Supplementary Information (SI) for ChemComm.
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Supporting Information

Electrochemistry-Enabled Ir-Catalyzed C-H/N-N Bond Activation Facilitates [3+2] Annulation of Phenidones with Propiolates

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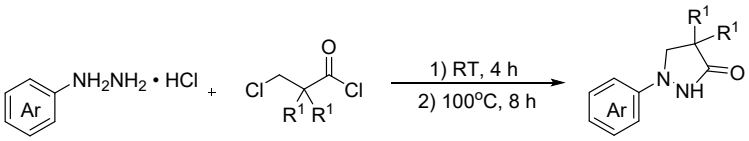
1. General information

All glassware was oven-dried at 100 °C for 3 h and cooled down under the atmospheric environment. All the reaction prepared using the solvent of methanol (AR) was purchased from Adamas. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. The instrument for electrolysis is dual display potentiostat (DJS-292B) (made in China) and the carbon rod (d: 6 mm) was purchased from Xuzhou Xinke Instrument and Meter Co. LTD. The thin-layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (b. p. 60-90 °C). ^{1}H, ^{13}C and ^{19}F NMR data were recorded with Bruker Advance III (500 MHz) spectrometers with tetramethylsilane as an internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. All chemical shifts are reported relative to tetramethylsilane and *d*-solvent peaks (77.00 ppm, $CDCl_3$, 44.00 ppm, DMSO-d_6).

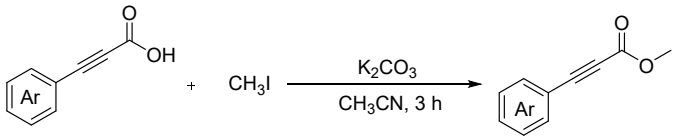
2. General procedure for synthesis

(1) Synthesis of phenidone derivatives



Phenylhydrazine hydrochloride derivatives (34.3 mmol, 1.0 equiv.) was dissolved in pyridine (100 mL). The solution was cooled in an ice bath and 3-chloro-2,2-dimethylpropionyl chloride derivatives (34.3 mmol, 1.0 equiv.) was added over 5 min. The reaction was allowed to warm to room temperature, and then stirred for 4 hours. After that, the reaction was moved to an oil bath stirring for 8 hours at 100 °C and then cooled to room temperature. Next, the reaction solution was poured into a 500 mL beaker, diluted with 150 mL DCM. And then, poured 150 mL aqueous HCl (3 M) into the beaker, stirred with a glass rod. The organic phase was separated and washed with 150 mL aqueous HCl (3 M) again. After that, the organic phase was washed with saturated sodium bicarbonate solution and saturated sodium chloride solution respectively. Then the organic layer was dried over anhydrous Na_2SO_4, and evaporated to dryness. The crude product was purified by flash chromatography over silica gel using PE/EA (3:1) to afford the corresponding products.

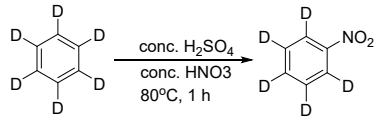
(2) Synthesis of methyl phenylpropiolate derivatives



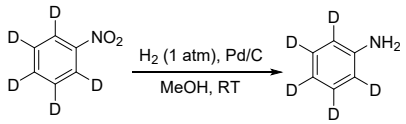
CH_3I (2.2 mmol) and K_2CO_3 (2.2 mmol) were added to the solution of phenylpropiolic acids (2 mmol) in acetonitrile and the obtained mixture was stirred at room temperature. The reaction was monitored by TLC until the starting disappeared.

After 3 hours, the mixture was extracted with ether (3 x 5 mL). The combined ether part was purified by column chromatography on silica gel (dichloromethane: hexane = 1:3) to give pure methyl 3-phenylpropiolate derivatives.

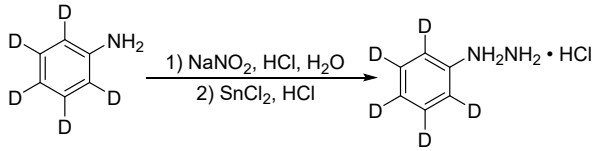
(3) Synthesis of $[D]_5$-1a



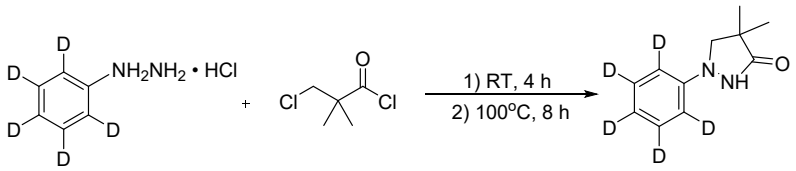
Concentrated nitric acid and concentrated sulfuric acid (1:1 v/v) were mixed together in a 25 mL round-bottom flask held in an ice-water bath. $[D]_6$-benzene (5.0 mL, 56.0 mmol) was added drop-wise at room temperature and the reaction was allowed to stir at 80 °C for 1h. The reaction mixture was poured into ice-water and extracted with DCM. The product was used without further purification (5.4 g, 75%).



Crude $[D]_5$-nitrobenzene was dissolved in MeOH and Pd/C (10 mol%) was added then the reaction was held under H_2 atmosphere (1 atm) at room temperature for overnight. The reaction mixture was checked by TLC and filtered over celite then the solvent removed under reduced pressure. The crude $[D]_5$-aniline was used without further purification (3.2 g, 77%).

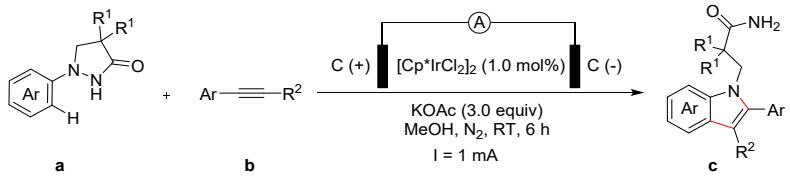


To a solution of $[D]_5$-aniline (1.0 g, 10 mmol) in 10 ml of 37% HCl was added drop wise the solution of $NaNO_2$ (718 mg，10.4 mmol) in 10 mL of H_2O while cooling with an ice-water bath. The reaction mixture was stirred at 0 °C for 1 h to give a clear solution. Then to the solution was added drop wise a solution of $SnCl_2$ (2.67g，14mmol) in 20 mL of 37% HCl at 0 °C. Then the mixture was stirred at room temperature for 2 h. The solid product was filtered, washed with 37% HCl and dried in a vacuum desiccator. The $[D]_5$-phenylhydrazine hydrochloride could be used in subsequent reactions without further purification (3.7 g, 77%).



$[D]_5$-phenylhydrazine hydrochloride (5 g, 34.3 mmol, 1.0 equiv.) was dissolved in pyridine (100 mL). The solution was cooled in an ice bath and 3-chloro-2,2-dimethylpropionyl chloride (5.3 g, 34.3 mmol, 1.0 equiv.) was added over 5 min. The reaction was allowed to warm to room temperature, and then stirred for 4 hours. After that, the reaction was moved to an oil bath stirring for 8 hours at 100 ℃ and then cooled to room temperature. Next, the reaction solution was poured into a 500 mL beaker, diluted with 150 mL DCM. And then, poured 150 mL aqueous HCl (3 M) into the beaker, stirred with a glass rod. The organic phase was separated and washed with 150 mL aqueous HCl (3 M) again. After that, the organic phase was washed with saturated sodium bicarbonate solution and saturated sodium chloride solution respectively. Then the organic layer was dried over anhydrous Na_2SO_4, and evaporated to dryness. The crude product was purified by flash chromatography over silica gel using PE/EA (3:1) to afford the corresponding $[D]_5$-pyrazolidinone 1a-$[D]_5$.

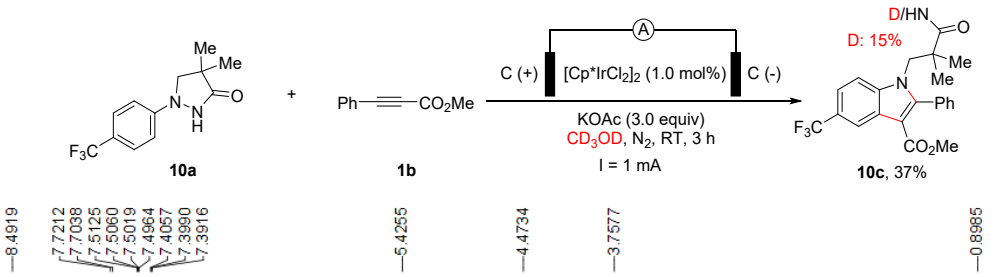
3. General procedure



In an oven-dried undivided three-necked flask (25 mL) equipped with a stir bar, **a** (0.5 mmol), $[Cp^*IrCl_2]_2$ (1.0 mol%) and KOAc (0.75 mmol) were combined and added. The flask was equipped with a carbon rods (ϕ = 6 mm, merge in solution 1.5 cm) as the anode and carbon rods (ϕ = 6 mm, merge in solution 1.5 cm) as the cathode and was then charged with nitrogen. Under the protection of nitrogen, **b** (0.25 mmol) and MeOH (6.0 mL) were slowly injected into the reaction flask. The reaction mixture was stirred and electrolyzed at a constant current of 1 mA (0.42 mA/cm^2) under RT for 6 h. When the reaction was finished, the solution was concentrated in a vacuum. The desired product **c** was subjected to column chromatography on silica gel.

4. Mechanism study

(1) Deuteration experiments



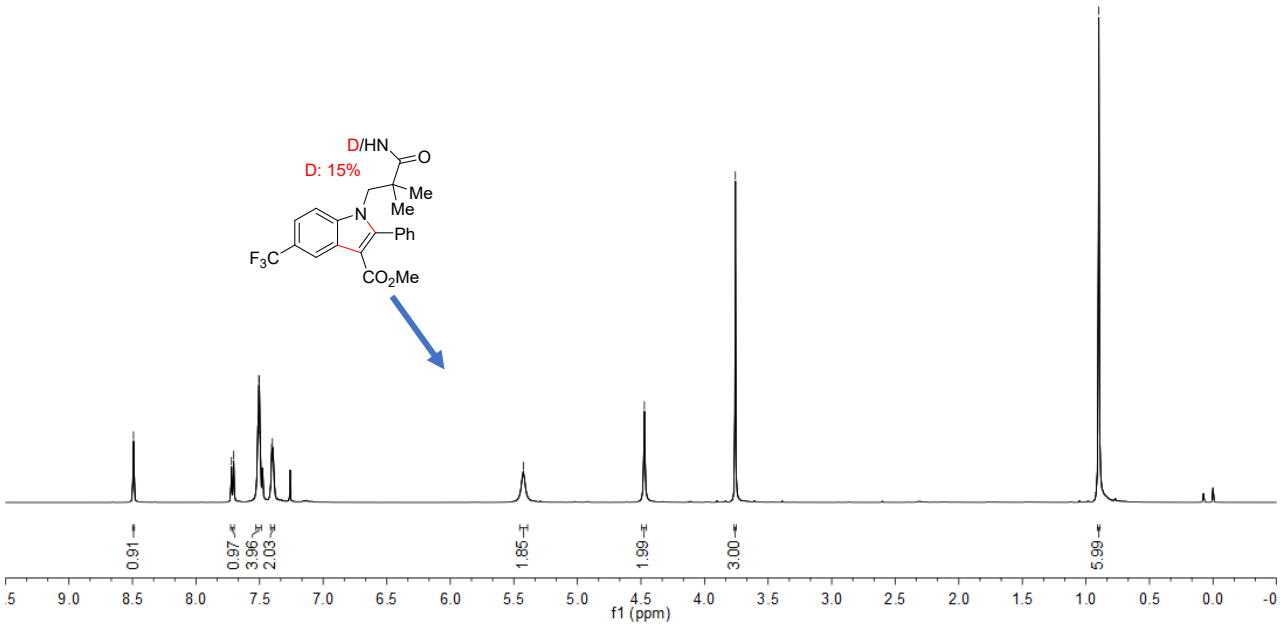
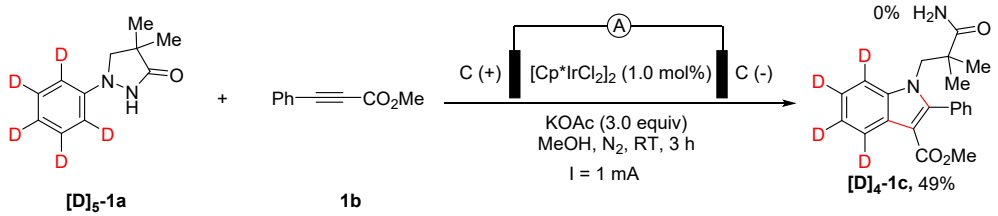


Figure S1. ^{1}H NMR results of **10c**.

In an oven-dried undivided three-necked flask (25 mL) equipped with a stir bar, **10a** (0.25 mmol), $[Cp^*IrCl_2]_2$ (1.0 mol%) and KOAc (0.75 mmol) were combined and added. The flask was equipped with a carbon rods (ϕ = 6 mm, merge in

solution 1.5 cm) as the anode and carbon rods (ϕ = 6 mm, merge in solution 1.5 cm) as the cathode and was then charged with nitrogen. Under the protection of nitrogen, **1b** (0.25 mmol) and CD_3OD (6.0 mL) were slowly injected into the reaction flask. The reaction mixture was stirred and electrolyzed at a constant current of 1 mA (0.42 mA/cm^2) under RT for 3 h. When the reaction was finished, the solution was concentrated in a vacuum. The desired product **10c** was subjected to column chromatography on silica gel (yield: 37%, Deuteration: 15%).



In an oven-dried undivided three-necked flask (25 mL) equipped with a stir bar, **[D]$_5$-1a** (0.5 mmol), [Cp*IrCl$_2$]$_2$ (1.0 mol%) and KOAc (0.75 mmol) were combined and added. The flask was equipped with a carbon rods (ϕ = 6 mm, merge in solution 1.5 cm) as the anode and carbon rods (ϕ = 6 mm, merge in solution 1.5 cm) as the cathode and was then charged with nitrogen. Under the protection of nitrogen, **1b** (0.25 mmol) and MeOH (6.0 mL) were slowly injected into the reaction flask. The reaction mixture was stirred and electrolyzed at a constant current of 1 mA (0.42 mA/cm^2) under RT for 3 h. When the reaction was finished, the solution was concentrated in a vacuum. The desired product **[D]$_4$-1c** was subjected to column chromatography on silica gel (yield: 49%, Deuteration: 0%).

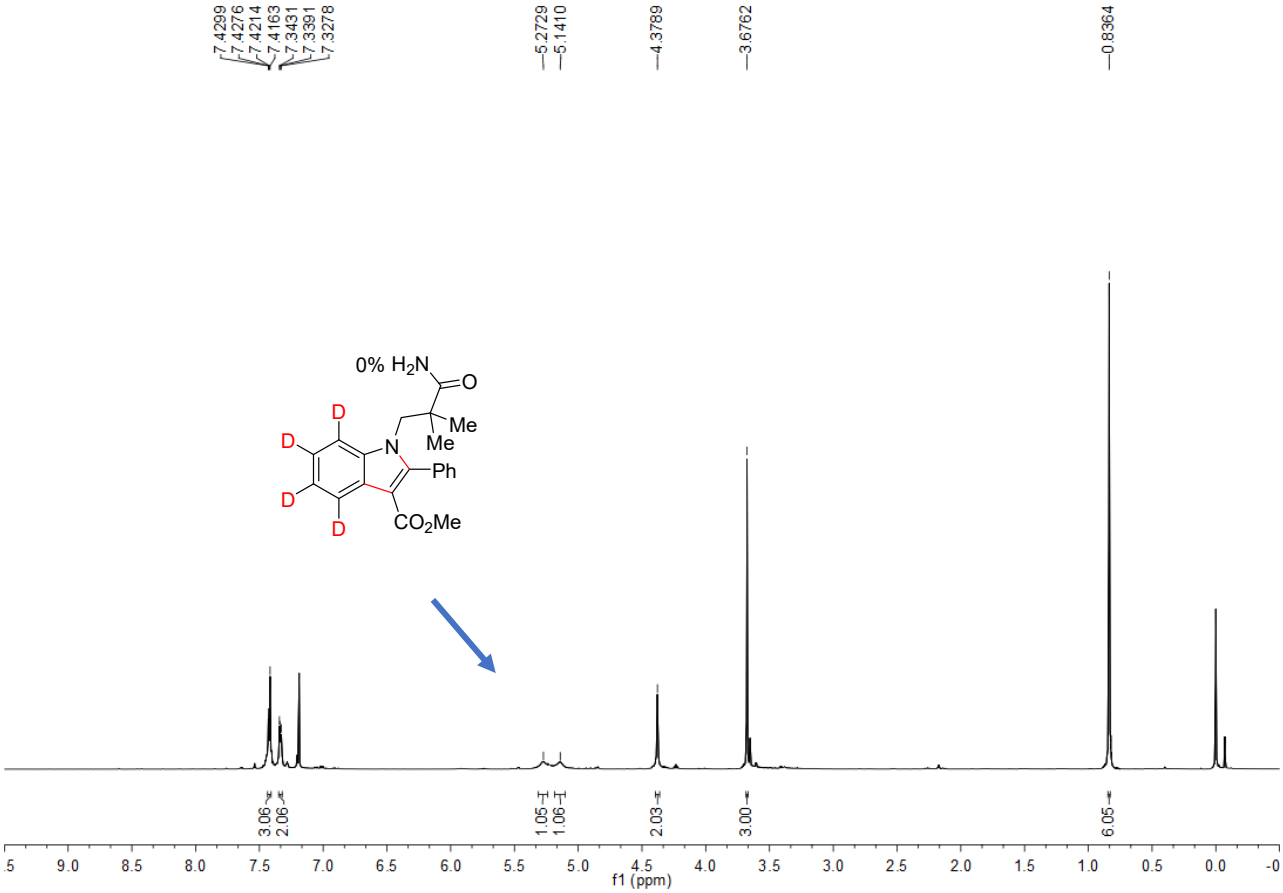
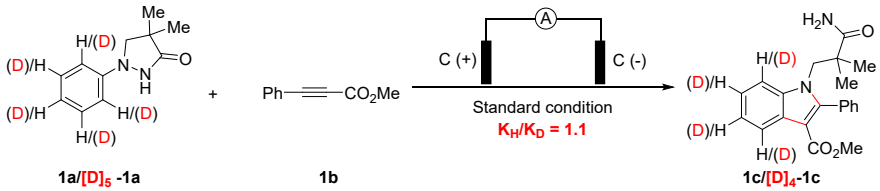


Figure S2. ^{1}H NMR results of **[D]$_4$-1c**.

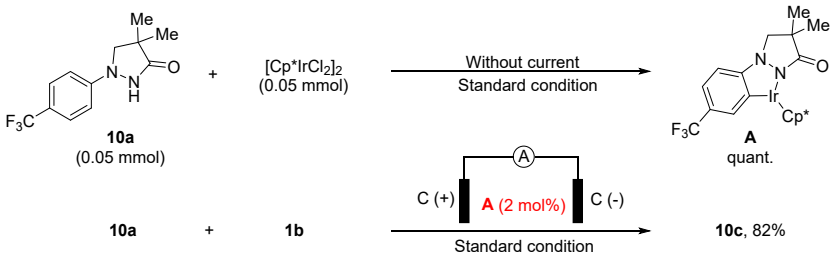
(2) Kinetic Isotope Effect experiments



1a/[D]$_5$ -1a **1b** **1c/[D]$_4$-1c**

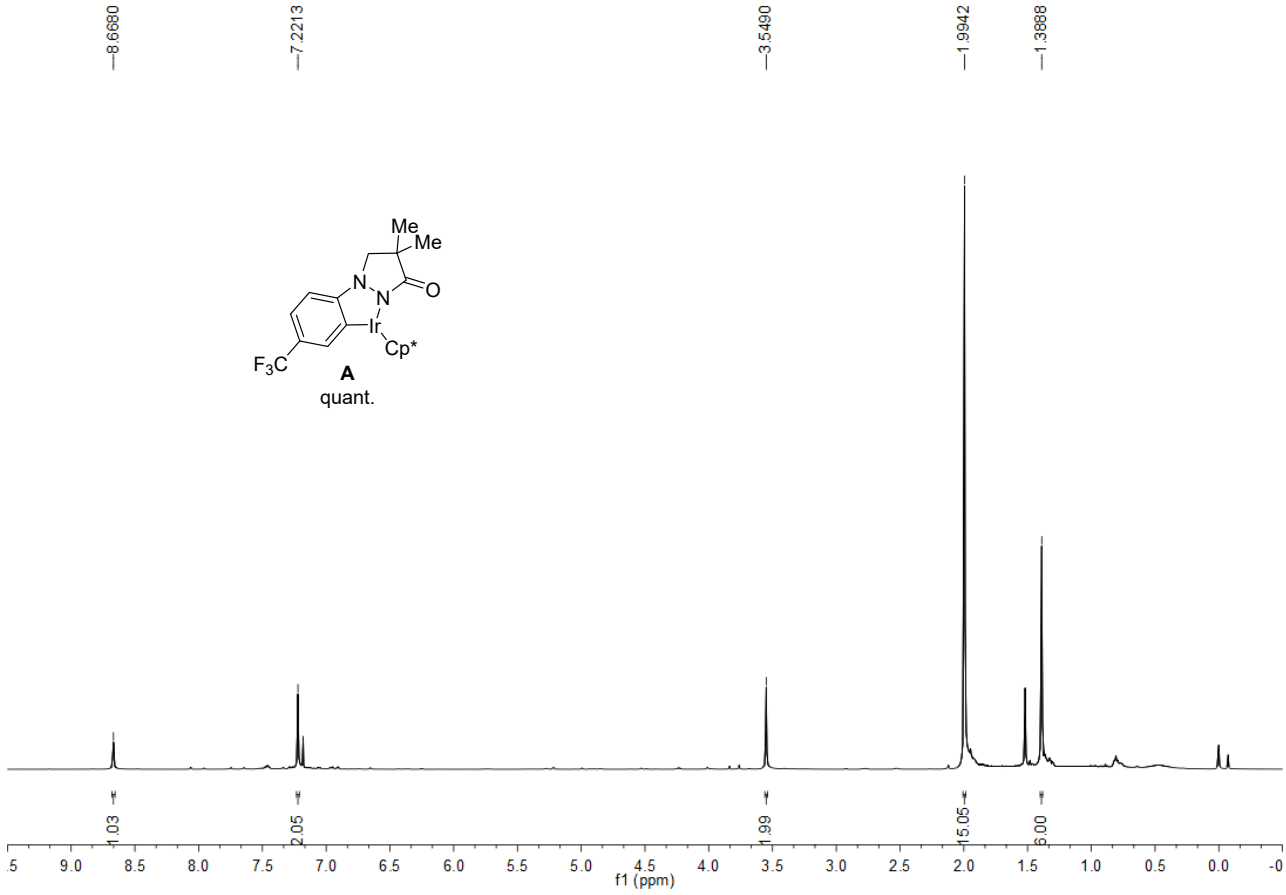
In an oven-dried undivided three-necked flask (25 mL) equipped with a stir bar, **1a** (0.5 mmol) or **[D]$_5$-1a** (0.5 mmol), [Cp*IrCl$_2$]$_2$ (1.0 mol%) and KOAc (0.75 mmol) were combined and added. The flask was equipped with a carbon rods (ϕ = 6 mm, merge in solution 1.5 cm) as the anode and carbon rods (ϕ = 6 mm, merge in solution 1.5 cm) as the cathode and was then charged with nitrogen. Under the protection of nitrogen, **1b** (0.25 mmol) and MeOH (6.0 mL) were slowly injected into the reaction flask. The reaction mixture was stirred and electrolyzed at a constant current of 1 mA (0.42 mA/cm^2) under RT for 1 h. When the reaction was finished, the solution was concentrated in a vacuum. The desired product **1c** (Yield: 24%) or **[D]$_4$-1c** (Yield: 22%) was subjected to column chromatography on silica gel. K_H/K_D = 1.1, this result is the average of three parallel experiments.

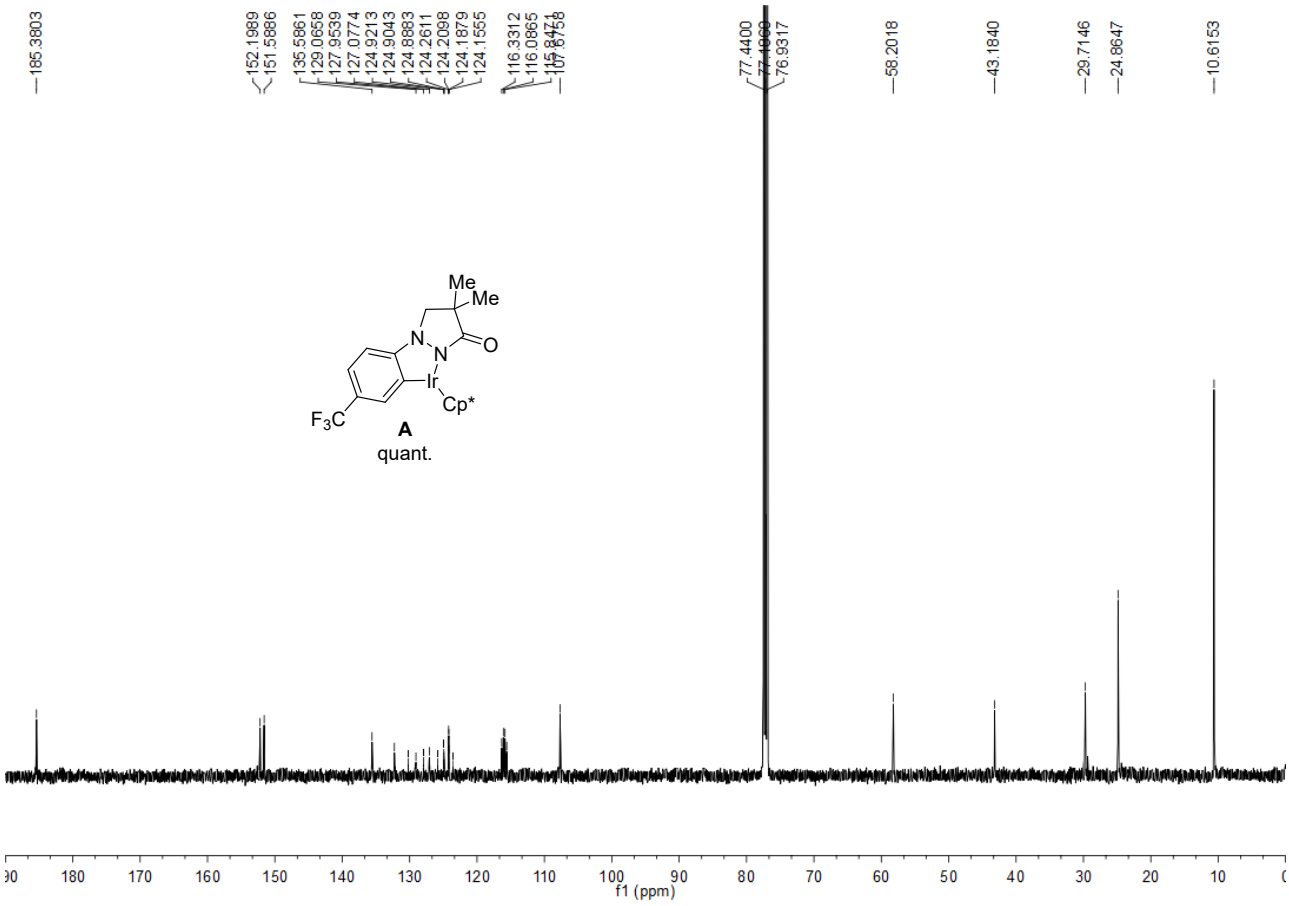
(3) Ir catalytic species



In an oven-dried undivided three-necked flask (25 mL) equipped with a stir bar, **10a** (0.05 mmol), [Cp*IrCl$_2$]$_2$ (0.05 mmol) and KOAc (0.15 mmol) were combined and added. The flask was then charged with nitrogen. Under the protection of nitrogen, CH_3CN (6.0 mL) were slowly injected into the reaction flask. The reaction mixture was stirred under RT for 6 h. When the reaction was finished, the solution was concentrated in a vacuum. The desired product **A** was subjected to column chromatography on silica gel.

In an oven-dried undivided three-necked flask (25 mL) equipped with a stir bar, **10a** (0.5 mmol), **A** (1.0 mol%) and KOAc (0.75 mmol) were combined and added. The flask was equipped with a carbon rods (ϕ = 6 mm, merge in solution 1.5 cm) as the anode and carbon rods (ϕ = 6 mm, merge in solution 1.5 cm) as the cathode and was then charged with nitrogen. Under the protection of nitrogen, **1b** (0.25 mmol) and MeOH (6.0 mL) were slowly injected into the reaction flask. The reaction mixture was stirred and electrolyzed at a constant current of 1 mA (0.42 mA/cm^2) under RT for 6 h. When the reaction was finished, the solution was concentrated in a vacuum. The desired product **10c** was subjected to column chromatography on silica gel (yield: 82%).


8.6680
7.2213
3.5490
1.9942
1.3888
Me
Me
N
N
O
Ir
Cp*
F3C
A
quant.
1.03
2.05
1.99
15.05
6.00
f1 (ppm)


185.3803
152.1989
151.5886
135.5861
129.0658
127.9539
127.0774
124.9213
124.9043
124.8883
124.2611
124.2098
124.1879
124.1555
116.3312
116.0865
77.4400
76.9317
58.2018
43.1840
29.7146
24.8647
10.6153
Me
Me
N
N
O
Ir
Cp*
F3C
A
quant.
f1 (ppm)

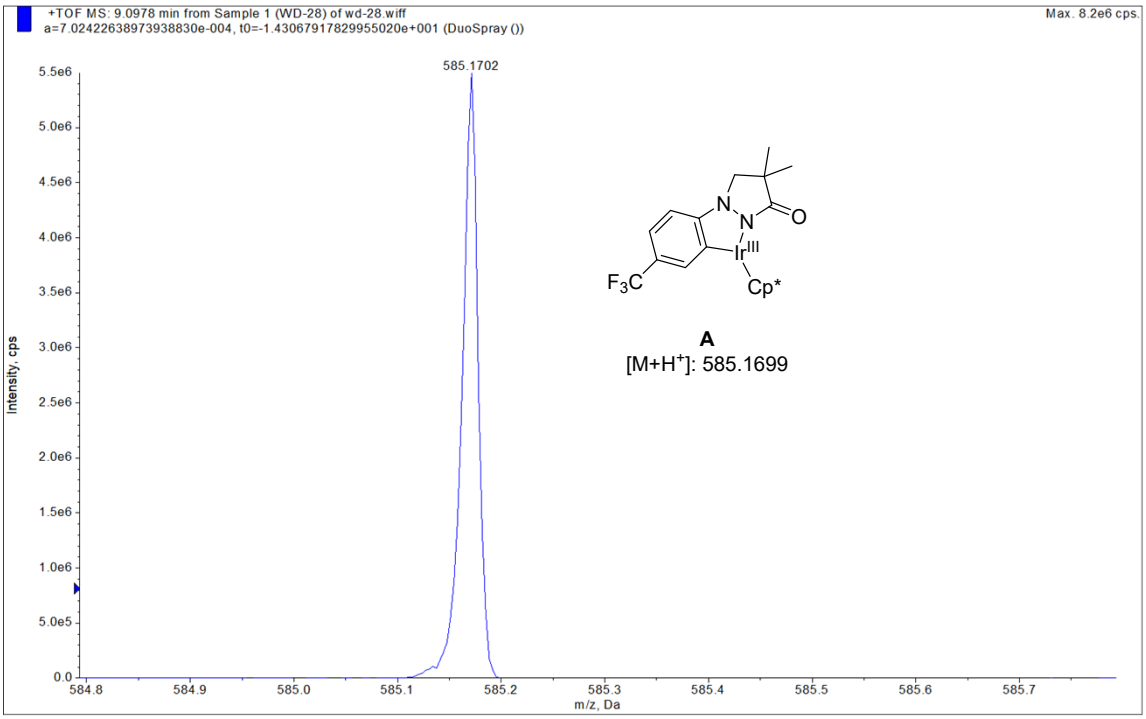
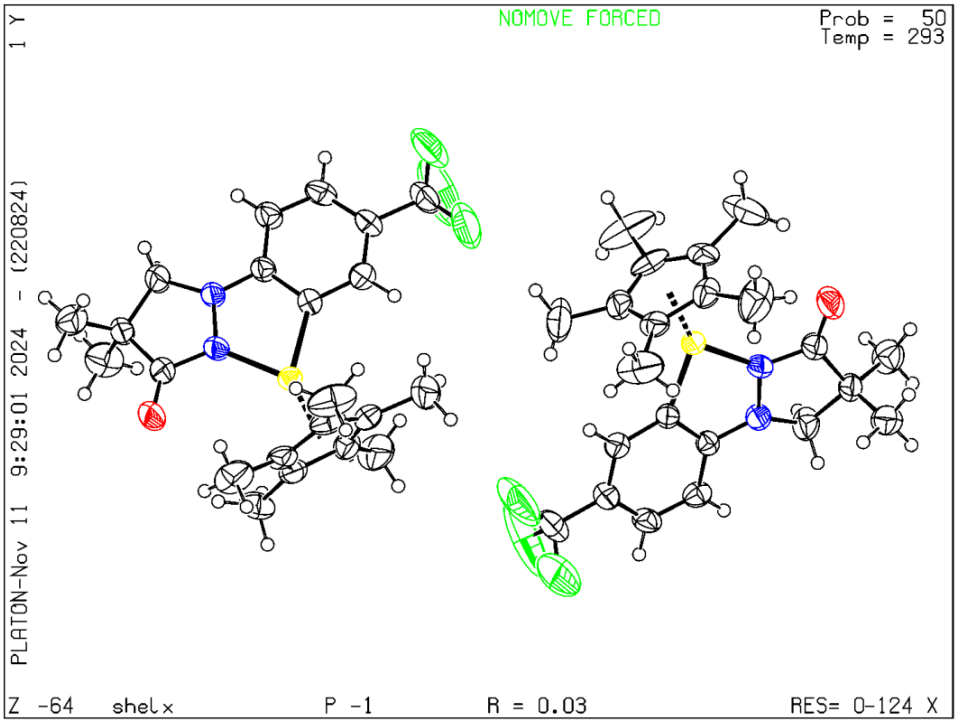


Figure S3. ^{1}H NMR, ^{13}C NMR, and HRMS results of **A**.

Compound A: red solid was obtained by column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.67 (s, 1H), 7.22 (s, 2H), 3.55 (s, 2H), 1.99 (s, 15H), 1.39 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 185.3, 152.2, 151.5, 135.5, 129.0, 129.05 (q, J = 267.3 Hz), 127.0, 124.94 – 124.88 (m), 124.28 – 124.14 (m), 115.96 (q, J = 32.4 Hz), 107.6, 58.2, 43.1, 29.7, 24.8, 10.6. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{22}H_{27}IrN_2OF_3$: 585.1699; found: 585.1702.

The crystal structure of **A** (CCDC: 2385192)



The diffractometer was equipped with a low temperature device and used MoK_α radiation (λ = 0.71073 Å). All data were integrated with SAINT and a multi-scan absorption correction using TWINABS was applied. The structure was solved by direct methods using SHELXT and refined by full-matrix least-squares methods against F^2 by SHELXL-2018/3. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen

atoms were refined isotropic on calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. Crystallographic data for the structures reported here have been deposited with the Cambridge Crystallographic Data Centre. CCDC 2385192 contain the supplementary crystallographic data for this paper.

