

Supporting Information

Modular Synthesis of C₂-Symmetric Nitrogen-Containing Polyaromatics via Visible Light-enabled Tandem Reduction/Aza-6 π Electrocyclization

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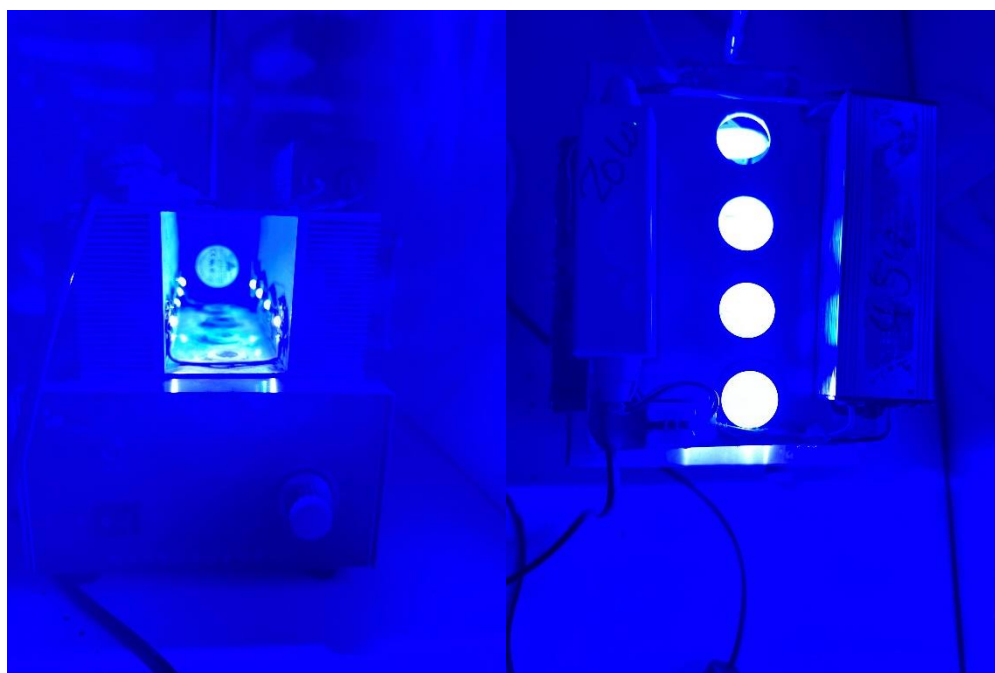
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1. General Information

General Methods. ^1H NMR spectra were recorded on 500 MHz spectrophotometers. Chemical shifts (δ) are reported in ppm from the resonance of tetramethyl silane as the internal standard (TMS: 0.00 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. All NMR spectra were recorded on a Bruker spectrometer at 500 MHz (^1H NMR), 125 MHz (^{13}C NMR) and 471 MHz (^{19}F NMR). HRMS was recorded on Bruker micrOTOF II ESI-TOF. Optical rotations were measured with a polarimeter. All air- and moisture-sensitive reactions were performed under an atmosphere of Nitrogen in fire dried glassware. The manipulations for cyclization reactions were carried out with standard Schlenk techniques. Flash column chromatography was performed using 200-300 mesh silica gel. Melting point was detected on INESA SGW[®] X-4. The heat source used in all heating reactions are oil bath. The following figure shows the reactors used in the reaction. The photoreactor contains eight lamp beads, each with a power of 10 W. The color of light is blue, with a maximum wavelength of 450 nm. Each reaction vessel is illuminated by two LEDs from both sides, with the LEDs located 1 cm away from the reaction vessel. The material of the vessel is quartz glass.



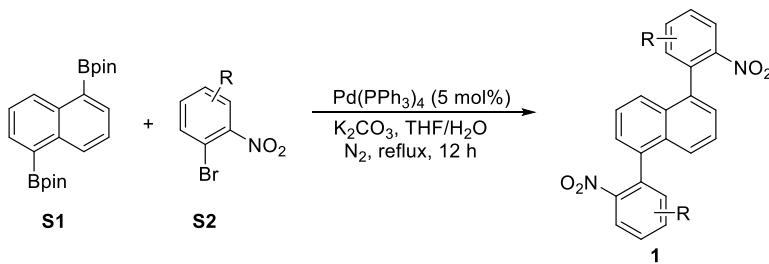
Supplementary Figure 1. Photoreactor used in this research (2 x 10 W blue LEDs, 1.0 cm from the light source to the irradiation vessel)

2. Prepare Substrate and Characteration Data of Substrates

2.1 Materials

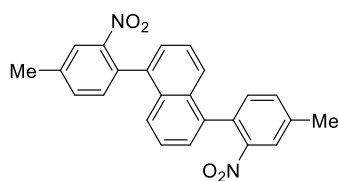
All the solvents were treated according to standard methods and all chemicals were used without purification. All reductants, additives, and substrates **2** were purchased commercially unless noted otherwise.

2.2 Prepare Nitroarenes Substrate 1



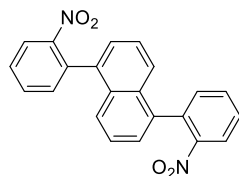
Procedure A: To a solution of 1,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalene **S1** (1.0 eq, 760.2 mg, 2.0 mmol) in THF/ H_2O (10.0/1.0 mL) was added 1-bromo-2-nitrobenzene (2.0 eq, 4 mmol), $\text{Pd(PPh}_3)_4$ (5 mol%, 115.5 mg, 0.1 mmol) and K_2CO_3 (8.0 eq, 2.21 g, 16 mmol) at rt. Then the mixture was bubbled with N_2 for 5 min followed by heated to reflux in oil bath. After stirring for 12 h, the reaction mixture was cooled down to room temperature and extracted with EtOAc. The combined organic layers were then washed with brine, dried over anhydrous Na_2SO_4 , and concentrated under reduced pressure to give crude product, which was purified by column chromatography on silica gel (PE/EtOAc = 10:1 as eluent) to afford **1**.

1,5-Bis(4-methyl-2-nitrophenyl)naphthalene (**1a**)



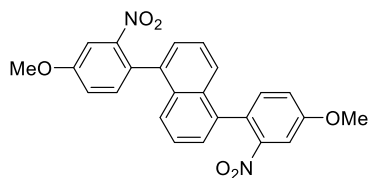
Yellow solid, 565.9 mg, 71% yield, $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.98 – 7.87 (m, 2H), 7.56 – 7.48 (m, 4H), 7.46 – 7.29 (m, 6H), 2.55 (s, 6H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 149.6, 139.3, 136.0, 133.5, 133.1, 132.4, 131.7, 126.3, 125.7, 125.4, 124.5, 21.0. **HRMS** (ESI) m/z : $[\text{M}+\text{H}]^+$ for $\text{C}_{24}\text{H}_{19}\text{N}_2\text{O}_4$ calcd 399.1339, found 399.1340.

1,5-Bis(2-nitrophenyl)naphthalene (**1b**)



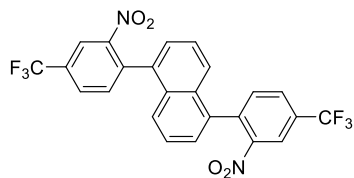
Yellow solid, 495.3 mg, 67% yield, $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.15 – 8.06 (m, 2H), 7.78 – 7.69 (m, 2H), 7.67 – 7.61 (m, 2H), 7.60 – 7.54 (m, 2H), 7.52 – 7.48 (m, 2H), 7.46 – 7.40 (m, 2H), 7.38 – 7.32 (m, 2H), $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 149.8, 136.0, 135.3, 133.3, 132.7, 131.6, 128.8, 126.3, 125.8, 125.5, 124.2. **HRMS** (ESI) m/z : $[\text{M}+\text{H}]^+$ for $\text{C}_{22}\text{H}_{15}\text{N}_2\text{O}_4$ calcd 371.1026, found 371.1029.

1,5-Bis(4-methoxy-2-nitrophenyl)naphthalene (1c)



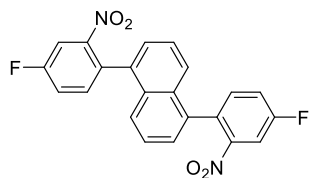
Yellow solid, 535.1 mg, 62% yield, $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.63 – 7.58 (m, 2H), 7.53 – 7.43 (m, 4H), 7.43 – 7.38 (m, 2H), 7.37 – 7.27 (m, 4H), 3.97 (s, 6H), $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 159.5, 150.1, 135.9, 134.1, 132.0, 127.4, 126.5, 125.8, 125.4, 119.1, 109.1, 56.0. **HRMS** (ESI) m/z : $[\text{M}+\text{H}]^+$ for $\text{C}_{24}\text{H}_{19}\text{N}_2\text{O}_6$ calcd 431.1238, found 431.1238.

1,5-Bis(2-nitro-4-(trifluoromethyl)phenyl)naphthalene (1d)



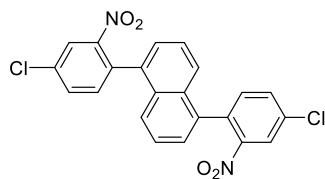
Yellow solid, 528.1 mg, 52% yield, $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.38 (s, 2H), 8.05 – 7.96 (m, 2H), 7.80 – 7.72 (m, 2H), 7.53 – 7.44 (m, 4H), 7.41 – 7.34 (m, 2H), $^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ 62.79, $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 149.7, 138.7, 134.7, 134.3, 131.7 (q, $J = 21.4$ Hz), 131.2, 129.3 (q, $J = 3.8$ Hz), 126.6, 126.3, 125.8, 122.9 (q, $J = 273.4$), 121.7 (q, $J = 3.8$), **HRMS** (ESI) m/z : $[\text{M}+\text{H}]^+$ for $\text{C}_{24}\text{H}_{13}\text{F}_6\text{N}_2\text{O}_4$ calcd 507.0774, found 507.0774.

1,5-Bis(4-fluoro-2-nitrophenyl)naphthalene (1e)



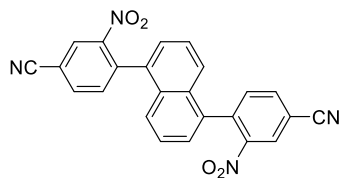
Yellow solid, 685.1 mg, 84% yield, $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.90 – 7.80 (m, 2H), 7.59 – 7.40 (m, 8H), 7.37 – 7.31 (m, 2H), $^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ 110.13, $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 161.7 (d, $J = 253.3$ Hz), 149.9 (d, $J = 7.6$ Hz), 135.1, 134.8 (d, $J = 8.8$ Hz), 131.6, 131.3 (d, $J = 1.3$ Hz), 126.7, 126.0, 125.6, 120.2 (d, $J = 21.4$ Hz), 112.0 (d, $J = 26.5$), **HRMS** (ESI) m/z : $[\text{M}+\text{H}]^+$ for $\text{C}_{22}\text{H}_{13}\text{F}_2\text{N}_2\text{O}_4$ calcd 407.0838, found 407.0836.

1,5-Bis(4-chloro-2-nitrophenyl)naphthalene (1f)



Yellow solid, 671.2 mg, 76% yield, $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.02 (d, $J = 2$ Hz, 2H), 7.68 – 7.57 (m, 2H), 7.47 – 7.30 (m, 6H), 7.28 – 7.22 (m, 2H), $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 149.9, 135.0, 134.7, 134.3, 133.6, 132.9, 131.4, 126.6, 126.0, 125.6, 124.5, **HRMS** (ESI) m/z : $[\text{M}+\text{H}]^+$ for $\text{C}_{22}\text{H}_{13}\text{Cl}_2\text{N}_2\text{O}_4$ calcd 439.0247, found 439.0247.

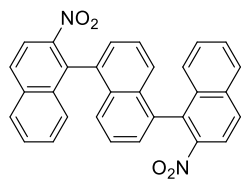
4,4'-(Naphthalene-1,5-diyl)bis(3-nitrobenzonitrile) (1g)



Yellow solid, 221.1 mg, 26% yield, $^1\text{H NMR}$ (500 MHz, $\text{DMSO}-d_6$) δ 8.83 – 8.73 (m, 2H), 8.42 – 8.27 (m, 2H), 7.92 (d, $J = 8$ Hz, 1H), 7.81 (d, $J = 7.5$ Hz, 1H), 7.61 – 7.44 (m, 6H), $^{13}\text{C NMR}$ The solubility of this compound is

very low in various deuterated solvents, leading it failed to obtain ^{13}C NMR signal. **HRMS** (ESI) m/z : $[\text{M}+\text{H}]^+$ for $\text{C}_{24}\text{H}_{13}\text{N}_4\text{O}_4$ calcd 421.0931, found 421.0933.

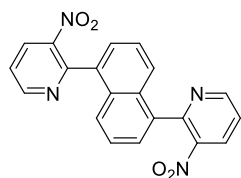
2,2''-Dinitro-1,1':5',1''-ternaphthalene (1h)



Gray solid, 718.0 mg, 76% yield, ^1H NMR (500 MHz, CDCl_3) δ 9.14 – 9.09 (m, 2H), 8.44 – 8.36 (m, 2H), 8.29 – 8.21 (m, 2H), 7.89 – 7.76 (m, 2H), 7.70 – 7.62 (m, 4H), 7.55 – 7.46 (m, 4H), ^{13}C NMR (126 MHz, CDCl_3) δ 147.3, 134.8, 133.3, 133.3, 133.0, 132.6, 129.6, 128.7, 128.5, 128.3, 128.0, 127.3, 126.5, 126.1, 120.4. **HRMS**

(ESI) m/z : $[\text{M}+\text{H}]^+$ for $\text{C}_{30}\text{H}_{19}\text{N}_2\text{O}_4$ calcd 471.1339, found 471.1341.

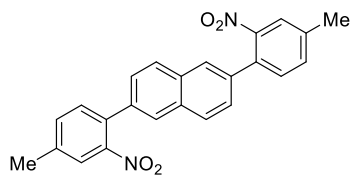
1,5-Bis(3-nitropyridin-2-yl)naphthalene (1i)



Yellow solid, 105.0 mg, 14% yield, ^1H NMR (500 MHz, DMSO-d_6) δ 9.00 (d, J = 4.5 Hz, 2H), 8.40 (d, J = 8.5 Hz, 2H), 7.67 – 7.58 (m, 4H), 7.54 – 7.46 (m, 4H), ^{13}C NMR The solubility of this compound is very low in various deuterated solvents, leading it failed to obtain ^{13}C NMR signal. **HRMS** (ESI) m/z : $[\text{M}+\text{H}]^+$ for

$\text{C}_{20}\text{H}_{13}\text{N}_4\text{O}_4$ calcd 373.0931, found 373.0934.

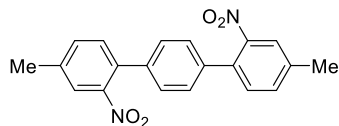
2,6-Bis(4-methyl-2-nitrophenyl)naphthalene (1j)



Yellow solid, 652.6 mg, 82% yield, ^1H NMR (500 MHz, CDCl_3) δ 7.88 (d, J = 8.5 Hz, 2H), 7.81 (s, 2H), 7.75 (s, 2H), 7.49 – 7.45 (m, 2H), 7.44 – 7.38 (m, 4H), ^{13}C NMR (126 MHz, CDCl_3) δ 149.1, 138.9, 135.7, 133.5, 133.2, 132.7, 132.1, 128.5, 126.8, 126.6, 124.6, 20.9. **HRMS** (ESI) m/z : $[\text{M}+\text{H}]^+$

for $\text{C}_{24}\text{H}_{19}\text{N}_2\text{O}_4$ calcd 399.1339, found 399.1339.

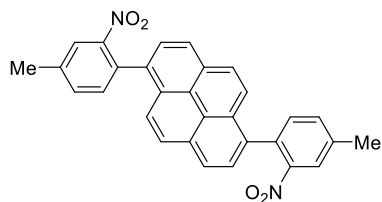
4,4''-Dimethyl-2,2''-dinitro-1,1':4',1''-terphenyl (1k)



Yellow solid, 388.1 mg, 56% yield, ^1H NMR (500 MHz, CDCl_3) δ 7.69 (s, 2H), 7.44 (d, J = 9.5 Hz, 2H), 7.37 (d, J = 7.5 Hz, 2H), 7.34 (s, 4H), 2.48 (s, 6H), ^{13}C NMR (126 MHz, CDCl_3) δ 149.1, 138.9, 137.2, 133.1, 132.9, 131.8,

128.3, 124.5, 20.9. **HRMS** (ESI) m/z : $[\text{M}+\text{H}]^+$ for $\text{C}_{20}\text{H}_{17}\text{N}_2\text{O}_4$ calcd 349.1183, found 349.1182.

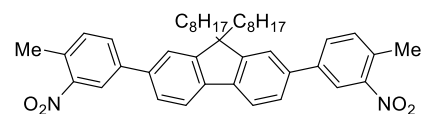
1,6-Bis(4-methyl-2-nitrophenyl)pyrene (1l)



Yellow solid, 592.5 mg, 63% yield, ^1H NMR (500 MHz, CDCl_3) δ 8.19 (d, J = 7.5 Hz, 2H), 8.06 – 8.00 (m, 2H), 7.97 (s, 2H), 7.86 (d, J = 9.5 Hz, 2H), 7.80 – 7.72 (m, 2H), 7.59 – 7.53 (m, 2H), 7.50 – 7.43 (m, 2H), ^{13}C NMR (126 MHz, CDCl_3) δ 149.8, 149.8, 139.3, 133.4, 133.4, 133.3,

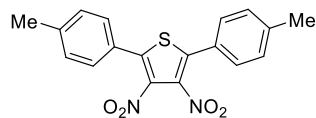
133.3, 132.8, 132.8, 130.9, 129.1, 129.1, 128.1, 128.1, 126.8, 126.7, 124.9, 124.8, 124.8, 124.7, 124.6, 124.6, 21.1. **HRMS** (ESI) m/z : $[M+H]^+$ for $C_{30}H_{21}N_2O_4$ calcd 473.1496, found 473.1499.

2,7-Bis(4-methyl-3-nitrophenyl)-9,9-dioctyl-9H-fluorene (1m)



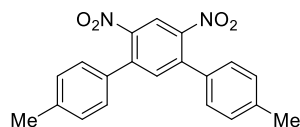
Yellow solid, 715.1 mg, 54% yield, **1H NMR** (500 MHz, $CDCl_3$) δ 7.74 (d, J = 7.5 Hz, 2H), 7.66 (s, 2H), 7.44 – 7.38 (m, 4H), 7.31 – 7.27 (m, 2H), 7.25 – 7.23 (m, 2H), 2.48 (s, 2H), 1.99 – 1.90 (m, 4H), 1.24 – 1.16 (m, 4H), 1.53 – 1.03 (m, 16H), 0.80 (t, J = 7.5 Hz, 6H), 0.73 – 0.64 (m, 4H), **^{13}C NMR** (126 MHz, $CDCl_3$) δ 151.5, 149.5, 140.5, 138.5, 136.3, 133.9, 132.8, 131.7, 126.8, 124.4, 122.6, 120.1, 55.4, 40.3, 31.8, 30.0, 29.2, 29.2, 23.7, 22.6, 20.9, 14.1. **HRMS** (ESI) m/z : $[M+H]^+$ for $C_{43}H_{53}N_2O_4$ calcd 661.4000, found 661.4000.

3,4-Dinitro-2,5-di-p-tolylthiophene (1n)



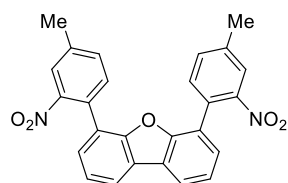
Yellow solid, 473.5 mg, 67% yield, **1H NMR** (500 MHz, $CDCl_3$) δ 7.37 – 7.42 (m, 4H), 7.28 (d, J = 8.0 Hz, 4H), **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.3, 140.8, 136.6, 129.9, 128.9, 125.3, 21.4. **HRMS** (ESI) m/z : $[M+H]^+$ for $C_{18}H_{15}N_2O_4S$ calcd 355.0747, found 355.0748.

4,4''-Dimethyl-4',6'-dinitro-1,1':3',1''-terphenyl (1o)



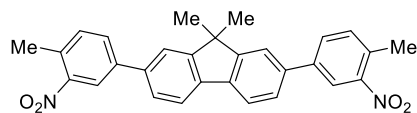
Yellow solid, 540.6 mg, 78% yield, **1H NMR** (500 MHz, $CDCl_3$) δ 8.39 (s, H), 7.53 (s, 1H), 7.29 – 7.22 (m, 8H), **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.2, 140.2, 139.6, 135.7, 132.5, 129.8, 127.7, 120.8, 21.3. **HRMS** (ESI) m/z : $[M+H]^+$ for $C_{20}H_{17}N_2O_4$ calcd 349.1183, found 349.1187.

4,6-Bis(4-methyl-2-nitrophenyl)dibenzo[b,d]furan (1p)



Yellow solid, 458.6 mg, 52% yield, **1H NMR** (500 MHz, $CDCl_3$) δ 7.97 (dd, J = 7.5, 1.4 Hz, 2H), 7.77 (s, 2H), 7.52 – 7.48 (m, 2H), 7.47 – 7.44 (m, 2H), 7.42 – 7.38 (m, 2H), 7.38 – 7.35 (m, 2H), 2.48 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 153.0, 148.9, 139.3, 133.7, 132.8, 128.0, 127.2, 124.9, 124.4, 123.5, 122.4, 120.8, 21.0. **HRMS** (ESI) m/z : $[M+H]^+$ for $C_{26}H_{19}N_2O_5$ calcd 439.1288, found 439.1291.

9,9-dimethyl-2,7-bis(4-methyl-3-nitrophenyl)-9H-fluorene (1q)

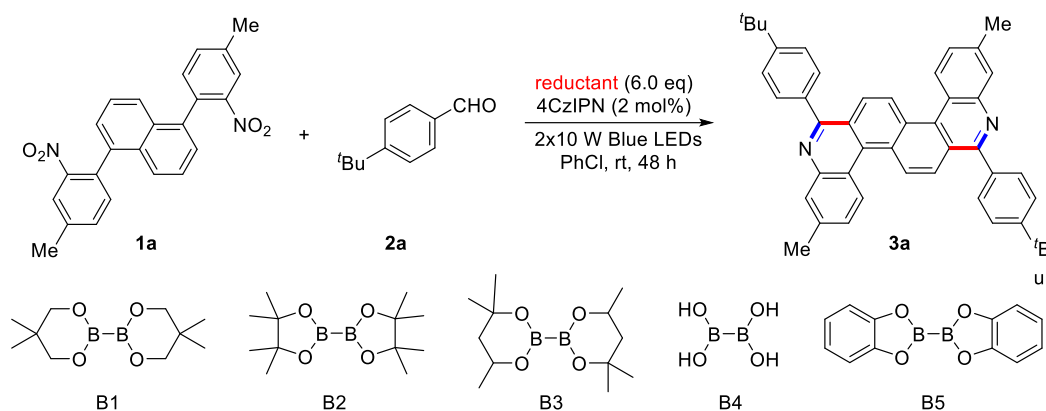


Yellow solid, 549.1 mg, 59% yield, **1H NMR** (500 MHz, $CDCl_3$) δ 7.76 (d, J = 8.0 Hz, 2H), 7.67 (s, 2H), 7.45 – 7.39 (m, 4H), 7.35 (d, J = 1.6 Hz, 2H), 7.29 (dd, J = 7.8, 1.7 Hz, 2H), 2.48 (s, 6H), 1.51 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 154.3, 149.3, 138.6, 138.6, 136.5, 133.8, 133.0, 131.8, 127.1, 124.4,

122.3, 120.4, 47.2, 27.1, 20.9. **HRMS** (ESI) m/z : $[M+H]^+$ for $C_{29}H_{25}N_2O_4$ calcd 465.1809, found 465.1811.

3. Details for the Condition Optimization

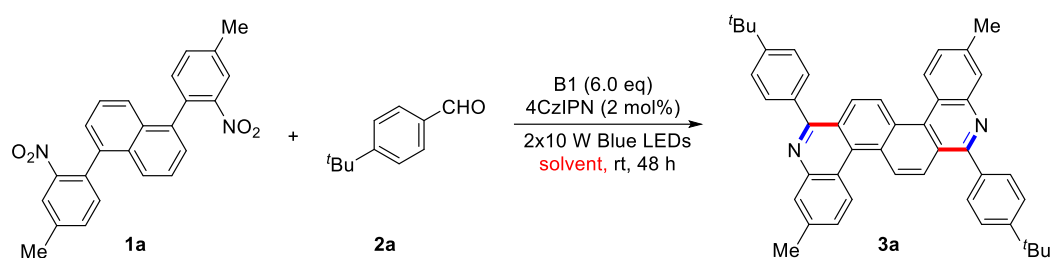
Table S1 Screen of Reductants. ^[a]



Entry	reductant	Yield of 3a (%) ^[b]
1	Zn powder	0
2	Fe powder	0
3	Mn powder	0
4	B1	46
5	B2	42
6	B3	40
7	B4	0
8	B5	0

^[a] Reactions were performed with **1a** (1.0 eq, 0.1 mmol, 39.8 mg), **2a** (3.0 eq, 0.6 mmol, 48.7 mg), Reductant (6.0 eq, 0.6 mmol), 4CzIPN (0.002 mmol, 1.6 mg, 2 mol%) in PhCl (4 mL, 0.05 M) under irradiation of 2 x 10 W blue LED at rt for 48 h. ^[b] Isolated yield.

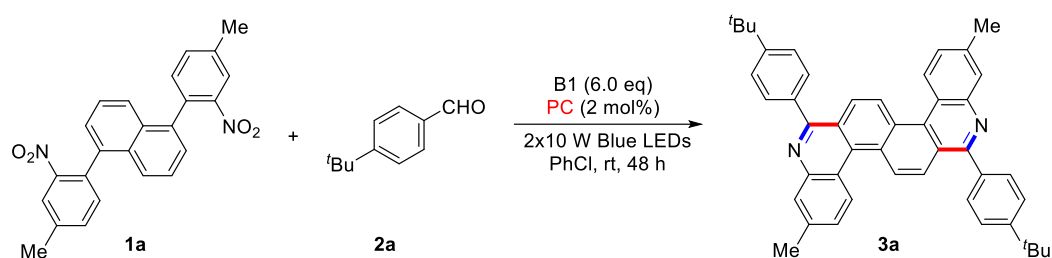
Table S2 The Effect of solvent. ^[a]



Entry	solvent	Yield of 3a (%) ^[b]
1	acetonitrile	0
2	DCE	21
3	THF	6
4	1,4-dioxane	5
5	DMF	0
6	DMSO	trace
7	acetone	trace
8	ethyl acetate	5
9	ethanol	0
10	isopropanol	9
11	HFIP	0
12	toluene	30
13	PhF	35
14	ethylbenzene	24
15	paraxylene	33
16	PhCF ₃	36

^[a] Reactions were performed with **1a** (1.0 eq, 0.1 mmol, 39.8 mg), **2a** (3.0 eq, 0.6 mmol, 48.7 mg), B1 (6.0 eq, 0.6 mmol, 135.5 mg), 4CzIPN (0.002 mmol, 1.6 mg, 2 mol%) in solvent (4 mL, 0.05 M) under irradiation of 2 x 10 W blue LED at rt for 48 h. ^[b] Isolated yield.

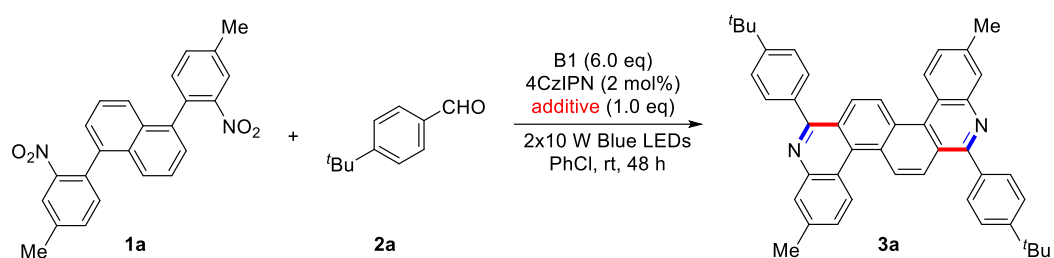
Table S3 The Effect of photocatalysts. ^[a]



Entry	photocatalyst	Yield of 3a (%) ^[b]
1	/	37
2	Mes-Acr-MeClO ₄	41
3	Rose Bengal	26
4	TPTBF ₄	36
5	Eosin Y	37
6	Ru(bpy) ₃ Cl ₂ ·6H ₂ O	40
7	<i>fac</i> -Ir(ppy) ₃	trace
8	Ir(ppy) ₂ (dtbbpy)PF ₆	25
9	Ir[dF(CF ₃)ppy] ₂ (dtbbpy)PF ₆	38

^[a] Reactions were performed with **1a** (1.0 eq, 0.1 mmol, 39.8 mg), **2a** (3.0 eq, 0.6 mmol, 48.7 mg), B1 (6.0 eq, 0.6 mmol, 135.5 mg), PC (0.002 mmol, 2 mol%) in PhCl (4 mL, 0.05 M) under irradiation of 2x10 W blue LED at rt for 48 h. ^[b] Isolated yield.

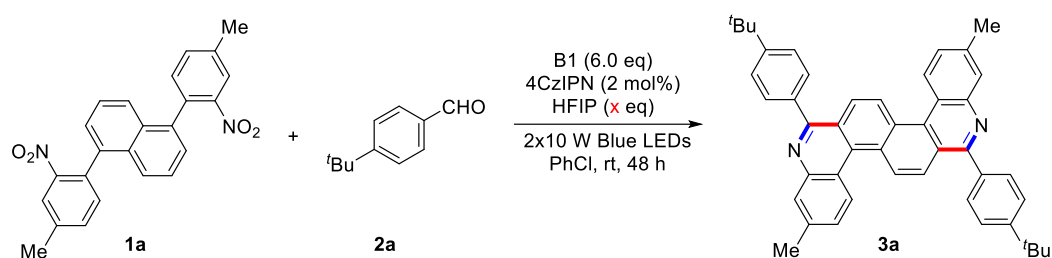
Table S4 The Effect of Additives. ^[a]



Entry	additive	Yield of 3a (%) ^[b]
1	CH ₃ COOH	56
2	CF ₃ COOH	61
3	B(C ₆ F ₅) ₃	46
4	AlCl ₃	34
5	HFIP	63

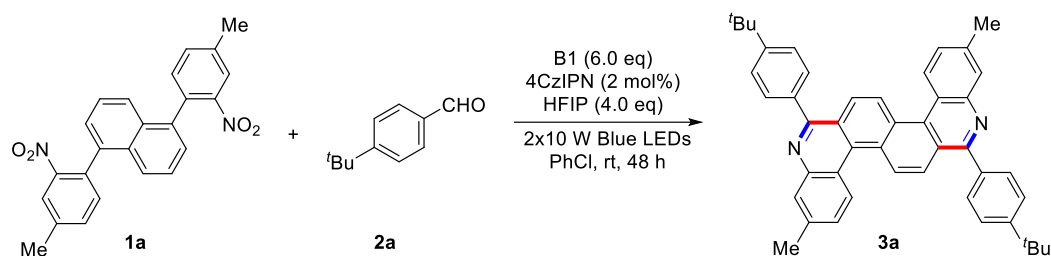
^[a] Reactions were performed with **1a** (1.0 eq, 0.1 mmol, 39.8 mg), **2a** (3.0 eq, 0.6 mmol, 48.7 mg), B1 (6.0 eq, 0.6 mmol, 135.5 mg), 4CzIPN (0.002 mmol, 1.6 mg, 2 mol%), additive (1.0 eq, 0.1 mmol) in PhCl (4 mL, 0.05 M) under irradiation of 2 x 10 W blue LED at rt for 48 h. ^[b] Isolated yield.

Table S5 The Effect of Equivalent of HFIP ^[a]



Entry	Equivalent of HFIP	Yield of 3a (%) ^[b]
1	1.0	63
2	2.0	67
3	4.0	75
4	6.0	75
5	10.0	70
6	20.0	42
7 ^[c]	4.0	74
8 ^[d]	4.0	63

^[a] Reactions were performed with **1a** (1.0 eq, 0.1 mmol, 39.8 mg), **2a** (3.0 eq, 0.6 mmol, 48.7 mg), B1 (6.0 eq, 0.6 mmol, 135.5 mg), 4CzIPN (0.002 mmol, 1.6 mg, 2 mol%), HFIP in PhCl (4 mL, 0.05 M) under irradiation of 2 x 10 W blue LED at rt for 48 h. ^[b] Isolated yield. ^[c] MgSO₄ (2.0 eq, 0.2 mmol, 24.1 mg) was added. ^[d] 4Å MS (25.0 mg) was added.

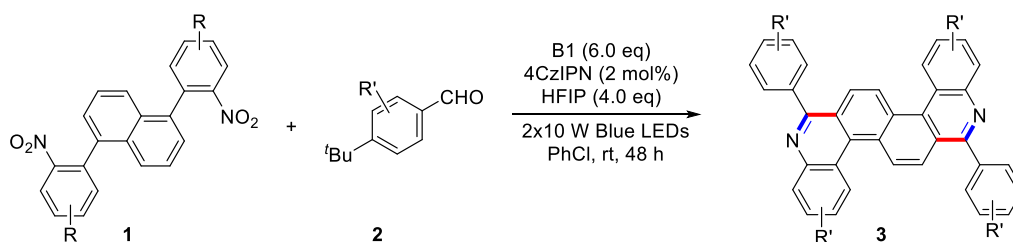
Table S6 Control experiment ^[a]

Entry	deviation from the standard conditions	Yield of 3a (%) ^[b]
1	dark	0
2	N ₂	73
3	air	75

^[a] Reactions were performed with **1a** (1.0 eq, 0.1 mmol, 39.8 mg), **2a** (3.0 eq, 0.6 mmol, 48.7 mg), B1 (6.0 eq, 0.6 mmol, 135.5 mg), 4CzIPN (0.002 mmol, 1.6 mg, 2 mol%), HFIP (4.0 eq, 0.4 mmol, 67.2 mg) in PhCl (4 mL, 0.05 M) under irradiation of 2 x 10 W blue LED at rt for 48 h. ^[b] Isolated yield.

4. General Procedures and Characterization

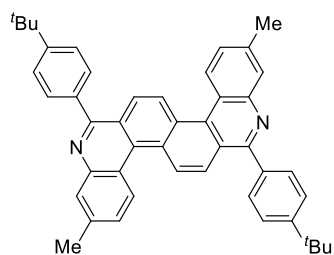
4.1. General Procedures B



In a flask dried tube, nitroarene (**1a**, 1.0 eq, 0.1 mmol) and B₂nep₂ (6.0 eq, 0.6 mmol, 135.5 mg), 4CzIPN (0.002 mmol, 1.6 mg, 2 mol%) were dissolved into PhCl (4 mL, directly used as received, without further purification to remove trace amount of water). Then 4-(tert-butyl)benzaldehyde (**2a**, 3.0 eq, 0.3 mmol) and HFIP (4.0 eq, 0.4 mmol, 67.2 mg) were added to the mixture. The resulting solution was sealed and stirred at room temperature under the irradiation of 2x10 W blue LEDs. After stirring for 48 h, the reaction mixture was concentrated under reduced pressure to remove HFIP. The result solution was purified by column chromatography on silica gel (PE/EtOAc = 10:1 as eluent) to afford **3**.

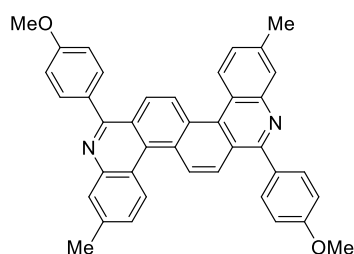
4.2 Characterization of Products

7,15-Bis(4-(tert-butyl)phenyl)-2,10-dimethylphenanthridino[10,9-k]phenanthridine (3a)



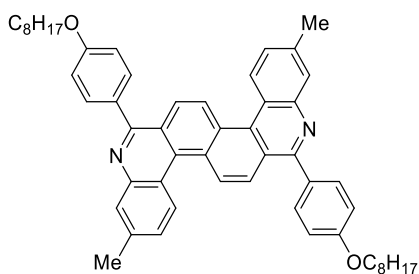
Yellow solid, 47.3 mg, 75% yield, $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 9.10 (d, $J = 9.0$ Hz, 2H), 8.81 (d, $J = 8.5$ Hz, 2H), 8.22 (d, $J = 9.0$ Hz, 2H), 8.18 (s, 2H), 7.75 (d, $J = 8.5$ Hz, 4H), 7.62 (d, $J = 8.5$ Hz, 4H), 7.52 (dd, $J = 8.5$, 2.0 Hz, 2H), 2.64 (s, 6H), 1.43 (s, 18H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 160.3, 151.8, 146.0, 139.0, 137.0, 132.1, 131.2, 129.9, 129.7, 128.6, 127.4, 127.0, 125.5, 125.3, 123.8, 121.4, 34.8, 31.4, 21.6. **HRMS** (ESI) m/z : $[\text{M}+\text{H}]^+$ for $\text{C}_{46}\text{H}_{43}\text{N}_2$ calcd 623.3421, found 623.3419.

7,15-Bis(4-methoxyphenyl)-2,10-dimethylphenanthridino[10,9-k]phenanthridine (3b)



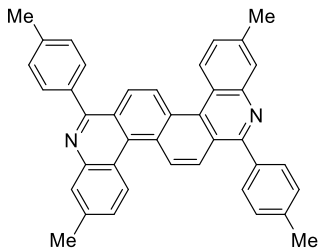
Yellow solid, 38.9 mg, 68% yield, $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 9.08 (d, $J = 9.0$ Hz, 2H), 8.79 (d, $J = 8.5$ Hz, 2H), 8.21 – 8.15 (m, 4H), 7.77 (d, $J = 8.5$ Hz, 4H), 7.52 (dd, $J = 8.5$, 2.0 Hz, 2H), 7.13 (d, $J = 9.0$ Hz, 4H), 3.93 (s, 6H), 2.64 (s, 6H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 160.2, 159.8, 145.9, 139.1, 132.4, 132.2, 131.4, 131.2, 129.8, 128.6, 127.4, 127.0, 125.2, 123.8, 121.3, 114.0, 55.5, 21.5. **HRMS** (ESI) m/z : $[\text{M}+\text{H}]^+$ for $\text{C}_{40}\text{H}_{31}\text{N}_2\text{O}_2$ calcd 571.2380, found 571.2381.

2,10-Dimethyl-7,15-bis(4-(octyloxy)phenyl)phenanthridino[10,9-k]phenanthridine (3c)



Yellow solid, 54.7 mg, 71% yield, $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 9.07 – 9.00 (m, 2H), 8.79 – 8.73 (m, 2H), 8.19 – 8.13 (m, 4H), 7.73 (d, $J = 9.0$ Hz, 4H), 7.50 (d, $J = 8.5$ Hz, 2H), 7.10 (d, $J = 8.5$ Hz, 4H), 4.07 (t, $J = 6.6$ Hz, 4H), 2.62 (s, 6H), 1.89 – 1.82 (m, 4H), 1.55 – 1.47 (m, 4H), 1.43 – 1.28 (m, 16H), 0.91 (t, $J = 6.8$ Hz, 6H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 159.9, 159.8, 145.9, 139.0, 132.2, 132.1, 131.4, 131.1, 129.8, 128.5, 127.3, 127.0, 125.2, 123.8, 121.3, 114.6, 68.3, 31.9, 29.4, 29.3, 26.1, 22.7, 21.5, 14.1. **HRMS** (ESI) m/z : $[\text{M}+\text{H}]^+$ for $\text{C}_{54}\text{H}_{59}\text{N}_2\text{O}_2$ calcd 767.4571, found 767.4572.

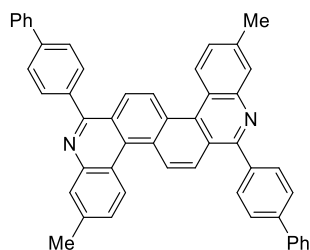
2,10-Dimethyl-7,15-di-p-tolylphenanthridino[10,9-k]phenanthridine (3d)



Yellow solid, 28.5 mg, 53% yield, $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 9.09 (d, $J = 9.0$ Hz, 2H), 8.80 (d, $J = 8.5$ Hz, 2H), 8.21 – 8.14 (m, 4H), 7.70 (d, $J = 8.0$ Hz, 4H), 7.53 (dd, $J = 8.5$, 2.0 Hz, 2H), 7.41 (d, $J = 8.0$ Hz, 4H), 2.64 (s, 6H), 2.51 (s, 6H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 160.3, 145.9, 139.1, 138.6,

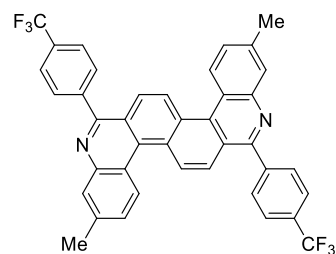
137.0, 132.1, 131.2, 129.9, 129.9, 129.2, 128.6, 127.4, 127.0, 125.3, 123.8, 121.4, 21.6, 21.4. **HRMS** (ESI) m/z : $[M+H]^+$ for $C_{40}H_{31}N_2$ calcd 539.2482, found 539.2482.

7,15-Di([1,1'-biphenyl]-4-yl)-2,10-dimethylphenanthridino[10,9-k]phenanthridine (3e)



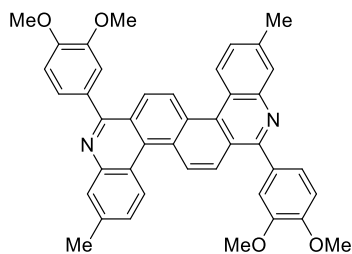
Yellow solid, 20.1 mg, 30% yield, **1H NMR** (500 MHz, $CDCl_3$) δ 9.14 (d, J = 9.0 Hz, 2H), 8.84 (d, J = 8.5 Hz, 2H), 8.26 (d, J = 9.0 Hz, 2H), 8.22 (s, 2H), 7.91 (d, J = 8.0 Hz, 4H), 7.84 (d, J = 8.0 Hz, 4H), 7.73 (d, J = 7.0 Hz, 4H), 7.56 (dd, J = 8.5, 2.0 Hz, 2H), 7.52 (t, J = 7.7 Hz, 4H), 7.42 (t, J = 7.5 Hz, 2H), 2.66 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.9, 145.7, 141.8, 140.8, 139.3, 132.3, 131.3, 130.5, 129.8, 128.9, 127.6, 127.6, 127.3, 127.3, 127.1, 125.3, 123.7, 121.4, 21.6. **HRMS** (ESI) m/z : $[M+H]^+$ for $C_{50}H_{35}N_2$ calcd 663.2795, found 663.2790.

2,10-Dimethyl-7,15-bis(4-(trifluoromethyl)phenyl)phenanthridino[10,9-k]phenanthridine (3f)



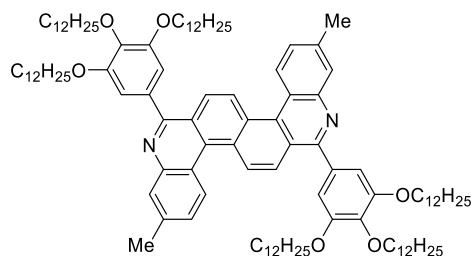
Yellow solid, 13.1 mg, 20% yield, **1H NMR** (500 MHz, $CDCl_3$) δ 9.14 (d, J = 9.0 Hz, 2H), 8.84 (d, J = 8.5 Hz, 2H), 8.20 (s, 2H), 8.09 (d, J = 9.0 Hz, 2H), 7.95 (d, J = 8.0 Hz, 4H), 7.89 (d, J = 8.0 Hz, 4H), 7.60 (dd, J = 8.5, 2.0 Hz, 2H), 2.67 (s, 6H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -62.57. **^{13}C NMR** δ 158.6, 145.8, 143.4, 139.6, 132.3, 131.3, 130.9 (q, J = 32.8 Hz), 130.4, 130.0, 129.3, 127.7, 127.0, 125.6 (q, J = 3.8 Hz), 124.7, 124.2 (q, J = 273.4 Hz), 123.4, 121.5, 21.6. **HRMS** (ESI) m/z : $[M+H]^+$ for $C_{40}H_{25}F_6N_2$ calcd 647.1916, found 647.1919.

7,15-Bis(3,4-dimethoxyphenyl)-2,10-dimethylphenanthridino[10,9-k]phenanthridine (3g)



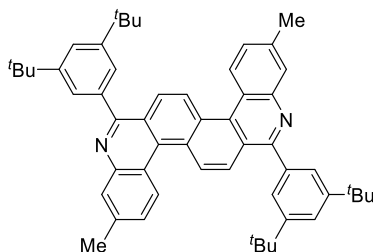
Yellow solid, 41.1 mg, 65% yield, **1H NMR** (500 MHz, $CDCl_3$) δ 9.11 (d, J = 9.0 Hz, 2H), 8.81 (d, J = 8.5 Hz, 2H), 8.23 (d, J = 9.0 Hz, 2H), 8.19 (s, 2H), 7.54 (dd, J = 8.5, 2.0 Hz, 2H), 7.39 (d, J = 2.0 Hz, 2H), 7.35 (dd, J = 8.0, 2.0 Hz, 2H), 7.09 (d, J = 8.5 Hz, 2H), 4.01 (s, 6H), 3.98 (s, 6H), 2.65 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.9, 149.7, 149.1, 145.8, 139.2, 132.5, 132.3, 131.2, 129.8, 128.7, 127.4, 127.0, 125.3, 123.8, 122.9, 121.3, 113.3, 111.1, 56.1, 56.1, 21.6. **HRMS** (ESI) m/z : $[M+H]^+$ for $C_{42}H_{35}N_2O_4$ calcd 631.2591, found 631.2590.

2,10-Dimethyl-7,15-bis(3,4,5-tris(dodecyloxy)phenyl)phenanthridino[10,9-k]phenanthridine (3h)



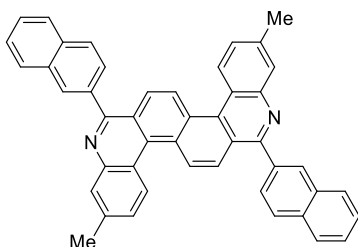
Brown solid, 101.5 mg, 63% yield, $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 9.14 (d, $J = 9.5$ Hz, 2H), 8.83 (d, $J = 9.0$ Hz, 2H), 8.25 – 8.19 (m, 4H), 7.57 (dd, $J = 8.5, 2.0$ Hz, 2H), 6.97 (s, 4H), 4.11 – 4.03 (m, 12H), 2.66 (s, 6H), 1.88 – 1.80 (m, 12H), 1.57 – 1.44 (m, 12H), 1.38 – 1.20 (m, 96H), 0.91 – 0.84 (m, 18H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 160.3, 153.2, 145.8, 139.2, 139.0, 134.8, 132.2, 131.2, 129.9, 128.8, 127.4, 127.0, 125.4, 123.8, 121.4, 108.8, 73.6, 69.3, 32.0, 31.9, 30.4, 29.8, 29.8, 29.8, 29.7, 29.7, 29.7, 29.5, 29.5, 29.4, 29.4, 26.2, 26.1, 22.7, 22.7, 21.6, 14.1, 14.1. **HRMS** (ESI) m/z : $[\text{M}+\text{H}]^+$ for $\text{C}_{110}\text{H}_{171}\text{N}_2\text{O}_6$ calcd 1616.3132, found 1616.3137.

7,15-Bis(3,5-di-tert-butylphenyl)-2,10-dimethylphenanthridino[10,9-k]phenanthridine (3i)



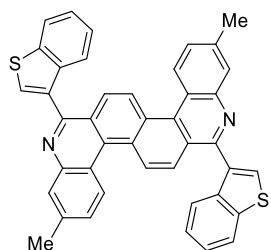
Yellow solid, 26.6 mg, 36% yield, $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 9.14 (d, $J = 9.0$ Hz, 2H), 8.84 (d, $J = 8.5$ Hz, 2H), 8.21 (s, 2H), 8.16 (d, $J = 9.0$ Hz, 2H), 7.63 – 7.58 (m, 6H), 7.55 (dd, $J = 8.5, 2.0$ Hz, 2H), 2.65 (s, 6H), 1.42 (s, 36H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 161.4, 150.8, 145.9, 139.0, 139.0, 132.2, 131.2, 129.9, 128.6, 127.4, 127.0, 125.5, 124.2, 124.0, 122.9, 121.5, 35.1, 31.6, 21.6. **HRMS** (ESI) m/z : $[\text{M}+\text{H}]^+$ for $\text{C}_{54}\text{H}_{59}\text{N}_2$ 7 calcd 35.4673, found 735.4675.

2,10-Dimethyl-7,15-di(naphthalen-2-yl)phenanthridino[10,9-k]phenanthridine (3j)



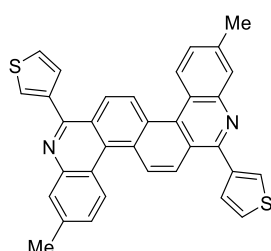
Yellow solid, 22.1 mg, 36% yield, $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 9.10 (d, $J = 9.0$ Hz, 2H), 8.83 (d, $J = 8.5$ Hz, 2H), 8.29 (s, 2H), 8.23 – 8.16 (m, 4H), 8.06 (d, $J = 8.5$ Hz, 2H), 7.98 (d, $J = 9.5$ Hz, 4H), 7.93 (d, $J = 8.5$ Hz, 2H), 7.62 – 7.51 (m, 6H), 2.64 (s, 6H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 160.1, 145.9, 139.3, 137.3, 133.4, 133.3, 132.3, 131.3, 129.9, 129.5, 128.9, 128.5, 128.2, 127.9, 127.6, 127.5, 127.1, 126.7, 126.5, 125.3, 123.9, 121.4, 21.6. **HRMS** (ESI) m/z : $[\text{M}+\text{H}]^+$ for $\text{C}_{46}\text{H}_{31}\text{N}_2$ calcd 611.2482, found 611.2482.

7,15-Bis(benzo[b]thiophen-3-yl)-2,10-dimethylphenanthridino[10,9-*k*]phenanthridine (3k)



Yellow solid, 19.4 mg, 31% yield, $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 9.12 (d, J = 9.0 Hz, 2H), 8.84 (d, J = 8.5 Hz, 2H), 8.21 (s, 2H), 8.11 (d, J = 9.0 Hz, 2H), 8.02 (d, J = 8.0 Hz, 2H), 7.86 (s, 2H), 7.72 (d, J = 7.5 Hz, 2H), 7.57 (dd, J = 8.5, 2.0 Hz, 2H), 7.46 – 7.41 (m, 2H), 7.38 – 7.33 (m, 2H), 2.66 (s, 6H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 155.2, 146.1, 140.3, 139.4, 139.2, 135.5, 132.2, 131.4, 129.9, 129.1, 127.9, 127.7, 127.1, 125.0, 124.8, 124.7, 124.6, 123.8, 122.7, 121.6, 21.6. **HRMS** (ESI) m/z : $[\text{M}+\text{H}]^+$ for $\text{C}_{42}\text{H}_{27}\text{N}_2\text{S}_2$ calcd 623.1610, found 623.1611.

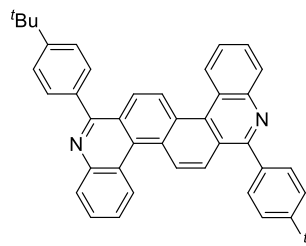
2,10-Dimethyl-7,15-di(thiophen-3-yl)phenanthridino[10,9-*k*]phenanthridine (3l)



Yellow solid, 28.7 mg, 55% yield, $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 9.12 (d, J = 9.0 Hz, 2H), 8.80 (d, J = 8.5 Hz, 2H), 8.33 (d, J = 9.0 Hz, 2H), 8.18 (s, 2H), 7.84 (dd, J = 3.0, 1.3 Hz, 2H), 7.64 (dd, J = 5.0, 1.3 Hz, 2H), 7.59 – 7.52 (m, 4H), 2.66 (s, 6H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 155.5, 145.9, 140.9, 139.2, 132.2, 131.2, 129.8, 129.5, 128.8, 127.6, 127.0, 126.6, 125.9, 124.8, 123.9, 121.4, 21.6.

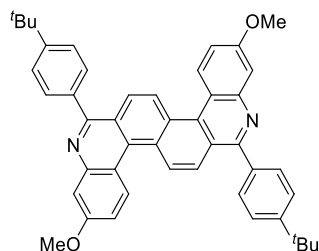
HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ for $\text{C}_{34}\text{H}_{23}\text{N}_2\text{S}_2$ calcd 523.1297, found 523.1296.

