

Iodo-Cycloisomerization of Aryl(indol-3-yl)methane-tethered-propargyl alcohols to 3-Iodocarbazoles via Selective 1,2-Alkyl-Migration

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I. X-ray data and crystal structures

The compounds **2k**, **2t** & **4d** were further confirmed by Single Crystal X-ray analysis.

X-ray data of Compound **2k**:

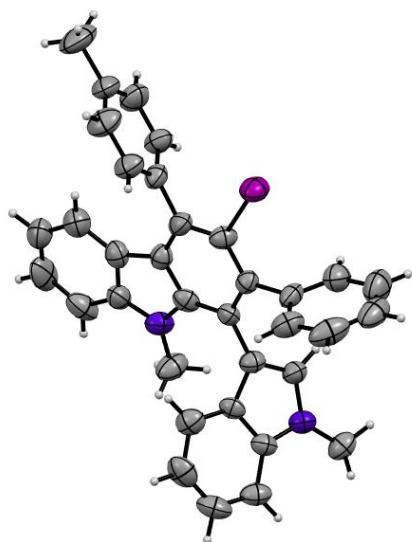


Figure S1. ORTEP representation of compound **2k** and thermal ellipsoids are drawn with 50% probability.

Table S1. Crystal data and structure refinement for **2k.**

Identification code	shelx	
Empirical formula	C ₃₆ H ₂₇ IN ₂ O	
Formula weight	630.49	
Temperature	293(2) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 15.8788(8) Å b = 9.3570(4) Å c = 21.2905(9) Å	a= 90°. b= 92.120(4)°. g = 90°.
Volume	3161.1(2) Å ³	
Z	4	
Density (calculated)	1.325 Mg/m ³	
Absorption coefficient	8.175 mm ⁻¹	
F(000)	1272	
Crystal size	0.200 x 0.200 x 0.180 mm ³	

Theta range for data collection	5.090 to 66.577°.
Index ranges	-16<=h<=18, -6<=k<=11, -25<=l<=22
Reflections collected	11205
Independent reflections	5563 [R(int) = 0.0886]
Completeness to theta = 66.577°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.3208 and 0.2917
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	5563 / 0 / 364
Goodness-of-fit on F ²	0.995
Final R indices [I>2sigma(I)]	R1 = 0.0746, wR2 = 0.1787
R indices (all data)	R1 = 0.1362, wR2 = 0.2304
Extinction coefficient	n/a
Largest diff. peak and hole	0.772 and -0.475 e.Å ⁻³

X-ray data of Compound 2t:

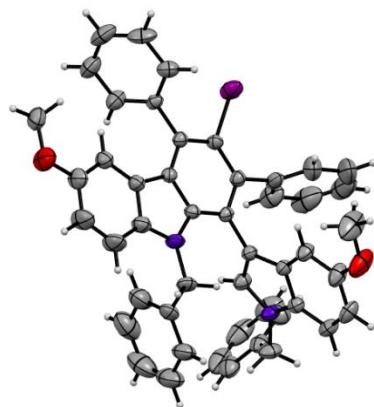


Figure S2. ORTEP representation of compound **2t** and thermal ellipsoids are drawn with 50% probability.

Table S2.Crystal data and structure refinement for 2t.

Identification code	ysr15_a
Empirical formula	C ₄₈ H ₃₇ IN ₂ O ₂
Formula weight	800.70
Temperature	299(2) K
Wavelength	0.71073 Å

Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	$a = 11.5071(18) \text{ \AA}$	$a = 90^\circ$
	$b = 38.741(5) \text{ \AA}$	$b = 113.662(6)^\circ$
	$c = 9.4077(14) \text{ \AA}$	$\gamma = 90^\circ$
Volume	$3841.3(10) \text{ \AA}^3$	
Z	4	
Density (calculated)	1.385 Mg/m^3	
Absorption coefficient	0.876 mm^{-1}	
F(000)	1632	
Crystal size	$0.6 \times 0.4 \times 0.14 \text{ mm}^3$	
Theta range for data collection	$2.44 \text{ to } 25.00^\circ$	
Index ranges	$-13 \leq h \leq 13, -46 \leq k \leq 46, -11 \leq l \leq 11$	
Reflections collected	37647	
Independent reflections	6744 [$R(\text{int}) = 0.0436$]	
Completeness to theta = 25.00°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7452 and 0.5388	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6744 / 0 / 478	
Goodness-of-fit on F^2	0.992	
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0409, wR_2 = 0.0914$	
R indices (all data)	$R_1 = 0.0556, wR_2 = 0.0976$	
Largest diff. peak and hole	0.764 and $-1.136 \text{ e.\AA}^{-3}$	

X-ray data of Compound 4d:

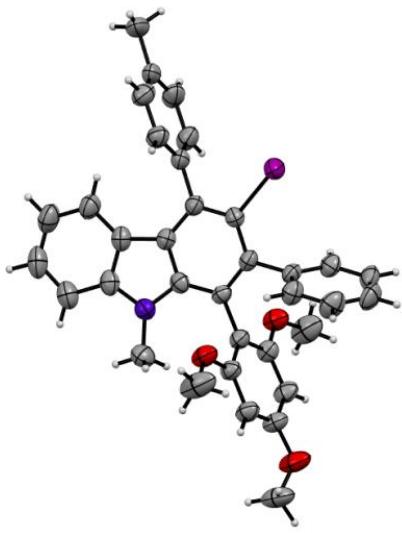


Figure S3. ORTEP representation of compound **4d** and thermal ellipsoids are drawn with 50% probability.

Table S3. Crystal data and structure refinement for 4d.

Identification code	shelx		
Empirical formula	$C_{34}H_{29}INO_4$		
Formula weight	642.48		
Temperature	293(2) K		
Wavelength	1.54184 Å		
Crystal system	Monoclinic		
Space group	I 2/a		
Unit cell dimensions	$a = 14.6664(12)$ Å	$a = 90^\circ$	
	$b = 10.0810(6)$ Å	$b = 97.759(7)^\circ$	
	$c = 40.221(2)$ Å	$g = 90^\circ$	
Volume	$5892.4(7)$ Å ³		
Z	8		
Density (calculated)	1.448 Mg/m ³		
Absorption coefficient	8.847 mm ⁻¹		
F(000)	2600		
Theta range for data collection	4.438 to 72.087°.		
Index ranges	$-17 \leq h \leq 14, -12 \leq k \leq 11, -34 \leq l \leq 49$		
Reflections collected	11753		
Independent reflections	5662 [R(int) = 0.0470]		
Completeness to theta = 67.684°	99.9 %		

Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	5662 / 0 / 366
Goodness-of-fit on F ²	1.026
Final R indices [I>2sigma(I)]	R1 = 0.0490, wR2 = 0.1282
R indices (all data)	R1 = 0.0664, wR2 = 0.1439
Extinction coefficient	n/a
Largest diff. peak and hole	0.842 and -0.578 e. \AA^{-3}

II. Computational Studies

Computational Methods:

The geometries of all the structures in Figure S1 and Figure S2 were fully optimized with the Gaussian 09 package¹ by using the Becke three-parameter exchange functional² and Lee, Yang, and Parr² (B3LYP) nonlocal correlation functional, with the 6-31G* basis set for the main group atoms and the LANL2DZ electron core potential and its associated basis set for Iodine. The stationary points were characterized by means of harmonic normal vibrational mode analysis and are reported in the supporting information Table S2. The local minimum are characterized by the absence of imaginary frequencies and for all the transition structures, the vibration related to the imaginary frequency corresponds to the nuclear motion along the reaction coordinate. The optimized geometries and vibrational harmonic frequencies have been employed to calculate the partition function and Gibbs Free Energies at 1 atm and 298.15 K using transition state theory. Single point high level energy corrections have been calculated at Truhlar's M06 functional³ with the def2-tzvpp basis set employing Gaussian09 suite of programs.⁴ The effect of solvent has been included using the solvation model based on density (SMD)⁵ with ethyl acetate as solvent as implemented in the Gaussian 09 package.

References:

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Detailed mechanism and study of 1,2-migration:

The detailed energies and free energy corrections in atomic units are reported in Table S1 for prototype starting systems (**1**) as depicted in schemes **2**. The system **1a** as depicted in Figure S1 prefers 1,2-alkyl migration over 1,2-vinyl migration. The 1,2-alkyl migration reaction follows a two-step mechanism through two transition states (**TS1-1a** and **TS2-1a**) separated by an intermediate local minimum (**Int-1a**). The activation barrier for the 1,2-alkyl migration is 11.82 kcal/mol and is lower compared to 19.23 kcal/mol, for the single step 1,2-Vinyl migration. Also, the final product of the 1,2-alkyl migration (**B-1a**) is also energetically preferred over 1,2-vinyl migration (**C-1a**) by 9.98 kcal/mol.

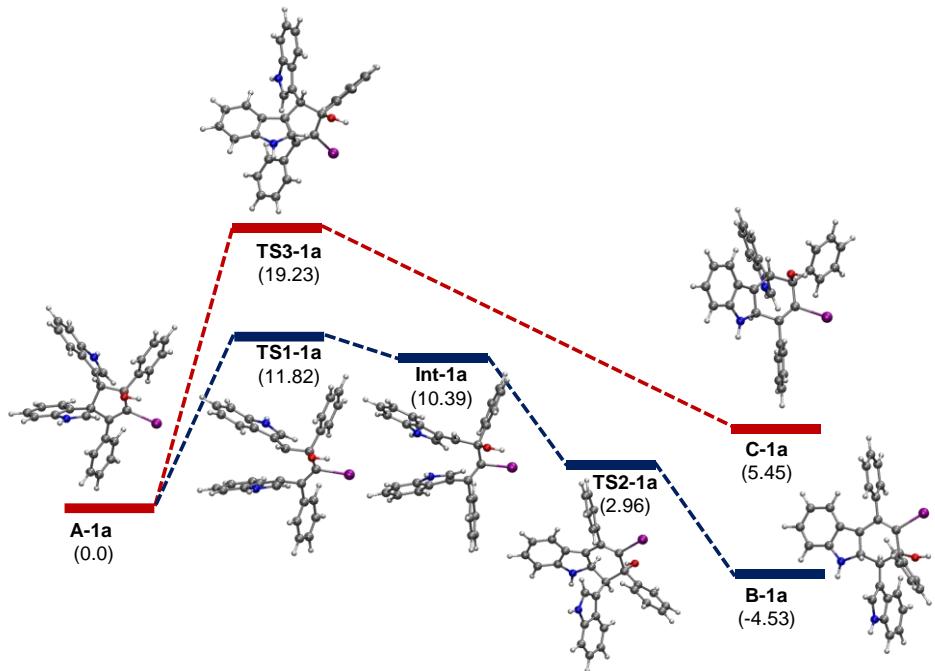


Figure S4 Energy profile of substrate **1a**

Table S4. The summary of the energy profile followed in the 1,2-alkyl and 1,2-vinyl migration reactions followed by systems **1a**.

System	E	Elect+ ZPE	G	H	E-Solvent	G-Final
Reaction-1:						
1,2-alkyl Migration						
A-1a	-1429.68342	-1429.20614	-1429.26775	-1429.17639	-1429.71409	-1429.29842
TS1-1a	-1429.67486	-1429.19919	-1429.26066	-1429.16955	-1429.69378	-1429.27959
Int-1a	-1429.67733	-1429.20155	-1429.26429	-1429.17115	-1429.69490	-1429.28187
TS2-1a	-1429.68283	-1429.20640	-1429.26840	-1429.17691	-1429.70813	-1429.29370
B-1a	-1429.70335	-1429.22574	-1429.28750	-1429.19599	-1429.72149	-1429.30564
D-1a	-1429.32644	-1428.86139	-1428.92340	-1428.83167	-1429.31722	-1428.91419
1a	-1352.94430	-1352.50653	-1352.56723	-1352.47818	-1352.91330	-1352.53623
Reaction- 1: 1,2- vinyl Migration						
TS3-1a	-1429.65603	-1429.18047	-1429.24159	-1429.15102	-1429.68222	-1429.26777
C-1a	-1429.68131	-1429.20453	-1429.26802	-1429.17449	-1429.70304	-1429.28974

Table S5. Energies (in a. u.) and Cartesian coordinates (in Å) of all the stationary points discussed in the text. All geometry optimization calculations have been performed at B3LYP/6-31G* level of theory and single-point energy calculations at M062X/def2-SVP level of theory.

<u>Reaction Type 1</u>			
<u>1. A-1a, Energy=-1429.68342</u>			
C	5.513537	-0.019308	0.525979
C	4.155239	-0.063148	0.811503
C	3.241300	-0.225570	-0.245038
C	3.742282	-0.334579	-1.568422
C	5.108612	-0.292905	-1.863752
C	5.985925	-0.133404	-0.798218
C	1.800644	-0.326315	-0.325359
C	1.494975	-0.476342	-1.664011
N	2.649604	-0.476169	-2.405829
C	0.887656	-0.244171	0.848288
C	0.018476	1.143868	0.863256
C	-1.288740	0.689869	0.173616
C	-1.411581	-0.648332	0.273750
C	-0.242146	-1.326885	0.991579
C	-0.204950	1.467655	2.302710
N	0.366325	2.598875	2.624944
C	0.958733	3.226928	1.494984
C	0.737491	2.390667	0.392003
C	1.181873	2.815307	-0.855692
C	1.843760	4.045917	-0.948602
C	2.063111	4.849421	0.177687
C	1.614135	4.449170	1.438206
O	-0.541288	-1.336527	2.405304
H	1.019166	2.212120	-1.740235
H	2.194081	4.386335	-1.917981
H	2.581772	5.796658	0.071752
H	1.767599	5.065699	2.318554
H	0.387948	2.982265	3.566177
H	-0.698170	0.823672	3.019325
H	1.495981	-0.303552	1.754607
C	0.188086	-2.719852	0.550946
H	-1.161131	-2.068203	2.569213
H	2.696635	-0.645207	-3.399774
H	0.537859	-0.591214	-2.150637
H	5.471439	-0.384978	-2.883529
H	7.054467	-0.099108	-0.987741
H	3.813343	0.020581	1.840277
H	6.228219	0.100789	1.334783
C	0.890809	-3.523222	1.461395
C	1.335542	-4.793911	1.094280
C	1.083980	-5.281517	-0.188335
C	0.388458	-4.487895	-1.102391
C	-0.052329	-3.216316	-0.736688
H	1.088445	-3.152918	2.462105
H	1.876877	-5.401584	1.813583
H	1.424563	-6.272554	-0.473606
H	0.180883	-4.860735	-2.101322
H	-0.599948	-2.621300	-1.459151
I	-3.228162	-1.704103	-0.057813
C	-2.228526	1.679729	-0.392727
C	-2.628512	2.808655	0.341405

C	-2.720632	1.518259	-1.698876
C	-3.512422	3.737452	-0.204695
H	-2.271378	2.953741	1.358022
C	-3.596516	2.452992	-2.248387
H	-2.410120	0.659508	-2.285898
C	-3.997600	3.563100	-1.502609
H	-3.823552	4.596089	0.383087
H	-3.965298	2.313294	-3.260277
H	-4.682309	4.289450	-1.930199

2. TS1-1a, Energy=-1429.67486

C	5.038264	1.005454	1.785306
C	3.694703	0.898270	1.433659
C	3.203524	1.186365	0.144141
C	4.101939	1.608247	-0.840661
C	5.451309	1.718685	-0.508578
C	5.914758	1.420967	0.785431
C	1.750893	0.978166	0.181194
C	1.462581	0.555309	1.504573
N	2.593489	0.521604	2.216849
C	0.885329	1.158341	-0.887274
C	-0.621079	1.347384	-0.952628
O	-0.887409	1.450912	-2.359701
C	-1.442387	0.184256	-0.383880
C	-1.032036	-1.110369	-0.393509
C	0.257771	-1.474596	-1.008063
C	0.711513	-1.086025	-2.271276
N	1.947813	-1.626606	-2.499465
C	2.335926	-2.382322	-1.403494
C	1.286700	-2.311268	-0.446468
C	1.436388	-2.986776	0.781788
C	2.600501	-3.707565	1.008955
C	3.623774	-3.767159	0.038843
C	3.508846	-3.105973	-1.179725
H	0.640174	-2.971564	1.519165
H	2.723975	-4.249493	1.941816
H	4.518188	-4.347526	0.244607
H	4.297908	-3.155540	-1.924170
H	2.449996	-1.568356	-3.373586
H	0.191486	-0.514379	-3.025712
H	5.388871	0.780863	2.788020
H	6.971697	1.520277	1.010957
H	6.160412	2.045831	-1.262671
H	3.764548	1.851123	-1.844275
H	1.349981	1.508688	-1.806054
H	0.514763	0.276098	1.938932
H	-1.835185	1.649947	-2.461968
C	-0.822433	2.723160	-0.276253
H	2.649019	0.241089	3.188302
C	-0.721538	3.882838	-1.056650
C	-0.839470	5.143837	-0.466549
C	-1.046244	5.258543	0.906766
C	-1.134784	4.103883	1.692703
C	-1.014570	2.847145	1.107073
H	-0.564060	3.796377	-2.125947
H	-0.769362	6.033526	-1.085367
H	-1.139779	6.237984	1.366371

H	-1.308014	4.185390	2.761881
H	-1.107807	1.961185	1.727723
I	-3.528973	0.671733	-0.087924
C	-1.810605	-2.249588	0.176033
C	-2.021383	-3.405194	-0.592749
C	-2.295560	-2.214986	1.493606
C	-2.728651	-4.485922	-0.067711
H	-1.640224	-3.449602	-1.608733
C	-2.986073	-3.303637	2.023875
H	-2.130749	-1.332103	2.104627
C	-3.210527	-4.439330	1.242053
H	-2.899037	-5.366163	-0.680632
H	-3.351044	-3.263874	3.046175
H	-3.754314	-5.284756	1.653260

3. Int-1a, Energy=-1429.67733

C	5.038264	1.005454	1.785306
C	3.694703	0.898270	1.433659
C	3.203524	1.186365	0.144141
C	4.101939	1.608247	-0.840661
C	5.451309	1.718685	-0.508578
C	5.914758	1.420967	0.785431
C	1.750893	0.978166	0.181194
C	1.462581	0.555309	1.504573
N	2.593489	0.521604	2.216849
C	0.885329	1.158341	-0.887274
C	-0.621079	1.347384	-0.952628
O	-0.887409	1.450912	-2.359701
C	-1.442387	0.184256	-0.383880
C	-1.032036	-1.110369	-0.393509
C	0.257771	-1.474596	-1.008063
C	0.711513	-1.086025	-2.271276
N	1.947813	-1.626606	-2.499465
C	2.335926	-2.382322	-1.403494
C	1.286700	-2.311268	-0.446468
C	1.436388	-2.986776	0.781788
C	2.600501	-3.707565	1.008955
C	3.623774	-3.767159	0.038843
C	3.508846	-3.105973	-1.179725
H	0.640174	-2.971564	1.519165
H	2.723975	-4.249493	1.941816
H	4.518188	-4.347526	0.244607
H	4.297908	-3.155540	-1.924170
H	2.449996	-1.568356	-3.373586
H	0.191486	-0.514379	-3.025712
H	5.388871	0.780863	2.788020
H	6.971697	1.520277	1.010957
H	6.160412	2.045831	-1.262671
H	3.764548	1.851123	-1.844275
H	1.349981	1.508688	-1.806054
H	0.514763	0.276098	1.938932
H	-1.835185	1.649947	-2.461968
C	-0.822433	2.723160	-0.276253
H	2.649019	0.241089	3.188302
C	-0.721538	3.882838	-1.056650
C	-0.839470	5.143837	-0.466549
C	-1.046244	5.258543	0.906766

C	-1.134784	4.103883	1.692703
C	-1.014570	2.847145	1.107073
H	-0.564060	3.796377	-2.125947
H	-0.769362	6.033526	-1.085367
H	-1.139779	6.237984	1.366371
H	-1.308014	4.185390	2.761881
H	-1.107807	1.961185	1.727723
I	-3.528973	0.671733	-0.087924
C	-1.810605	-2.249588	0.176033
C	-2.021383	-3.405194	-0.592749
C	-2.295560	-2.214986	1.493606
C	-2.728651	-4.485922	-0.067711
H	-1.640224	-3.449602	-1.608733
C	-2.986073	-3.303637	2.023875
H	-2.130749	-1.332103	2.104627
C	-3.210527	-4.439330	1.242053
H	-2.899037	-5.366163	-0.680632
H	-3.351044	-3.263874	3.046175
H	-3.754314	-5.284756	1.653260

4. TS2-1a, Energy=-1429.68283

C	-5.720173	1.091564	0.359807
C	-4.426785	0.789076	0.761875
C	-3.362081	1.031146	-0.126512
C	-3.651489	1.571668	-1.406991
C	-4.953607	1.877814	-1.818803
C	-5.981076	1.631420	-0.917956
N	-2.447709	1.710626	-2.070089
C	-1.421086	1.282030	-1.260897
C	-1.929454	0.853315	-0.052640
C	-1.210217	0.338504	1.164244
C	-0.525038	-1.088582	1.097838
O	-0.295633	-1.561004	2.435117
C	0.893709	-1.017809	0.485909
C	1.631653	0.132276	0.314121
C	1.055592	1.366129	0.764323
C	1.370561	2.707822	0.506934
C	0.342419	3.514343	1.133587
N	-0.522319	2.723225	1.792428
C	-0.134737	1.331686	1.676079
C	0.331797	4.918438	1.005733
C	1.340820	5.491307	0.260554
C	2.366402	4.719570	-0.366516
C	2.393044	3.352208	-0.253170
C	-1.455579	-2.078426	0.398042
H	-1.967369	0.220295	1.948677
H	-0.396538	-0.841849	3.075535
H	0.230785	1.002045	2.662457
H	-1.375673	3.037638	2.233287
H	-0.438297	5.519285	1.477988
H	1.361249	6.571462	0.146705
H	3.173330	2.767103	-0.722480
H	3.134482	5.232900	-0.935208
H	-0.404381	1.309190	-1.625125
H	-2.337667	2.048999	-3.014108
H	-5.154215	2.289359	-2.803947

H	-7.004839	1.854295	-1.202889
H	-4.251677	0.355783	1.743715
H	-6.549564	0.904275	1.035221
C	-2.277646	-2.912341	1.163796
C	-3.171237	-3.786532	0.541255
C	-3.249374	-3.839867	-0.849918
C	-2.427447	-3.012958	-1.619541
C	-1.539587	-2.136484	-0.999909
H	-2.201681	-2.892612	2.244462
H	-3.799254	-4.431898	1.148598
H	-3.941080	-4.523639	-1.333295
H	-2.475852	-3.052009	-2.703959
H	-0.905875	-1.502413	-1.611878
I	1.800021	-2.891814	0.117972
C	2.993251	0.168830	-0.305919
C	4.124292	0.370931	0.498106
C	3.148425	0.044657	-1.694197
C	5.393217	0.438165	-0.078604
H	4.012979	0.463427	1.575205
C	4.417628	0.121037	-2.268909
H	2.277108	-0.118078	-2.323065
C	5.541384	0.316974	-1.462333
H	6.264752	0.582802	0.552979
H	4.528679	0.022631	-3.344777
H	6.529243	0.370771	-1.910194

5. B-1a.com, Energy=-1429.70335

C	-3.707198	0.752960	-0.927168
C	-2.688832	0.689869	0.096496
C	-3.343425	0.811050	1.308310
N	-4.693146	0.951247	1.092932
C	-4.952212	0.918621	-0.266263
C	-3.686531	0.677386	-2.331936
C	-4.885058	0.782143	-3.024287
C	-6.110317	0.954846	-2.345423
C	-6.163574	1.023066	-0.958991
C	-1.217196	0.552547	-0.143116
C	-0.656330	-0.933581	-0.148790
C	0.880554	-0.910018	-0.276919
C	1.701815	0.153621	-0.000370
C	1.076412	1.365084	0.457596
C	-0.364609	1.353198	0.862904
N	-0.694765	2.757499	0.988571
C	0.393792	3.524672	0.815309
C	1.537360	2.688816	0.506209
C	0.504016	4.929604	0.874920
C	1.745436	5.475084	0.626710
C	2.888348	4.674811	0.320539
C	2.800147	3.307042	0.255867
O	-1.222526	-1.462308	-1.332360
H	-0.993183	0.936099	-1.145344
C	-1.083913	-1.723327	1.097094
H	-1.196310	-2.433789	-1.294265
H	3.668923	2.702744	0.031045
H	3.838591	5.166364	0.140867
H	1.863148	6.554259	0.666820

H	-0.354923	5.550255	1.107448
H	-1.637285	3.082042	1.157447
H	-2.957051	0.778502	2.318404
H	-5.389419	1.038444	1.817982
H	-7.107507	1.148756	-0.436207
H	-7.030130	1.030187	-2.917613
H	-4.884812	0.723306	-4.108632
H	-2.753817	0.515970	-2.863974
H	-0.458232	0.871670	1.850062
C	-2.322261	-2.382993	1.087217
C	-2.752247	-3.099076	2.205026
C	-1.960206	-3.156697	3.353376
C	-0.730186	-2.498148	3.375375
C	-0.292381	-1.791762	2.253093
H	-2.952893	-2.327960	0.206280
H	-3.709002	-3.612556	2.175855
H	-2.295081	-3.717200	4.221227
H	-0.099552	-2.547365	4.258365
H	0.687222	-1.322281	2.276424
I	1.728175	-2.732206	-0.970532
C	3.183585	0.147924	-0.208059
C	4.044462	0.027424	0.891977
C	3.722572	0.308303	-1.492736
C	5.427640	0.056283	0.707270
H	3.634156	-0.095555	1.891047
C	5.105709	0.343866	-1.672703
H	3.060077	0.403642	-2.348525
C	5.959687	0.217098	-0.574168
H	6.087725	-0.047718	1.563384
H	5.515271	0.467275	-2.670946
H	7.036038	0.240802	-0.716731

II. Reaction Type 2

6. TS3-1a, Energy=-1429.65603

C	-5.098502	2.489472	-0.612237
C	-3.868767	1.925459	-0.919513
C	-2.978665	1.621240	0.127703
C	-3.371799	1.902350	1.463324
C	-4.611150	2.471200	1.779028
C	-5.466266	2.759400	0.723822
C	-1.652928	1.053263	0.187238
C	-1.303929	1.007847	1.519382
N	-2.327272	1.519797	2.284358
C	-0.854257	0.598620	-1.004444
C	0.534272	1.208949	-1.074870
C	1.539886	0.683029	-1.975258
C	1.607352	-0.253131	-0.473103
C	0.667141	-1.224895	-0.400186
C	-0.673536	-0.975162	-1.130592
N	2.541590	1.620344	-2.089585
C	2.287876	2.698787	-1.261244
C	1.027583	2.499544	-0.633633
C	0.511310	3.509811	0.202024
C	1.265889	4.656981	0.396331
C	2.530650	4.814277	-0.210552
C	3.064350	3.840155	-1.044034

O	-0.416230	-1.231861	-2.522036
H	-1.389996	0.900232	-1.912347
H	1.356810	-0.026869	-2.769800
H	3.422728	1.452997	-2.555633
H	-0.498434	-2.191139	-2.663625
C	-1.908144	-1.747525	-0.681031
H	4.031186	3.968403	-1.520090
H	3.095985	5.723472	-0.029285
H	-0.459721	3.398585	0.665682
H	0.878457	5.451645	1.025737
H	-2.325617	1.577784	3.291558
H	-0.400662	0.649201	1.992851
H	-4.894379	2.678354	2.807143
H	-6.436852	3.200472	0.929874
H	-3.606399	1.720101	-1.954278
H	-5.794237	2.727550	-1.411251
C	-2.163227	-2.071604	0.659313
C	-3.329248	-2.745427	1.018053
C	-4.266901	-3.100497	0.046348
C	-4.033401	-2.767176	-1.286852
C	-2.865964	-2.091987	-1.647351
H	-1.456453	-1.799665	1.433652
H	-3.503374	-2.994646	2.060736
H	-5.173656	-3.627308	0.328549
H	-4.759551	-3.026199	-2.051704
H	-2.709716	-1.820913	-2.686245
I	1.154970	-3.110270	0.439367
C	2.905212	-0.137216	0.221805
C	2.970048	0.425963	1.505315
C	4.084807	-0.602527	-0.384691
C	4.191389	0.512913	2.174050
H	2.065332	0.798415	1.975894
C	5.301177	-0.522617	0.289749
H	4.042057	-1.057613	-1.371274
C	5.356332	0.038098	1.569237
H	4.231299	0.949325	3.167576
H	6.204449	-0.901332	-0.179250
H	6.305387	0.101783	2.093180

7. C-1a, Energy=-1429.68131

C	-5.765455	1.002687	0.443926
C	-4.455952	0.899637	-0.005171
C	-3.460067	0.471732	0.891214
C	-3.830562	0.160532	2.225821
C	-5.148419	0.261003	2.684621
C	-6.108279	0.687218	1.775757
C	-2.037066	0.243166	0.782957
C	-1.611138	-0.173803	2.027676
N	-2.680151	-0.224432	2.888833
C	-1.237499	0.498433	-0.474115
C	-0.400792	1.709033	-0.312078
C	0.750788	1.646910	0.634542
C	1.590044	0.370215	0.434040
C	1.070365	-0.659140	-0.256741
C	-0.273645	-0.652293	-1.013596
N	1.471023	2.888295	0.361117
C	0.818139	3.625092	-0.548853

C	-0.361741	2.908194	-0.993958
C	1.140634	4.890839	-1.084159
C	0.295282	5.395015	-2.049754
C	-0.866613	4.697824	-2.516418
C	-1.197904	3.471686	-2.006821
O	0.014876	-0.192509	-2.338844
C	-1.045332	-1.967133	-1.036060
H	2.326930	3.147093	0.833005
H	-2.076357	2.934835	-2.348442
H	-1.480989	5.160371	-3.281270
H	0.518526	6.366341	-2.482276
H	2.016159	5.438929	-0.752790
H	-1.941685	0.643566	-1.296617
H	0.390114	1.680973	1.672907
H	0.501562	-0.898482	-2.800095
H	-2.638670	-0.547116	3.844076
H	-0.628042	-0.469951	2.366227
H	-5.412255	0.012997	3.708740
H	-7.142216	0.776107	2.094936
H	-4.215009	1.140640	-1.037670
H	-6.543182	1.328726	-0.240138
C	-1.804464	-2.281801	-2.171819
C	-2.568808	-3.448930	-2.214854
C	-2.591668	-4.312229	-1.119643
C	-1.846641	-4.001129	0.020211
C	-1.082598	-2.836666	0.063248
H	-1.794810	-1.612243	-3.025581
H	-3.145020	-3.680679	-3.105896
H	-3.184327	-5.221765	-1.152478
H	-1.855086	-4.669688	0.876200
H	-0.499756	-2.618335	0.951522
I	2.325994	-2.370182	-0.652873
C	2.936216	0.445619	1.075143
C	3.057457	0.316544	2.467363
C	4.080537	0.725887	0.311493
C	4.305154	0.435784	3.081809
H	2.179131	0.099292	3.070899
C	5.325150	0.850291	0.929497
H	3.994664	0.828919	-0.766477
C	5.440145	0.703595	2.314096
H	4.389458	0.316552	4.157979
H	6.205730	1.056409	0.328074
H	6.410711	0.796316	2.792304

