Supplementary Information (SI) for ChemComm.

Supporting Information

Synthesis of 2-CF_3-Indoles or 2-CF_3-Indolin-3-ones *via* Anaerobic or Aerobic Reactions of *N*-Phenylpyridin-2-amines with TFISYs

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I. General experimental information

Commercial reagents were used without further purification. All solvents were purified and dried according to standard methods prior to use. *N*-Arylpyridin-2-amines **1**[1] and CF_3-imidoyl sulfoxonium ylides **2**[2] were prepared based on literature procedures. Melting points were recorded with a micro melting point apparatus and uncorrected. The ^1H NMR spectra were recorded at 400 MHz or 600 MHz. The ^{13}C NMR spectra were recorded at 100 MHz or 150 MHz. The ^{19}F NMR spectra were recorded at 376 MHz or 565 MHz. Chemical shifts were expressed in parts per million (δ), and were reported as s (singlet), d (doublet), t (triplet), dd (doublet of doublets), m (multiplet), etc. The coupling constants *J* were given in Hz. High-resolution mass spectra (HRMS) were recorded with a ThermoScientific Orbitrap Explories MX mass spectrometer or a BRUKER compact mass spectrometer. All reactions were monitored by thin layer chromatography (TLC) using silica gel plates (silica gel 60 F254 0.25 mm), and components were visualized by observation under UV light (254 and 365 nm).

II. Experimental procedures and spectroscopic data

1. General procedure for the synthesis of pyridinyl arylamines 1[1]

To a flask equipped with a stir bar were added aniline (10 mmol) and 2-bromopyridine (10 mmol). The resulting mixture was stirred at 160 °C (oil bath) for 6 h. Upon completion, it was quenched with saturated $NaHCO_3$, and extracted with EtOAc (3 × 10 mL). The combined organic phases were washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography by using *n*-hexanes/ethyl acetate (2:1) as eluent to give the corresponding product. All the pyridinyl arylamines are known compounds. For *N*-phenylpyridin-2-amine **1a**, a white solid was obtained in 83% yield, and its NMR data were consistent with the reported data.

***N*-phenylpyridin-2-amine (1a)**

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21-8.20 (m, 1H), 7.51-7.46 (m, 1H), 7.33-7.32 (m, 4H), 7.07-7.03 (m, 1H), 6.88 (t, *J* = 8.4 Hz, 1H), 6.75-6.71 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.0, 148.5, 140.5, 137.7, 129.3, 122.8, 120.4, 115.1, 108.2.

[1] (a) Mishra, N. K.; Choi, M.; Jo, H.; Oh, Y.; Sharma, S.; Han, S. H.; Jeong, T.; Han, S.; Lee, S.-Y.; Kim, I. S. Direct C−H Alkylation and Indole Formation of Anilines with Diazo Compounds under Rhodium Catalysis. *Chem. Commun*. **2015**, *51*, 17229−17232. (b) Wang, Y.; Jia, D.; Zeng, J.; Liu, Y.; Bu, X.; Yang, X. Benzocarbazole Synthesis *via* Visible-Light-Accelerated Rh(III)-Catalyzed C−H Annulation of Aromatic Amines with Bicyclic Alkenes. *Org. Lett*. **2021**, *23*, 7740−7745.

2. General procedure for the synthesis of CF_3-imidoyl sulfoxonium ylides 2[2]

2.1 Preparation of fluorinated imidoyl chlorides

To a flask equipped with a stir bar were charged with PPh_3 (37.5 mmol), Et_3N (15 mmol), CCl_4 (20 mL) and trifluoroacetic acid (15 mmol). The solution was stirred at 0 °C (ice bath) for 10 min. Afterwards, amine (15 mmol) dissolved in CCl_4 (20 mL) was added. The resulting mixture was refluxed (oil bath) with stirring for 3 h.

Upon completion, it was added with petroleum ether (20 mL), filtered, and washed with petroleum ether (3 × 5 mL). The combined filtrates were concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using petroleum ether as eluent to afford the corresponding product.

2.2 Preparation of CF_3-imidoyl sulfoxonium ylides

To a flask equipped with a stir bar were charged with trimethylsulfoxonium iodide (30 mmol), THF (150 mL) and *t*-BuOK (30 mmol). The mixture was stirred at room temperature for 2 h. Then, fluorinated imidoyl chloride (10 mmol) was added. The resulting mixture was stirred at room temperature for 3 h. Upon completion, it was filtered through a plug of celite, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography by using petroleum ether/ethyl acetate (2:1) as the eluent to afford the corresponding product. All the CF_3-imidoyl sulfoxonium ylides (TFISYs) are known compounds. For CF_3-imidoyl sulfoxonium ylide **2r**, a yellow solid was obtained in 75% yield, and its NMR data were consistent with the reported data.

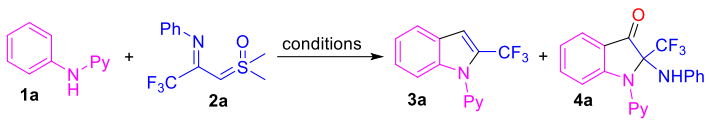
(*E*)-3-(Dimethyl(oxo)-λ^6-sulfaneylidene)-1,1,1-trifluoro-*N*-(*m*-tolyl)propan-2-imine (**2r**)

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.13 (t, *J* = 7.8 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 6.63 (s, 1H), 6.60 (d, *J* = 7.8 Hz, 1H), 4.07 (s, 1H), 3.38 (s, 6H), 2.31 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 150.4, 149.0, 138.1, 128.3, 123.1, 121.3, 117.6, 59.1, 41.3, 21.4. ^{19}F NMR (565 MHz, $CDCl_3$): δ -62.57.

[2] (a) Zhang, Y.; Ling, S.; Li, P.; Chen, Z.; Wu, X.-F. Rh(III)-Catalyzed Dual C−H Activation/Cascade Annulation of Benzimidates and CF_3-Imidoyl Sulfoxonium Ylides for the Synthesis of Trifluoromethyl Decorated Benzo[*de*][1,8]naphthyridines. *Org. Lett*. **2022**, *24,* 8864−8869. (b) Wen, S.; Tian, Q.; Chen, Y.; Zhang, Y.; Cheng, G. Annulation of CF_3−Imidoyl Sulfoxonium Ylides with 1,3-Dicarbonyl Compounds: Access to 1,2,3-Trisubstituted 5-Trifluoromethylpyrroles. *Org. Lett.* **2021**, *23*, 7407−7411.

3. Optimization studies

Table S1. Optimization for the Formation of **3a** and **4a**[a]

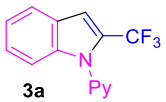


Entry	Additive 1	Additive 2	Solvent	Yield (%)[b]	
				3a	**4a**
1	$AgSbF_6$		TFE	68	ND
2	$AgNTf_2$		TFE	48	ND
3	AgOAc		TFE	58	ND
4	AgF		TFE	60	ND
5	AgOTf		TFE	62	ND
6	$AgSbF_6$		HFIP	31	ND
7	$AgSbF_6$		MeOH	ND	ND
8	$AgSbF_6$		EtOH	trace	ND
9	$AgSbF_6$		MeCN	ND	ND
10	$AgSbF_6$		dioxane	ND	ND
11	$AgSbF_6$		DCE	trace	ND
12	$AgSbF_6$	$Cu(OAc)_2$	TFE	8	25
13	$AgSbF_6$	$Cu(OAc)_2·H_2O$	TFE	7	23
14	$AgSbF_6$	$CuCl_2$	TFE	trace	14
15	$AgSbF_6$	$CuBr_2$	TFE	trace	10
16[c]	**$AgSbF_6$**		**TFE**	**81**	**ND**
17[d]	$AgSbF_6$	$Cu(OAc)_2$	TFE	trace	52
18[d,e]	$AgSbF_6$	$Cu(OAc)_2$	TFE	trace	61
19[d,e,f]	**$AgSbF_6$**	**$Cu(OAc)_2$**	**TFE**	**trace**	**66**
20[c,g]	$AgSbF_6$		TFE	80	ND
21[c,h]	$AgSbF_6$		TFE	76	ND
22[d,e,f,i]	$AgSbF_6$	$Cu(OAc)_2$	TFE	trace	trace
23[d,e,f,j]	$AgSbF_6$	$Cu(OAc)_2$	TFE	trace	trace
24[d,e,f,k]	$AgSbF_6$	$Cu(OAc)_2$	TFE	ND	ND
25[d,e,f,l]	$AgSbF_6$	$Cu(OAc)_2$	TFE	trace	36
26[d,e,f]	$AgSbF_6$	BPO	TFE	ND	ND
27[d,e,f]	$AgSbF_6$	TEMPO	TFE	ND	ND
28[d,e,f]	$AgSbF_6$	CH_3COOOH	TFE	ND	ND

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), $[RhCp^*Cl_2]_2$ (4 mol%), additive 1 (0.04 mmol), additive 2 (0.1 mmol), solvent (2 mL), sealed tube, 50 °C, air, 12 h. [b]Isolated yields. [c]Under argon. [d]Under oxygen. [e]TFE (1.5 mL), EtOH (0.5 mL). [f]**2a** (0.4 mmol). [g]60 °C. [h]14 h. [i]$[Ru(p\text{-cymene})Cl_2]_2$ as the catalyst. [j]$[IrCp^*Cl_2]_2$ as the catalyst. [k]$CoCp^*(CO)I_2$ as the catalyst. [l]$[RhCp^*(MeCN)_3](SbF_6)_2$ as the catalyst.

4. Typical procedure for the synthesis of 3a and spectroscopic data of 3a-3q

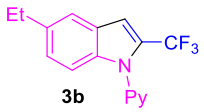
To a reaction tube equipped with a stir bar were added *N*-phenylpyridin-2-amine (**1a**, 34.0 mg, 0.2 mmol), $[RhCp^*Cl_2]_2$ (4.9 mg, 0.008 mmol), $AgSbF_6$ (13.7 mg, 0.04 mmol), CF_3-imidoyl sulfoxonium ylide (**2a**, 79.0 mg, 0.3 mmol) and TFE (2 mL). The tube was then sealed, and the mixture was stirred at 50 °C (oil bath) under argon for 12 h. Upon completion, it was cooled to room temperature, filtered through a pad of celite and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/dichloromethane (5:1) as eluent to afford **3a**. Other products **3b-3q** were obtained in a similar manner.



3a

1-(Pyridin-2-yl)-2-(trifluoromethyl)-1*H*-indole (3a)

Eluent: petroleum ether/dichloromethane (5:1). White solid (42.5 mg, 81%), mp 55.6-56.5°C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.69 (d, J = 3.0 Hz, 1H), 7.92 (td, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1H), 7.72 (d, J = 7.8 Hz, 1H), 7.49 (d, J = 7.8 Hz, 1H), 7.42 (dd, J_1 = 7.2 Hz, J_2 = 5.4 Hz, 1H), 7.31-7.30 (m, 2H), 7.25-7.22 (m, 1H), 7.15 (s, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 150.3, 149.8, 138.7, 138.6, 127.5 (q, $^2J_{C\text{-}F}$ = 37.1 Hz), 126.0, 125.4, 123.5, 122.2, 121.8, 121.7, 121.2 (q, $^1J_{C\text{-}F}$ = 266.9 Hz), 111.5, 107.5 (q, $^3J_{C\text{-}F}$ = 5.0 Hz). ^{19}F NMR (565 MHz, $CDCl_3$): δ -56.86 (s). HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{10}F_3N_2$ 263.0791; Found 263.0794.

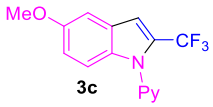


3b

5-Ethyl-1-(pyridin-2-yl)-2-(trifluoromethyl)-1*H*-indole (3b)

Eluent: petroleum ether/dichloromethane (5:1). Colorless oil (48.8 mg, 84%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.66-8.65 (m, 1H), 7.88 (td, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1H), 7.51 (s, 1H), 7.45 (d, J = 7.8 Hz, 1H), 7.38-7.36 (m, 1H), 7.24-7.23 (m, 1H), 7.16 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1H), 7.08 (s, 1H), 2.74 (q, J = 7.8 Hz, 2H), 1.27 (t, J = 7.8 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 150.4, 149.7, 138.6, 138.0, 137.3, 127.4 (q, $^2J_{C\text{-}F}$ = 37.4

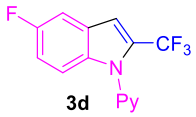
Hz), 126.22, 126.16, 123.3, 121.5, 121.3 (q, $^{1}J_{C\text{-}F}$ = 266.7 Hz), 120.4, 111.3, 107.3 (q, $^{3}J_{C\text{-}F}$ = 4.7 Hz), 28.9, 16.3. ^{19}F NMR (565 MHz, $CDCl_3$): δ -56.73 (s). HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{13}F_3N_2Na$ 313.0923; Found 313.0928.



3c

5-Methoxy-1-(pyridin-2-yl)-2-(trifluoromethyl)-1*H*-indole (3c)

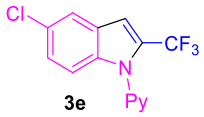
Eluent: petroleum ether/dichloromethane (5:1). Colorless oil (45.6 mg, 78%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.67-8.66 (m, 1H), 7.89 (td, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1H), 7.46 (d, J = 8.4 Hz, 1H), 7.40-7.38 (m, 1H), 7.23 (d, J = 9.0 Hz, 1H), 7.12 (d, J = 2.4 Hz, 1H), 7.06 (s, 1H), 6.97 (dd, J_1 = 9.0 Hz, J_2 = 2.4 Hz, 1H), 3.85 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 155.5, 150.4, 149.7, 138.6, 133.9, 127.6 (q, $^{2}J_{C\text{-}F}$ = 36.8 Hz), 126.5, 123.4, 121.4, 121.1 (q, $^{1}J_{C\text{-}F}$ = 266.3 Hz), 116.2, 112.5, 107.2 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 102.8, 55.8. ^{19}F NMR (565 MHz, $CDCl_3$): δ -56.72 (s). HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{12}F_3N_2O$ 293.0896; Found 293.0901.



3d

5-Fluoro-1-(pyridin-2-yl)-2-(trifluoromethyl)-1*H*-indole (3d)

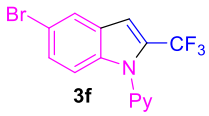
Eluent: petroleum ether/dichloromethane (5:1). White solid (48.2 mg, 86%), mp 78.9-79.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68-8.66 (m, 1H), 7.92 (td, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.47 (d, J = 7.6 Hz, 1H), 7.44-7.41 (m, 1H), 7.35 (dd, J_1 = 8.8 Hz, J_2 = 2.8 Hz, 1H), 7.26-7.23 (m, 1H), 7.10 (s, 1H), 7.06 (td, J_1 = 9.2 Hz, J_2 = 2.4 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 158.7 (d, $^{1}J_{C\text{-}F}$ = 236.8 Hz), 150.0, 149.8, 138.8, 135.3, 128.8 (q, $^{2}J_{C\text{-}F}$ = 38.4 Hz), 126.3 (d, $^{3}J_{C\text{-}F}$ = 11.0 Hz), 123.7, 121.6 (d, $^{4}J_{C\text{-}F}$ = 1.4 Hz), 120.9 (q, $^{1}J_{C\text{-}F}$ = 266.9 Hz), 114.2 (d, $^{2}J_{C\text{-}F}$ = 26.5 Hz), 112.7 (d, $^{3}J_{C\text{-}F}$ = 9.5 Hz), 107.2 (q, $^{3}J_{C\text{-}F}$ = 4.2 Hz), 106.8 (d, $^{2}J_{C\text{-}F}$ = 23.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ -57.08 (s), -121.78 (td, J_1 = 7.5 Hz, J_2 = 3.4 Hz). HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_9F_4N_2$ 281.0696; Found 281.0703.



3e

5-Chloro-1-(pyridin-2-yl)-2-(trifluoromethyl)-1*H*-indole (3e)

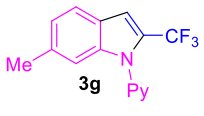
Eluent: petroleum ether/dichloromethane (5:1). Colorless oil (48.5 mg, 82%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.67-8.66 (m, 1H), 7.92 (td, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 7.68 (d, J = 1.8 Hz, 1H), 7.45 (d, J = 7.8 Hz, 1H), 7.43-7.41 (m, 1H), 7.26-7.22 (m, 2H), 7.07 (s, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 149.9, 149.8, 138.8, 137.1, 128.7 (q, $^{2}J_{C\text{-}F}$ = 37.5 Hz), 127.5, 126.9, 125.8, 123.8, 121.6, 121.5, 120.9 (q, $^{1}J_{C\text{-}F}$ = 266.4 Hz), 112.8, 106.8 (q, $^{3}J_{C\text{-}F}$ = 4.7 Hz). ^{19}F NMR (565 MHz, $CDCl_3$): δ -57.11 (s). HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_9ClF_3N_2$ 297.0401; Found 297.0405.



3f

5-Bromo-1-(pyridin-2-yl)-2-(trifluoromethyl)-1*H*-indole (3f)

Eluent: petroleum ether/dichloromethane (5:1). Colorless oil (54.6 mg, 80%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.68 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H), 7.93 (td, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1H), 7.85 (d, J = 1.8 Hz, 1H), 7.47-7.42 (m, 2H), 7.39 (dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 1H), 7.18 (d, J = 9.0 Hz, 1H), 7.07 (s, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 149.9, 149.8, 138.8, 137.3, 128.8 (q, $^{2}J_{C\text{-}F}$ = 38.1 Hz), 128.4, 127.5, 124.6, 123.8, 121.6, 120.8 (q, $^{1}J_{C\text{-}F}$ = 268.8 Hz), 115.0, 113.2, 106.7 (q, $^{3}J_{C\text{-}F}$ = 3.0 Hz). ^{19}F NMR (565 MHz, $CDCl_3$): δ -57.10 (s). HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_9BrF_3N_2$ 340.9896; Found 340.9903.

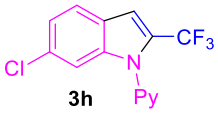


3g

6-Methyl-1-(pyridin-2-yl)-2-(trifluoromethyl)-1*H*-indole (3g)

Eluent: petroleum ether/dichloromethane (5:1). Colorless oil (47.0 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69-8.67 (m, 1H), 7.90 (td, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H), 7.58 (d, J = 8.4 Hz, 1H), 7.46 (d, J = 8.0 Hz, 1H), 7.42-7.38 (m, 1H), 7.09-7.05 (m, 3H), 2.41 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 150.4, 149.8, 139.1,

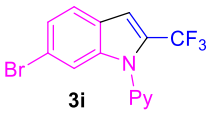
138.7, 135.6, 126.8 (q, $^{2}J_{C\text{-}F}$ = 37.6 Hz), 123.8, 123.5, 121.8, 121.3 (q, $^{1}J_{C\text{-}F}$ = 266.3 Hz), 111.2, 107.4 (q, $^{3}J_{C\text{-}F}$ = 5.0 Hz), 22.0. ^{19}F NMR (376 MHz, $CDCl_3$): δ -56.70 (s). HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{11}F_3N_2Na$ 299.0767; Found 299.0772.



3h

6-Chloro-1-(pyridin-2-yl)-2-(trifluoromethyl)-1*H*-indole (3h)

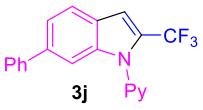
Eluent: petroleum ether/dichloromethane (5:1). White solid (53.9 mg, 91%), mp 61.1-62.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H), 7.93 (td, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.62 (d, J = 8.4 Hz, 1H), 7.47-7.42 (m, 2H), 7.31-7.30 (m, 1H), 7.20 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1H), 7.11 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 149.9, 149.7, 139.0, 138.9, 131.4, 128.1 (q, $^{2}J_{C\text{-}F}$ = 37.5 Hz), 124.4, 123.9, 123.1, 122.8, 121.6, 120.9 (q, $^{1}J_{C\text{-}F}$ = 267.0 Hz), 111.6, 107.4 (q, $^{3}J_{C\text{-}F}$ = 3.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ -57.05 (s). HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{14}H_8ClF_3N_2Na$ 319.0220; Found 319.0227.



3i

6-Bromo-1-(pyridin-2-yl)-2-(trifluoromethyl)-1*H*-indole (3i)

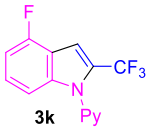
Eluent: petroleum ether/dichloromethane (5:1). White solid (61.4 mg, 90%), mp 76.0-76.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.70 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H), 7.95 (td, J_1 = 7.6 Hz, J_2 = 2.0 Hz, 1H), 7.58 (d, J = 8.4 Hz, 1H), 7.48-7.44 (m, 3H), 7.34 (dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz, 1H), 7.11 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 149.9, 149.7, 139.3, 138.9, 128.0 (q, $^{2}J_{C\text{-}F}$ = 36.8 Hz), 125.4, 124.8, 123.9, 123.4, 121.7, 120.9 (q, $^{1}J_{C\text{-}F}$ = 267.2 Hz), 119.2, 114.6, 107.4 (q, $^{3}J_{C\text{-}F}$ = 3.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ -57.08 (s). HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_9BrF_3N_2$ 340.9896; Found 340.9905.



3j

6-Phenyl-1-(pyridin-2-yl)-2-(trifluoromethyl)-1*H*-indole (3j)

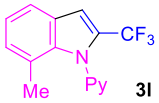
Eluent: petroleum ether/dichloromethane (5:1). White solid (57.5 mg, 85%), mp 100.3-100.7 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.73 (dd, J_1 = 4.2 Hz, J_2 = 1.2 Hz, 1H), 7.94 (td, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1H), 7.81 (d, J = 8.4 Hz, 1H), 7.60 (d, J_1 = 7.8 Hz, 2H), 7.55-7.51 (m, 3H), 7.45-7.43 (m, 3H), 7.35 (t, J = 7.2 Hz, 1H), 7.21 (s, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 150.2, 149.9, 141.8, 139.3, 139.1, 138.8, 128.8, 128.0 (q, $^{2}J_{C\text{-}F}$ = 38.3 Hz), 127.6, 127.2, 125.3, 123.7, 122.5, 121.93, 121.85, 121.2 (q, $^{1}J_{C\text{-}F}$ = 267.2 Hz), 110.0, 107.4 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz). ^{19}F NMR (565 MHz, $CDCl_3$): δ -56.84 (s). HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{13}F_3N_2Na$ 361.0923; Found 361.0929.



3k

4-Fluoro-1-(pyridin-2-yl)-2-(trifluoromethyl)-1*H*-indole (3k)

Eluent: petroleum ether/dichloromethane (5:1). White solid (28.0 mg, 50%), mp 62.7-63.7 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.68 (dd, J_1 = 4.8 Hz, J_2 = 1.8 Hz, 1H), 7.92 (td, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1H), 7.48 (d, J = 7.8 Hz, 1H), 7.44-7.42 (m, 1H), 7.24-7.21 (m, 2H), 7.06 (d, J = 8.4 Hz, 1H), 6.89 (dd, J_1 = 10.2 Hz, J_2 = 8.4 Hz, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 156.8 (d, $^{1}J_{C\text{-}F}$ = 248.1 Hz), 149.90, 149.87, 140.9 (d, $^{3}J_{C\text{-}F}$ = 9.2 Hz), 138.8, 127.6 (q, $^{2}J_{C\text{-}F}$ = 38.1 Hz), 126.1 (d, $^{3}J_{C\text{-}F}$ = 7.8 Hz), 123.9, 121.7, 120.8 (q, $^{1}J_{C\text{-}F}$ = 266.7 Hz), 115.6 (d, $^{2}J_{C\text{-}F}$ = 22.4 Hz), 107.6 (d, $^{4}J_{C\text{-}F}$ = 3.9 Hz), 106.5 (d, $^{2}J_{C\text{-}F}$ = 18.9 Hz), 103.4 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz). ^{19}F NMR (565 MHz, $CDCl_3$): δ -57.16 (s), -120.59 (dd, J_1 = 9.0 Hz, J_2 = 5.1 Hz). HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_9F_4N_2$ 281.0696; Found 281.0702.

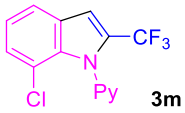


3l

7-Methyl-1-(pyridin-2-yl)-2-(trifluoromethyl)-1*H*-indole (3l)

Eluent: petroleum ether/dichloromethane (5:1). Colorless oil (49.2 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.62 (dd, J_1 = 5.2 Hz, J_2 = 1.2 Hz, 1H), 7.85 (td, J_1 = 8.0 Hz, J_2 = 2.4 Hz, 1H), 7.56 (d, J = 8.0 Hz, 1H), 7.47 (d,

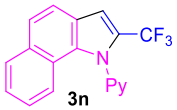
J = 7.6 Hz, 1H), 7.45-7.42 (m, 1H), 7.13-7.09 (m, 2H), 7.03 (d, J = 7.2 Hz, 1H), 1.80 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 151.7, 149.1, 138.1, 138.0, 128.3 (q, $^2J_{C\text{-}F}$ = 37.7 Hz), 127.7, 126.5, 124.4, 122.5, 121.8, 121.2 (q, $^1J_{C\text{-}F}$ = 265.3 Hz), 120.2, 107.0 (q, $^3J_{C\text{-}F}$ = 4.0 Hz), 18.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ -57.65 (s). HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{11}F_3N_2Na$ 299.0767; Found 299.0771.



3m

7-Chloro-1-(pyridin-2-yl)-2-(trifluoromethyl)-1*H*-indole (3m)

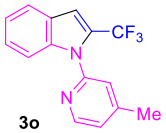
Eluent: petroleum ether/dichloromethane (5:1). Colorless oil (37.4 mg, 63%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.62 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H), 7.88 (td, J_1 = 7.6 Hz, J_2 = 2.0 Hz, 1H), 7.63 (dd, J_1 = 8.0 Hz, J_2 = 0.4 Hz, 1H), 7.51 (d, J = 7.6 Hz, 1H), 7.48-7.44 (m, 1H), 7.28 (d, J = 7.6 Hz, 1H), 7.16-7.12 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 150.3, 148.9, 137.9, 134.8, 129.6 (q, $^2J_{C\text{-}F}$ = 38.2 Hz), 128.5, 126.7, 124.6, 124.5, 122.3, 121.1, 120.7 (q, $^1J_{C\text{-}F}$ = 267.5 Hz), 117.8, 107.0 (q, $^3J_{C\text{-}F}$ = 3.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ -58.05 (s). HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_9ClF_3N_2$ 297.0401; Found 297.0403.



3n

1-(Pyridin-2-yl)-2-(trifluoromethyl)-1*H*-benzo[*g*]indole (3n)

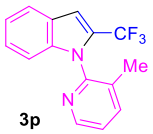
Eluent: petroleum ether/dichloromethane (5:1). White solid (37.5 mg, 60%), mp 96.2-97.1 °C. ^1H NMR (600 MHz, $CDCl_3$): δ 8.77 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H), 8.01 (td, J_1 = 7.8 Hz, J_2 = 2.4 Hz, 1H), 7.90 (d, J = 7.8 Hz, 1H), 7.73 (d, J = 8.4 Hz, 1H), 7.61 (d, J = 9.0 Hz, 1H), 7.60-7.56 (m, 2H), 7.40-7.37 (m, 1H), 7.24 (s, 1H), 7.17-7.14 (m, 1H), 6.68 (d, J = 8.4 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 152.0, 150.2, 139.0, 133.5, 129.3, 127.1 (q, $^2J_{C\text{-}F}$ = 37.6 Hz), 132.8, 125.6, 125.0, 124.9, 124.0, 123.4, 123.2, 122.3, 121.1 (q, $^1J_{C\text{-}F}$ = 266.6 Hz), 120.9, 120.8, 107.9 (q, $^3J_{C\text{-}F}$ = 4.5 Hz). ^{19}F NMR (565 MHz, $CDCl_3$): δ -56.84 (s). HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{12}F_3N_2$ 313.0947; Found 313.0949.



3o

1-(4-Methylpyridin-2-yl)-2-(trifluoromethyl)-1*H*-indole (3o)

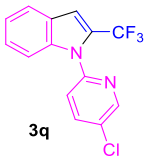
Eluent: petroleum ether/dichloromethane (5:1). White solid (50.8 mg, 92%), mp 79.9-80.4 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.54 (d, J = 4.8 Hz, 1H), 7.73 (d, J = 7.8 Hz, 1H), 7.34-7.30 (m, 3H), 7.25-7.23 (m, 2H), 7.15 (s, 1H), 2.48 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 150.32, 150.29, 149.4, 138.8, 127.5 (q, $^{2}J_{C\text{-}F}$ = 37.1 Hz), 125.9, 125.3, 124.6, 122.4, 122.2, 121.7, 121.2 (q, $^{1}J_{C\text{-}F}$ = 266.8 Hz), 111.6, 107.3 (q, $^{3}J_{C\text{-}F}$ = 3.7 Hz), 21.1. ^{19}F NMR (565 MHz, $CDCl_3$): δ -56.91 (s). HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{11}F_3N_2Na$ 299.0767; Found 299.0772.



3p

1-(3-Methylpyridin-2-yl)-2-(trifluoromethyl)-1*H*-indole (3p)

Eluent: petroleum ether/dichloromethane (5:1). Colorless oil (51.4 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H), 7.77-7.73 (m, 2H), 7.40 (dd, J_1 = 7.6 Hz, J_2 = 4.4 Hz, 1H), 7.29-7.19 (m, 2H), 7.13 (s, 1H), 6.84 (dd, J_1 = 7.6 Hz, J_2 = 0.4 Hz, 1H), 2.00 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 148.8, 147.5, 140.0, 138.4, 132.7, 127.3 (q, $^{2}J_{C\text{-}F}$ = 37.5 Hz), 125.7, 125.2, 124.8, 122.3, 121.5, 121.1 (q, $^{1}J_{C\text{-}F}$ = 267.0 Hz), 110.8, 106.2 (q, $^{3}J_{C\text{-}F}$ = 4.7 Hz), 16.7. ^{19}F NMR (376 MHz, $CDCl_3$): δ -58.85 (s). HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{12}F_3N_2$ 277.0947; Found 277.0951.



3q

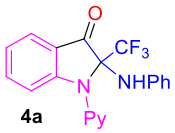
1-(5-Chloropyridin-2-yl)-2-(trifluoromethyl)-1*H*-indole (3q)

Eluent: petroleum ether/dichloromethane (3:1). Colorless oil (39.2 mg, 66%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.63 (d, J = 3.0 Hz, 1H), 7.89 (dd, J_1 = 8.4 Hz, J_2 = 3.0 Hz, 1H), 7.72 (d, J = 8.4 Hz, 1H), 7.44 (d, J = 8.4 Hz,

1H), 7.35-7.29 (m, 2H), 7.26-7.23 (m, 1H), 7.16 (s, 1H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ 148.6, 148.4, 138.6, 138.4, 131.8, 127.4 (q, $^{2}J_{C-F}$ = 38.1 Hz), 126.0, 125.6, 122.33, 122.28, 122.1, 121.1 (q, $^{1}J_{C-F}$ = 266.9 Hz), 111.3, 108.0 (q, $^{3}J_{C-F}$ = 3.3 Hz). ^{19}F NMR (565 MHz, $CDCl_3$): δ -56.81 (s). HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_9ClF_3N_2$ 297.0401; Found 297.0404.

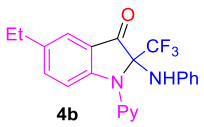
5. Typical procedure for the synthesis of 4a and spectroscopic data of 4a-4aa

To a reaction tube equipped with a stir bar were added *N*-phenylpyridin-2-amine (**1a**, 34.0 mg, 0.2 mmol), $[RhCp^*Cl_2]_2$ (4.9 mg, 0.008 mmol), $AgSbF_6$ (13.7 mg, 0.04 mmol), $Cu(OAc)_2$ (18.2 mg, 0.1 mmol), CF_3-imidoyl sulfoxonium ylide (**2a**, 105.3 mg, 0.4 mmol), TFE (1.5 mL) and EtOH (0.5 mL). The tube was then sealed, and the mixture was stirred at 50 °C (oil bath) under oxygen for 12 h. Upon completion, it was cooled to room temperature, filtered through a pad of celite and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/dichloromethane (1:1) as eluent to afford **4a**. Other products **4b-4aa** were obtained in a similar manner.



2-(Phenylamino)-1-(pyridin-2-yl)-2-(trifluoromethyl)indolin-3-one (4a)

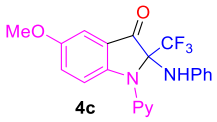
Eluent: petroleum ether/dichloromethane (1:1). Yellow solid (48.8 mg, 66%), mp 104.9-105.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H), 7.75 (d, J = 7.6 Hz, 1H), 7.64-7.60 (m, 2H), 7.54 (d, J = 8.4 Hz, 1H), 7.29 (d, J = 8.4 Hz, 1H), 7.11-7.02 (m, 4H), 6.79 (t, J = 7.6 Hz, 1H), 6.57 (d, J = 7.6 Hz, 2H), 5.02 (s, 1H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ 192.0, 156.8, 151.5, 148.7, 141.6, 138.4, 138.2, 129.4, 125.0, 122.2 (q, $^{1}J_{C-F}$ = 289.1 Hz), 121.7, 121.3, 120.9, 120.7, 117.7, 116.4, 114.5, 81.3 (q, $^{2}J_{C-F}$ = 28.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ -75.92 (s). HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{14}F_3N_3NaO$ 392.0981; Found 392.0976.



4b

5-Ethyl-2-(phenylamino)-1-(pyridin-2-yl)-2-(trifluoromethyl)indolin-3-one (4b)

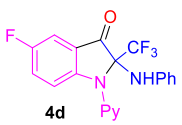
Eluent: petroleum ether/dichloromethane (1:1). Yellow solid (48.5 mg, 61%), mp 140.6-141.6 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.42-8.41 (m, 1H), 7.60-7.58 (m, 2H), 7.52-7.47 (m, 2H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.05-7.01 (m, 3H), 6.77 (t, *J* = 7.2 Hz, 1H), 6.55 (d, *J* = 7.8 Hz, 2H), 5.04 (s, 1H), 2.67 (q, *J* = 7.2 Hz, 2H), 1.26 (t, *J* = 7.8 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 192.1, 155.2, 151.8, 148.5, 141.7, 138.8, 138.1, 138.0, 129.3, 123.2, 122.3 (q, $^{1}J_{C\text{-}F}$ = 288.5 Hz), 121.2, 121.1, 120.4, 117.1, 116.4, 114.8, 81.5 (q, $^{2}J_{C\text{-}F}$ = 27.0 Hz), 28.0, 15.3. ^{19}F NMR (565 MHz, $CDCl_3$): δ -75.88 (s). HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{18}F_3N_3NaO$ 420.1294; Found 420.1290.



4c

5-Methoxy-2-(phenylamino)-1-(pyridin-2-yl)-2-(trifluoromethyl)indolin-3-one (4c)

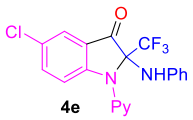
Eluent: petroleum ether/dichloromethane (1:1). Yellow solid (32.7 mg, 41%), mp 162.2-162.5 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.39 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H), 7.61 (d, *J* = 9.0 Hz, 1H), 7.60-7.57 (m, 1H), 7.29-7.27 (m, 2H), 7.18 (d, *J* = 2.4 Hz, 1H), 7.04-7.01 (m, 3H), 6.77 (t, *J* = 7.8 Hz, 1H), 6.54 (d, *J* = 7.8 Hz, 2H), 5.02 (s, 1H), 3.83 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 192.2, 155.0, 152.0, 151.8, 148.4, 141.6, 138.0, 129.3, 128.2, 122.3 (q, $^{1}J_{C\text{-}F}$ = 288.9 Hz), 121.5, 121.2, 120.1, 116.8, 116.6, 116.3, 104.9, 81.7 (q, $^{2}J_{C\text{-}F}$ = 27.8 Hz), 55.9. ^{19}F NMR (565 MHz, $CDCl_3$): δ -75.97 (s). HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{16}F_3N_3NaO_2$ 422.1087; Found 422.1084.



4d

5-Fluoro-2-(phenylamino)-1-(pyridin-2-yl)-2-(trifluoromethyl)indolin-3-one (4d)

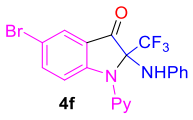
Eluent: petroleum ether/dichloromethane (3:1). Yellow solid (33.3 mg, 43%), mp 128.5-129.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44-8.42 (m, 1H), 7.65-7.61 (m, 2H), 7.41-7.34 (m, 2H), 7.29 (d, J = 8.4 Hz, 1H), 7.11-7.03 (m, 3H), 6.80 (t, J = 7.6 Hz, 1H), 6.56-6.54 (m, 2H), 4.98 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 191.8 (d, $^{4}J_{C\text{-}F}$ = 3.9 Hz), 157.6 (d, $^{1}J_{C\text{-}F}$ = 242.4 Hz), 153.3, 151.4, 148.5, 141.4, 138.3, 129.5, 126.0 (d, $^{2}J_{C\text{-}F}$ = 24.5 Hz), 122.1 (q, $^{1}J_{C\text{-}F}$ = 289.1 Hz), 121.5, 120.9, 117.4, 116.7 (d, $^{3}J_{C\text{-}F}$ = 7.5 Hz), 116.3, 109.9 (d, $^{2}J_{C\text{-}F}$ = 23.1 Hz), 81.8 (q, $^{2}J_{C\text{-}F}$ = 28.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ -75.99 (s), -120.66 (td, J_1 = 7.9 Hz, J_2 = 4.1 Hz). HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{13}F_4N_3NaO$ 410.0887; Found 410.0886.



4e

5-Chloro-2-(phenylamino)-1-(pyridin-2-yl)-2-(trifluoromethyl)indolin-3-one (4e)

Eluent: petroleum ether/dichloromethane (1:1). Yellow solid (45.2 mg, 56%), mp 131.9-132.4 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.44 (dd, J_1 = 4.8 Hz, J_2 = 1.8 Hz, 1H), 7.69 (d, J = 1.8 Hz, 1H), 7.66-7.63 (m, 1H), 7.58-7.54 (m, 2H), 7.28 (d, J = 8.4 Hz, 1H), 7.12 (dd, J_1 = 7.2 Hz, J_2 = 4.8 Hz, 1H), 7.07-7.05 (m, 2H), 6.81 (t, J = 7.2 Hz, 1H), 6.55 (d, J = 7.8 Hz, 2H), 4.97 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 190.7, 157.2, 151.0, 148.8, 145.1, 141.5, 138.5, 129.5, 125.8, 122.5, 122.0 (q, $^{1}J_{C\text{-}F}$ = 288.9 Hz), 121.53, 121.49, 119.0, 118.1, 116.3, 114.8, 81.6 (q, $^{2}J_{C\text{-}F}$ = 27.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ -75.95 (s). HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{13}ClF_3N_3NaO$ 426.0591; Found 426.0594.

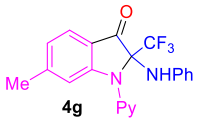


4f

5-Bromo-2-(phenylamino)-1-(pyridin-2-yl)-2-(trifluoromethyl)indolin-3-one (4f)

Eluent: petroleum ether/dichloromethane (1:1). Yellow solid (49.3 mg, 55%), mp 123.9-124.3 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δδ 8.44 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H), 7.84 (d, J = 1.8 Hz, 1H), 7.68 (dd, J_1 = 9.0 Hz, J_2 = 1.8 Hz, 1H), 7.64 (td, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 7.51 (d, J = 9.0 Hz, 1H), 7.28 (d, J = 8.4 Hz, 1H), 7.11 (dd, J_1 = 7.2 Hz, J_2 = 4.8 Hz, 1H), 7.07-7.05 (m, 2H), 6.81 (t, J = 7.2 Hz, 1H), 6.55 (d, J = 7.8 Hz, 2H), 4.98 (br

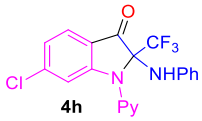
s, 1H).. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 190.9, 155.6, 151.1, 148.7, 141.4, 140.8, 138.4, 129.5, 127.2, 122.2, 122.0 (q, $^{1}J_{C\text{-}F}$ = 288.7 Hz), 121.5, 121.2, 117.8, 116.6, 116.3, 114.1, 81.6 (q, $^{2}J_{C\text{-}F}$ = 28.1 Hz). ^{19}F NMR (565 MHz,$CDCl_3$): δ -75.94 (s). HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{13}BrF_3N_3NaO$ 470.0086; Found 470.0089.



4g

6-Methyl-2-(phenylamino)-1-(pyridin-2-yl)-2-(trifluoromethyl)indolin-3-one (4g)

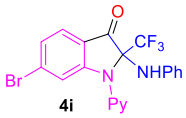
Eluent: petroleum ether/dichloromethane (3:1). Yellow solid (51.4 mg, 67%), mp 144.0-145.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.46 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H), 7.66-7.61 (m, 2H), 7.31 (s, 1H), 7.27 (d, J = 9.2 Hz, 1H), 7.11-7.08 (m, 1H), 7.04 (t, J = 8.0 Hz, 2H), 6.88 (d, J = 8.0 Hz, 1H), 6.79 (t, J = 7.6 Hz, 1H), 6.58 (d, J = 8.0 Hz, 2H), 5.00 (s, 1H), 2.42 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 191.1, 157.2, 151.5, 150.6, 148.7, 141.7, 138.3, 129.4, 124.8, 123.4, 122.3 (q, $^{1}J_{C\text{-}F}$ = 288.2 Hz), 121.2, 120.9, 118.6, 118.0, 116.3, 114.4, 81.5 (q, $^{2}J_{C\text{-}F}$ = 28.4 Hz), 23.0. ^{19}F NMR (376 MHz, $CDCl_3$): δ -76.02 (s). HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{16}F_3N_3NaO$ 406.1138; Found 406.1132.



4h

6-Chloro-2-(phenylamino)-1-(pyridin-2-yl)-2-(trifluoromethyl)indolin-3-one (4h)

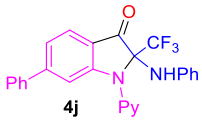
Eluent: petroleum ether/dichloromethane (1:1). Yellow solid (41.2 mg, 51%), mp 108.1-109.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.49 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H), 7.68-7.65 (m, 2H), 7.58 (d, J = 1.8 Hz, 1H), 7.29 (d, J = 8.4 Hz, 1H), 7.16-7.14 (m, 1H), 7.09-7.06 (m, 2H), 7.03 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 6.83 (t, J = 7.2 Hz, 1H), 6.58 (d, J = 7.8 Hz, 2H), 4.97 (s, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 190.7, 157.2, 151.0, 148.8, 145.1, 141.5, 138.5, 129.5, 125.8, 122.5, 122.0 (q, $^{1}J_{C\text{-}F}$ = 288.9 Hz), 121.53, 121.49, 119.0, 118.1, 116.3, 114.8, 81.6 (q, $^{2}J_{C\text{-}F}$ = 27.9 Hz). ^{19}F NMR (565 MHz, $CDCl_3$): δ -76.00 (s). HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{13}ClF_3N_3NaO$ 426.0591; Found 426.0596.



4i

6-Bromo-2-(phenylamino)-1-(pyridin-2-yl)-2-(trifluoromethyl)indolin-3-one (4i)

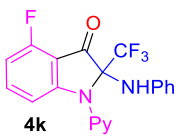
Eluent: petroleum ether/dichloromethane (1:1). Yellow solid (37.7 mg, 42%), mp 98.6-99.9°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H), 7.76 (d, J = 1.6 Hz, 1H), 7.66 (td, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.28 (d, J = 8.4 Hz, 1H), 7.18 (dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz, 1H), 7.16-7.13 (m, 1H), 7.10-7.06 (m, 2H), 6.82 (t, J = 7.2 Hz, 1H), 6.58 (d, J = 7.6 Hz, 2H), 4.98 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 191.0, 157.1, 150.9, 148.8, 141.4, 138.5, 134.2, 129.5, 125.7, 125.3, 122.0 (q, $^{1}J_{C\text{-}F}$ = 288.6 Hz), 121.53, 121.52, 119.3, 118.1, 117.8, 116.3, 81.5 (q, $^{2}J_{C\text{-}F}$ = 28.0 Hz). ^{19}F NMR (376 MHz,$CDCl_3$): δ -75.98 (s). HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{13}BrF_3N_3NaO$ 470.0086; Found 470.0089.



4j

6-Phenyl-2-(phenylamino)-1-(pyridin-2-yl)-2-(trifluoromethyl)indolin-3-one (4j)

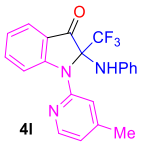
Eluent: petroleum ether/dichloromethane (1:1). Yellow solid (53.5 mg, 60%), mp 197.0-197.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H), 7.81 (d, J = 8.4 Hz, 1H), 7.70 (s, 1H), 7.64-7.61 (m, 3H), 7.45 (t, J = 6.6 Hz, 2H), 7.41-7.39 (m, 1H), 7.32 (d, J = 8.4 Hz, 1H), 7.28 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 7.10 (dd, J_1 = 7.2 Hz, J_2 = 4.8 Hz, 1H), 7.07-7.04 (m, 2H), 6.80 (t, J = 7.2 Hz, 1H), 6.62 (d, J = 7.8 Hz, 2H), 5.05 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 191.4, 157.2, 151.6, 151.5, 148.8, 141.7, 140.0, 138.3, 129.4, 129.0, 128.9, 127.6, 125.3, 122.3 (q, $^{1}J_{C\text{-}F}$ = 288.6 Hz), 121.4, 121.3, 121.0, 119.6, 117.9, 116.5, 112.7, 81.7 (q, $^{2}J_{C\text{-}F}$ = 27.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ -75.86 (s). HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{18}F_3N_3NaO$ 468.1294; Found 468.1290.



4k

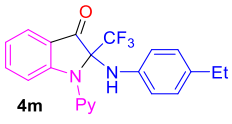
4-Fluoro-2-(phenylamino)-1-(pyridin-2-yl)-2-(trifluoromethyl)indolin-3-one (4k)

Eluent: petroleum ether/dichloromethane (3:1). Yellow solid (41.1 mg, 53%), mp 122.8-123.2 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.48-8.47 (m, 1H), 7.67-7.64 (m, 1H), 7.58-7.54 (m, 1H), 7.28-7.25 (m, 2H), 7.16-7.13 (m, 1H), 7.09-7.07 (m, 2H), 6.82 (t, *J* = 7.2 Hz, 1H), 6.66 (t, *J* = 8.4 Hz, 1H), 6.63-6.61 (m, 2H), 4.98 (s, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 188.0, 158.9 (d, $^{1}J_{C\text{-}F}$ = 262.2 Hz), 157.4 (d, $^{3}J_{C\text{-}F}$ = 5.1 Hz), 151.0, 148.8, 141.5, 140.1 (d, $^{3}J_{C\text{-}F}$ = 10.1 Hz), 138.5, 129.5, 122.0 (q, $^{1}J_{C\text{-}F}$ = 288.0 Hz), 121.6, 121.5, 118.5, 116.5, 110.0 (d, $^{4}J_{C\text{-}F}$ = 2.7 Hz), 109.5 (d, $^{2}J_{C\text{-}F}$ = 17.3 Hz), 107.9 (d, $^{2}J_{C\text{-}F}$ = 18.0 Hz), 81.6 (q, $^{2}J_{C\text{-}F}$ = 28.5 Hz). ^{19}F NMR (565 MHz, $CDCl_3$): δ -75.99 (s), -109.78 – -109.81 (m). HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{13}F_4N_3NaO$ 410.0887; Found 410.0886.



1-(4-Methylpyridin-2-yl)-2-(phenylamino)-2-(trifluoromethyl)indolin-3-one (4l)

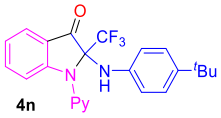
Eluent: petroleum ether/dichloromethane (1:1). Yellow solid (50.6 mg, 66%), mp 106.5-107.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (d, *J* = 5.2 Hz, 1H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.62-7.58 (m, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.09 (s, 1H), 7.07-7.01 (m, 3H), 6.93 (d, *J* = 5.2 Hz, 1H), 6.79 (t, *J* = 7.6 Hz, 1H), 6.60 (d, *J* = 8.0 Hz, 2H), 5.03 (s, 1H), 2.27 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 192.1, 157.1, 151.6, 149.7, 148.3, 141.8, 138.4, 129.3, 124.9, 122.24 (q, $^{1}J_{C\text{-}F}$ = 288.8 Hz), 122.19, 121.5, 121.3, 120.6, 118.3, 116.7, 114.4, 81.3 (q, $^{2}J_{C\text{-}F}$ = 27.4 Hz), 21.2. ^{19}F NMR (376 MHz, $CDCl_3$): δ -75.86 (s). HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{16}F_3N_3NaO$ 406.1138; Found 406.1136.



2-{(4-Ethylphenyl)amino}-1-(pyridin-2-yl)-2-(trifluoromethyl)indolin-3-one (4m)

Eluent: petroleum ether/dichloromethane (1:1). Yellow solid (40.5 mg, 51%), mp 92.4-93.1 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.46 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.65-7.59 (m, 2H), 7.55 (d, *J*

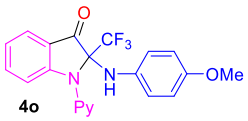
= 8.4 Hz, 1H), 7.33 (d, J = 8.4 Hz, 1H), 7.10 (dd, J_1 = 7.2 Hz, J_2 = 4.8 Hz, 1H), 7.04 (t, J = 7.2 Hz, 1H), 6.87 (d, J = 9.0 Hz, 2H), 6.53 (d, J = 8.4 Hz, 2H), 4.94 (s, 1H), 2.45 (q, J = 7.8 Hz, 2H), 1.09 (t, J = 7.8 Hz, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 192.3, 156.8, 151.6, 148.6, 139.4, 138.3, 138.2, 137.2, 128.7, 124.9, 122.2 (q, $^1J_{C-F}$ = 288.5 Hz), 121.6, 120.8, 120.7, 117.8, 116.8, 114.4, 81.5 (q, $^2J_{C-F}$ = 27.3 Hz), 27.9, 15.5. ^{19}F NMR (565 MHz, $CDCl_3$): δ -75.90 (s). HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{18}F_3N_3NaO$ 420.1294; Found 420.1284.



4n

2-{(4-(*tert*-Butyl)phenyl)amino}-1-(pyridin-2-yl)-2-(trifluoromethyl)indolin-3-one (4n)

Eluent: petroleum ether/dichloromethane (1:1). Yellow solid (48.5 mg, 57%), mp 65.3-65.8 °C. ^1H NMR (600 MHz, $CDCl_3$): δ 8.46 (dd, J_1 = 4.2 Hz, J_2 = 1.2 Hz, 1H), 7.74 (dd, J_1 = 7.8 Hz, J_2 = 0.6 Hz, 1H), 7.64-7.60 (m, 2H), 7.56 (d, J = 7.8 Hz, 1H), 7.32 (d, J = 8.4 Hz, 1H), 7.11-7.09 (m, 1H), 7.06-7.03 (m, 3H), 6.53-6.51 (m, 2H), 4.94 (s, 1H), 1.17 (s, 9H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 192.3, 156.8, 151.6, 148.6, 144.0, 139.0, 138.4, 138.2, 126.2, 124.9, 122.2 (q, $^1J_{C-F}$ = 288.8 Hz), 121.6, 120.9, 120.7, 117.9, 116.1, 114.4, 81.4 (q, $^2J_{C-F}$ = 27.8 Hz), 34.0, 31.3. ^{19}F NMR (565 MHz, $CDCl_3$): δ -75.94 (s). HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{22}F_3N_3NaO$ 448.1607; Found 448.1619.

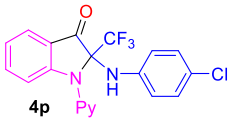


4o

2-{(4-Methoxyphenyl)amino}-1-(pyridin-2-yl)-2-(trifluoromethyl)indolin-3-one (4o)

Eluent: petroleum ether/dichloromethane (1:1). Yellow solid (39.9 mg, 50%), mp 125.8-126.1 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.48 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H), 7.71-7.65 (m, 2H), 7. 60-7.56 (m, 1H), 7.51 (d, J = 8.4 Hz, 1H), 7.38 (d, J =8.4 Hz, 1H), 7.13-7.10 (m, 1H), 7.01 (t, J = 7.2 Hz, 1H), 6.67-6.64 (m, 2H), 6.62-6.59 (m, 2H), 4.99 (s, 1H), 3.64 (s, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 192.1, 156.9, 155.0, 151.8, 148.7, 138.3, 138.2, 134.9, 125.0, 122.3 (q, $^1J_{C-F}$ = 289.2 Hz), 121.6, 120.8, 120.7, 119.9, 117.4, 114.6, 113.9, 82.1 (q, $^2J_{C-F}$ =

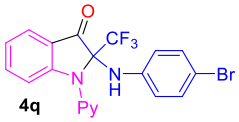
26.6 Hz), 55.4. ^{19}F NMR (376 MHz, $CDCl_3$): δ -75.65 (s). HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{16}F_3N_3NaO_2$ 422.1087; Found 422.1096.



4p

2-{(4-Chlorophenyl)amino}-1-(pyridin-2-yl)-2-(trifluoromethyl)indolin-3-one (4p)

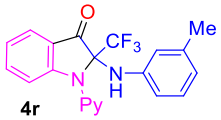
Eluent: petroleum ether/dichloromethane (1:1). Yellow solid (38.8 mg, 48%), mp 102.1-102.7 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.46-8.45 (m, 1H), 7.75 (dd, J_1 = 7.8 Hz, J_2 = 0.6 Hz, 1H), 7.67-7.61 (m, 2H), 7.51 (d, J = 8.4 Hz, 1H), 7.29 (d, J = 7.8 Hz, 1H), 7.13-7.11 (m, 1H), 7.07 (t, J = 7.2 Hz, 1H), 7.01-6.99 (m, 2H), 6.56-6.53 (m, 2H), 5.07 (s, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 191.6, 156.8, 151.4, 148.8, 140.3, 138.6, 138.3, 129.3, 126.6, 125.1, 122.1 (q, $^1J_{C-F}$ = 289.1 Hz), 121.9, 121.0, 120.6, 118.2, 117.4, 114.4, 81.3 (q, $^2J_{C-F}$ = 27.9 Hz). ^{19}F NMR (565 MHz, $CDCl_3$): δ -75.83 (s). HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{13}ClF_3N_3NaO$ 426.0591; Found 426.0594.



4q

2-{(4-Bromophenyl)amino}-1-(pyridin-2-yl)-2-(trifluoromethyl)indolin-3-one (4q)

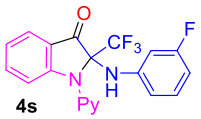
Eluent: petroleum ether/dichloromethane (1:1). Yellow solid (40.3 mg, 45%), mp 128.8-129.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (dd, J_1 = 4.8 Hz, J_2 = 0.8 Hz, 1H), 7.75 (d, J = 7.6 Hz, 1H), 7.68-7.60 (m, 2H), 7.51 (d, J = 8.4 Hz, 1H), 7.28 (d, J = 8.0 Hz, 1H), 7.15-7.10 (m, 3H), 7.07 (t, J = 7.2 Hz, 1H), 6.49 (d, J = 8.8 Hz, 2H), 5.08 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 191.6, 156.8, 151.4, 148.8, 140.8, 138.6, 138.3, 132.2, 125.1, 122.1 (q, $^1J_{C-F}$ = 288.8 Hz), 121.9, 121.0, 120.6, 118.5, 117.4, 114.4, 113.9, 81.2 (q, $^2J_{C-F}$ = 28.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ -75.84 (s). HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{13}BrF_3N_3NaO$ 470.0086; Found 470.0087.



4r

1-(Pyridin-2-yl)-2-(*m*-tolylamino)-2-(trifluoromethyl)indolin-3-one (4r)

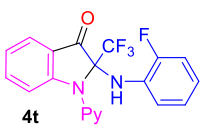
Eluent: petroleum ether/dichloromethane (1:1). Yellow solid (46.0 mg, 60%), mp 125.8-126.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H), 7.75 (d, J = 7.2 Hz, 1H), 7.66-7.60 (m, 2H), 7.56 (d, J = 8.4 Hz, 1H), 7.31 (d, J = 8.4 Hz, 1H), 7.13-7.10 (m, 1H), 7.05 (t, J = 8.0 Hz, 1H), 6.91 (t, J = 7.6 Hz, 1H), 6.62 (d, J = 7.6 Hz, 1H), 6.45 (s, 1H), 6.33 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 4.93 (s, 1H), 2.13 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 192.2, 156.8, 151.6, 148.6, 141.7, 139.2, 138.4, 138.3, 129.3, 124.8, 122.25, 122.24 (q, $^{1}J_{C\text{-}F}$ = 289.0 Hz), 121.7, 120.9, 120.7, 117.8, 117.7, 114.4, 113.0, 81.3 (q, $^{2}J_{C\text{-}F}$ = 28.0 Hz), 21.4. ^{19}F NMR (376 MHz, $CDCl_3$): δ -75.94 (s). HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{16}F_3N_3NaO$ 406.1138; Found 406.1124.



4s

2-{(3-Fluorophenyl)amino}-1-(pyridin-2-yl)-2-(trifluoromethyl)indolin-3-one (4s)

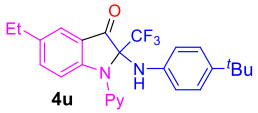
Eluent: petroleum ether/dichloromethane (1:1). Yellow solid (31.0 mg, 40%), mp 130.1-130.8 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.47-8.46 (m, 1H), 7.77 (dd, J_1 = 7.8 Hz, J_2 = 0.6 Hz, 1H), 7.66-7.62 (m, 2H), 7.52 (d, J = 8.4 Hz, 1H), 7.28 (d, J = 7.8 Hz, 1H), 7.13-7.11 (m, 1H), 7.09-7.06 (m, 1H), 7.01-6.97 (m, 1H), 6.51-6.48 (m, 1H), 6.36-6.34 (m, 1H), 6.32-6.30 (m, 1H), 5.13 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 191.5, 163.4 (d, $^{1}J_{C\text{-}F}$ = 243.3 Hz), 156.8, 151.4, 148.8, 143.4 (d, $^{3}J_{C\text{-}F}$ = 10.5 Hz), 138.6, 138.3, 130.6 (d, $^{3}J_{C\text{-}F}$ = 9.6 Hz), 125.1, 122.1 (q, $^{1}J_{C\text{-}F}$ = 288.7 Hz), 122.0, 121.0, 120.5, 117.5, 114.4, 112.1 (d, $^{4}J_{C\text{-}F}$ = 2.8 Hz), 108.1 (d, $^{2}J_{C\text{-}F}$ = 21.2 Hz), 103.9 (d, $^{2}J_{C\text{-}F}$ = 25.9 Hz), 81.0 (q, $^{2}J_{C\text{-}F}$ = 27.9 Hz). ^{19}F NMR (565 MHz, $CDCl_3$): δ -75.89 (s), -111.58 – -111.63 (m). HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{13}F_4N_3NaO$ 410.0887; Found 410.0884.



4t

2-{(2-Fluorophenyl)amino}-1-(pyridin-2-yl)-2-(trifluoromethyl)indolin-3-one (4t)

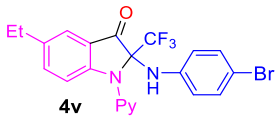
Eluent: petroleum ether/dichloromethane (1:1). Yellow oil (27.9 mg, 36%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.43 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H), 7.77 (d, J = 7.6 Hz, 1H), 7.67-7.62 (m, 2H), 7.55 (d, J = 8.4 Hz, 1H), 7.26 (d, J = 8.4 Hz, 1H), 7.12-7.07 (m, 2H), 6.98-6.93 (m, 1H), 6.74-6.70 (m, 2H), 6.39-6.35 (m, 1H), 5.27 (d, J = 2.8 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 191.8, 157.0, 152.2 (d, $^{1}J_{C\text{-}F}$ = 239.5 Hz), 151.2, 148.7, 138.5, 138.3, 130.2 (d, $^{2}J_{C\text{-}F}$ = 10.7 Hz), 125.0, 124.7 (d, $^{4}J_{C\text{-}F}$ = 3.5 Hz), 122.2 (q, $^{1}J_{C\text{-}F}$ = 288.8 Hz), 121.9, 121.04, 120.96 (d, $^{3}J_{C\text{-}F}$ = 7.3 Hz), 120.6, 117.6 (d, $J_{C\text{-}F}$ = 1.3 Hz), 115.4 (d, $J_{C\text{-}F}$ = 1.8 Hz), 115.1 (d, $^{2}J_{C\text{-}F}$ = 18.7 Hz), 114.8, 80.6 (q, $^{2}J_{C\text{-}F}$ = 28.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ -75.95 (s), -133.14 – -133.20 (m). HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{13}F_4N_3NaO$ 410.0887; Found 410.0872.



4u

2-{(4-(*tert*-Butyl)phenyl)amino}-5-ethyl-1-(pyridin-2-yl)-2-(trifluoromethyl)indolin-3-one (4u)

Eluent: petroleum ether/dichloromethane (1:1). Yellow solid (61.7 mg, 68%), mp 87.7-88.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.43-8.41 (m, 1H), 7.61-7.53 (m, 3H), 7.47 (dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz, 1H), 7.31 (d, J = 8.0 Hz, 1H), 7.06-7.02 (m, 3H), 6.52-6.49 (m, 2H), 4.96 (s, 1H), 2.66 (q, J = 7.6 Hz, 2H), 1.26 (t, J = 7.2 Hz, 3H), 1.17 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 192.4, 155.2, 151.8, 148.5, 143.8, 139.1, 138.7, 138.1, 137.8, 126.2, 123.1, 122.3 (q, $^{1}J_{C\text{-}F}$ = 288.5 Hz), 121.0, 120.4, 117.4, 116.0, 114.7, 81.6 (q, ^{2}J = 28.3 Hz), 34.0, 31.3, 28.0, 15.3. ^{19}F NMR (565 MHz, $CDCl_3$): δ -75.87 (s). HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{26}F_3N_3NaO$ 476.1920; Found 476.1914.

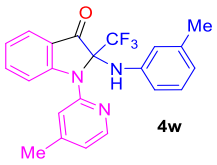


4v

2-{(4-Bromophenyl)amino}-5-ethyl-1-(pyridin-2-yl)-2-(trifluoromethyl)indolin-3-one (4v)

Eluent: petroleum ether/dichloromethane (1:1). Yellow oil (52.4 mg, 55%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H), 7.65-7.60 (m, 1H), 7.57 (s, 1H), 7.51-7.46 (m, 2H), 7.28 (d, J = 8.0 Hz, 1H), 7.14-7.11 (m, 2H), 7.09-7.05 (m, 1H), 6.49-6.45 (m, 2H), 5.09 (s, 1H), 2.67 (q, J = 7.6 Hz, 2H), 1.26 (t, J = 7.6

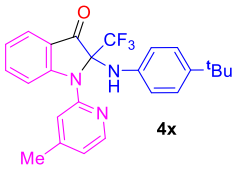
Hz, 3H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ 191.7, 155.1, 151.6, 148.6, 140.9, 139.0, 138.22, 138.20, 132.2, 123.3, 122.2 (q, $^{1}J_{C\text{-}F}$ = 288.8 Hz), 120.9, 120.5, 118.4, 116.9, 114.7, 113.8, 81.4 (q, ^{2}J = 28.1 Hz), 28.0, 15.2. ^{19}F NMR (376 MHz, $CDCl_3$): δ -75.81 (s). HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{17}BrF_3N_3NaO$ 498.0399; Found 498.0404.



4w

1-(4-Methylpyridin-2-yl)-2-(*m*-tolylamino)-2-(trifluoromethyl)indolin-3-one (4w)

Eluent: petroleum ether/dichloromethane (1:1). Yellow solid (52.4 mg, 66%), mp 137.4-137.8 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.32 (d, J = 5.4 Hz, 1H), 7.73 (dd, J_1 = 7.8 Hz, J_2 = 0.6 Hz, 1H), 7.61-7.58 (m, 1H), 7.48 (d, J = 8.4 Hz, 1H), 7.11 (s, 1H), 7.02 (t, J = 7.2 Hz, 1H), 6.94 (d, J = 4.2 Hz, 1H), 6.91 (t, J = 8.4 Hz, 1H), 6.62 (d, J = 7.8 Hz, 1H), 6.47 (s, 1H), 6.36 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 4.95 (s, 1H), 2.28 (s, 3H), 2.13 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 192.2, 157.1, 151.7, 149.6, 148.3, 141.8, 139.1, 138.4, 129.2, 124.8, 122.3, 122.23 (q, $^{1}J_{C\text{-}F}$ = 289.8 Hz), 122.21, 121.4, 120.6, 118.4, 117.9, 114.3, 113.4, 81.3 (q, ^{2}J = 28.0 Hz), 21.4, 21.2. ^{19}F NMR (565 MHz, $CDCl_3$): δ -75.88 (s). HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{18}F_3N_3NaO$ 420.1294; Found 420.1291.

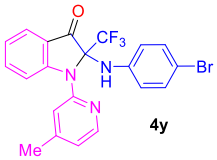


4x

2-{(4-(*tert*-Butyl)phenyl)amino}-1-(4-methylpyridin-2-yl)-2-(trifluoromethyl)indolin-3-one (4x)

Eluent: petroleum ether/dichloromethane (3:1). Yellow solid (57.1 mg, 65%), mp 117.9-118.3 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.31 (d, J = 5.4 Hz, 1H), 7.73 (dd, J_1 = 7.8 Hz, J_2 = 0.6 Hz, 1H), 7.61-7.58 (m, 1H), 7.48 (d, J = 8.4 Hz, 1H), 7.12 (s, 1H), 7.06-7.02 (m, 3H), 6.93 (d, J = 5.4 Hz, 1H), 6.54-6.52 (m, 2H), 4.92 (br s, 1H), 2.28 (s, 3H), 1.18 (s, 9H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 192.3, 157.1, 151.7, 149.6, 148.3, 144.0, 139.2,

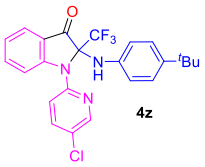
138.3, 126.2, 124.9, 122.2 (q, $^{1}J_{C\text{-}F}$ = 288.7 Hz), 122.1, 121.4, 120.7, 118.4, 116.4, 114.3, 81.4 (q, ^{2}J = 28.2 Hz), 34.0, 31.3, 21.1. ^{19}F NMR (565 MHz, $CDCl_3$): δ -75.86 (s). HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{25}H_{24}F_3N_3NaO$ 462.1764; Found 462.1762.



4y

2-{(4-Bromophenyl)amino}-1-(4-methylpyridin-2-yl)-2-(trifluoromethyl)indolin-3-one (4y)

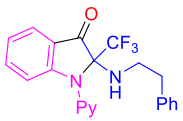
Eluent: petroleum ether/dichloromethane (1:1). Yellow solid (55.5 mg, 60%), mp 164.3-164.6 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.31 (d, *J* = 5.4 Hz, 1H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.62-7.60 (m, 1H), 7.44 (d, *J* = 8.4 Hz, 1H), 7.16-7.14 (m, 2H), 7.08 (s, 1H), 7.05 (t, *J* = 7.8 Hz, 1H), 6.95 (d, *J* = 4.8 Hz, 1H), 6.53-6.50 (m, 2H), 5.07 (s, 1H), 2.31 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 191.6, 157.1, 151.5, 149.8, 148.5, 141.0, 138.6, 132.2, 125.1, 122.3, 122.1 (q, $^{1}J_{C\text{-}F}$ = 288.9 Hz), 121.7, 120.5, 118.8, 118.1, 114.2, 114.0, 81.2 (q, ^{2}J = 28.7 Hz), 21.3. ^{19}F NMR (565 MHz, $CDCl_3$): δ -75.80 (s). HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{15}BrF_3N_3NaO$ 484.0243; Found 484.0249.



4z

2-{(4-(*tert*-Butyl)phenyl)amino}-1-(5-chloropyridin-2-yl)-2-(trifluoromethyl)indolin-3-one (4z)

Eluent: petroleum ether/dichloromethane (3:1). Yellow solid (49.7 mg, 54%), mp 139.5-139.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (d, *J* = 2.4 Hz, 1H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.64-7.57 (m, 3H), 7.32 (d, *J* = 8.8 Hz, 1H), 7.10-7.04 (m, 3H), 6.49 (d, *J* = 8.8 Hz, 2H), 4.88 (s, 1H), 1.18 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 192.1, 156.2, 149.9, 147.1, 144.2, 138.8, 138.4, 137.9, 128.3, 126.3, 124.9, 122.2 (q, $^{1}J_{C\text{-}F}$ = 289.1 Hz), 122.0, 120.9, 118.4, 115.9, 114.7, 81.3 (q, ^{2}J = 28.3 Hz), 34.0, 31.3. ^{19}F NMR (376 MHz, $CDCl_3$): δ -75.90 (s). HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{21}ClF_3N_3NaO$ 482.1217; Found 482.1205.



4aa

2-(Phenethylamino)-1-(pyridin-2-yl)-2-(trifluoromethyl)indolin-3-one (4aa)

Eluent: petroleum ether/dichloromethane (1:1). Yellow oil (30.8 mg, 39%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, *J* = 3.2 Hz, 1H), 7.65-7.58 (m, 2H), 7.46 (t, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 8.4 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 1H), 7.19-7.15 (m, 2H), 7.13-7.09 (m, 1H), 7.05-7.00 (m, 3H), 6.90 (t, *J* = 7.2 Hz, 1H), 3.11 (br s, 1H), 2.80-2.63 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 192.6, 157.6, 149.0, 139.0, 138.3, 138.2, 129.0, 128.5, 126.3, 125.2, 122.3 (q, $^{1}J_{C\text{-}F}$ = 285.7 Hz), 121.3, 120.5, 120.2, 117.0, 84.2 (q, $^{2}J_{C\text{-}F}$ = 27.8 Hz), 43.6, 36.0. ^{19}F NMR (376 MHz, $CDCl_3$): δ -75.72 (s). HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{18}F_3N_3NaO$ 420.1294; Found 420.1292.

6. Gram-Scale Synthesis of 3a and 4a

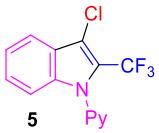
To a reaction tube equipped with a stir bar were added **1a** (0.85 g, 5 mmol), $[RhCp^*Cl_2]_2$ (123.6 mg, 0.2 mmol), $AgSbF_6$ (343.6 mg, 1 mmol), **2a** (1.97 g, 7.5 mmol) and TFE (20 mL). The tube was then sealed, and the mixture was stirred at 50 °C (oil bath) under argon for 40 h. Upon completion, it was cooled to room temperature, filtered through a pad of celite and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/dichloromethane (5:1) as eluent to afford **3a** (870 mg, 66%).