Table 1. Crystal data and structure refinement for shelx

CCDC number	2385192
Empirical formula	$C_{22}H_{26}F_3IrN_2O$
Formula weight	583.65
Temperature [K]	293(2)
Crystal system	triclinic
Space group (number)	$P\bar{1}$ (2)
a [Å]	13.152(2)
b [Å]	13.561(2)
c [Å]	14.160(2)
α [°]	75.977(5)
β [°]	83.773(5)
γ [°]	62.963(4)
Volume [Å^3]	2182.6(6)
Z	4
ρ_{calc} [gcm^{-3}]	1.776
μ [mm^{-1}]	6.157
F(000)	1136
Crystal size [mm^3]	0.230×0.220×0.200
Crystal colour	red
Crystal shape	block
Radiation	MoK_α (λ=0.71073 Å)
2θ range [°]	4.57 to 50.05 (0.84 Å)
Index ranges	−15 ≤ h ≤ 15 −16 ≤ k ≤ 16 −16 ≤ l ≤ 16
Reflections collected	34657
Independent reflections	7700 R_{int} = 0.0385 R_{sigma} = 0.0341
Completeness to θ = 25.000°	99.9 %
Data / Restraints / Parameters	7700/0/537
Absorption correction	0.5151/0.7457
T_{min}/T_{max} (method)	(multi-scan)
Goodness-of-fit on F^2	1.023
Final *R* indexes	R_1 = 0.0277
[$I \geq 2\sigma(I)$]	wR_2 = 0.0535
Final *R* indexes	R_1 = 0.0423
[all data]	wR_2 = 0.0583
Largest peak/hole [eÅ^{-3}]	0.98/−0.59

Table 2. Atomic coordinates and U_{eq} [Å^2] for shelx

Atom	*x*	*y*	*z*	U_{eq}
Ir1	0.16127(2)	0.64340(2)	0.22909(2)	0.03268(6)
Ir2	0.35909(2)	0.89995(2)	0.72857(2)	0.03507(6)
N4	0.3686(3)	0.8720(4)	0.8701(3)	0.0390(10)
N1	0.2066(3)	0.5494(4)	0.1332(3)	0.0394(10)
O2	0.4986(4)	0.9258(4)	0.9075(3)	0.0734(14)
O1	0.0437(3)	0.5708(4)	0.0699(3)	0.0718(14)
N3	0.2957(4)	0.8319(4)	0.9282(3)	0.0422(11)
C5	0.2277(4)	0.8150(4)	0.8747(4)	0.0329(11)
C35	0.3330(4)	0.5720(4)	0.2375(3)	0.0329(11)
N2	0.3227(3)	0.4838(4)	0.1189(3)	0.0467(12)

C4	0.1489(4)	0.7739(4)	0.9192(4)	0.0412(13)
H4	0.145810	0.751957	0.986601	0.049
C6	0.2388(4)	0.8457(4)	0.7721(4)	0.0358(12)
C15	0.5025(5)	0.9377(6)	0.6553(4)	0.0519(16)
C17	0.4000(5)	1.0349(5)	0.6411(4)	0.0483(14)
C7	0.1619(4)	0.8366(4)	0.7176(4)	0.0418(13)
H7	0.164642	0.856535	0.650103	0.050
C34	0.4037(4)	0.5828(4)	0.2975(4)	0.0412(13)
H34	0.369974	0.631040	0.340468	0.049
C21	0.3783(6)	0.9077(6)	0.5734(4)	0.0545(16)
C12	0.4274(5)	0.8915(5)	0.9334(4)	0.0460(14)
C24	0.1469(5)	0.5228(5)	0.0762(4)	0.0470(14)
C19	0.3226(5)	1.0175(5)	0.5903(4)	0.0475(14)
C30	0.5107(4)	0.4363(4)	0.1721(4)	0.0454(14)
H30	0.545709	0.387473	0.129819	0.055
C32	0.5219(4)	0.5245(4)	0.2957(4)	0.0417(13)
C29	0.3912(4)	0.4963(4)	0.1745(4)	0.0370(12)
C37	0.0701(5)	0.6653(5)	0.3633(4)	0.0479(14)
C3	0.0774(5)	0.7672(5)	0.8607(4)	0.0459(14)
H3	0.024566	0.740794	0.888490	0.055
F3	0.6727(5)	0.5614(6)	0.3170(4)	0.156(3)
C14	0.4893(6)	0.8545(5)	0.6171(4)	0.0585(18)
C38	-0.0074(4)	0.6692(5)	0.2940(4)	0.0447(14)
C2	0.0828(5)	0.7996(5)	0.7591(4)	0.0461(14)
C39	-0.0265(4)	0.7621(5)	0.2175(4)	0.0463(14)
F2	0.5393(4)	0.6149(5)	0.4106(4)	0.144(2)
C31	0.5746(5)	0.4503(5)	0.2320(4)	0.0481(14)
H31	0.653706	0.410486	0.230986	0.058
C10	0.3083(5)	0.9782(5)	1.0656(4)	0.0579(16)
H10A	0.347353	1.024743	1.057294	0.087
H10B	0.285613	0.964301	1.132400	0.087
H10C	0.241835	1.016499	1.024640	0.087
C40	0.0399(5)	0.8168(5)	0.2357(4)	0.0519(15)
C9	0.3878(5)	0.8655(5)	1.0379(4)	0.0433(13)
C36	0.0944(5)	0.7594(5)	0.3275(4)	0.0505(15)
C8	0.3260(6)	0.7959(5)	1.0298(4)	0.0569(16)
H8A	0.375902	0.715159	1.047126	0.068
H8B	0.258750	0.813467	1.070790	0.068
F1	0.6470(6)	0.4471(5)	0.4264(4)	0.162(3)
C25	0.2289(4)	0.4265(5)	0.0287(4)	0.0451(14)
C28	0.3459(5)	0.4118(6)	0.0531(5)	0.0616(18)
H28A	0.394335	0.333475	0.083379	0.074
H28B	0.383231	0.434397	-0.005081	0.074
C44	-0.0548(5)	0.5850(6)	0.3052(5)	0.0673(19)
H44A	-0.067775	0.578467	0.242023	0.101
H44B	-0.125581	0.610219	0.340156	0.101
H44C	-0.001341	0.512412	0.340493	0.101
F4	0.0119(6)	0.8243(8)	0.6073(4)	0.193(4)
C11	0.4882(5)	0.8004(5)	1.1087(4)	0.0639(18)
H11A	0.535117	0.727054	1.094602	0.096
H11B	0.460089	0.791534	1.174111	0.096
H11C	0.532555	0.841682	1.101886	0.096
C42	0.0385(6)	0.9228(5)	0.1716(6)	0.085(2)
H42A	0.104393	0.930170	0.185126	0.128
H42B	-0.029398	0.987219	0.184039	0.128

H42C	0.039510	0.919205	0.104645	0.128
C33	0.5937(6)	0.5375(7)	0.3609(6)	0.0657(18)
C1	0.0021(7)	0.7948(8)	0.6979(6)	0.076(2)
C43	-0.1050(5)	0.8046(6)	0.1326(5)	0.076(2)
H43A	-0.068489	0.826529	0.074531	0.114
H43B	-0.173945	0.869009	0.143347	0.114
H43C	-0.123055	0.745701	0.125569	0.114
C26	0.2096(6)	0.3231(5)	0.0749(5)	0.073(2)
H26A	0.220714	0.305485	0.144005	0.110
H26B	0.262753	0.259794	0.048339	0.110
H26C	0.133071	0.338617	0.061643	0.110
F5	0.0014(8)	0.6996(6)	0.7116(6)	0.208(4)
C23	0.1081(6)	0.5820(6)	0.4593(4)	0.080(2)
H23A	0.115705	0.509824	0.453541	0.120
H23B	0.052457	0.609229	0.508297	0.120
H23C	0.180287	0.573719	0.477286	0.120
C27	0.2054(5)	0.4594(6)	-0.0799(4)	0.0642(18)
H27A	0.126781	0.480189	-0.090683	0.096
H27B	0.253303	0.396296	-0.108871	0.096
H27C	0.221450	0.522617	-0.108879	0.096
F6	-0.1030(5)	0.8558(8)	0.7146(5)	0.197(4)
C20	0.2047(6)	1.1066(7)	0.5553(5)	0.093(3)
H20A	0.160797	1.070468	0.543335	0.140
H20B	0.210841	1.156302	0.496282	0.140
H20C	0.167537	1.149742	0.604167	0.140
C16	0.6111(6)	0.9190(9)	0.6999(5)	0.116(4)
H16A	0.592176	0.959444	0.751215	0.174
H16B	0.654227	0.946268	0.650826	0.174
H16C	0.655689	0.839487	0.725755	0.174
C13	0.5788(7)	0.7366(6)	0.6153(6)	0.112(3)
H13A	0.628197	0.708166	0.670645	0.168
H13B	0.622691	0.737609	0.556638	0.168
H13C	0.542769	0.688319	0.617503	0.168
C41	0.1563(6)	0.7989(6)	0.3815(6)	0.084(2)
H41A	0.208358	0.735462	0.427466	0.126
H41B	0.102086	0.854577	0.415411	0.126
H41C	0.198103	0.831795	0.336090	0.126
C22	0.3370(8)	0.8555(8)	0.5140(5)	0.111(3)
H22A	0.353722	0.779196	0.547558	0.166
H22B	0.374717	0.854622	0.452029	0.166
H22C	0.256060	0.899080	0.504323	0.166
C18	0.3740(8)	1.1427(6)	0.6725(5)	0.097(3)
H18A	0.292776	1.186449	0.676054	0.145
H18B	0.405284	1.186005	0.626054	0.145
H18C	0.407236	1.124094	0.735283	0.145

U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Table 3. Anisotropic displacement parameters [Å²] for shelx.

The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2(a^*)^2U_{11} + k^2(b^*)^2U_{22} + \ldots + 2hka^*b^*U_{12}\,]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ir1	0.02875(11)	0.03250(12)	0.03238(12)	−0.00689(9)	−0.00025(8)	−0.00987(9)
Ir2	0.03632(12)	0.04230(13)	0.02965(12)	−0.00741(9)	0.00356(9)	−0.02102(10)
N4	0.038(2)	0.048(3)	0.039(3)	−0.009(2)	0.005(2)	−0.027(2)
N1	0.027(2)	0.042(3)	0.047(3)	−0.014(2)	−0.0031(19)	−0.011(2)
O2	0.091(3)	0.126(4)	0.050(3)	−0.028(3)	0.013(2)	−0.086(3)
O1	0.035(2)	0.100(4)	0.089(3)	−0.056(3)	−0.004(2)	−0.020(2)

N3	0.050(3)	0.059(3)	0.029(2)	−0.007(2)	0.004(2)	−0.035(2)
C5	0.033(3)	0.030(3)	0.036(3)	−0.008(2)	−0.002(2)	−0.013(2)
C35	0.036(3)	0.028(3)	0.033(3)	−0.001(2)	−0.006(2)	−0.013(2)
N2	0.025(2)	0.055(3)	0.062(3)	−0.035(2)	−0.001(2)	−0.008(2)
C4	0.045(3)	0.037(3)	0.042(3)	−0.006(2)	0.008(3)	−0.021(3)
C6	0.031(3)	0.035(3)	0.037(3)	−0.011(2)	−0.003(2)	−0.010(2)
C15	0.046(4)	0.087(5)	0.028(3)	0.004(3)	0.008(2)	−0.044(4)
C17	0.069(4)	0.048(4)	0.037(3)	−0.010(3)	0.011(3)	−0.036(3)
C7	0.039(3)	0.049(3)	0.037(3)	−0.012(3)	0.001(2)	−0.019(3)
C34	0.042(3)	0.037(3)	0.043(3)	−0.009(2)	0.000(2)	−0.016(3)
C21	0.070(4)	0.078(5)	0.039(3)	−0.020(3)	0.014(3)	−0.052(4)
C12	0.050(3)	0.057(4)	0.041(3)	−0.013(3)	0.004(3)	−0.032(3)
C24	0.037(3)	0.060(4)	0.045(3)	−0.020(3)	−0.002(3)	−0.018(3)
C19	0.042(3)	0.067(4)	0.027(3)	−0.001(3)	0.001(2)	−0.023(3)
C30	0.035(3)	0.042(3)	0.060(4)	−0.017(3)	−0.004(3)	−0.013(3)
C32	0.035(3)	0.041(3)	0.052(3)	−0.006(3)	−0.009(2)	−0.019(3)
C29	0.030(3)	0.035(3)	0.044(3)	−0.011(2)	−0.004(2)	−0.010(2)
C37	0.048(3)	0.057(4)	0.036(3)	−0.013(3)	0.003(3)	−0.021(3)
C3	0.042(3)	0.049(3)	0.058(4)	−0.014(3)	0.008(3)	−0.030(3)
F3	0.144(5)	0.322(9)	0.111(4)	−0.077(5)	0.020(3)	−0.187(6)
C14	0.063(4)	0.054(4)	0.041(3)	−0.006(3)	0.031(3)	−0.019(3)
C38	0.038(3)	0.052(4)	0.041(3)	−0.013(3)	0.008(2)	−0.018(3)
C2	0.042(3)	0.052(4)	0.053(4)	−0.018(3)	0.000(3)	−0.024(3)
C39	0.025(3)	0.046(3)	0.052(4)	−0.016(3)	0.004(2)	−0.001(3)
F2	0.084(3)	0.197(6)	0.192(6)	−0.138(5)	−0.019(4)	−0.046(4)
C31	0.030(3)	0.046(3)	0.065(4)	−0.009(3)	−0.005(3)	−0.014(3)
C10	0.051(4)	0.067(4)	0.055(4)	−0.013(3)	0.001(3)	−0.025(3)
C40	0.039(3)	0.037(3)	0.064(4)	−0.014(3)	0.016(3)	−0.005(3)
C9	0.051(3)	0.055(4)	0.034(3)	−0.013(3)	0.001(2)	−0.030(3)
C36	0.039(3)	0.055(4)	0.059(4)	−0.032(3)	0.012(3)	−0.015(3)
C8	0.080(5)	0.071(4)	0.037(3)	−0.010(3)	0.005(3)	−0.051(4)
F1	0.199(6)	0.139(5)	0.158(5)	0.031(4)	−0.138(5)	−0.085(5)
C25	0.038(3)	0.049(3)	0.054(4)	−0.023(3)	−0.003(3)	−0.018(3)
C28	0.039(3)	0.077(5)	0.082(5)	−0.054(4)	0.006(3)	−0.020(3)
C44	0.061(4)	0.085(5)	0.075(5)	−0.015(4)	0.014(3)	−0.053(4)
F4	0.202(6)	0.433(12)	0.062(3)	−0.020(5)	−0.018(4)	−0.254(8)
C11	0.065(4)	0.067(4)	0.051(4)	−0.010(3)	−0.005(3)	−0.022(4)
C42	0.073(5)	0.039(4)	0.116(6)	−0.011(4)	0.033(4)	−0.011(4)
C33	0.044(4)	0.082(5)	0.079(5)	−0.027(4)	−0.014(4)	−0.028(4)
C1	0.067(5)	0.122(7)	0.074(5)	−0.030(5)	−0.002(4)	−0.065(5)
C43	0.042(4)	0.081(5)	0.060(4)	−0.009(4)	−0.011(3)	0.011(4)
C26	0.065(5)	0.059(4)	0.088(5)	−0.011(4)	−0.002(4)	−0.022(4)
F5	0.296(10)	0.167(6)	0.244(9)	−0.001(6)	−0.150(7)	−0.162(7)
C23	0.082(5)	0.112(6)	0.033(4)	0.001(4)	−0.001(3)	−0.041(5)
C27	0.050(4)	0.071(5)	0.064(4)	−0.026(4)	0.003(3)	−0.016(4)
F6	0.072(4)	0.335(11)	0.218(7)	−0.148(8)	−0.019(4)	−0.074(5)
C20	0.057(5)	0.118(7)	0.059(5)	0.015(4)	−0.005(4)	−0.016(5)
C16	0.072(5)	0.231(11)	0.063(5)	0.007(6)	−0.008(4)	−0.099(7)
C13	0.110(7)	0.065(5)	0.094(6)	−0.001(4)	0.058(5)	−0.001(5)
C41	0.067(5)	0.104(6)	0.109(6)	−0.070(5)	0.012(4)	−0.040(5)
C22	0.175(9)	0.186(9)	0.061(5)	−0.065(6)	0.040(5)	−0.147(8)
C18	0.161(8)	0.082(6)	0.083(6)	−0.033(4)	0.030(5)	−0.083(6)

Table 4. Bond lengths and angles for shelx

Atom–Atom	Length [Å]
Ir1–N1	1.948(4)
Ir1–C35	2.017(5)
Ir1–C37	2.143(5)

Ir1–C36	2.174(5)
Ir1–C40	2.179(5)
Ir1–C38	2.213(5)
Ir1–C39	2.250(5)
Ir2–N4	1.955(4)
Ir2–C6	2.013(5)
Ir2–C19	2.144(5)
Ir2–C21	2.167(6)
Ir2–C14	2.175(5)
Ir2–C17	2.197(5)
Ir2–C15	2.257(5)
N4–C12	1.385(6)
N4–N3	1.406(5)
N1–C24	1.391(6)
N1–N2	1.396(5)
O2–C12	1.211(6)
O1–C24	1.212(6)
N3–C5	1.357(6)
N3–C8	1.440(6)
C5–C4	1.413(7)
C5–C6	1.421(7)
C35–C34	1.402(7)
C35–C29	1.420(7)
N2–C29	1.349(6)
N2–C28	1.422(6)
C4–C3	1.364(7)
C4–H4	0.9300
C6–C7	1.401(7)
C15–C17	1.383(8)
C15–C14	1.446(9)
C15–C16	1.513(8)
C17–C19	1.439(8)
C17–C18	1.509(8)
C7–C2	1.370(7)
C7–H7	0.9300
C34–C32	1.388(7)
C34–H34	0.9300
C21–C19	1.398(8)
C21–C14	1.434(9)
C21–C22	1.497(8)
C12–C9	1.528(7)
C24–C25	1.519(7)
C19–C20	1.511(8)
C30–C31	1.355(7)
C30–C29	1.404(7)
C30–H30	0.9300
C32–C31	1.406(7)
C32–C33	1.481(8)
C37–C36	1.417(8)
C37–C38	1.465(7)
C37–C23	1.505(8)
C3–C2	1.402(7)
C3–H3	0.9300
F3–C33	1.281(8)
C14–C13	1.499(8)

C38–C39	1.391(7)
C38–C44	1.502(8)
C2–C1	1.475(8)
C39–C40	1.452(8)
C39–C43	1.494(8)
F2–C33	1.294(8)
C31–H31	0.9300
C10–C9	1.528(8)
C10–H10A	0.9600
C10–H10B	0.9600
C10–H10C	0.9600
C40–C36	1.419(8)
C40–C42	1.496(8)
C9–C11	1.524(8)
C9–C8	1.528(7)
C36–C41	1.506(8)
C8–H8A	0.9700
C8–H8B	0.9700
F1–C33	1.290(8)
C25–C26	1.517(8)
C25–C27	1.518(8)
C25–C28	1.526(7)
C28–H28A	0.9700
C28–H28B	0.9700
C44–H44A	0.9600
C44–H44B	0.9600
C44–H44C	0.9600
F4–C1	1.259(8)
C11–H11A	0.9600
C11–H11B	0.9600
C11–H11C	0.9600
C42–H42A	0.9600
C42–H42B	0.9600
C42–H42C	0.9600
C1–F5	1.261(9)
C1–F6	1.279(9)
C43–H43A	0.9600
C43–H43B	0.9600
C43–H43C	0.9600
C26–H26A	0.9600
C26–H26B	0.9600
C26–H26C	0.9600
C23–H23A	0.9600
C23–H23B	0.9600
C23–H23C	0.9600
C27–H27A	0.9600
C27–H27B	0.9600
C27–H27C	0.9600
C20–H20A	0.9600
C20–H20B	0.9600
C20–H20C	0.9600
C16–H16A	0.9600
C16–H16B	0.9600
C16–H16C	0.9600
C13–H13A	0.9600

C13–H13B	0.9600
C13–H13C	0.9600
C41–H41A	0.9600
C41–H41B	0.9600
C41–H41C	0.9600
C22–H22A	0.9600
C22–H22B	0.9600
C22–H22C	0.9600
C18–H18A	0.9600
C18–H18B	0.9600
C18–H18C	0.9600
Atom–Atom–Atom	Angle [°]
N1–Ir1–C35	78.16(18)
N1–Ir1–C37	141.8(2)
C35–Ir1–C37	116.5(2)
N1–Ir1–C36	174.1(2)
C35–Ir1–C36	107.2(2)
C37–Ir1–C36	38.3(2)
N1–Ir1–C40	136.4(2)
C35–Ir1–C40	128.0(2)
C37–Ir1–C40	64.1(2)
C36–Ir1–C40	38.1(2)
N1–Ir1–C38	112.50(19)
C35–Ir1–C38	151.3(2)
C37–Ir1–C38	39.3(2)
C36–Ir1–C38	64.1(2)
C40–Ir1–C38	63.2(2)
N1–Ir1–C39	110.86(18)
C35–Ir1–C39	166.0(2)
C37–Ir1–C39	63.4(2)
C36–Ir1–C39	63.4(2)
C40–Ir1–C39	38.2(2)
C38–Ir1–C39	36.31(19)
N4–Ir2–C6	78.29(18)
N4–Ir2–C19	149.0(2)
C6–Ir2–C19	113.4(2)
N4–Ir2–C21	170.1(2)
C6–Ir2–C21	105.8(2)
C19–Ir2–C21	37.8(2)
N4–Ir2–C14	132.1(2)
C6–Ir2–C14	129.5(2)
C19–Ir2–C14	63.7(2)
C21–Ir2–C14	38.6(2)
N4–Ir2–C17	117.68(19)
C6–Ir2–C17	147.2(2)
C19–Ir2–C17	38.7(2)
C21–Ir2–C17	63.6(2)
C14–Ir2–C17	62.8(2)
N4–Ir2–C15	111.16(18)
C6–Ir2–C15	167.5(2)
C19–Ir2–C15	62.9(2)
C21–Ir2–C15	63.5(2)
C14–Ir2–C15	38.0(2)
C17–Ir2–C15	36.1(2)

C12–N4–N3	106.3(4)
C12–N4–Ir2	134.5(3)
N3–N4–Ir2	118.9(3)
C24–N1–N2	107.2(4)
C24–N1–Ir1	133.8(3)
N2–N1–Ir1	118.8(3)
C5–N3–N4	112.6(4)
C5–N3–C8	133.3(4)
N4–N3–C8	112.6(4)
N3–C5–C4	121.5(5)
N3–C5–C6	115.2(4)
C4–C5–C6	123.2(5)
C34–C35–C29	115.0(4)
C34–C35–Ir1	130.2(4)
C29–C35–Ir1	114.7(3)
C29–N2–N1	113.5(4)
C29–N2–C28	132.3(4)
N1–N2–C28	114.1(4)
C3–C4–C5	118.2(5)
C3–C4–H4	120.9
C5–C4–H4	120.9
C7–C6–C5	114.8(5)
C7–C6–Ir2	130.4(4)
C5–C6–Ir2	114.8(3)
C17–C15–C14	107.2(5)
C17–C15–C16	127.9(7)
C14–C15–C16	124.9(7)
C17–C15–Ir2	69.6(3)
C14–C15–Ir2	67.9(3)
C16–C15–Ir2	128.7(4)
C15–C17–C19	109.1(5)
C15–C17–C18	125.5(6)
C19–C17–C18	125.4(6)
C15–C17–Ir2	74.3(3)
C19–C17–Ir2	68.7(3)
C18–C17–Ir2	123.8(4)
C2–C7–C6	123.1(5)
C2–C7–H7	118.5
C6–C7–H7	118.5
C32–C34–C35	122.8(5)
C32–C34–H34	118.6
C35–C34–H34	118.6
C19–C21–C14	107.3(5)
C19–C21–C22	127.8(7)
C14–C21–C22	124.7(7)
C19–C21–Ir2	70.2(3)
C14–C21–Ir2	71.0(3)
C22–C21–Ir2	127.9(4)
O2–C12–N4	123.8(5)
O2–C12–C9	125.9(5)
N4–C12–C9	110.3(4)
O1–C24–N1	122.3(5)
O1–C24–C25	127.4(5)
N1–C24–C25	110.3(4)
C21–C19–C17	108.3(5)

C21–C19–C20	126.5(6)
C17–C19–C20	125.1(6)
C21–C19–Ir2	72.0(3)
C17–C19–Ir2	72.6(3)
C20–C19–Ir2	124.7(4)
C31–C30–C29	119.4(5)
C31–C30–H30	120.3
C29–C30–H30	120.3
C34–C32–C31	119.5(5)
C34–C32–C33	121.1(5)
C31–C32–C33	119.4(5)
N2–C29–C30	122.4(5)
N2–C29–C35	114.8(4)
C30–C29–C35	122.8(5)
C36–C37–C38	107.7(5)
C36–C37–C23	126.5(6)
C38–C37–C23	125.7(6)
C36–C37–Ir1	72.0(3)
C38–C37–Ir1	72.9(3)
C23–C37–Ir1	124.7(4)
C4–C3–C2	120.8(5)
C4–C3–H3	119.6
C2–C3–H3	119.6
C21–C14–C15	108.0(5)
C21–C14–C13	125.5(7)
C15–C14–C13	126.3(7)
C21–C14–Ir2	70.4(3)
C15–C14–Ir2	74.0(3)
C13–C14–Ir2	125.1(4)
C39–C38–C37	108.0(5)
C39–C38–C44	127.2(6)
C37–C38–C44	124.8(5)
C39–C38–Ir1	73.3(3)
C37–C38–Ir1	67.8(3)
C44–C38–Ir1	123.6(4)
C7–C2–C3	120.0(5)
C7–C2–C1	120.5(6)
C3–C2–C1	119.5(5)
C38–C39–C40	108.0(5)
C38–C39–C43	127.5(6)
C40–C39–C43	124.4(6)
C38–C39–Ir1	70.4(3)
C40–C39–Ir1	68.2(3)
C43–C39–Ir1	129.1(4)
C30–C31–C32	120.4(5)
C30–C31–H31	119.8
C32–C31–H31	119.8
C9–C10–H10A	109.5
C9–C10–H10B	109.5
H10A–C10–H10B	109.5
C9–C10–H10C	109.5
H10A–C10–H10C	109.5
H10B–C10–H10C	109.5
C36–C40–C39	108.2(5)
C36–C40–C42	127.3(6)
C39–C40–C42	124.2(6)
C36–C40–Ir1	70.8(3)
C39–C40–Ir1	73.6(3)
C42–C40–Ir1	126.4(4)
C11–C9–C12	111.6(5)
C11–C9–C10	109.3(5)
C12–C9–C10	107.9(5)
C11–C9–C8	112.9(5)
C12–C9–C8	102.0(4)
C10–C9–C8	112.9(5)
C37–C36–C40	107.9(5)
C37–C36–C41	126.1(6)
C40–C36–C41	125.7(6)
C37–C36–Ir1	69.7(3)
C40–C36–Ir1	71.2(3)
C41–C36–Ir1	129.5(4)
N3–C8–C9	102.3(4)
N3–C8–H8A	111.3
C9–C8–H8A	111.3
N3–C8–H8B	111.3
C9–C8–H8B	111.3
H8A–C8–H8B	109.2
C26–C25–C27	110.2(5)
C26–C25–C24	107.6(5)
C27–C25–C24	109.7(5)
C26–C25–C28	112.6(5)
C27–C25–C28	113.1(5)
C24–C25–C28	103.2(4)
N2–C28–C25	104.7(4)
N2–C28–H28A	110.8
C25–C28–H28A	110.8
N2–C28–H28B	110.8
C25–C28–H28B	110.8
H28A–C28–H28B	108.9
C38–C44–H44A	109.5
C38–C44–H44B	109.5
H44A–C44–H44B	109.5
C38–C44–H44C	109.5
H44A–C44–H44C	109.5
H44B–C44–H44C	109.5
C9–C11–H11A	109.5
C9–C11–H11B	109.5
H11A–C11–H11B	109.5
C9–C11–H11C	109.5
H11A–C11–H11C	109.5
H11B–C11–H11C	109.5
C40–C42–H42A	109.5
C40–C42–H42B	109.5
H42A–C42–H42B	109.5
C40–C42–H42C	109.5
H42A–C42–H42C	109.5
H42B–C42–H42C	109.5
F3–C33–F1	104.2(6)
F3–C33–F2	104.9(7)
F1–C33–F2	103.7(7)

F3–C33–C32	114.0(6)
F1–C33–C32	113.5(6)
F2–C33–C32	115.3(6)
F4–C1–F5	105.3(8)
F4–C1–F6	104.1(8)
F5–C1–F6	99.5(7)
F4–C1–C2	116.3(6)
F5–C1–C2	115.3(8)
F6–C1–C2	114.2(7)
C39–C43–H43A	109.5
C39–C43–H43B	109.5
H43A–C43–H43B	109.5
C39–C43–H43C	109.5
H43A–C43–H43C	109.5
H43B–C43–H43C	109.5
C25–C26–H26A	109.5
C25–C26–H26B	109.5
H26A–C26–H26B	109.5
C25–C26–H26C	109.5
H26A–C26–H26C	109.5
H26B–C26–H26C	109.5
C37–C23–H23A	109.5
C37–C23–H23B	109.5
H23A–C23–H23B	109.5
C37–C23–H23C	109.5
H23A–C23–H23C	109.5
H23B–C23–H23C	109.5
C25–C27–H27A	109.5
C25–C27–H27B	109.5
H27A–C27–H27B	109.5
C25–C27–H27C	109.5
H27A–C27–H27C	109.5
H27B–C27–H27C	109.5
C19–C20–H20A	109.5
C19–C20–H20B	109.5
H20A–C20–H20B	109.5
C19–C20–H20C	109.5
H20A–C20–H20C	109.5
H20B–C20–H20C	109.5
C15–C16–H16A	109.5
C15–C16–H16B	109.5
H16A–C16–H16B	109.5
C15–C16–H16C	109.5
H16A–C16–H16C	109.5
H16B–C16–H16C	109.5
C14–C13–H13A	109.5
C14–C13–H13B	109.5
H13A–C13–H13B	109.5
C14–C13–H13C	109.5
H13A–C13–H13C	109.5
H13B–C13–H13C	109.5
C36–C41–H41A	109.5
C36–C41–H41B	109.5
H41A–C41–H41B	109.5
C36–C41–H41C	109.5
H41A–C41–H41C	109.5
H41B–C41–H41C	109.5
C21–C22–H22A	109.5
C21–C22–H22B	109.5
H22A–C22–H22B	109.5
C21–C22–H22C	109.5
H22A–C22–H22C	109.5
H22B–C22–H22C	109.5
C17–C18–H18A	109.5
C17–C18–H18B	109.5
H18A–C18–H18B	109.5
C17–C18–H18C	109.5
H18A–C18–H18C	109.5
H18B–C18–H18C	109.5

Table 5. Torsion angles for shelx

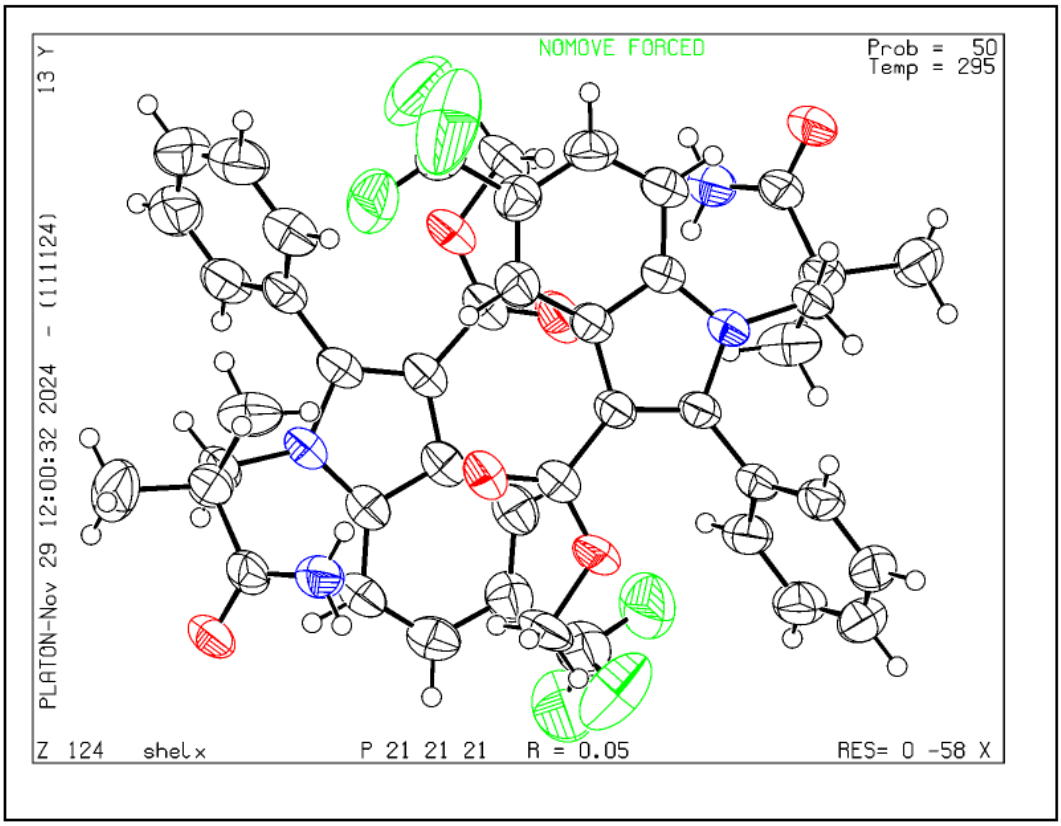
Atom–Atom–Atom–Atom	Torsion Angle [°]
C12–N4–N3–C5	176.6(4)
Ir2–N4–N3–C5	1.5(5)
C12–N4–N3–C8	−15.5(6)
Ir2–N4–N3–C8	169.4(4)
N4–N3–C5–C4	179.4(4)
C8–N3–C5–C4	14.9(9)
N4–N3–C5–C6	−2.9(6)
C8–N3–C5–C6	−167.5(6)
C24–N1–N2–C29	−176.3(5)
Ir1–N1–N2–C29	−1.1(6)
C24–N1–N2–C28	0.0(7)
Ir1–N1–N2–C28	175.2(4)
N3–C5–C4–C3	175.1(5)
C6–C5–C4–C3	−2.3(7)
N3–C5–C6–C7	−175.1(4)
C4–C5–C6–C7	2.5(7)
N3–C5–C6–Ir2	3.1(6)
C4–C5–C6–Ir2	−179.3(4)
C14–C15–C17–C19	−2.6(6)
C16–C15–C17–C19	176.0(5)
Ir2–C15–C17–C19	−60.2(4)
C14–C15–C17–C18	178.2(5)
C16–C15–C17–C18	−3.2(9)
Ir2–C15–C17–C18	120.6(6)
C14–C15–C17–Ir2	57.6(4)
C16–C15–C17–Ir2	−123.8(6)
C5–C6–C7–C2	−0.8(7)
Ir2–C6–C7–C2	−178.6(4)
C29–C35–C34–C32	0.3(7)
Ir1–C35–C34–C32	178.2(4)
N3–N4–C12–O2	179.4(6)
Ir2–N4–C12–O2	−6.7(9)
N3–N4–C12–C9	−1.6(6)
Ir2–N4–C12–C9	172.3(4)
N2–N1–C24–O1	−176.2(6)
Ir1–N1–C24–O1	9.6(9)
N2–N1–C24–C25	5.3(6)
Ir1–N1–C24–C25	−168.9(4)
C14–C21–C19–C17	2.3(6)

C22–C21–C19–C17	−172.9(6)
Ir2–C21–C19–C17	64.0(4)
C14–C21–C19–C20	178.1(5)
C22–C21–C19–C20	2.9(10)
Ir2–C21–C19–C20	−120.2(6)
C14–C21–C19–Ir2	−61.7(4)
C22–C21–C19–Ir2	123.1(6)
C15–C17–C19–C21	0.2(6)
C18–C17–C19–C21	179.4(5)
Ir2–C17–C19–C21	−63.5(4)
C15–C17–C19–C20	−175.7(5)
C18–C17–C19–C20	3.5(9)
Ir2–C17–C19–C20	120.6(5)
C15–C17–C19–Ir2	63.7(4)
C18–C17–C19–Ir2	−117.1(6)
C35–C34–C32–C31	−0.7(8)
C35–C34–C32–C33	−179.5(5)
N1–N2–C29–C30	178.9(5)
C28–N2–C29–C30	3.5(10)
N1–N2–C29–C35	0.7(7)
C28–N2–C29–C35	−174.8(6)
C31–C30–C29–N2	−178.1(5)
C31–C30–C29–C35	0.0(8)
C34–C35–C29–N2	178.3(5)
Ir1–C35–C29–N2	0.0(6)
C34–C35–C29–C30	0.0(7)
Ir1–C35–C29–C30	−178.2(4)
C5–C4–C3–C2	0.4(8)
C19–C21–C14–C15	−3.9(6)
C22–C21–C14–C15	171.5(5)
Ir2–C21–C14–C15	−65.0(4)
C19–C21–C14–C13	−179.1(5)
C22–C21–C14–C13	−3.7(9)
Ir2–C21–C14–C13	119.7(6)
C19–C21–C14–Ir2	61.2(4)
C22–C21–C14–Ir2	−123.5(6)
C17–C15–C14–C21	4.0(6)
C16–C15–C14–C21	−174.7(5)
Ir2–C15–C14–C21	62.7(4)
C17–C15–C14–C13	179.2(5)
C16–C15–C14–C13	0.5(9)
Ir2–C15–C14–C13	−122.2(6)
C17–C15–C14–Ir2	−58.7(4)
C16–C15–C14–Ir2	122.7(5)
C36–C37–C38–C39	1.4(6)
C23–C37–C38–C39	176.4(6)
Ir1–C37–C38–C39	−62.7(4)
C36–C37–C38–C44	−179.5(5)
C23–C37–C38–C44	−4.4(9)
Ir1–C37–C38–C44	116.4(5)
C36–C37–C38–Ir1	64.1(4)
C23–C37–C38–Ir1	−120.8(6)
C6–C7–C2–C3	−1.0(8)
C6–C7–C2–C1	178.4(6)
C4–C3–C2–C7	1.2(8)
C4–C3–C2–C1	−178.1(6)
C37–C38–C39–C40	1.2(6)
C44–C38–C39–C40	−177.9(5)

Ir1–C38–C39–C40	−58.0(4)
C37–C38–C39–C43	−176.0(5)
C44–C38–C39–C43	4.9(9)
Ir1–C38–C39–C43	124.8(6)
C37–C38–C39–Ir1	59.2(4)
C44–C38–C39–Ir1	−119.9(6)
C29–C30–C31–C32	−0.3(8)
C34–C32–C31–C30	0.7(8)
C33–C32–C31–C30	179.5(6)
C38–C39–C40–C36	−3.4(6)
C43–C39–C40–C36	173.9(5)
Ir1–C39–C40–C36	−62.7(4)
C38–C39–C40–C42	−177.5(5)
C43–C39–C40–C42	−0.1(9)
Ir1–C39–C40–C42	123.2(6)
C38–C39–C40–Ir1	59.3(4)
C43–C39–C40–Ir1	−123.4(5)
O2–C12–C9–C11	−44.0(8)
N4–C12–C9–C11	137.0(5)
O2–C12–C9–C10	76.2(7)
N4–C12–C9–C10	−102.8(5)
O2–C12–C9–C8	−164.7(6)
N4–C12–C9–C8	16.2(6)
C38–C37–C36–C40	−3.5(6)
C23–C37–C36–C40	−178.5(6)
Ir1–C37–C36–C40	61.2(4)
C38–C37–C36–C41	170.6(5)
C23–C37–C36–C41	−4.4(9)
Ir1–C37–C36–C41	−124.7(6)
C38–C37–C36–Ir1	−64.7(4)
C23–C37–C36–Ir1	120.3(6)
C39–C40–C36–C37	4.3(6)
C42–C40–C36–C37	178.1(5)
Ir1–C40–C36–C37	−60.3(4)
C39–C40–C36–C41	−169.9(5)
C42–C40–C36–C41	3.9(9)
Ir1–C40–C36–C41	125.6(6)
C39–C40–C36–Ir1	64.5(4)
C42–C40–C36–Ir1	−121.7(6)
C5–N3–C8–C9	−170.1(5)
N4–N3–C8–C9	25.3(6)
C11–C9–C8–N3	−143.4(5)
C12–C9–C8–N3	−23.5(6)
C10–C9–C8–N3	92.0(5)
O1–C24–C25–C26	−67.2(8)
N1–C24–C25–C26	111.2(5)
O1–C24–C25–C27	52.7(8)
N1–C24–C25–C27	−128.9(5)
O1–C24–C25–C28	173.6(7)
N1–C24–C25–C28	−8.1(6)
C29–N2–C28–C25	170.4(6)
N1–N2–C28–C25	−5.1(7)
C26–C25–C28–N2	−108.2(6)
C27–C25–C28–N2	126.0(5)
C24–C25–C28–N2	7.5(6)
C34–C32–C33–F3	−128.6(7)
C31–C32–C33–F3	52.5(9)
C34–C32–C33–F1	112.2(7)

C31–C32–C33–F1	−66.6(9)
C34–C32–C33–F2	−7.2(10)
C31–C32–C33–F2	174.0(6)
C7–C2–C1–F4	1.1(12)
C3–C2–C1–F4	−179.6(8)

C7–C2–C1–F5	125.2(9)
C3–C2–C1–F5	−55.4(11)
C7–C2–C1–F6	−120.3(8)
C3–C2–C1–F6	59.1(11)



The diffractometer was equipped with a low temperature device and used MoK_α radiation (λ = 0.71073 Å). All data were integrated with SAINT and a MULTI-SCAN absorption correction using SADABS was applied. The structure was solved by direct methods using SIR-92 and refined by full-matrix least-squares methods against F^2 by SHELXL-2018/3. All non-hydrogen atoms were refined with anisotropic displacement parameters. All C-bound hydrogen atoms were refined isotropic on calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. Crystallographic data for the structures reported here have been deposited with the Cambridge Crystallographic Data Centre. CCDC 2360016 contain the supplementary crystallographic data for this paper.

