

Supporting Information

Pd-Catalyzed Synthesis of 9,9'-Bifluorenylidene Derivatives via Dual C-H Activation of Bis-biaryl Alkynes

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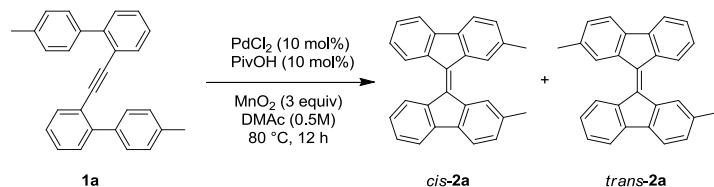
General Information. GC-MS analysis was performed on an Agilent 6890N GC interfaced to an Agilent 5973 mass-selective detector (30 m x 0.25 mm capillary column, HP-5MS). ¹H NMR and ¹³C NMR spectra were recorded on JEOL JNM AL 400 (400 MHz) and JEOL JNM AL 700 (700 MHz) spectrometers. ¹H NMR spectra are reported as follows: chemical shift in ppm (δ) relative to the chemical shift of CDCl₃ at 7.26 ppm, CD₂Cl₂ at 5.32 ppm, Acetone-*d*₆ at 2.04 ppm, integration, multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broadened), and coupling constants (Hz). ¹³C NMR spectra were recorded on JEOL JNM AL 400 (100.5 MHz) and JEOL JNM AL 400 (176.0 MHz) spectrometers with complete proton decoupling, and chemical shift reported in ppm (δ) relative to the central line for CDCl₃ at 77 ppm, CD₂Cl₂ at 53.8 ppm, Acetone-*d*₆ at 29.8 ppm. High-resolution mass spectra were obtained on a BRUKER APEXIII spectrometer and JEOL JMS-700 MStation operator. Column chromatography was carried out employing silica gel 60 N (spherical, neutral, 40~100 μ m, KANTO Chemical Co.) and Silica gel 60 (Merck). Analytical thin-layer chromatography (TLC) was performed on 0.2 mm precoated plate Kieselgel 60 F254 (Merck).

Materials. Anhydrous solvents (WAKO), palladium catalysts (Aldrich), activated MnO₂ (Aldrich) were purchased and used as received. The *cis*-**2a** and *trans*-**2a** were determined by noe and 2D NMR. The products **2b**, **2l**, and **2l'** were unambiguously confirmed by ¹H- and ¹³C NMR comparing with the reported literature.¹⁻³ The structures of new products were determined by ¹H, ¹³C NMR, and high-resolution mass.

References:

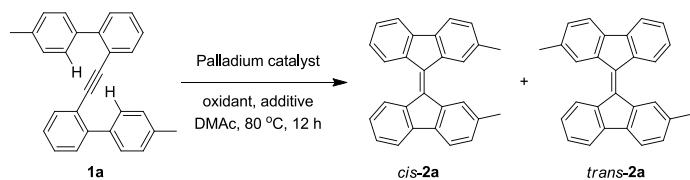
1. Kim, H. U.; Kim, J.-H.; Suh, H.; Kwak, J.; Kim, D.; Grimsdale, A. C.; Yoon, S. C.; Hwang, D.-H. *Chem. Commun.* **2013**, 49, 10950.
2. Assadi, N.; Pogodin, S.; Israel Agranat, I. *Eur. J. Org. Chem.* **2011**, 6773.
3. Levy, A.; Goldschmidt, M.; Agranat, I. *Lett. Org. Chem.* **2006**, 3, 579.

General procedure for Pd-catalyzed annulations of various bis-biphenyl alkynes



To an anhydrous DMAC (0.4 mL, 0.5 M) solution were added bis-biphenyl alkyne (**1a**) (0.2 mmol), PdCl₂ (3.5 mg, 0.02 mmol), PivOH (2 mg, 0.02 mmol), and MnO₂ (53 mg, 0.6 mmol). The reaction vial was purged with N₂ atmosphere and capped. The reaction mixture was stirred at room temperature for 5 min and then heated at 80 °C for 12 hours. After cooling to room temperature, the reaction mixture was passed through a short silica (Merck) pad using CH₂Cl₂/hexanes or EtOAc/Hexane as an eluent. After concentration, the residue was purified by quick silica gel (Merck) chromatography using a mixture of hexane and CH₂Cl₂ [100:1 to 50:1 (v/v)] as eluent to afford the product **2a** in 93 % yield as a red solid.

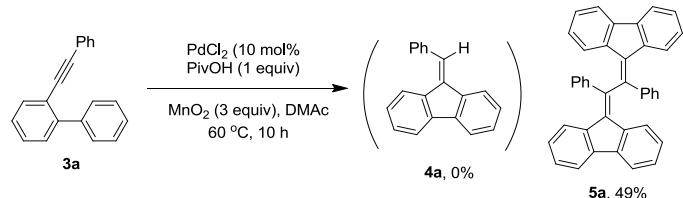
Table S1. Detailed optimization of reaction conditions^a



entry	[Pd] (10 mol%)	oxidant (2 equiv)	additive (10 mol%)	solvent (0.5 M)	yield of 2a (%) ^b
1	PdCl ₂	-	-	DMAC	3
2	Pd(OAc) ₂	-	-	DMAC	<1
3	PdCl ₂	K ₂ S ₂ O ₈	-	DMAC	5
4	PdCl ₂	Ag ₂ O	-	DMAC	4
5	PdCl ₂	<i>o</i> -chloronil	-	DMAC	0
6	PdCl ₂	CuCl ₂	-	DMAC	0
7	PdCl ₂	PhI(OAc) ₂	-	DMAC	trace
8	PdCl ₂	MnO ₂	-	DMAC	43
9	PdCl ₂	MnO ₂	PivOH	DMAC	82
10 ^c	PdCl ₂	O ₂	PivOH	DMAC	6
11	PdCl ₂	K ₂ S ₂ O ₈	PivOH	DMAC	18
12	PdCl ₂	Ag ₂ O	PivOH	DMAC	0
13	PdCl ₂	<i>o</i> -chloronil	PivOH	DMAC	0
14	PdCl ₂	CuCl ₂	PivOH	DMAC	0
15	PdCl ₂	PhI(OAc) ₂	PivOH	DMAC	trace
16	Pd(OAc) ₂	MnO ₂	PivOH	DMAC	12
17	Pd(OPiv) ₂	MnO ₂	PivOH	DMAC	4
18	Pd(OPiv) ₂	MnO ₂	-	DMAC	5
19	Pd ₂ (dba) ₃	MnO ₂	PivOH	DMAC	3
20	Pd(CH ₃ CN) ₄ (BF ₄) ₂	MnO ₂	PivOH	DMAC	5
21	PdBr ₂	MnO ₂	PivOH	DMAC	69
22	PdI ₂	MnO ₂	PivOH	DMAC	14
23	PdCl ₂ /AgOTf ^d	MnO ₂	PivOH	DMAC	9
24	-	MnO ₂	PivOH	DMAC	0
25	NiCl ₂	MnO ₂	PivOH	DMAC	0
26	PtCl ₂	MnO ₂	PivOH	DMAC	trace
27	Rh(PPh ₃) ₃ Cl	MnO ₂	PivOH	DMAC	0
28	PdCl ₂	MnO ₂	PivOH	DCE	trace
29	PdCl ₂	MnO ₂	PivOH	Toluene	0
30	PdCl ₂	MnO ₂	PivOH	1,4-Dioxane	0
31	PdCl ₂	MnO ₂ ^e	PivOH	DMAC	98 (93)
32 ^f	PdCl ₂	MnO ₂ ^e	PivOH	DMAC	87

^a Reaction conditions: **1a** (0.2 mmol), Pd catalyst (10 mol%), oxidant (2 equiv), DMAC (0.5 M), under N₂ atmosphere, 80 °C for 12 h. ^b ¹H NMR yield determined using CH₂Br₂ as an internal standard. The isolated yields are shown in parentheses. ^c The reaction time is 48 hours. ^d The ratio of is 1:2. ^e MnO₂ (3 equiv) was used. ^f The reaction carried out at room temperature for 24 hours. The ratio of *cis*-**2a** and *trans*-**2a** is 4:1.

Procedure for Pd-catalyzed annulation of 2-(phenylethynyl)-1,1'-biphenyl (**3a**)



To an anhydrous DMAc (0.6 mL, 0.5 M) solution were added 2-(phenylethynyl)-1,1'-biphenyl **3a** (0.3 mmol), PdCl₂ (5.3 mg, 0.03 mmol), PivOH (30 mg, 0.3 mmol), and MnO₂ (79 mg, 0.6 mmol). The reaction vial was purged with N₂ and capped. The reaction mixture was stirred at room temperature for 5 min and then heated at 60 °C for 10 hours. After cooling to room temperature, the reaction mixture was passed through a short silica (Merck) pad using CH₂Cl₂/hexanes as an eluent. After concentration, the residue was purified by silica gel (Merck) chromatography using a mixture of hexane and CH₂Cl₂ [10:1 to 3:1 (v/v)] as eluent to afford product **5a** in 49 % yield as a yellow solid (poor solubility in CH₂Cl₂). The structure of **5a** was determined by 1D- and 2D-NMR as well as HRMS.

Figure S1. ¹H NMR spectra changes for isomerization of *cis*-**2a** to *trans*-**2a**

As shown in Table 1, entry 15, the reaction of **1a** at room temperature gave the corresponding product **2a** as a 4:1 mixture of *cis*- and *trans*-isomers, which was determined by ¹H NMR spectrum. This ratio was changed to 2:1 after 3 days at room temperature and 1.3:1 after 8 days at same temperature. Finally, a 1:1 ratio of *cis*-**2a** and *trans*-**2a** was obtained at 80 °C after 12 h. These ratio changes clearly indicate that the reaction should proceed through a *cis*-annulation manner to produce *cis*-**2a** followed by isomerization of *cis*-**2a** to give *trans*-**2a**.

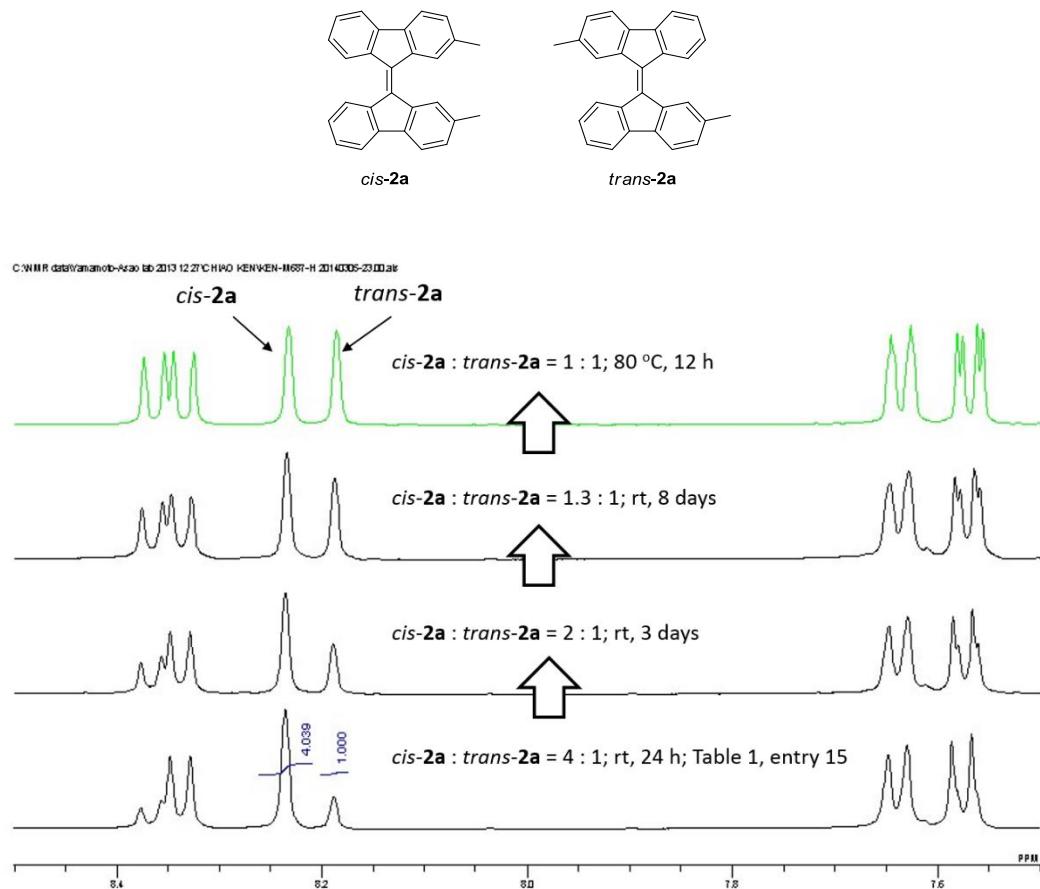
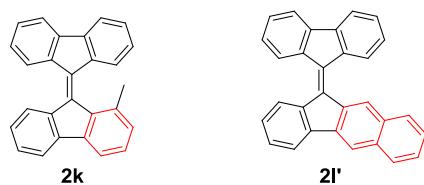
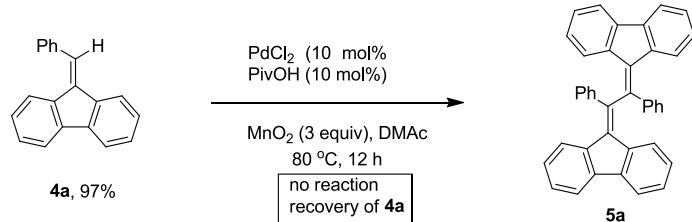


Figure S2. The structures of by-products **2k** and **2l'** in Table 2.



Scheme S1. Reaction of 4a with under our standard conditions for formation of 5a.

In order to confirm whether the reaction proceed through cation radical dimerization pathway from **4a**,¹ we carried out the following reaction. The reaction of **4a** prepared following the Gevorgyan's conditions (Scheme S3a) under our standard Pd-catalyzed conditions did not produce any expected products including the dimerization product **5a**. This result indicates that the potential cation radical dimerization pathway is unlike for the formation of **5a** from **4a** or **3a** under our new catalytic system.



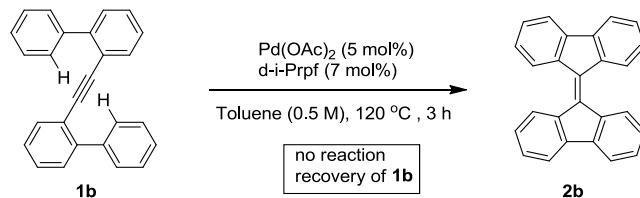
Reference

1. (a) Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1986**, *108*, 7356. (b) Kim, K. S.; Son, S. H.; Joo, Y. H.; Jung, D. I.; Hahn, C. S. *Chem. Lett.* **1987**, 2251.

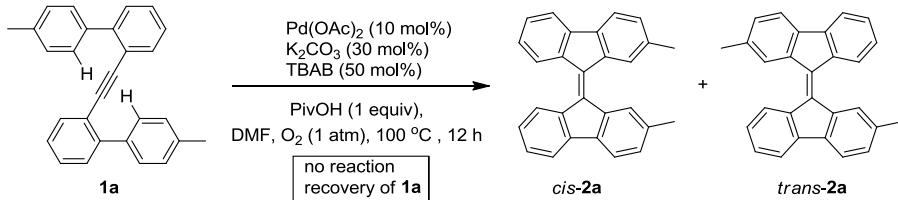
Scheme S2. Reactions of 1a using Gevorgyan, Jiao, and Itami's conditions

The bis-biarylalkyne **1b** with Gevorgyan did not produce any products including the expected product **2b** and **1b** was recovered in quantitative yield (Schemes S2a). The Jiao's condition for the reaction of **1a** was totally inactive (Scheme S2b). The reaction of **1a** under the Itami's condition gave only a 10% yield of the corresponding product **2a** (1:1) along with decomposition of **1a** (Scheme S2c).

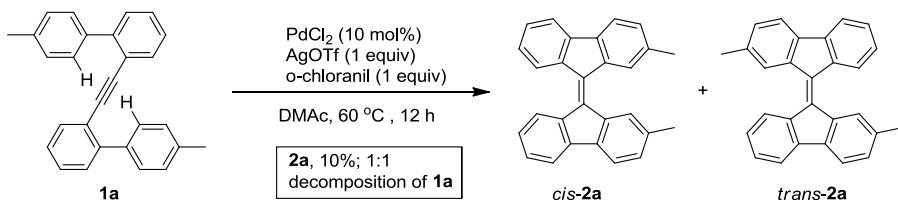
(a) Gevorgyan's condition²



(b) Jiao's condition³



(c) Itami's condition⁴



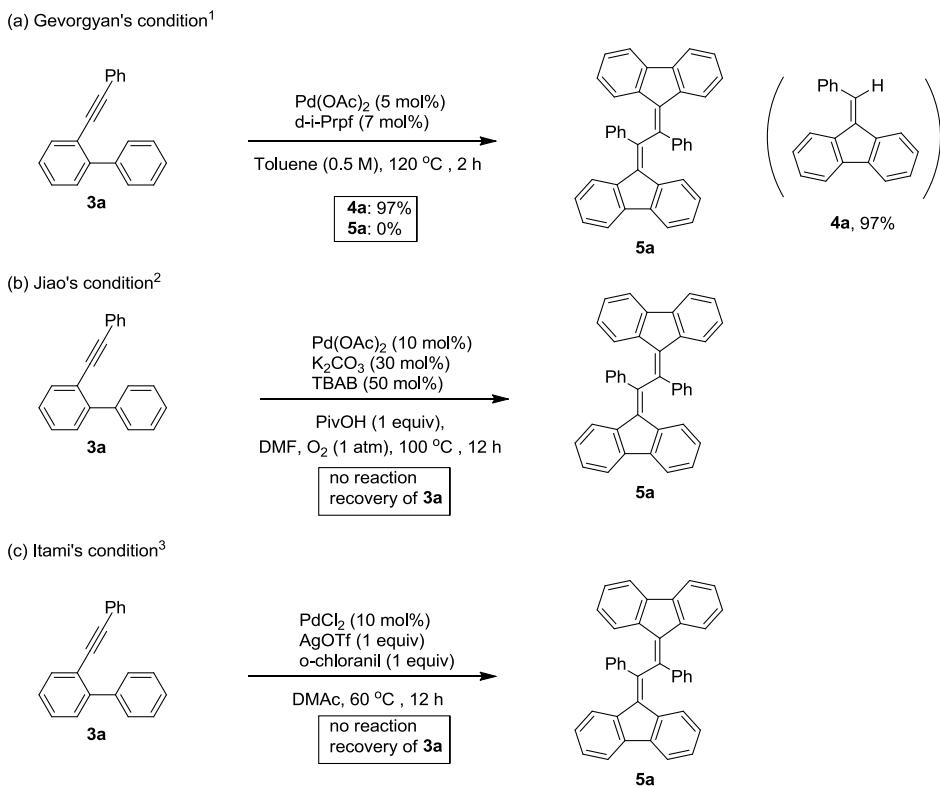
References:

2. Chernyak, N.; Gevorgyan, V. *J. Am. Chem. Soc.* **2008**, *130*, 5636.

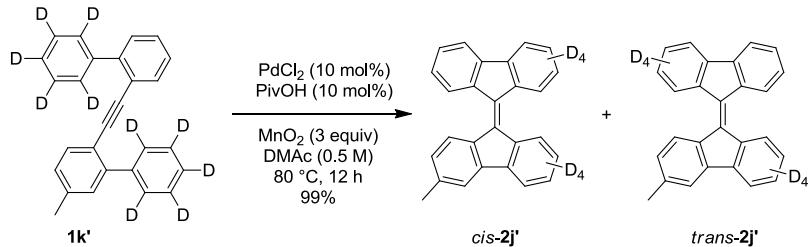
3. Shi, Z.; Ding, S.; Cui, Y.; Jiao, N. *Angew. Chem., Int. Ed.* **2009**, *48*, 7895.
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Scheme S3. Reactions of **3a using Gevorgyan, Jiao, and Itami's conditions**

The reaction of *o*-alkynyl biaryl **3a** with Gevorgyan's condition produced the corresponding product **4a** in 97% yield without formation of the dimerization product **5a**, which is consistent with the reported literature. The reactions of **3a** with Jiao and Itami's conditions did not afford **4a** and **5a**, and **3a** was recovered mainly with some decomposition. These results combined with the observations in Scheme S1 indicate that our new catalytic system is unique for implementation of the present double cyclization, which may proceed under totally different pathway compared with the previously reported methodologies.¹



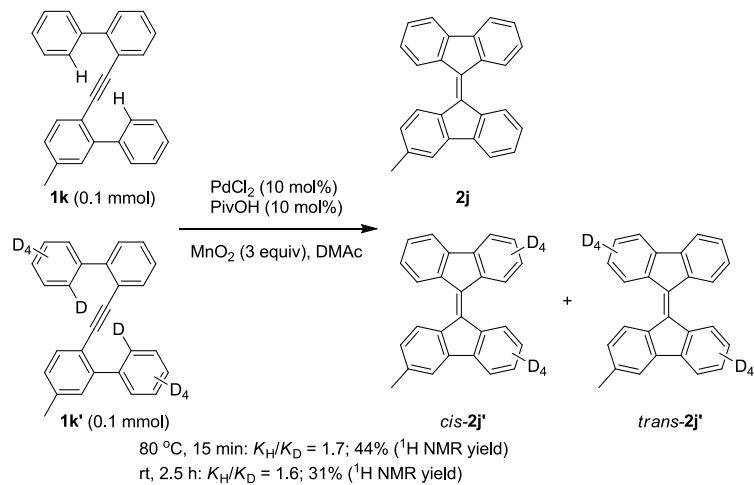
Scheme S4. Procedure for Pd-catalyzed annulations of deuterated bis-biphenyl alkynes (1k'**)**



To an anhydrous DMAc (0.4 mL, 0.5 M) solution were added deuterated bis-biphenyl alkyne (**1k'**) (0.2 mmol), PdCl₂ (3.5 mg, 0.02 mmol), PivOH (2 mg, 0.02 mmol), and MnO₂ (53 mg, 0.6 mmol). The reaction vial was purged with N₂ and capped. The reaction mixture was stirred at room temperature for 5 min and then heated at 80 °C for 12 hours. After cooling to room temperature, the reaction mixture was filtered through a short silica (Merck) pad using EtOAc/Hexane as an eluent. After concentration, the

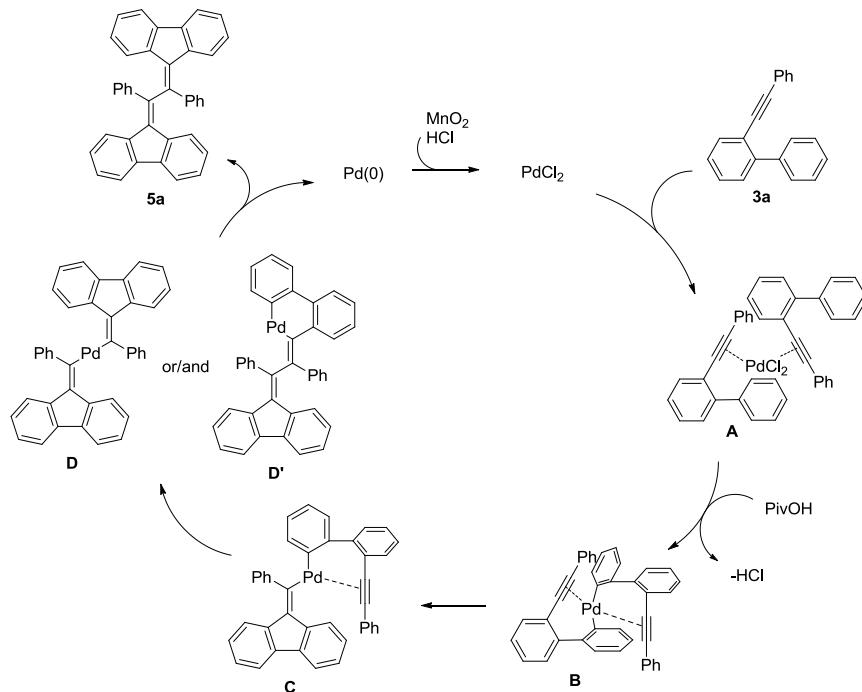
residue was purified by quick silica gel (Merck) chromatography using a mixture of hexane and CH_2Cl_2 [100:1 to 50:1 (v/v)] as eluent, affording a mixture of *cis*-**2j'** and *trans*-**2j'** in 99 % yield as a red solid.

