Supporting Information

Synthesis of Benzofuro- and Indolo[3,2-*b*]indoles via Palladium-Catalyzed Double *N*-Arylation and Their Physical Properties

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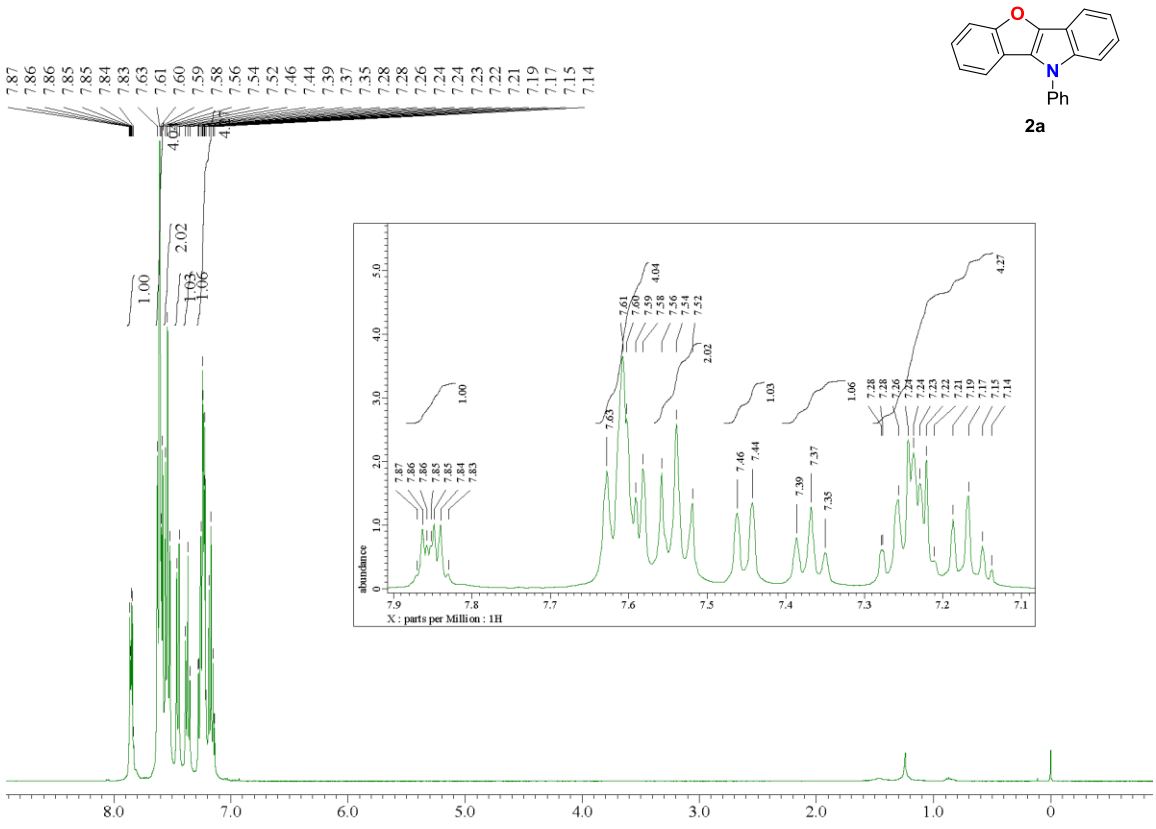


Figure S1. ^{1}H NMR spectrum of **2a** ($CDCl_3$).

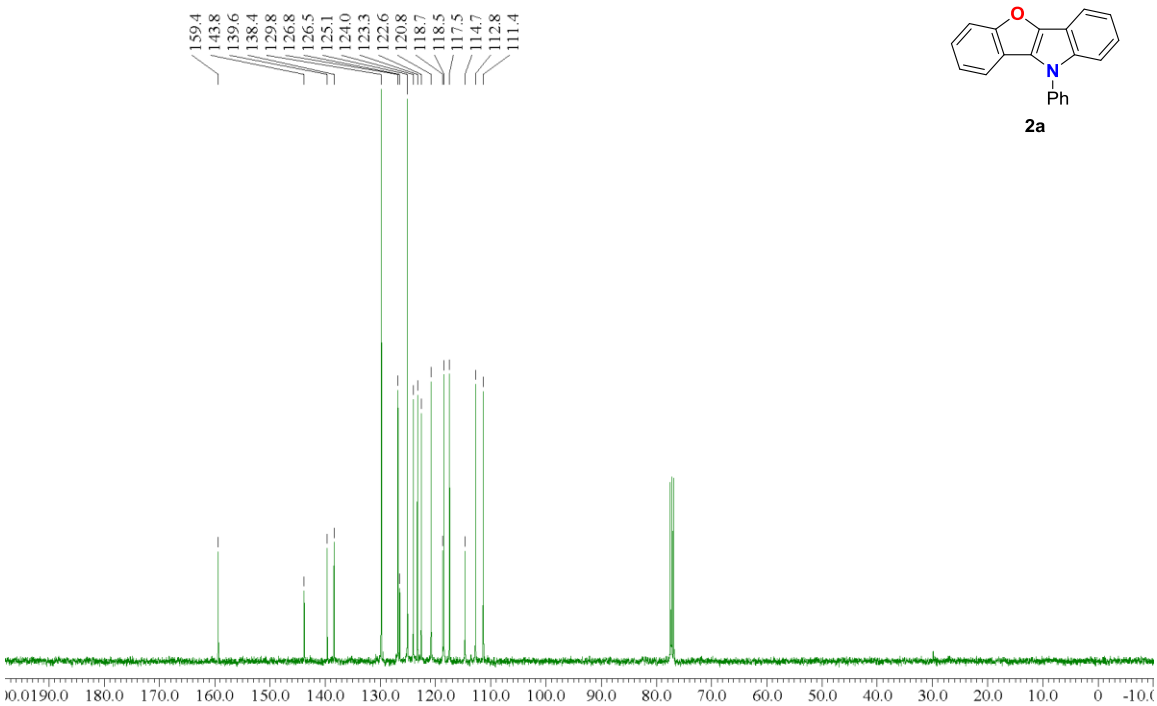


Figure S2. ^{13}C NMR spectrum of **2a** ($CDCl_3$).

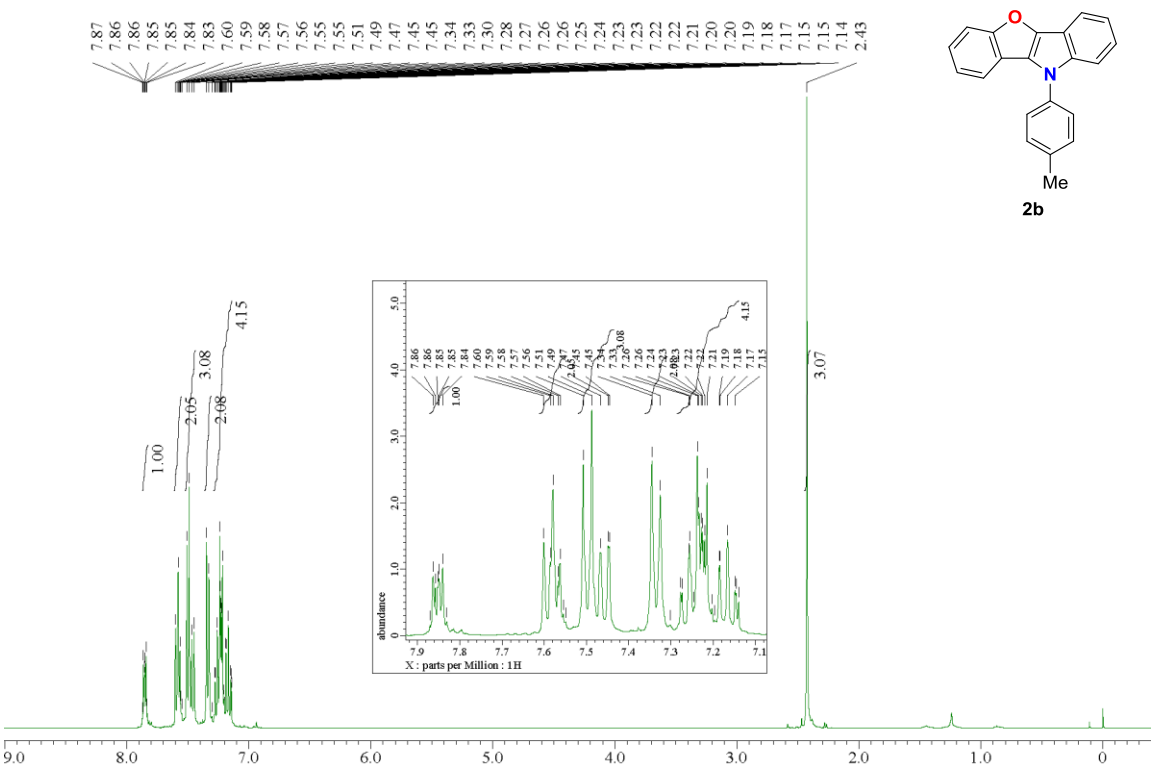


Figure S3. ^{1}H NMR spectrum of **2b** ($CDCl_3$).

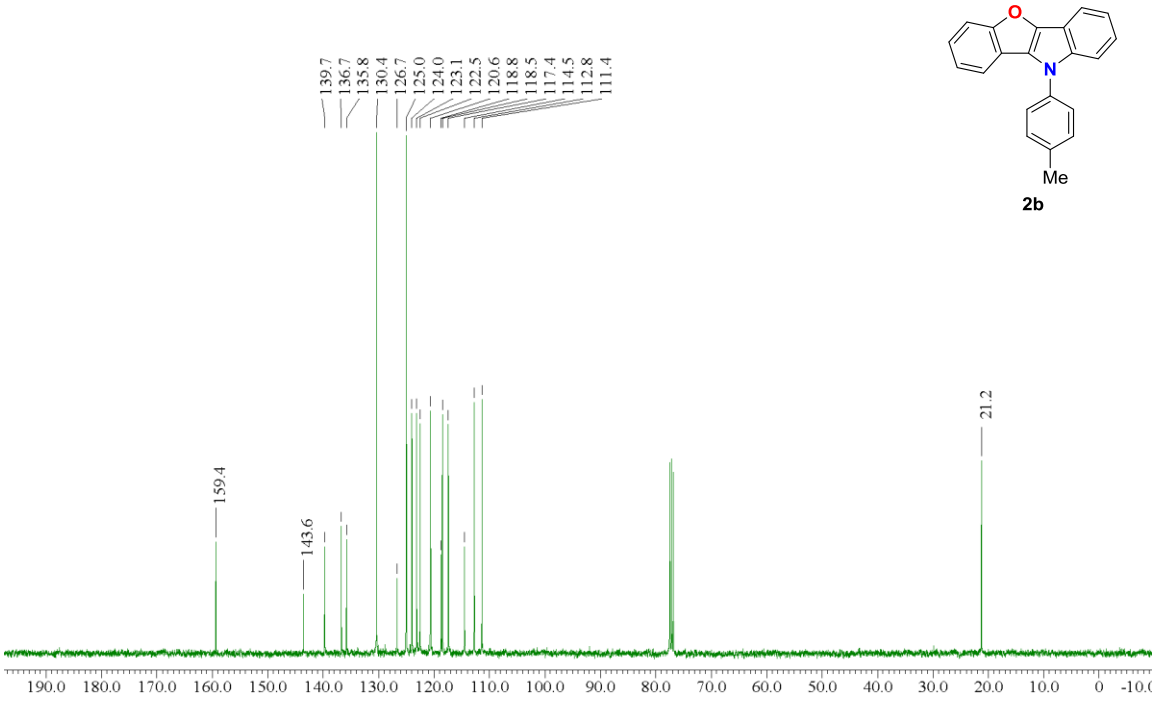


Figure S4. ^{13}C NMR spectrum of **2b** ($CDCl_3$).

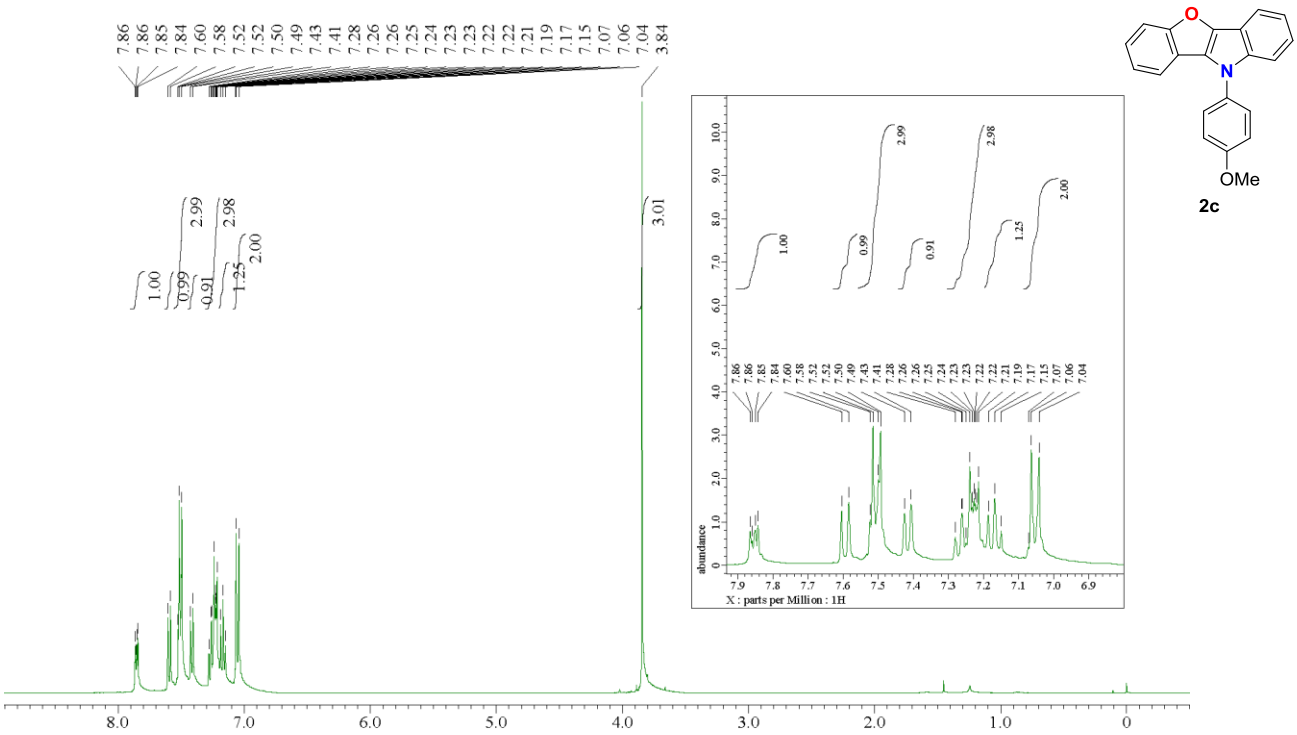


Figure S5. ^{1}H NMR spectrum of **2c** ($CDCl_3$).

