Electronic Supplementary Information

Continuous flow synthesis of indoles by Pd-catalyzed deoxygenation of 2-nitrostilbenes with carbon monoxide

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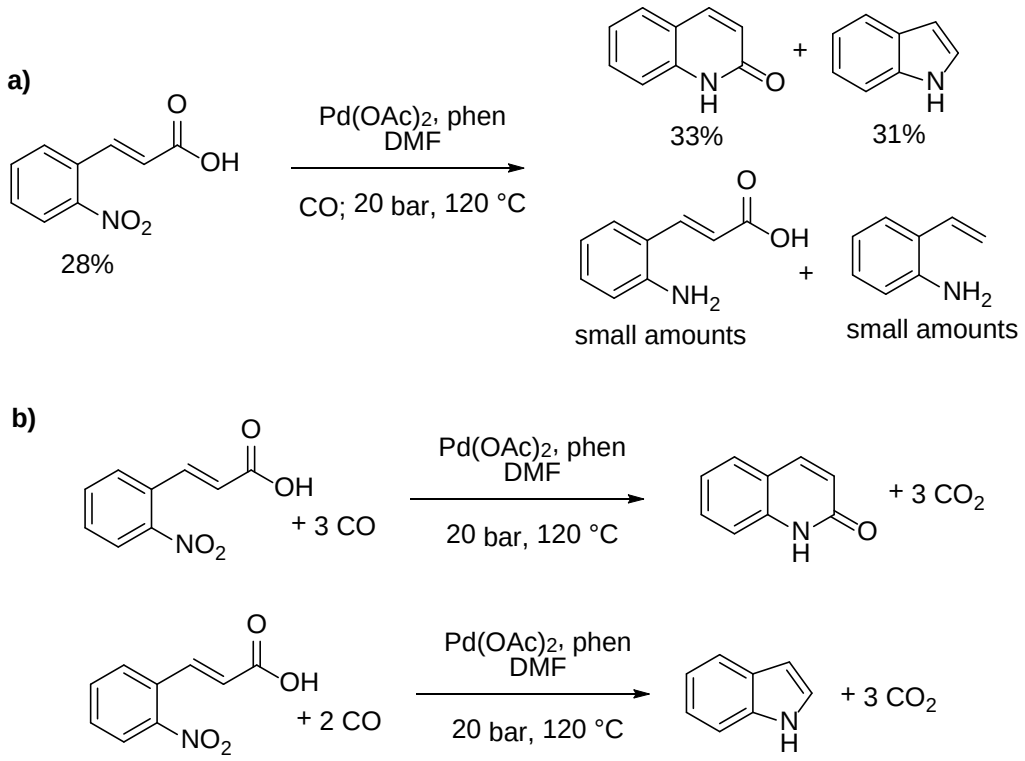


Scheme S1 $Pd(OAc)_2$ catalyzed reduction of 2-nitrocinnamic acid with CO: a) HPLC peak area integration at 215 nm. Conditions: 5 mol% $Pd(OAc)_2$ and 5 mol% 1,10- phenanthroline (phen) in DMF as solvent; 120 °C reaction temperature; 20 bar pressure, ~30 min residence time. b) Balanced equation; hydrogen (*e.g.* from a water-gas shift reaction with water impurities in DMF) might be involved in the reduction of the nitro group.

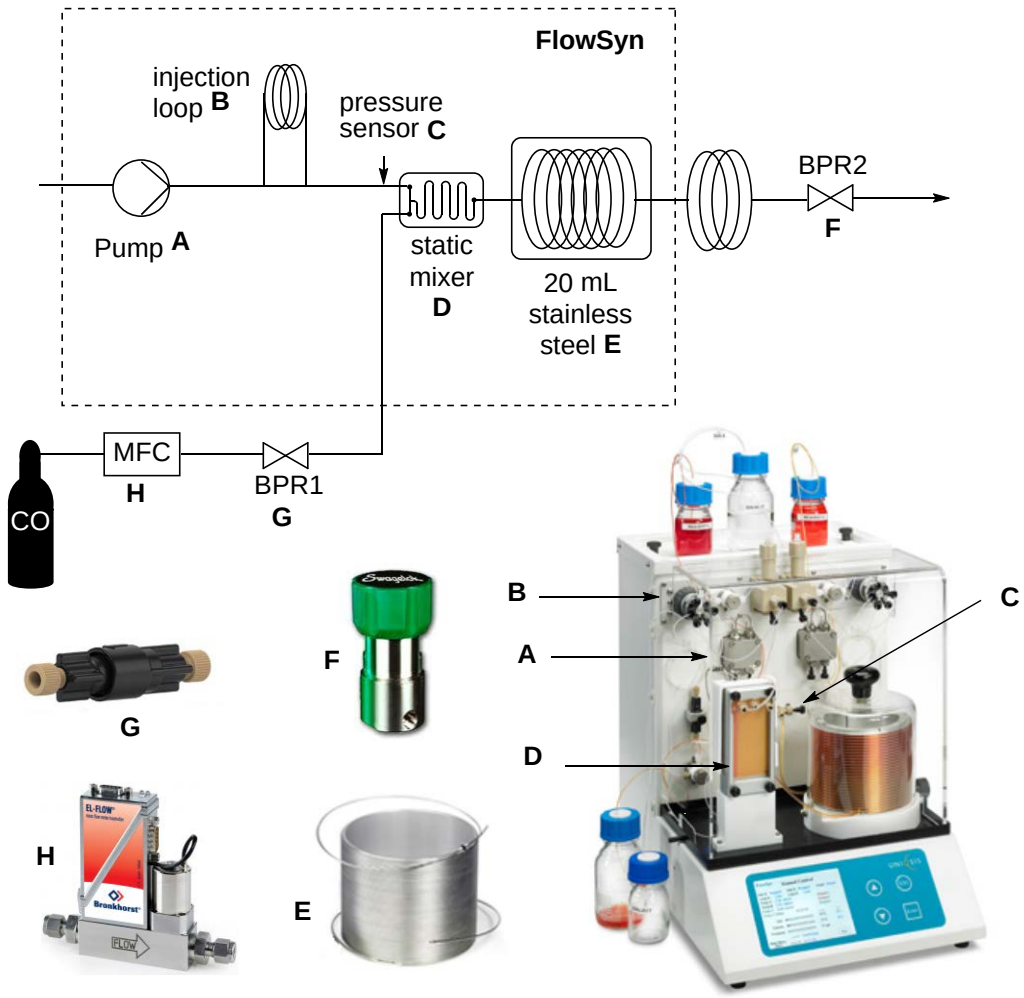
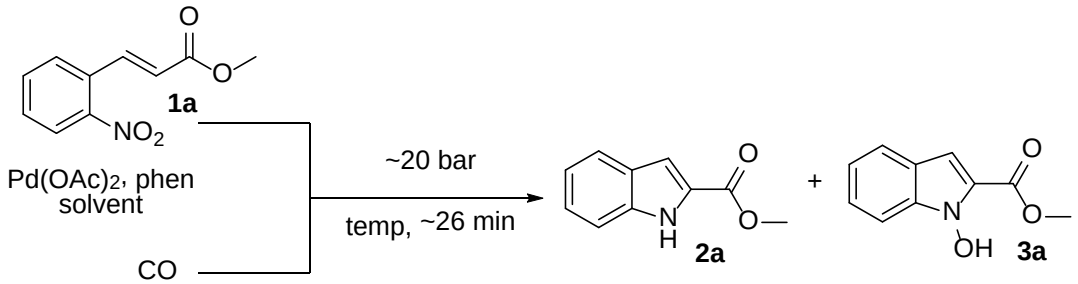


Fig S1 Schematic diagram of the flow reactor for aerobic oxidation. Pump **A**, injection loop **B**, pressure sensor **C**, static mixer **D** and stainless steel coil **E** are part of the Uniqsis FlowSyn (www.uniqsis.com). Mass flow controller **H** was purchased from Bronkhorst (www.bronkhorst.com); adjustable back pressure regulator **F** was purchased from Swagelok (www.swagelok.com); fixed back pressure regulator H was purchased from IDEX Health & Science (www.idex-hs.com).

Table S1 Palladium catalyzed reductive cyclization in a microwave reactor [a]



time [min]	MeCN **1a** [%][b]	MeCN **2a** [%][b]	MeCN **3a** [%][b]	ethyl acetate **1a** [%][b]	ethyl acetate **2a** [%][b]	ethyl acetate **3a** [%][b]	toluene **1a** [%][b]	toluene **2a** [%][b]	toluene **3a** [%][b]
0	100	0	0	100	0	0	100	0	0
10	96	2	2	98	1	1	95	2	3
20	90	8	2	94	2	4	89	5	6
30	89	11	0	92	3	6	86	8	6

[a] Conditions: 0.9 mmol substrate **1a**, 1 mol% $Pd(OAc)_2$, 2 mol% 1,10-phenanthroline, 20 mol% tributylamine in 3 mL solvent. 110 °C; Biotage vial filled with CO, subjected to microwave heating in a Biotage Initiator$^+$. [b] HPLC peak area integration at 215 nm.

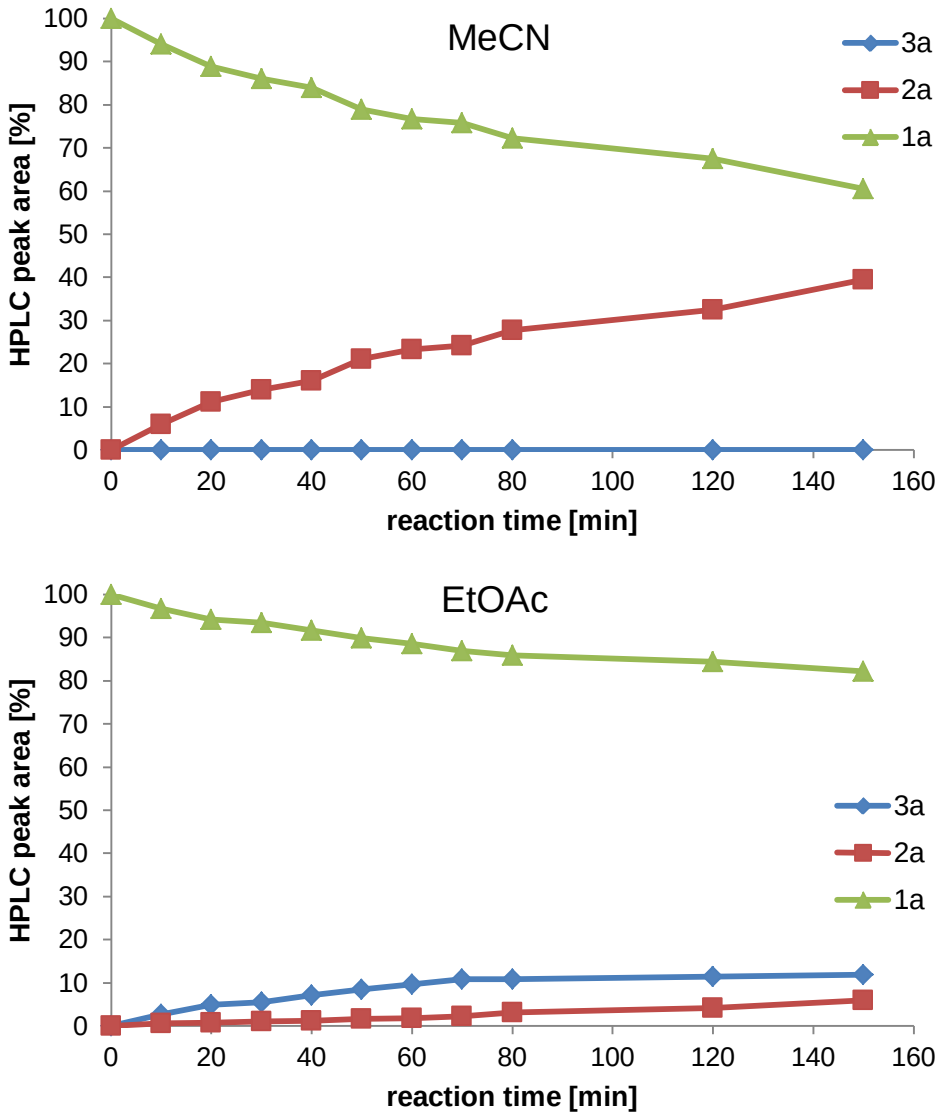


Fig S2 Palladium catalyzed reductive cyclization under reflux conditions. Conditions: 0.9 mmol substrate **1a**, 1 mol% $Pd(OAc)_2$, 2 mol% 1,10-phenanthroline, 20 mol% tributylamine in 3 mL solvent. Oil bath; reaction temperature boiling point of solvent; CO bubbled through reaction mixture. Reaction was monitored by HPLC (215 nm).

Table S2 Influence of amount of CO (MeCN as solvent) [a]

flow rate liquid [mL/min]	flow rate CO [mL/min]	CO [equiv]	**1a** [%][b]	**2a** [%][b]	others [%][b]
0.5	3	0.8	50	48	2
0.5	5	1.4	32	65	3
0.5	7	1.9	25	73	3
0.5	10	2.8	25	72	2

[a] Conditions: 0.9 mmol substrate **1a**, 1 mol% $Pd(OAc)_2$, 4 mol% 1,10-phenanthroline in 3 mL MeCN. ~20 bar pressure; 120 °C; residence time; ~30 min. [b] HPLC peak area integration at 215 nm.

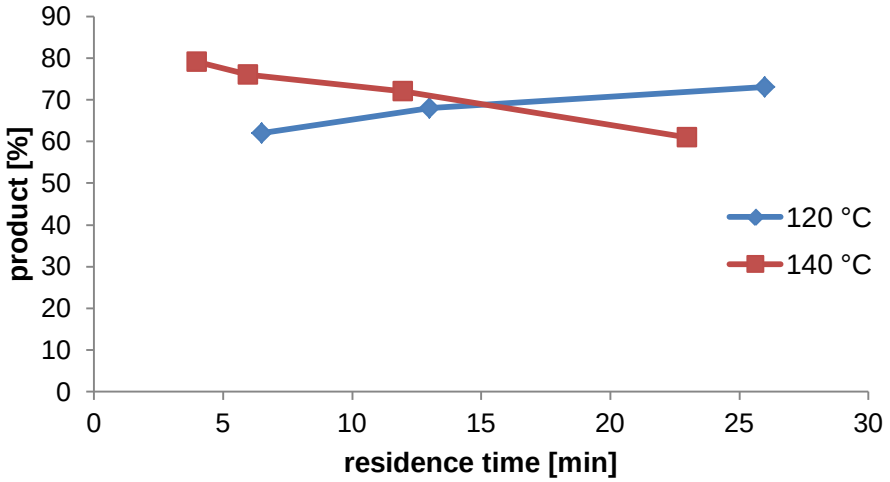


Fig S3 Product formed at 120 °C and 140 °C with different residence times (conditions see Table S2).

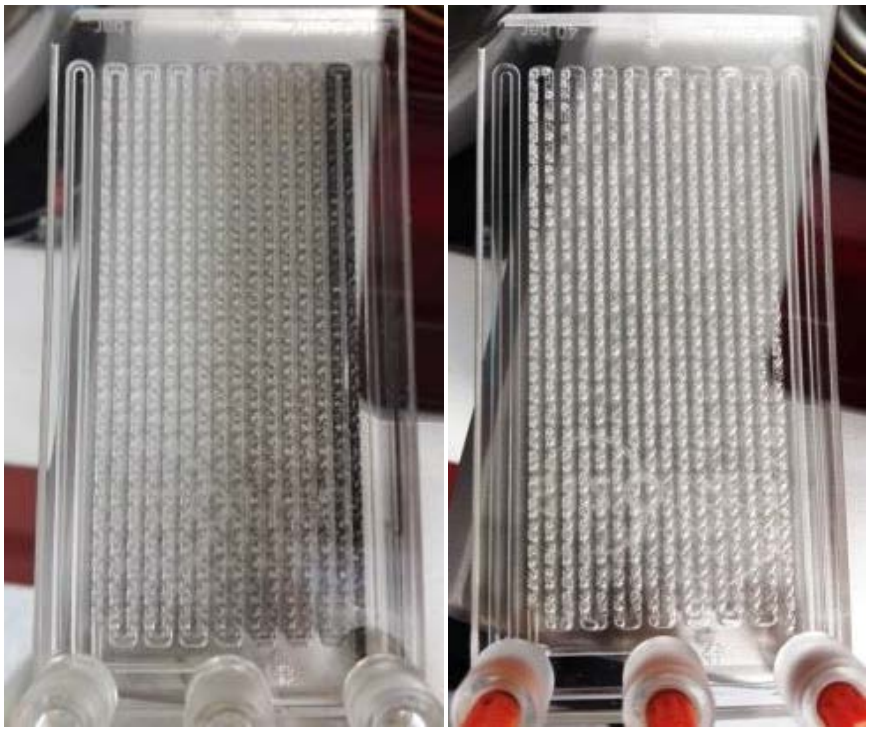
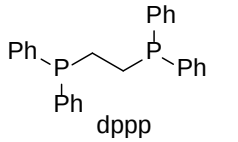
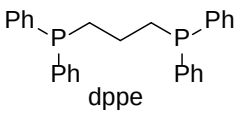
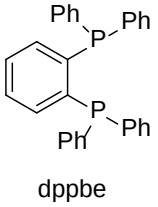


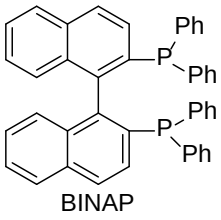
Fig S4 Palladium(0) deposited on the channels of the static mixer immediately upon contact of $Pd(OAc)_2$ with CO (left). The palladium(0) precipitate can be fully removed from the chip with aqua regia (right). For large scale synthesis, cleaning cycles could be implemented to avoid accumulation of Pd(0) on the channels of the microreactor.

