Supporting Information

One-pot synthesis of benzo[*b*]fluorenones via a cobalt-catalyzed MHP-directed [3+2] annulation/ring-opening/dehydration sequence

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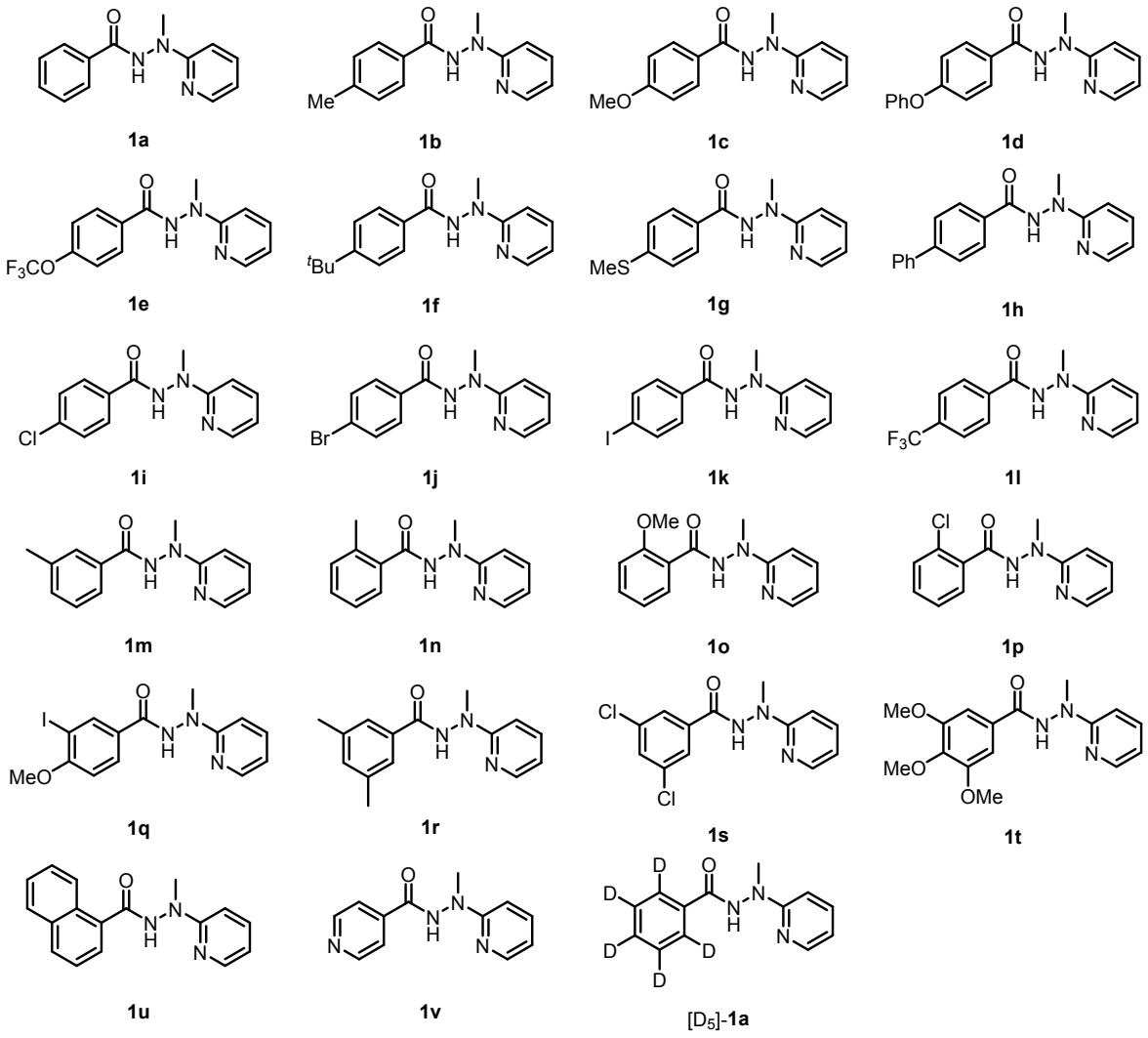
1. Materials and Methods

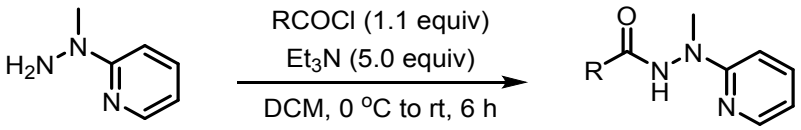
All reactions were carried out under Argon atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. All the chemicals were purchased commercially, and used without further purification. Anhydrous THF was distilled from sodium-benzophenone. Dichloromethane was distilled from calcium hydride. TFE and HFIP were used directly without distillation. Thin-layer chromatography (TLC) was conducted with 0.25 mm Tsingdao silica gel plates (60F-254) and visualized by exposure to UV light (254 nm) or stained with potassium permanganate. Flash column chromatography was performed on Tsingdao silica gel (200-300 mesh) and neutral aluminum oxide (200-300 mesh). ^{1}H NMR spectra were recorded on Bruker spectrometers (at 400 or 500 MHz) and reported relative to deuterated solvent signals or tetramethylsilane internal standard signals. Data for ^{1}H NMR spectra were reported as follows: chemical shift (δ/ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad.), coupling constant (*J*/Hz), and integration. ^{13}C NMR spectra were recorded on Bruker Spectrometers (100 or 125 MHz). Data for ^{13}C NMR spectra were reported in terms of chemical shift. ^{19}F NMR spectra were recorded on Bruker Spectrometers (376 MHz). High-resolution mass spectrometry (HRMS) was conducted on Bruker Apex IV RTMS.

2. General Procedure for the Preparation of Starting Materials



Hydrazides **1a-1v** and [D_5]-**1a** were known compounds and the spectral data matched those reported in the literature.[1]

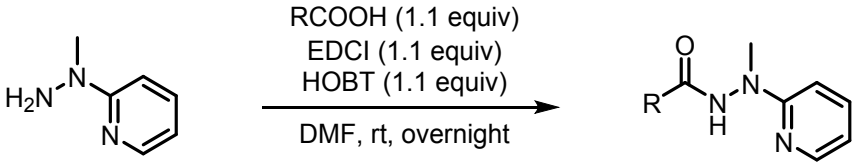
Representative method A: (1a, 1b, 1c, 1e, 1f, 1h, 1i, 1j, 1k, 1l, 1m, 1n, 1o, 1p, 1r, 1s, 1u)



To a stirred mixture of 2-(1-methylhydrazinyl)pyridine (5.0 mmol) and Et_3N (25.0 mmol) in dry CH_2Cl_2 (20 mL) was added benzoyl chloride (5.5 mmol) dropwise under Ar atmosphere at 0 °C. After stirring at ambient temperature

for 6 h, the resulting mixture was washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on neutral alumina (eluting with *n*-hexanes/EtOAc = 3:1 to 1:1) to give the desired product.

Representative method B:[2] (1d, **1g**, **1q**, **1t**, [D_5]-**1a)**

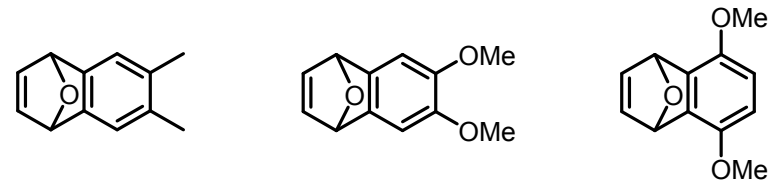


A mixture of 2-(1-methylhydrazinyl)pyridine (5.0 mmol), carboxylic acid (5.5 mmol), EDCI (5.5 mmol), and HOBT (5.5 mmol) in anhydrous DMF (20 mL) was stirred at room temperature overnight. Water (100 mL) was added and the mixture was extracted with EtOAc (20 mL x 3). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on neutral alumina (eluting with *n*-hexanes/EtOAc = 3:1 to 1:1) to give the desired product.

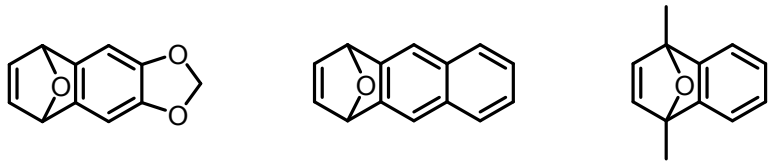
Representative method C: (1v)

A solution of isonicotinic acid (5.0 mmol) was refluxed in $SOCl_2$ (5 mL) for 2 h and cooled to ambient temperature. The excess of $SOCl_2$ was removed under vacuum to give the corresponding acid choloride. The acid choloride was then dissolved in dry CH_2Cl_2 (5 mL) and added dropwise to a dry CH_2Cl_2 (20 mL) solution containing 2-(1-methylhydrazinyl)pyridine (5.0 mmol) and Et_3N (25.0 mmol) at 0 ^oC. After stirring at ambient temperature for 6 h, the resulting mixture was washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on neutral alumina (eluting with *n*-hexanes/EtOAc = 3:1 to 1:1) to afford the corresponding product.

General procedure for the synthesis of substituted 1,4-dihydro-1,4-epoxynaphthalenes

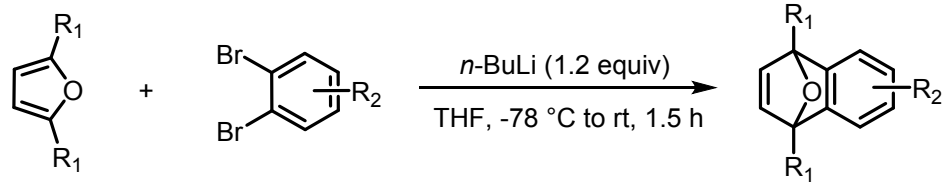


2b **2c** **2d**



2e **2f** **2g**

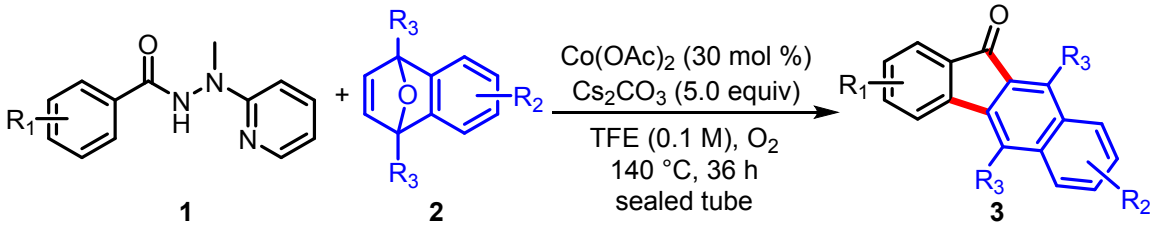
Compounds **2b**-**2g** were prepared according to known literature procedures.[3] Compounds **2b**-**2g** were known compounds and the spectral data matched those reported in the literature.[4]



To a stirred solution of substituted 1,2-dibromobenzene (7.0 mmol) in anhydrous THF (15 mL) under Ar and freshly distilled furan (15 mL) at -78 °C was added *n*-BuLi (2.5 M in hexane, 3.4 mL, 8.4 mmol, 1.2 equiv) dropwise. The solution was stirred at -78 °C for 1.5 h. Then, distillated water (20 mL) was added to the reaction mixture, which was left to warm up to room temperature. Et_2O was added to the reaction mixture and the organic phase was separated. The aqueous solution was extracted with Et_2O (20 mL x 3) and the combined organic solution was dried over $MgSO_4$. The Et_2O was then removed in vacuo and the resulting mixture was purified by a flash silica gel column using a mixture of *n*-hexane/EtOAc as eluent to give the desired pure product. Note that freshly prepared LDA was used rather than *n*-BuLi for compound **2d** and anhydrous toluene was used as the solvent for

compound **2g**.

3. General Procedure for the [3+2] Annulation/Ring-Opening/Dehydration Sequence

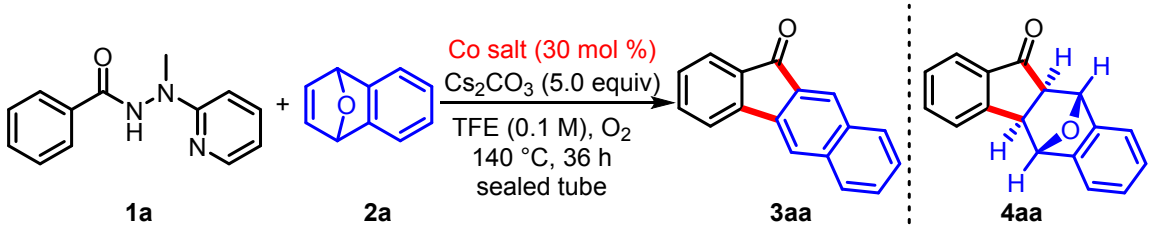


1 **2** **3**

A 25-mL oven-dried sealed tube was charged with hydrazide **1** (0.40 mmol), bicyclic alkene **2** (0.20 mmol), $Co(OAc)_2$ (10.6 mg, 0.06 mmol), and Cs_2CO_3 (325.8 mg, 1.00 mmol). The tube was evacuated and filled with O_2 (1 atm), and TFE (2.0 mL) was added. The tube was stirred at 140 °C for 36 h. After cooling to room temperature, the reaction mixture was diluted with EtOAc (5.0 mL), filtered through a plug of *Celite*, and concentrated in vacuo. The residue was purified by column chromatography on silica gel, eluting with *n*-hexanes/EtOAc (40:1, v/v) to afford corresponding product **3**.

4. Details of Optimization Studies

Table S1. Optimization Studies to Find Suitable Co Salt[a]



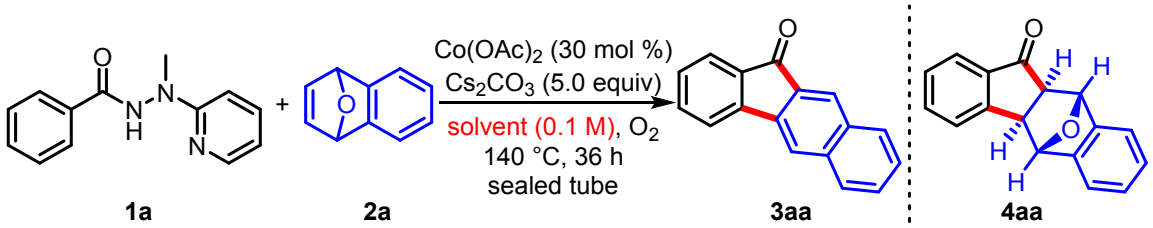
1a **2a** **3aa** **4aa**

entry	Co salt	yield of **3aa** (%)[b]	yield of **4aa** (%)[b]
1	**$Co(OAc)_2$**	**81**	**ND**

2	$Co(acac)_2$	71	ND
3	$Co(acac)_3$	71	ND
4	CoC_2O_4	67	trace
5	$CoCl_2$	68	ND
6	$CoBr_2$	70	ND
7	CoI_2	66	trace

[a]Reaction conditions: **1a** (0.4 mmol), **2a** (0.2 mmol), Co salt (30 mol %), Cs_2CO_3 (5.0 equiv), TFE (2.0 mL), O_2 (1 atm), 140 °C, 36 h, sealed tube. [b]Isolated yield. ND = not detectable.

Table S2. Optimization Studies to Find Suitable Solvent[a]



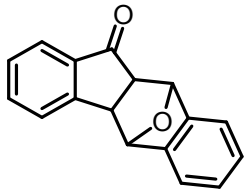
1a **2a** **3aa** **4aa**

entry	solvent	yield of **3aa** (%)[b]	yield of **4aa** (%)[b]
1	**TFE**	**81**	**ND**
2	EtOH	trace	ND
3[c]	HFIP	13	58
4	CH_3CN	trace	ND
5	DCE	trace	5
6	THF	trace	ND
7	toluene	ND	ND
8	DMF	trace	ND

[a]Reaction conditions: **1a** (0.4 mmol), **2a** (0.2 mmol), $Co(OAc)_2$ (30 mol %), Cs_2CO_3 (5.0 equiv), solvent (2.0 mL), O_2 (1 atm), 140 °C, 36 h, sealed tube. [b]Isolated yield. [c]We recently carried out the base-promoted ring-

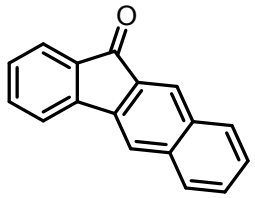
opening/dehydration (or aromatization) reaction of dihydroepoxybenzofluorenone **4aa** under the optimal reaction conditions with HFIP instead of TFE as the solvent and found that only **3aa** was isolated in 11% yield with the recovery of most of the unreacted **4aa**. By comparison, the yield of **3aa** was 97% when TFE was used as the solvent (see Scheme 4c-1). We speculate that the ring-opening/dehydration sequence was less effective in HFIP, due to lowered basicity of Cs_2CO_3 in this solvent. ND = not detectable.

5. Analytical Data of Products



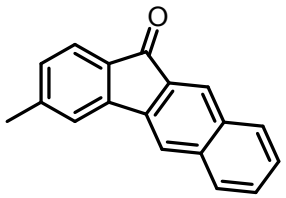
4aa

4b,5,10,10a-Tetrahydro-11*H*-5,10-epoxybenzo[*b*]fluoren-11-one (**4aa**), a light yellow solid, mp 169.1–171.6 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.0 Hz, 1H), 7.71–7.68 (m, 2H), 7.46–7.42 (m, 2H), 7.38–7.36 (m, 1H), 7.24–7.23 (m, 2H), 5.63 (s, 1H), 5.34 (s, 1H), 3.55 (d, *J* = 6.0 Hz, 1H), 2.89 (d, *J* = 5.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.3, 154.3, 145.4, 144.6, 139.9, 135.3, 128.4, 127.3, 127.1, 126.0, 124.0, 119.7, 119.6, 83.1, 82.2, 55.3, 48.5. MS (*m/z*) [$M^{+\cdot}$, 248.10] (M^+, 3%), (M+1, 1%), 247.10 (4%), 231.10 (12%), 220.10 (7%), 219.10 (7%), 203.10 (5%), 202.10 (6%), 192.10 (6%), 191.05 (19%), 190.20 (8%), 189.10 (23%), 165.10 (15%), 164.10 (4%), 163.10 (5%), 119.05 (9%), 118.10 (100%), 115.10 (5%), 102.10 (6%), 90.10 (11%), 89.05 (13%), 76.00 (4%), 63.00 (6%). HRMS calculated for $C_{17}H_{12}NaO_2$ ($M + Na^+$): 271.0730, found 271.0727.



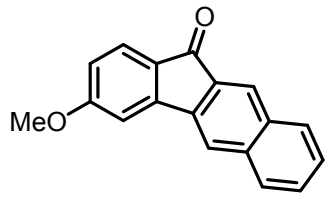
3aa

11*H*-Benzo[*b*]fluoren-11-one (**3aa**), a yellow solid (37.2 mg, 81%), mp 148.5–150.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.79–7.77 (m, 2H), 7.72 (d, *J* = 7.2 Hz, 1H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.54–7.50 (m, 2H), 7.46–7.42 (m, 1H), 7.31 (t, *J* = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.0, 144.7, 138.3, 136.8, 136.0, 134.9, 133.5, 132.7, 130.7, 129.1, 128.9, 128.7, 126.8, 125.6, 124.3, 120.9, 119.0. MS (*m/z*) [$M^{+\cdot}$, 230.10] (M^+, 100%), (M+1, 19%), 202.10 (28%), 201.00 (17%), 200.00 (21%), 175.10 (5%). HRMS calculated for $C_{17}H_{11}O$ (M + H^+): 231.0804, found 231.0805.



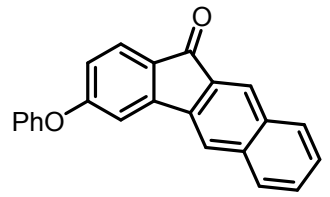
3ba

3-Methyl-11*H*-benzo[*b*]fluoren-11-one (**3ba**), a yellow solid (40.0 mg, 82%), mp 138.0–139.6 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.78–7.76 (m, 2H), 7.60 (d, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 7.0 Hz, 1H), 7.45–7.42 (m, 2H), 7.10 (d, *J* = 7.5 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.6, 146.1, 145.2, 138.4, 136.8, 134.0, 133.7, 133.4, 130.7, 130.0, 128.8, 128.7, 126.8, 125.3, 124.3, 121.6, 118.8, 22.2. MS (*m/z*) [$M^{+\cdot}$, 244.10] (M^+, 100%), (M+1, 19%), 216.10 (11%), 215.10 (59%), 214.20 (7%), 213.10 (18%). 189.10 (10%), 187.10 (5%). HRMS calculated for $C_{18}H_{13}O$ (M + H^+): 245.0961, found 245.0960.



3ca

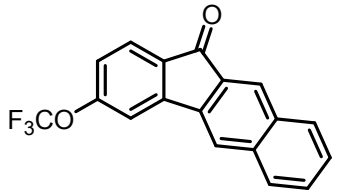
3-Methoxy-11*H*-benzo[*b*]fluoren-11-one (**3ca**), a yellow solid (29.1 mg, 56%), mp 134.0–136.9 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.78–7.75 (m, 2H), 7.66 (d, *J* = 8.5 Hz, 1H), 7.51 (t, *J* = 7.0 Hz, 1H), 7.44 (t, *J* = 7.0 Hz, 1H), 7.11 (d, *J* = 2.0 Hz, 1H), 6.78 (dd, *J* = 8.0, 2.0 Hz, 1H), 3.92 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.5, 165.6, 147.4, 137.8, 136.6, 133.9, 133.8, 130.6, 129.5, 128.7, 128.7, 126.9, 126.3, 124.9, 118.9, 114.6, 106.3, 55.8. MS (*m/z*) [$M^{+\cdot}$, 260.10] (M^+, 100%), (M+1, 17%), 231.10 (9%), 230.10 (11%), 217.10 (18%), 203.10 (5%). 202.10 (11%), 201.10 (4%), 200.00 (5%), 190.10 (7%), 189.10 (45%), 188.10 (11%), 187.00 (12%). HRMS calculated for $C_{18}H_{13}O_2$ ($M + H^+$): 261.0910, found 261.0914.



3da

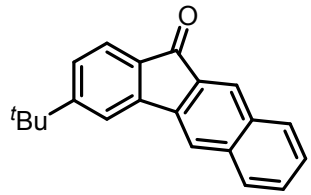
3-Phenoxy-11*H*-benzo[*b*]fluoren-11-one (**3da**), a yellow solid (38.0 mg, 59%), mp 151.0–152.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.71–7.69 (m, 2H), 7.53–7.50 (m, 1H), 7.47–7.44 (m, 3H), 7.28–7.25 (m, 1H), 7.21 (d, *J* = 2.0 Hz, 1H), 7.16 (d, *J* = 7.5 Hz, 2H), 6.88 (dd, *J* = 8.0, 2.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.4, 164.1, 155.5, 147.4, 137.6, 136.7, 133.8, 133.6, 131.0, 130.7, 130.2, 128.8, 128.8, 127.0, 126.4, 125.2, 124.8, 120.3, 119.2, 118.1, 109.9. MS (*m/z*) [$M^{+\cdot}$, 322.10] (M^+, 100%), (M+1, 23%), 321.20 (10%),

294.15 (8%), 293.10 (7%), 266.10 (8%). 265.05 (29%), 264.10 (3%), 263.10 (8%), 201.10 (8%), 200.00 (12%), 189.10 (16%), 188.10 (6%), 187.10 (8%), 77.10 (5%). HRMS calculated for $C_{23}H_{15}O_2$ (M + H^+): 323.1067, found 323.1065.



3ea

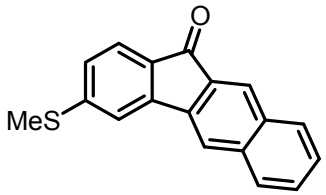
3-(Trifluoromethoxy)-11*H*-benzo[*b*]fluoren-11-one (**3ea**), a yellow solid (48.8 mg, 78%), mp 162.1–165.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.86–7.83 (m, 2H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.57 (td, *J* = 8.0, 1.0 Hz, 1H), 7.52–7.48 (m, 2H), 7.15 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.2, 154.3, 147.1, 136.9, 136.8, 134.2, 133.9, 132.7, 130.9, 129.3, 129.0, 127.4, 126.1, 126.0, 121.0, 120.4 (q, *J* = 256.2 Hz), 119.8, 113.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.4. MS (*m/z*) [$M^{+\cdot}$, 314.10] (M^+, 100%), (M+1, 19%), 229.00 (2%), 217.10 (14%), 190.10 (6%), 189.10 (40%), 188.10 (10%), 187.10 (14%), 69.00 (8%). HRMS calculated for $C_{18}H_{10}F_3O_2$ (M + H^+): 315.0627, found 315.0630.



3fa

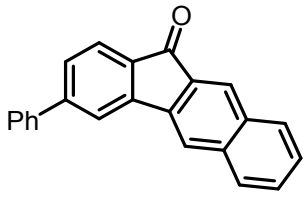
3-(*tert*-Butyl)-11*H*-benzo[*b*]fluoren-11-one (**3fa**), a yellow solid (38.3 mg, 67%), mp 154.2–155.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.86–7.85 (m, 2H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 1.0 Hz, 1H), 7.68 (d, *J* = 7.5 Hz, 1H), 7.54–7.51 (m, 1H), 7.46–7.43 (m, 1H), 7.38 (dd, *J* = 7.5, 1.5 Hz, 1H), 1.42 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.7, 159.4, 145.0,

138.7, 136.9, 134.0, 133.7, 133.5, 130.7, 128.8, 128.7, 126.8, 126.5, 125.3, 124.2, 118.7, 117.9, 35.6, 31.2. MS (*m/z*) [$M^{+\cdot}$, 286.10] (M^+, 83%), (M+1, 18%), 272.10 (20%), 271.10 (100%), 253.10 (5%), 244.10 (7%). 243.10 (35%), 239.10 (9%), 231.10 (10%), 230.20 (11%), 229.10 (18%), 228.10 (28%), 227.10 (8%), 226.10 (18%), 215.10 (16%), 214.10 (3%), 213.10 (5%), 203.10 (5%), 202.10 (18%), 201.10 (8%), 200.10 (13%), 121.60 (13%). HRMS calculated for $C_{21}H_{19}O$ ($M + H^+$): 287.1430, found 287.1429.



3ga

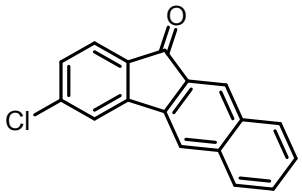
3-(Methylthio)-11*H*-benzo[*b*]fluoren-11-one (**3ga**), a yellow solid (39.7 mg, 72%), mp 151.4–153.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.75–7.72 (m, 2H), 7.57 (d, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.0 Hz, 1H), 7.44–7.40 (m, 2H), 7.06 (d, *J* = 7.5 Hz, 1H), 2.56 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.8, 148.4, 145.2, 137.7, 136.6, 133.8, 133.4, 132.8, 130.7, 128.8, 128.7, 127.0, 125.3, 124.5, 119.0, 117.2, 15.0. MS (*m/z*) [$M^{+\cdot}$, 276.10] (M^+, 100%), (M+1, 22%), (M+2, 8%), 260.90 (10%), 244.10 (5%), 243.10 (23%), 233.10 (8%), 232.00 (15%), 231.10 (4%), 230.10 (10%), 229.10 (1%), 215.20 (7%), 202.20 (8%), 201.10 (8%), 200.10 (14%), 189.10 (20%), 188.10 (6%), 187.10 (9%). HRMS calculated for $C_{18}H_{13}OS$ ($M + H^+$): 277.0682, found 277.0682.



3ha

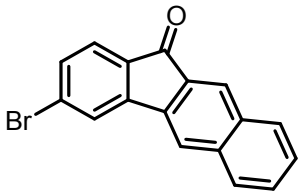
3-Phenyl-11*H*-benzo[*b*]fluoren-11-one (**3ha**), a yellow solid (46.4 mg,

76%), mp 171.0–174.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.82 (s, 3H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 7.5 Hz, 1H), 7.66 (d, *J* = 7.0 Hz, 2H), 7.53–7.49 (m, 4H), 7.46–7.42 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.5, 148.0, 145.5, 140.2, 138.2, 136.9, 135.0, 133.7, 133.3, 130.8, 129.0, 128.9, 128.8, 128.5, 128.1, 127.3, 126.9, 125.5, 124.8, 119.6, 119.0. MS (*m/z*) [$M^{+\cdot}$, 306.05] (M^+, 100%), (M+1, 24%), 278.10 (5%), 277.10 (8%), 276.10 (26%), 275.15 (3%), 274.05 (8%). HRMS calculated for $C_{23}H_{15}O$ (M + H^+): 307.1117, found 307.1119.



3ia

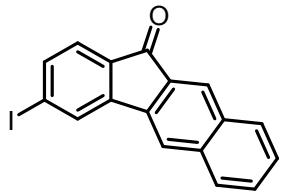
3-Chloro-11*H*-benzo[*b*]fluoren-11-one (**3ia**), a yellow solid (44.3 mg, 84%), mp 218.0–220.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.85–7.83 (m, 2H), 7.68–7.67 (m, 2H), 7.58 (t, *J* = 7.0 Hz, 1H), 7.50 (t, *J* = 7.0 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.6, 146.4, 141.4, 137.1, 136.8, 134.5, 133.9, 132.7, 130.9, 129.3, 129.2, 128.9, 127.4, 126.0, 125.5, 121.5, 119.7. MS (*m/z*) [$M^{+\cdot}$, 264.00] (M^+, 100%), (M+1, 18%), (M+2, 33%), (M+3, 8%), 238.10 (8%), 237.00 (4%), 236.10 (18%), 229.00 (1%), 229.90 (1%), 201.00 (17%), 200.10 (31%), 199.10 (7%), 198.00 (5%), 174.10 (5%). HRMS calculated for $C_{17}H_{10}ClO$ (M + H^+): 265.0415, found 265.0415.



