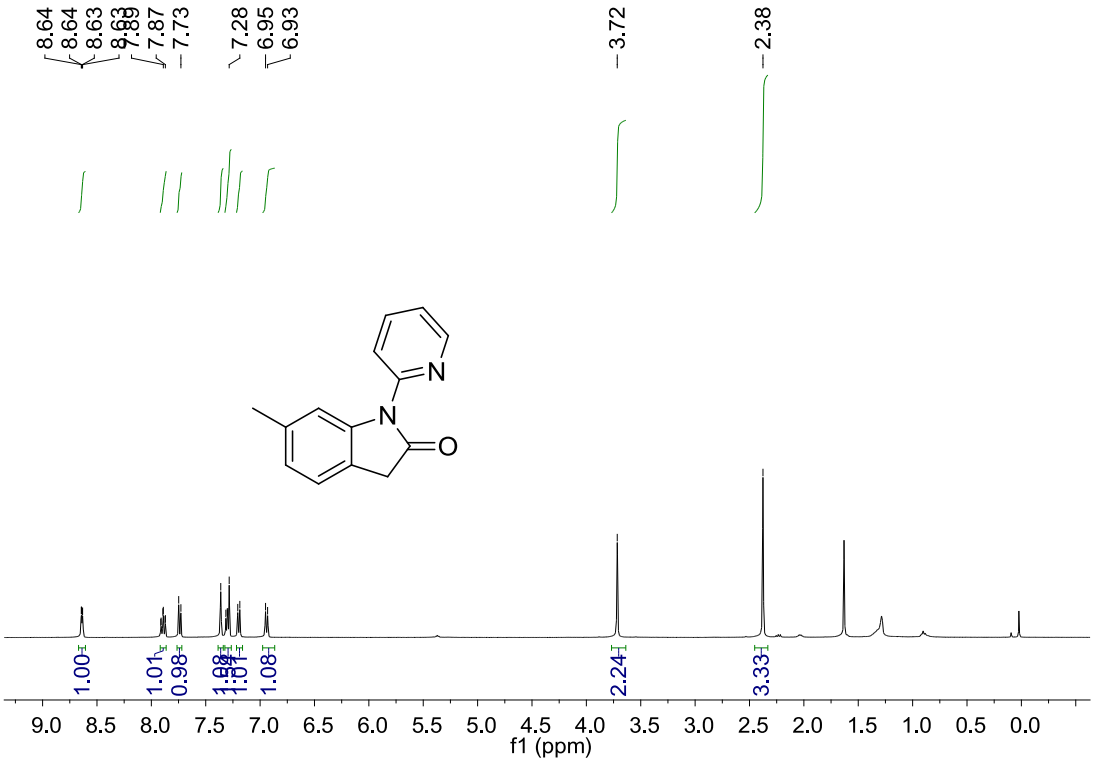
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3k**



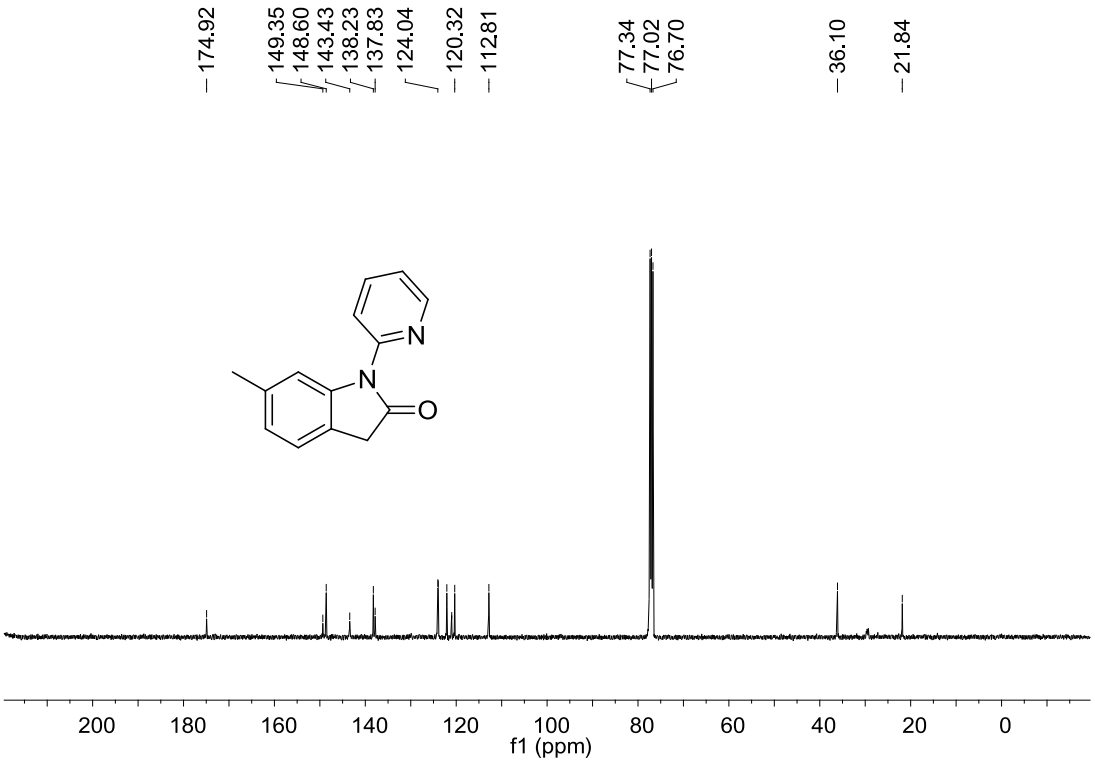
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **3k**



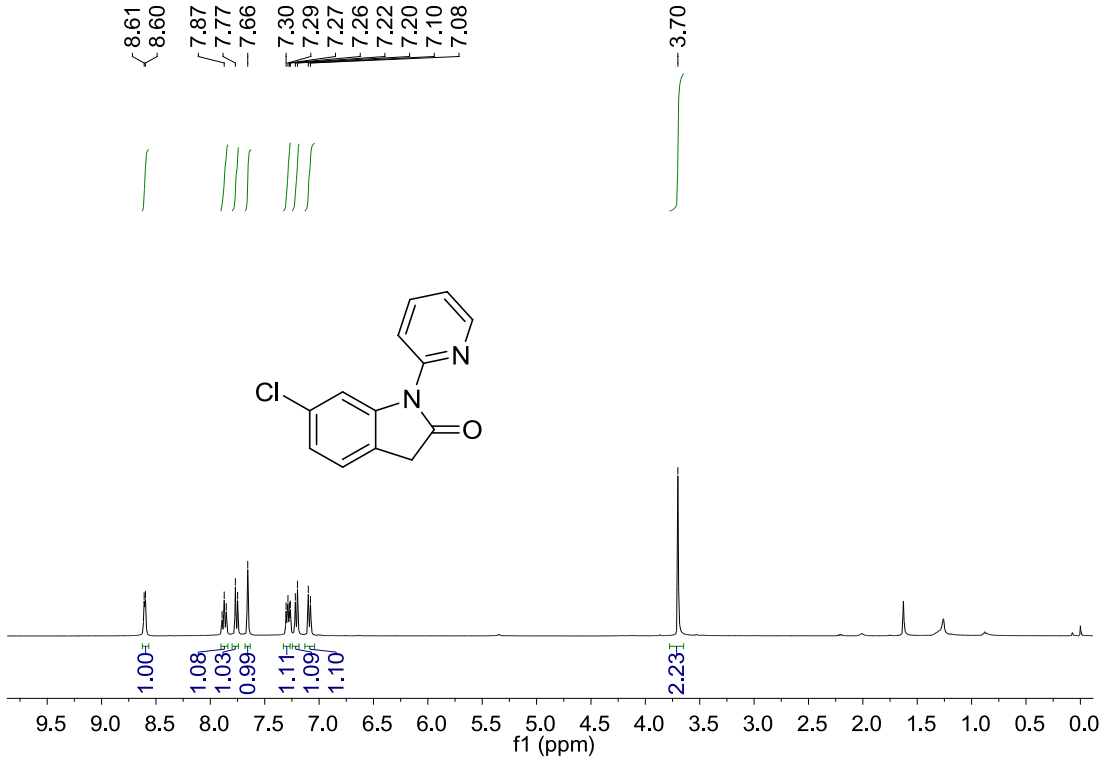
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3l**



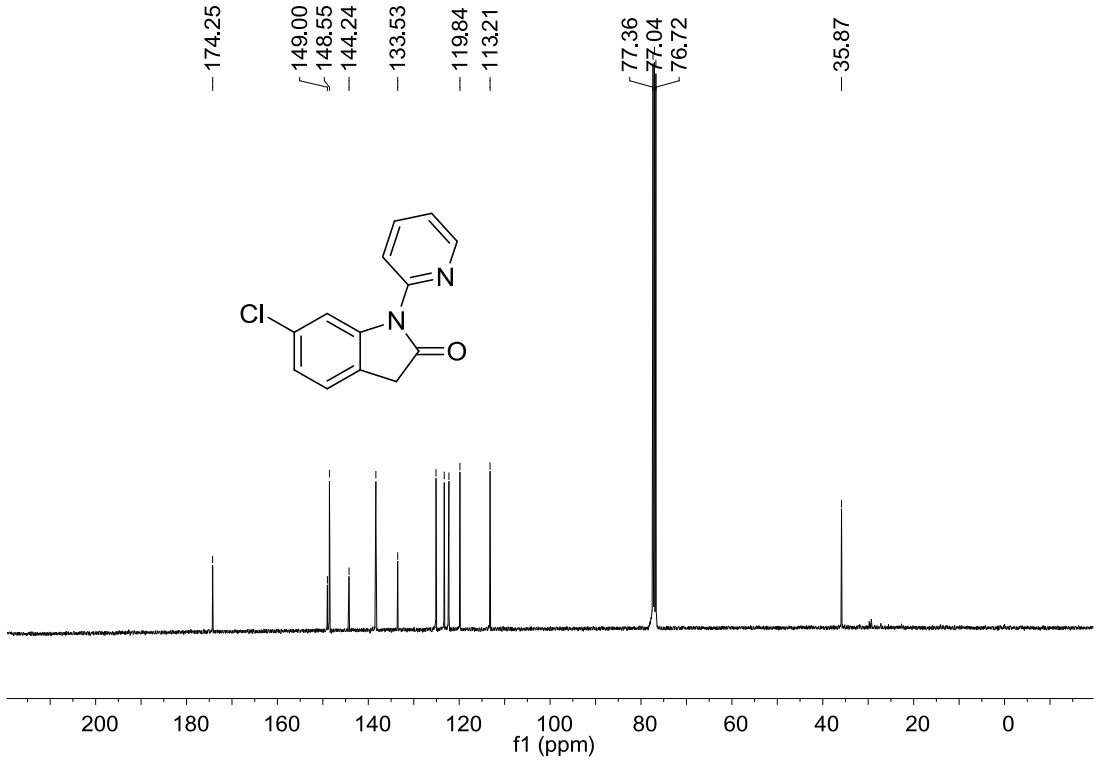
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **3l**



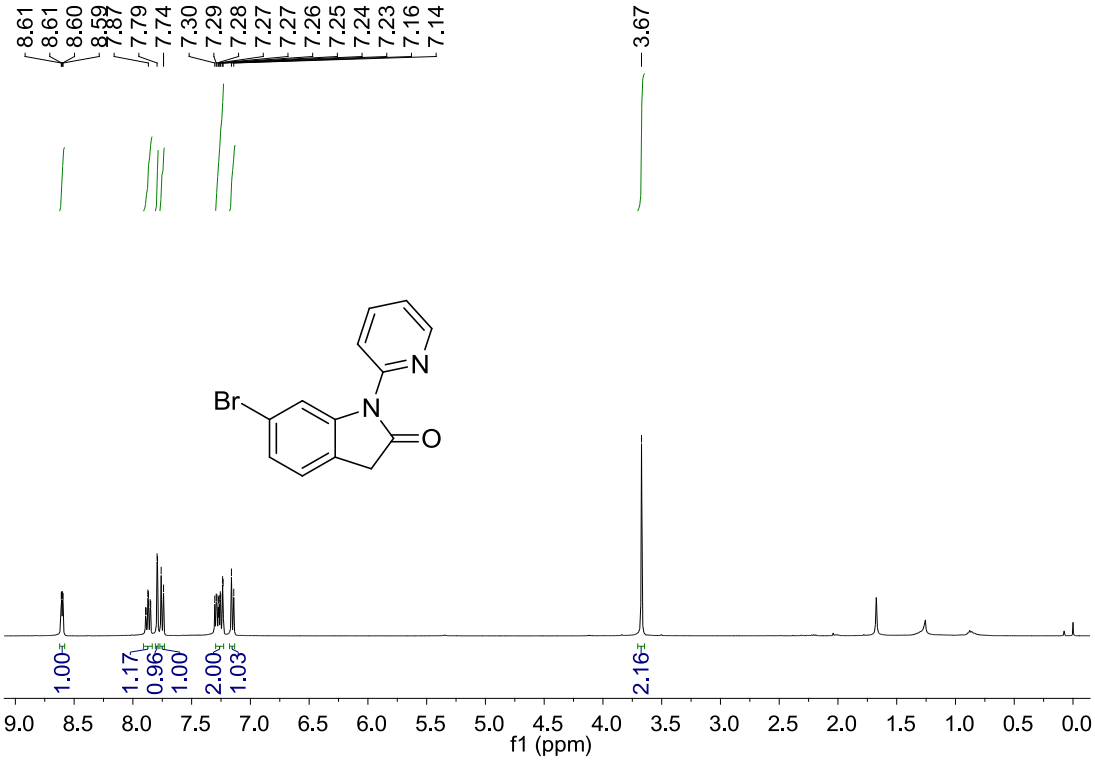
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3m**



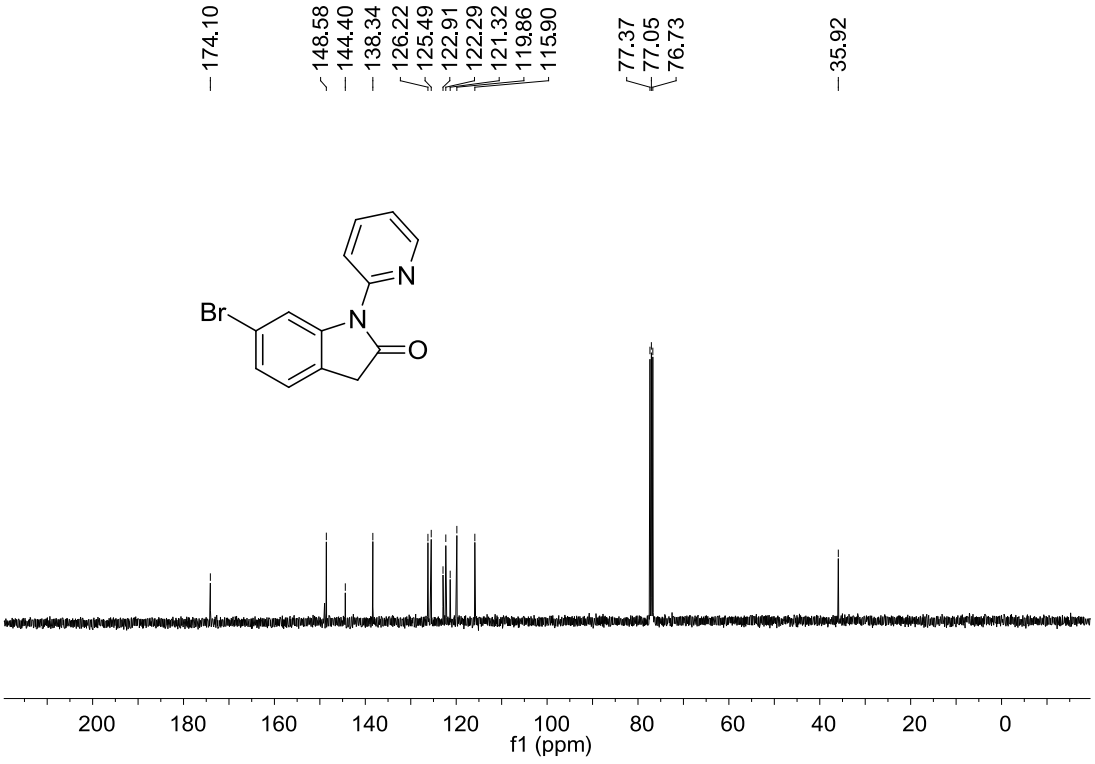
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **3m**