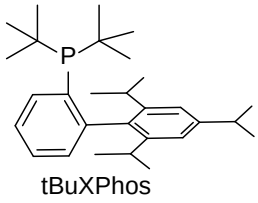
Table S3 Reductive cyclization in the presence of various phosphine ligands [a]

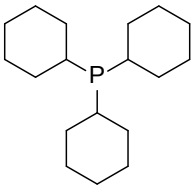


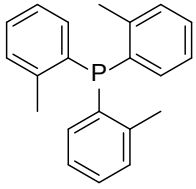


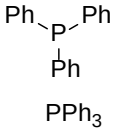


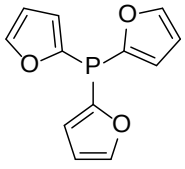








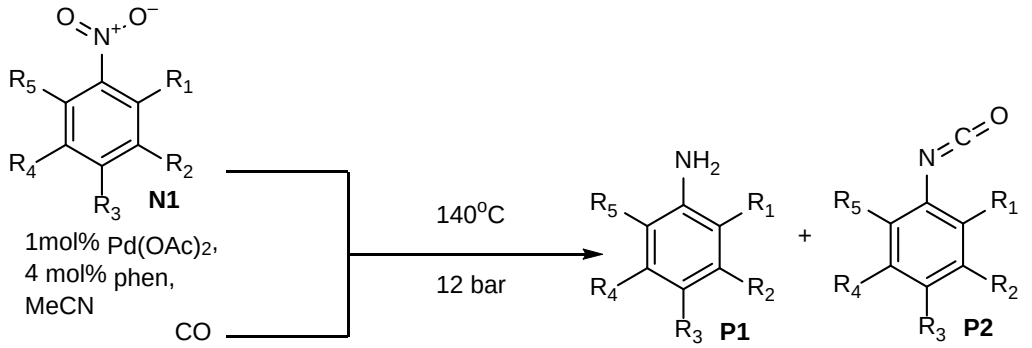




	ligand [mol%]	**1a** [%][b]	**2a** [%][b]	**3a** [%][b]	others [%][b]
1	PCy_3 (4)	98	2	0	0
2	$P(o\text{-}tol)_3$ (4)	93	7	0	0
3	tBuXPhos (4)	93	1	6	0
4	TFP (4)	99	0	1	0
5	PPh_3 (4)	92	0	3	5
6	dppe (4)	98	1	1	0
7	dppp (4)	92	6	0	2
8	dppbe (4)	95	2	1	2
9	BINAP (4)	92	8	0	0
10	phen/dppe (2:2)	43	55	2	0
11	phen/dppp (3:1)	27	52	19	2
12	phen/dppp (1:1)	40	42	16	2
13	phen/dppp (2:2)	15	56	26	3
14	phen/dppp (1:3)	49	19	28	4

[a] Conditions: 0.9 mmol substrate **1a**, 1 mol% $Pd(OAc)_2$ and 4 mol% ligand in 3 mL MeCN. Flow rate gas/liquid: 8/0.5 mL/min (~2.2 equivalent of CO). ~20 bar pressure; 140 °C; 4 min residence time. [b] HPLC peak area integration at 215 nm.

Table S4 Palladium catalyzed reduction of nitro arenes [a]



	R_1	R_2	R_3	R_4	R_5	N1 [%][b]	P1 [%][b]	P2 [%][b]	others [%][b]
1	Cl	H	H	H	H	100	0	0	0
2	OEt	H	H	OEt	H	100	0	0	0
3	H	H	Br	H	H	100	0	0	0
4	NH_2	H	H	Cl	H	100	0	0	0
5[c]	H	NH_2	Cl	H	H	100	0	0	0
6[c]	H	Cl	Cl	H	H	100	0	0	0
7	H	H	OH	H	H	100	0	0	0
8	H	NO_2	H	H	Cl	100	0	0	0
9	H	H	CH=CHCOOEt	H	H	100	0	0	0
10	H	COOMe	H	H	H	100	0	0	0
11	F	H	OEt	H	H	100	0	0	0
12	I	H	H	H	H	100	0	0	0

[a] Conditions: 0.9 mmol substrate, 1 mol% $Pd(OAc)_2$ and 4 mol% ligand in 3 mL MeCN. Flow rate gas/liquid: 8/0.5 mL/min (~2.2 equivalent of CO). ~12 bar pressure; 140 °C; 4 min residence time. [b] Reaction was monitored by HPLC (215 nm). [c] 20 equiv. MeOH. Even in the presence of methanol as proton source no reduction to aniline or other reduction products was observed.

Table S5 Comparison of reactions with/without nitrobenzene in the mixture [a]

	1f[b] [%]	**2f**[b] [%]
Without $PhNO_2$	19	81
With $PhNO_2$[c]	99	1

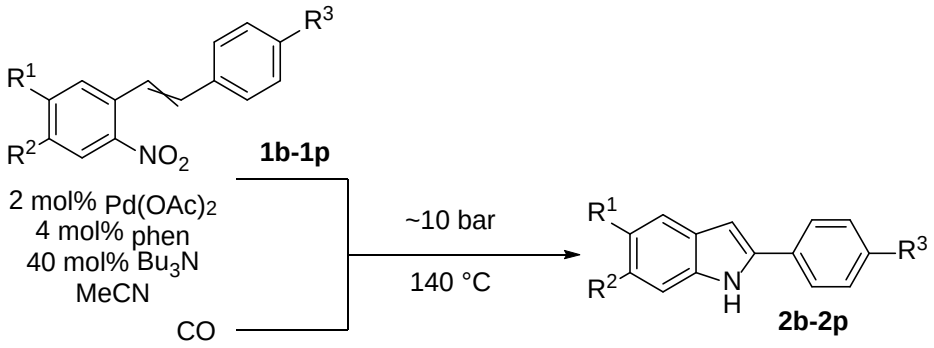
[a] Conditions: 0.9 mmol substrate **1f**, 2 mol% $Pd(OAc)_2$ and 4 mol% ligand 20 mol% tributylamine in 3 mL MeCN. Flow rate gas/liquid: 8/0.5 mL/min (~2.2 equivalent of CO). ~12 bar pressure; 140 °C; residence time: 4 min. [b] Reaction was monitored by HPLC (215 nm). [c] The mixture contained 10% of $PhNO_2$.

Table S6 ICPMS analysis of the reaction mixture [a]

sample	sample [mg]	Pd determined [mg/kg]	Pd determined [mg]	Pd expected [mg][b]	Pd determined [%]
control	6.5	126500	0.822	0.822	
blank	30.9	885	0.027	0.822	3
1x[c]	186.7	2124	0.397	0.822	48
1a	440.5	1114	0.491	0.822	60
1f	216.8	334	0.072	0.822	9
1g	229.1	181	0.041	0.822	5
wash	10 (mL)	289 (mg/L)	2.890		
		sum	3.92	4.11	95

[a] A stock solution of 12.1 mg $Pd(OAc)_2$ (1 mol%), 19.5 mg 1,10-phenanthroline (2 mol%) and 43 µL tributylamine (20 mol%) in 18 mL MeCN was prepared. Three mL of this solution were pipetted to 0.9 mmol of substrate (**1x**, **1a**, **1f** or **1g**). The solutions, inclusive a blank (no substrate dissolved), were pumped through the glass mixer under standard conditions (flow rate gas/liquid: 8/0.5 mL/min (~2.2 equivalent of CO). ~12 bar pressure; 140 °C). The control sample was not processed. The solvent was evaporated under reduced pressure and the samples were analyzed by ICPMS after microwave digestion. The glass chip was washed by rinsing through with 10 mL of aqua regia. [b] The amount of palladium measured for the control sample was used as reference value (deviation from the weighted amount of Pd is attributed to weighting and pipette error). [c] **1x** = stilbene of undisclosed structure.

Table S7 Continuous flow reductive cyclization of *o*-nitrostilbenes **3** with CO as terminal reductant [a]



	R^1,R^2	R^3	starting material (E/Z)	first pass (rt= 15 min)[b]	second pass (rt= 30 min)[b]	yield [%][b]
1b	H,CF_3	CN	(58/42)	57(12/88)	89(0/100)	80
1c		H	(55/45)	98(30/70)	-.	90
1d		*t*Bu	(53/47)	57(44/56)	95(45/55)	85
1e		F	(68/32)	90(47/53)	-	83
1f	H,H	CN	(43/57)	95(-/-)	-	90
1g		H	(52/48)	81(25/75)	81(24/76)	70
1h		*t*Bu	(47/53)	37(32/68)	39(32/68)	n.d.
1i		F	(38/62)	14(13/87)	16(17/83)	n.d.
***E*-1j**	H,NMe_2	CN	(100/0)	50(96/4)	83(94/6)	n.d.
***Z*-1j**		CN	(0/100)	57(1/99)	95(96/4)	74
1k		H	(44/56)	16(26/73)	25(35/65)	n.d.
1l		*t*Bu	(48/52)	13(40/60)	14(40/60)	n.d.
1m		F	(41/59)	6(22/78)	14(22/78)	n.d.
1n	Cl,H	CN	(59/41)	41(4/96)	-.	40
1o		H	(60/40)	51(20/80)	58(20/80)	45
1p		F	(54/46)	87(27/73)	-	80

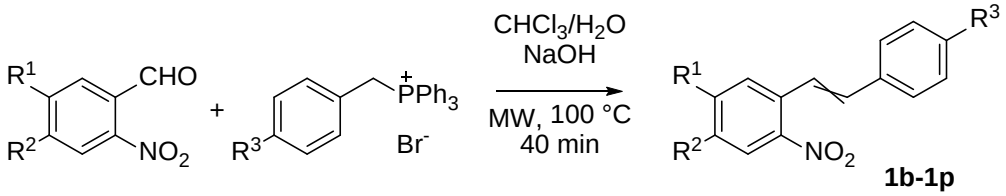
[a] Conditions: 0.9 mmol substrate **1**, 2 mol% $Pd(OAc)_2$ and 4 mol% ligand, 20 mol% tributylamine in 3 mL MeCN. Flow rate gas/liquid: 8/0.5 mL/min (~2.2 equivalent of CO). ~12 bar pressure; 140 °C. [b] Conversion according HPLC peak area integration at 215 nm. In parenthesis is the E/Z ratio of the remaining starting material.

General Procedure for Stilbene Synthesis under Microwave Conditions

Into a 30 mL microwave process vial equipped with a magnetic stir bar were placed 2.0 mmol of the respective aldehyde **1a-d**, 2.0 mmol of Wittig reagent (phosphoium ylide **2a-d**), 1 equiv of NaOH, 7 mL of chloroform and 7 mL of distilled water. The vials were sealed by capping and the samples were irradiated in an Anton Paar Monowave 300 for 40 min (fixed hold time) at 100 °C

(~6 bar). After the reaction time has elapsed, the mixtures were cooled to 55 °C by compressed air. The product was extracted with dichloromethane in 3 portions of 30 mL. The dichlormethane fractions were comined, dried over sodium sulphate and the solvent was then evaporated under reduced pressure. The residue was purified by column chromatography on silica gel using ethyl acetate and petroleum ether (20:80) to give E/Z mixtures of the stilbene **3** as coloured solids. This approach was suitable for all stilbenes and provided pure stilbene products as mixture of E and Z isomers (HPLC at 215 nm) in high yields (see Table S9 for a summary).

Table S8 Synthesis of *o*-nitrostilbenes **1b**-**1p** by an aqueous/$CHCl_3$-biphasic Wittig reaction [a]



1b-1p

	R^1,R^2	R^3	E/Z	yield [mg][b]	yield [%][b]
1b	H,CF_3	CN	58/42	521	82
1c		H	55/45	421	72
1d		*t*Bu	53/47	469	67
1e		F	68/32	523	84
1f	H,H	CN	43/57	422	84
1g		H	52/48	361	80
1h		*t*Bu	47/53	350	62
1i		F	38/62	380	78
***E*-1j**	H,NMe_2	CN	-	160	23
***Z*-1j**		CN	-	355	51
1k		H	44/56	429	80
1l		*t*Bu	48/52	331	51
1m		F	41/59	423	74
1n	Cl,H	CN	59/41	417	73
1o		H	60/40	418	80
1p		F	54/46	478	86

[a]Conditions: Microwave heating for 40 min at 100 °C (see Experimental Section for details). [b]Isolated yields after purification by column chromatography on silica gel. Purity of compounds was determined by ^{1}H NMR, HPLC and GC-MS analysis. Four nitroaldehydes and four benzyl phosphonium bromides with either electron-donating, -neutral or -withdrawing substituents on the phenyl ring have been selected as the starting materials. The Wittig reaction proceeded to completion within 40 min at 100 °C for all attempted combinations of aldehyde and phosphonium salts.

(E/Z)-4-(2-Nitro-4-(trifluoromethyl)styryl)benzonitrile (1b): Yellow solid; isolated yield: 82% (520 mg, 1.64 mmol), ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 10.47 (s, 1H), 8.40 (d, *J* = 0.8 Hz, 8H), 8.29 (s, 3H), 8.13 – 8.02 (m, 2H), 7.95 – 7.86 (m, 6H), 7.75 (s, 1H), 7.74 – 7.60 (m, 21H), 7.55 – 7.45 (m, 15H), 7.31 (d, *J* = 8.1 Hz, 8H), 7.20 – 7.10 (m, 18H), 7.05 (d, *J* = 12.2 Hz, 8H), 6.88 (d, *J* = 12.2 Hz, 8H). Z:E 42:58 (^{1}H NMR). (MS) (EI): m/z : 318 $[M]^+$.

(E/Z)-2-Nitro-1-styryl-4-(trifluoromethyl)benzene (1c): Yellow solid; isolated yield: 72% (421 mg, 1.44 mmol), ^{1}H NMR (300 MHz, $CDCl_3$ TMS) δ 8.29 (t, *J* = 9.3 Hz, 76H), 8.15 (d, *J* = 0.6 Hz, 26H), 8.06 – 7.91 (m, 10H), 7.78 (dt, *J* = 8.8, 5.0 Hz, 55H), 7.73 – 7.08 (m, 573H), 7.08 – 6.68 (m, 307H), 1.47 (s, 13H), 1.13 (dt, *J* = 30.3, 11.2 Hz, 6H). Z:E 45:55 (^{1}H NMR). MS (EI): m/z: 293 $[M]^+$.

(E/Z)-1-(4-(tert-Butyl)styryl)-2-nitro-4-(trifluoromethyl)benzene (1d): Yellow solid, isolated yield: 67% (469 mg, 1.34 mmol), ^{1}H NMR (300 MHz, $CDCl_3$ TMS) δ 8.28 (d, *J* = 0.7 Hz, 25H), 8.15 (d, *J* = 0.7 Hz, 18H), 7.84 (d, *J* = 8.3 Hz, 19H), 7.75 (dd, *J* = 8.5, 1.5 Hz, 19H), 7.45 (dddd, *J* = 13.8, 8.5, 7.3, 1.6 Hz, 145H), 7.22 – 7.07 (m, 84H), 7.07 – 6.61 (m, 107H), 1.95 – 1.68 (m, 5H), 1.48 (s, 15H), 1.25 (dd, *J* = 20.0, 7.3 Hz, 394H), 1.05 (dd, *J* = 20.4, 14.5 Hz, 16H), 0.82 (dd, *J* = 16.1, 6.6 Hz, 11H). Z:E 47:53 (^{1}H NMR). MS (EI): m/z: 349 $[M]^+$.

(E/Z)-1-(4-Fluorostyryl)-2-nitro-4-(trifluoromethyl)benzene (1e): Yellow solid; isolated yield: 84% (523 mg, 1.68 mmol), ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23 (d, *J* = 0.7 Hz, 9H), 8.10 (s, 4H), 7.79 (d, *J* = 8.3 Hz, 4H), 7.73 (d, *J* = 1.5 Hz, 3H), 7.70 (d, *J* = 1.5 Hz, 1H), 7.53 (dd, *J* = 8.2, 1.3 Hz, 11H), 7.46 – 7.37 (m, 14H), 7.29 (d, *J* = 8.1 Hz, 11H), 7.06 (s, 3H), 6.99 (t, *J* = 3.6 Hz, 4H), 6.93 (ddd, *J* = 11.5, 5.2, 3.0 Hz, 28H), 6.84 – 6.56 (m, 38H), 1.17 (dd, *J* = 24.5, 14.5 Hz, 1H). Z:E 32:68 (^{1}H NMR). MS (EI): m/z: 311 $[M]^+$.

(E/Z)-4-(2-Nitrostyryl)benzonitrile (1f): Yellow solid; isolated yield: 84% (421 mg, 1.68 mmol), ^{1}H NMR (300 MHz, $CDCl_3$ TMS) δ 8.16 – 8.00 (m, 27H), 7.95 (dd, *J* = 8.2, 1.2 Hz, 8H), 7.74 – 7.65 (m, 12H), 7.63 – 7.51 (m, 6H), 7.38 (dt, *J* = 3.5, 1.3 Hz, 15H), 7.12 – 7.04 (m, 12H), 7.01 (d, *J* = 2.4 Hz, 2H), 6.97 (d, *J* = 6.4 Hz, 3H), 6.70 (d, *J* = 12.1 Hz, 28H), 5.23 (s, 8H), 2.35 (s, 7H), 1.50 (d, *J* = 9.1 Hz, 11H), 1.24 – 0.81 (m, 7H). Z:E 57:43 (^{1}H NMR). MS (EI): m/z : 250 $[M]^+$.

(E/Z)-1-Nitro-2-styrylbenzene (1g): Yellow solid; isolated yield: 80% (361 mg, 1.60 mmol), ^{1}H NMR (300 MHz, $CDCl_3$ TMS) δ 8.03 – 7.96 (m, 1H), 7.87 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.68 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.52 (dd, *J* = 4.7, 4.0 Hz, 1H), 7.50 – 7.43 (m, 2H), 7.35 – 7.26 (m, 4H), 7.21 –

7.16 (m, 1H), 7.07 (dt, *J* = 5.1, 2.9 Hz, 3H), 6.99 – 6.94 (m, 2H), 6.81 (d, *J* = 12.1 Hz, 1H), 6.68 (d, *J* = 12.1 Hz, 1H). Z:E 48:52 (^{1}H NMR). MS (EI): m/z : 225$[M]^+$.

(E/Z)-1-(4-(tert-Butyl)styryl)-2-nitrobenzene (1h): Yellow solid; isolated yield: 62% (350 mg, 1.24 mmol), ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.54 – 7.47 (m, 1H), 7.37 (d, *J* = 6.4 Hz, 1H), 7.31 (d, *J* = 12.1 Hz, 3H), 7.22 (d, *J* = 2.8 Hz, 1H), 7.12 – 7.06 (m, 3H), 7.04 (d, *J* = 2.7 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 2H), 6.85 (s, 1H), 6.79 (d, *J* = 2.8 Hz, 1H), 6.76 (d, *J* = 2.7 Hz, 1H), 6.68 – 6.62 (m, 2H), 6.60 (d, *J* = 2.8 Hz, 1H), 6.52 – 6.41 (m, 1H), 2.91 (d, *J* = 3.0 Hz, 12H).
Z:E 53:47 (^{1}H NMR). MS (EI): m/z : 281$[M]^+$.