Table 1. Crystal data and structure refinement for shelx

CCDC number	2360016
Empirical formula	$C_{22}H_{21}F_3N_2O_3$
Formula weight	418.41
Temperature [K]	295(2)
Crystal system	orthorhombic
Space group (number)	$P2_12_12_1$ (19)
a [Å]	12.159(2)
b [Å]	15.314(3)
c [Å]	22.569(4)
α [°]	90
β [°]	90
γ [°]	90
Volume [Å^3]	4202.8(13)
Z	8
ρ_{calc} [gcm^{-3}]	1.323
μ [mm^{-1}]	0.106
F(000)	1744

Crystal size [mm^3]	0.340×0.220×0.200
Crystal colour	colourless
Crystal shape	block
Radiation	MoK_α (λ=0.71073 Å)
2θ range [°]	3.80 to 52.00 (0.81 Å)
Index ranges	−14 ≤ h ≤ 14 −18 ≤ k ≤ 18 −27 ≤ l ≤ 24
Reflections collected	39452
Independent reflections	8216 R_{int} = 0.0442 R_{sigma} = 0.0379
Completeness to θ = 25.242°	99.8 %
Data / Restraints / Parameters	8216/0/543
Absorption correction	0.7026/0.7457
T_{min}/T_{max} (method)	(MULTI-SCAN)
Goodness-of-fit on F^2	1.021
Final R indexes	R_1 = 0.0477
[I≥2σ(I)]	wR_2 = 0.1071
Final R indexes	R_1 = 0.0778
[all data]	wR_2 = 0.1242
Largest peak/hole [eÅ^{-3}]	0.20/−0.22
Flack X parameter	−0.1(3)

Table 2. Atomic coordinates and U_{eq} [Å^2] for shelx

Atom	x	y	z	U_{eq}
C1	0.1200(3)	0.8407(2)	0.52082(16)	0.0496(8)
C2	0.2151(3)	0.8472(3)	0.48683(17)	0.0580(10)
H2	0.283752	0.833691	0.502505	0.070
C3	0.2034(3)	0.8742(3)	0.42944(18)	0.0638(11)
H3	0.265512	0.879181	0.405618	0.077
C4	0.1004(4)	0.8944(3)	0.40578(17)	0.0625(10)
C5	0.0053(3)	0.8888(3)	0.43953(17)	0.0585(10)
H5	-0.062790	0.902999	0.423491	0.070
C6	0.0148(3)	0.8611(2)	0.49834(17)	0.0513(9)
C7	-0.0628(3)	0.8438(2)	0.54481(17)	0.0510(9)
C8	-0.1820(3)	0.8574(3)	0.54116(19)	0.0551(9)
C9	-0.3493(3)	0.8522(3)	0.5952(2)	0.0769(13)
H9A	-0.384613	0.822875	0.562818	0.115
H9B	-0.365304	0.913567	0.593304	0.115
H9C	-0.376126	0.828997	0.632003	0.115
C10	-0.0044(3)	0.8117(2)	0.59289(17)	0.0494(9)
C11	-0.0429(3)	0.7719(2)	0.64891(16)	0.0506(9)
C12	-0.0932(3)	0.8200(3)	0.6930(2)	0.0670(11)
H12	-0.101857	0.879994	0.688519	0.080
C13	-0.1311(4)	0.7790(4)	0.7440(2)	0.0801(14)
H13	-0.164841	0.811445	0.773747	0.096

C14	-0.1187(4)	0.6913(4)	0.7503(2)	0.0889(15)
H14	-0.143929	0.664165	0.784591	0.107
C15	-0.0697(4)	0.6426(3)	0.7072(2)	0.0829(14)
H15	-0.062045	0.582638	0.712015	0.099
C16	-0.0318(3)	0.6824(3)	0.6568(2)	0.0657(11)
H16	0.001808	0.648976	0.627477	0.079
C17	0.1975(3)	0.7915(2)	0.61948(18)	0.0545(9)
H17A	0.254703	0.761423	0.597551	0.065
H17B	0.170437	0.751488	0.649447	0.065
C18	0.2495(3)	0.8705(3)	0.65094(17)	0.0572(10)
C19	0.1614(4)	0.9275(3)	0.6806(2)	0.0746(13)
H19A	0.112406	0.950036	0.650925	0.112
H19B	0.120548	0.893008	0.708441	0.112
H19C	0.196155	0.975176	0.700904	0.112
C20	0.3282(4)	0.8343(4)	0.6982(2)	0.0961(18)
H20A	0.383107	0.798691	0.679439	0.144
H20B	0.363120	0.881832	0.718504	0.144
H20C	0.287513	0.799663	0.726041	0.144
C21	0.3197(3)	0.9219(3)	0.60625(17)	0.0539(9)
C22	0.0946(4)	0.9215(4)	0.3425(2)	0.0790(13)
C23	-0.1780(3)	1.1091(2)	0.56607(15)	0.0462(8)
C24	-0.2852(3)	1.1286(2)	0.54828(15)	0.0469(8)
C25	-0.3738(3)	1.1275(3)	0.58723(17)	0.0595(10)
H25	-0.444489	1.141830	0.574830	0.071
C26	-0.3522(3)	1.1045(3)	0.64478(17)	0.0649(11)
H26	-0.409655	1.102717	0.671935	0.078
C27	-0.2455(3)	1.0834(3)	0.66371(16)	0.0569(10)
C28	-0.1580(3)	1.0858(2)	0.62501(17)	0.0549(9)
H28	-0.087245	1.072276	0.637757	0.066
C29	0.0113(3)	1.1114(2)	0.51601(17)	0.0510(9)
C30	0.1761(3)	1.1226(3)	0.4600(2)	0.0702(12)
H30A	0.195690	1.064450	0.471814	0.105
H30B	0.213173	1.164024	0.484882	0.105
H30C	0.197632	1.131765	0.419495	0.105
C31	-0.1748(3)	1.1499(2)	0.46895(15)	0.0440(8)
C32	-0.1442(3)	1.1800(2)	0.40883(15)	0.0458(8)
C33	-0.1021(3)	1.1228(3)	0.36743(17)	0.0597(10)
H33	-0.095105	1.063934	0.376768	0.072
C34	-0.0702(4)	1.1524(3)	0.31212(18)	0.0705(12)
H34	-0.041222	1.113380	0.284671	0.085
C35	-0.0811(4)	1.2383(3)	0.29764(19)	0.0726(12)
H35	-0.059796	1.257793	0.260338	0.087
C36	-0.1234(3)	1.2959(3)	0.33814(19)	0.0671(11)
H36	-0.130570	1.354646	0.328335	0.081
C37	-0.1553(3)	1.2670(3)	0.39343(17)	0.0541(9)
H37	-0.184503	1.306334	0.420583	0.065
C38	-0.3797(3)	1.1723(2)	0.45242(16)	0.0514(9)

H38A	-0.357584	1.211500	0.420851	0.062
H38B	-0.432094	1.203287	0.477038	0.062
C39	-0.4388(3)	1.0929(3)	0.42431(16)	0.0581(10)
C40	-0.3589(4)	1.0357(3)	0.39080(18)	0.0743(13)
H40A	-0.321354	1.070045	0.361521	0.111
H40B	-0.306314	1.011507	0.417924	0.111
H40C	-0.398355	0.989317	0.371674	0.111
C41	-0.5252(4)	1.1328(4)	0.3817(2)	0.0946(18)
H41A	-0.575129	1.168842	0.403773	0.142
H41B	-0.488609	1.167506	0.352285	0.142
H41C	-0.565381	1.086701	0.362657	0.142
C42	-0.2278(5)	1.0609(4)	0.72676(19)	0.0779(13)
C43	-0.1086(3)	1.1222(2)	0.51531(15)	0.0459(8)
C44	-0.5035(3)	1.0449(3)	0.47231(17)	0.0533(9)
N1	0.1070(2)	0.81116(19)	0.57859(13)	0.0485(7)
N2	0.2851(3)	0.9986(2)	0.58733(15)	0.0629(9)
H2A	0.323164	1.027252	0.561779	0.075
H2B	0.224454	1.019964	0.600551	0.075
N3	-0.2826(2)	1.15220(18)	0.48841(13)	0.0462(7)
N4	-0.4720(3)	0.9651(2)	0.48812(16)	0.0660(9)
H4A	-0.507899	0.937165	0.514946	0.079
H4B	-0.415817	0.941392	0.471512	0.079
O1	0.4064(2)	0.88967(19)	0.58799(14)	0.0711(8)
O2	-0.2291(2)	0.8830(2)	0.49690(13)	0.0742(8)
O3	-0.2318(2)	0.8391(2)	0.59158(14)	0.0711(8)
O4	-0.5839(2)	1.08056(19)	0.49535(13)	0.0681(8)
O5	0.0628(2)	1.0865(2)	0.55849(13)	0.0733(8)
O6	0.0583(2)	1.1341(2)	0.46548(12)	0.0637(7)
F1	-0.0050(3)	0.9254(3)	0.32043(13)	0.1242(13)
F2	0.1343(4)	1.0011(3)	0.33376(14)	0.1402(15)
F3	0.1527(3)	0.8704(3)	0.30767(12)	0.1329(14)
F4	-0.1294(3)	1.0298(2)	0.73877(11)	0.1029(10)
F5	-0.2924(4)	0.9955(3)	0.74453(16)	0.1550(18)
F6	-0.2468(5)	1.1227(3)	0.76269(13)	0.186(3)

U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Table 3. Anisotropic displacement parameters [Å²] for shelx.

The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2(a^*)^2U_{11} + k^2(b^*)^2U_{22} + \ldots + 2hka^*b^*U_{12}\,]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.042(2)	0.051(2)	0.057(2)	−0.0081(17)	−0.0030(17)	0.0048(17)
C2	0.038(2)	0.067(2)	0.068(2)	−0.010(2)	0.0013(18)	0.0086(18)
C3	0.055(2)	0.071(3)	0.066(2)	−0.010(2)	0.012(2)	0.005(2)
C4	0.064(3)	0.066(3)	0.057(2)	−0.0091(19)	−0.002(2)	0.011(2)
C5	0.054(2)	0.056(2)	0.066(2)	−0.0104(19)	−0.0070(19)	0.0078(19)
C6	0.042(2)	0.048(2)	0.064(2)	−0.0073(18)	−0.0027(17)	0.0058(16)
C7	0.0363(18)	0.049(2)	0.068(2)	−0.0046(18)	−0.0032(17)	0.0036(16)
C8	0.039(2)	0.053(2)	0.074(3)	−0.0062(19)	−0.004(2)	0.0072(17)
C9	0.034(2)	0.097(4)	0.100(3)	0.011(3)	0.004(2)	0.015(2)

C10	0.0324(18)	0.0471(19)	0.069(2)	−0.0048(17)	0.0035(17)	0.0023(15)
C11	0.0323(18)	0.055(2)	0.065(2)	−0.0014(18)	−0.0016(17)	−0.0013(16)
C12	0.051(2)	0.074(3)	0.076(3)	−0.014(2)	0.001(2)	0.000(2)
C13	0.059(3)	0.116(4)	0.066(3)	−0.017(3)	0.007(2)	−0.007(3)
C14	0.068(3)	0.115(5)	0.084(3)	0.021(3)	0.006(3)	−0.011(3)
C15	0.066(3)	0.078(3)	0.105(4)	0.023(3)	0.010(3)	0.001(3)
C16	0.044(2)	0.063(3)	0.090(3)	0.003(2)	0.007(2)	0.0030(19)
C17	0.0329(19)	0.058(2)	0.072(2)	0.0077(19)	−0.0047(17)	0.0022(16)
C18	0.041(2)	0.069(2)	0.061(2)	0.0091(19)	−0.0059(17)	−0.0106(18)
C19	0.067(3)	0.083(3)	0.074(3)	−0.015(2)	0.017(2)	−0.023(2)
C20	0.078(3)	0.122(4)	0.088(3)	0.038(3)	−0.038(3)	−0.033(3)
C21	0.034(2)	0.060(2)	0.068(2)	0.0066(19)	−0.0092(17)	−0.0080(18)
C22	0.080(3)	0.094(4)	0.064(3)	−0.018(3)	0.003(3)	0.018(3)
C23	0.0384(19)	0.0461(19)	0.054(2)	−0.0003(16)	0.0021(15)	0.0013(15)
C24	0.0384(19)	0.051(2)	0.0518(19)	−0.0012(16)	0.0051(16)	0.0009(16)
C25	0.041(2)	0.077(3)	0.061(2)	0.002(2)	0.0072(18)	0.0047(19)
C26	0.058(3)	0.080(3)	0.057(2)	−0.002(2)	0.0167(19)	0.001(2)
C27	0.063(3)	0.057(2)	0.051(2)	−0.0022(18)	0.0033(18)	0.0024(19)
C28	0.049(2)	0.058(2)	0.057(2)	−0.0020(18)	−0.0038(18)	0.0017(18)
C29	0.038(2)	0.055(2)	0.060(2)	−0.0019(18)	0.0003(18)	0.0040(17)
C30	0.0297(19)	0.096(3)	0.085(3)	−0.006(3)	0.0069(19)	0.004(2)
C31	0.0325(17)	0.0456(19)	0.054(2)	0.0013(16)	0.0051(15)	0.0004(14)
C32	0.0292(17)	0.054(2)	0.055(2)	0.0030(17)	0.0012(15)	−0.0020(15)
C33	0.049(2)	0.066(2)	0.064(2)	0.002(2)	0.0125(19)	0.0015(19)
C34	0.059(3)	0.095(3)	0.057(2)	−0.002(2)	0.012(2)	0.003(2)
C35	0.063(3)	0.098(4)	0.057(2)	0.019(3)	0.004(2)	−0.008(2)
C36	0.056(3)	0.070(3)	0.075(3)	0.022(2)	0.000(2)	−0.010(2)
C37	0.042(2)	0.057(2)	0.064(2)	0.0018(18)	0.0027(17)	−0.0052(17)
C38	0.0316(18)	0.060(2)	0.063(2)	0.0115(17)	0.0024(16)	0.0014(16)
C39	0.0384(19)	0.080(3)	0.056(2)	0.008(2)	−0.0034(17)	−0.0115(19)
C40	0.067(3)	0.090(3)	0.065(3)	−0.016(2)	0.017(2)	−0.023(2)
C41	0.054(3)	0.157(5)	0.073(3)	0.044(3)	−0.016(2)	−0.024(3)
C42	0.085(4)	0.093(3)	0.055(3)	0.005(3)	0.006(2)	0.008(3)
C43	0.0335(18)	0.0488(19)	0.0553(19)	0.0024(16)	0.0029(15)	0.0023(15)
C44	0.034(2)	0.069(3)	0.058(2)	0.0057(19)	−0.0017(17)	−0.0076(18)
N1	0.0311(15)	0.0533(17)	0.0611(18)	−0.0031(14)	−0.0023(13)	0.0041(13)
N2	0.0495(19)	0.062(2)	0.077(2)	0.0129(17)	0.0100(17)	0.0011(16)
N3	0.0314(15)	0.0536(16)	0.0537(16)	0.0034(13)	0.0029(13)	0.0012(13)
N4	0.0498(19)	0.069(2)	0.079(2)	0.0153(18)	0.0124(17)	0.0048(16)
O1	0.0342(14)	0.0784(19)	0.101(2)	0.0233(17)	0.0079(14)	0.0100(13)
O2	0.0465(16)	0.096(2)	0.0805(19)	0.0029(17)	−0.0091(15)	0.0154(16)
O3	0.0333(13)	0.095(2)	0.0848(19)	0.0057(16)	0.0001(14)	0.0111(14)
O4	0.0383(15)	0.0794(18)	0.0865(19)	0.0186(16)	0.0114(13)	0.0012(13)
O5	0.0445(15)	0.102(2)	0.0738(18)	0.0135(17)	−0.0065(14)	0.0149(16)
O6	0.0283(12)	0.093(2)	0.0702(17)	0.0069(15)	0.0009(12)	0.0004(13)
F1	0.100(2)	0.198(4)	0.0749(18)	0.009(2)	−0.0179(17)	0.030(2)
F2	0.215(4)	0.127(3)	0.0789(19)	0.021(2)	0.002(2)	−0.028(3)

F3	0.140(3)	0.194(4)	0.0646(16)	−0.033(2)	0.0024(18)	0.071(3)
F4	0.110(2)	0.134(3)	0.0644(15)	0.0136(16)	−0.0122(16)	0.019(2)
F5	0.151(3)	0.210(4)	0.104(2)	0.078(3)	−0.016(2)	−0.061(3)
F6	0.345(7)	0.153(3)	0.0593(17)	−0.031(2)	−0.017(3)	0.121(4)

Table 4. Bond lengths and angles for shelx

Atom–Atom	Length [Å]
C1–N1	1.389(5)
C1–C2	1.391(5)
C1–C6	1.411(5)
C2–C3	1.367(5)
C2–H2	0.9300
C3–C4	1.397(6)
C3–H3	0.9300
C4–C5	1.387(6)
C4–C22	1.490(6)
C5–C6	1.398(5)
C5–H5	0.9300
C6–C7	1.436(5)
C7–C10	1.387(5)
C7–C8	1.465(5)
C8–O2	1.217(5)
C8–O3	1.319(5)
C9–O3	1.445(4)
C9–H9A	0.9600
C9–H9B	0.9600
C9–H9C	0.9600
C10–N1	1.393(4)
C10–C11	1.480(5)
C11–C12	1.382(5)
C11–C16	1.389(5)
C12–C13	1.391(7)
C12–H12	0.9300
C13–C14	1.358(7)
C13–H13	0.9300
C14–C15	1.363(7)
C14–H14	0.9300
C15–C16	1.371(6)
C15–H15	0.9300
C16–H16	0.9300
C17–N1	1.467(4)
C17–C18	1.539(5)
C17–H17A	0.9700
C17–H17B	0.9700
C18–C19	1.535(6)
C18–C20	1.536(6)
C18–C21	1.537(5)
C19–H19A	0.9600
C19–H19B	0.9600
C19–H19C	0.9600
C20–H20A	0.9600
C20–H20B	0.9600
C20–H20C	0.9600
C21–O1	1.235(5)
C21–N2	1.319(5)
C22–F1	1.310(6)
C22–F3	1.315(5)
C22–F2	1.326(6)
C23–C24	1.397(5)
C23–C28	1.399(5)
C23–C43	1.437(5)
C24–C25	1.390(5)
C24–N3	1.399(4)
C25–C26	1.372(5)
C25–H25	0.9300
C26–C27	1.403(6)
C26–H26	0.9300
C27–C28	1.377(5)
C27–C42	1.480(6)
C28–H28	0.9300
C29–O5	1.207(4)
C29–O6	1.322(5)
C29–C43	1.468(5)
C30–O6	1.449(4)
C30–H30A	0.9600
C30–H30B	0.9600
C30–H30C	0.9600
C31–N3	1.384(4)
C31–C43	1.386(5)
C31–C32	1.481(5)
C32–C33	1.380(5)
C32–C37	1.383(5)
C33–C34	1.383(5)
C33–H33	0.9300
C34–C35	1.362(7)
C34–H34	0.9300
C35–C36	1.371(6)
C35–H35	0.9300
C36–C37	1.380(5)
C36–H36	0.9300

C37–H37	0.9300
C38–N3	1.465(4)
C38–C39	1.548(5)
C38–H38A	0.9700
C38–H38B	0.9700
C39–C40	1.511(6)
C39–C44	1.528(5)
C39–C41	1.549(6)
C40–H40A	0.9600
C40–H40B	0.9600
C40–H40C	0.9600
C41–H41A	0.9600
C41–H41B	0.9600
C41–H41C	0.9600
C42–F6	1.267(6)
C42–F4	1.316(6)
C42–F5	1.335(6)
C44–O4	1.234(4)
C44–N4	1.329(5)
N2–H2A	0.8600
N2–H2B	0.8600
N4–H4A	0.8600
N4–H4B	0.8600
Atom–Atom–Atom	Angle [°]
N1–C1–C2	129.5(3)
N1–C1–C6	107.9(3)
C2–C1–C6	122.6(3)
C3–C2–C1	117.3(4)
C3–C2–H2	121.4
C1–C2–H2	121.4
C2–C3–C4	121.5(4)
C2–C3–H3	119.3
C4–C3–H3	119.3
C5–C4–C3	121.6(4)
C5–C4–C22	120.3(4)
C3–C4–C22	118.1(4)
C4–C5–C6	118.1(4)
C4–C5–H5	120.9
C6–C5–H5	120.9
C5–C6–C1	118.9(4)
C5–C6–C7	134.0(3)
C1–C6–C7	107.0(3)
C10–C7–C6	107.5(3)
C10–C7–C8	126.9(4)
C6–C7–C8	125.6(4)

O2–C8–O3	124.0(3)
O2–C8–C7	123.9(4)
O3–C8–C7	112.0(3)
O3–C9–H9A	109.5
O3–C9–H9B	109.5
H9A–C9–H9B	109.5
O3–C9–H9C	109.5
H9A–C9–H9C	109.5
H9B–C9–H9C	109.5
C7–C10–N1	108.6(3)
C7–C10–C11	130.7(3)
N1–C10–C11	120.2(3)
C12–C11–C16	118.5(4)
C12–C11–C10	122.4(4)
C16–C11–C10	119.0(4)
C11–C12–C13	120.1(4)
C11–C12–H12	119.9
C13–C12–H12	119.9
C14–C13–C12	119.8(5)
C14–C13–H13	120.1
C12–C13–H13	120.1
C13–C14–C15	121.0(5)
C13–C14–H14	119.5
C15–C14–H14	119.5
C14–C15–C16	119.8(5)
C14–C15–H15	120.1
C16–C15–H15	120.1
C15–C16–C11	120.7(4)
C15–C16–H16	119.6
C11–C16–H16	119.6
N1–C17–C18	115.9(3)
N1–C17–H17A	108.3
C18–C17–H17A	108.3
N1–C17–H17B	108.3
C18–C17–H17B	108.3
H17A–C17–H17B	107.4
C19–C18–C20	109.8(4)
C19–C18–C21	112.5(3)
C20–C18–C21	107.1(3)
C19–C18–C17	111.2(3)
C20–C18–C17	107.0(4)
C21–C18–C17	109.1(3)
C18–C19–H19A	109.5
C18–C19–H19B	109.5
H19A–C19–H19B	109.5

C18–C19–H19C	109.5
H19A–C19–H19C	109.5
H19B–C19–H19C	109.5
C18–C20–H20A	109.5
C18–C20–H20B	109.5
H20A–C20–H20B	109.5
C18–C20–H20C	109.5
H20A–C20–H20C	109.5
H20B–C20–H20C	109.5
O1–C21–N2	121.3(4)
O1–C21–C18	119.3(4)
N2–C21–C18	119.4(3)
F1–C22–F3	107.3(4)
F1–C22–F2	103.8(5)
F3–C22–F2	105.2(5)
F1–C22–C4	114.9(4)
F3–C22–C4	112.4(4)
F2–C22–C4	112.4(4)
C24–C23–C28	119.4(3)
C24–C23–C43	106.8(3)
C28–C23–C43	133.8(3)
C25–C24–C23	122.6(3)
C25–C24–N3	129.1(3)
C23–C24–N3	108.2(3)
C26–C25–C24	117.0(4)
C26–C25–H25	121.5
C24–C25–H25	121.5
C25–C26–C27	121.7(4)
C25–C26–H26	119.2
C27–C26–H26	119.2
C28–C27–C26	121.0(3)
C28–C27–C42	120.2(4)
C26–C27–C42	118.7(4)
C27–C28–C23	118.4(3)
C27–C28–H28	120.8
C23–C28–H28	120.8
O5–C29–O6	123.0(3)
O5–C29–C43	124.0(4)
O6–C29–C43	113.0(3)
O6–C30–H30A	109.5
O6–C30–H30B	109.5
H30A–C30–H30B	109.5
O6–C30–H30C	109.5
H30A–C30–H30C	109.5
H30B–C30–H30C	109.5
N3–C31–C43	108.6(3)
N3–C31–C32	121.4(3)
C43–C31–C32	129.9(3)
C33–C32–C37	118.5(3)
C33–C32–C31	121.0(3)
C37–C32–C31	120.4(3)
C32–C33–C34	120.5(4)
C32–C33–H33	119.8
C34–C33–H33	119.8
C35–C34–C33	120.4(4)
C35–C34–H34	119.8
C33–C34–H34	119.8
C34–C35–C36	119.9(4)
C34–C35–H35	120.1
C36–C35–H35	120.1
C35–C36–C37	120.1(4)
C35–C36–H36	120.0
C37–C36–H36	120.0
C36–C37–C32	120.6(4)
C36–C37–H37	119.7
C32–C37–H37	119.7
N3–C38–C39	115.9(3)
N3–C38–H38A	108.3
C39–C38–H38A	108.3
N3–C38–H38B	108.3
C39–C38–H38B	108.3
H38A–C38–H38B	107.4
C40–C39–C44	114.0(4)
C40–C39–C38	111.2(3)
C44–C39–C38	109.1(3)
C40–C39–C41	110.7(4)
C44–C39–C41	106.3(3)
C38–C39–C41	105.1(4)
C39–C40–H40A	109.5
C39–C40–H40B	109.5
H40A–C40–H40B	109.5
C39–C40–H40C	109.5
H40A–C40–H40C	109.5

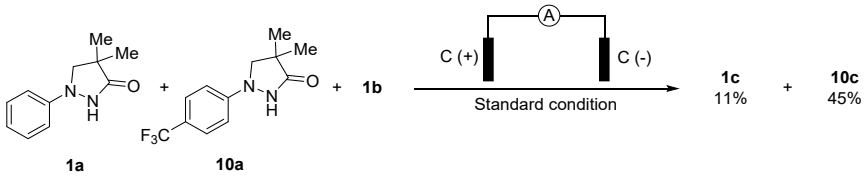
H40B–C40–H40C	109.5
C39–C41–H41A	109.5
C39–C41–H41B	109.5
H41A–C41–H41B	109.5
C39–C41–H41C	109.5
H41A–C41–H41C	109.5
H41B–C41–H41C	109.5
F6–C42–F4	107.8(5)
F6–C42–F5	105.1(5)
F4–C42–F5	101.6(4)
F6–C42–C27	114.5(4)
F4–C42–C27	114.5(4)
F5–C42–C27	112.2(4)
C31–C43–C23	107.7(3)
C31–C43–C29	128.3(3)
C23–C43–C29	124.0(3)
O4–C44–N4	121.5(4)
O4–C44–C39	119.6(4)
N4–C44–C39	119.0(4)
C1–N1–C10	109.0(3)
C1–N1–C17	124.9(3)
C10–N1–C17	125.8(3)
C21–N2–H2A	120.0
C21–N2–H2B	120.0
H2A–N2–H2B	120.0
C31–N3–C24	108.7(3)
C31–N3–C38	126.4(3)
C24–N3–C38	124.9(3)
C44–N4–H4A	120.0
C44–N4–H4B	120.0
H4A–N4–H4B	120.0
C8–O3–C9	118.3(3)
C29–O6–C30	118.0(3)

Table 5. Torsion angles for shelx

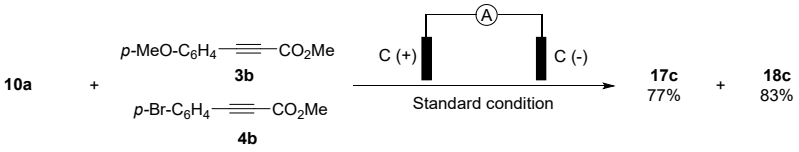
Atom–Atom–Atom–Atom	Torsion Angle [°]
N1–C1–C2–C3	176.4(4)
C6–C1–C2–C3	−0.3(6)
C1–C2–C3–C4	−0.1(6)
C2–C3–C4–C5	0.6(6)
C2–C3–C4–C22	−178.8(4)
C3–C4–C5–C6	−0.7(6)
C22–C4–C5–C6	178.6(4)
C4–C5–C6–C1	0.3(5)
C4–C5–C6–C7	−176.6(4)
N1–C1–C6–C5	−177.1(3)
C2–C1–C6–C5	0.2(5)
N1–C1–C6–C7	0.6(4)
C2–C1–C6–C7	177.9(3)
C5–C6–C7–C10	175.7(4)
C1–C6–C7–C10	−1.5(4)
C5–C6–C7–C8	−4.0(7)
C1–C6–C7–C8	178.8(3)
C10–C7–C8–O2	−177.3(4)
C6–C7–C8–O2	2.3(6)
C10–C7–C8–O3	3.0(6)
C6–C7–C8–O3	−177.4(3)
C6–C7–C10–N1	1.9(4)
C8–C7–C10–N1	−178.5(3)
C6–C7–C10–C11	−170.3(4)
C8–C7–C10–C11	9.4(7)
C7–C10–C11–C12	−71.6(5)
N1–C10–C11–C12	117.0(4)
C7–C10–C11–C16	106.0(5)
N1–C10–C11–C16	−65.4(5)
C16–C11–C12–C13	0.3(6)
C10–C11–C12–C13	177.9(4)
C11–C12–C13–C14	−0.2(7)
C12–C13–C14–C15	−0.2(8)
C13–C14–C15–C16	0.3(8)
C14–C15–C16–C11	−0.2(7)
C12–C11–C16–C15	−0.2(6)
C10–C11–C16–C15	−177.8(4)
N1–C17–C18–C19	51.4(4)
N1–C17–C18–C20	171.2(3)
N1–C17–C18–C21	−73.3(4)
C19–C18–C21–O1	165.7(4)
C20–C18–C21–O1	45.1(5)
C17–C18–C21–O1	−70.3(4)
C19–C18–C21–N2	−15.5(5)
C20–C18–C21–N2	−136.2(4)
C17–C18–C21–N2	108.4(4)
C5–C4–C22–F1	−10.2(7)
C3–C4–C22–F1	169.1(4)
C5–C4–C22–F3	−133.3(5)
C3–C4–C22–F3	46.1(6)
C5–C4–C22–F2	108.2(5)
C3–C4–C22–F2	−72.4(6)
C28–C23–C24–C25	1.2(6)

C43–C23–C24–C25	−176.5(3)
C28–C23–C24–N3	178.2(3)
C43–C23–C24–N3	0.6(4)
C23–C24–C25–C26	−1.2(6)
N3–C24–C25–C26	−177.6(4)
C24–C25–C26–C27	0.4(6)
C25–C26–C27–C28	0.5(7)
C25–C26–C27–C42	178.7(4)
C26–C27–C28–C23	−0.5(6)
C42–C27–C28–C23	−178.7(4)
C24–C23–C28–C27	−0.3(5)
C43–C23–C28–C27	176.6(4)
N3–C31–C32–C33	−115.5(4)
C43–C31–C32–C33	69.6(5)
N3–C31–C32–C37	65.9(5)
C43–C31–C32–C37	−109.0(4)
C37–C32–C33–C34	1.0(6)
C31–C32–C33–C34	−177.7(4)
C32–C33–C34–C35	−0.7(6)
C33–C34–C35–C36	0.3(7)
C34–C35–C36–C37	−0.2(7)
C35–C36–C37–C32	0.5(6)
C33–C32–C37–C36	−0.9(5)
C31–C32–C37–C36	177.7(3)
N3–C38–C39–C40	−51.7(4)
N3–C38–C39–C44	74.9(4)
N3–C38–C39–C41	−171.5(3)
C28–C27–C42–F6	113.9(6)
C26–C27–C42–F6	−64.3(7)
C28–C27–C42–F4	−11.4(6)
C26–C27–C42–F4	170.4(4)
C28–C27–C42–F5	−126.5(5)
C26–C27–C42–F5	55.3(6)
N3–C31–C43–C23	−1.6(4)
C32–C31–C43–C23	173.8(3)
N3–C31–C43–C29	−178.6(3)
C32–C31–C43–C29	−3.2(6)
C24–C23–C43–C31	0.6(4)
C28–C23–C43–C31	−176.6(4)
C24–C23–C43–C29	177.8(3)
C28–C23–C43–C29	0.7(6)
O5–C29–C43–C31	−179.8(4)
O6–C29–C43–C31	2.0(6)
O5–C29–C43–C23	3.6(6)
O6–C29–C43–C23	−174.7(3)
C40–C39–C44–O4	−167.5(4)
C38–C39–C44–O4	67.6(4)
C41–C39–C44–O4	−45.2(5)
C40–C39–C44–N4	12.2(5)
C38–C39–C44–N4	−112.7(4)
C41–C39–C44–N4	134.5(4)
C2–C1–N1–C10	−176.5(4)
C6–C1–N1–C10	0.6(4)
C2–C1–N1–C17	9.3(6)
C6–C1–N1–C17	−173.6(3)
C7–C10–N1–C1	−1.6(4)
C11–C10–N1–C1	171.6(3)
C7–C10–N1–C17	172.6(3)
C11–C10–N1–C17	−14.3(5)
C18–C17–N1–C1	80.7(4)
C18–C17–N1–C10	−92.6(4)
C43–C31–N3–C24	2.0(4)
C32–C31–N3–C24	−173.9(3)
C43–C31–N3–C38	−175.7(3)
C32–C31–N3–C38	8.5(5)
C25–C24–N3–C31	175.2(4)
C23–C24–N3–C31	−1.6(4)
C25–C24–N3–C38	−7.1(6)
C23–C24–N3–C38	176.1(3)
C39–C38–N3–C31	92.4(4)
C39–C38–N3–C24	−84.8(4)
O2–C8–O3–C9	−1.6(6)
C7–C8–O3–C9	178.0(4)
O5–C29–O6–C30	4.4(6)
C43–C29–O6–C30	−177.3(3)

(4) Competition experiments



In an oven-dried undivided three-necked flask (25 mL) equipped with a stir bar, **1a** (0.125 mmol), **10a** (0.125 mmol), $[Cp^*IrCl_2]_2$ (1.0 mol%) and KOAc (0.375 mmol) were combined and added. The flask was equipped with a carbon rods (ϕ = 6 mm, merge in solution 1.5 cm) as the anode and carbon rods (ϕ = 6 mm, merge in solution 1.5 cm) as the cathode and was then charged with nitrogen. Under the protection of nitrogen, **1b** (0.125 mmol) and MeOH (6.0 mL) were slowly injected into the reaction flask. The reaction mixture was stirred and electrolyzed at a constant current of 1 mA (0.42 mA/cm^2) under RT for 6 h. When the reaction was finished, the solution was concentrated in a vacuum. The desired product **1c** and **10c** was subjected to column chromatography on silica gel (**1c**: 11%, **10c**: 45%).



In an oven-dried undivided three-necked flask (25 mL) equipped with a stir bar, **10a** (0.25 mmol), $[Cp^*IrCl_2]_2$ (1.0 mol%) and KOAc (0.375 mmol) were combined and added. The flask was equipped with a carbon rods (ϕ = 6 mm, merge in solution 1.5 cm) as the anode and carbon rods (ϕ = 6 mm, merge in solution 1.5 cm) as the cathode and was then charged with nitrogen. Under the protection of nitrogen, **3b** (0.125 mmol), **4b** (0.125 mmol) and MeOH (6.0 mL) were slowly injected into the reaction flask. The reaction mixture was stirred and electrolyzed at a constant current of 1 mA (0.42 mA/cm^2) under RT for 6 h. When the reaction was finished, the solution was concentrated in a vacuum. The desired product **17c** and **18c** was subjected to column chromatography on silica gel (**17c**: 77%, **18c**: 83%).

(5) Cyclic voltammetry

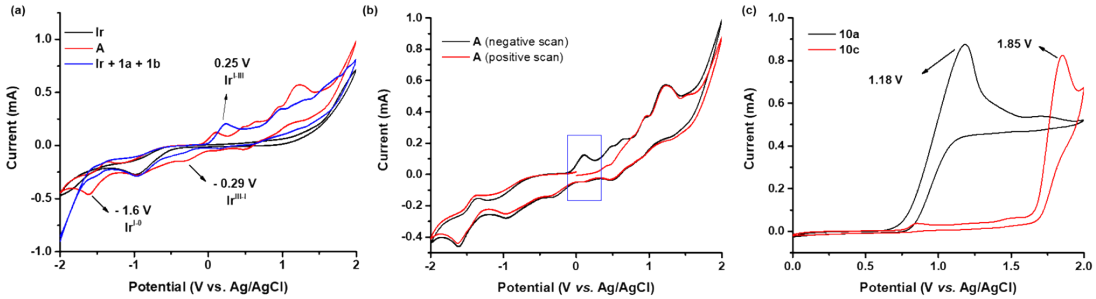
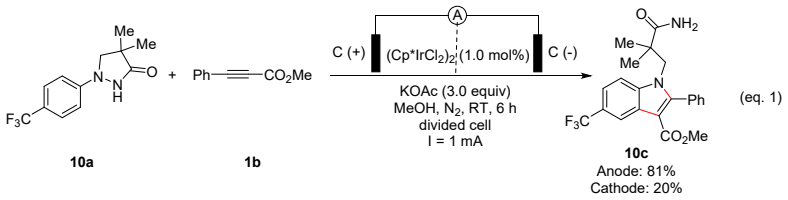


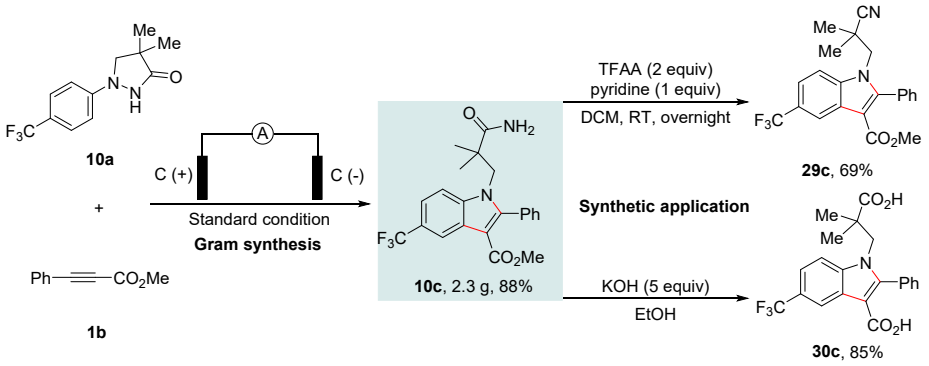
Figure S4. Cyclic voltammograms at glassy carbon as work electrode, Ag/AgCl as the reference electrode, Pt (1 x 1 cm^2) as counter electrode in 0.1 M $^nBu_4NBF_4$ in CH_3OH, scan rate 100 mV/s, **A** (0.025 mM), **10a** (0.25 mM), **1b** (0.25 mM), **10c** (0.25 mM), KOAc (0.75 mM), $(Cp^*IrCl_2)_2$ (2.0 mg). (a) negative scan. (b) positive scan, no oxidation peak at 0.25 V was observed during the positive scan, while an obvious oxidation peak appeared at 0.25 V (Ir^I to Ir^{III}) during the negative scan, indicating that the Ir^{III} produced by reduction elimination is more easily oxidized by the anode. (c) Substrates (**10a**: 1.18 V *vs.* Ag/AgCl) and products (**10c**: 1.85 V *vs.* Ag/AgCl) have higher oxidation potentials and will not be preferentially oxidized under given conditions.

