

**SUPPORTING INFORMATION**

**Stereoselective Synthesis of Spiro Cyclohexadiene-Pyrazolones via  
Organic Base and/or Hydrogen Bonding Assisted [3+3] Annulation  
Reaction**

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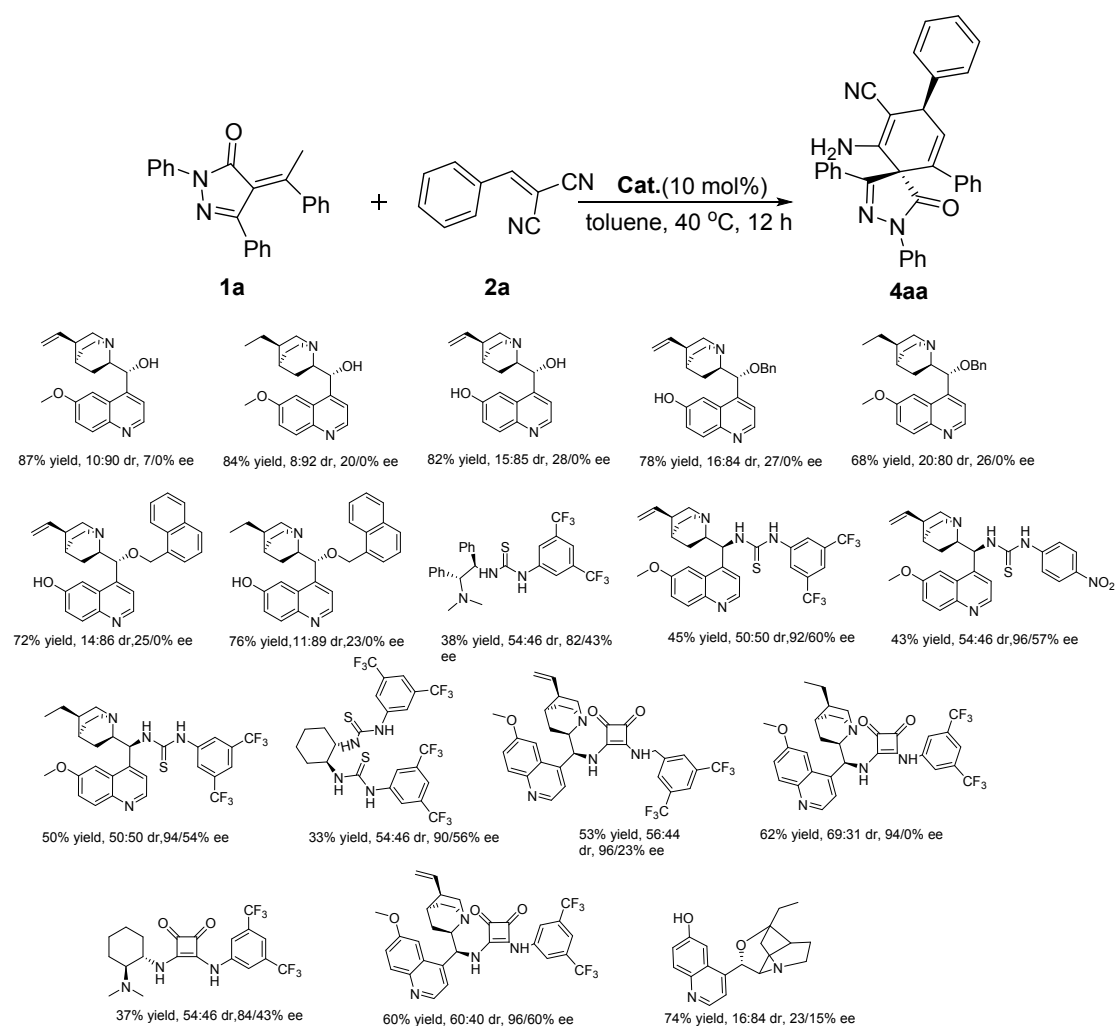
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## 1. General information

Unless otherwise noted, all reactions were carried out under an atmosphere of nitrogen in oven-dried glasswares with magnetic stirring, all reagents obtained from commercial suppliers were used without further purification. Reactions were monitored by thin-layer chromatography (TLC) on silica gel precoated glass plates ( $0.2 \pm 0.03$  mm thickness, GF-254, particle size 0.01–0.04 mm) from Yantai Chemical Industry Research Institute. TLC was visualized by UV fluorescence (254 nm). Flash column chromatography was performed with silica gel (particle size 0.04–0.05 mm).  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectroscopic data were recorded using Bruker AMX-400 instrument and calibrated by using the residual solvent peaks as an internal reference ( $\text{CDCl}_3$  [ $^1\text{H}$ : 7.26,  $^{13}\text{C}$ : 77.23]). Coupling constants ( $J$ ) are given in Hz. High-resolution mass spectra (HRMS) for all the compounds were determined on a Micromass GCT-TOF mass spectrometer with ESI or CI resource. High performance liquid chromatography (HPLC) was performed on Agilent 1200 Series chromatographs using a Daicel Chiralpak IA-H, or AD-H column ( $0.46 \text{ cm} \times 25 \text{ cm}$ ). The racemic compounds for HPLC spectrum were obtained by DABCO catalyzed reactions, with the exception of **4ab**, **4na**, **4ca**, **4ha** and **4ua** catalyzed by  $\text{Et}_3\text{N}$ . X-ray data were recorded on a Rigaku Mercury CCD/AFC diffractometer. Optical rotations are reported as follows:  $[\alpha]_{20}^{\text{D}}$  (c in g per 100 mL, solvent).

## 2. Screening of catalysts and condition optimization

### Scheme S1. Optimization of the reaction conditions<sup>a</sup>



<sup>a</sup>) Unless otherwise noted, reactions were carried out with **1a** (0.12 mmol), **2a** (0.1 mmol), and 10 mol% **Cat.** in toluene (1.0 mL) at 40 °C

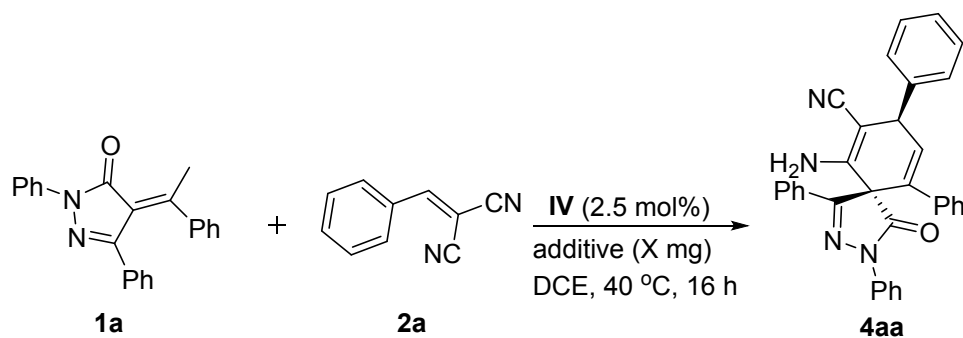
### Table S1. Optimization of solvents<sup>a</sup>

entry	solvent	yield (%) <sup>b</sup>	dr <sup>c</sup>	ee (%) <sup>d</sup>
1	THF	< 5%	--	--
2	Et <sub>2</sub> O	< 5%	--	--
3	EA	< 5%	--	--

4	dixone	< 5%	--	--
5	<i>o</i> -xylene	54	58:42	96/56
6	<i>m</i> -xylene	55	55:45	96/64
7	<i>p</i> -xylene	52	57:43	91/68
8	mesitylene	70	57:43	91/71
9	PhCF <sub>3</sub>	55	63:37	96/71
10	PhF <sub>5</sub>	52	65:35	96/78
11	1,4-F <sub>2</sub> Ph	50	64:36	97/77
12	PhF	47	65:35	81/35
13	toluene	60	40:60	60/96
14	HFIP	trace	--	--
<b>15</b>	<b>DCE</b>	67	70:30	97/62
16	DCM	60	65:35	94/58

a) Unless otherwise noted, reactions were carried out with **1a** (0.12 mmol), **2a** (0.1 mmol), and 10 mol% **IV** in corresponding solvent (1.0 mL) at 40 °C for 12 h. b) Isolated yield. c) Measured from the <sup>1</sup>H NMR of the crude reaction material. d) Determined by chiral HPLC.

**Table S2. Optimization of additives <sup>a</sup>**

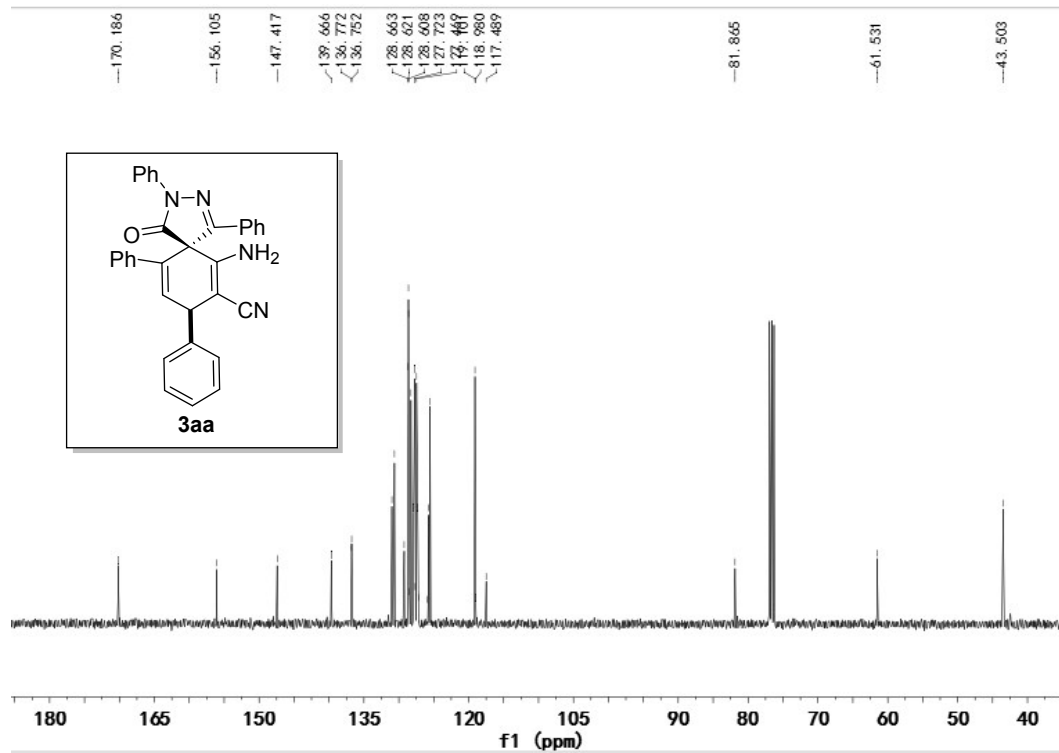
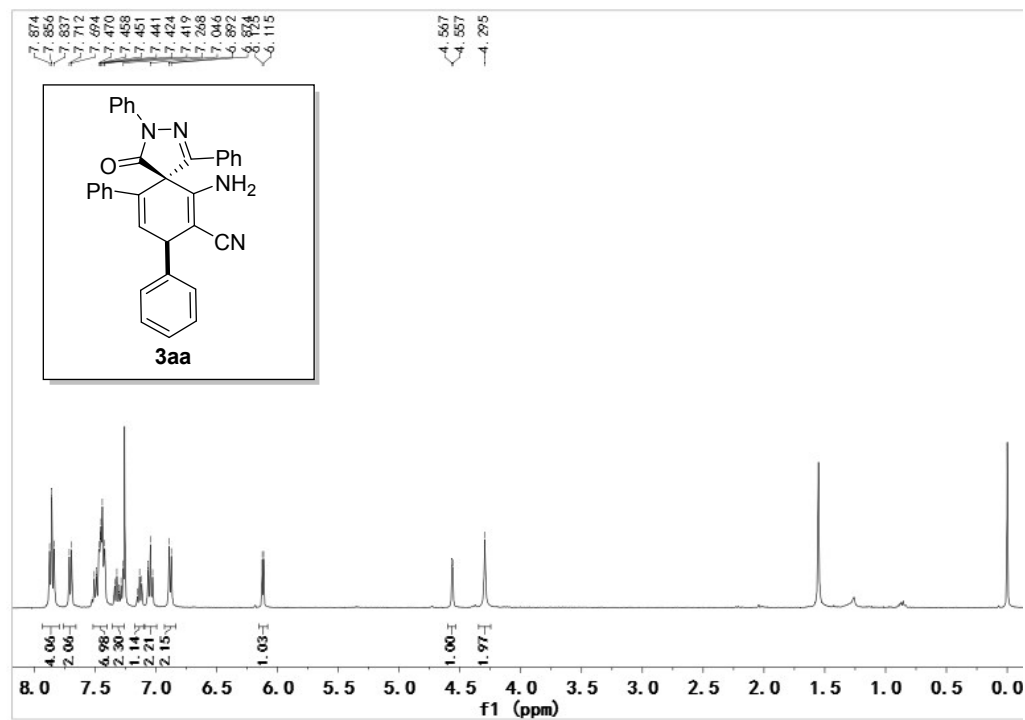


entry	additive	X	yield (%) <sup>b</sup>	<i>dr</i> <sup>c</sup>	<i>ee</i> (%) <sup>d</sup>
1	LiBr	20	trace	--	--
2	Tf <sub>2</sub> NH	20	trace	--	--
3	3 Å MS	25	55	75:25	97/55
4	4 Å MS	25	50	75:25	97/50
4	5 Å MS	25	51	75:25	97/54
4	CsF	20	trace	--	--
5 <sup>e</sup>	KI	20	58	66:34	91/61
7	Ph <sub>3</sub> P	20	56	70:30	97/60
8	Ph <sub>3</sub> PO	20	58	66:34	97/60
9	K <sub>3</sub> PO <sub>4</sub>	20	69	60:40	96/55
10	PhCOOH	20	trace	--	--
11	Trip-CPA	5	trace	--	--
12	Cu(OTf) <sub>2</sub>	5	trace	--	--

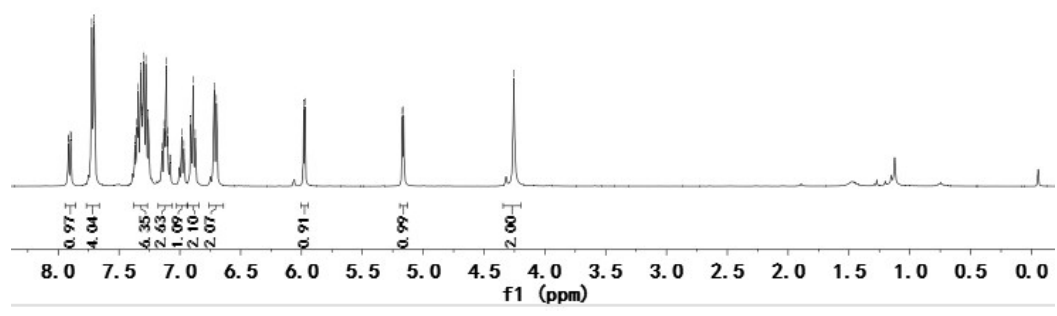
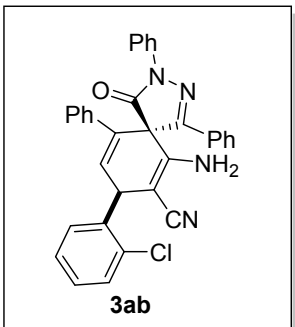
a) Unless otherwise noted, reactions were carried out with **1a** (0.12 mmol), **2a** (0.1 mmol), and 2.5 mol% **IV** in DCE (1.0 mL) at 40 °C for 16 h. b) Isolated yield. c)

Measured from the  $^1\text{H}$  NMR of the crude reaction material. <sup>d)</sup> Determined by chiral HPLC.

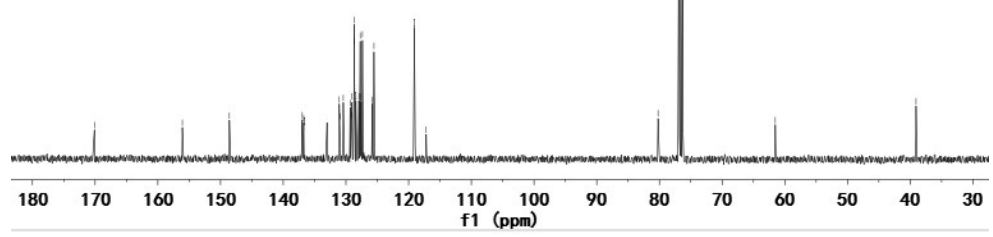
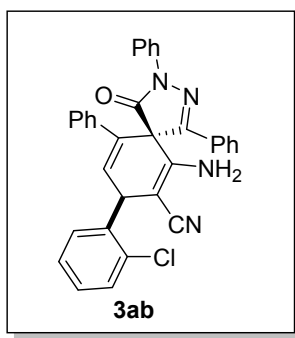
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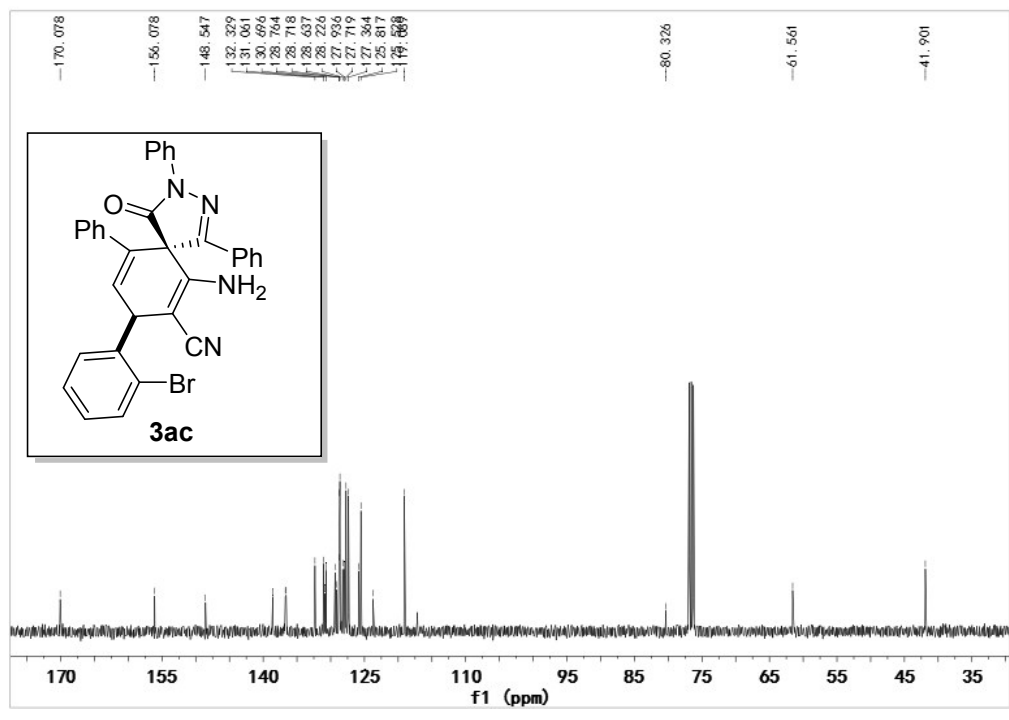
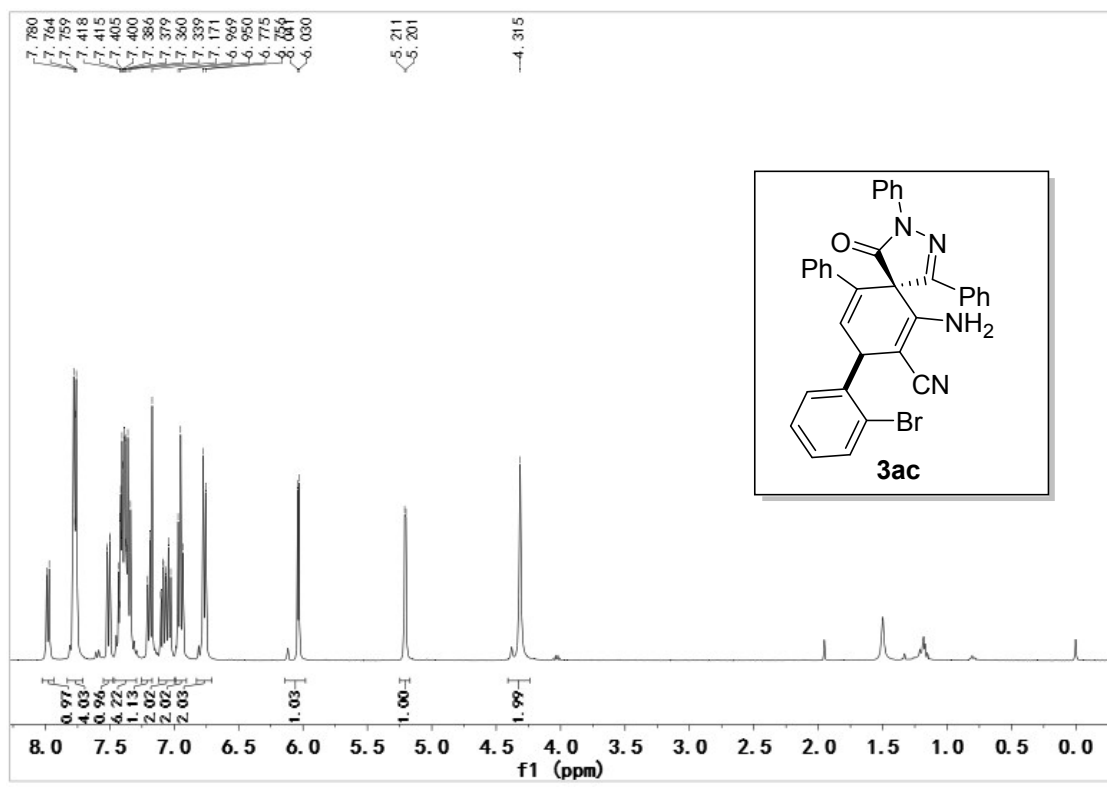


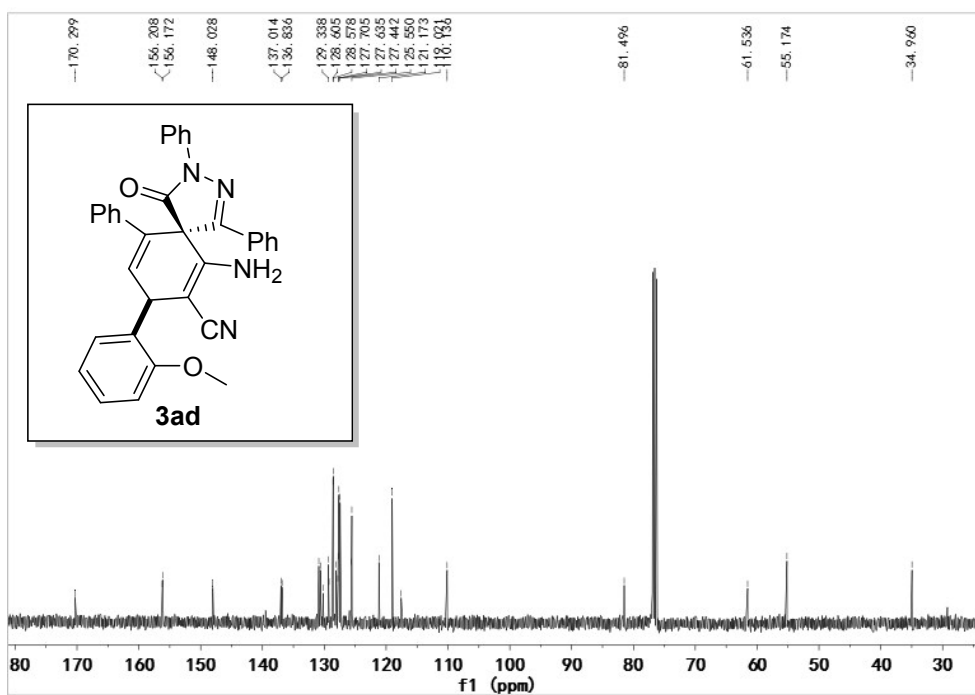
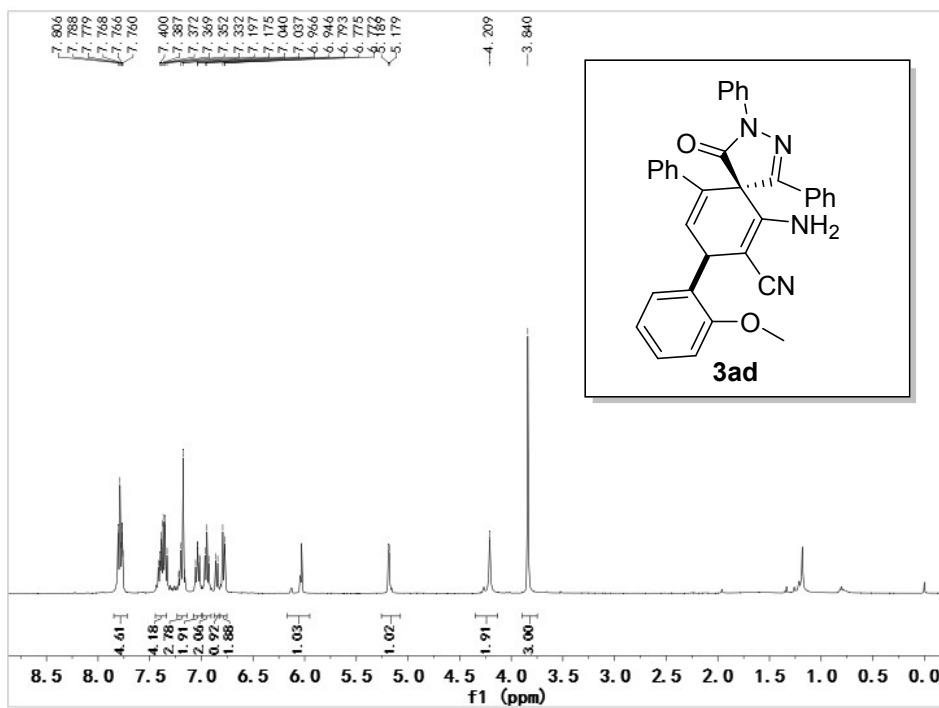
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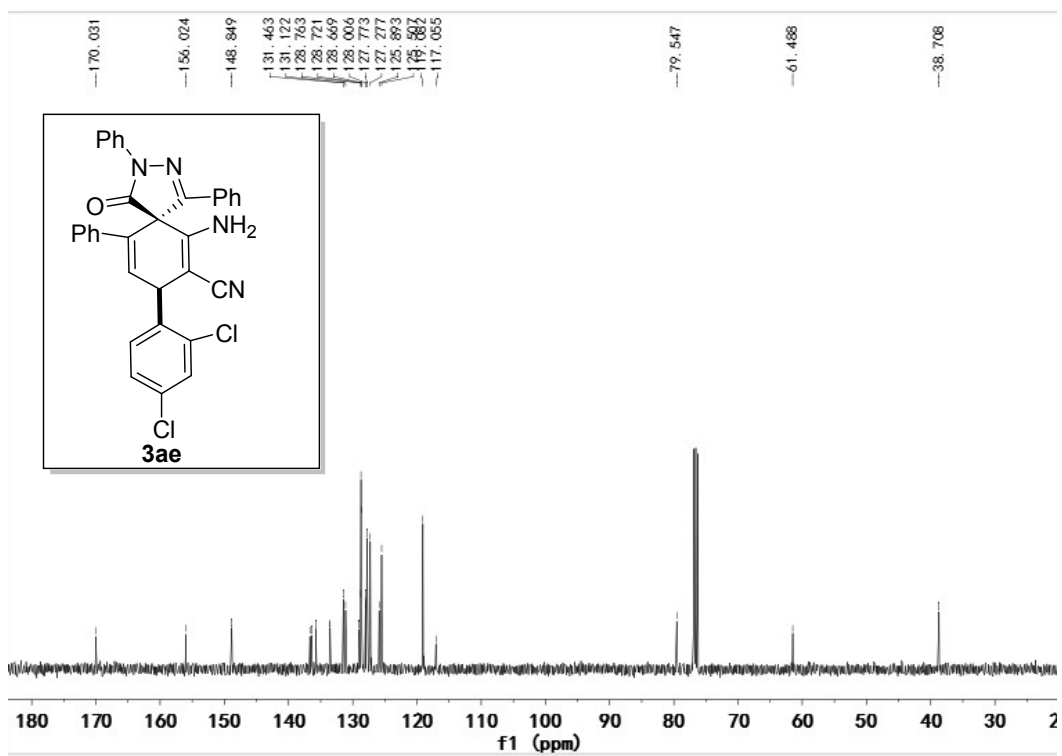
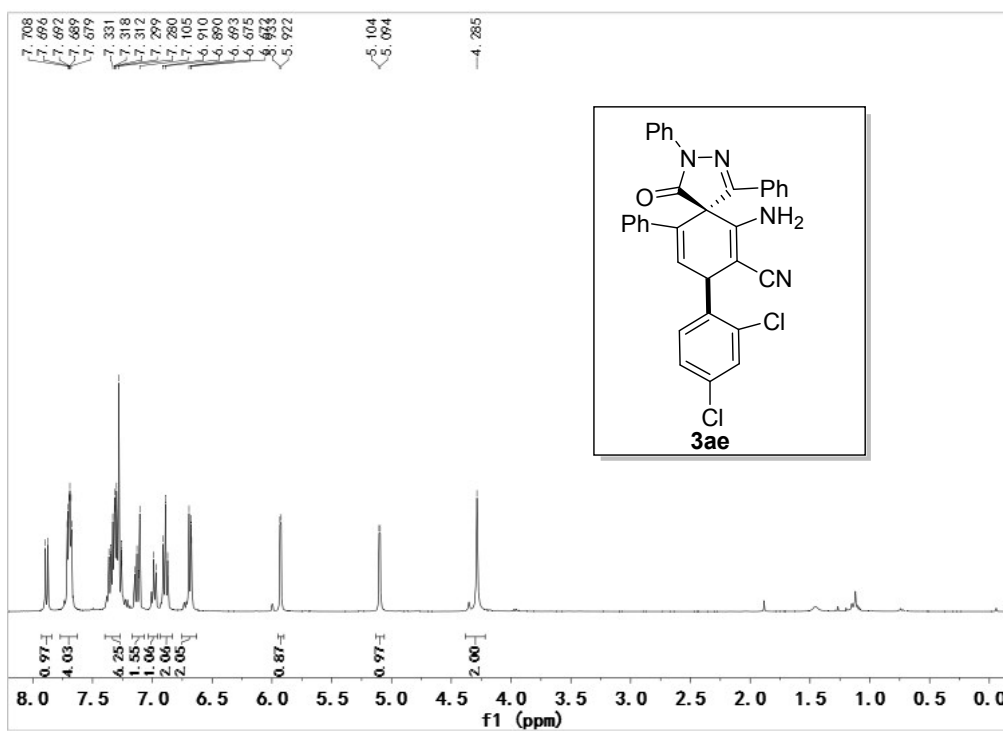
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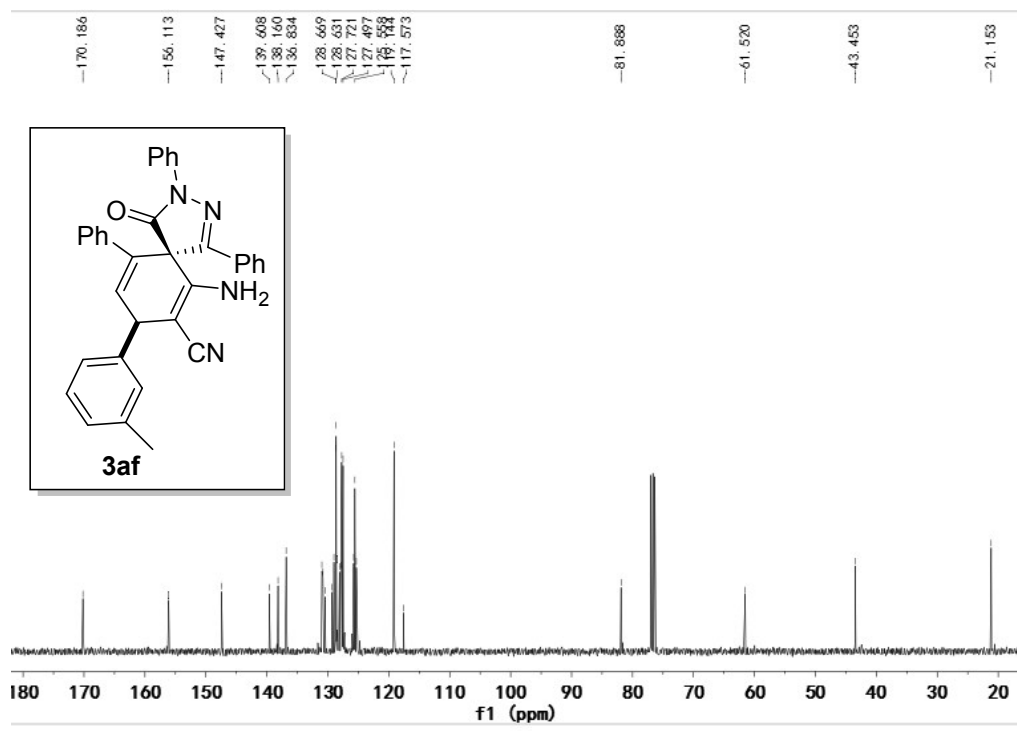
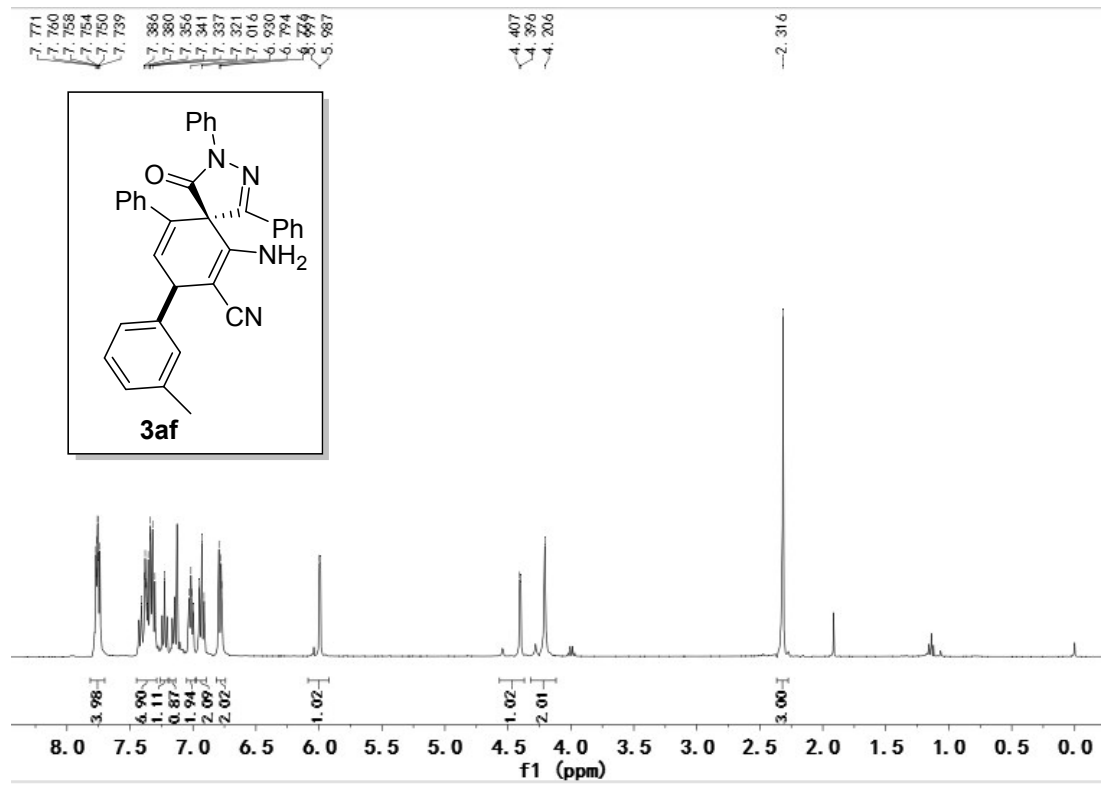


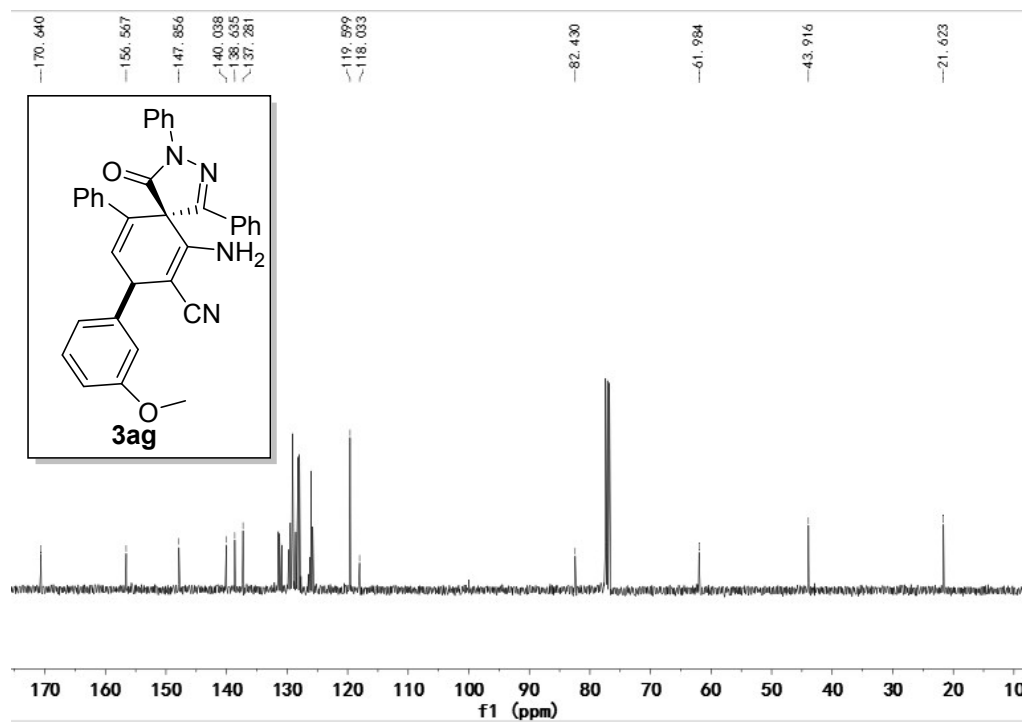
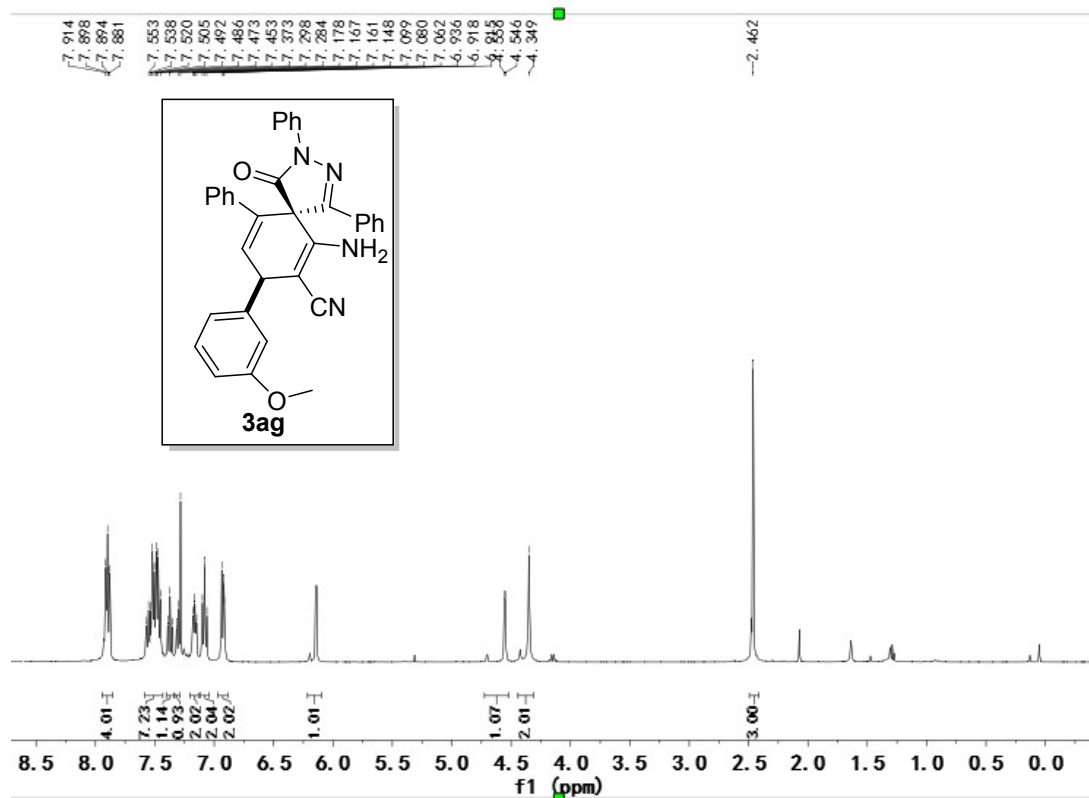


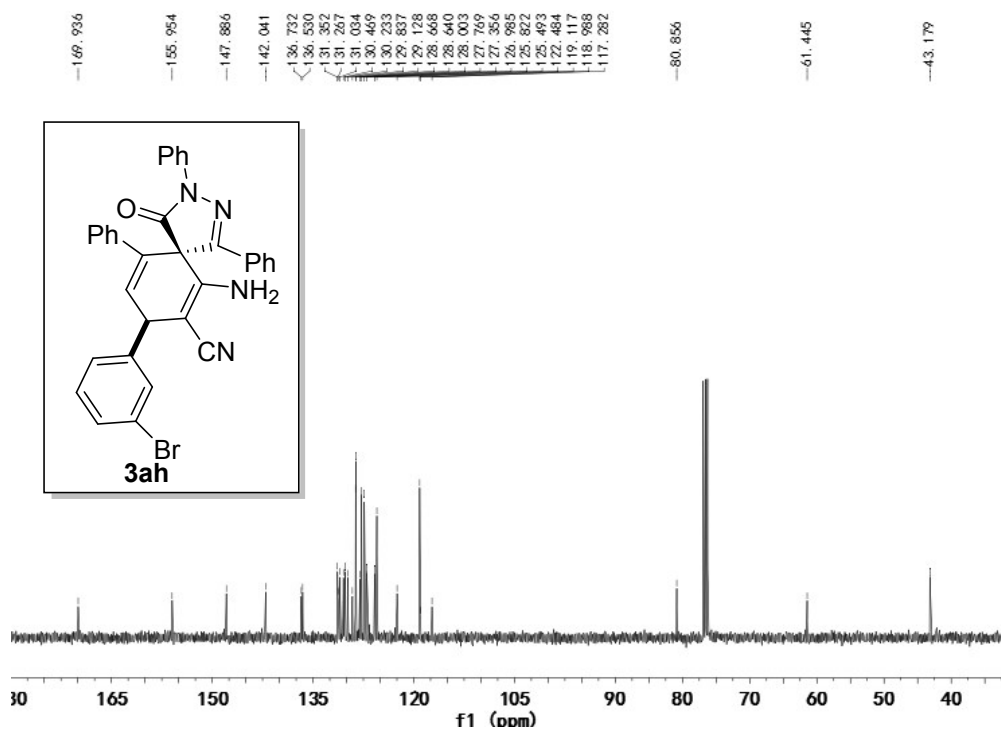
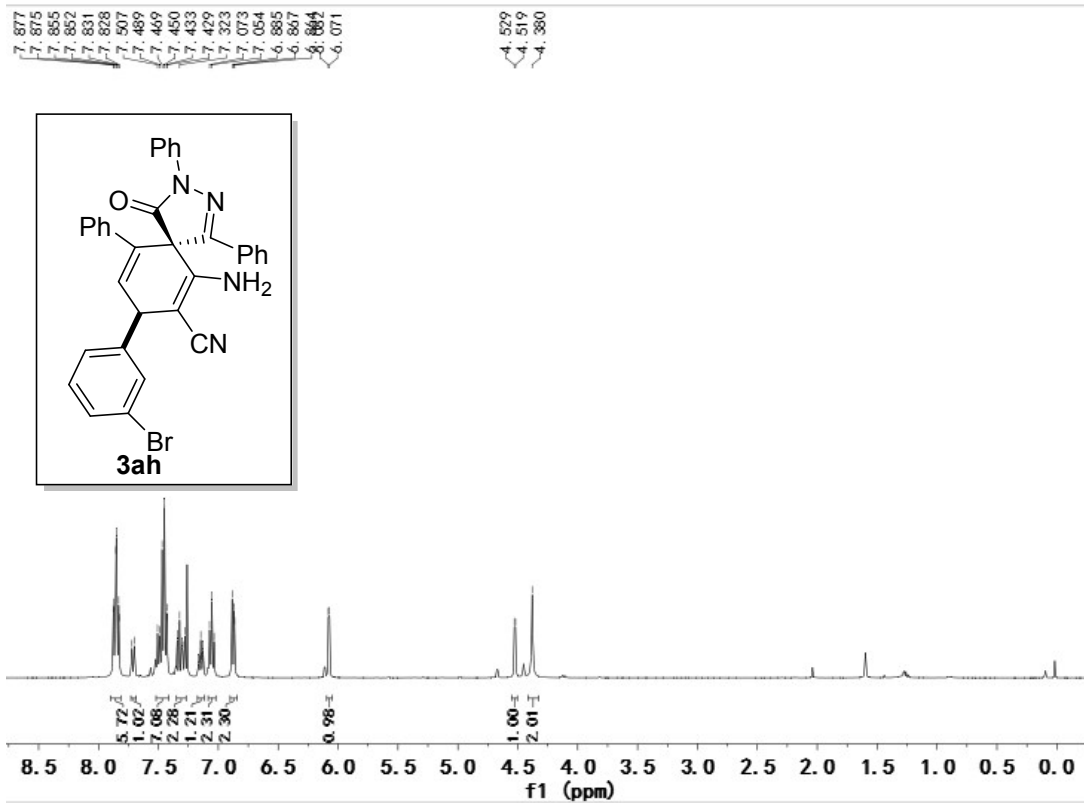


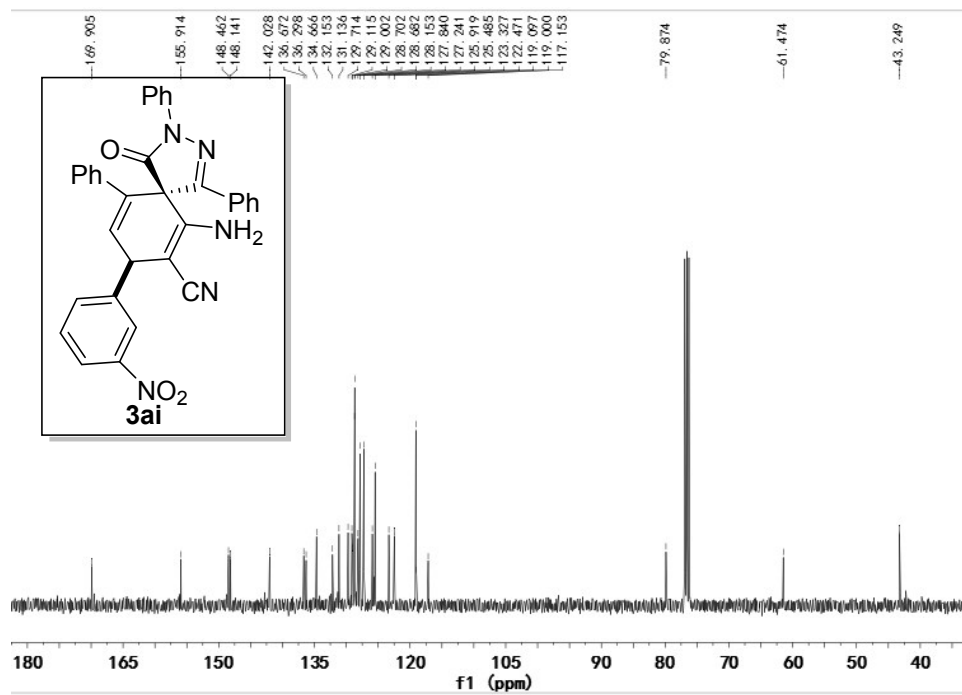
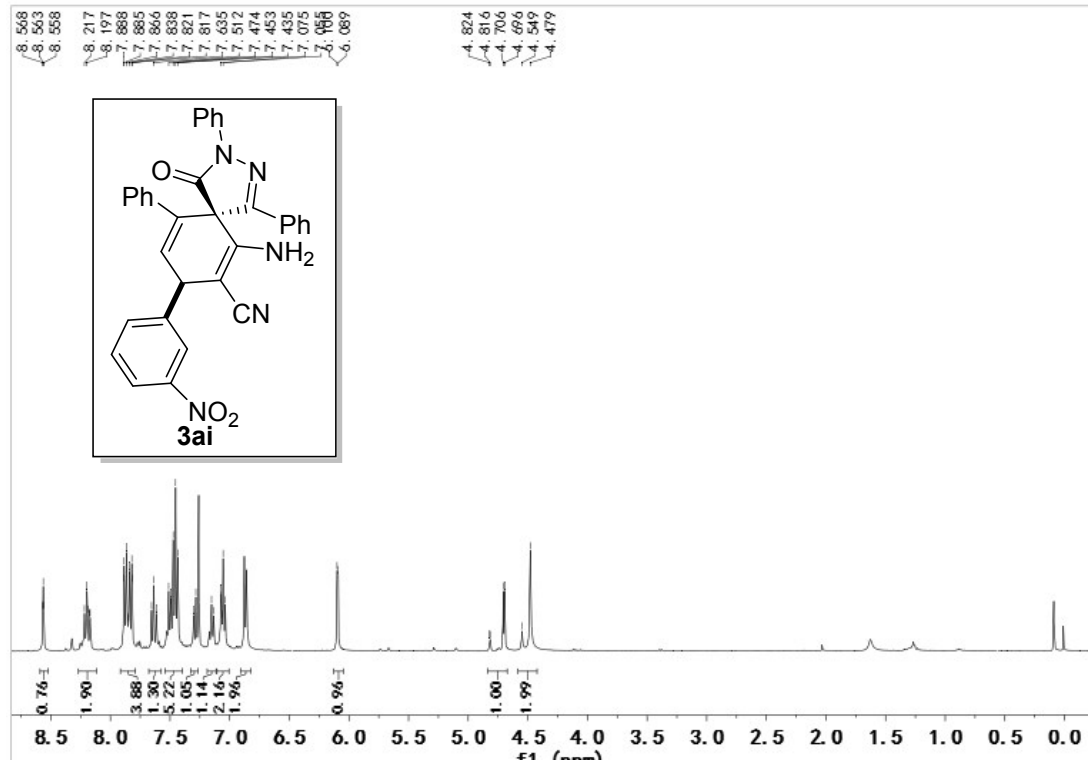


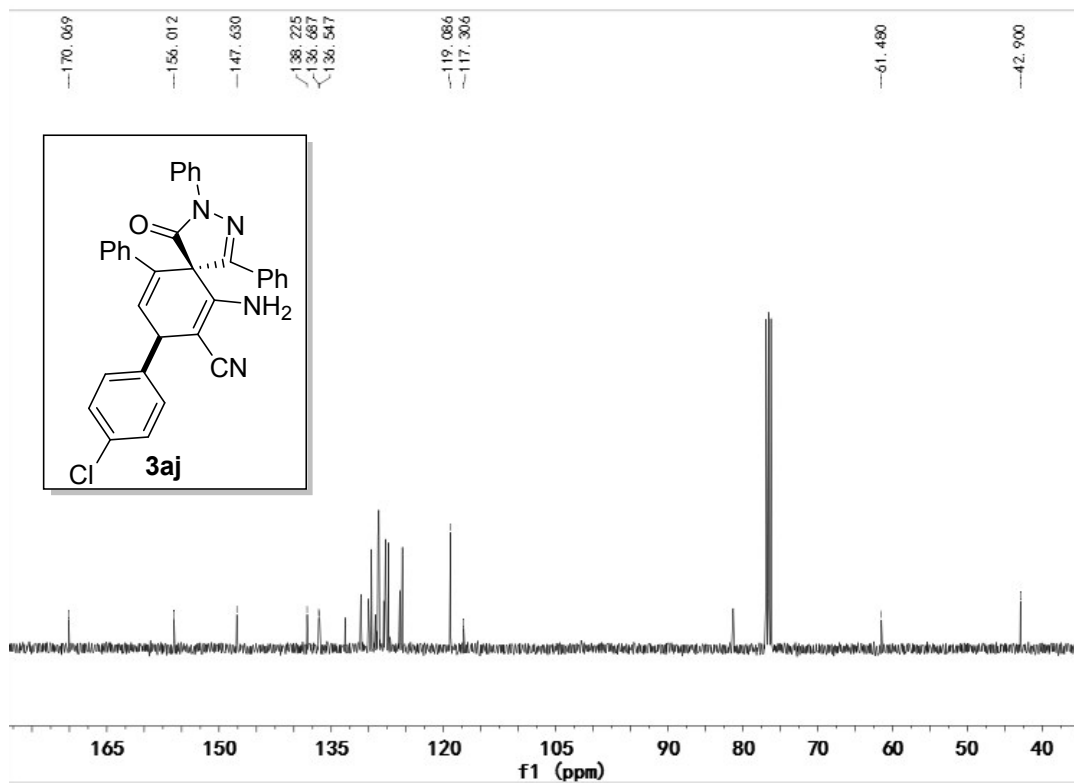
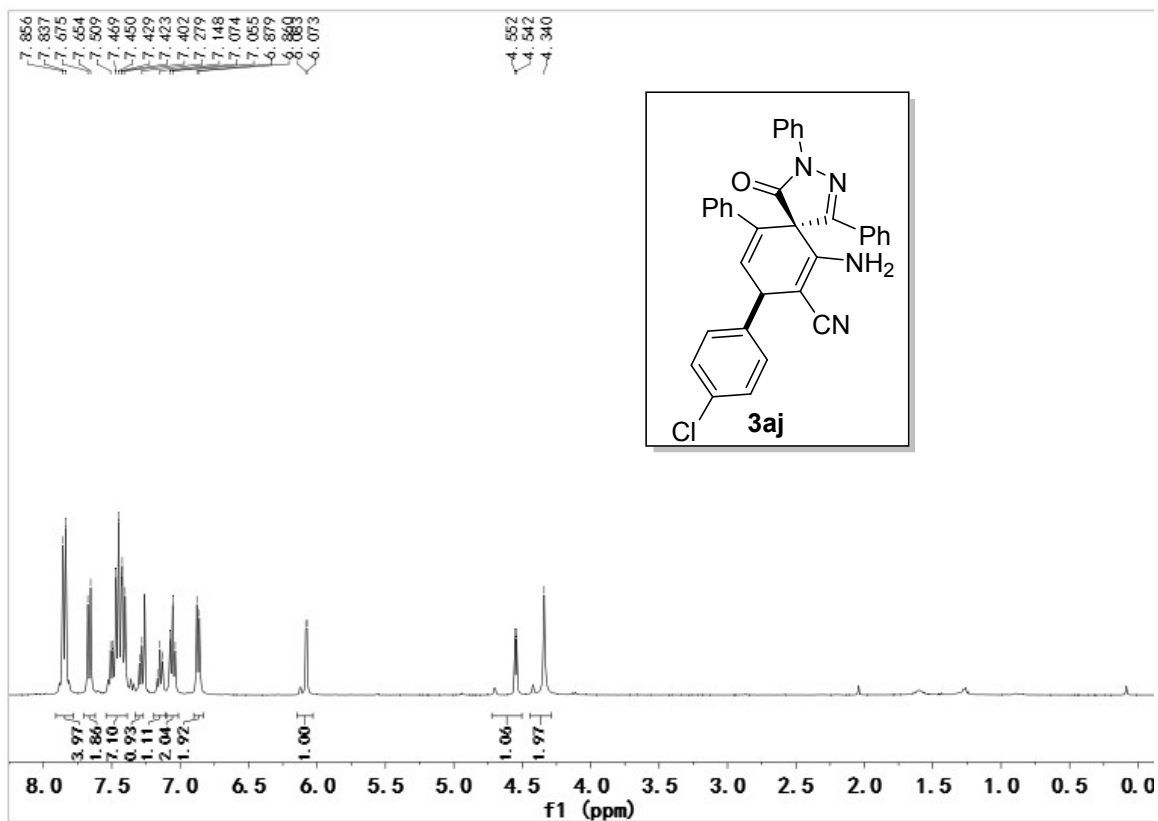