7,15-Bis(4-(*tert*-butyl)phenyl)phenanthridino[10,9-*k*]phenanthridine (3m)



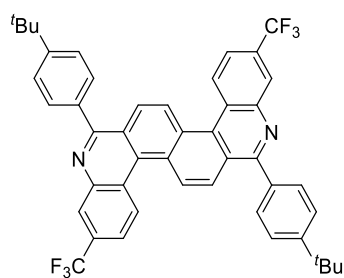
Yellow solid, 25.2 mg, 42% yield, $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 9.18 (d, J = 9.0 Hz, 2H), 8.94 (d, J = 8.5 Hz, 2H), 8.43 (dd, J = 8.5, 1.5 Hz, 2H), 8.27 (d, J = 9.0 Hz, 2H), 7.86 – 7.81 (m, 2H), 7.78 (d, J = 8.5 Hz, 4H), 7.75 – 7.70 (m, 2H), 7.64 (d, J = 8.5 Hz, 4H), 1.44 (s, 18H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 160.3, 152.1, 145.5, 136.6, 132.2, 131.4, 130.3, 129.7, 129.0, 127.9, 127.3, 126.9, 125.6, 125.5, 124.2, 123.5, 34.9, 31.4. **HRMS** (ESI) m/z : $[\text{M}+\text{H}]^+$ for $\text{C}_{44}\text{H}_{39}\text{N}_2$ calcd 595.3108, found 595.3110.

7,15-Bis(4-(*tert*-butyl)phenyl)-2,10-dimethoxyphenanthridino[10,9-*k*]phenanthridine (3n)



Yellow solid, 35.2 mg, 54% yield, $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 9.00 (d, J = 9.0 Hz, 2H), 8.81 (d, J = 9.0 Hz, 2H), 8.18 (d, J = 9.0 Hz, 2H), 7.78 (d, J = 3.0 Hz, 2H), 7.74 (d, J = 8.5 Hz, 4H), 7.62 (d, J = 8.5 Hz, 4H), 7.33 (dd, J = 9.0, 3.0 Hz, 2H), 4.01 (s, 6H), 1.43 (s, 18H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 160.8, 160.0, 151.8, 147.6, 137.0, 132.4, 131.1, 129.6, 128.4, 126.8, 125.5, 125.3, 123.1, 118.3, 118.0, 109.7, 55.6, 34.8, 31.4. **HRMS** (ESI) m/z : $[\text{M}+\text{H}]^+$ for $\text{C}_{46}\text{H}_{43}\text{N}_2\text{O}_2$ calcd 655.3319, found 655.3321.

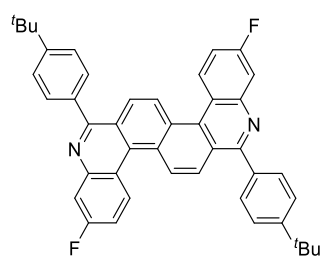
7,15-Bis(4-(*tert*-butyl)phenyl)-2,10-bis(trifluoromethyl)phenanthridino[10,9-*k*]phenanthridine (3o)



Yellow solid, 23.5 mg, 32% yield, ^1H NMR (400 MHz, CDCl_3) δ 9.20 (d, J = 9.0 Hz, 2H), 9.04 (d, J = 8.5 Hz, 2H), 8.72 (s, 2H), 8.38 (d, J = 9.0 Hz, 2H), 7.91 (dd, J = 9.0, 2.0 Hz, 2H), 7.79 (d, J = 8.0 Hz, 4H), 7.67 (d, J = 8.5 Hz, 4H), 1.45 (s, 18H). ^{19}F NMR (471 MHz, CDCl_3) δ -62.42. ^{13}C NMR (100 MHz, CDCl_3) δ 161.8, 152.6, 145.1, 136.1, 131.6, 131.4, 130.7 (q, J = 32.8 Hz), 129.7, 128.6, 128.2, 126.0, 125.7, 125.4, 125.1, 124.0 (q, J = 272.2

Hz), 122.5 (q, J = 3.8 Hz), 34.9, 31.4. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ for $\text{C}_{46}\text{H}_{37}\text{F}_6\text{N}_2$ calcd 731.2855, found 731.2854.

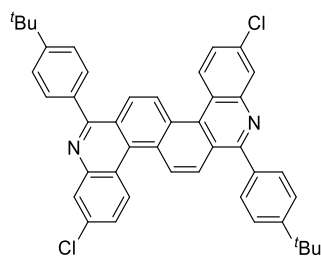
7,15-Bis(4-(*tert*-butyl)phenyl)-2,10-difluorophenanthridino[10,9-*k*]phenanthridine (3p)



Yellow solid, 25.9 mg, 41% yield, ^1H NMR (500 MHz, CDCl_3) δ 9.05 (d, J = 9.0 Hz, 2H), 8.90 (dd, J = 9.0, 6.0 Hz, 2H), 8.26 (d, J = 9.0 Hz, 2H), 8.03 (dd, J = 10.0, 3.0 Hz, 2H), 7.75 (d, J = 8.5 Hz, 4H), 7.64 (d, J = 8.5 Hz, 4H), 7.51 – 7.44 (m, 2H), 1.44 (s, 18H). ^{19}F NMR (471 MHz, CDCl_3) δ -111.09. ^{13}C NMR (126 MHz, CDCl_3) δ 162.5 (d, J = 250.5 Hz), 161.6, 152.2, 147.2

(d, J = 12.6 Hz), 136.5, 132.1, 131.1, 129.7, 129.2 (d, J = 8.8 Hz), 127.5, 125.7, 125.6, 123.8, 120.3 (d, 2.5 Hz), 116.1 (d, J = 23.9 Hz), 114.7 (d, J = 20.2 Hz), 34.9, 31.4. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ for $\text{C}_{44}\text{H}_{37}\text{F}_2\text{N}_2$ calcd 631.2919, found 631.2920.

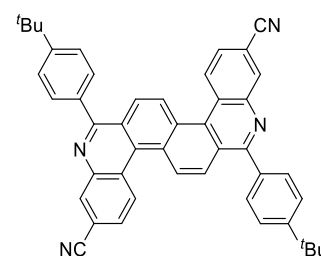
7,15-Bis(4-(*tert*-butyl)phenyl)-2,10-dichlorophenanthridino[10,9-*k*]phenanthridine (3q)



Yellow solid, 40.3 mg, 61% yield, ^1H NMR (500 MHz, CDCl_3) δ 9.04 (d, J = 9.0 Hz, 2H), 8.81 (d, J = 9.0 Hz, 2H), 8.37 (d, J = 2.5 Hz, 2H), 8.26 (d, J = 9.0 Hz, 2H), 7.76 – 7.71 (m, 4H), 7.66 – 7.61 (m, 6H), 1.44 (s, 18H). ^{13}C NMR (126 MHz, CDCl_3) δ 161.5, 152.3, 146.5, 136.4, 134.6, 131.9, 131.2, 129.7, 129.6, 128.4, 127.7, 127.3, 125.7, 125.6, 124.2, 121.9, 34.9, 31.4.

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ for $\text{C}_{44}\text{H}_{37}\text{Cl}_2\text{N}_2$ calcd 663.2328, found 663.2330.

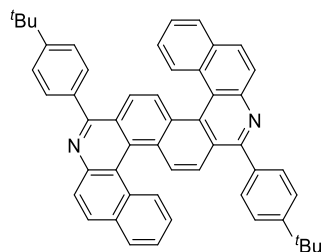
7,15-Bis(4-(*tert*-butyl)phenyl)phenanthridino[10,9-*k*]phenanthridine-2,10-dicarbonitrile (3r)



Yellow solid, 14.5 mg, 22% yield, ^1H NMR (500 MHz, CDCl_3) δ 9.17 (d, J = 9.0 Hz, 2H), 8.99 (d, J = 9.0 Hz, 2H), 8.74 (d, J = 2.0 Hz, 2H), 8.40 (d, J = 9.0 Hz, 2H), 7.89 (dd, J = 9.0, 2.0 Hz, 2H), 7.78 (d, J = 8.5 Hz, 4H), 7.67 (d, J = 8.5 Hz, 4H), 1.45 (s, 18H). ^{13}C NMR (126 MHz, CDCl_3) δ 162.3, 152.8,

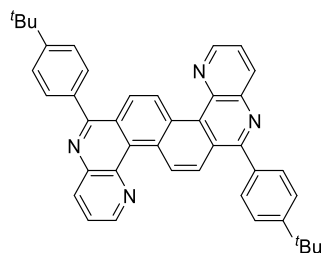
145.0, 135.8, 135.7, 131.4, 129.7, 128.9, 128.4, 128.0, 126.2, 126.2, 125.8, 125.4, 118.5, 112.4, 34.9, 31.4. **HRMS** (ESI) m/z : $[M+H]^+$ for $C_{46}H_{37}N_4$ calcd 645.3013, found 645.3012.

9,19-Bis(4-(*tert*-butyl)phenyl)benzo[*a*]benzo[1,2]phenanthridino[10,9-*k*]phenanthridine (3s)



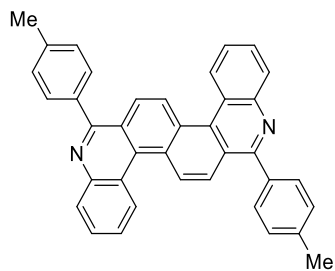
Yellow solid, 17.5 mg, 25% yield, **1H NMR** (500 MHz, $CDCl_3$) δ 8.78 (d, J = 8.5 Hz, 2H), 8.48 (d, J = 9.0 Hz, 2H), 8.29 (d, J = 9.0 Hz, 2H), 8.16 (d, J = 9.0 Hz, 2H), 8.05 (d, J = 9.5 Hz, 2H), 7.90 (d, J = 9.0 Hz, 2H), 7.76 (d, J = 8.5 Hz, 4H), 7.62 (t, J = 6.9 Hz, 2H), 7.58 (d, J = 8.3 Hz, 4H), 7.46 (t, J = 8.4 Hz, 2H), 1.38 (s, 18H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.7, 152.1, 145.0, 136.1, 132.6, 132.1, 131.9, 130.5, 129.8, 129.8, 129.3, 128.5, 128.4, 128.0, 127.0, 125.7, 125.6, 125.5, 123.2, 120.0, 34.8, 31.4. **HRMS** (ESI) m/z : $[M+H]^+$ for $C_{52}H_{43}N_2$ calcd 695.3421, found 695.3420.

7,15-bis(4-(*tert*-butyl)phenyl)naphtho[2,1-*c*:6,5-*c'*]bis([1,5]naphthyridine) (3t)



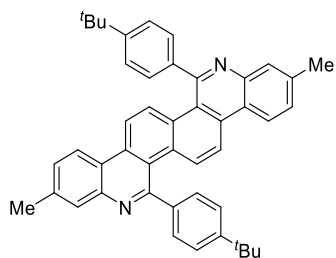
Gray solid, 8.6 mg, 14% yield, **1H NMR** (500 MHz, $CDCl_3$) δ 11.46 (d, J = 9.5 Hz, 2H), 9.19 (dd, J = 4.0, 2.0 Hz, 2H), 8.67 (dd, J = 8.0, 2.0 Hz, 2H), 8.53 (d, J = 9.5 Hz, 2H), 7.81 (d, J = 8.0 Hz, 4H), 7.77 (dd, J = 8.0, 4.0 Hz, 2H), 7.66 (d, J = 8.0 Hz, 4H), 1.46 (s, 18H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.3, 152.1, 148.5, 142.7, 140.7, 138.2, 136.9, 132.6, 132.3, 129.9, 129.8, 127.1, 126.5, 125.6, 123.2, 34.9, 31.4. **HRMS** (ESI) m/z : $[M+H]^+$ for $C_{42}H_{37}N_4$ calcd 597.3013, found 597.3011.

7,15-Di-*p*-tolylphenanthridino[10,9-*k*]phenanthridine (3u)



Yellow solid, 23.1 mg, 45% yield, **1H NMR** (500 MHz, $CDCl_3$) δ 9.16 (d, J = 9.0 Hz, 2H), 8.94 (d, J = 8.5 Hz, 2H), 8.40 (d, J = 9.5 Hz, 2H), 8.22 (d, J = 9.1 Hz, 2H), 7.83 (t, J = 7.6 Hz, 2H), 7.73 (d, J = 7.9 Hz, 6H), 7.42 (d, J = 7.7 Hz, 4H), 2.51 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.3, 145.7, 138.8, 136.9, 132.1, 131.3, 130.5, 129.9, 129.3, 128.9, 127.9, 127.3, 126.8, 125.4, 124.2, 123.5, 21.4. **HRMS** (ESI) m/z : $[M+H]^+$ for $C_{38}H_{27}N_2$ calcd 511.2169, found 511.2171.

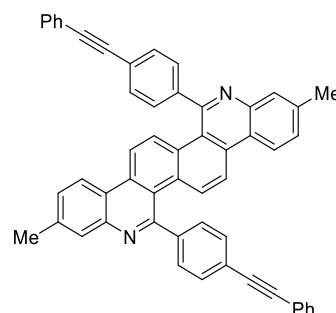
7,15-Bis(4-(*tert*-butyl)phenyl)phenanthridino[8,7-*i*]phenanthridine (3v)



Yellow solid, 28.3 mg, 48% yield, $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.38 (d, J = 8.5 Hz, 2H), 8.19 – 8.11 (m, 4H), 8.05 (s, 2H), 7.62 (d, J = 8.5 Hz, 4H), 7.52 (d, J = 8.5 Hz, 4H), 7.49 (dd, J = 8.5, 2.0 Hz, 2H), 2.61 (s, 6H), 1.41 (s, 18H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 158.8, 151.9, 144.0, 140.9, 139.6, 133.7, 131.6, 130.8, 129.1, 128.9, 126.1, 122.0, 121.0, 120.7, 118.5, 34.8, 31.4, 21.7. **HRMS** (ESI) m/z : $[\text{M}+\text{H}]^+$ for $\text{C}_{46}\text{H}_{43}\text{N}_2$ calcd 623.3421, found

623.3423.

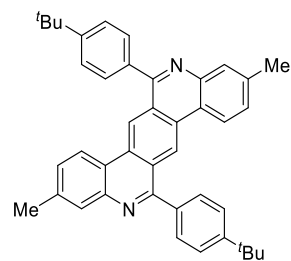
2,10-Dimethyl-7,15-bis(4-(phenylethynyl)phenyl)phenanthridino[8,7-*i*]phenanthridine (3w)



Yellow solid, 31.9 mg, 45% yield, $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.43 (d, J = 8.5 Hz, 2H), 8.30 (d, J = 9.5 Hz, 2H), 8.18 (d, J = 9.5 Hz, 2H), 8.06 (s, 2H), 7.77 – 7.73 (m, 4H), 7.72 – 7.68 (m, 4H), 7.62 – 7.58 (m, 4H), 7.53 (dd, J = 8.5, 1.8 Hz, 2H), 7.41 – 7.36 (m, 6H), 2.62 (s, 6H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 158.0, 144.4, 143.9, 139.8, 133.8, 132.4, 131.7, 131.6, 130.5, 129.4, 129.3, 128.5, 128.4, 123.6, 123.2, 122.2, 120.9, 120.8, 118.9, 90.7,

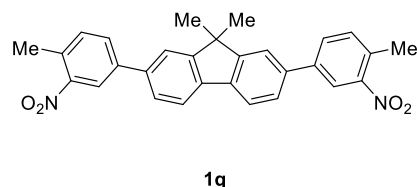
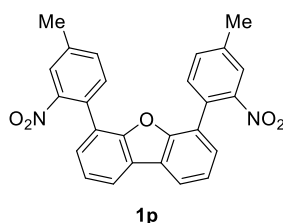
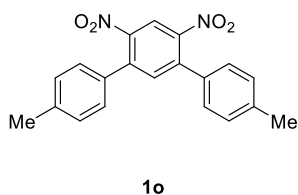
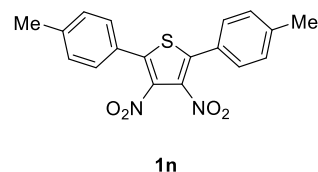
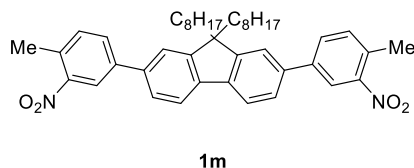
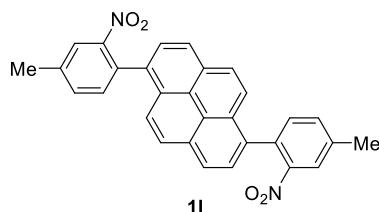
89.4, 21.6. **HRMS** (ESI) m/z : $[\text{M}+\text{H}]^+$ for $\text{C}_{54}\text{H}_{35}\text{N}_2$ calcd 711.2792, found 711.2796.

6,13-Bis(4-(*tert*-butyl)phenyl)-3,10-dimethylquinolino[4,3-*j*]phenanthridine (3x)

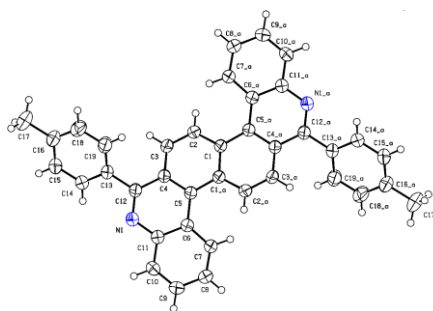
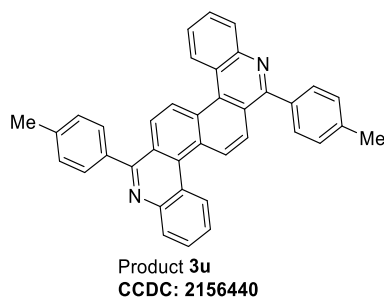


Yellow solid, 10.4 mg, 18% yield, $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.93 (s, 2H), 8.53 (d, J = 8.5 Hz, 2H), 8.00 (s, 2H), 7.53 (d, J = 8.5 Hz, 3H), 7.17 – 6.86 (m, 7H), 2.62 (s, 6H), 1.35 (s, 18H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 158.8, 150.5, 144.6, 140.3, 139.3, 134.1, 129.3, 128.5, 127.2, 124.5, 121.9, 120.7, 119.9, 34.5, 31.3, 21.6. **HRMS** (ESI) m/z : $[\text{M}+\text{H}]^+$ for $\text{C}_{42}\text{H}_{41}\text{N}_2$ calcd 573.3264, found 573.3265.

4.3 Unsuccessful Substrates

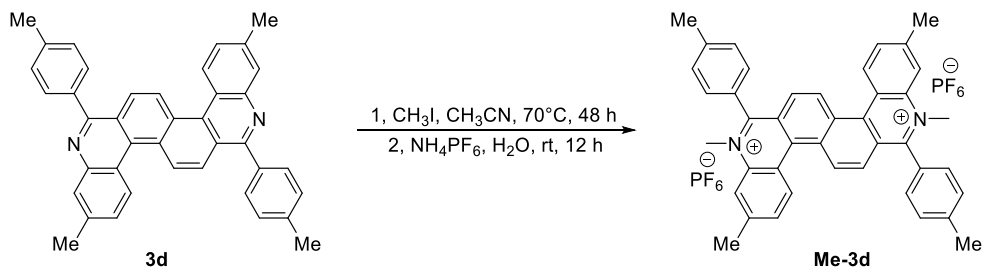


5. X-Ray Structure of Products 3u



6. Preparation of Designed Photocatalyst

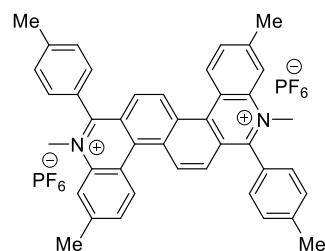
6.1. General Procedures C



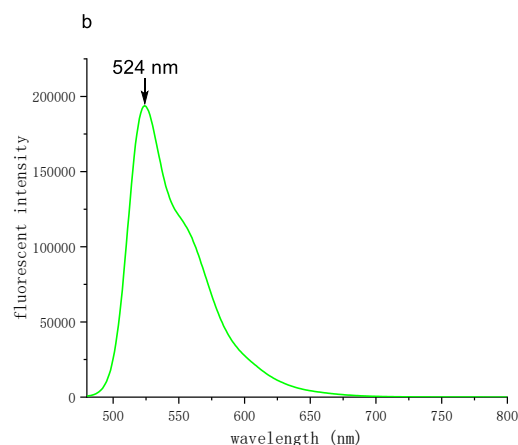
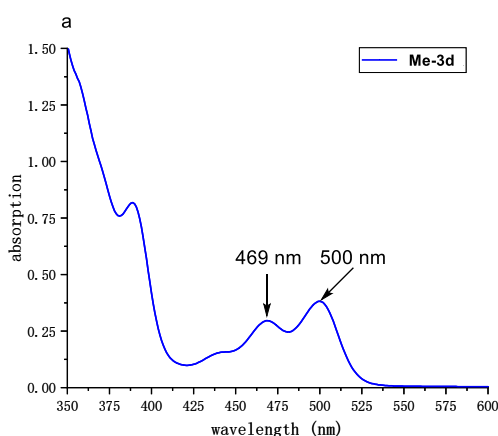
Based on previous work,^[1] in a flame-dried 10 mL Schlenk tube equipped with a magnetic stirrer bar was charged with **3d** (269.3 mg, 0.5 mmol, 1.0 eq), followed by the addition of CH₃CN (5 mL). Then, CH₃I (709.7 mg, 5.0 mmol, 10.0 eq) was added. The mixture was stirred for 48 h at 70 °C (heated by oil bath). The mixture was cooled to rt and after adding ether, a brown solid precipitated. Then, the mixture was filtered. The obtained red solid was dissolved in H₂O (5 mL), then NH₄PF₆ (326.0 mg, 2.0 mmol, 4.0 eq)

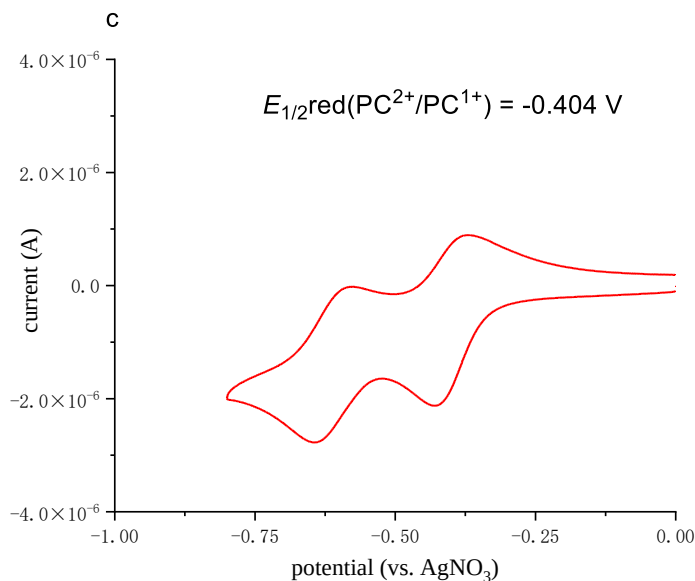
was added. The mixture was stirred at room temperature for 12 h, then filtered through Celite and extracted with CH₂Cl₂ (5 mL x 3). The combined organic layers were collected and dried over with Na₂SO₄, and concentrated under reduced pressure to give crude product, which was purified by column chromatography on silica gel (CH₂Cl₂/MeOH = 10:1 as eluent) to afford **Me-3d** in 66% yield.

6.2. Characterization of Me-3d



Red solid, ¹H NMR (500 MHz, DMSO-d₆) δ 9.26 (d, J = 9.0 Hz, 2H), 9.01 (d, J = 8.5 Hz, 2H), 8.71 (s, 2H), 8.05 (d, J = 9.0 Hz, 2H), 7.79 (d, J = 9.0 Hz, 2H), 7.73 (d, J = 8.0 Hz, 4H), 7.68 (d, J = 8.0 Hz, 4H), 4.44 (s, 6H), 2.80 (s, 6H), 2.56 (s, 6H). ¹⁹F NMR (471 MHz, DMSO-d₆) δ -69.4, -71.0. ¹³C NMR (126 MHz, DMSO-d₆) δ 162.4, 144.7, 142.2, 137.1, 134.9, 132.7, 132.1, 130.8, 130.5, 129.7, 129.6, 128.8, 128.2, 125.9, 123.3, 120.6, 44.5, 22.2, 21.7. HRMS (ESI) m/z for: C₄₂H₃₆N₂²⁺ [M-2PF₆]²⁻ calcd 858.2162, found 858.2166.





Supplementary Figure 2. (a) UV/vis absorption spectra of **Me-3d** in CH_2Cl_2 (1×10^{-5} M). (b) Fluorescent intensity for **Me-3d** in CH_2Cl_2 (1×10^{-5} M), $\lambda_{\text{em}} = 469$ nm. (c) Cyclic voltammetry (CV) was taken using a CHI660D potentiostation. CV measurement of **Me-3d** was carried out in 0.1 M of CH_3CN at a scan rate of 100 mV/s with the protection of Ar. The working electrode is a glassy carbon, the counter electrode is a Pt wire, and the reference electrode is Ag/AgCl. The results are as follow; **Me-3d** ($E_{1/2\text{red}}(\text{PC}^{2+}/\text{PC}^+) = -0.404$ V vs SCE in CH_3CN) $*E_{1/2\text{red}}(*\text{PC}^{2+}/\text{PC}^+) = E_{1/2\text{red}}(\text{PC}^{2+}/\text{PC}^+) + E_{0,0} = -0.404 + 2.425 = 2.02$ V (vs SCE).

7. Application of Me-3d in C-H Amination

7.1. General Procedure D



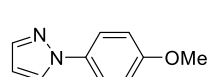
To a flask dried tube containing a Teflon-coated magnetic stir bar was added the arene (0.2 mmol, 1 eq), 0.2 mg of acridinium tetrafluoroborate (0.0002 mmol, 0.1 mol%), 27.2 mg of pyrazole (0.4 mmol, 2 eq), and 6.3 mg of (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (0.04 mmol, 0.2 eq.). The solids were dissolved in 1,2-Dichloroethane (2.0 mL). The vial was sealed with a Teflon-lined septum screw cap. The septum was pierced with a disposable steel needle connected to an oxygen-filled balloon. A vent needle was inserted and the reaction medium was sparged for 5 minutes by bubbling oxygen through the mixture. The vent needle was removed, and the oxygen balloon was maintained, providing approximately

1 atm of oxygen to the vial headspace for the course of the reaction. The resulting solution was stirred at room temperature under the irradiation of 2 x 10 W blue LEDs. After stirring for 48 h, the reaction mixture was concentrated in vacuo and purified by column chromatography on silica gel with Petroleum ether/ethyl acetate with the eluent noted for each substrate.

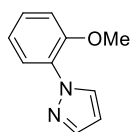
7.2. Characterization of Products

The NMR data were consistent with literature values.^[2-4]

1-(4-Methoxyphenyl)-1H-pyrazole (5a), 1-(2-Methoxyphenyl)-1H-pyrazole (5a'). Yellow oil, 25.5 mg, 73% yield as an inseparable mixture of **5a** and **5a'**. The para:ortho ratio of the inseparable mixture was 8:1 as determined by ¹H NMR of the isolated product.

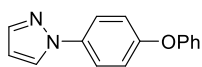


¹H NMR (500 MHz, CDCl₃) δ 7.82 (s, 1H), 7.69 (s, 1H), 7.59 (d, *J* = 9.0 Hz, 2H), 6.97 (d, *J* = 8.5 Hz, 2H), 6.43 (s, 1H), 3.84 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 158.3, 140.6, 134.1, 126.8, 120.9, 114.5, 107.2, 55.6.

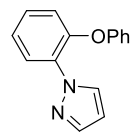


¹H NMR (500 MHz, CDCl₃) δ 8.03 (s, 1H), 7.73 – 7.70 (m, 1H), 7.69 (m, 1H), 7.32 – 7.27 (m, 1H), 7.09 – 7.02 (m, 2H), 6.43 (s, 1H), 3.88 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 151.4, 140.1, 131.6, 128.0, 125.3, 121.2, 112.3, 106.1, 56.0.

1-(4-Phenoxyphenyl)-1H-pyrazole (6a) and 1-(2-Phenoxyphenyl)-1H-pyrazole (6a'). Yellow solid, 38.2 mg, 81% yield as an inseparable mixture of **5b** and **5b'**. The para:ortho ratio of the mixture was 10.5:1 as determined by ¹H NMR of the isolated product.

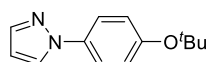


¹H NMR (500 MHz, CDCl₃) δ 7.85 (d, *J* = 2.5 Hz, 1H), 7.71 (d, *J* = 2.0 Hz, 1H), 7.64 (d, *J* = 9.0 Hz, 2H), 7.35 (dd, *J* = 8.5, 7.5 Hz, 2H), 7.14 – 7.10 (m, 1H), 7.08 (d, *J* = 9.0 Hz, 2H), 7.05–7.01 (m, 2H), 6.45 (t, *J* = 2.0 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 157.1, 155.8, 141.0, 136.0, 129.9, 126.8, 123.5, 120.9, 119.7, 118.9, 107.5.

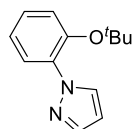


¹H NMR (500 MHz, CDCl₃) δ 8.07 (d, *J* = 2.5 Hz, 1H), 7.91 – 7.88 (m, 1H), 7.70 (d, *J* = 1.5 Hz, 1H), 7.32 – 7.27 (m, 2H), 7.25 (d, *J* = 4.0 Hz, 2H), 7.11 – 7.10 (m, 1H), 7.08 (d, *J* = 9.0 Hz, 1H), 6.98 – 6.94 (m, 2H), 6.36 (t, *J* = 2.0 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 156.7, 147.8, 140.5, 132.3, 131.2, 130.1, 127.8, 125.3, 124.5, 120.6, 118.2, 106.8.

1-(4-(*tert*-butoxy)phenyl)-1H-pyrazole (5c) and 1-(2-(*tert*-butoxy)phenyl)-1H-pyrazole (5c'). Yellow solid, 26.0 mg, in 60% as an inseparable mixture of **5c** and **5c'**. The para:ortho ratio of the mixture was 6.5:1 as determined by ¹H NMR of the isolated product.

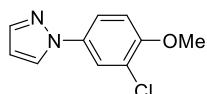


¹H NMR (500 MHz, CDCl₃) δ 7.85 (d, J = 2.5 Hz, 1H), 7.70 (d, J = 1.5 Hz, 1H), 7.57 (d, J = 9.0 Hz, 2H), 7.07 (d, J = 9.0 Hz, 2H), 6.48 (s, 1H), 1.41 (s, 9H). **¹³C NMR** (126 MHz, CDCl₃) δ 154.0, 140.8, 136.1, 126.8, 125.0, 120.0, 107.3, 79.0, 28.8.



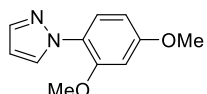
¹H NMR (500 MHz, CDCl₃) δ 8.07 (d, J = 2.5 Hz, 1H), 7.73 – 7.67 (m, 2H), 7.26 – 7.13 (m, 3H), 6.46 (s, 1H), 1.17 (s, 9H). **¹³C NMR** (126 MHz, CDCl₃) δ 147.0, 130.1, 135.7, 131.9, 127.3, 125.4, 124.4, 106.1, 81.0, 28.2.

1-(3-Chloro-4-methoxyphenyl)-1H-pyrazole (**5d**).



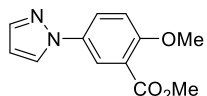
Yellow solid, 25.9 mg, 62% yield. **¹H NMR** (500 MHz, CDCl₃) δ 7.82 (d, J = 3.0 Hz, 1H), 7.74 (d, J = 2.5 Hz, 1H), 7.69 (d, J = 2.0 Hz, 1H), 7.54 (dd, J = 9.0, 2.5 Hz, 1H), 6.98 (d, J = 8.5 Hz, 1H), 6.45 (t, J = 2.2 Hz, 1H), 3.91 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 153.7, 141.0, 134.2, 126.8, 123.2, 121.7, 118.6, 112.4, 107.6, 56.5.

1-(2,4-Dimethoxyphenyl)-1H-pyrazole (**5e**).



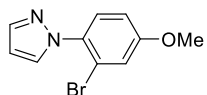
Yellow oil, 32.9 mg, 80% yield. **¹H NMR** (500 MHz, CDCl₃) δ 7.86 (d, J = 2.5 Hz, 1H), 7.68 (d, J = 2.0 Hz, 1H), 7.54 (d, J = 8.5 Hz, 1H), 6.62 – 6.52 (m, 2H), 6.40 (t, J = 2.0 Hz, 1H), 3.85 (s, 3H), 3.83 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 159.8, 152.9, 139.8, 131.4, 126.5, 123.7, 105.8, 104.6, 55.9, 55.6.

Methyl 2-methoxy-5-(1H-pyrazol-1-yl) benzoate (**5f**).

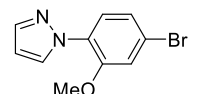


Yellow oil, 32.1 mg, 69% yield. **¹H NMR** (500 MHz, CDCl₃) δ 8.09 (d, J = 3.0 Hz, 1H), 7.88 (d, J = 2.5 Hz, 1H), 7.83 (dd, J = 9.0, 3.0 Hz, 1H), 7.70 (d, J = 1.5 Hz, 1H), 7.06 (d, J = 9.0 Hz, 1H), 6.46 (t, J = 2.2 Hz, 1H), 3.94 (s, 3H), 3.92 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 165.8, 157.7, 141.0, 133.4, 126.8, 124.5, 122.6, 120.5, 113.0, 107.6, 56.4, 52.2.

1-(2-Bromo-4-methoxyphenyl)-1H-pyrazole (5g**). 1-(4-Bromo-2-methoxyphenyl)-1H-pyrazole (**5g'**).** Yellow oil, 28.9 mg, 57% yield as an inseparable mixture of **5g** and **5g'**. The para:ortho ratio of the mixture was 10:1 as determined by ¹H NMR of the isolated product.



¹H NMR (500 MHz, CDCl₃) δ 7.71 (dd, J = 9.0, 2.0 Hz, 1H), 7.39 (d, J = 4.0 Hz, 1H), 7.21 (d, J = 3.0 Hz, 1H), 6.93 (dd, J = 8.5, 2.7 Hz, 2H), 6.43 (t, J = 2.7 Hz, 1H), 3.84 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 159.9, 140.5, 133.3, 131.5, 129.0, 119.9, 118.4, 113.9, 106.3, 55.8.



¹H NMR (500 MHz, CDCl₃) δ 7.73 (dd, J = 9.0, 2.0 Hz, 1H), 7.44 (d, J = 3.5 Hz, 1H), 7.03 (d, J = 2.5 Hz, 1H), 6.89 (dd, J = 8.7, 2.7 Hz, 2H), 6.44 (t, J = 2.5 Hz, 1H), 3.84 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 159.7, 140.6, 131.4, 129.9, 128.7, 115.4, 113.4, 106.3, 55.9.

8. Application of Me-3d in C-H Trifluoromethylation

8.1. General Procedure E

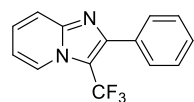


To a flask dried tube containing a Teflon-coated magnetic stir bar was added imidazo[1,2-*a*]pyridine **6a** (58.3 mg, 0.3 mmol, 1.5 eq), $\text{CF}_3\text{SO}_2\text{Na}$ (31.2 mg, 0.2 mmol, 1.0 eq), **Me-3d** (0.2 mg, 0.0002 mmol, 0.1 mol%) and 1,2-Dichloroethane (2.0 mL). The reaction mixture was stirred with a 2 x 10 W blue LED irradiation at room temperature for 24 h, filtered through a pad of celite and then washed with CH_2Cl_2 (10 mL×3). The solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel (elute: Petroleum ether/ethyl acetate) to give the desired product **7a**.

8.2. Characterization of Products

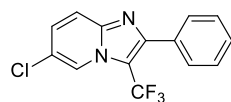
The NMR data were consistent with literature values.^[5]

2-Phenyl-3-(trifluoromethyl)imidazo[1,2-*a*]pyridine (**7a**)



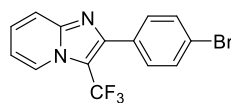
Yellow solid, 37.3 mg, 71% yield; ^1H NMR (500 MHz, CDCl_3) δ 8.32 (d, J = 7.0 Hz, 1H), 7.78-7.65 (m, 3H), 7.51-7.35 (m, 4H), 7.00 (t, J = 7.5 Hz, 1H); ^{19}F NMR (471 MHz, CDCl_3) δ -57.65. ^{13}C NMR (126 MHz, CDCl_3) δ 148.1, 146.1, 132.9, 129.6 (q, J = 1.8 Hz), 129.0, 128.2, 127.0, 125.5 (q, J = 4.0 Hz), 121.8 (q, J = 268.0 Hz), 118.1, 113.9, 109.3 (q, J = 38.2 Hz).

6-Chloro-2-phenyl-3-(trifluoromethyl)imidazo[1,2-*a*]pyridine (**7b**)



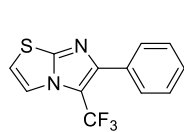
White solid, 50.3 mg, 85% yield, ^1H NMR (500 MHz, CDCl_3) δ 8.35 (s, 1H), 7.73-7.64 (m, 3H), 7.52-7.42 (m, 3H), 7.39-7.34 (m, 1H); ^{19}F NMR (471 MHz, CDCl_3) δ -57.67. ^{13}C NMR (126 MHz, CDCl_3) δ 148.8 (q, J = 2.4 Hz), 144.5, 132.4, 129.5 (q, J = 1.8 Hz), 129.2, 128.5, 128.3, 123.4 (q, J = 3.9 Hz), 122.4, 121.5 (q, J = 268.3 Hz), 118.4, 110.1 (q, J = 39.7).

2-(4-Bromophenyl)-3-(trifluoromethyl)imidazo[1,2-*a*]pyridine (**7c**)



White solid 27.4 mg, 40% yield, ^1H NMR (500 MHz, CDCl_3) δ 8.31 (d, J = 7.0 Hz, 1H), 7.73 (d, J = 9.5 Hz, 1H), 7.65-7.54 (m, 4H), 7.45-7.36 (m, 1H), 7.01 (t, J = 7.0 Hz, 1H). ^{19}F NMR (471 MHz, CDCl_3) δ -57.64. ^{13}C NMR (126 MHz, CDCl_3) δ 146.9 (q, J = 2.9 Hz), 146.2, 131.8, 131.4, 131.2 (q, J = 1.8 Hz), 127.2, 125.5 (q, J = 3.8 Hz), 123.5, 121.8 (q, J = 267.9 Hz), 118.1, 114.2, 109.7 (q, J = 39.8 Hz).

6-phenyl-5-(trifluoromethyl)imidazo[2,1-*b*]thiazole (7d)



Yellow oil, 44.1 mg, 82% yield, ^1H NMR (500 MHz, CDCl_3) δ 7.71 (d, J = 7.0 Hz, 2H),

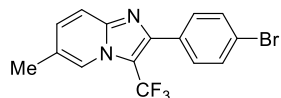
7.59 (dd, J = 4.5, 1.0 Hz, 1H), 7.49–7.38 (m, 3H), 6.99 (d, J = 4.5 Hz, 1H). ^{19}F NMR

(471 MHz, CDCl_3) δ -56.33. ^{13}C NMR (126 MHz, CDCl_3) δ 151.5, 149.1 (q, J = 2.8

Hz), 132.6, 128.9, 128.8 (q, J = 1.9 Hz), 128.4, 121.6 (q, J = 267.4 Hz), 119.0 (q, J = 2.0 Hz), 114.3,

111.8 (q, J = 40.8 Hz).

2-(4-Bromophenyl)-6-methyl-3-(trifluoromethyl)imidazo[1,2-*a*]pyridine (7e)



White solid, 35.7 mg, 50% yield, ^1H NMR (500 MHz, CDCl_3) δ 8.07 (s, 1H),

7.66 – 7.51 (m, 5H), 7.24 (dd, J = 9.0, 1.5 Hz, 1H), 2.41 (s, 3H). ^{19}F NMR (471

MHz, CDCl_3) δ -57.69. ^{13}C NMR (126 MHz, CDCl_3) δ 146.5 (q, J = 2.3 Hz), 145.2, 132.1, 131.4, 131.1

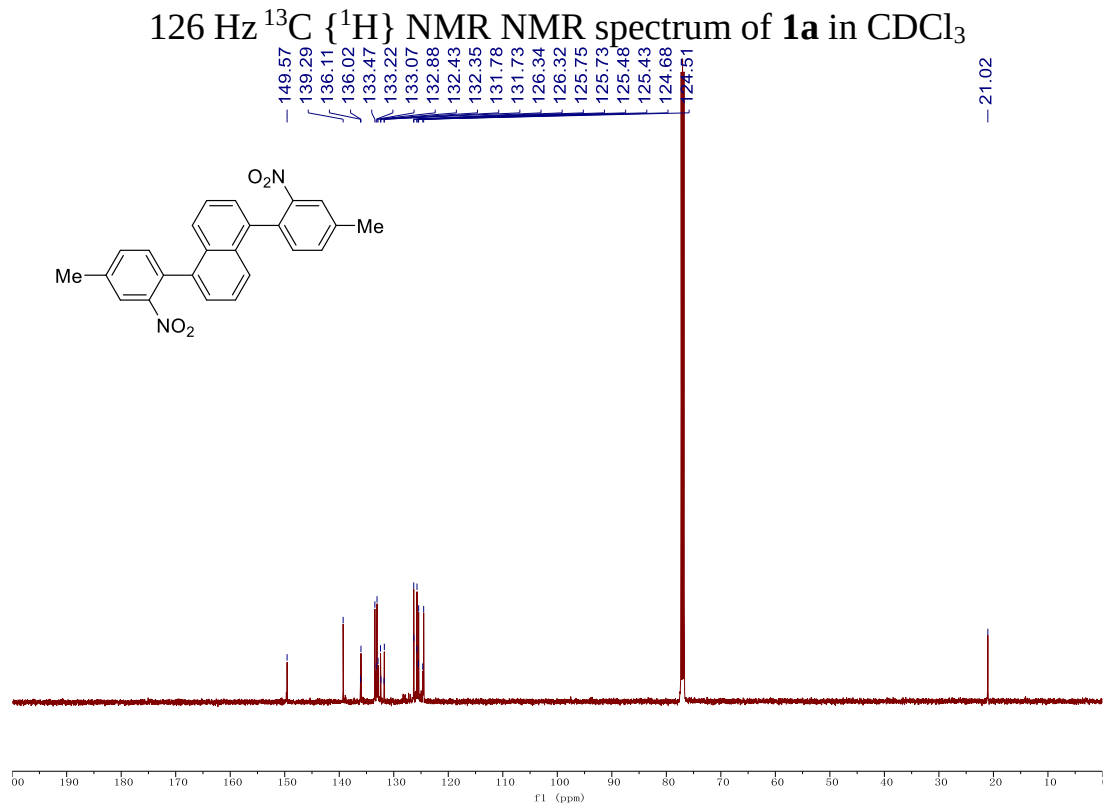
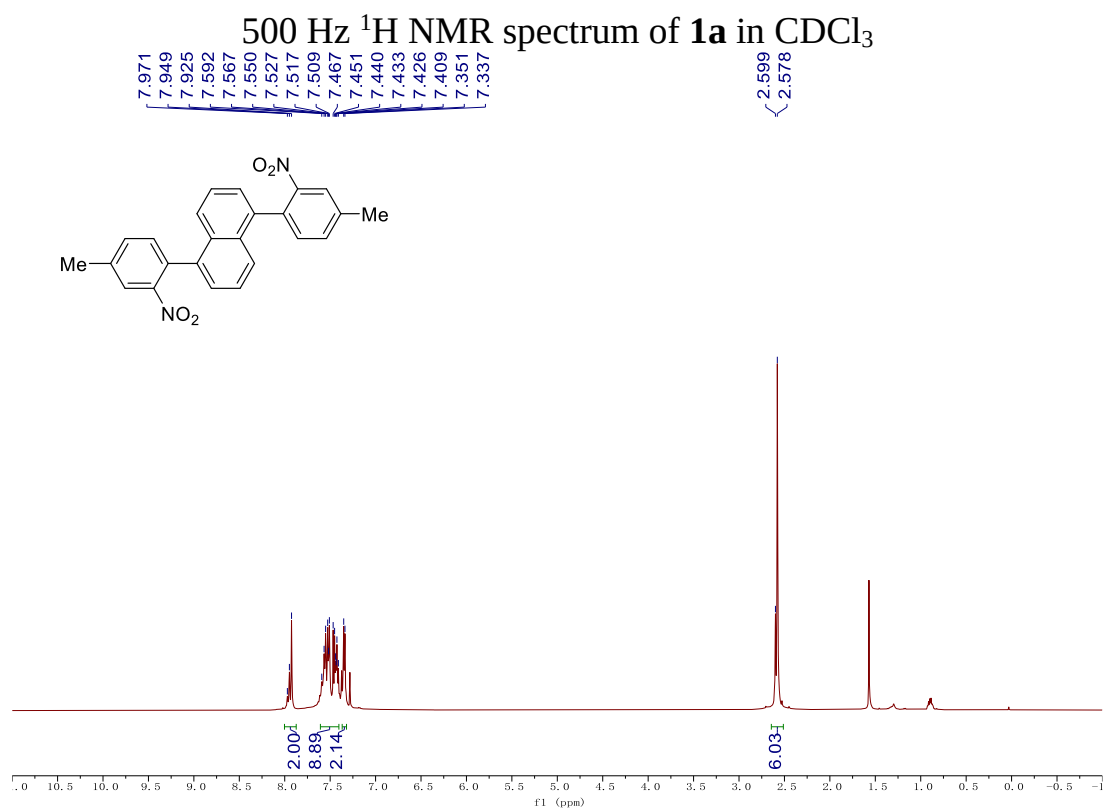
(q, J = 1.8 Hz), 130.3, 124.1, 123.3, 123.2 (q, J = 3.7 Hz), 121.9 (q, J = 267.9 Hz), 117.3, 109.3 (q, J =

39.6 Hz), 18.4. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ for $\text{C}_{15}\text{H}_{11}\text{BrF}_3\text{N}_2$ calcd 355.0052, found 355.0053.

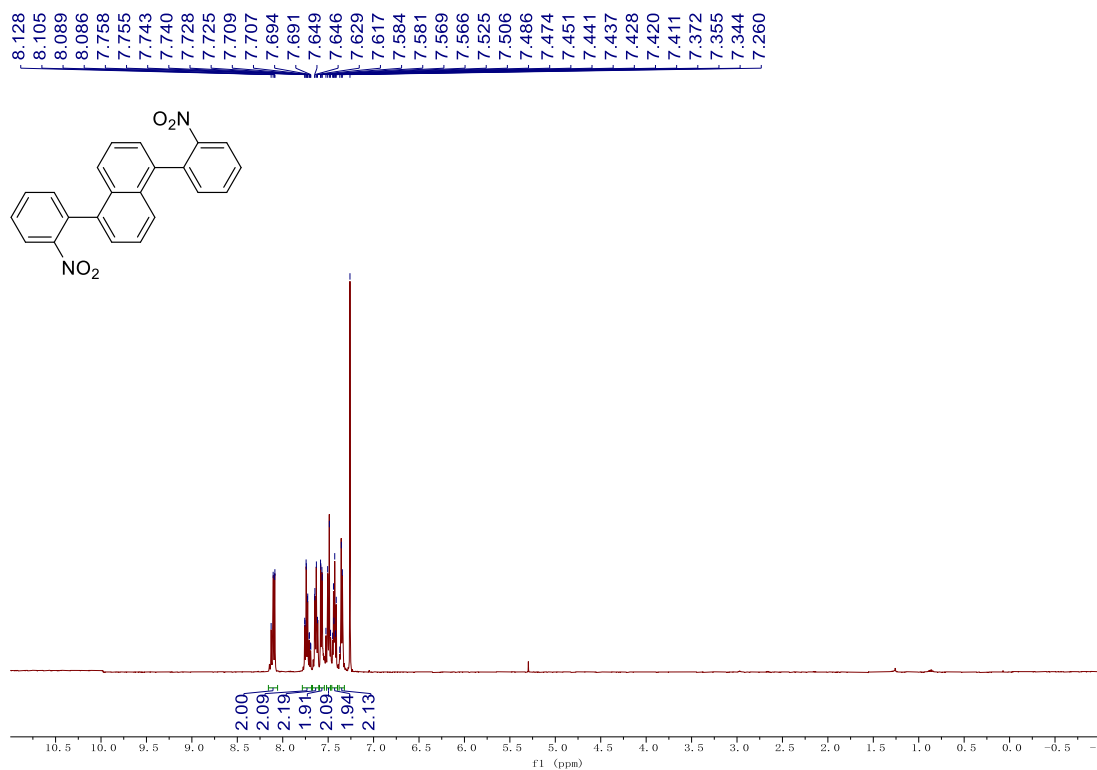
9. Reference

- 1, X. Jiang, W. Xiong, S. Deng, F. D. Lu, Y. Jia, Q. Yang, W. J. Xiao, *Nat. Catal.* **2022**, 5, 788–797.
- 2, N. A. Romero, K. A. Margrey, N. E. Tay, D. A. Nicewicz, *Science* **2015**, 349, 1326–1330.
- 3, K. A. Margrey, J. B. McManus, S. Bonazzi, F. Zecri, D. A. Nicewicz, *J. Am. Chem. Soc.* **2017**, 139, 11288–11299.
- 4, L. Zhang, L. Liardet, J. Luo, D. Ren, M. Grätzel, X. Hu, *Nat. Catal.* **2019**, 2, 366–373.
- 5, X. Mi, Y. Kong, H. Yang, J. Zhang, C. Pi, X. Cui, *Eur. J. Org. Chem.* **2020**, 1019–1022.