III. NMR Spectra of Synthesized Compounds

SYDJ- 105

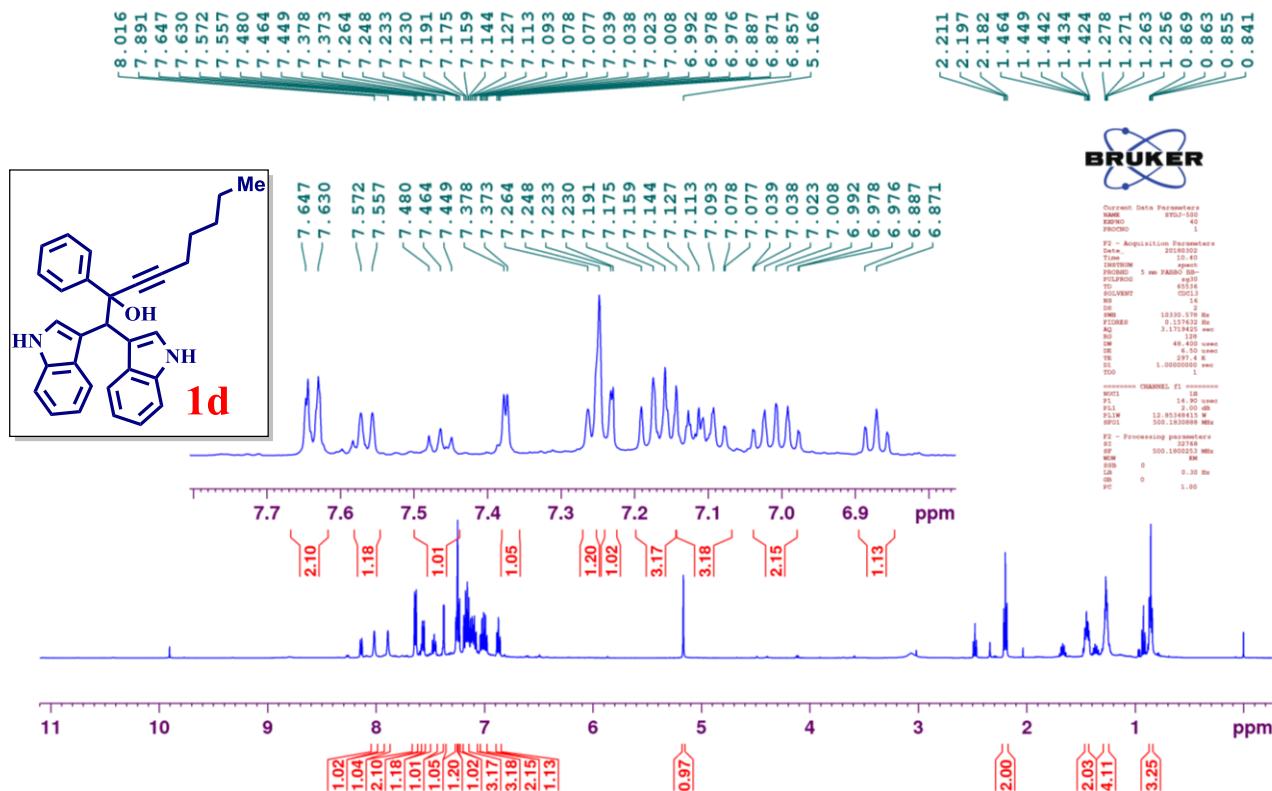


Figure S5 ^1H NMR in CDCl_3

SYDJ- 105

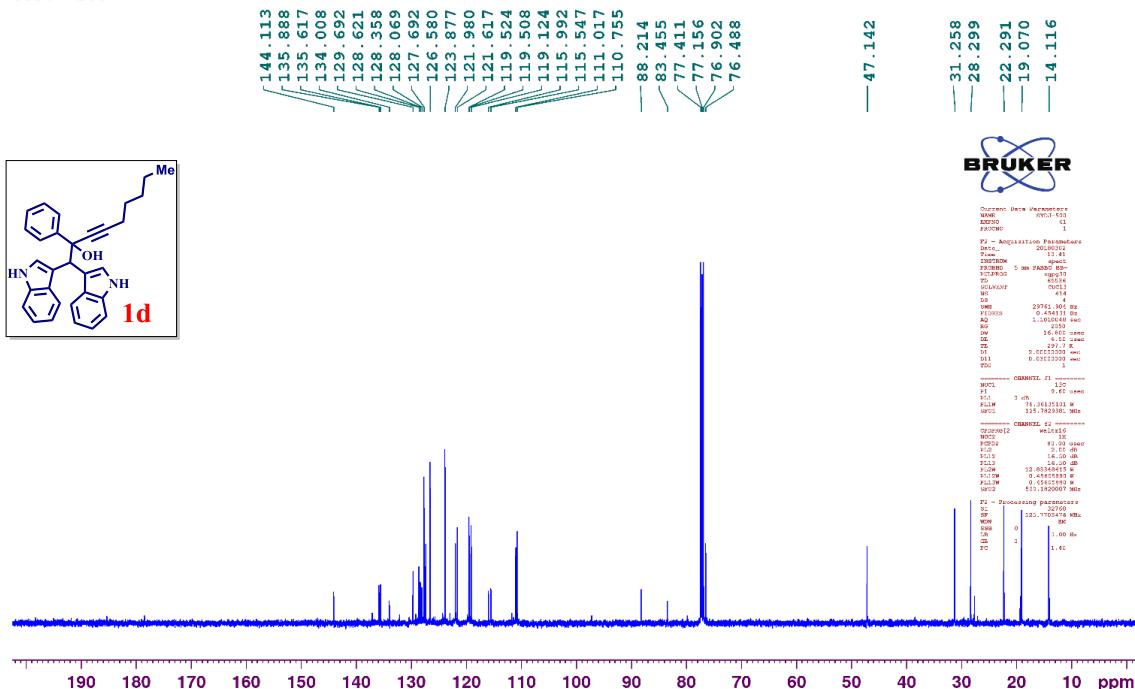
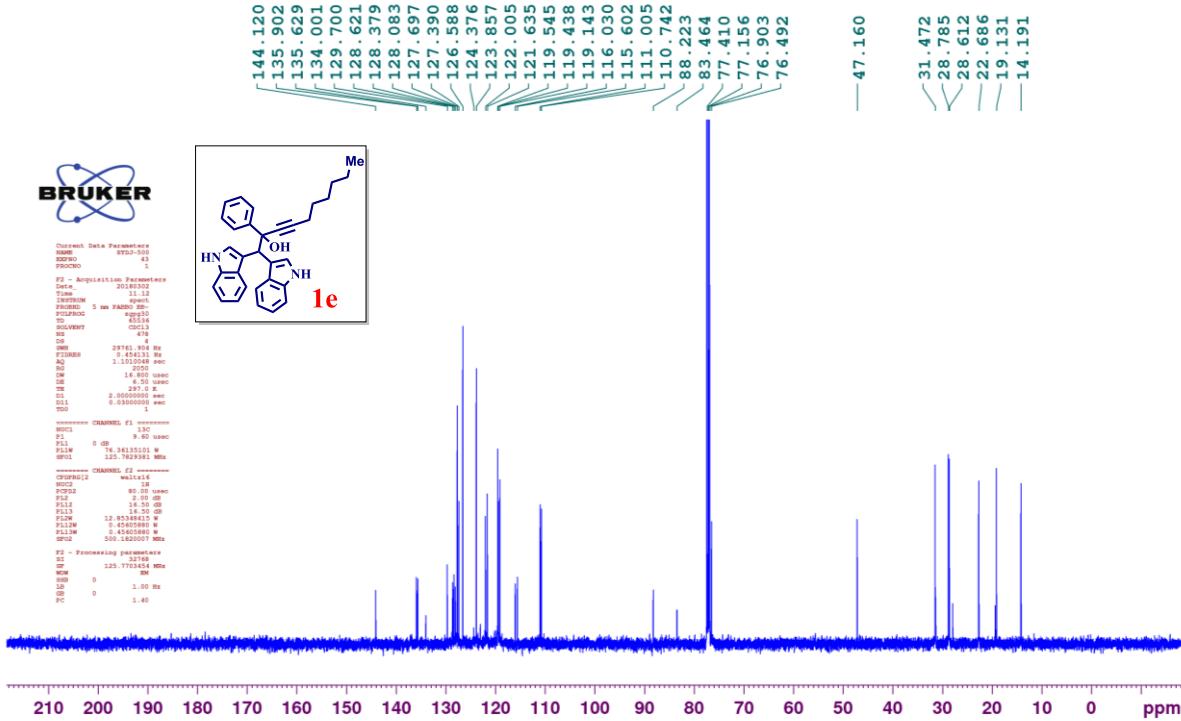
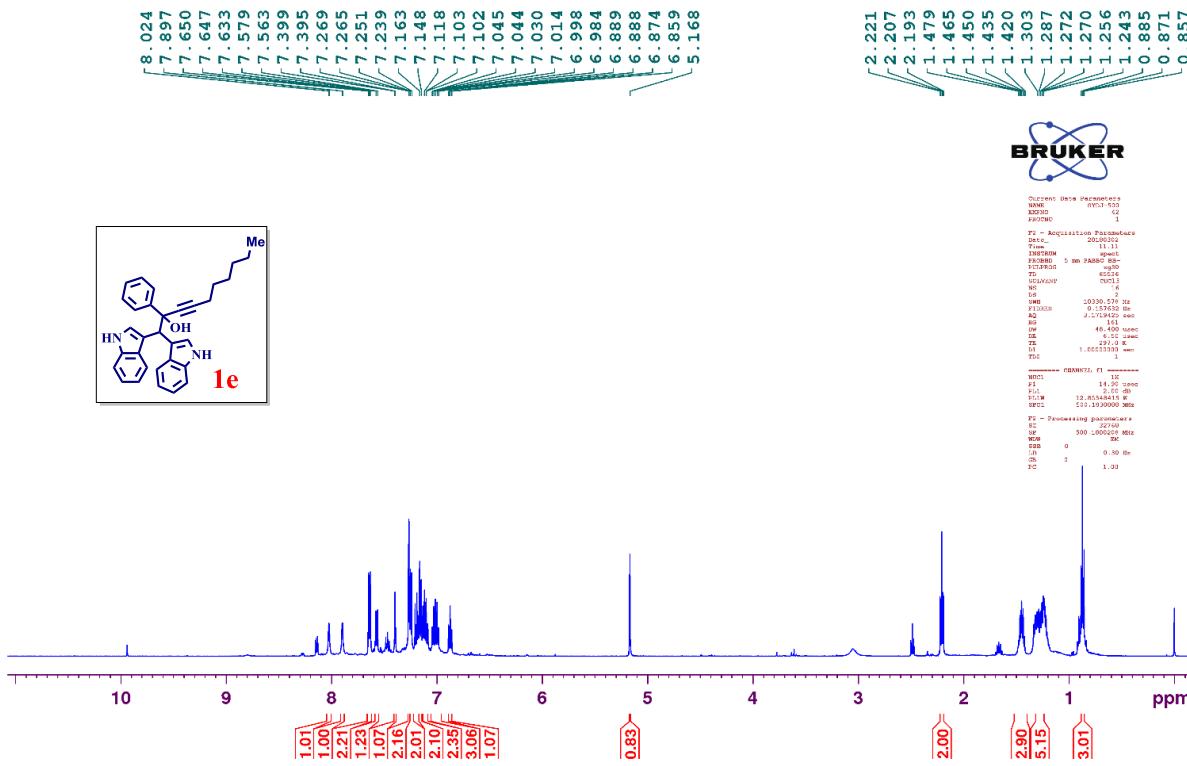


Figure S6 ^{13}C NMR in CDCl_3



SYDJ-92

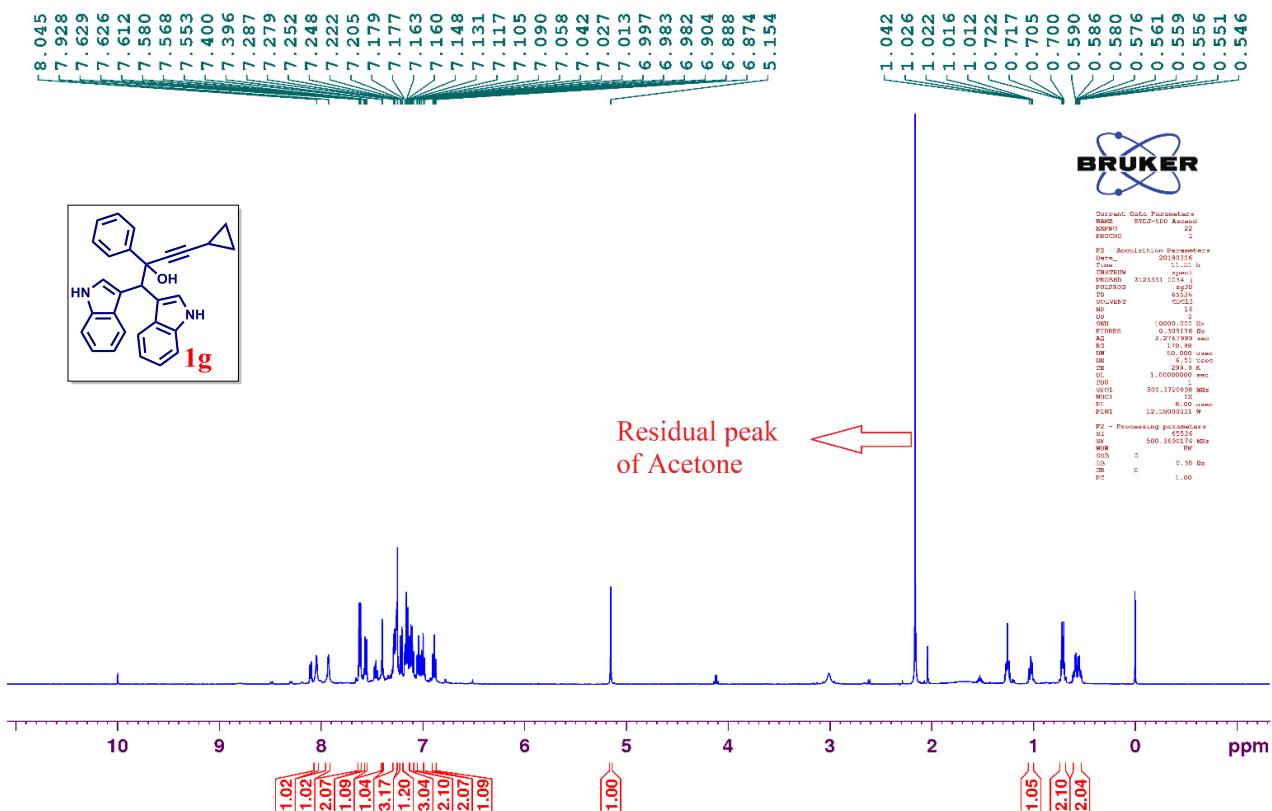


Figure S9 ^1H NMR in CDCl_3

SYDJ-92

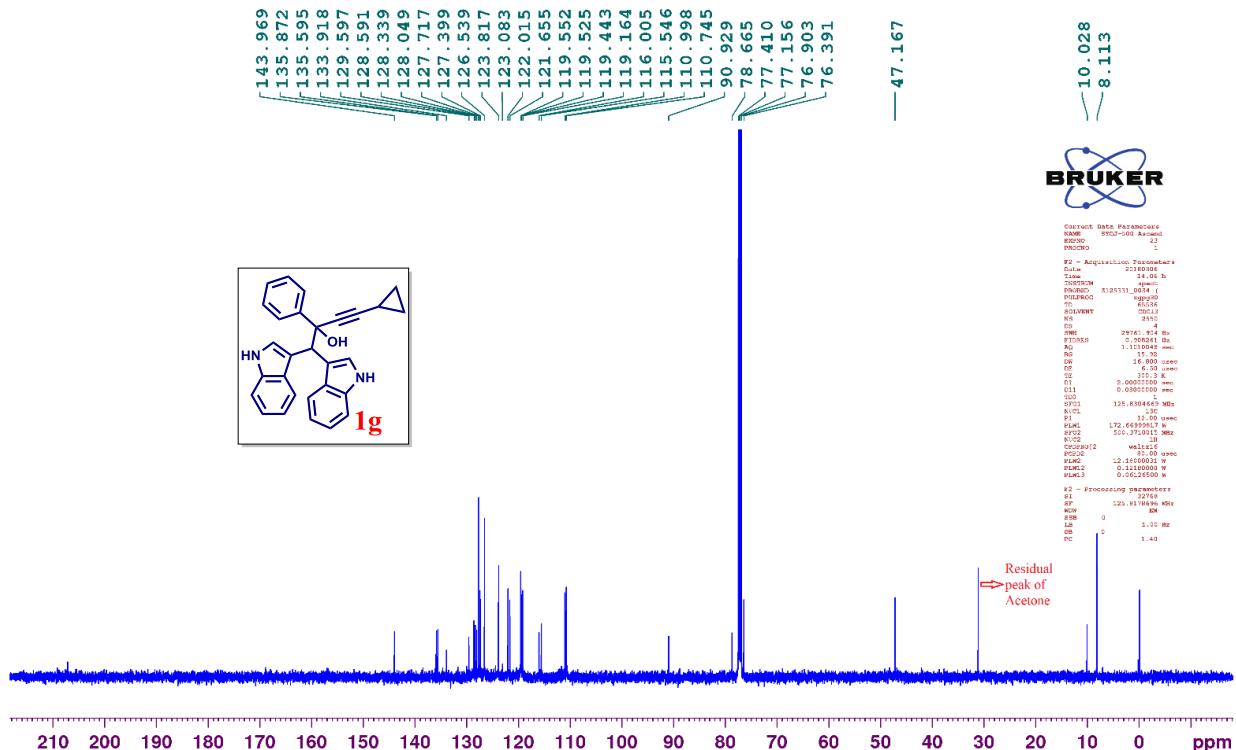


Figure S10 ^{13}C NMR in CDCl_3

SYDJ-108a

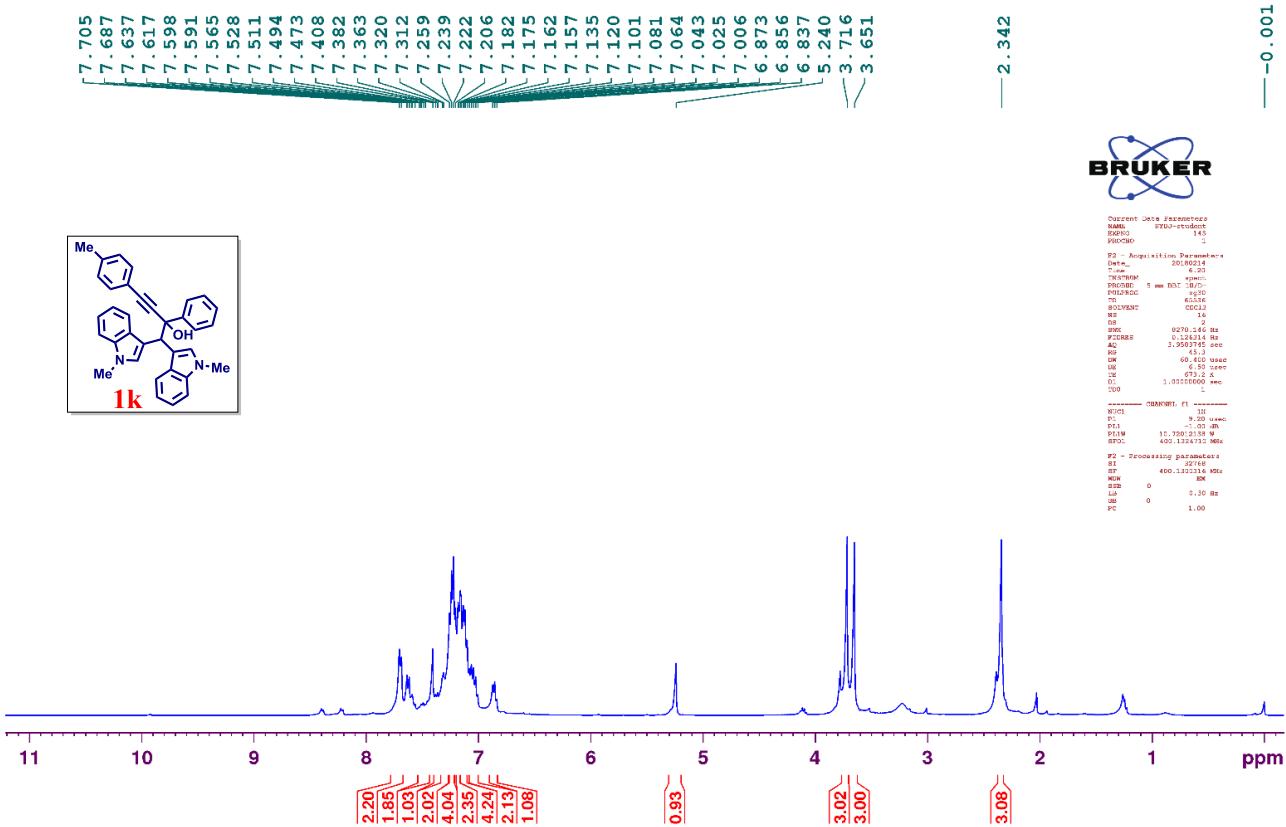


Figure S11 ^1H NMR in CDCl_3

SYDJ-108a

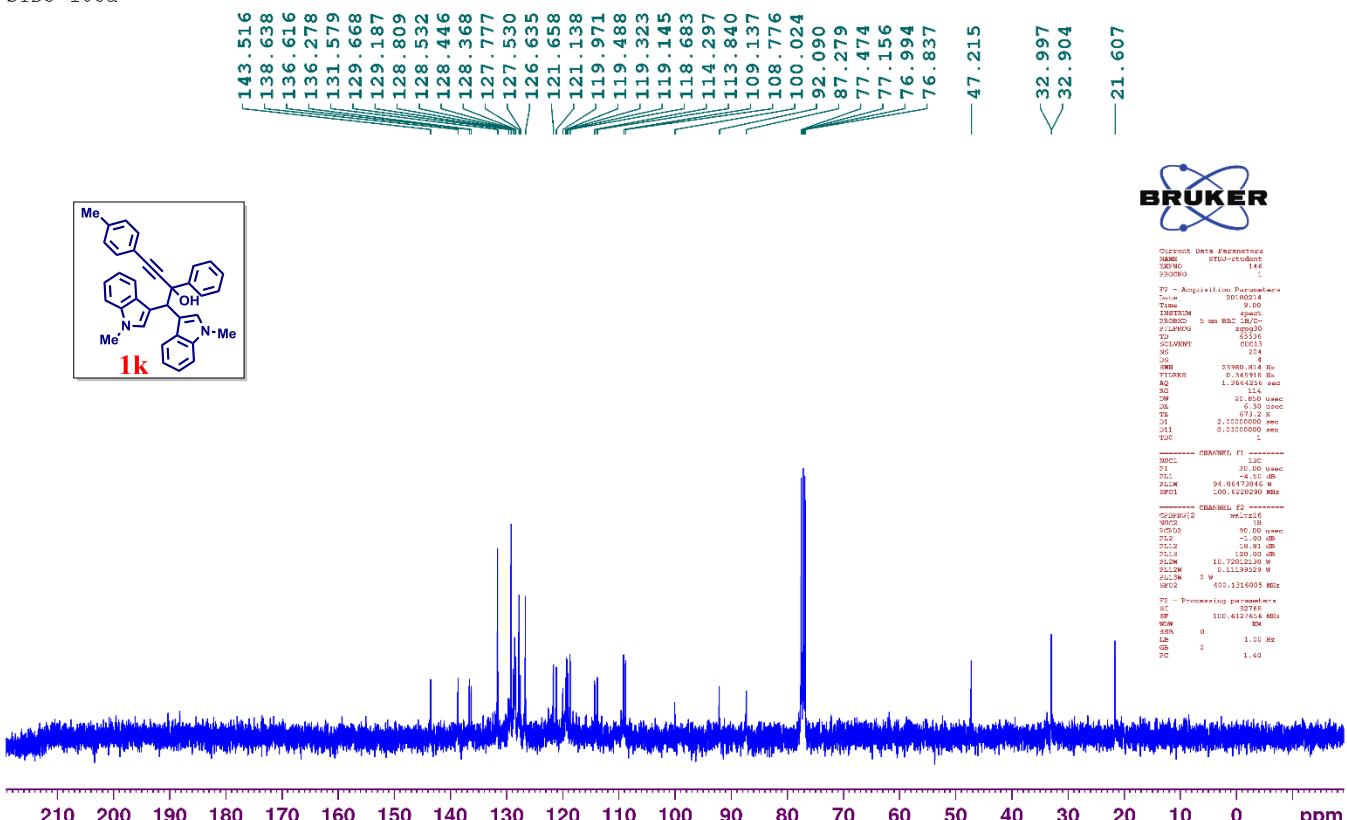
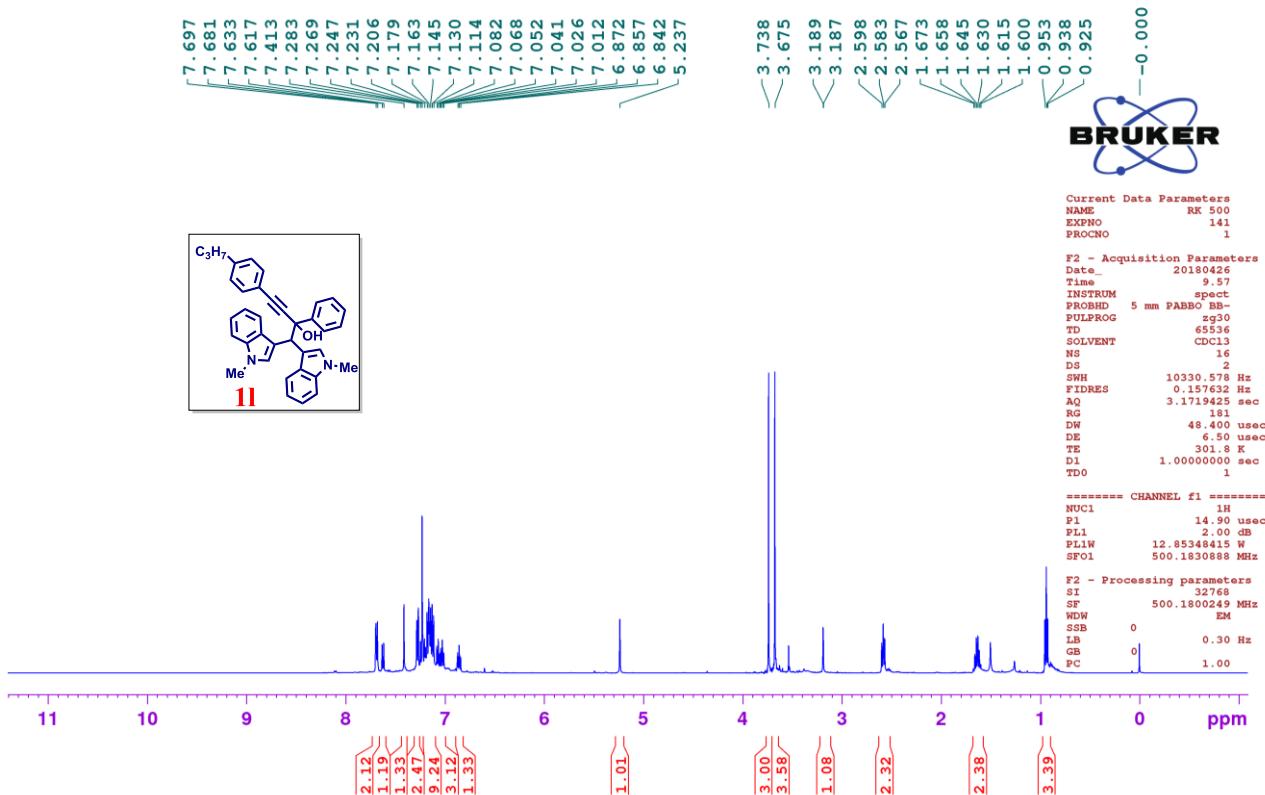
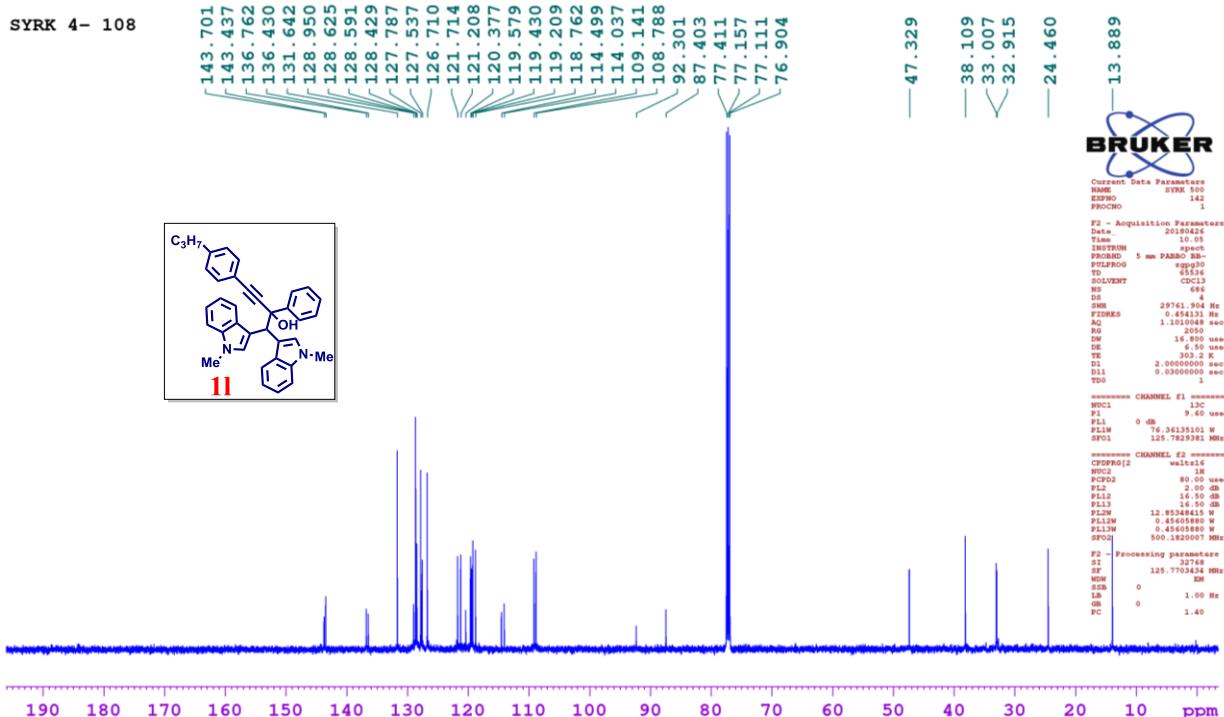