To a reaction tube equipped with a stir bar were added **1a** (0.85 g, 5 mmol), $[RhCp^*Cl_2]_2$ (123.6 mg, 0.2 mmol), $AgSbF_6$ (343.6 mg, 1 mmol), $Cu(OAc)_2$ (454.1 mg, 2.5 mmol), **2a** (2.63 g, 10 mmol), TFE (15 mL) and EtOH (5 mL). The tube was then sealed, and the mixture was stirred at 50 °C (oil bath) under oxygen for 30 h. Upon completion, it was cooled to room temperature, filtered through a pad of celite and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/dichloromethane (1:1) as eluent to afford **4a** (923 mg, 50%).

7. Structural elaborations of 3

7.1 Synthesis of 5

To a reaction tube equipped with a stir bar were added **3a** (52.4 mg, 0.2 mmol), $CHCl_3$ (3.0 mL) and *N*-chlorosuccinimide (26.7 mg, 0.2 mmol) with stirring. The mixture was stirred at 100 °C under air for 5 h. Upon completion, it was concentrated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/dichloromethane (3:1) as eluent to afford **5**.



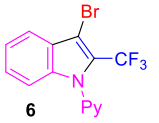
5

3-Chloro-1-(pyridin-2-yl)-2-(trifluoromethyl)-1*H*-indole (5)

Eluent: petroleum ether/dichloromethane (3:1). Colorless oil (30.9 mg, 52%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.68 (d, J = 3.6 Hz, 1H), 7.94 (td, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1H), 7.77 (d, J = 7.8 Hz, 1H), 7.46-7.44 (m, 2H), 7.36 (t, J = 7.2 Hz, 1H), 7.31 (t, J = 7.2 Hz, 1H), 7.23 (d, J = 8.4 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 150.0, 149.9, 138.7, 136.9, 126.6, 125.0, 123.9, 122.4, 122.3 (q, $^2J_{C\text{-}F}$ = 36.9), 122.0, 120.9 (q, $^1J_{C\text{-}F}$ = 268.8), 119.8, 111.7 (q, $^3J_{C\text{-}F}$ = 2.7), 111.5. ^{19}F NMR (565 MHz, $CDCl_3$): δ -54.84. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_9ClF_3N_2$ 297.0401; Found 297.0404.

7.2 Synthsis of 6

To a reaction tube equipped with a stir bar were added **3a** (52.4 mg, 0.2 mmol), $CHCl_3$ (3.0 mL) and *N*-bromosuccinimide (35.6 mg, 0.2 mmol) with stirring. The mixture was stirred at room temperature under air for 5 h. Upon completion, it was concentrated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/dichloromethane (3:1) as eluent to afford **6**.



6

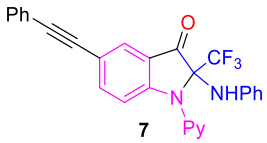
3-Bromo-1-(pyridin-2-yl)-2-(trifluoromethyl)-1*H*-indole (6)

Eluent: petroleum ether/dichloromethane (3:1). Colorless oil (51.9 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (dd, J_1 = 5.2 Hz, J_2 = 2.0 Hz, 1H), 7.94 (td, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.73 (d, J = 7.6 Hz, 1H), 7.46-7.44 (m, 2H), 7.38-7.30 (m, 2H), 7.20 (d, J = 8.0 Hz, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 150.2, 149.9, 138.8, 137.5, 126.6, 124.2 (q, $^{2}J_{C-F}$ = 36.8 Hz), 124.0, 122.5, 122.1, 121.0, 120.9 (q, $^{1}J_{C-F}$ = 269.1 Hz), 111.4, 97.3 (q, $^{3}J_{C-F}$ = 2.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ -54.50 (s). HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_9BrF_3N_2$ 340.9896; Found 340.9898.

8. Structural elaborations of 4

8.1 Synthesis of 7

To a reaction tube equipped with a stir bar were added **4f** (46.8 mg, 0.1 mmol), ethynylbenzene (16.5 μL, 0.15 mmol), PPh_3 (5.2 mg, 0.02 mmol), K_3PO_4 (25.5 mg, 0.12 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) and DMSO (1 mL). The resulting mixture was then stirred at 80°C (oil bath) under argon for 24 h. Upon completion, it was diluted with ethyl acetate (20 mL) and washed with water and brine. The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with petroleum ether/dichloromethane (1:1) as eluent to give **7**.



7

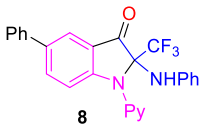
2-(Phenylamino)-5-(phenylethynyl)-1-(pyridin-2-yl)-2-(trifluoromethyl)indolin-3-one (7)

Eluent: petroleum ether/dichloromethane (1:1). Yellow oil (32.2 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49-8.47 (m, 1H), 7.91 (d, J = 1.6 Hz, 1H), 7.75 (dd, J_1 = 8.8 Hz, J_2 = 1.6 Hz, 1H), 7.67-7.63 (m, 1H), 7.55-7.51 (m, 3H), 7.37-7.33 (m, 3H), 7.31-7.29 (m, 1H), 7.15-7.11 (m, 1H), 7.09-7.05 (m, 2H), 6.84-6.80 (m, 1H), 6.59-6.57 (m, 2H), 5.00 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 191.2, 156.0, 151.2, 148.8, 141.5, 141.2, 138.4, 131.6, 129.5, 128.5, 127.9, 123.0, 122.2 (q, $^{1}J_{C-F}$ = 267.0 Hz), 121.5, 121.3, 120.6, 117.9, 116.8, 116.5, 114.5,

89.7, 87.9, 81.6 (q, $^{2}J_{C\text{-}F}$ = 28.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ -75.86 (s). HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{28}H_{18}F_3N_3NaO$ 492.1294; Found 492.1291.

8.2 Synthsis of 8

To a reaction tube equipped with a stir bar were added with **4f** (49.7 mg, 0.1 mmol), phenylboronic acid (18.3 mg, 0.15 mmol), PPh_3 (15.7 mg, 0.06 mmol), K_2CO_3 (55.3 mg, 0.4 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol) and dioxane (1 mL). The tube was then sealed, and the mixture was stirred at 80 °C (oil bath) under argon for 24 h. Upon completion, it was diluted with water and extracted with ethyl acetate (10 mL × 3). The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1) as eluent to give **8**.



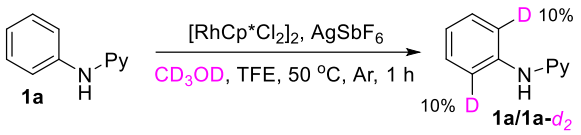
8

5-Phenyl-2-(phenylamino)-1-(pyridin-2-yl)-2-(trifluoromethyl)indolin-3-one (8)

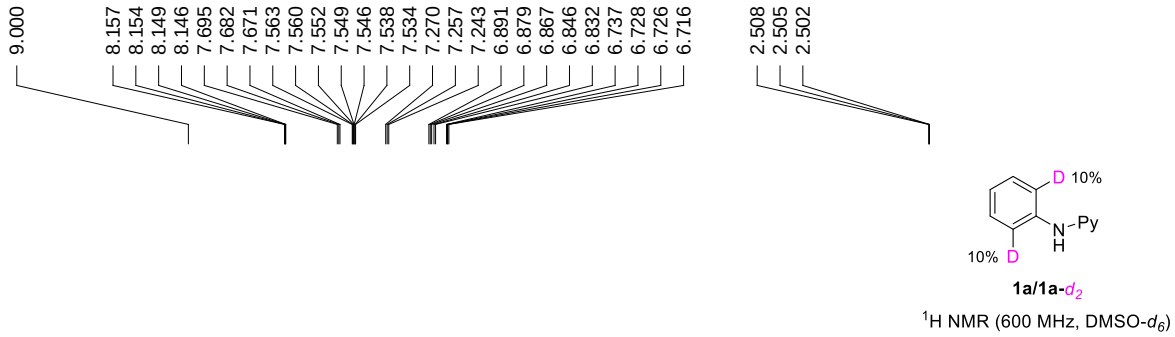
Eluent: petroleum ether/dichloromethane (1:1). Yellow oil (31.5 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47-8.45 (m, 1H), 7.97 (d, J = 2.0 Hz, 1H), 7.89 (dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 1H), 7.67-7.62 (m, 2H), 7.60-7.58 (m, 2H), 7.47-7.43 (m, 2H), 7.38-7.32 (m, 2H), 7.12-7.084 (m, 1H), 7.076-7.04 (m, 2H), 6.82-6.78 (m, 1H), 6.61-6.59 (m, 2H), 5.03 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 192.1, 156.0, 151.5, 148.7, 141.6, 139.3, 138.3, 137.4, 135.1, 129.4, 129.0, 127.6, 126.7, 122.7, 122.3 (q, $^{1}J_{C\text{-}F}$ = 288.5 Hz), 121.4, 121.3, 120.8, 117.5, 116.4, 115.2, 81.7 (q, $^{2}J_{C\text{-}F}$ = 28.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ -75.82 (s). HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{18}F_3N_3NaO$ 468.1294; Found 468.1289.

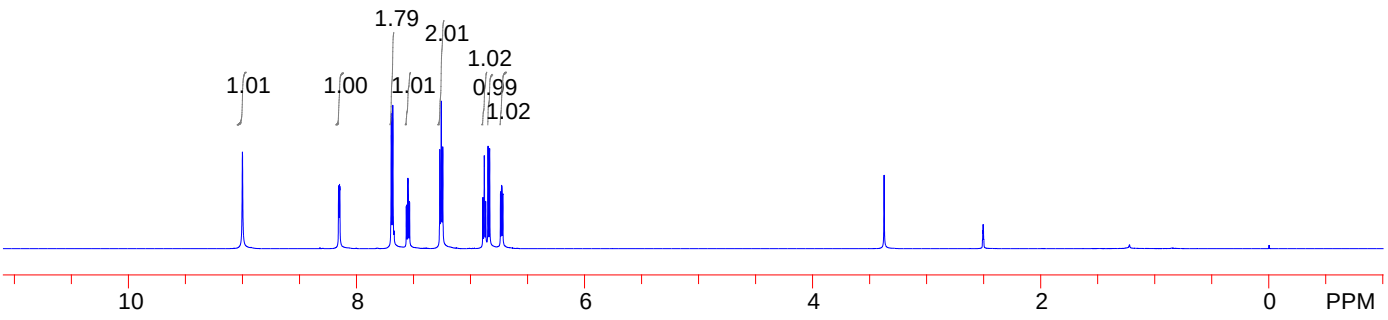
III. Mechanistic studies

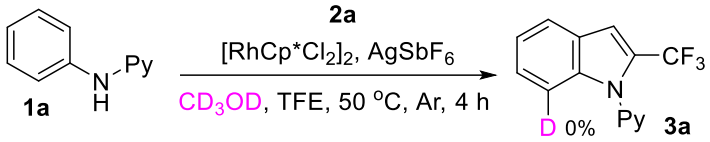
1. Studies on the reversibility of C−H bond activation



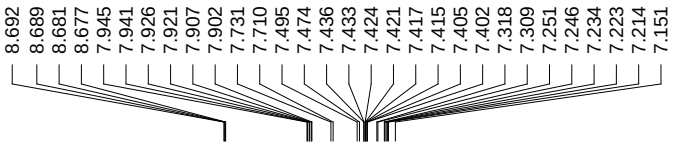
To a reaction tube equipped with a stir bar were added **1a** (34.0 mg, 0.2 mmol), $[RhCp^*Cl_2]_2$ (4.9 mg, 0.008 mmol), $AgSbF_6$ (13.7 mg, 0.04 mmol), TFE (2 mL) and CD_3OD (0.16 mL, 4 mmol). The tube was then sealed, and the mixture was stirred at 50 °C (oil bath) under argon for 1 h. It was then cooled to room temperature, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (3:1) as eluent to afford **1a** and **1a**-d_2. Upon analyzing the ^{1}H NMR spectrum of the product, the deuteration percentage at the *ortho*-site of the phenyl ring was determined as 10%. This result indicates that *ortho*-C−H bond cleavage has occurred.

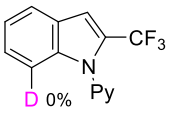






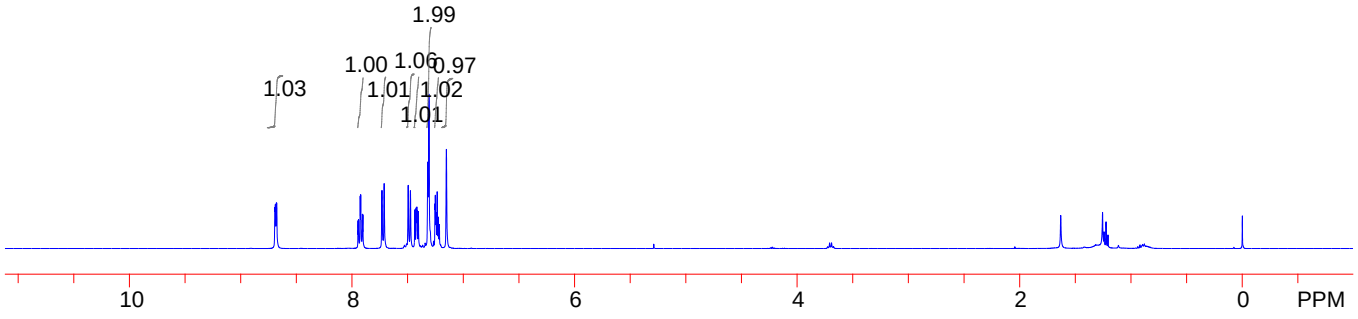
To a reaction tube equipped with a stir bar were added **1a** (34.0 mg, 0.2 mmol), $[RhCp^*Cl_2]_2$ (4.9 mg, 0.008 mmol), $AgSbF_6$ (13.7 mg, 0.04 mmol), **2a** (79.0 mg, 0.3 mmol), TFE (2 mL) and CD_3OD (0.16 mL, 4 mmol). The tube was then sealed, and the mixture was stirred at 50 °C (oil bath) under argon for 4 h. It was then cooled to room temperature, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/dichloromethane (5:1) as eluent to afford **3a**. Upon analyzing the ^1H NMR spectrum of the product, no deuteration onto the remaining (unreacted) *ortho*-position of the phenyl ring was found. This result shows that the C−H bond breaking process should be irreversible in the presence of **2a**.



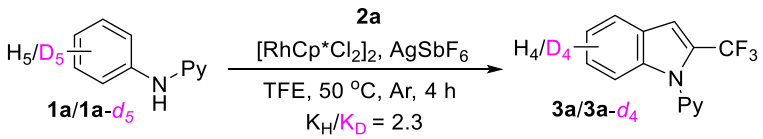


3a

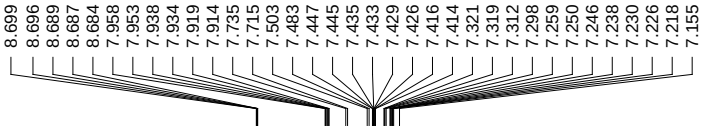
^1H NMR (400 MHz, $CDCl_3$)

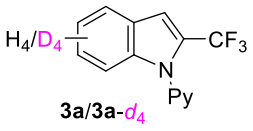


2. Kinetic isotope effect study

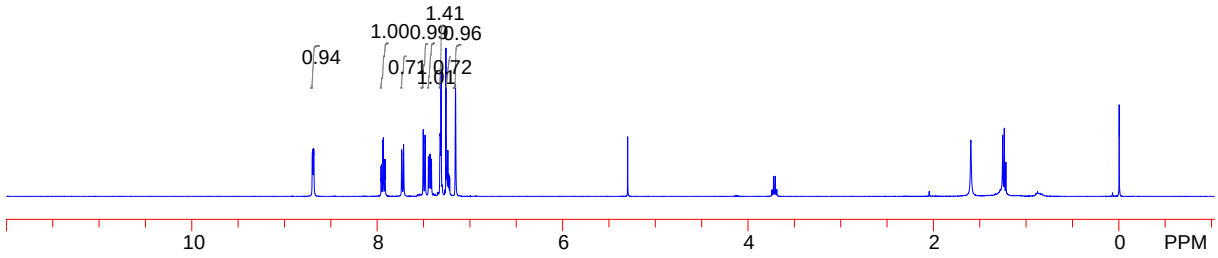


To a reaction tube equipped with a stir bar were added **1a** (34.0 mg, 0.2 mmol), **1a**-d_5 (35.0 mg, 0.2 mmol), $[RhCp^*Cl_2]_2$ (4.9 mg, 0.008 mmol), $AgSbF_6$ (13.7 mg, 0.04 mmol), **2a** (52.7 mg, 0.2 mmol) and TFE (2 mL). The tube was then sealed, and the mixture was stirred at 50 °C (oil bath) under argon for 4 h. It was then cooled to room temperature, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/dichloromethane (5:1) as eluent to afford **3a** and **3a**-d_4. Upon analyzing the ^{1}H NMR spectrum of the mixture, the ratio of **3a** to **3a**-d_4 was determined to be 0.7:0.3. Accordingly, the intermolecular KIE value (k_H/k_D) was calculated to be about 2.3. This result shows that the *ortho* C−H bond cleavage process is likely involved in the turnover-determining step

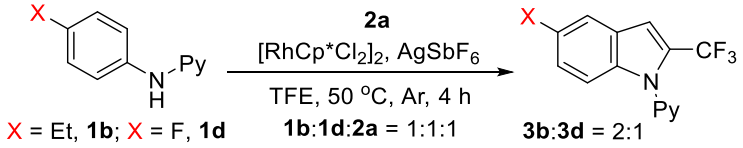




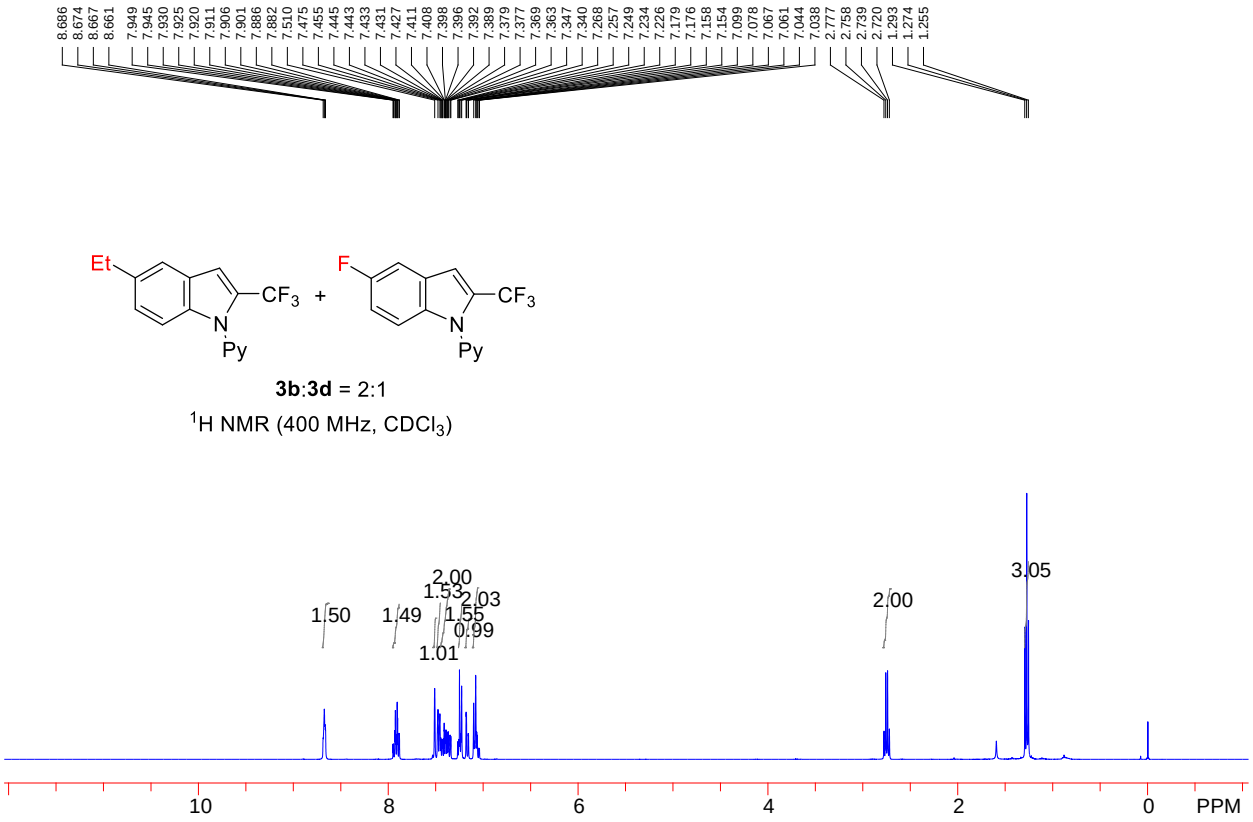
^{1}H NMR (400 MHz, $CDCl_3$)



3. Competing experiments between 1b and 1d



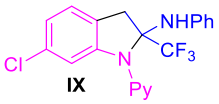
To a reaction tube equipped with a stir bar were added with *N*-(4-ethylphenyl)pyridin-2-amine (**1b**, 39.7 mg, 0.2 mmol), *N*-(4-fluorophenyl)pyridin-2-amine (**1d**, 37.6 mg, 0.2 mmol), **2a** (52.7 mg, 0.2 mmol), $[RhCp^*Cl_2]_2$ (4.9 mg, 0.008 mmol), $AgSbF_6$ (13.7 mg, 0.04 mmol) and TFE (2 mL). The tube was then sealed and the mixture was stirred 50 °C (oil bath) under argon for 4 h. Afterwards, it was cooled to room temperature and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/dichloromethane (5:1) as eluent to afford a mixture of **3b** and **3d**. Upon analyzing the ^1H NMR spectrum of the mixture, the ratio of **3b** to **3d** was determined to be about 2:1. This result shows that the presence of an electron-donating group facilitates this reaction obviously, indicating that the C−H cleavage step might occur *via* an electrophilic aromatic substitution (SEAr) process.



4. Control Experiments

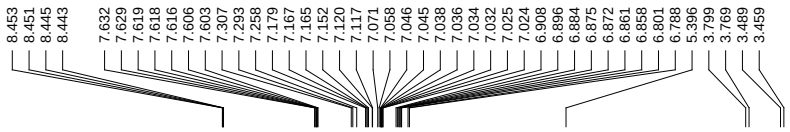
4.1. To a reaction tube equipped with a stir bar were added **1h** (40.9 mg, 0.2 mmol), **2a** (79.0 mg, 0.3 mmol), $[RhCp^*Cl_2]_2$ (4.9 mg, 0.008 mmol), $AgSbF_6$ (13.7 mg, 0.04 mmol) and TFE (2 mL). The tube was then sealed, and the mixture was stirred at 50 °C (oil bath) under argon for 6 h. The resulting mixture was then cooled to room temperature, filtered and concentrated under reduced pressure. The residue was purified by silica gel

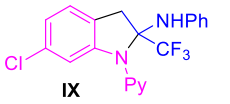
column chromatography using petroleum ether/dichloromethane (3:1) as eluent to afford **IX**.



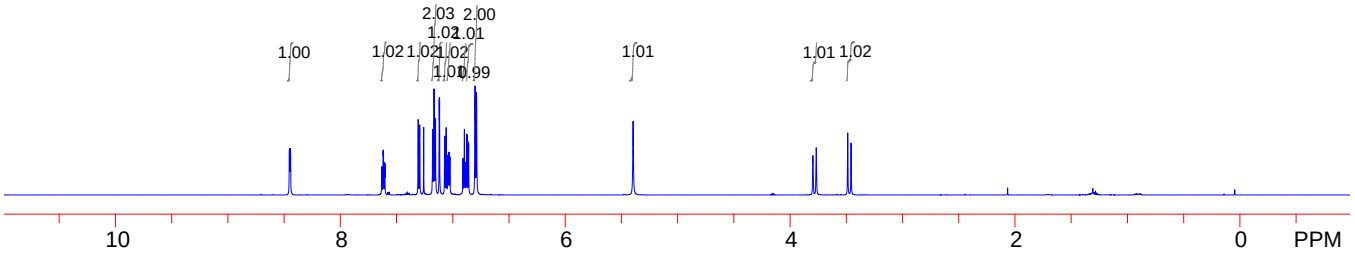
6-Chloro-*N*-phenyl-1-(pyridin-2-yl)-2-(trifluoromethyl)indolin-2-amine (IX)

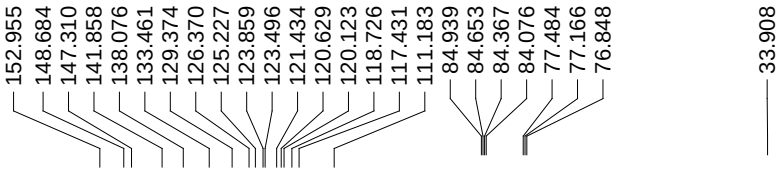
Eluent: petroleum ether/dichloromethane (3:1). Colorless oil (39.7 mg, 51%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.45 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H), 7.63-7.60 (m, 1H), 7.30 (d, J = 8.4 Hz, 1H), 7.18-7.15 (m, 2H), 7.12 (d, J = 1.8 Hz, 1H), 7.06 (d, J = 7.8 Hz, 1H), 7.05-7.02 (m, 1H), 6.90 (t, J = 7.2 Hz, 1H), 6.87 (dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 1H), 6.79 (d, J = 7.8 Hz, 2H), 5.40 (s, 1H), 3.78 (d, J = 18.0 Hz, 1H), 3.47 (d, J = 18.0 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 153.0, 148.7, 147.3, 141.9, 138.1, 133.5, 129.4, 125.2, 124.9 (q, $^{1}J_{C\text{-}F}$ = 287.4 Hz), 123.9, 121.4, 120.6, 120.1, 118.7, 117.4, 111.2, 84.5 (q, $^{2}J_{C\text{-}F}$ = 28.6 Hz), 33.9. ^{19}F NMR (376 MHz, $CDCl_3$): δ -80.54 (s). HRMS (ESI) *m/z*: $[M\text{-}PhNH_2+H]^+$ Calcd for $C_{14}H_9ClF_3N_2$ 297.0401; Found 297.0400.

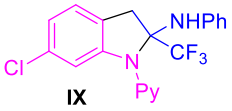




^{1}H NMR (600 MHz, $CDCl_3$)

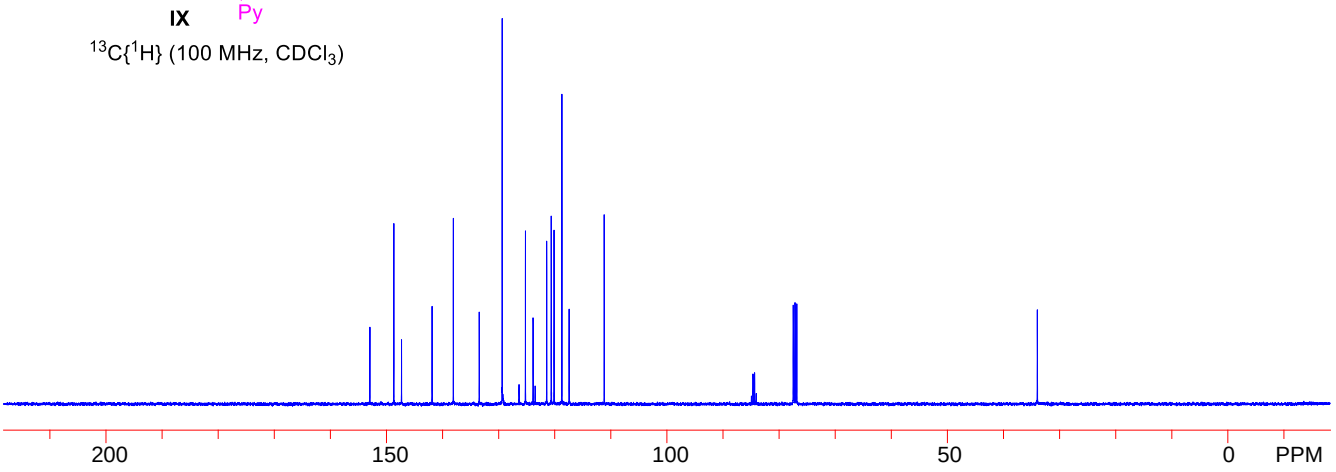


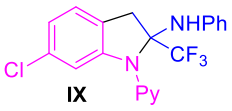




IX

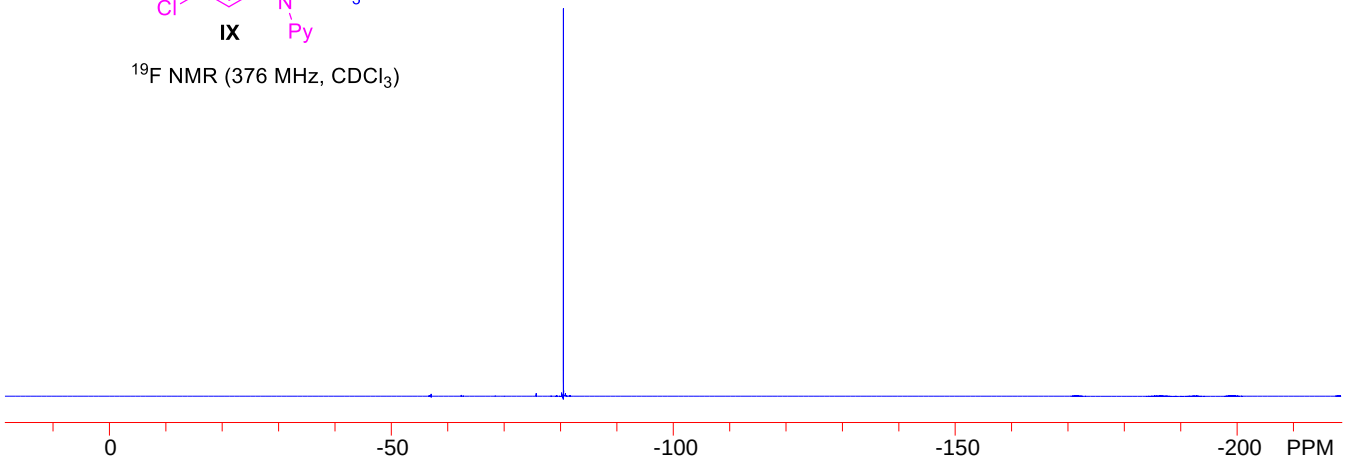
$^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$)





IX

^{19}F NMR (376 MHz, $CDCl_3$)

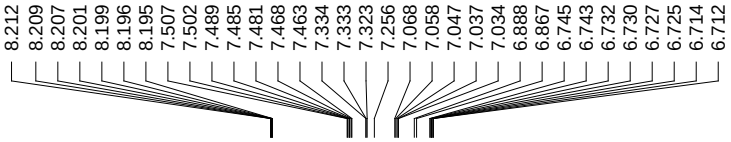


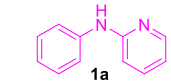
4.2. To a reaction tube equipped with a stir bar were added **IX** (39.0 mg, 0.1 mmol), $[RhCp^*Cl_2]_2$ (2.5 mg, 0.004 mmol), $AgSbF_6$ (6.9 mg, 0.02 mmol) and TFE (1 mL). The tube was then sealed, and the mixture was stirred at 50 °C (oil bath) under argon for 5 h. The resulting mixture was then cooled to room temperature, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/dichloromethane (3:1) as eluent to afford **3h** (18.7 mg, 63%).

To a reaction tube equipped with a stir bar were added **IX** (39.0 mg, 0.1 mmol), $AgSbF_6$ (6.9 mg, 0.02 mmol) and TFE (1 mL). The tube was then sealed, and the mixture was stirred at 50 °C (oil bath) under argon for 5 h. The resulting mixture was then cooled to room temperature, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/dichloromethane (3:1) as eluent to afford **3h** (23.1 mg, 78%).

To a reaction tube equipped with a stir bar were added **IX** (39.0 mg, 0.1 mmol), $AgSbF_6$ (6.9 mg, 0.02 mmol), $Cu(OAc)_2$ (9.1 mg, 0.05 mmol), TFE (0.75 mL) and EtOH (0.25 mL). The tube was then sealed, and the mixture was stirred at 50 °C (oil bath) under oxygen for 5 h. The resulting mixture was then cooled to room temperature, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/dichloromethane (3:1) as eluent to afford **3h** (10.1 mg, 34%). Meanwhile, the formation of **4h** was not observed.

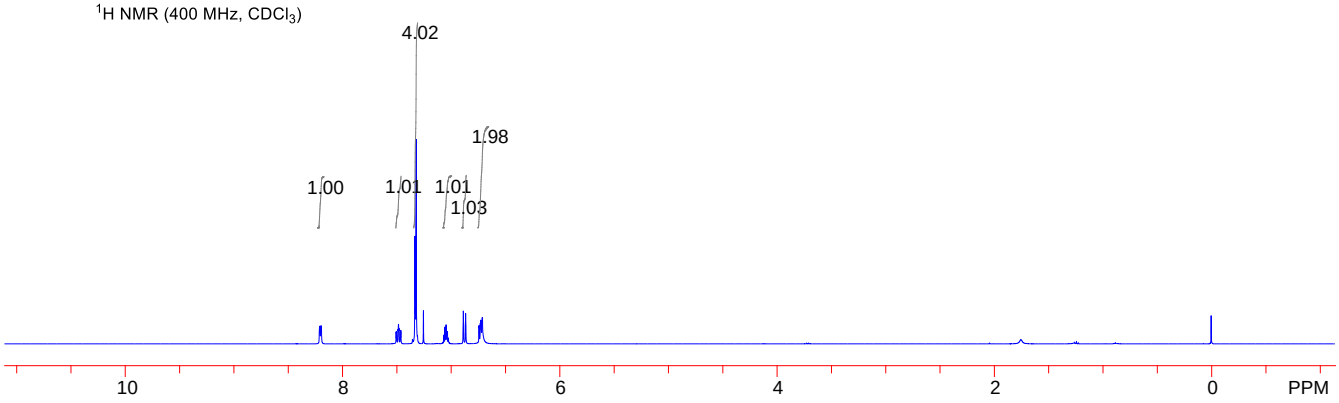
IV. Copies of NMR spectra of 1a and 2r

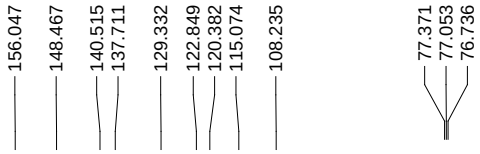


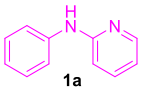


1a

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

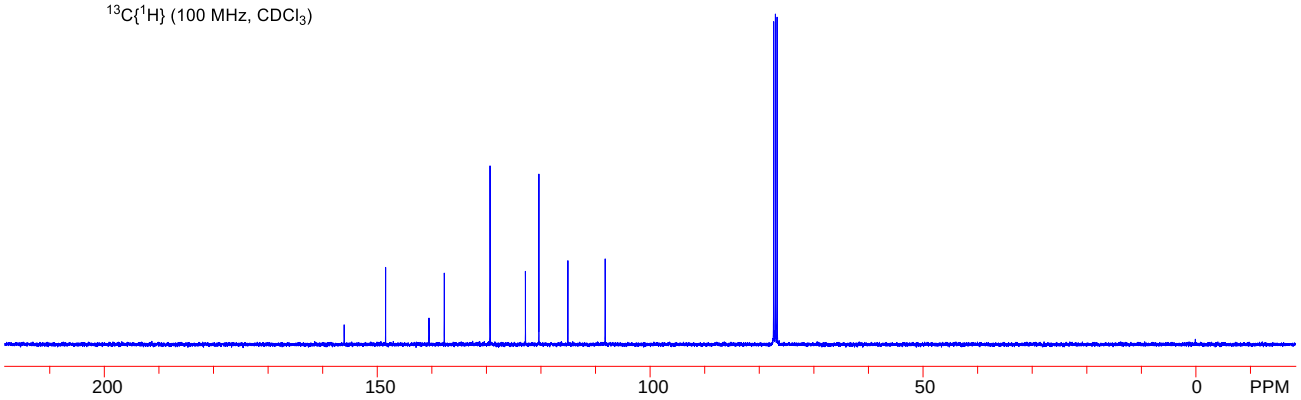


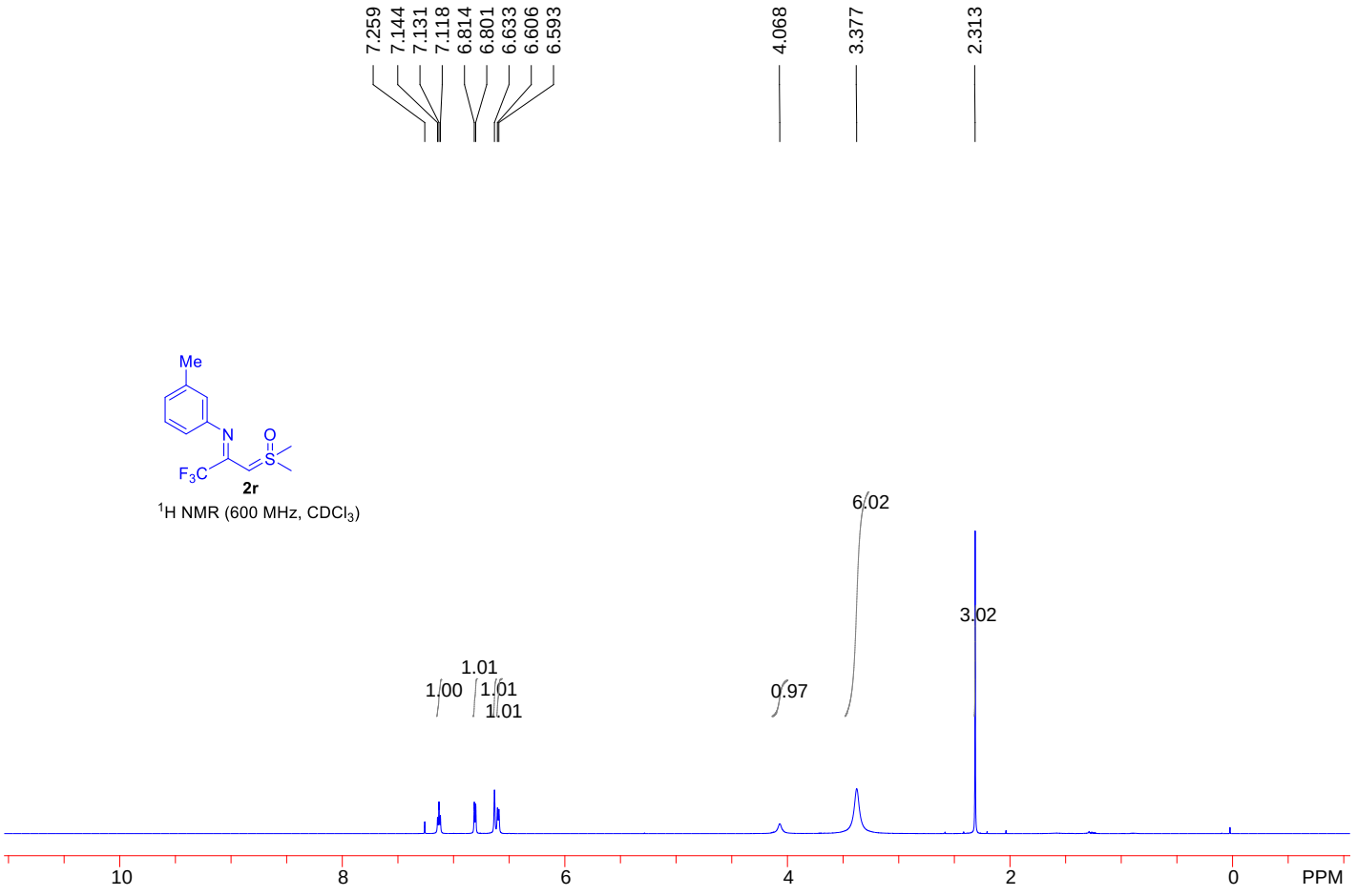


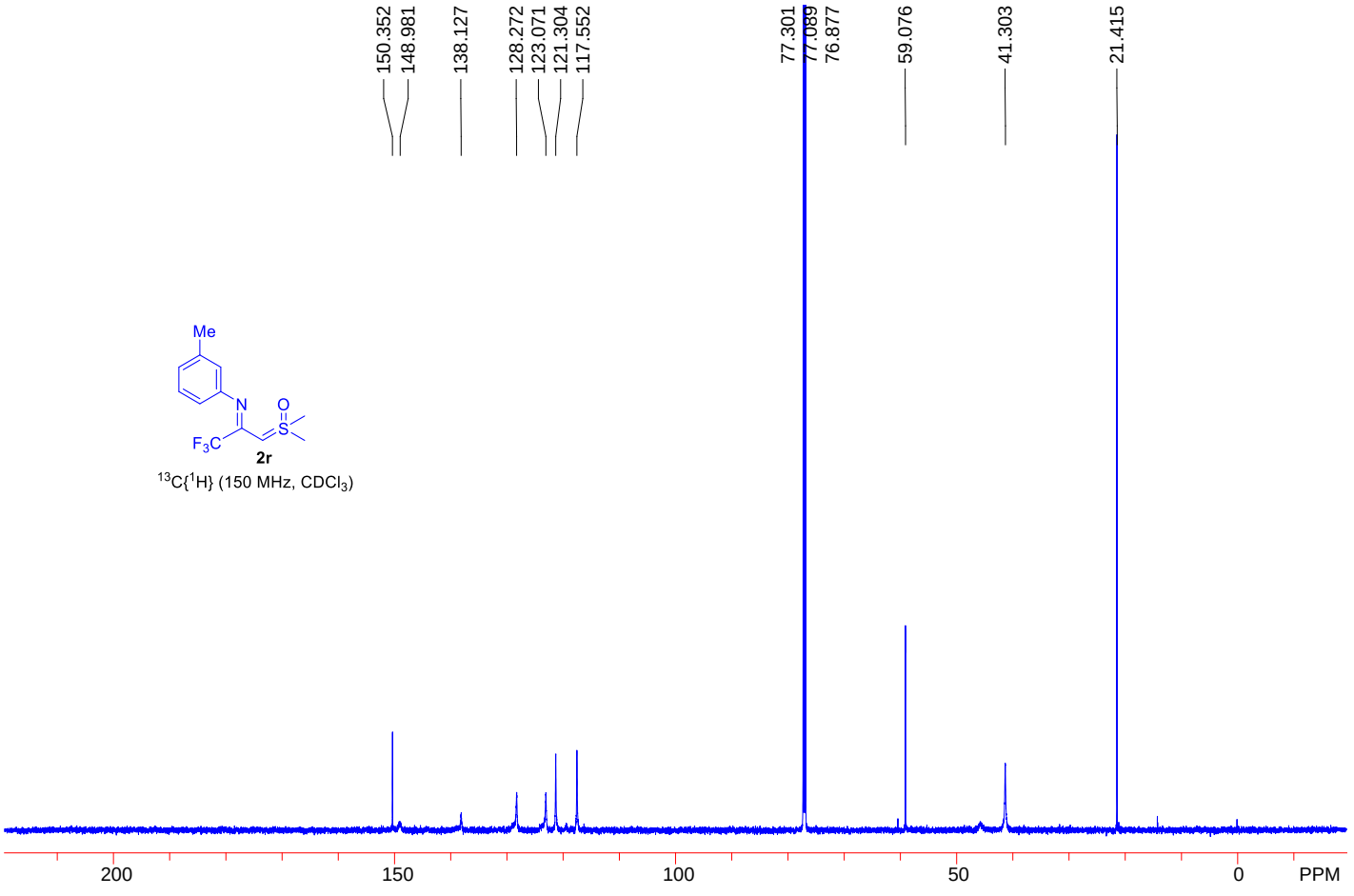


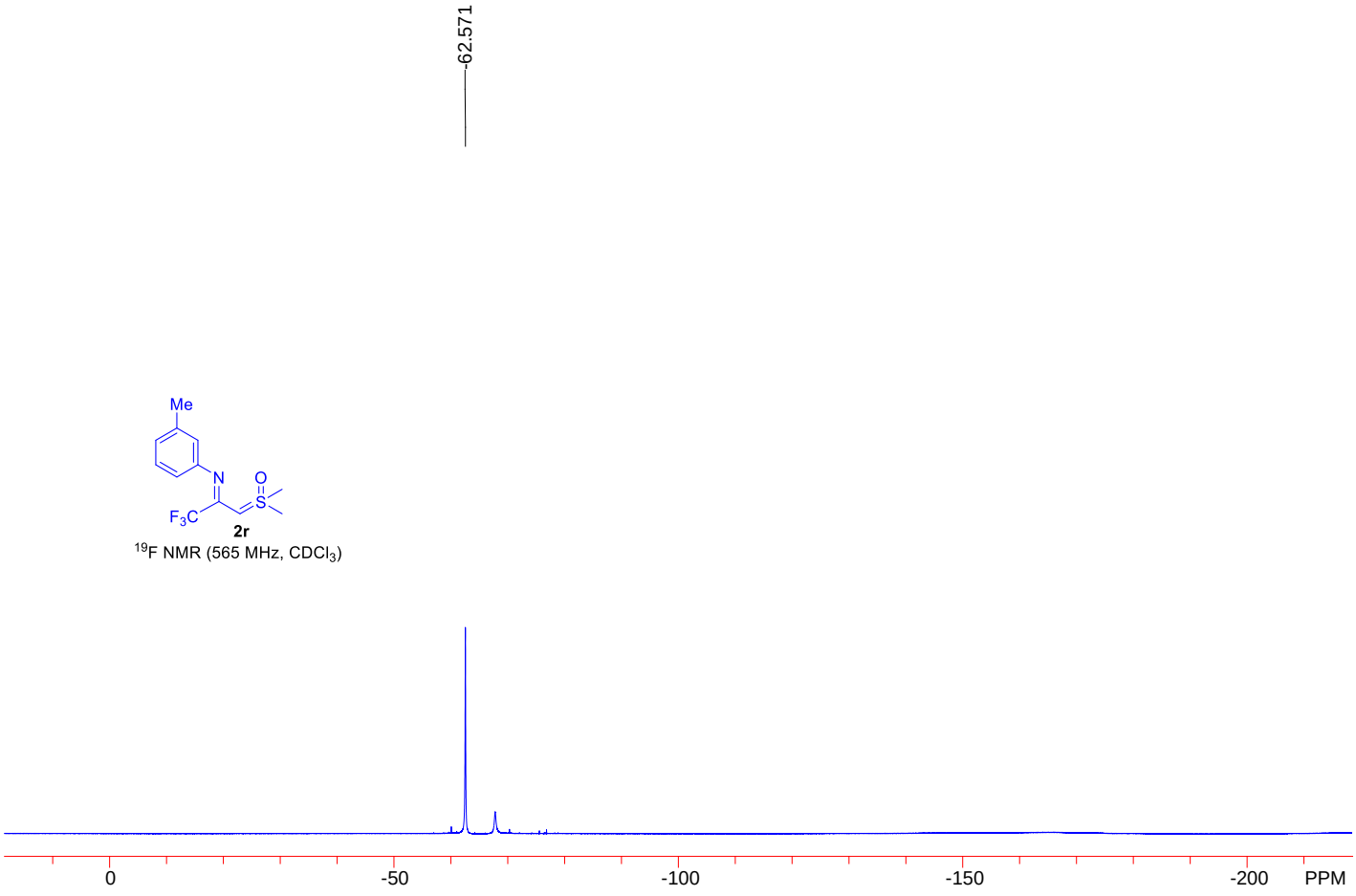
1a

$^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$)

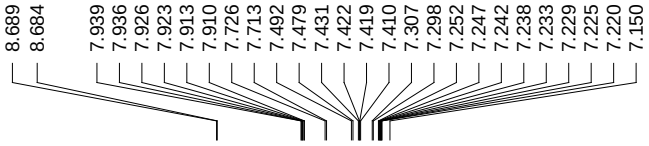


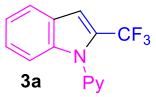

7.259
7.144
7.131
7.118
6.814
6.801
6.633
6.606
6.593
4.068
3.377
2.313
Me
N
O
S
F3C
2r
1H NMR (600 MHz, CDCl3)
6.02
3.02
1.01
1.00
1.01
1.01
0.97
10
8
6
4
2
0
PPM


150.352
148.981
138.127
128.272
123.071
121.304
117.552
77.301
77.089
76.877
59.076
41.303
21.415
Me
N
O
S
F3C
2r
13C{1H} (150 MHz, CDCl3)
200
150
100
50
0
PPM

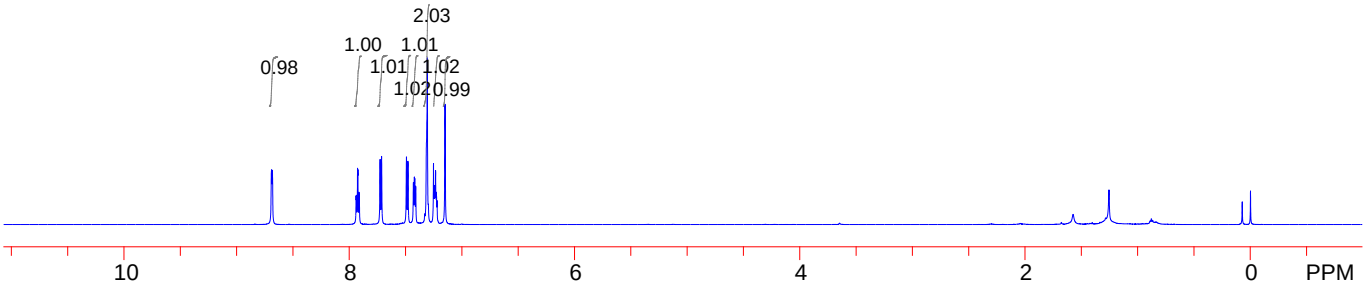

-62.571
Me
N
O
S
F3C
2r
19F NMR (565 MHz, CDCl3)
0
-50
-100
-150
-200
PPM

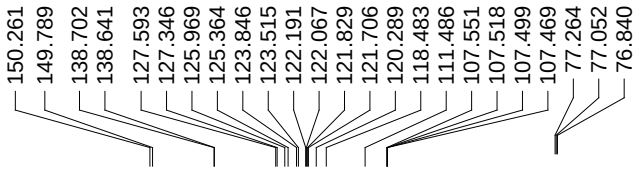
V. Copies of NMR spectra of 3a-3q

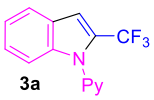




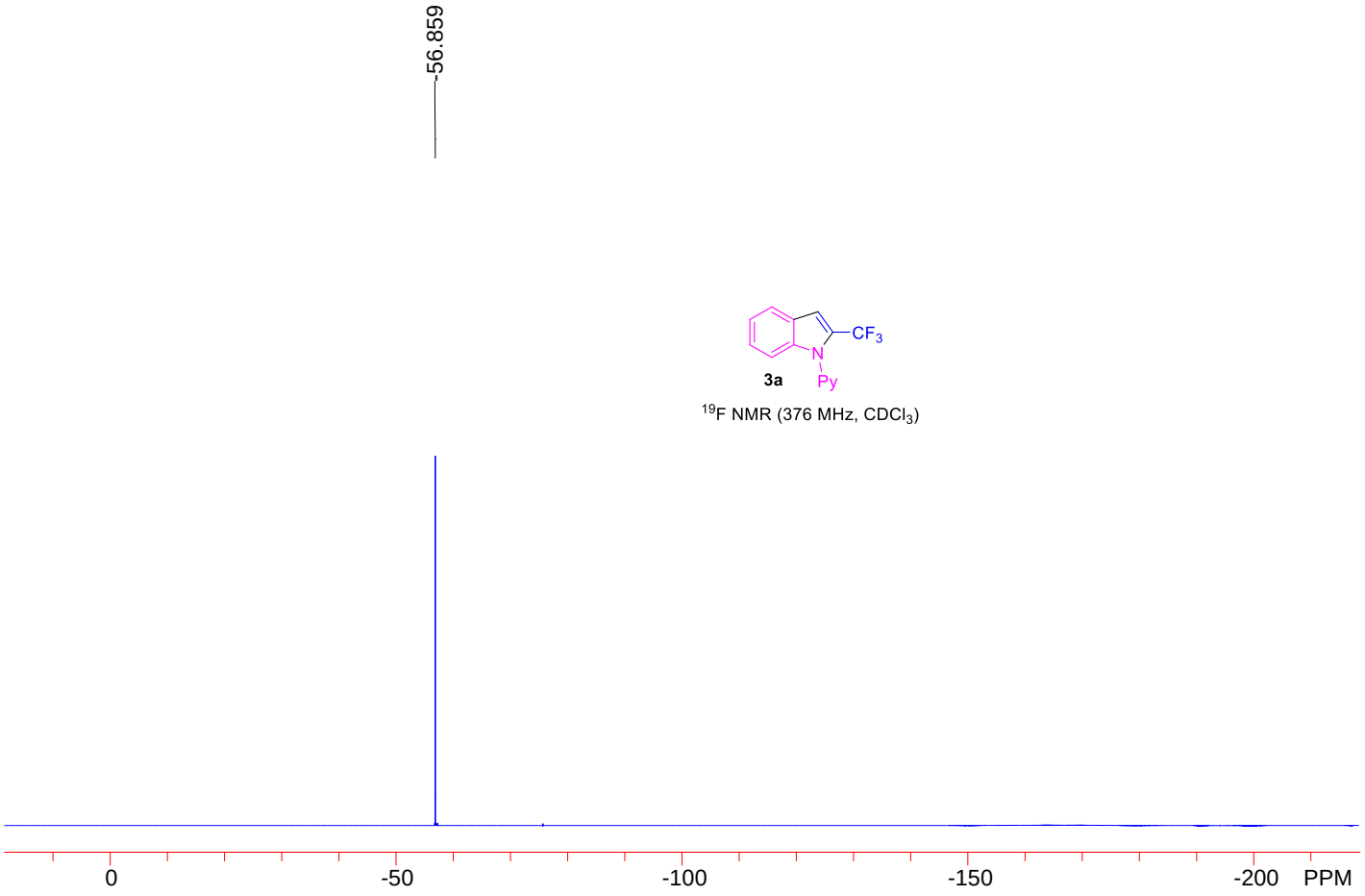
^{1}H NMR (600 MHz, $CDCl_3$)

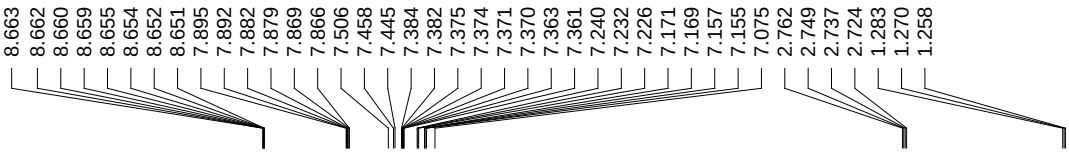


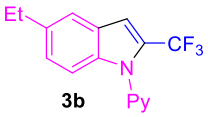




^{13}C NMR (150 MHz, $CDCl_3$)

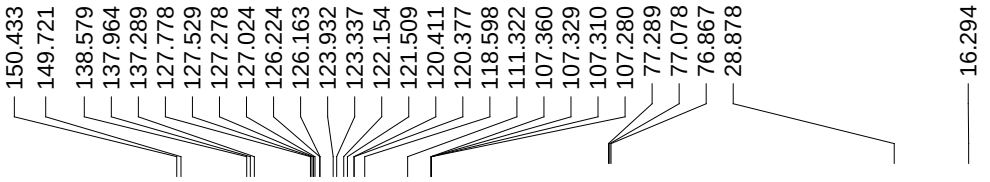

-56.859
CF3
N
Py
3a
19F NMR (376 MHz, CDCl3)
0
-50
-100
-150
-200
PPM

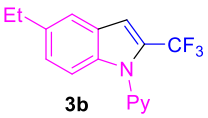




3b

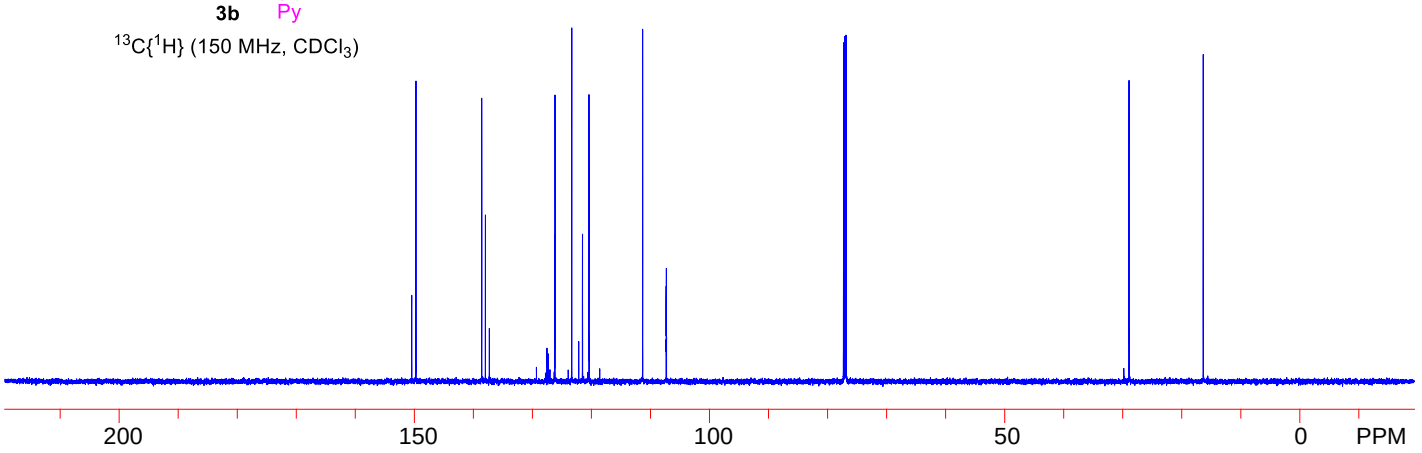
^{1}H NMR (600 MHz, $CDCl_3$)

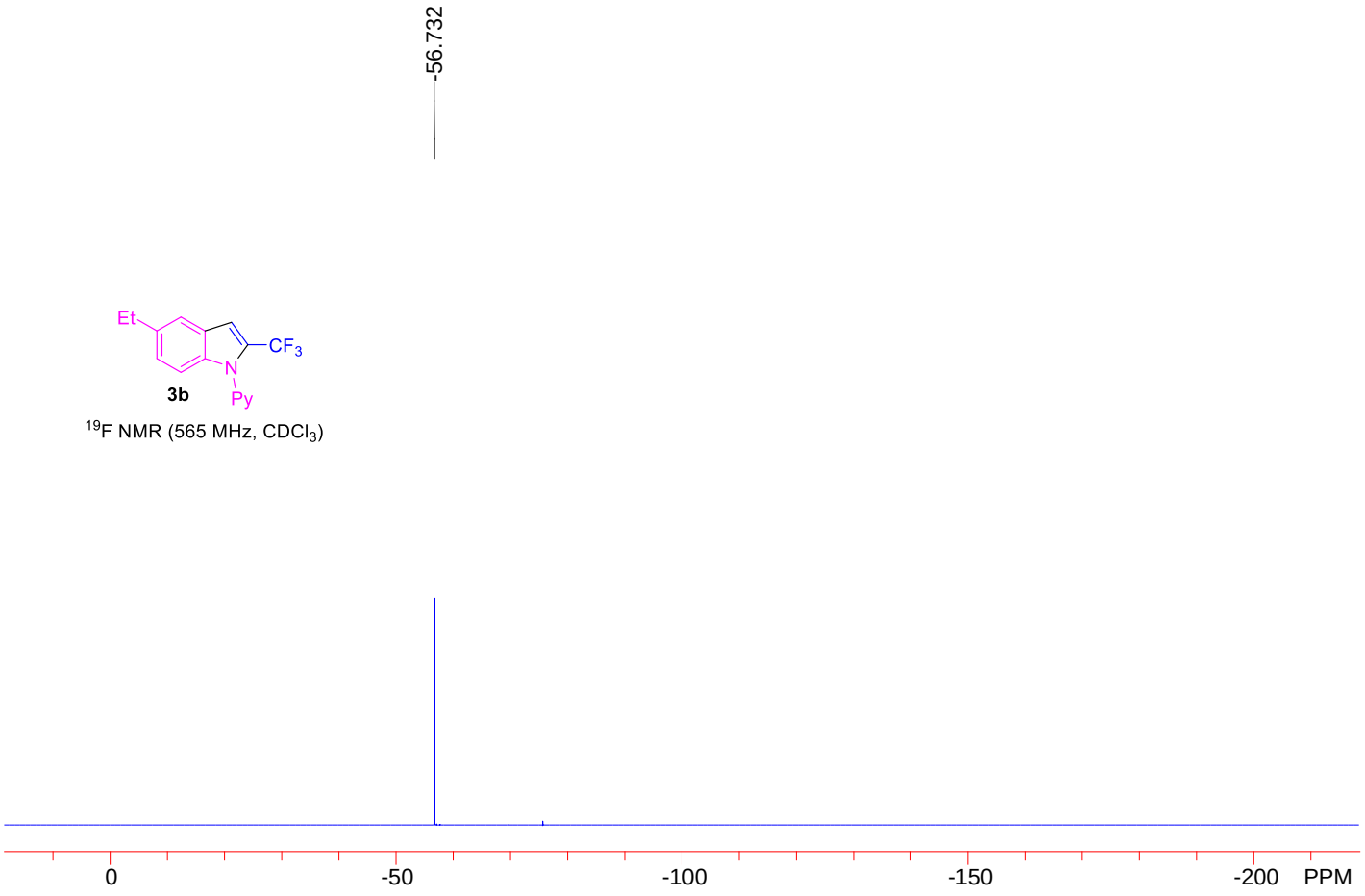


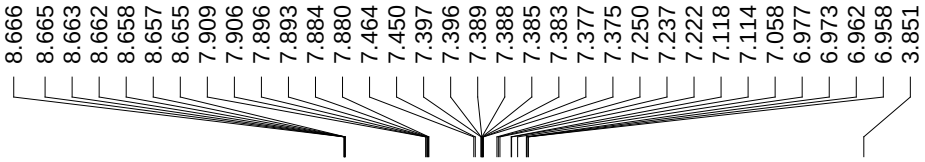


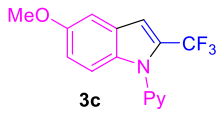
3b

$^{13}C\{^{1}H\}$ (150 MHz, $CDCl_3$)



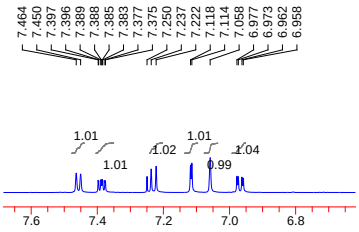

-56.732
Et
CF3
N
Py
3b
19F NMR (565 MHz, CDCl3)
0
-50
-100
-150
-200
PPM

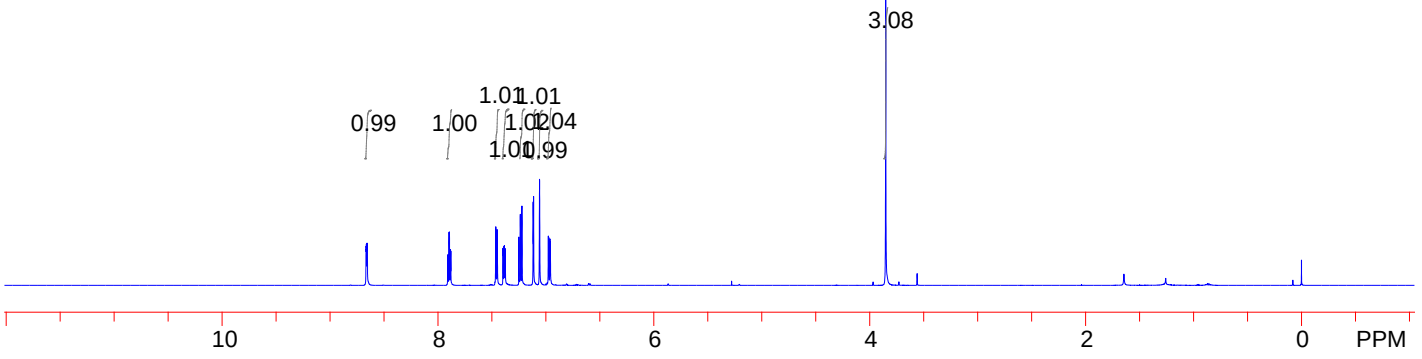


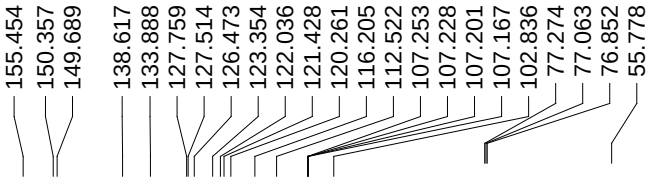


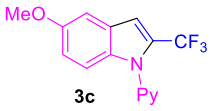
3c

^{1}H NMR (600 MHz, $CDCl_3$)



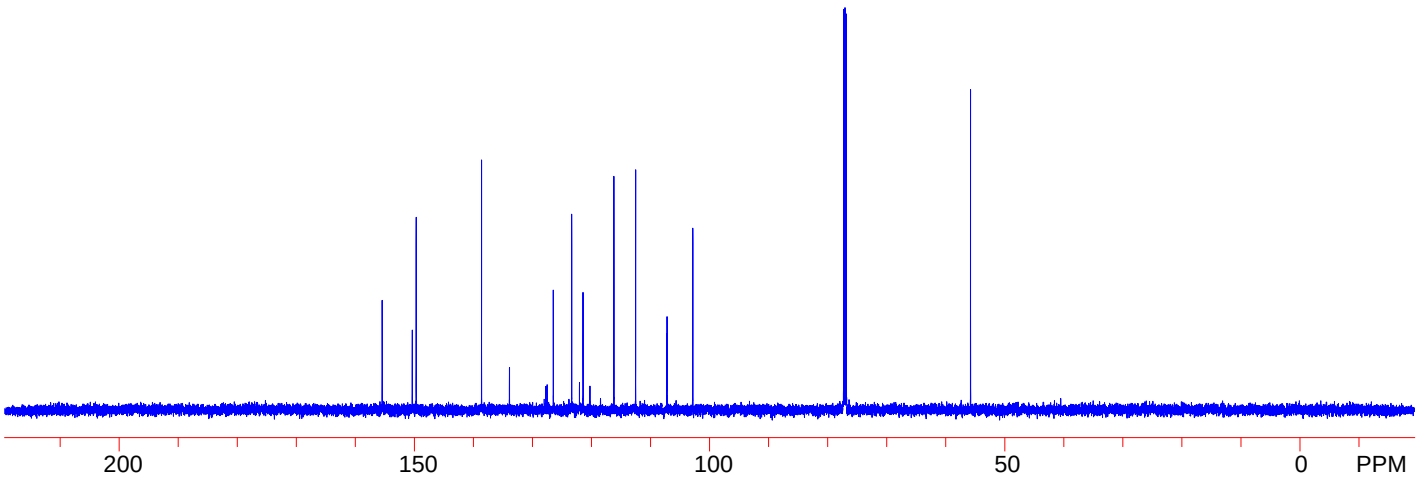


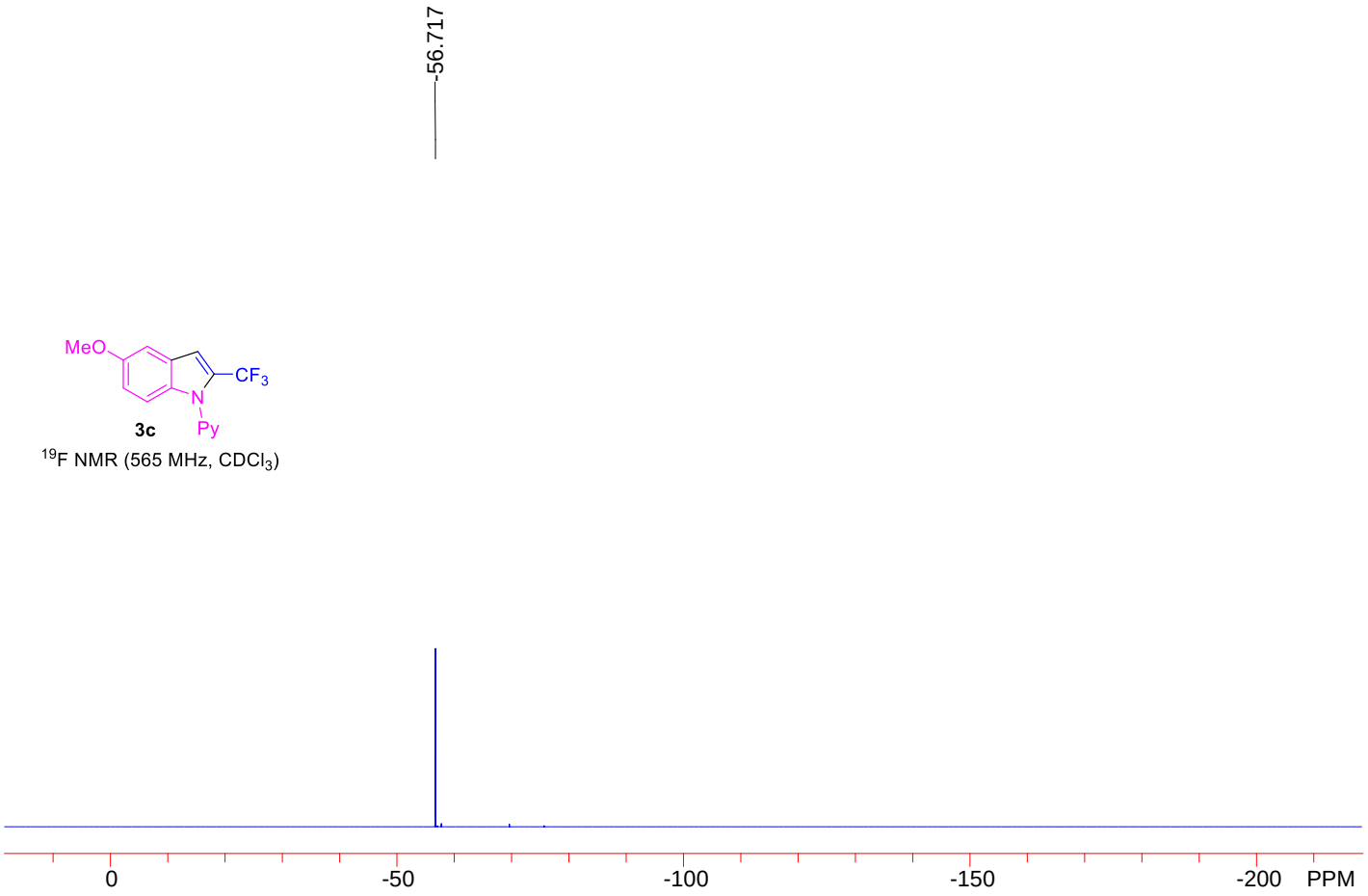




3c

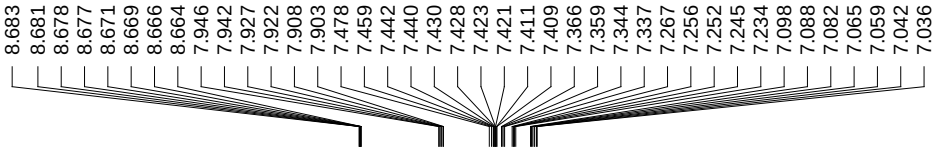
^{13}C{^{1}H} (150 MHz, $CDCl_3$)