3ja

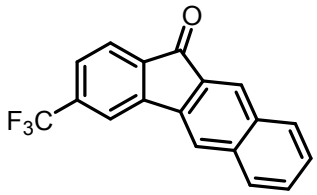
3-Bromo-11*H*-benzo[*b*]fluoren-11-one (**3ja**), a yellow solid (35.1 mg,

57%), mp 228.0–231.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.86–7.83 (m, 3H), 7.61–7.56 (m, 2H), 7.52–7.47 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.5, 146.5, 137.1, 136.8, 134.8, 133.9, 132.6, 132.2, 130.9, 130.1, 129.3, 128.9, 127.4, 126.1, 125.7, 124.4, 119.7. MS (*m/z*) [$M^{+\cdot}$, 308.00] (M^+, 100%), (M+1, 18%), (M+2, 98%), (M+3, 16%), 229.10 (2%), 230.10 (1%), 202.10 (7%), 201.10 (46%), 200.10 (53%), 199.10 (11%), 198.00 (7%), 175.00 (5%), 174.10 (7%), 100.10 (5%). HRMS calculated for $C_{17}H_{10}BrO$ ($M + H^+$): 308.9910, found 308.9902.



3ka

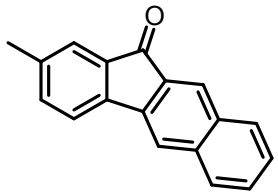
3-Iodo-11*H*-benzo[*b*]fluoren-11-one (**3ka**), a yellow solid (53.4 mg, 75%), mp 223.1–226.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (s, 1H), 8.07 (s, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.82–7.81 (m, 2H), 7.70 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.57 (td, *J* = 7.5, 0.5 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.44 (d, *J* = 7.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.1, 146.2, 138.2, 137.0, 136.7, 135.4, 133.8, 132.3, 130.9, 130.4, 129.2, 128.9, 127.3, 126.1, 125.5, 119.6, 102.9. MS (*m/z*) [$M^{+\cdot}$, 356.00] (M^+, 100%), (M+1, 18%), 230.10 (2%), 229.10 (7%), 202.10 (6%), 201.10 (39%), 200.10 (35%), 199.10 (7%), 198.10 (5%), 175.10 (3%), 174.10 (4%). HRMS calculated for $C_{17}H_{10}IO$ ($M + H^+$): 356.9771, found 356.9765.



3la

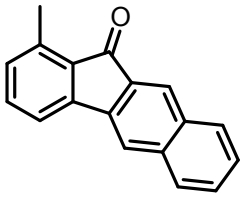
3-(Trifluoromethyl)-11*H*-benzo[*b*]fluoren-11-one (**3la**), a yellow solid

(45.3 mg, 76%), mp 204.0–207.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.92–7.89 (m, 3H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 7.5 Hz, 1H), 7.60–7.57 (m, 2H), 7.50 (t, *J* = 7.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.7, 145.2, 138.5, 137.0, 136.9, 136.3 (q, *J* = 31.2 Hz), 133.8, 132.2, 131.0, 129.5, 129.0, 127.5, 126.4, 126.1 (q, *J* = 3.8 Hz), 124.6, 123.6 (q, *J* = 271.2 Hz), 112.0, 118.0 (q, *J* = 3.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.2. MS (*m/z*) [$M^{+\cdot}$, 298.10] (M^+, 100%), (M+1, 18%), 279.10 (5%), 270.00 (12%), 269.05 (14%), 251.10 (8%), 250.10 (2%), 249.00 (6%), 229.00 (1%), 220.10 (9%), 200.10 (9%). HRMS calculated for $C_{18}H_{10}F_3O$ ($M + H^+$): 299.0678, found 299.0677.



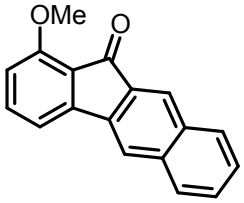
3ma

2-Methyl-11*H*-benzo[*b*]fluoren-11-one (**3ma**), a yellow solid (38.0 mg, 78%), mp 152.2–155.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.69 (s, 1H), 7.50–7.48 (m, 3H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.2, 142.3, 139.4, 138.5, 137.0, 136.4, 135.6, 133.4, 133.1, 130.7, 128.8, 128.6, 126.6, 125.4, 124.8, 120.8, 118.5, 21.4. MS (*m/z*) [$M^{+\cdot}$, 244.10] (M^+, 100%), (M+1, 19%), 243.10 (17%), 216.10 (17%), 215.10 (69%), 214.10 (8%), 213.10 (17%), 189.05 (11%), 188.00 (3%), 187.10 (5%). HRMS calculated for $C_{18}H_{13}O$ ($M + H^+$): 245.0961, found 245.0965.



3na

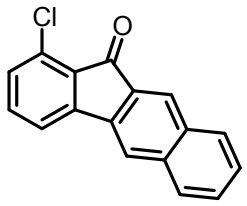
1-Methyl-11*H*-benzo[*b*]fluoren-11-one (**3na**), a yellow solid (30.7 mg, 63%), mp 151.0–153.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.80–7.79 (m, 2H), 7.54–7.51 (m, 2H), 7.45 (td, *J* = 8.0, 1.0 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.07 (d, *J* = 7.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.2, 145.3, 139.6, 138.1, 136.9, 134.3, 133.7, 133.2, 133.1, 131.7, 130.7, 128.7, 126.7, 125.0, 118.7, 118.4, 18.0. MS (*m/z*) [$M^{+\cdot}$, 244.10] (M^+, 100%), (M+1, 20%), 243.20 (9%), 216.10 (12%), 215.10 (58%), 214.10 (7%), 213.10 (19%), 189.10 (10%), 188.10 (3%), 187.00 (5%). HRMS calculated for $C_{18}H_{13}O$ (M + H^+): 245.0961, found 245.0961.



3oa

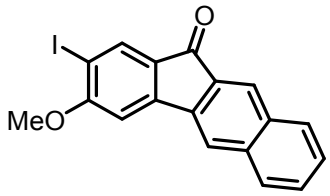
1-Methoxy-11*H*-benzo[*b*]fluoren-11-one (**3oa**), a yellow solid (35.9 mg, 69%), mp 197.0–200.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.82 (s, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.53–7.48 (m, 2H), 7.45 (td, *J* = 8.0, 1.0 Hz, 1H), 7.29 (d, *J* = 7.0 Hz, 1H), 6.83 (d, *J* = 8.5 Hz, 1H), 4.00 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.0, 158.6, 146.9, 137.6, 137.0, 136.6, 133.8, 133.2, 130.6, 128.7, 128.6, 126.8, 125.0, 122.8, 119.1, 113.3, 112.5, 56.0. MS (*m/z*) [$M^{+\cdot}$, 260.10] (M^+, 69%), (M+1, 12%), 259.10 (28%), 232.10 (21%), 231.00 (100%), 230.00 (19%). 229.00 (2%), 214.20 (13%), 213.10 (6%), 203.00 (21%), 202.10 (44%), 201.00 (24%), 200.00 (24%), 189.10 (13%), 188.00 (8%), 187.10 (15%), 101.00 (5%). HRMS

calculated for $C_{18}H_{13}O_2$ ($M + H^+$): 261.0910, found 261.0913.



3pa

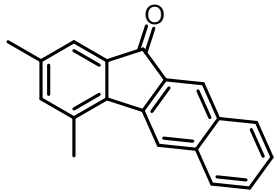
1-Chloro-11*H*-benzo[*b*]fluoren-11-one (**3pa**), a yellow solid (35.3 mg, 67%), mp 206.4–209.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.83 (s, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 7.2 Hz, 1H), 7.54 (td, *J* = 7.6, 1.2 Hz, 1H), 7.49–7.41 (m, 2H), 7.23 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.0, 146.8, 136.7, 136.5, 135.3, 133.7, 132.8, 132.3, 131.4, 130.8, 130.7, 129.0, 128.8, 127.1, 125.8, 119.4, 119.2. MS (*m/z*) [$M^{+\cdot}$, 264.00] (M^+, 100%), (M+1, 20%), (M+2, 35%), (M+3, 6%), 238.10 (7%), 237.10 (3%), 236.00 (20%), 229.10 (1%), 201.10 (23%), 200.10 (38%), 199.10 (9%), 198.10 (5%), 174.00 (5%). HRMS calculated for $C_{17}H_{10}ClO$ ($M + H^+$): 265.0415, found 265.0416.



3qa

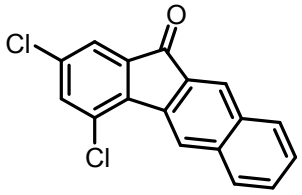
2-Iodo-3-methoxy-11*H*-benzo[*b*]fluoren-11-one (**3qa**), a yellow solid (48.6 mg, 63%), mp 258.1–261.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 8.10 (s, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.85 (s, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.55 (td, *J* = 7.6, 1.2 Hz, 1H), 7.48 (td, *J* = 7.6, 1.2 Hz, 1H), 7.10 (s, 1H), 4.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.2, 163.2, 147.5, 137.2, 136.5, 135.9, 133.8, 133.0, 130.7, 130.6, 128.9, 128.7, 127.1, 125.3, 119.0, 102.7, 86.4, 56.8. MS (*m/z*) [$M^{+\cdot}$, 386.00] (M^+, 100%), (M+1, 19%), 343.00 (5%), 260.15 (1%), 244.00 (19%), 230.10 (4%), 229.10 (8%), 227.90 (1%),

216.10 (5%), 202.10 (7%), 201.10 (19%), 200.10 (15%), 188.10 (10%), 187.10 (15%). HRMS calculated for $C_{18}H_{12}IO_2$ ($M + H^+$): 386.9876, found 386.9879.



3ra

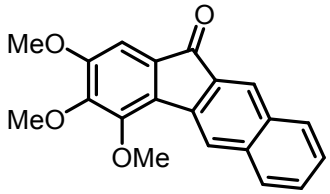
2,4-Dimethyl-11*H*-benzo[*b*]fluoren-11-one (**3ra**), a yellow solid (45.4 mg, 88%), mp 175.0–177.6 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.73 (d, J = 8.0 Hz, 1H), 7.67 (d, J = 8.0 Hz, 1H), 7.63 (s, 1H), 7.44 (t, J = 7.0 Hz, 1H), 7.37 (t, J = 7.0 Hz, 1H), 7.26 (s, 1H), 6.98 (s, 1H), 2.50 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.3, 140.0, 139.2, 138.9, 138.0, 137.0, 136.8, 134.1, 133.4, 132.7, 130.4, 128.9, 128.6, 126.6, 125.0, 122.4, 121.6, 21.1, 20.3. MS (*m/z*) [$M^{+\cdot}$, 258.10] (M^+, 100%), (M+1, 23%), 243.10 (17%), 230.10 (5%), 229.10 (19%), 228.10 (22%), 227.10 (10%), 226.10 (14%), 216.10 (9%), 215.10 (51%), 213.10 (8%), 202.10 (9%), 189.10 (5%). HRMS calculated for $C_{19}H_{15}O$ ($M + H^+$): 259.1117, found 259.1119.



3sa

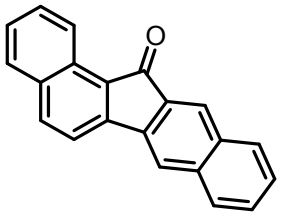
2,4-Dichloro-11*H*-benzo[*b*]fluoren-11-one (**3sa**), a yellow solid (55.4 mg, 93%), mp 197.2–199.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (s, 1H), 8.08 (s, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.78 (d, J = 8.0 Hz, 1 H), 7.55 (t, J = 7.0 Hz, 1H), 7.49–7.47 (m, 2H), 7.38 (d, J = 1.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.3, 139.3, 139.0, 136.8, 135.9, 135.2, 135.2, 133.2, 132.0, 130.6, 130.6, 129.4, 127.7, 126.3, 123.6, 123.0. MS (*m/z*) [$M^{+\cdot}$, 298.00] (M^+,

100%), (M+1, 18%), (M+2, 66%), (M+3, 12%), (M+4, 11%), 272.00 (10%), 271.10 (3%), 270.00 (15%), 264.10 (1%), 262.90 (1%), 234.95 (7%), 234.10 (6%), 201.00 (7%), 200.00 (38%), 199.10 (14%), 198.00 (12%). HRMS calculated for $C_{17}H_9Cl_2O$ ($M + H^+$): 299.0025, found 299.0027.



3ta

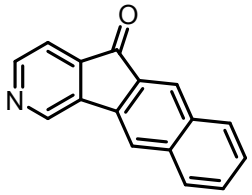
2,3,4-Trimethoxy-11*H*-benzo[*b*]fluoren-11-one (**3ta**), a yellow solid (56.3 mg, 88%), mp 194.5–197.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.99 (s, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.50 (td, *J* = 8.0, 1.0 Hz, 1H), 7.41 (td, *J* = 8.0, 1.0 Hz, 1H), 7.09 (s, 1H), 4.10 (s, 3H), 4.00 (s, 3H), 3.91 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.2, 154.9, 149.8, 148.4, 137.3, 137.0, 133.2, 132.9, 131.9, 130.9, 130.6, 128.8, 128.8, 126.6, 125.2, 121.4, 103.5, 61.1, 60.6, 56.4. MS (*m/z*) [$M^{+\cdot}$, 320.10] (M^+, 100%), (M+1, 23%), 305.10 (19%), 290.10 (8%), 277.10 (13%), 263.00 (6%), 262.00 (35%), 247.10 (24%), 234.10 (5%), 219.10 (10%), 218.20 (5%), 217.10 (12%), 191.00 (17%), 190.00 (3%), 189.05 (7%), 188.10 (3%), 187.10 (6%), 163.10 (22%), 162.10 (5%). HRMS calculated for $C_{20}H_{17}O_4$ ($M + H^+$): 321.1121, found 321.1122.



3ua

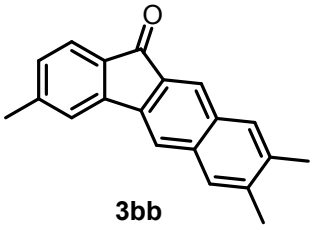
13*H*-Dibenzo[*a*,*h*]fluoren-13-one (**3ua**), a yellow solid (34.7 mg, 62%), mp 202.0–205.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.03 (d, *J* = 8.5 Hz, 1H),

8.02 (s, 1H), 7.96 (d, J = 8.0 Hz, 1H), 7.81 (d, J = 7.5 Hz, 1H), 7.75 (t, J = 8.5 Hz, 2H), 7.72–7.70 (m, 2H), 7.59 (td, J = 8.0, 1.0 Hz, 1H), 7.49 (td, J = 7.5, 1.0 Hz, 1H), 7.46–7.40 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.0, 146.4, 138.0, 136.7, 136.2, 134.2, 133.9, 133.4, 130.8, 130.1, 129.5, 129.4, 128.8, 128.8, 128.5, 126.9, 126.7, 125.0, 124.6, 118.8, 118.4. MS (*m/z*) [$M^{+\cdot}$, 280.10] (M^+, 100%), (M+1, 20%), 252.10 (18%), 251.10 (6%), 250.10 (23%), 249.10 (4%), 248.10 (5%), 224.10 (4%). HRMS calculated for $C_{21}H_{13}O$ (M + H^+): 281.0961, found 281.0963.



3va

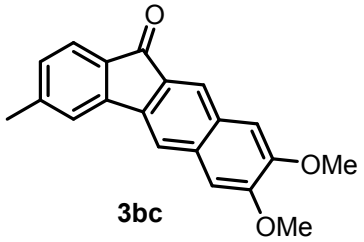
5*H*-Benzo[5,6]indeno[1,2-*c*]pyridin-5-one (**3va**), a yellow solid (16.2 mg, 35%), mp 182.2–185.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.08 (s, 1H), 8.70 (d, J = 3.0 Hz, 1H), 8.21 (s, 1H), 7.95 (s, 1H), 7.89 (d, J = 8.5 Hz, 1H), 7.84 (d, J = 8.5 Hz, 1H), 7.59 (td, J = 8.0, 1.0 Hz, 1H), 7.55 (d, J = 4.5 Hz, 1H), 7.51 (td, J = 8.0, 1.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.3, 151.0, 143.5, 141.8, 138.0, 137.0, 136.5, 133.7, 131.6, 131.1, 129.7, 129.0, 127.6, 127.2, 120.3, 117.2. MS (*m/z*) [$M^{+\cdot}$, 231.10] (M^+, 100%), (M+1, 24%), 204.10 (9%), 203.10 (21%), 202.10 (8%), 201.10 (7%), 177.00 (10%), 176.10 (25%), 175.10 (14%), 174.10 (10%), 150.00 (9%), 149.05 (4%). HRMS calculated for $C_{16}H_{10}NO$ (M + H^+): 232.0757, found 232.0757.



3bb

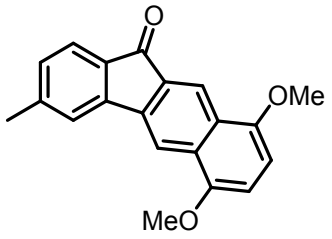
3,7,8-Trimethyl-11*H*-benzo[*b*]fluoren-11-one (**3bb**), a yellow solid (39.7

mg, 73%), mp 224.0–227.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.67 (s, 1H), 7.61 (d, *J* = 7.5 Hz, 1H), 7.58 (s, 1H), 7.53 (s, 1H), 7.45 (s, 1H), 7.10 (d, *J* = 7.5 Hz, 1H), 2.45 (s, 3H), 2.41 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.8, 145.9, 145.4, 139.0, 137.7, 136.6, 135.6, 134.0, 132.7, 132.4, 130.4, 129.6, 128.6, 124.6, 124.2, 121.4, 117.9, 22.2, 20.3, 20.0. MS (*m/z*) [$M^{+\cdot}$, 272.10] (M^+, 100%), (M+1, 19%), 271.10 (10%), 257.10 (25%), 242.20 (3%), 239.20 (5%), 229.10 (16%), 228.10 (12%), 227.10 (7%), 226.10 (11%), 215.10 (6%), 214.10 (2%), 213.20 (5%), 202.00 (7%). HRMS calculated for $C_{20}H_{17}O$ ($M + H^+$): 273.1274, found 273.1274.



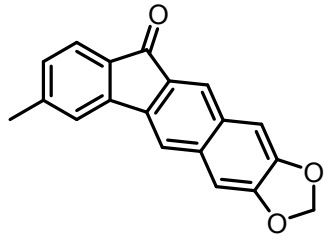
3bc

7,8-Dimethoxy-3-methyl-11*H*-benzo[*b*]fluoren-11-one (**3bc**), a yellow solid (44.3 mg, 73%), mp 181.2–183.9 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.65 (s, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.40 (s, 1H), 7.13 (s, 1H), 7.09–7.08 (m, 2H), 4.02 (s, 3H), 4.00 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.9, 151.6, 149.9, 145.8, 145.4, 137.7, 133.8, 133.0, 132.0, 129.4, 129.1, 124.2, 123.9, 121.2, 117.4, 109.3, 107.6, 56.0, 22.2. MS (*m/z*) [$M^{+\cdot}$, 304.10] (M^+, 100%), (M+1, 22%), 289.10 (7%), 262.10 (7%), 261.10 (37%), 246.10 (7%), 243.10 (5%), 233.10 (9%), 232.10 (5%), 231.10 (20%), 219.00 (9%), 218.10 (48%), 215.10 (5%), 203.10 (5%), 202.10 (9%), 190.10 (6%), 189.05 (23%), 188.20 (5%), 187.10 (6%). HRMS calculated for $C_{20}H_{17}O_3$ ($M + H^+$): 305.1172, found 305.1170.



3bd

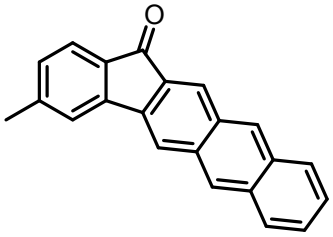
6,9-Dimethoxy-3-methyl-11*H*-benzo[*b*]fluoren-11-one (**3bd**), a yellow solid (49.2 mg, 81%), mp 209.0–211.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 0.4 Hz, 1H), 8.11 (s, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.46 (s, 1H), 7.08 (dd, *J* = 7.6, 0.4 Hz, 1H), 6.72 (d, *J* = 8.4 Hz, 1H), 6.62 (d, *J* = 8.4 Hz, 1H), 3.92 (s, 3H), 3.91 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.9, 151.6, 149.8, 145.8, 145.3, 138.3, 133.8, 132.6, 129.6, 128.9, 126.0, 124.1, 121.6, 119.8, 113.0, 107.2, 104.7, 55.7, 22.1. MS (*m/z*) [$M^{+\cdot}$, 304.10] (M^+, 71%), (M+1, 16%), 290.10 (22%), 289.10 (100%), 274.10 (18%), 273.10 (4%), 261.10 (9%), 247.10 (6%), 246.10 (31%), 218.10 (13%), 192.00 (12%), 190.95 (3%), 189.95 (10%), 189.05 (21%), 163.00 (10%). HRMS calculated for $C_{20}H_{17}O_3$ ($M + H^+$): 305.1172, found 305.1171.



3be

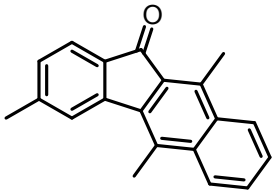
7-Methyl-10*H*-indeno[1',2':6,7]naphtho[2,3-*d*][1,3]dioxol-10-one (**3be**), a yellow solid (37.4 mg, 65%), mp 246.0–249.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.65 (s, 1H), 7.59 (d, *J* = 7.5 Hz, 1H), 7.43 (s, 1H), 7.15 (s, 1H), 7.11–7.10 (m, 2H), 6.08 (s, 2H), 2.45 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.9, 149.9, 148.2, 145.8, 145.3, 138.0, 134.6, 133.7, 132.2, 130.6, 129.6, 124.3, 124.3, 121.2, 118.1, 106.8, 105.2, 101.6, 22.2. MS (*m/z*)

[$M^{+\cdot}$, 288.10] (M^+, 100%), (M+1, 20%), 287.10 (17%), 232.00 (7%), 231.10 (7%), 230.10 (6%), 229.00 (2%), 203.10 (8%), 202.10 (22%), 201.00 (13%), 200.10 (18%). HRMS calculated for $C_{19}H_{13}O_3$ (M + H^+): 289.0859, found 289.0858.



3bf

3-Methyl-13*H*-indeno[1,2-*b*]anthracen-13-one (**3bf**), a yellow solid (40.1 mg, 68%), mp 220.0–222.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 8.24 (s, 1H), 8.22 (s, 1H), 7.91 (s, 1H), 7.89 (s, 1H), 7.84 (s, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.50–7.43 (m, 3H), 7.11 (d, *J* = 7.6 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.0, 146.1, 145.1, 136.2, 134.6, 133.4, 133.4, 133.2, 132.1, 131.1, 130.4, 130.1, 128.3, 128.0, 127.3, 126.9, 126.3, 126.1, 124.2, 121.7, 118.5, 22.2. MS (*m/z*) [$M^{+\cdot}$, 294.10] (M^+, 100%), (M+1, 23%), 266.10 (7%), 265.10 (27%), 264.10 (5%), 263.10 (15%), 132.65 (4%). HRMS calculated for $C_{22}H_{15}O$ (M + H^+): 295.1117, found 295.1118.



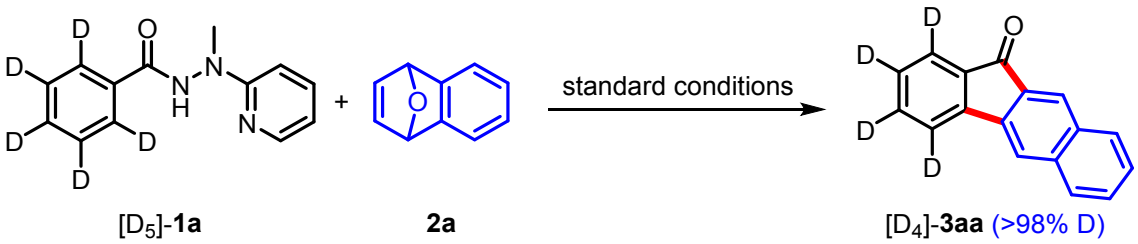
3bg

3,5,10-Trimethyl-11*H*-benzo[*b*]fluoren-11-one (**3bg**), a yellow solid (35.3 mg, 65%), mp 143.0–145.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.4 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 7.64–7.61 (m, 2H), 7.56 (td, *J* = 8.0, 1.2 Hz, 1H), 7.51–7.47 (m, 1H), 7.10 (d, *J* = 7.6 Hz, 1H), 2.98 (s, 3H), 2.80 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.4, 145.2, 145.2,

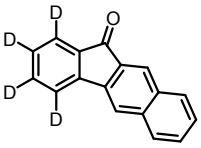
136.4, 136.1, 135.4, 134.8, 134.0, 129.1, 128.8, 128.2, 127.6, 126.4, 126.2, 125.2, 124.9, 123.9, 22.5, 14.9, 12.2. MS (*m/z*) [$M^{+\cdot}$, 272.10] (M^+, 100%), (M+1, 20%), 271.10 (8%), 257.10 (21%), 243.10 (5%), 242.20 (3%), 241.10 (4%), 240.20 (3%), 239.10 (8%), 230.10 (9%), 229.10 (49%), 228.10 (37%), 227.10 (12%), 226.10 (16%), 215.10 (7%), 202.10 (10%). HRMS calculated for $C_{20}H_{17}O$ ($M + H^+$): 273.1274, found 273.1271.

6. Preliminary Mechanistic Experiments

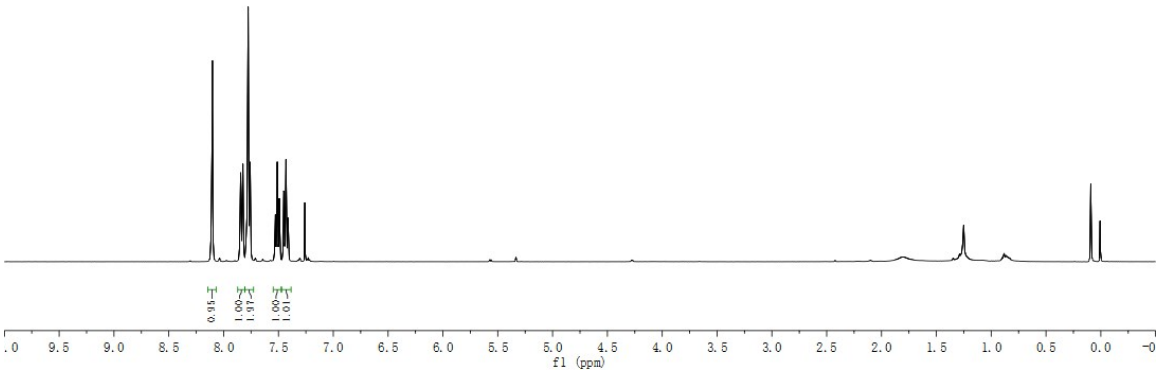
Deuterium labeling experiment



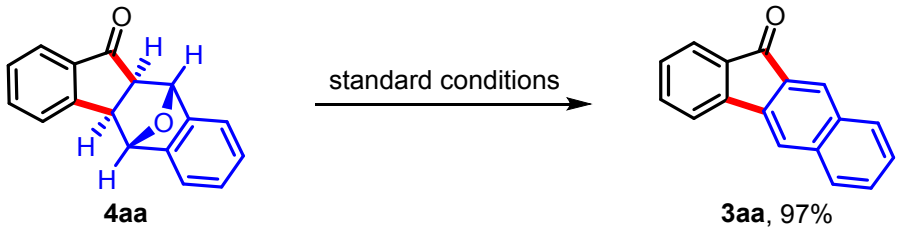
[D_5]-**1a** **2a** [D_4]-**3aa** (>98% D)



[D_4]-**3aa** (>98% D)

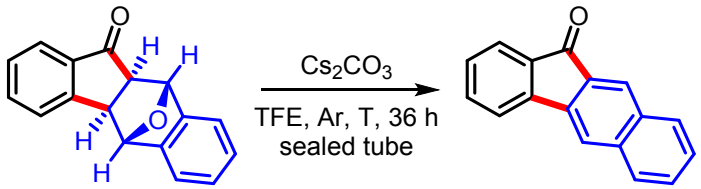


Ring-opening/dehydration:



4aa **3aa**, 97%

A 25-mL oven-dried sealed tube was charged with **4aa** (49.6 mg, 0.20 mmol), $Co(OAc)_2$ (10.6 mg, 0.06 mmol), and Cs_2CO_3 (325.8 mg, 1.00 mmol). The tube was evacuated and filled with O_2 (1 atm), and TFE (2.0 mL) was added. The tube was stirred at 140 °C for 36 h. After cooling to room temperature, the reaction mixture was diluted with EtOAc (5.0 mL), filtered through a plug of *Celite*, and concentrated in vacuo. The residue was purified by column chromatography on silica gel, eluting with *n*-hexanes/EtOAc (40:1, v/v) to afford corresponding product **3aa** in 97% yield.



4aa **3aa**

Cs_2CO_3 (equiv)	T (°C)	**3aa** (%)
2.0	140	89
2.0	130	72
2.0	120	30
/	140	0

A 25-mL oven-dried sealed tube was charged with **4aa** (49.6 mg, 0.20 mmol), Cs_2CO_3 (130.3 mg, 0.40 mmol). The tube was evacuated and filled with Ar (1 atm), and TFE (2.0 mL) was added. The tube was stirred at specified temperature for 36 h. After cooling to room temperature, the reaction mixture was concentrated in vacuo and purified by column chromatography on silica gel, eluting with *n*-hexanes/EtOAc (40:1, v/v) to afford corresponding product **3aa**.

7. References

1. a) S. Zhai, S. Qiu, X. Chen, J. Wu, H. Zhao, C. Tao, Y. Li, B. Cheng, H. Wang and H.

Zhai, *Chem. Commun.*, 2018, **54**, 98; b) S. Qiu, S. Zhai, H. Wang, C. Tao, H. Zhao and H. Zhai, *Adv. Synth. Catal.*, 2018, **360**, 3271.

2. S.-Y. Yan, Y.-J. Liu, B. Liu, Y.-H. Liu and B.-F. Shi, *Chem. Commun.*, 2015, **51**, 4069.

3. P. Gandeepan, P. Rajamalli and C.-H. Cheng, *Angew. Chem., Int. Ed.*, 2016, **55**, 4308.

4. a) Y. Cheng, K. Parthasarathy and C. Bolm, *Eur. J. Org. Chem.*, 2017, **2017**, 1203; b) M. Christl and S. Groetsch, *Eur. J. Org. Chem.*, 2000, **2000**, 1871; c) M. S. Newman, H. M. Dali and W. M. Hung, *J. Org. Chem.*, 1975, **40**, 262; d) D. Yang, P. Hu, Y. Long, Y. Wu, H. Zeng, H. Wang and X. Zuo, *Beilstein J. Org. Chem.*, 2009, **5**, 53.

