

Supplementary Information for Accessing Gold p-Acid Reactivity under Electrochemical Anode Oxidation (EAO) through Oxidation Relay

Shuyao Zhang, Jingwen Wei, Xiaohan Ye, Angel Perez & Xiaodong Shi

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1. General Methods and Materials

All of the reactions dealing with air and/or moisture-sensitive compounds were carried out under an atmosphere of argon using oven/flame-dried glassware and standard syringe/septa techniques. Unless otherwise noted, all commercial reagents and solvents were obtained from the commercial provider and used without further purification. ^1H NMR and ^{13}C NMR spectra were recorded on Agilent 400/600 MHz spectrometers. Chemical shifts were reported relative to internal tetramethylsilane (δ 0.00 ppm) or CDCl_3 (δ 7.26 ppm) for ^1H and CDCl_3 (δ 77.00 ppm) for ^{13}C . Flash column chromatography was performed on 230-430 mesh silica gel. Analytical thin layer chromatography was performed with precoated glass baked plates (250 μ) and visualized by fluorescence and by charring after treatment with potassium permanganate stain.

2. General Procedures

2.0 General procedure for the ElectraSyn Set-up

Handmade cell connection with IKA ElectraSyn



1. Remove the top cover



2. Wind a thin wire and attach to the screw on cathode(-)



3. Assemble both graphite electrode and Pt electrode.



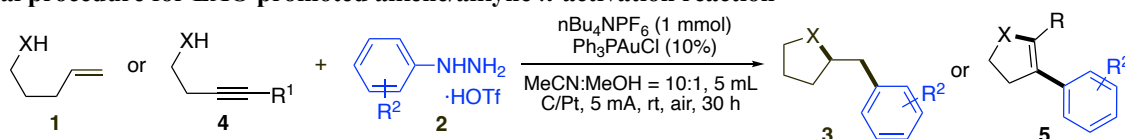
4. Complete the vial set up



5. Connection the vials to IKA Carousel

Supplementary Fig. 1. ElectraSyn Set-up

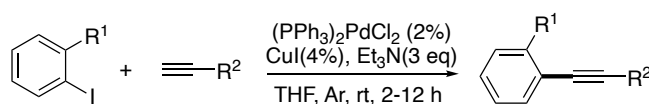
2.1 General procedure for EAO promoted alkene/alkyne π -activation reaction



Supplementary Fig. 2. General procedure for EAO promoted alkene/alkyne π -activation reaction

To a 10 mL ElectraSyn screwed vial with 387 mg $n\text{Bu}_4\text{NPF}_6$ (1 mmol) in $\text{MeCN}:\text{MeOH} = 10:1$ (5.5 mL), alkene **1** or alkyne **4** (0.5 mmol, 1.0 equiv.), Ph_3PAuCl (0.05 mmol, 10 mol%) and the first batch of aryl hydrazine HOTf salt **2** (0.5 mmol, 1.0 equiv) was added. The vial was placed on IKA Carousel and run under constant current at 5 mA for 10 h. After the time is over, the cap was opened and another 1 eq hydrazine was added, then the reaction was performed under same condition for another 10 h. This step was repeated twice until all 3 eq hydrazine HOTf salt **2** was consumed. the solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel to give desired product **3** or **5**.

2.2 General procedure for the synthesis of different internal alkyne **4**



Supplementary Fig. 3. General procedure for the synthesis of different internal alkyne **4**

All alkyne substrates **4** were synthesized with literature reported Sonogashira coupling strategy. To a round bottom flask was added iodobenzene substrate (5 mmol, 1 eq), $(\text{PPh}_3)_2\text{PdCl}_2$ (0.1 mmol, 2%) and CuI (0.2 mmol, 4%). The flask was capped

and flushed with Ar. THF (25 mL, 0.2 M), Et₃N (15 mmol, 3 eq) and terminal alkyne (6 mmol, 1.2 eq) were added in sequence. The reaction was stirred under rt for 2-12 h (monitored by TLC). Once the reaction finished, the mixture was filtrated and washed with EA. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel to get the desired product **4**.

3. Condition Optimization and Substrate Scope Screening

3.1 Optimization studies of EAO promoted alkene/alkyne π -activation reaction

Supplementary Table 1 | Reaction optimization

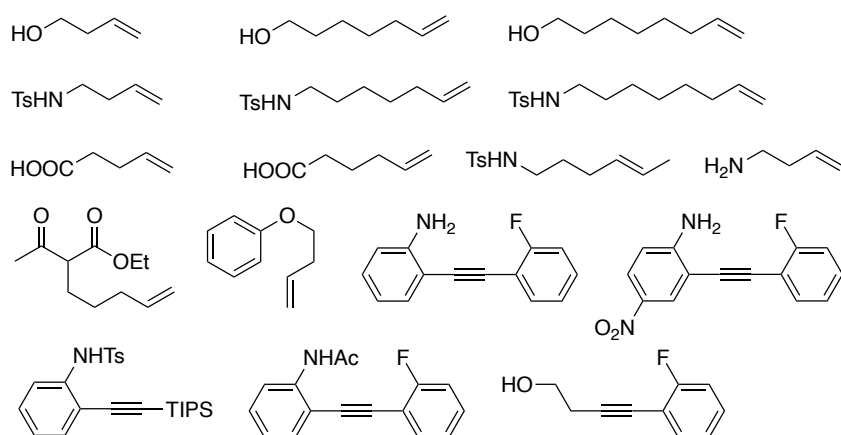
Entry	Condition Variation	Yield		Note
		3a	4ad	
1	none	32%	29%	-
2	MeCN 5 mL only	trace	19%	Gold decomposition
3	MeCN:MeOH = 4:1, 5 mL	16%	30%	-
4	MeCN:MeOH = 1:1, 5 mL	12%	26%	-
5	MeCN:MeOH = 1:4, 5 mL	6%	32%	-
6	Only MeOH	trace	24%	-
7	Ph ₃ PAu(TA-Me)OTf instead	12%	46%	-
8	JohnPhosAuCl instead	0%	43%	Gold decomposition
9	MeDalPhosAuCl instead	trace	37%	Gold decomposition
10	Ph ₂ P(N ₁ Bn)BTAAuCl instead	7%	44%	-
11	dppm(AuBr) ₂ instead	trace	41%	Gold decomposition
12	IPrAuNTf ₂ instead	0%	48%	Gold decomposition
13	(2-MePh) ₃ PAuCl instead	trace	36%	Gold decomposition
14	nBu ₄ NBF ₄ (1 mmol)	15%	31%	-
15	LiClO ₄ (1 mmol)	37%	32%	-
16	nBu ₄ NPF ₆ (0.5 mmol)	38%	37%	-
17	nBu ₄ NPF ₆ (1.5 mmol)	35%	40%	-
18	nBu ₄ NPF ₆ (1 mmol) + LiClO ₄ (0.5 mmol)	35%	41%	-
19	EtOH instead of MeOH	20%	27%	-
20	iPrOH instead of MeOH	17%	28%	-
21	tBuOH instead of MeOH	10%	22%	-
22	HFIP instead of MeOH	4%	9%	Gold decomposition
23	CF ₃ CH ₂ OH instead of MeOH	0%	6%	Gold decomposition
24	H ₂ O instead of MeOH	6%	33%	-
25	DCM instead of MeOH	0%	48%	Gold decomposition
26	2 eq alkene instead	33%	25%	-
27	45 °C	trace	44%	Gold decomposition
28	45 °C, O ₂	5%	14%	Gold decomposition
29	rt, N ₂	6%	43%	Gold decomposition
30	rt, O ₂	24%	9%	-
31	3 mA, 15 h	32%	27%	-

32	2 mA, 25 h	35%	23%	-
33	10 mA, 5 h	9%	37%	Gold decomposition
34	double alkene and hydrazine (20 h)	34%	35%	-
35	Double alkene, hydrazine and gold (20 h)	54%	22%	-
36	0.5 mmol alkene, 1.5 mmol hydrazine, 0.05 mmol gold (30 h)	70%	21%	-
37	0.5 mmol alkene, 1.5 mmol hydrazine, 0.05 mmol gold, 0.5 mmol nBu ₄ NPF ₆ (30 h)	70%	23%	-
38	0.5 mmol alkene, 1.5 mmol hydrazine, 0.05 mmol gold (add 0.5 mmol hydrazine, run 10 h, repeat 3 times)	92%	18%	-

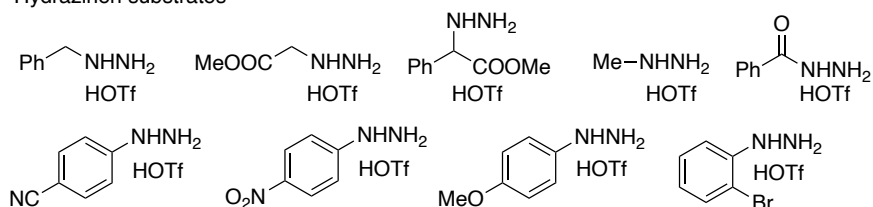
3.2 Substrate scope of failed alkenes/hydrazines

We tested various different alkene and hydrazine substrates. Attached is a list of substrates that is not reactive or will decompose under optimized conditions.

alkene/alkyne substrates

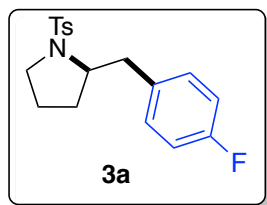


Hydrazinen substrates



Supplementary Fig. 4. Substrate scope of failed alkenes/hydrazines

4. Compound Characterization



2-(4-fluorobenzyl)-1-tosylpyrrolidine

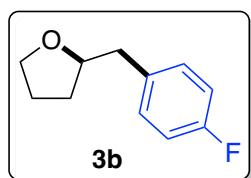
3a was prepared following the general procedure 2.1 and purified by column chromatography (hexane:EA = 5:1) as a white solid.

¹H NMR (600 MHz, Chloroform-*d*) δ 7.75 (d, J = 8.3 Hz, 2H), 7.35 – 7.29 (m, 2H), 7.21 (dd, J = 8.5, 5.5 Hz, 2H), 6.98 (t, J = 8.7 Hz, 2H), 3.83 – 3.75 (m, 1H), 3.36 (dddd, J = 10.1, 5.4, 4.2, 2.7 Hz, 1H), 3.20 – 3.09 (m, 2H), 2.79 (dd, J = 13.5, 9.1 Hz, 1H), 2.43 (s, 3H), 1.64 – 1.58 (m, 2H), 1.48 – 1.41 (m, 2H).

¹³C NMR (151 MHz, CDCl₃) δ 161.71 (d, J = 244.7 Hz), 143.40, 134.64, 134.06, 131.07 (d, J = 7.9 Hz), 129.70, 127.52, 115.21 (d, J = 21.1 Hz), 61.44, 49.26, 41.76, 29.86, 23.81, 21.53.

¹⁹F NMR (564 MHz, Chloroform-*d*) δ -116.75.

HRMS m/z (ESI) calcd. for C₁₈H₂₁FN₂O₂S⁺ (M+H)⁺ 334.1272, found 334.1315.



2-(4-fluorobenzyl)tetrahydrofuran

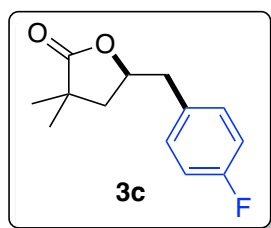
3b was prepared following the general procedure 2.1 and purified by column chromatography (hexane:EA = 20:1) as a colorless oil.

¹H NMR (600 MHz, Chloroform-*d*) δ 7.21 – 7.16 (m, 2H), 6.97 (t, J = 8.7 Hz, 1H), 4.03 (dq, J = 7.7, 6.3 Hz, 1H), 3.88 (ddd, J = 8.3, 7.1, 6.2 Hz, 1H), 3.74 (td, J = 8.0, 6.3 Hz, 1H), 2.86 (dd, J = 13.8, 6.7 Hz, 1H), 2.74 (dd, J = 13.8, 6.0 Hz, 1H), 1.93 (dddd, J = 11.2, 8.2, 6.2, 4.8 Hz, 1H), 1.90 – 1.81 (m, 2H), 1.56 – 1.51 (m, 1H).

¹³C NMR (151 MHz, Chloroform-*d*) δ 161.53 (d, J = 243.5 Hz), 134.68, 130.59 (d, J = 7.8 Hz), 115.08 (d, J = 21.0 Hz), 79.95, 68.00, 41.04, 30.96, 25.63.

¹⁹F NMR (564 MHz, Chloroform-*d*) δ -117.40.

HRMS m/z (ESI) calcd. for C₁₁H₁₄FO⁺ (M+H)⁺ 181.1023, found 181.1051.



5-(4-fluorobenzyl)-3,3-dimethyldihydrofuran-2(3H)-one

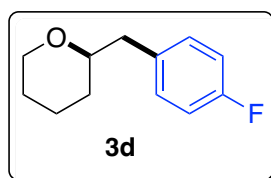
3c was prepared following the general procedure 2.1 and purified by column chromatography (hexane:EA = 20:1) as a colorless oil.

¹H NMR (600 MHz, Chloroform-*d*) δ 7.20 (dd, J = 8.5, 5.5 Hz, 2H), 7.01 (t, J = 8.7 Hz, 2H), 4.60 (ddt, J = 10.0, 6.8, 5.8 Hz, 1H), 3.04 (dd, J = 14.2, 6.8 Hz, 1H), 2.88 (dd, J = 14.2, 5.8 Hz, 1H), 2.09 (dd, J = 12.7, 5.8 Hz, 1H), 1.80 (dd, J = 12.7, 10.0 Hz, 1H), 1.24 (d, J = 2.2 Hz, 6H).

¹³C NMR (151 MHz, Chloroform-*d*) δ 181.68, 161.93 (d, J = 245.5 Hz), 131.96, 130.89 (d, J = 8.0 Hz), 115.46 (d, J = 21.3 Hz), 42.83, 40.75, 40.44, 24.97, 24.41.

¹⁹F NMR (564 MHz, Chloroform-*d*) δ -115.94.

HRMS m/z (ESI) calcd. for C₁₃H₁₆FO₂⁺ (M+H)⁺ 223.1129, found 223.1158.



2-(4-fluorobenzyl)tetrahydro-2H-pyran

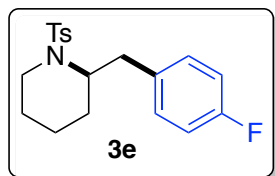
3d was prepared following the general procedure 2.1 and purified by column chromatography (hexane:EA = 20:1) as a colorless oil.

¹H NMR (600 MHz, Chloroform-*d*) δ 7.16 (dd, J = 8.4, 5.6 Hz, 2H), 6.96 (t, J = 8.7 Hz, 2H), 4.01 – 3.93 (m, 1H), 3.48 – 3.36 (m, 2H), 2.82 (dd, J = 13.9, 7.0 Hz, 1H), 2.62 (dd, J = 13.9, 6.1 Hz, 1H), 1.81 (dq, J = 11.7, 2.5 Hz, 1H), 1.56 (td, J = 13.6, 12.6, 7.2 Hz, 2H), 1.51 – 1.40 (m, 2H), 1.28 (tdd, J = 12.8, 10.8, 5.0 Hz, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 161.48 (d, J = 242.7 Hz), 134.50, 130.71 (d, J = 7.9 Hz), 114.97 (d, J = 20.8 Hz), 78.71, 68.67, 42.29, 31.43, 26.01, 23.48.

¹⁹F NMR (564 MHz, Chloroform-*d*) δ -117.45.

HRMS m/z (ESI) calcd. for C₁₂H₁₆FO⁺ (M+H)⁺ 195.1180, found 195.1217.



2-(4-fluorobenzyl)-1-tosylpiperidine

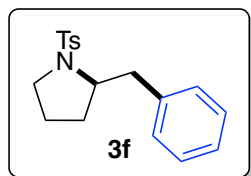
3e was prepared following the general procedure 2.1 and purified by column chromatography (hexane:EA = 5:1) as a pale yellow solid.

¹H NMR (600 MHz, Chloroform-*d*) δ 7.59 (d, J = 8.1 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 7.14 – 7.04 (m, 2H), 6.94 (t, J = 8.7 Hz, 2H), 4.30 – 4.19 (m, 1H), 3.84 – 3.72 (m, 1H), 3.07 (td, J = 13.4, 2.5 Hz, 1H), 2.92 – 2.75 (m, 2H), 2.40 (s, 3H), 1.60 (qd, J = 16.8, 13.0 Hz, 3H), 1.53 – 1.35 (m, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 161.60 (d, J = 244.4 Hz), 142.90, 138.33, 134.28, 130.55 (d, J = 7.8 Hz), 129.59, 126.95, 115.31 (d, J = 21.0 Hz), 54.44, 40.88, 35.03, 26.16, 24.83, 21.50, 18.35.

¹⁹F NMR (564 MHz, Chloroform-*d*) δ -116.66.

HRMS m/z (ESI) calcd. for C₁₉H₂₃FNO₂S⁺ (M+H)⁺ 348.1428, found 348.1439.



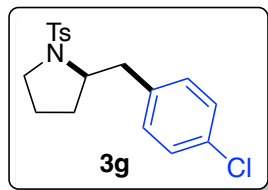
2-benzyl-1-tosylpyrrolidine

3f was prepared following the general procedure 2.1 and purified by column chromatography (hexane:EA = 5:1) as a colorless oil.

¹H NMR (600 MHz, Chloroform-*d*) δ 7.76 (d, J = 8.2 Hz, 2H), 7.31 (dd, J = 11.7, 7.7 Hz, 4H), 7.23 (dd, J = 16.0, 7.3 Hz, 3H), 3.82 (ddt, J = 9.7, 7.7, 3.4 Hz, 1H), 3.48 – 3.33 (m, 1H), 3.25 (dd, J = 13.3, 3.5 Hz, 1H), 3.13 (dt, J = 10.1, 7.6 Hz, 1H), 2.75 (dd, J = 13.3, 9.7 Hz, 1H), 2.43 (s, 3H), 1.70 – 1.59 (m, 2H), 1.54 – 1.36 (m, 2H).

¹³C NMR (151 MHz, CDCl₃) δ 143.35, 138.53, 134.63, 129.69, 129.66, 128.45, 127.54, 126.43, 61.63, 49.28, 42.75, 29.85, 23.81, 21.56.

HRMS m/z (ESI) calcd. for C₁₈H₂₂NO₂S⁺ (M+H)⁺ 316.1366, found 316.1412.



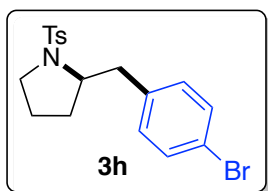
2-(4-chlorobenzyl)-1-tosylpyrrolidine

3g was prepared following the general procedure 2.1 and purified by column chromatography (hexane:EA = 5:1) as a pale yellow oil.

¹H NMR (600 MHz, Chloroform-*d*) δ 7.74 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 7.29 – 7.26 (m, 2H), 7.19 (d, J = 8.4 Hz, 2H), 3.78 (dh, J = 11.4, 3.5, 2.7 Hz, 1H), 3.36 (ddd, J = 10.4, 6.2, 3.8 Hz, 1H), 3.20 – 3.08 (m, 2H), 2.79 (dd, J = 13.4, 9.1 Hz, 1H), 2.43 (s, 3H), 1.63 – 1.55 (m, 2H), 1.50 – 1.40 (m, 2H).

¹³C NMR (151 MHz, CDCl₃) δ 143.47, 136.84, 134.48, 132.32, 131.04, 129.73, 128.55, 127.52, 61.30, 49.27, 41.96, 29.88, 23.84, 21.57.

HRMS m/z (ESI) calcd. for C₁₈H₂₁ClNO₂S⁺ (M+H)⁺ 350.0976, found 350.1001.



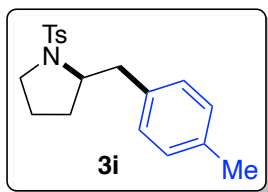
2-(4-bromobenzyl)-1-tosylpyrrolidine

3h was prepared following the general procedure 2.1 and purified by column chromatography (hexane:EA = 5:1) as a white solid.

¹H NMR (600 MHz, Chloroform-*d*) δ 7.74 (d, J = 8.0 Hz, 2H), 7.42 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 8.1 Hz, 2H), 3.78 (td, J = 8.2, 6.8, 3.7 Hz, 1H), 3.36 (ddd, J = 10.4, 6.3, 3.8 Hz, 1H), 3.13 (tt, J = 14.2, 5.5 Hz, 2H), 2.78 (dd, J = 13.4, 9.1 Hz, 1H), 2.43 (s, 3H), 1.70 – 1.54 (m, 2H), 1.45 (ddt, J = 11.9, 9.3, 5.5 Hz, 2H).

¹³C NMR (151 MHz, CDCl₃) δ 143.48, 137.36, 134.48, 131.51, 131.45, 129.73, 127.52, 120.40, 61.23, 49.27, 42.02, 29.89, 23.84, 21.57.

HRMS m/z (ESI) calcd. for C₁₈H₂₁BrNO₂S⁺ (M+H)⁺ 394.0471, found 394.0510.



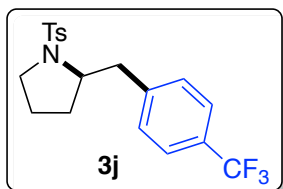
2-(4-methylbenzyl)-1-tosylpyrrolidine

3i was prepared following the general procedure 2.1 and purified by column chromatography (hexane:EA = 5:1) as colorless oil.

¹H NMR (600 MHz, Chloroform-*d*) δ 7.75 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 7.9 Hz, 2H), 7.12 (q, J = 8.0 Hz, 4H), 3.83 – 3.77 (m, 1H), 3.40 (ddd, J = 10.7, 7.1, 4.4 Hz, 1H), 3.24 – 3.19 (m, 1H), 3.12 (dt, J = 9.9, 7.3 Hz, 1H), 2.70 (dd, J = 13.3, 9.7 Hz, 1H), 2.42 (s, 3H), 2.33 (s, 3H), 1.73 – 1.60 (m, 2H), 1.50 – 1.35 (m, 2H).

¹³C NMR (151 MHz, CDCl₃) δ 143.29, 135.93, 135.42, 134.66, 129.64, 129.50, 129.11, 127.52, 61.73, 49.24, 42.28, 29.78, 23.78, 21.53, 21.06.

HRMS m/z (ESI) calcd. for C₁₉H₂₄NO₂S⁺ (M+H)⁺ 330.1522, found 330.1551.



1-tosyl-2-(4-(trifluoromethyl)benzyl)pyrrolidine

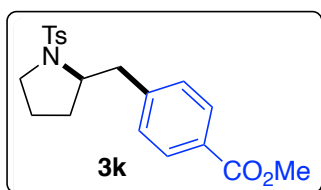
3j was prepared following the general procedure 2.1 and purified by column chromatography (hexane:EA = 10:1) as white solid.

¹H NMR (600 MHz, Chloroform-*d*) δ 7.75 (d, J = 7.9 Hz, 2H), 7.56 (d, J = 7.9 Hz, 2H), 7.37 (d, J = 7.9 Hz, 2H), 7.33 (d, J = 7.9 Hz, 2H), 3.82 (tt, J = 7.6, 3.6 Hz, 1H), 3.37 (ddd, J = 10.2, 6.5, 4.0 Hz, 1H), 3.27 (dd, J = 13.4, 3.5 Hz, 1H), 3.14 (dt, J = 10.4, 7.1 Hz, 1H), 2.88 (dd, J = 13.3, 9.2 Hz, 1H), 2.43 (s, 3H), 1.68 – 1.51 (m, 2H), 1.46 (dq, J = 12.4, 7.2, 6.7 Hz, 2H).

¹³C NMR (151 MHz, CDCl₃) δ 143.56, 142.52, 134.38, 130.02, 129.77, 128.81 (q, J = 32.4, 32.0 Hz), 127.52, 125.35, 125.32, 61.15, 49.28, 42.47, 29.96, 23.84, 21.56.

¹⁹F NMR (564 MHz, Chloroform-*d*) δ -62.34.

HRMS m/z (ESI) calcd. for C₁₉H₂₁F₃NO₂S⁺ (M+H)⁺ 384.1240, found 384.1278.



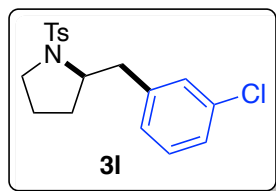
Methyl 4-((1-tosylpyrrolidin-2-yl)methyl)benzoate

3k was prepared following the general procedure 2.1 and purified by column chromatography (hexane:EA = 3:1) as yellow solid.

¹H NMR (600 MHz, Chloroform-*d*) δ 7.97 (d, J = 8.2 Hz, 2H), 7.75 (d, J = 8.3 Hz, 2H), 7.36 – 7.29 (m, 4H), 3.91 (s, 3H), 3.83 (tt, J = 7.1, 3.5 Hz, 1H), 3.40 – 3.35 (m, 1H), 3.27 (dd, J = 13.3, 3.6 Hz, 1H), 3.13 (dt, J = 10.0, 6.9 Hz, 1H), 2.87 (dd, J = 13.3, 9.2 Hz, 1H), 2.43 (s, 3H), 1.65 – 1.58 (m, 2H), 1.51 – 1.41 (m, 2H).

¹³C NMR (151 MHz, CDCl₃) δ 167.07, 143.86, 143.47, 134.51, 129.72, 128.44, 127.51, 61.14, 52.07, 49.23, 42.68, 29.97, 23.82, 21.54.

HRMS m/z (ESI) calcd. for C₂₀H₂₄NO₄S⁺ (M+H)⁺ 374.1421, found 374.1449.



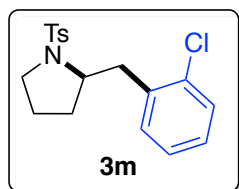
2-(3-chlorobenzyl)-1-tosylpyrrolidine

3l was prepared following the general procedure 2.1 and purified by column chromatography (hexane:EA = 5:1) as pale yellow oil.

¹H NMR (600 MHz, Chloroform-*d*) δ 7.75 (d, J = 8.3 Hz, 2H), 7.34 – 7.30 (m, 2H), 7.22 (qd, J = 7.3, 1.5 Hz, 3H), 7.14 (dt, J = 7.2, 1.6 Hz, 1H), 3.81 (ddt, J = 10.4, 6.6, 3.4 Hz, 1H), 3.39 (ddd, J = 10.8, 6.8, 4.1 Hz, 1H), 3.21 (dd, J = 13.4, 3.6 Hz, 1H), 3.14 (dt, J = 9.9, 7.3 Hz, 1H), 2.75 (dd, J = 13.4, 9.5 Hz, 1H), 2.43 (s, 3H), 1.71 – 1.61 (m, 2H), 1.52 – 1.41 (m, 2H).

¹³C NMR (151 MHz, CDCl₃) δ 143.45, 140.49, 134.62, 134.17, 129.73, 129.61, 127.88, 127.62, 127.53, 126.67, 61.24, 49.22, 42.35, 29.94, 23.84, 21.54.

HRMS m/z (ESI) calcd. for C₁₈H₂₁ClNO₂S⁺ (M+H)⁺ 350.0976, found 350.1006.



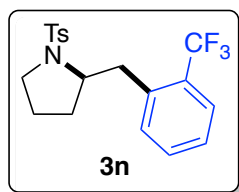
2-(2-chlorobenzyl)-1-tosylpyrrolidine

3m was prepared following the general procedure 2.1 and purified by column chromatography (hexane:EA = 5:1) as colorless oil.

¹H NMR (600 MHz, Chloroform-*d*) δ 7.77 (d, J = 8.2 Hz, 2H), 7.35 (dd, J = 7.9, 1.4 Hz, 1H), 7.32 (td, J = 4.8, 2.4 Hz, 3H), 7.21 (td, J = 7.4, 1.4 Hz, 1H), 7.17 (td, J = 7.6, 1.8 Hz, 1H), 3.93 (ddd, J = 10.1, 7.8, 3.9 Hz, 1H), 3.47 (ddd, J = 10.1, 7.2, 4.3 Hz, 1H), 3.41 (dd, J = 13.4, 4.3 Hz, 1H), 3.17 (ddd, J = 10.0, 8.2, 7.0 Hz, 1H), 2.92 (dd, J = 13.4, 9.8 Hz, 1H), 2.42 (s, 3H), 1.86 – 1.74 (m, 1H), 1.64 (ddt, J = 13.8, 6.6, 3.9 Hz, 1H), 1.56 – 1.49 (m, 1H), 1.35 (ddt, J = 12.7, 9.5, 7.3 Hz, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 143.36, 136.36, 134.56, 134.38, 132.00, 129.68, 129.58, 127.96, 127.58, 126.86, 60.32, 49.29, 39.51, 29.74, 23.90, 21.56.

HRMS m/z (ESI) calcd. for C₁₈H₂₁ClNO₂S⁺ (M+H)⁺ 350.0976, found 350.1008.



1-tosyl-2-(2-(trifluoromethyl)benzyl)pyrrolidine

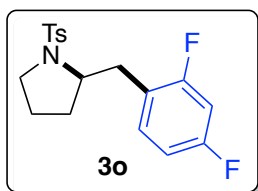
3n was prepared following the general procedure 2.1 and purified by column chromatography (hexane:EA = 10:1) as colorless oil.

¹H NMR (600 MHz, Chloroform-*d*) δ 7.75 (d, J = 8.3 Hz, 2H), 7.63 (d, J = 7.9 Hz, 1H), 7.53 – 7.47 (m, 2H), 7.32 (t, J = 7.8 Hz, 3H), 3.99 (tq, J = 8.6, 4.4, 3.8 Hz, 1H), 3.47 (ddd, J = 10.1, 7.1, 4.3 Hz, 1H), 3.40 (dd, J = 14.2, 4.9 Hz, 1H), 3.20 (ddd, J = 10.2, 8.2, 6.8 Hz, 1H), 3.04 – 2.95 (m, 1H), 2.43 (s, 3H), 1.87 – 1.76 (m, 1H), 1.57 – 1.49 (m, 2H), 1.42 – 1.32 (m, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 143.41, 137.18, 134.66, 132.10, 131.74, 129.72, 129.07 (q, J = 32.0, 32.0 Hz), 127.52, 126.52, 126.09, 126.05, 61.17, 49.07, 38.27, 29.73, 23.83, 21.56.

¹⁹F NMR (564 MHz, Chloroform-*d*) δ -58.61.

HRMS m/z (ESI) calcd. for C₁₉H₂₁F₃NO₂S⁺ (M+H)⁺ 384.1240, found 384.1265.



2-(2,4-difluorobenzyl)-1-tosylpyrrolidine

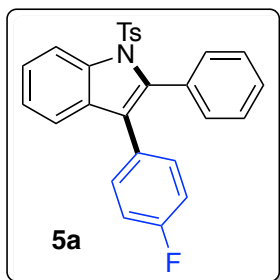
3o was prepared following the general procedure 2.1 and purified by column chromatography (hexane:EA = 5:1) as yellow oil.

¹H NMR (600 MHz, Chloroform-*d*) δ 7.74 (d, J = 8.3 Hz, 2H), 7.36 – 7.31 (m, 2H), 7.11 – 7.03 (m, 2H), 6.99 – 6.94 (m, 1H), 3.77 (tt, J = 7.4, 3.6 Hz, 1H), 3.37 (ddd, J = 9.5, 6.9, 4.3 Hz, 1H), 3.18 – 3.09 (m, 2H), 2.78 (dd, J = 13.5, 9.0 Hz, 1H), 2.44 (s, 3H), 1.66 – 1.58 (m, 2H), 1.51 – 1.38 (m, 2H).

¹³C NMR (151 MHz, CDCl₃) δ 143.55, 135.33, 134.40, 129.77, 127.52, 125.62, 118.36 (d, J = 16.6 Hz), 117.12 (d, J = 17.0 Hz), 61.14, 49.27, 41.77, 29.93, 23.84, 21.57.

¹⁹F NMR (564 MHz, Chloroform-*d*) δ -138.08, -141.25.

HRMS m/z (ESI) calcd. for C₁₈H₂₀F₂NO₂S⁺ (M+H)⁺ 352.1177, found 352.1189.



3-(4-fluorophenyl)-2-phenyl-1-tosyl-1H-indole

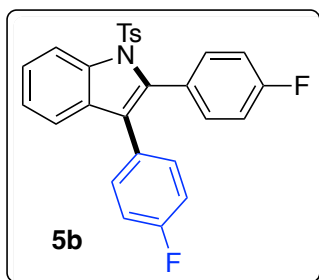
5a was prepared following the general procedure 2.1 and purified by column chromatography (hexane:EA = 10:1) as white solid.

¹H NMR (600 MHz, Chloroform-*d*) δ 8.41 (d, J = 8.4 Hz, 1H), 7.47 – 7.41 (m, 2H), 7.35 (dd, J = 12.2, 7.9 Hz, 4H), 7.32 – 7.27 (m, 4H), 7.23 (d, J = 7.3 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H), 7.05 (dd, J = 8.4, 5.5 Hz, 2H), 6.92 (t, J = 8.5 Hz, 2H), 2.32 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 144.67, 137.12, 136.91, 135.31, 132.05, 131.45 (d, J = 8.0 Hz), 130.72, 130.26, 129.36, 128.63, 127.39, 126.96, 125.29, 124.24, 123.69, 119.74, 116.24, 115.29 (d, J = 21.3 Hz), 21.62.

¹⁹F NMR (564 MHz, Chloroform-*d*) δ -114.90.

HRMS m/z (ESI) calcd. for C₂₇H₂₁FNO₂S⁺ (M+H)⁺ 442.1272, found 442.1317.



2,3-bis(4-fluorophenyl)-1-tosyl-1H-indole

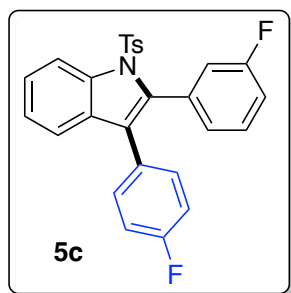
5b was prepared following the general procedure 2.1 and purified by column chromatography (hexane:EA = 10:1) as white solid.

¹H NMR (600 MHz, Chloroform-*d*) δ 8.41 (dd, J = 9.0, 1.0 Hz, 1H), 7.43 (ddd, J = 7.7, 6.7, 1.6 Hz, 2H), 7.34 – 7.29 (m, 3H), 7.20 – 7.16 (m, 2H), 7.11 – 7.08 (m, 2H), 7.06 – 7.02 (m, 3H), 7.00 – 6.96 (m, 2H), 6.96 – 6.92 (m, 2H), 2.33 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 163.70, 162.65, 162.05, 161.02, 144.79, 137.15, 135.73, 135.38, 133.86 (d, J = 8.4 Hz), 131.42 (d, J = 8.1 Hz), 130.11, 129.40, 129.27, 128.38, 126.86, 126.69, 126.67, 125.44, 124.31, 123.97, 119.77, 116.23, 115.40 (d, J = 21.5 Hz), 114.61 (d, J = 21.7 Hz), 21.59.

¹⁹F NMR (564 MHz, Chloroform-*d*) δ -112.15, -114.60.

HRMS m/z (ESI) calcd. for C₂₇H₂₀F₂NO₂S⁺ (M+H)⁺ 460.1177, found 460.1193.



2-(3-fluorophenyl)-3-(4-fluorophenyl)-1-tosyl-1*H*-indole

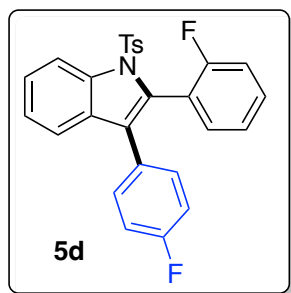
5c was prepared following the general procedure 2.1 and purified by column chromatography (hexane:EA = 10:1) as white solid.

¹H NMR (600 MHz, Chloroform-*d*) δ 8.40 (dt, J = 8.2, 1.0 Hz, 1H), 7.44 (ddd, J = 9.0, 7.6, 1.1 Hz, 2H), 7.38 – 7.35 (m, 2H), 7.31 (ddd, J = 8.1, 7.1, 1.0 Hz, 1H), 7.28 (dd, J = 8.0, 5.9 Hz, 1H), 7.13 – 7.10 (m, 2H), 7.09 – 7.03 (m, 4H), 6.97 – 6.93 (m, 2H), 6.90 (ddd, J = 9.5, 2.6, 1.5 Hz, 1H), 2.33 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 162.74, 162.61, 161.10, 160.97, 144.92, 137.17, 135.15, 131.39 (d, J = 7.9 Hz), 130.14, 129.46, 128.93 (d, J = 8.1 Hz), 127.93, 126.91, 125.63, 124.39, 124.31, 119.93, 118.98, 116.26, 115.67 (d, J = 21.3 Hz), 115.46 (d, J = 21.6 Hz), 21.62.

¹⁹F NMR (564 MHz, Chloroform-*d*) δ -113.71, -114.44.

HRMS m/z (ESI) calcd. for C₂₇H₂₀F₂NO₂S⁺ (M+H)⁺ 460.1177, found 460.1207.



2-(2-fluorophenyl)-3-(4-fluorophenyl)-1-tosyl-1*H*-indole

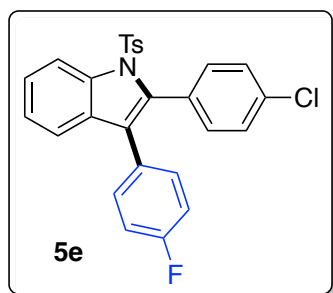
5d was prepared following the general procedure 2.1 and purified by column chromatography (hexane:EA = 10:1) as white solid.

¹H NMR (600 MHz, Chloroform-*d*) δ 8.35 (dt, J = 8.5, 0.8 Hz, 1H), 7.48 (dt, J = 7.9, 1.0 Hz, 1H), 7.46 – 7.40 (m, 3H), 7.40 – 7.36 (m, 1H), 7.30 (td, J = 7.5, 1.0 Hz, 1H), 7.16 (td, J = 7.4, 1.8 Hz, 1H), 7.14 – 7.07 (m, 5H), 7.05 (ddd, J = 9.5, 8.3, 1.1 Hz, 1H), 6.94 (t, J = 8.7 Hz, 2H), 2.34 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 144.81, 136.92, 135.46, 133.78, 131.16 (d, J = 7.6 Hz), 131.04 (d, J = 7.8 Hz), 129.81, 129.52, 126.95, 125.46, 124.72, 124.03, 123.29, 119.88, 115.63, 115.43 (d, J = 7.4 Hz), 115.29 (d, J = 7.8 Hz), 21.63.

¹⁹F NMR (564 MHz, Chloroform-*d*) δ -110.23, -114.58.

HRMS m/z (ESI) calcd. for C₂₇H₂₀F₂NO₂S⁺ (M+H)⁺ 460.1177, found 460.1209.



2-(4-chlorophenyl)-3-(4-fluorophenyl)-1-tosyl-1*H*-indole

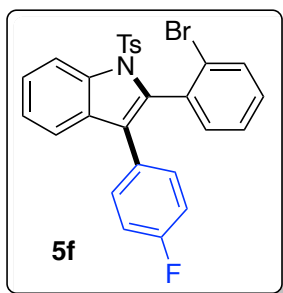
5e was prepared following the general procedure 2.1 and purified by column chromatography (hexane:EA = 10:1) as pale yellow solid.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.40 (d, J = 8.4 Hz, 1H), 7.42 (d, J = 8.0 Hz, 2H), 7.31 (dd, J = 12.0, 8.5 Hz, 5H), 7.16 (d, J = 8.2 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H), 7.03 (dd, J = 8.6, 5.6 Hz, 2H), 6.95 (t, J = 8.7 Hz, 2H), 2.33 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 163.12, 144.85, 135.19, 134.77, 133.25, 131.42 (d, J = 8.0 Hz), 129.42, 129.24, 127.76, 126.86, 125.56, 124.41, 119.84, 116.32, 115.48 (d, J = 21.4 Hz), 21.60.

¹⁹F NMR (564 MHz, Chloroform-*d*) δ -114.41.

HRMS m/z (ESI) calcd. for C₂₇H₂₀ClFNO₂S⁺ (M+H)⁺ 476.0882, found 476.0912.



2-(2-bromophenyl)-3-(4-fluorophenyl)-1-tosyl-1*H*-indole

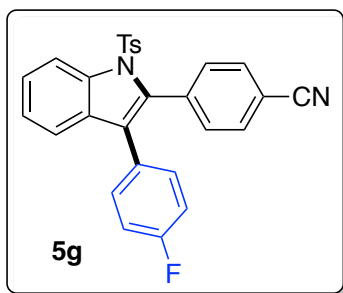
5f was prepared following the general procedure 2.1 and purified by column chromatography (hexane:EA = 10:1) as pale yellow solid.

¹H NMR (600 MHz, Chloroform-*d*) δ 8.38 (dt, *J* = 8.4, 0.9 Hz, 1H), 7.58 – 7.54 (m, 1H), 7.54 – 7.49 (m, 3H), 7.45 (ddd, *J* = 8.5, 7.2, 1.3 Hz, 1H), 7.35 – 7.30 (m, 1H), 7.28 (dd, *J* = 7.2, 1.9 Hz, 2H), 7.22 (dd, *J* = 6.8, 2.5 Hz, 1H), 7.17 – 7.10 (m, 4H), 6.97 – 6.90 (m, 2H), 2.35 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 162.72, 161.09, 144.90, 136.38, 135.89, 134.48, 133.98, 132.42, 131.08 (d, *J* = 7.7 Hz), 130.52, 129.59, 129.40, 128.36, 127.25, 126.86, 126.33, 125.46, 123.89, 123.50, 120.00, 115.37 (d, *J* = 8.8 Hz), 115.26, 21.65.

¹⁹F NMR (564 MHz, Chloroform-*d*) δ -114.63.

HRMS *m/z* (ESI) calcd. for C₂₇H₂₀BrFNO₂S⁺ (*M*+*H*)⁺ 522.0356, found 522.0381.



4-(3-(4-fluorophenyl)-1-tosyl-1*H*-indol-2-yl)benzonitrile

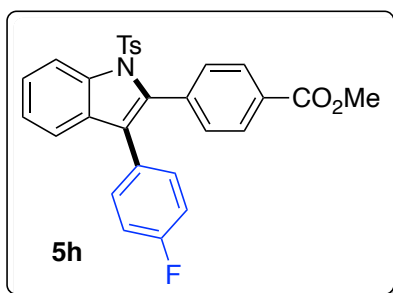
5g was prepared following the general procedure 2.1 and purified by column chromatography (hexane:EA = 5:1) as white solid.

¹H NMR (600 MHz, Chloroform-*d*) δ 8.39 (d, *J* = 8.4 Hz, 1H), 7.60 (d, *J* = 8.1 Hz, 2H), 7.47 (ddd, *J* = 8.5, 7.1, 1.3 Hz, 1H), 7.40 (dd, *J* = 16.9, 8.0 Hz, 3H), 7.32 (dd, *J* = 15.5, 7.9 Hz, 3H), 7.11 (d, *J* = 8.1 Hz, 2H), 7.02 – 6.94 (m, 4H), 2.33 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 149.14, 148.87, 148.61, 145.16, 137.47, 135.78, 134.70, 134.65, 132.50, 131.42 (d, *J* = 8.0 Hz), 131.18, 129.54, 126.77, 126.14, 125.66, 124.76, 120.16, 116.46, 115.73 (d, *J* = 21.7 Hz), 112.18, 21.65.

¹⁹F NMR (564 MHz, Chloroform-*d*) δ -113.68.

HRMS *m/z* (ESI) calcd. for C₂₈H₂₀FN₂O₂S⁺ (*M*+*H*)⁺ 467.1224, found 467.1256.



methyl 4-(3-(4-fluorophenyl)-1-tosyl-1*H*-indol-2-yl)benzoate

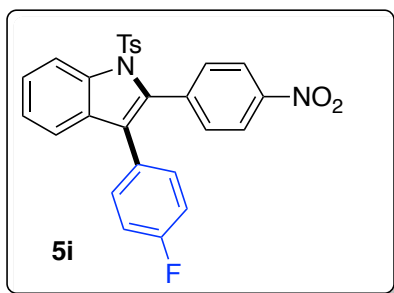
5h was prepared following the general procedure 2.1 and purified by column chromatography (hexane:EA = 4:1) as white solid.

¹H NMR (600 MHz, Chloroform-*d*) δ 8.40 (dt, *J* = 8.4, 0.9 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 2H), 7.49 – 7.38 (m, 2H), 7.36 – 7.31 (m, 5H), 7.12 – 7.08 (m, 2H), 7.04 – 6.99 (m, 2H), 6.96 – 6.90 (m, 2H), 3.94 (s, 3H), 2.33 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 166.80, 162.73, 161.09, 144.92, 137.34, 135.68, 135.57, 134.92, 131.97, 131.40 (d, *J* = 8.2 Hz), 130.31, 129.97, 129.44, 128.59, 128.06, 126.84, 125.72, 124.80, 124.49, 119.95, 116.35, 115.49 (d, *J* = 21.7 Hz), 52.27, 21.61.

¹⁹F NMR (564 MHz, Chloroform-*d*) δ -114.29.

HRMS *m/z* (ESI) calcd. for C₂₉H₂₄FO₄S⁺ (*M*+*H*)⁺ 500.1326, found 500.1352.



3-(4-fluorophenyl)-2-(4-nitrophenyl)-1-tosyl-1*H*-indole

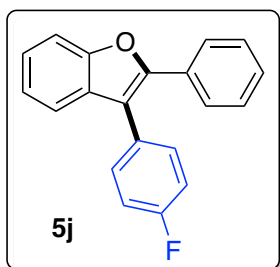
5i was prepared following the general procedure 2.1 and purified by column chromatography (hexane:EA = 3:1) as yellow solid.