(E/Z)-1-(4-Fluorostyryl)-2-nitrobenzene (1i): Yellow solid; isolated yield: 78% (380 mg, 1.56 mmol), ^{1}H NMR (300 MHz, $CDCl_3$ TMS) δ 8.10 – 7.92 (m, 20H), 7.85 (dd, *J* = 8.2, 1.2 Hz, 7H), 7.64 (dd, *J* = 7.9, 1.1 Hz, 8H), 7.50 (ddd, *J* = 8.0, 7.4, 0.8 Hz, 9H), 7.45 – 7.37 (m, 26H), 7.36 – 7.25 (m, 55H), 7.20 – 7.07 (m, 21H), 7.02 – 6.88 (m, 61H), 6.77 (dd, *J* = 5.6, 3.4 Hz, 23H), 6.73 – 6.70 (m, 10H), 6.61 (d, *J* = 12.1 Hz, 21H), 3.38 (s, 1H), 1.53 (s, 1H), 1.38 – 1.13 (m, 1H), 0.77 (d, *J* = 7.0 Hz, 1H). Z:E 62:38 (^{1}H NMR). MS (EI): m/z : 243$[M]^+$.

(E)-4-(4-(Dimethylamino)-2-nitrostyryl)benzonitrile (*E*-1j): Dark red solid; isolated yield: 23% (160 mg, 0.46 mmol), ^{1}H NMR (300 MHz, $CDCl_3$ TMS) δ 7.55 (s, 1H), 7.53 (d, *J* = 2.4 Hz, 1H), 7.48 (d, *J* = 2.0 Hz, 1H), 7.46 (s, 1H), 7.09 (d, *J* = 2.8 Hz, 1H), 6.85 (s, 1H), 6.83 (d, *J* = 2.8 Hz, 1H), 6.81 (s, 1H), 6.80 (s, 1H), 2.99 (s, 1H). E:Z 100:0 (^{1}H NMR). MS (EI): m/z : 293 $[M]^+$.

(Z)-4-(4-(Dimethylamino)-2-nitrostyryl)benzonitrile (*Z*-1j): Dark red solid; isolated yield: 51% (355 mg, 1.02 mmol), ^{1}H NMR (300 MHz, $CDCl_3$ TMS) δ 7.41 – 7.36 (m, 1H), 7.27 (d, *J* = 2.8 Hz, 1H), 7.14 (d, *J* = 8.2 Hz, 1H), 6.91 (s, 1H), 6.88 (d, *J* = 4.1 Hz, 1H), 6.62 (d, *J* = 2.7 Hz, 1H), 6.59 (d, *J* = 2.8 Hz, 1H), 6.54 (s, 1H), 6.50 (s, 1H), 2.96 (s, 3H). E:Z 0:100 (^{1}H NMR). MS (EI): m/z: 293 $[M]^+$.

(E/Z)-N,N-Dimethyl-3-nitro-4-styrylaniline (1k): Red solid; isolated yield: 80% (428 mg, 1.60 mmol), ^{1}H NMR (300 MHz, $CDCl_3$ TMS) δ 7.54 – 7.47 (m, 1H), 7.37 (d, *J* = 6.4 Hz, 1H), 7.31 (d, *J* = 12.1 Hz, 3H), 7.22 (d, *J* = 2.8 Hz, 1H), 7.12 – 7.06 (m, 3H), 7.04 (d, *J* = 2.7 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 2H), 6.85 (s, 1H), 6.79 (d, *J* = 2.8 Hz, 1H), 6.76 (d, *J* = 2.7 Hz, 1H), 6.68 – 6.62 (m, 2H), 6.60 (d, *J* = 2.8 Hz, 1H), 6.52 – 6.41 (m, 1H). Z:E 56:44 (^{1}H NMR). MS (EI): m/z : 268$[M]^+$.

(E/Z)-4-(4-(tert-Butyl)styryl)-N,N-dimethyl-3-nitroaniline (1l): Red solid; isolated yield: 51% (331 mg, 1.02 mmol), ^{1}H NMR (300 MHz, $CDCl_3$ TMS) δ 7.54 – 7.47 (m, 1H), 7.37 (d, *J* = 6.4 Hz, 1H), 7.31 (d, *J* = 12.1 Hz, 3H), 7.22 (d, *J* = 2.8 Hz, 1H), 7.12 – 7.06 (m, 3H), 7.04 (d, *J* = 2.7

Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 2H), 6.85 (s, 1H), 6.79 (d, *J* = 2.8 Hz, 1H), 6.76 (d, *J* = 2.7 Hz, 1H), 6.68 – 6.62 (m, 2H), 6.60 (d, *J* = 2.8 Hz, 1H), 6.52 – 6.41 (m, 1H), 2.91 (s, *J* = 3.0 Hz, 5H), 2.90 (s, 6H). Z:E 52:48 (^{1}H NMR). MS (EI): m/z : 324$[M]^+$.

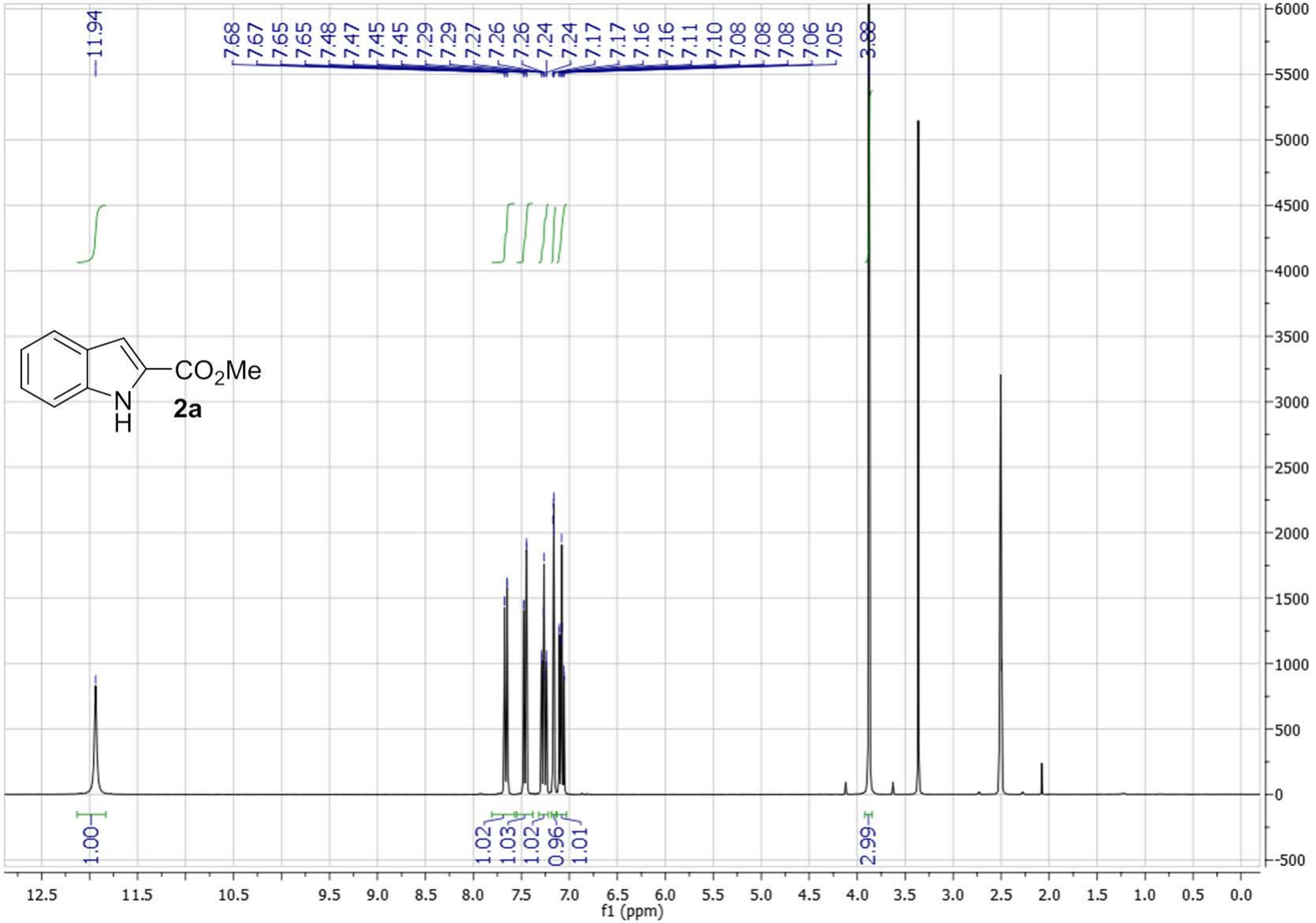
(E/Z)-4-(4-Fluorostyryl)-N,N-dimethyl-3-nitroaniline (1m): Red solid; isolated yield: 74% (423 mg, 1.48 mmol), ^{1}H NMR (300 MHz, $CDCl_3$ TMS) δ 7.50 – 7.40 (m, 1H), 7.33 (ddd, *J* = 8.3, 5.0, 2.9 Hz, 2H), 7.18 (d, *J* = 2.8 Hz, 2H), 7.01 (dd, *J* = 4.9, 2.4 Hz, 2H), 6.99 – 6.95 (m, 4H), 6.90 (ddd, *J* = 9.9, 4.8, 2.6 Hz, 3H), 6.77 (dd, *J* = 4.4, 2.7 Hz, 2H), 6.76 – 6.70 (m, 4H), 6.65 (d, *J* = 11.9 Hz, 2H), 6.56 (dd, *J* = 8.7, 2.8 Hz, 2H), 6.47 – 6.40 (m, 2H). Z:E 59:41 (^{1}H NMR). MS (EI): m/z : 286$[M]^+$.

(E/Z)-4-(5-Chloro-2-nitrostyryl)benzonitrile (1n): Yellow solid; isolated yield: 73% (416 mg, 1.46 mmol),^{1}H NMR (300 MHz, $CDCl_3$ TMS) δ 8.04 (d, *J* = 8.8 Hz, 1H), 7.94 (d, *J* = 8.8 Hz, 1H), 7.67 – 7.61 (m, 1H), 7.62 – 7.56 (m, 1H), 7.47 – 7.40 (m, 2H), 7.39 – 7.32 (m, 1H), 7.11 – 7.04 (m, 3H), 7.02 (s, 1H), 6.96 (d, *J* = 3.6 Hz, 1H), 6.91 (s, 1H), 6.73 (d, *J* = 12.1 Hz, 1H). Z:E 41:59 (^{1}H NMR). MS (EI): m/z: 284$[M]^+$.

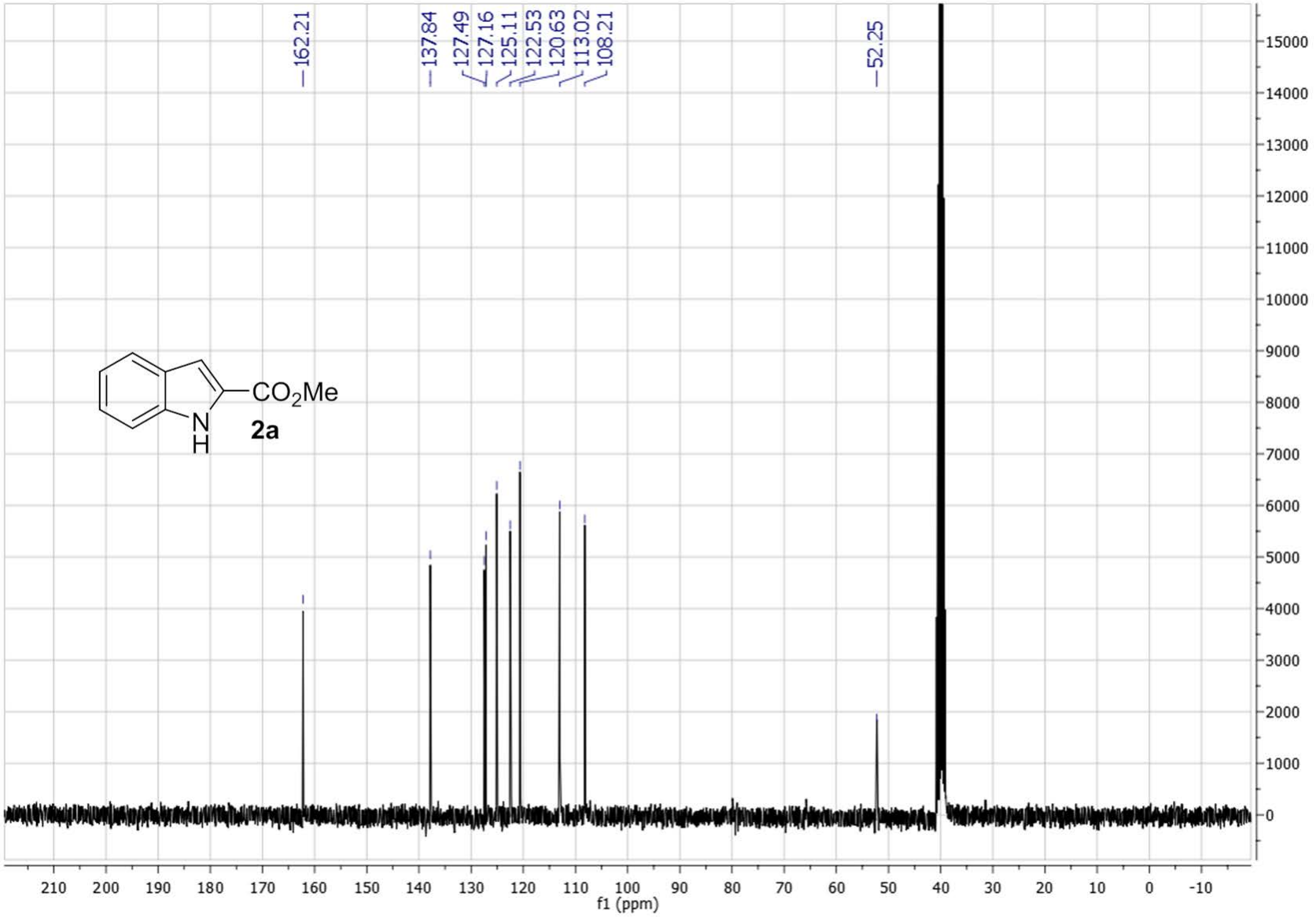
(E/Z)-4-Chloro-1-nitro-2-styrylbenzene (1o): Yellow solid; isolated yield: 80% (418 mg, 1.61 mmol),^{1}H NMR (300 MHz, $CDCl_3$ TMS) δ 7.98 (d, *J* = 8.8 Hz, 1H), 7.88 (d, *J* = 8.8 Hz, 1H), 7.66 (d, *J* = 2.2 Hz, 1H), 7.54 (s, 1H), 7.46 (dd, *J* = 5.6, 4.8 Hz, 1H), 7.36 – 7.25 (m, 3H), 7.17 – 7.10 (m, 4H), 7.05 (s, 1H), 7.02 – 6.95 (m, 2H), 6.74 (d, *J* = 1.9 Hz, 2H). Z:E 40:60 (^{1}H NMR). MS (EI): m/z: 259 $[M]^+$.

(E/Z)-4-Chloro-2-(4-fluorostyryl)-1-nitrobenzene (1p): Yellow solid; isolated yield: 86% (477 mg, 1.72 mmol),^{1}H NMR (300 MHz, $CDCl_3$ TMS) δ 7.99 (d, *J* = 8.8 Hz, 1H), 7.89 (d, *J* = 8.8 Hz, 1H), 7.64 (d, *J* = 2.2 Hz, 1H), 7.48 – 7.39 (m, 1H), 7.29 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.14 (d, *J* = 2.2 Hz, 1H), 7.06 – 6.91 (m, 3H), 6.87 – 6.78 (m, 2H), 6.76 (s, 1H), 6.71 (d, *J* = 8.0 Hz, 2H), 6.66 (s, 1H). Z:E 46:54 (^{1}H NMR). MS (EI): m/z : 277 $[M]^+$.