8. ^{1}H, ^{13}C and ^{19}F NMR Spectra

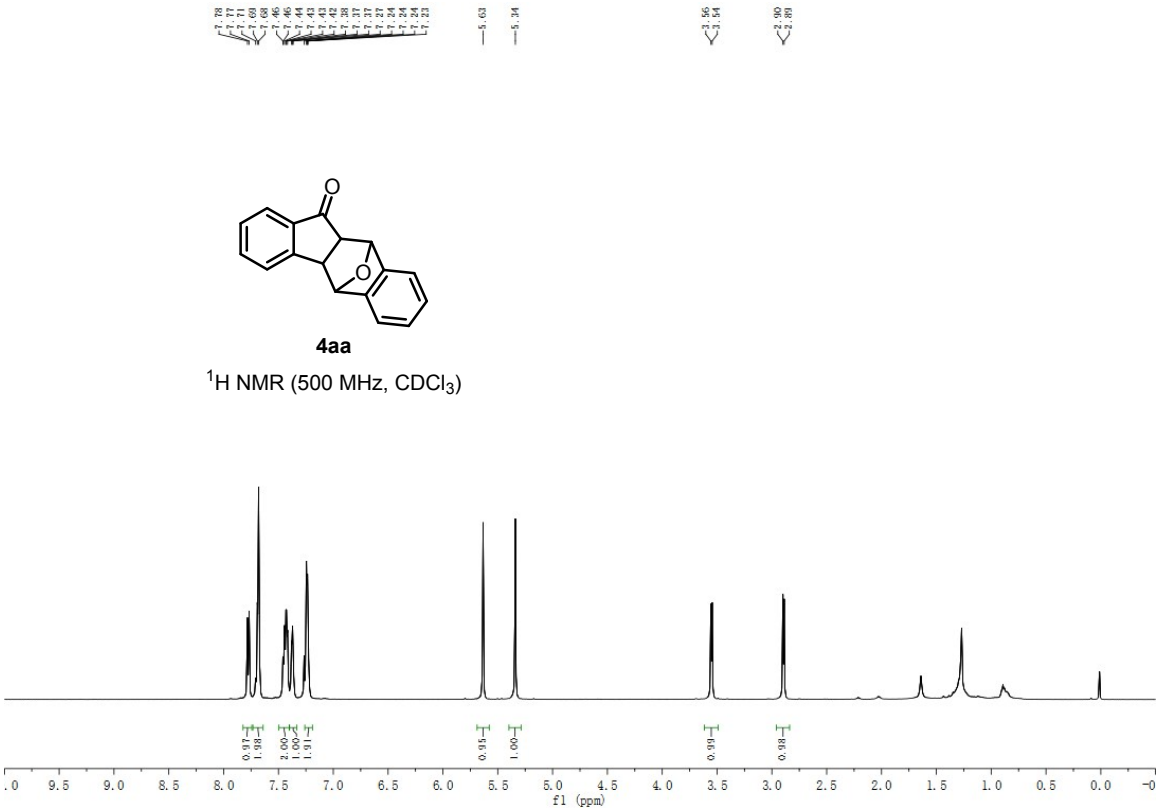


Fig. S1. ^{1}H NMR Spectrum of **4aa**

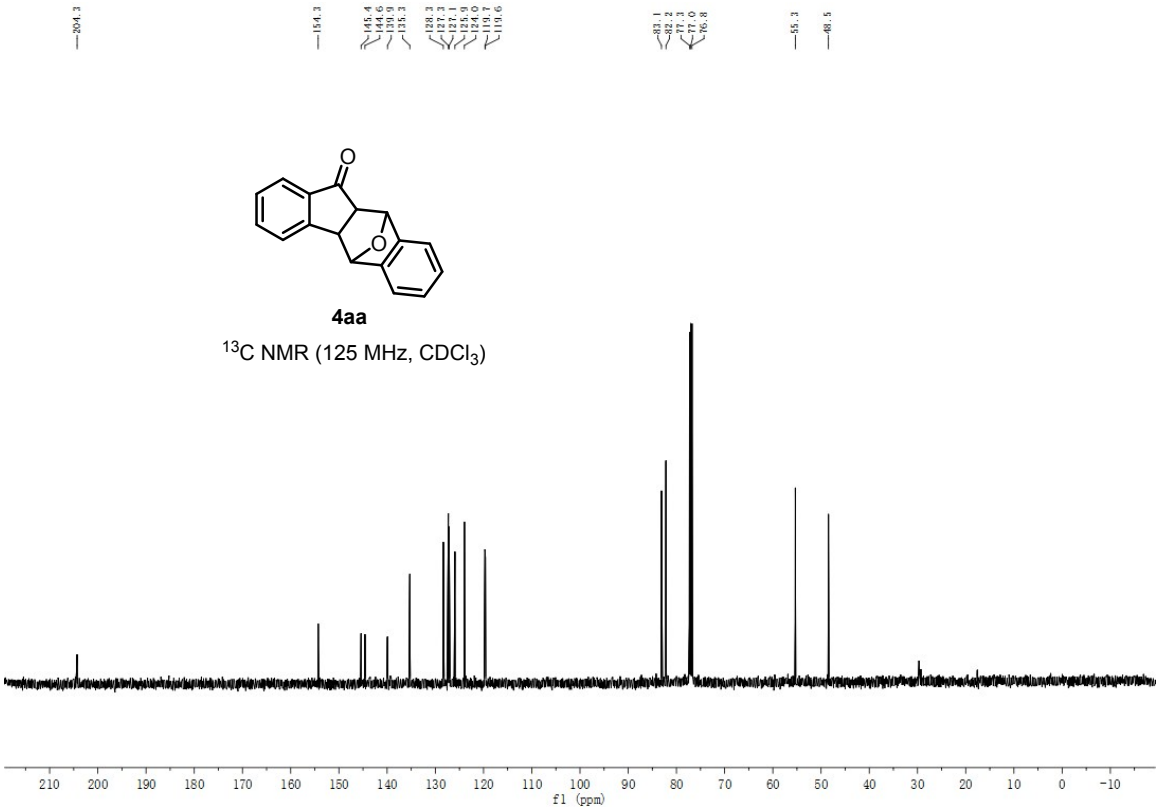


Fig. S2. ^{13}C NMR Spectrum of **4aa**

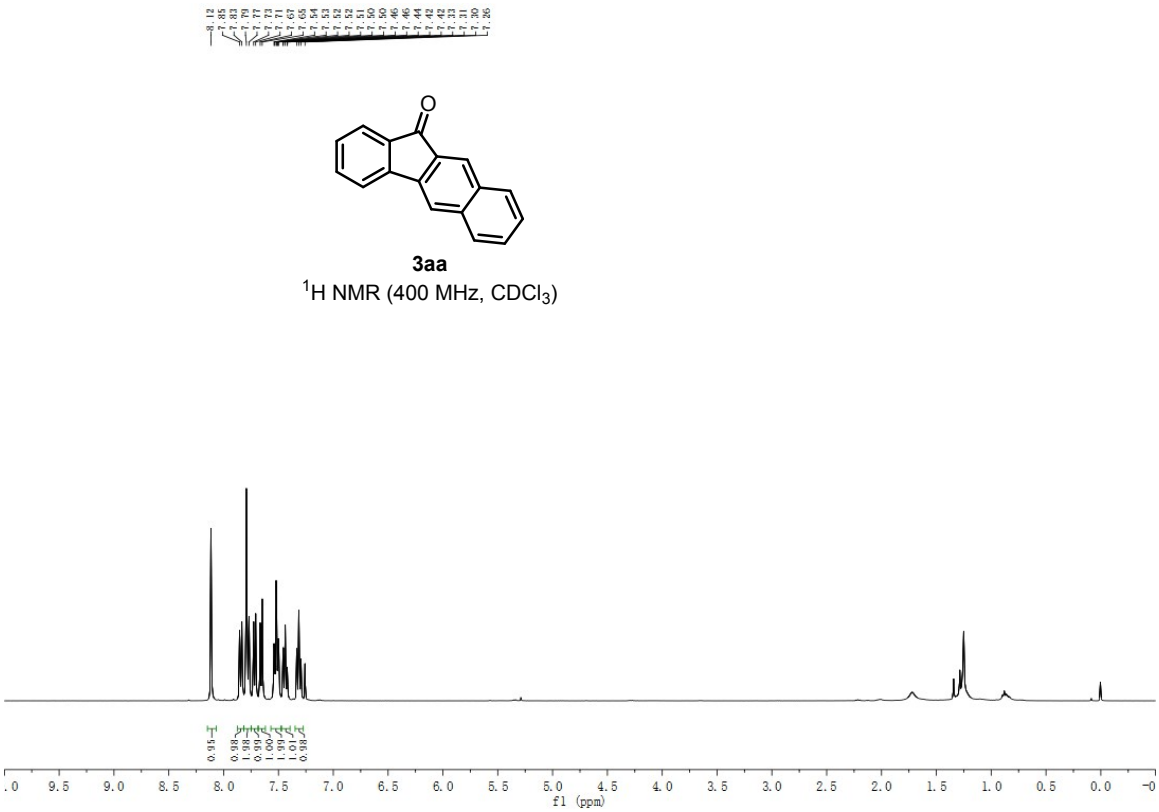


Fig. S3. ^{1}H NMR Spectrum of **3aa**

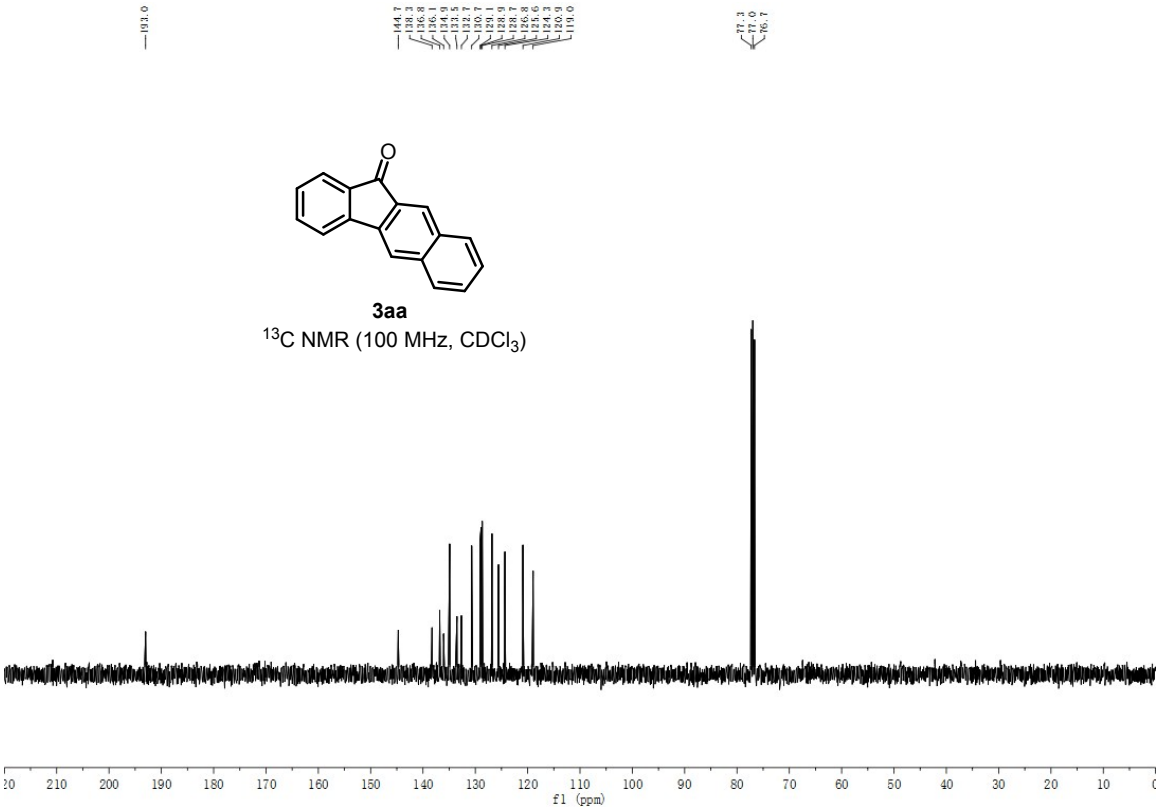


Fig. S4. ^{13}C NMR Spectrum of **3aa**

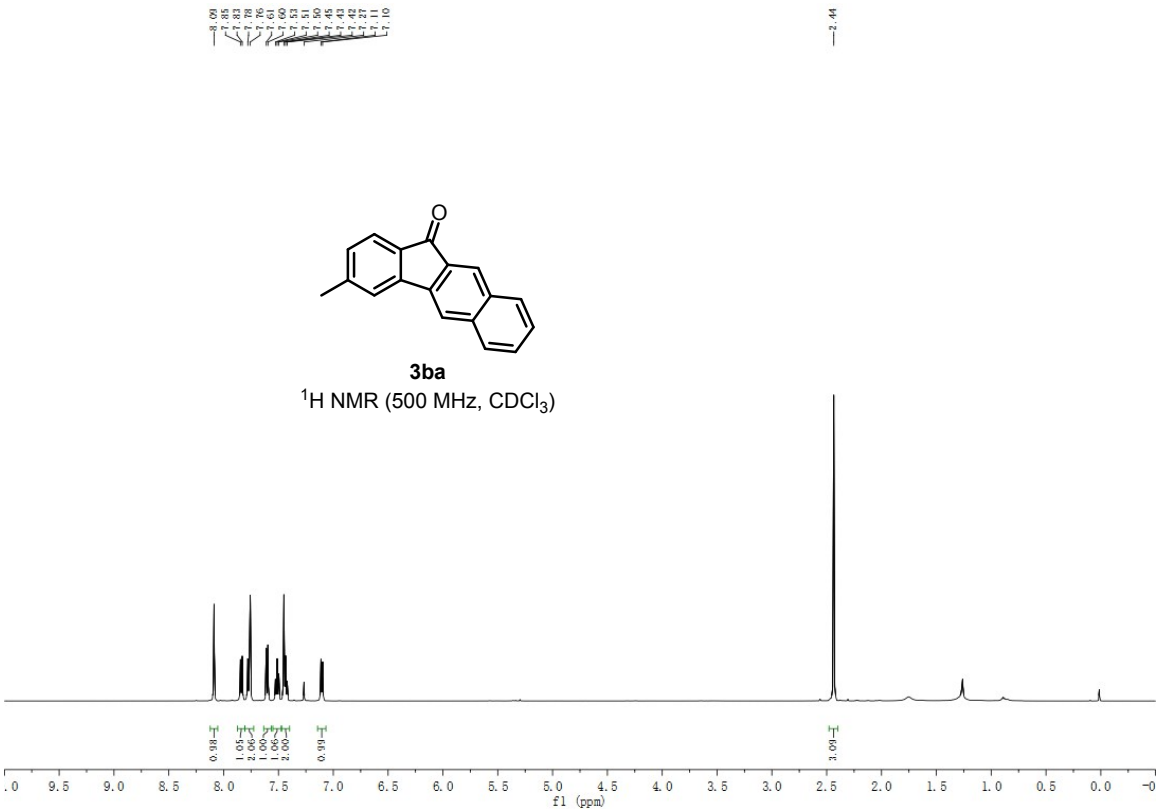


Fig. S5. ^{1}H NMR Spectrum of **3ba**

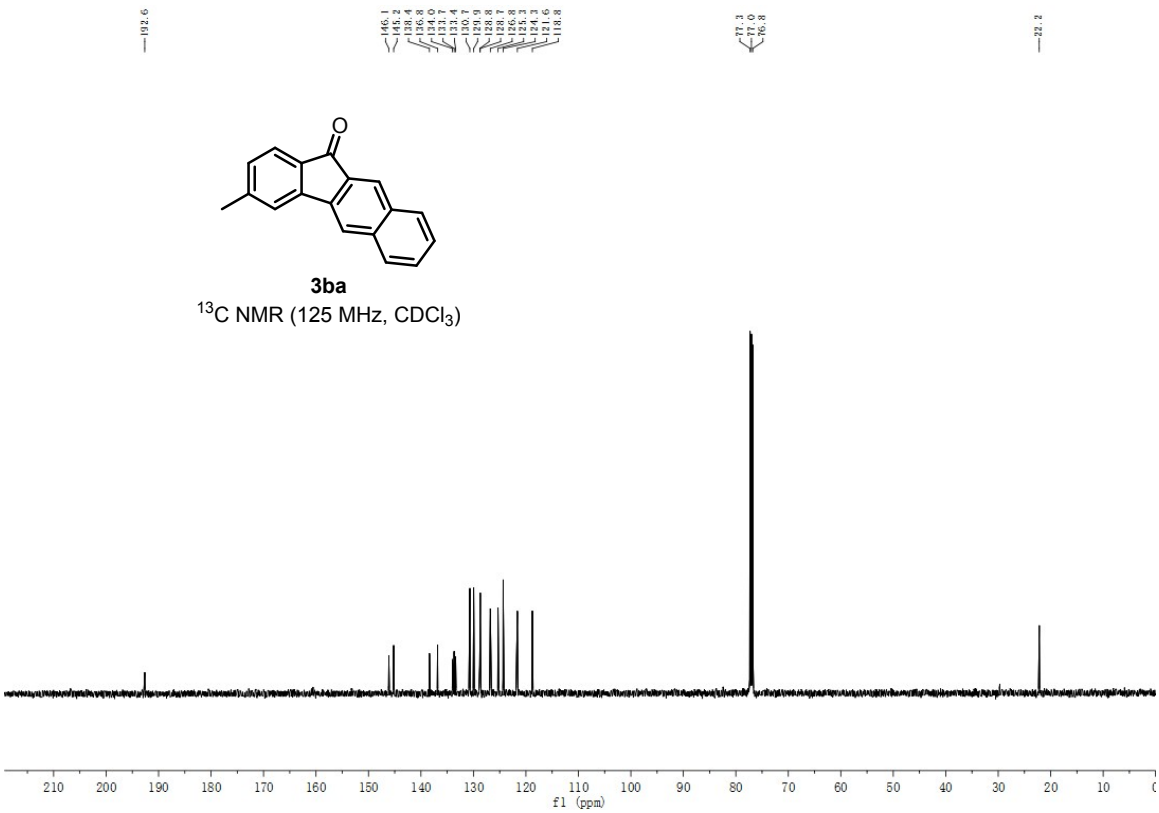


Fig. S6. ^{13}C NMR Spectrum of **3ba**

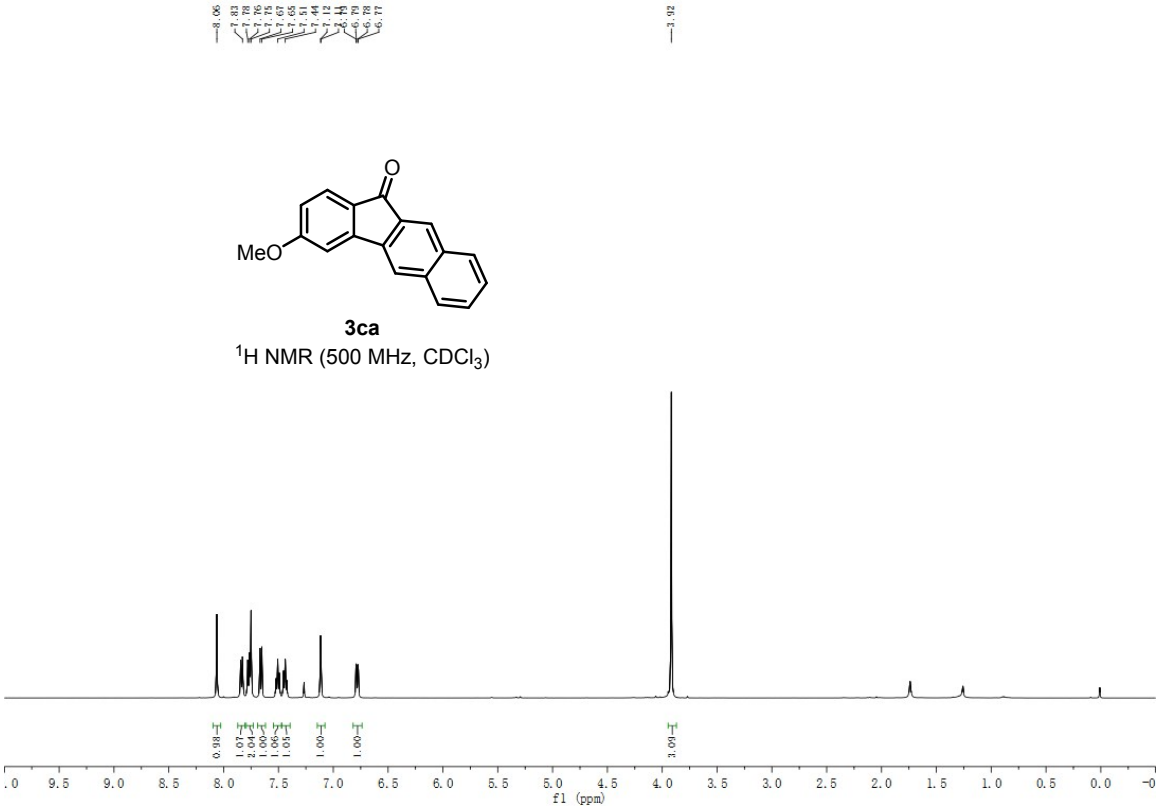
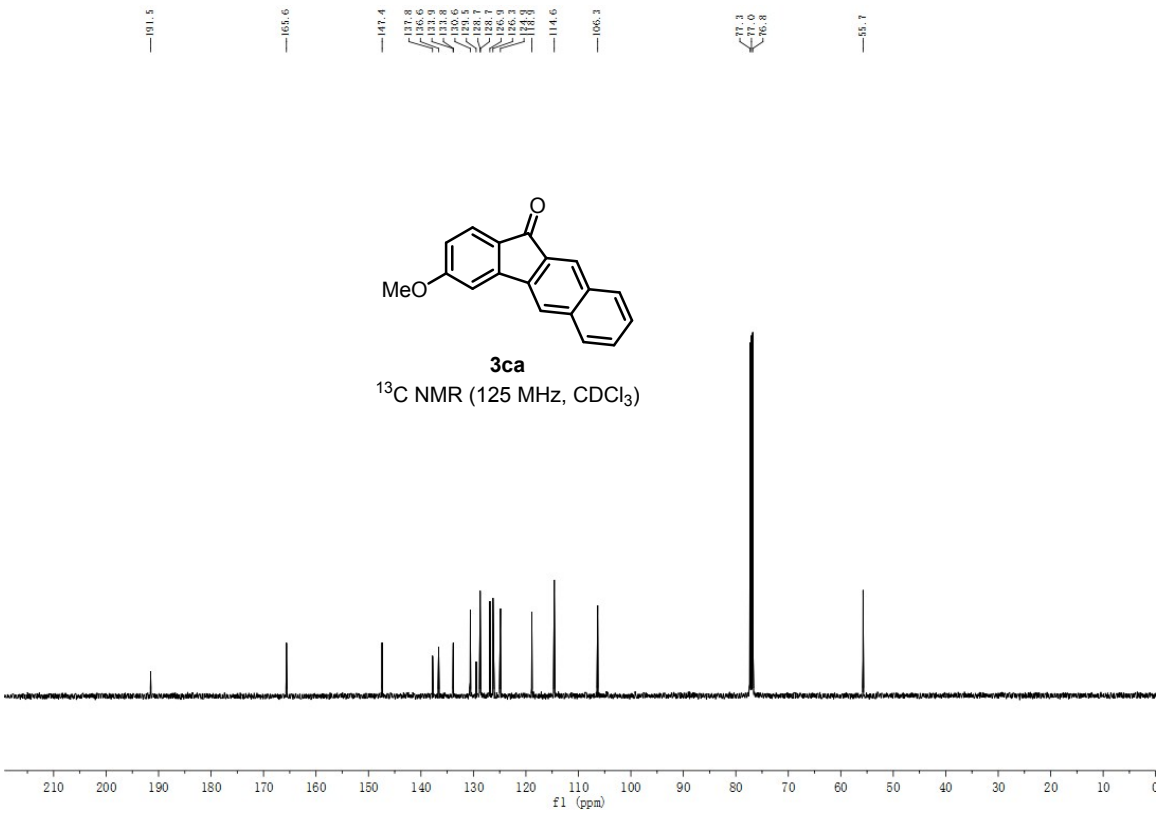


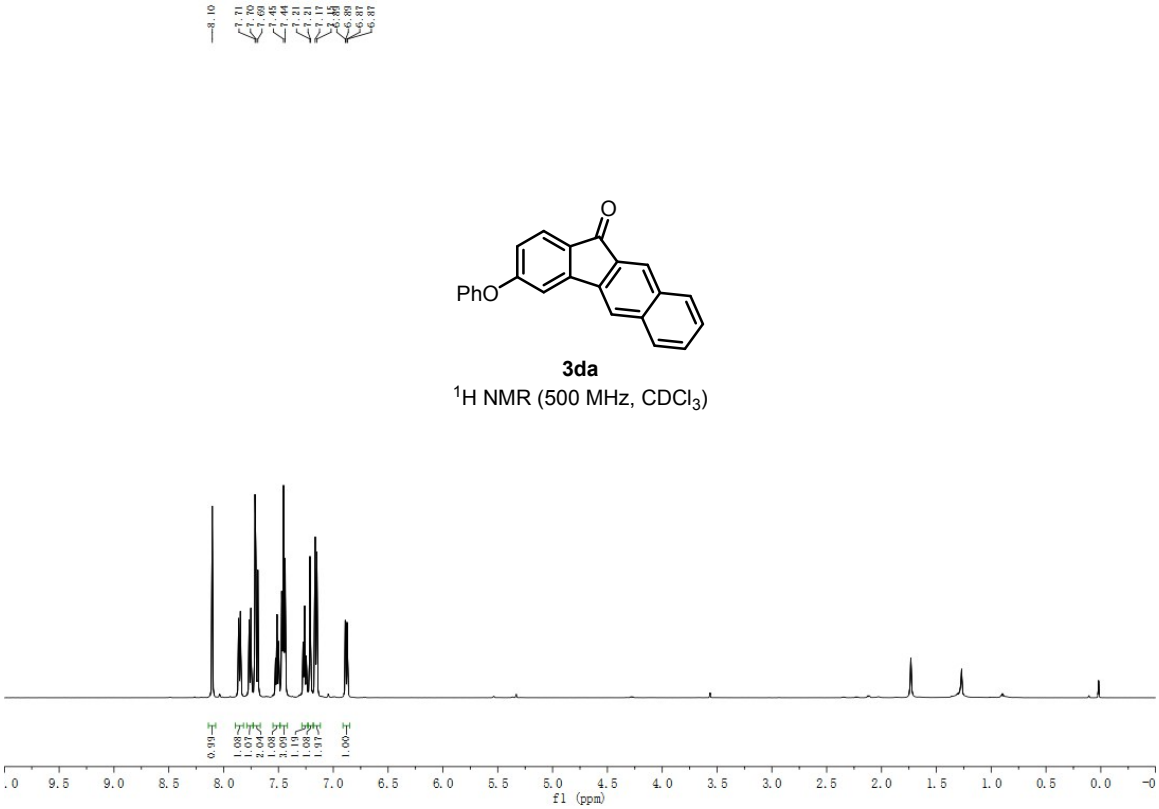
Fig. S7. ^{1}H NMR Spectrum of **3ca**



3ca

^{13}C NMR (125 MHz, $CDCl_3$)

Fig. S8. ^{13}C NMR Spectrum of **3ca**



3da

^{1}H NMR (500 MHz, $CDCl_3$)

