Supporting Information for

TfOH catalyzed synthesis of 9-arylfluorenes via tandem reaction under warm and efficient conditions

Qingcui Li, Wengang Xu, Jiaxing Hu, Xiaoqing Chen, Fanglin Zhang* and Hua Zheng*

College of Chemical Engineering , Wuhan University of Technology, Luoshi Road 205, Wuhan, Hubei, 430070, China; E-mail: fanglinzhang0210@gmail.com or zhenghua.whut@126.com

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Ⅰ. General information

All reactions were performed in air. Solvents were dried by the standard procedures. ^{1}H and ^{13}C NMR spectra were determined in $CDCl_3$ or DMSO-d_6 on a Varian-Inova 400MHz or 600 MHz spectrometer and chemical shifts were reported in ppm from internal TMS (δ). Column chromatography was performed with 300-400 mesh silica gel using flash column techniques. All of the reagents were used directly as obtained commercially unless otherwise noted. 2-arylbenzaldehydes (**1**),[1] [1,1':4',1''-terphenyl]-2',5'-dicarbaldehyde (**4**),[2] 2-phenoxybenzaldehyde (**6**)[3] and [1,1'-biphenyl]-2-ylmethylene diacetate (**8**) [4] were prepared according to the reported procedures.

References

1 J. Zhao, D. Yue, M. A. Campo and R. C. Larock, *J. Am. Chem. Soc.*, 2007, 129, 5288.

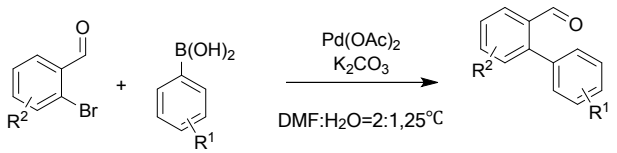
2 Z. Xie, B. Yang, L. Liu, M. Li, D. Lin, Y. Ma, G. Cheng and S. Liu, *Journal of Physical Organic Chemistry*, 2005, 18, 962.

3 J. Chen, X. Wang, X. Zheng, J. Ding, M. Liu and H. Wu, *Tetrahedron*, 2012, 68, 8905.

4 S. A. POURMOUSAVI and Z. ZINATI, *Turk J Chem*, 2009, 33, 385.

Ⅱ. Noncommercial Compounds

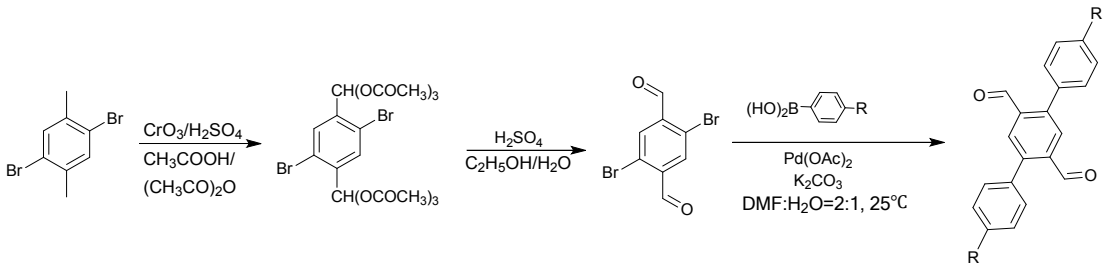
Preparation of 2-arylbenzaldehydes (1a, 1b, 1c, 1d, 1e, 1f, 1g, 1h, 1i, 1j, 1k, 1l, 1m, 1n, 1o)



Typical procedure for the preparation of 2-arylbenzaldehydes (1a, 1b, 1c, 1d, 1e, 1f, 1g, 1i, 1j, 1k, 1l, 1m, 1n, 1o)

5.0 mmol of arylboronic acid were added to 15 ml of a 2:1 DMF/H_2O solution containing 5.0 mmol of 2-bromobenzaldehyde derivative and 5.0 mmol of Na_2CO_3 and the reaction mixture was stirred for 2 min. $Pd(OAc)_2$ (5 mol %) was then added and the flask was flushed with N_2, sealed and allowed to stir at 25℃ overnight. The reaction mixture was extracted with EtOAc (3 x 50 ml). The combined organic layers were washed with water three times, dried over anhydrous Na_2SO_4 and concentrated under vacuum to yield the crude product, which was purified by column chromatography on silica gel using petroleum ether /ethyl acetate as eluent.

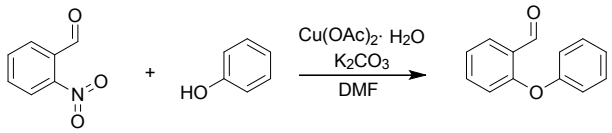
Preparation of [1,1':4',1''-terphenyl]-2',5'-dicarbaldehyde (4a, 4b)



Typical procedure for the preparation of [1,1':4',1''-terphenyl]-2',5'-dicarbaldehyde (4 a, 4b)

Sulfuric acid (14 ml) was added dropwise to a suspension containing 15 mmol 1,4-dibromo-2,5-dimethylbenzene, 20 ml acetic acid and 40 ml acetic anhydride at 0 ℃. 6.5 mmol CrO_3 was then added to the mixture in portions. The resulting mixture was stirred vigorously at this temperature for a further 5 h until the reaction was completed. The greenish slurry was poured into ice–water and filtered. The white solid was washed with water and cold methanol. The diacetate was then hydrolyzed by refluxing with a mixture of 20 ml water, 20 ml ethanol and 2 ml sulfuric acid for 5 h. After the mixture had cooled, the pale yellow product was separated by filtration. The crude product was purified by recrystallization from chloroform. Then, 5.0 mmol of arylboronic acid were added to 15 ml of a 2:1 DMF/H_2O solution containing 2.5 mmol of 2,5-dibromoterephthalaldehyde, the product from the last step and 5.0 mmol of Na_2CO_3 and the reaction mixture was stirred for 2 min. $Pd(OAc)_2$ (5 mol %) was then added and the flask was flushed with N_2, sealed and allowed to stir at 25℃ overnight. The reaction mixture was extracted with EtOAc (3 x 50 ml). The combined organic layers were washed with water three times, dried over anhydrous Na_2SO_4 and concentrated under vacuum to yield the crude product, which was purified by column chromatography on silica gel using petroleum ether /ethyl acetate as eluent.

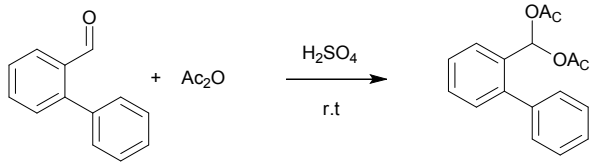
Preparation of 2-phenoxybenzaldehyde (6)



Typical procedure for the preparation of 2-phenoxybenzaldehyde (6)

Under N_2 atmosphere, a Schlenk tube was charged with 2-nitrobenzaldehyde (5 mmol), phenol (10 mmol), $Cu(OAc)_2{\cdot}H_2O$ (5 mol %), and Cs_2CO_3 (10 mmol) in DMF (20 ml) at room temperature. After that, the mixture was stirred constantly at 100 °C for 4 h. After the completion of the reaction, as monitored by TLC, the reaction mixture was cooled to room temperature, diluted with ethyl acetate, and filtrated. The filtrate concentrated under vacuum, and the resulting residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to afford 2-phenoxybenzaldehyde.

Preparation of [1,1'-biphenyl]-2-ylmethylene diacetate (8)



Procedure for the preparation of [1,1'-biphenyl]-2-ylmethylene diacetate (8)

A mixture of aldehyde (5 mmol), Ac_2O (20 mmol), and H_2SO_4 (1 mol %) was stirred at room temperature. After completion of the reaction, the mixture was extracted with EtOAc. The combined organic layers were washed with saturated $NaHCO_3$ solution (3 × 10 mL) and water (10 ml) and then dried (Na_2SO_4). The solvents were removed on a rotary evaporator to give almost pure product.

Ⅲ. Experimental Procedures

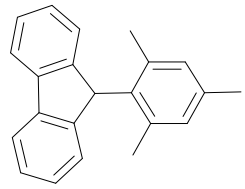
Typical procedure for the preparation of 9-mesityl -9H-fluorene

2-phenylbenzaldehyde (0.5 mmol) and mesitylene (2.5 mmol) were added to the glassware with 5 ml DCE. Then, TfOH (0.05 mmol) and Ac_2O (1.0 mmol) were added to the reaction mixture successively. The reaction was stirred at room temperature monitored by TLC. After that, the reaction mixture was quenched with water. The aqueous layer was extracted three times with 50 ml EtOAc. The combined organic layers were dried with anhydrous Na_2SO_4, filtered. The solvent was evaporated under reduced pressure and the crude mixture was purified by silica gel column chromatography for pure product.

Especially stated reaction conditons: **3ae** (benzene as solvent in relux); **3af** (1.1 mmol **2f**); **3ag** (1.1 mmol **2g**); **4** (0.5 mmol [1,1':4',1"-terphenyl]-2',5'-dicarbaldehyde (**4**), 5 mmol mesitylene, 0.1 mmol TfOH, 2.0 mmol Ac_2O**)**

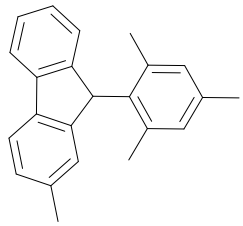
IV. Compound characterizations and NMR spectra

9-mesityl -9H-fluorene (3aa)



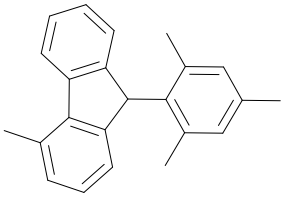
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 7.6, 0.7 Hz, 2H), 7.54 – 7.47 (m, 2H), 7.41 – 7.35 (m, 4H), 7.16 (s, 1H), 6.79 (s, 1H), 5.63 (s, 1H), 2.81 (s, 3H), 2.41 (s, 3H), 1.24 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 147.32, 141.01, 137.93, 137.76, 136.28, 133.99, 130.65, 128.94, 127.27, 126.91, 124.26, 120.10, 49.87, 21.85, 20.97, 18.78.

9-mesityl-2-methyl-9H-fluorene（3ba）



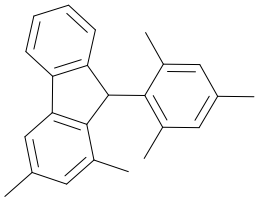
^{1}H NMR (400 MHz, CDCl3) δ 7.95 (d, J = 7.6 Hz, 1H), 7.88 (d, J = 7.7 Hz, 1H), 7.57 – 7.48 (m, 1H), 7.42 – 7.33 (m, 3H), 7.22 (d, J = 12.3 Hz, 2H), 6.85 (s, 1H), 5.64 (s, 1H), 2.85 (s, 3H), 2.52 (s, 3H), 2.46 (s, 3H), 1.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.54, 147.15, 141.15, 138.48, 138.09, 137.84, 137.26, 136.30, 134.29, 130.68, 128.96, 127.86, 126.91, 126.84, 124.91, 124.24, 119.91, 119.83, 49.74, 21.95, 21.78, 21.07, 18.90.

9-mesityl-4-methyl-9H-fluorene (3ca)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.7 Hz, 1H), 7.64 – 7.49 (m, 1H), 7.45 – 7.40 (m, 2H), 7.32 (dd, *J* = 7.6, 4.6 Hz, 2H), 7.20 (s, 1H), 6.99 (s, 1H), 6.84 (s, 1H), 5.65 (s, 1H), 2.95 (s, 3H), 2.85 (s, 3H), 2.46 (s, 3H), 1.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.80, 147.77, 142.02, 139.09, 137.99, 137.82, 136.26, 134.38, 133.24, 130.68, 129.22, 128.94, 127.09, 127.00, 126.87, 126.63, 124.17, 123.31, 121.76, 49.88, 21.90, 21.25, 21.03, 18.88.

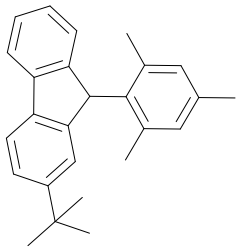
9-mesityl-1,3-dimethyl-9H-fluorene (3da)



^{1}H NMR (400 MHz, CDCl3) δ 7.91 (d, J = 7.6 Hz, 1H), 7.64 (s, 1H), 7.48 (t, J = 7.2 Hz, 1H), 7.37 – 7.28 (m, 2H), 7.13 (s, 1H), 7.01 (s, 1H), 6.95 (s, 1H), 6.76 (s, 1H), 5.54 (s, 1H), 2.83 (s, 3H), 2.58 (s, 3H), 2.40 (s, 3H), 2.08 (s, 3H), 1.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.10, 142.57, 141.36, 141.33, 137.79, 137.67,

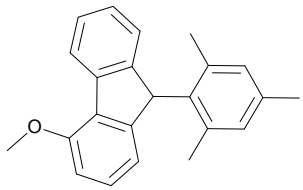
137.07, 136.74, 135.92, 134.41, 133.78, 130.52, 129.75, 129.10, 127.05, 126.84, 124.20, 119.77, 118.42, 77.49, 77.17, 76.85, 49.19, 22.14, 21.57, 20.97, 18.57, 18.52.

2-(tert-butyl)-9-mesityl-9H-fluorene (3ea)



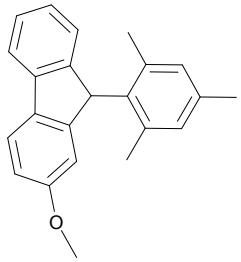
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.8 Hz, 1H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.60 (t, *J* = 10.5 Hz, 1H), 7.52 (dd, *J* = 8.6, 3.7 Hz, 1H), 7.44 (d, *J* = 13.7 Hz, 1H), 7.37 (d, *J* = 4.3 Hz, 2H), 7.21 (s, 1H), 6.84 (s, 1H), 5.66 (s, 1H), 2.87 (s, 3H), 2.46 (s, 3H), 1.50 (s, 9H), 1.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.79, 147.47, 147.30, 141.05, 138.47, 138.04, 137.75, 136.11, 134.25, 130.70, 128.95, 127.09, 126.89, 126.84, 124.19, 124.09, 121.04, 119.81, 119.72, 50.05, 35.05, 31.79, 21.96, 21.04, 19.01.

9-mesityl-4-methoxy-9H-fluorene (3fa)



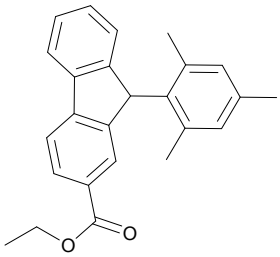
^{1}H NMR (600 MHz, CDCl3) δ 8.31 (1 H, d, J 7.5), 7.47 (1 H, t, J 7.1), 7.30 (3 H, dd, J 13.9, 6.4), 7.11 (1 H, s), 6.98 (1 H, d, J 8.1), 6.94 (1 H, d, J 7.4), 6.76 (1 H, s), 5.58 (1 H, s), 4.12 (3 H, s), 2.76 (3 H, s), 2.38 (3 H, s), 1.23 (3 H, s).^{13}C NMR (151 MHz, CDCl3) δ 156.12, 149.24, 146.55, 140.25, 138.05, 137.69, 136.19, 134.04, 130.53, 128.98, 128.83, 128.19, 126.84, 126.31, 123.90, 123.49, 116.55, 108.83, 55.39, 50.18, 21.77, 20.93, 18.76.

9-mesityl-2-methoxy-9H-fluorene (3ga)



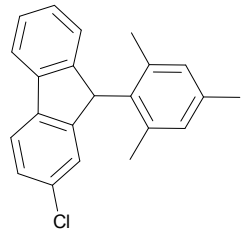
^{1}H NMR (400 MHz, CDCl3) δ 7.76 (d, J = 8.4 Hz, 2H), 7.46 – 7.33 (m, 1H), 7.21 (d, J = 4.4 Hz, 2H), 7.06 (s, 1H), 7.02 – 6.95 (m, 1H), 6.81 (s, 1H), 6.71 (s, 1H), 5.48 (s, 1H), 3.82 (s, 3H), 2.71 (s, 3H), 2.33 (s, 3H), 1.18 (s, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 159.73, 149.19, 146.63, 140.84, 137.97, 137.63, 136.19, 133.96, 133.93, 130.52, 128.77, 126.79, 126.02, 123.98, 120.75, 119.14, 113.08, 109.54, 55.56, 49.82, 21.73, 20.87, 18.73.

ethyl 9-mesityl-9H-fluorene-2-carboxylate (3ia)



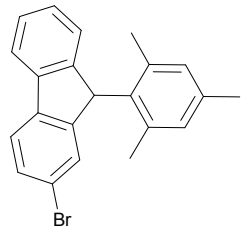
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.23 (1 H, d, *J* 8.0), 8.11 – 7.82 (3 H, m), 7.41 (3 H, ddd, *J* 36.5, 22.0, 7.4), 7.13 (1 H, s), 6.75 (1 H, s), 5.60 (1 H, s), 2.78 (3 H, s), 2.38 (4 H, s), 1.47 (3 H, t, *J* 7.1), 1.39 (1 H, s), 1.19 (3 H, s), 1.13 – 0.90 (1 H, m). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.87, 148.50, 147.30, 145.41, 139.84, 137.79, 137.70, 136.49, 133.14, 130.71, 129.29, 129.08, 128.89, 128.43, 127.15, 127.00, 125.37, 124.39, 120.93, 119.75, 60.95, 49.82, 21.85, 21.29, 20.91, 18.76, 14.49.

2-chloro-9-mesityl-9H-fluorene （3ja）



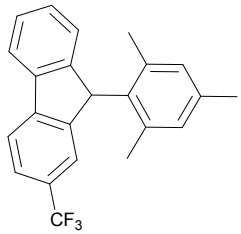
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.6 Hz, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.64 – 7.56 (m, 1H), 7.52 – 7.44 (m, 2H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.31 (d, *J* = 7.5 Hz, 1H), 7.14 (s, 1H), 6.78 (s, 1H), 5.56 (s, 1H), 2.77 (s, 3H), 2.40 (s, 3H), 1.23 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 149.35, 147.06, 139.96, 139.92, 137.83, 137.73, 136.63, 133.09, 130.74, 130.12, 129.06, 127.71, 127.42, 127.13, 124.27, 121.39, 121.20, 120.19, 49.79, 21.83, 20.98, 18.84.

2-bromo-9-mesityl-9H-fluorene (3ka)

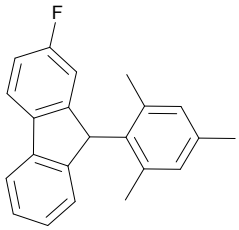


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (1 H, d, *J* 7.6), 7.84 (1 H, d, *J* 8.1), 7.50 (2 H, dd, *J* 14.9, 7.6), 7.37 (3 H, q, *J* 7.7), 7.17 (1 H, s), 6.82 (1 H, s), 5.59 (1 H, s), 2.80 (3 H, s), 2.43 (3 H, s), 1.27 (3 H, s).^{13}C NMR (101 MHz, $CDCl_3$) δ 149.09, 147.21, 139.95, 139.57, 137.85, 137.75, 136.65, 133.19, 133.13, 130.78, 129.10, 127.61, 127.31, 127.15, 124.57, 124.31, 121.03, 120.19, 49.83, 21.85, 21.00, 18.86.

9-mesityl-2-(trifluoromethyl)-9H-fluorene (3la)



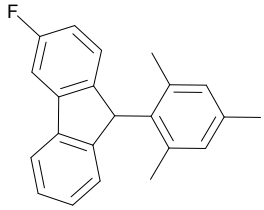
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (d, 1H), 7.98 (d, *J* = 7.6 Hz, 1H), 7.79 (d, *J* = 10.7 Hz, 1H), 7.63 (s, 1H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.38 (d, *J* = 7.5 Hz, 1H), 7.18 (s, 1H), 6.81 (s, 1H), 5.64 (s, 1H), 2.81 (s, 3H), 2.41 (s, 3H), 1.22 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.07, 147.79, 144.36, 139.51, 137.80, 137.73, 136.77, 132.80, 130.82, 129.16, 128.51, 127.24, 124.41, 124.32, 124.30, 121.13, 121.11, 120.82, 120.17, 49.95, 21.78, 20.90, 18.77.