(6) Divided cell electrolysis experiments



In an oven-dried divided H-cell (10.0 mL, anion exchange membrane) equipped with a stir bar, **10a** (0.25 mmol), $[Cp^*IrCl_2]_2$ (1.0 mol%) and KOAc (0.375 mmol) were combined and added in anode and cathode, respectively. The H-cell was equipped with a carbon rods (ϕ = 6 mm, merge in solution 1.5 cm) as the anode and carbon rods (ϕ = 6 mm, merge in solution 1.5 cm) as the cathode and was then charged with nitrogen. Under the protection of nitrogen, **3b** (0.125 mmol), **4b** (0.125 mmol) and MeOH (6.0 mL) were slowly injected into the reaction, respectively. The reaction mixture was stirred and electrolyzed at a constant current of 1 mA (0.42 mA/cm^2) under RT for 6 h. When the reaction was finished, the solution was concentrated in a vacuum. The desired product **10c** was subjected to column chromatography on silica gel (**Anode**: 81%, **Cathode**: 20%).

5. Gram-scale synthesis and Synthetic application



(1) Gram-scale synthesis

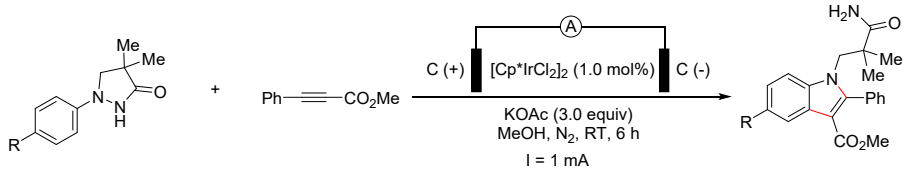
In an oven-dried undivided three-necked flask (500 mL) equipped with a stir bar, **10a** (12.5 mmol), $[Cp^*IrCl_2]_2$ (1.0 mol%) and KOAc (18.75 mmol) were combined and added. The flask was equipped with a carbon rods (ϕ = 6 mm, merge in solution 3 cm) as the anode and carbon rods (ϕ = 6 mm, merge in solution 3 cm) as the cathode and was then charged with nitrogen. Under the protection of nitrogen, **1b** (6.25 mmol) and MeOH (300.0 mL) were slowly injected into the reaction flask. The reaction mixture was stirred and electrolyzed at a constant current of 1 mA (0.85 mA/cm^2) under RT for 300 h. When the reaction was finished, the solution was concentrated in a vacuum. The desired product **10c** was subjected to column chromatography on silica gel (yield: 88%).

(2) Synthetic application

In an oven-dried round-bottom flask (10 mL) equipped with a stir bar, **10c** (0.25 mmol), TFAA (0.5 mmol), pyridine (0.25 mmol), DCM (4.0 mL) were combined and added. The reaction mixture was stirred under room temperature for overnight. Upon completion of the reaction, the reaction mixture was concentrated to remove the solvent, and then the pure product **29c** was obtained by flash column chromatography on silica gel (yield: 69%).

In an oven-dried round-bottom flask (10 mL) equipped with a stir bar, **10c** (0.25 mmol), KOH (1.25 mmol), EtOH (4.0 mL) were combined and added. The reaction mixture was stirred under room temperature for overnight. Upon completion of the reaction, the reaction mixture was concentrated to remove the solvent, and then the pure product **30c** was obtained by flash column chromatography on silica gel (yield: 85%).

6. Hammett plot Analysis



Entry	R	Conv.	σ_{para}	Log (conv.R/conv.H)
1	OMe	0.54	-0.268	-0.04
2	Me	0.57	-0.17	-0.022
3	H	0	0	0
4	F	0.73	0.062	0.085
5	Cl	0.75	0.227	0.096
6	CF_3	0.86	0.53	0.156
7	CN	0.98	1	0.213

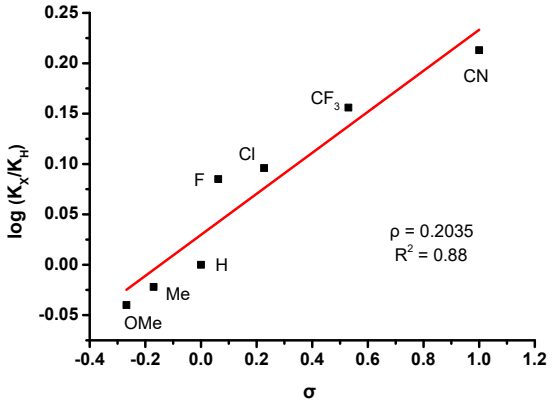
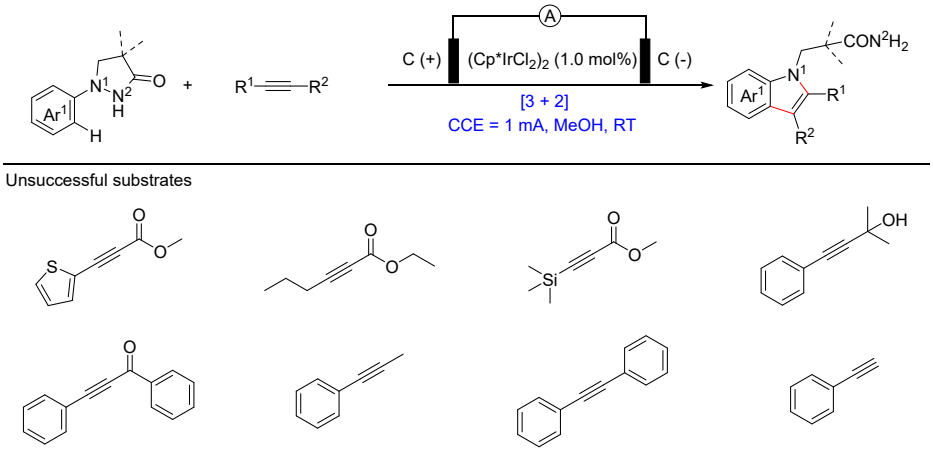
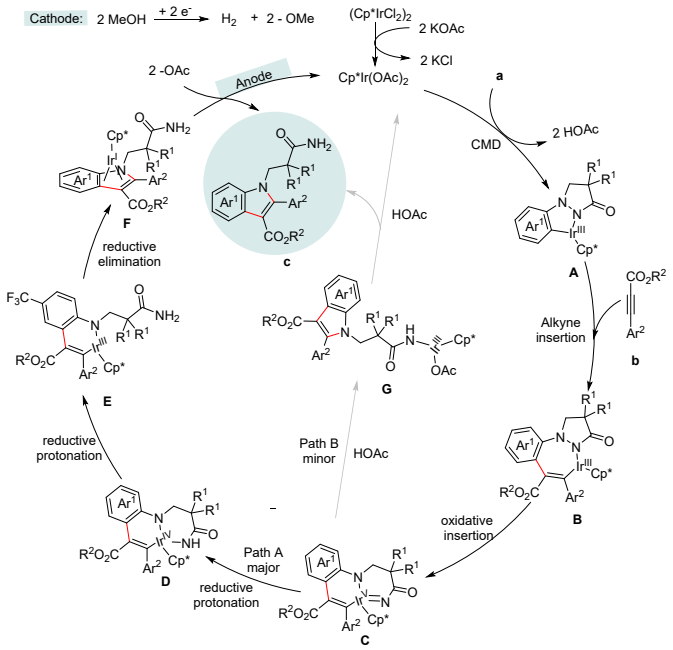


Figure S5. Hammett plot of relative initial rates.



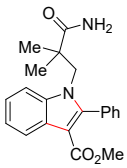
Scheme S1. Limitation of substrate scope.



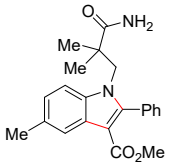
Scheme S2. Proposed reaction mechanism.

On the basis of our experimental results and previous reports, a possible catalytic mechanism is proposed for the Ir-catalyzed electrochemical C-H/N-N [3+2] annulation of phenidones with propiolates (Scheme S2). Initially, the active catalyst $Cp^*Ir(OAc)_2$ is generated via ligand exchange between $(Cp^*IrCl_2)_2$ and KOAc. Then, the *in situ* generated Ir^{III} catalyst undergoes a CMD process with phenidones, resulting in the formation of complex **A**. The subsequent step involves the regioselective insertion of alkynes, followed through Ir^{III} oxidative insertion into the activated N–N bond to obtain Ir^{V} complex **C**. Then, the $N{=}Ir^{V}$ intermediate **C** maybe undergoes a coherent reductive protonation to generate intermediate **E**, which subsequently undergoes reductive elimination to form the Ir^{I} complex **F**. However, the transition from steps C to D to E currently lacks clarity and is subject to further investigation in future studies. Finally, the catalytic cycle can be completed by regenerating Ir^{III} through anodic oxidation of Ir^{I} complex **F** assisted by $^{-}$OAc and releasing the desired product (Path A, major). Certainly, the possibility of the catalytic pathway via HOAc protonation cannot be entirely disregarded (Path B, minor).

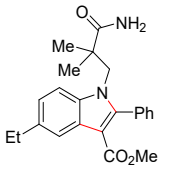
7. Detail descriptions for products



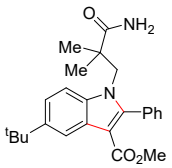
methyl 1-(3-amino-2,2-dimethyl-3-oxopropyl)-2-phenyl-1*H*-indole-3-carboxylate (1c): white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 60% isolated yield (26.3 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (m, 1H), 7.56 (m, 1H), 7.44 (m, 3H), 7.35 (m, 2H), 7.20 (dd, J = 6.1, 3.2 Hz, 2H), 5.28 (s, 2H), 4.38 (s, 2H), 3.68 (s, 3H), 0.84 (s, 6H).^{13}C NMR (126 MHz, DMSO) δ 178.1, 164.9, 147.3, 137.5, 131.7, 131.7, 129.2, 128.1, 126.3, 122.9, 122.1, 121.4, 112.8, 105.4, 50.9, 50.7, 43.9, 24.6. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{21}H_{23}N_2O_3$: 351.1703; found: 351.1712.



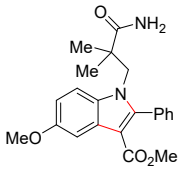
methyl 1-(3-amino-2,2-dimethyl-3-oxopropyl)-5-methyl-2-phenyl-1*H*-indole-3-carboxylate (2c): white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 57% isolated yield (25.9 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.49 (m, 4H), 7.39 (m, 2H), 7.08 (dd, *J* = 8.5, 1.4 Hz, 1H), 5.44 (d, *J* = 29.2 Hz, 2H), 4.40 (s, 2H), 3.73 (s, 3H), 2.49 (s, 3H), 0.88 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.0, 165.6, 147.0, 135.4, 131.7, 131.5, 131.2, 128.9, 128.0, 126.6, 124.5, 121.3, 111.5, 105.7, 50.8, 50.7, 43.9, 24.2, 21.5. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{22}H_{25}N_2O_3$: 365.1860; found: 365.1865. m. p. = 115-117 °C.



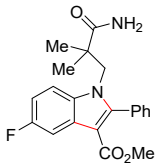
methyl 1-(3-amino-2,2-dimethyl-3-oxopropyl)-5-ethyl-2-phenyl-1*H*-indole-3-carboxylate (3c): white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 56% isolated yield (26.4 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.54 (m, 4H), 7.40 (m, 2H), 7.10 (dd, *J* = 8.5, 1.7 Hz, 1H), 5.59 (d, *J* = 106.3 Hz, 2H), 4.40 (s, 2H), 3.72 (s, 3H), 2.77 (q, *J* = 7.6 Hz, 2H), 1.30 (t, *J* = 7.6 Hz, 3H), 0.88 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.3, 165.6, 147.0, 138.4, 135.6, 131.6, 131.2, 128.9, 128.0, 126.6, 123.5, 120.1, 116.3, 111.6, 105.8, 50.8, 50.7, 43.9, 29.1, 24.2, 16.4. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{23}H_{27}N_2O_3$: 379.2016; found: 379.2018. m. p. = 116-118 °C.



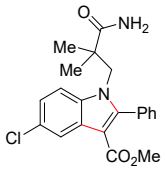
methyl 1-(3-amino-2,2-dimethyl-3-oxopropyl)-5-(tert-butyl)-2-phenyl-1*H*-indole-3-carboxylate (4c): white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 48% isolated yield (24.3 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (d, *J* = 1.5 Hz, 1H), 7.53 (d, *J* = 8.8 Hz, 1H), 7.48 (d, *J* = 6.1 Hz, 3H), 7.38 (m, 3H), 5.32 (d, *J* = 37.2 Hz, 2H), 4.41 (s, 2H), 3.72 (s, 3H), 1.42 (s, 9H), 0.91 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.9, 165.6, 146.9, 145.3, 135.3, 131.7, 131.2, 128.8, 128.0, 126.2, 121.3, 117.4, 111.2, 106.1, 50.9, 50.7, 43.9, 34.8, 31.8, 24.3. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{25}H_{31}N_2O_3$: 407.2329; found: 407.2328. m. p. = 120-122 °C.



methyl 1-(3-amino-2,2-dimethyl-3-oxopropyl)-5-methoxy-2-phenyl-1*H*-indole-3-carboxylate (5c): white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 54% isolated yield (25.7 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 2.5 Hz, 1H), 7.51 (m, 4H), 7.39 (m, 2H), 6.90 (dd, *J* = 9.0, 2.6 Hz, 1H), 5.46 (d, *J* = 36.4 Hz, 2H), 4.39 (s, 2H), 3.89 (s, 3H), 3.70 (s, 3H), 0.88 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.0, 165.6, 155.9, 147.1, 132.0, 131.5, 131.1, 128.9, 128.0, 127.3, 113.1, 112.7, 105.7, 103.1, 55.7, 51.0, 50.7, 43.9, 24.2. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{22}H_{25}N_2O_4$: 365.1860; found: 381.1813. m. p. = 110-112 °C.

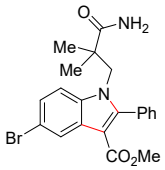


methyl 1-(3-amino-2,2-dimethyl-3-oxopropyl)-5-fluoro-2-phenyl-1*H*-indole-3-carboxylate (6c): white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 73% isolated yield (33.6 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 9.9, 2.6 Hz, 1H), 7.55 (dd, *J* = 9.0, 4.4 Hz, 1H), 7.50 (dd, *J* = 5.5, 1.5 Hz, 3H), 7.42 (m, 2H), 7.00 (td, *J* = 9.0, 2.6 Hz, 1H), 5.32 (d, *J* = 53.5 Hz, 2H), 4.43 (s, 2H), 3.74 (s, 3H), 0.89 (s, 6H). ^{13}C NMR (126 MHz, DMSO) δ 178.1, 164.5, 158.90 (d, *J* = 234.8 Hz), 148.8, 134.1, 131.6, 131.3, 129.3, 128.2, 127.03 (d, *J* = 11.0 Hz), 114.32 (d, *J* = 9.6 Hz), 111.09 (d, *J* = 25.8 Hz), 106.18 (d, *J* = 24.8 Hz), 105.52 (d, *J* = 4.2 Hz), 51.1, 51.0, 43.9, 24.6. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{21}H_{22}N_2O_3F$: 369.1609; found: 369.1627. m. p. = 135-137 °C.

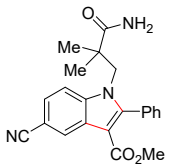


methyl 1-(3-amino-2,2-dimethyl-3-oxopropyl)-5-chloro-2-phenyl-1*H*-indole-3-carboxylate (7c): white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 75% isolated yield (36.1 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 2.0 Hz, 1H), 7.55 (d, *J* = 8.8 Hz, 1H), 7.50 (dd, *J* = 5.2, 1.7 Hz, 3H), 7.41 (m, 2H), 7.21 (dd, *J* = 8.8, 2.1 Hz, 1H), 5.32 (d, *J* = 52.1 Hz, 2H), 4.42 (s, 2H), 3.75 (s, 3H), 0.89 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.7, 165.0, 148.1, 135.4,

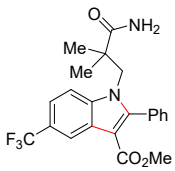
131.1, 130.9, 129.2, 128.1, 128.1, 127.4, 123.3, 121.2, 112.9, 105.9, 51.0, 50.9, 43.8, 24.2. HRMS (ESI) *m/z:* $[M+Na]^+$ calcd for $C_{21}H_{21}N_2O_3ClNa$: 407.1133; found: 407.1337. m. p. = 129-131 °C.



methyl 1-(3-amino-2,2-dimethyl-3-oxopropyl)-5-bromo-2-phenyl-1*H*-indole-3-carboxylate (8c): white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 80% isolated yield (42.9 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (d, *J* = 1.8 Hz, 1H), 7.53 (m, 4H), 7.41 (m, 2H), 7.33 (dd, *J* = 8.8, 1.9 Hz, 1H), 5.44 (d, *J* = 16.9 Hz, 2H), 4.41 (s, 2H), 3.74 (s, 3H), 0.88 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.7, 164.9, 147.9, 135.7, 131.1, 130.8, 129.2, 128.1, 127.9, 125.9, 124.3, 115.8, 113.4, 105.8, 51.0, 50.9, 43.8, 24.2. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{21}H_{22}N_2O_3Br$: 429.0808; found: 429.0809. m. p. = 127-129 °C.

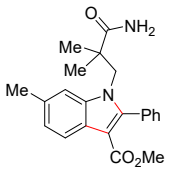


methyl 1-(3-amino-2,2-dimethyl-3-oxopropyl)-5-cyano-2-phenyl-1*H*-indole-3-carboxylate (9c): white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 98% isolated yield (45.9 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55 (s, 1H), 7.73 (d, *J* = 8.7 Hz, 1H), 7.54 (m, 3H), 7.47 (d, *J* = 8.6 Hz, 1H), 7.44 (m, 2H), 5.47 (s, 2H), 4.48 (s, 2H), 3.77 (s, 3H), 0.90 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.5, 164.5, 149.1, 138.6, 131.0, 130.3, 129.6, 128.2, 127.4, 126.1, 125.8, 120.2, 112.8, 106.8, 105.4, 51.1, 51.1, 43.8, 24.2. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{22}H_{22}N_3O_3$: 376.1656; found: 376.1661. m. p. = 114-116 °C.

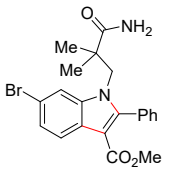


methyl 1-(3-amino-2,2-dimethyl-3-oxopropyl)-2-phenyl-5-(trifluoromethyl)-1*H*-indole-3-carboxylate (10c): white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 86% isolated yield (44.9 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 (s, 1H), 7.73 (d, *J* = 8.7 Hz, 1H), 7.51 (dd, *J* = 5.5, 4.2 Hz, 4H), 7.42 (m, 2H), 5.49 (d, *J* = 36.2 Hz, 2H), 4.48 (s, 2H), 3.76 (s,

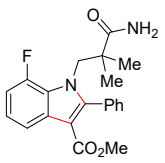
3H), 0.90 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.1, 164.9, 148.6, 138.4, 131.0, 130.6, 129.4, 128.1, 125.8, 125.07 (q, J = 271.7 Hz), 124.47 (q, J = 31.9 Hz), 119.69 (q, J = 3.4 Hz), 119.55 (q, J = 4.2 Hz), 112.2, 106.9, 51.0, 43.8, 24.1. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{22}H_{22}N_2O_3F_3$: 419.1577; found: 419.1588. m. p. = 119-121 °C.



methyl 1-(3-amino-2,2-dimethyl-3-oxopropyl)-6-methyl-2-phenyl-1*H*-indole-3-carboxylate (11c): white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 54% isolated yield (24.6 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, J = 8.2 Hz, 1H), 7.47 (t, J = 6.2 Hz, 3H), 7.39 (s, 3H), 7.10 (d, J = 8.2 Hz, 1H), 5.31 (d, J = 16.0 Hz, 2H), 4.41 (s, 2H), 3.74 (s, 3H), 2.48 (s, 3H), 0.90 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.9, 165.5, 146.5, 137.5, 132.9, 131.5, 131.2, 128.9, 128.0, 124.1, 123.9, 121.3, 111.6, 106.1, 50.7, 50.6, 44.0, 24.3, 21.9. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{22}H_{25}N_2O_3$: 365.1860; found: 365.1865. m. p. = 117-119 °C.

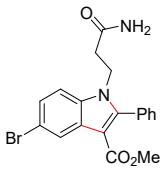


methyl 1-(3-amino-2,2-dimethyl-3-oxopropyl)-6-bromo-2-phenyl-1*H*-indole-3-carboxylate (12c): white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 48% isolated yield (25.8 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, J = 8.6 Hz, 1H), 7.78 (d, J = 1.1 Hz, 1H), 7.51 (m, 3H), 7.40 (m, 2H), 7.35 (dd, J = 8.6, 1.4 Hz, 1H), 5.60 (d, J = 144.4 Hz, 2H), 4.40 (s, 2H), 3.73 (s, 3H), 0.89 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.8, 165.0, 147.4, 137.8, 131.1, 130.9, 129.2, 128.1, 125.4, 125.2, 123.0, 116.6, 114.7, 106.4, 50.9, 43.9, 24.2. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{21}H_{22}N_2O_3Br$: 429.0808; found: 429.0809. m. p. = 112-114 °C.

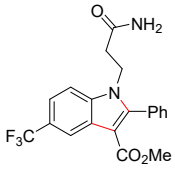


methyl 1-(3-amino-2,2-dimethyl-3-oxopropyl)-7-fluoro-2-phenyl-1*H*-indole-3-carboxylate (13c): white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 22%

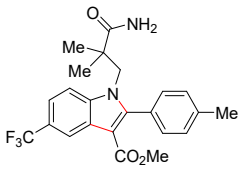
isolated yield (10.1 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.0 Hz, 1H), δ 7.46 (t, *J* = 12.5 Hz, 5H)., 7.18 (td, *J* = 8.0, 4.6 Hz, 1H), 6.99 (dd, *J* = 13.2, 7.9 Hz, 1H), 5.23 (d, *J* = 33.7 Hz, 2H), 4.63 (s, 2H), 3.73 (s, 3H), 0.94 (s, 6H). ^{13}C NMR (126 MHz, DMSO) δ 177.7, 164.5, 149.81 (d, *J* = 244.4 Hz), 148.6, 130.7, 130.04 (d, *J* = 4.3 Hz), 129.4, 128.1, 125.68 (d, *J* = 8.2 Hz), 122.65 (d, *J* = 7.1 Hz), 117.83 (d, *J* = 3.0 Hz), 109.39 (d, *J* = 19.1 Hz), 106.62 (d, *J* = 1.1 Hz), 52.33 (d, *J* = 6.3 Hz), 51.1, 44.2, 23.4. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{21}H_{22}N_2O_3F$: 369.1609; found: 369.1627. m. p. = 104-106 °C.



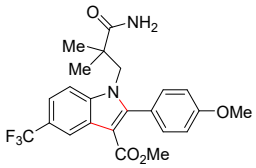
methyl 1-(3-amino-3-oxopropyl)-5-bromo-2-phenyl-1*H*-indole-3-carboxylate (14c): white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 51% isolated yield (25.6 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (d, *J* = 1.6 Hz, 1H), 7.50 (dd, *J* = 4.9, 1.7 Hz, 3H), 7.41 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.38 (m, 3H), 5.30 (d, *J* = 51.2 Hz, 2H), 4.32 (t, *J* = 7.6 Hz, 2H), 3.73 (s, 3H), 2.43 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.3, 164.9 147.2, 134.4, 130.8, 129.8, 129.4, 128.4, 128.2, 126.1, 124.7, 115.8, 111.6, 105.5, 50.9, 39.8, 35.3. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{19}H_{18}N_2O_3Br$: 401.0495; found: 401.0514. m. p. = 108-110 °C.



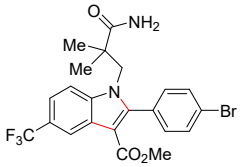
methyl 1-(3-amino-3-oxopropyl)-2-phenyl-5-(trifluoromethyl)-1*H*-indole-3-carboxylate (15c): white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 58% isolated yield (28.3 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.49 (t, *J* = 8.6 Hz, 2H), 7.42 (dd, *J* = 7.7, 2.7 Hz, 3H), 7.30 (m, 2H), 5.40 (d, *J* = 90.2 Hz, 2H), 4.29 (t, *J* = 7.7 Hz, 2H), 3.67 (s, 3H), 2.36 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.5, 164.8, 147.9, 137.1, 130.6, 129.8, 129.5, 128.5, 126.1, 125.06 (q, *J* = 271.8 Hz), 124.65 (q, *J* = 32.2 Hz), 120.01 – 119.84 (m), 110.5, 106.6, 51.0, 39.9, 35.3. HRMS (ESI) *m/z:* $[M+Na]^+$ calcd for $C_{20}H_{17}N_2O_3F_3Na$: 413.1083; found: 413.1100. m. p. = 111-113 °C.



methyl 1-(3-amino-2,2-dimethyl-3-oxopropyl)-2-(p-tolyl)-5-(trifluoromethyl)-1*H*-indole-3-carboxylate (16c): white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 71% isolated yield (38.3 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.62 (d, *J* = 8.7 Hz, 1H), 7.39 (d, *J* = 8.7 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.3 Hz, 2H), 5.41 (d, *J* = 50.6 Hz, 2H), 4.39 (s, 2H), 3.69 (s, 3H), 2.37 (s, 3H), 0.82 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.8, 164.9, 149.0, 139.4, 138.3, 130.9, 128.9, 127.6, 125.8, 125.10 (q, *J* = 271.6 Hz), 124.39 (q, *J* = 31.9 Hz), 119.74 – 119.27 (m), 112.2, 106.8, 51.0, 43.9, 24.2, 21.5. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{23}H_{24}N_2O_3F_3$: 433.1734; found: 433.1741. m. p. = 119-121 °C.

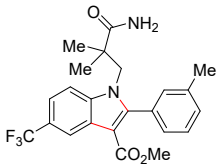


methyl 1-(3-amino-2,2-dimethyl-3-oxopropyl)-2-(4-methoxyphenyl)-5-(trifluoromethyl)-1*H*-indole-3-carboxylate (17c): white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 86% isolated yield (48.2 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.62 (d, *J* = 8.7 Hz, 1H), 7.39 (d, *J* = 8.7 Hz, 1H), 7.23 (d, *J* = 8.2 Hz, 2H), 6.95 (d, *J* = 8.3 Hz, 2H), 5.40 (d, *J* = 39.7 Hz, 2H), 4.40 (s, 2H), 3.81 (s, 3H), 3.70 (s, 3H), 0.83 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.7, 164.9, 160.2, 148.7, 138.3, 132.4, 125.8, 125.10 (q, *J* = 271.6 Hz), 124.40 (q, *J* = 31.7 Hz), 122.6, 119.78 – 119.24 (m), 113.6, 112.1, 106.8, 55.2, 51.0, 43.9, 24.2. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{23}H_{24}N_2O_4F_3$: 449.1683; found: 449.1691. m. p. = 117-119 °C.

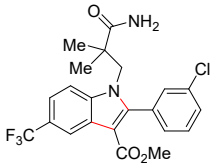


methyl 1-(3-amino-2,2-dimethyl-3-oxopropyl)-2-(4-bromophenyl)-5-(trifluoromethyl)-1*H*-indole-3-carboxylate (18c): white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 96% isolated yield (59.6 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.63 (d, *J* = 8.8 Hz, 1H), 7.58 (d, *J* = 8.5 Hz, 2H), 7.42 (dd, *J* = 8.8, 1.4 Hz, 1H), 7.21 (d, *J* = 8.3 Hz, 2H), 5.41 (d, *J*

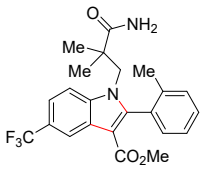
= 58.3 Hz, 2H), 4.38 (s, 2H), 3.71 (s, 3H), 0.86 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.5, 164.7, 147.1, 138.4, 132.7, 131.5, 129.6, 125.7, 124.99 (q, *J* = 270.2 Hz), 124.70 (q, *J* = 28.6 Hz), 124.0, 119.97 (q, *J* = 3.6 Hz), 119.70 (q, *J* = 3.9 Hz), 117.9, 112.2, 107.3, 51.1, 44.0, 24.3, 21.2. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{22}H_{21}N_2O_3F_3Br$: 497.0682; found: 497.0687. m. p. = 120-122 °C.



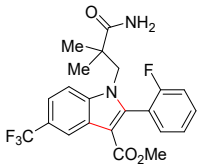
methyl 1-(3-amino-2,2-dimethyl-3-oxopropyl)-2-(m-tolyl)-5-(trifluoromethyl)-1*H*-indole-3-carboxylate (19c): white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 56% isolated yield (30.3 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.70 (d, *J* = 8.7 Hz, 1H), 7.48 (d, *J* = 8.7 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 7.7 Hz, 1H), 7.20 (t, *J* = 7.7 Hz, 2H), 5.46 (d, *J* = 23.5 Hz, 2H), 4.47 (d, *J* = 15.1 Hz, 2H), 3.77 (s, 3H), 2.44 (s, 3H), 0.91 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.9, 164.8, 148.9, 138.3, 137.8, 131.3, 130.6, 130.1, 128.3, 128.0, 125.8, 125.08 (q, *J* = 272.2 Hz), 124.45 (q, *J* = 32.3 Hz), 119.67 – 119.47 (m), 112.1, 106.9, 51.1, 51.0, 43.8, 21.5. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{23}H_{24}N_2O_3F_3$: 433.1734; found: 433.1741. m. p. = 125-127 °C.



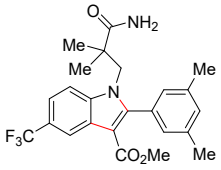
methyl 1-(3-amino-2,2-dimethyl-3-oxopropyl)-2-(3-chlorophenyl)-5-(trifluoromethyl)-1*H*-indole-3-carboxylate (20c): white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 68% isolated yield (38.4 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.64 (d, *J* = 8.7 Hz, 1H), 7.44 (m, 2H), 7.39 (d, *J* = 7.5 Hz, 1H), 7.34 (s, 1H), 7.23 (d, *J* = 7.3 Hz, 1H), 5.42 (d, *J* = 44.6 Hz, 2H), 4.38 (s, 2H), 3.70 (s, 3H), 0.87 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.5, 164.6, 146.6, 138.4, 134.1, 132.5, 131.1, 129.5, 129.4, 125.6, 124.99 (q, *J* = 272.0 Hz), 124.70 (q, *J* = 32.0 Hz), 120.02 (q, *J* = 3.4 Hz), 119.72 (q, *J* = 4.3 Hz), 112.3, 107.4, 51.2, 51.1, 43.9, 24.2. HRMS (ESI) *m/z:* $[M+Na]^+$ calcd for $C_{22}H_{20}N_2O_3F_3ClNa$: 475.1007; found: 475.1013. m. p. = 122-124 °C.



methyl 1-(3-amino-2,2-dimethyl-3-oxopropyl)-2-(o-tolyl)-5-(trifluoromethyl)-1*H*-indole-3-carboxylate (21c): white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 22% isolated yield (11.9 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (s, 1H), 7.73 (d, *J* = 8.7 Hz, 1H), 7.50 (dd, *J* = 8.7, 1.5 Hz, 1H), 7.43 (m, 1H), 7.34 (dd, *J* = 7.7, 3.6 Hz, 2H), 7.31 (d, *J* = 1.8 Hz, 1H), 5.49 (s, 2H), 4.30 (dd, *J* = 324.3, 14.9 Hz, 2H), 3.76 (s, 3H), 2.04 (s, 3H), 0.97 (d, *J* = 15.7 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.5, 164.8, 147.9, 137.1, 130.6, 129.8, 129.5, 128.5, 126.1, 125.06 (q, *J* = 271.8 Hz), 124.65 (q, *J* = 32.2 Hz), 120.00 – 119.79 (m), 110.5, 106.6, 51.0, 39.9, 22.6, 14.1. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{23}H_{24}N_2O_3F_3$: 433.1734; found: 433.1741. m. p. = 114-116 °C.

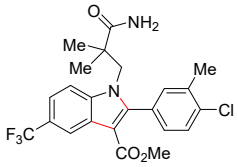


methyl 1-(3-amino-2,2-dimethyl-3-oxopropyl)-2-(2-fluorophenyl)-5-(trifluoromethyl)-1*H*-indole-3-carboxylate (22c): white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 31% isolated yield (16.9 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.65 (d, *J* = 8.8 Hz, 1H), 7.48 (m, 2H), 7.28 (m, 2H), 7.16 (t, *J* = 9.0 Hz, 1H), 5.33 (d, *J* = 21.0 Hz, 2H), 4.35 (s, 2H), 3.72 (s, 3H), 0.88 (d, *J* = 8.9 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.5, 164.5, 160.43 (d, *J* = 248.9 Hz), 142.0, 138.7, 131.89 (d, *J* = 8.3 Hz), 125.7, 125.02 (q, *J* = 271.8 Hz), 124.56 (q, *J* = 31.8 Hz), 124.06 (d, *J* = 3.5 Hz), 119.91 (q, *J* = 5.2 Hz), 119.66 (q, *J* = 4.2 Hz), 119.11 (d, *J* = 15.2 Hz), 115.96 (d, *J* = 21.7 Hz), 112.2, 108.1, 51.6, 51.1, 43.9, 24.2. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{22}H_{21}N_2O_3F_4$: 437.1483; found: 437.1490. m. p. = 118-120 °C.

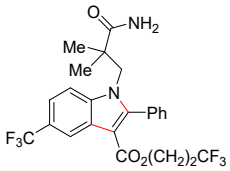


methyl 1-(3-amino-2,2-dimethyl-3-oxopropyl)-2-(3,5-dimethylphenyl)-5-(trifluoromethyl)-1*H*-indole-3-carboxylate (23c): white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 46% isolated yield (25.7 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (s,

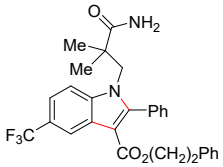
1H), 7.62 (d, J = 8.7 Hz, 1H), 7.39 (d, J = 8.7 Hz, 1H), 7.05 (s, 1H), 6.92 (s, 2H), 5.35 (s, 2H), 4.38 (s, 2H), 3.70 (s, 3H), 2.32 (s, 6H), 0.84 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.0, 164.9, 149.2, 138.3, 137.6, 131.0, 130.4, 128.6, 125.8, 125.11 (q, J = 271.8 Hz), 124.36 (q, J = 31.9 Hz), 119.54 (q, J = 3.2 Hz), 119.47 (q, J = 4.3 Hz), 112.1, 106.8, 51.0, 51.0, 43.8, 24.2, 21.3. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{24}H_{26}N_2O_3F_3$: 447.1980; found: 447.1893. m. p. = 177-179 °C.



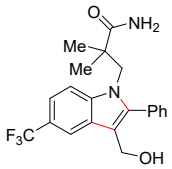
methyl 1-(3-amino-2,2-dimethyl-3-oxopropyl)-2-(3-chloro-4-methylphenyl)-5-(trifluoromethyl)-1*H*-indole-3-carboxylate (24c): white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 57% isolated yield (33.3 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.62 (d, J = 8.7 Hz, 1H), 7.42 (m, 2H), 7.17 (s, 1H), 7.12 (d, J = 8.1 Hz, 1H), 5.45 (d, J = 93.5 Hz, 2H), 4.37 (d, J = 15.4 Hz, 2H), 3.70 (s, 3H), 2.38 (s, 3H), 0.85 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.7, 164.8, 147.5, 138.4, 136.1, 135.7, 133.1, 130.0, 129.1, 128.9, 125.02 (q, J = 272.3 Hz), 124.57 (q, J = 32.1 Hz), 119.82 (q, J = 3.4 Hz), 119.63 (q, J = 4.2 Hz), 112.2, 107.2, 51.1, 51.1, 43.9, 20.2. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{23}H_{23}N_2O_3F_3Cl$: 467.1344; found: 467.1348. m. p. = 172-174 °C.



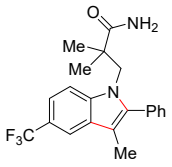
3,3,3-trifluoropropyl 1-(3-amino-2,2-dimethyl-3-oxopropyl)-2-phenyl-5-(trifluoromethyl)-1*H*-indole-3-carboxylate (25c): white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 34% isolated yield (21.2 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.65 (d, J = 8.7 Hz, 1H), 7.47 (m, 4H), 7.32 (dd, J = 6.5, 2.9 Hz, 2H), 5.37 (s, 2H), 4.40 (s, 2H), 4.30 (t, J = 6.3 Hz, 2H), 2.34 (m, 2H), 0.84 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.7, 163.8, 148.9, 138.4, 131.0, 130.7, 129.5, 128.1, 125.9, 125.41 (q, J = 271.8 Hz), 125.37 (q, J = 277.2 Hz), 124.74 (q, J = 31.9 Hz), 119.88 (q, J = 3.4 Hz), 119.44 (q, J = 4.4 Hz), 115.5, 112.3, 106.3, 56.57 (q, J = 3.8 Hz), 51.2, 43.8, 33.37 (q, J = 29.2 Hz), 24.2. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{24}H_{23}N_2O_3F_6$: 501.1607; found: 501.1606. m. p. = 125-127 °C.



phenethyl 1-(2,2-dimethyl-3-oxobutyl)-2-phenyl-5-(trifluoromethyl)-1*H*-indole-3-carboxylate (26c): white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 58% isolated yield (36.8 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.61 (d, *J* = 8.8 Hz, 1H), 7.40 (dd, *J* = 8.8, 5.5 Hz, 4H), 7.30 (m, 2H), 7.19 (m, 2H), 7.12 (d, *J* = 7.1 Hz, 1H), 7.07 (d, *J* = 7.7 Hz, 2H), 5.38 (d, *J* = 42.2 Hz, 2H), 4.37 (s, 2H), 4.33 (t, *J* = 6.9 Hz, 2H), 2.81 (t, *J* = 6.8 Hz, 2H), 0.81 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.8, 164.3, 148.5, 138.4, 138.0, 131.1, 130.8, 129.3, 128.7, 128.4, 128.1, 126.4, 125.9, 125.07 (q, *J* = 271.7 Hz), 124.48 (q, *J* = 31.9 Hz), 119.76 – 119.58 (m), 112.1, 107.0, 64.5, 51.1, 43.8, 35.0, 24.2. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{29}H_{28}N_2O_3F$: 509.2047; found: 509.2048. m. p. = 119-121 °C.