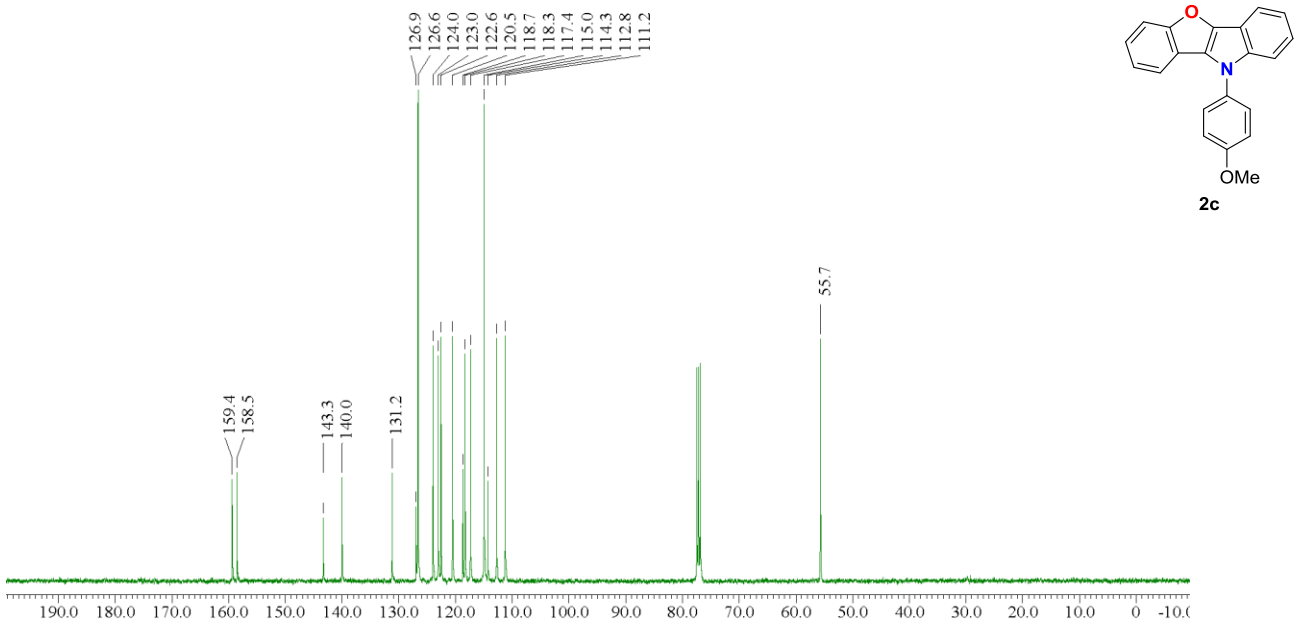


Figure S6. ^{13}C NMR spectrum of **2c** ($CDCl_3$).

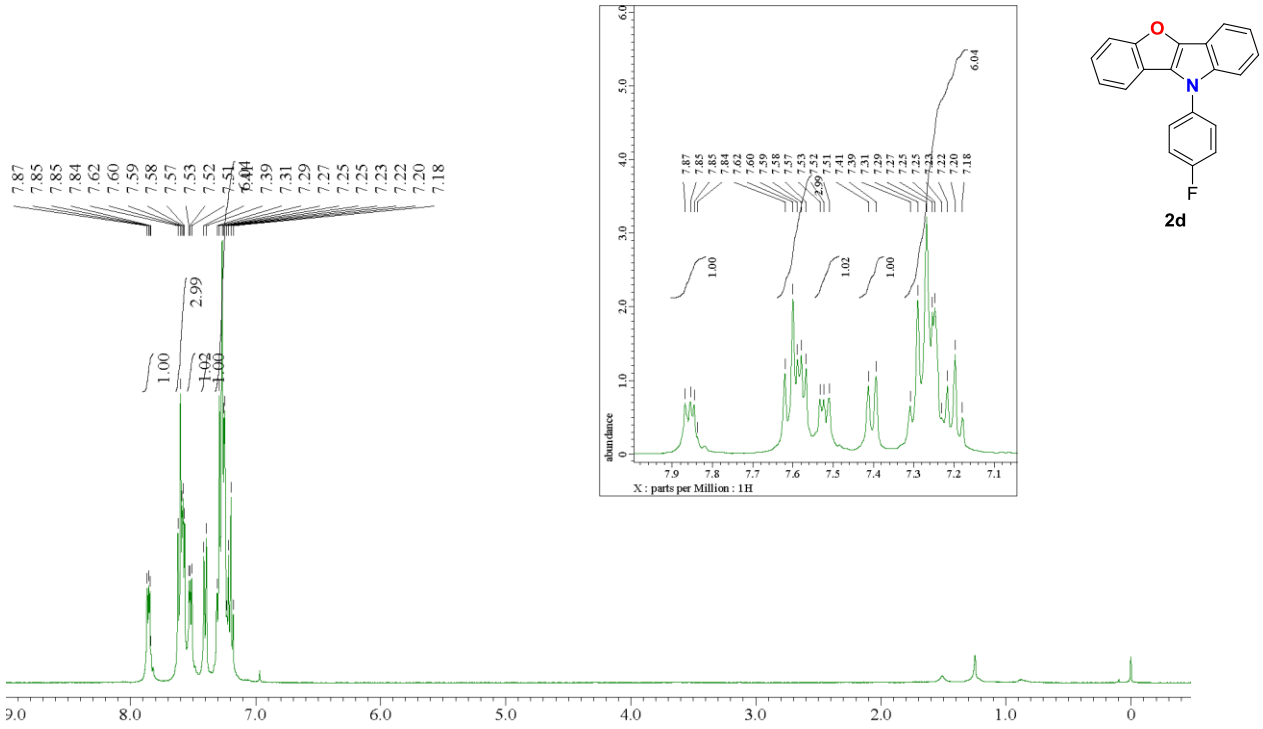


Figure S7. ^{1}H NMR spectrum of **2d** ($CDCl_3$).

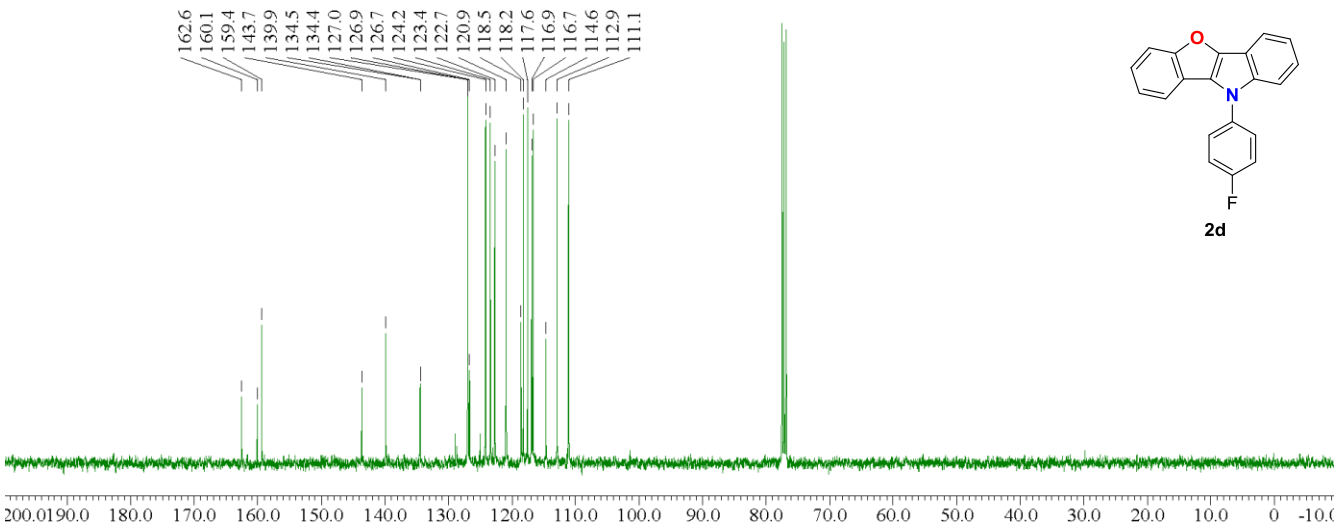


Figure S8. ^{13}C NMR spectrum of **2d** ($CDCl_3$).

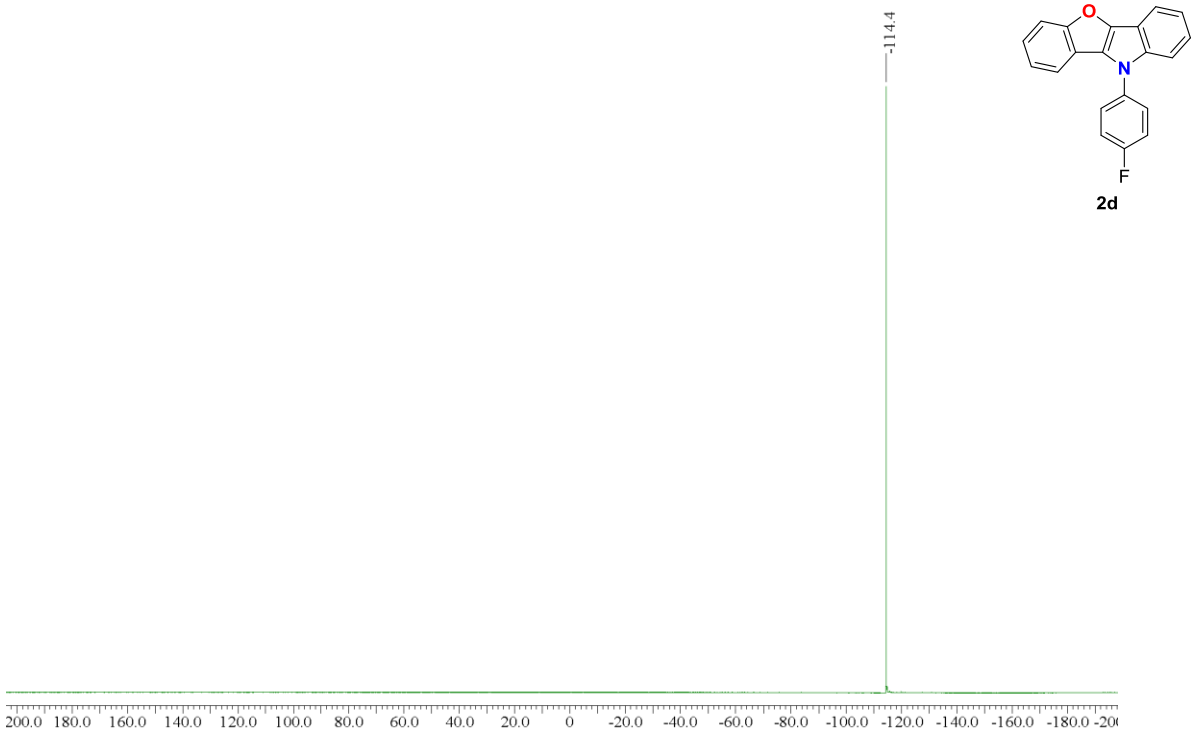


Figure S9. ^{19}F NMR spectrum of **2d** ($CDCl_3$).

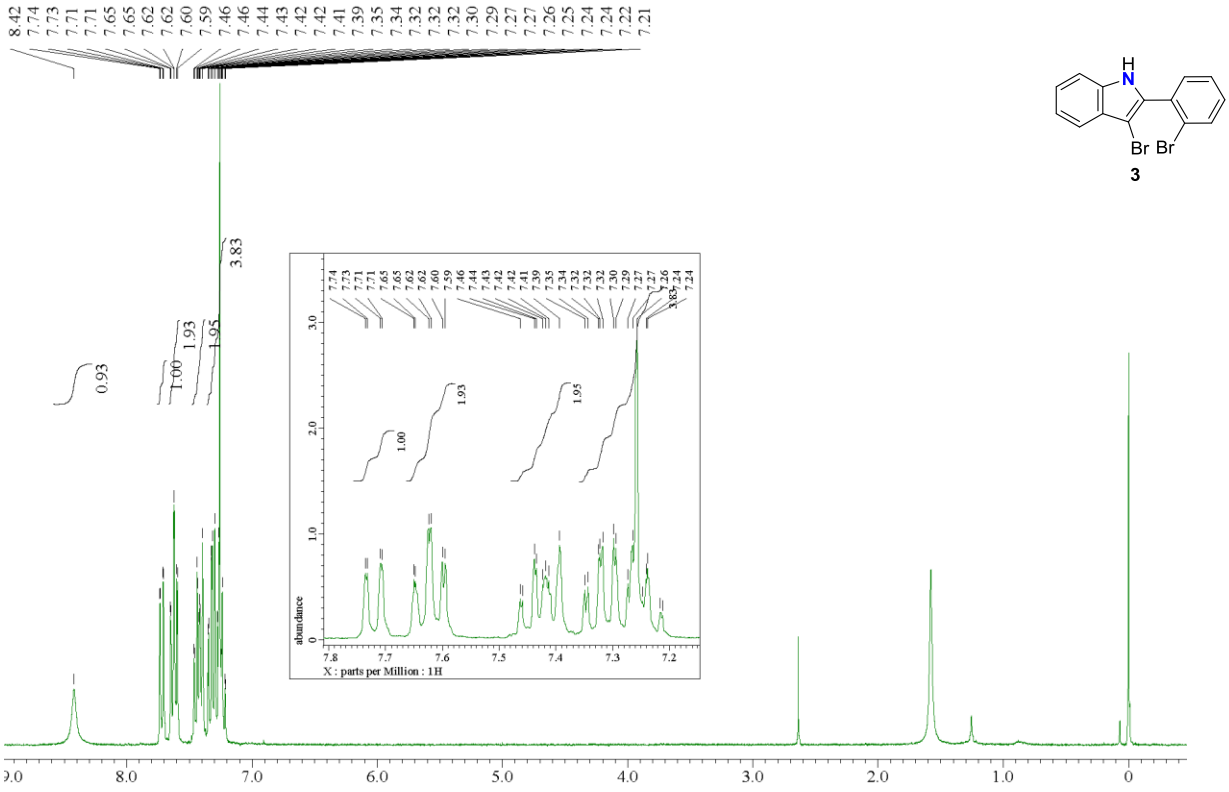


Figure S10. ^{1}H NMR spectrum of **3** ($CDCl_3$).