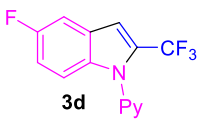




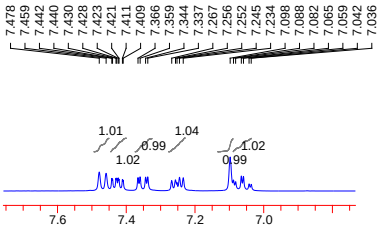
3c

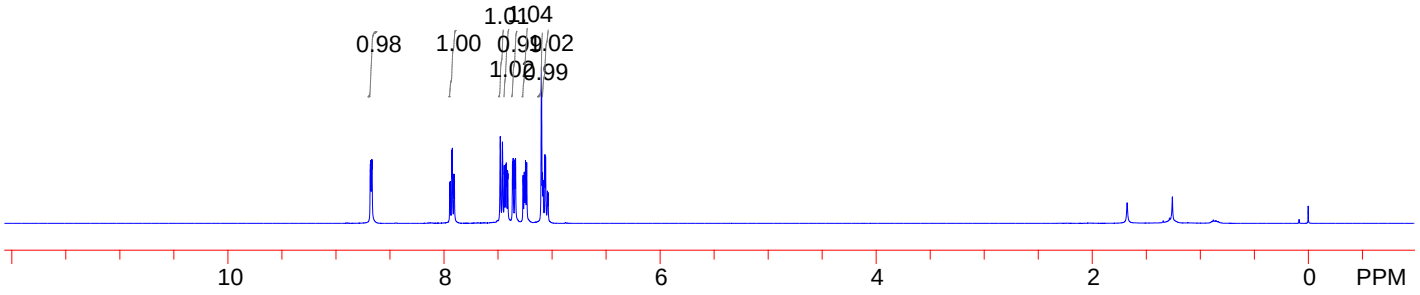
^{19}F NMR (565 MHz, $CDCl_3$)

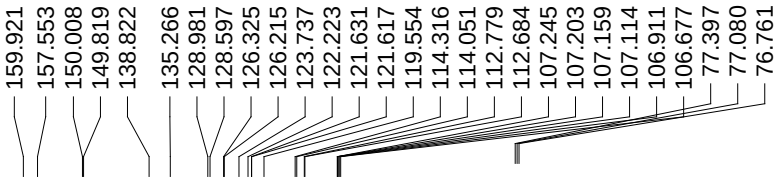


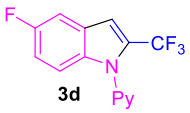


^{1}H NMR (400 MHz, $CDCl_3$)

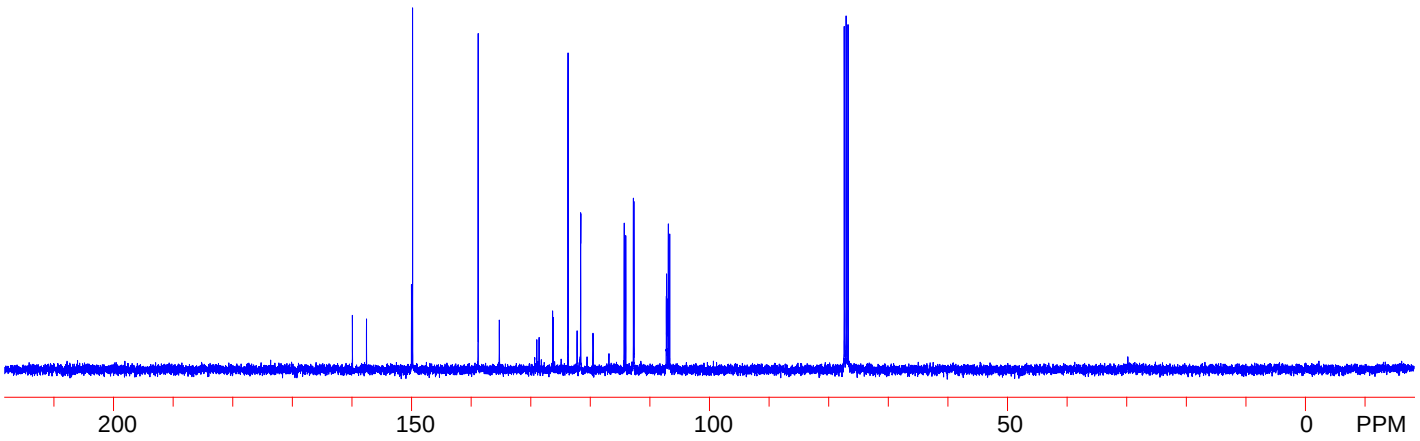


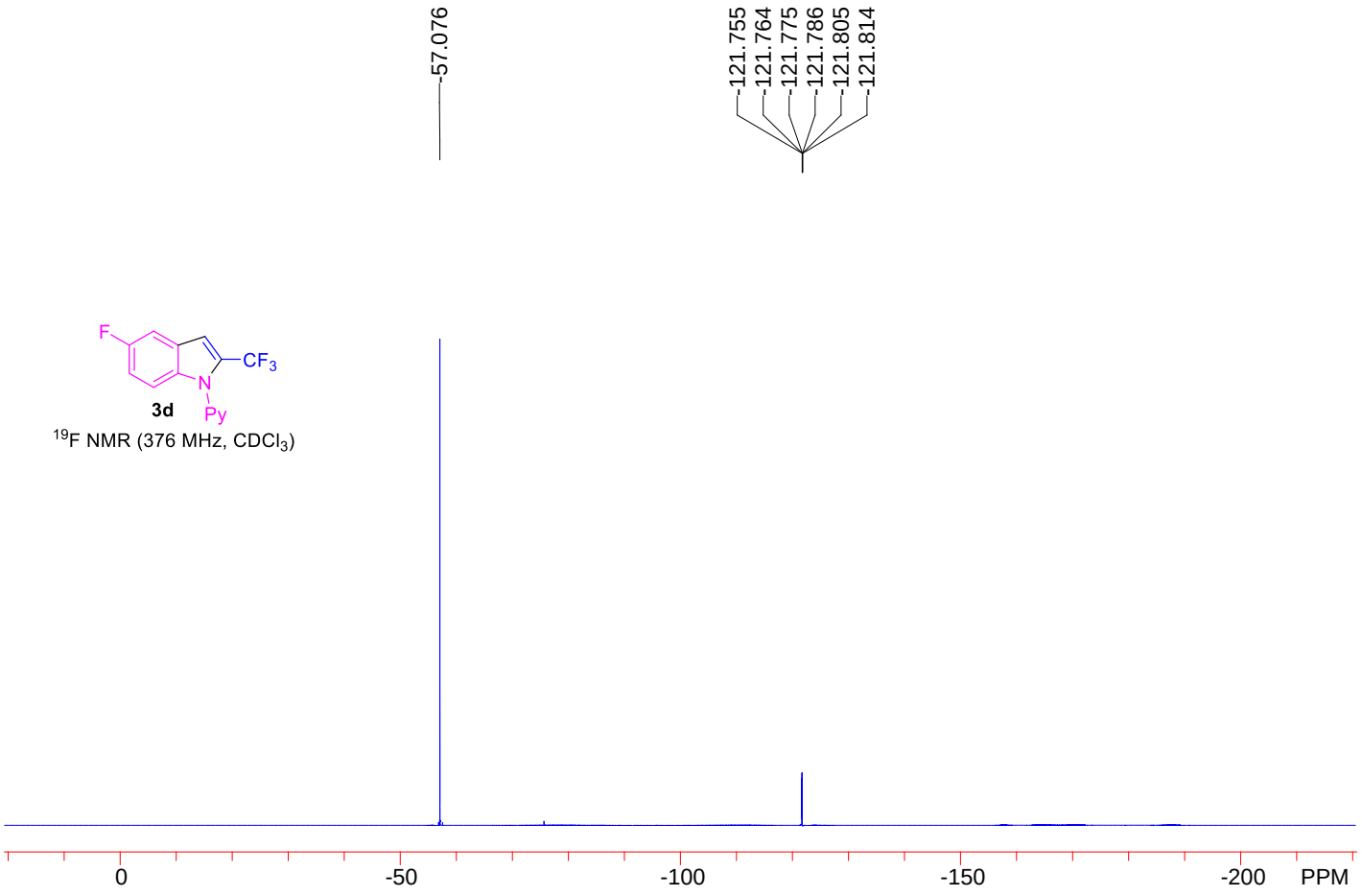


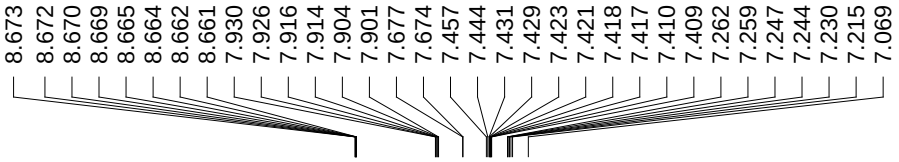


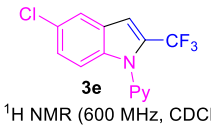


^{13}C{^{1}H} (100 MHz, $CDCl_3$)



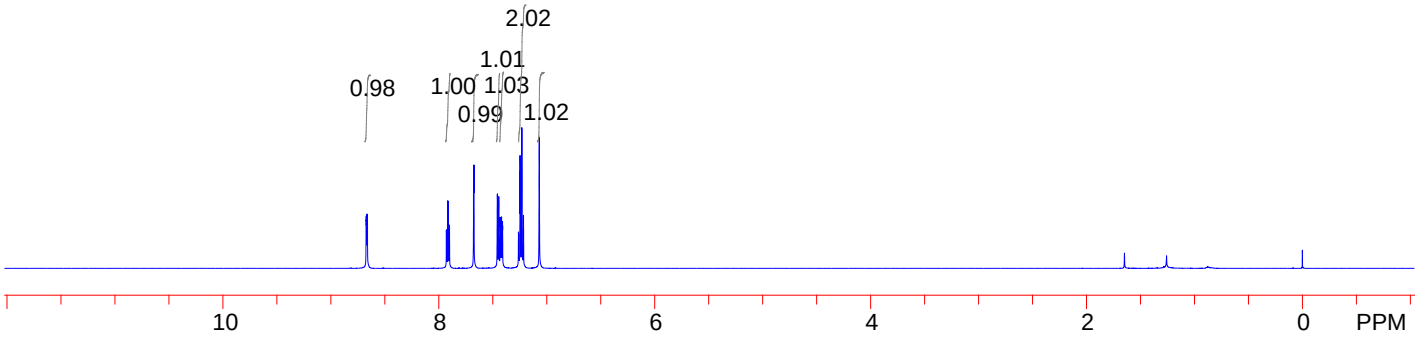

-57.076
-121.755
-121.764
-121.775
-121.786
-121.805
-121.814
F
CF3
N
Py
3d
19F NMR (376 MHz, CDCl3)
0
-50
-100
-150
-200
PPM

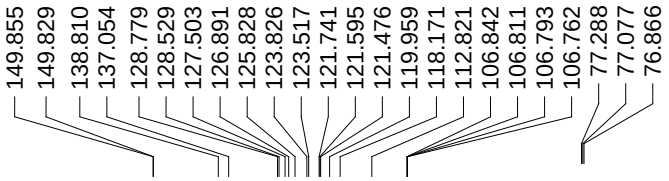


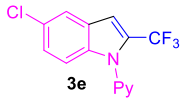


3e

^{1}H NMR (600 MHz, $CDCl_3$)

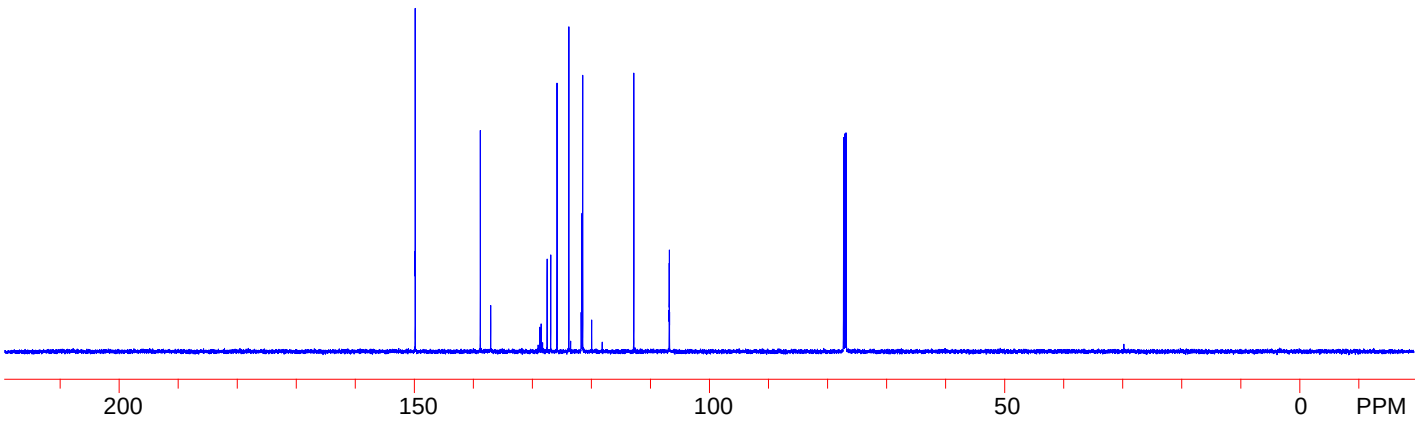


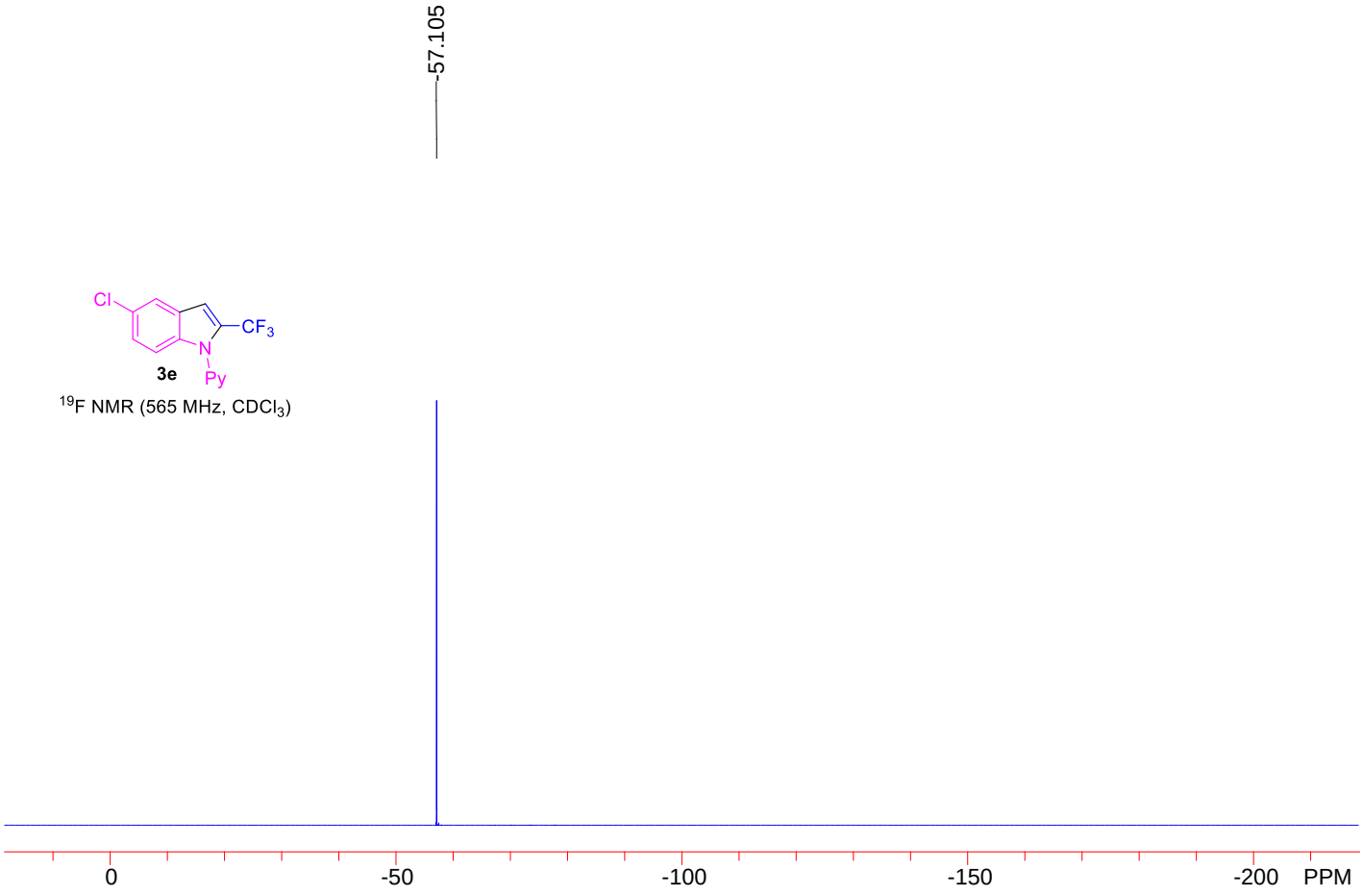


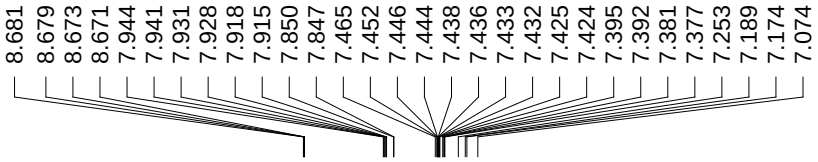


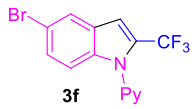
3e

$^{13}C\{^{1}H\}$ (150 MHz, $CDCl_3$)



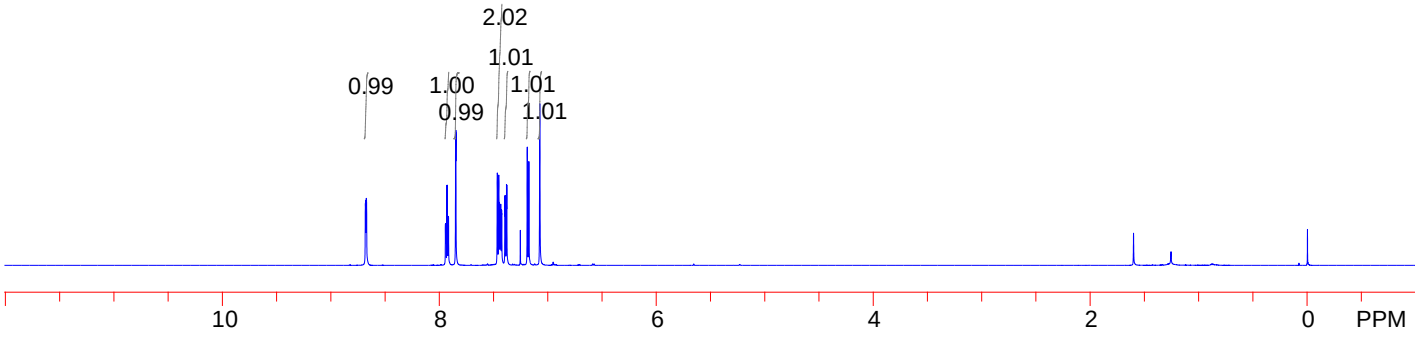

-57.105
Cl
CF3
N
Py
3e
19F NMR (565 MHz, CDCl3)
0
-50
-100
-150
-200
PPM

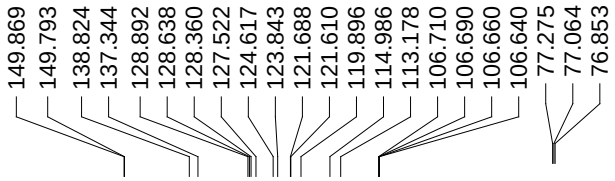


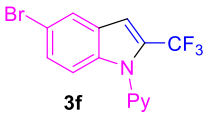


3f

^{1}H NMR (600 MHz, $CDCl_3$)

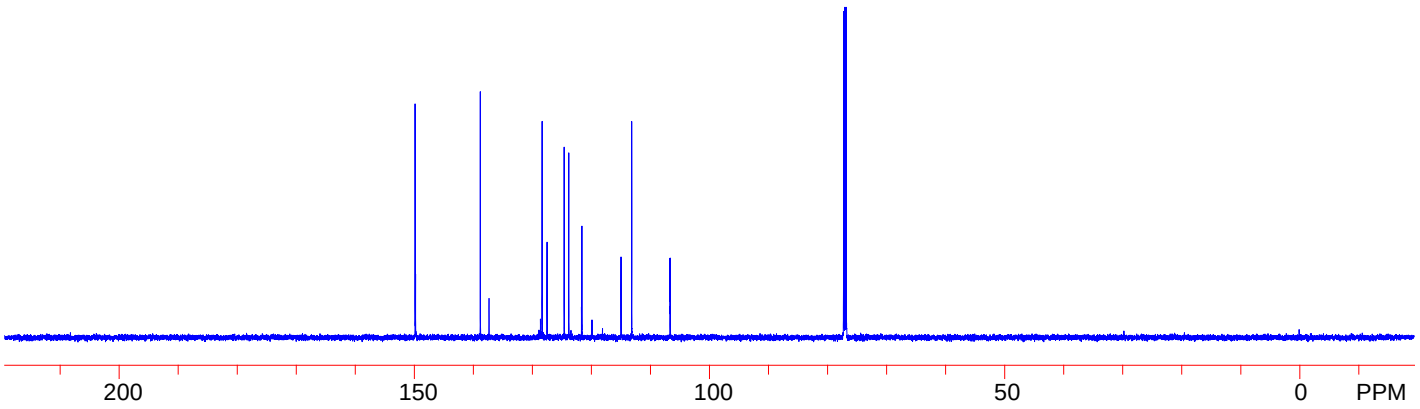


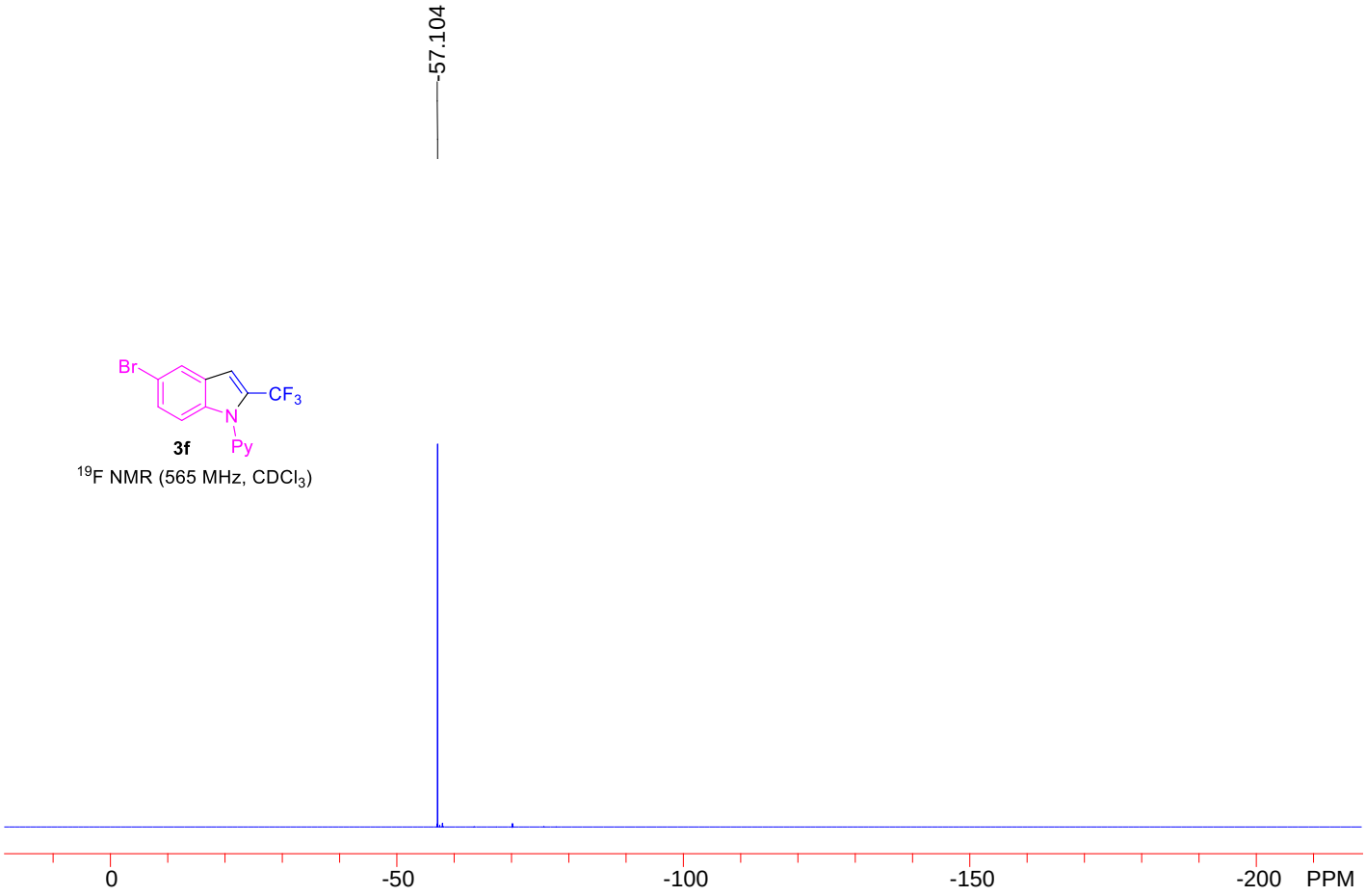


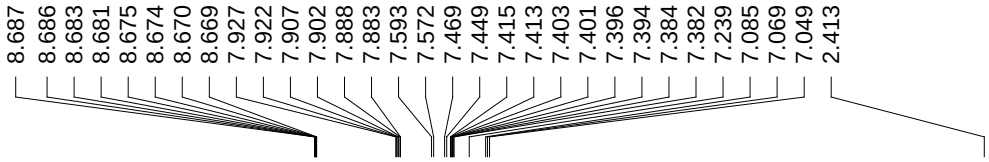


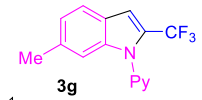
3f

^{13}C{^{1}H} (150 MHz, $CDCl_3$)



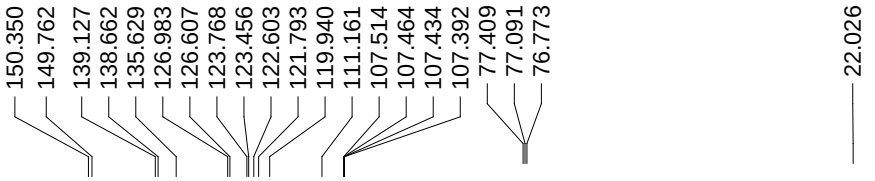

-57.104
Br
CF3
N
Py
3f
19F NMR (565 MHz, CDCl3)
0
-50
-100
-150
-200
PPM

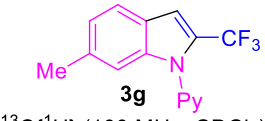




3g

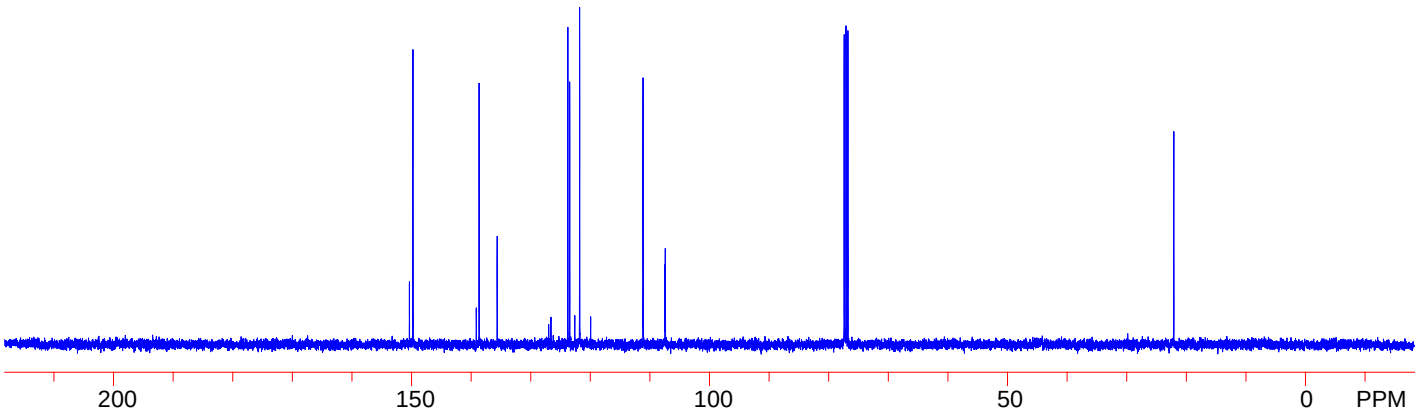
^{1}H NMR (400 MHz, $CDCl_3$)

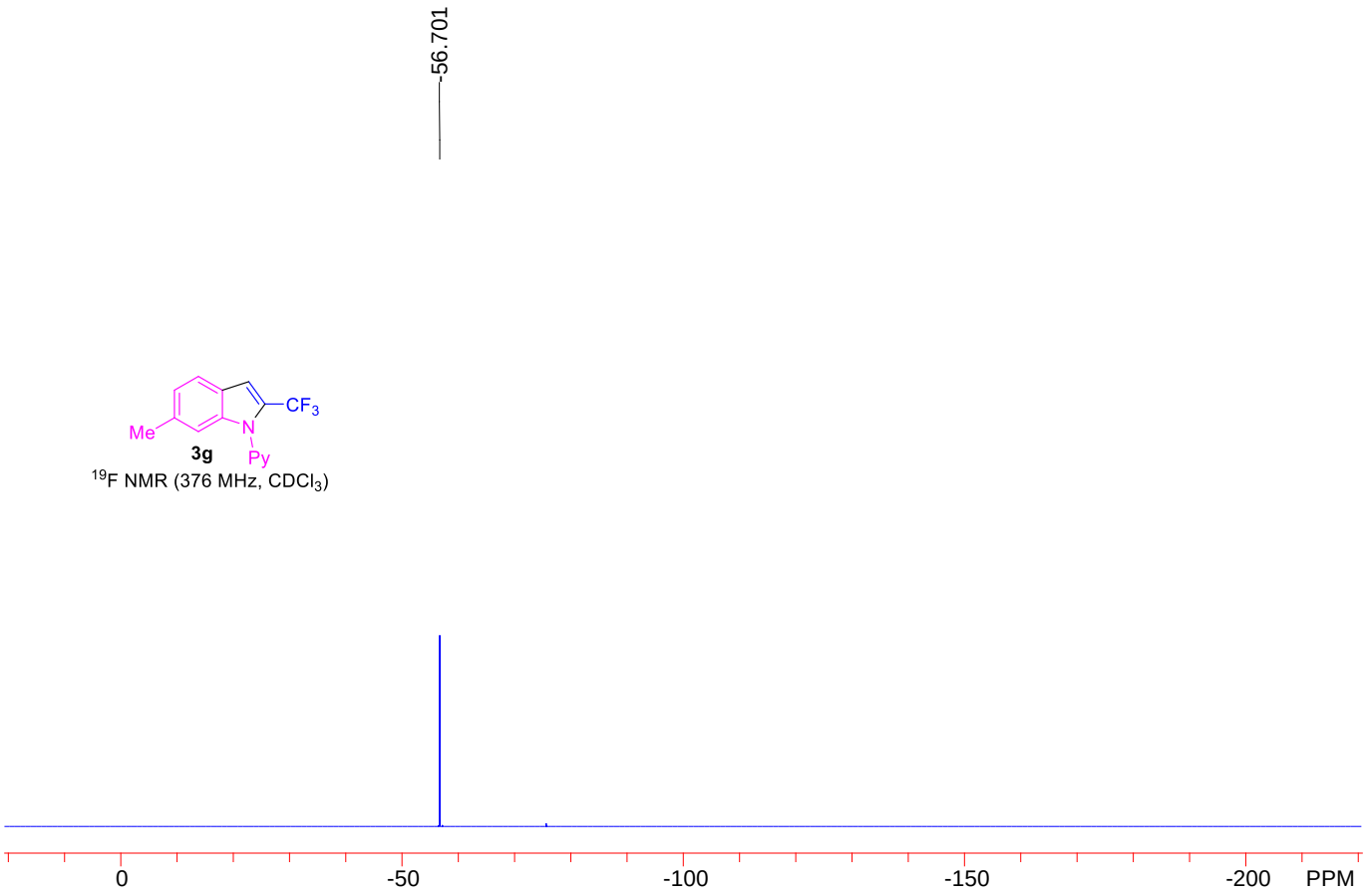




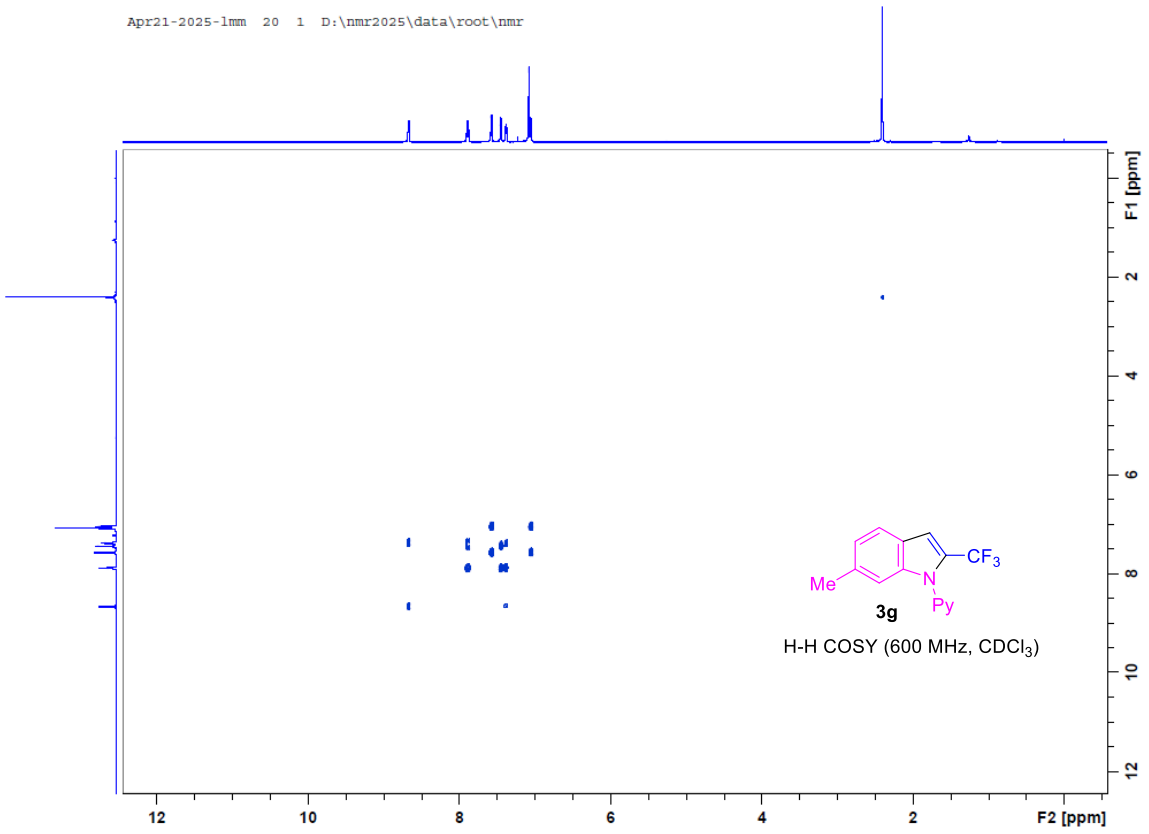
3g

$^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$)

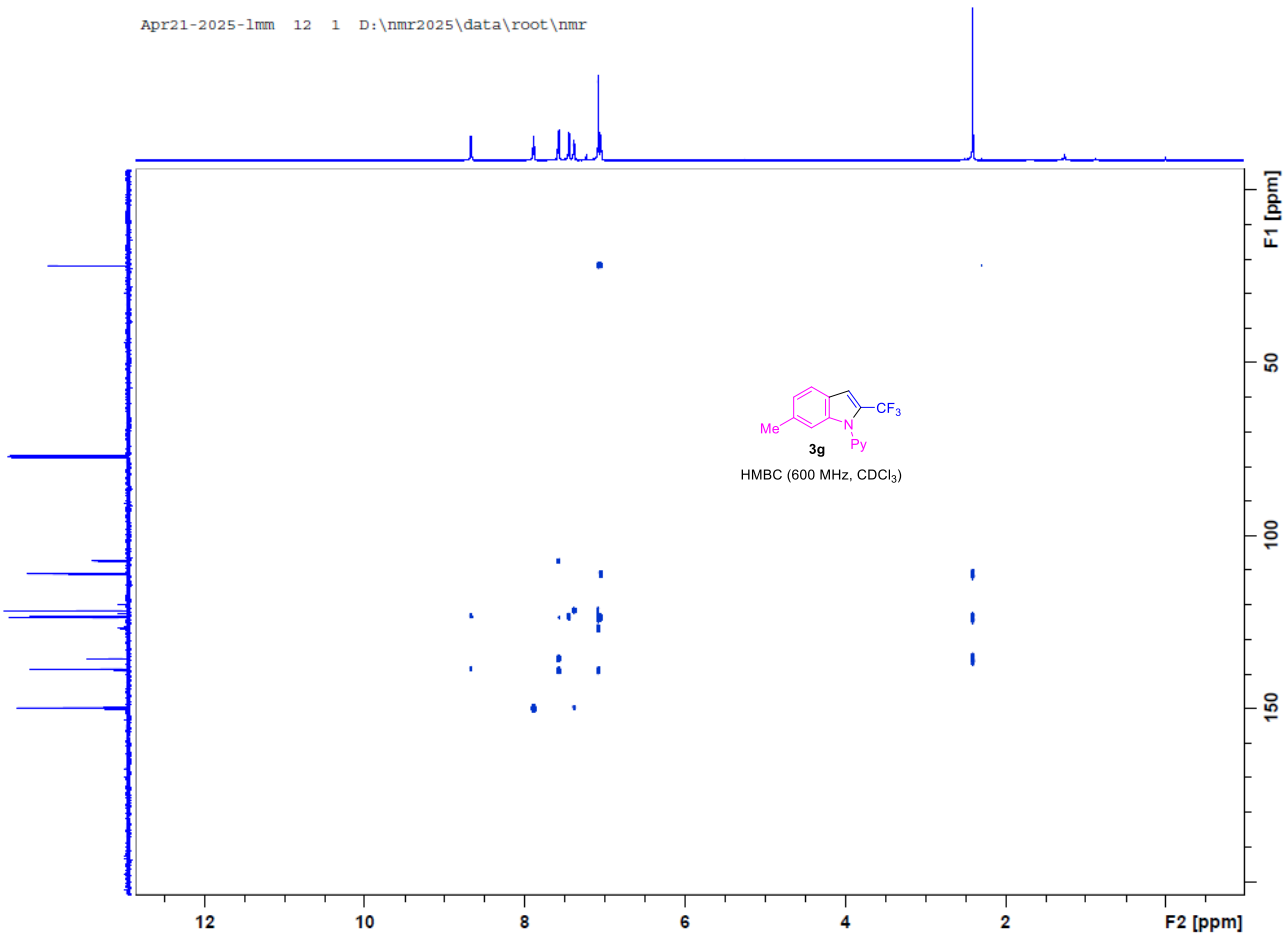




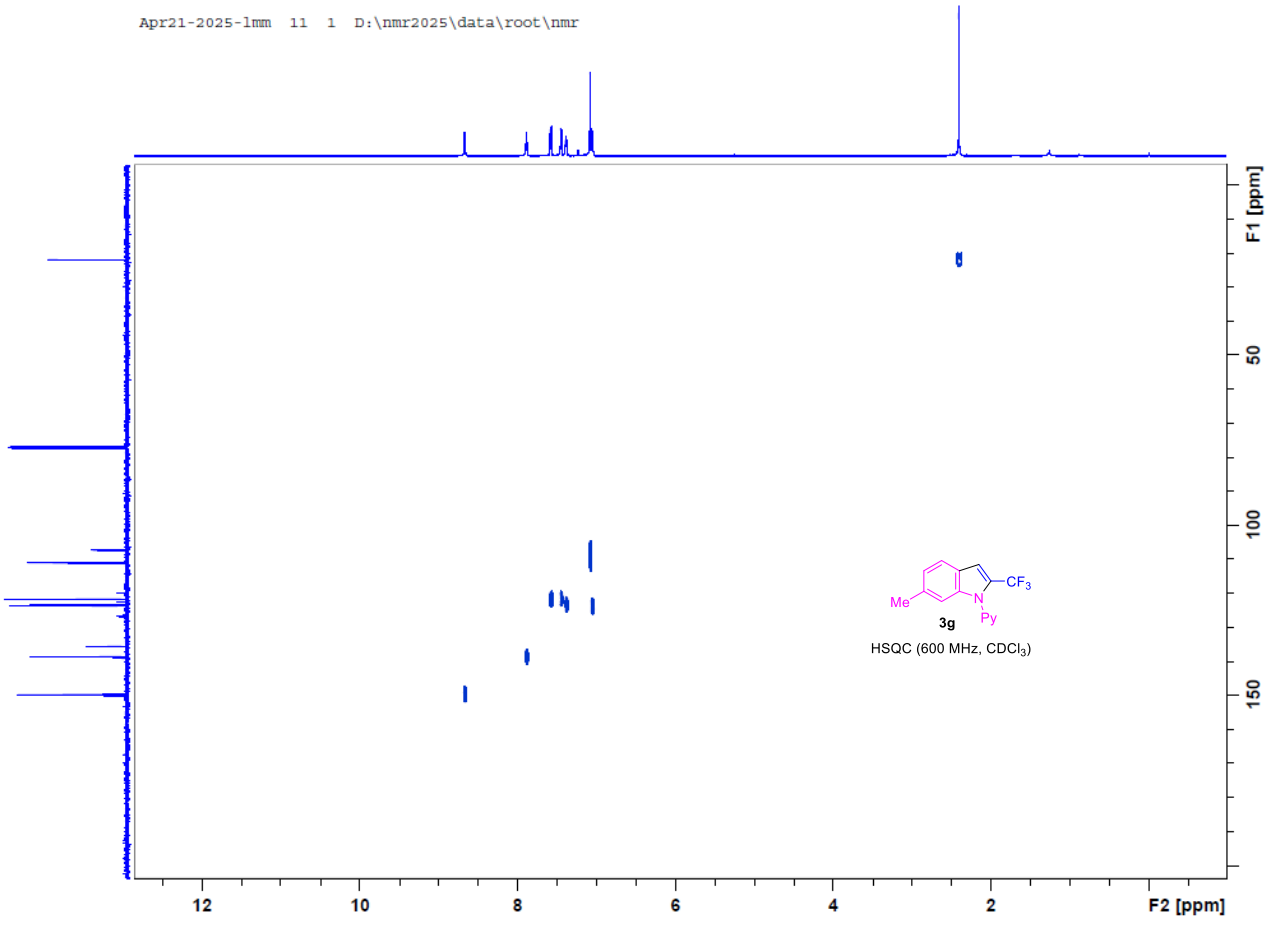
^{19}F NMR (376 MHz, $CDCl_3$)



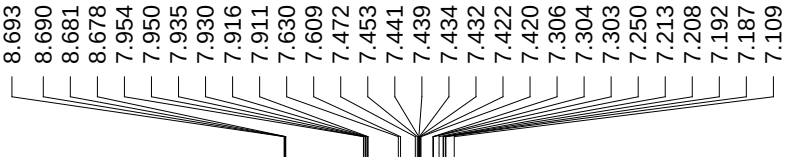
H-H COSY (600 MHz, $CDCl_3$)

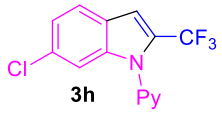


HMBC (600 MHz, $CDCl_3$)

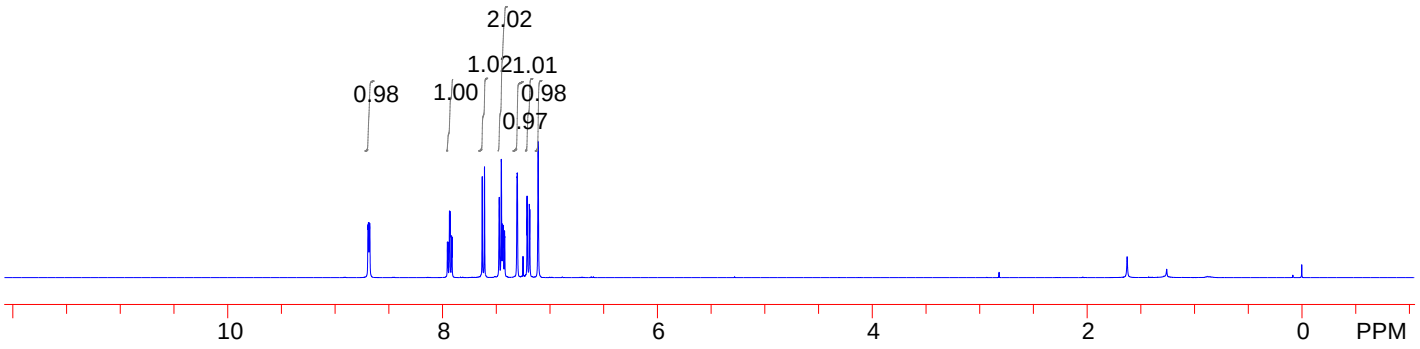


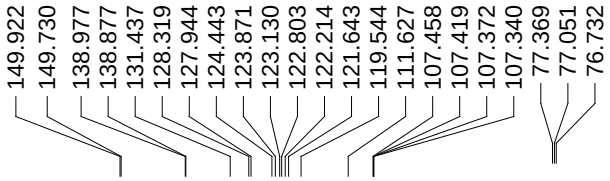
HSQC (600 MHz, $CDCl_3$)

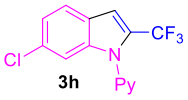




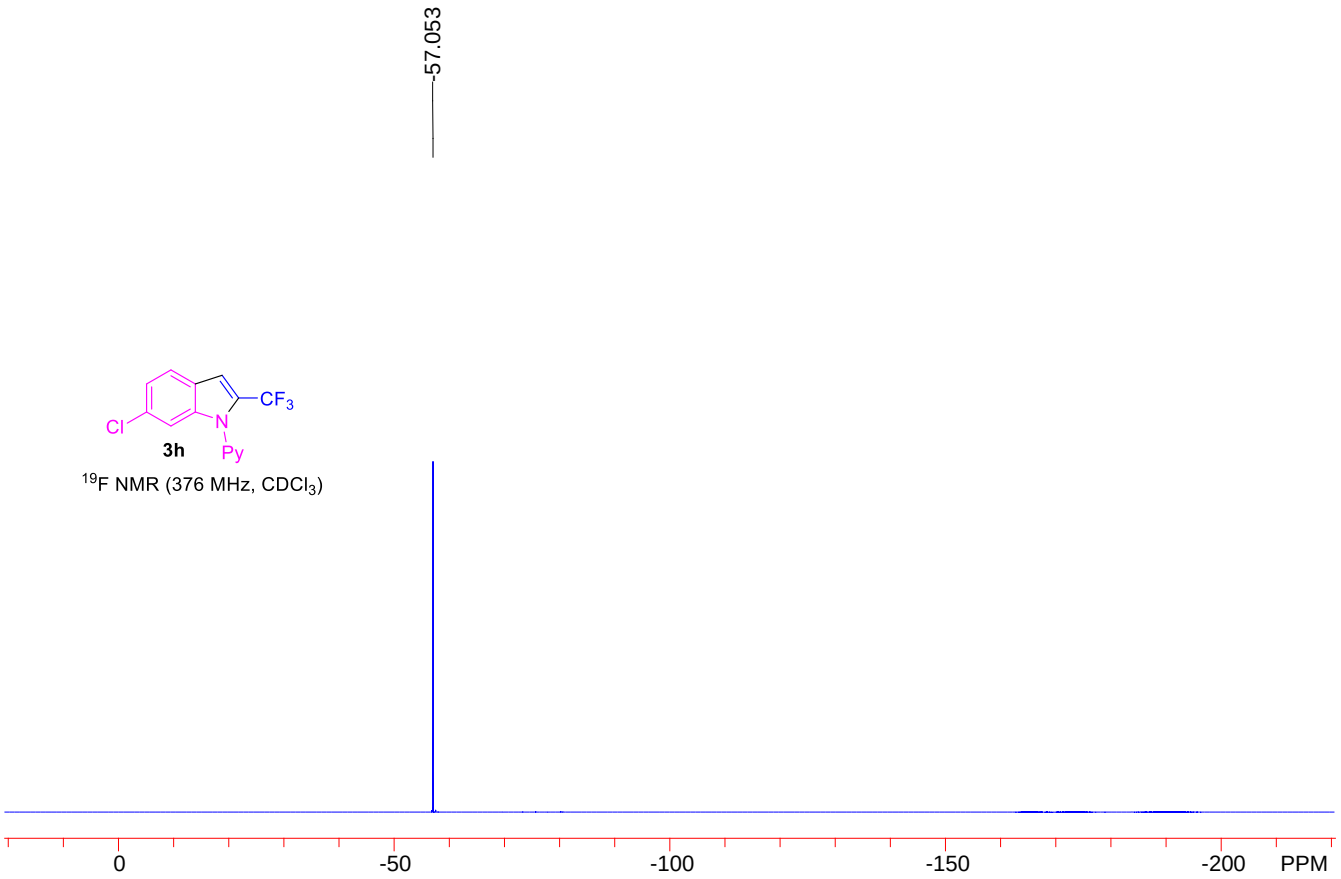
^{1}H NMR (400 MHz, $CDCl_3$)



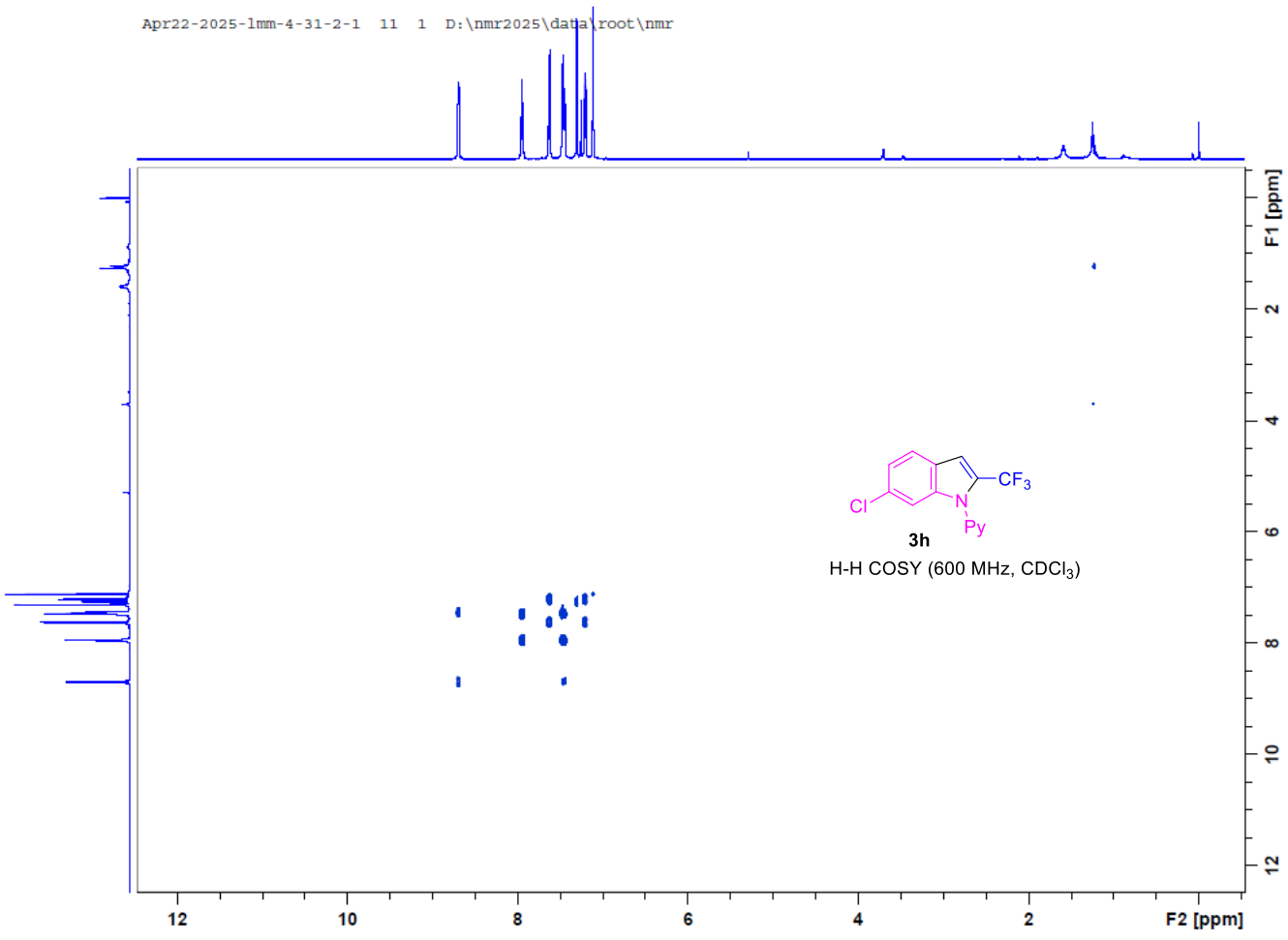




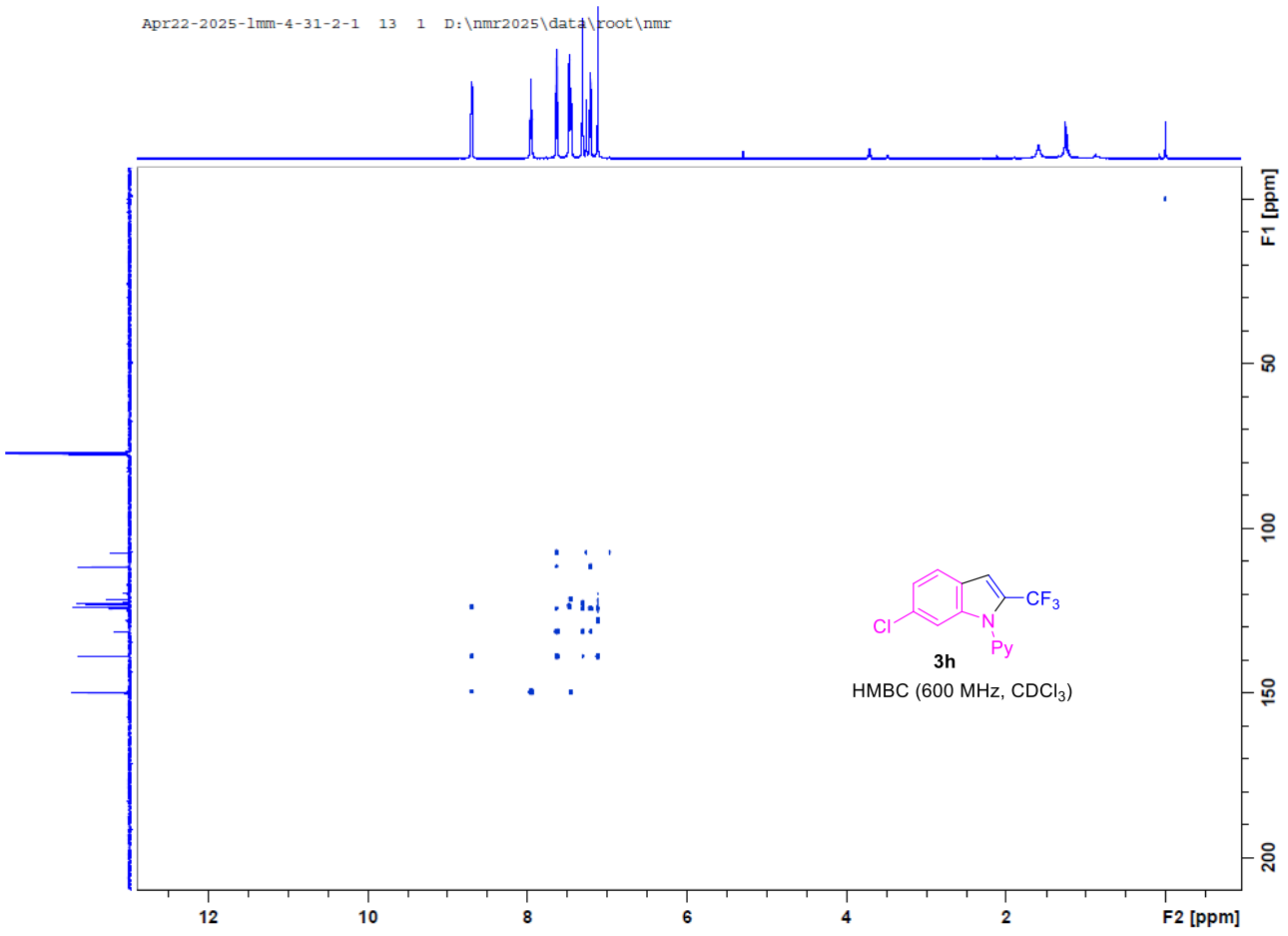
$^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$)



^{19}F NMR (376 MHz, $CDCl_3$)

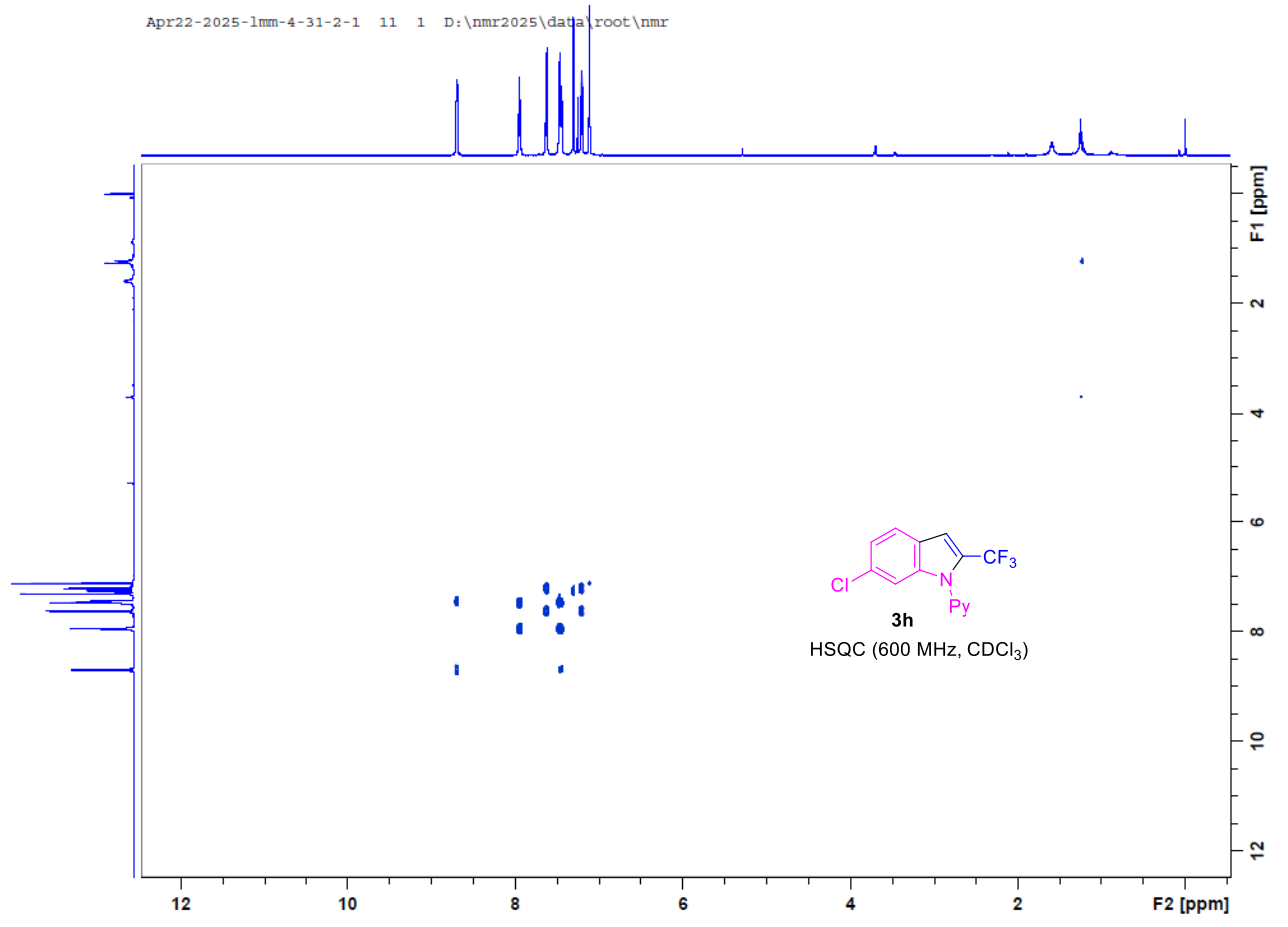


H-H COSY (600 MHz, $CDCl_3$)



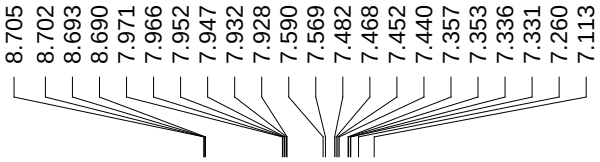
3h

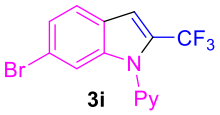
HMBC (600 MHz, $CDCl_3$)



3h

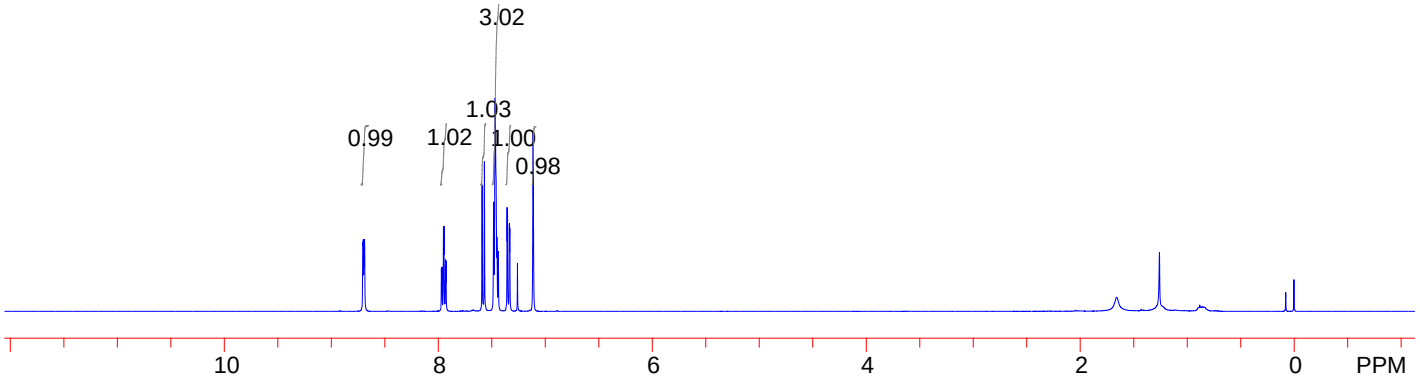
HSQC (600 MHz, $CDCl_3$)