Scheme S5. Intermolecular kinetic isotope effect measurements



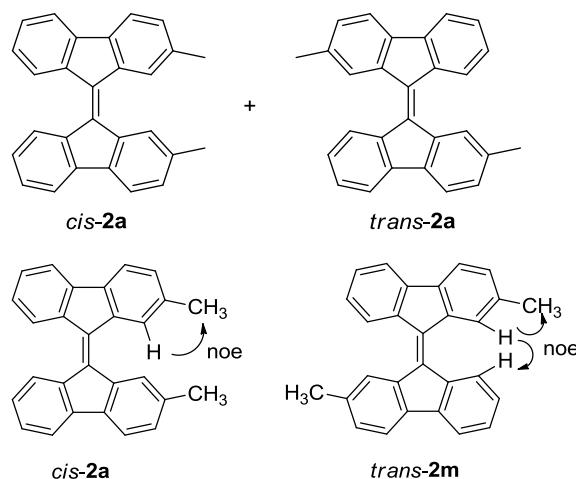
To a DMAc solution (0.5 M, 0.4 mL) were added **1k** (0.1 mmol) and **1k'** (0.1 mmol), PdCl₂ (3.5 mg, 0.02 mmol), PivOH (2 mg, 0.02 mmol), and MnO₂ (53 mg, 0.6 mmol) under an N₂ atmosphere at room temperature. The reaction mixture was heated at 80 °C for 15 min or stirred at room temperature for 2.5 h. The reaction mixture was allowed to cool down to room temperature and was passed through a short silica (Merck) plug with DCM/Hexane as eluent. The filtrate was concentrated under vacuum and the kinetic isotope effect was analyzed from the crude ¹H NMR spectrum without further purification.

Scheme S6. Proposed mechanism for Pd-catalyzed dimerization of 3a (Alternative possibility for the formation of 5a was suggested by a referee, see: Masui, K.; Ikegami, H.; Mori, A. *J. Am. Chem. Soc.* **2004**, 126, 5074.



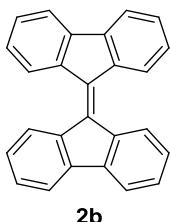
Analytical data of compounds

(Z and E)-2,2'-Dimethyl-9,9'-bifluorenylidene (2a) (for noe and 2D NMR, see NMR spectra)



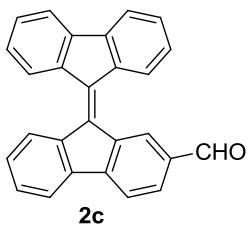
Red solid; ^1H NMR (400 MHz, CDCl_3) δ 8.42 (d, J = 7.6 Hz, 2H, *trans*-**2a**), 8.39 (d, J = 8.0 Hz, 2H, *cis*-**2a**), 8.29 (s, 2H, *cis*-**2a**), 8.24 (s, 2H, *trans*-**2a**), 7.70–7.65 (m, 4H), 7.63–7.57 (m, 4H), 7.37–7.30 (m, 4H), 7.25–7.15 (m, 8H), 2.40 (s, 6H), 2.40 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 141.3, 141.2, 140.9, 140.8, 138.7(4), 138.7(1), 138.4(4), 138.4(1), 138.2, 138.1, 136.4, 136.3, 129.9, 129.8, 128.9, 127.0(9), 127.0(6), 126.5, 126.4, 126.2(5), 126.2(0), 119.5, 119.4(9), 119.4(4), 21.7(8), 21.7(2); HRMS (MALDI): [m/z]: calcd for $\text{C}_{28}\text{H}_{20}$, 356.15595; found, 356.15591.

9,9'-Bifluorenylidene (2b)



Red solid; ^1H NMR (400 MHz, CDCl_3) δ 8.41 (d, J = 7.6 Hz, 4H), 7.72 (d, J = 7.2 Hz, 4H), 7.35 (dd, J = 7.2, 7.2 Hz, 4H), 7.23 (dd, J = 7.6, 7.6 Hz, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 141.1, 140.8, 138.1, 129.0, 126.7, 126.5, 119.7; HRMS (APCI): $[\text{M}+\text{H}]^+$: calcd for $\text{C}_{26}\text{H}_{17}$, 329.13248; found, 329.13244.

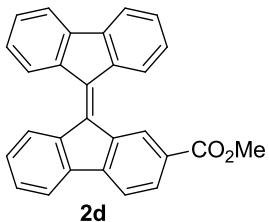
9,9'-Bifluorenylidene]-2-carbaldehyde (2c)



Red solid; ^1H NMR (400 MHz, CDCl_3) δ 9.97 (s, 1H), 8.87 (s, 1H), 8.46 (d, J = 7.6 Hz, 1H), 8.37 (d, J = 7.6 Hz, 1H), 8.27 (d, J = 8.0 Hz, 1H), 7.92–7.85 (m, 2H), 7.82 (d, J = 7.2 Hz, 1H), 7.71 (dd, J = 7.6, 2.8 Hz, 2H), 7.45–7.28 (m, 4H), 7.26–7.17 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 191.5, 145.9, 142.7, 141.5(7), 141.5(0), 139.5, 139.1, 138.7, 138.3, 137.7(7), 137.7(4), 135.0, 129.8, 129.7(3), 129.7(2), 129.1, 128.4,

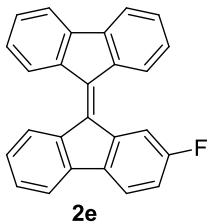
128.1, 127.1, 126.9, 126.5, 120.8, 120.1, 120.0, 119.9; HRMS (APCI): $[M+H]^+$: calcd for $C_{27}H_{17}O$, 357.12739; found, 357.12736.

Methyl [9,9'-bifluorenylidene]-2-carboxylate (2d)



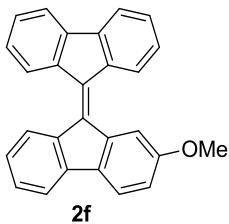
Red solid; 1H NMR (400 MHz, $CDCl_3$) δ 9.05 (s, 1H), 8.42 (d, J = 8.0 Hz, 1H), 8.35 (d, J = 8.0 Hz, 1H), 8.28 (d, J = 8.0 Hz, 1H), 8.04 (dd, J = 8.0, 0.8 Hz, 1H), 7.80–7.73 (m, 2H), 7.72–7.65 (m, 2H), 7.40–7.15 (m, 6H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 144.7, 142.2, 141.4(9), 141.4(4), 139.8, 139.3, 138.9, 137.9, 137.8, 130.1, 129.5, 129.1, 128.3, 127.7(9), 127.7(5), 127.0, 126.9, 126.8, 126.6, 126.5, 120.6, 119.9, 119.8, 119.4, 52.1; HRMS (APCI): $[M+H]^+$: calcd for $C_{28}H_{19}O_2$, 387.13796; found, 387.13793.

2-Fluoro-9,9'-bifluorenylidene (2e)



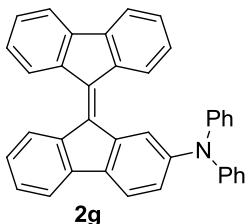
Red solid; 1H NMR (400 MHz, $CDCl_3$) δ 8.40–8.30 (m, 3H), 8.07 (dd, J = 10.0, 2.0 Hz, 1H), 7.73–7.65 (m, 2H), 7.65–7.58 (m, 2H), 7.38–7.27 (m, 3H), 7.26–7.15 (m, 3H), 7.08–7.00 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1 (d, J^1 = 241.7 Hz), 141.9, 141.3, 141.2, 140.3, 139.8, 139.7, 139.6, 138.0 (d, J^8 = 1.6 Hz), 137.9, 137.6, 137.1 (d, J^7 = 2.4 Hz), 129.4 (d, J^6 = 5.7 Hz), 129.1, 126.9, 126.8, 126.5, 126.3, 120.5 (d, J^4 = 8.3 Hz), 119.8 (d, J^5 = 7.4 Hz), 119.4, 115.8 (d, J^3 = 23.9 Hz), 113.1 (d, J^2 = 24.7 Hz); HRMS (APCI): $[M+H]^+$: calcd for $C_{26}H_{16}F$, 347.12306; found, 347.12302.

2-Methoxy-9,9'-bifluorenylidene (2f)



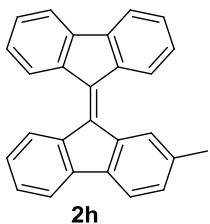
Dark red solid; 1H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, J = 7.6 Hz, 1H), 8.39 (d, J = 8.0 Hz, 1H), 8.32 (d, J = 7.6 Hz, 1H), 7.98 (d, J = 2.4 Hz, 1H), 7.70 (d, J = 7.6 Hz, 2H), 7.60–7.54 (m, 2H), 7.37–7.10 (m, 6H), 6.90 (dd, J = 8.0, 2.0 Hz, 1H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 141.4, 141.2, 141.1(6), 141.1(2), 140.9, 139.5, 138.1, 138.0(5), 138.0(3), 134.6, 129.1, 129.0, 126.7, 126.6(7), 126.6(2), 126.5, 126.2, 125.7, 120.4, 119.8, 119.7, 119.0, 115.7, 111.7, 55.6; HRMS (APCI): $[M+H]^+$: calcd for $C_{27}H_{19}O$, 359.14304; found, 359.14303.

***N,N*-Diphenyl-[9,9'-bifluorenylidene]-2-amine (2g)**



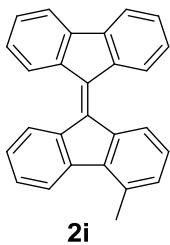
Dark red solid; ^1H NMR (400 MHz, CDCl_3) δ 8.37 (d, J = 8.0 Hz, 1H), 8.34 (d, J = 7.6 Hz, 1H), 8.00 (d, J = 2.0 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.65-7.55 (m, 4H), 7.33-7.23 (m, 6H), 7.21-7.06 (m, 8H), 7.05-6.98 (m, 2H), 6.80-6.73 (1H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.6, 147.0, 141.2, 141.1, 140.9, 140.8, 140.2, 139.4, 137.9, 137.7, 136.2, 129.1(8), 129.1(2), 129.0, 128.8, 126.7, 126.6, 126.2, 126.0, 125.6, 123.9, 123.7, 122.4, 120.3, 119.6, 119.5, 119.2; HRMS (APCI): $[\text{M}+\text{H}]^+$: calcd for $\text{C}_{38}\text{H}_{26}\text{N}$, 496.20598; found, 496.20590.

2-Methyl-9,9'-bifluorenylidene (2h)



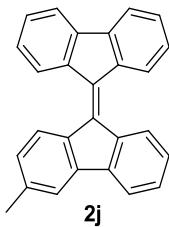
Red solid; ^1H NMR (400 MHz, CDCl_3) δ 8.50-8.35 (m, 3H), 8.25 (s, 1H), 7.75-7.67 (m, 2H), 7.65 (d, J = 7.2 Hz, 1H), 7.58 (d, J = 7.6 Hz, 1H), 7.40-7.27 (m, 3H), 7.26-7.10 (m, 4H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 141.2, 141.1, 141.0(7), 141.0(3), 140.4, 138.7, 138.3, 138.1(4), 138.1(1), 136.3, 129.9, 128.9, 128.8, 127.0, 126.6, 126.5(8), 126.5(3), 126.5(1), 126.3, 126.2, 119.7(2), 119.7(0), 119.5, 119.4, 21.7; HRMS (APCI): $[\text{M}+\text{H}]^+$: calcd for $\text{C}_{27}\text{H}_{19}$, 343.14813; found, 343.14811.

4-Methyl-9,9'-bifluorenylidene (2i)



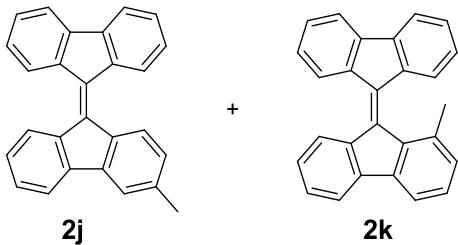
Red solid; ^1H NMR (400 MHz, CDCl_3) δ 8.44 (d, J = 8.0 Hz, 1H), 8.39 (d, J = 8.0 Hz, 2H), 8.32-8.27 (m, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.70 (d, J = 7.6 Hz, 2H), 7.38-7.29 (m, 3H), 7.25-7.17 (m, 3H), 7.15-7.07 (m, 2H), 2.73 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 142.1, 141.4, 141.1, 140.4, 139.1, 138.6(3), 138.6(0), 138.3, 132.8, 131.7, 129.0, 128.9, 126.7, 126.6(8), 126.6(3), 126.6(0), 126.2, 126.0, 124.5, 123.1, 119.7(7), 119.7(5), 21.1; HRMS (MALDI): $[\text{m}/\text{z}]$: calcd for $\text{C}_{27}\text{H}_{18}$, 342.14030; found, 342.14036.

3-Methyl-9,9'-bifluorenylidene (2j)



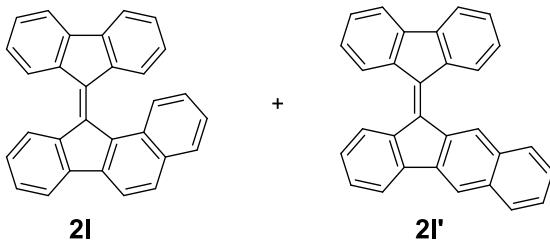
Red solid; ^1H NMR (400 MHz, CD_2Cl_2) δ 8.40-8.30 (m, 3H), 8.24 (d, J = 8.0 Hz, 1H), 7.75-7.67 (m, 3H), 7.54 (s, 1H), 7.37-7.30 (m, 3H), 7.25-7.15 (m, 3H), 7.04 (d, J = 8.0 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 141.7, 141.5, 141.3, 141.2, 140.1, 140.0, 138.8, 138.5, 138.4, 135.9, 129.3, 129.1, 128.1, 127.0(6), 127.0(4), 126.9, 126.8(4), 126.8(0), 120.7, 120.0(9), 120.0(0), 21.9; HRMS (MALDI): [m/z]: calcd for $\text{C}_{27}\text{H}_{18}$, 342.14030; found, 342.14027.

3-Methyl-9,9'-bifluorenylidene (2j) and 1-methyl-9,9'-bifluorenylidene (2k) (4:1)



Red solid; ^1H NMR (400 MHz, CDCl_3) δ 8.46 (d, J = 8.0 Hz, 1H, **2k**), 8.38 (d, J = 7.6 Hz, 3H, **2j**), 8.34 (d, J = 7.6 Hz, 1H, **2k**), 8.26 (d, J = 8.0 Hz, 1H, **2j**), 7.75 (d, J = 7.2 Hz, 1H, **2k**), 7.71 (d, J = 7.2 Hz, 2H, **2j**; 2H, **2k**), 7.68 (d, J = 7.2 Hz, 1H, **2j**), 7.63 (d, J = 7.2 Hz, 1H, **2k**), 7.51 (s, 1H, **2j**), 7.40-7.27 (m, 3H, **2j**; 5H, **2k**), 7.24-7.12 (m, 3H, **2j**; 4H, **2k**), 7.03 (d, J = 8.0 Hz, 1H, **2j**), 2.46 (s, 3H, **2j**), 2.29 (s, 3H, **2k**); ^{13}C NMR (100 MHz, CDCl_3) δ **2j&2k**, 142.0, 141.5, 141.4, 141.2, 141.0, 140.9, 140.7, 140.5, 140.1(8), 140.1(1), 139.8, 139.6, 139.5(4), 139.5(0), 138.5, 138.2(9), 138.2(5), 138.1, 137.6, 136.9, 135.6, 130.9, 129.1, 128.9, 128.8, 128.7, 128.5, 128.2, 127.7, 127.5, 126.9(8), 126.9(1), 126.8, 126.6(7), 126.6(4), 126.5(4), 126.5(2), 126.4, 124.6, 120.4, 120.0, 119.7(9), 119.7(5), 119.6(8), 119.6(6), 117.3, 23.9, 21.8; HRMS (MALDI): [m/z]: calcd for $\text{C}_{27}\text{H}_{18}$, 342.14030; found, 342.14035.

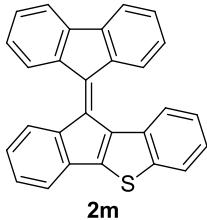
11-(9H-Fluoren-9-ylidene)-11H-benzo[a]fluorine (2l) and 11-(9H-fluoren-9-ylidene)-11H-benzo[b]fluorine (2l') (1.9:1)



Dark red solid; ^1H NMR (400 MHz, CDCl_3) δ 8.89 (s, 1H, **2l'**), 8.60 (d, J = 8.0 Hz, 1H, **2l'**), 8.47 (d, J = 8.0 Hz, 1H, **2l**), 8.46 (d, J = 8.0 Hz, 1H, **2l'**), 8.43 (d, J = 7.6 Hz, 1H, **2l**; 1H, **2l'**), 8.09 (s, 1H, **2l'**), 8.03 (d, J = 8.4 Hz, 1H, **2l**), 7.95-7.82 (m, 2H, **2l'**; 3H, **2l**), 7.80-7.72 (m, 3H, **2l'**; 1H, **2l**), 7.70 (dd, J = 7.2, 7.2 Hz, 2H, **2l**), 7.52-7.30 (m, 5H, **2l'**; 3H, **2l**), 7.30-7.19 (m, 3H, **2l'**; 4H, **2l**), 7.16 (dd, J = 7.6, 7.6 Hz, 1H, **2l**), 6.90 (dd, J = 7.6, 7.6 Hz, 1H, **2l**); ^{13}C NMR (100 MHz, CDCl_3) δ **2l&2l'**, 142.3, 142.0(7), 142.0(3), 140.9(9), 140.9(7),

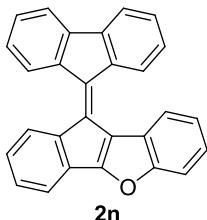
140.8(6), 140.8(5), 140.3, 140.1, 140.0, 139.9, 139.7, 139.5, 139.3, 138.4, 138.3(9), 138.3(4), 138.1, 136.8, 133.9, 133.8, 132.9, 132.0, 131.6, 129.6, 129.3(4), 129.3(1), 129.2(5), 129.2(1), 128.8(8), 128.8(3), 128.7, 128.6, 128.5, 128.3, 128.2, 127.9, 127.3, 127.2, 126.8, 126.7, 126.6(4), 126.6(2), 126.5, 126.3, 126.1, 125.7(3), 125.7(0), 124.7, 124.6, 120.5, 120.0, 119.8, 119.7, 119.5, 119.4, 118.3, 117.8; HRMS (MALDI): [m/z]: calcd for $C_{30}H_{18}$, 378.14030; found, 378.14035.

10-(9*H*-Fluoren-9-ylidene)-10*H*-benzo[*b*]indeno[2,1-*d*]thiophene (2m)



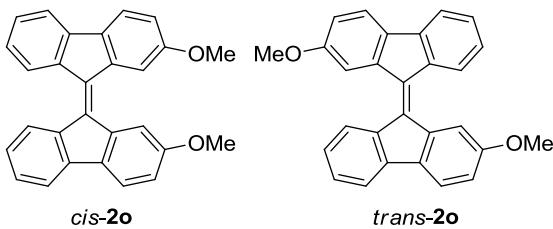
Dark red solid; 1H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, J = 8.0 Hz, 1H), 8.32 (d, J = 8.4 Hz, 1H), 7.82 (d, J = 7.6 Hz, 1H), 7.76 (d, J = 7.6 Hz, 1H), 7.72 (d, J = 7.2 Hz, 1H), 7.67 (d, J = 7.6 Hz, 1H), 7.60 (d, J = 7.6 Hz, 1H), 7.45–7.10 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 143.6, 141.8, 141.7, 140.5, 139.0, 138.5, 138.3, 136.8, 136.2, 134.7, 133.5, 129.0, 128.8(8), 128.8(6), 128.4, 127.8, 126.7, 126.6(9), 126.6(6), 125.8, 125.4, 124.7, 123.9, 123.8, 120.1, 119.9, 119.6; HRMS (APCI): [M+H] $^+$: calcd for $C_{28}H_{17}S$, 385.10455; found, 385.10451.

10-(9*H*-Fluoren-9-ylidene)-10*H*-indeno[1,2-*b*]benzofuran (2n)



Dark red solid; 1H NMR (400 MHz, $CDCl_3$) δ 8.40–8.30 (m, 2H), 7.94 (d, J = 8.0 Hz, 1H), 7.80–7.70 (m, 2H), 7.60–7.50 (m, 2H), 7.45–7.10 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 160.7, 141.6, 141.1, 140.7, 138.7, 138.6, 137.7, 130.8, 130.7, 128.9, 128.8, 128.3, 128.1, 127.2, 127.1(8), 127.1(3), 126.8, 126.7, 124.5, 123.8, 123.2, 122.9, 120.4, 120.1, 119.6, 118.4, 112.3; HRMS (MALDI): [m/z]: calcd for $C_{28}H_{16}O$, 368.11957; found, 368.11955.