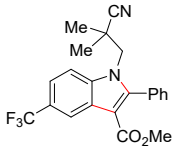


3-(3-(hydroxymethyl)-2-phenyl-5-(trifluoromethyl)-1*H*-indol-1-yl)-2,2-dimethylpropanamide (27c): white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 81% isolated yield (39.5 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.55 (d, *J* = 8.7 Hz, 1H), 7.36 (t, *J* = 1.7 Hz, 1H), 7.32 (dd, *J* = 13.7, 6.1 Hz, 4H), 7.23 (d, *J* = 7.0 Hz, 2H), 5.29 (s, 2H), 4.43 (s, 2H), 4.38 (s, 2H), 0.74 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.1, 142.3, 138.7, 130.9, 130.7, 127.1, 125.30 (q, *J* = 267.6 Hz), 122.47 (q, *J* = 31.8 Hz), 118.84 (q, *J* = 9.2 Hz), 116.54 (q, *J* = 8.6 Hz), 112.1, 111.7, 63.1, 51.1, 44.3, 23.9. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{21}H_{22}N_2O_2F_3$: 391.1628; found: 391.1633. m. p. = 145-147 °C.

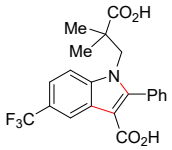


2,2-dimethyl-3-(3-methyl-2-phenyl-5-(trifluoromethyl)-1*H*-indol-1-yl)-propanamide (28c): white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 34% isolated yield (15.9 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.44 (dd, *J* = 14.5, 7.4 Hz, 3H), 7.37 (d, *J* = 7.3 Hz, 1H), 7.34 (s, 1H), 7.29 (s, 1H), 7.27 (s, 1H), 5.62 (s, 1H), 5.30 (s, 1H), 4.42 (s, 2H), 2.17 (s, 3H),

0.80 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.1, 139.4, 138.6, 131.8, 131.0, 128.6, 128.2, 127.7, 125.48 (q, *J* = 271.4 Hz), 121.63 (q, *J* = 31.7 Hz), 118.44 (q, *J* = 3.4 Hz), 116.29 (q, *J* = 4.2 Hz), 111.4, 110.8, 51.1, 44.4, 24.0, 9.2. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{21}H_{22}N_2OF_3$: 375.1679; found: 375.1689. m. p. = 130-132 °C.



methyl 1-(2-cyano-2-methylpropyl)-2-phenyl-5-(trifluoromethyl)-1*H*-indole-3-carboxylate (29c): white solid was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 69% isolated yield (34.5 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.67 (d, *J* = 8.7 Hz, 1H), 7.51 (d, *J* = 8.7 Hz, 1H), 7.48 (m, 3H), 7.36 (m, 2H), 4.32 (s, 2H), 3.70 (s, 3H), 1.06 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.6, 148.0, 138.0, 131.1, 130.1, 129.6, 128.3, 126.1, 125.01 (q, *J* = 32.0 Hz), 124.94 (q, *J* = 272.0 Hz), 123.5, 120.17 – 119.85 (m), 111.8, 107.8, 51.1, 50.7, 34.1, 25.7. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{22}H_{20}N_2O_2F_3$: 401.1471; found: 401.1475. m. p. = 125-127 °C.

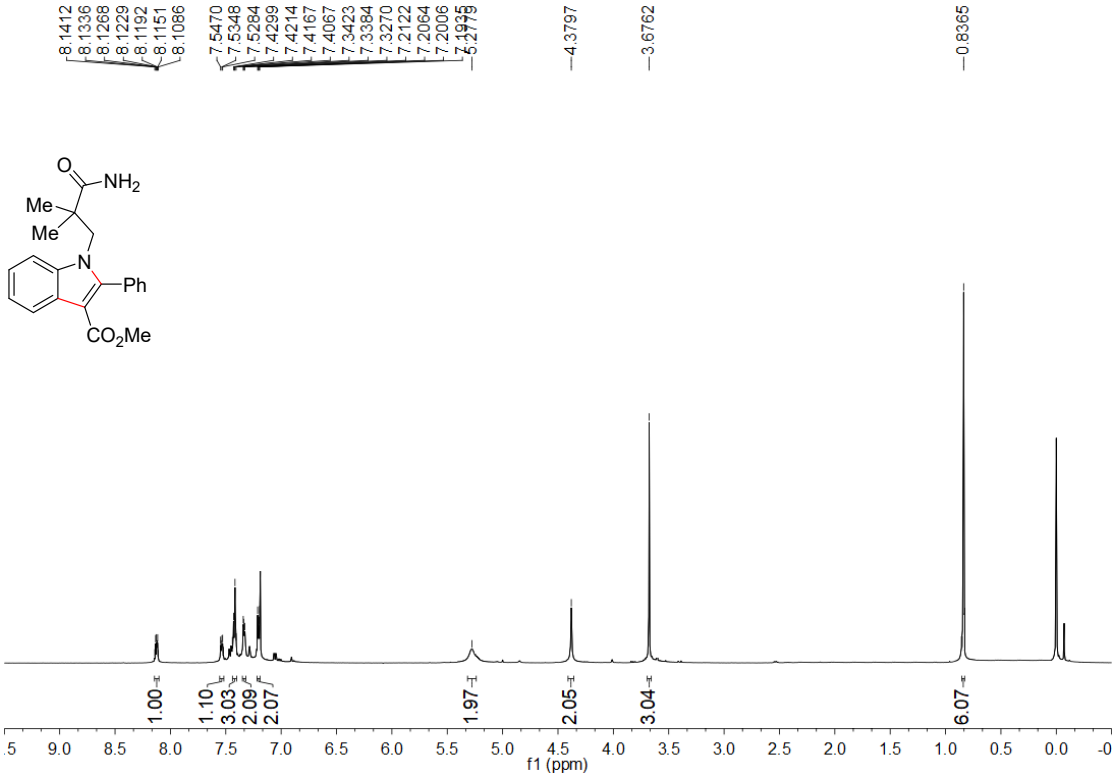


1-(2-carboxy-2-methylpropyl)-2-phenyl-5-(trifluoromethyl)-1*H*-indole-3-carboxylic acid (30c): yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/1) with 85% isolated yield (43.0 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (s, 1H), 7.62 (d, *J* = 8.7 Hz, 1H), 7.40 (dd, *J* = 9.4, 6.9 Hz, 4H), 7.33 (s, 2H), 6.39 (s, 1H), 5.38 (s, 1H), 4.40 (d, *J* = 11.2 Hz, 2H), 0.81 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.9, 168.9, 149.2, 138.5, 131.1, 130.4, 129.4, 128.2, 126.3, 125.02 (q, *J* = 265.3 Hz), 124.69 (q, *J* = 31.6 Hz), 120.08 – 119.65 (m), 112.1, 106.4, 51.0, 43.8, 24.1. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{21}H_{19}NO_4F_3$: 406.1261; found: 406.1264.

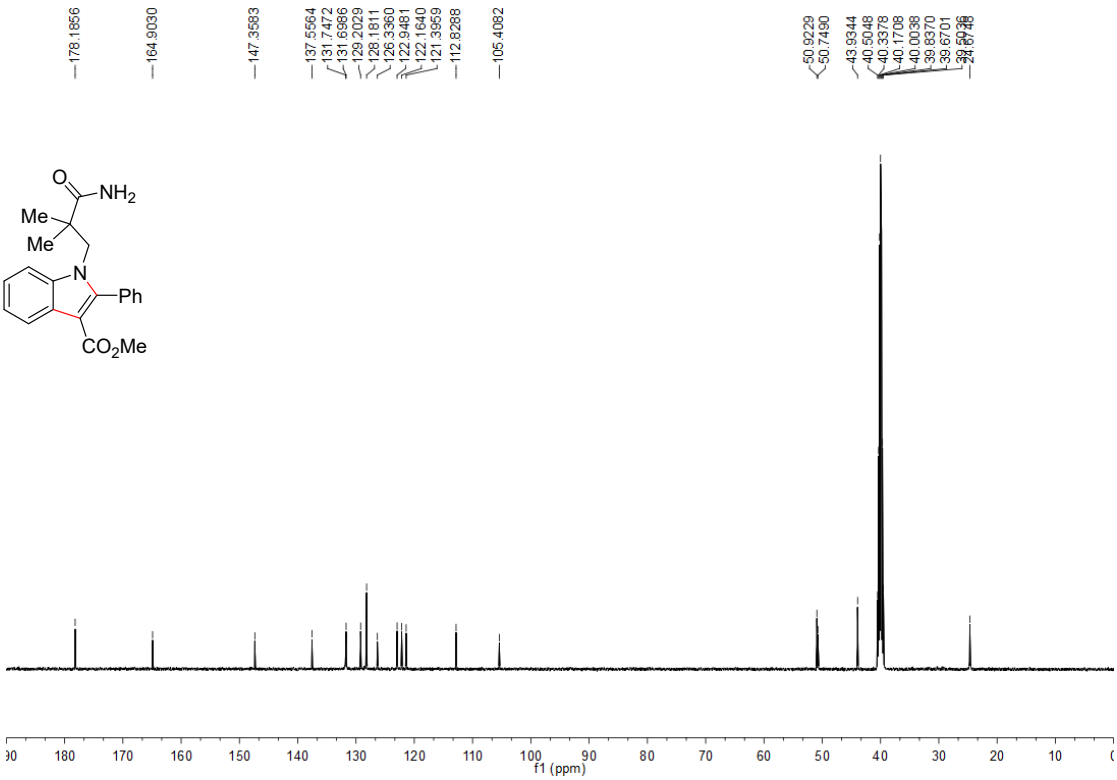
8. Copies of product NMR Spectra

1c

^{1}H NMR



^{13}C NMR



2c

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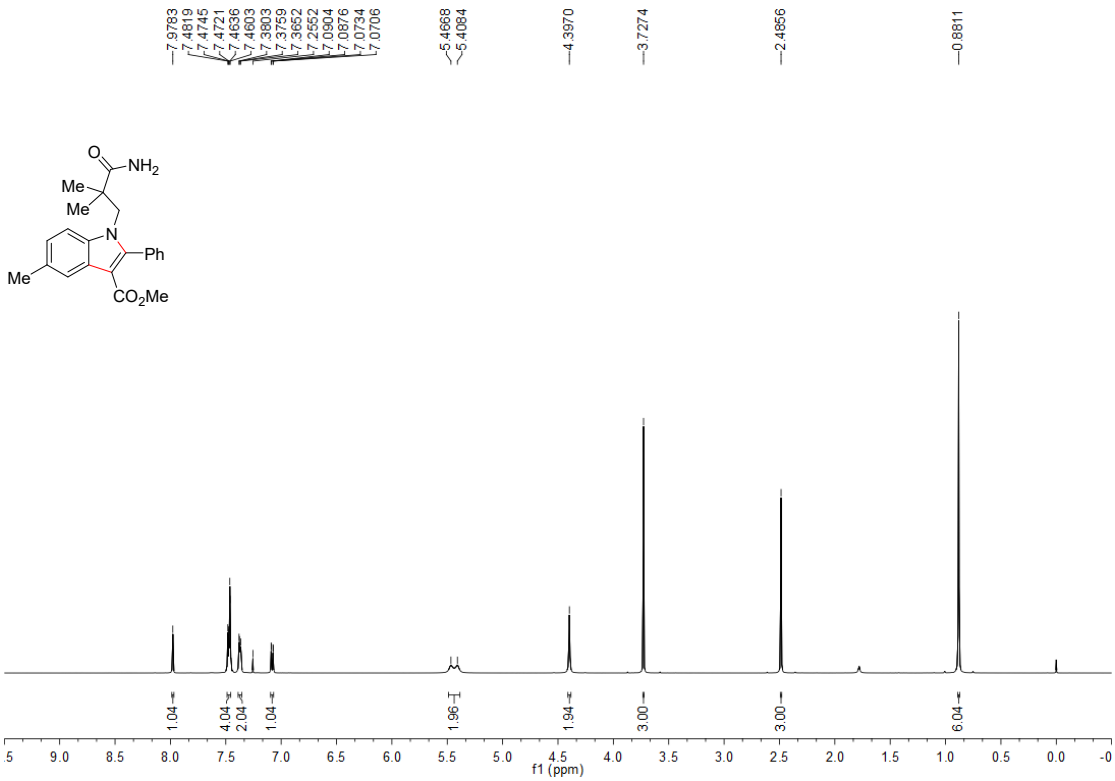

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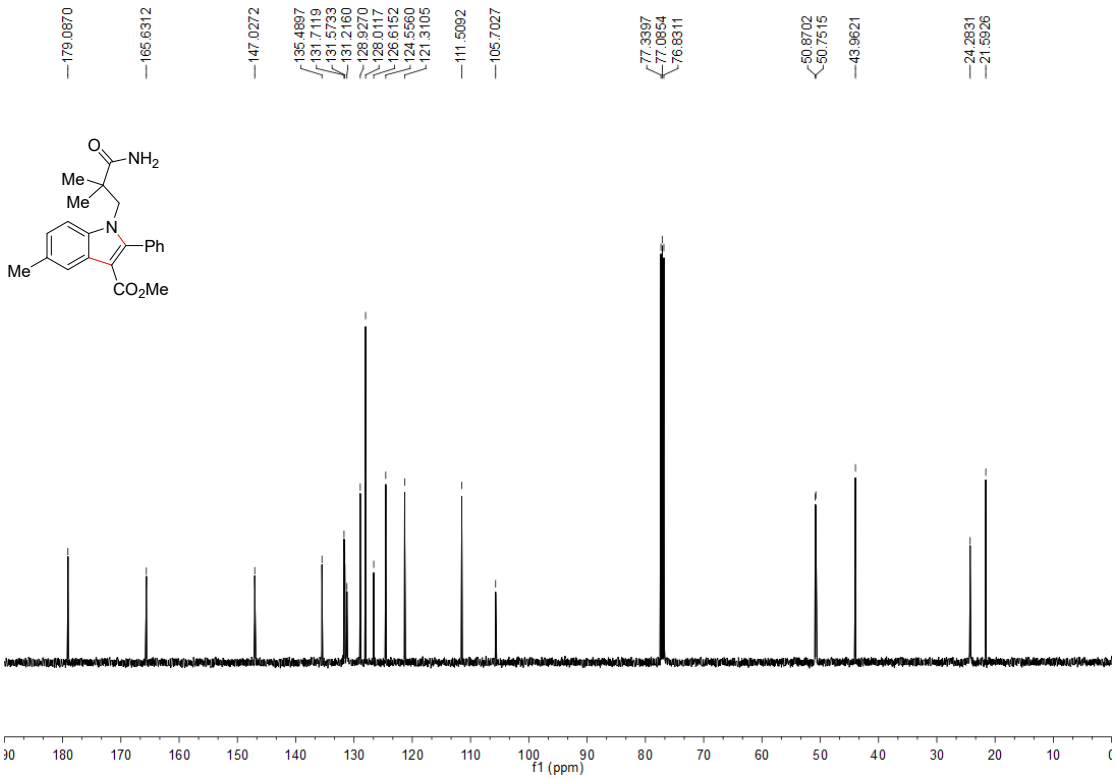

3c

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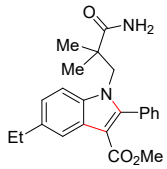

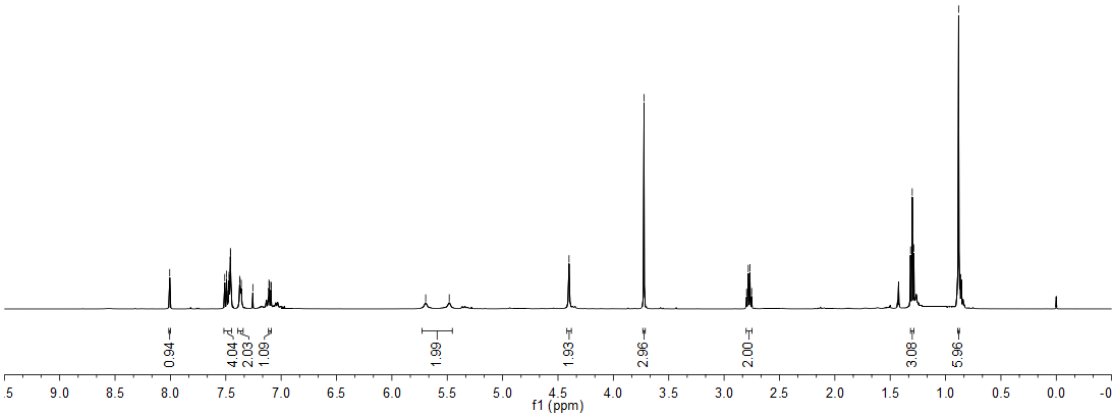

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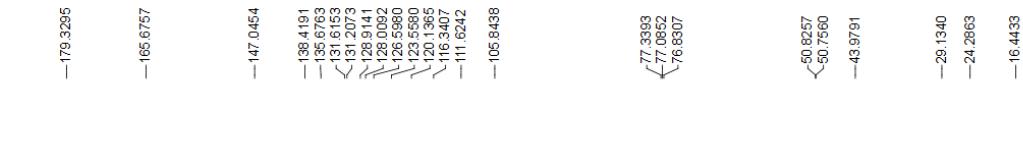

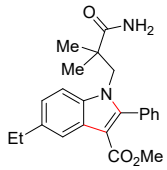

4c

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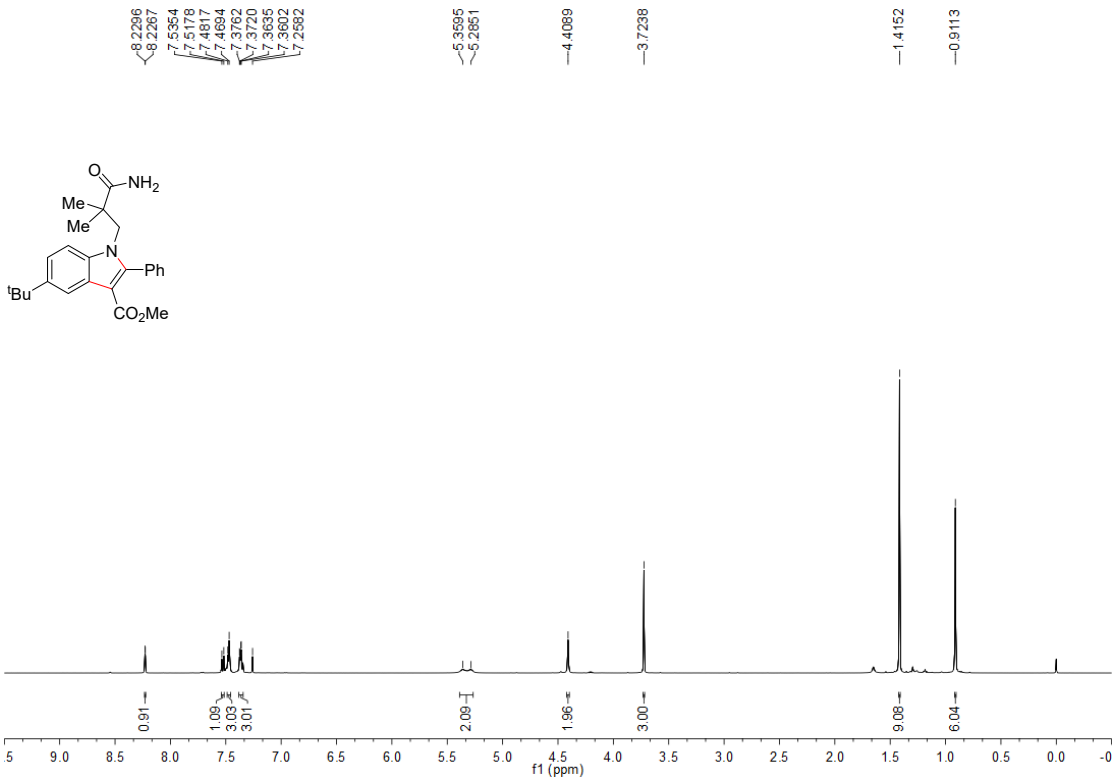

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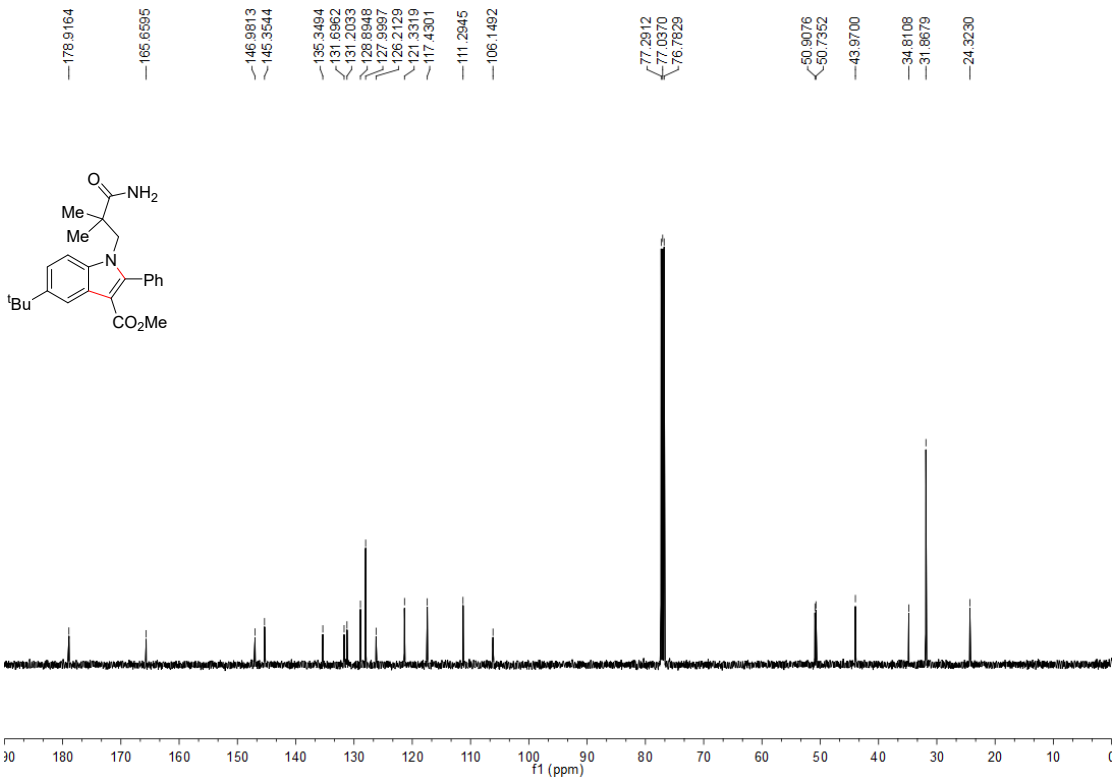

5c

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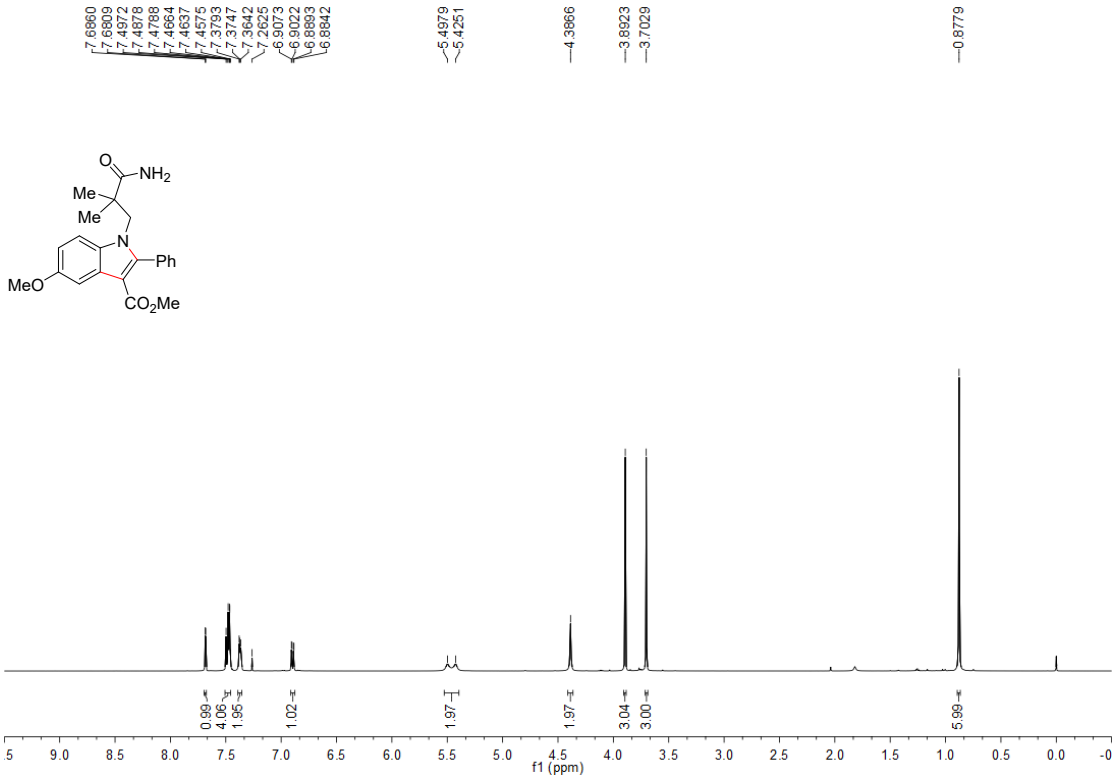
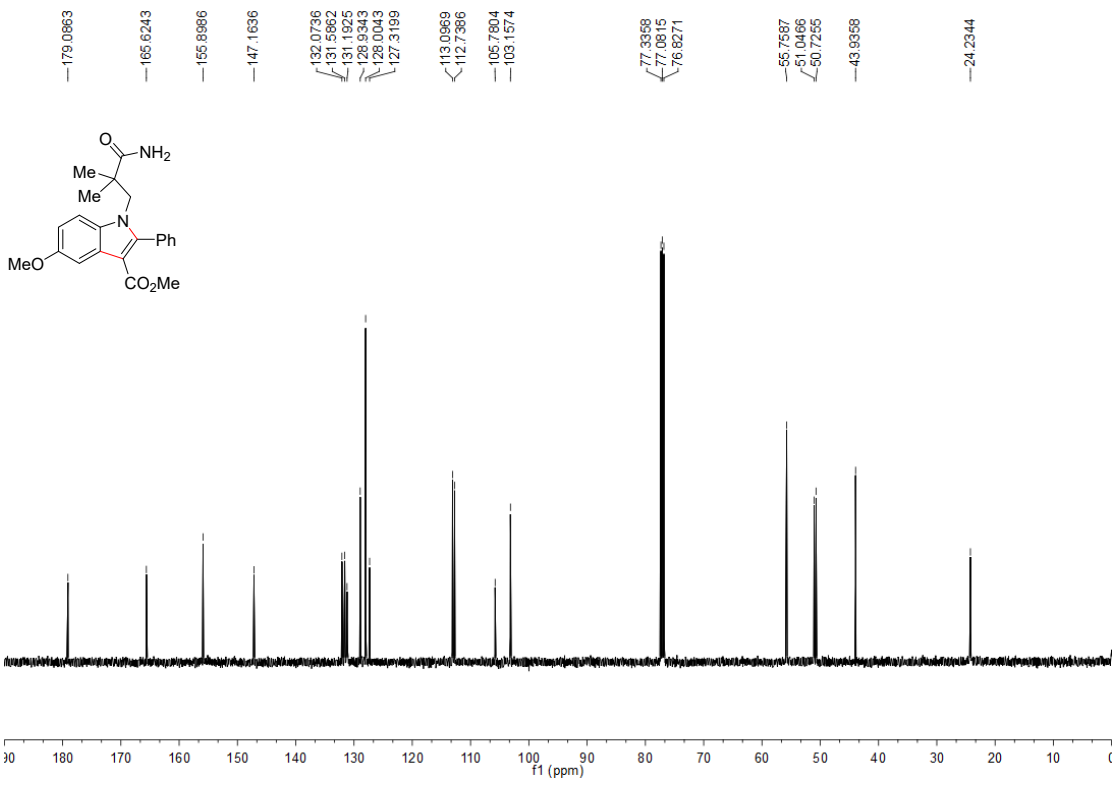


^{13}C NMR



6c

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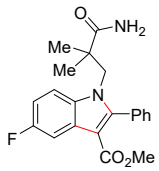

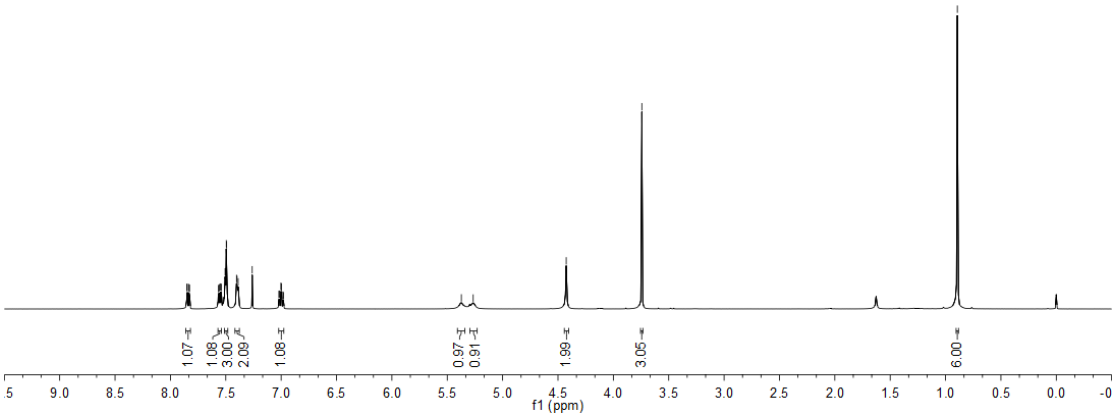

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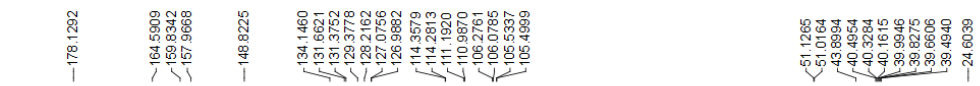

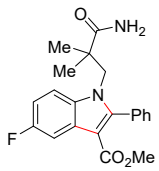

7c

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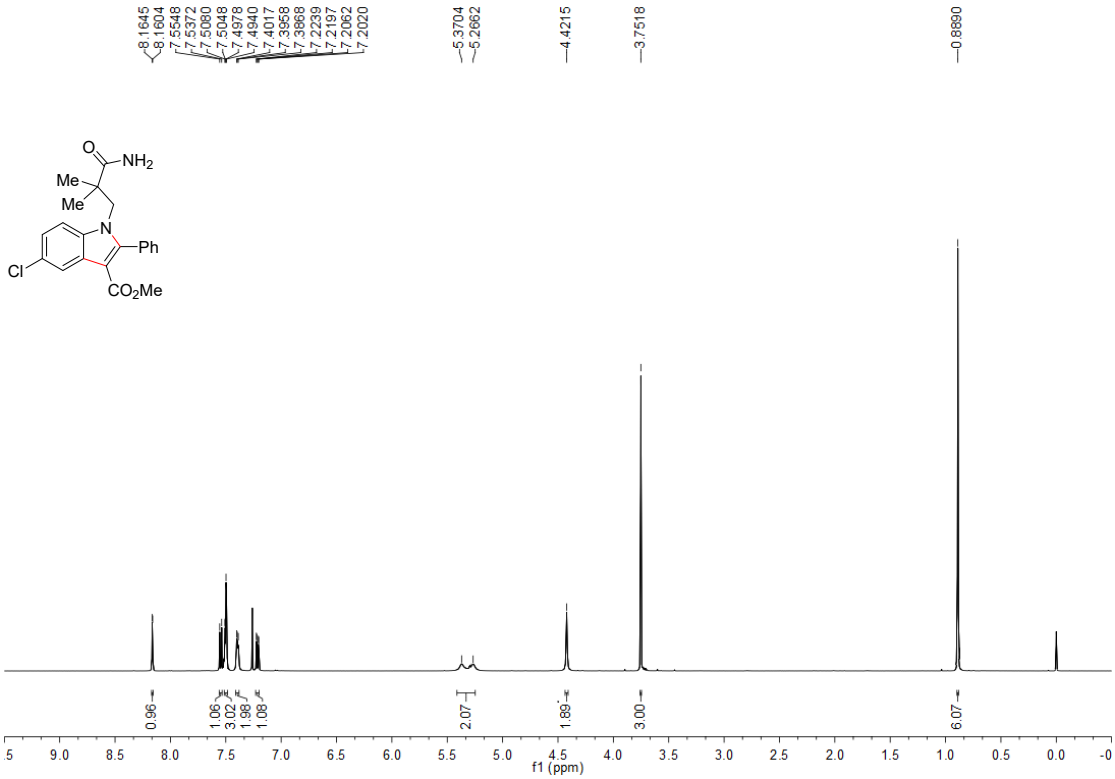
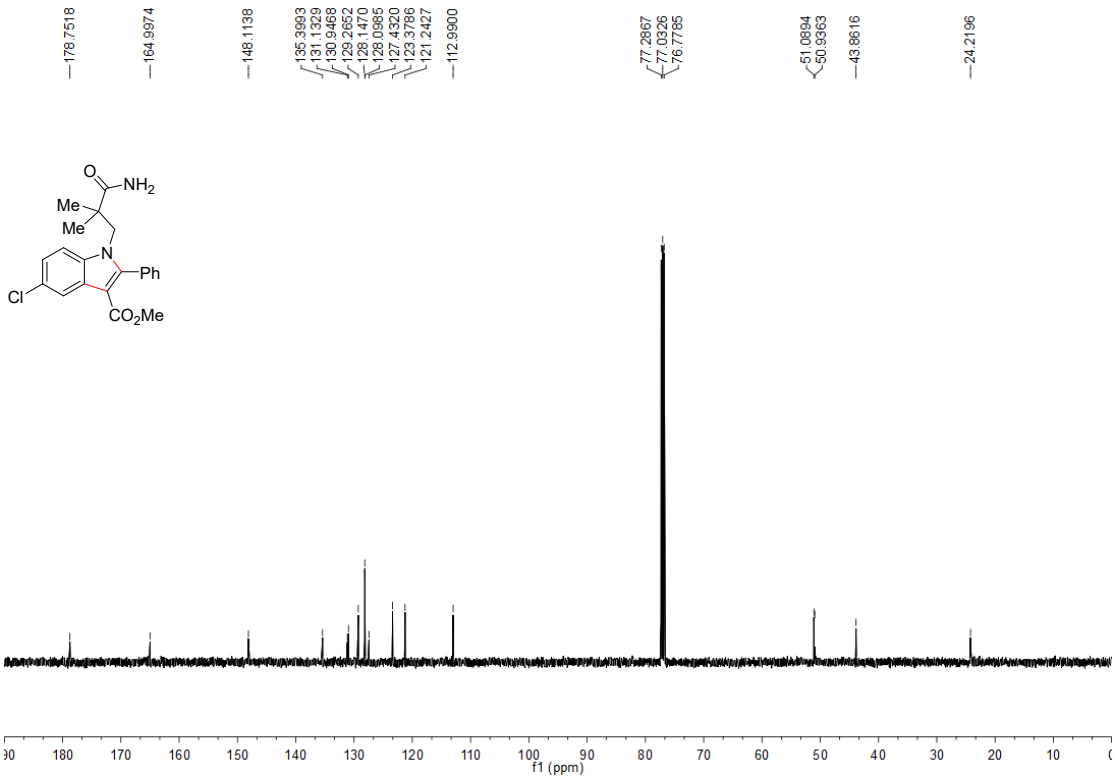


^{13}C NMR



8c

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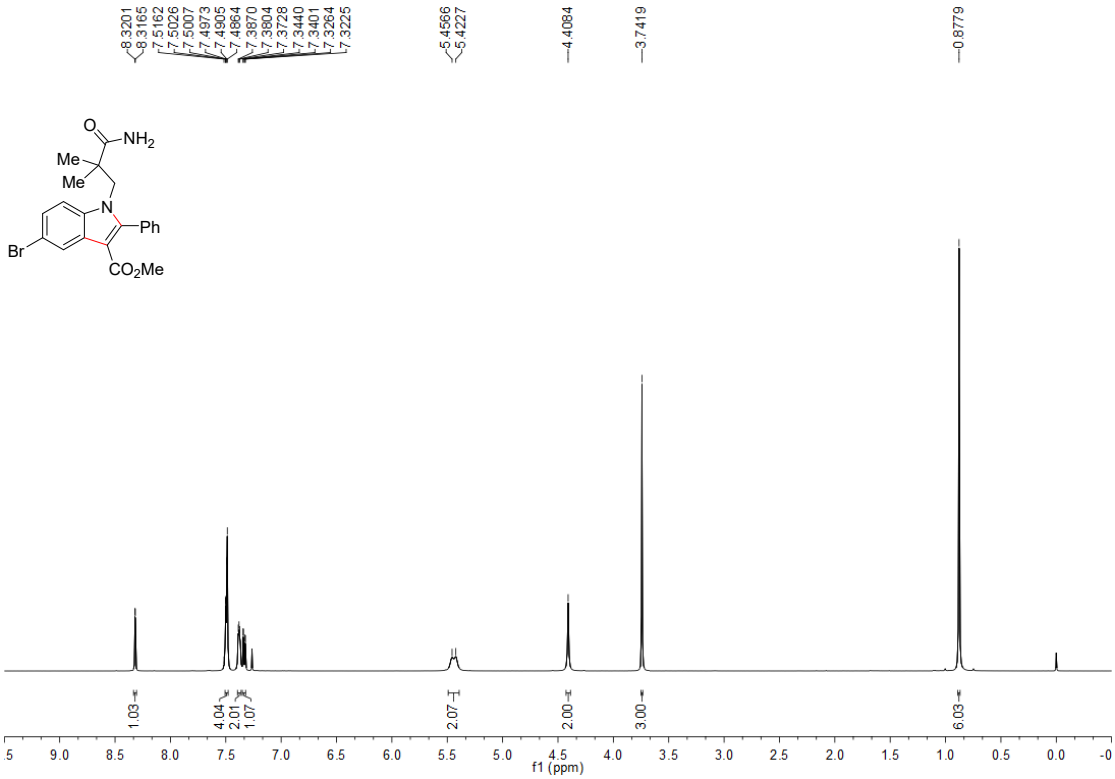