Fig. S9. ^{1}H NMR Spectrum of **3da**

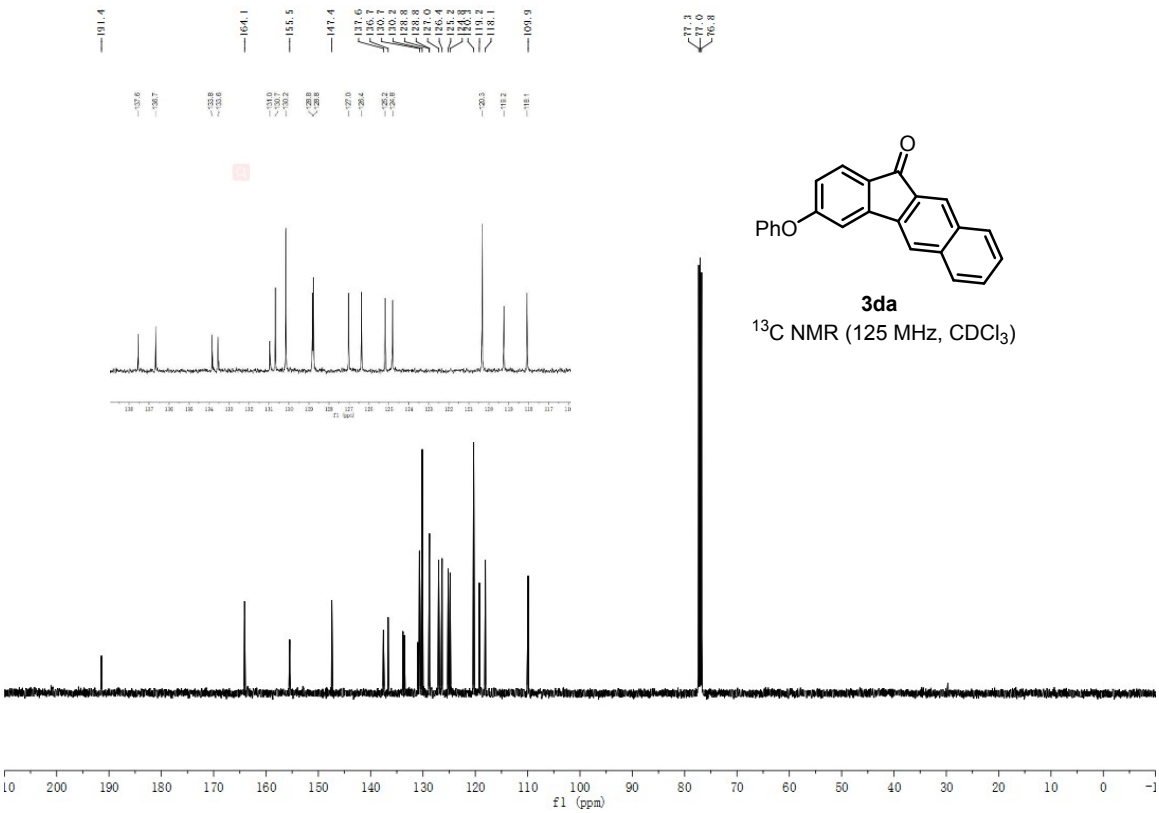


Fig. S10. ^{13}C NMR Spectrum of **3da**

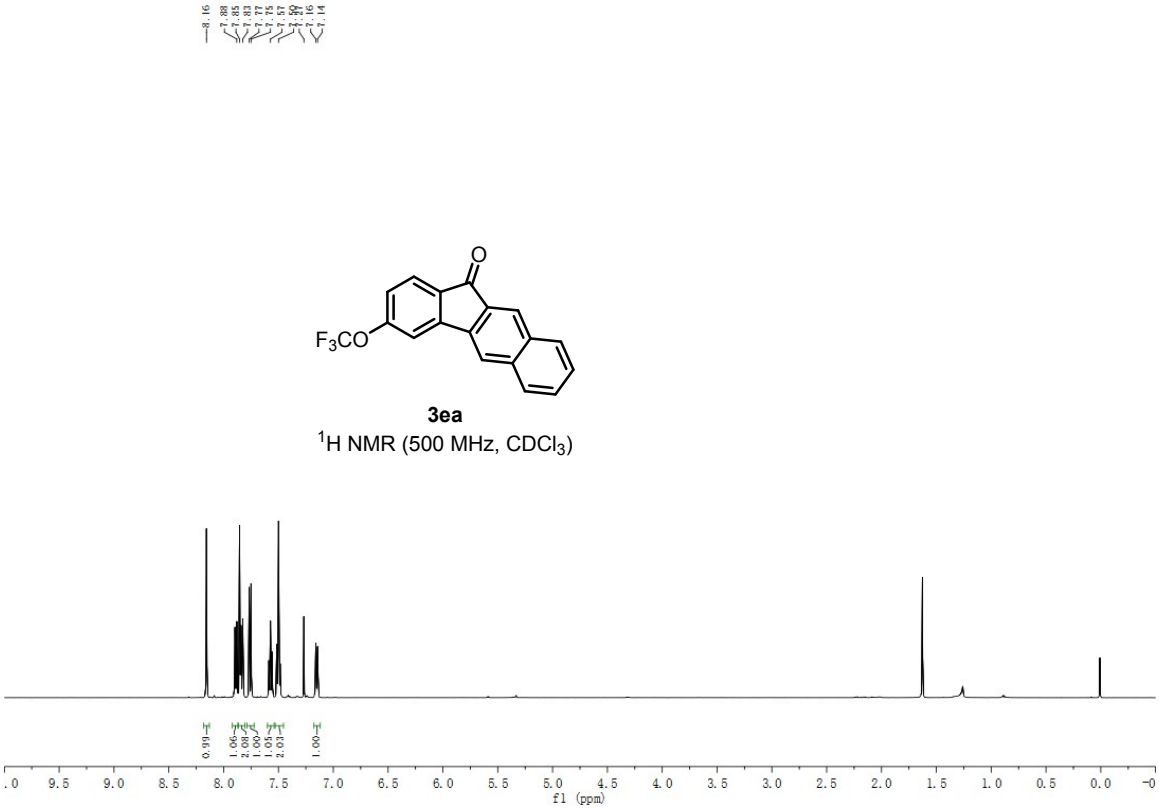


Fig. S11. ^{1}H NMR Spectrum of **3ea**

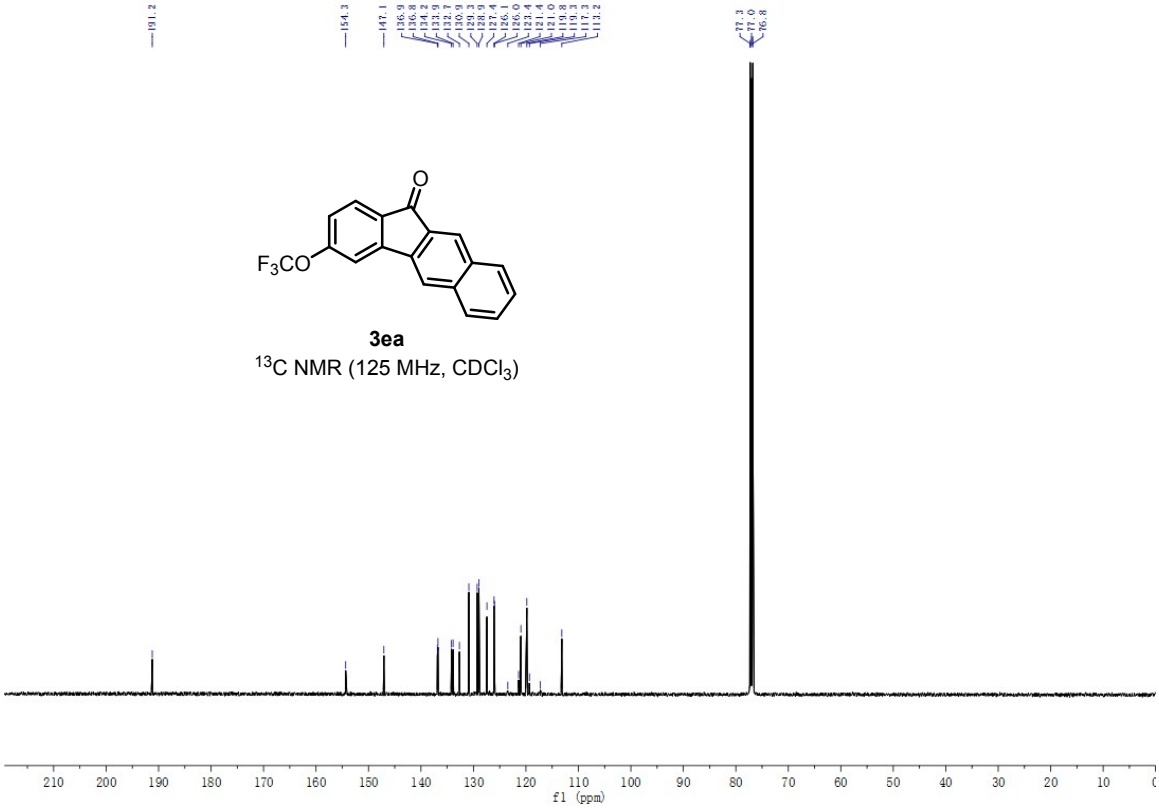


Fig. S12. ^{13}C NMR Spectrum of **3ea**

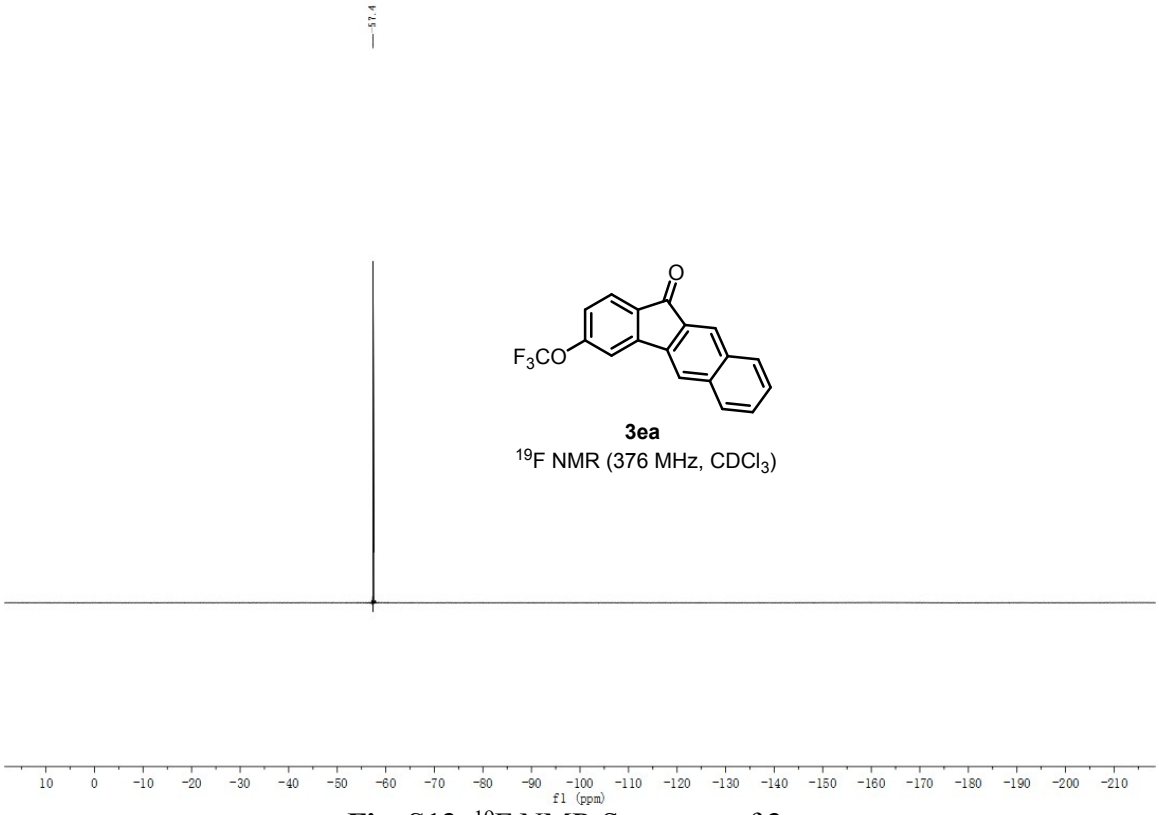


Fig. S13. ^{19}F NMR Spectrum of **3ea**

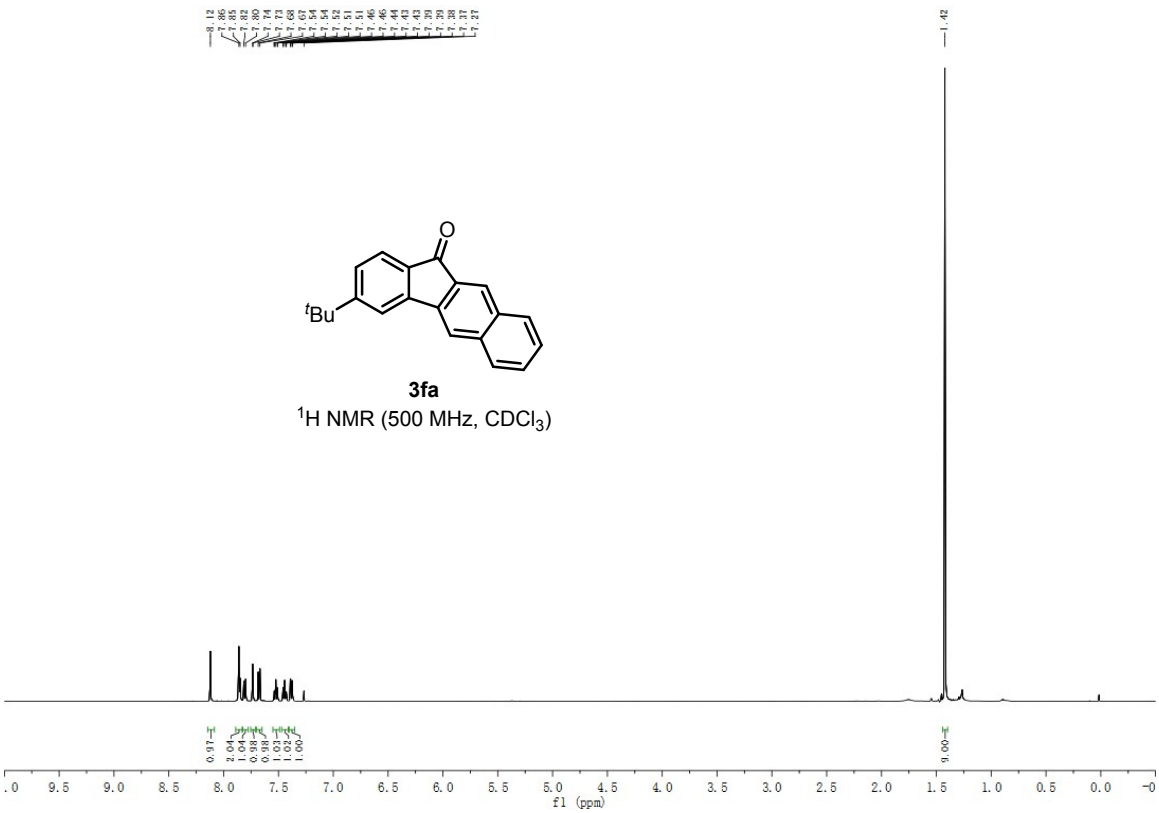


Fig. S14. ^{1}H NMR Spectrum of **3fa**

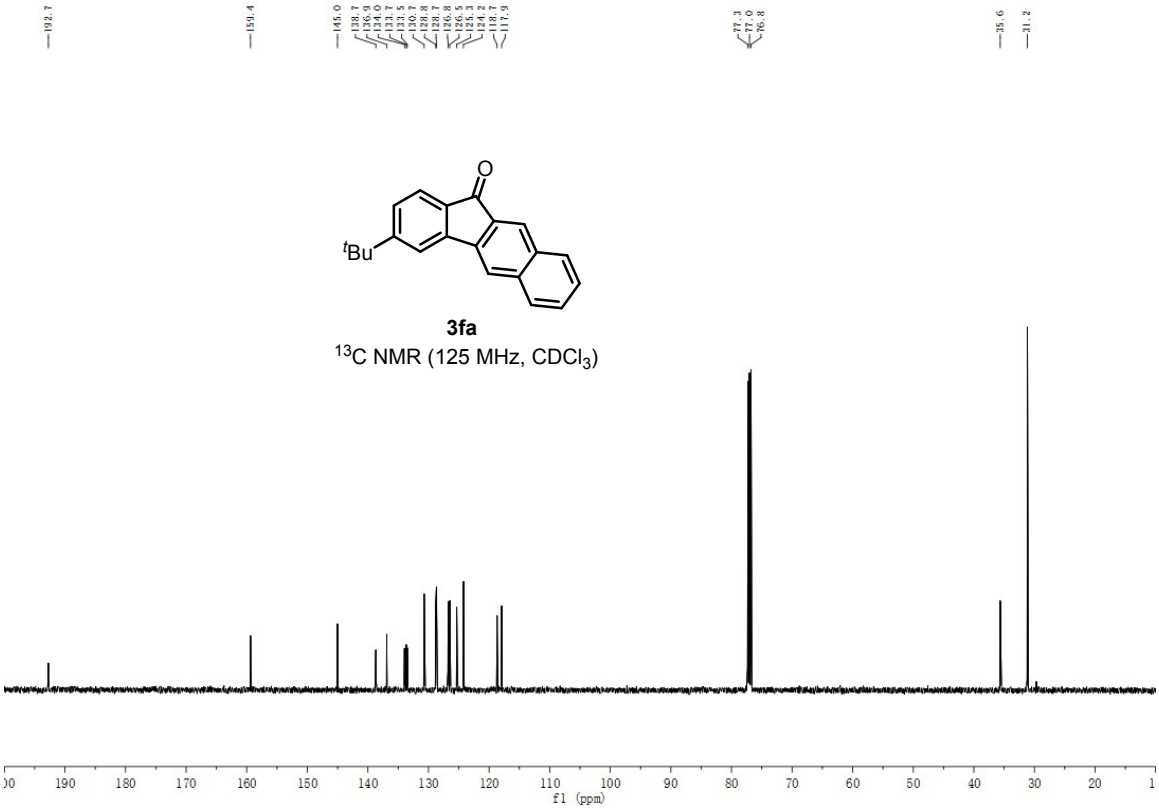


Fig. S15. ^{13}C NMR Spectrum of **3fa**

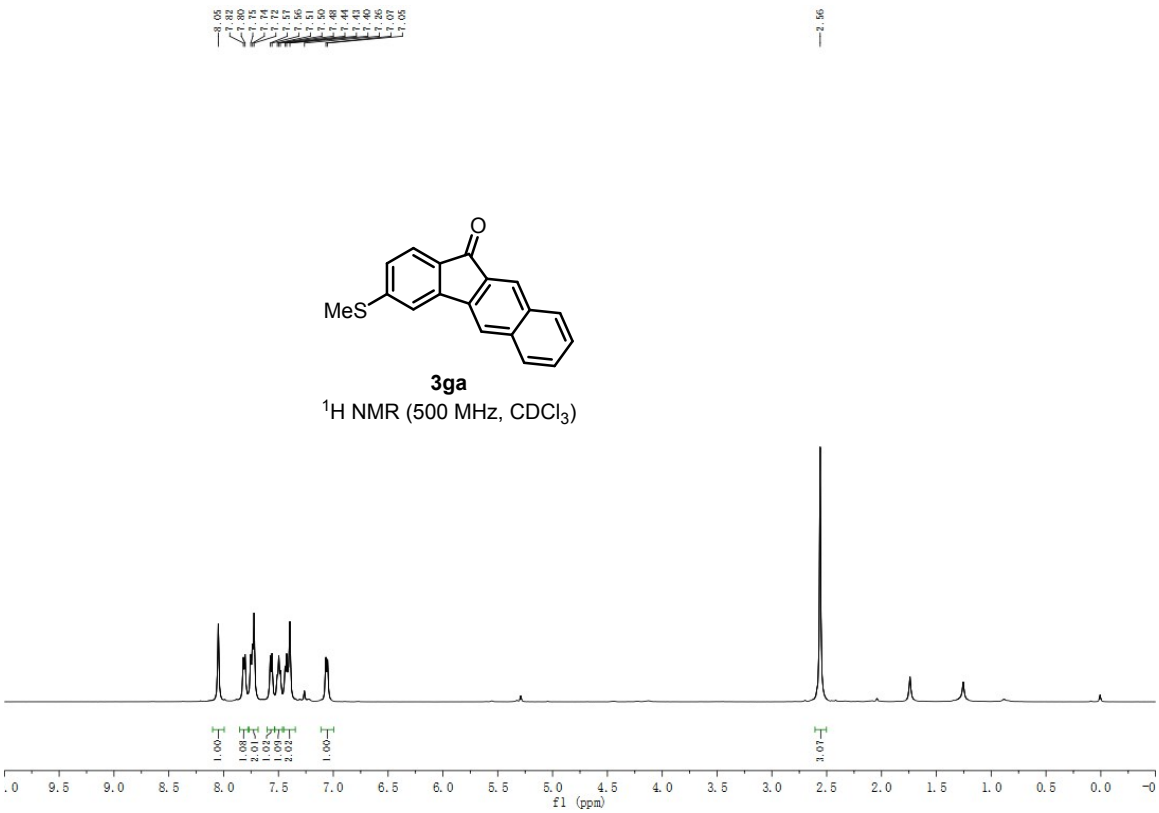


Fig. S16. ^{1}H NMR Spectrum of **3ga**

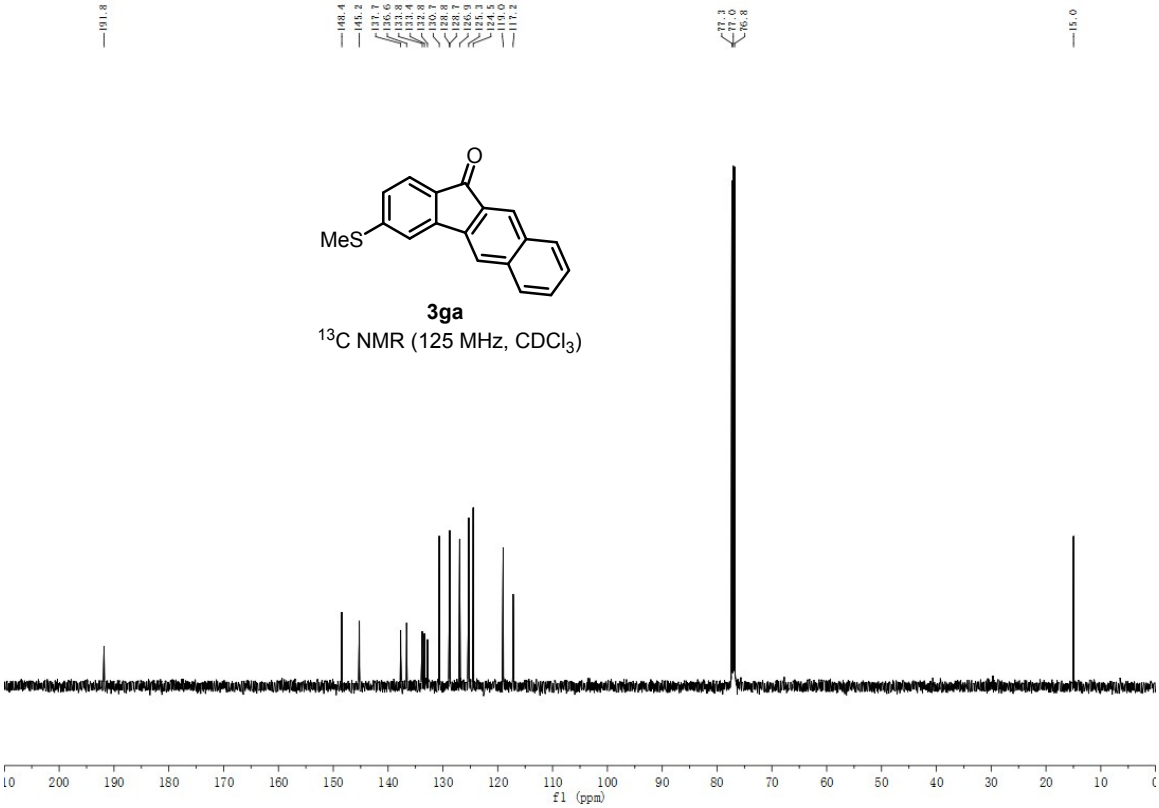


Fig. S17. ^{13}C NMR Spectrum of **3ga**

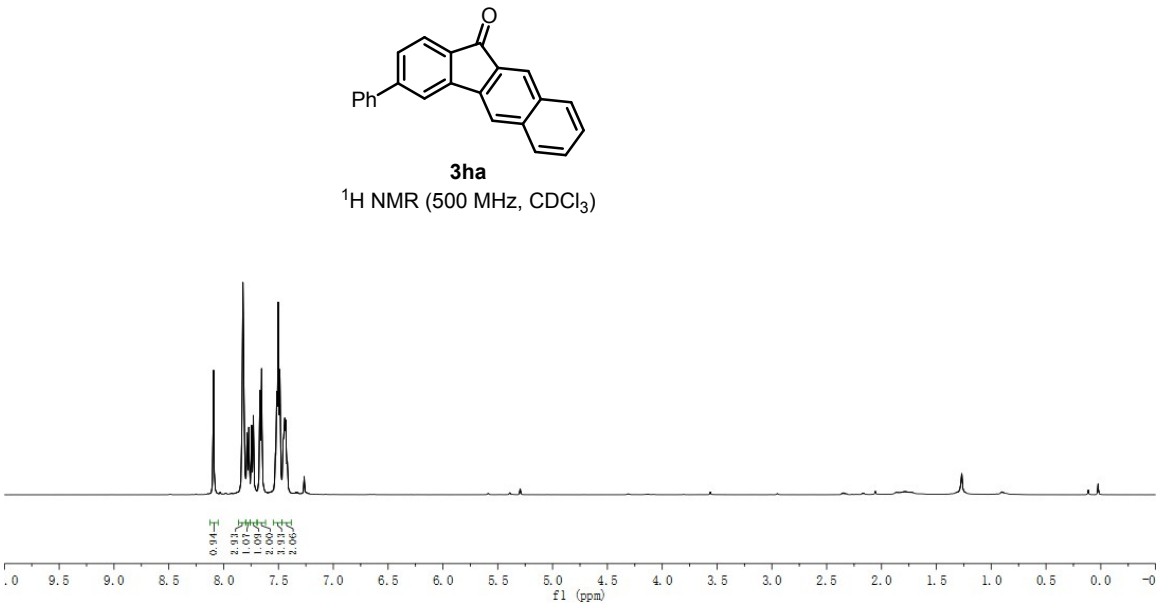