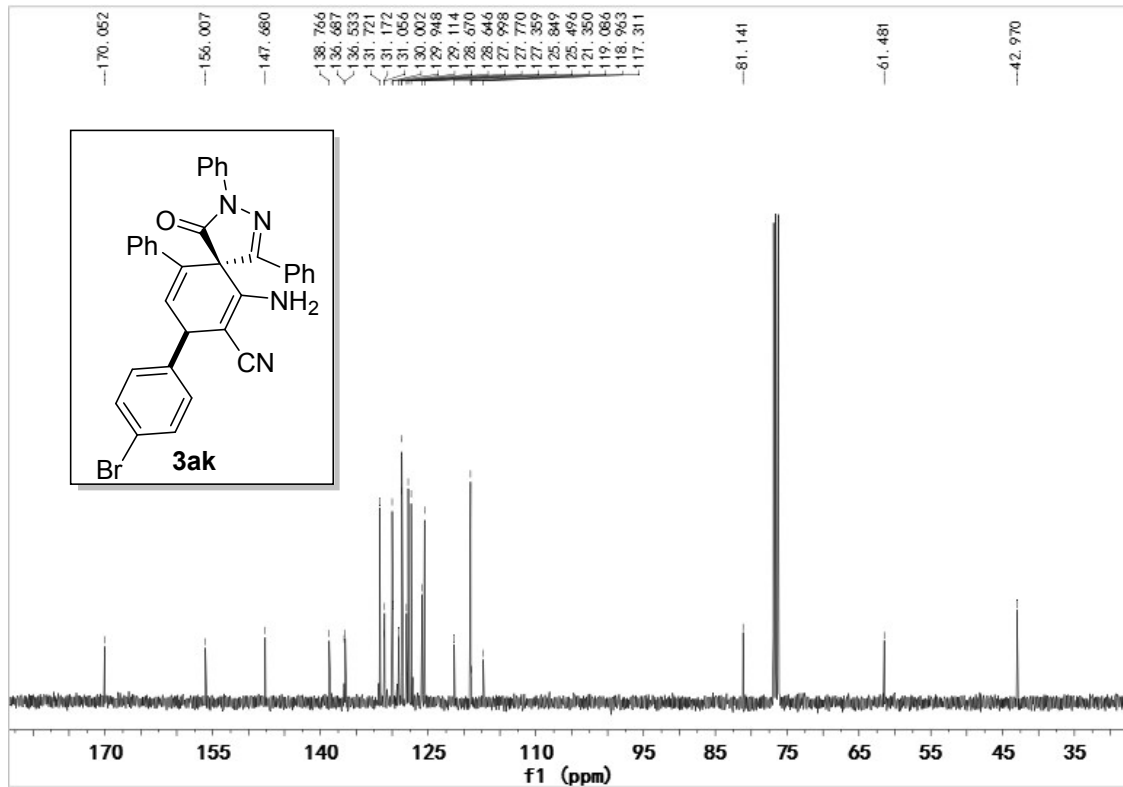
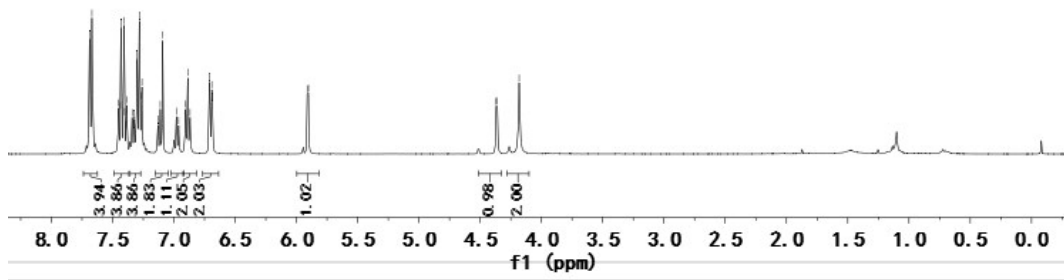
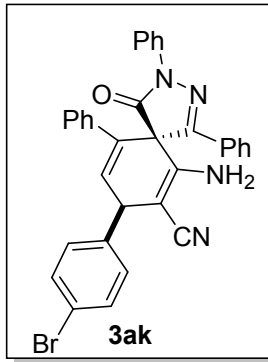


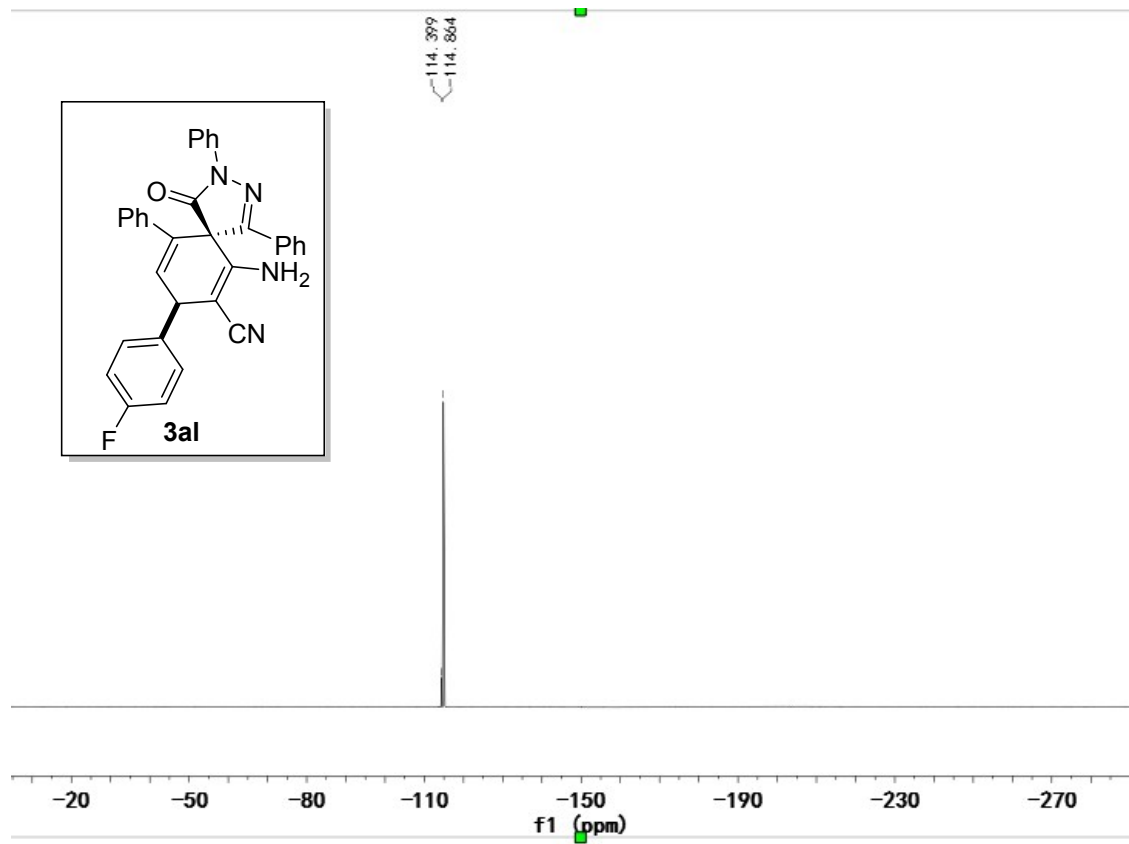
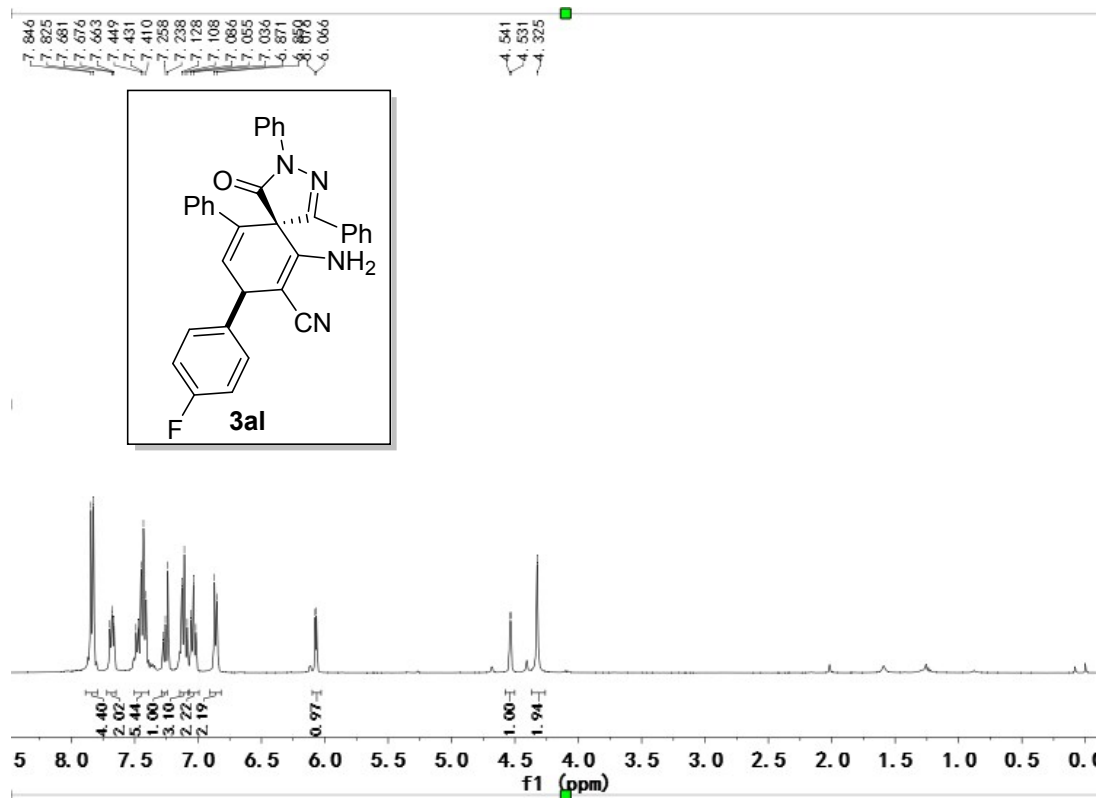




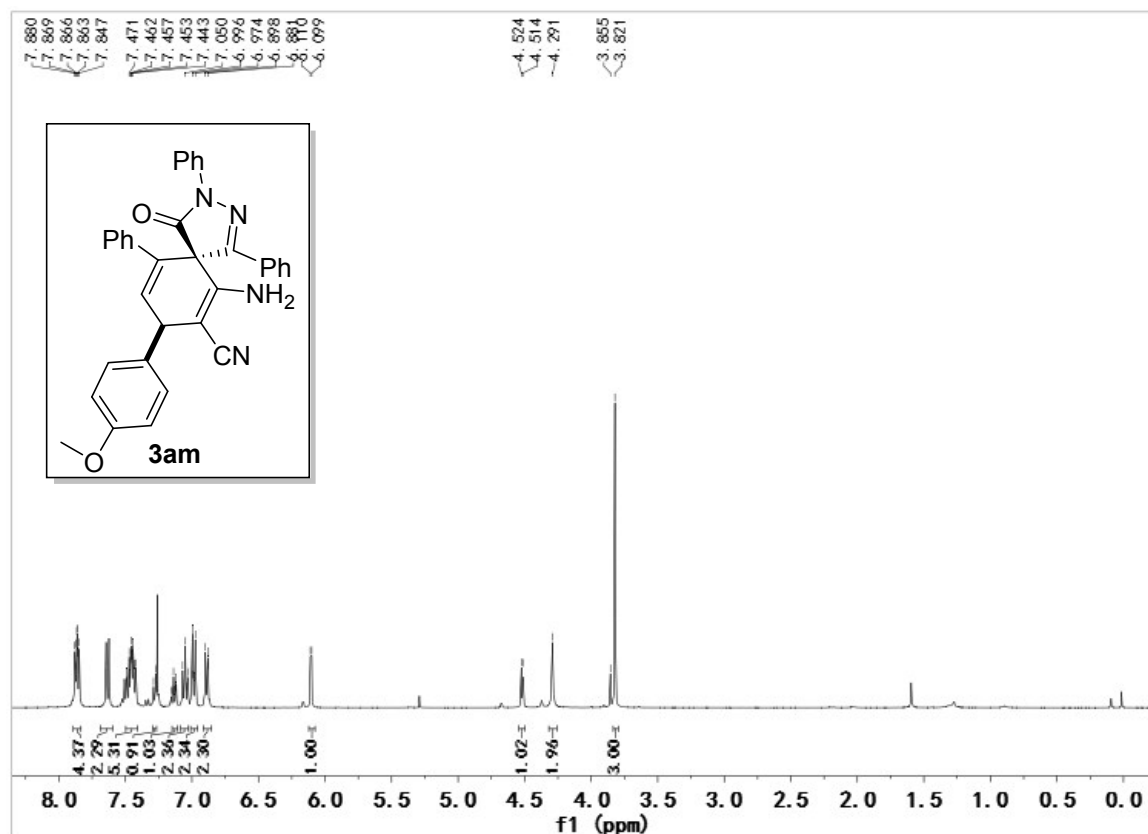
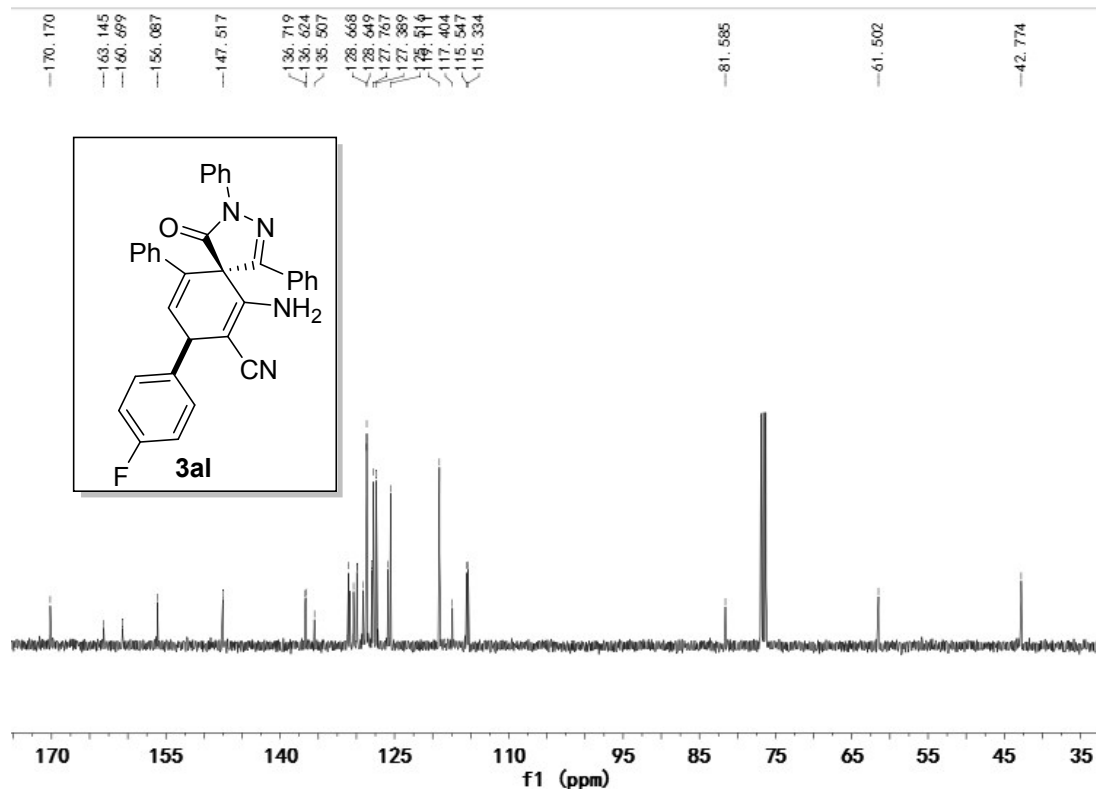
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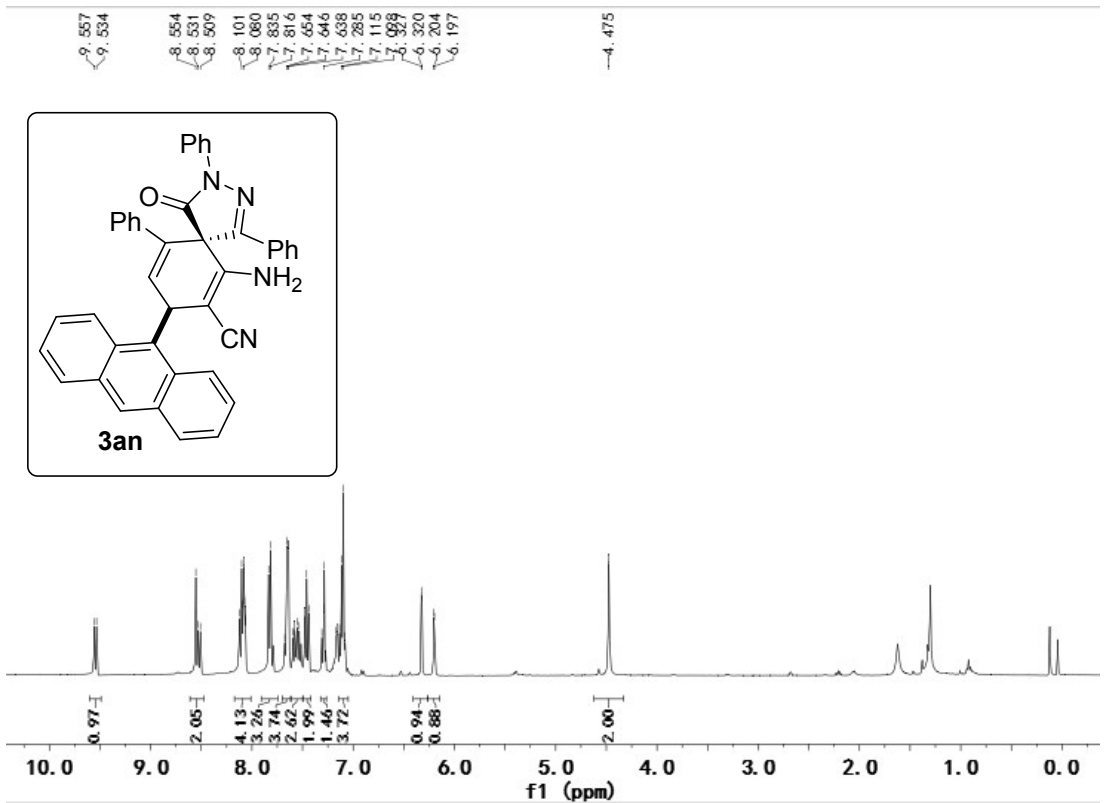
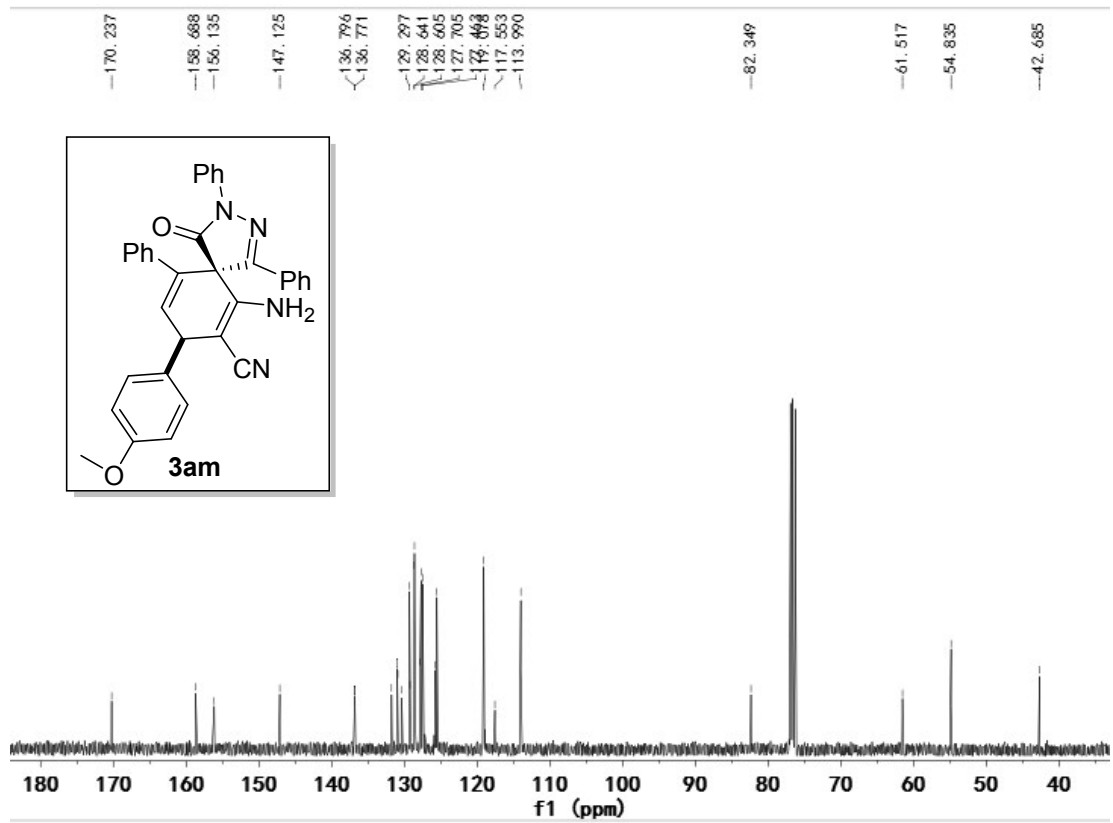
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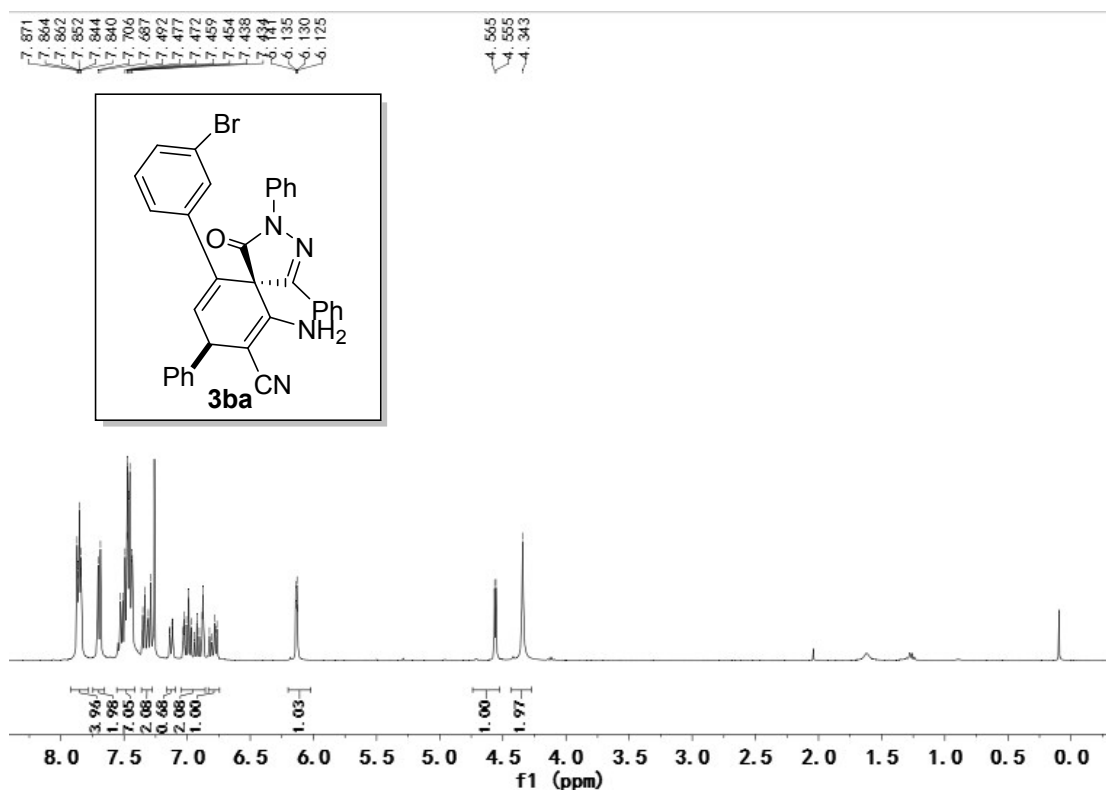
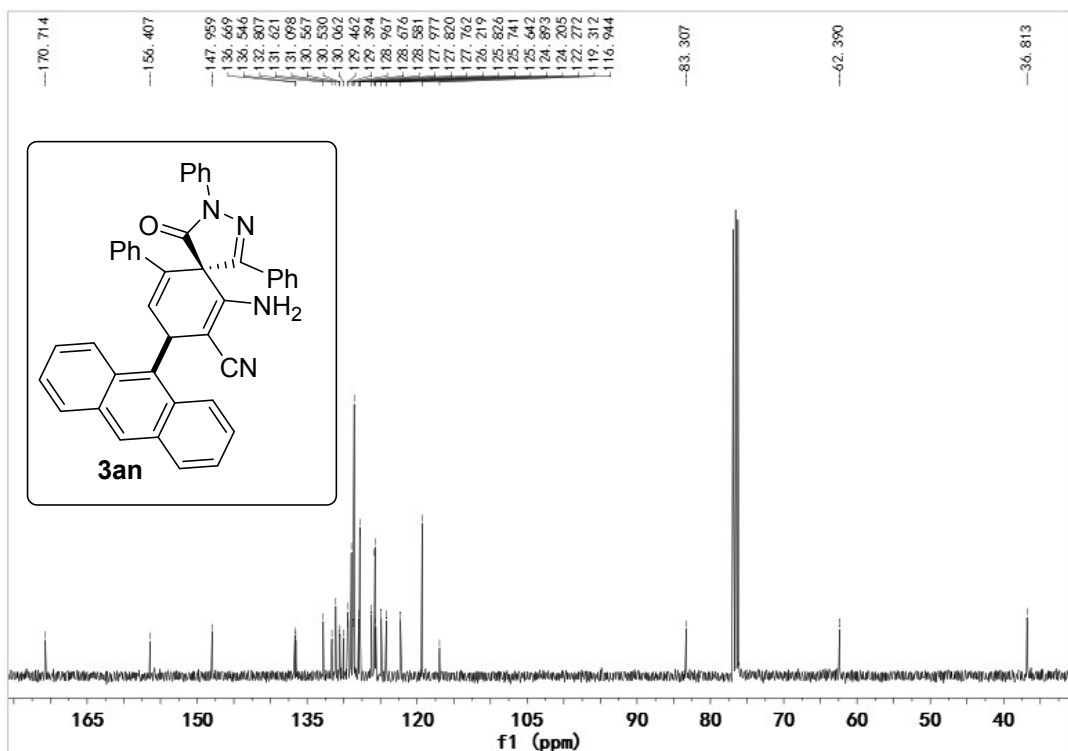


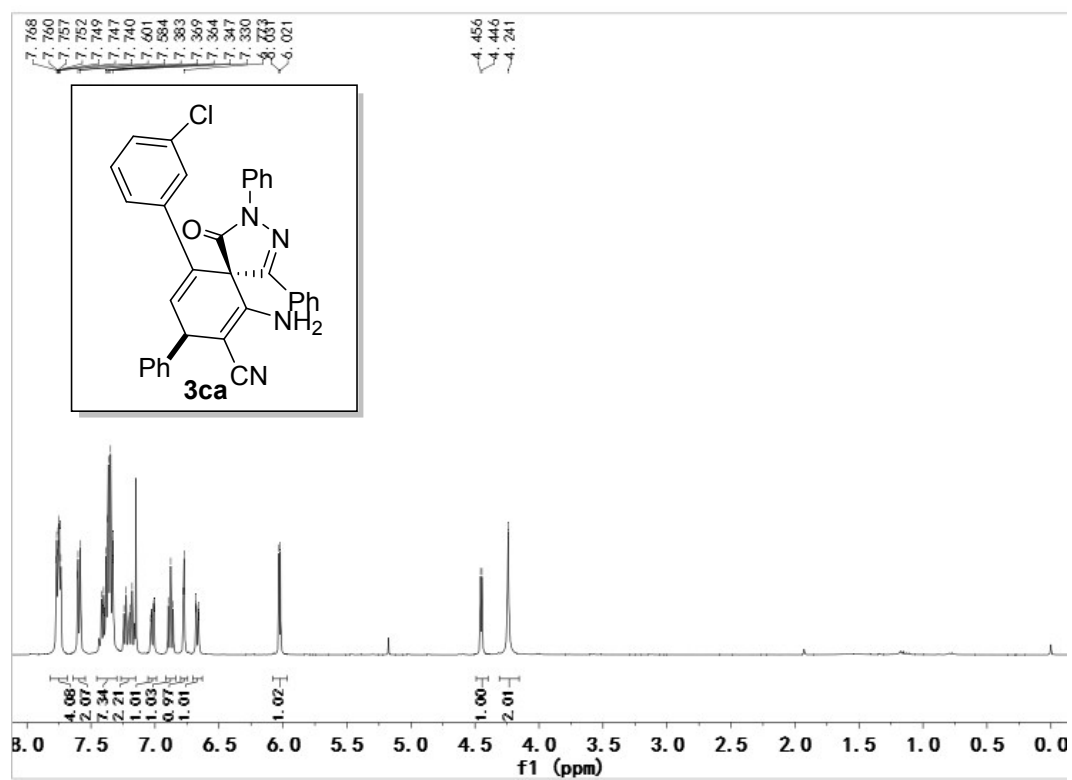
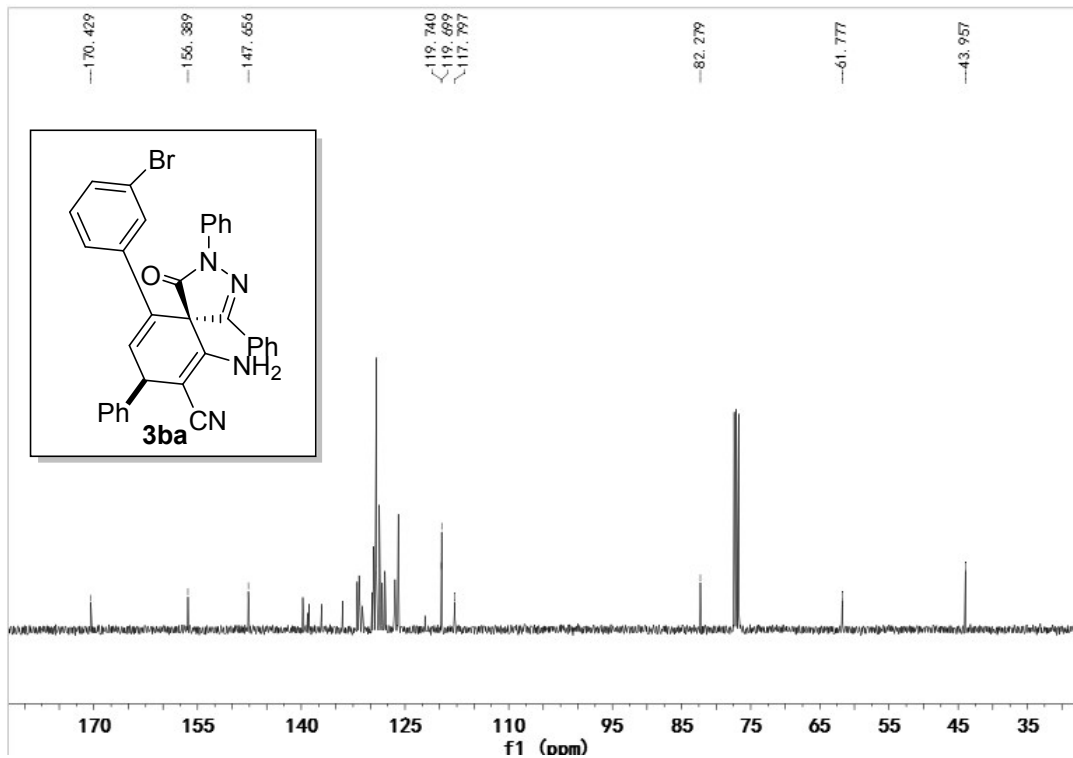


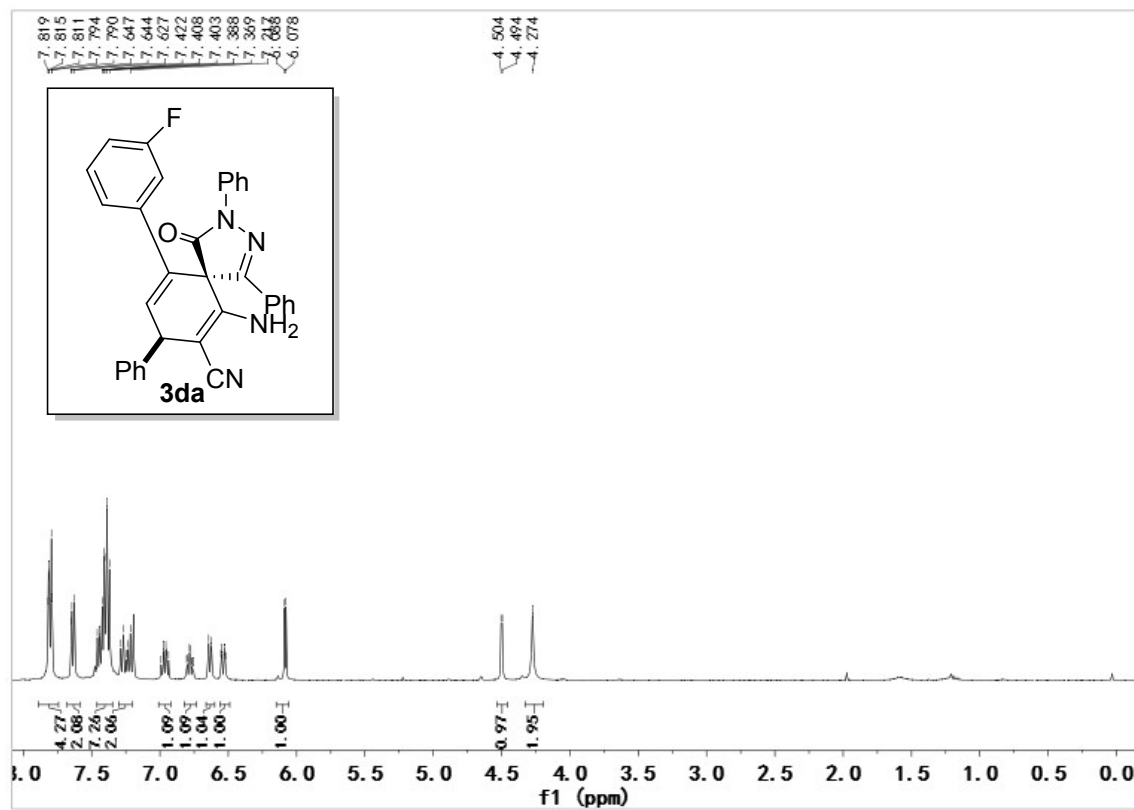
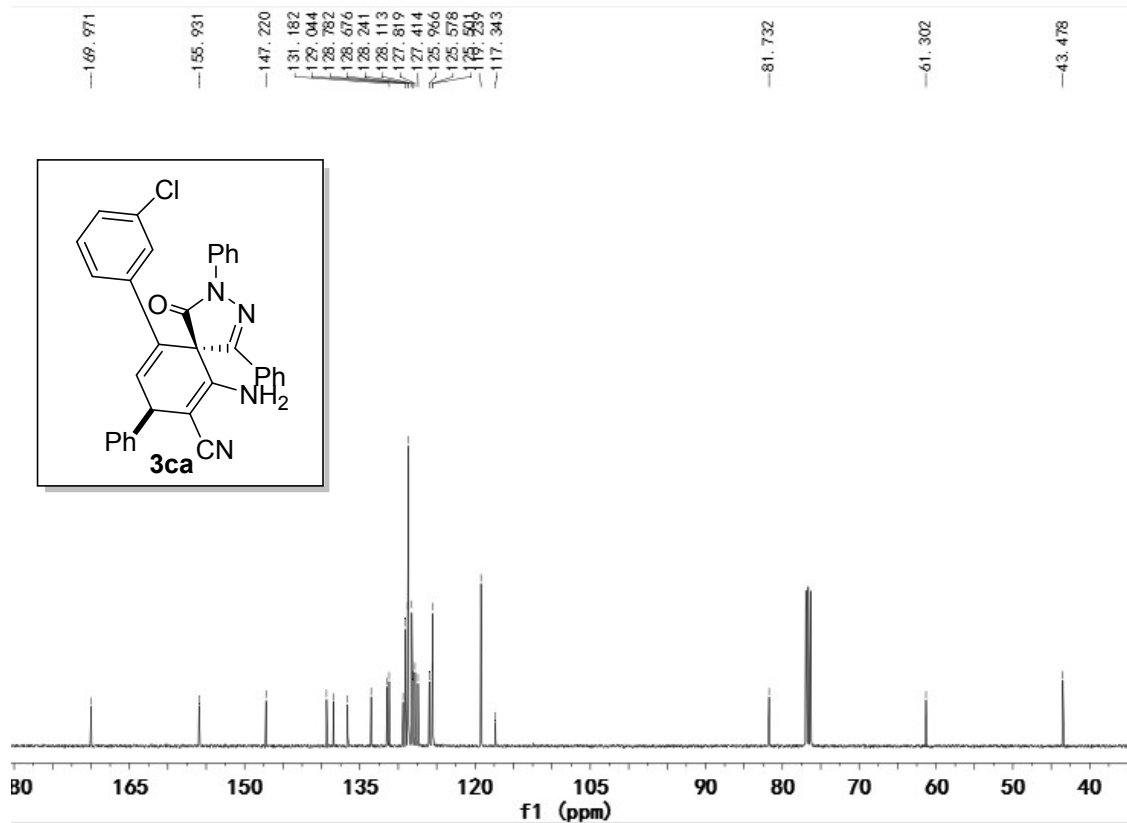


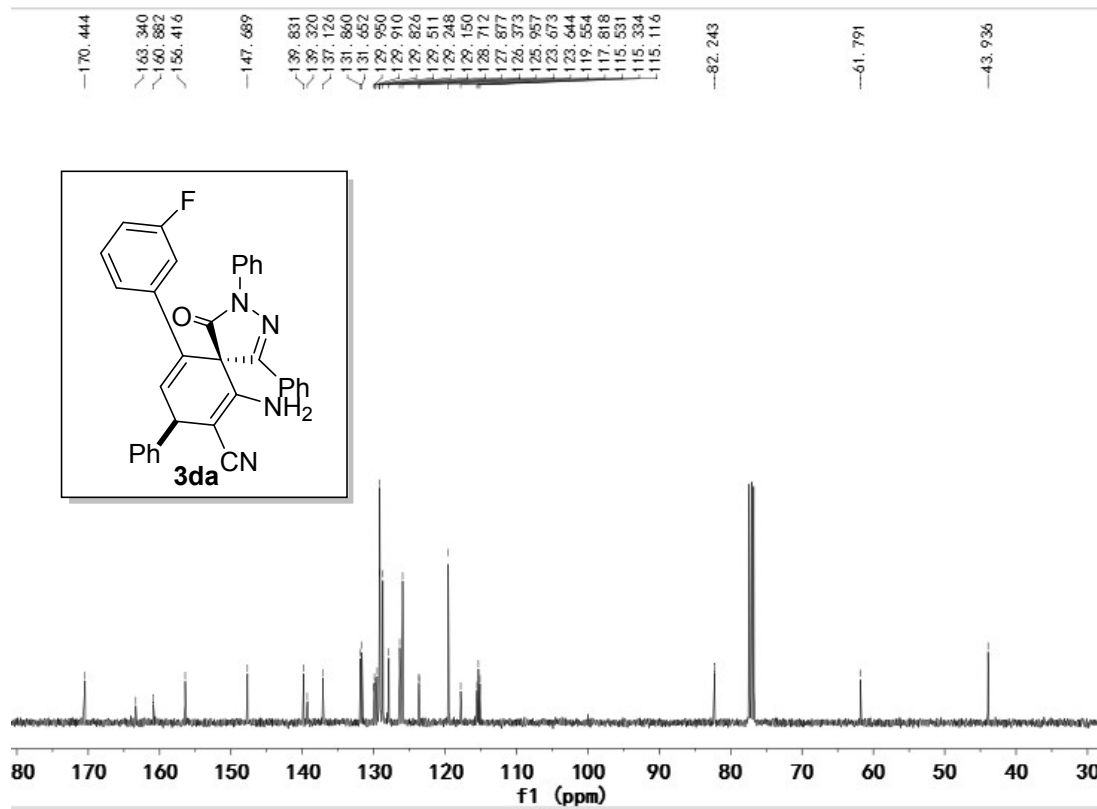
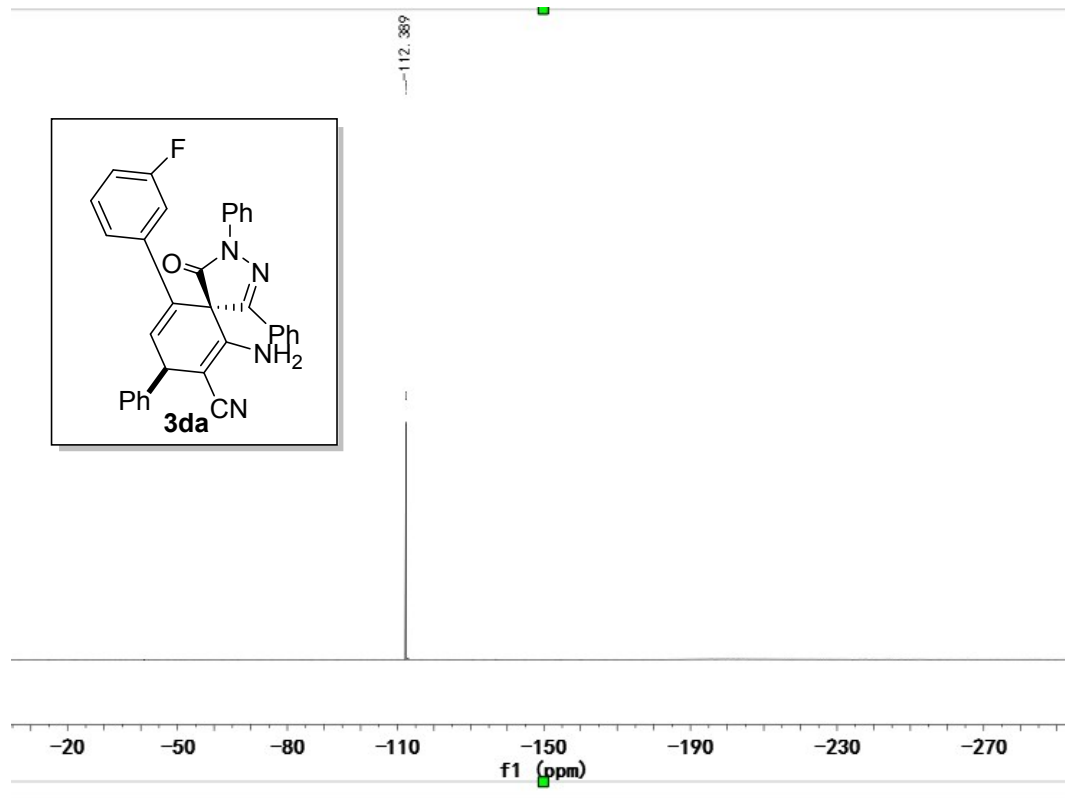


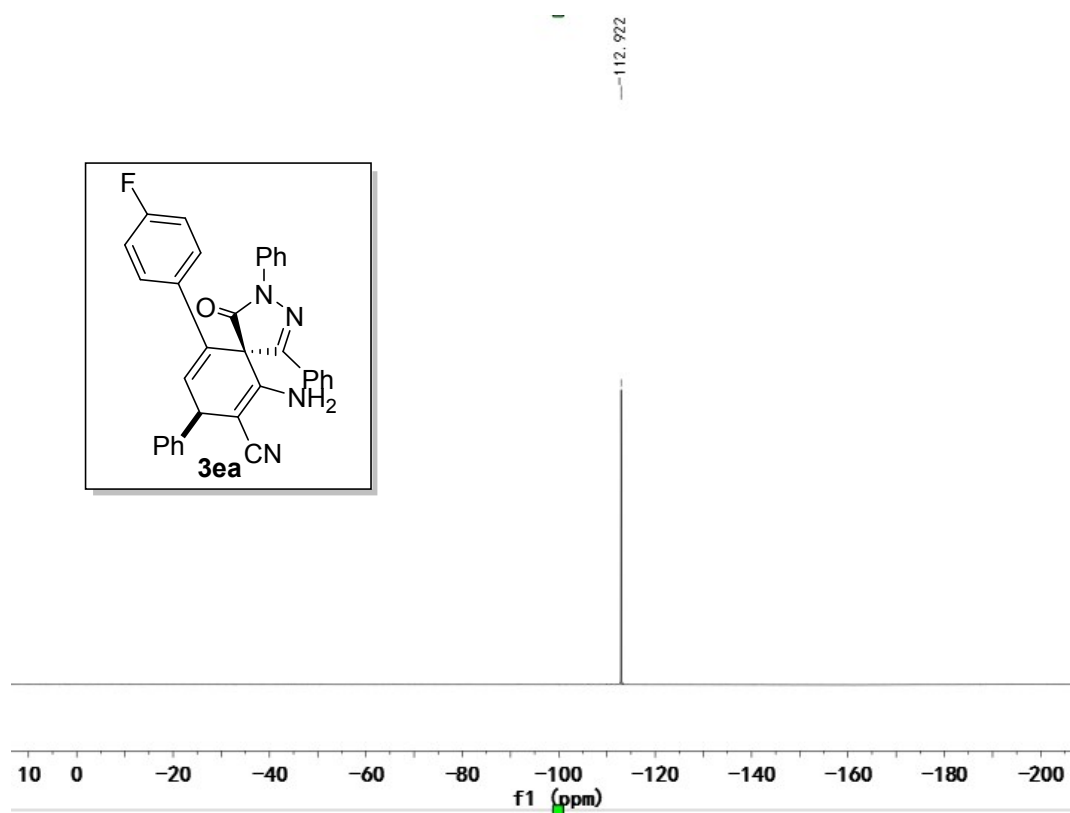
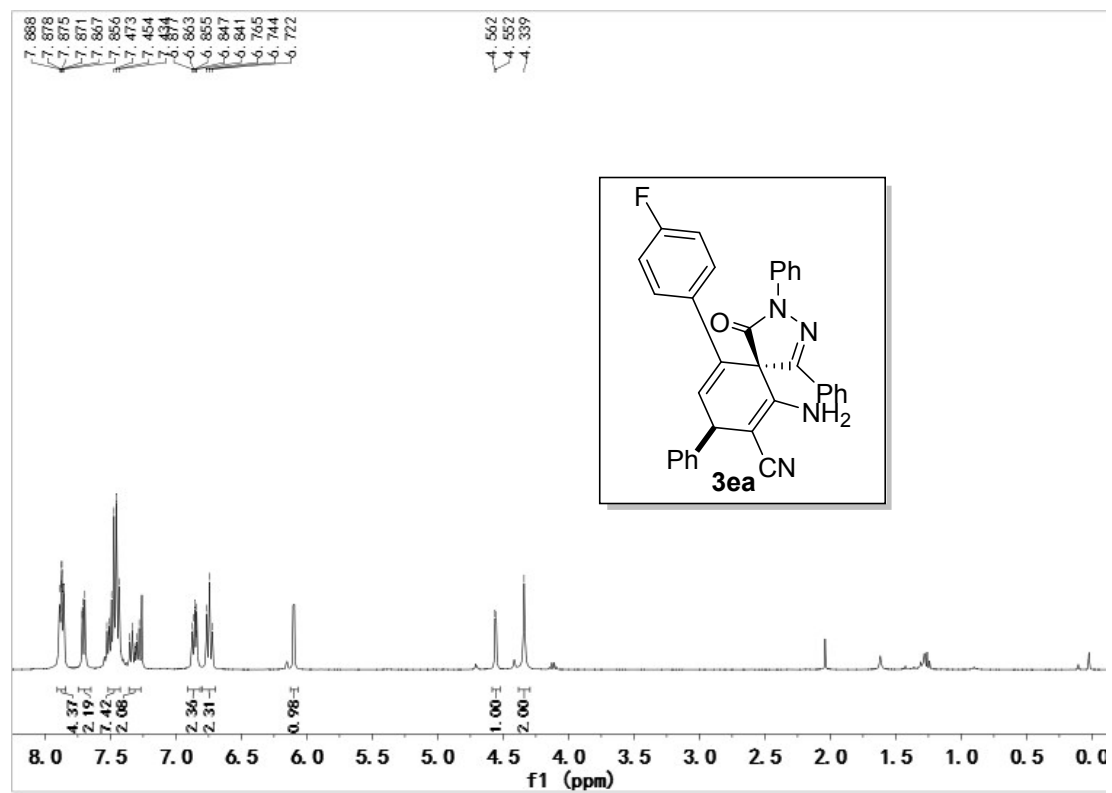


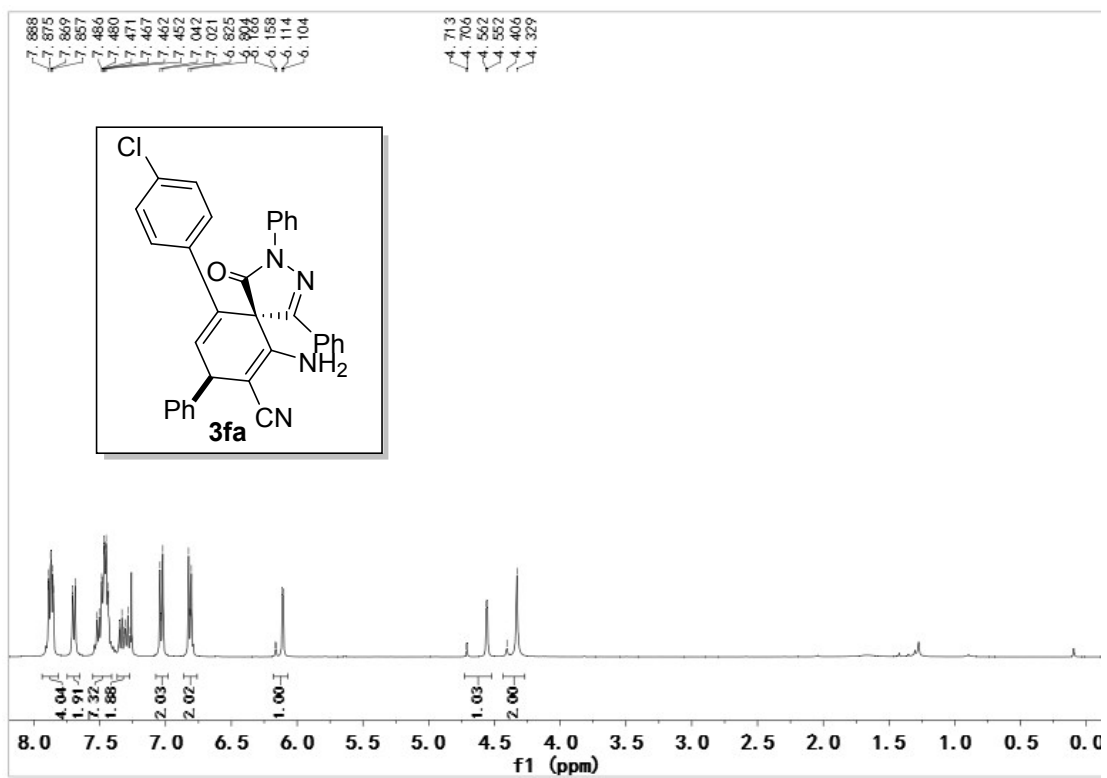
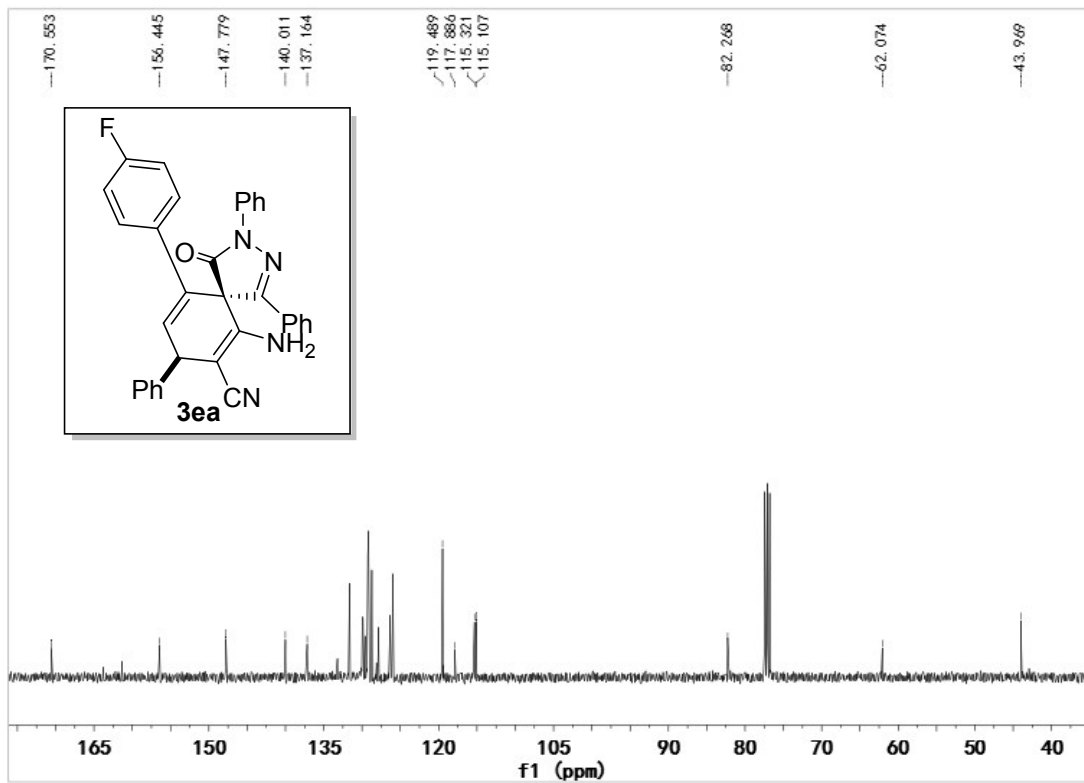




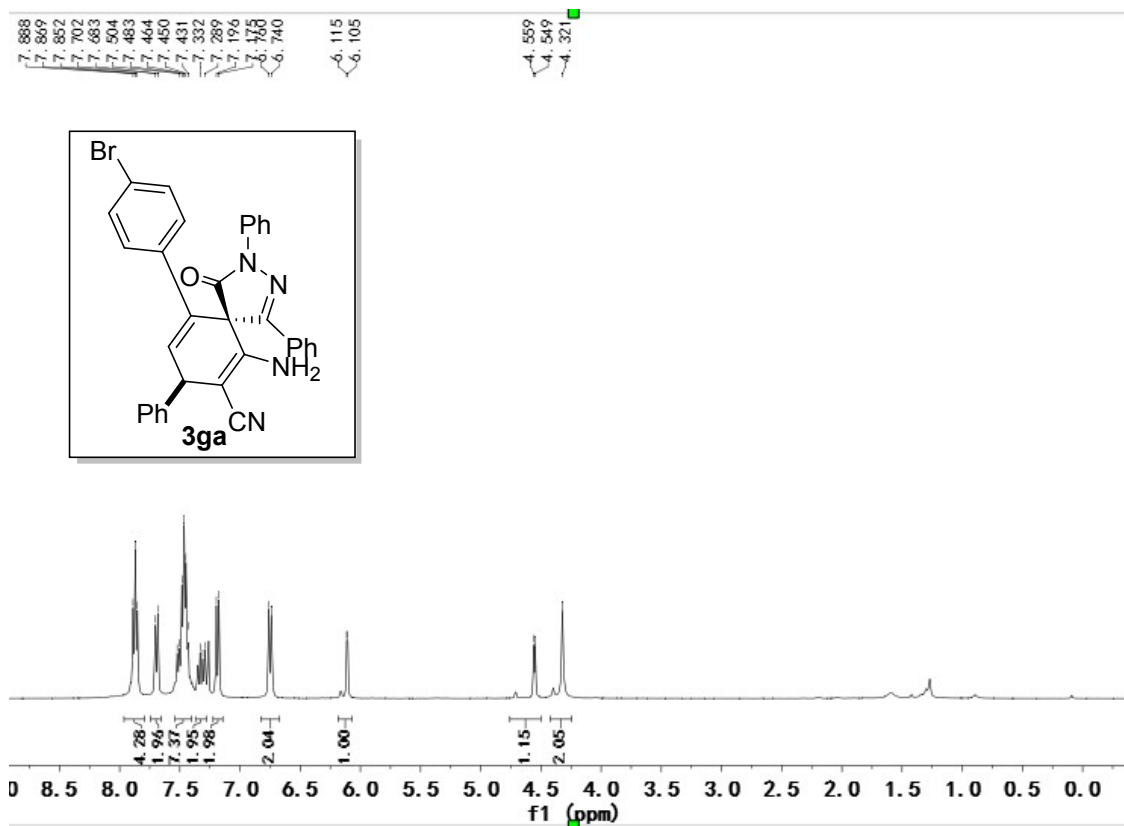
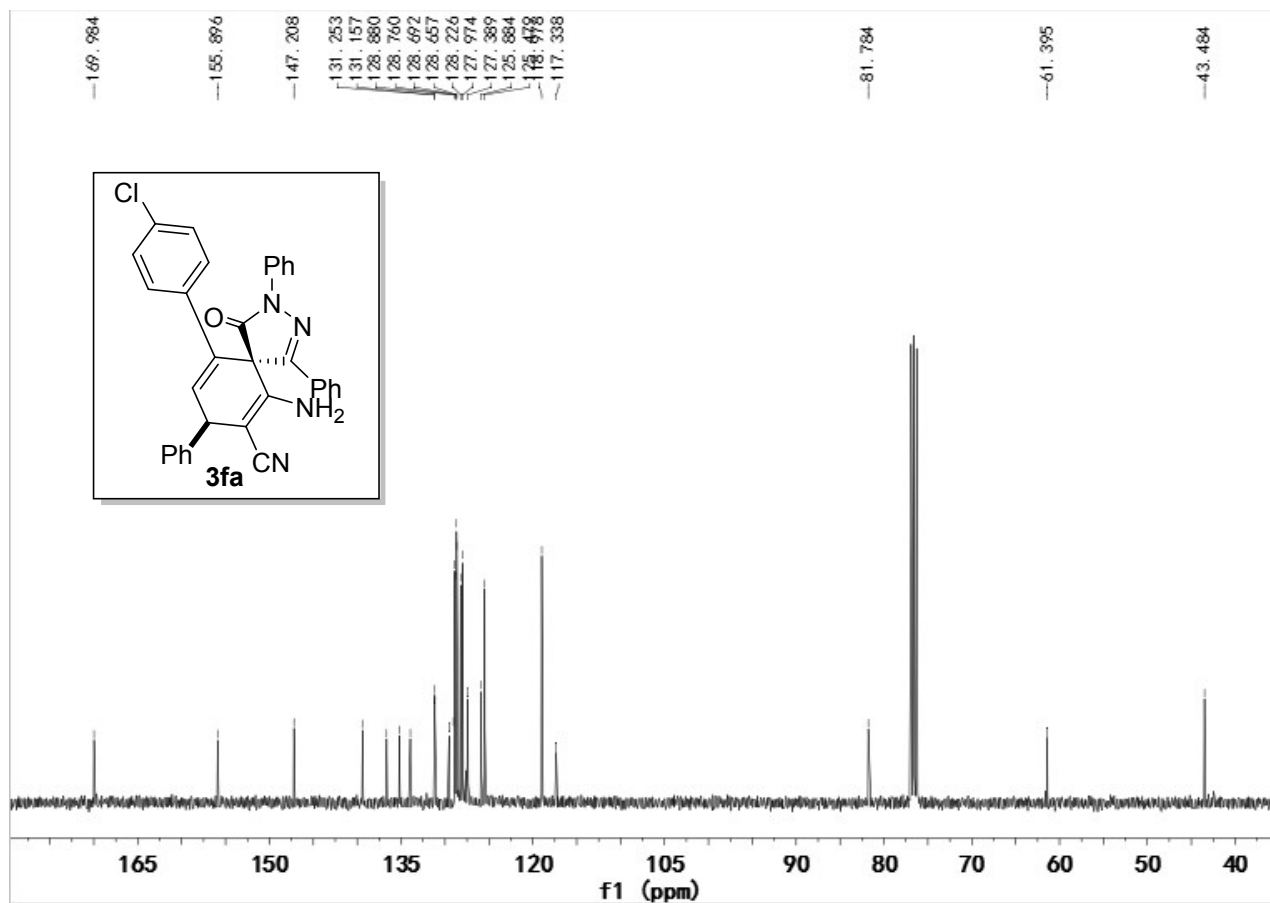