Figure S12 ^{13}C NMR in CDCl_3

Figure S13 ^1H NMR in CDCl_3 

SYDJ-145

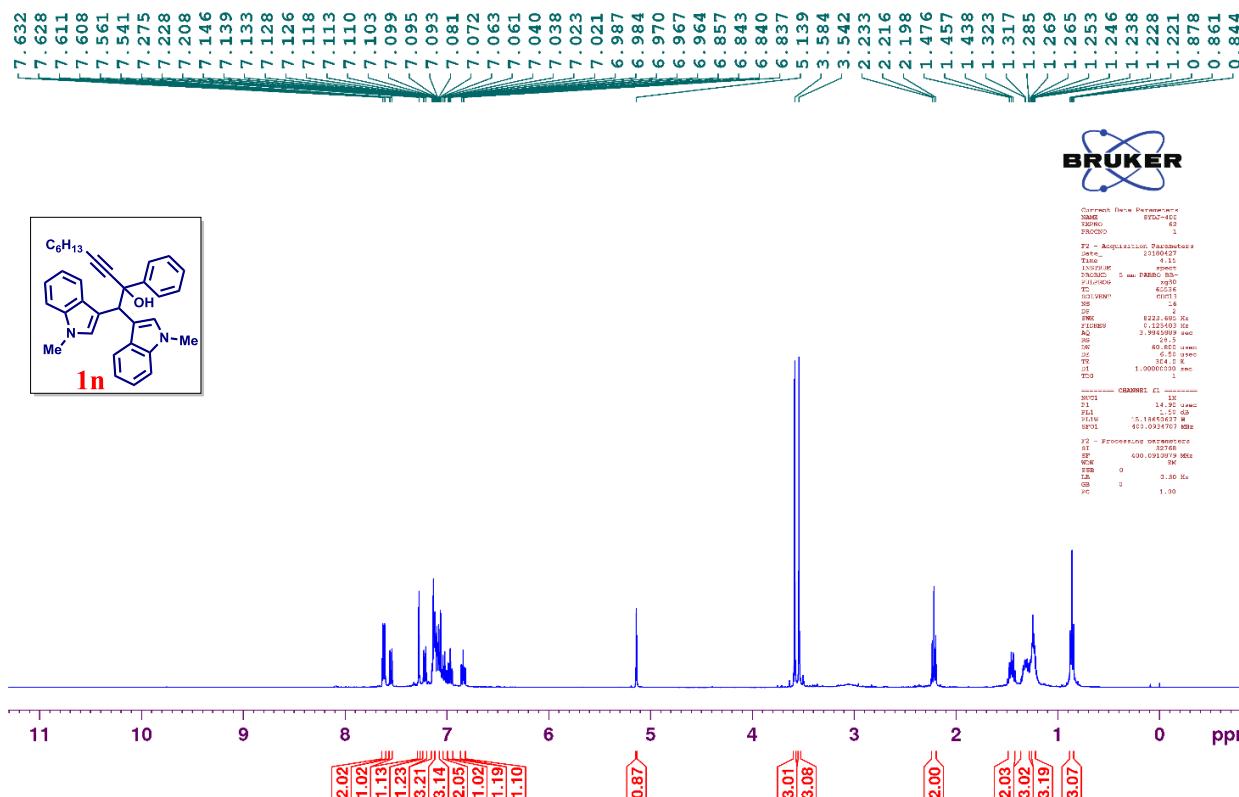


Figure S15 ¹H NMR in CDCl₃

SYDJ-145

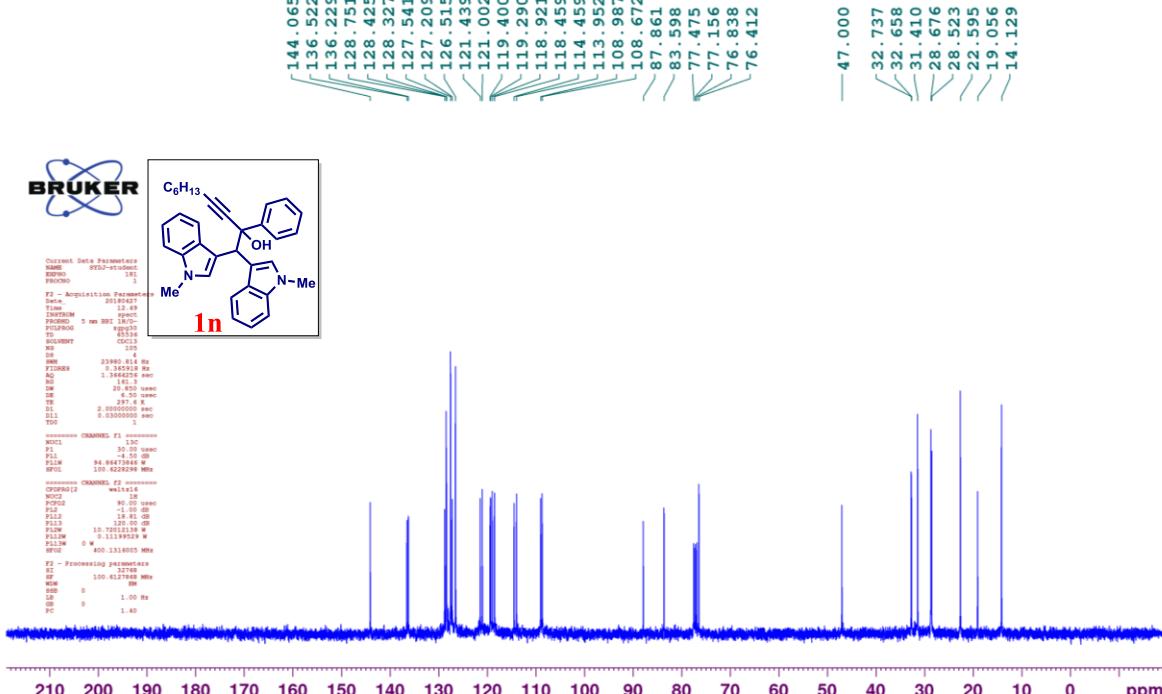
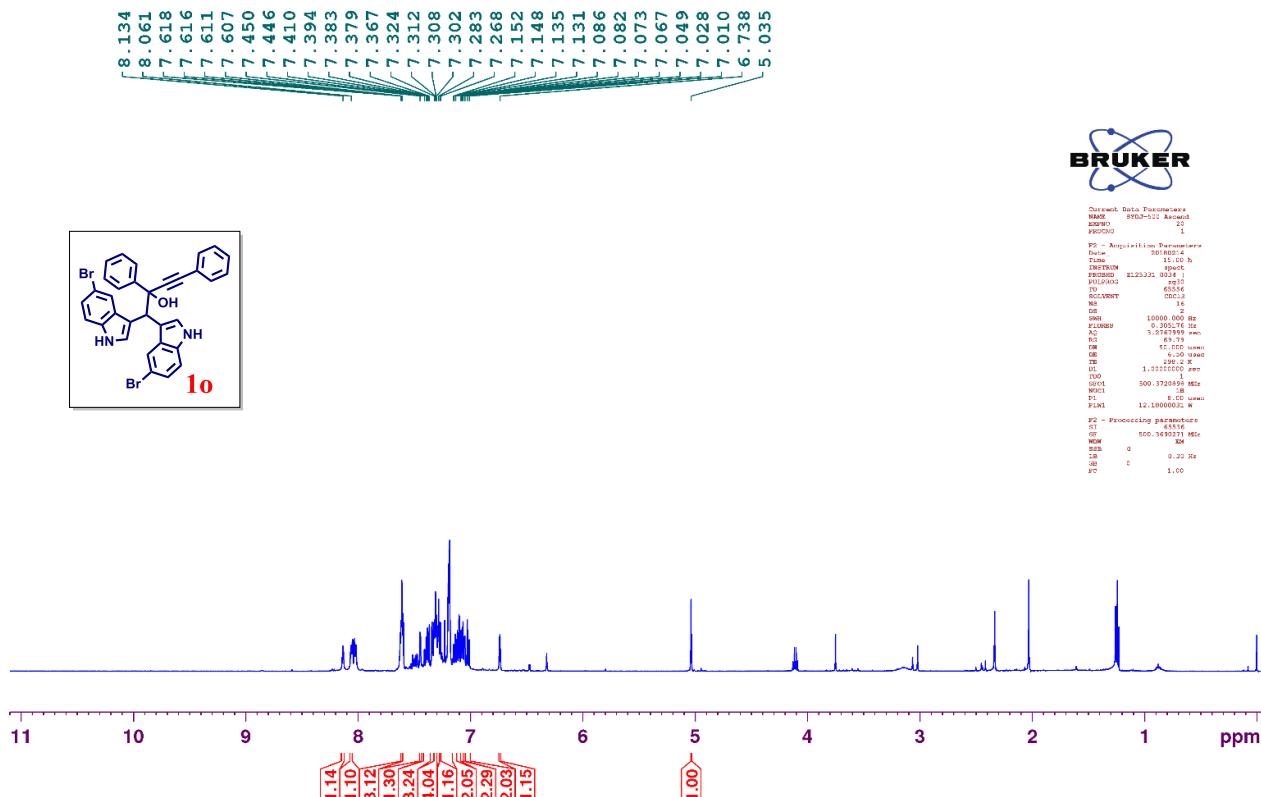
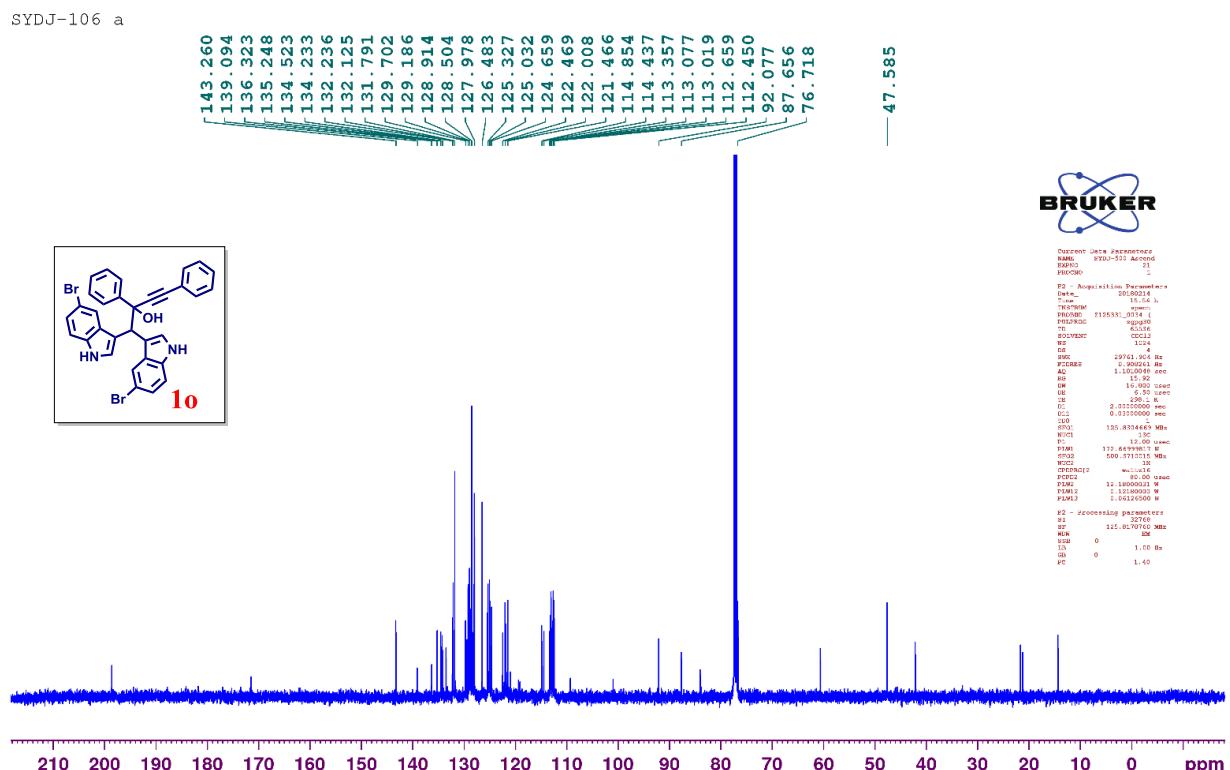


Figure S16 ¹³C NMR in CDCl₃

Figure S17 ^1H NMR in CDCl_3 Figure S18 ^{13}C NMR in CDCl_3

SYDJ-107 a

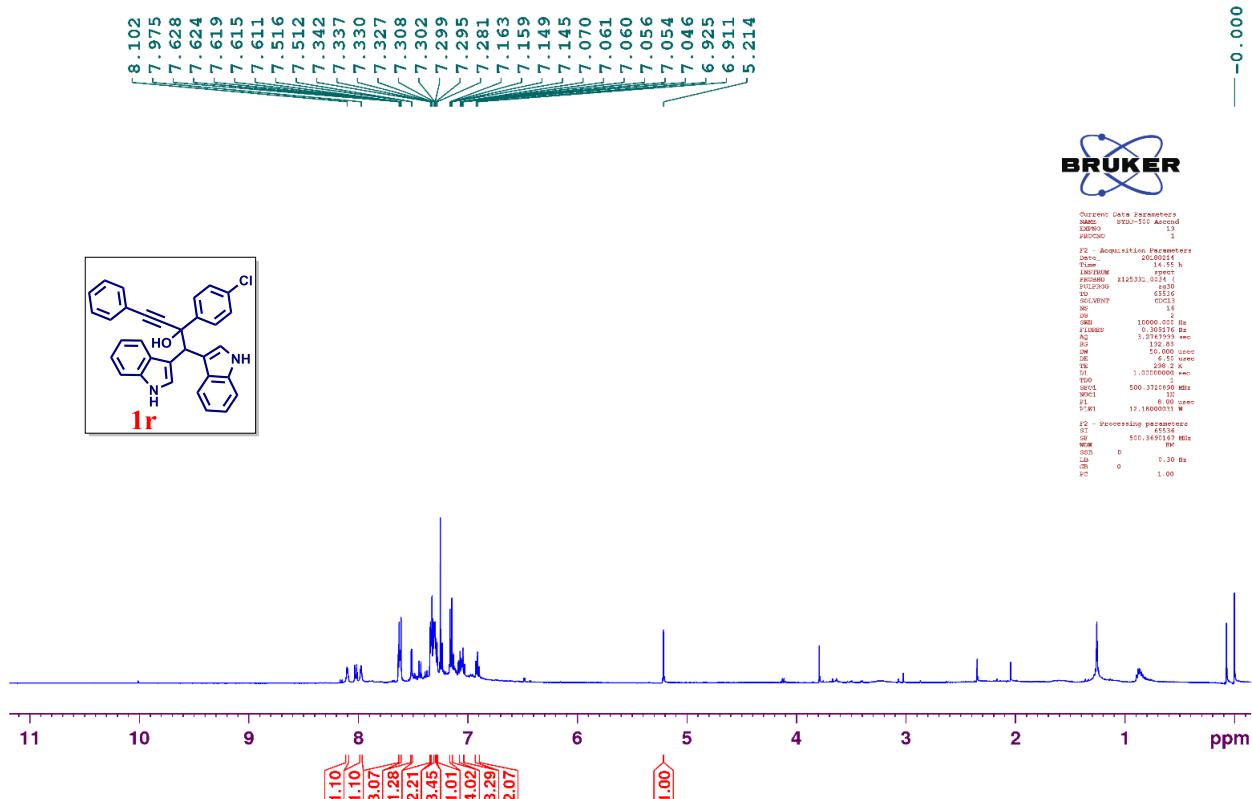


Figure S19 ^1H NMR in CDCl_3

SYDJ-107 (A)

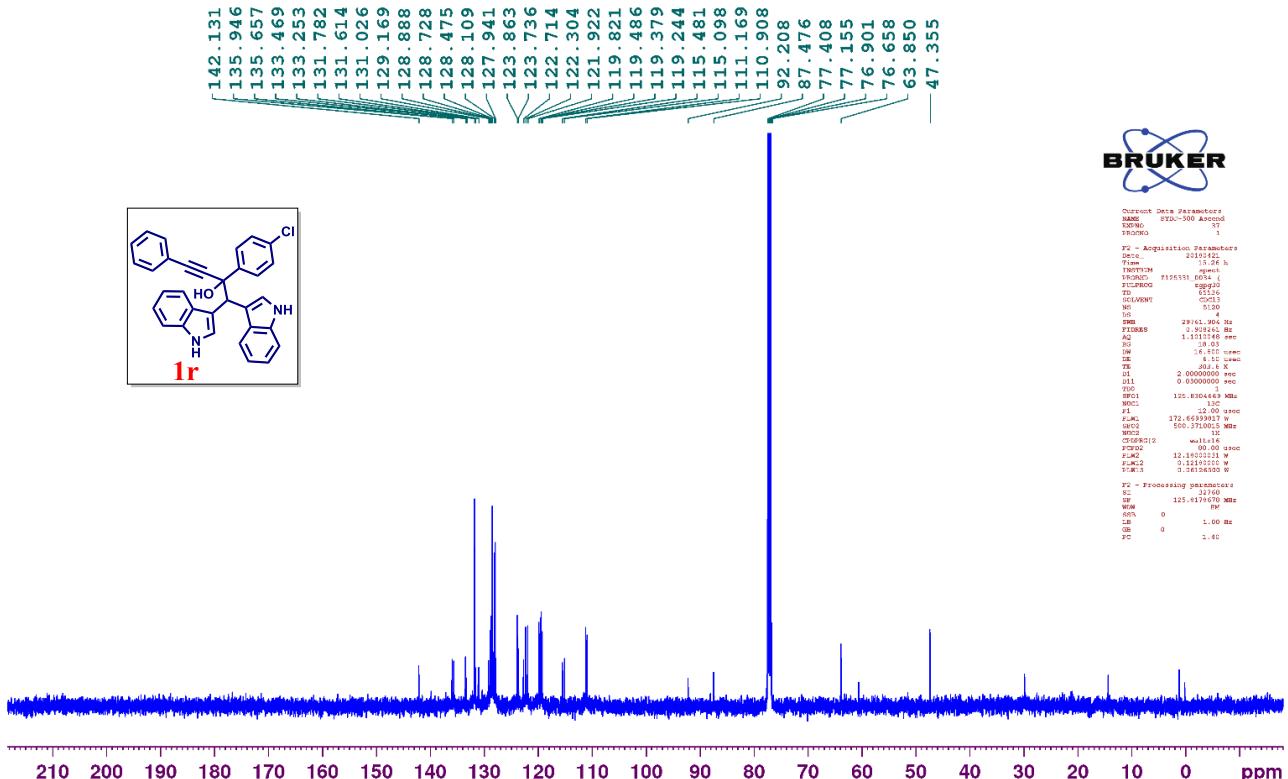


Figure S20 ^{13}C NMR in CDCl_3

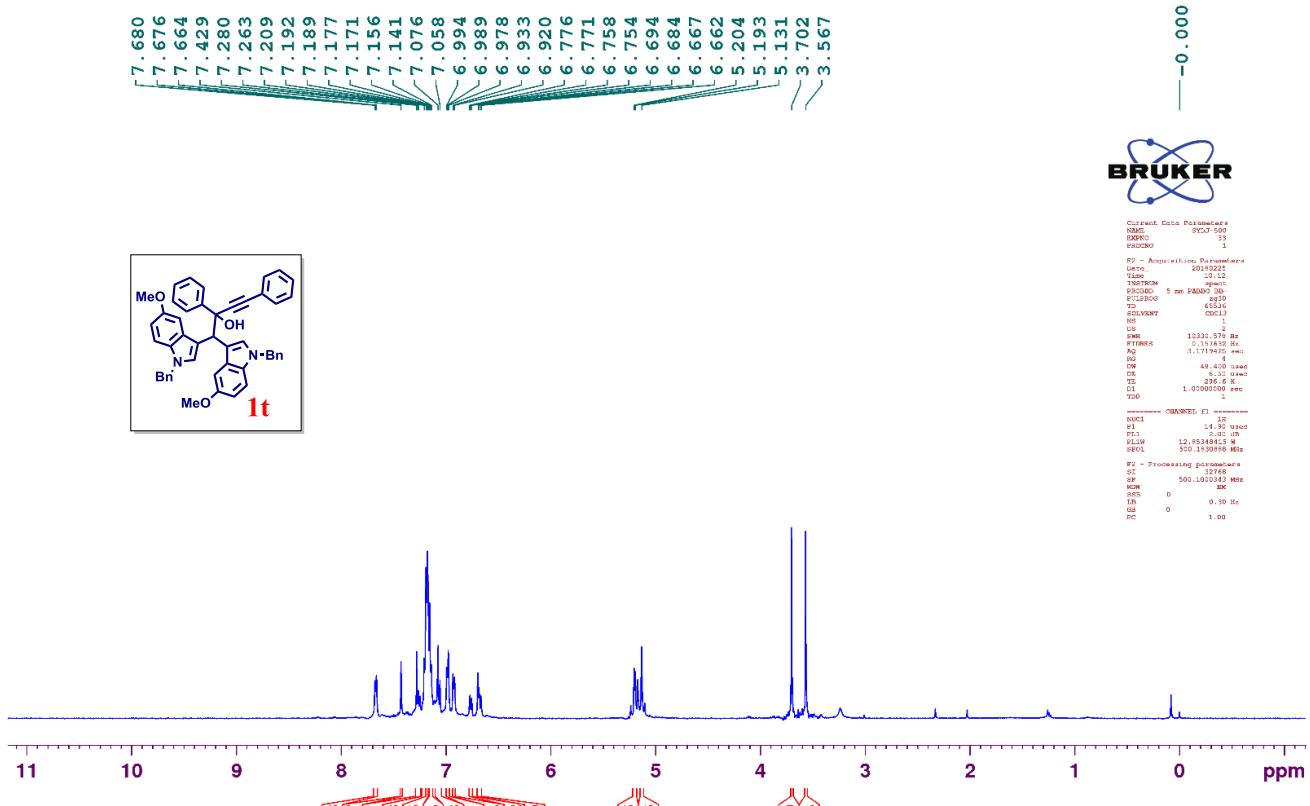


Figure S21 ^1H NMR in CDCl_3

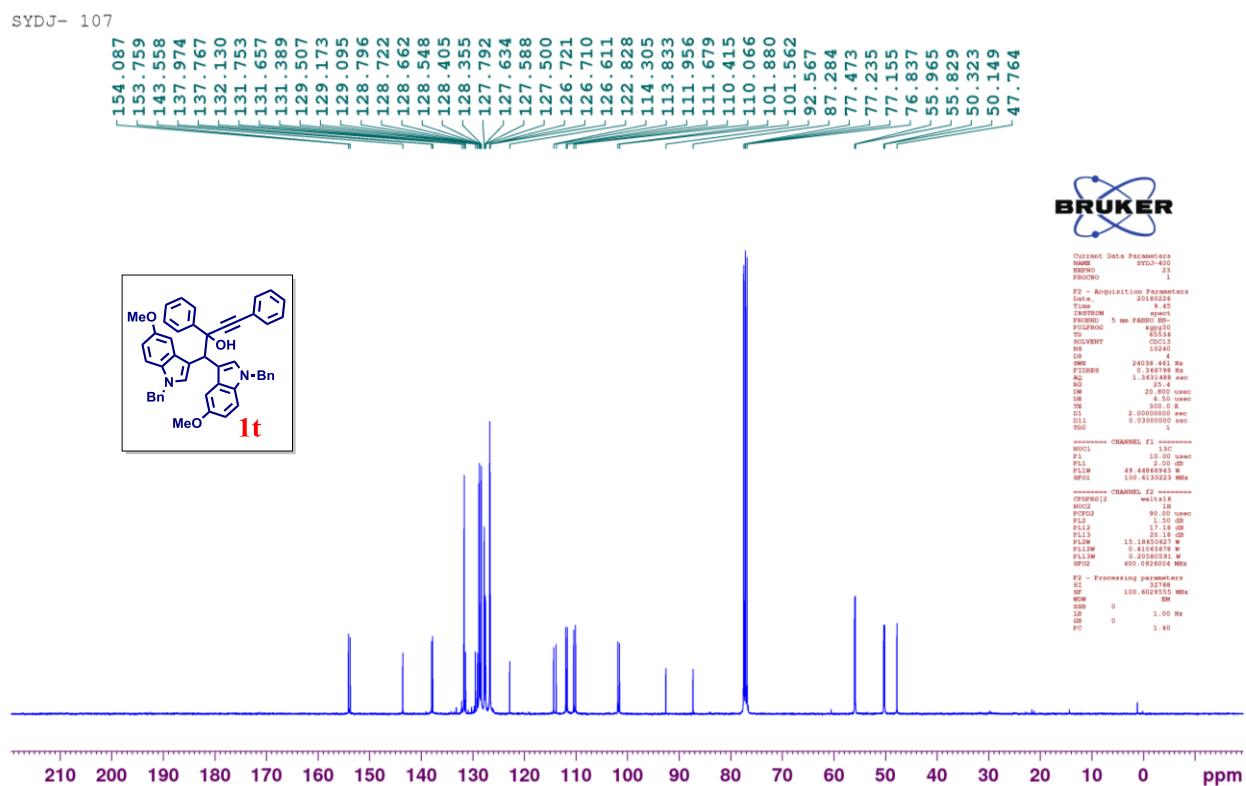
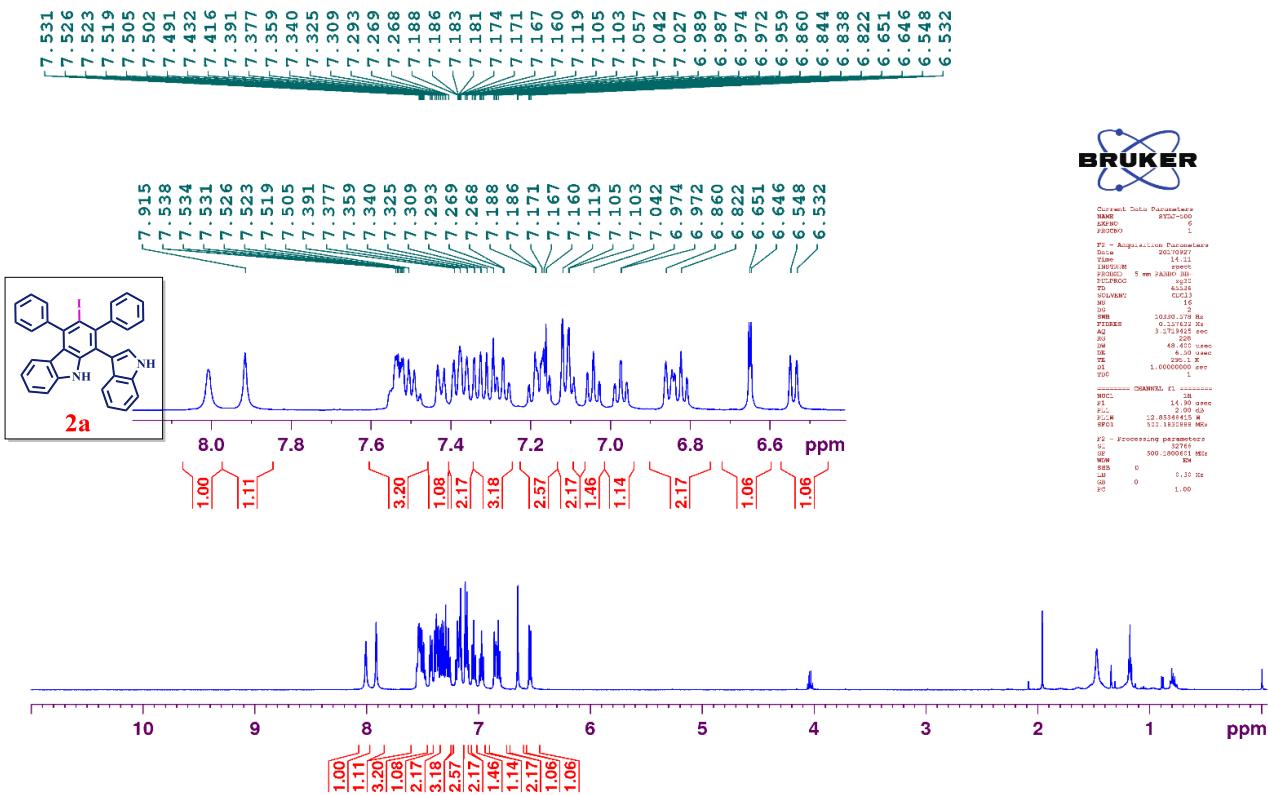
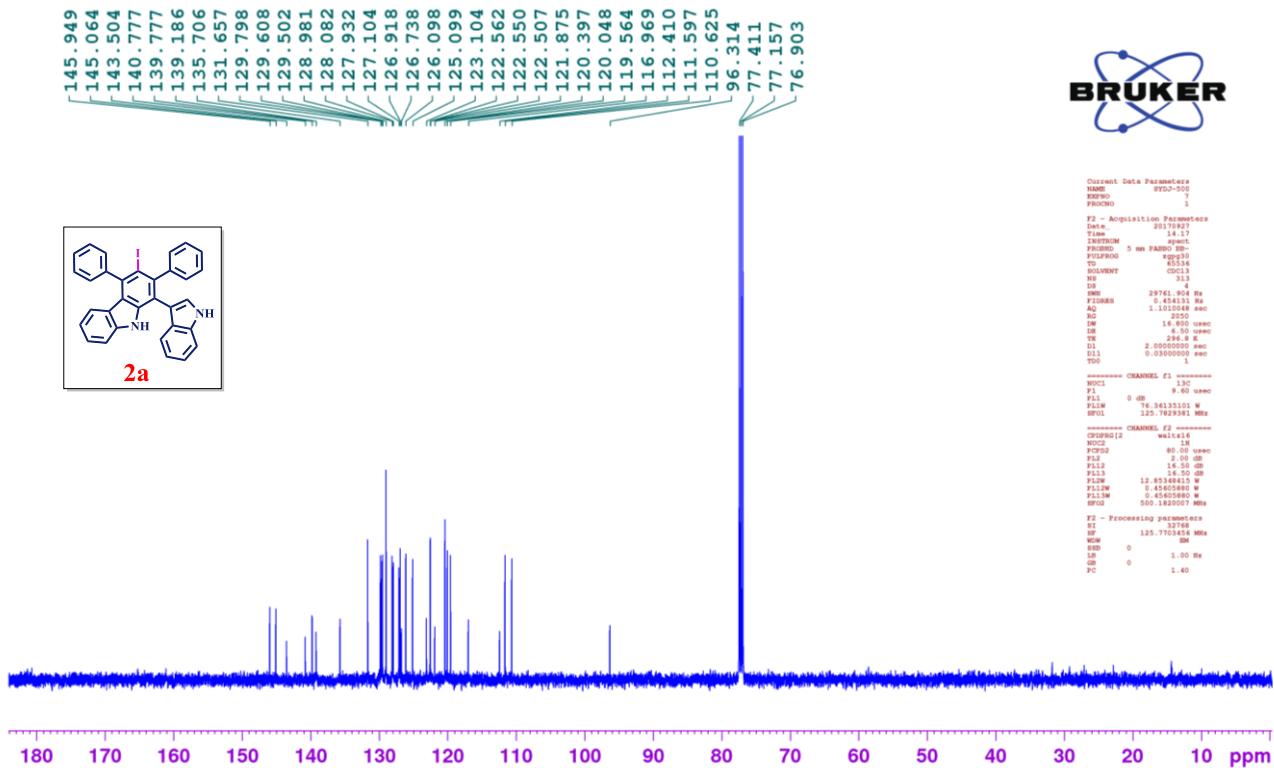