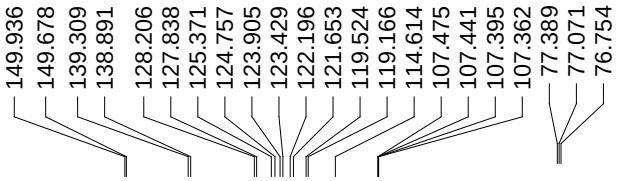


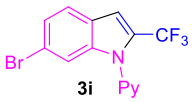


3i

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

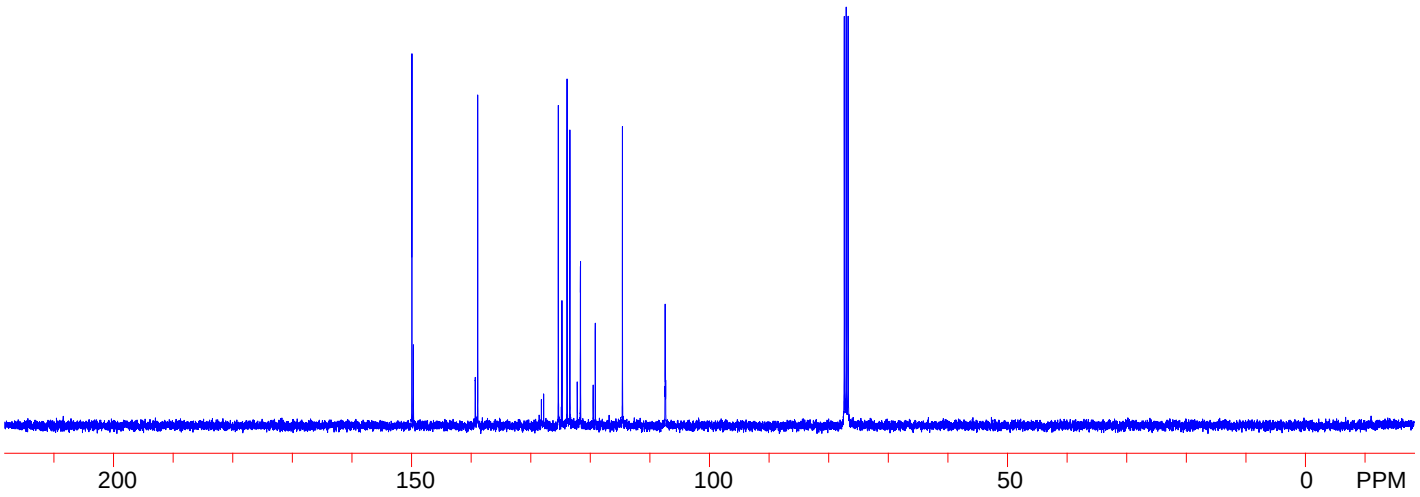


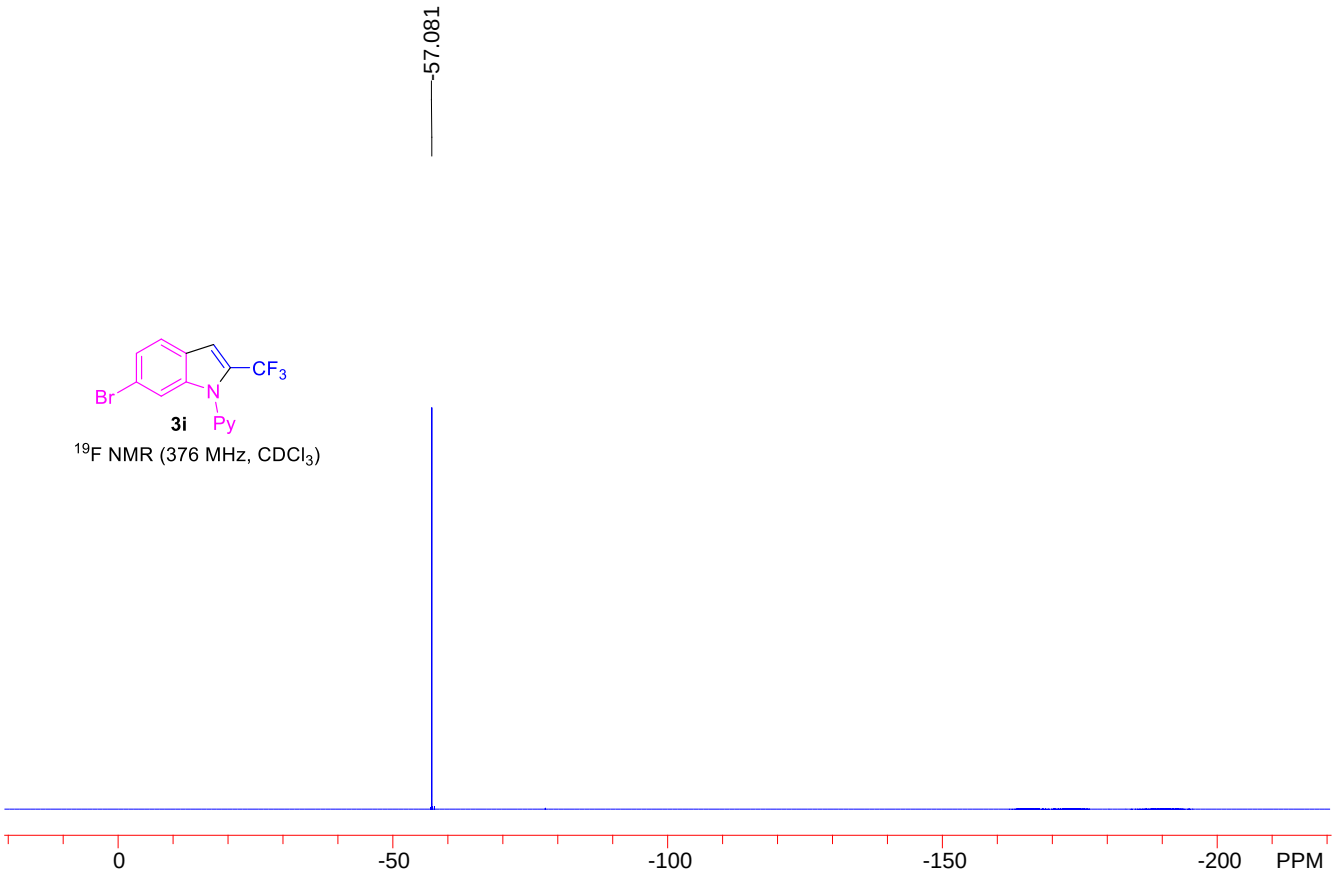


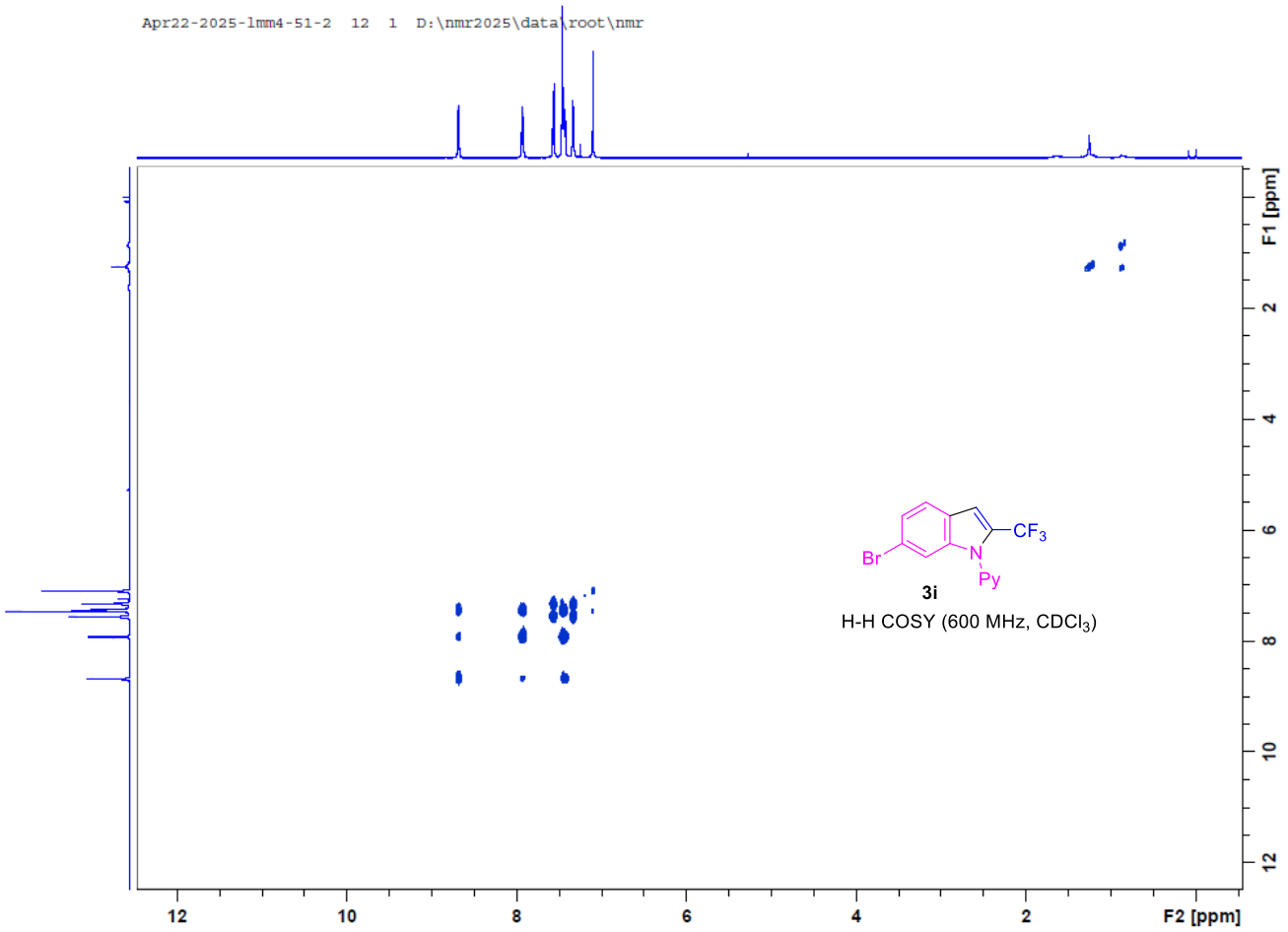


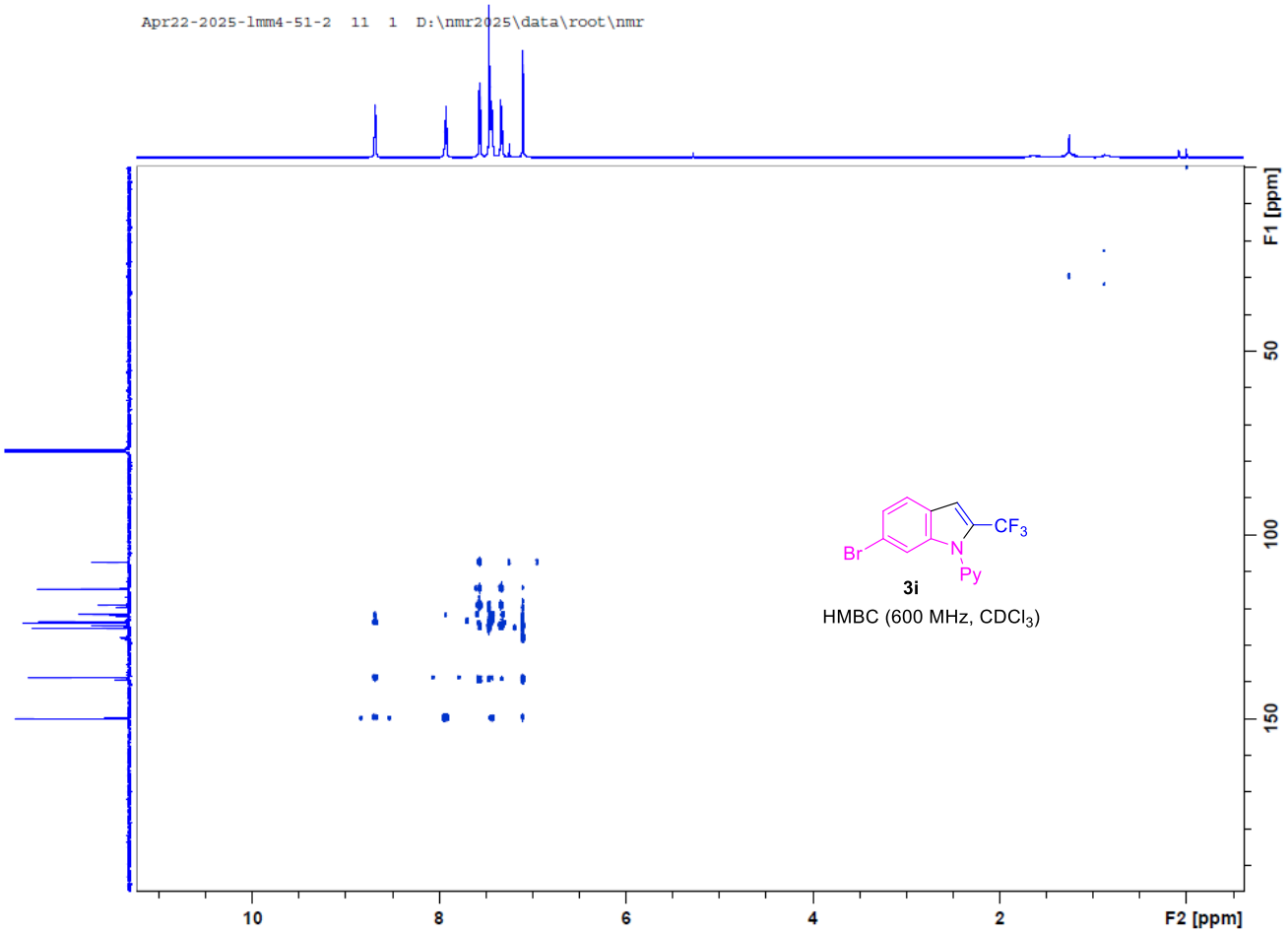
3i

$^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$)



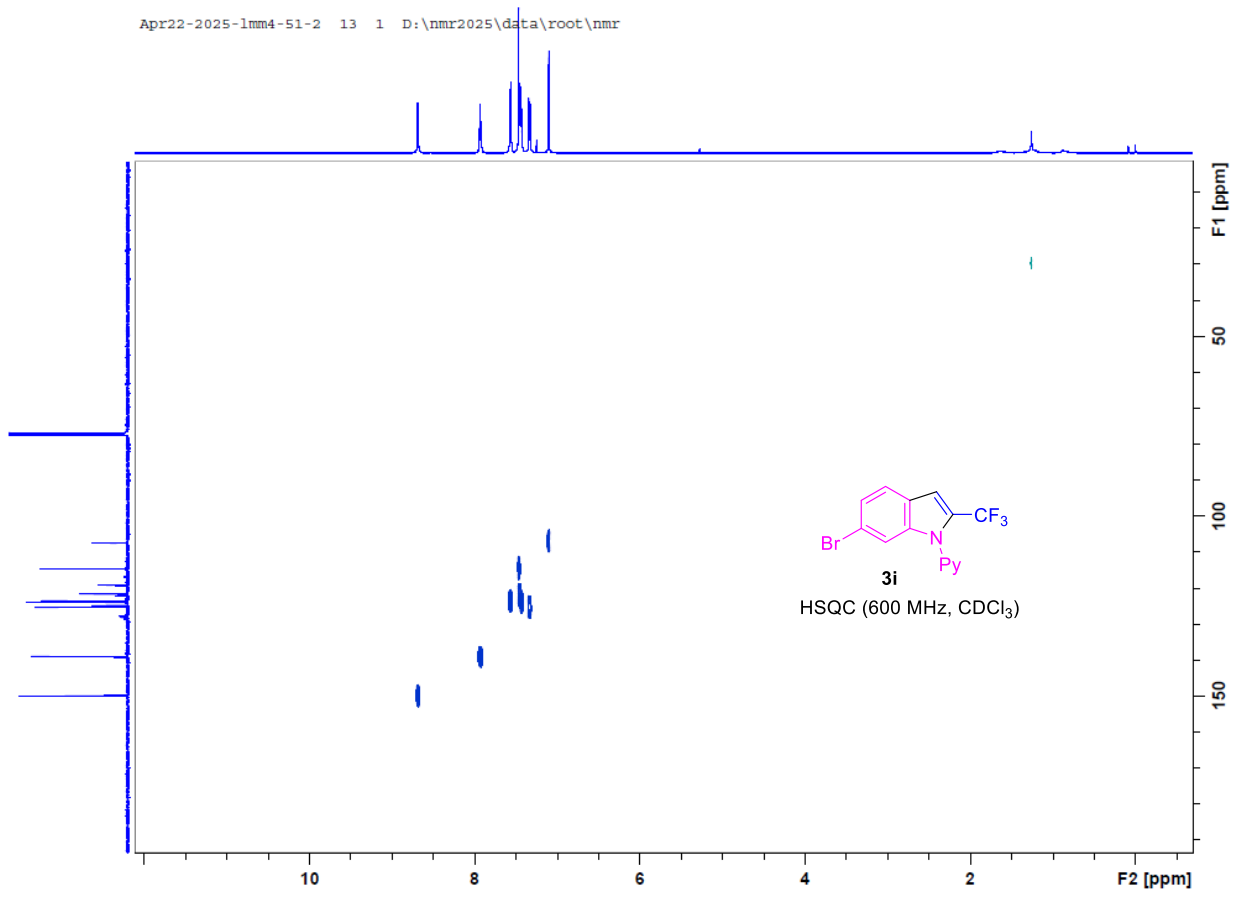

-57.081
Br
CF3
N
Py
3i
19F NMR (376 MHz, CDCl3)
0
-50
-100
-150
-200
PPM


Apr22-2025-lmm4-51-2 12 1 D:\nmr2025\data\root\nmr
F1 [ppm]
F2 [ppm]
Br
CF3
N
Py
3i
H-H COSY (600 MHz, CDCl3)



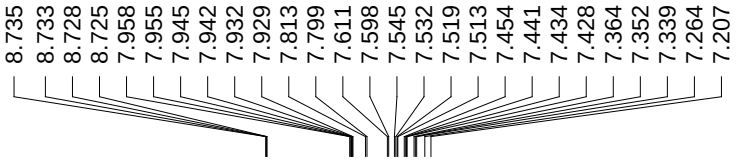
3i

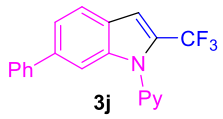
HMBC (600 MHz, $CDCl_3$)



3i

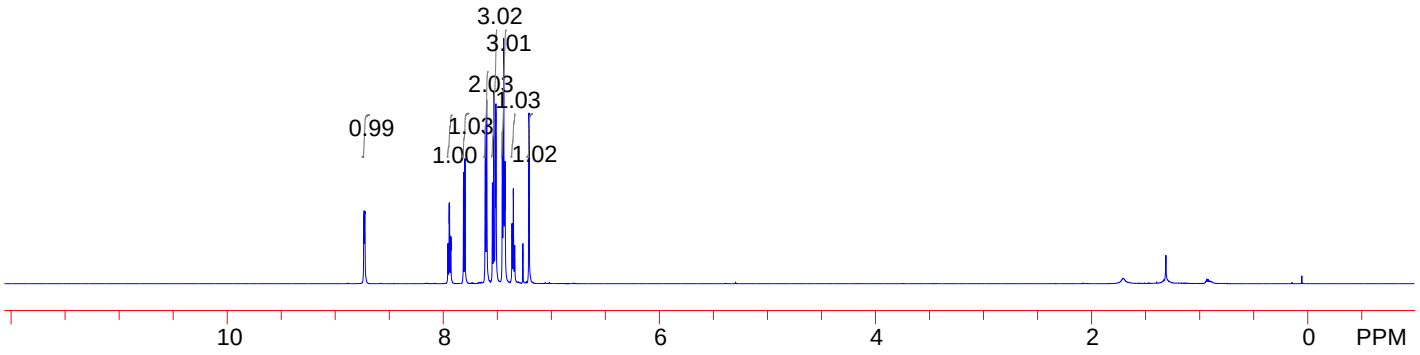
HSQC (600 MHz, $CDCl_3$)

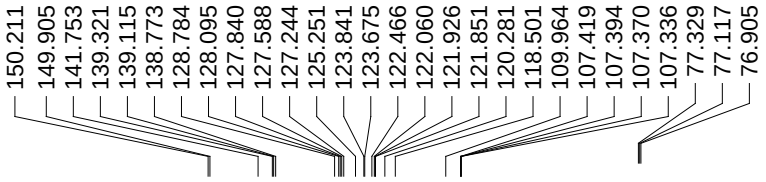


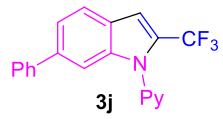


3j

^{1}H NMR (600 MHz, $CDCl_3$)

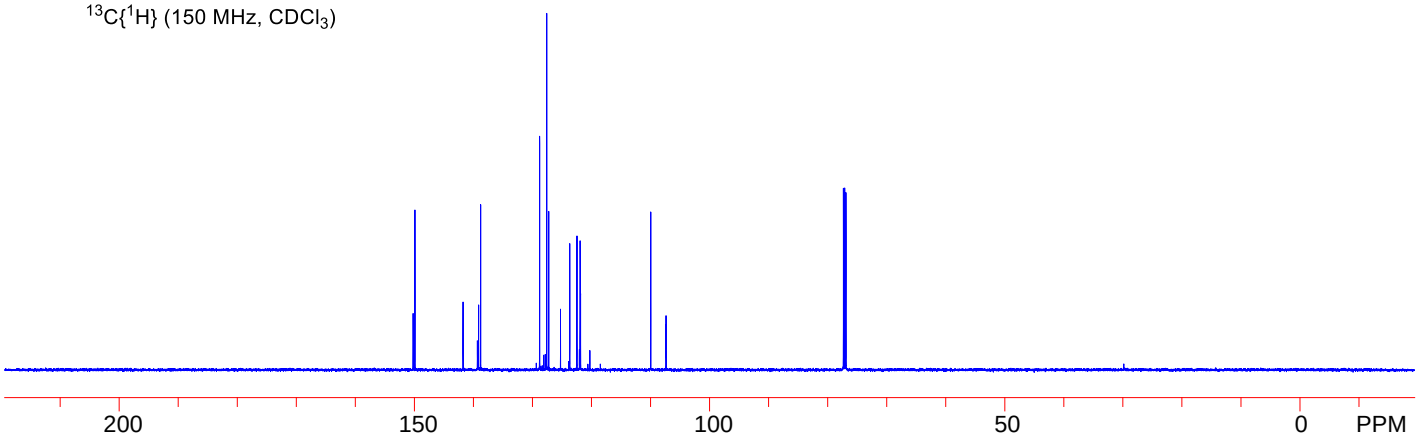


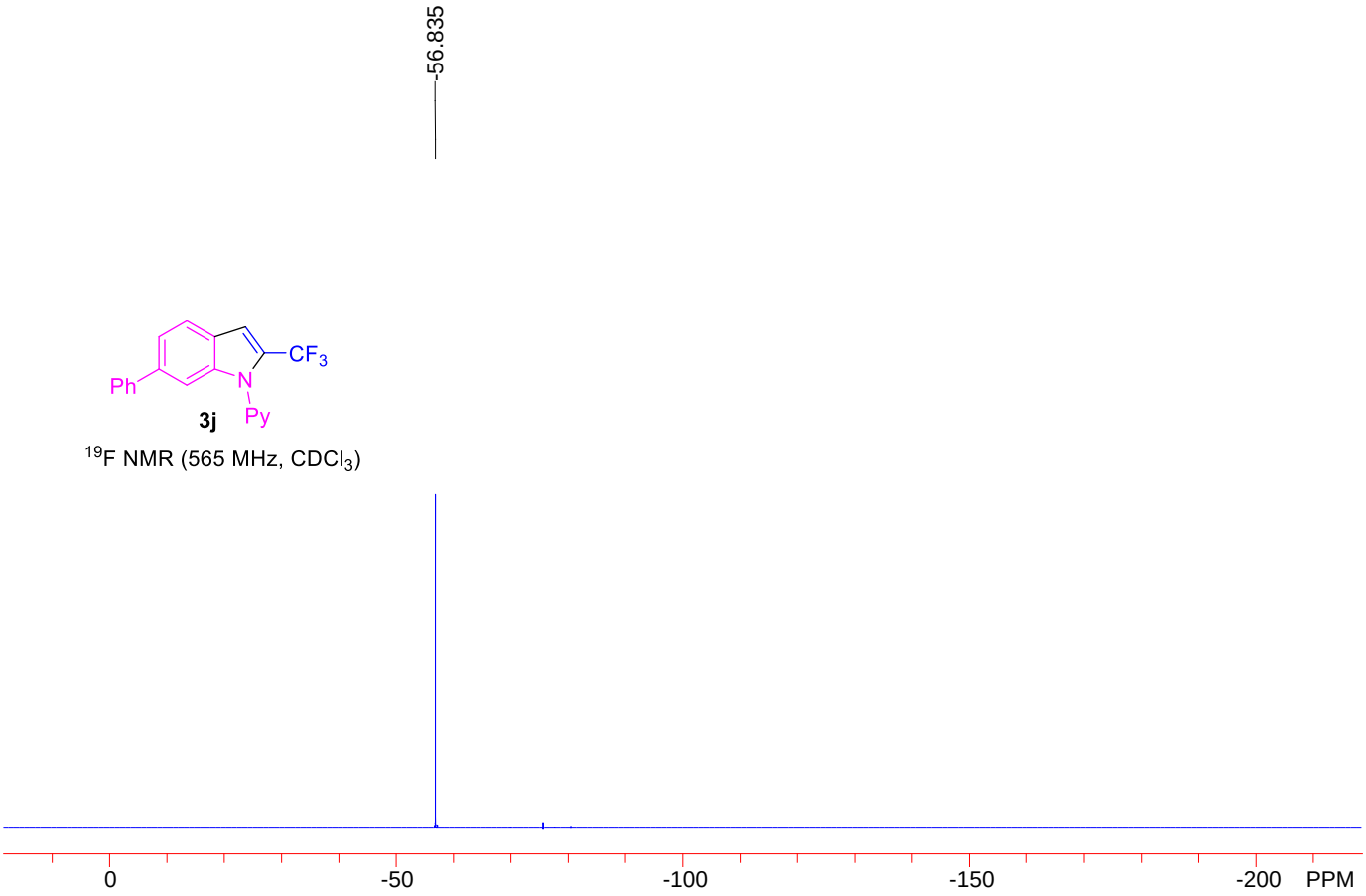




3j

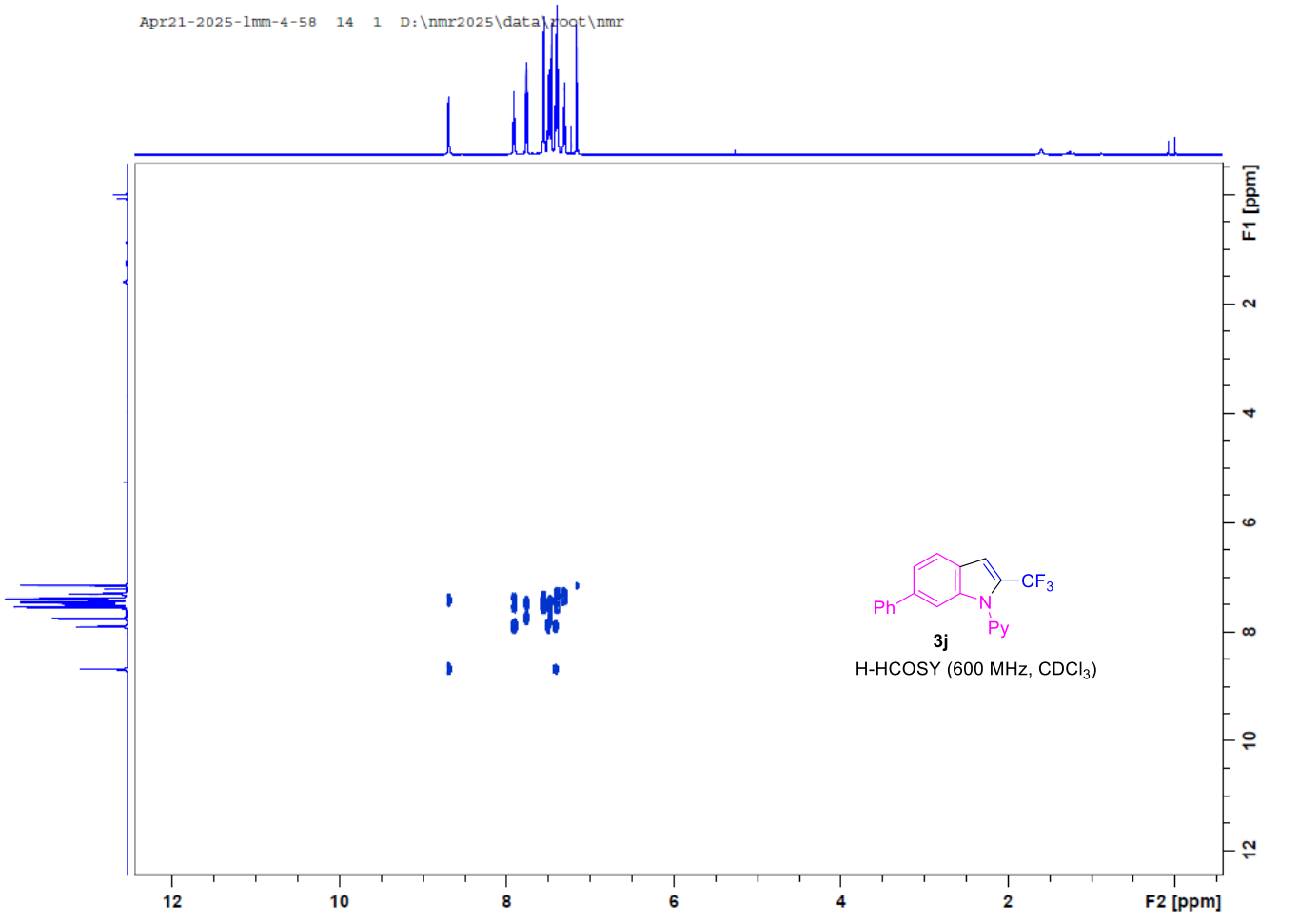
$^{13}C\{^{1}H\}$ (150 MHz, $CDCl_3$)





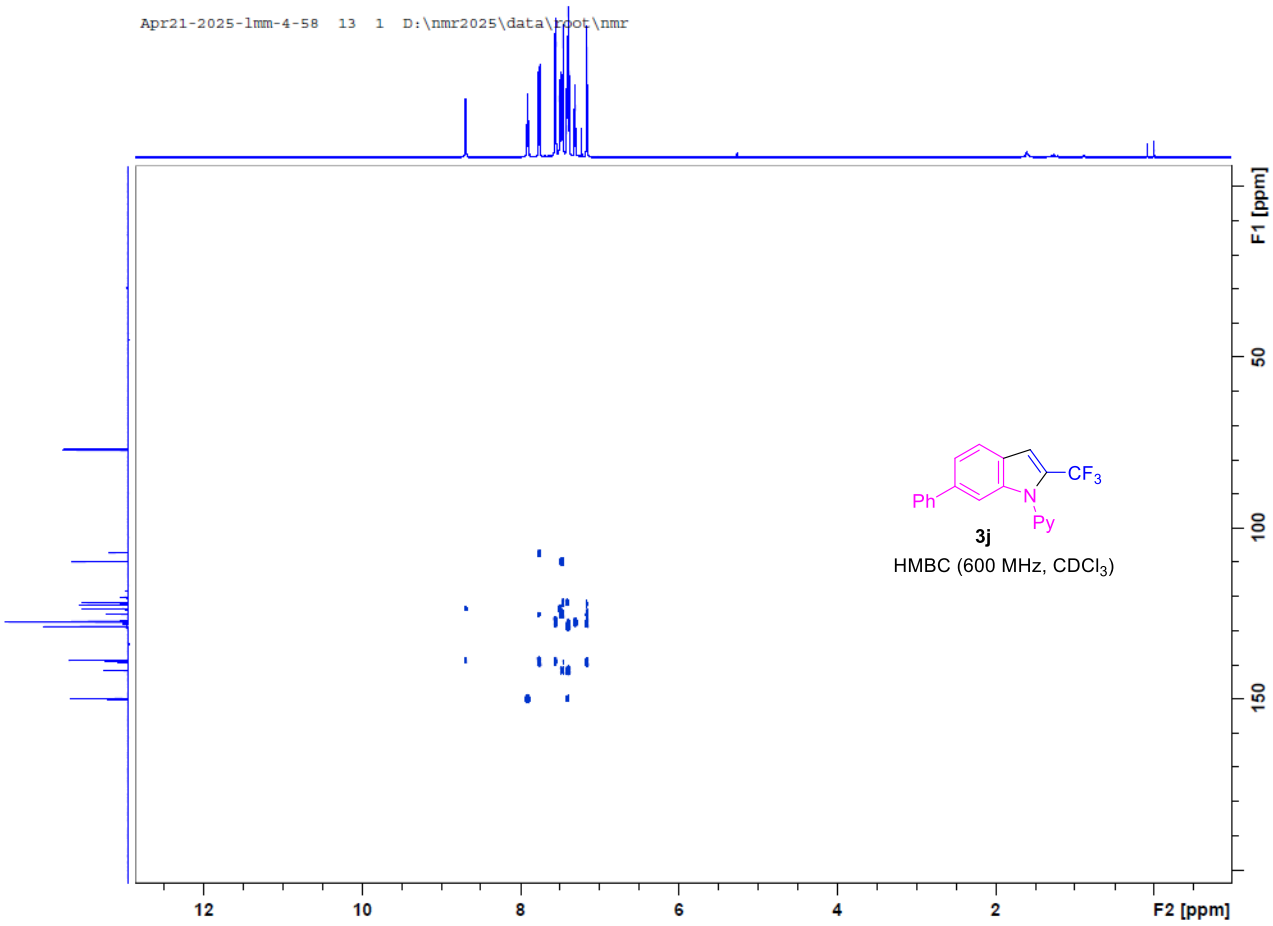
3j

^{19}F NMR (565 MHz, $CDCl_3$)



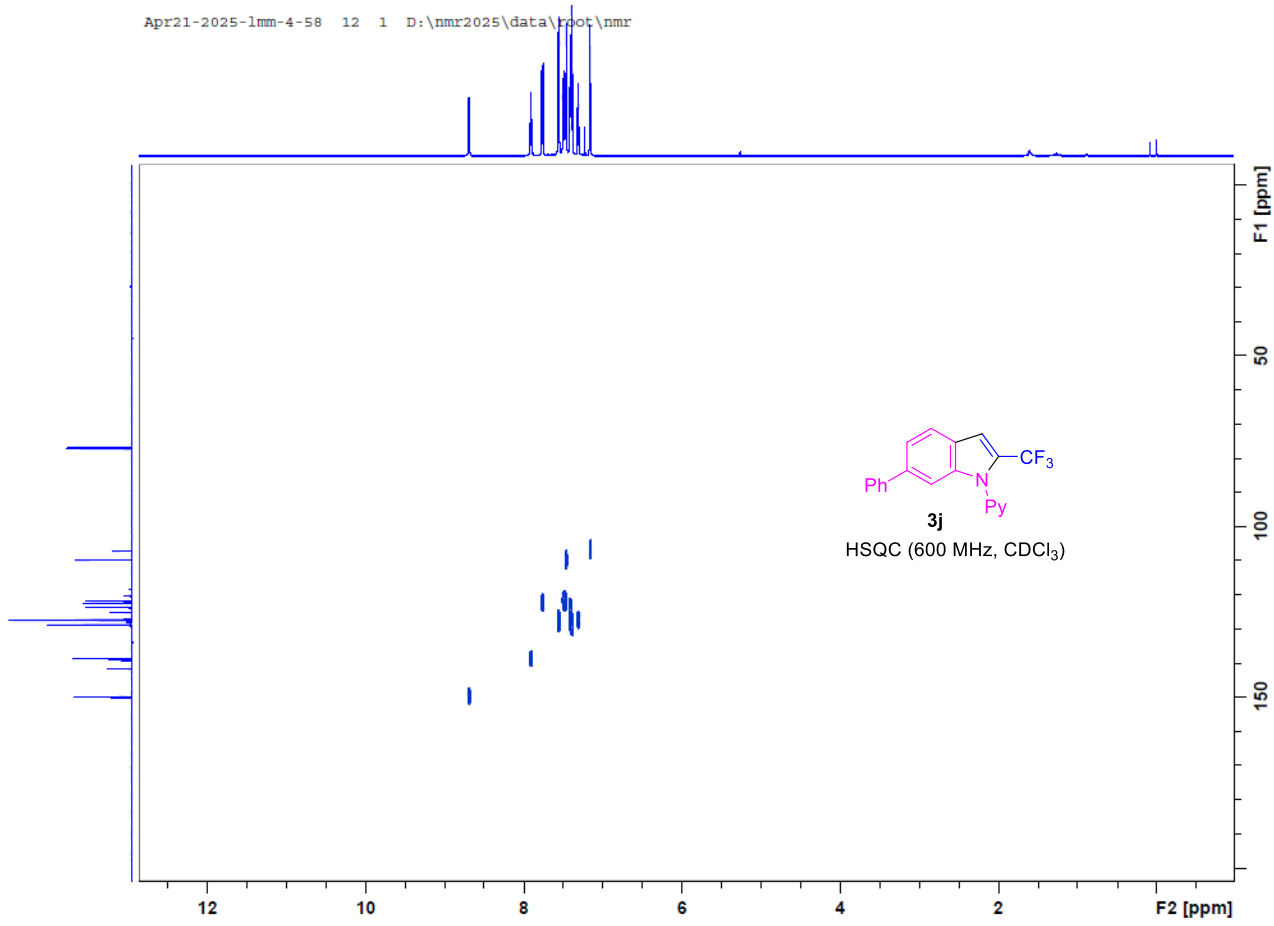
3j

H-HCOSY (600 MHz, $CDCl_3$)



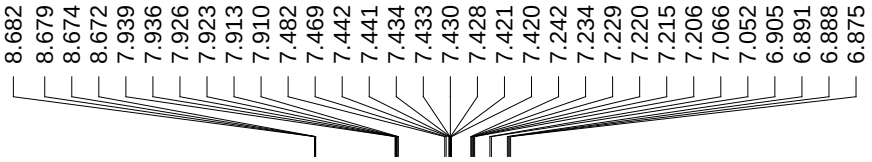
3j

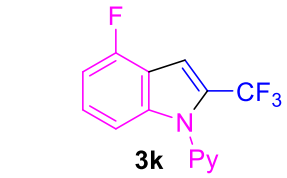
HMBC (600 MHz, $CDCl_3$)



3j

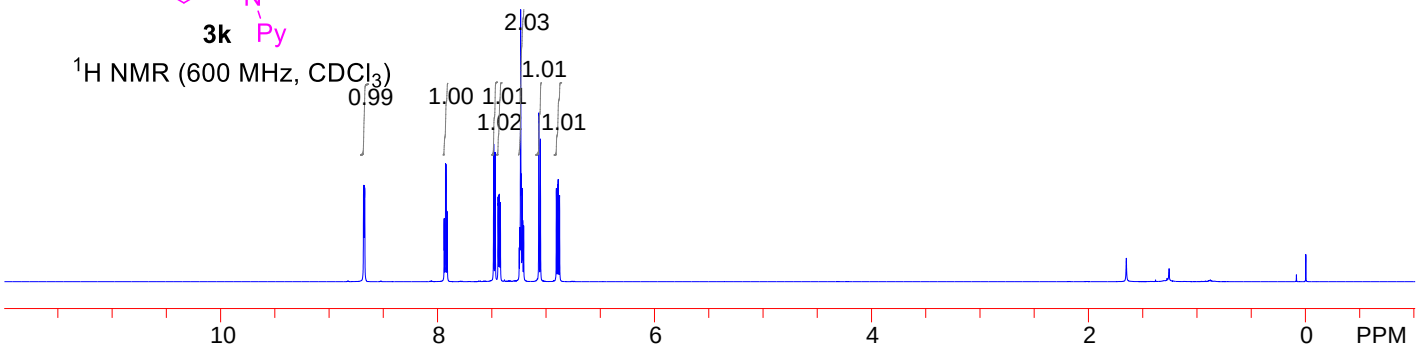
HSQC (600 MHz, $CDCl_3$)

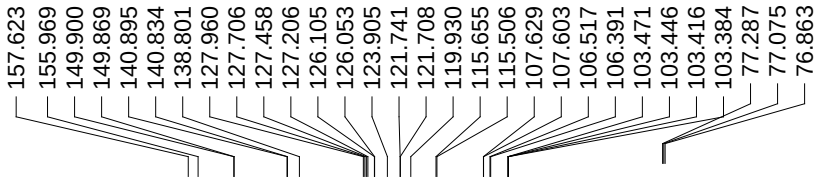


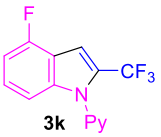


3k

^{1}H NMR (600 MHz, $CDCl_3$)

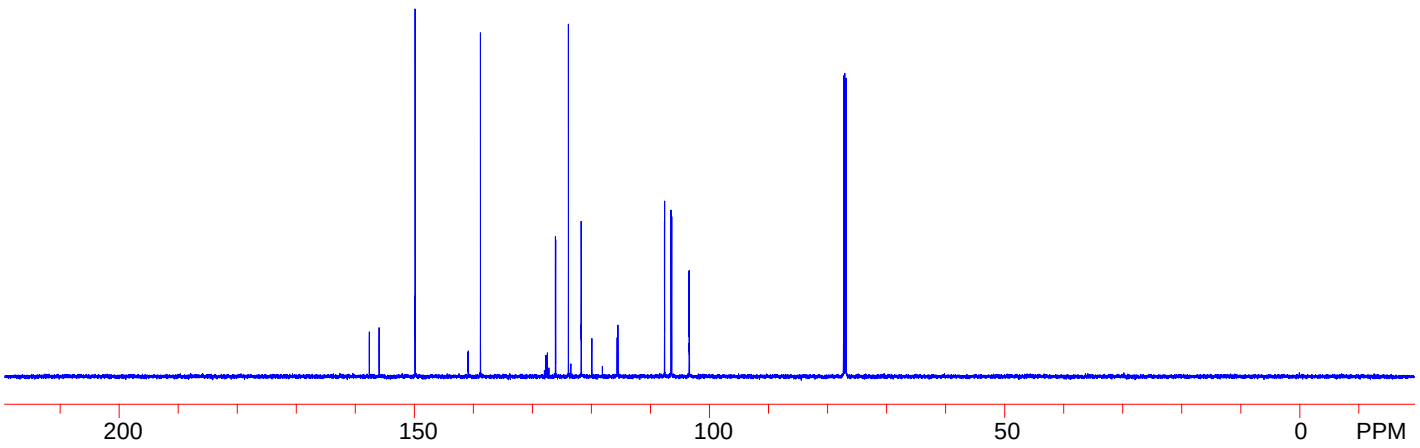


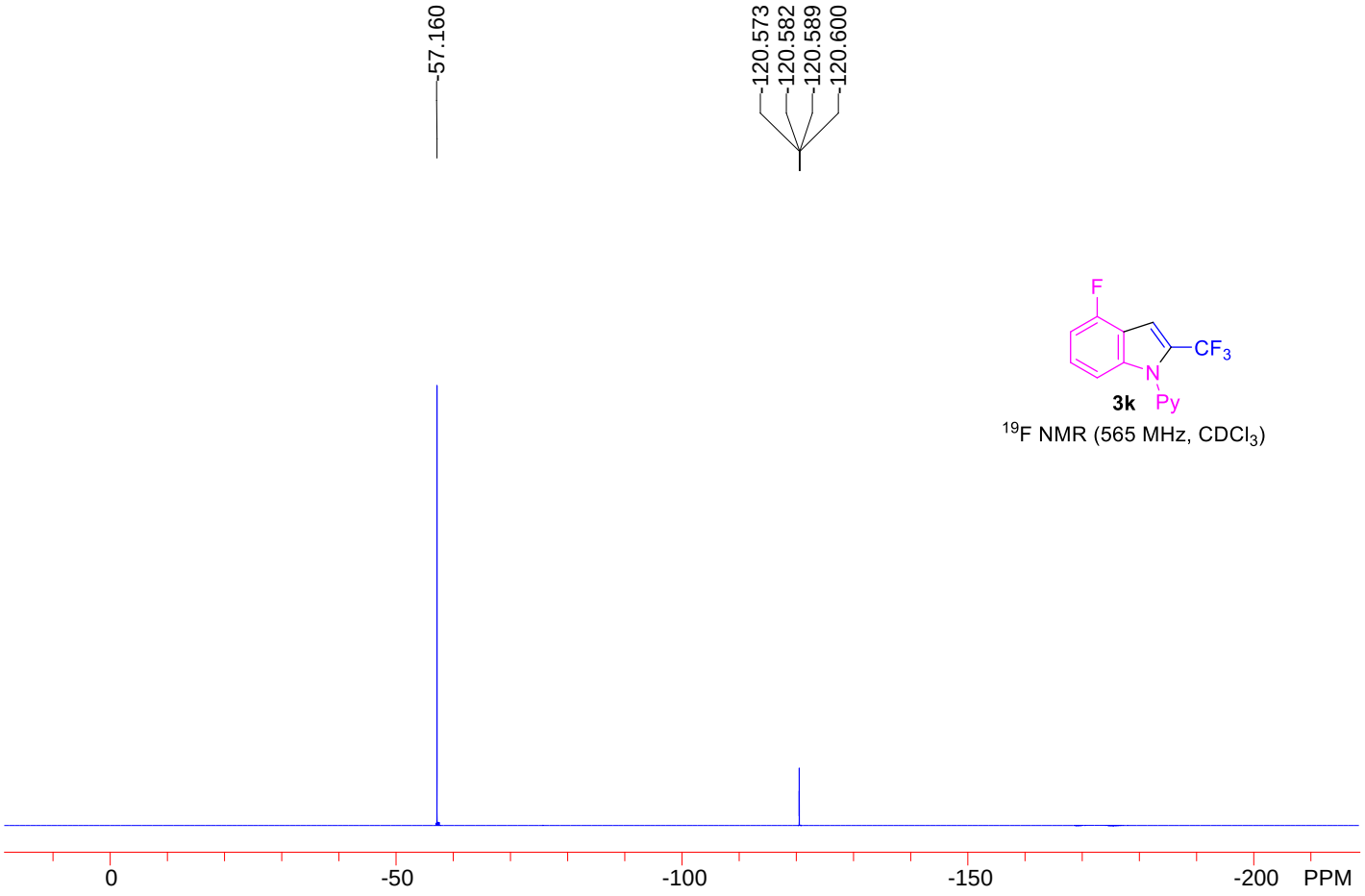


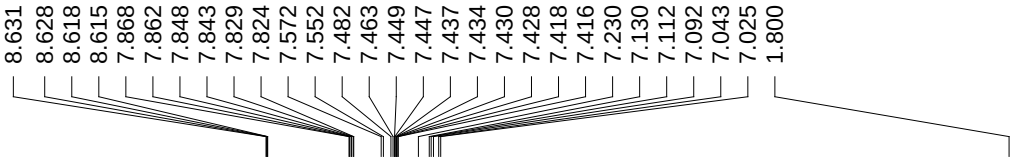


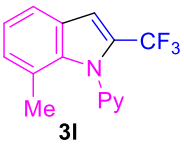
3k

$^{13}C\{^{1}H\}$ (150 MHz, $CDCl_3$)



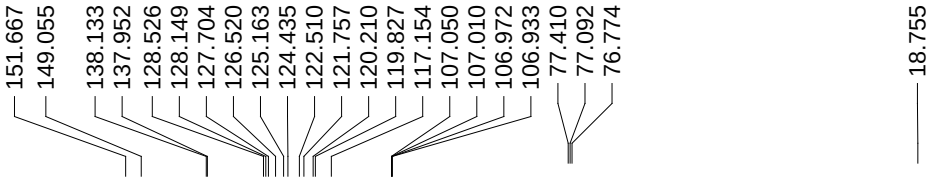

-57.160
-120.573
-120.582
-120.589
-120.600
F
CF3
N
Py
3k
19F NMR (565 MHz, CDCl3)
0
-50
-100
-150
-200
PPM

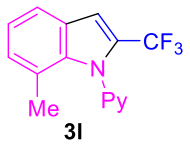




3l

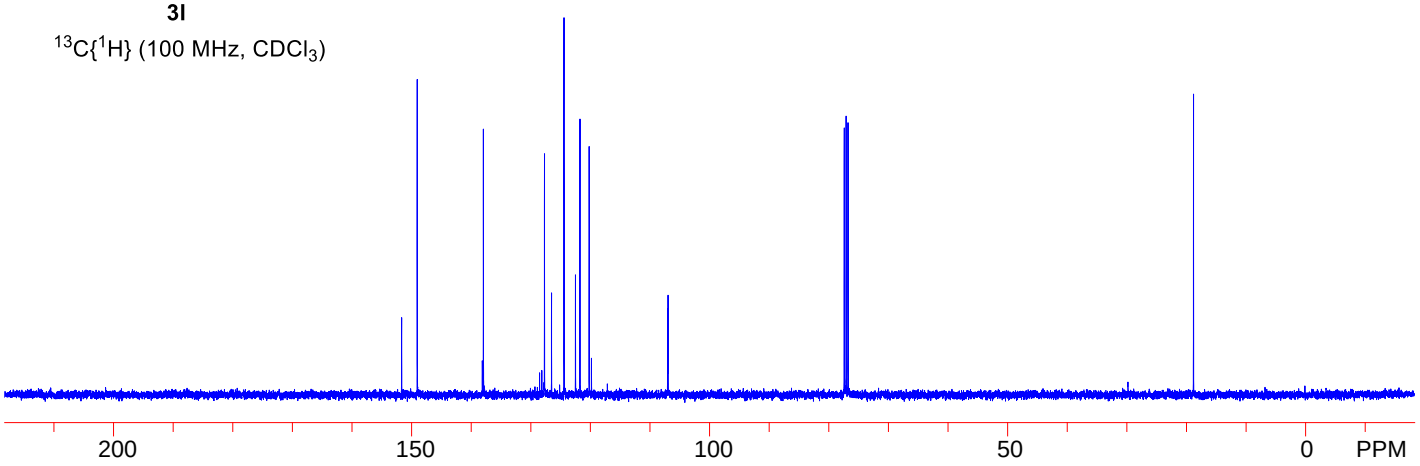
^{1}H NMR (400 MHz, $CDCl_3$)

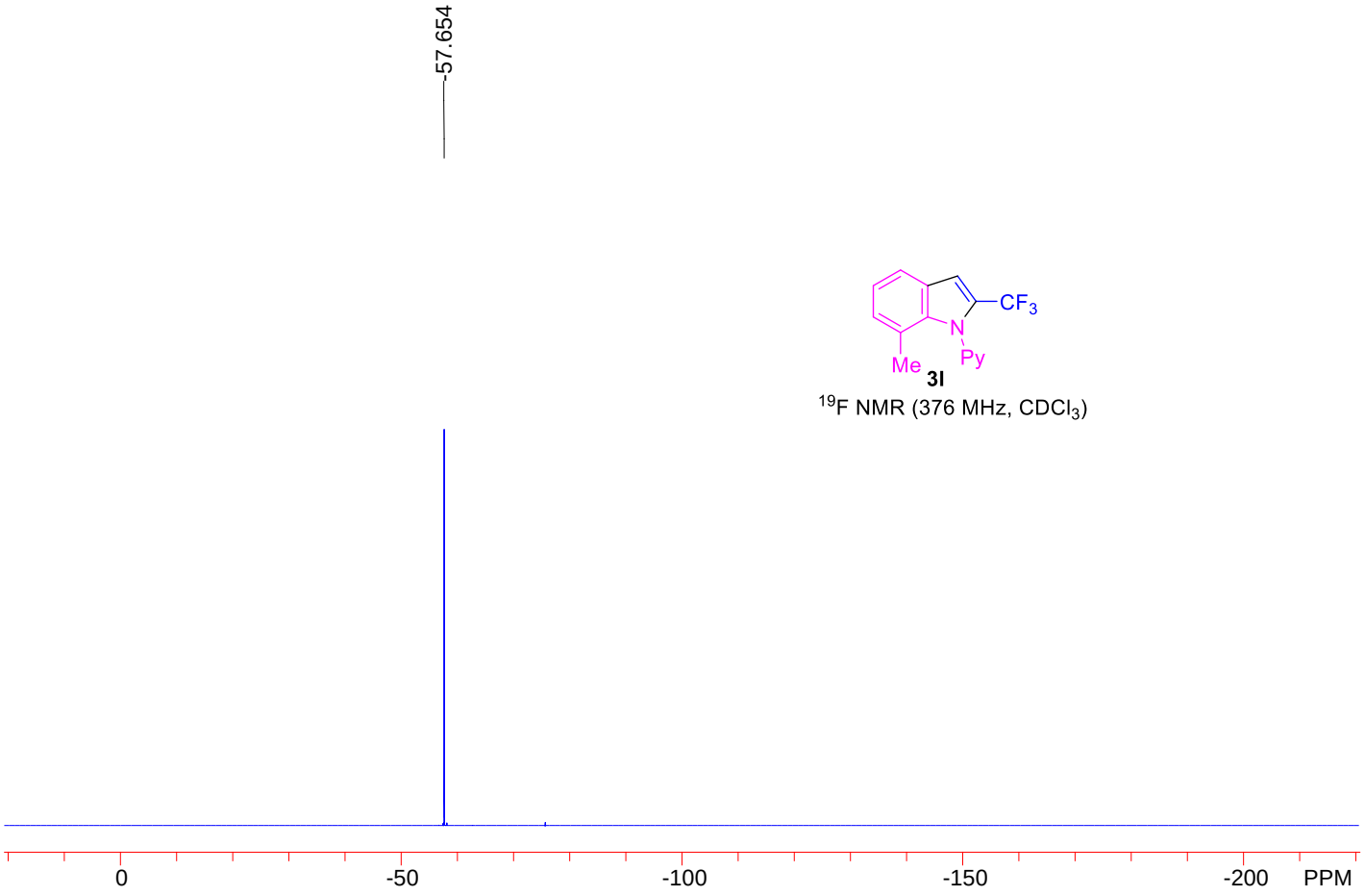




3l

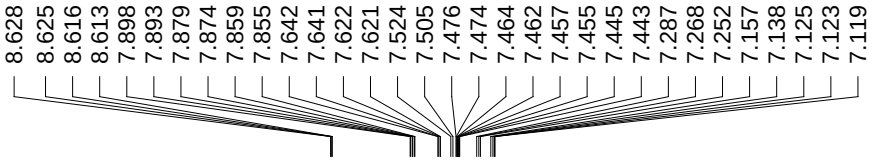
$^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$)

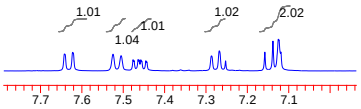


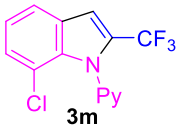


3l

^{19}F NMR (376 MHz, $CDCl_3$)

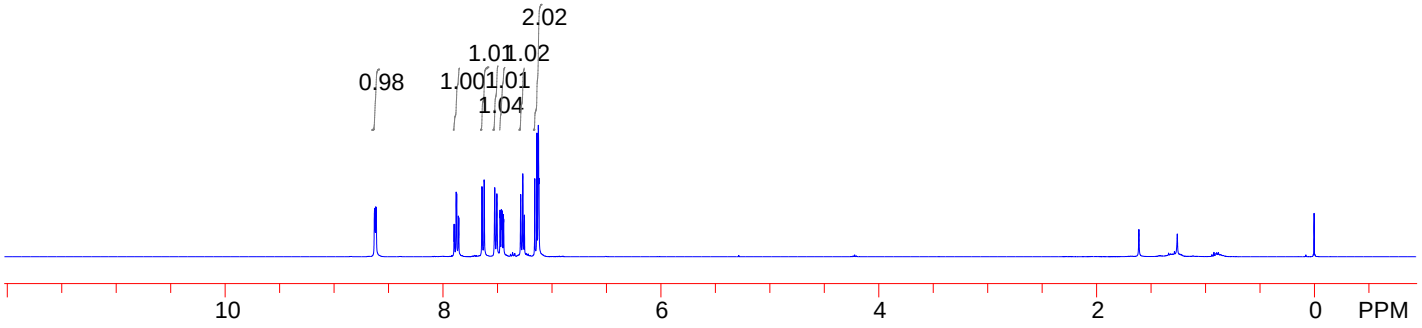


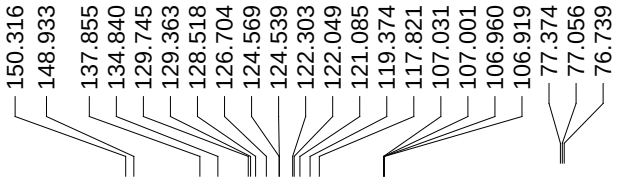


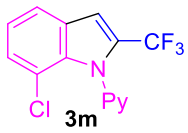


3m

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

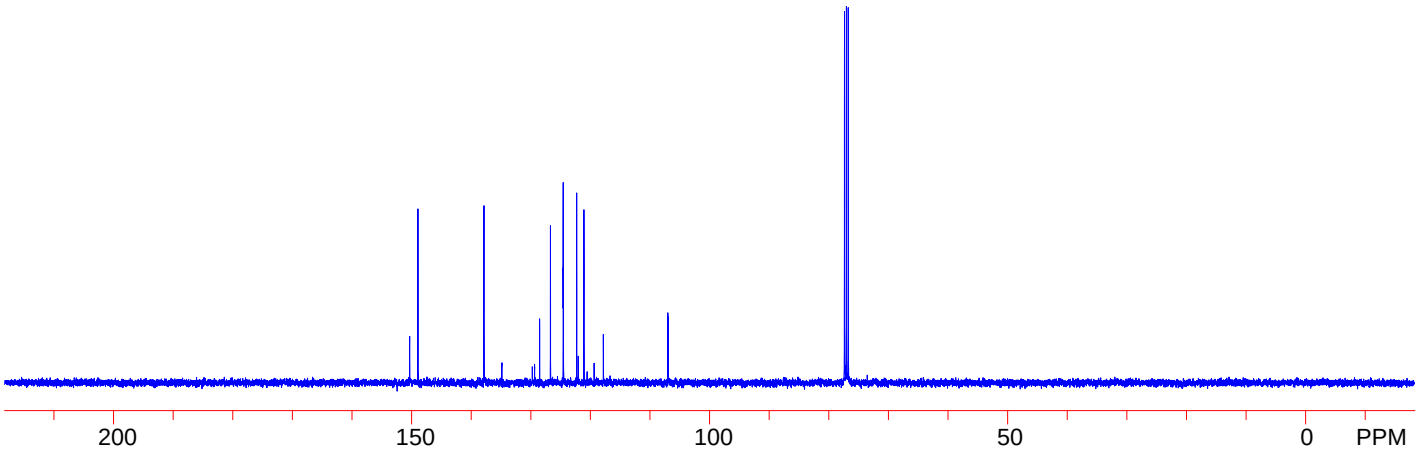


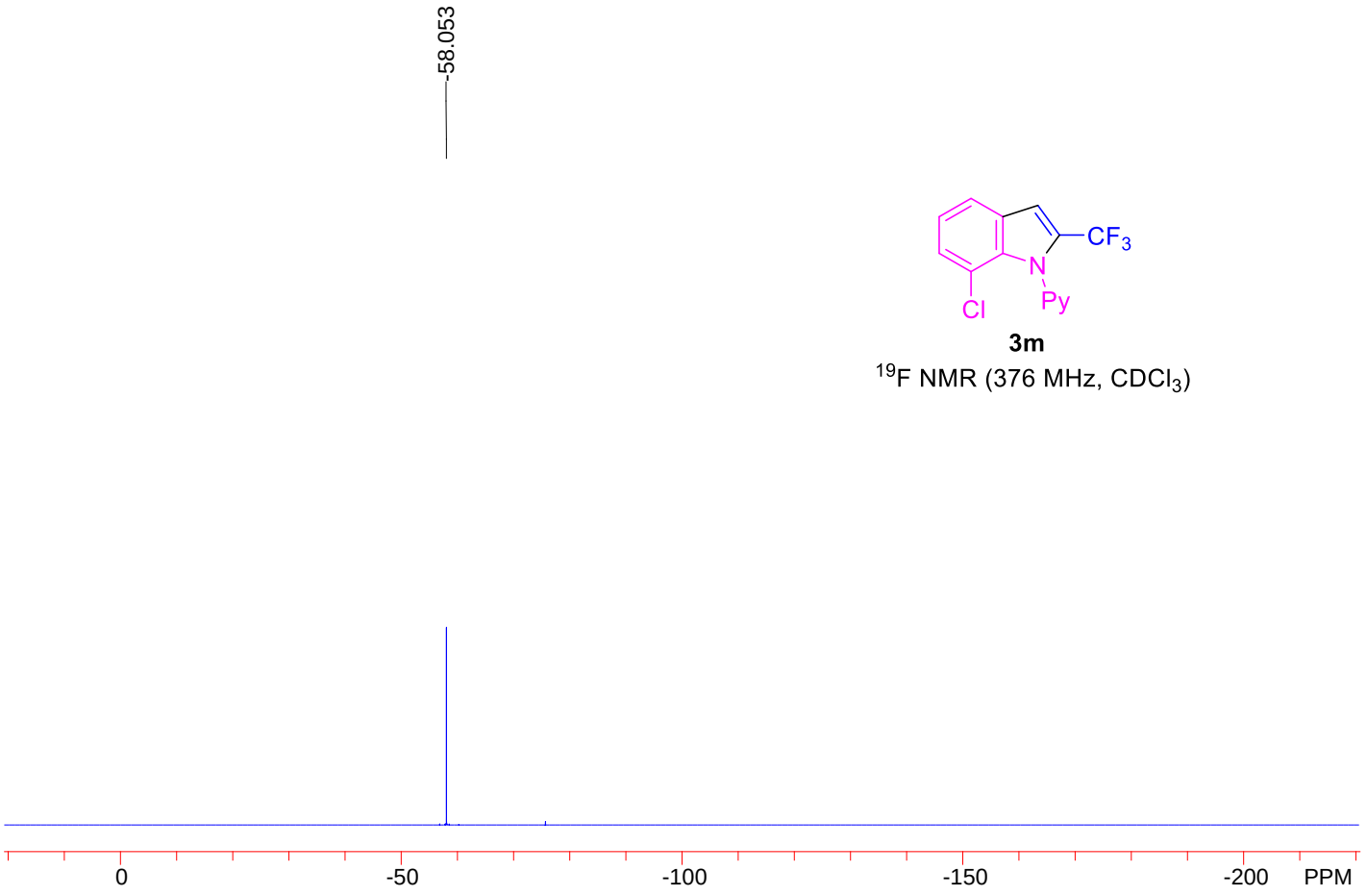




3m

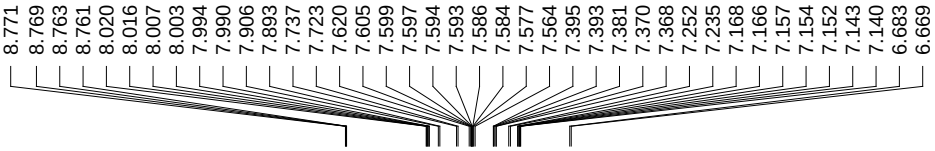
$^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$)

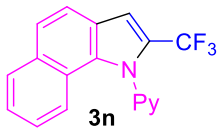




3m

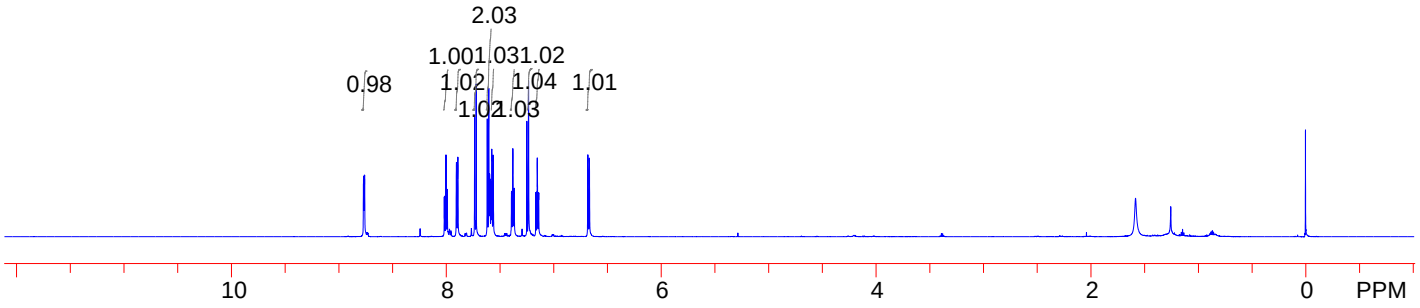
^{19}F NMR (376 MHz, $CDCl_3$)

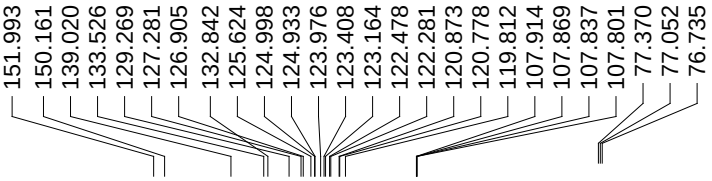


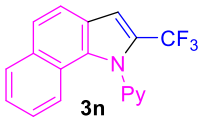


3n

^{1}H NMR (600 MHz, $CDCl_3$)

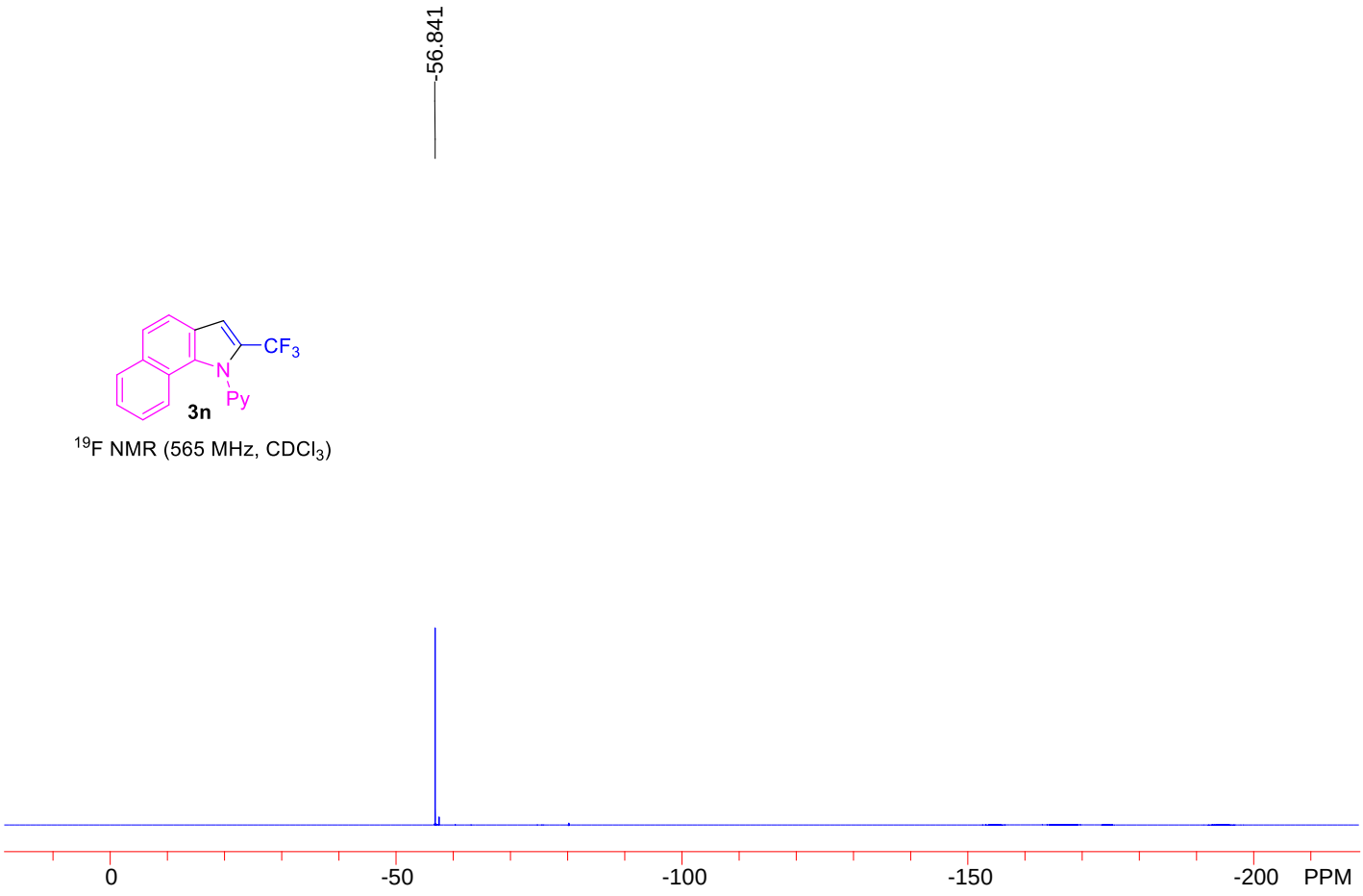




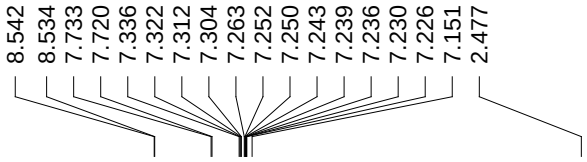


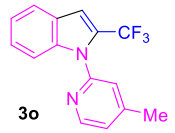
3n

^{13}C{^{1}H} (100 MHz, $CDCl_3$)



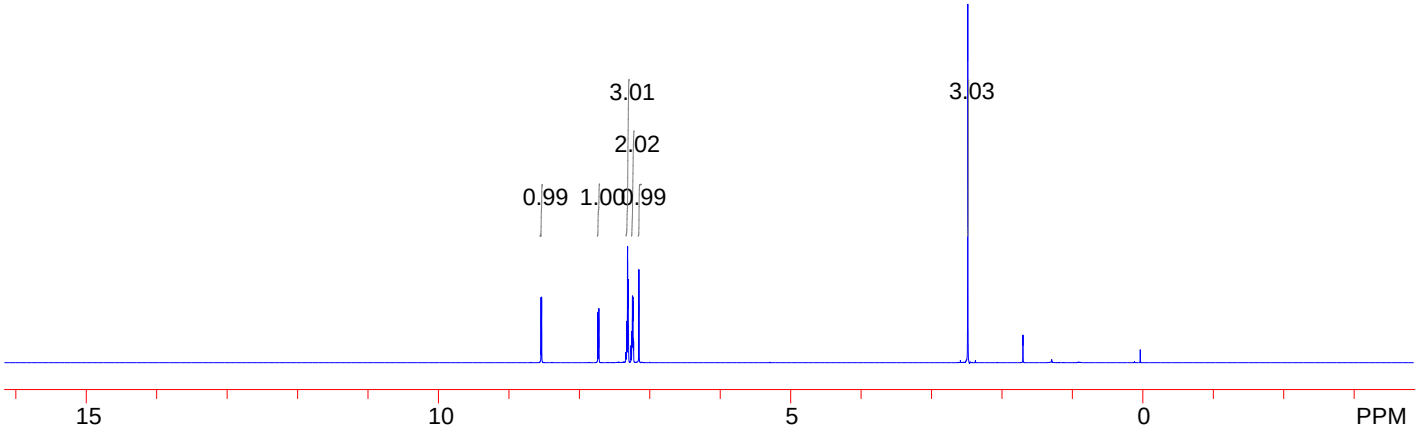
^{19}F NMR (565 MHz, $CDCl_3$)

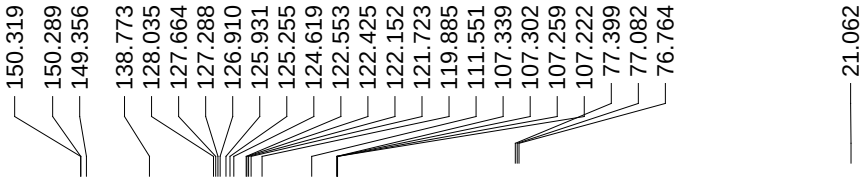


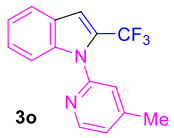


3o

^{1}H NMR (600 MHz, $CDCl_3$)