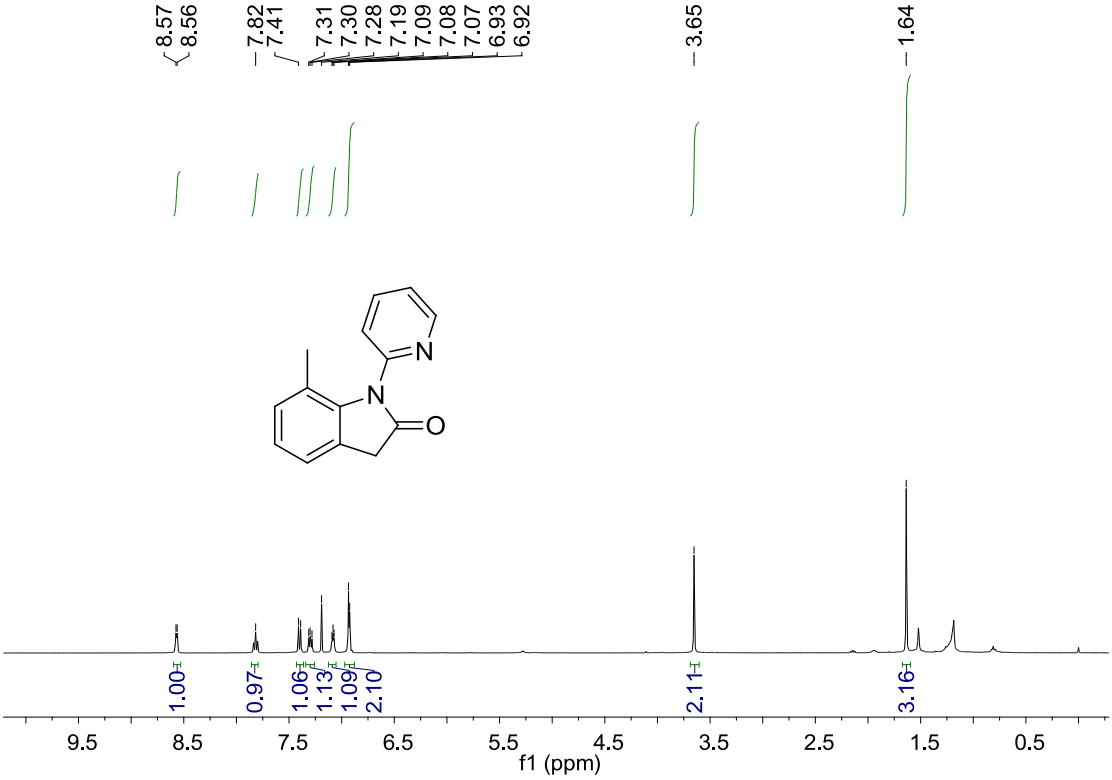
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3n**



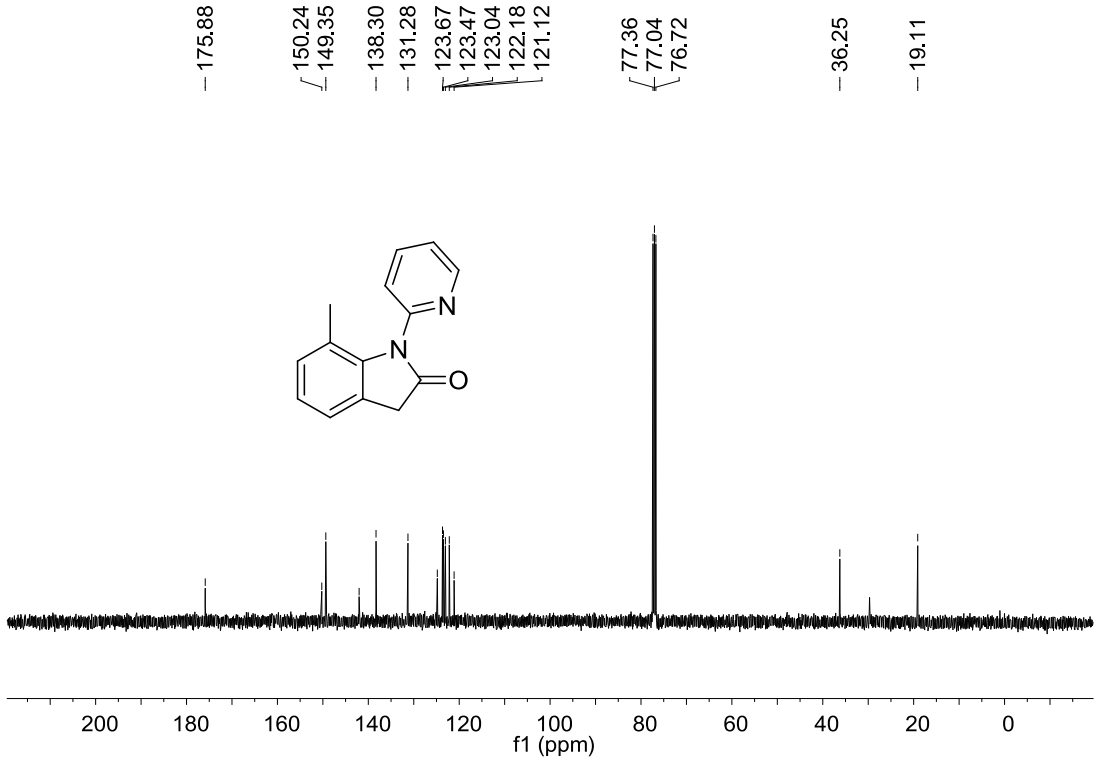
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **3n**



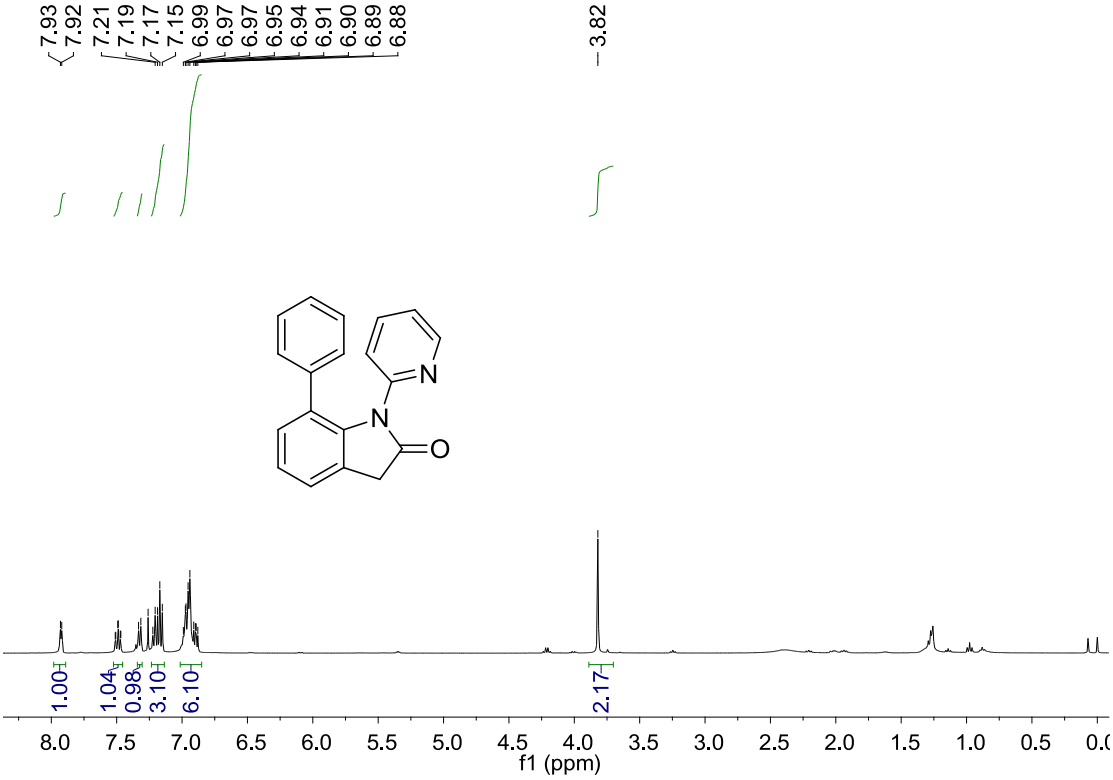
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3o**



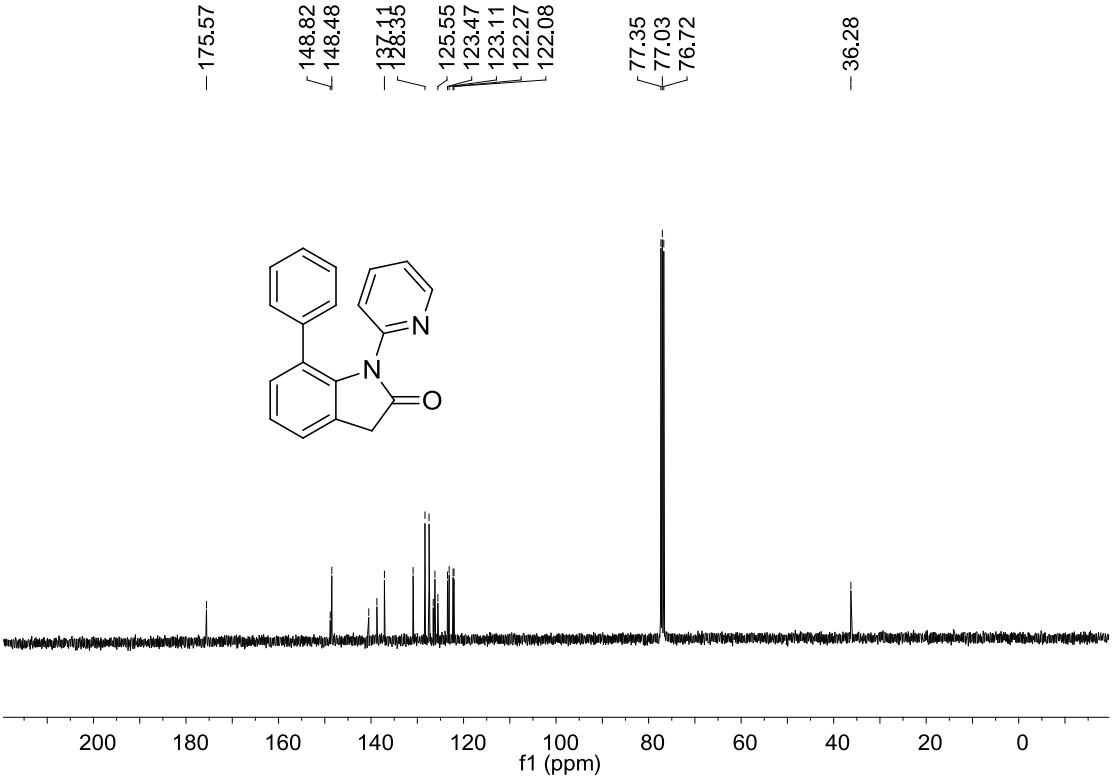
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **3o**



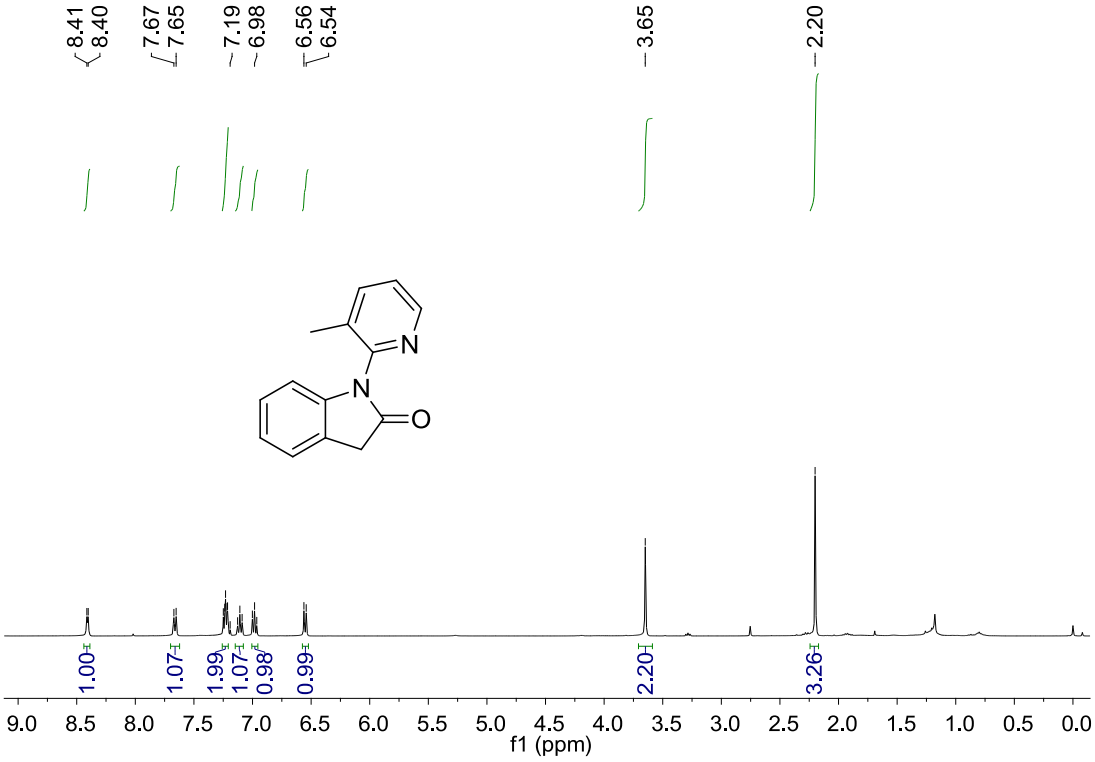
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3p**