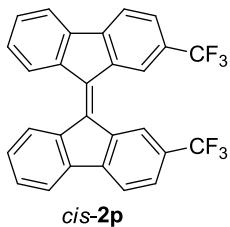
(*Z* and *E*)-2,2'-Dimethoxy-9,9'-bifluorenylidene (2o)



Dark red solid; 1H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, J = 8.0 Hz, 2H, *trans*-2o), 8.31 (d, J = 8.0 Hz, 2H, *cis*-2o), 8.04 (d, J = 2.8 Hz, 2H, *cis*-2o), 7.97 (d, J = 2.4 Hz, 2H, *trans*-2o), 7.60–7.52 (m, 8H), 7.30–7.26 (m, 4H), 7.15–7.08 (m, 4H), 6.93–6.86 (m, 4H), 3.79 (s, 6H), 3.78 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0(4), 159.0(0), 141.4, 141.3, 141.1, 139.5, 139.4, 138.0, 137.9, 134.6, 134.5, 129.2, 129.1, 126.5, 126.2, 125.7,

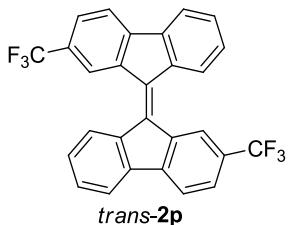
125.6, 120.4(5), 120.4(0), 119.1, 119.0, 115.7, 111.6, 111.4, 55.6, 55.5; HRMS (APCI): [M+H]⁺: calcd for C₂₈H₂₁O₂, 389.15361; found, 389.15354.

(Z)-2,2'-Bis(trifluoromethyl)-9,9'-bifluorenylidene (*cis*-2p)



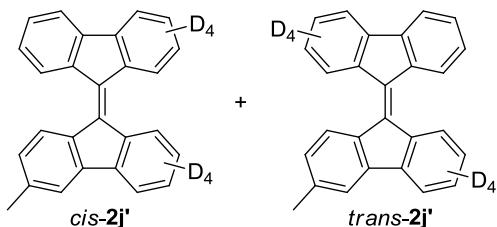
Red solid; ¹H NMR (400 MHz, Acetone-*d*₆) δ 8.54 (s, 2H), 8.45 (d, *J* = 8.0 Hz, 2H), 8.08 (d, *J* = 7.6 Hz, 2H), 7.98 (d, *J* = 7.6 Hz, 2H), 7.77-7.70 (m, 2H), 7.53-7.45 (m, 2H), 7.42-7.35 (m, 2H); ¹³C NMR (175 MHz, Acetone-*d*₆) δ 145.9, 141.9, 141.3, 139.3, 139.0, 131.7, 129.8, 129.7 (q, *J*² = 32.0 Hz), 127.9, 127.7, 125.8 (q, *J*¹ = 269.6 Hz), 124.6, 122.6, 122.2; HRMS (APCI): [m/z]: calcd for C₂₈H₁₄F₆, 464.09942; found, 464.09939.

(E)-2,2'-Bis(trifluoromethyl)-9,9'-bifluorenylidene (*trans*-2p)



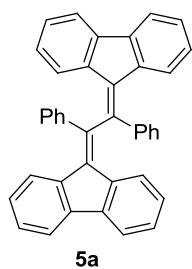
Red solid; ¹H NMR (400 MHz, CDCl₃) δ 8.63 (s, 2H), 8.30 (d, *J* = 8.0 Hz, 2H), 7.85-7.70 (m, 4H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.42 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.32 (dd, *J* = 7.6, 7.6 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 144.1 (q, *J*⁴ = 1.6 Hz), 140.7, 140.0, 138.1, 137.8, 129.9, 128.9 (q, *J*² = 32.2 Hz), 128.1, 126.7, 126.2 (q, *J*³ = 4.1 Hz), 124.2 (q, *J*¹ = 270.6 Hz), 123.3 (q, *J*³ = 4.1 Hz), 120.8, 120.0; HRMS (APCI): [m/z]: calcd for C₂₈H₁₄F₆, 464.09942; found, 464.09938.

(E and Z)-Deuterated 3-methyl-9,9'-bifluorenylidene (2j')



¹H NMR (400 MHz, CD₂Cl₂) δ 8.37 (d, *J* = 8.0 Hz, 1H), 8.24 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.54 (s, 1H), 7.33 (dd, *J* = 7.2, 7.2 Hz, 1H), 7.22 (dd, *J* = 7.2, 7.2 Hz, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 2.45 (s, 3H); HRMS (MALDI): [M]⁺: calcd for C₂₇H₁₀D₈, 350.19052; found, 350.19048.

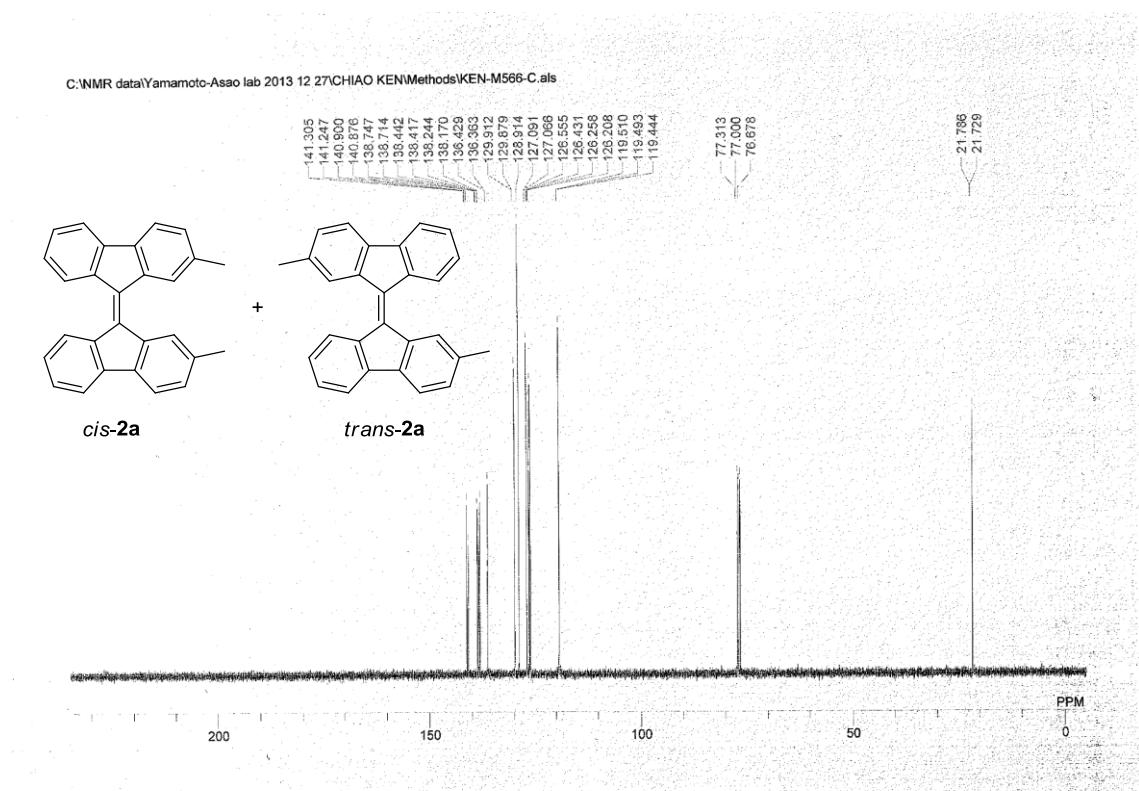
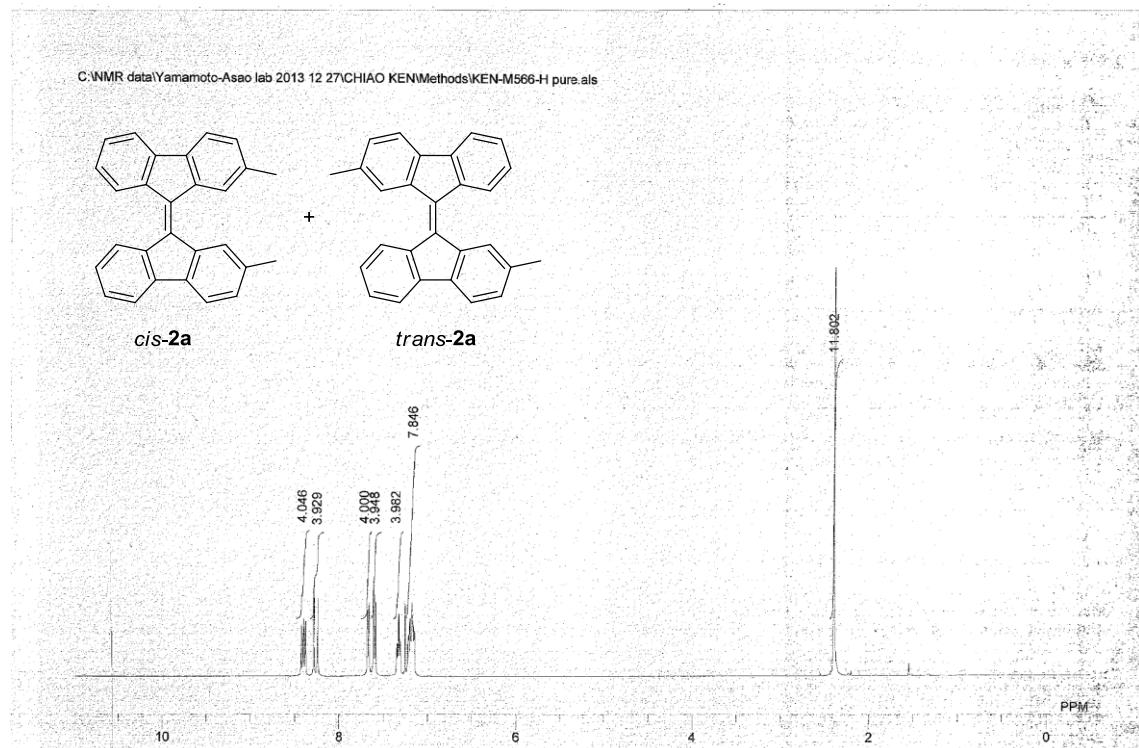
1,2-Di(9H-fluoren-9-ylidene)-1,2-diphenylethane (5a)

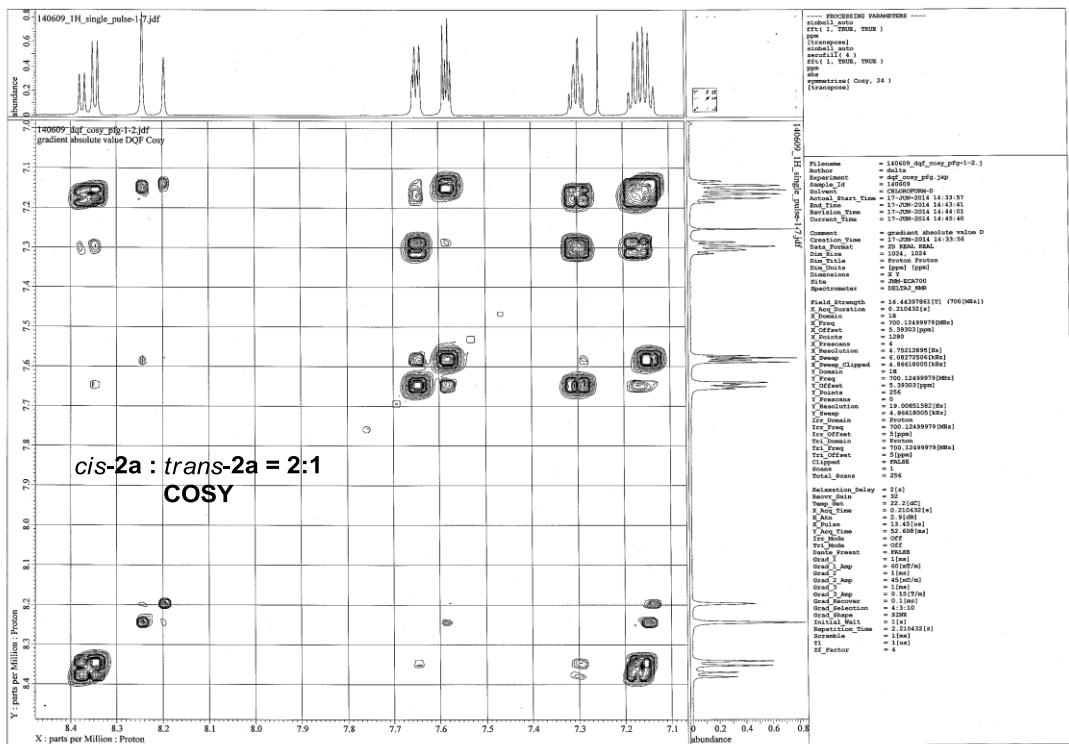
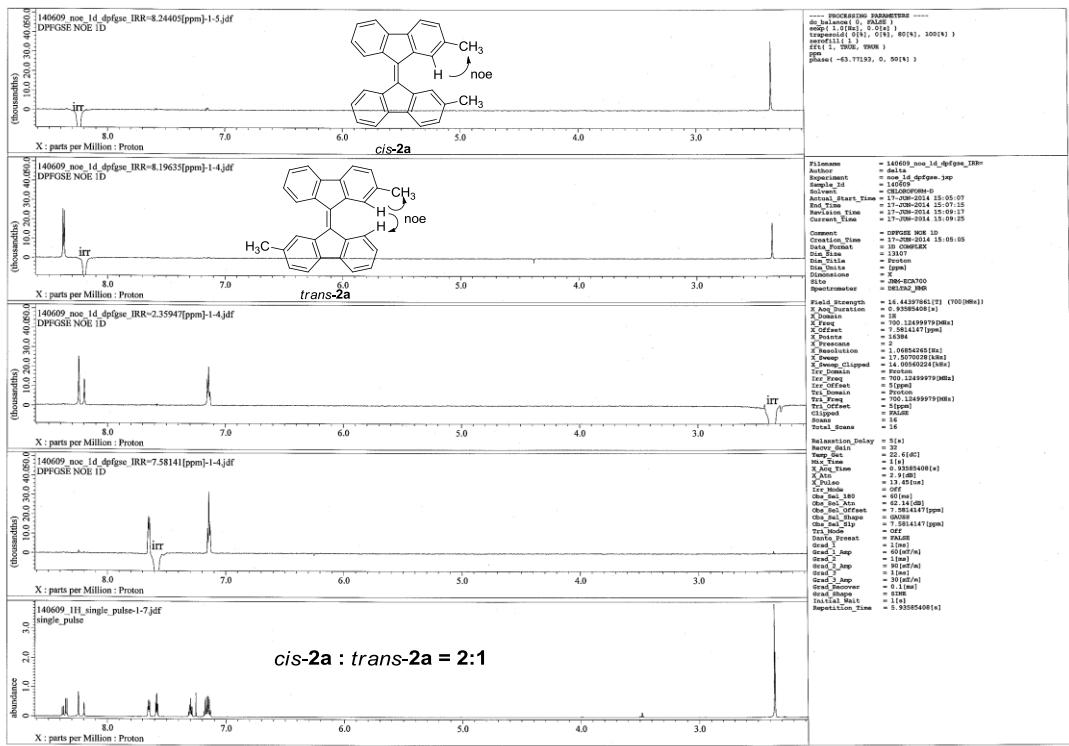


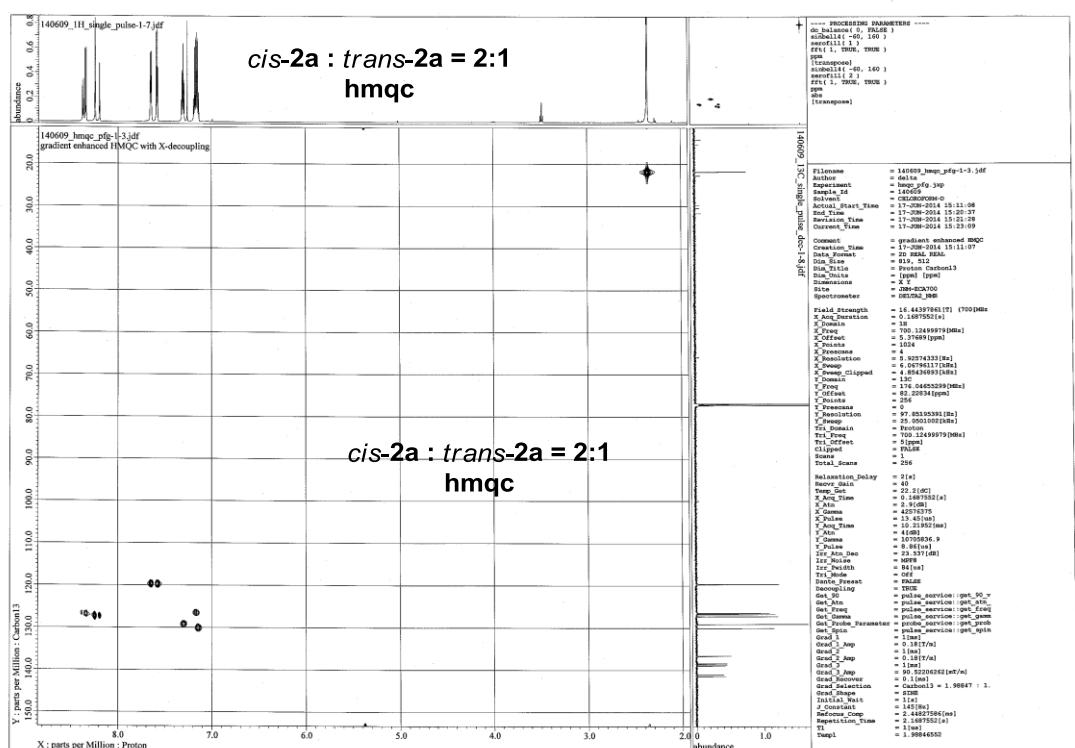
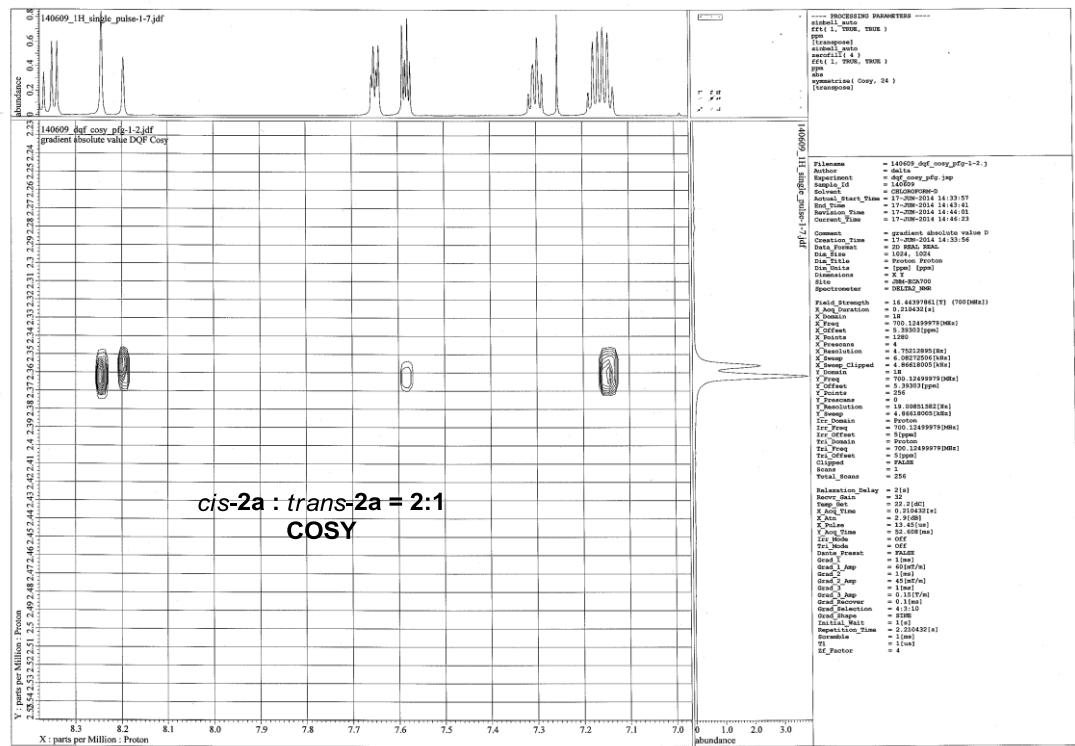
5a

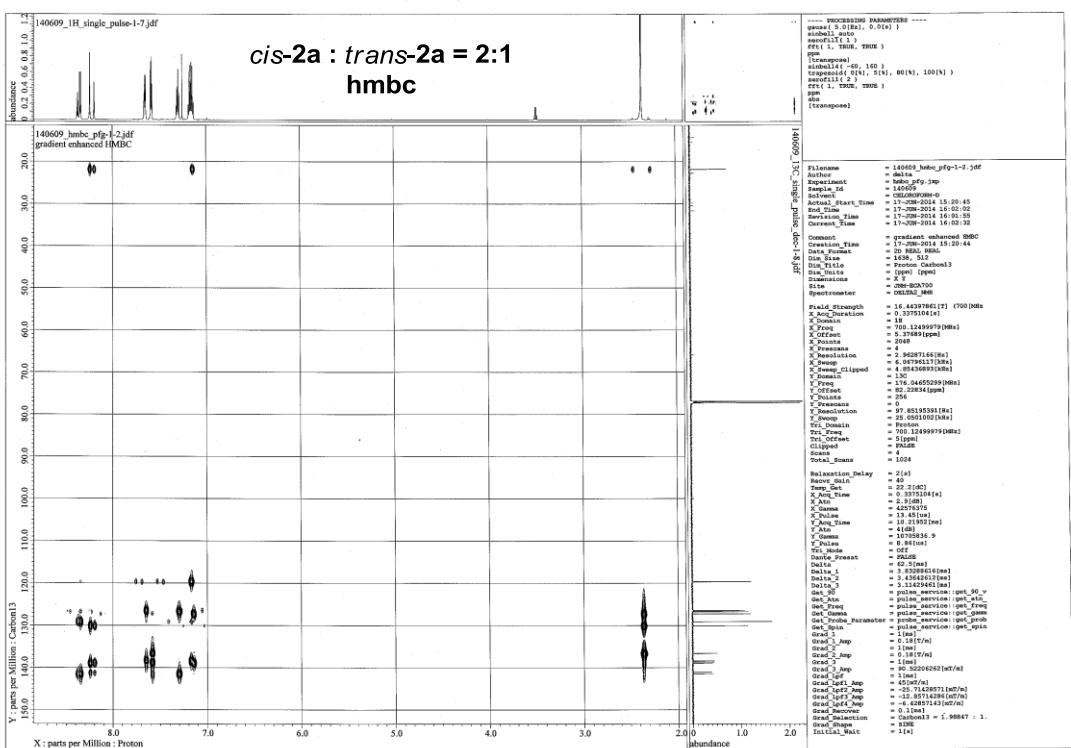
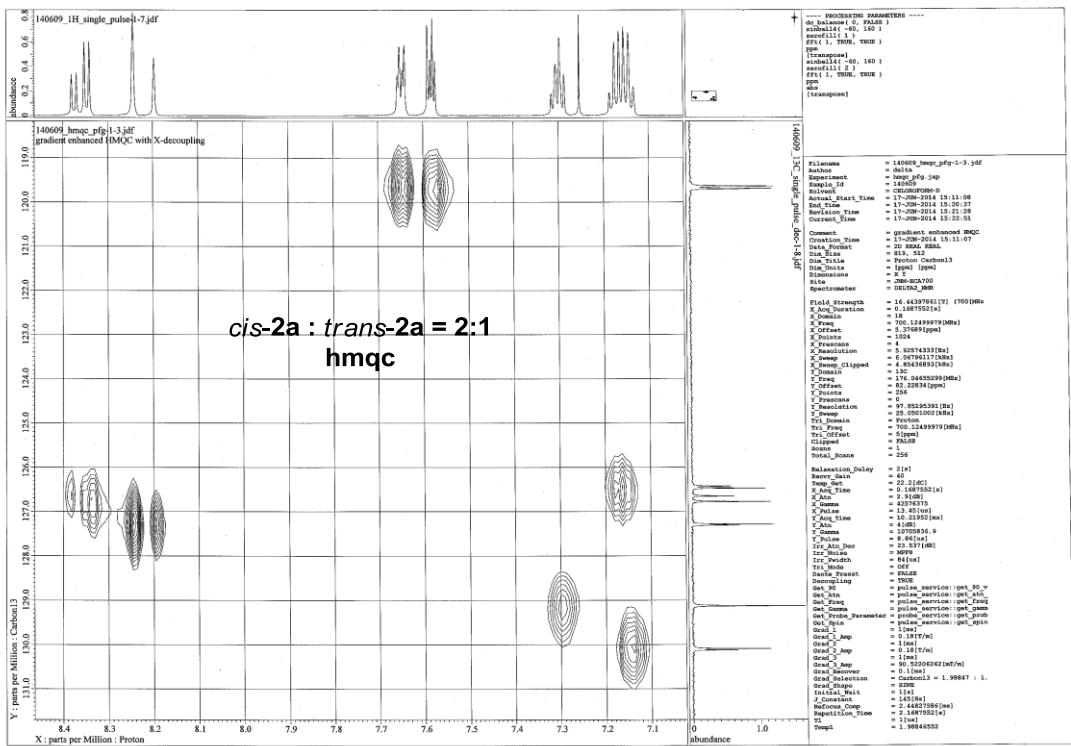
Yellow solid; ^1H NMR (400 MHz, CD_2Cl_2) δ 8.20 (d, J = 7.6 Hz, 2H), 7.75–7.60 (m, 6H), 7.45–7.20 (m, 8H), 7.16 (dd, J = 7.6, 7.6 Hz, 2H), 7.00–6.90 (m, 6H), 6.74 (d, J = 8.0 Hz, 2H); ^{13}C NMR (175 MHz, CD_2Cl_2) δ 143.9, 141.1, 140.9, 139.8, 138.8, 138.1, 135.8, 132.0, 129.2, 128.7(9), 128.7(4), 128.6, 127.9, 127.6, 126.8, 125.8, 124.2, 119.7(8), 119.7(0); HRMS (MALDI): [m/z]: calcd for $\text{C}_{40}\text{H}_{26}$, 506.20290; found, 506.20294.