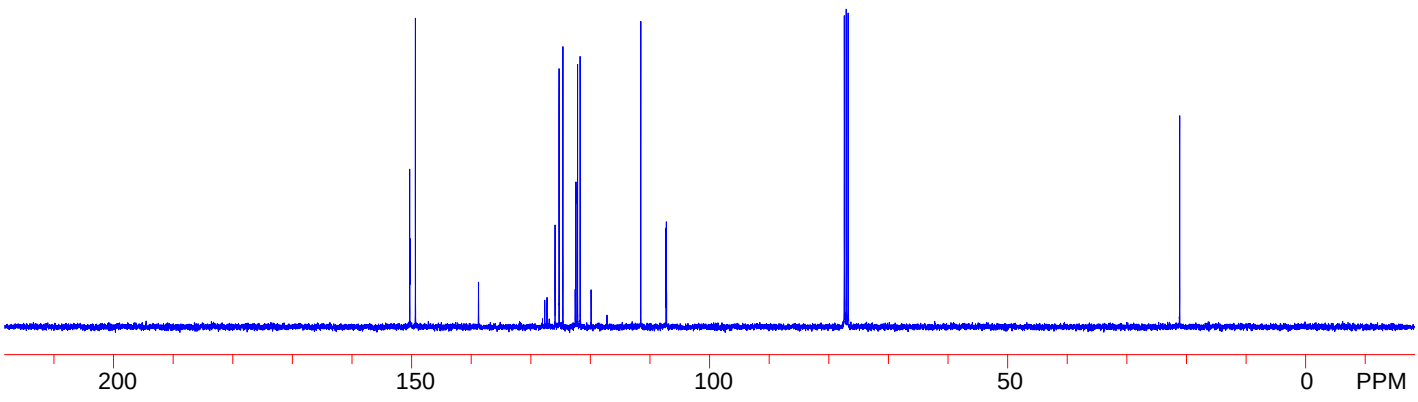


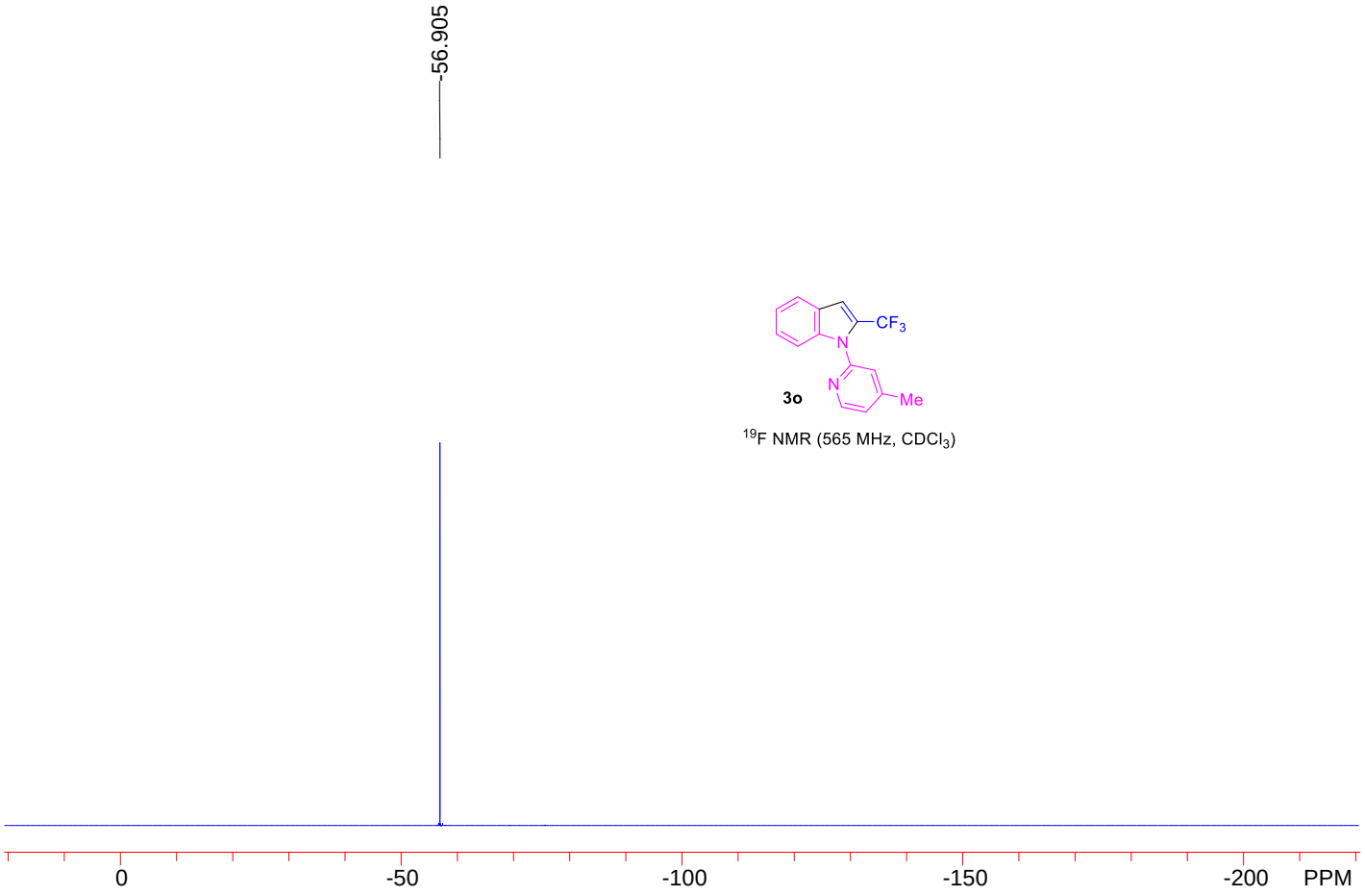


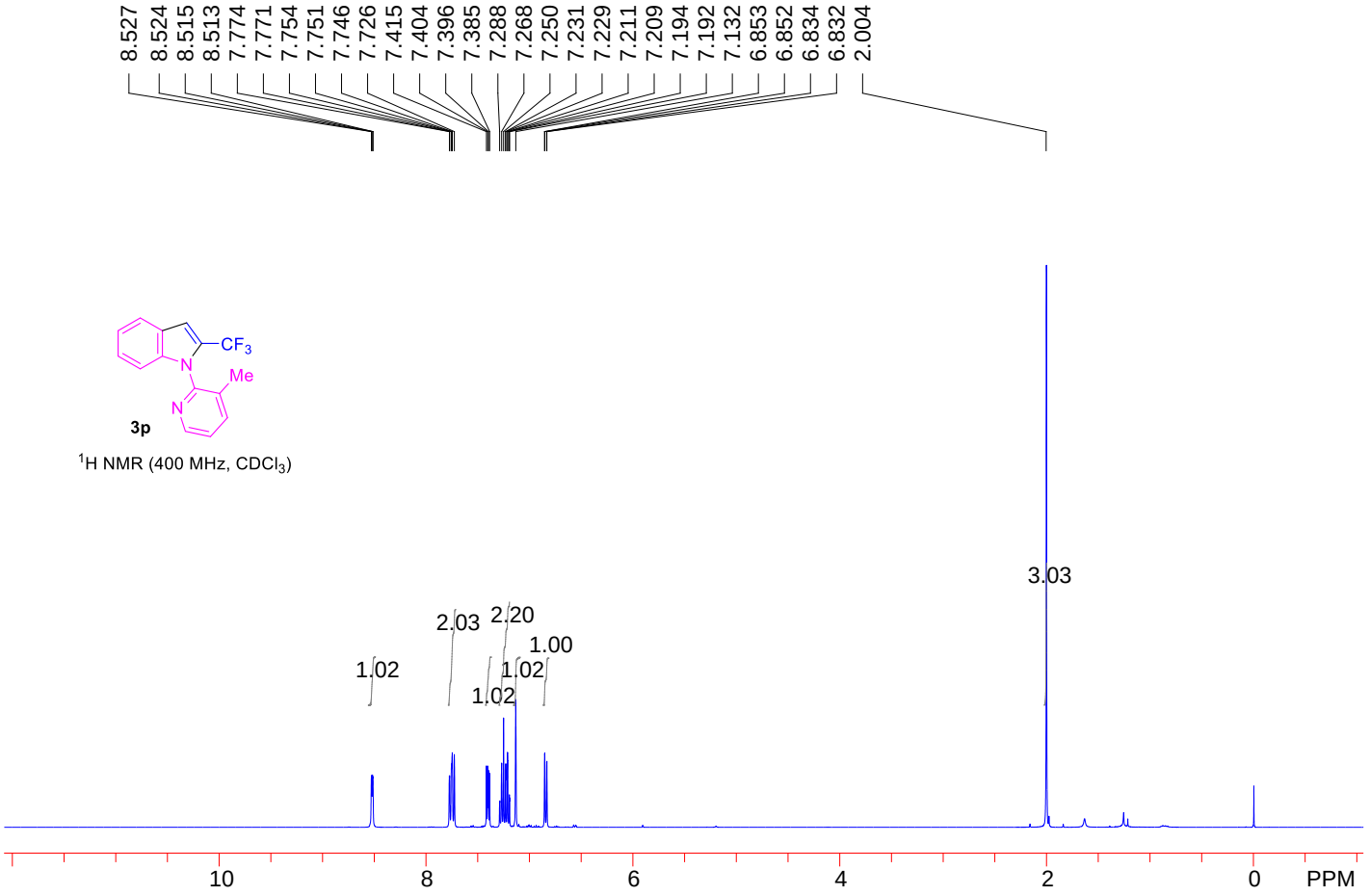


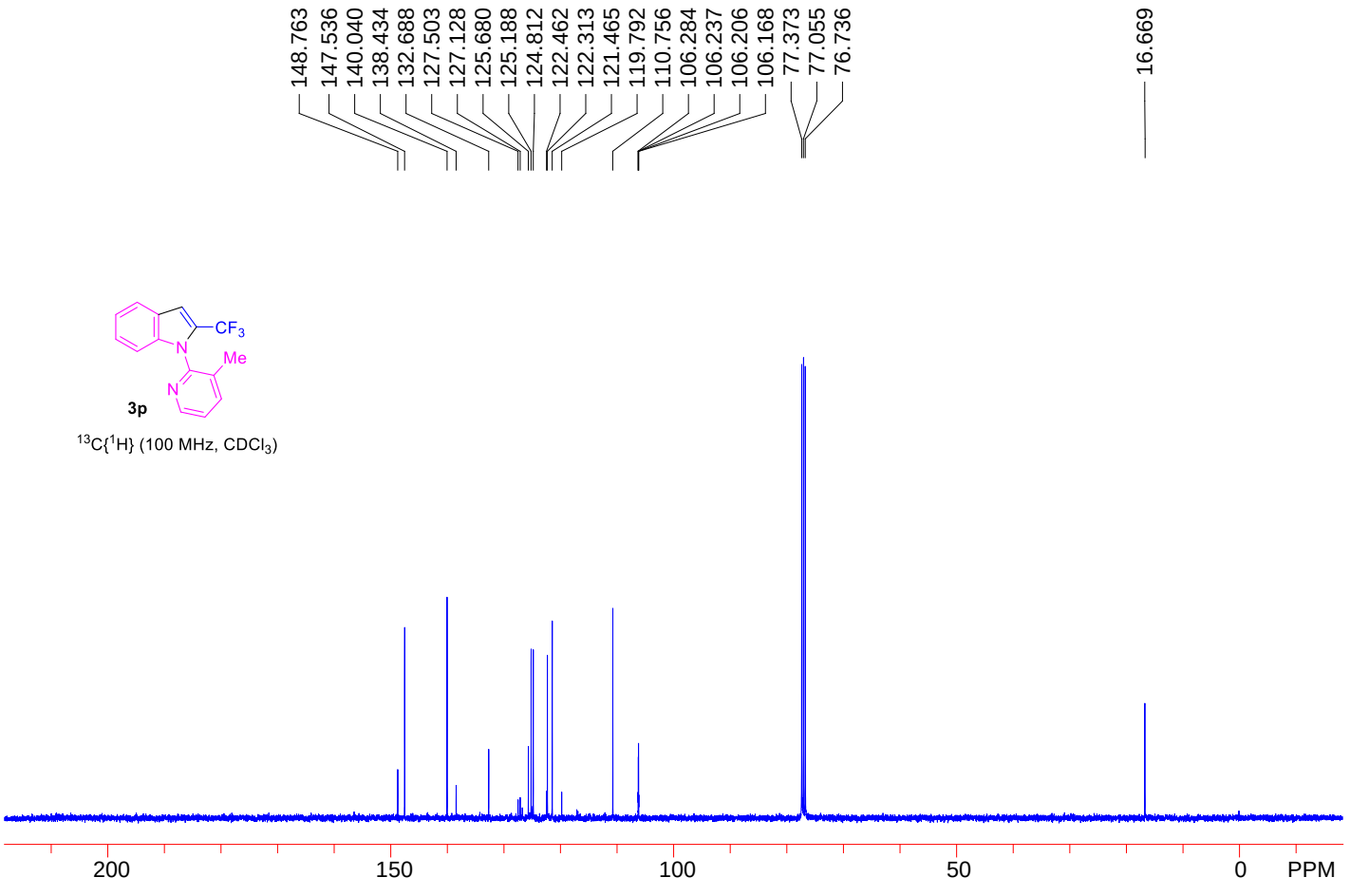
3o

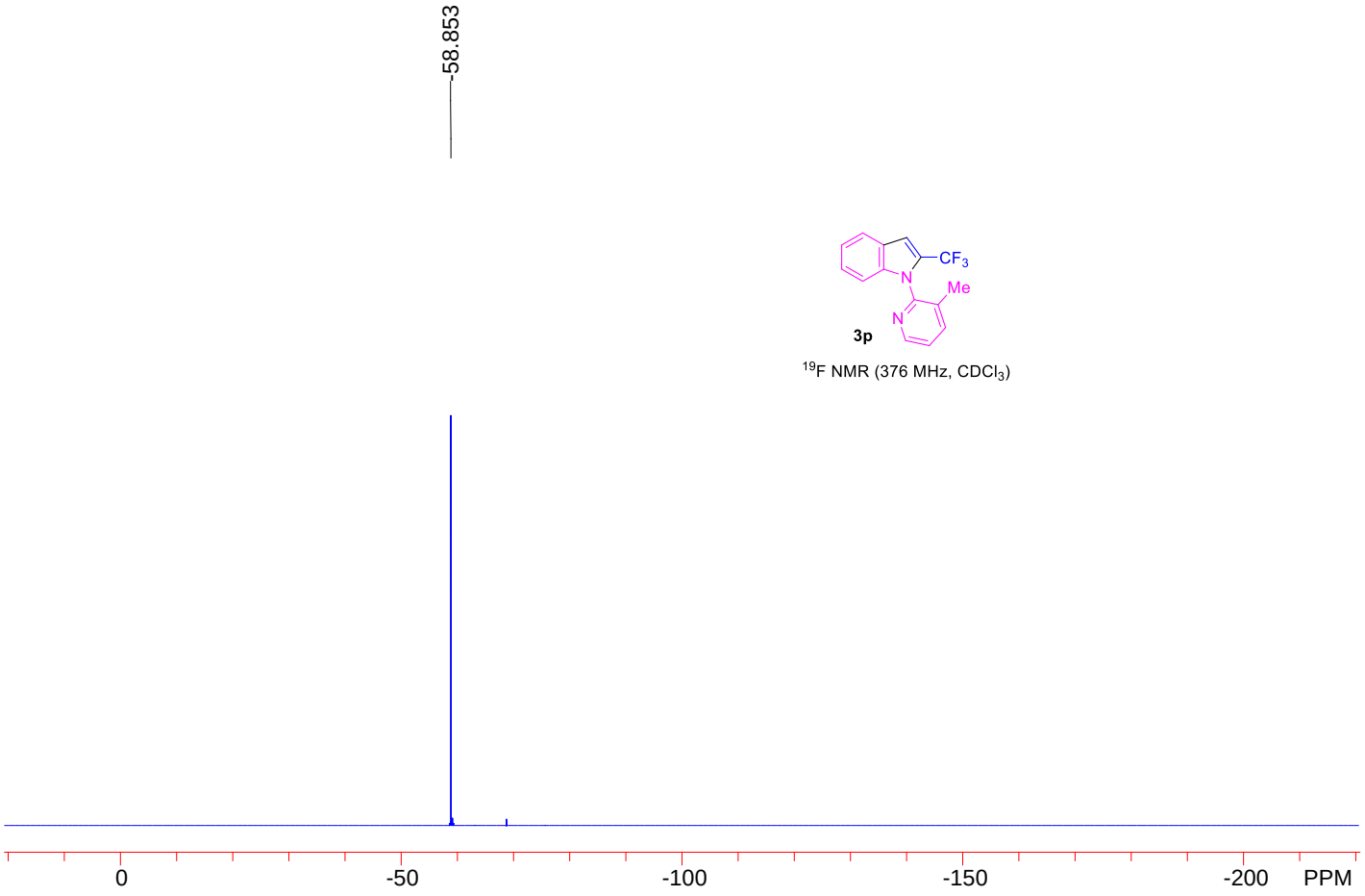
$^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$)




-56.905
CF3
N
N
Me
3o
19F NMR (565 MHz, CDCl3)
0
-50
-100
-150
-200
PPM

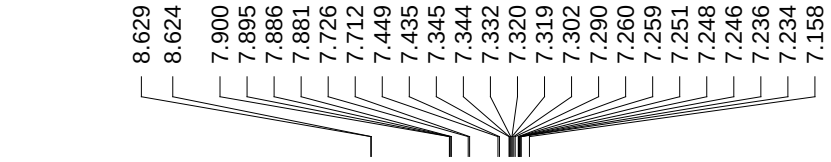

8.527
8.524
8.515
8.513
7.774
7.771
7.754
7.751
7.746
7.726
7.415
7.404
7.396
7.385
7.288
7.268
7.250
7.231
7.229
7.211
7.209
7.194
7.192
7.132
6.853
6.852
6.834
6.832
2.004
CF3
N
Me
N
3p
1H NMR (400 MHz, CDCl3)
3.03
2.03
2.20
1.00
1.02
1.02
1.02
10
8
6
4
2
0
PPM

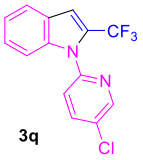

148.763
147.536
140.040
138.434
132.688
127.503
127.128
125.680
125.188
124.812
122.462
122.313
121.465
119.792
110.756
106.284
106.237
106.206
106.168
77.373
77.055
76.736
16.669
CF3
N
Me
N
3p
13C{1H} (100 MHz, CDCl3)
200
150
100
50
0
PPM



3p

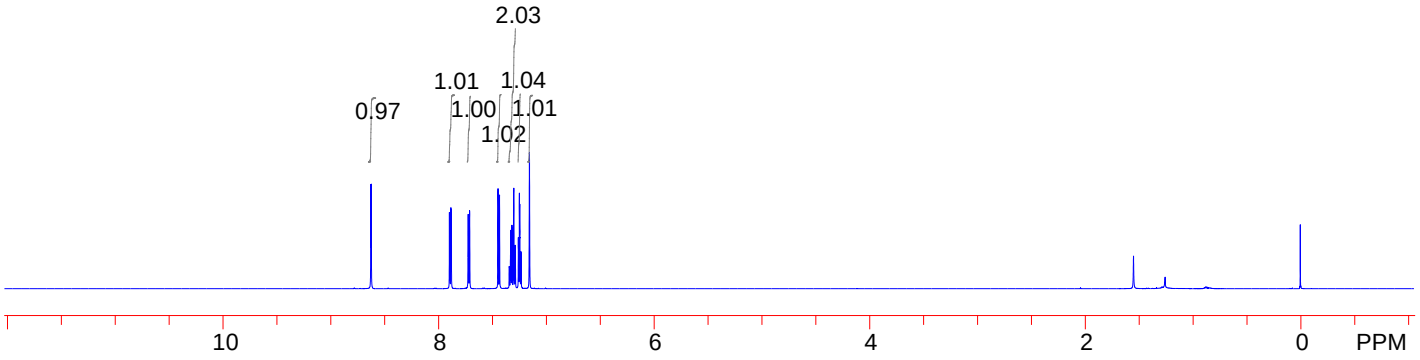
^{19}F NMR (376 MHz, $CDCl_3$)

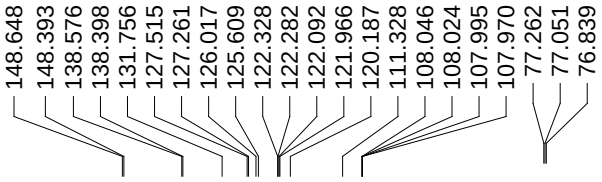


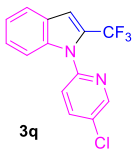


3q

^{1}H NMR (600 MHz, $CDCl_3$)

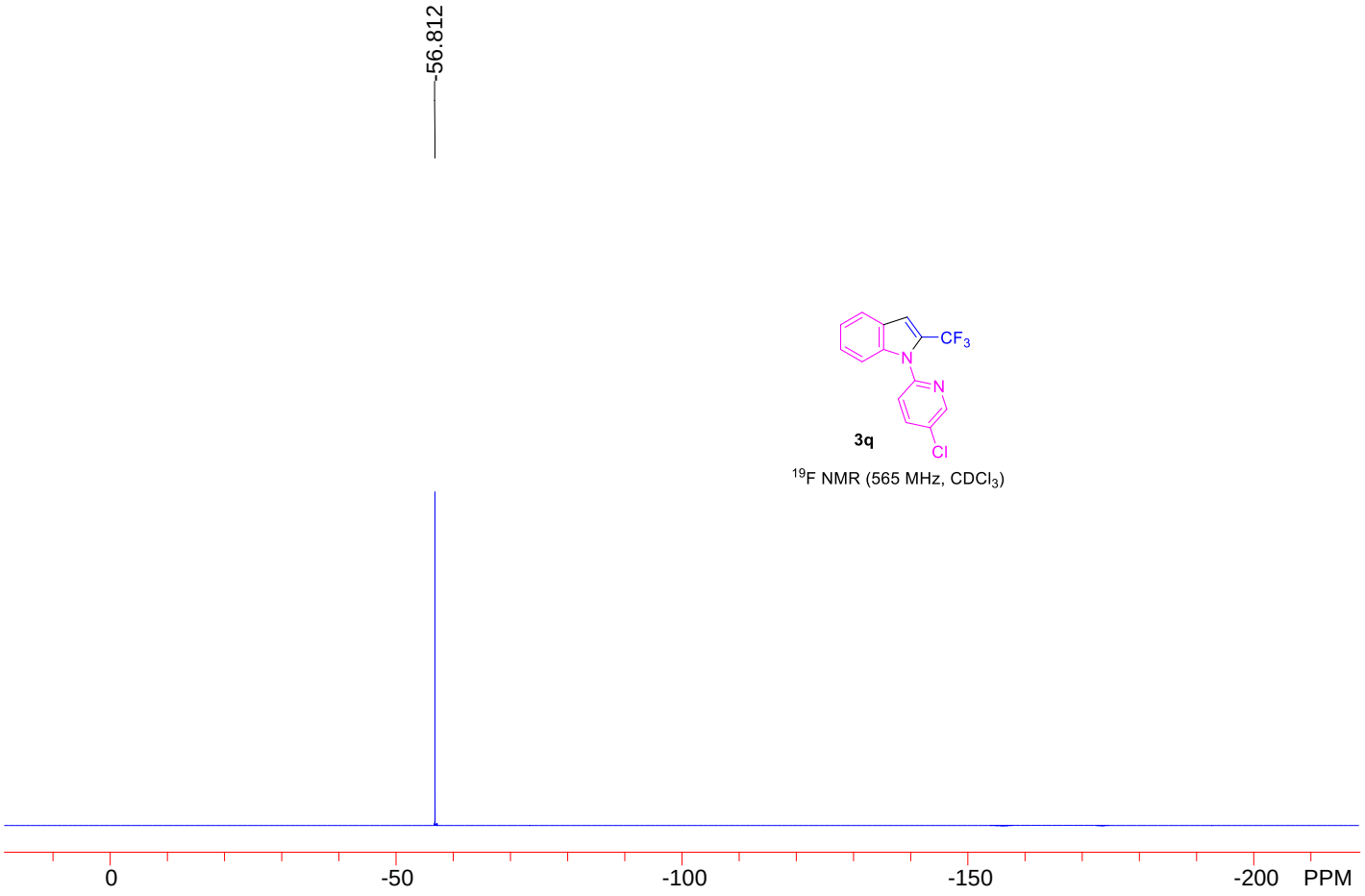






3q

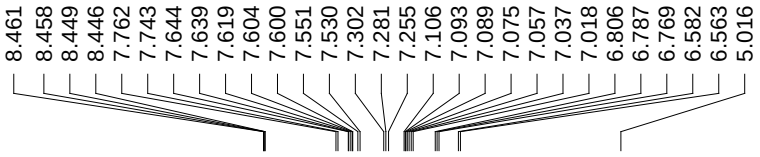
$^{13}C\{^{1}H\}$ (150 MHz, $CDCl_3$)

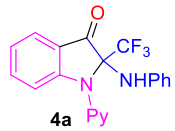


3q

^{19}F NMR (565 MHz, $CDCl_3$)

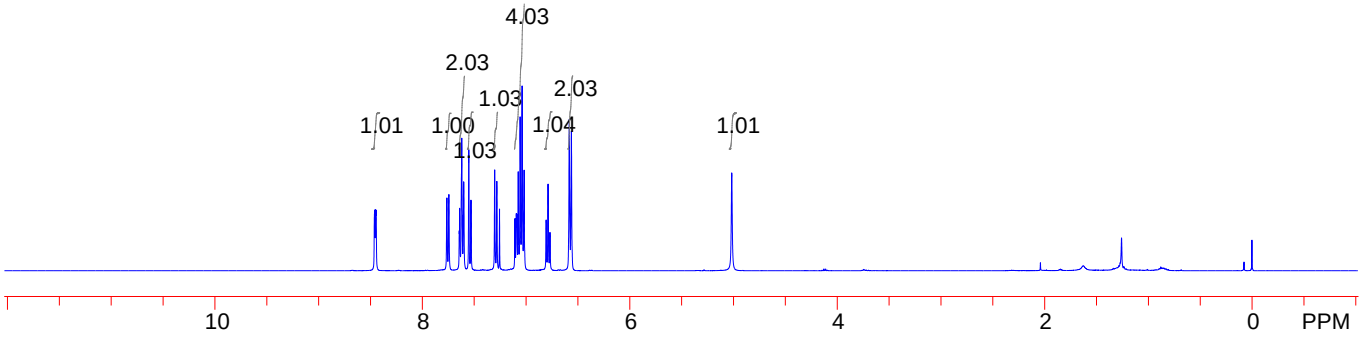
VI. NMR spectra of 4a-4aa

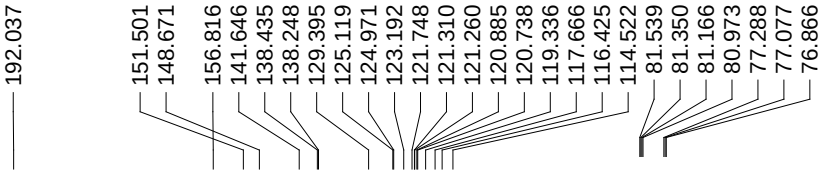


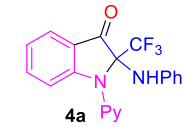


4a

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

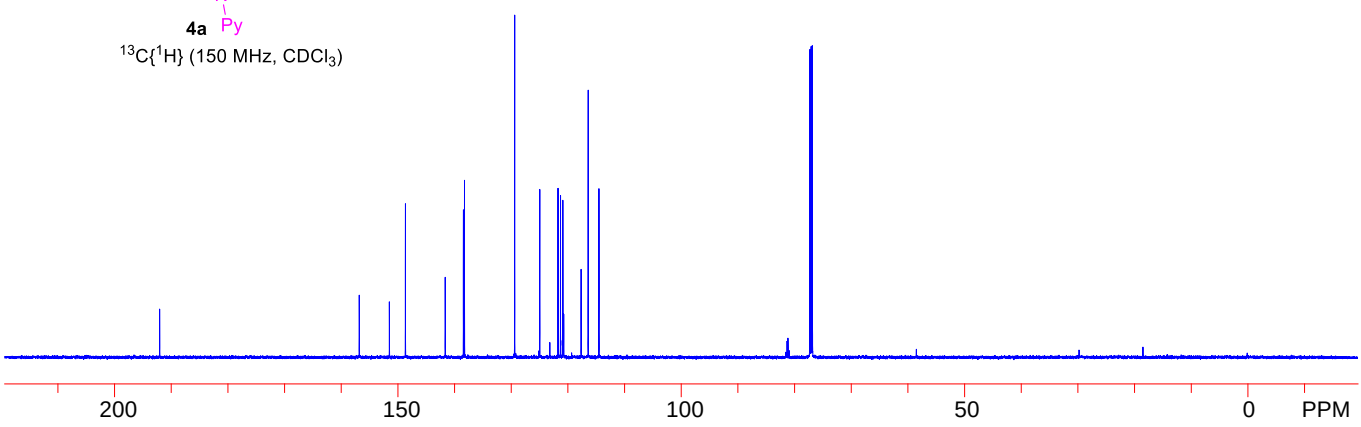


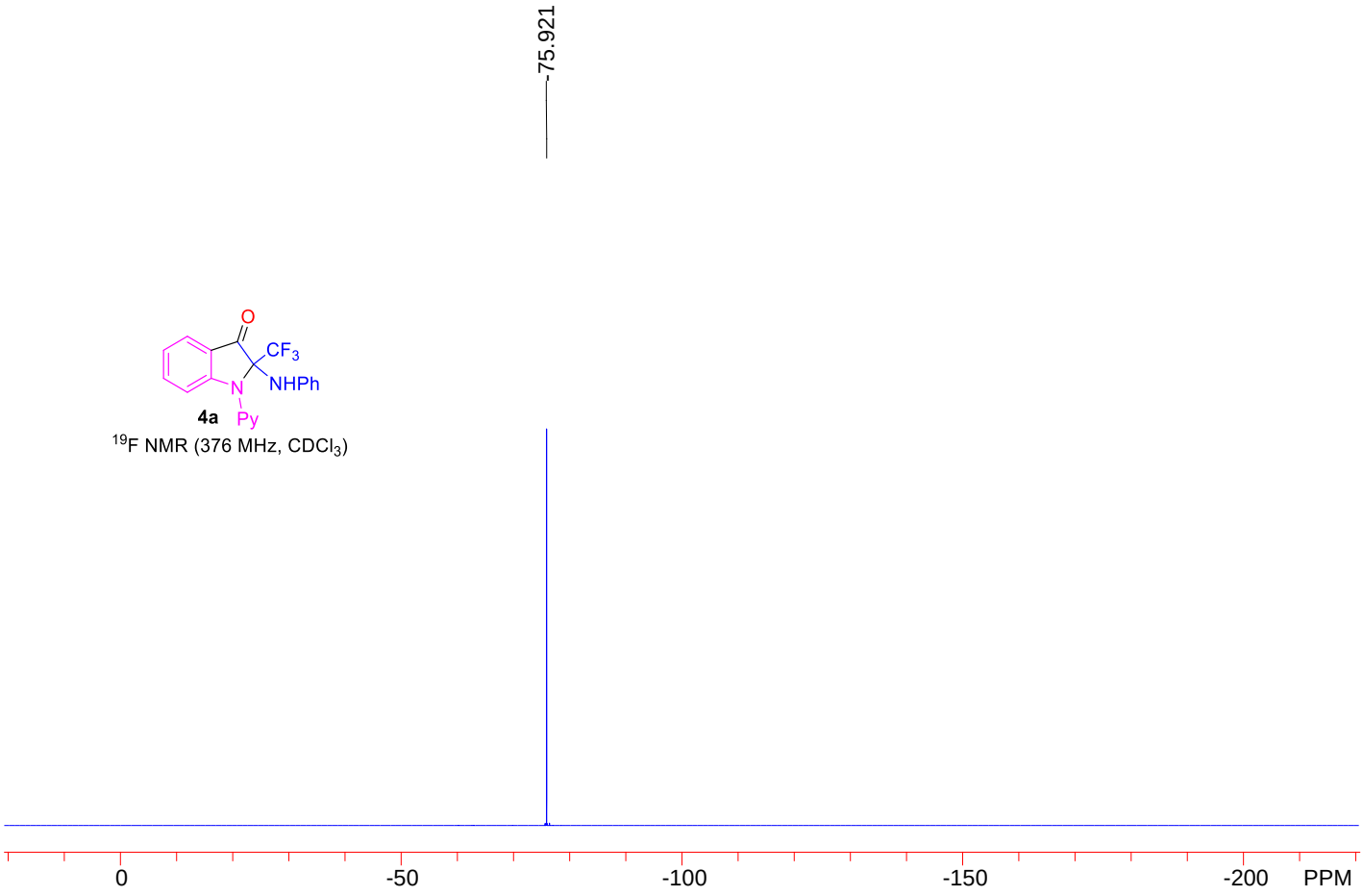


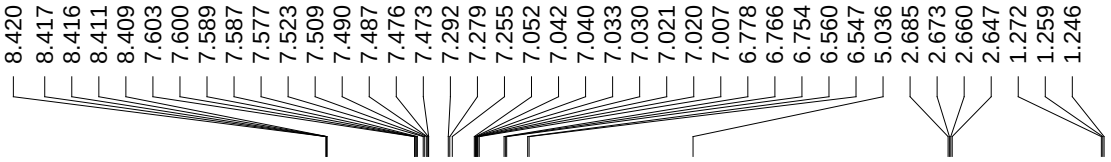


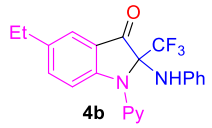
4a

$^{13}C\{^{1}H\}$ (150 MHz, $CDCl_3$)



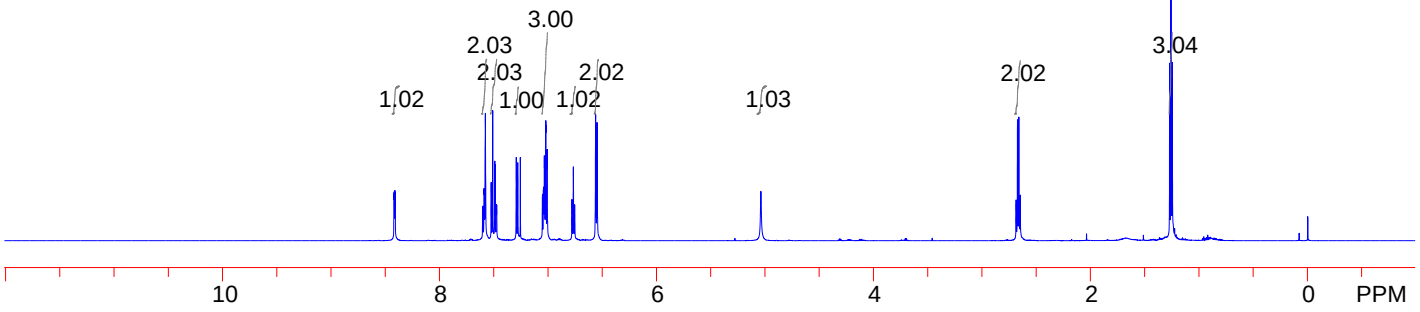

-75.921
O
CF3
NHPh
N
Py
4a
19F NMR (376 MHz, CDCl3)
0
-50
-100
-150
-200
PPM

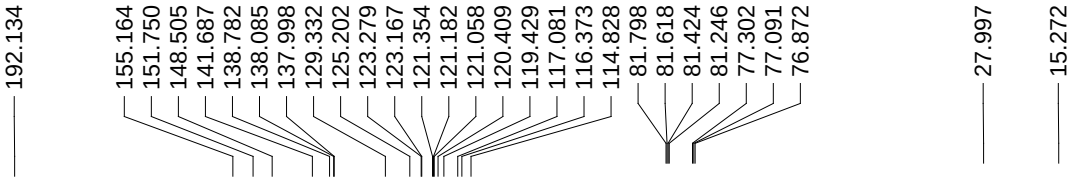


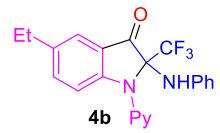


4b

^{1}H NMR (600 MHz, $CDCl_3$)

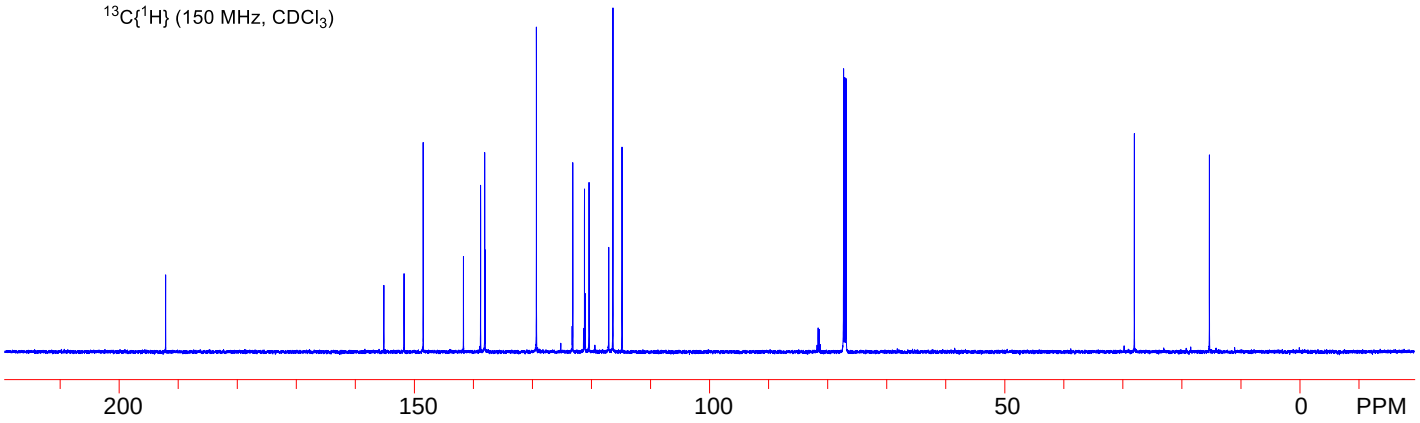


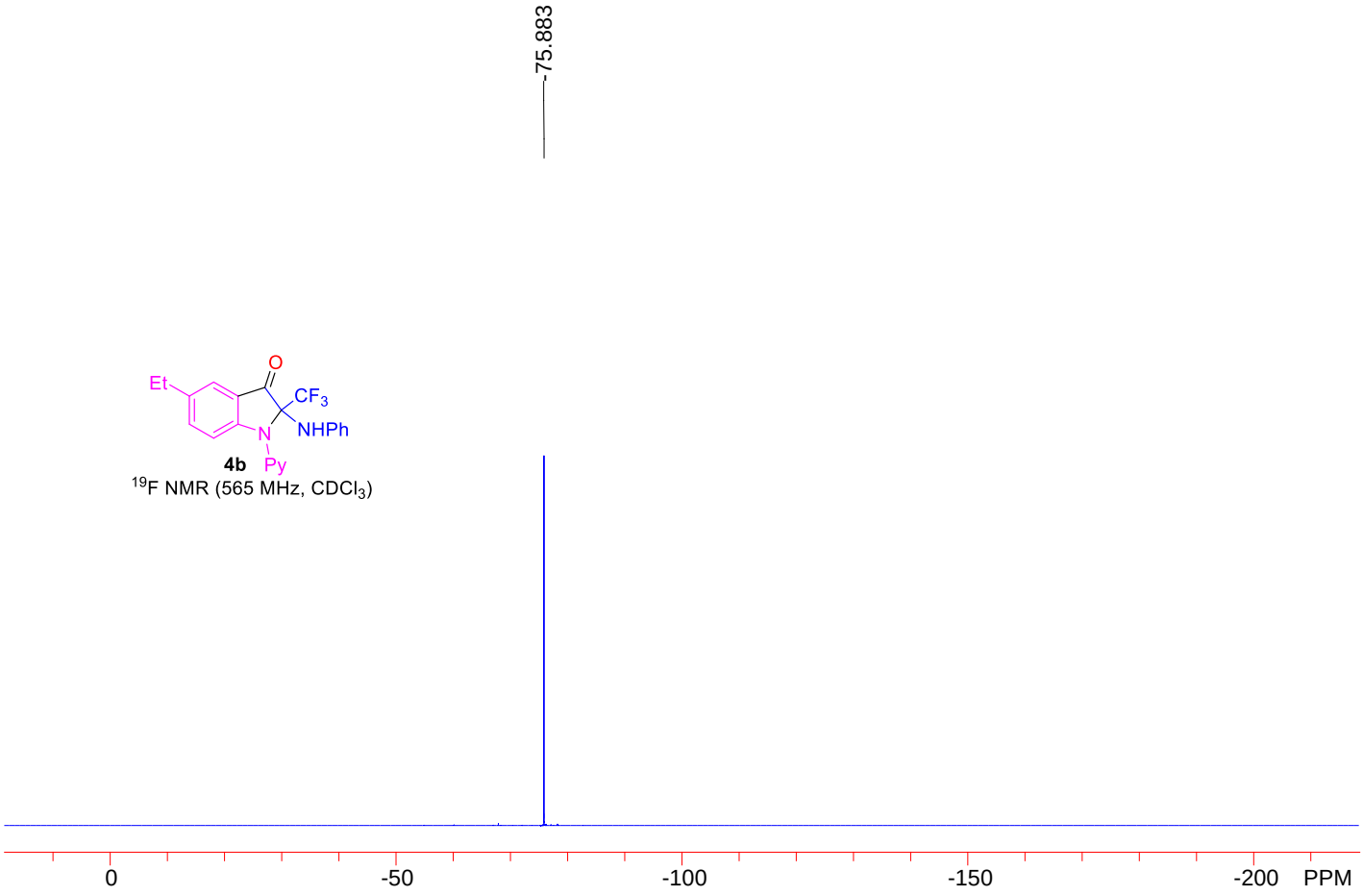




4b

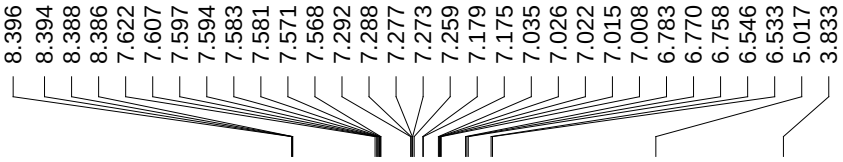
$^{13}C\{^{1}H\}$ (150 MHz, $CDCl_3$)

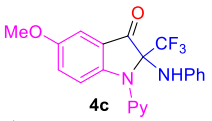




4b

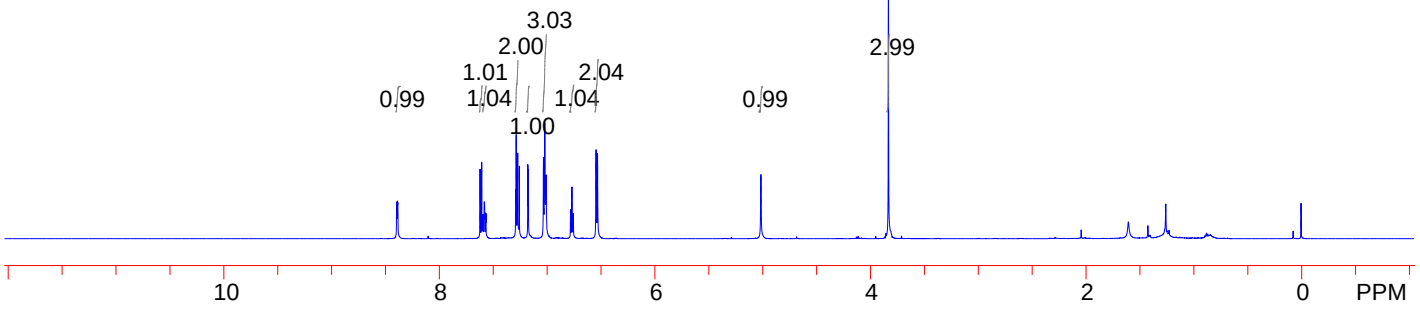
^{19}F NMR (565 MHz, $CDCl_3$)

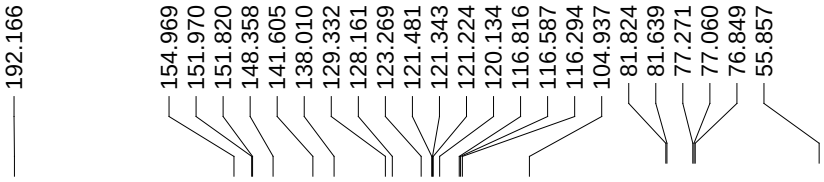


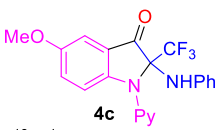


4c

^{1}H NMR (600 MHz, $CDCl_3$)

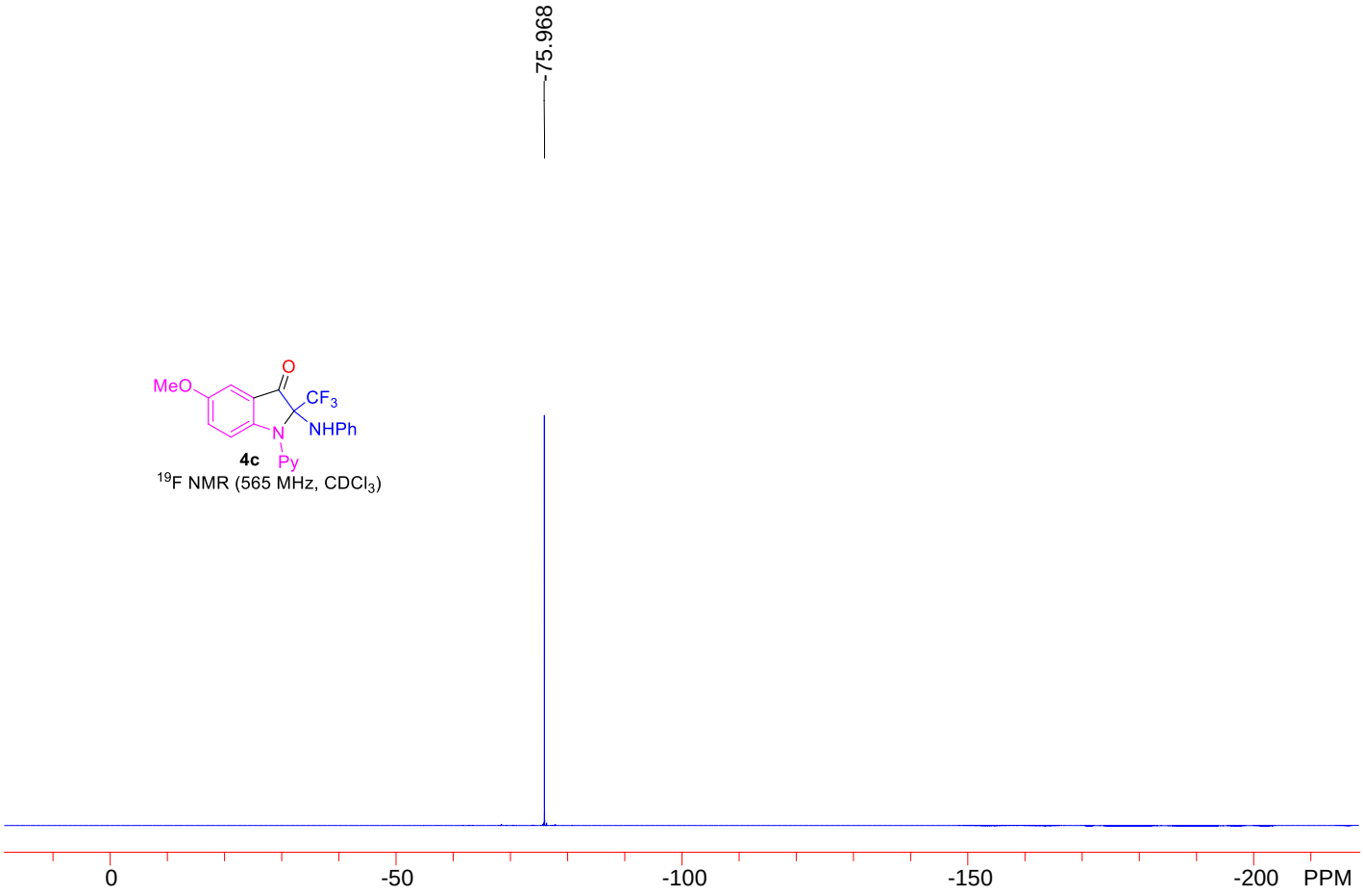


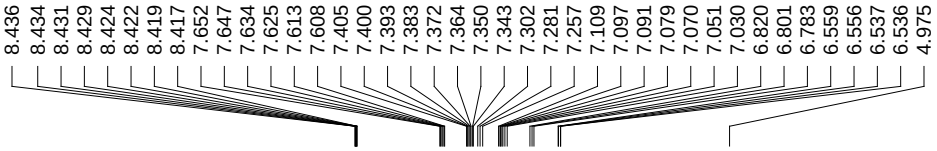


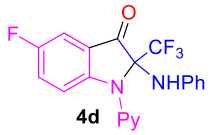


4c

$^{13}C\{^{1}H\}$ (150 MHz, $CDCl_3$)

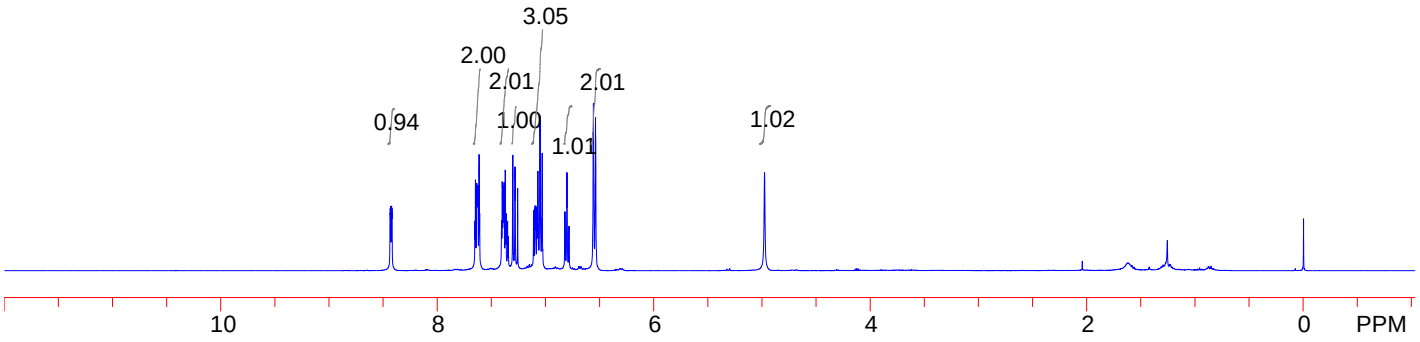

-75.968
MeO
O
CF3
NHPh
N
Py
4c
19F NMR (565 MHz, CDCl3)
0
-50
-100
-150
-200
PPM

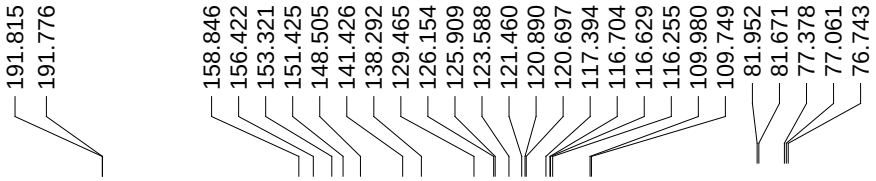


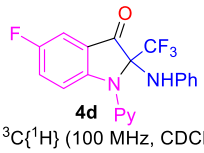


4d

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

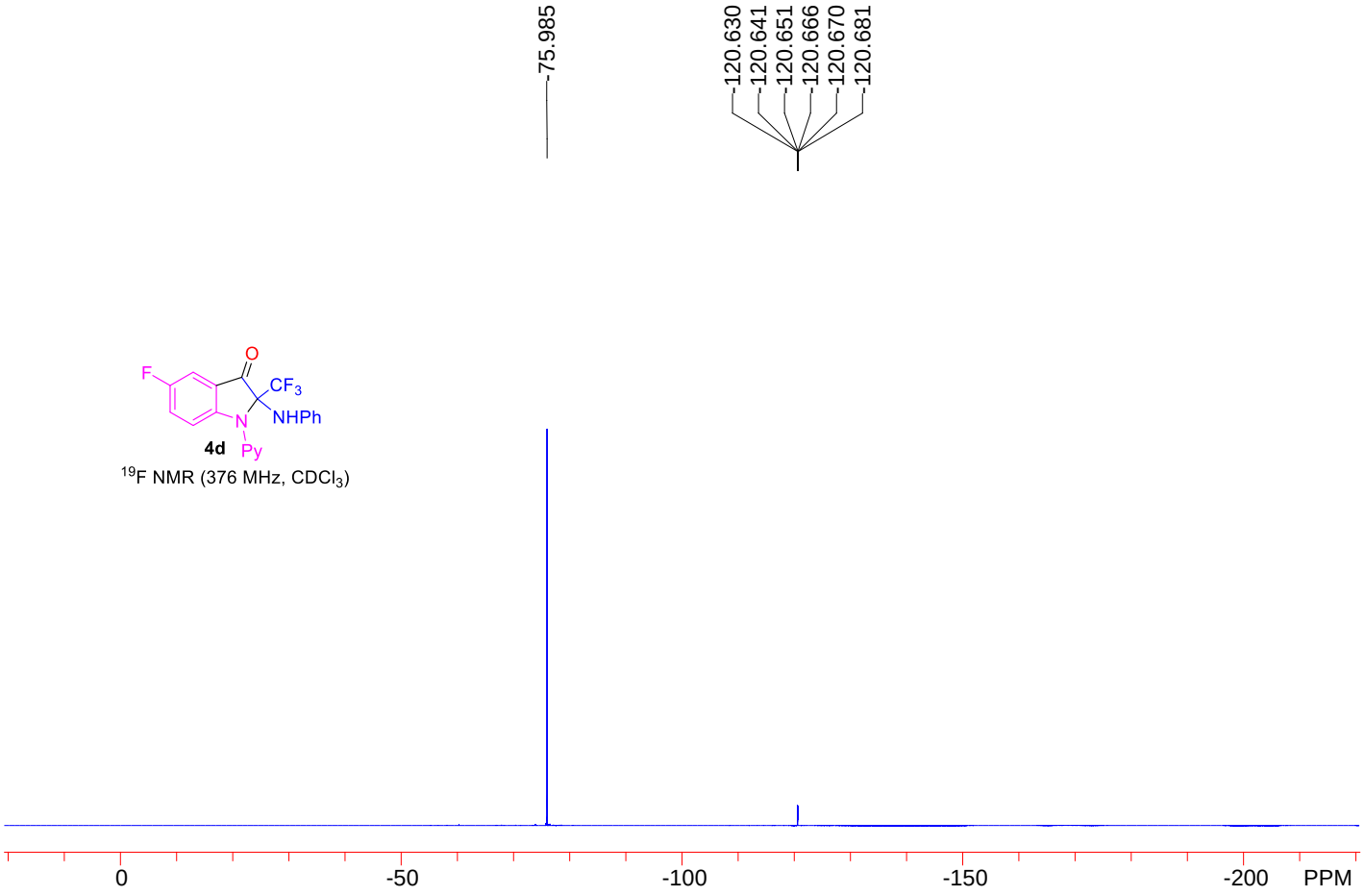


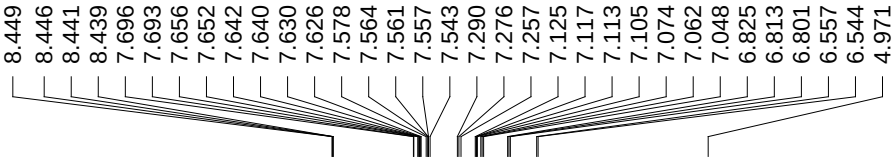


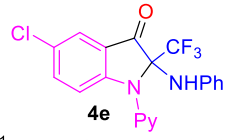


4d

$^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$)

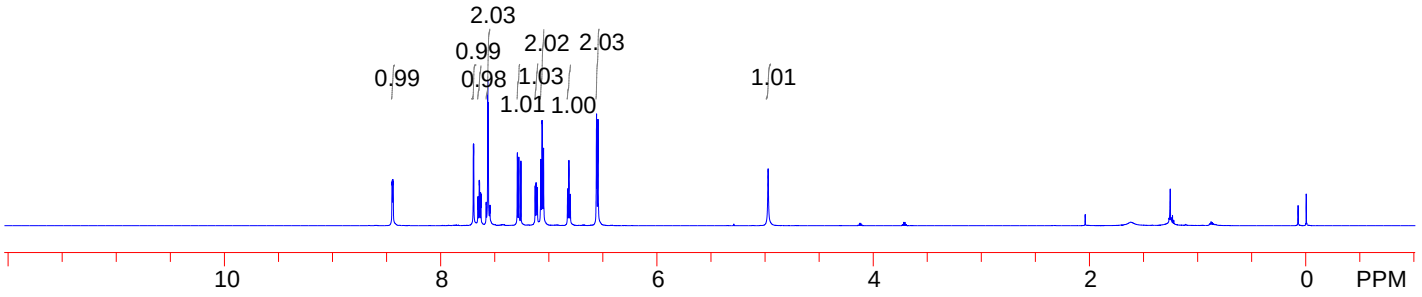

-75.985
-120.630
-120.641
-120.651
-120.666
-120.670
-120.681
F
O
CF3
NHPh
N
Py
4d
19F NMR (376 MHz, CDCl3)
0
-50
-100
-150
-200
PPM

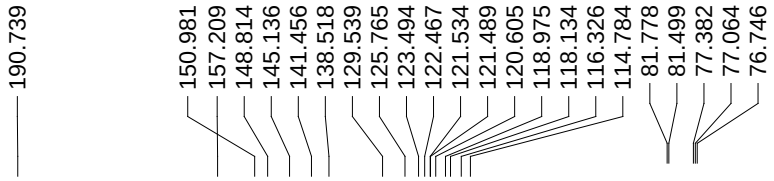


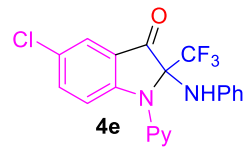


4e

^{1}H NMR (600 MHz, $CDCl_3$)

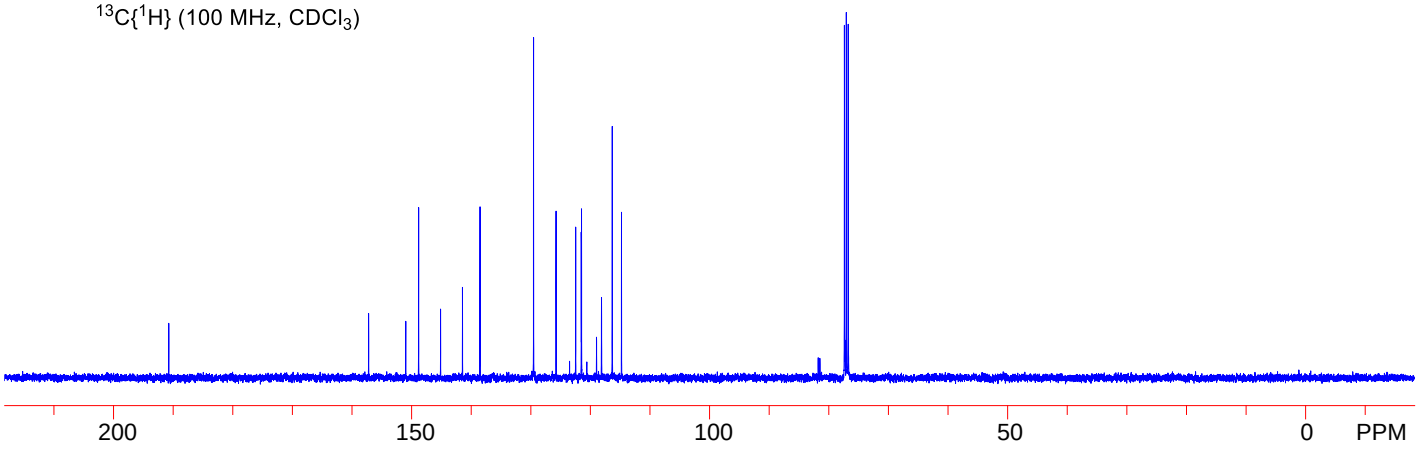


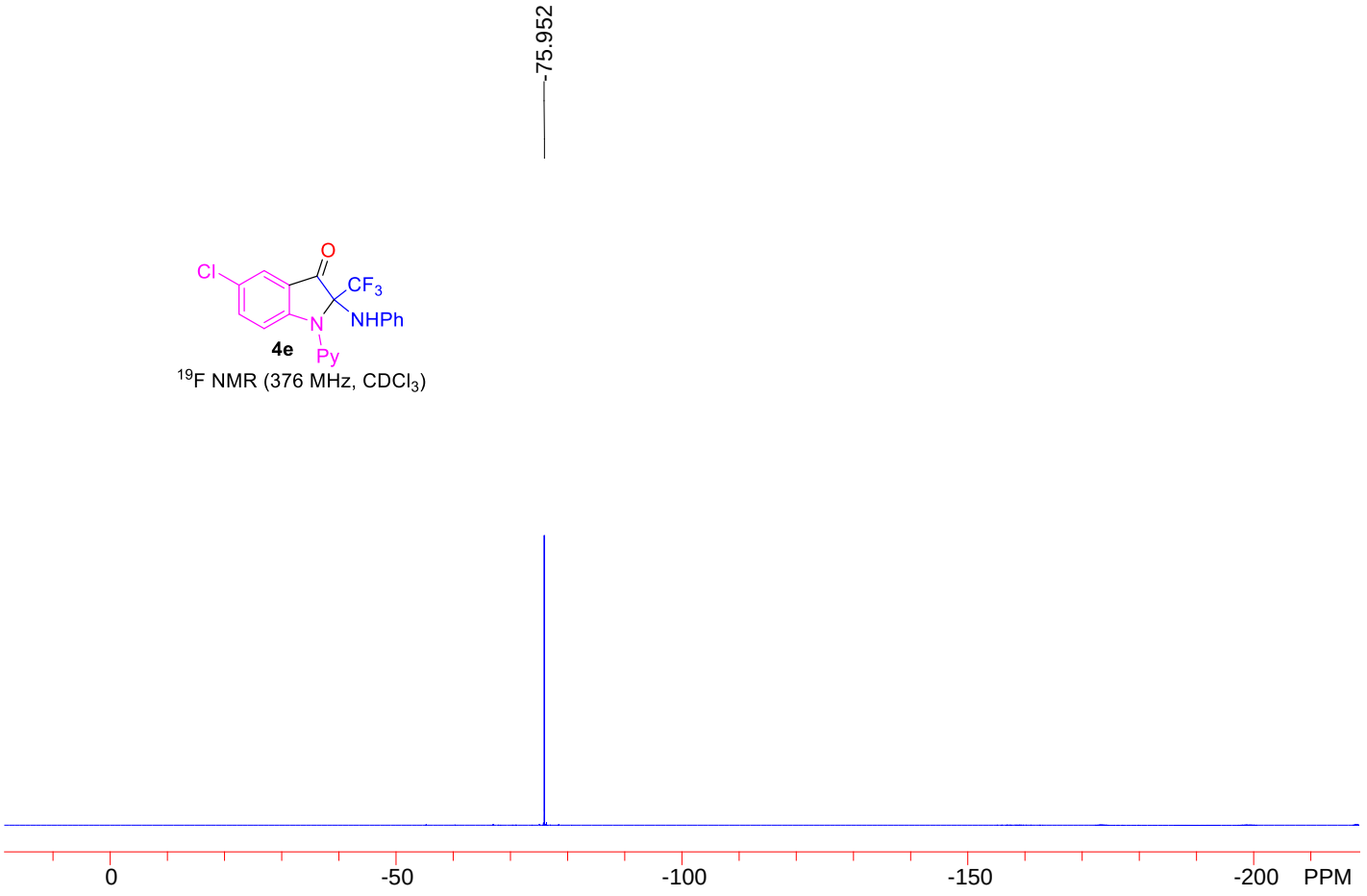




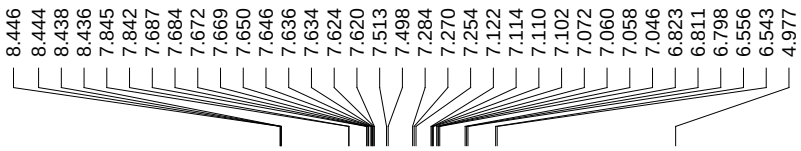
4e

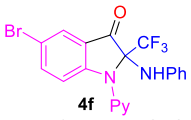
$^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$)





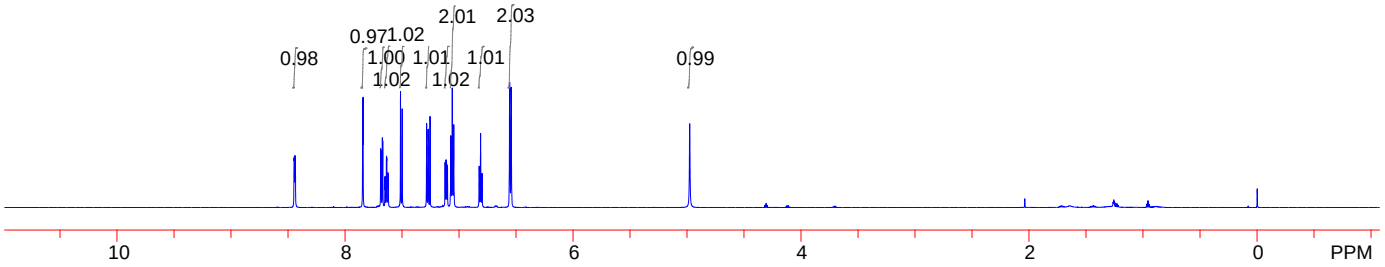
^{19}F NMR (376 MHz, $CDCl_3$)

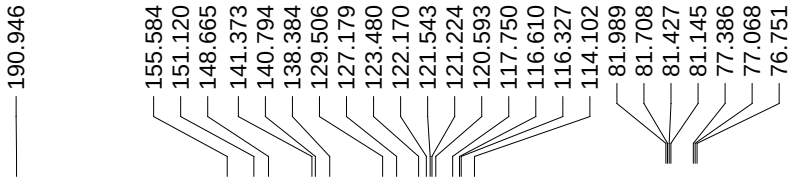


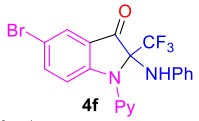


4f

^{1}H NMR (600 MHz, $CDCl_3$)

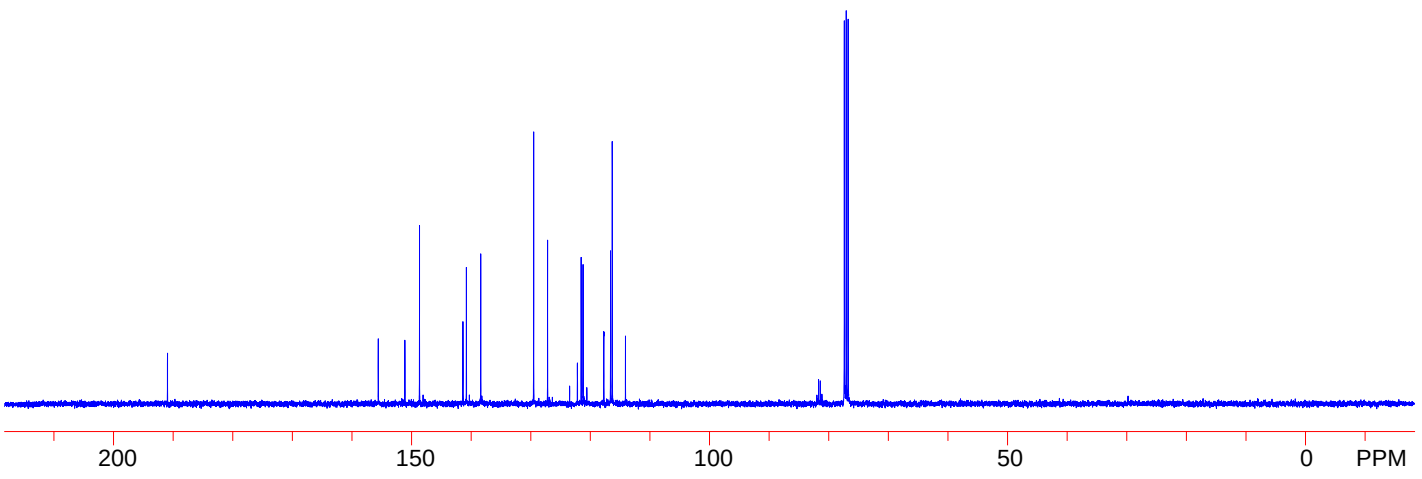


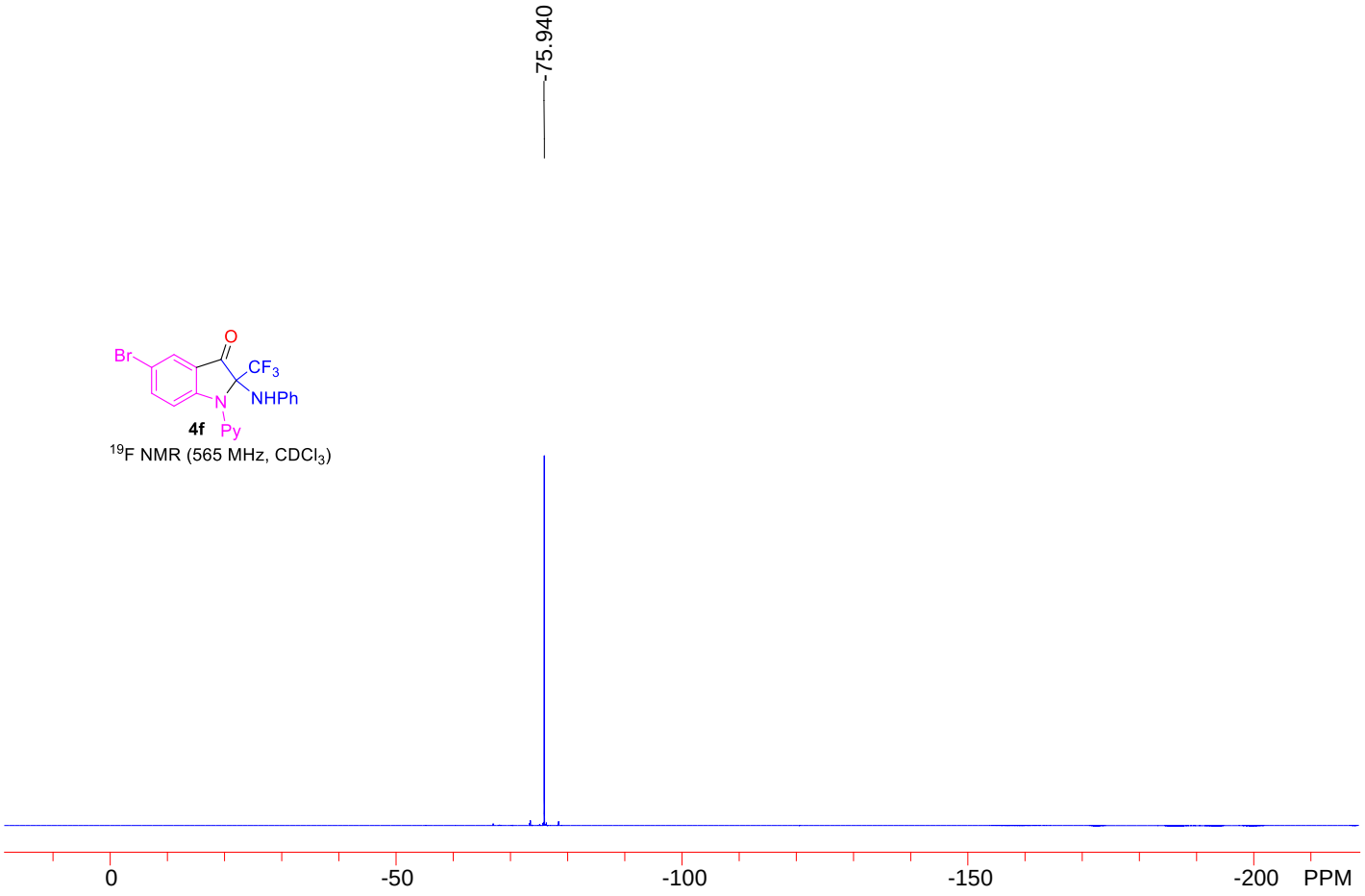


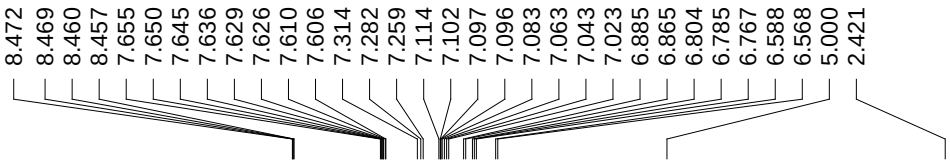


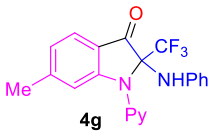
4f

$^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$)