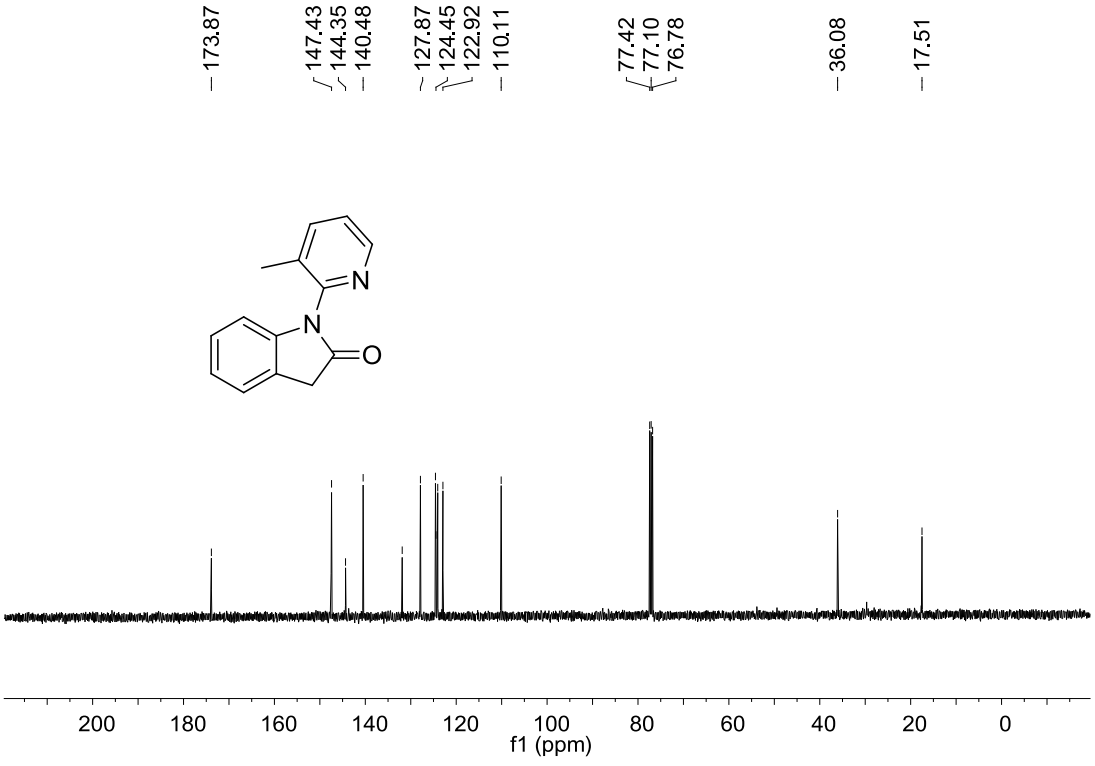
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **3p**



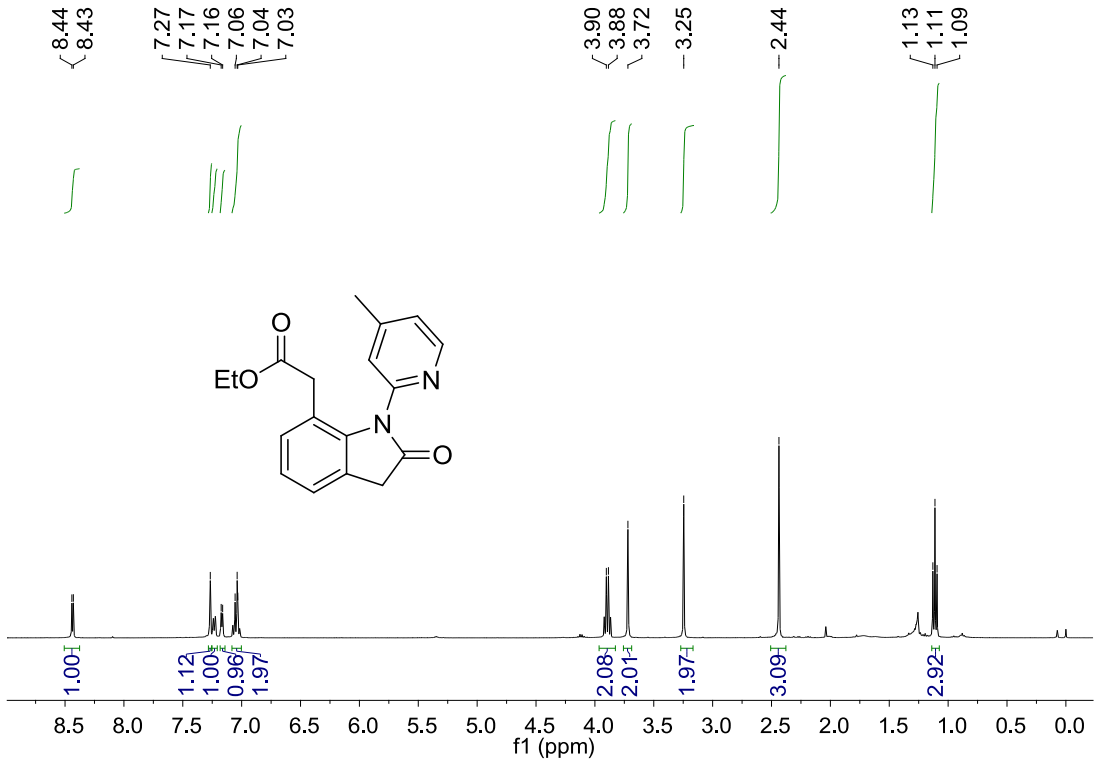
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3q**



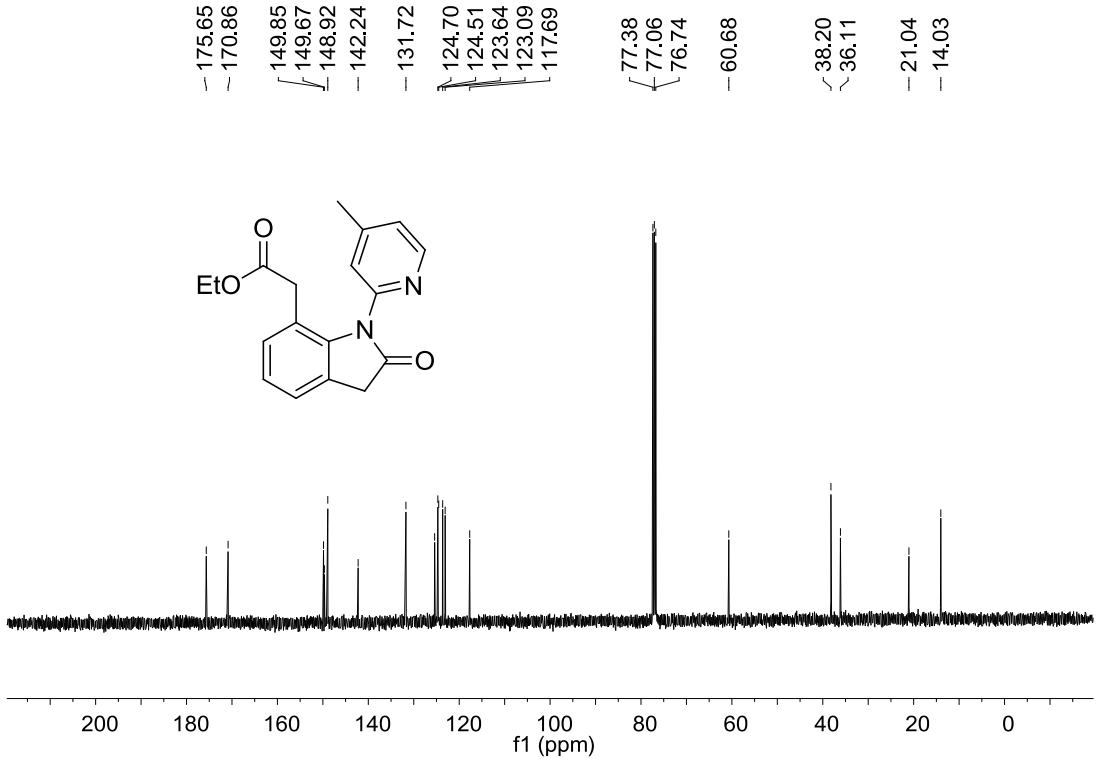
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **3q**



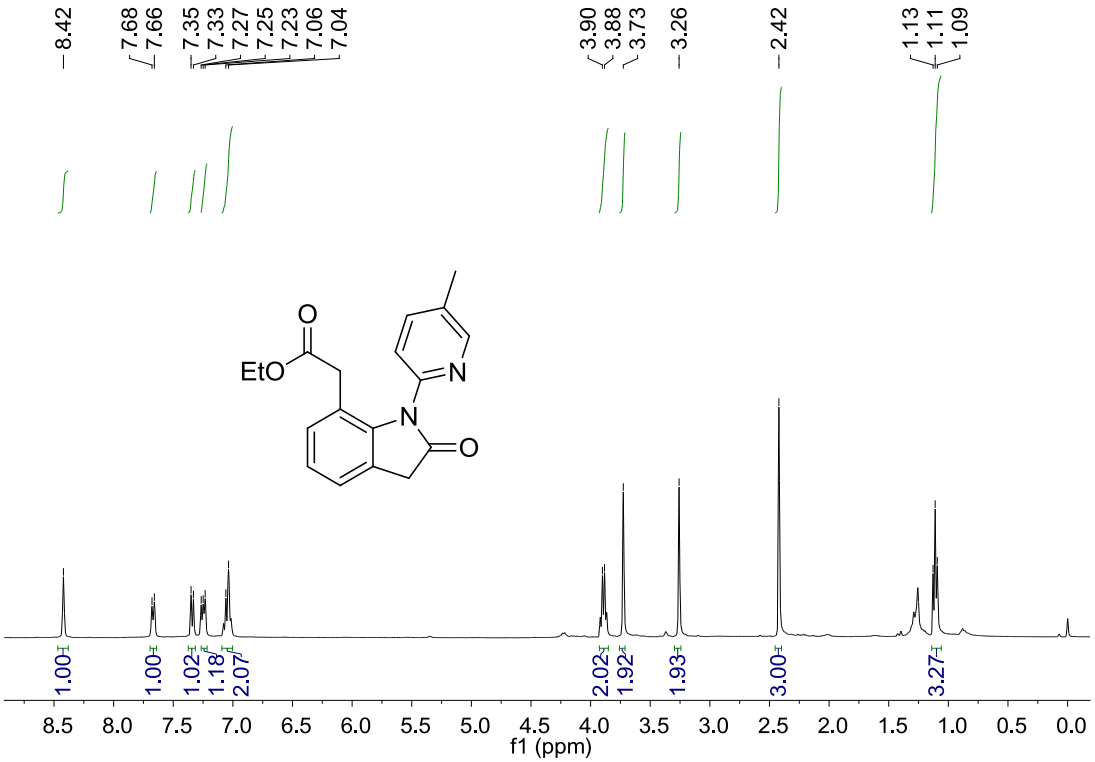
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3r**



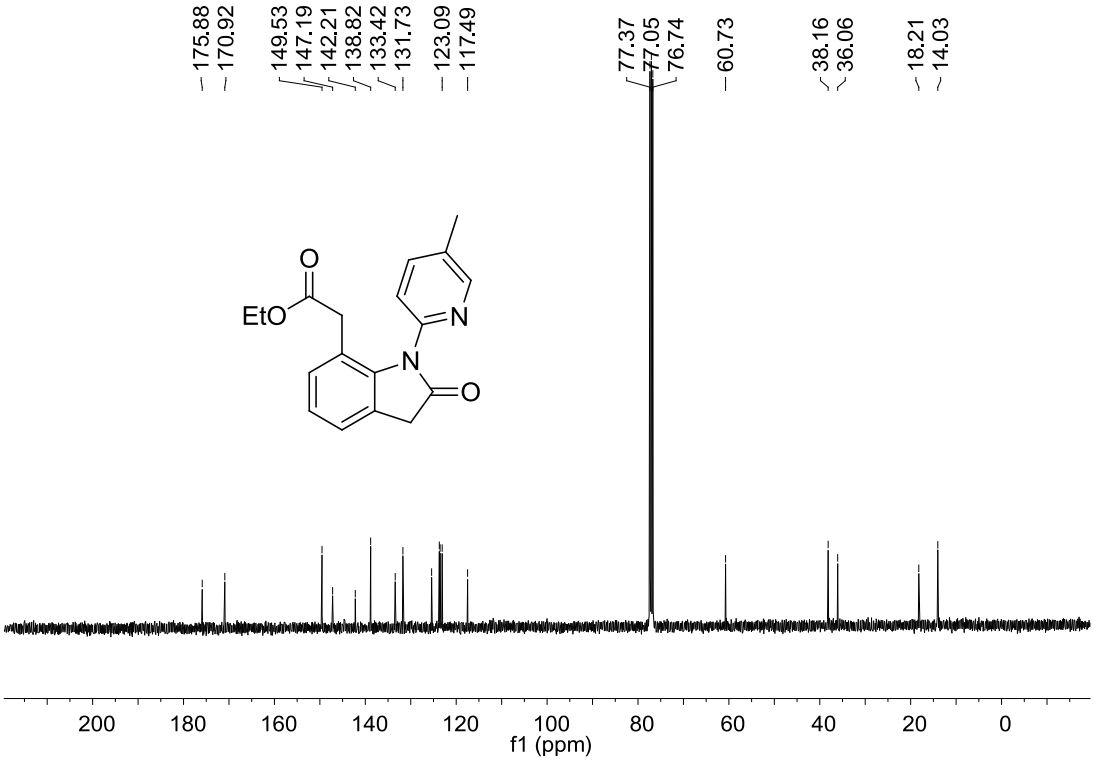
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **3r**



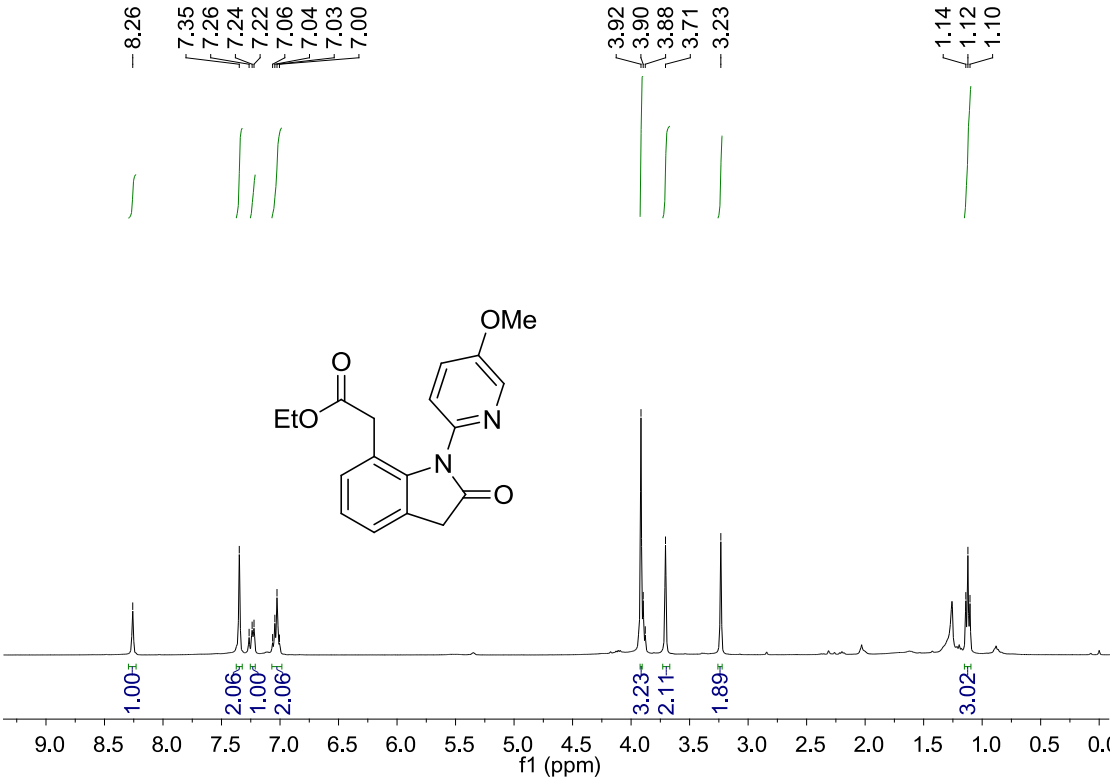
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3s**