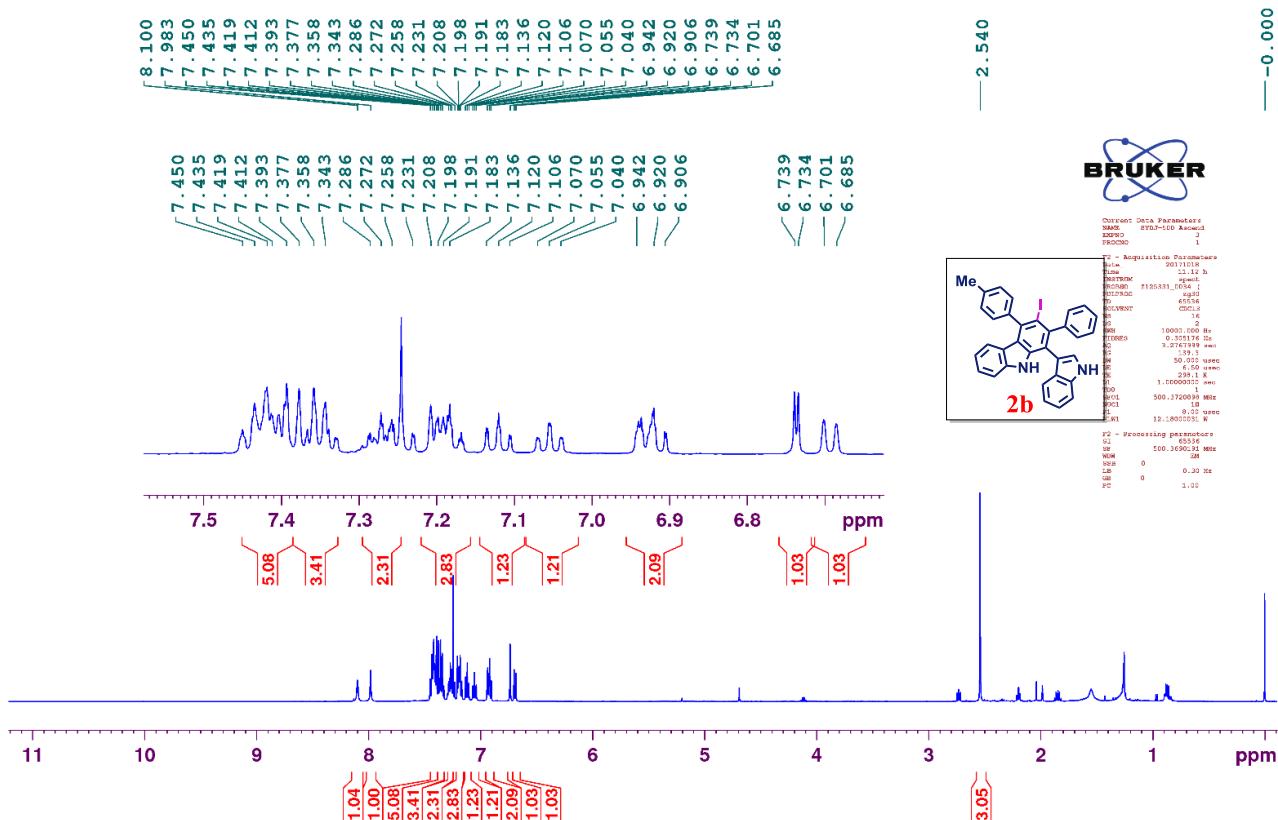
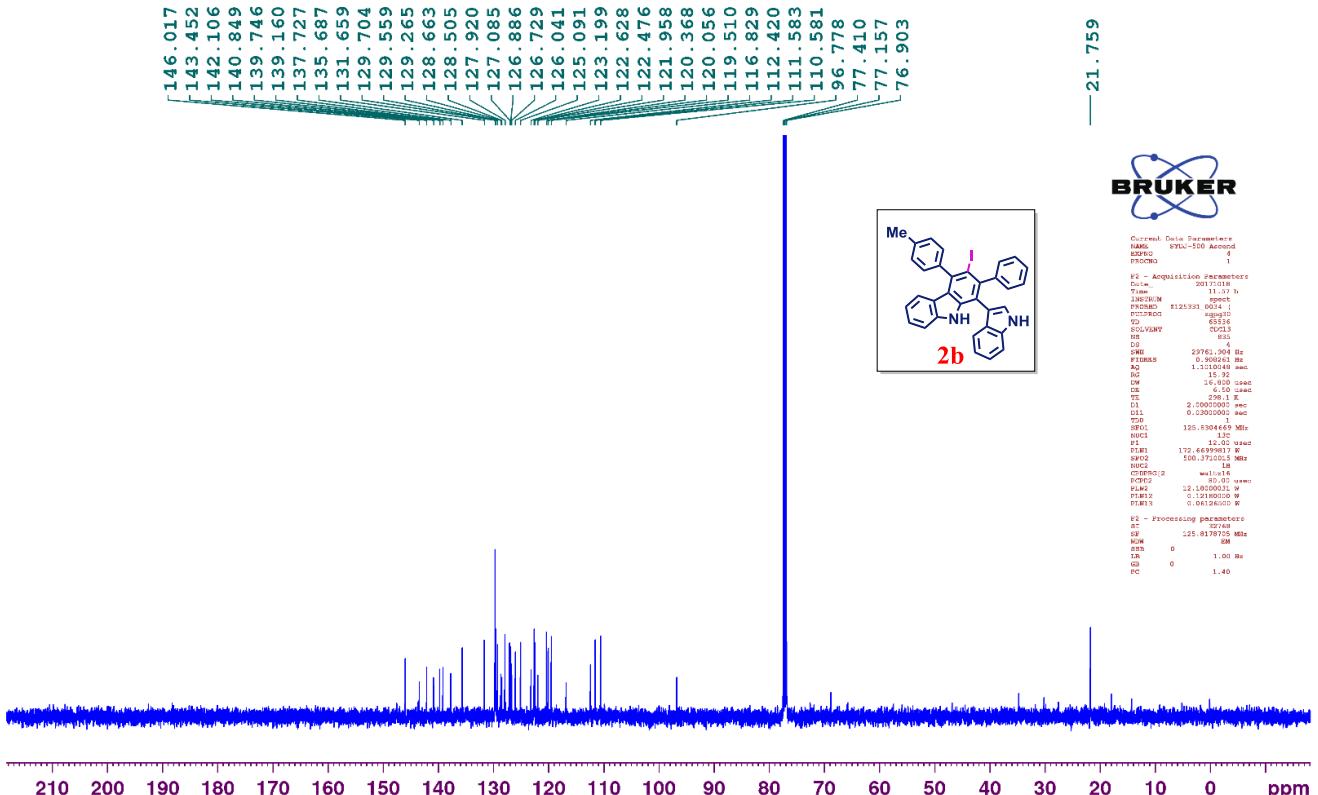
Figure S22 ^{13}C NMR in CDCl_3

SYDJ-43

Figure S23 ¹H NMR in CDCl₃

SYDJ-41

Figure S24 ¹³C NMR in CDCl₃

Figure S25 ^1H NMR in CDCl_3 Figure S26 ^{13}C NMR in CDCl_3

SYDJ-45-A

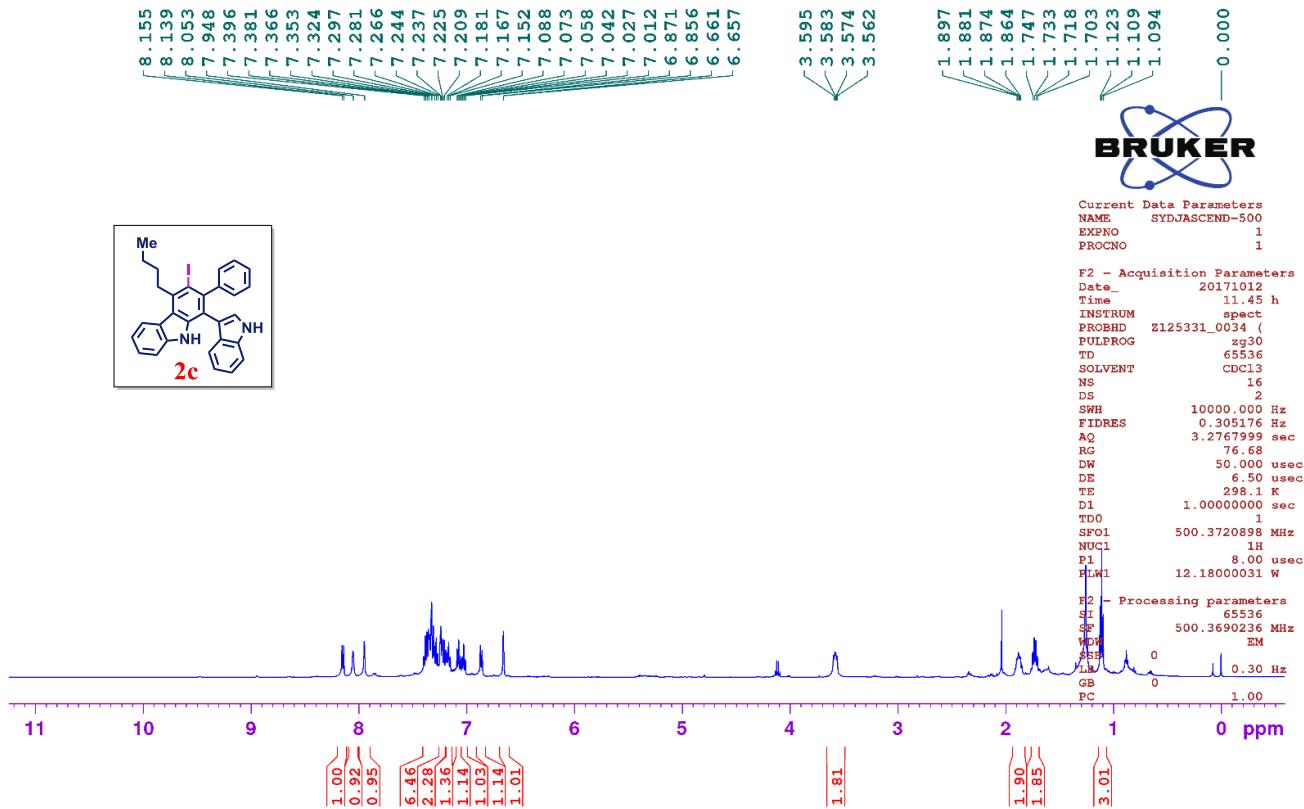


Figure S27 ^1H NMR in CDCl_3

SYDJ-45-A

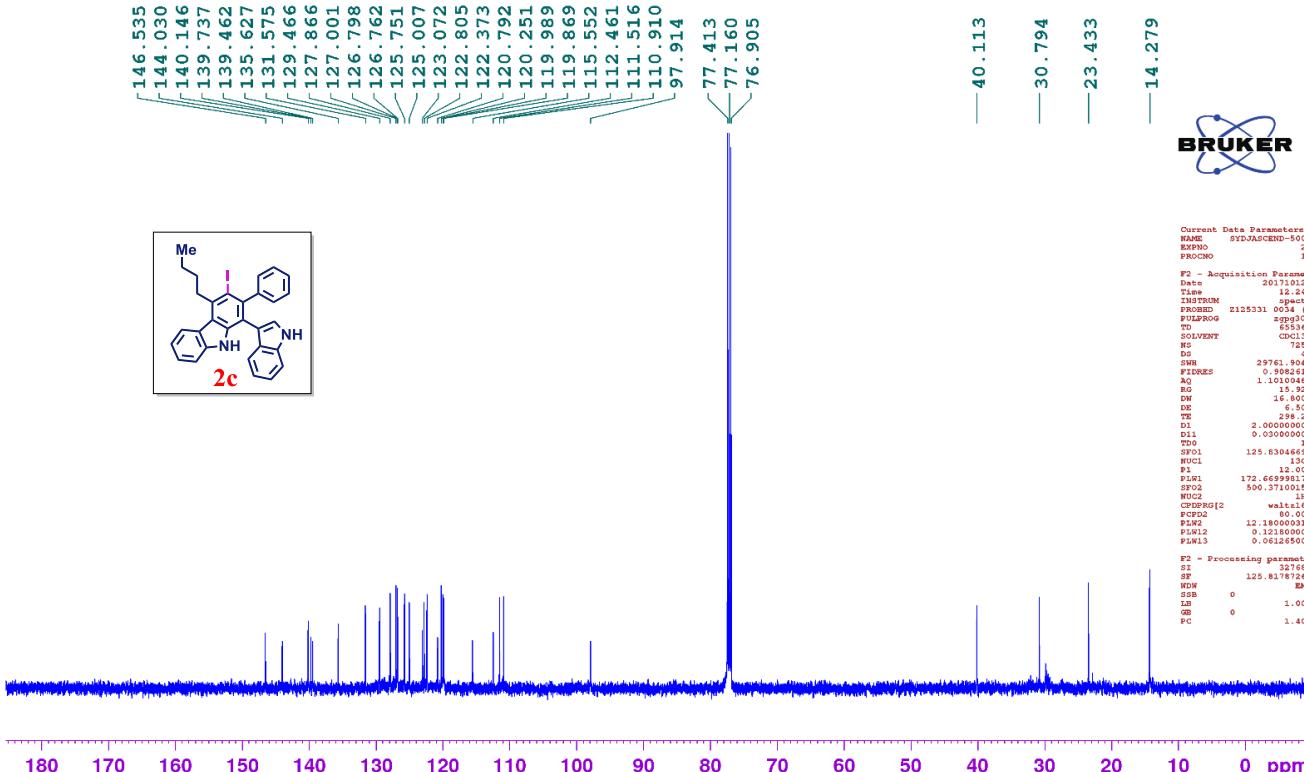


Figure S28 ^{13}C NMR in CDCl_3

SYDJ-46 (A)

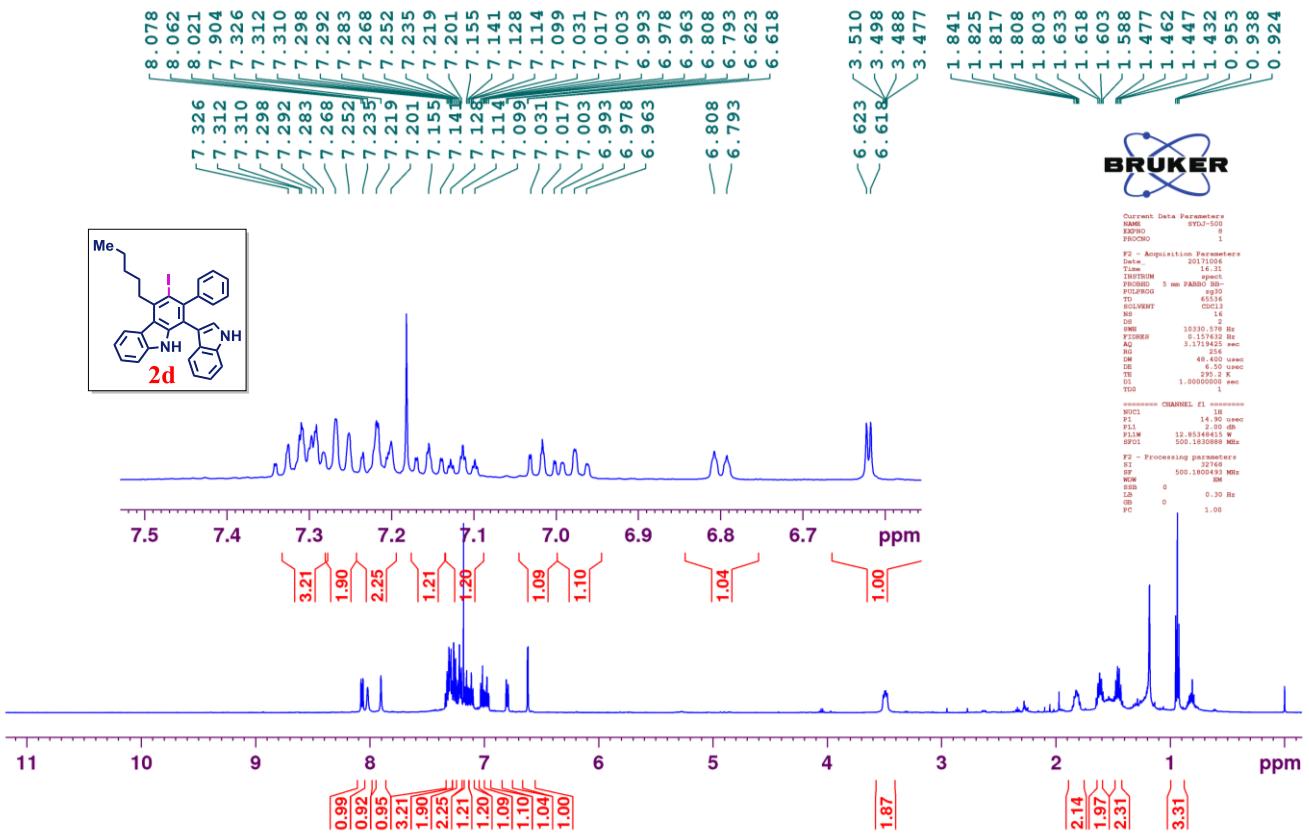


Figure S29 ^1H NMR in CDCl_3

SYDJ-46 (A)