¹H NMR (600 MHz, Chloroform-*d*) δ 8.39 (d, *J* = 8.4 Hz, 1H), 8.17 (d, *J* = 8.8 Hz, 2H), 7.52 – 7.44 (m, 3H), 7.44 – 7.40 (m, 1H), 7.37 – 7.29 (m, 3H), 7.12 (d, *J* = 8.2 Hz, 2H), 7.04 – 6.92 (m, 4H), 2.34 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 149.95, 134.57, 132.69, 131.42 (d, *J* = 8.2 Hz), 130.40, 129.58, 126.77, 126.27, 124.85, 124.29, 124.12, 123.08, 122.67, 120.23, 116.50, 115.80 (d, *J* = 21.9 Hz), 21.66.

¹⁹F NMR (564 MHz, Chloroform-*d*) δ -113.51.

HRMS *m/z* (ESI) calcd. for C₂₇H₂₀FN₂O₄S⁺ (M+H)⁺ 487.1122, found 487.1168.



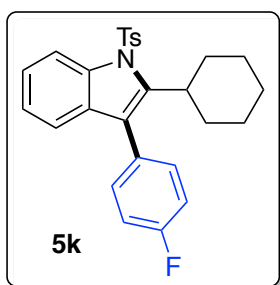
3-(4-fluorophenyl)-2-phenylbenzofuran

5j was prepared following the general procedure 2.1 and purified by column chromatography (hexane:EA = 40:1) as white solid.

¹H NMR (600 MHz, Chloroform-*d*) δ 7.66 – 7.61 (m, 2H), 7.56 (dt, *J* = 8.2, 0.8 Hz, 1H), 7.49 – 7.44 (m, 3H), 7.36 – 7.30 (m, 4H), 7.27 – 7.23 (m, 1H), 7.19 – 7.15 (m, 2H).

¹³C NMR (151 MHz, CDCl₃) δ 163.20, 161.56, 153.97, 150.67, 131.46 (d, *J* = 7.9 Hz), 130.50, 130.16, 128.83, 128.55, 127.02, 124.96, 124.84, 123.05, 119.83, 116.49, 116.12 (d, *J* = 21.4 Hz), 111.23, 101.33.

¹⁹F NMR (564 MHz, Chloroform-*d*) δ -114.19.



2-cyclohexyl-3-(4-fluorophenyl)-1-tosyl-1*H*-indole

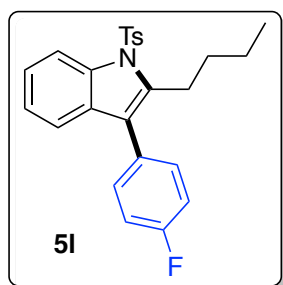
5k was prepared following the general procedure 2.1 and purified by column chromatography (hexane:EA = 10:1) as colorless oil.

¹H NMR (600 MHz, Chloroform-*d*) δ 8.28 (dd, *J* = 8.4, 0.9 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.30 (ddd, *J* = 8.5, 7.2, 1.3 Hz, 1H), 7.24 (d, *J* = 8.2 Hz, 2H), 7.22 – 7.19 (m, 2H), 7.16 (td, *J* = 7.5, 0.9 Hz, 1H), 7.12 – 7.07 (m, 2H), 6.97 (dt, *J* = 7.7, 1.0 Hz, 1H), 3.51 – 3.40 (m, 1H), 2.38 (s, 3H), 1.66 – 1.60 (m, 6H), 1.26 – 1.12 (m, 4H).

¹³C NMR (151 MHz, CDCl₃) δ 163.10, 161.46, 144.64, 142.22, 136.94, 135.85, 132.39 (d, *J* = 8.2 Hz), 132.07, 130.30, 129.79, 126.30, 124.39, 123.38, 121.63, 118.95, 115.20, 115.10 (d, *J* = 12.4 Hz), 38.03, 33.40, 27.10, 25.82, 21.62.

¹⁹F NMR (564 MHz, Chloroform-*d*) δ -114.72.

HRMS *m/z* (ESI) calcd. for C₂₇H₂₇FN₂O₂S⁺ (M+H)⁺ 448.1741, found 448.1774.



2-butyl-3-(4-fluorophenyl)-1-tosyl-1*H*-indole

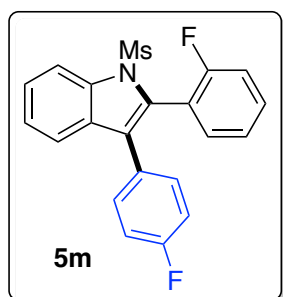
5l was prepared following the general procedure 2.1 and purified by column chromatography (hexane:EA = 10:1) as colorless oil.

¹H NMR (600 MHz, Chloroform-*d*) δ 8.22 (d, J = 8.4 Hz, 1H), 7.63 (d, J = 8.4 Hz, 2H), 7.32 – 7.23 (m, 4H), 7.22 – 7.17 (m, 3H), 7.17 – 7.12 (m, 2H), 3.00 – 2.92 (m, 2H), 2.34 (s, 3H), 1.74 – 1.65 (m, 2H), 1.27 (dq, J = 14.8, 7.5 Hz, 2H), 0.82 (t, J = 7.4 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 163.00, 161.37, 144.66, 138.78, 136.56, 135.91, 131.60 (d, J = 7.9 Hz), 130.63, 129.76, 129.23, 126.33, 124.43, 123.79, 122.66, 119.09, 115.63 (d, J = 21.3 Hz), 115.31, 33.38, 26.59, 22.53, 21.60, 13.70.

¹⁹F NMR (564 MHz, Chloroform-*d*) δ -114.58.

HRMS m/z (ESI) calcd. for C₂₅H₂₅FN₂O₂S⁺ (M+H)⁺ 422.1585, found 422.1619.



2-(2-fluorophenyl)-3-(4-fluorophenyl)-1-(methylsulfonyl)-1*H*-indole

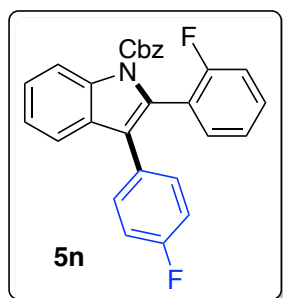
5m was prepared following the general procedure 2.1 and purified by column chromatography (hexane:EA = 10:1) as white solid.

¹H NMR (600 MHz, Chloroform-*d*) δ 8.15 (dt, J = 8.5, 0.9 Hz, 1H), 7.60 (dt, J = 7.9, 1.0 Hz, 1H), 7.46 (ddd, J = 8.4, 7.2, 1.3 Hz, 1H), 7.43 – 7.35 (m, 2H), 7.25 – 7.21 (m, 3H), 7.14 – 7.08 (m, 2H), 7.00 (t, J = 8.7 Hz, 2H), 3.09 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 162.90, 162.06, 161.26, 160.43, 136.43, 133.39, 131.25 (d, J = 8.6 Hz), 131.17 (d, J = 7.8 Hz), 129.95, 129.64, 128.13, 125.73, 124.22, 123.87, 120.19, 119.31, 119.21, 115.54 (d, J = 21.6 Hz), 115.22 (d, J = 21.8 Hz), 114.71, 40.59.

¹⁹F NMR (564 MHz, Chloroform-*d*) δ -111.74, -114.32.

HRMS m/z (ESI) calcd. for C₂₁H₁₆F₂NO₂S⁺ (M+H)⁺ 384.0864, found 384.0894.



benzyl 2-(2-fluorophenyl)-3-(4-fluorophenyl)-1*H*-indole-1-carboxylate

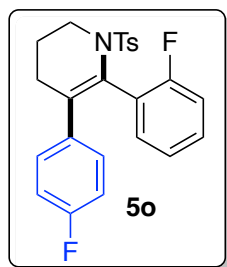
5n was prepared following the general procedure 2.1 and purified by column chromatography (hexane:EA = 10:1) as white solid.

¹H NMR (600 MHz, Chloroform-*d*) δ 8.30 (d, J = 8.4 Hz, 1H), 7.54 (d, J = 7.8 Hz, 1H), 7.40 (ddd, J = 8.5, 7.3, 1.2 Hz, 1H), 7.33 – 7.28 (m, 4H), 7.22 – 7.18 (m, 3H), 7.13 (dd, J = 7.7, 1.9 Hz, 2H), 7.05 (td, J = 7.4, 1.8 Hz, 1H), 7.00 – 6.89 (m, 4H), 5.23 (d, J = 8.0 Hz, 2H).

¹³C NMR (151 MHz, CDCl₃) δ 161.84, 161.10, 160.20, 158.72, 151.34, 136.38, 134.39, 132.03, 131.39 (d, J = 8.0 Hz), 130.17 (d, J = 8.0 Hz), 129.60, 129.30, 128.53, 128.51, 125.42, 123.53, 123.46, 123.14, 119.62, 115.84, 115.37 (d, J = 21.5 Hz), 114.96 (d, J = 21.3 Hz), 68.87.

¹⁹F NMR (564 MHz, Chloroform-*d*) δ -113.00, -114.91.

HRMS m/z (ESI) calcd. for $C_{28}H_{20}F_2NO_2^+$ ($M+H$) $^+$ 440.1457, found 440.1489.



6-(2-fluorophenyl)-5-(4-fluorophenyl)-1-tosyl-1,2,3,4-tetrahydropyridine

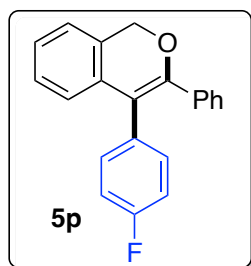
5o was prepared following the general procedure 2.1 and purified by column chromatography (hexane:EA = 10:1) as white solid.

1H NMR (600 MHz, Chloroform- d) δ 7.45 (d, J = 7.9 Hz, 2H), 7.17 (d, J = 7.9 Hz, 2H), 7.07 (dt, J = 7.7, 5.6 Hz, 2H), 6.88 (qd, J = 8.1, 6.0 Hz, 3H), 6.77 (t, J = 8.5 Hz, 2H), 6.63 (dd, J = 10.0, 8.1 Hz, 1H), 3.84 (s, 2H), 2.39 (d, J = 18.2 Hz, 5H), 1.82 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.10, 164.58, 162.18, 161.04, 143.11, 137.55, 137.00, 132.76, 130.57, 130.14 (d, J = 7.7 Hz), 129.72, 129.43 (d, J = 8.4 Hz), 129.27, 127.17, 123.20, 114.85 (d, J = 22.3 Hz), 114.68 (d, J = 21.2 Hz), 46.21, 29.69, 22.86, 21.58.

^{19}F NMR (564 MHz, Chloroform- d) δ -113.85, -115.69.

HRMS m/z (ESI) calcd. for $C_{24}H_{22}F_2NO_2S^+$ ($M+H$) $^+$ 426.1334, found 426.1355.



4-(4-fluorophenyl)-3-phenyl-1H-isochromene

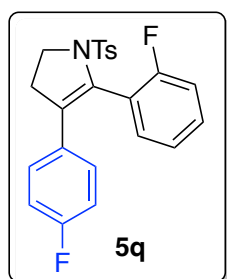
5p was prepared following the general procedure 2.1 and purified by column chromatography (hexane:EA = 40:1) as white solid.

1H NMR (600 MHz, Chloroform- d) δ 7.24 – 7.12 (m, 10H), 7.04 (ddd, J = 8.7, 7.7, 1.2 Hz, 2H), 6.80 (d, J = 7.4 Hz, 1H), 5.28 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 151.64, 135.18, 133.60, 133.20 (d, J = 8.0 Hz), 128.58, 128.05, 127.66, 126.82, 123.74, 122.80, 115.94, 115.66 (d, J = 21.1 Hz), 68.76.

^{19}F NMR (564 MHz, Chloroform- d) δ -115.19.

HRMS m/z (ESI) calcd. for $C_{21}H_{16}FO^+$ ($M+H$) $^+$ 303.1180, found 303.1200.



5-(2-fluorophenyl)-4-(4-fluorophenyl)-1-tosyl-2,3-dihydro-1H-pyrrole

5q was prepared following the general procedure 2.1 and purified by column chromatography (hexane:EA = 10:1) as pale yellow oil.

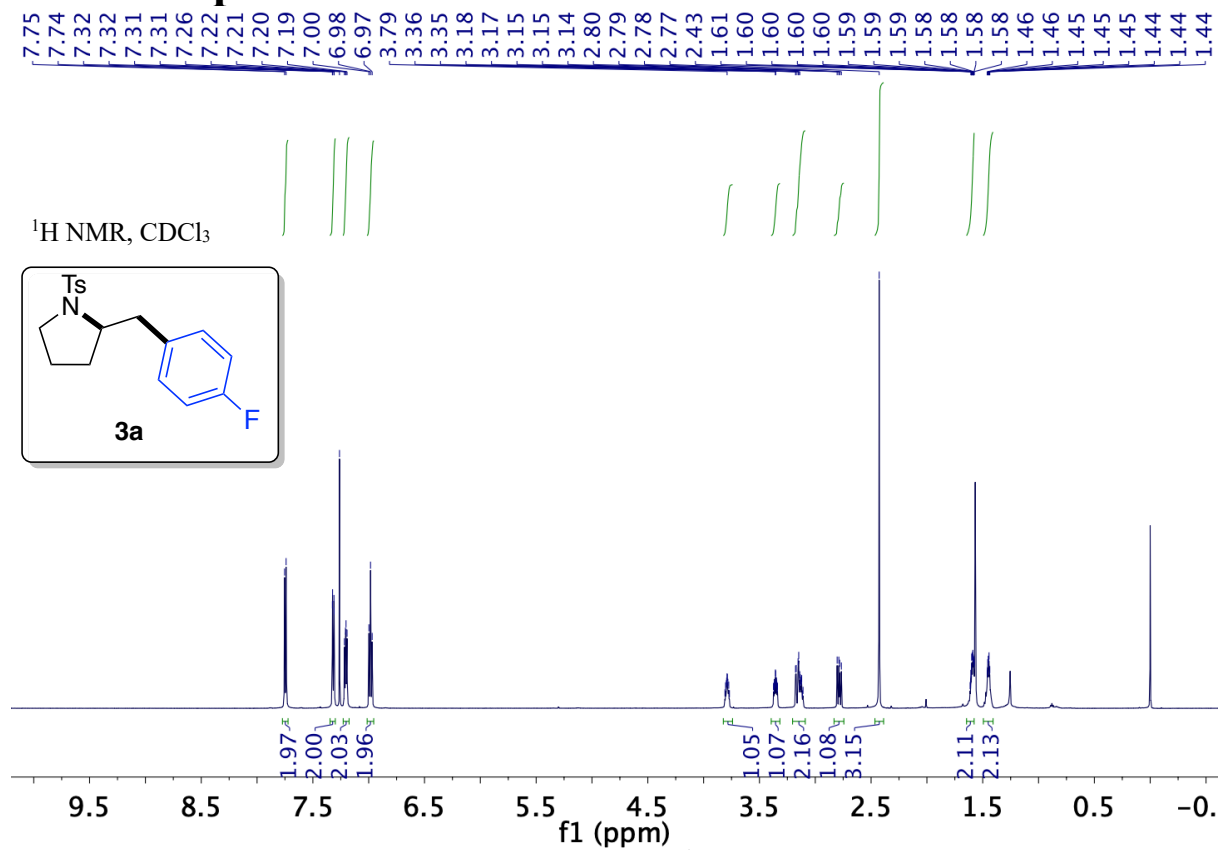
1H NMR (600 MHz, Chloroform- d) δ 7.62 (d, J = 8.3 Hz, 2H), 7.40 – 7.33 (m, 2H), 7.28 (d, J = 8.0 Hz, 3H), 7.15 (td, J = 7.5, 1.1 Hz, 1H), 7.02 (ddd, J = 10.1, 8.3, 1.1 Hz, 1H), 6.86 – 6.76 (m, 4H), 4.08 (t, J = 8.6 Hz, 2H), 2.59 (t, J = 8.6 Hz, 2H), 2.44 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 160.94, 143.83, 134.96, 132.36, 131.70, 131.21, 130.86 (d, J = 8.2 Hz), 129.56, 128.03 (d, J = 8.0 Hz), 127.78, 127.35, 125.56, 124.02, 123.61, 122.25, 120.63, 115.97 (d, J = 21.4 Hz), 115.16 (d, J = 21.6 Hz), 49.30, 33.07, 21.67.

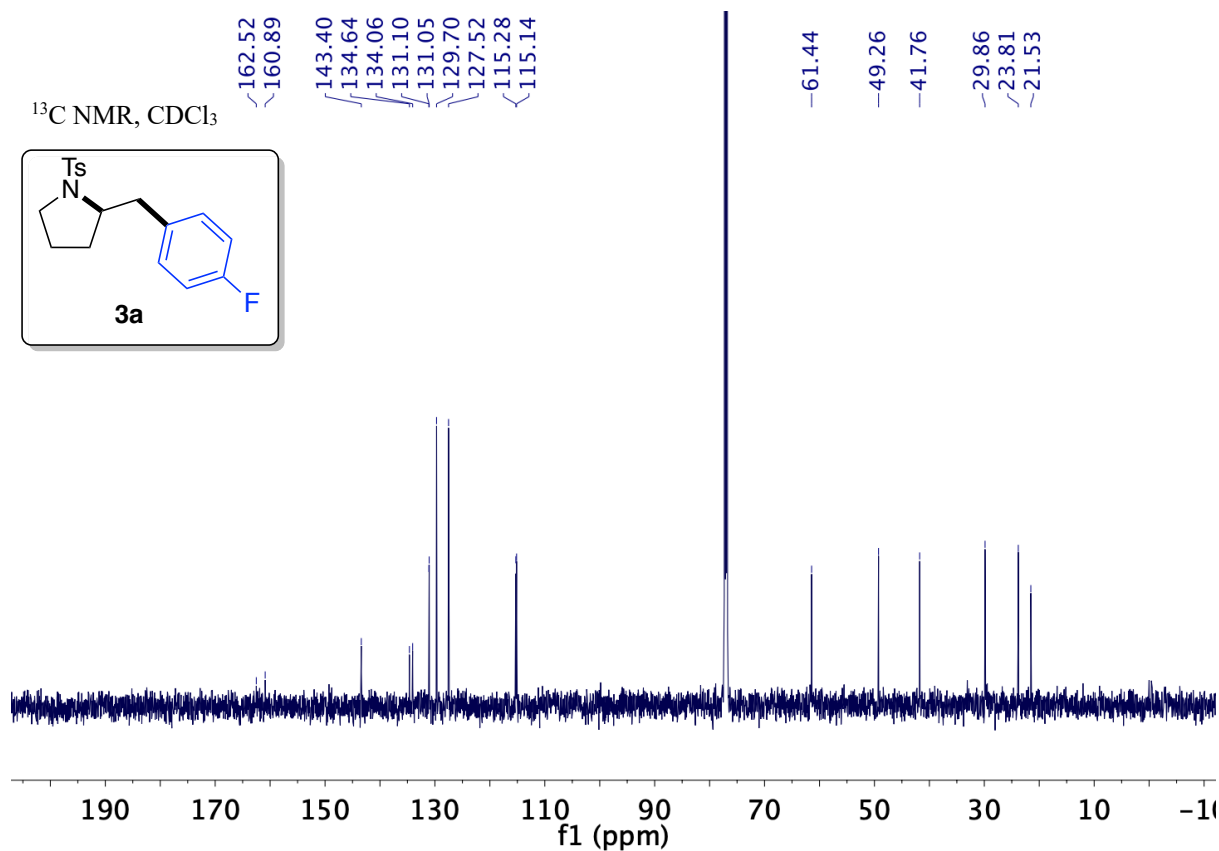
^{19}F NMR (564 MHz, Chloroform- d) δ -111.31, -114.17.

HRMS m/z (ESI) calcd. for $\text{C}_{23}\text{H}_{20}\text{F}_2\text{NO}_2\text{S}^+$ (M+H)⁺ 412.1177, found 412.1199.

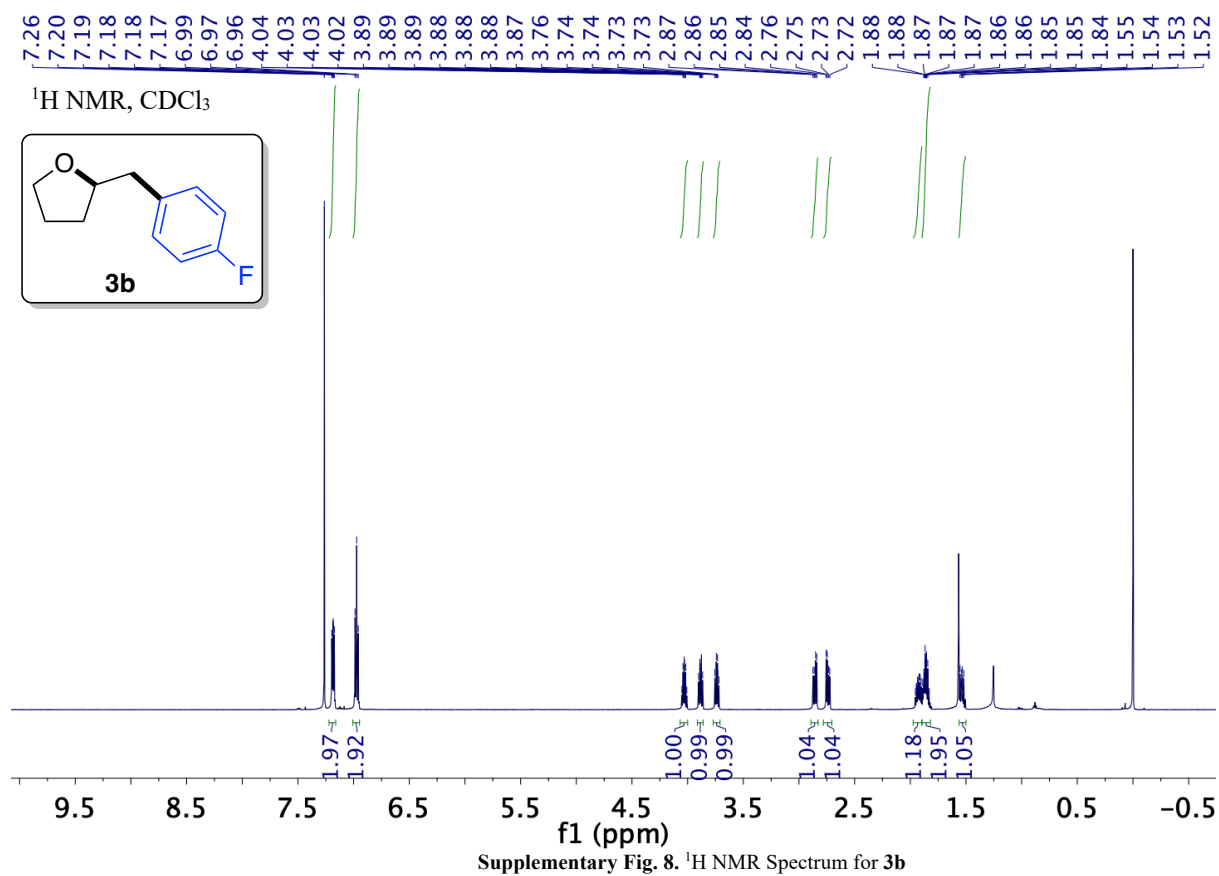
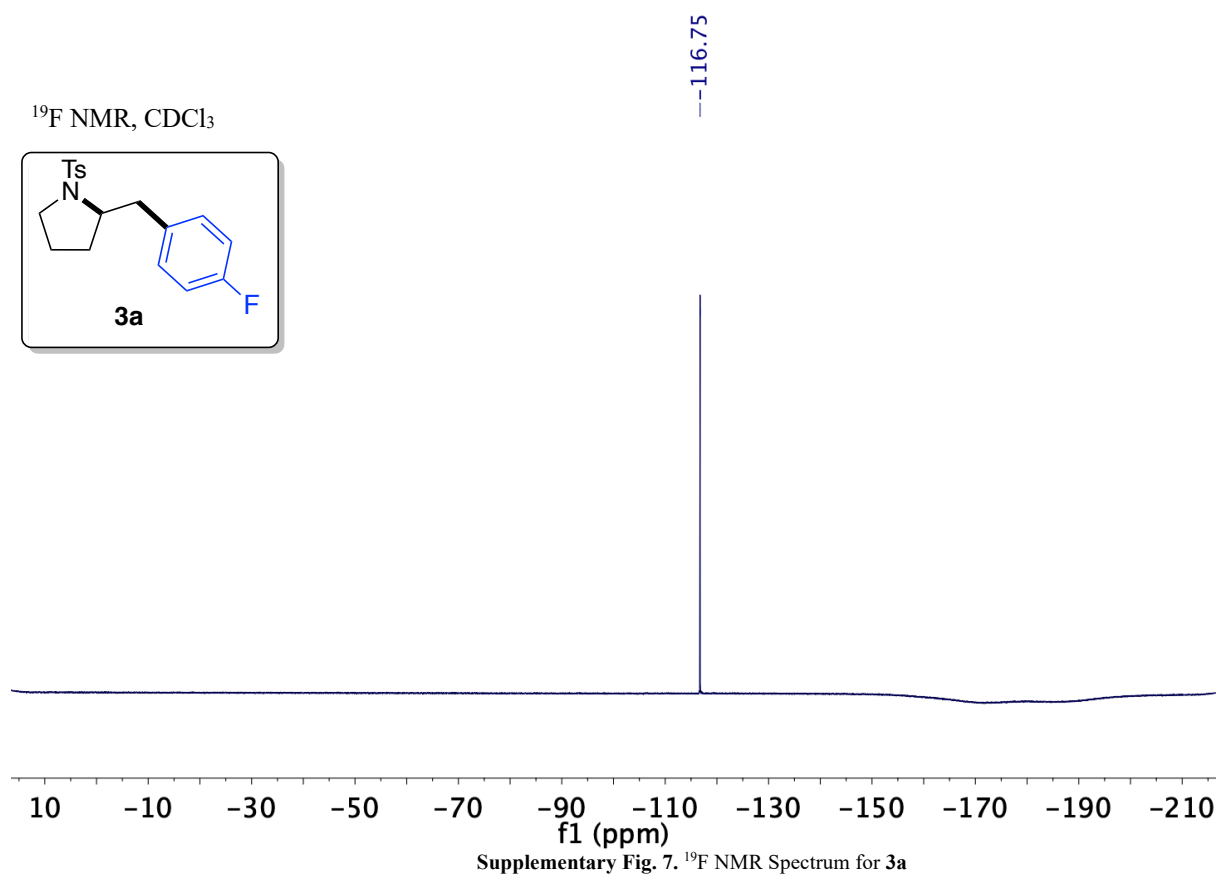
5. NMR Spectra Data

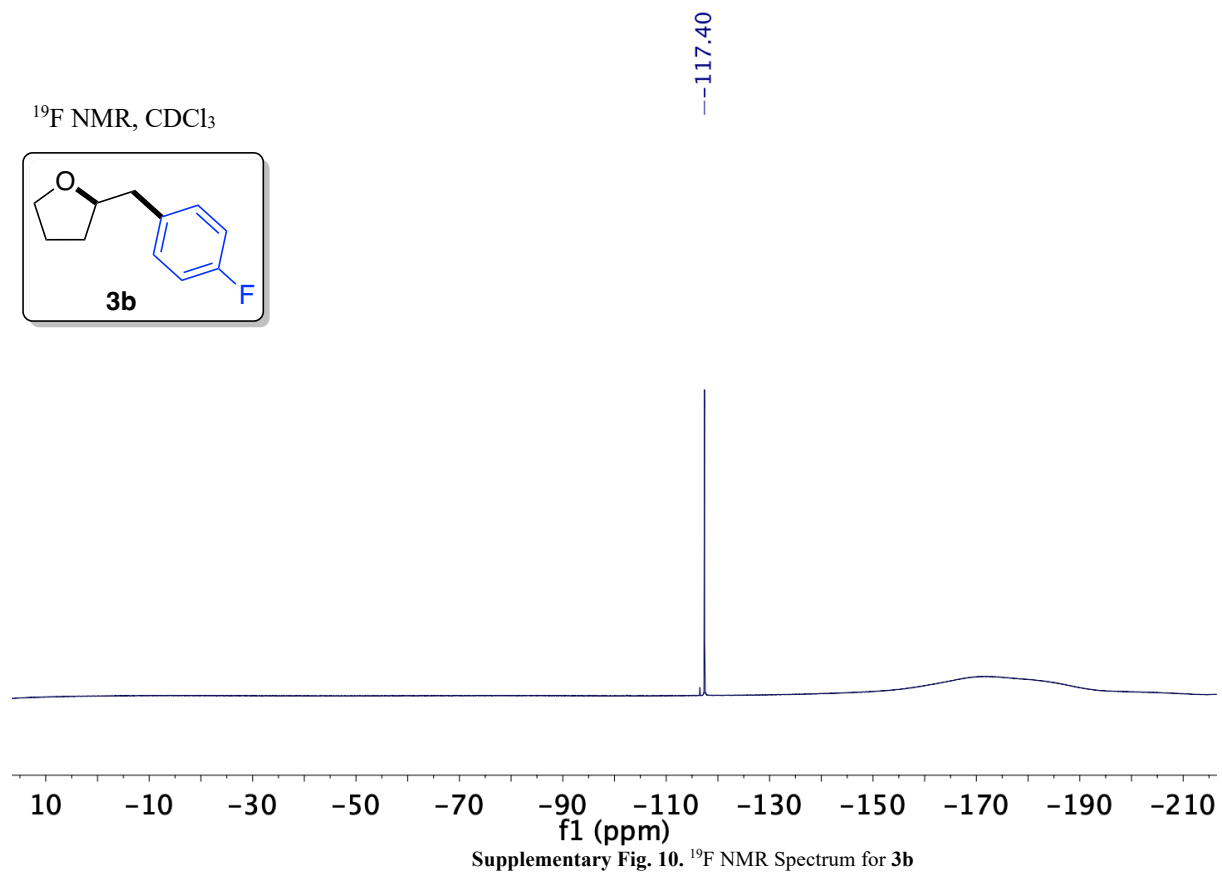
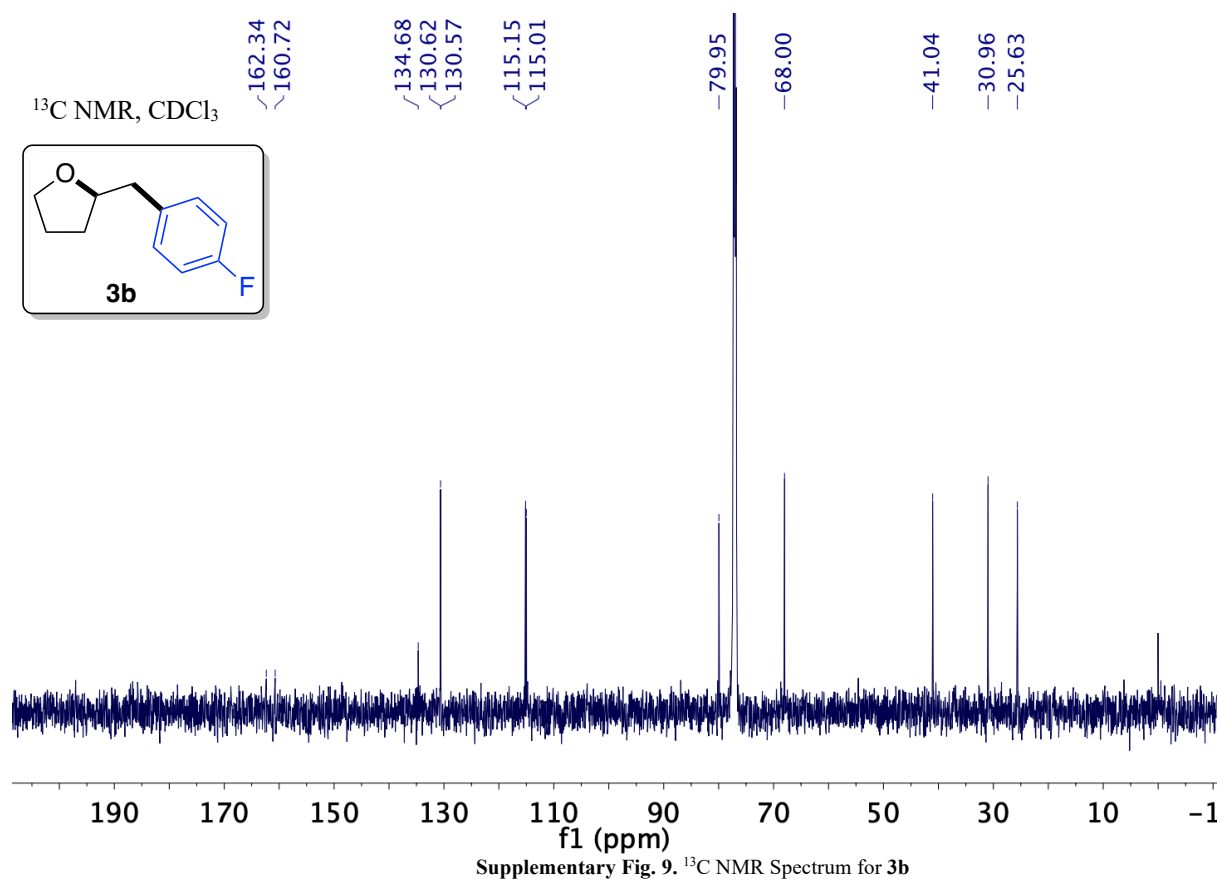


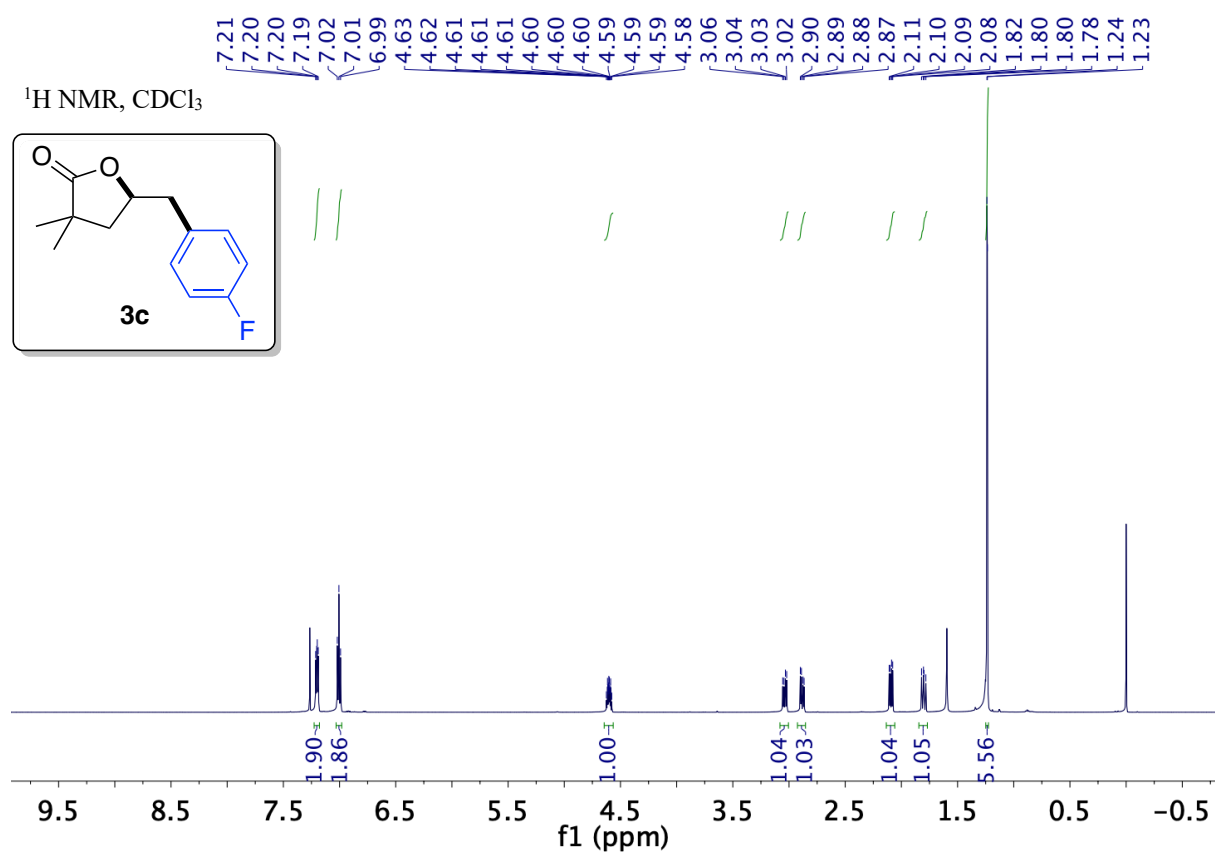
Supplementary Fig. 5. ¹H NMR Spectrum for **3a**



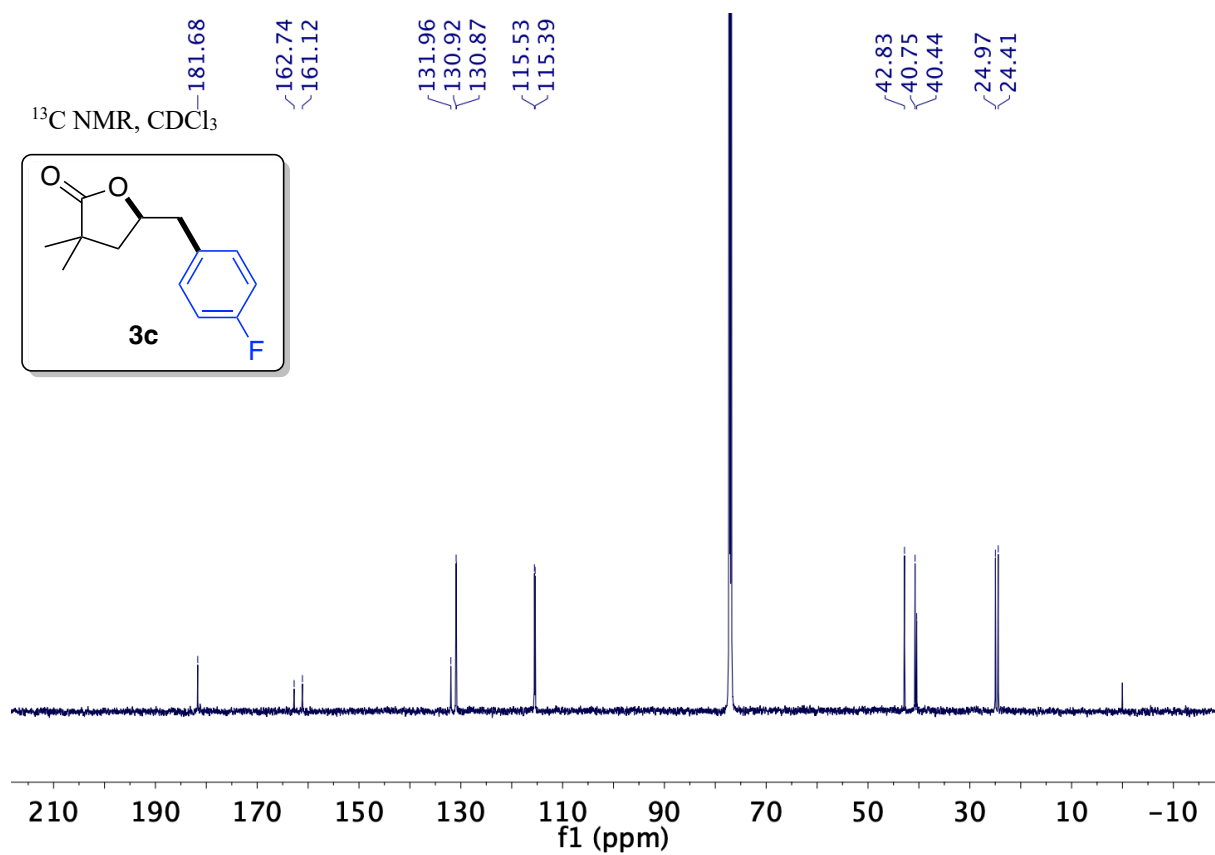
Supplementary Fig. 6. ¹³C NMR Spectrum for **3a**



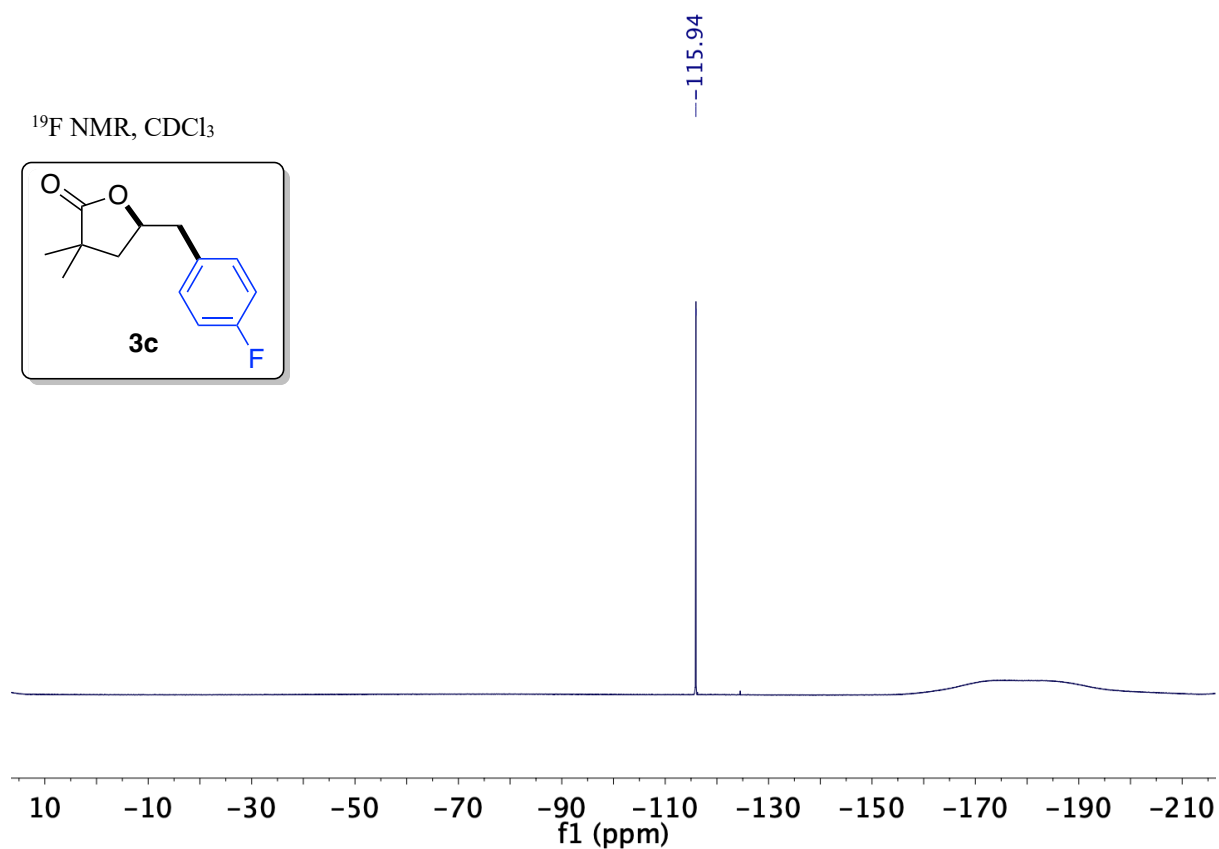




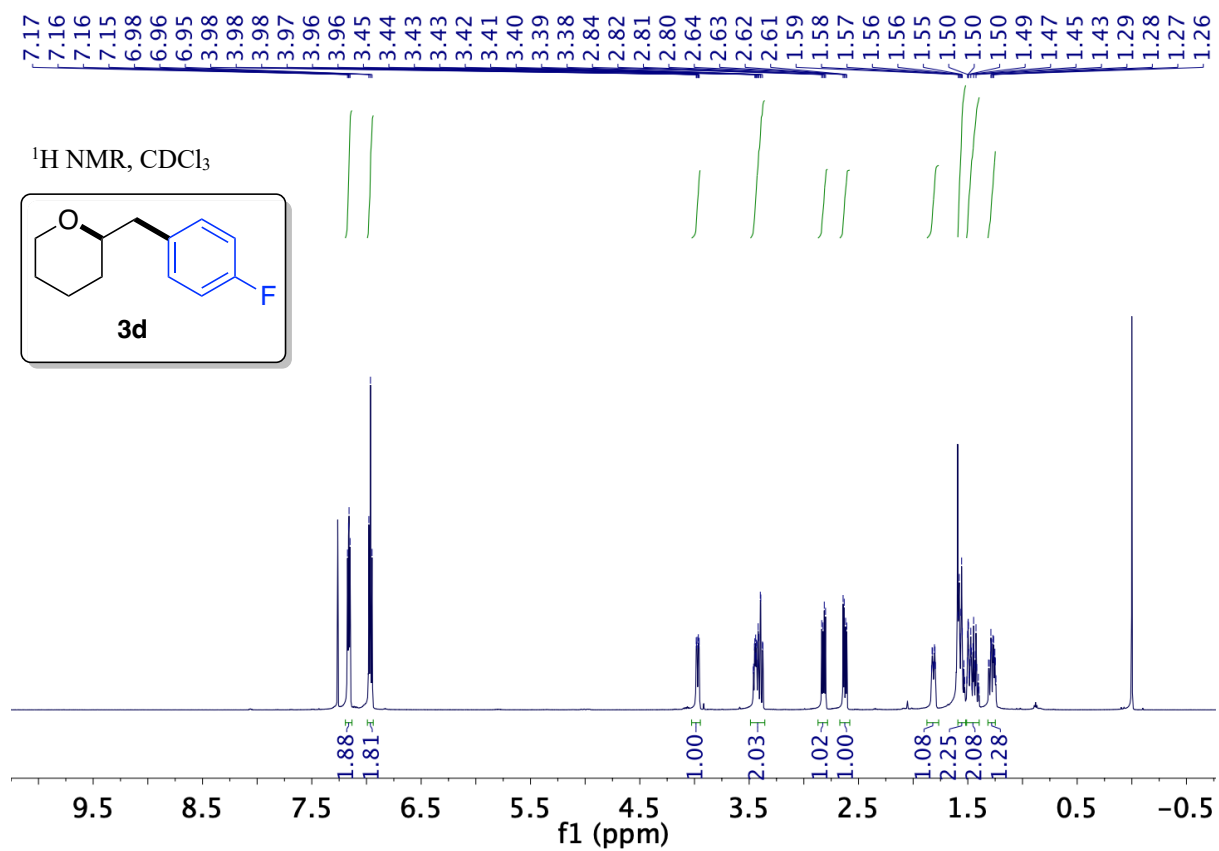
Supplementary Fig. 11. ¹H NMR Spectrum for **3c**