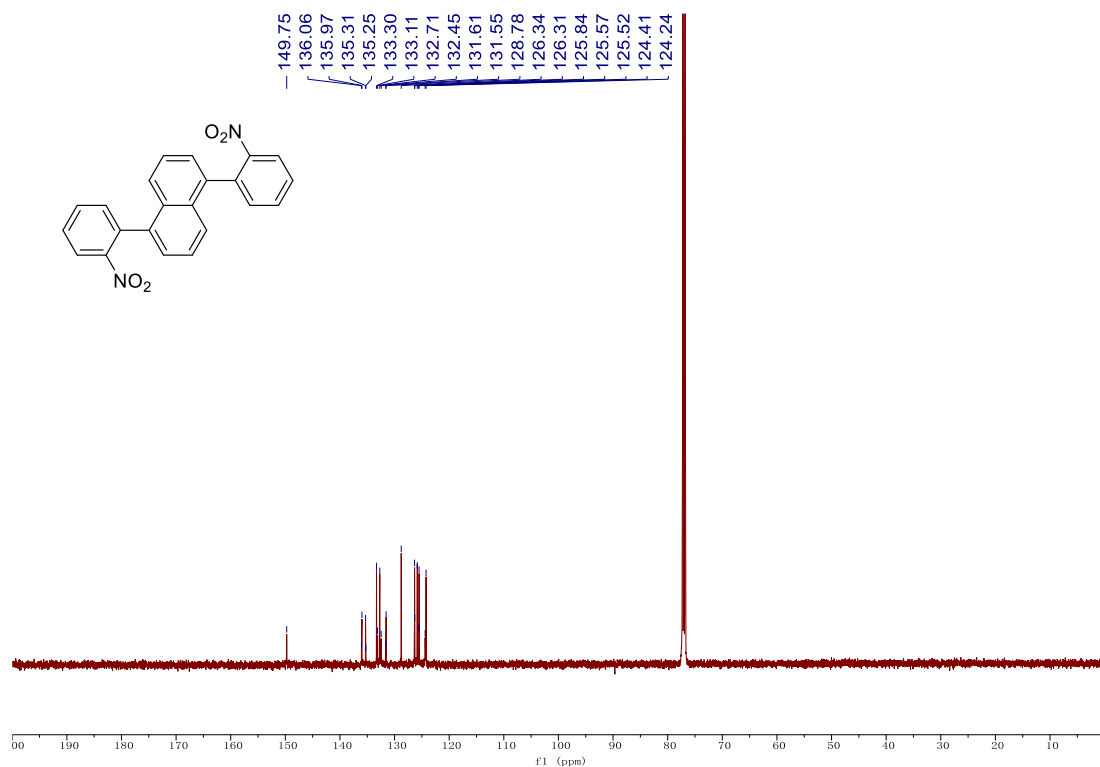
10. NMR Spectra



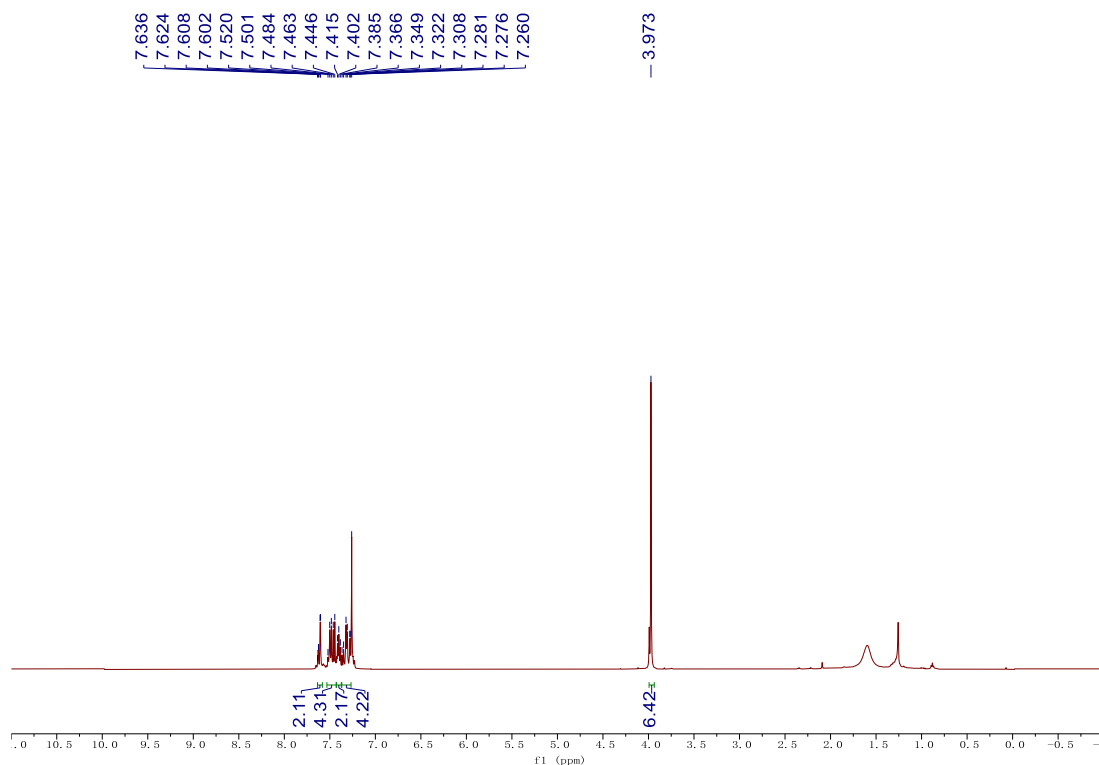
500 Hz ^1H NMR spectrum of **1b** in CDCl_3



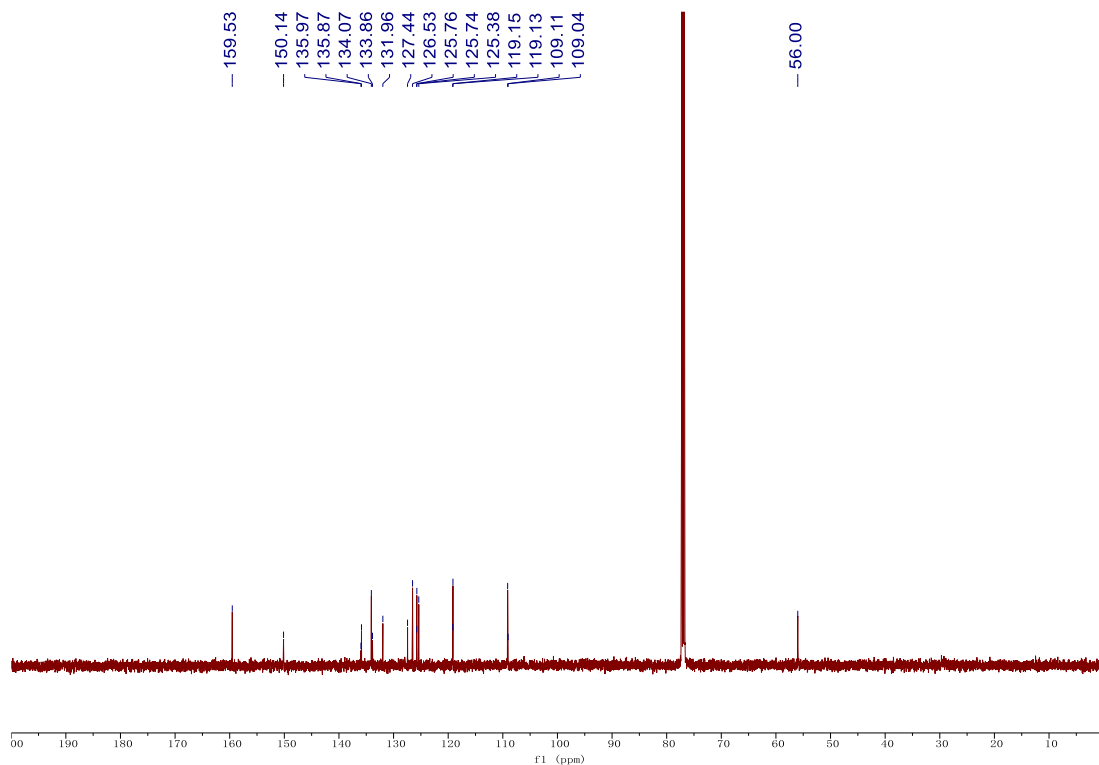
126 Hz ^{13}C $\{^1\text{H}\}$ NMR spectrum of **1b** in CDCl_3



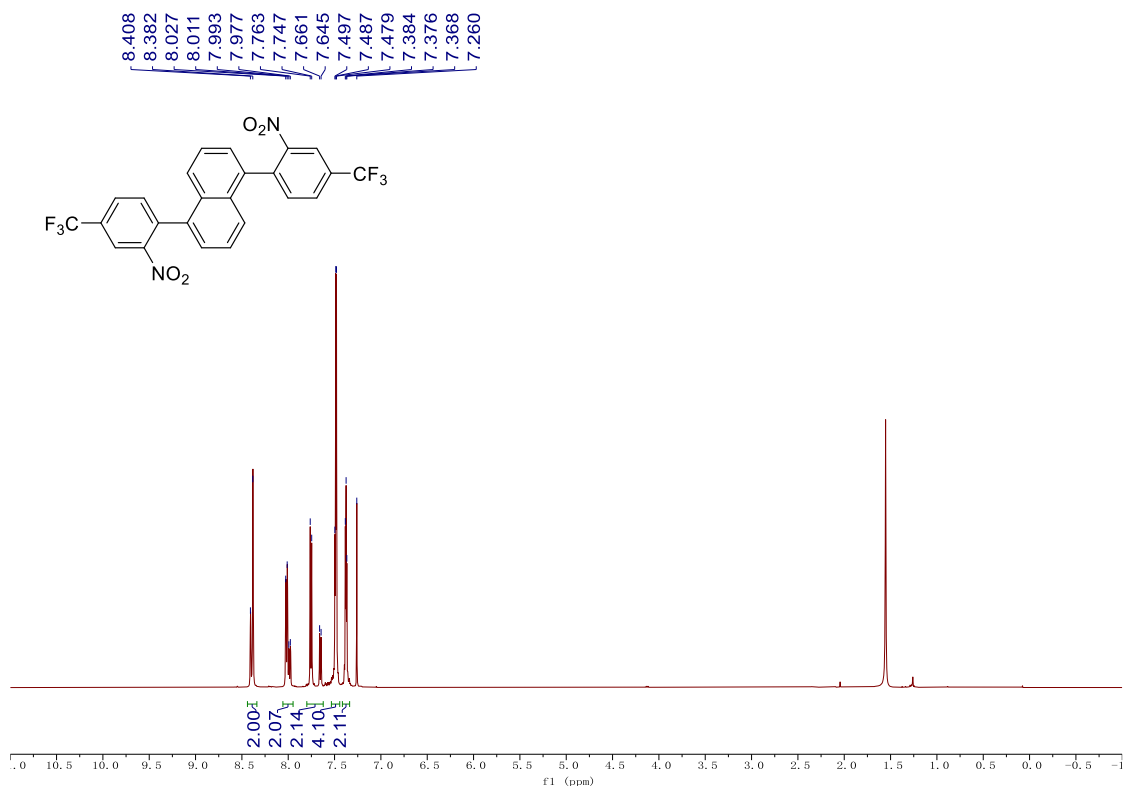
500 Hz ^1H NMR spectrum of **1c** in CDCl_3



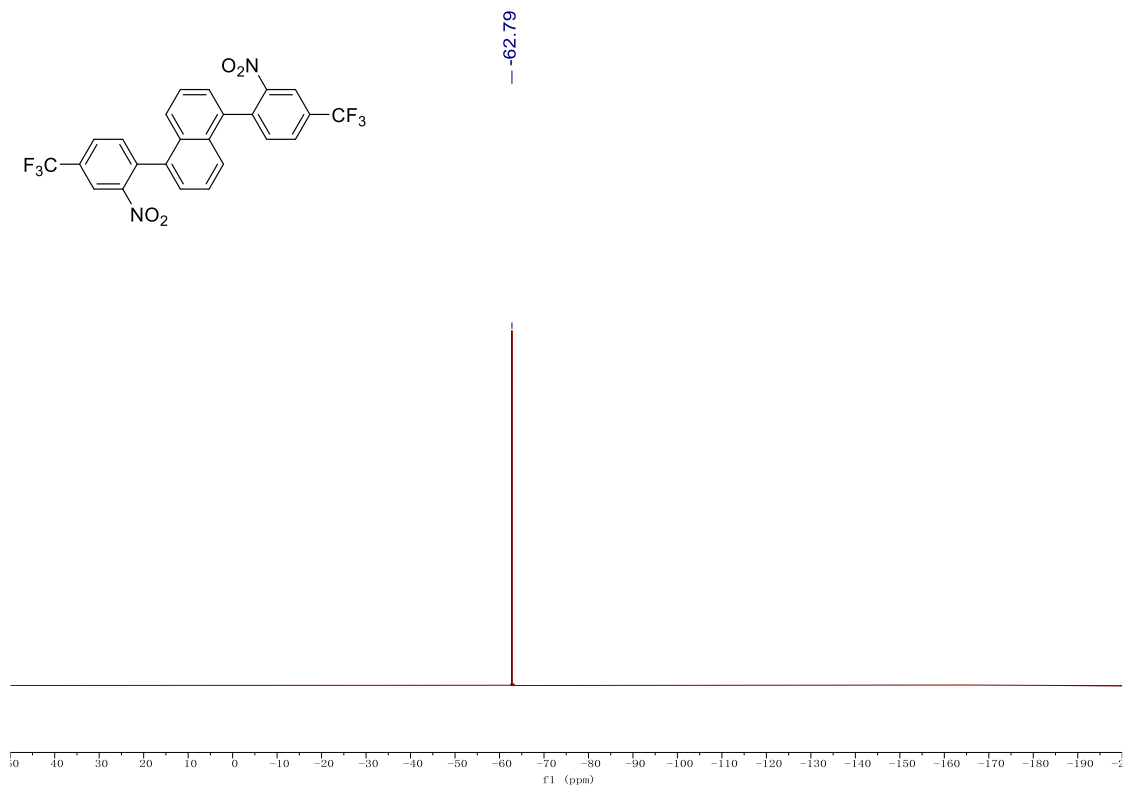
126 Hz ^{13}C $\{^1\text{H}\}$ NMR spectrum of **1c** in CDCl_3



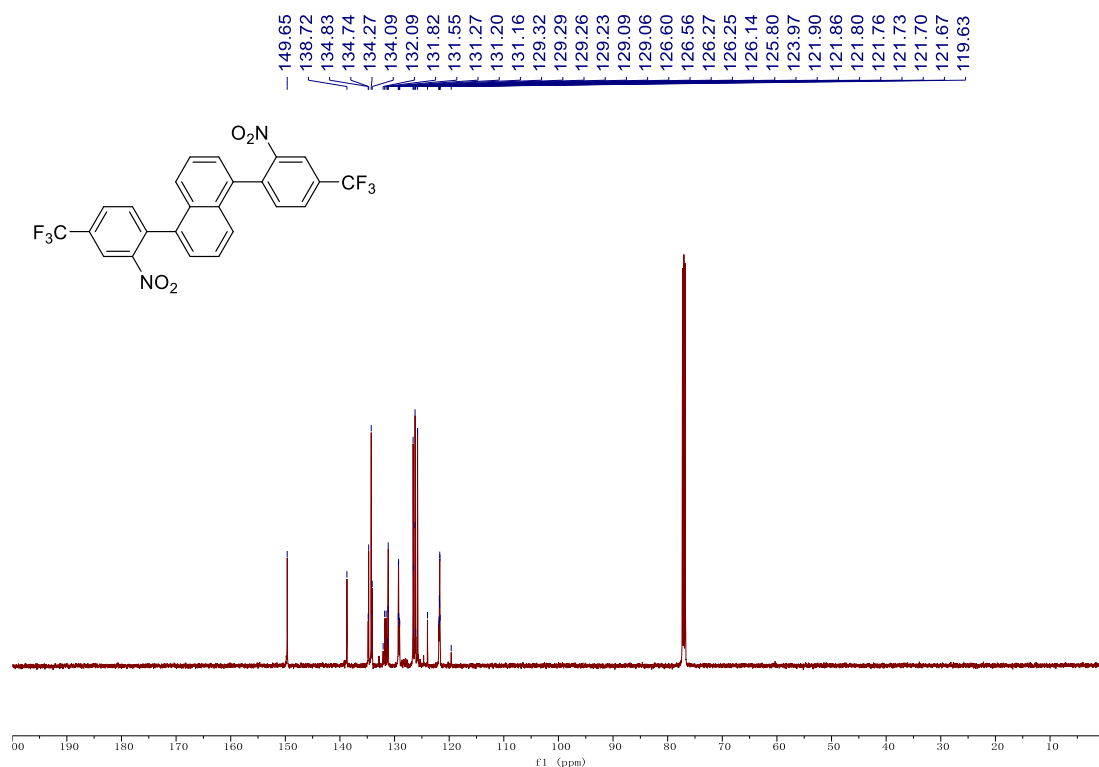
500 Hz ^1H NMR spectrum of **1d** in CDCl_3



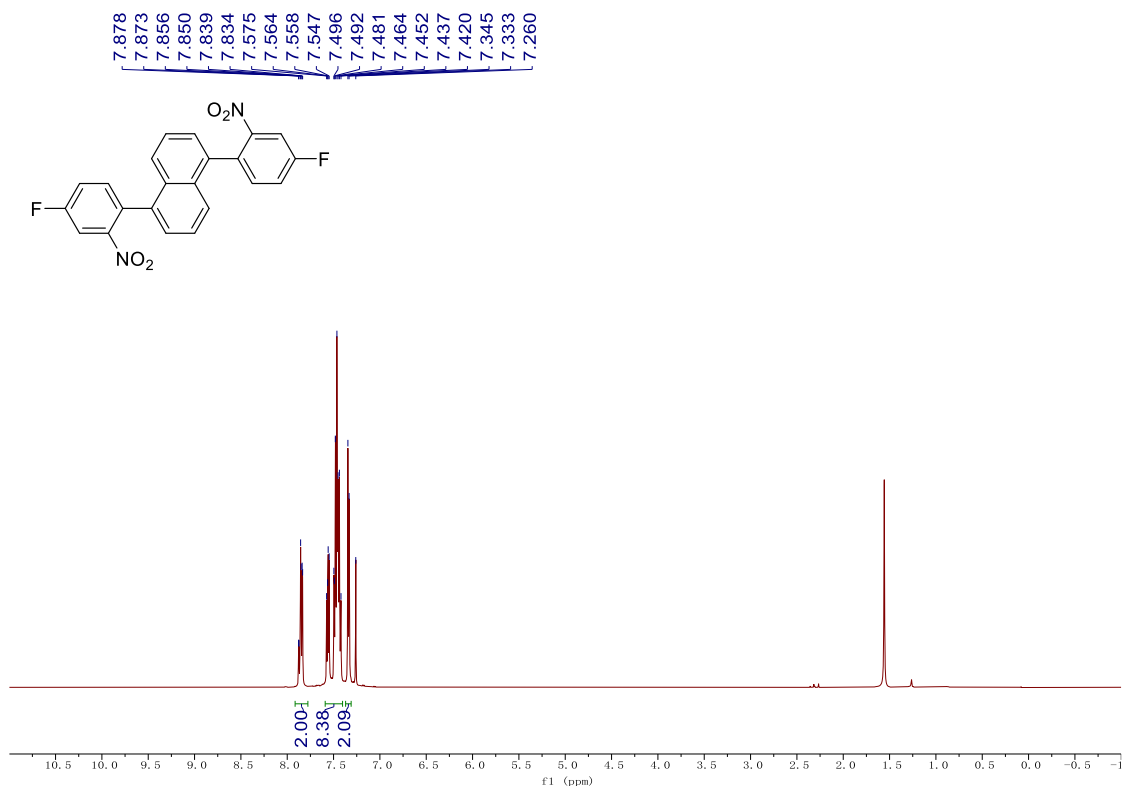
471 Hz ^{19}F $\{^1\text{H}\}$ NMR spectrum of **1d** in CDCl_3



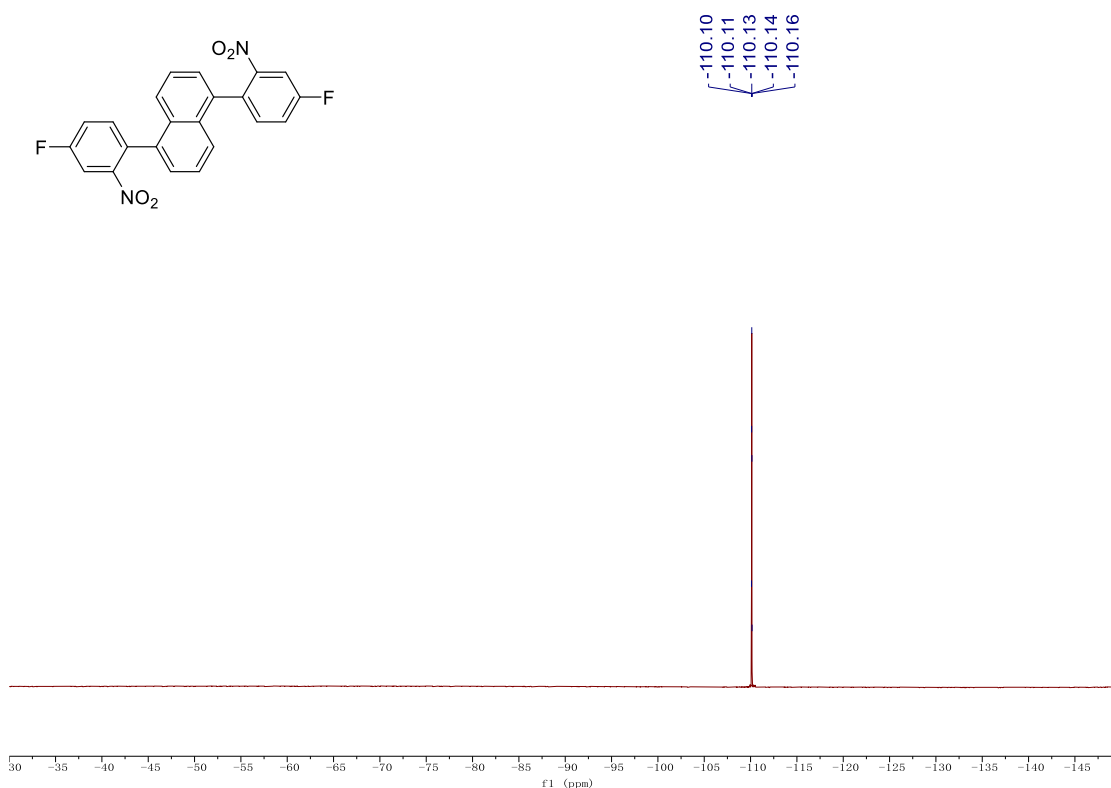
126 Hz ^{13}C $\{^1\text{H}\}$ NMR spectrum of **1d** in CDCl_3



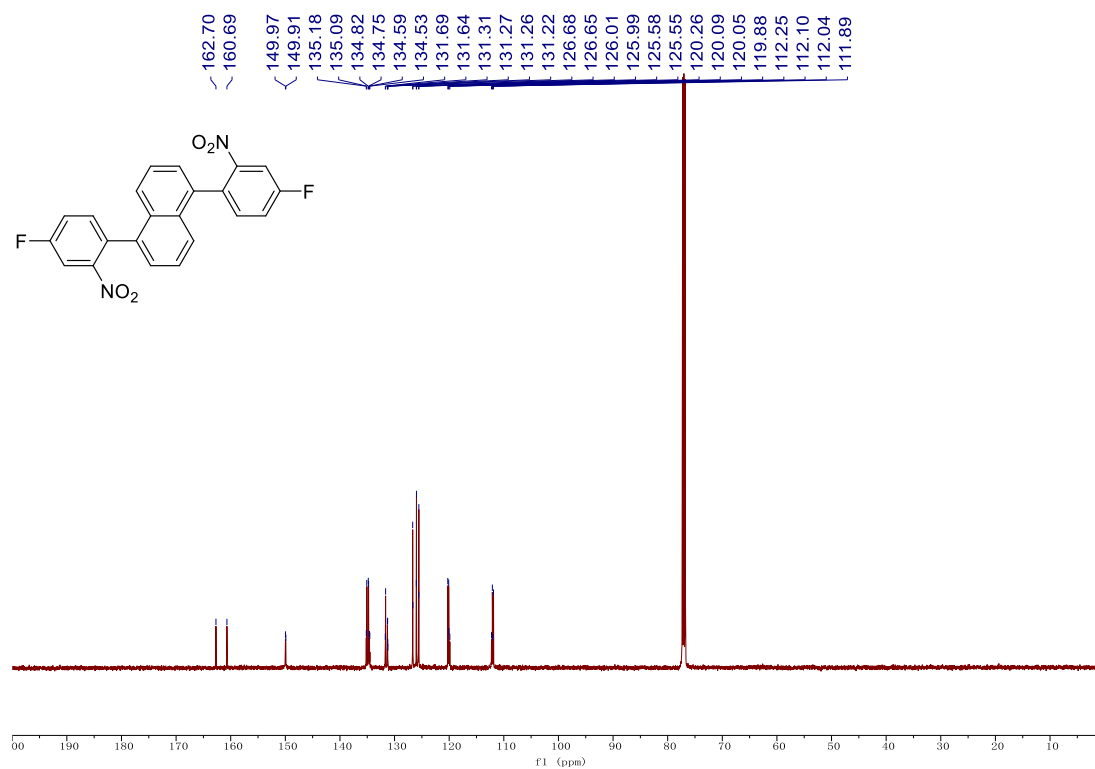
500 Hz ^1H NMR spectrum of **1e** in CDCl_3



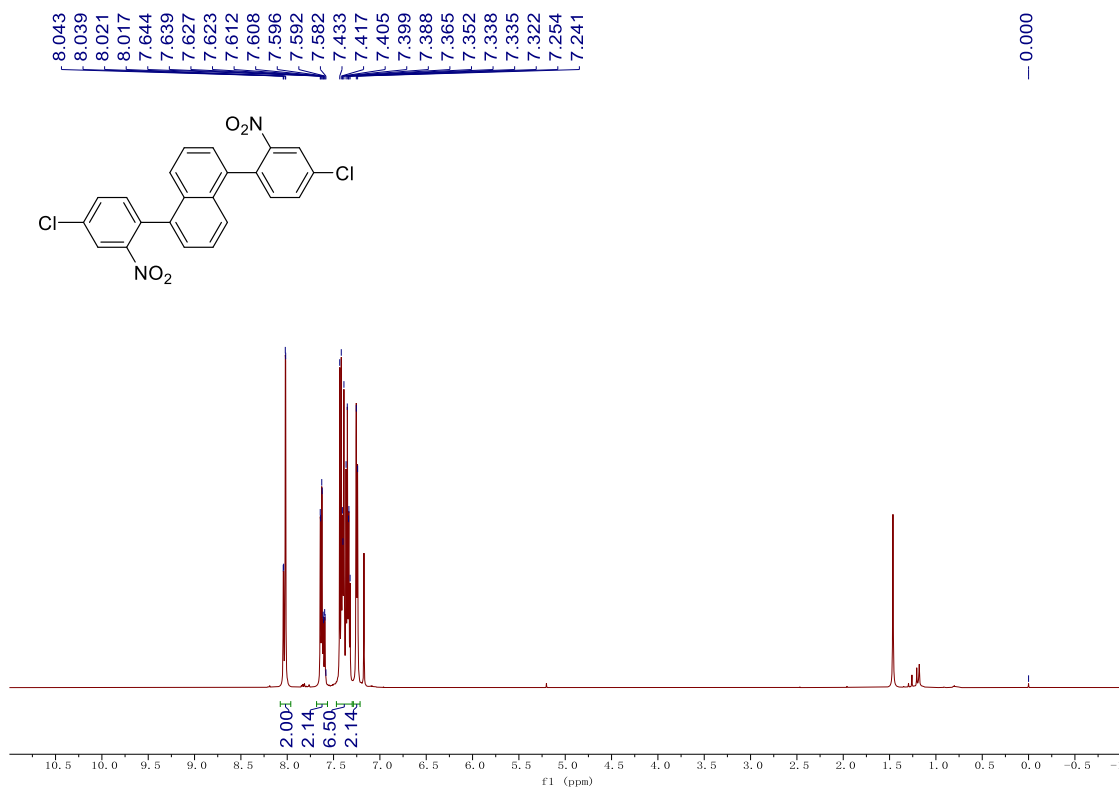
471 Hz ^{19}F $\{^1\text{H}\}$ NMR spectrum of **1e** in CDCl_3



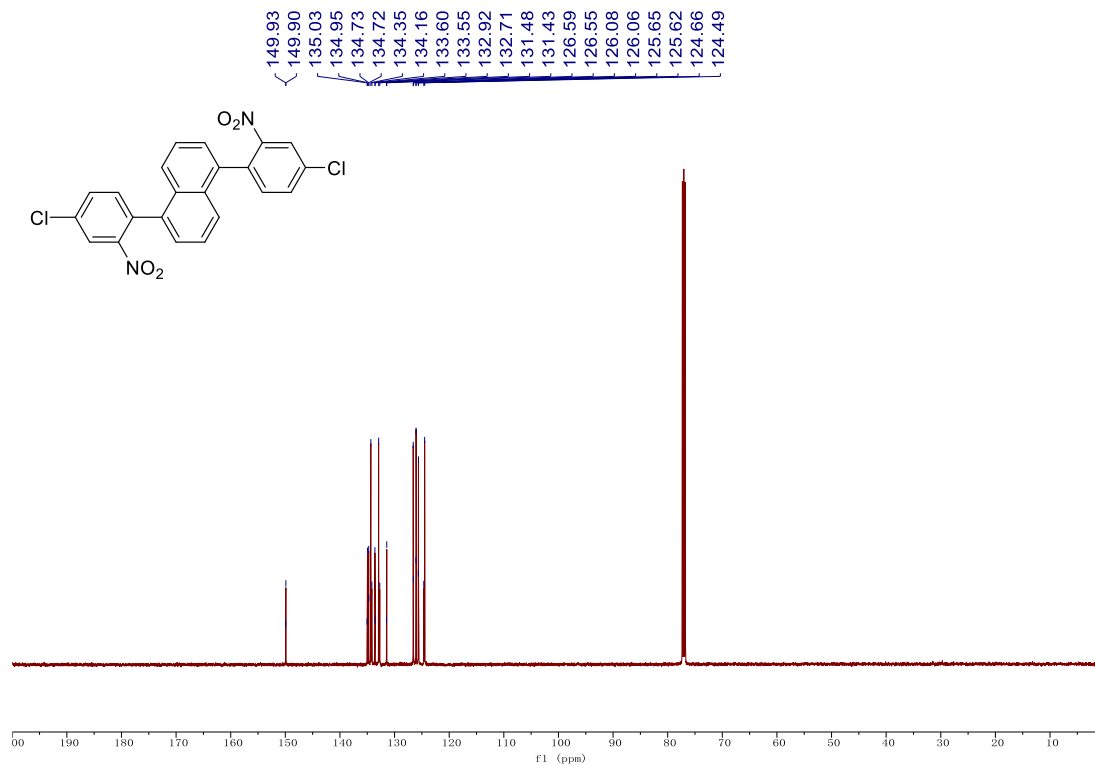
126 Hz ^{13}C $\{^1\text{H}\}$ NMR spectrum of **1e** in CDCl_3



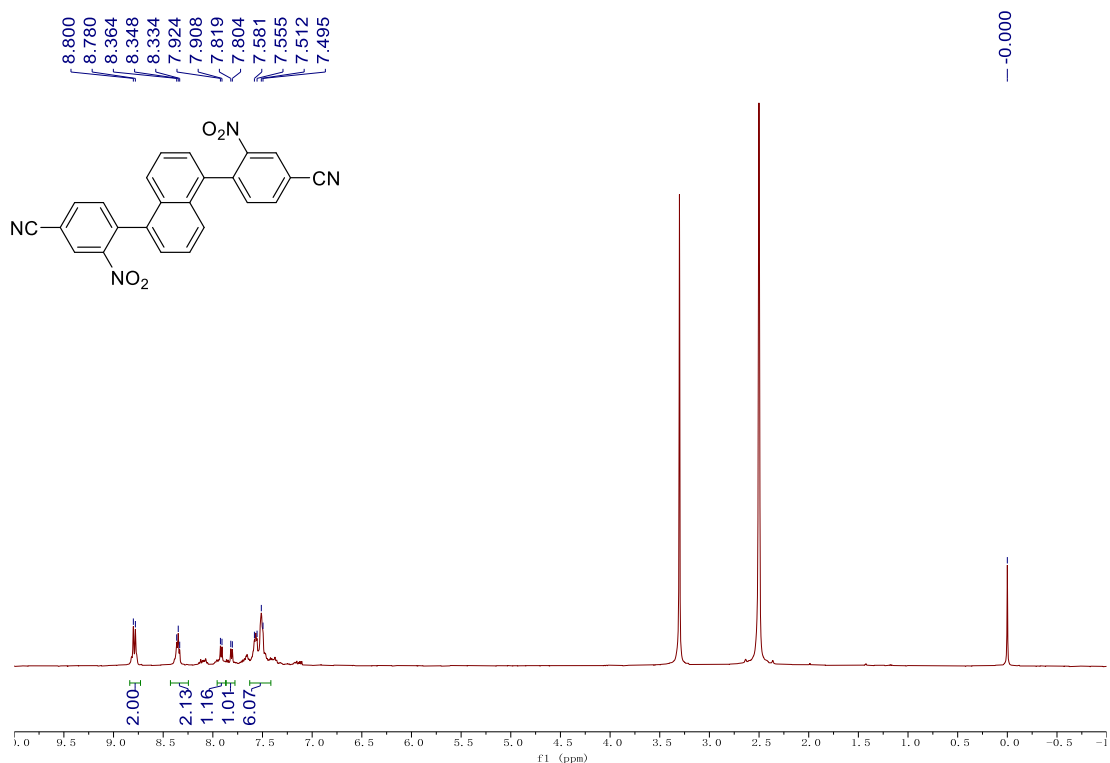
500 Hz ^1H NMR spectrum of **1f** in CDCl_3



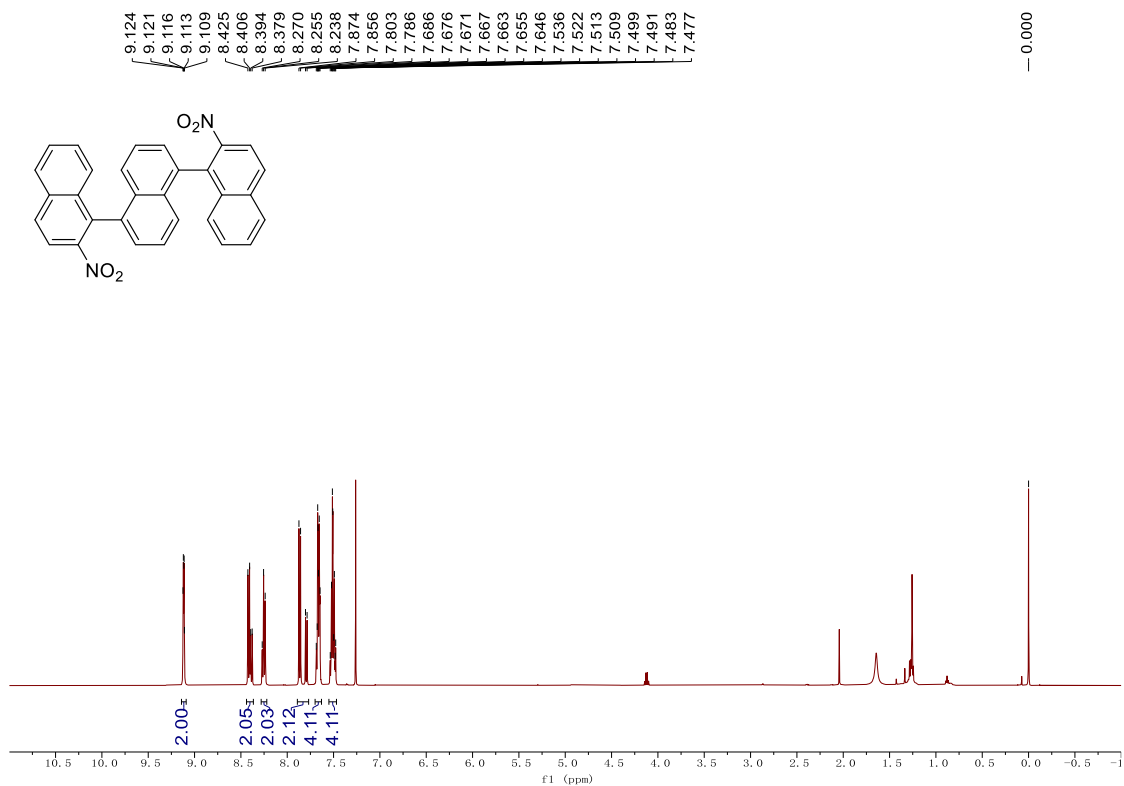
126 Hz ^{13}C $\{^1\text{H}\}$ NMR spectrum of **1f** in CDCl_3



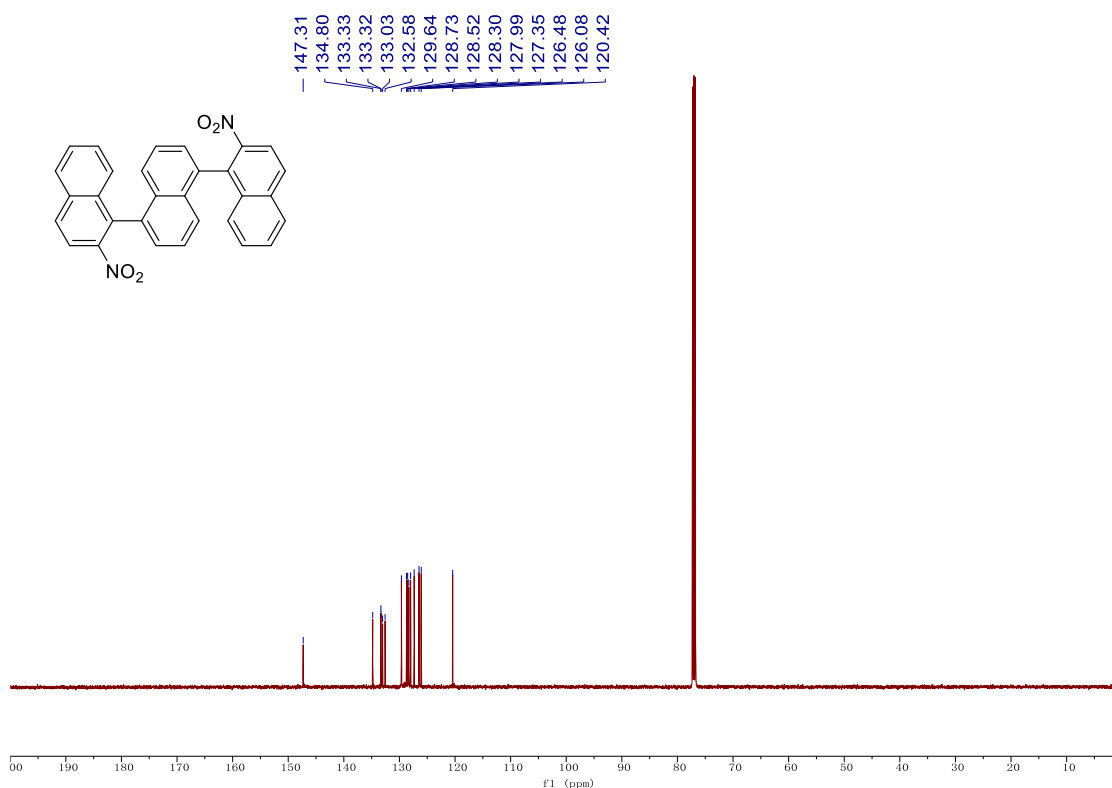
500 Hz ^1H NMR spectrum of **1g** in DMSO- d_6



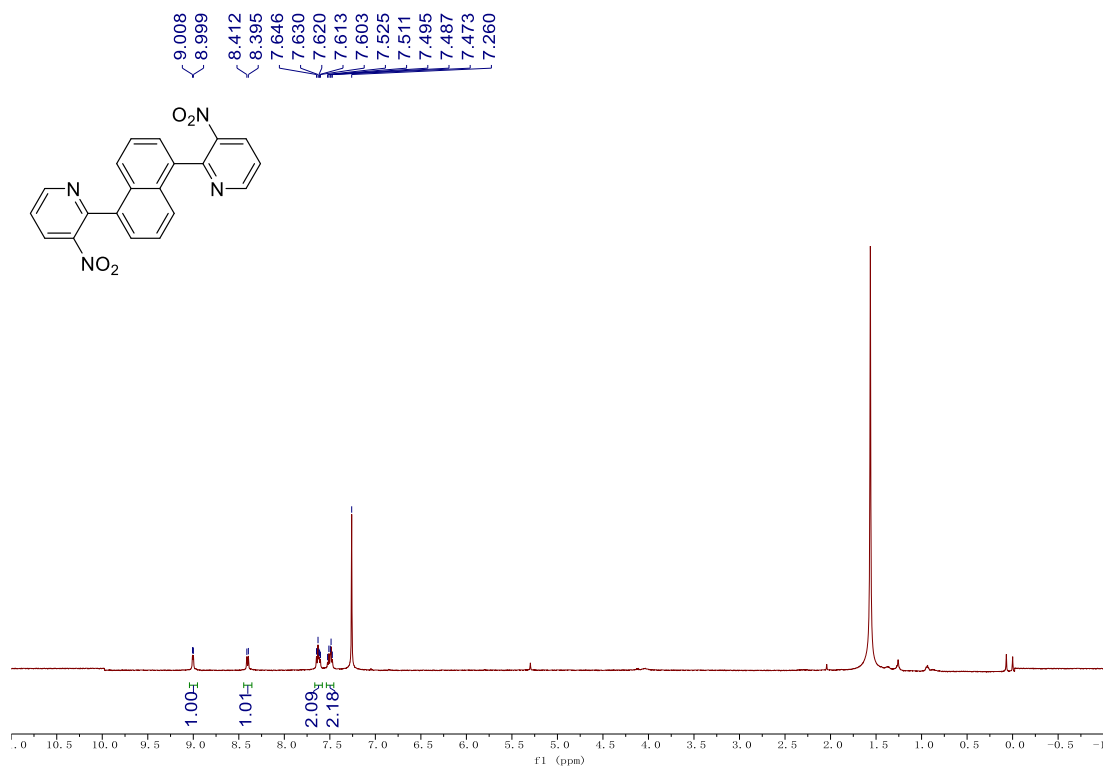
500 Hz ^1H NMR spectrum of **1h** in CDCl_3



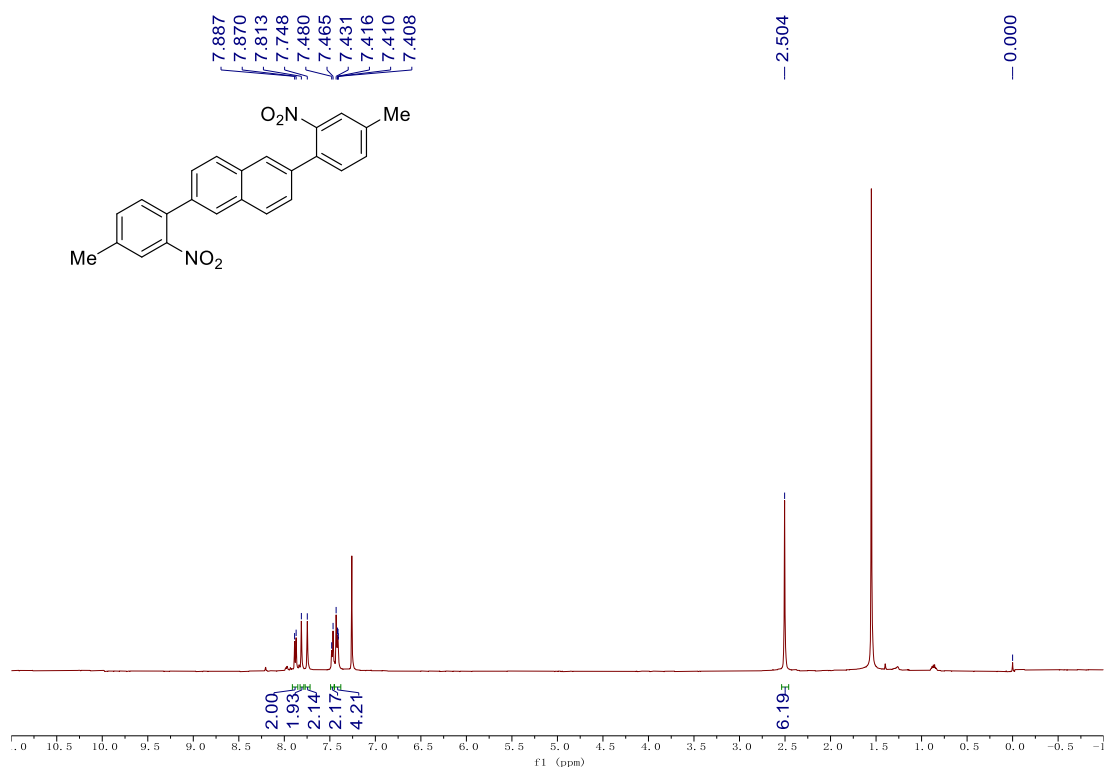
126 Hz ^{13}C $\{^1\text{H}\}$ NMR spectrum of **1h** in CDCl_3



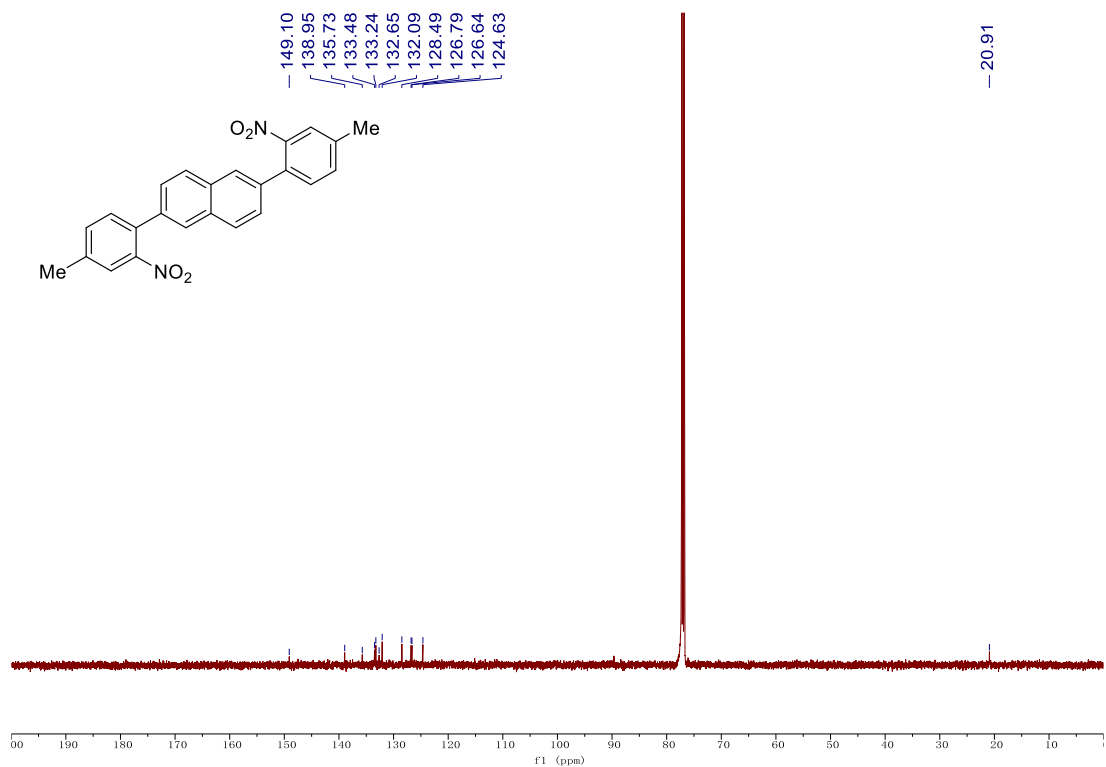
500 Hz ^1H NMR spectrum of **1i** in CDCl_3



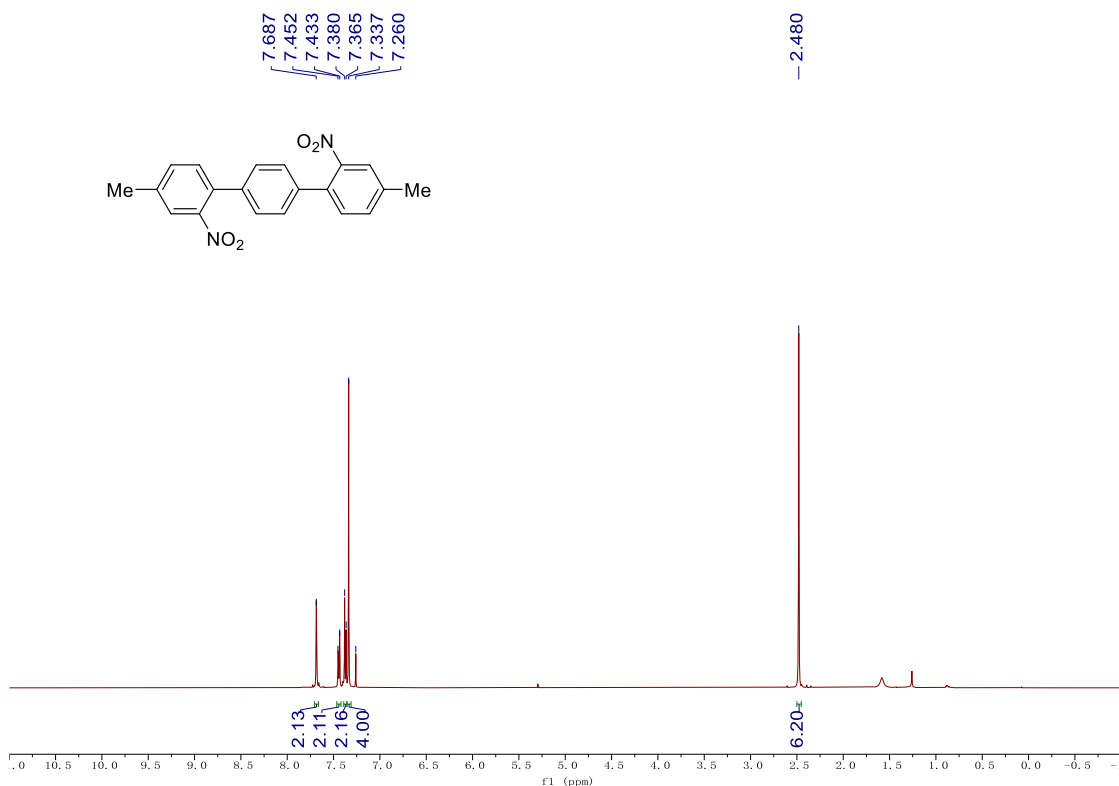
500 Hz ^1H NMR spectrum of **1j** in CDCl_3



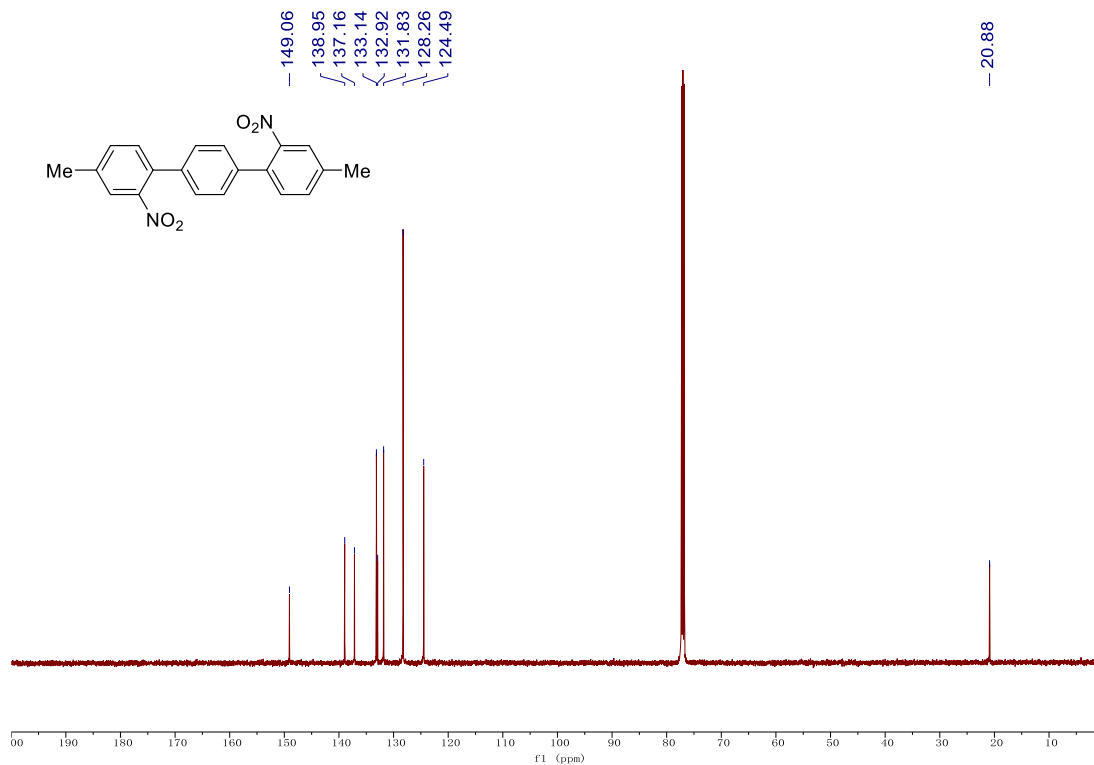
126 Hz ^{13}C $\{^1\text{H}\}$ NMR spectrum of **1j** in CDCl_3