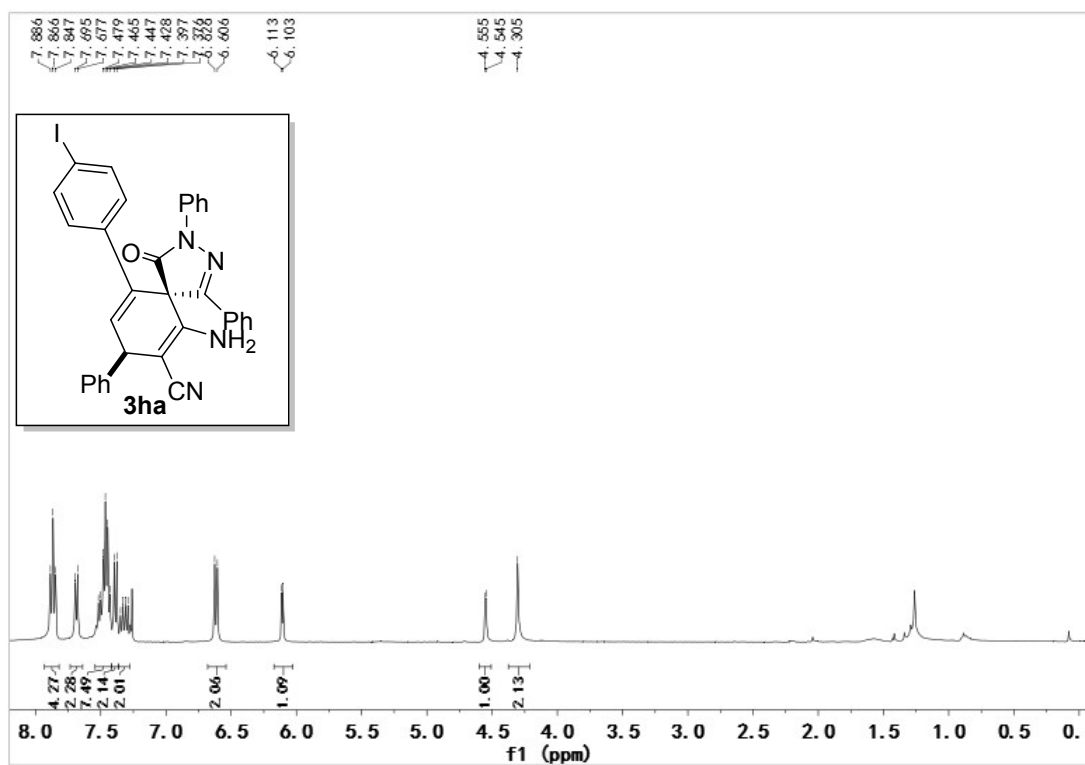
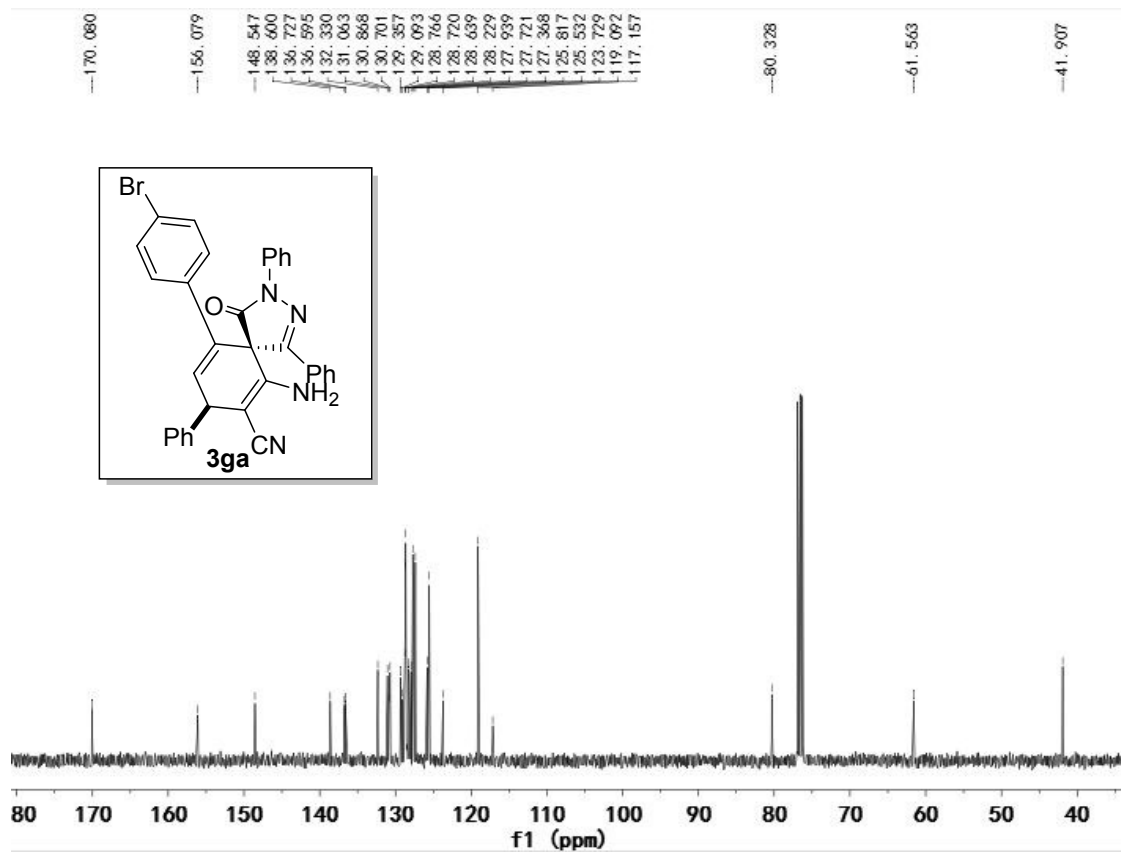


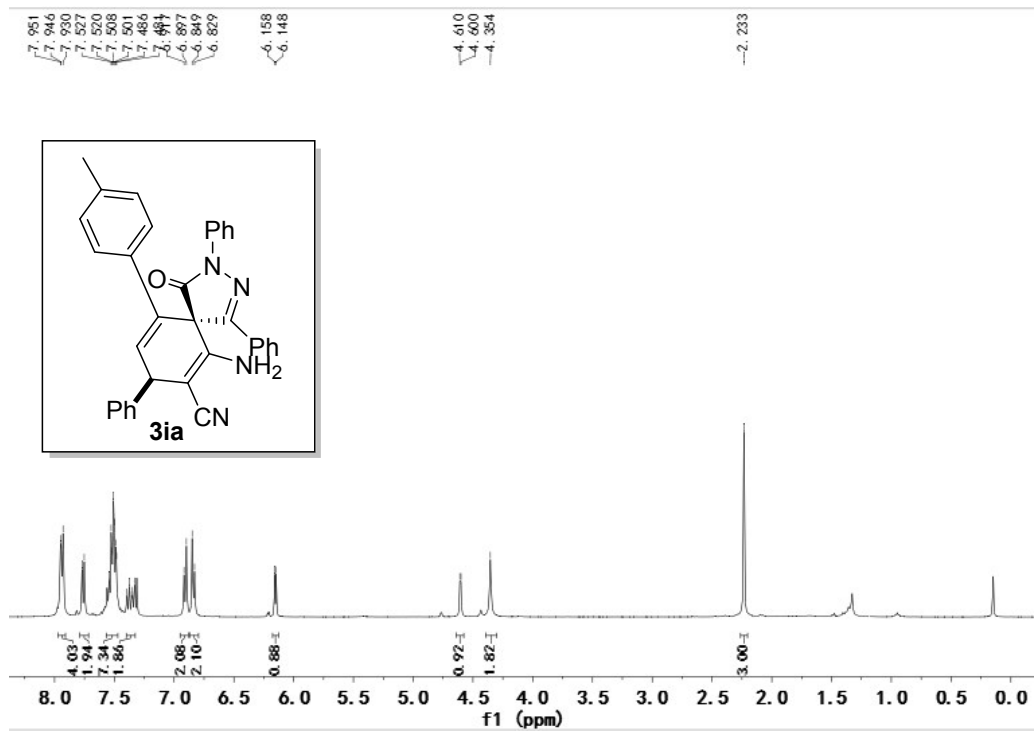
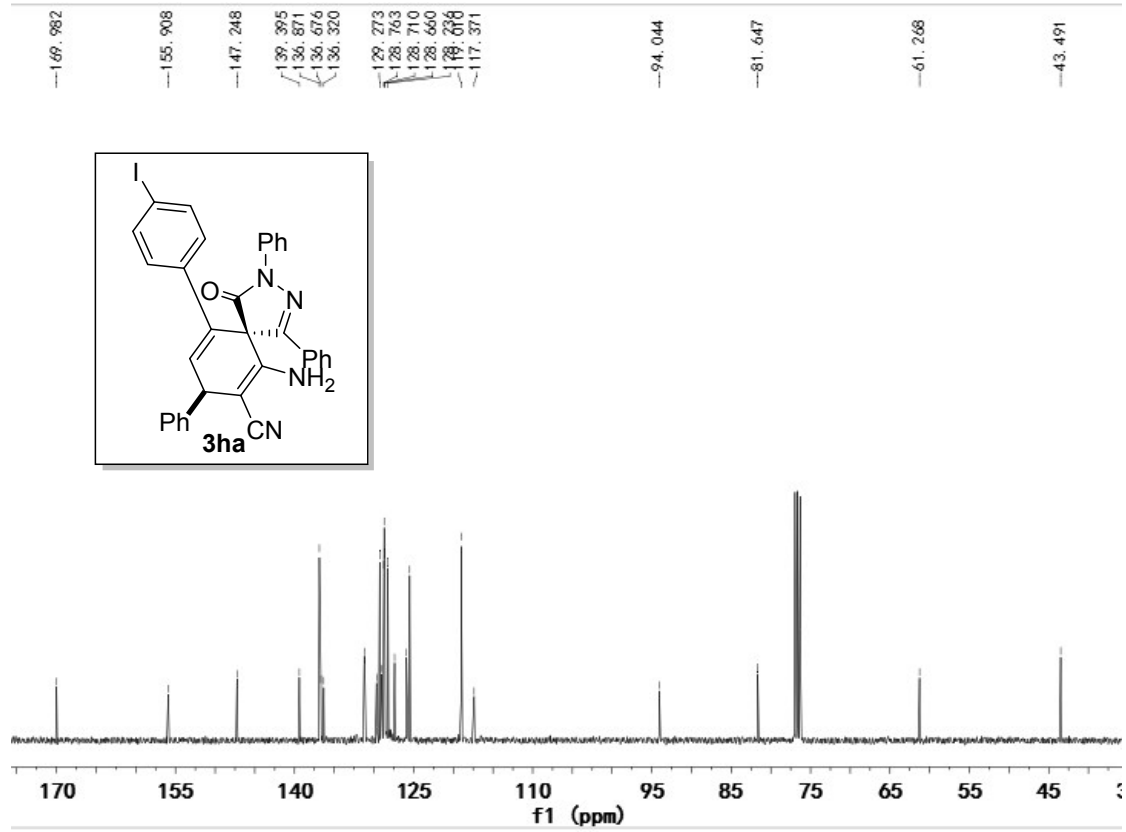


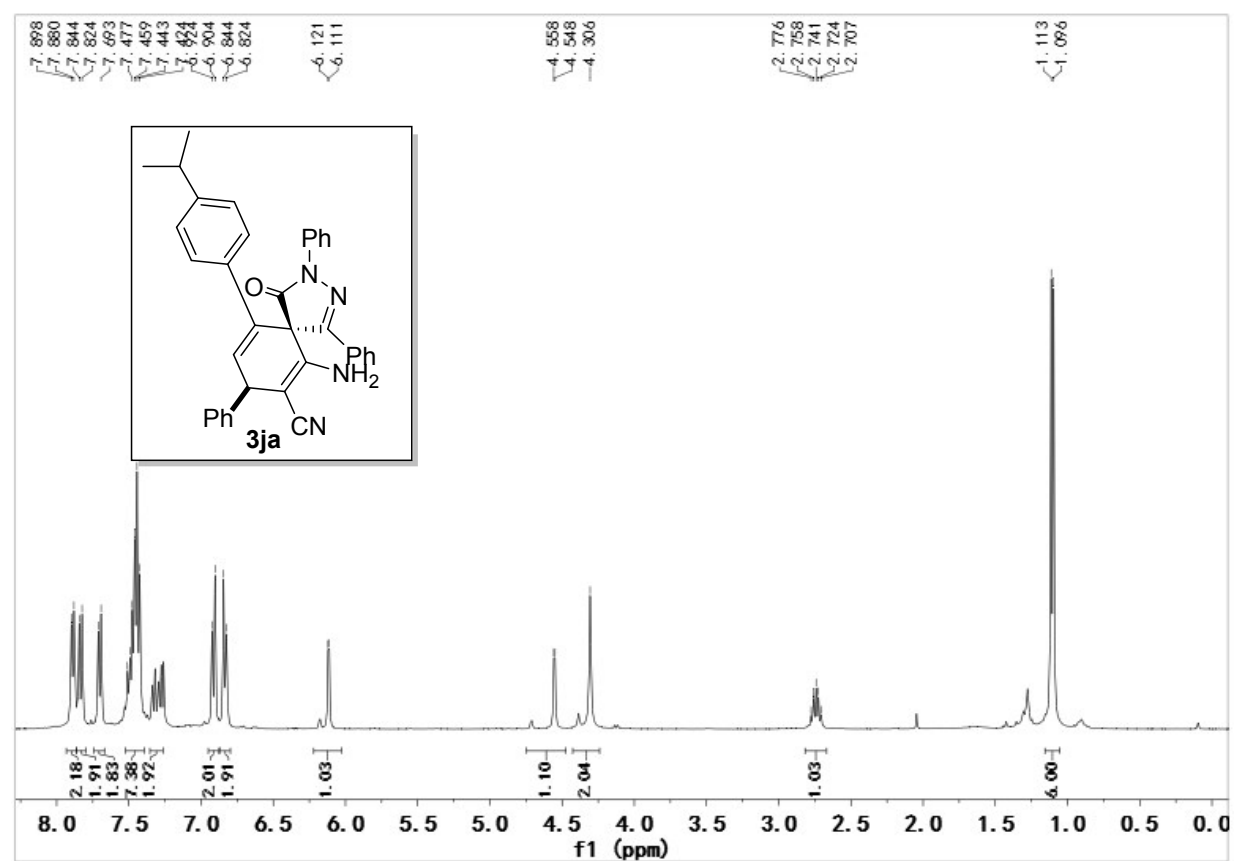
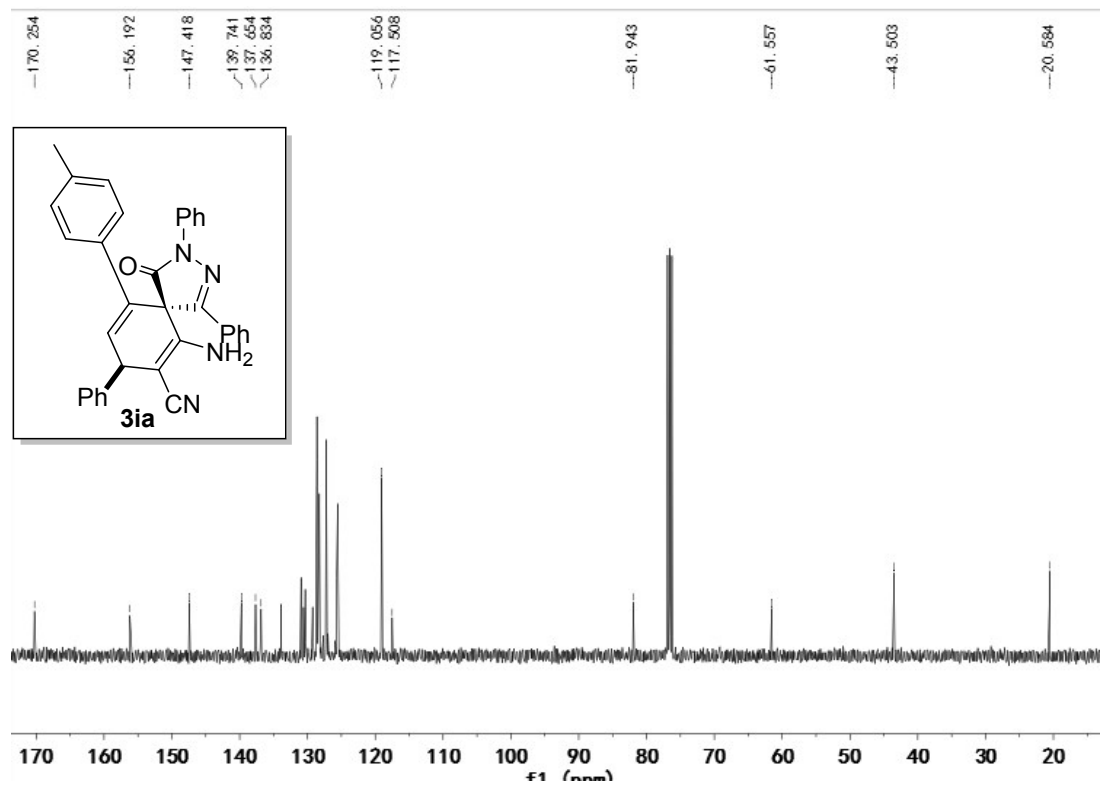


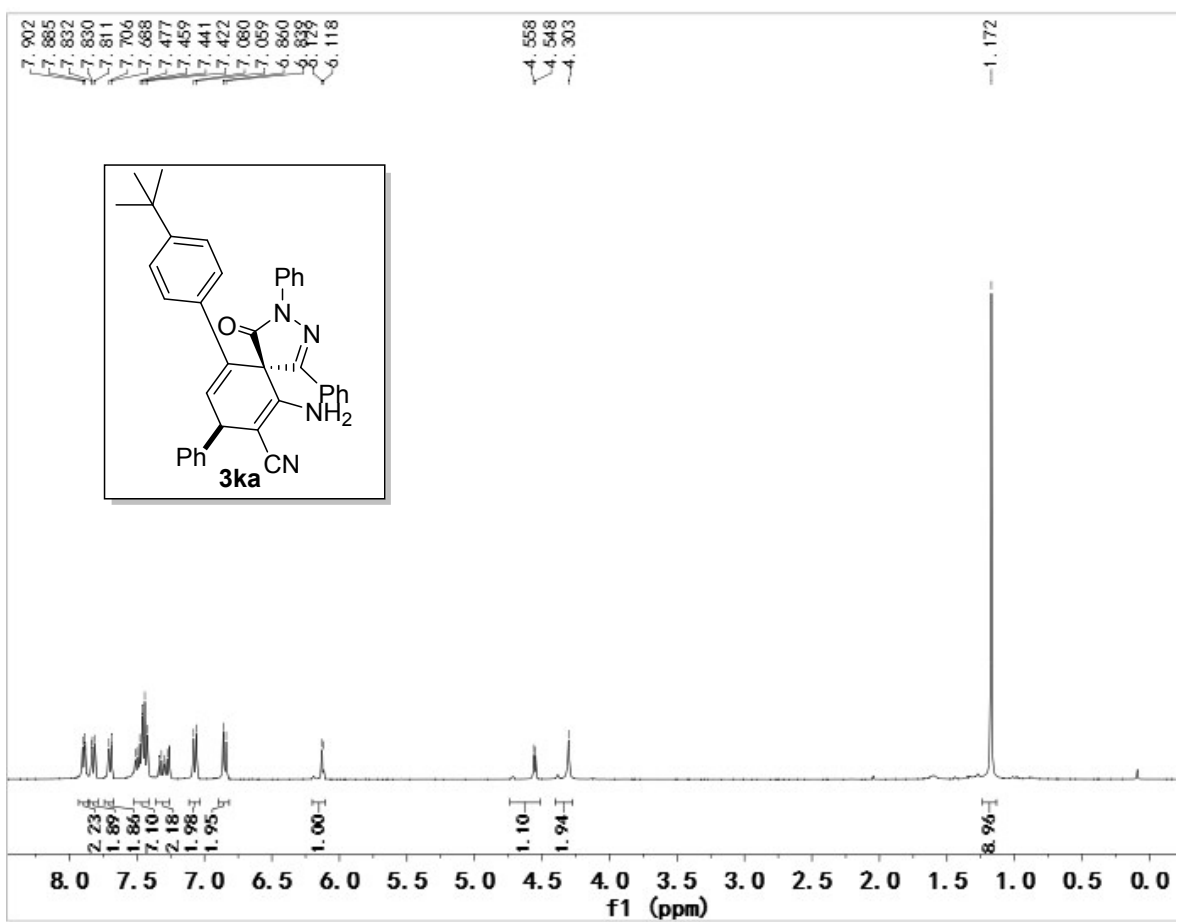
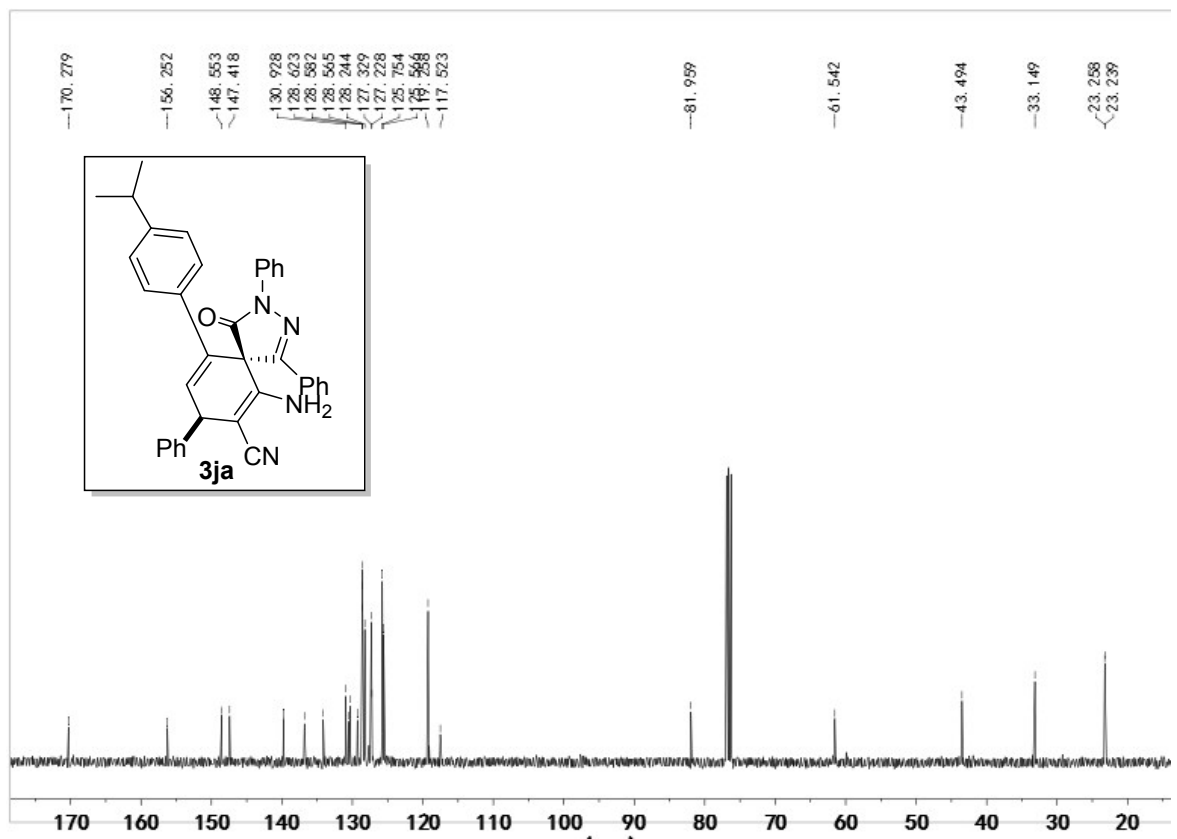


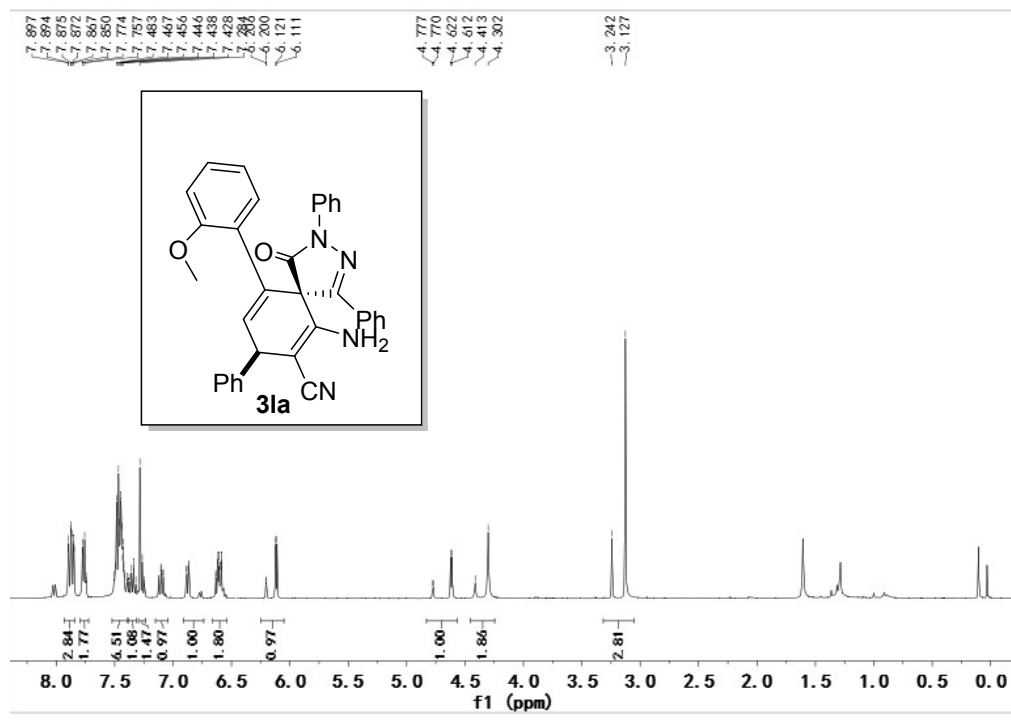
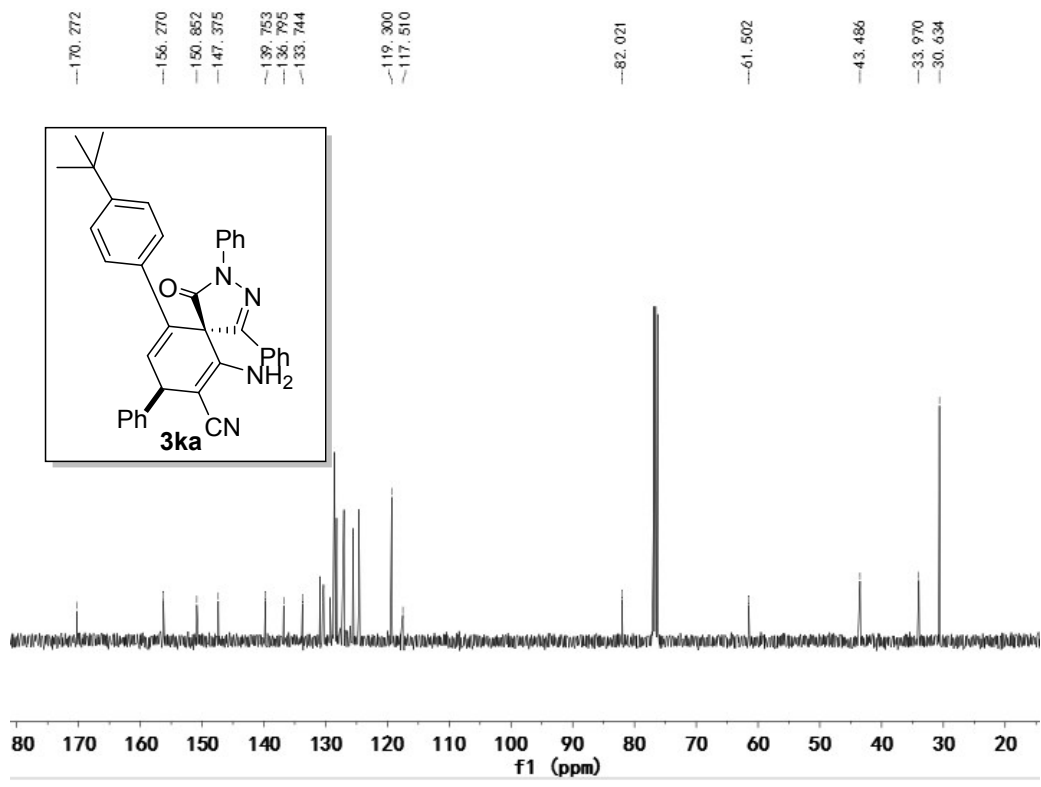


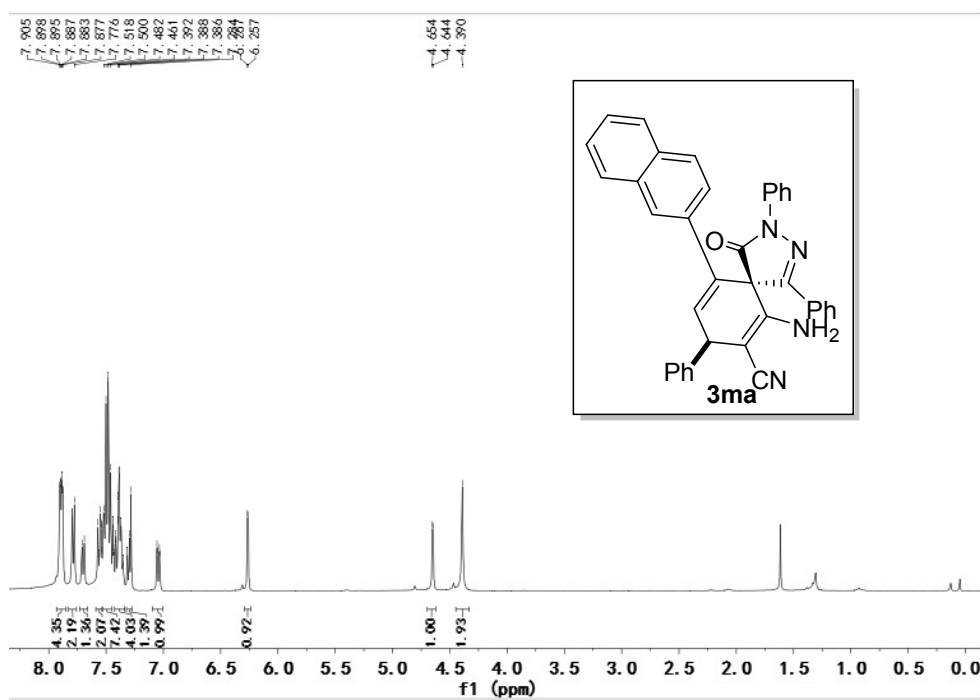
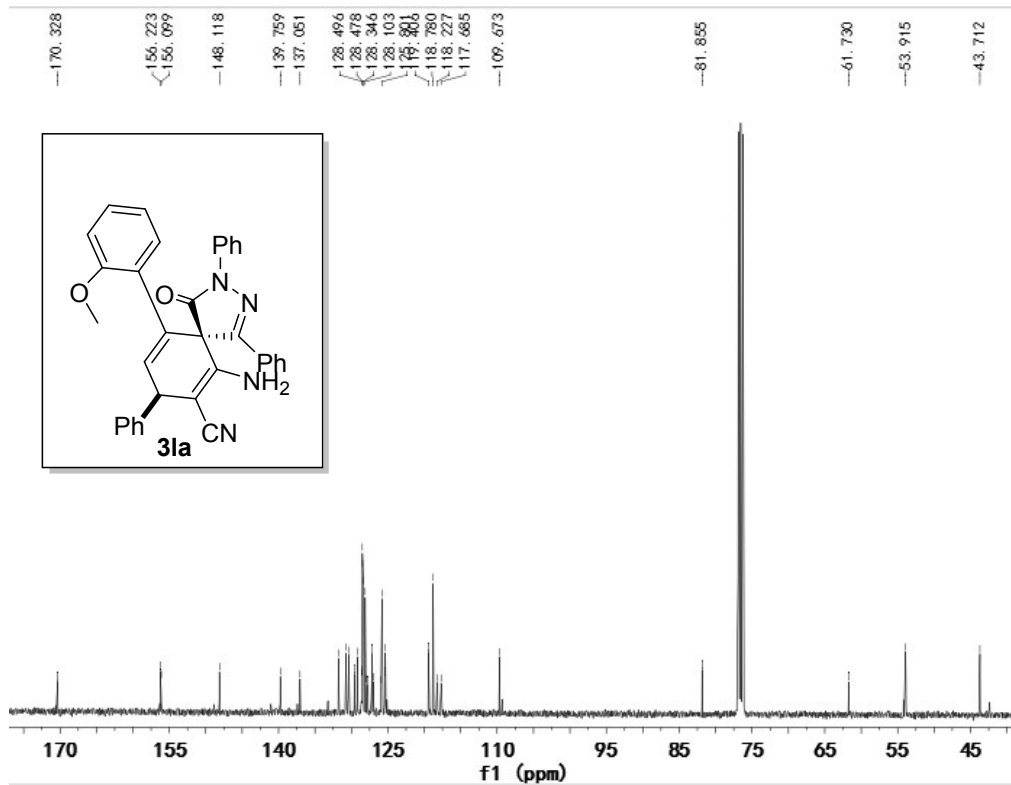


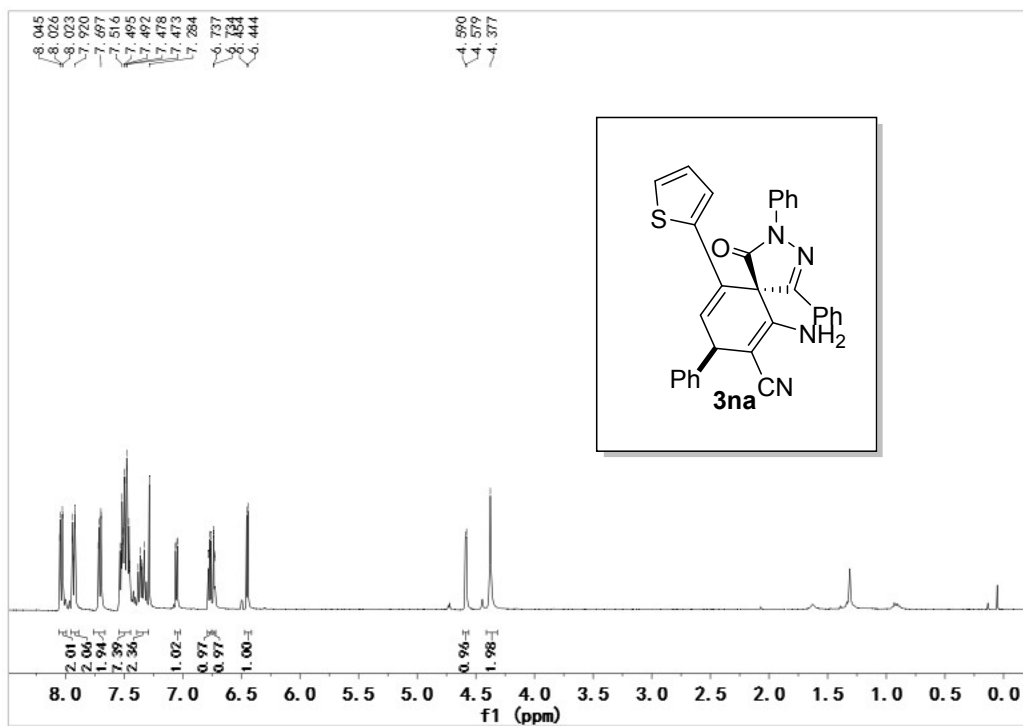
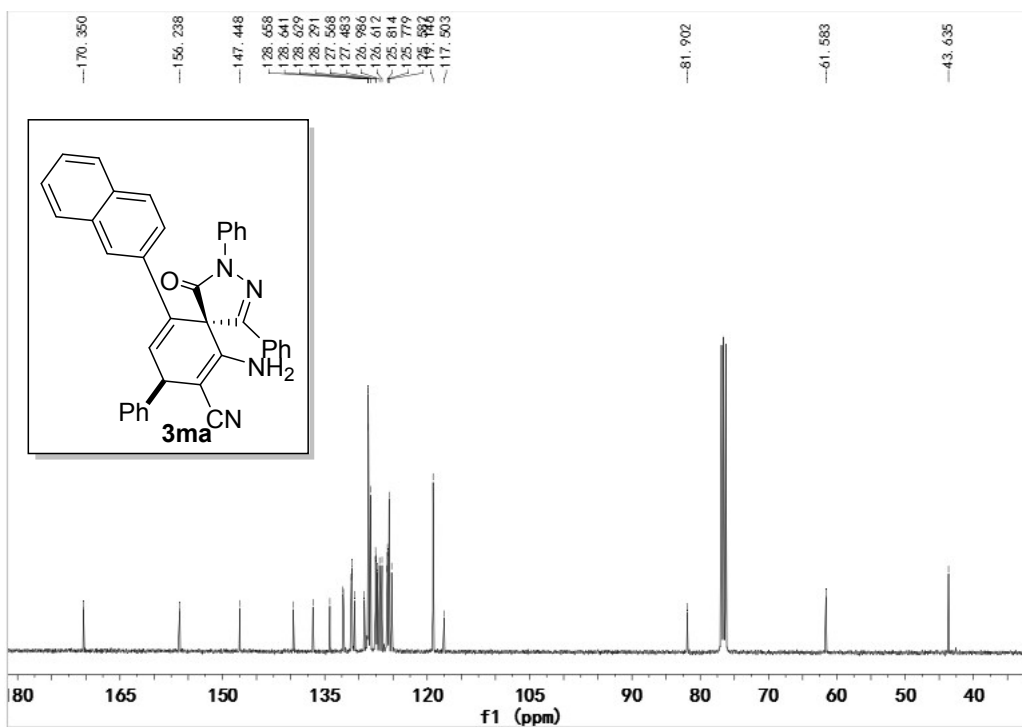




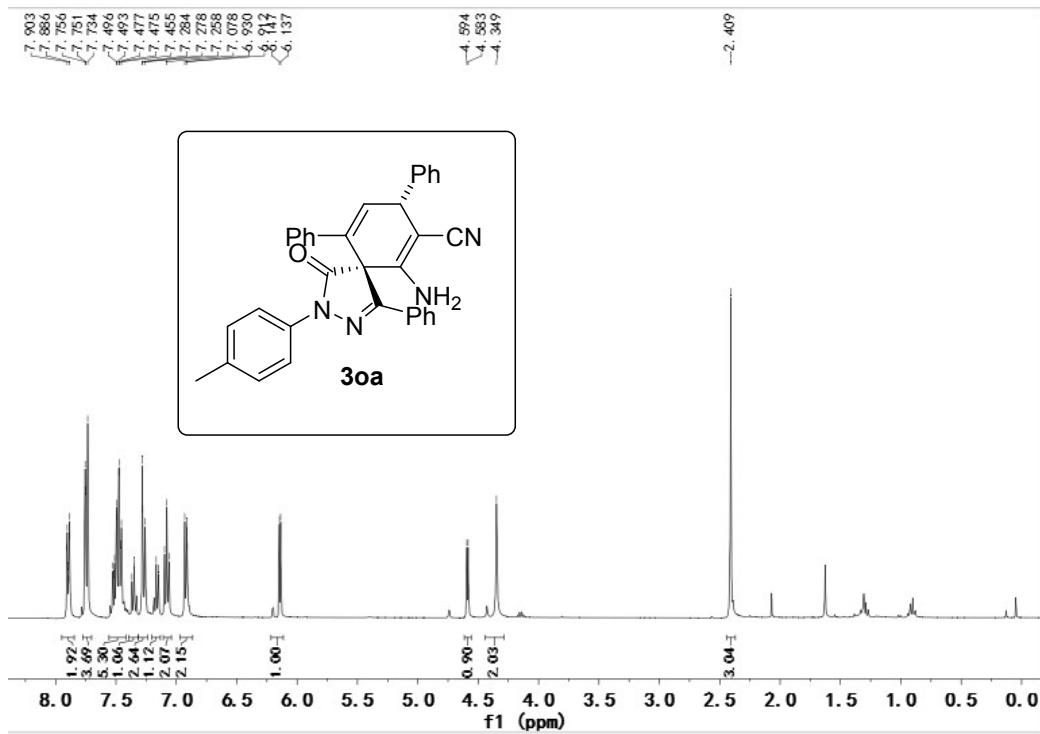
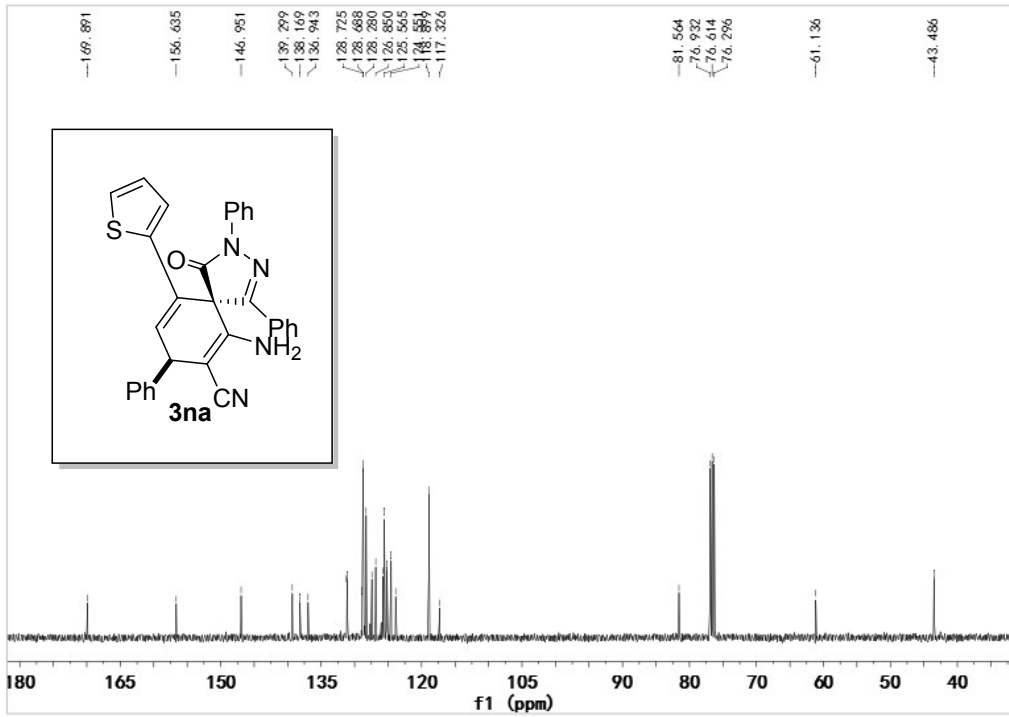


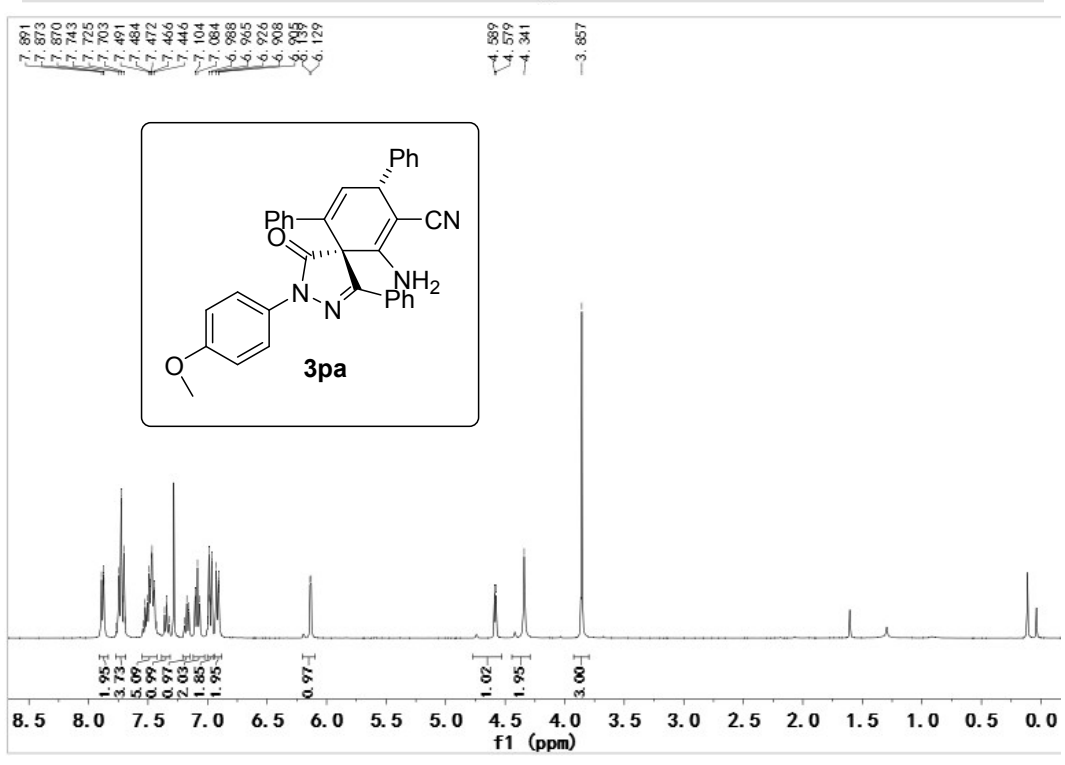
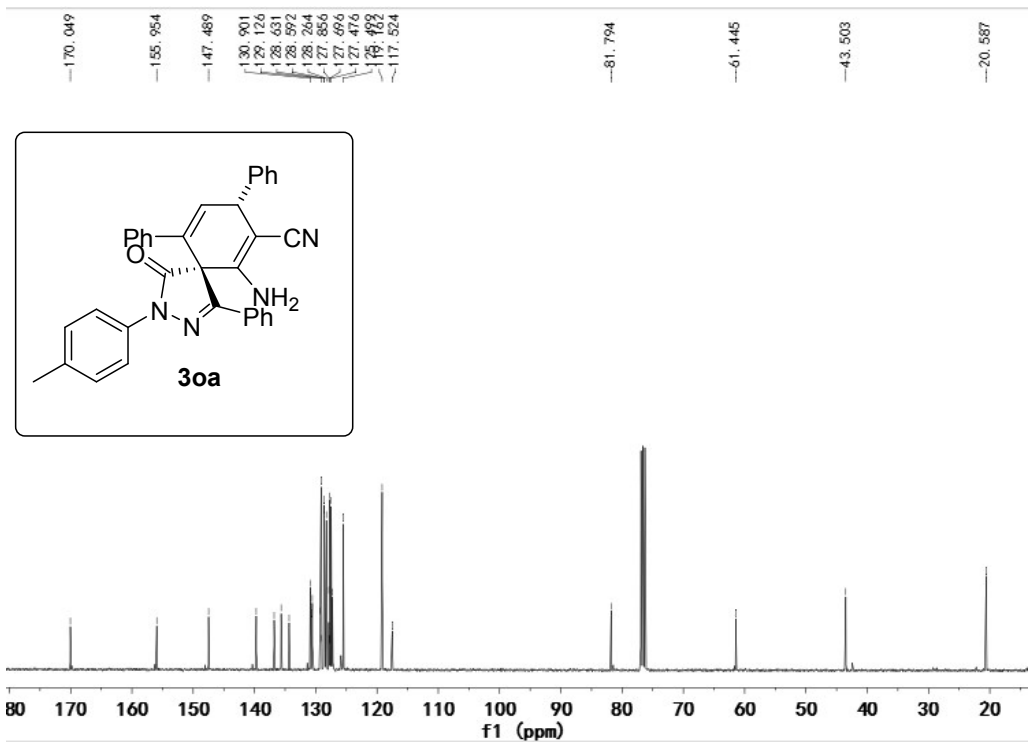


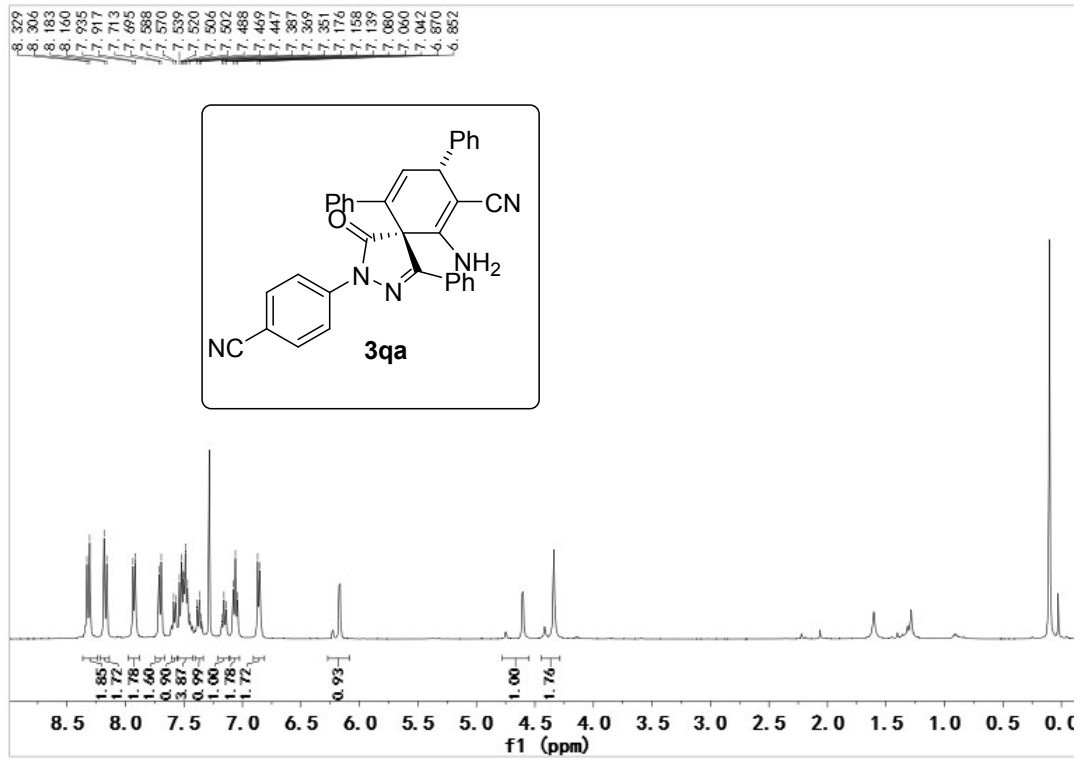
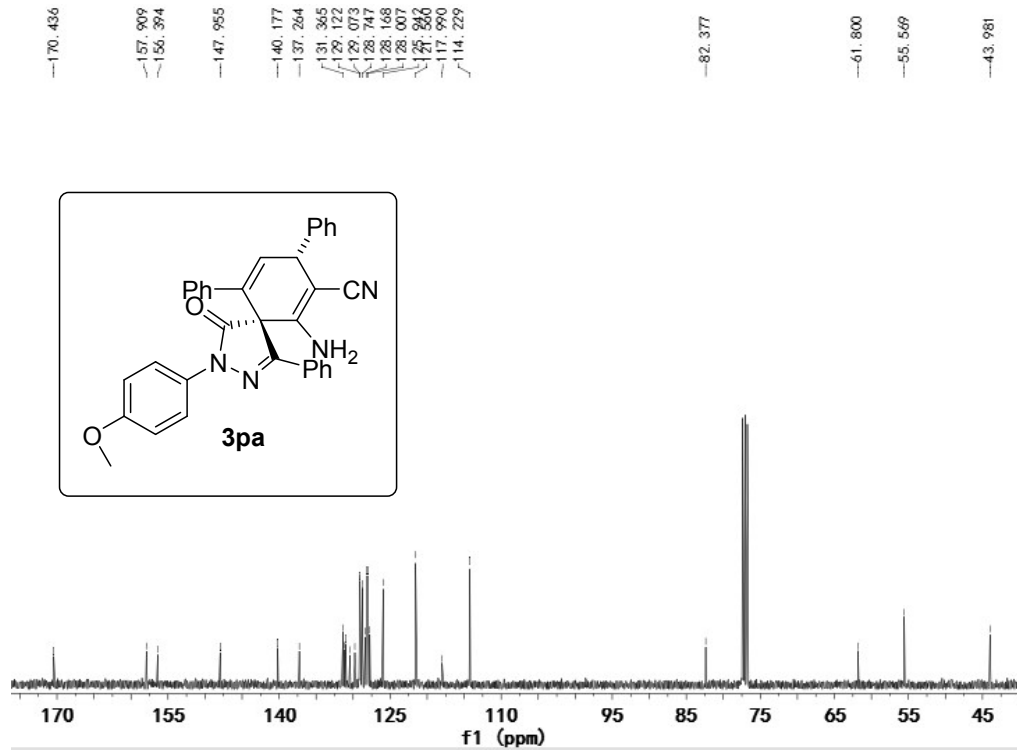


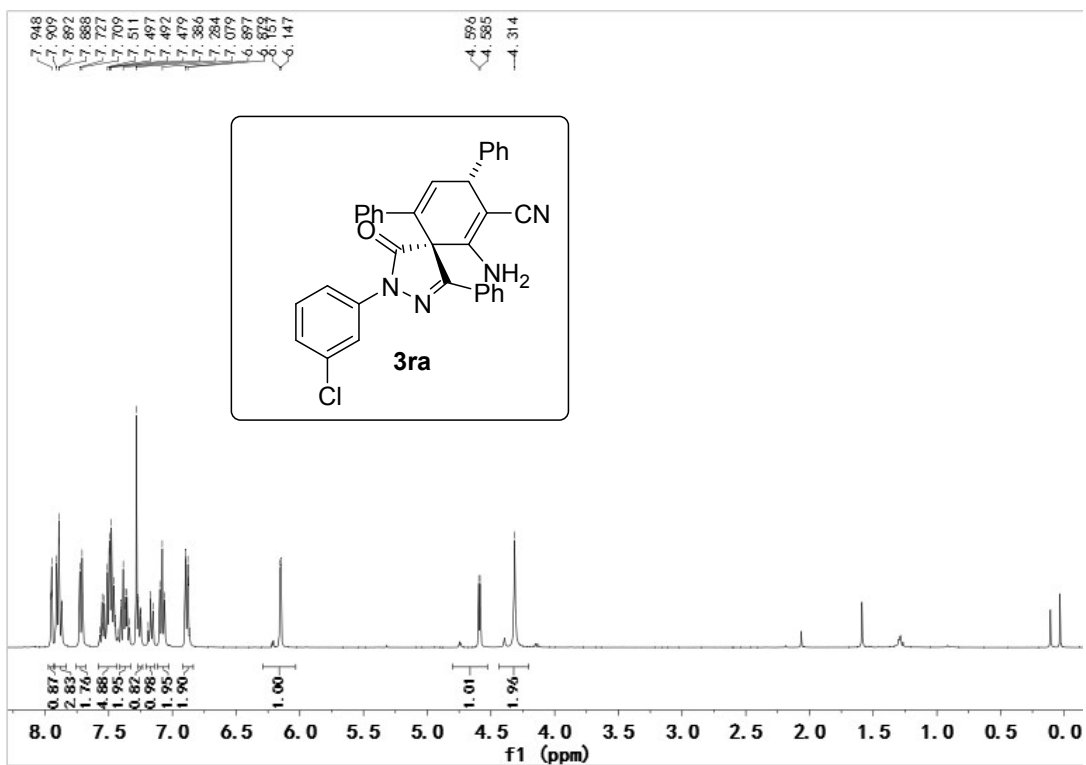
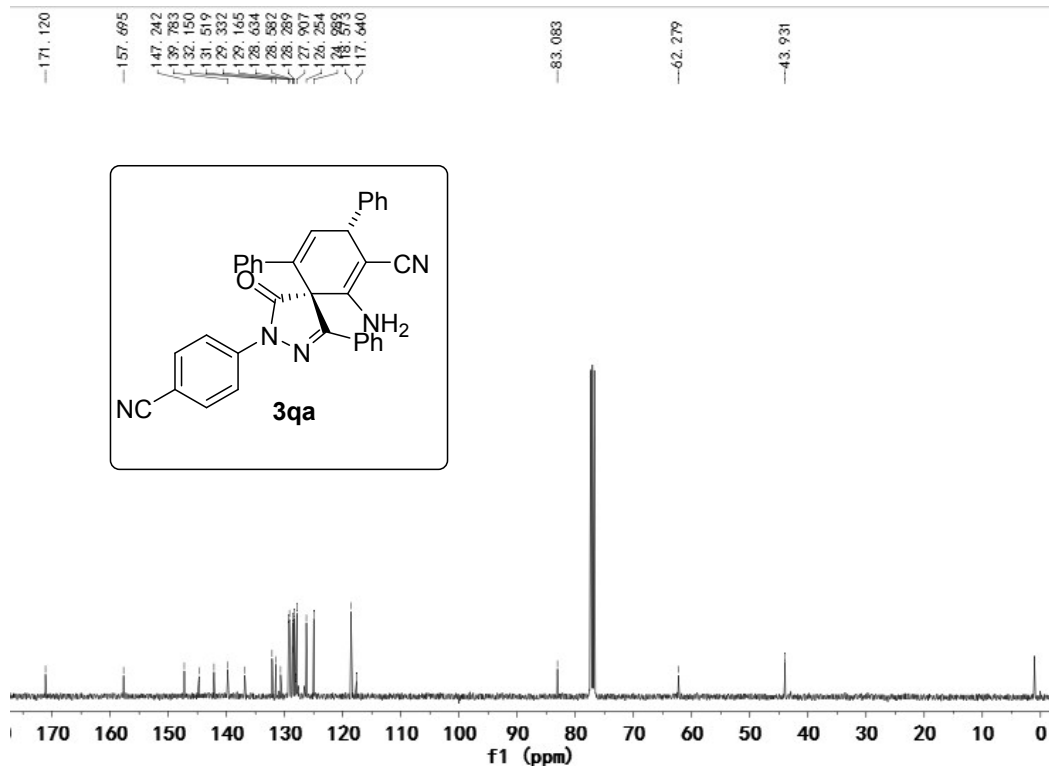