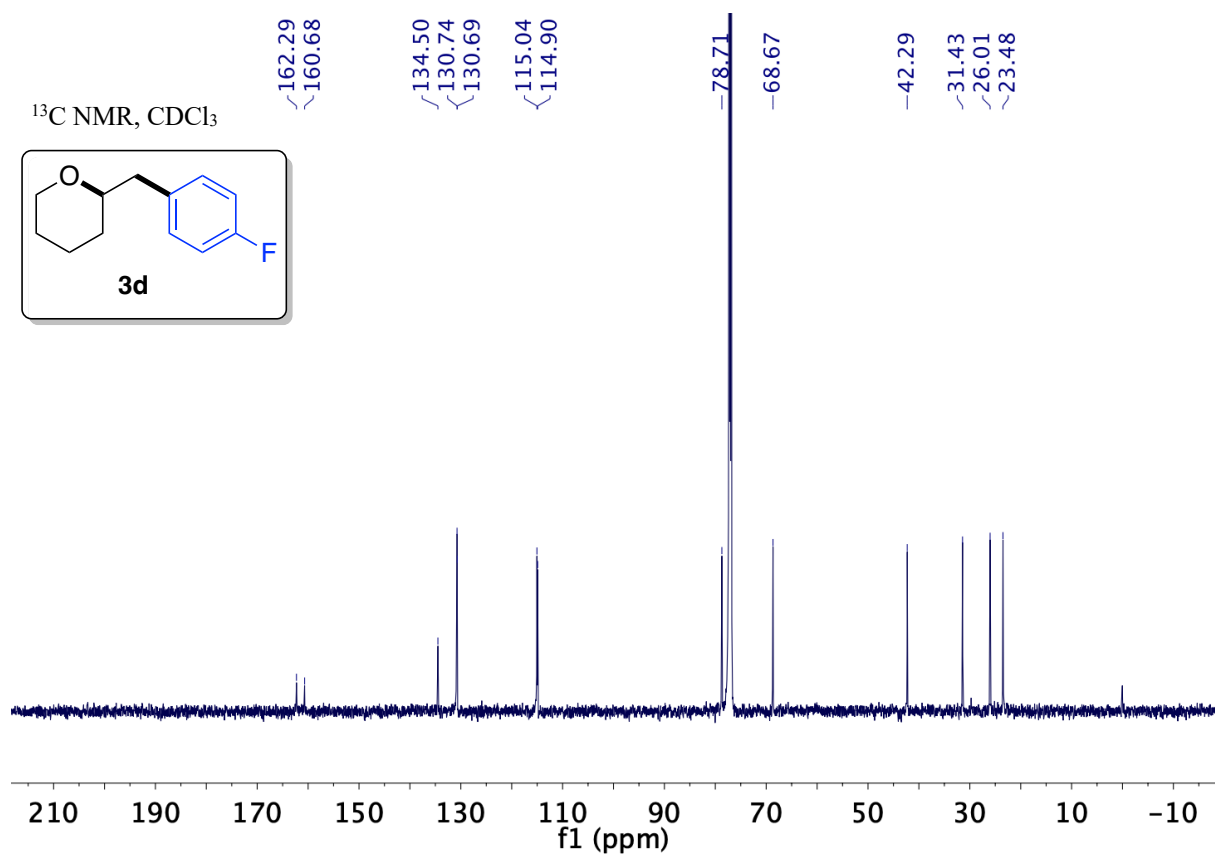
Supplementary Fig. 12. ¹³C NMR Spectrum for **3c**



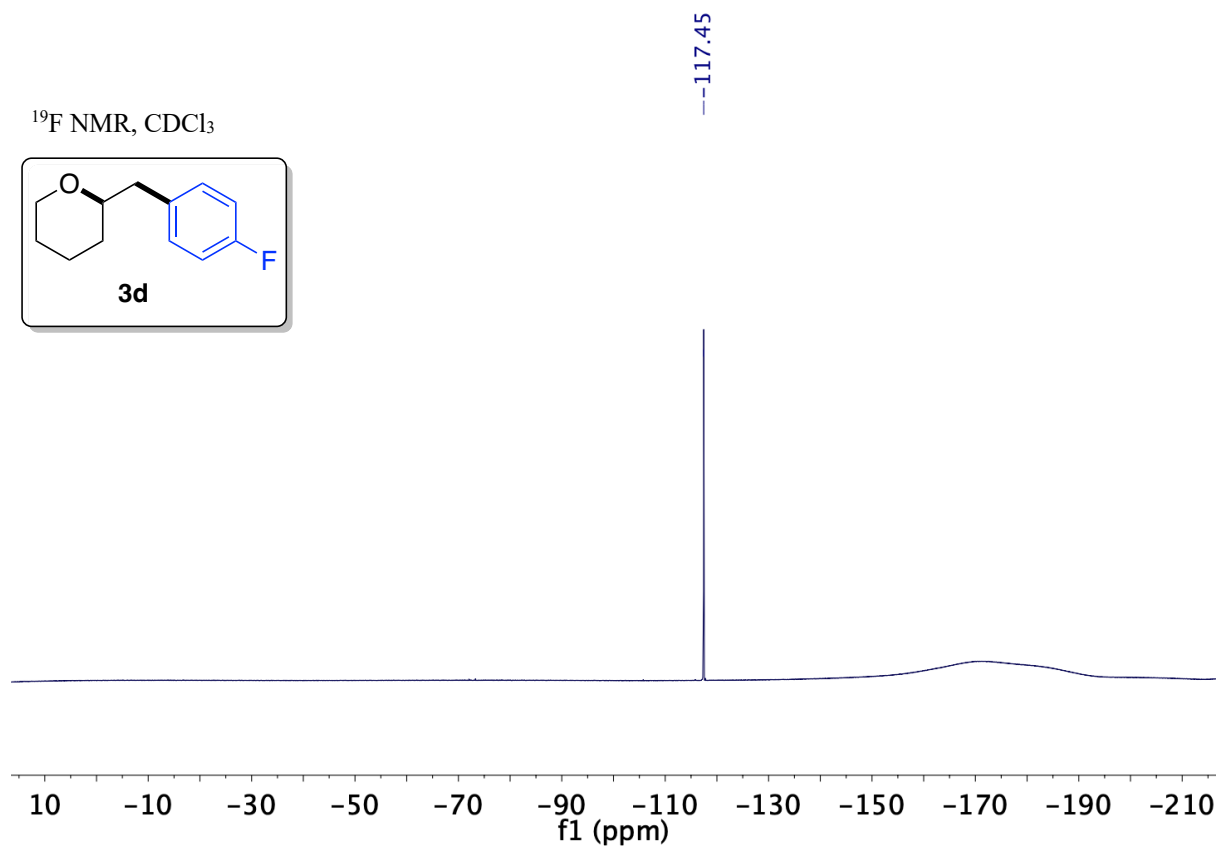
Supplementary Fig. 13. ¹⁹F NMR Spectrum for **3c**



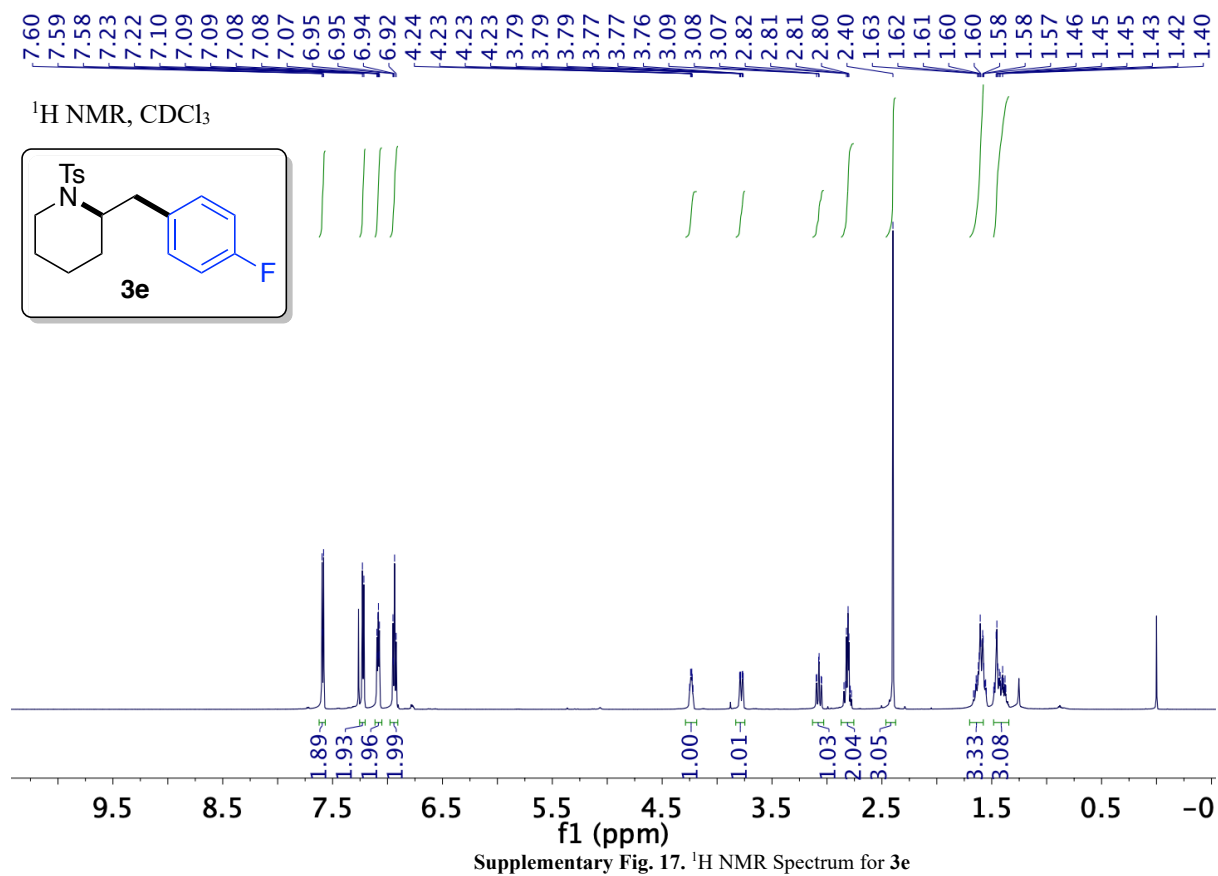
Supplementary Fig. 14. ¹H NMR Spectrum for **3d**



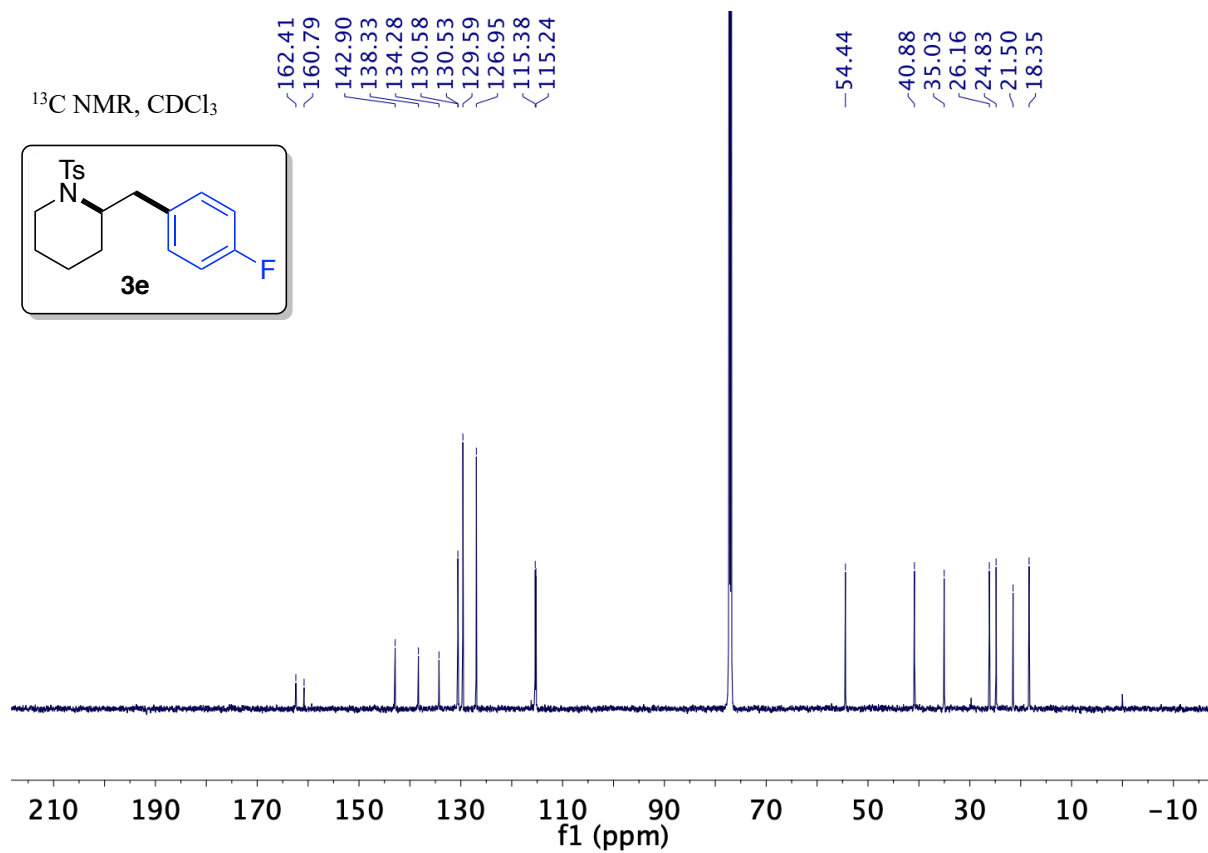
Supplementary Fig. 15. ¹³C NMR Spectrum for **3d**



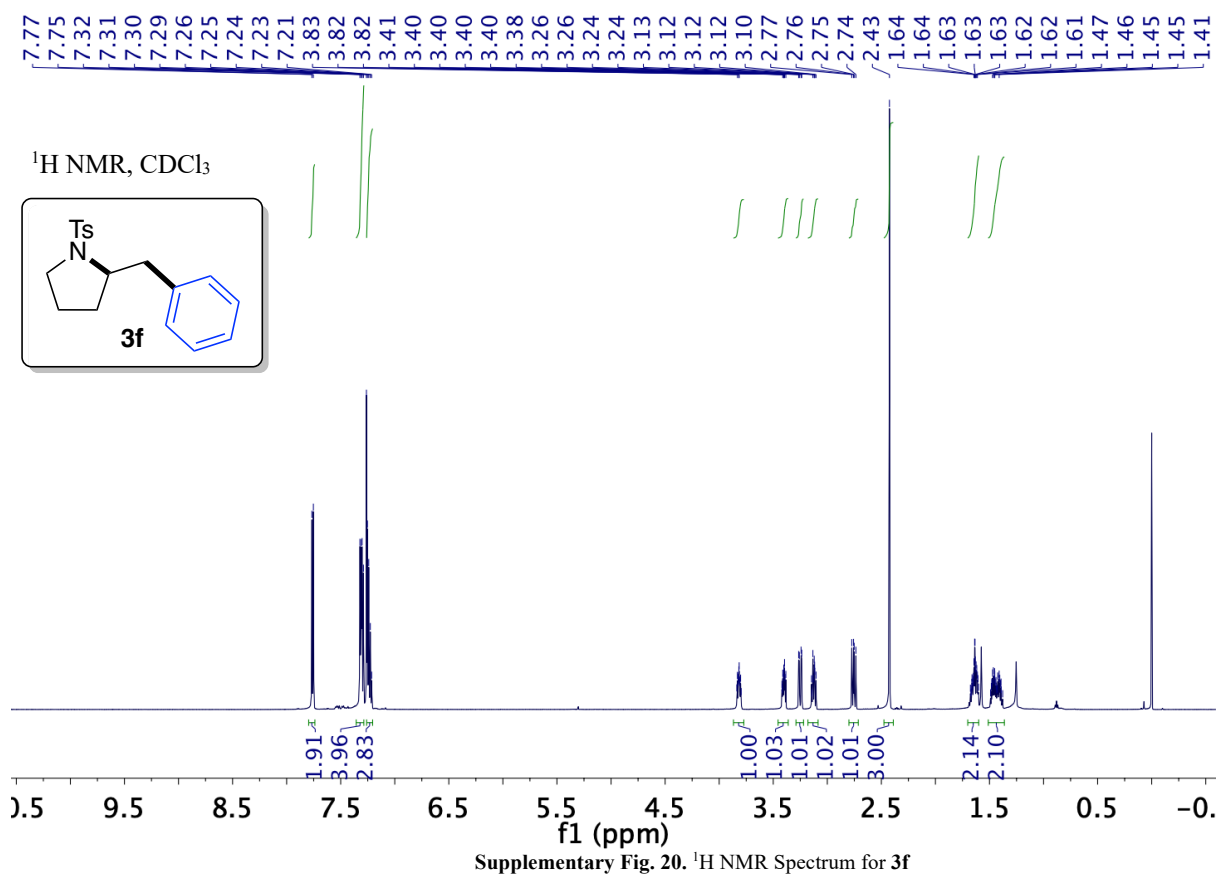
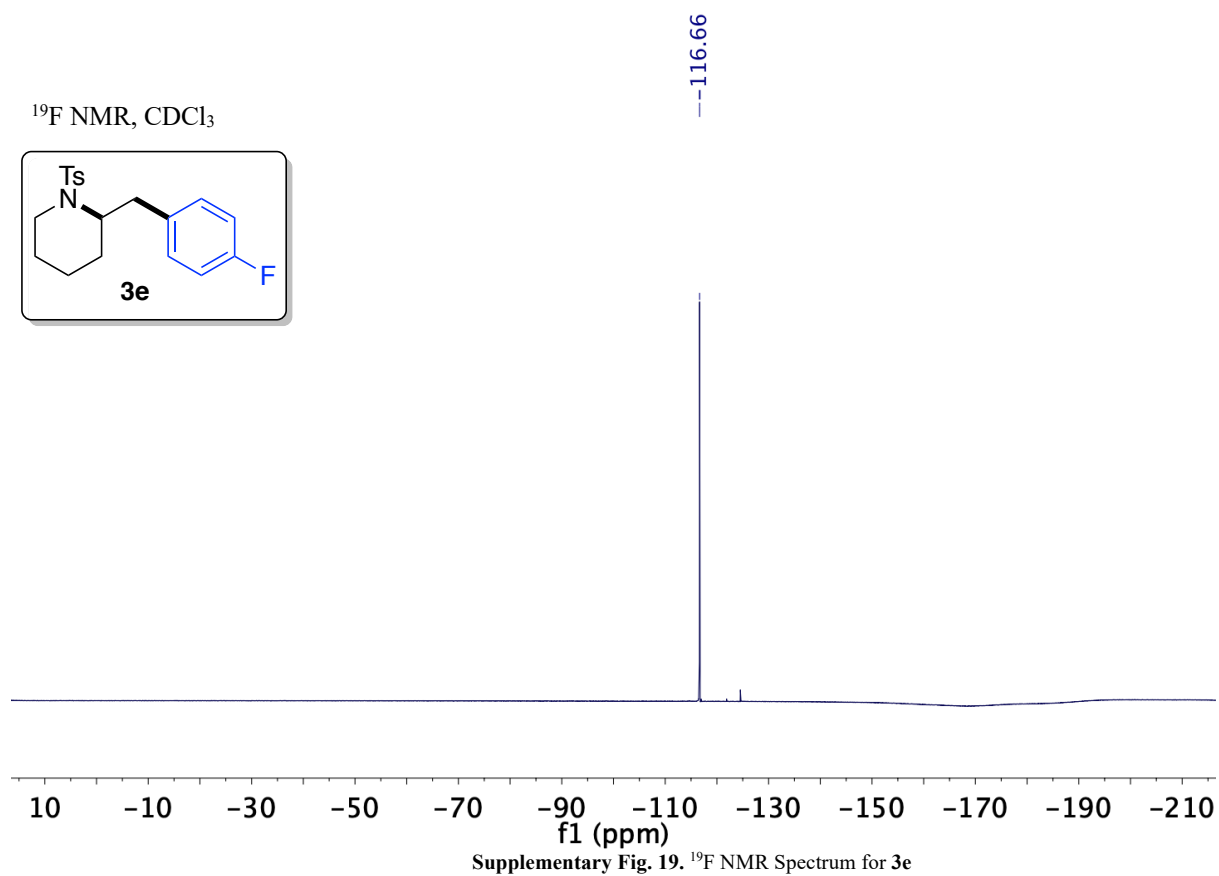
Supplementary Fig. 16. ¹⁹F NMR Spectrum for **3d**

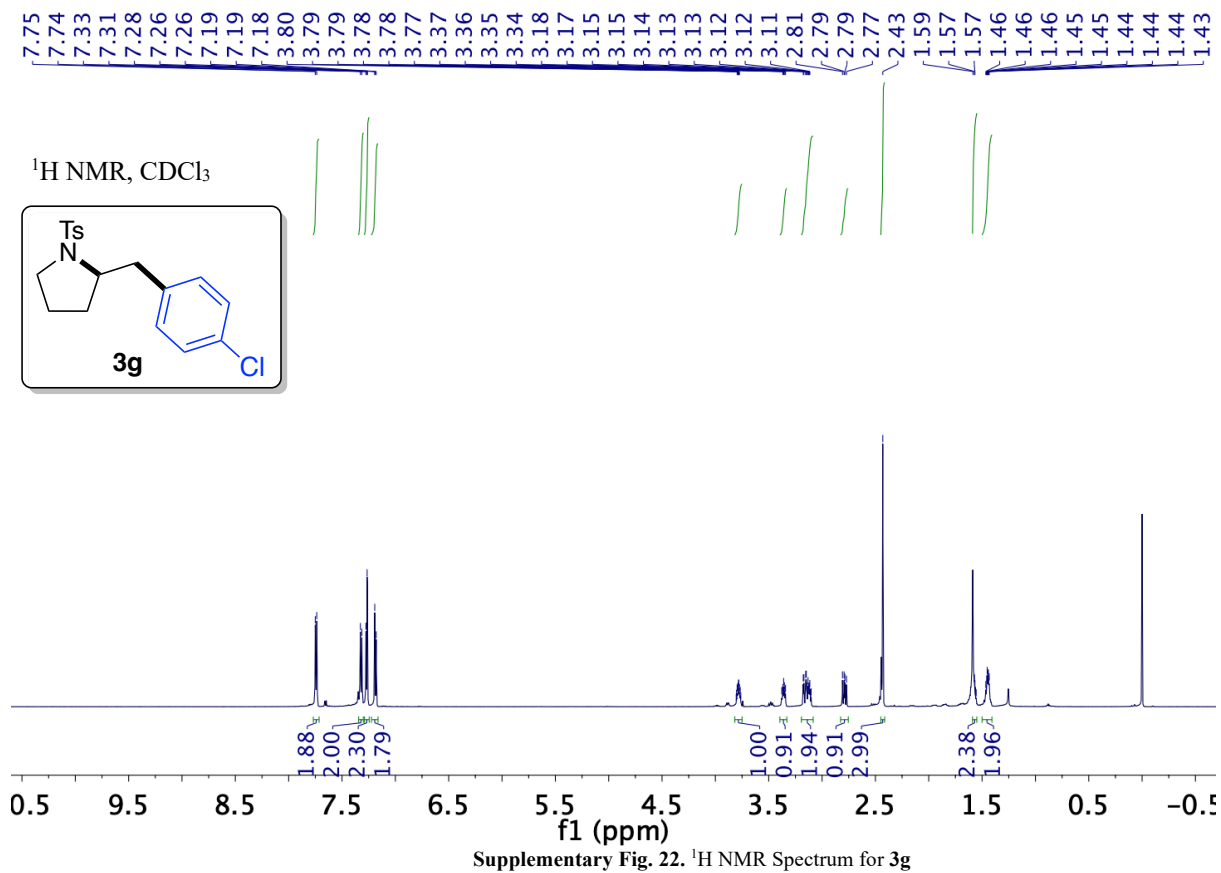
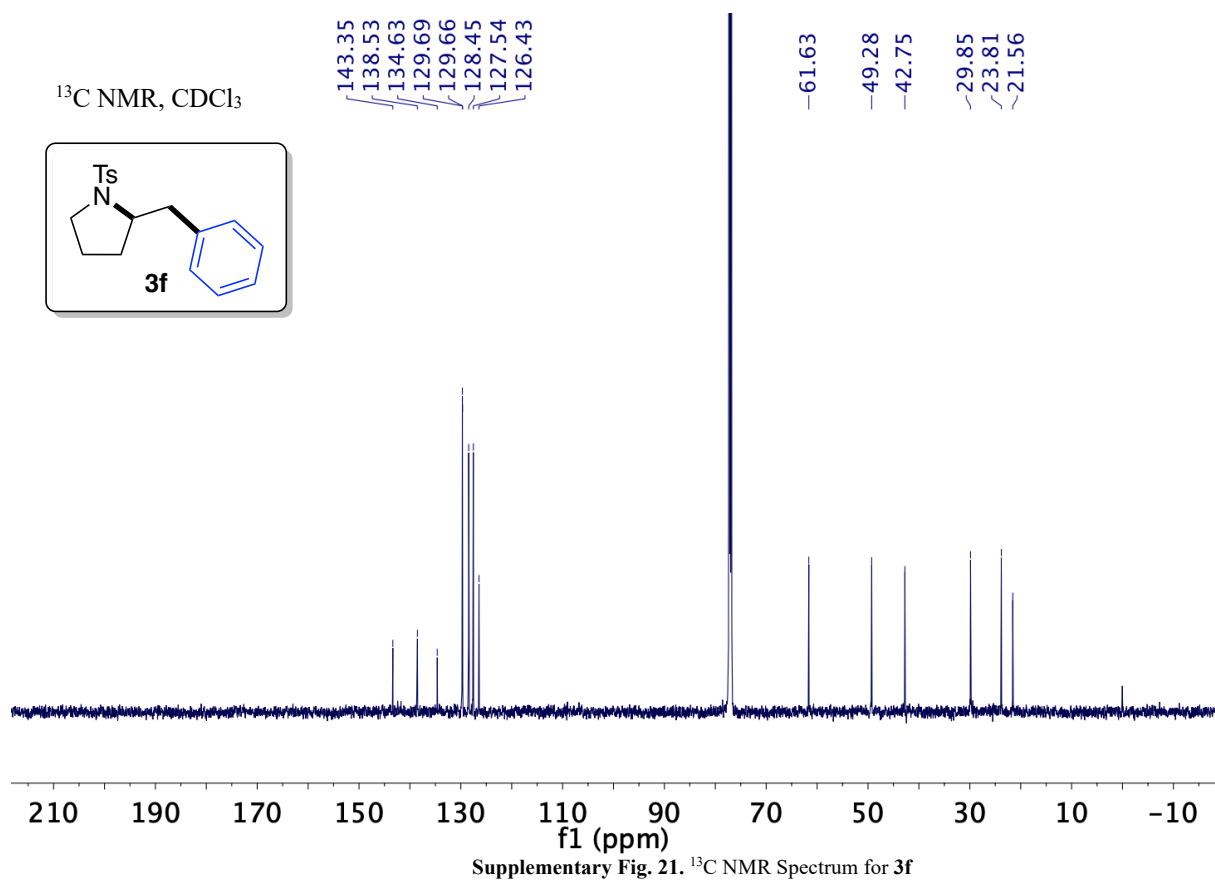


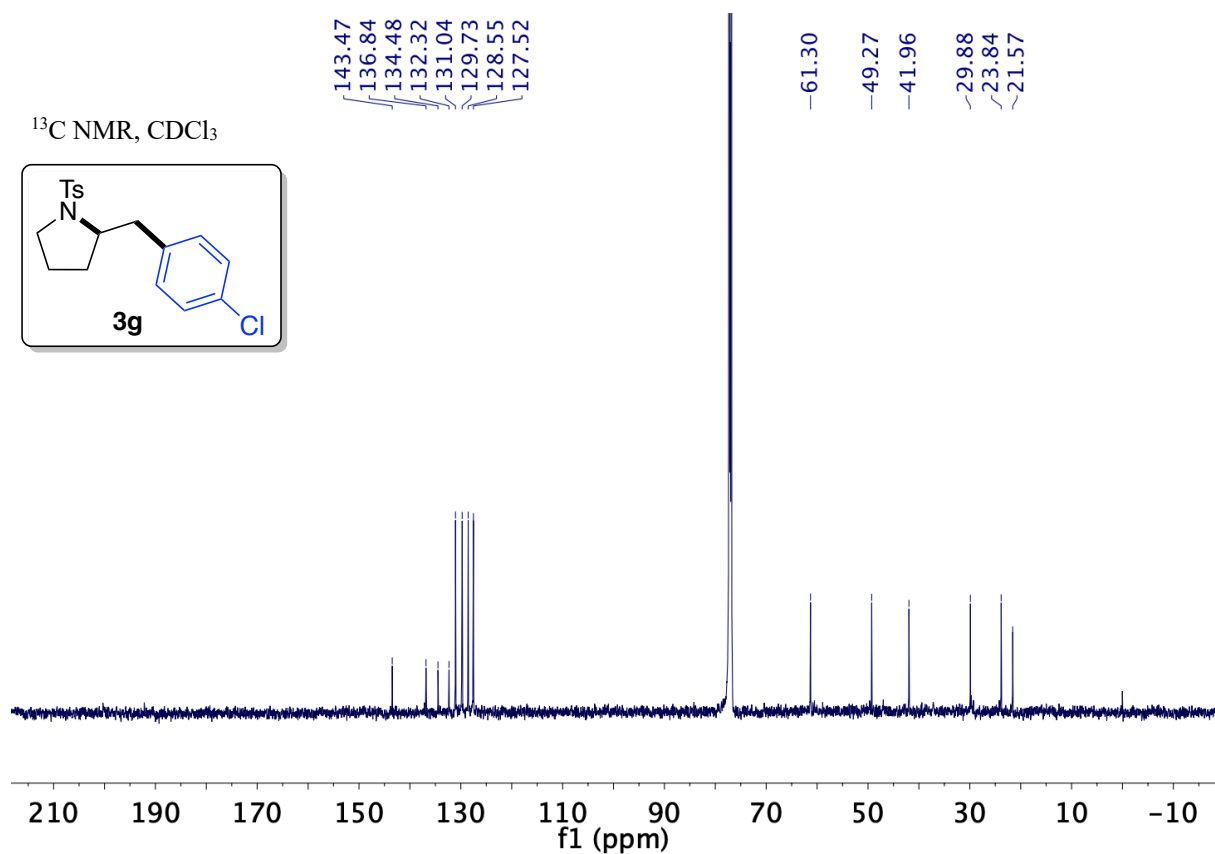
Supplementary Fig. 17. ¹H NMR Spectrum for **3e**



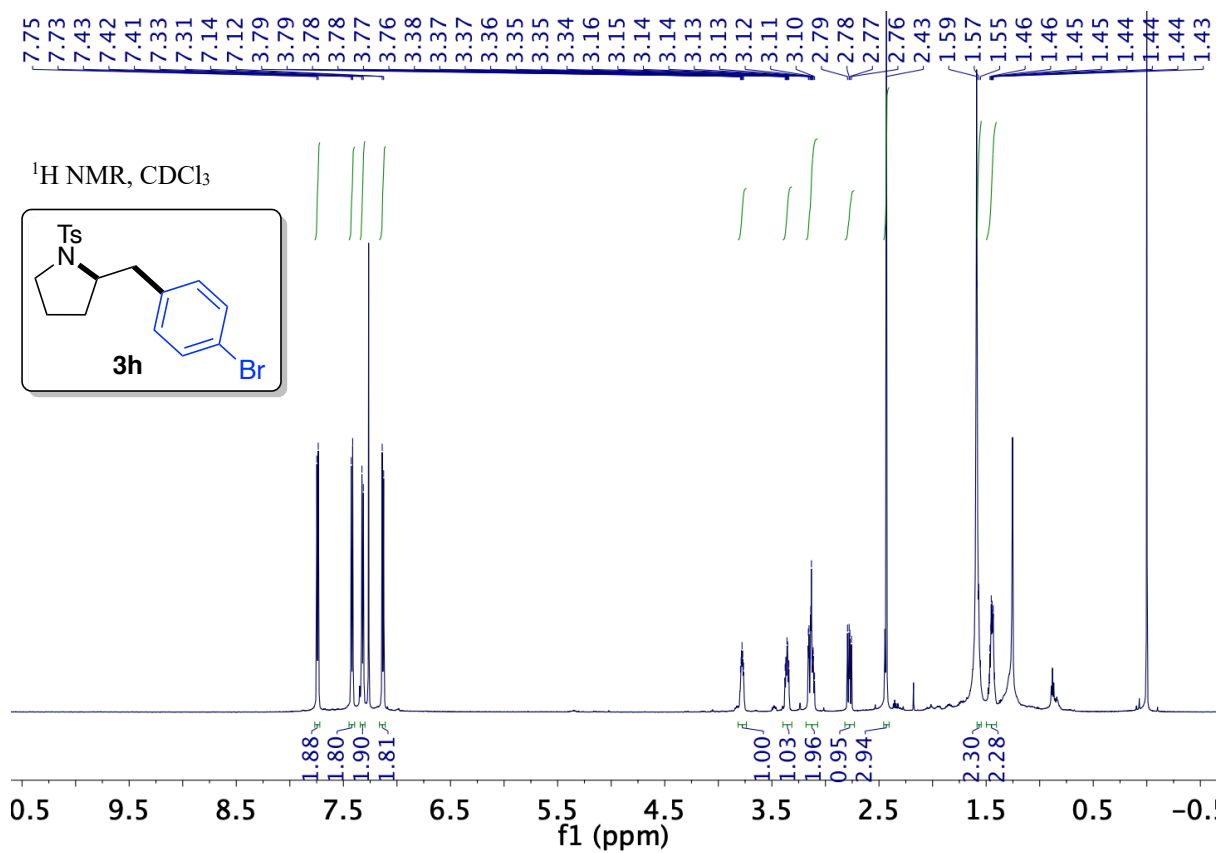
Supplementary Fig. 18. ¹³C NMR Spectrum for **3e**



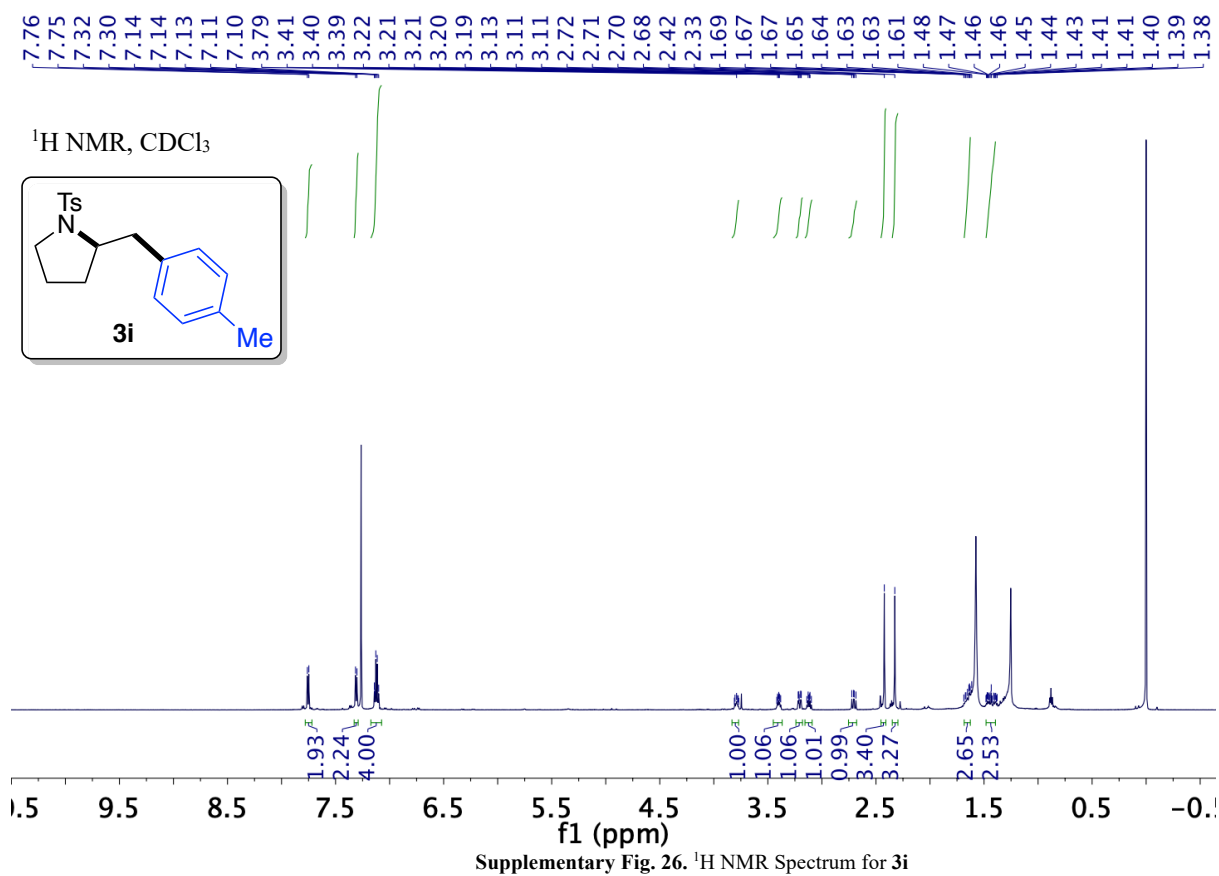
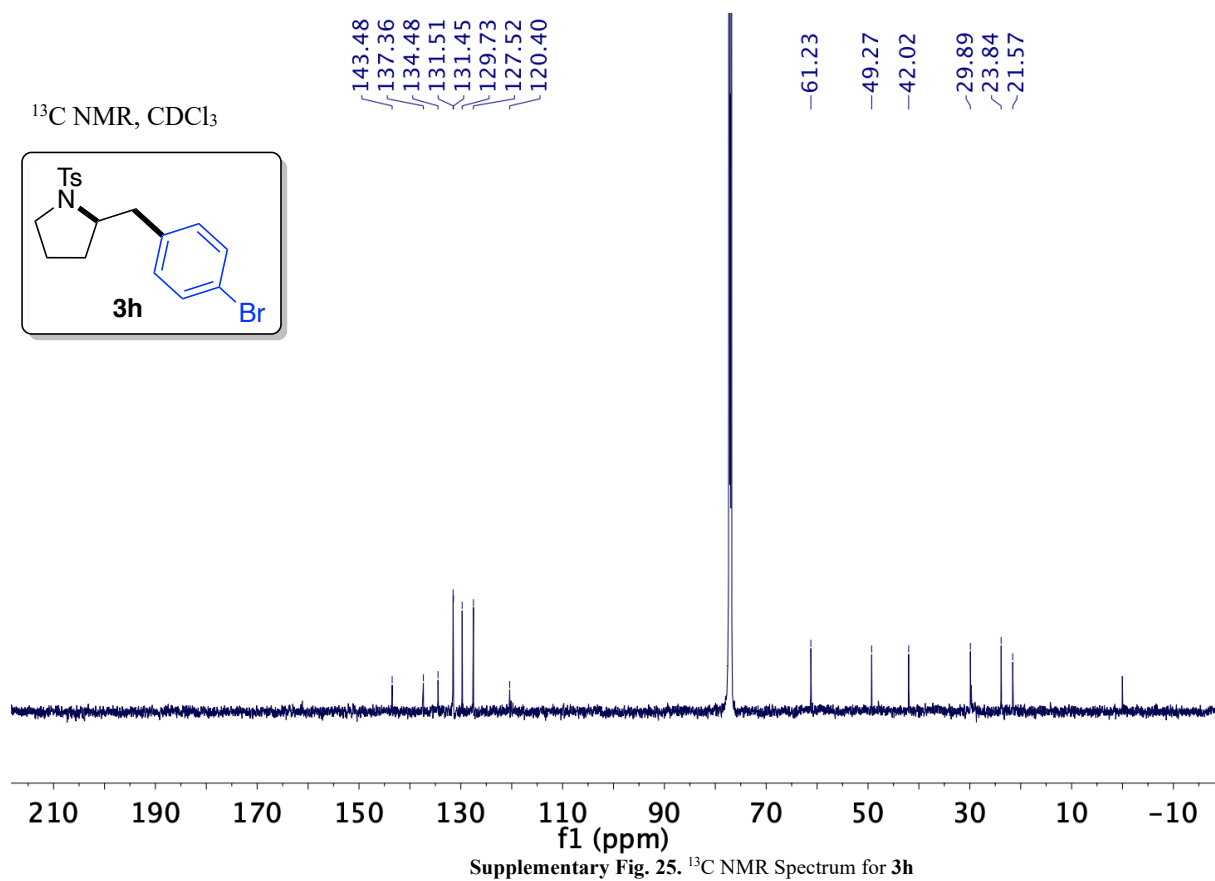