2-fluoro-9-mesityl-9H-fluorene (3ma)

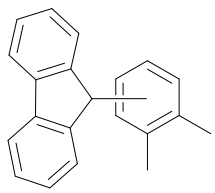
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.75 (m, 2H), 7.50 (t, *J* = 6.5 Hz, 1H), 7.35 (s, 2H), 7.20 (dd, *J* = 14.4, 5.2 Hz, 1H), 7.17 (s, 1H), 7.07 (d, *J* = 8.5 Hz, 1H), 6.81 (s, 1H), 5.58 (s, 1H), 2.79 (s, 3H), 2.42 (s, 3H), 1.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.11, 161.67, 149.64, 149.56, 147.17, 140.14, 137.86, 137.73, 137.01, 136.61, 133.37, 130.73, 129.07, 127.09, 126.98, 124.24, 121.09, 121.01, 119.81, 114.26, 114.03, 111.71, 111.48, 49.92, 21.83, 20.99, 18.82.

3-fluoro-9-mesityl-9H-fluorene （3na）



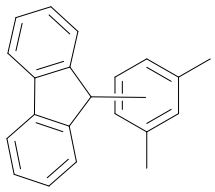
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (1 H, d, *J* 7.5), 7.63 (1 H, d, *J* 8.8), 7.53 (1 H, t, *J* 7.2), 7.41 (1 H, t, *J* 7.3), 7.37 (1 H, d, *J* 7.3), 7.28 (1 H, t, *J* 6.1), 7.18 (1 H, s), 7.08 (1 H, t, *J* 8.7), 6.81 (1 H, s), 5.58 (1 H, s), 2.81 (3 H, s), 2.43 (3 H, s), 1.26 (3 H, s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.94, 161.53, 148.25, 142.93, 142.84, 142.63, 140.22, 140.19, 137.84, 137.74, 136.49, 133.63, 130.77, 129.07, 127.93, 127.09, 125.24, 125.15, 124.41, 120.42, 114.23, 114.01, 107.26, 107.03, 49.27, 21.88, 20.99, 18.79.

9-(dimethylphenyl)-9H-fluorene（3ab）



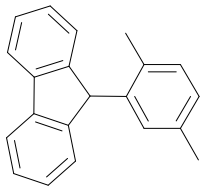
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (2 H, t, *J* 11.4), 7.58 (1 H, d, *J* 7.3), 7.46 (4 H, ddd, *J* 11.6, 8.5, 4.1), 7.37 (2 H, dd, *J* 6.2, 1.1), 7.27 – 7.20 (1 H, m), 7.14 (1 H, t, *J* 8.8), 6.94 (2 H, dd, *J* 23.3, 8.0), 6.39 (1 H, d, *J* 7.7), 5.61 (1 H, s), 5.10 (1 H, s), 2.80 (1 H, s), 2.53 (1 H, s), 2.33 (3 H, s), 2.29 (3 H, s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.70, 148.27, 147.68, 141.23, 141.07, 140.68, 139.99, 139.00, 138.31, 138.03, 137.03, 136.90, 136.55, 135.11, 134.88, 131.05, 130.00, 129.68, 129.52, 129.33, 128.43, 127.35, 127.27, 127.18, 127.08, 125.91, 125.41, 125.18, 124.68, 120.07, 119.99, 119.89, 56.74, 54.24, 21.33, 20.51, 19.84, 19.47.

9-(dimethylphenyl)-9H-fluorene（3ac）



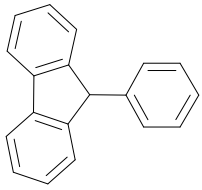
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (t, *J* = 10.3 Hz, 1H), 7.53 (t, *J* = 12.5 Hz, 1H), 7.49 – 7.38 (m, 1H), 7.35 – 7.29 (m, 2H), 7.20 (d, *J* = 4.5 Hz, 2H), 7.19 – 7.10 (m, 2H), 6.93 – 6.65 (m, 1H), 6.31 (d, *J* = 7.8 Hz, 1H), 5.41 (s, 1H), 5.02 (s, 1H), 2.81 (d, *J* = 17.1 Hz, 3H), 2.45 – 2.19 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.13, 147.56, 142.18, 139.20, 137.45, 137.13, 136.76, 136.00, 133.01, 132.69, 132.55, 131.05, 129.35, 127.52, 127.32, 126.98, 126.61, 126.31, 125.00, 124.60, 123.09, 122.57, 122.18, 55.84, 49.59, 20.39, 18.18.

9-(2,5-dimethylphenyl)-9H-fluorene （3ad）



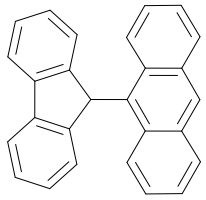
^{1}H NMR(400 MHz, $CDCl_3$) δ 7.93 (3 H, d, *J* 7.6), 7.57 – 7.45 (4 H, m), 7.39 (2 H, d, *J* 6.3), 7.16 – 6.94 (2 H, m), 6.33 (1 H, s), 5.50 (1 H, s), 2.84 (3 H, s), 2.56 (2 H, s), 2.14 (3 H, s), 1.23 (2 H, s).^{13}C NMR δ (101 MHz, $CDCl_3$) δ 148.63, 141.26, 139.89, 135.12, 134.20, 133.60, 133.11, 131.63, 130.34, 127.98, 127.63, 127.38, 127.30, 127.18, 125.21, 124.82, 56.36, 50.10, 21.07, 20.92, 20.12, 17.81.

9-phenyl-9H-fluorene （3ae）



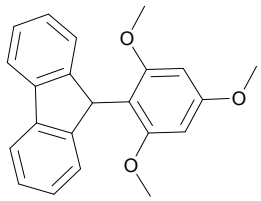
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (2 H, d, *J* 7.6), 7.48 (2 H, t, *J* 7.4), 7.42 (2 H, d, *J* 7.2), 7.37 – 7.33 (4 H, m), 7.20 (1 H, d, *J* 1.7), 7.19 (1 H, s), 5.14 (1 H, s).^{13}C NMR (101 MHz, $CDCl_3$) δ 147.99 (s), 141.69 (s), 141.10 (s), 128.76 (s), 128.42 (s), 127.39 (s), 126.90 (s), 125.41 (s), 119.95 (s), 54.55 (s).

9-(9H-fluoren-9-yl)anthracene （3af）



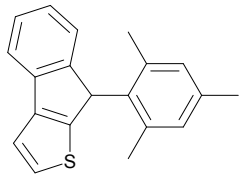
^{1}H NMR (400 MHz, $CDCl_3$, DMSO-d_6) δ 8.48 (d, *J* = 8.9 Hz, 1H), 8.28 (s, 1H), 7.94 (d, *J* = 8.3 Hz, 1H), 7.82 (d, *J* = 7.6 Hz, 2H), 7.72 (d, *J* = 8.5 Hz, 1H), 7.40 (dt, *J* = 14.7, 6.8 Hz, 2H), 7.24 (t, *J* = 7.5 Hz, 2H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.96 (t, *J* = 7.4 Hz, 2H), 6.85 (d, *J* = 7.5 Hz, 2H), 6.70 – 6.57 (m, 1H), 6.50 (d, *J* = 9.0 Hz, 1H), 6.31 (s, 1H), 2.73 (s, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 148.79, 140.00, 132.09, 131.76, 131.60, 131.40, 129.50, 129.26, 128.74, 127.66, 127.29, 127.01, 126.50, 125.44, 124.93, 124.79, 124.63, 124.20, 123.70, 120.39, 48.69.

9-(2,4,6-trimethoxyphenyl)-9H-fluorene （3ag）



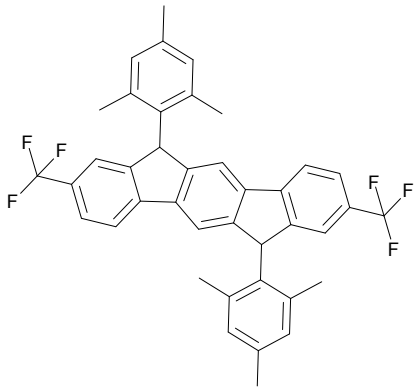
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.5 Hz, 2H), 7.43 (t, *J* = 7.1 Hz, 2H), 7.33 (dt, *J* = 14.6, 7.3 Hz, 4H), 6.42 (s, 1H), 6.06 (s, 1H), 5.75 (s, 1H), 4.06 (s, 3H), 3.88 (s, 3H), 3.07 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 160.22, 159.85, 159.75, 148.88, 141.14, 126.61, 126.16, 123.71, 119.49, 110.62, 92.59, 91.08, 56.34, 55.81, 55.32, 43.76.

8-mesityl-8H-indeno[2,1-b]thiophene （3oa）



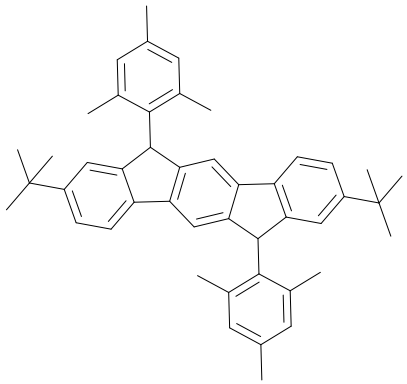
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.5 Hz, 1H), 7.40 (dd, *J* = 14.3, 5.1 Hz, 3H), 7.25 – 7.16 (m, 2H), 7.06 (s, 1H), 6.74 (s, 1H), 5.53 (s, 1H), 2.72 (s, 3H), 2.34 (s, 3H), 1.31 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 150.50, 149.08, 146.36, 138.71, 138.02, 137.22, 136.52, 133.07, 130.65, 129.02, 128.60, 126.83, 124.94, 124.04, 119.28, 118.73, 47.70, 21.70, 20.92, 18.42.

6,12-dimesityl-2,8-bis(trifluoromethyl)-6,12-dihydroindeno[1,2-b]fluorine (5a)



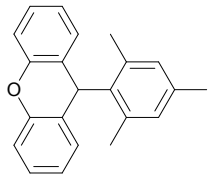
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.0 Hz, 2H), 7.77 (s, 2H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.51 (s, 2H), 7.17 (s, 2H), 6.75 (s, 2H), 5.66 (s, 2H), 2.83 (s, 6H), 2.38 (s, 7H), 1.12 (s, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 148.09, 147.56, 143.89, 140.25, 137.85, 137.69, 136.93, 132.92, 130.90, 129.22, 125.85, 124.23, 123.15, 121.05, 121.02, 120.41, 116.71, 49.62, 21.91, 20.90, 18.59.

2,8-di-tert-butyl-6,12-dimesityl-6,12-dihydroindeno[1,2-b]fluorine (5b)



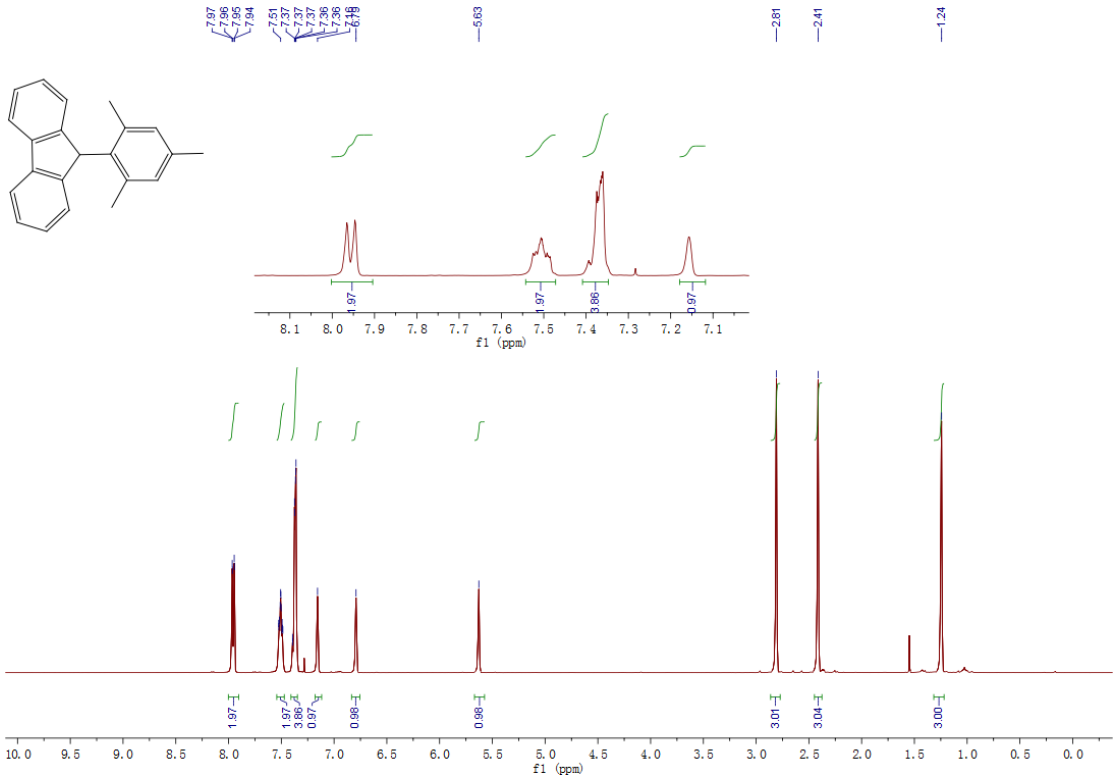
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.9 Hz, 2H), 7.61 (d, *J* = 12.6 Hz, 2H), 7.41 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.25 (s, 2H), 7.13 (s, 2H), 6.72 (d, *J* = 11.3 Hz, 2H), 5.59 (s, 2H), 2.81 (s, 6H), 2.37 (s, 6H), 1.33 (s, 18H), 1.21 (d, *J* = 5.0 Hz, 1H), 1.13 (s, 5H).^{13}C NMR (101 MHz, $CDCl_3$) δ 150.26, 147.52, 146.37, 140.19, 138.47, 138.07, 137.75, 135.98, 134.65, 130.58, 128.79, 123.89, 120.76, 119.49, 115.47, 49.64, 34.88, 31.62, 21.97, 20.93, 18.69.

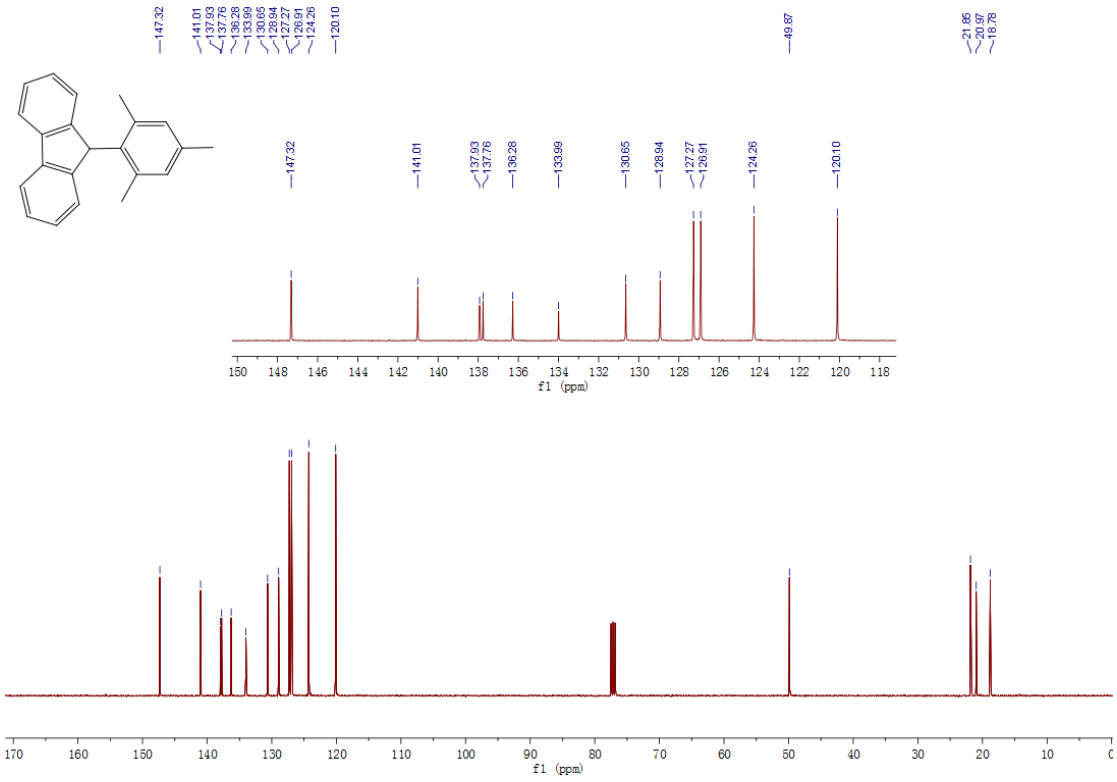
9-mesityl-9H-xanthene (7)



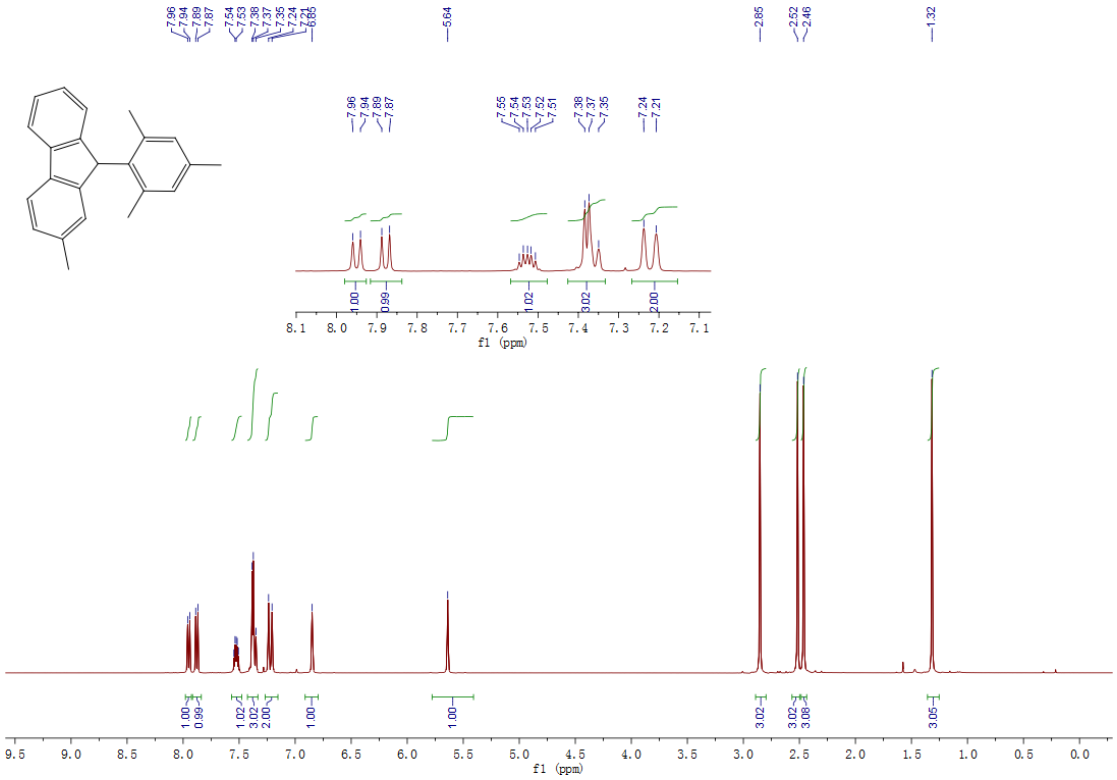
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.3 Hz, 2H), 7.22 – 7.15 (m, 2H), 7.12 (s, 1H), 7.00 (dd, *J* = 10.5, 4.2 Hz, 2H), 6.89 (d, *J* = 6.3 Hz, 3H), 6.02 (s, 1H), 2.67 (s, 3H), 2.41 (d, *J* = 13.2 Hz, 3H), 1.79 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 151.03, 137.90, 137.62, 137.15, 136.61, 131.63, 128.78, 128.23, 127.77, 123.91, 123.21, 116.18, 37.29, 21.38, 21.04, 20.78.