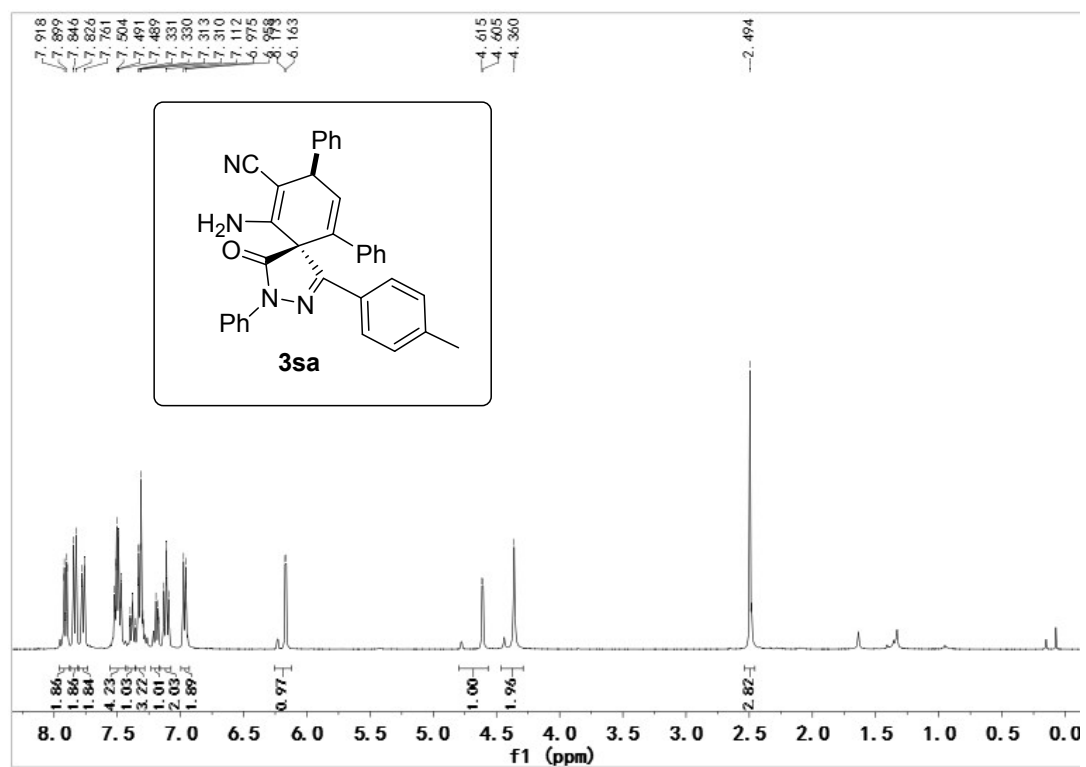
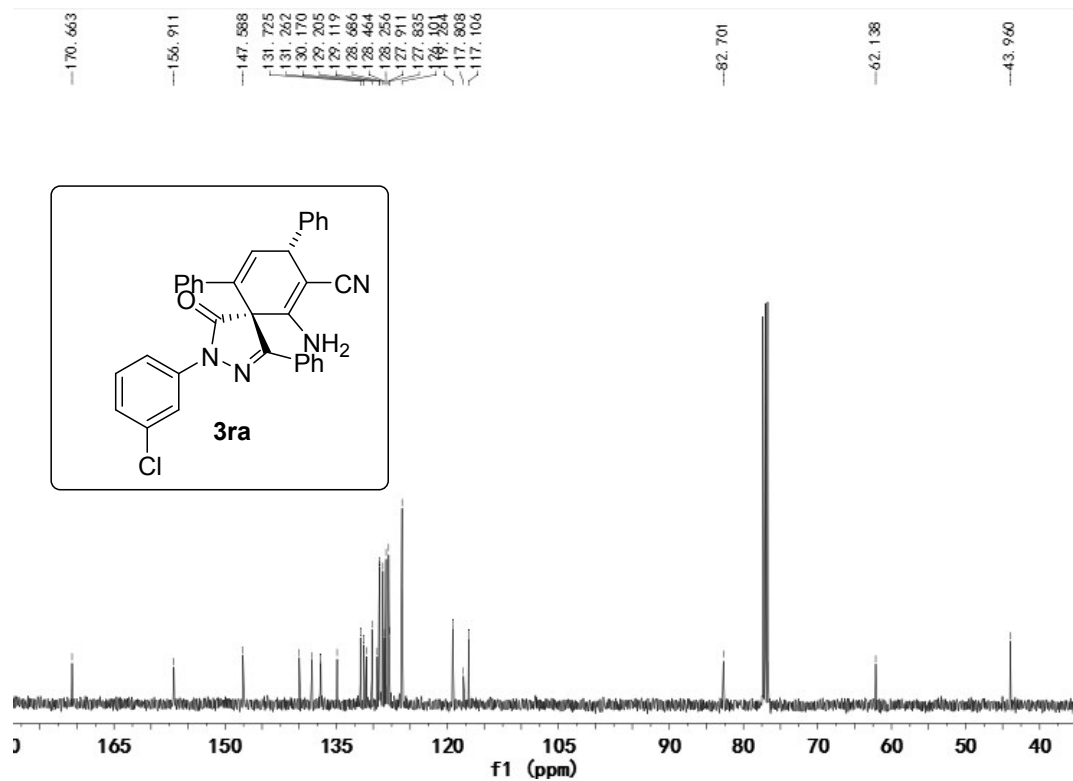


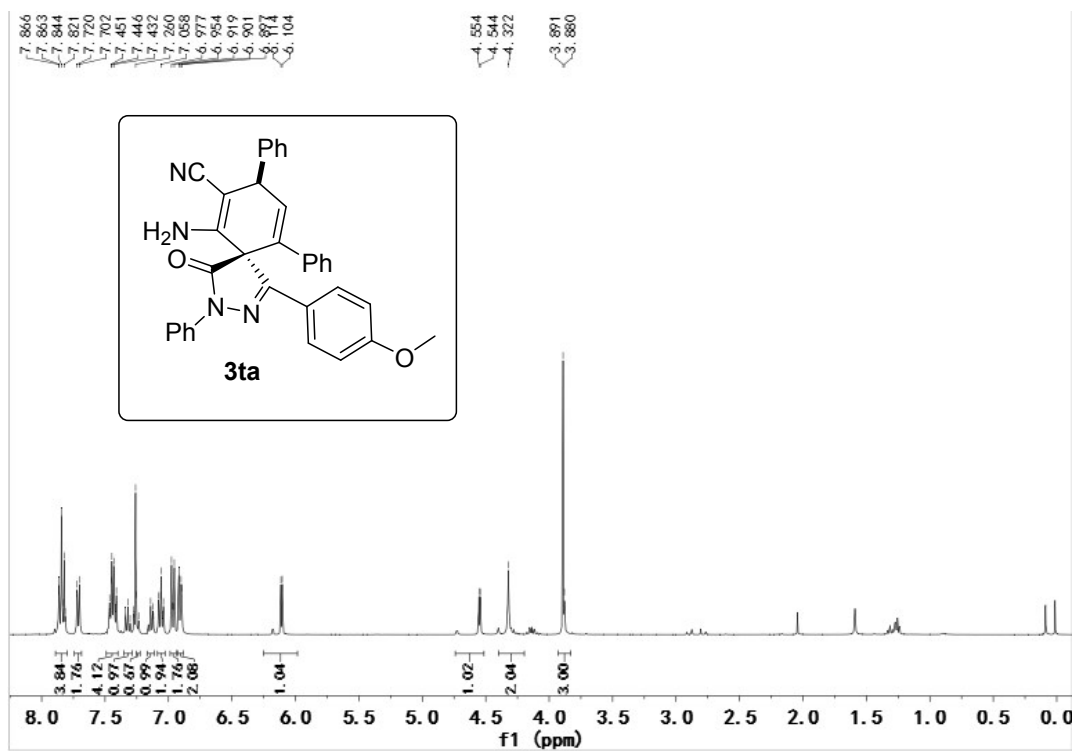
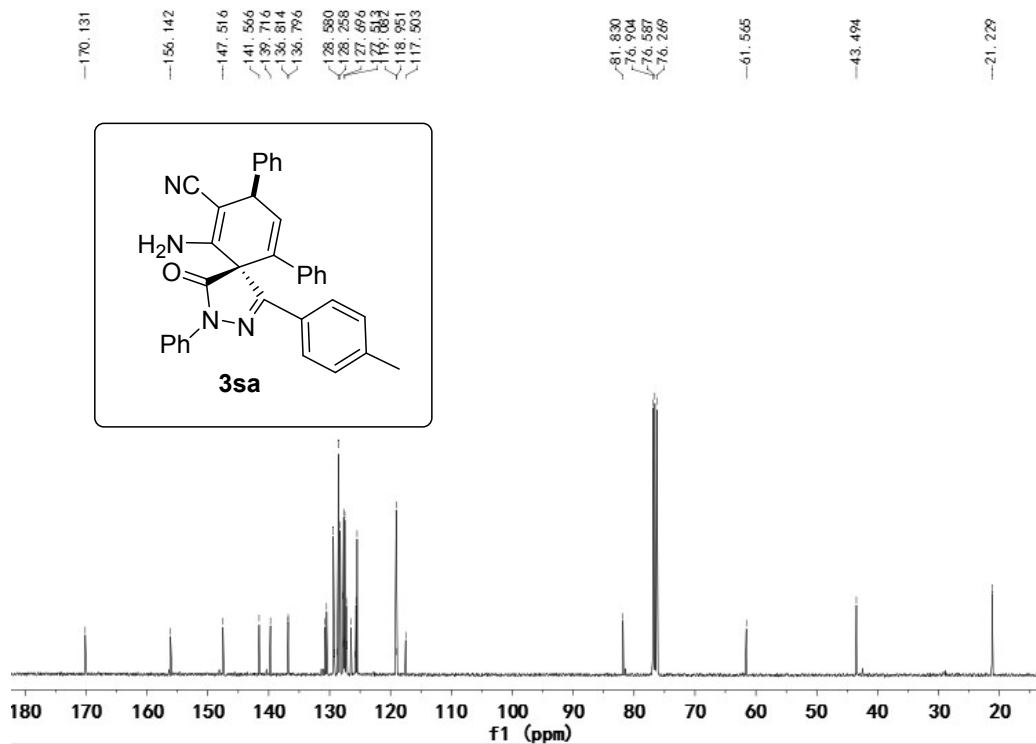


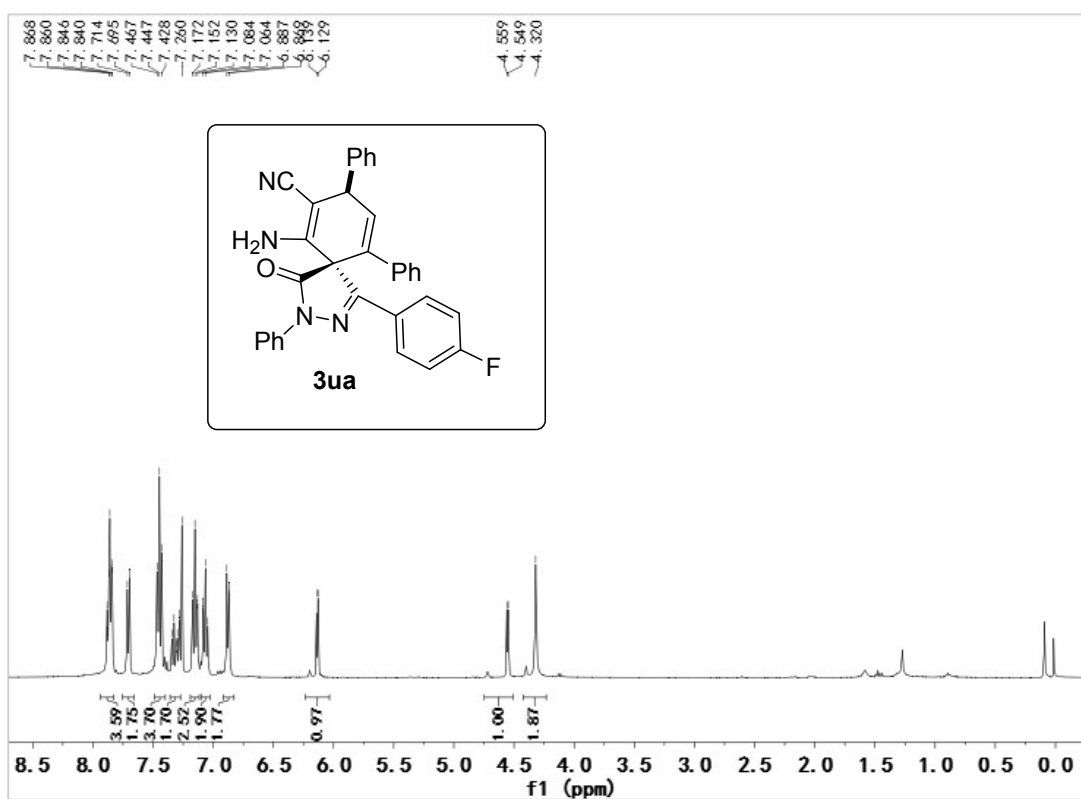
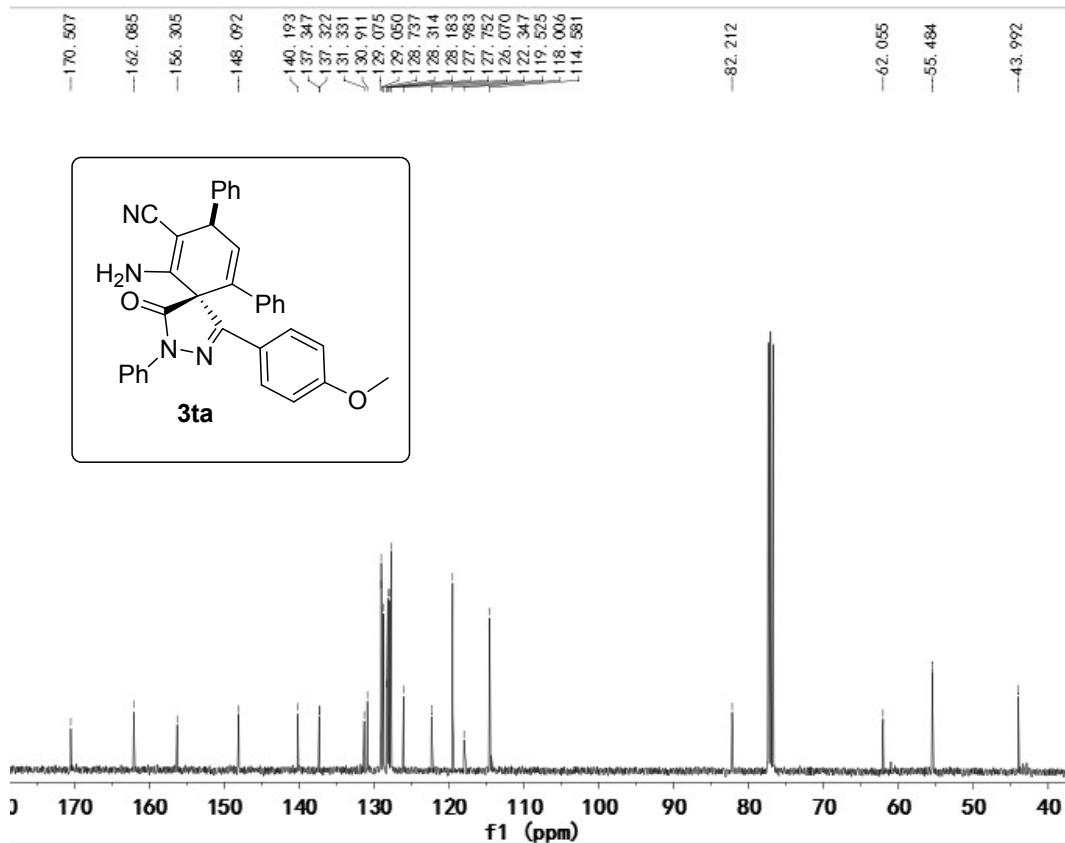


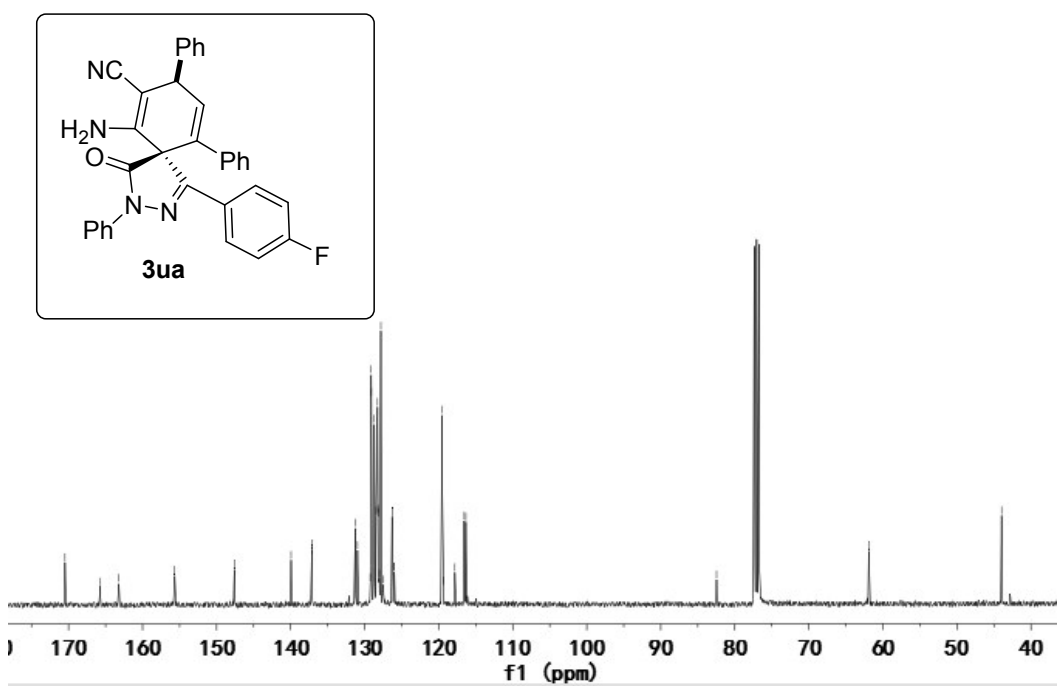
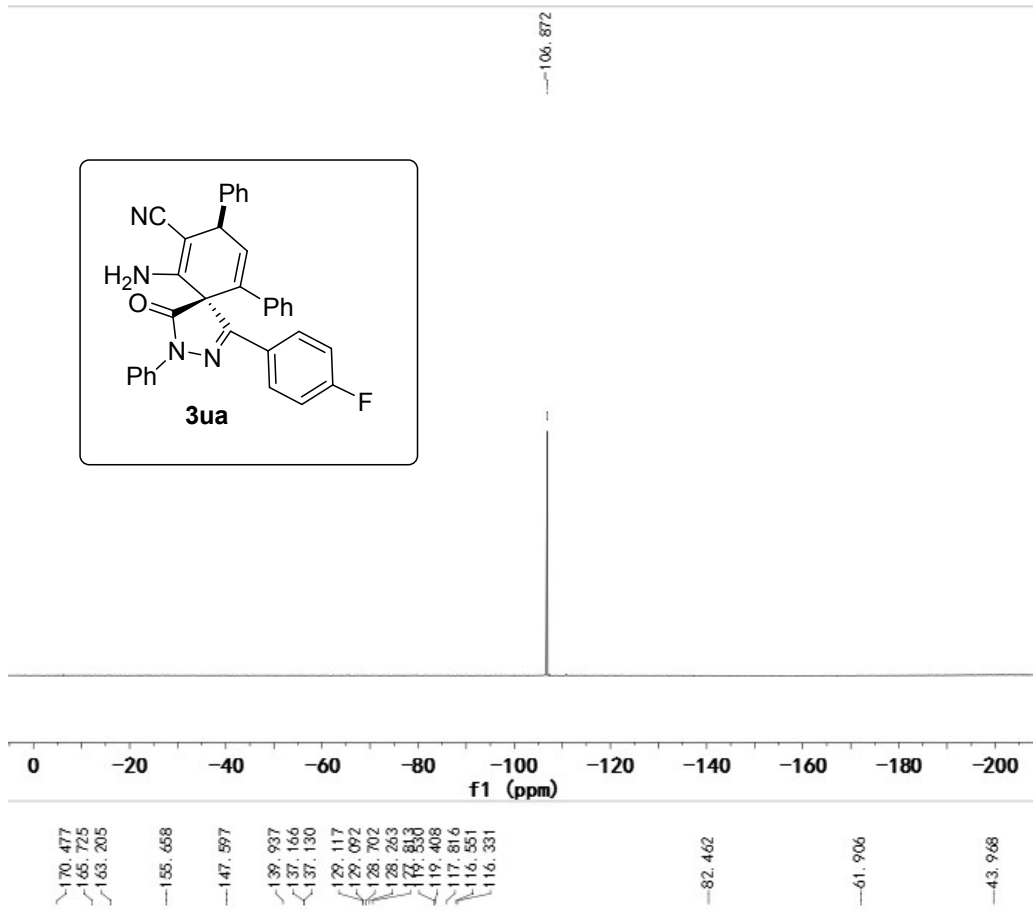




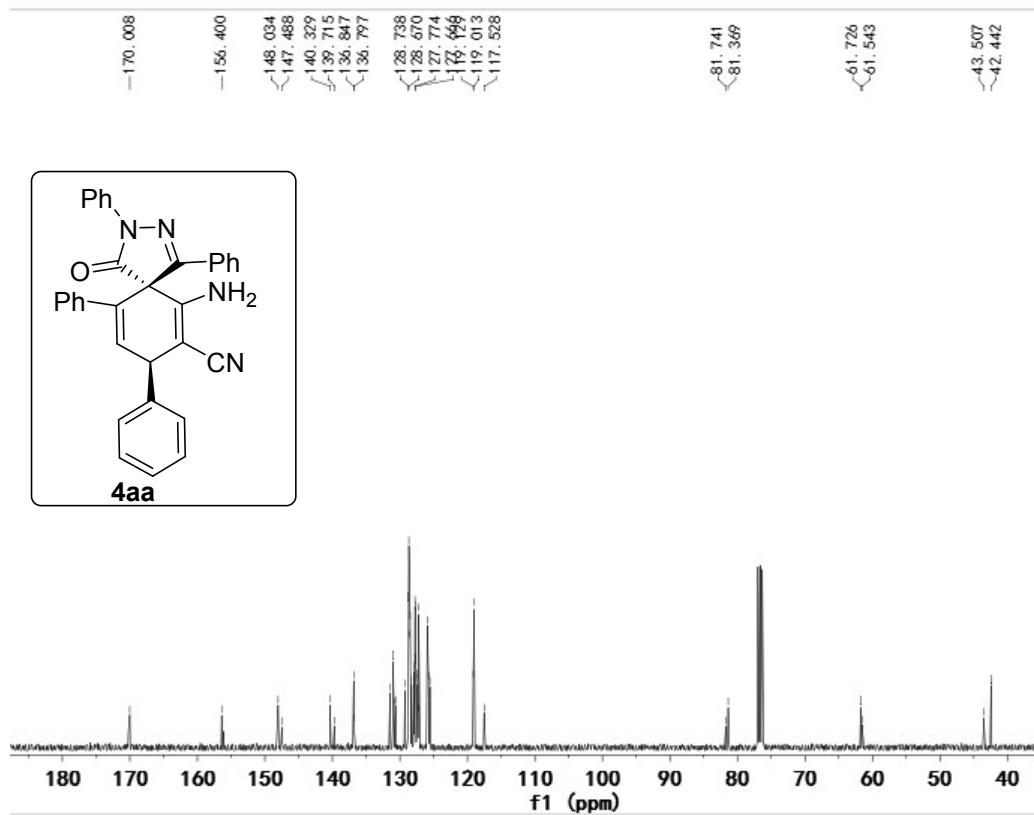
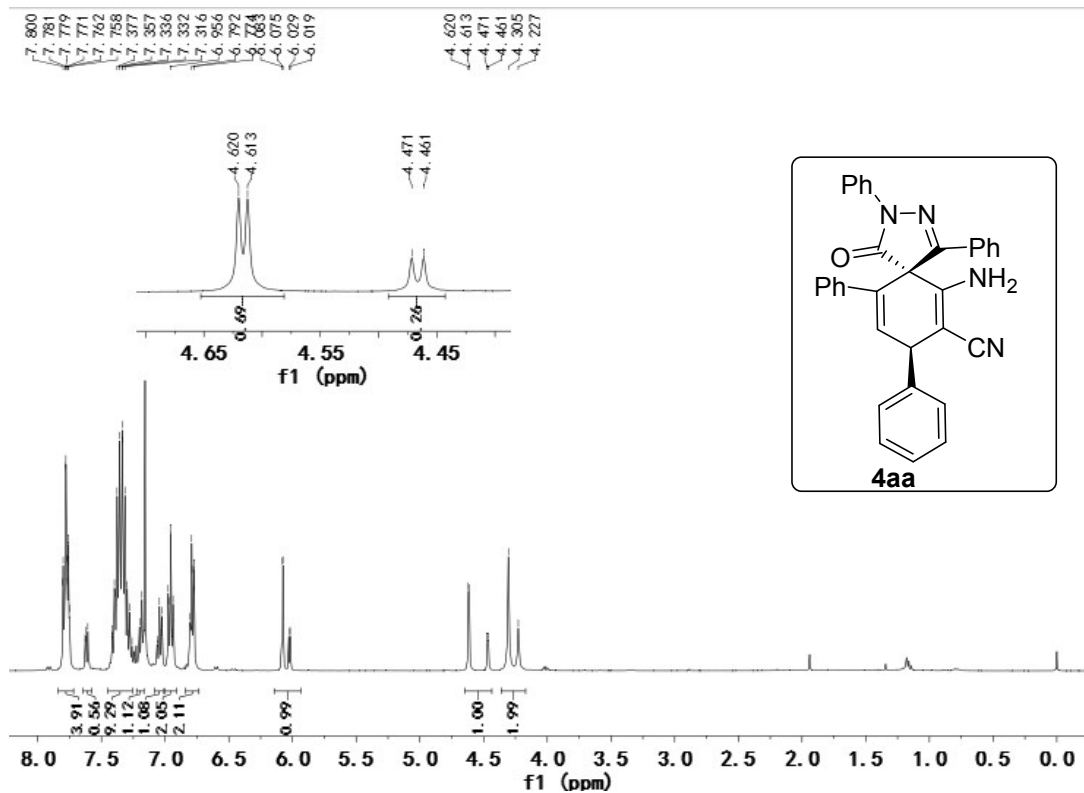


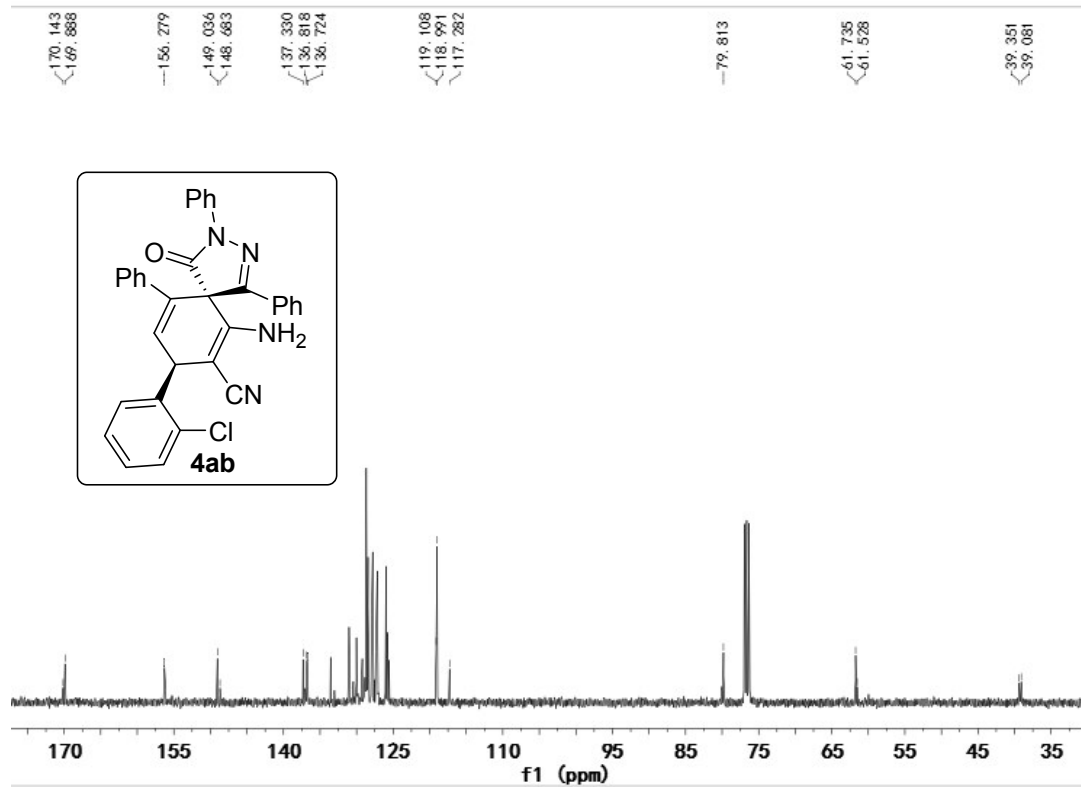
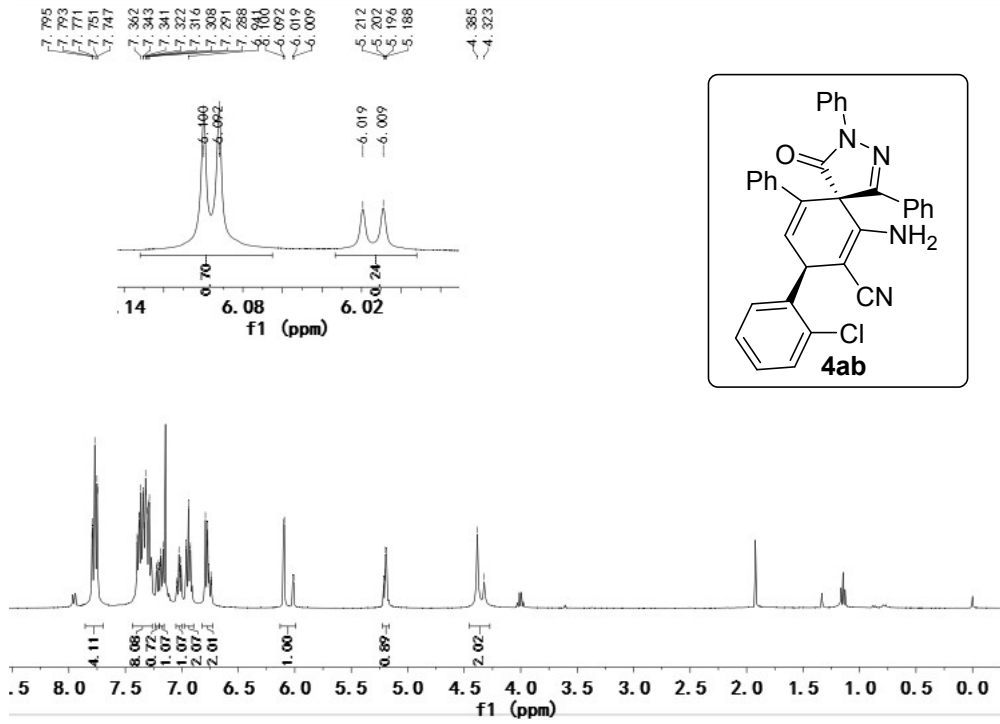


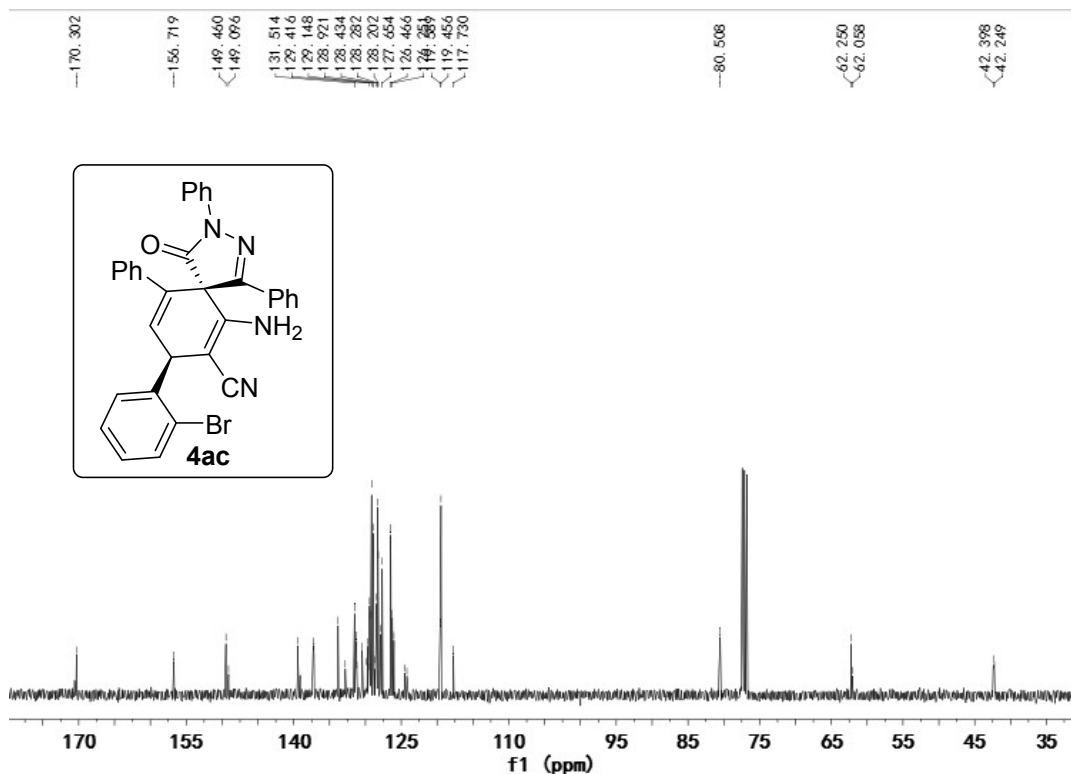
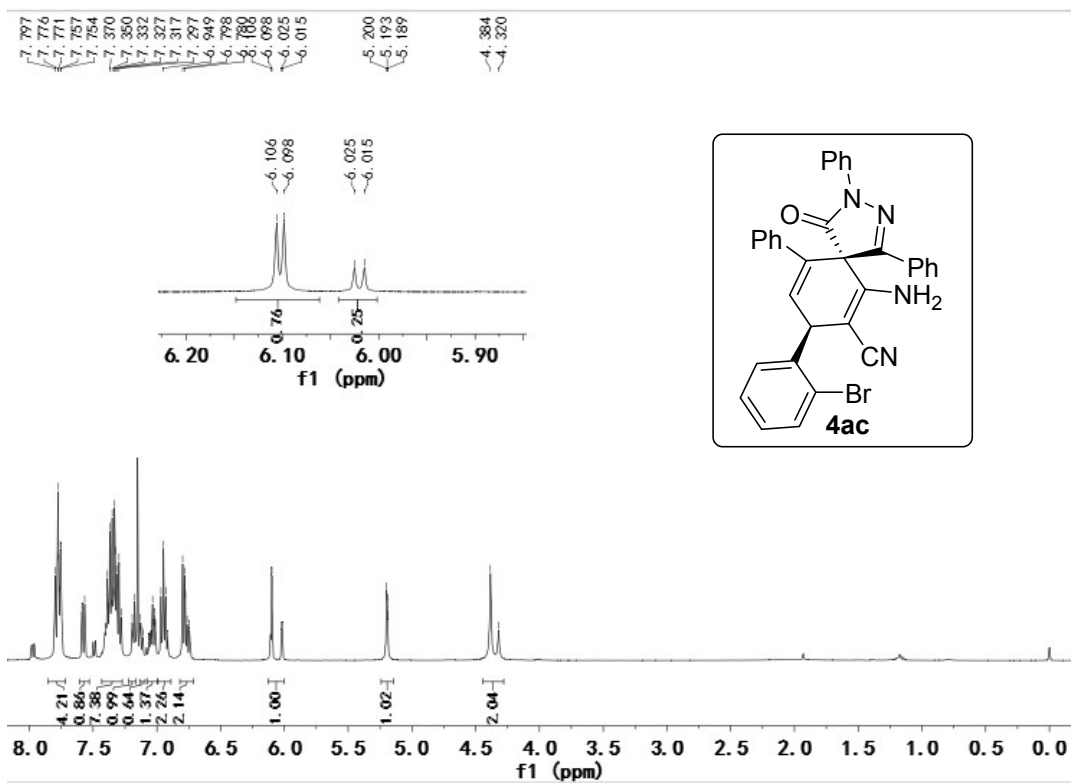


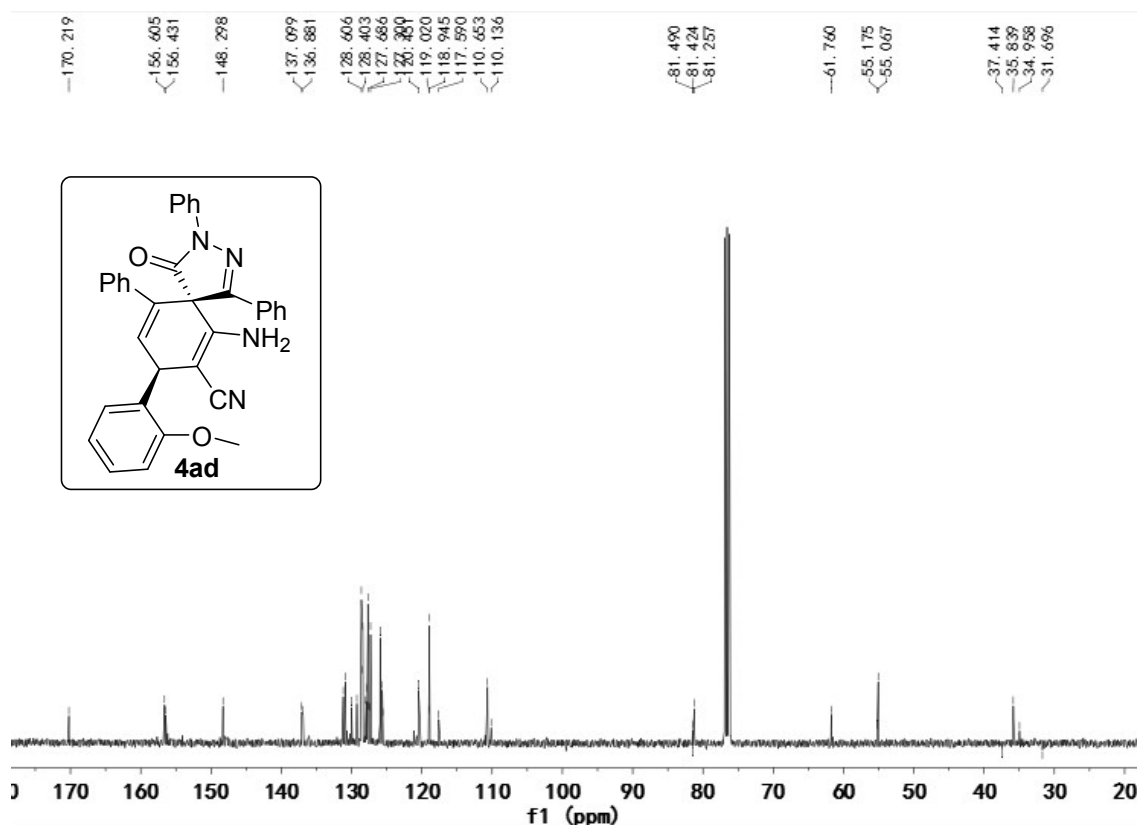
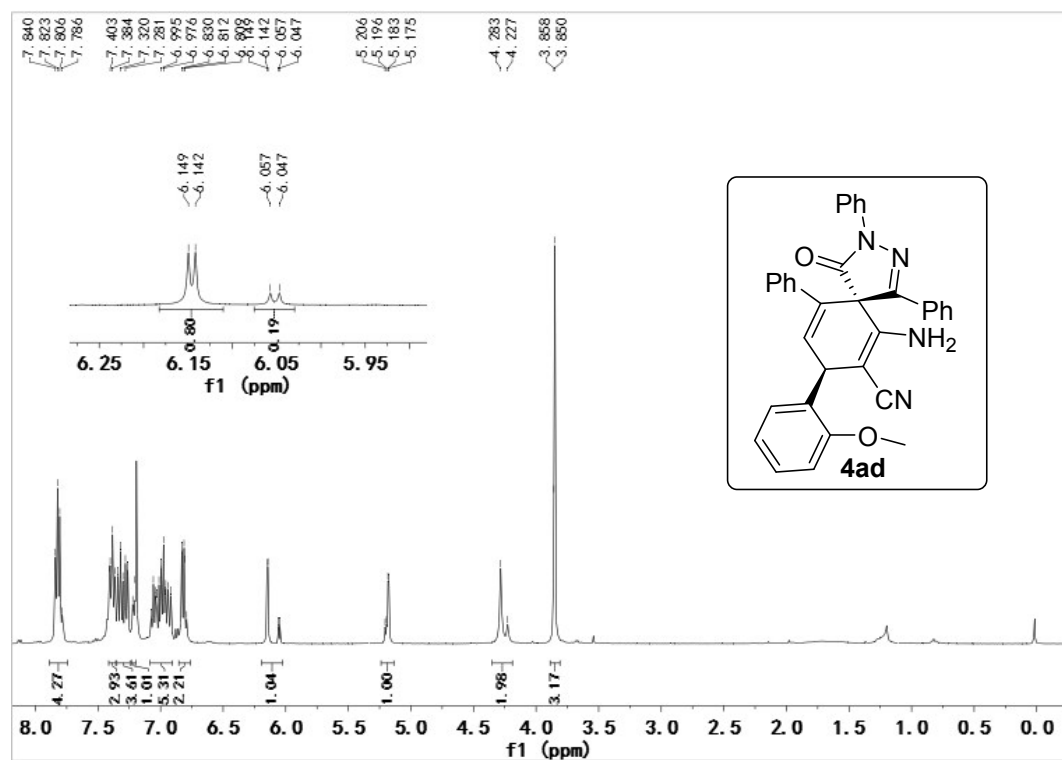


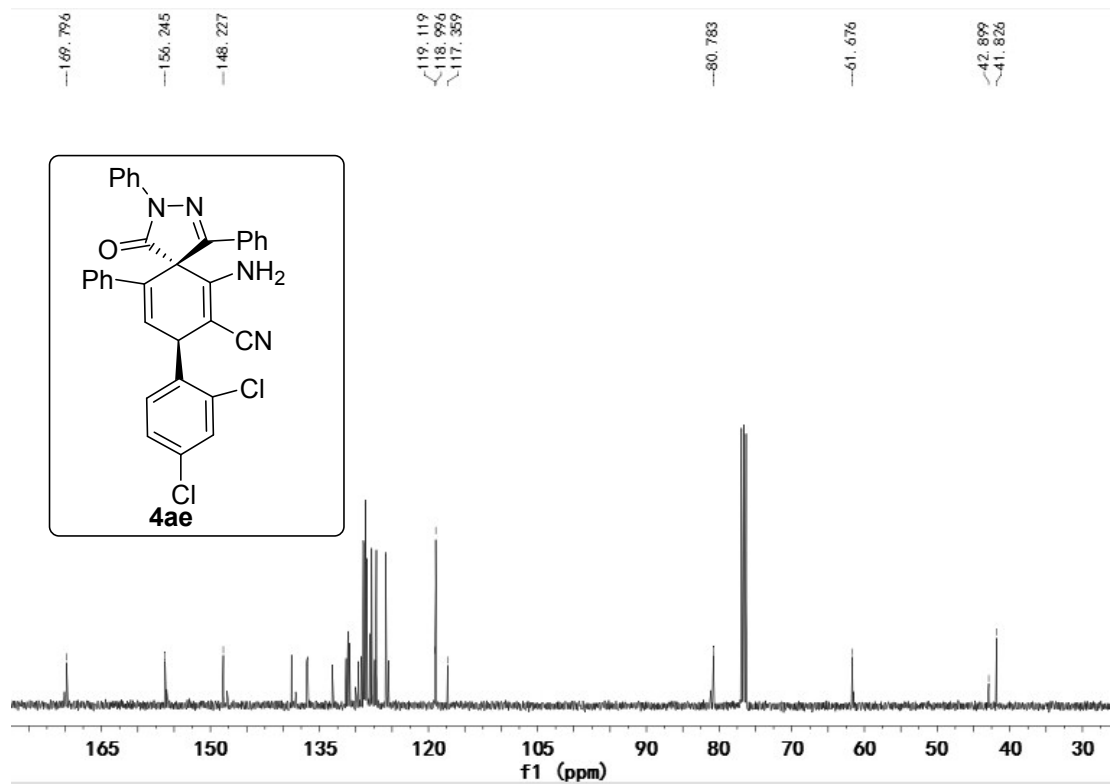
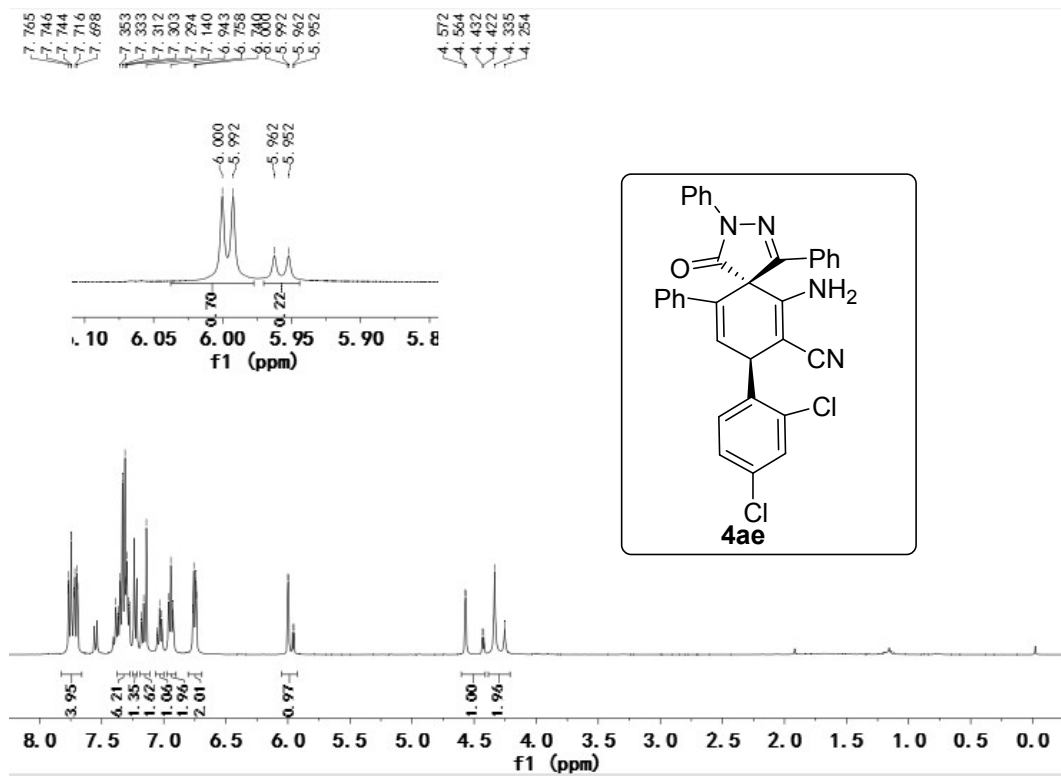


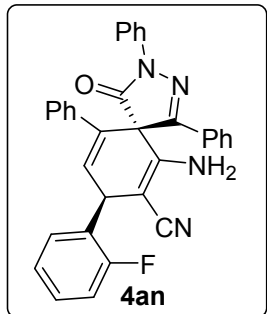
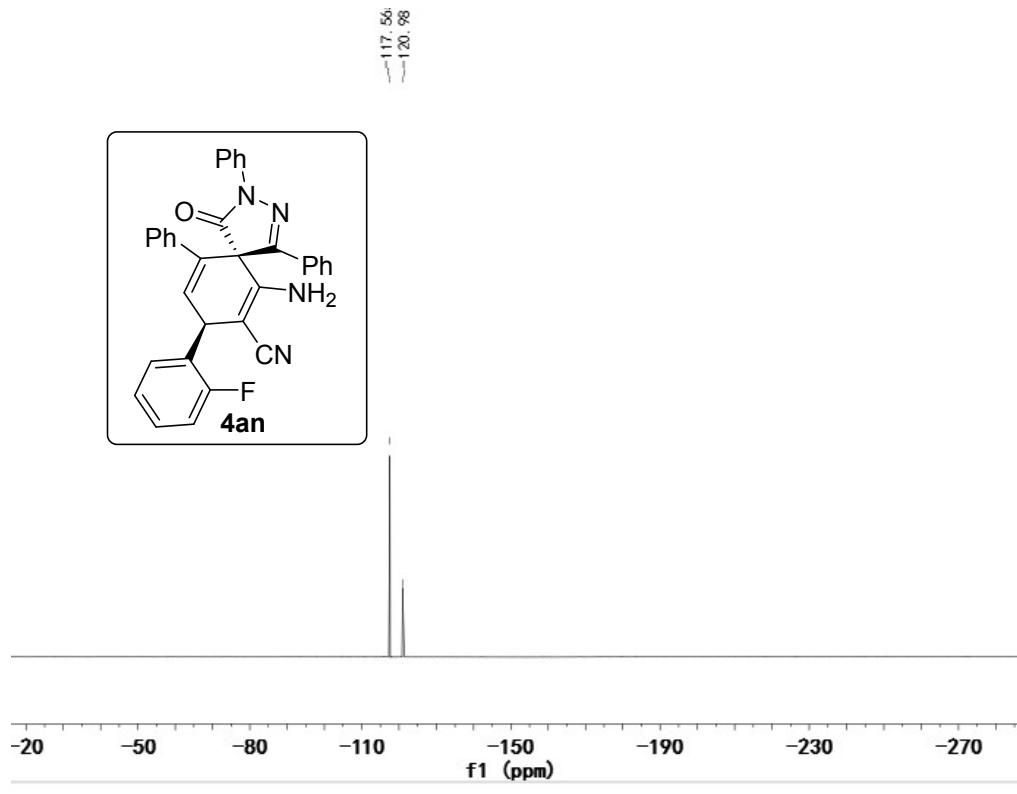
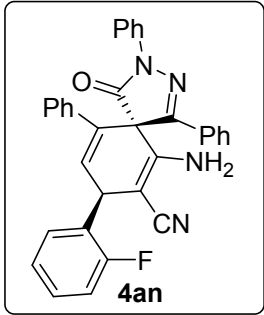
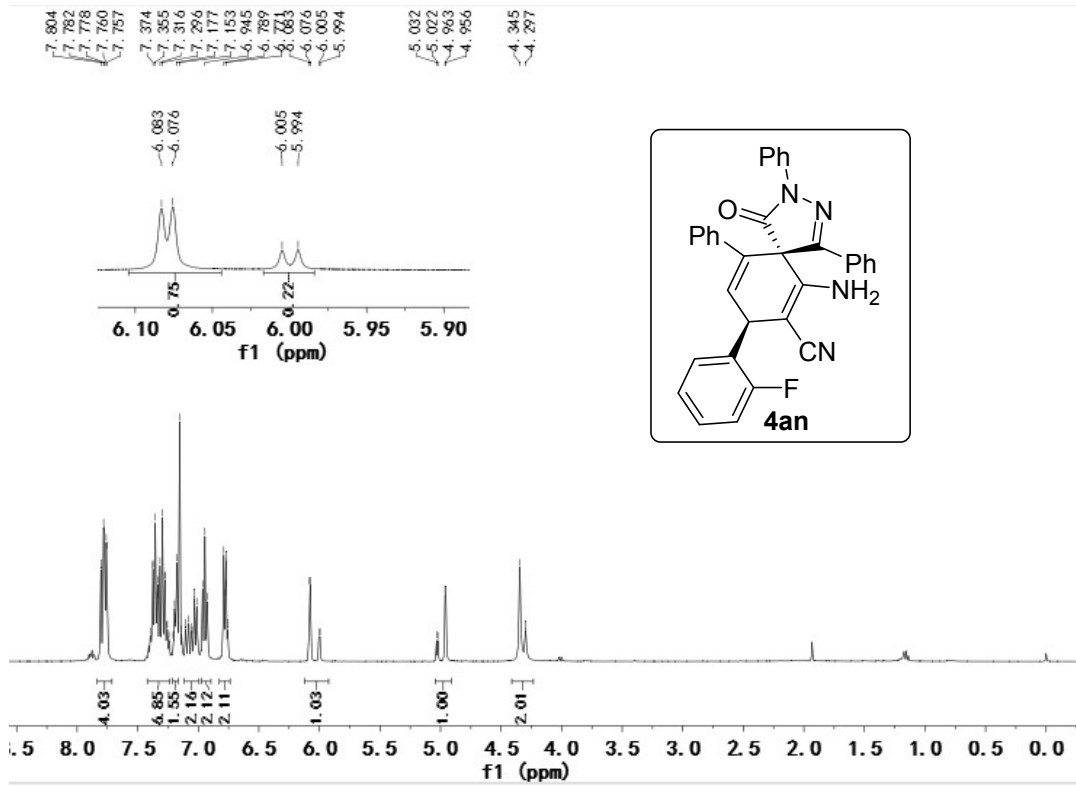


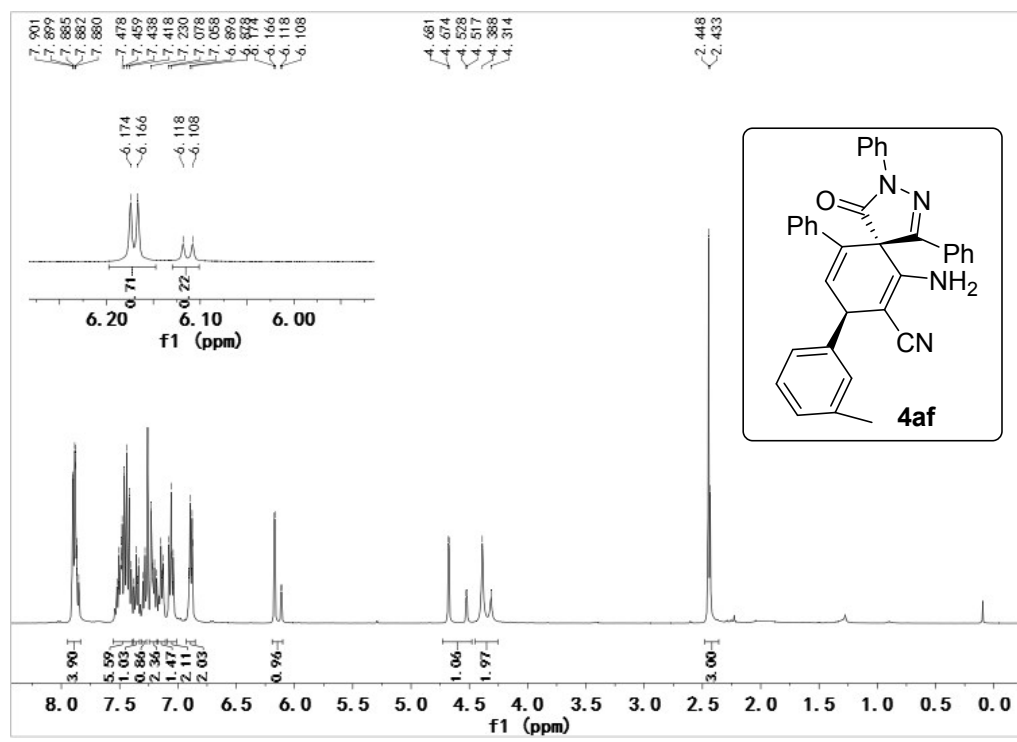
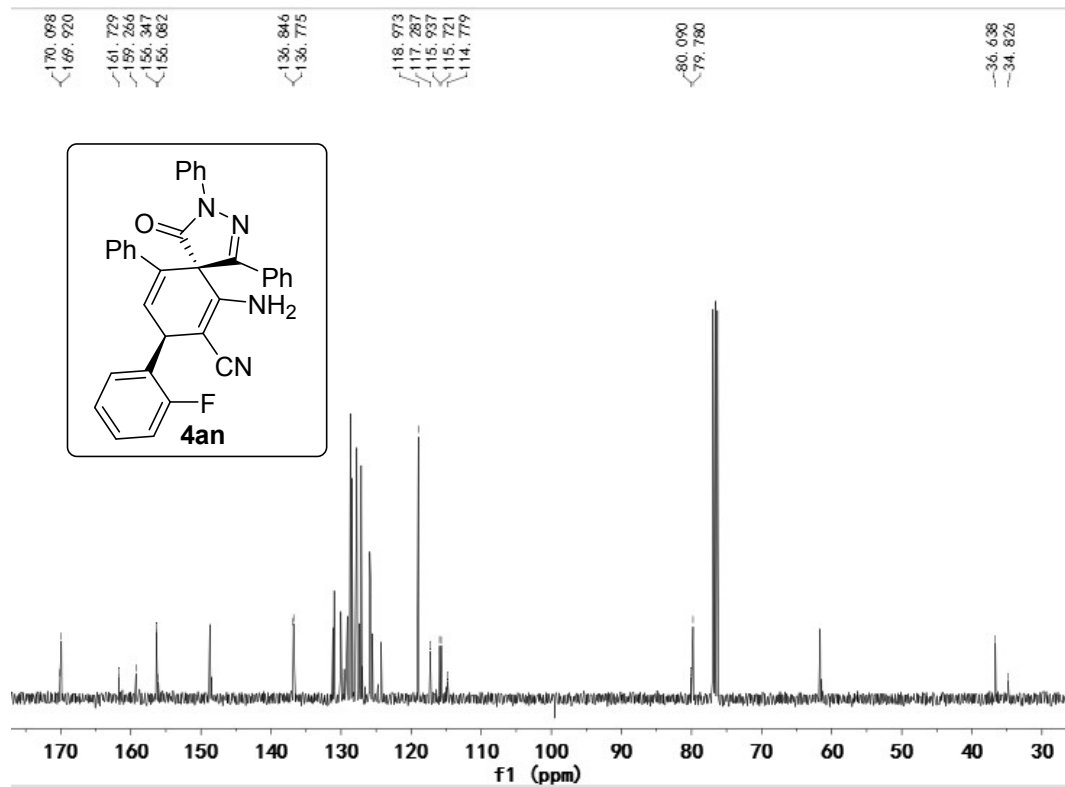