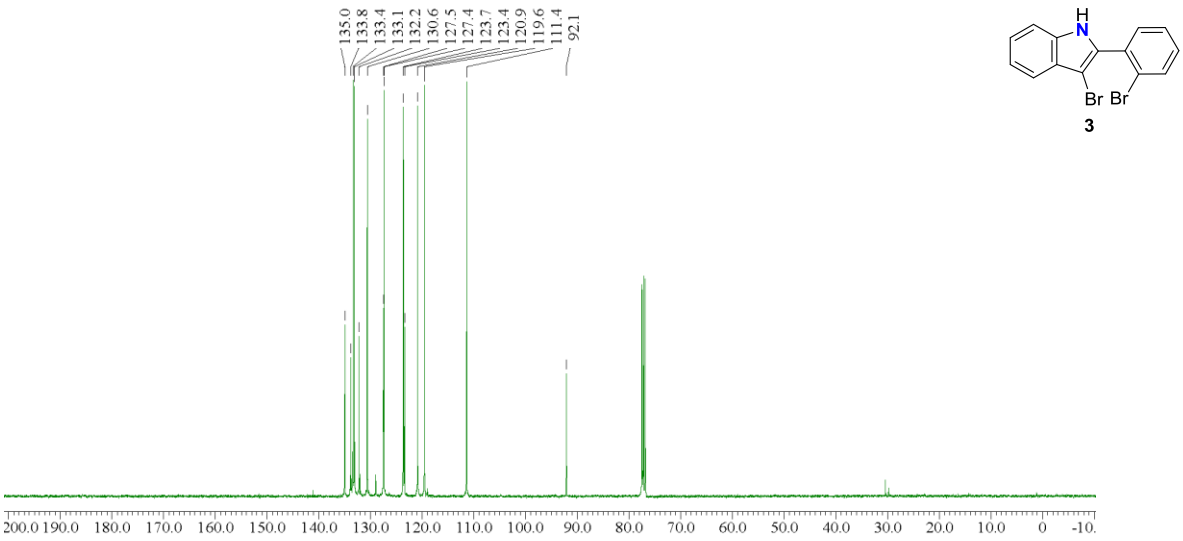


Figure S11. ^{13}C NMR spectrum of **3** ($CDCl_3$).

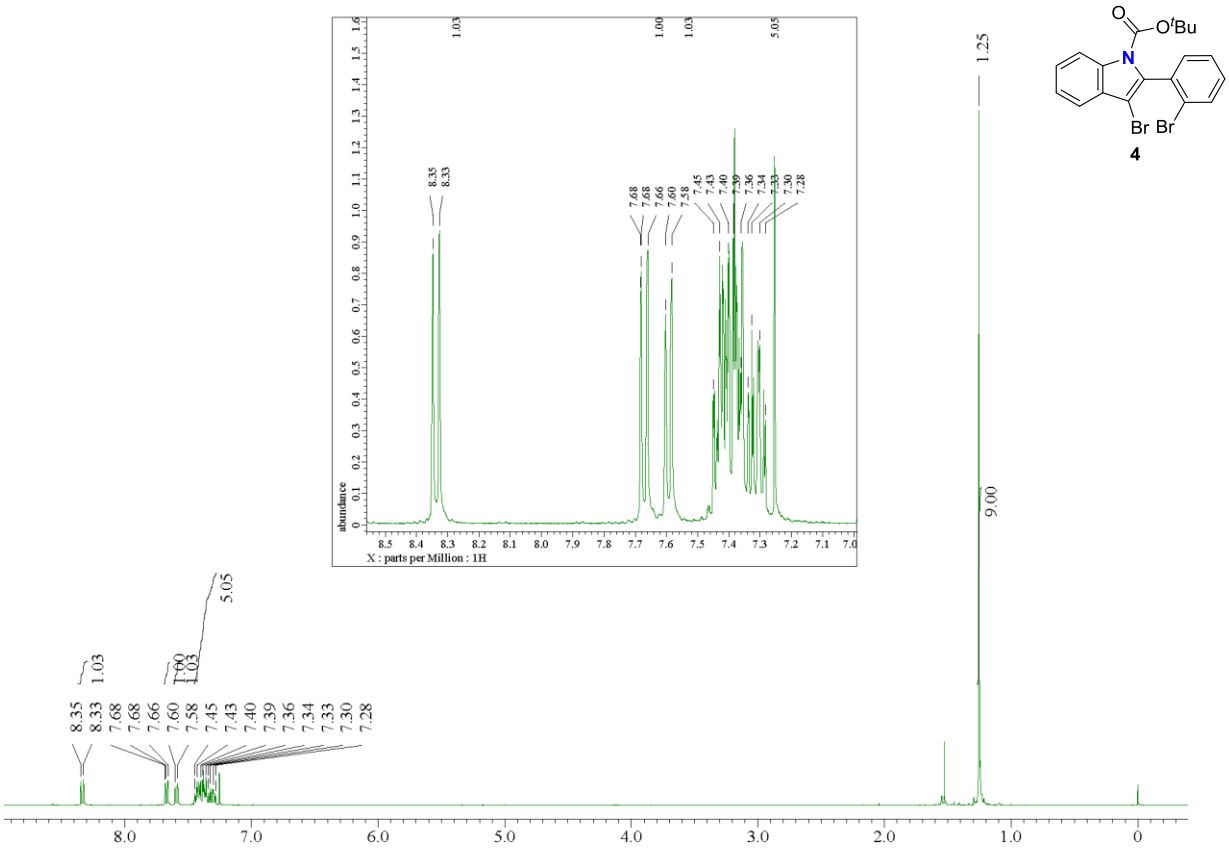


Figure S12. ^{1}H NMR spectrum of **4** ($CDCl_3$).

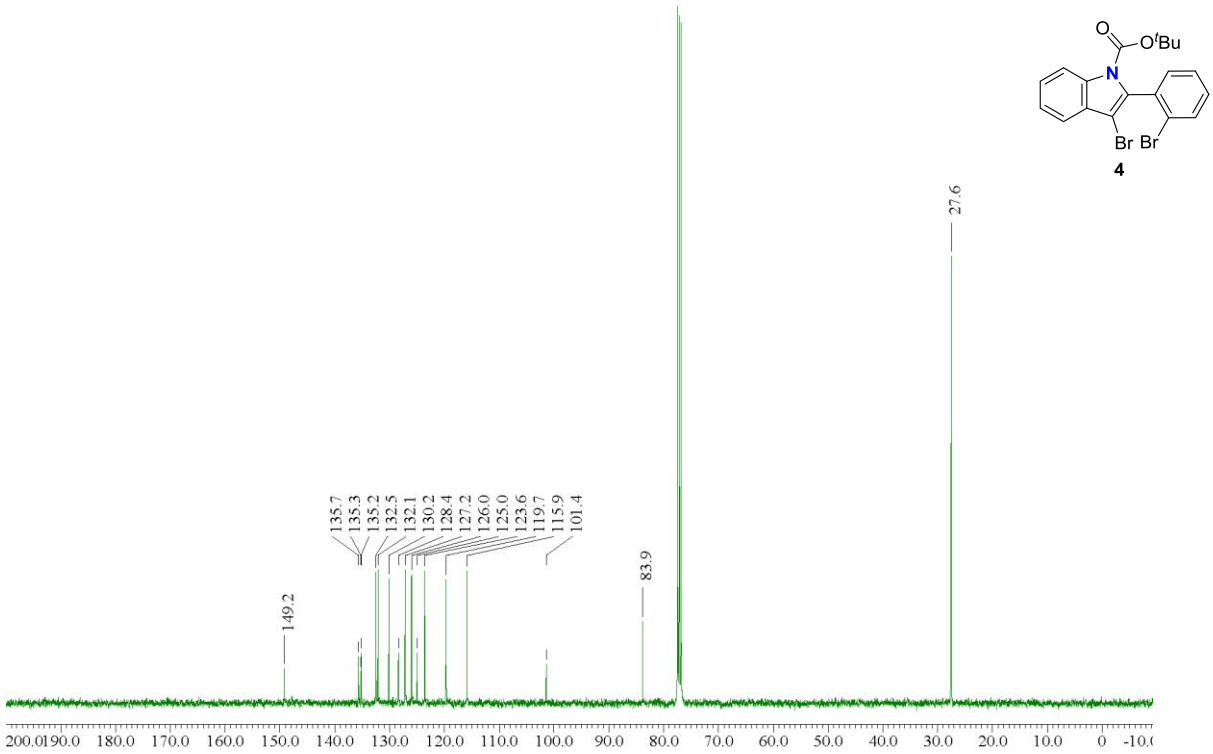


Figure S13. ^{13}C NMR spectrum of **4** ($CDCl_3$).

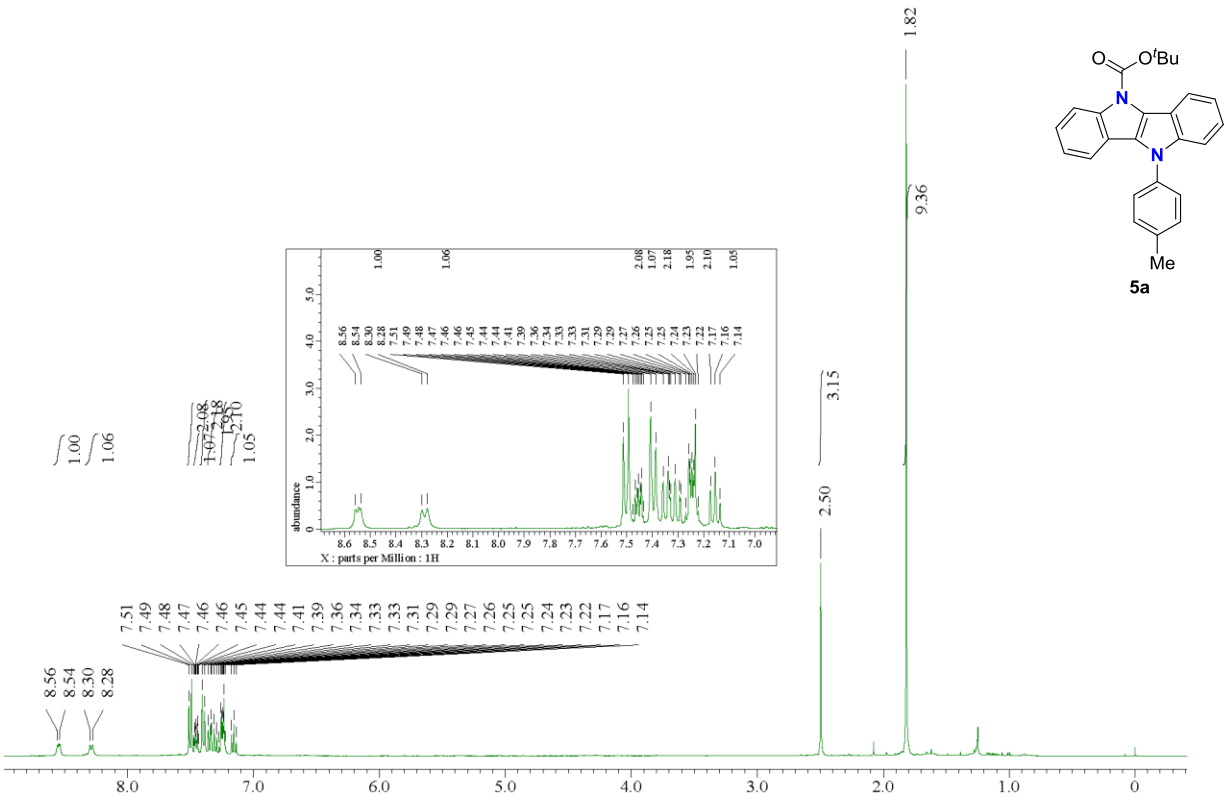


Figure S14. ^{1}H NMR spectrum of **5a** ($CDCl_3$).