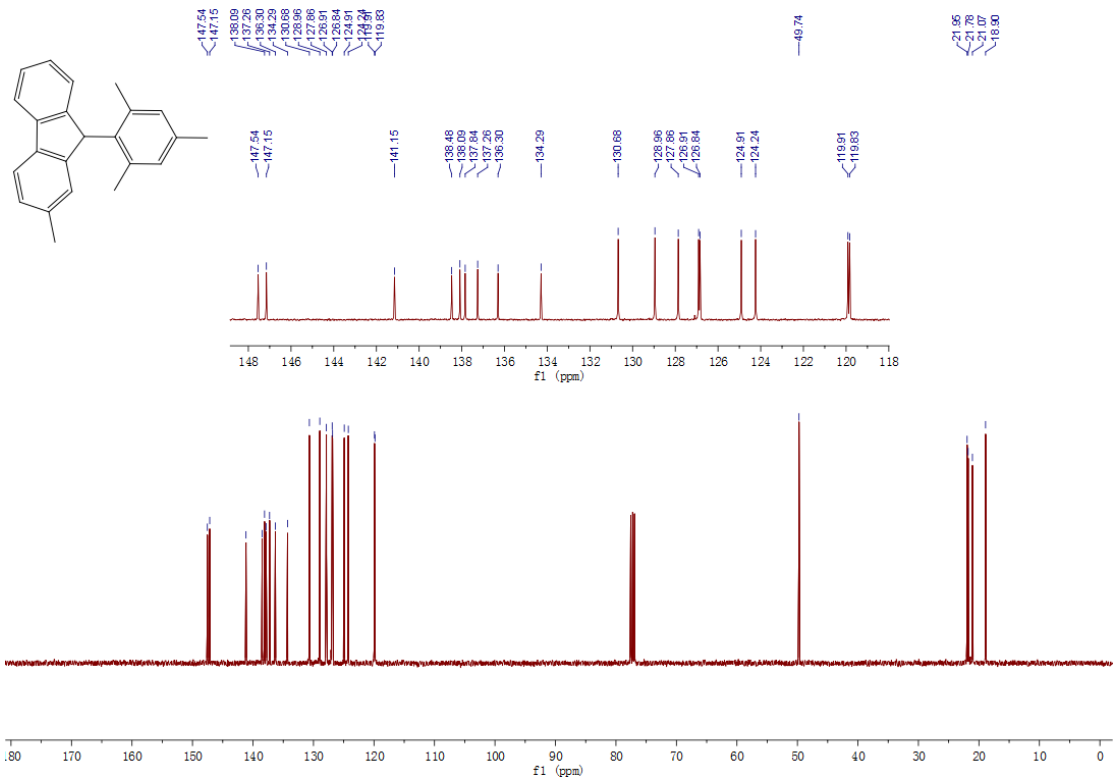
3aa



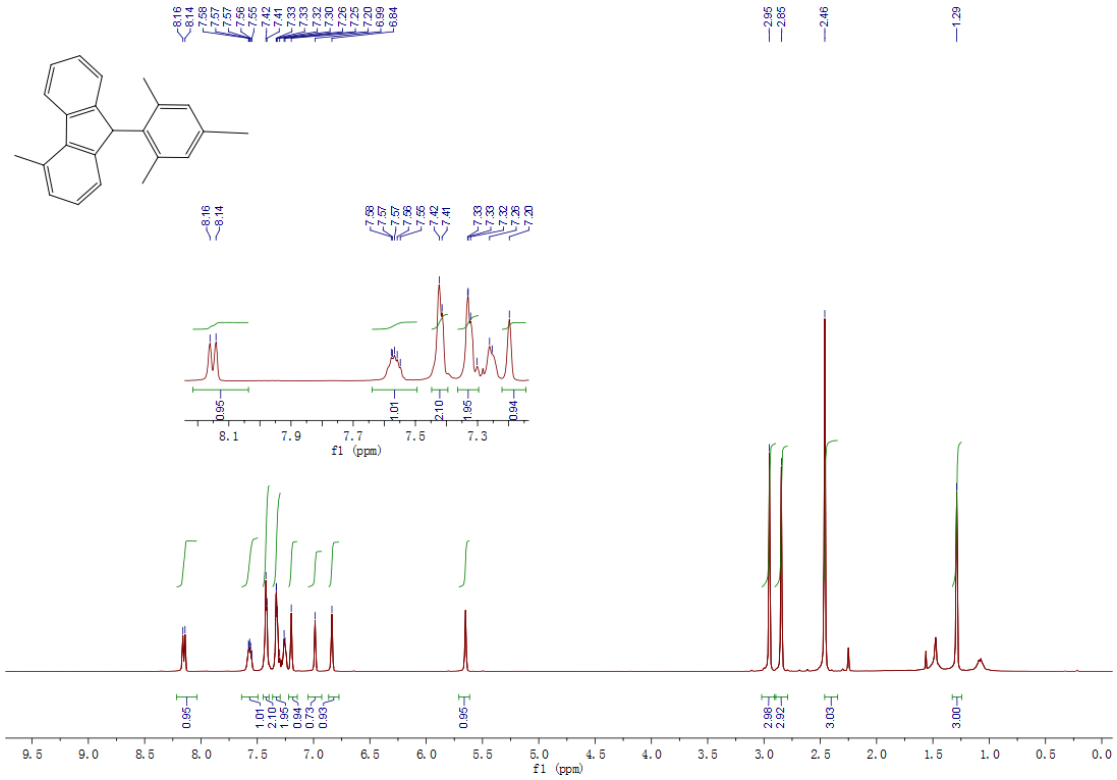


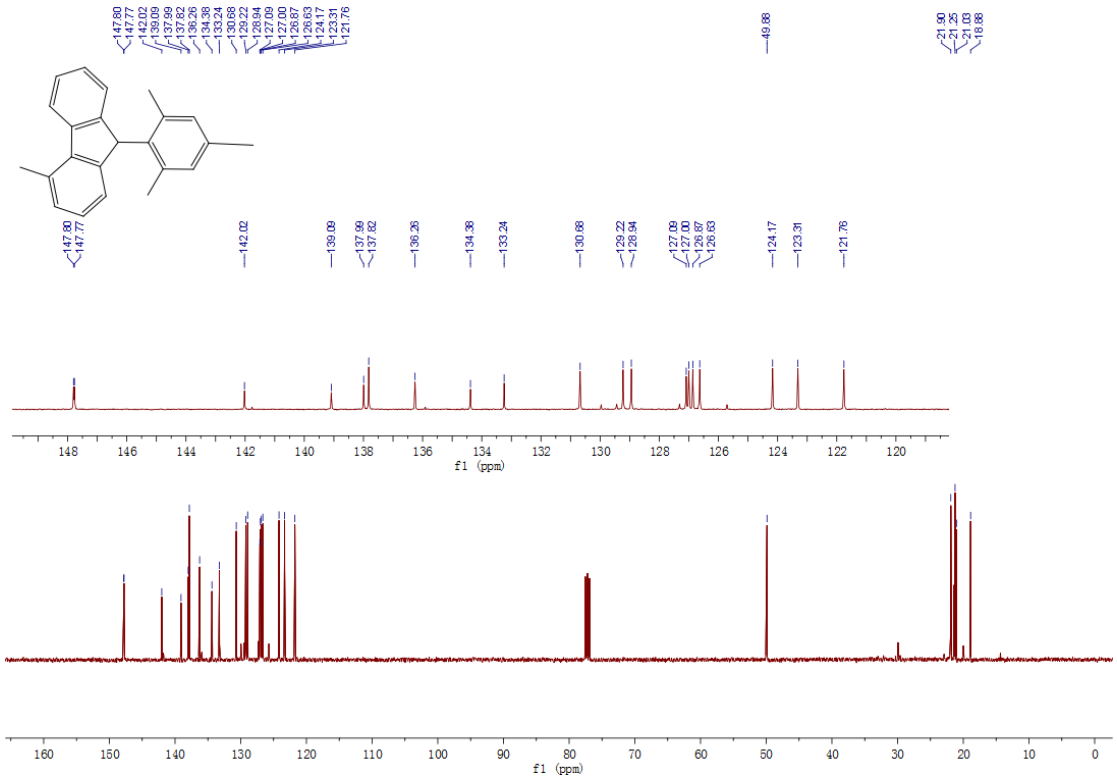
3ba



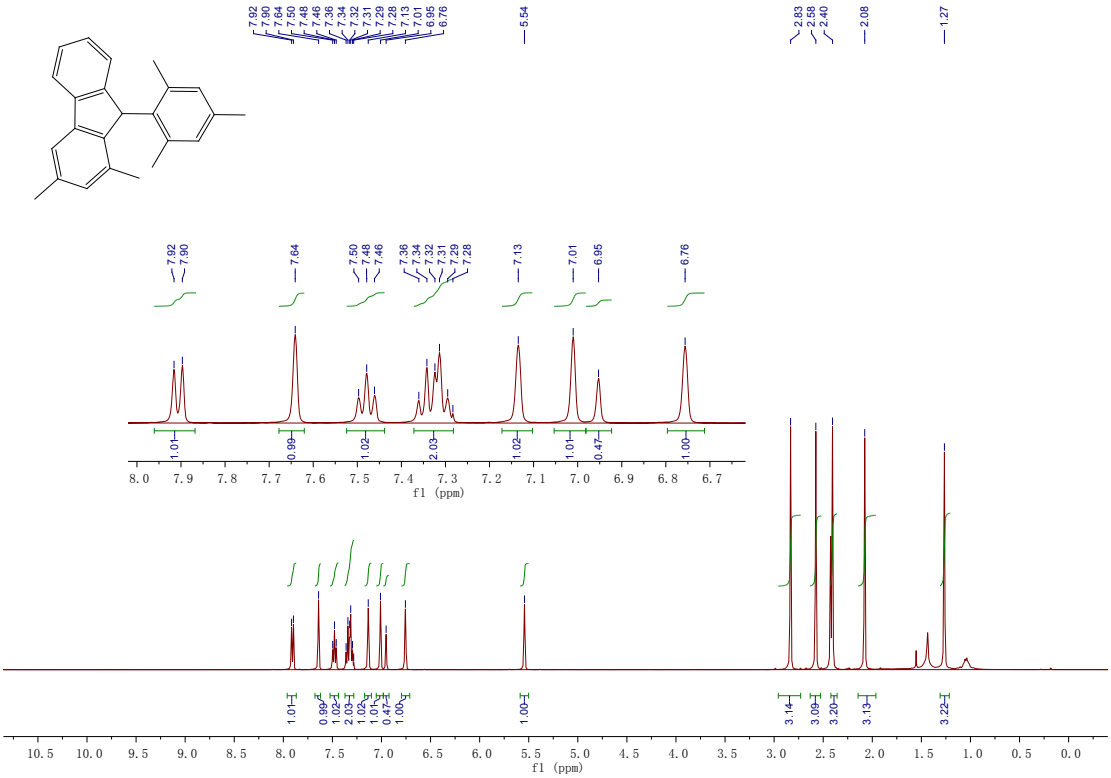


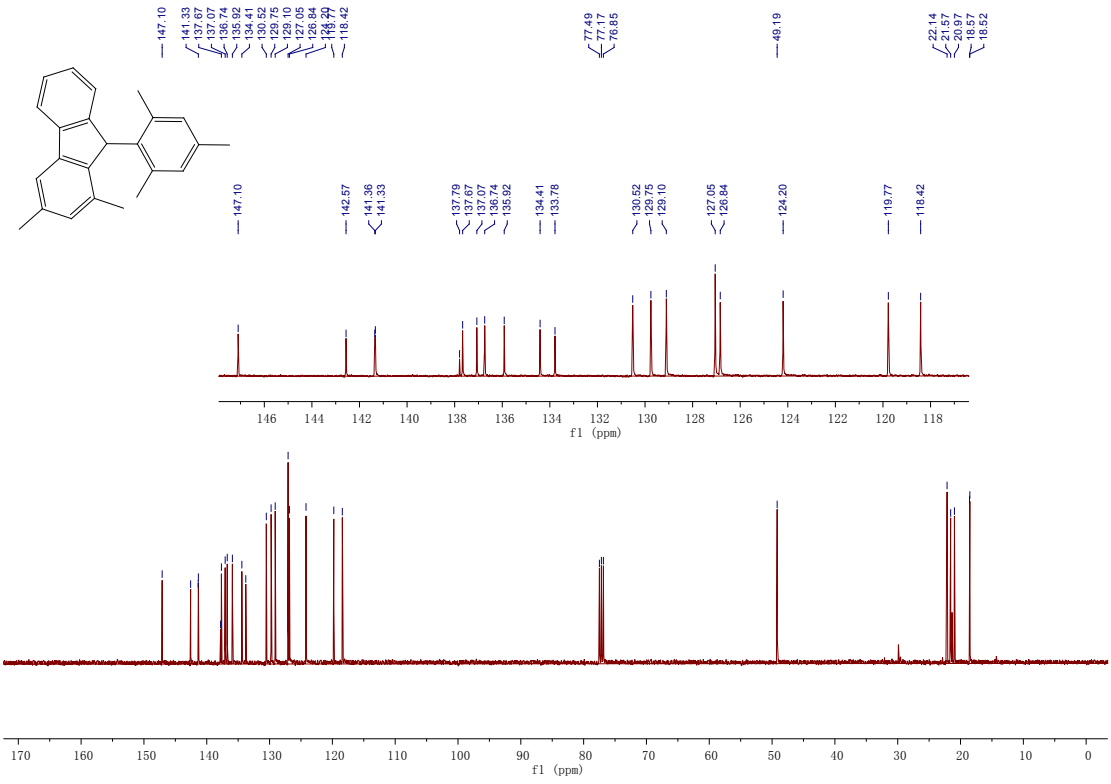
3ca


8.16
8.14
7.58
7.57
7.57
7.56
7.55
7.42
7.41
7.33
7.33
7.32
7.30
7.26
7.25
7.20
6.89
6.84
2.95
2.85
2.46
1.29
f1 (ppm)

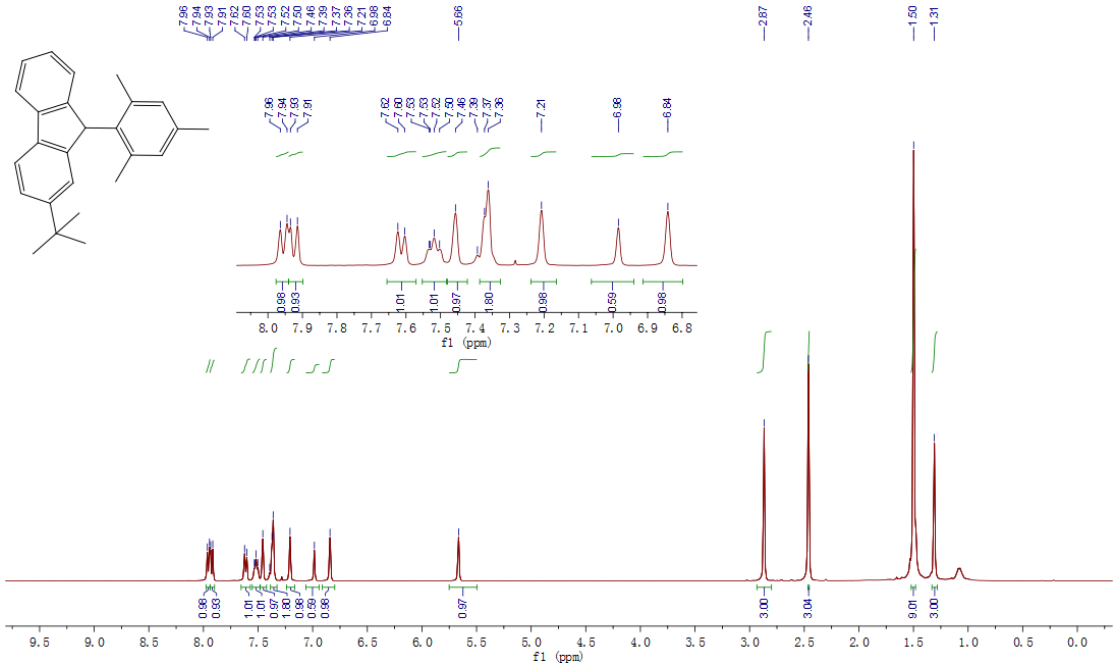

147.80
147.77
142.02
139.09
137.99
137.82
136.26
134.38
133.24
130.68
129.22
128.94
127.09
127.00
126.87
126.63
124.17
123.31
121.76
49.88
21.90
21.25
21.03
18.88
f1 (ppm)