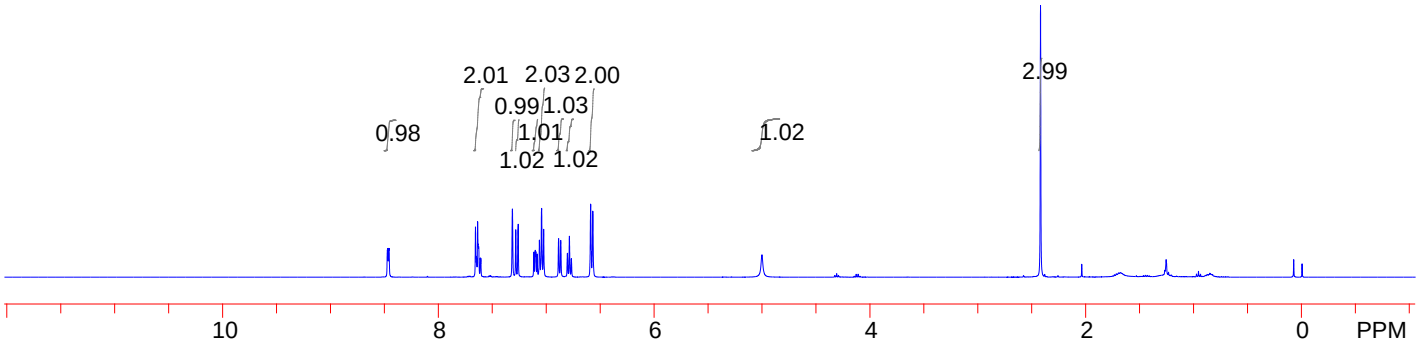

-75.940
Br
O
CF3
NHPh
N
Py
4f
19F NMR (565 MHz, CDCl3)
0
-50
-100
-150
-200
PPM

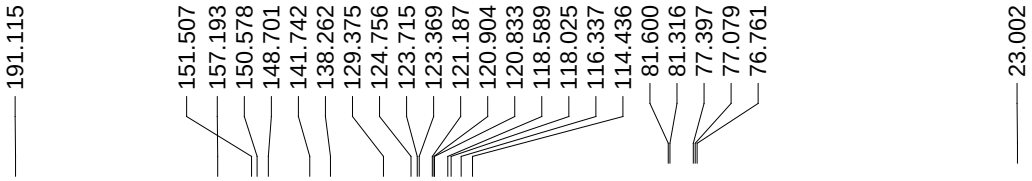


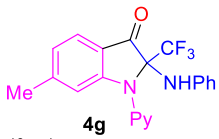


4g

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

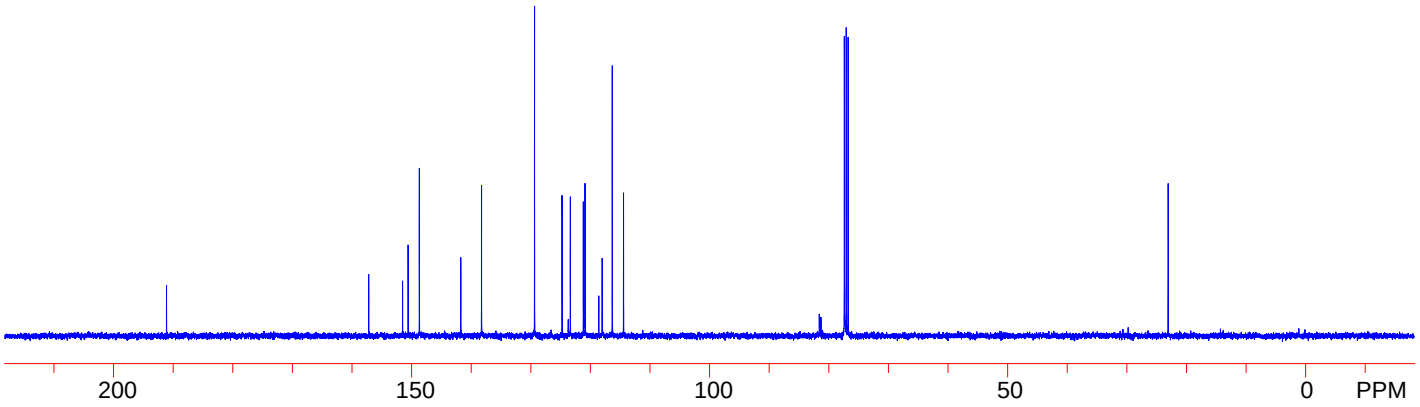


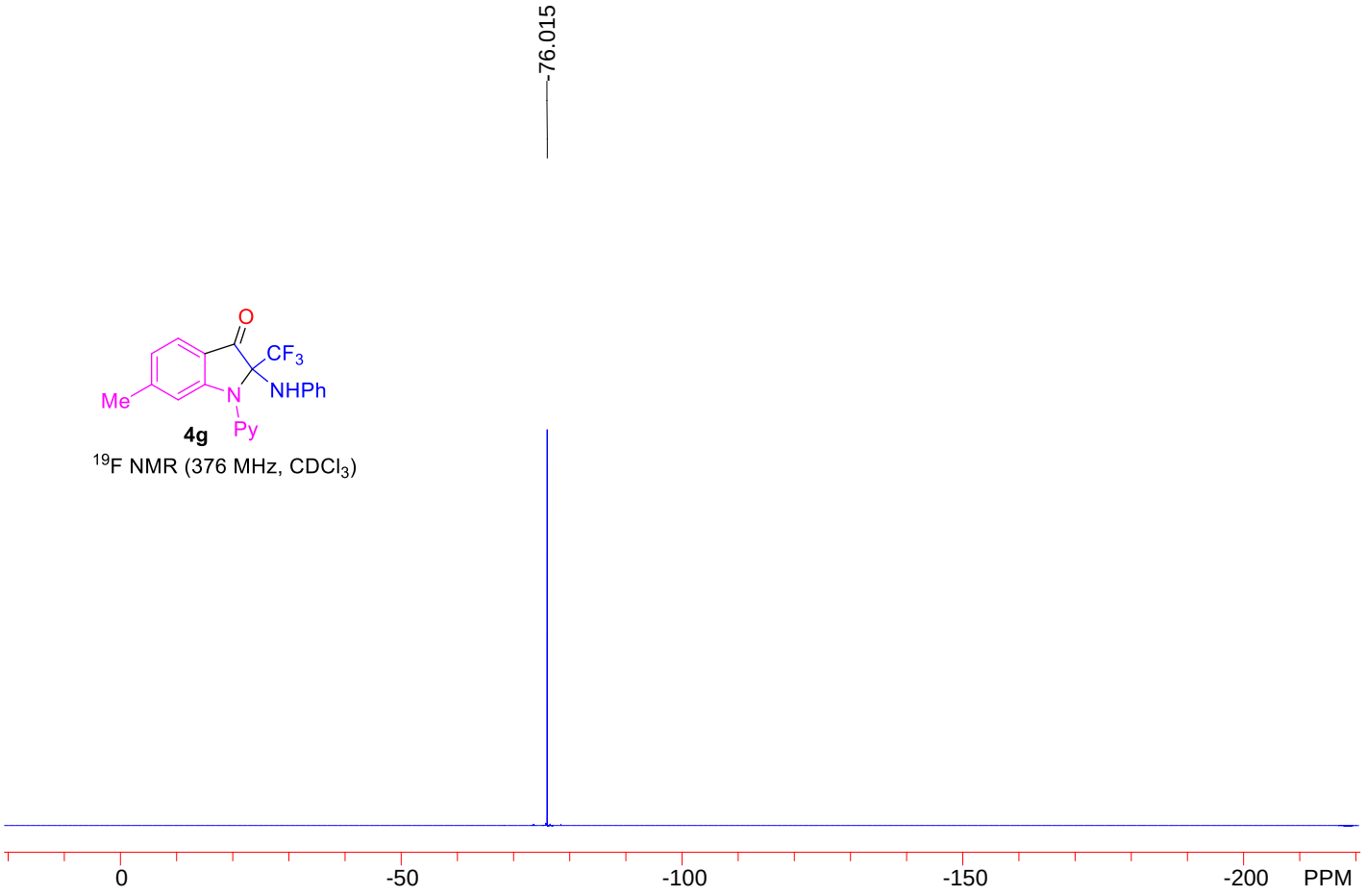




4g

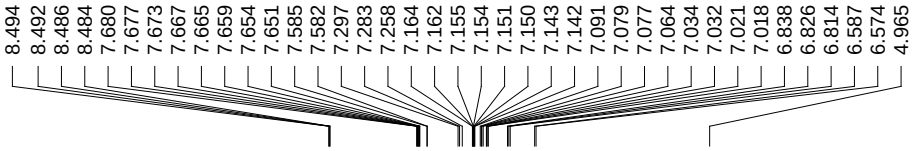
$^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$)

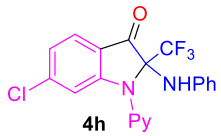




4g

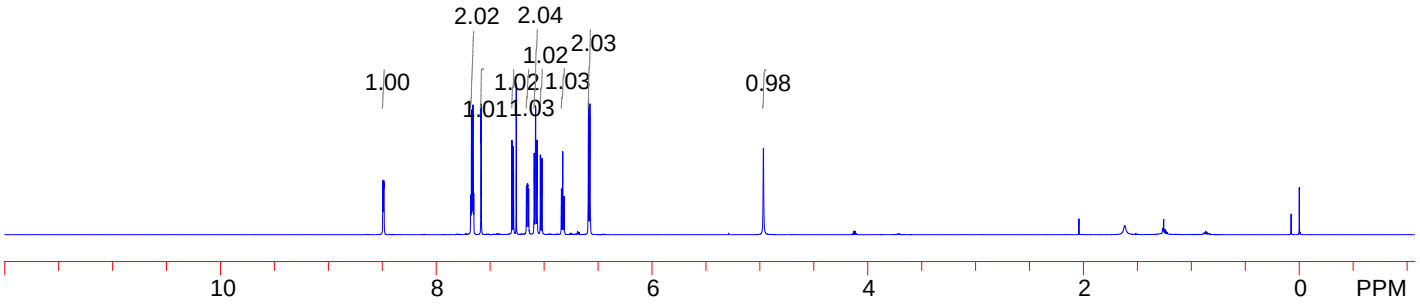
^{19}F NMR (376 MHz, $CDCl_3$)

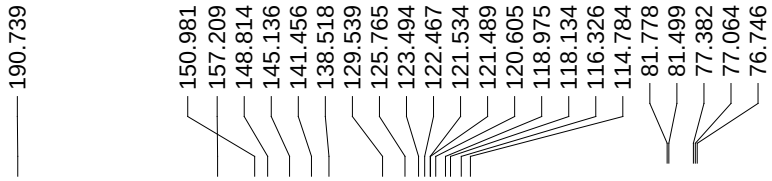


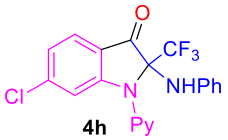


4h

^{1}H NMR (600 MHz, $CDCl_3$)

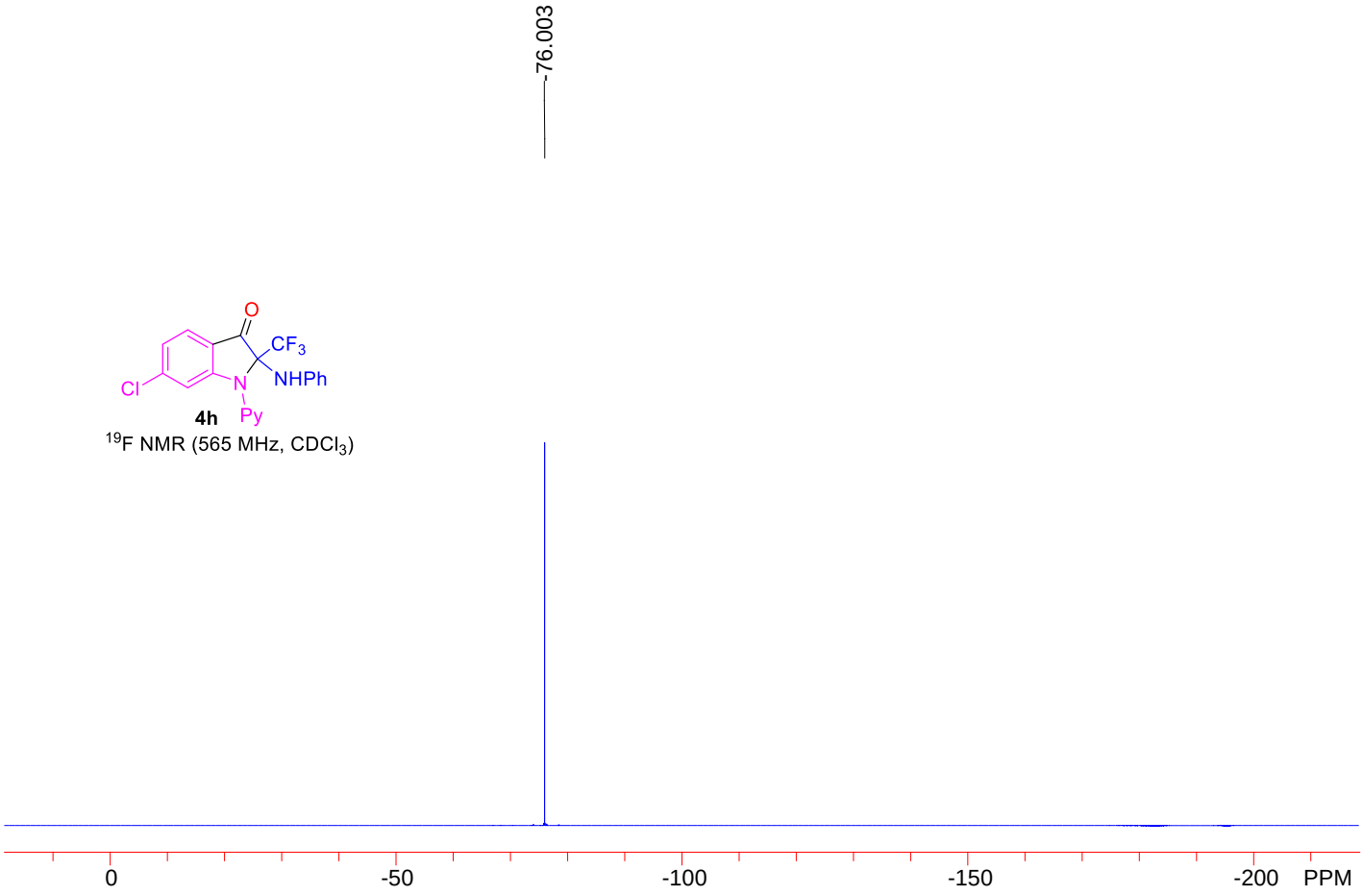






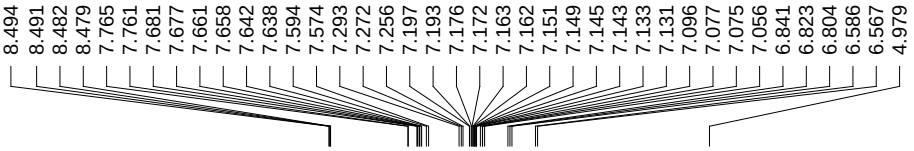
4h

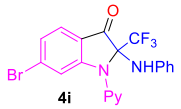
$^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$)



4h

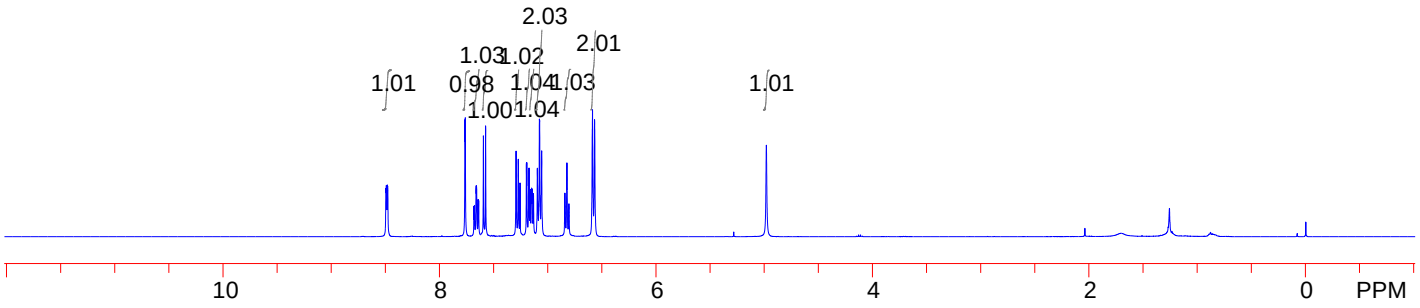
^{19}F NMR (565 MHz, $CDCl_3$)

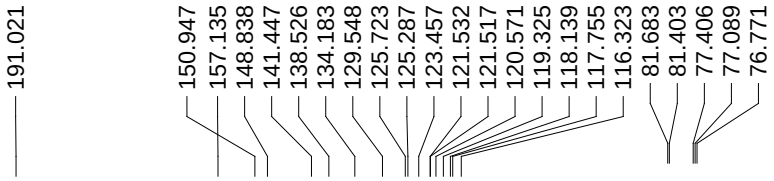


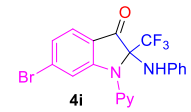


4i

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

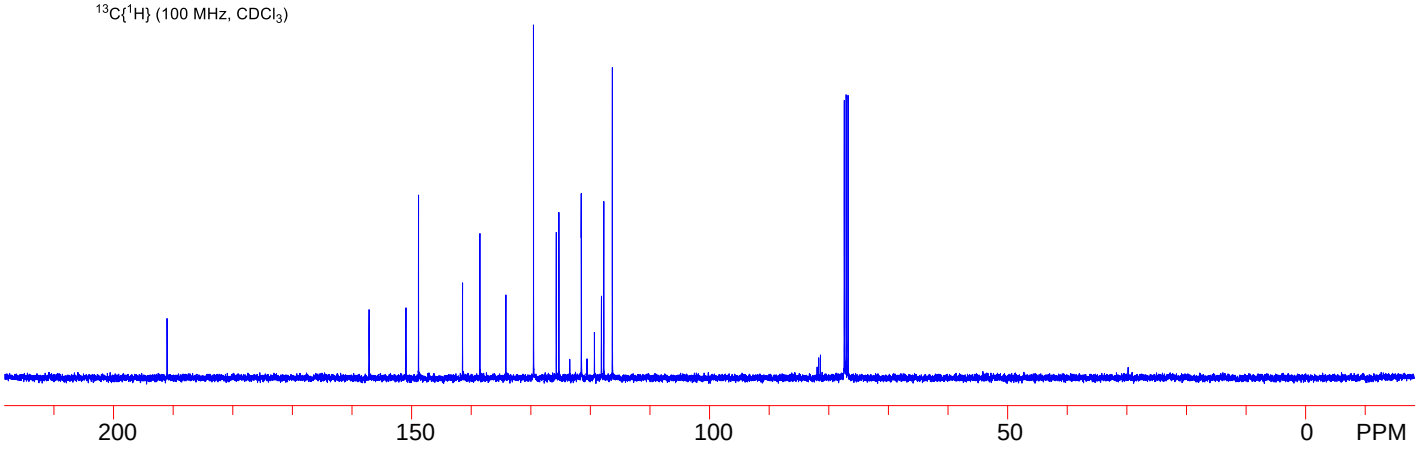


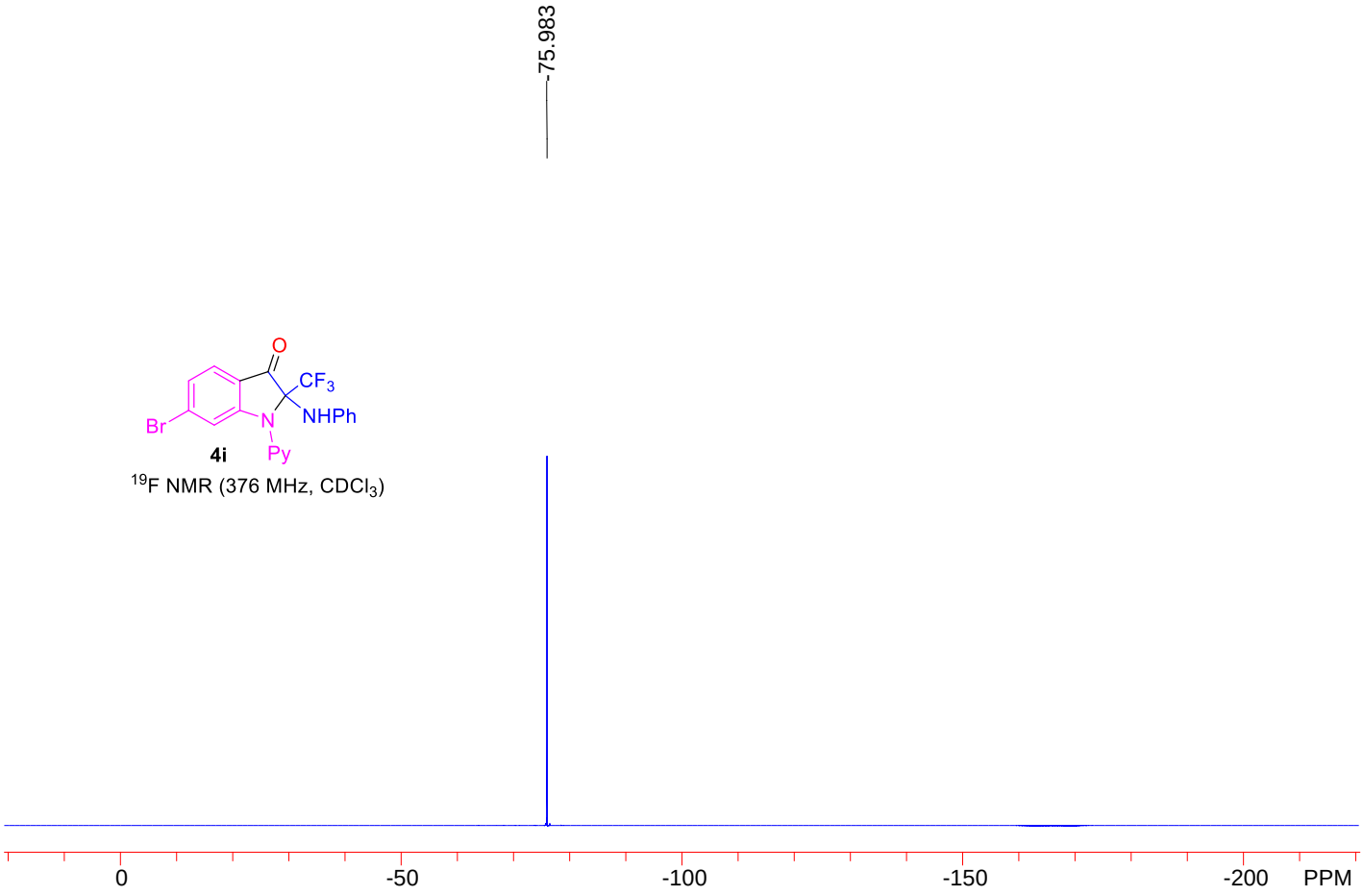


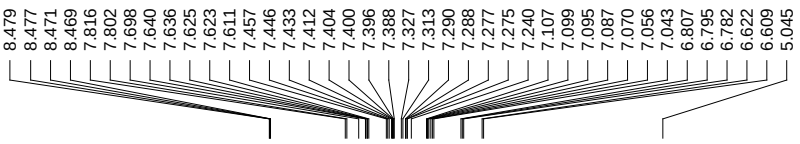


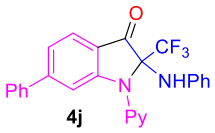
4i

^{13}C{^{1}H} (100 MHz, $CDCl_3$)



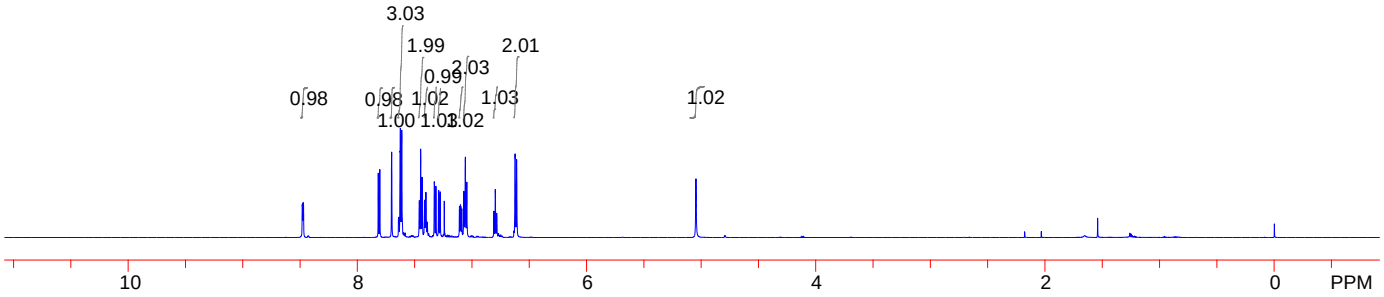

-75.983
O
CF3
NHPh
Br
N
Py
4i
19F NMR (376 MHz, CDCl3)
0
-50
-100
-150
-200
PPM

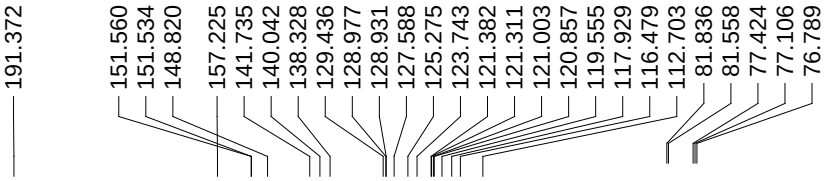


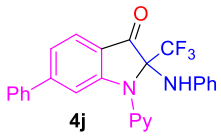


4j

^{1}H NMR (600 MHz, $CDCl_3$)

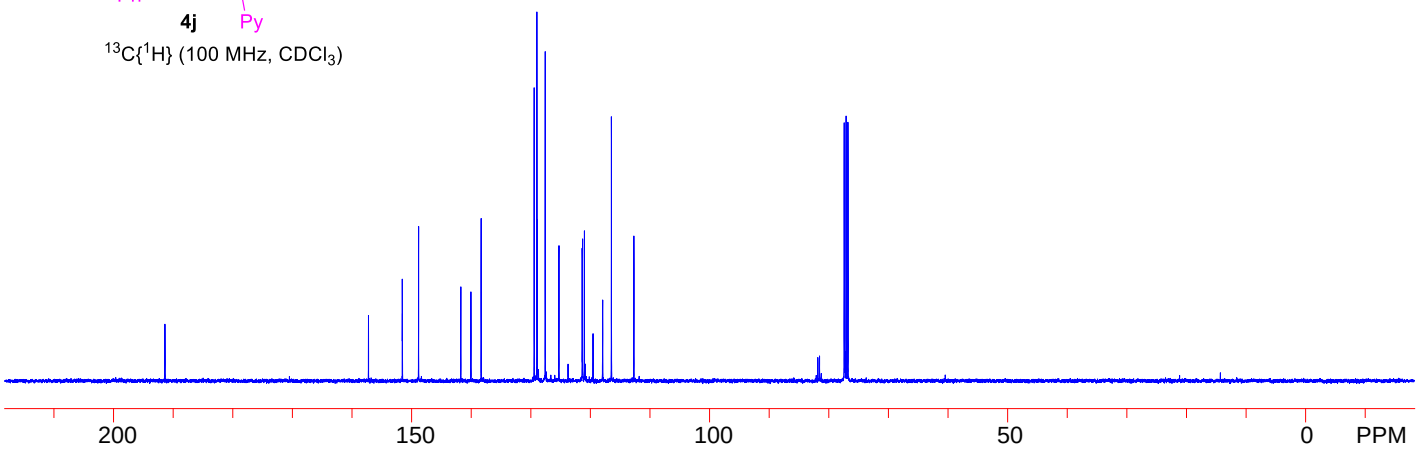


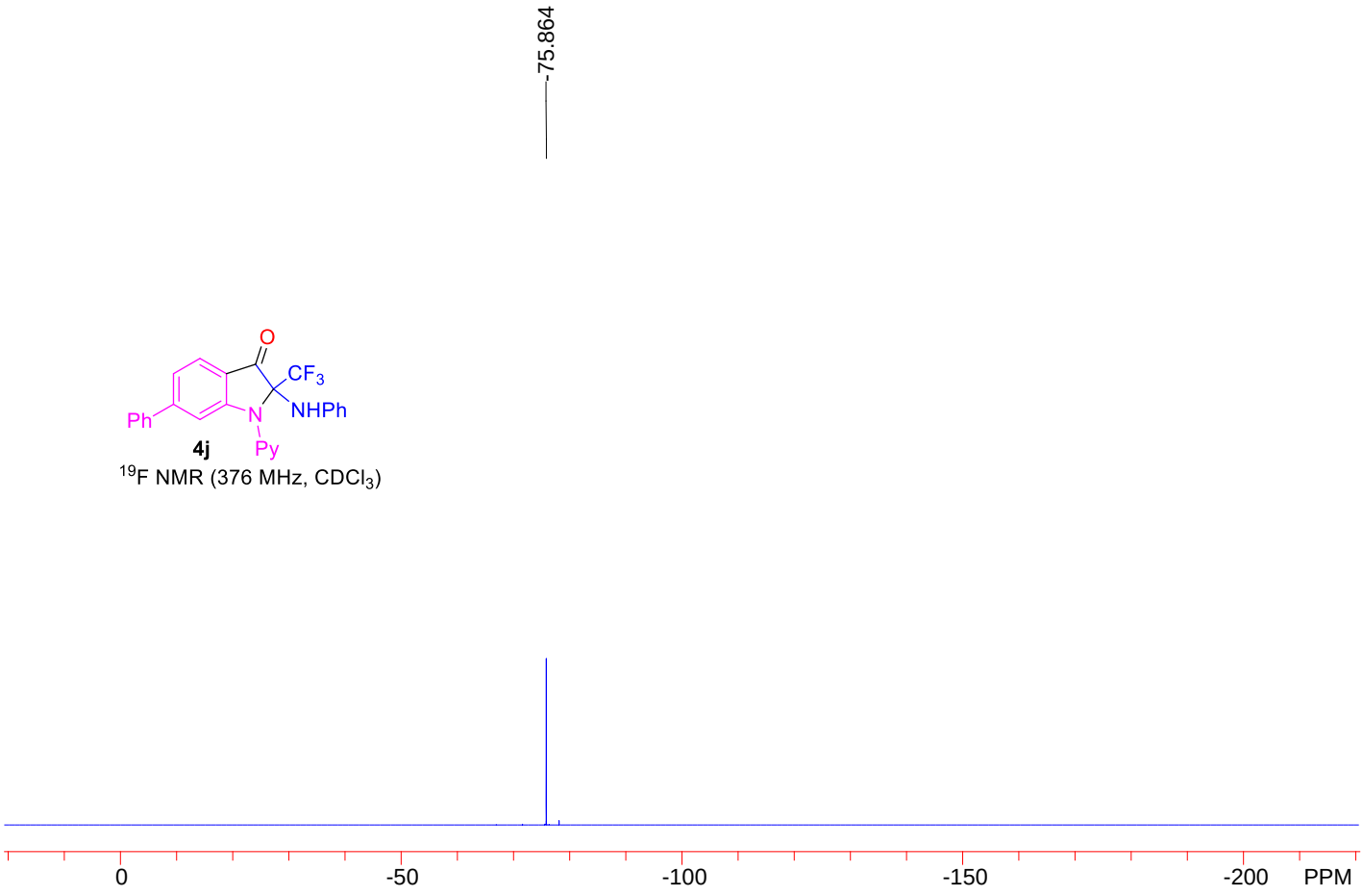


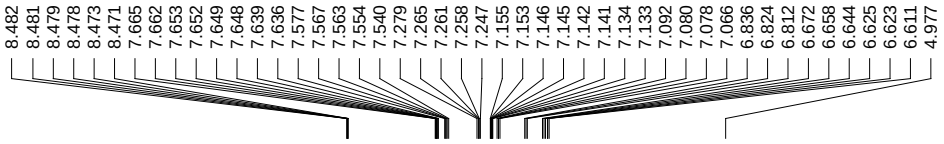


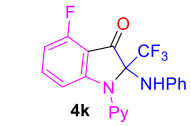
4j

$^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$)



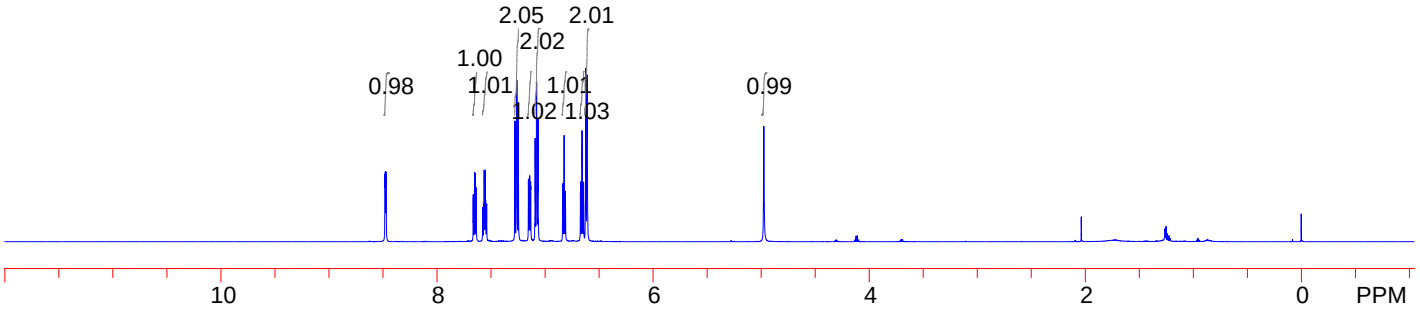

-75.864
O
CF3
NHPh
Ph
N
Py
4j
19F NMR (376 MHz, CDCl3)
0
-50
-100
-150
-200
PPM

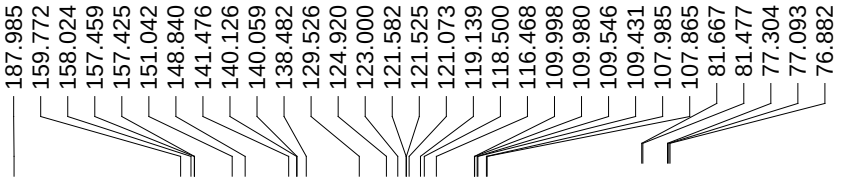


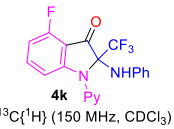


4k

^{1}H NMR (600 MHz, $CDCl_3$)

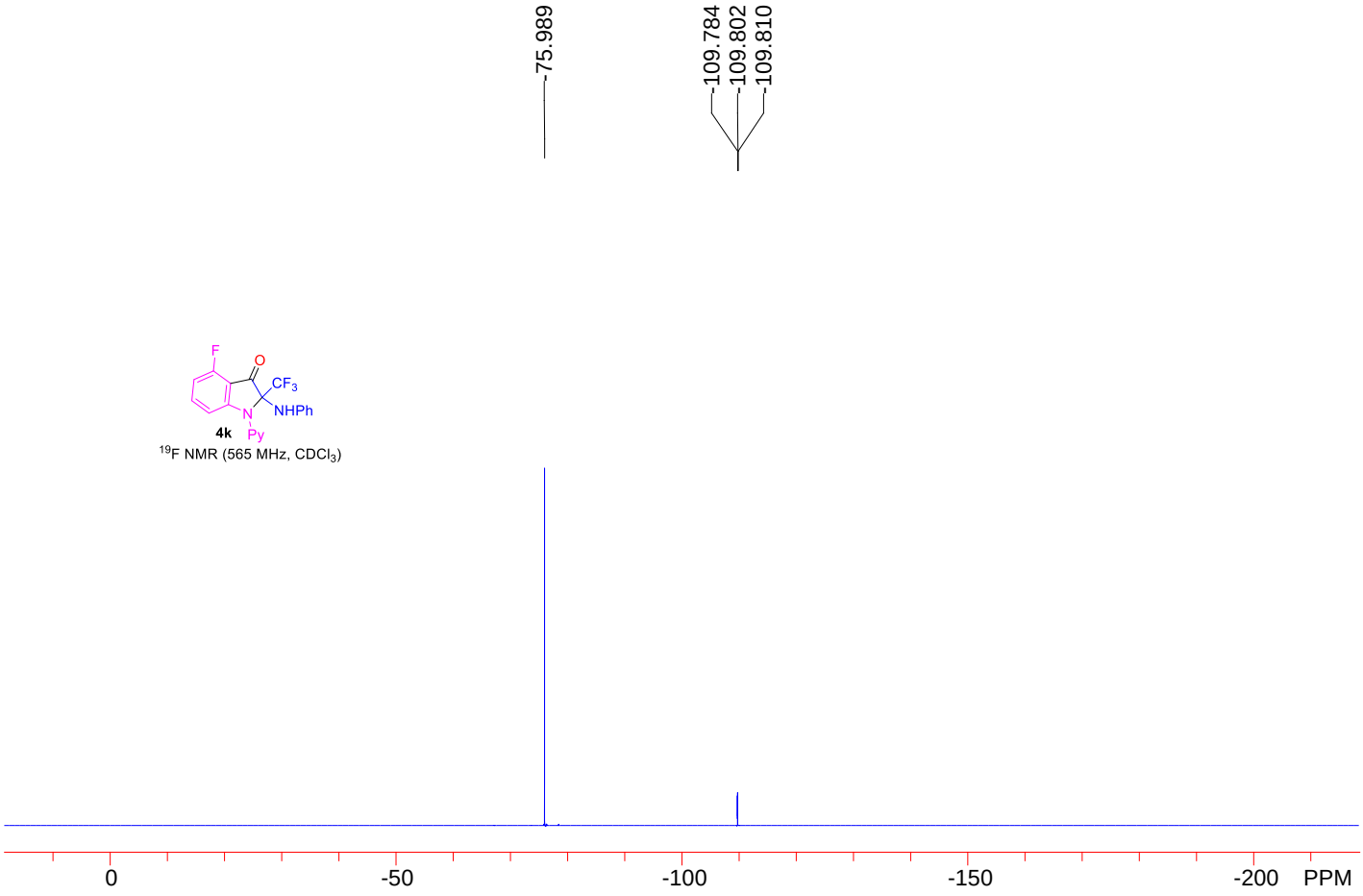


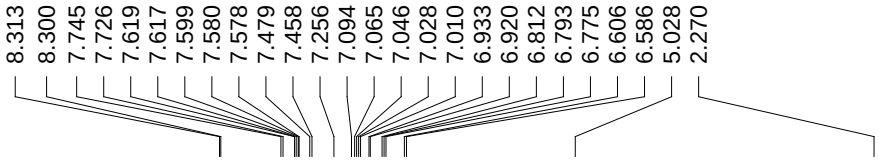


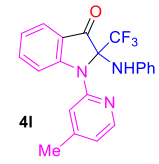


4k

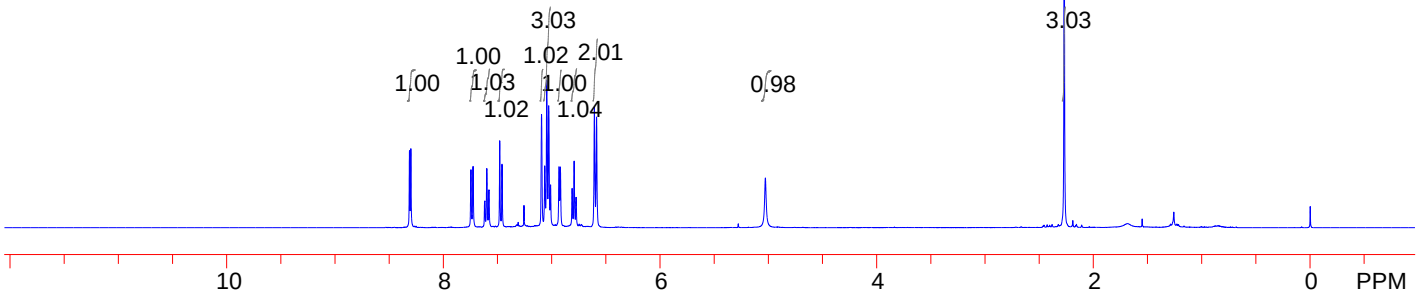
$^{13}C\{^{1}H\}$ (150 MHz, $CDCl_3$)

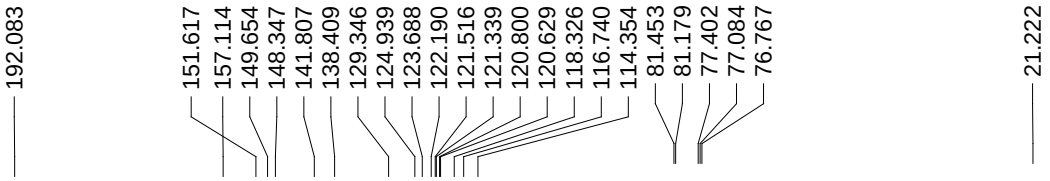

-75.989
-109.784
-109.802
-109.810
F
O
CF3
NHPh
N
Py
4k
19F NMR (565 MHz, CDCl3)
0
-50
-100
-150
-200
PPM

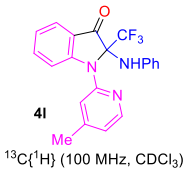




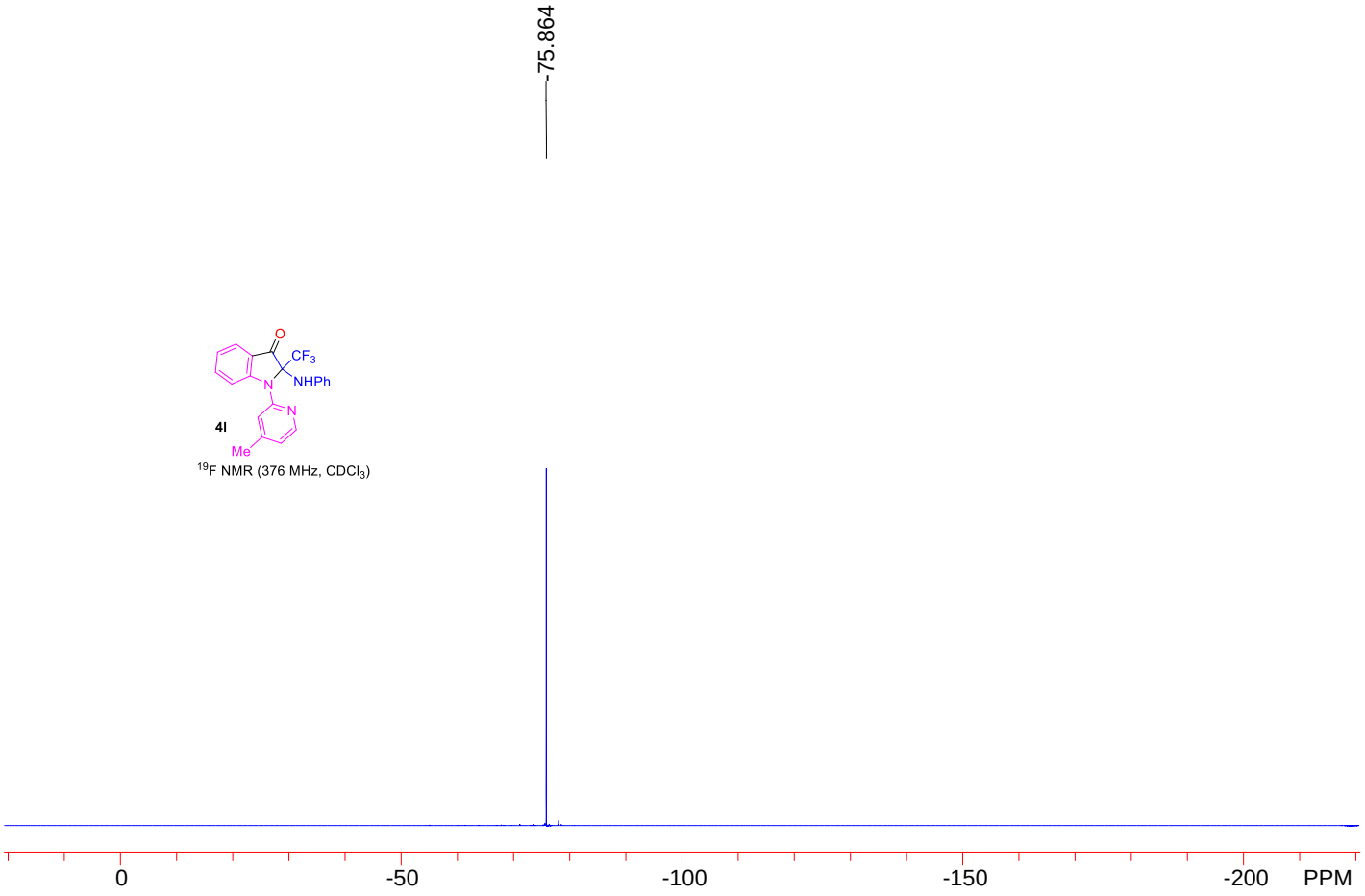
^{1}H NMR (400 MHz, $CDCl_3$)

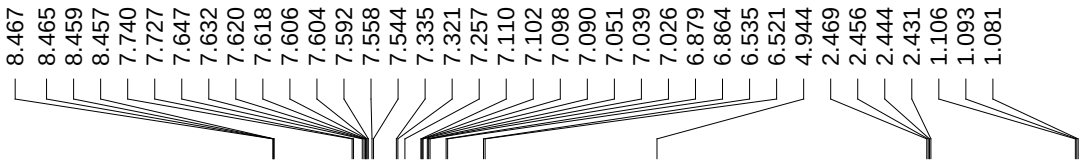


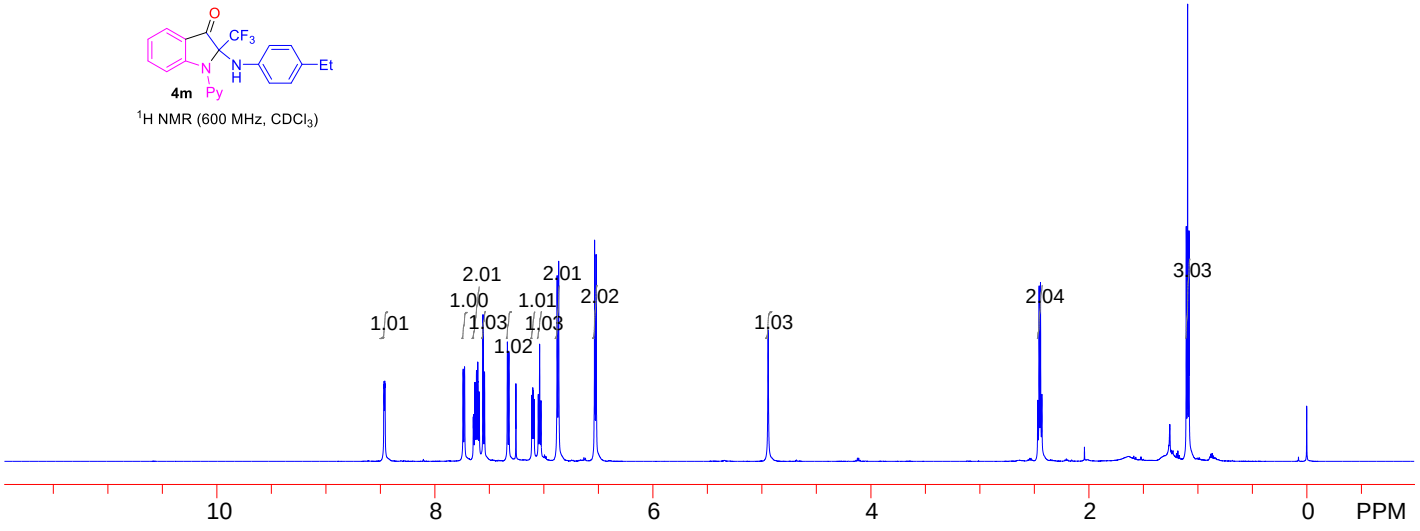


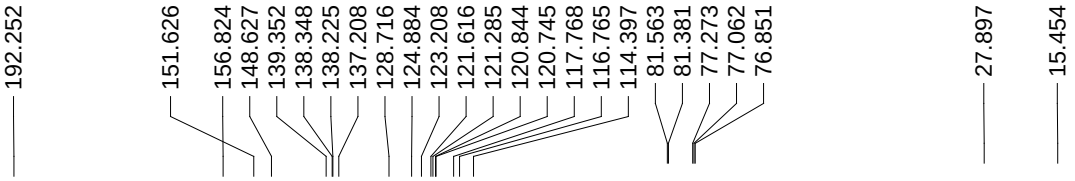


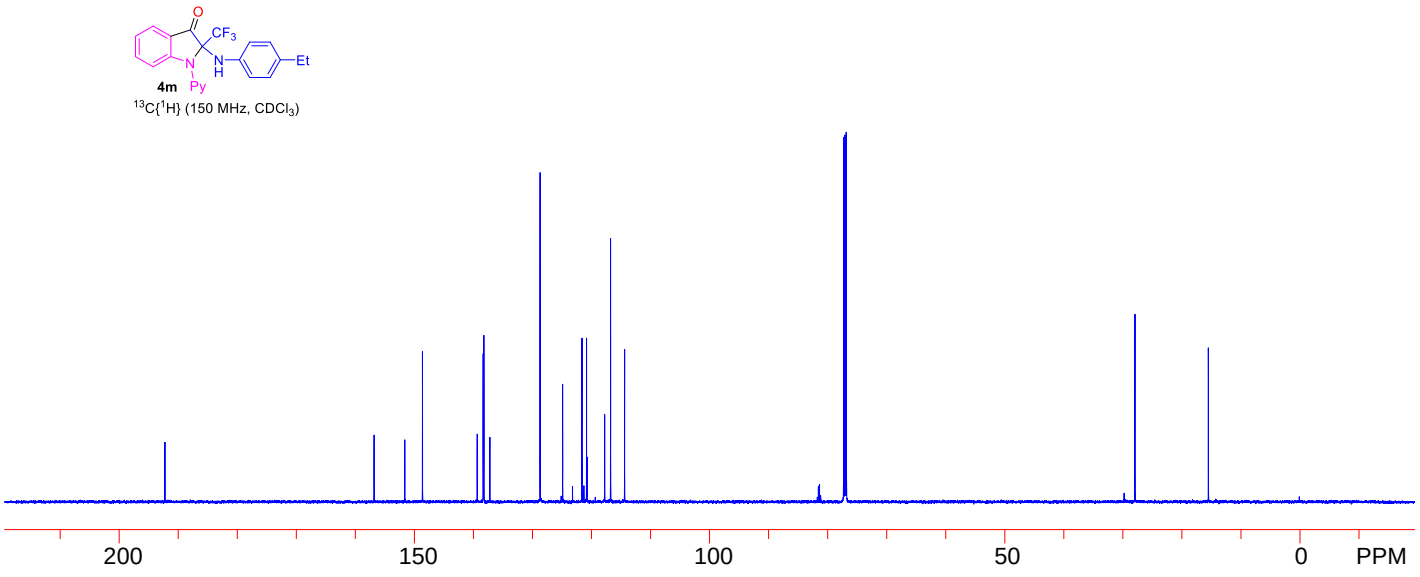
^{13}C{^{1}H} (100 MHz, $CDCl_3$)

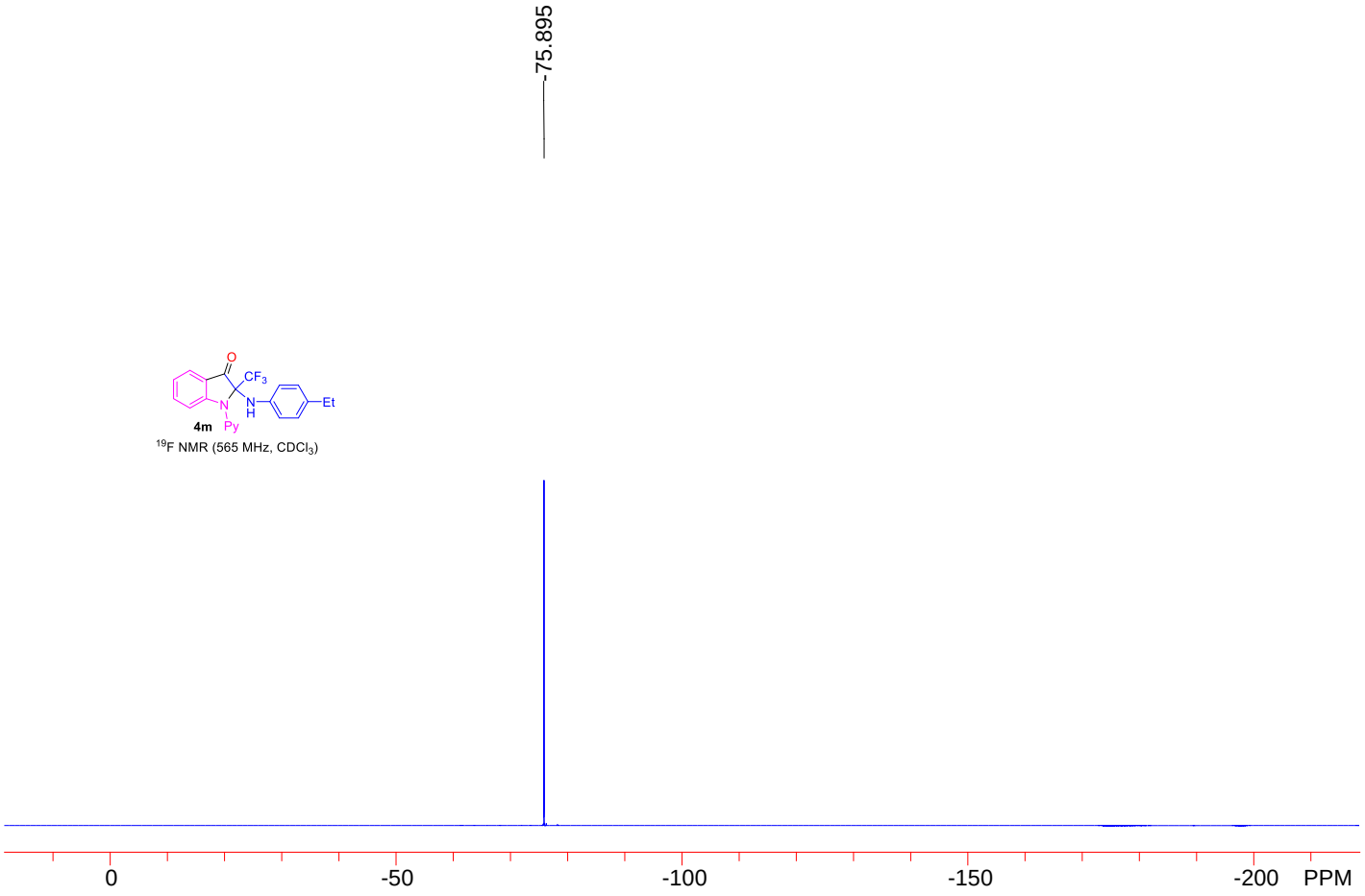

-75.864
O
CF3
NHPh
N
N
Me
4l
19F NMR (376 MHz, CDCl3)
0
-50
-100
-150
-200
PPM

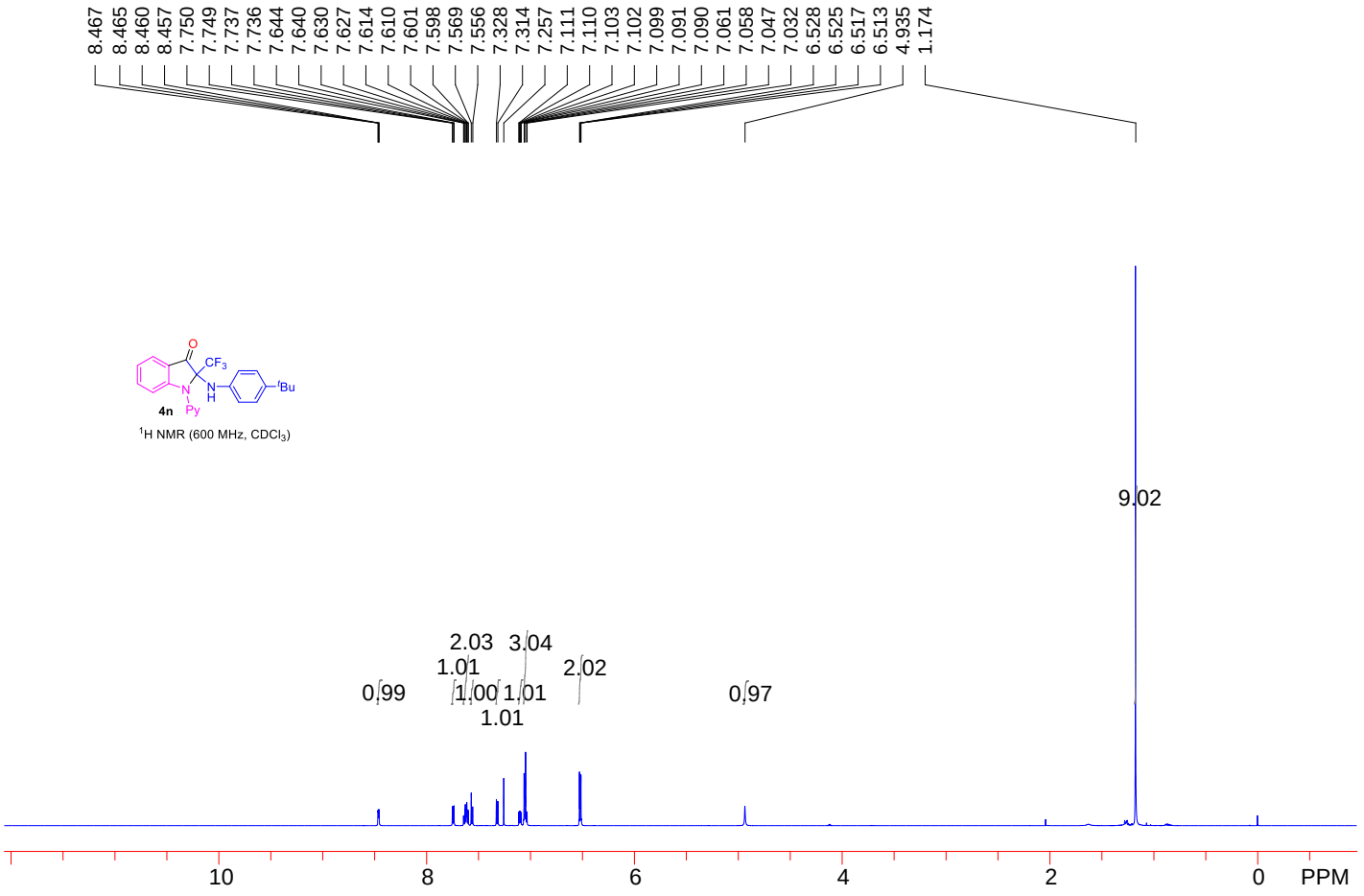

8.467
8.465
8.459
8.457
7.740
7.727
7.647
7.632
7.620
7.618
7.606
7.604
7.592
7.558
7.544
7.335
7.321
7.257
7.110
7.102
7.098
7.090
7.051
7.039
7.026
6.879
6.864
6.535
6.521
4.944
2.469
2.456
2.444
2.431
1.106
1.093
1.081


O
CF3
N
H
Et
4m
Py
1H NMR (600 MHz, CDCl3)
1.01
2.01
1.00
1.03
1.02
1.01
1.03
2.01
2.02
1.03
2.04
3.03
10
8
6
4
2
0
PPM


192.252
151.626
156.824
148.627
139.352
138.348
138.225
137.208
128.716
124.884
123.208
121.616
121.285
120.844
120.745
117.768
116.765
114.397
81.563
81.381
77.273
77.062
76.851
27.897
15.454


O
CF3
N
H
Et
4m
Py
13C{1H} (150 MHz, CDCl3)
200
150
100
50
0
PPM


-75.895
O
CF3
N
H
Et
N
Py
4m
19F NMR (565 MHz, CDCl3)
0
-50
-100
-150
-200
PPM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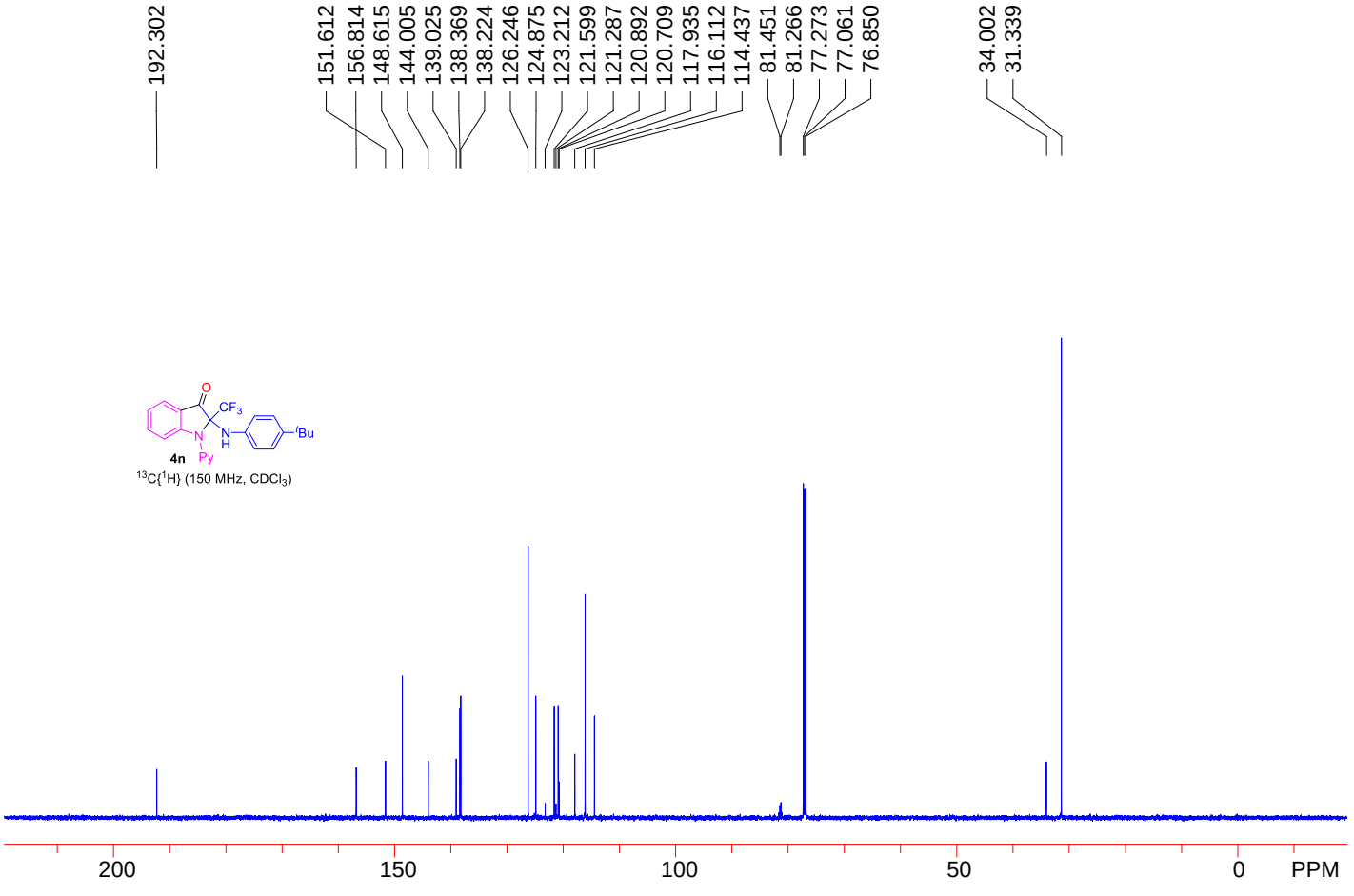
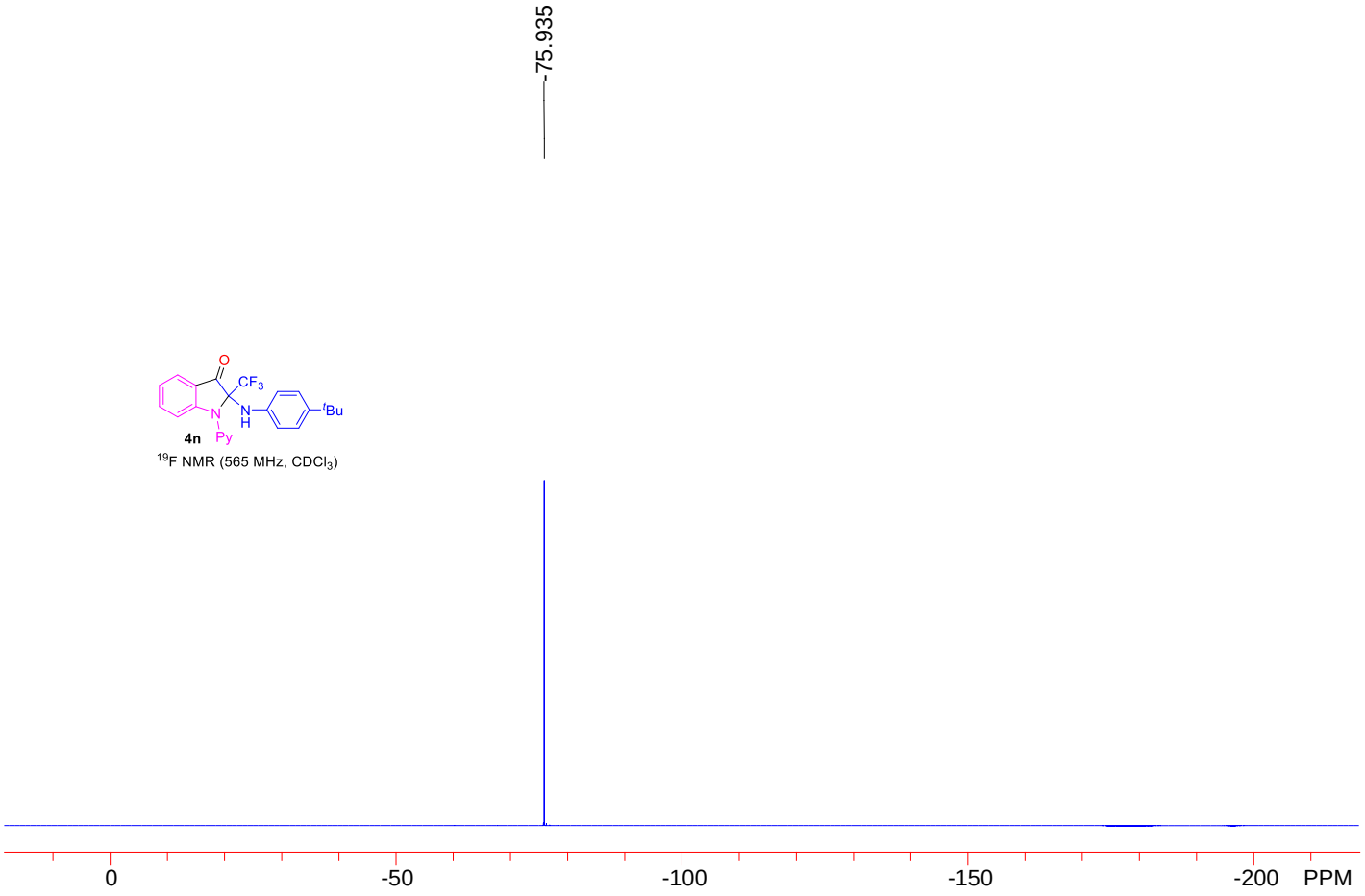
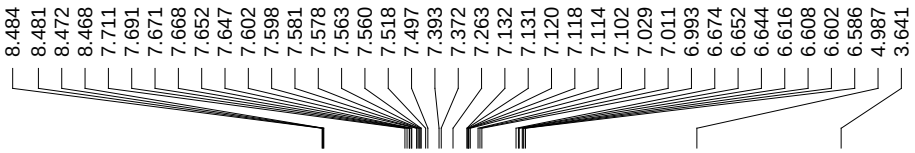
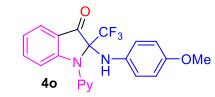
8.465
8.460
8.457
7.750
7.749
7.737
7.736
7.644
7.640
7.630
7.627
7.614
7.610
7.601
7.598
7.569
7.556
7.328
7.314
7.257
7.111
7.110
7.103
7.102
7.099
7.091
7.090
7.061
7.058
7.047
7.032
6.528
6.525
6.517
6.513
4.935
1.174
4n
Py
CF3
tBu
1H NMR (600 MHz, CDCl3)
9.02
2.03
3.04
1.01
2.02
0.99
1.00
1.01
1.01
0.97
10
8
6
4
2
0
PPM


192.302
151.612
156.814
148.615
144.005
139.025
138.369
138.224
126.246
124.875
123.212
121.599
121.287
120.892
120.709
117.935
116.112
114.437
81.451
81.266
77.273
77.061
76.850
34.002
31.339
4n
Py
CF3
tBu
13C{1H} (150 MHz, CDCl3)
200
150
100
50
0
PPM