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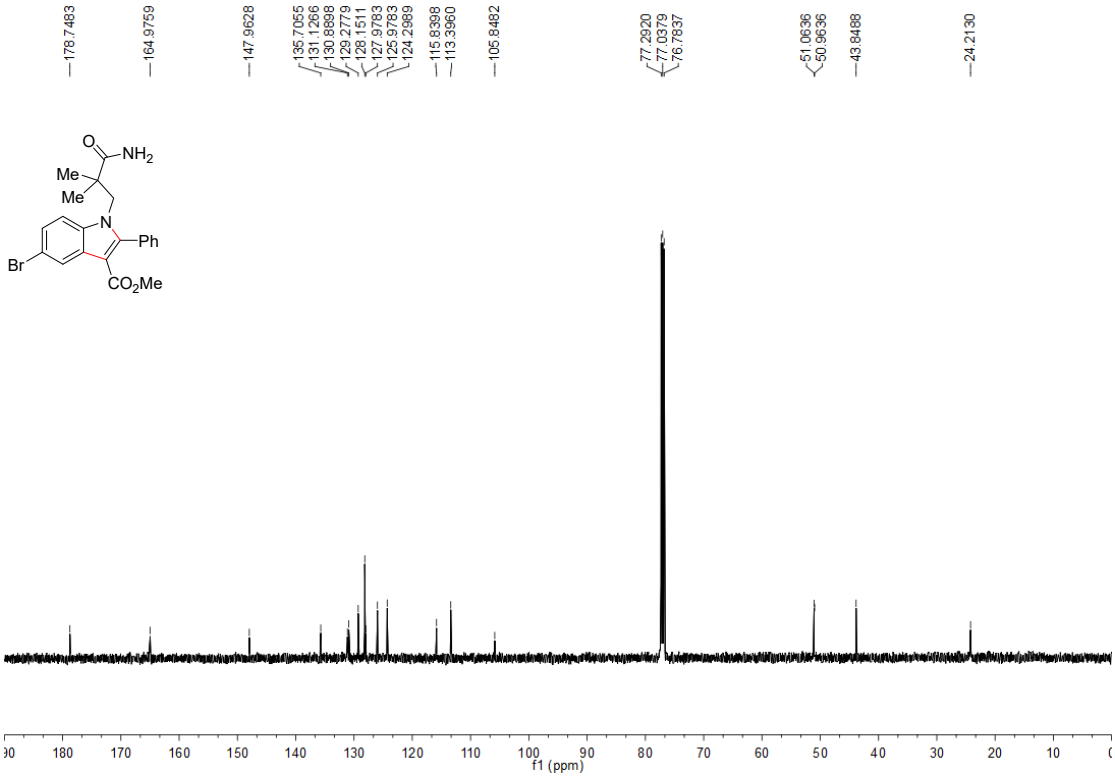

9c

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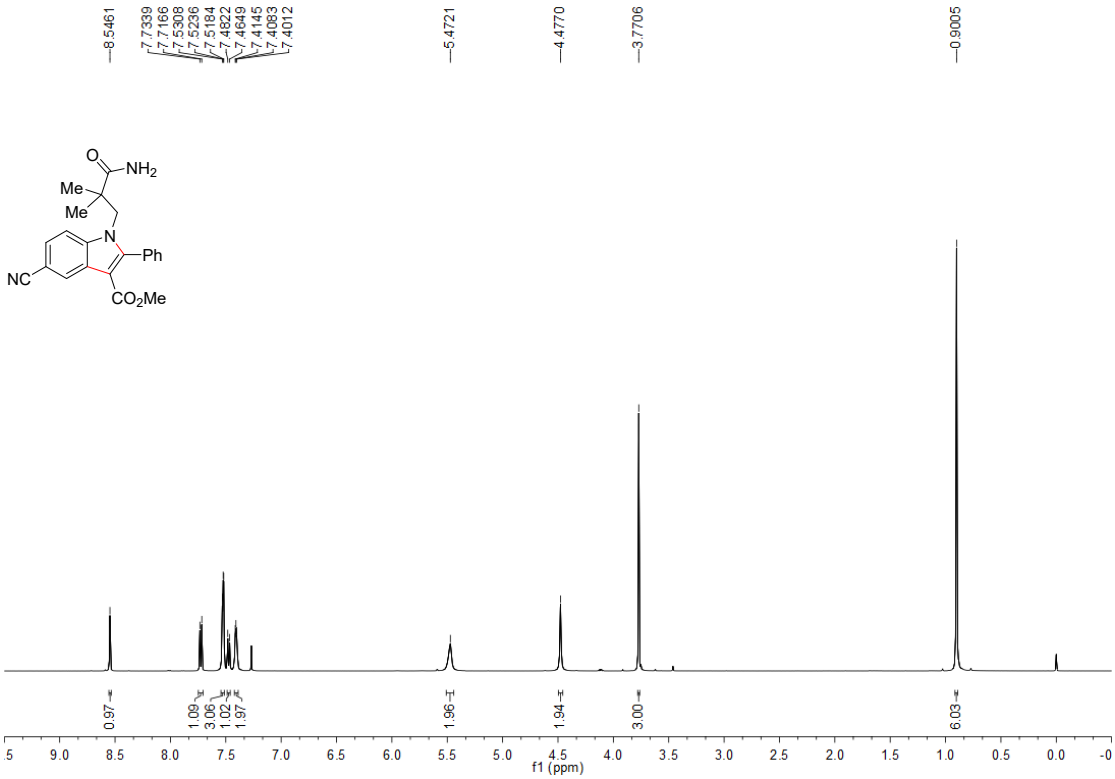

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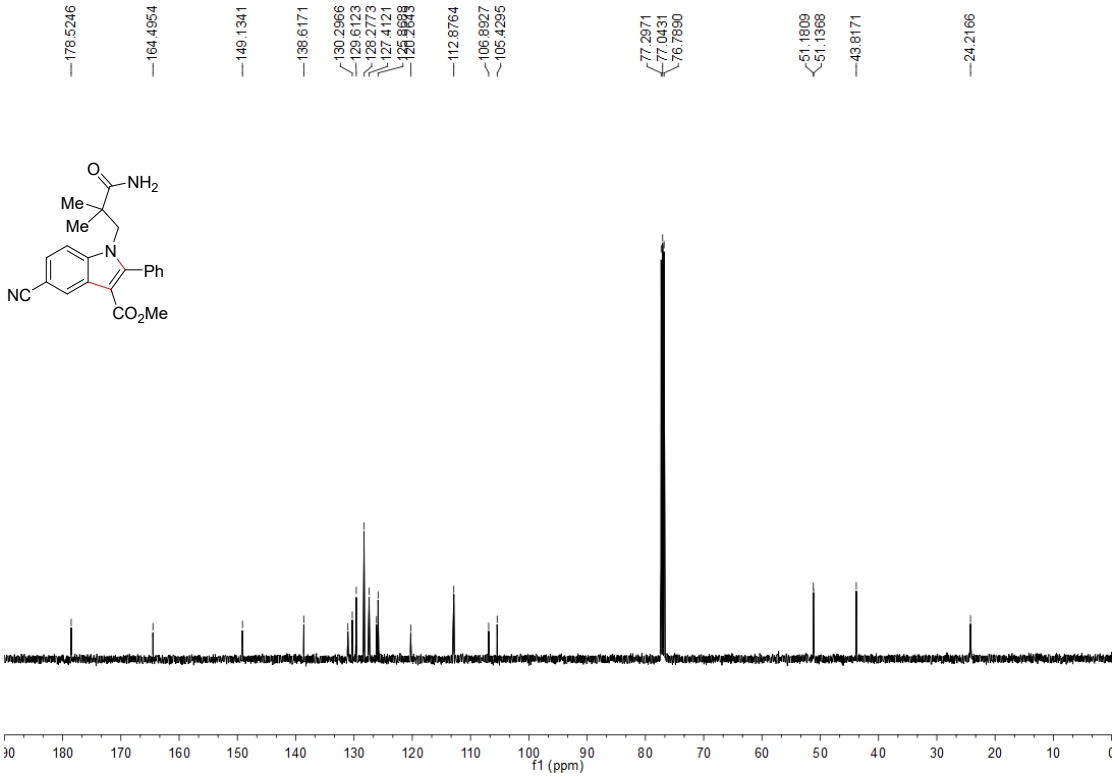

10c

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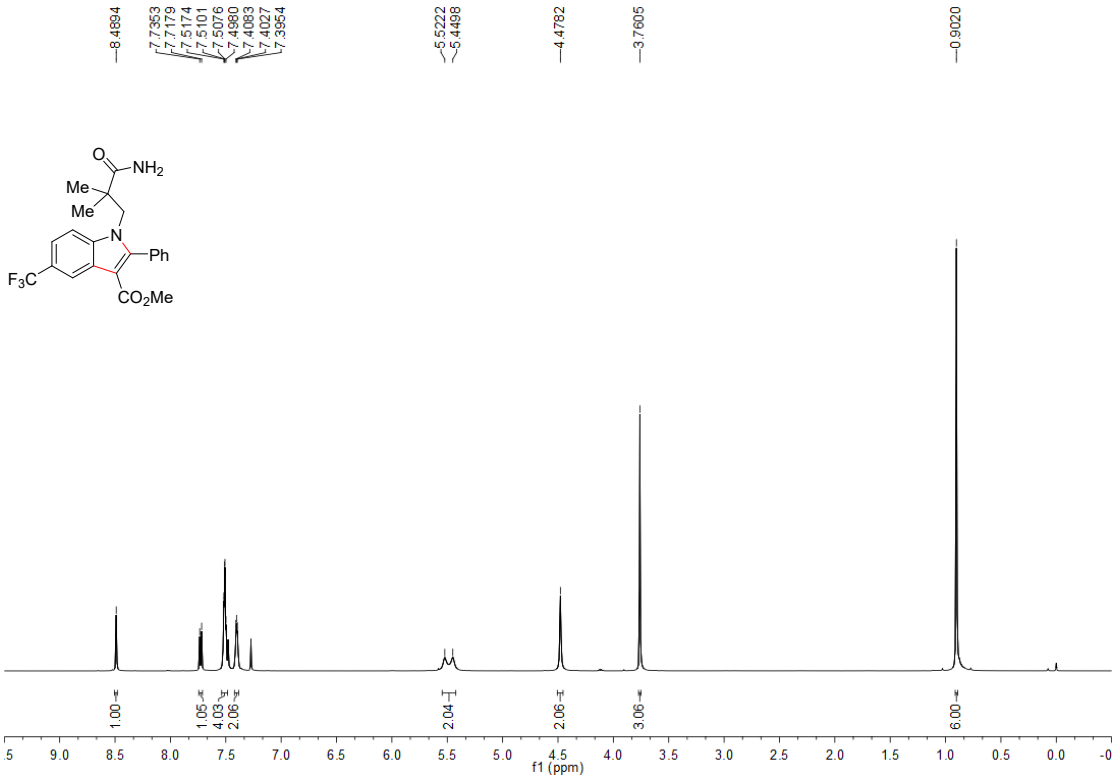

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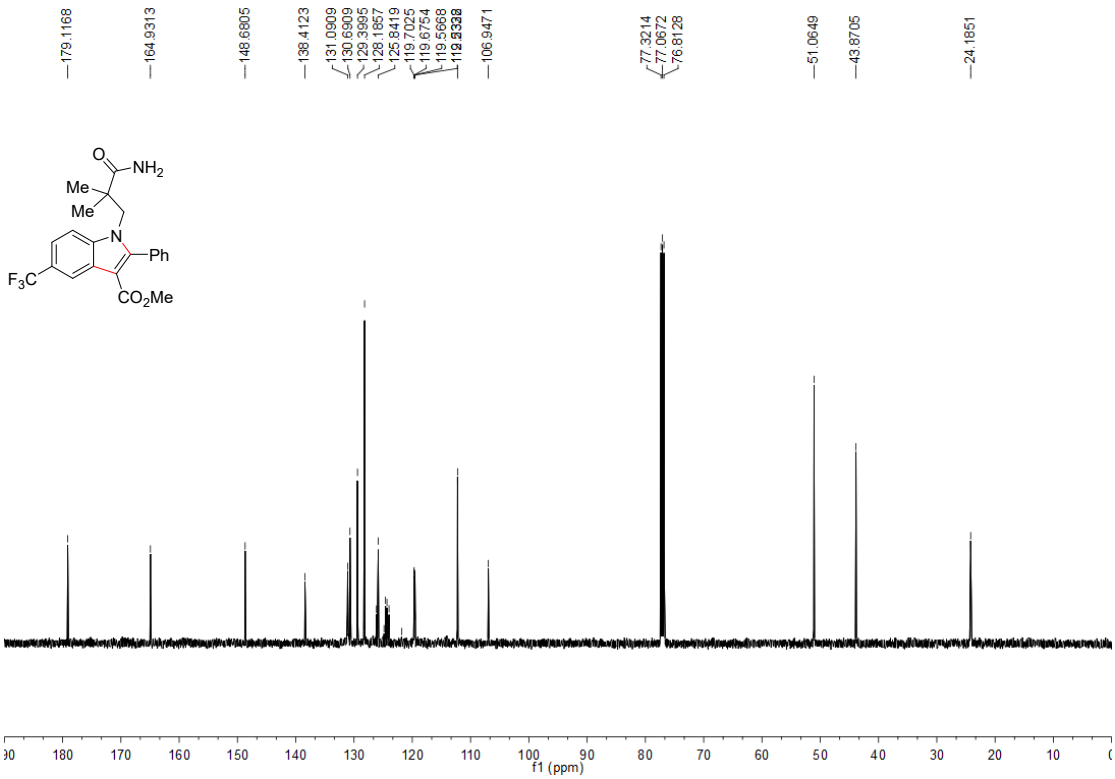

11c

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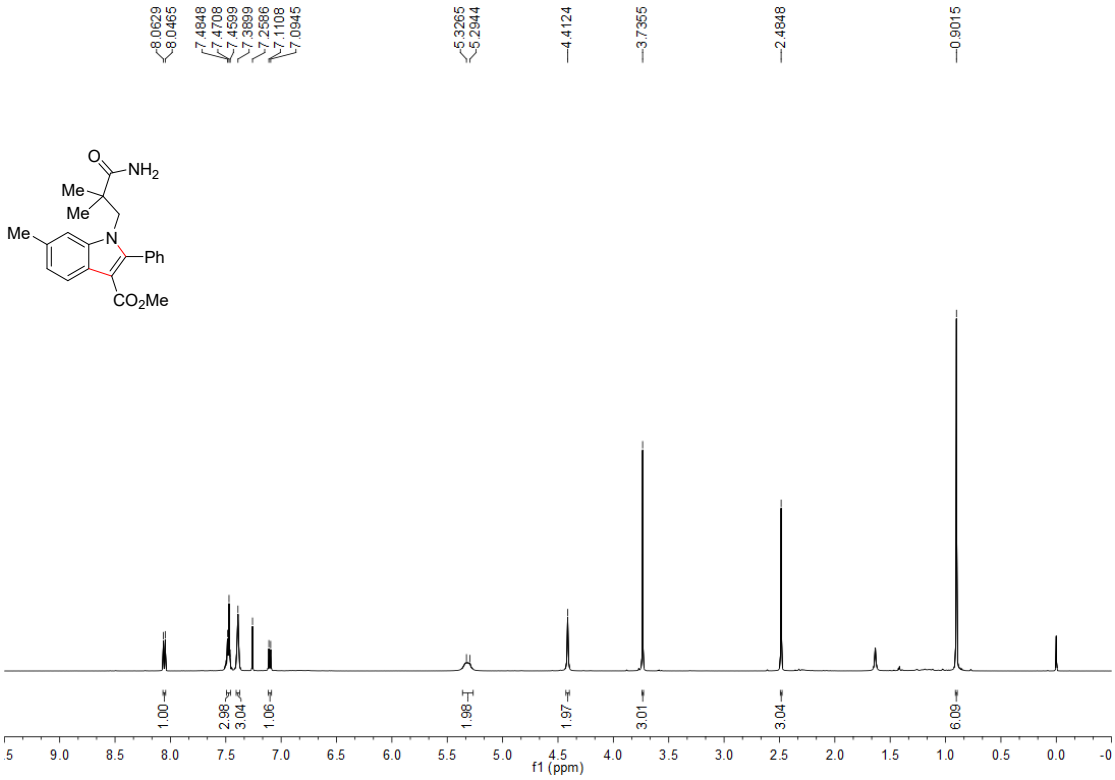
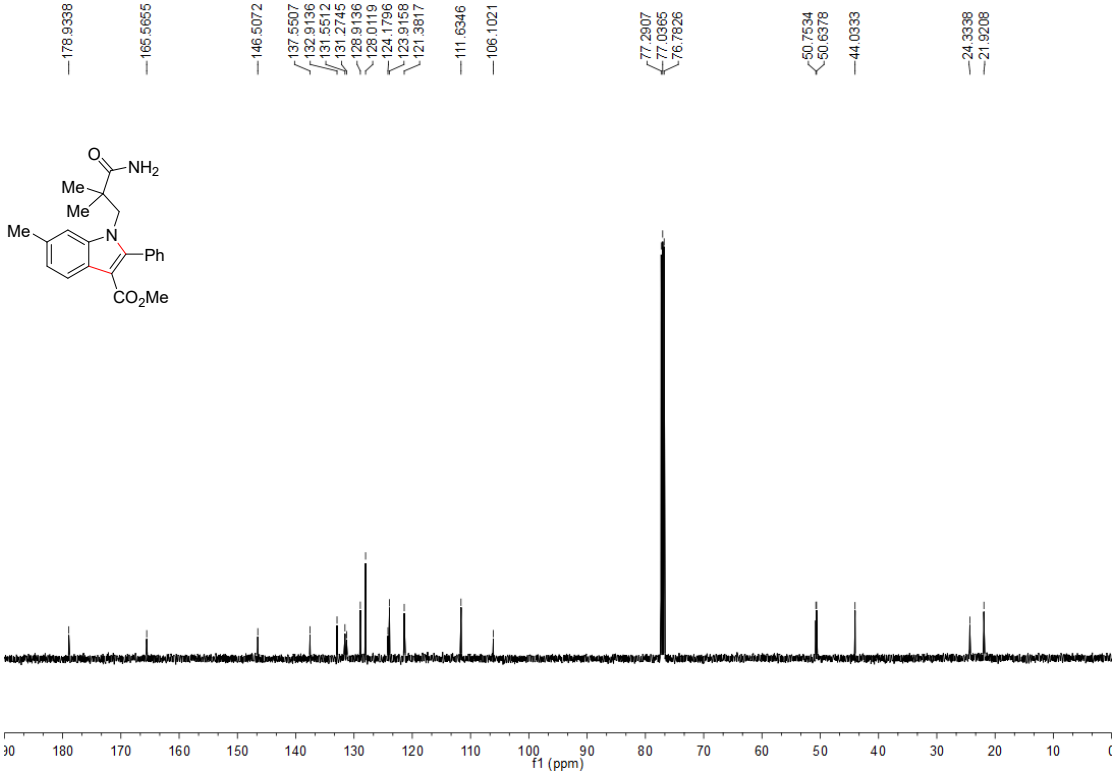


^{13}C NMR



12c

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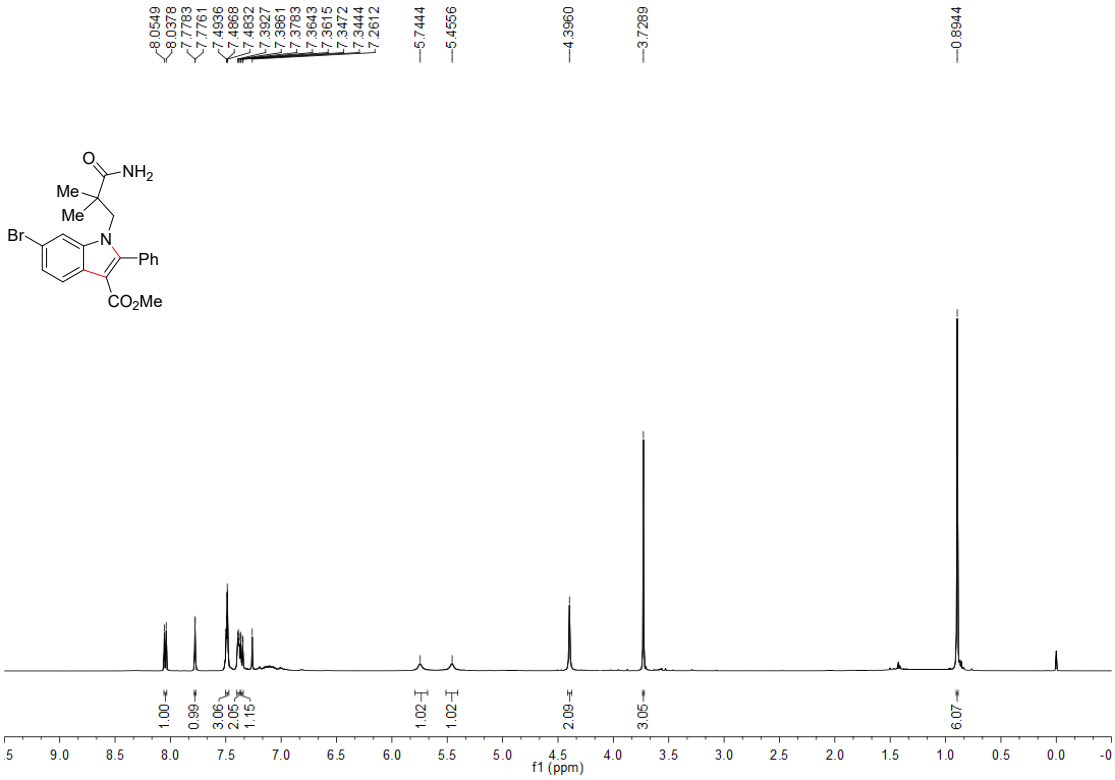

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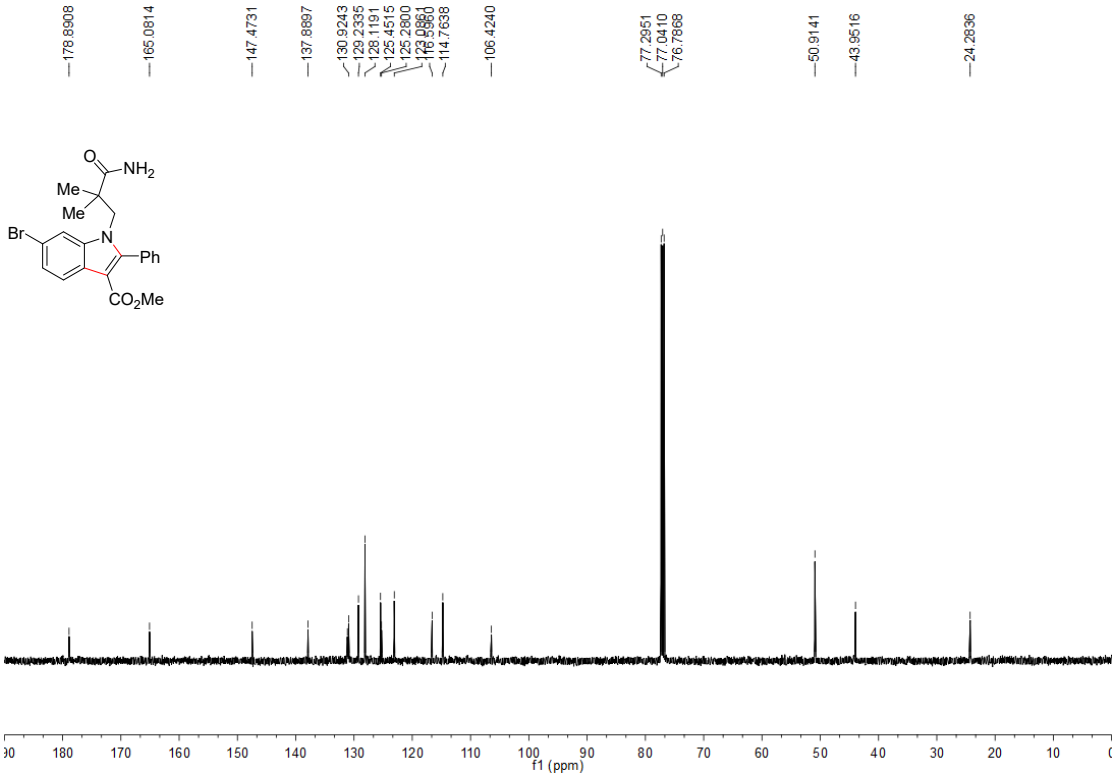

13c

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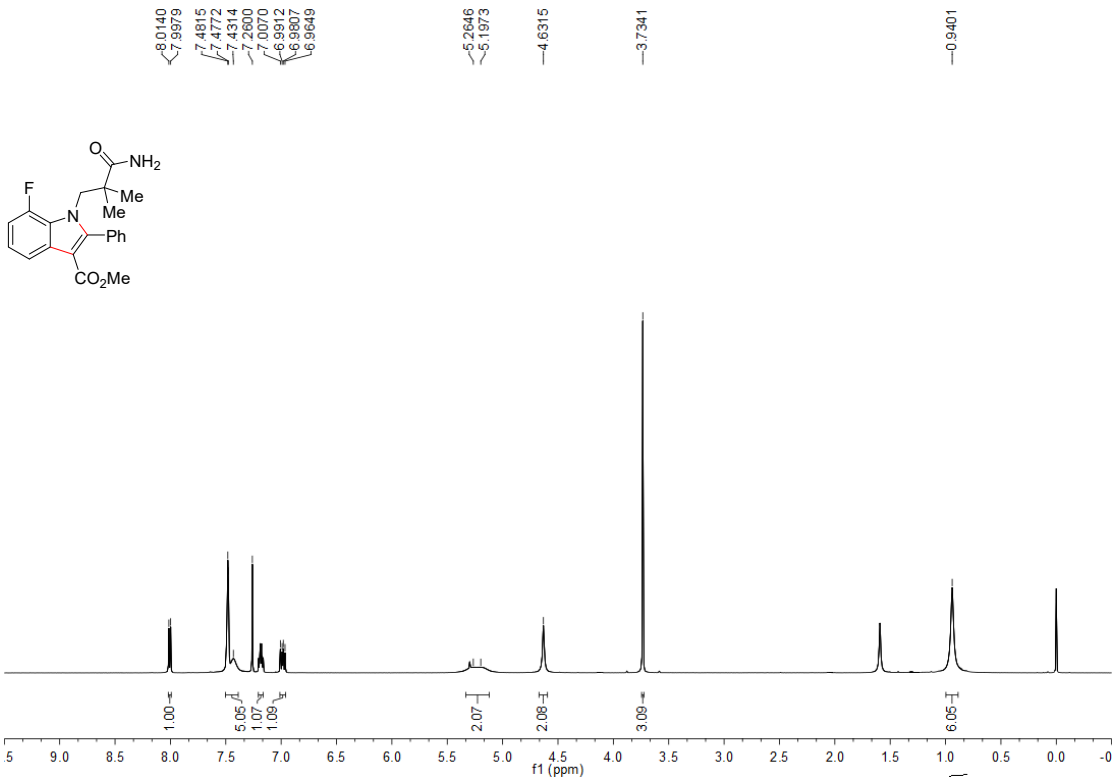

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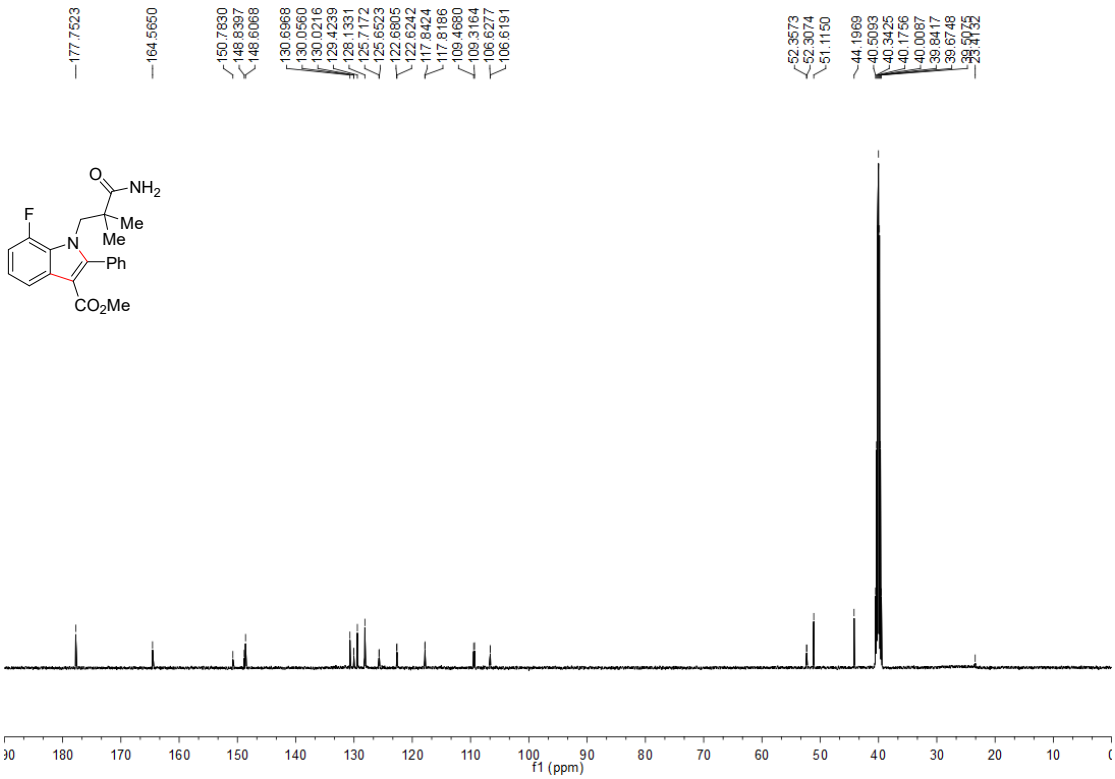

14c

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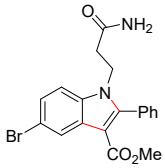

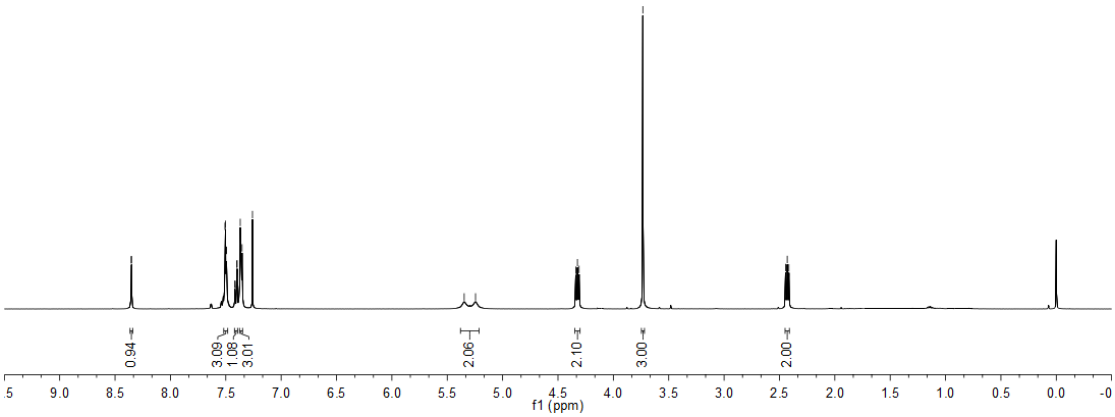

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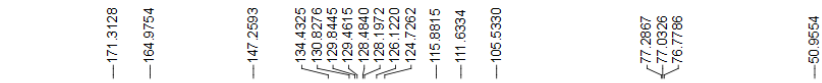

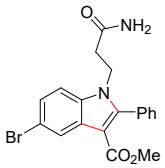

15c

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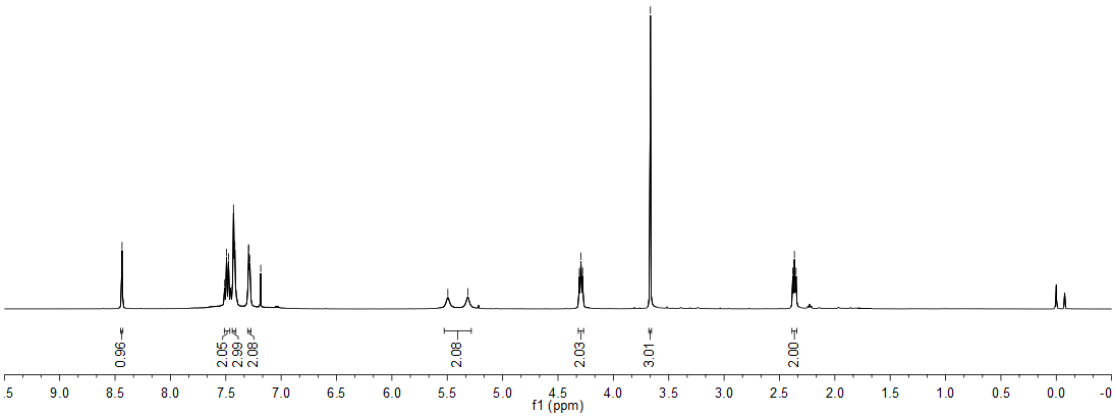

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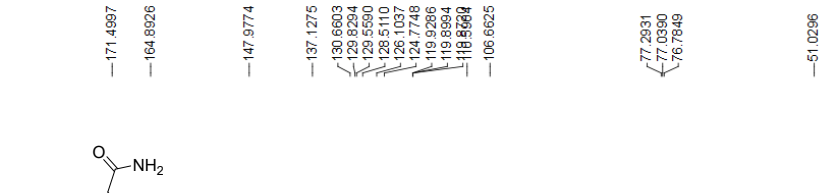
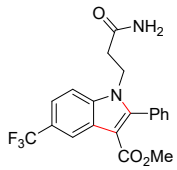
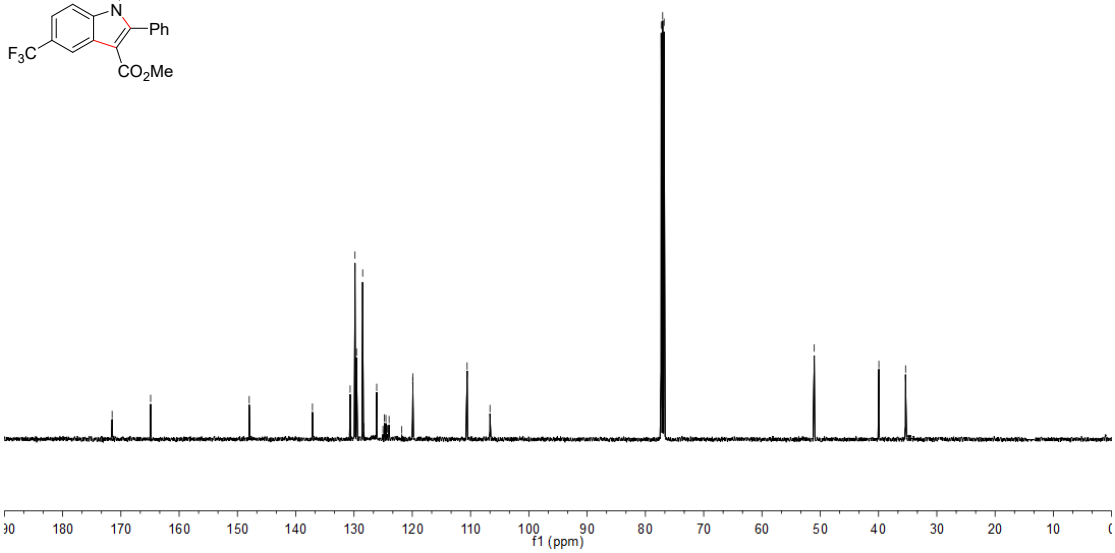
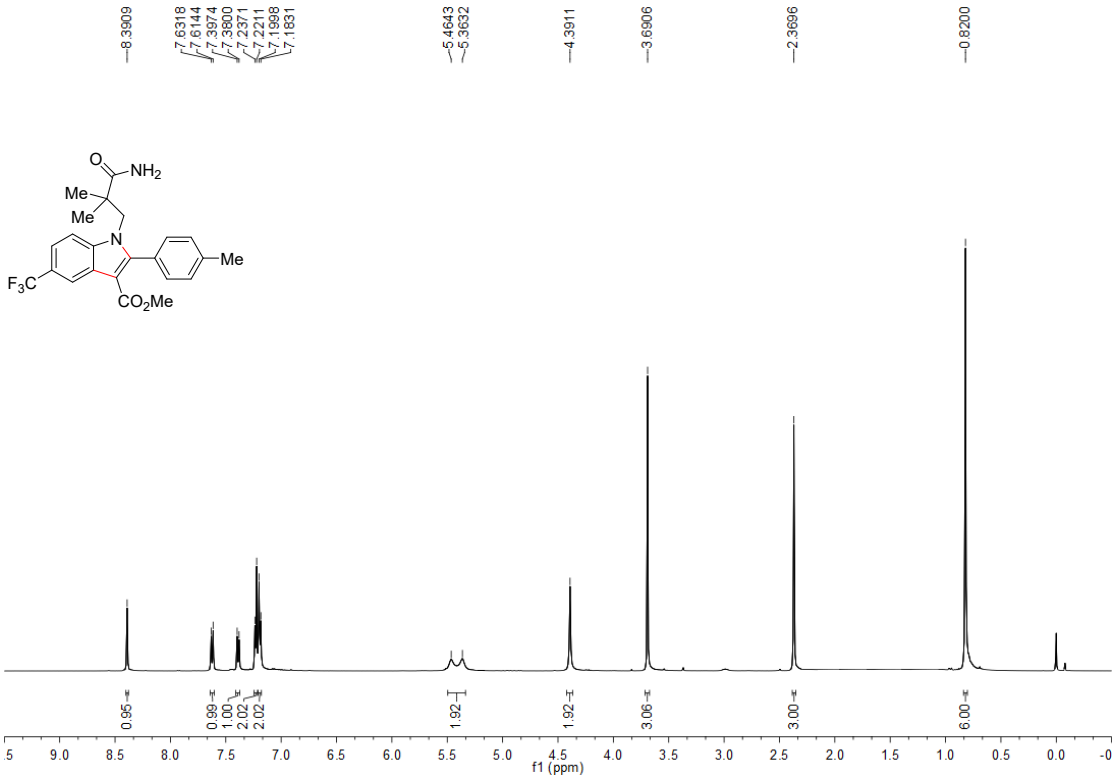