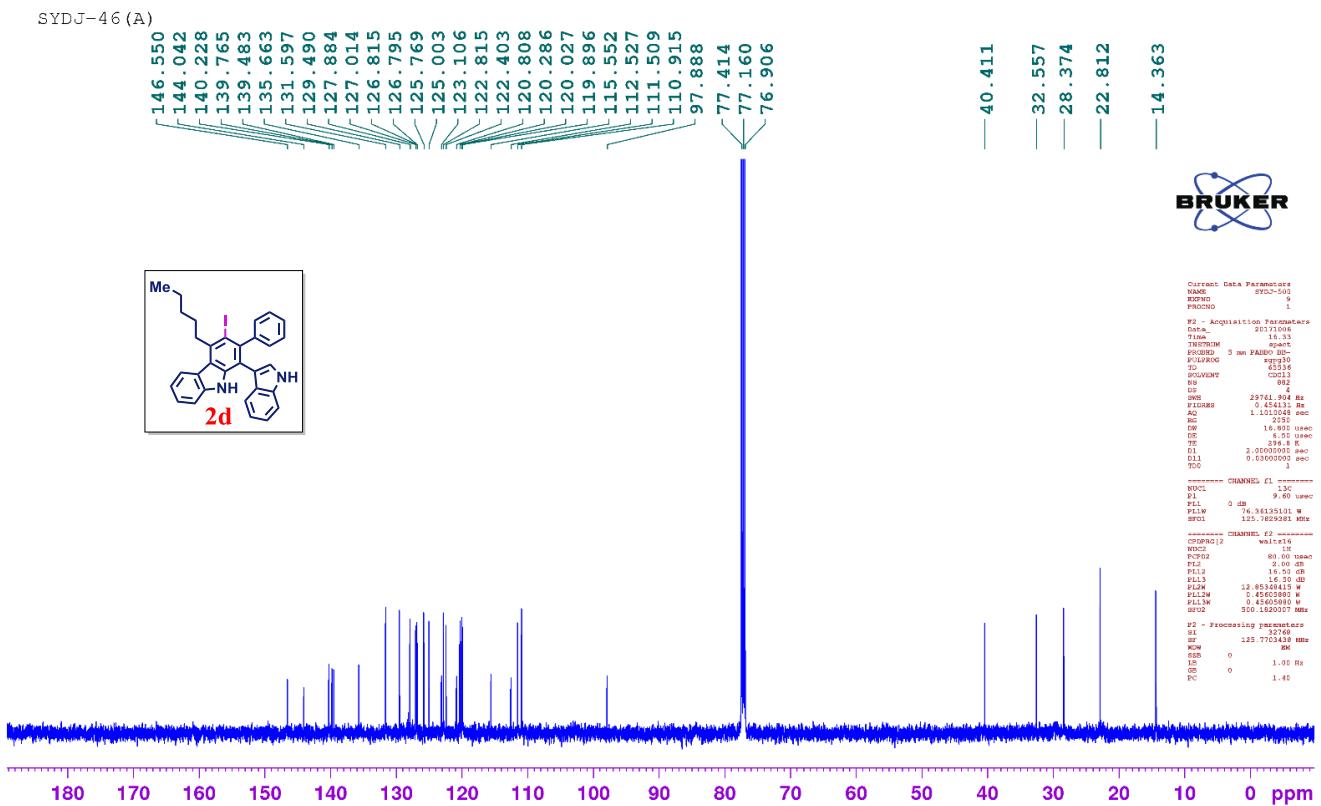


Figure S30 ^{13}C NMR in CDCl_3

SYDJ- 61

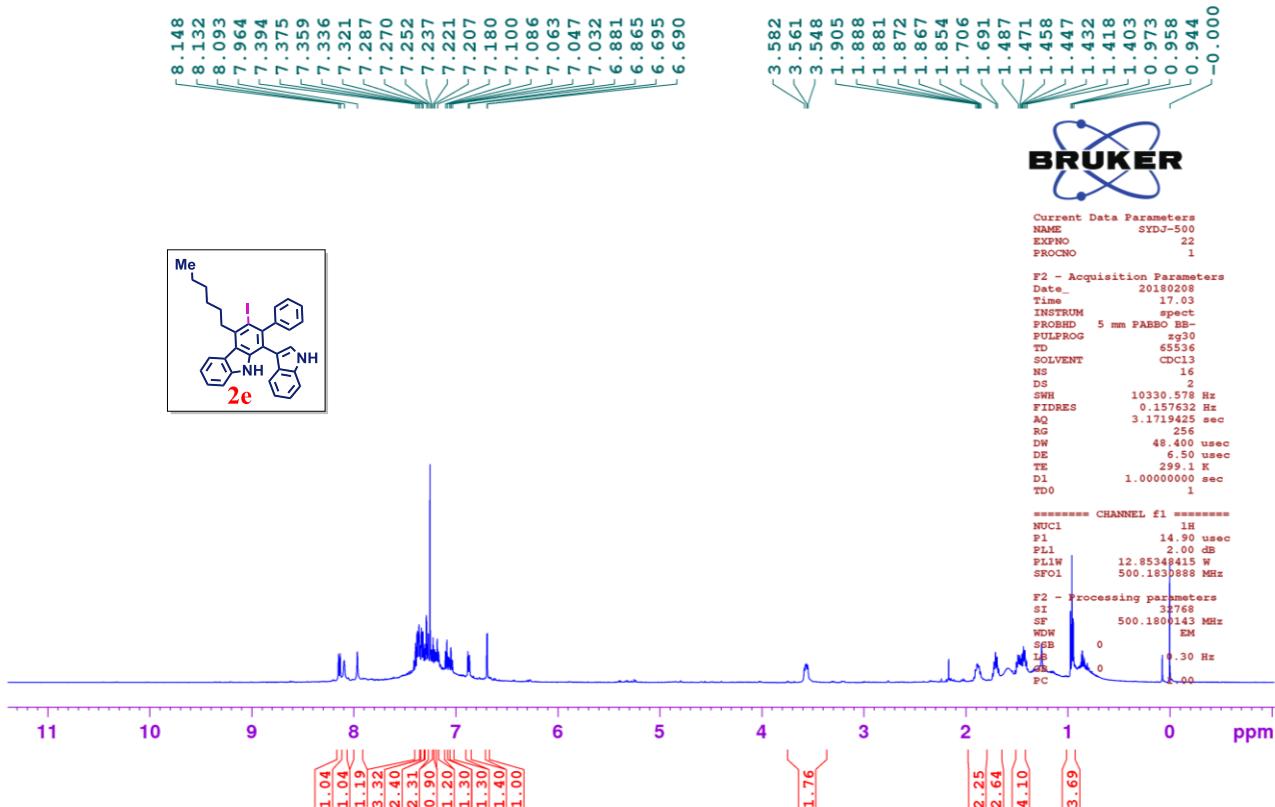


Figure S31 ^1H NMR in CDCl_3

SYDJ- 61

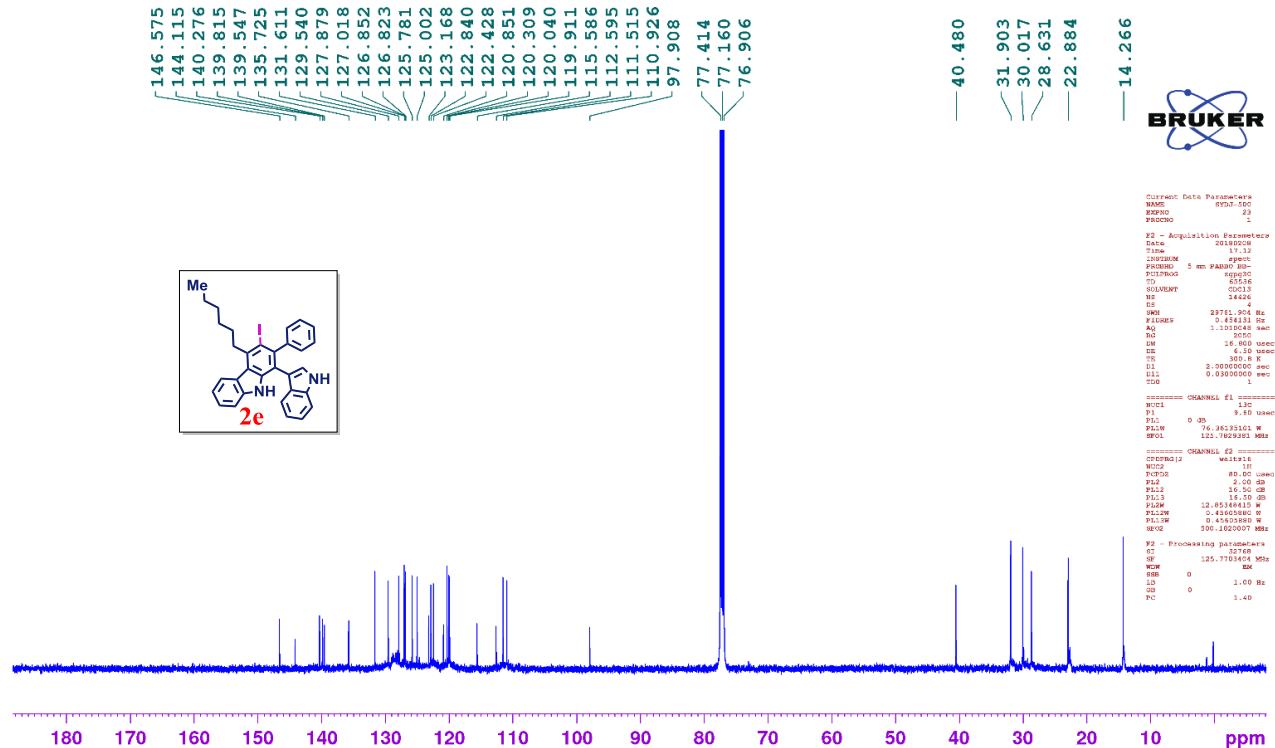
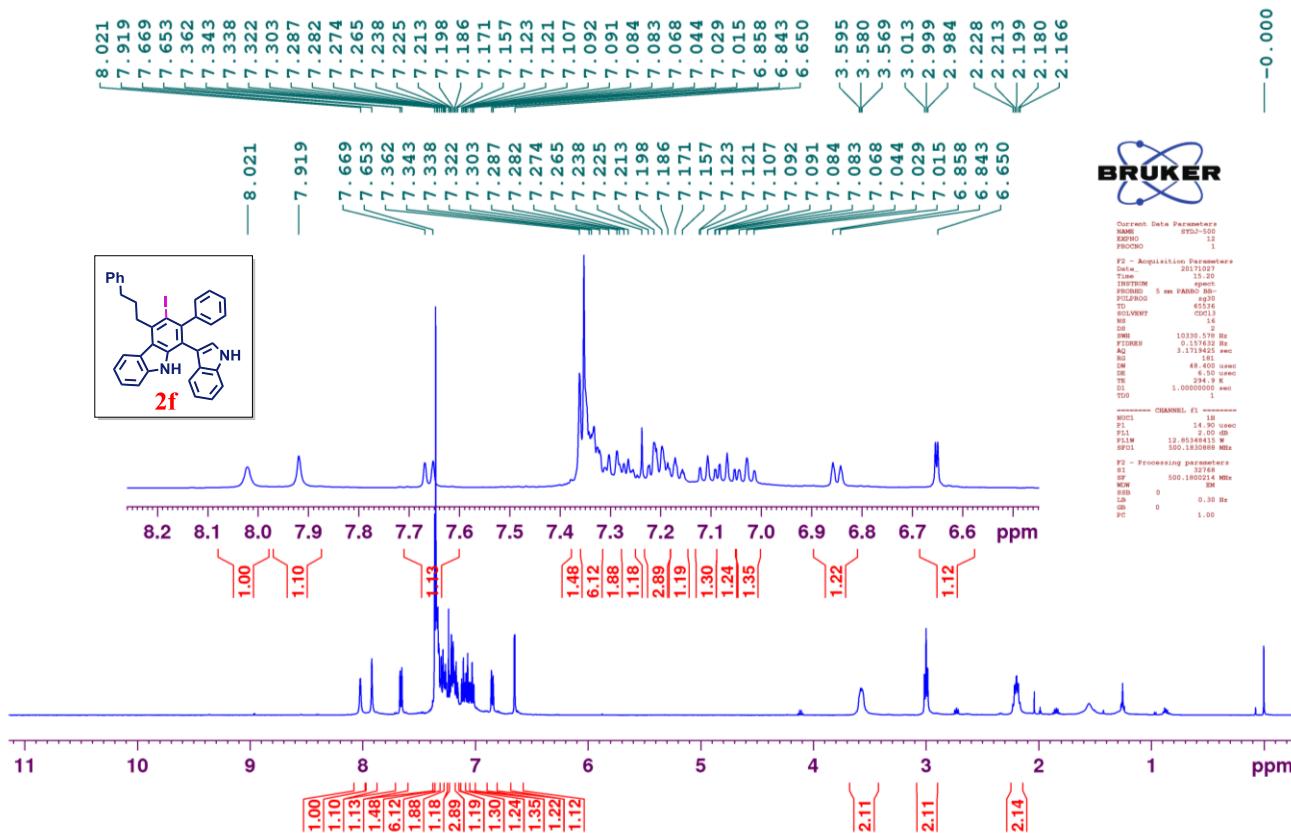
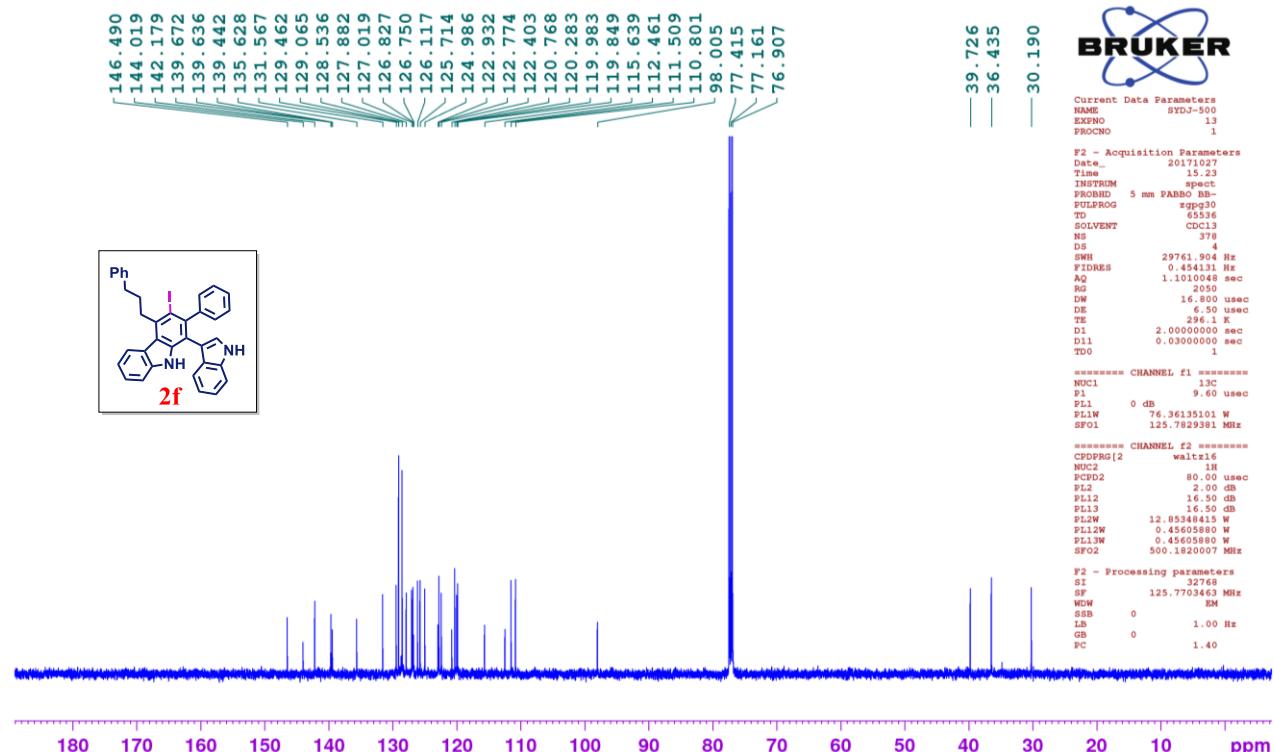
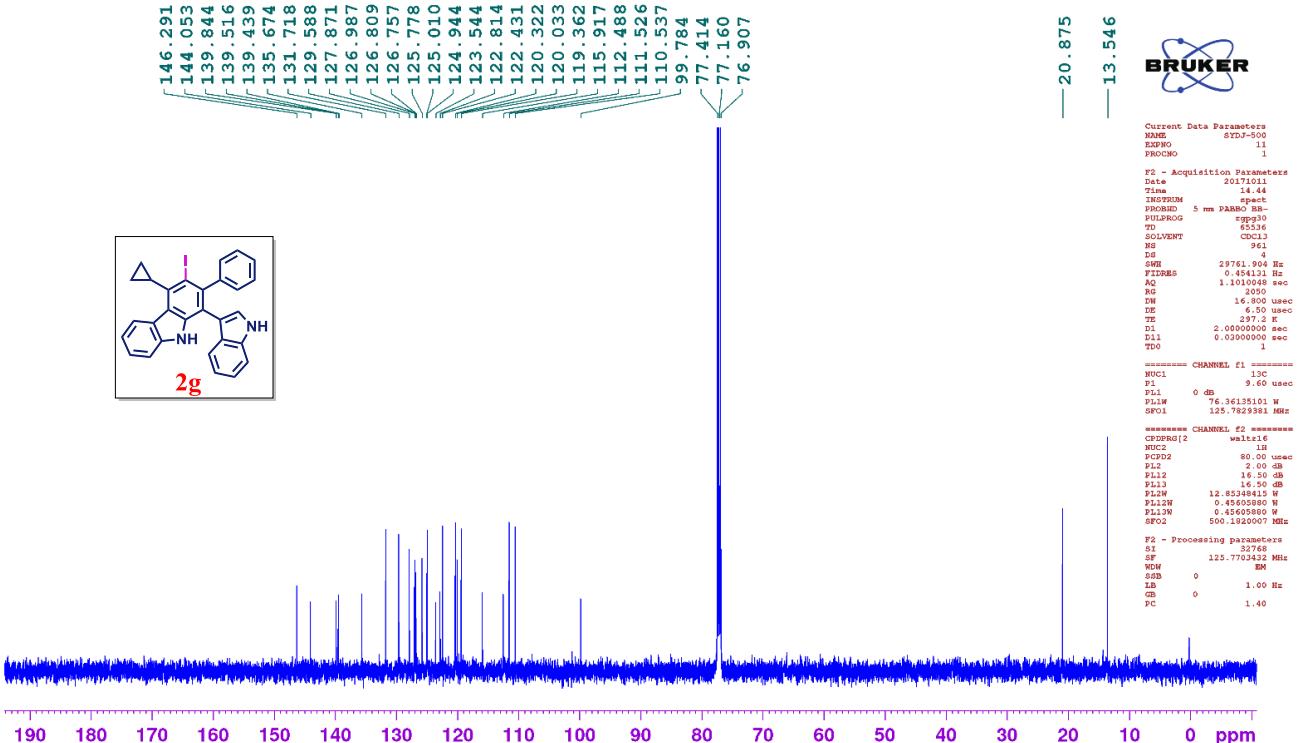
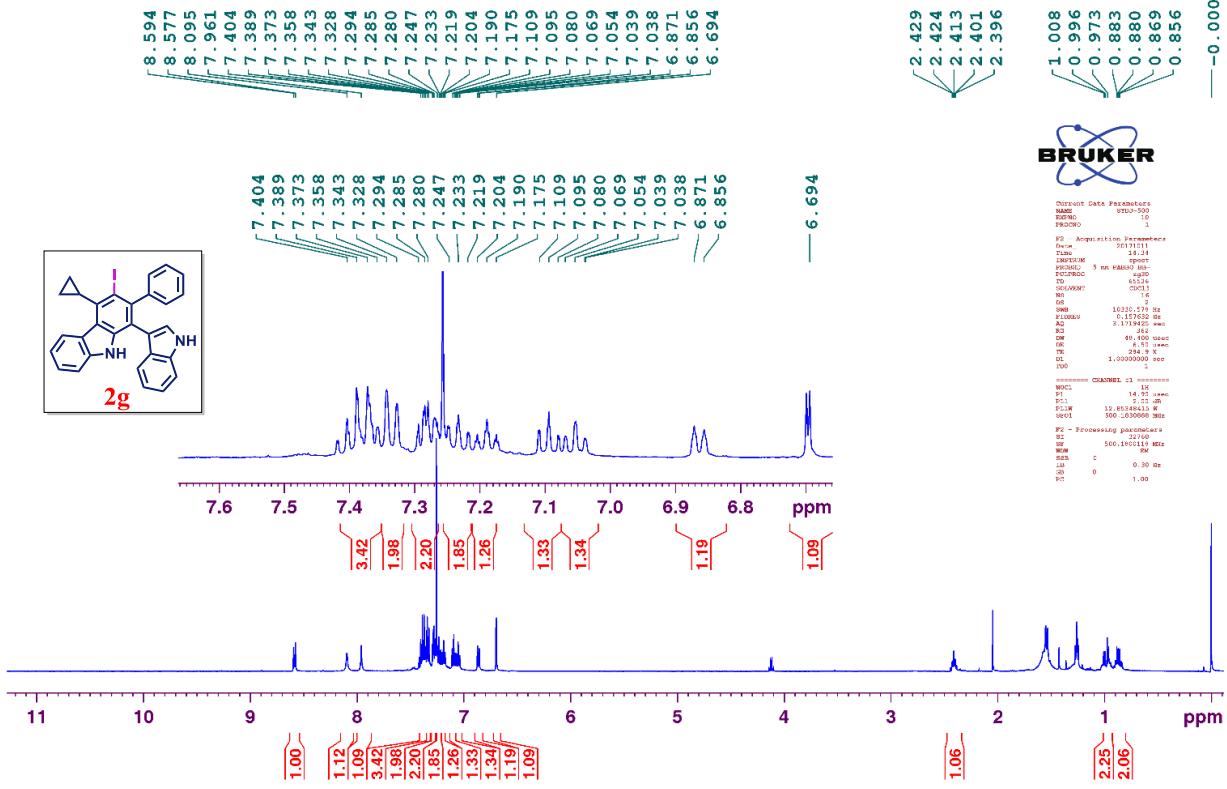
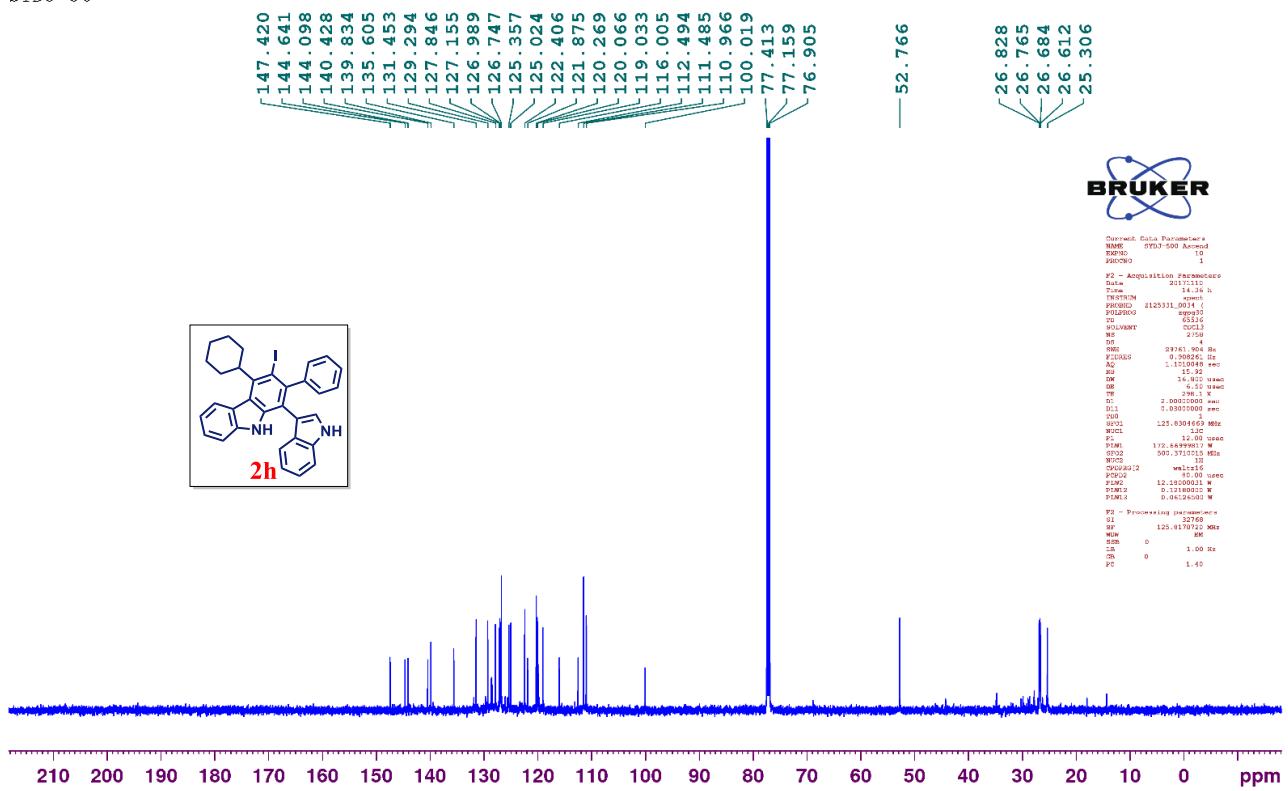
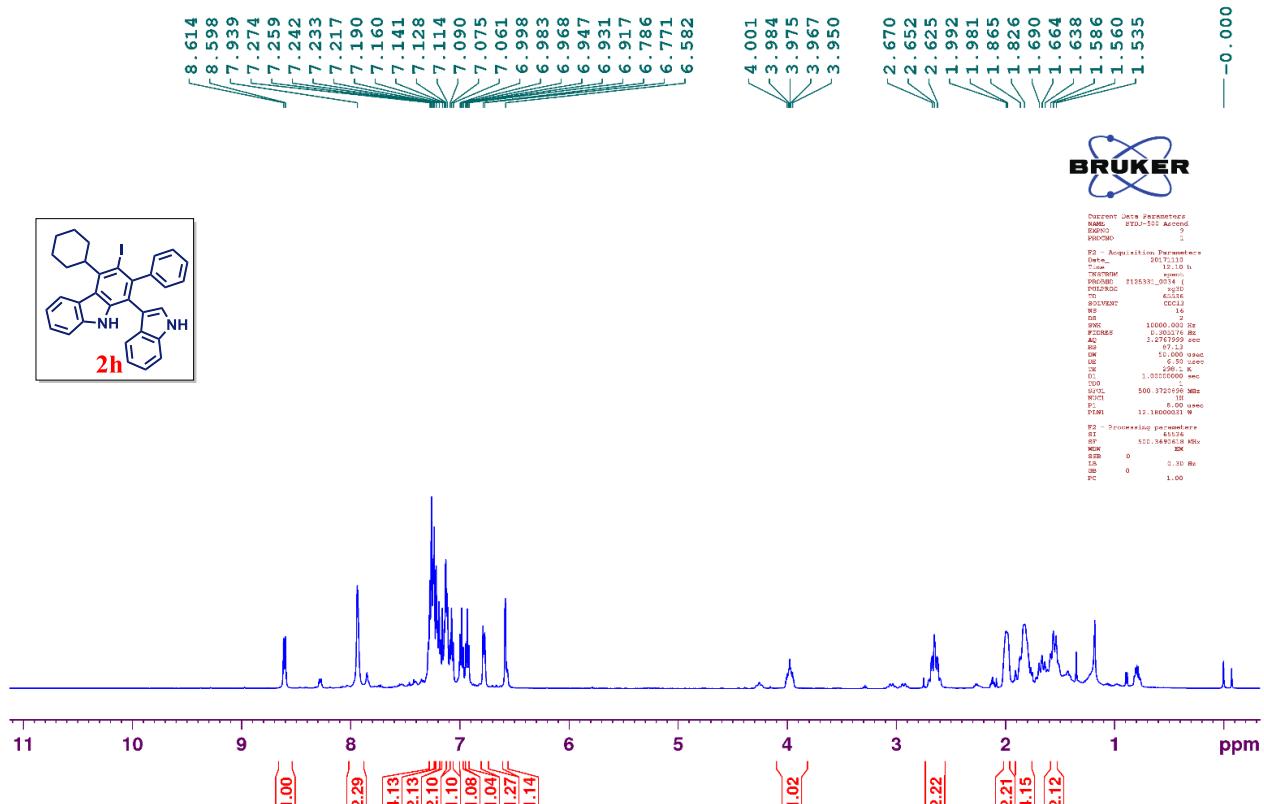
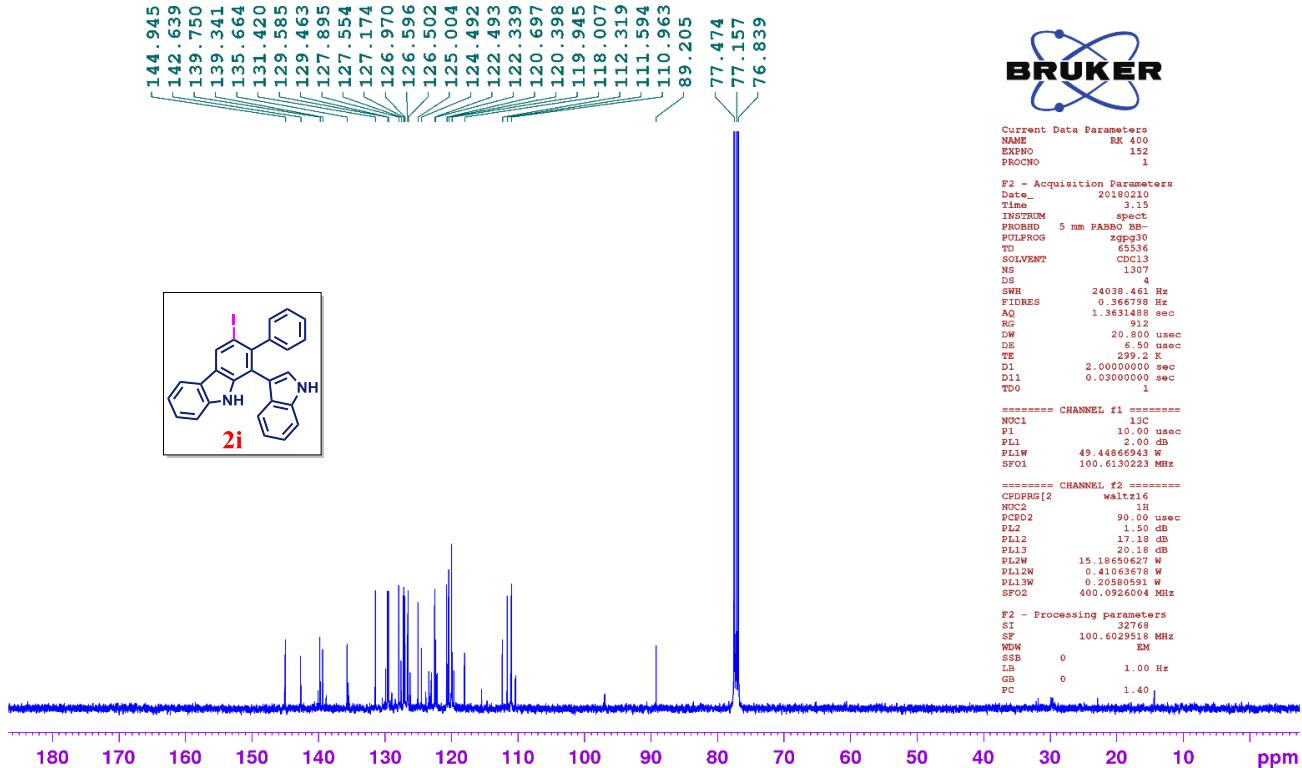
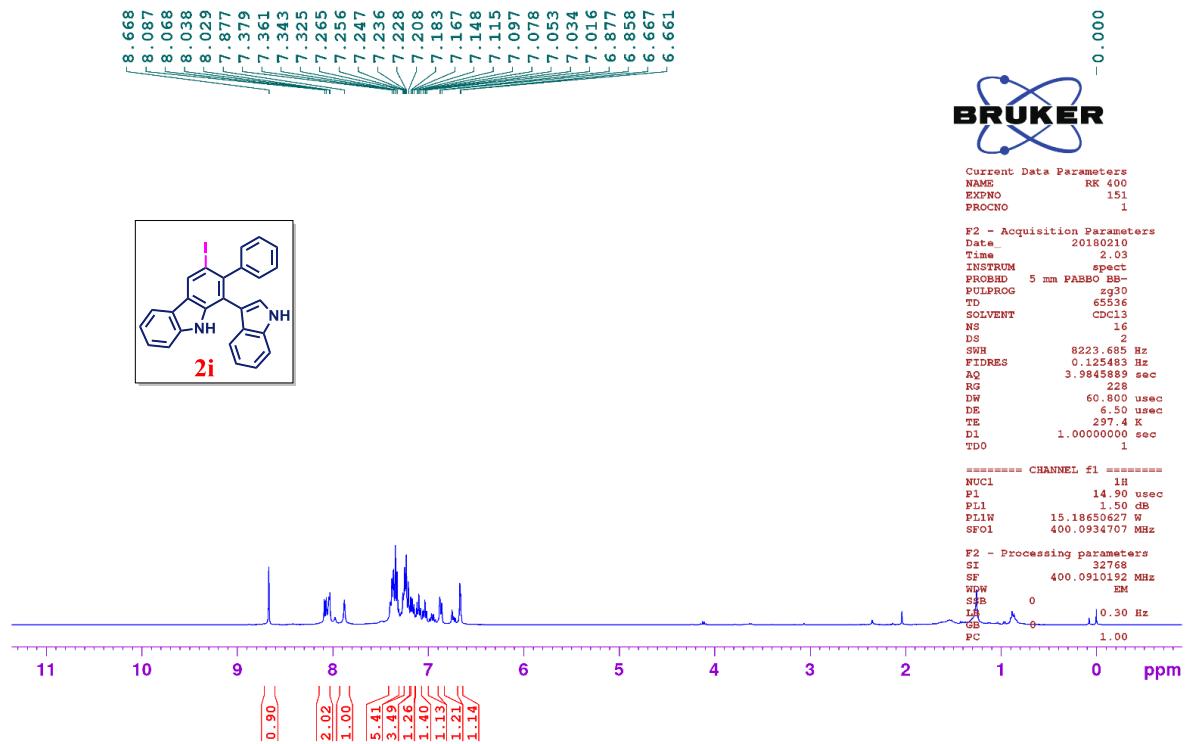


Figure S32 ^{13}C NMR in CDCl_3

Figure S33 ^1H NMR in CDCl_3 Figure S34 ^{13}C NMR in CDCl_3

**Figure S36 ^{13}C NMR in CDCl_3**





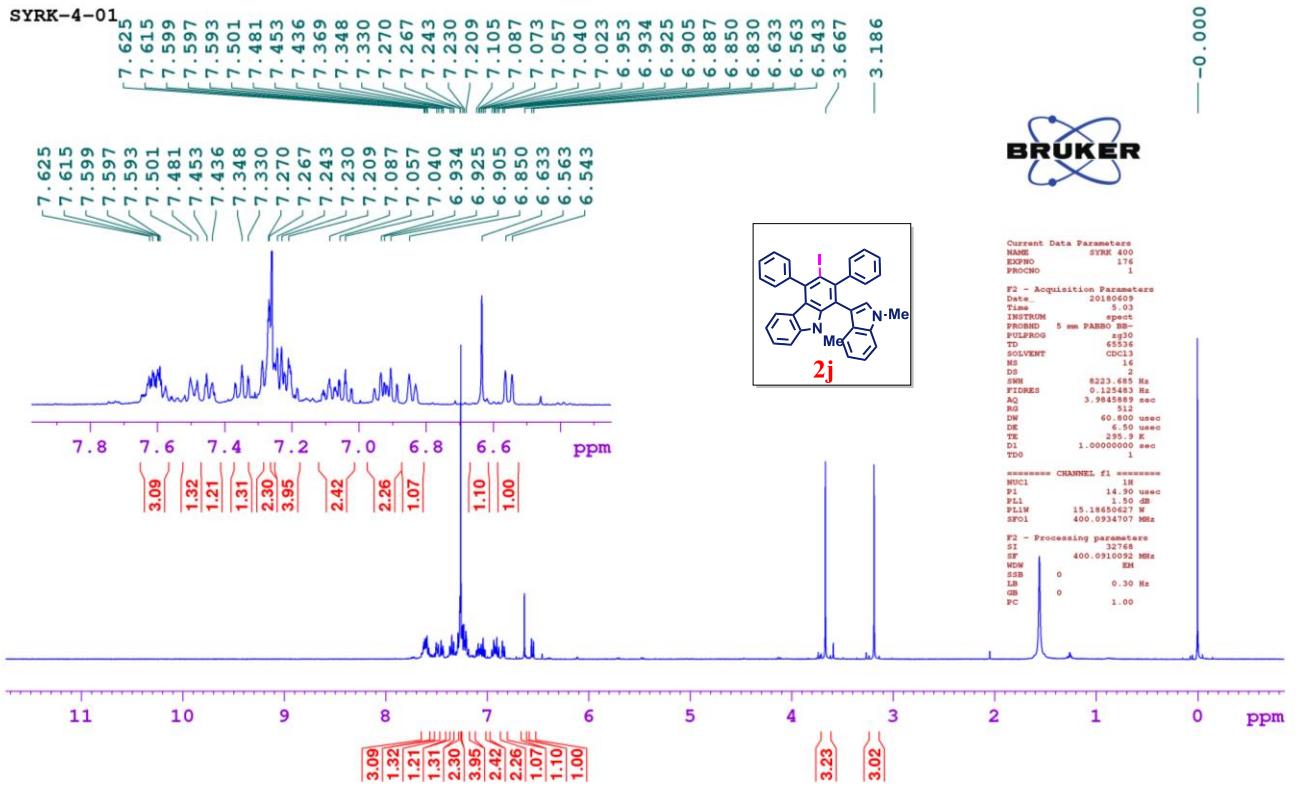


Figure S41 ¹H NMR in CDCl₃

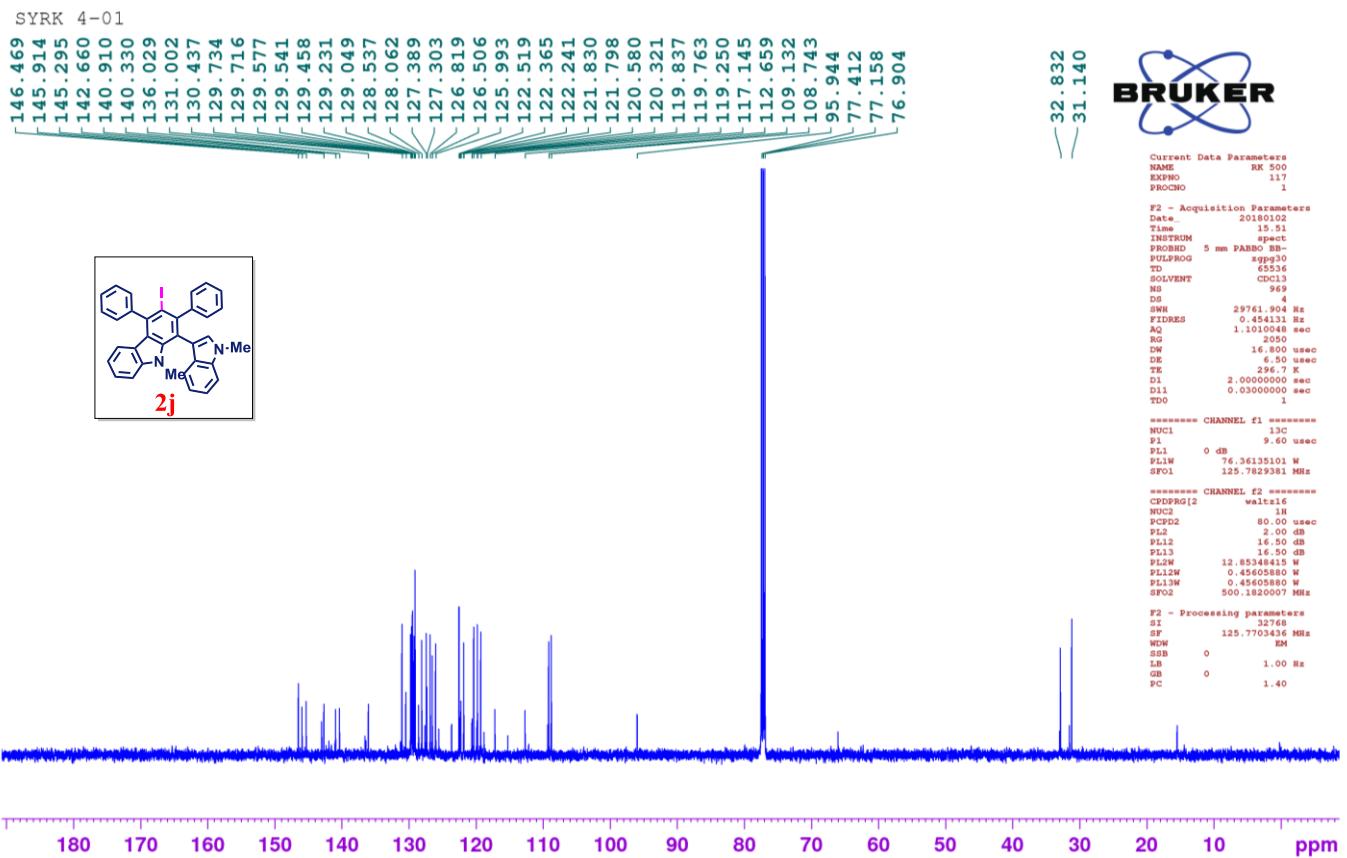
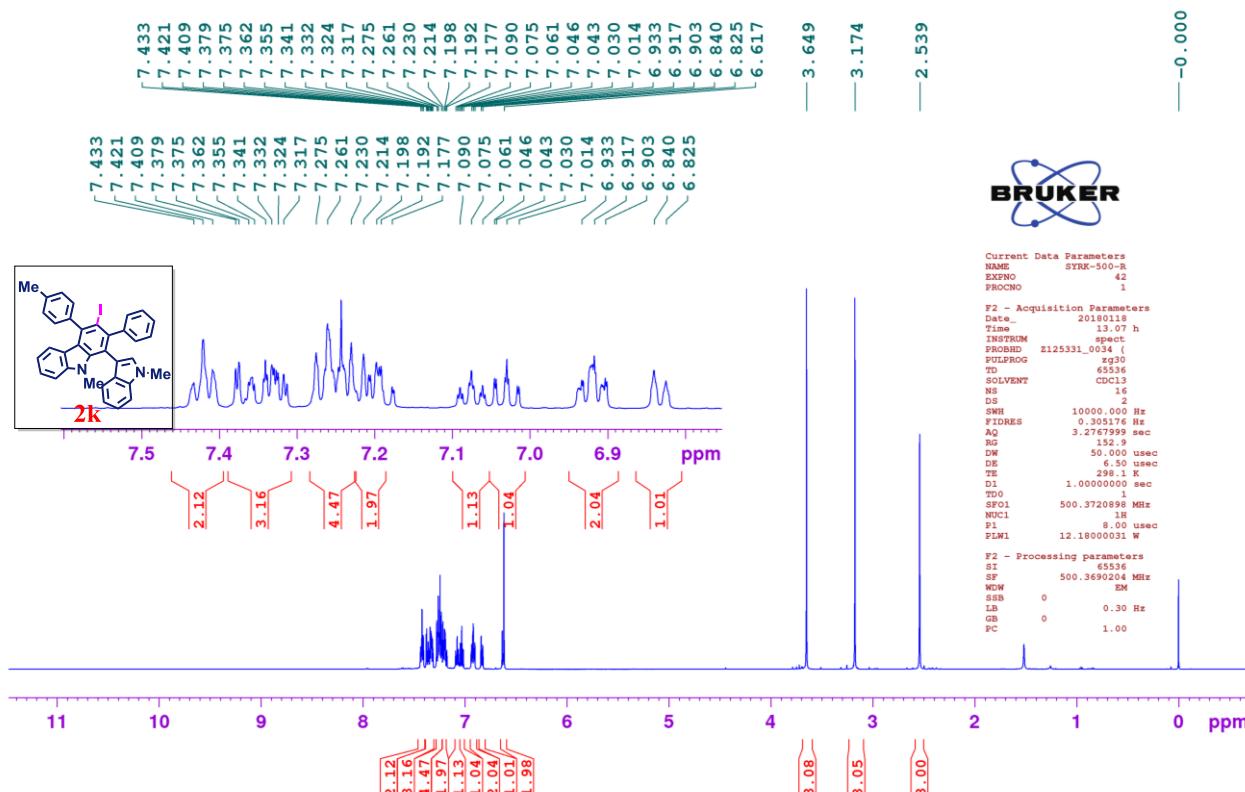
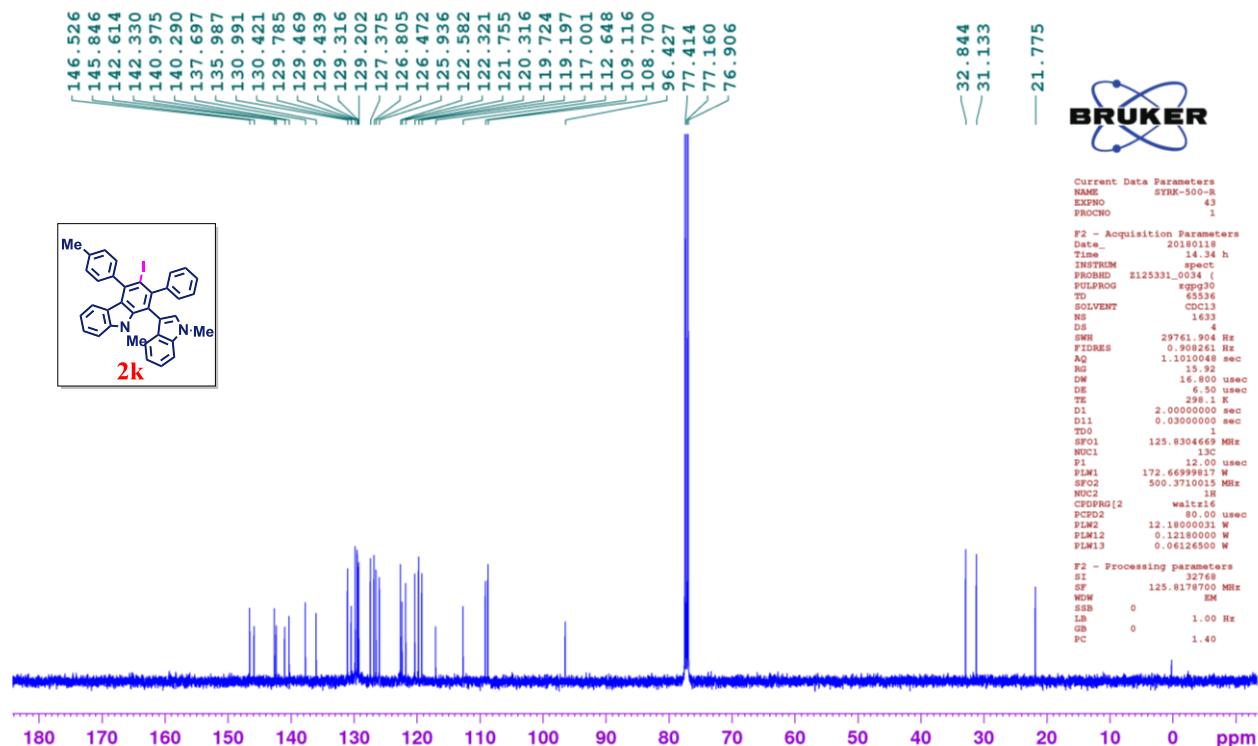