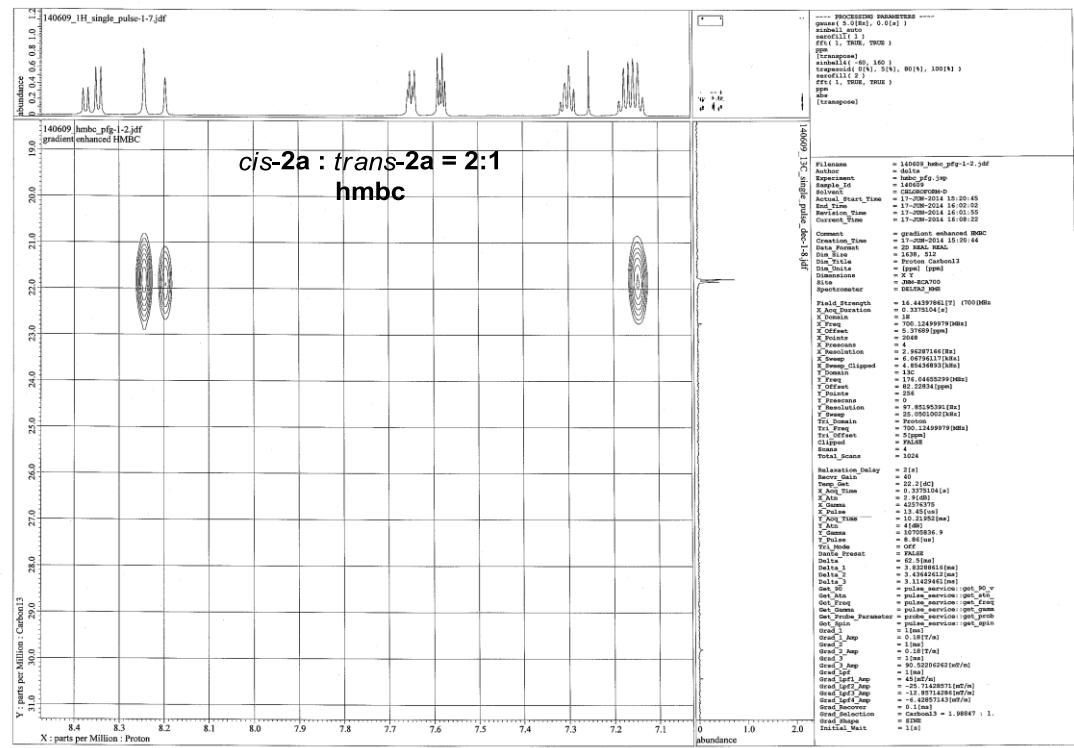
NMR Spectra



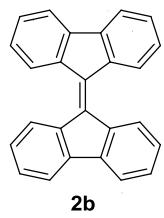




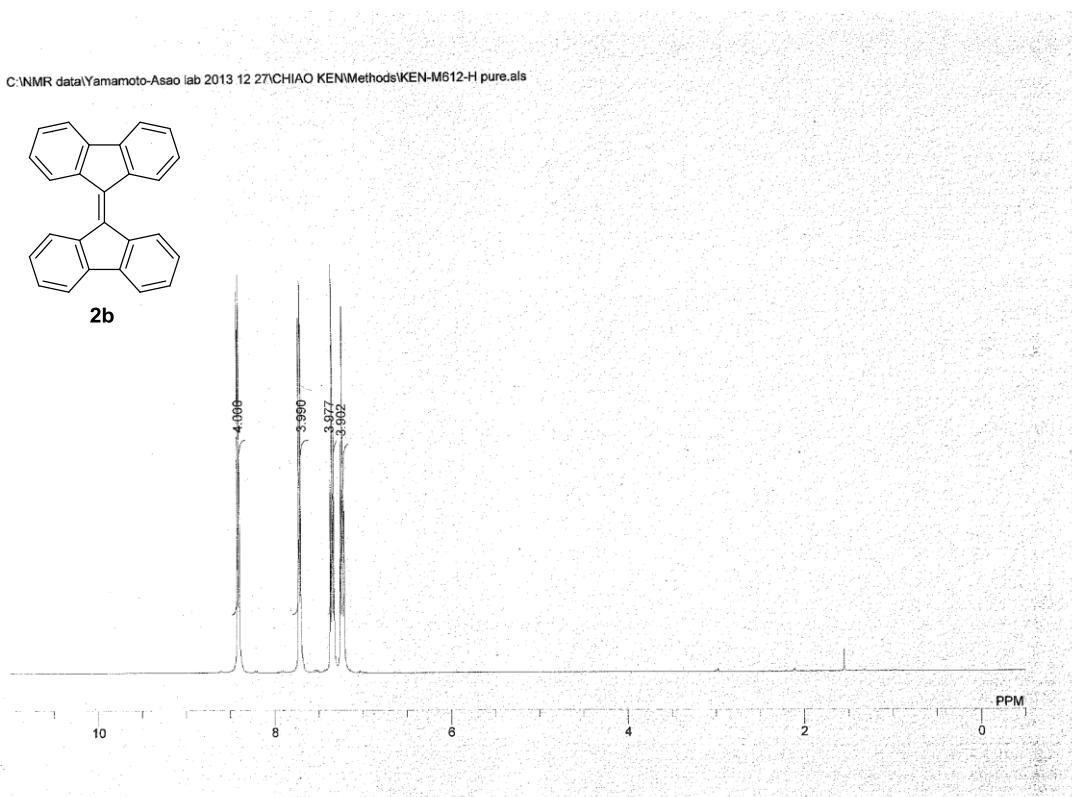




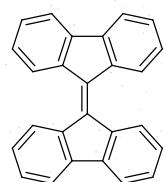
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2b



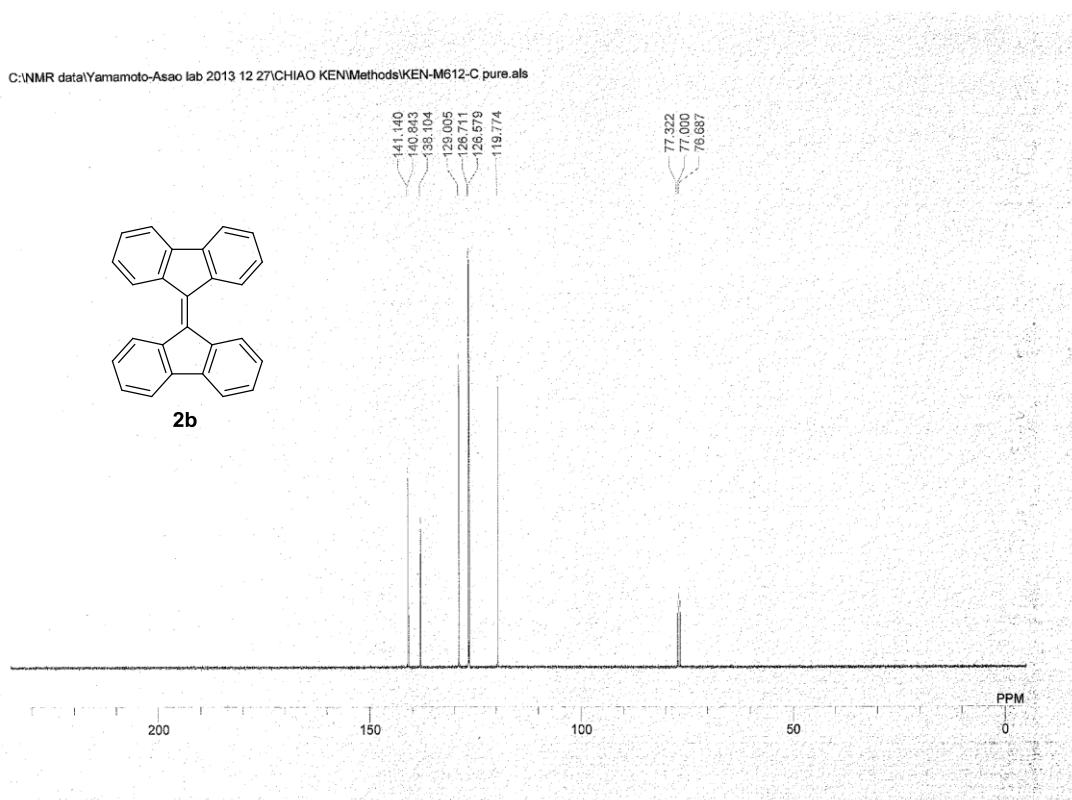
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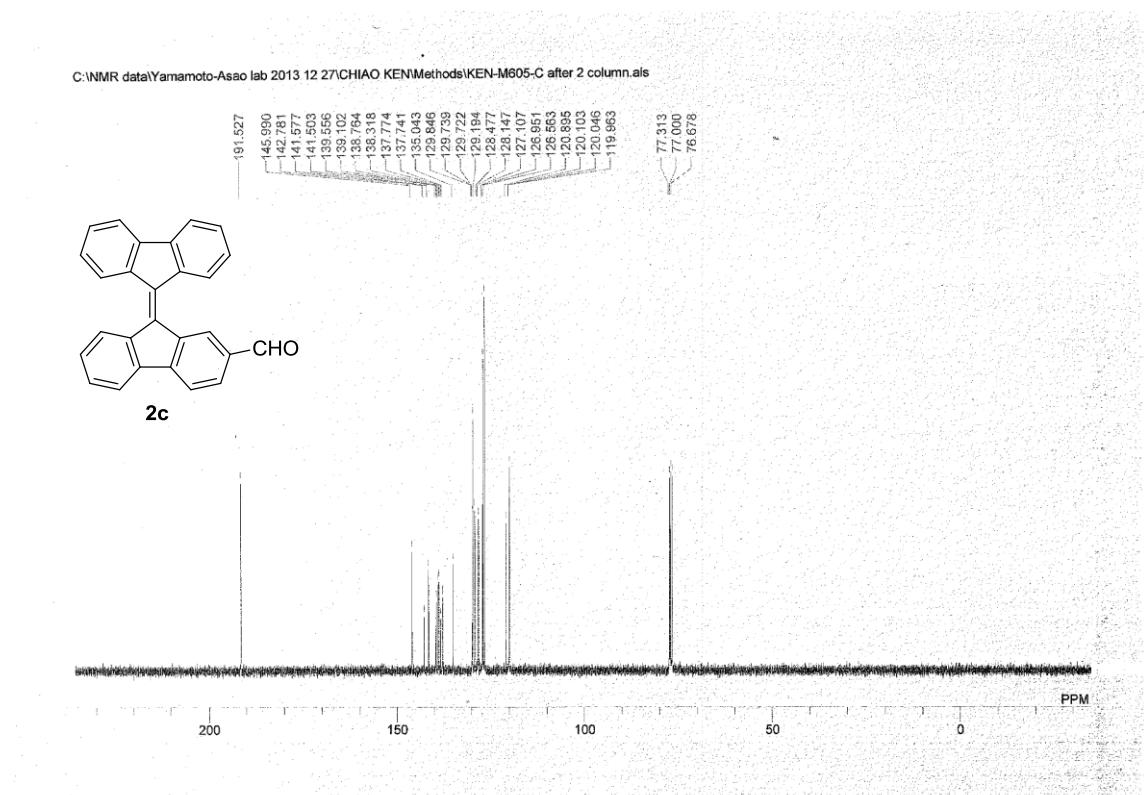
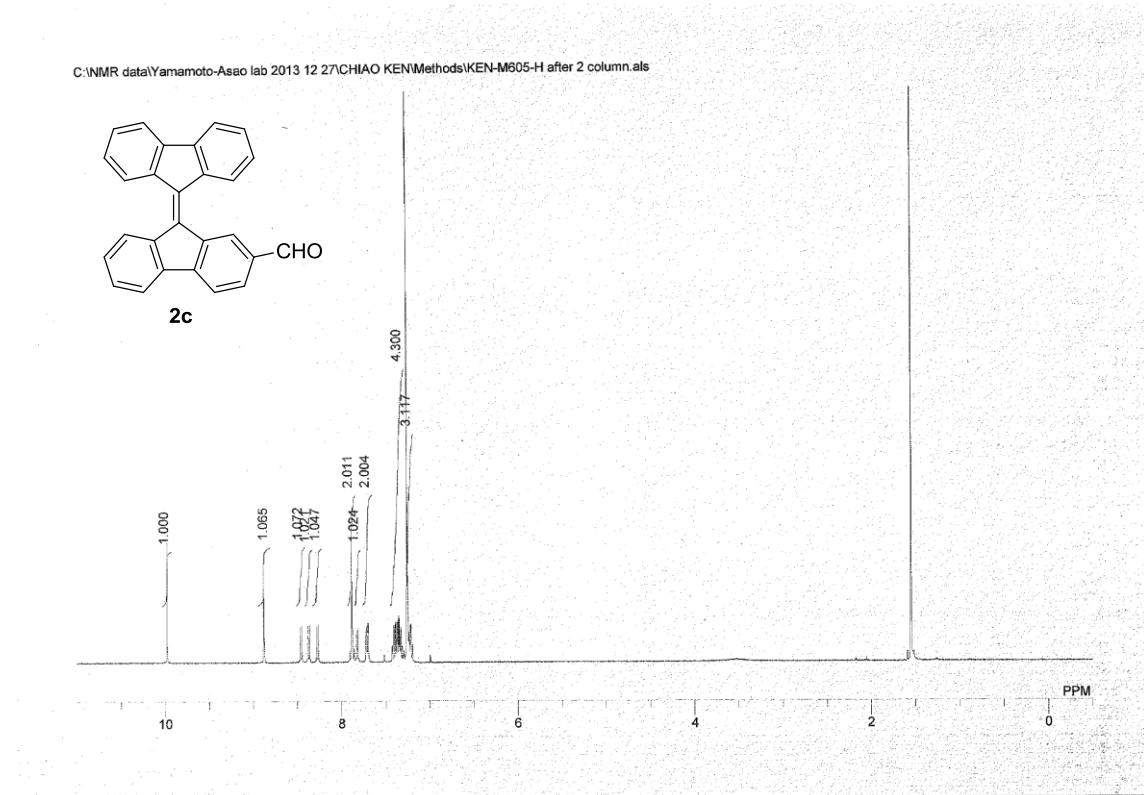


2b

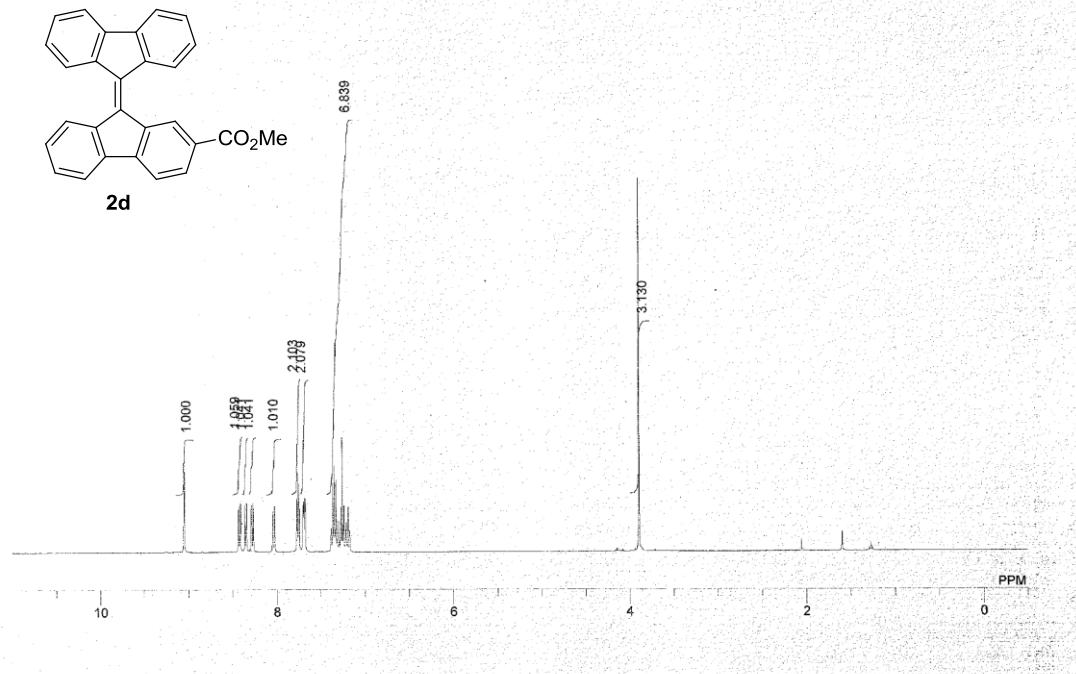
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129.005
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126.579
119.774