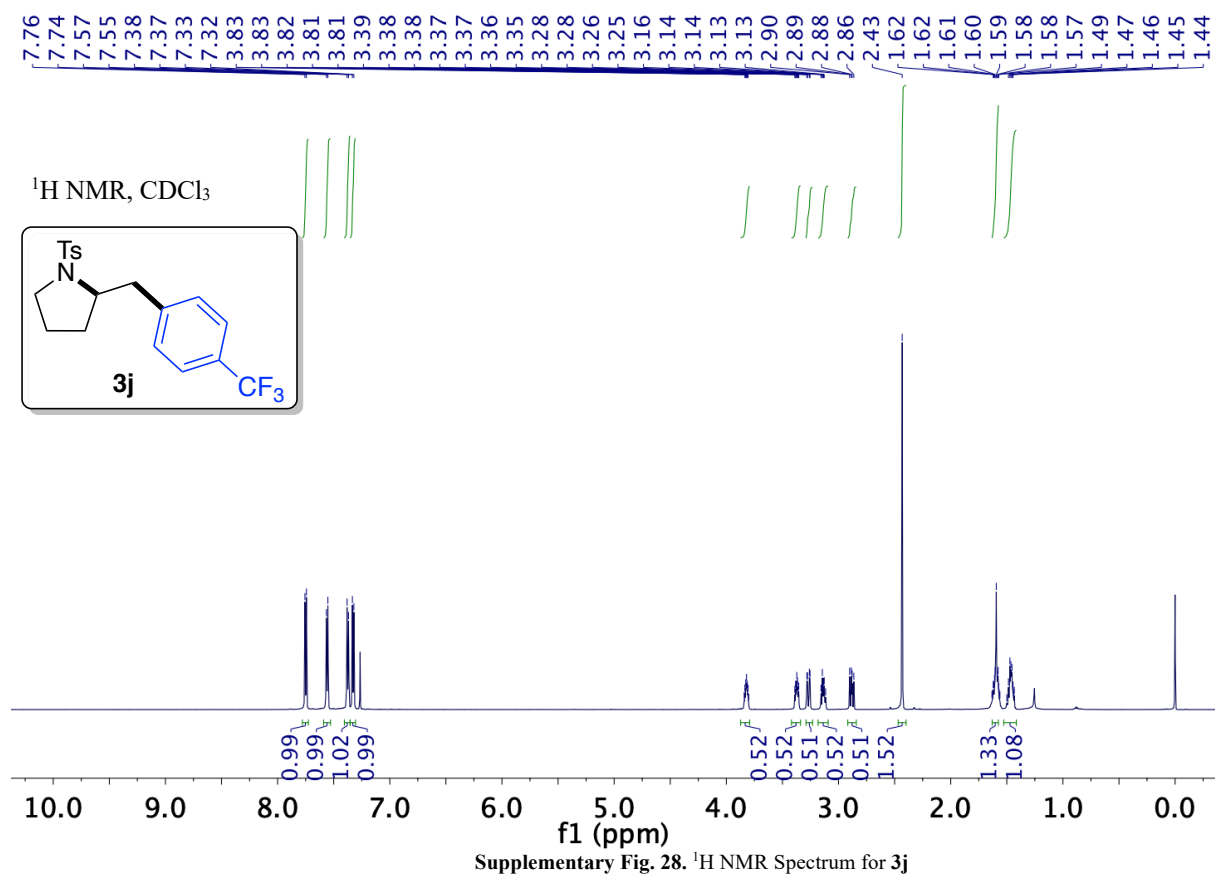
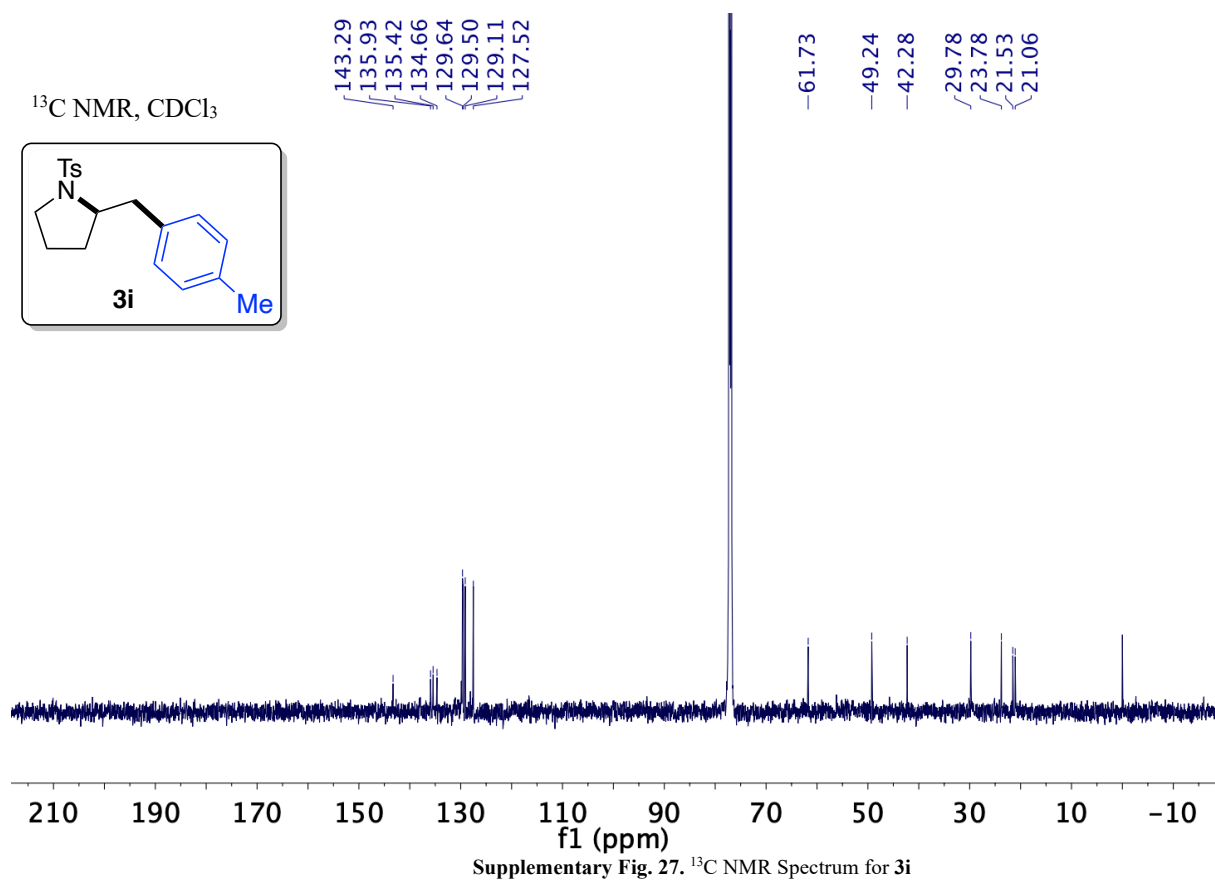


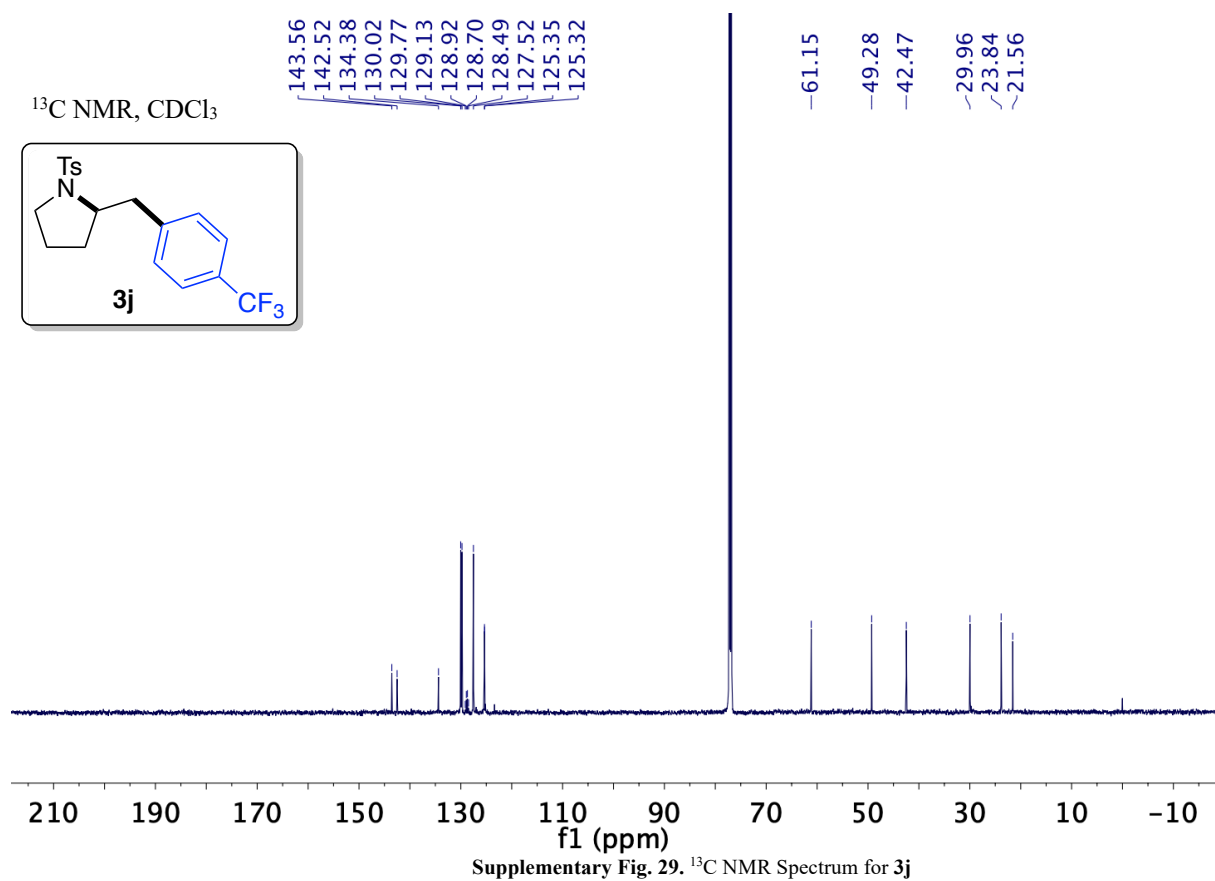
Supplementary Fig. 23. ¹³C NMR Spectrum for **3g**



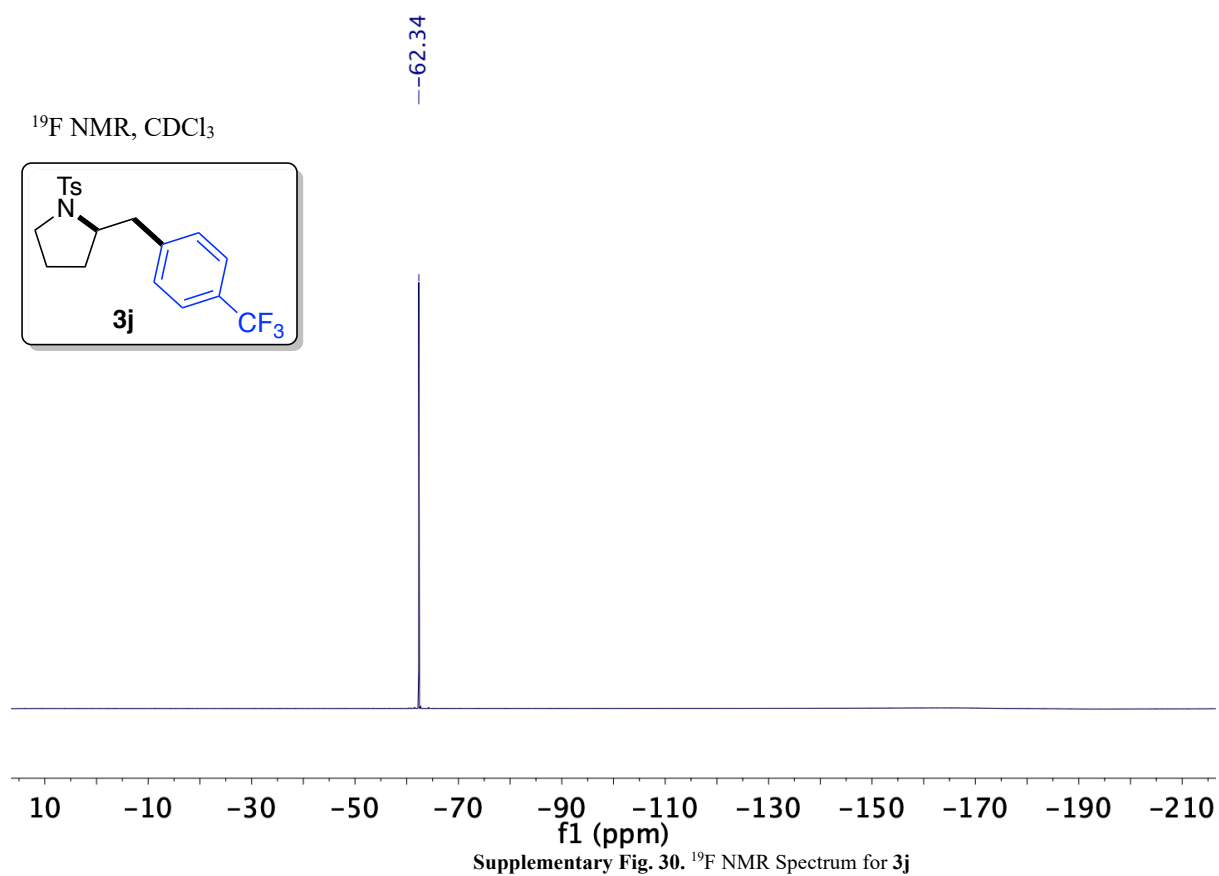
Supplementary Fig. 24. ¹H NMR Spectrum for **3h**



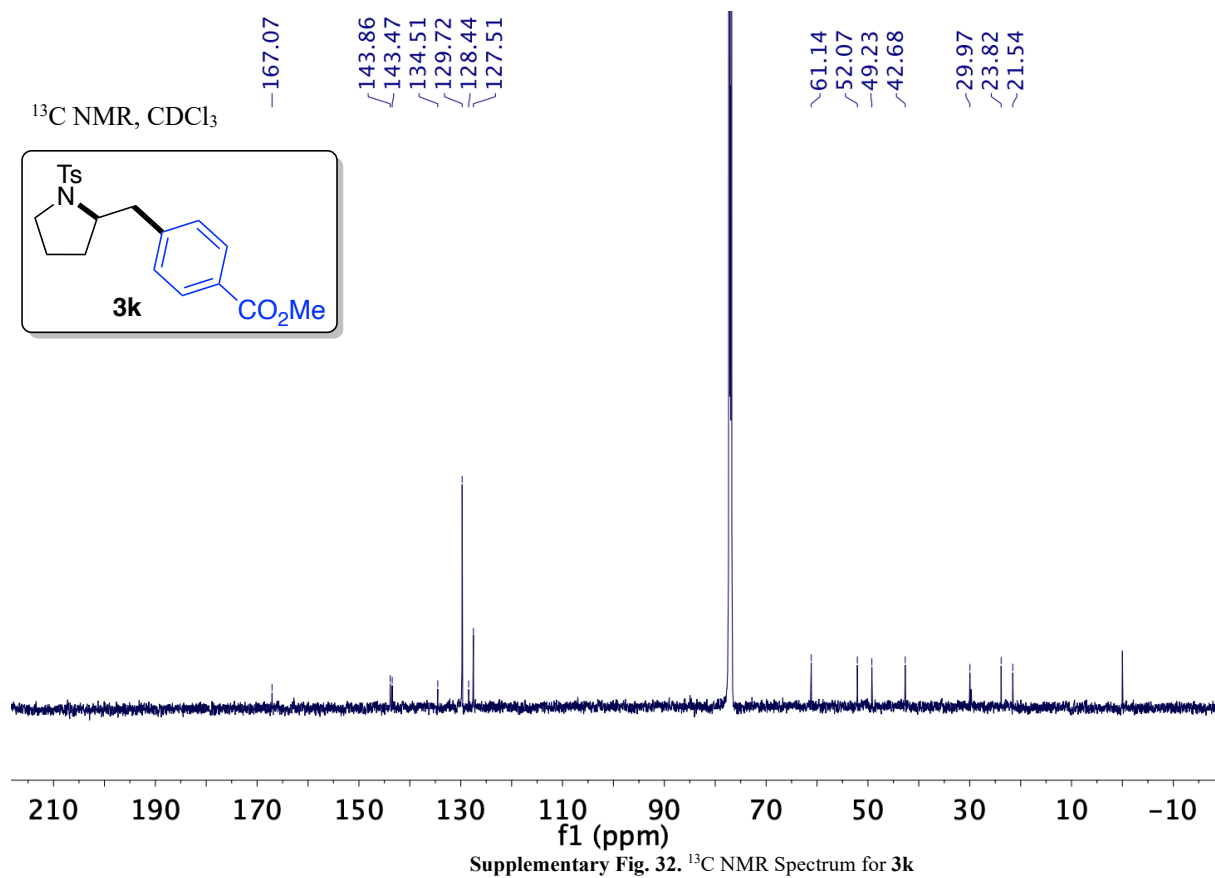
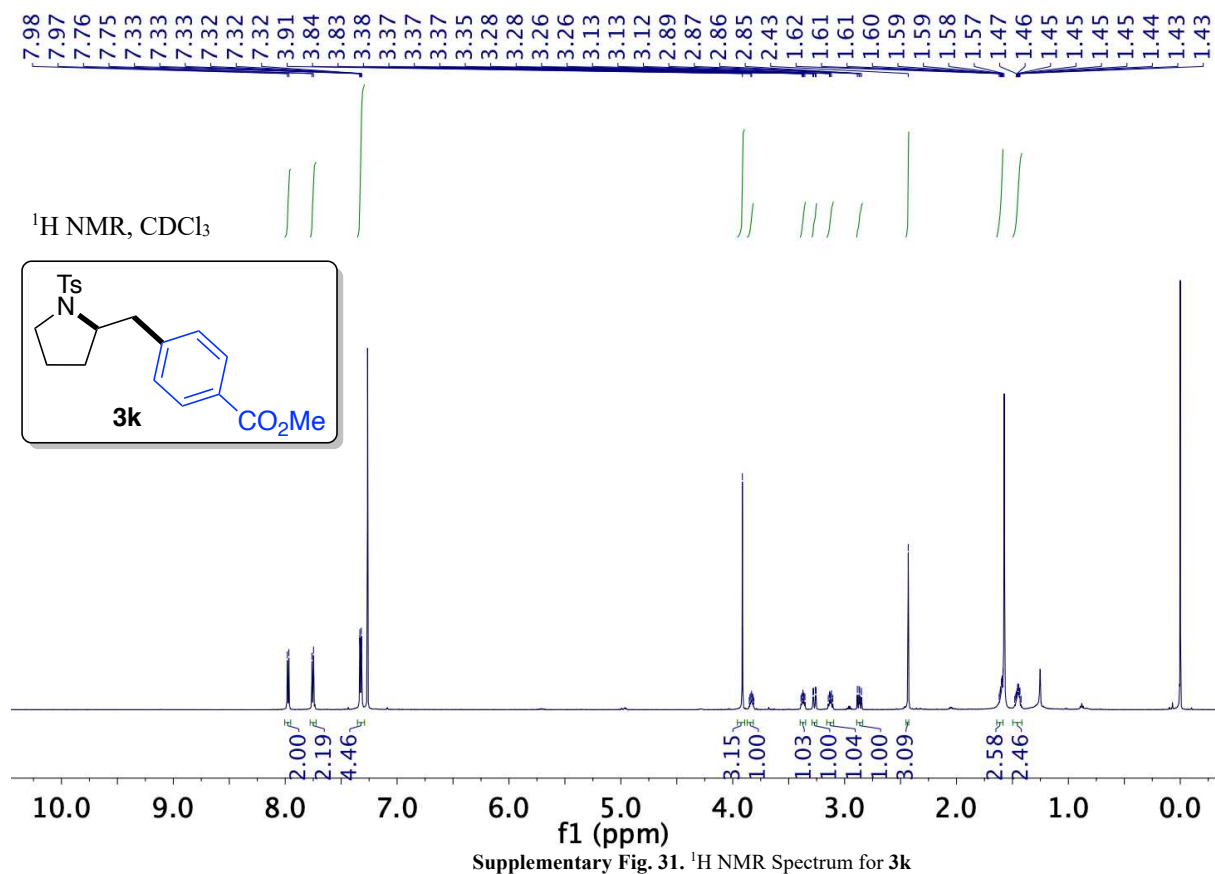


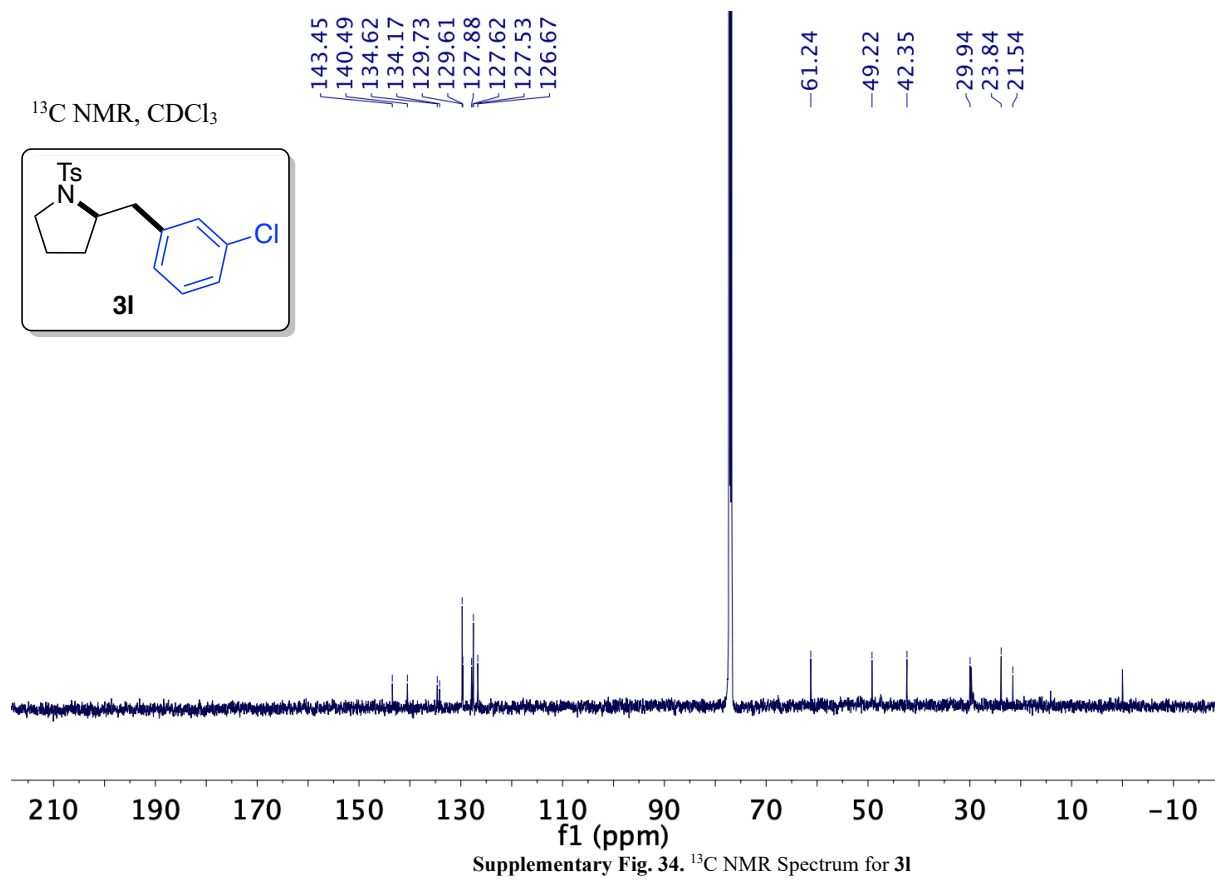
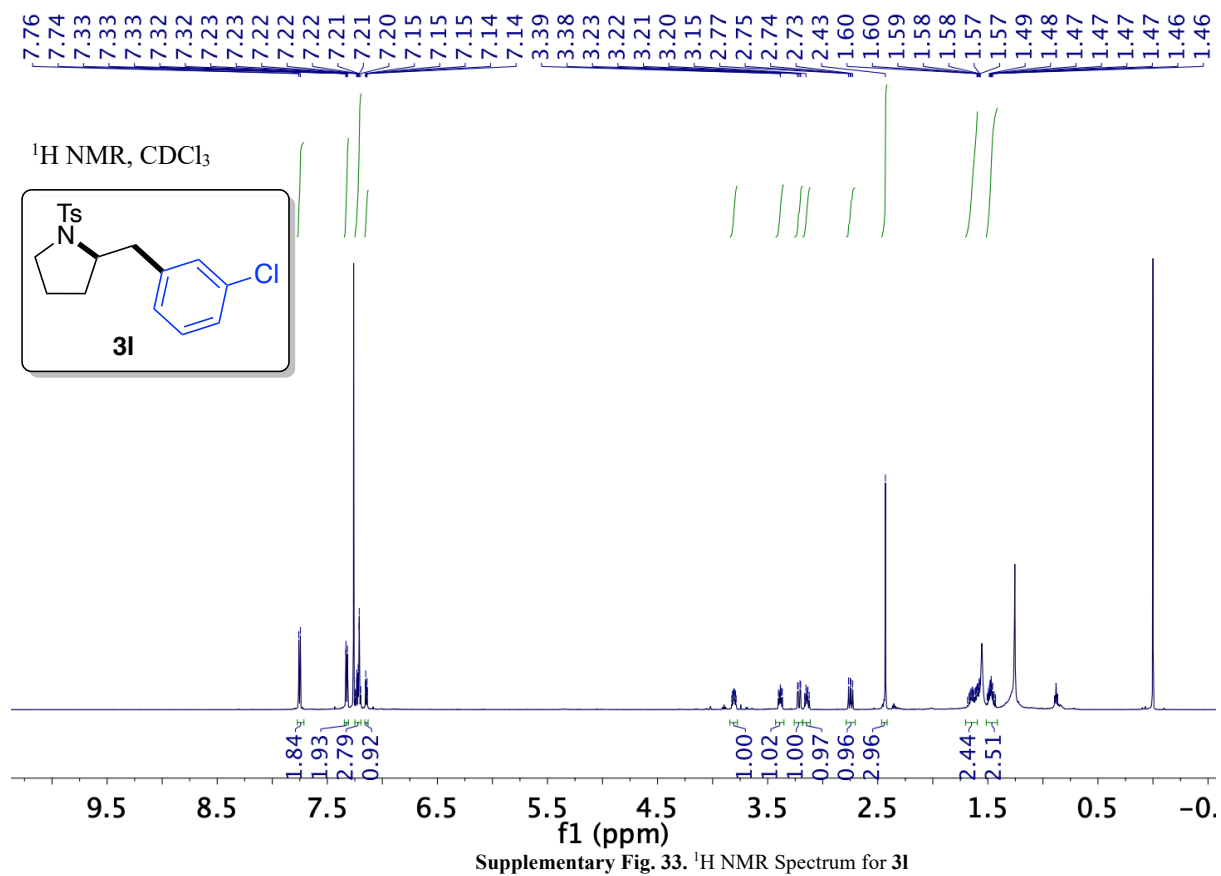


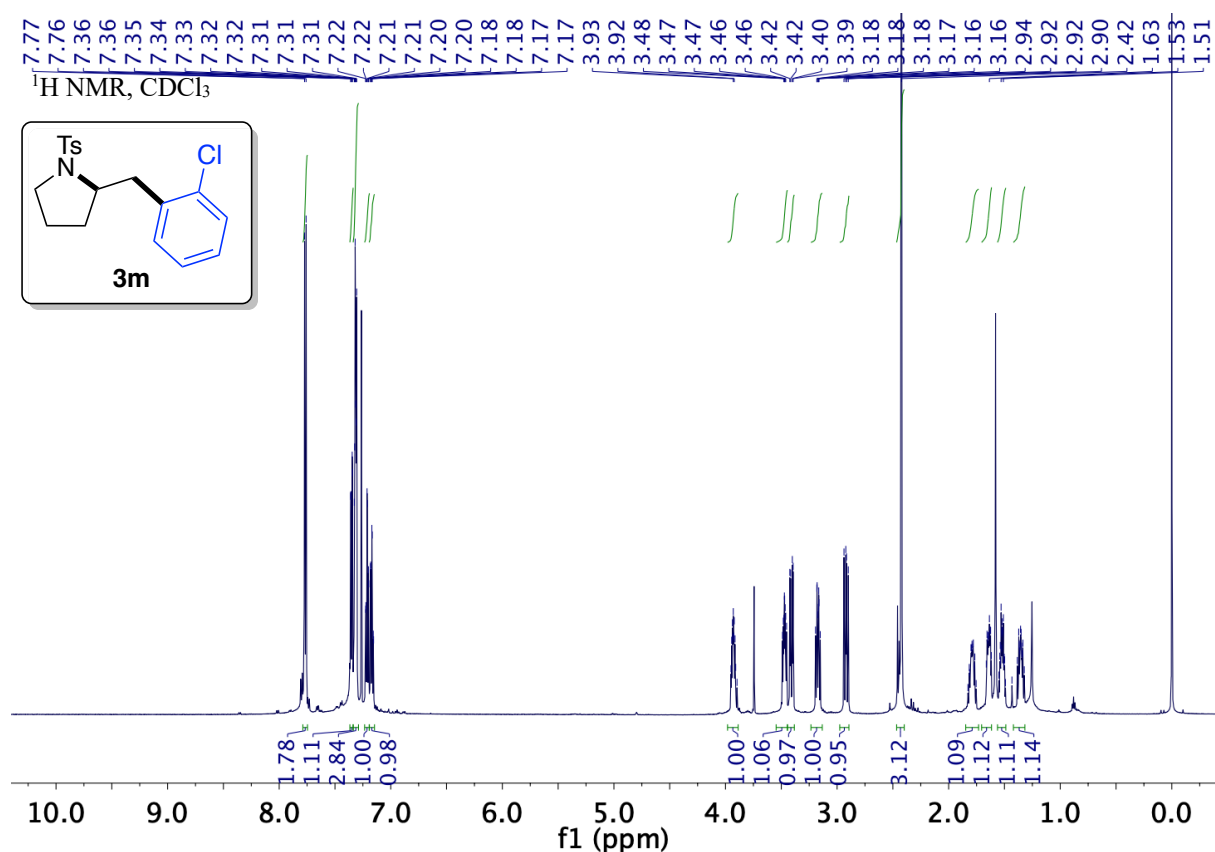
Supplementary Fig. 29. ¹³C NMR Spectrum for **3j**



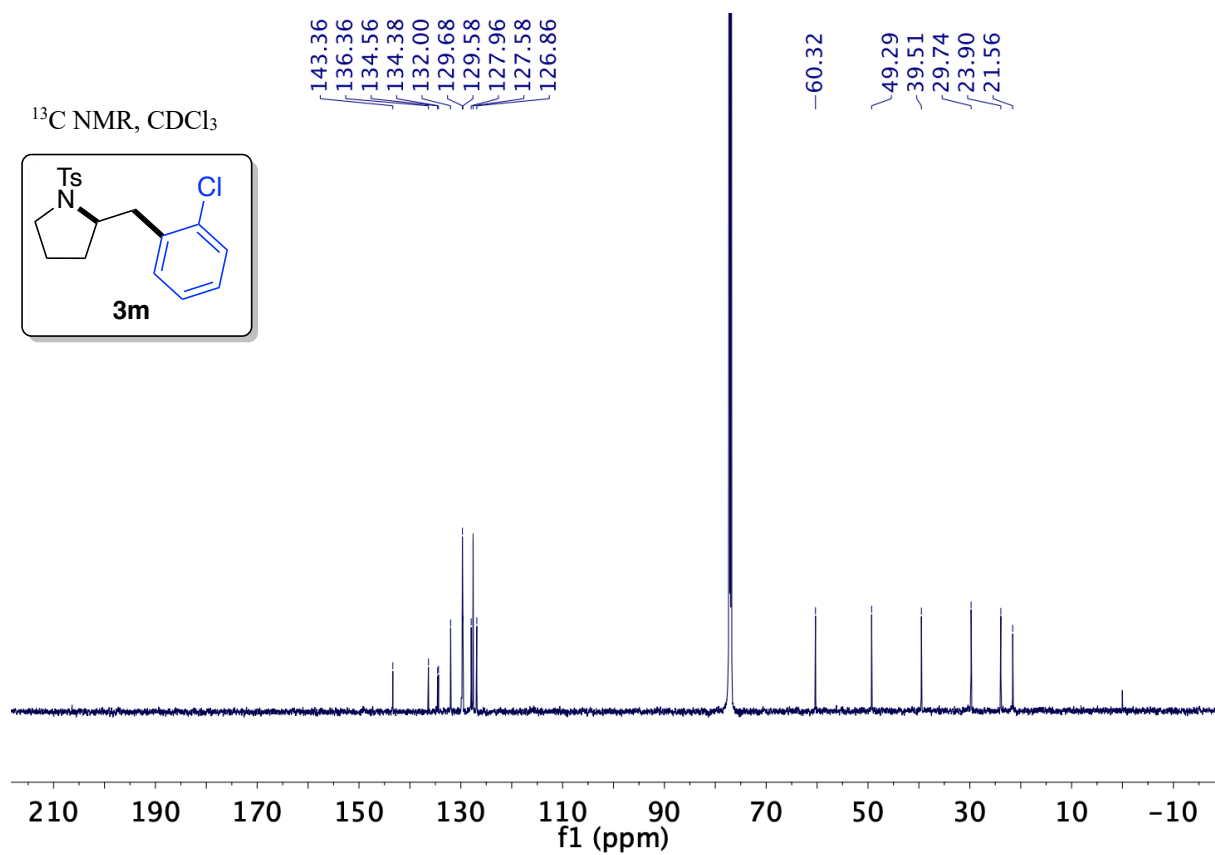
Supplementary Fig. 30. ¹⁹F NMR Spectrum for **3j**



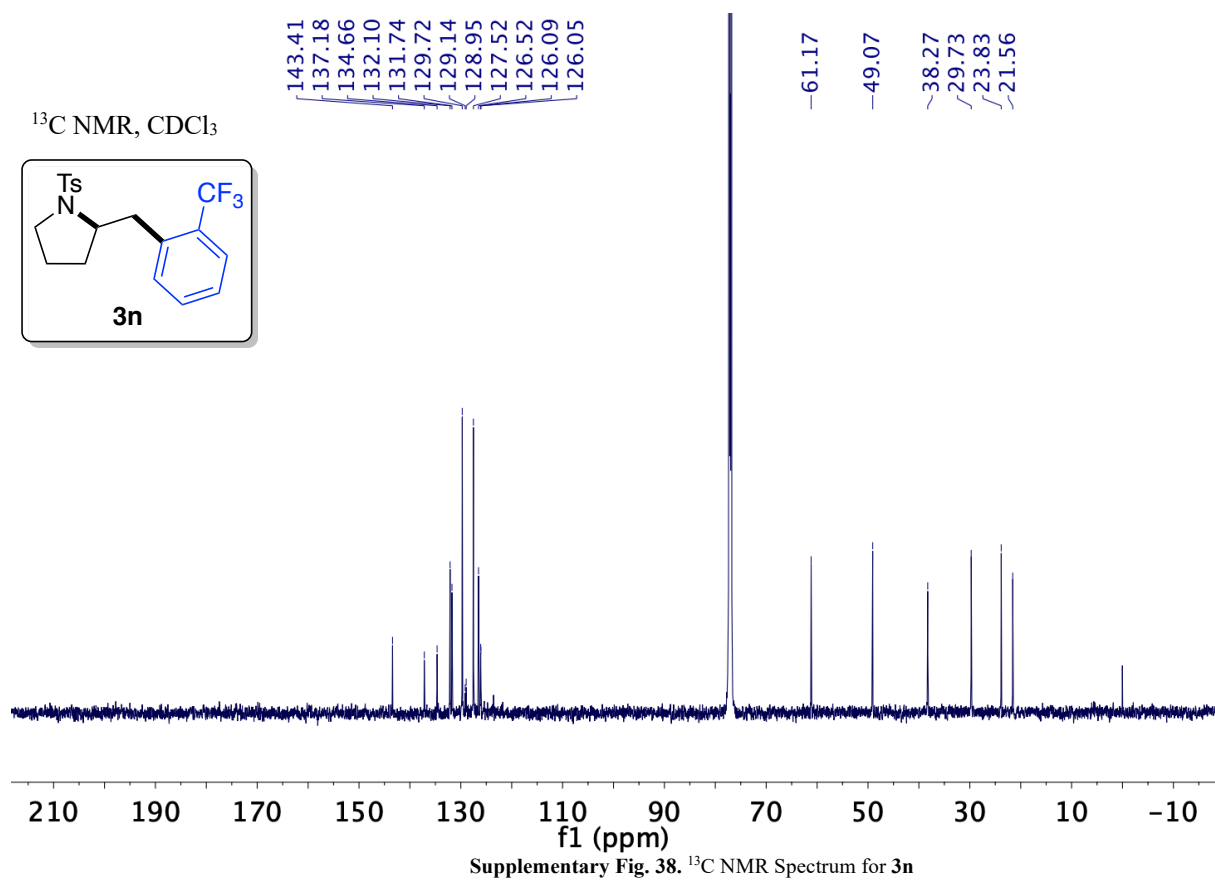
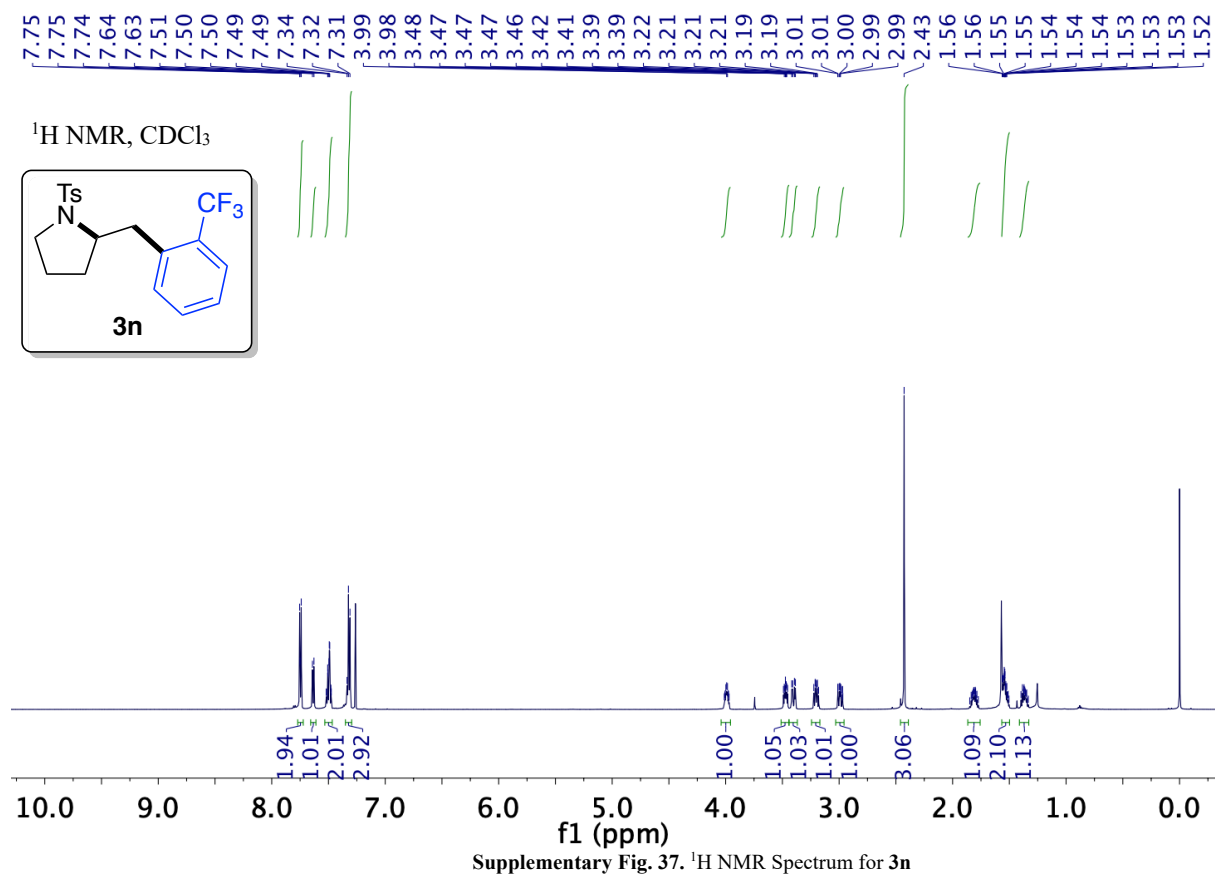


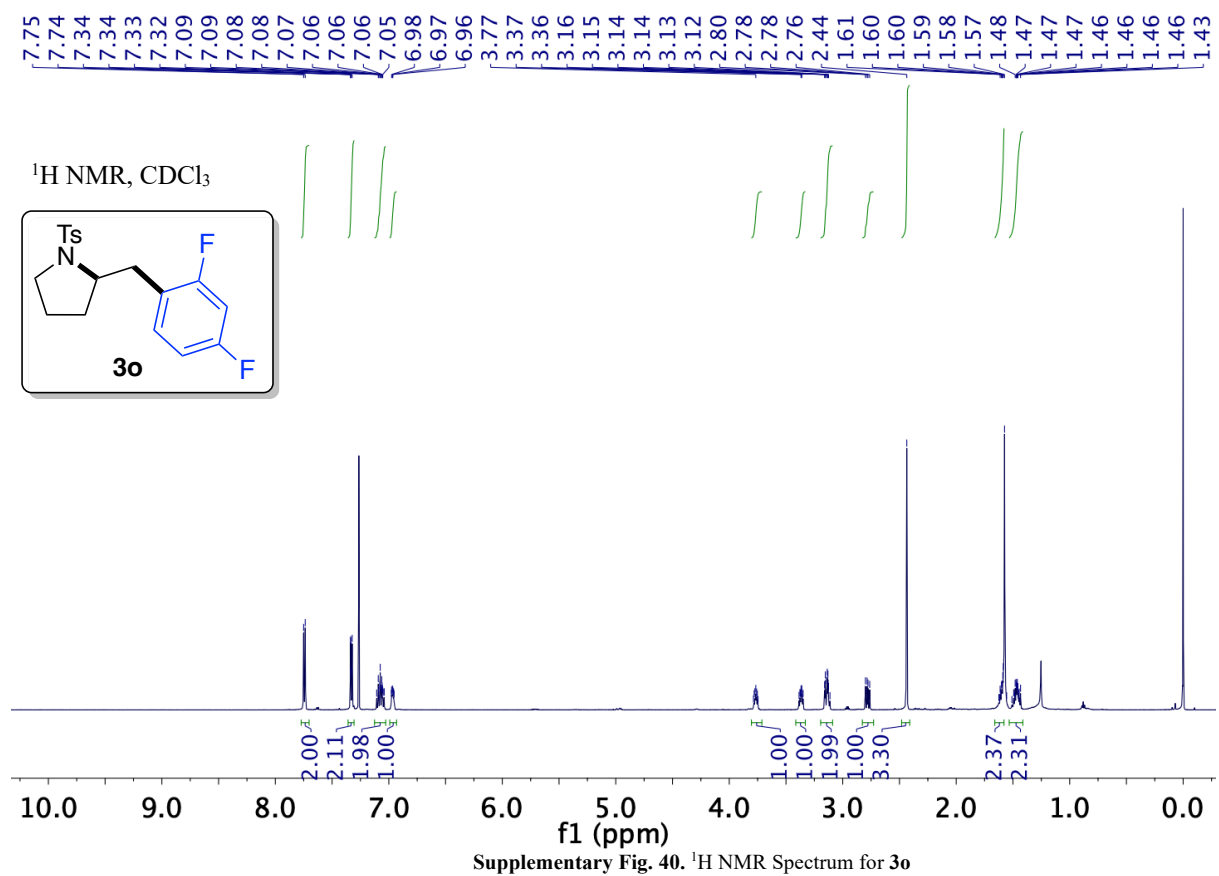
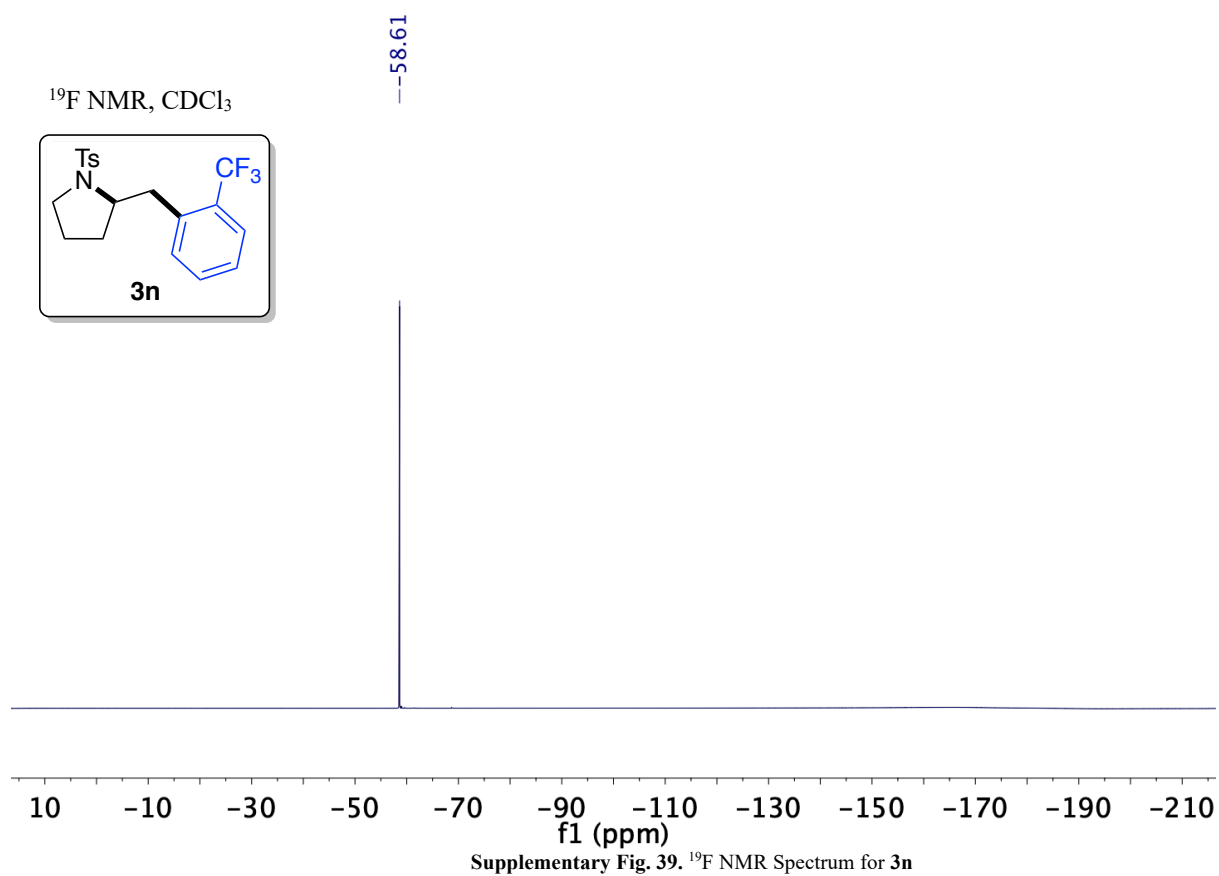