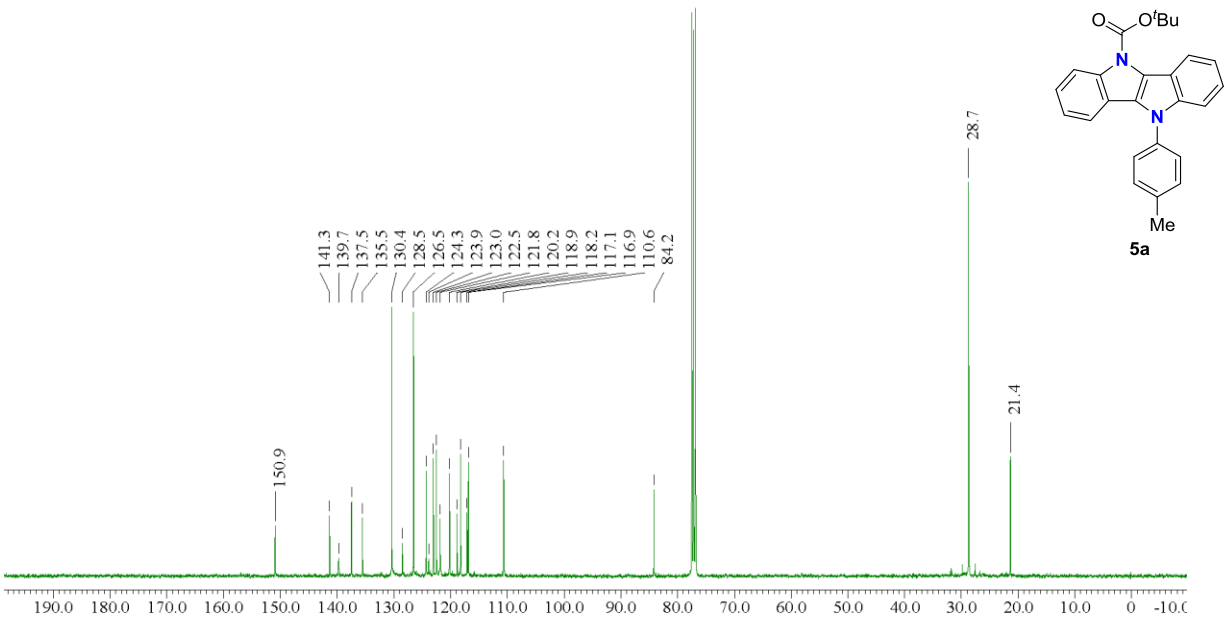


Figure S15. ^{13}C NMR spectrum of **5a** ($CDCl_3$).

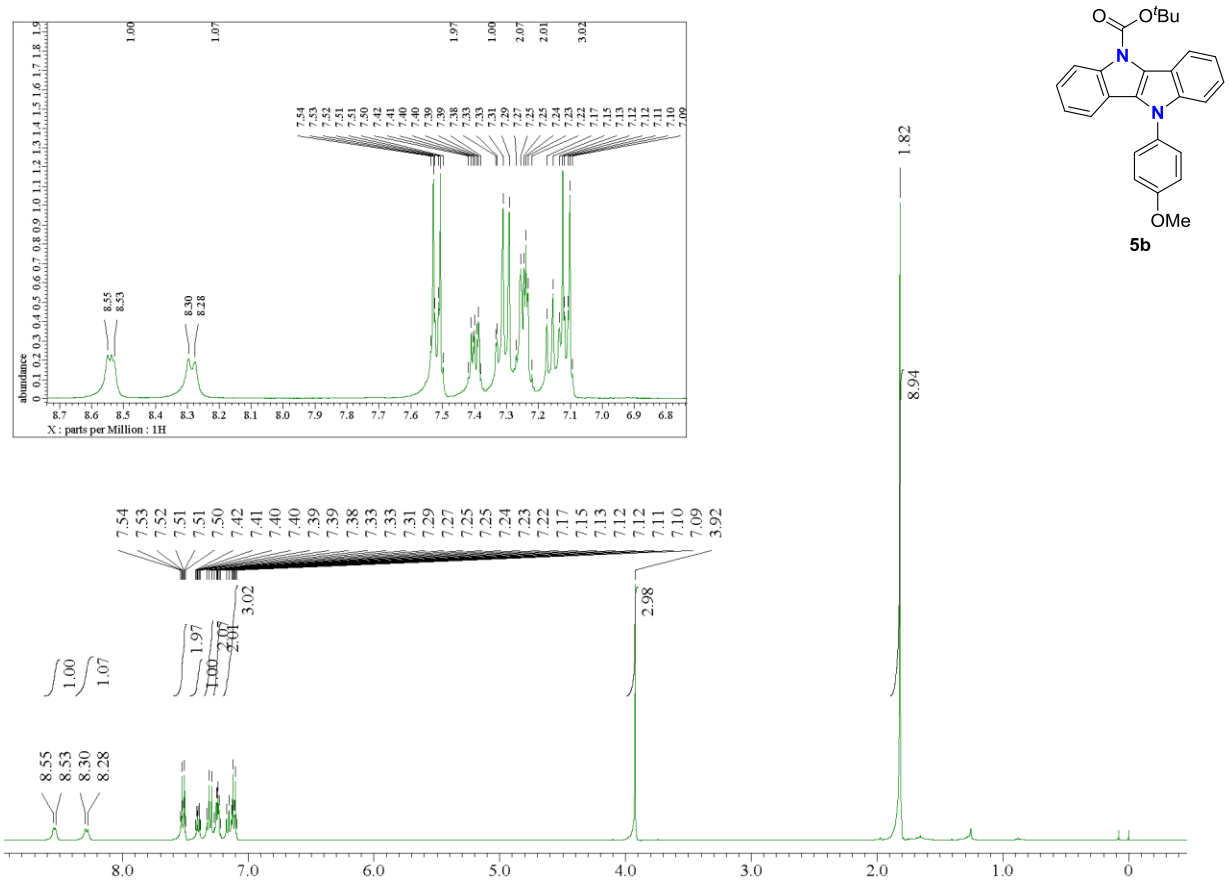


Figure S16. ^{1}H NMR spectrum of **5b** ($CDCl_3$).

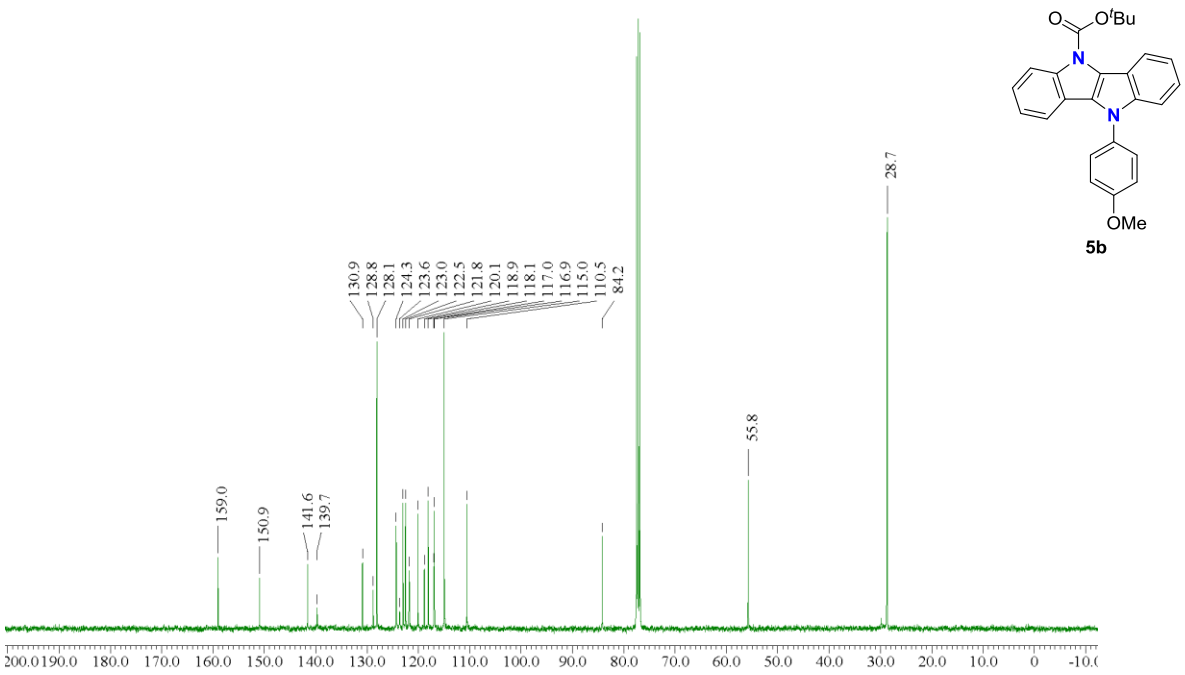


Figure S17. ^{13}C NMR spectrum of **5b** ($CDCl_3$).

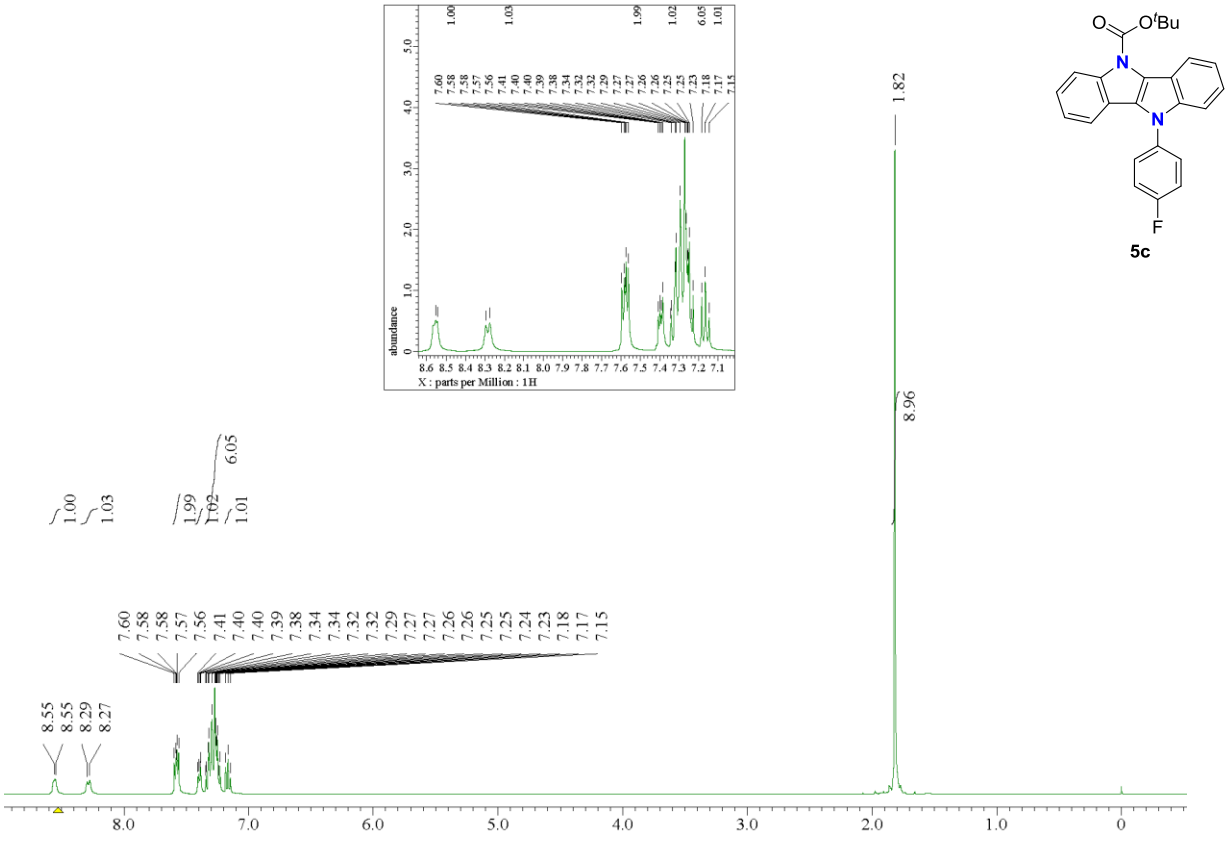


Figure S18. ^{1}H NMR spectrum of **5c** ($CDCl_3$).

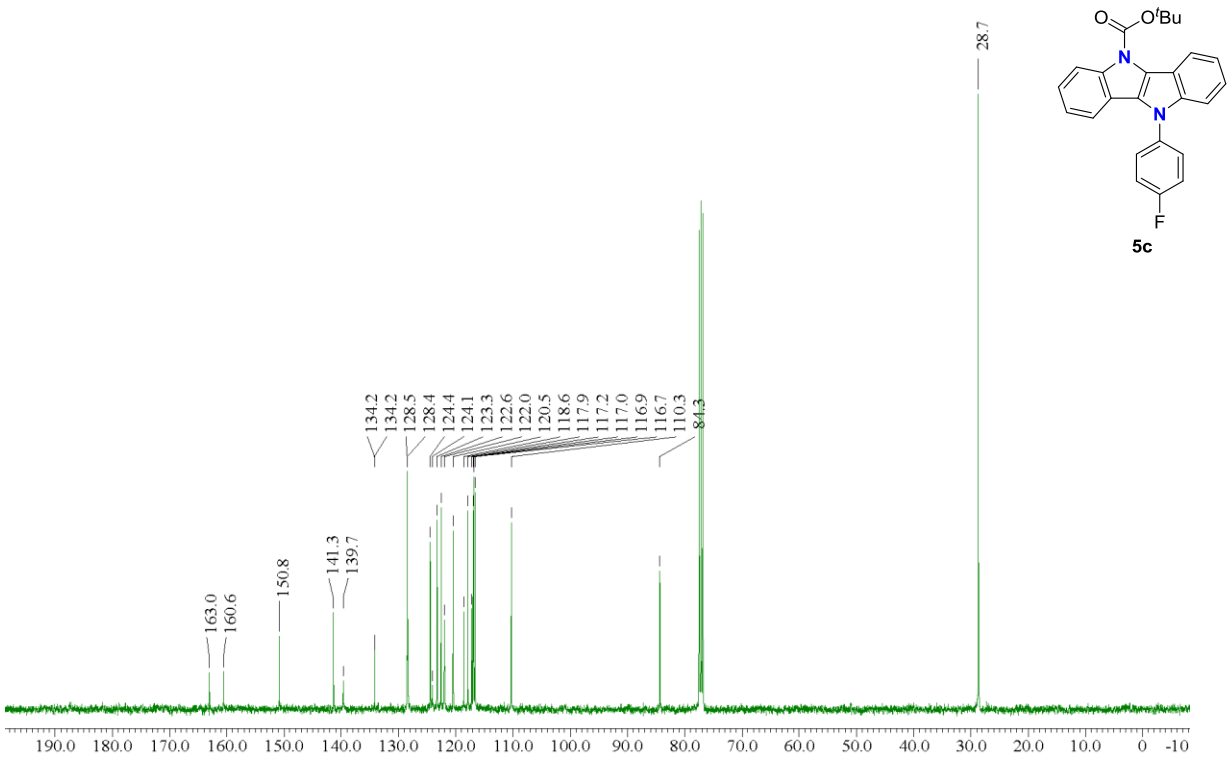


Figure S19. ^{13}C NMR spectrum of **5c** ($CDCl_3$).