77.322
77.000
76.687

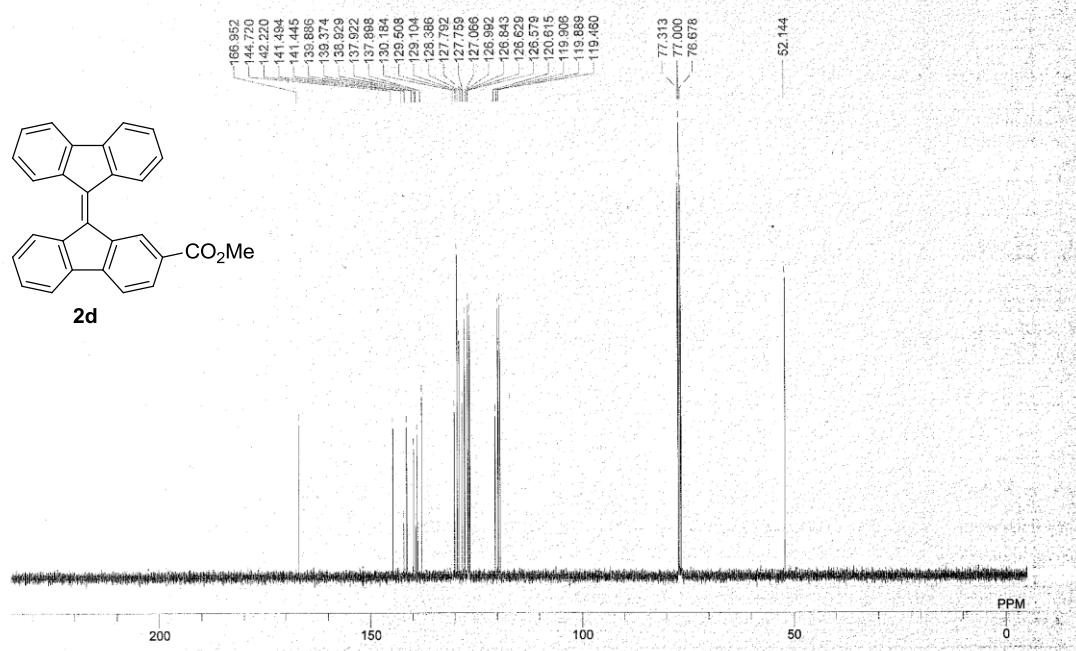


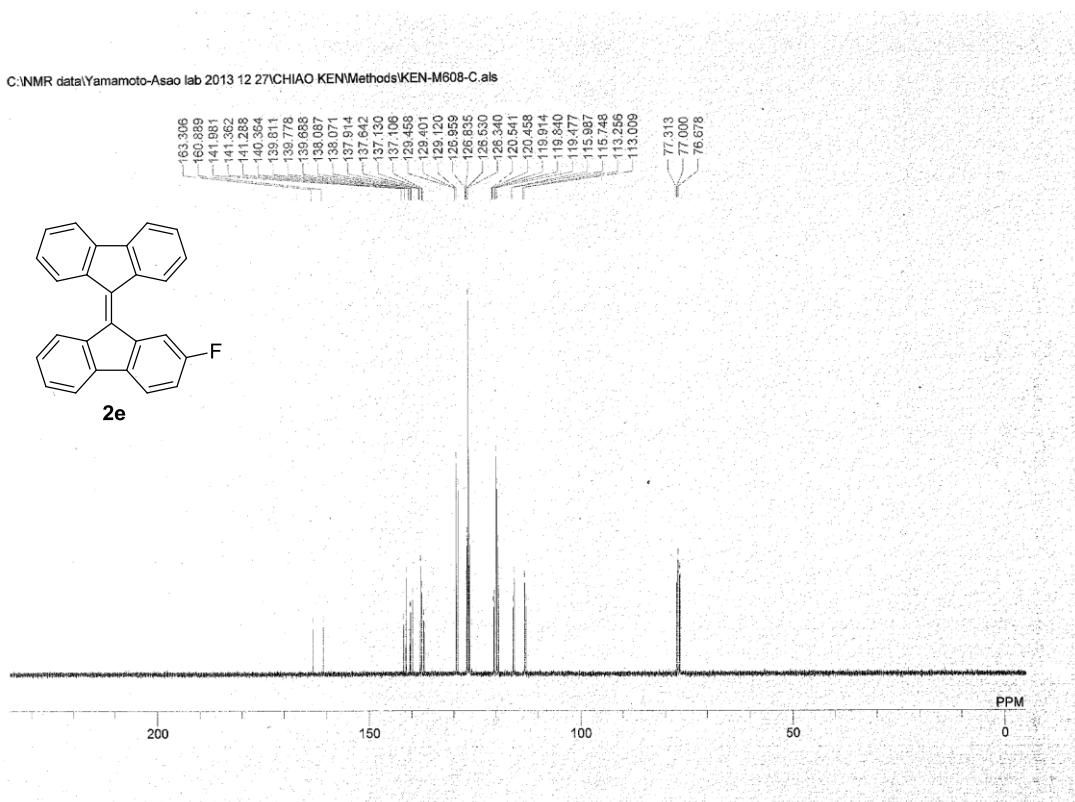
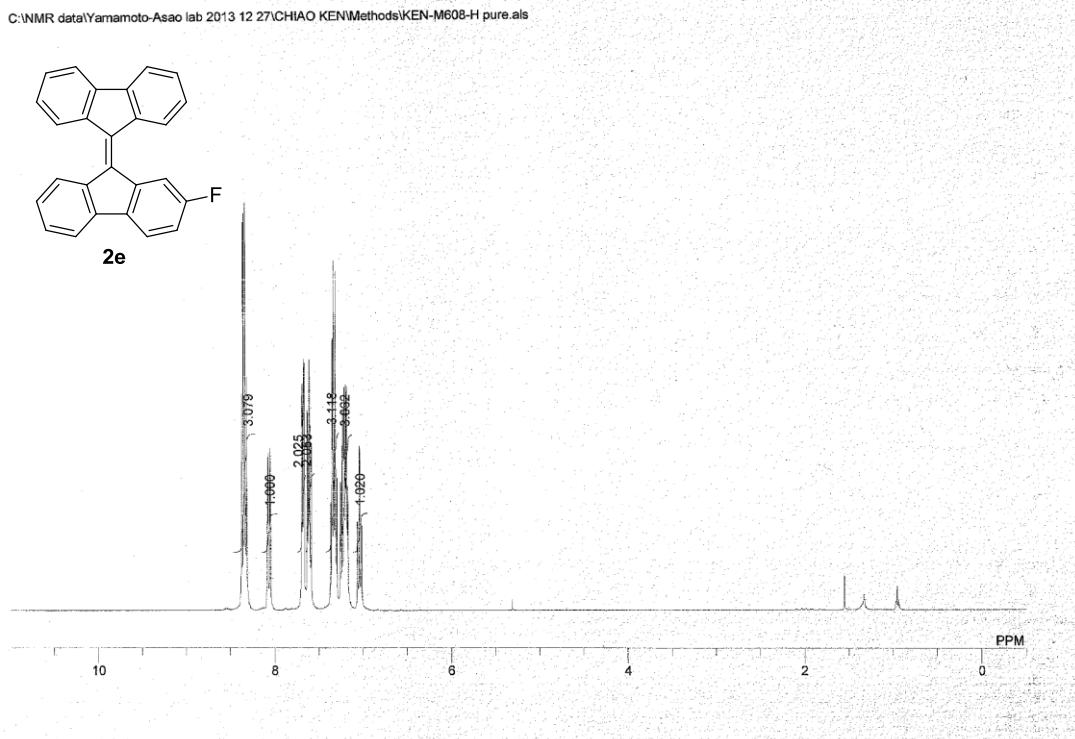


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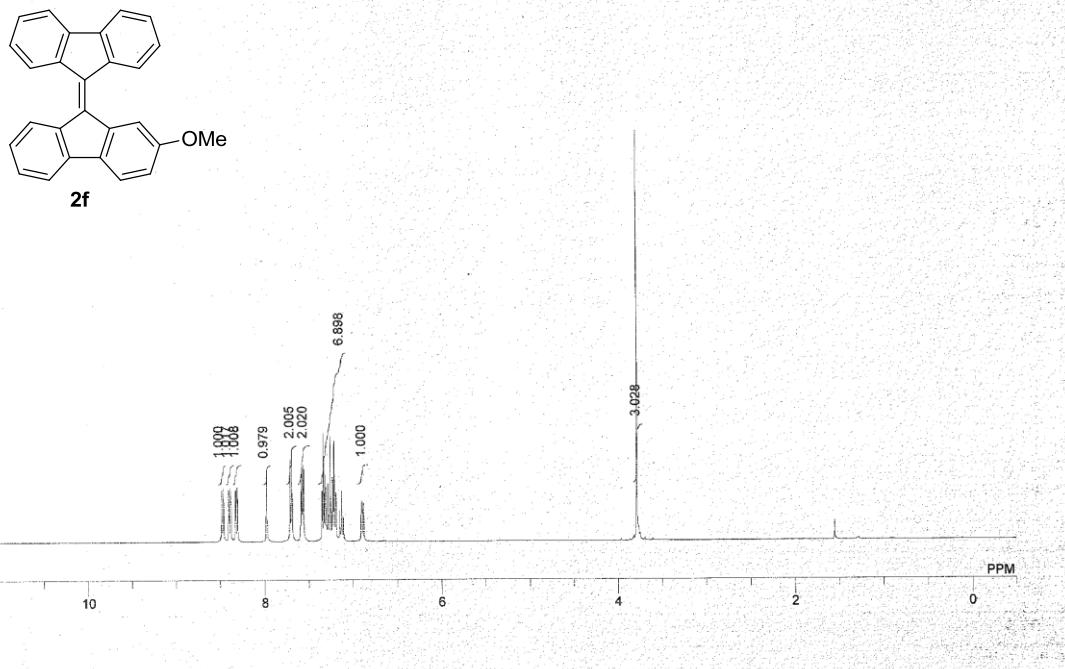


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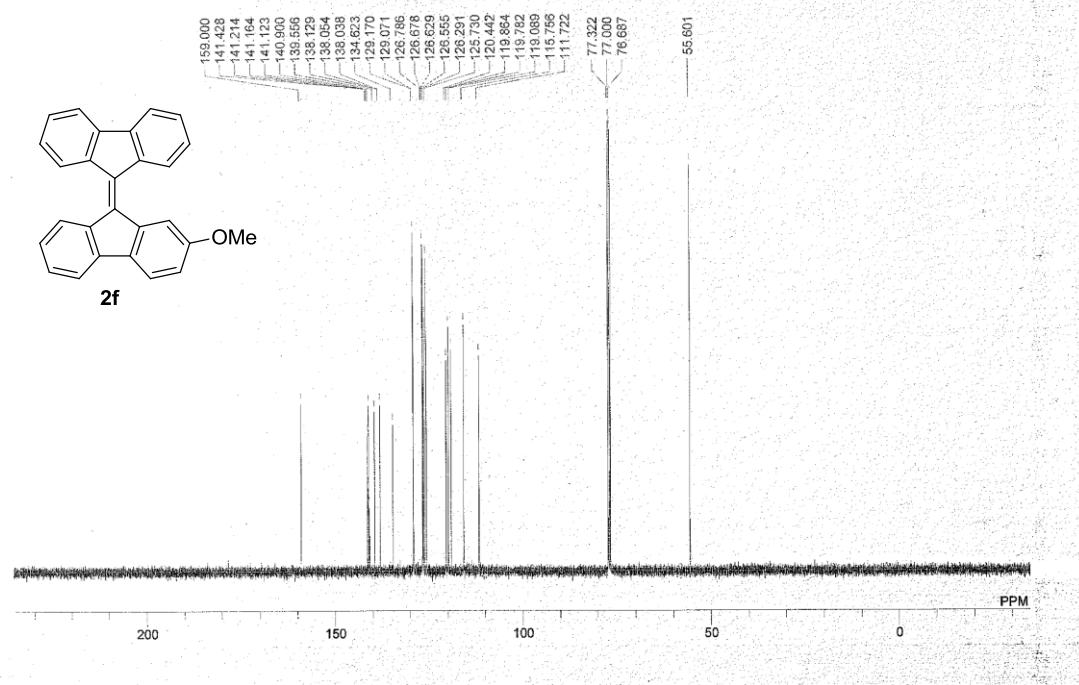