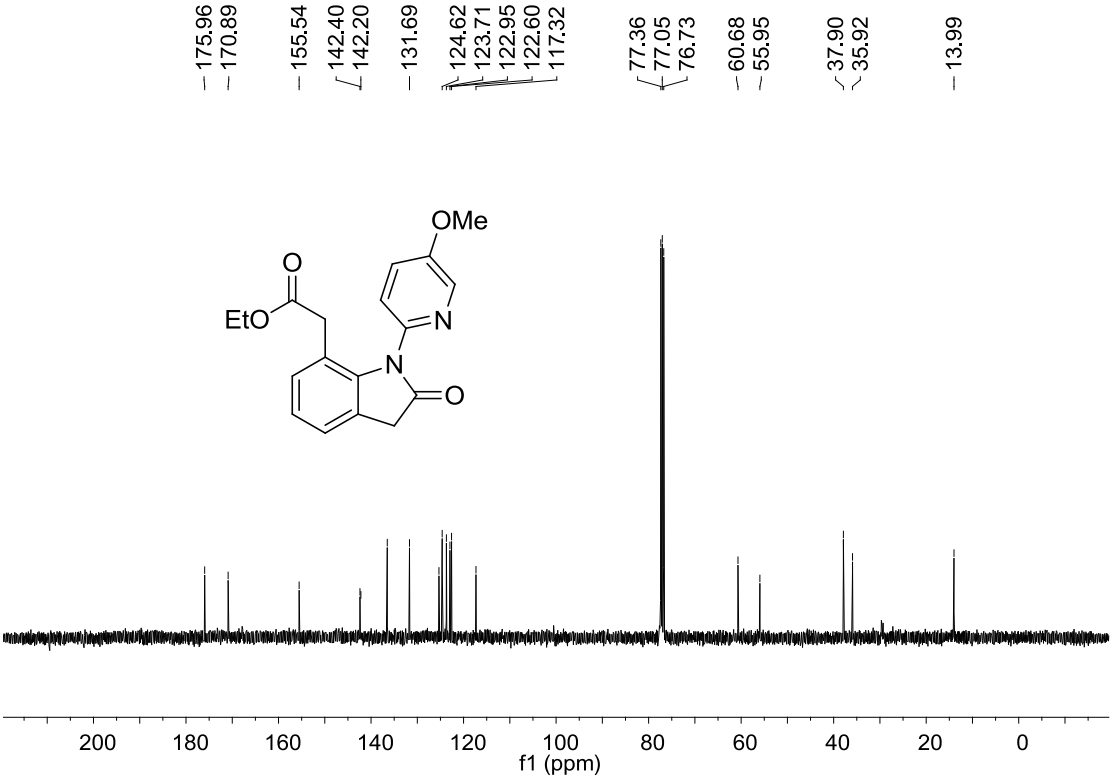
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **3s**



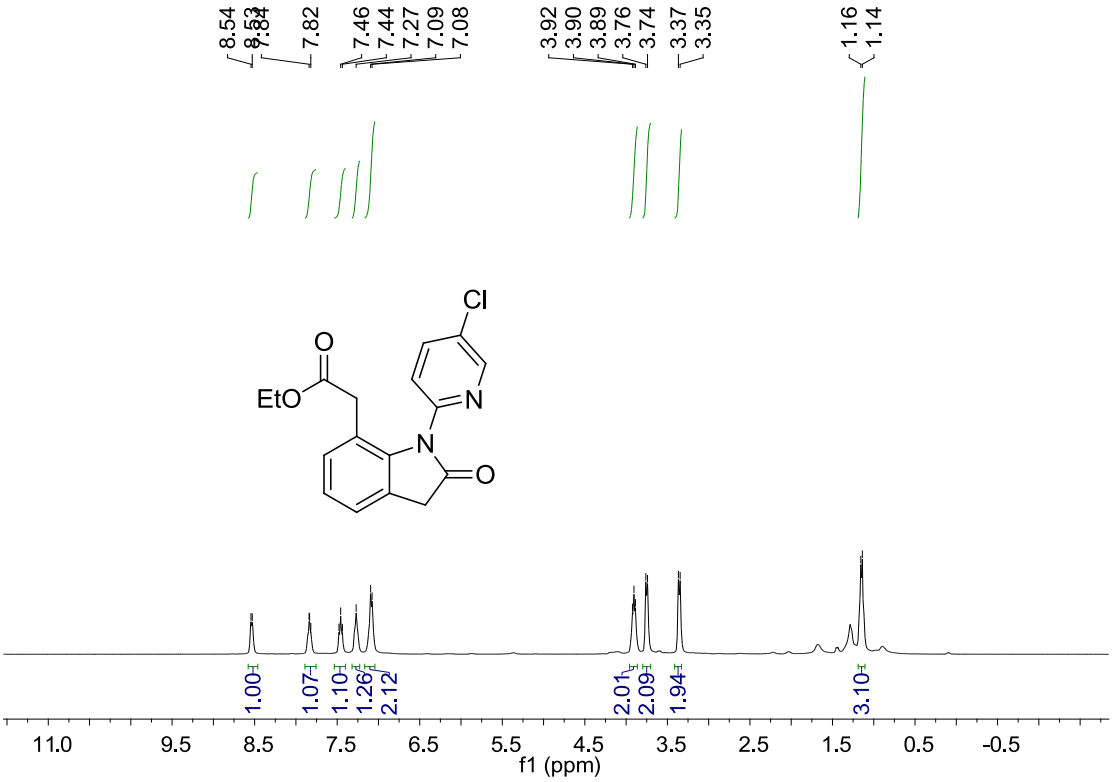
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3t**



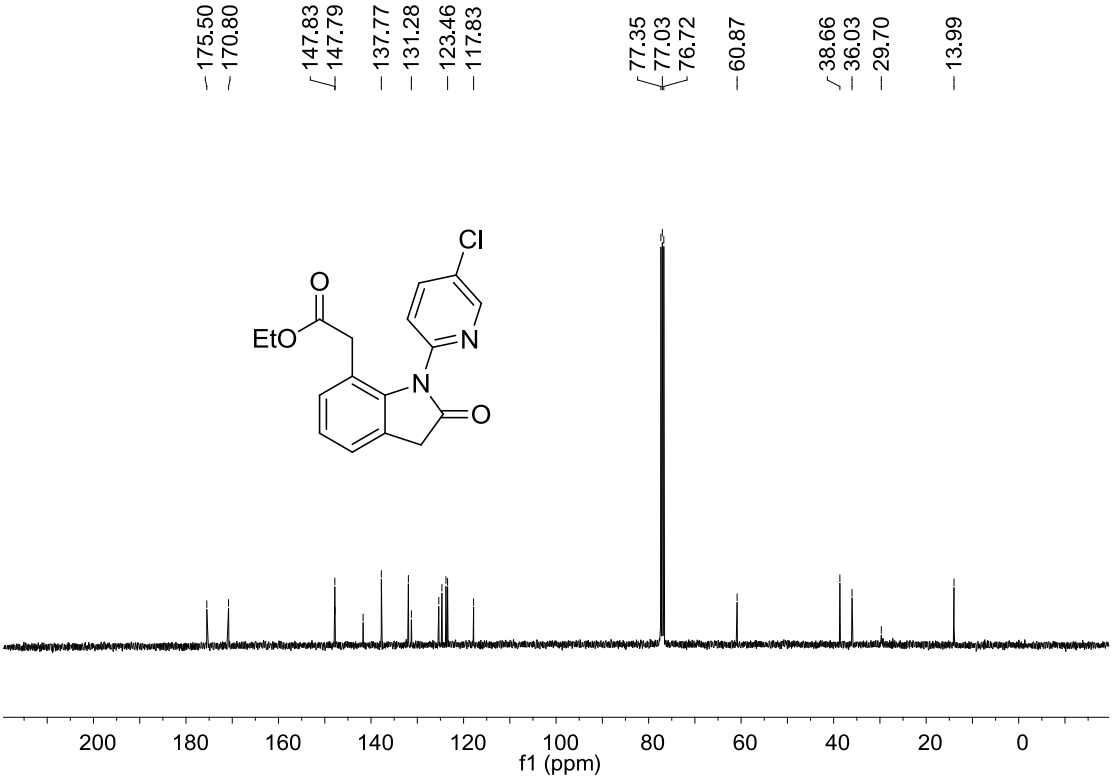
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **3t**



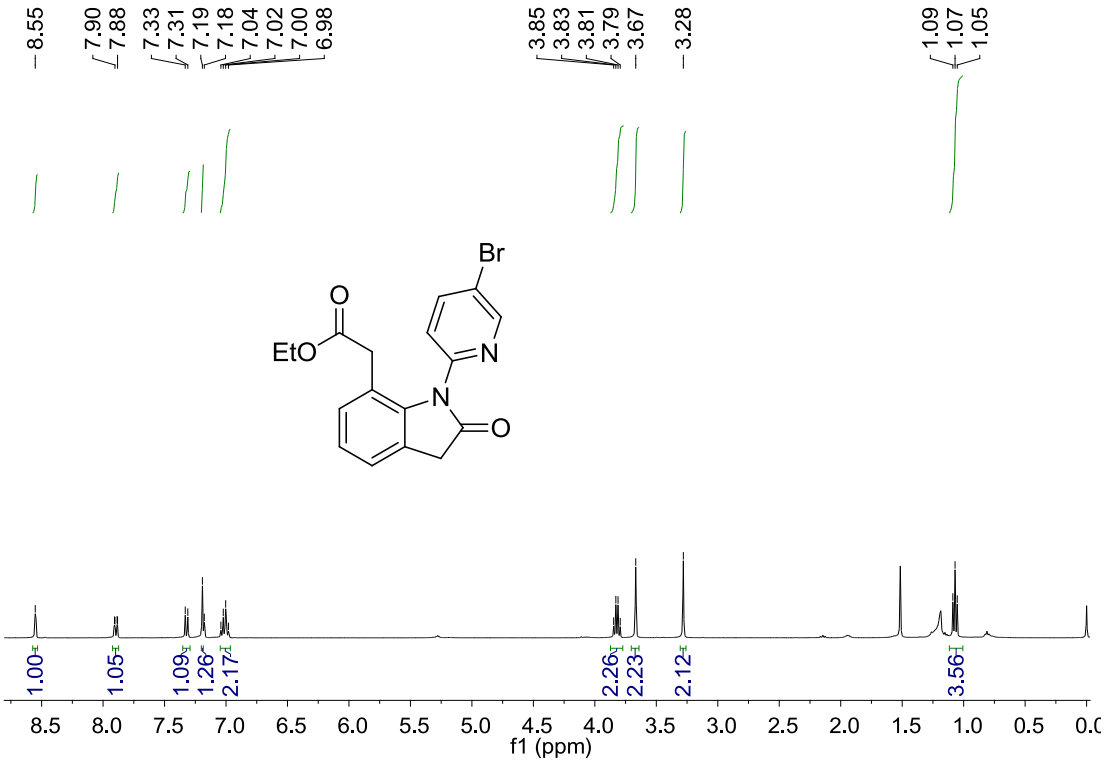
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3u**



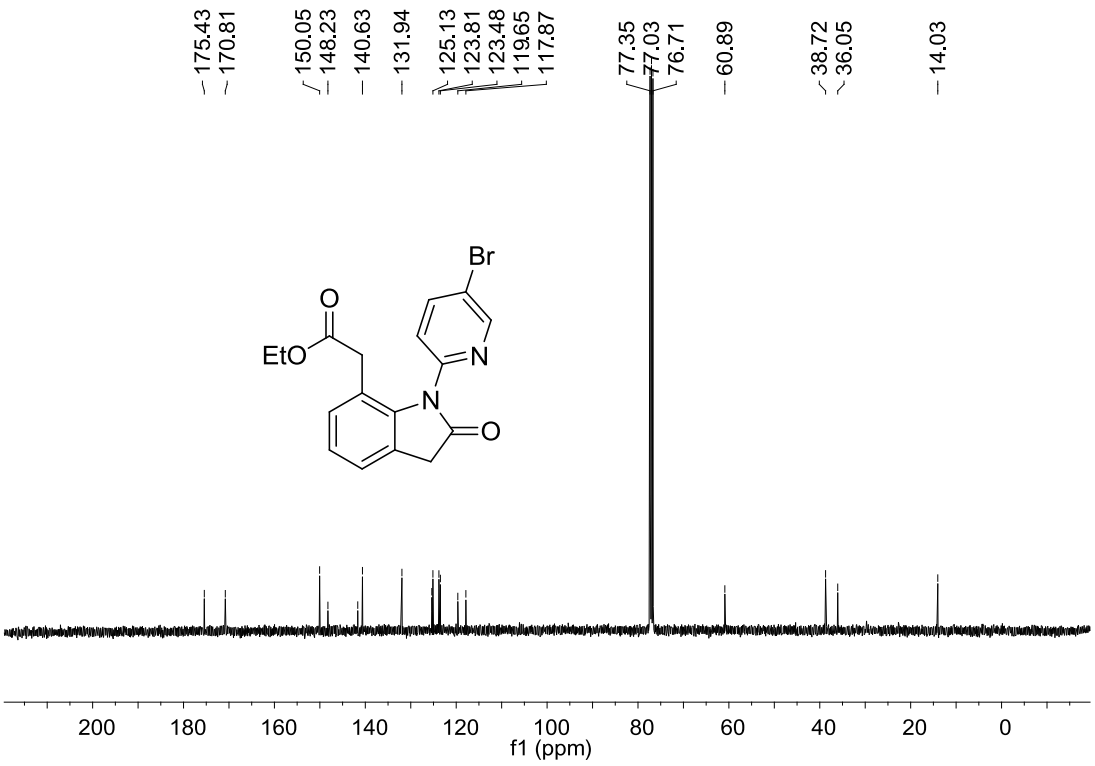
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **3u**



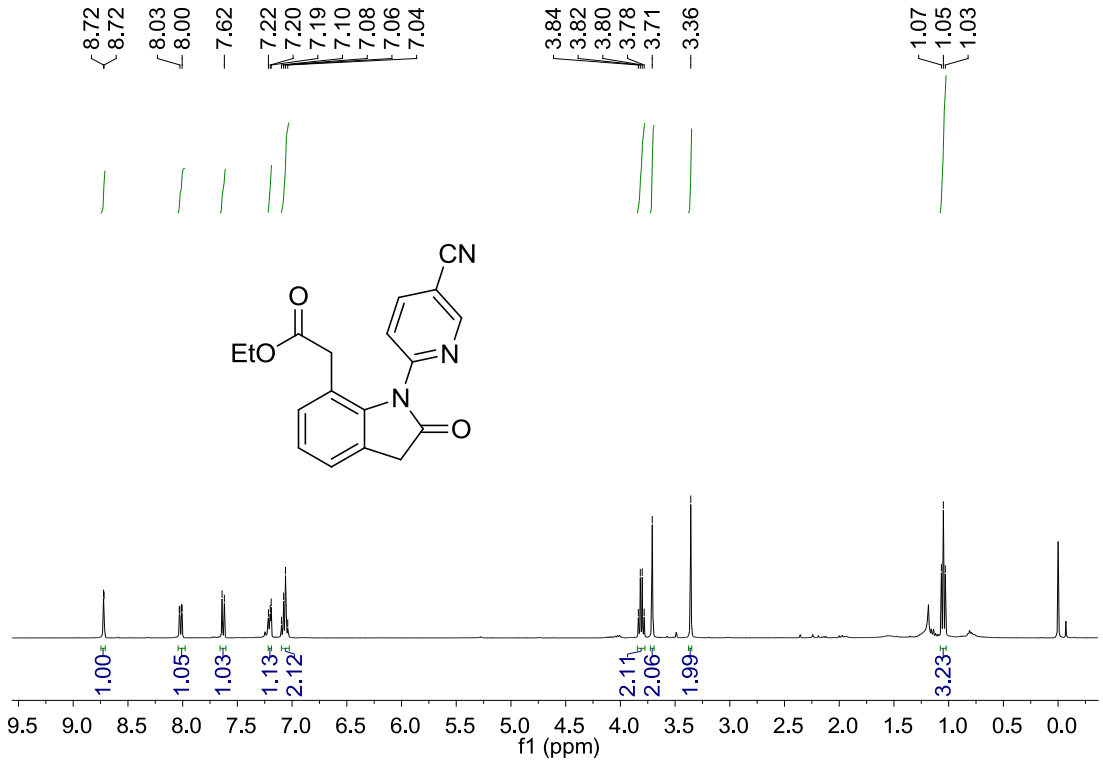
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3v**