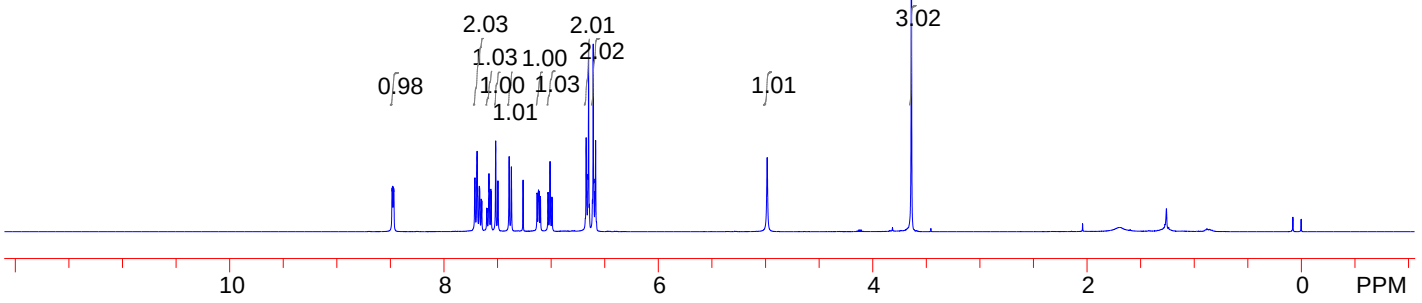

-75.935
O
CF3
N
H
tBu
Py
4n
19F NMR (565 MHz, CDCl3)
0
-50
-100
-150
-200
PPM

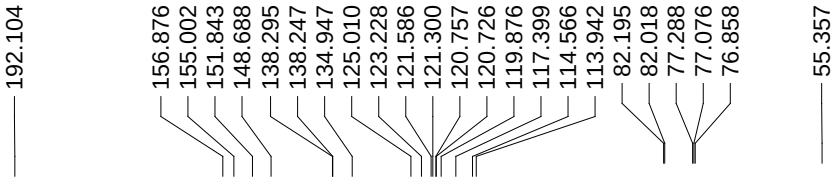


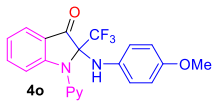


4o

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

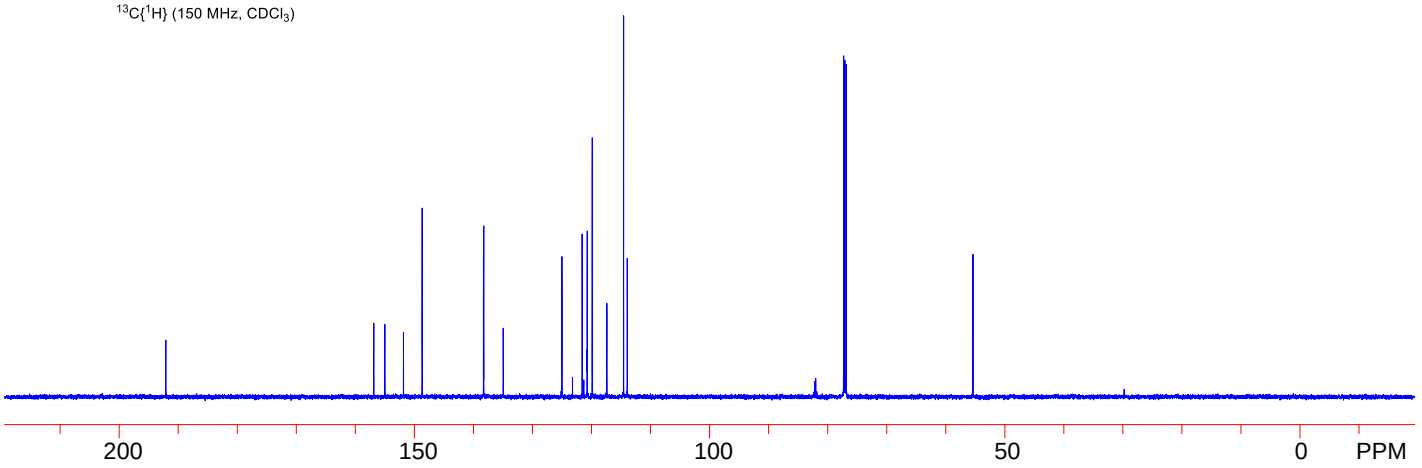


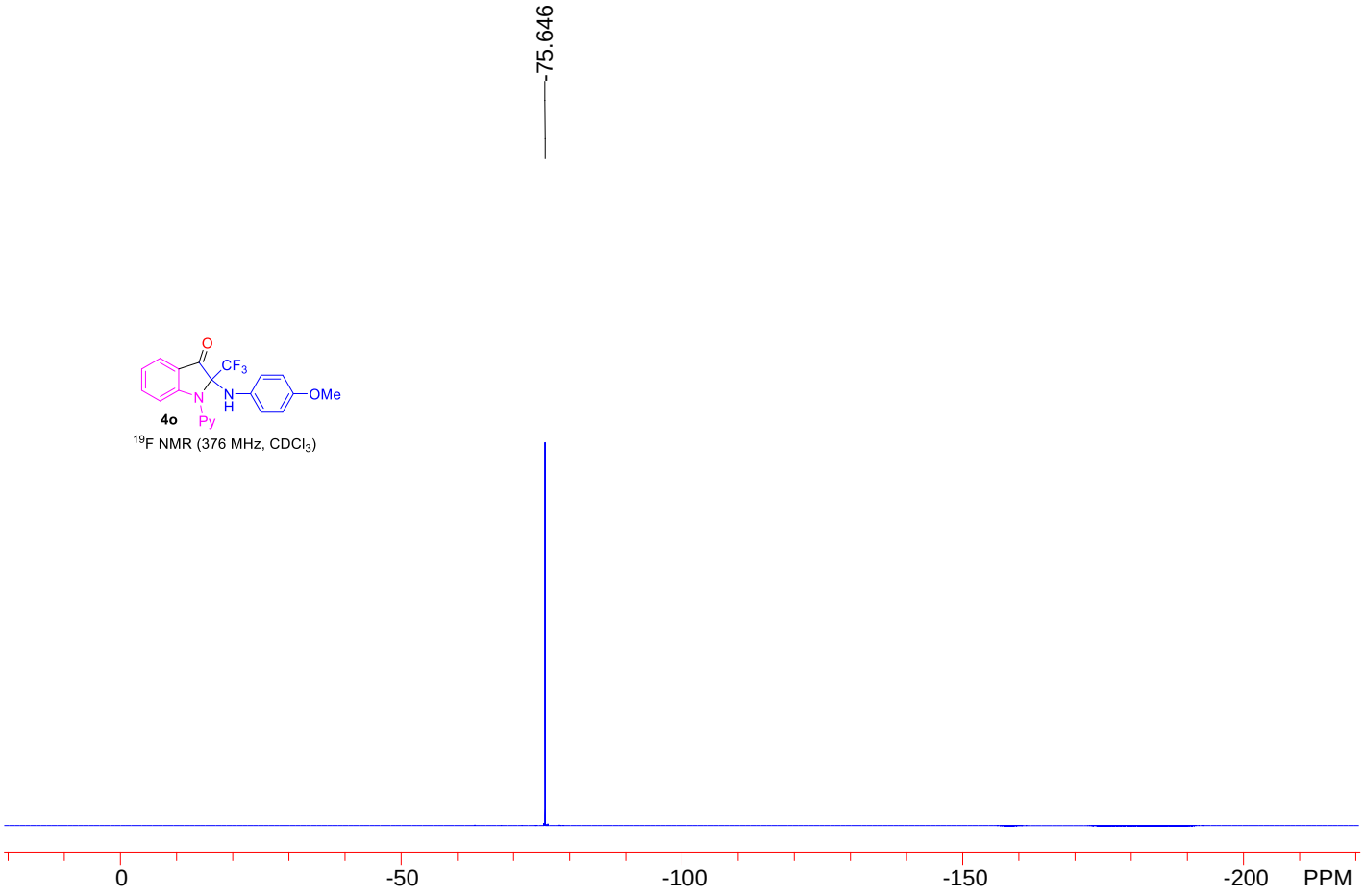


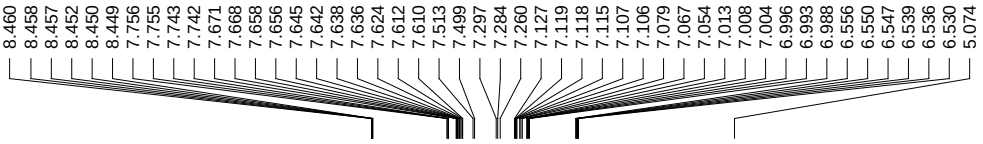


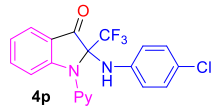
4o

$^{13}C\{^{1}H\}$ (150 MHz, $CDCl_3$)

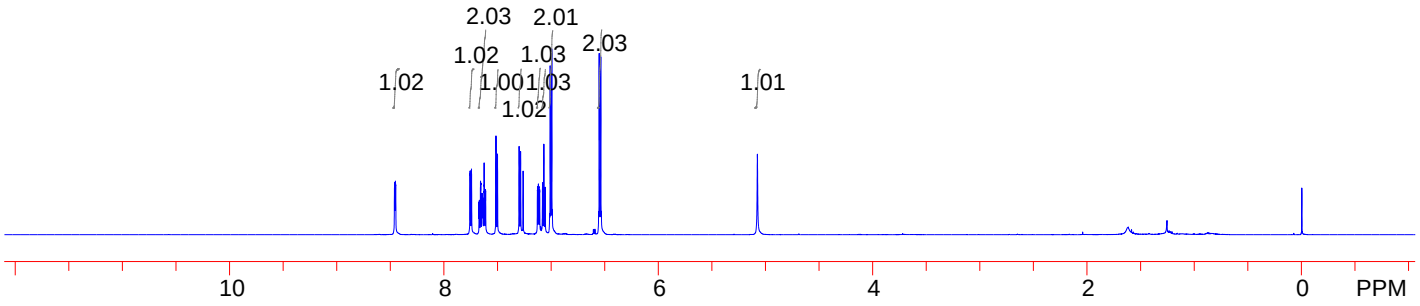


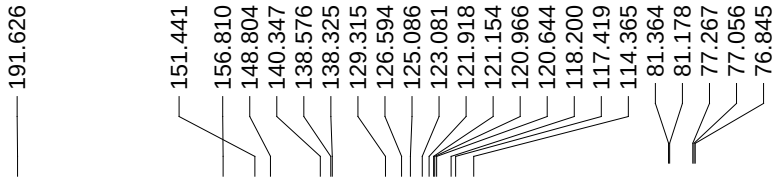

-75.646
O
CF3
N
H
OMe
4o
Py
19F NMR (376 MHz, CDCl3)
0
-50
-100
-150
-200
PPM

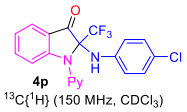




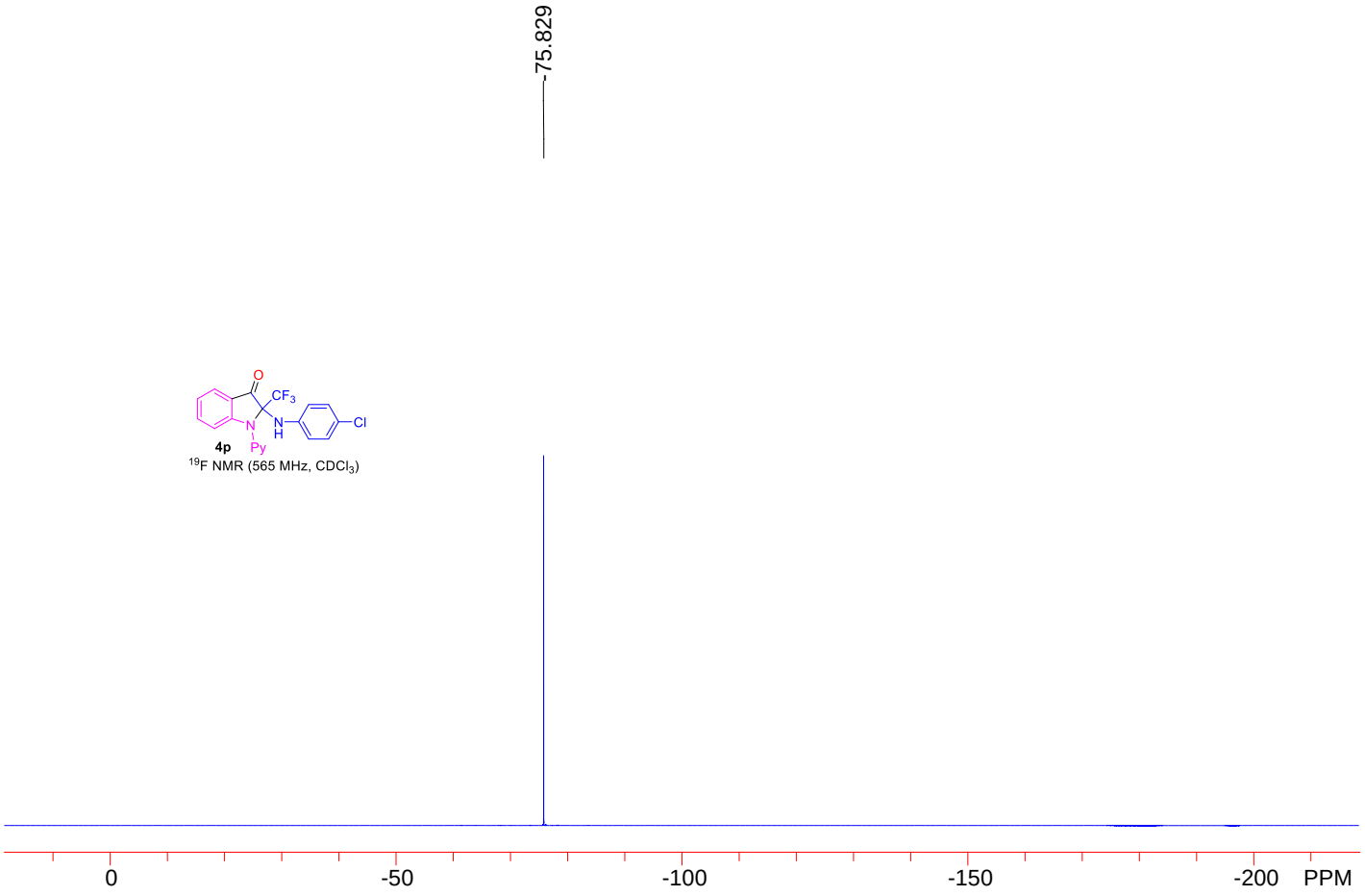
^{1}H NMR (600 MHz, $CDCl_3$)

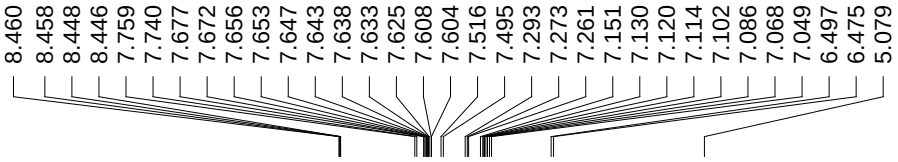


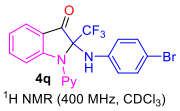




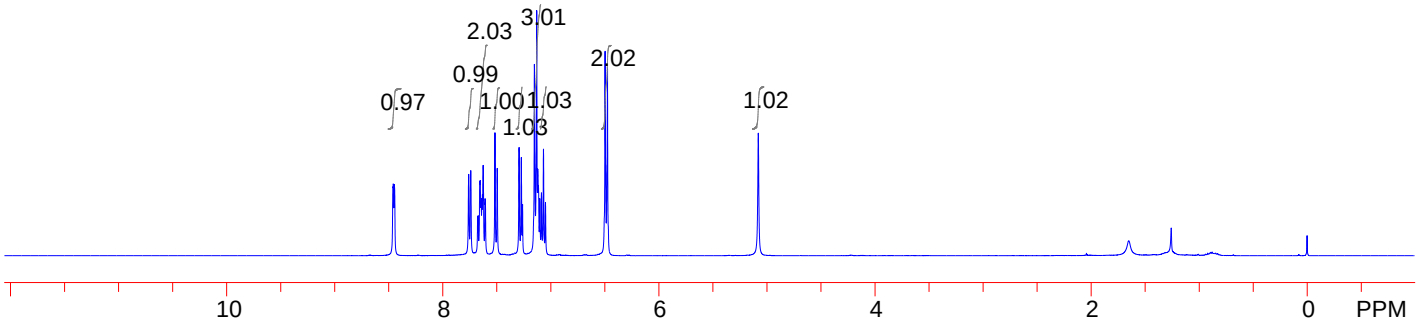
$^{13}C\{^{1}H\}$ (150 MHz, $CDCl_3$)

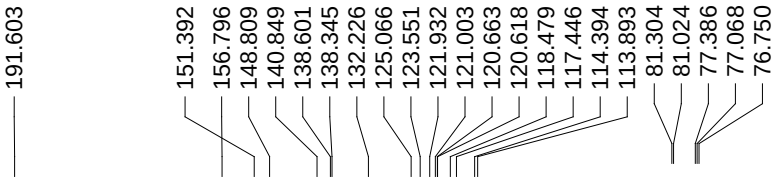

-75.829
O
CF3
N
H
Cl
N
Py
4p
19F NMR (565 MHz, CDCl3)
0
-50
-100
-150
-200
PPM

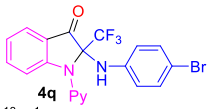




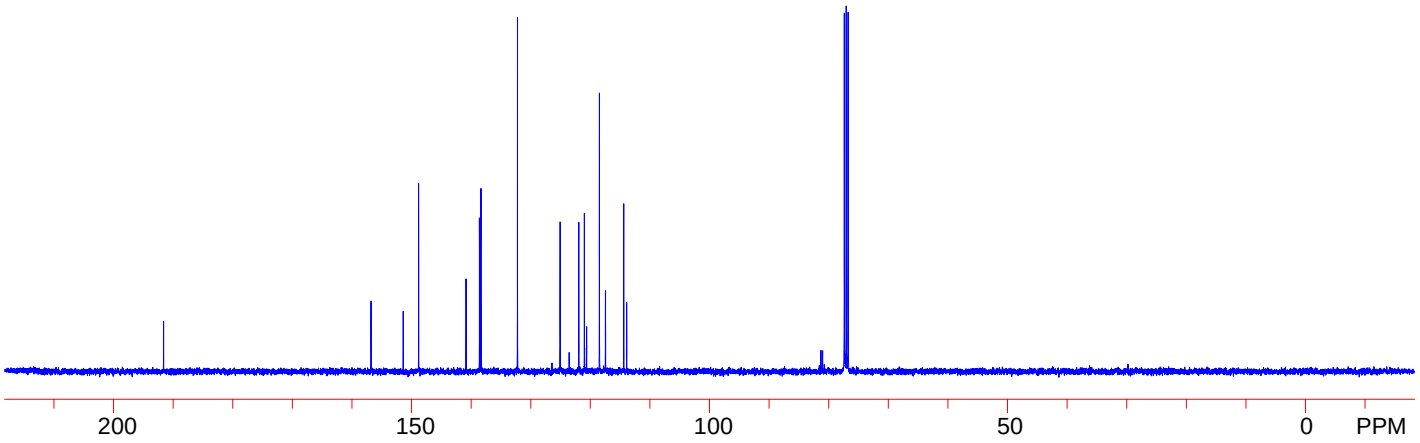
^{1}H NMR (400 MHz, $CDCl_3$)

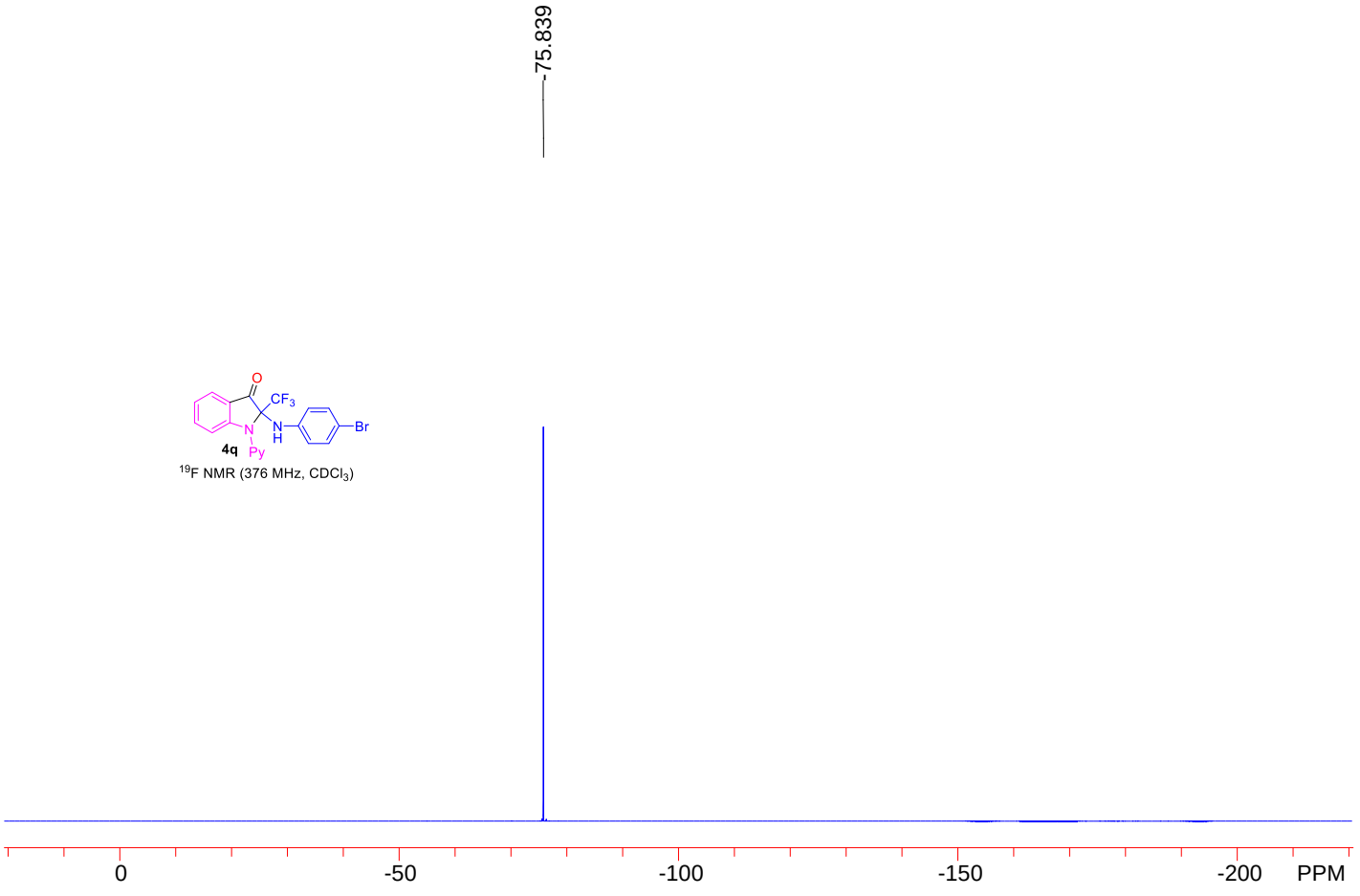


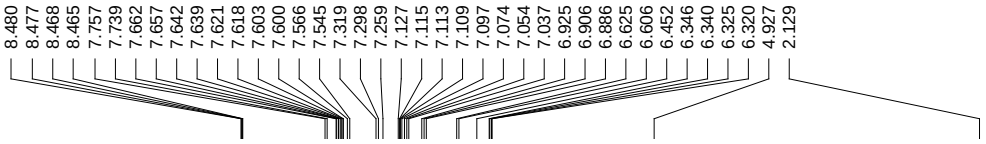


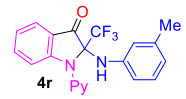


$^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$)



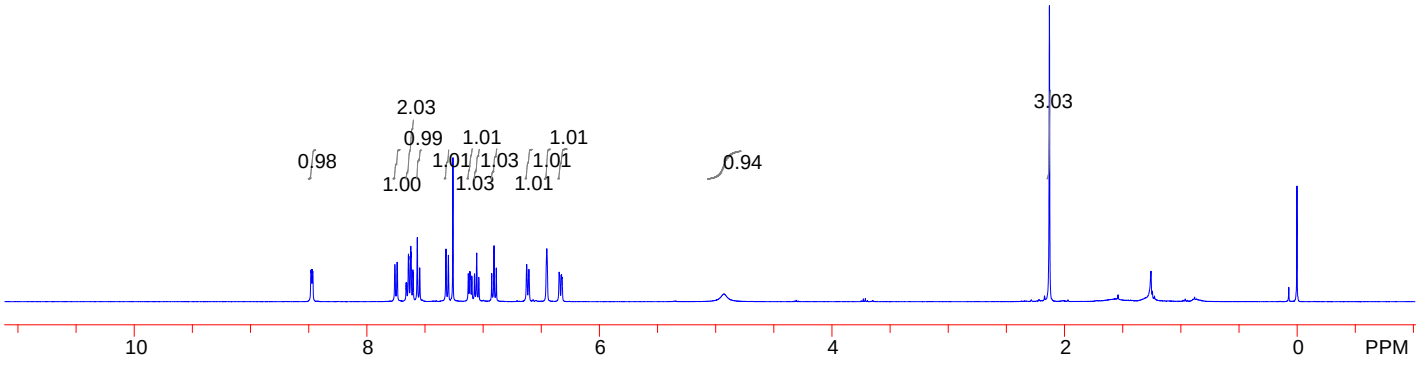

-75.839
O
CF3
N
H
Br
4q
Py
19F NMR (376 MHz, CDCl3)
0
-50
-100
-150
-200
PPM

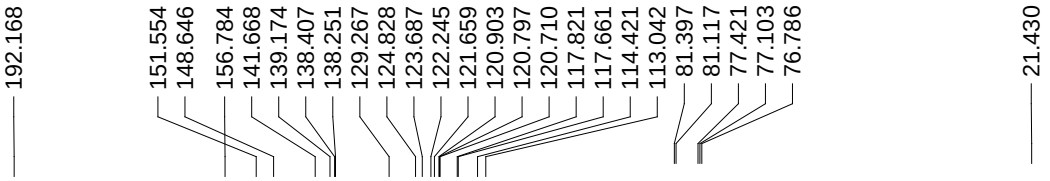


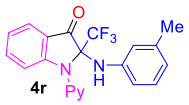


4r

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

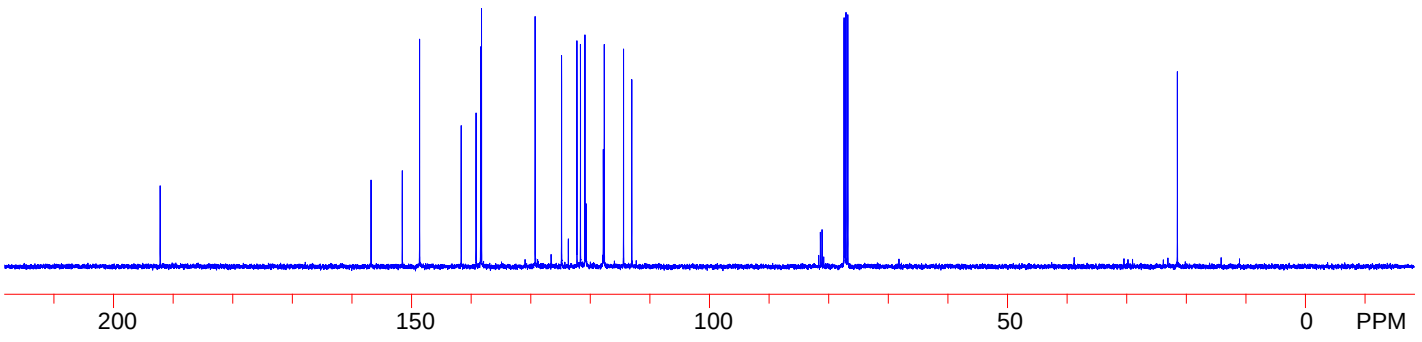


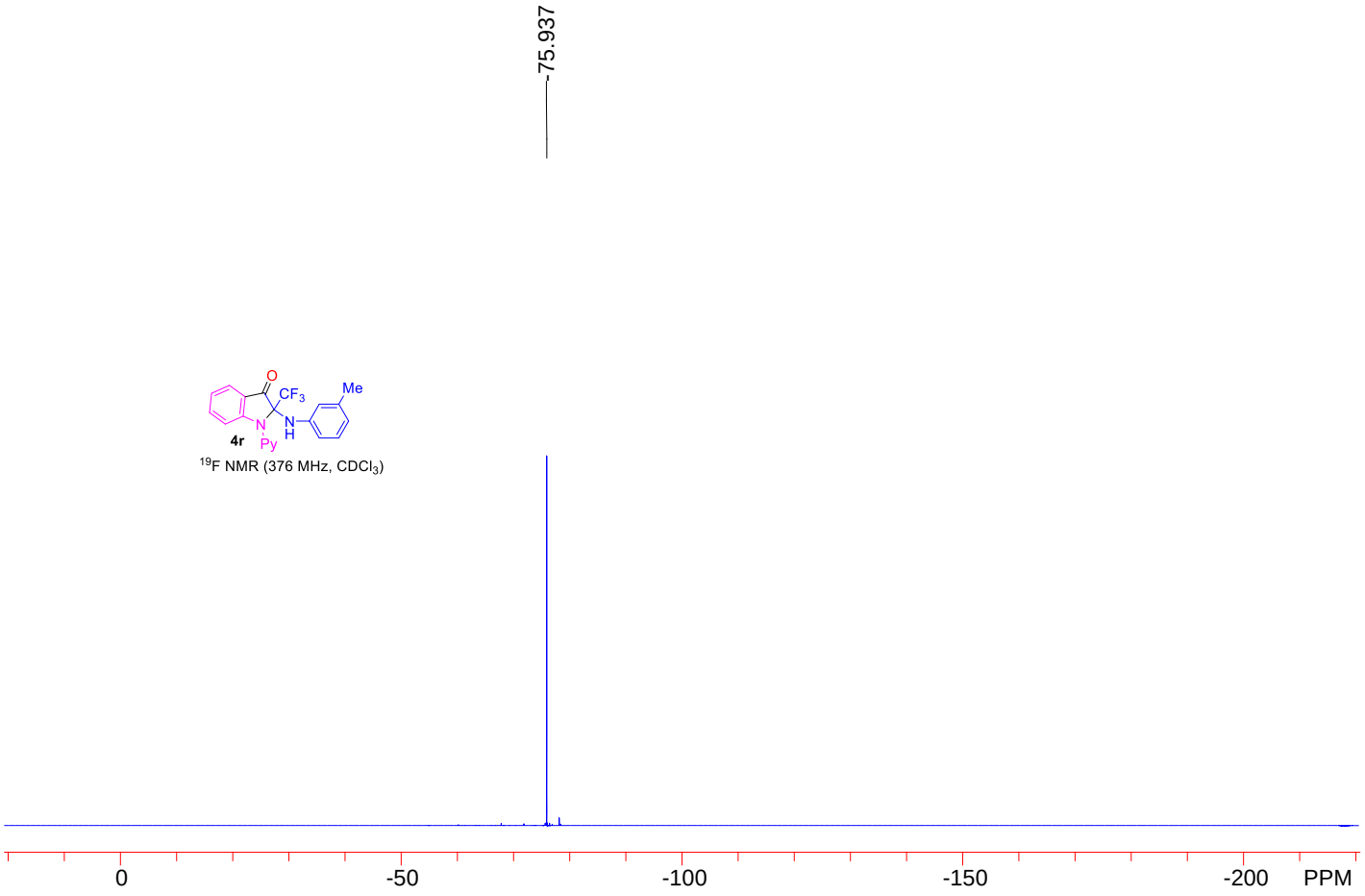


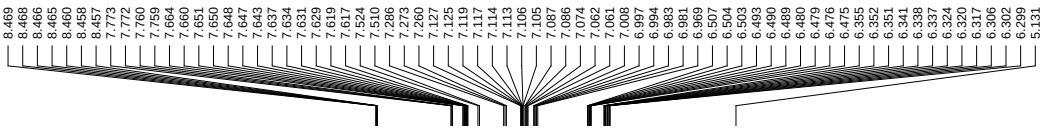


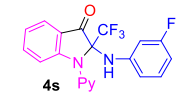
4r

$^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$)



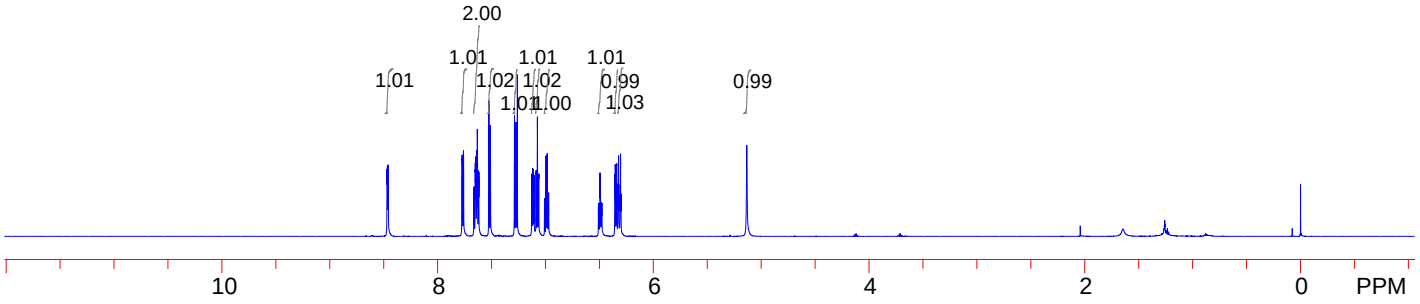

-75.937
O
CF3
Me
N
H
N
Py
4r
19F NMR (376 MHz, CDCl3)
0
-50
-100
-150
-200
PPM

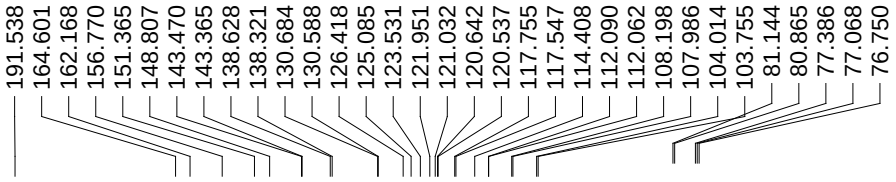


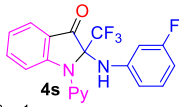


4s

^{1}H NMR (600 MHz, $CDCl_3$)

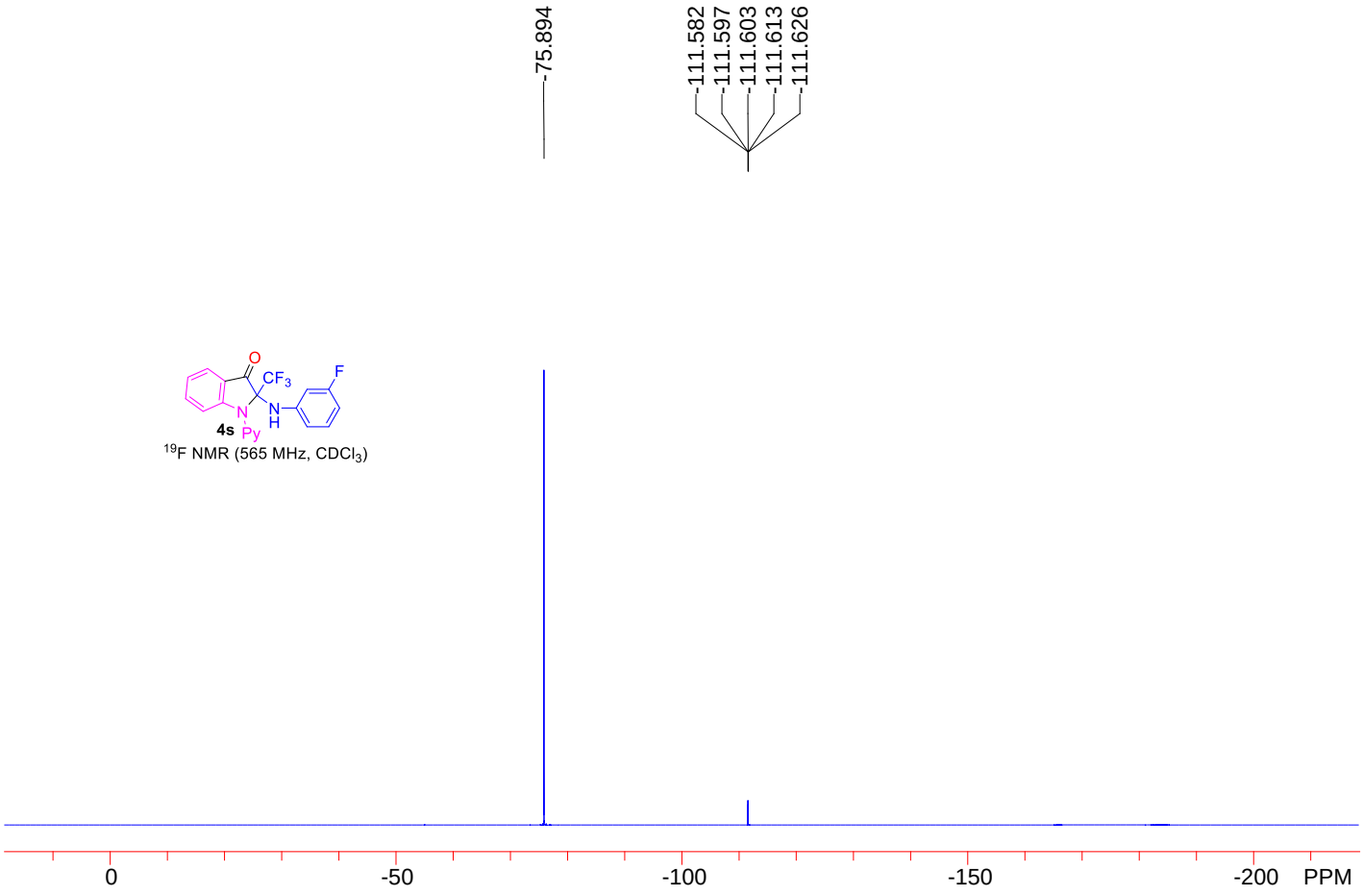


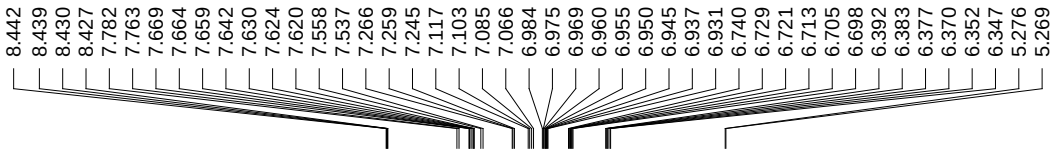


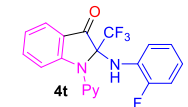


4s

$^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$)

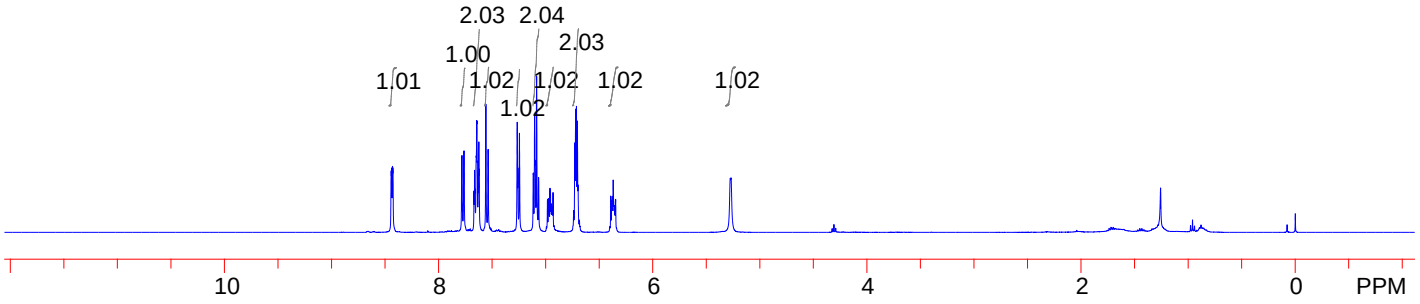

-75.894
-111.582
-111.597
-111.603
-111.613
-111.626
O
CF3
F
N
H
N
4s Py
19F NMR (565 MHz, CDCl3)
0
-50
-100
-150
-200
PPM

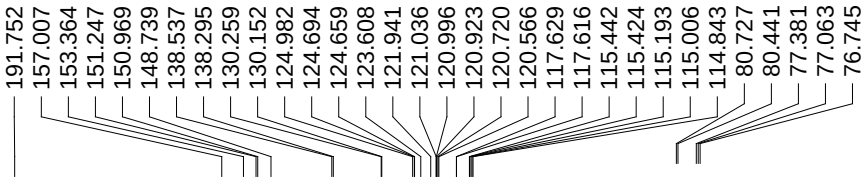


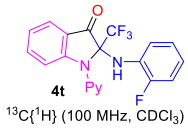


4t

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

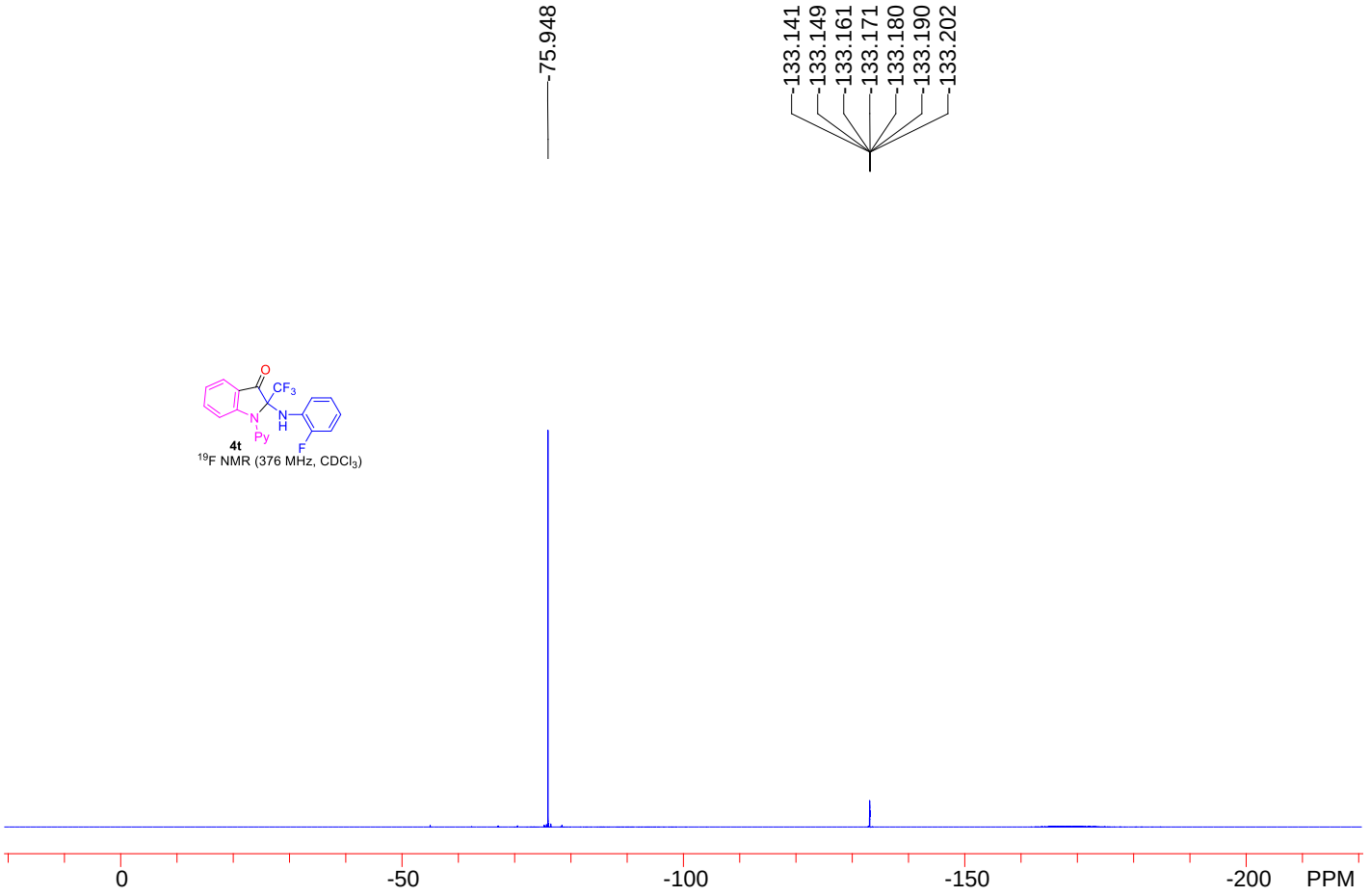


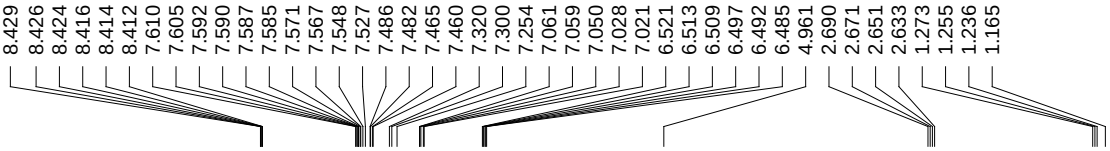


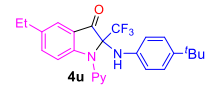


4t

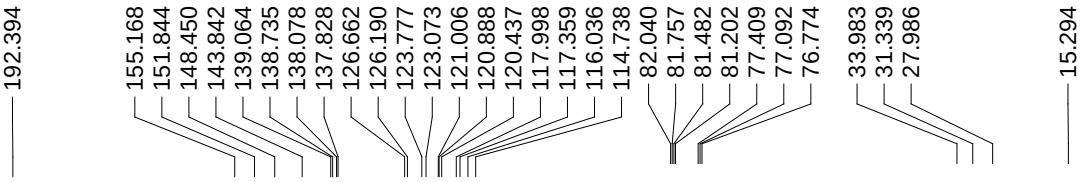
^{13}C{^{1}H} (100 MHz, $CDCl_3$)

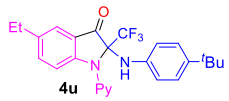

-75.948
-133.141
-133.149
-133.161
-133.171
-133.180
-133.190
-133.202
4t
19F NMR (376 MHz, CDCl3)
0
-50
-100
-150
-200
PPM



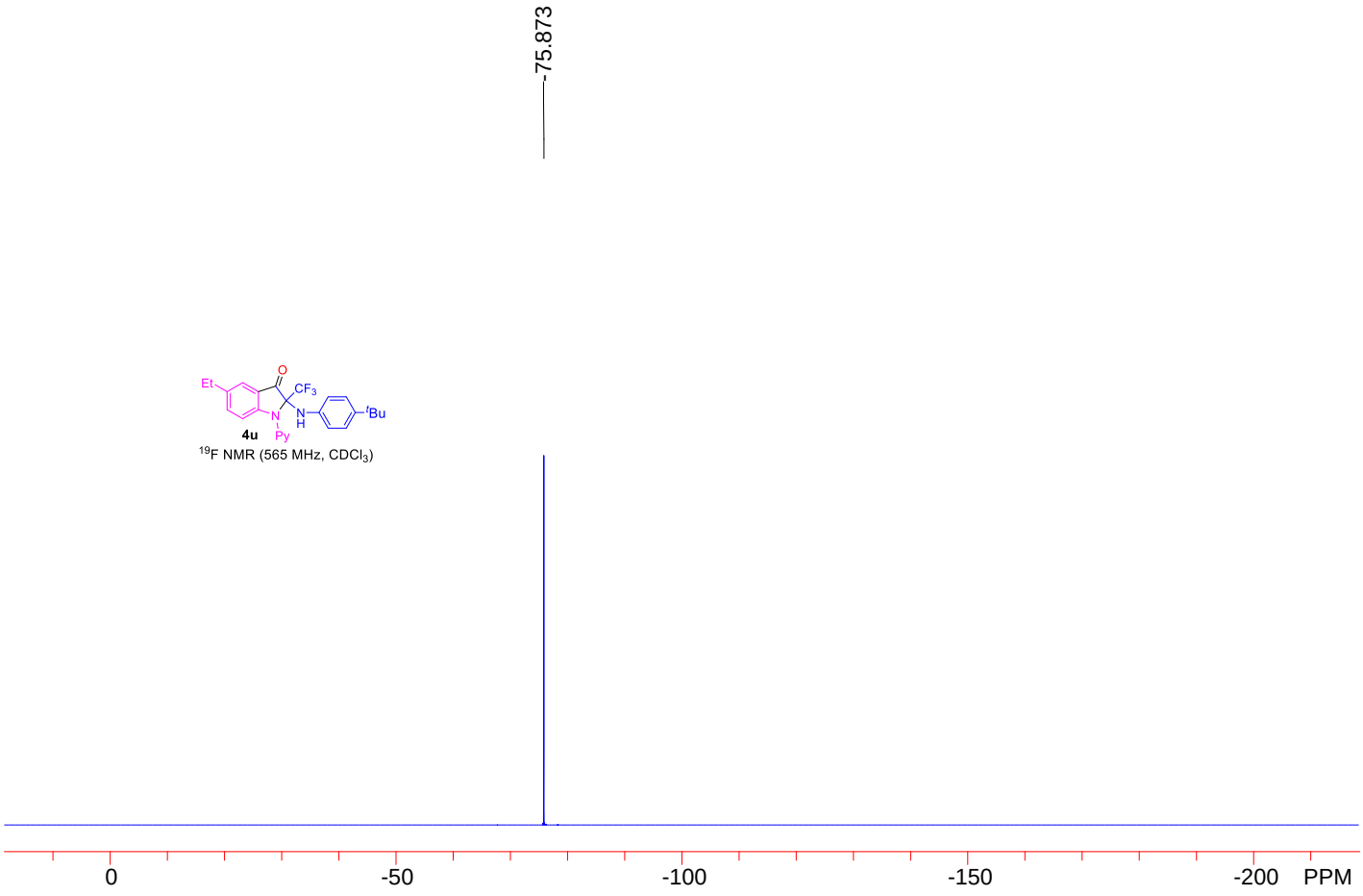


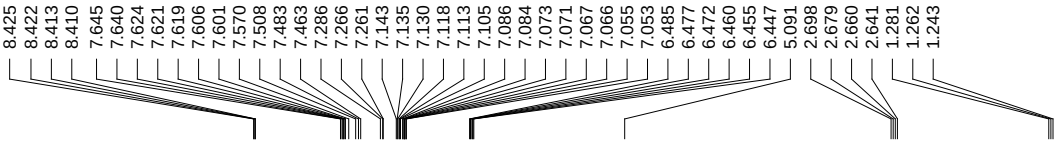
^{1}H NMR (400 MHz, $CDCl_3$)

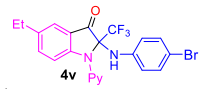




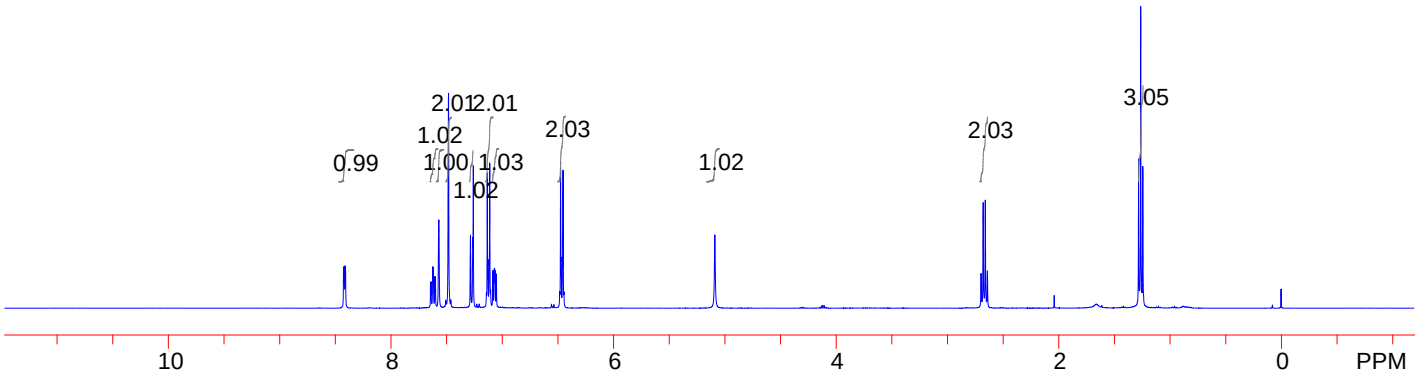
^{13}C{^{1}H} (100 MHz, $CDCl_3$)

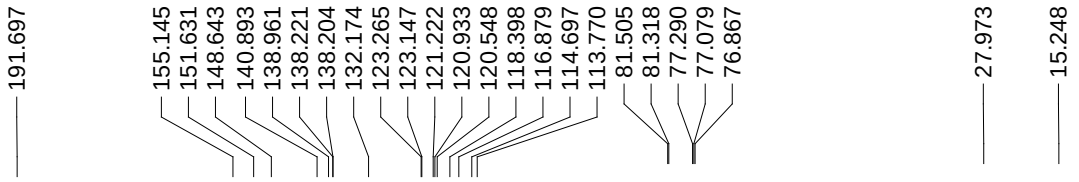

-75.873
Et
O
CF3
N
H
tBu
Py
4u
19F NMR (565 MHz, CDCl3)
0
-50
-100
-150
-200
PPM

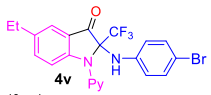




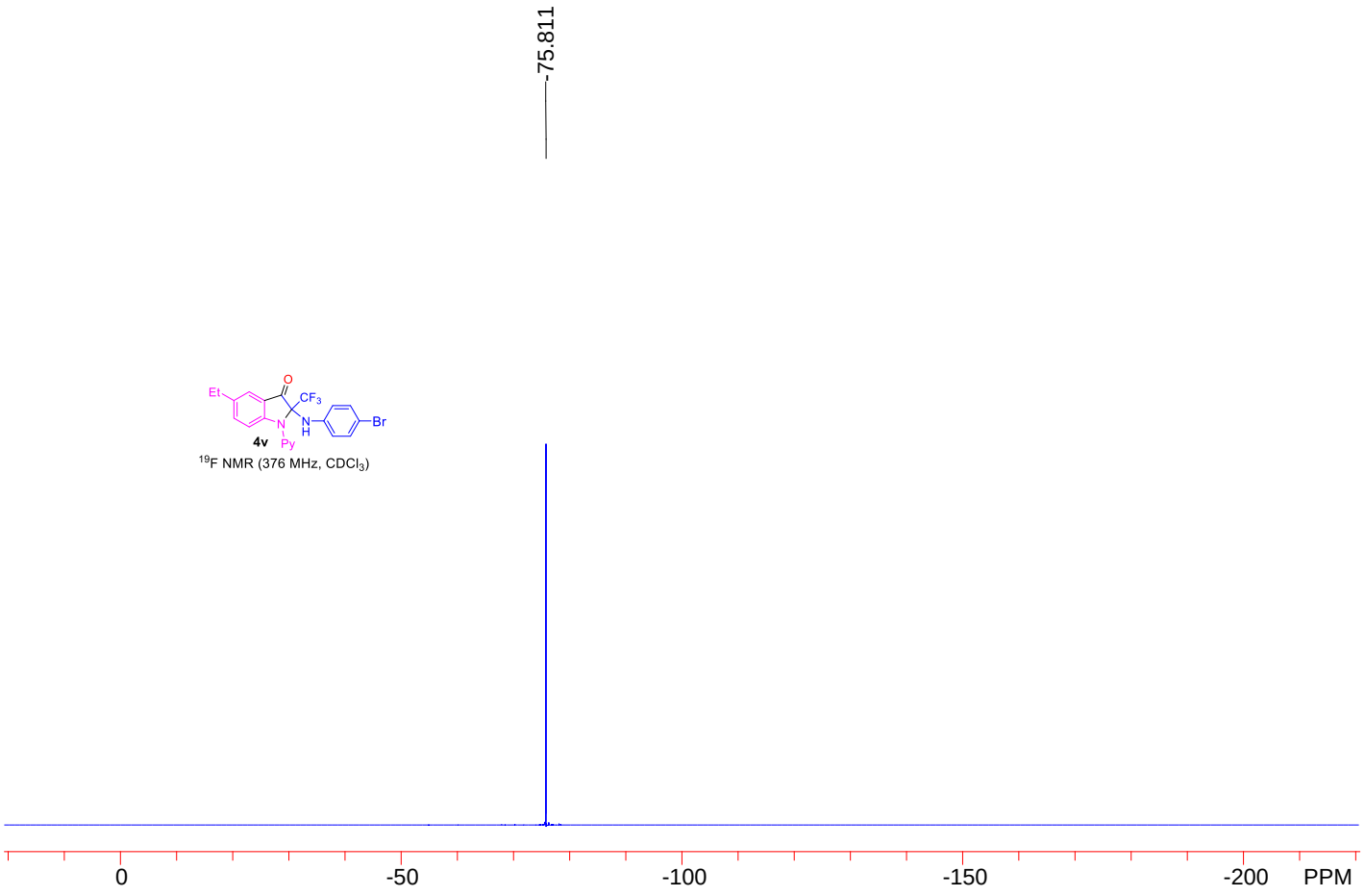
^{1}H NMR (400 MHz, $CDCl_3$)

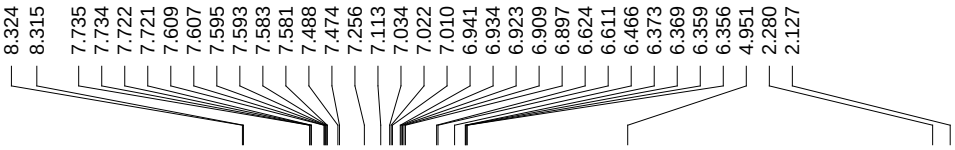


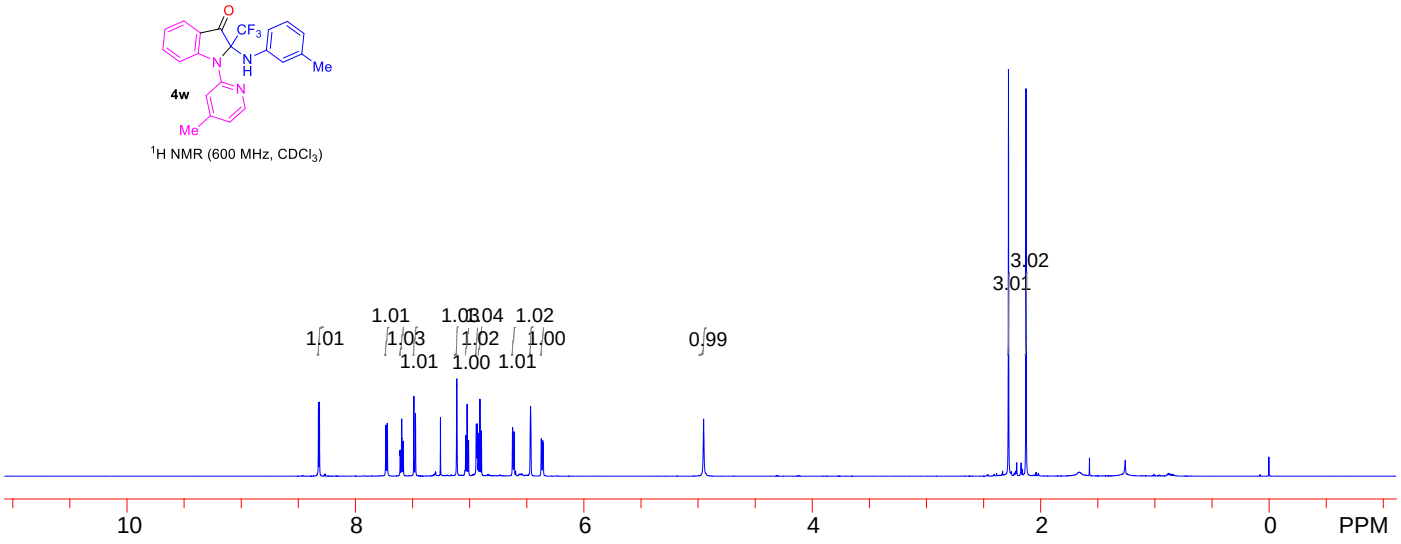


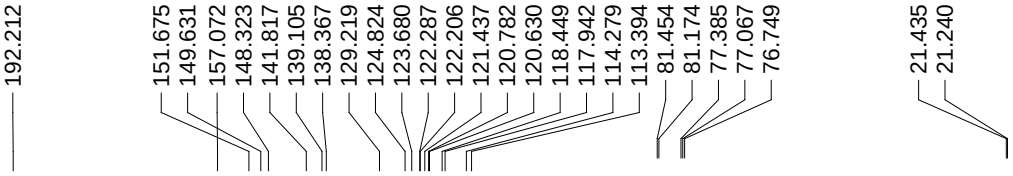


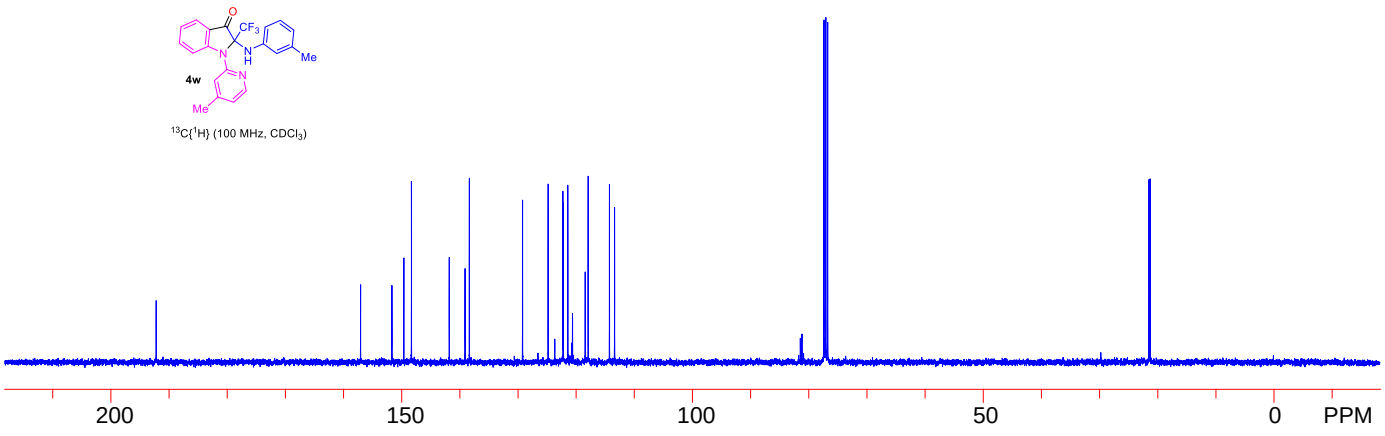
$^{13}C\{^{1}H\}$ (150 MHz, $CDCl_3$)

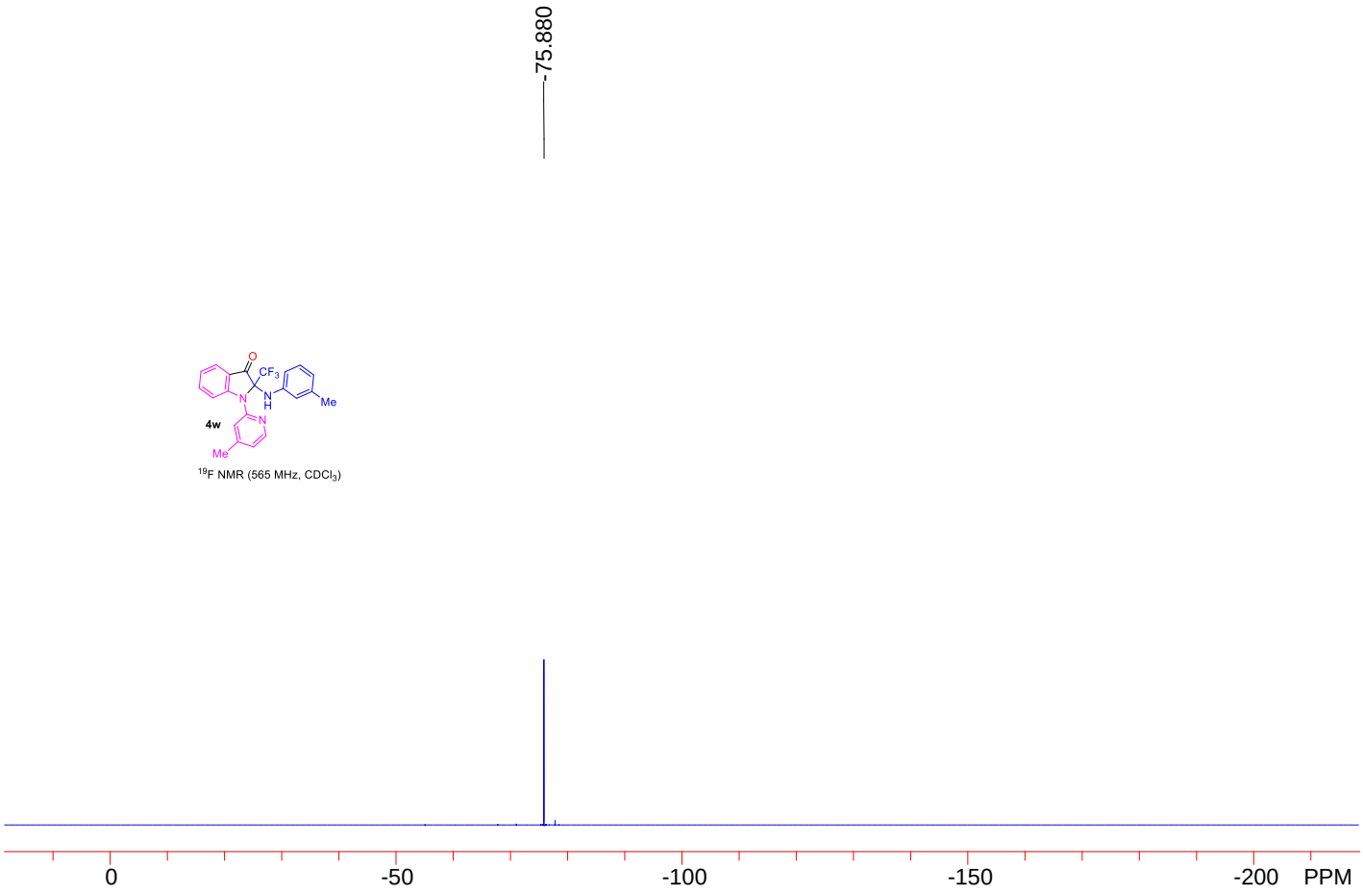

-75.811
Et
O
CF3
N
H
Br
N
Py
4v
19F NMR (376 MHz, CDCl3)
0
-50
-100
-150
-200
PPM

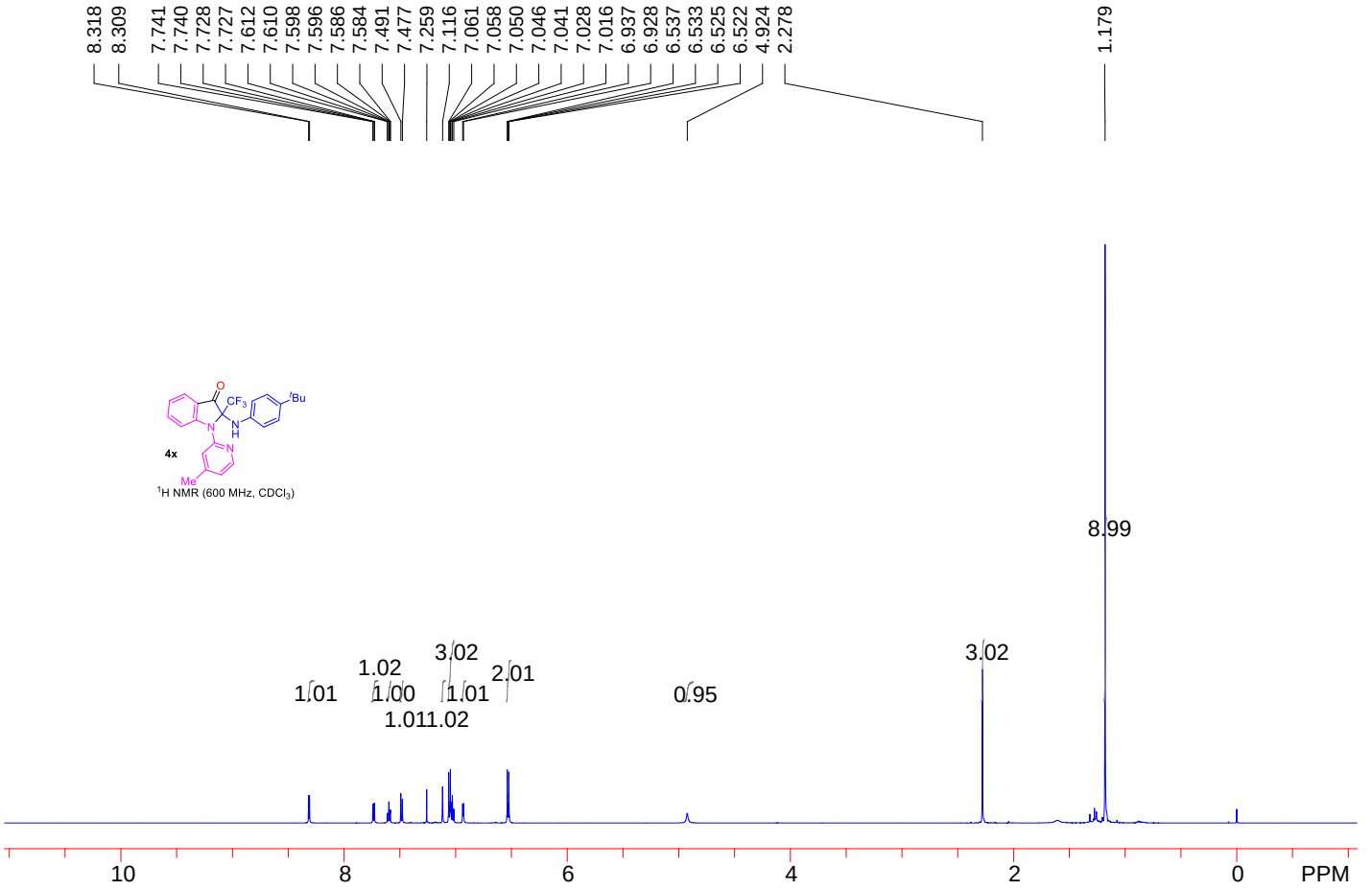

8.324
8.315
7.735
7.734
7.722
7.721
7.609
7.607
7.595
7.593
7.583
7.581
7.488
7.474
7.256
7.113
7.034
7.022
7.010
6.941
6.934
6.923
6.909
6.897
6.624
6.611
6.466
6.373
6.369
6.359
6.356
4.951
2.280
2.127