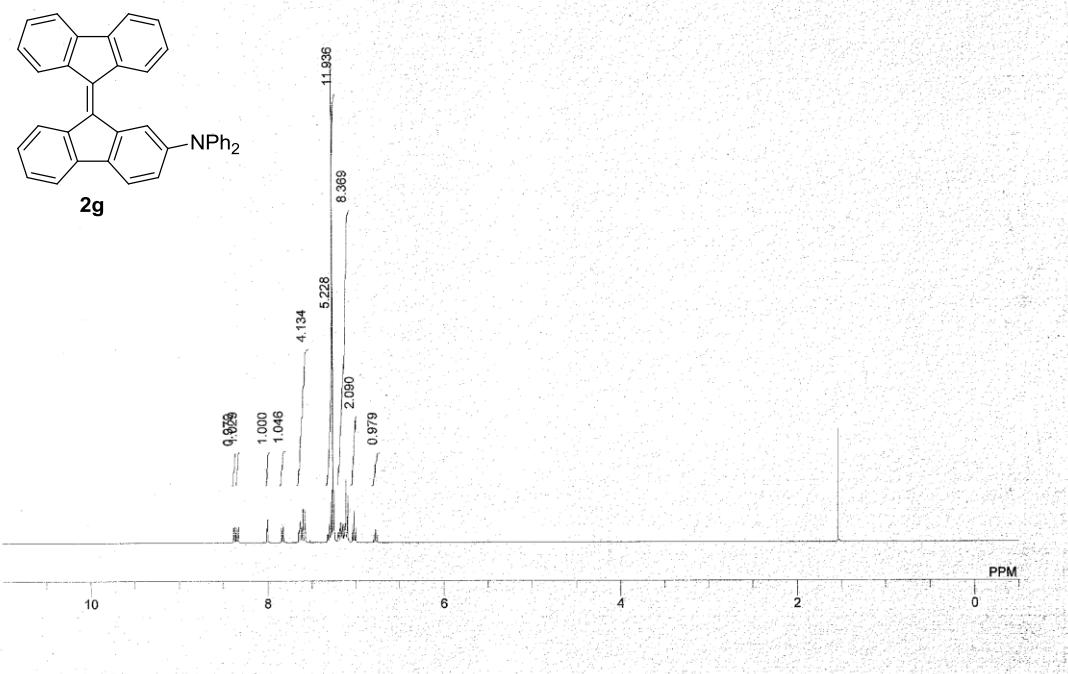
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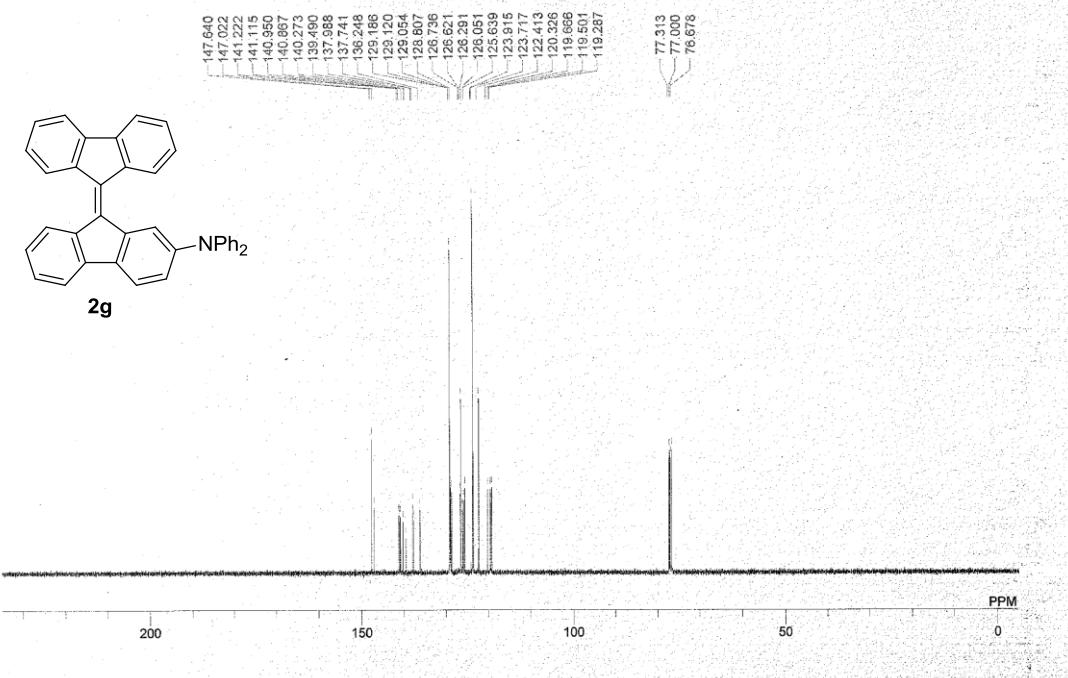
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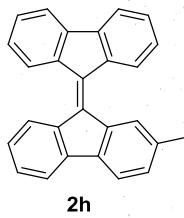
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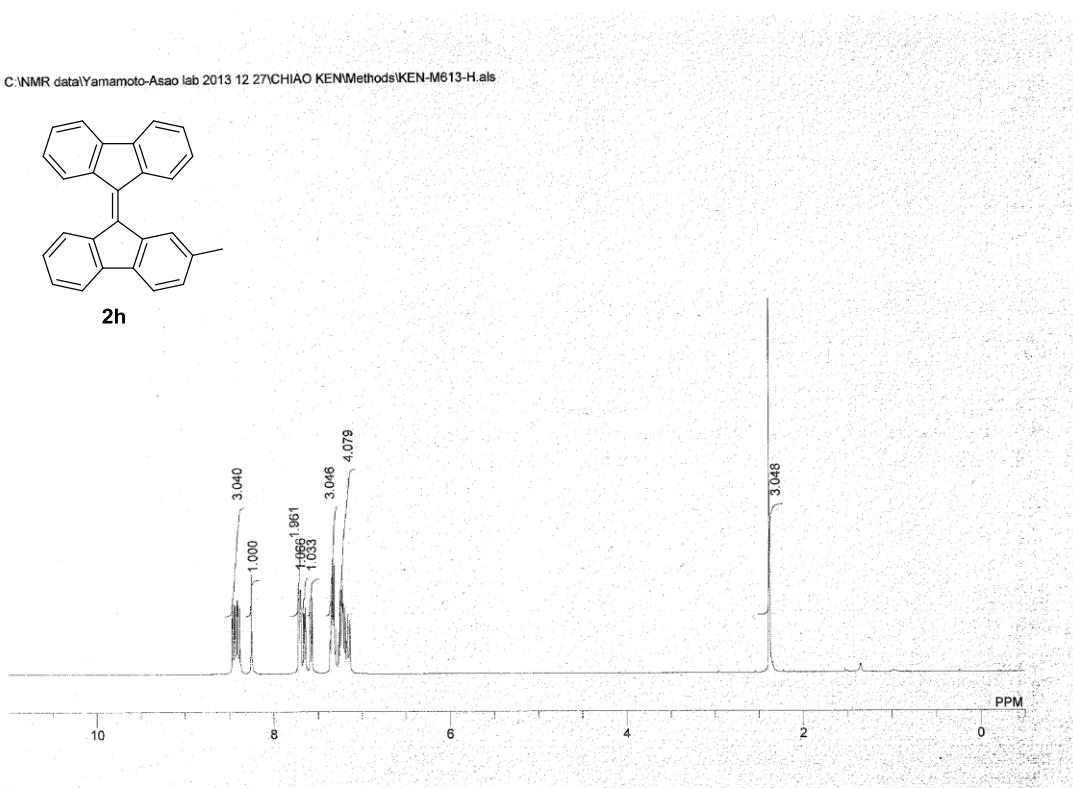
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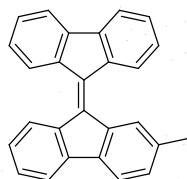
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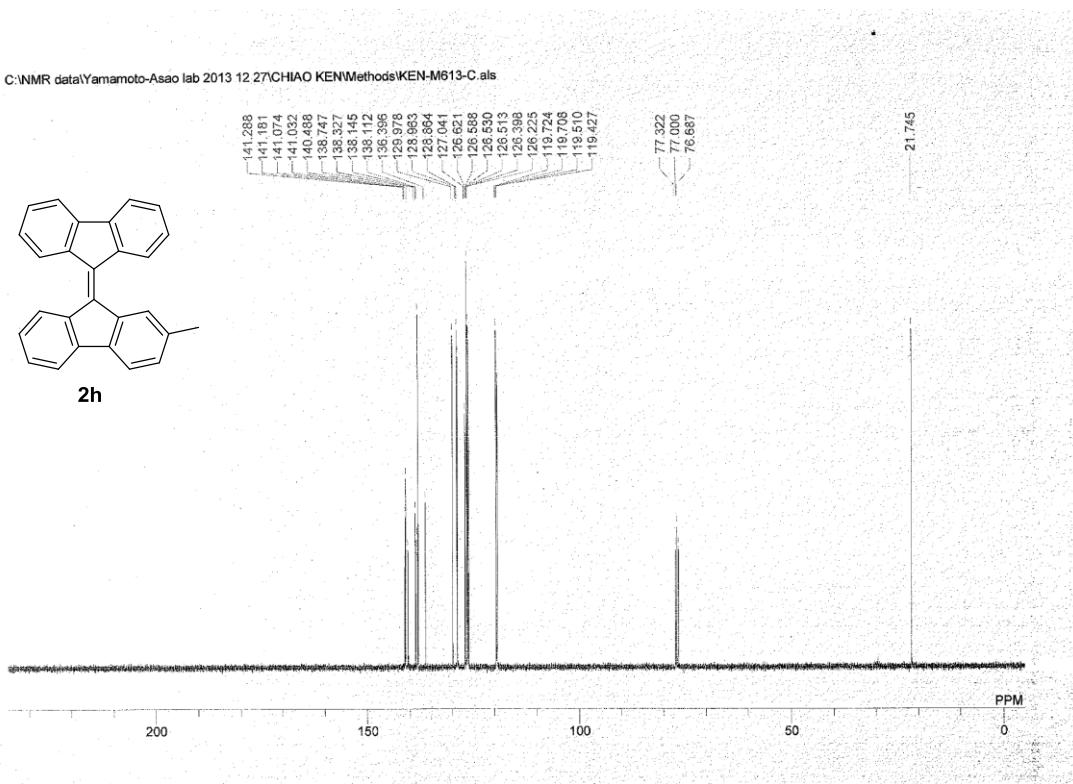
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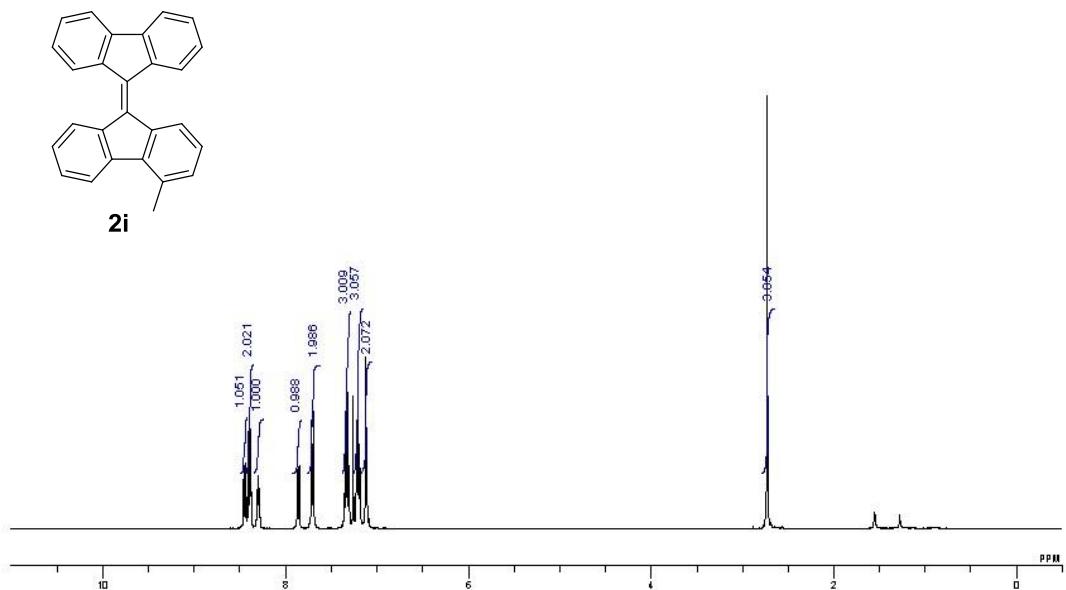
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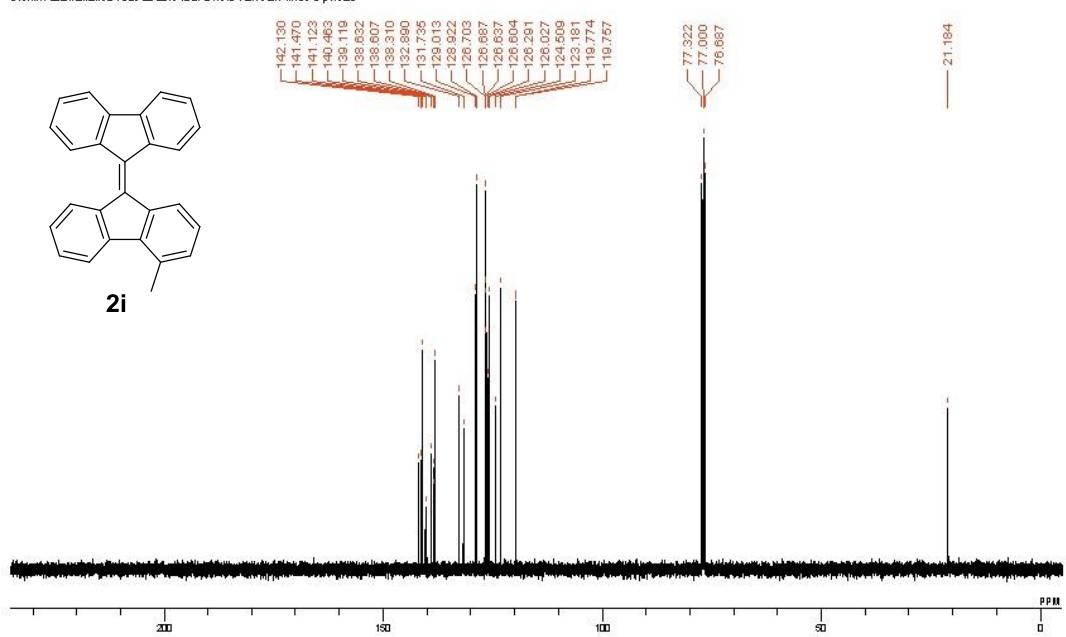
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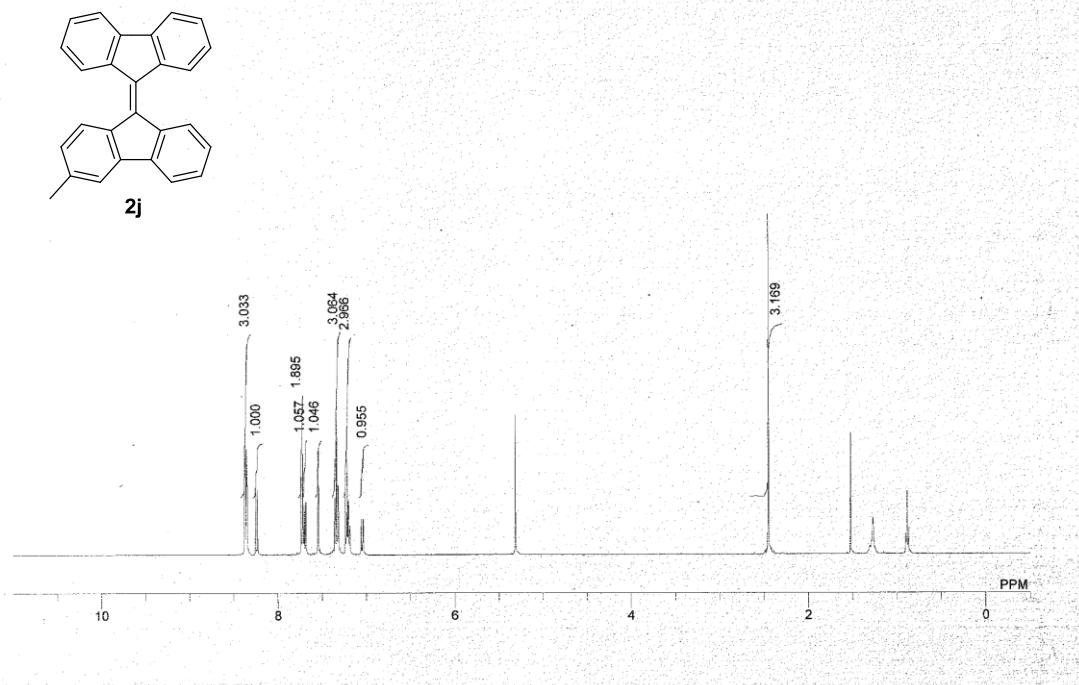
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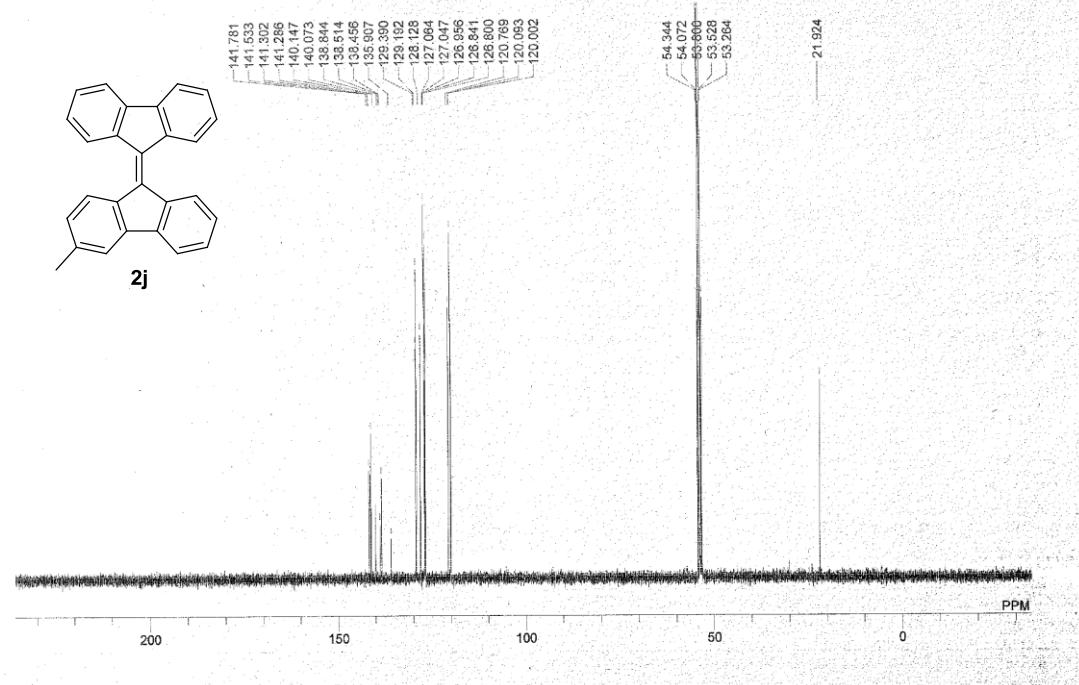
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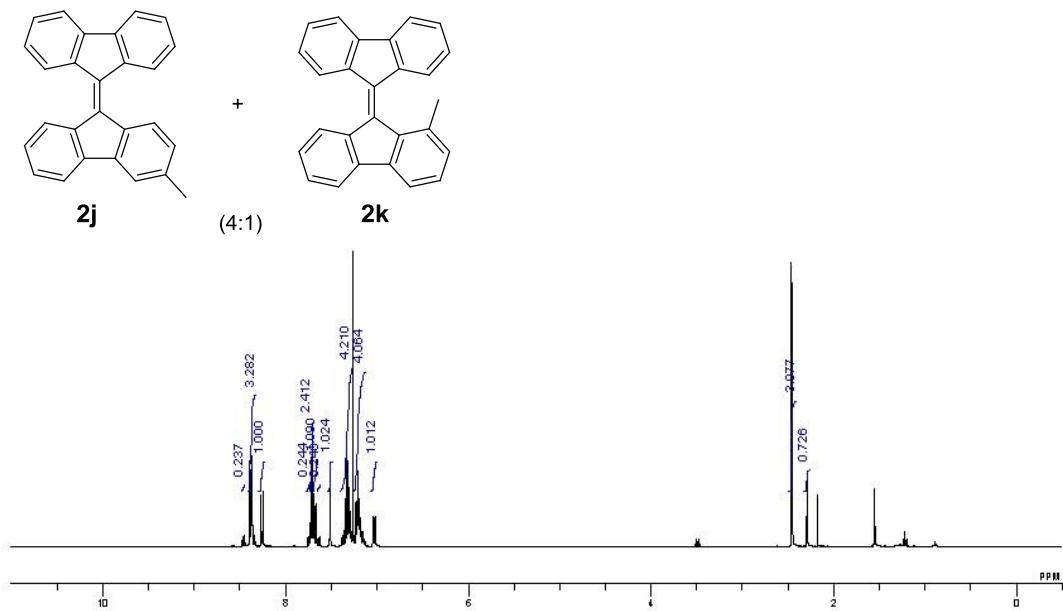
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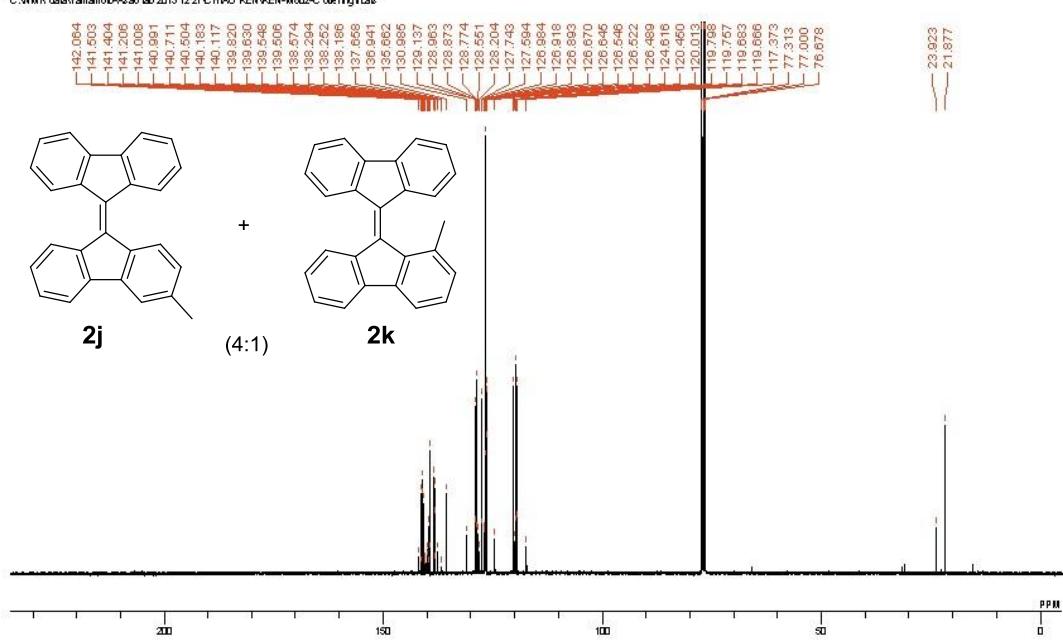
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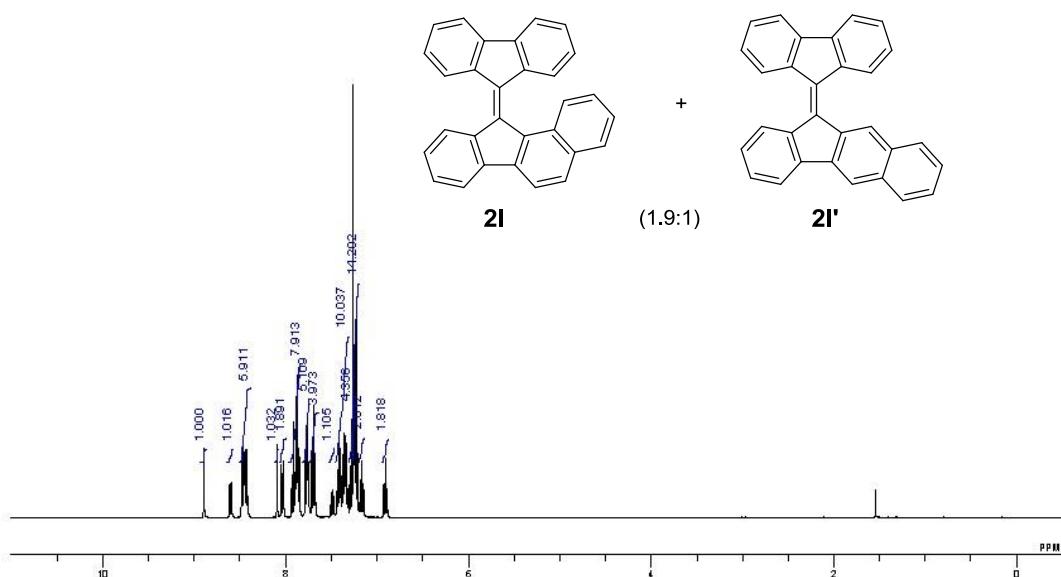
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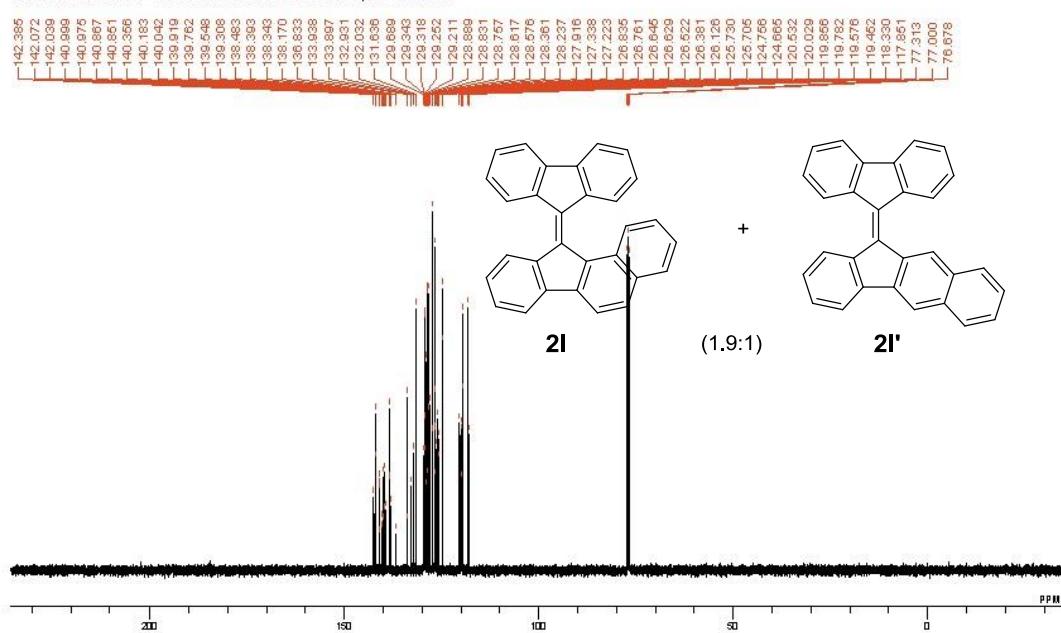
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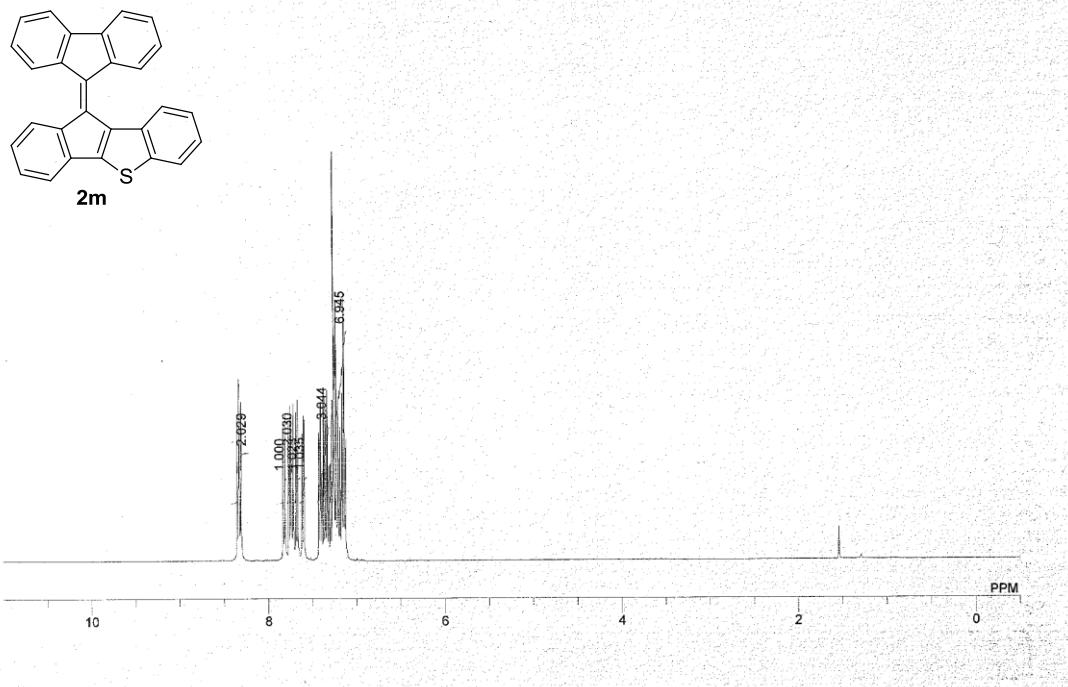
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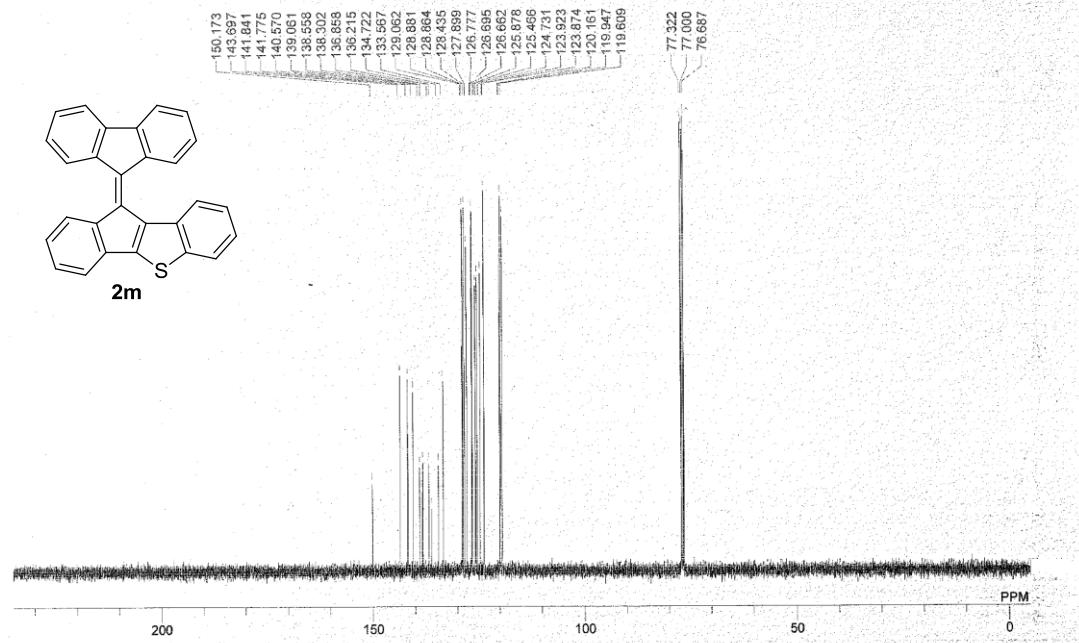
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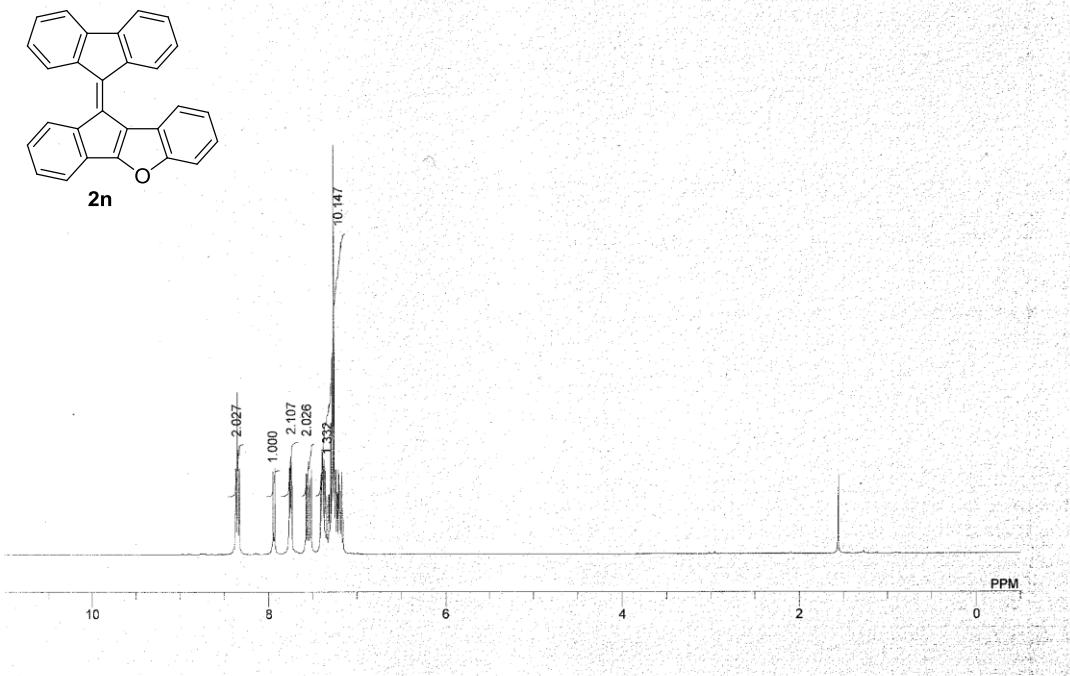
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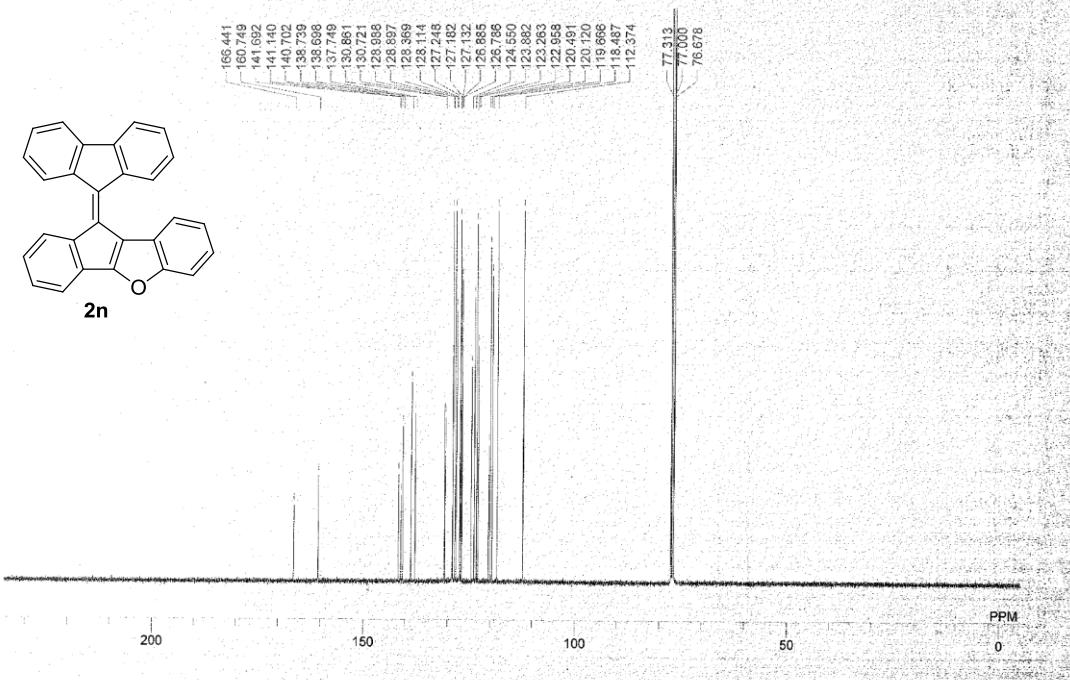
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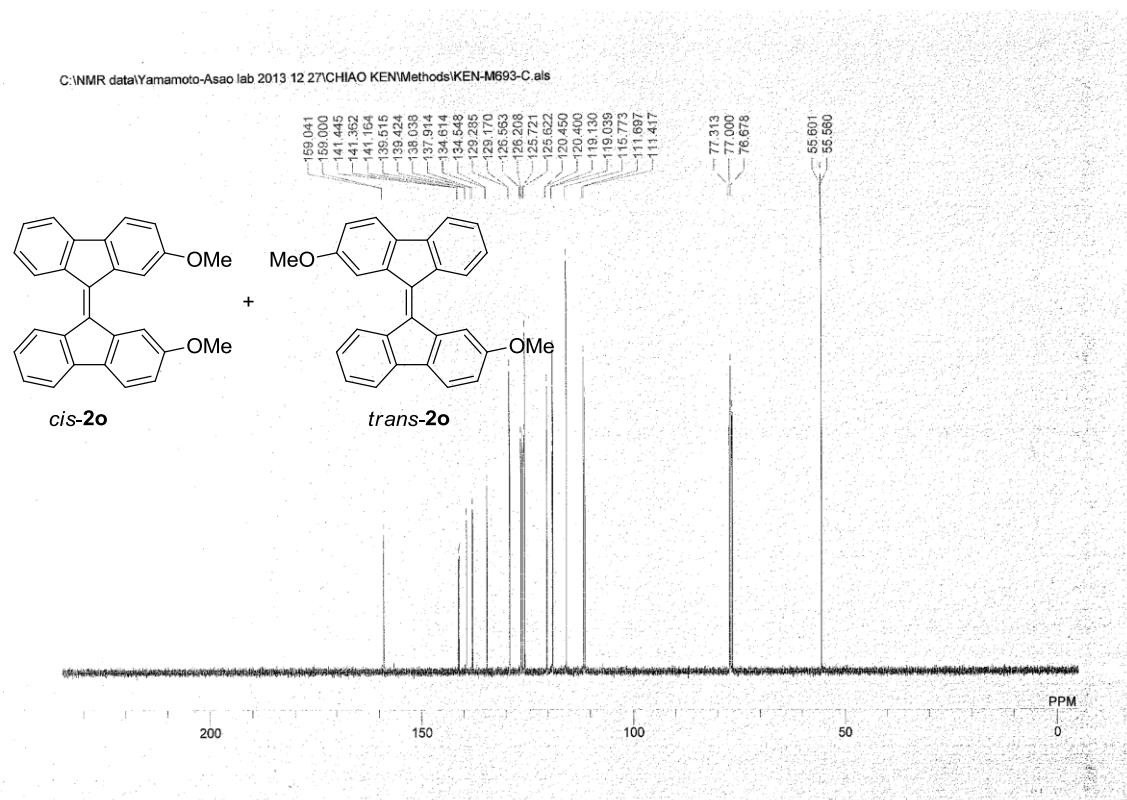
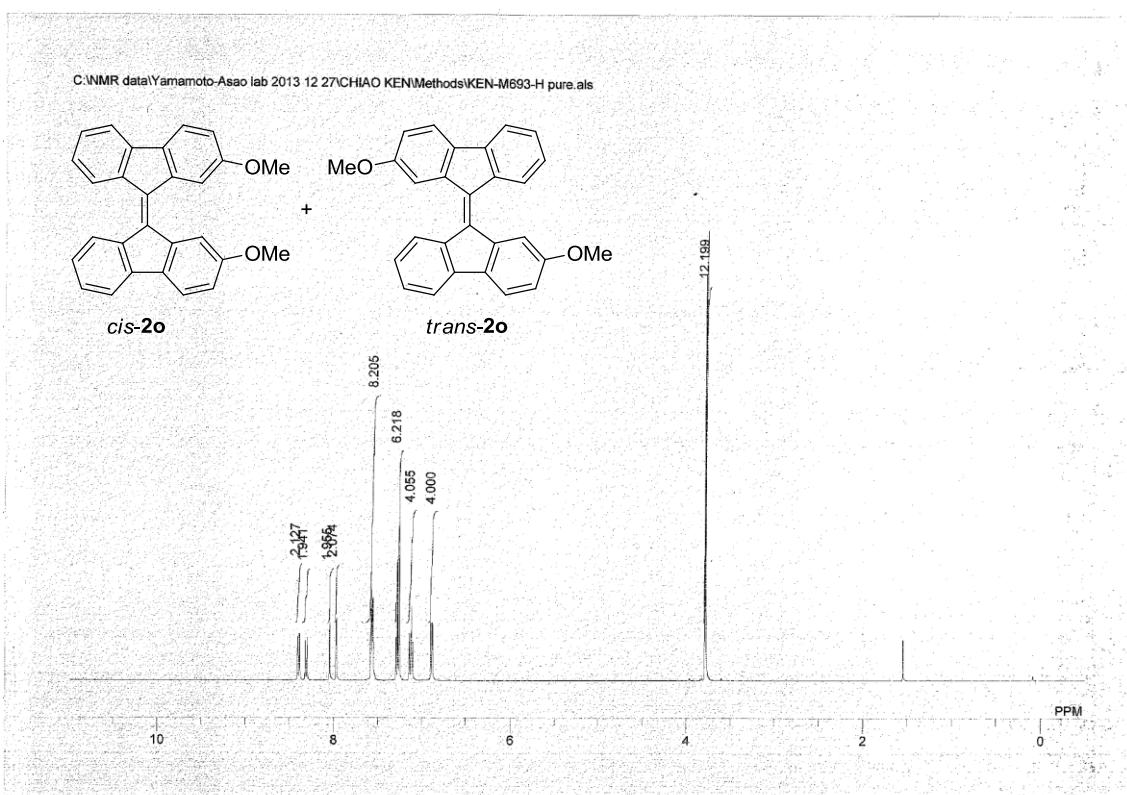