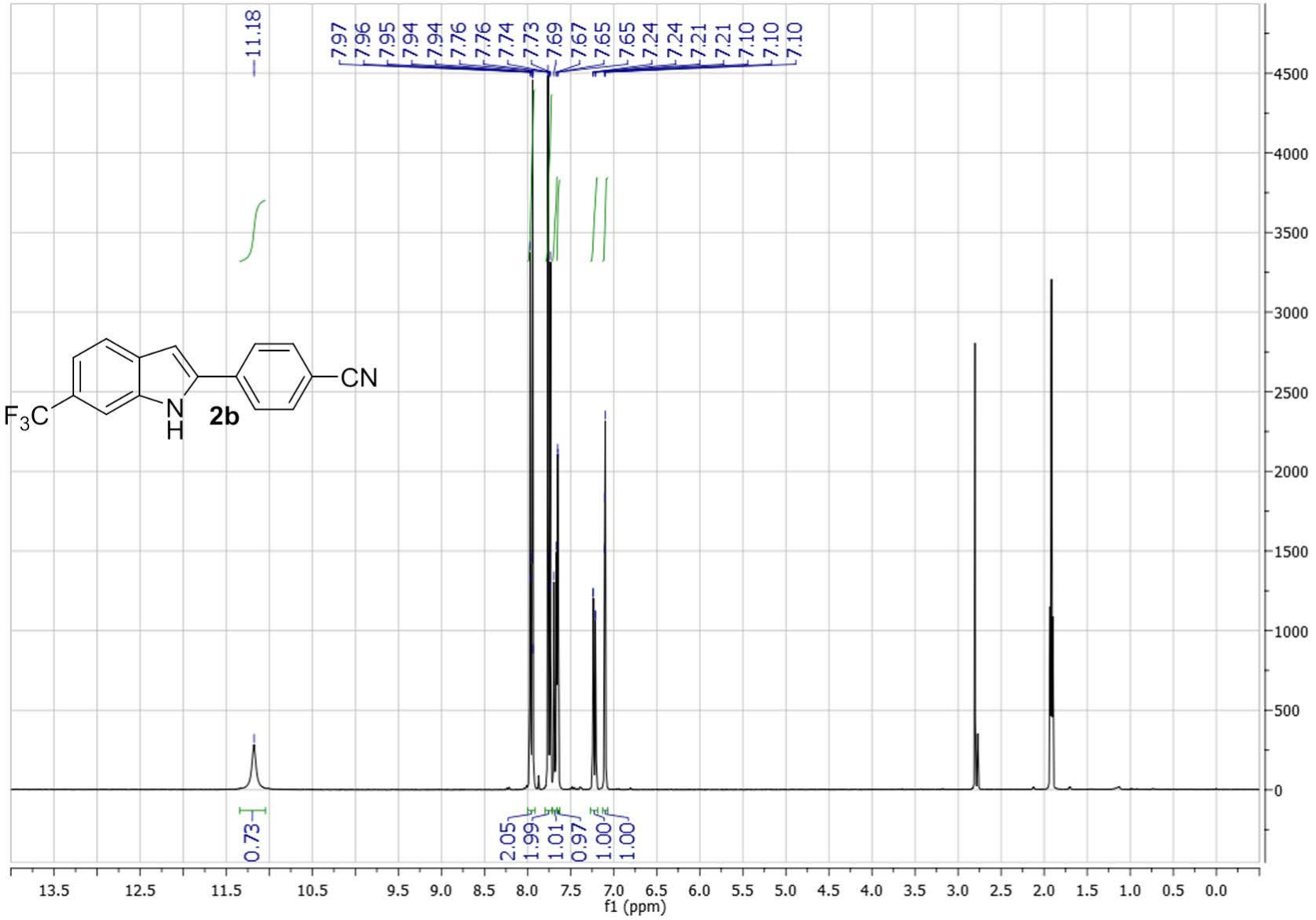
Methyl *1H*-indole-2-carboxylate (2a) ^{1}H NMR (300 MHz, DMSO)



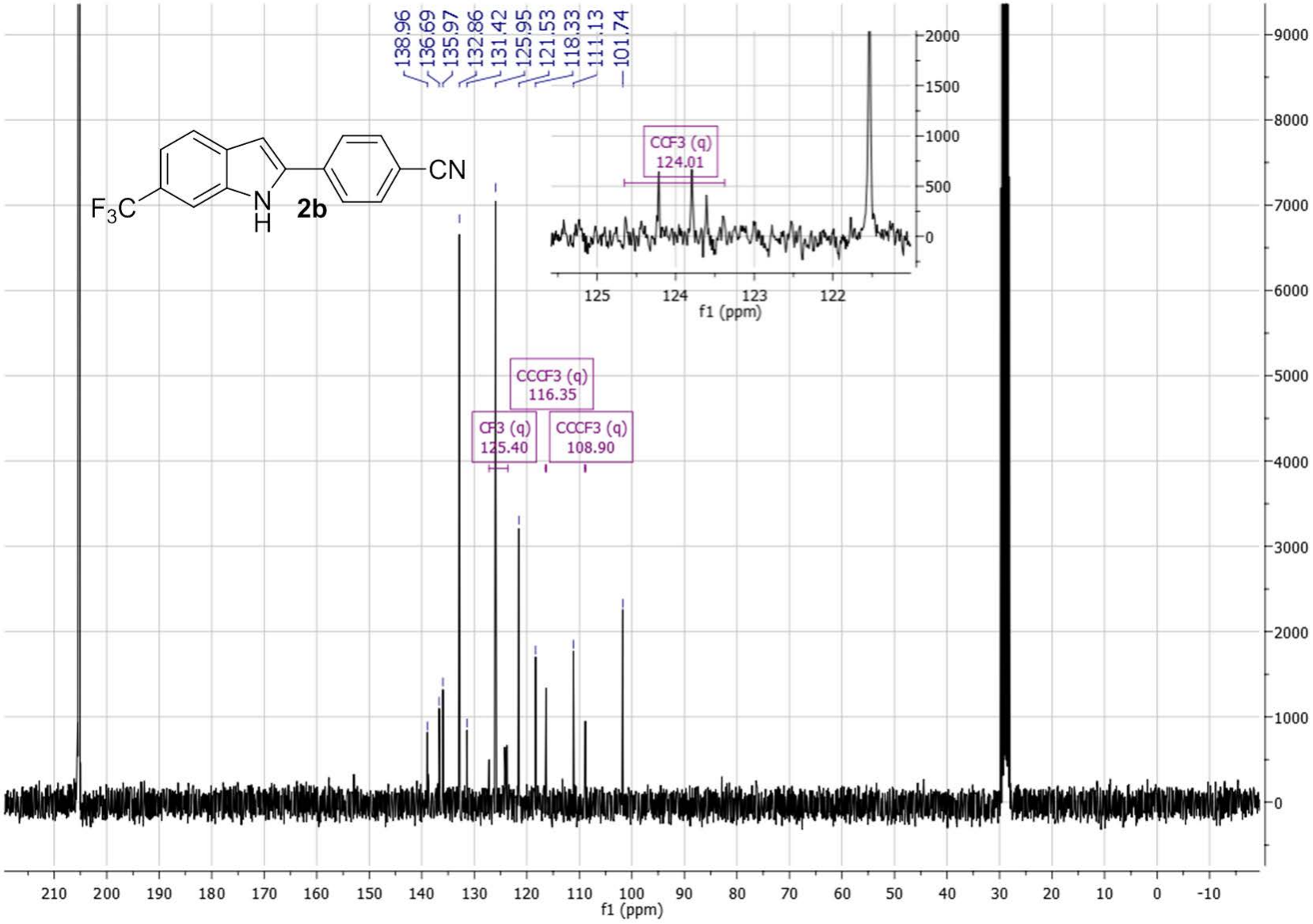
^{13}C NMR (75 MHz, DMSO)



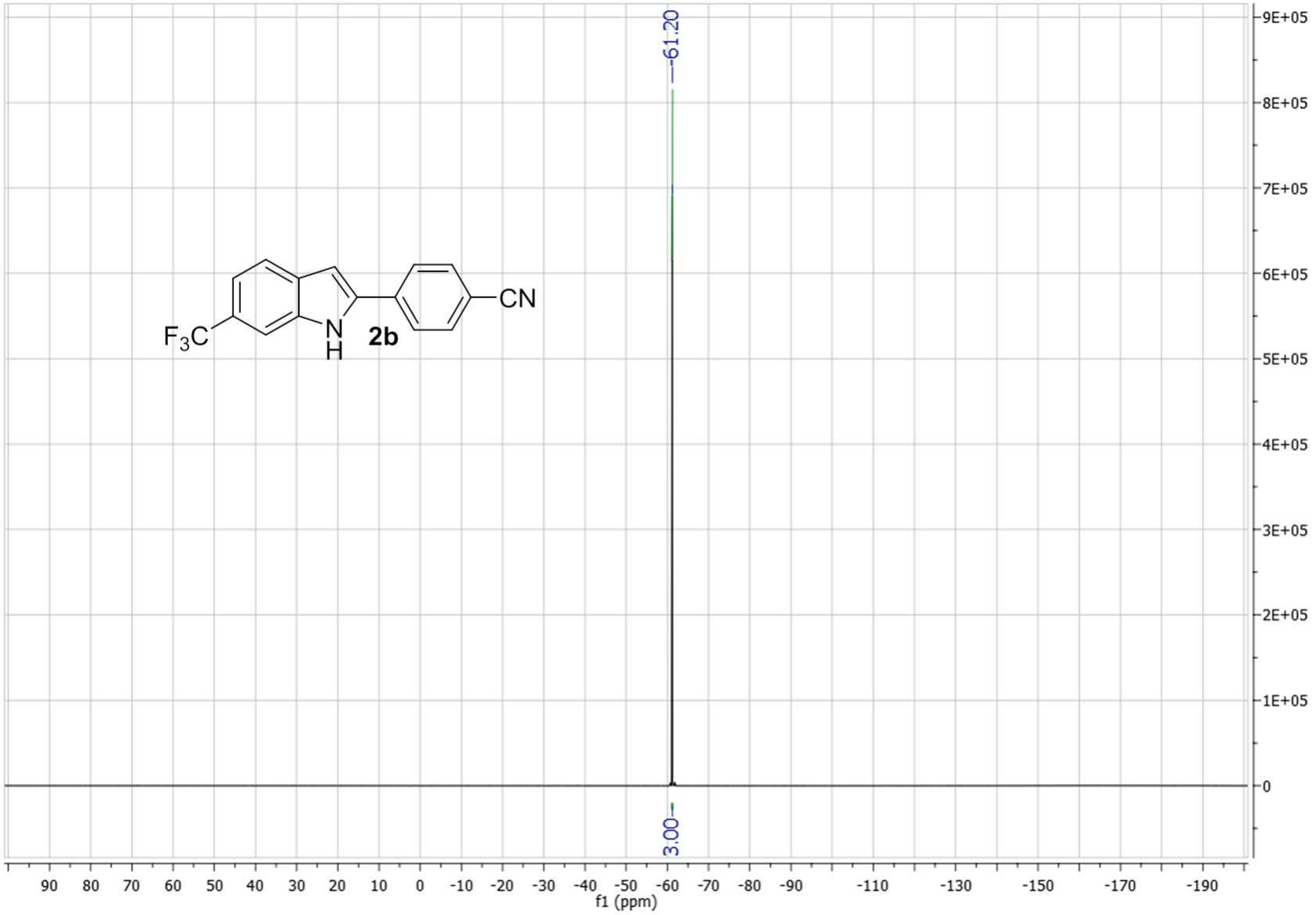
4-(6-(Trifluoromethyl)-*1H*-indol-2-yl)benzonitrile (2b) ^{1}H NMR (300 MHz, acetone-d_6)



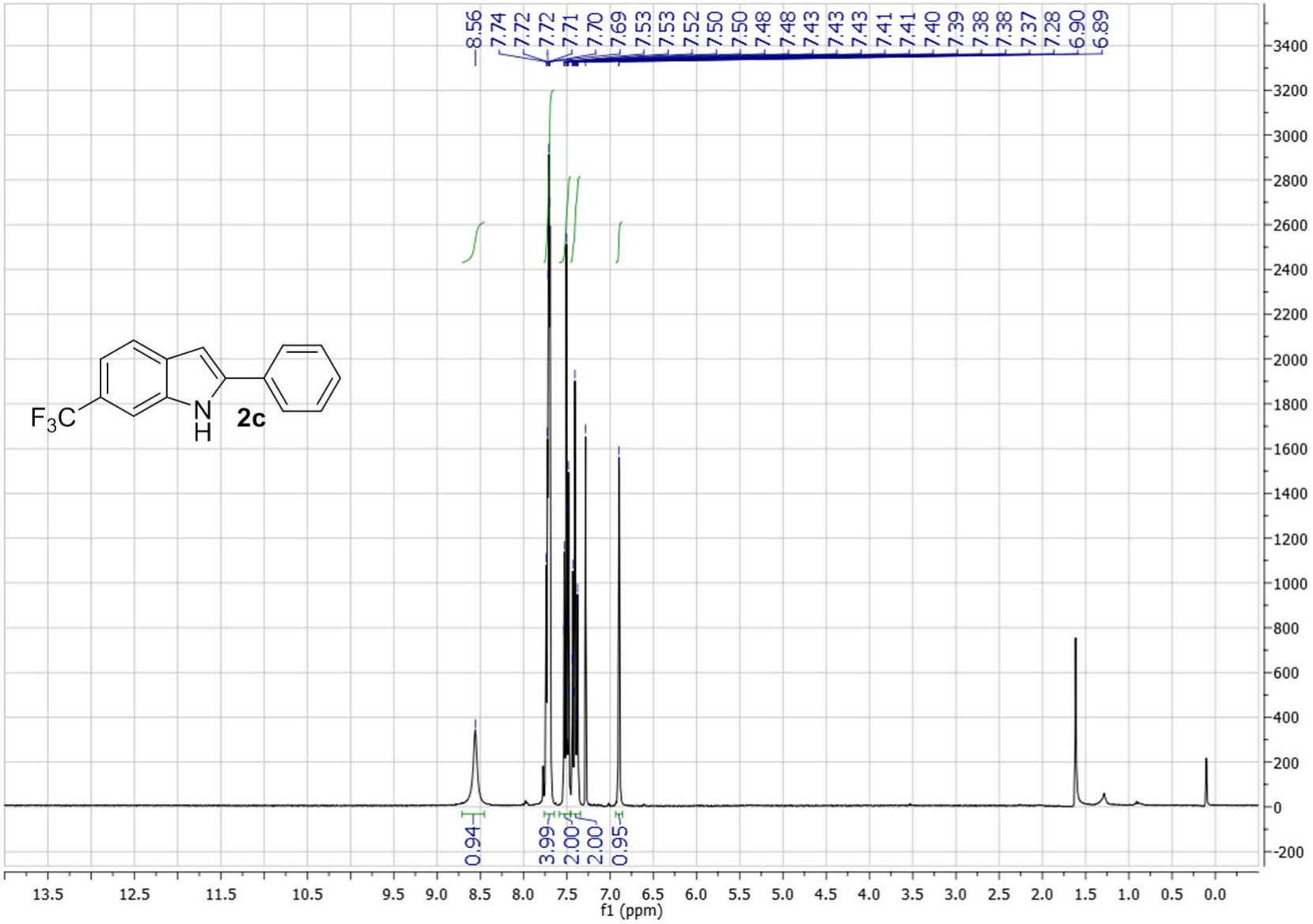
^{13}C NMR (75 MHz, acetone-d_6)



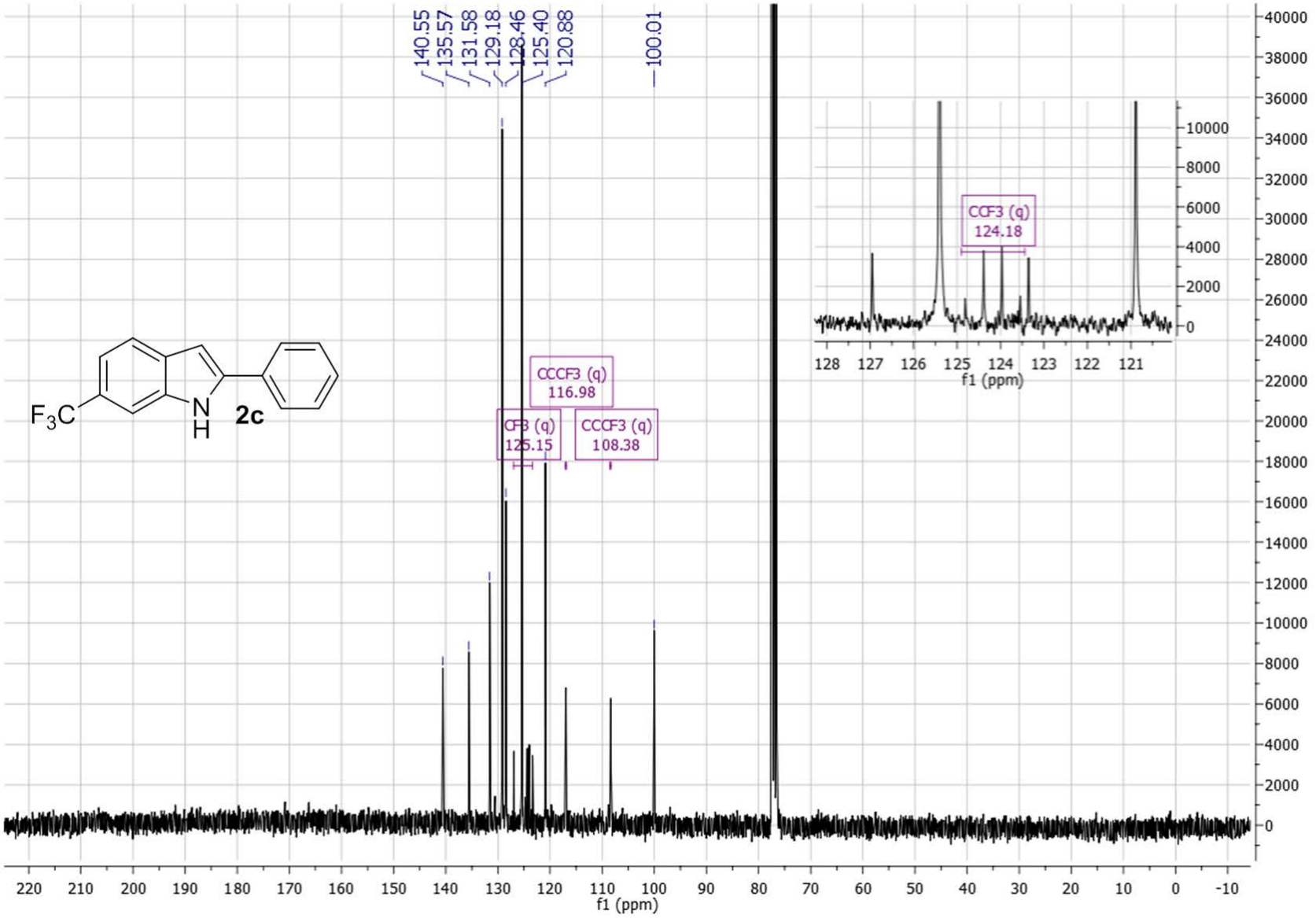
^{19}F NMR (282 MHz, acetone-d_6)