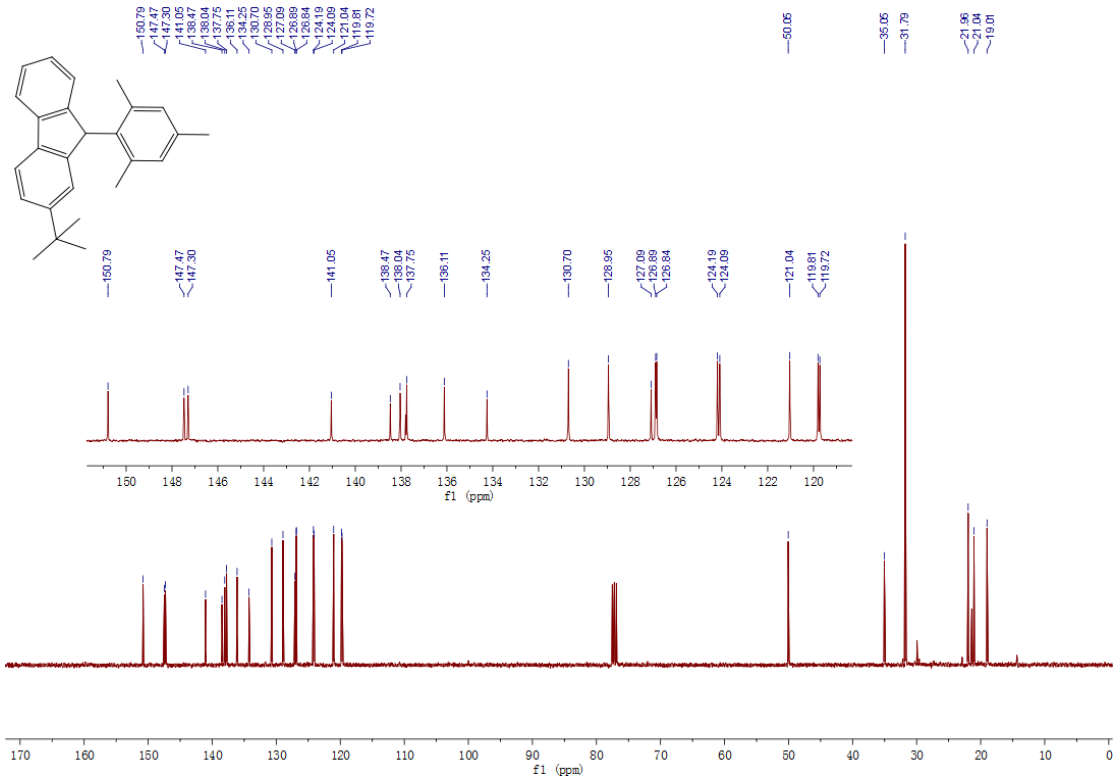
3da



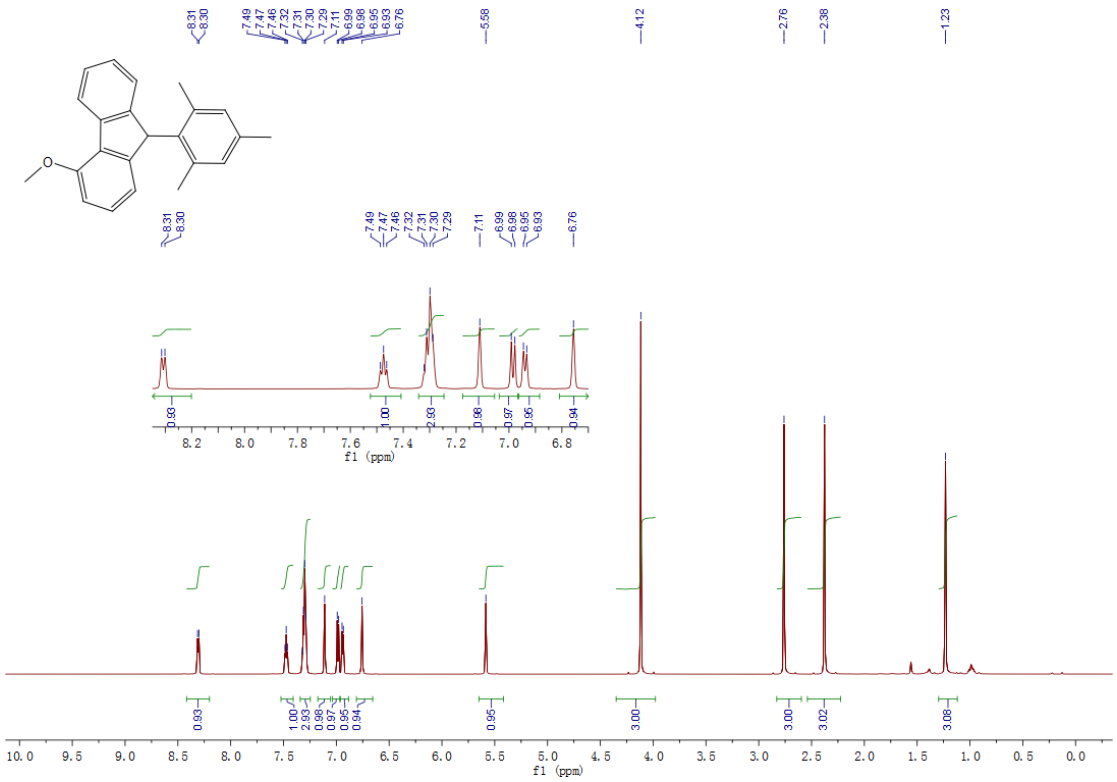


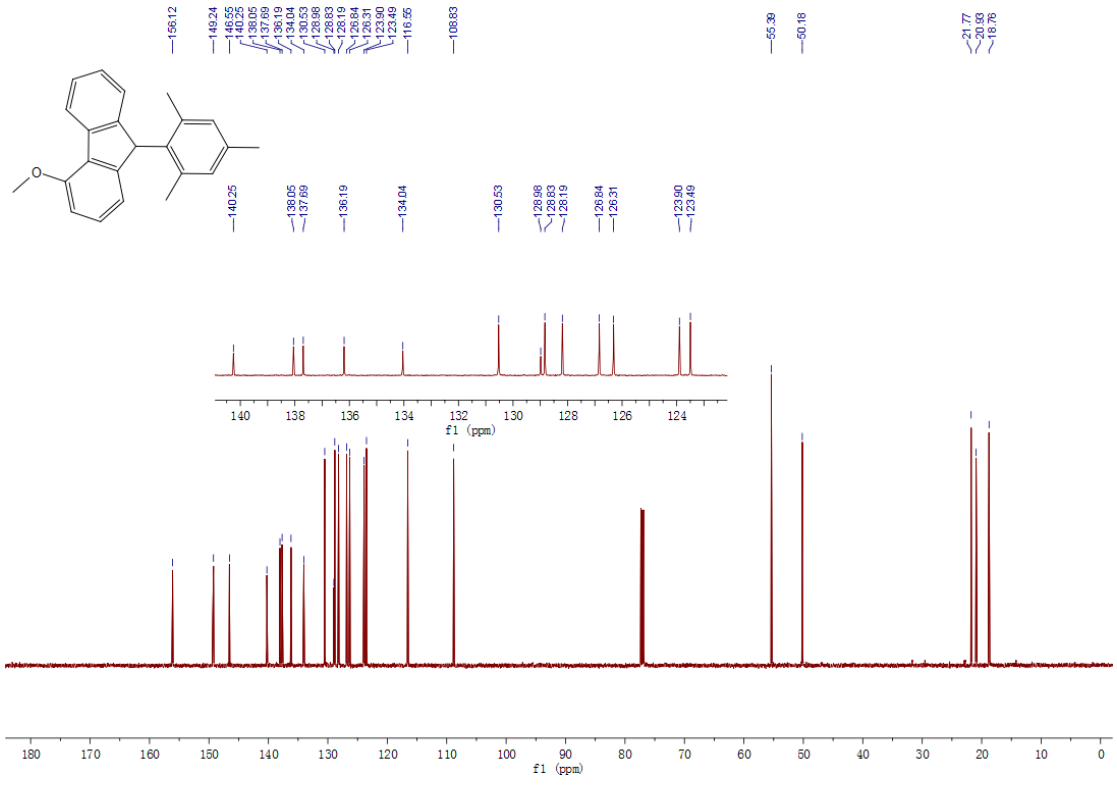
3ea





3fa


8.31
8.30
7.49
7.47
7.46
7.32
7.31
7.30
7.29
7.11
6.99
6.98
6.95
6.93
6.76
5.58
4.12
2.76
2.38
1.23
f1 (ppm)


156.12
149.24
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140.25
138.05
137.69
136.19
134.04
130.53
128.98
128.83
128.19
126.84
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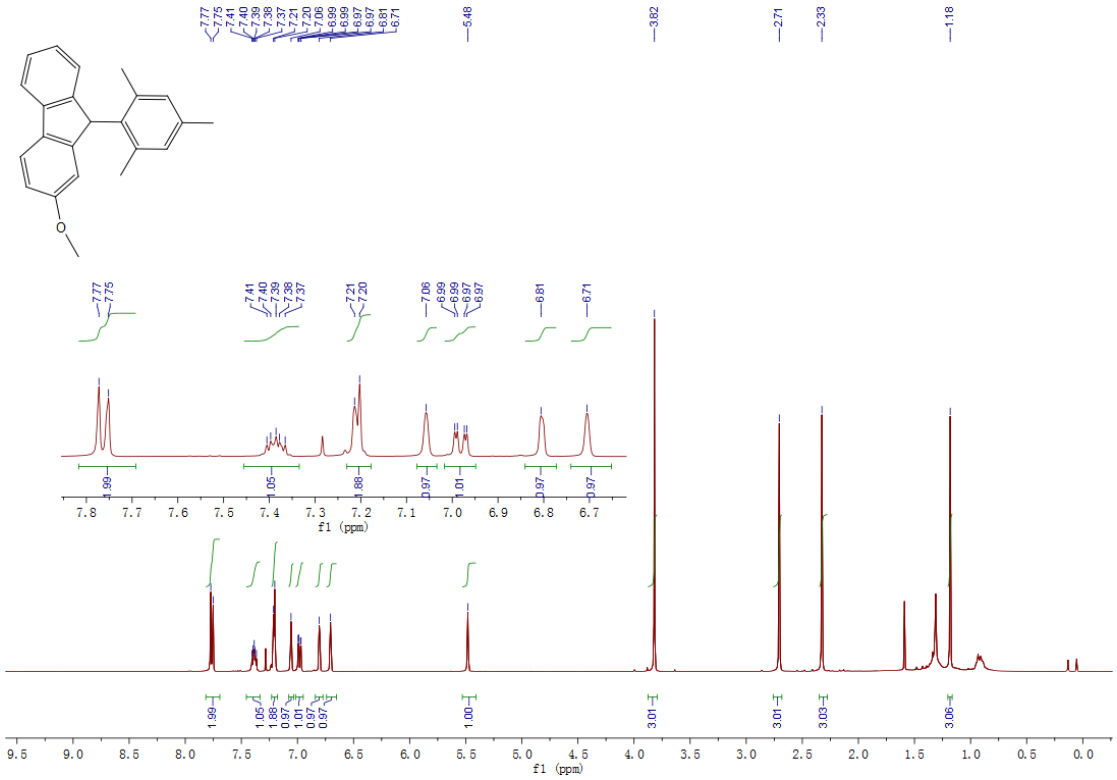
21.77
20.93
18.76
f1 (ppm)

3ga


7.77
7.75
7.41
7.40
7.39
7.38
7.37
7.21
7.20
7.06
6.99
6.99
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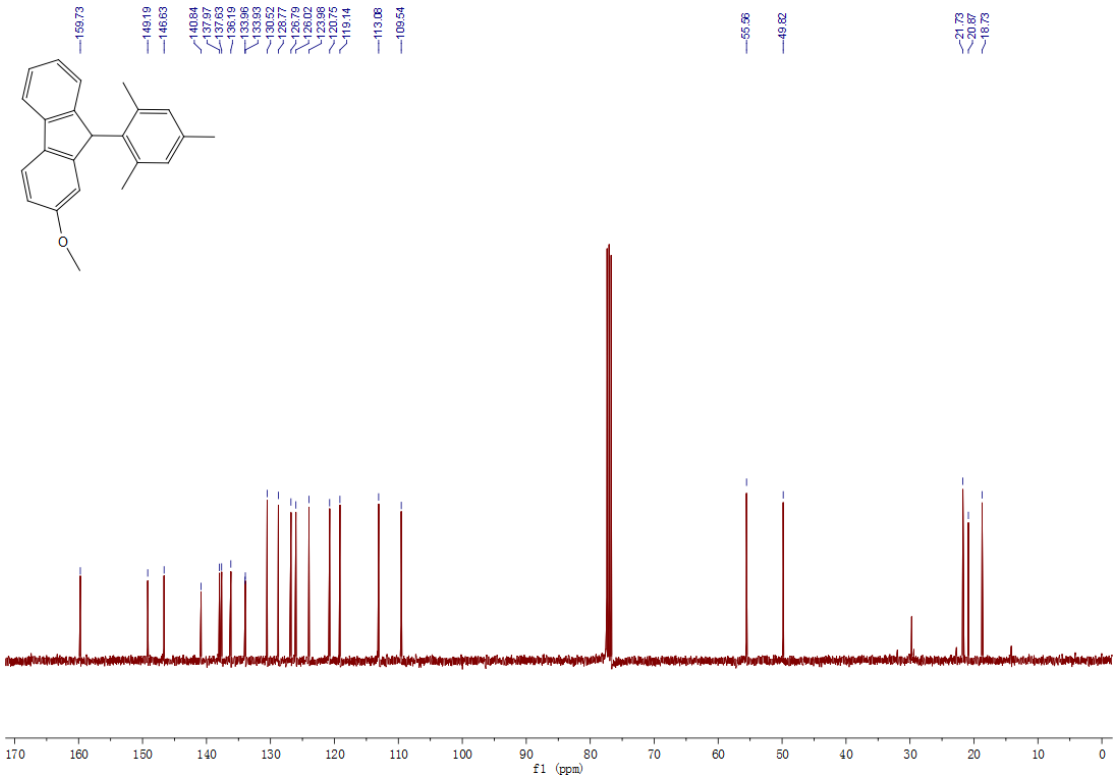
6.97
6.81
6.71
5.48
3.82
2.71
2.33
1.18
f1 (ppm)


159.73
149.19
146.63
140.84
137.97
137.63
136.19
133.96
133.93
130.52
128.77
126.79
126.02
123.98
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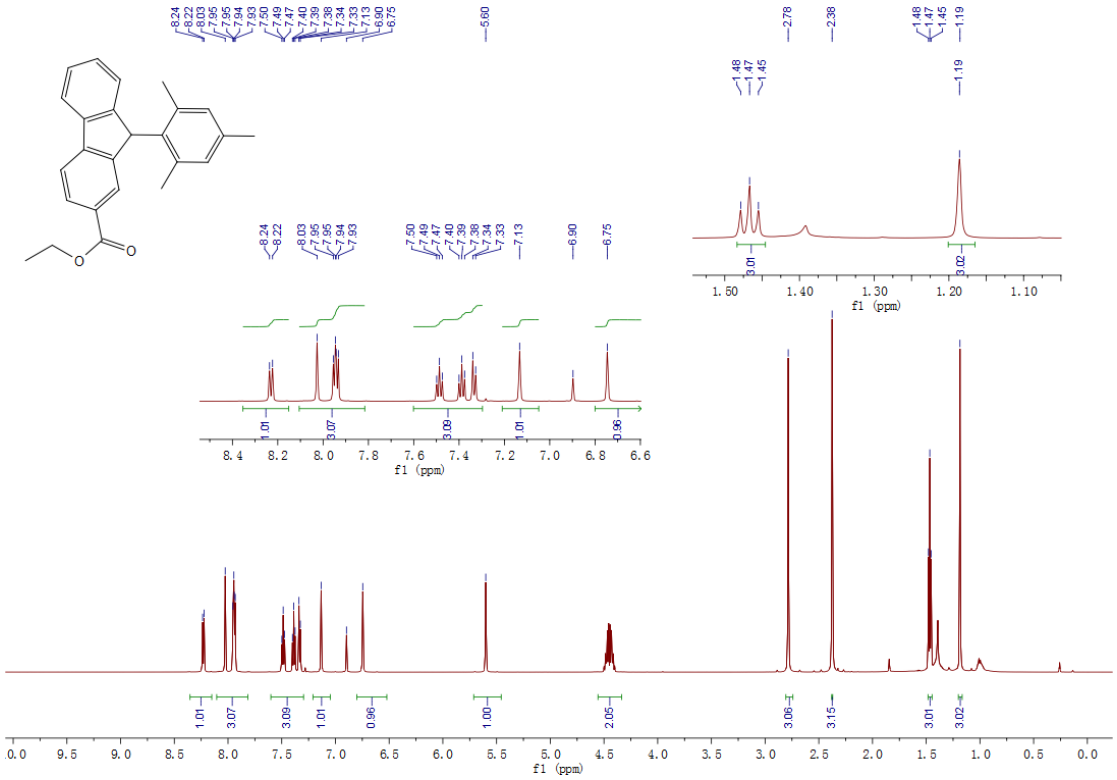
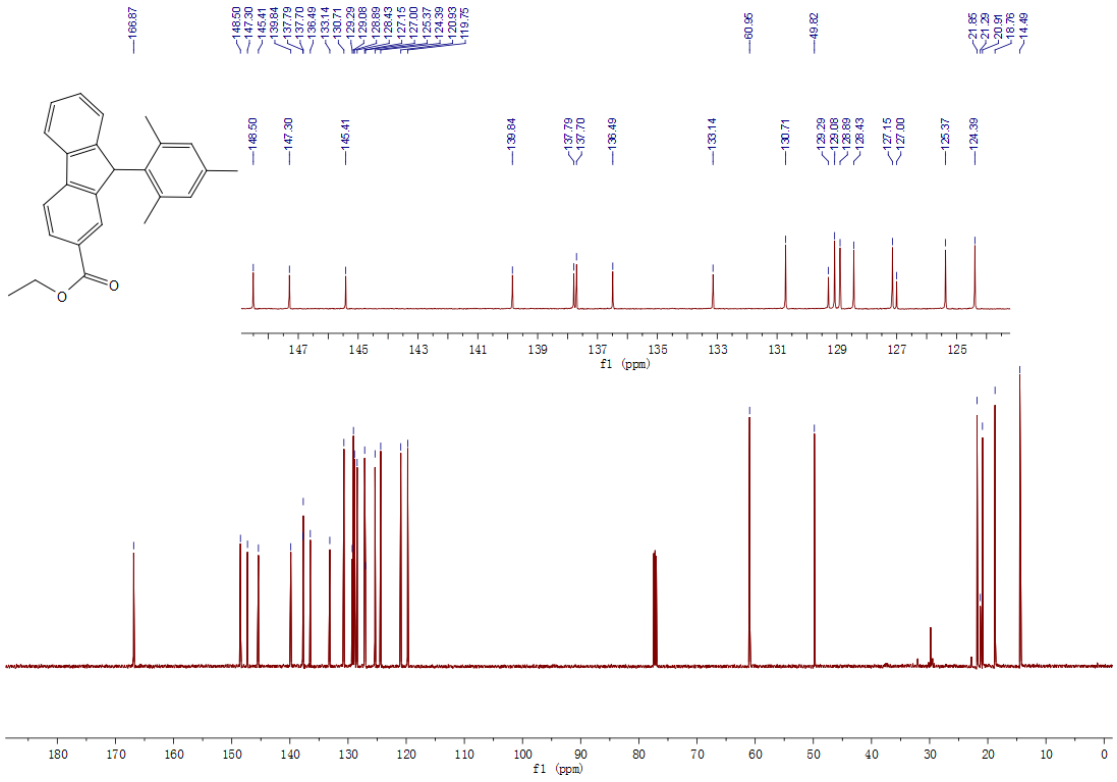
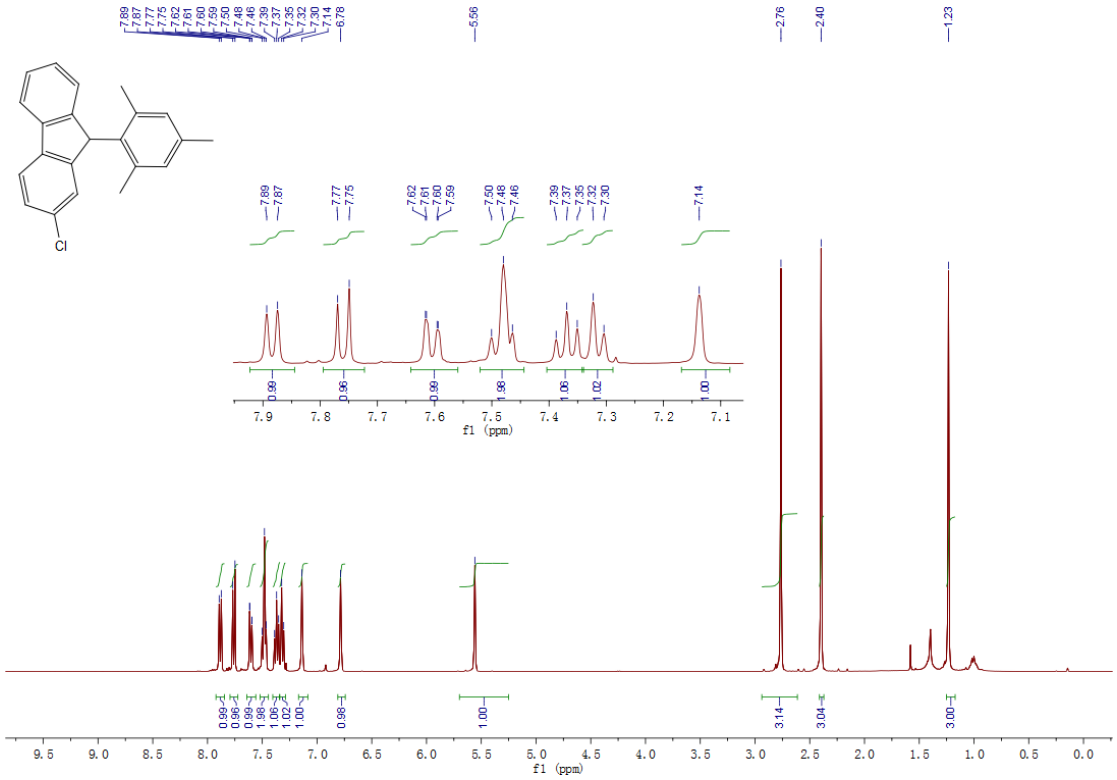
113.08
109.54
55.56
49.82
21.73
20.87
18.73
f1 (ppm)