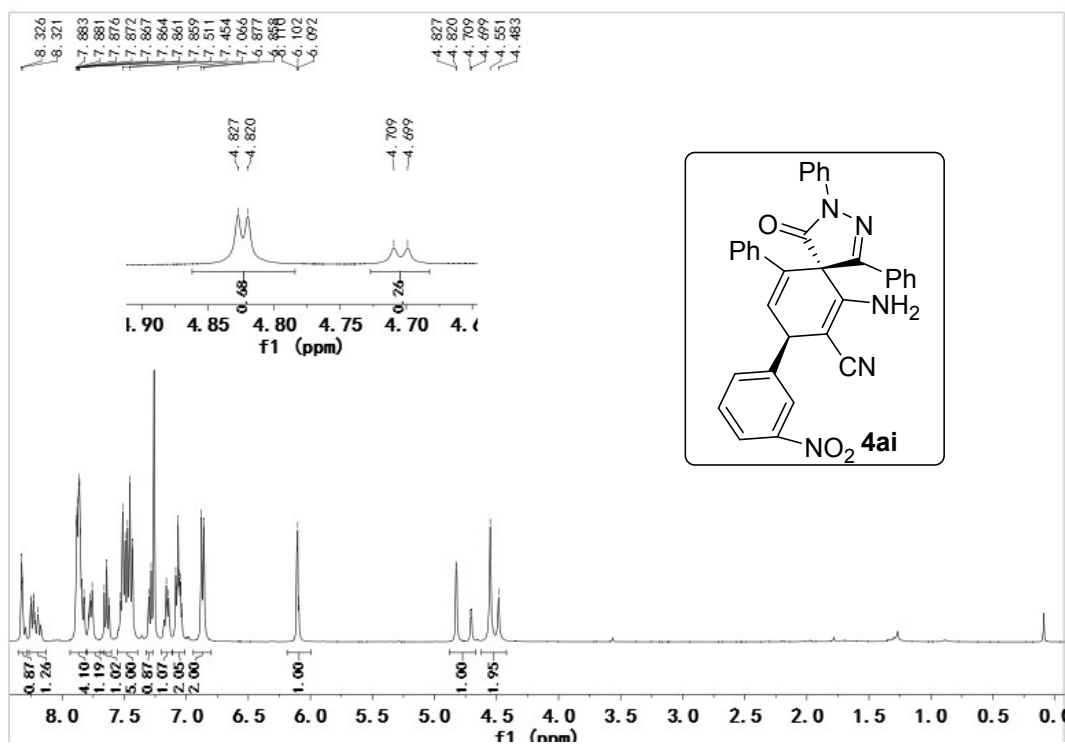
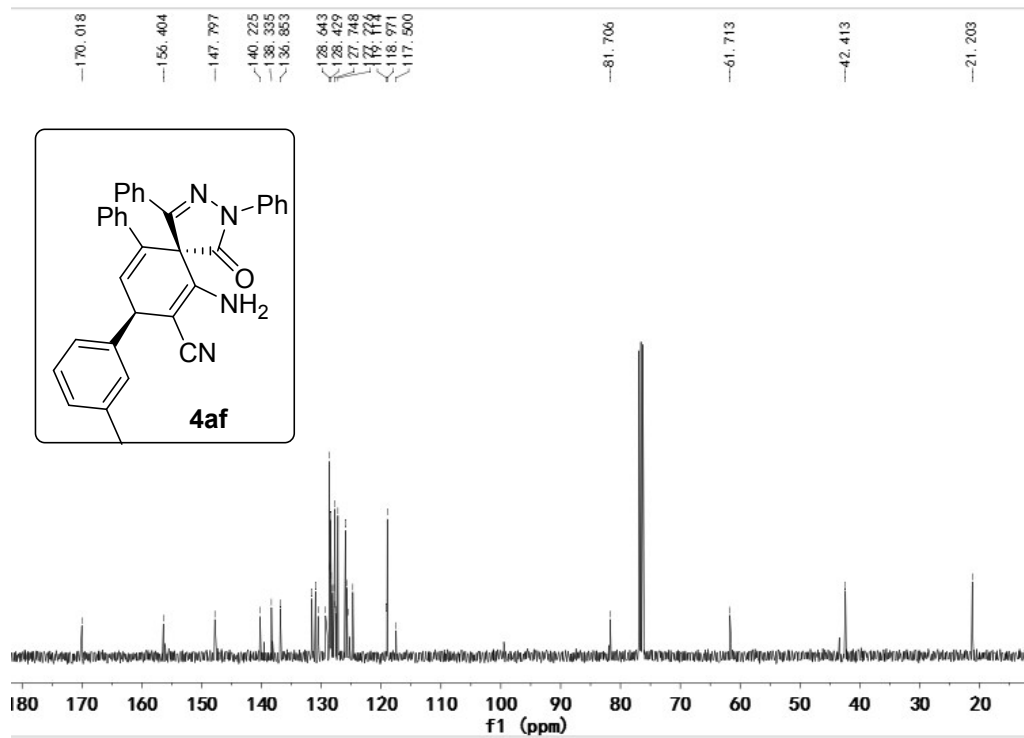




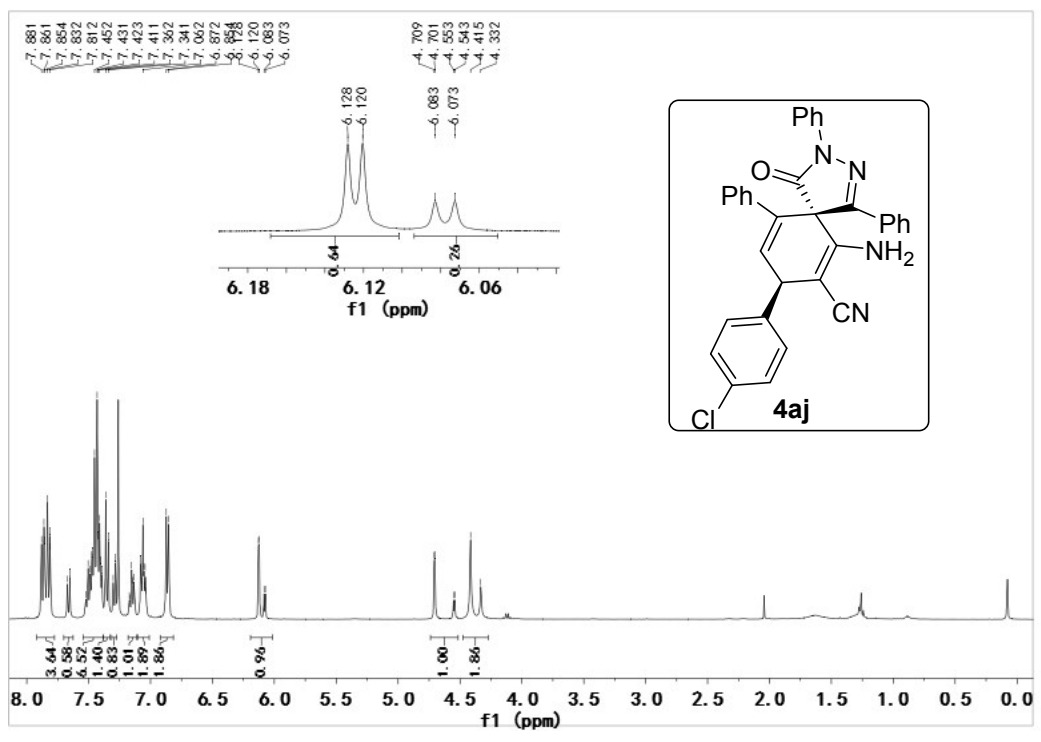
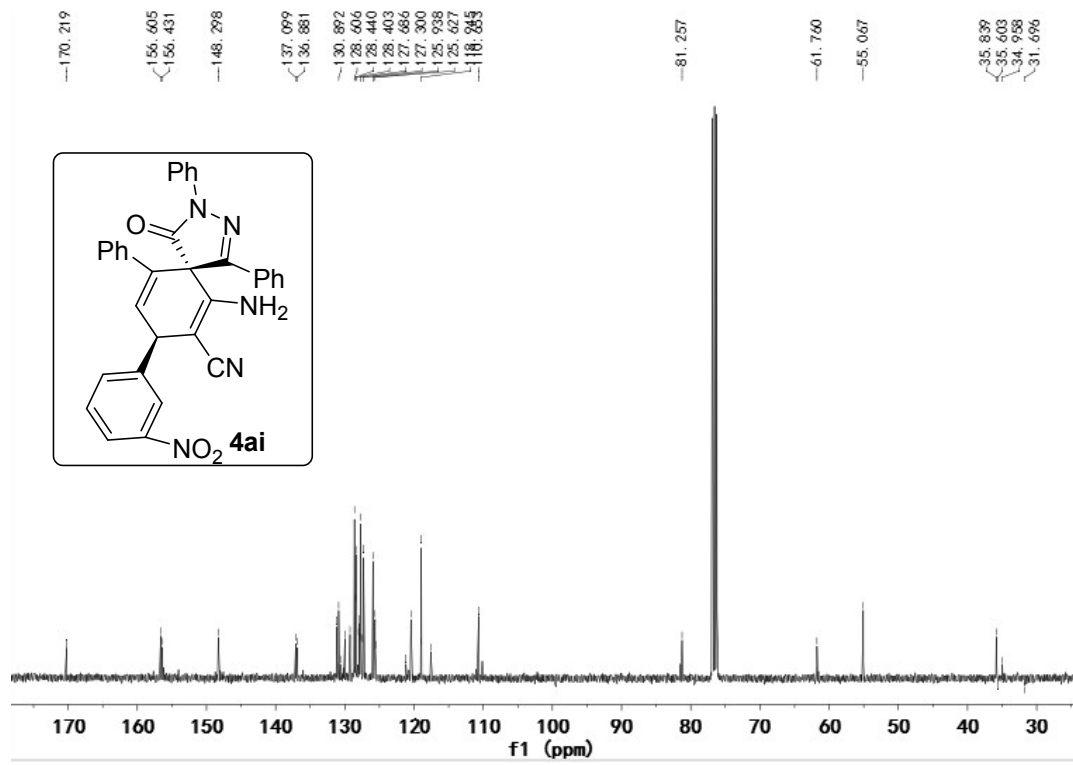


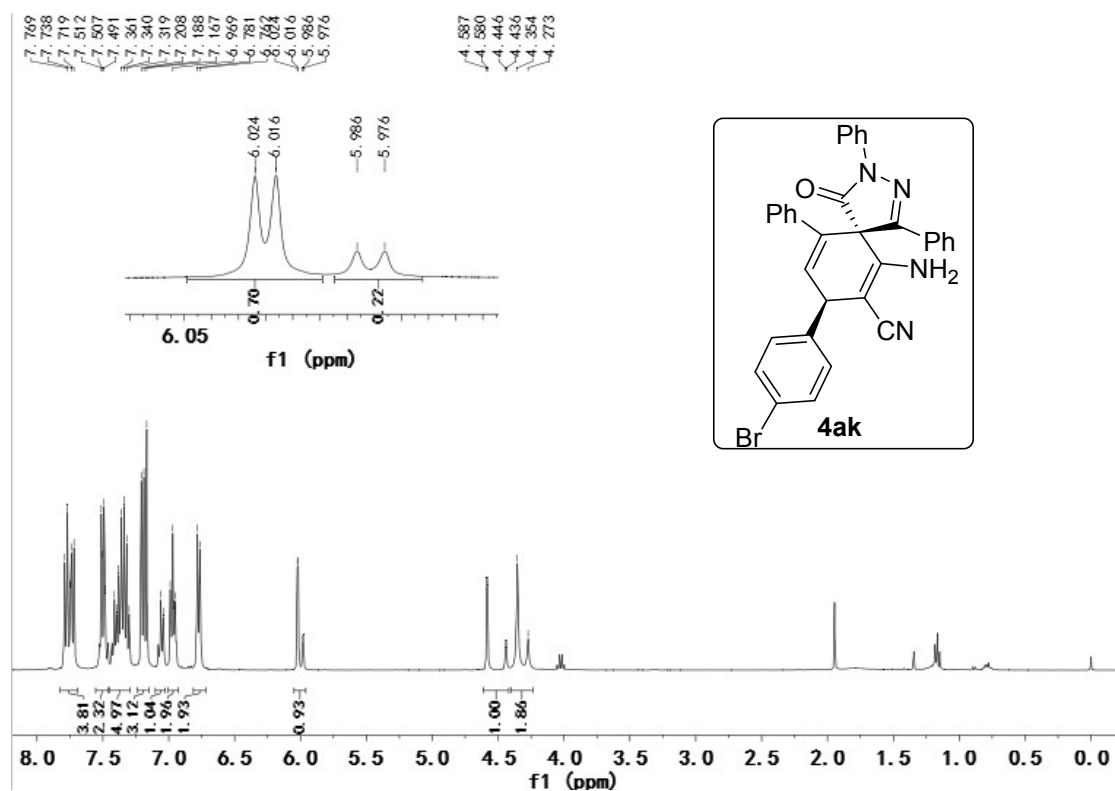
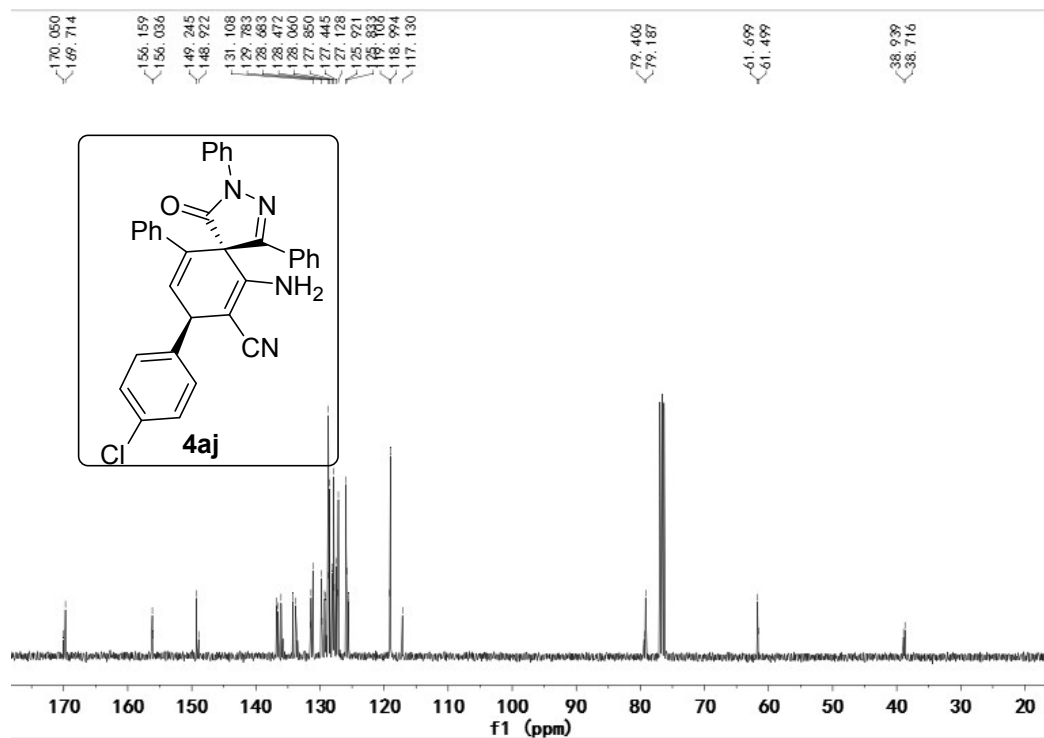


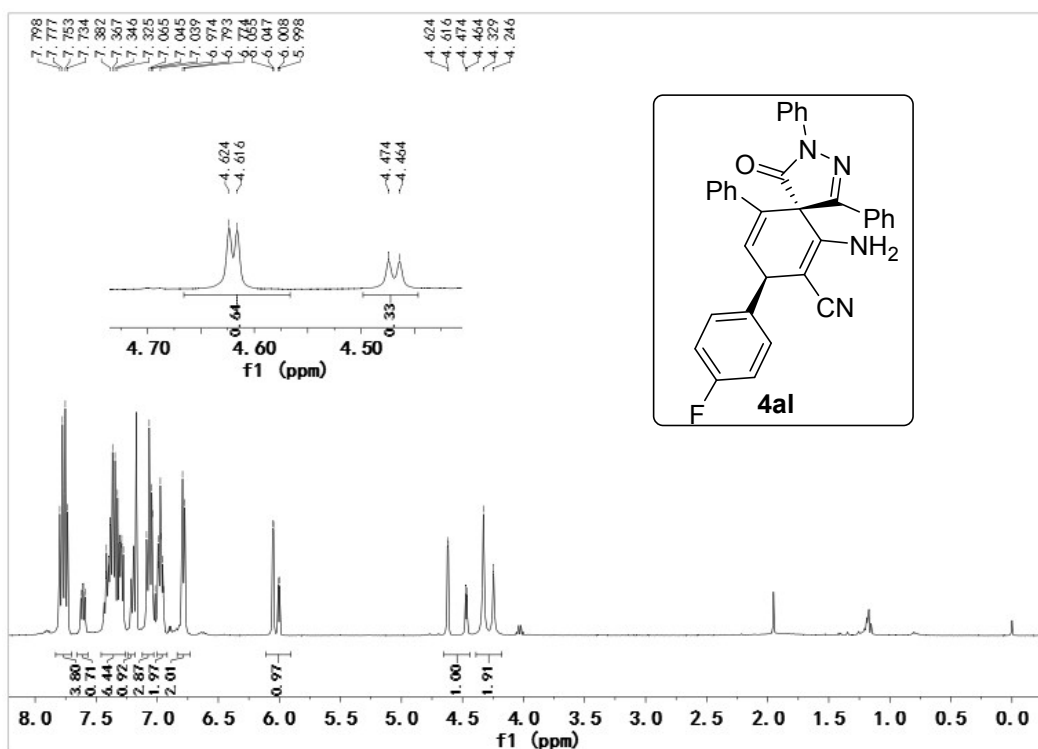
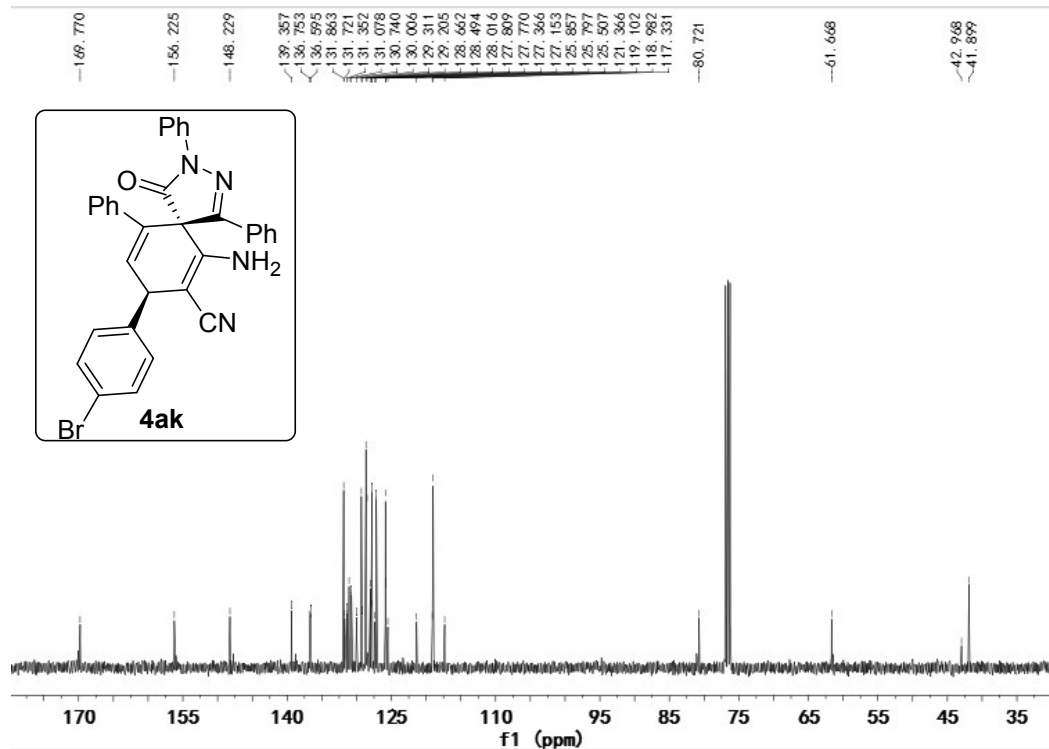


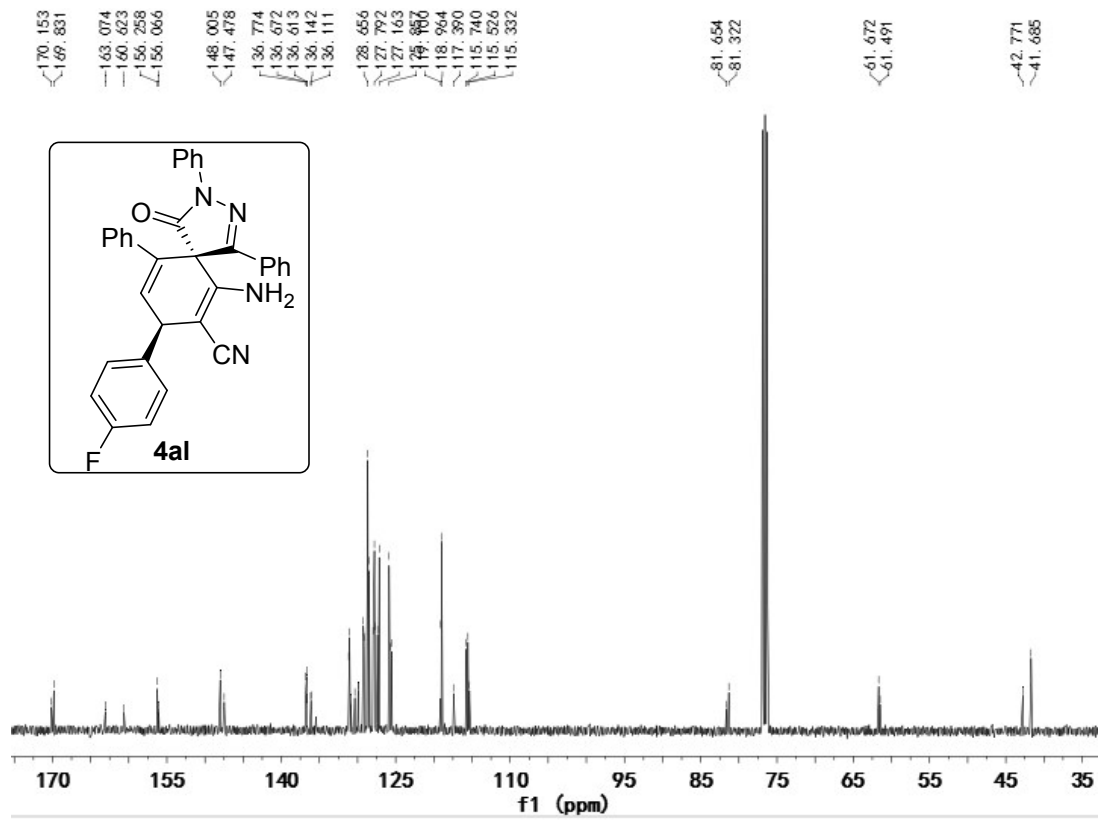
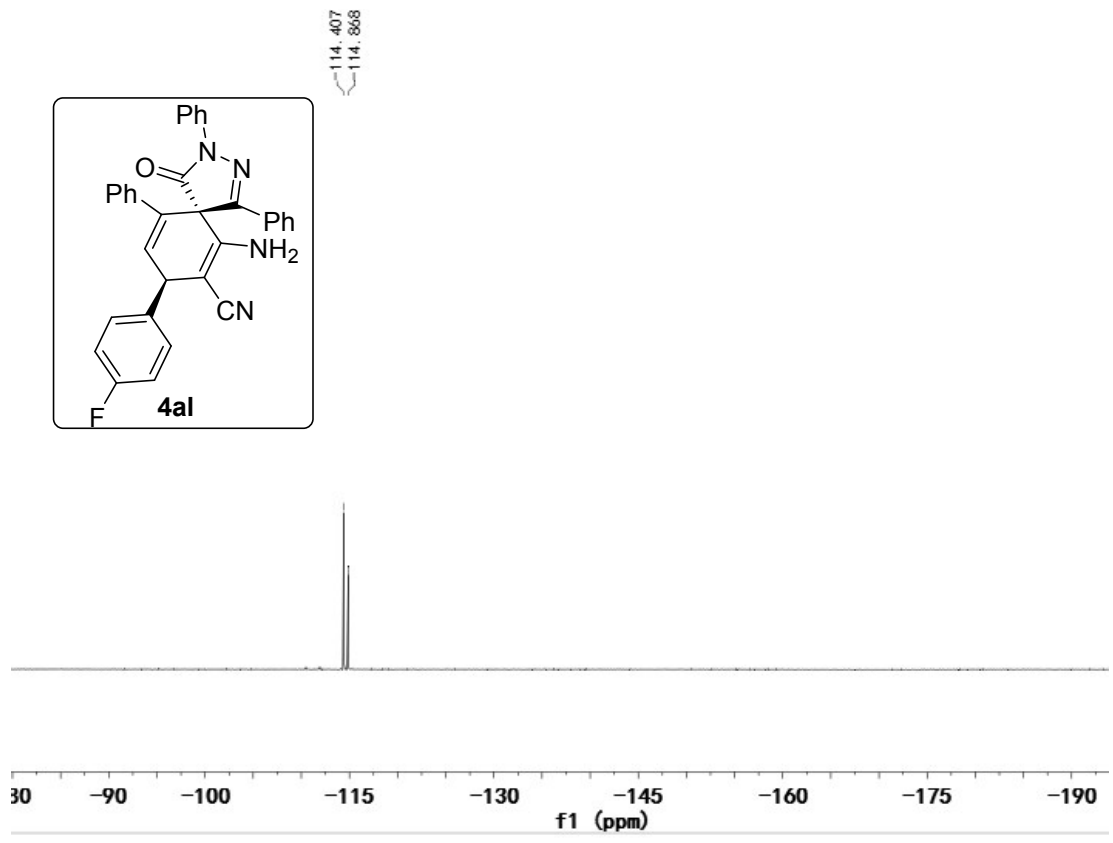


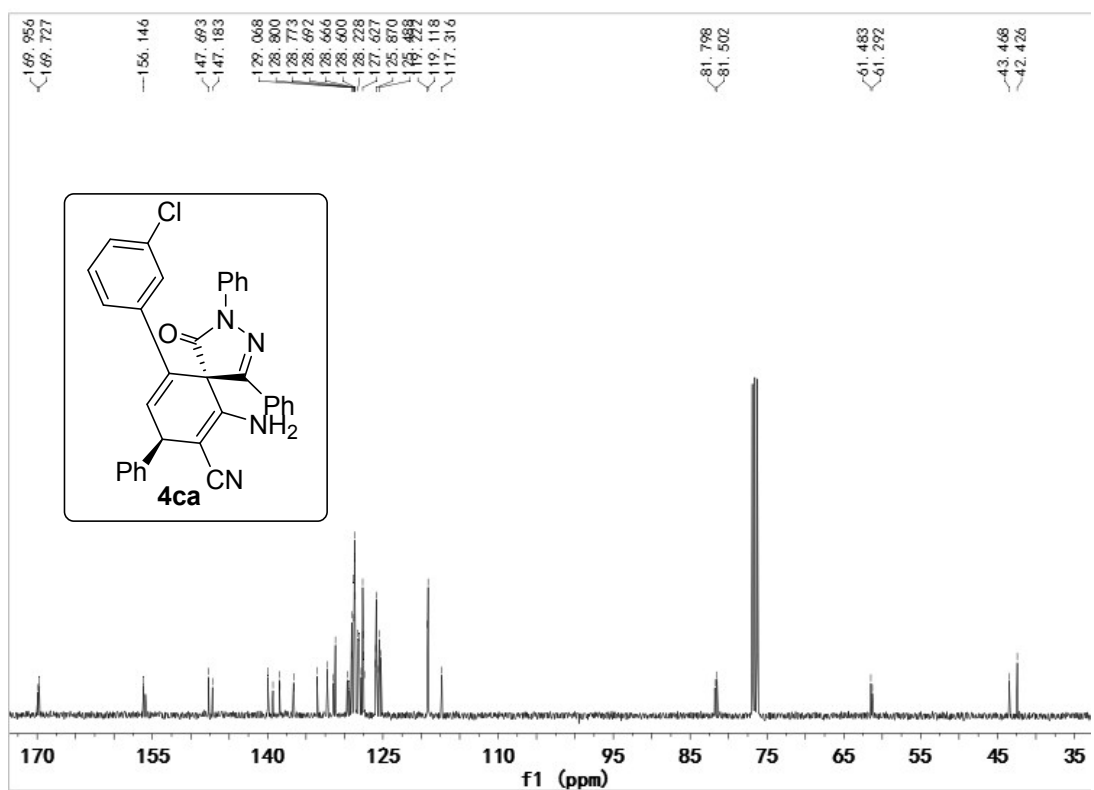
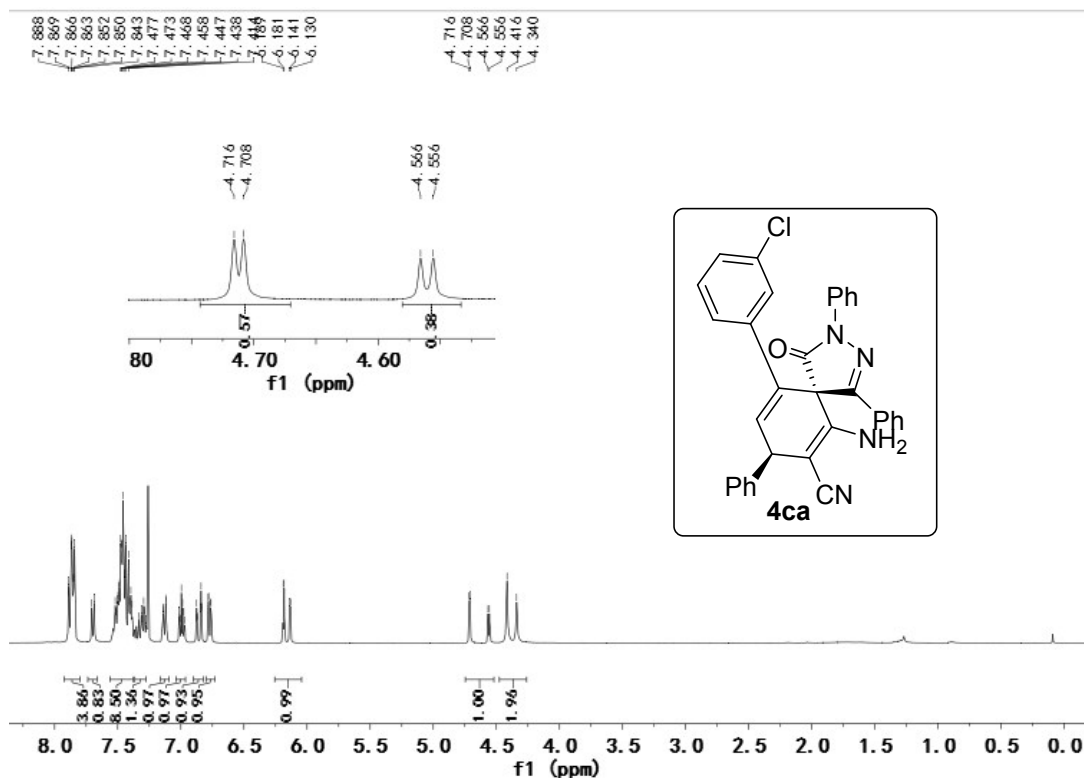


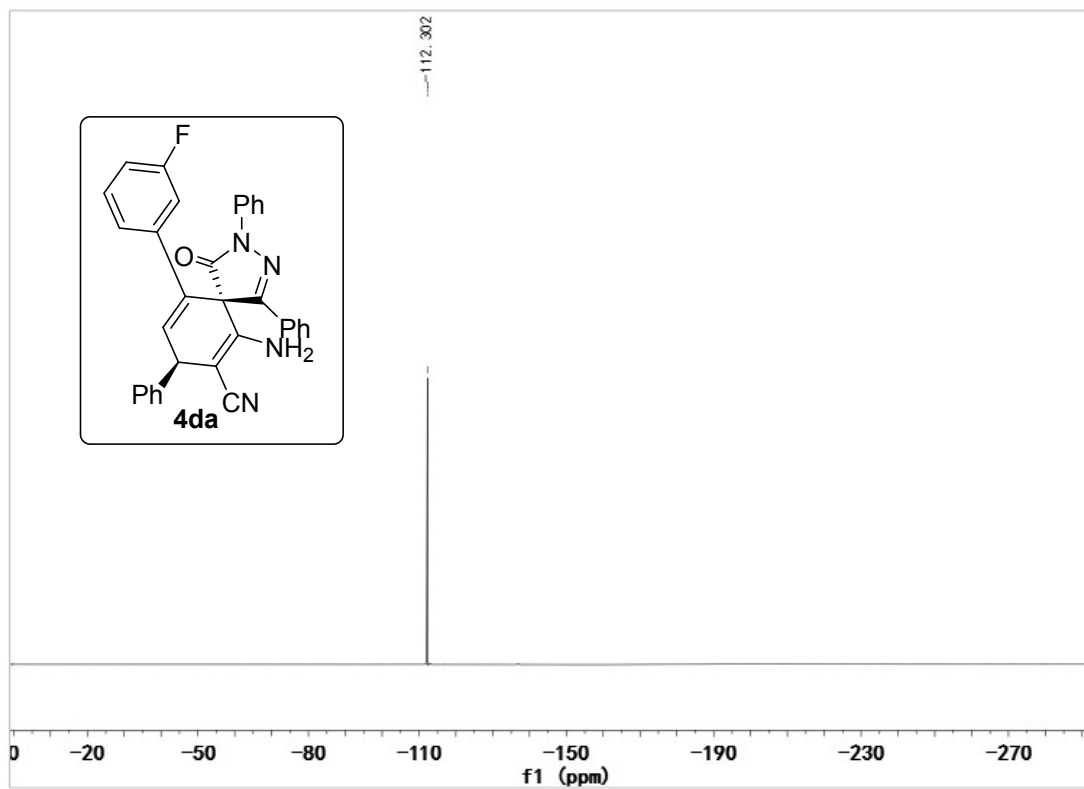
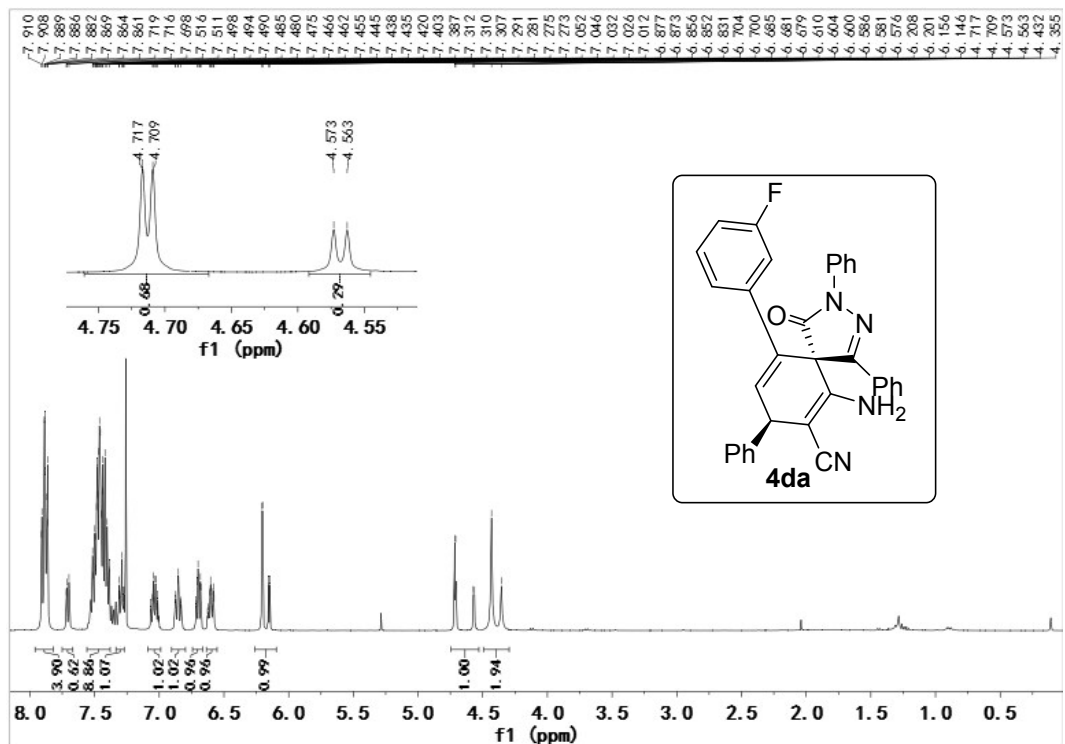


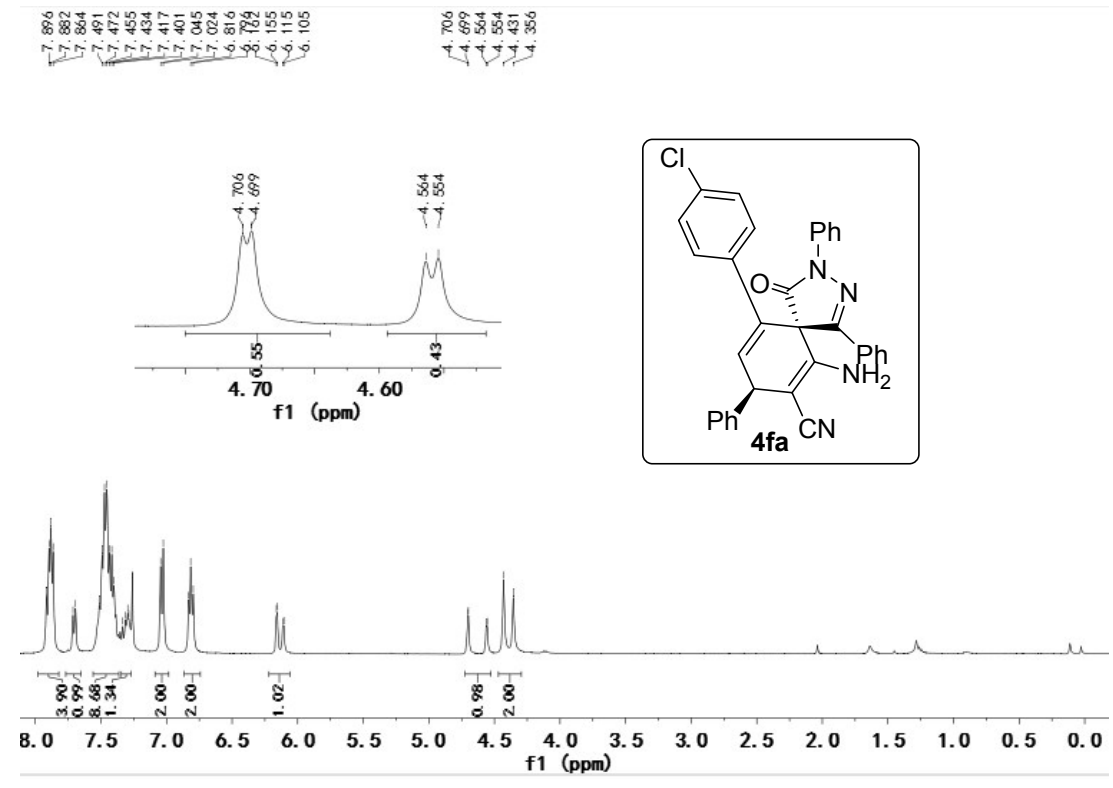
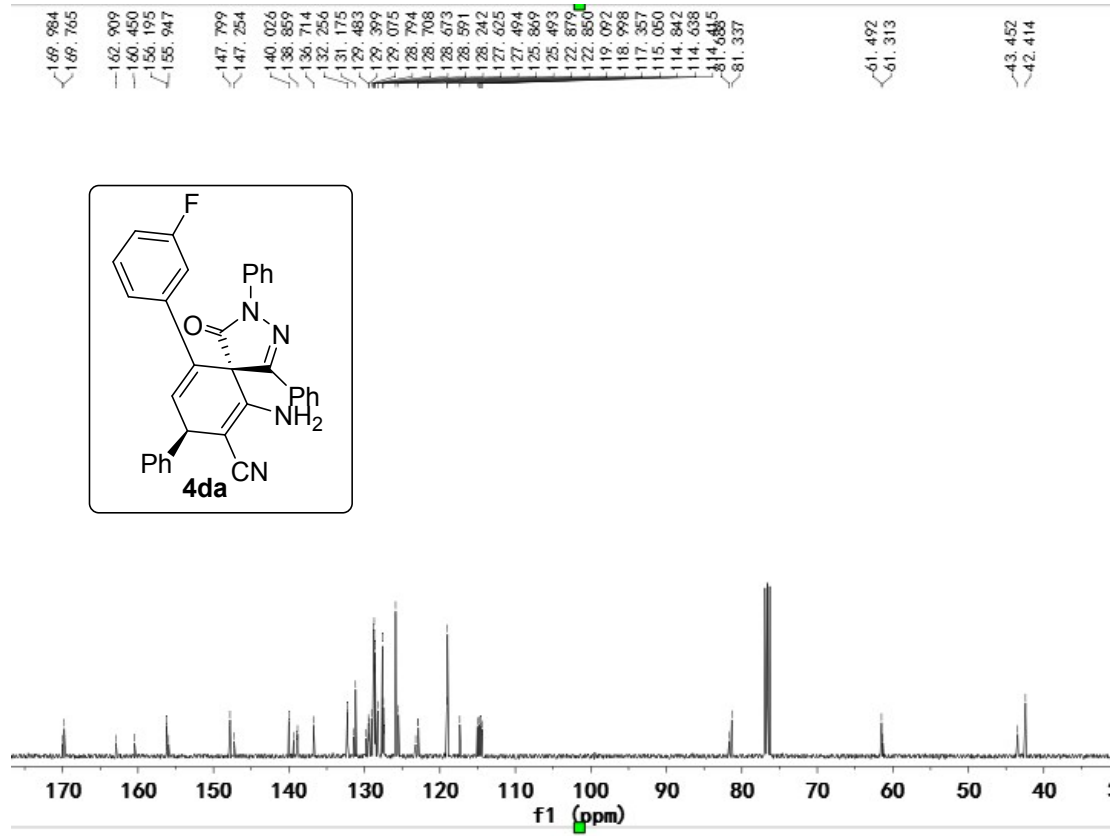


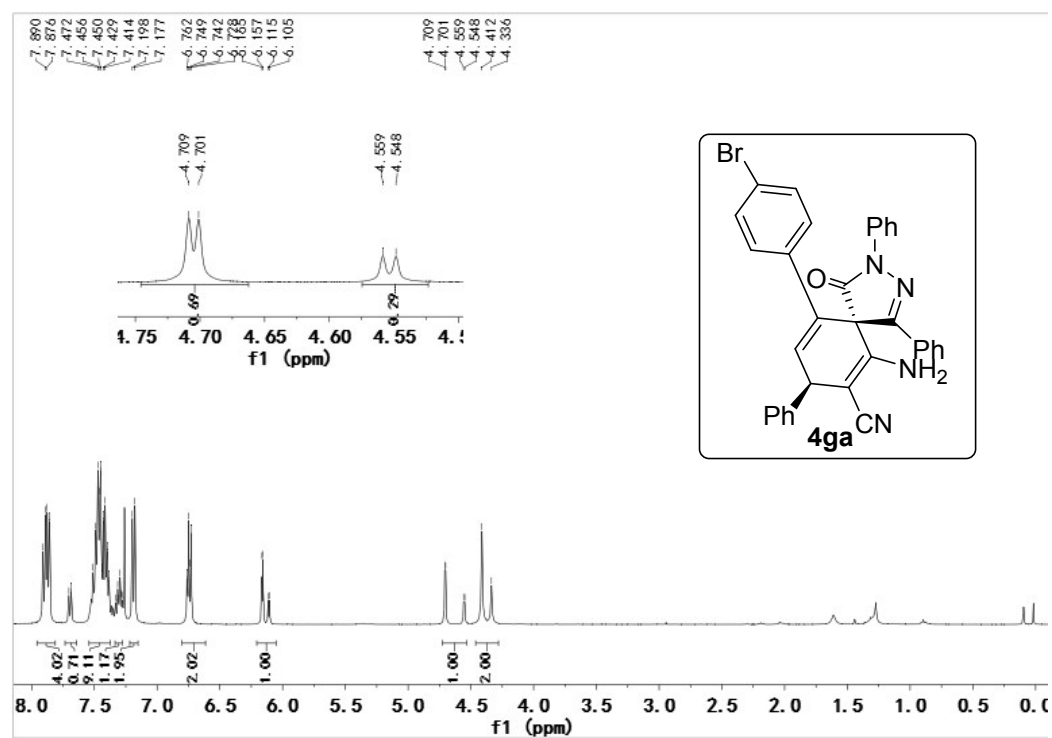
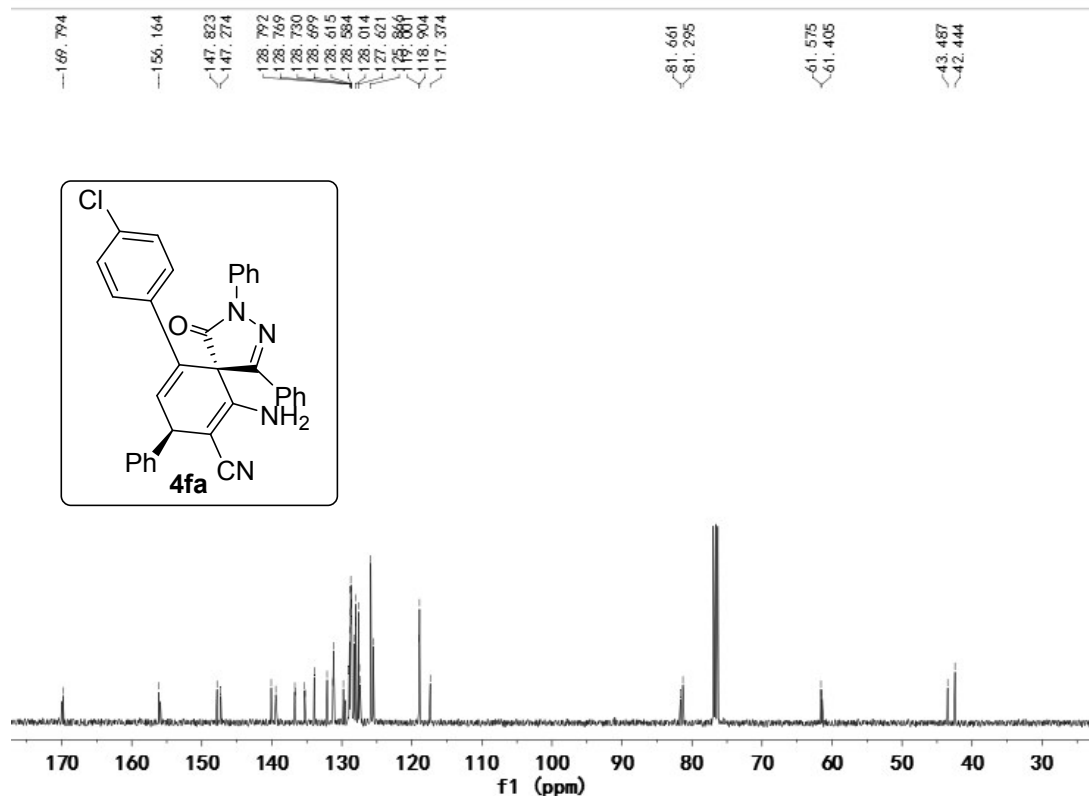




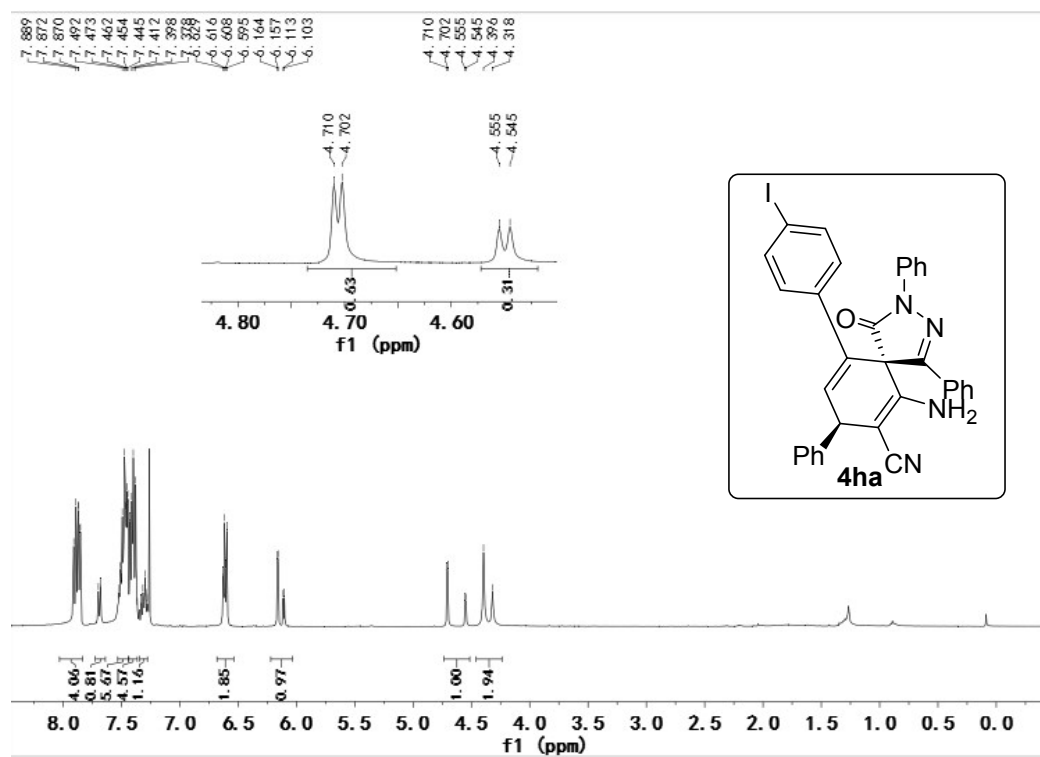
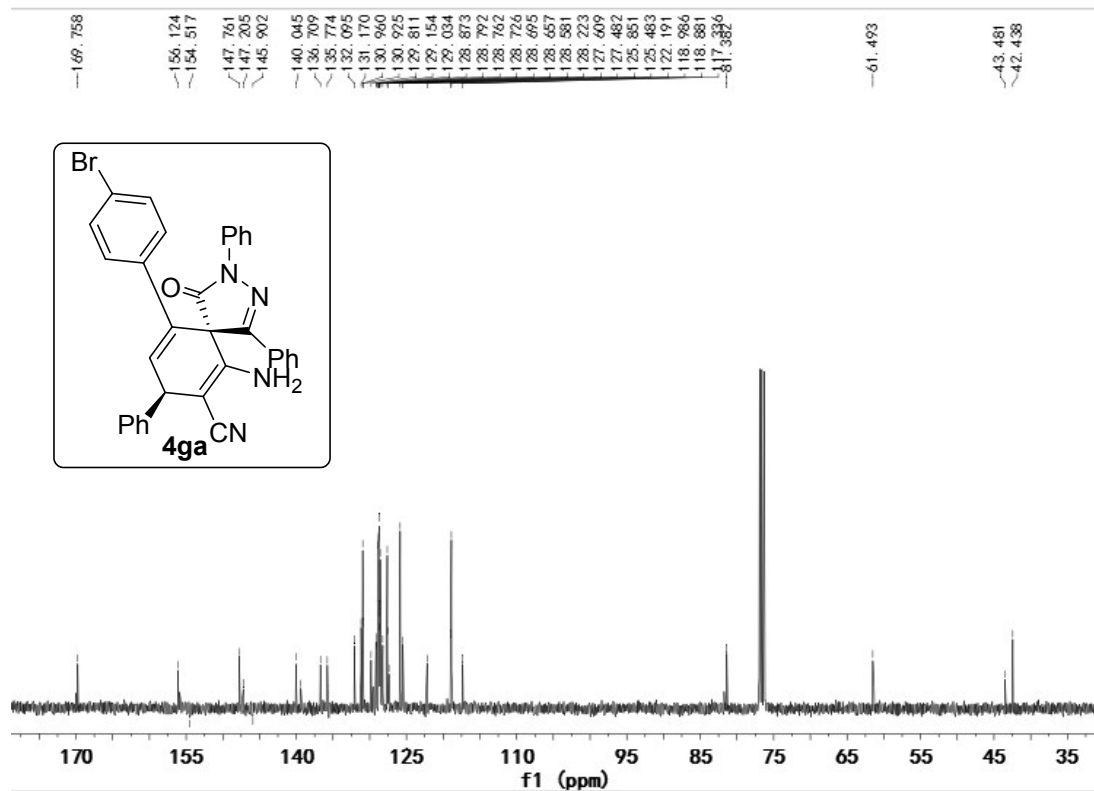


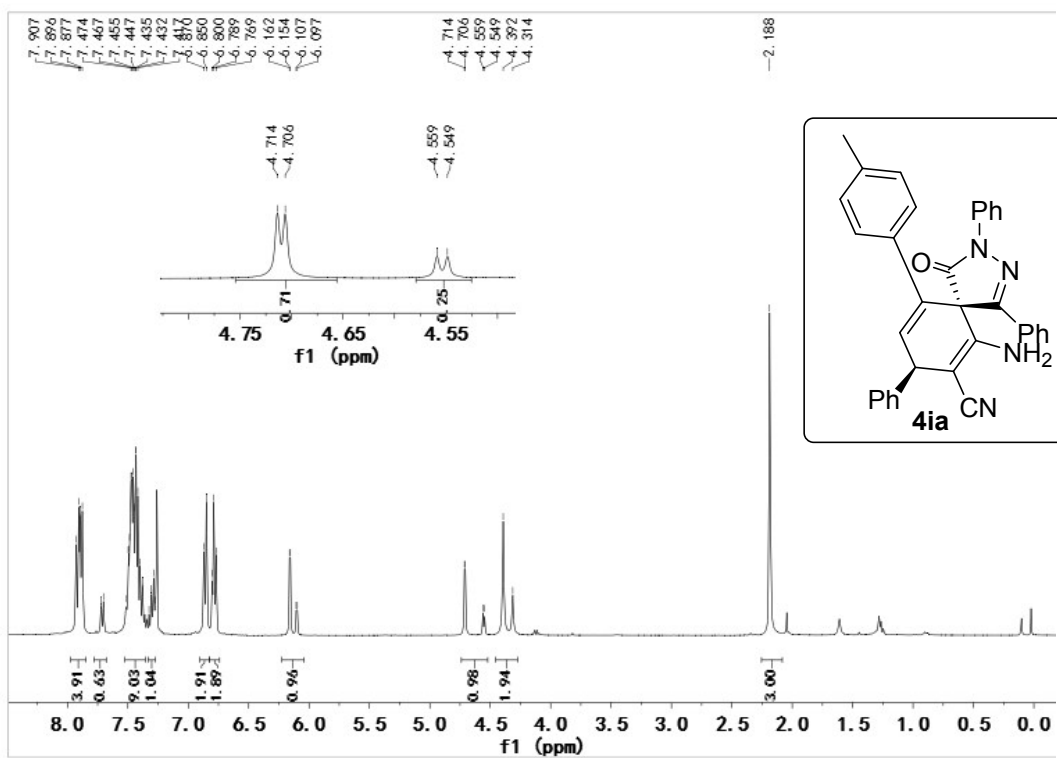
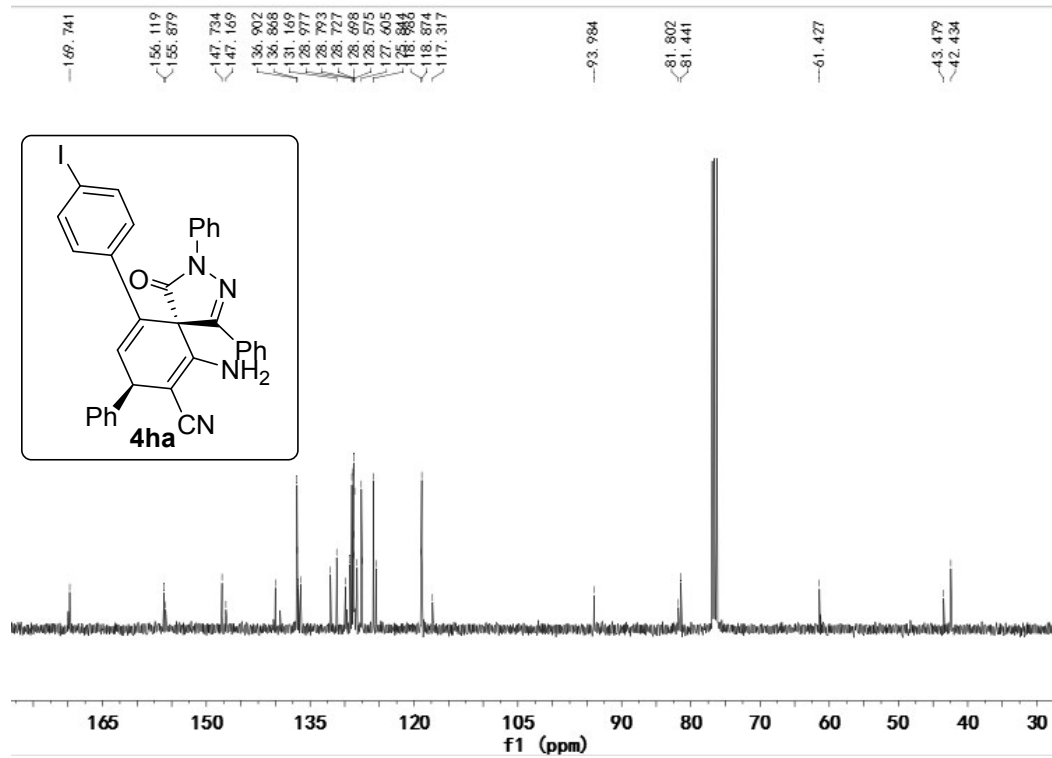