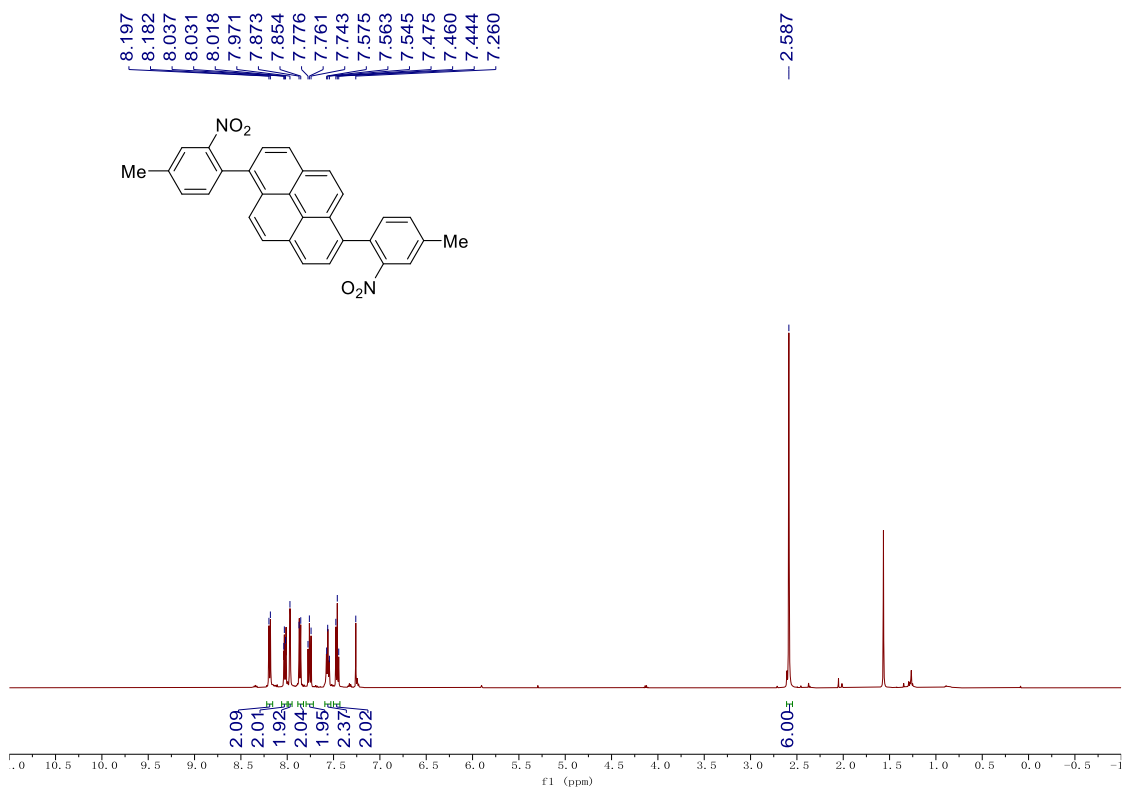
500 Hz ^1H NMR spectrum of **1k** in CDCl_3



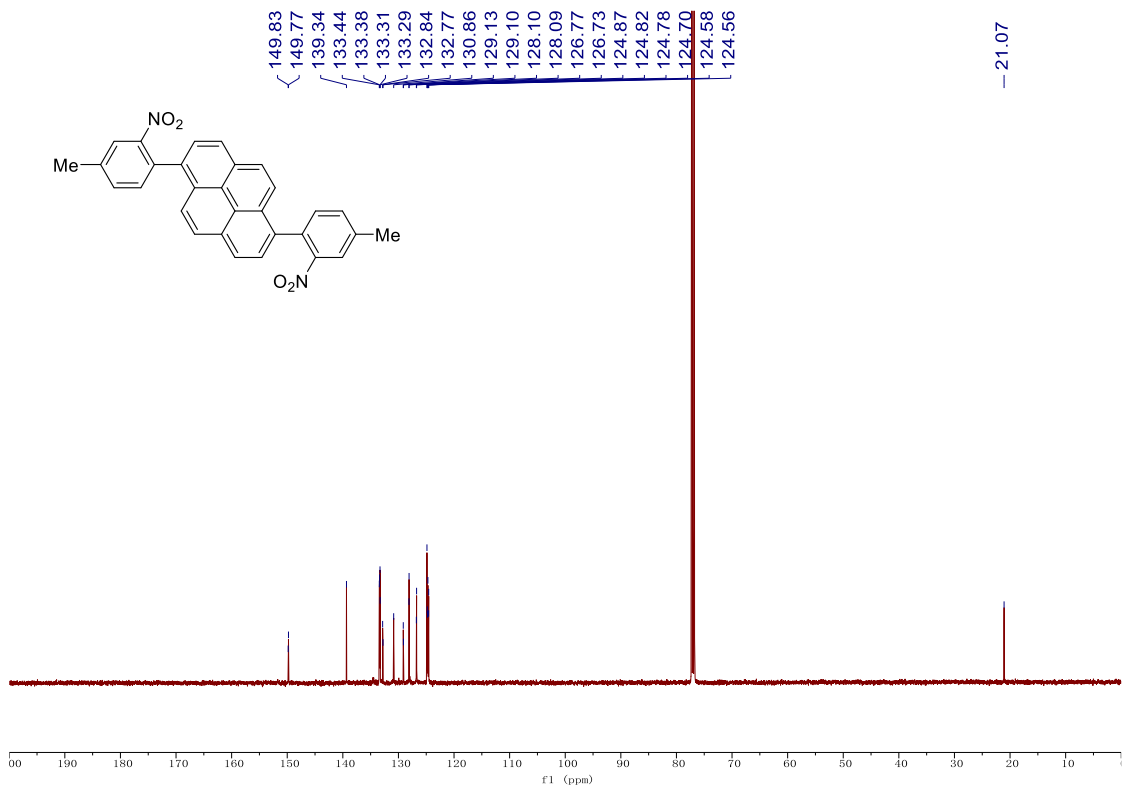
126 Hz ^{13}C $\{^1\text{H}\}$ NMR spectrum of **1k** in CDCl_3

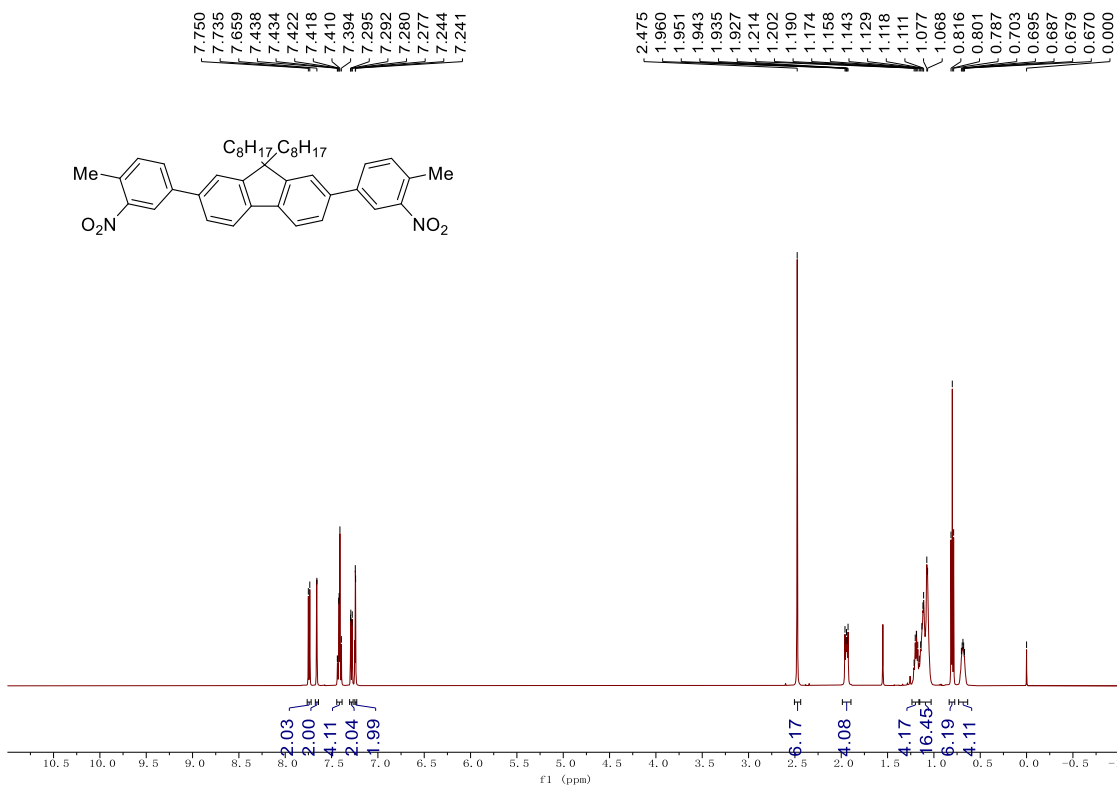


500 Hz ^1H NMR spectrum of **11** in CDCl_3

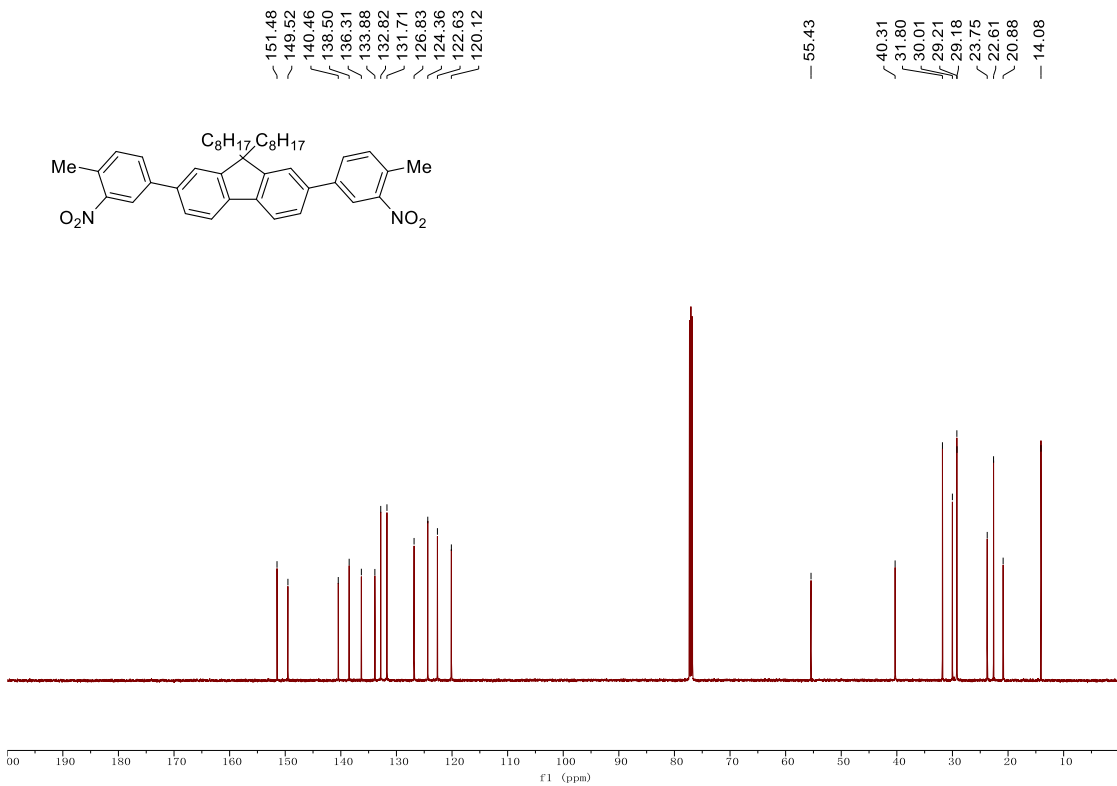


126 Hz ^{13}C $\{^1\text{H}\}$ NMR spectrum of **11** in CDCl_3

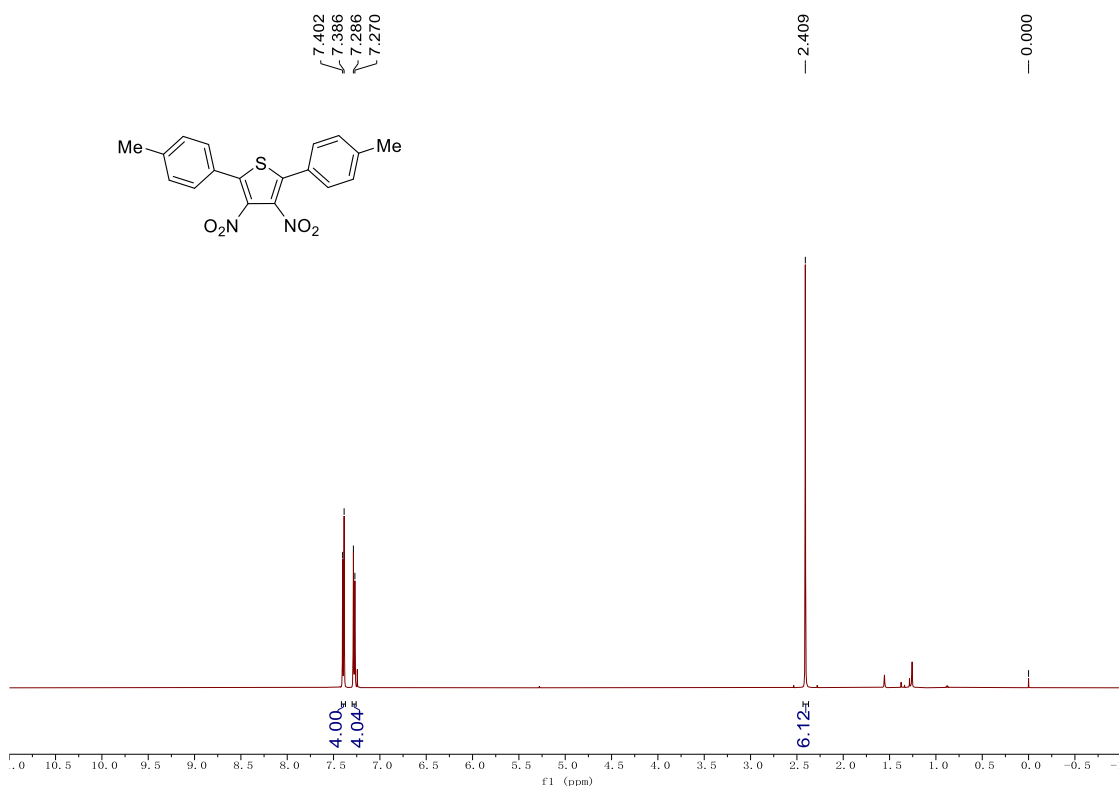


500 Hz ^1H NMR spectrum of **1m** in CDCl_3 

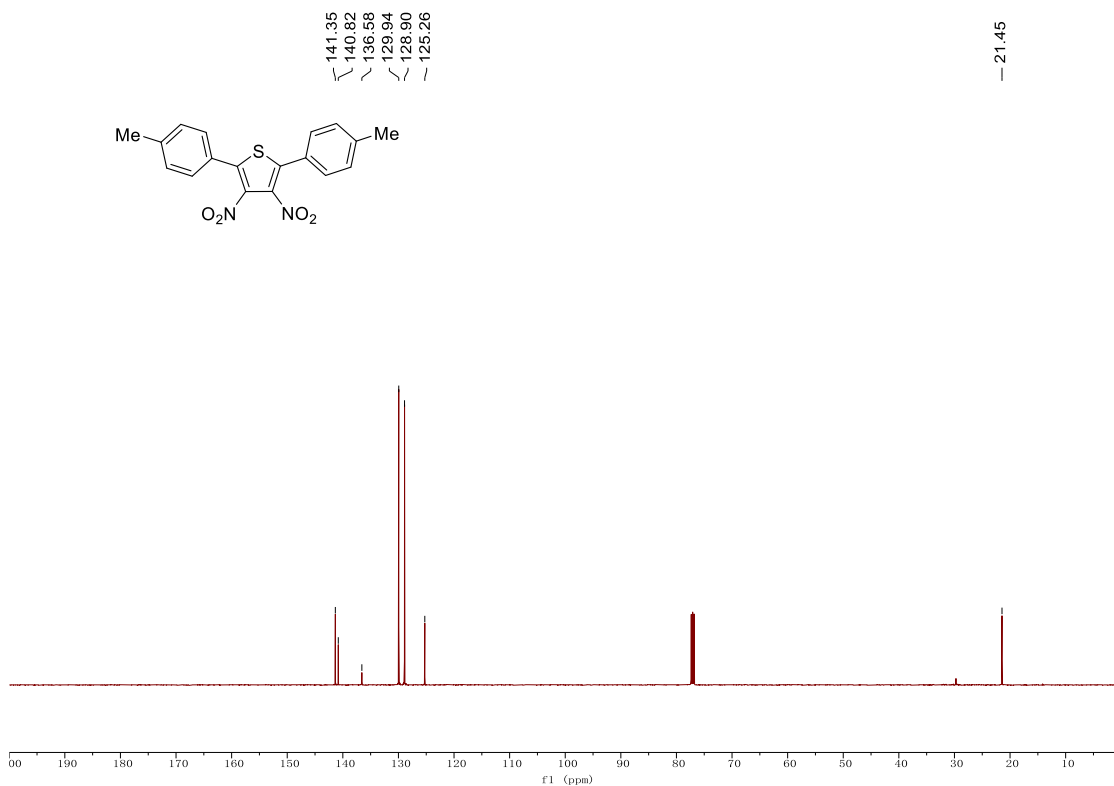
126 Hz ^{13}C $\{^1\text{H}\}$ NMR spectrum of **1m** in CDCl_3



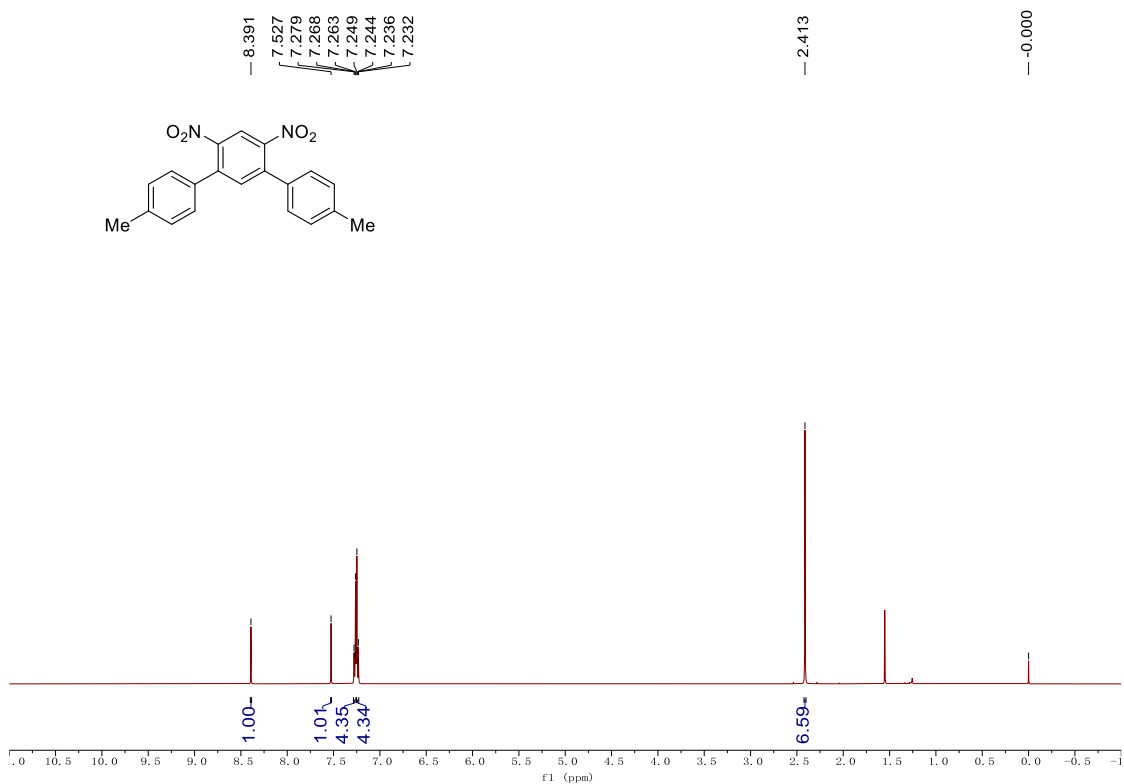
500 Hz ^1H NMR spectrum of **1n** in CDCl_3



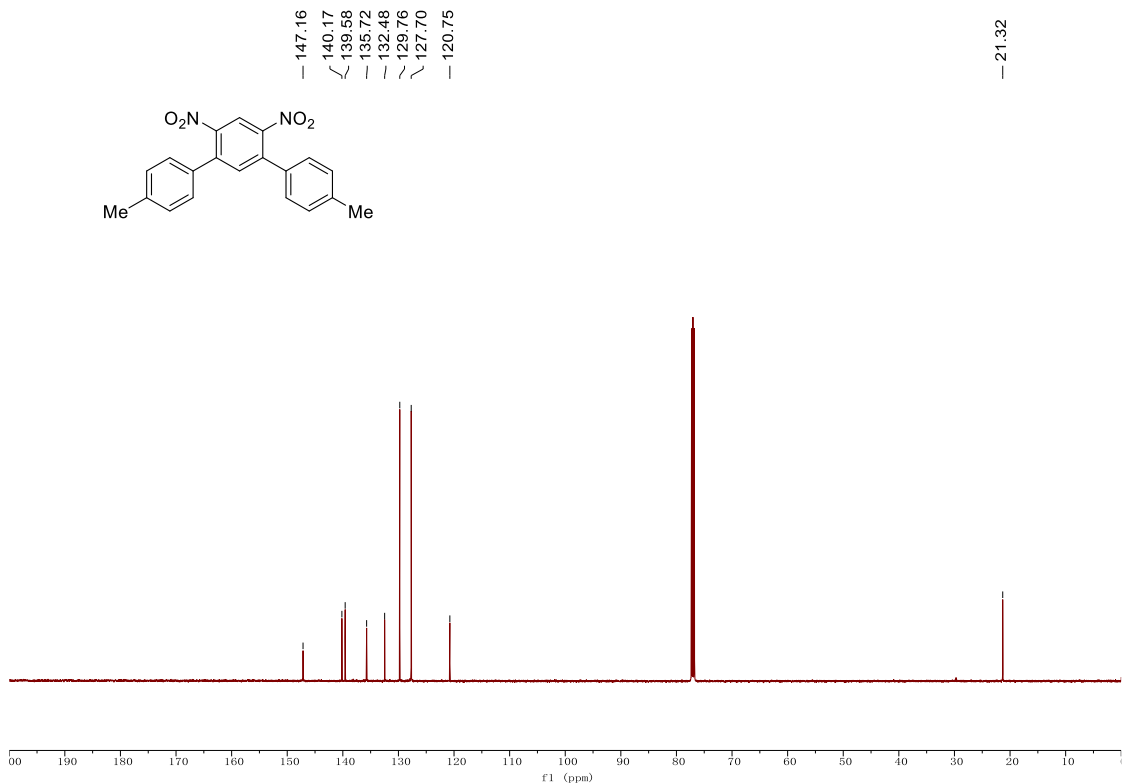
126 Hz ^{13}C $\{^1\text{H}\}$ NMR spectrum of **1n** in CDCl_3



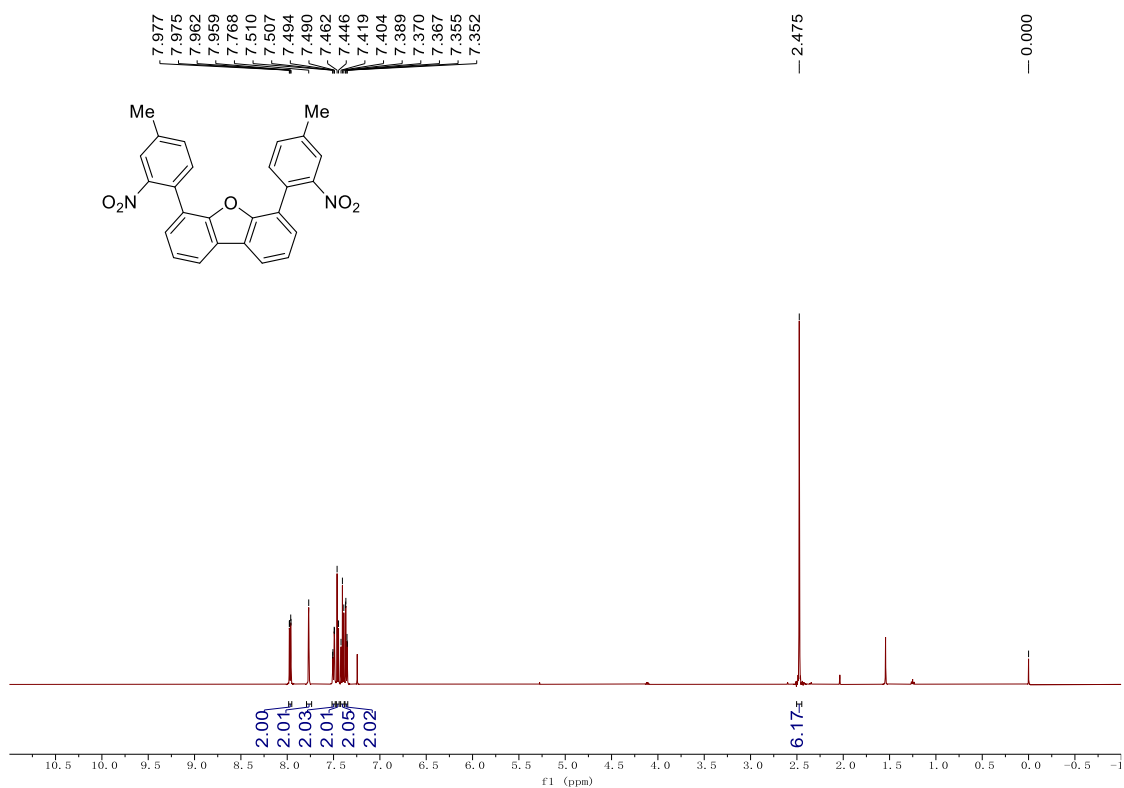
500 Hz ^1H NMR spectrum of **1o** in CDCl_3



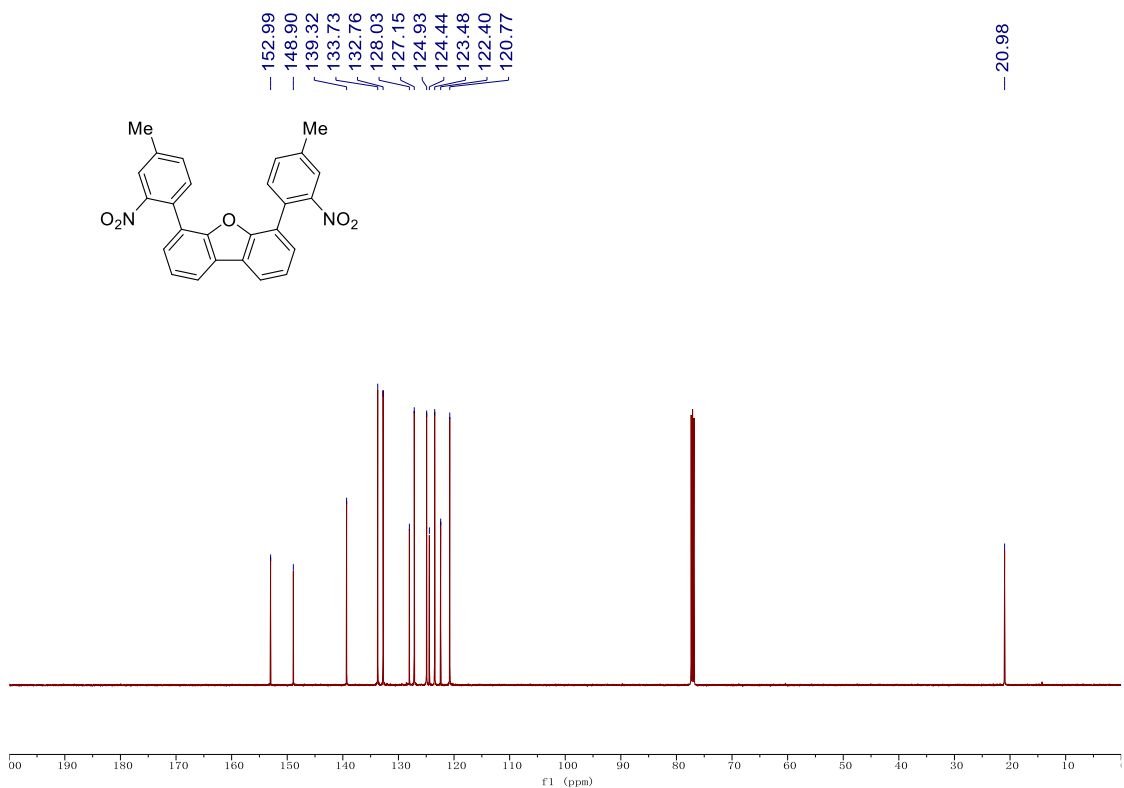
126 Hz ^{13}C $\{^1\text{H}\}$ NMR spectrum of **1o** in CDCl_3



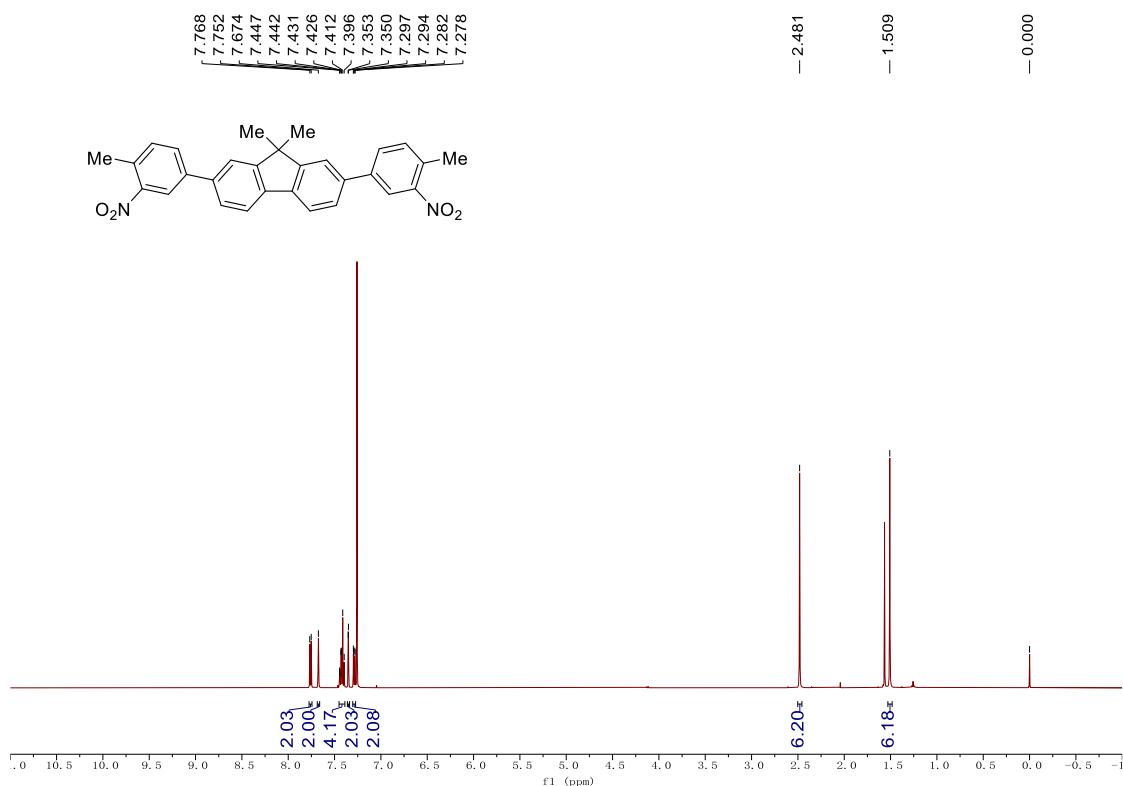
500 Hz ^1H NMR spectrum of **1p** in CDCl_3



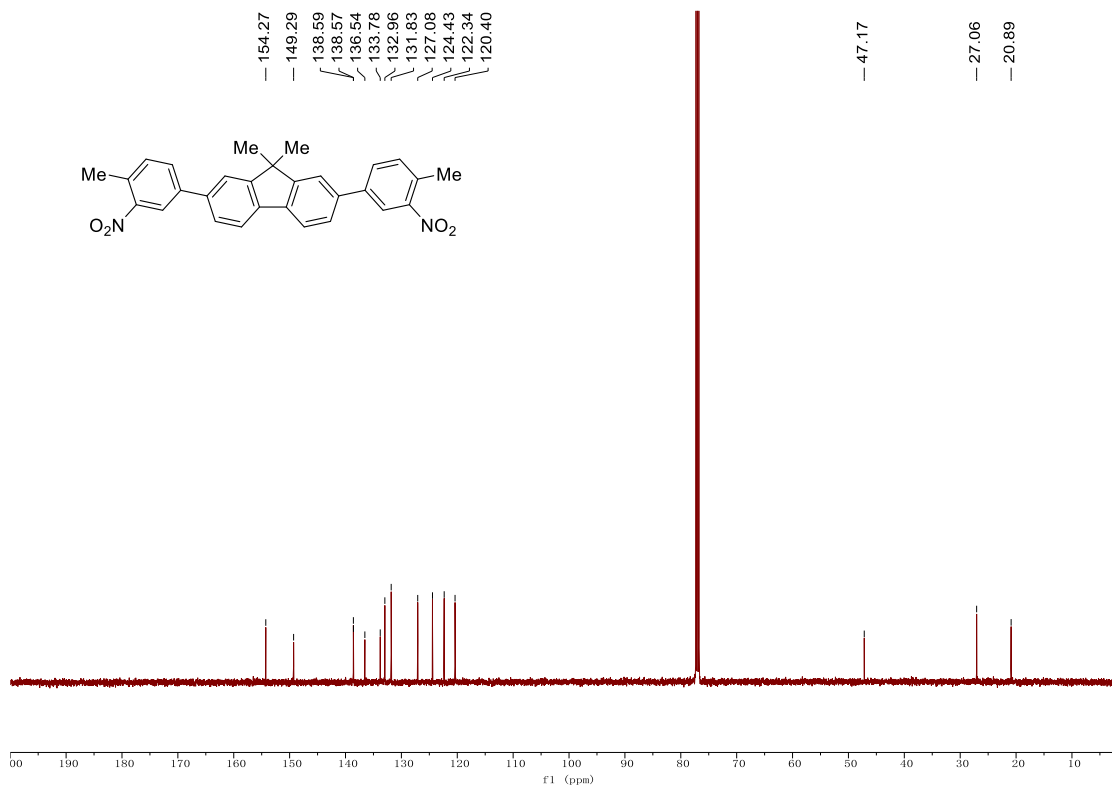
126 Hz ^{13}C $\{^1\text{H}\}$ NMR spectrum of **1p** in CDCl_3



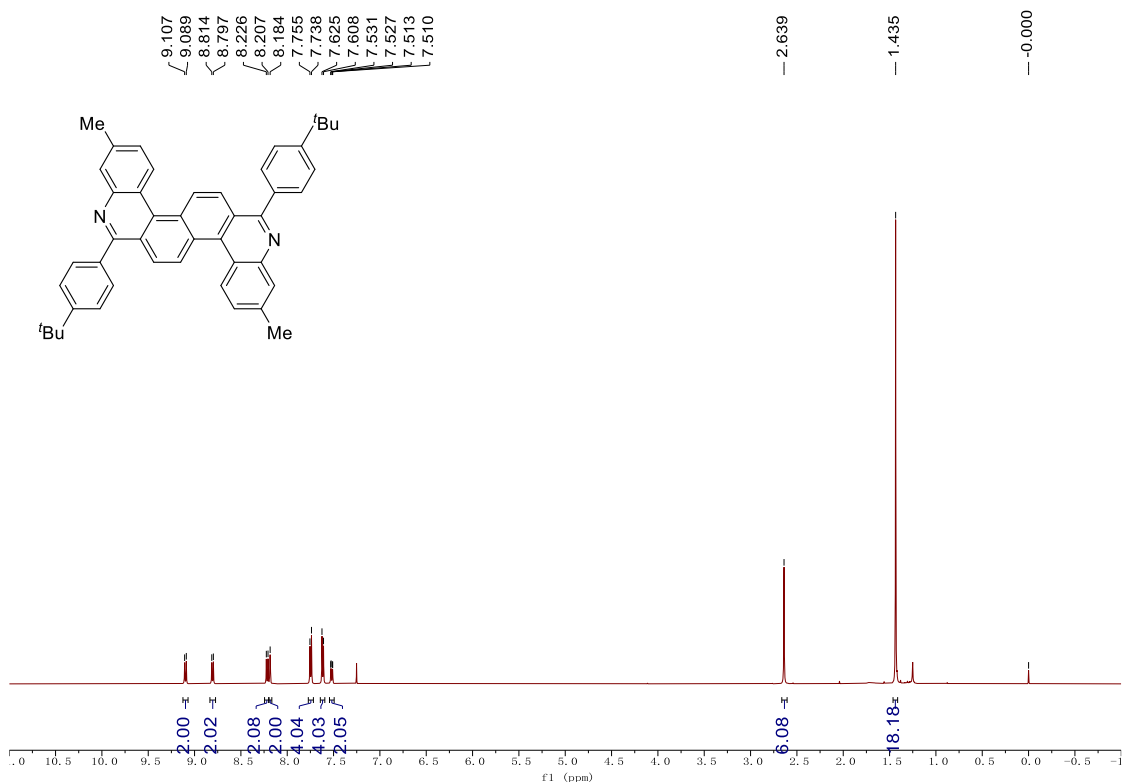
500 Hz ^1H NMR spectrum of **1q** in CDCl_3



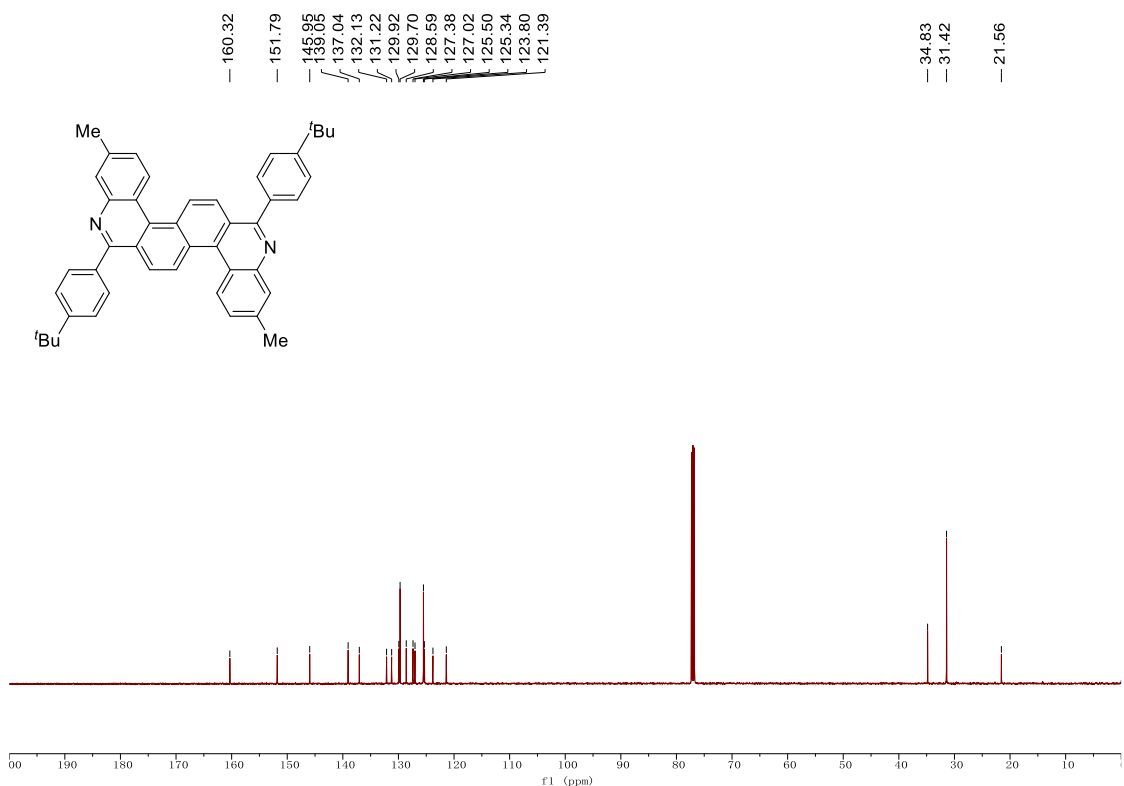
126 Hz ^{13}C $\{^1\text{H}\}$ NMR spectrum of **1q** in CDCl_3



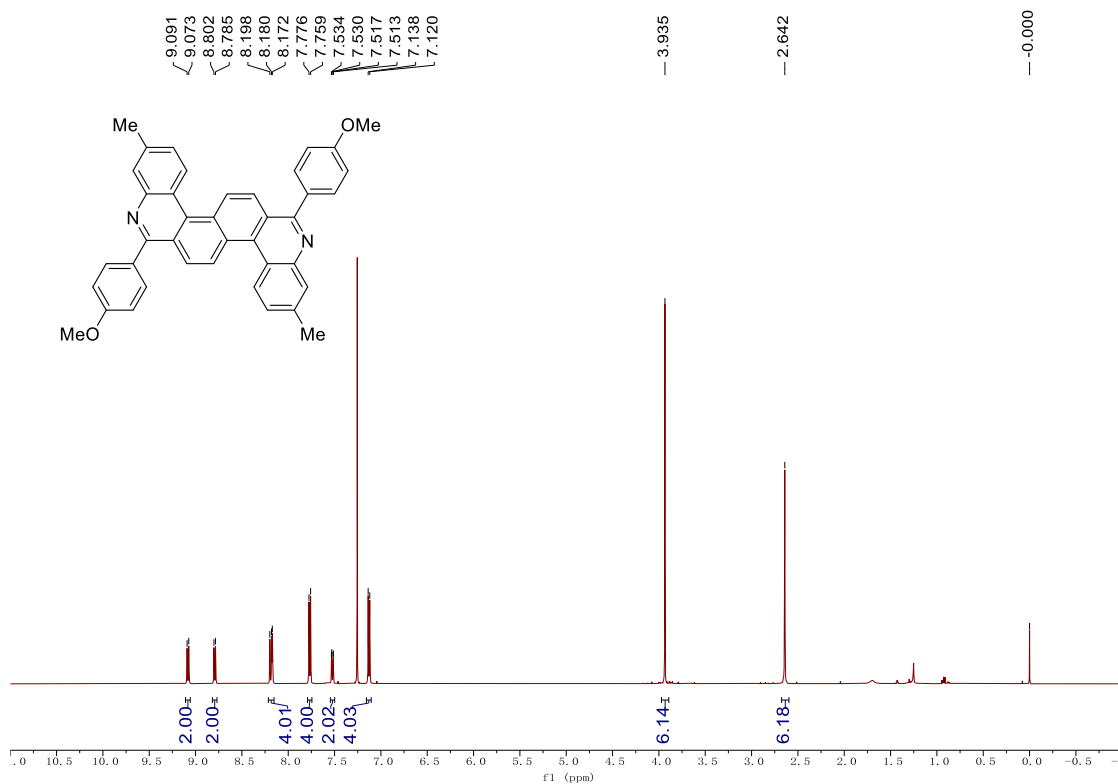
500 Hz ^1H NMR spectrum of **3a** in CDCl_3



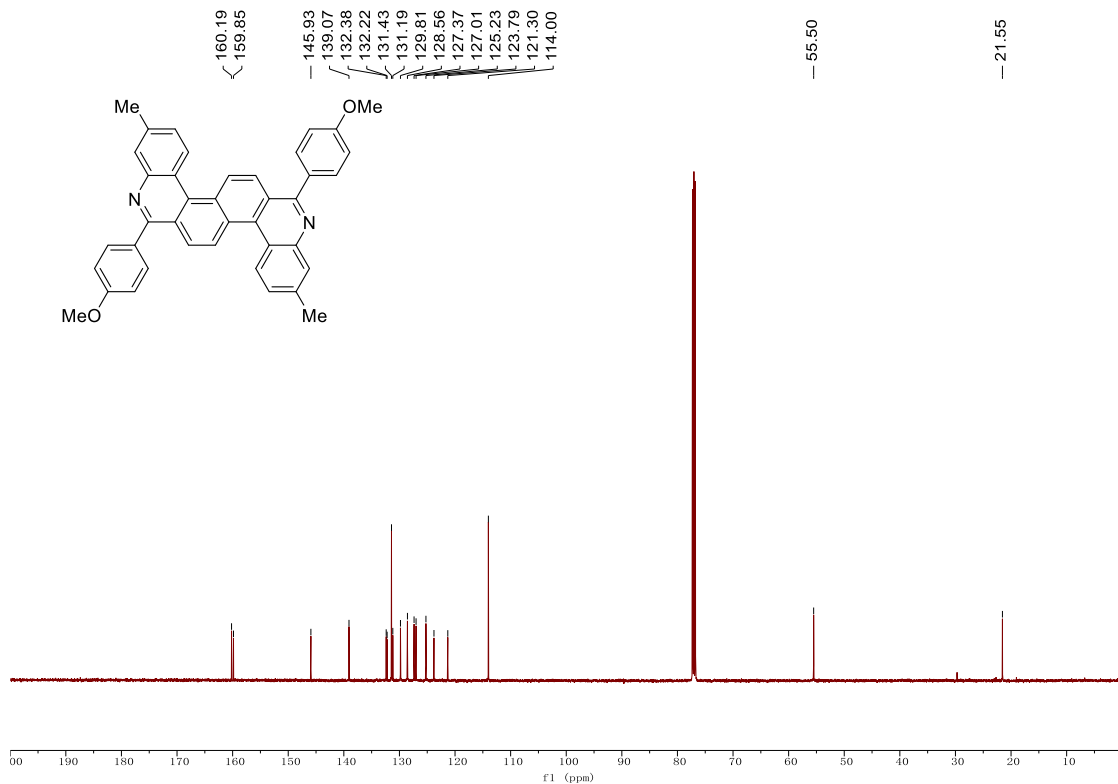
126 Hz ^{13}C { ^1H } NMR spectrum of **3a** in CDCl_3



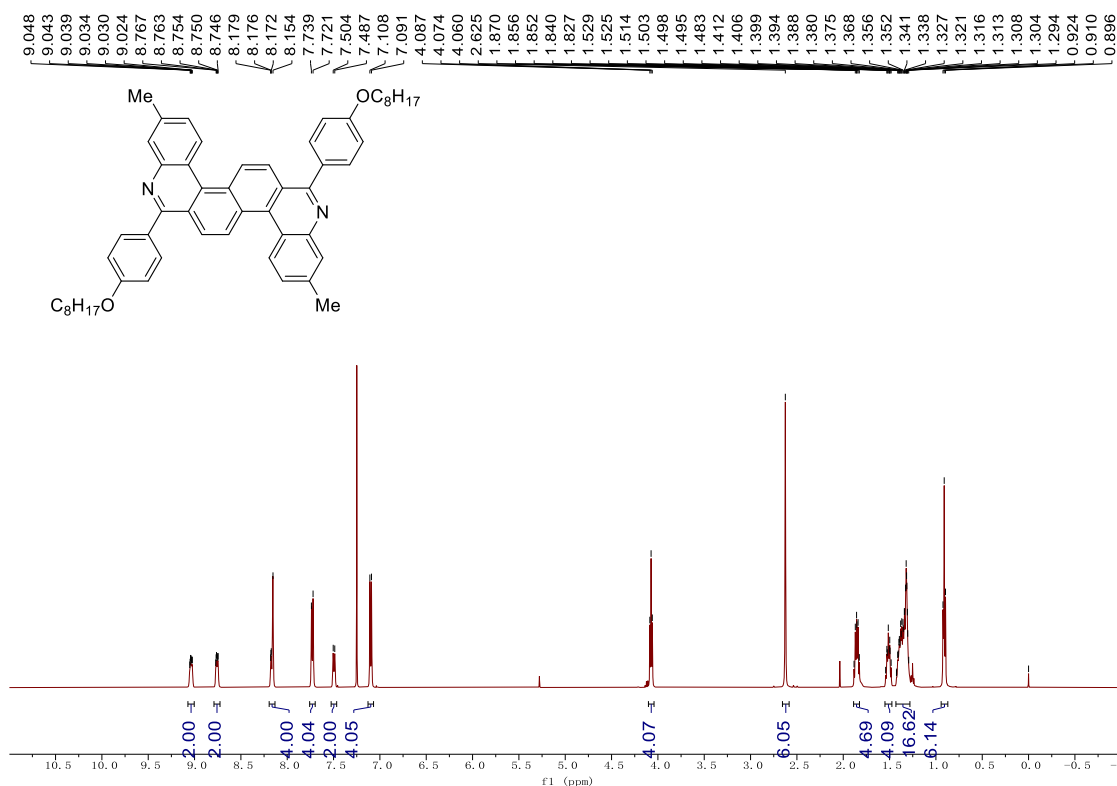
500 Hz ^1H NMR spectrum of **3b** in CDCl_3



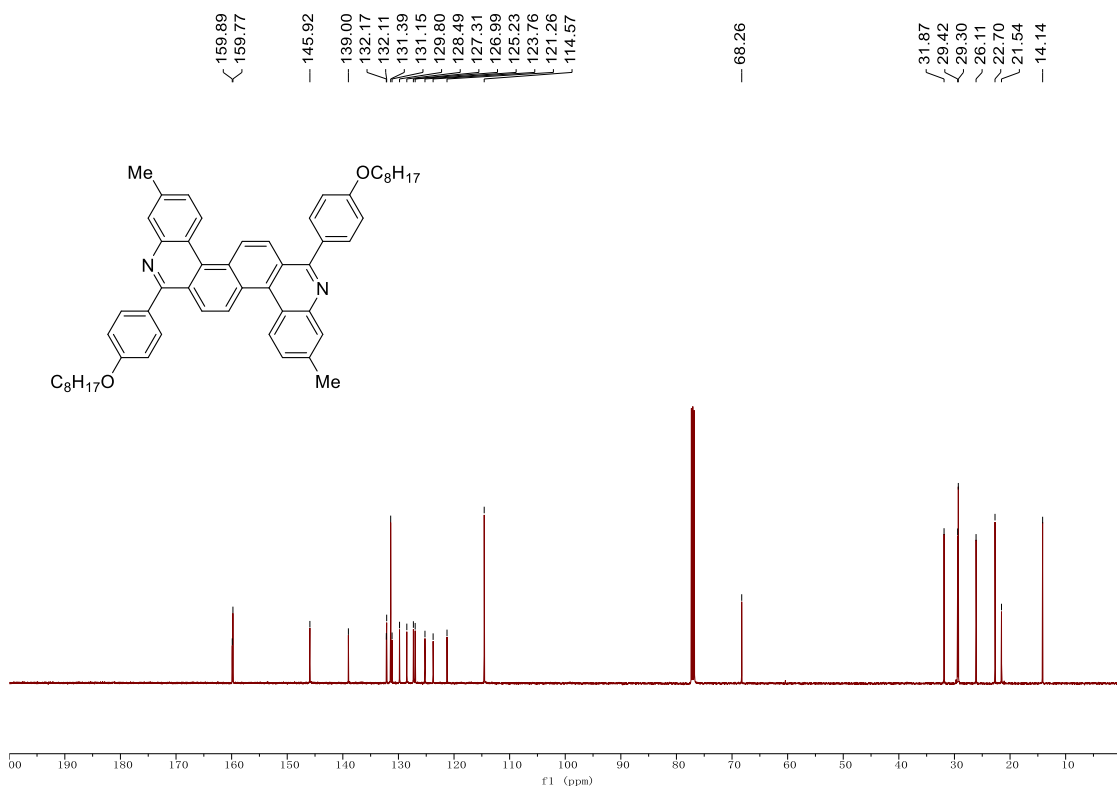
126 Hz ^{13}C { ^1H } NMR spectrum of **3b** in CDCl_3