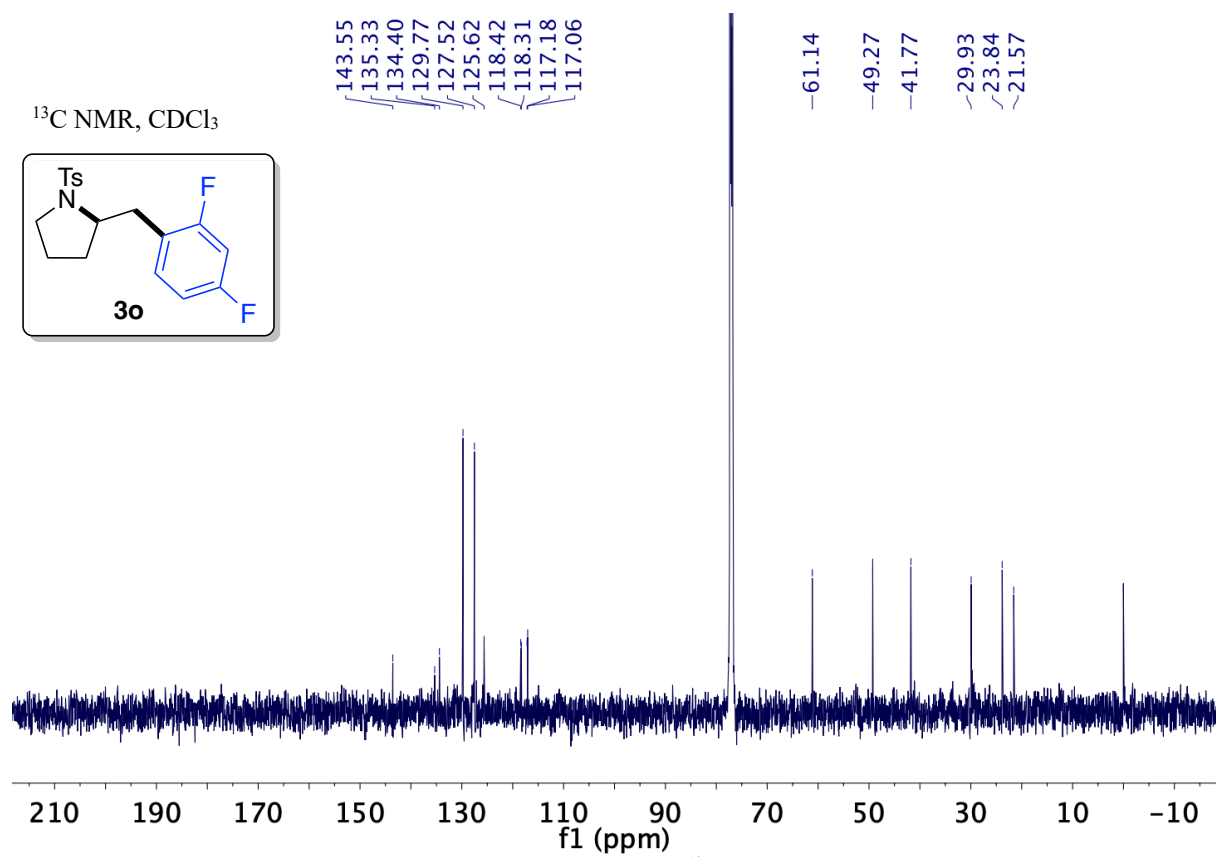
Supplementary Fig. 35. ¹H NMR Spectrum for **3m**



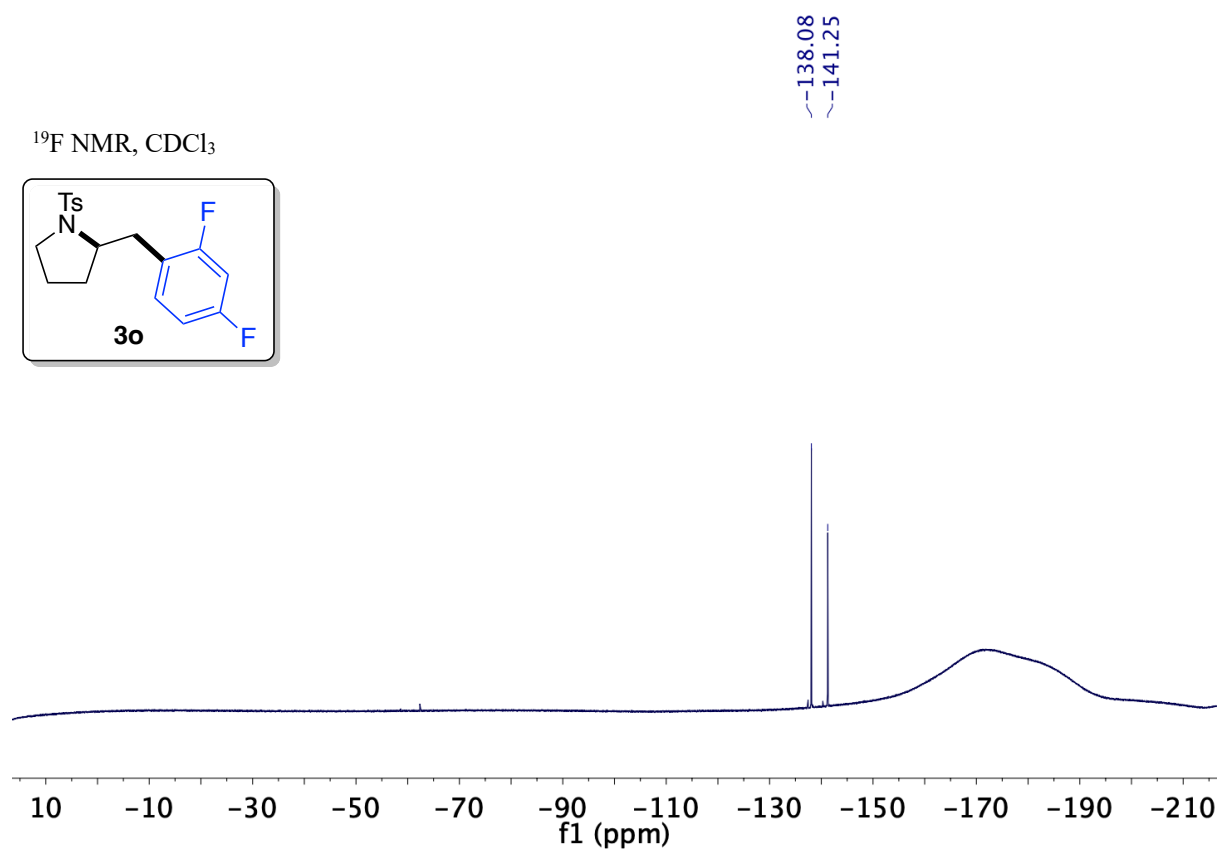
Supplementary Fig. 36. ¹³C NMR Spectrum for **3m**



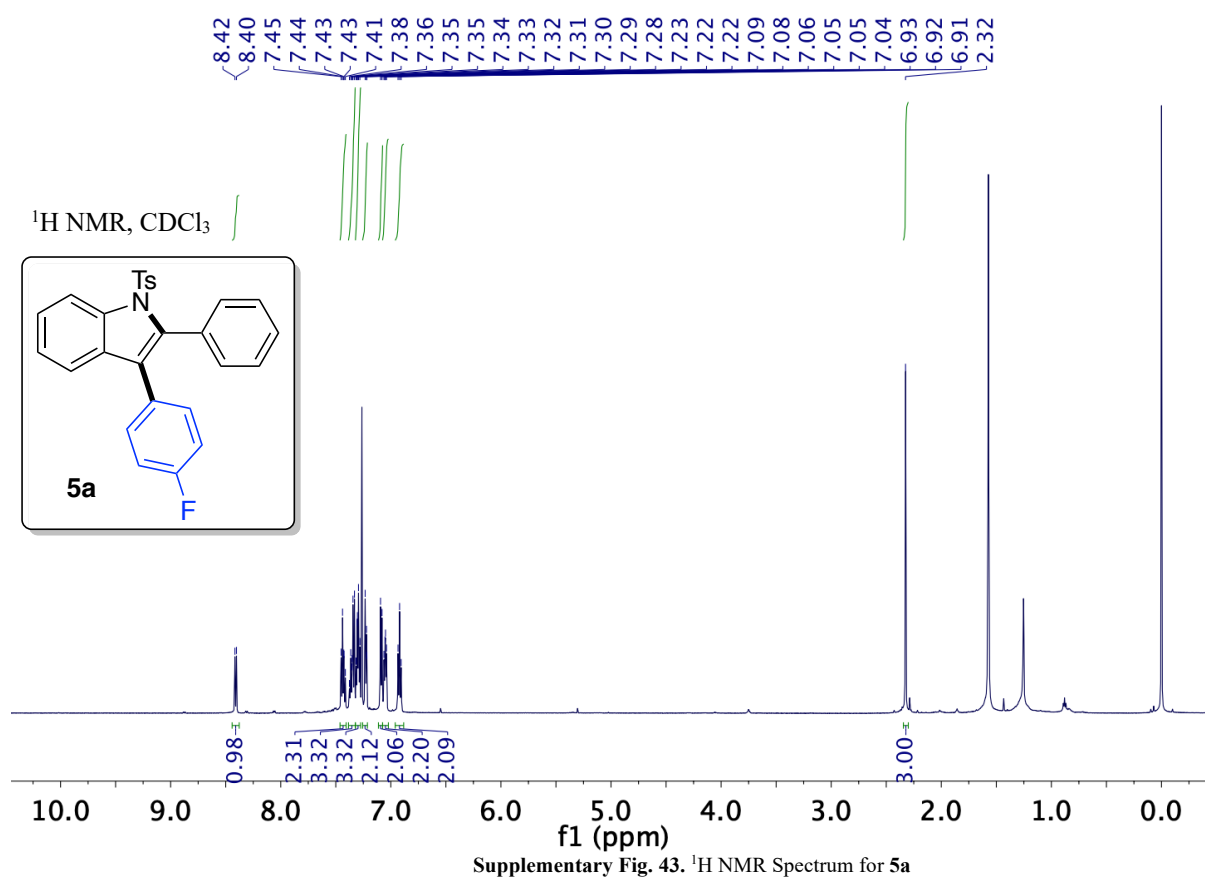




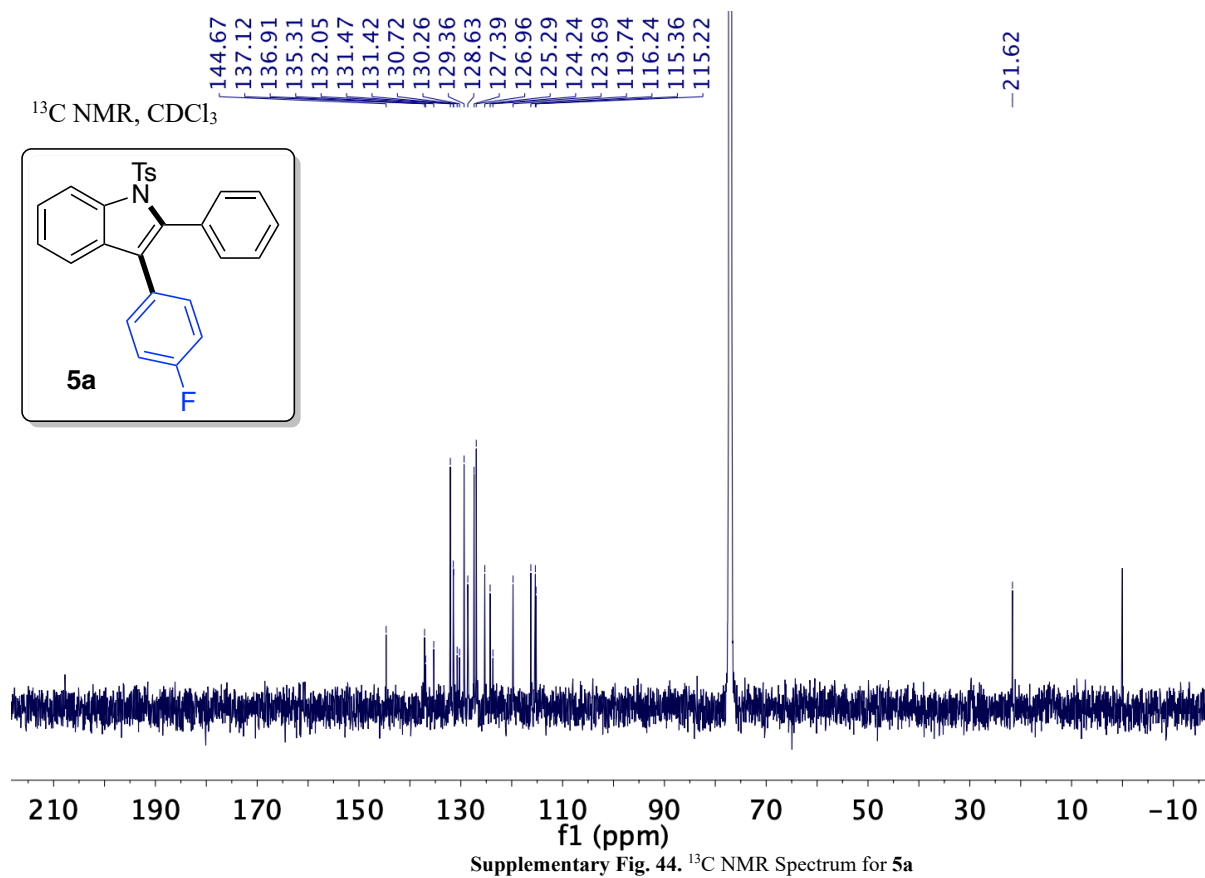
Supplementary Fig. 41. ¹³C NMR Spectrum for **3o**



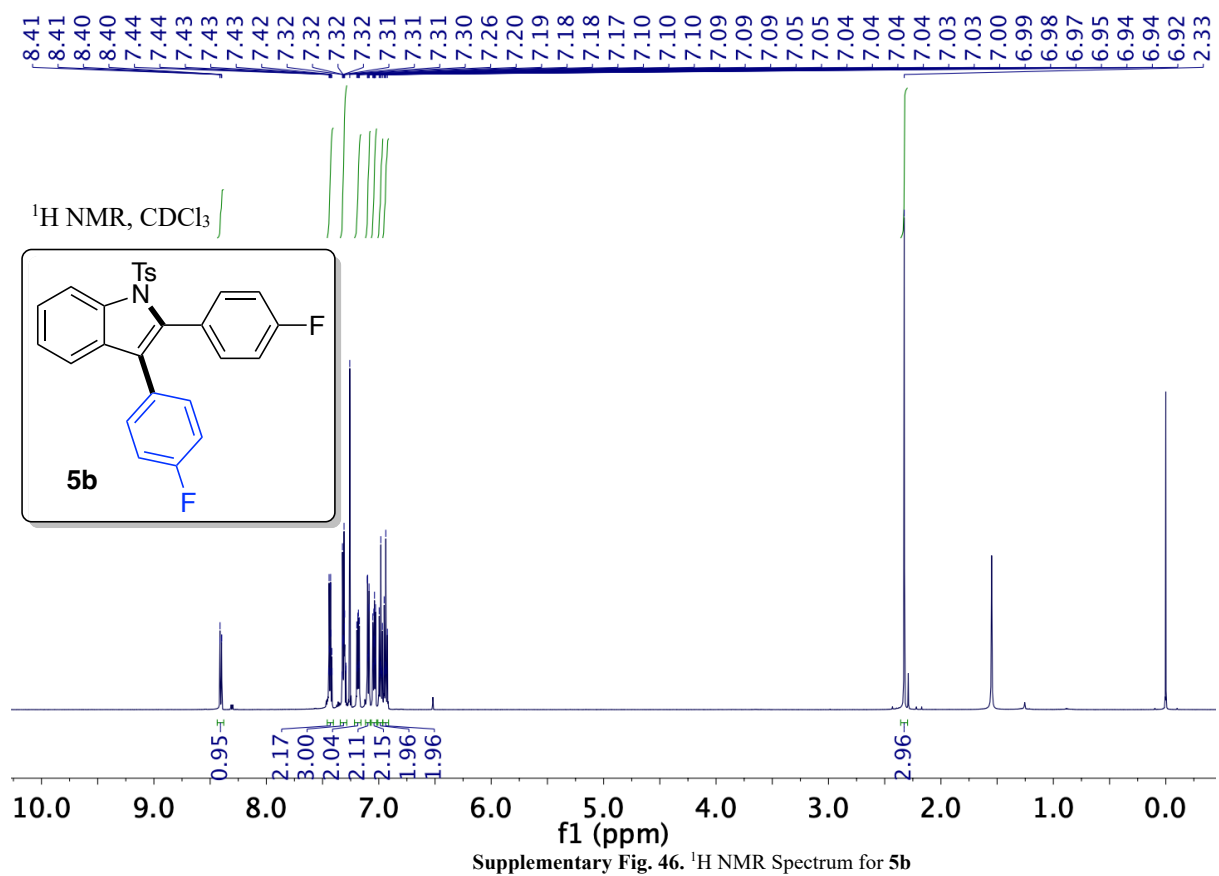
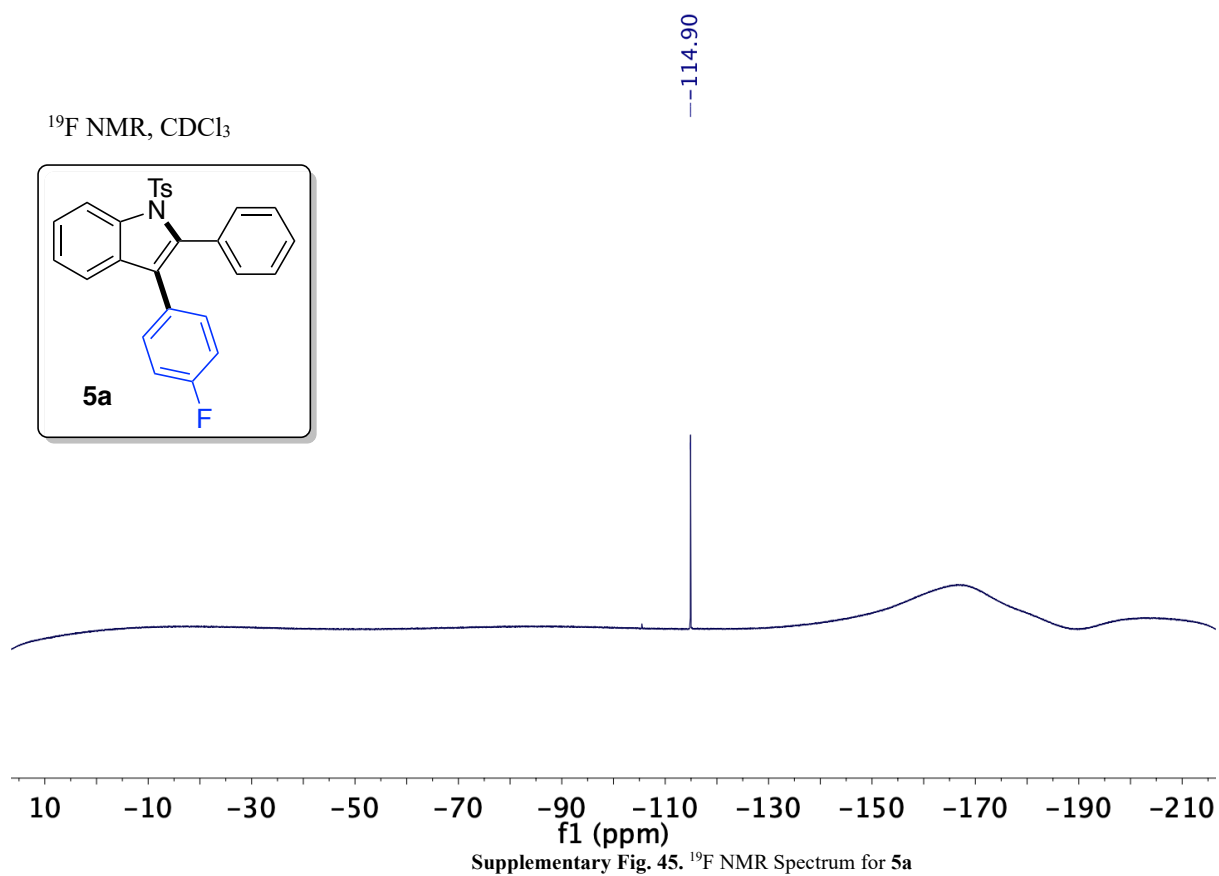
Supplementary Fig. 42. ¹⁹F NMR Spectrum for **3o**

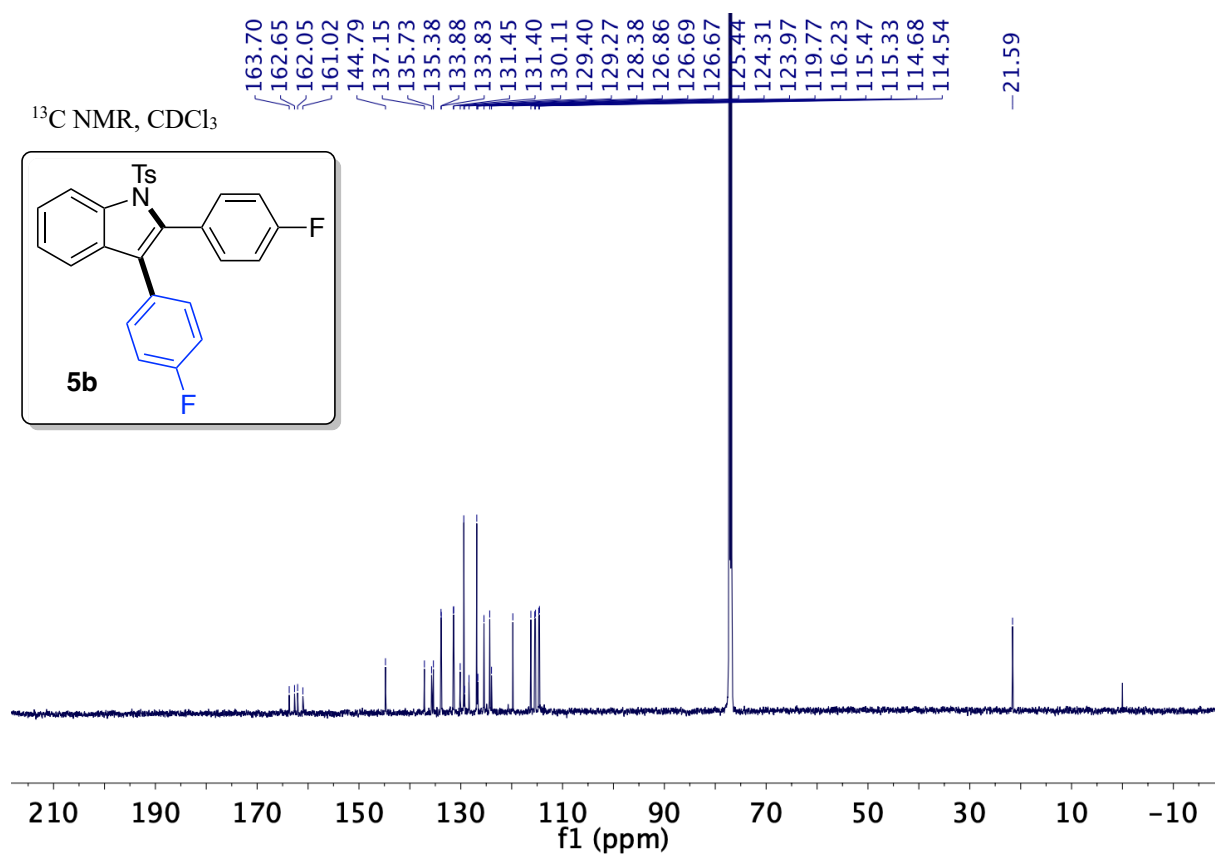


Supplementary Fig. 43. ¹H NMR Spectrum for **5a**

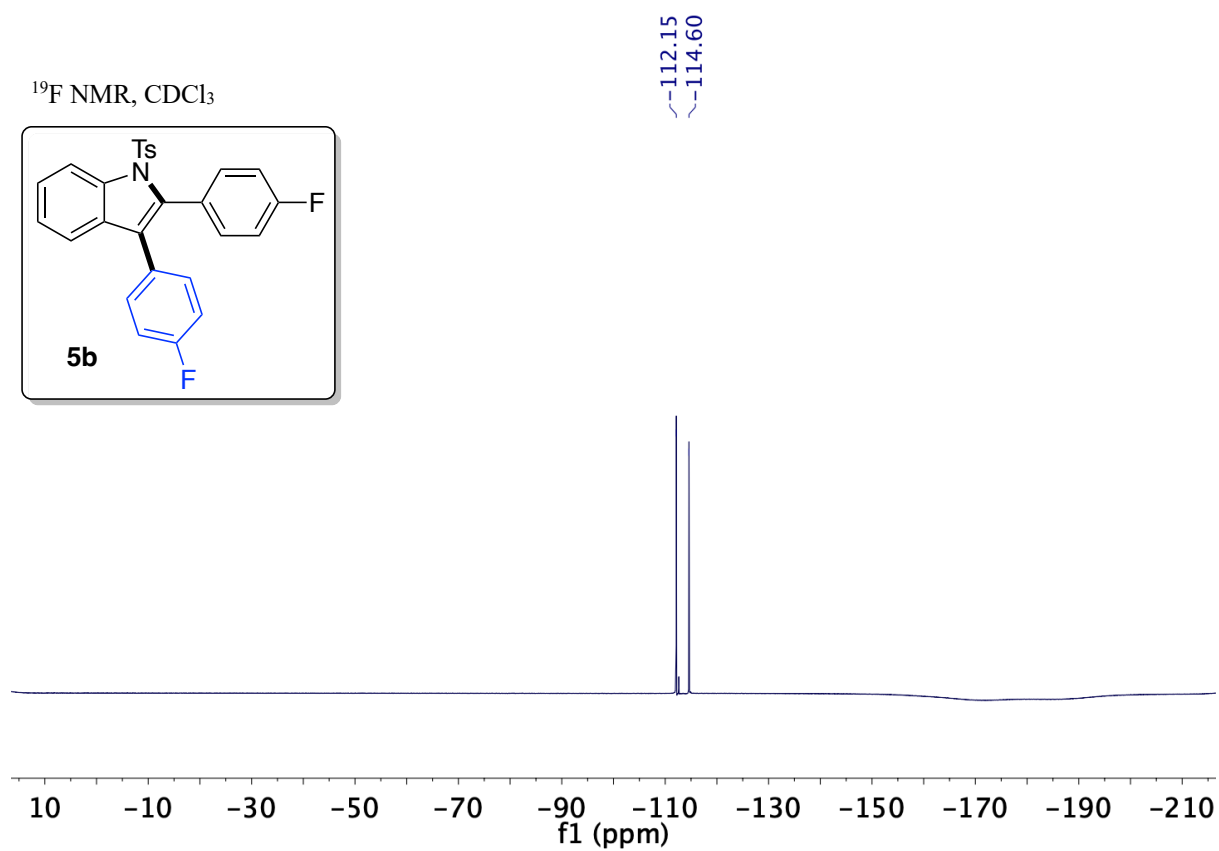


Supplementary Fig. 44. ¹³C NMR Spectrum for **5a**

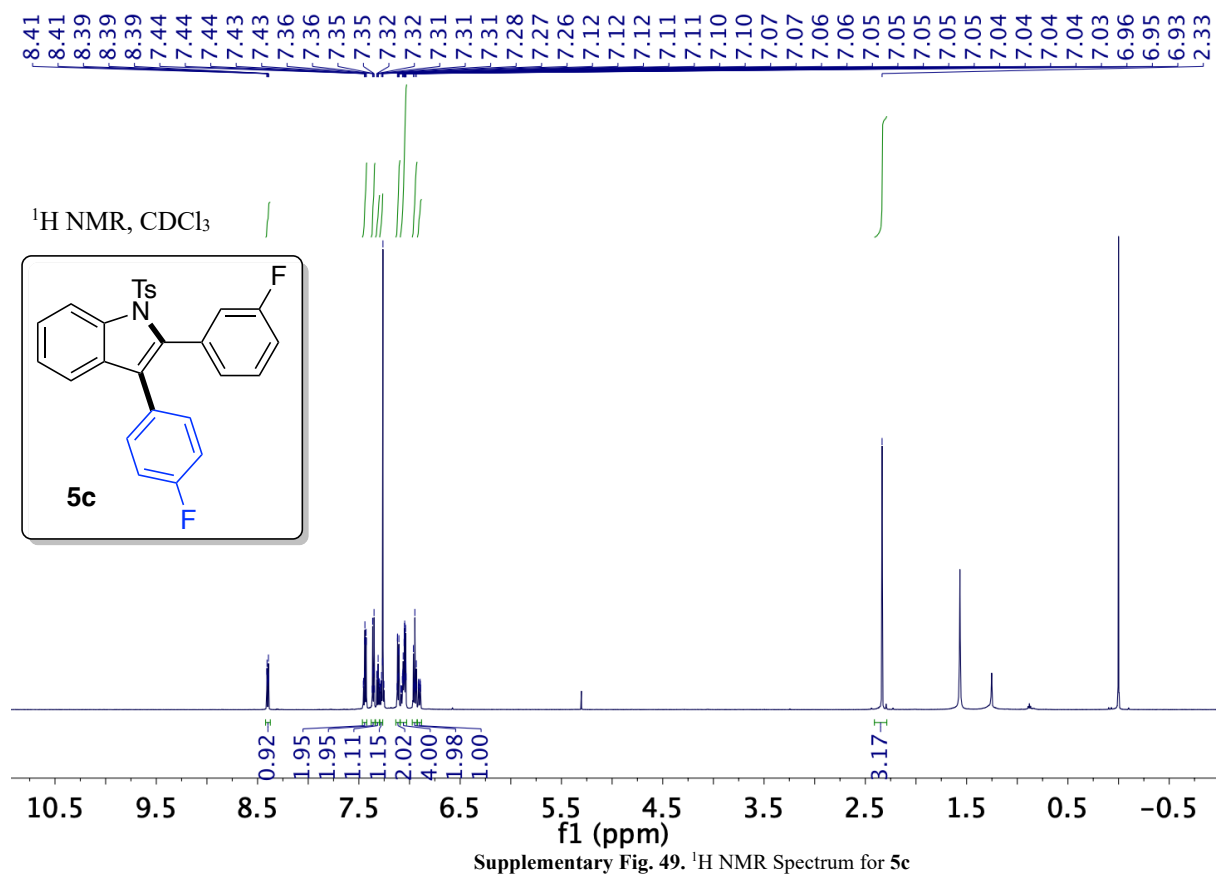




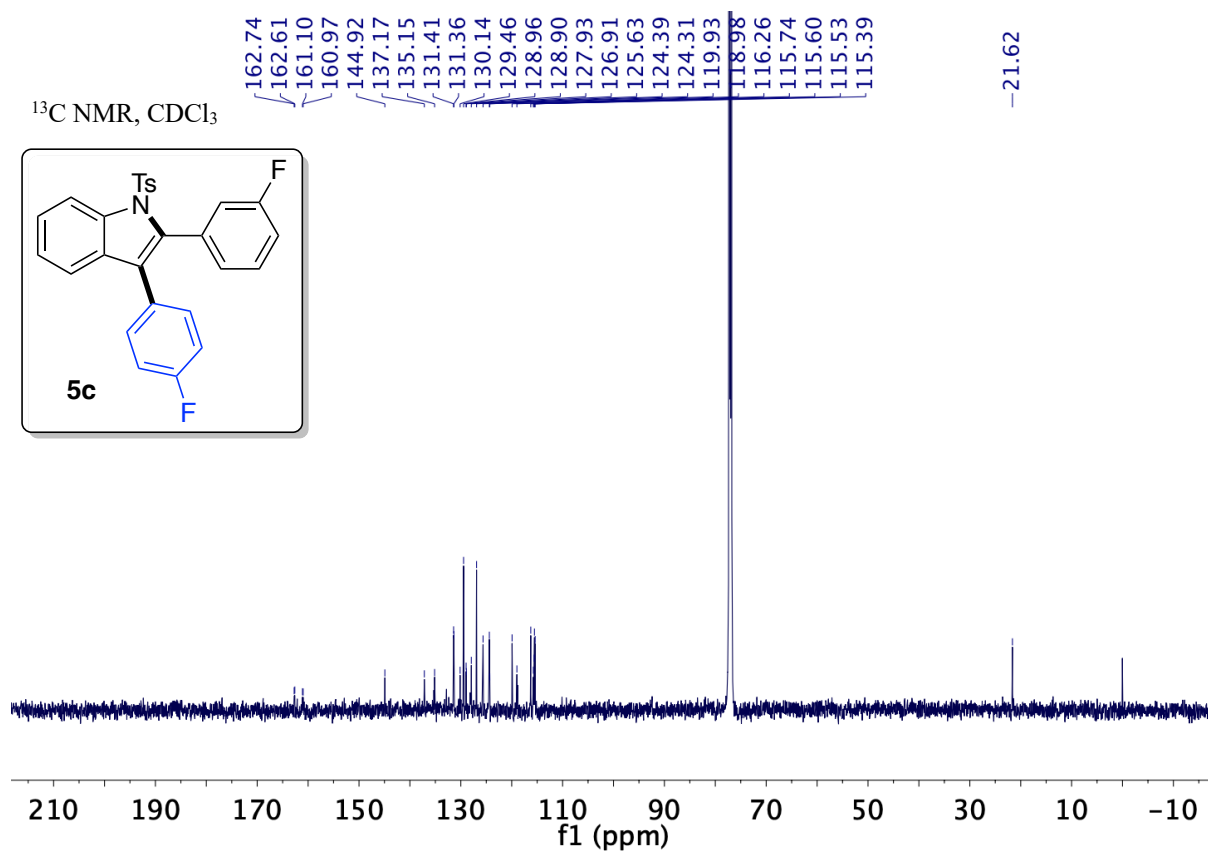
Supplementary Fig. 47. ¹³C NMR Spectrum for **5b**



Supplementary Fig. 48. ¹⁹F NMR Spectrum for **5b**

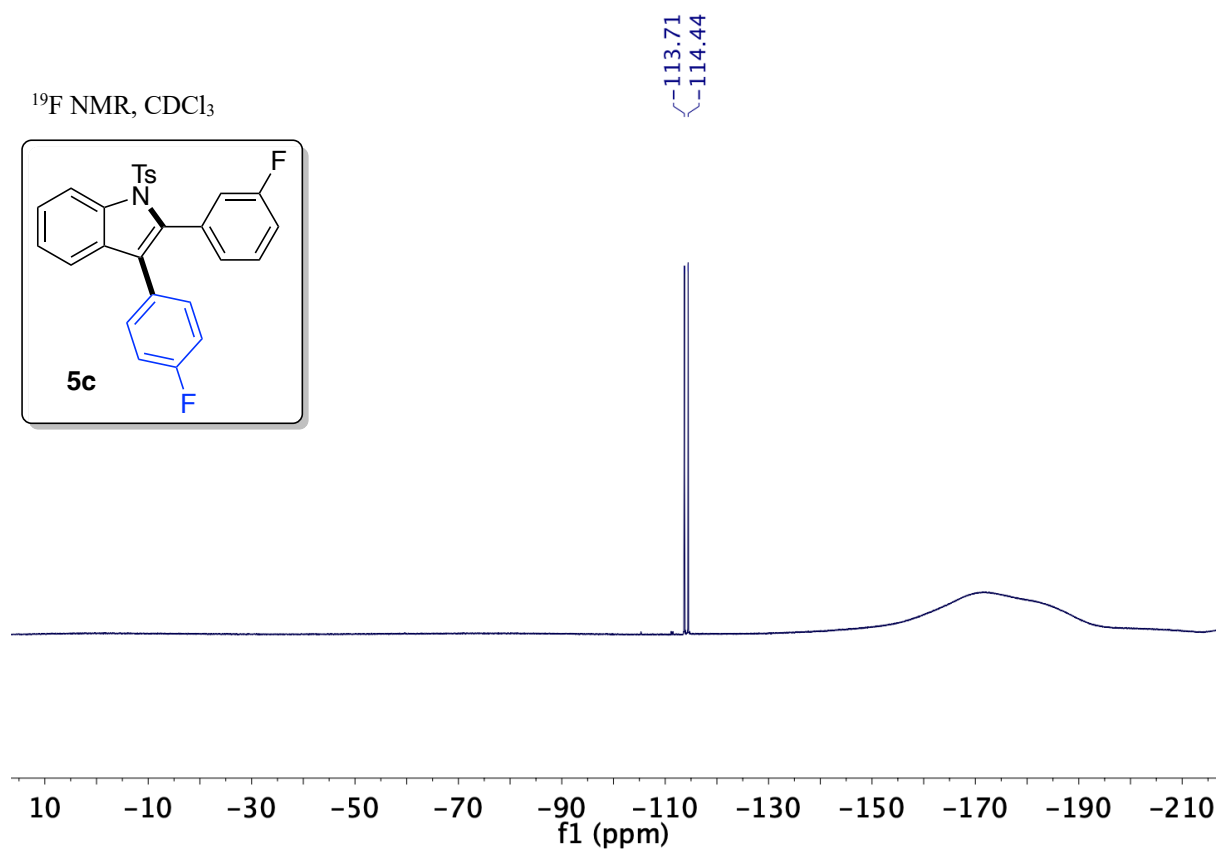
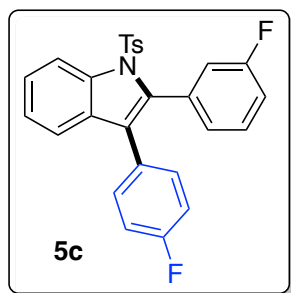


Supplementary Fig. 49. ¹H NMR Spectrum for **5c**



Supplementary Fig. 50. ¹³C NMR Spectrum for **5c**

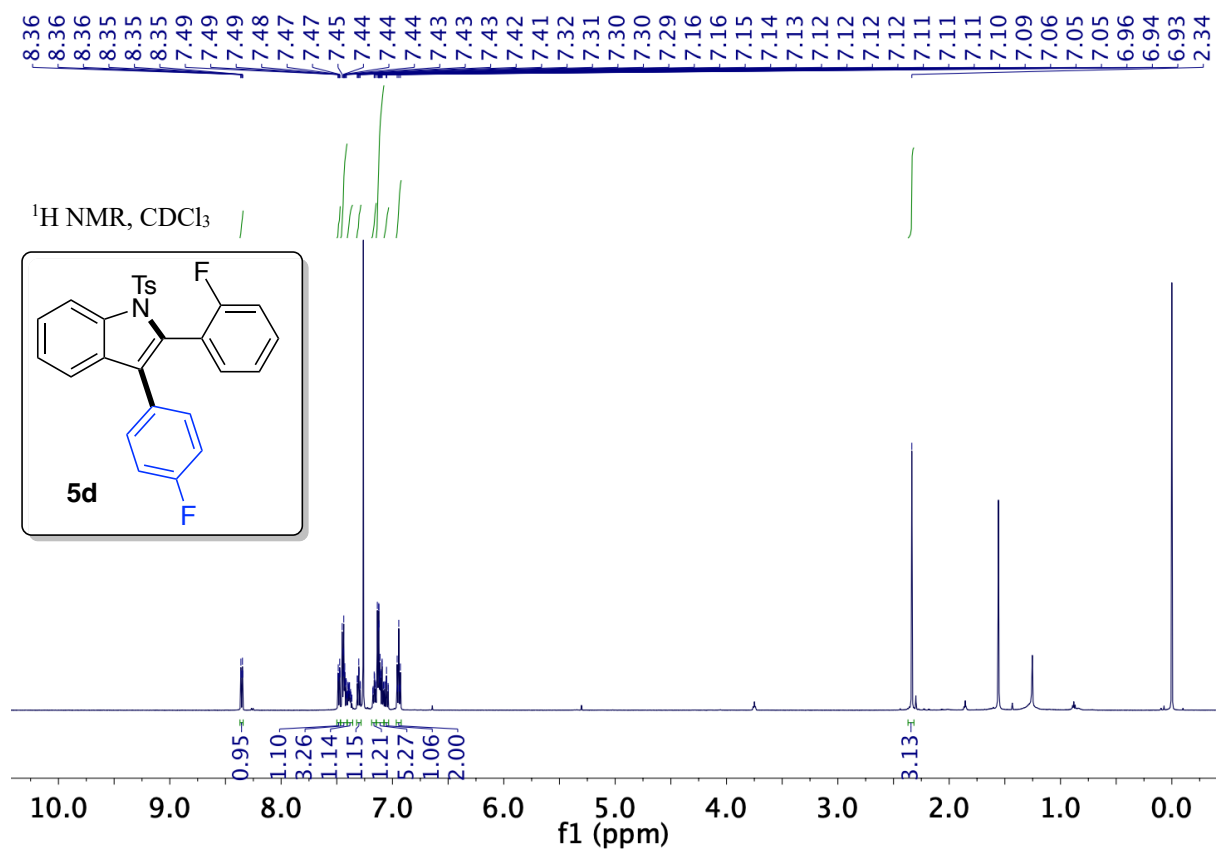
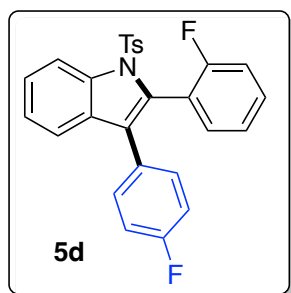
^{19}F NMR, CDCl_3



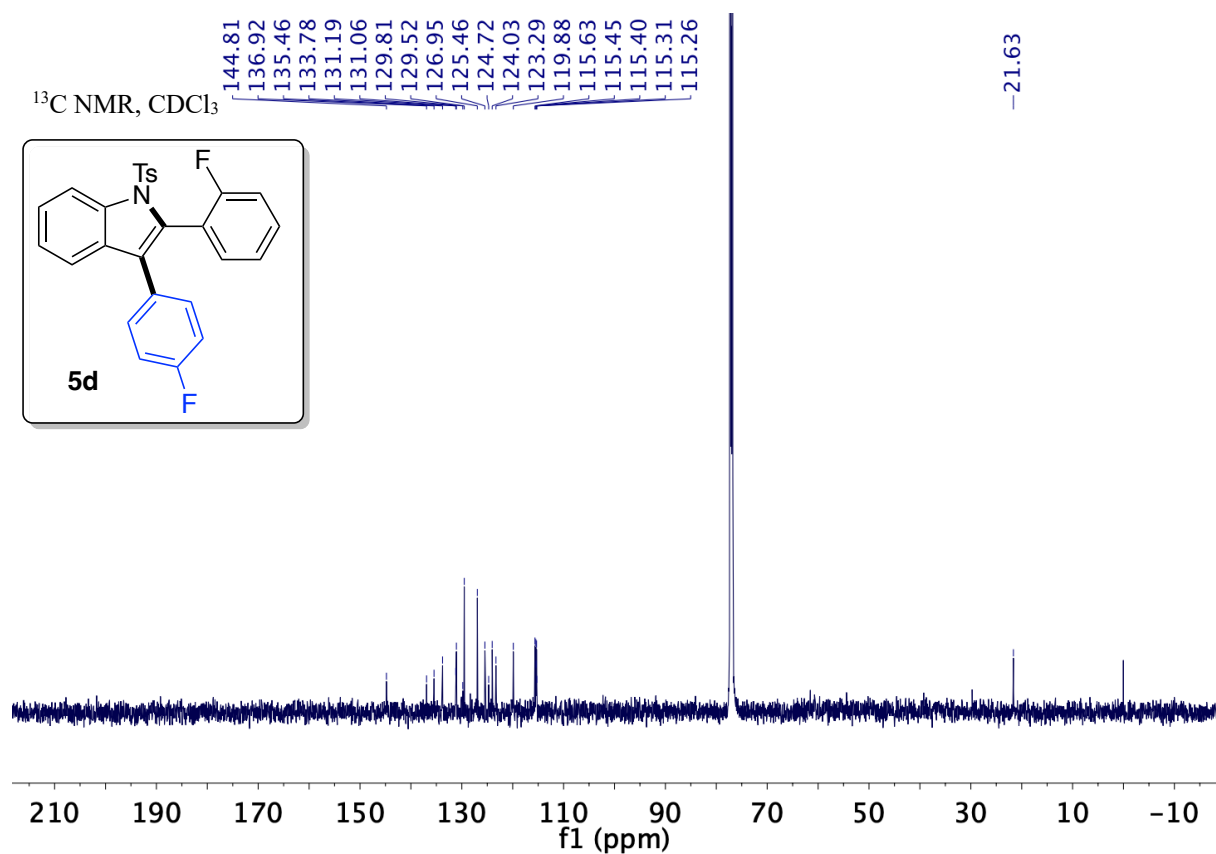
Supplementary Fig. 51. ^{19}F NMR Spectrum for **5c**

8.36 8.36 8.35 8.35 7.49 7.49 7.48 7.47 7.45 7.44 7.44 7.44 7.43 7.43 7.43 7.42 7.41 7.32 7.31 7.30 7.30 7.29 7.16 7.16 7.15 7.14 7.13 7.12 7.12 7.12 7.11 7.11 7.10 7.09 7.06 7.05 7.05 6.96 6.94 6.93 2.34