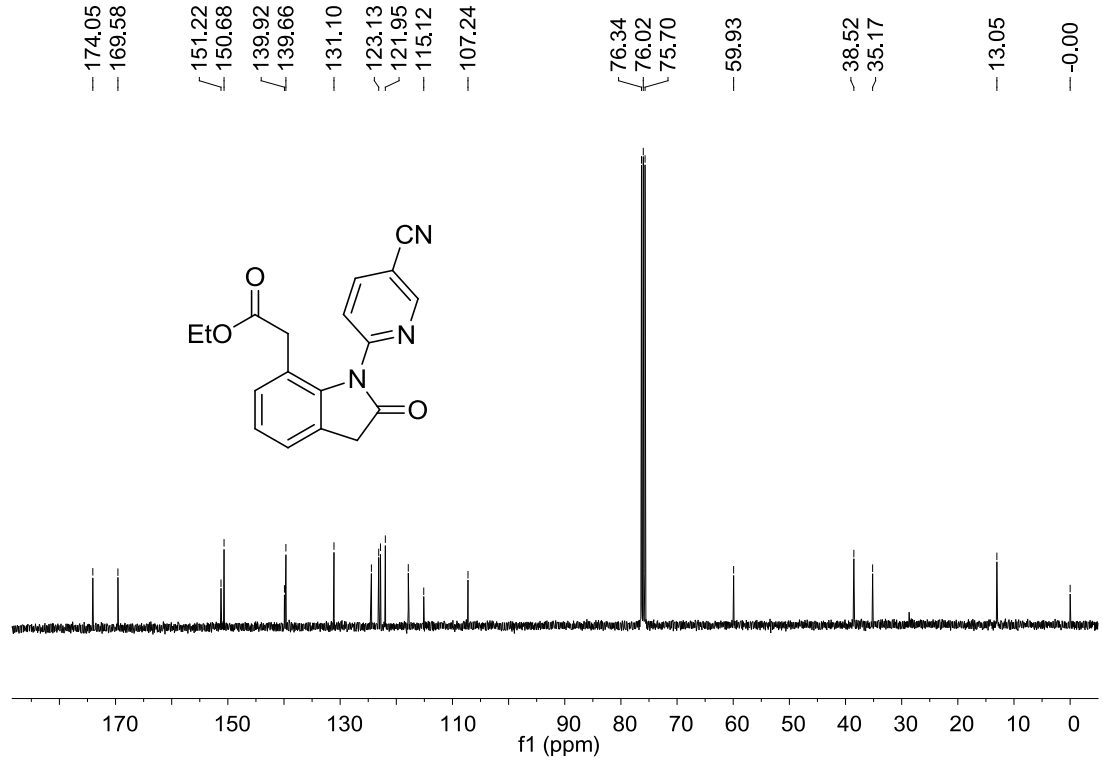
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **3v**



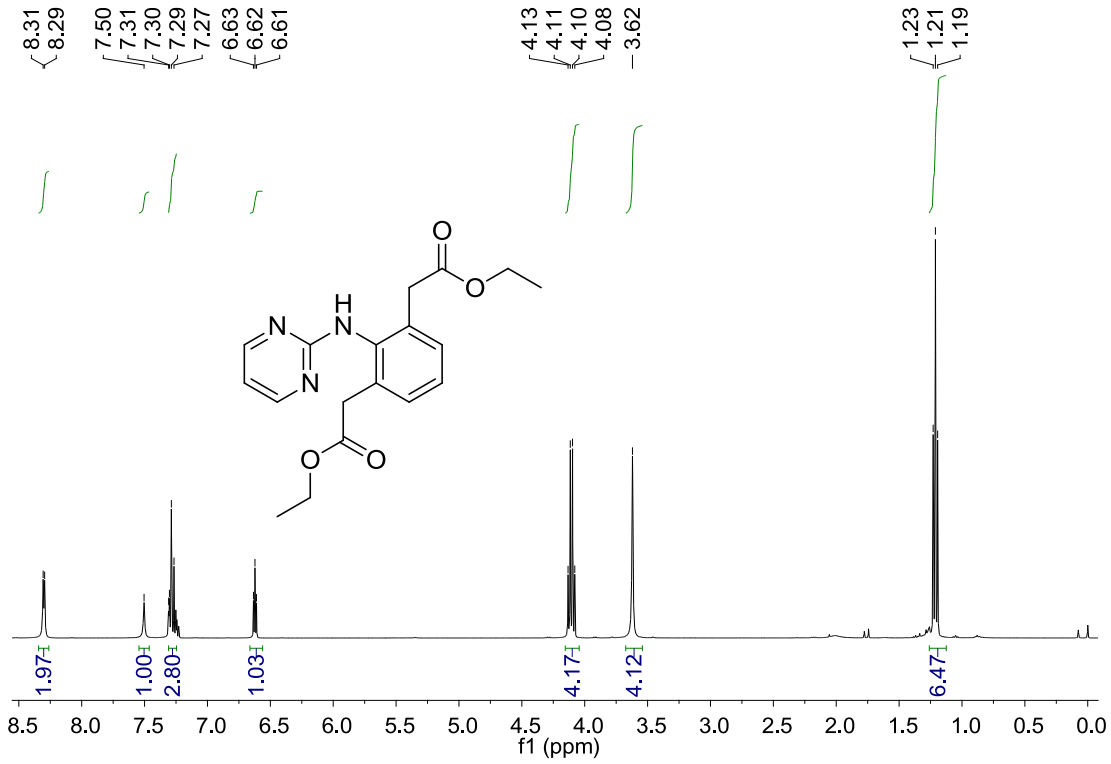
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3w**



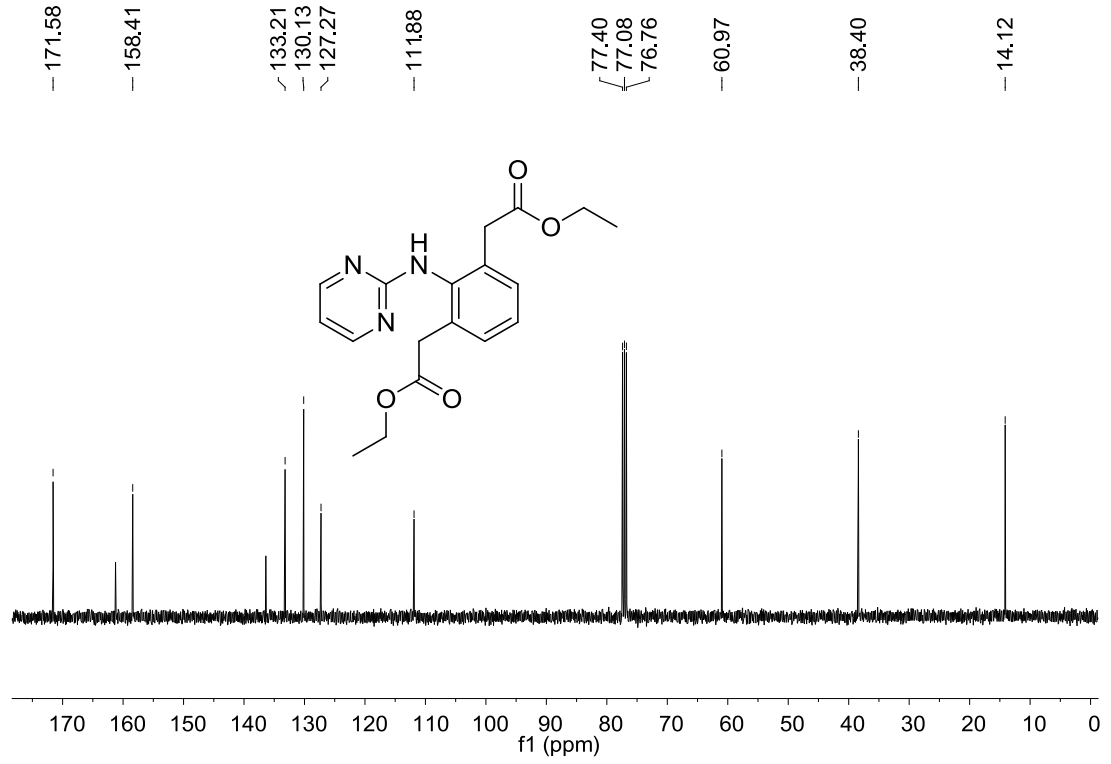
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **3w**



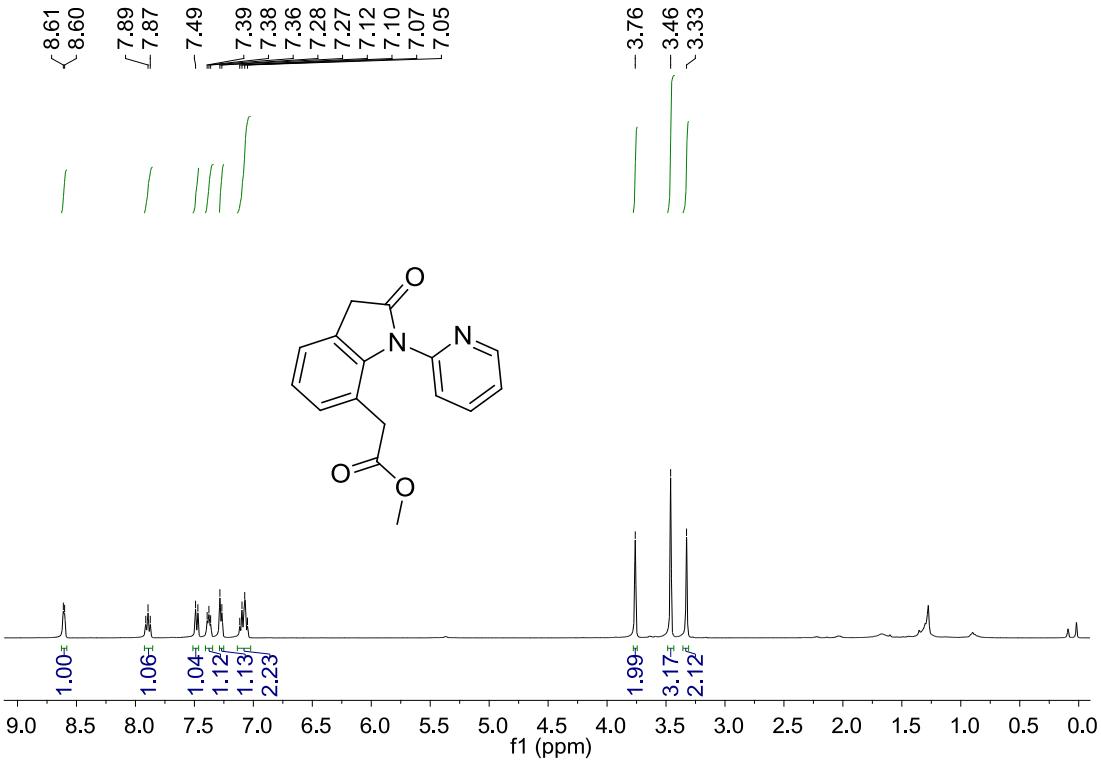
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3x**



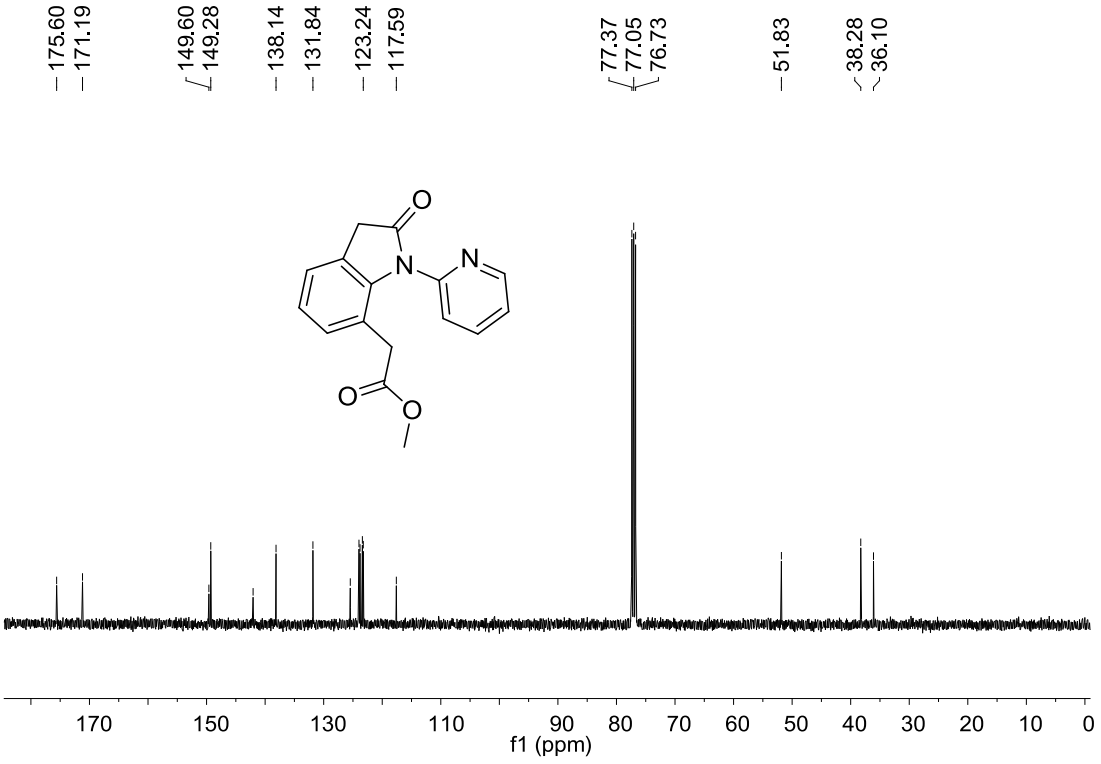
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **3x**