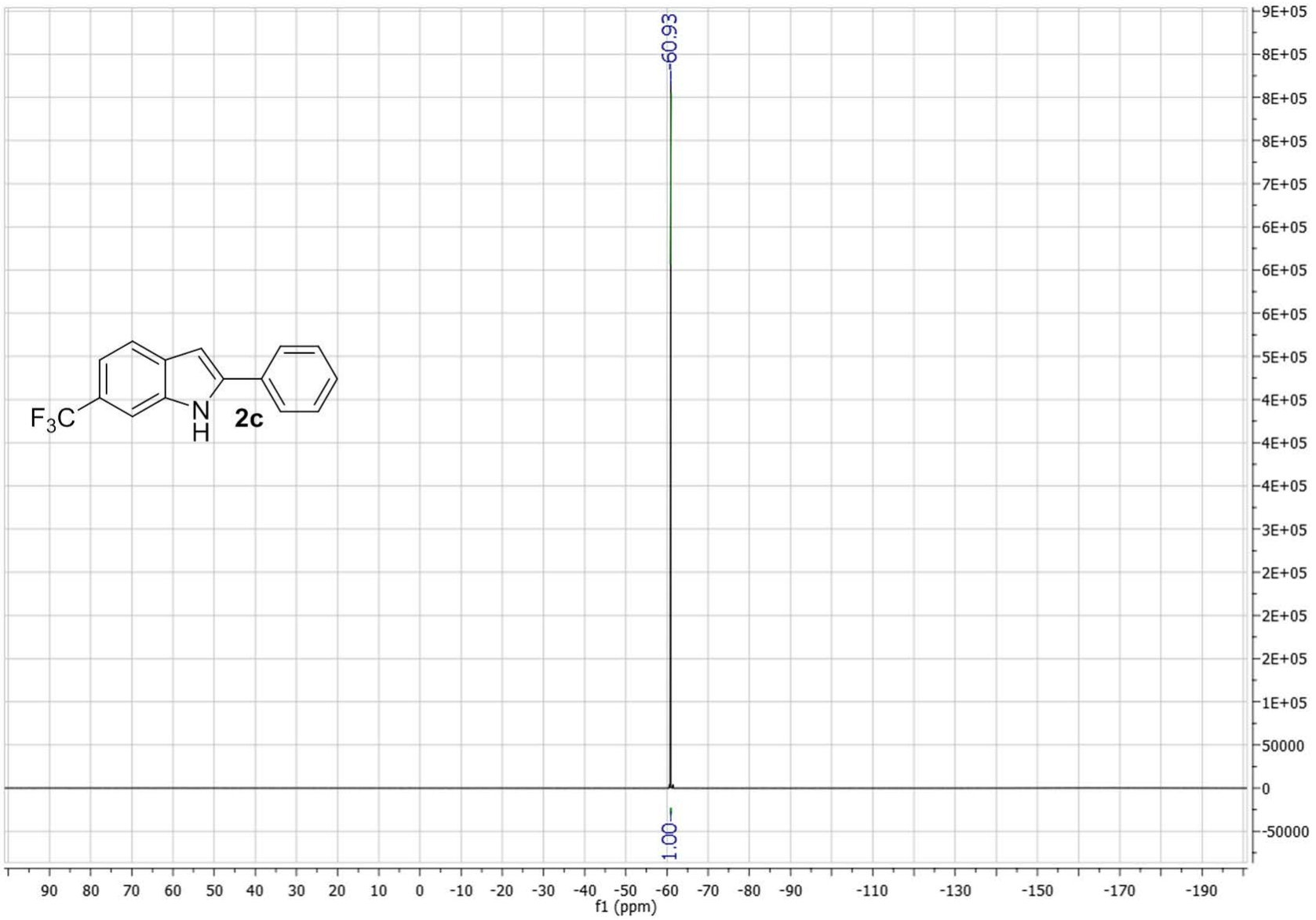
2-Phenyl-6-(trifluoromethyl)-*1H*-indole (2c) ^{1}H NMR (300 MHz, $CDCl_3$)



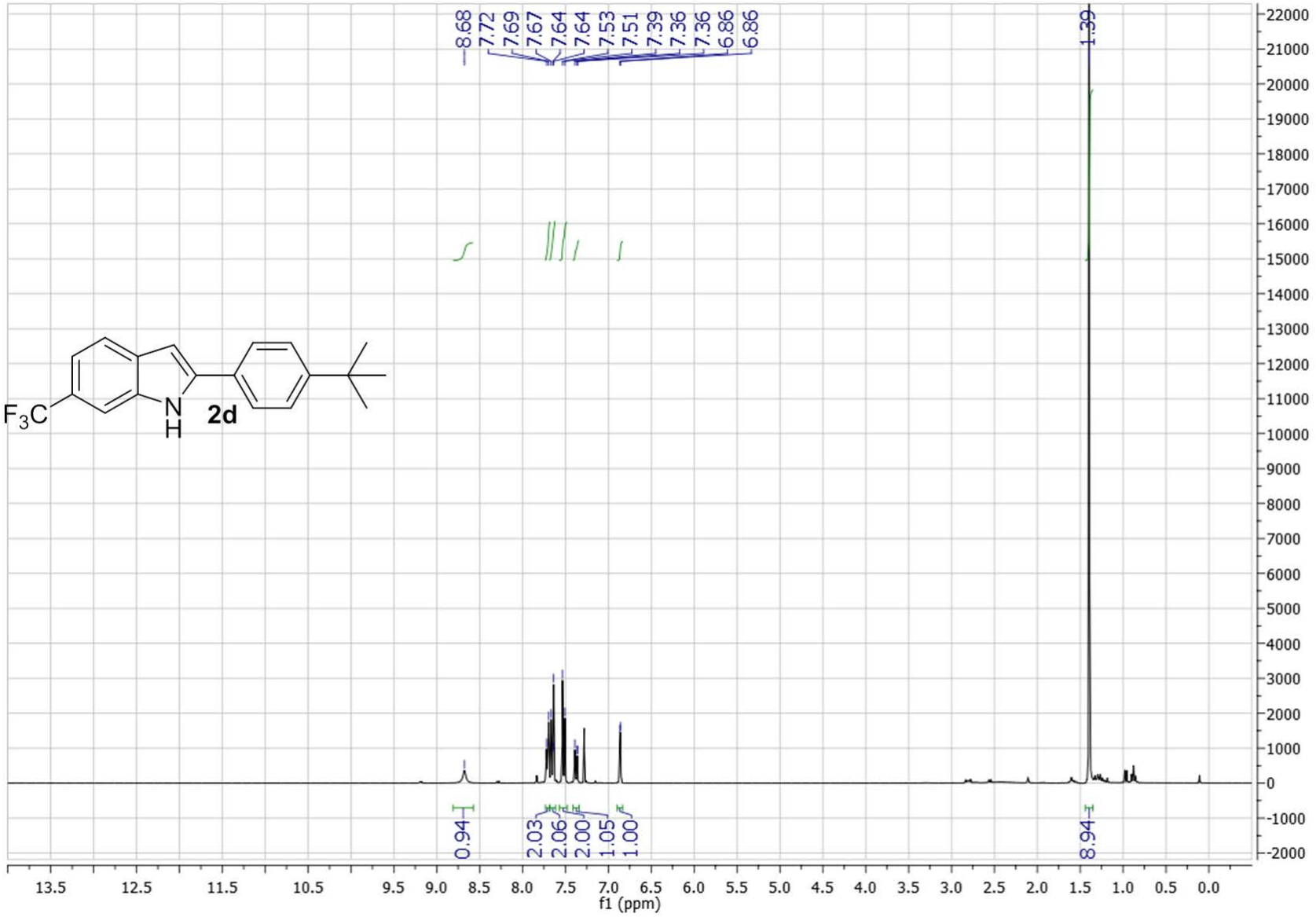
^{13}C NMR (75 MHz, $CDCl_3$)



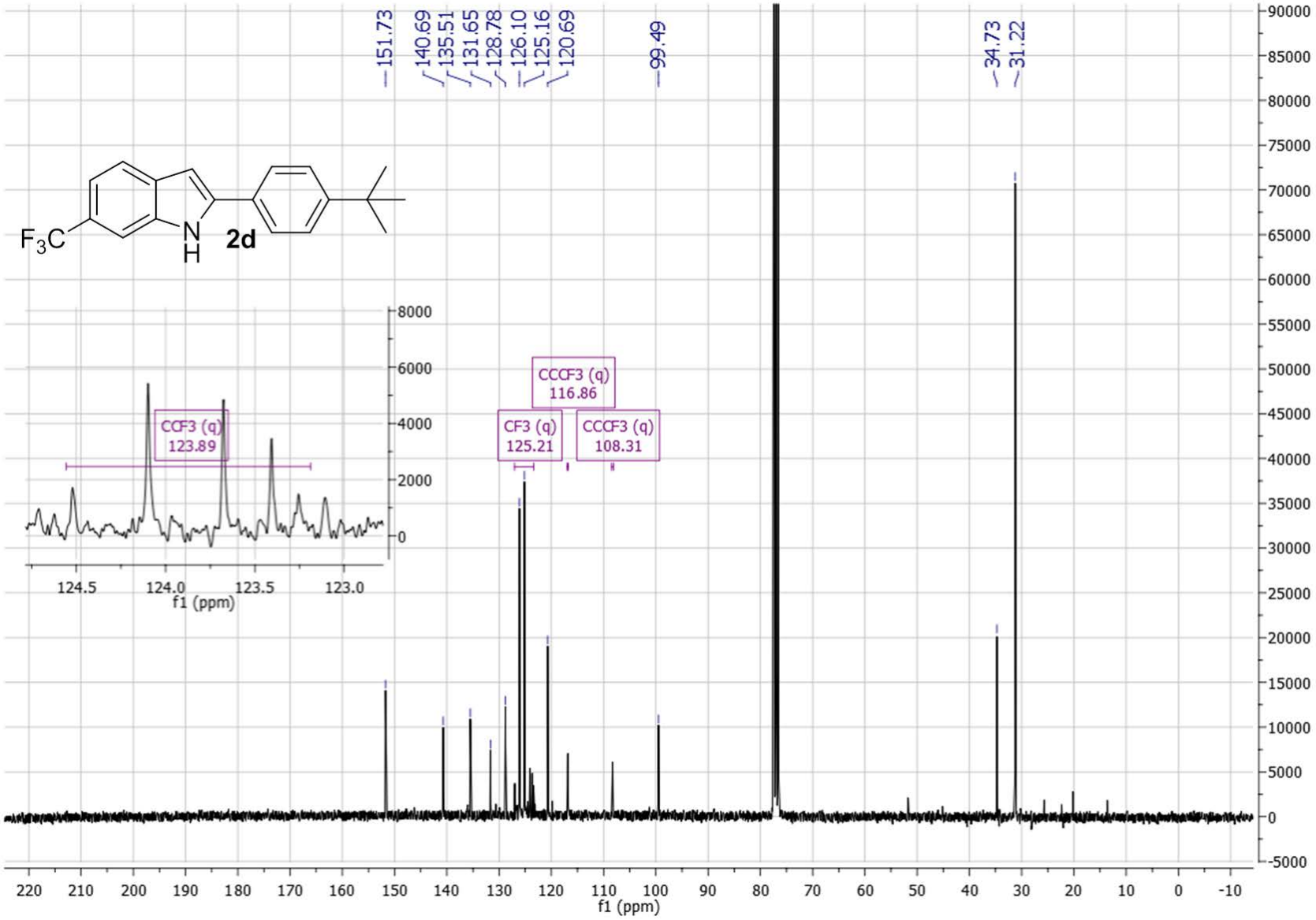
^{19}F NMR (282 MHz, $CDCl_3$)



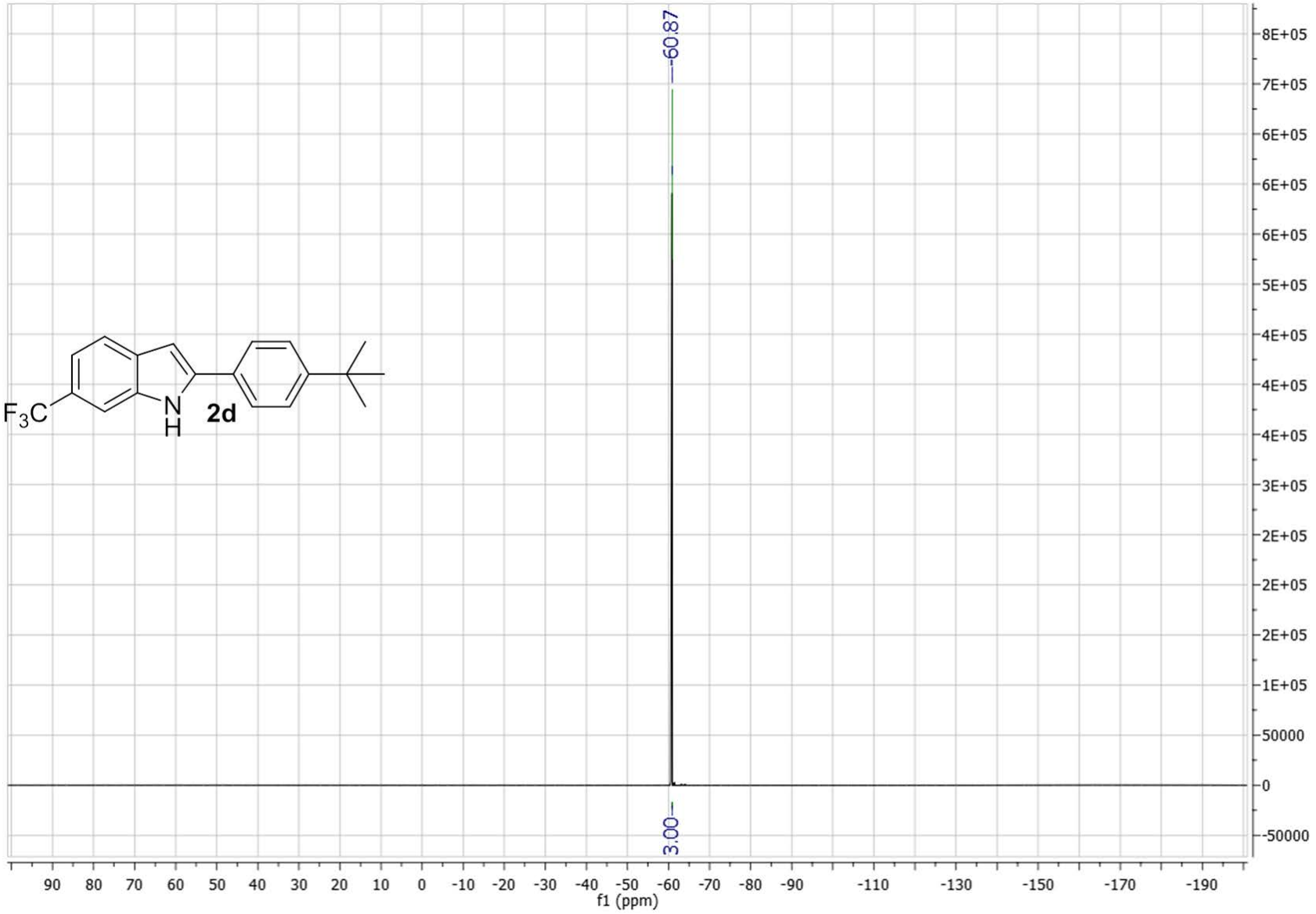
2-(4-(tert-Butyl)phenyl)-6-(trifluoromethyl)-*1H*-indole (2d) ^{1}H NMR (300 MHz, $CDCl_3$)



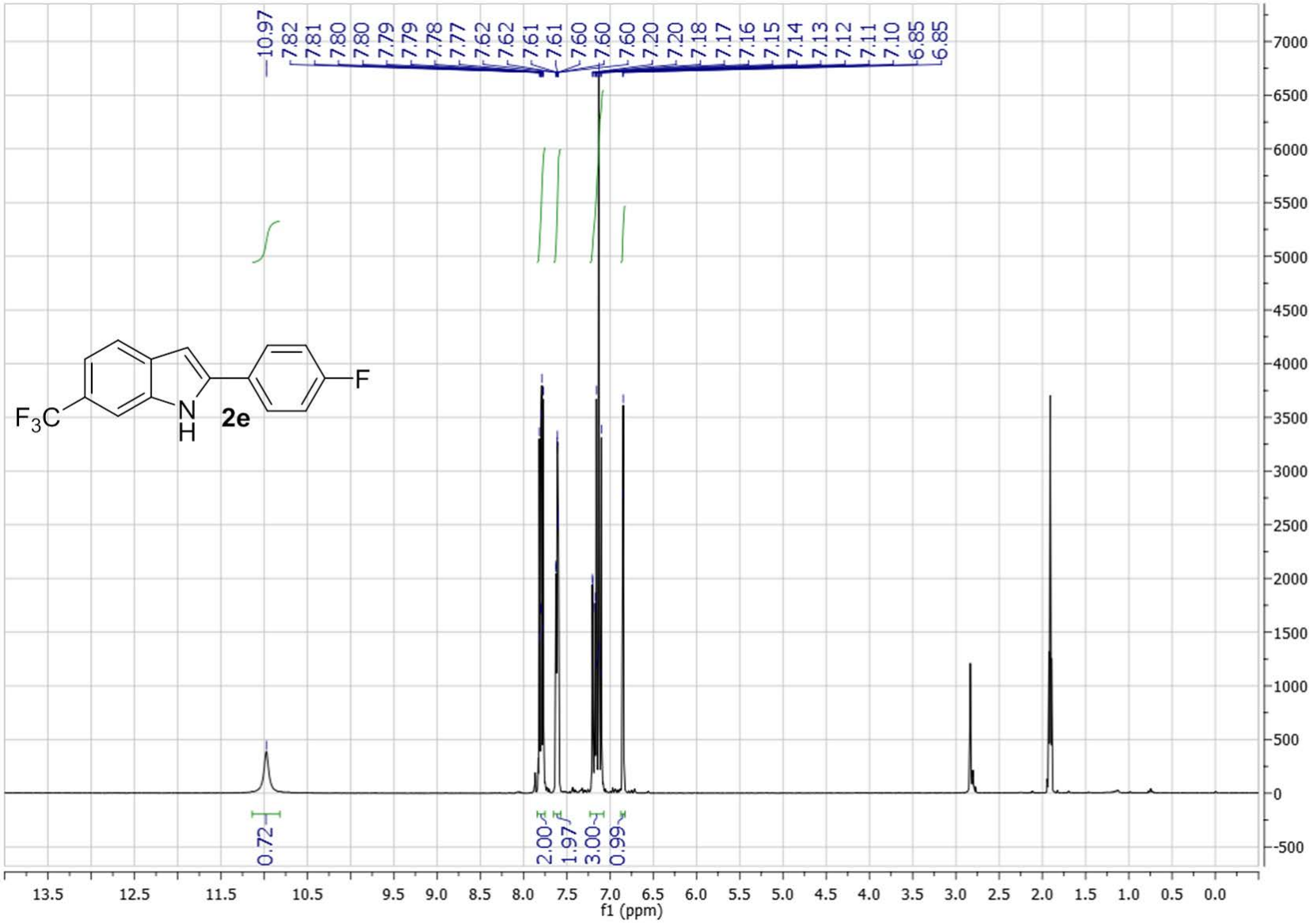
^{13}C NMR (75 MHz, $CDCl_3$)