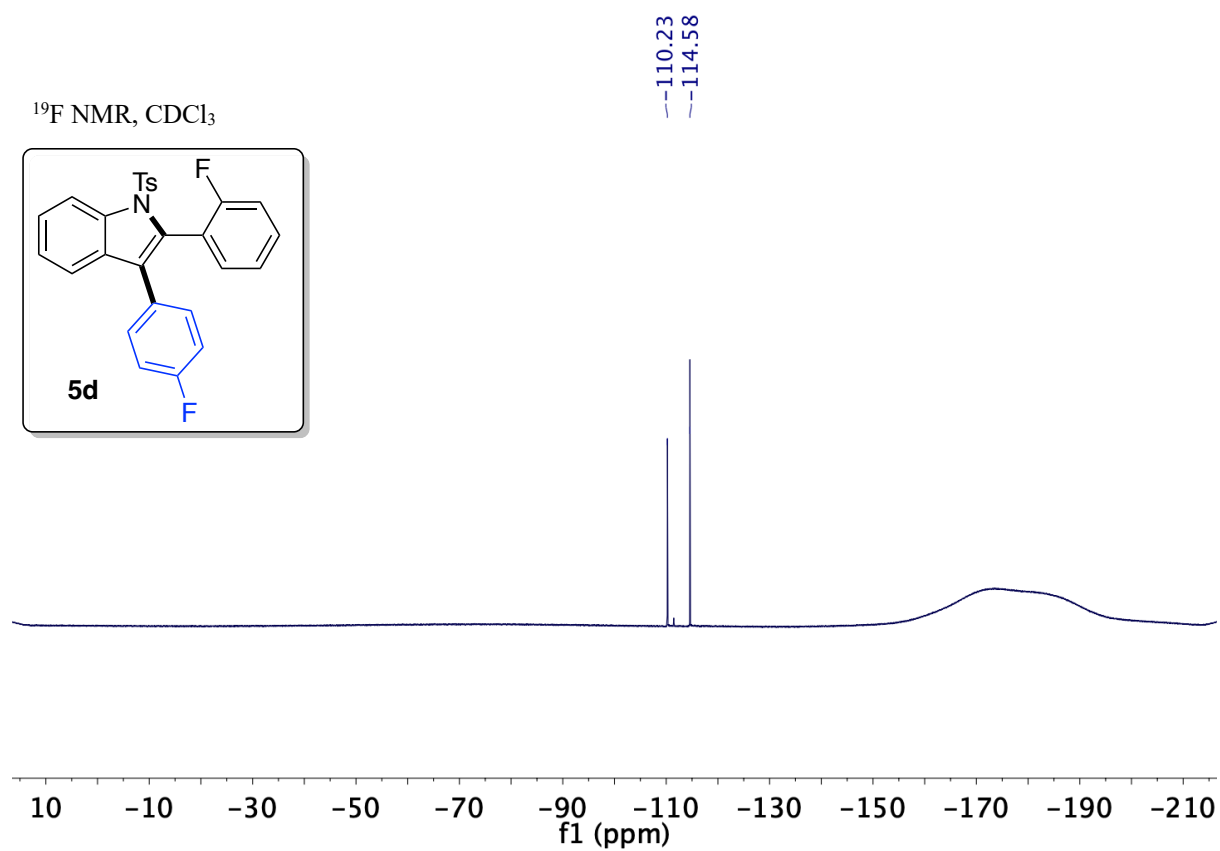
^1H NMR, CDCl_3



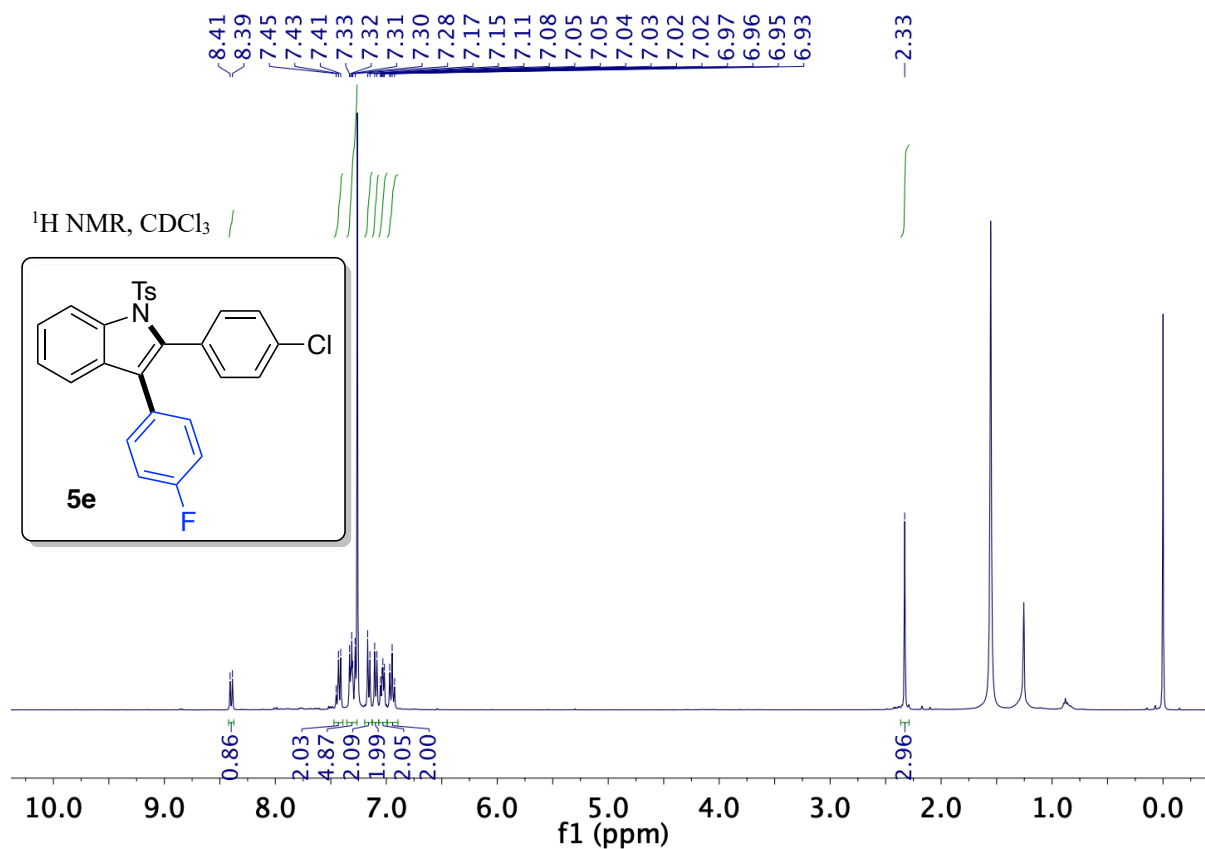
Supplementary Fig. 52. ^1H NMR Spectrum for **5d**



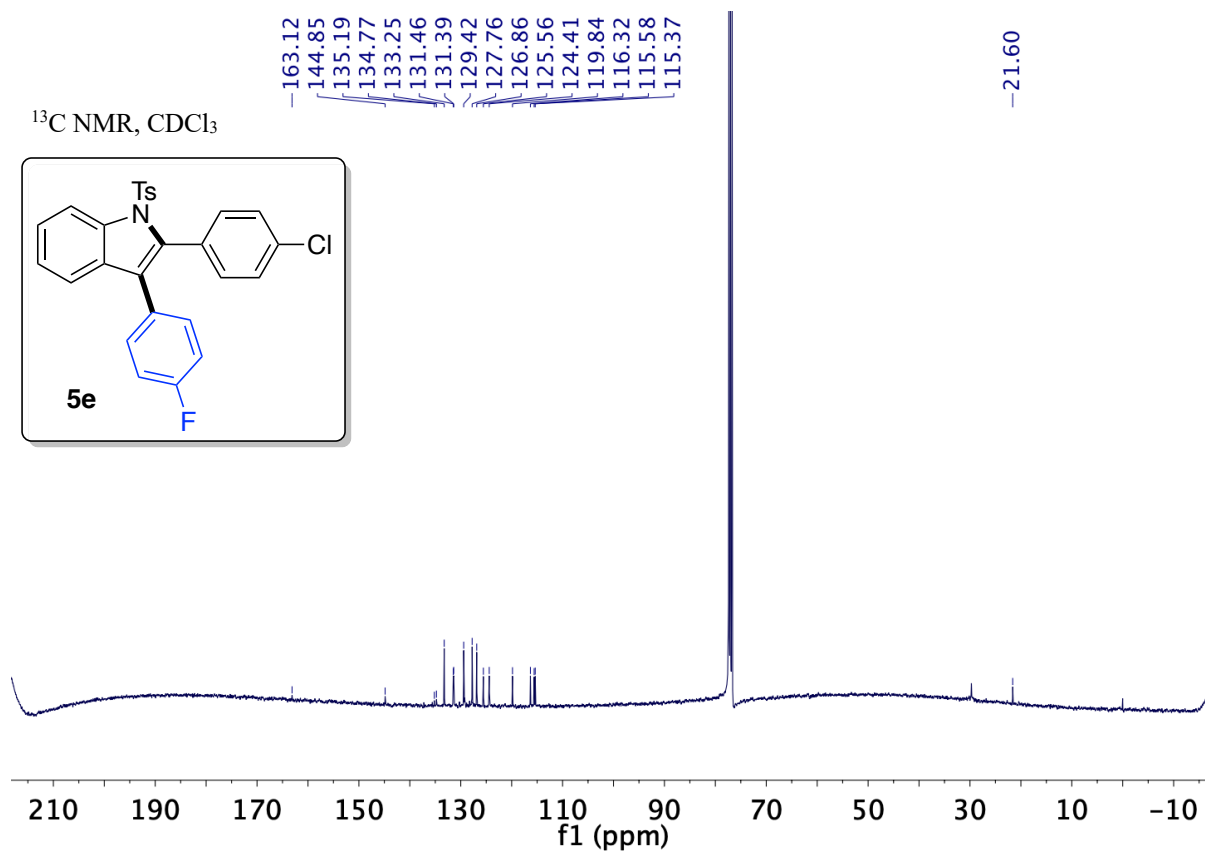
Supplementary Fig. 53. ¹³C NMR Spectrum for **5d**



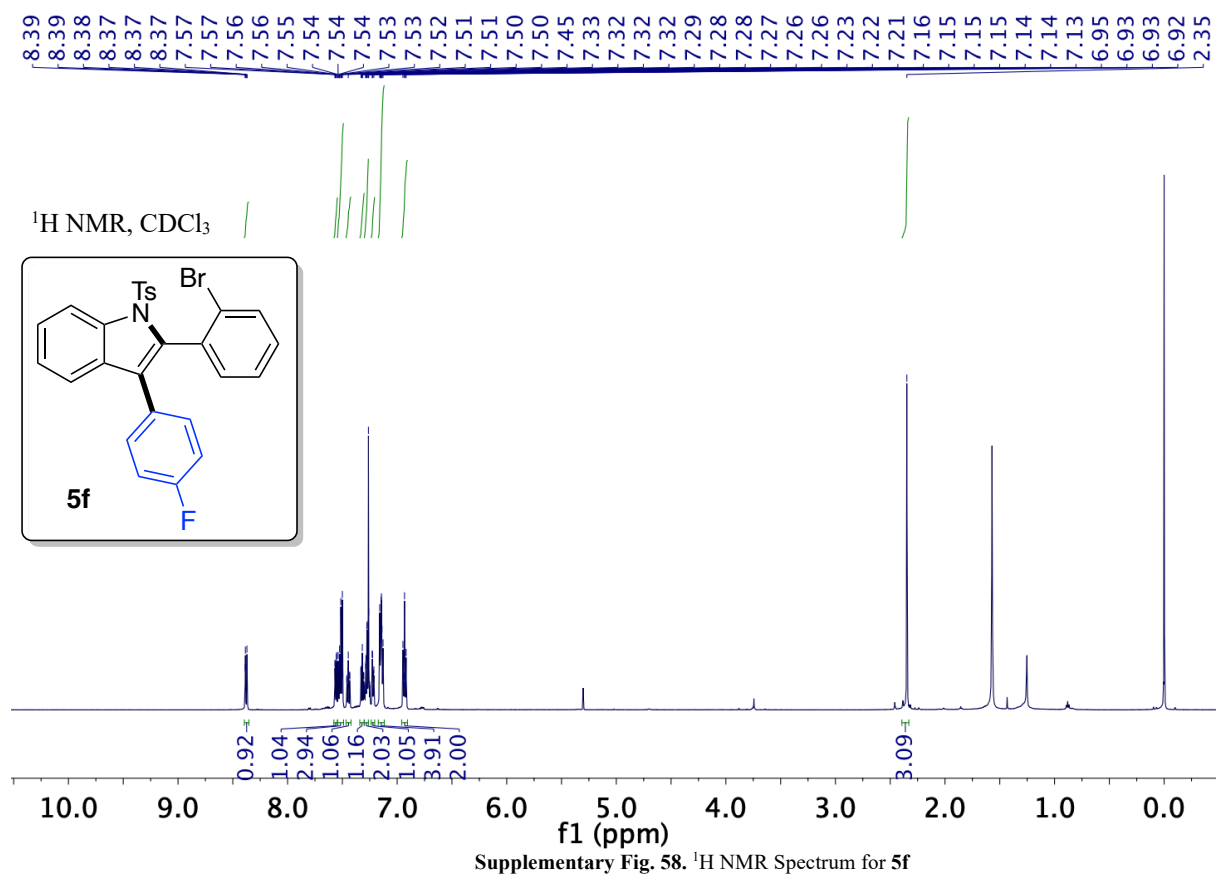
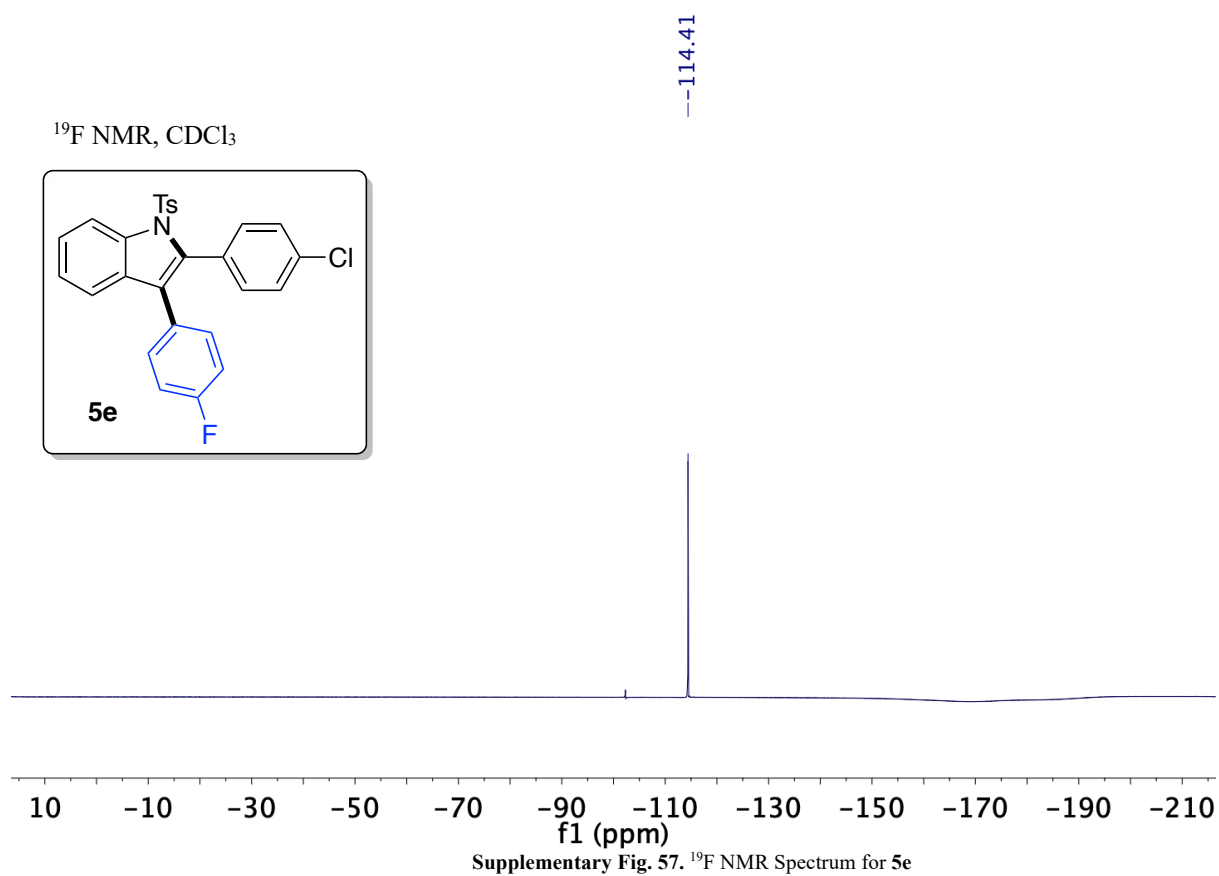
Supplementary Fig. 54. ¹⁹F NMR Spectrum for **5d**

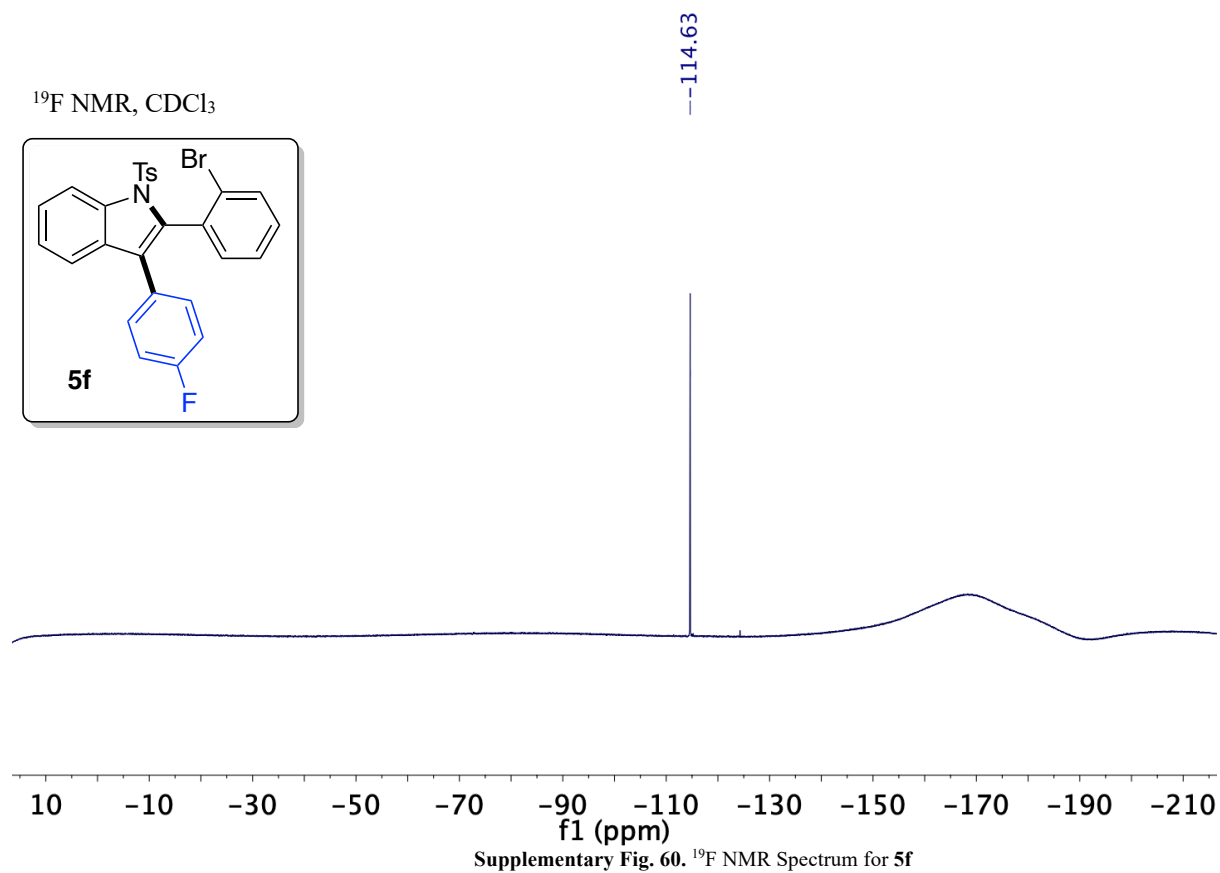
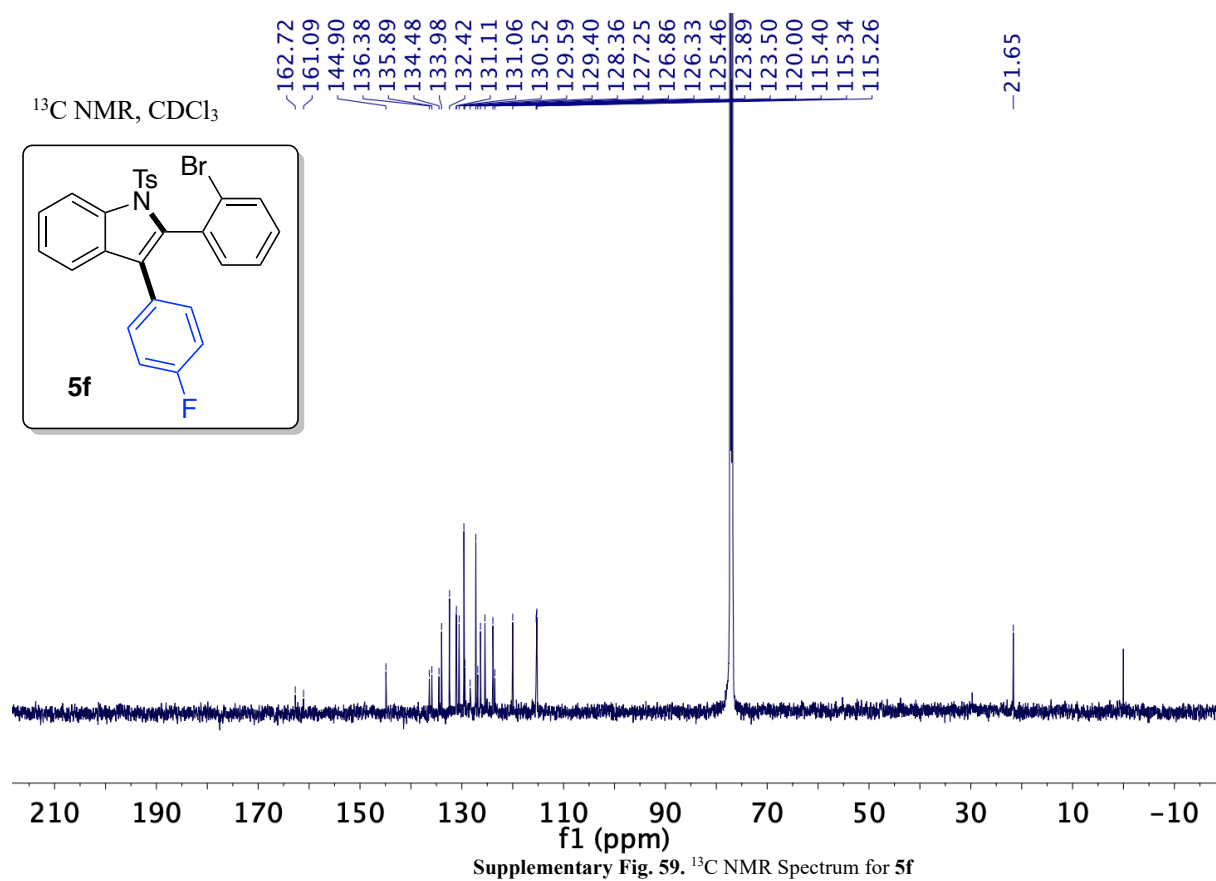


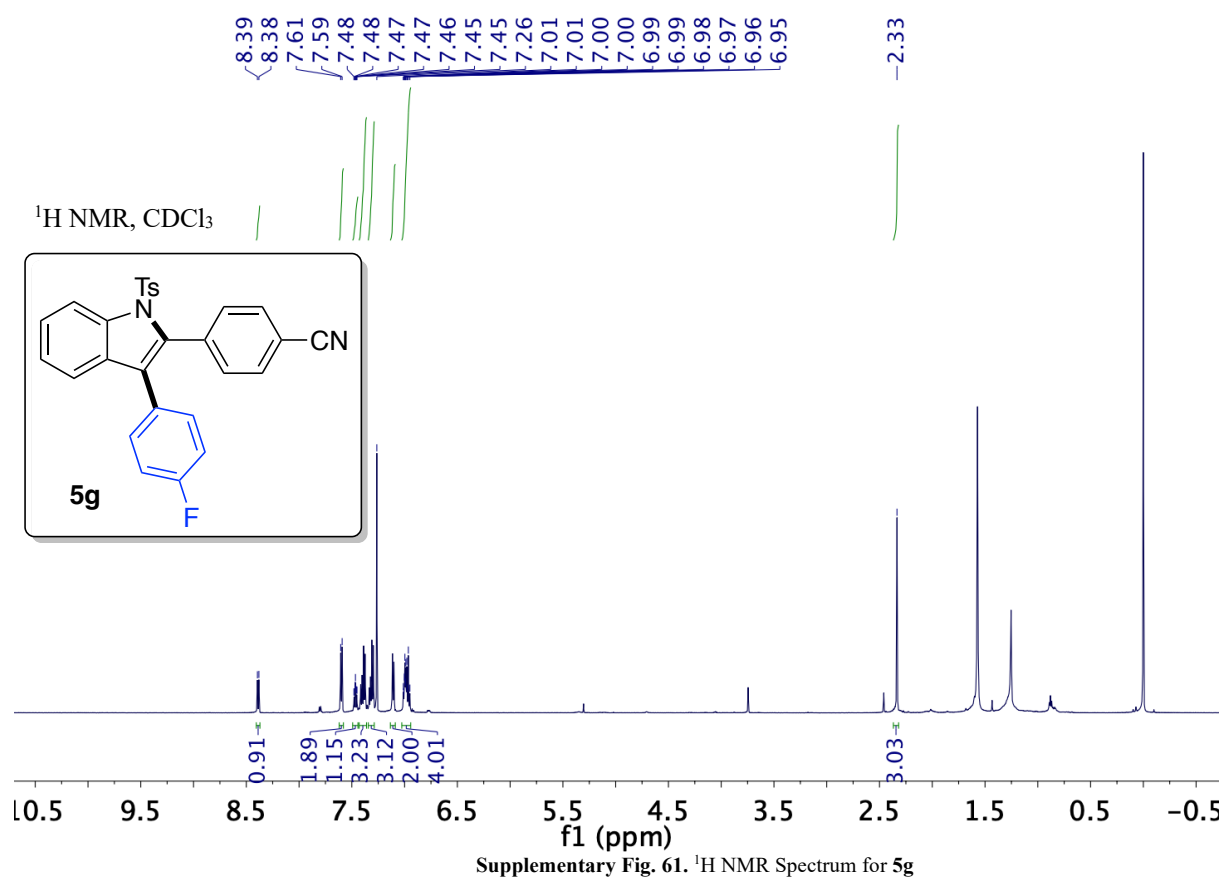
Supplementary Fig. 55. ¹H NMR Spectrum for **5e**



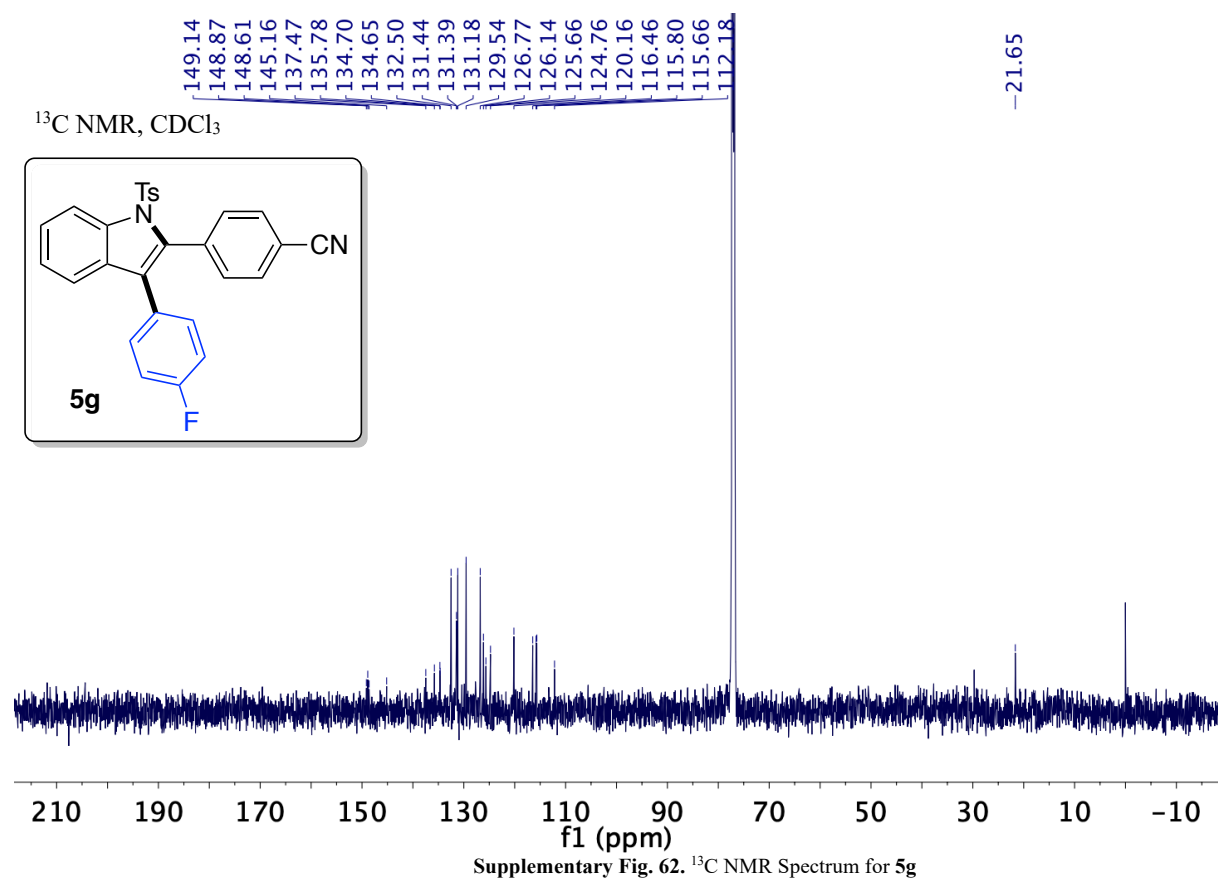
Supplementary Fig. 56. ¹³C NMR Spectrum for **5e**



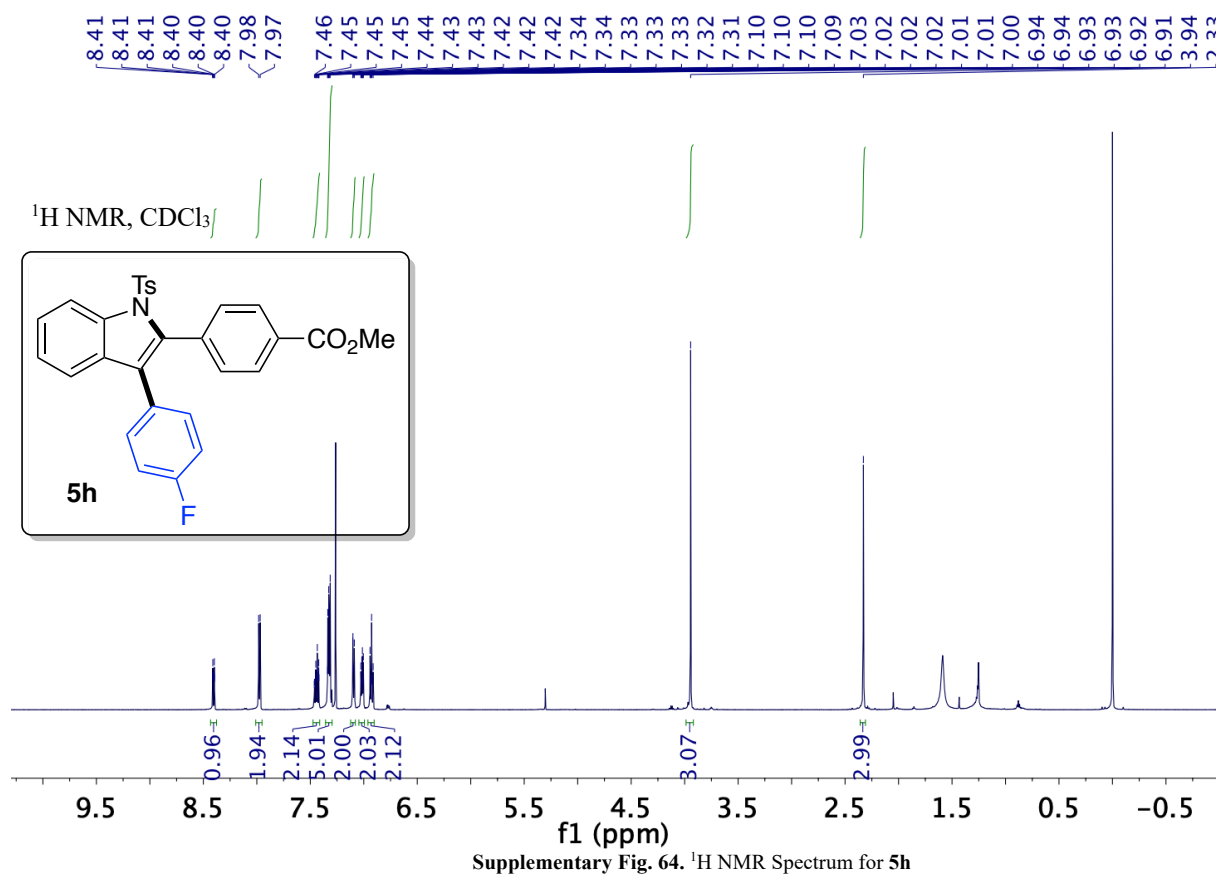
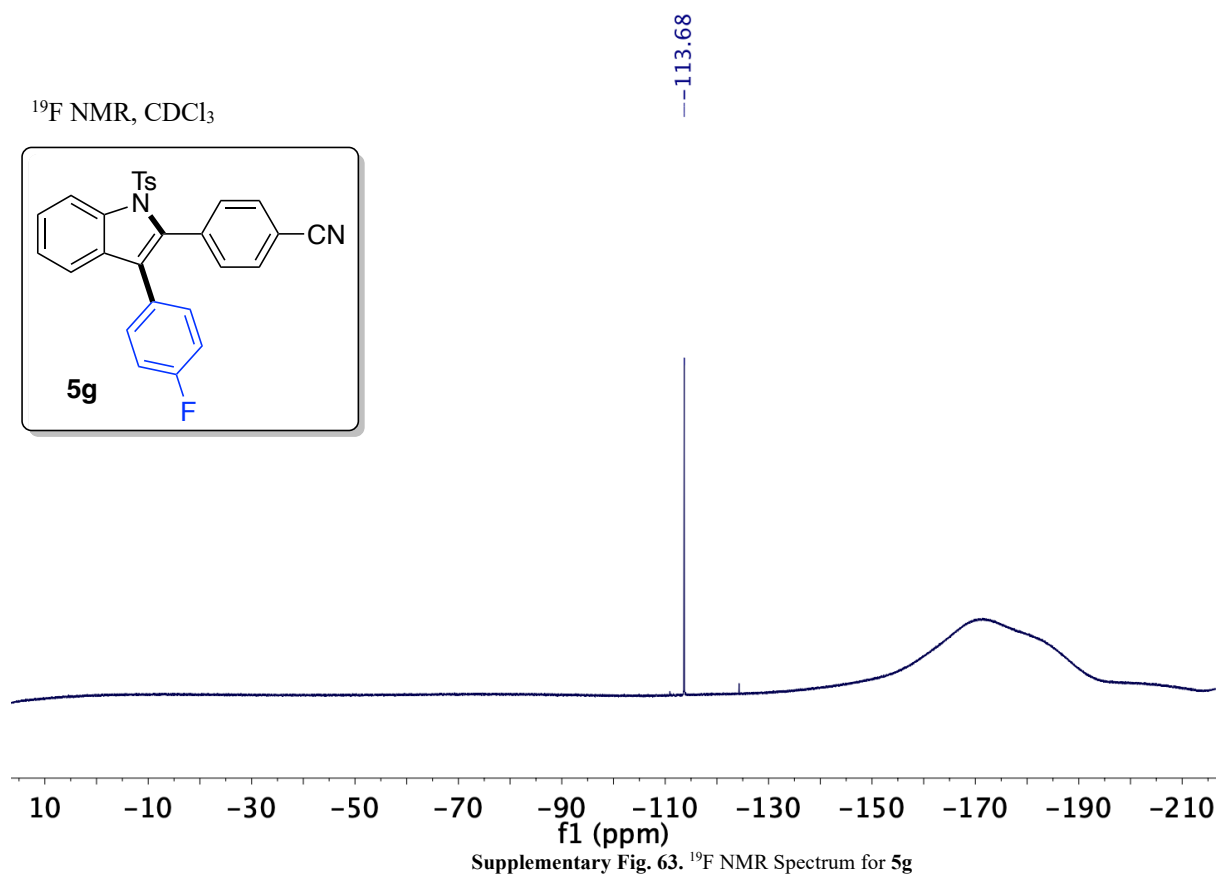


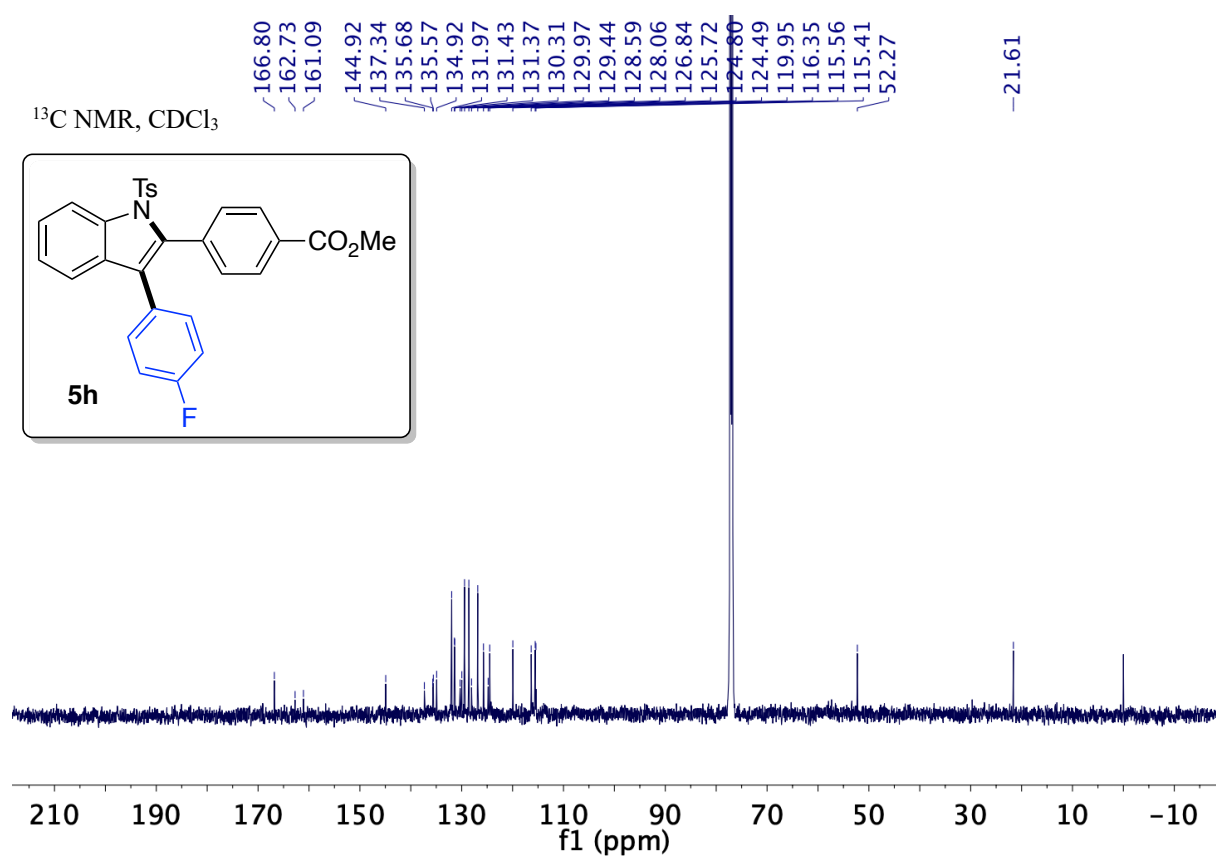


Supplementary Fig. 61. ¹H NMR Spectrum for **5g**

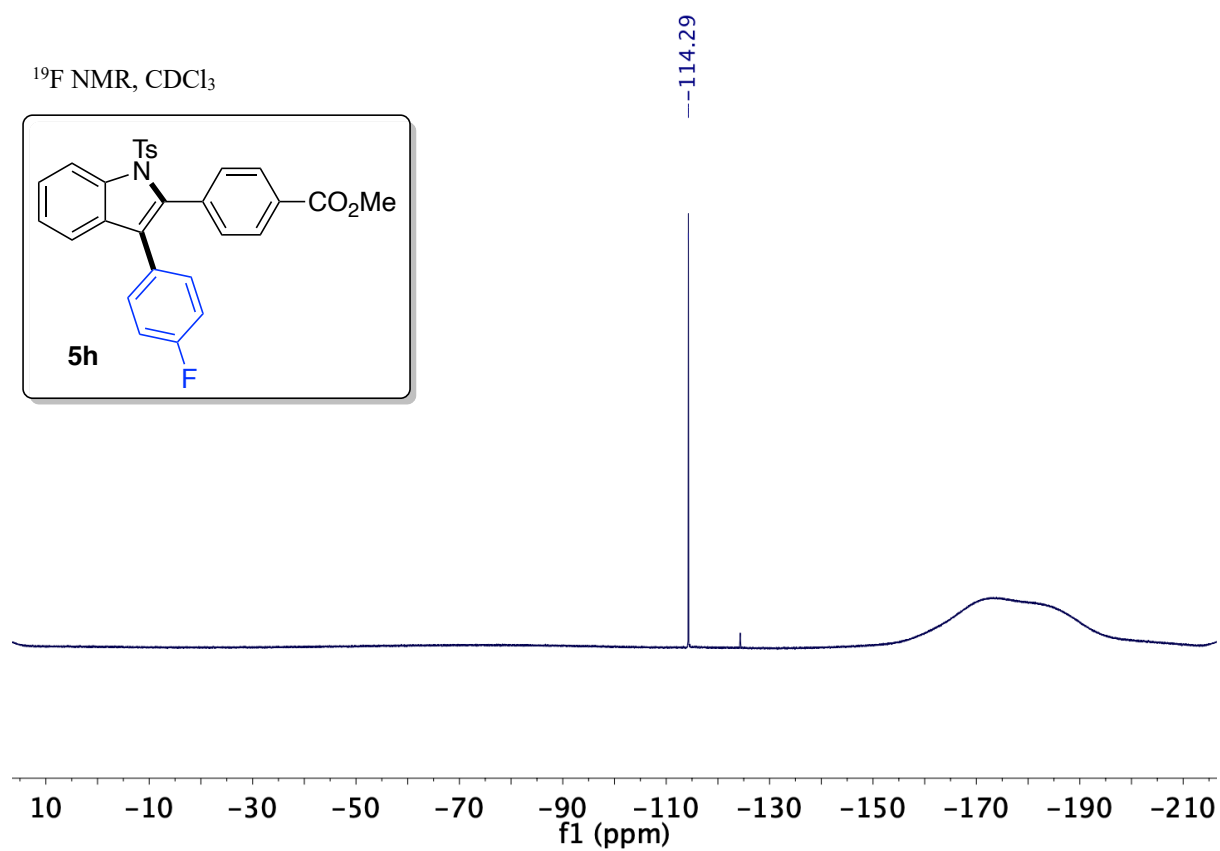


Supplementary Fig. 62. ¹³C NMR Spectrum for **5g**

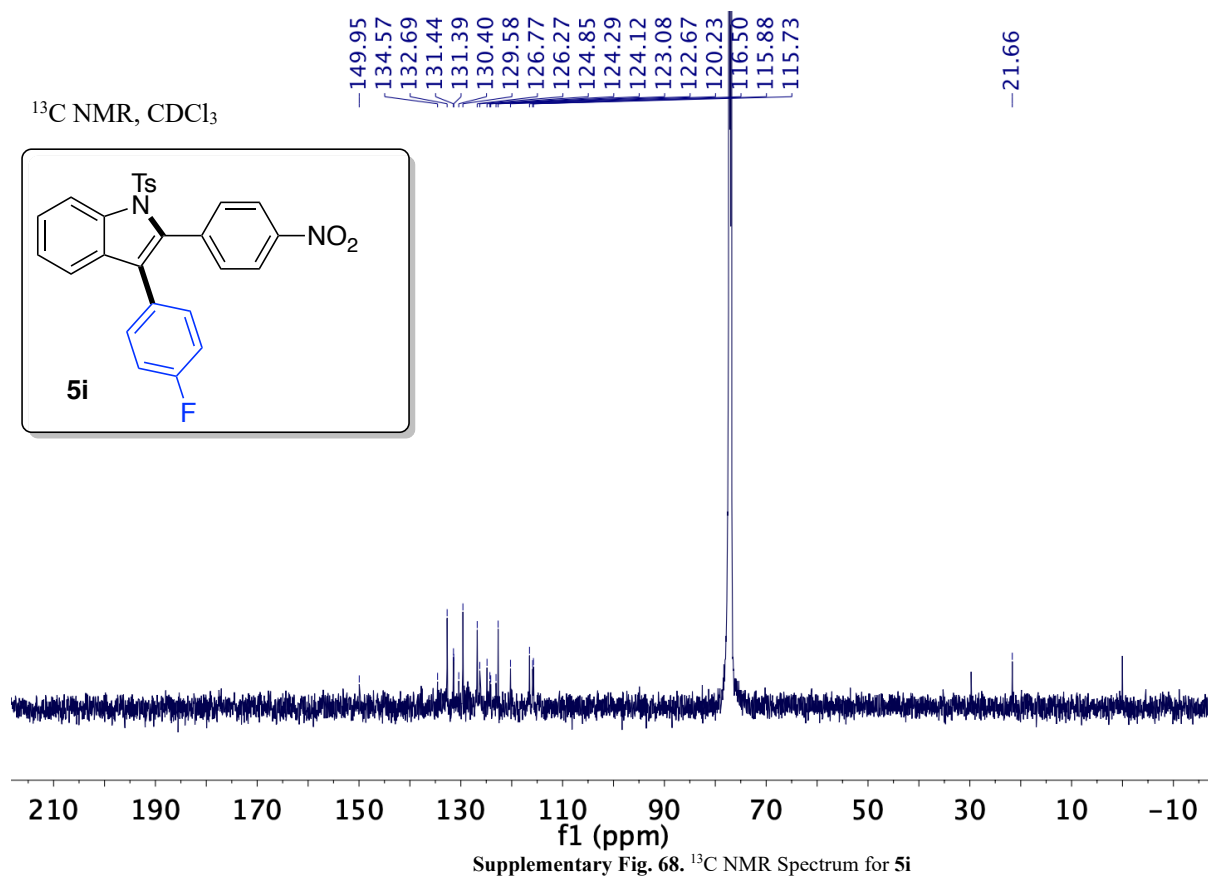
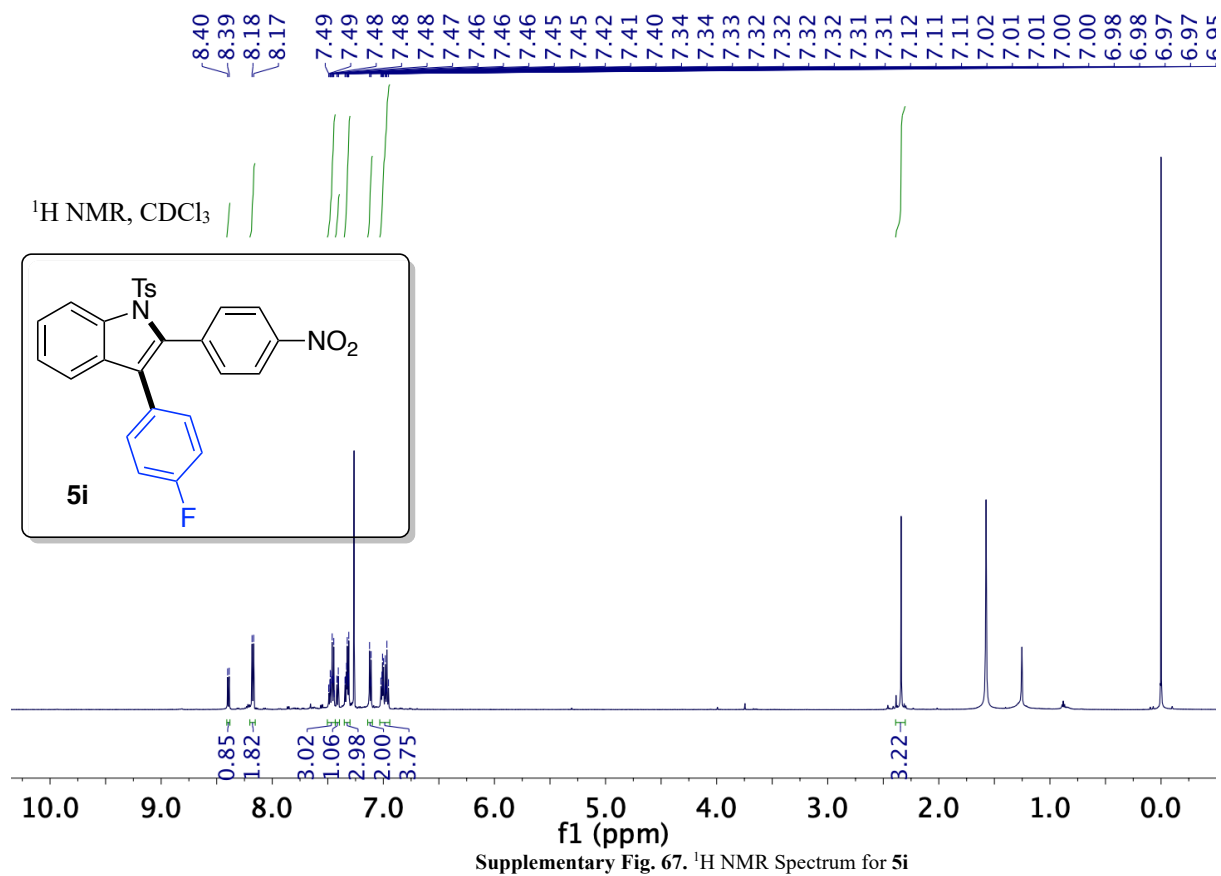