Figure S42 ¹³C NMR in CDCl₃

Figure S43 ^1H NMR in CDCl_3 Figure S44 ^{13}C NMR in CDCl_3

SYRK--4- 109 R

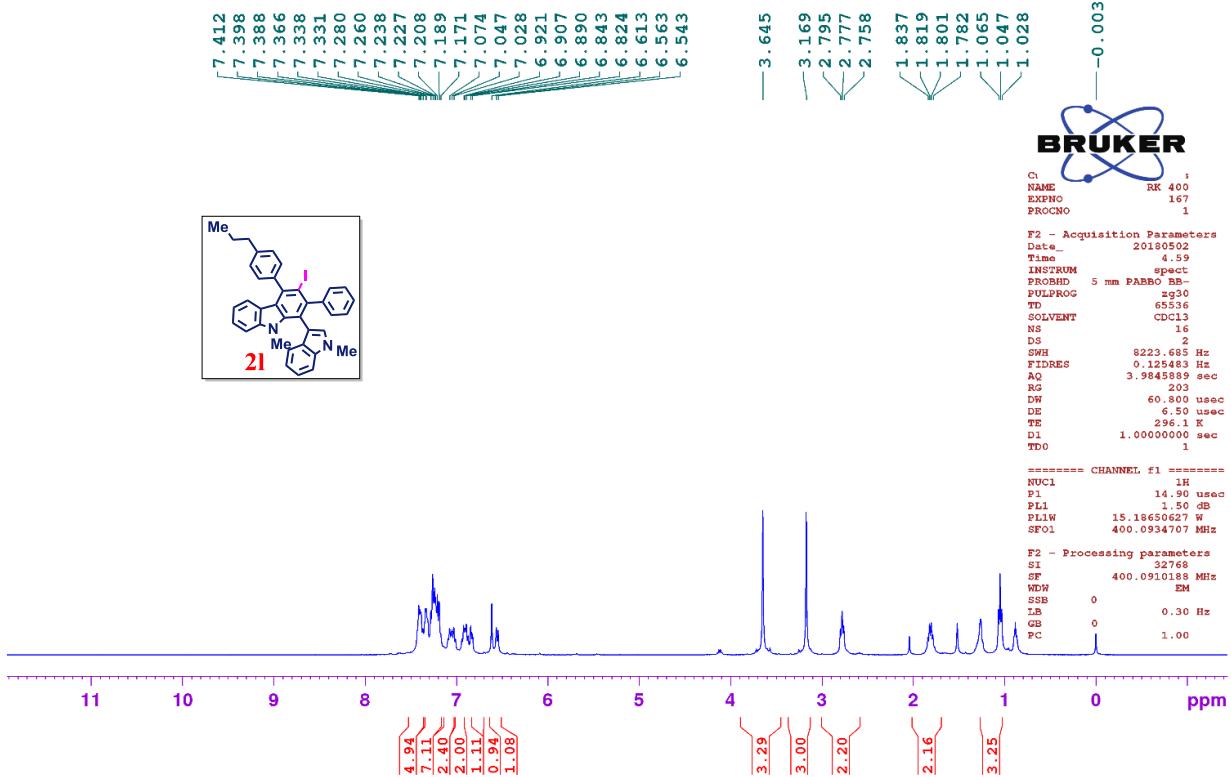


Figure S45 ¹H NMR in CDCl₃

SYRK--4- 109 R

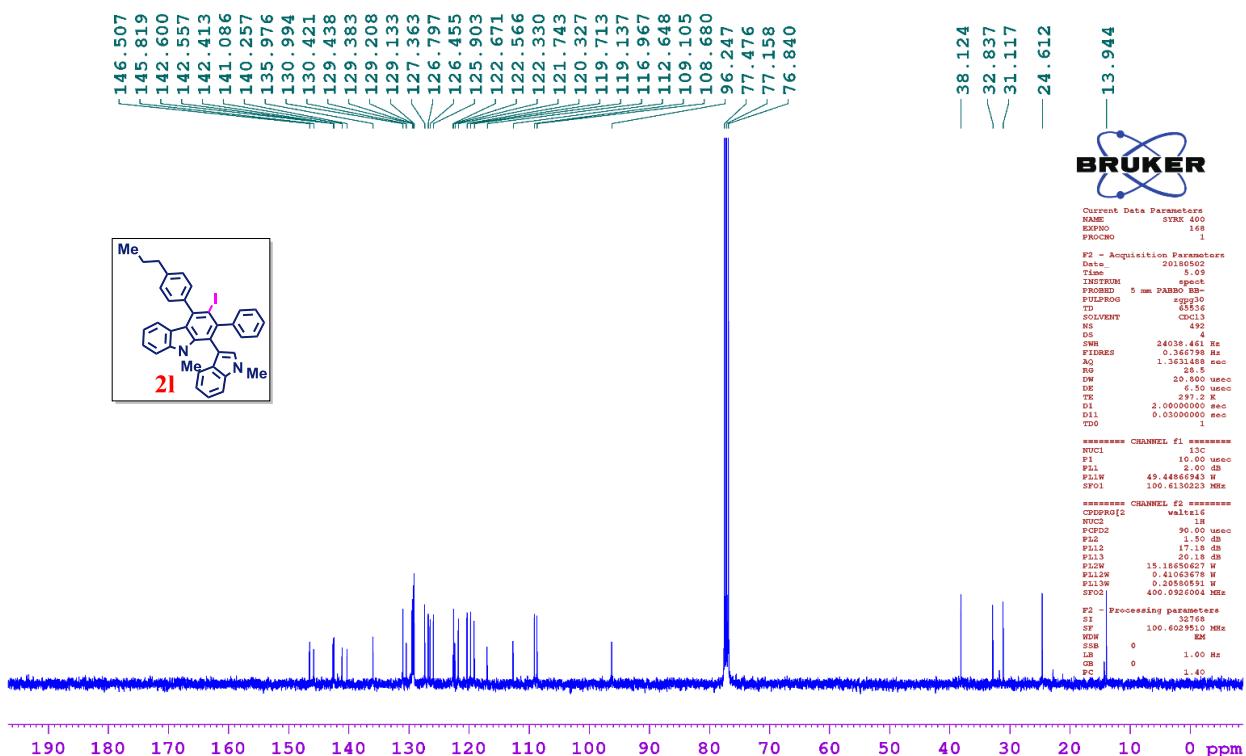


Figure S46 ¹³C NMR in CDCl₃

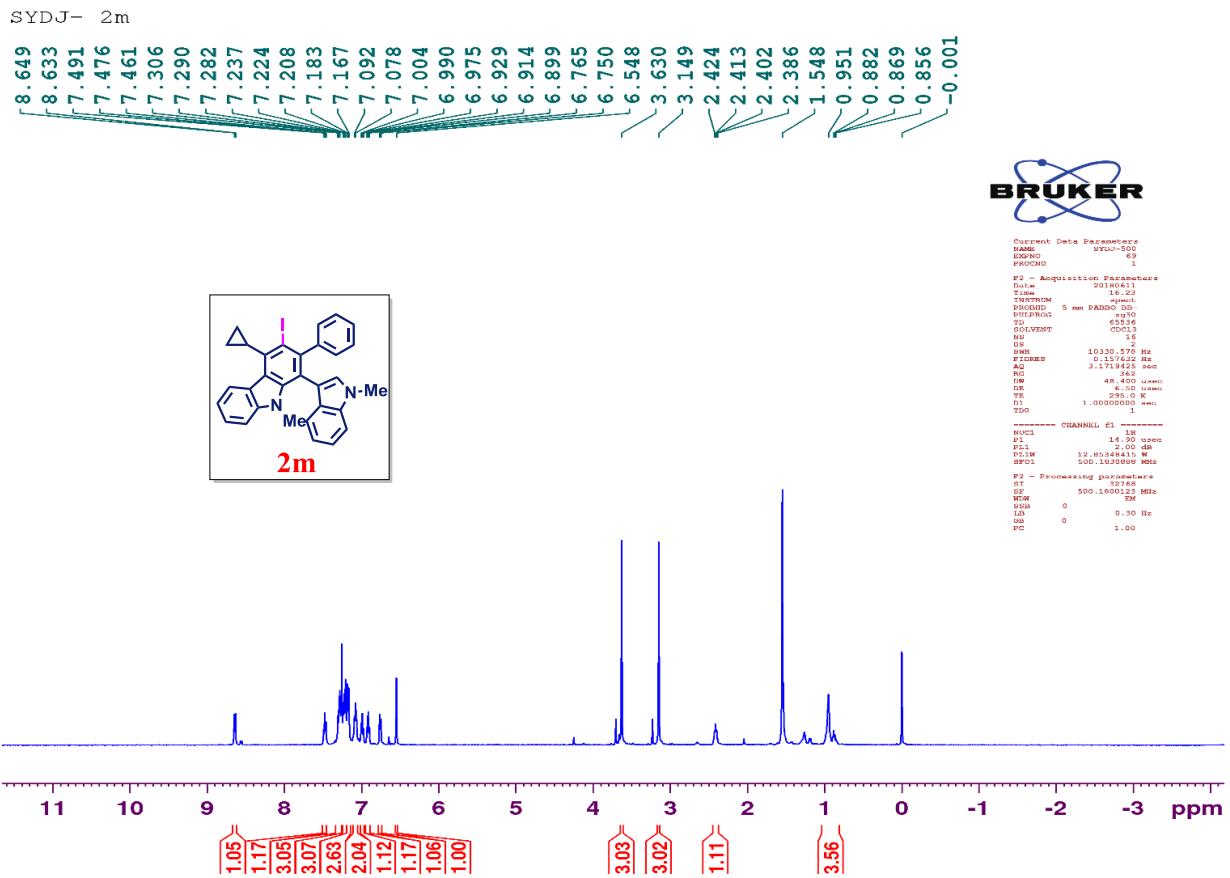


Figure S47 ^1H NMR in CDCl_3

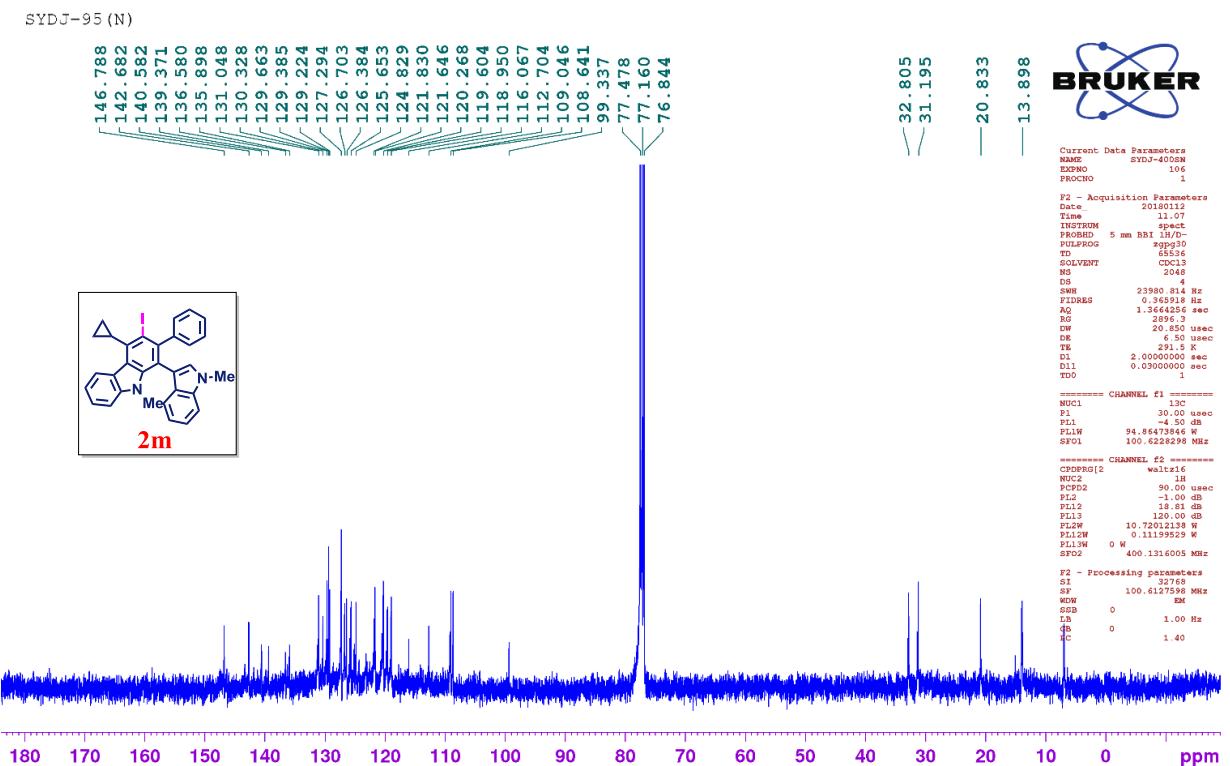
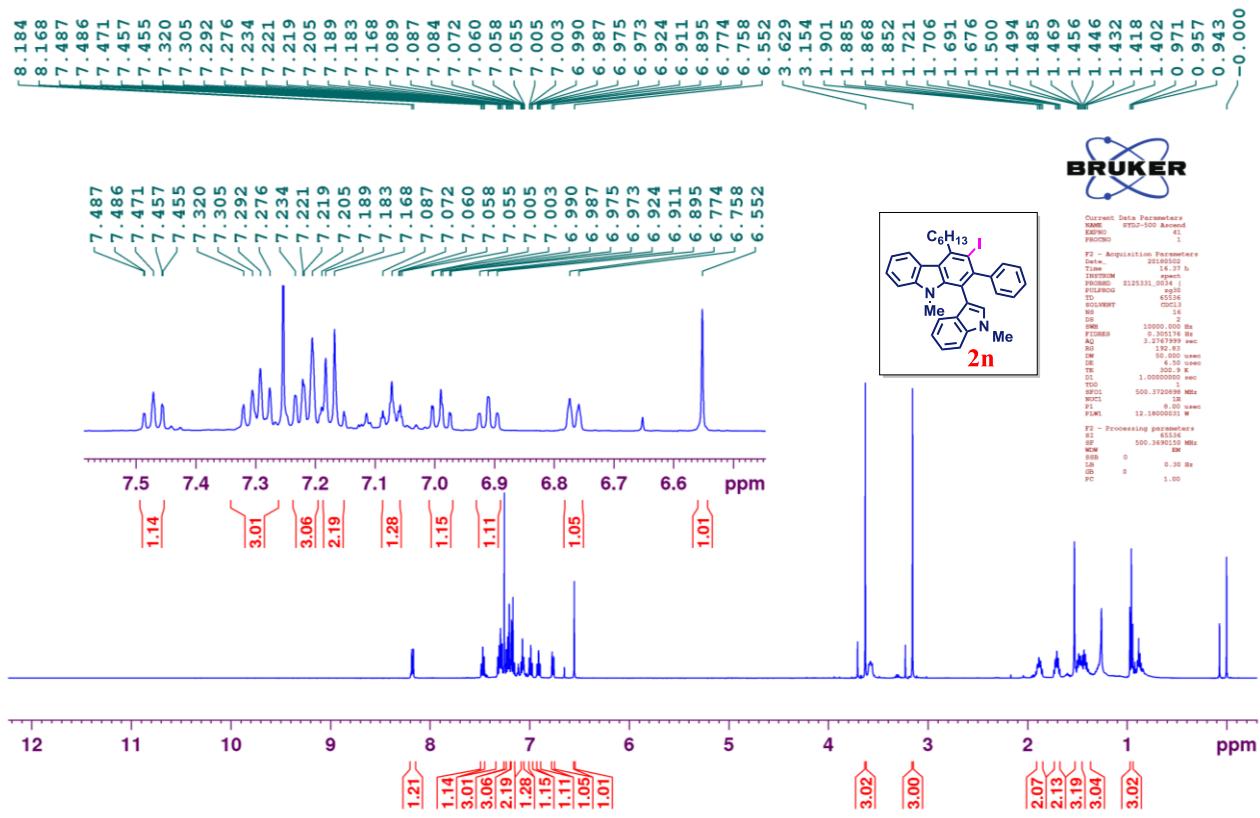
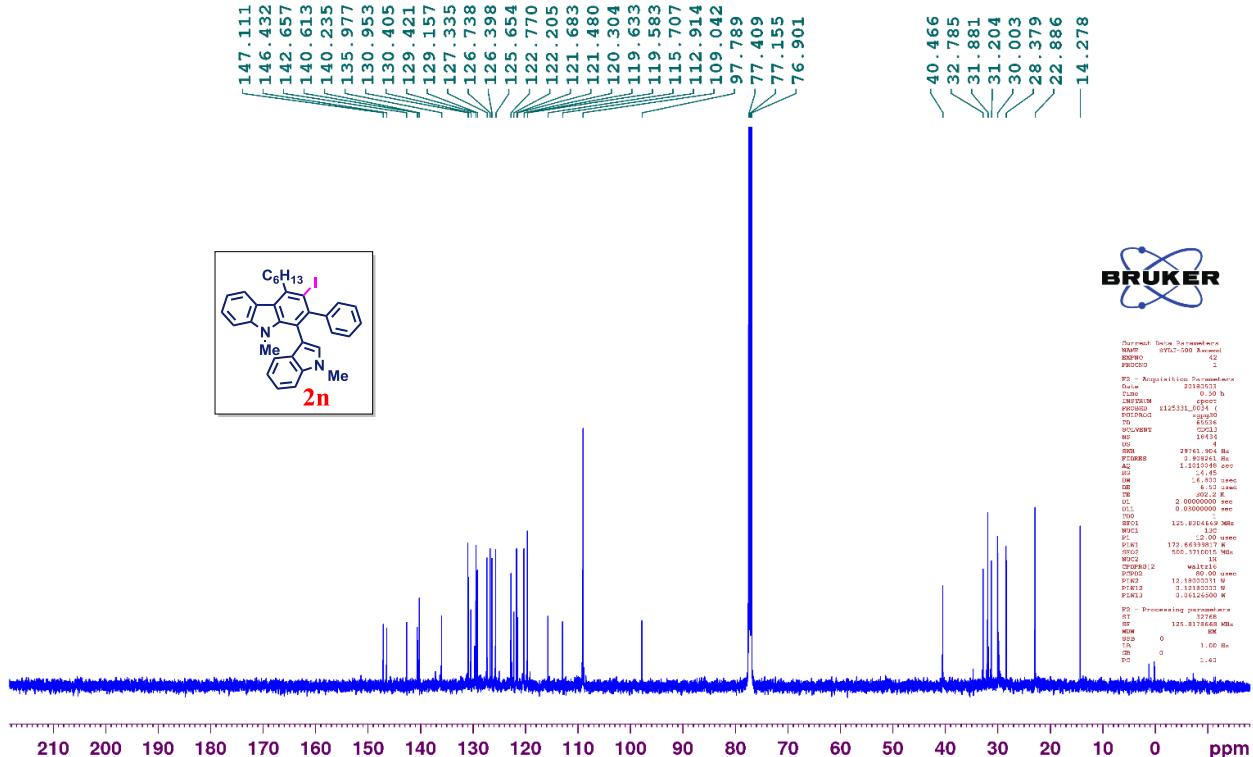
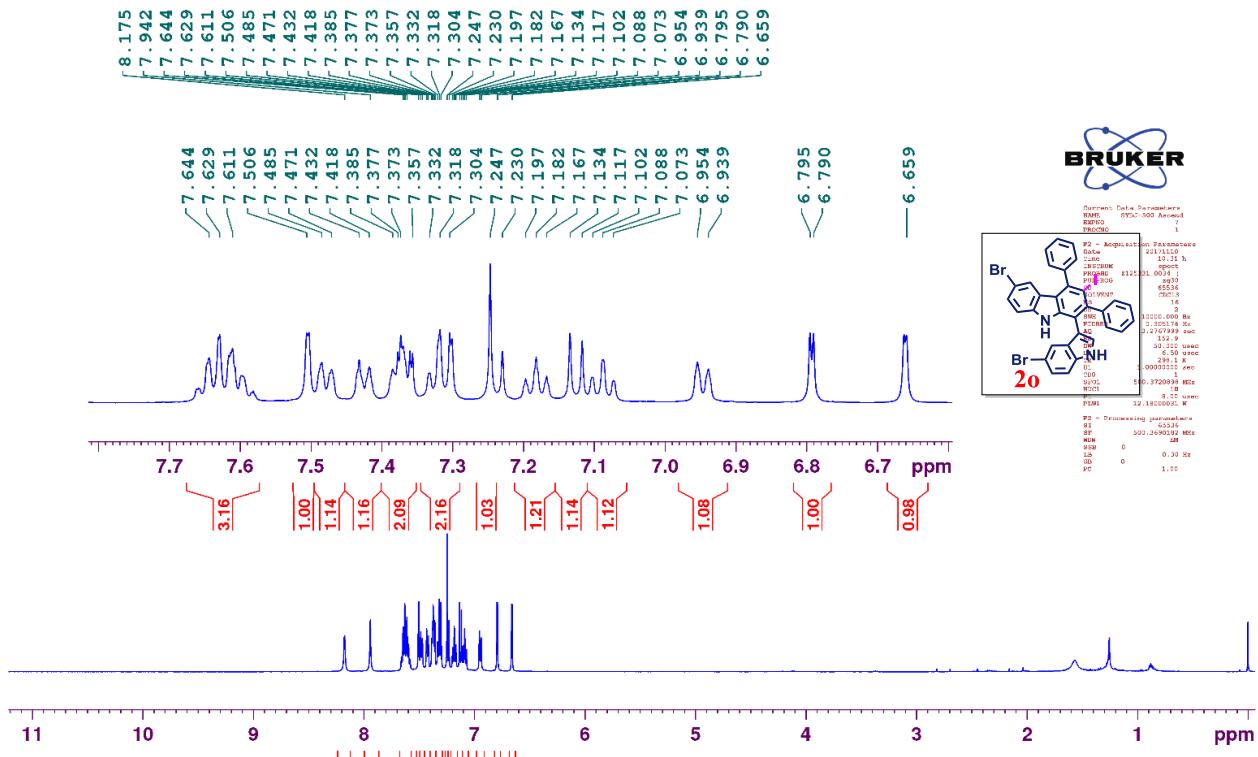
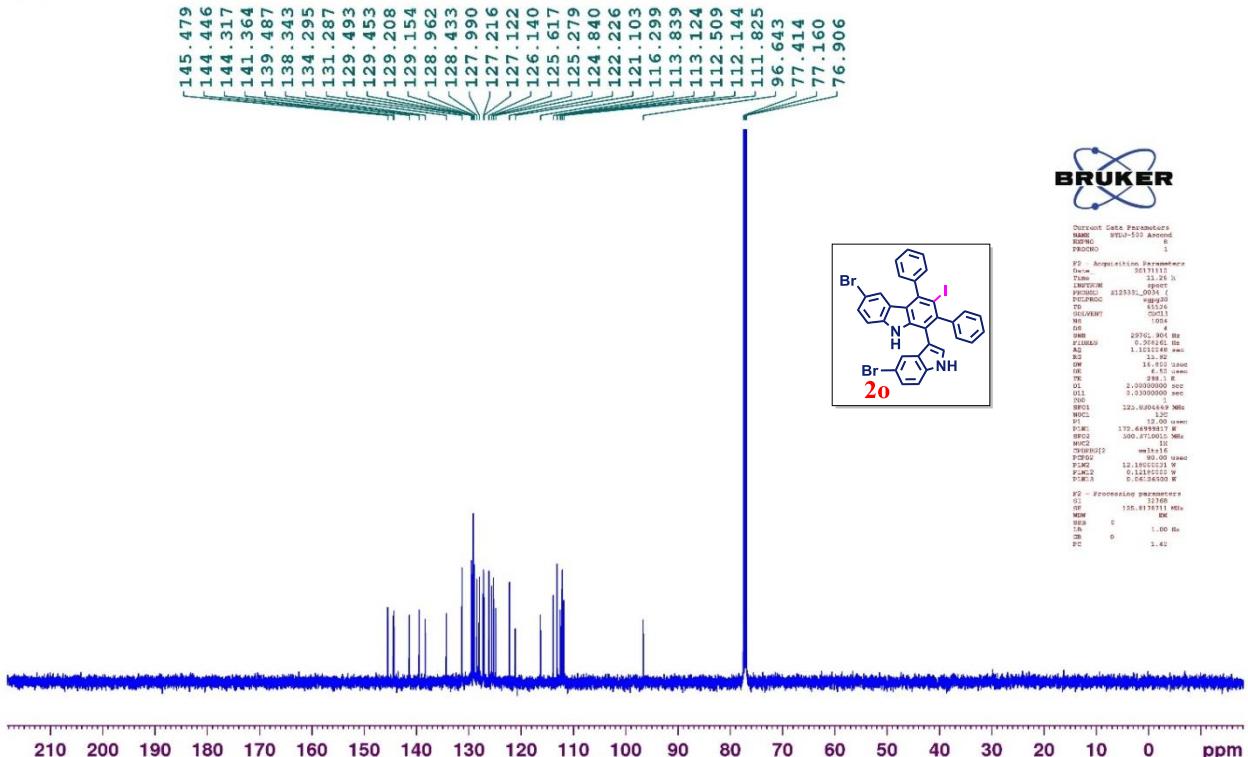
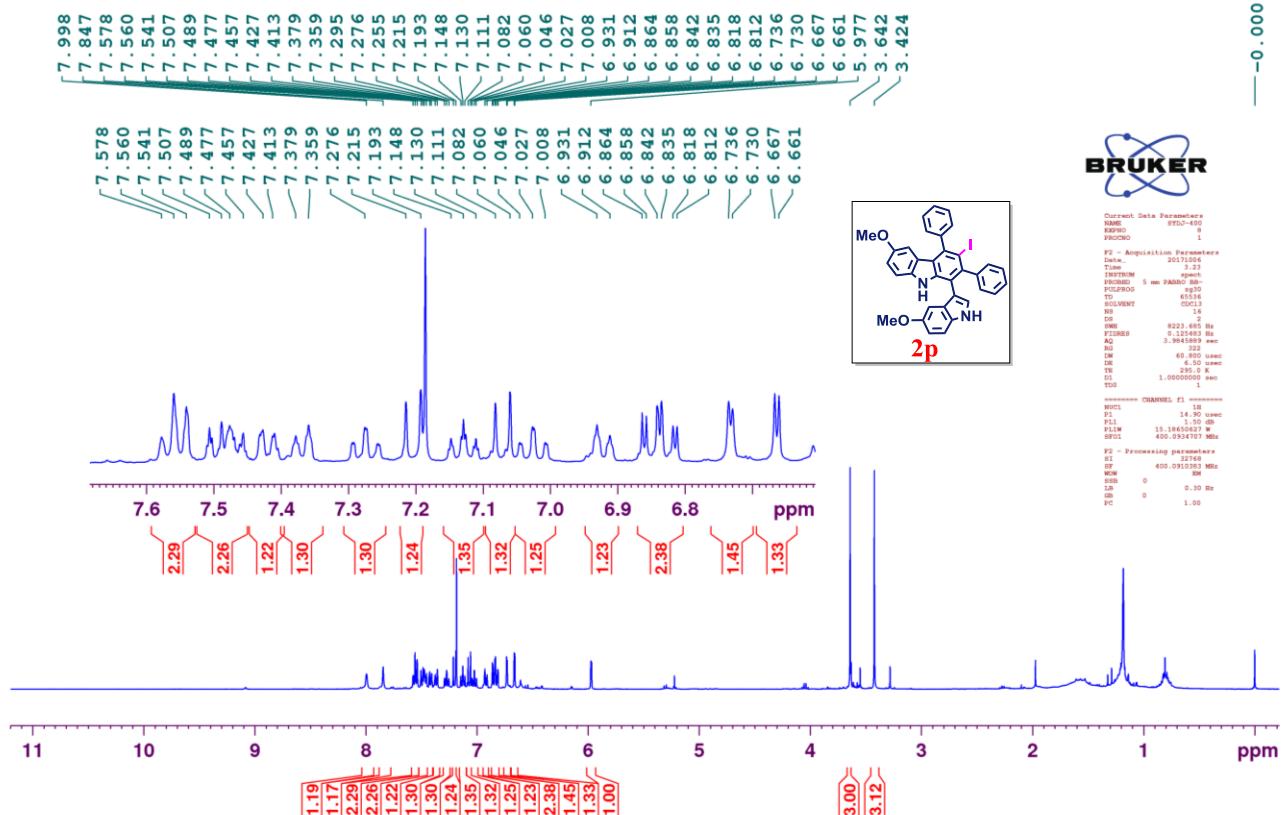


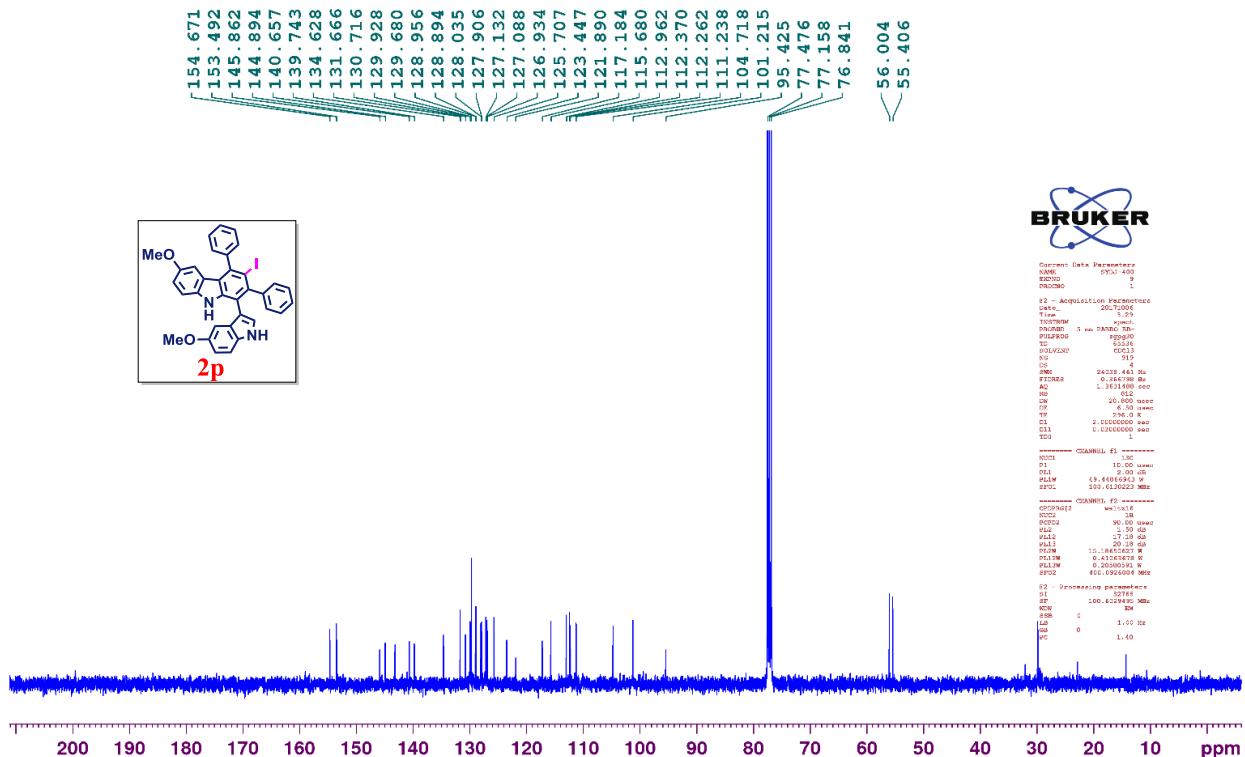
Figure S48 ^{13}C NMR in CDCl_3

Figure S49 ^1H NMR in CDCl_3 Figure S50 ^{13}C NMR in CDCl_3

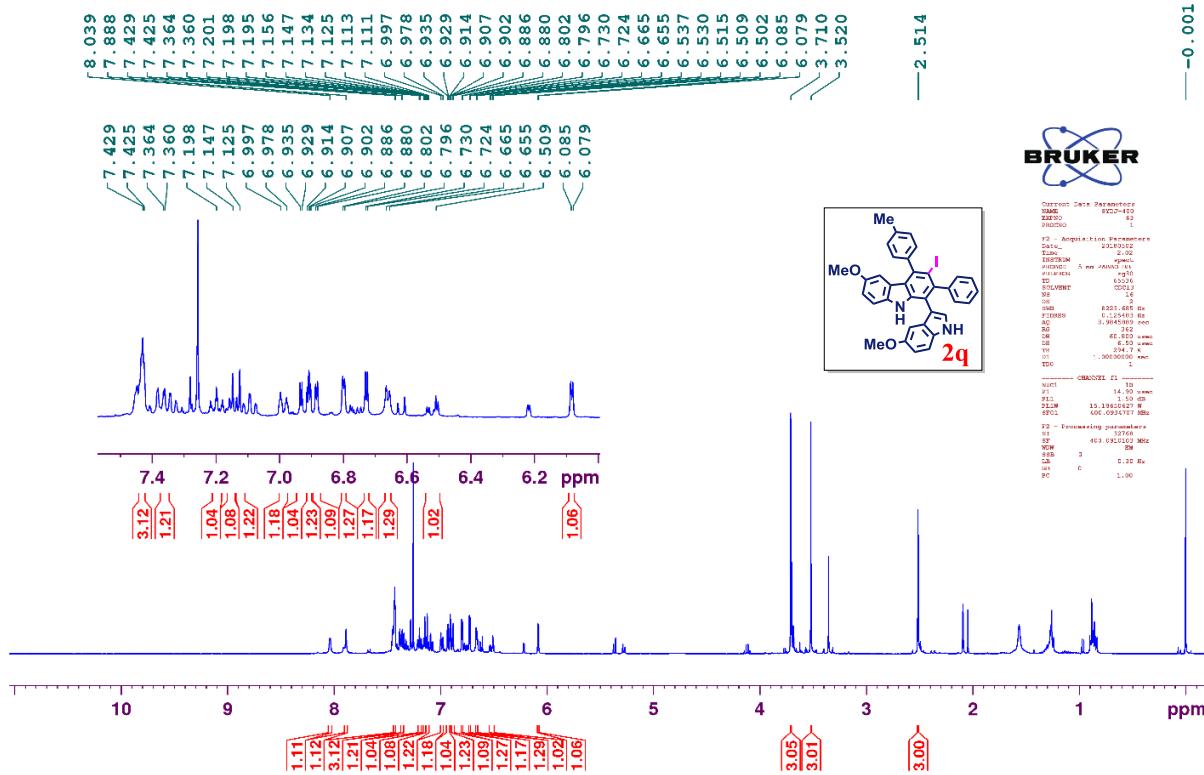
Figure S51 ^1H NMR in CDCl_3 Figure S52 ^{13}C NMR in CDCl_3