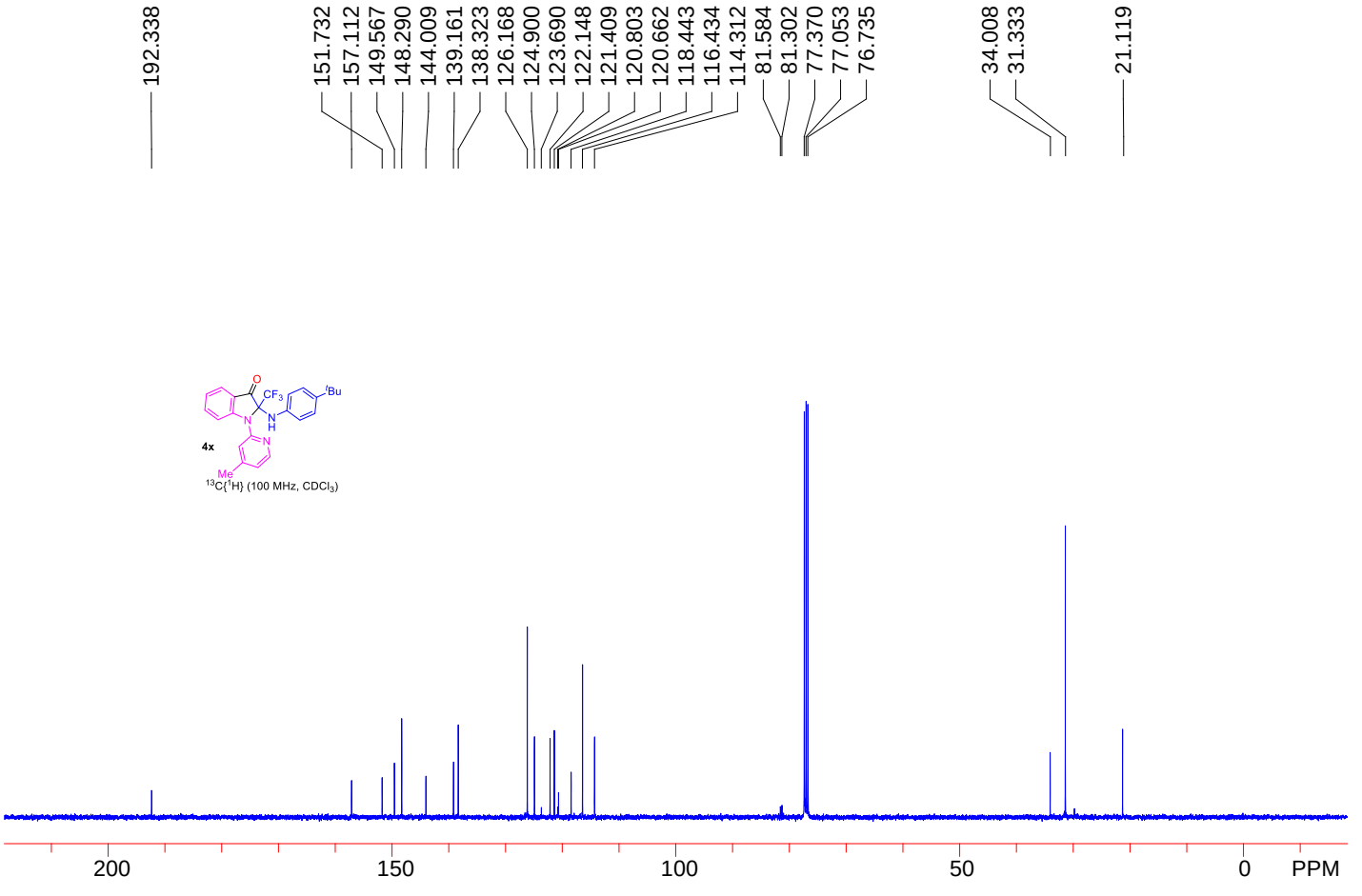

4w
^{1}H NMR (600 MHz, CDCl$_3$)
3.02
3.01
1.01
1.01
1.03
1.01
1.01
1.02
1.00
1.04
1.00
1.02
1.01
1.00
0.99
10
8
6
4
2
0
PPM

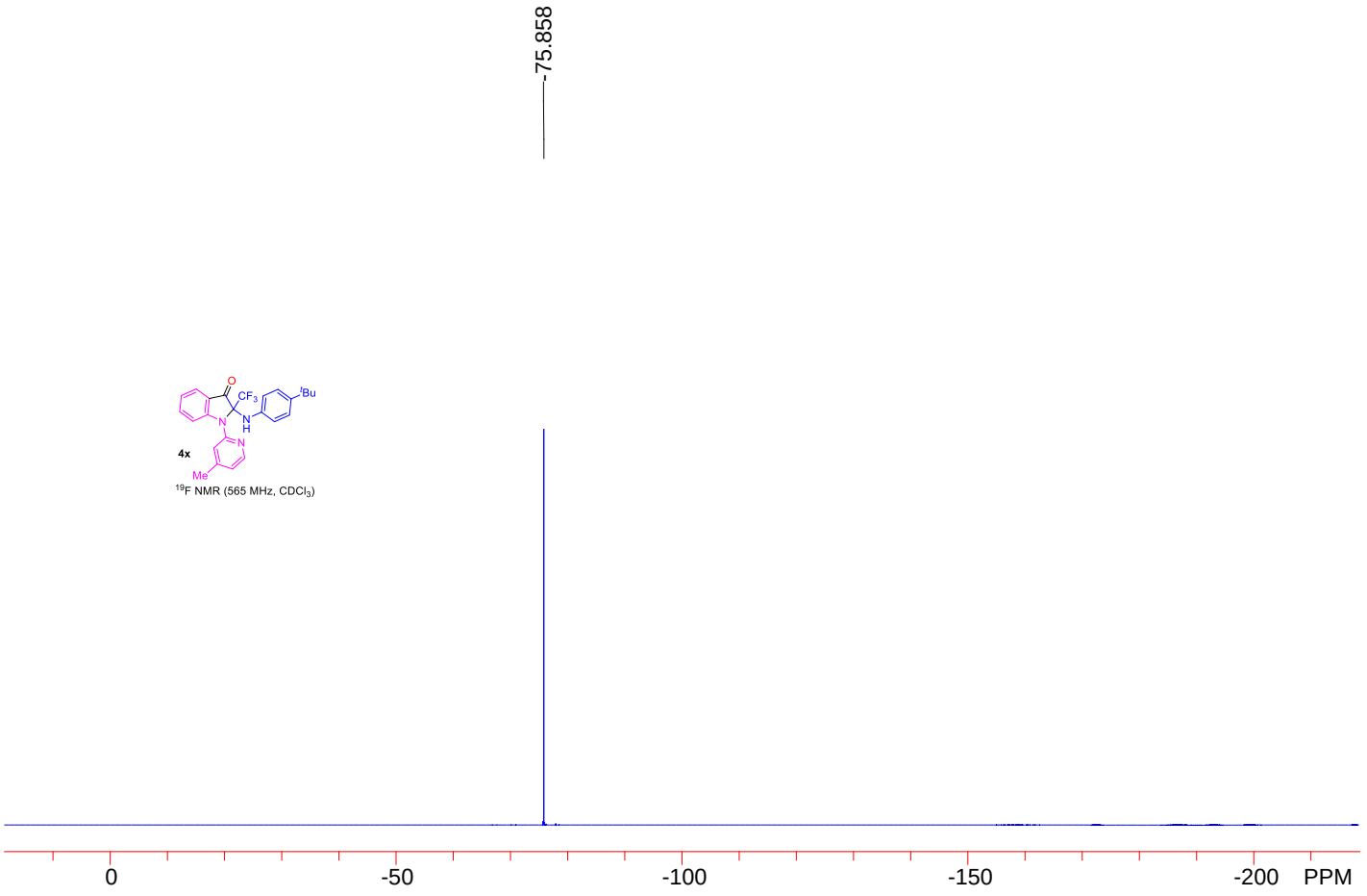

192.212
151.675
149.631
157.072
148.323
141.817
139.105
138.367
129.219
124.824
123.680
122.287
122.206
121.437
120.782
120.630
118.449
117.942
114.279
113.394
81.454
81.174
77.385
77.067
76.749
21.435
21.240

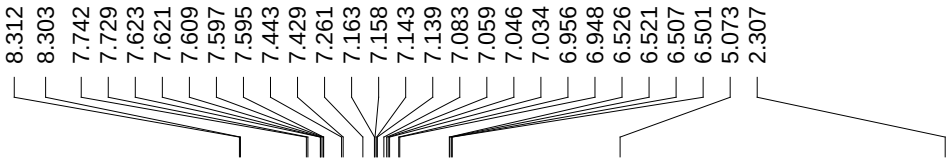

4w
^{13}C{^{1}H} (100 MHz, CDCl$_3$)
200
150
100
50
0
PPM

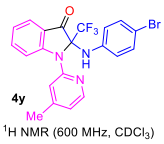

-75.880
4w
^{19}F NMR (565 MHz, CDCl$_3$)
0
-50
-100
-150
-200
PPM


8.318
8.309
7.741
7.740
7.728
7.727
7.612
7.610
7.598
7.596
7.586
7.584
7.491
7.477
7.259
7.116
7.061
7.058
7.050
7.046
7.041
7.028
7.016
6.937
6.928
6.537
6.533
6.525
6.522
4.924
2.278
1.179
4x
^{1}H NMR (600 MHz, CDCl$_3$)
8.99
3.02
3.02
2.01
1.02
1.01
1.00
1.01
1.01
1.02
0.95
10
8
6
4
2
0
PPM

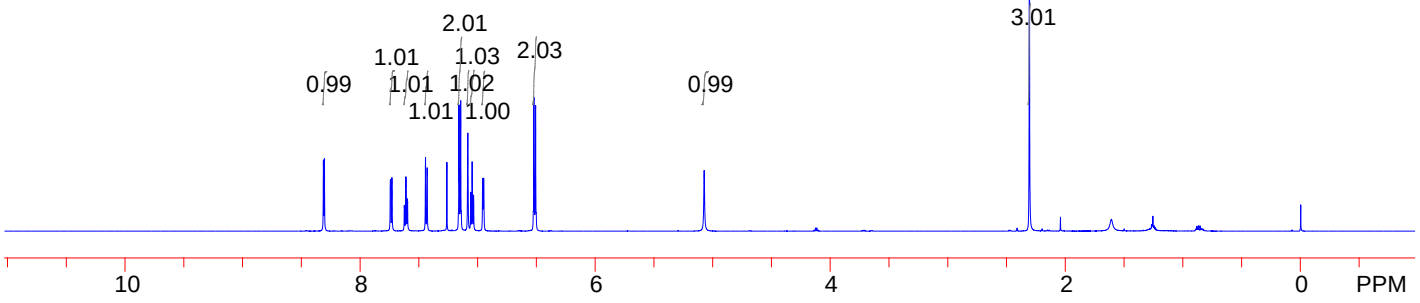

192.338
151.732
157.112
149.567
148.290
144.009
139.161
138.323
126.168
124.900
123.690
122.148
121.409
120.803
120.662
118.443
116.434
114.312
81.584
81.302
77.370
77.053
76.735
34.008
31.333
21.119
4x
^{13}C{^{1}H} (100 MHz, CDCl$_3$)
200
150
100
50
0
PPM

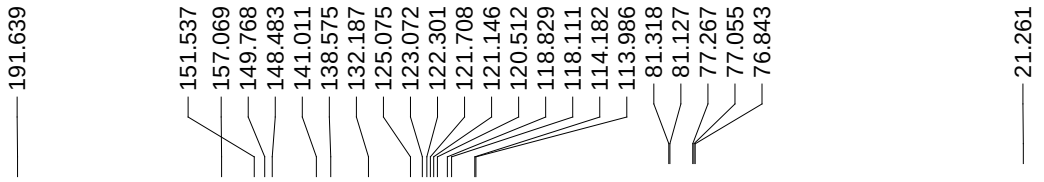

-75.858
O
CF3
tBu
NH
N
4x
Me
19F NMR (565 MHz, CDCl3)
0
-50
-100
-150
-200
PPM

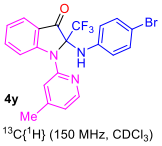




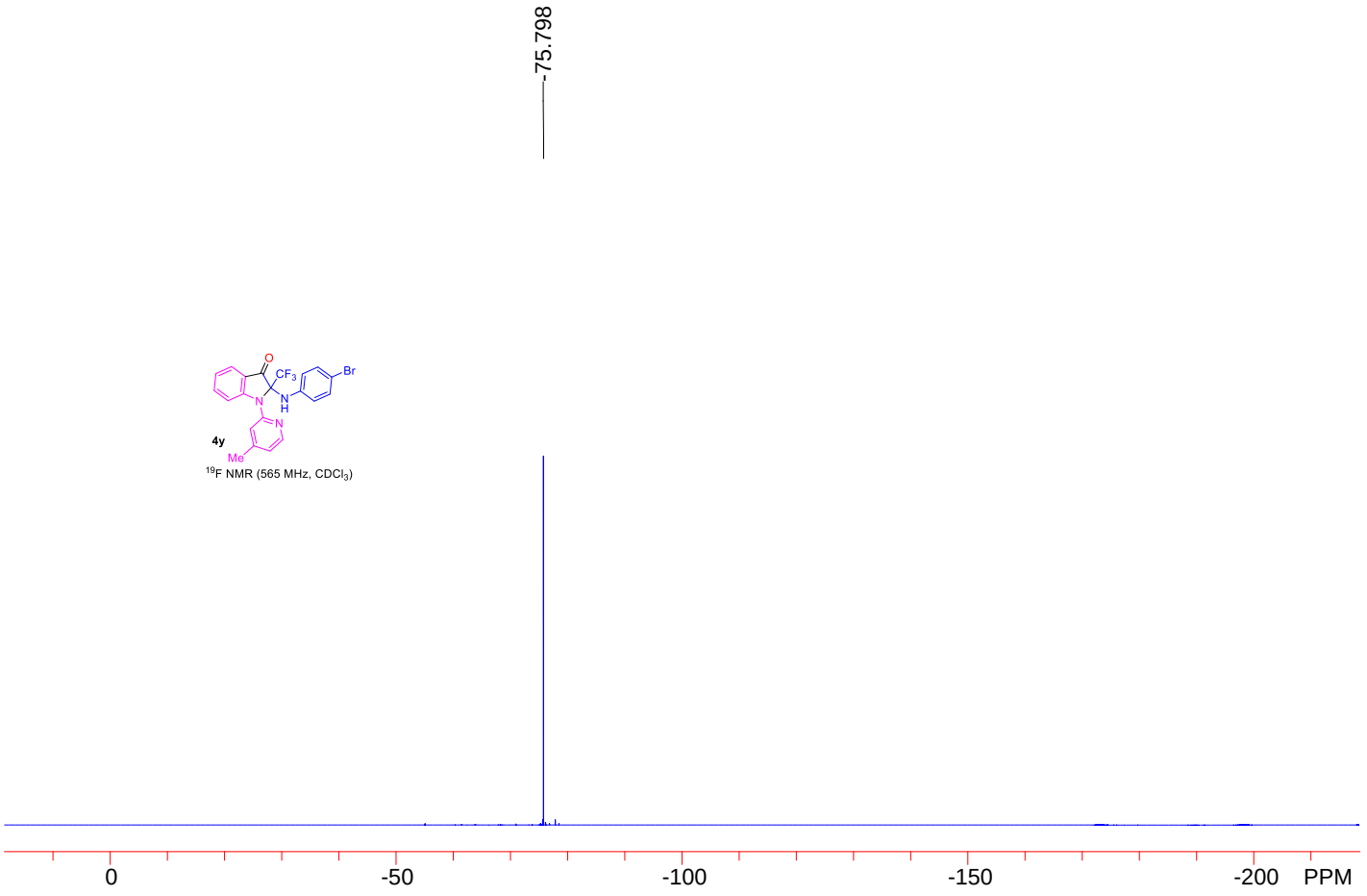
^{1}H NMR (600 MHz, $CDCl_3$)

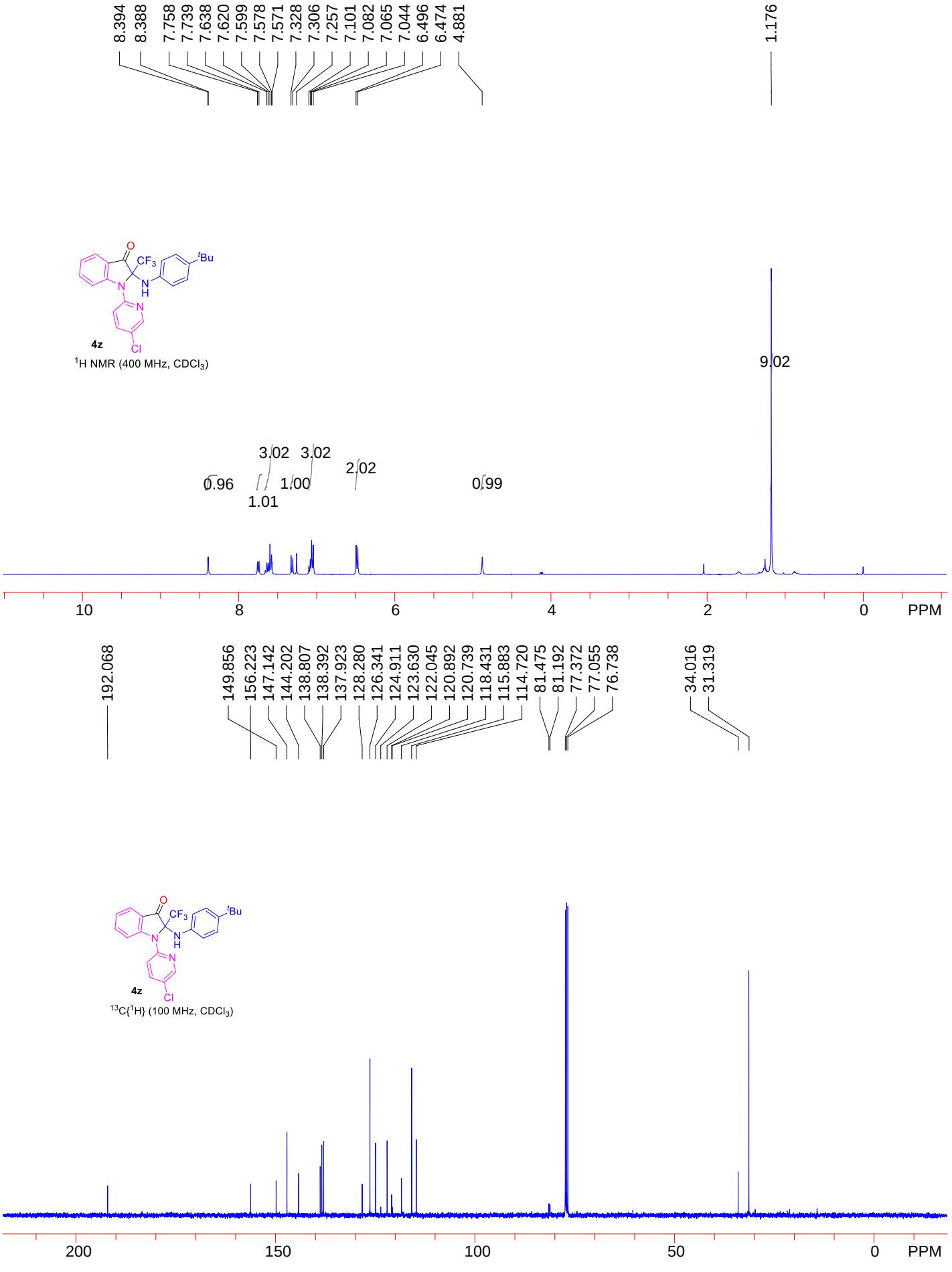


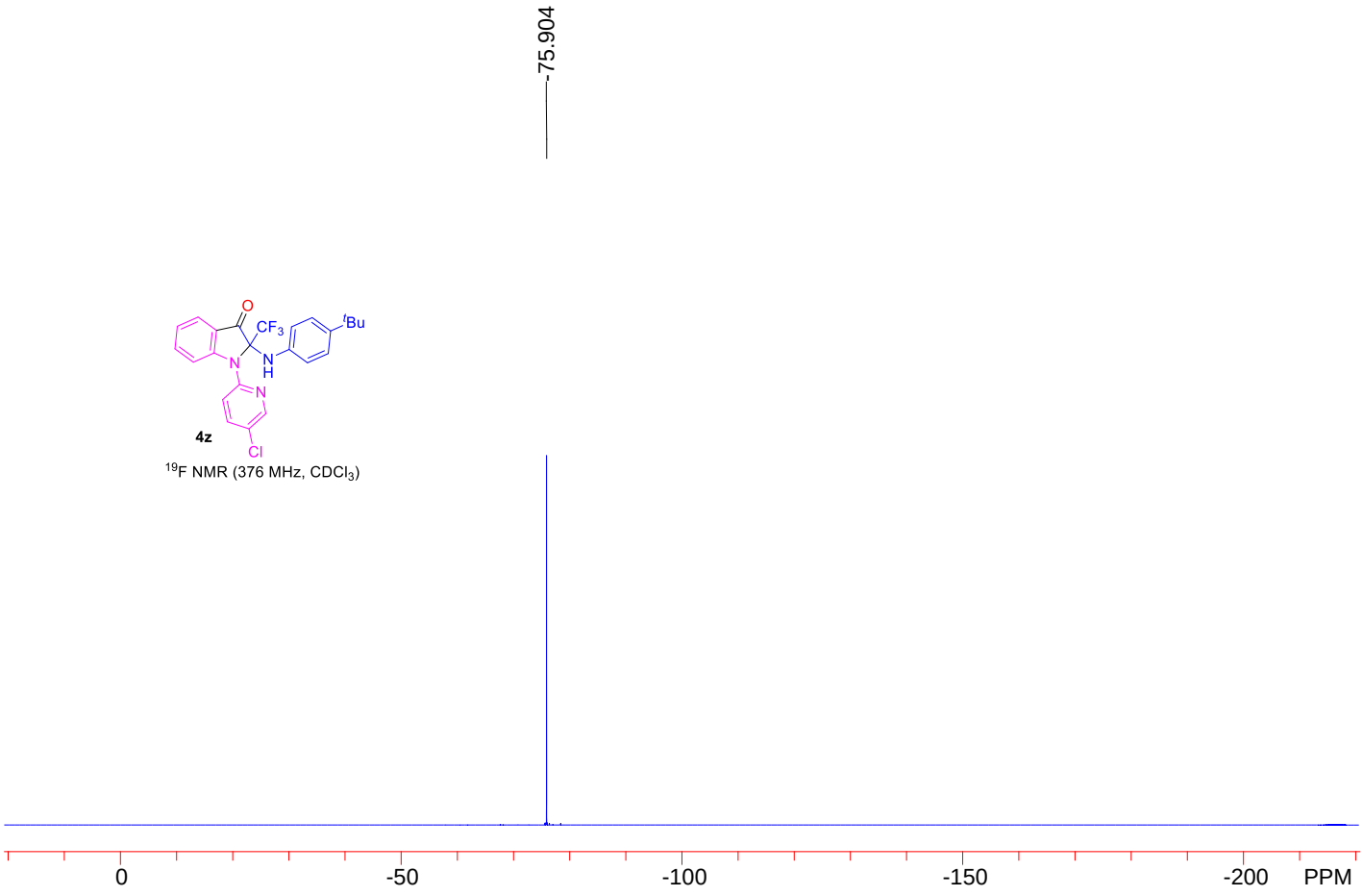


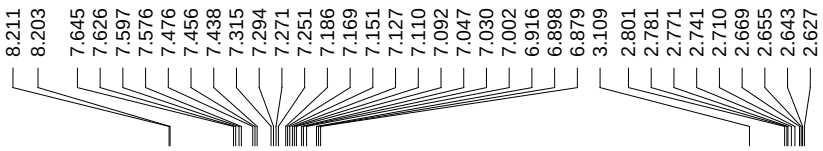


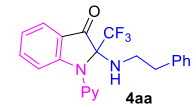
$^{13}C\{^{1}H\}$ (150 MHz, $CDCl_3$)


-75.798
O
CF3
Br
N
H
N
Me
4y
19F NMR (565 MHz, CDCl3)
0
-50
-100
-150
-200
PPM


8.394
8.388
7.758
7.739
7.638
7.620
7.599
7.578
7.571
7.328
7.306
7.257
7.101
7.082
7.065
7.044
6.496
6.474
4.881
1.176
4z
1H NMR (400 MHz, CDCl3)
9.02
3.02
3.02
2.02
0.96
1.00
1.01
0.99
10
8
6
4
2
0
PPM
192.068
149.856
156.223
147.142
144.202
138.807
138.392
137.923
128.280
126.341
124.911
123.630
122.045
120.892
120.739
118.431
115.883
114.720
81.475
81.192
77.372
77.055
76.738
34.016
31.319
4z
13C{1H} (100 MHz, CDCl3)
200
150
100
50
0
PPM

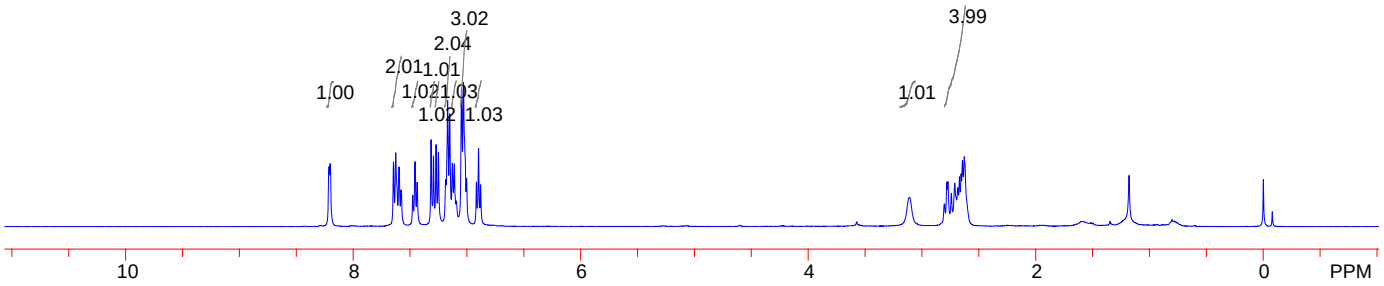

-75.904
O
CF3
tBu
N
H
N
Cl
4z
19F NMR (376 MHz, CDCl3)
0
-50
-100
-150
-200
PPM

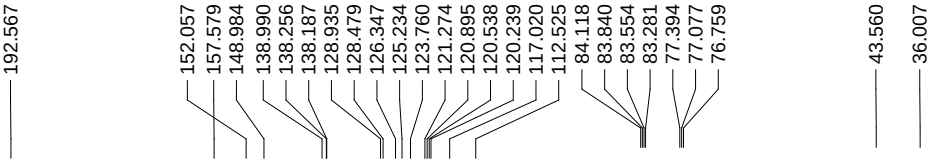


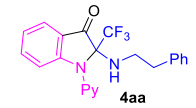


4aa

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

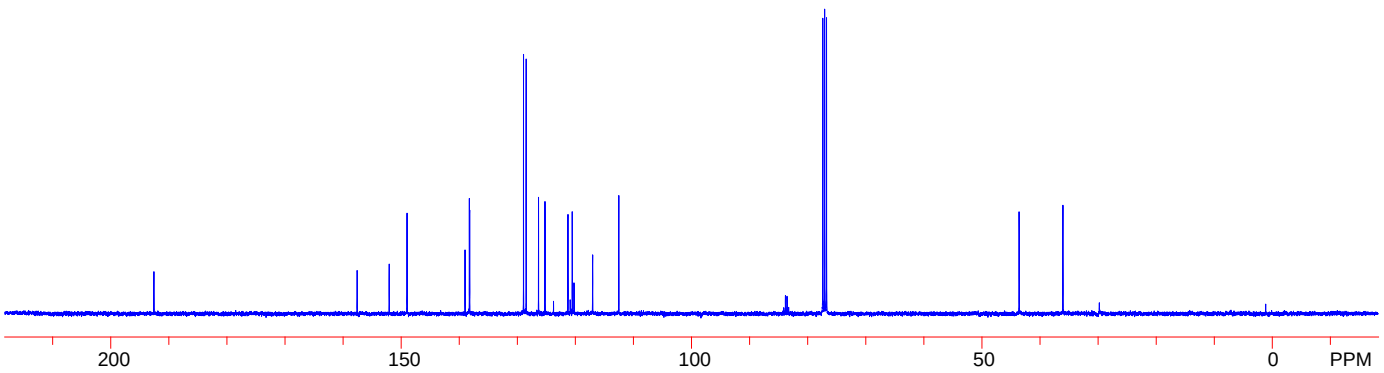


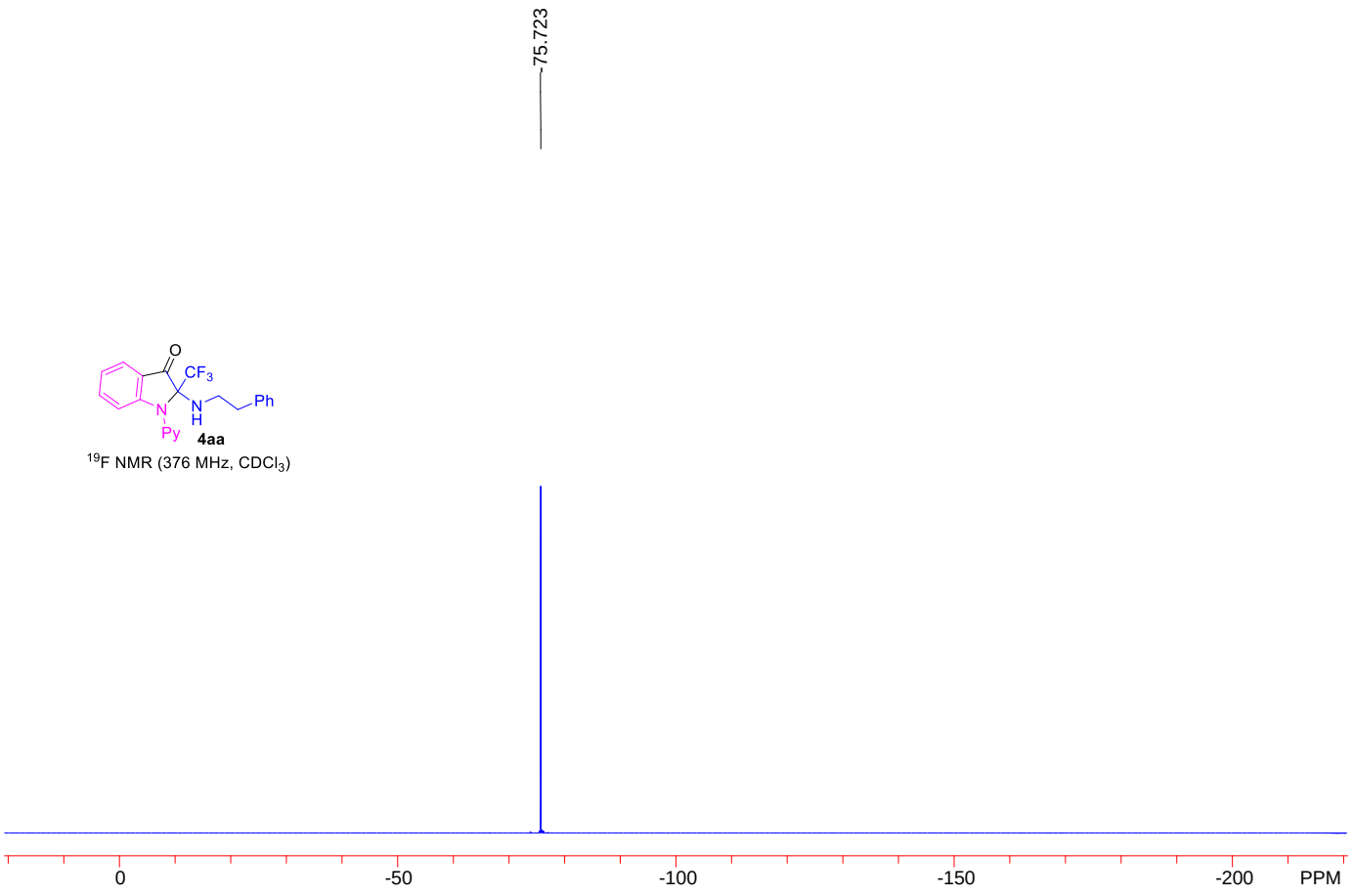




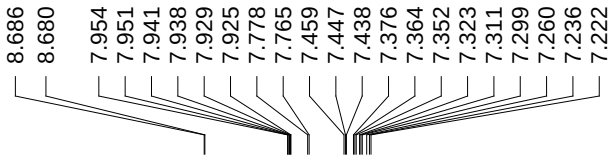
4aa

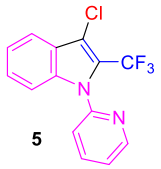
^{13}C{^{1}H} (100 MHz, $CDCl_3$)




75.723
O
CF3
N
H
Ph
Py
4aa
19F NMR (376 MHz, CDCl3)
0
-50
-100
-150
-200
PPM

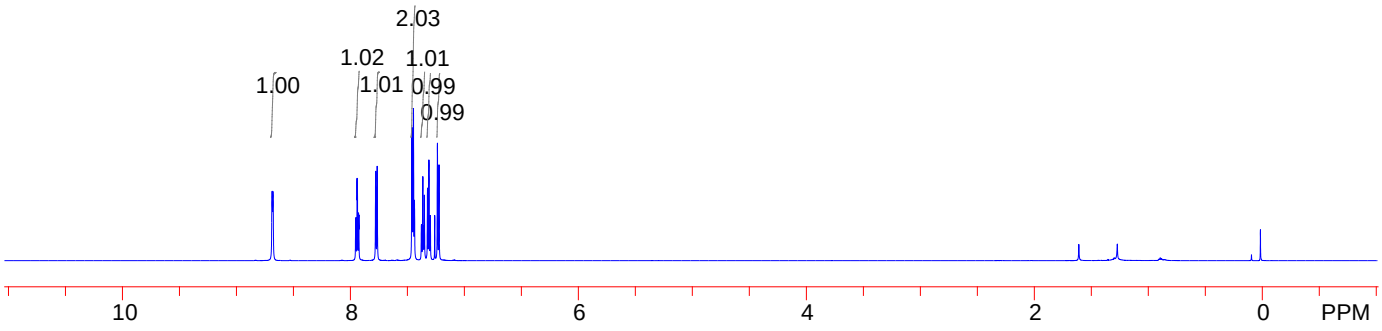
VII. Copies of NMR spectra of 5-8

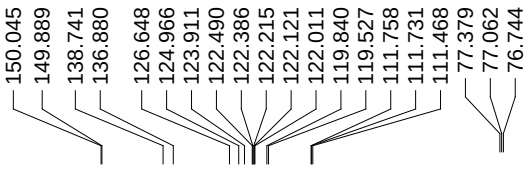


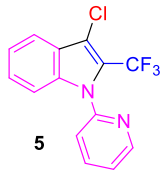


5

^{1}H NMR (600 MHz, $CDCl_3$)

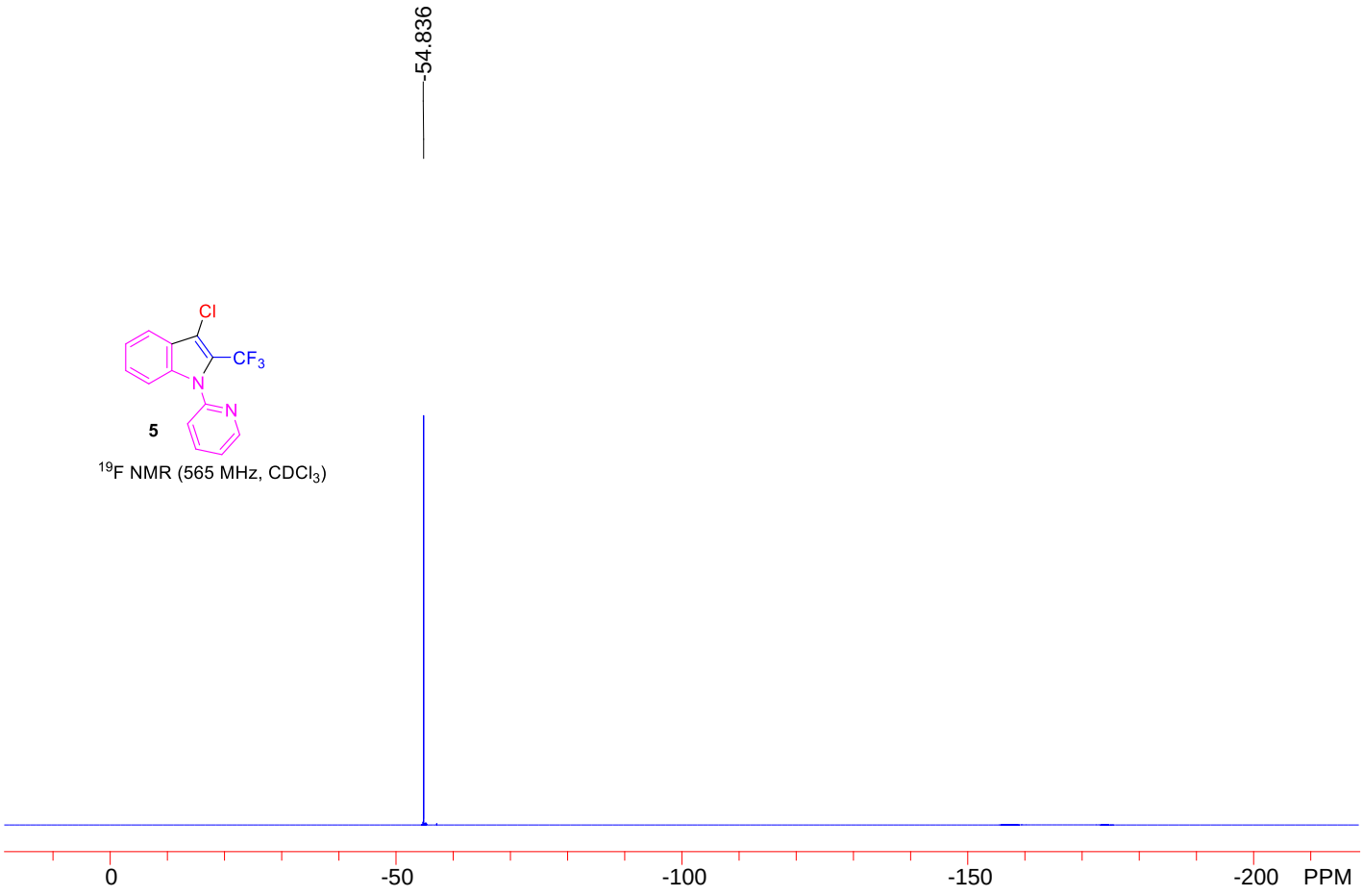






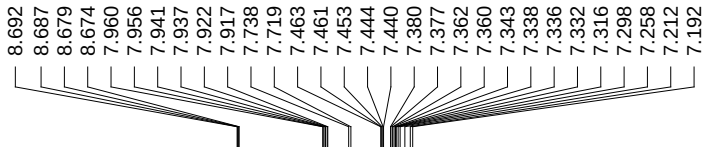
5

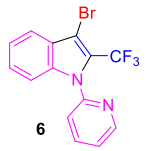
$^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$)



5

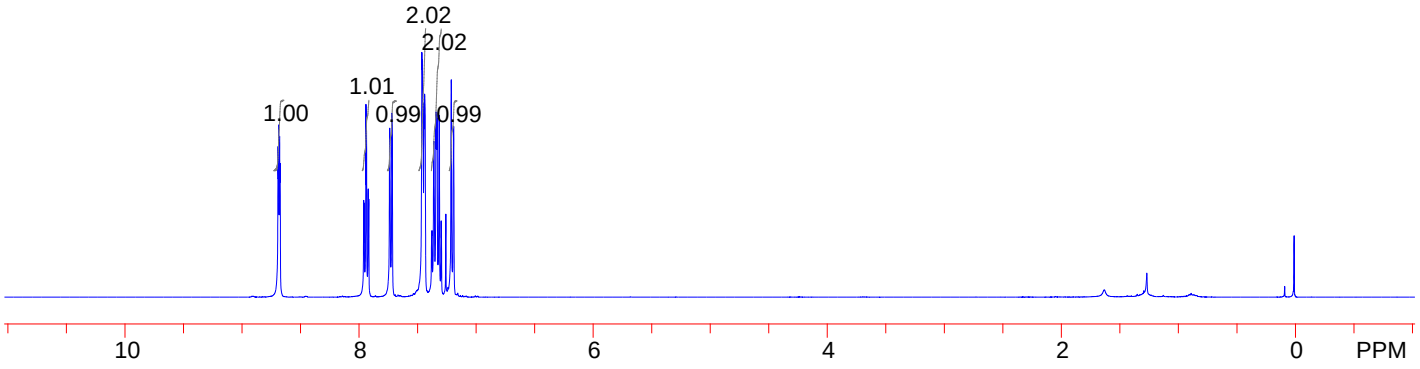
^{19}F NMR (565 MHz, $CDCl_3$)

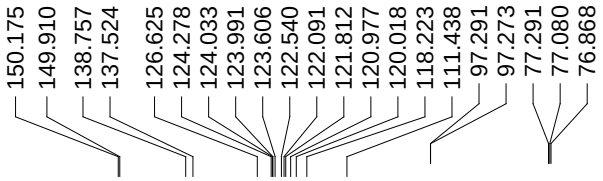


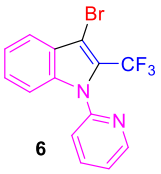


6

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

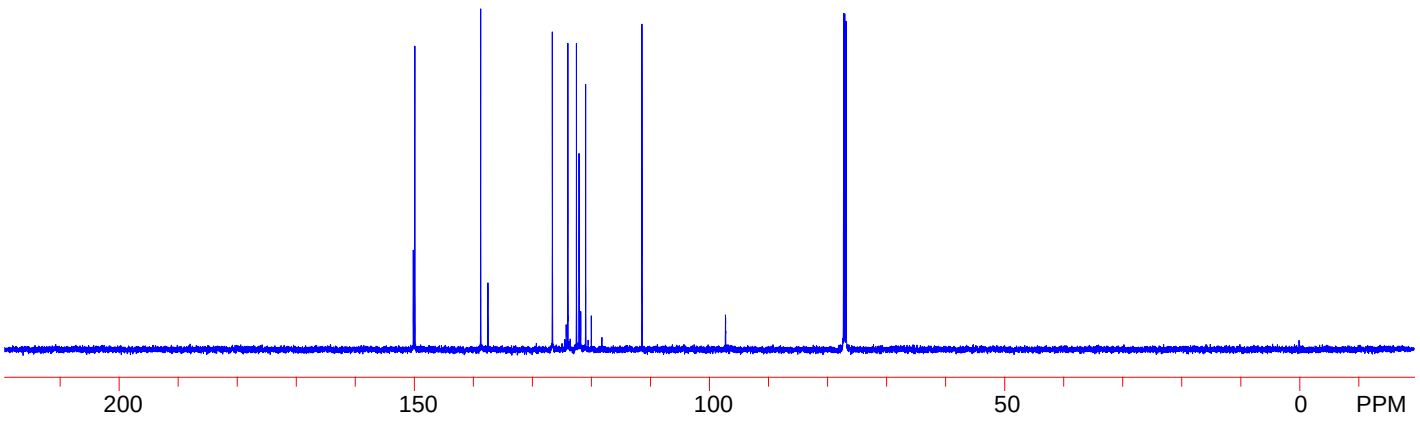


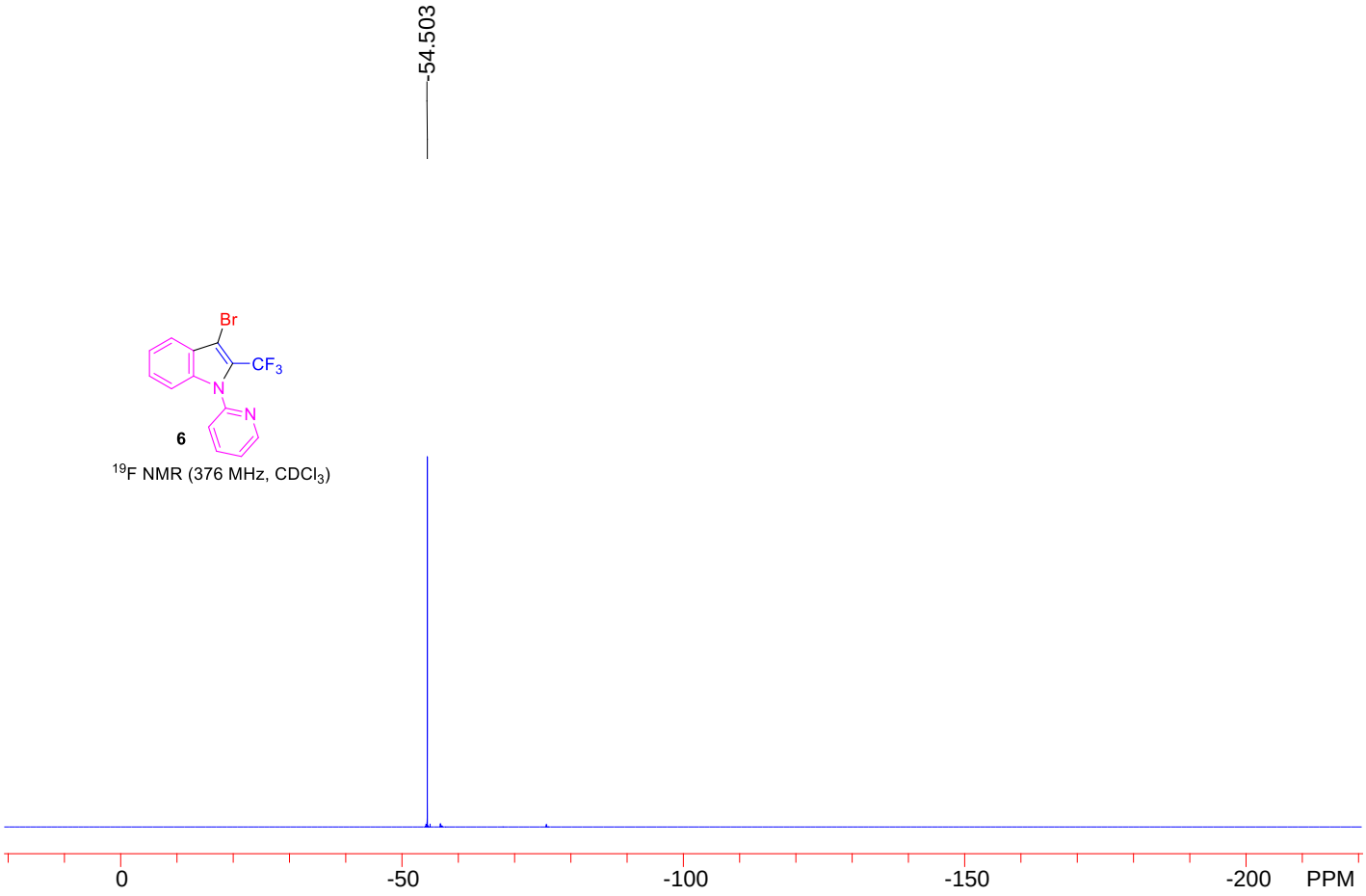




6

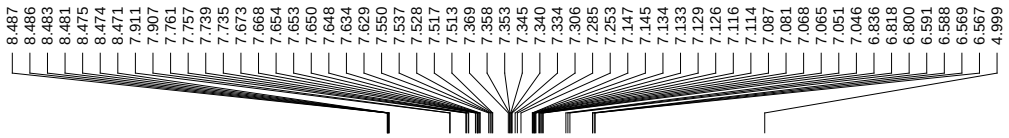
$^{13}C\{^{1}H\}$ (150 MHz, $CDCl_3$)

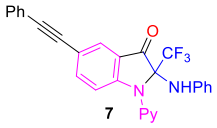




6

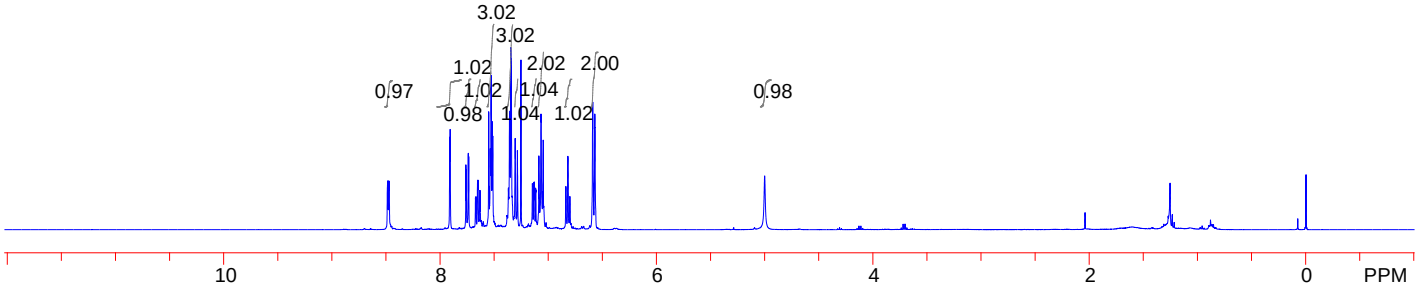
^{19}F NMR (376 MHz, $CDCl_3$)

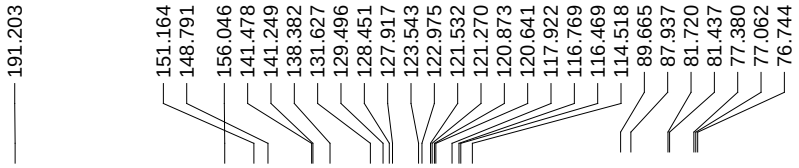


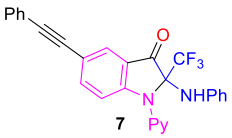


7

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

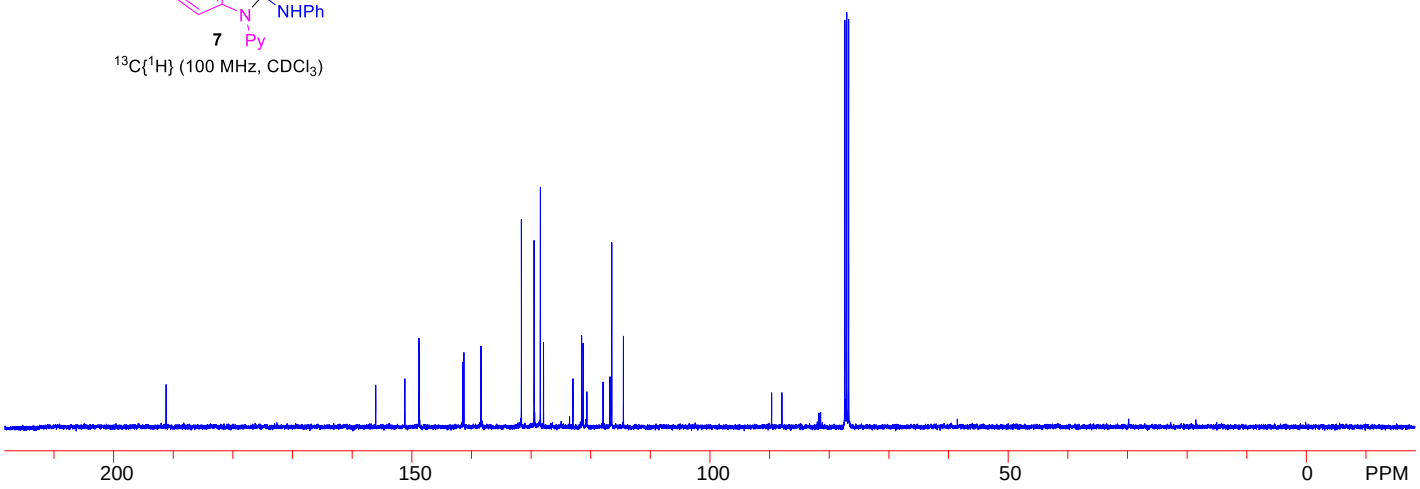


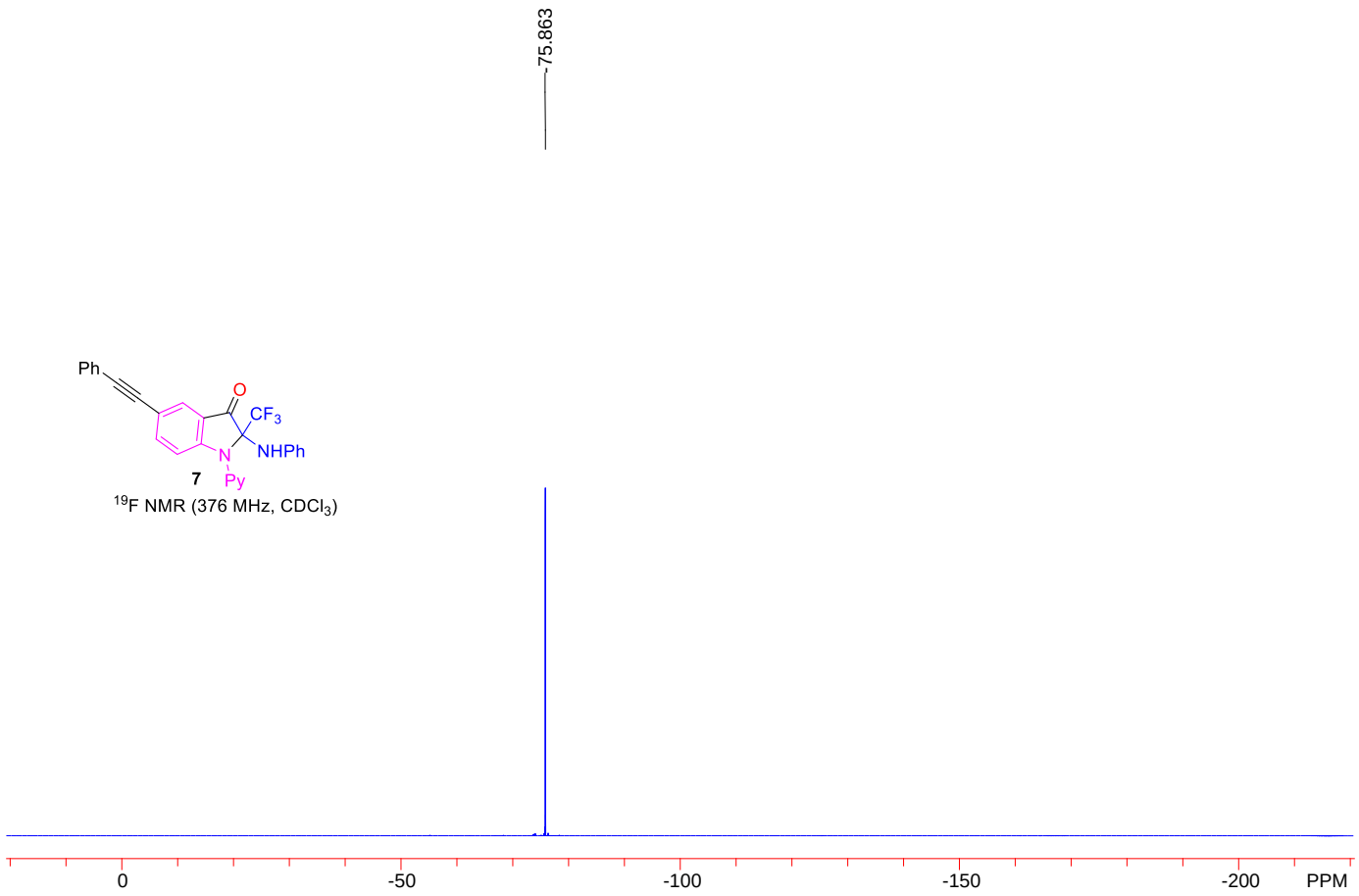


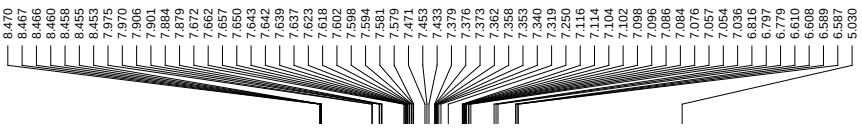


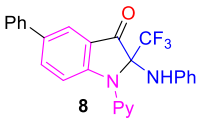
7

$^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$)



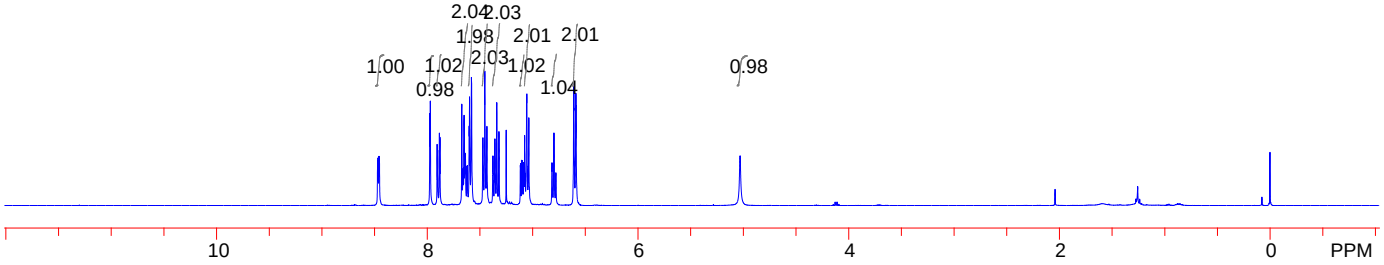

75.863
Ph
O
CF3
NHPh
N
Py
7
19F NMR (376 MHz, CDCl3)
0
-50
-100
-150
-200
PPM

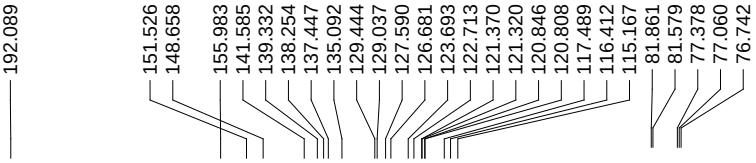


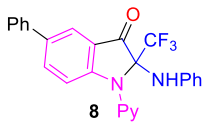


8

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

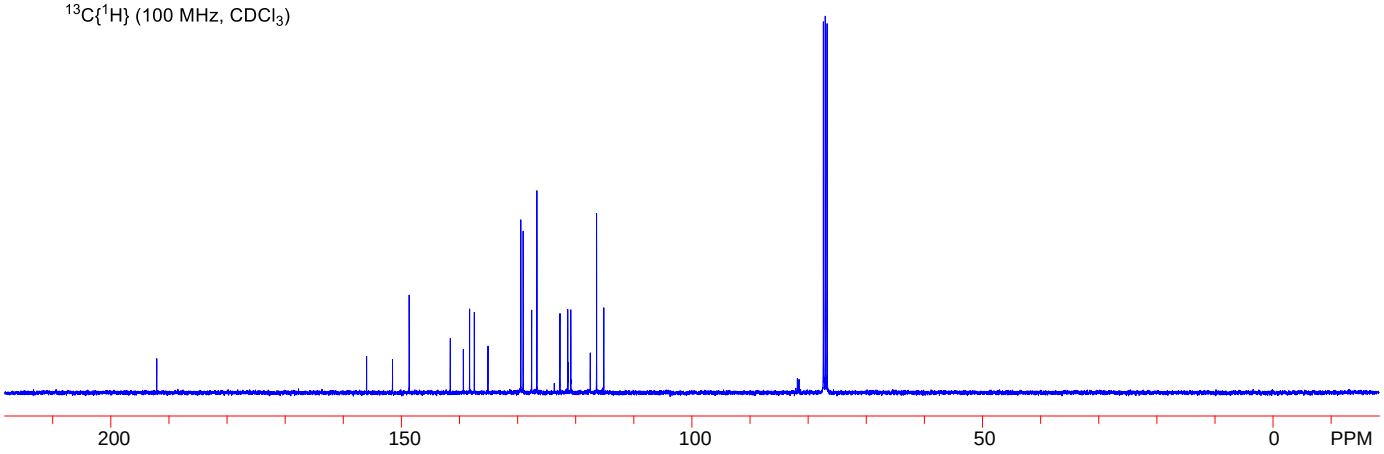


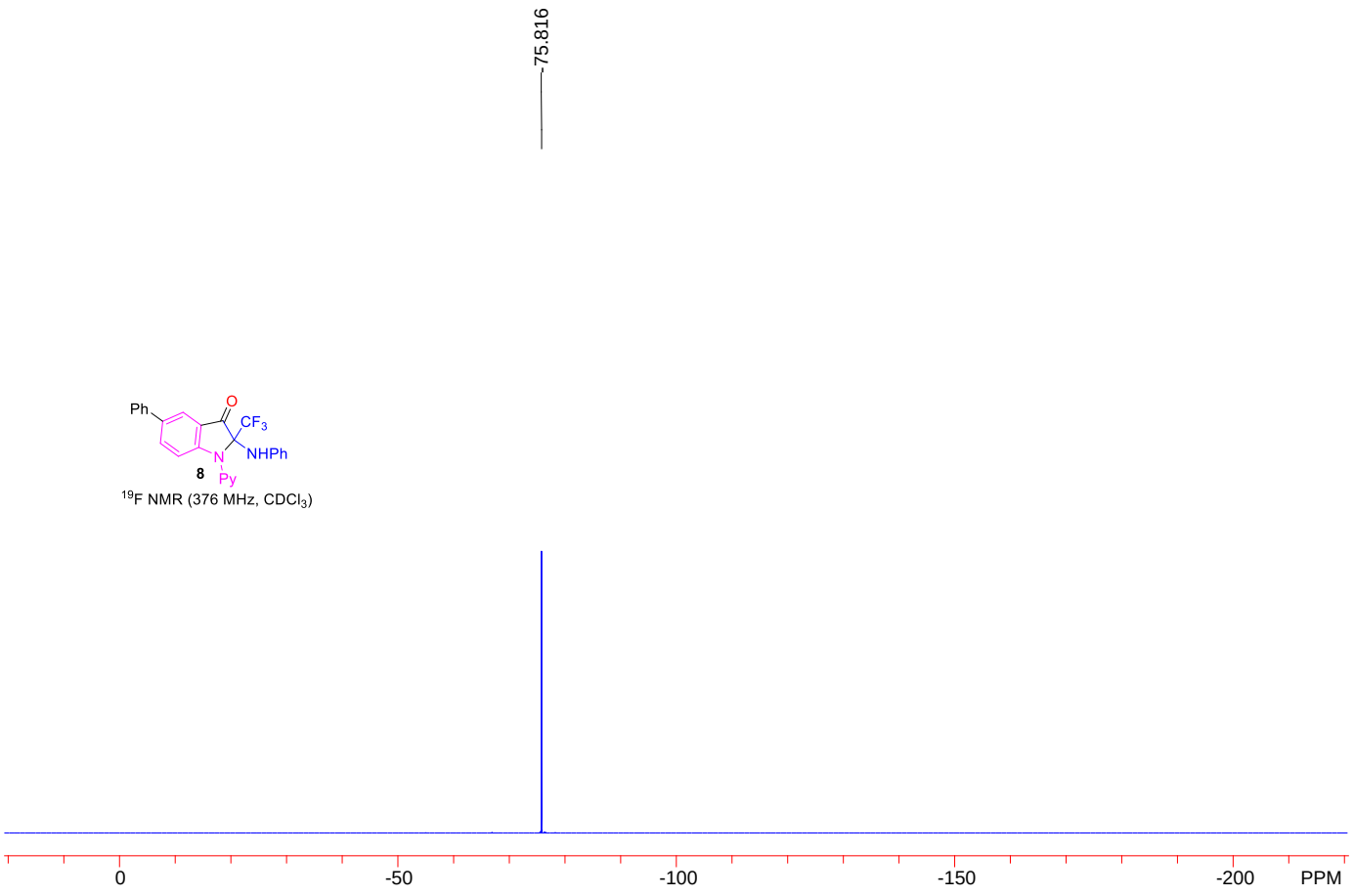




8

^{13}C{^{1}H} (100 MHz, $CDCl_3$)




75.816
Ph
O
CF3
NHPh
N
Py
8
19F NMR (376 MHz, CDCl3)
0
-50
-100
-150
-200
PPM

VIII. X-ray crystal structure and data of 3o

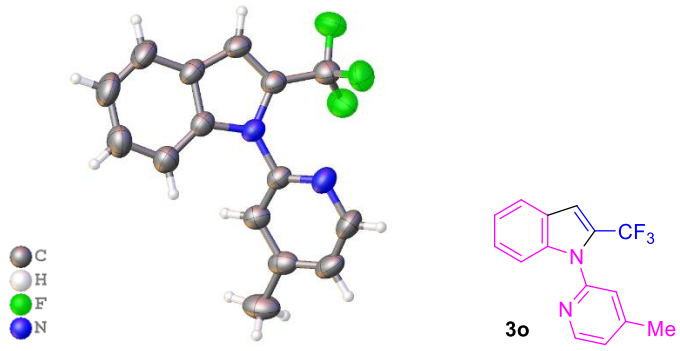


Fig. S1 X-ray crystal structure of **3o** with 50% ellipsoid probability

X-ray structure determination. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent from an ethyl ether solution of **3o**. Crystal data collection and refinement parameters of **3o** are summarized in Table S1. Intensity data were collected at 293 K on a SuperNova Dual diffractometer using mirror-monochromated Cu Kα radiation, λ = 1.54184 Å. The data were corrected for decay, Lorentz, and polarization effects as well as absorption and beam corrections based on the multi-scan technique. Using Olex2, the structure was solved with the SHELXS structure solution program using Direct Methods and refined with the SHELXL refinement package using Least Squares minimisation. Nonhydrogen atoms were refined with anisotropic displacement parameters. The H-atoms were either located or calculated and subsequently treated with a riding model.

Table S1 Crystallographic data and structure refinement results of **3o**

Empirical formula	$C_{15}H_{11}F_3N_2$
Formula weight	276.26
Temp, K	293 (2)
Crystal system	monoclinic
Space group	$P2_1/n$
a, Å	11.7069(5)
b, Å	7.8689(3)
c, Å	14.4296(6)
α (°)	90
β (°)	105.523(4)
γ (°)	90

Volume, Å^3	1280.77(9)
Z	4
ρ_{calc}, g cm^{-3}	1.433
λ, Å	1.54184
μ, mm^{-1}	0.998
No. of data collected	5302
No. of unique data	2430
R_{int}	0.0283
Goodness-of-fit on F^2	1.108
R_1, wR_2 ($I>=2\sigma(I)$)	0.0552, 0.1570
R_1, wR_2 (all data)	0.0606, 0.1636

IX. X-ray crystal structure and data of 4a

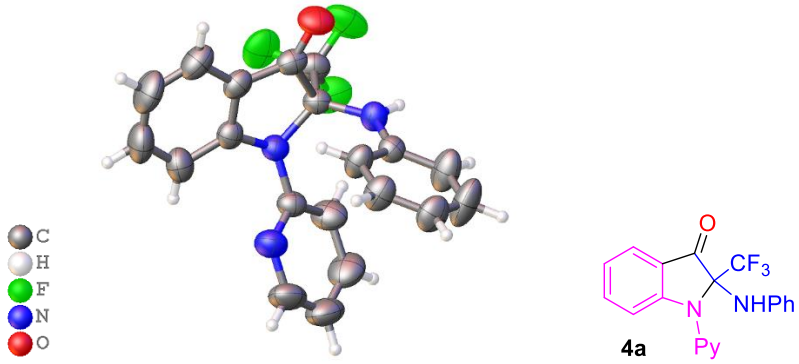


Fig. S2 X-ray crystal structure of **4a** with 50% ellipsoid probability

X-ray structure determination. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent from a petroleum ether/ethyl acetate (10:1) solution of **4a**. Crystal data collection and refinement parameters of **4a** are summarized in Table S2. Intensity data were collected at 293 K on a SuperNova Dual diffractometer using mirror-monochromated Cu Kα radiation, λ = 1.54184 Å. The data were corrected for decay, Lorentz, and polarization effects as well as absorption and beam corrections based on the multi-scan technique. Using Olex2, the structure was solved with the SHELXS structure solution program using Direct Methods and refined with the SHELXL refinement package using Least Squares minimisation. Nonhydrogen atoms were refined with anisotropic displacement parameters. The H-atoms were either located or calculated and subsequently treated with a riding model.

Table S2 Crystallographic data and structure refinement results of **4a**

Empirical formula	$C_{20}H_{14}F_3N_3O$
Formula weight	369.34
Temp, K	293 (2)
Crystal system	orthorhombic
Space group	Pbca
a, Å	17.0044(6)
b, Å	10.7501(3)
c, Å	18.9380(6)
α (°)	90

β (°)	90
γ (°)	90
Volume, Å^3	3461.85(19)
Z	8
ρ_{calc}, g cm^{-3}	1.417
λ, Å	1.54184
μ, mm^{-1}	0.953
No. of data collected	9256
No. of unique data	3261
R_{int}	0.0273
Goodness-of-fit on F^2	1.050
R_1, wR_2 ($I>=2\sigma(I)$)	0.0522, 0.1637
R_1, wR_2 (all data)	0.0653, 0.1984