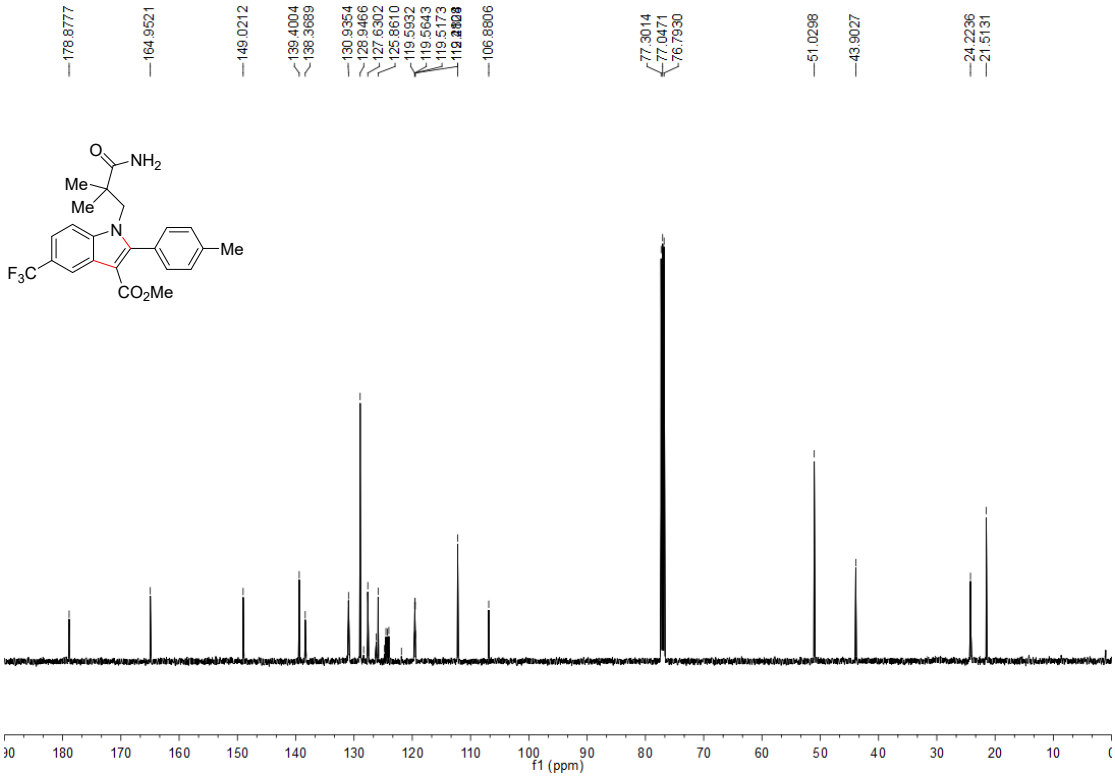


16c

^{1}H NMR

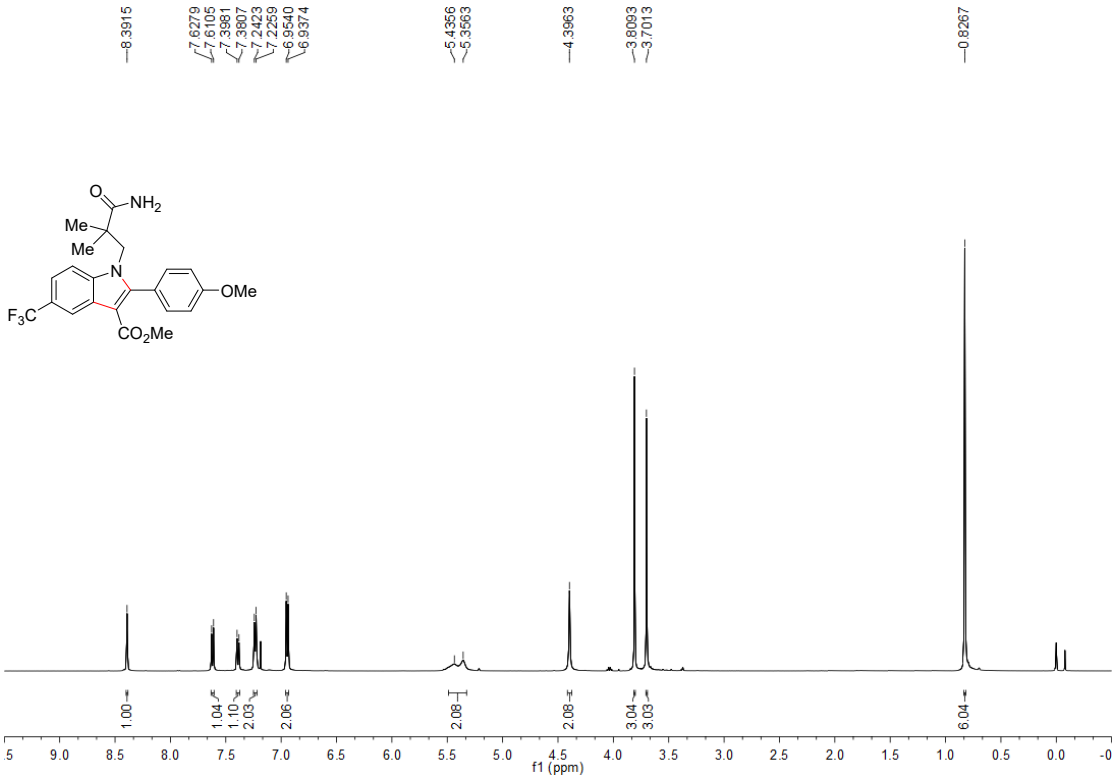


^{13}C NMR



17c

^{1}H NMR



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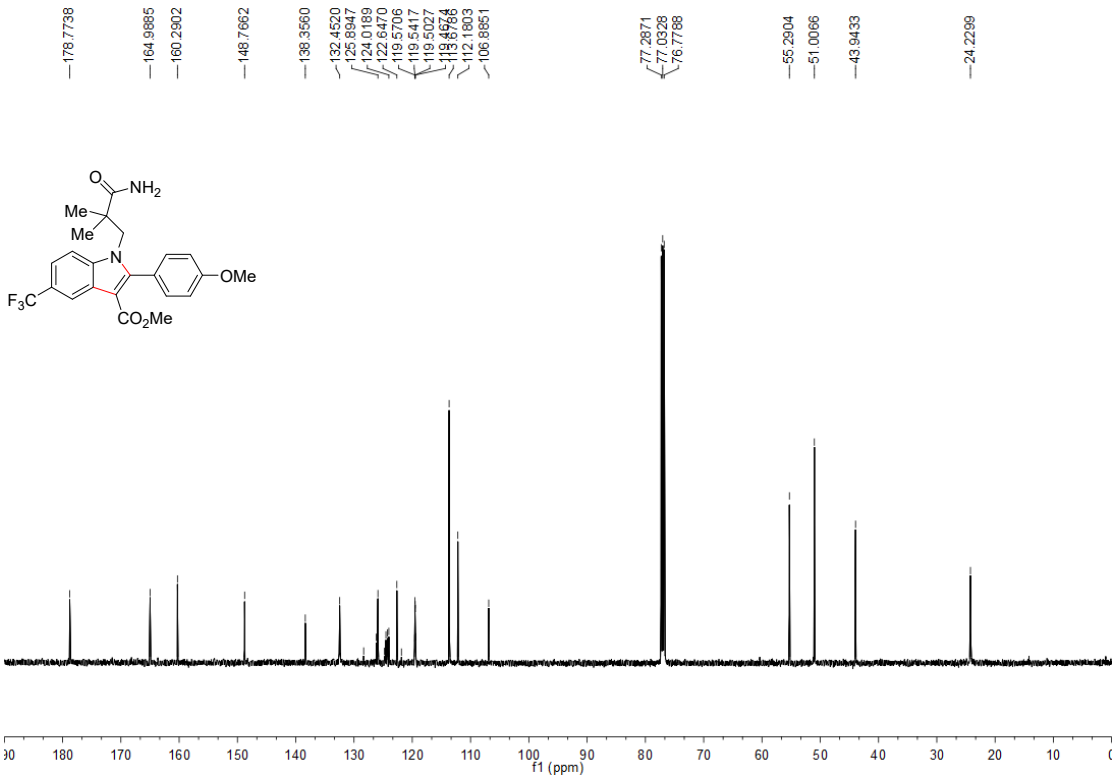
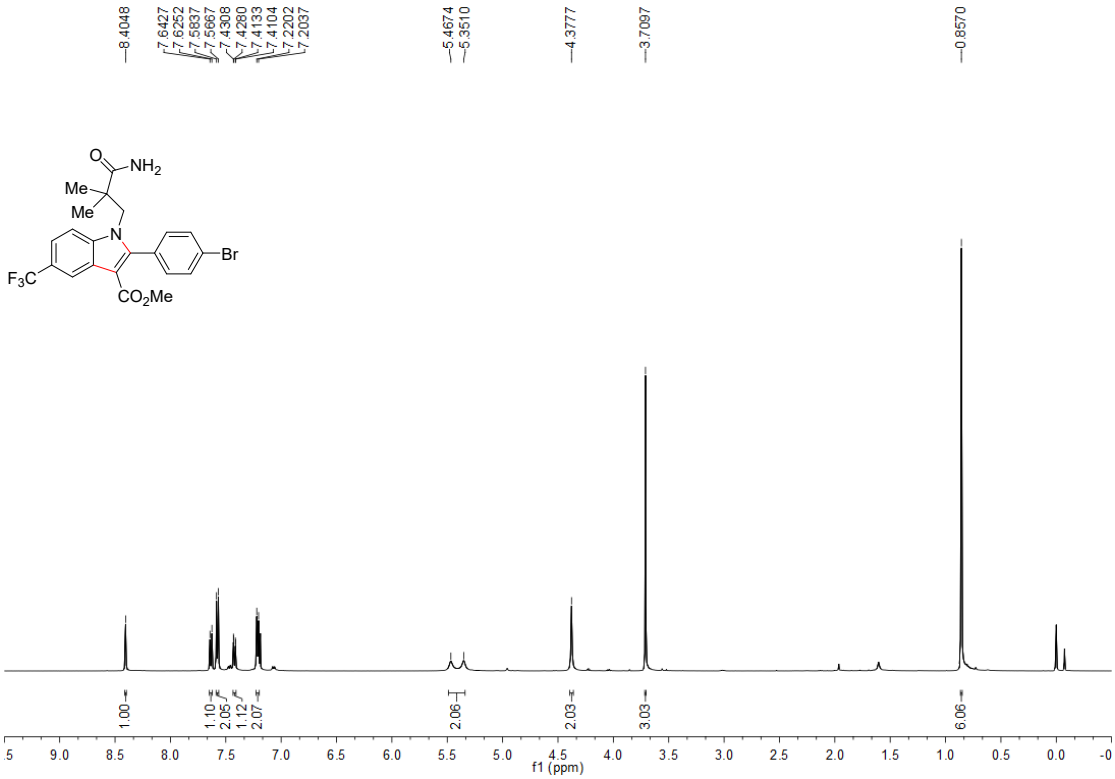


18c

^{1}H NMR



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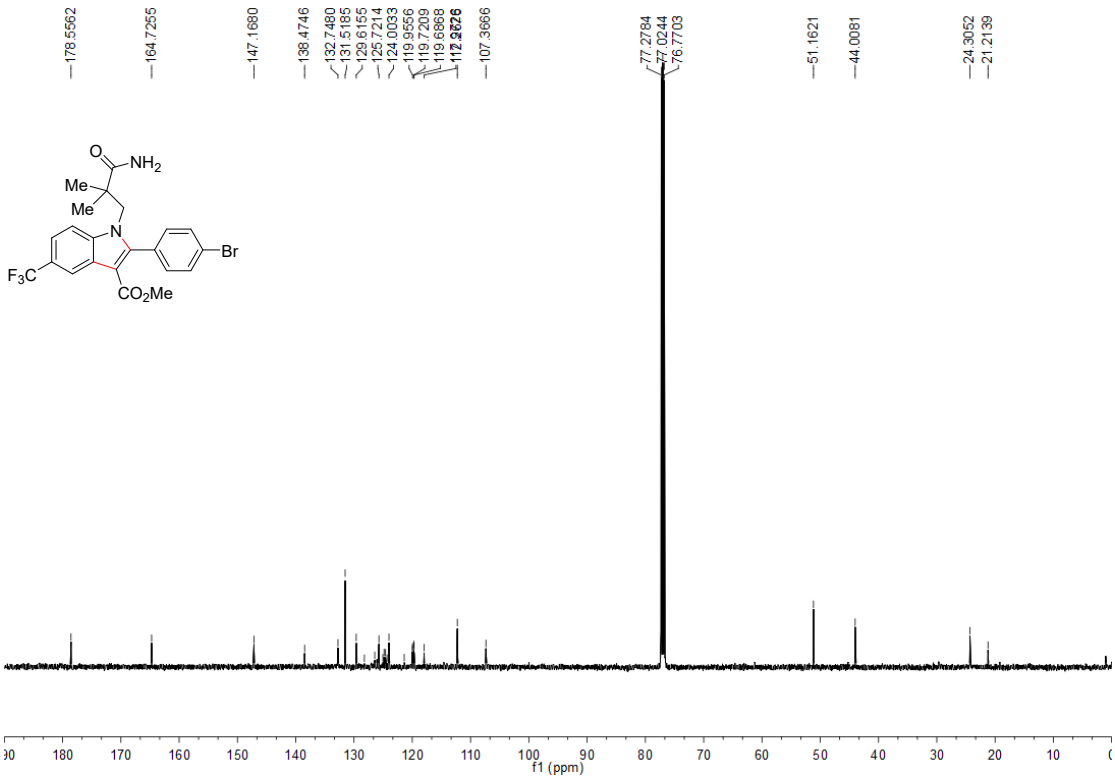

19c

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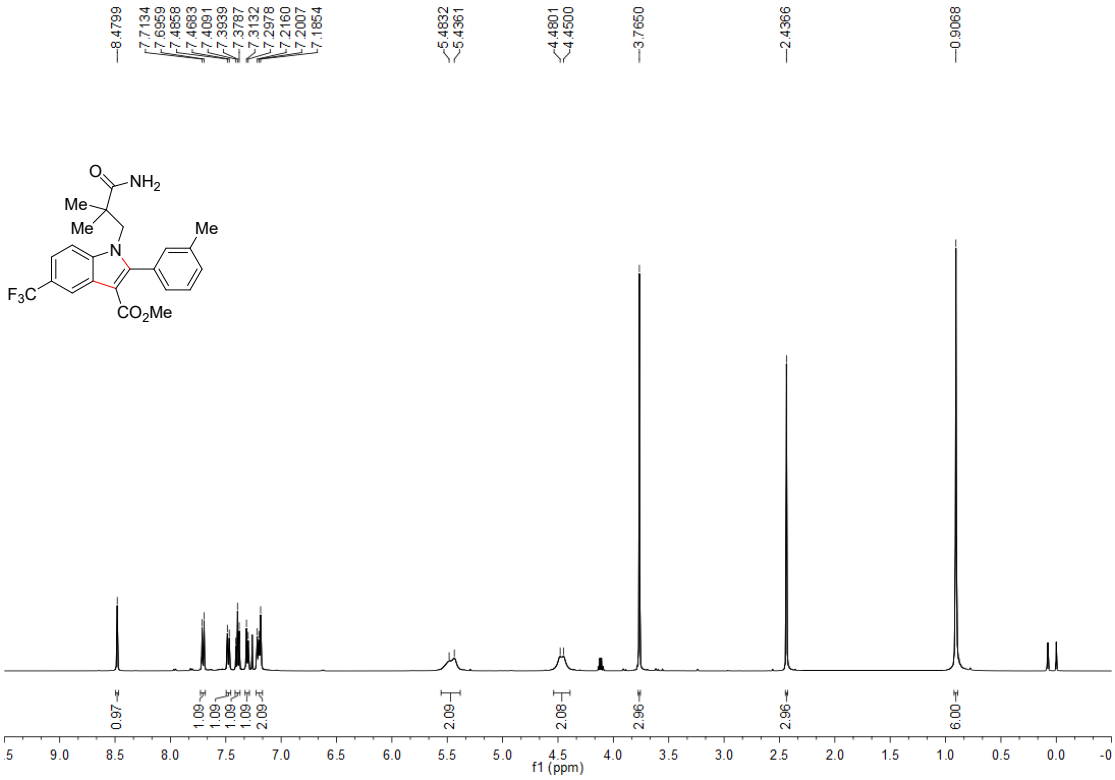

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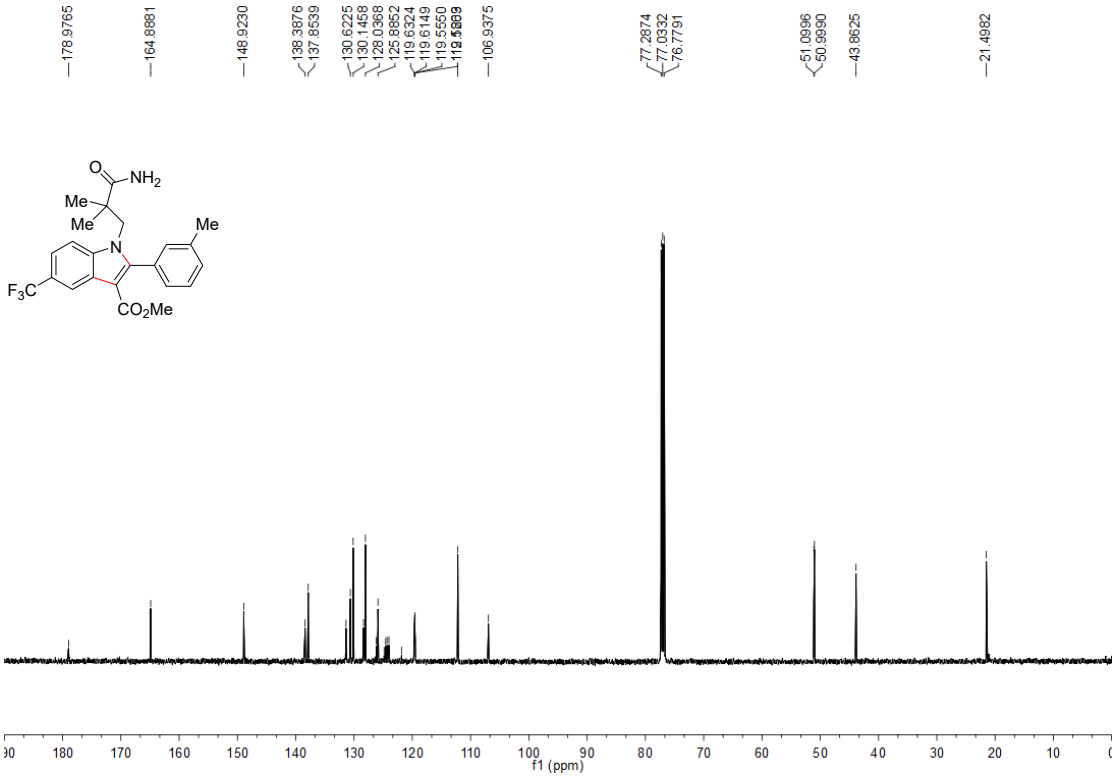

20c

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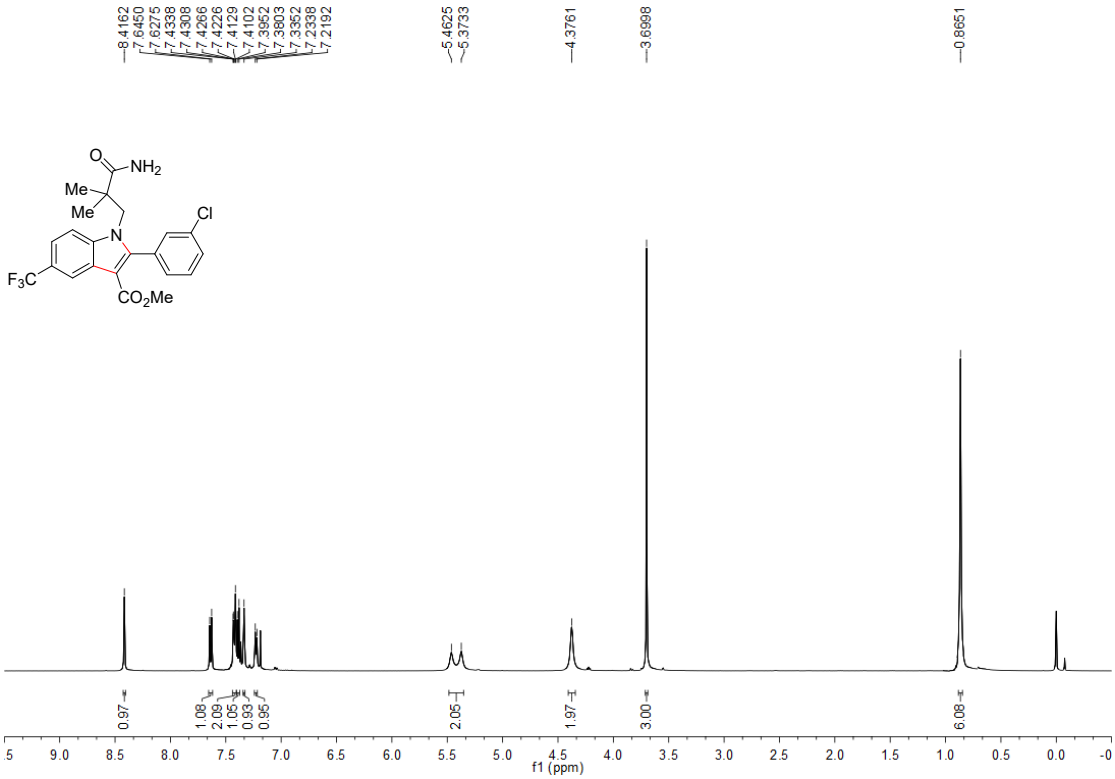

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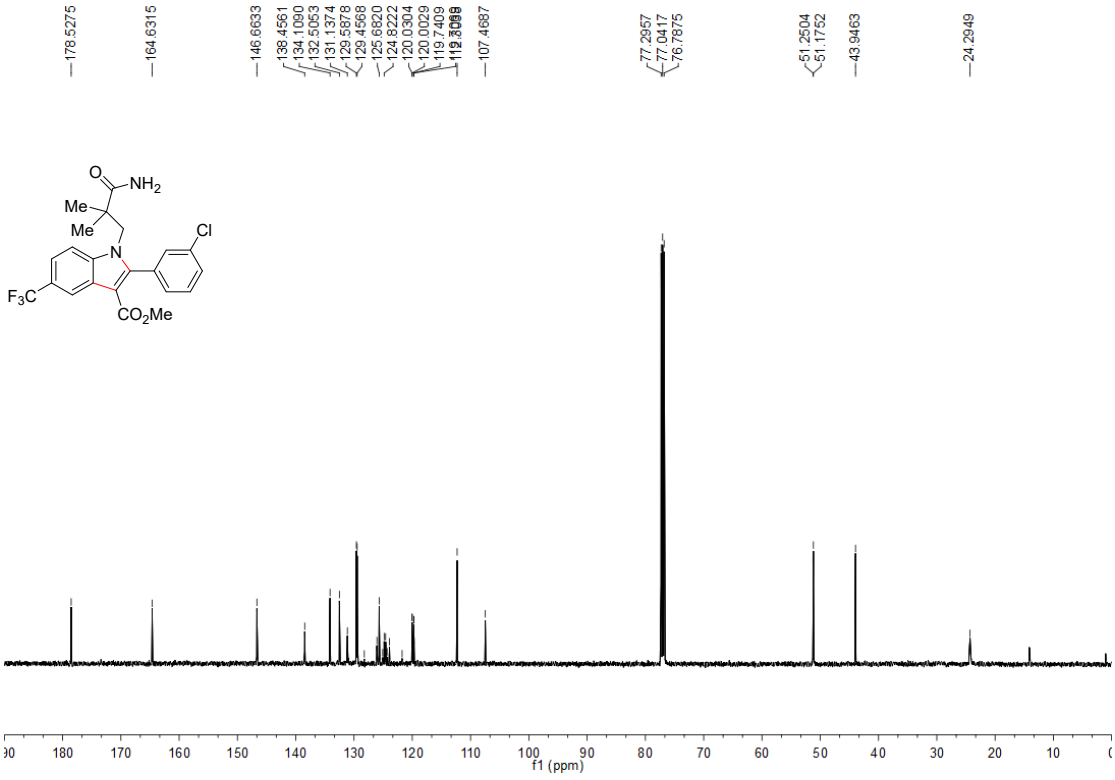
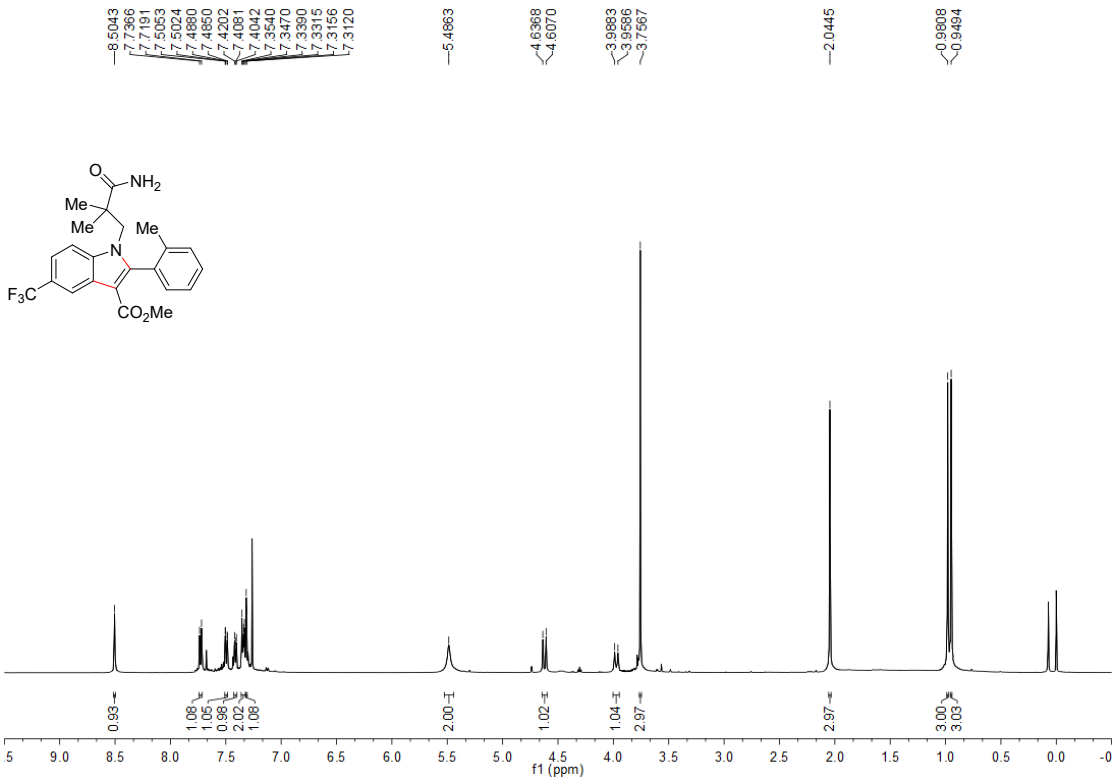


21c

^{1}H NMR



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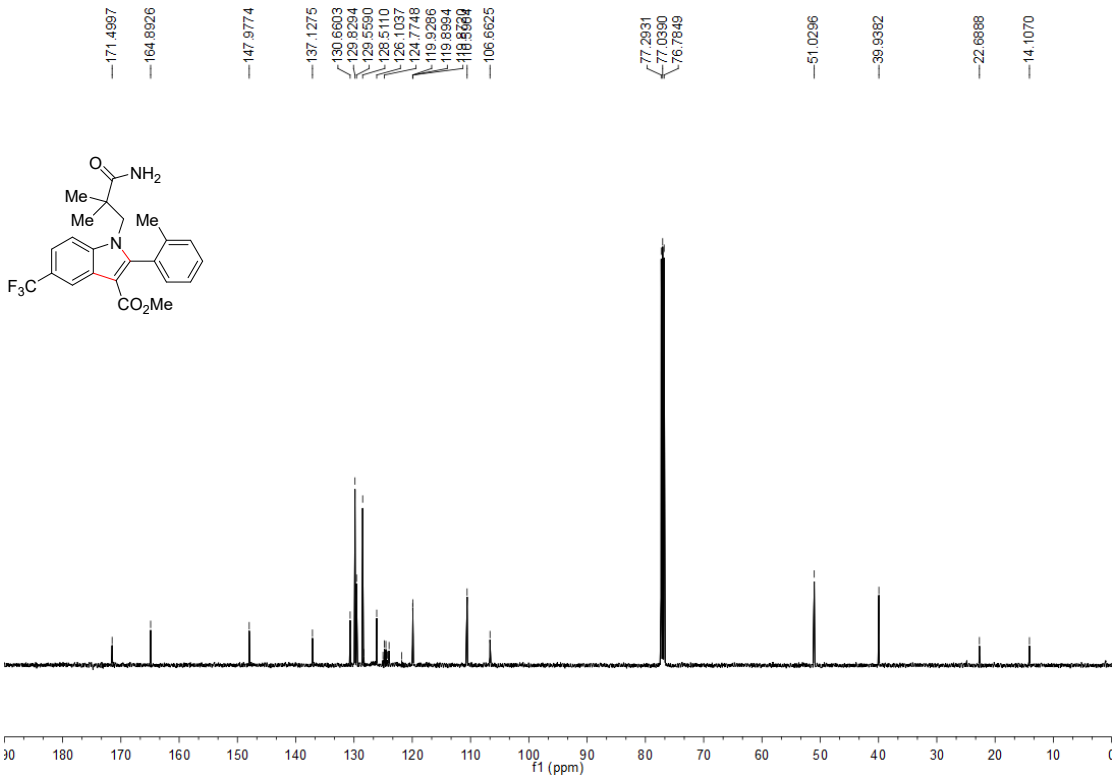

22c

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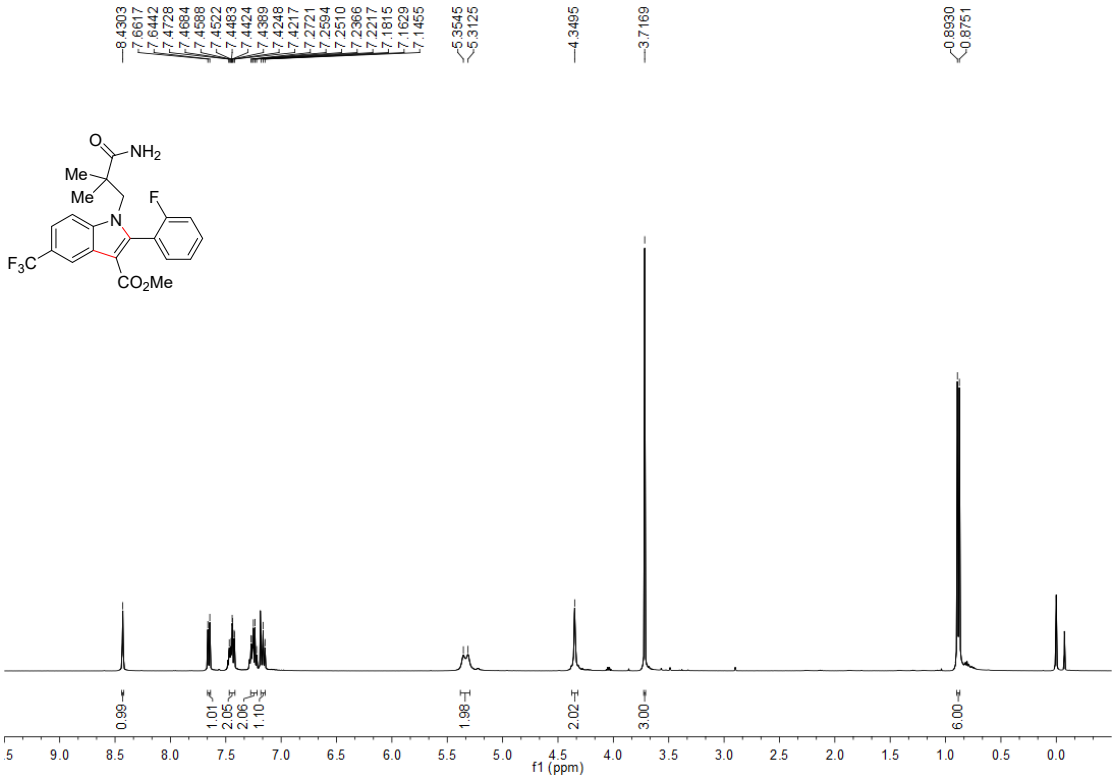

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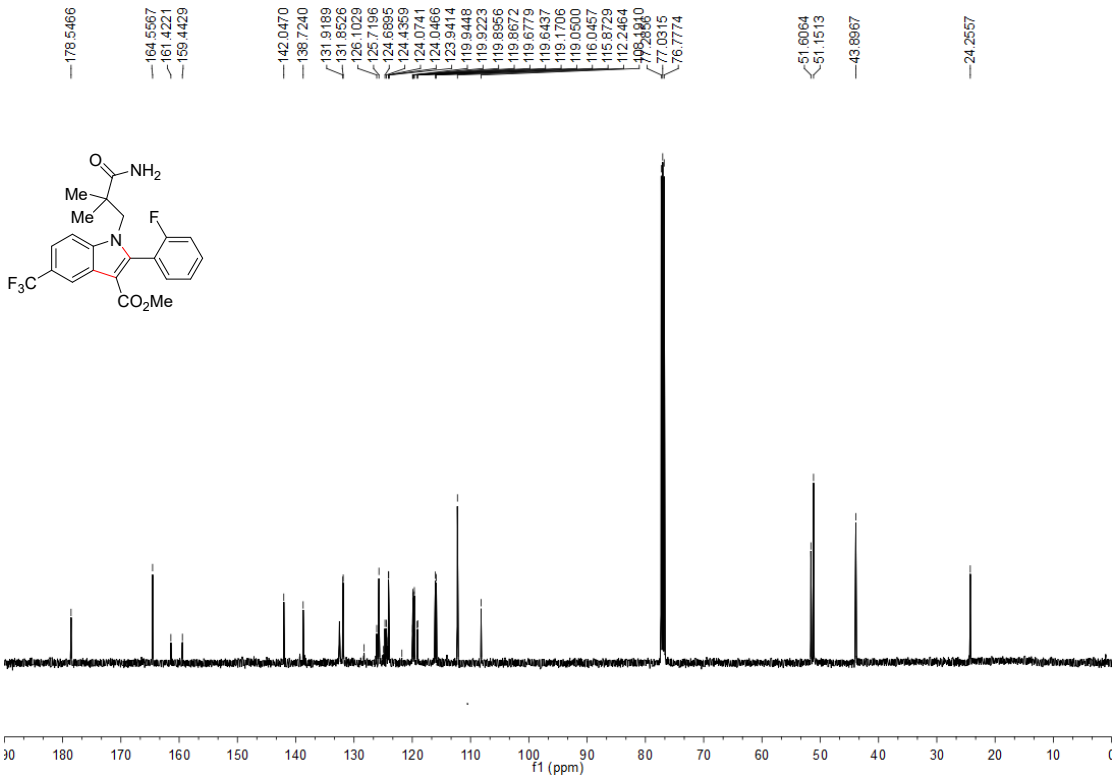

23c

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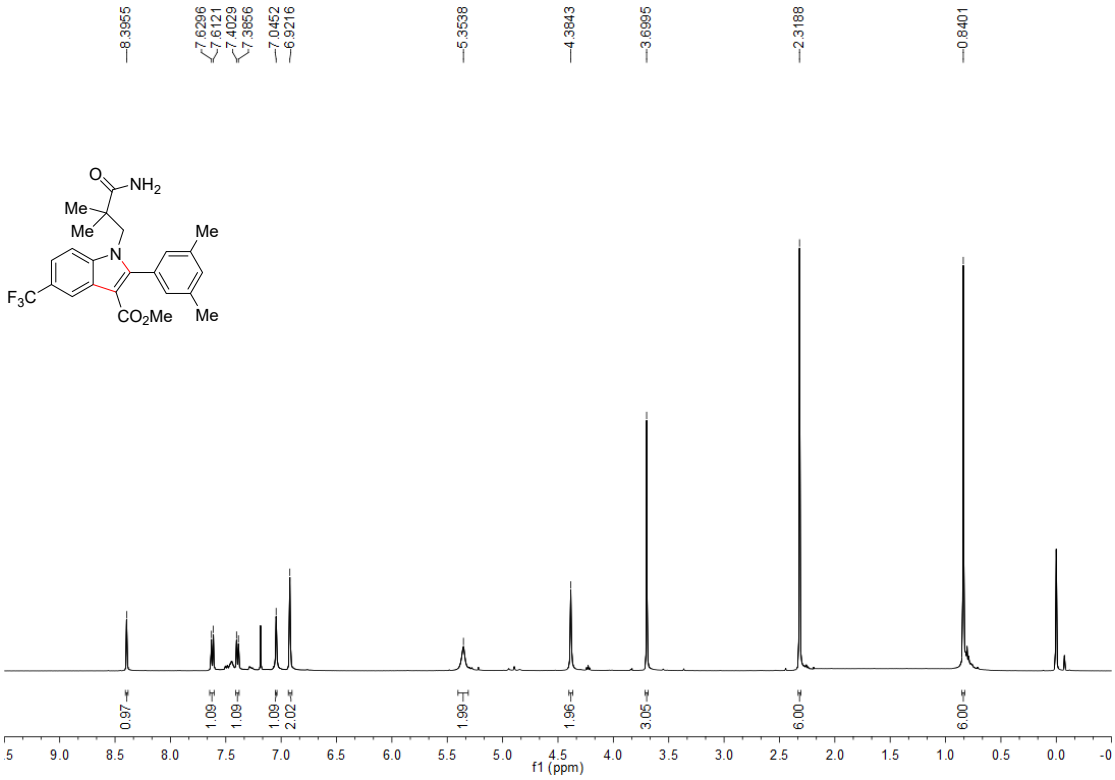