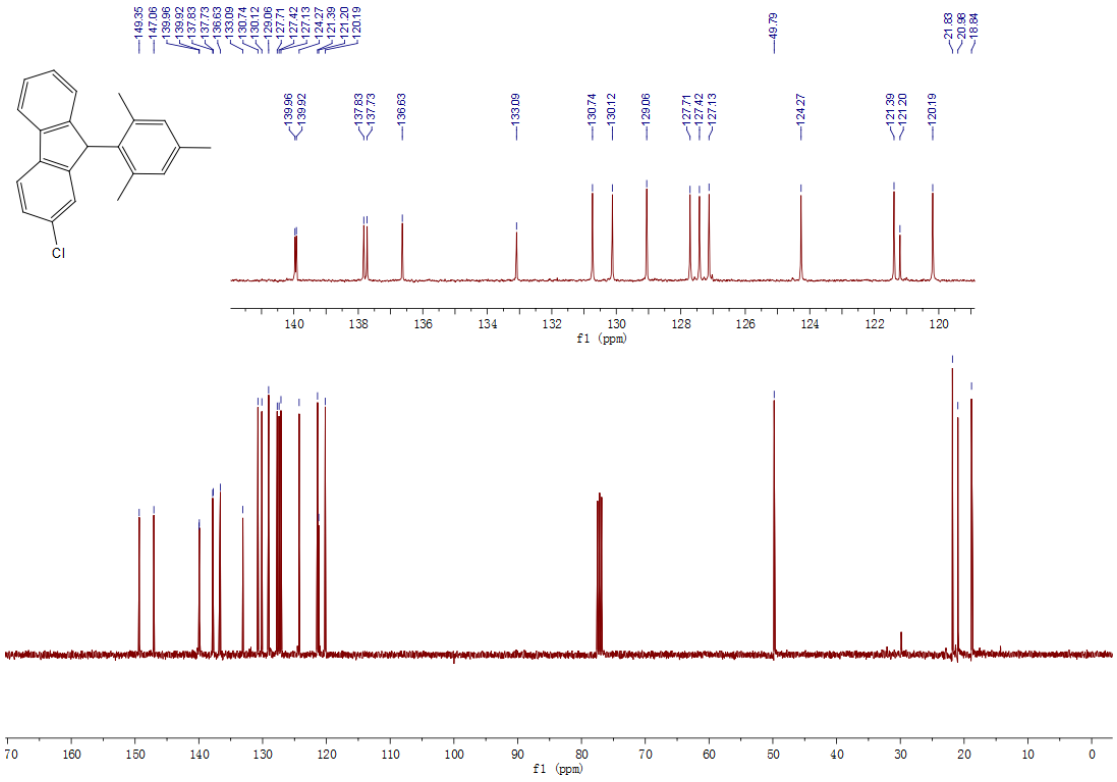
3ia



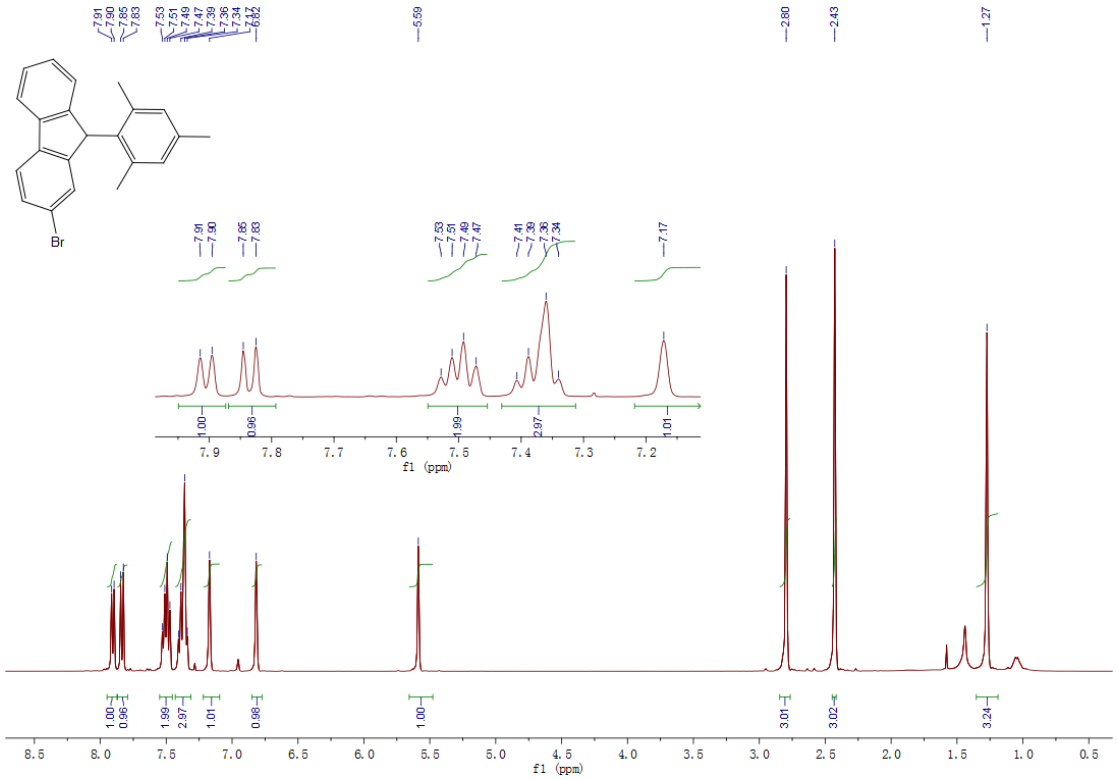


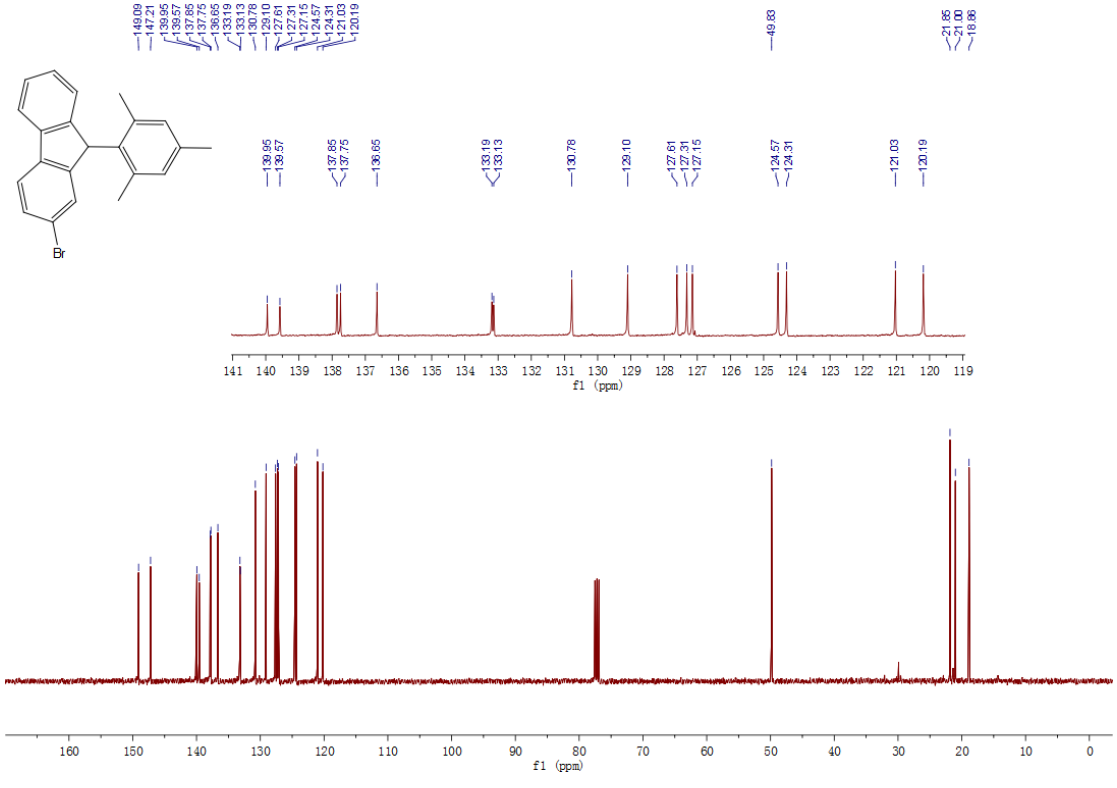
3ja



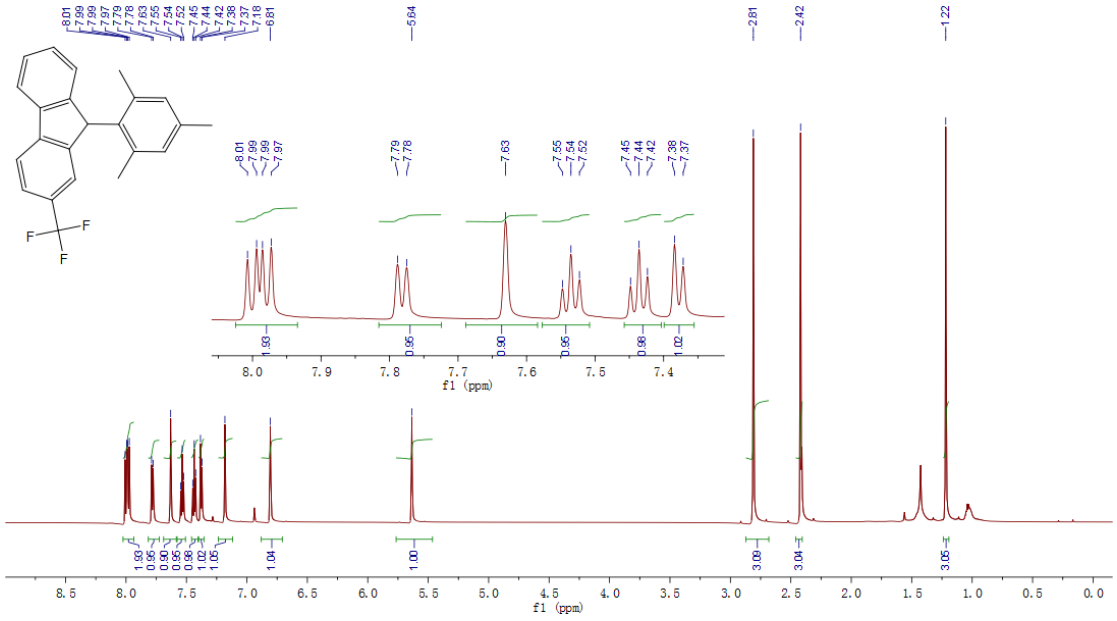


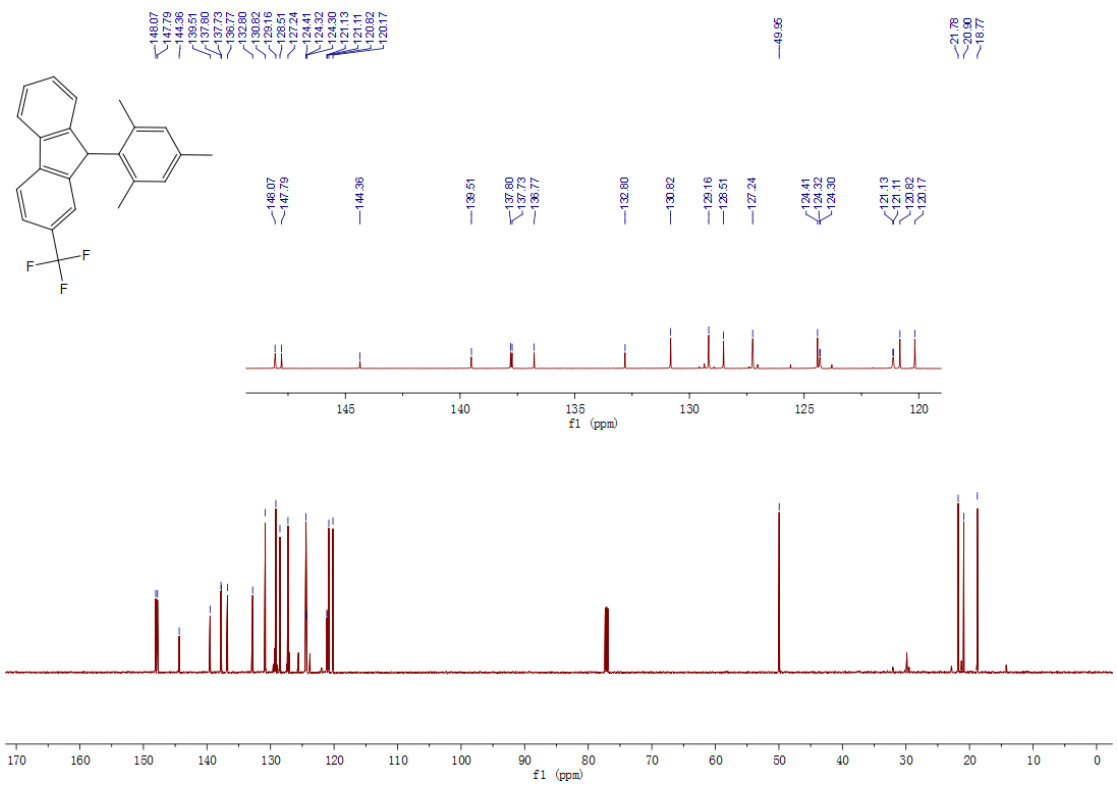
3ka



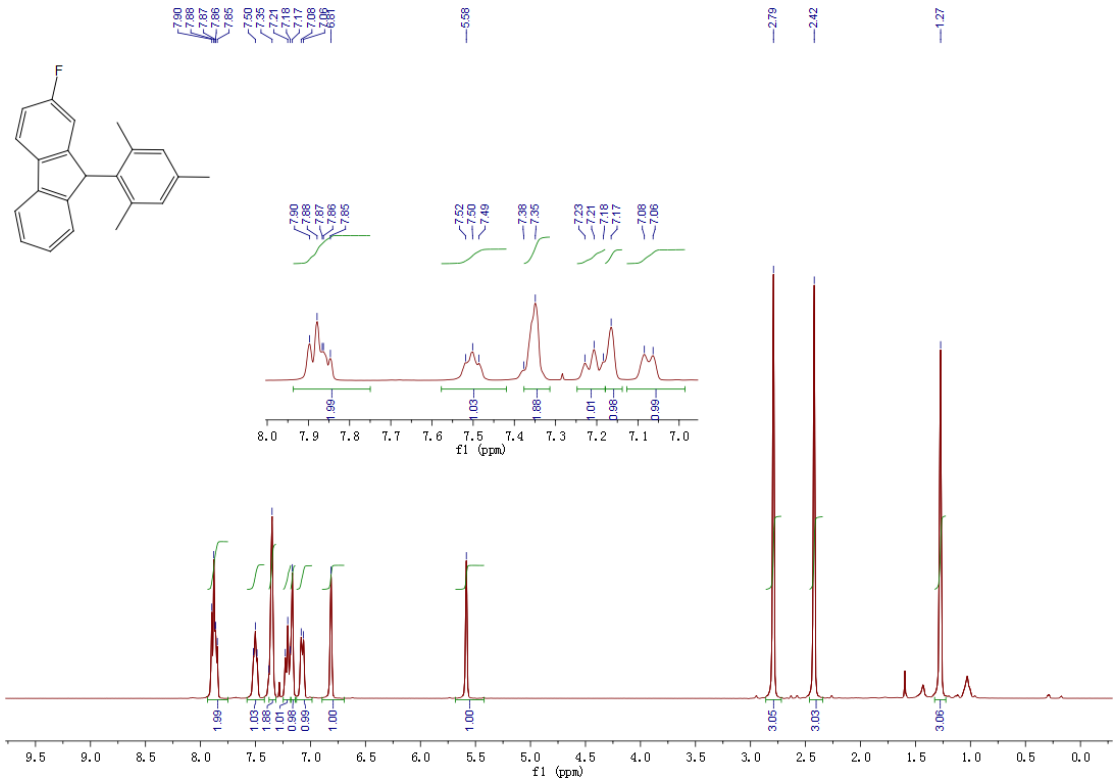


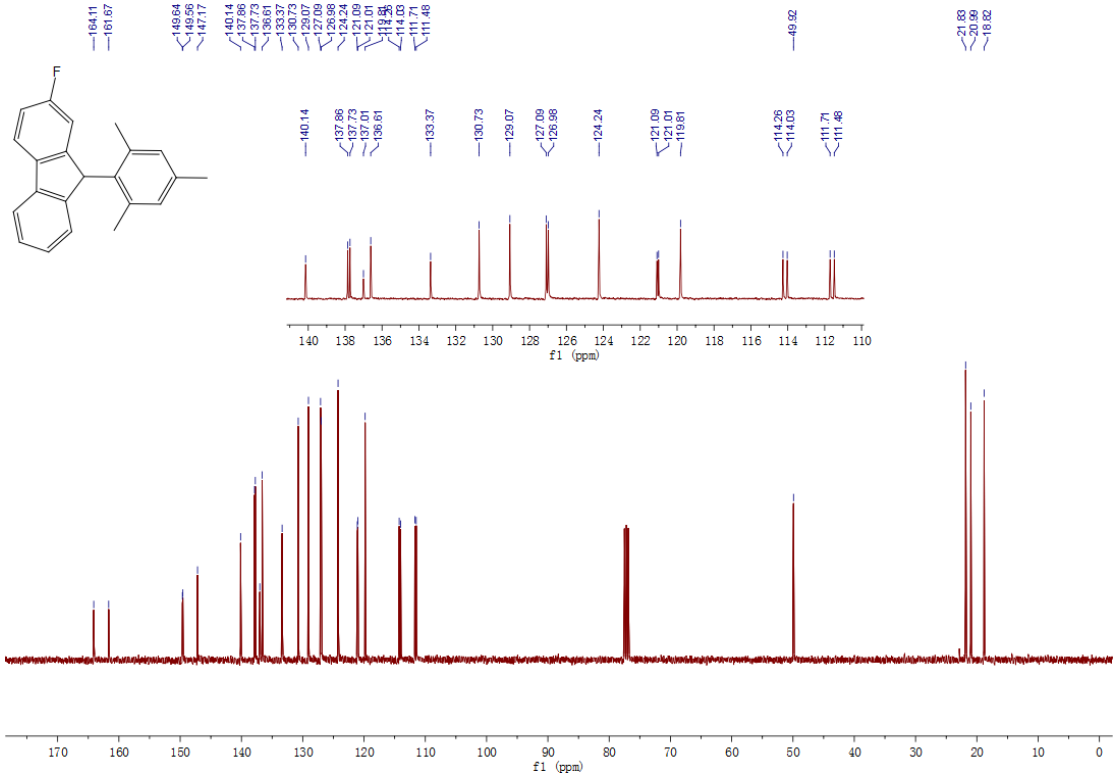
3la



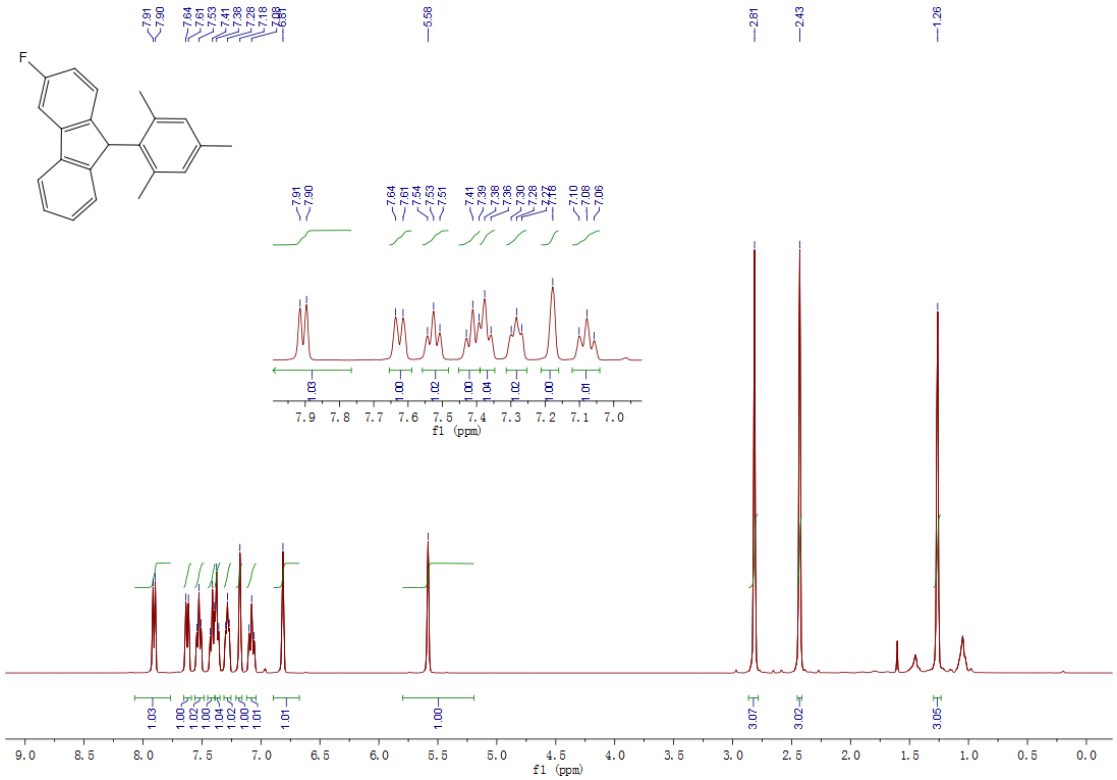


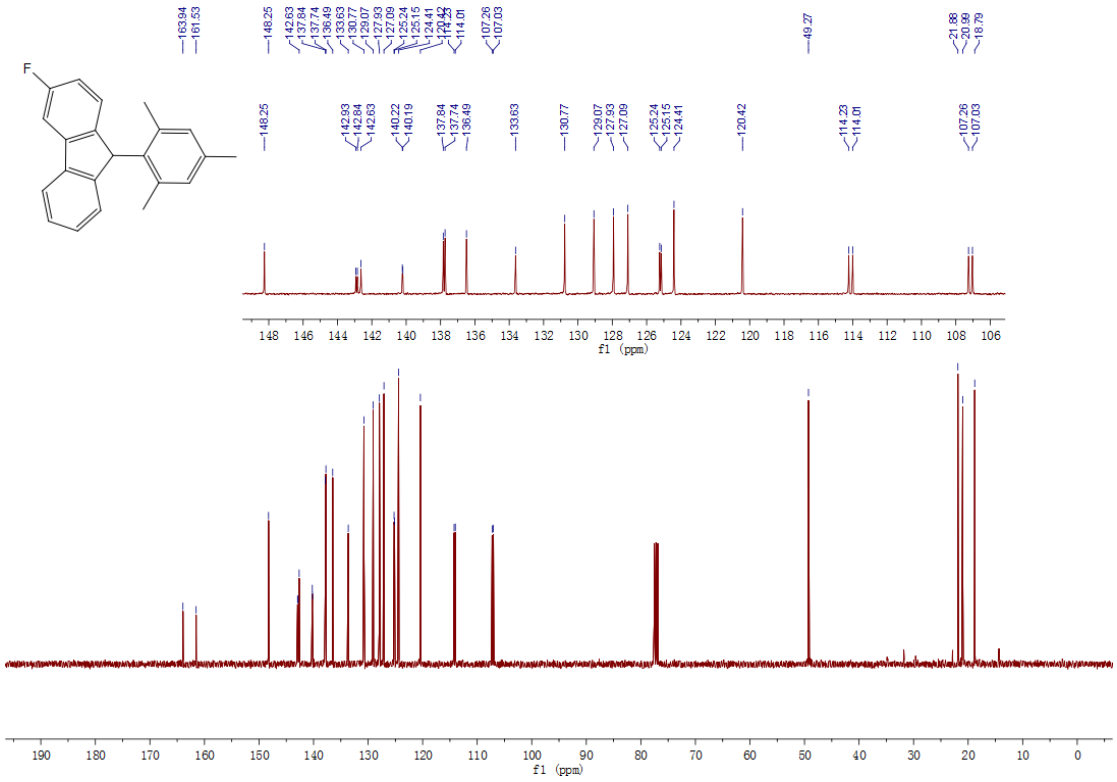
3ma



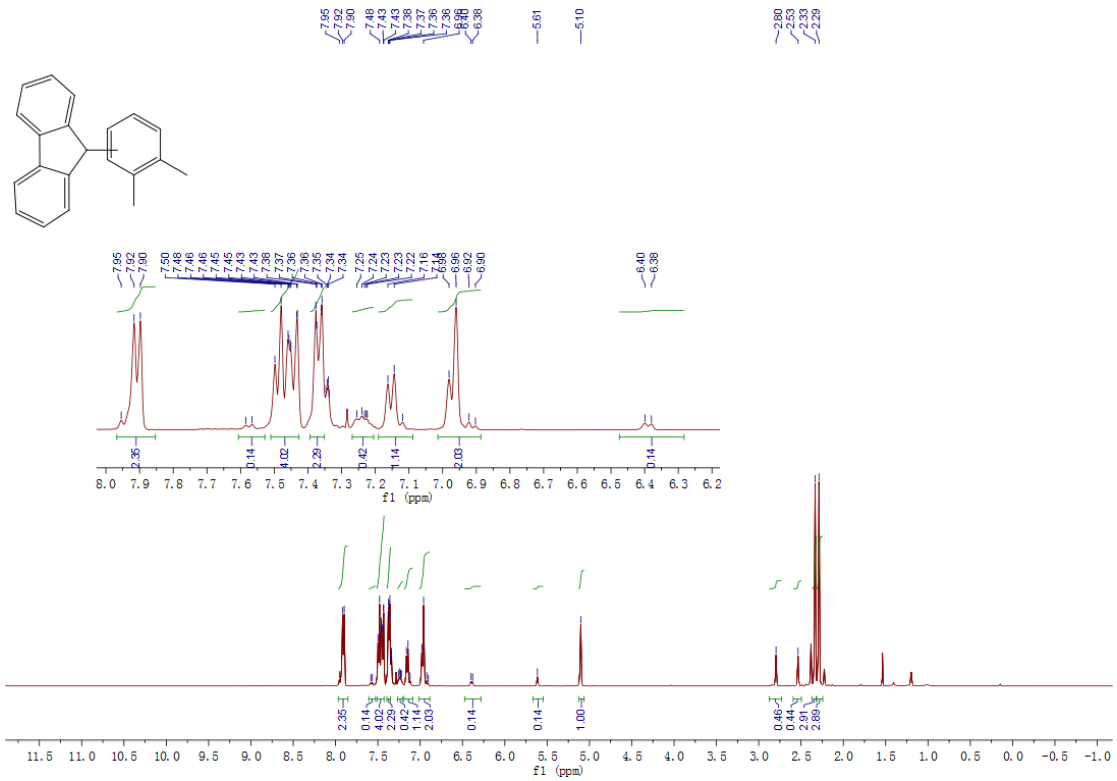


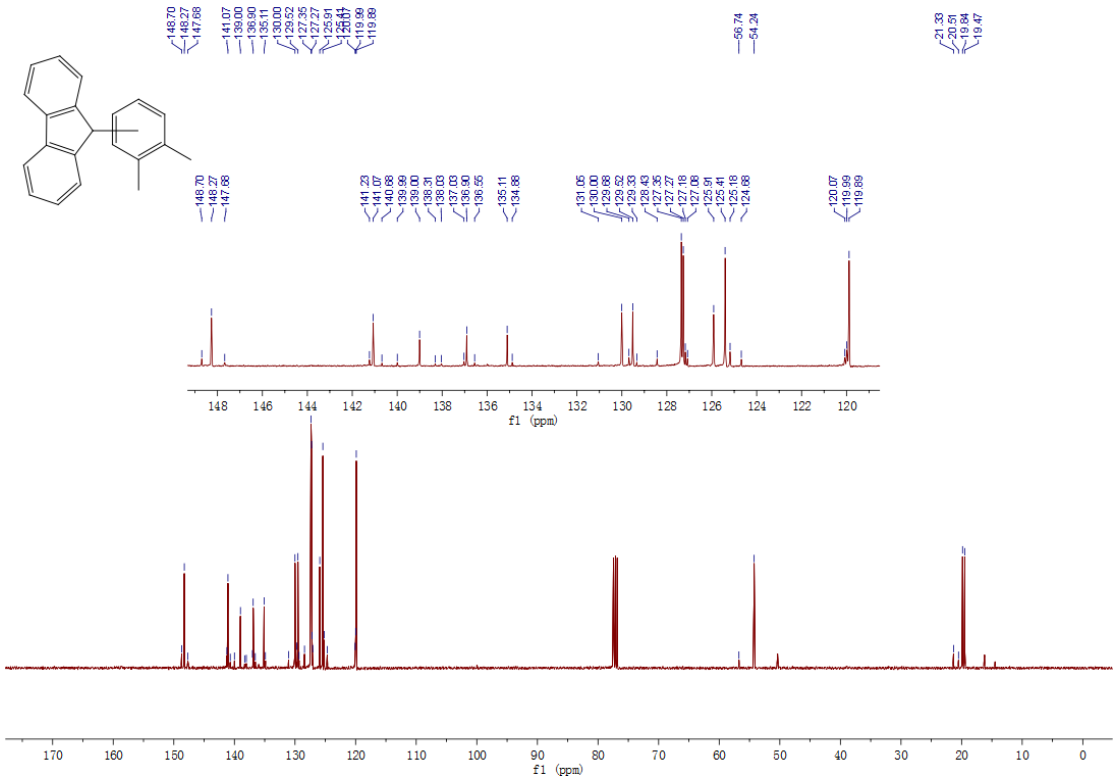
3na


F
7.91
7.90
7.64
7.61
7.53
7.41
7.39
7.38
7.36
7.30
7.28
7.18
7.08
6.81
5.58