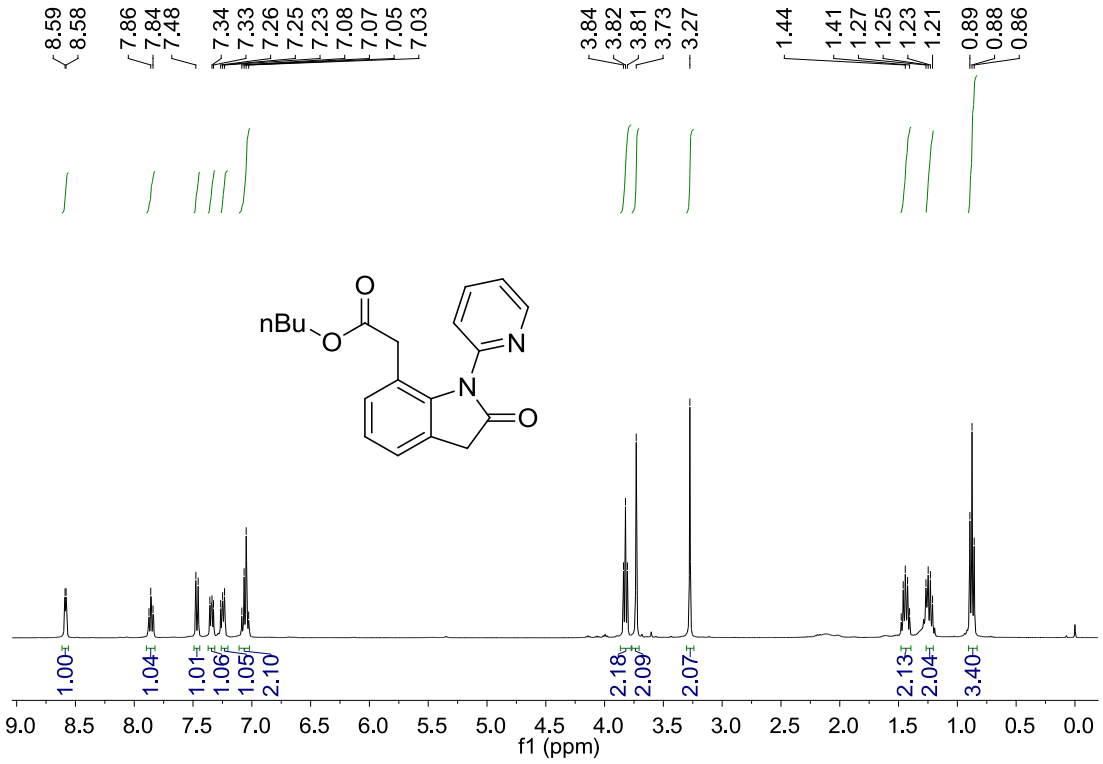
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3y**



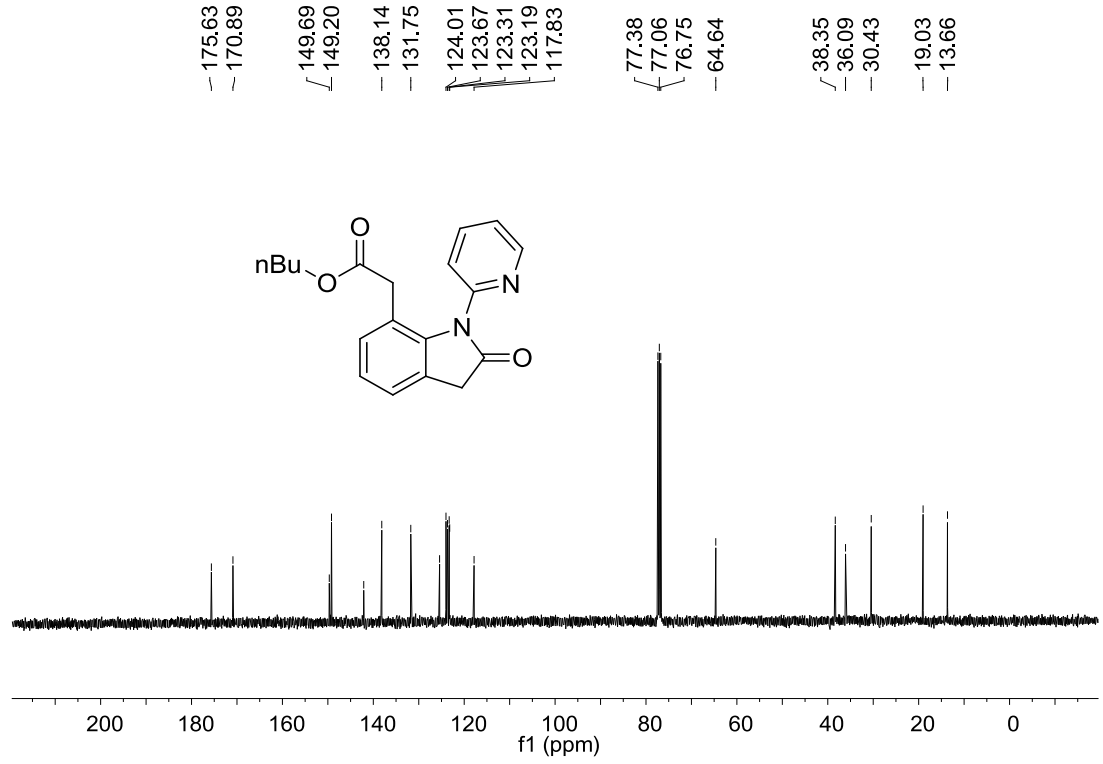
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **3y**



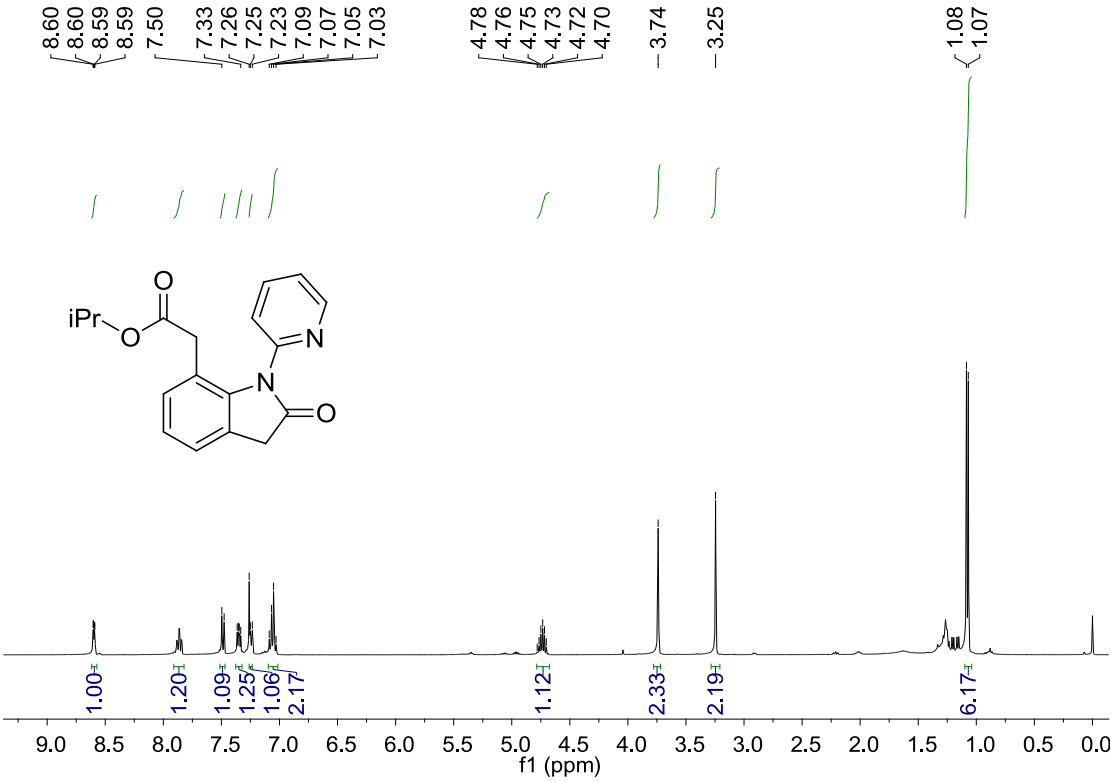
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3z**



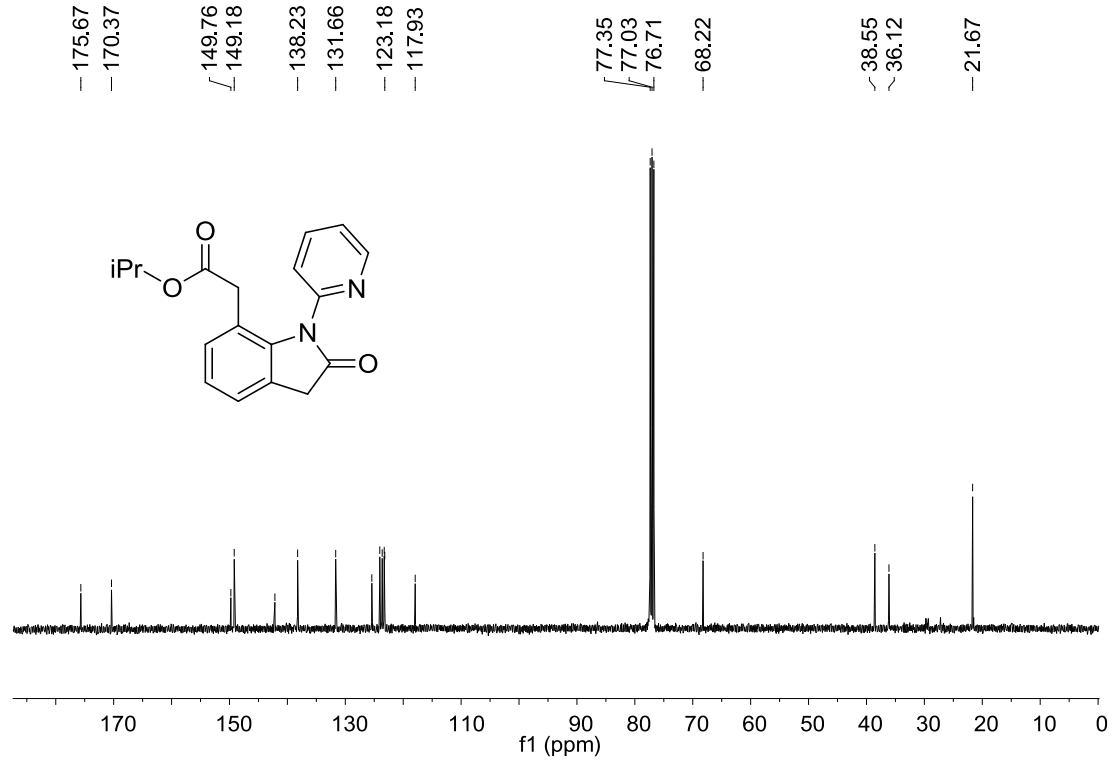
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **3z**



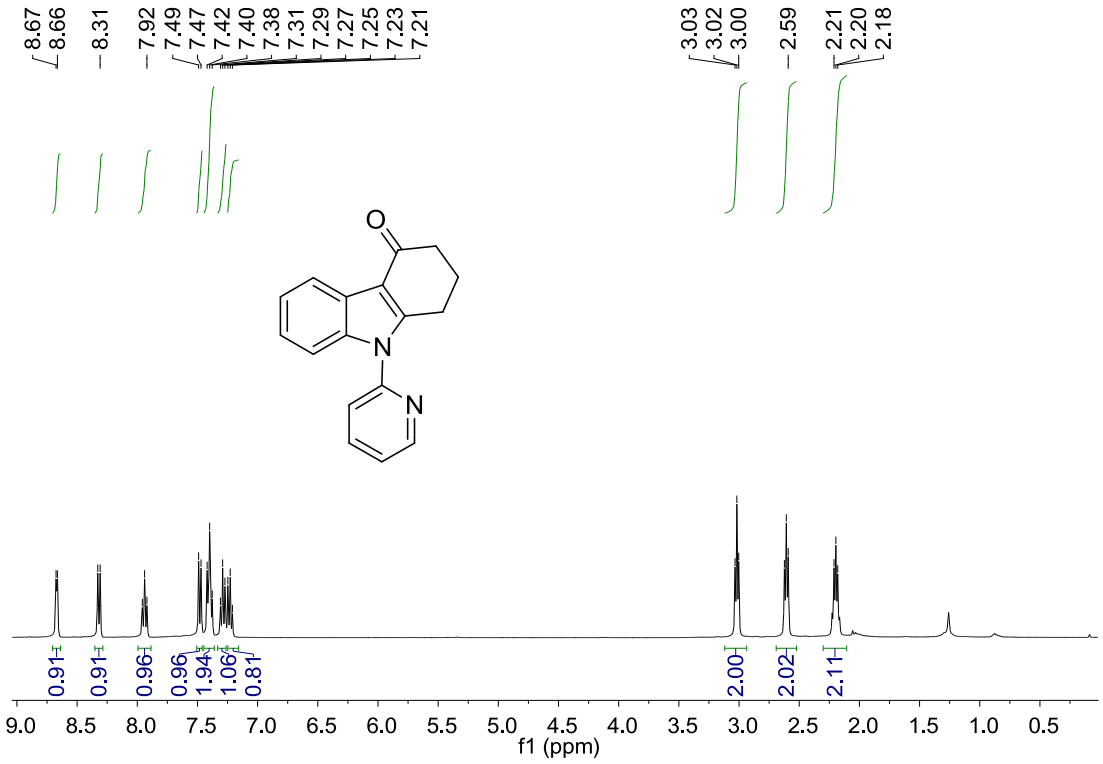
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3-1a**



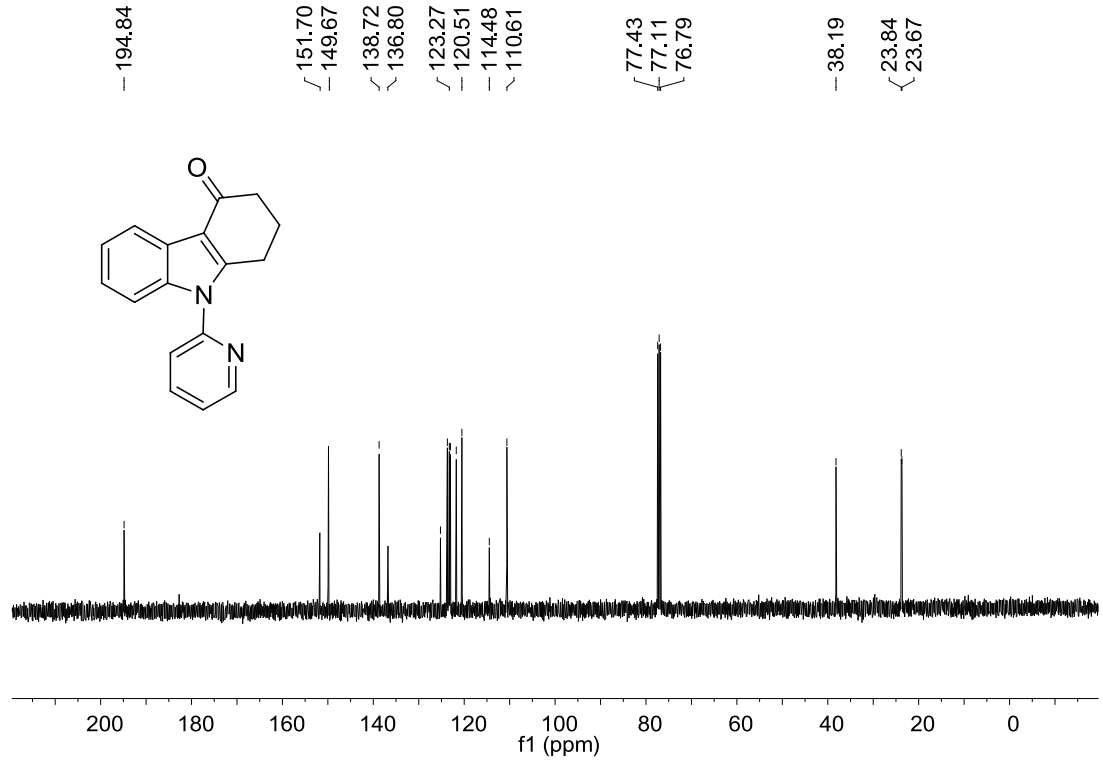
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **3-1a**