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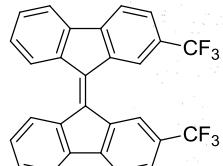


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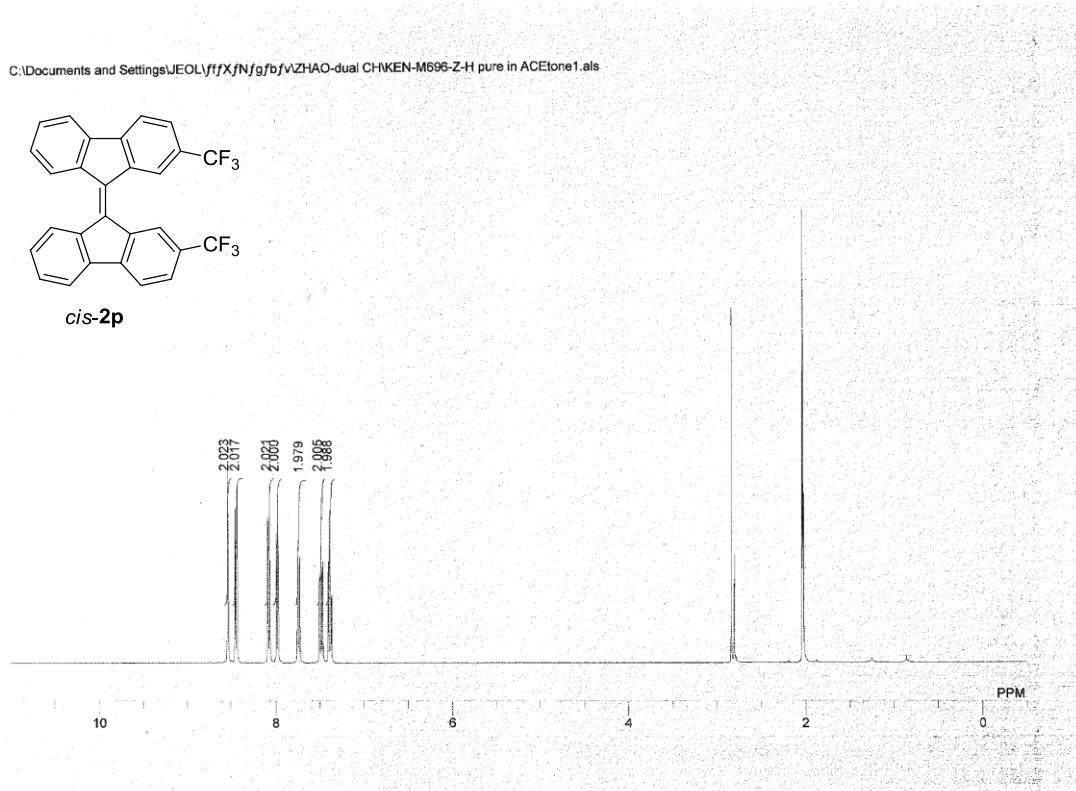




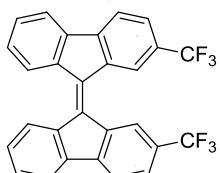
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cis-2p

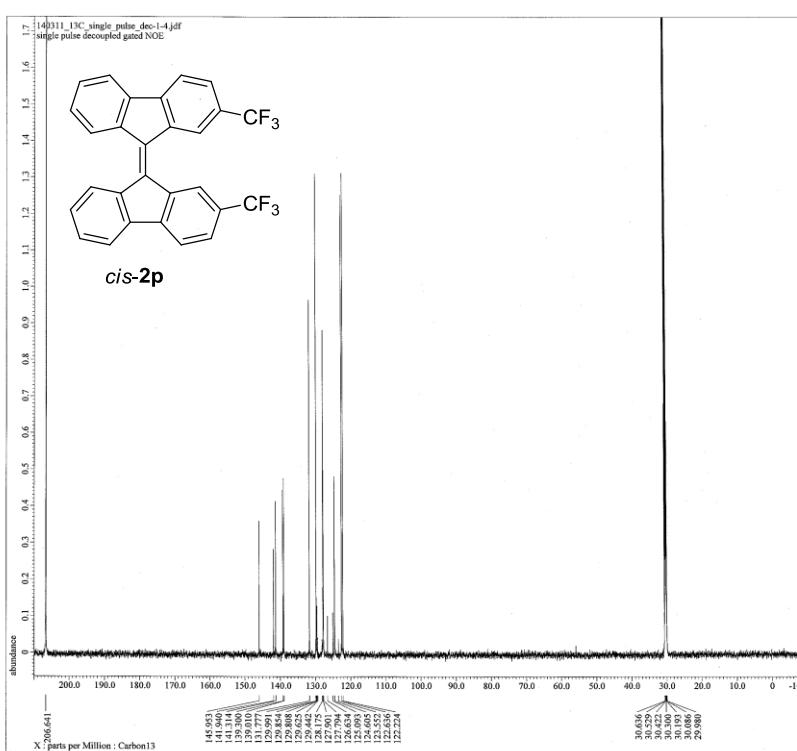


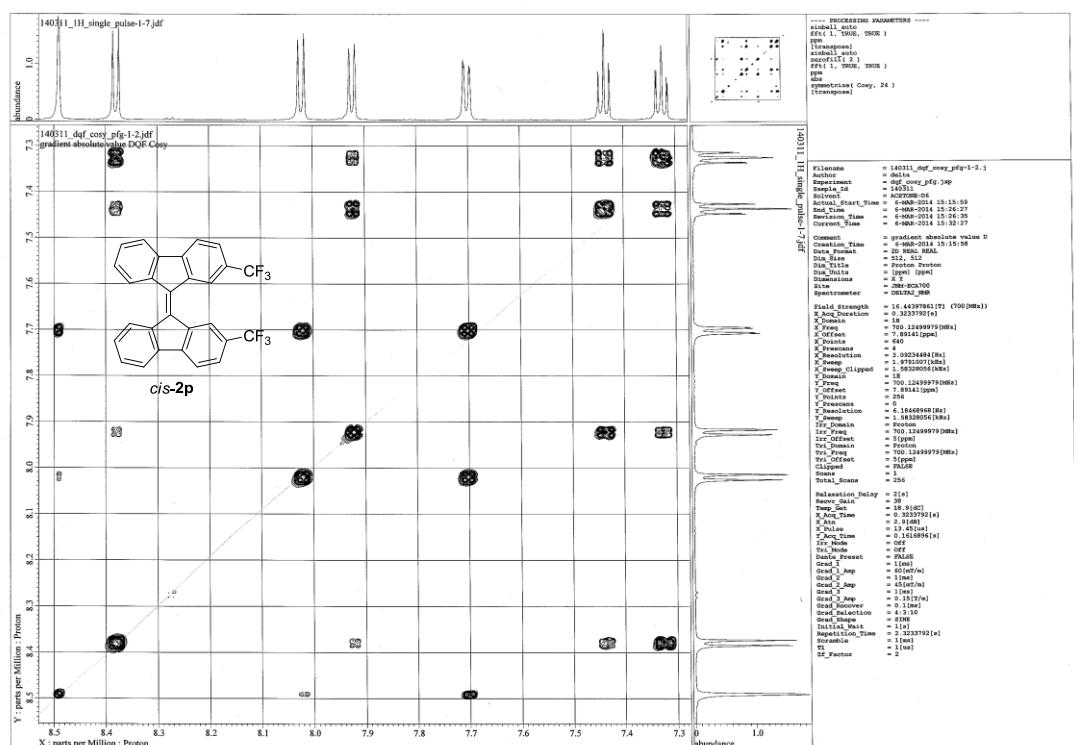
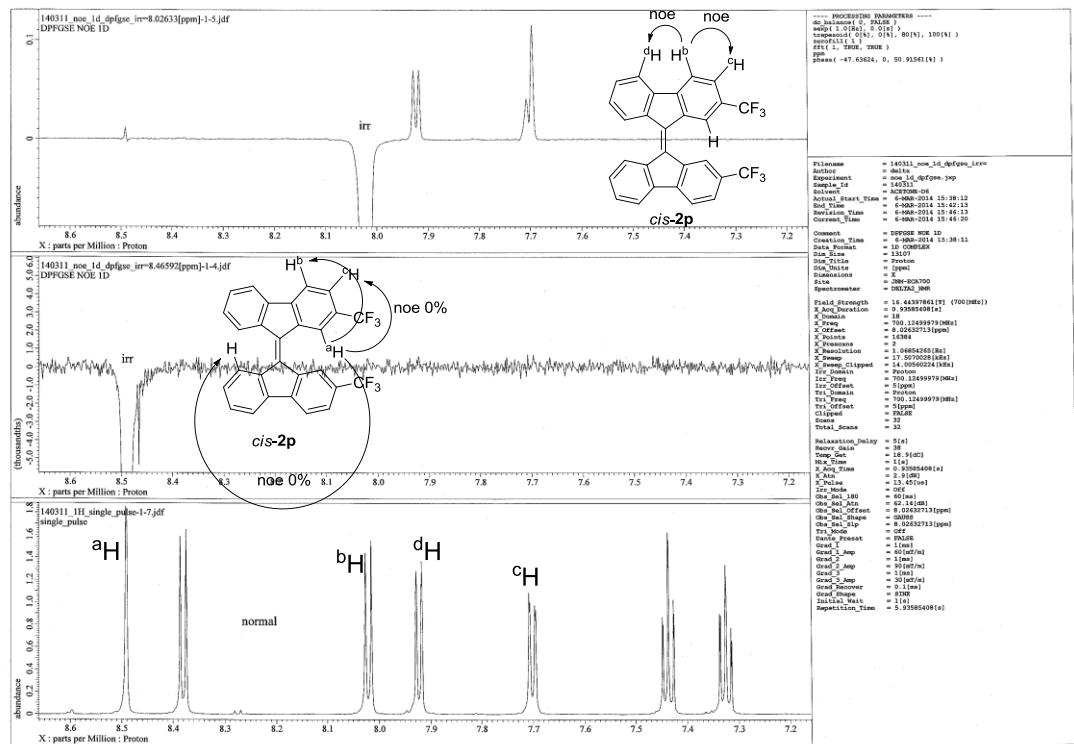
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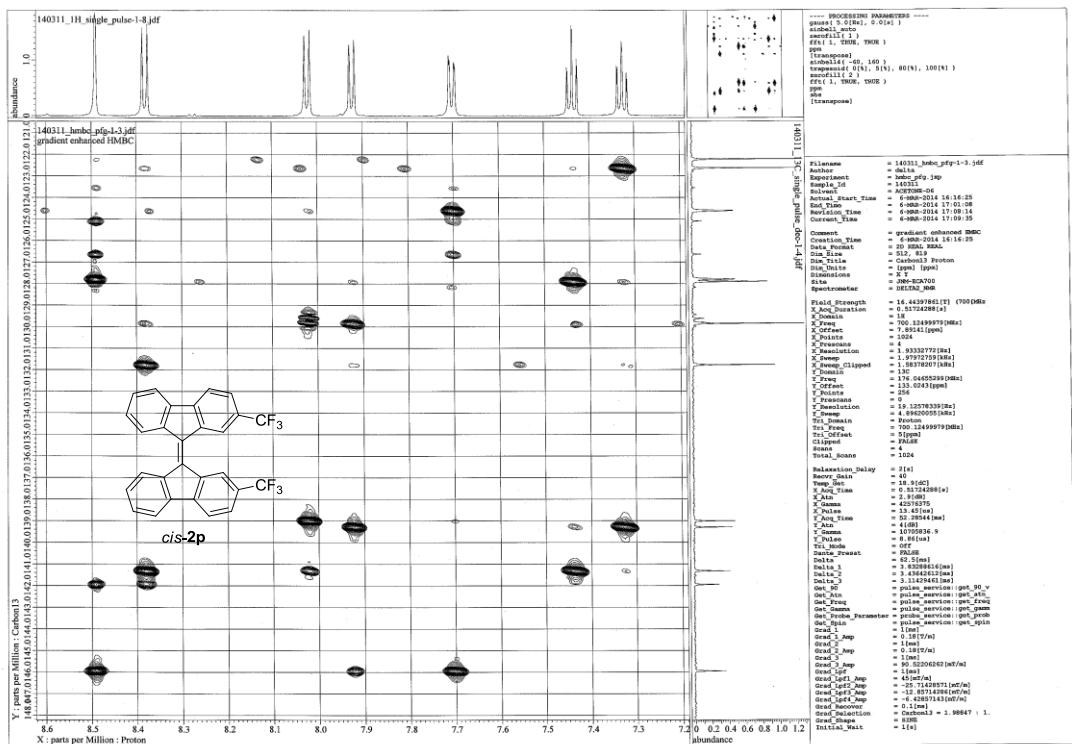
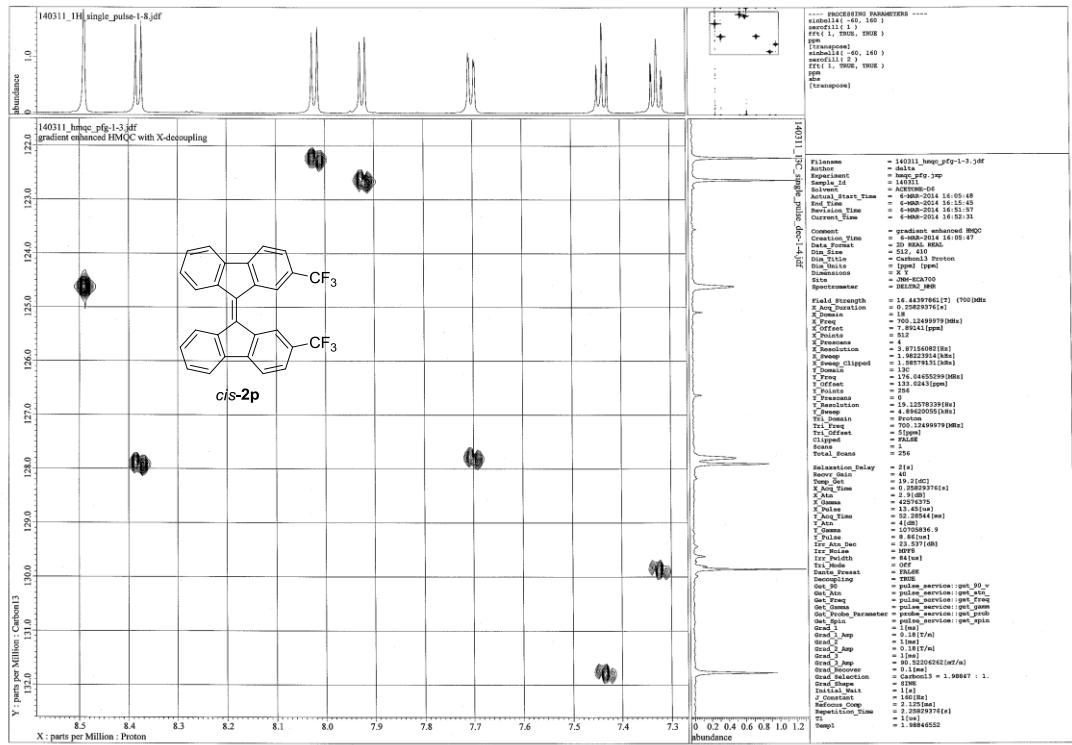


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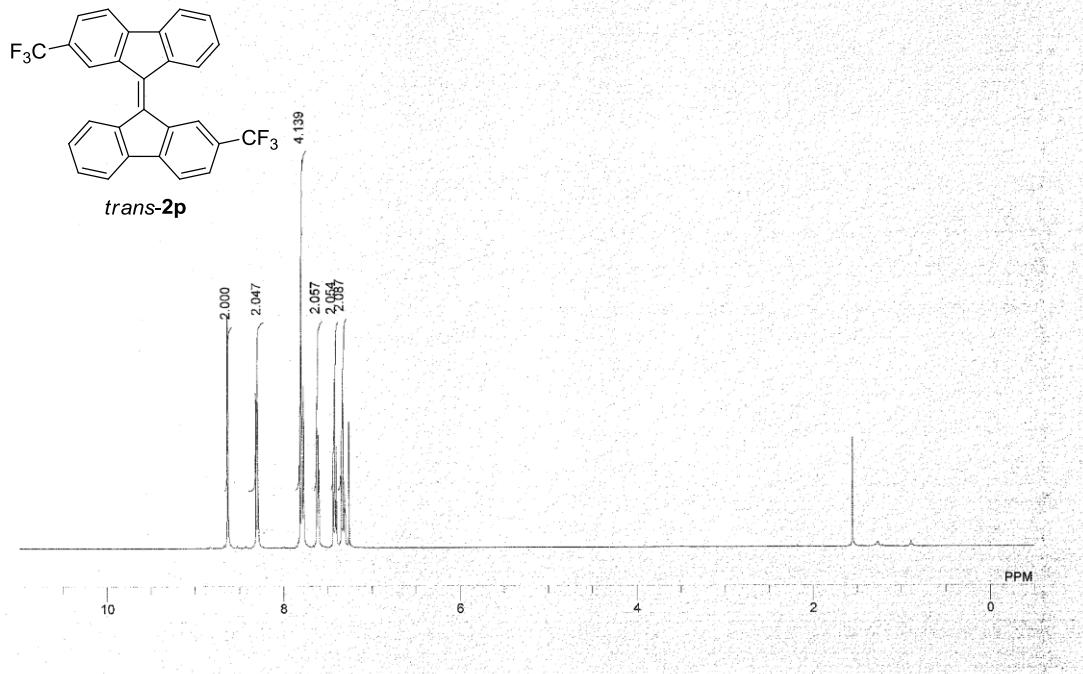
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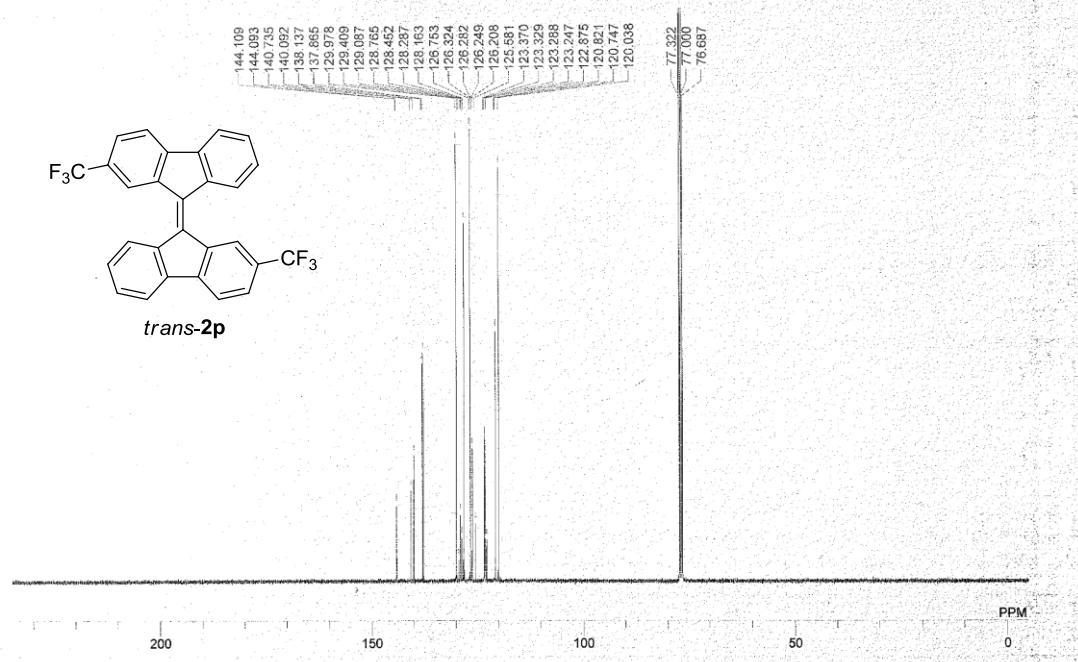