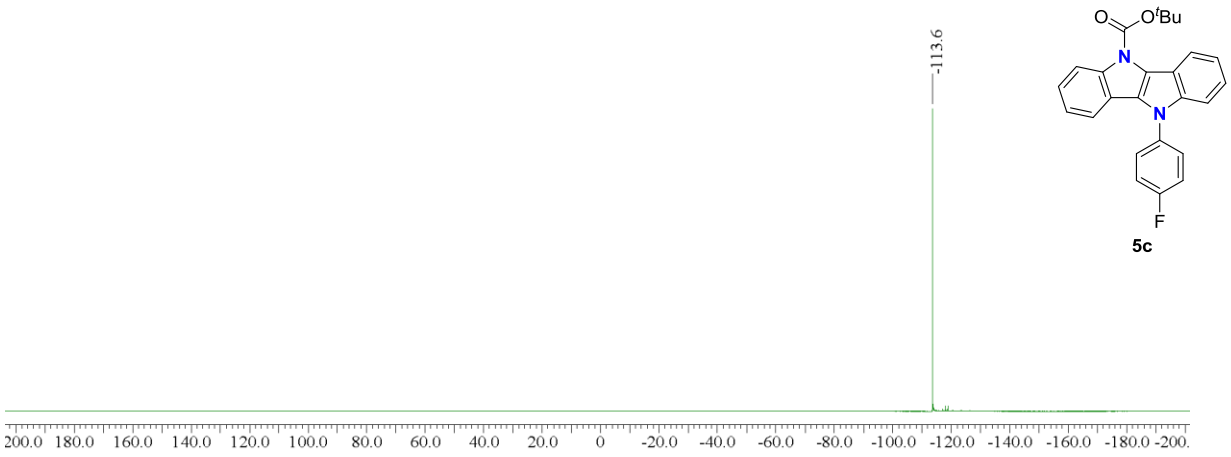


Figure S20. ^{19}F NMR spectrum of **5c** ($CDCl_3$).

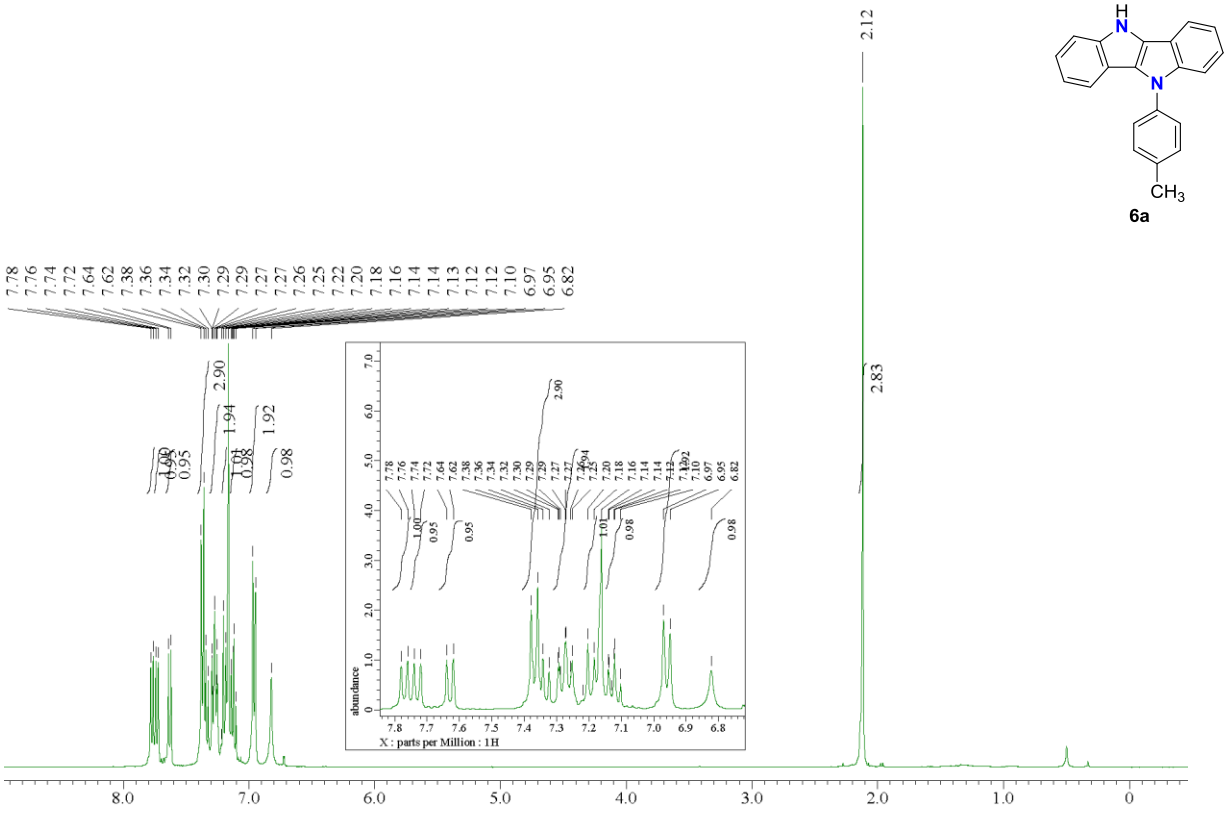


Figure S21. ^{1}H NMR spectrum of **6a** (C_6D_6).

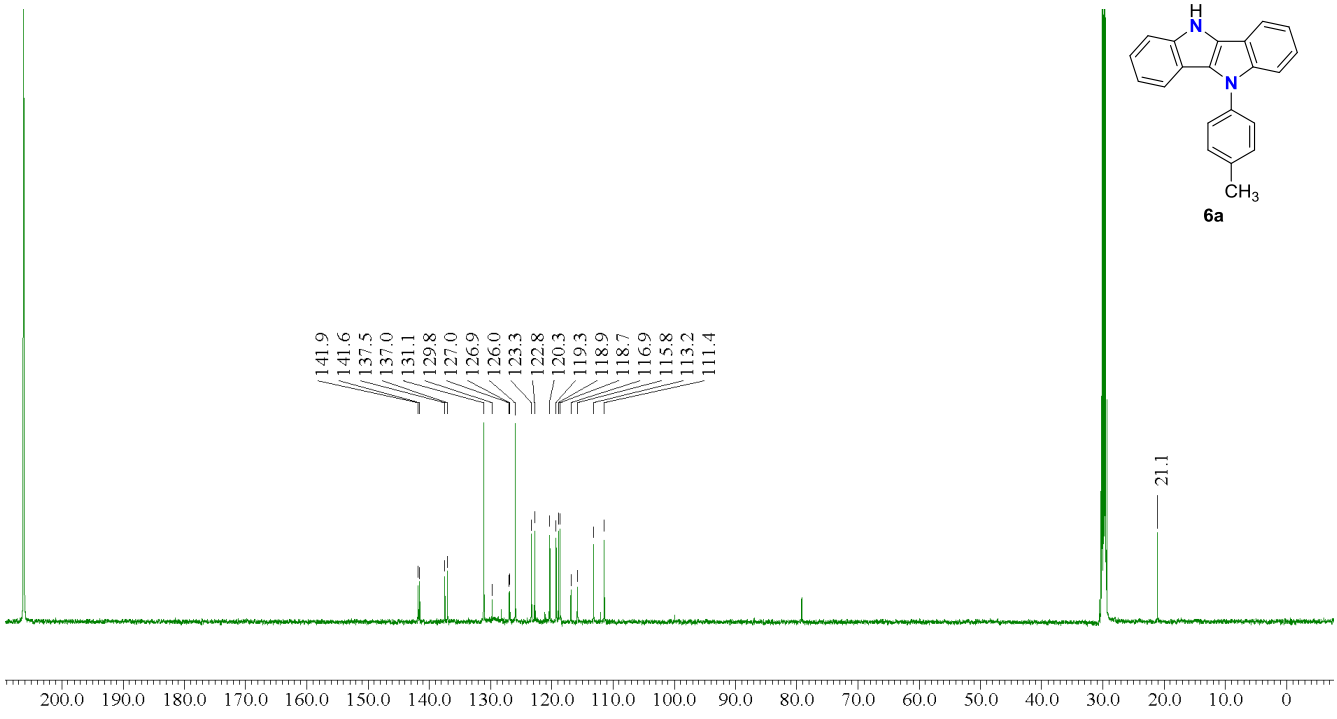


Figure S22. ^{13}C NMR spectrum of **6a** (acetone-d_6).

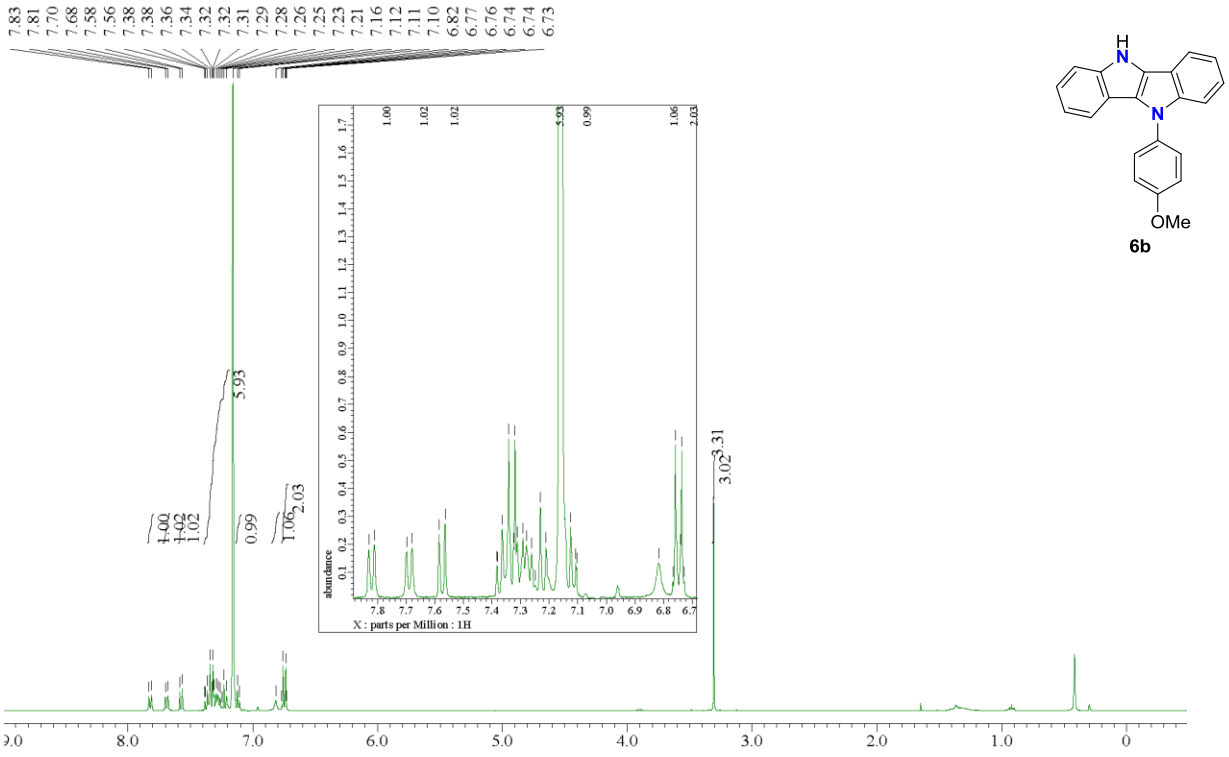


Figure S23. ^{1}H NMR spectrum of **6b** (C_6D_6).

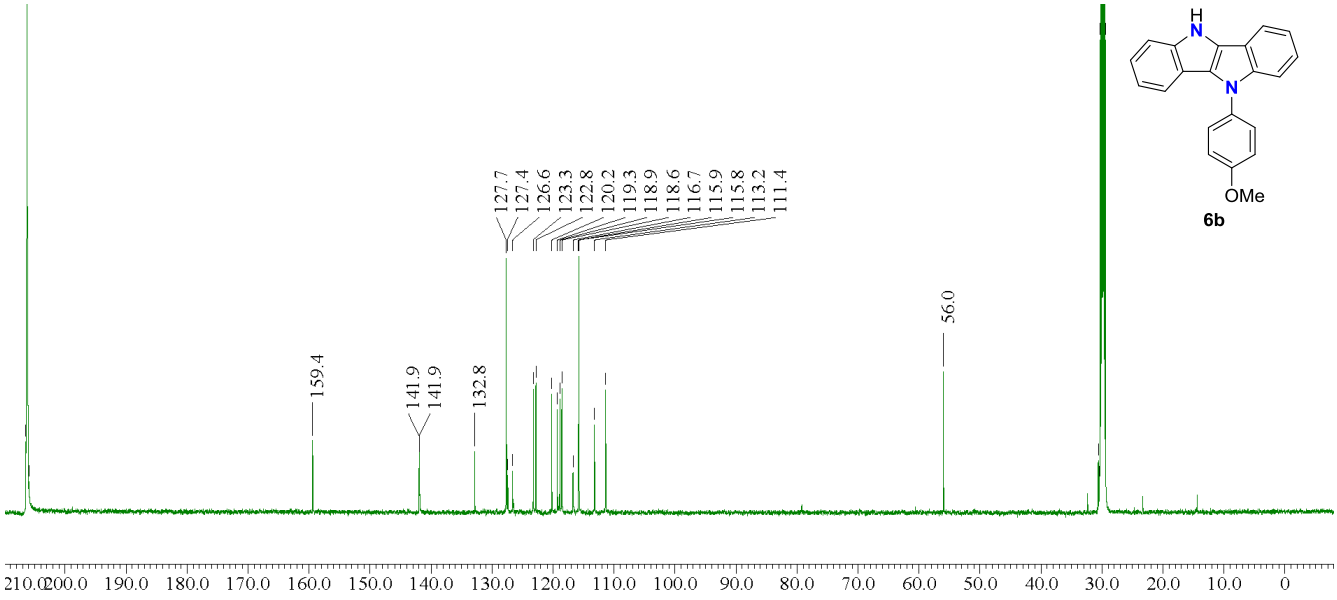


Figure S24. ^{13}C NMR spectrum of **6b** (acetone-d_6).