2.81
2.43
1.26
f1 (ppm)


F
163.94
161.53
148.25
142.63
137.84
137.74
136.49
133.63
130.77
129.07
127.93
127.09
125.24
125.15
124.41
120.42
114.23
114.01
107.26
107.03
49.27
21.88
20.96
18.79
f1 (ppm)

3ab





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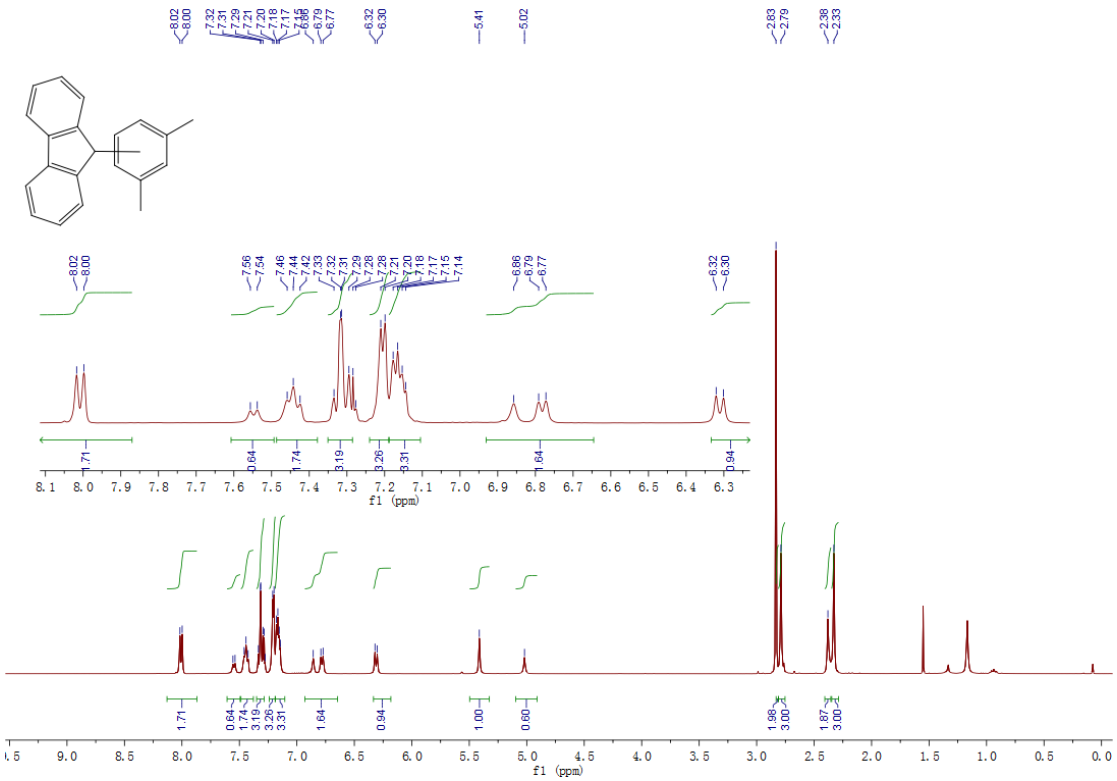

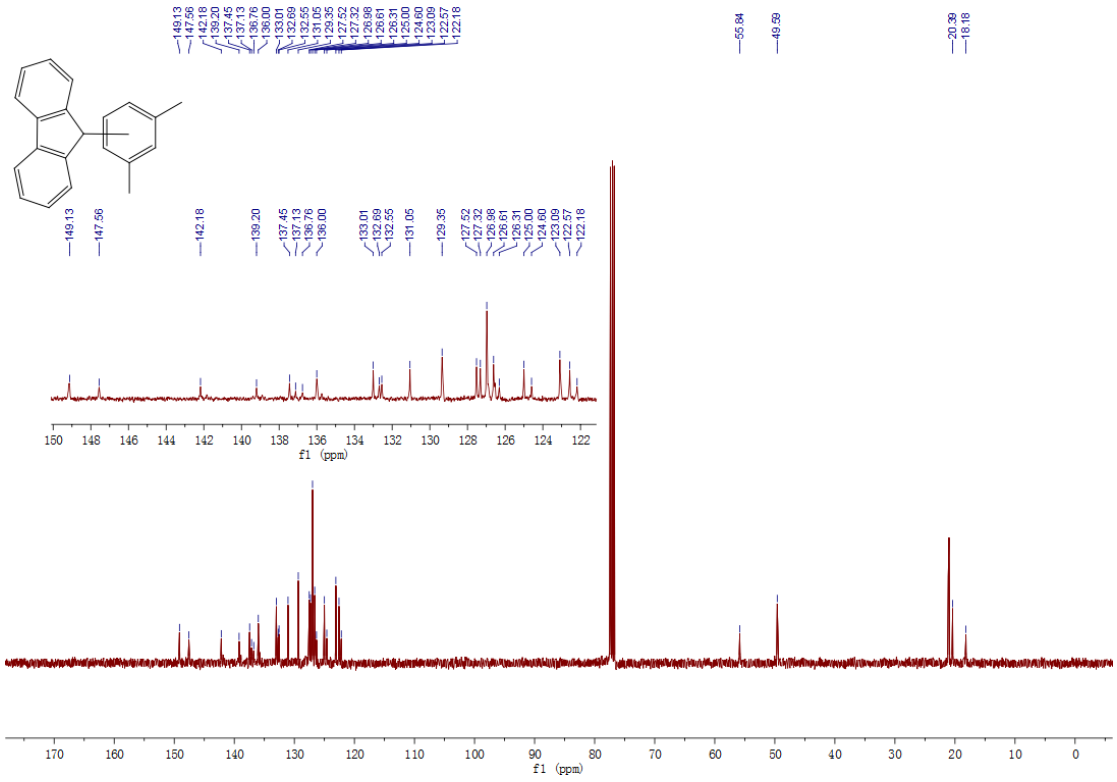

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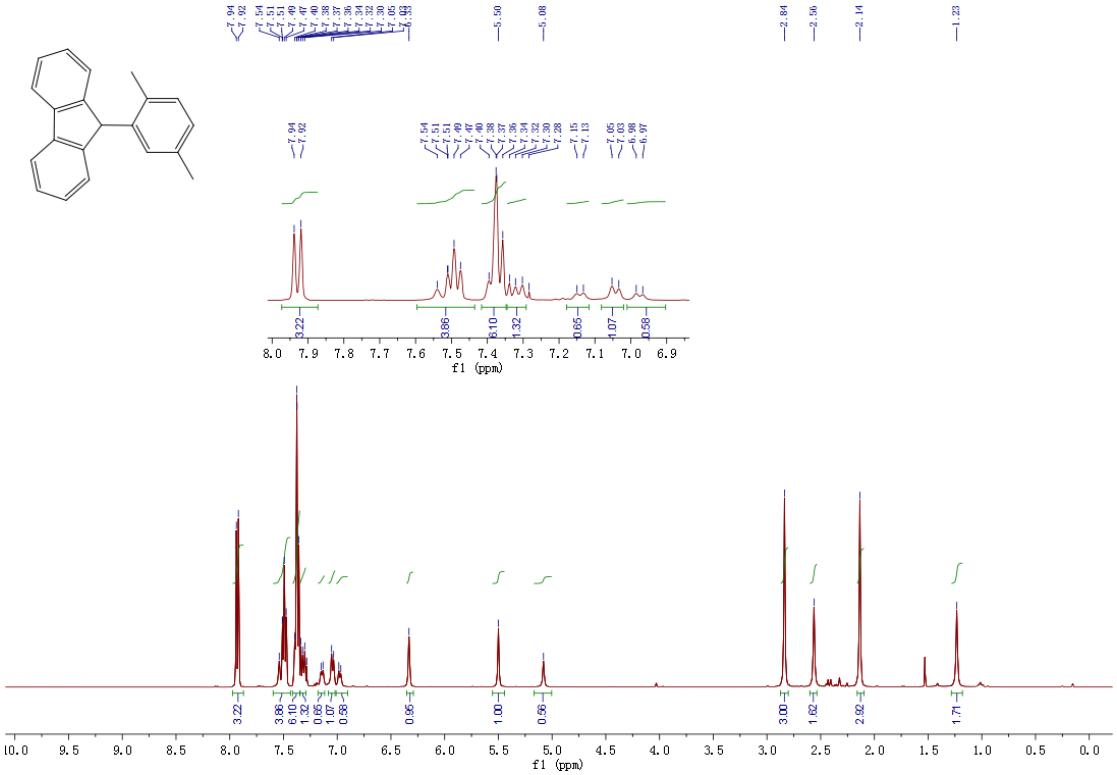

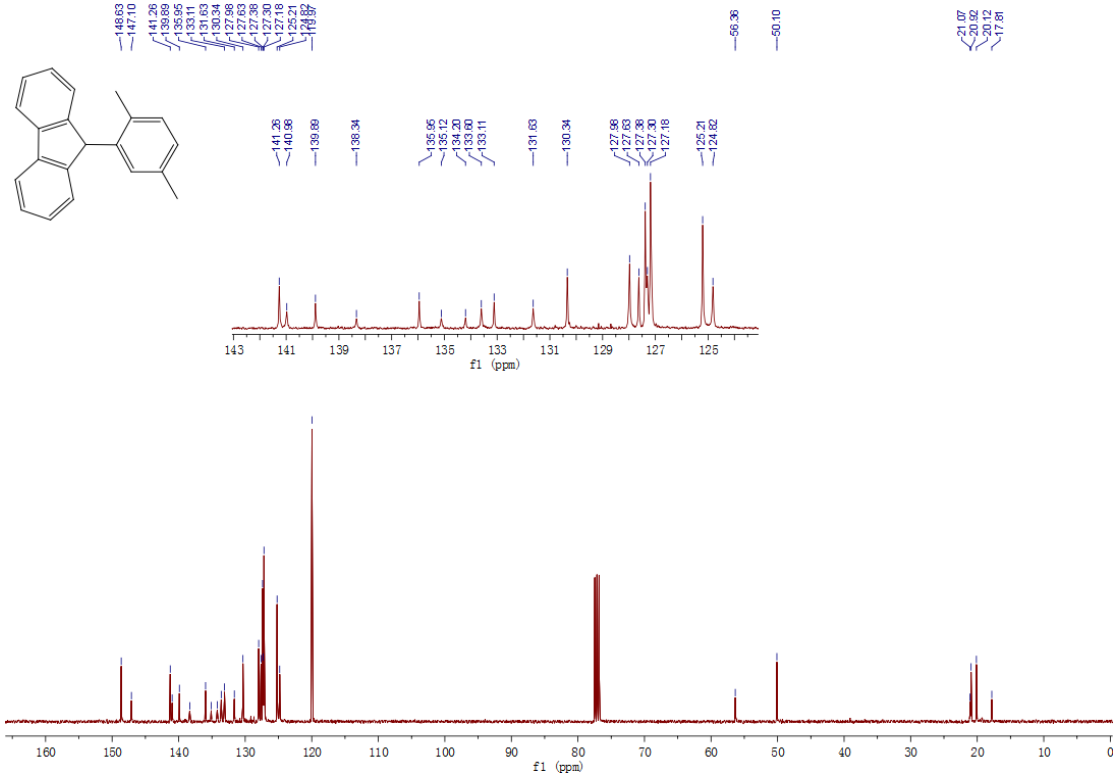

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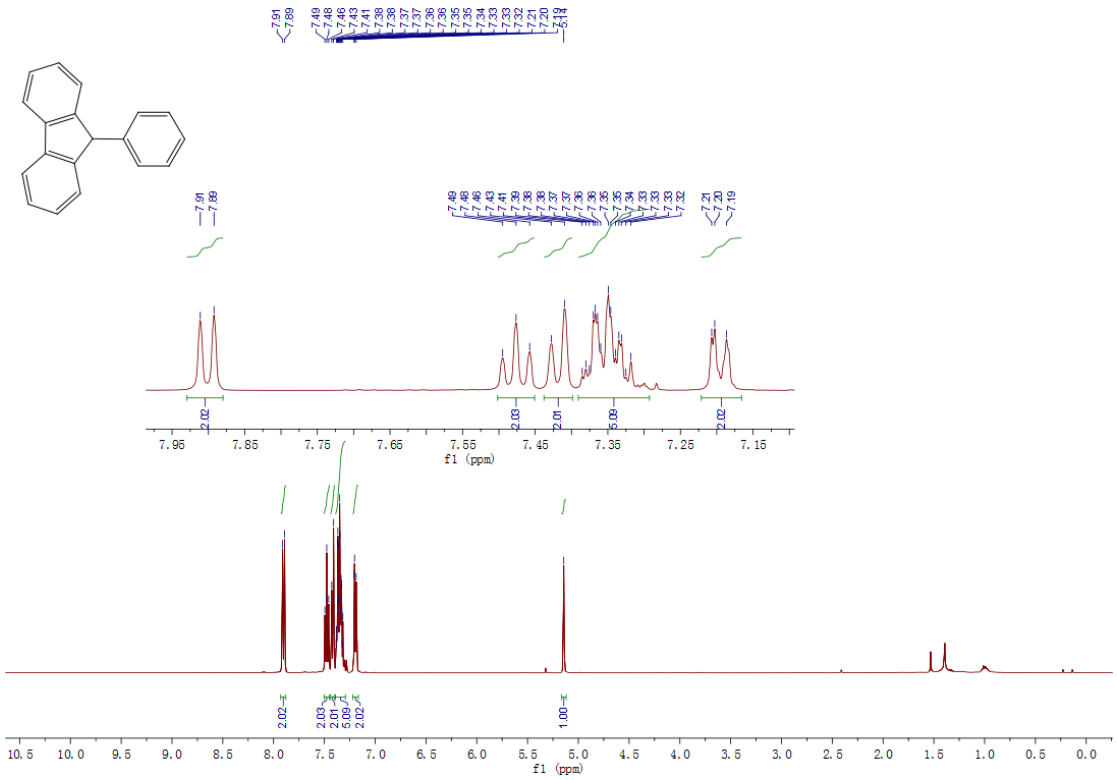