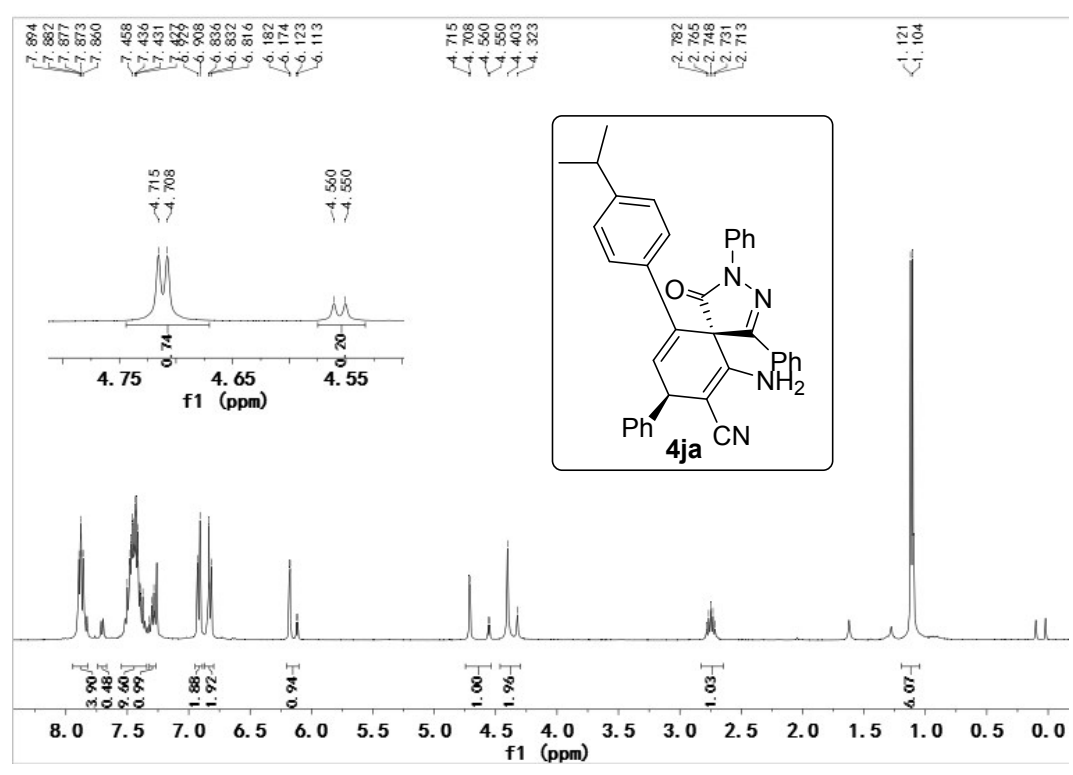
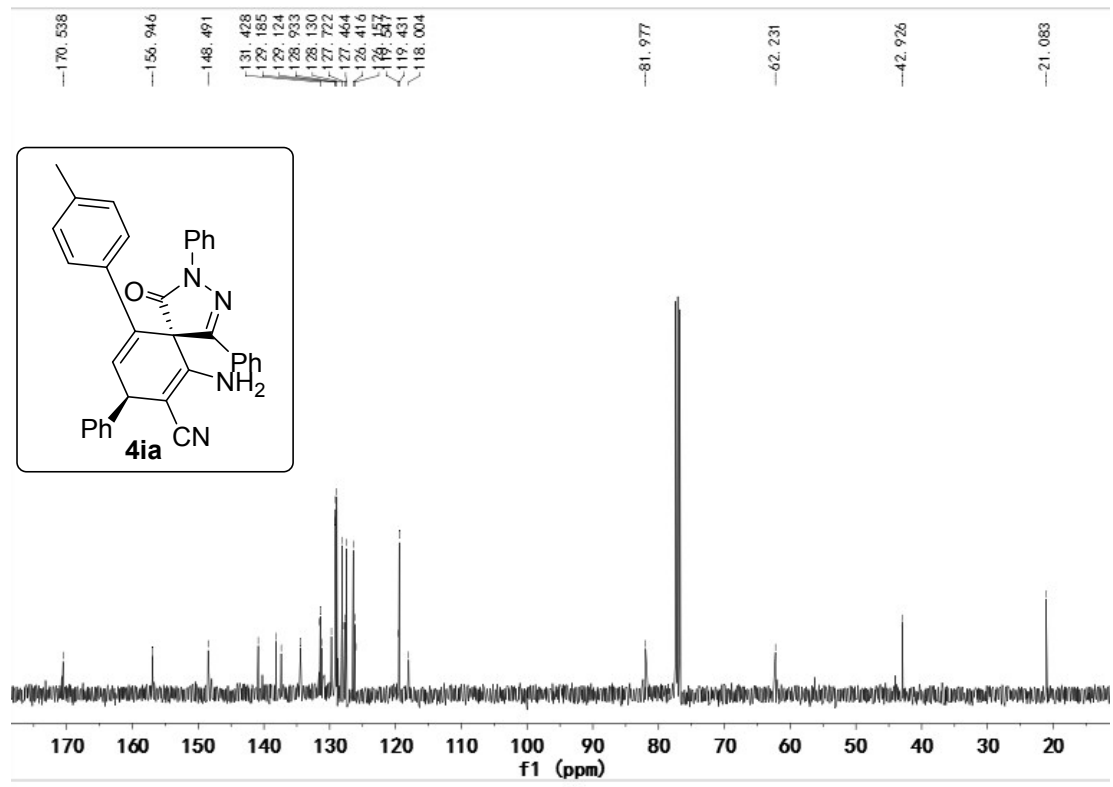


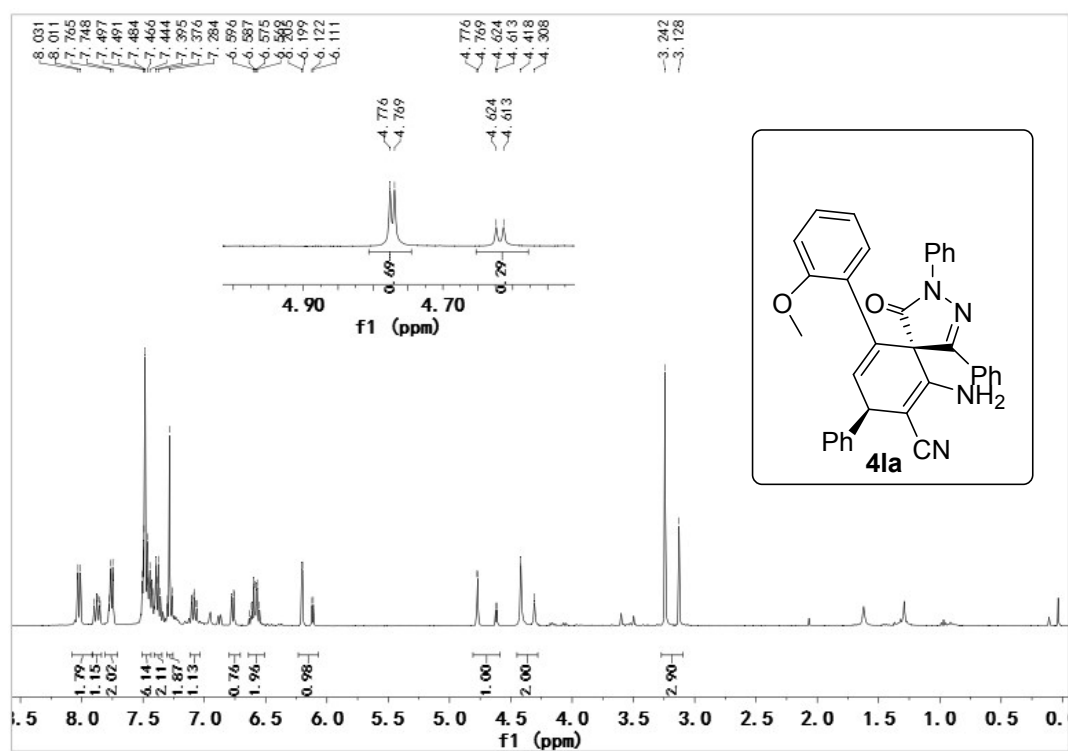
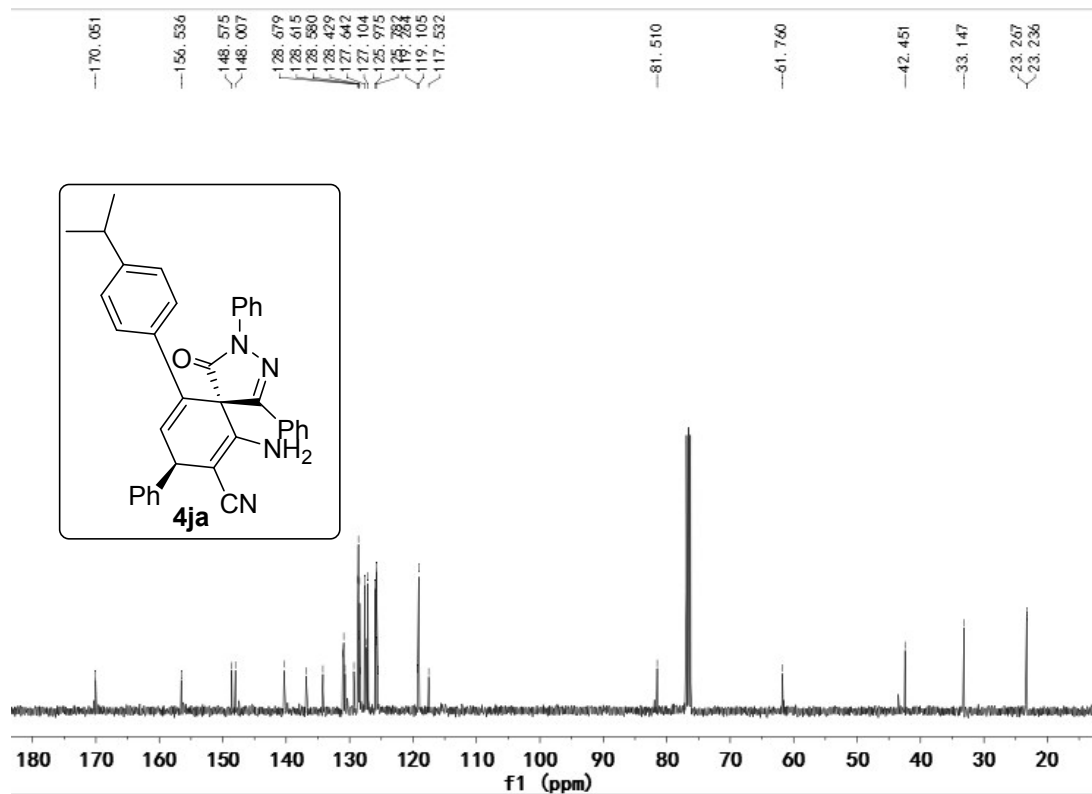


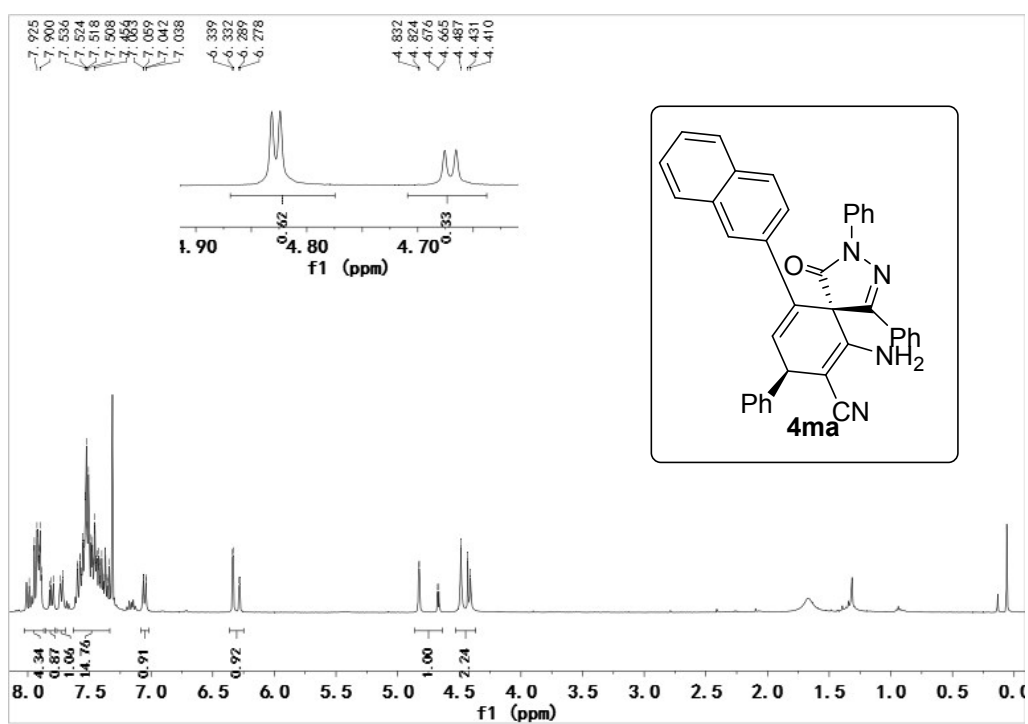
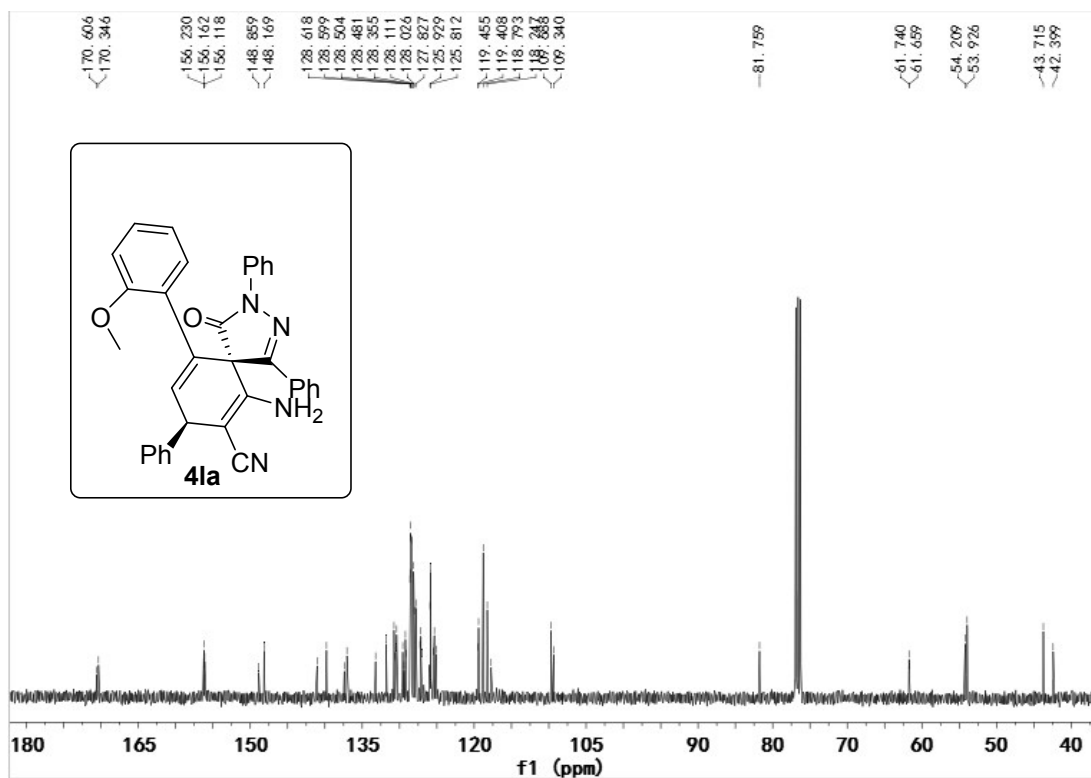


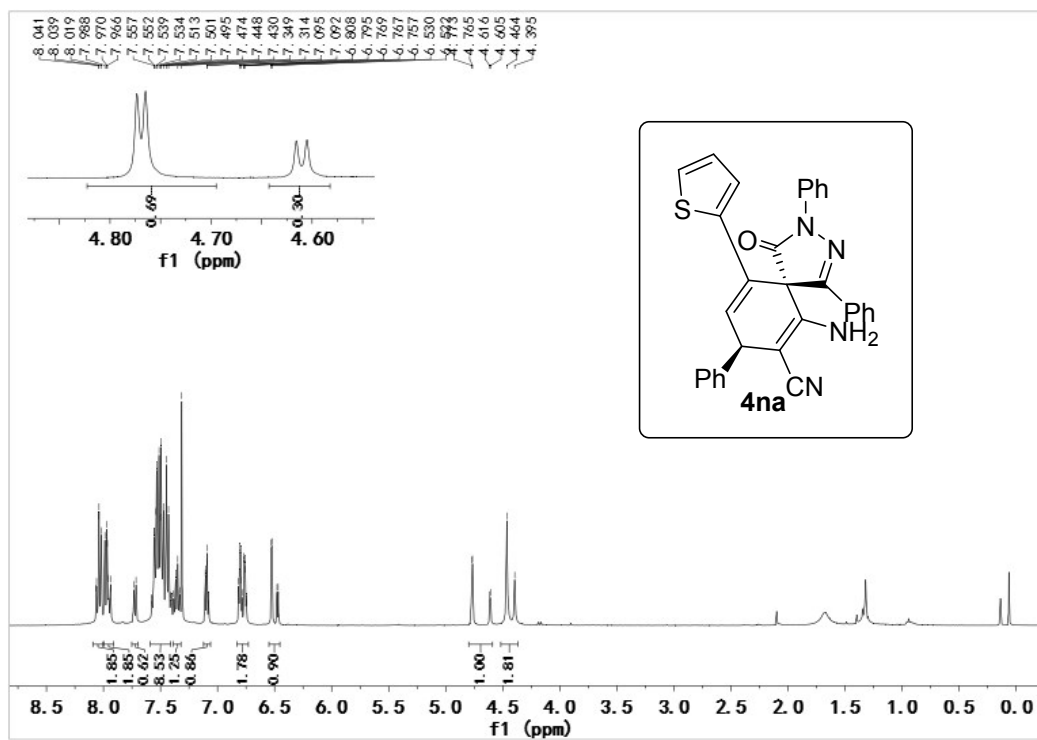
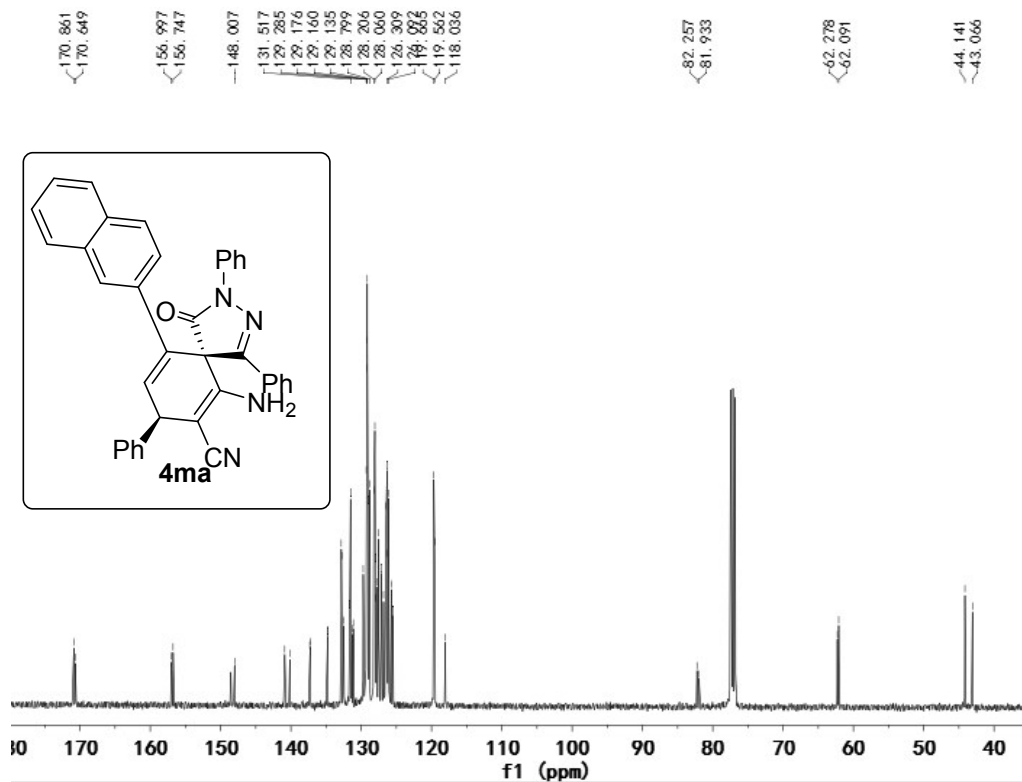


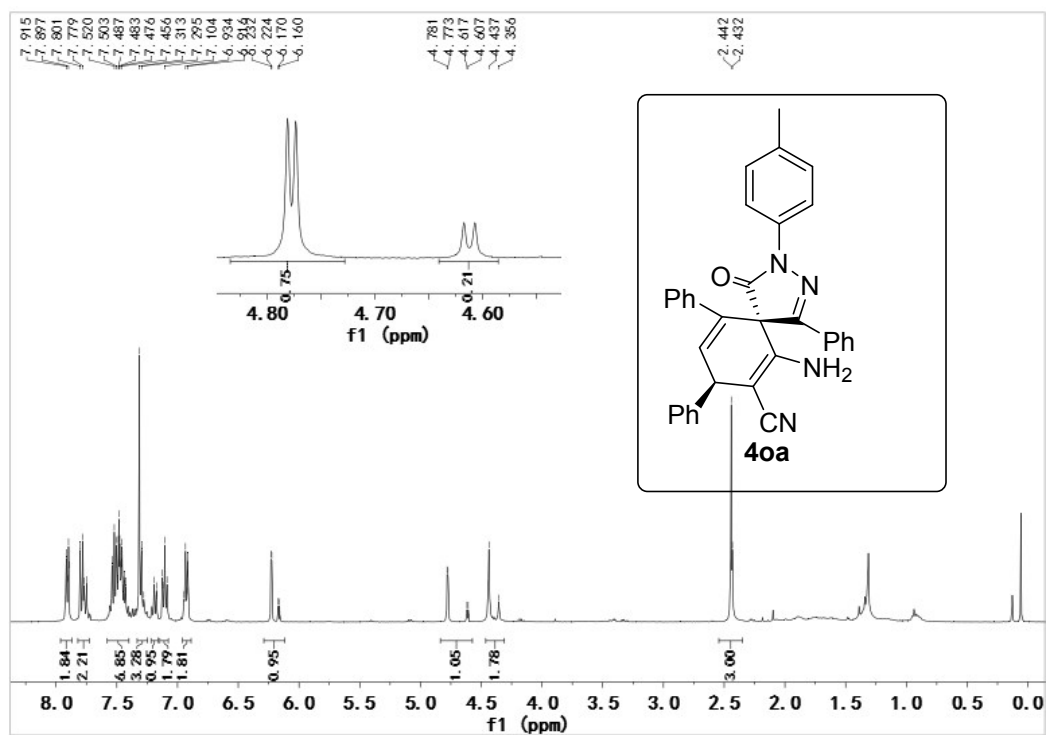
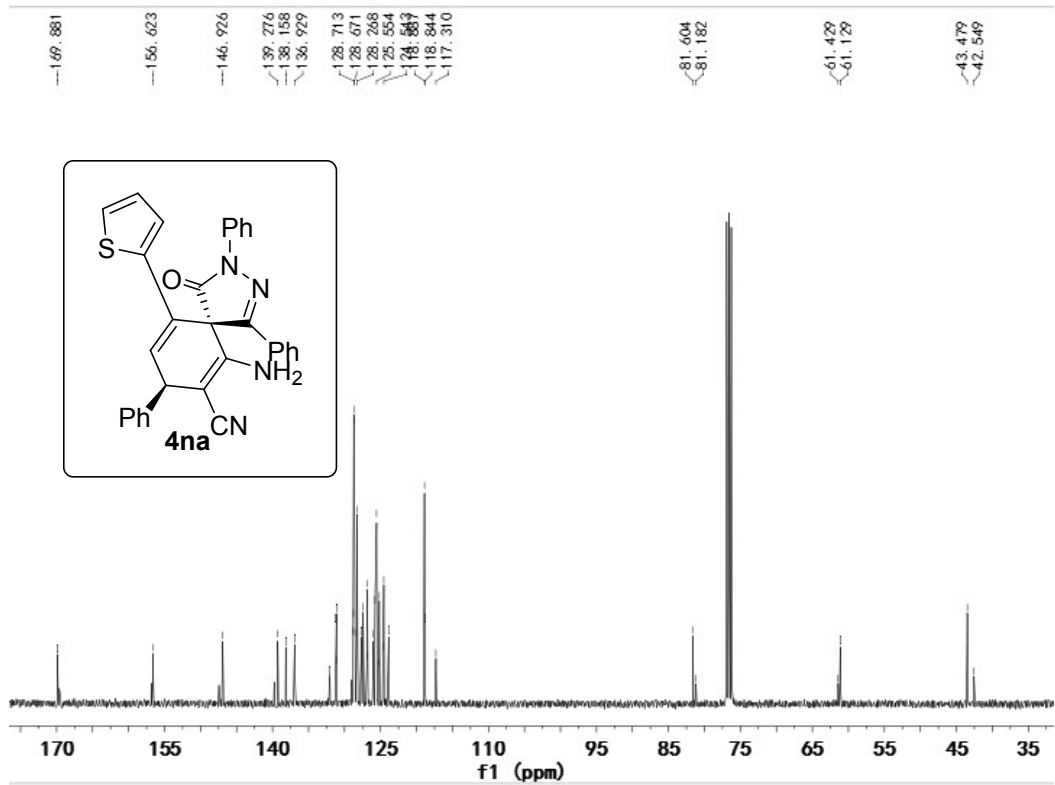


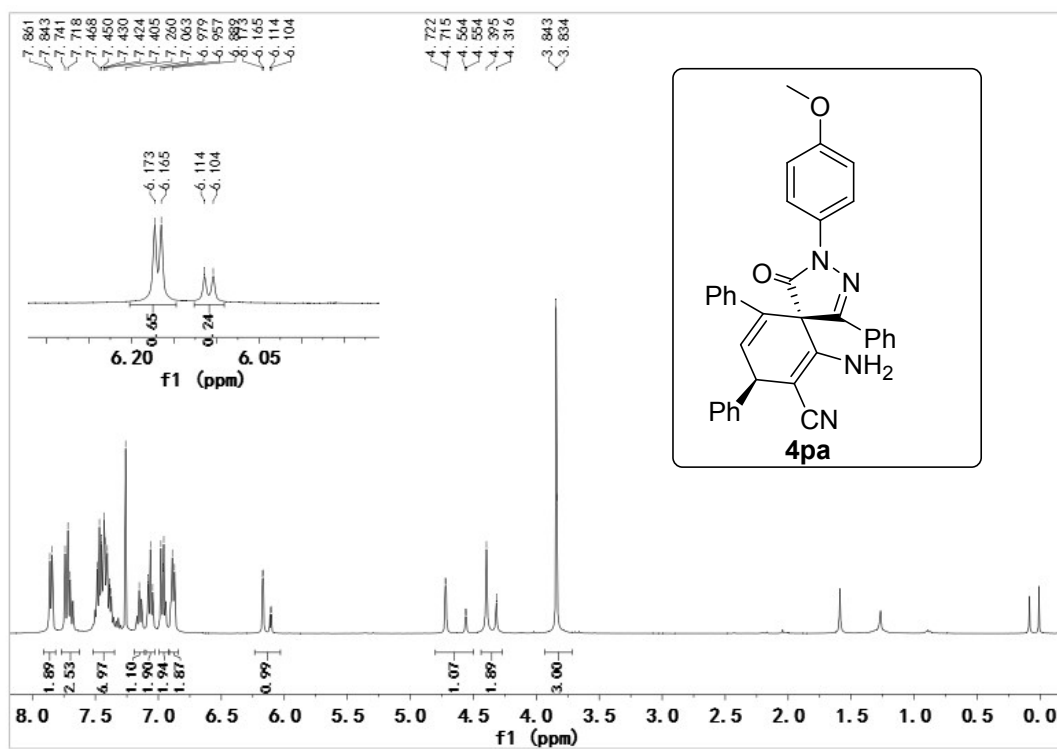
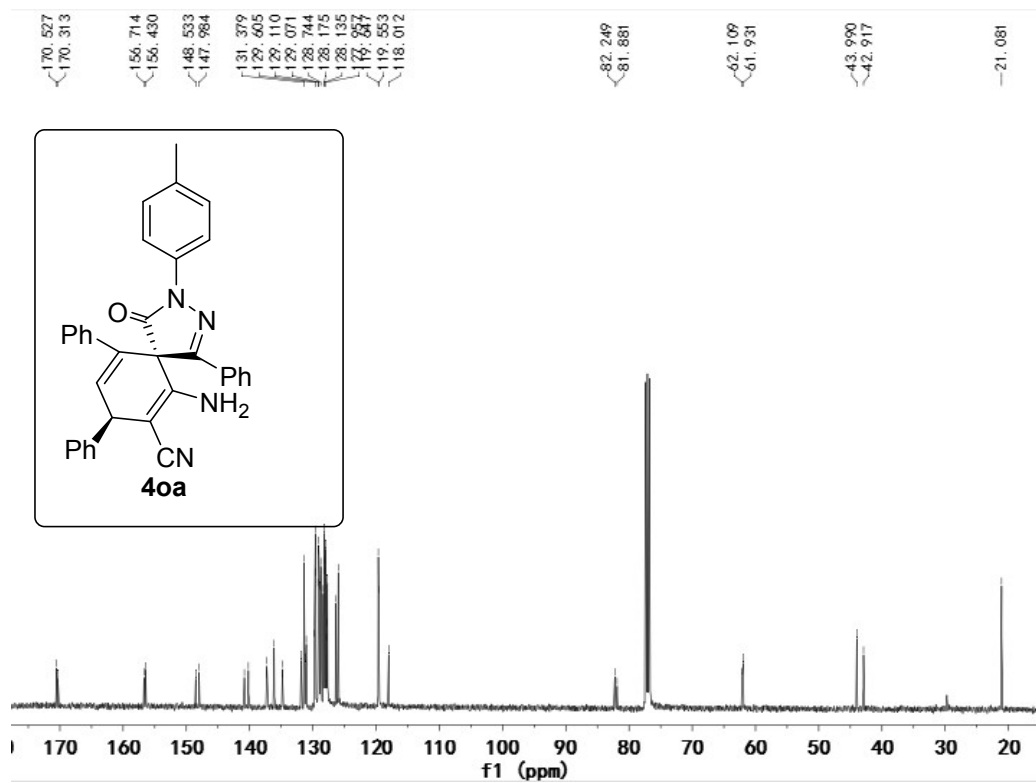




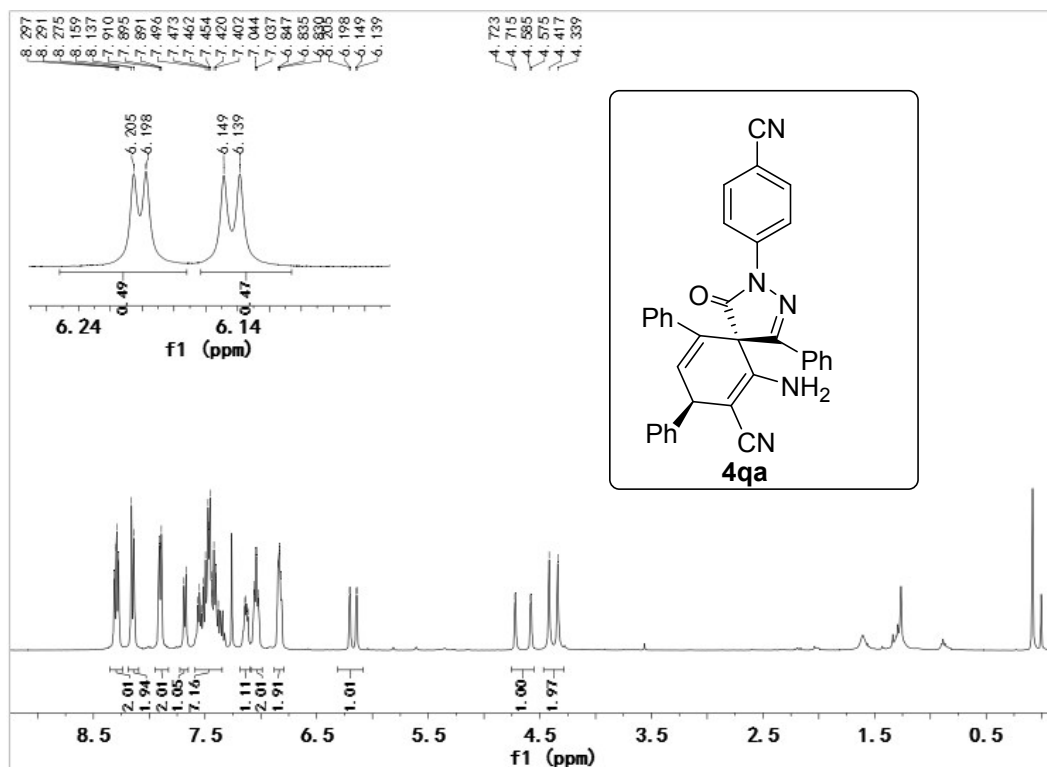
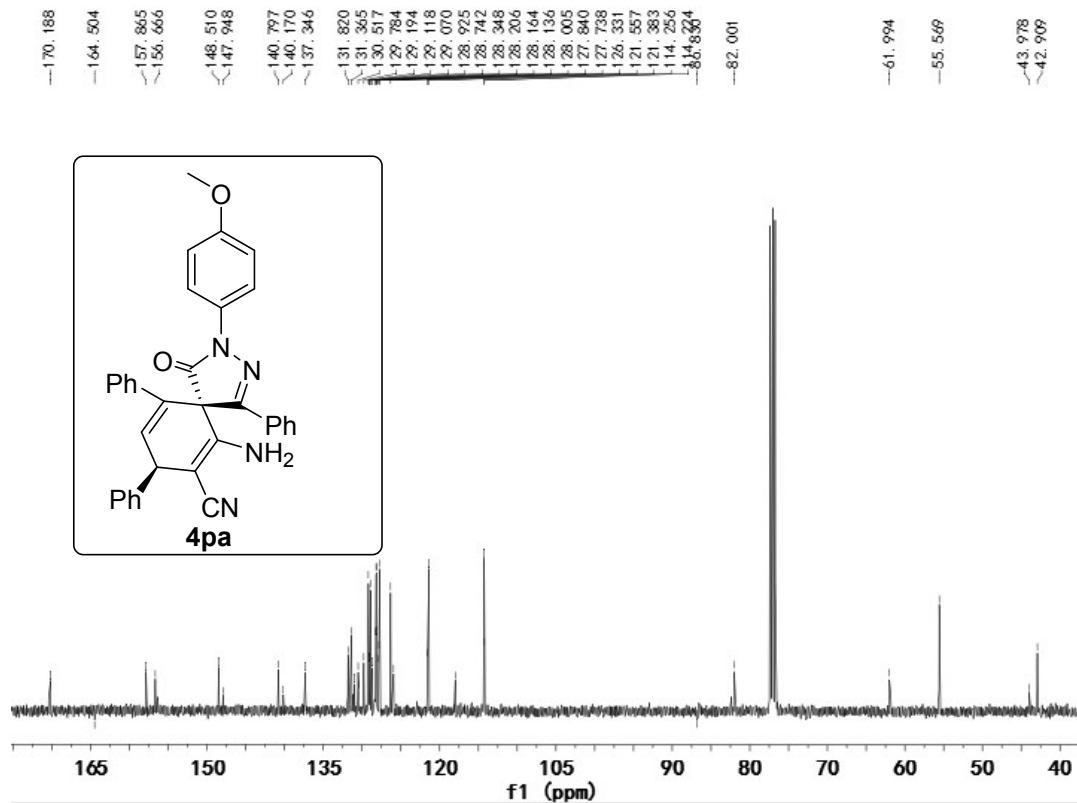


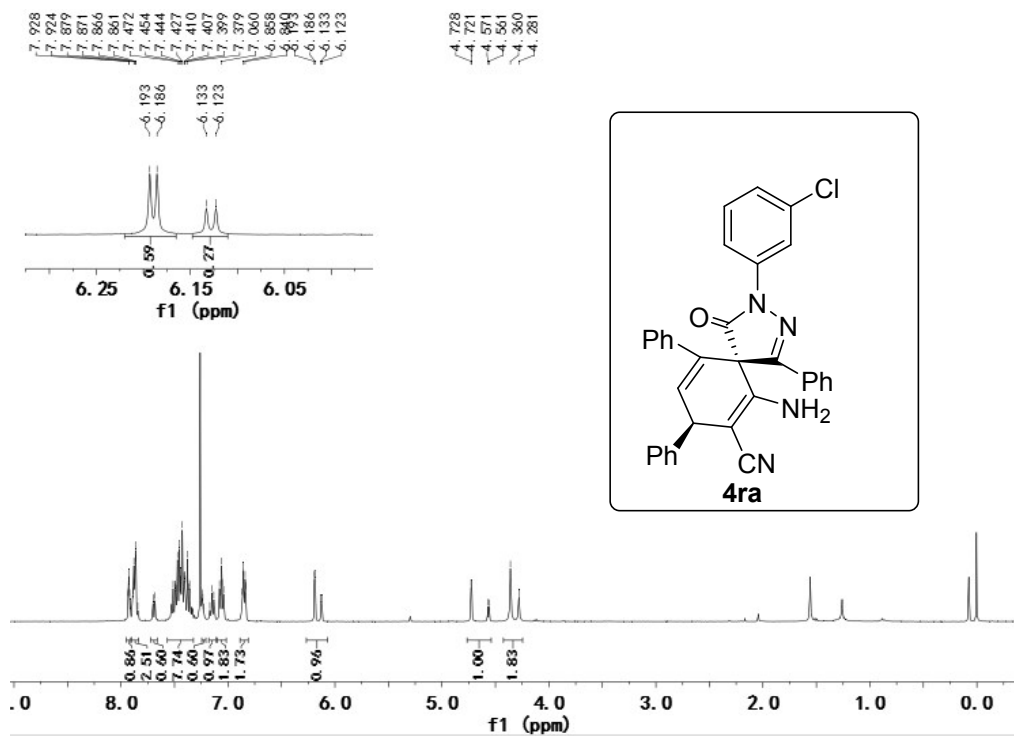
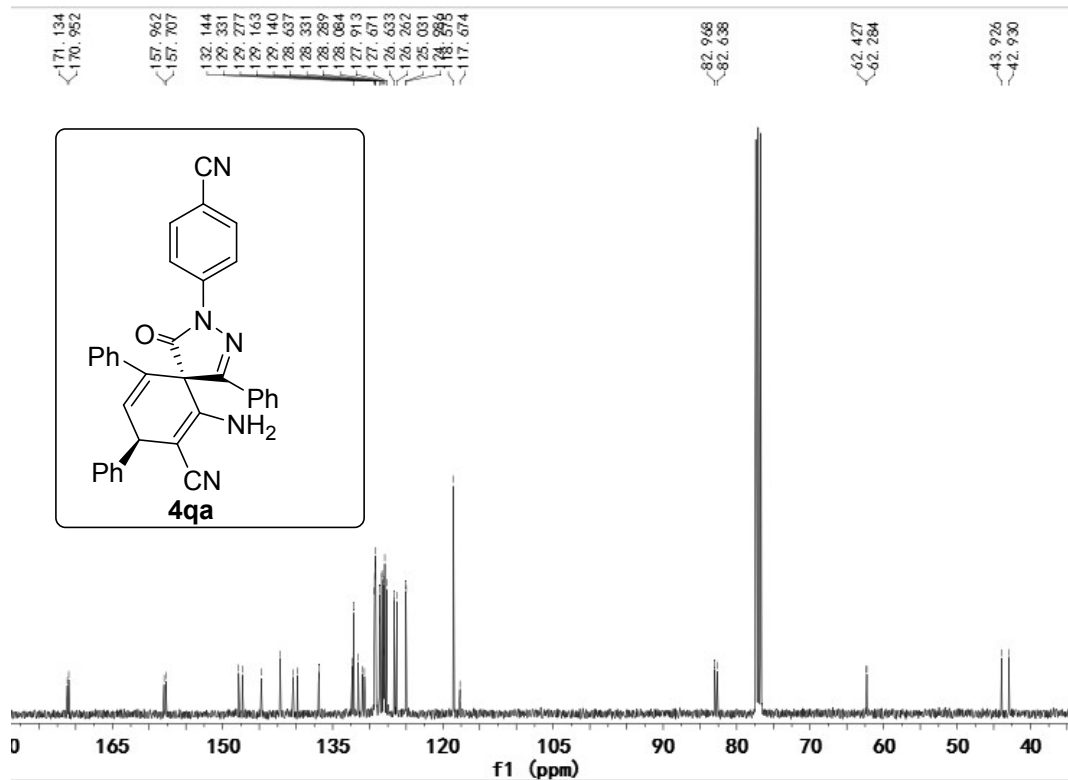


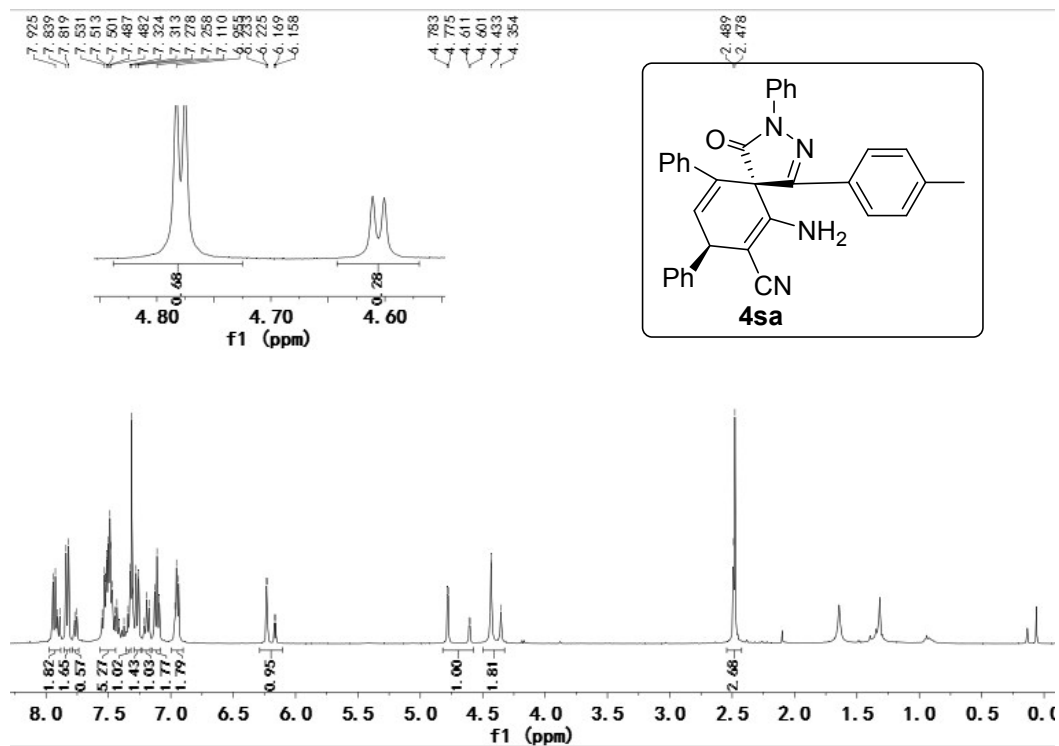
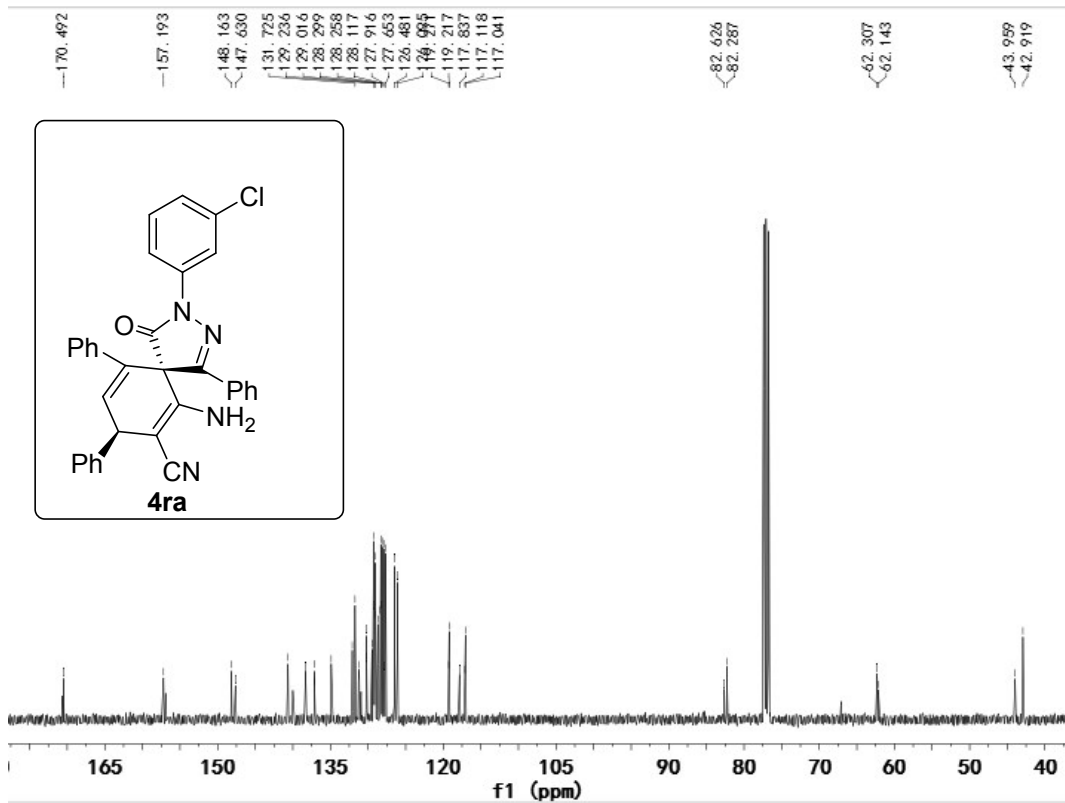


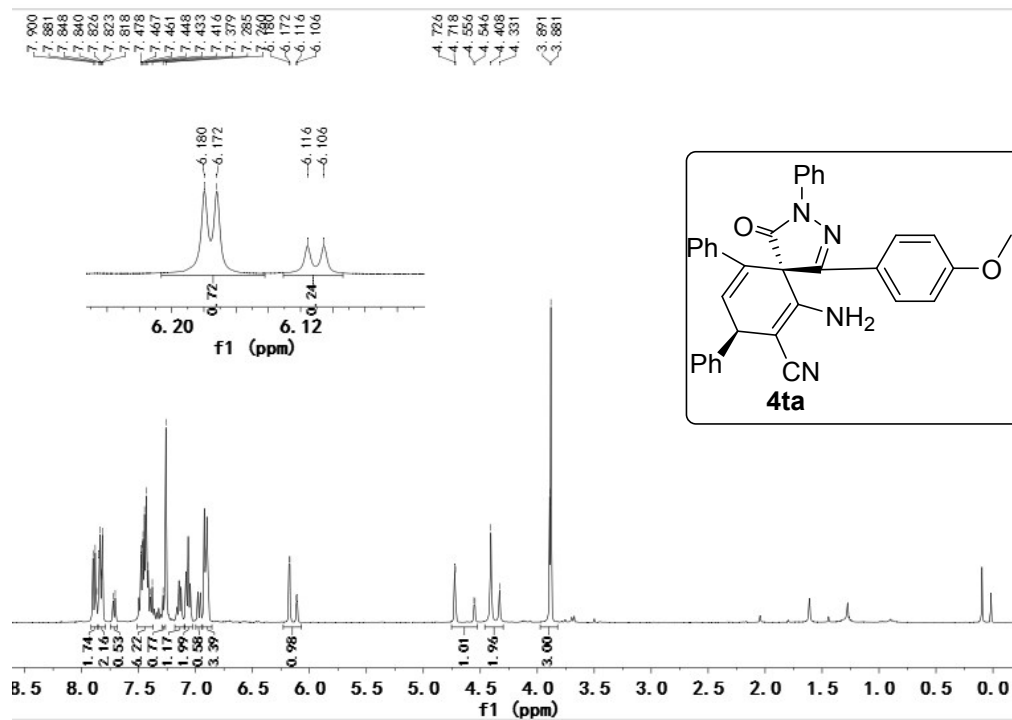
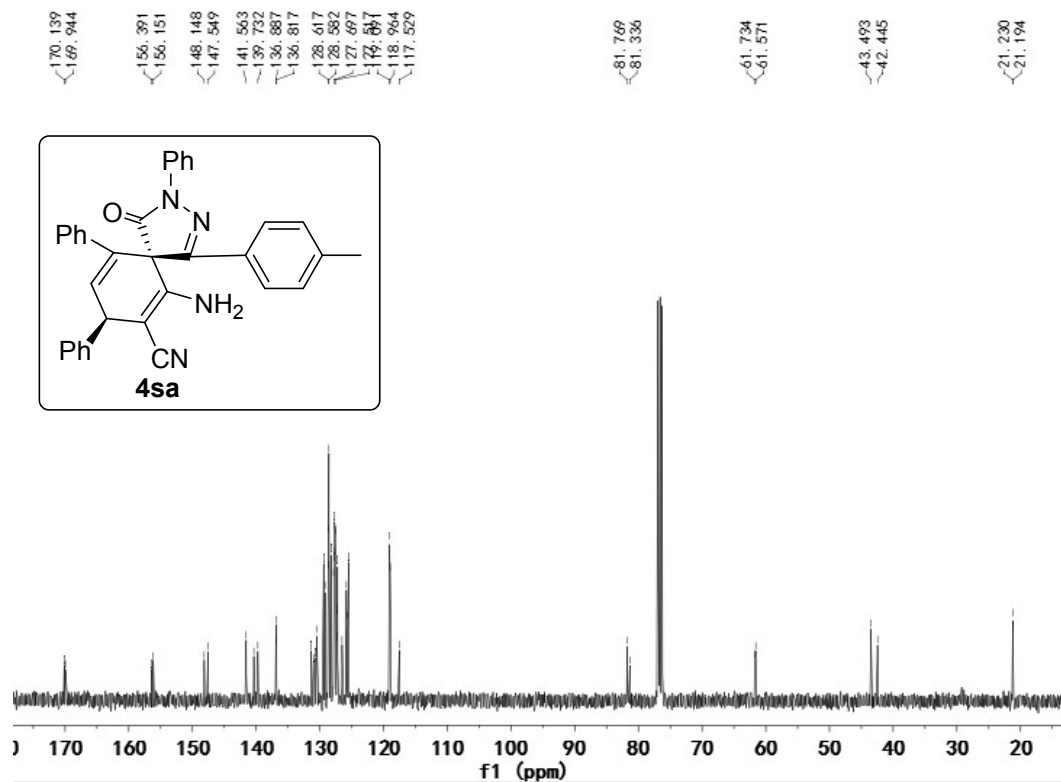


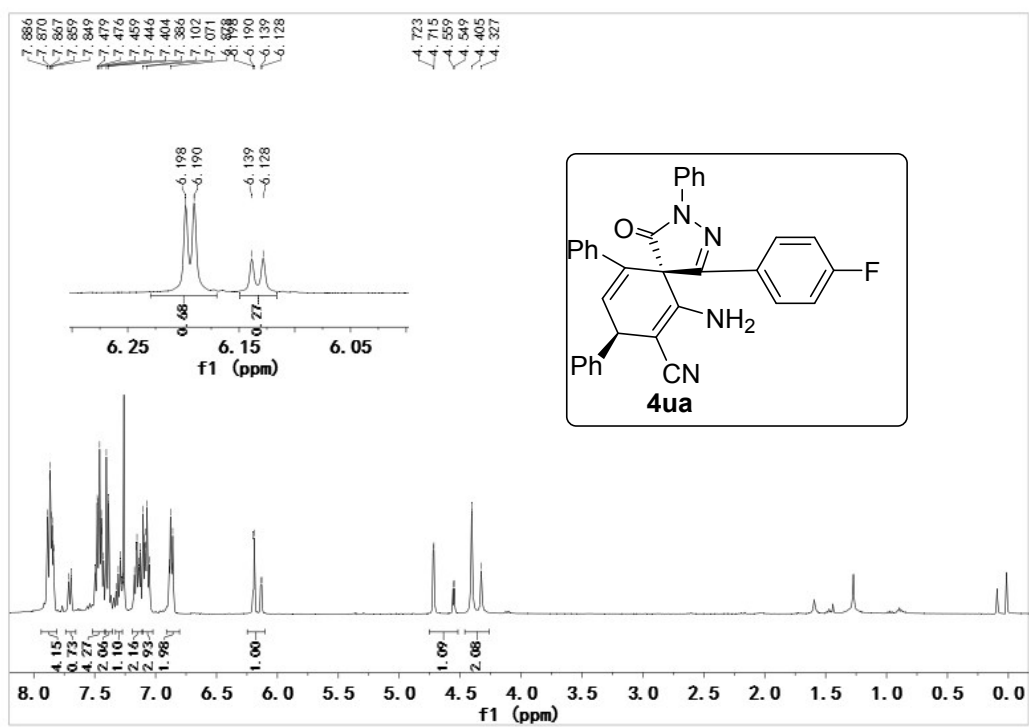
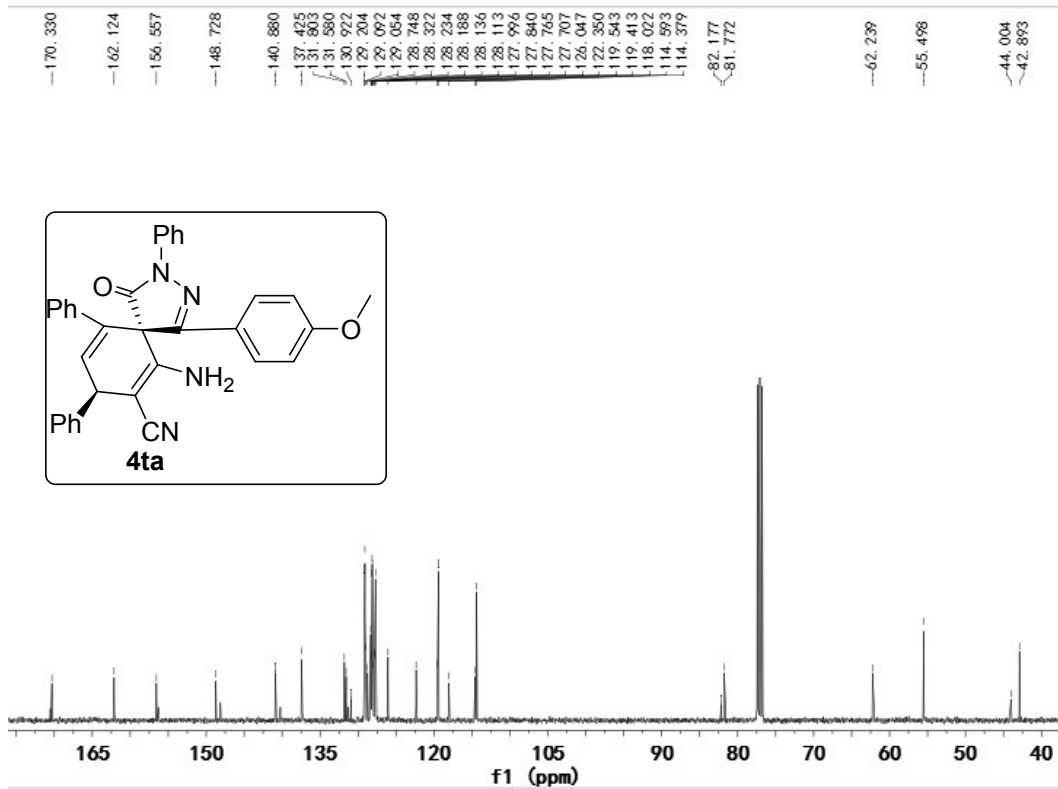