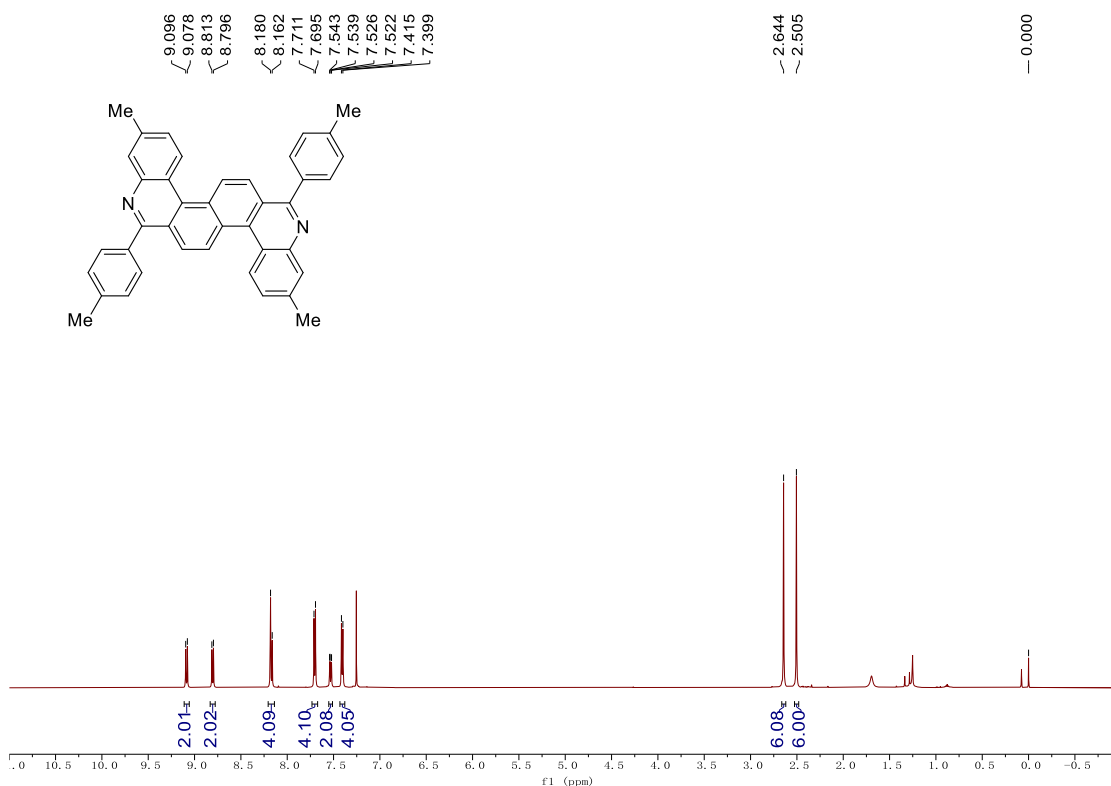
500 Hz ^1H NMR spectrum of **3c** in CDCl_3



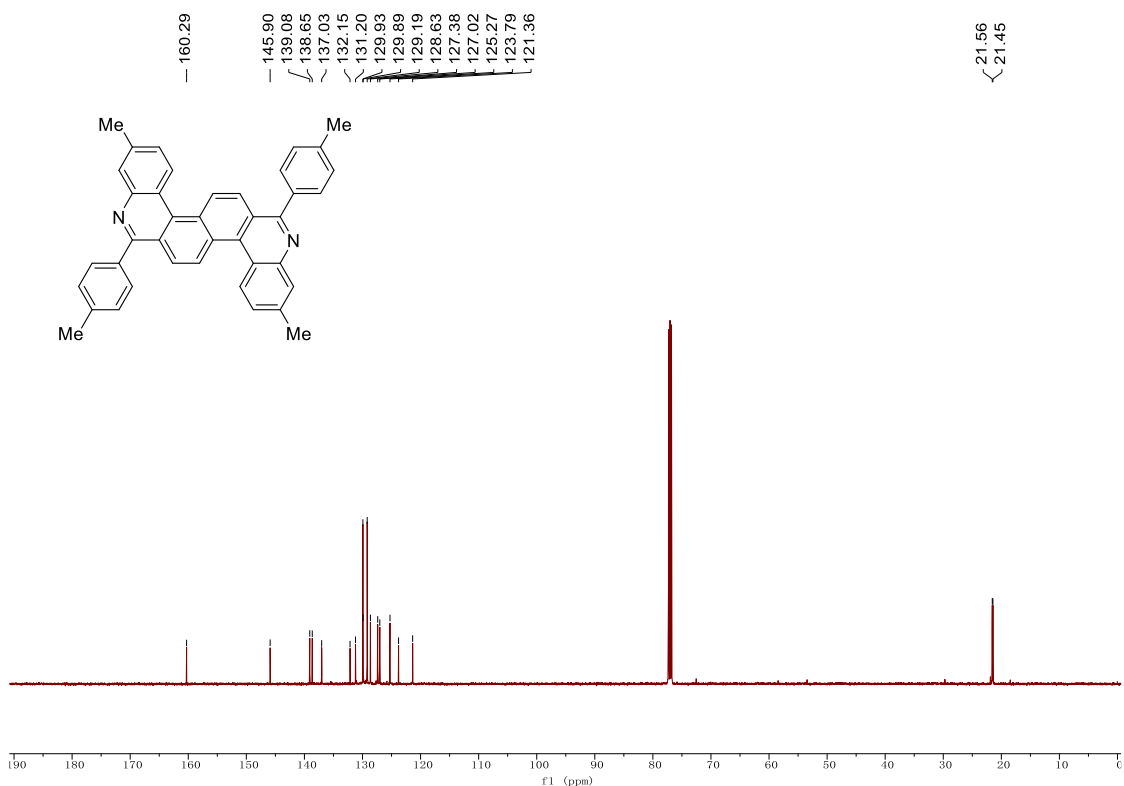
126 Hz ^{13}C { ^1H } NMR spectrum of **3c** in CDCl_3



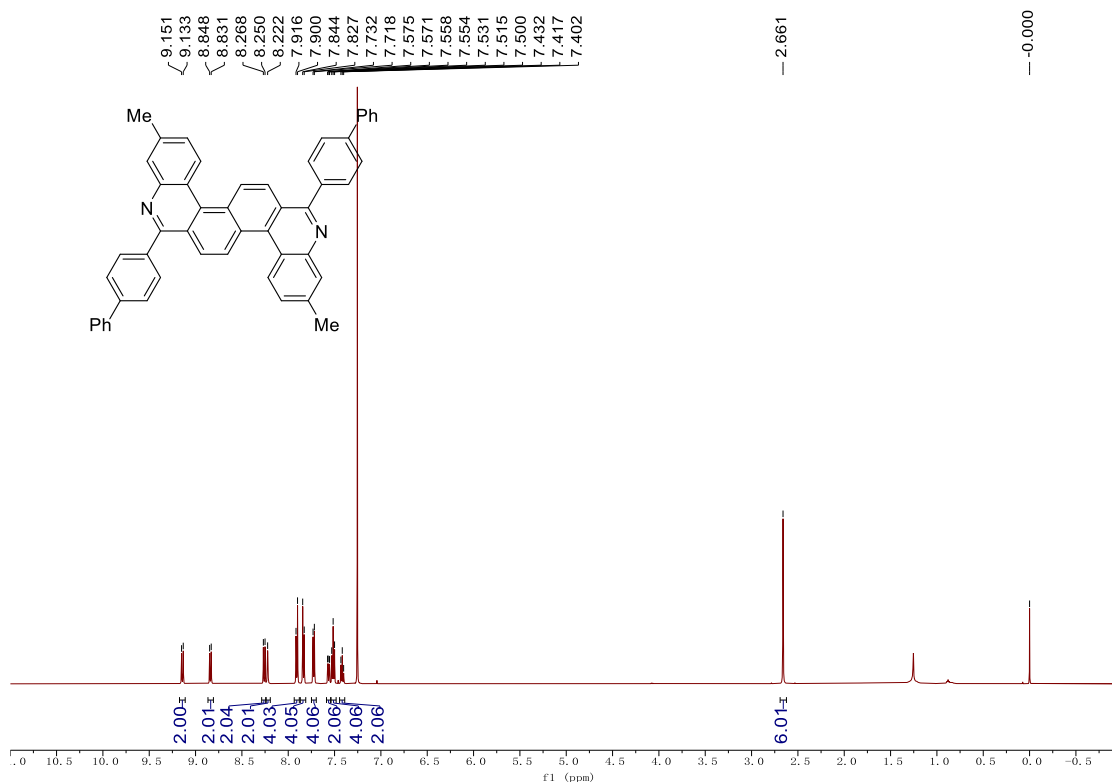
500 Hz ^1H NMR spectrum of **3d** in CDCl_3



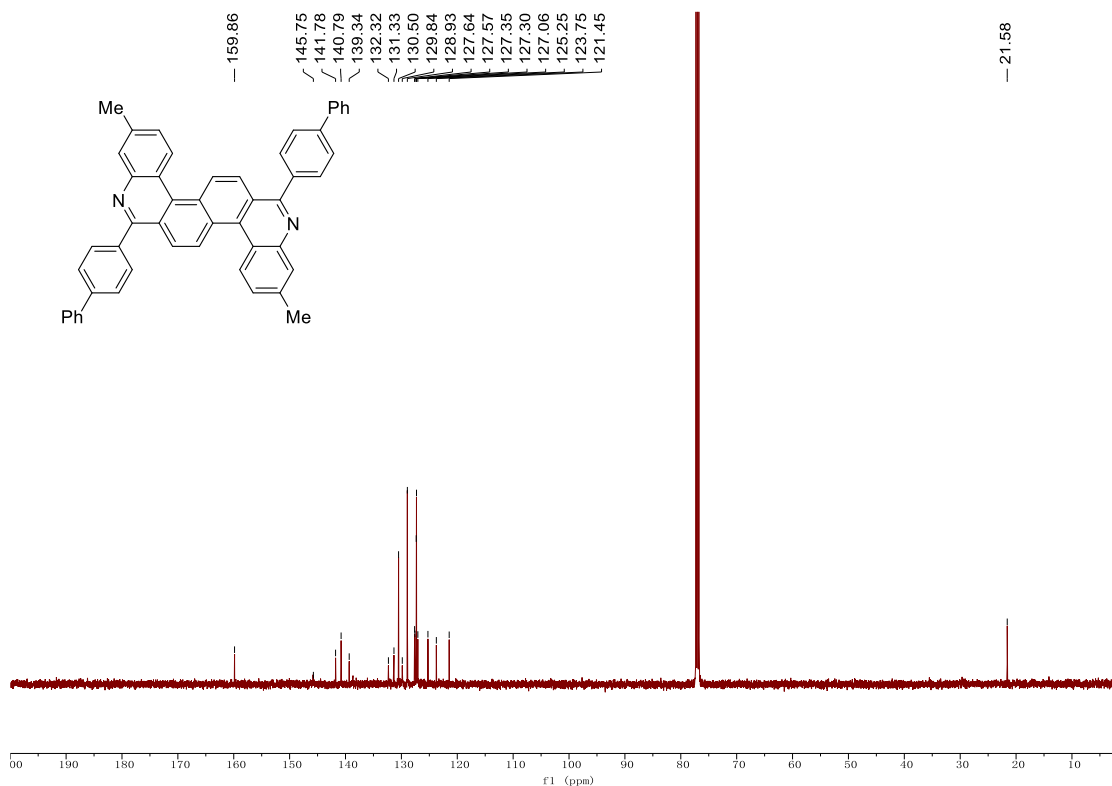
126 Hz ^{13}C { ^1H } NMR spectrum of **3d** in CDCl_3



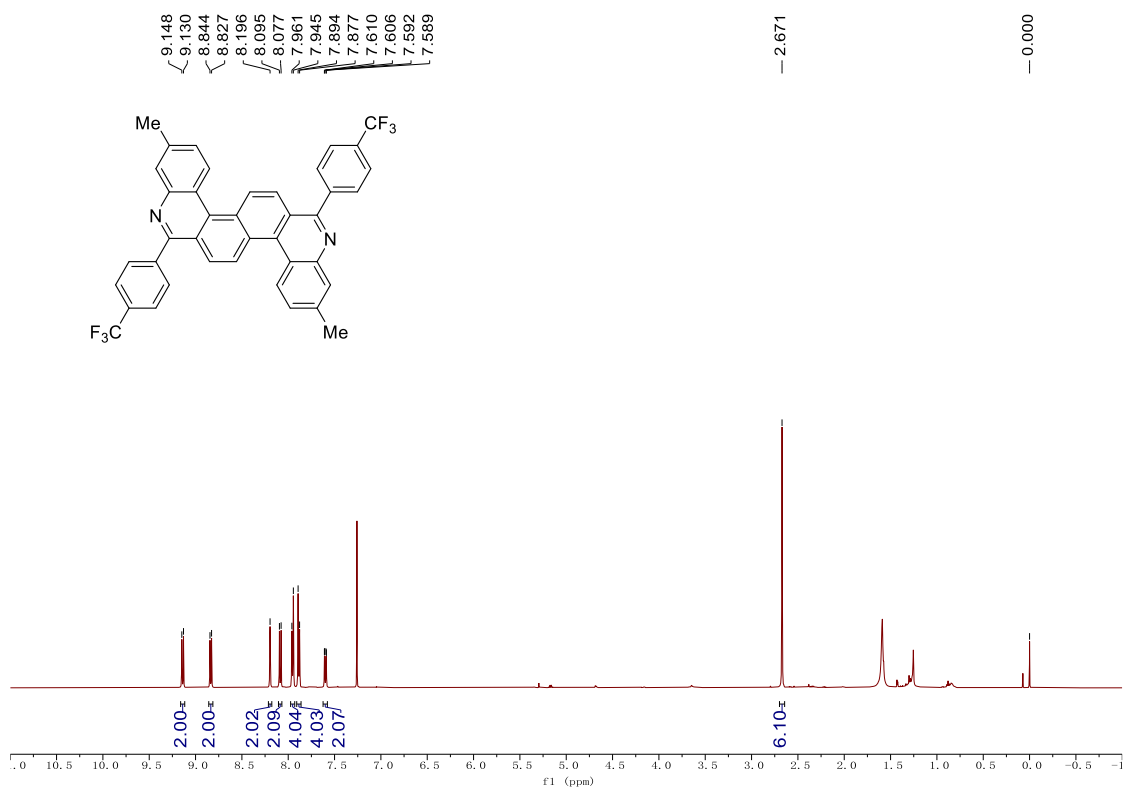
500 Hz ^1H NMR spectrum of **3e** in CDCl_3



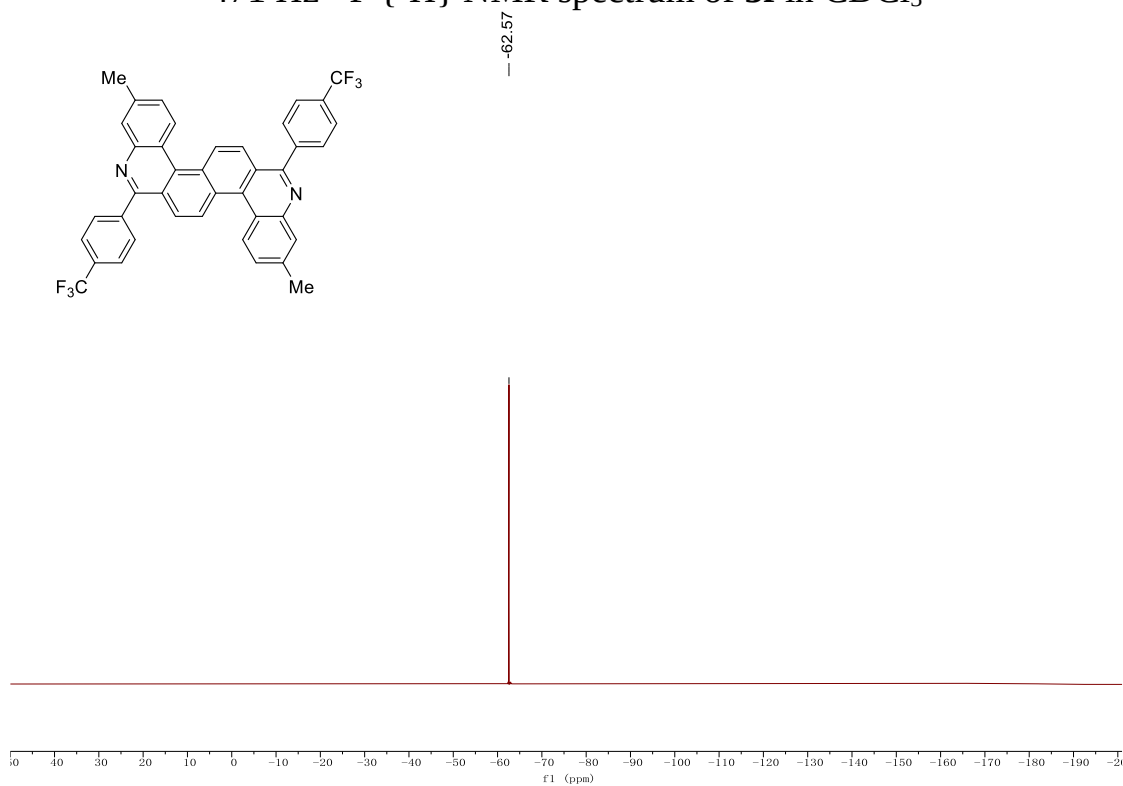
126 Hz ^{13}C $\{^1\text{H}\}$ NMR spectrum of **3e** in CDCl_3



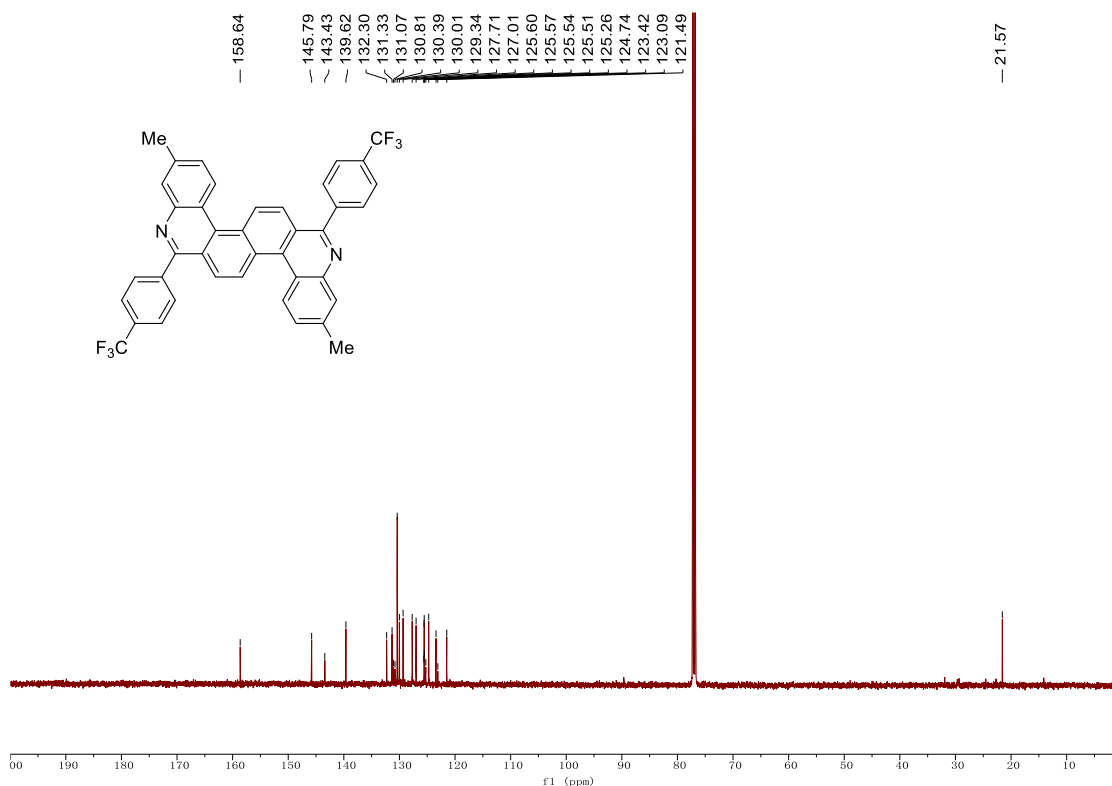
500 Hz ^1H NMR spectrum of **3f** in CDCl_3



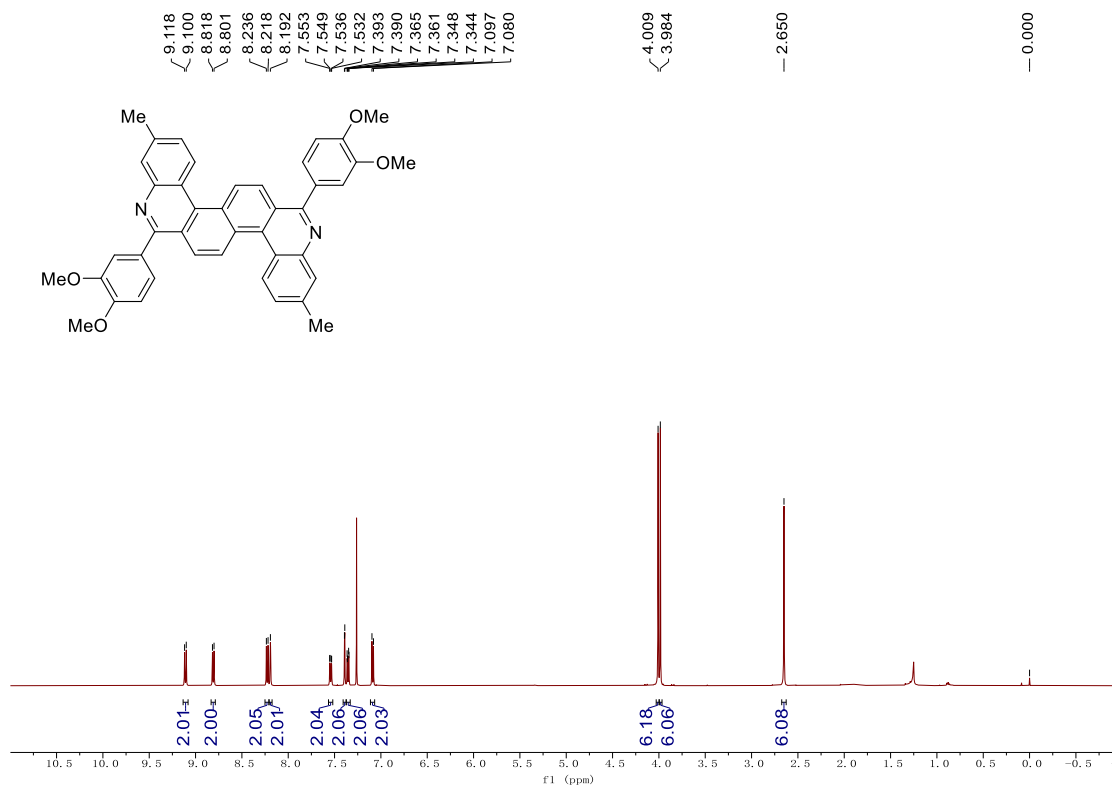
471 Hz ^{19}F $\{^1\text{H}\}$ NMR spectrum of **3f** in CDCl_3



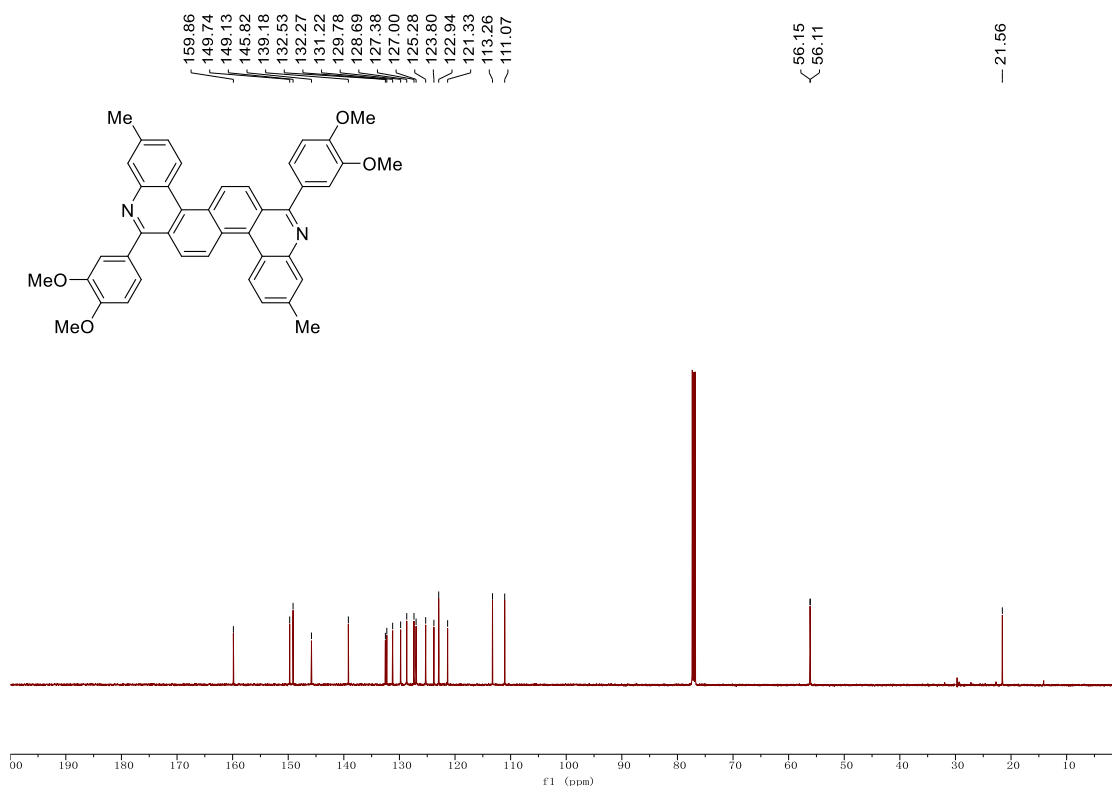
126 Hz ^{13}C $\{^1\text{H}\}$ NMR spectrum of **3f** in CDCl_3



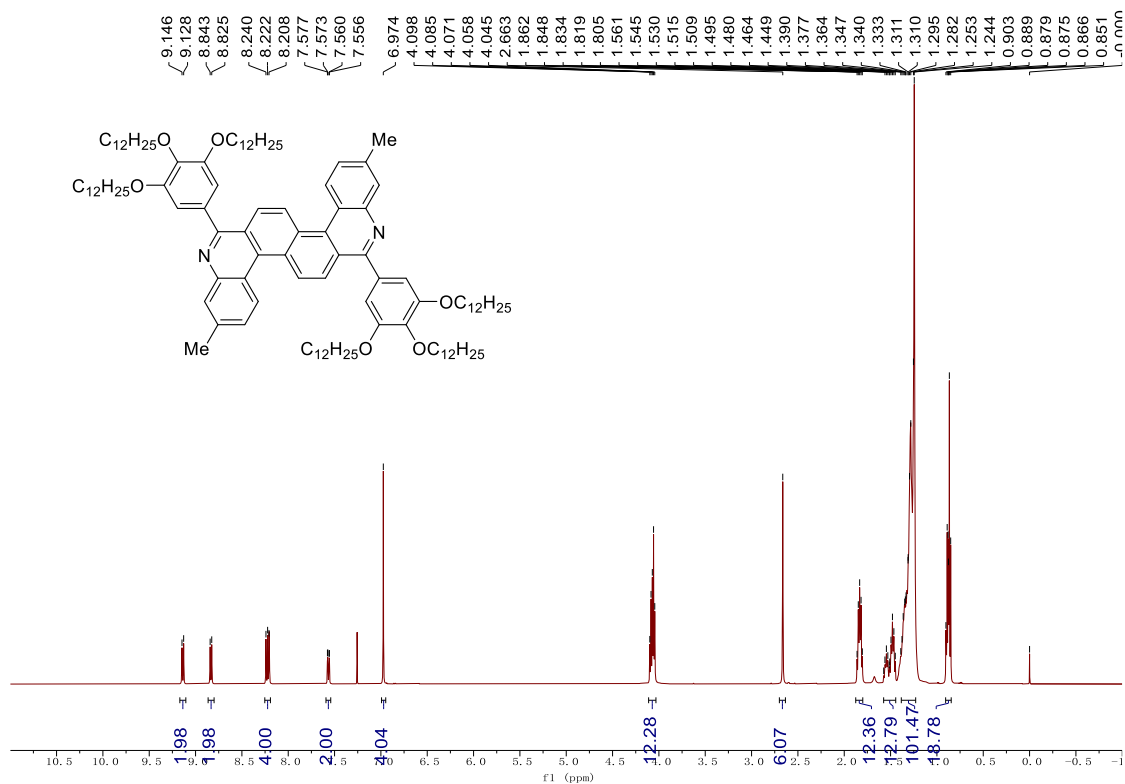
500 Hz ^1H NMR spectrum of **3g** in CDCl_3



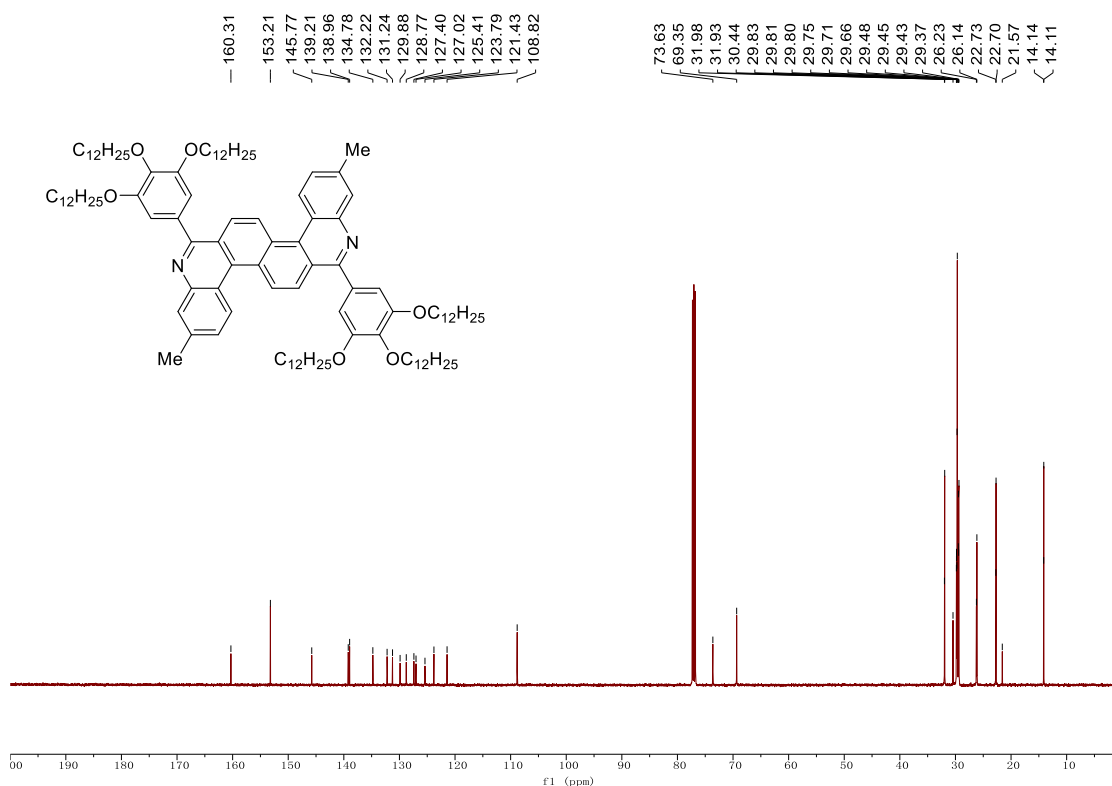
126 Hz ^{13}C $\{^1\text{H}\}$ NMR spectrum of **3g** in CDCl_3



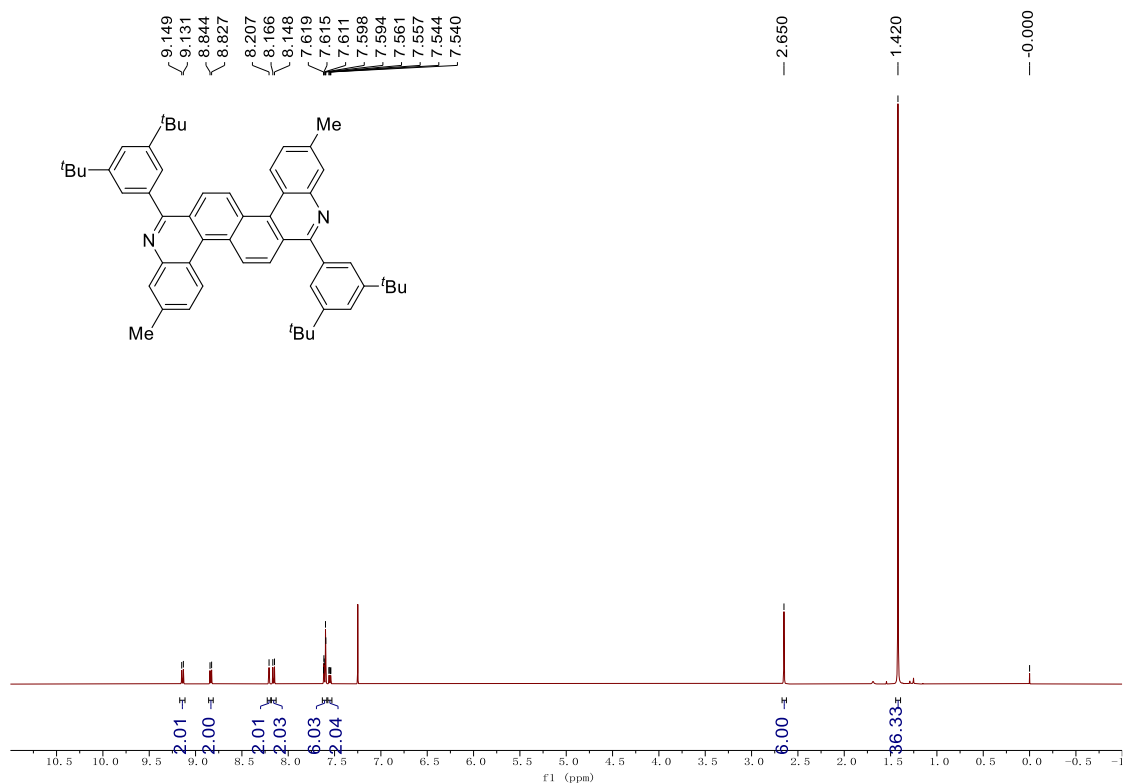
500 Hz ^1H NMR spectrum of **3h** in CDCl_3



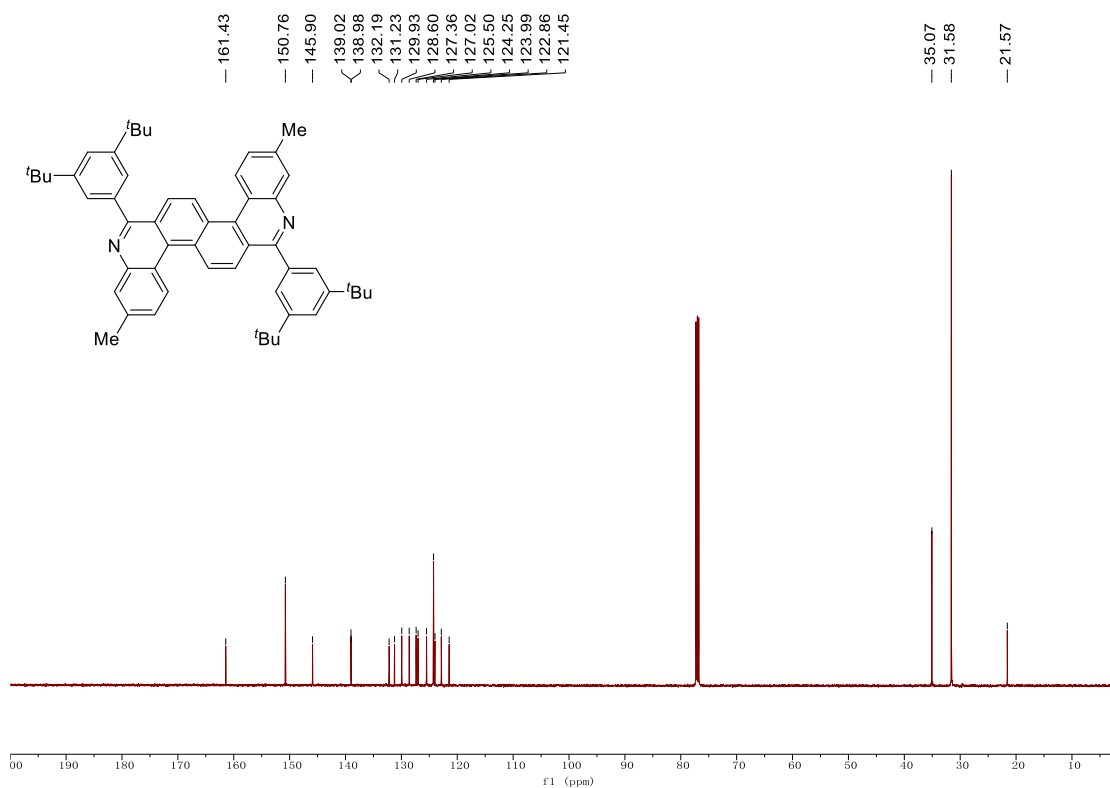
126 Hz ^{13}C $\{^1\text{H}\}$ NMR spectrum of **3h** in CDCl_3



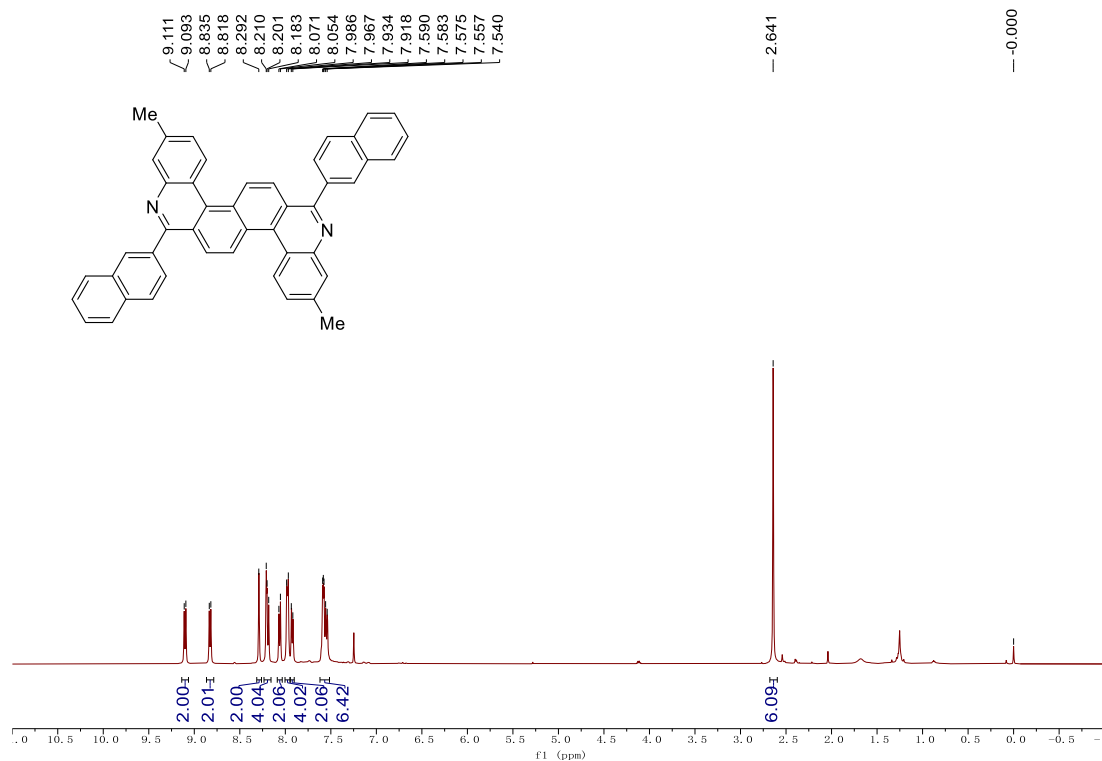
500 Hz ^1H NMR spectrum of **3i** in CDCl_3



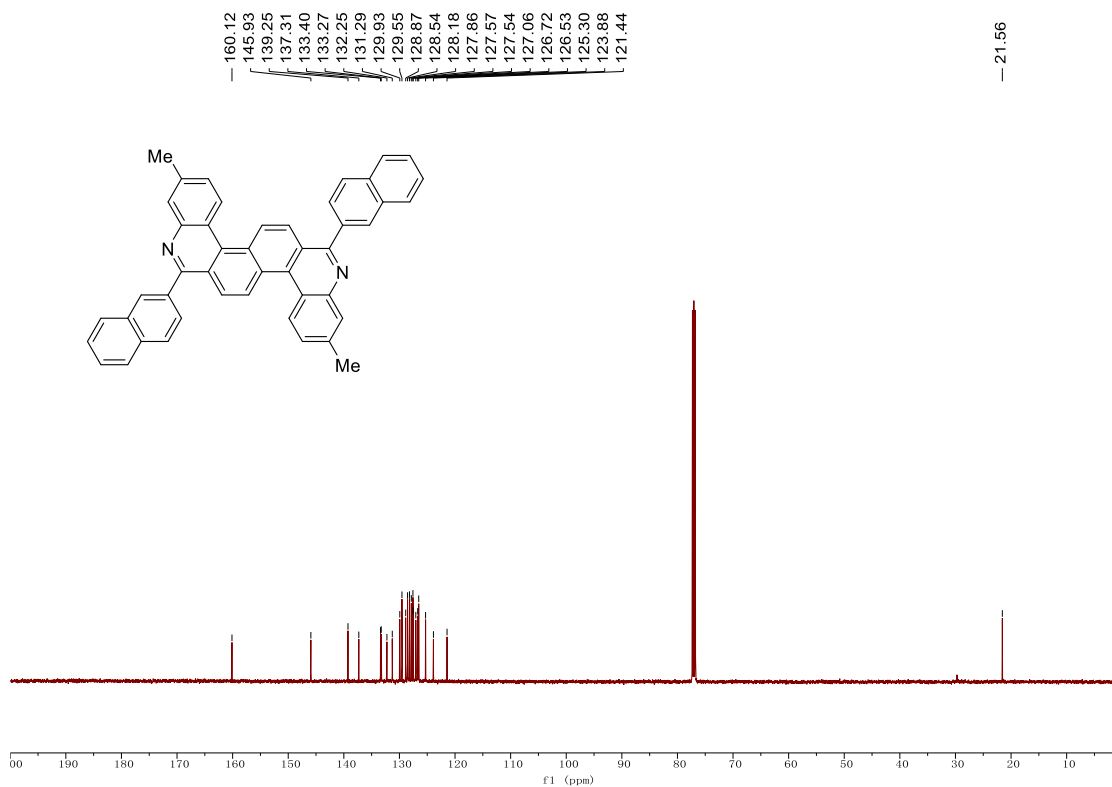
126 Hz ^{13}C $\{^1\text{H}\}$ NMR spectrum of **3i** in CDCl_3



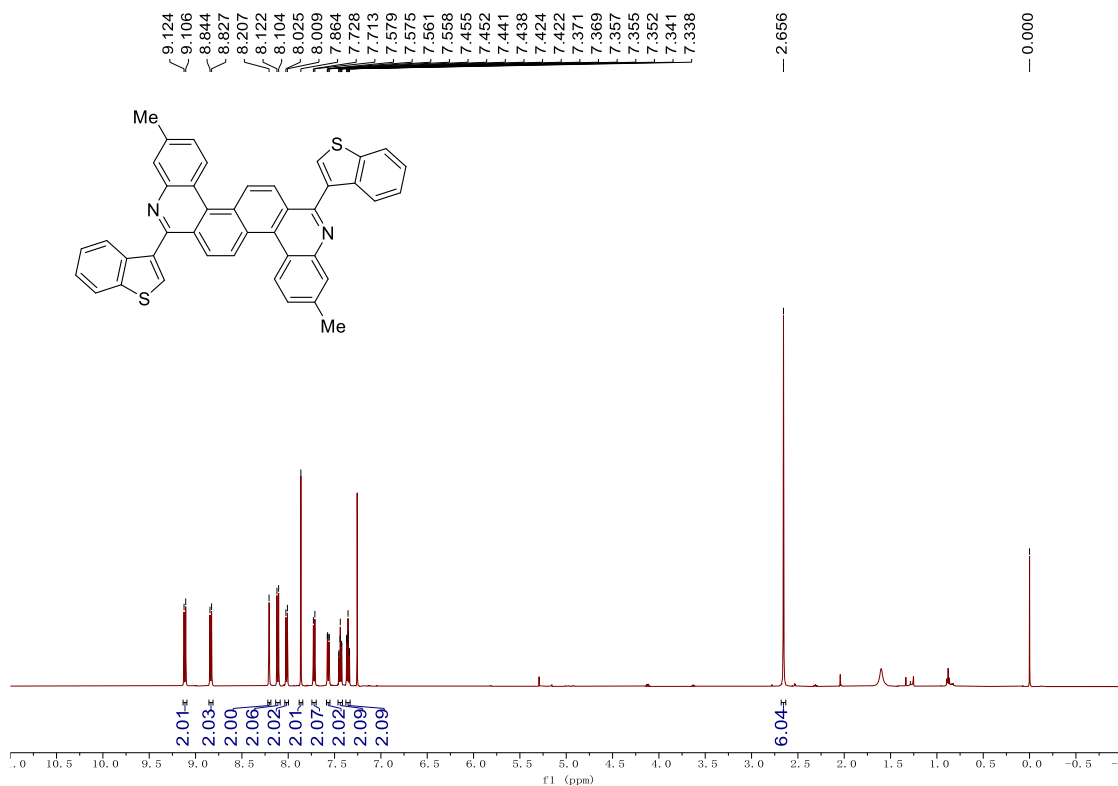
500 Hz ^1H NMR spectrum of **3j** in CDCl_3



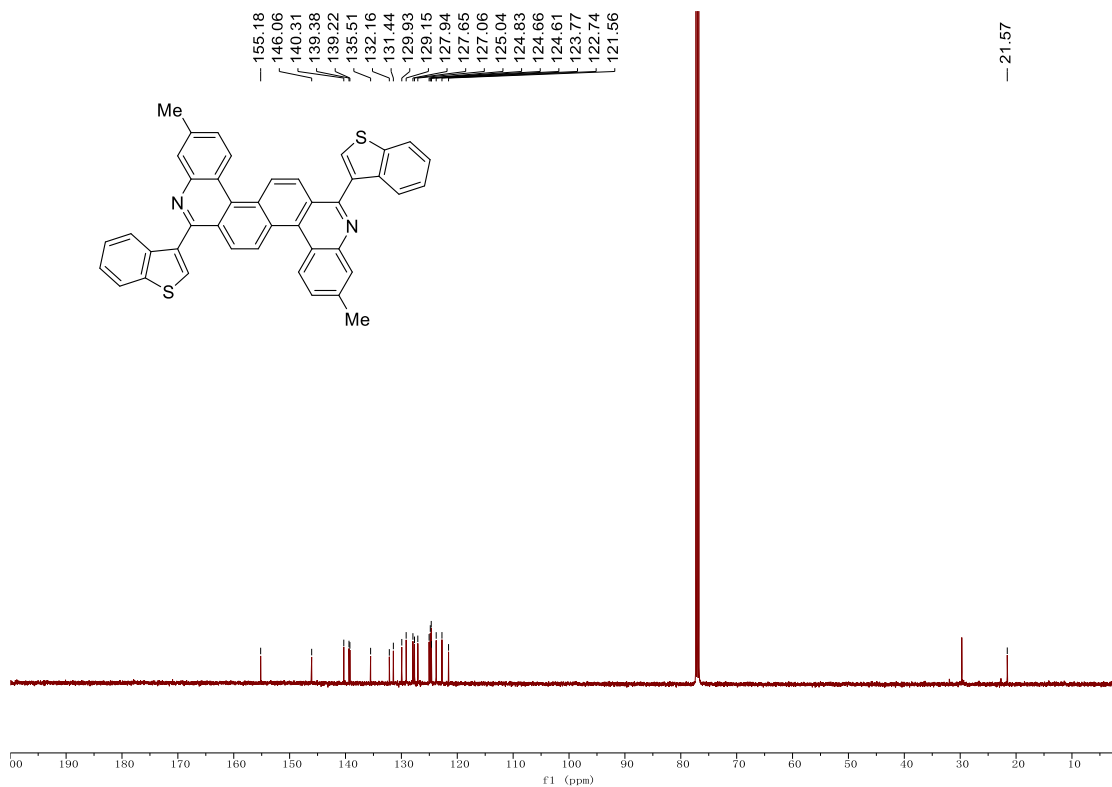
126 Hz ^{13}C $\{^1\text{H}\}$ NMR spectrum of **3j** in CDCl_3



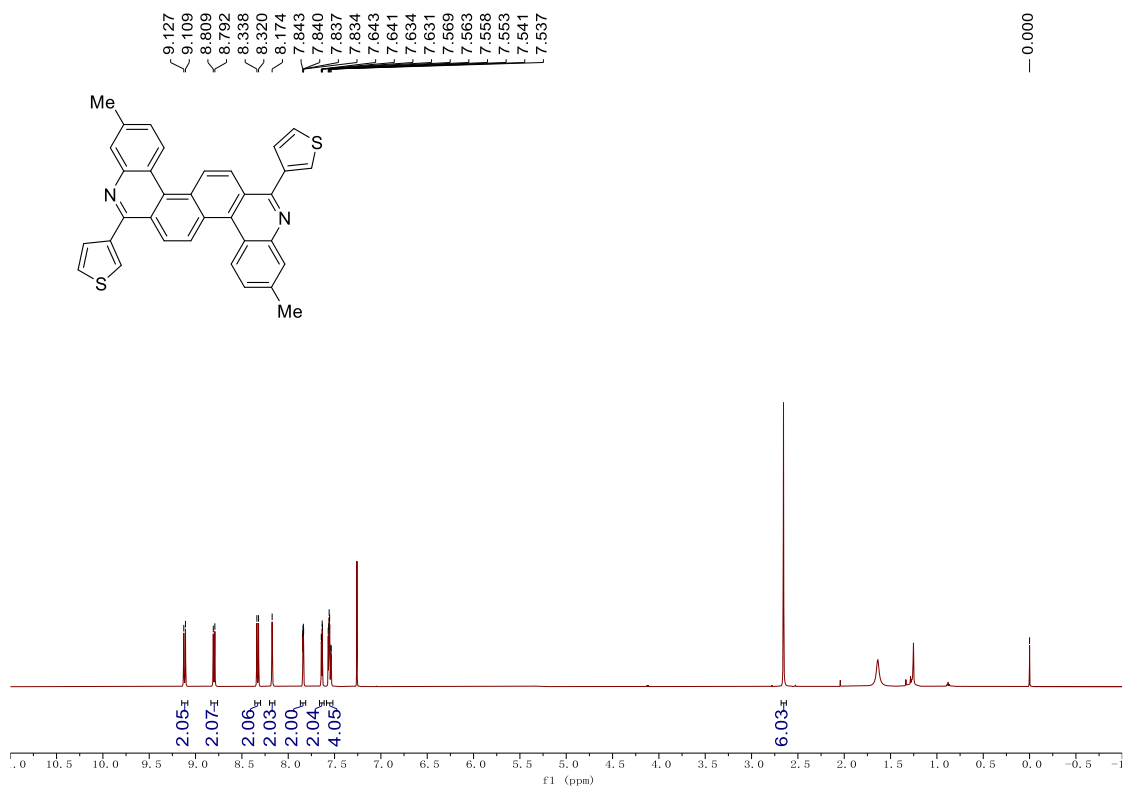
500 Hz ^1H NMR spectrum of **3k** in CDCl_3