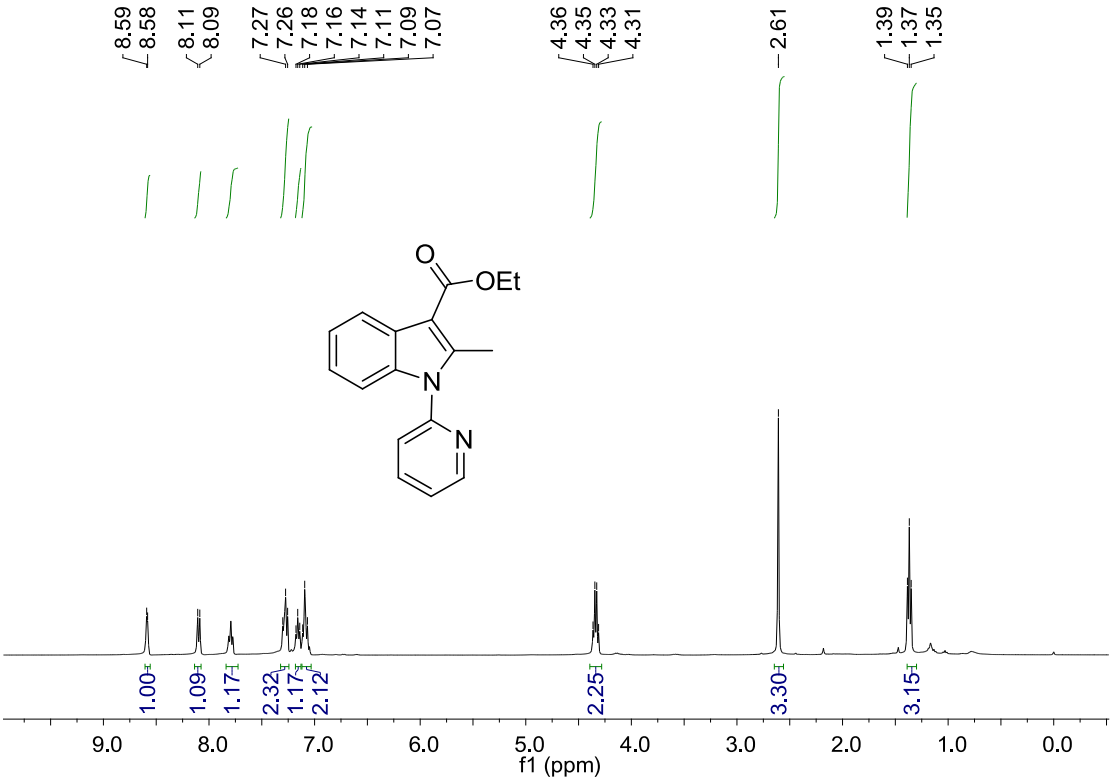
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4b**



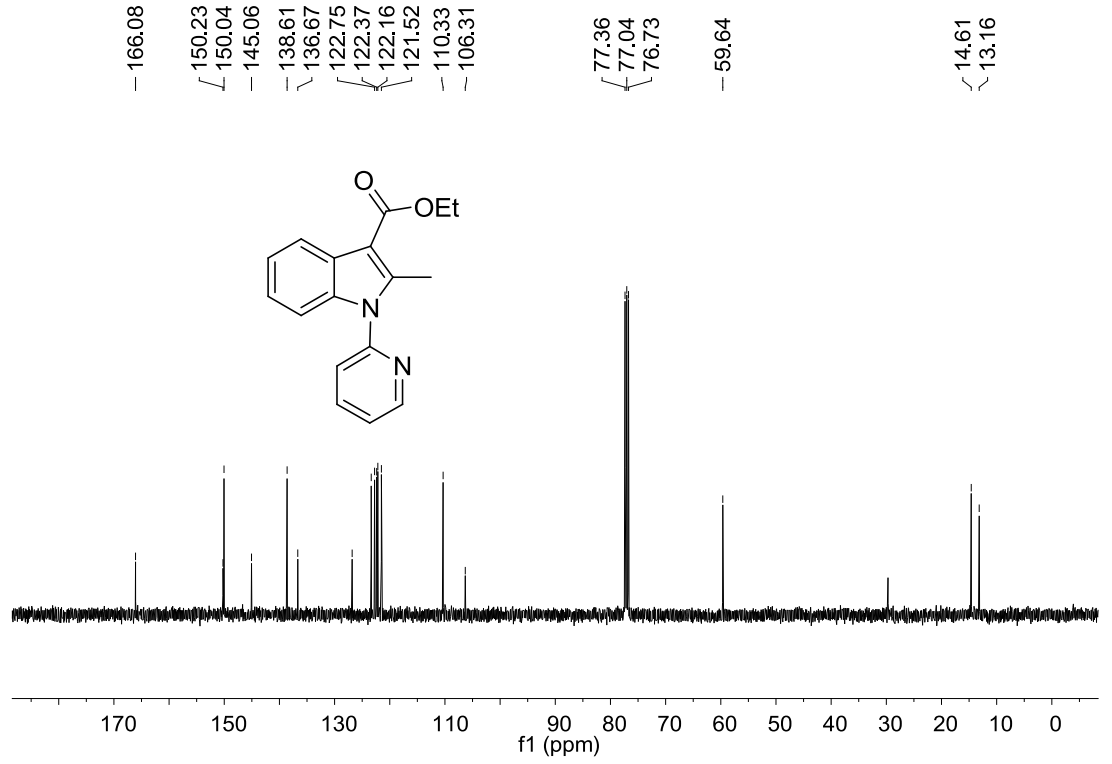
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **4b**



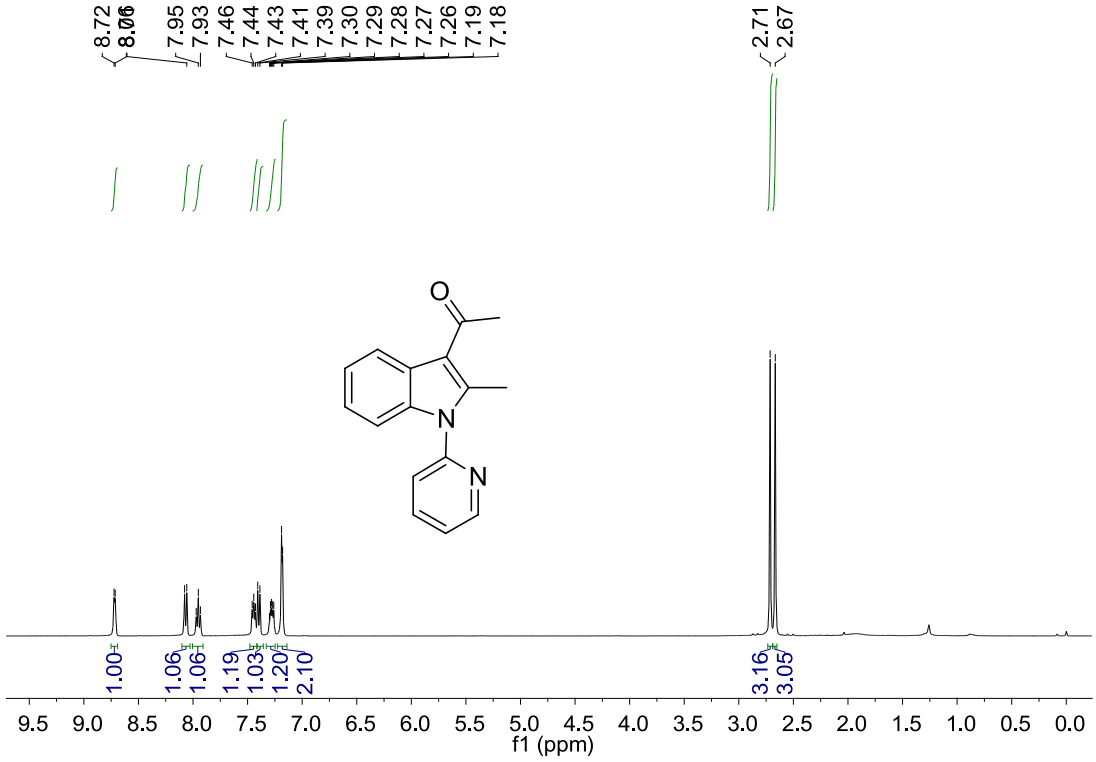
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4d**



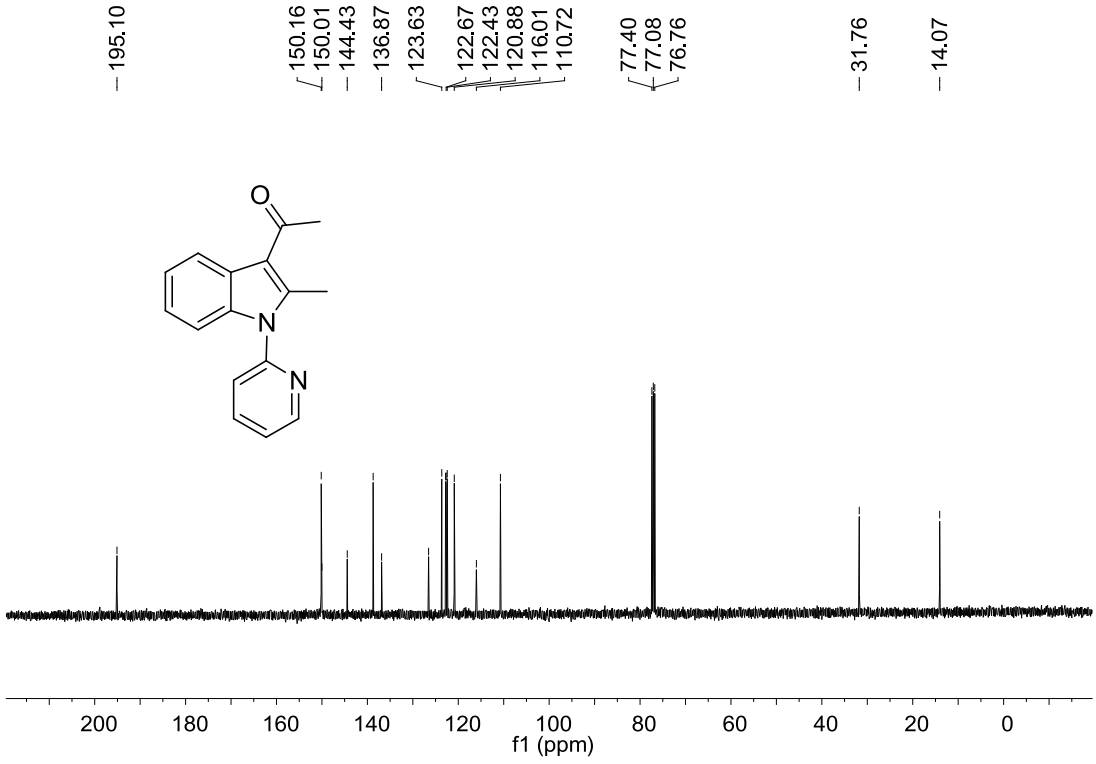
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **4d**



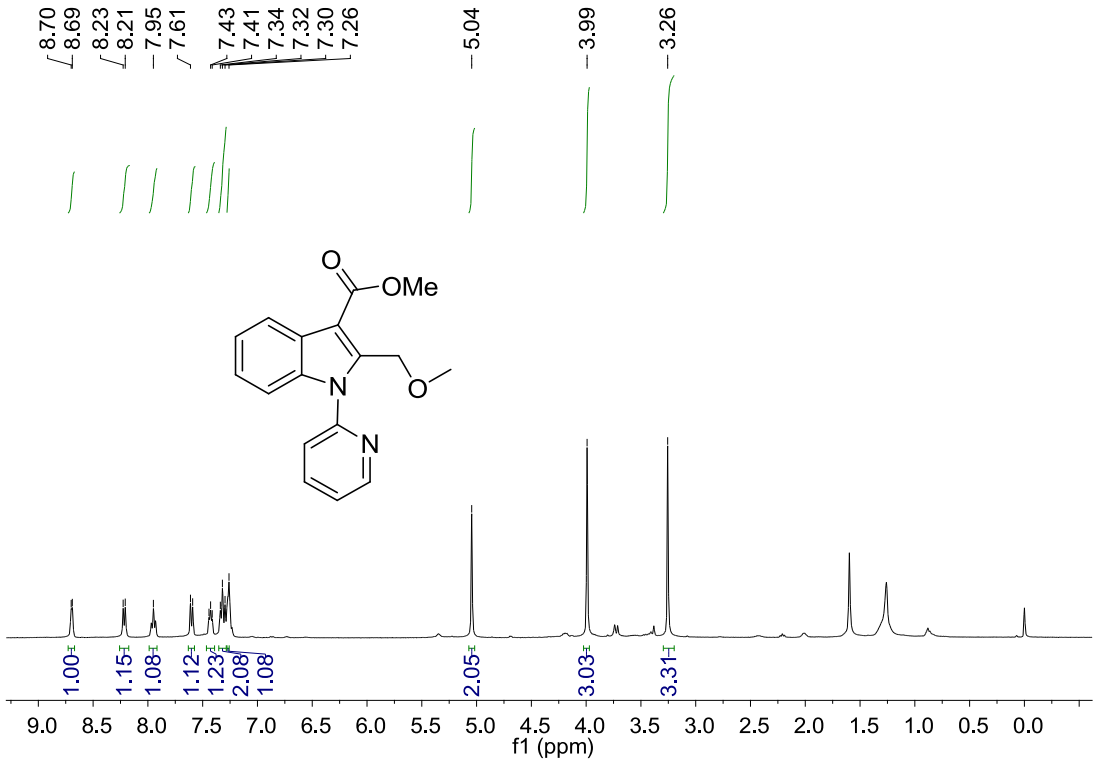
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4e**