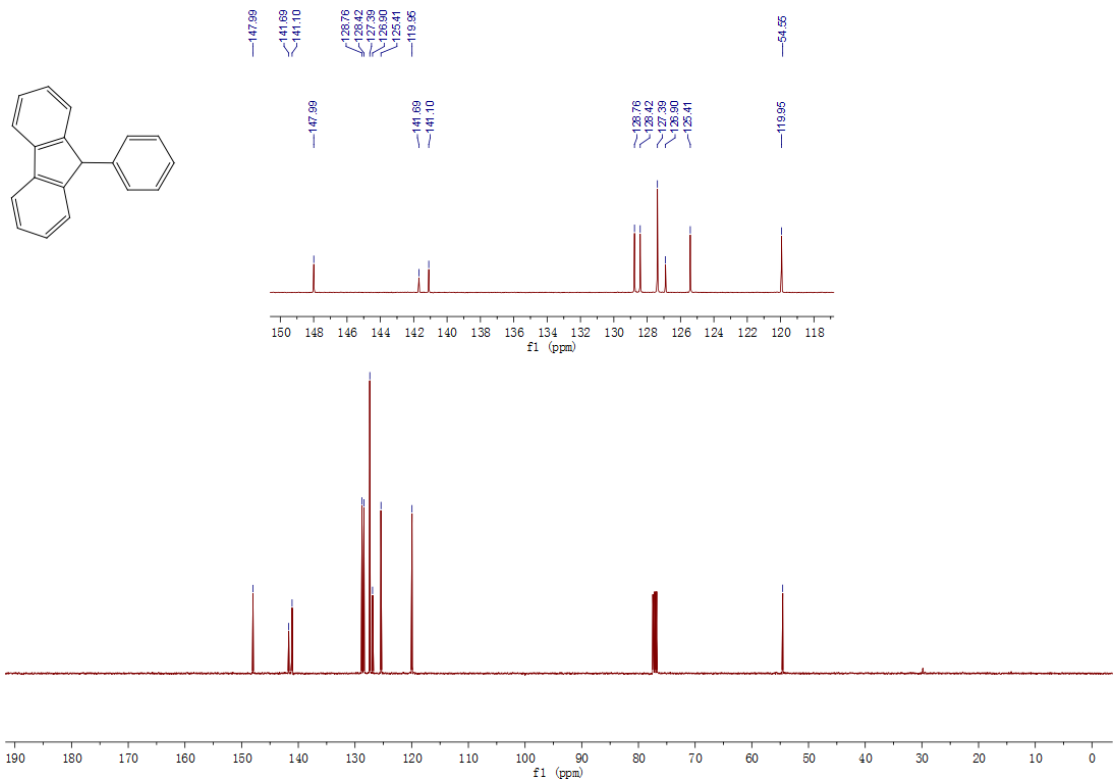

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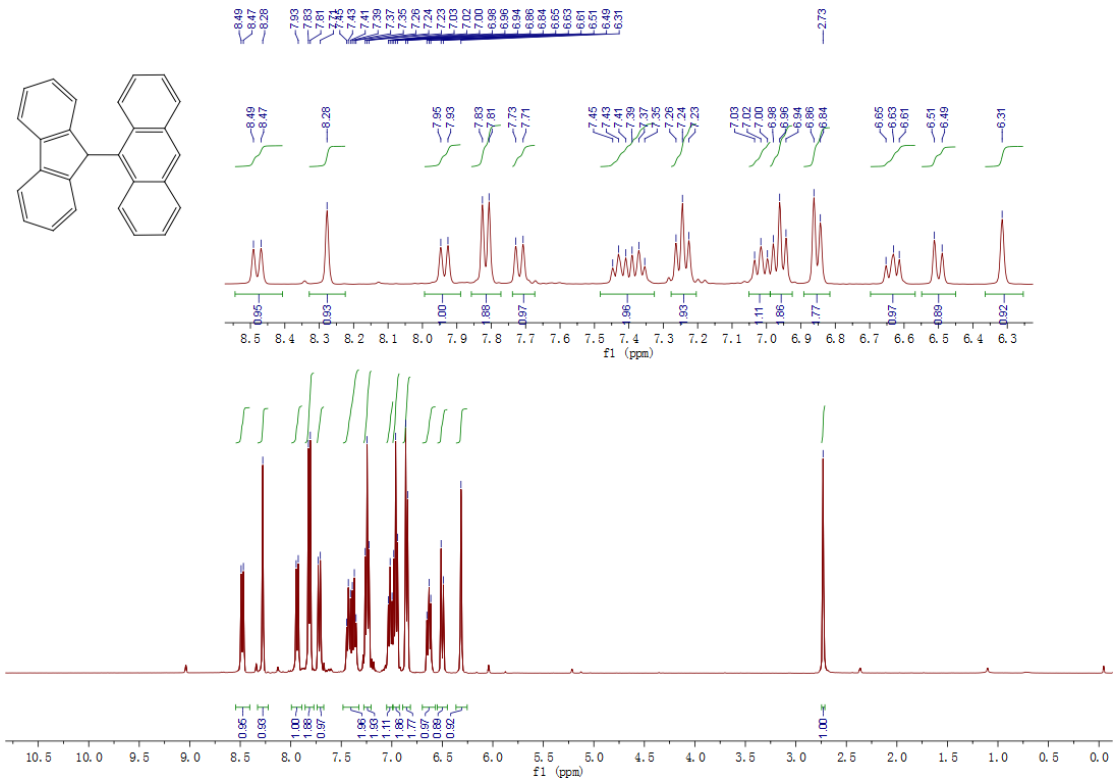

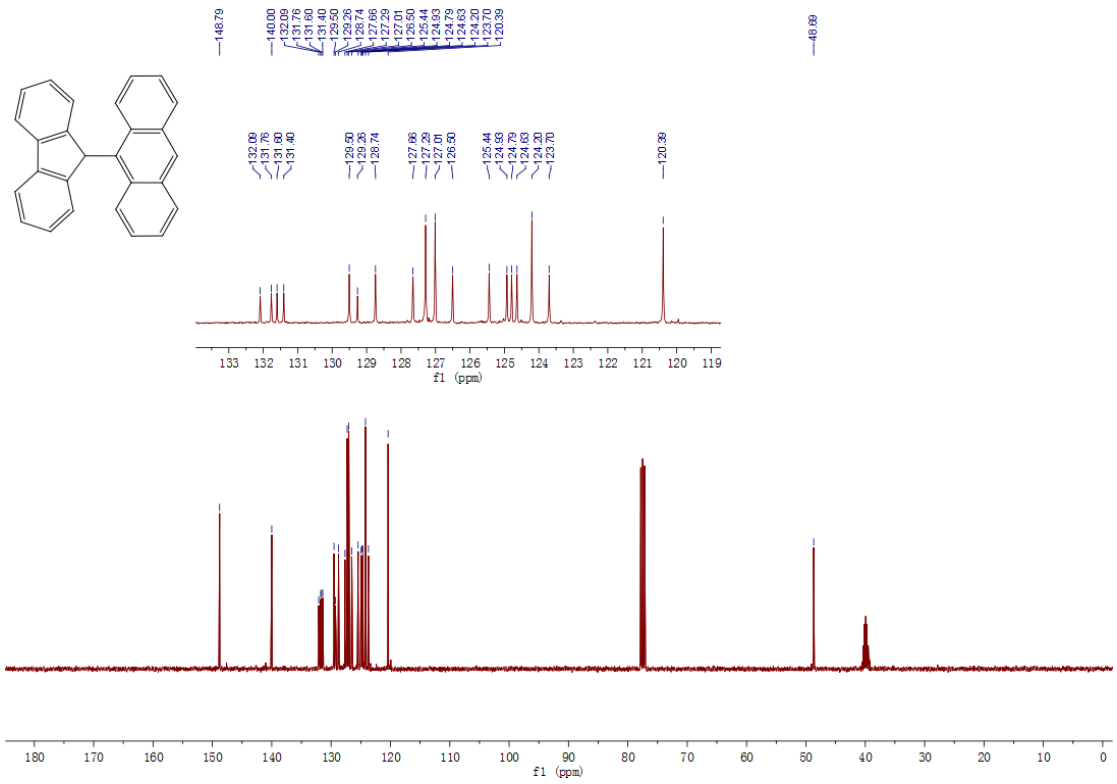

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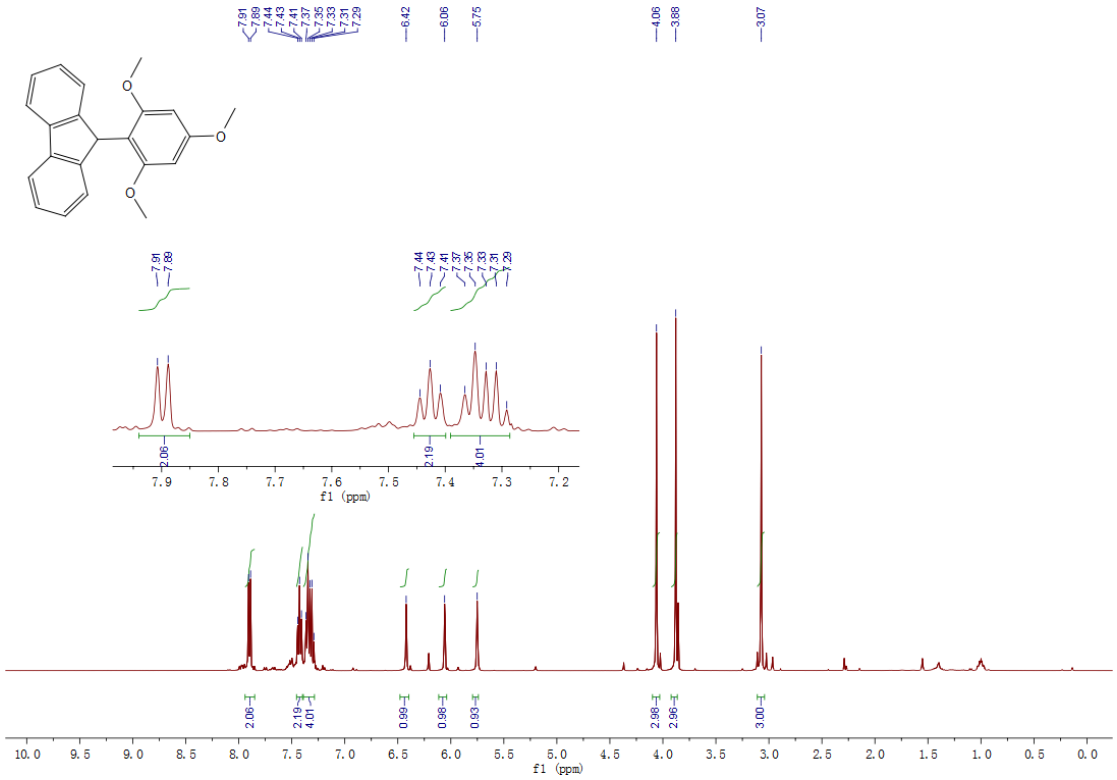
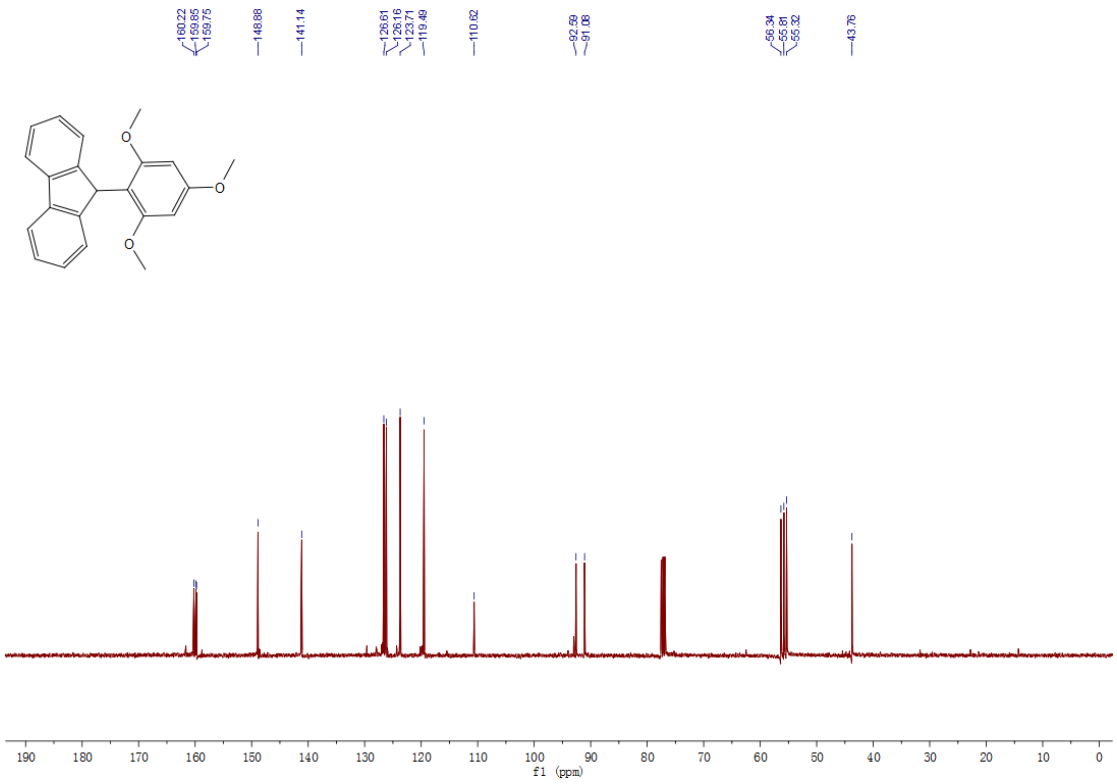
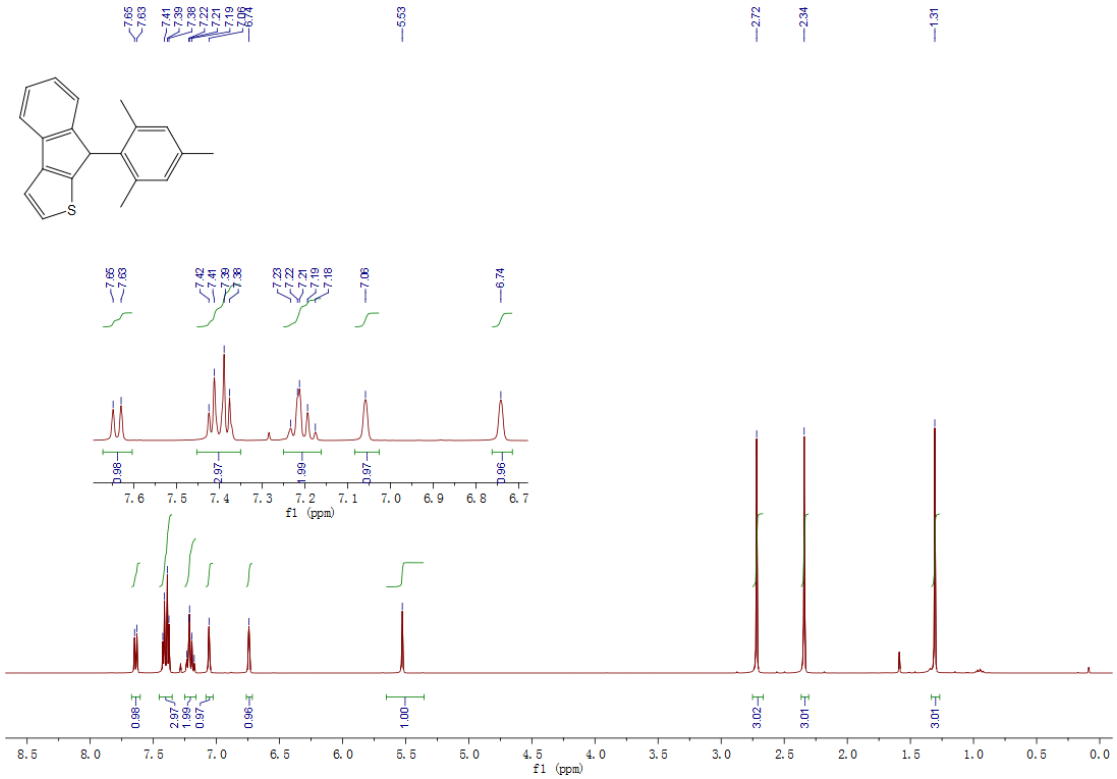
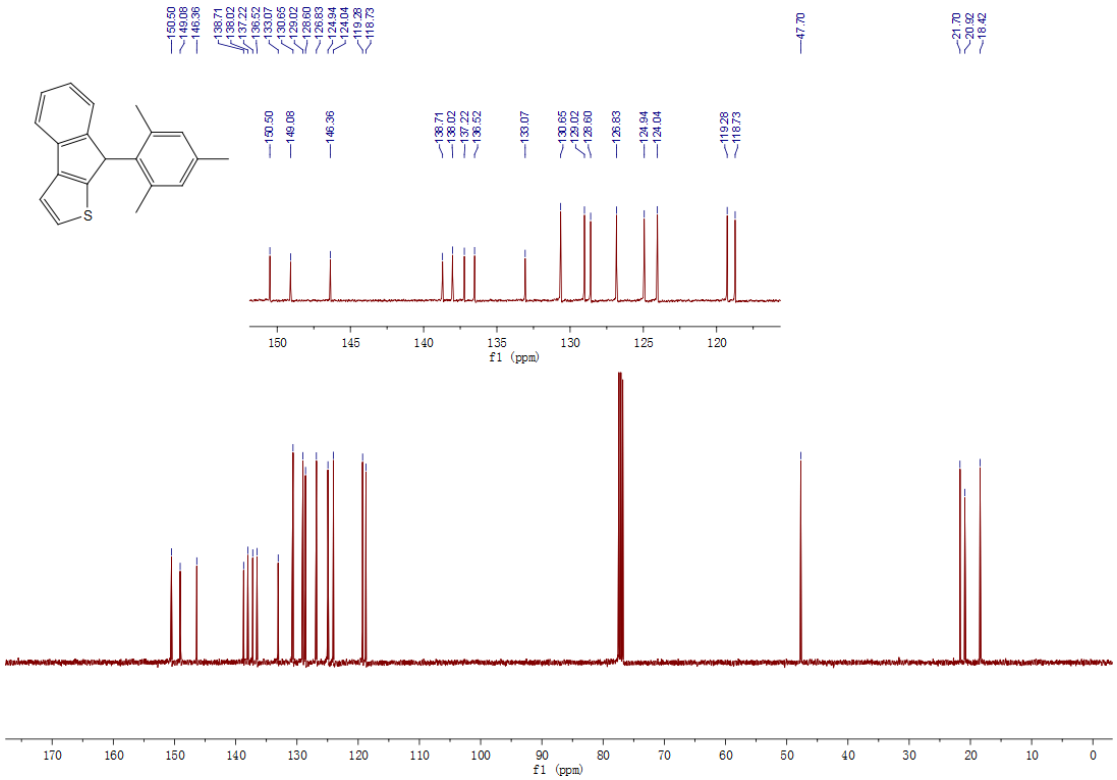