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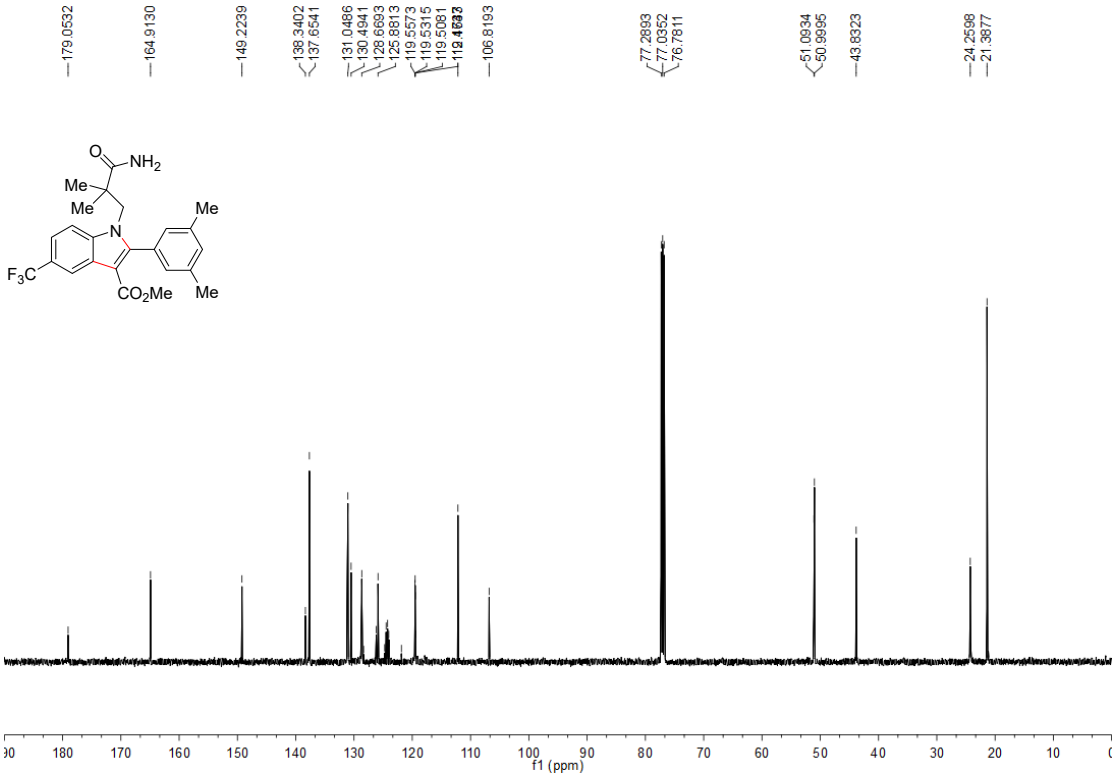

24c

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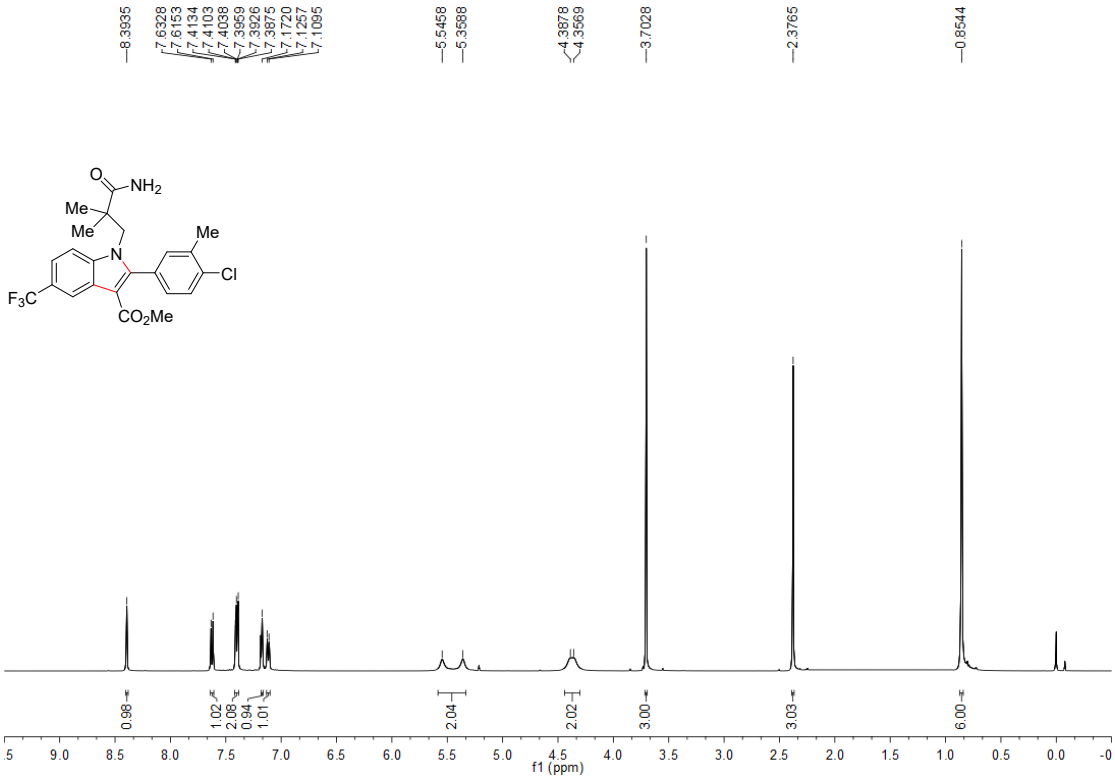

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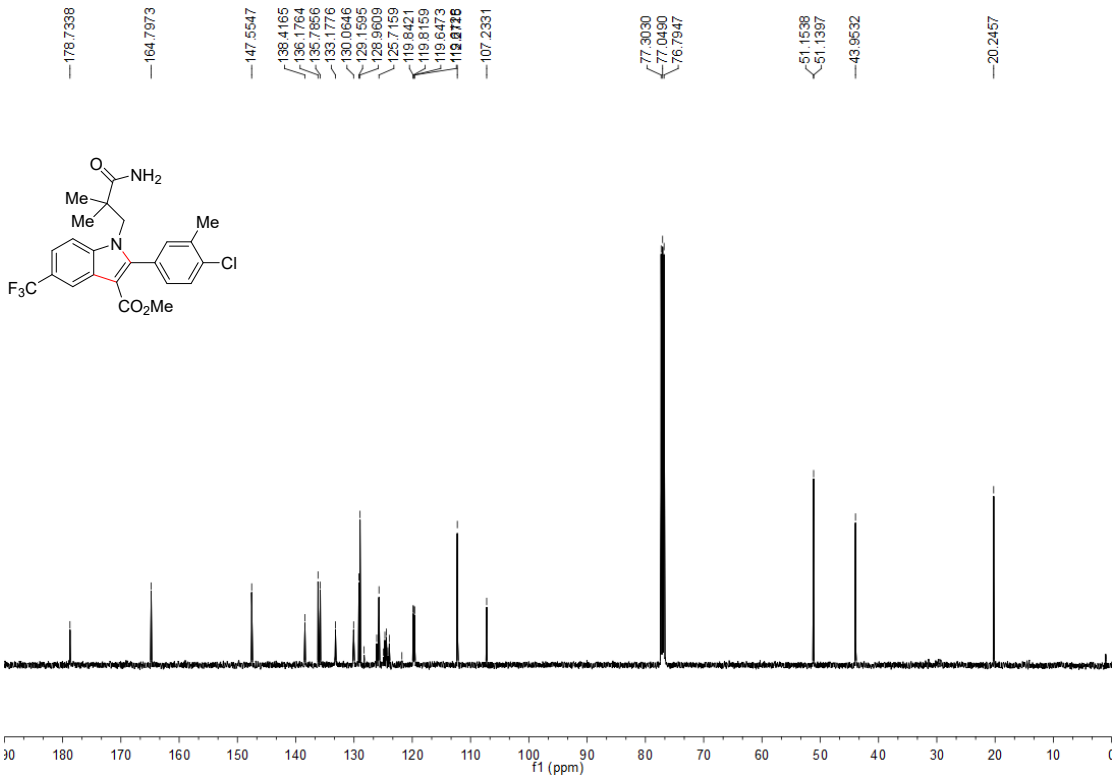

25c

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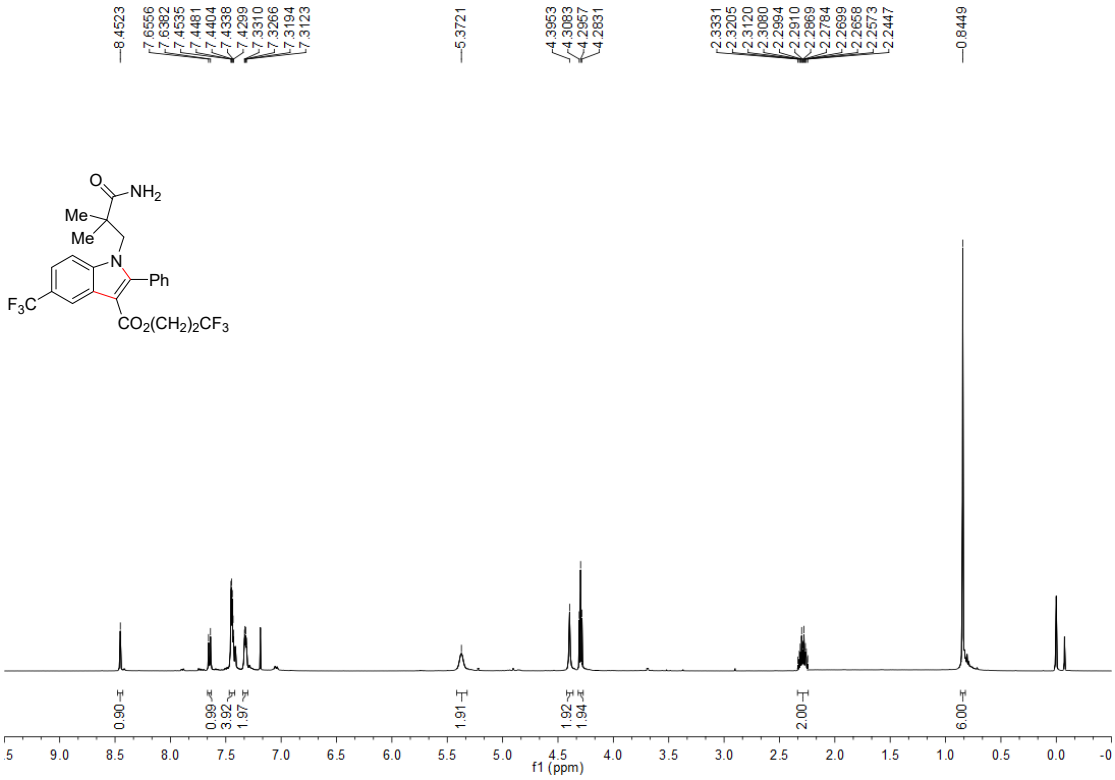

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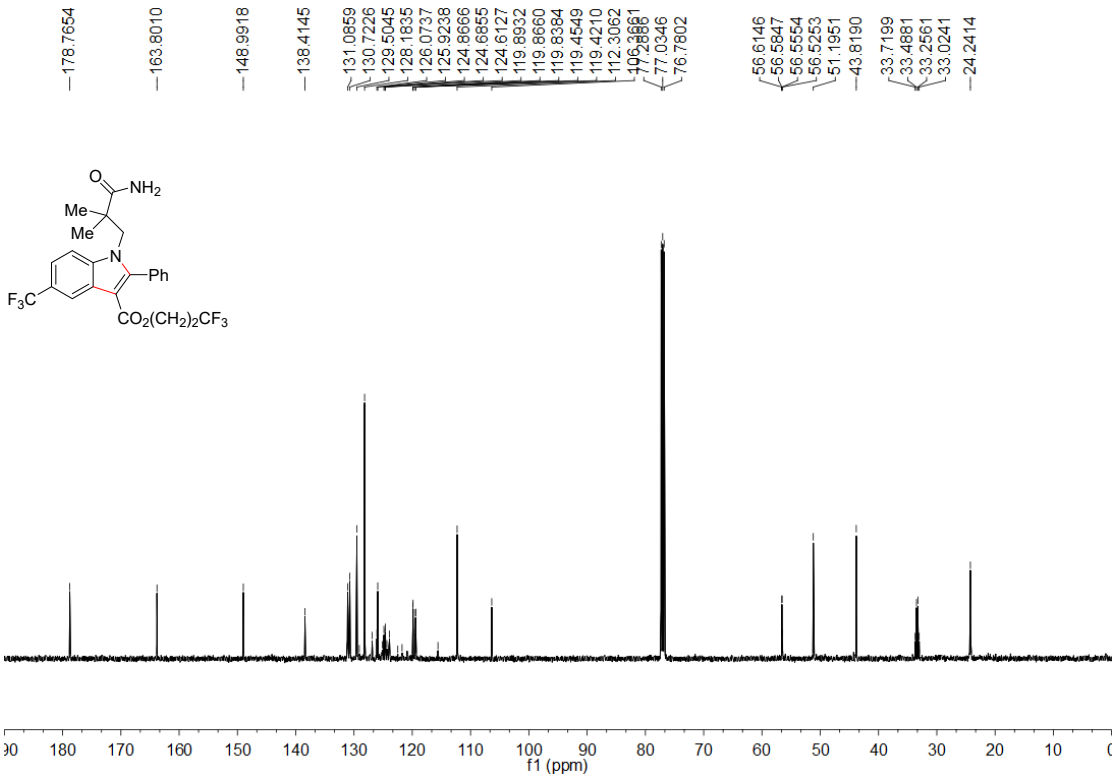
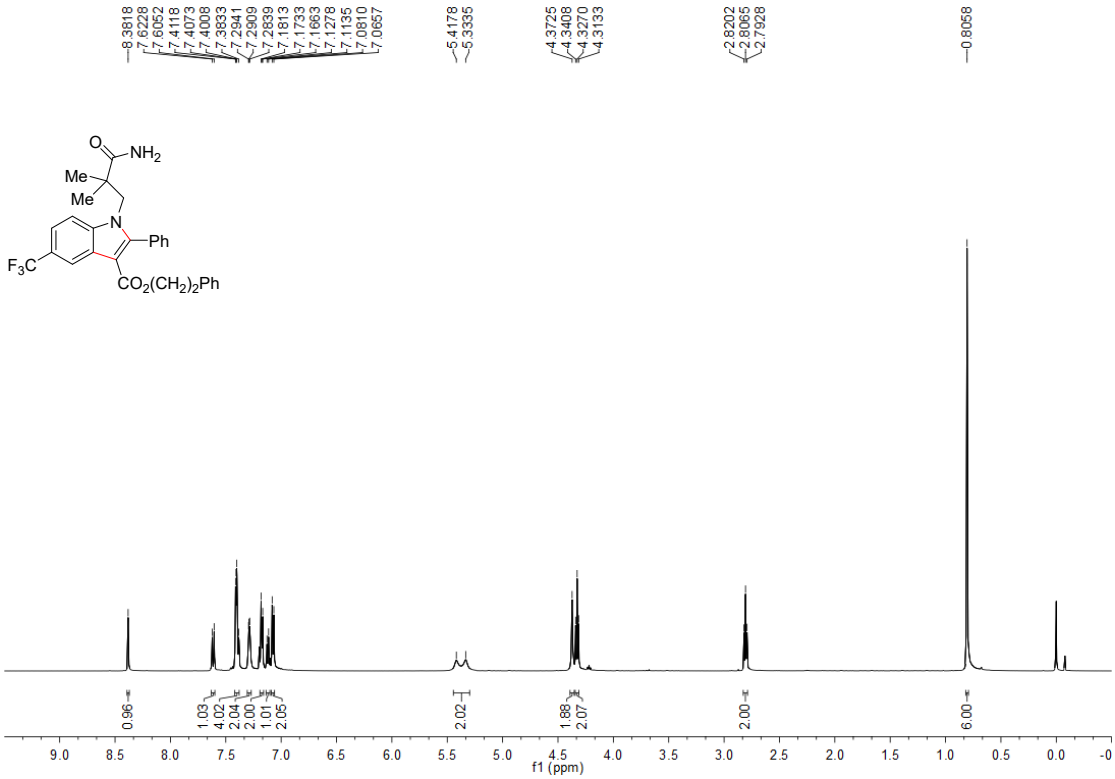
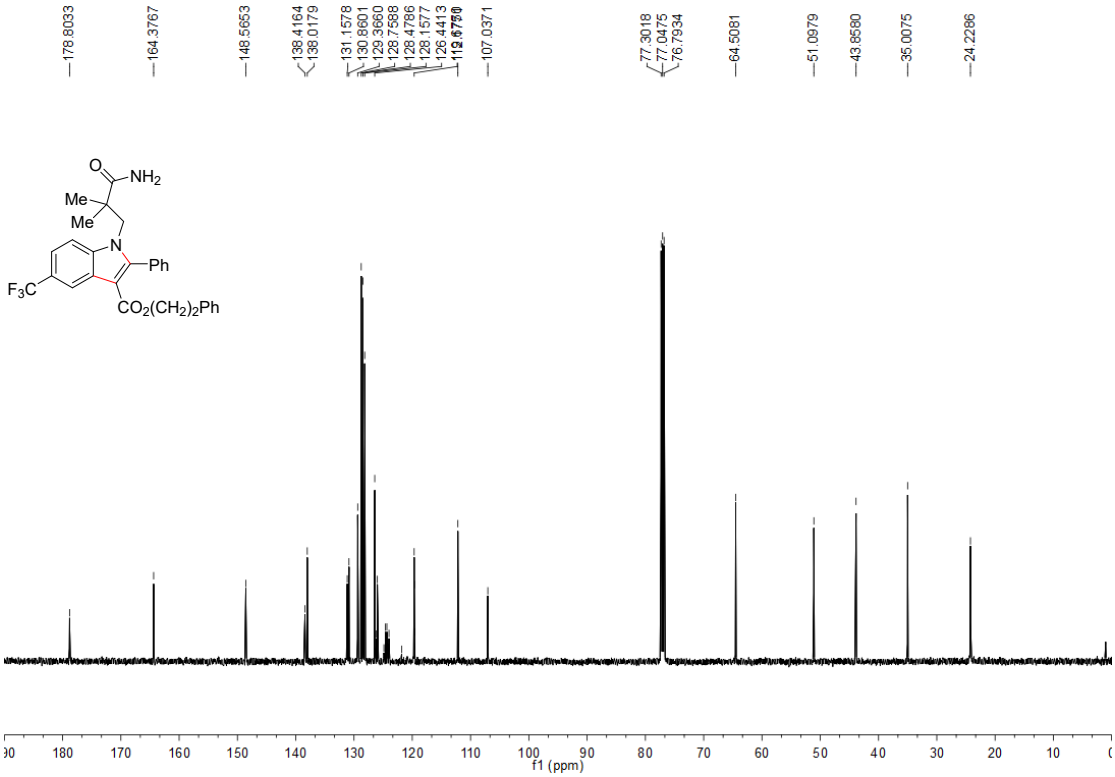


26c

^{1}H NMR

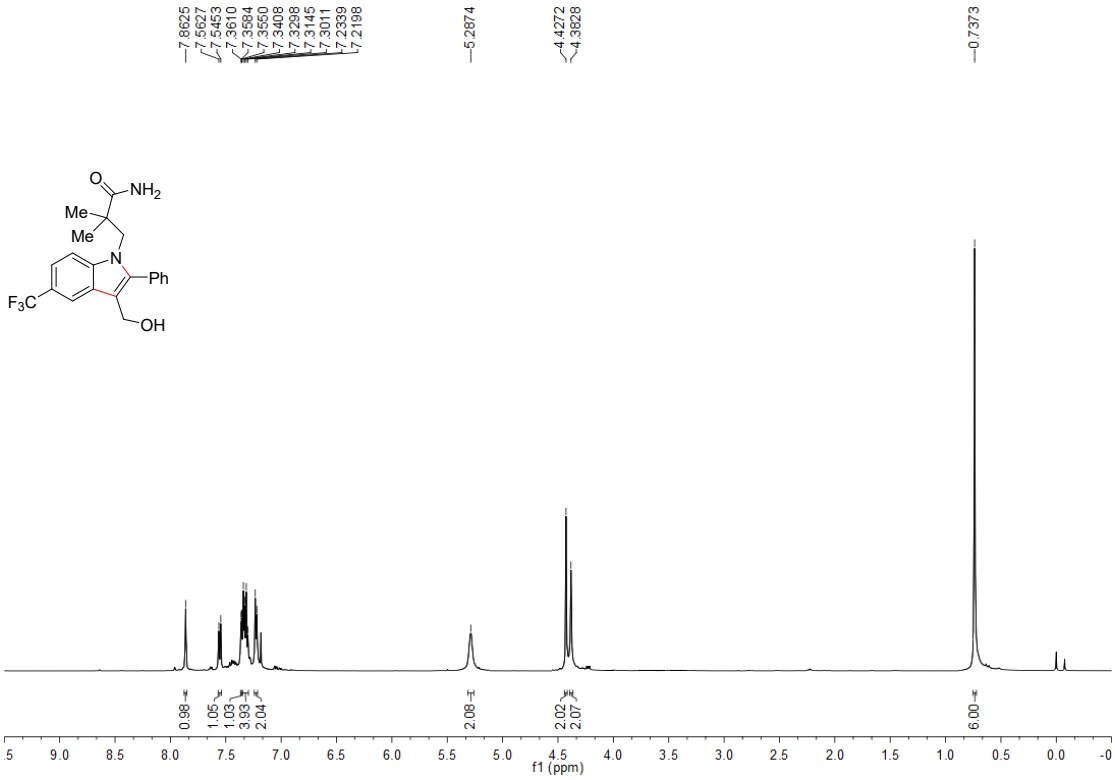


^{13}C NMR

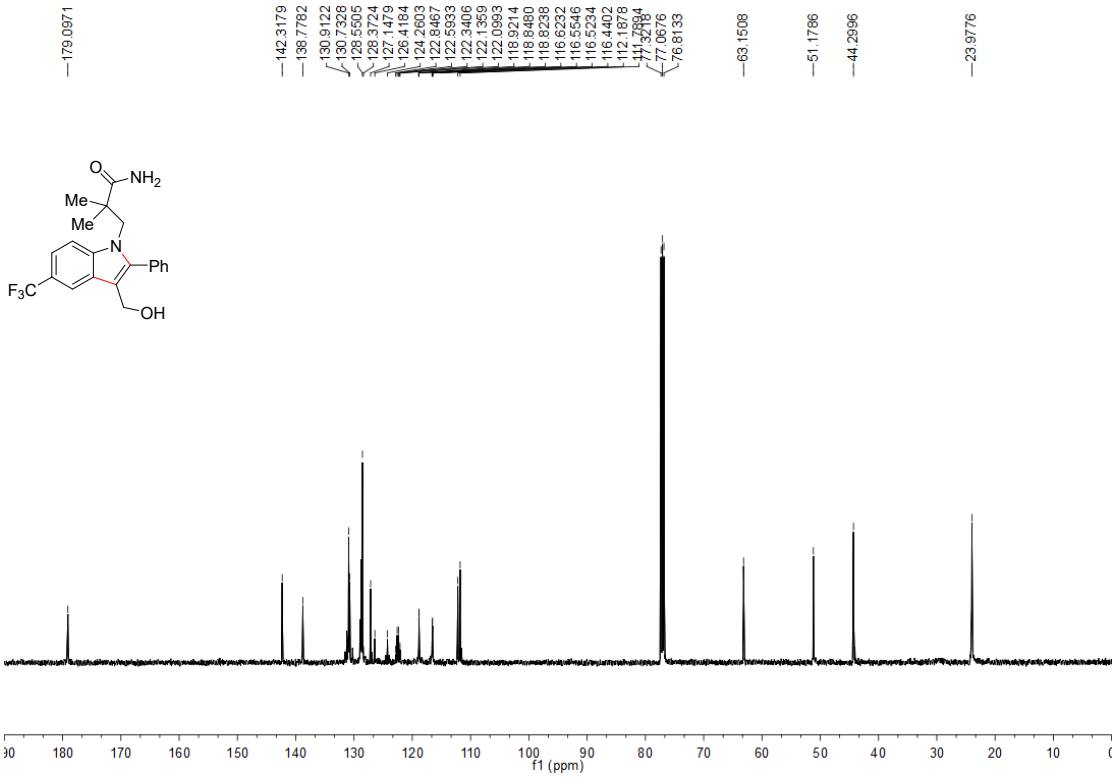


27c

^{1}H NMR

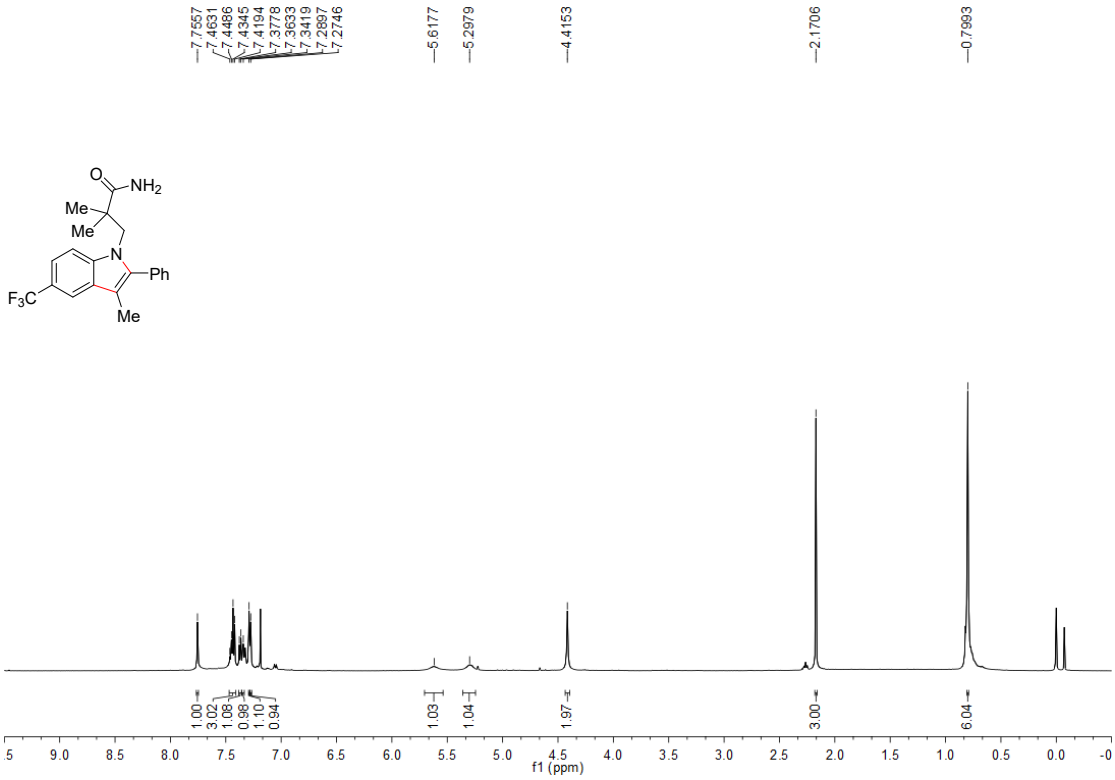


^{13}C NMR

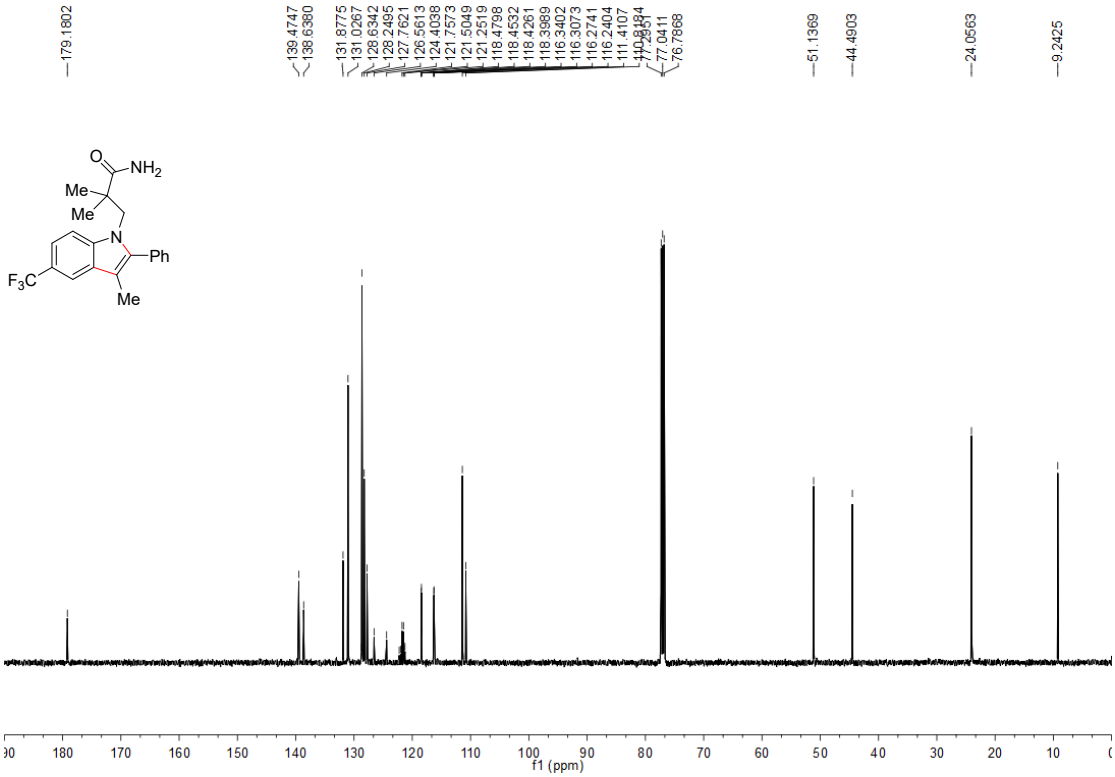


28c

^{1}H NMR

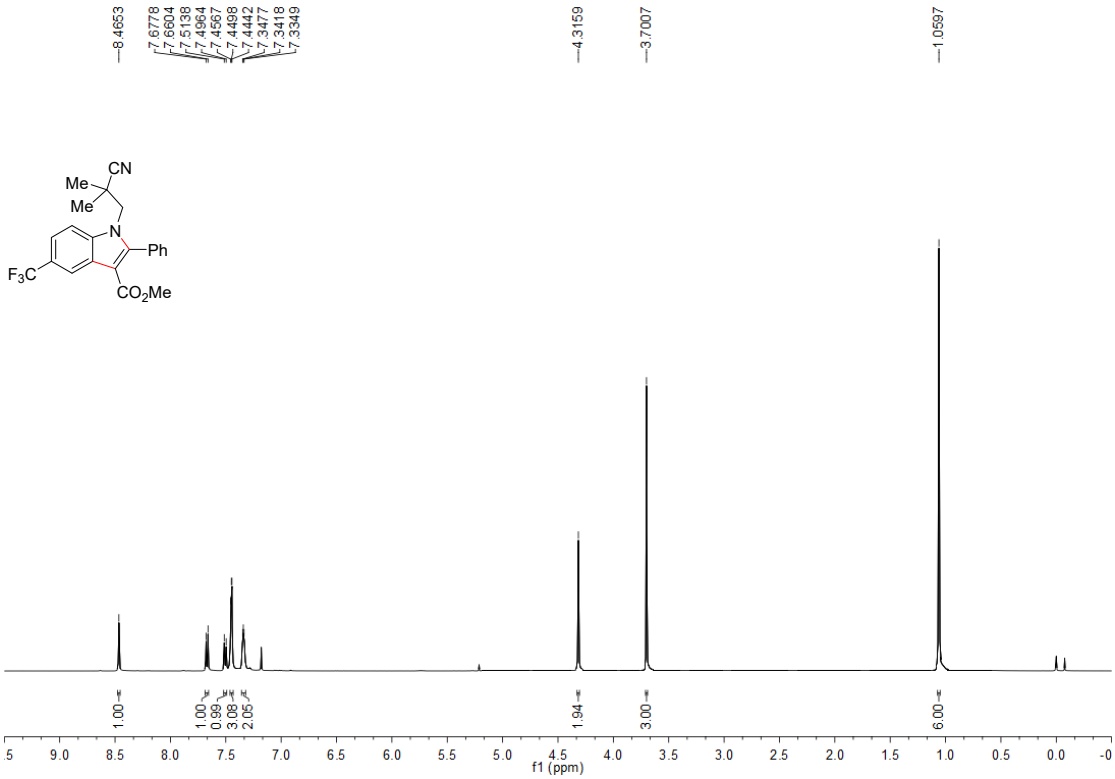


^{13}C NMR

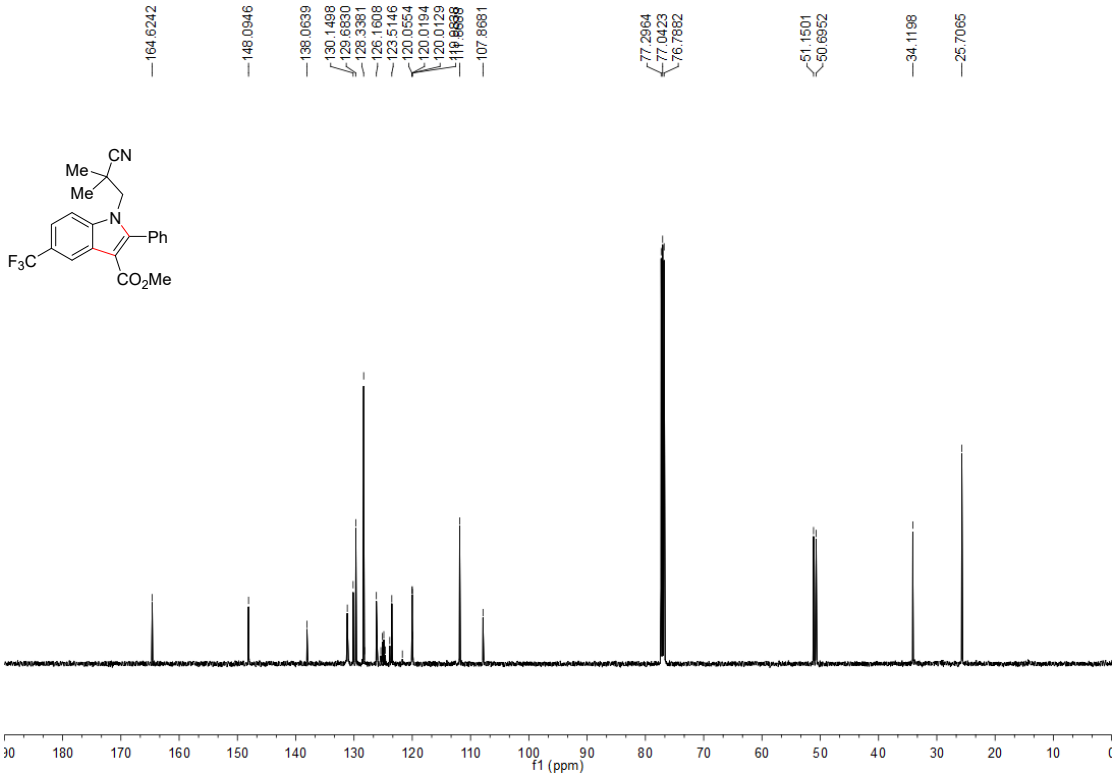


29c

^{1}H NMR

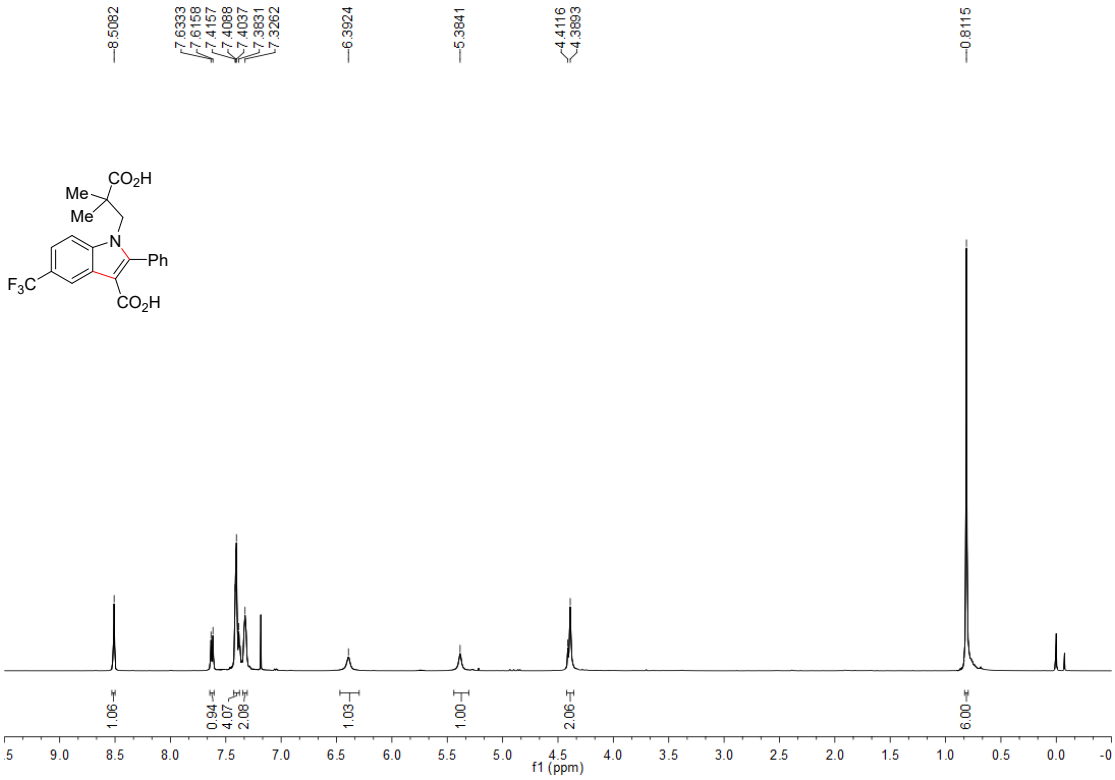


^{13}C NMR



30c

^{1}H NMR



^{13}C NMR