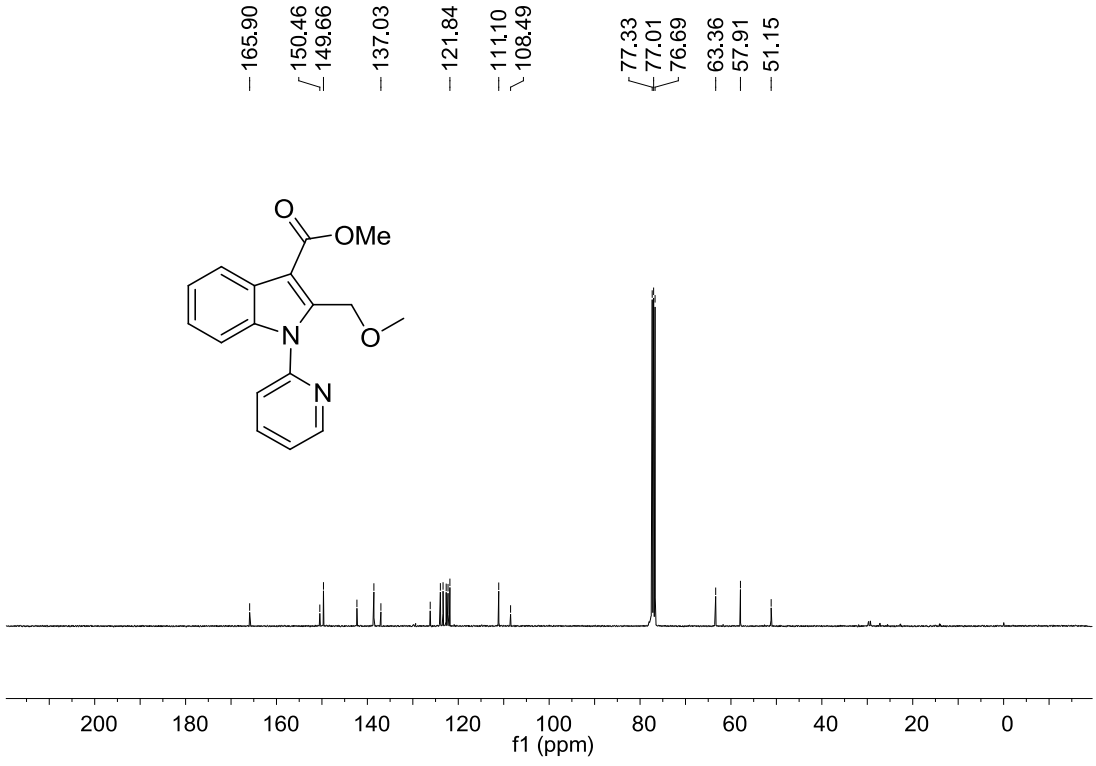
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **4e**



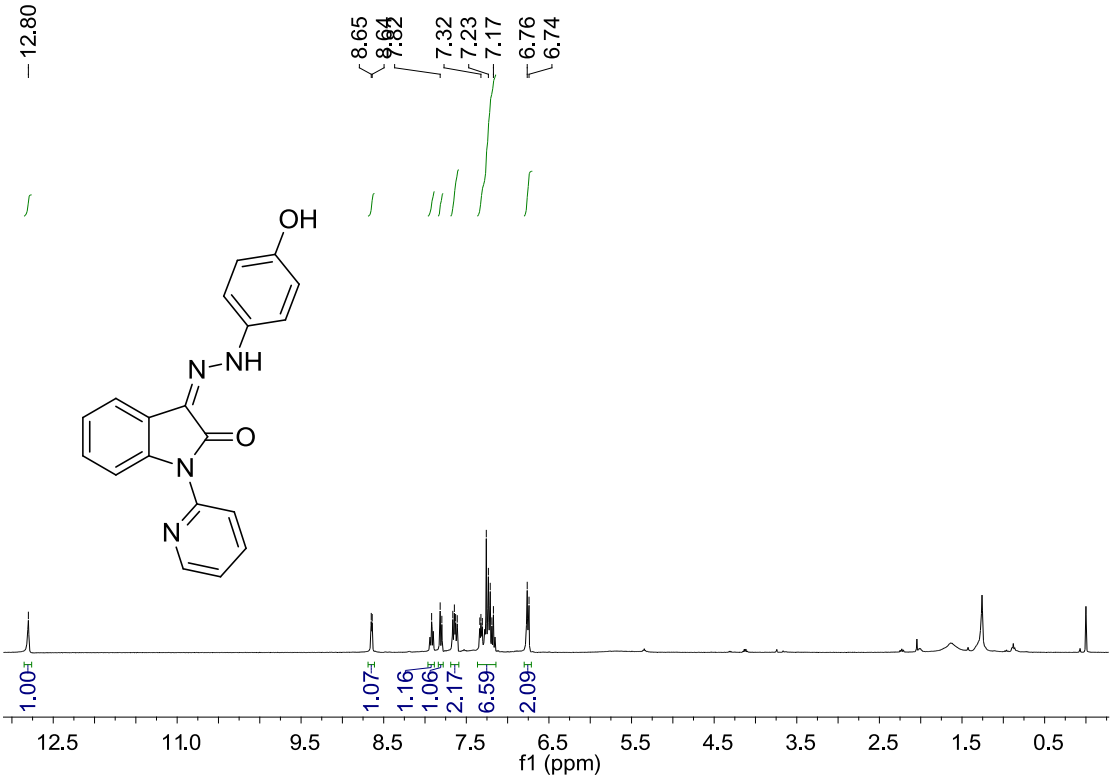
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4f**



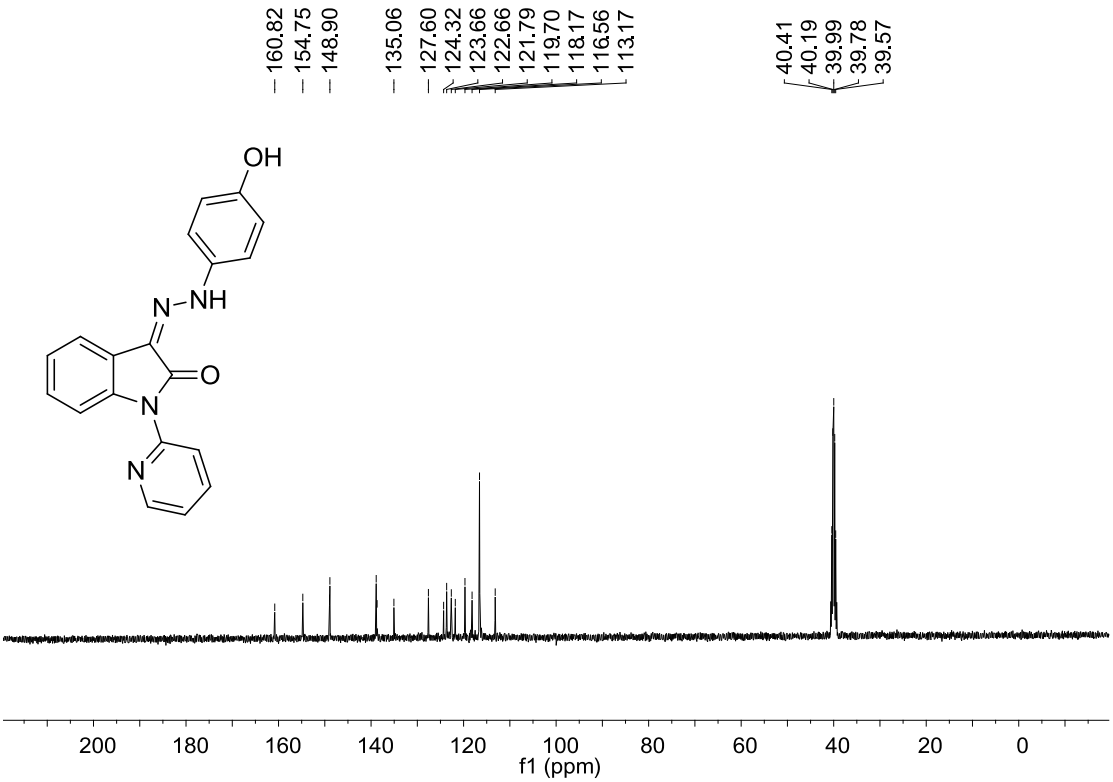
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **4f**



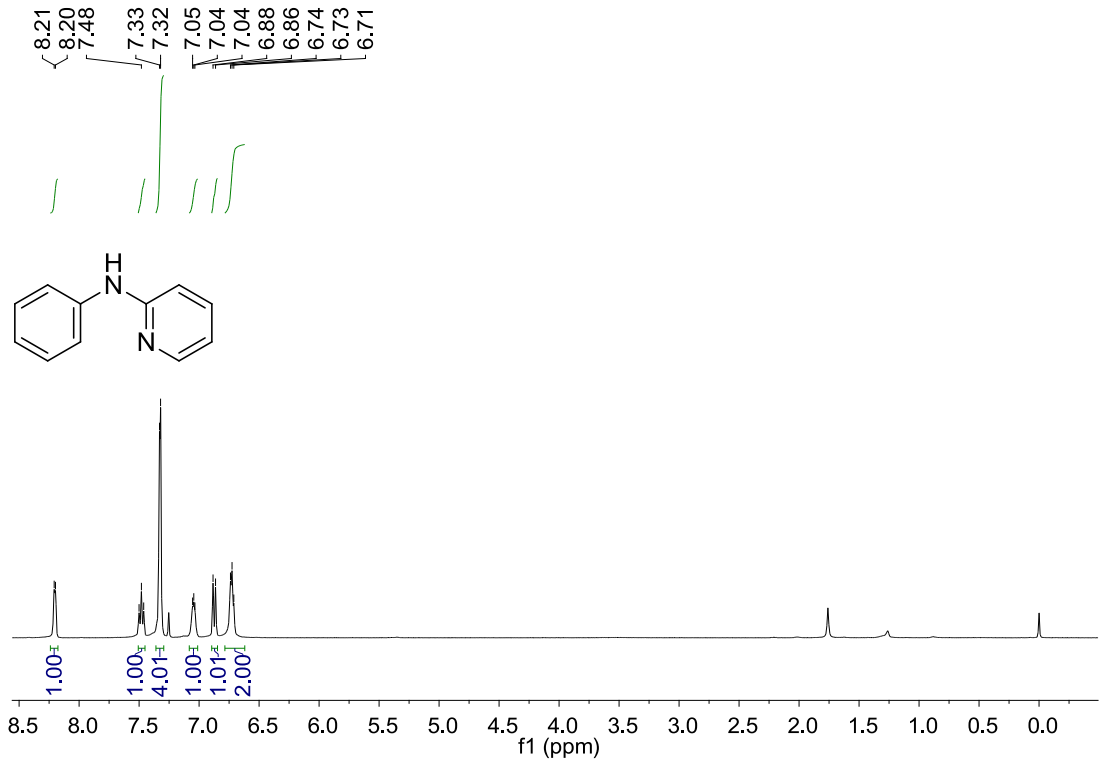
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6**



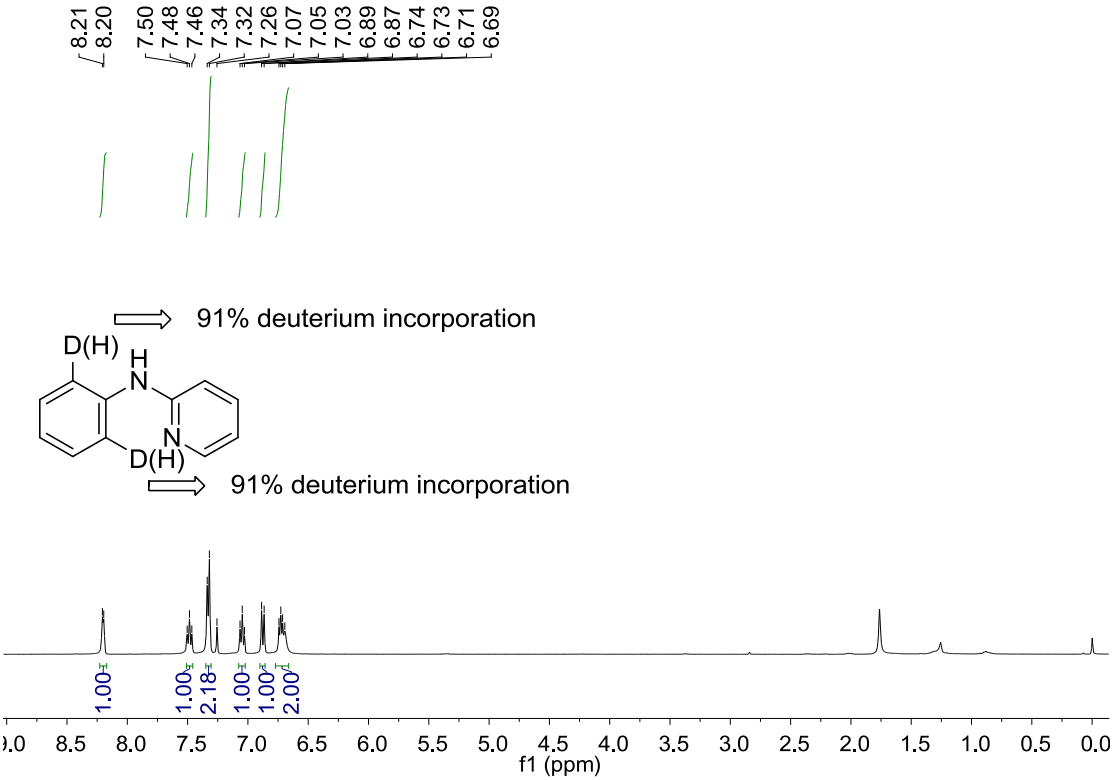
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **6**



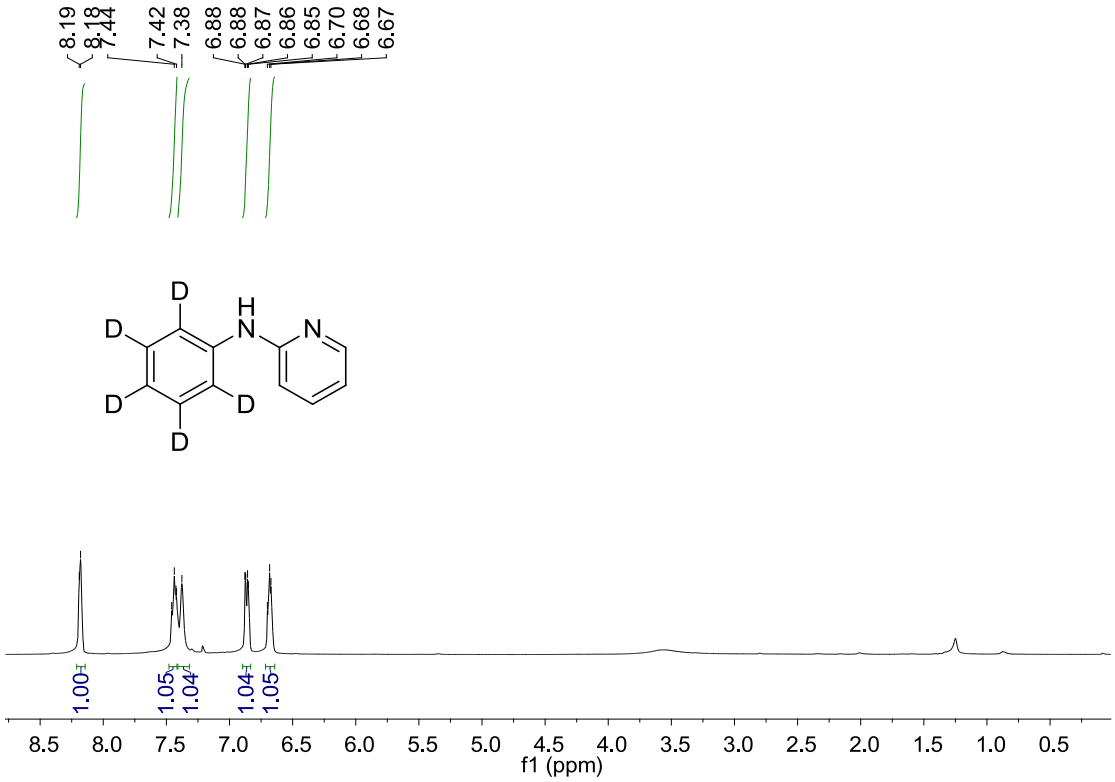
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1a**



^{1}H NMR spectrum (400 MHz, $CDCl_3$) of ***d*$_2$-1a**



^{1}H NMR spectrum (400 MHz, $CDCl_3$) of ***d_5*-1a**



^{1}H NMR spectrum (400 MHz, $CDCl_3$) of ***d_4*-4a**