Fig. S18. ^{1}H NMR Spectrum of **3ha**

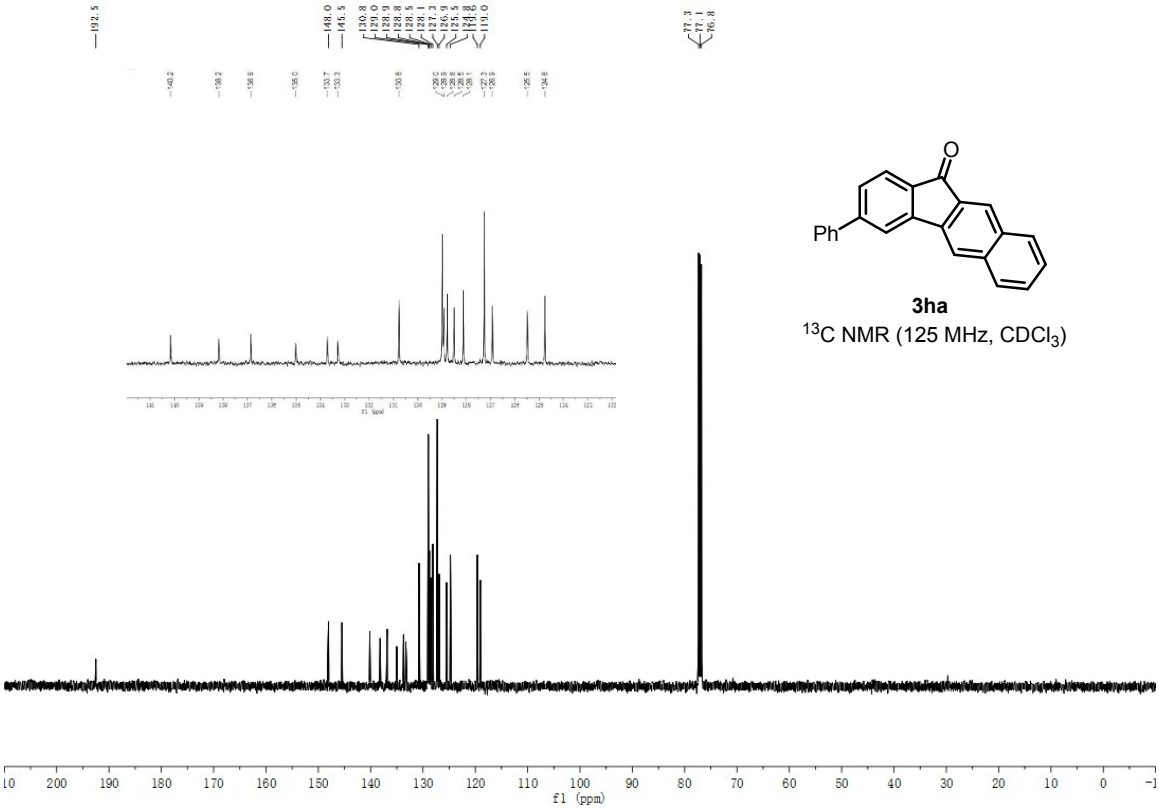


Fig. S19. ^{13}C NMR Spectrum of **3ha**

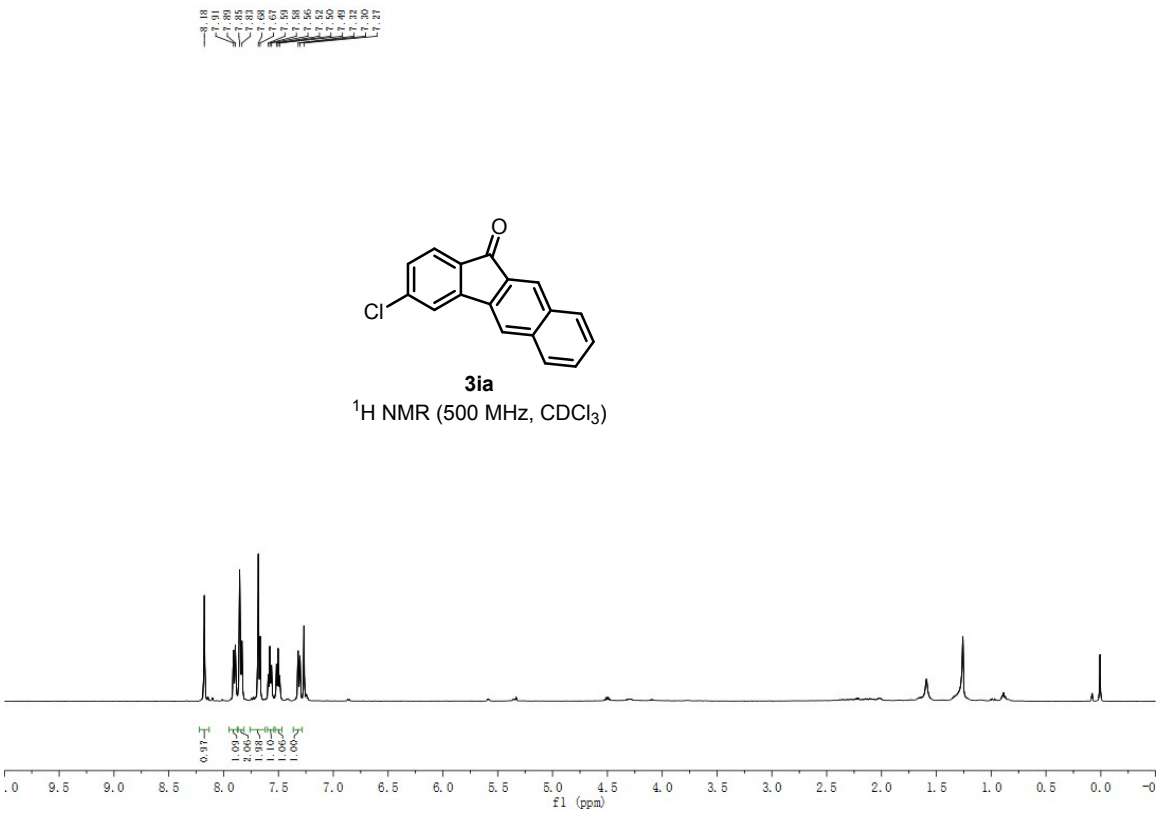


Fig. S20. ^{1}H NMR Spectrum of **3ia**

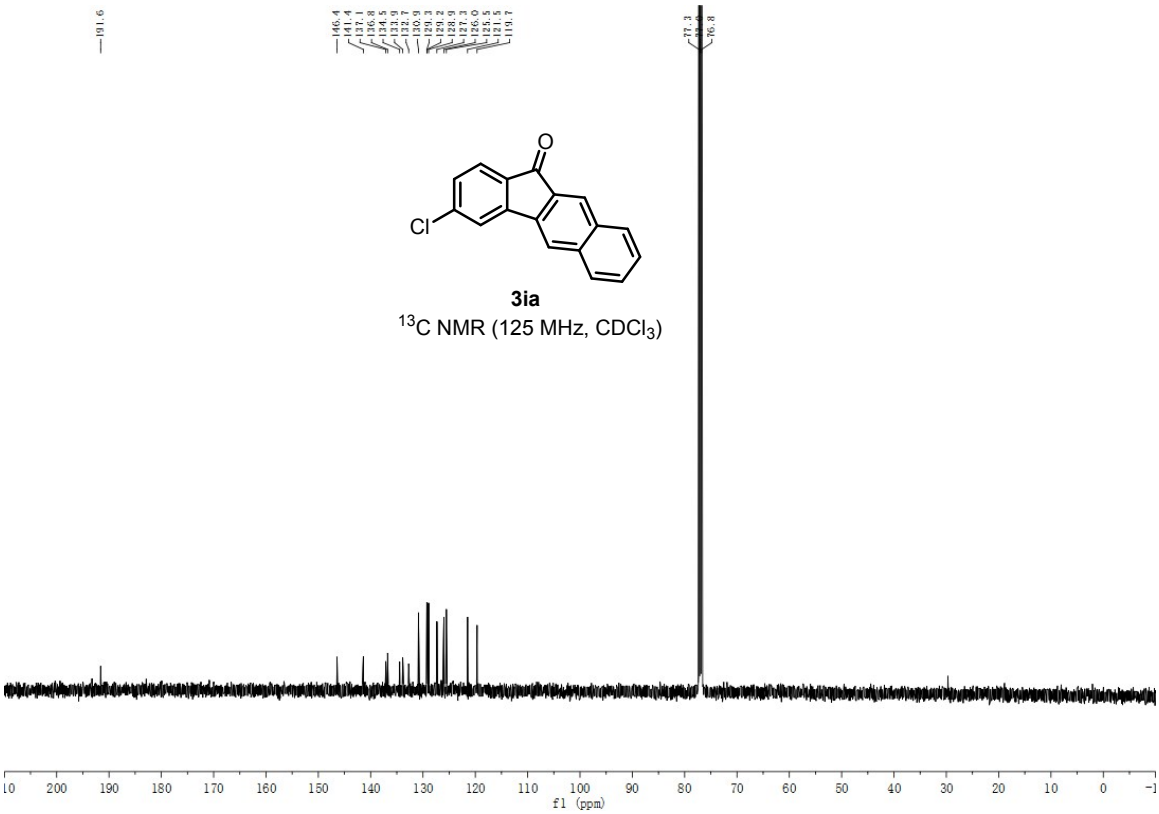
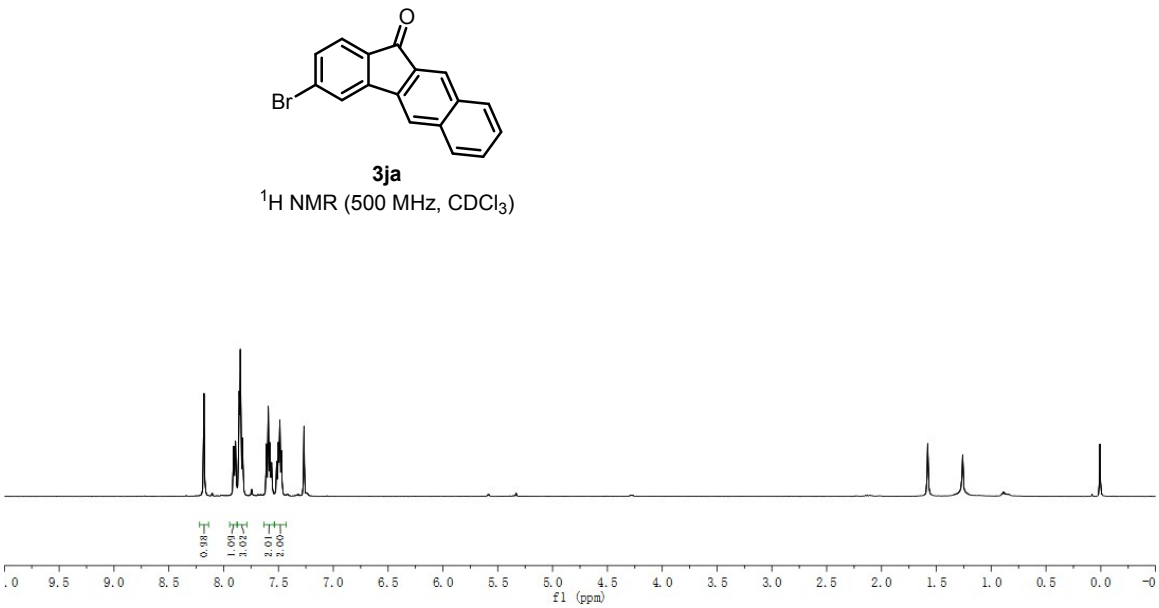


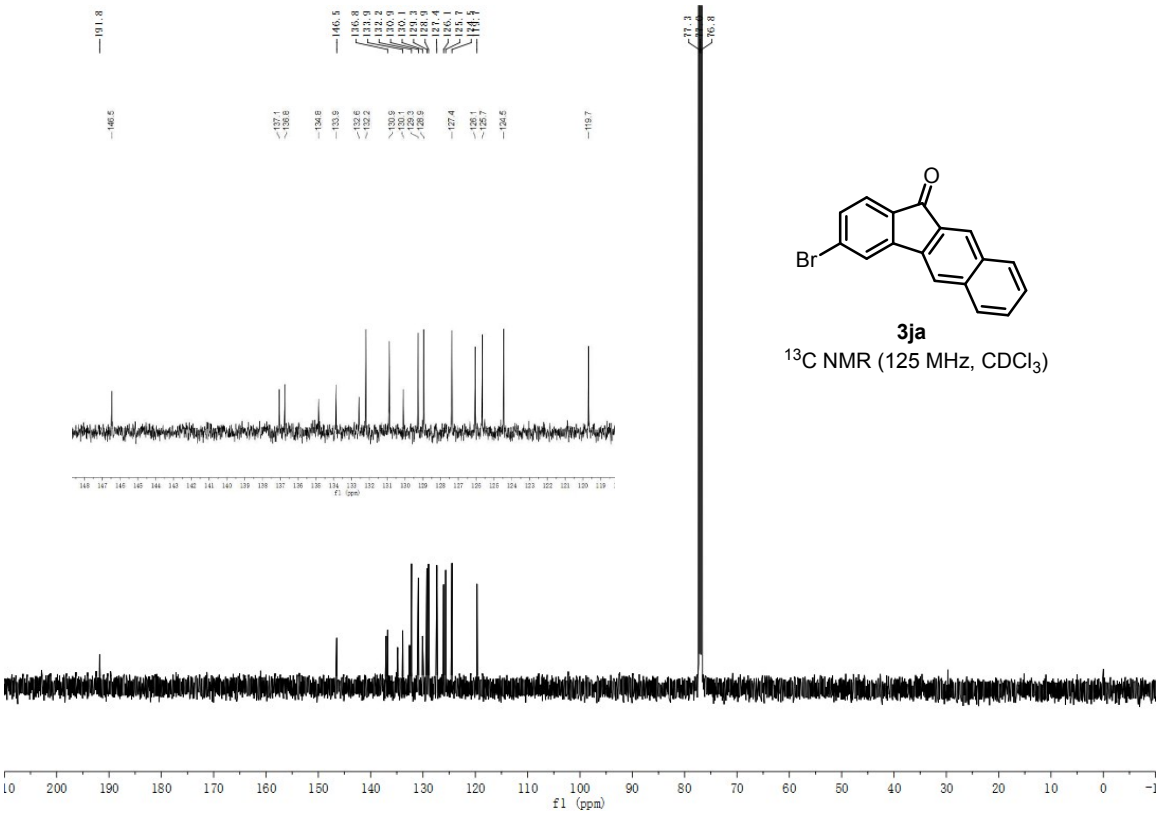
Fig. S21. ^{13}C NMR Spectrum of **3ia**



3ja

^{1}H NMR (500 MHz, $CDCl_3$)

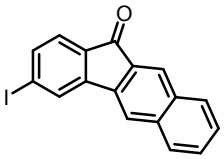
Fig. S22. ^{1}H NMR Spectrum of **3ja**



3ja

^{13}C NMR (125 MHz, $CDCl_3$)

Fig. S23. ^{13}C NMR Spectrum of **3ja**



3ka

^{1}H NMR (500 MHz, $CDCl_3$)

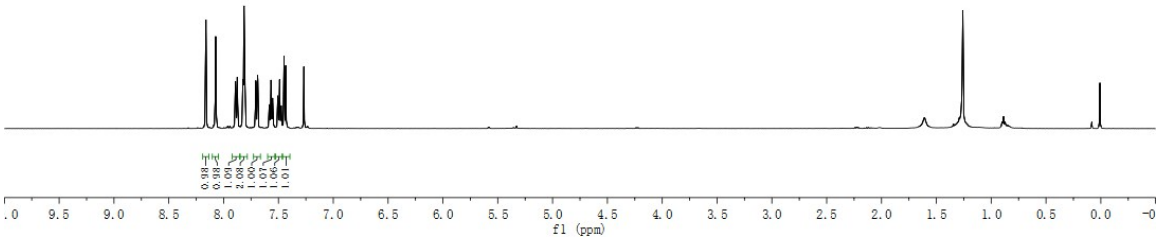
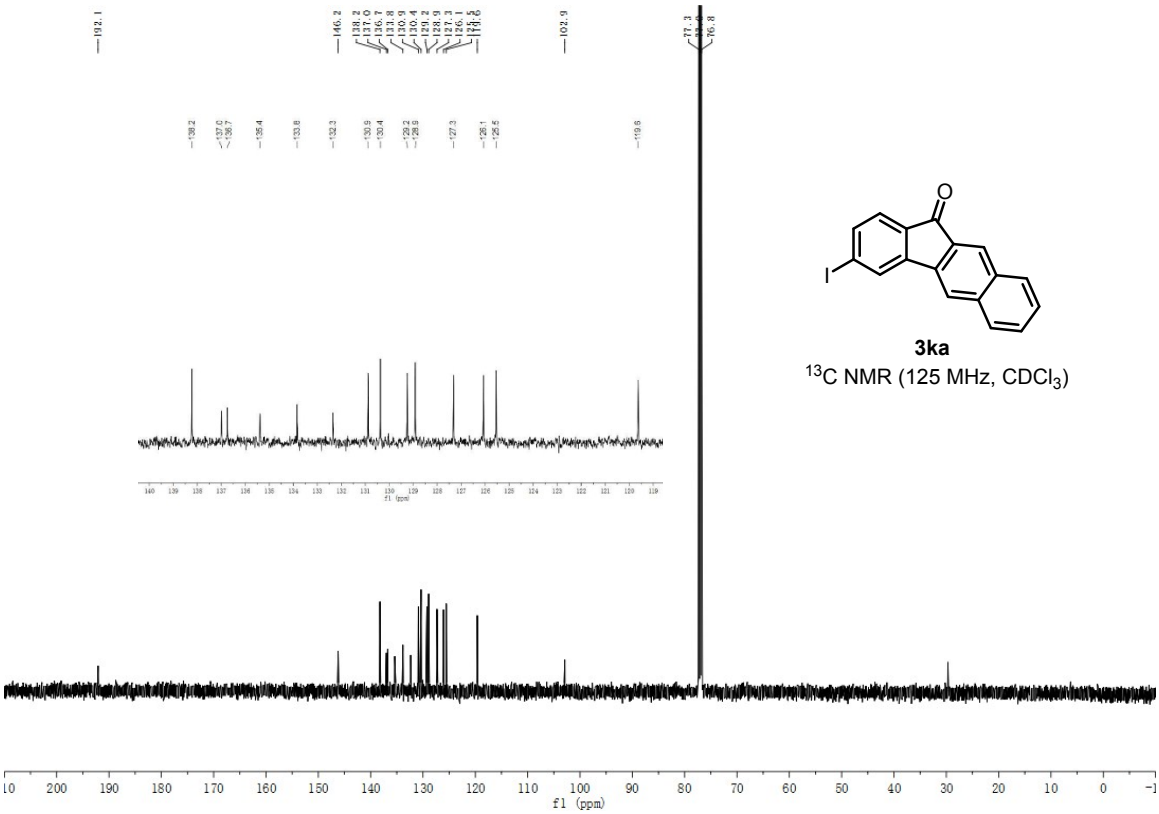


Fig. S24. ^{1}H NMR Spectrum of **3ka**



3ka

^{13}C NMR (125 MHz, $CDCl_3$)