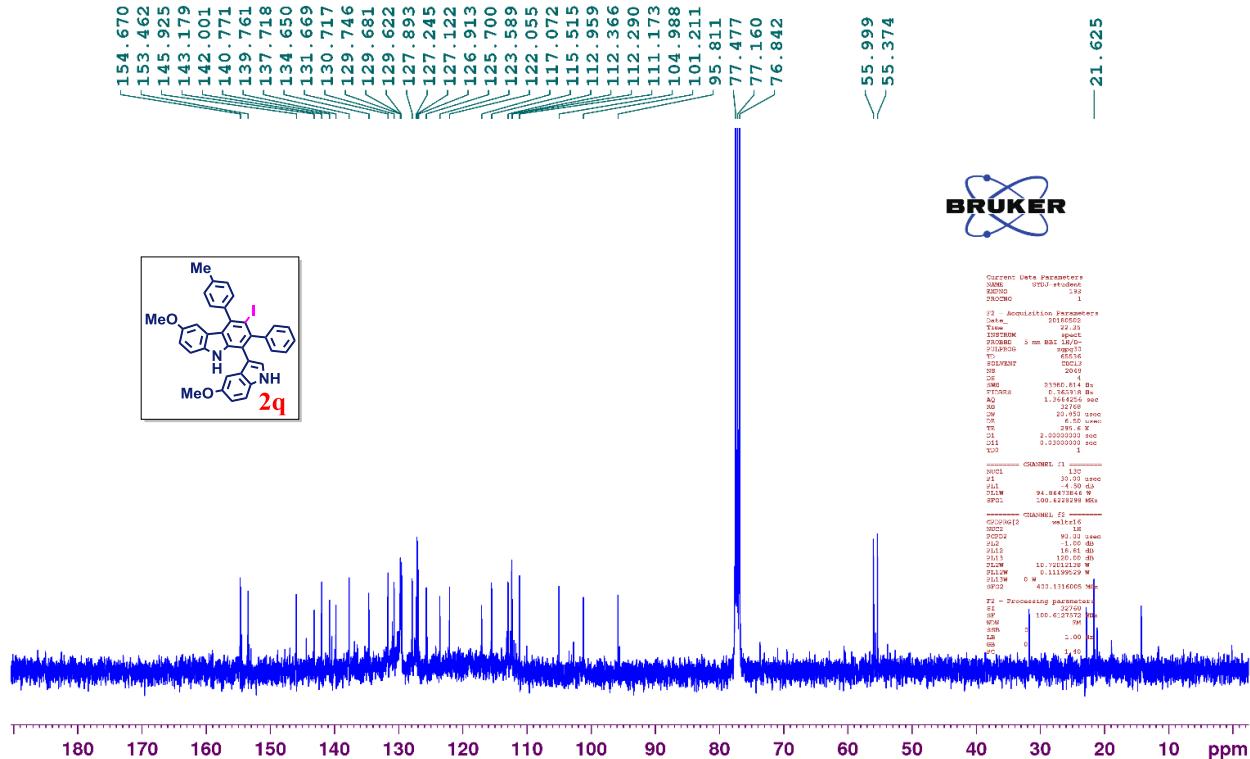
SYDJ-43-A



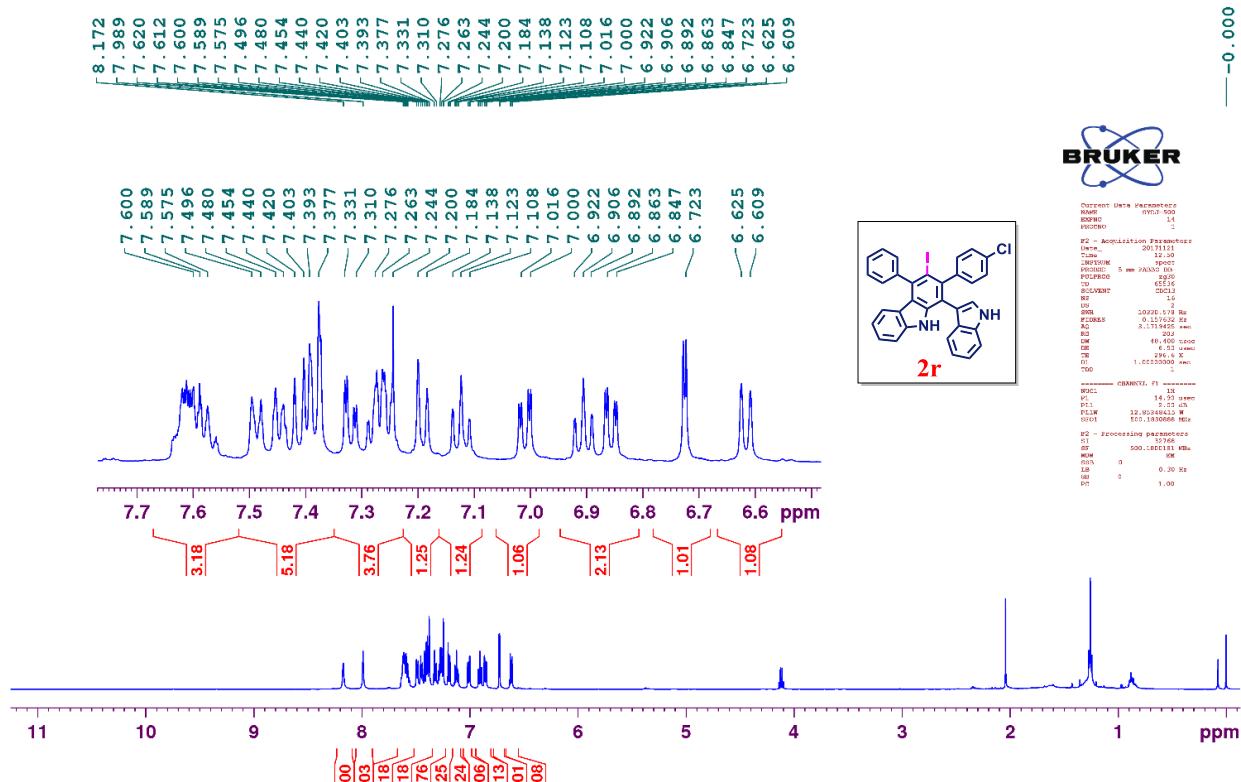
SYDJ-149



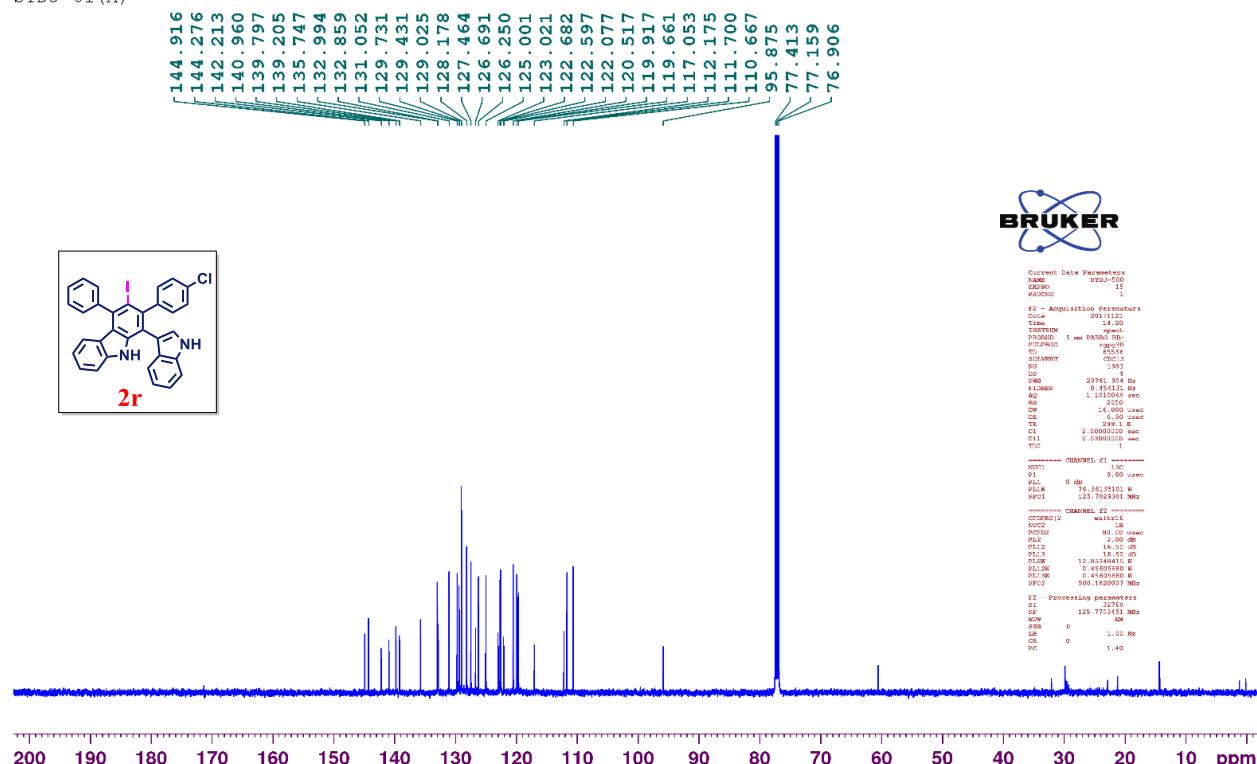
SYDJ-149



SYDJ-61 (A)



SYDJ-61 (A)



SYDJ-123

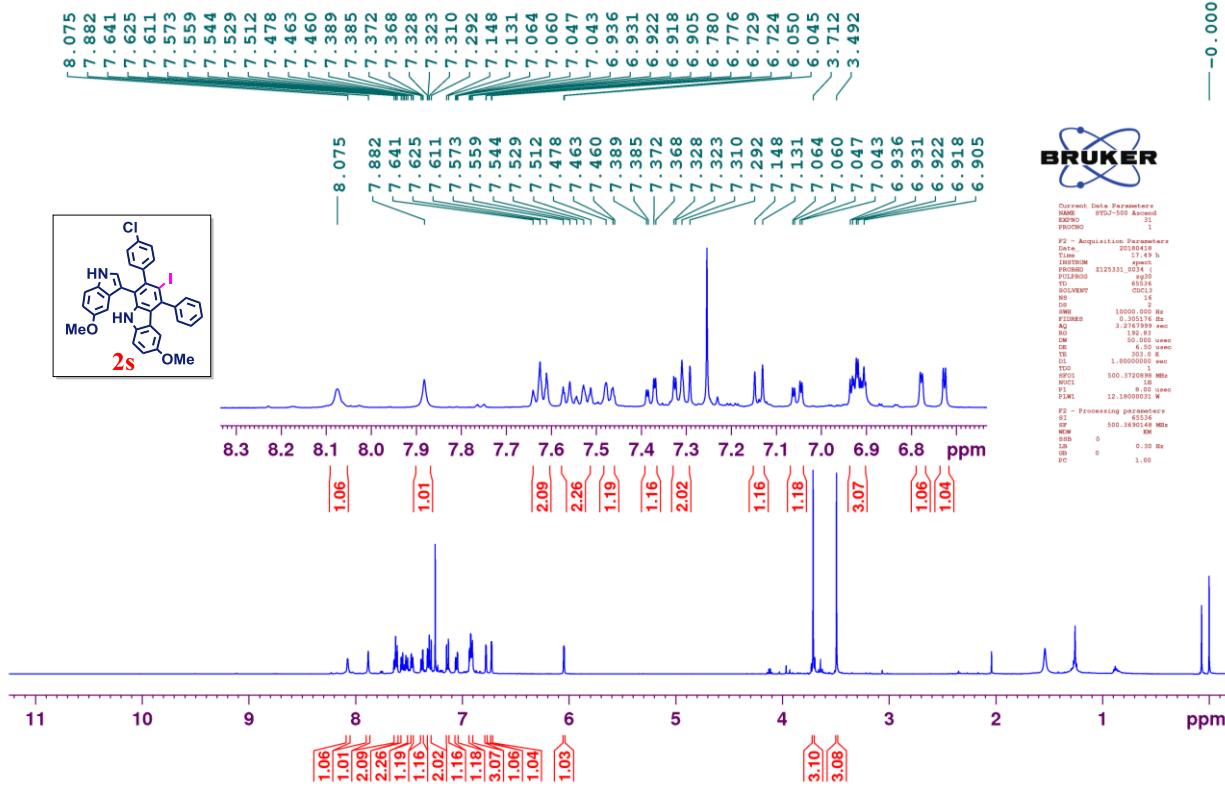


Figure S59 ^1H NMR in CDCl_3

SYDJ-123

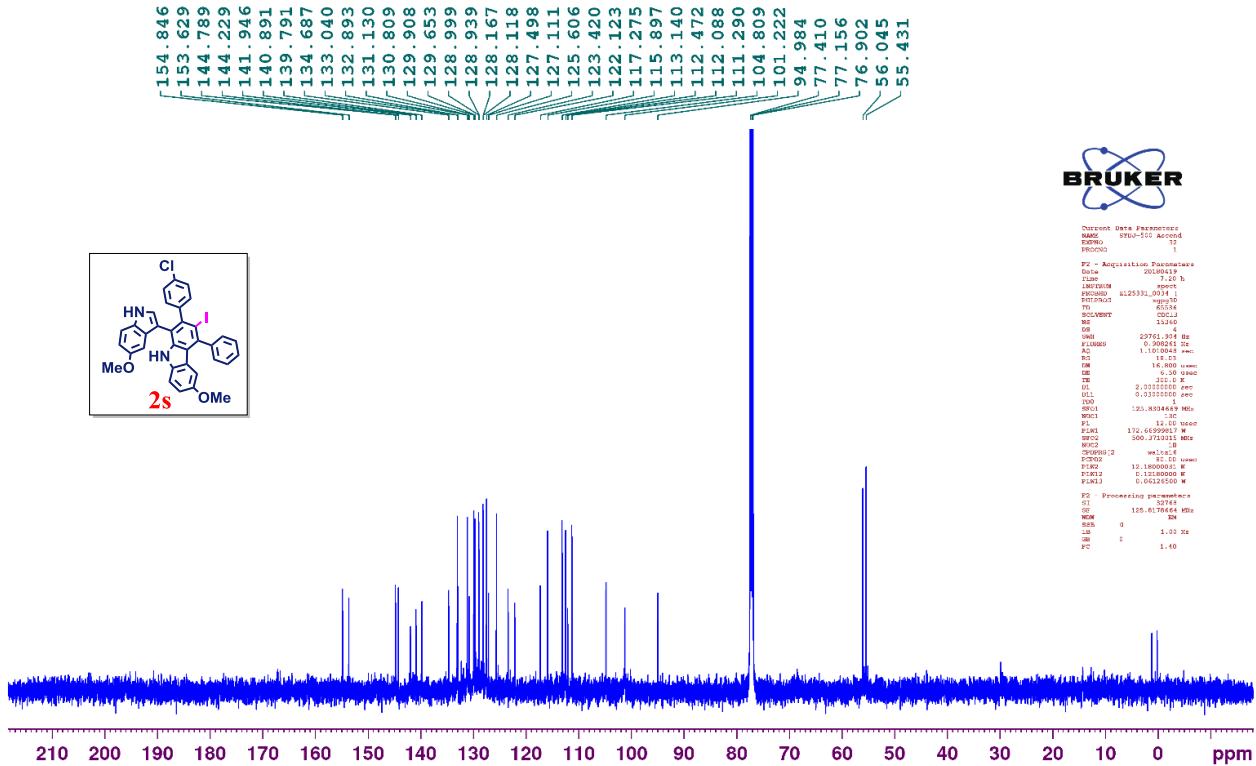
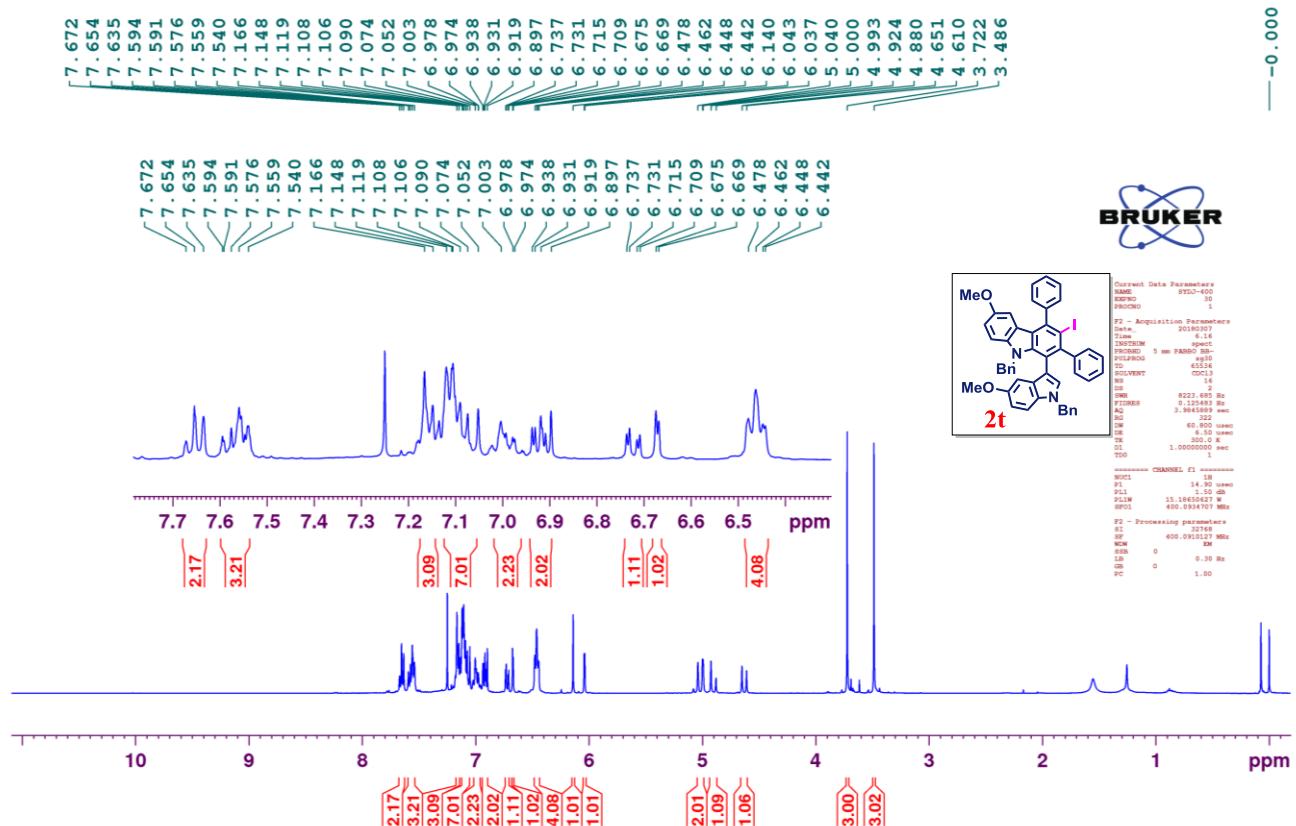
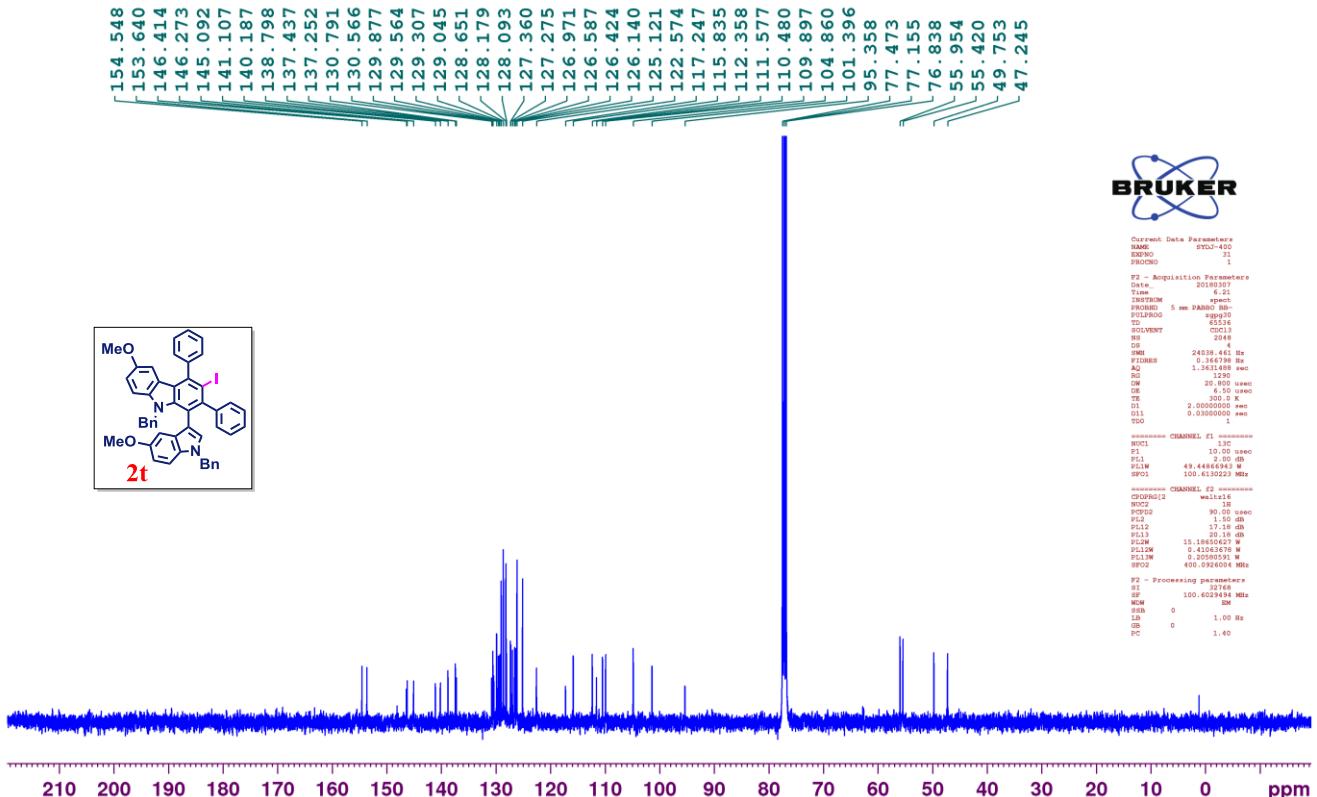
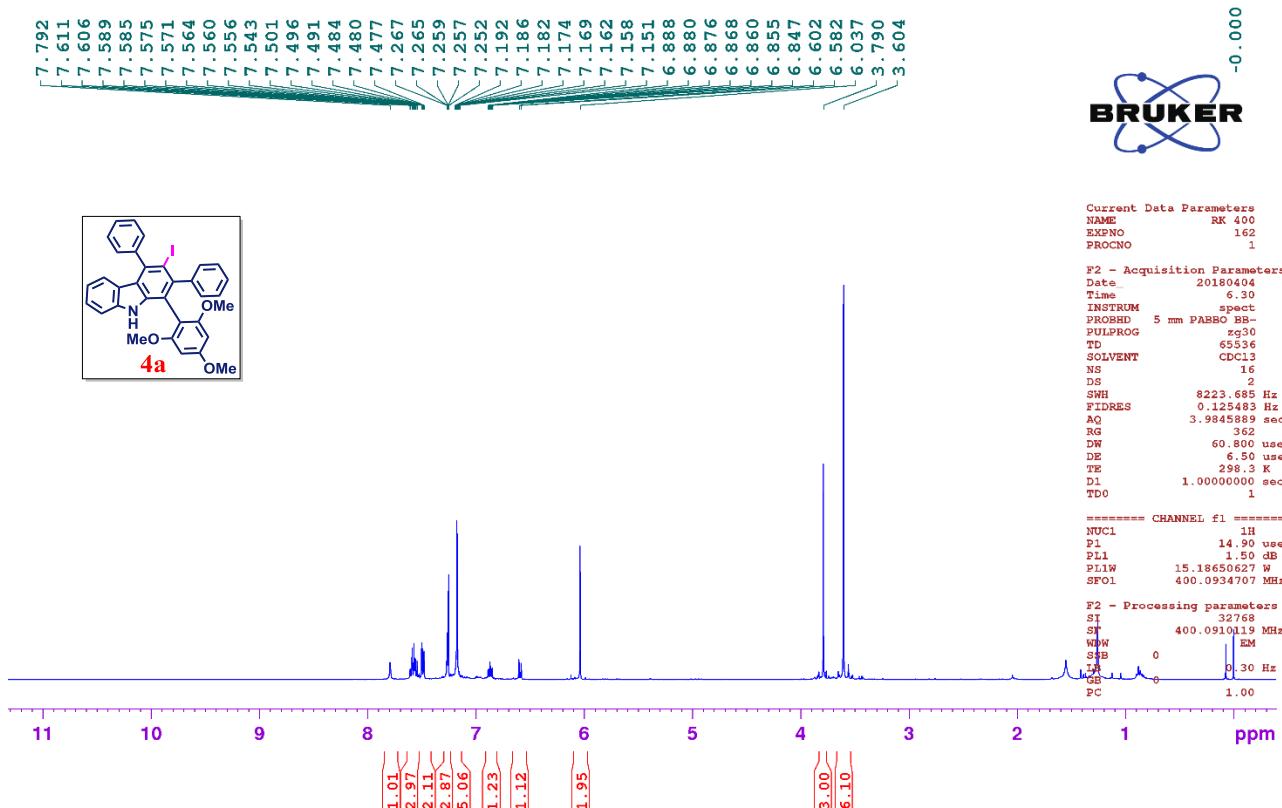