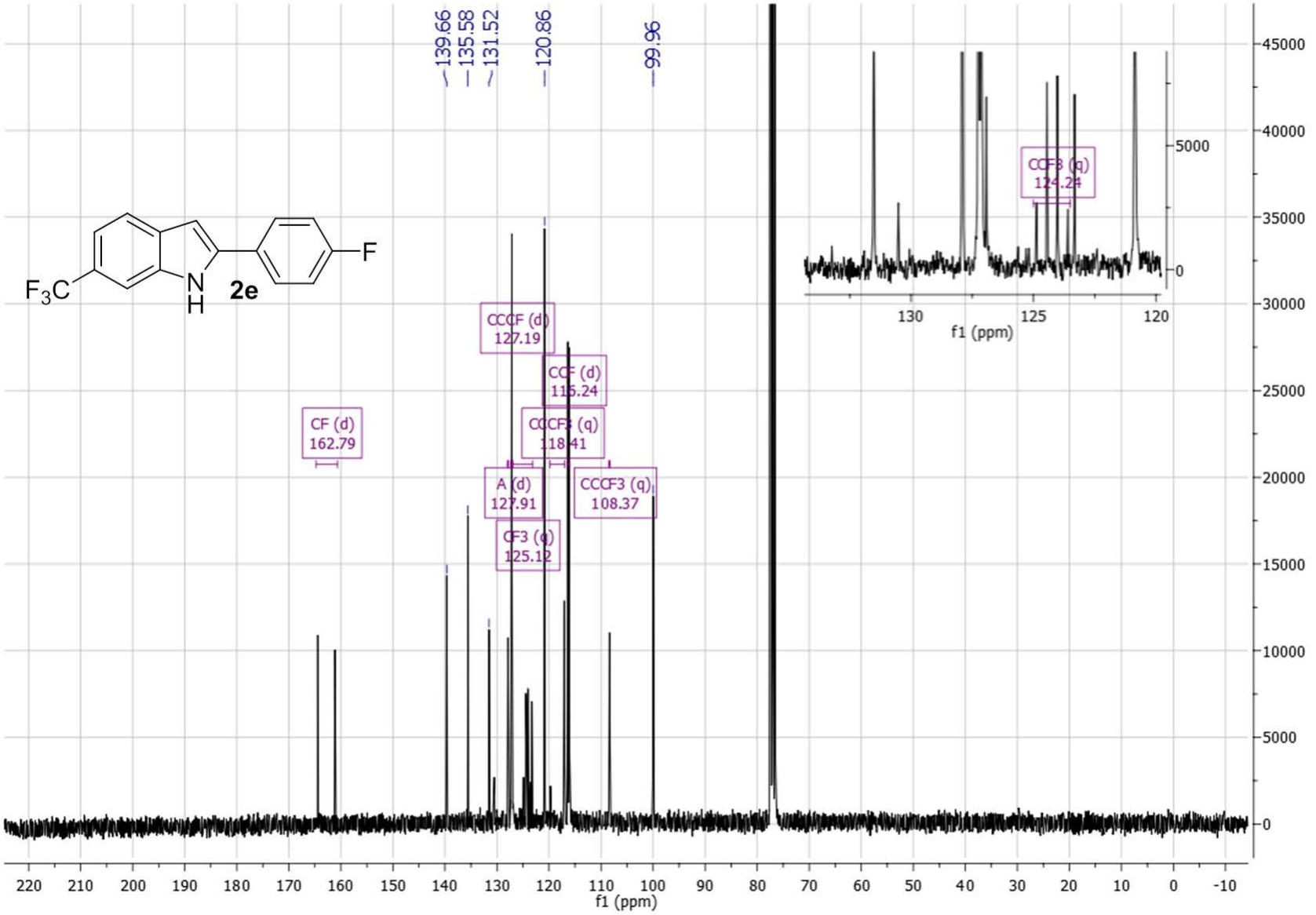
^{19}F NMR (282 MHz, $CDCl_3$)



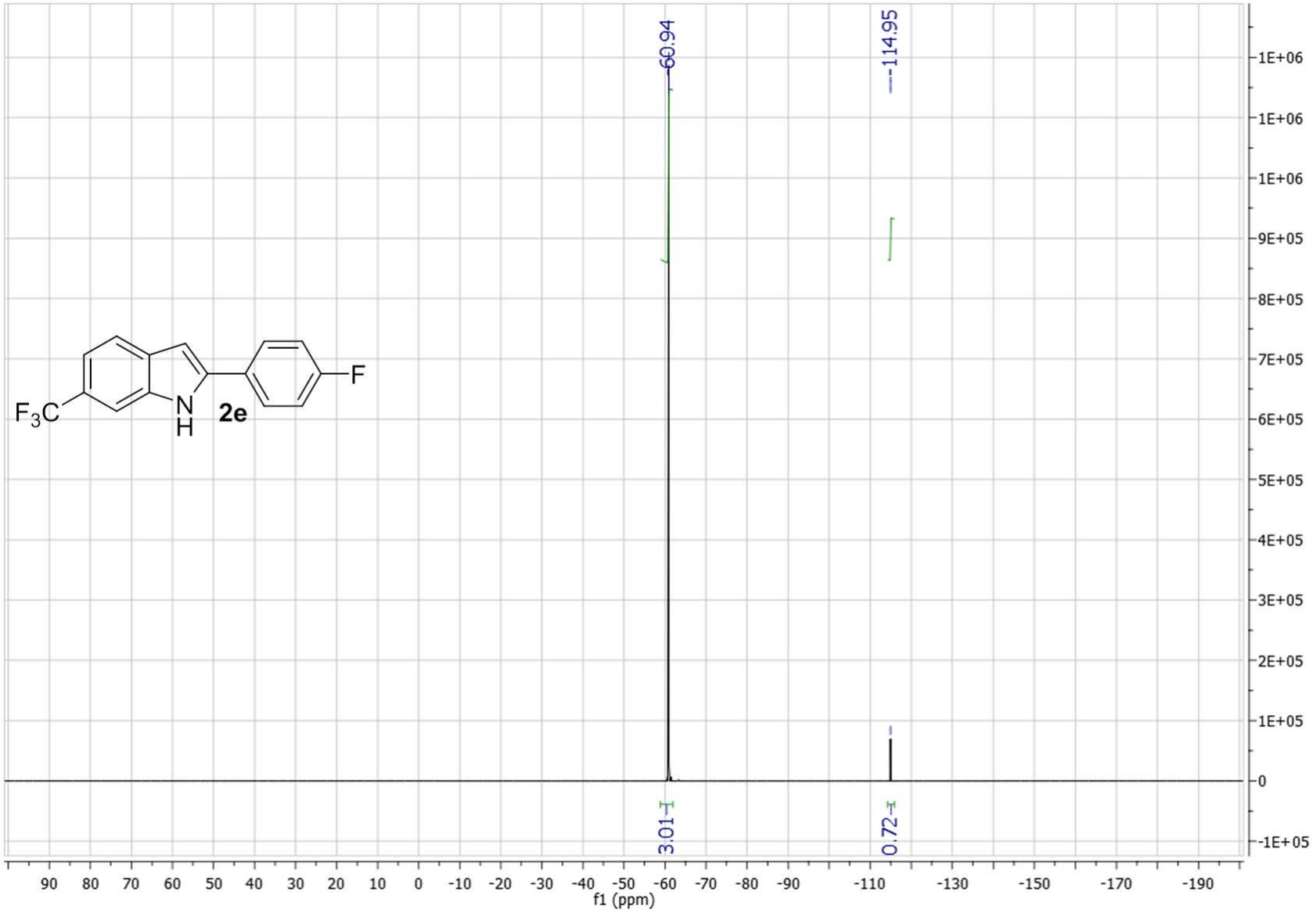
2-(4-Fluorophenyl)-6-(trifluoromethyl)-*1H*-indole (2e) ^{1}H NMR (300 MHz, acetone-d_6)



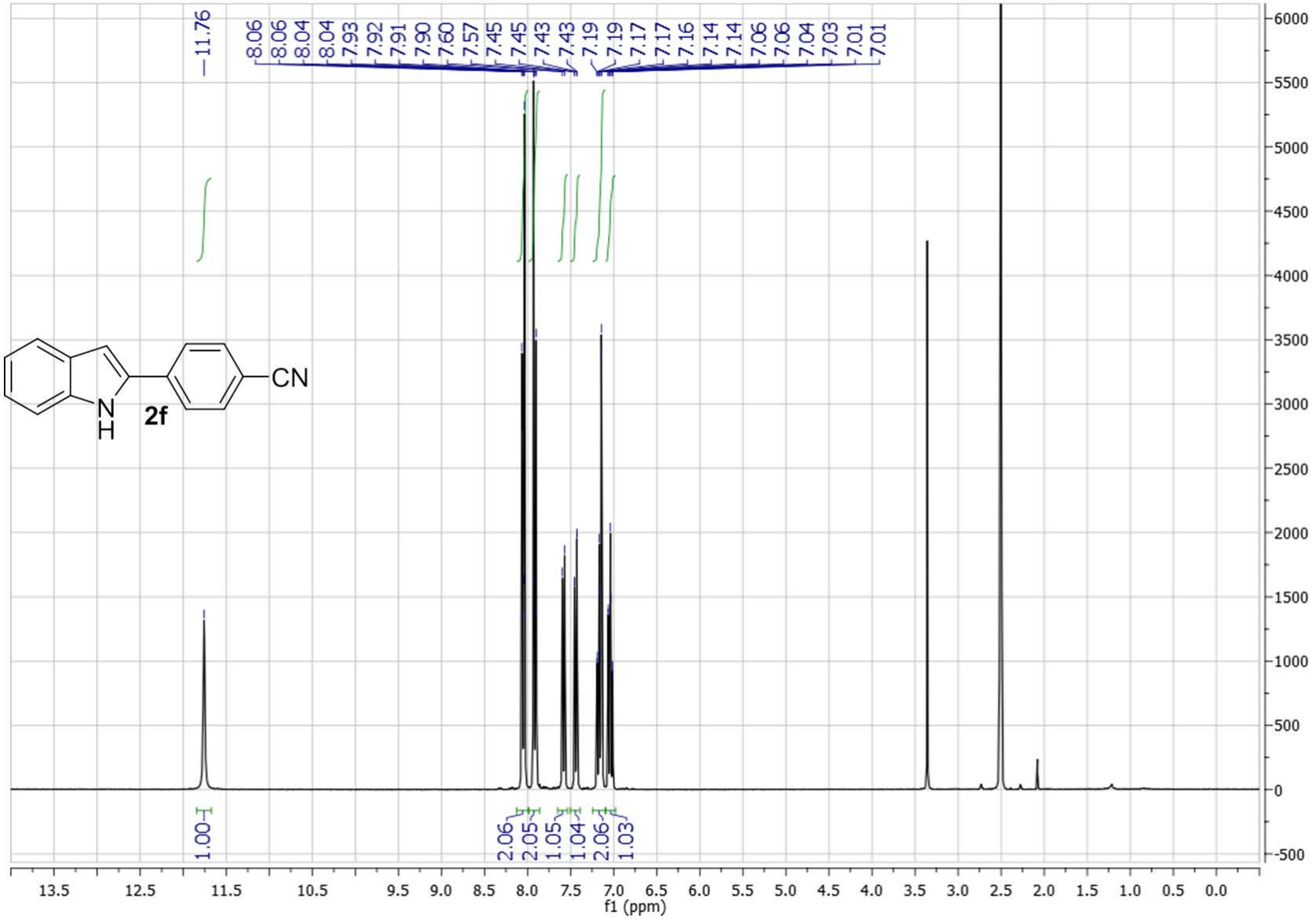
^{13}C NMR (75 MHz, $CDCl_3$)



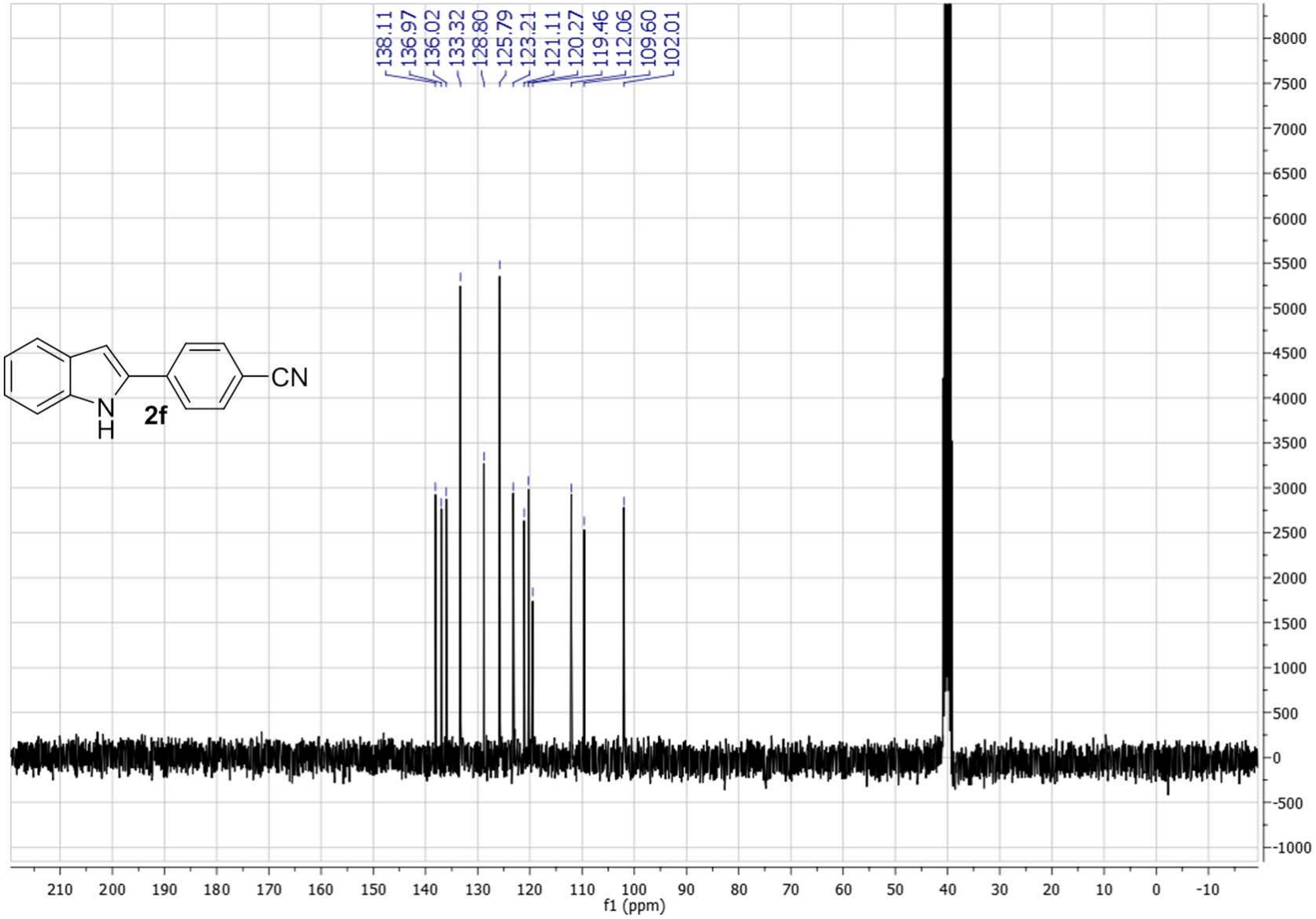
^{19}F NMR (282 MHz, acetone-d_6)



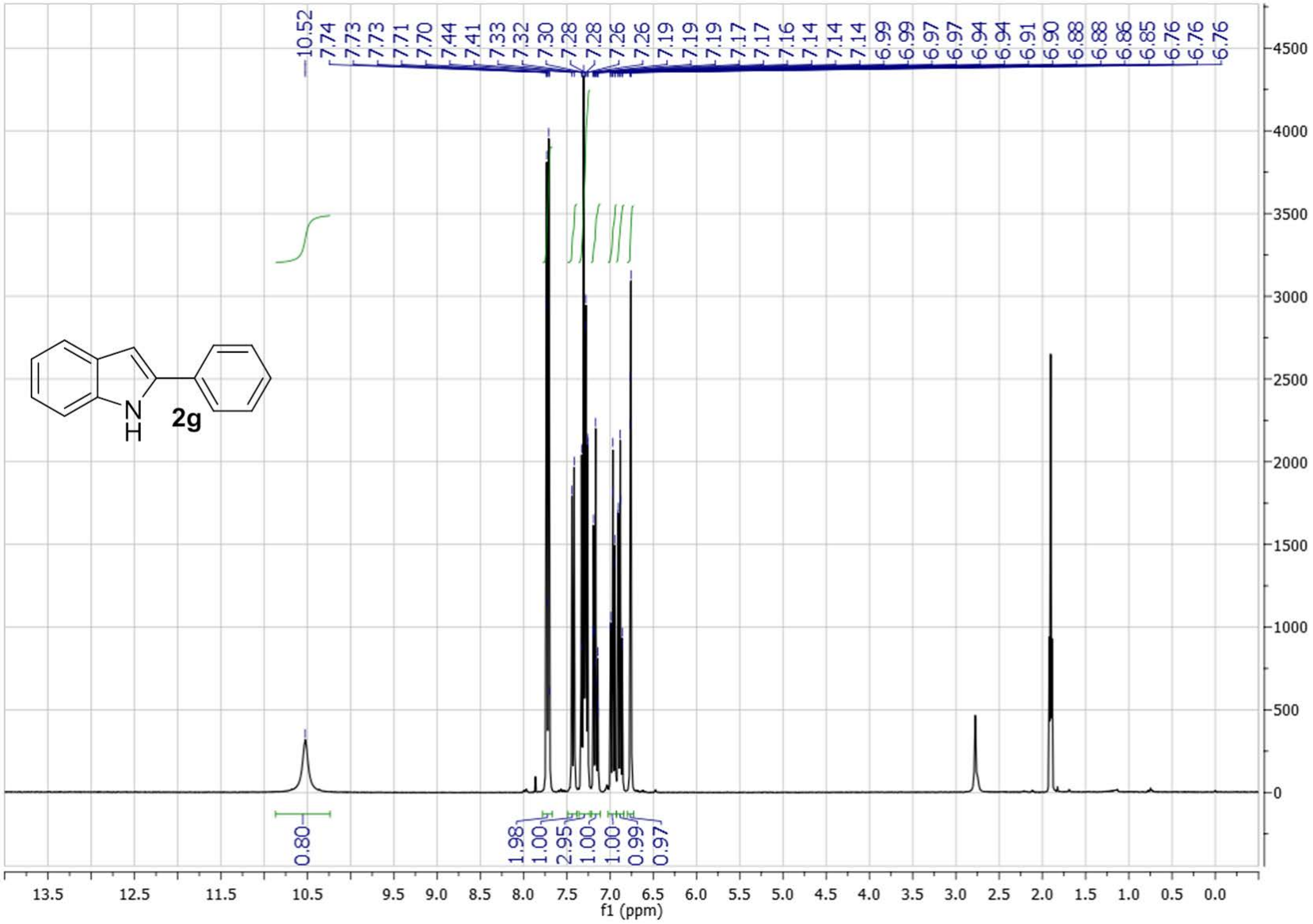
4-(*1H*-Indol-2-yl)benzonitrile (2f) ^{1}H NMR (300 MHz, DMSO-d_6)