Fig. S25. ^{13}C NMR Spectrum of **3ka**

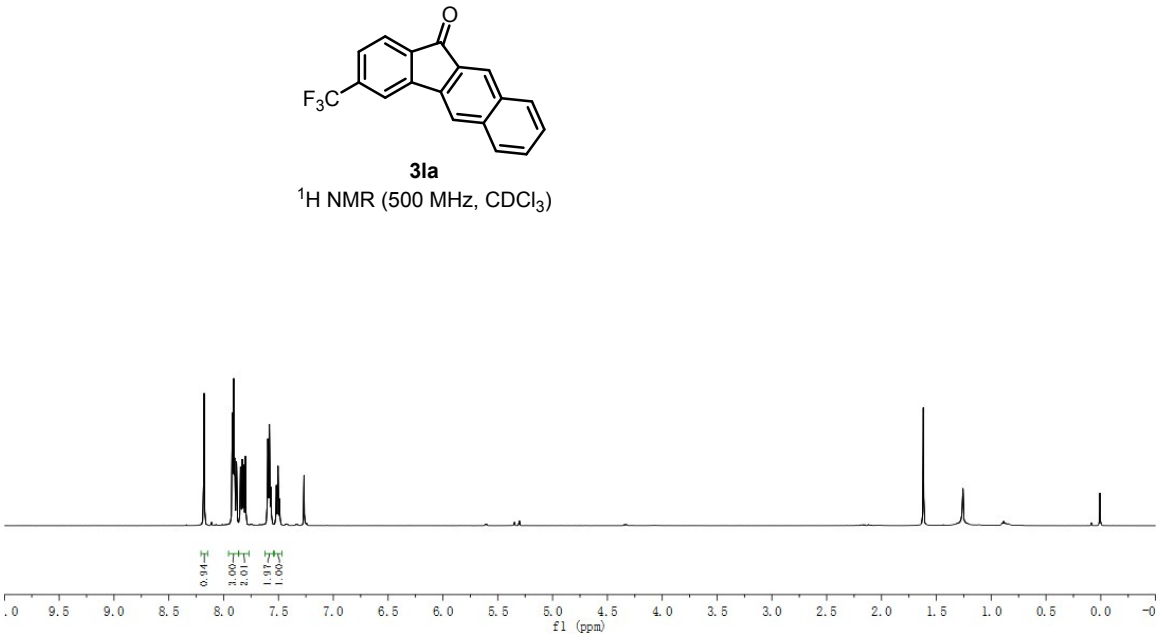


Fig. S26. ^{1}H NMR Spectrum of **3la**

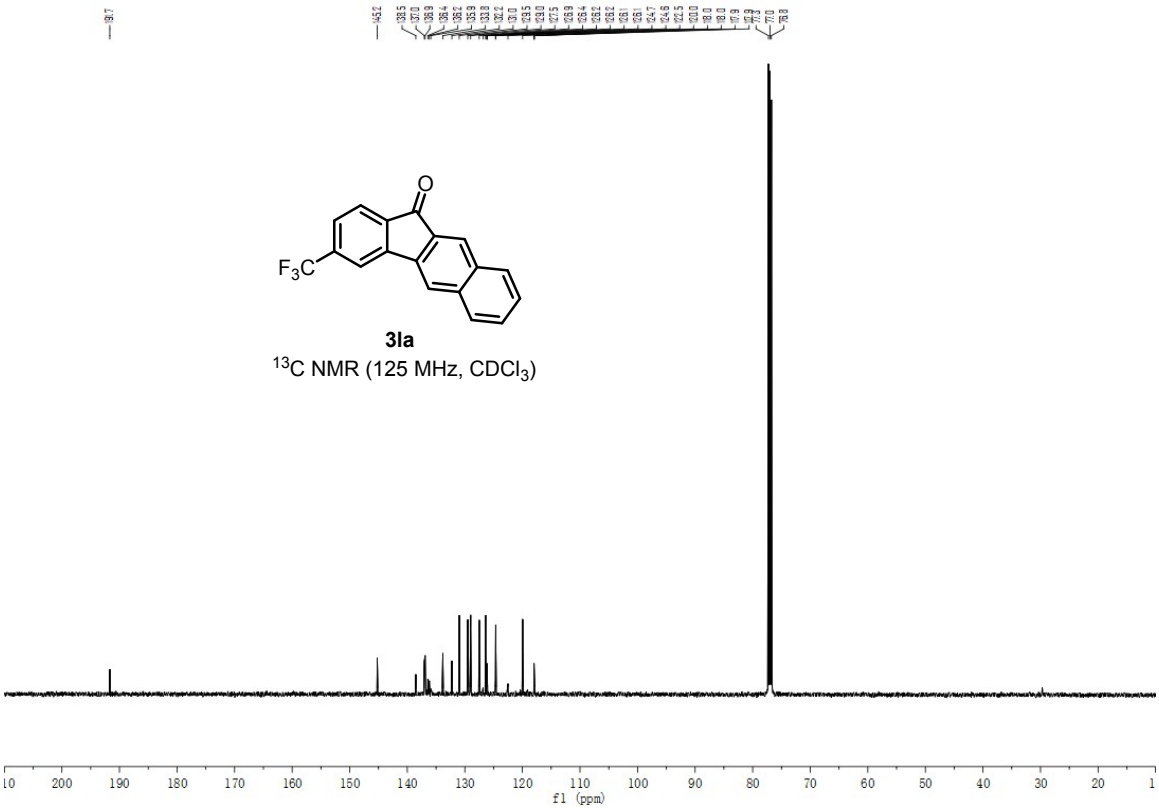


Fig. S27. ^{13}C NMR Spectrum of **3la**

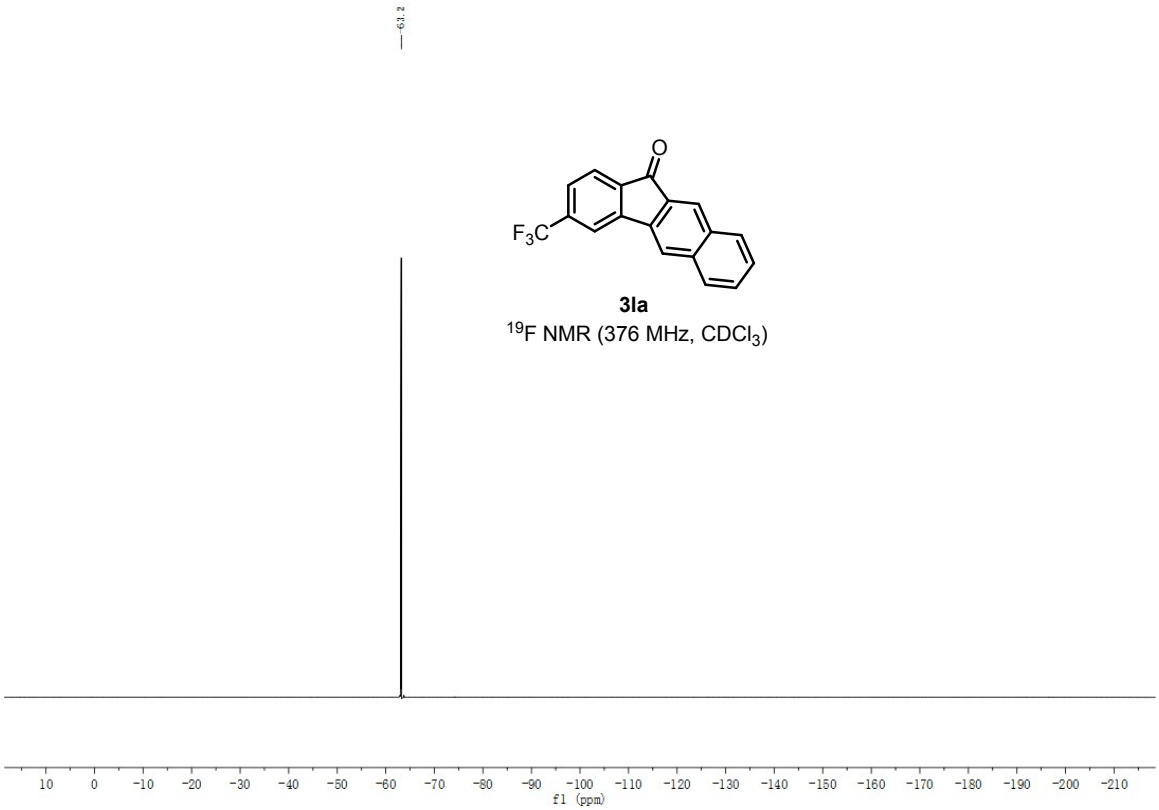


Fig. S28. ^{19}F NMR Spectrum of **3la**

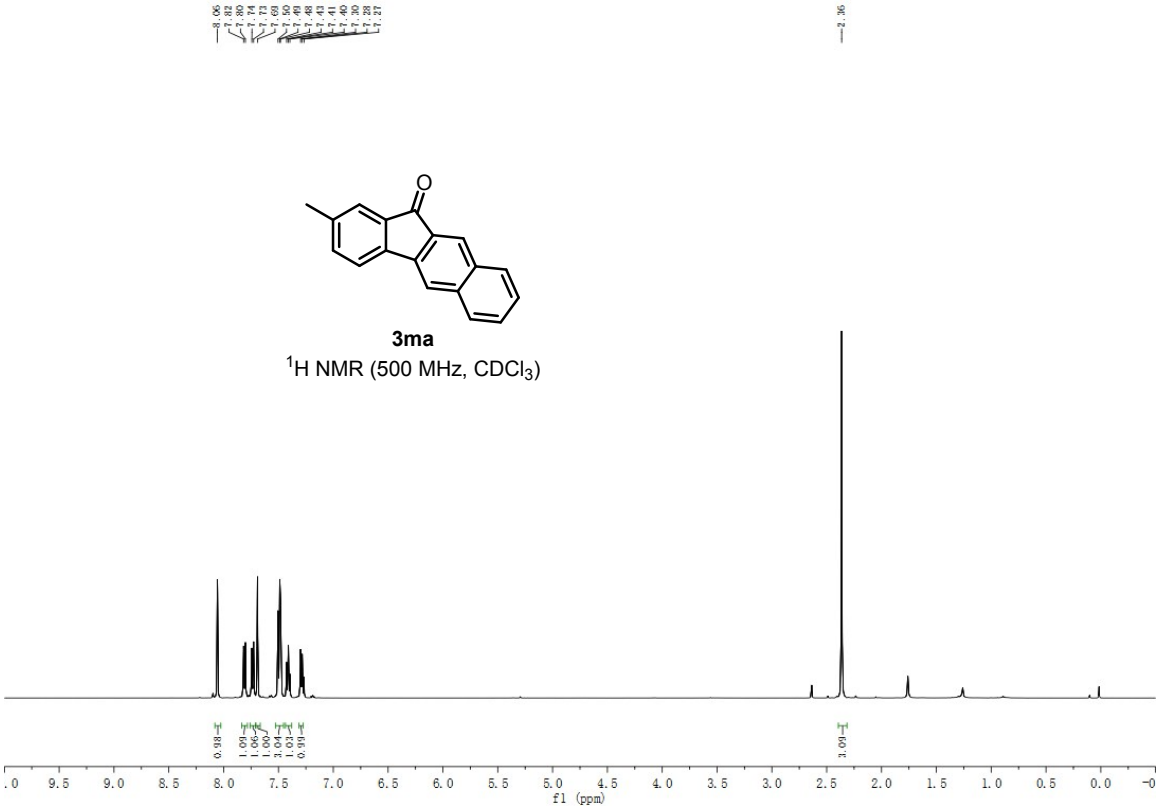


Fig. S29. ^{1}H NMR Spectrum of **3ma**

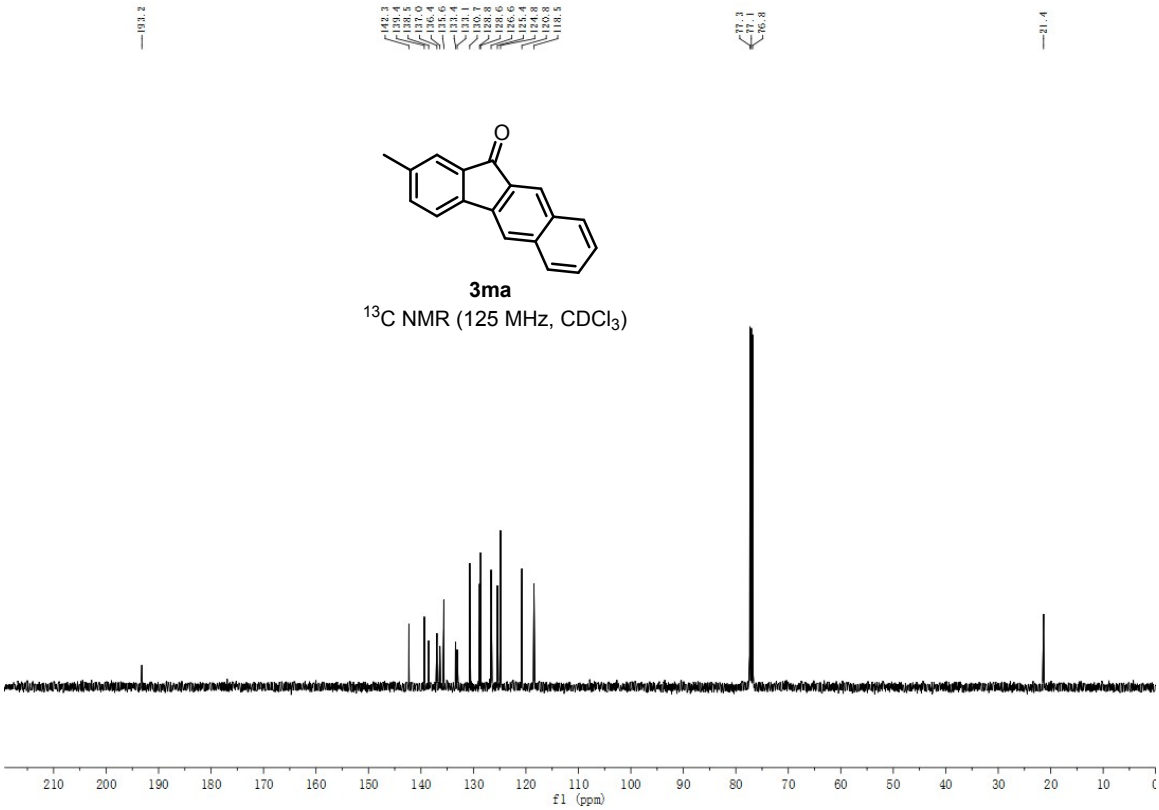


Fig. S30. ^{13}C NMR Spectrum of **3ma**

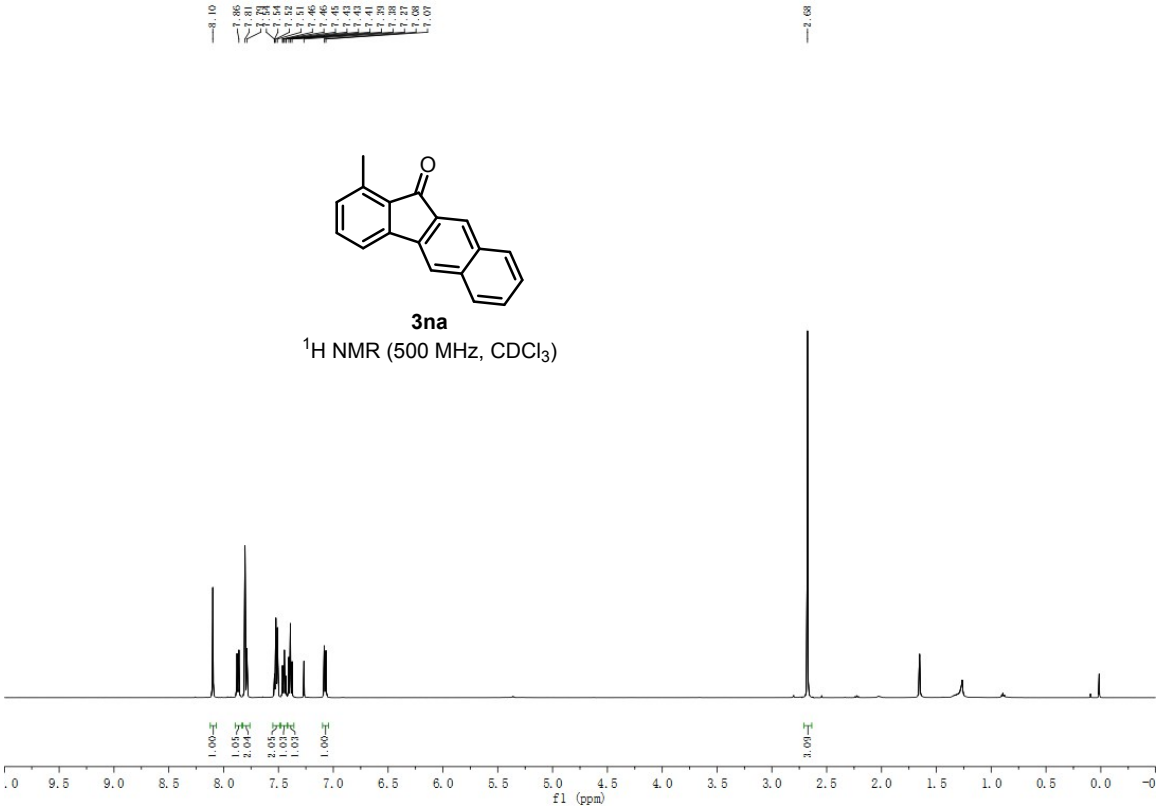


Fig. S31. ^{1}H NMR Spectrum of **3na**

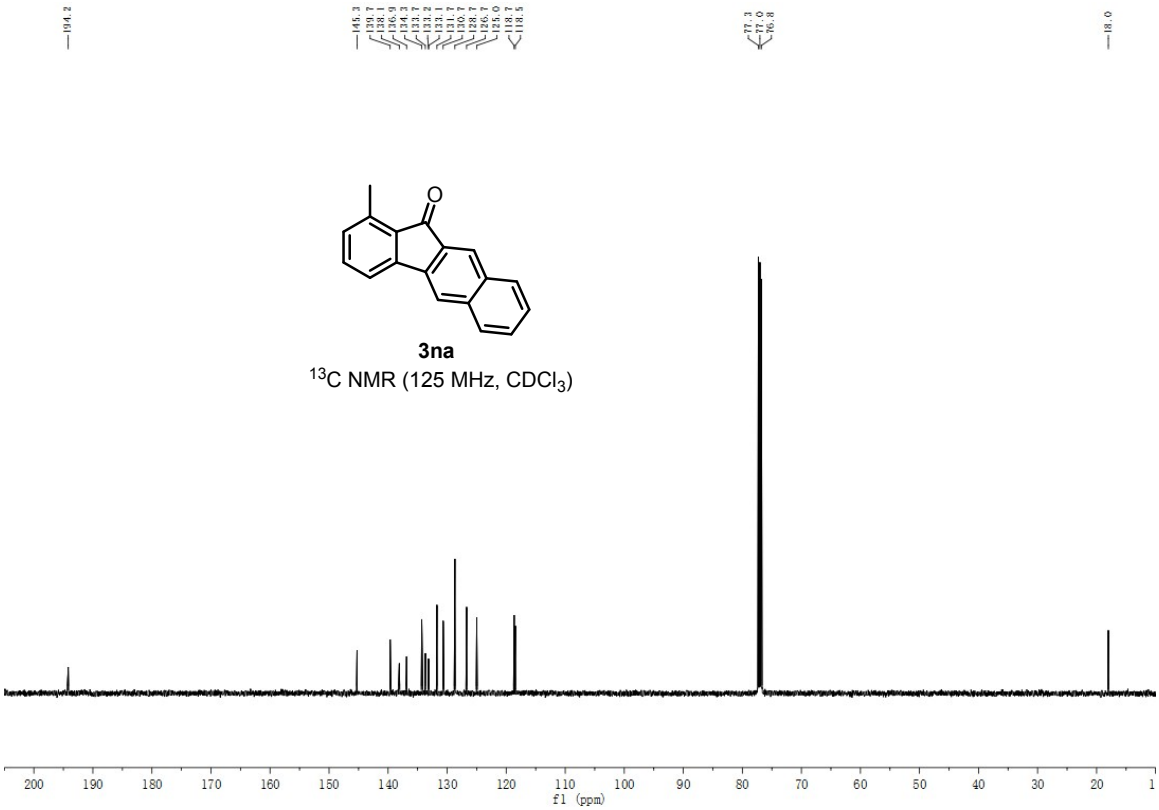


Fig. S32. ^{13}C NMR Spectrum of **3na**

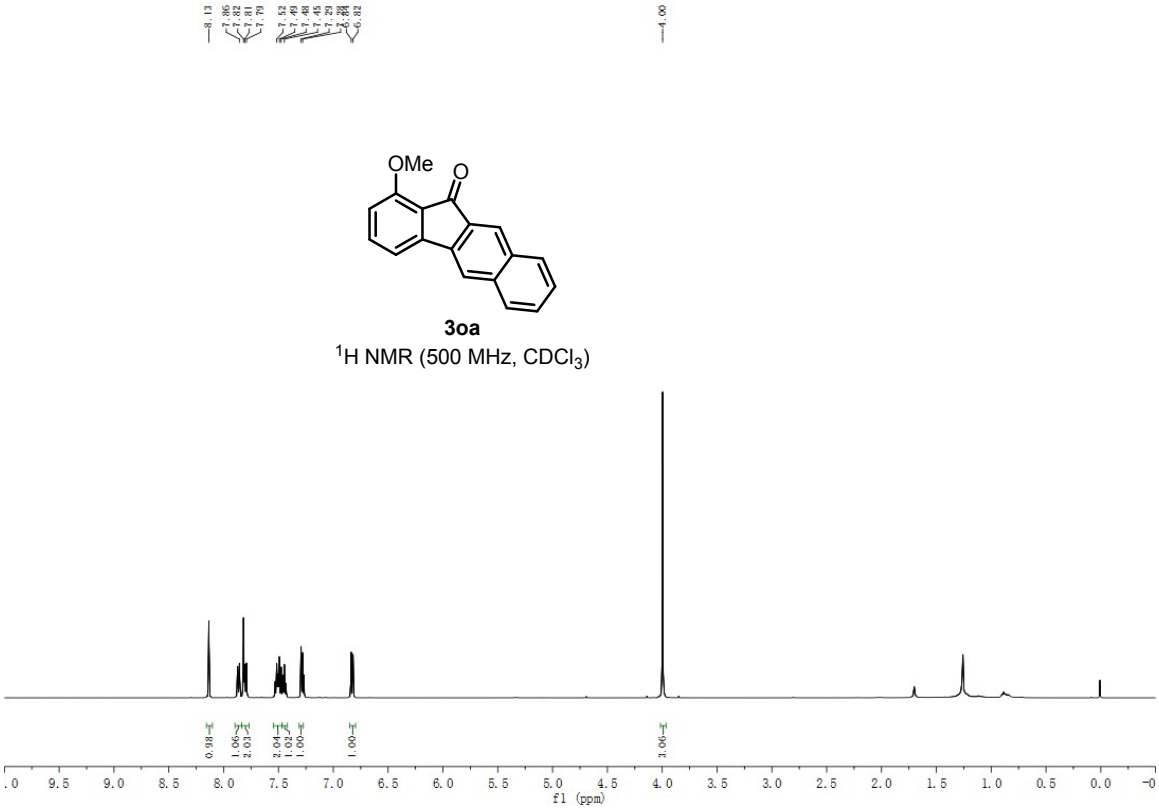
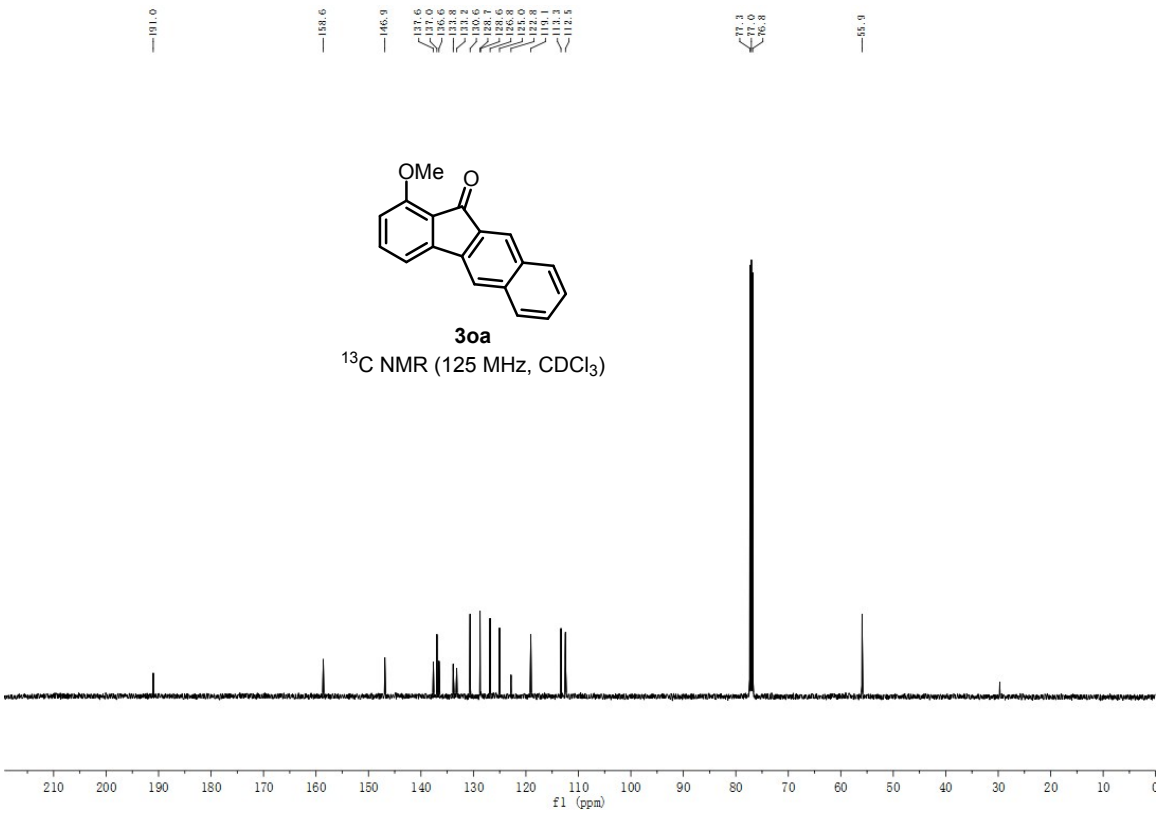


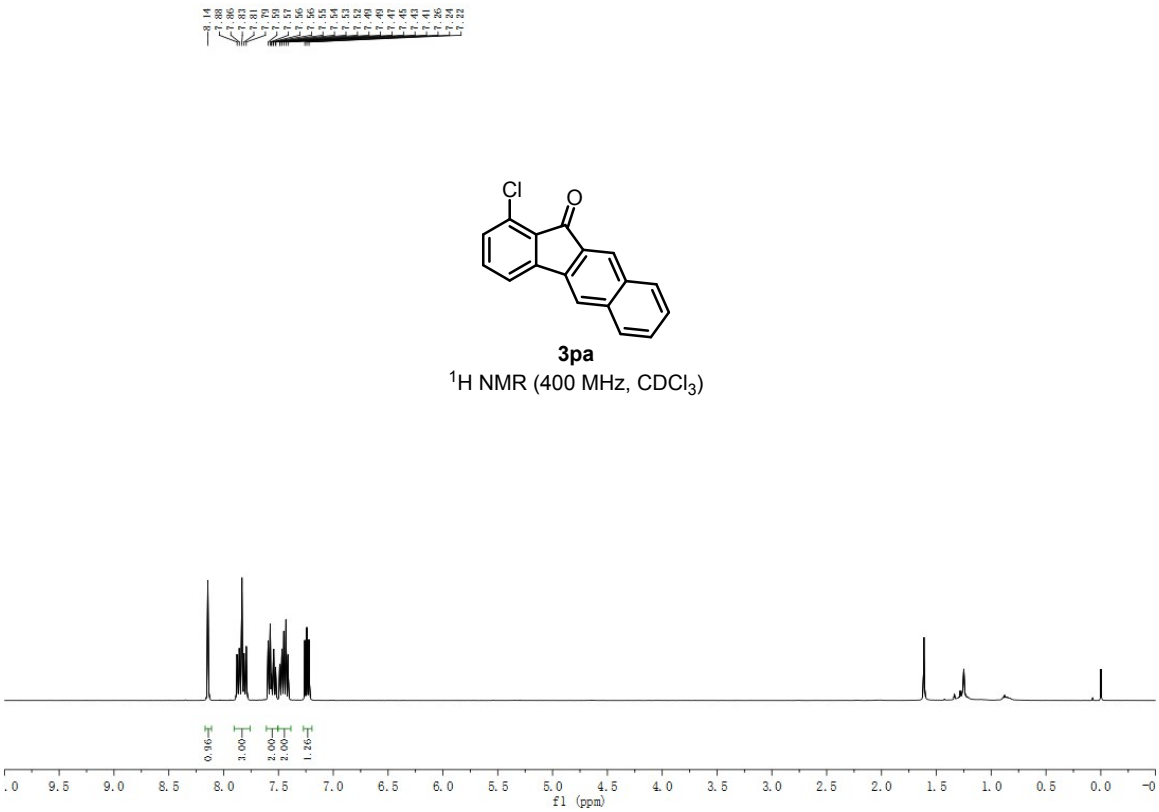
Fig. S33. ^{1}H NMR Spectrum of **3oa**



3oa

^{13}C NMR (125 MHz, $CDCl_3$)

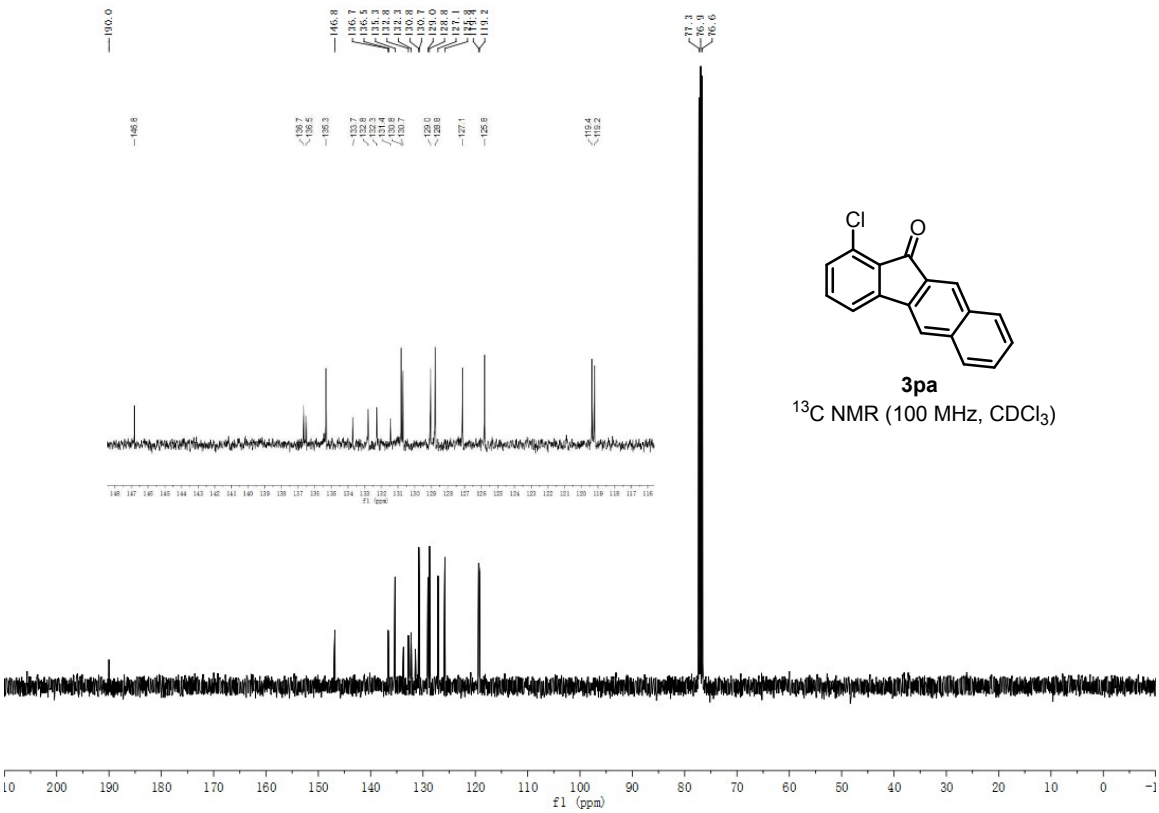
Fig. S34. ^{13}C NMR Spectrum of **3oa**



3pa

^{1}H NMR (400 MHz, $CDCl_3$)

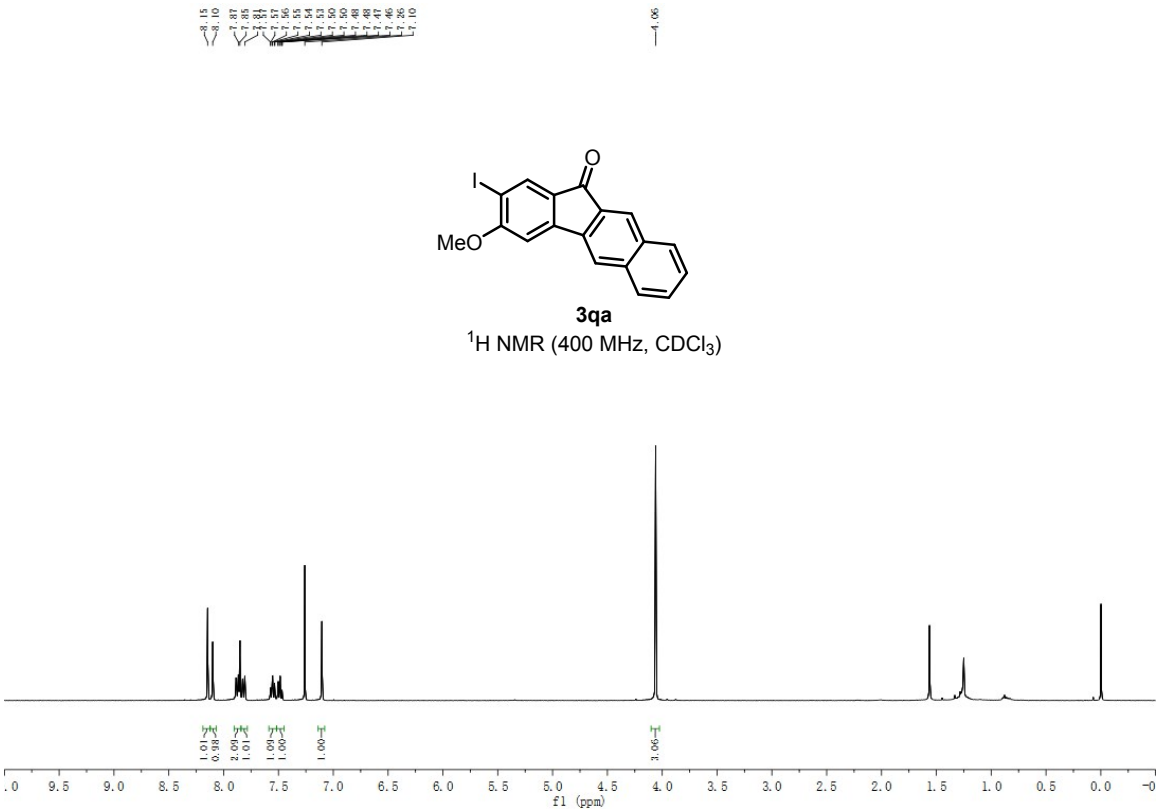
Fig. S35. ^{1}H NMR Spectrum of **3pa**



3pa

^{13}C NMR (100 MHz, $CDCl_3$)

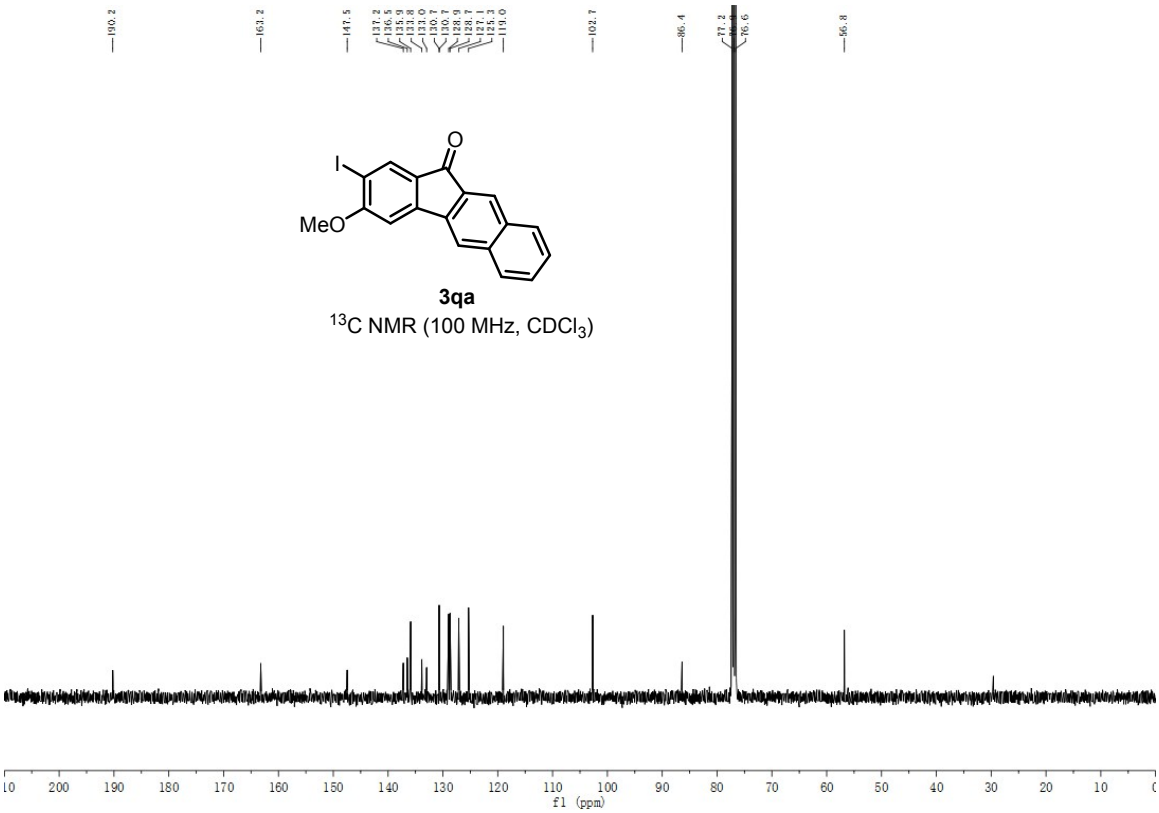
Fig. S36. ^{13}C NMR Spectrum of **3pa**



3qa

^{1}H NMR (400 MHz, $CDCl_3$)

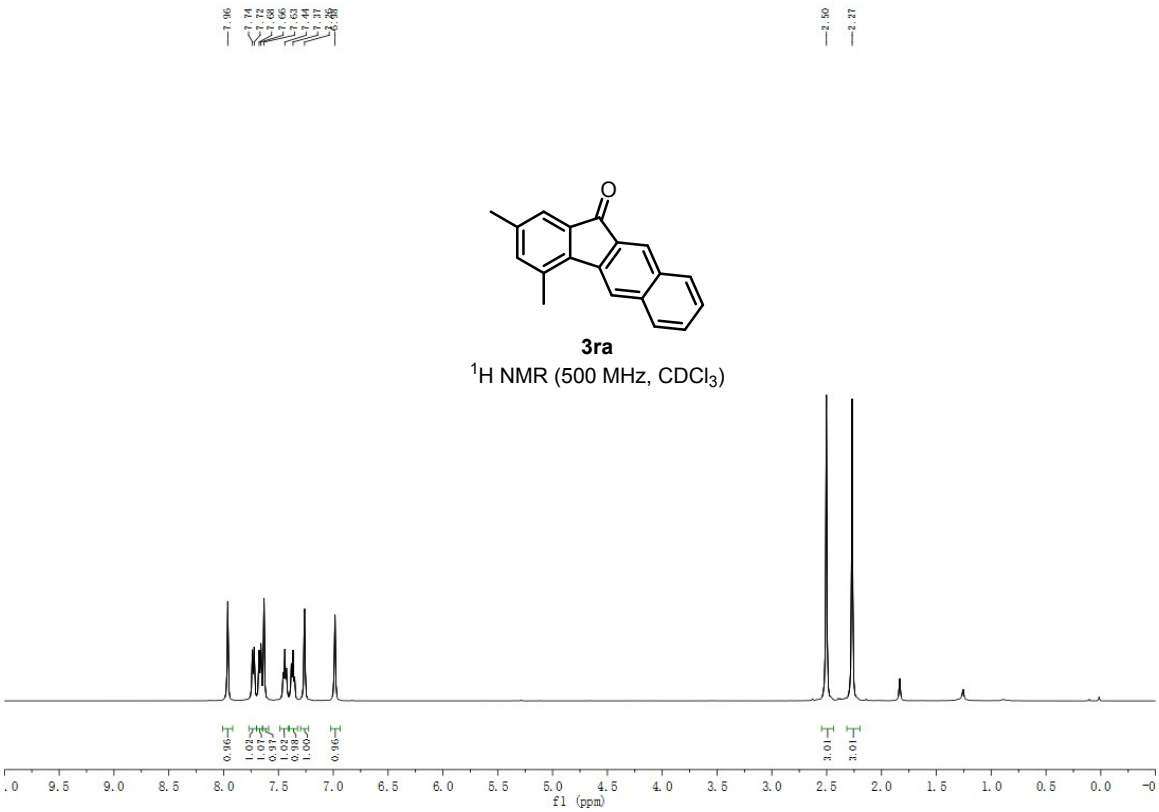
Fig. S37. ^{1}H NMR Spectrum of **3qa**



3qa

^{13}C NMR (100 MHz, $CDCl_3$)

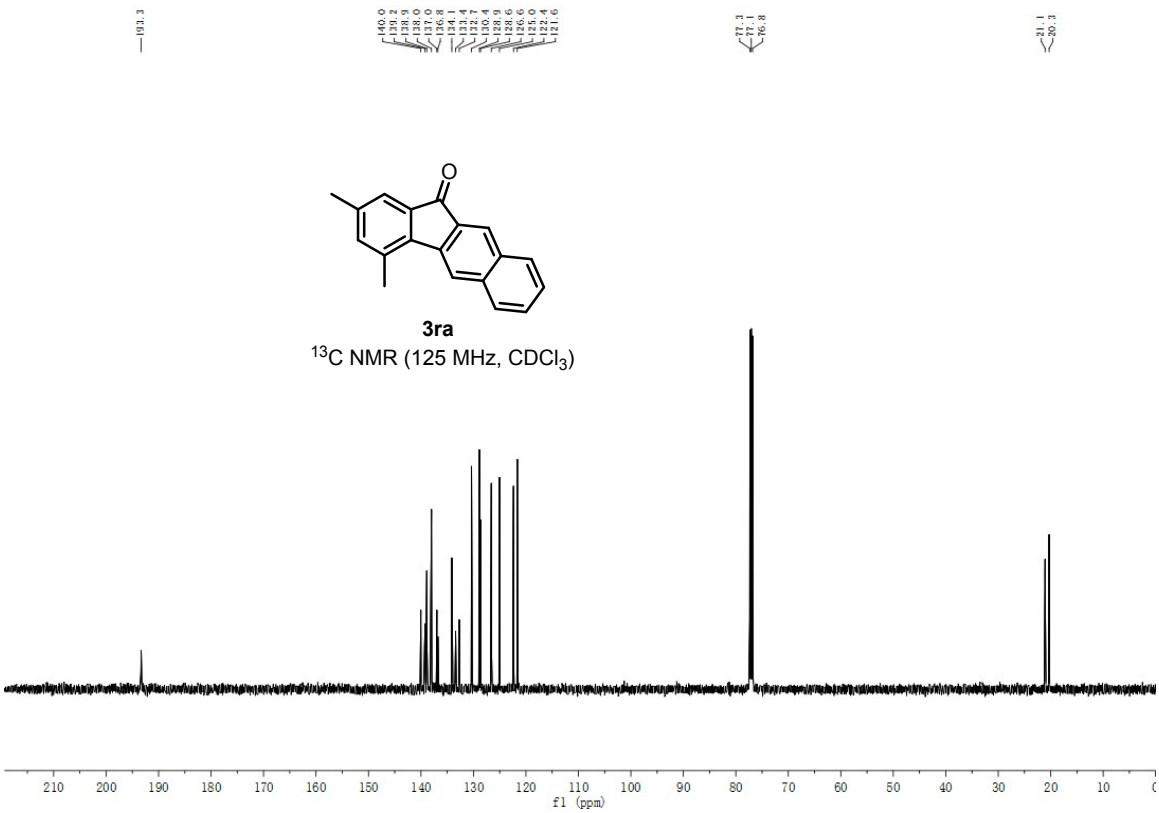
Fig. S38. ^{13}C NMR Spectrum of **3qa**



3ra

^{1}H NMR (500 MHz, $CDCl_3$)