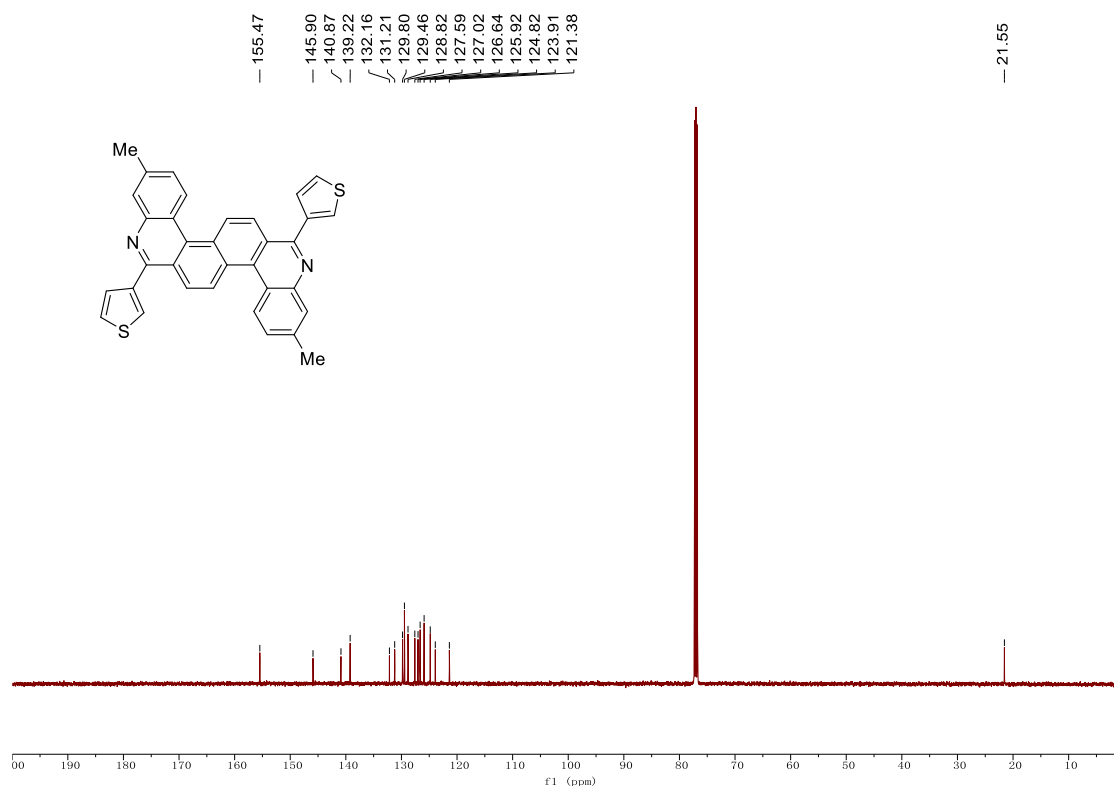
126 Hz ^{13}C $\{^1\text{H}\}$ NMR spectrum of **3k** in CDCl_3



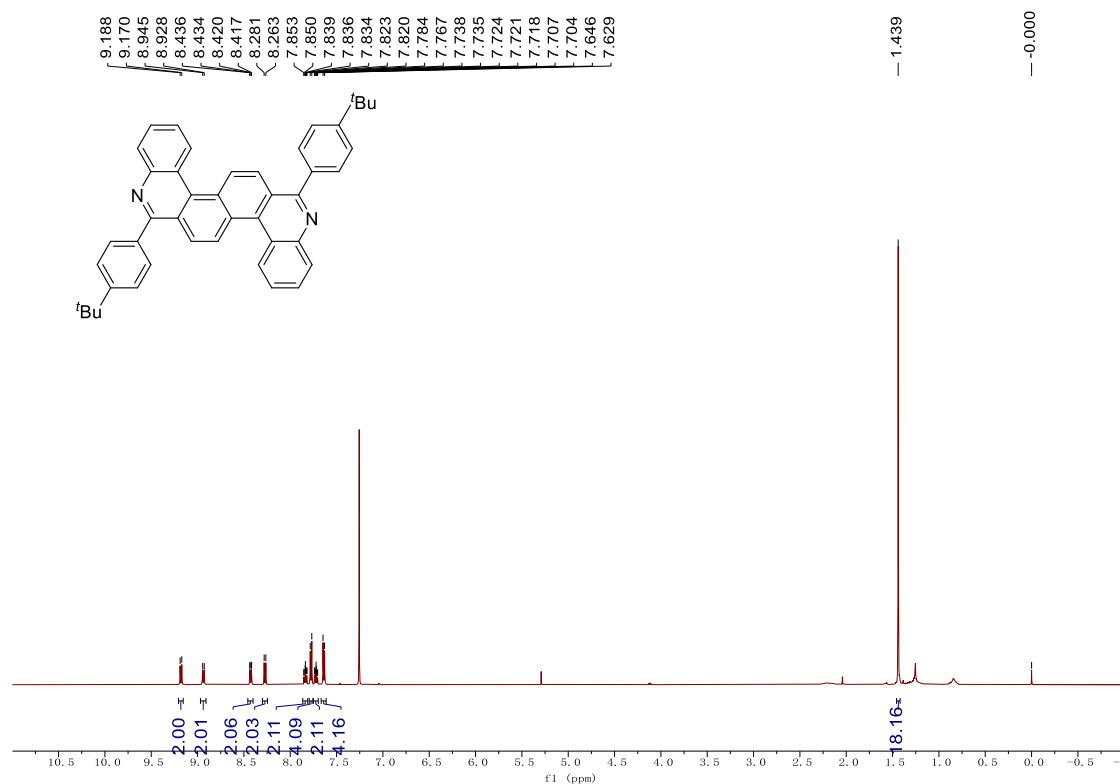
500 Hz ^1H NMR spectrum of **3l** in CDCl_3



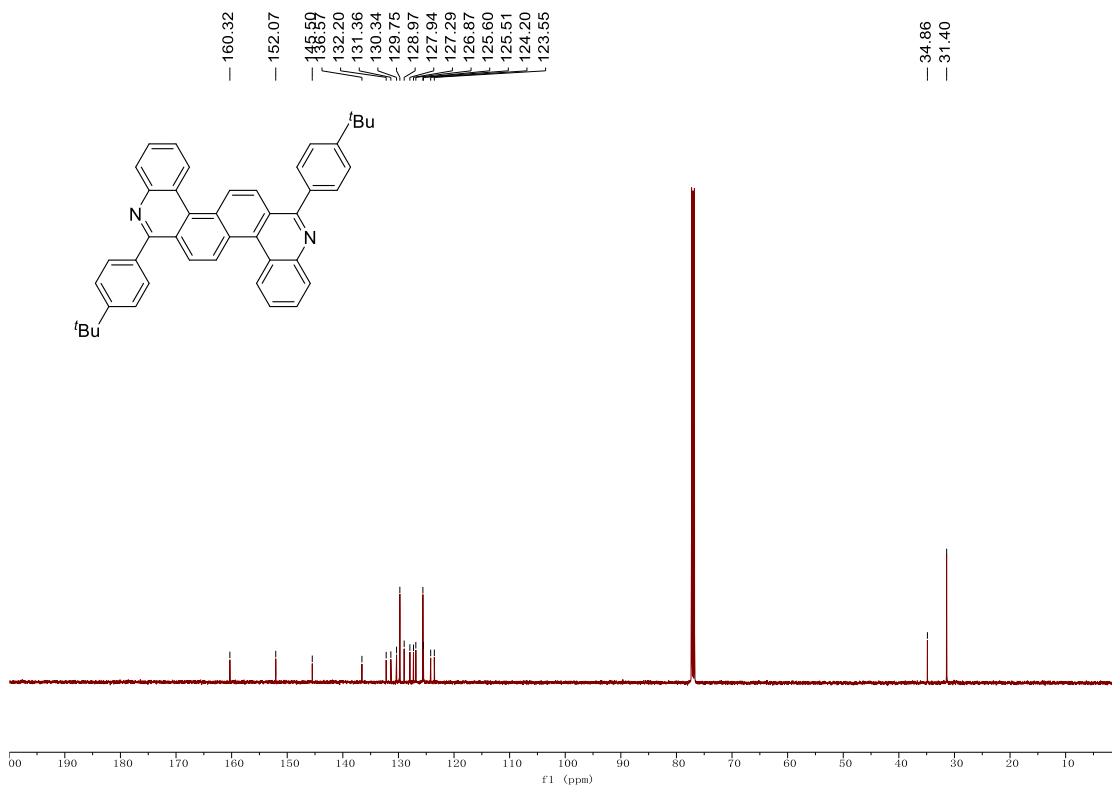
126 Hz ^{13}C $\{^1\text{H}\}$ NMR spectrum of **3l** in CDCl_3



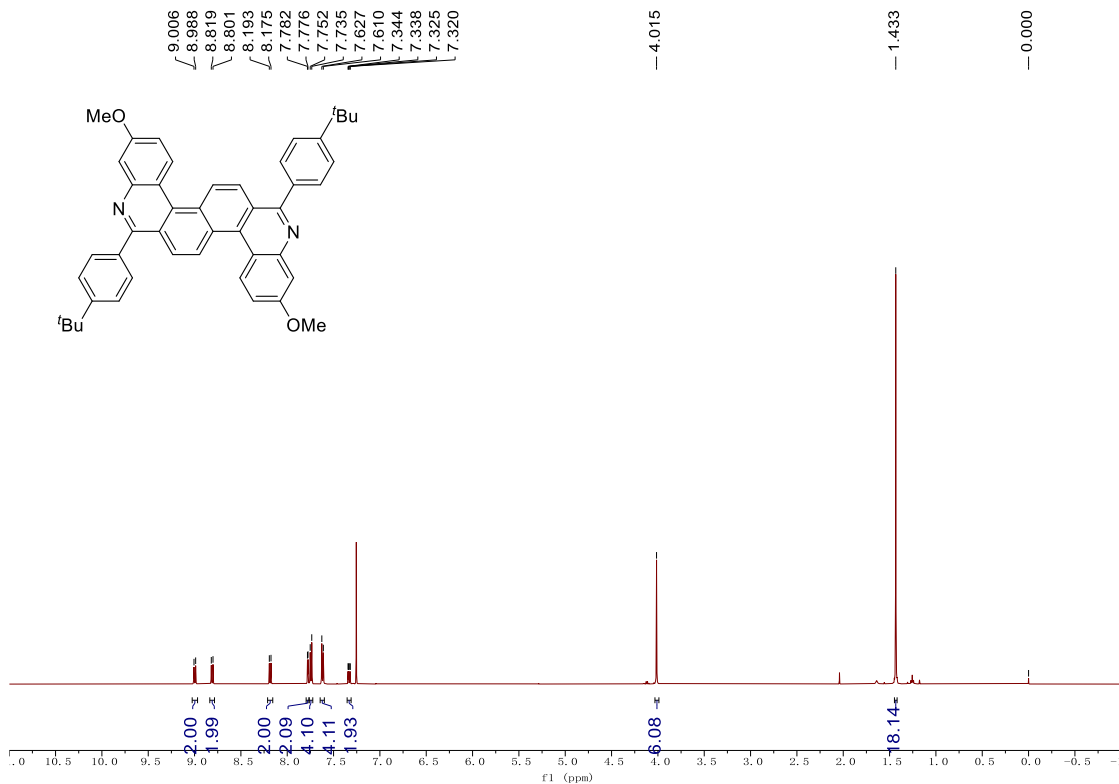
500 Hz ^1H NMR spectrum of **3m** in CDCl_3



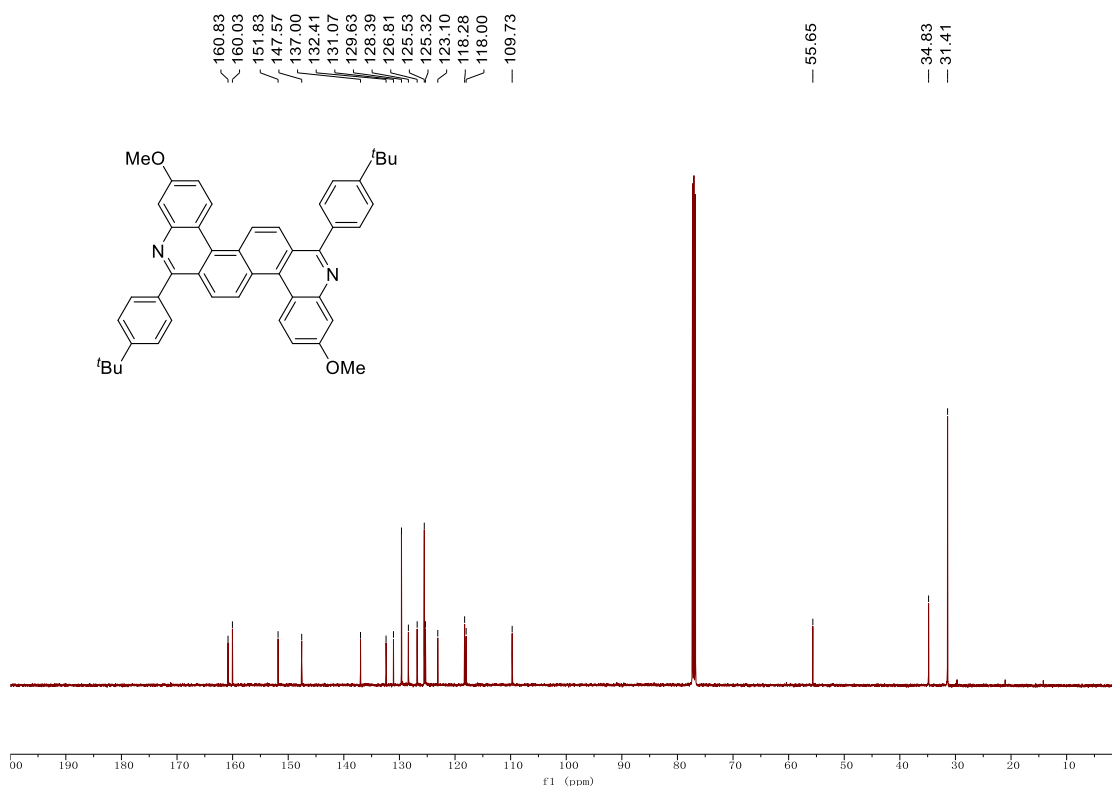
126 Hz ^{13}C $\{^1\text{H}\}$ NMR spectrum of **3m** in CDCl_3



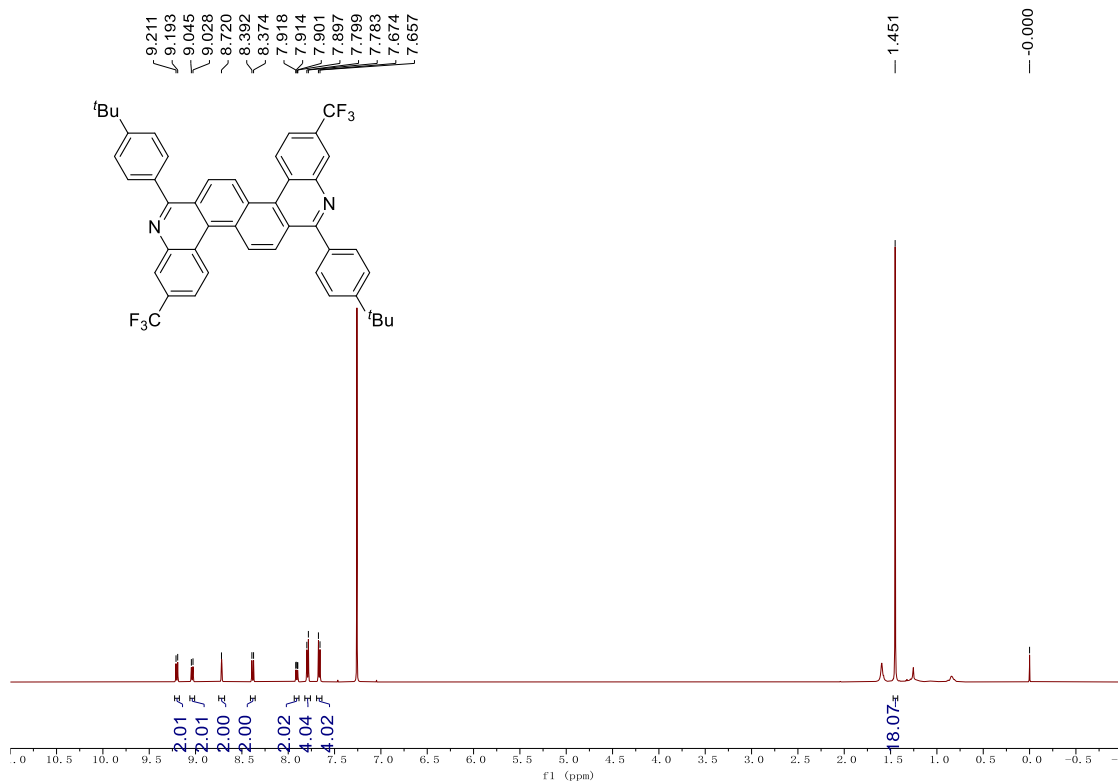
500 Hz ^1H NMR spectrum of **3n** in CDCl_3



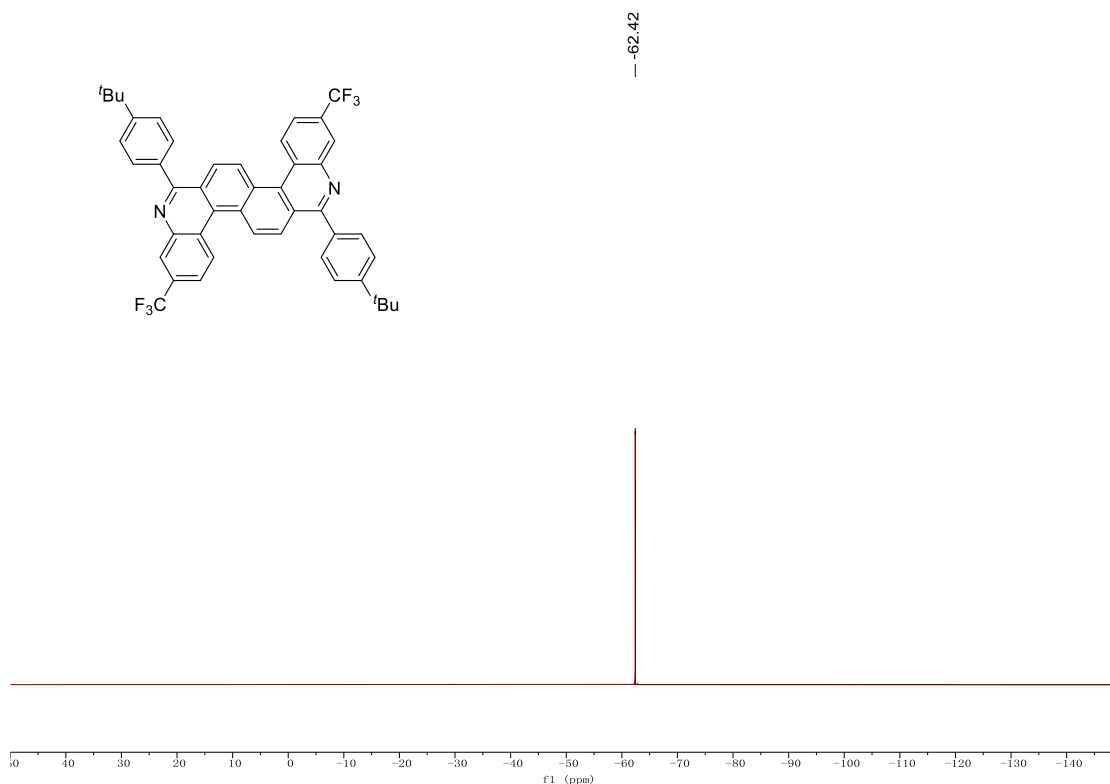
126 Hz ^{13}C $\{^1\text{H}\}$ NMR spectrum of **3n** in CDCl_3



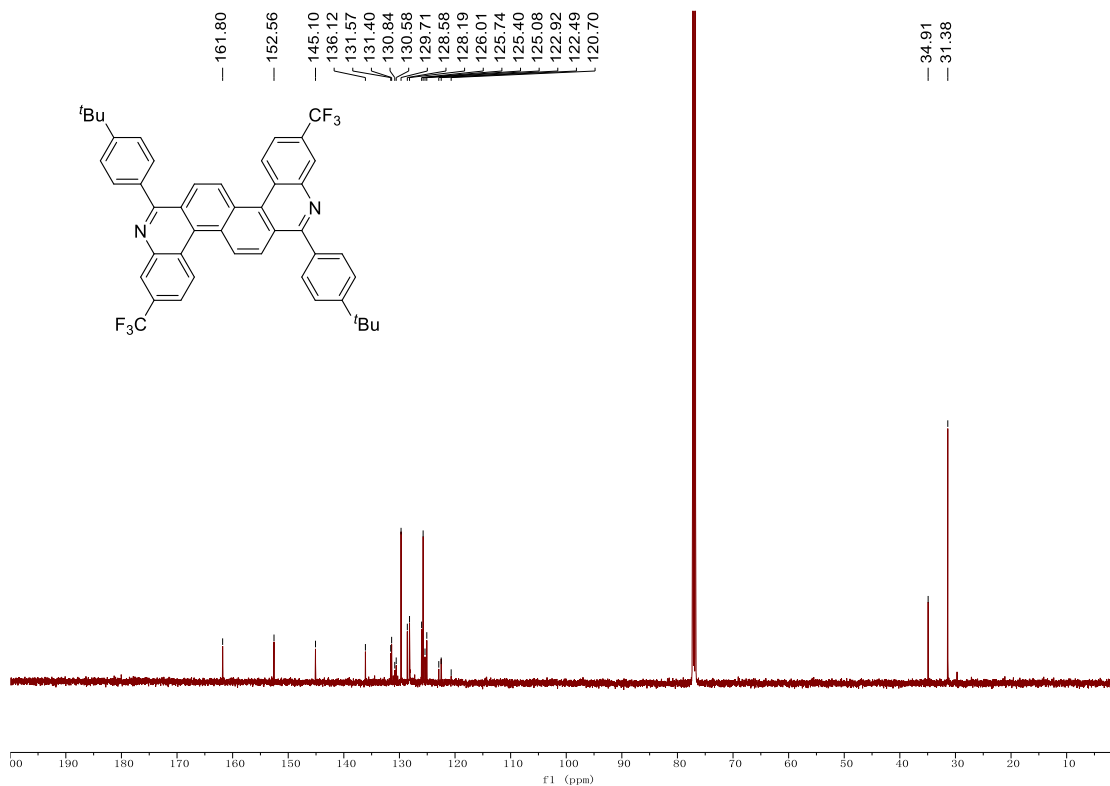
500 Hz ^1H NMR spectrum of **3o** in CDCl_3



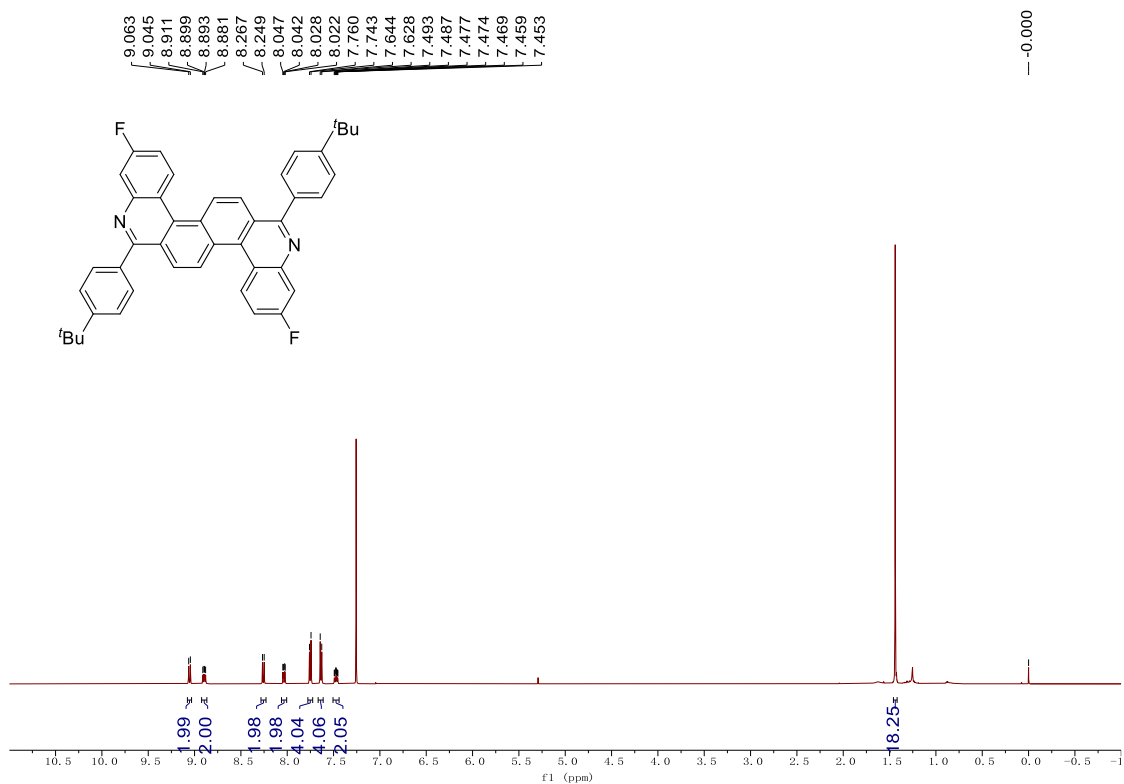
471 Hz ^{19}F $\{^1\text{H}\}$ NMR spectrum of **3o** in CDCl_3



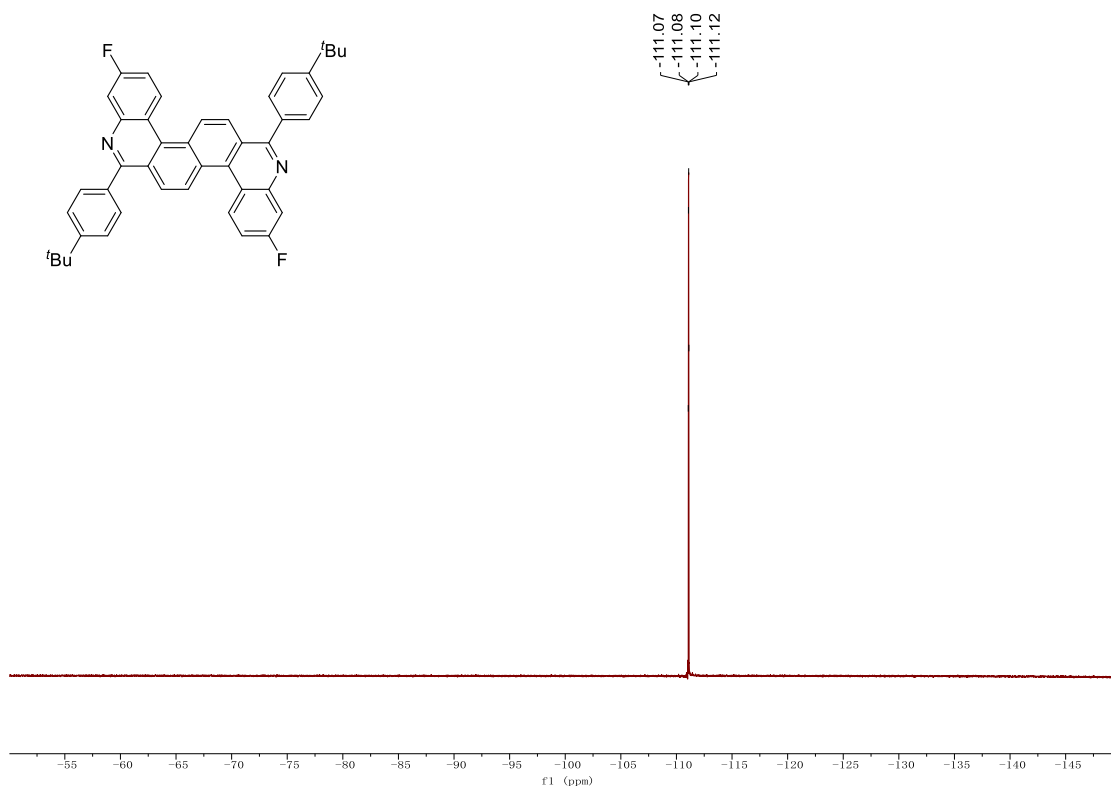
126 Hz ^{13}C $\{^1\text{H}\}$ NMR spectrum of **3o** in CDCl_3



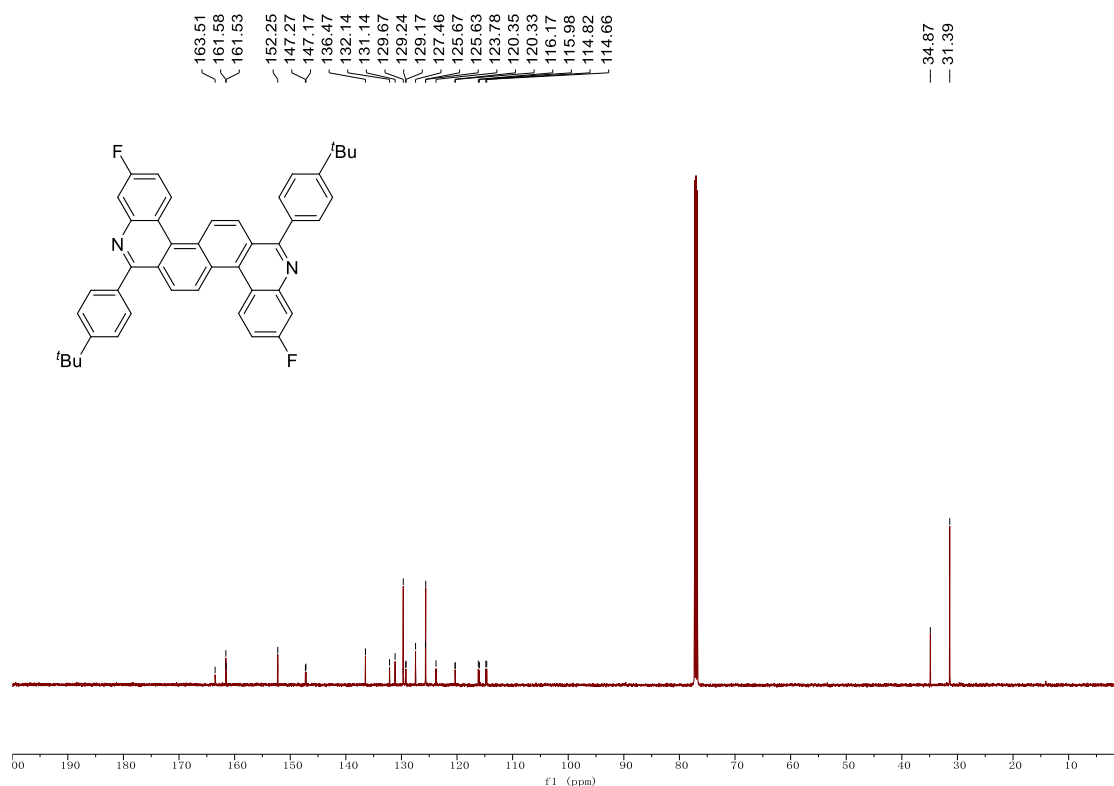
500 Hz ^1H NMR spectrum of **3p** in CDCl_3



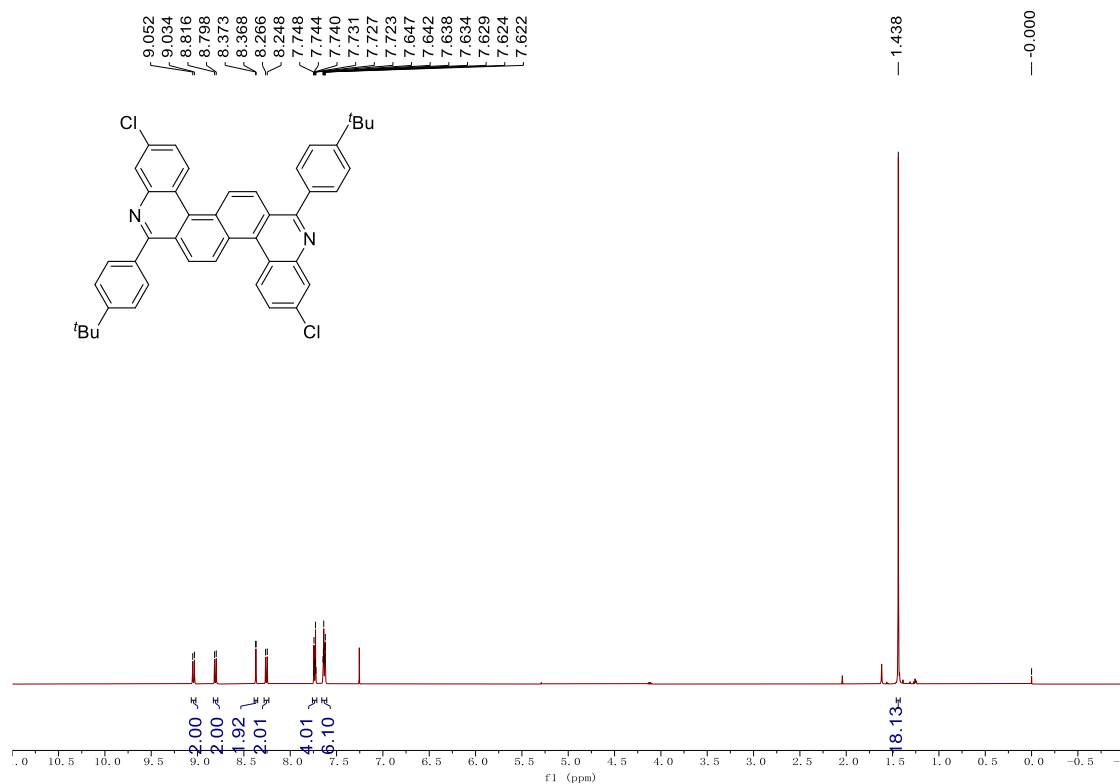
471 Hz ^{19}F { ^1H } NMR spectrum of **3p** in CDCl_3



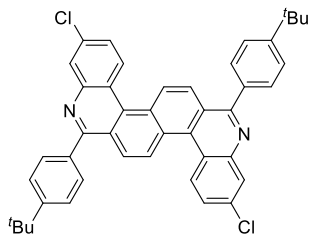
126 Hz ^{13}C $\{^1\text{H}\}$ NMR spectrum of **3p** in CDCl_3



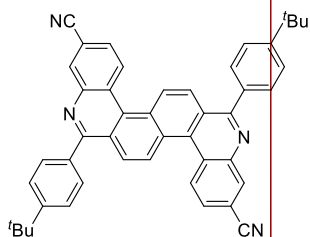
500 Hz ^1H NMR spectrum of **3q** in CDCl_3



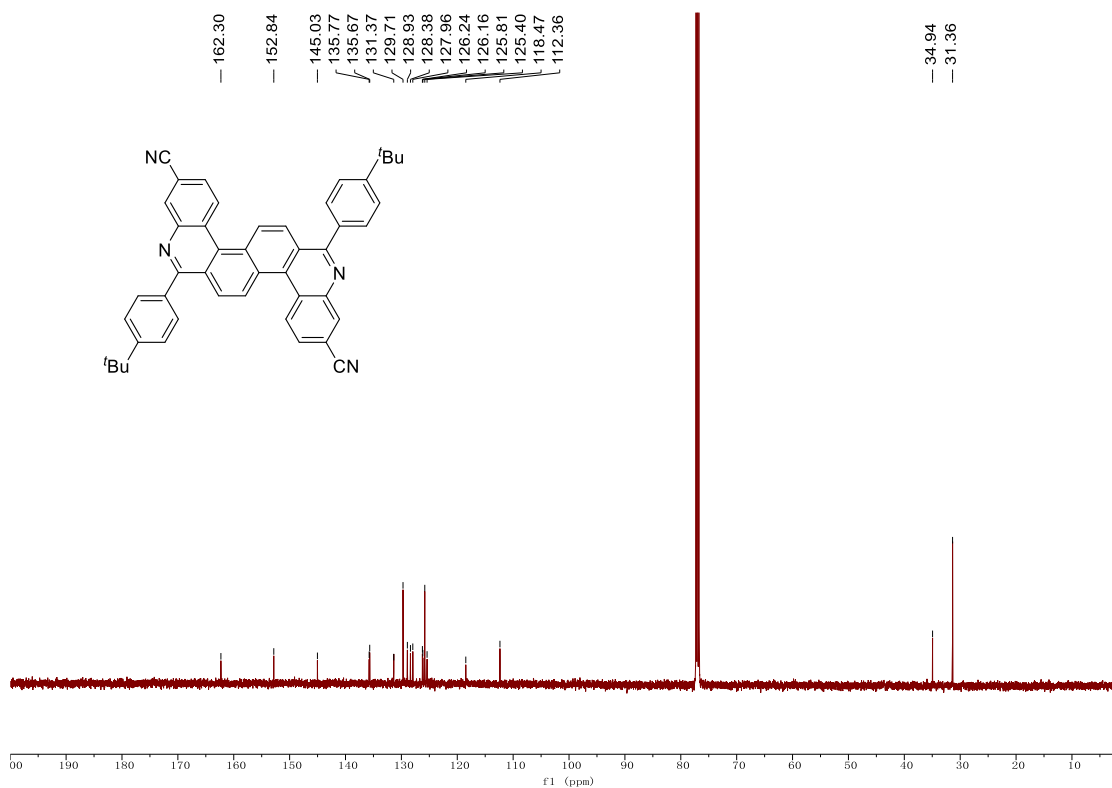
— 161.49
— 152.31
— 146.46
— 136.37
— 134.63
— 131.88
— 131.17
— 129.69
— 129.62
— 128.45
— 127.74
— 127.32
— 125.72
— 125.64
— 124.19
— 121.91



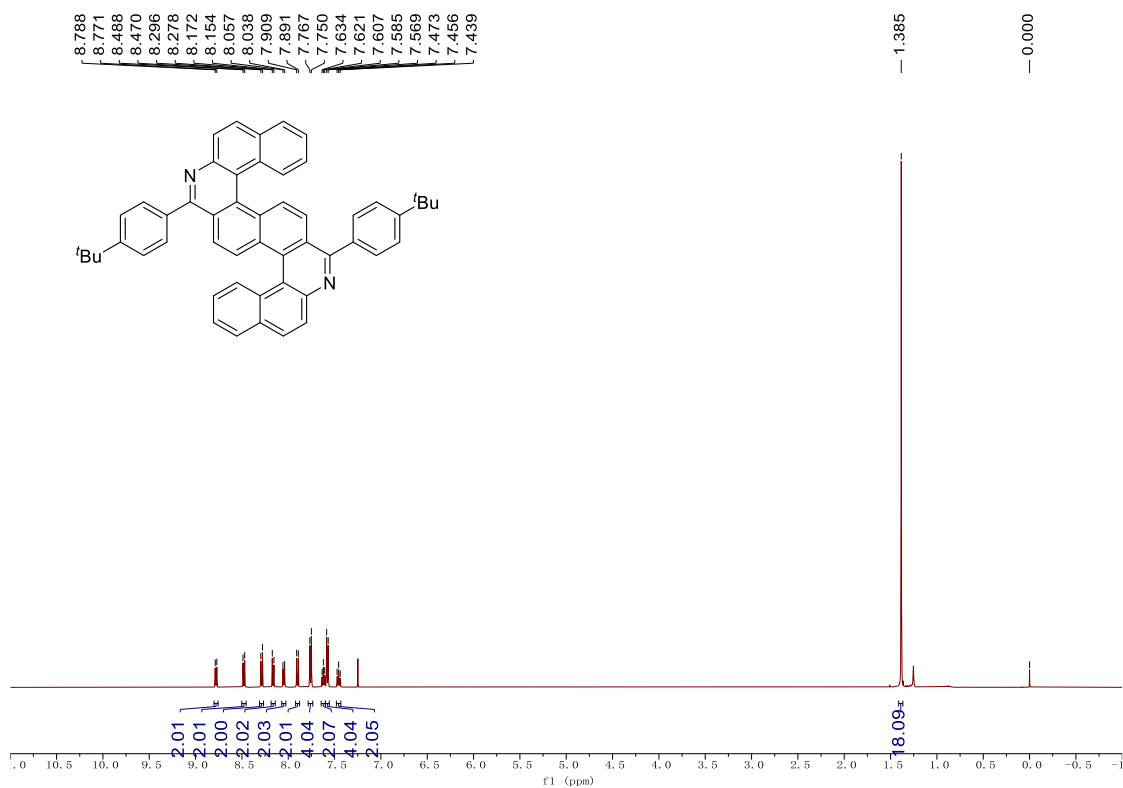
9.181
9.163
8.999
8.981
8.740
8.736
8.411
8.392
7.905
7.901
7.888
7.884
~~7.790~~
7.773
7.680
7.663



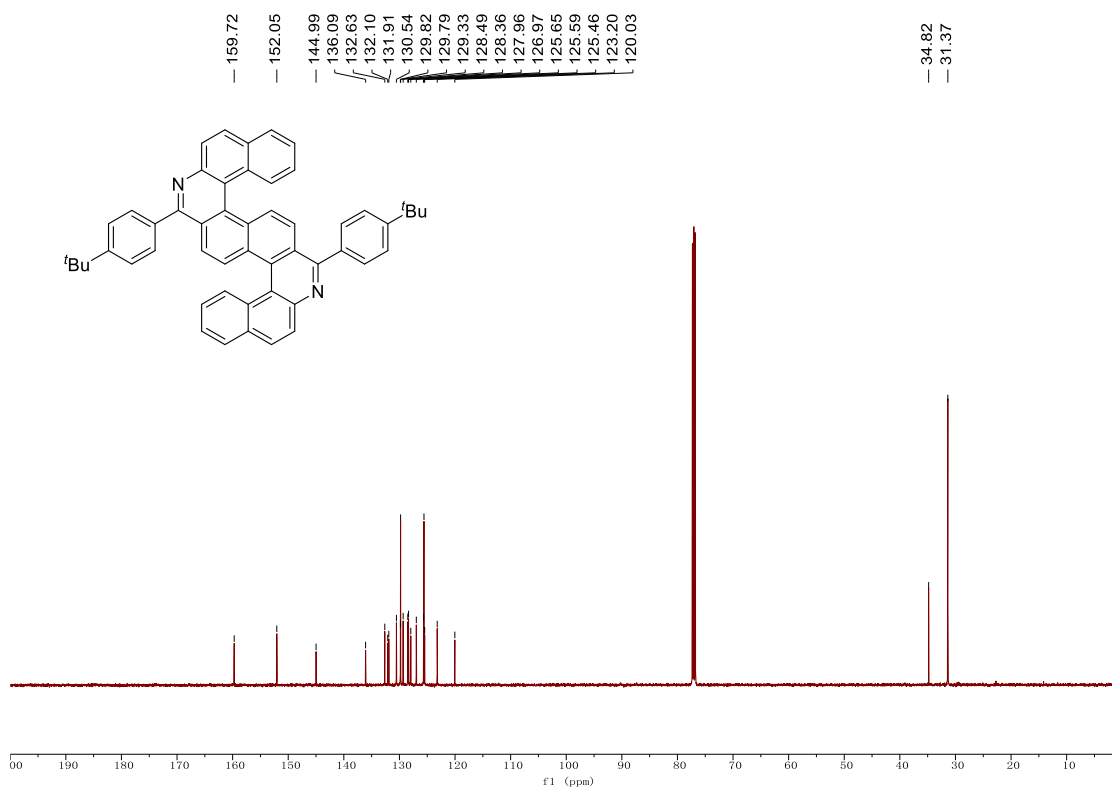
126 Hz ^{13}C $\{^1\text{H}\}$ NMR spectrum of **3r** in CDCl_3



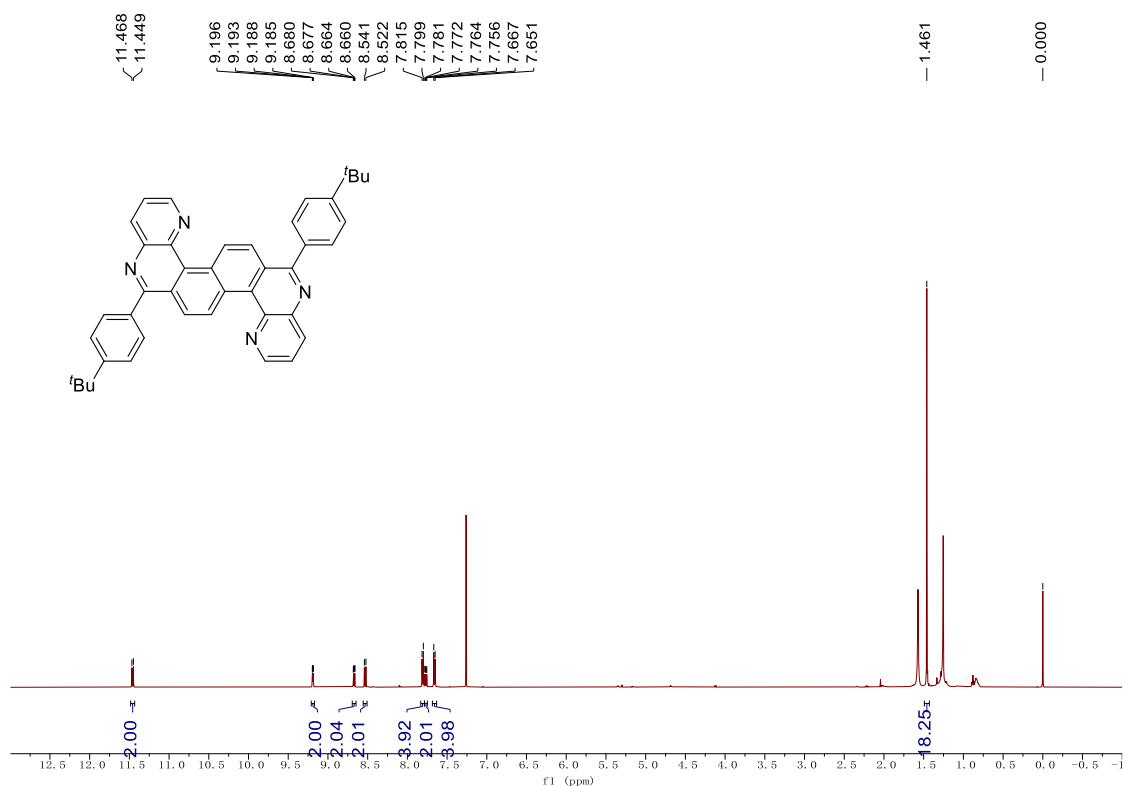
500 Hz ^1H NMR spectrum of **3s** in CDCl_3



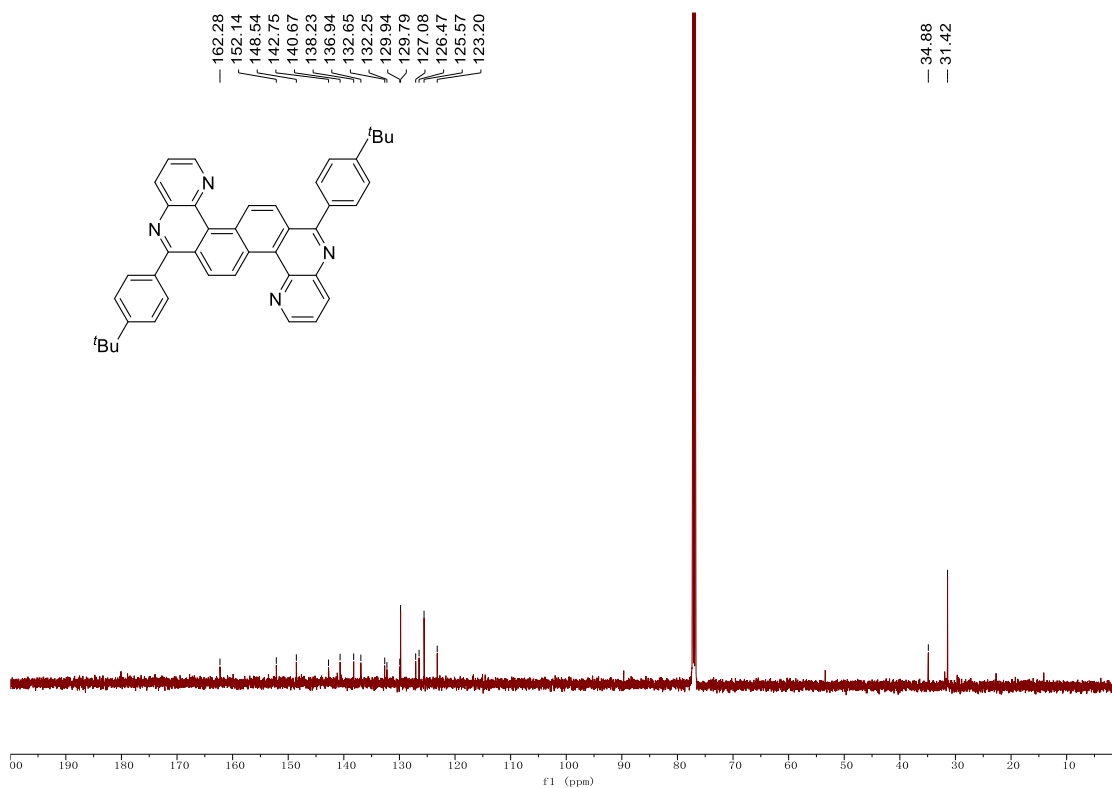
126 Hz ^{13}C $\{^1\text{H}\}$ NMR spectrum of **3s** in CDCl_3



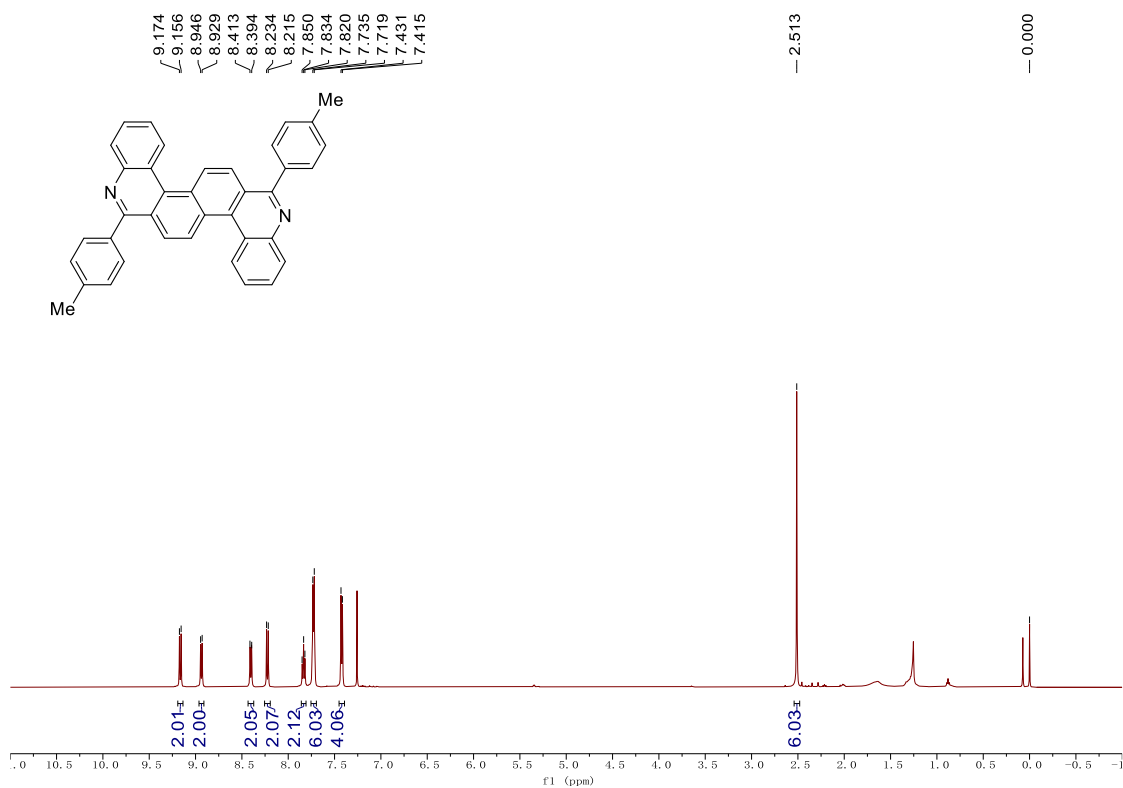
500 Hz ^1H NMR spectrum of **3t** in CDCl_3