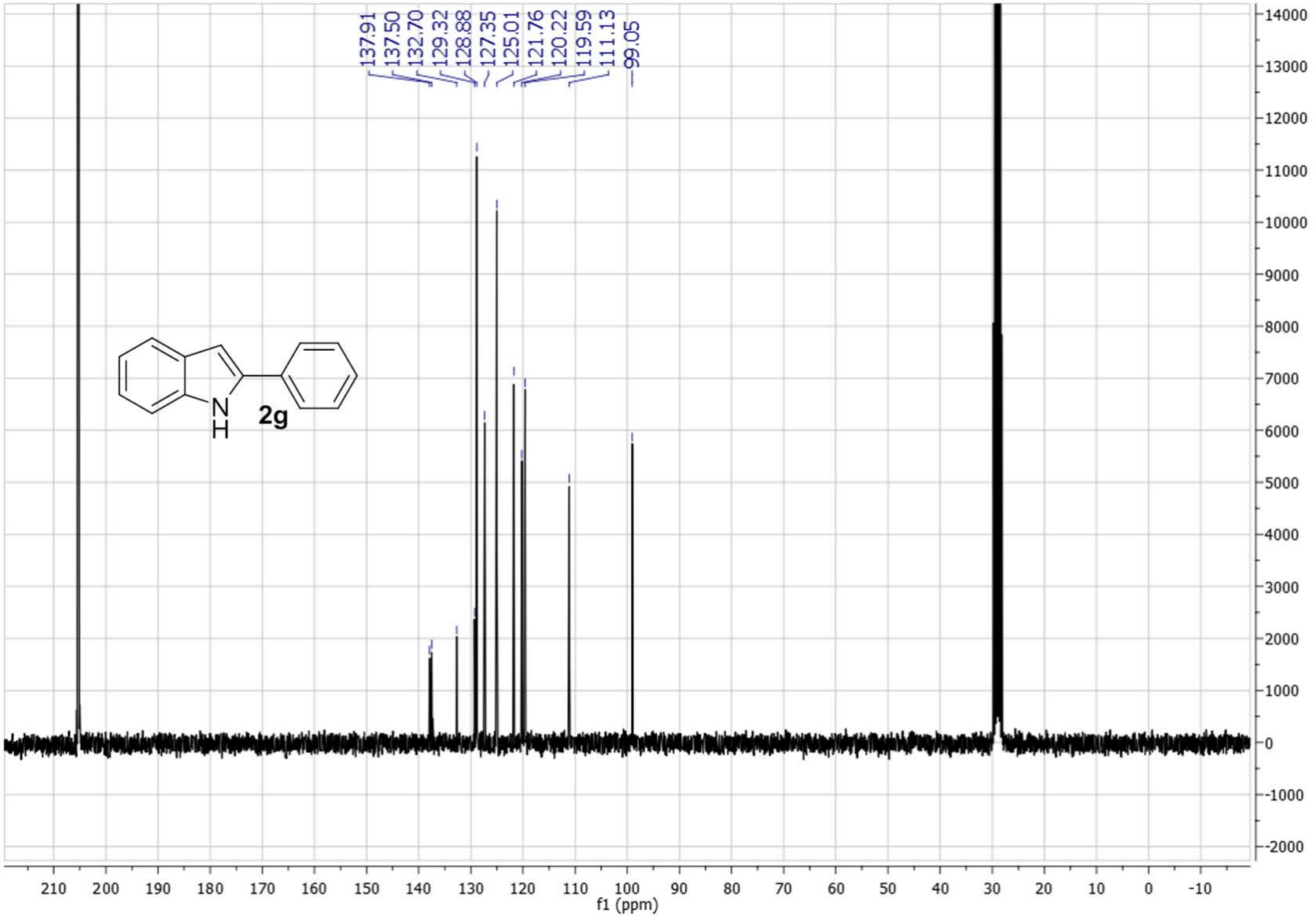
^{13}C NMR (75 MHz, DMSO-d_6)



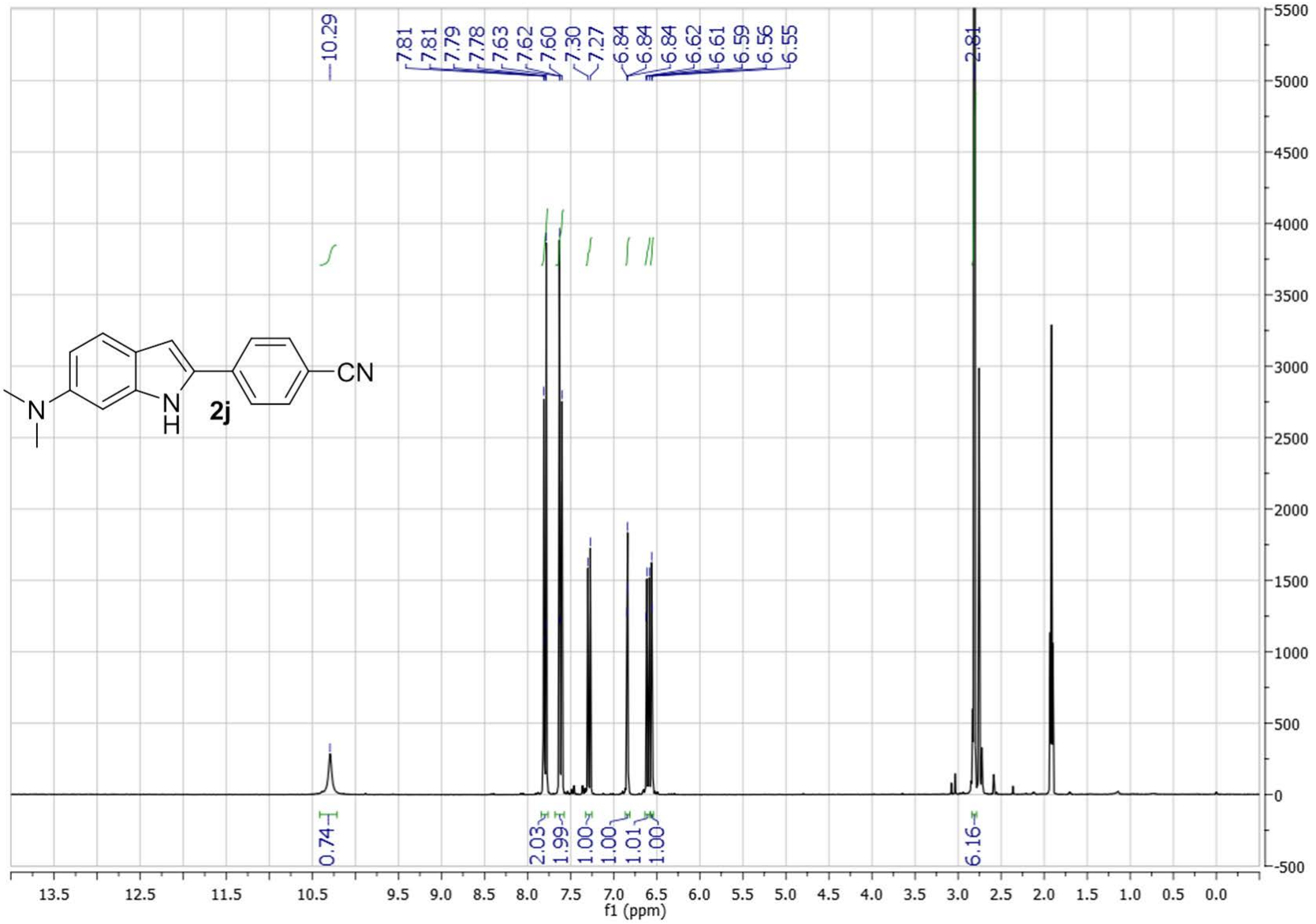
2-Phenyl-*1H*-indole (2g) ^{1}H NMR (300 MHz, acetone-d_6)



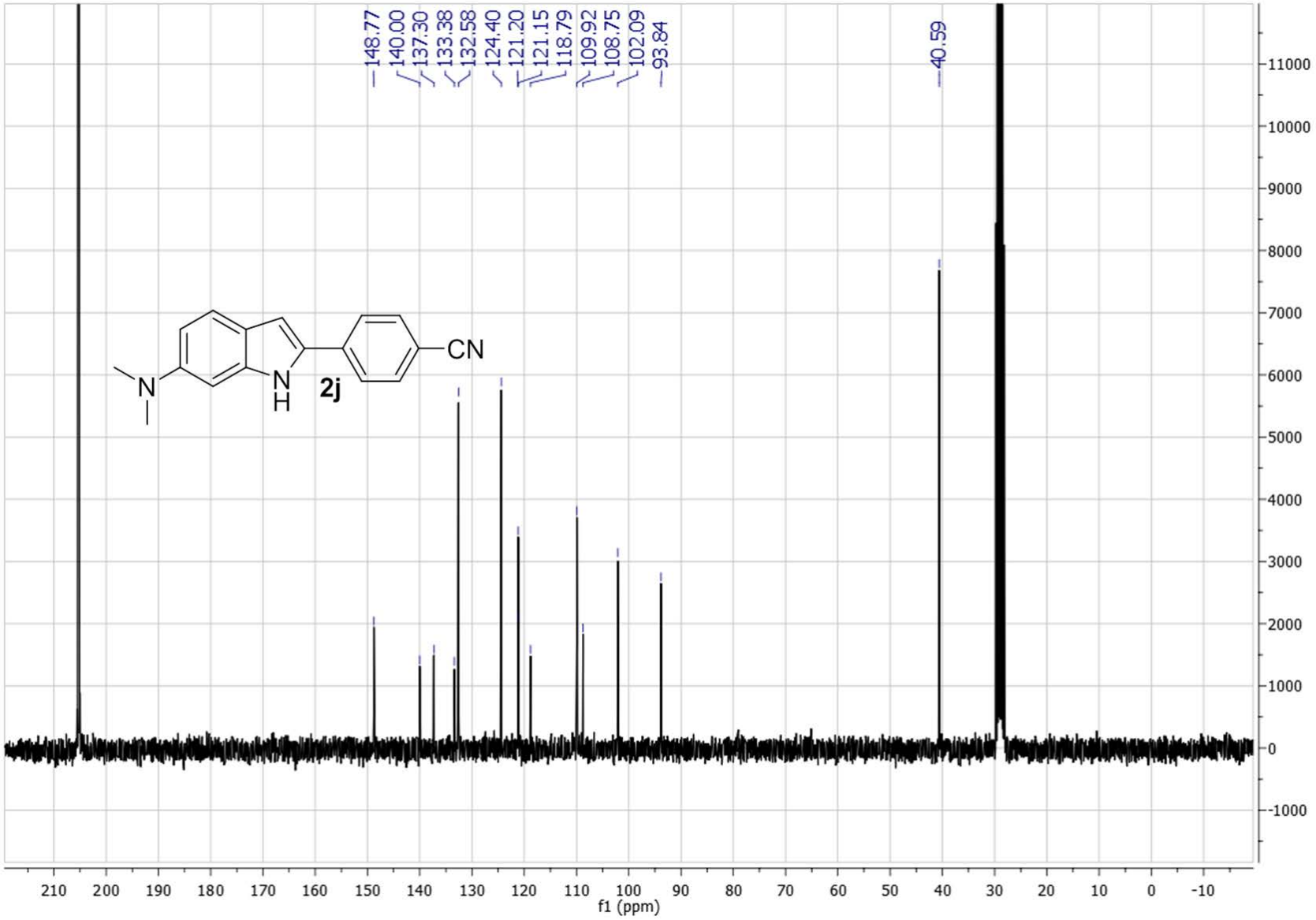
^{13}C NMR (75 MHz, acetone-d_6)



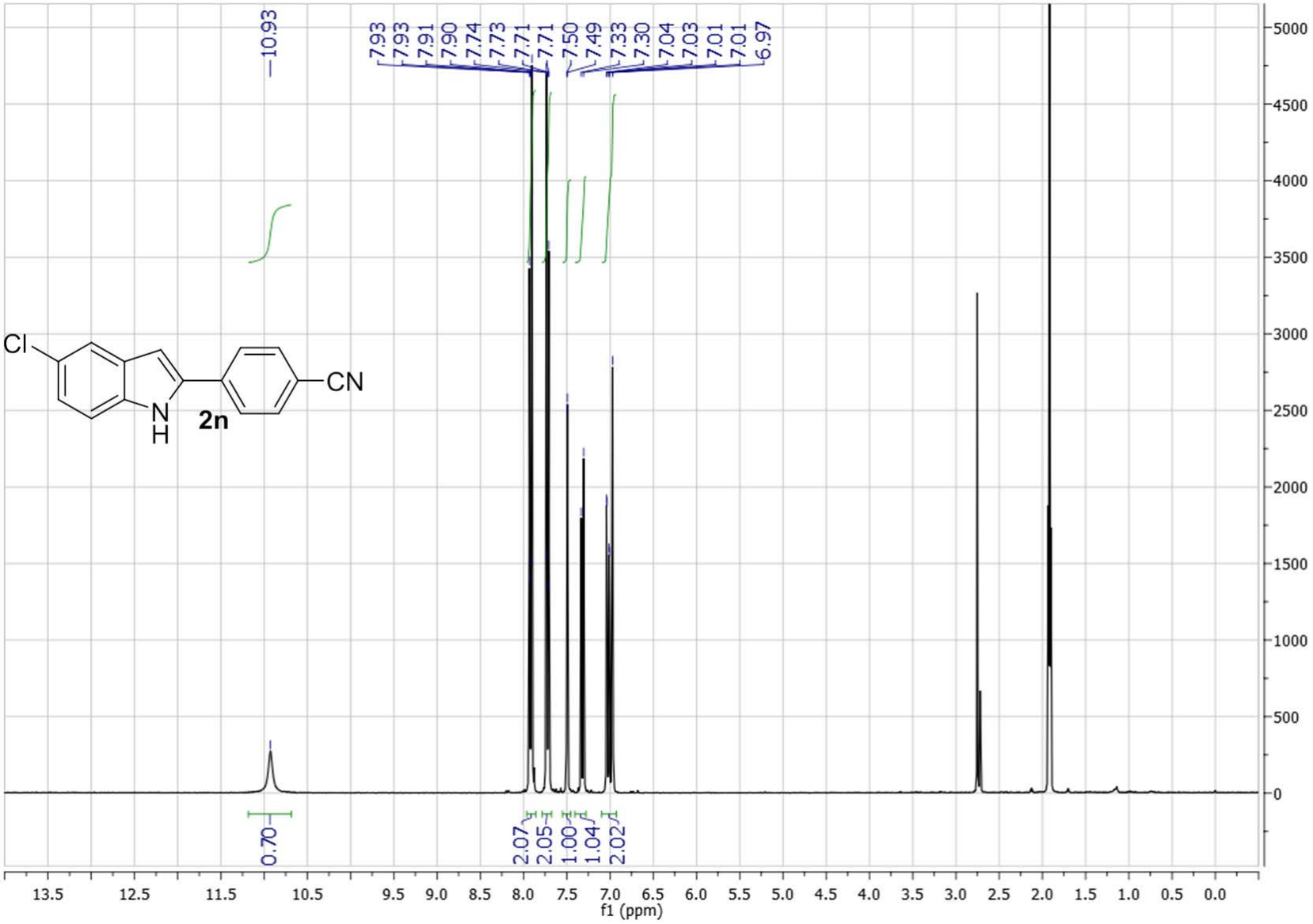
4-(6-(Dimethylamino)-*1H*-indol-2-yl)benzonitrile (2j) ^{1}H NMR (300 MHz, acetone-d_6)