7.91
7.89
7.44
7.43
7.41
7.37
7.35
7.33
7.31
7.29
6.42
6.06
5.75
4.06
3.88
3.07
2.06
2.19
4.01
0.99
0.98
0.93
2.98
2.96
3.00
f1 (ppm)

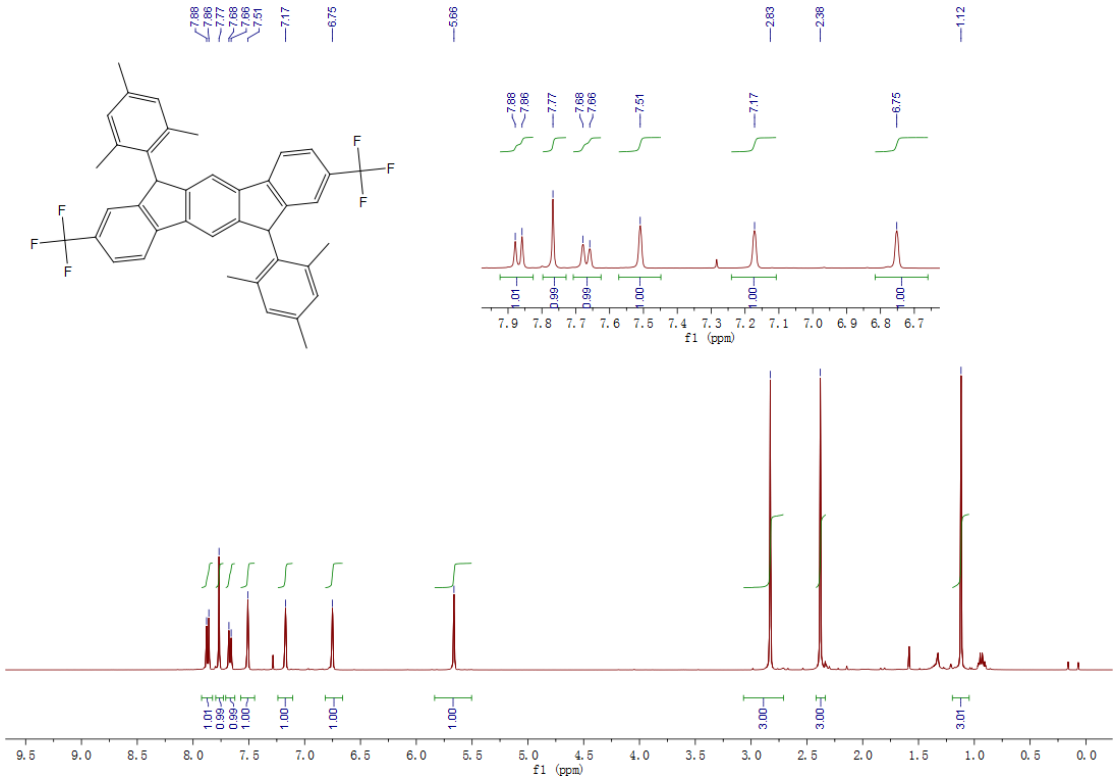

160.22
159.65
159.75
148.88
141.14
126.61
126.16
123.71
119.49
110.62
92.69
91.88
56.34
55.61
55.32
43.76
f1 (ppm)

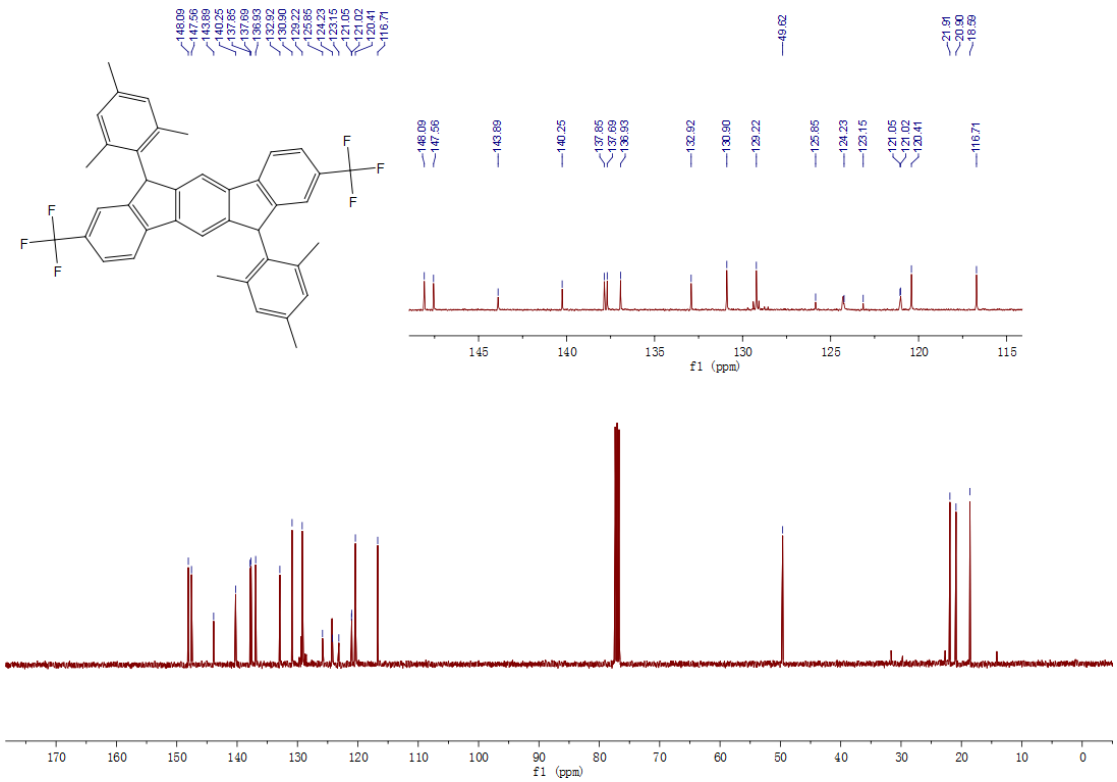
3oa


7.65
7.63
7.41
7.39
7.38
7.22
7.21
7.19
7.06
6.74
5.53
2.72
2.34
1.31
S
f1 (ppm)

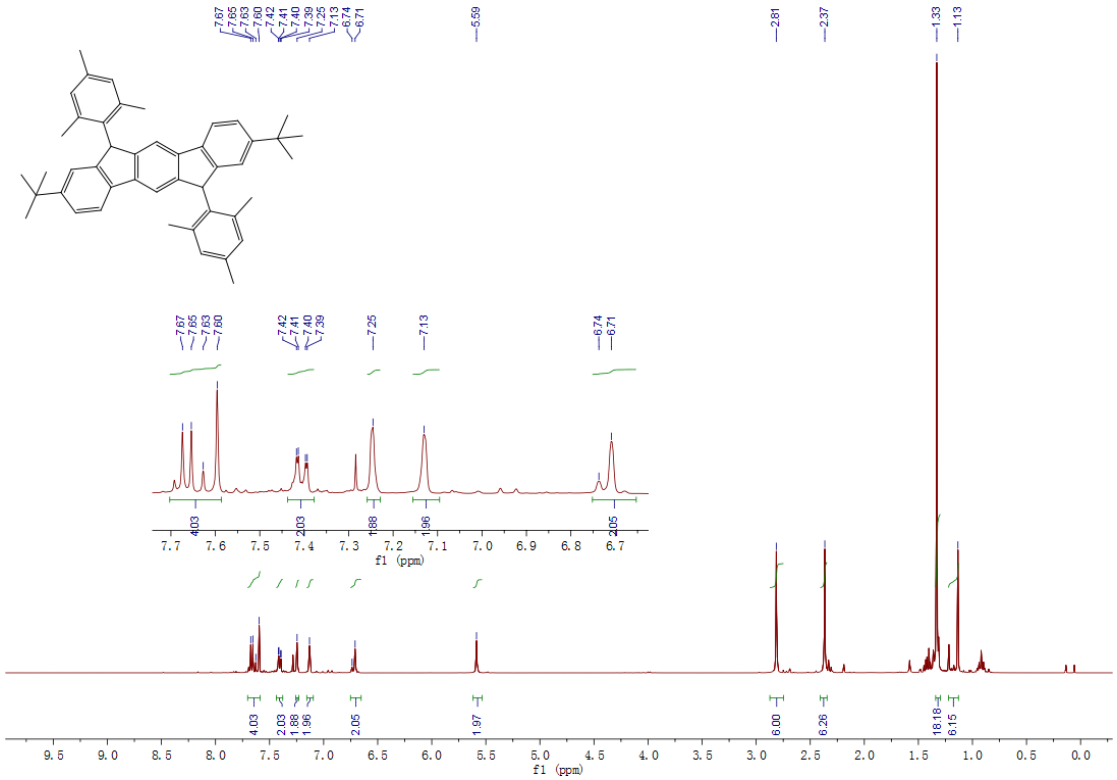

150.50
149.08
146.36
138.71
138.02
137.22
136.52
133.07
130.65
129.02
128.60
126.83
124.94
124.04
119.28
118.73
47.70
21.70
20.92
18.42
S
f1 (ppm)

5a


7.88
7.86
7.77
7.68
7.66
7.51
7.17
6.75
5.66
2.83
2.38
1.12
f1 (ppm)


148.09
147.56
143.89
140.25
137.85
137.69
136.93
132.92
130.90
129.22
125.85
124.23
123.15
121.05
121.02
120.41
116.71
49.62
21.91
20.90
18.59
f1 (ppm)

5b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7.63
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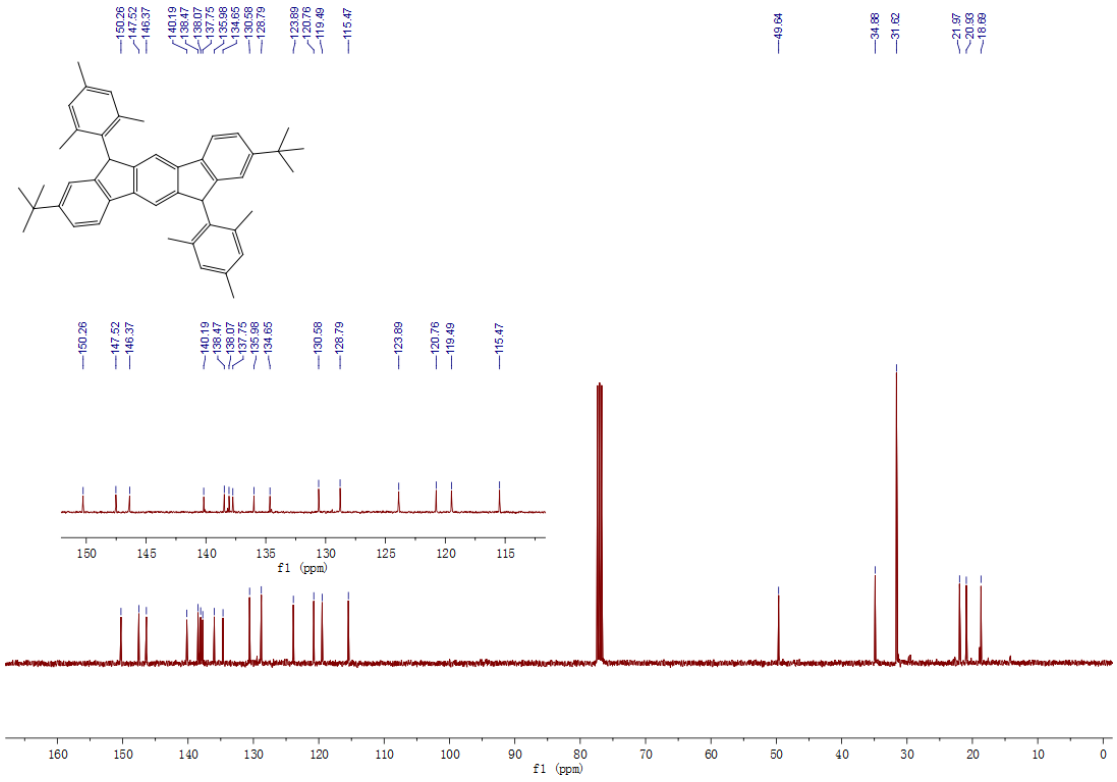
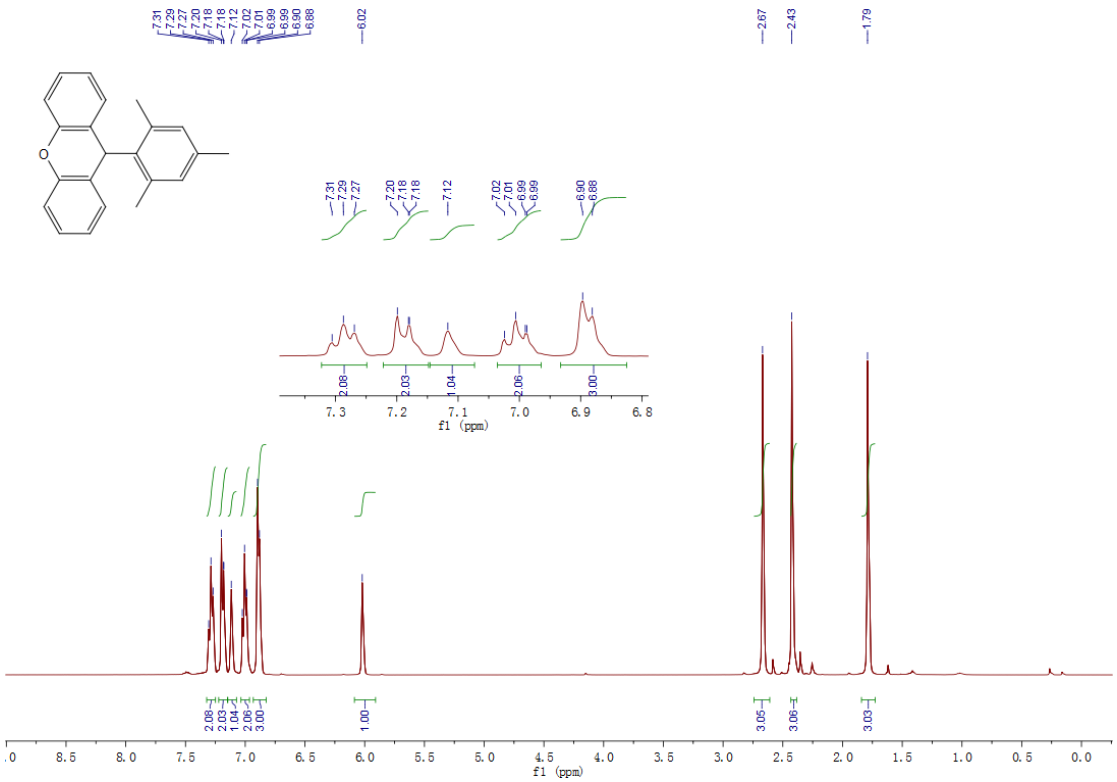
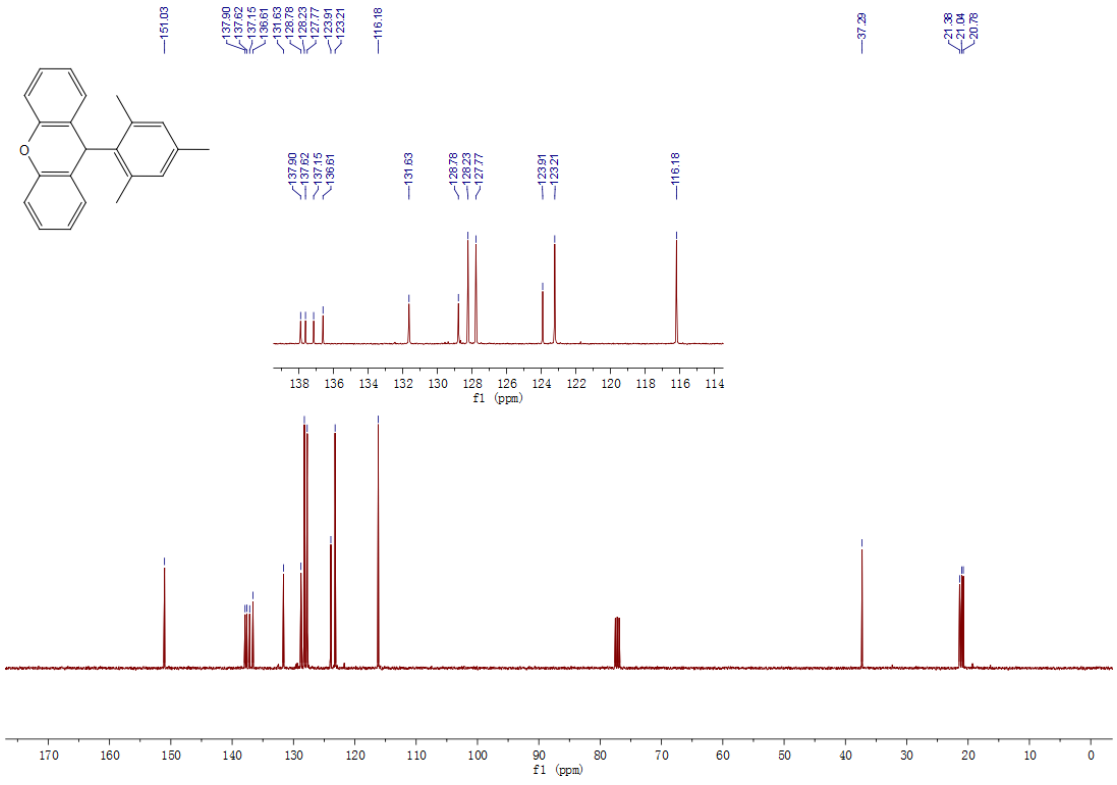
7.42
7.41
7.40
7.39
7.25
7.13
6.74
6.71
5.59
2.81
2.37
1.33
1.13
4.03
2.03
1.88
1.96
2.05
1.97
6.00
6.26
18.18
6.15
f1 (ppm)


150.26
147.52
146.37
140.19
138.47
138.07
137.75
135.98
134.85
130.58
128.79
123.89
120.76
119.49
115.47
49.64
34.88
31.62
21.97
20.93
18.89
f1 (ppm)

7


7.31
7.29
7.27
7.20
7.18
7.12
7.02
7.01
6.99
6.99
6.90
6.88
6.02
2.67
2.43
1.79
2.08
2.03
1.04
2.06
3.00
1.00
3.05
3.06
3.03
f1 (ppm)


151.03
137.90
137.62
137.15
136.61
131.63
128.78
128.23
127.77
123.91
123.21
116.18
37.29
21.38
21.04
20.78
f1 (ppm)