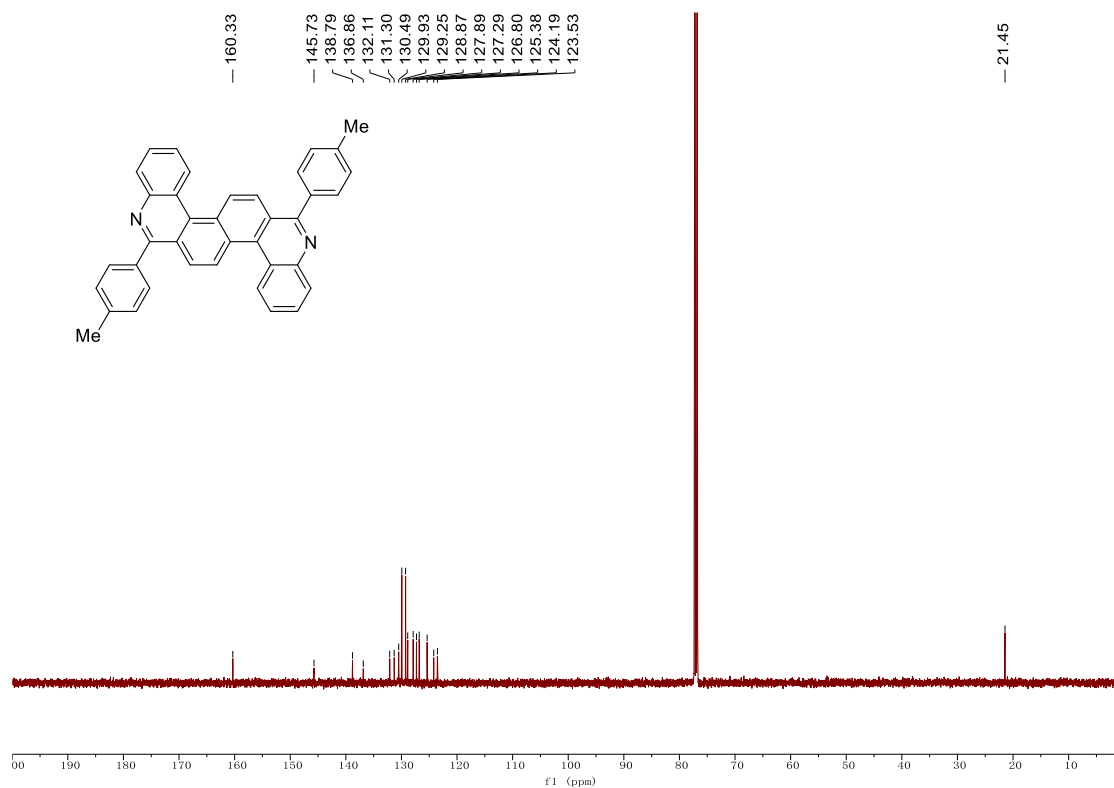
126 Hz ^{13}C $\{^1\text{H}\}$ NMR spectrum of **3t** in CDCl_3



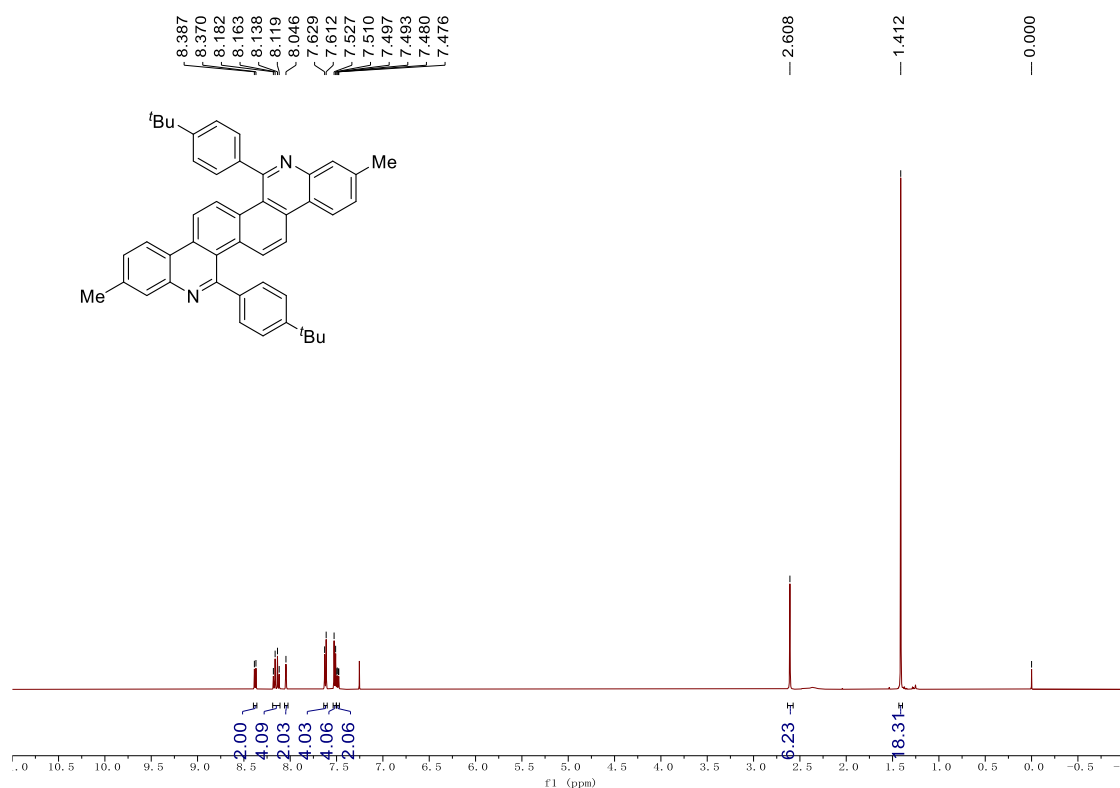
500 Hz ^1H NMR spectrum of **3u** in CDCl_3



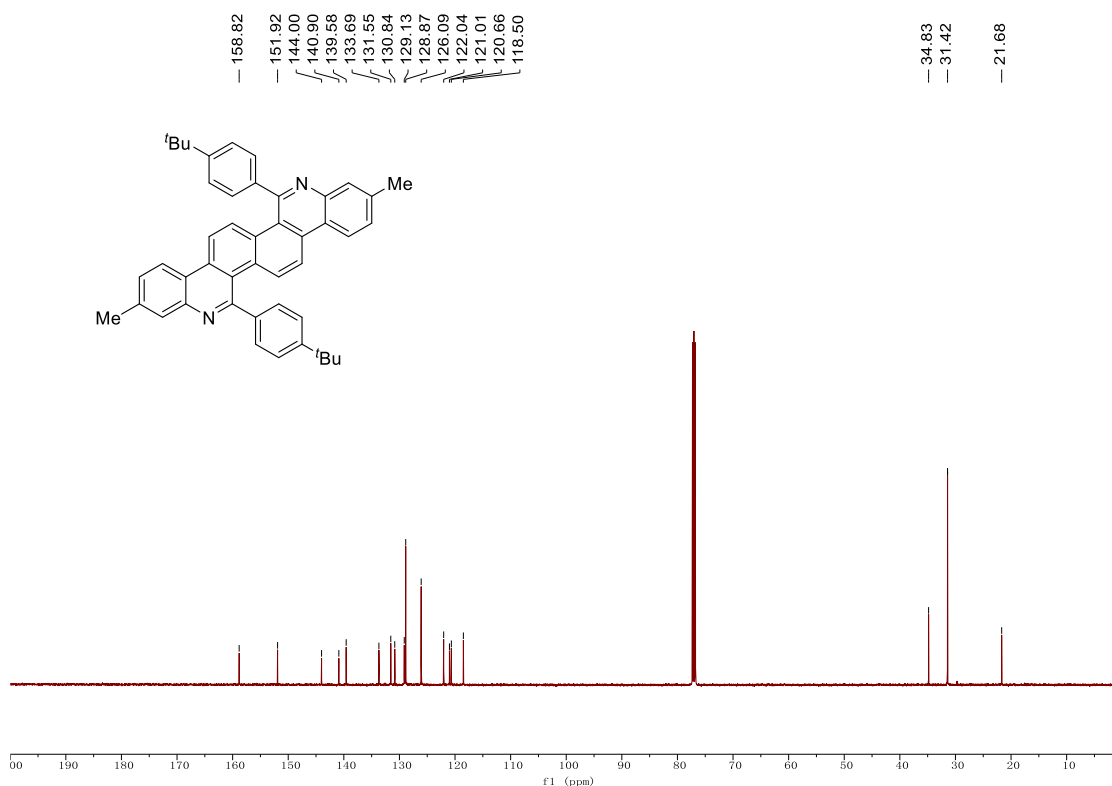
126 Hz ^{13}C $\{^1\text{H}\}$ NMR spectrum of **3u** in CDCl_3



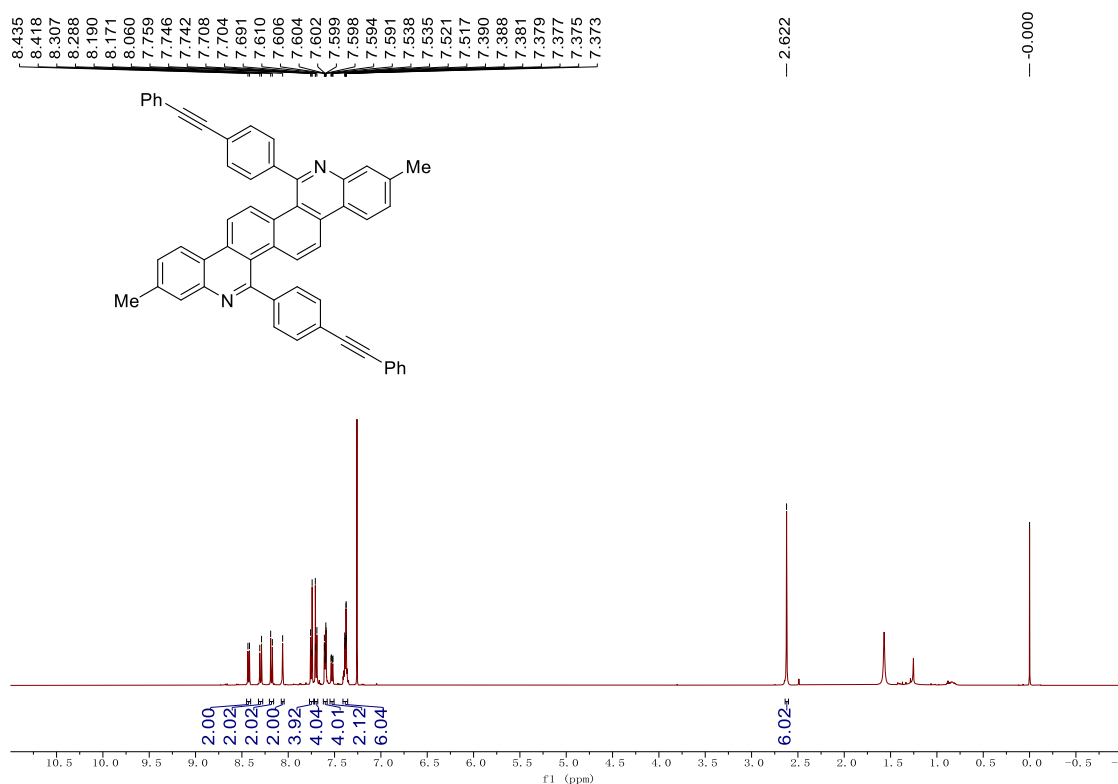
500 Hz ^1H NMR spectrum of **3v** in CDCl_3



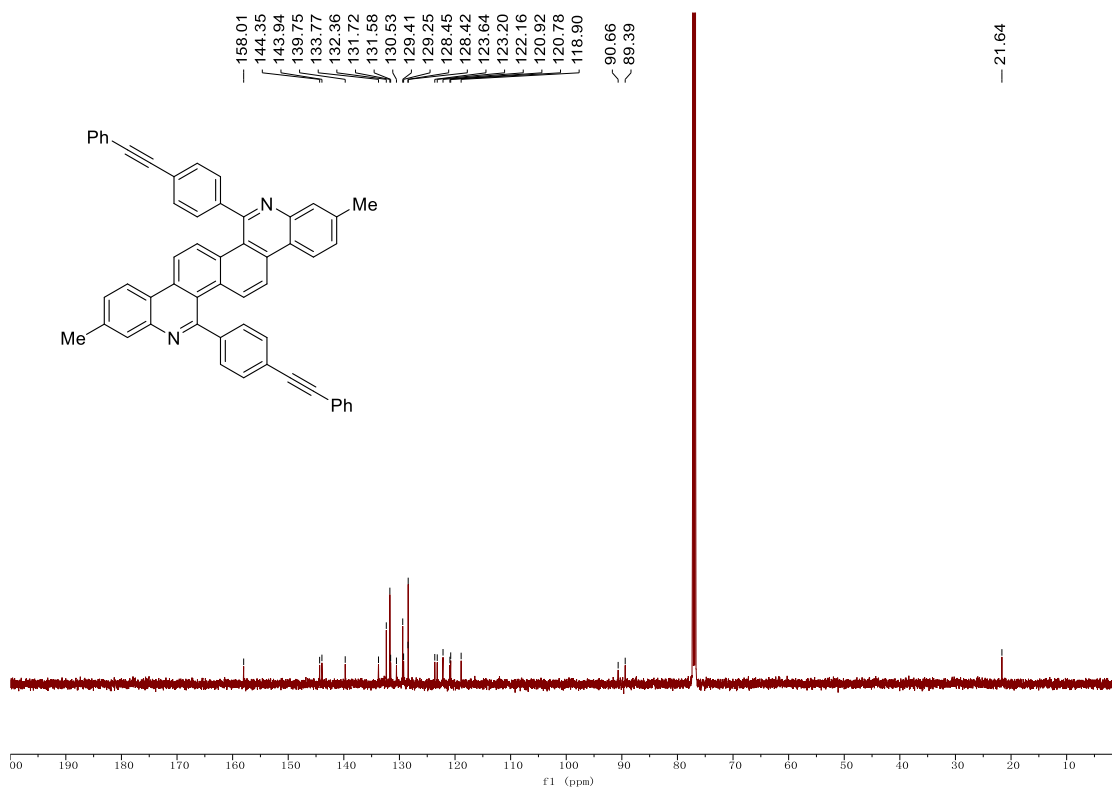
126 Hz ^{13}C $\{^1\text{H}\}$ NMR spectrum of **3v** in CDCl_3



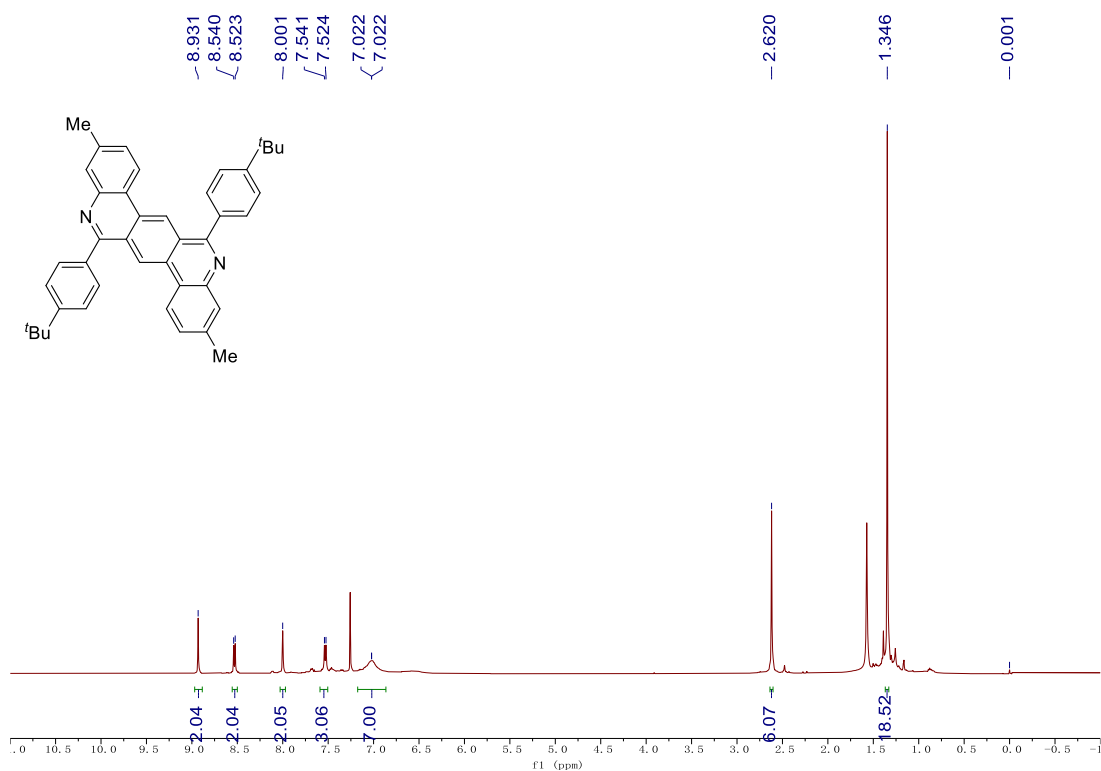
500 Hz ^1H NMR spectrum of **3w** in CDCl_3



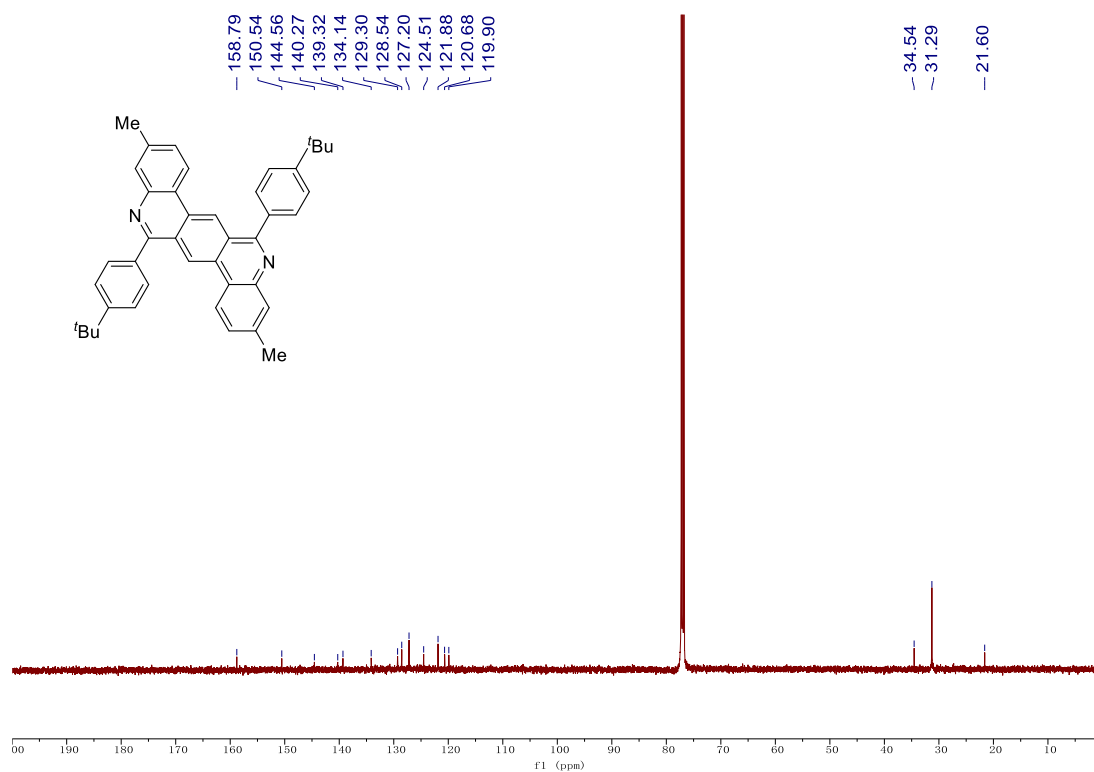
126 Hz ^{13}C $\{^1\text{H}\}$ NMR spectrum of **3w** in CDCl_3



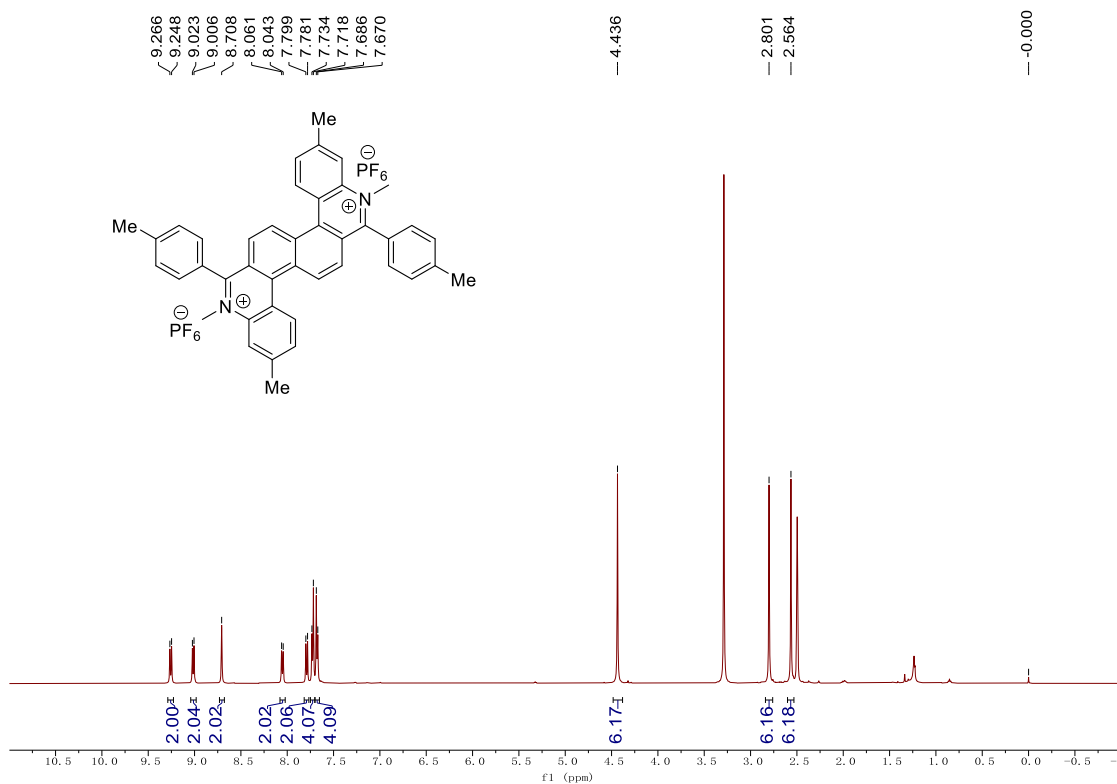
500 Hz ^1H NMR spectrum of **3x** in CDCl_3



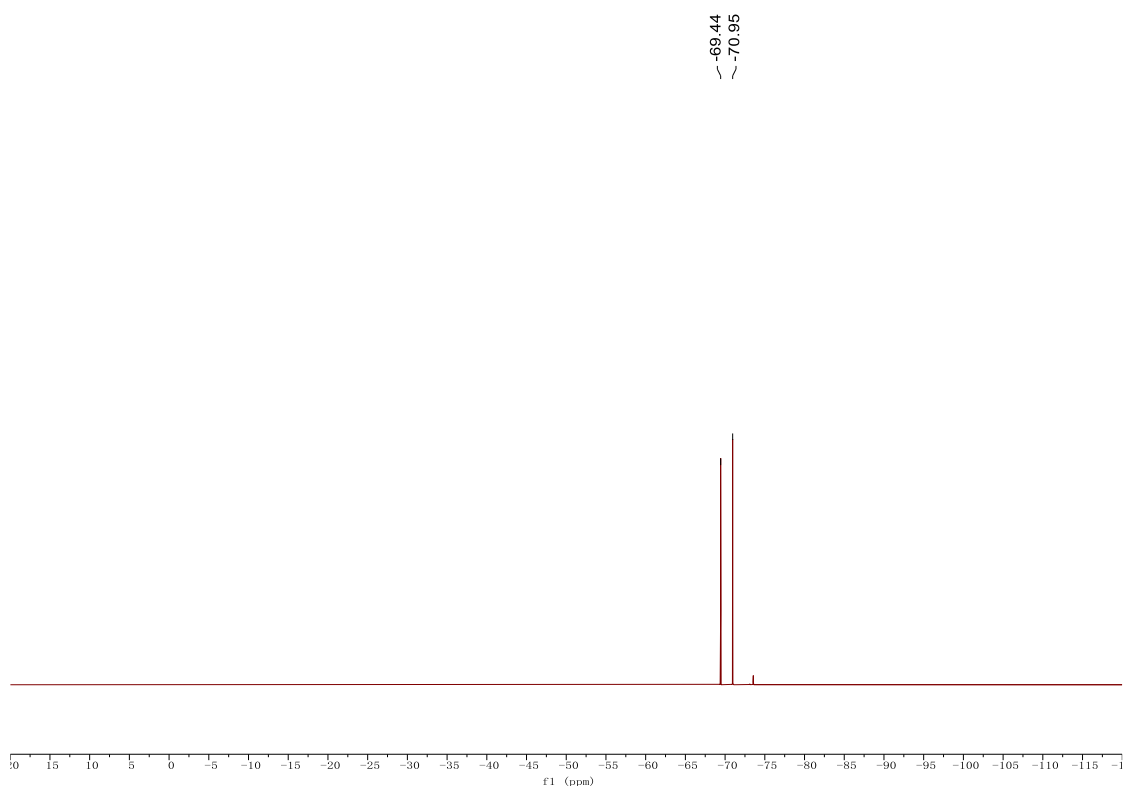
126 Hz ^{13}C $\{^1\text{H}\}$ NMR spectrum of **3x** in CDCl_3



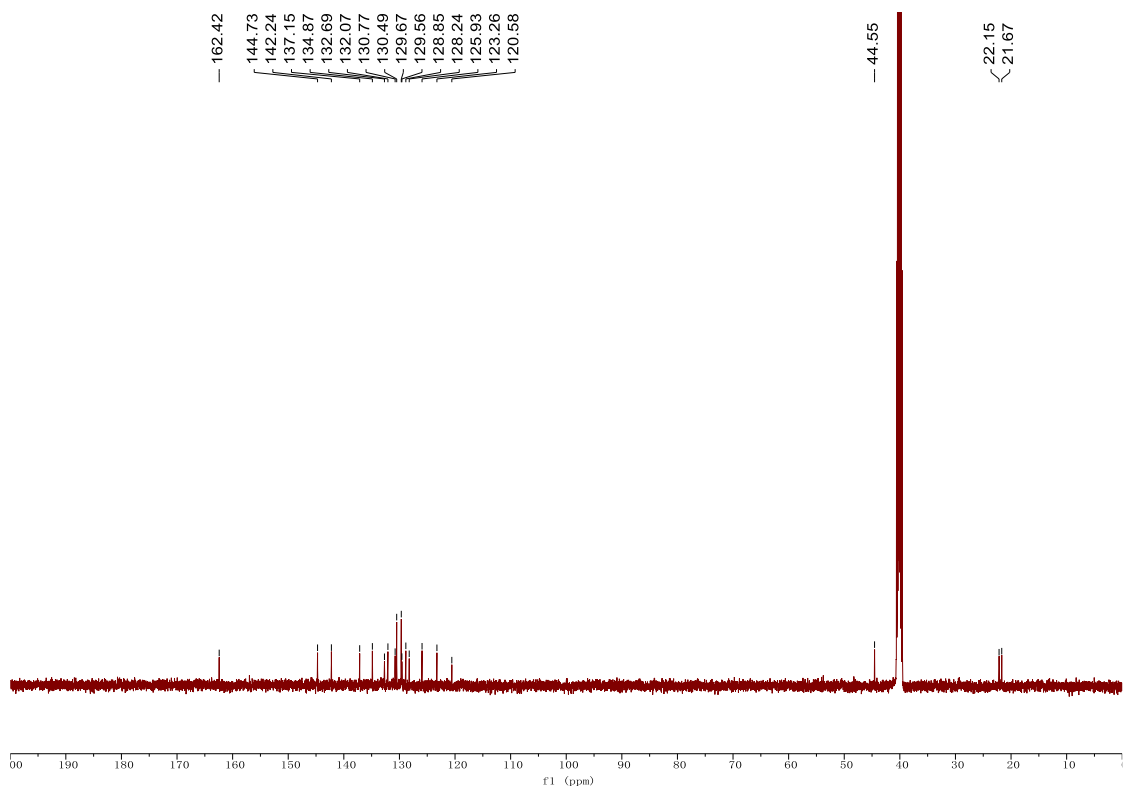
500 Hz ^1H NMR spectrum of **Me-3d** in CDCl_3



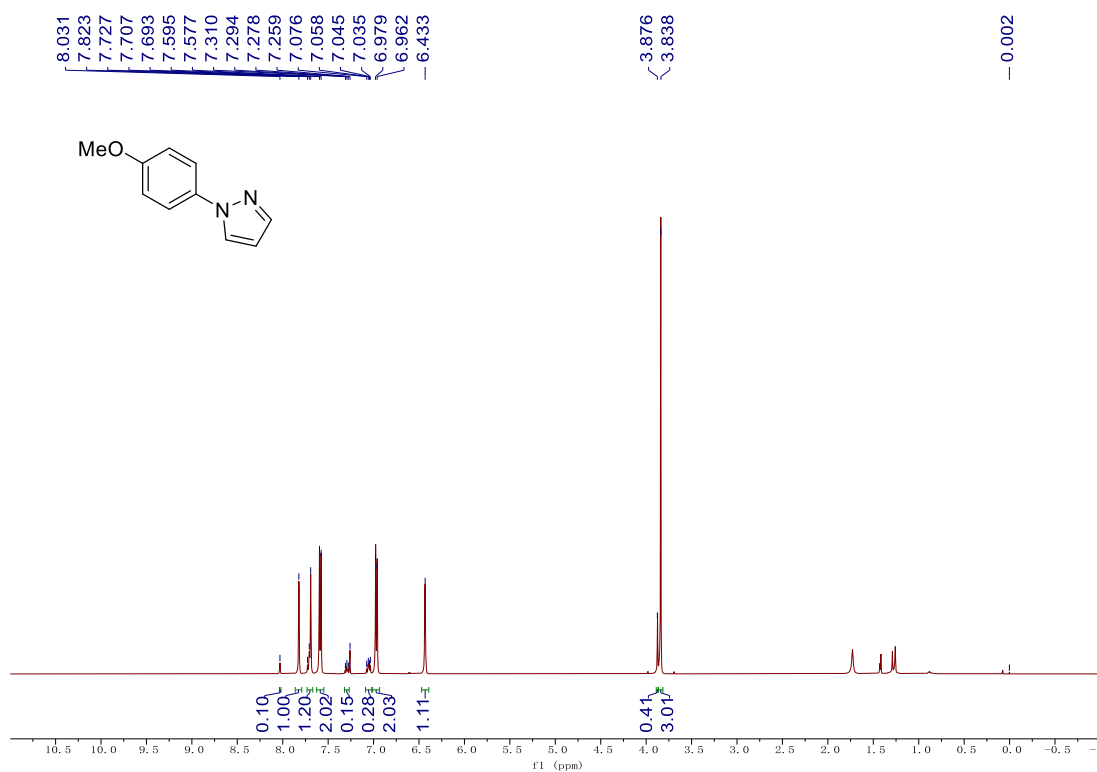
471 Hz ^{19}F $\{^1\text{H}\}$ NMR spectrum of **Me-3d** in CDCl_3



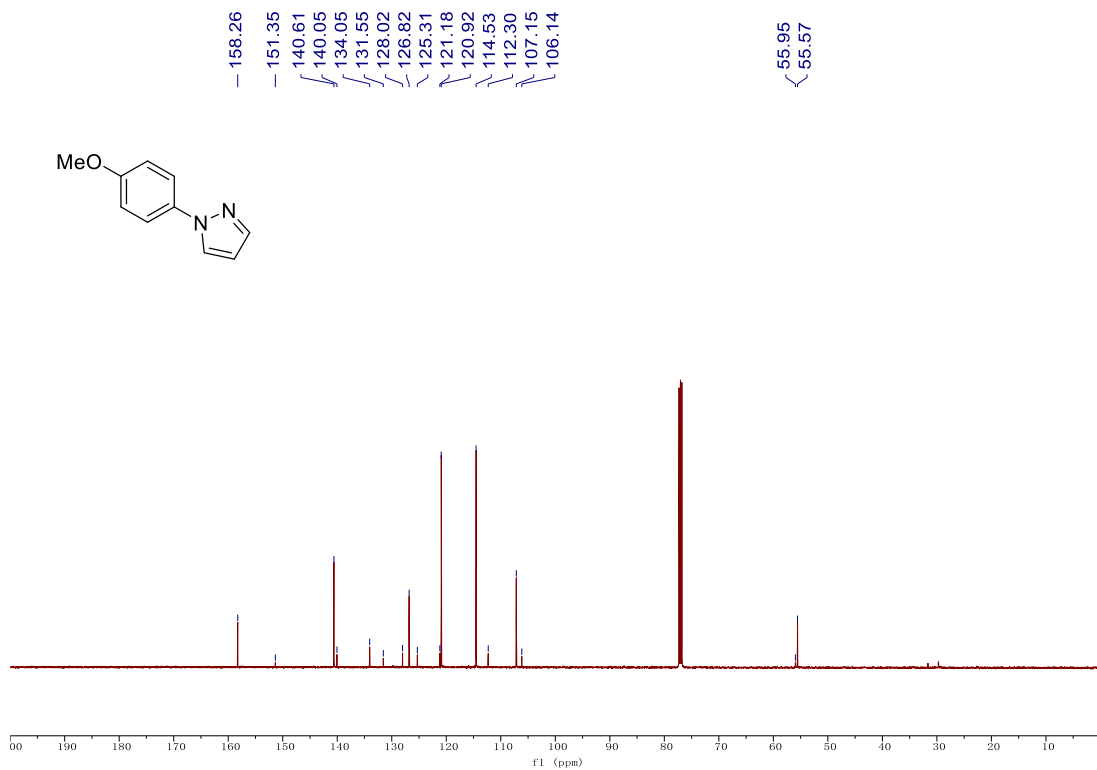
126 Hz ^{13}C $\{^1\text{H}\}$ NMR spectrum of **Me-3d** in CDCl_3



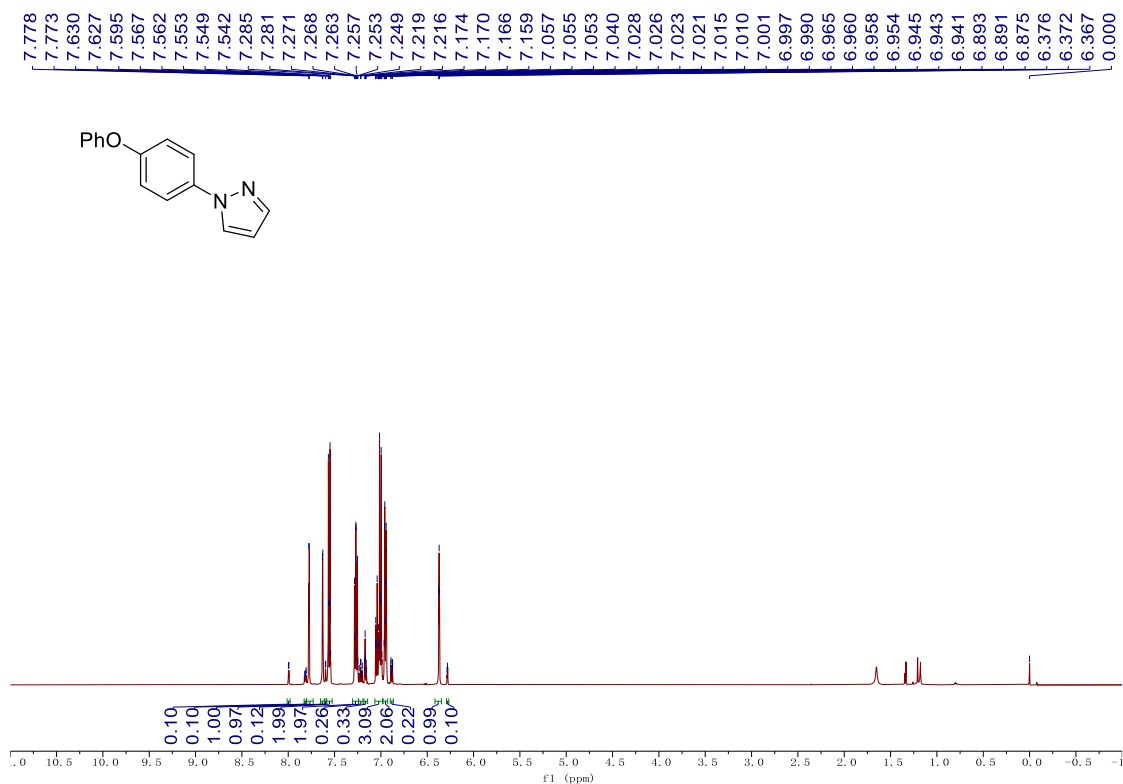
500 Hz ^1H NMR spectrum of **5a** in CDCl_3



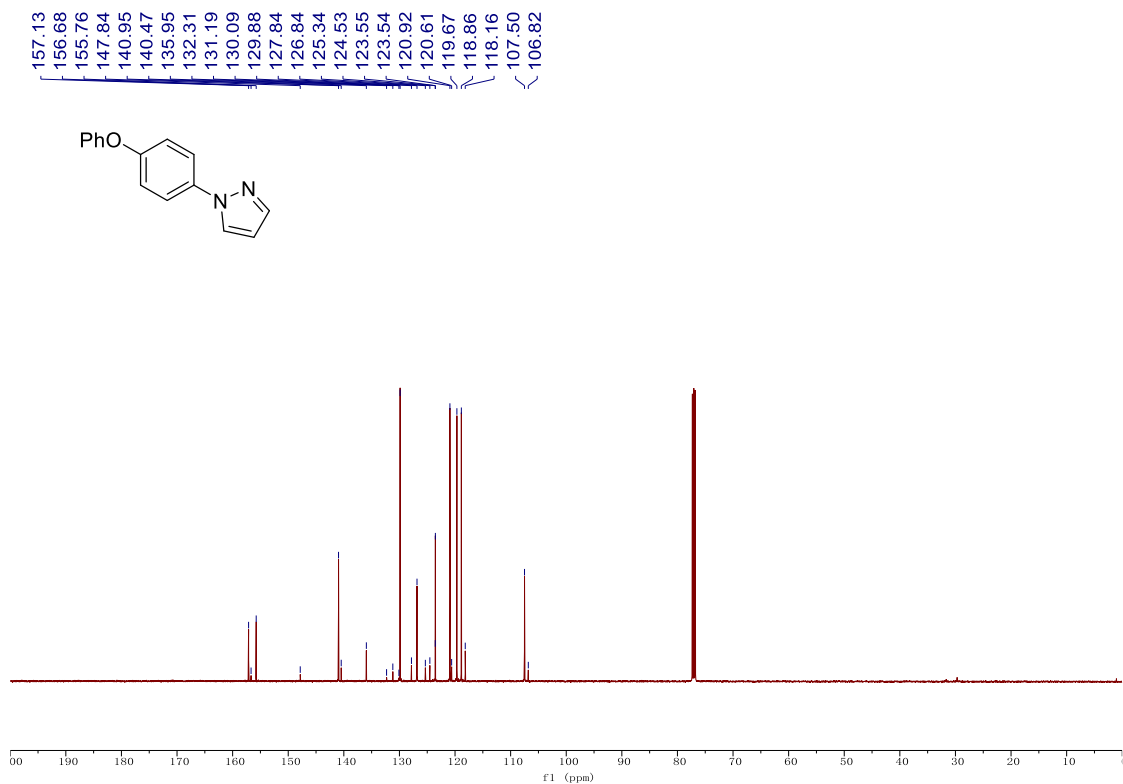
126 Hz ^{13}C { ^1H } NMR spectrum of **5a** in CDCl_3



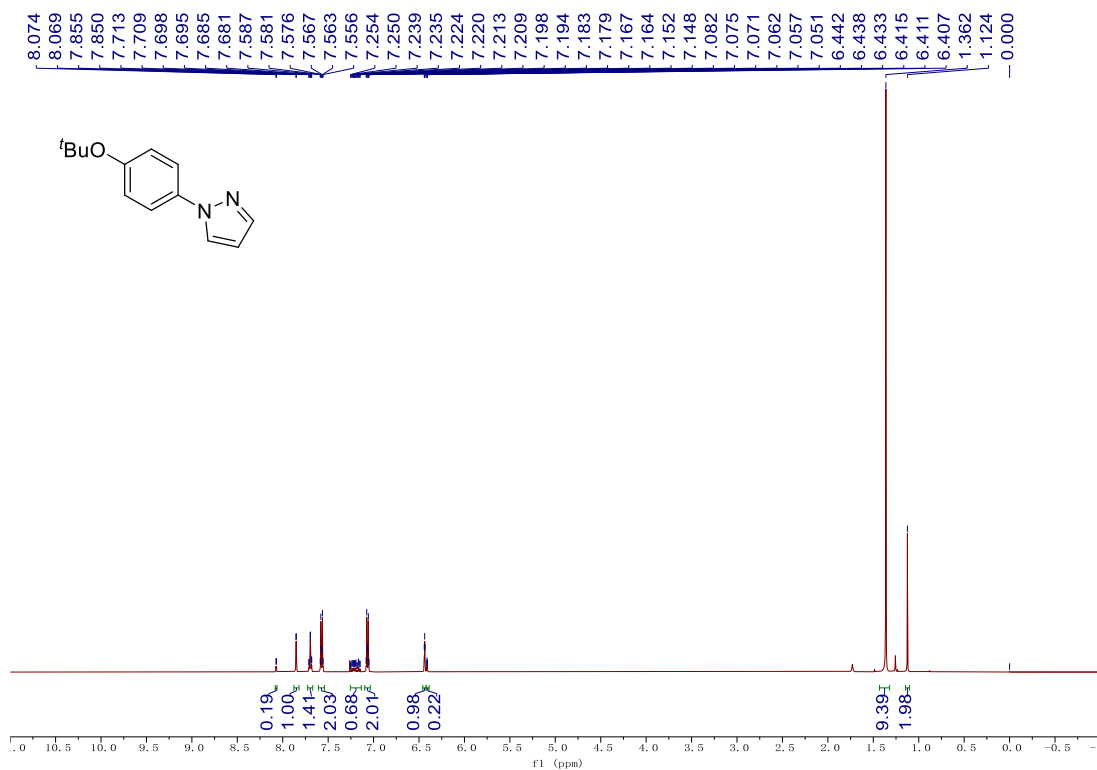
500 Hz ^1H NMR spectrum of **5b** in CDCl_3



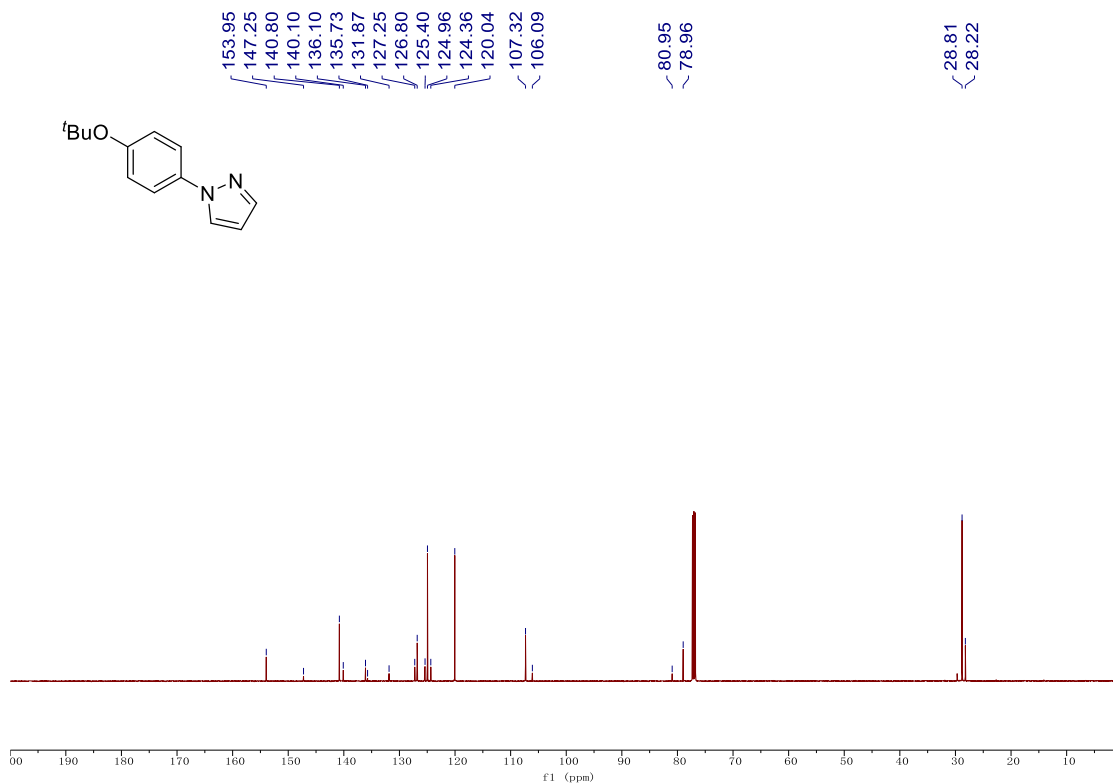
126 Hz ^{13}C $\{^1\text{H}\}$ NMR spectrum of **5b** in CDCl_3



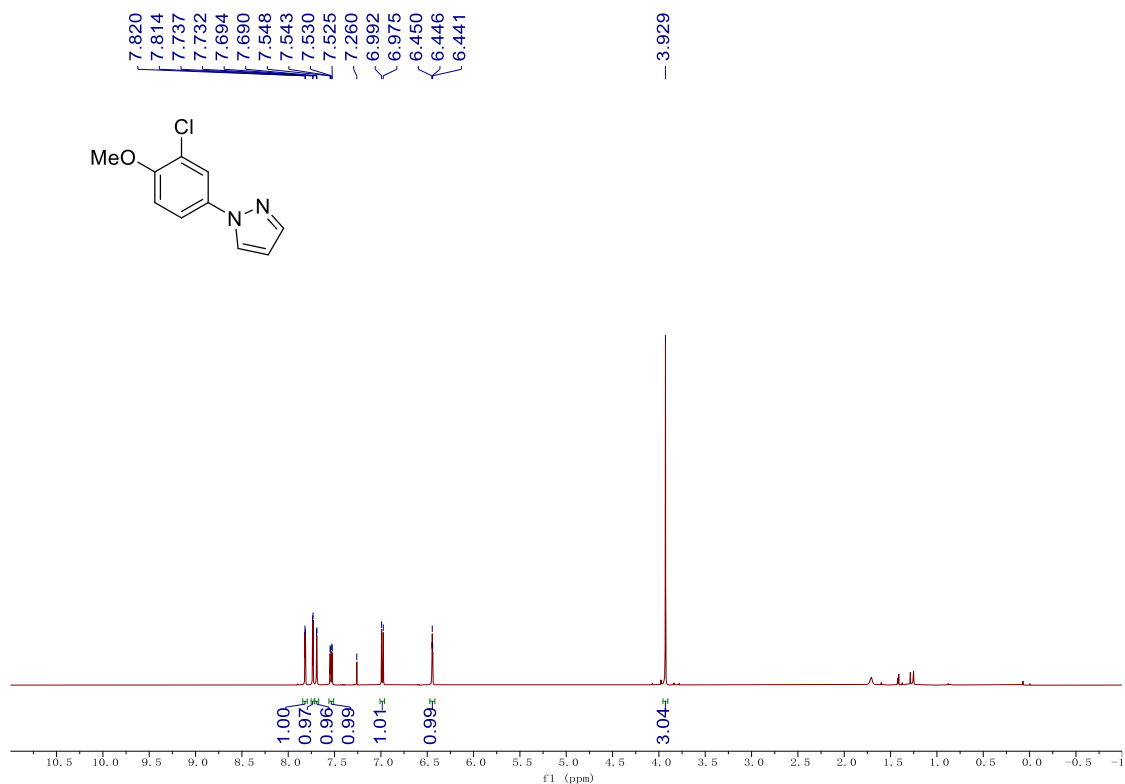
500 Hz ^1H NMR spectrum of **5c** in CDCl_3



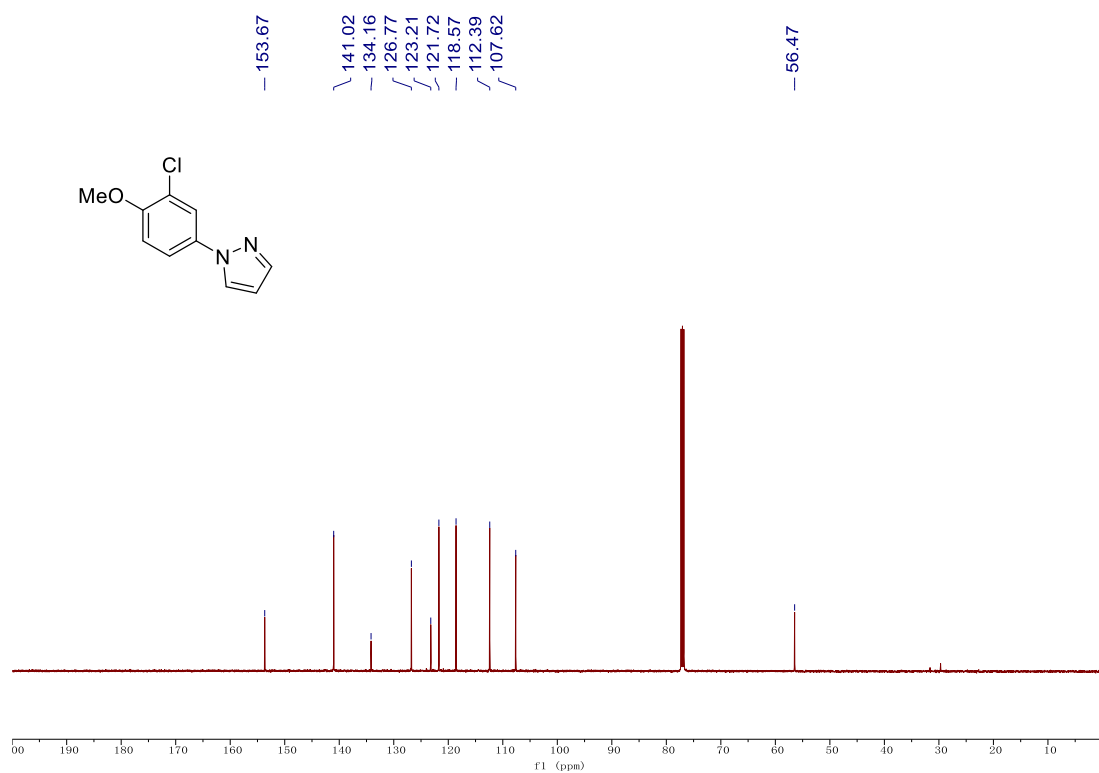
126 Hz ^{13}C $\{^1\text{H}\}$ NMR spectrum of **5c** in CDCl_3



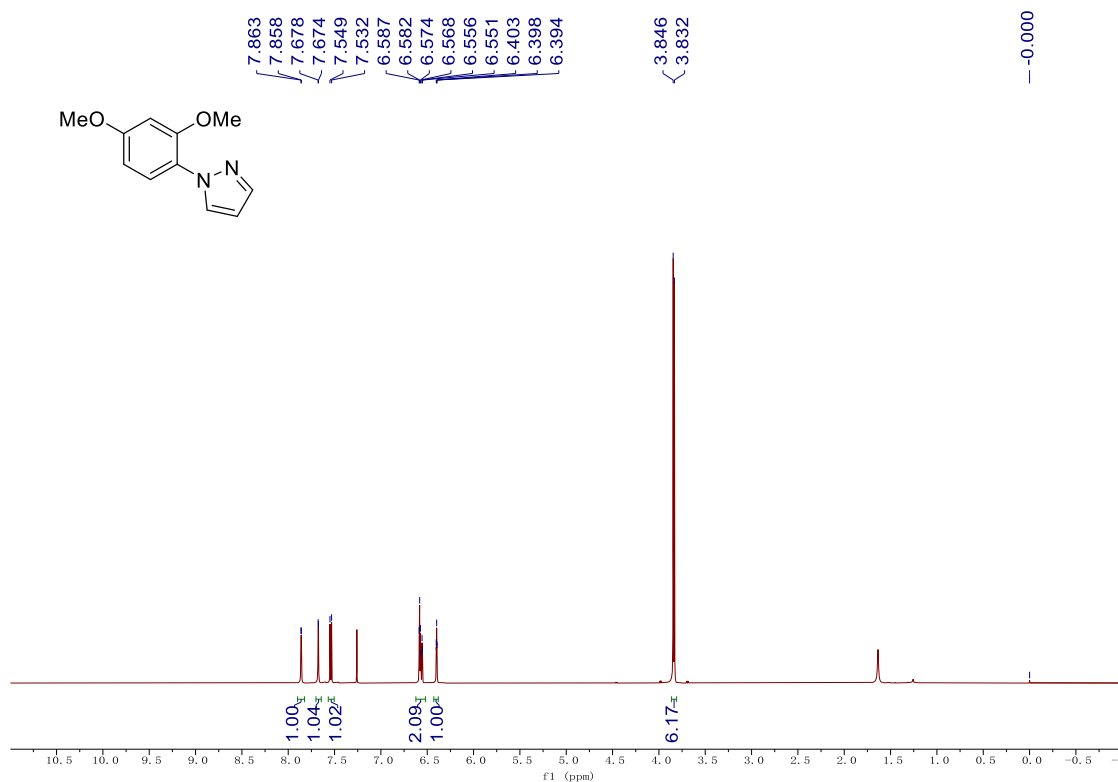
500 Hz ^1H NMR spectrum of **5d** in CDCl_3