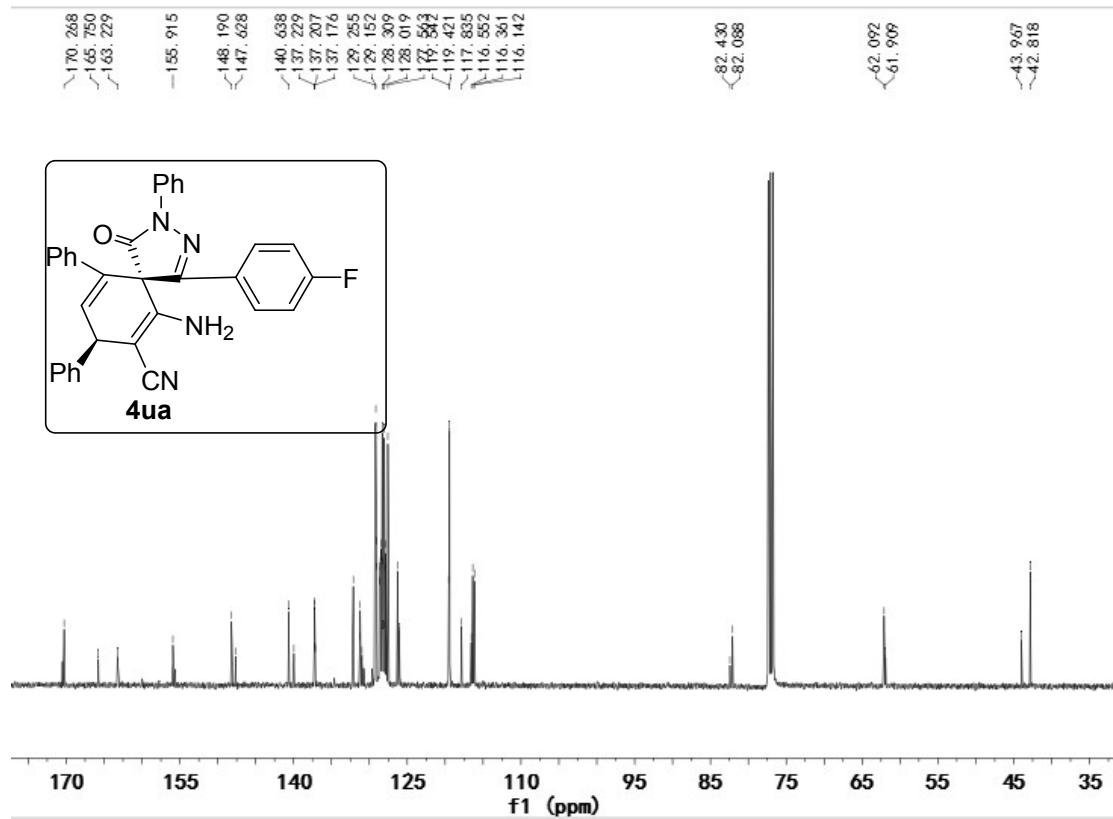
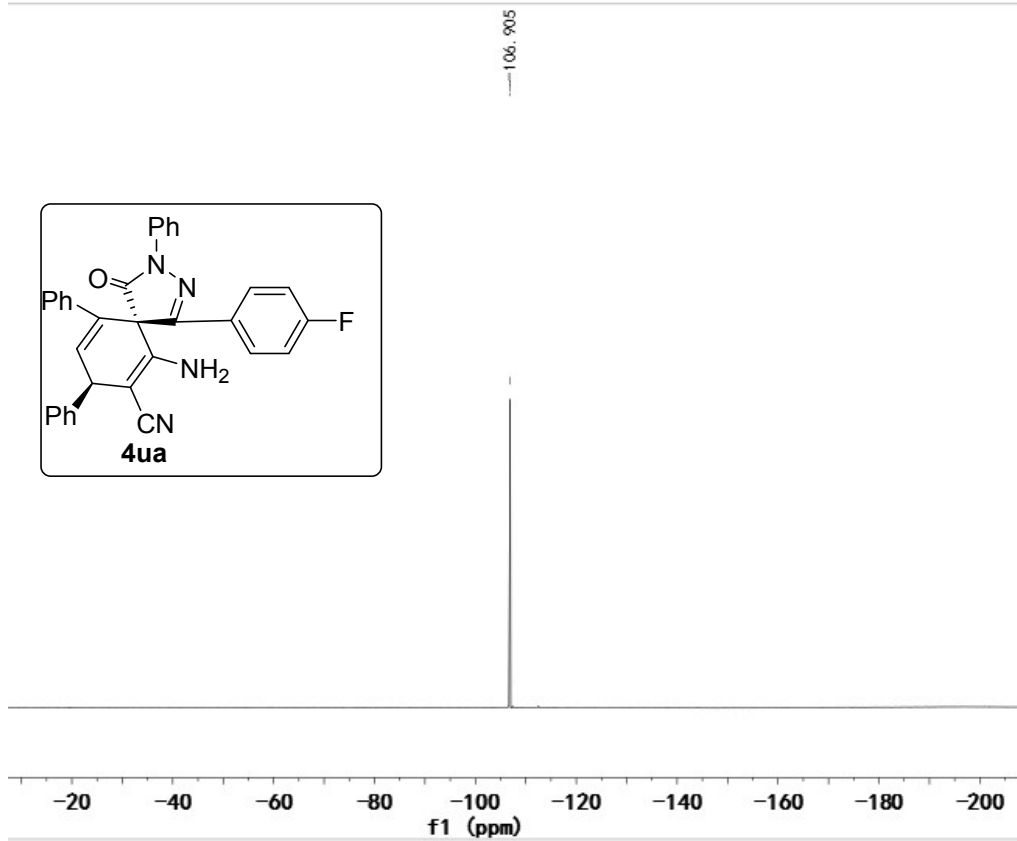


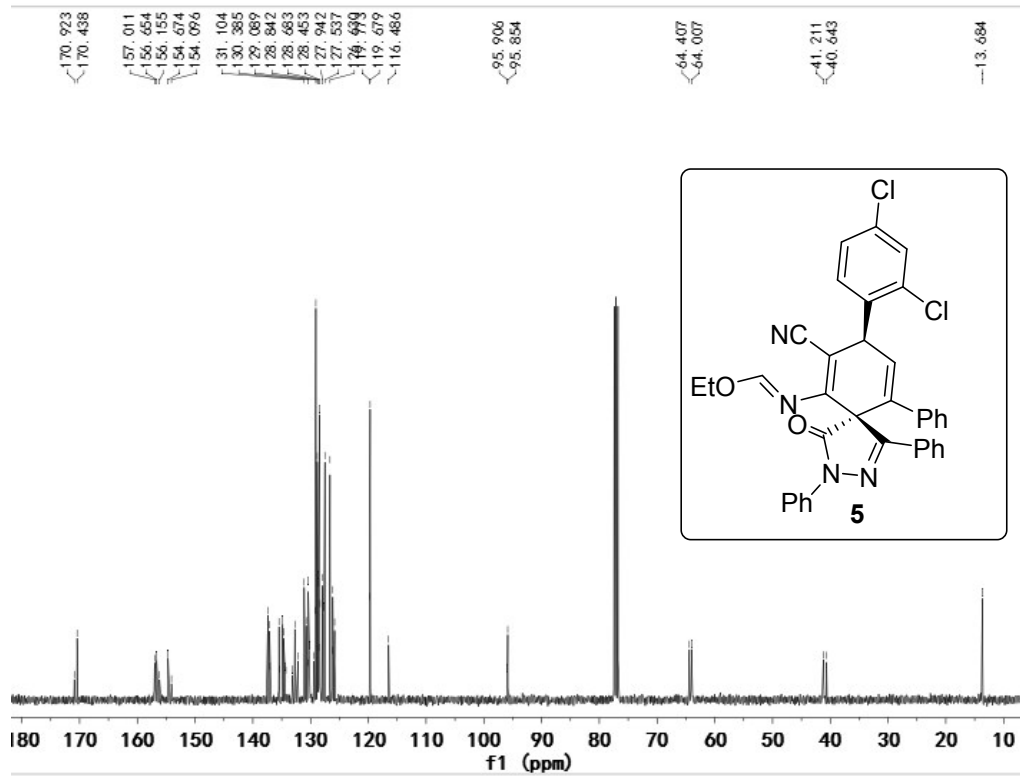
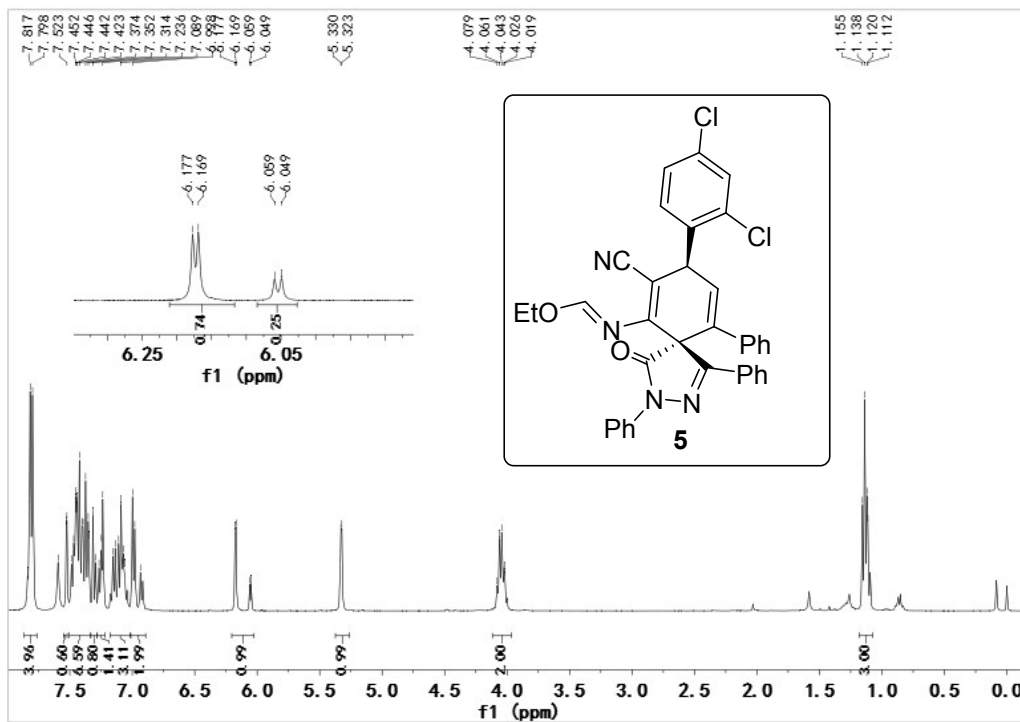


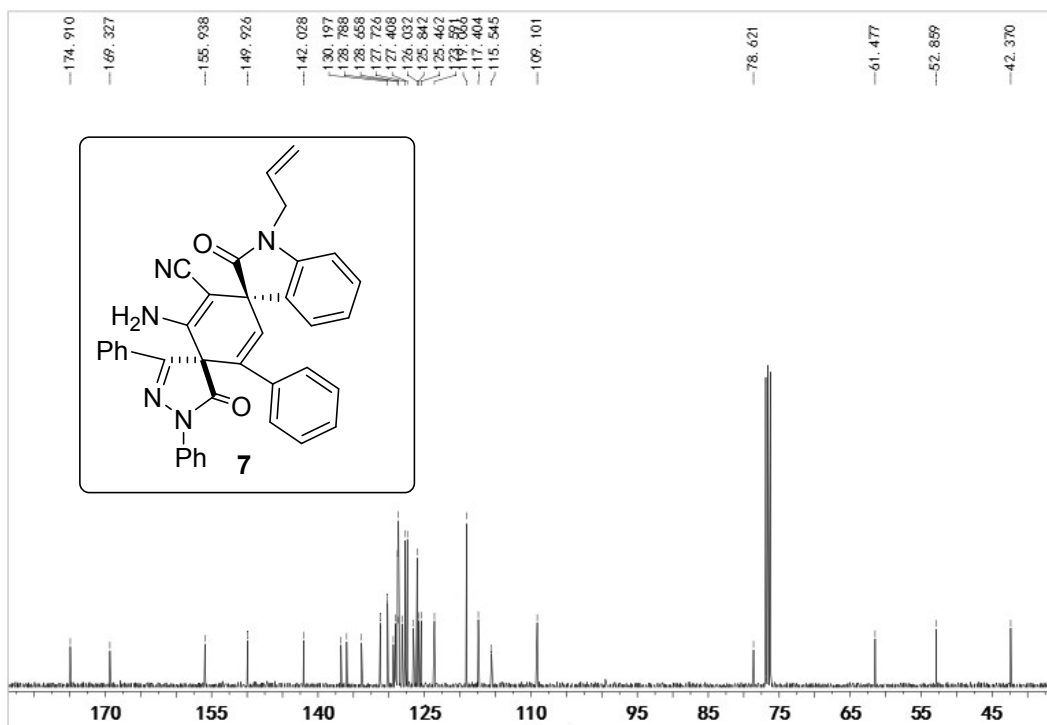
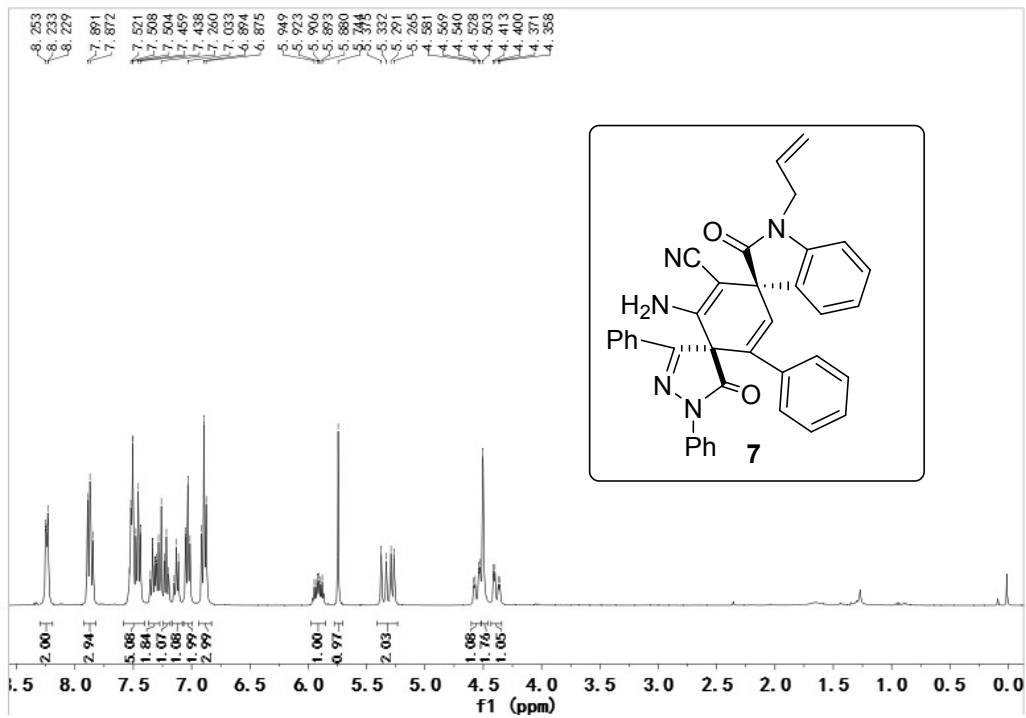




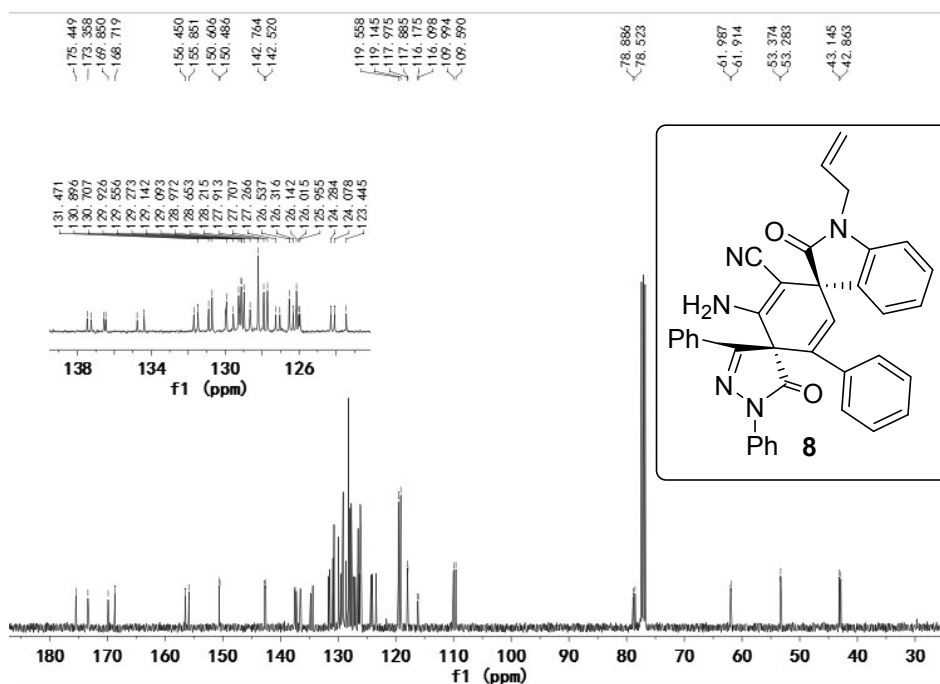
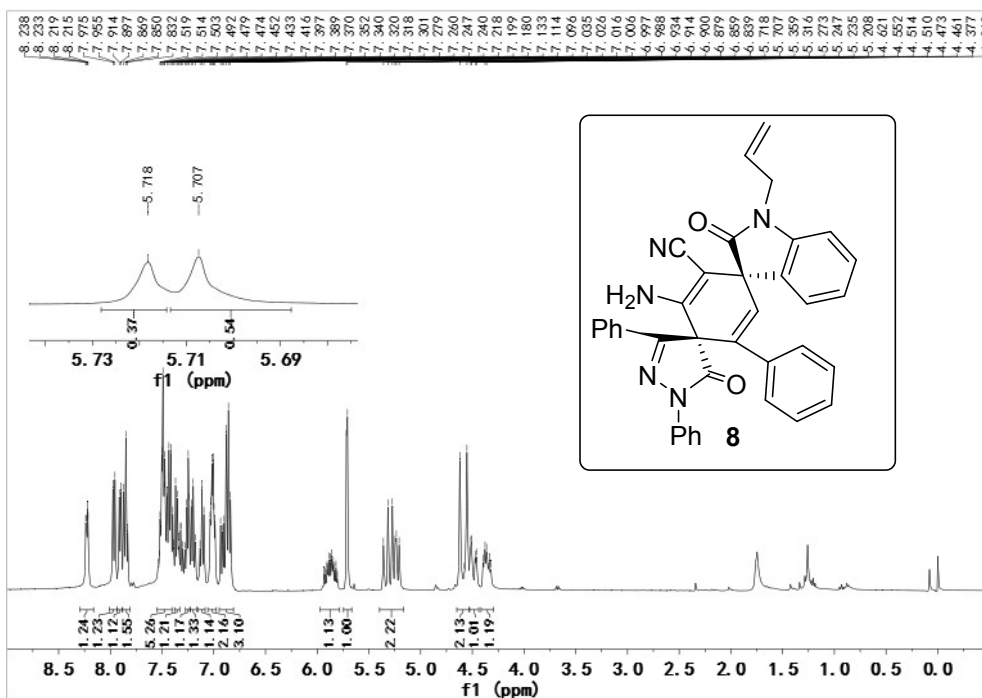




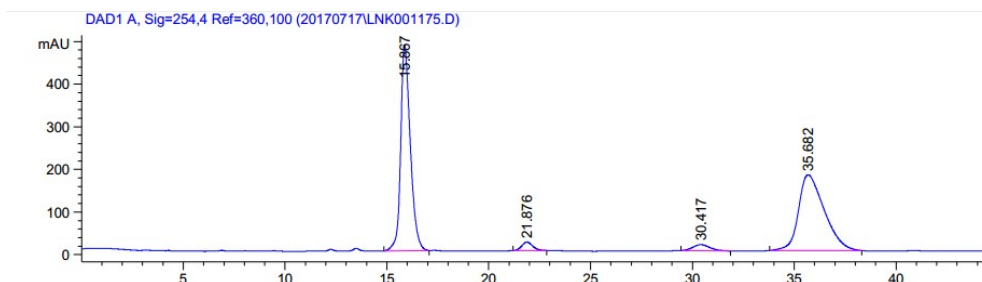






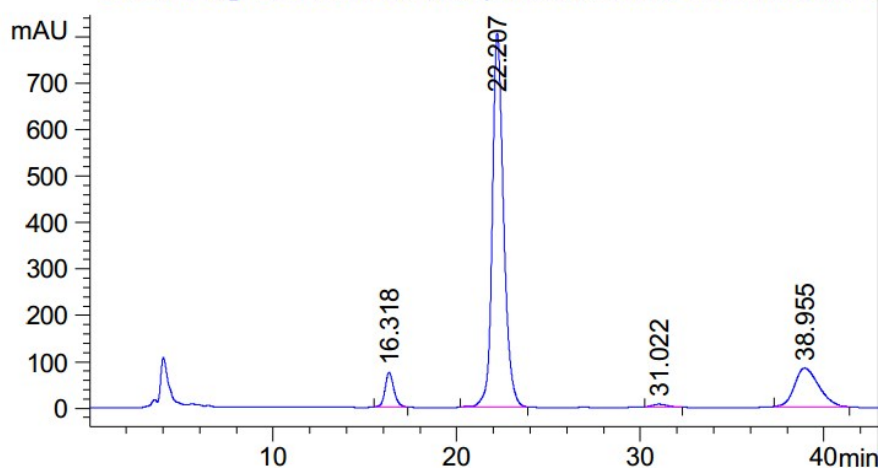


#### 4. HPLC profile spectrum of compounds 4aa



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.867	BB	0.4962	1.58726e4	481.97772	47.8776
2	21.876	BB	0.5748	744.11084	19.96746	2.2445
3	30.417	BB	0.8674	834.63892	14.37391	2.5176
4	35.682	BB	1.3252	1.57011e4	177.97485	47.3603

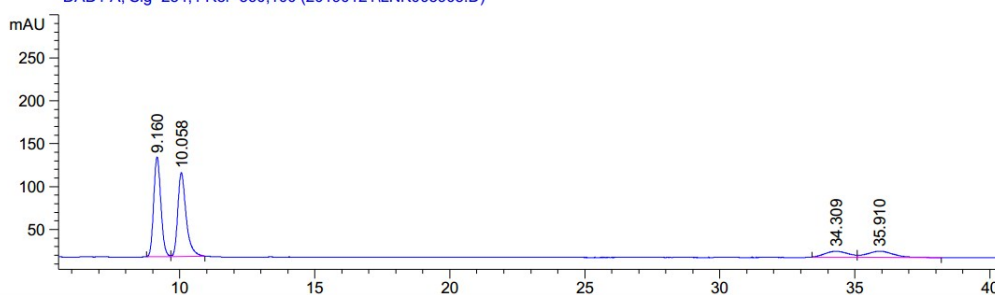
DAD1 A, Sig=254,4 Ref=360,100 (E:\WXW\DATA\ZHAOMIN\201710



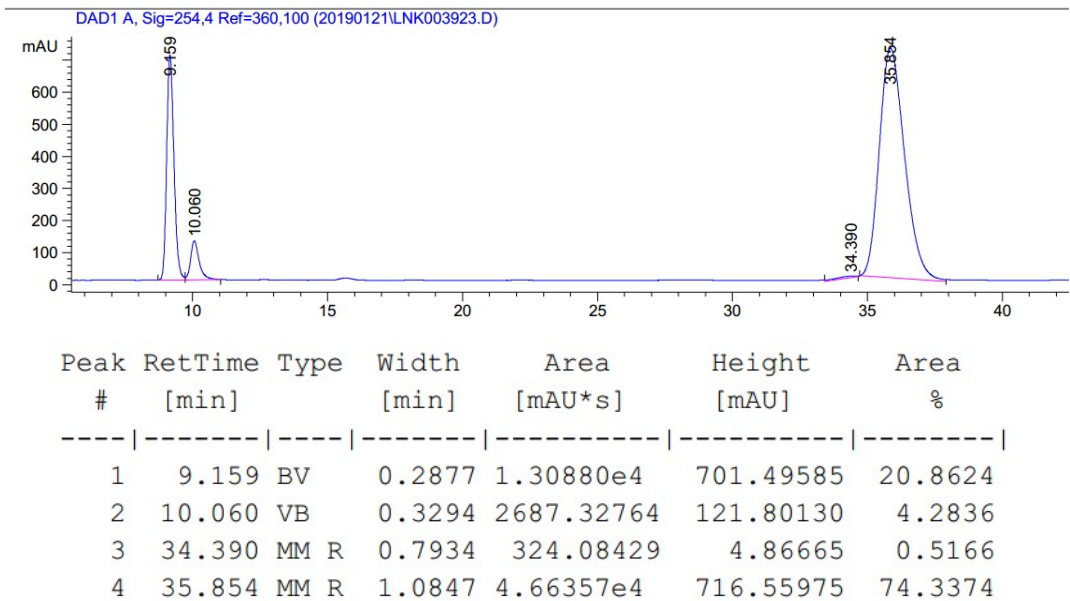
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.318	BB	0.5110	2523.99805	74.92770	5.5985
2	22.207	BB	0.6457	3.44928e4	805.25916	76.5085
3	31.022	BB	0.7842	363.22385	6.49716	0.8057
4	38.955	BB	1.3881	7703.56641	83.52045	17.0873

#### 4ab

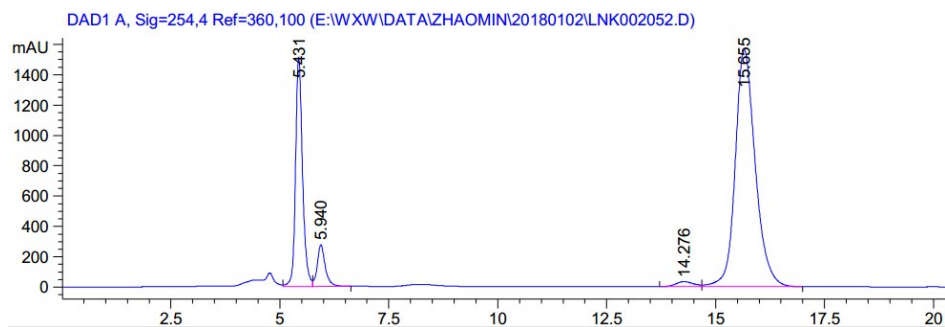
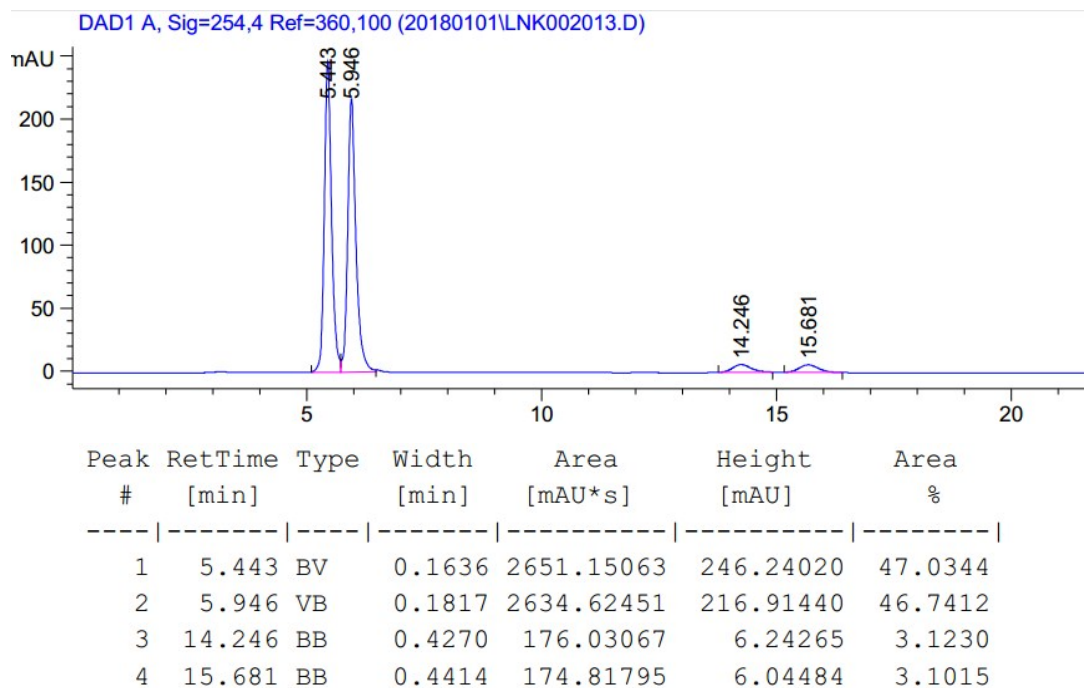
DAD1 A, Sig=254,4 Ref=360,100 (20190121\LNK003905.D)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.160	BV	0.2871	2143.62158	116.27102	41.8727
2	10.058	VB	0.3255	2105.93115	97.69395	41.1365
3	34.309	BV	0.7115	405.56577	6.80286	7.9222
4	35.910	VB	0.7783	464.25400	7.08667	9.0686



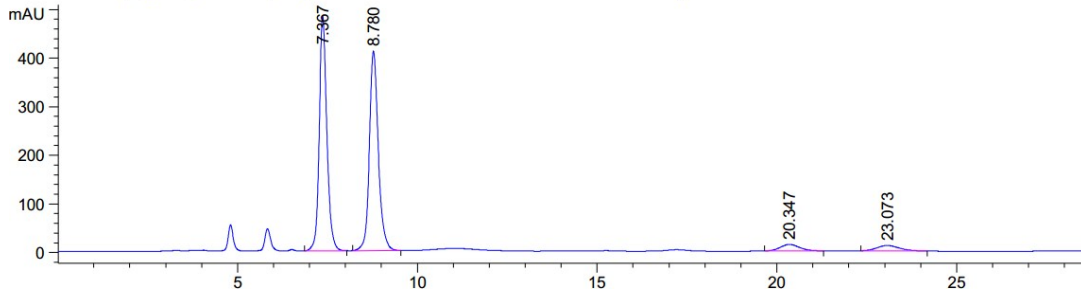
4ac



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.431	VV	0.1678	1.68087e4	1510.65173	23.5400
2	5.940	VB	0.1891	3521.86865	275.49597	4.9322
3	14.276	BV	0.4395	984.37726	34.02378	1.3786
4	15.655	VB	0.4878	5.00900e4	1563.38293	70.1492

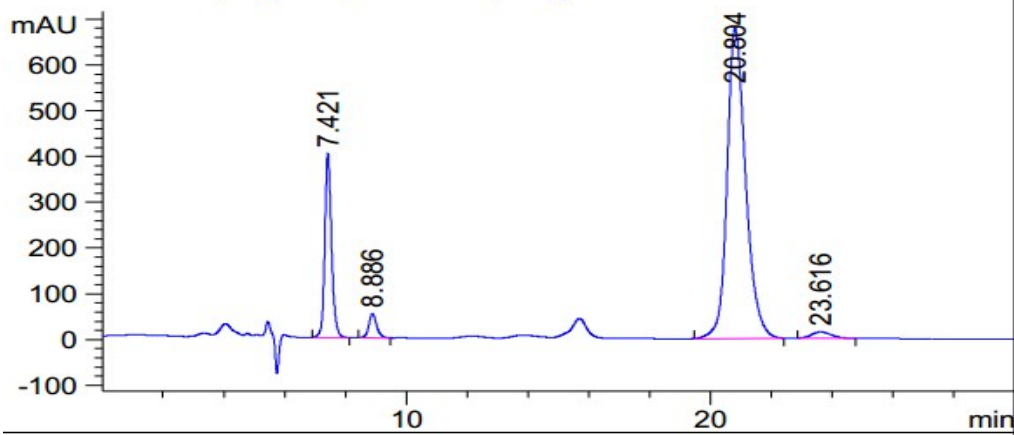
#### 4ad

DAD1 A, Sig=254,4 Ref=360,100 (E:\WXW\DATA\ZHAOMIN\20171024\LNK001530.D)



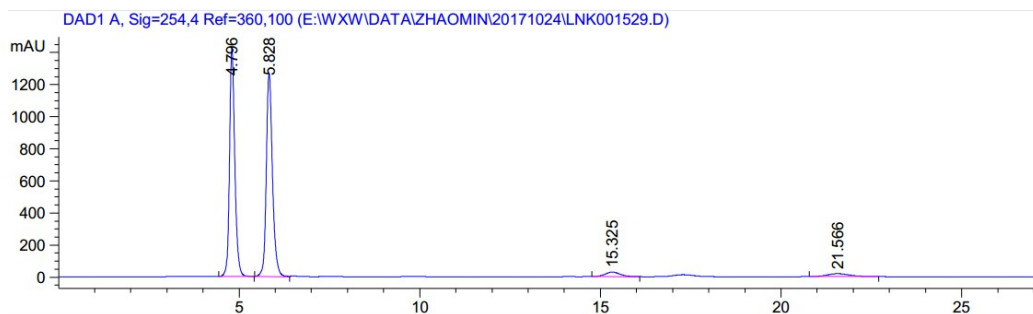
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.367	BB	0.2222	7128.84619	482.98984	46.7768
2	8.780	BB	0.2601	7113.71924	410.63330	46.6776
3	20.347	BB	0.5714	496.16669	13.35478	3.2557
4	23.073	BB	0.6732	501.39774	11.26589	3.2900

DAD1 A, Sig=254,4 Ref=360,100 (E:\WXW\DATA\ZHAOMIN\201801)

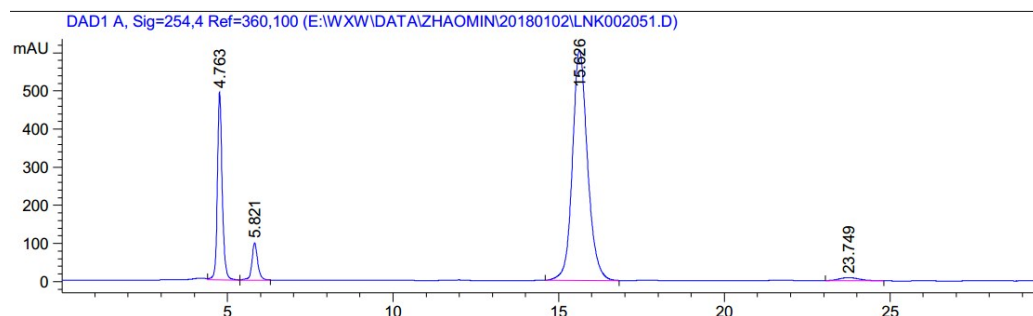


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.421	BB	0.2295	6124.40625	402.61902	16.7871
2	8.886	BB	0.2710	952.25586	53.15343	2.6102
3	20.804	BB	0.6435	2.87763e4	677.59387	78.8764
4	23.616	BB	0.6977	629.79559	13.87106	1.7263

#### 4ae

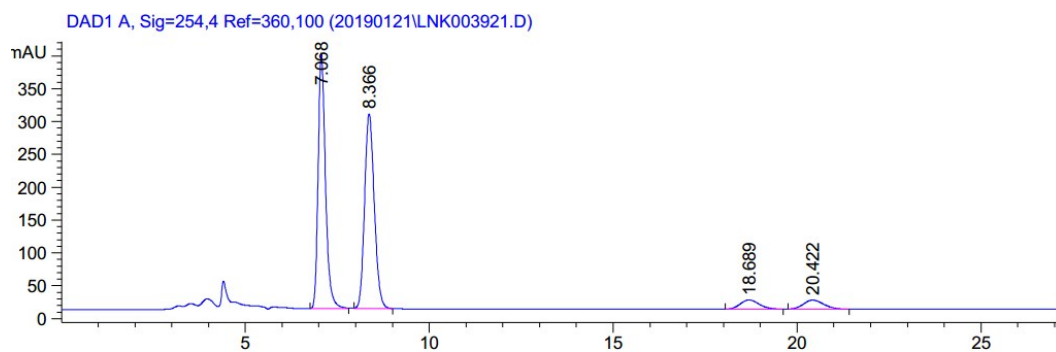


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.796	BB	0.1553	1.45718e4	1424.85962	47.1377
2	5.828	BV	0.1732	1.46770e4	1266.39063	47.4781
3	15.325	BB	0.4444	836.14368	28.65454	2.7048
4	21.566	BB	0.6777	828.30524	18.45390	2.6794



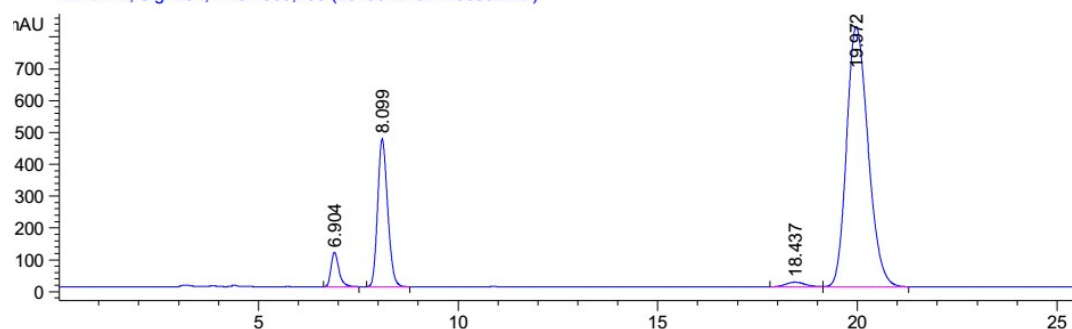
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.763	VV	0.1523	4989.60938	492.12366	19.4081
2	5.821	VB	0.1830	1189.68066	97.08310	4.6275
3	15.626	BB	0.4824	1.91734e4	603.94324	74.5785
4	23.749	BB	0.6571	356.29764	8.23003	1.3859

#### 4an



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.068	BB	0.2125	5395.79980	387.33557	45.5139
2	8.366	BB	0.2835	5429.60303	296.76395	45.7991
3	18.689	BB	0.5445	501.67517	13.98667	4.2317
4	20.422	BB	0.5572	528.18927	13.71792	4.4553

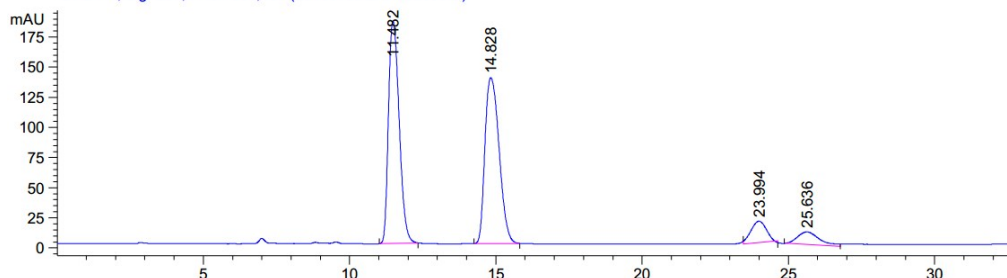
DAD1 A, Sig=254,4 Ref=360,100 (20190121\LNK003922.D)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.904	BB	0.2090	1498.06665	108.58165	3.6816
2	8.099	BB	0.2692	8110.86230	465.60507	19.9329
3	18.437	BV	0.5054	490.12799	14.53590	1.2045
4	19.972	VB	0.5824	3.05918e4	817.76996	75.1810

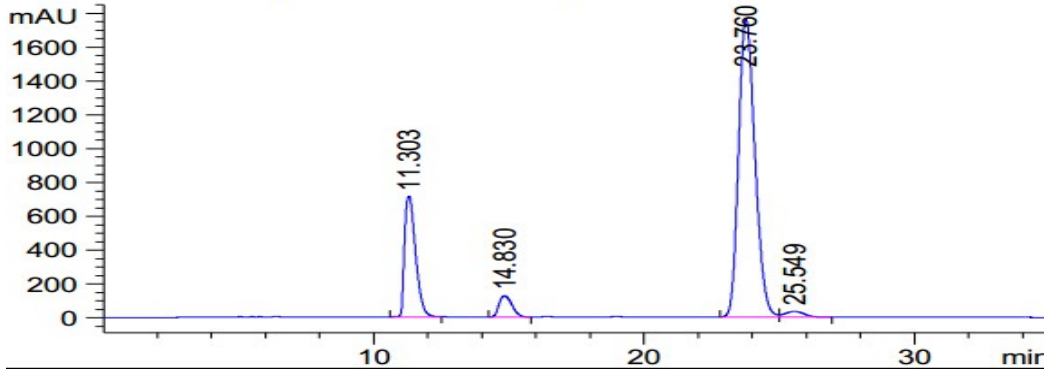
4af

DAD1 A, Sig=254,4 Ref=360,100 (20180102\LNK002065.D)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.482	BB	0.4056	4707.91162	184.54274	44.7538
2	14.828	BB	0.5405	4635.83740	137.80353	44.0687
3	23.994	MM R	0.6060	647.78247	17.81682	6.1579
4	25.636	MM R	0.8577	528.04858	10.26103	5.0197

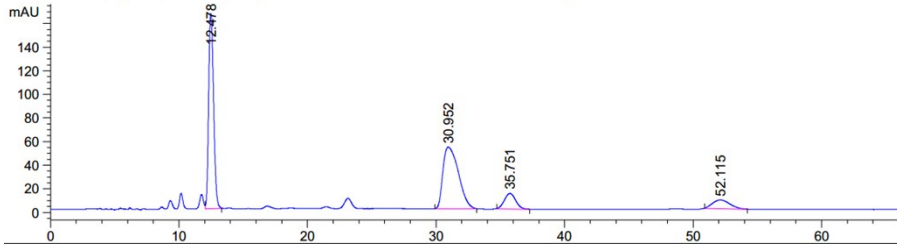
DAD1 A, Sig=254,4 Ref=360,100 (E:\WXW\DATA\ZHAOMIN\20180



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.303	BB	0.4370	2.01140e4	713.36975	20.0667
2	14.830	BB	0.5359	4130.03467	124.23204	4.1203
3	23.760	BV	0.6589	7.42989e4	1758.43665	74.1243
4	25.549	VB	0.7625	1692.61707	34.13572	1.6886

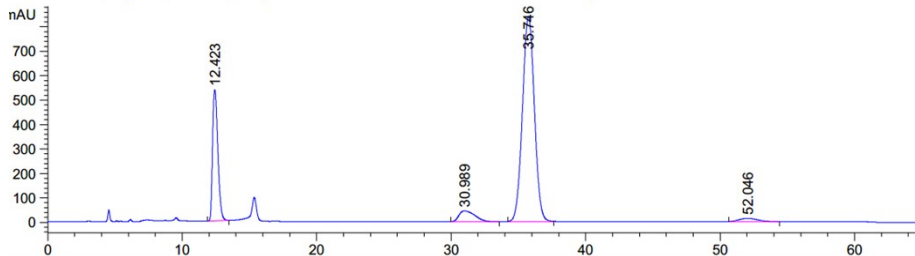
4ai

DAD1 A, Sig=254,4 Ref=360,100 (E:\WXW\DATA\ZHAOMIN\20180228\LNK002214.D)



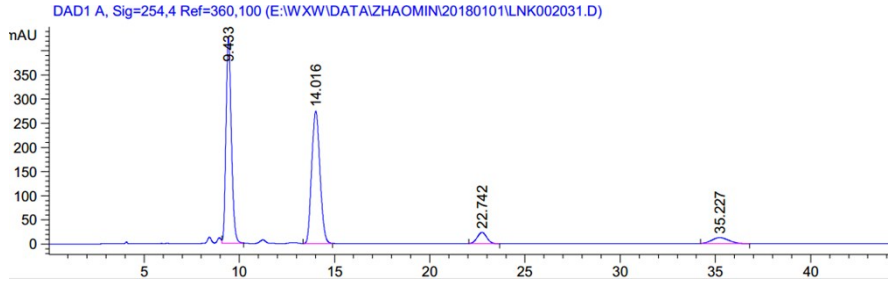
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.478	VB	0.4223	4393.02539	165.16379	42.7937
2	30.952	BB	1.2091	4389.38428	52.30492	42.7582
3	35.751	BB	0.8712	797.13763	13.18797	7.7651
4	52.115	BB	1.1138	686.04248	7.34398	6.6829

DAD1 A, Sig=254,4 Ref=360,100 (E:\WXW\DATA\ZHAOMIN\20180228\LNK002215.D)

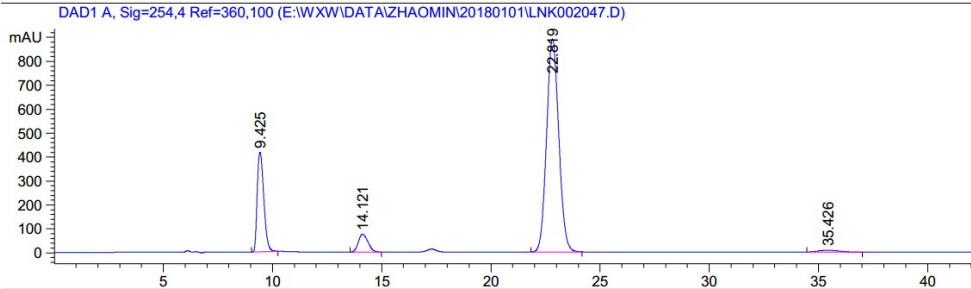


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.423	BB	0.4347	1.47417e4	536.30328	20.6591
2	30.989	BB	1.3416	3590.62329	43.93037	5.0319
3	35.746	BB	0.9690	5.17407e4	839.52179	72.5097
4	52.046	BB	1.3987	1283.90503	13.15385	1.7993

4aj



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.433	VB	0.3045	8358.18848	426.80356	45.7421
2	14.016	VB	0.4819	8314.65332	274.09131	45.5038
3	22.742	BB	0.5377	821.15259	23.38254	4.4939
4	35.227	BB	0.8692	778.42487	12.48856	4.2601

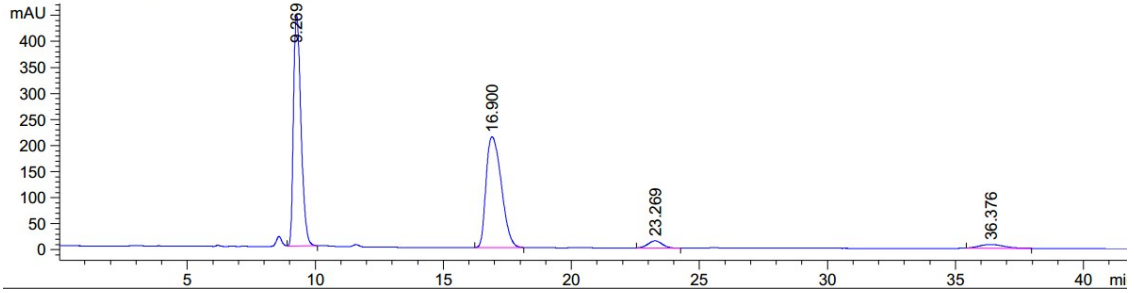


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.425	BB	0.3303	8719.50781	416.38519	18.9385
2	14.121	BB	0.4893	2297.96191	74.61008	4.9911
3	22.819	BB	0.6029	3.45202e4	889.31696	74.9767
4	35.426	BB	0.8361	503.56711	7.58978	1.0937

4ak

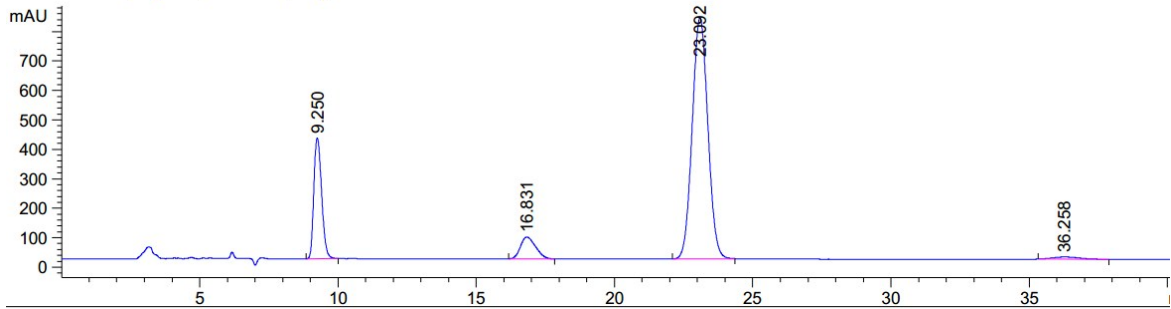


DAD1 A, Sig=254,4 Ref=360,100 (E:\WXW\DATA\ZHAOMIN\20180228\LNK002212.D)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.269	VB	0.3212	9099.91895	443.81271	48.1549
2	16.900	BB	0.6685	8795.99512	212.69055	46.5466
3	23.269	BB	0.5789	527.49841	13.77225	2.7914
4	36.376	BB	0.8334	473.76929	7.10972	2.5071

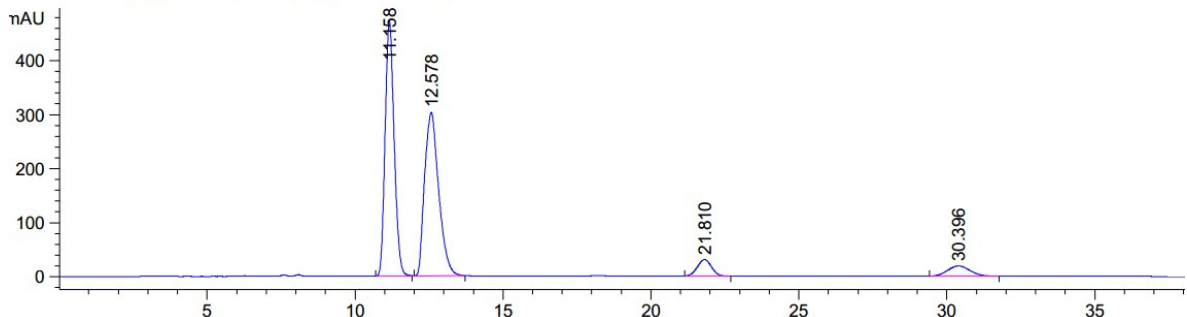
DAD1 C, Sig=210,8 Ref=360,100 (E:\WXW\DATA\ZHAOMIN\20180228\LNK002213.D)



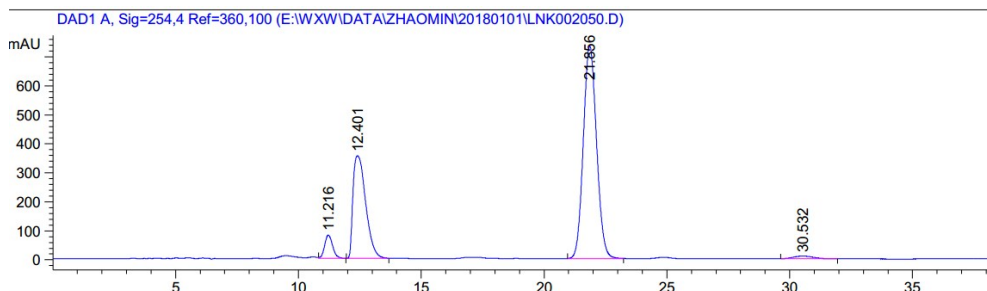
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.250	BB	0.3104	8032.92334	410.36209	18.4448
2	16.831	BB	0.5864	2841.07178	74.58701	6.5235
3	23.092	BB	0.6167	3.21758e4	818.36340	73.8805
4	36.258	BB	0.8182	501.35312	7.43965	1.1512

### 4al

DAD1 A, Sig=254,4 Ref=360,100 (SNAPSHOT.D)

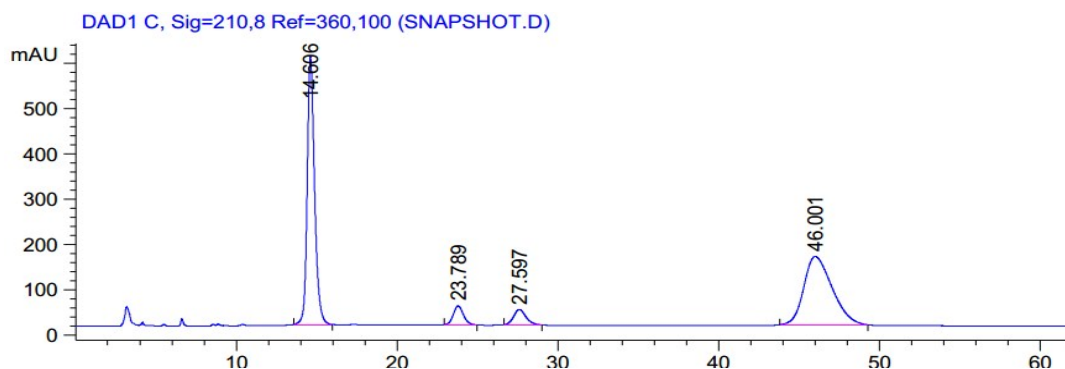


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.158	BB	0.3269	1.00175e4	473.29077	45.3022
2	12.578	BB	0.5218	1.00276e4	303.24808	45.3481
3	21.810	BB	0.5266	1046.60791	30.94072	4.7331
4	30.396	BB	0.8162	1020.84064	19.07943	4.6166

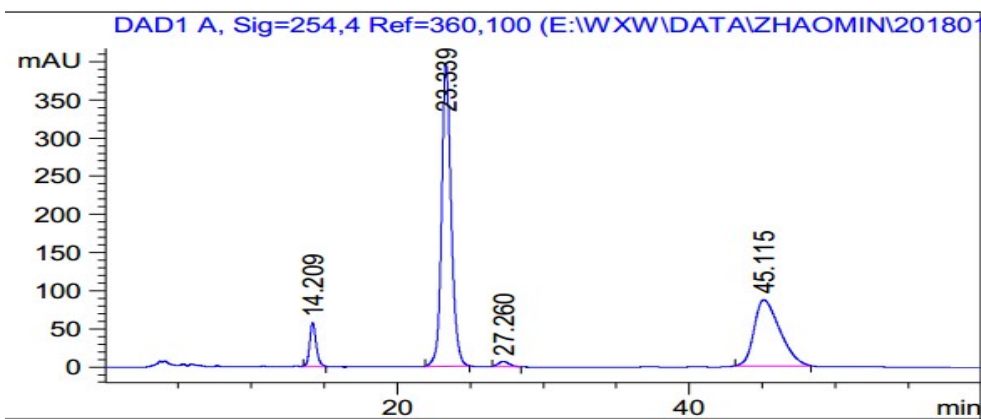


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.216	VB	0.3594	1848.90442	80.67911	4.3434
2	12.401	BB	0.5601	1.26892e4	354.06964	29.8093
3	21.856	BB	0.5847	2.74766e4	734.05243	64.5479
4	30.532	BB	0.7887	553.07794	9.59141	1.2993

#### 4ca

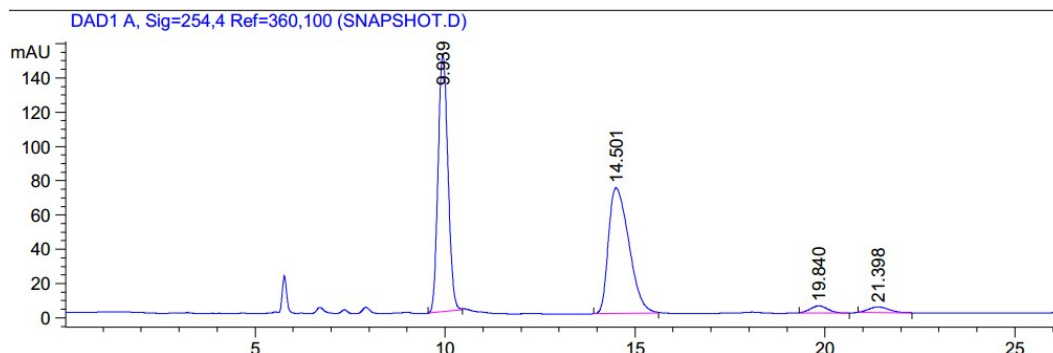


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.606	BB	0.4848	1.89169e4	592.07306	45.7974
2	23.789	BB	0.6816	1885.31592	42.32897	4.5643
3	27.597	BB	0.8285	1867.12695	34.44213	4.5203
4	46.001	BB	1.7531	1.86363e4	151.71902	45.1180

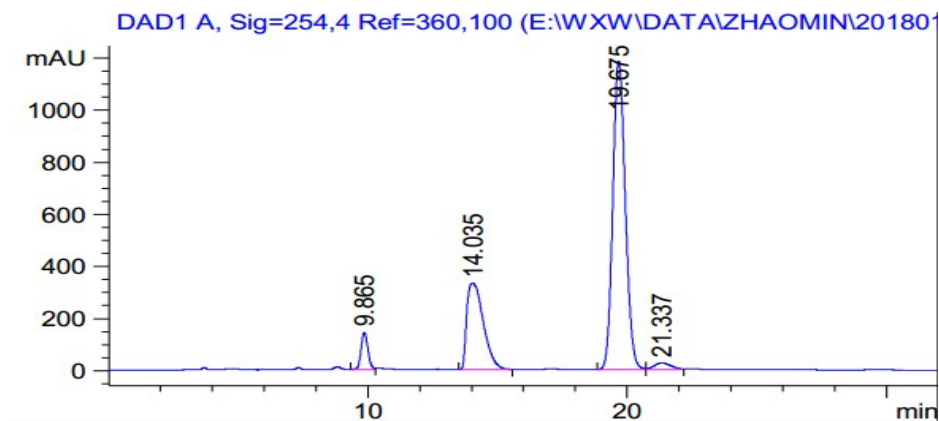


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.209	BB	0.4659	1762.58118	57.46173	5.7002
2	23.339	BB	0.6929	1.81484e4	397.29779	58.6920
3	27.260	BB	0.7380	368.39597	7.13978	1.1914
4	45.115	BB	1.8203	1.06420e4	86.80717	34.4164

4da

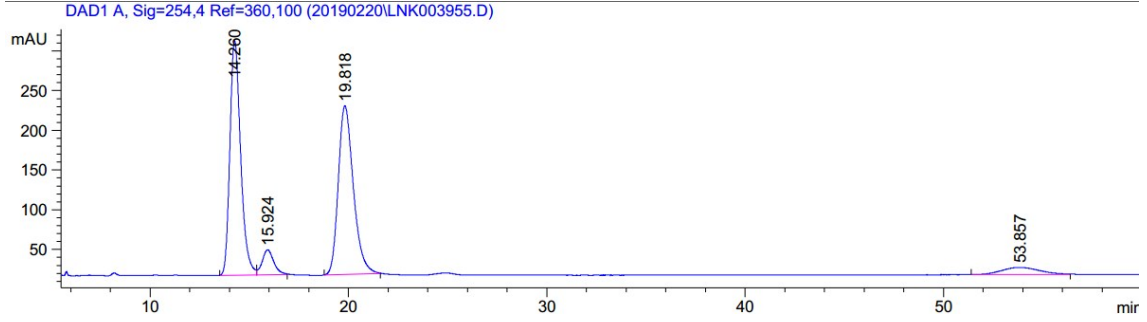


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.939	BB	0.2850	2716.88306	150.25201	47.4459
2	14.501	BB	0.6057	2752.22021	73.36610	48.0630
3	19.840	BB	0.4905	131.45578	4.11714	2.2957
4	21.398	BB	0.5718	125.71352	3.34981	2.1954