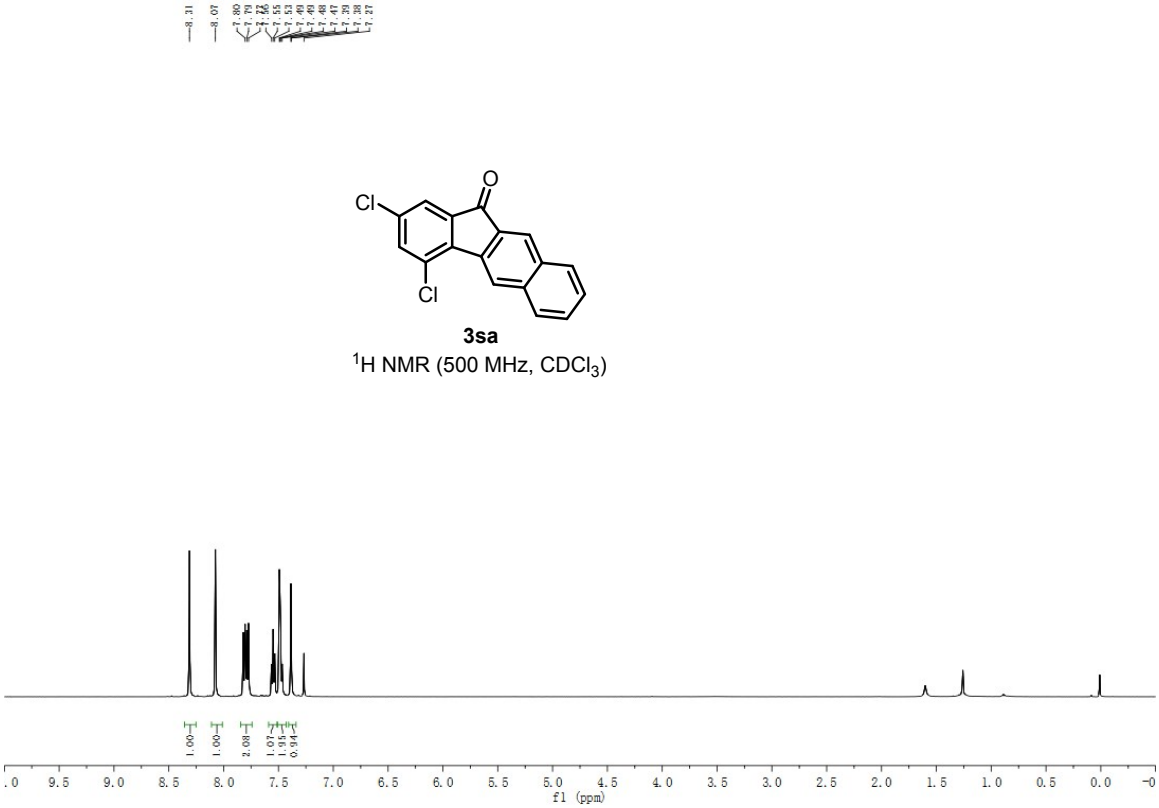
Fig. S39. ^{1}H NMR Spectrum of **3ra**



3ra

^{13}C NMR (125 MHz, $CDCl_3$)

Fig. S40. ^{13}C NMR Spectrum of **3ra**



3sa

^{1}H NMR (500 MHz, $CDCl_3$)

Fig. S41. ^{1}H NMR Spectrum of **3sa**

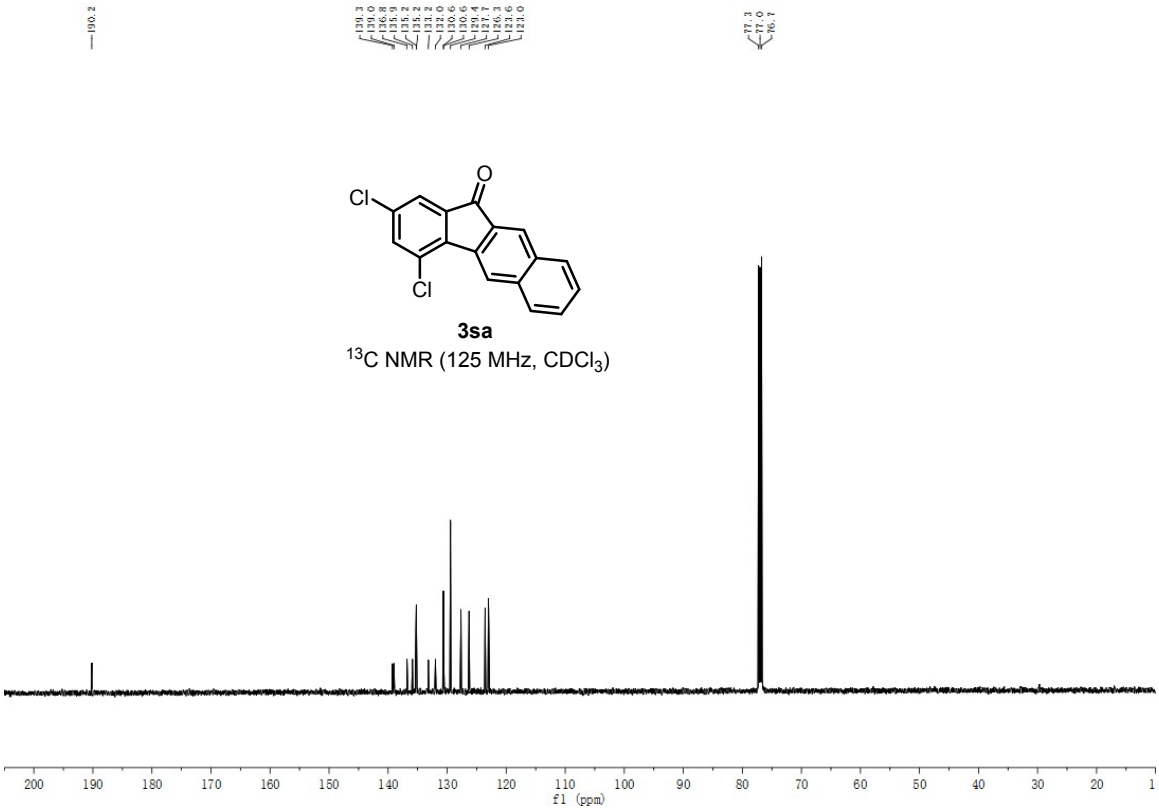


Fig. S42. ^{13}C NMR Spectrum of **3sa**

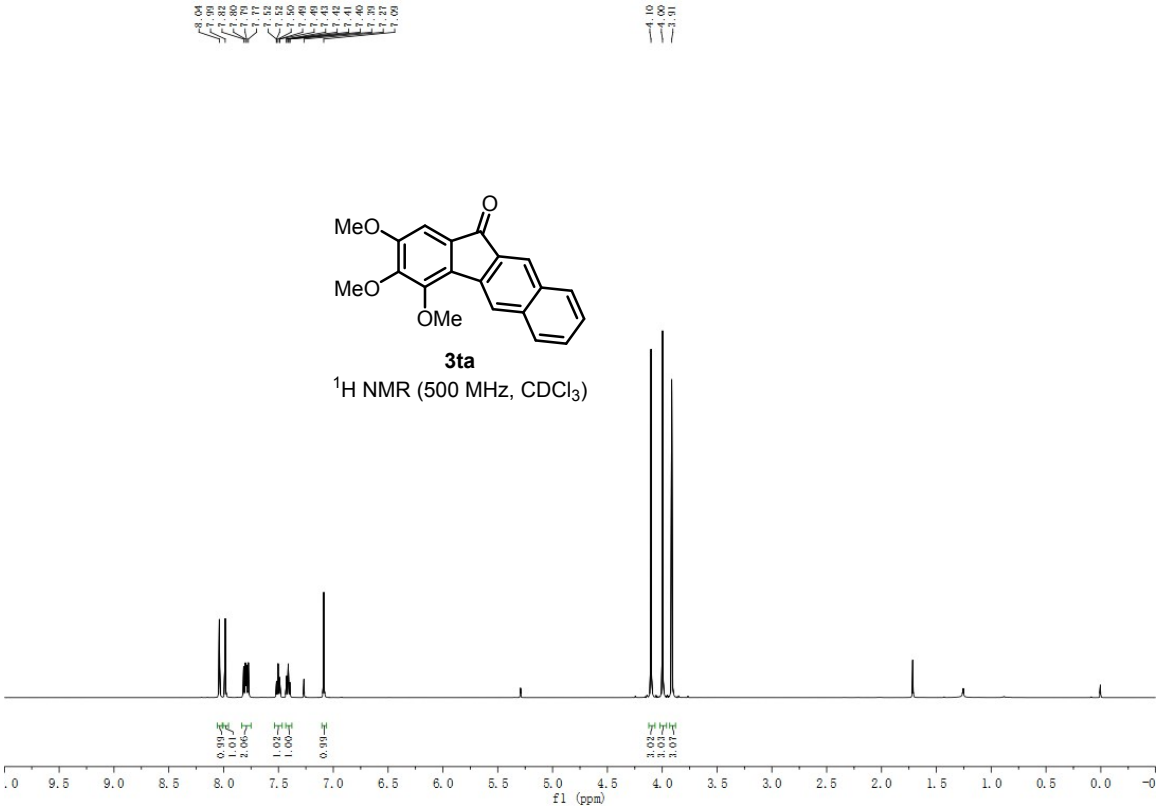
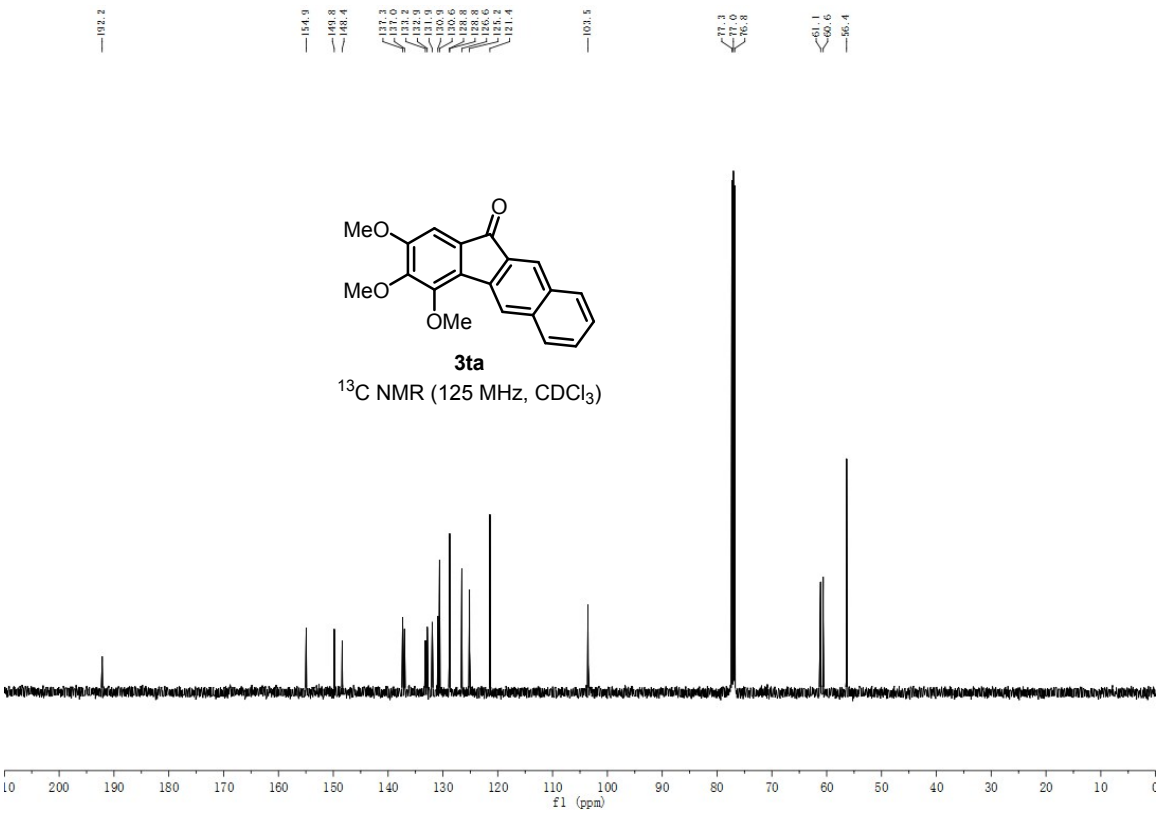


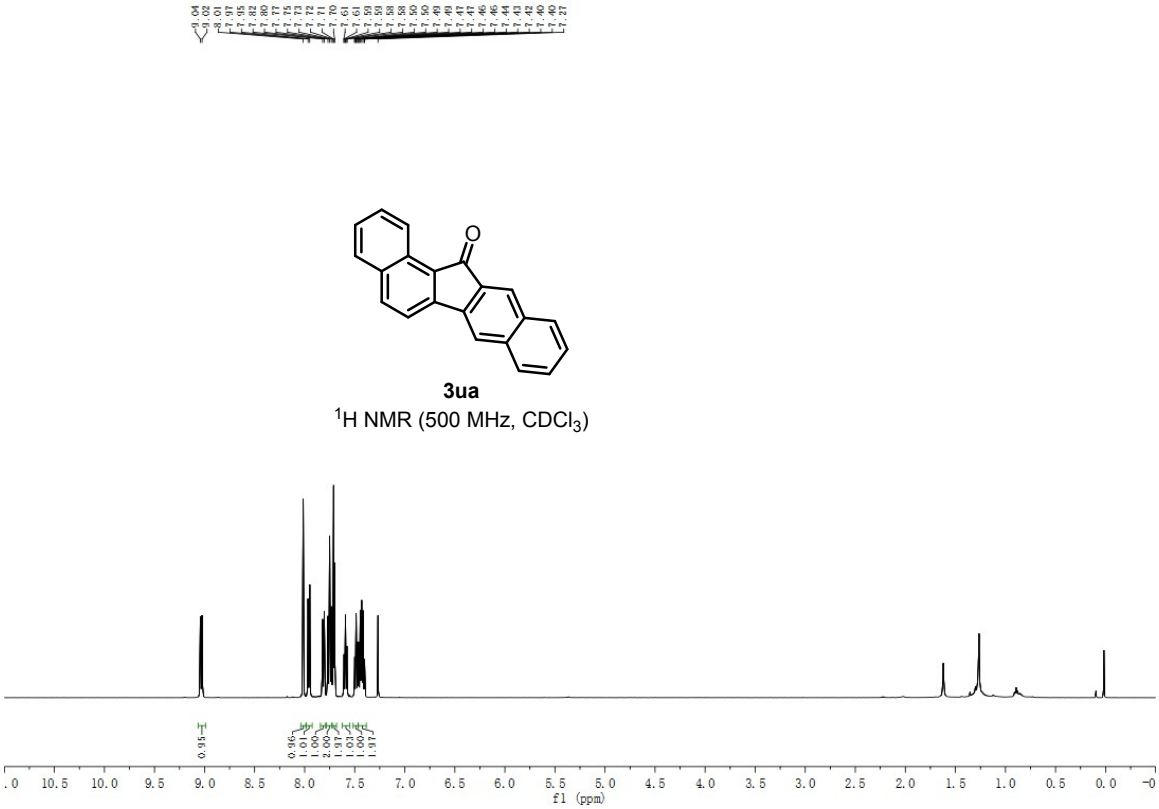
Fig. S43. ^{1}H NMR Spectrum of **3ta**



3ta

^{13}C NMR (125 MHz, $CDCl_3$)

Fig. S44. ^{13}C NMR Spectrum of **3ta**



3ua

^{1}H NMR (500 MHz, $CDCl_3$)

Fig. S45. ^{1}H NMR Spectrum of **3ua**

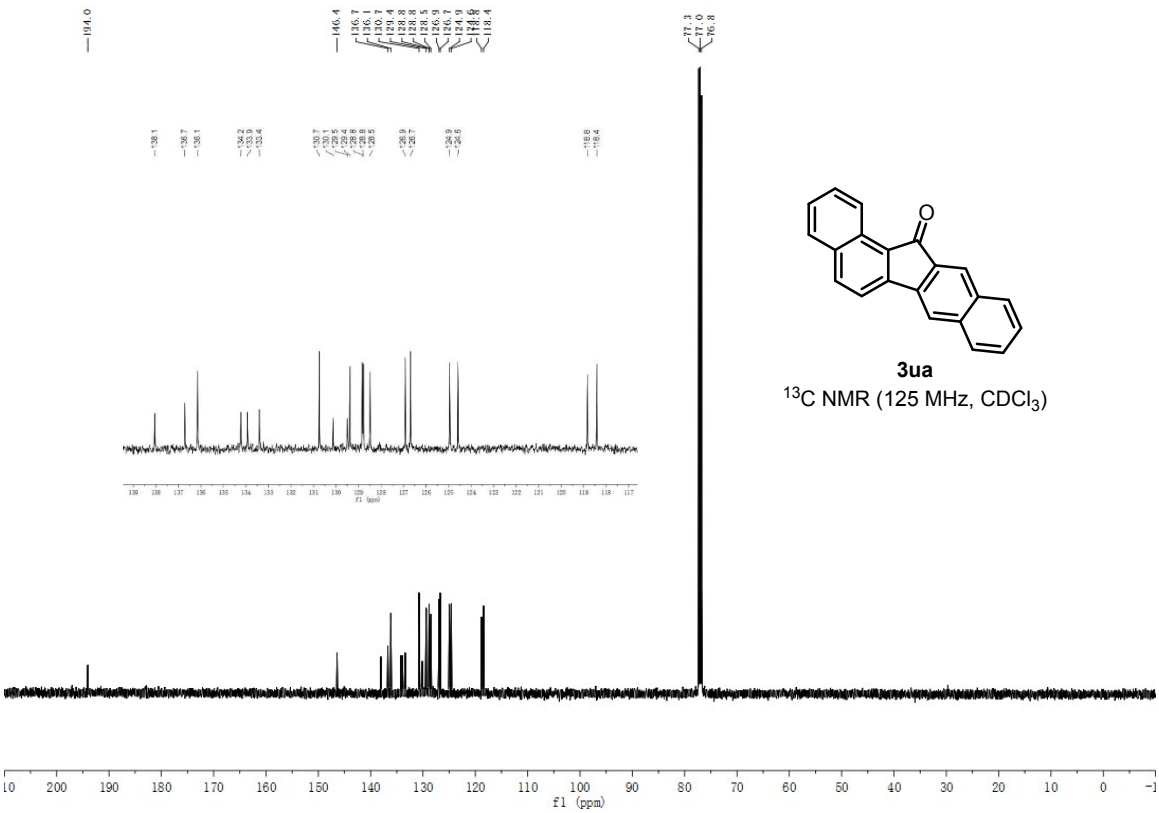


Fig. S46. ^{13}C NMR Spectrum of **3ua**

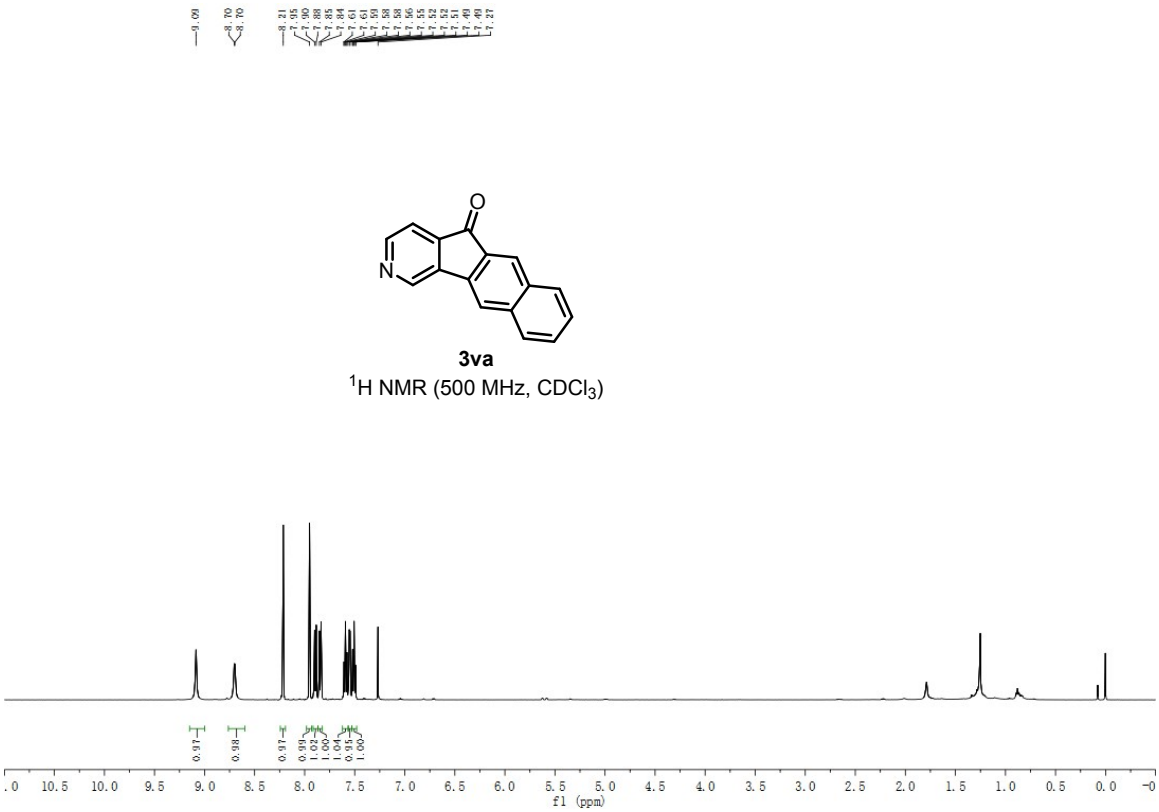
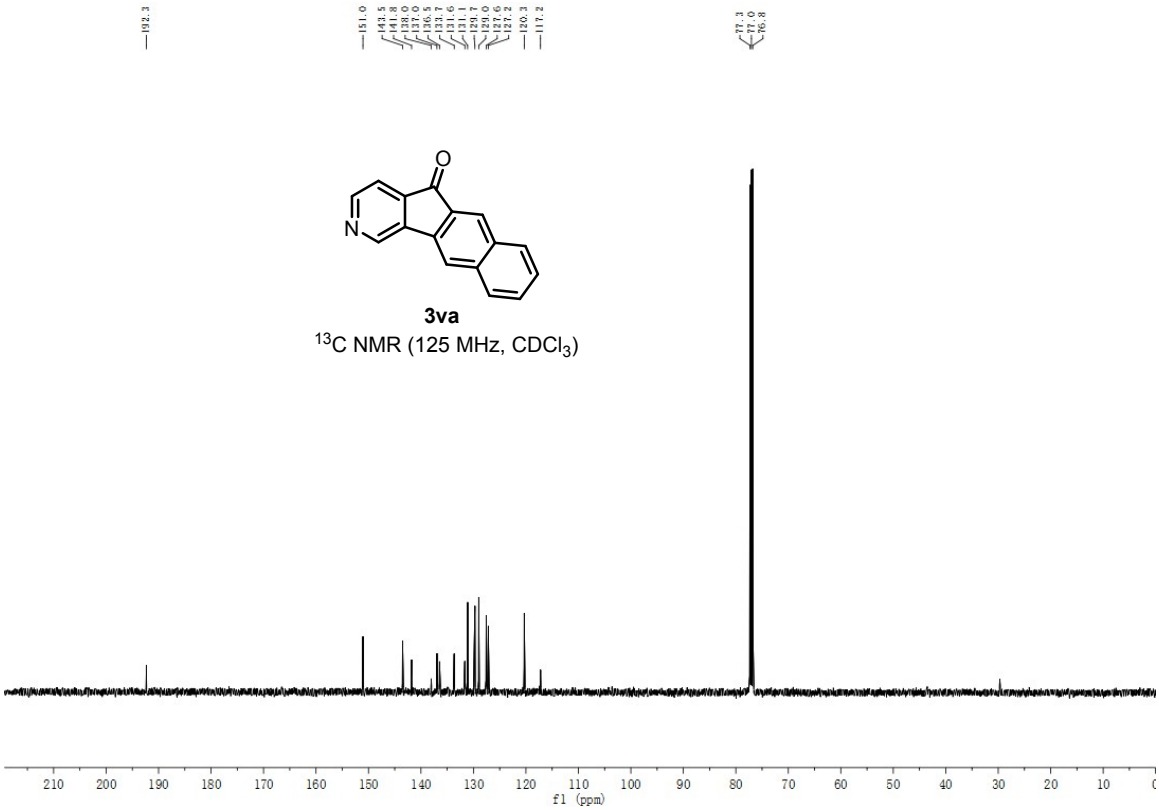


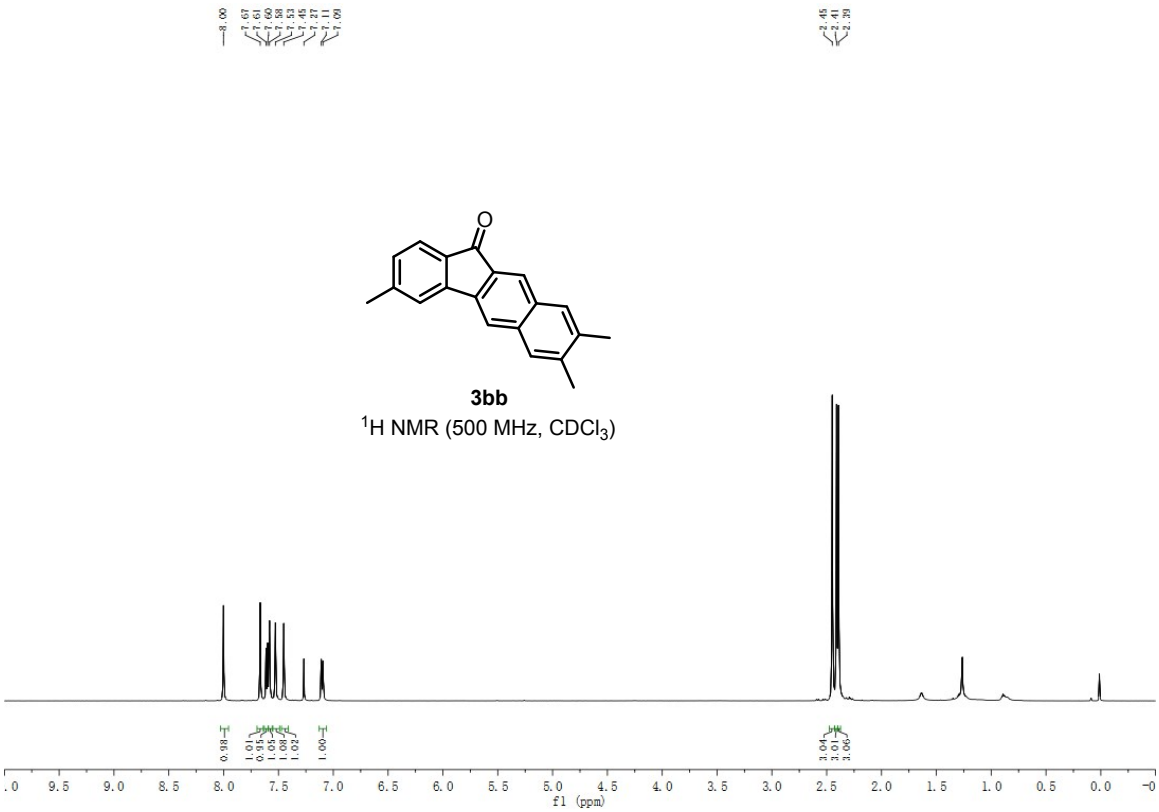
Fig. S47. ^{1}H NMR Spectrum of **3va**



3va

^{13}C NMR (125 MHz, $CDCl_3$)

Fig. S48. ^{13}C NMR Spectrum of **3va**



3bb

^{1}H NMR (500 MHz, $CDCl_3$)