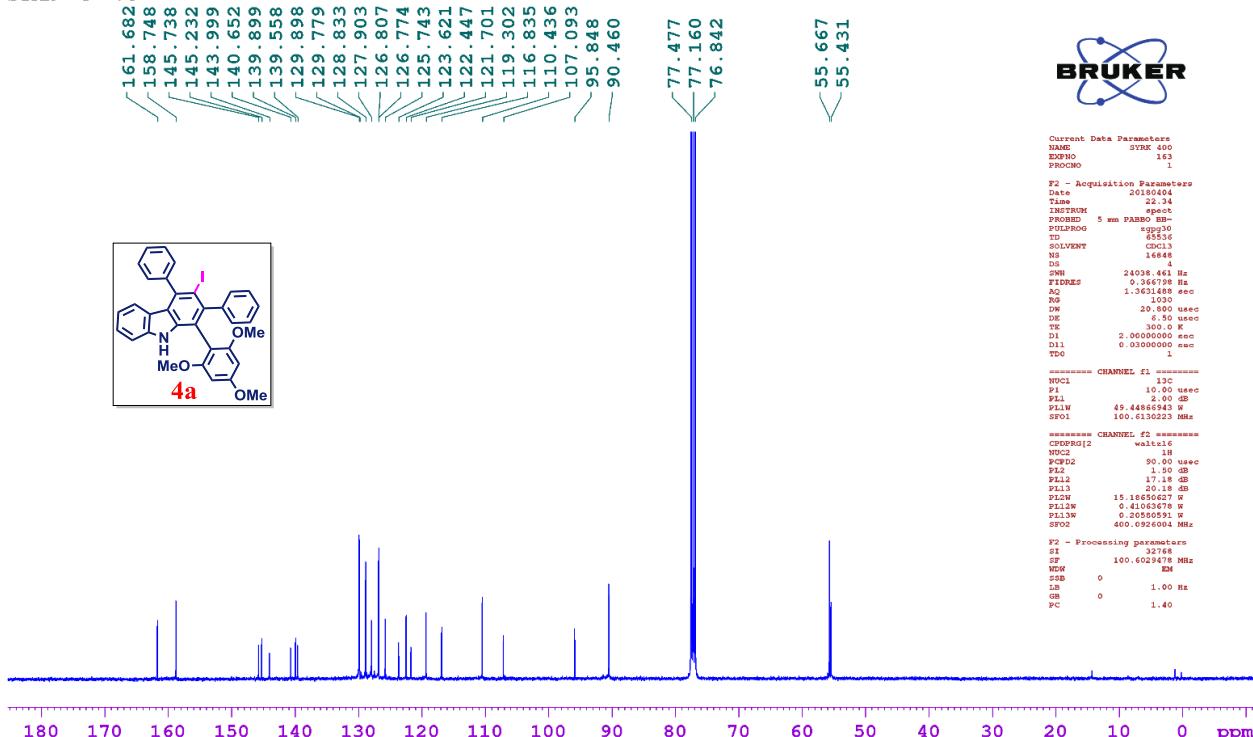
Figure S60 ^{13}C NMR in CDCl_3

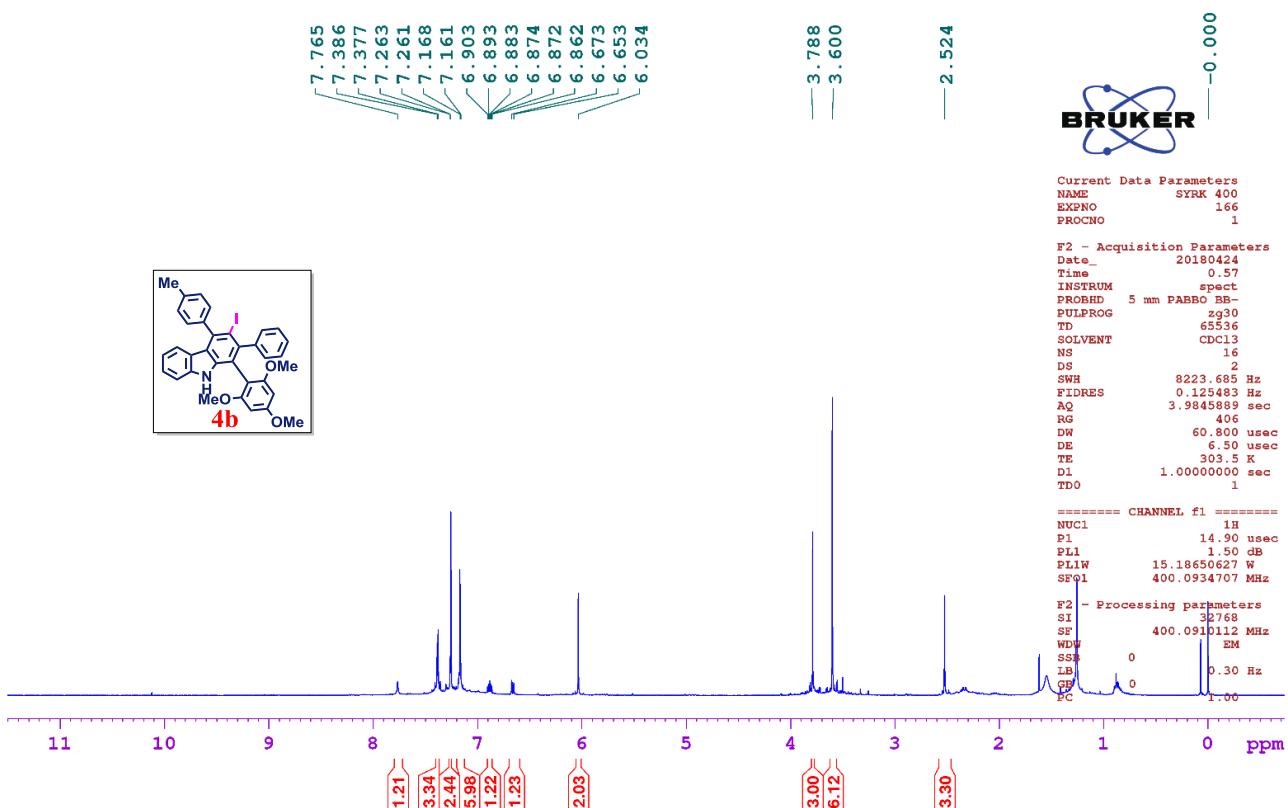
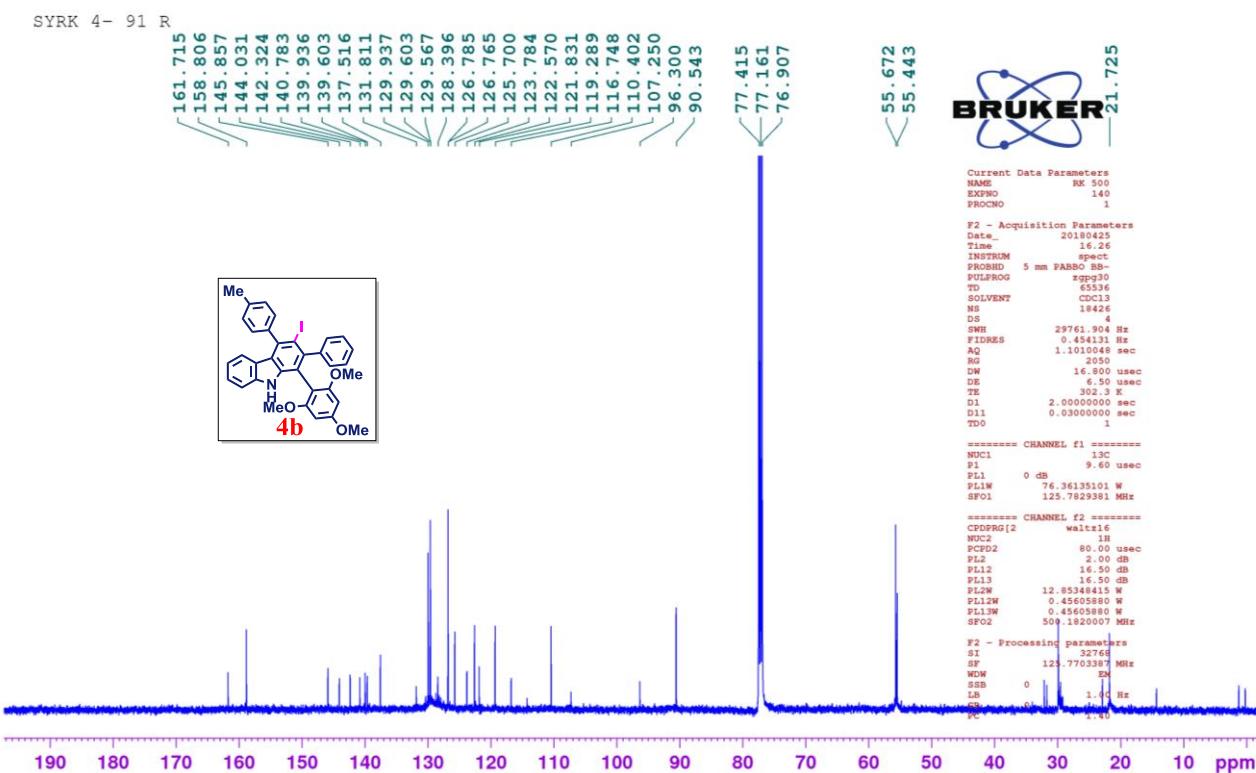
Figure S61 ^1H NMR in CDCl_3 Figure S62 ^{13}C NMR in CDCl_3

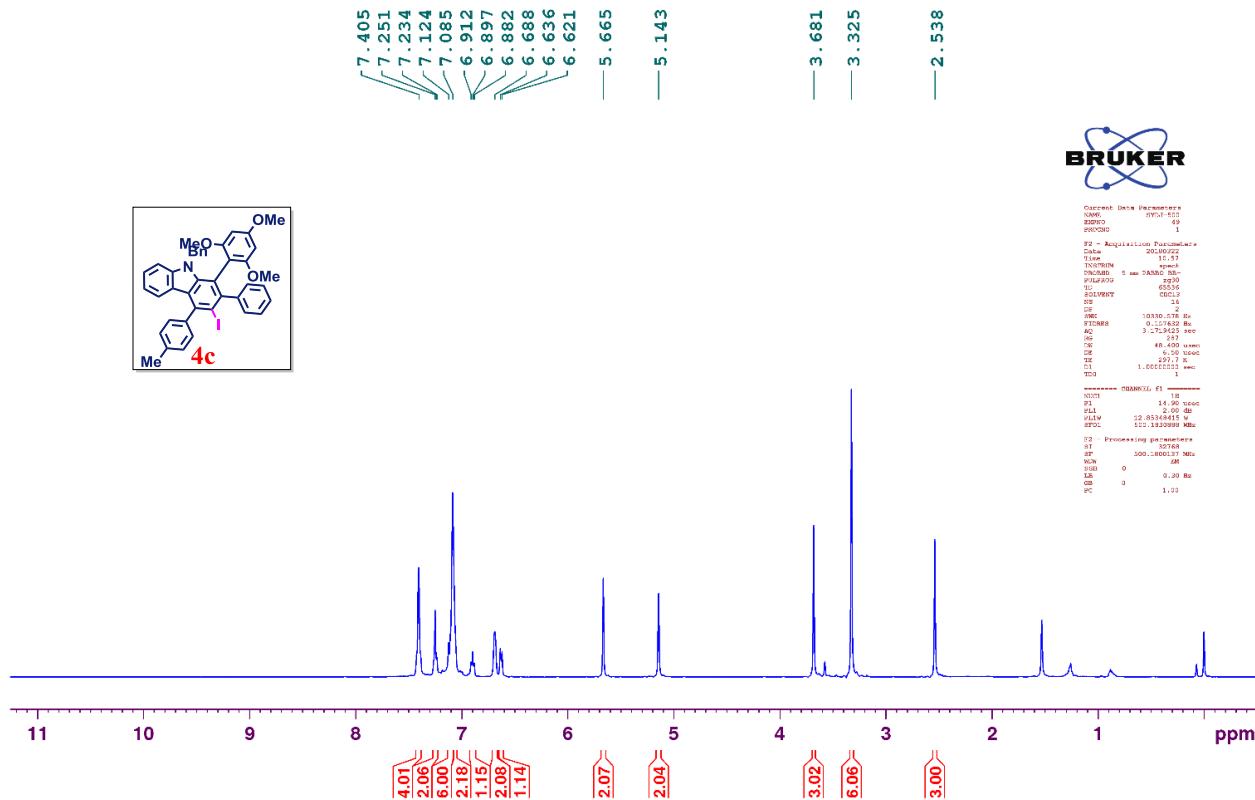
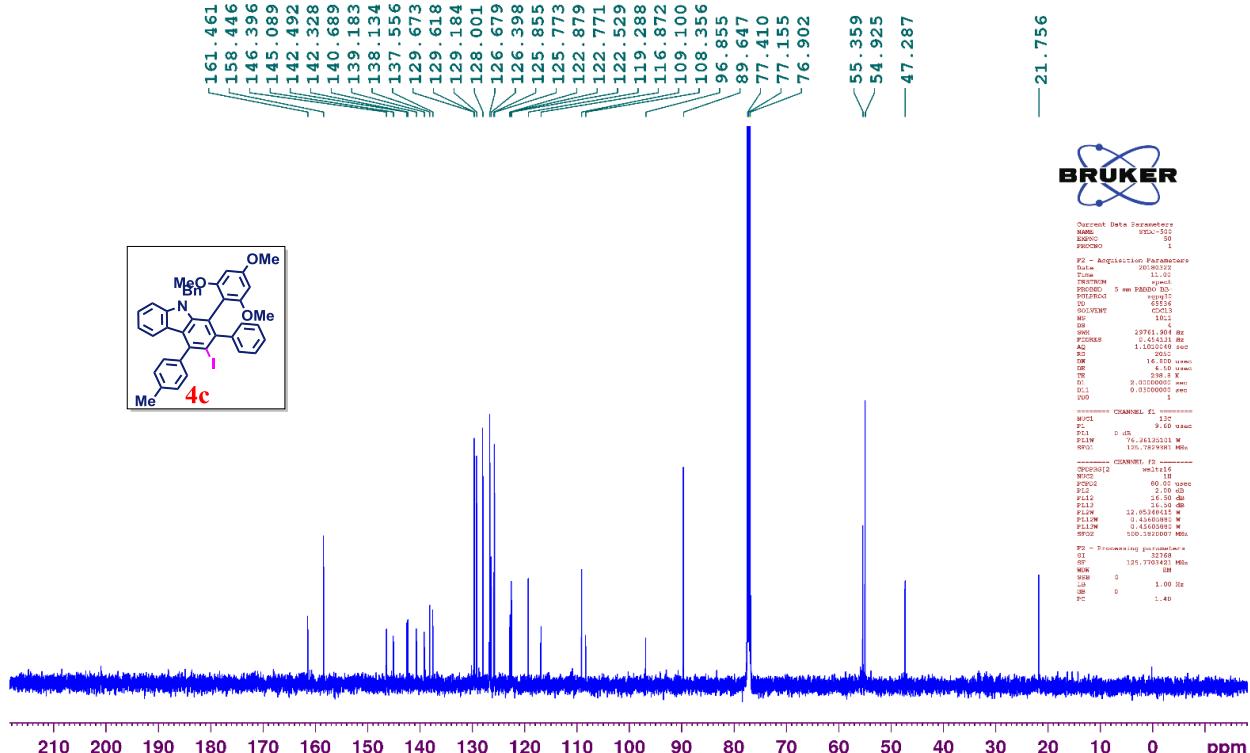
SYRK--4- 76

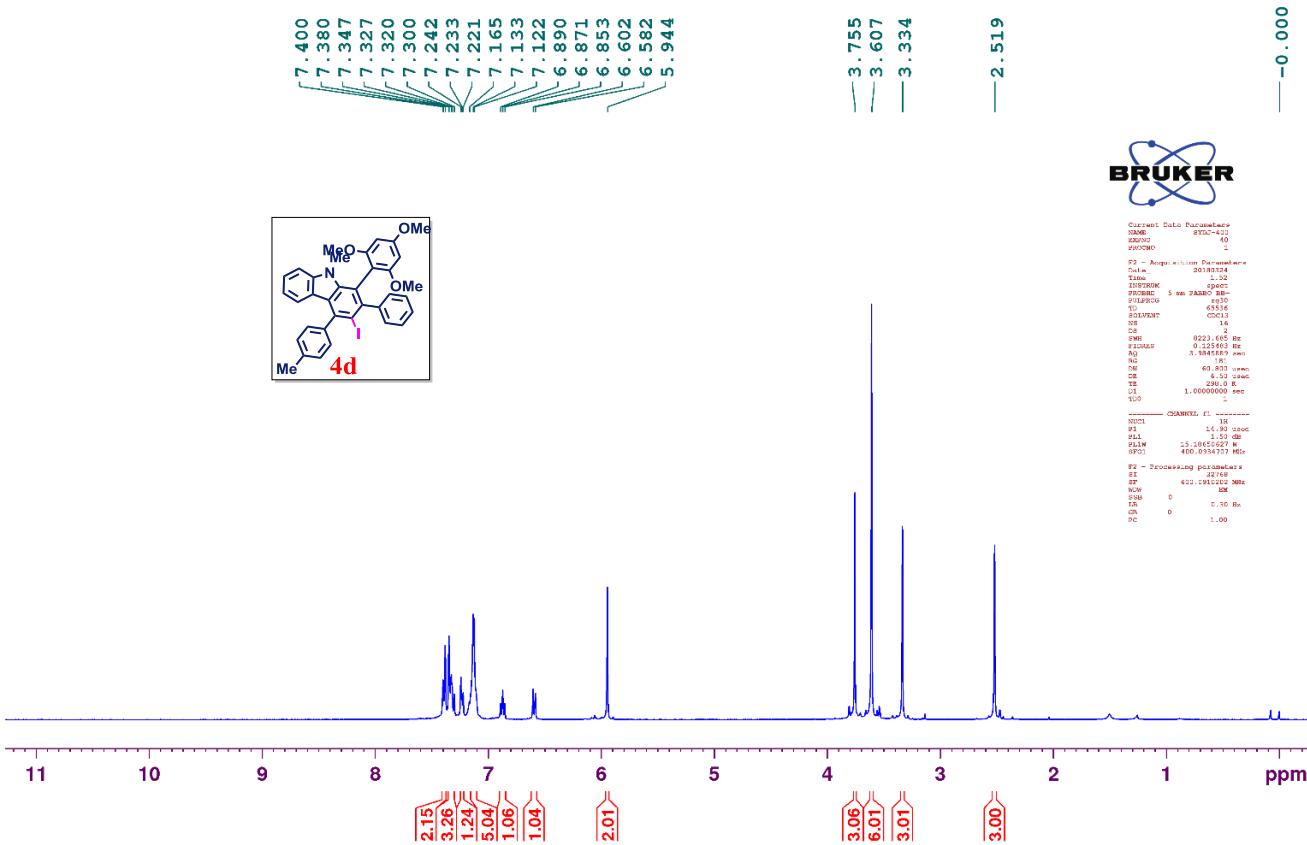
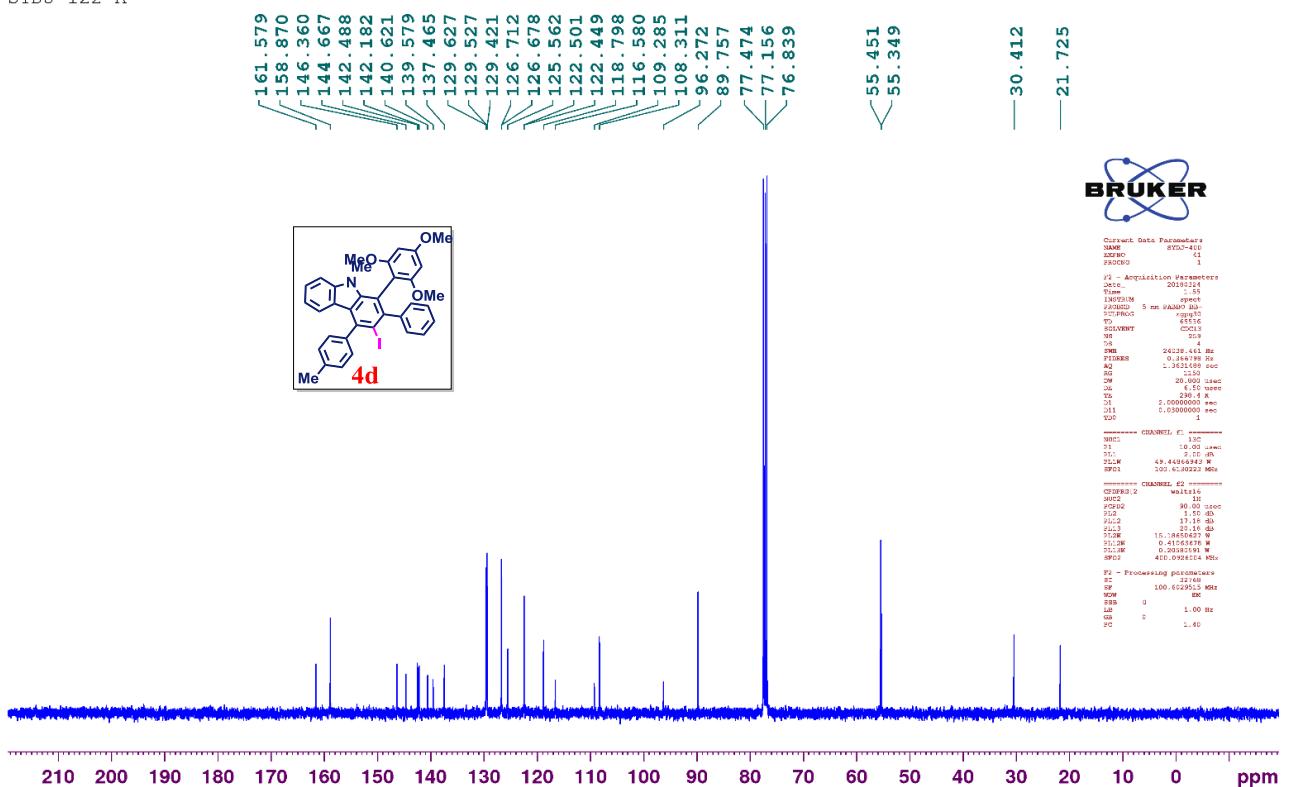
Figure S63 ^1H NMR in CDCl_3

SYRK--4- 76



Figure S65 ^1H NMR in CDCl_3 Figure S66 ^{13}C NMR in CDCl_3

Figure S67 ¹H NMR in CDCl₃Figure S68 ¹³C NMR in CDCl₃

**Figure S69 ¹H NMR in CDCl₃****Figure S70 ¹³C NMR in CDCl₃**

SYRK-3-181

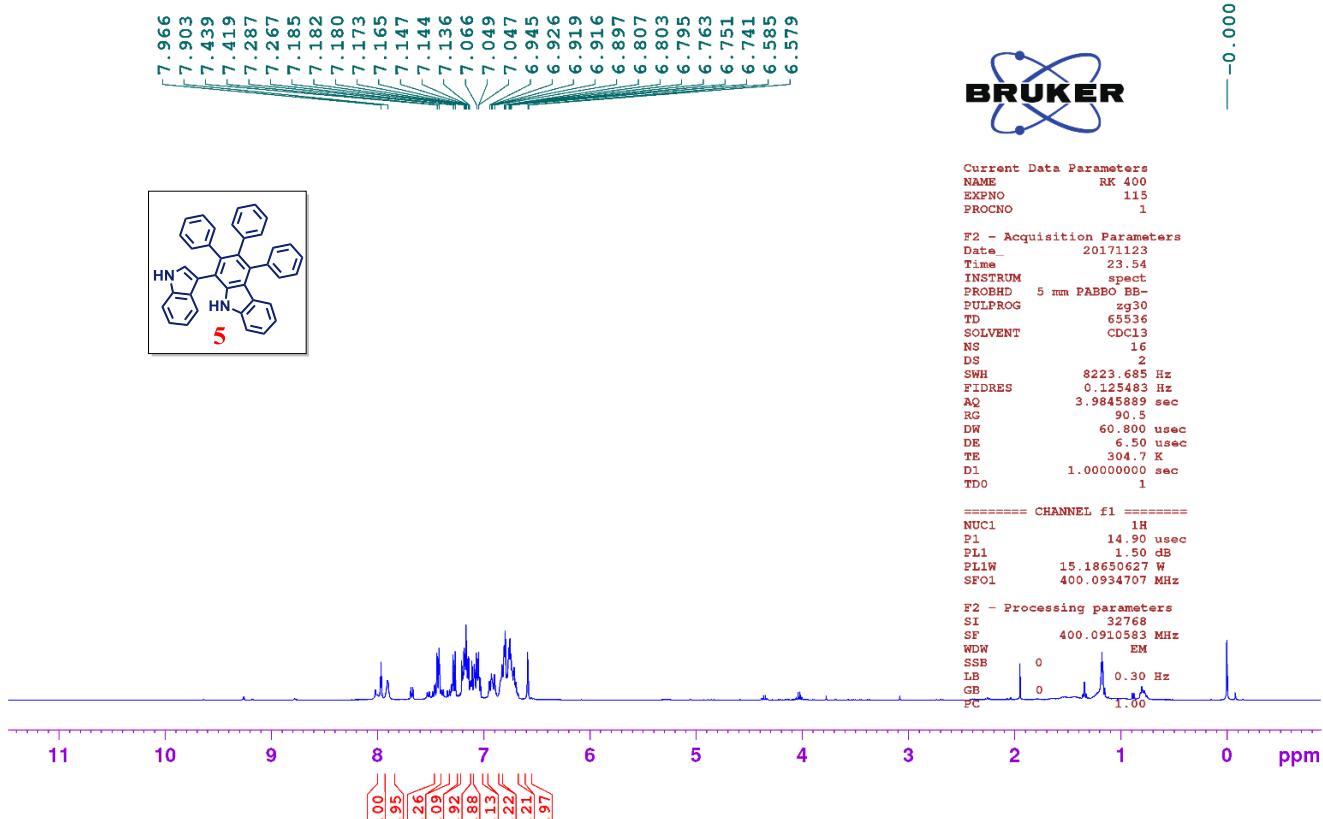


Figure S71 ¹H NMR in CDCl₃

SYRK-3-181

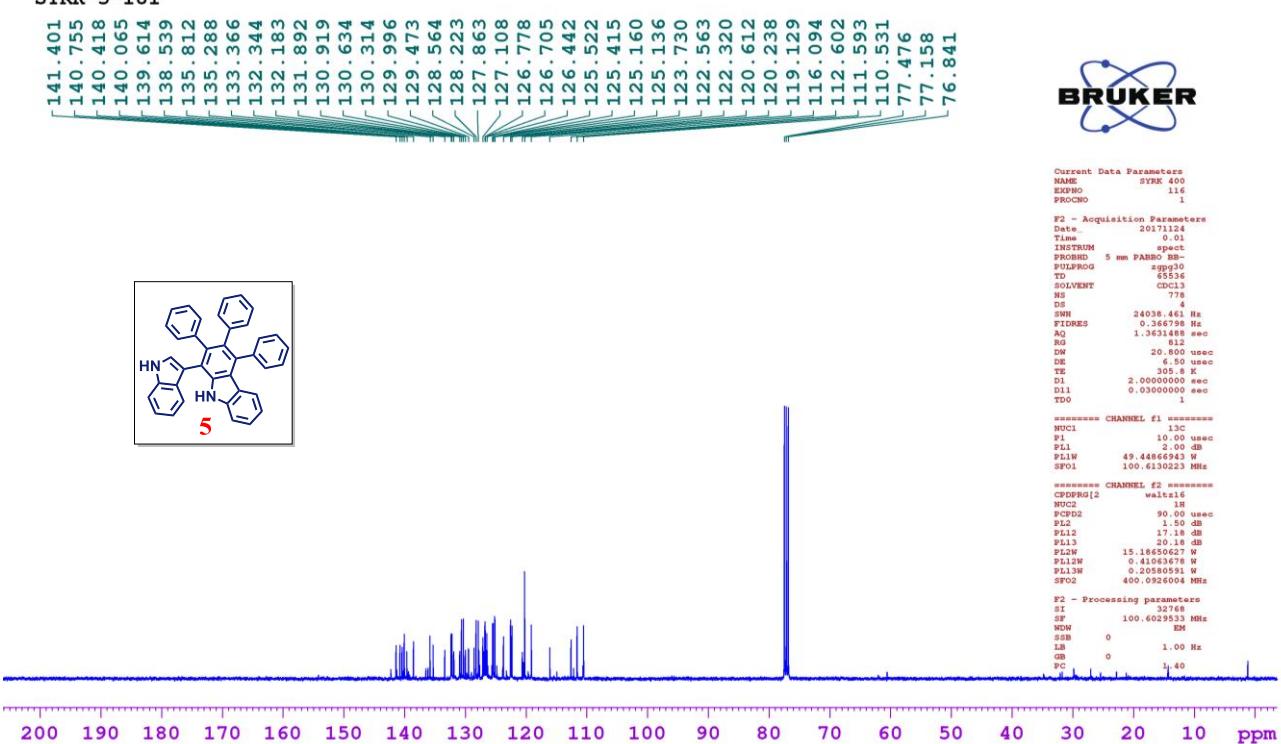
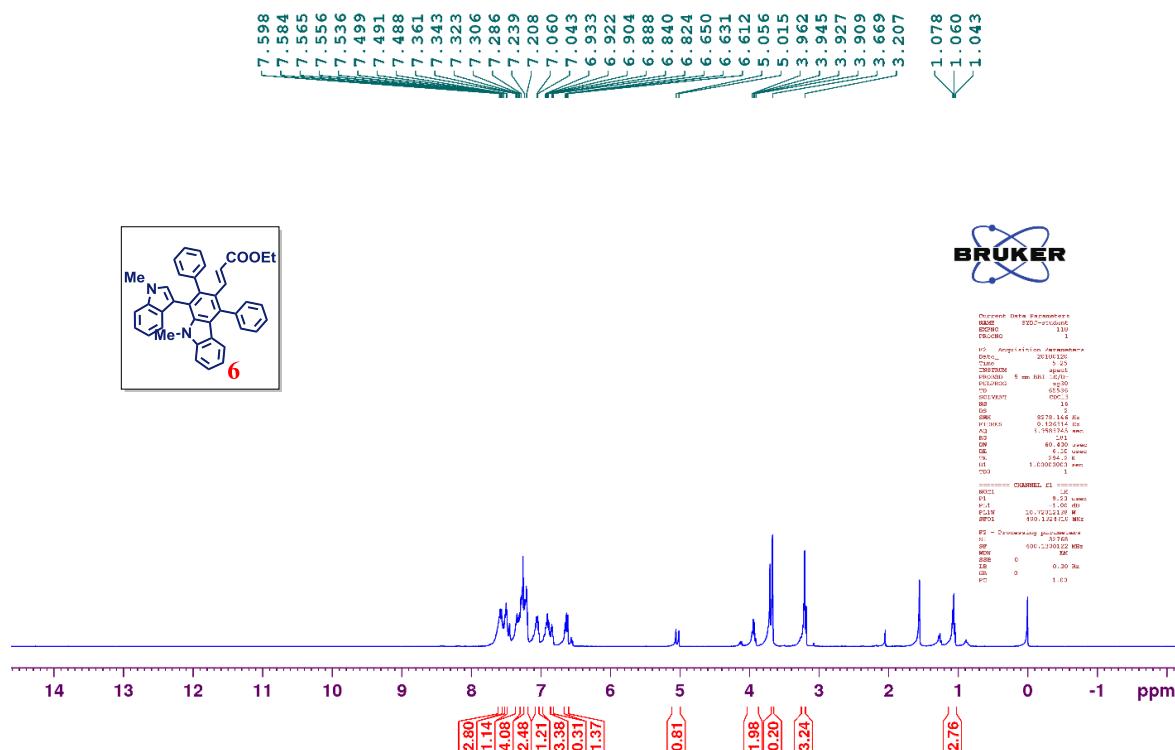
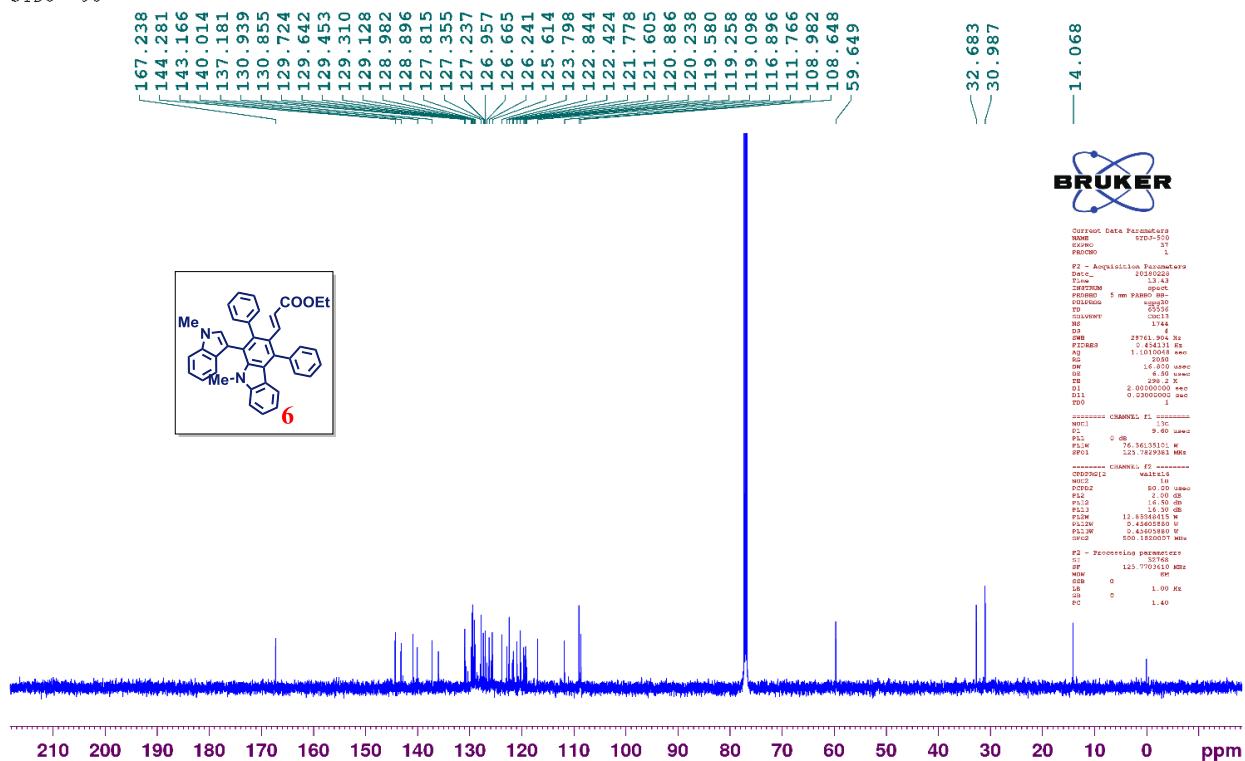


Figure S72 ¹³C NMR in CDCl₃

Figure S73 ¹H NMR in ^{CDCl}₃Figure S74 ¹³C NMR in ^{CDCl}₃