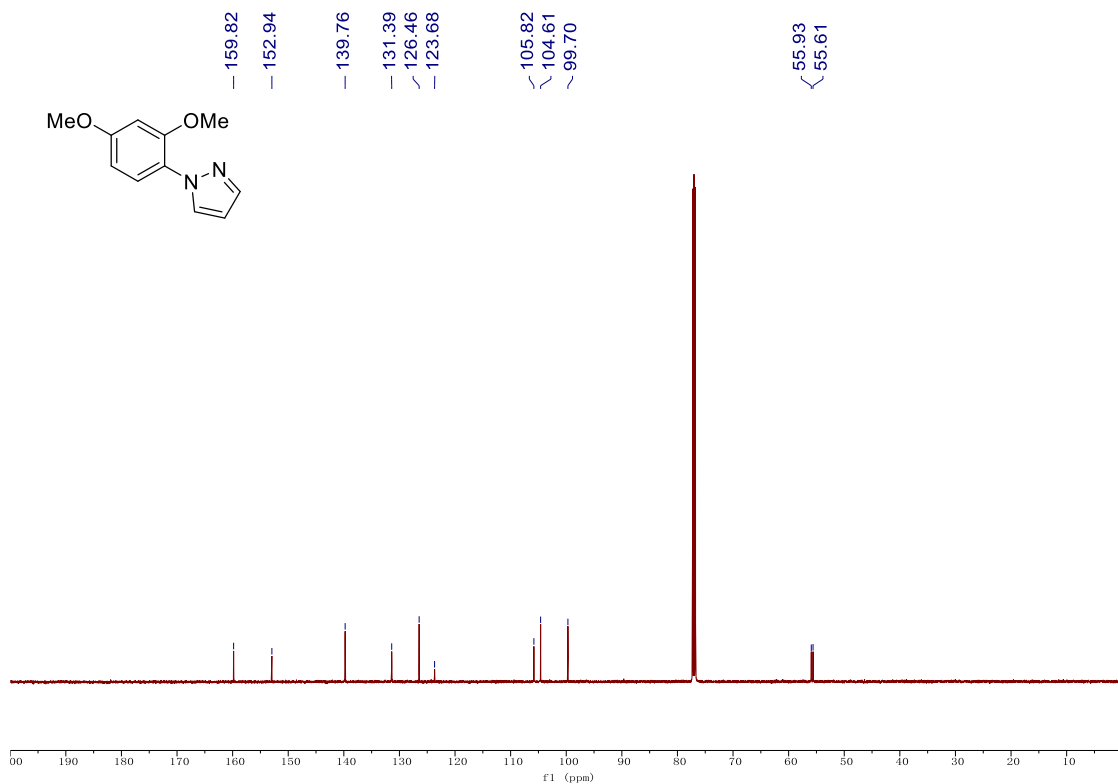
126 Hz ^{13}C { ^1H } NMR spectrum of **5d** in CDCl_3



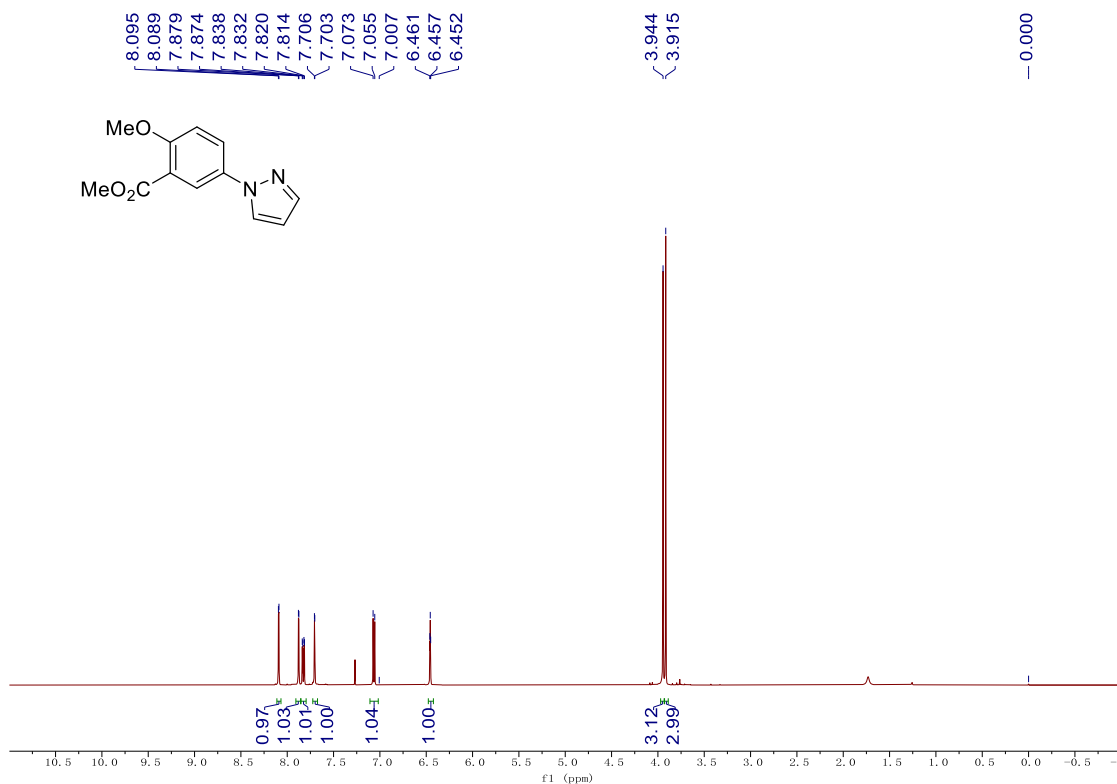
500 Hz ^1H NMR spectrum of **5e** in CDCl_3



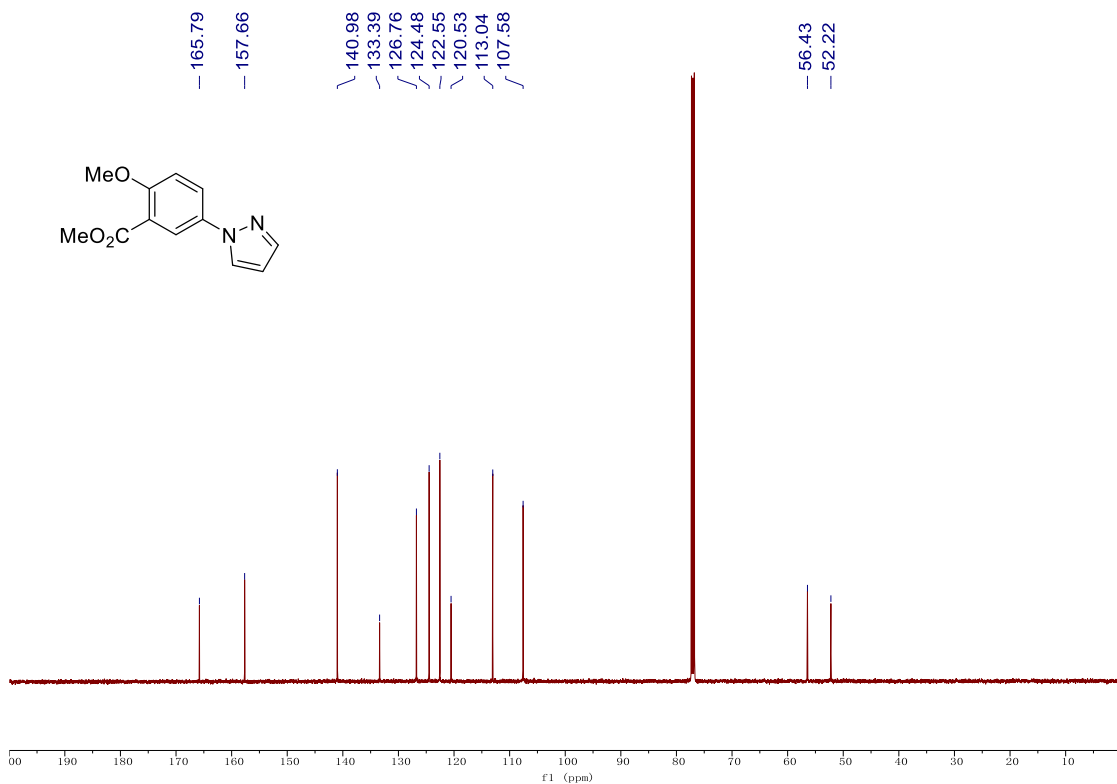
126 Hz ^{13}C $\{^1\text{H}\}$ NMR spectrum of **5e** in CDCl_3



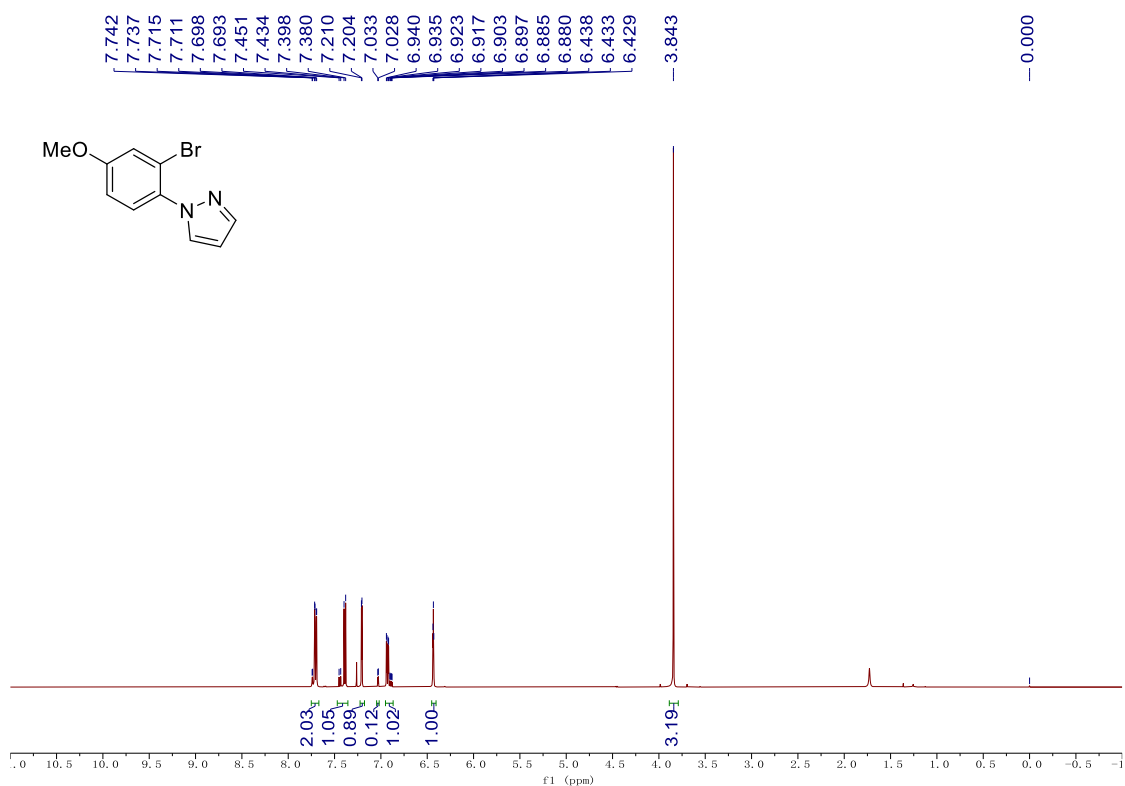
500 Hz ^1H NMR spectrum of **5f** in CDCl_3



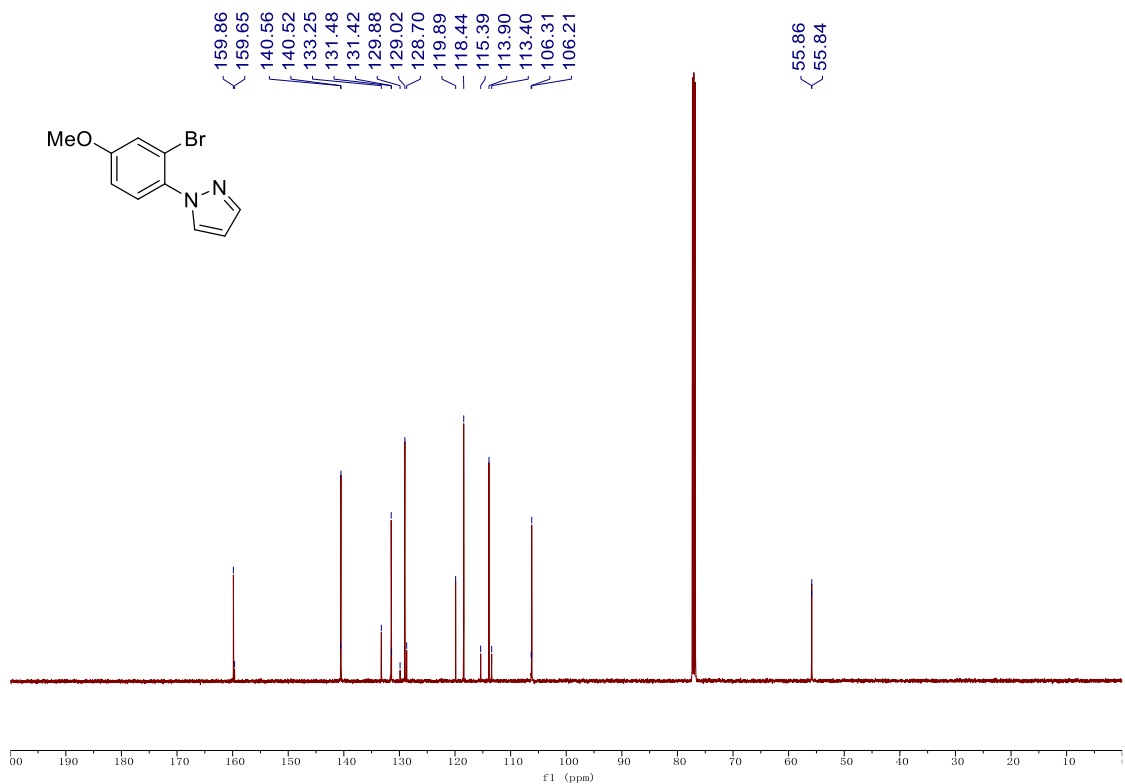
126 Hz ^{13}C $\{^1\text{H}\}$ NMR spectrum of **5f** in CDCl_3



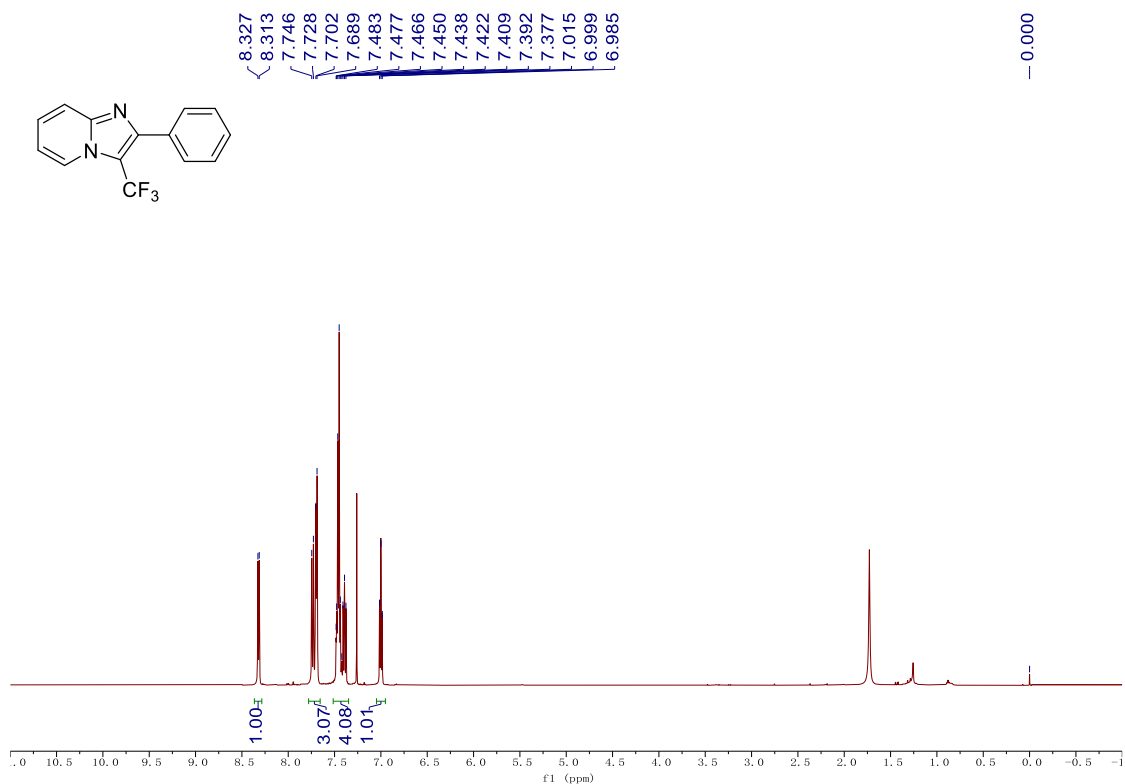
500 Hz ^1H NMR spectrum of **5g** in CDCl_3



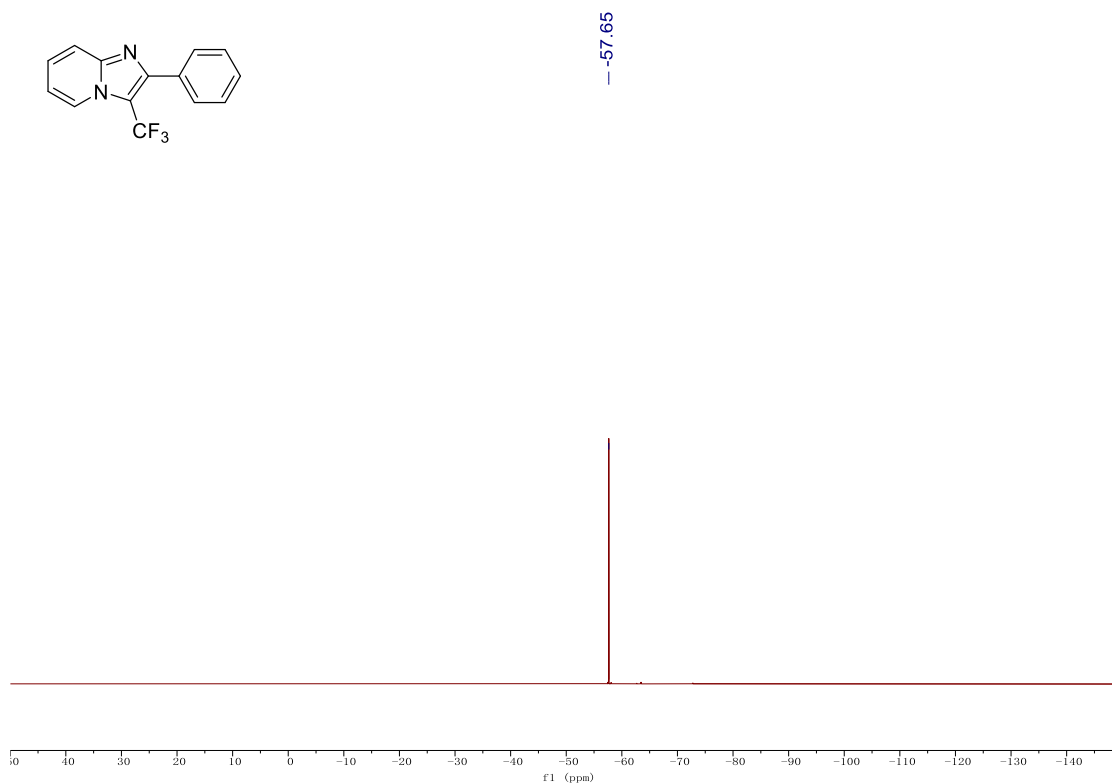
126 Hz ^{13}C $\{^1\text{H}\}$ NMR spectrum of **5g** in CDCl_3



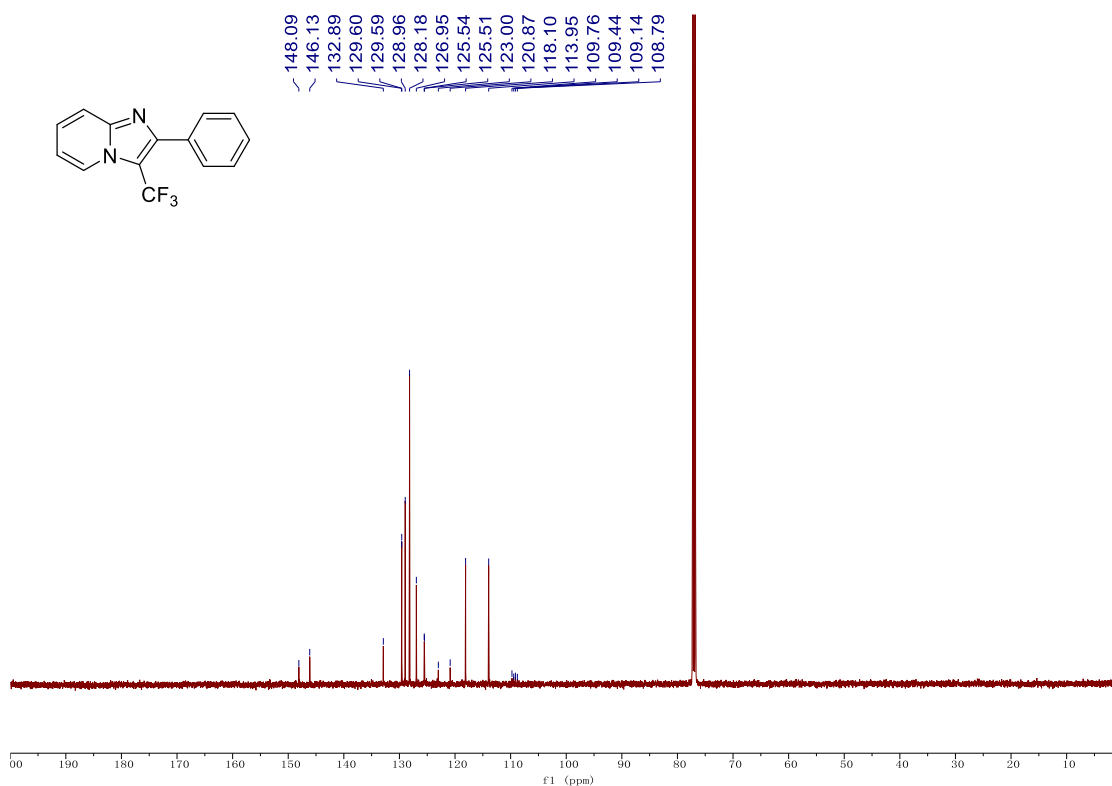
500 Hz ^1H NMR spectrum of **7a** in CDCl_3



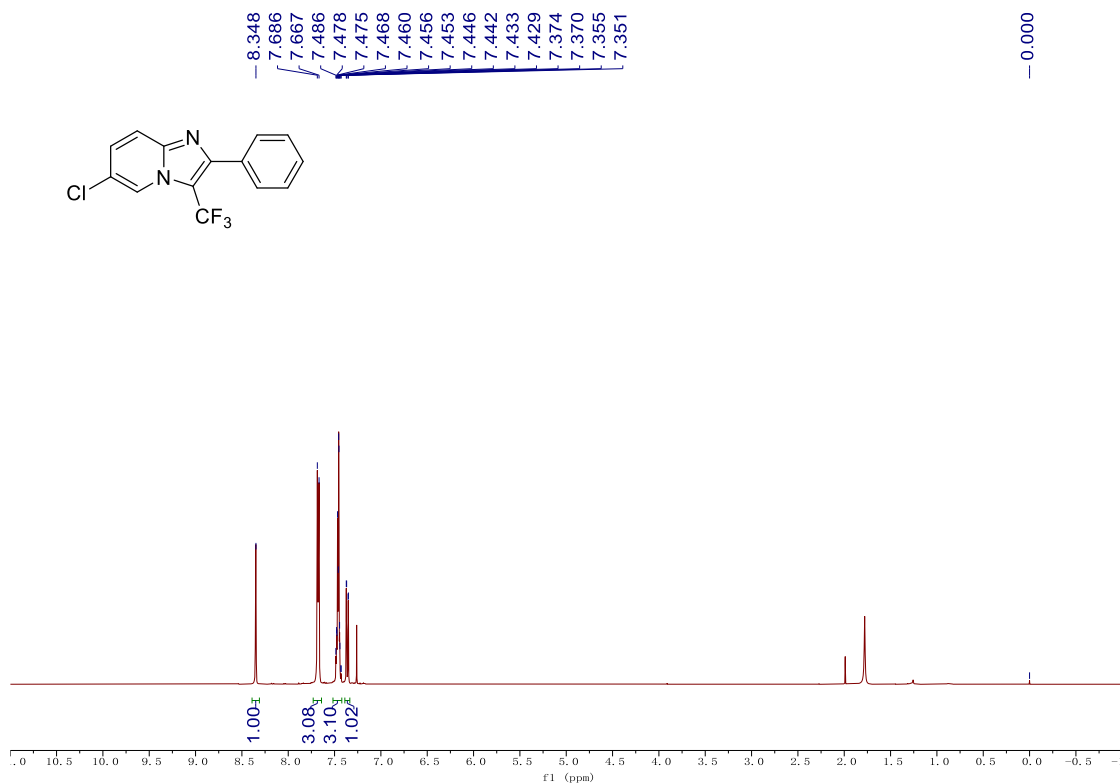
471 Hz ^{19}F $\{^1\text{H}\}$ NMR spectrum of **7a** in CDCl_3



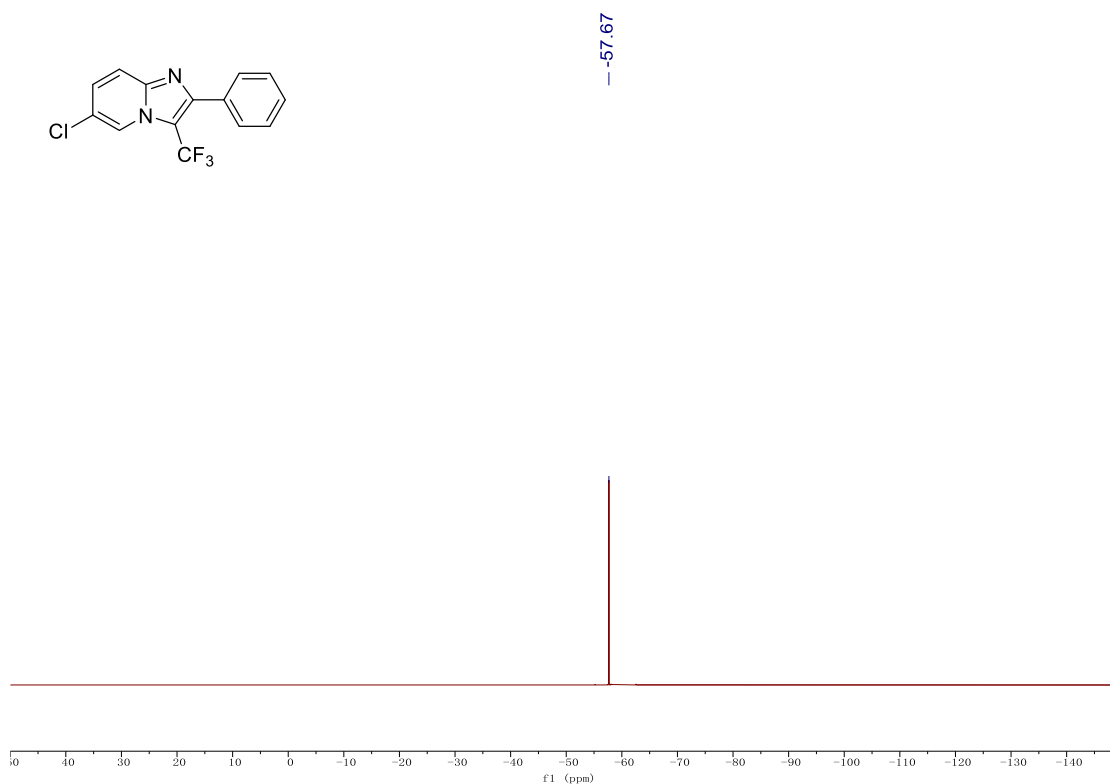
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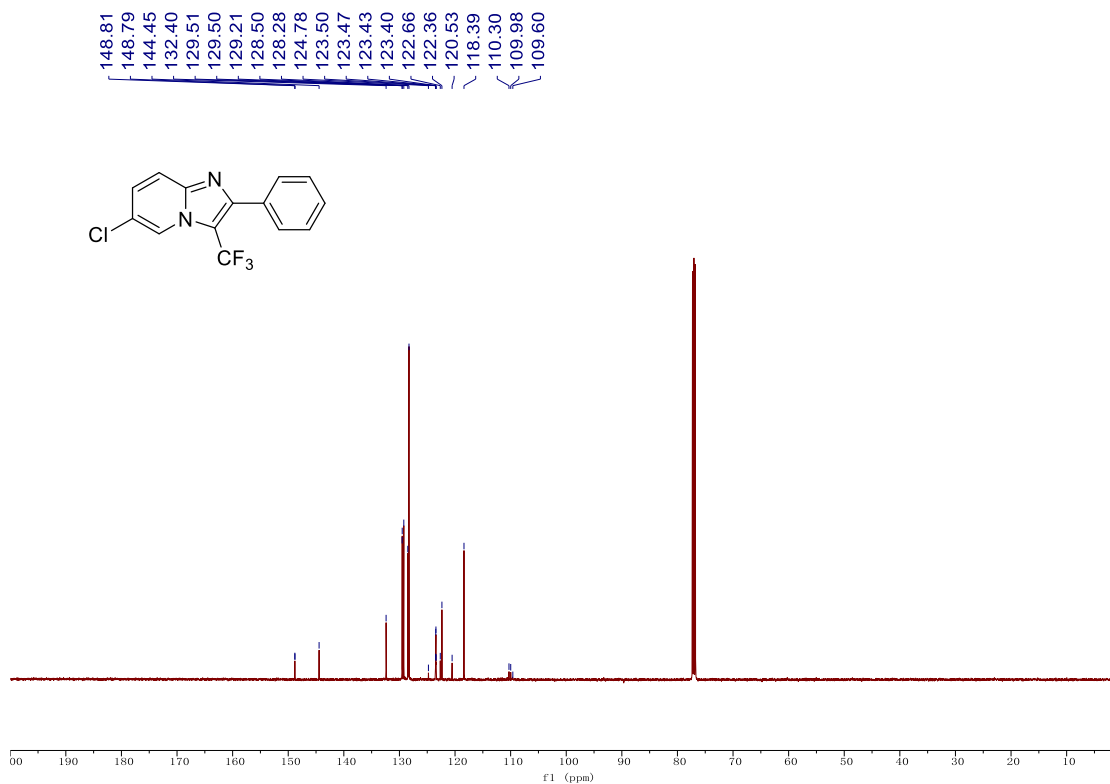
500 Hz ^1H NMR spectrum of **7b** in CDCl_3



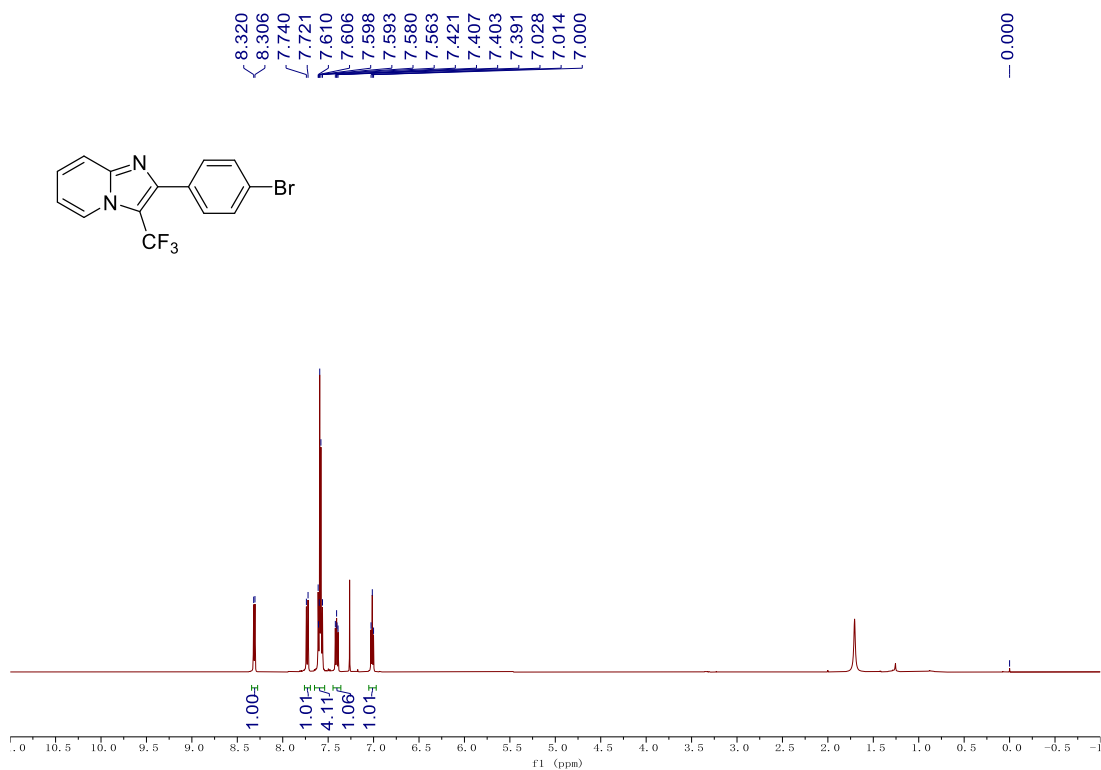
471 Hz ^{19}F $\{^1\text{H}\}$ NMR spectrum of **7b** in CDCl_3



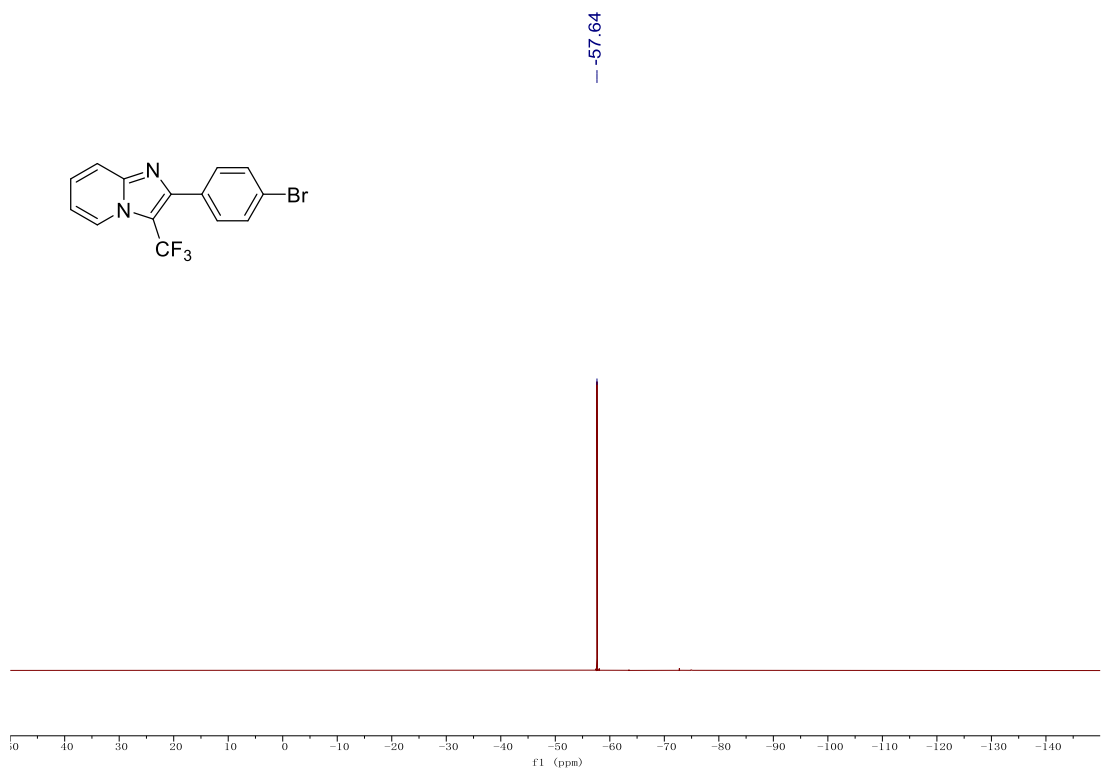
126 Hz ^{13}C $\{^1\text{H}\}$ NMR spectrum of **7b** in CDCl_3



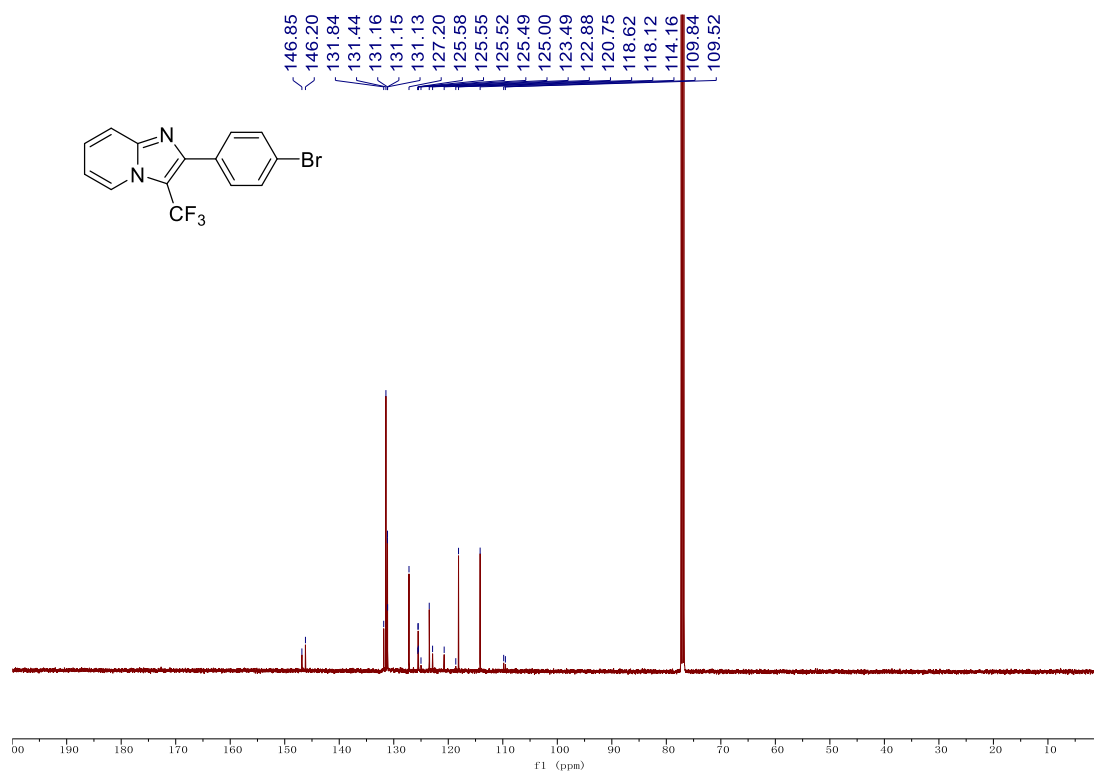
500 Hz ^1H NMR spectrum of **7c** in CDCl_3



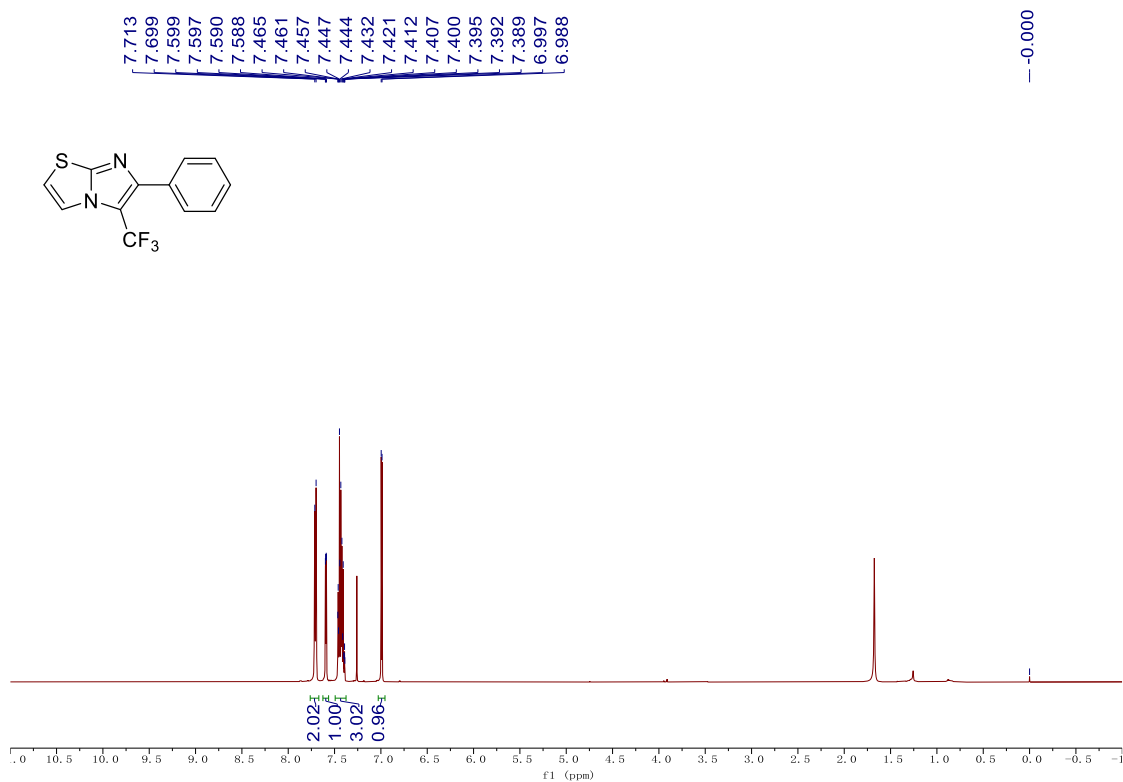
471 Hz ^{19}F $\{^1\text{H}\}$ NMR spectrum of **7c** in CDCl_3



126 Hz ^{13}C $\{^1\text{H}\}$ NMR spectrum of **7c** in CDCl_3



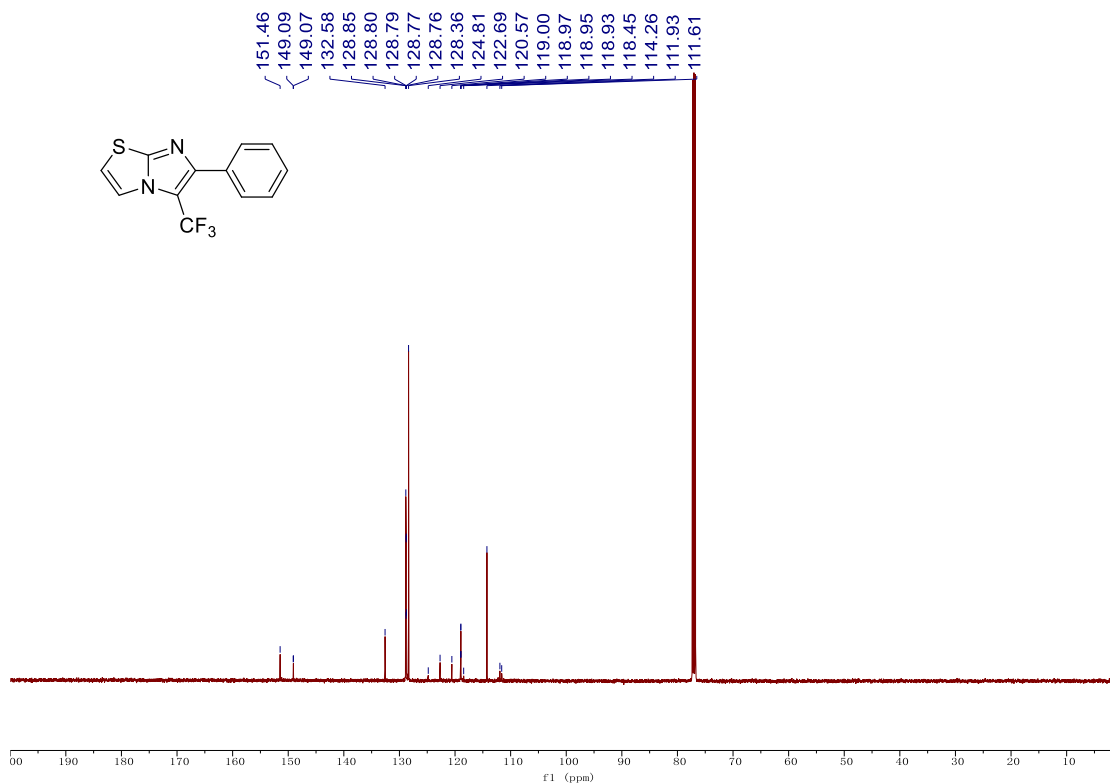
500 Hz ^1H NMR spectrum of **7d** in CDCl_3



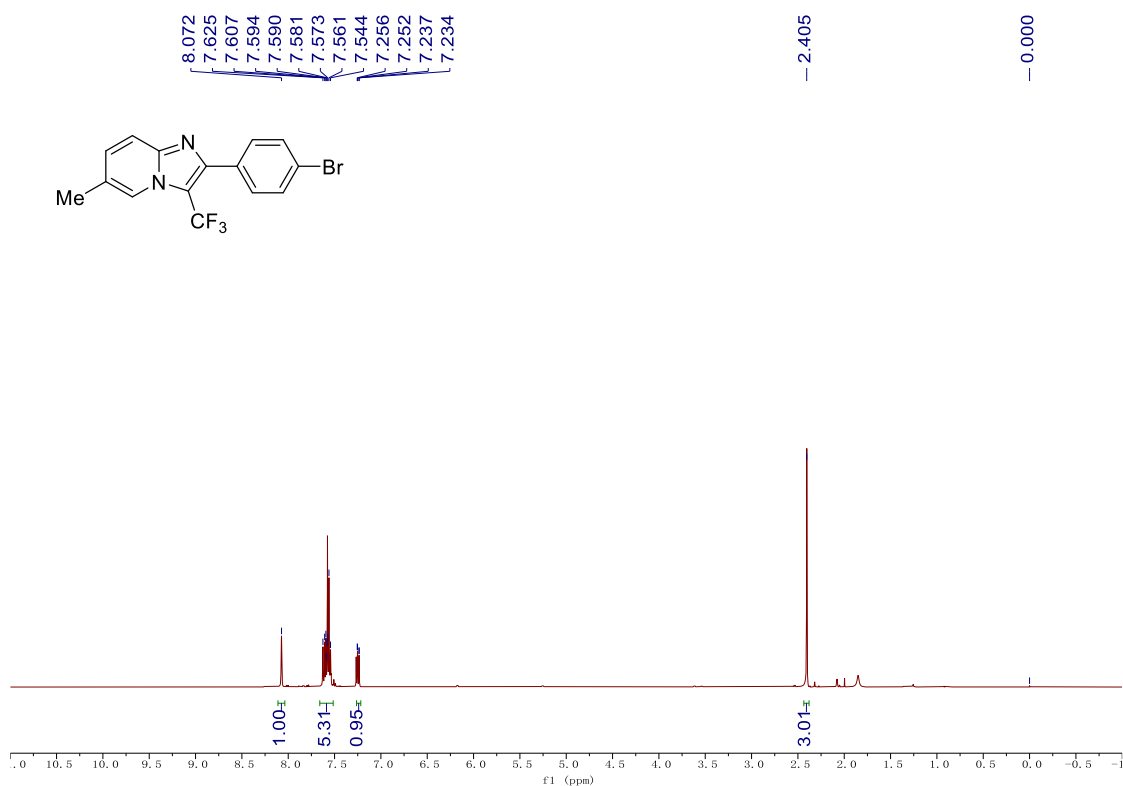
471 Hz ^{19}F $\{^1\text{H}\}$ NMR spectrum of **7d** in CDCl_3



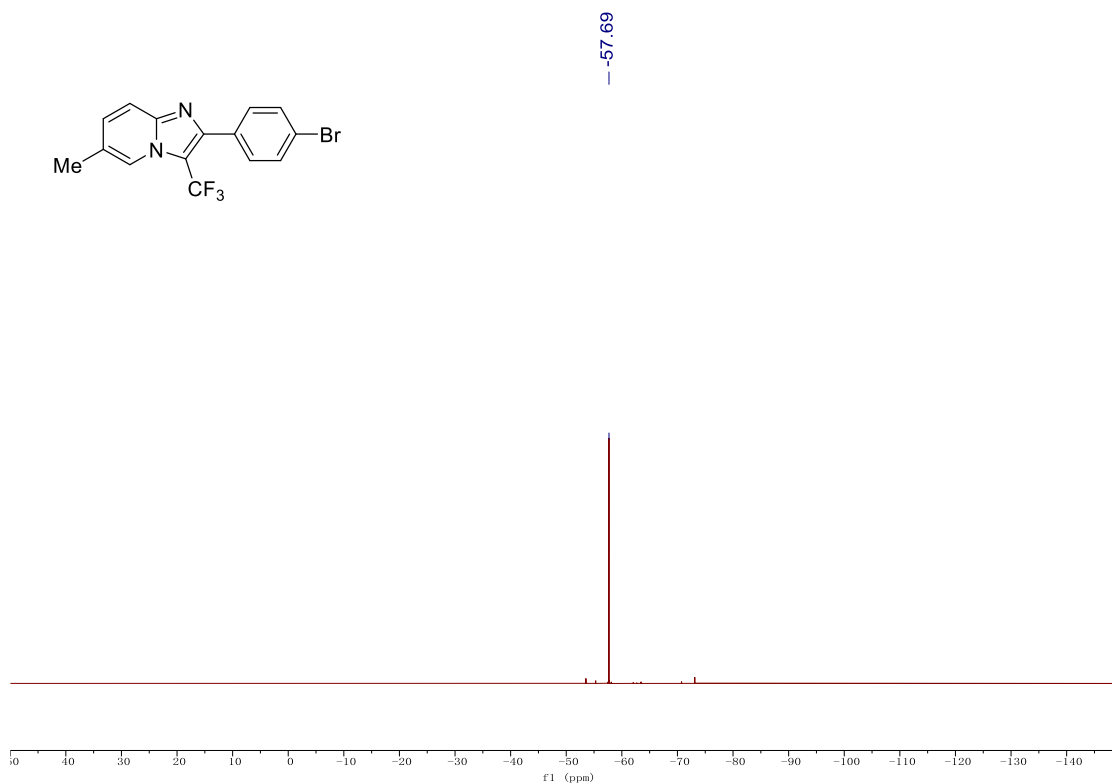
126 Hz ^{13}C $\{^1\text{H}\}$ NMR spectrum of **7d** in CDCl_3



500 Hz ^1H NMR spectrum of **7e** in CDCl_3



471 Hz ^{19}F { ^1H } NMR spectrum of **7e** in CDCl_3



126 Hz ^{13}C $\{^1\text{H}\}$ NMR spectrum of **7e** in CDCl_3