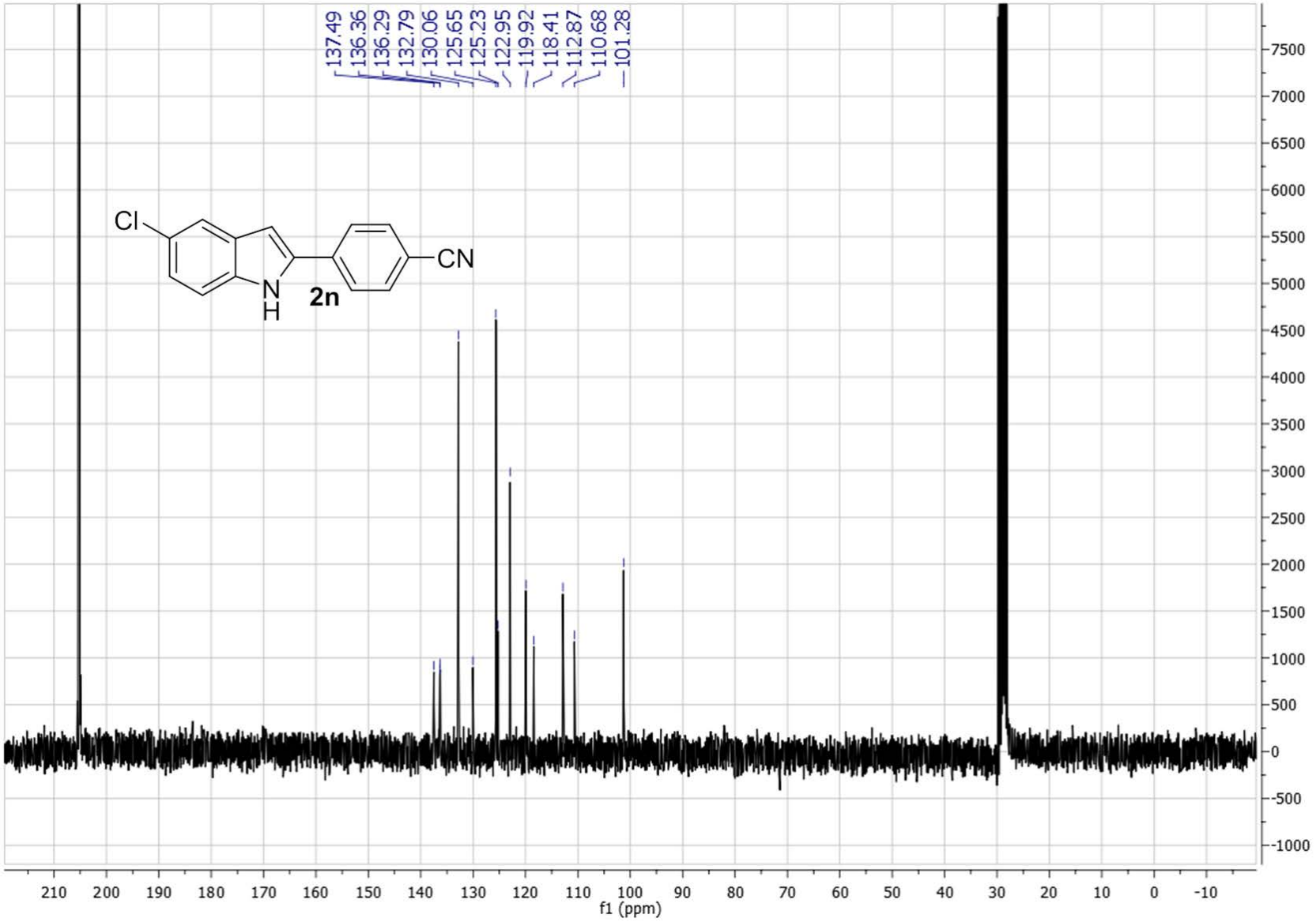
^{13}C NMR (75 MHz, acetone-d_6)



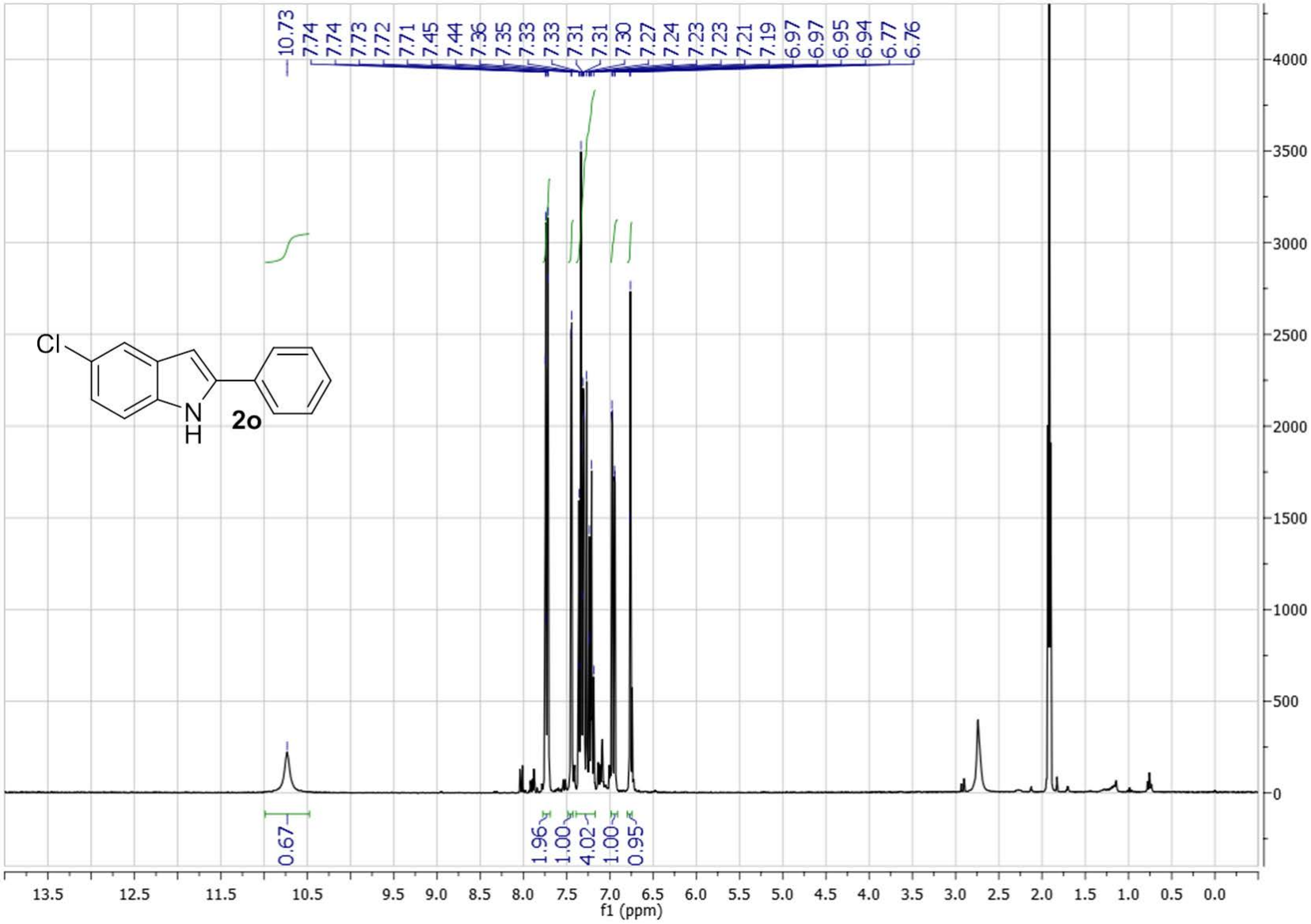
4-(5-Chloro-*1H*-indol-2-yl)benzonitrile (2n) ^{1}H NMR (300 MHz, acetone-d_6)



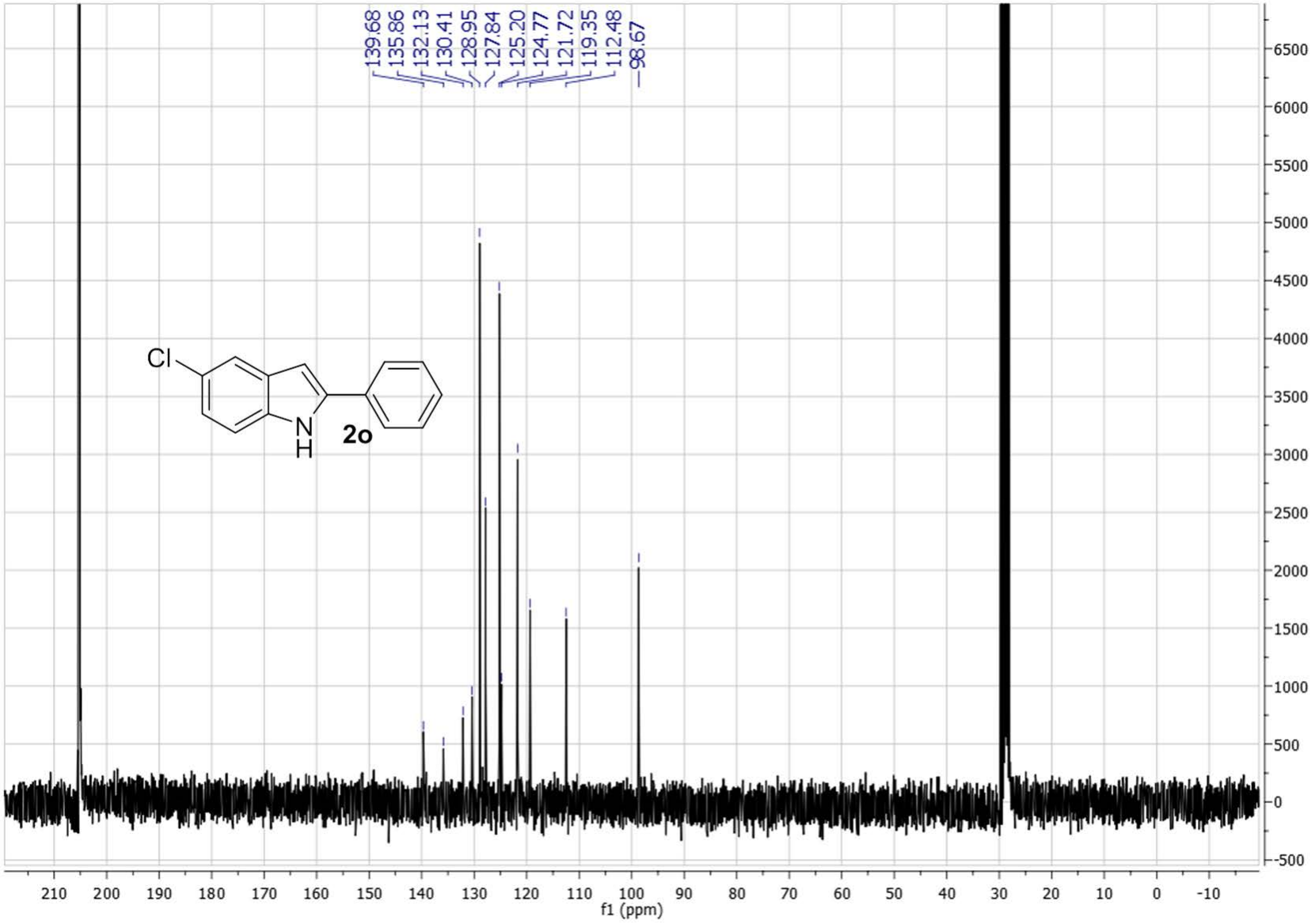
^{13}C NMR (75 MHz, acetone-d_6)



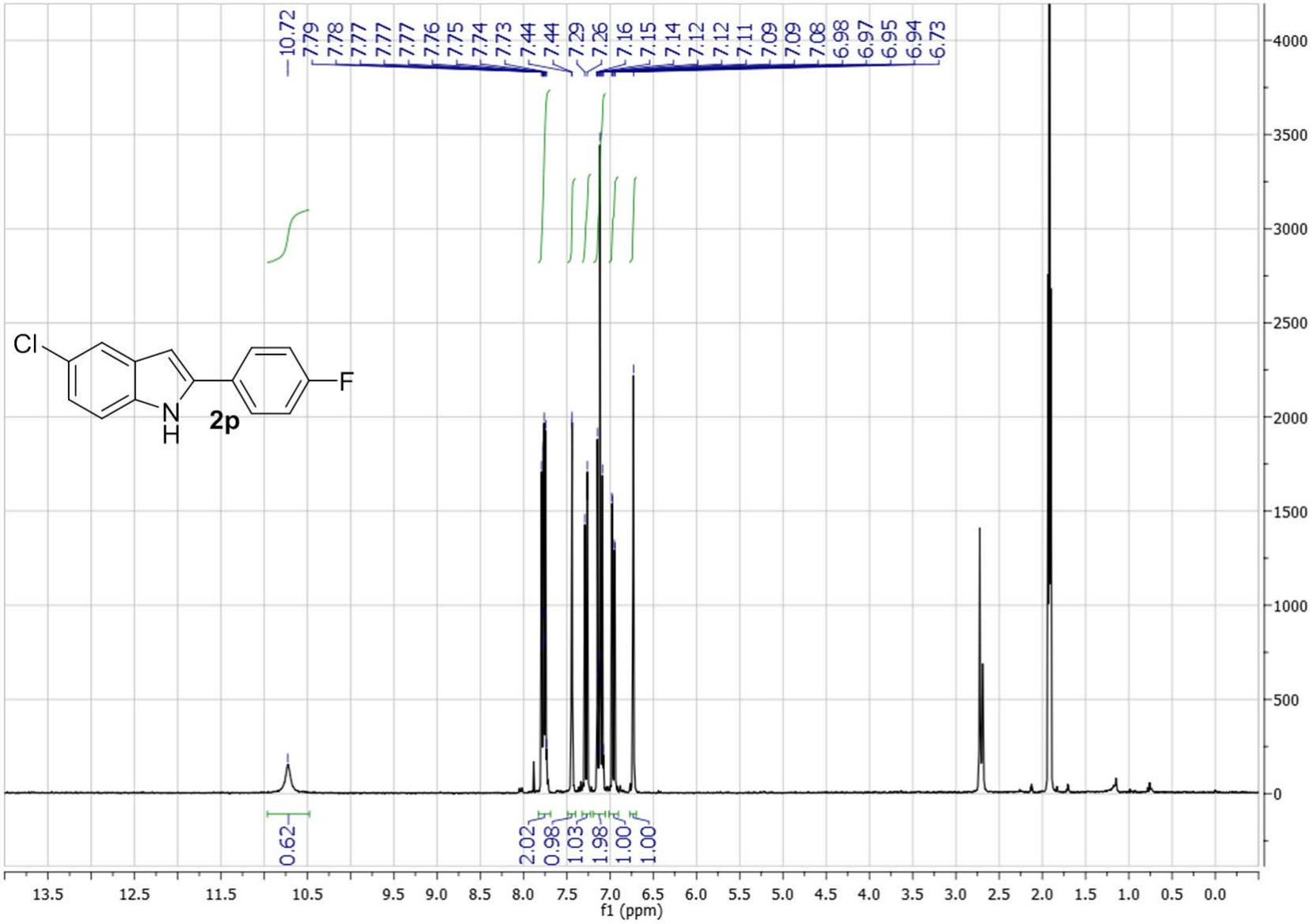
5-Chloro-2-phenyl-*1H*-indole (2o) ^{1}H NMR (300 MHz, acetone-d_6)



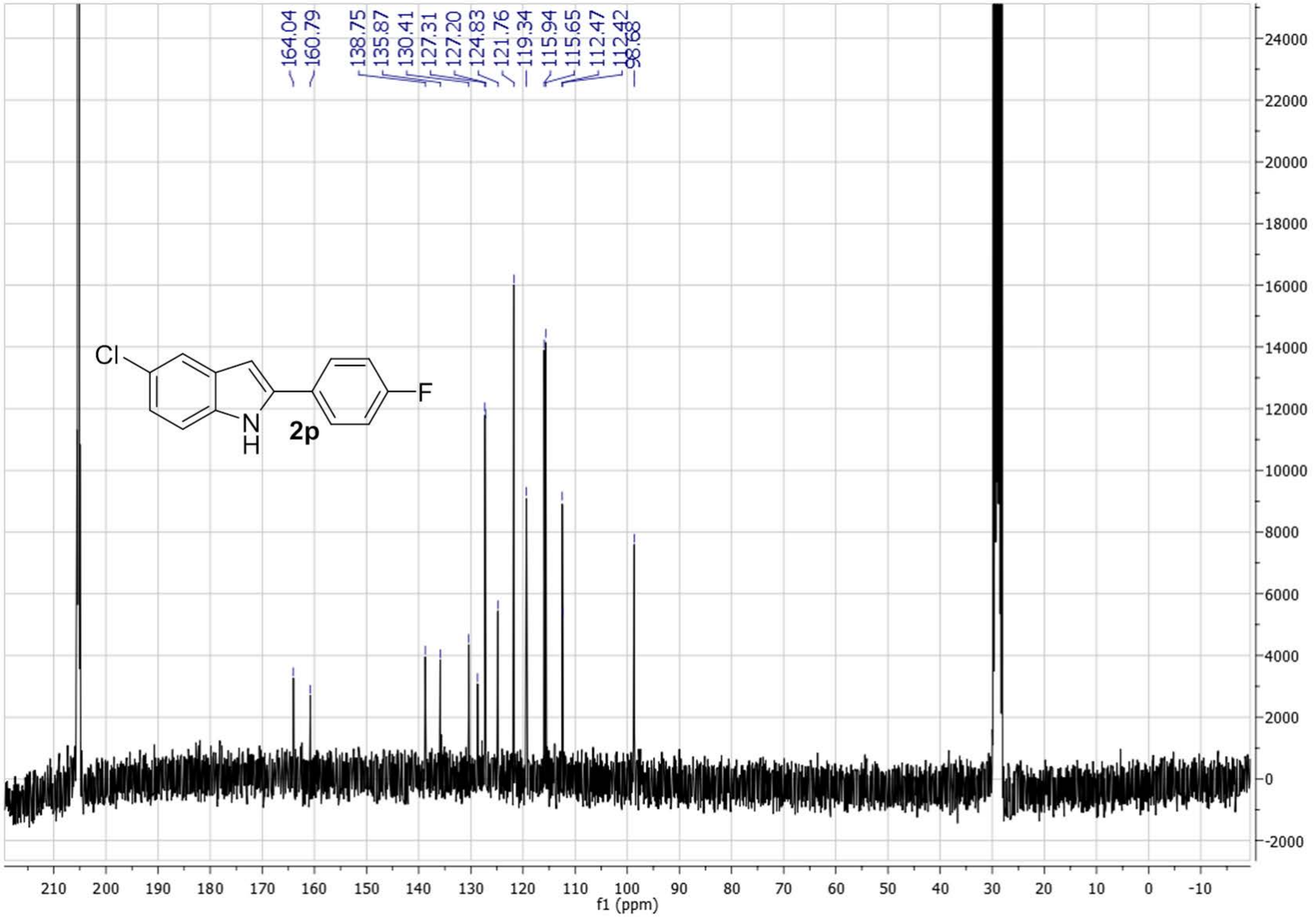
^{13}C NMR (75 MHz, acetone-d_6)



5-Chloro-2-(4-fluorophenyl)-*1H*-indole (2p) ^{1}H NMR (300 MHz, acetone-d_6)



^{13}C NMR (75 MHz, acetone-d_6)



^{19}F NMR (282 MHz, acetone-d_6)