Fig. S49. ^{1}H NMR Spectrum of **3bb**

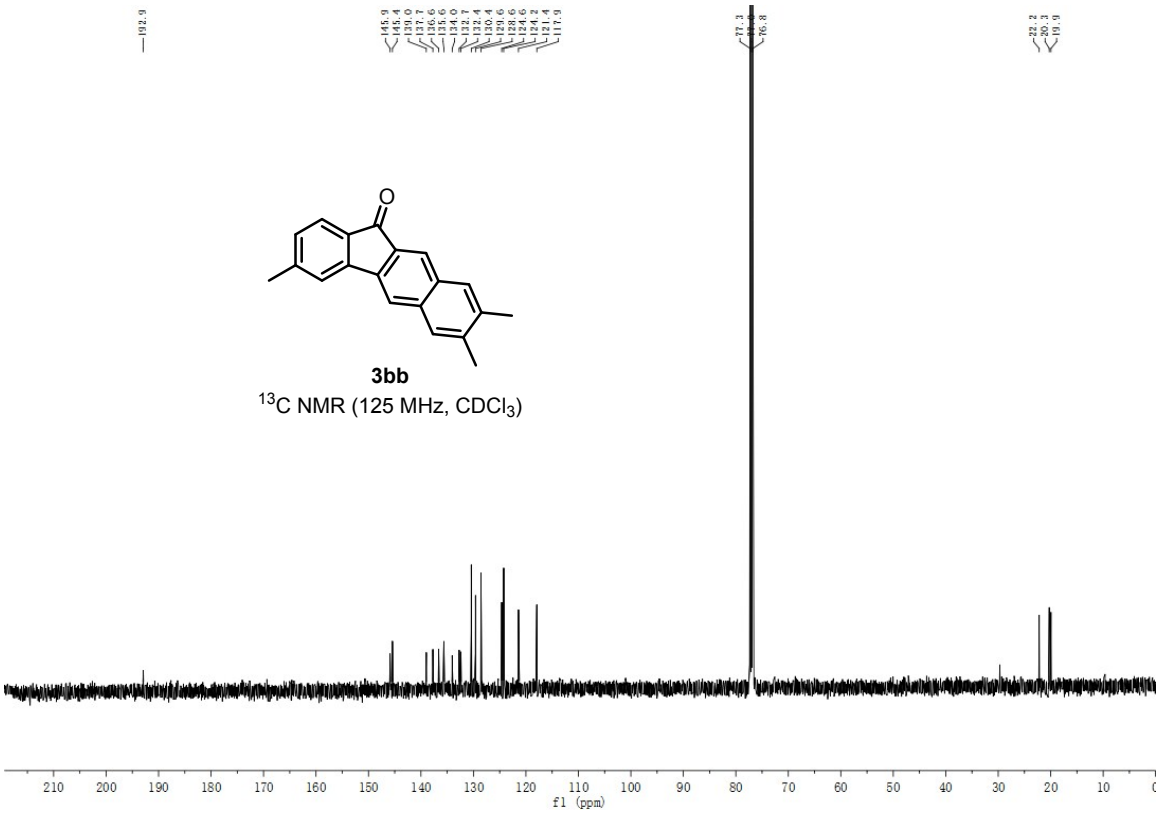


Fig. S50. ^{13}C NMR Spectrum of **3bb**

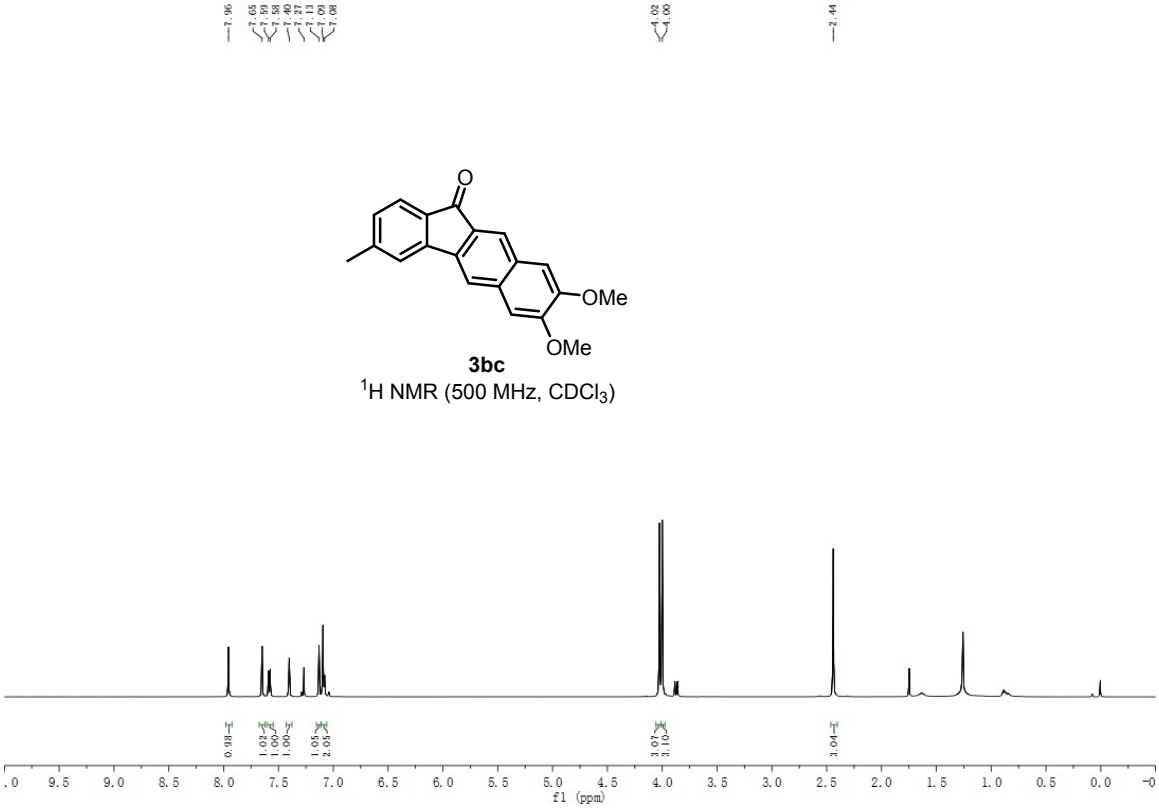


Fig. S51. ^{1}H NMR Spectrum of **3bc**

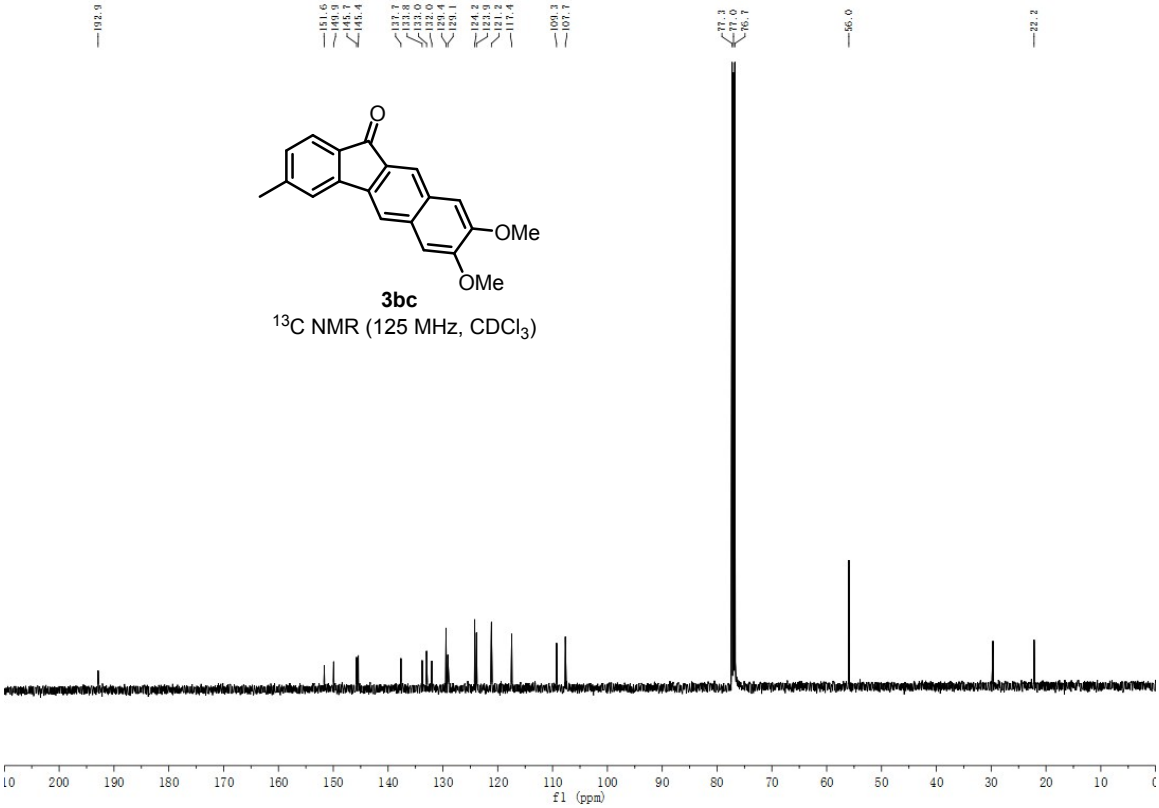


Fig. S52. ^{13}C NMR Spectrum of **3bc**

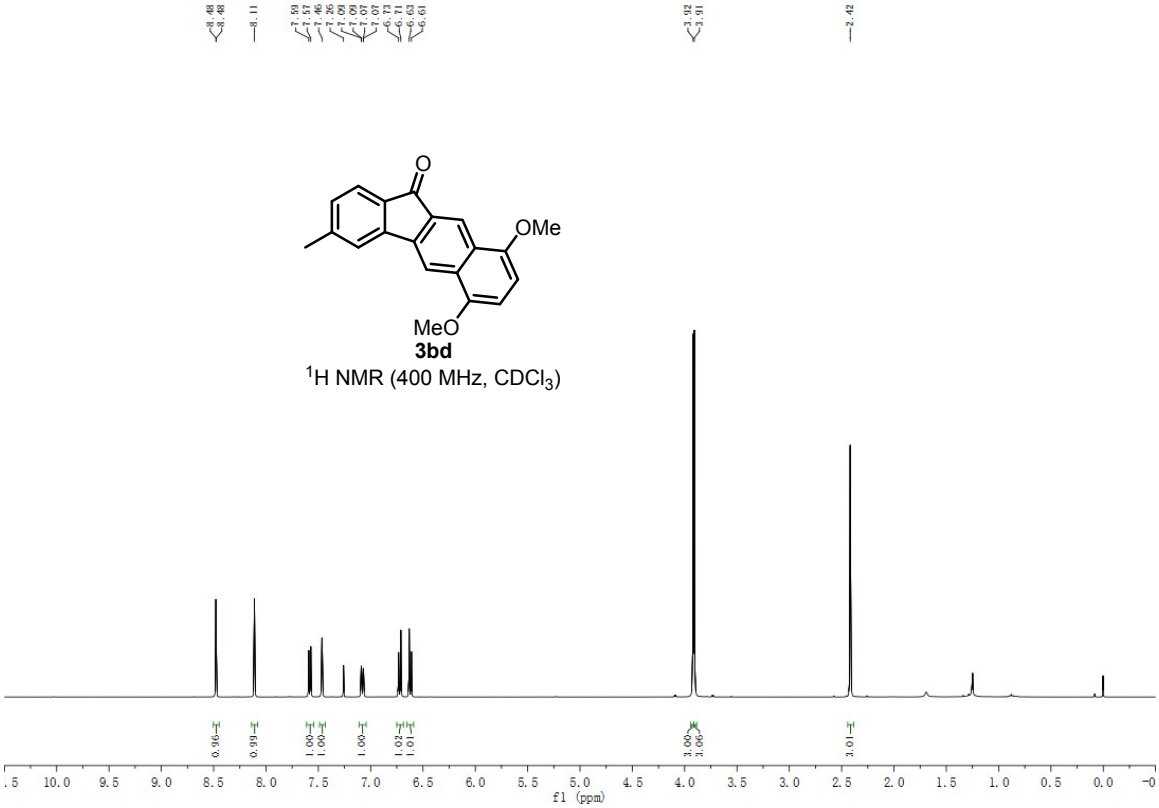
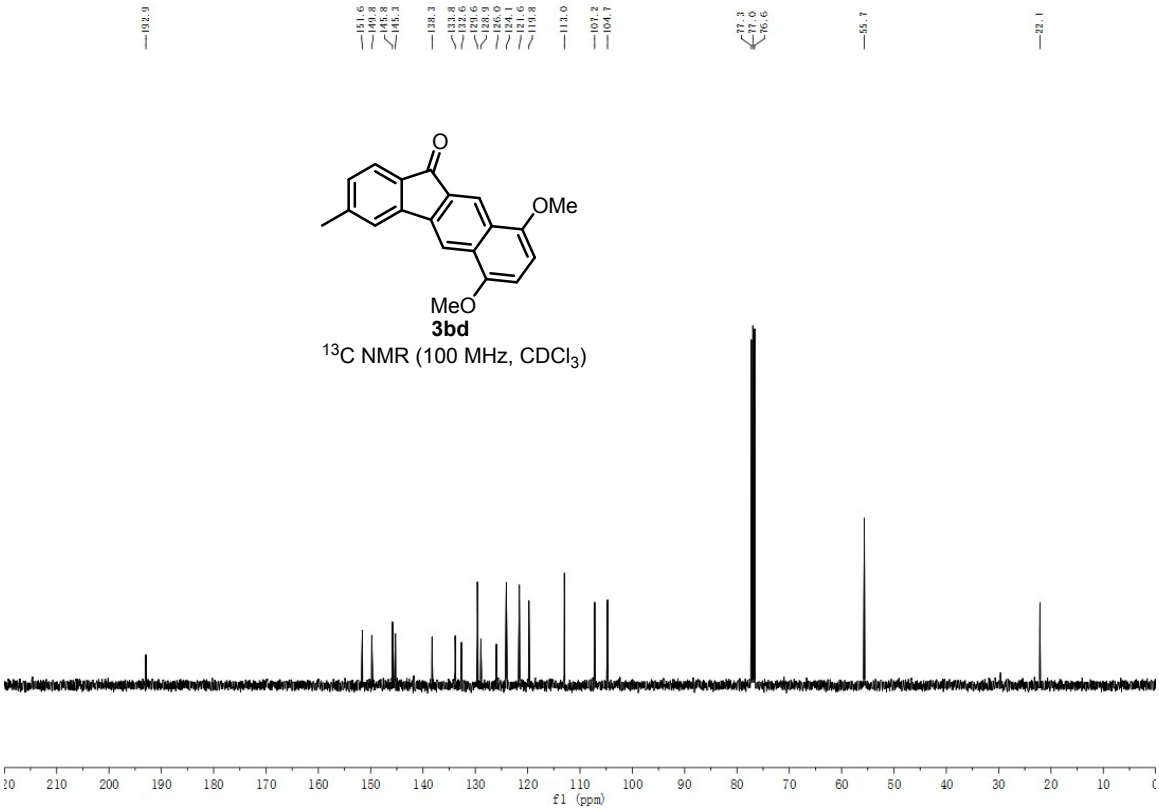


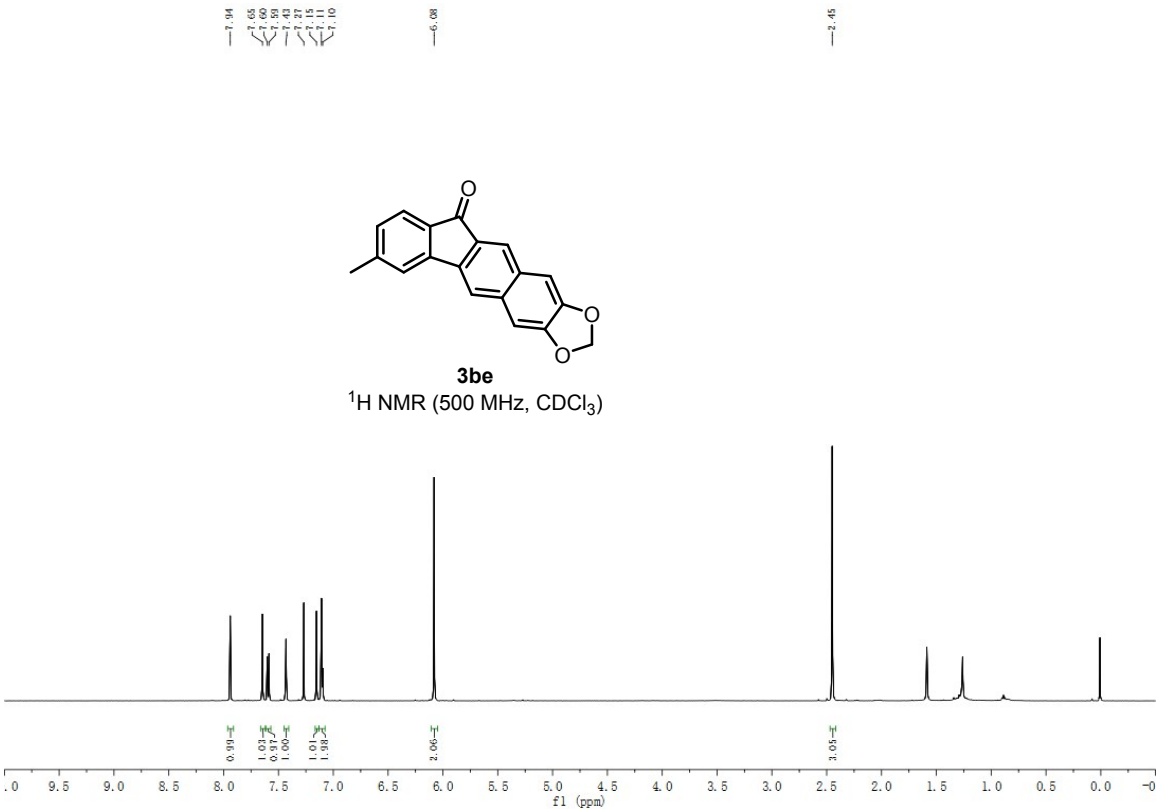
Fig. S53. ^{1}H NMR Spectrum of **3bd**



3bd

^{13}C NMR (100 MHz, $CDCl_3$)

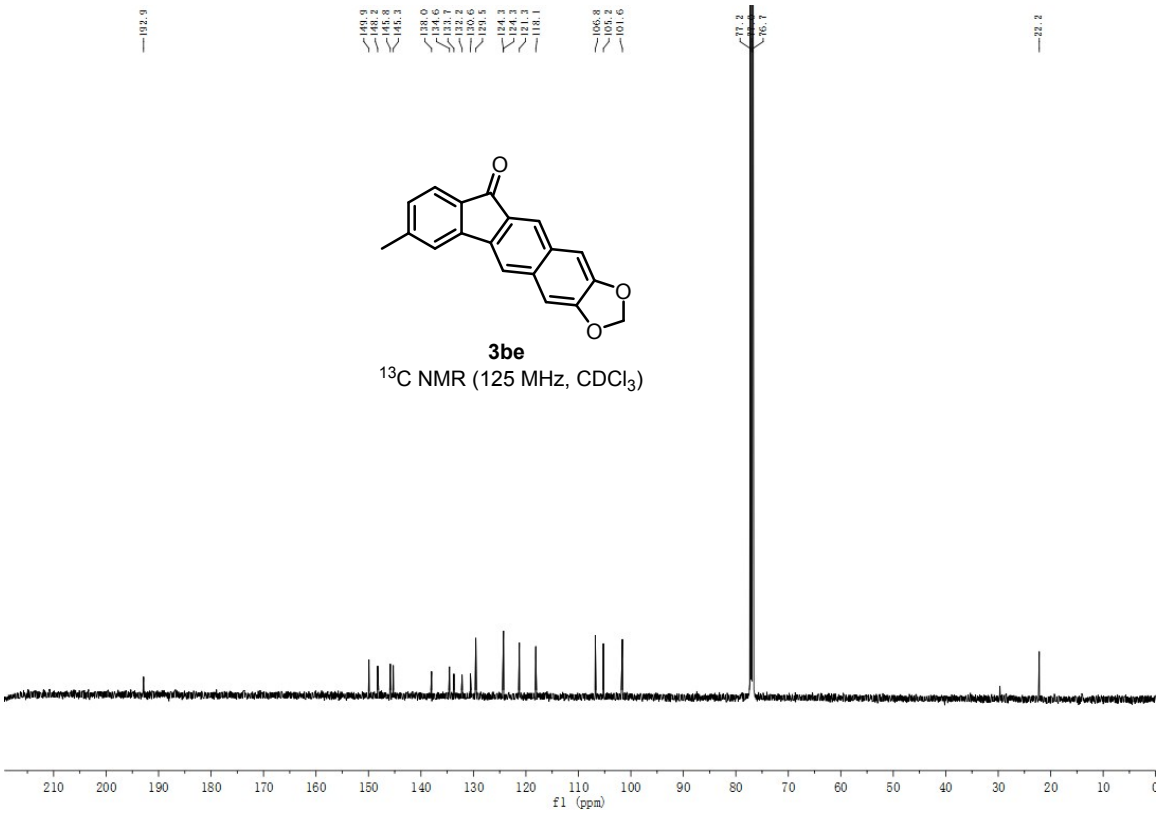
Fig. S54. ^{13}C NMR Spectrum of **3bd**



3be

^{1}H NMR (500 MHz, $CDCl_3$)

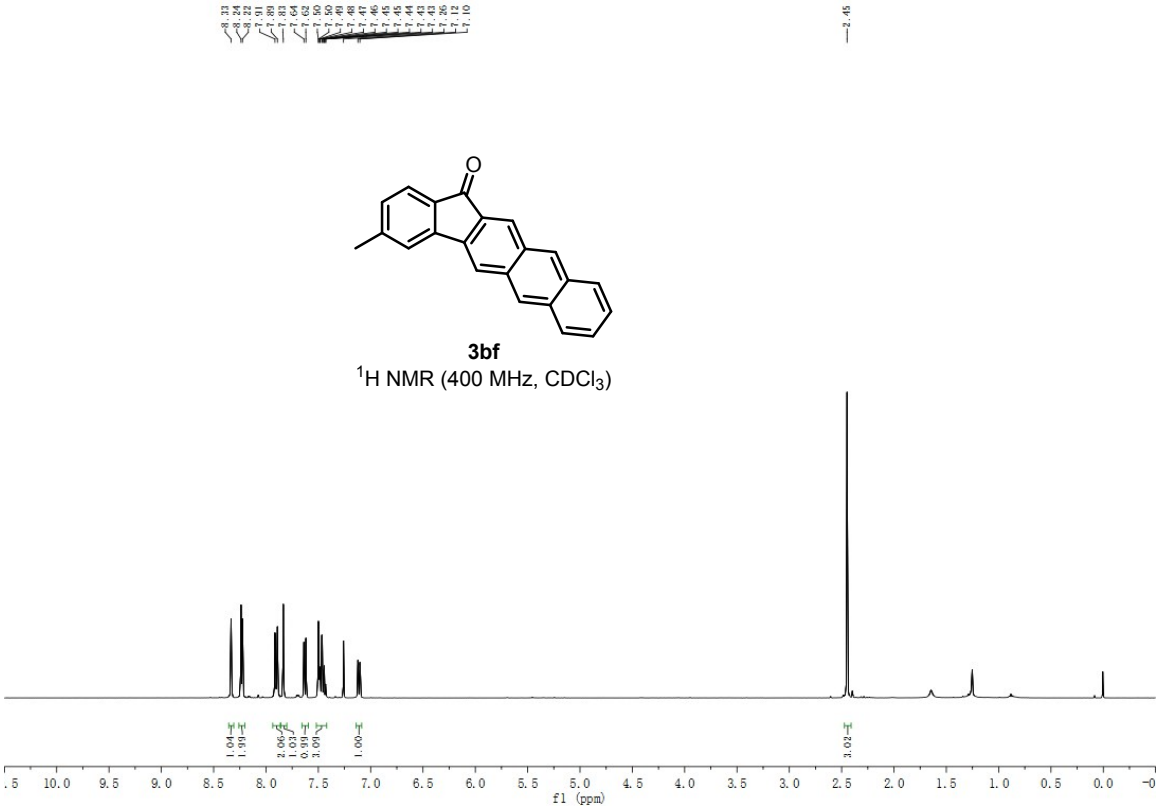
Fig. S55. ^{1}H NMR Spectrum of **3be**



3be

^{13}C NMR (125 MHz, $CDCl_3$)

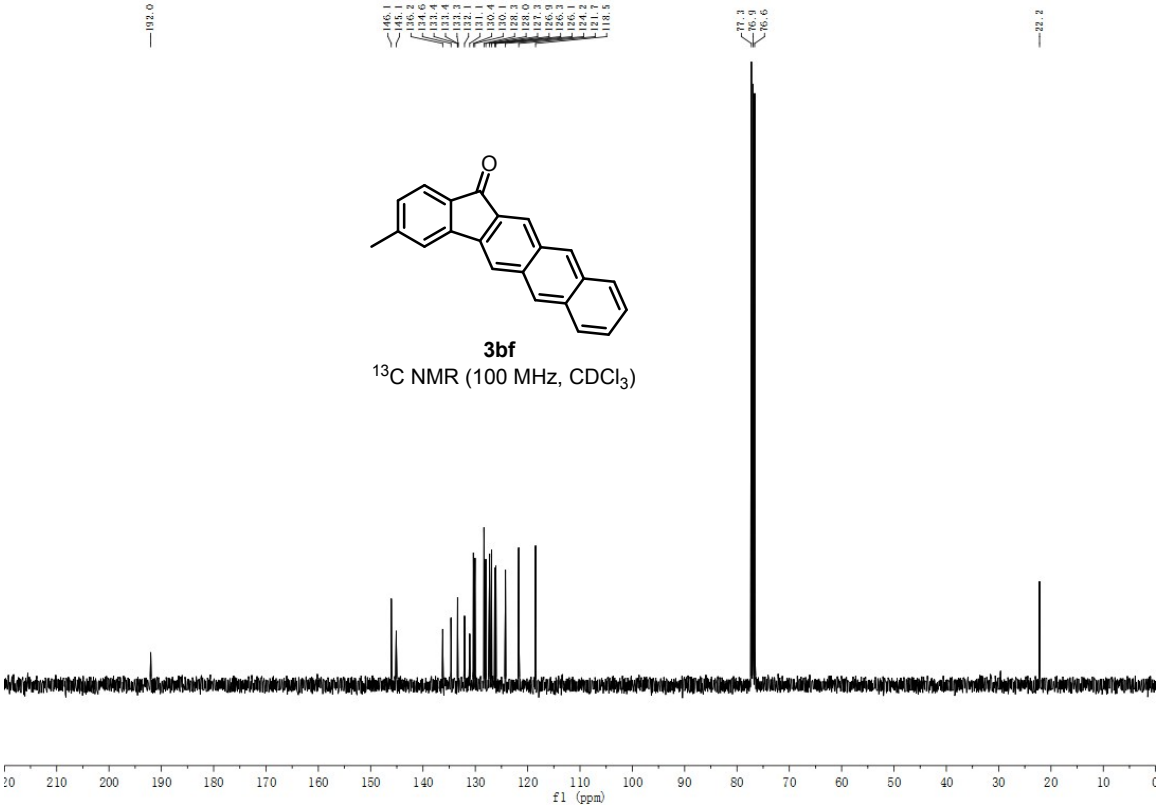
Fig. S56. ^{13}C NMR Spectrum of **3be**



3bf

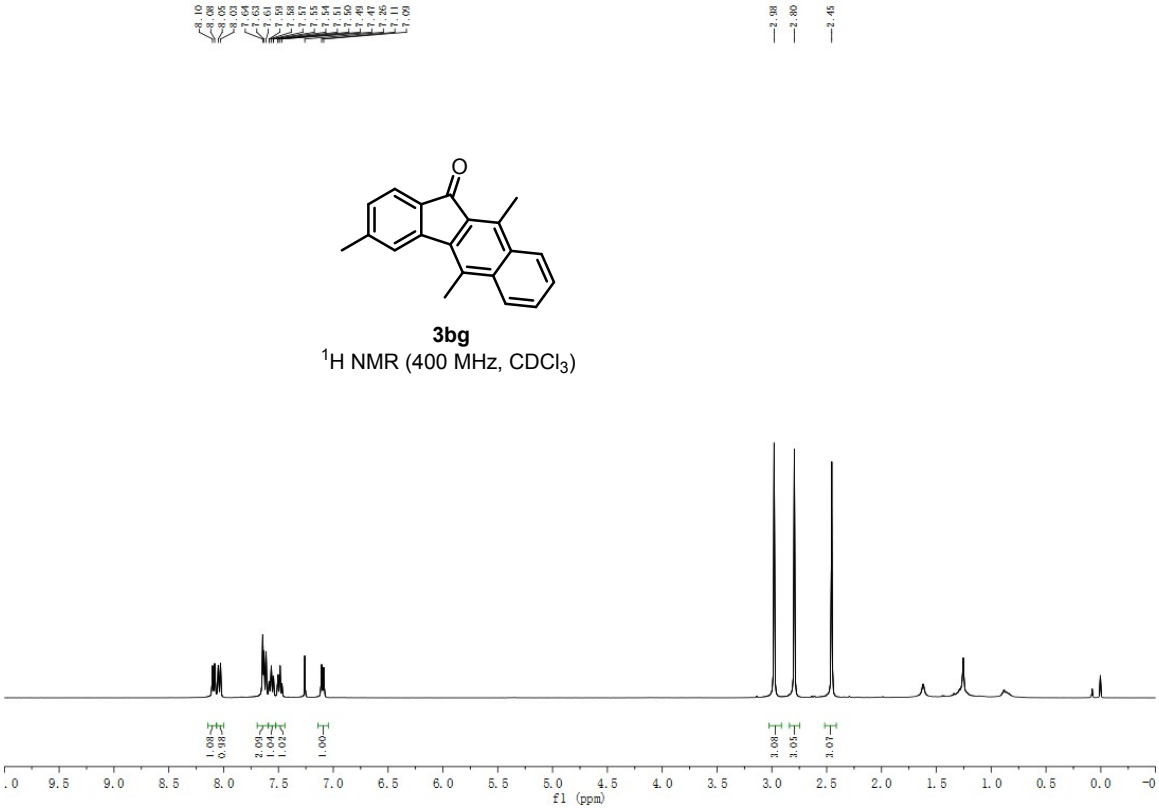
^{1}H NMR (400 MHz, $CDCl_3$)

Fig. S57. ^{1}H NMR Spectrum of **3bf**



3bf
^{13}C NMR (100 MHz, $CDCl_3$)

Fig. S58. ^{13}C NMR Spectrum of **3bf**



3bg
^{1}H NMR (400 MHz, $CDCl_3$)

Fig. S59. ^{1}H NMR Spectrum of **3bg**

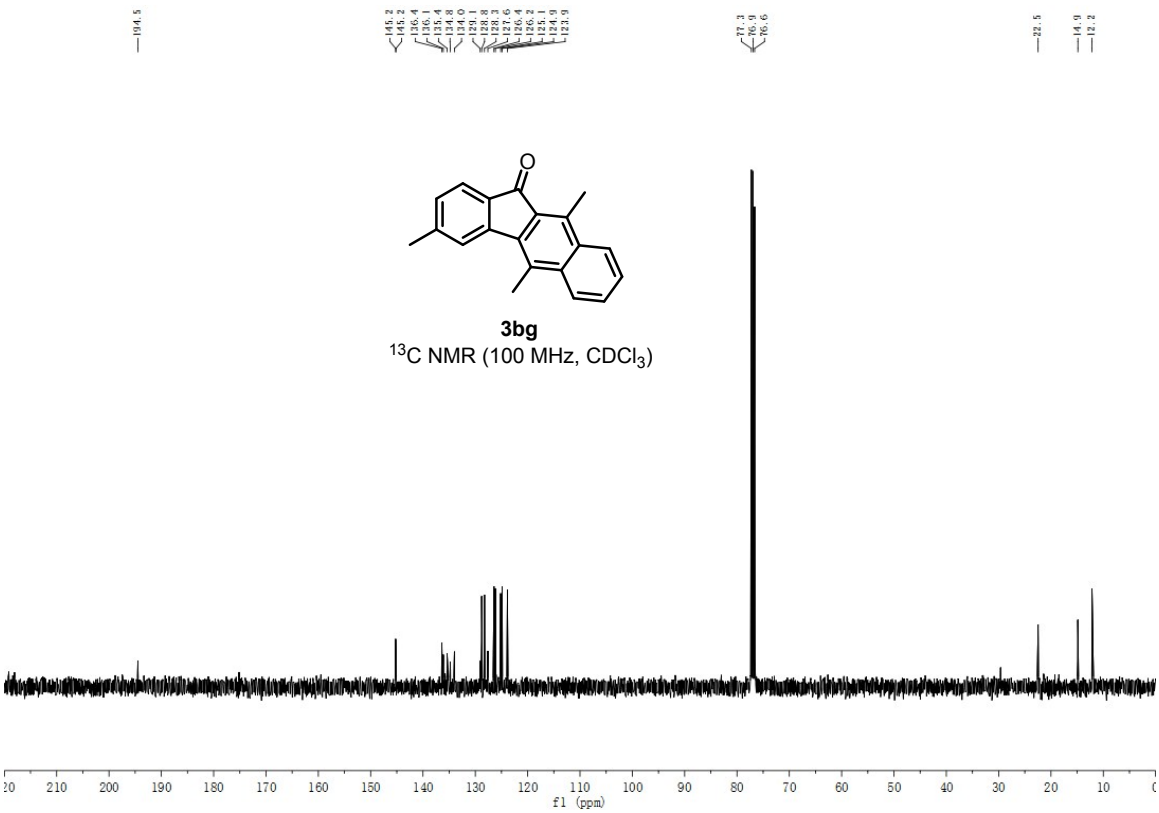


Fig. S60. ^{13}C NMR Spectrum of **3bg**