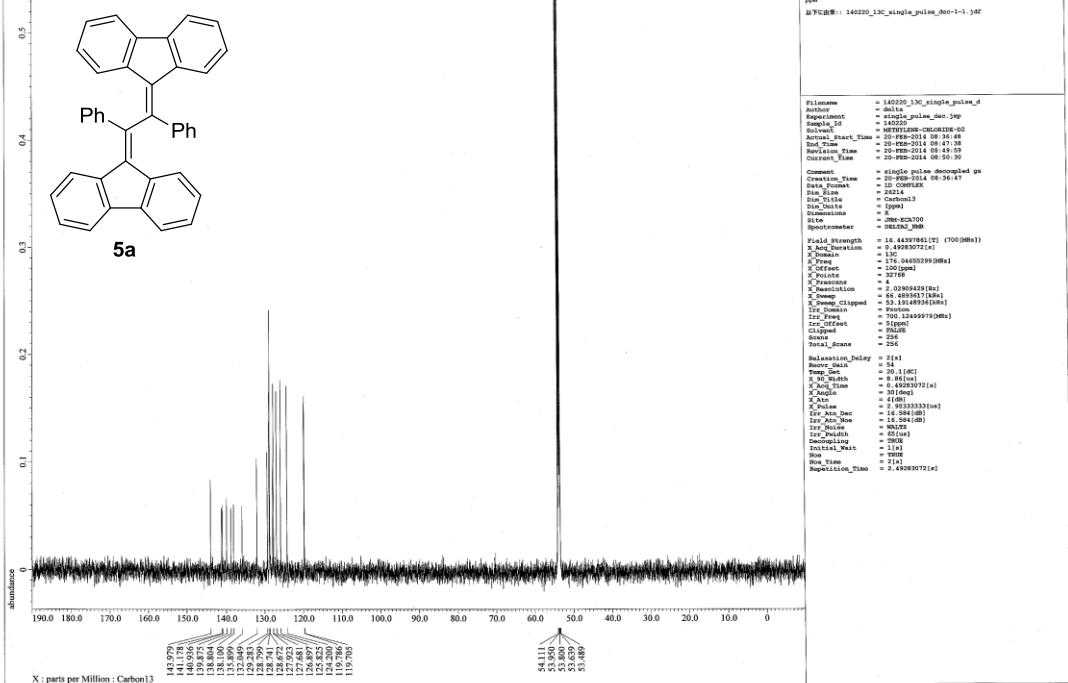
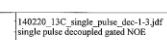
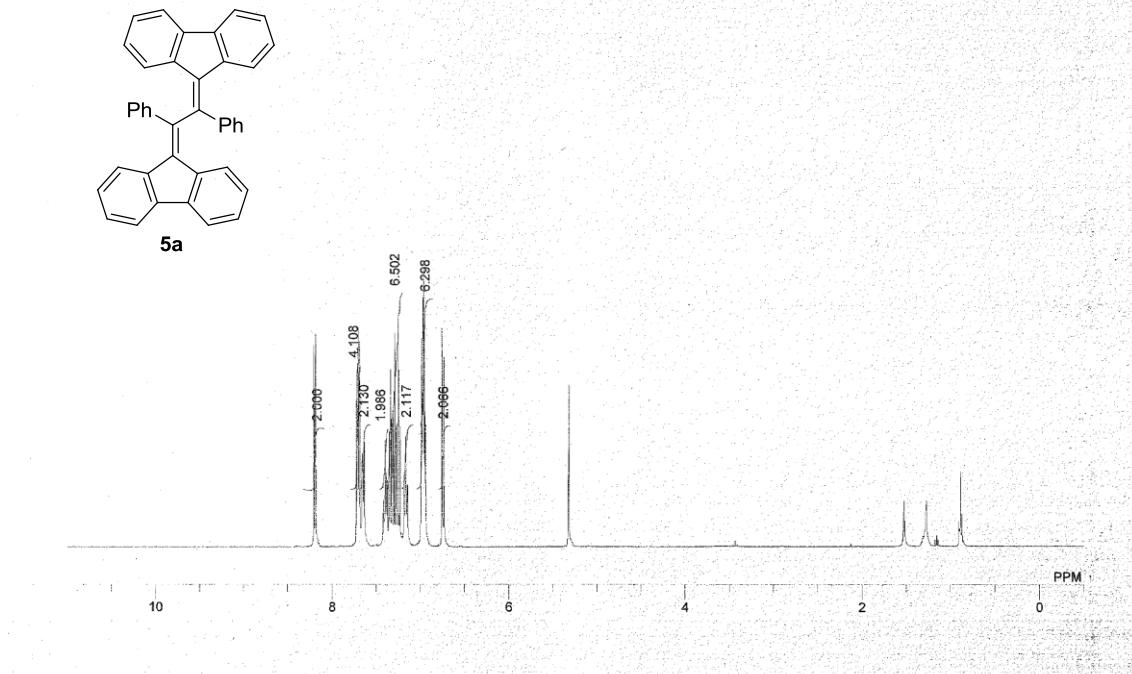
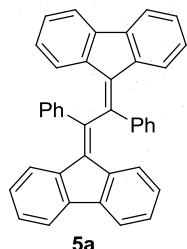
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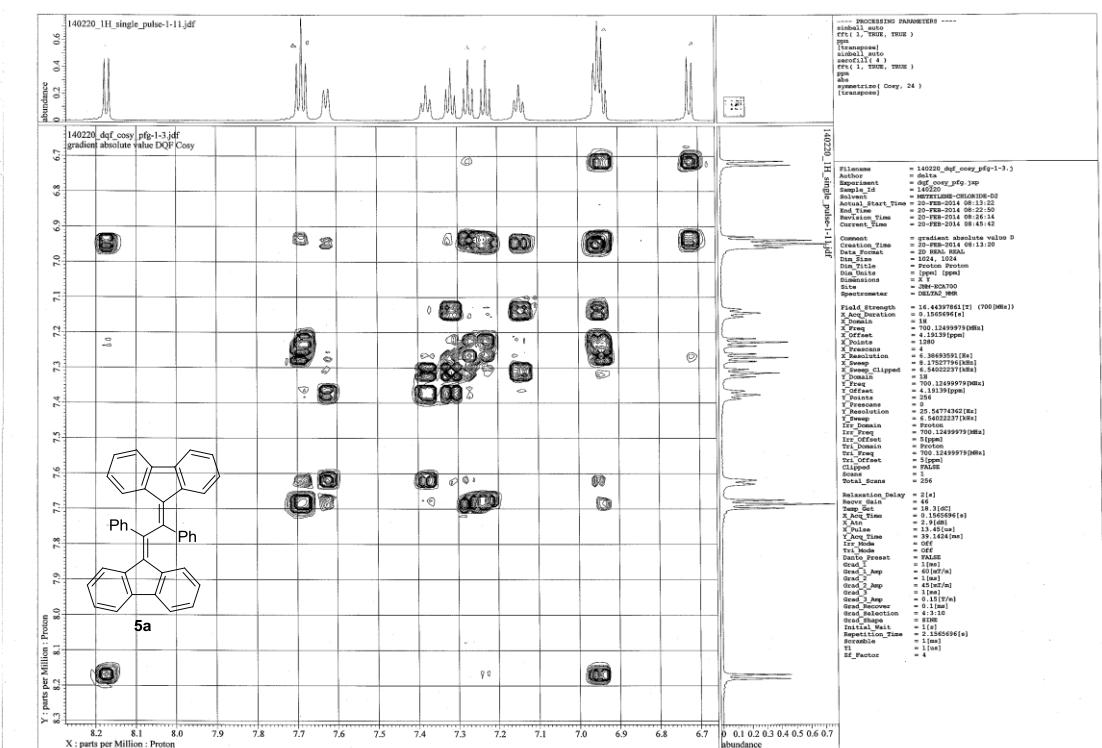
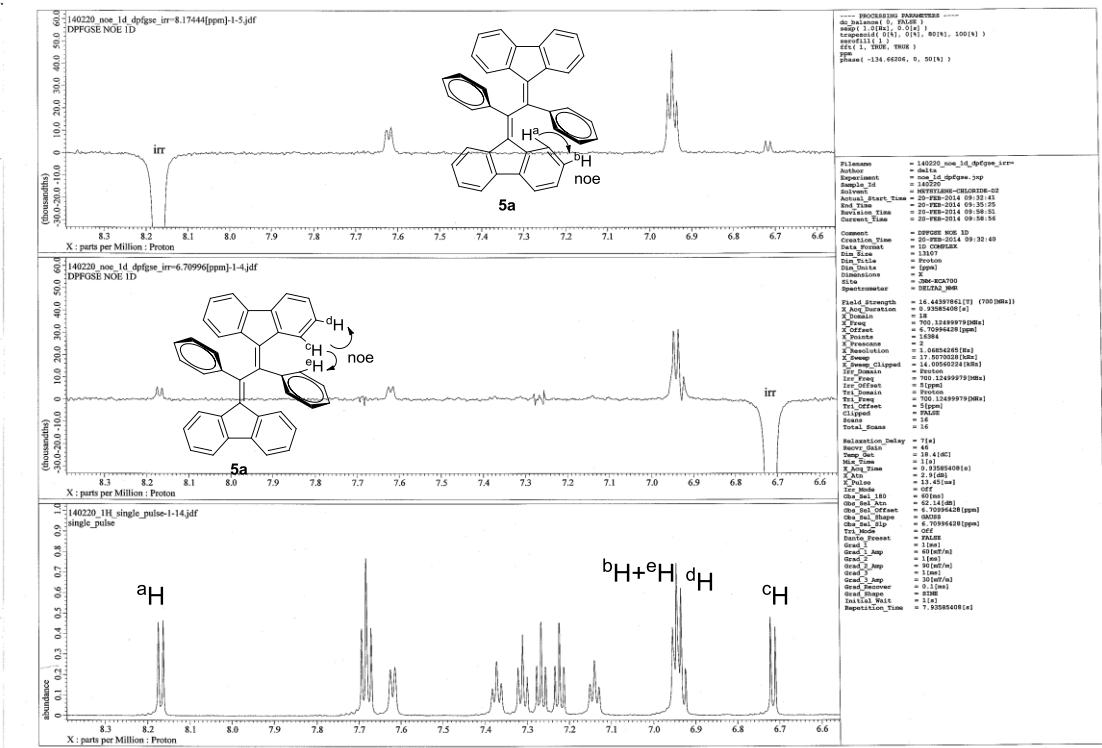


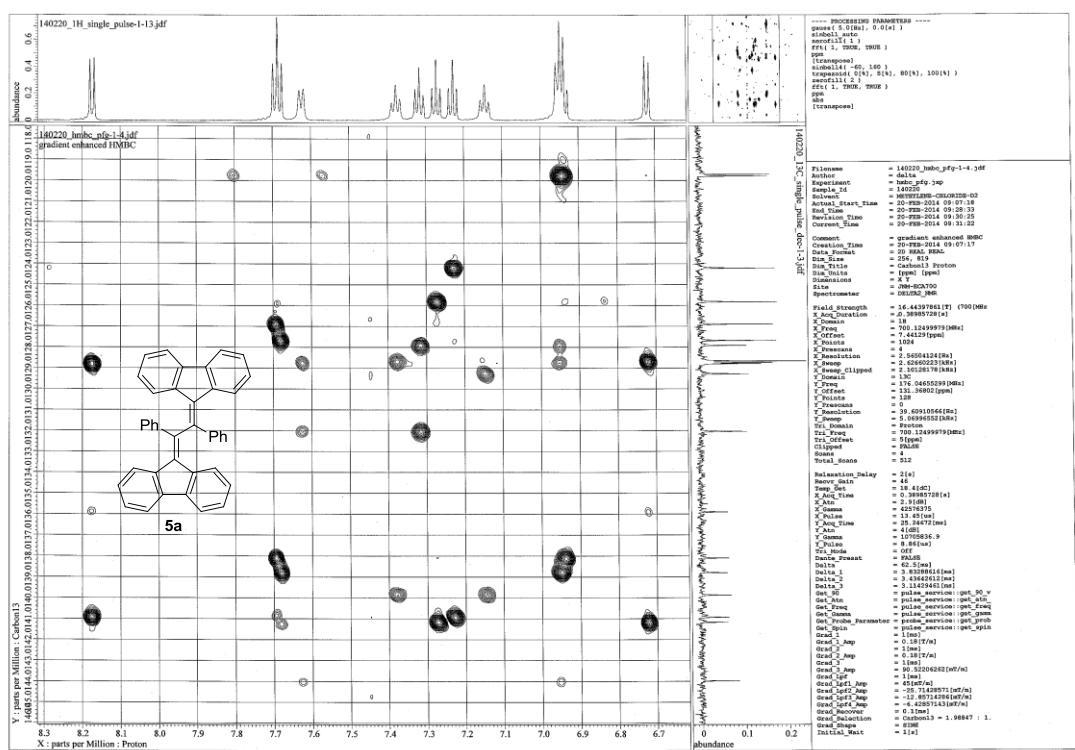
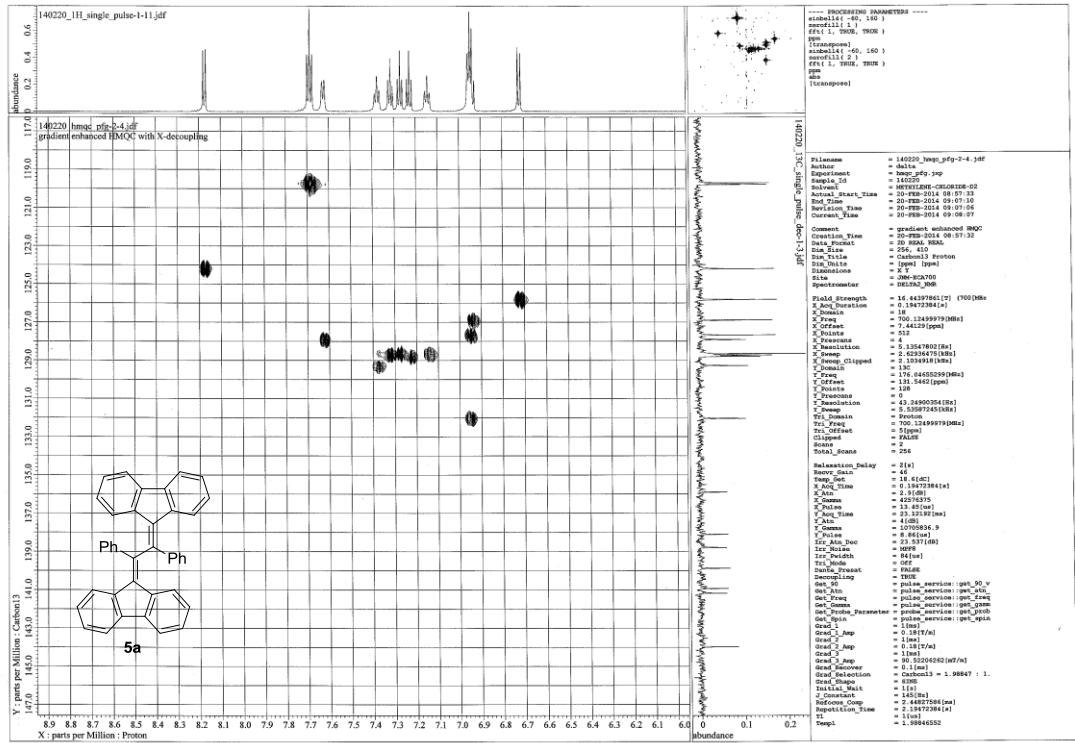
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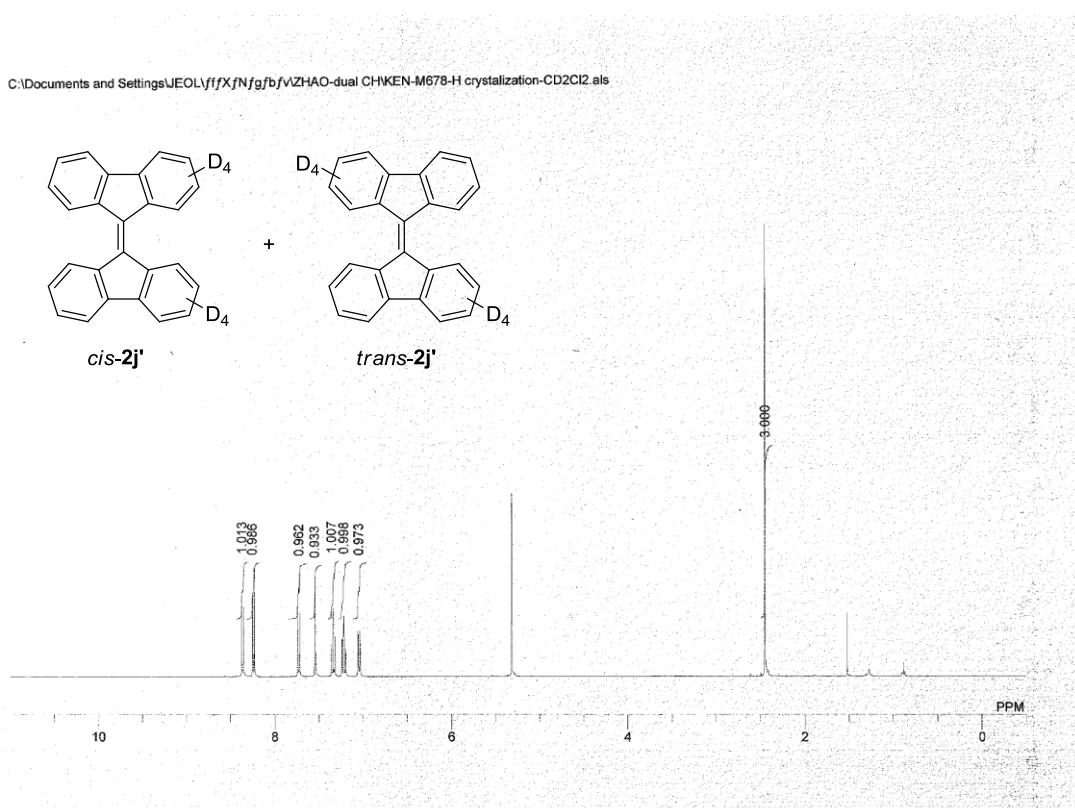


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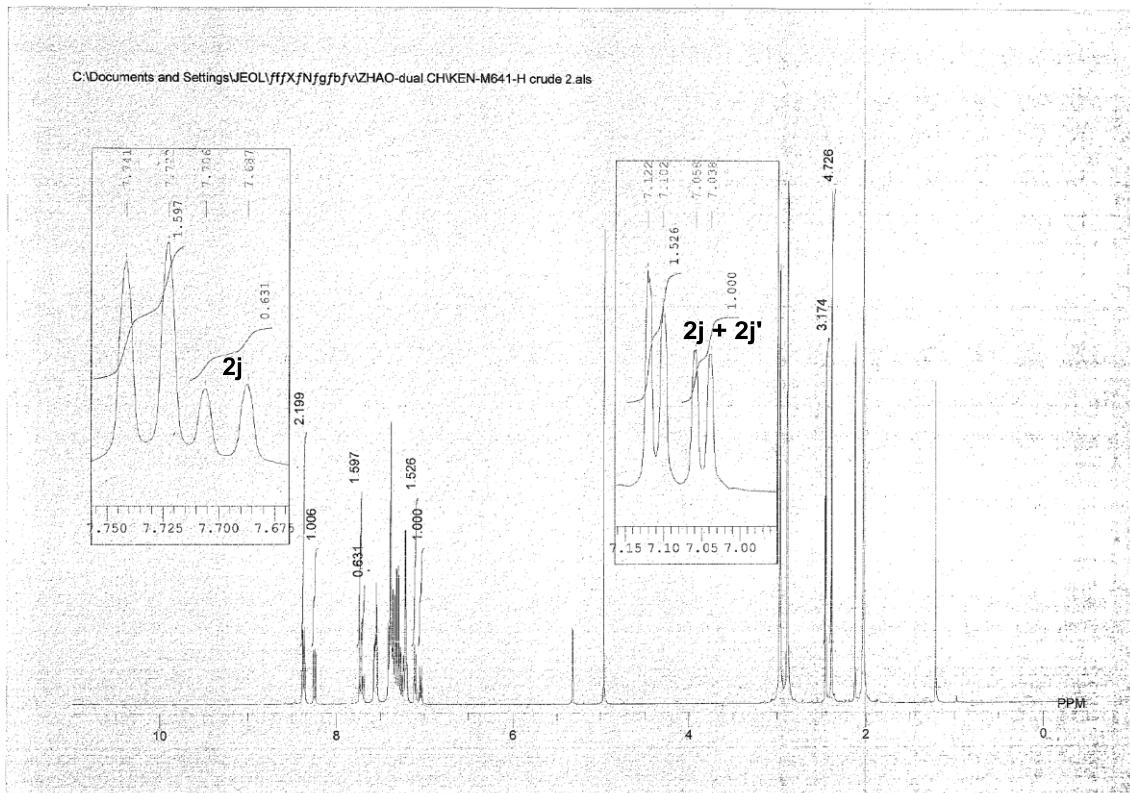








KIE experiment: 80 °C, 15 min: KIE = 1.7



KIE experiment: room temperature, 2.5 h: KIE = 1.6