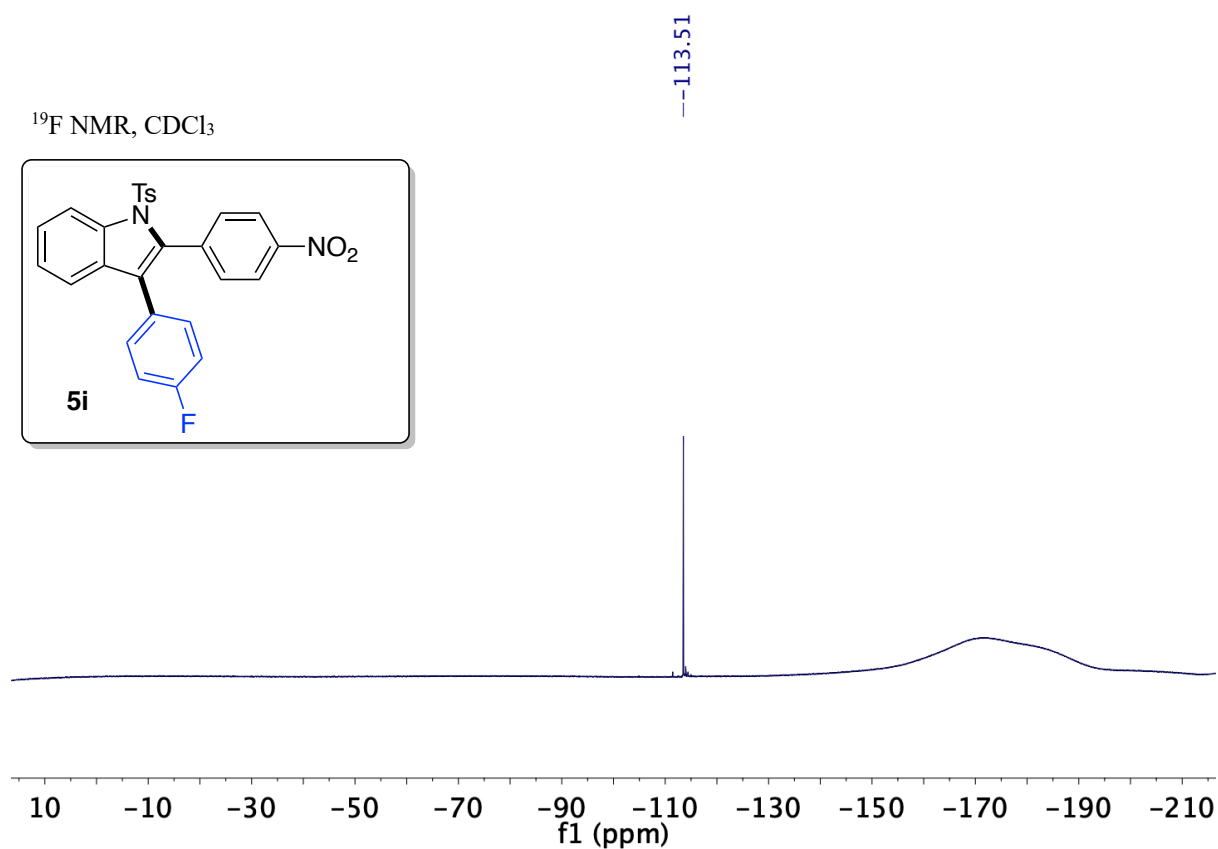
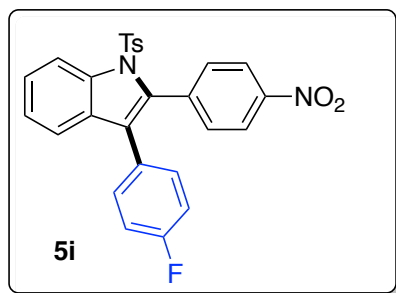
Supplementary Fig. 65. ¹³C NMR Spectrum for **5h**



Supplementary Fig. 66. ¹⁹F NMR Spectrum for **5h**



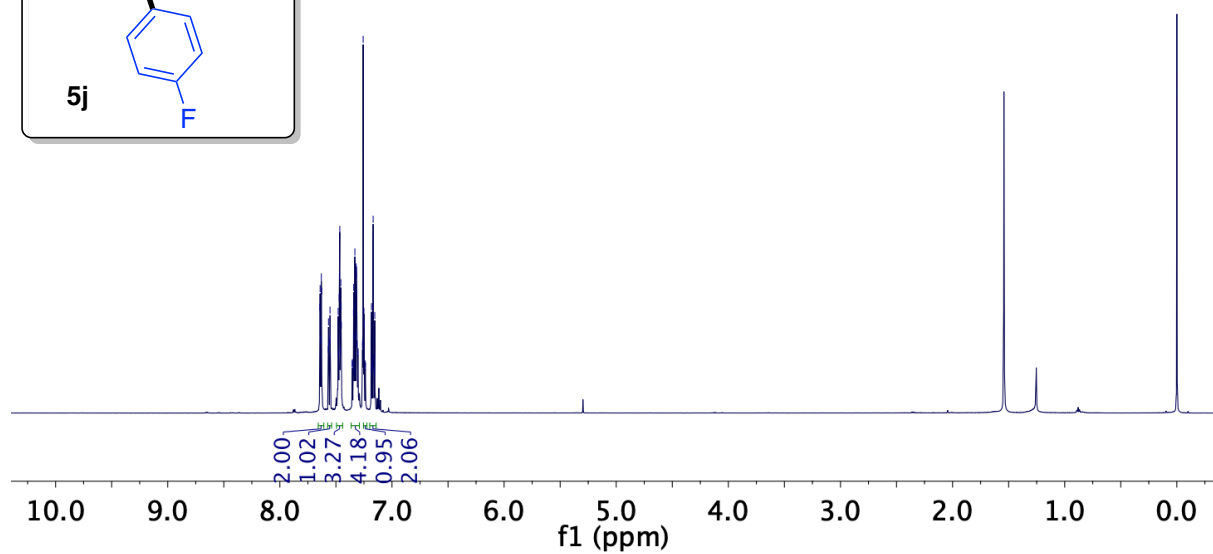
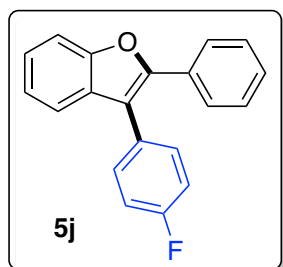
^{19}F NMR, CDCl_3



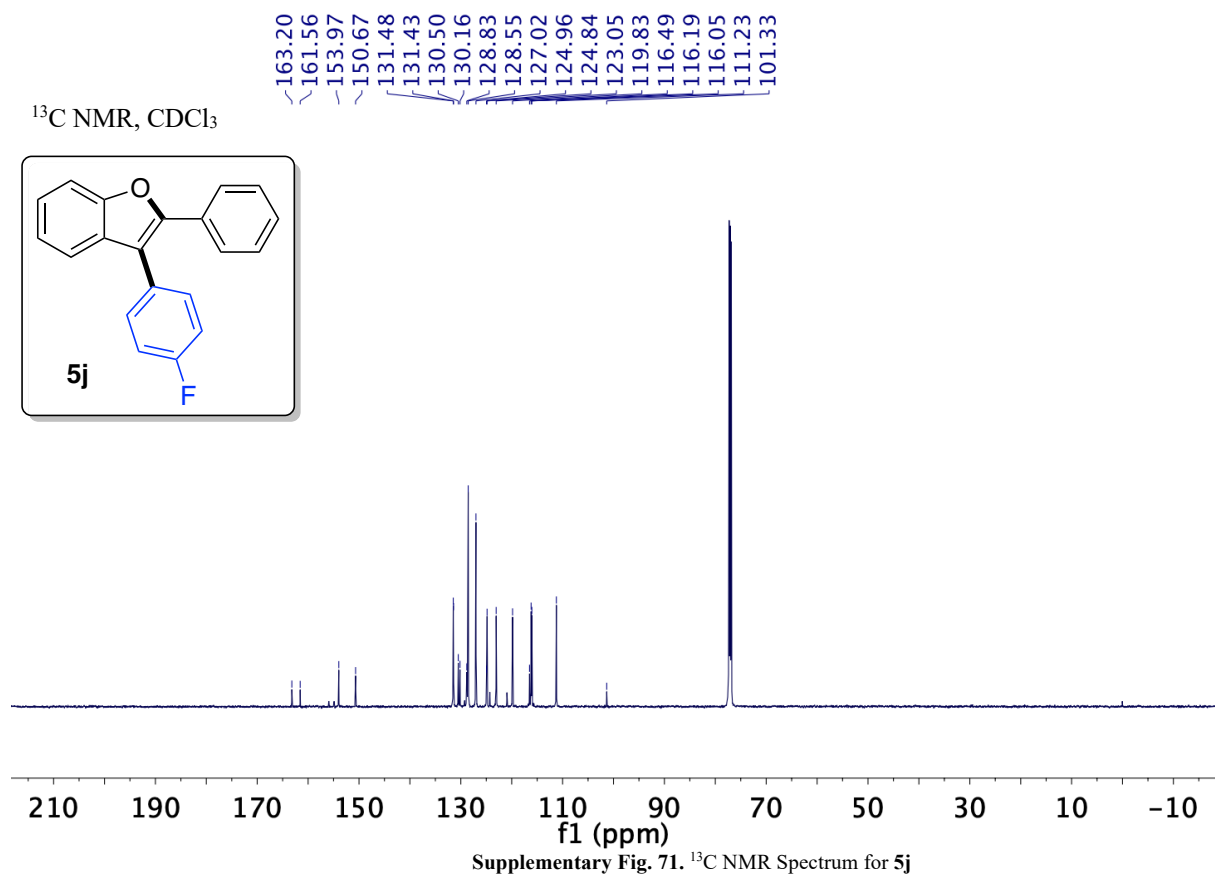
Supplementary Fig. 69. ^{19}F NMR Spectrum for **5i**

7.64
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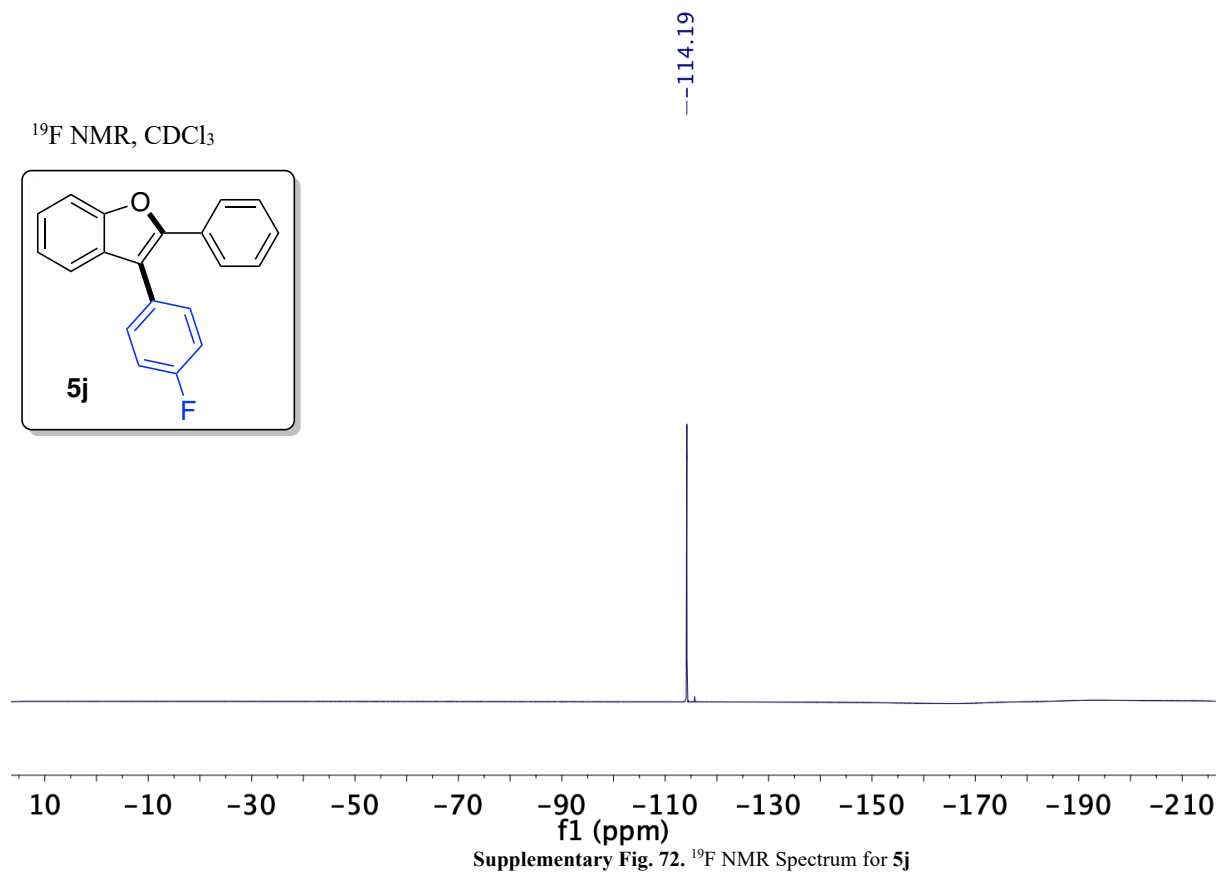
^1H NMR, CDCl_3



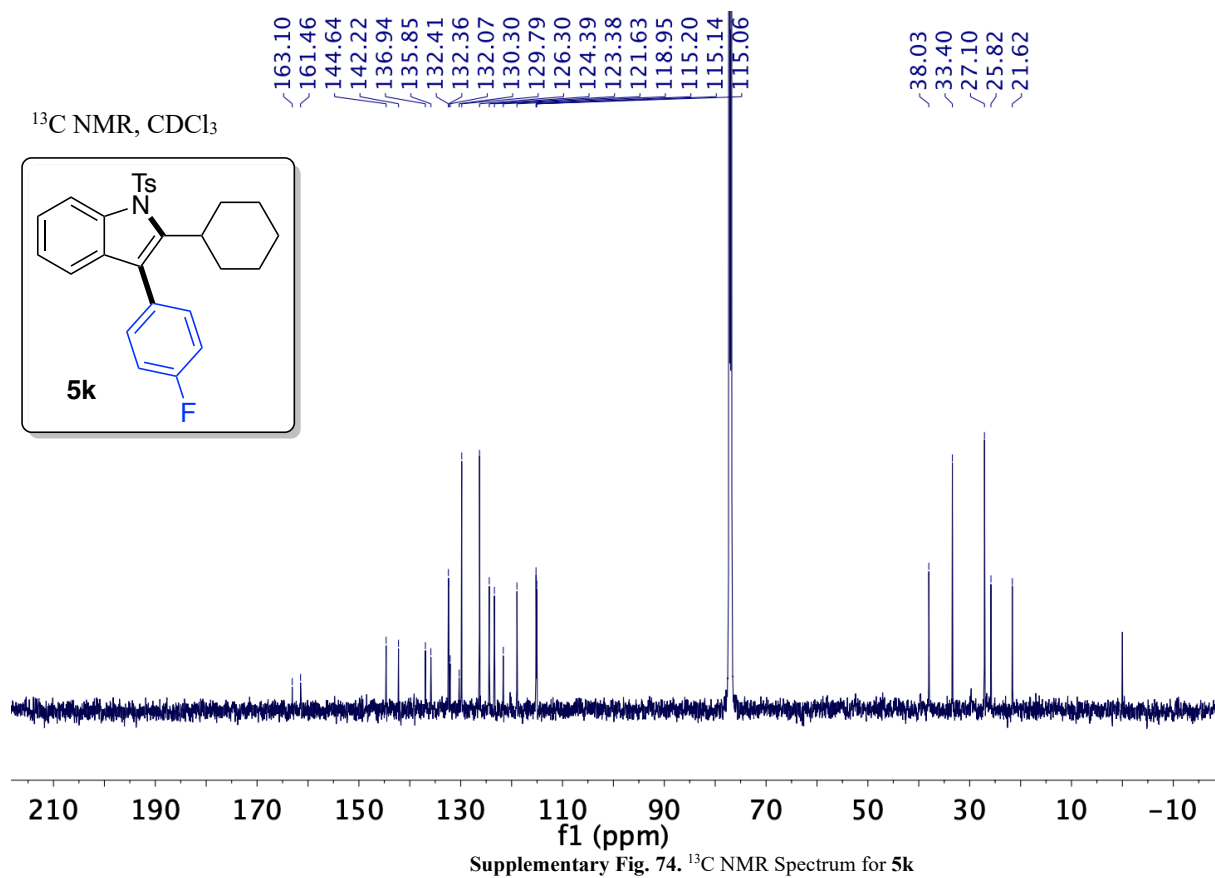
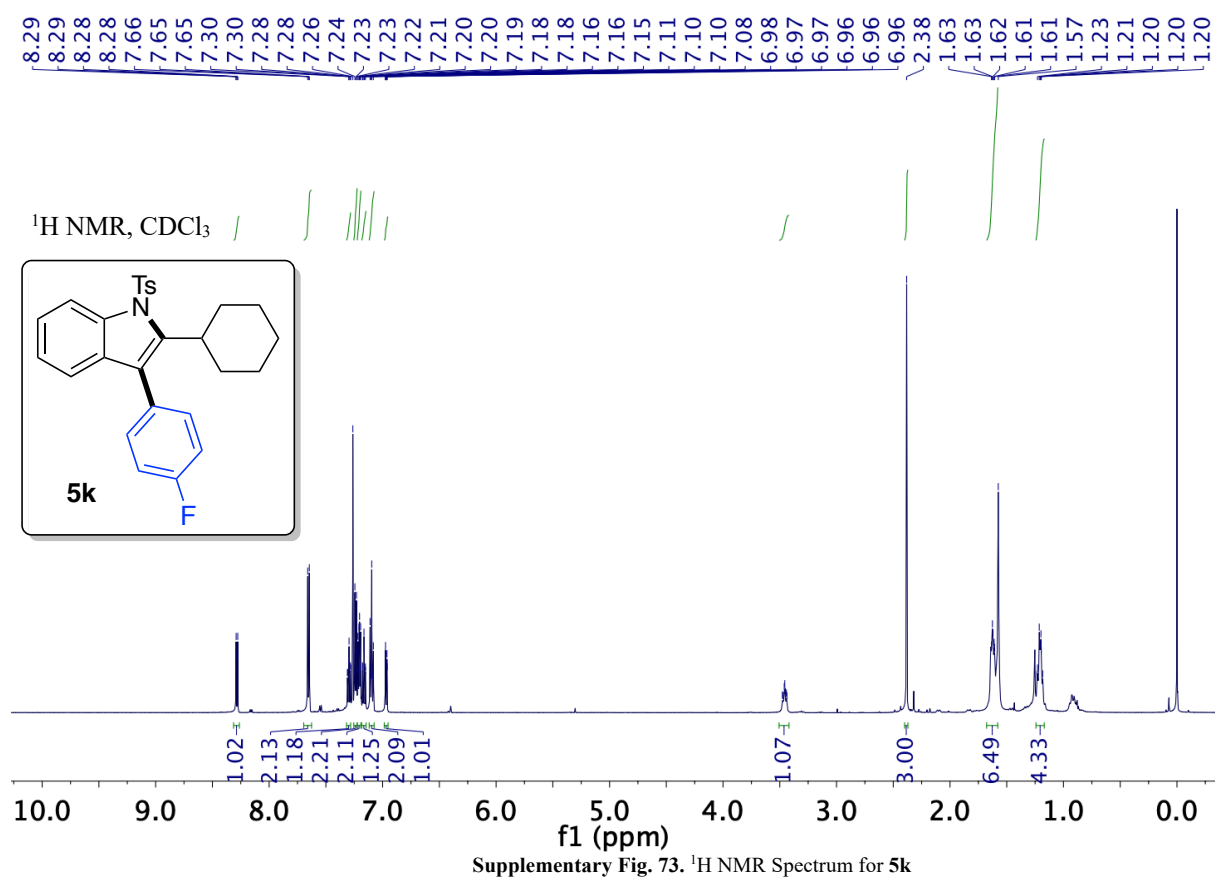
Supplementary Fig. 70. ^1H NMR Spectrum for **5j**

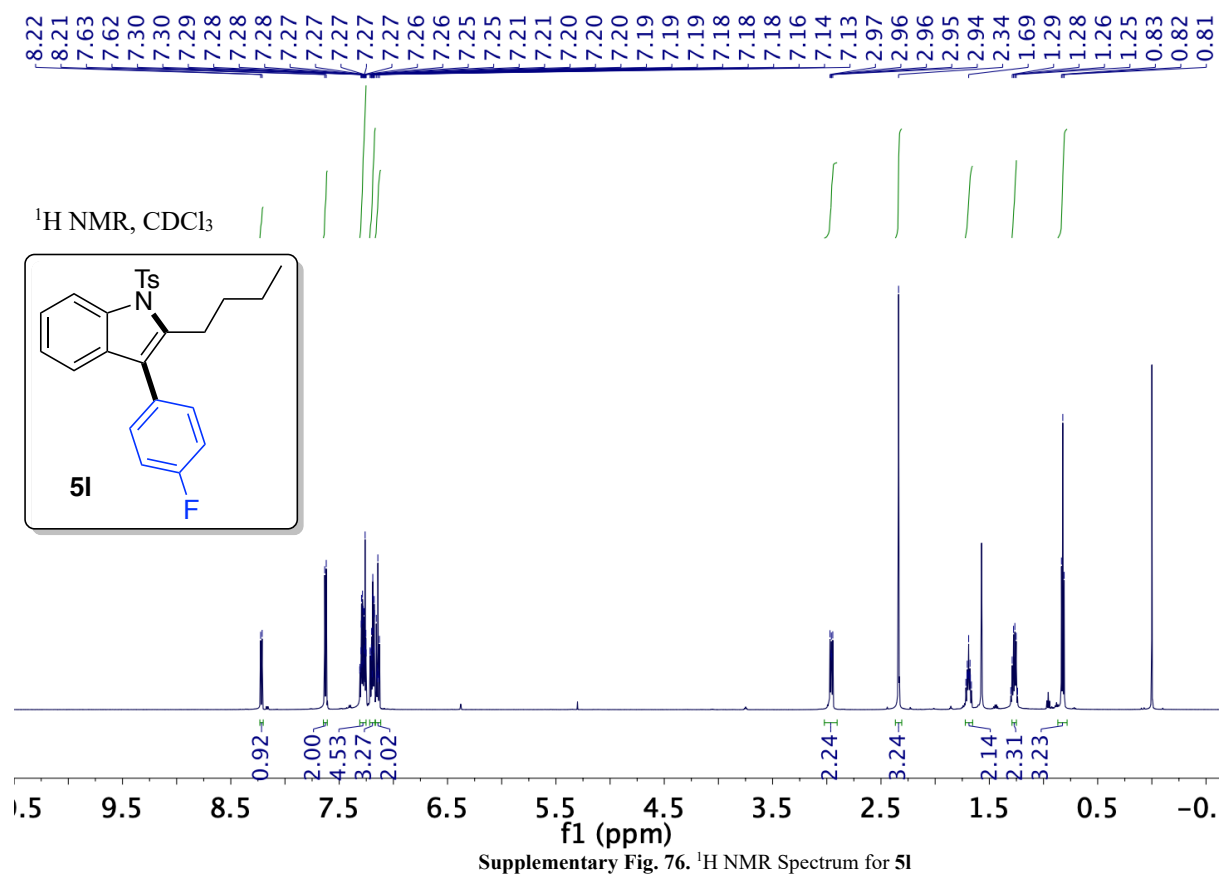
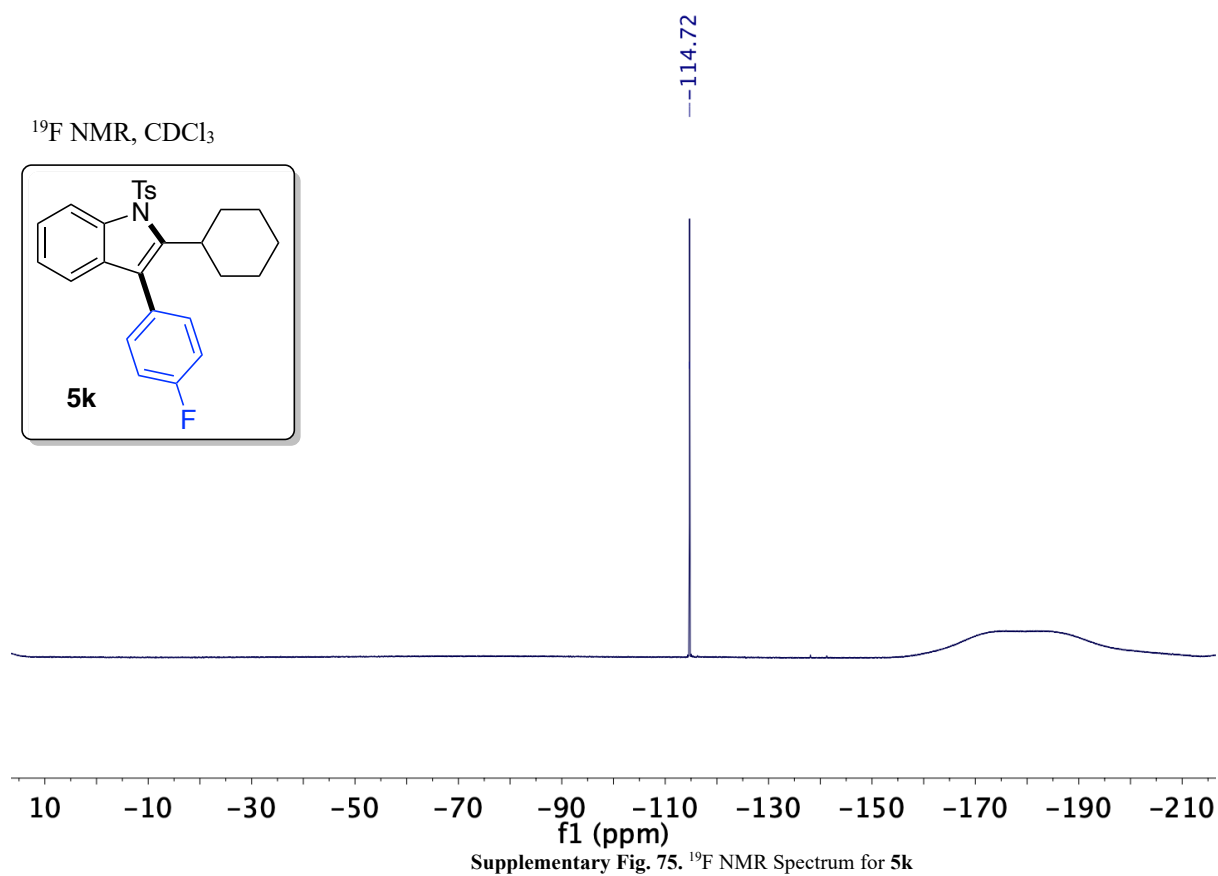


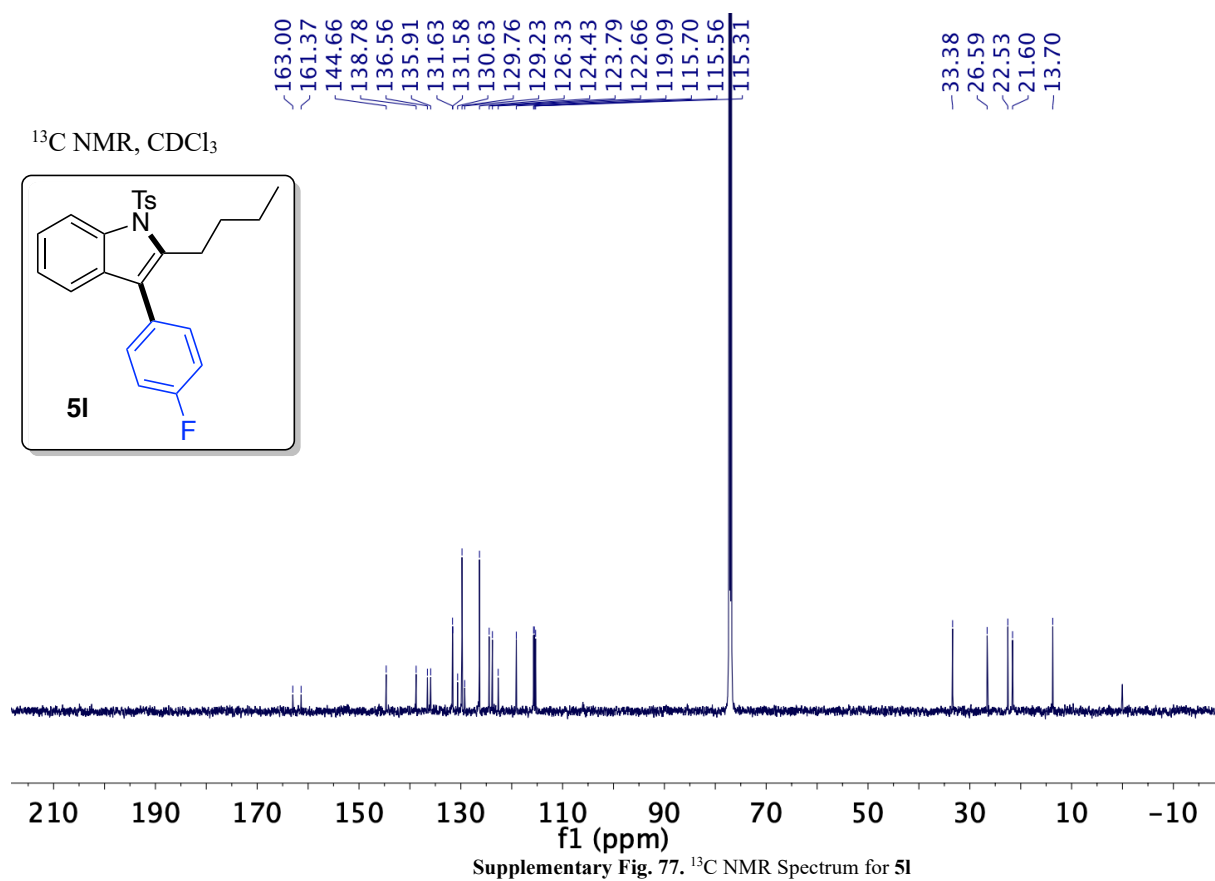
Supplementary Fig. 71. ¹³C NMR Spectrum for **5j**



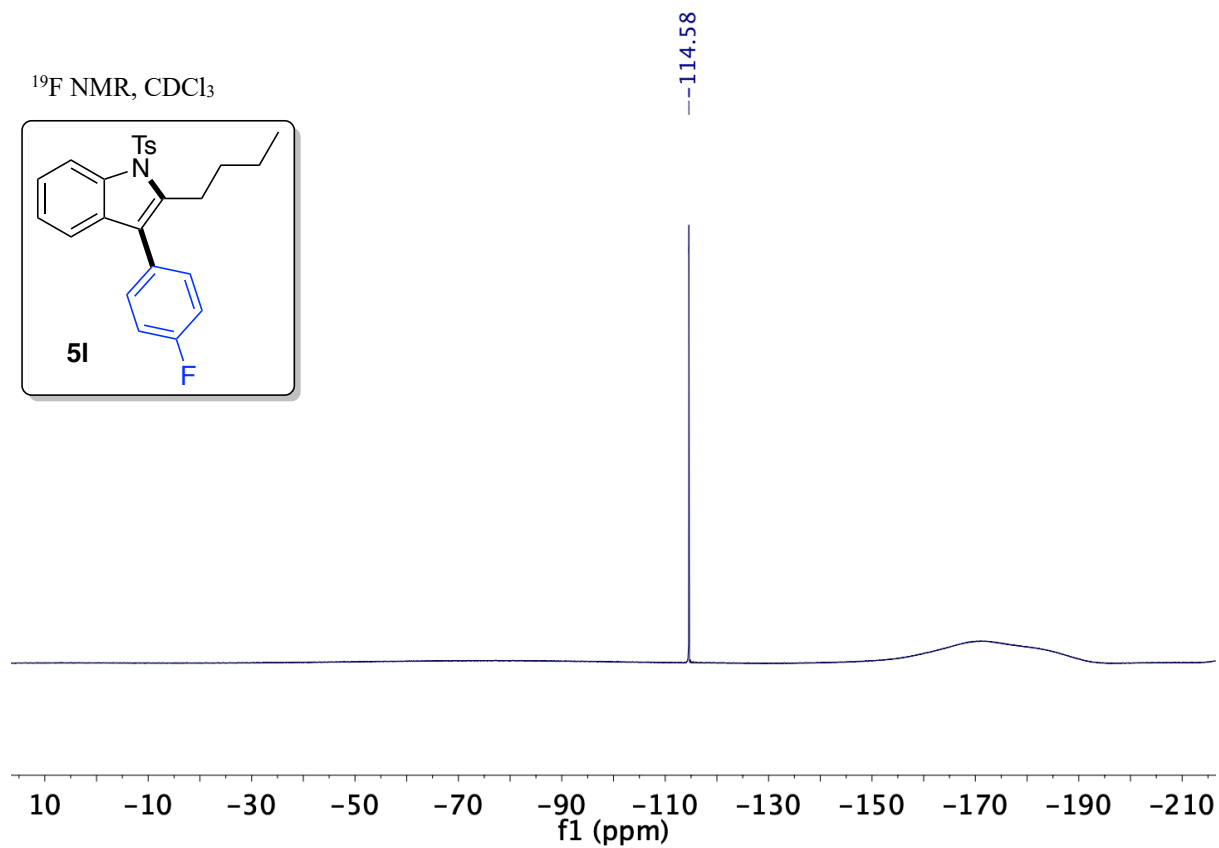
Supplementary Fig. 72. ¹⁹F NMR Spectrum for **5j**



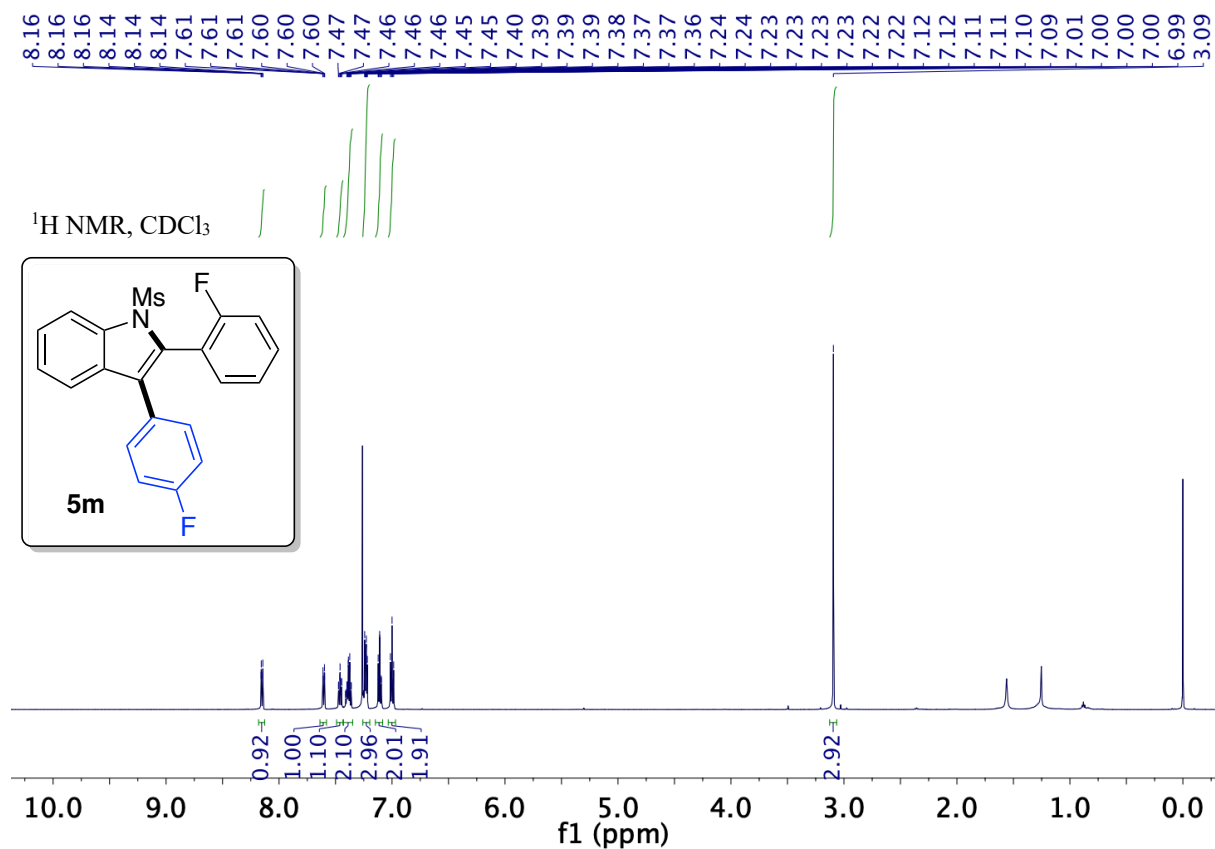




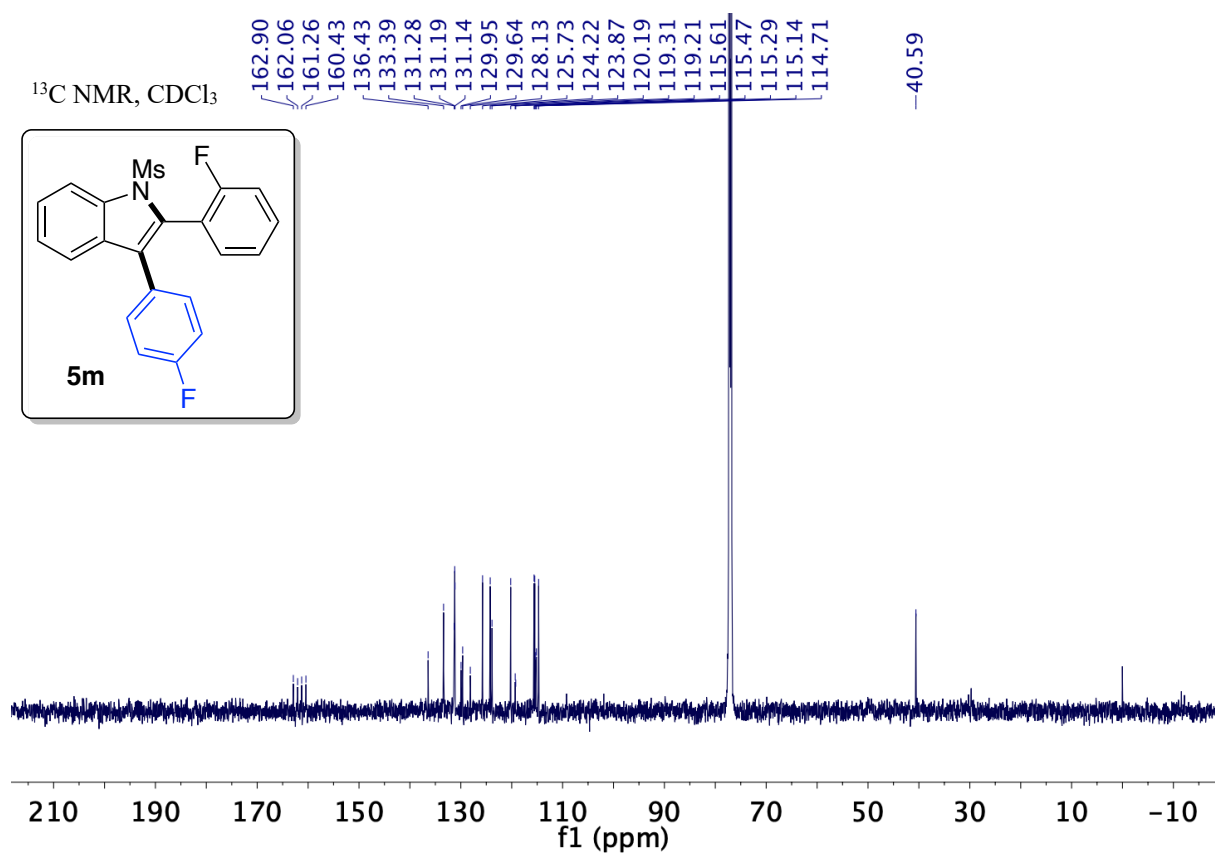
Supplementary Fig. 77. ¹³C NMR Spectrum for **5I**