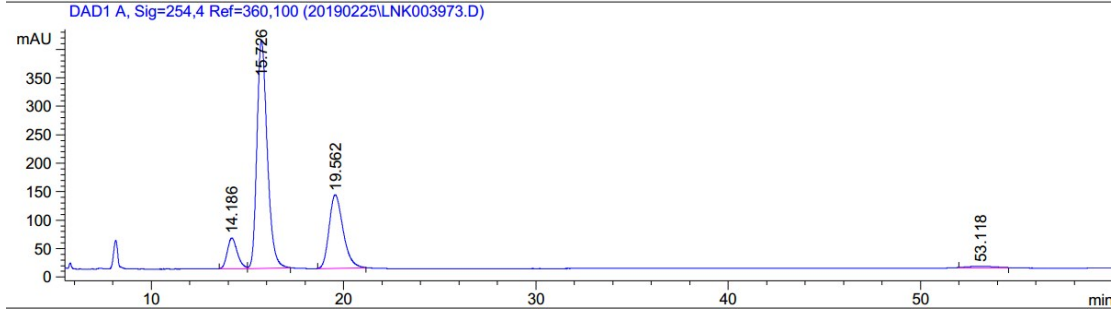


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.865	BV	0.2905	2625.63623	141.48164	4.5107
2	14.035	BB	0.6900	1.47350e4	331.86652	25.3140
3	19.675	BB	0.5201	3.96313e4	1185.09717	68.0844
4	21.337	BV	0.7115	1217.07593	26.02862	2.0909

**4fa**

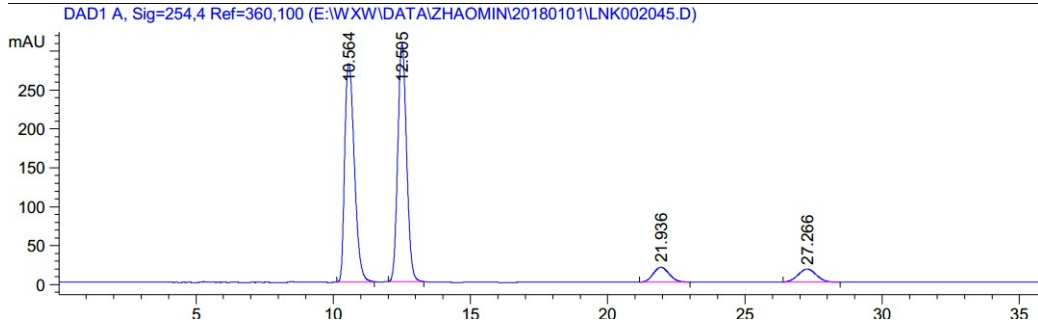


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.260	BB	0.5770	1.11063e4	295.18845	44.8053
2	15.924	BB	0.6115	1263.37683	31.39486	5.0967
3	19.818	BB	0.8045	1.12316e4	212.55714	45.3109
4	53.857	MM R	2.1986	1186.60864	8.99529	4.7870

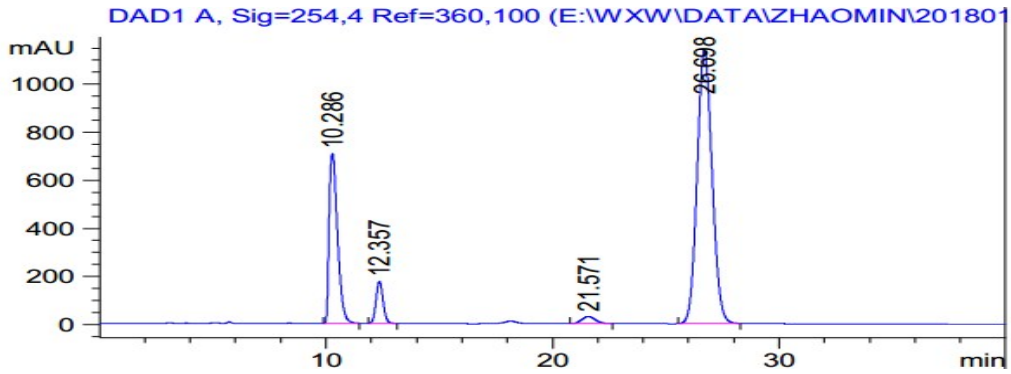


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.186	BV	0.5580	1963.17993	54.01295	8.2452
2	15.726	VB	0.5723	1.49737e4	400.42914	62.8884
3	19.562	BB	0.7741	6543.13037	129.35536	27.4806
4	53.118	MM R	1.8247	329.95038	3.01382	1.3858

**4ga**

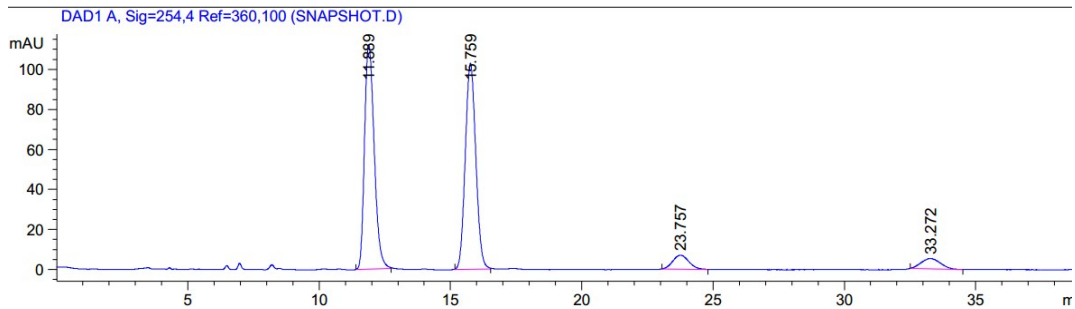


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.564	BB	0.3847	6863.06836	281.26978	44.9849
2	12.505	BB	0.3506	6840.53418	306.23340	44.8372
3	21.936	BB	0.6269	777.68292	19.18669	5.0974
4	27.266	BB	0.7041	775.11035	16.80664	5.0806

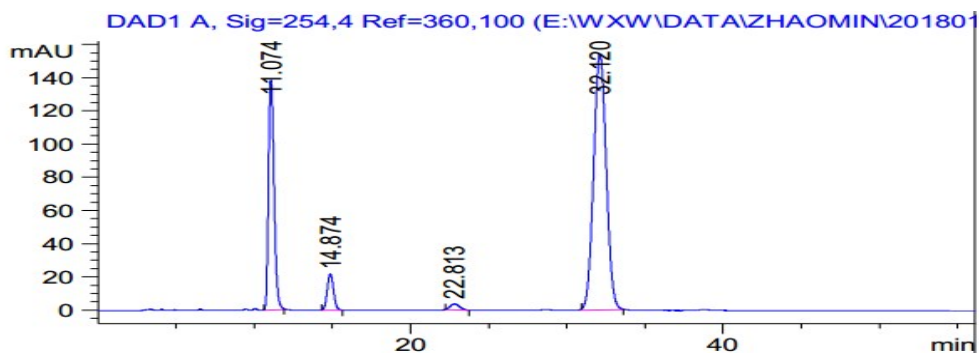


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.286	BB	0.3973	1.82455e4	706.37140	24.1436
2	12.357	BB	0.3410	3806.53174	174.18172	5.0371
3	21.571	BB	0.6359	1193.07422	29.25087	1.5788
4	26.698	BB	0.7169	5.23255e4	1136.94495	69.2406

#### 4ha

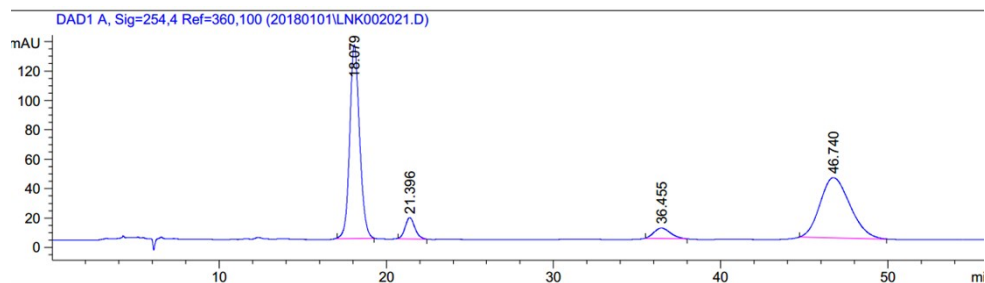


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.889	BB	0.4029	2869.59204	112.00312	45.5590
2	15.759	BB	0.4369	2861.90405	102.77763	45.4369
3	23.757	BB	0.6199	297.57581	7.02848	4.7244
4	33.272	BB	0.6706	269.56238	5.21915	4.2797

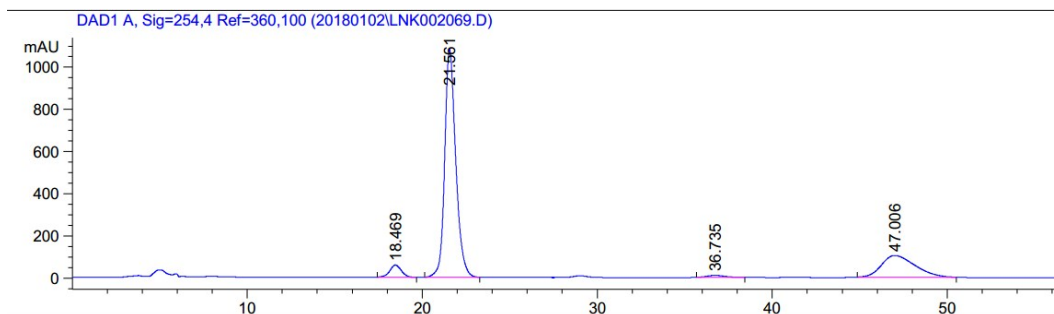


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.074	BB	0.3912	3433.91016	138.51617	26.7334
2	14.874	BB	0.4460	614.70026	21.86459	4.7855
3	22.813	BB	0.5943	150.42392	3.59381	1.1711
4	32.120	BB	0.8776	8645.97559	154.32677	67.3100

#### 4ia

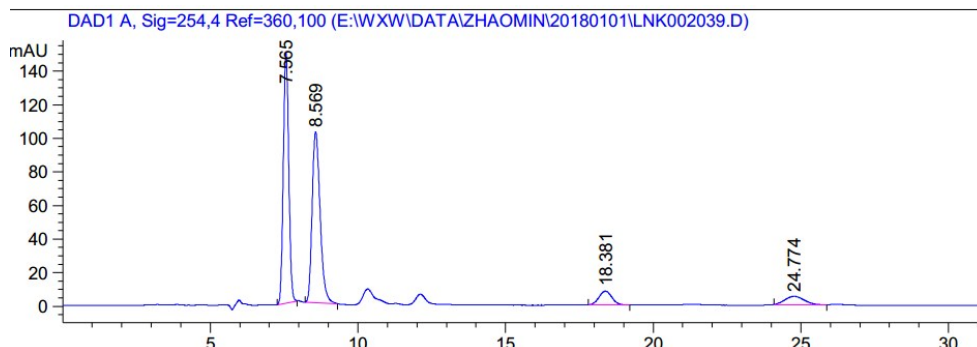


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.079	BB	0.6303	5414.84277	131.53760	46.6623
2	21.396	BB	0.6131	585.04651	14.48965	5.0416
3	36.455	BB	0.8339	492.54758	7.13043	4.2445
4	46.740	BB	1.6229	5111.87549	40.99157	44.0515

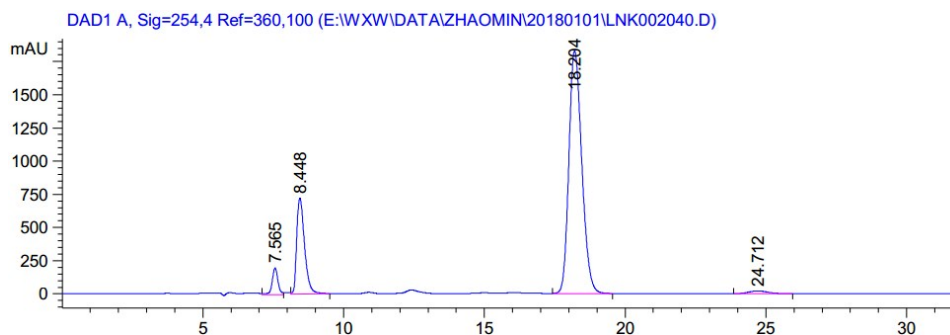


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.469	BB	0.7143	2711.56616	58.33255	4.1917
2	21.561	BB	0.6652	4.74612e4	1083.21875	73.3676
3	36.735	BB	0.9284	686.20422	9.61710	1.0608
4	47.006	BB	1.9260	1.38306e4	103.56478	21.3800

4ja

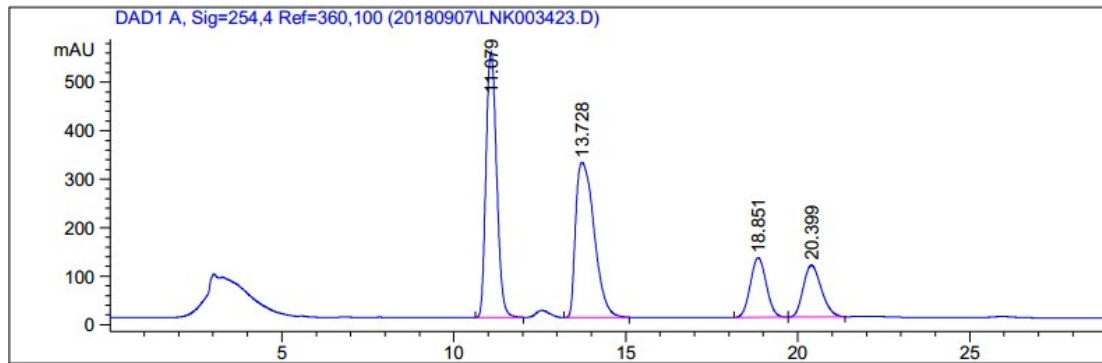


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.565	BB	0.2014	1909.74463	149.15356	44.3910
2	8.569	BB	0.2939	1917.96118	101.75131	44.5820
3	18.381	BB	0.4795	252.00247	8.27026	5.8577
4	24.774	BB	0.6385	222.38800	4.96601	5.1693

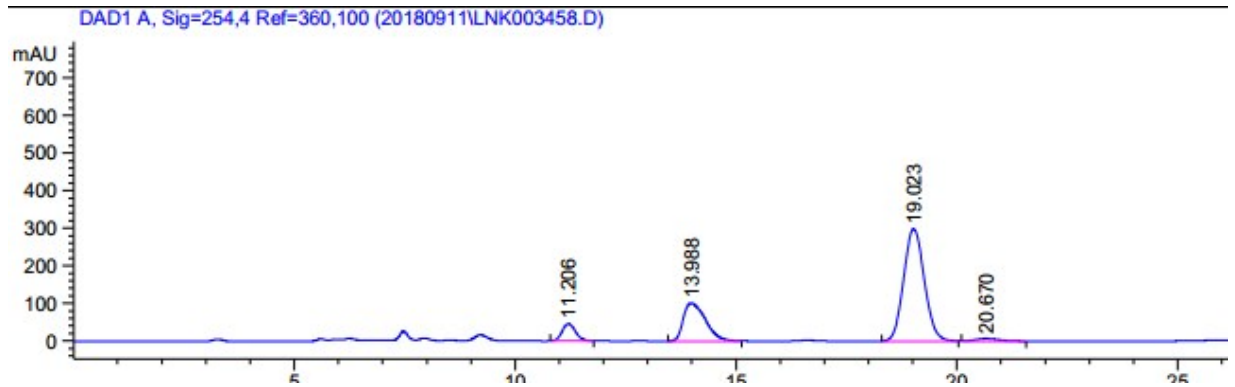


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.565	VV	0.2209	2925.07520	202.02441	3.8345
2	8.448	VB	0.2990	1.40558e4	722.28290	18.4257
3	18.204	BB	0.4922	5.83309e4	1828.60559	76.4658
4	24.712	BB	0.7313	971.82263	20.71782	1.2740

#### 4la



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.079	BB	0.3416	1.18163e4	547.96869	37.3156
2	13.728	VB	0.5958	1.19598e4	320.18869	37.7688
3	18.851	BB	0.5065	3979.33496	123.30418	12.5667
4	20.399	BB	0.5708	3910.39697	106.88630	12.3489

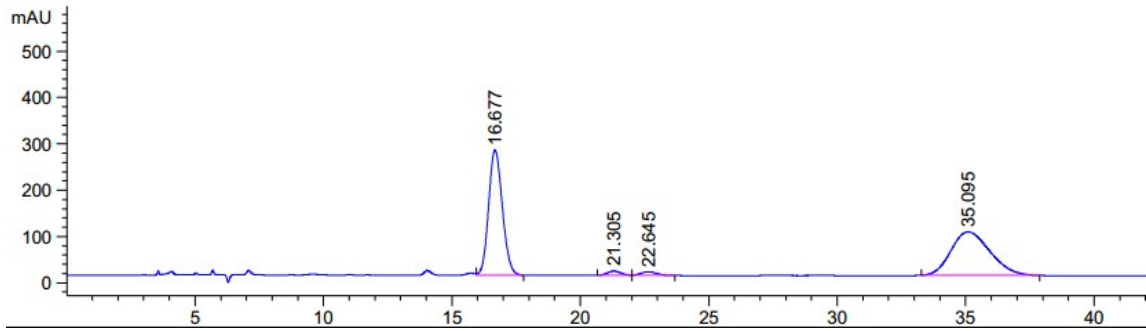


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.206	BB	0.3326	964.33167	45.62113	6.6395
2	13.988	BB	0.5637	3523.71997	101.32996	24.2609
3	19.023	BB	0.5088	9768.40723	299.24765	67.2558
4	20.670	BB	0.5828	267.80759	6.96214	1.8439

#### 4ma

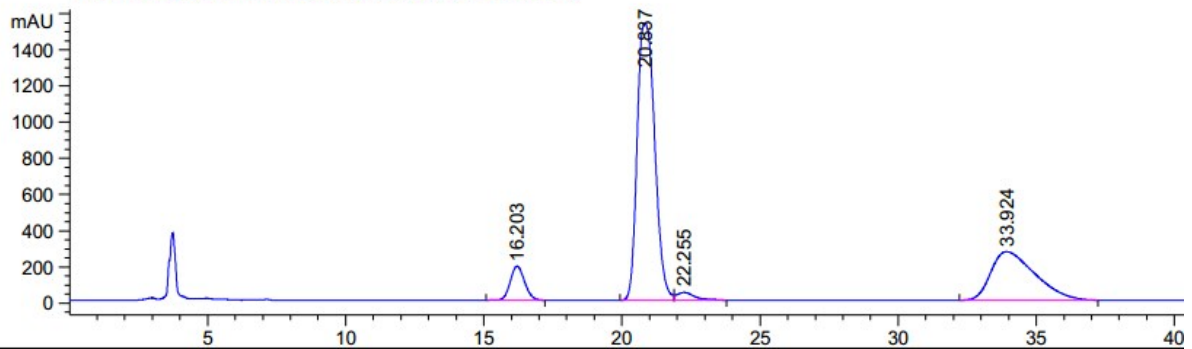


DAD1 A, Sig=254,4 Ref=360,100 (20180911\LNK003456.D)



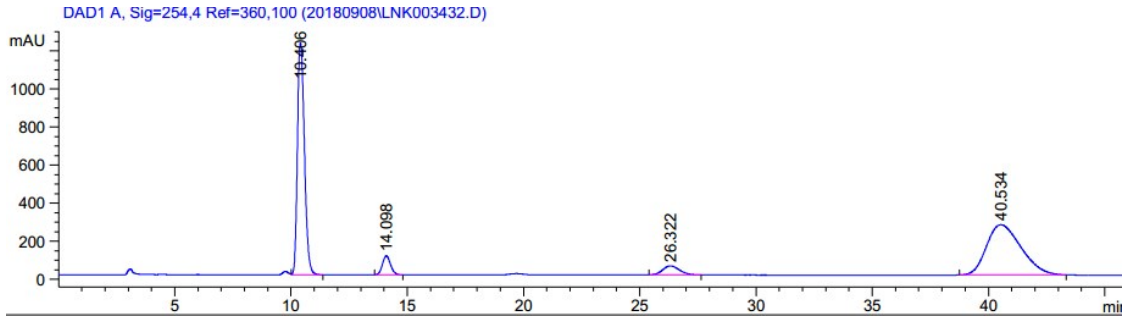
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.677	VB	0.5804	1.00694e4	270.46426	48.5126
2	21.305	BV	0.5558	336.58624	9.30873	1.6216
3	22.645	VB	0.6321	345.70663	8.12938	1.6655
4	35.095	BB	1.6029	1.00046e4	94.21230	48.2002

DAD1 A, Sig=254,4 Ref=360,100 (20180911\LNK003457.D)

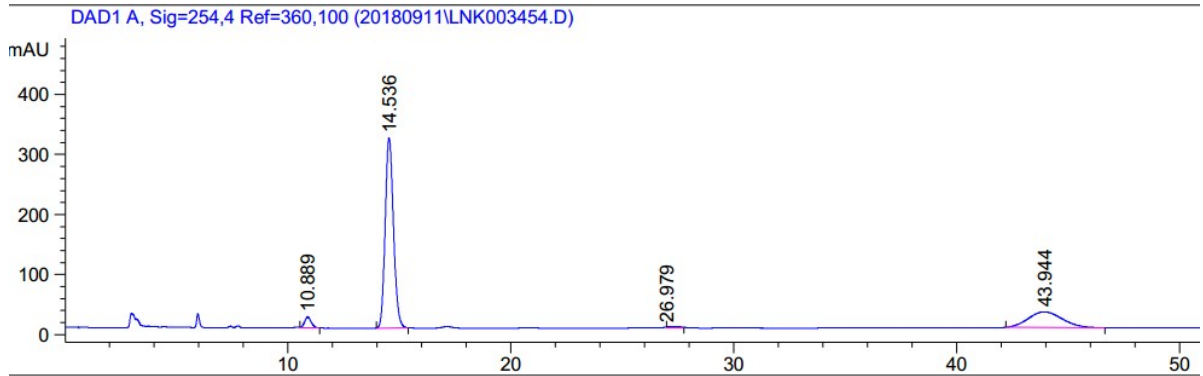


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.203	BB	0.5623	6823.99658	188.53024	6.4033
2	20.837	BV	0.7018	6.77640e4	1532.72839	63.5860
3	22.255	VB	0.6956	2060.57324	43.57943	1.9335
4	33.924	BB	1.6216	2.99221e4	269.03339	28.0772

4na

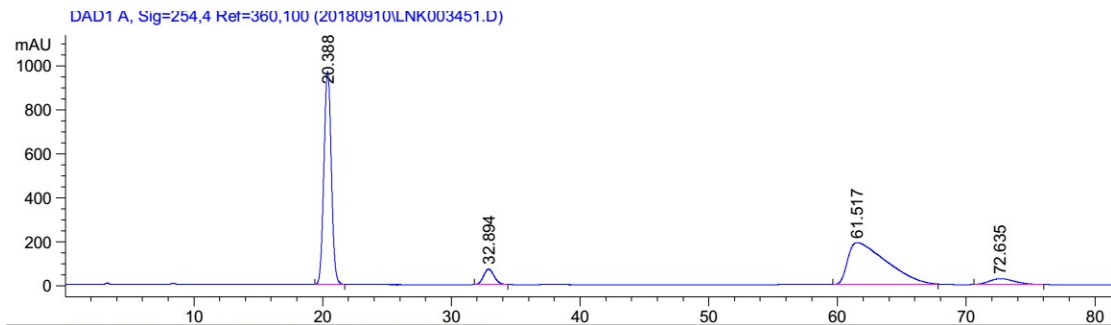


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.406	VB	0.3273	2.54397e4	1219.91138	44.2089
2	14.098	BB	0.3786	2448.89673	100.37071	4.2557
3	26.322	BB	0.7614	2379.55469	47.75035	4.1352
4	40.534	BB	1.5710	2.72761e4	264.07663	47.4002



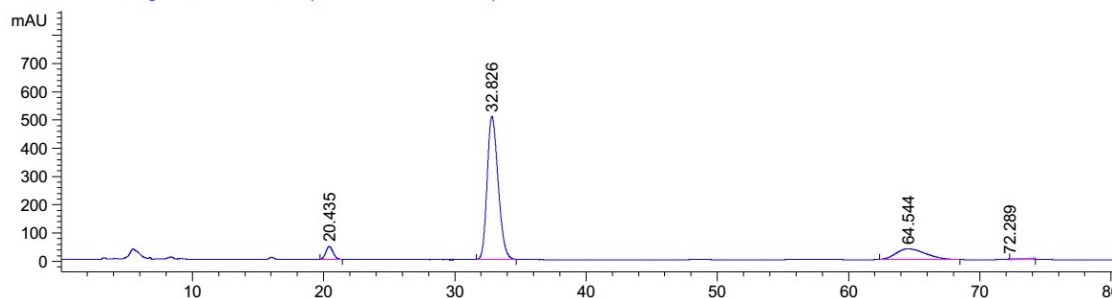
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.889	BB	0.3190	380.38766	18.26397	3.3385
2	14.536	BB	0.4008	8172.50195	316.96701	71.7263
3	26.979	MM R	0.5763	64.27321	7.20372e-1	0.5641
4	43.944	BB	1.2633	2776.84546	26.18272	24.3711

**40a**



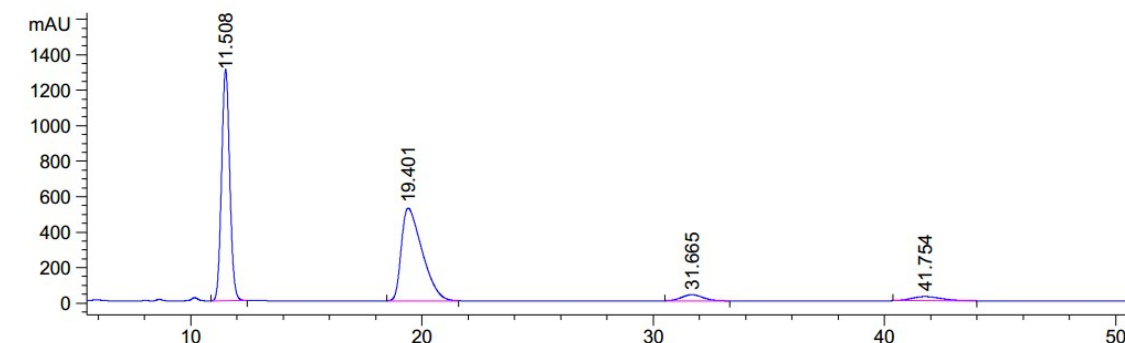
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.388	BB	0.6291	3.88491e4	970.39832	45.2241
2	32.894	BB	0.8722	4008.05371	70.61563	4.6658
3	61.517	BB	2.6621	3.94215e4	190.20027	45.8904
4	72.635	BB	1.6148	3624.87061	26.41745	4.2197

DAD1 A, Sig=254,4 Ref=360,100 (20180910LNK003450.D)



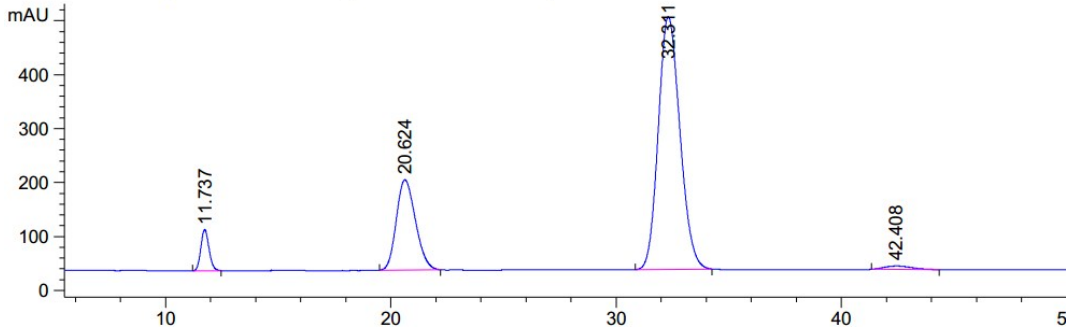
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.435	BB	0.6004	1801.82617	46.67205	4.8241
2	32.826	BB	0.9047	2.94858e4	506.82828	78.9436
3	64.544	BB	1.8420	5930.33350	37.80797	15.8776
4	72.289	MM R	0.8840	132.49513	2.70836	0.3547

#### 4pa



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.508	BB	0.3850	3.20802e4	1303.98730	46.5398
2	19.401	BB	0.9398	3.25986e4	522.54651	47.2918
3	31.665	BB	0.9110	2178.42407	34.38948	3.1603
4	41.754	BB	1.0609	2073.45142	23.28378	3.0080

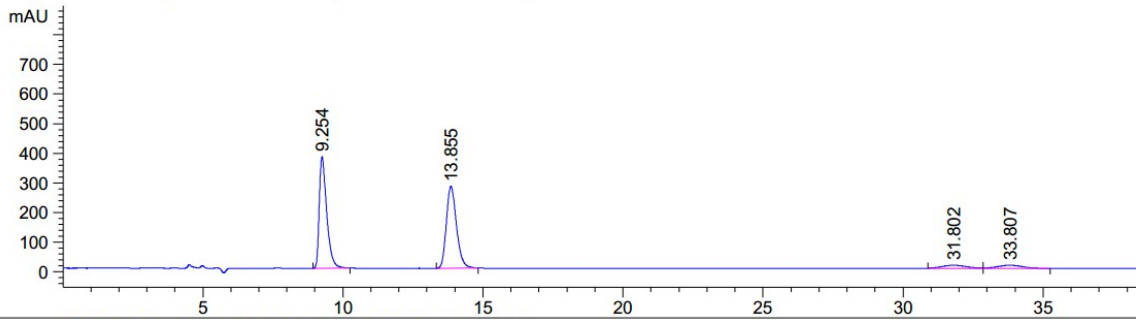
DAD1 C, Sig=210,8 Ref=360,100 (20190121\LNK003927.D)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.737	BB	0.3895	1939.28589	76.57458	4.4328
2	20.624	BB	0.8977	9917.28320	167.75404	22.6686
3	32.311	BB	1.0160	3.13381e4	468.73779	71.6316
4	42.408	BB	1.0019	554.29028	6.50614	1.2670

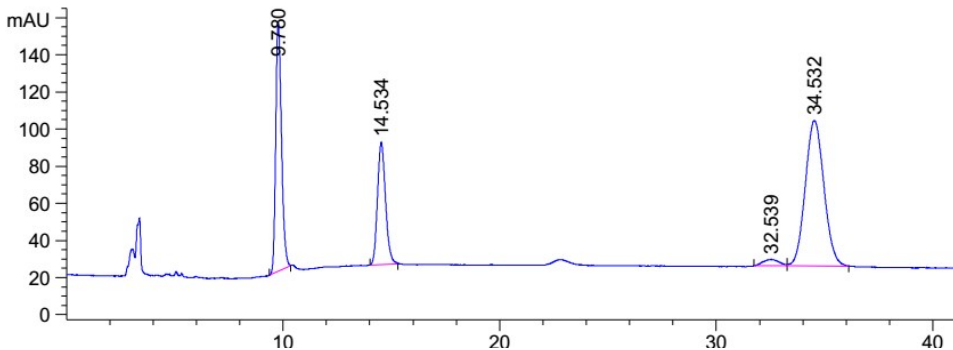
4qa

DAD1 A, Sig=254,4 Ref=360,100 (20190227\LNK003993.D)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.254	BB	0.2777	6978.85107	377.43103	45.9645
2	13.855	BB	0.3879	6968.08252	276.61566	45.8935
3	31.802	BV	0.7454	601.78363	10.30426	3.9635
4	33.807	VB	0.7154	634.42413	10.52291	4.1785

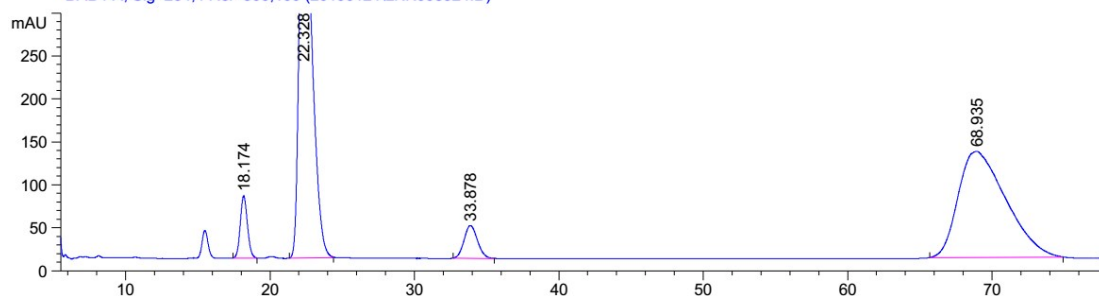
DAD1 C, Sig=210,8 Ref=360,100 (20190301\LNK003998.D)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.616	BV	0.2416	22.41961	1.27206	0.6263
2	5.067	VV	0.1434	9.76055	1.02205	0.2727
3	9.780	BB	0.2883	1013.92261	53.68915	28.3233
4	14.533	BB	0.3912	664.56439	25.91564	18.5642

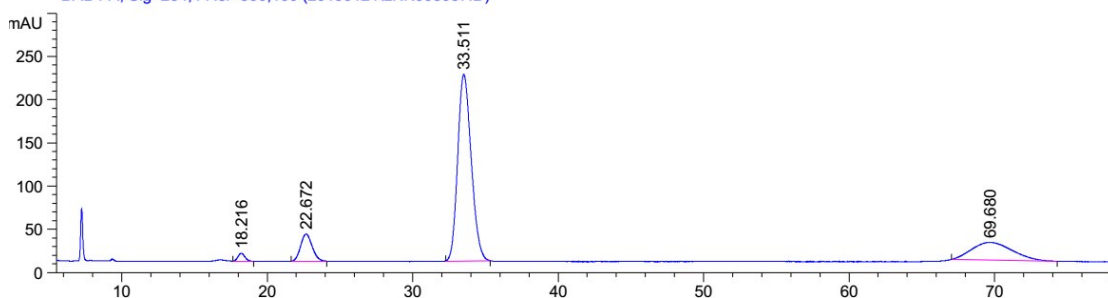
#### 4ra

DAD1 A, Sig=254,4 Ref=360,100 (20190121\LNK003924.D)



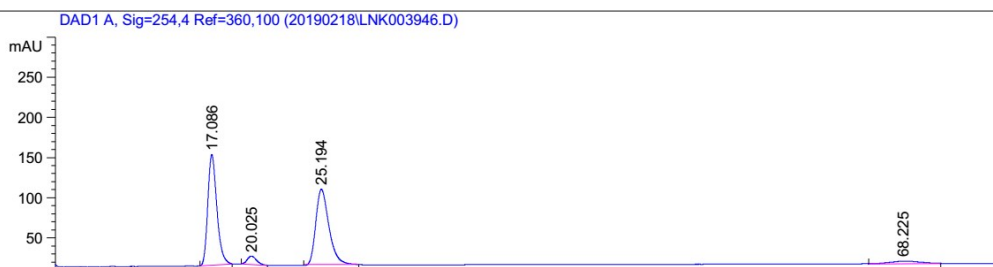
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.174	BB	0.5316	2513.71411	72.66383	4.0505
2	22.328	BB	0.9281	2.87736e4	476.77325	46.3650
3	33.878	BB	0.9063	2457.26465	38.20797	3.9596
4	68.935	BB	2.6880	2.83143e4	123.44321	45.6249

DAD1 A, Sig=254,4 Ref=360,100 (20190121\LNK003937.D)

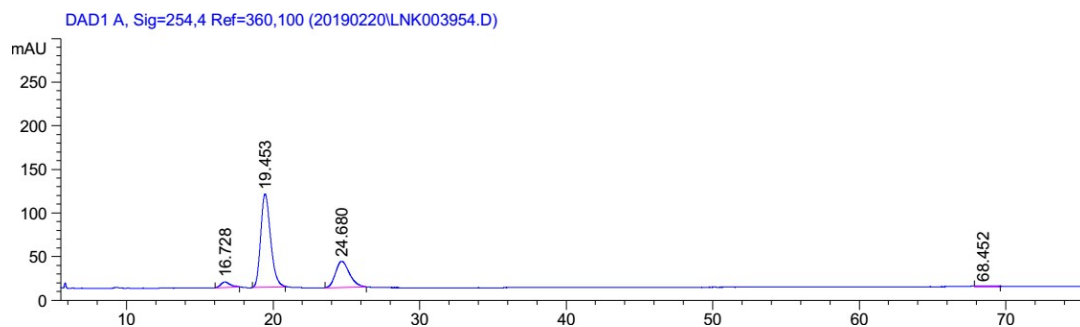


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.216	BB	0.4904	305.30771	9.12306	1.5212
2	22.672	BB	0.8176	1750.78662	31.54156	8.7233
3	33.511	BB	0.9975	1.40013e4	216.21440	69.7610
4	69.680	BB	2.2837	4012.97241	20.57299	19.9946

### 4sa

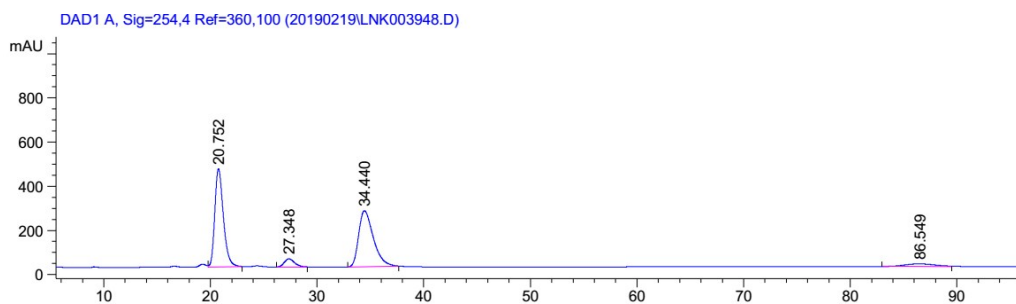


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.086	BB	0.7083	6424.97949	137.71626	46.6441
2	20.025	BB	0.5952	487.45416	10.46977	3.5388
3	25.194	MM R	1.1240	6335.46191	93.94252	45.9943
4	68.225	MM R	2.7877	526.56506	3.14812	3.8228



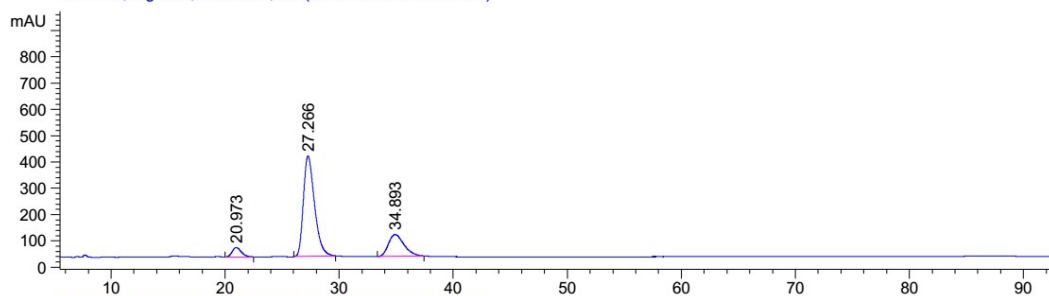
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.728	BB	0.6281	296.27661	6.39978	4.0201
2	19.453	BB	0.7192	5019.65039	107.02759	68.1102
3	24.680	BB	0.9019	1975.96240	30.02198	26.8113
4	68.452	MM R	1.5984	78.00200	8.13341e-1	1.0584
4	30.946	BB	0.8138	664.25830	10.47570	1.5118

### 4ta



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.752	VB	0.8541	2.48502e4	444.61746	45.8269
2	27.348	BB	0.9593	2484.14209	37.00160	4.5811
3	34.440	BB	1.4164	2.43423e4	253.92256	44.8901
4	86.549	MM R	3.4232	2549.65771	12.41372	4.7019

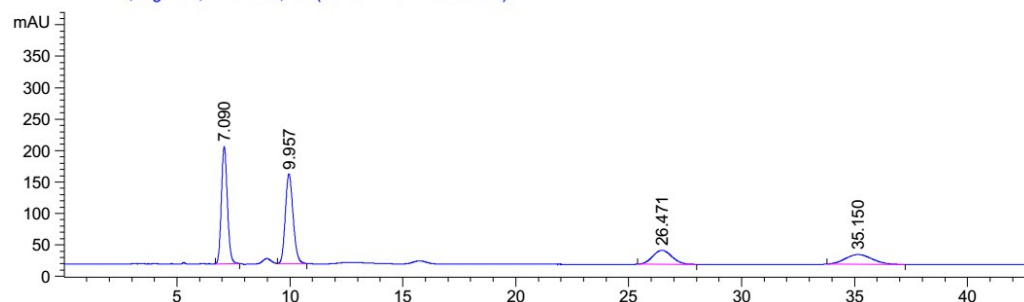
DAD1 A, Sig=254,4 Ref=360,100 (20190219\LNK003949.D)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.973	BB	0.8198	1984.73181	35.74358	5.5266
2	27.266	BB	1.0262	2.59580e4	382.27637	72.2814
3	34.893	BB	1.3726	7969.68896	83.27139	22.1920

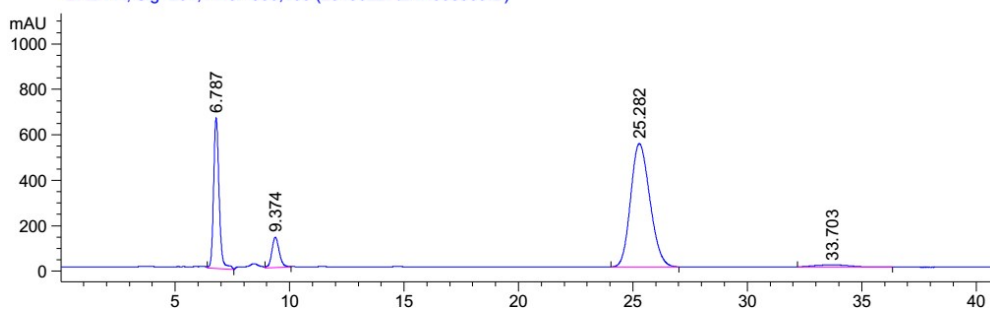
#### 4ua

DAD1 A, Sig=254,4 Ref=360,100 (20190227\LNK003988.D)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.090	BB	0.2842	3424.69727	186.51723	36.2074
2	9.957	VB	0.3690	3422.44678	143.10637	36.1836
3	26.471	BB	0.8113	1321.05334	22.29454	13.9668
4	35.150	BB	1.0124	1290.35669	15.54483	13.6422

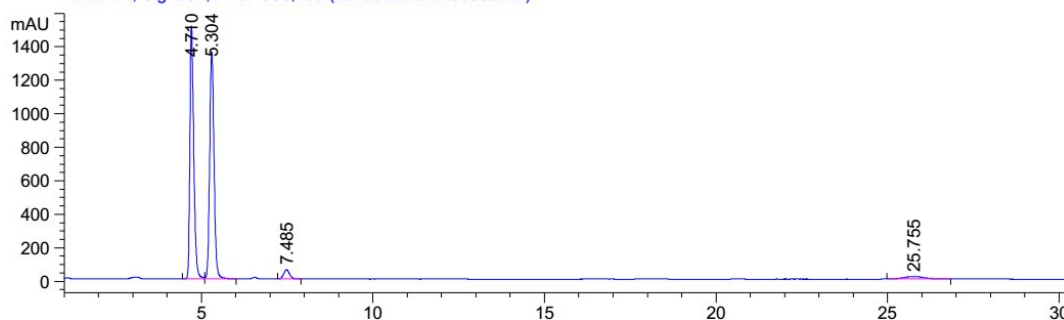
DAD1 A, Sig=254,4 Ref=360,100 (20190227LKNK003989.D)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.787	VV	0.2568	1.10790e4	663.39368	23.6601
2	9.374	VB	0.3472	2978.37769	133.03624	6.3606
3	25.282	BB	0.9090	3.17779e4	542.83453	67.8642
4	33.703	BB	1.2382	990.45007	9.37788	2.1152

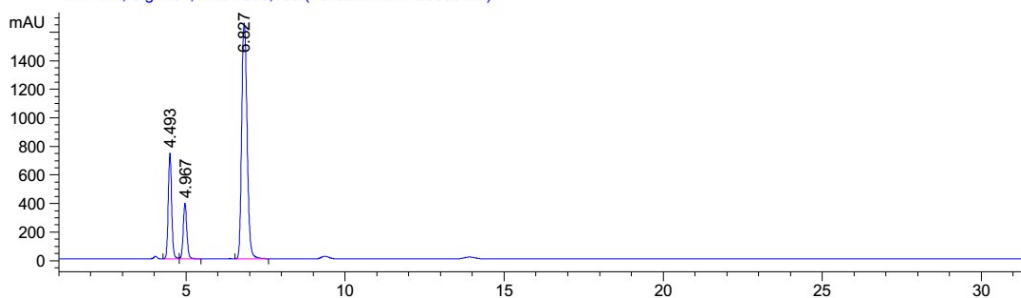
5

DAD1 A, Sig=254,4 Ref=360,100 (20190227LKNK003992.D)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.710	BV	0.1188	1.17752e4	1512.75781	46.7102
2	5.304	VB	0.1402	1.21142e4	1356.80481	48.0549
3	7.485	BB	0.1916	671.06683	54.50545	2.6620
4	25.755	BB	0.6388	648.61469	15.60917	2.5729

DAD1 A, Sig=254,4 Ref=360,100 (20190227LKNK003994.D)

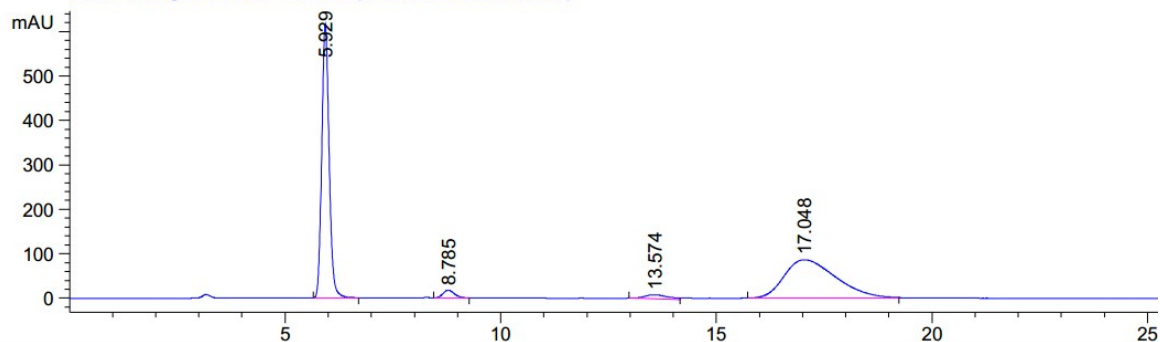




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.493	BV	0.1137	5468.62451	744.49805	19.4136
2	4.967	VB	0.1198	3072.37622	390.36728	10.9069
3	6.827	VB	0.1871	1.96280e4	1646.49976	69.6794

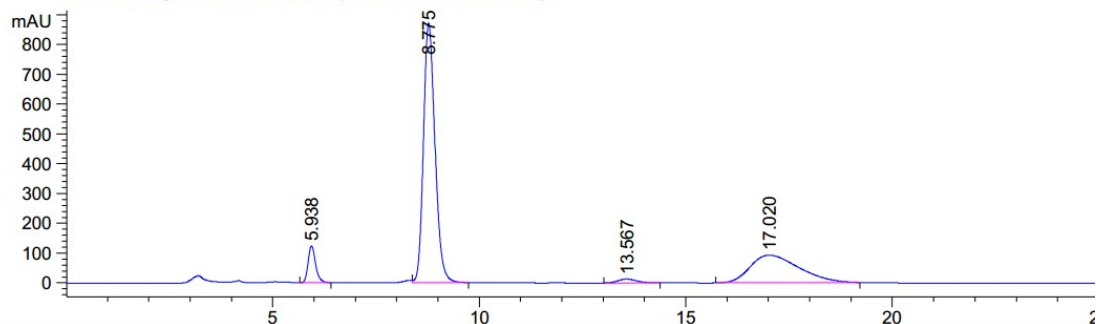
8

DAD1 A, Sig=254,4 Ref=360,100 (20181029\LNK003574.D)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.929	BB	0.1815	7261.36523	615.98218	48.1688
2	8.785	VB	0.2938	337.46716	17.75195	2.2386
3	13.574	MM R	0.6232	343.38284	9.18307	2.2779
4	17.048	BB	1.2198	7132.62256	86.15762	47.3148

DAD1 A, Sig=254,4 Ref=360,100 (20181029\LNK003575.D)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.938	VB	0.1883	1528.83716	123.64040	5.7636
2	8.775	VB	0.3005	1.69158e4	871.28900	63.7711
3	13.567	BB	0.4723	408.38867	13.14992	1.5396
4	17.020	BB	1.2397	7672.79150	92.69875	28.9258

## 5. Crystal data and ORTEP diagram for compound

X-ray data of **3ab**

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Empirical formula	C <sub>33</sub> H <sub>23</sub> ClN <sub>4</sub> O
Formula weight	527.00
Temperature	120 K
Wavelength	0.71073 Å
Crystal system, space group	triclinic, <i>P</i> -1
Unit cell dimensions	<i>a</i> = 9.3289 (4) Å, <i>α</i> = 87.2370 (10) deg. <i>b</i> = 10.9229 (5) Å, <i>β</i> = 78.6140 (10) deg. <i>c</i> = 12.8668 (6) Å, <i>γ</i> = 85.6810 (10) deg.
Volume	1280.91(10) Å <sup>3</sup>
Z, Calculated density	17, 1.730 Mg/cm <sup>3</sup>
Absorption coefficient	0.985 mm <sup>-1</sup>
F(000)	663
Crystal size	0.20 x 0.18 x 0.15 mm
Radiation	MoK $\alpha$ ( $\lambda$ = 0.71073)
Theta range for data collection	1.615 to 27.533 deg.
Index ranges	-12 ≤ <i>h</i> ≤ 12, -14 ≤ <i>k</i> ≤ 14, -16 ≤ <i>l</i> ≤ 16
Reflections collected	42789/5876 [ <i>R</i> (int) = 0.0327]
Completeness to theta = 25.242	99.8%
Absorption correction	multi-scan
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	5876/0/352
Goodness-of-fit on F <sup>2</sup>	1.148
Final R indexes [ <i>I</i> ≥ 2σ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0369, <i>wR</i> <sub>2</sub> = 0.1022
Final R indexes [all data]	<i>R</i> <sub>1</sub> = 0.0479, <i>wR</i> <sub>2</sub> = 0.1242
Largest diff. peak/hole / eÅ <sup>-3</sup>	0.571 and -0.515

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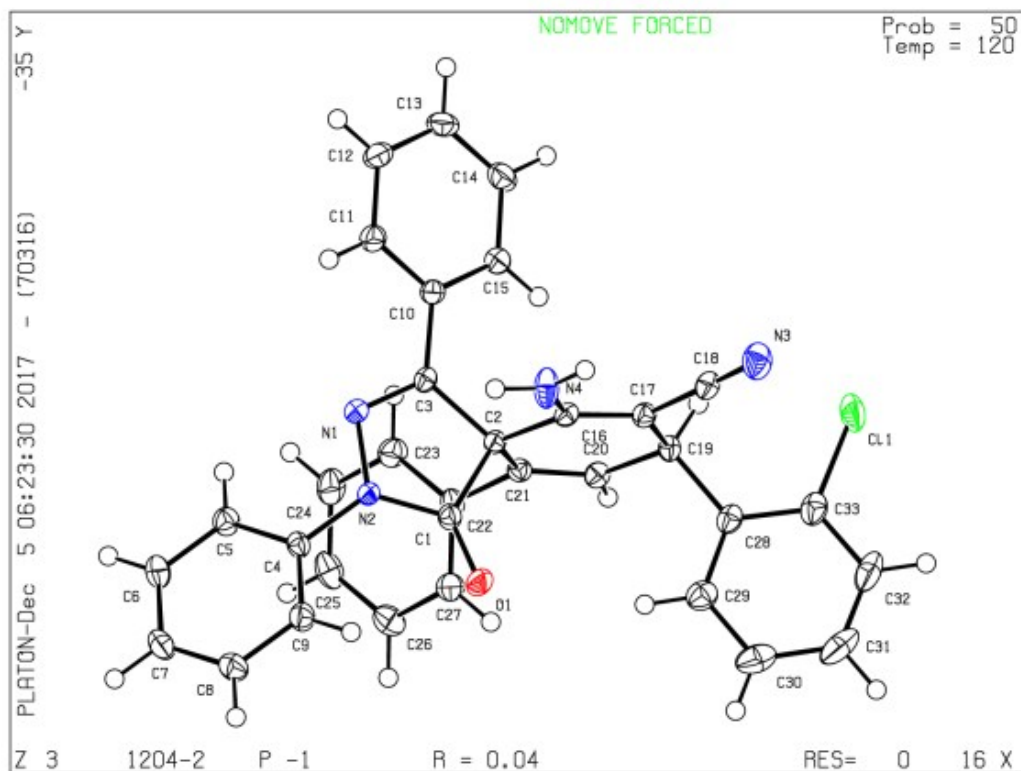


Figure S1. ORTEP drawing of **3ab**

The crystal was prepared from the solution of **3ab** in acetonitrile. CCDC 1821024 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

#### X-ray data of **4ab**

Empirical formula	$C_{33}H_{23}ClN_4O, CH_3CN$
Formula weight	568.06
Temperature	296.15 K
Wavelength	0.71073 Å
Crystal system, space group	orthorhombic, $P 21 21 21$
Unit cell dimensions	$a = 11.351(2)$ Å, $\alpha = 90$ deg. $b = 11.9996(17)$ Å, $\beta = 90$ deg. $c = 21.215(3)$ Å, $\gamma = 90$ deg.
Volume	$2889.7(8)$ Å <sup>3</sup>

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Z, Calculated density	4, 1.306 Mg/cm <sup>3</sup>
Absorption coefficient	0.170 mm <sup>-1</sup>
F(000)	1184
Crystal size	0.6 x 0.6 x 0.3 mm
Radiation	MoK $\alpha$ ( $\lambda = 0.71073$ )
Theta range for data collection	2.47 to 27.55 deg.
Limiting indices	$-7 \leq h \leq 15, -13 \leq k \leq 16, -27 \leq l \leq 28$
Reflections collected / unique	11645/ 7159 [ $R(\text{int}) = 0.0382$ ]
Completeness to theta = 25.242	99.6%
Absorption correction	Semi-empirical from equivalents
Refinement method	least-squares
Data / restraints / parameters	7159/2/386
Goodness-of-fit on F <sup>2</sup>	1.078
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0640, wR_2 = 0.1786$
Final R indexes [all data]	$R_1 = 0.0864, wR_2 = 0.1920$
Largest diff. peak/hole / e $\text{\AA}^{-3}$	0.317 and -0.279
Absolute structure parameter	0.02(5)

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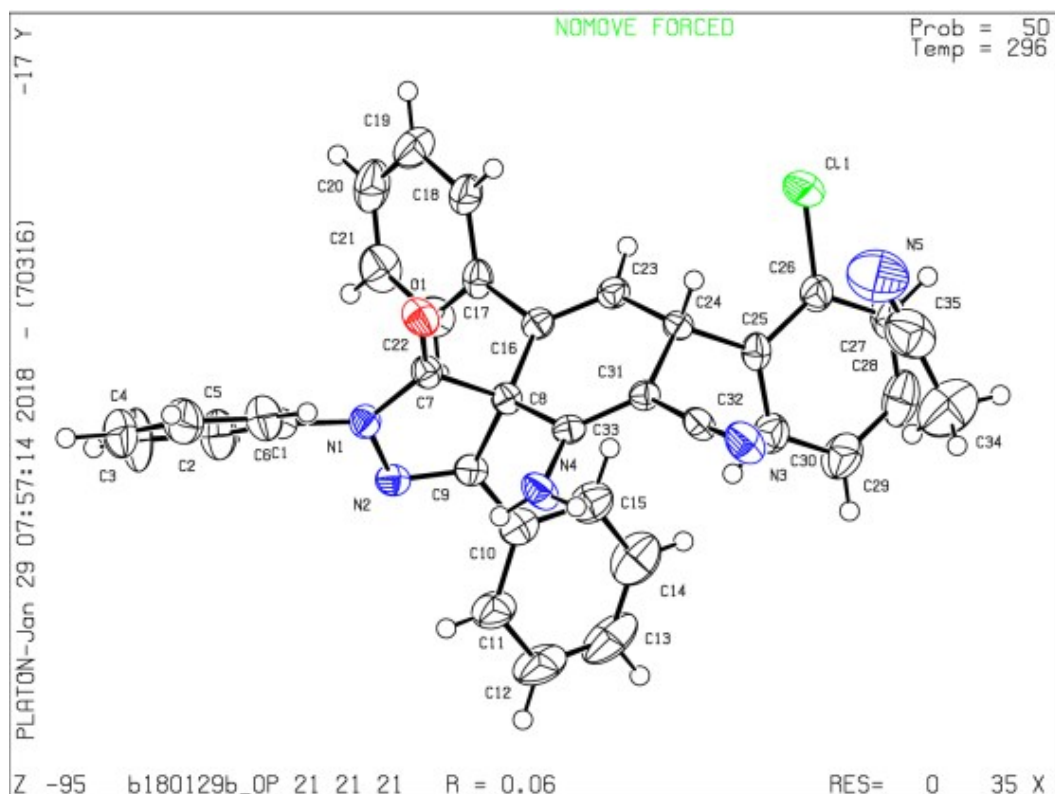


Figure S2. ORTEP drawing of **4ab**

The crystal was prepared from the solution of **4ab** in petroleum ether/n-hexane/ethyl acetate. CCDC 1820660 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).