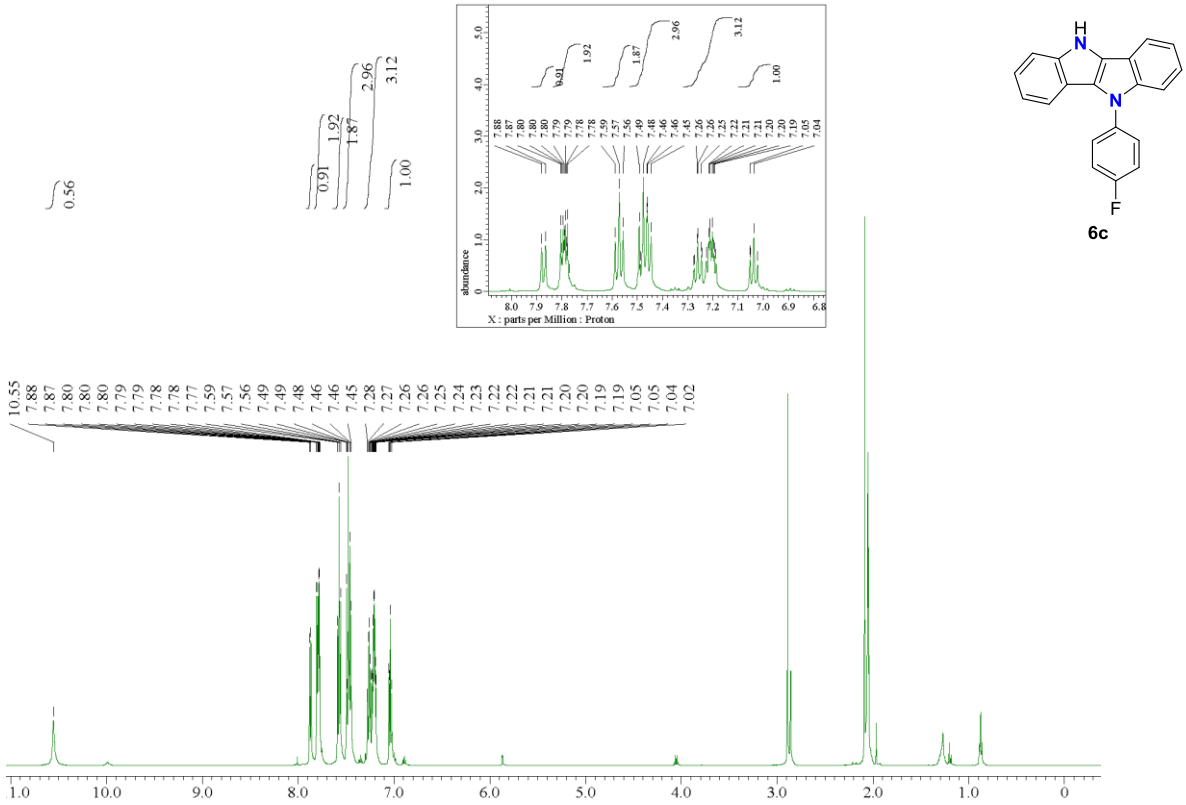


Figure S25. ^{1}H NMR spectrum of **6c** (acetone-d_6).

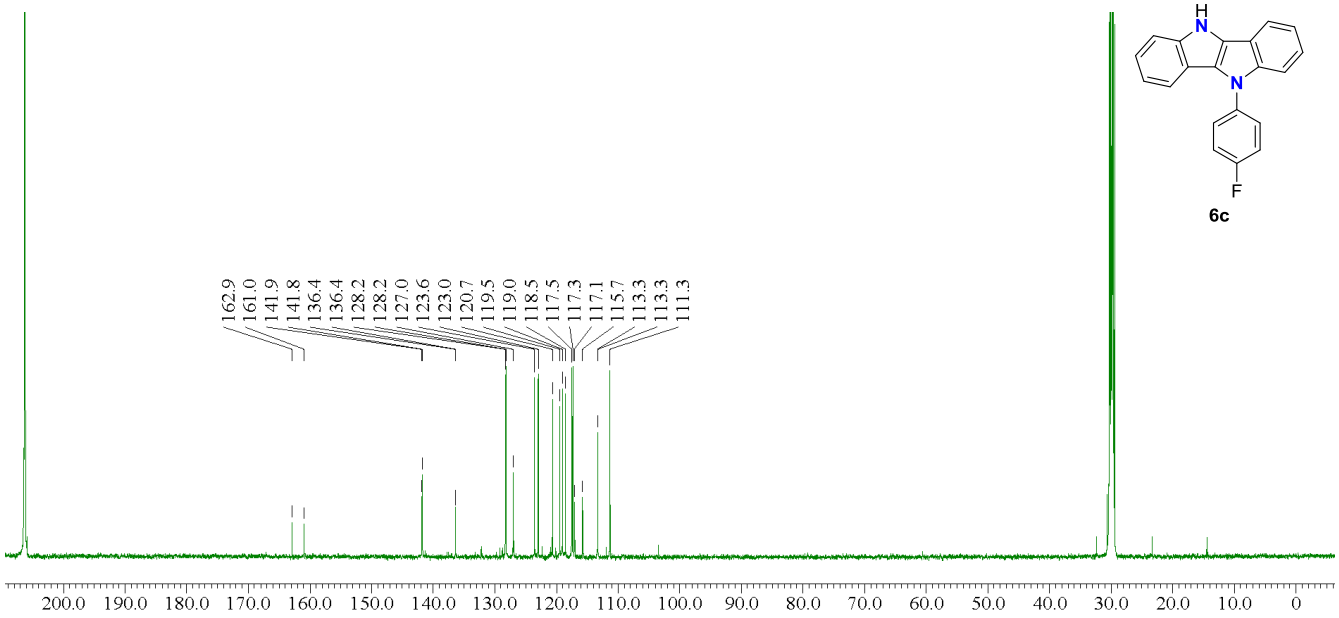
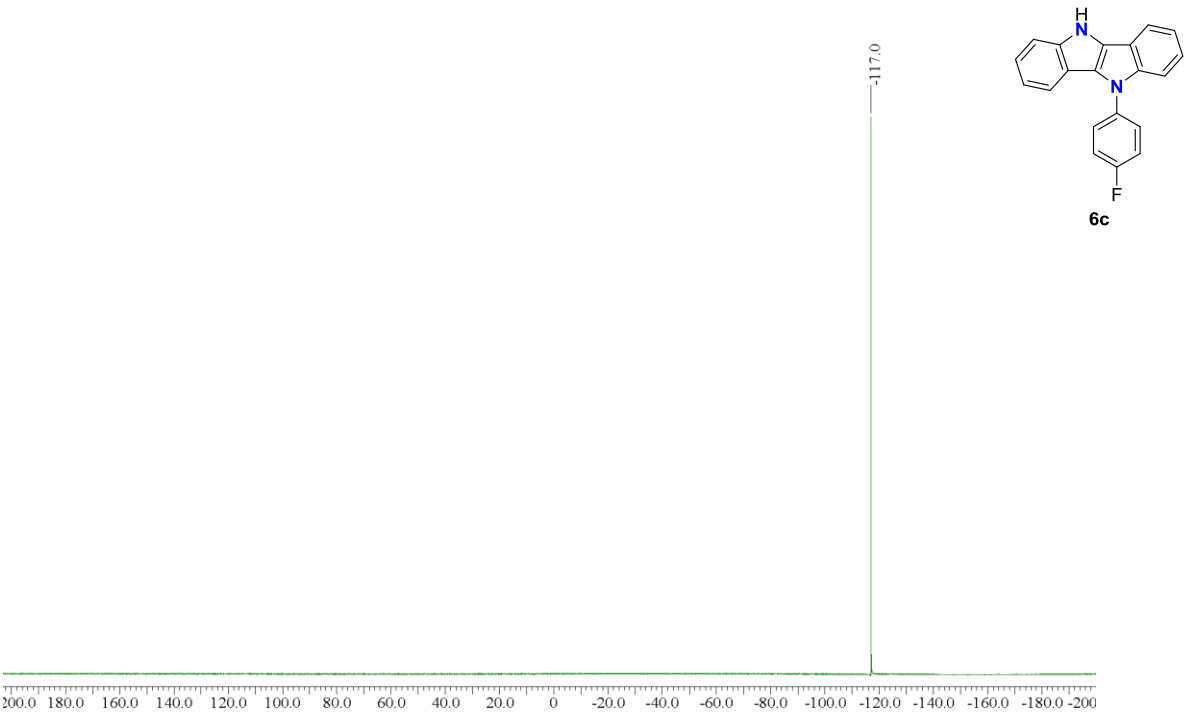
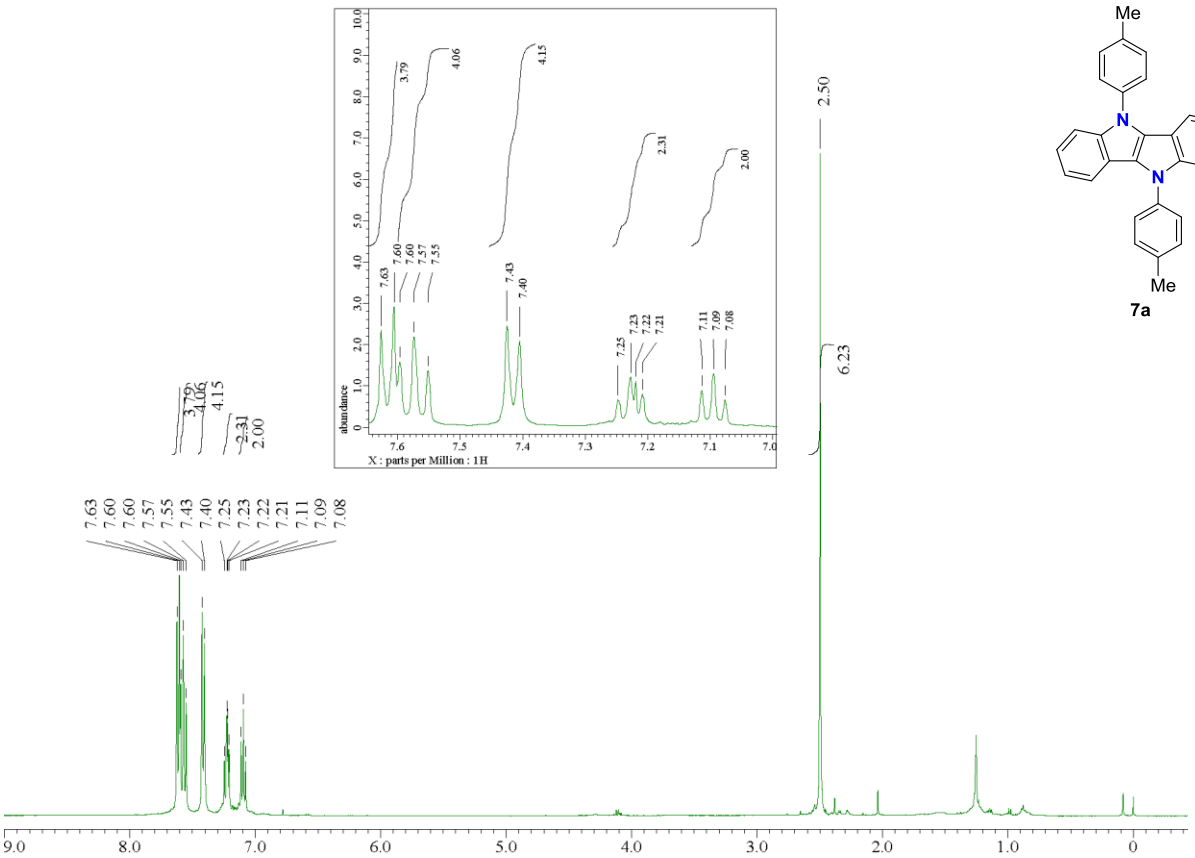


Figure S26. ^{13}C NMR spectrum of **6c** (acetone-d_6).



6c

Figure S27. ^{19}F NMR spectrum of **6c** (acetone-d_6).



7a

Figure S28. ^{1}H NMR spectrum of **7a** ($CDCl_3$).

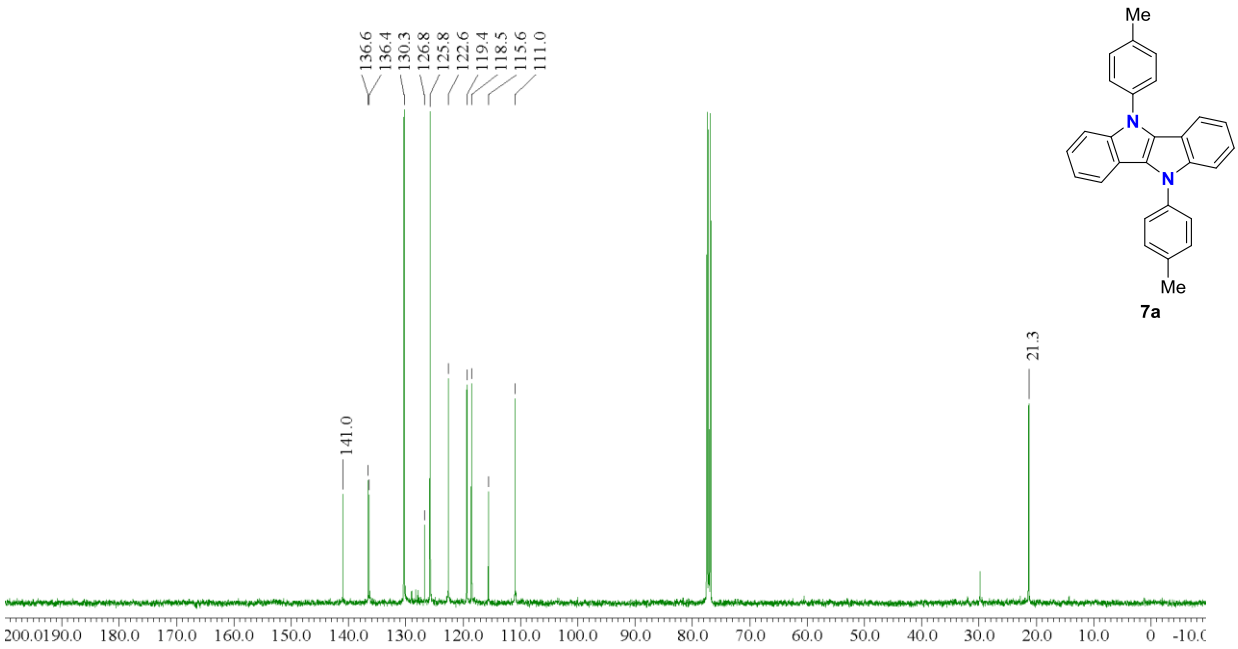


Figure S29. ^{13}C NMR spectrum of **7a** ($CDCl_3$).