Supplementary Fig. 78. ¹⁹F NMR Spectrum for **5I**

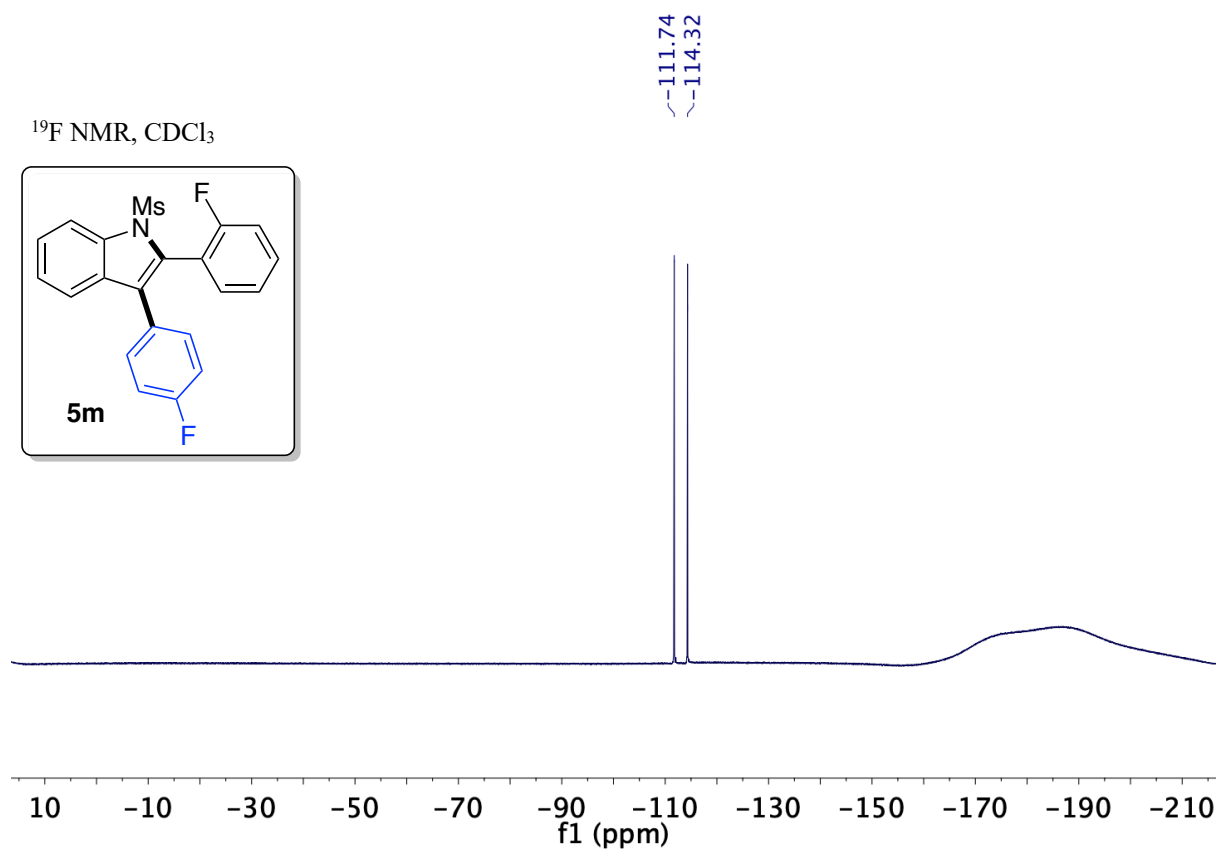
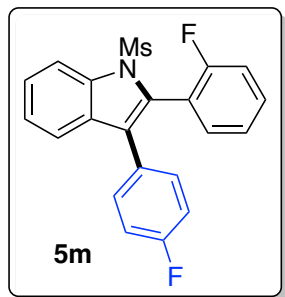


Supplementary Fig. 79. ¹H NMR Spectrum for **5m**

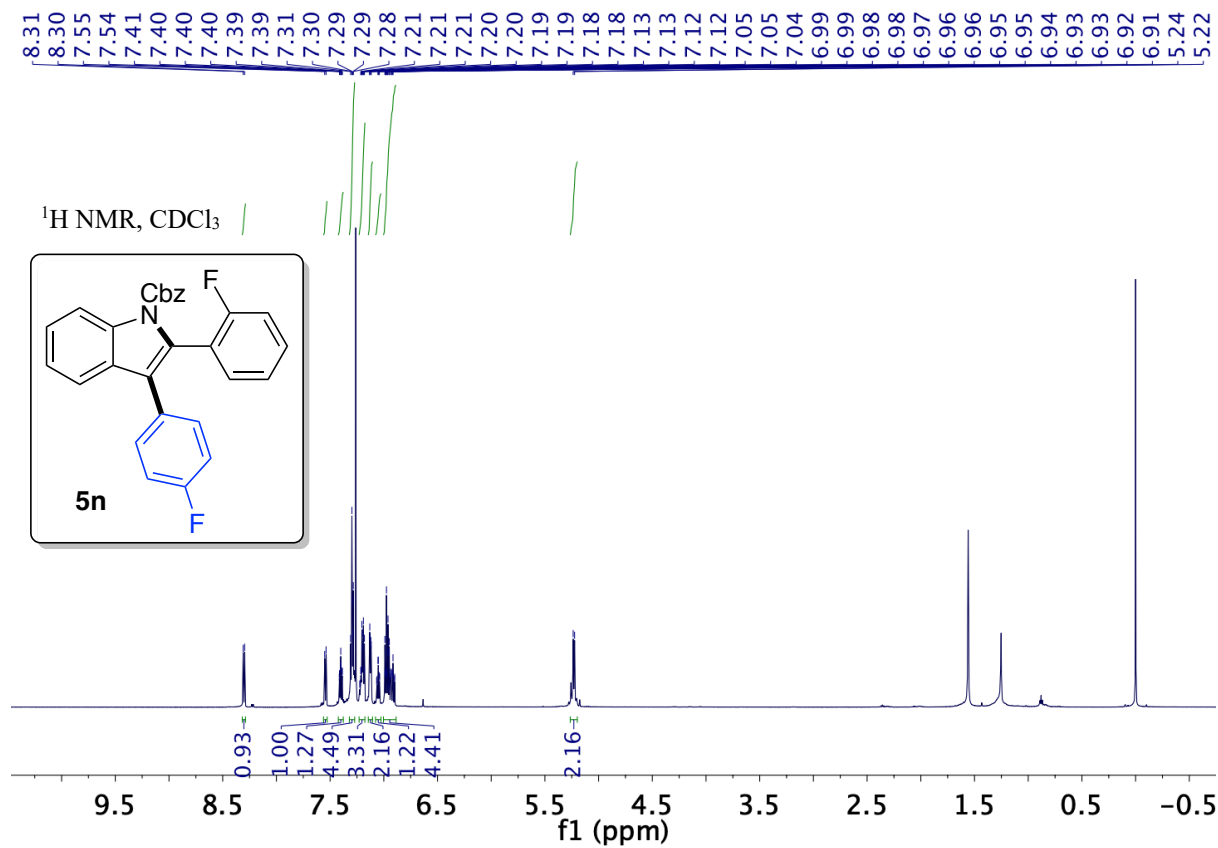


Supplementary Fig. 80. ¹³C NMR Spectrum for **5m**

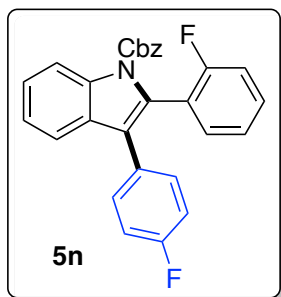
^{19}F NMR, CDCl_3

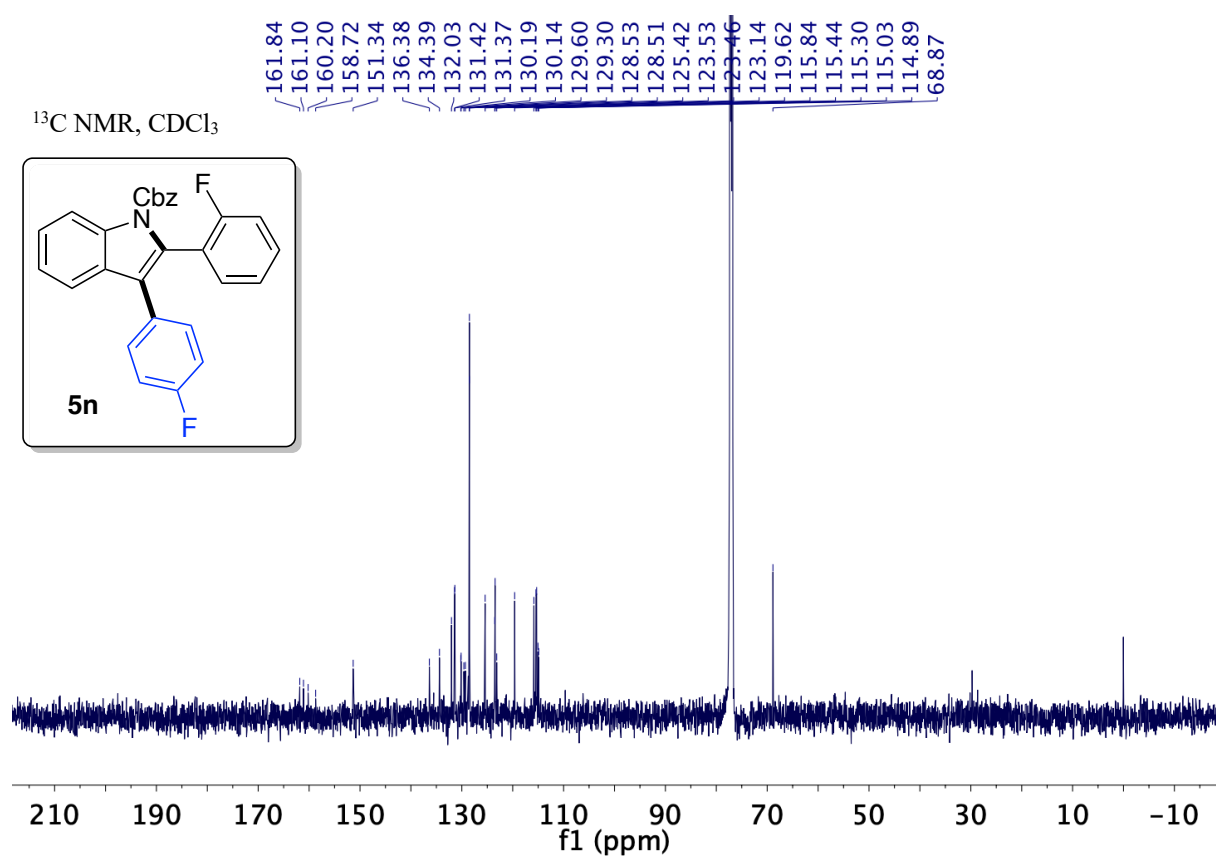


Supplementary Fig. 81. ^{19}F NMR Spectrum for **5m**

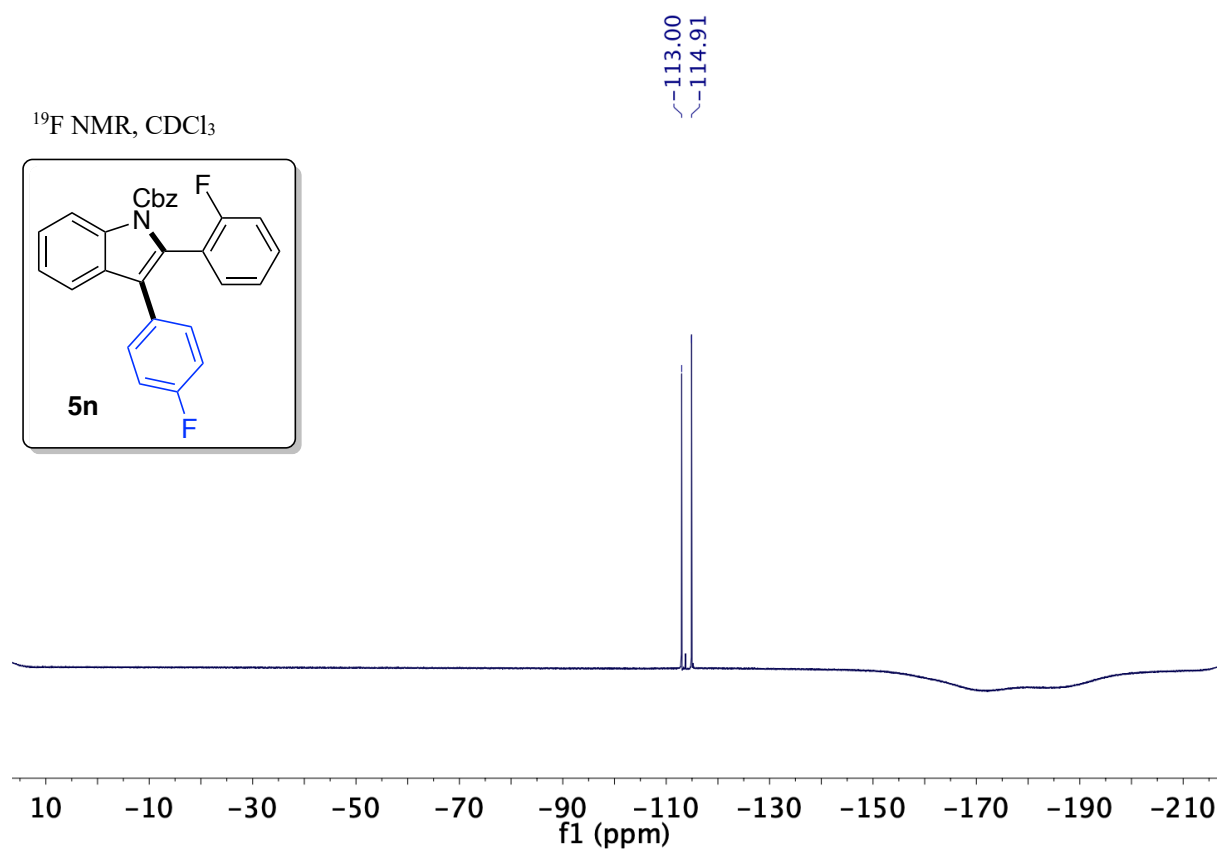


^1H NMR, CDCl_3

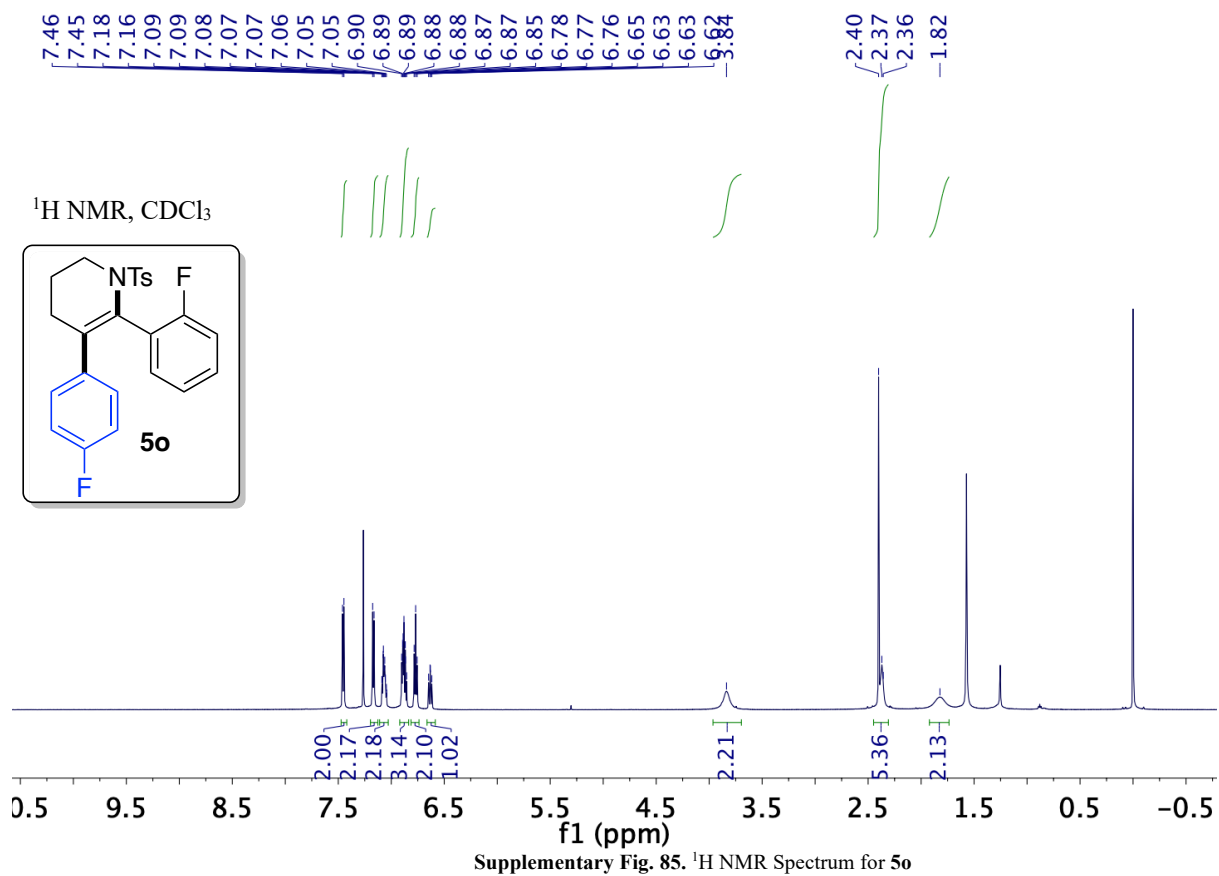




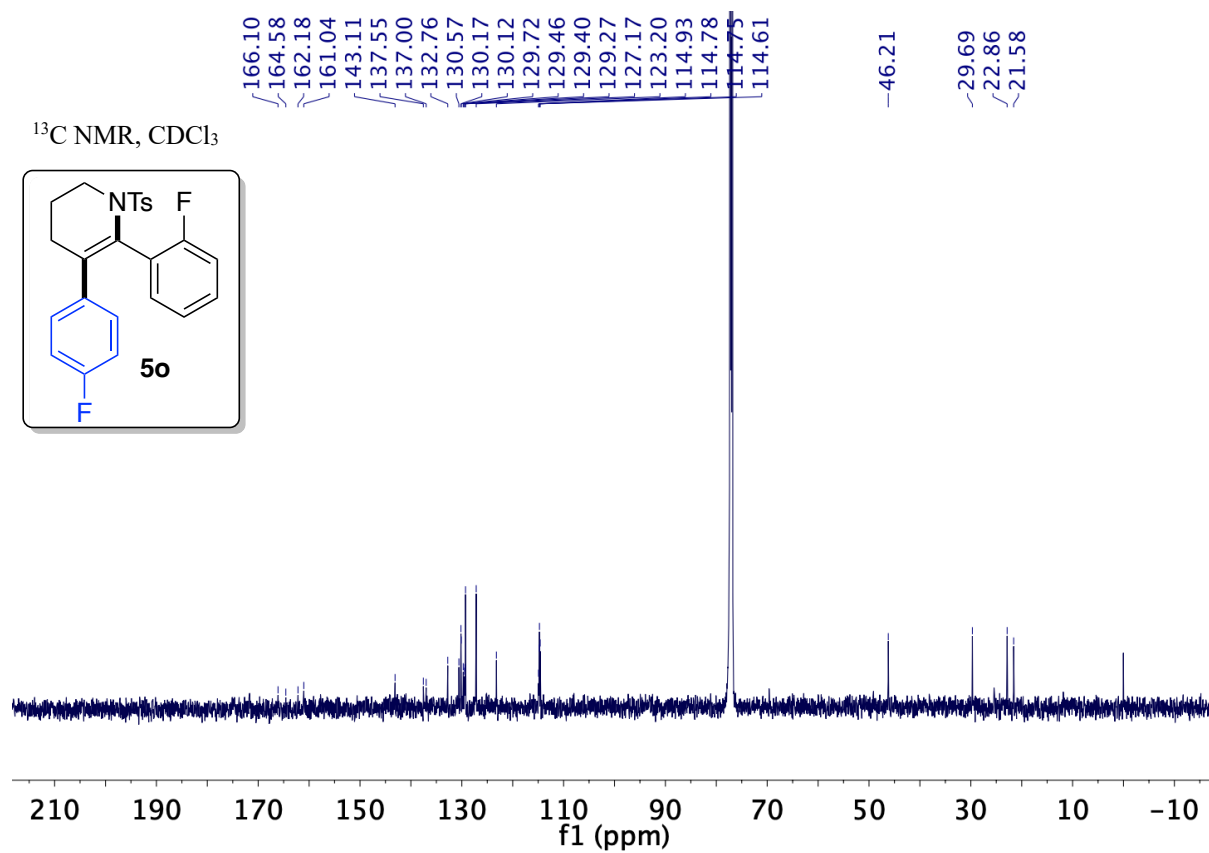
Supplementary Fig. 83. ¹³C NMR Spectrum for **5n**



Supplementary Fig. 84. ¹⁹F NMR Spectrum for **5n**

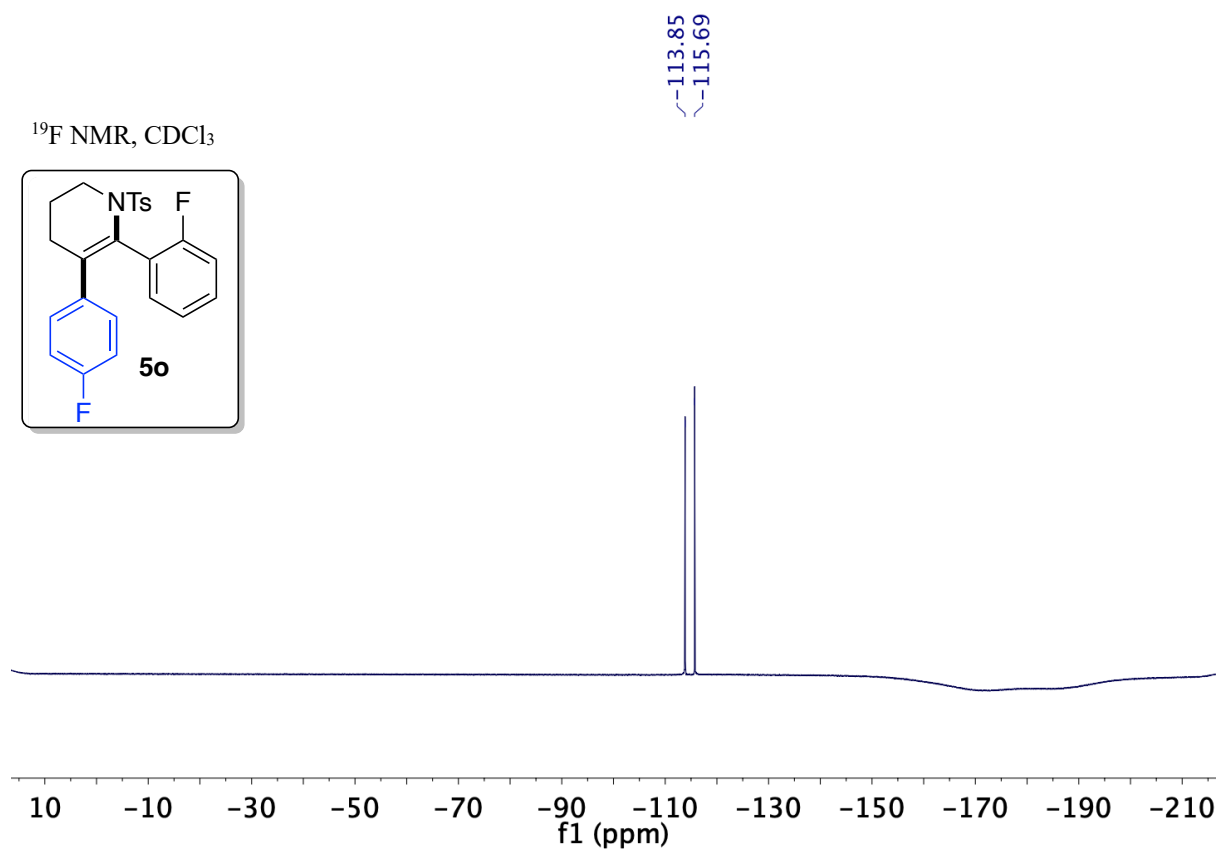
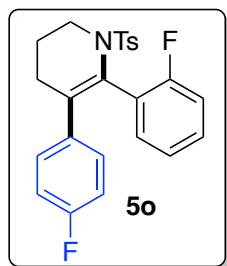


Supplementary Fig. 85. ¹H NMR Spectrum for **5o**



Supplementary Fig. 86. ¹³C NMR Spectrum for **5o**

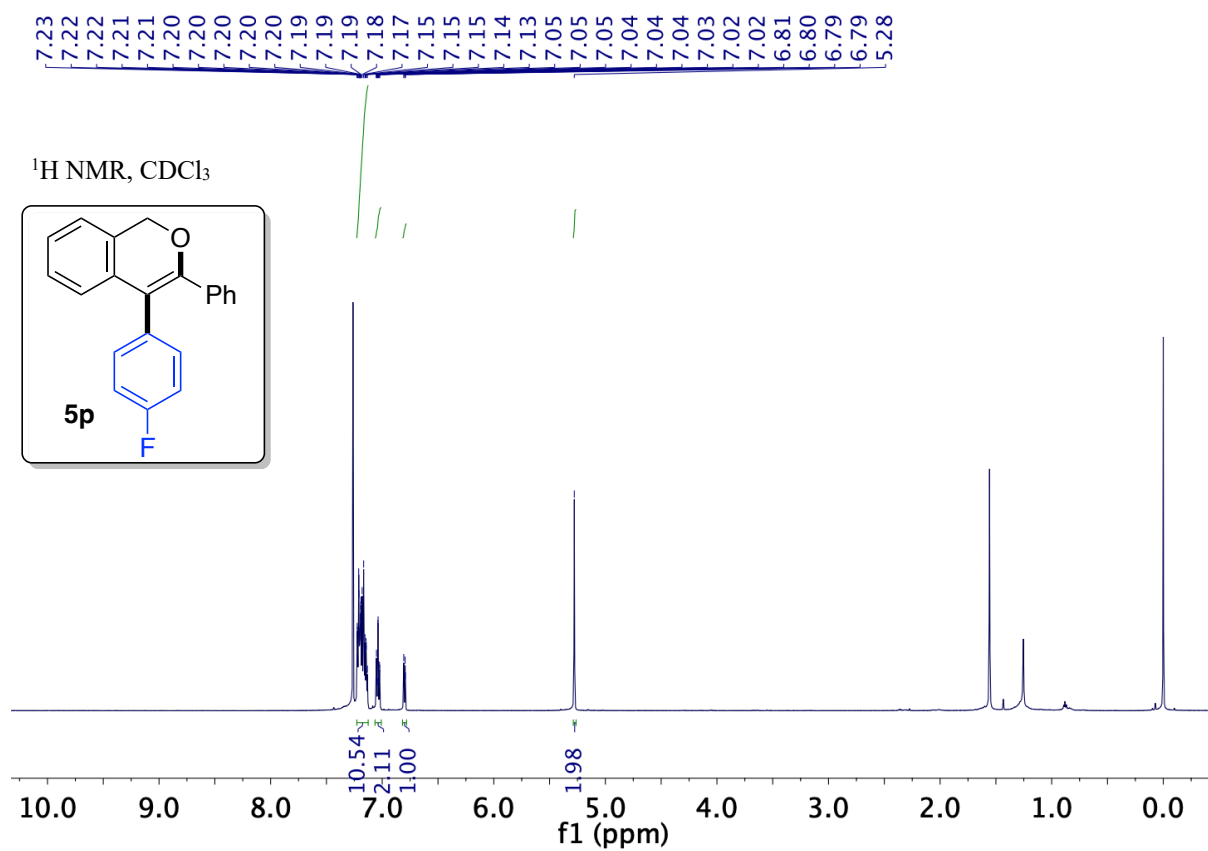
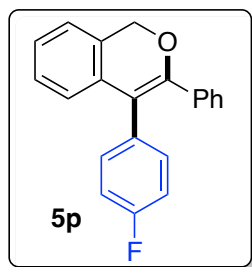
^{19}F NMR, CDCl_3



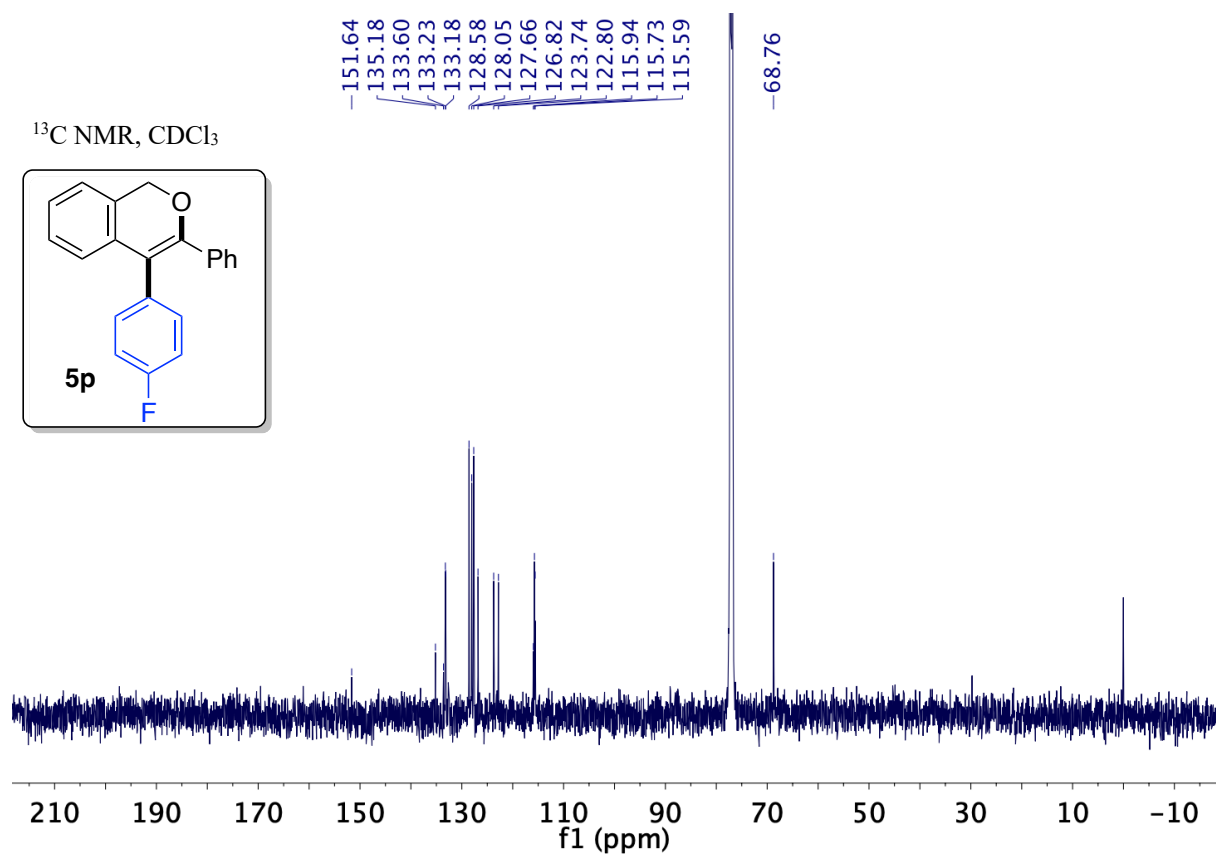
Supplementary Fig. 87. ^{19}F NMR Spectrum for **5o**

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7.04
7.04
7.03
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7.02
6.81
6.80
6.79
6.79
5.28

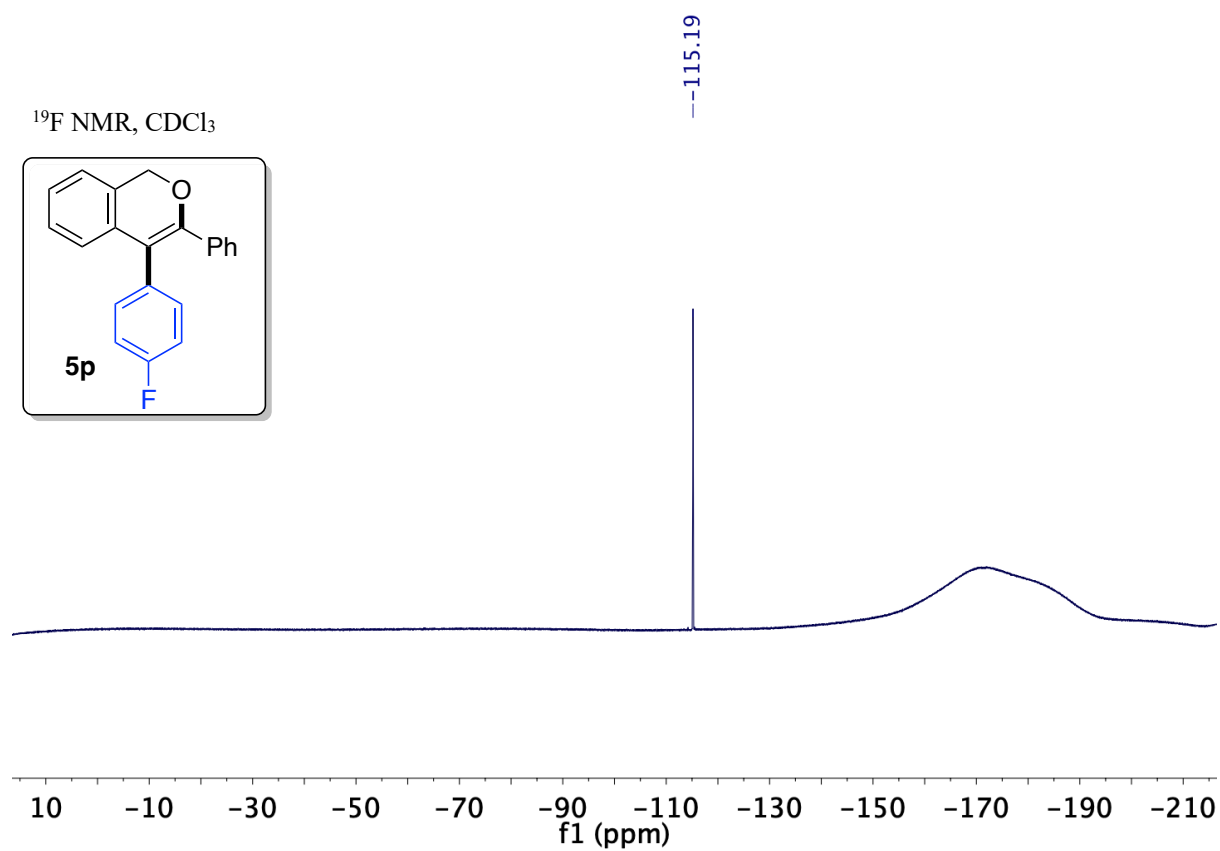
^1H NMR, CDCl_3



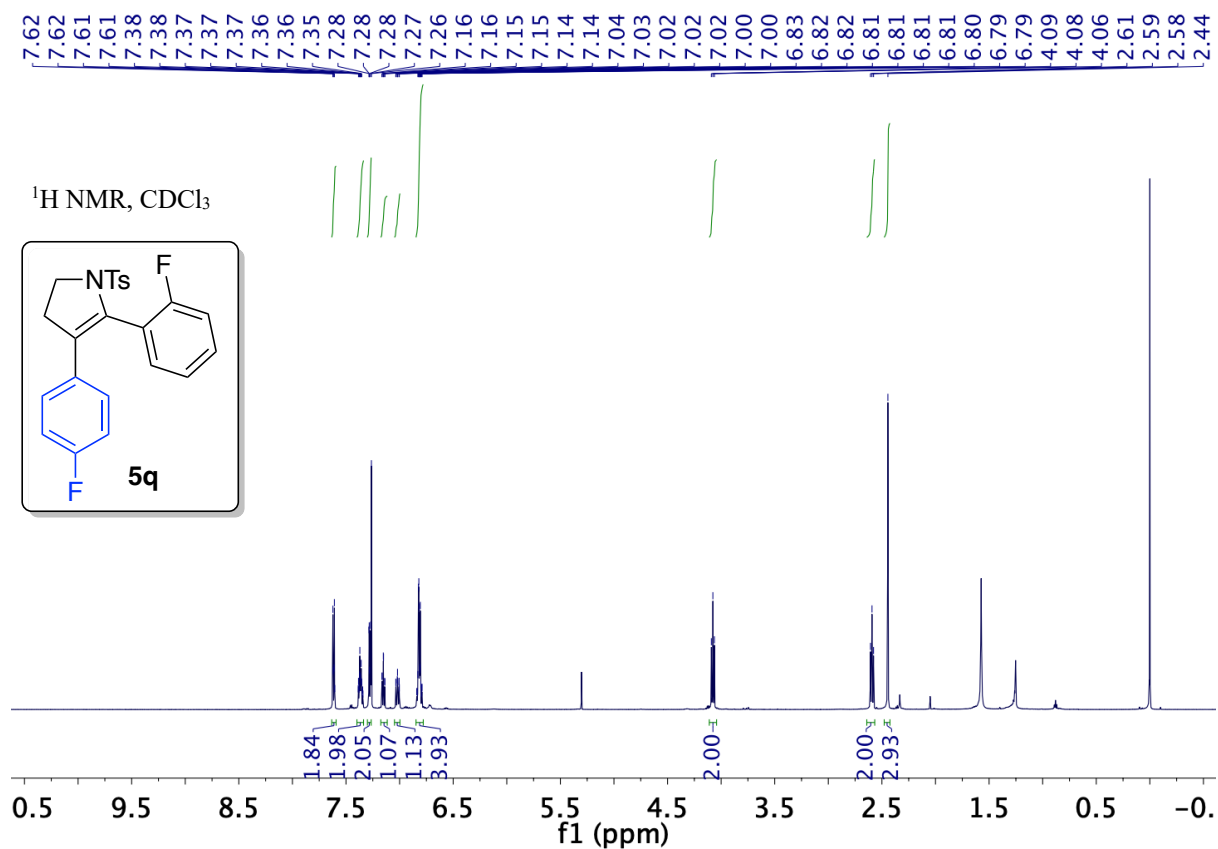
Supplementary Fig. 88. ^1H NMR Spectrum for **5p**



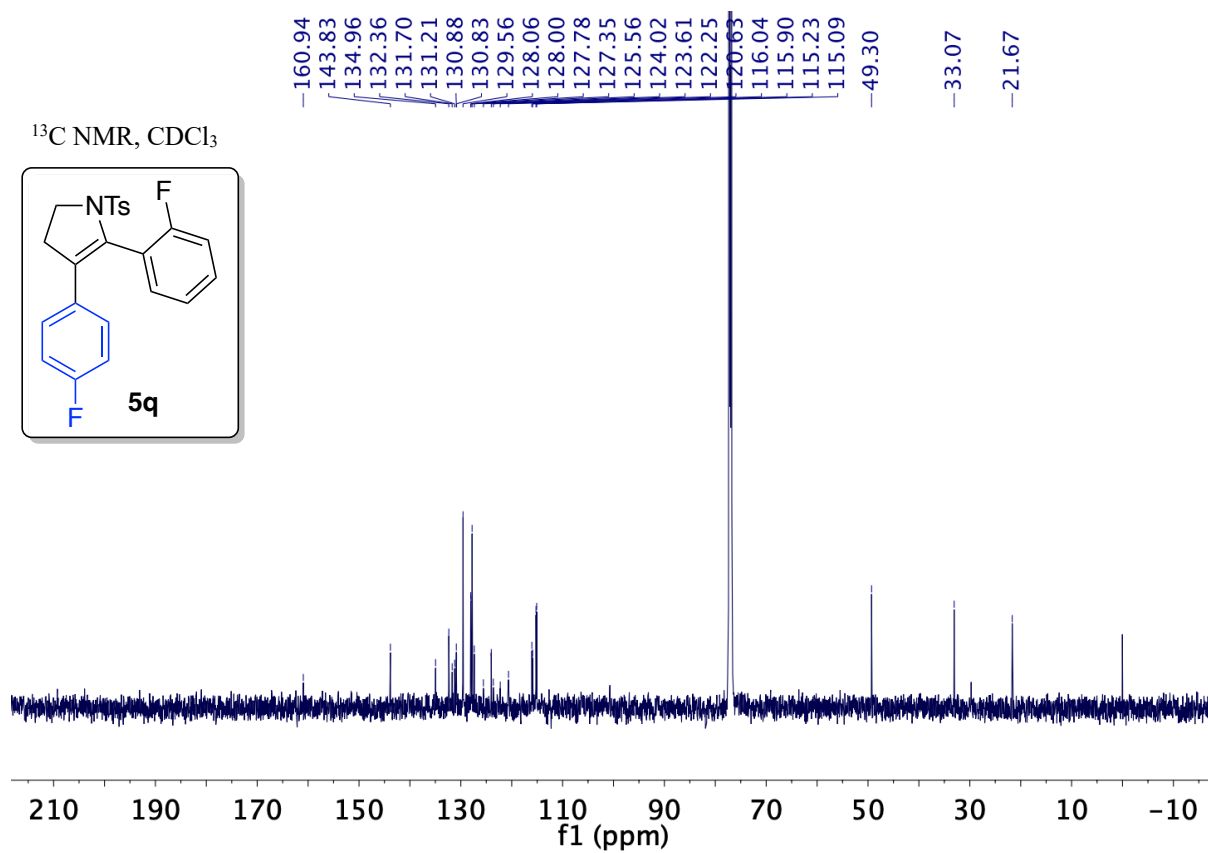
Supplementary Fig. 89. ¹³C NMR Spectrum for **5p**



Supplementary Fig. 90. ¹⁹F NMR Spectrum for **5p**

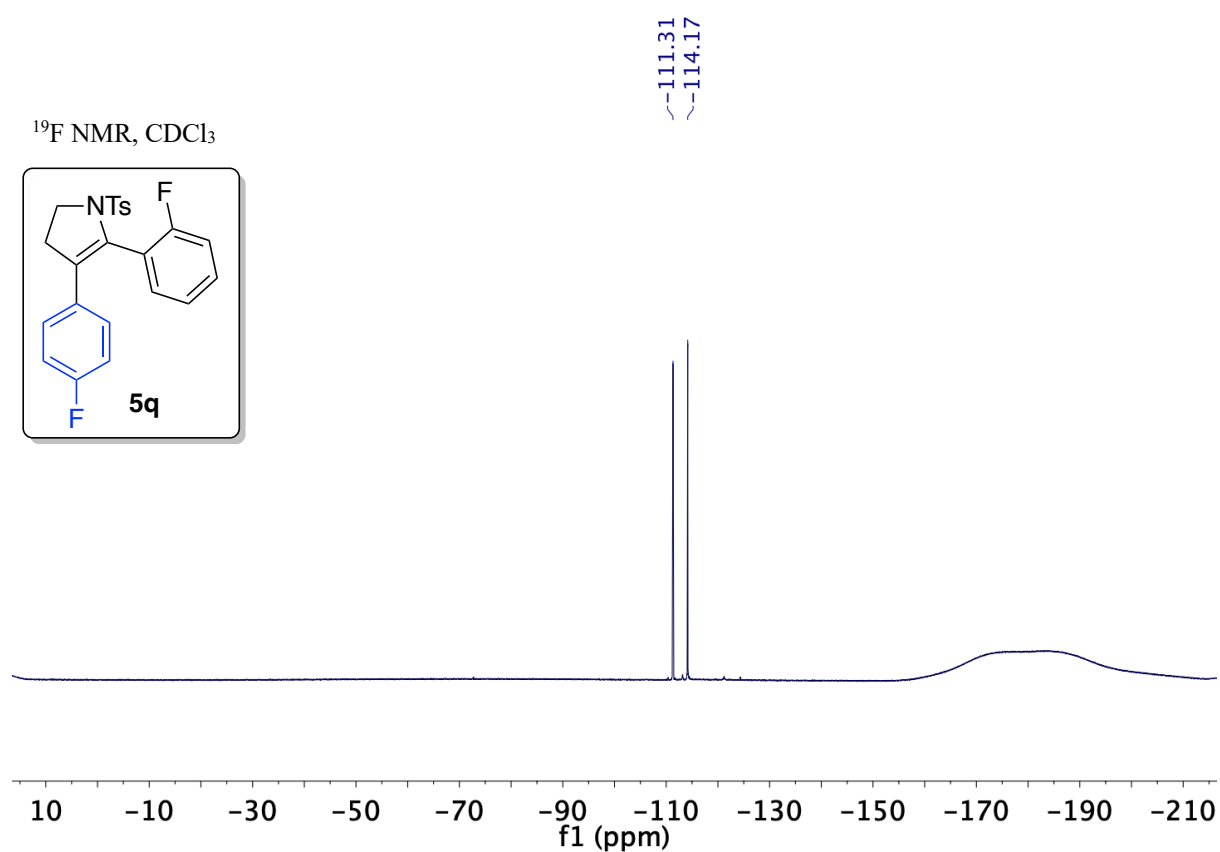
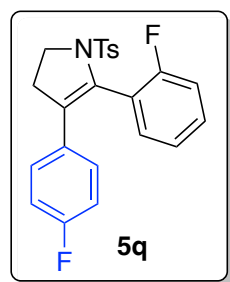


Supplementary Fig. 91. ¹H NMR Spectrum for **5q**



Supplementary Fig. 92. ¹³C NMR Spectrum for **5q**

^{19}F NMR, CDCl_3



Supplementary Fig. 93. ^{19}F NMR Spectrum for **5q**