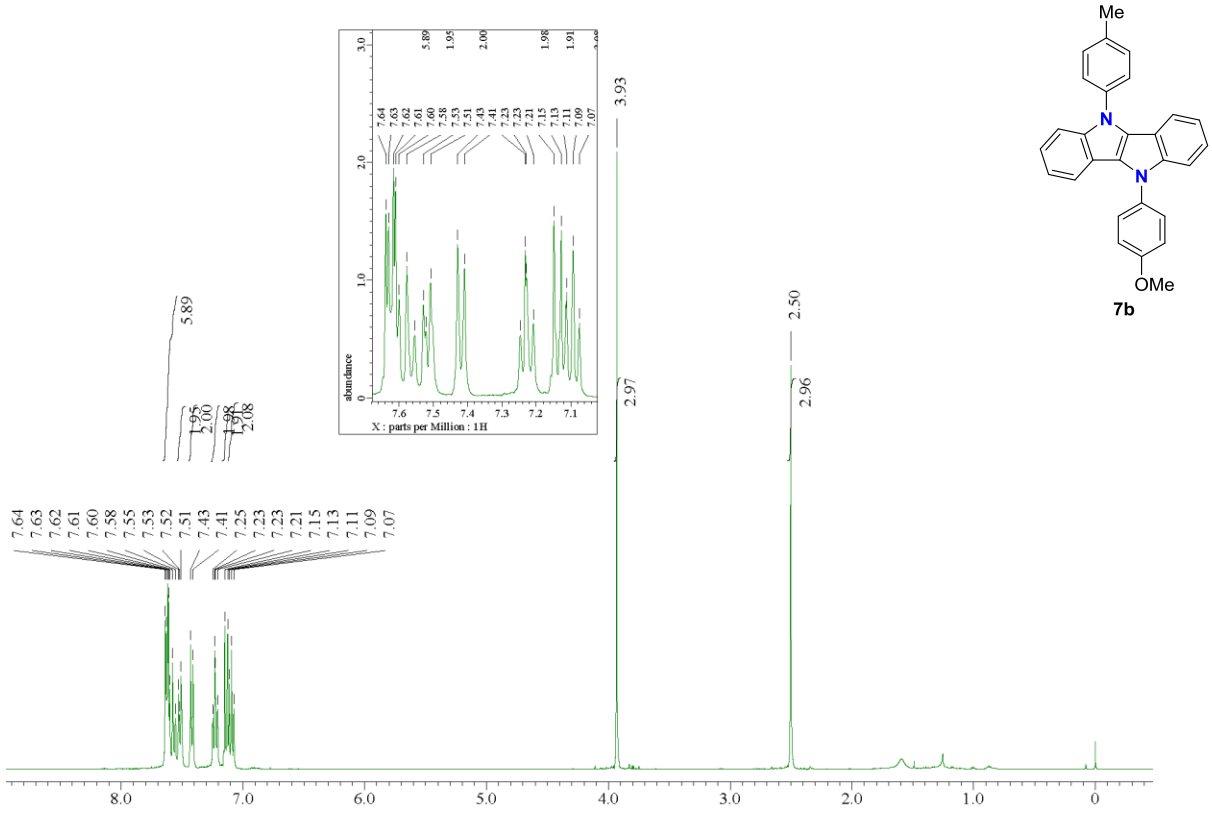


Figure S30. ^{1}H NMR spectrum of **7b** ($CDCl_3$).

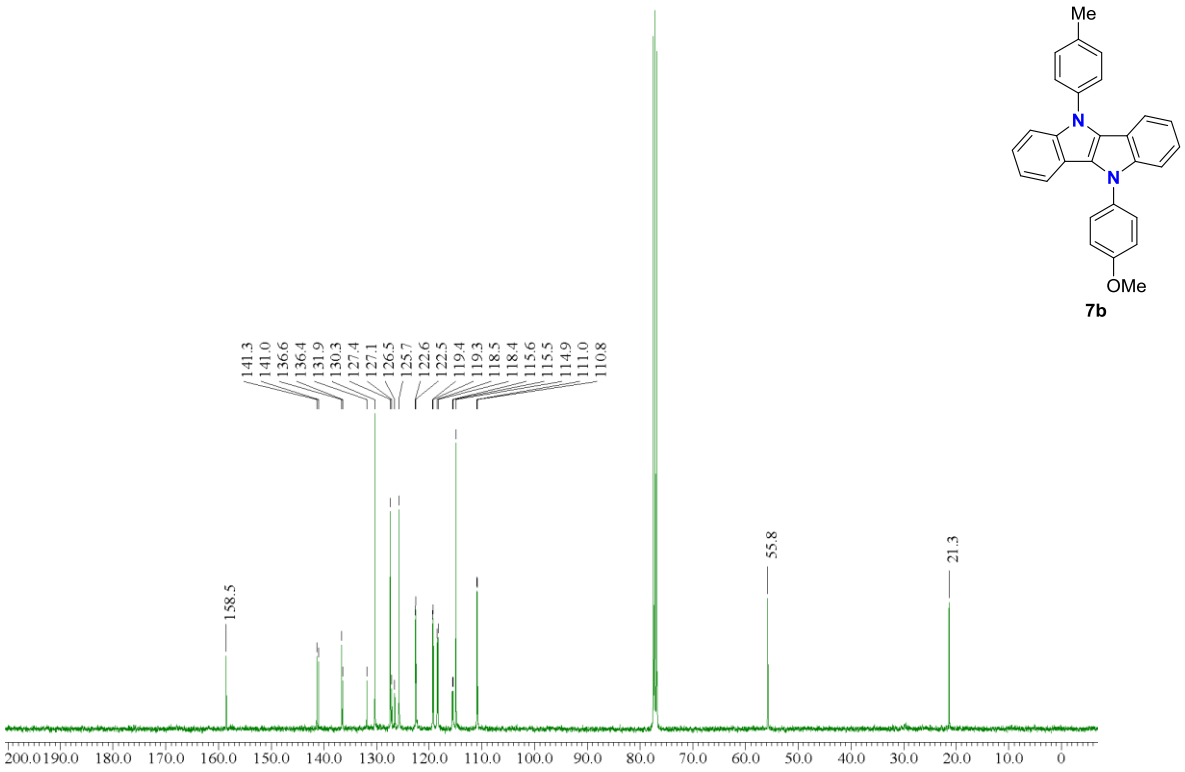
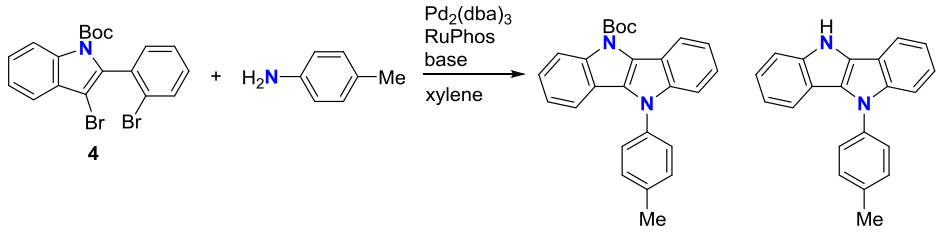


Figure S31. ^{13}C NMR spectrum of **7b** ($CDCl_3$).

Table S1. Optimization for Double *N*-Arylation of 4-Methylaniline with **4**[a]



entry	base	*T* (°C)	yield of **5a** (%)	yield of **6a** (%)
1	NaO^{t}Bu	120	21	42
2	NaO^{t}Bu	100	25	25
3	K_3PO_4	120	18	35

[a]Reaction conditions: **4** (1.0 equiv.), aniline (1.1 equiv.), $Pd_2(dba)_3$ (10 mol%), ligand (30 mol%), Base (3.0 equiv.), xylene, *T* (°C), 20 h.

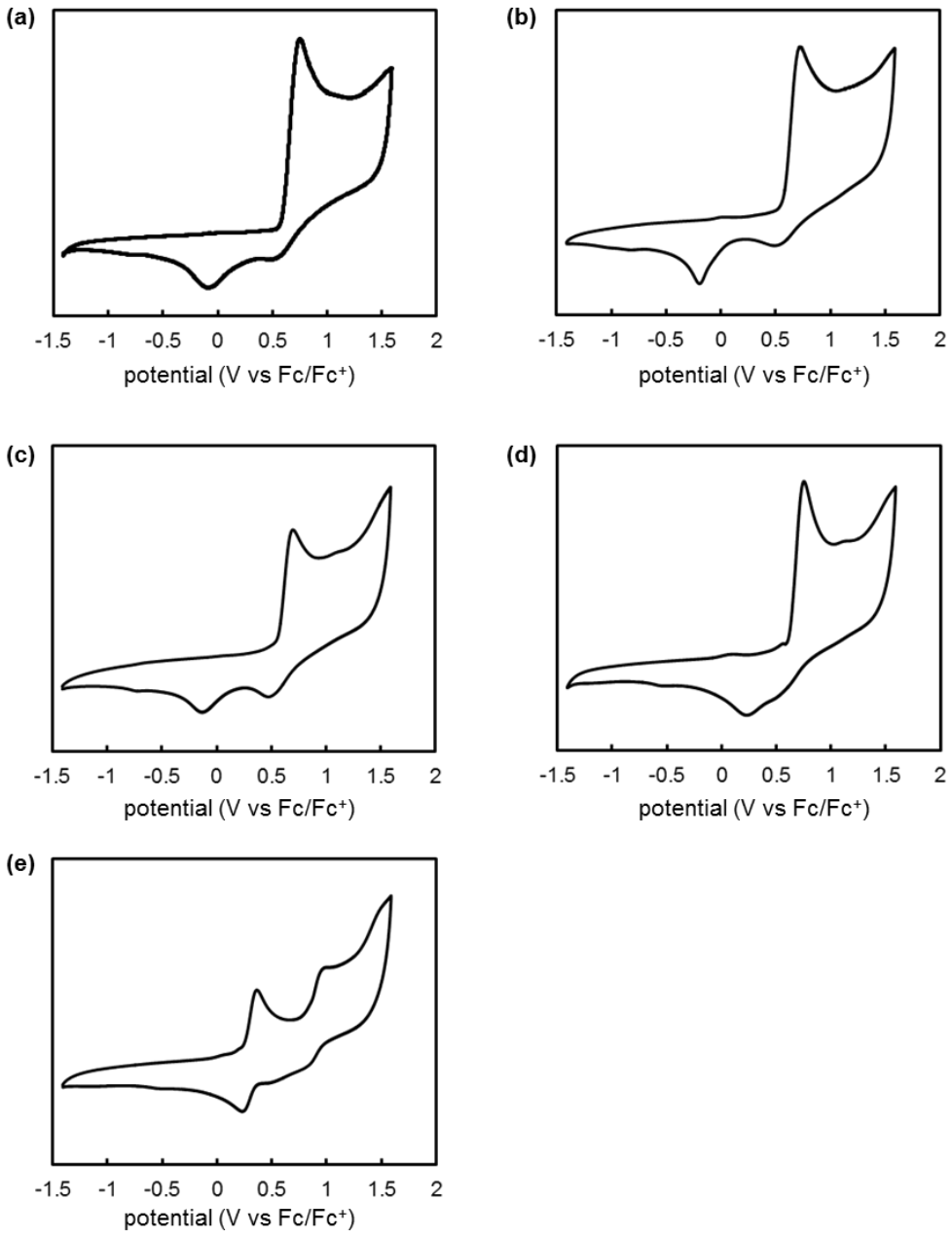


Figure S32. Cyclic voltammograms of (a) **2a**, (b) **2b**, (c) **2c**, (d) **2d**, and (e) **7a**

Table S2. Coordinates (Å) of the optimized structure for **2a** calculated at the B3LYP/6-31G(d) level of theory

atom	x	y	z
H	0.3686697	-4.4125	0.088951
C	1.0536495	-3.56998	0.07753
C	2.8497954	-1.35884	0.073294
C	0.5567559	-2.25745	0.039876
C	2.4280773	-3.76581	0.108887
C	3.3139972	-2.67097	0.114097
C	1.4684658	-1.14904	0.019137
H	2.8267747	-4.7759	0.137182
H	4.3847582	-2.85042	0.153809
H	3.5427879	-0.52447	0.091335
C	-0.7265339	-1.64645	0.034274
C	-0.6019929	-0.27798	0.008612
C	-1.9286639	0.271547	-0.05391
C	-4.7204402	0.454947	-0.14603
C	-2.761464	-0.88262	-0.04164
C	-2.5325589	1.536745	-0.1213
C	-3.9231111	1.612034	-0.16679
C	-4.1458819	-0.81626	-0.08297
H	-1.9282077	2.437765	-0.14266
H	-4.4012351	2.586086	-0.22086
H	-4.745773	-1.72039	-0.07064
H	-5.8019875	0.548089	-0.1819
N	0.7490474	0.057934	-0.01227
O	-2.034979	-2.05448	0.00888
C	1.2858782	1.371207	0.00651
C	2.3212403	3.972962	0.041817
C	0.7926423	2.311963	0.920544
C	2.296194	1.737318	-0.89247
C	2.8162128	3.031449	-0.86297
C	1.3039708	3.609624	0.927244
H	0.0217001	2.017542	1.625989
H	2.6531226	1.01541	-1.61966
H	3.5998204	3.307534	-1.56321
H	0.915323	4.333288	1.638519
H	2.7233506	4.981891	0.055578

Table S3. Coordinates (Å) of the optimized structure for **2b** calculated at the B3LYP/6-31G(d) level of theory

atom	x	y	z
H	3.175305	3.475598	0.090555
C	2.095145	3.364526	0.079367
C	-0.7389	3.072604	0.074042
C	1.517905	2.08514	0.041547
C	1.26218	4.475168	0.110459
C	-0.1387	4.328275	0.114674
C	0.089088	1.947096	0.021437
H	1.69489	5.471186	0.138845
H	-0.76827	5.212885	0.153384
H	-1.81895	2.972076	0.090194
C	1.991795	0.745262	0.033885
C	0.934463	-0.13262	0.007306
C	1.481255	-1.4602	-0.05376
C	3.320011	-3.56837	-0.1434
C	2.886745	-1.23595	-0.04155
C	1.010012	-2.78052	-0.11916
C	1.937366	-3.81955	-0.16332
C	3.816028	-2.26438	-0.08197
H	-0.05523	-2.98662	-0.13923
H	1.58423	-4.84567	-0.21548
H	4.880138	-2.05224	-0.0699
H	4.016864	-4.4008	-0.17844
N	-0.25707	0.586266	-0.01124
O	3.204603	0.105653	0.008958
C	-1.56649	0.03825	0.002374
C	-4.16265	-1.07484	0.029356
C	-1.89627	-0.96603	0.920806
C	-2.53636	0.484616	-0.90317
C	-3.81888	-0.06103	-0.87473
C	-3.17634	-1.51732	0.921596
H	-1.15304	-1.2993	1.638761
H	-2.27949	1.245024	-1.63361
H	-4.56253	0.299586	-1.58163
H	-3.41743	-2.29497	1.642686
C	-5.54295	-1.68968	0.025442
H	-5.82636	-2.04407	1.022301
H	-5.59335	-2.5524	-0.65254
H	-6.30082	-0.97204	-0.30631

Table S4. Coordinates (Å) of the optimized structure for **2c** calculated at the B3LYP/6-31G(d) level of theory

atom	x	y	z
H	-4.16783	2.731756	-0.21626
C	-3.09081	2.863147	-0.17088
C	-0.26406	3.210292	-0.07181
C	-2.24586	1.744201	-0.09202
C	-2.5243	4.130728	-0.19655
C	-1.12627	4.300218	-0.15332
C	-0.82332	1.929603	-0.02727
H	-3.16632	5.005031	-0.25647
H	-0.70875	5.302687	-0.18708
H	0.811707	3.350688	-0.04957
C	-2.40757	0.332455	-0.07028
C	-1.18119	-0.28429	0.007257
C	-1.41597	-1.69984	0.071605
C	-2.73136	-4.16883	0.134948
C	-2.83454	-1.79956	0.010352
C	-0.66034	-2.87803	0.171789
C	-1.32924	-4.10003	0.202483
C	-3.50745	-3.01176	0.037523
H	0.422725	-2.83658	0.22814
H	-0.75523	-5.01908	0.281646
H	-4.59089	-3.04688	-0.01191
H	-3.22259	-5.13723	0.161
N	-0.18308	0.683148	0.043945
O	-3.44521	-0.56534	-0.07344
C	1.217889	0.447106	0.083415
C	3.981149	-0.04371	0.16753
C	1.813165	-0.41134	-0.84346
C	2.017461	1.060157	1.060415
C	3.385447	0.826322	1.094288
C	3.185493	-0.67012	-0.79974
H	1.200913	-0.877	-1.6099
H	1.557401	1.709587	1.798369
H	4.015049	1.294844	1.843973
H	3.6187	-1.34363	-1.53005
O	5.328132	-0.2116	0.294399
C	5.986906	-1.07757	-0.61605
H	5.60778	-2.10554	-0.54189
H	7.041306	-1.06153	-0.33469
H	5.882796	-0.7286	-1.652

Table S5. Coordinates (Å) of the optimized structure for **2d** calculated at the B3LYP/6-31G(d) level of theory

atom	x	y	z
H	2.942663	3.647241	0.08829
C	1.87116	3.471519	0.078847
C	-0.94037	3.010401	0.077634
C	1.371683	2.159848	0.041849
C	0.972953	4.530182	0.111076
C	-0.41655	4.299884	0.1171
C	-0.04604	1.937242	0.024489
H	1.345195	5.550299	0.138812
H	-1.09789	5.145153	0.156405
H	-2.01264	2.845853	0.095431
C	1.924808	0.850326	0.032225
C	0.922284	-0.08947	0.006264
C	1.546937	-1.38205	-0.05418
C	3.509024	-3.37622	-0.14231
C	2.936496	-1.07395	-0.04299
C	1.155991	-2.72844	-0.11791
C	2.143961	-3.70993	-0.1611
C	3.925836	-2.04476	-0.08294
H	0.105445	-2.99994	-0.1385
H	1.852869	-4.75535	-0.21203
H	4.97525	-1.76899	-0.07175
H	4.254485	-4.16534	-0.17671
N	-0.31027	0.55762	-0.00873
O	3.173265	0.2845	0.006642
C	-1.58491	-0.06492	0.003688
C	-4.06655	-1.30546	0.02308
C	-1.86015	-1.0757	0.935012
C	-2.56879	0.314108	-0.91974
C	-3.82088	-0.29864	-0.90413
C	-3.10169	-1.7097	0.939608
H	-1.10207	-1.35637	1.659285
H	-2.34545	1.077098	-1.65788
H	-4.59537	-0.01915	-1.61056
H	-3.33302	-2.49488	1.651652
F	-5.27276	-1.90785	0.032456

Table S6. Coordinates (Å) of the optimized structure for **7a** calculated at the B3LYP/6-31G(d) level of theory

atom	x	y	z
H	2.259919	2.815261	-0.10569
C	1.177834	2.897867	-0.09644
C	-1.65615	3.136298	-0.06425
C	0.378948	1.742082	-0.06276
C	0.564805	4.145155	-0.11417
C	-0.83728	4.26208	-0.08874
C	-1.04918	1.876955	-0.07226
H	1.17643	5.042704	-0.14265
H	-1.29322	5.248361	-0.08774
H	-2.73626	3.234628	-0.037
C	0.609269	0.330264	-0.00742
C	-0.60979	-0.32661	-0.00621
C	-0.37968	-1.73845	-0.06136
C	0.836473	-4.25846	-0.08936
C	1.04839	-1.87337	-0.07369
C	-1.17866	-2.89421	-0.09275
C	-0.56568	-4.14151	-0.11144
C	1.655419	-3.13268	-0.06692
H	-2.26077	-2.81151	-0.09927
H	-1.17737	-5.03907	-0.13809
H	2.735614	-3.23091	-0.04232
H	1.292372	-5.24476	-0.08929
N	-1.64348	0.608516	-0.05261
C	-3.03302	0.327291	0.002114
C	-5.79842	-0.24529	0.116301
C	-3.53992	-0.52624	0.990266
C	-3.91259	0.893965	-0.92846
C	-5.2769	0.616254	-0.85791
C	-4.90339	-0.81136	1.034654
H	-2.86382	-0.95244	1.725096
H	-3.52348	1.538556	-1.71022
H	-5.94664	1.068165	-1.58608
H	-5.28037	-1.47486	1.809737
C	-7.27246	-0.57509	0.158685
H	-7.6047	-0.79604	1.178772
H	-7.50182	-1.4564	-0.45556
H	-7.87983	0.252629	-0.22285
N	1.642808	-0.60499	-0.05532
C	3.032657	-0.32523	-0.0014
C	5.797814	0.24976	0.105882
C	3.540673	0.531354	0.983272
C	3.910206	-0.88945	-0.93564
C	5.273978	-0.60856	-0.87015
C	4.903759	0.819657	1.02268
H	2.864821	0.964356	1.714339
H	3.518347	-1.52786	-1.7211
H	5.941168	-1.05262	-1.60547
H	5.280557	1.491341	1.790691
C	7.280083	0.533108	0.181718
H	7.7927	-0.19355	0.826535
H	7.477824	1.528253	0.594216
H	7.750109	0.477544	-0.8061

Table S7. The selected absorption peaks of **2** and **7a** calculated by TD–DFT method[a]

	electron transition	transition energy (eV)	wavelength (nm)	main transition configuration (CI expansion coefficient)	oscillator strength *f*
2a	$S_0 \rightarrow S_1$	3.91	317	**HOMO → LUMO (0.658)**	0.2401
				HOMO → LUMO+1 (0.143)	
				HOMO–1 → LUMO (−0.164)	
2b	$S_0 \rightarrow S_1$	3.90	318	**HOMO → LUMO (0.661)**	0.2413
				HOMO–1 → LUMO (−0.181)	
2c	$S_0 \rightarrow S_1$	3.88	319	**HOMO → LUMO (0.658)**	0.2089
				HOMO–1 → LUMO (−0.200)	
2d	$S_0 \rightarrow S_1$	3.90	318	**HOMO → LUMO (0.493)**	0.1189
				HOMO → LUMO+1 (0.478)	
				HOMO–1 → LUMO (−0.119)	
	$S_0 \rightarrow S_2$	3.95	314	**HOMO → LUMO+1 (0.516)**	0.1282
				HOMO → LUMO (−0.444)	
				HOMO–1 → LUMO (0.126)	
7a	$S_0 \rightarrow S_1$	3.61	344	**HOMO → LUMO (0.680)**	0.2447
				HOMO–1 → LUMO (−0.141)	

[a]Calculated at the B3LYP/6-31G(d) level of theory.

Table S8. HOMO and LUMO energy levels of **2** and **7a** calculated by DFT method[a]

	HOMO (eV)	LUMO (eV)	HOMO–LUMO energy gap (eV)
2a	–5.15	–0.90	4.25
2b	–5.11	–0.85	4.25
2c	–5.06	–0.81	4.25
2d	–5.22	–0.96	4.26
7a	–4.71	–0.66	4.05

[a]Calculated at the B3LYP/6-31G(d) level of theory.

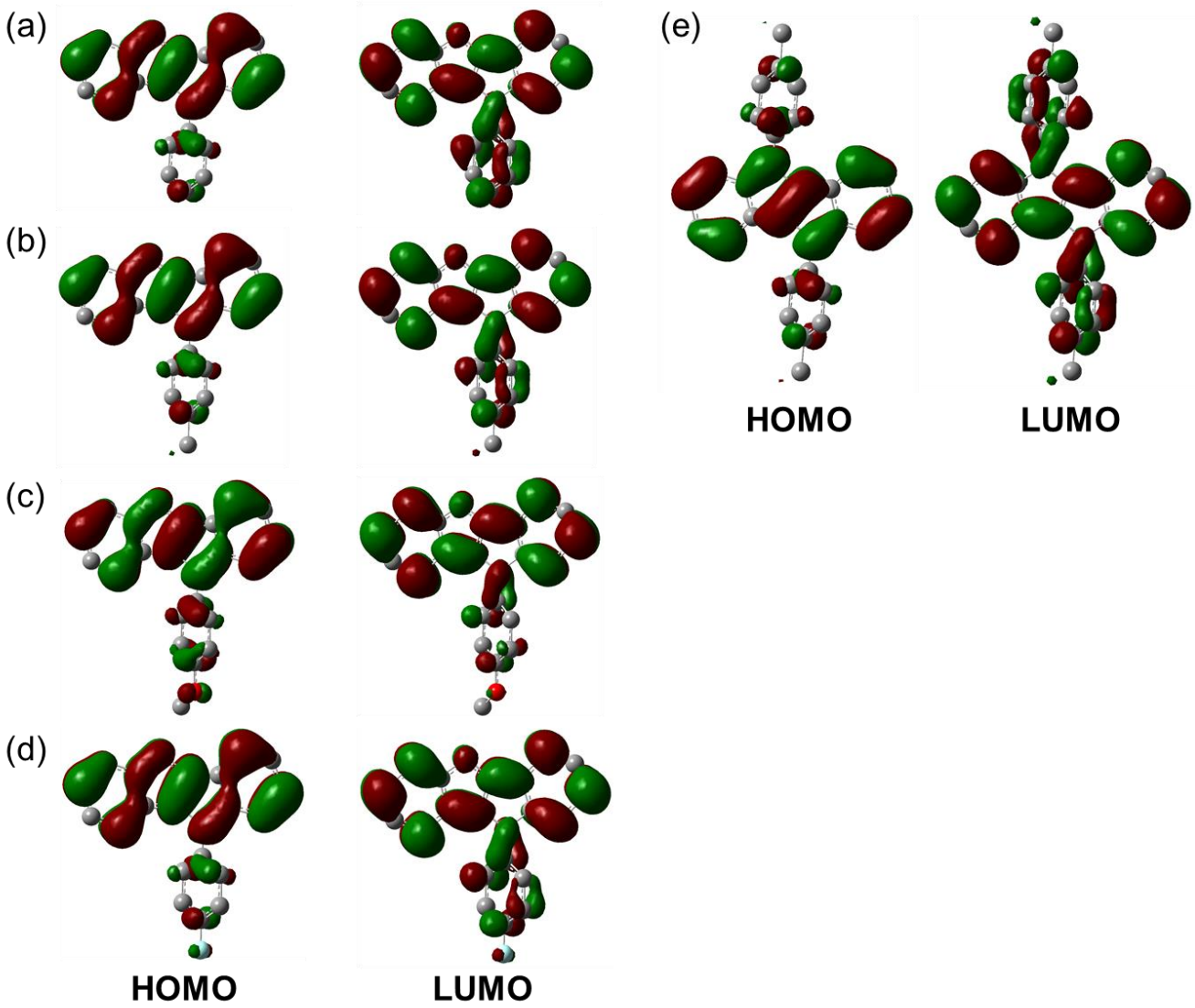


Figure S33. The HOMOs and LUMOs of (a) **2a**, (b) **2b**, (c) **2c**, (d) **2d**, and (e) **7a** calculated by DFT method at the B3LYP /6-31G(d) level of theory.