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# Electronic Supplementary Information

# Ni-catalysed Intramolecular Reductive Aminocarbonylation of 2-Haloaryl-tethered Nitroarenes for the Synthesis of Dibenzazepine-based Heterocycles

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## General Considerations

**General Analytical Information.** $^{1}H$, $^{13}C$ and $^{19}F$ NMR spectra were recorded on Bruker AV 400 MHz instrument at 400 MHz ($^{1}H$ NMR), 101 MHz ($^{13}C$ NMR), and 376 MHz ($^{19}F$ NMR). All $^{1}H$ NMR spectra were measured in parts per million (ppm) downfield from tetramethylsilane (TMS, 0 ppm), or were measured relative to the residual proton signals of $d_1$-chloroform ($CDCl_3$, 7.26 ppm) or dimethyl sulfoxide-$d_6$ (DMSO-$d_6$, 2.50 ppm). All $^{13}C$ NMR spectra were reported in ppm relative to residual carbon signals of $CHCl_3$ (77.16 ppm) or DMSO-$d_6$ (39.52 ppm) and were obtained with $^{1}H$ decoupling. Coupling constants (*J*) are reported in hertz (Hz). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), and m (multiplet). High resolution mass spectrometry (HRMS) spectra were obtained on a Bruker miorOTOF-QII instrument. Thin-layer chromatography (TLC) was performed on precoated GF254 silica gel plates (Qingdao Marine Chemical Inc.) and compounds were visualized with a UV light at 254 nm. Flash chromatography for purification of compounds were carried out using silica gel (200–300 mesh, Qingdao Marine Chemical Inc.).

**General Reagents Information.** Unless otherwise noted, commerically available materials were used without prior purification. Anhydrous *N*-methylpyrrolidone (NMP) was purchased from HEOWNS and it was added with anhydrous 3Å molecular sieves for storage. Chlorotrimethylsilane (TMSCl, 98% purity) was purchased from Energy Chemical and was stored in refrigerator for storage. 4,7-Diphenyl-1,10-phenanthroline (bathophenanthroline, Bphen, 99% purity) and manganese powder (Mn, 99.9%) were purchased from Bidepharm. Nickel(II) chloride ethylene glycol dimethyl ether complex ($Ni(dme)Cl_2$, 98.8% purity) was purchased from Bidepharm. Carbon monoxide (CO, 99.9% purity) was purchased from Tianjin Boliming Techology.

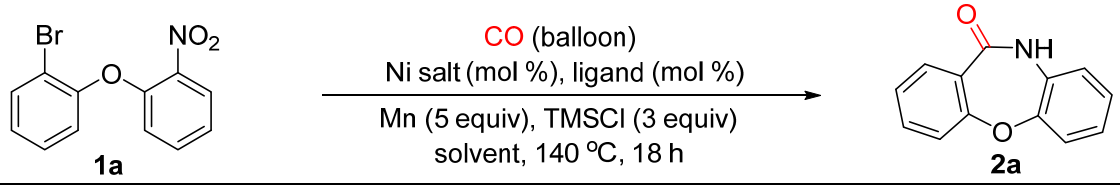
**General Manipulation Considerations.** All manipulations for reductive aminocarbonylation reaction were performed in Schlenk tubes. The eluents used for column chromatography were presented as ratios of solvent volumes. Yields reported in the publication are isolated yields

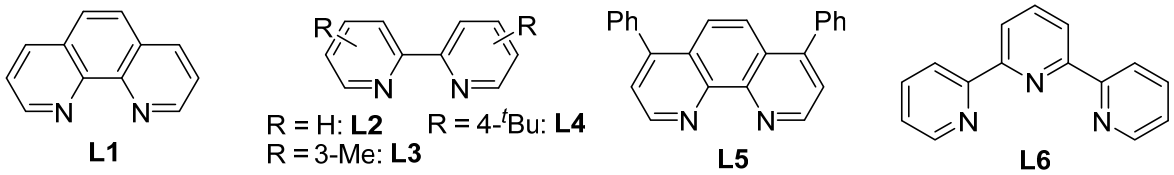
unless otherwise noted. All new starting materials and products were characterized by $^{1}H$ and $^{13}C$ NMR spectroscopies and high-resolution mass spectrometry (HRMS).

## Optimization of Reaction Conditions

**General procedure for optimizations of reaction conditions (Table 1 and Table S1).** An oven-dried 10 mL Schlenk tube equipped with a stir bar was sequentially charged with haloaryl-tethered nitroarene **1a** (0.2 mmol, 1 equiv), Mn powder, ligand, and Ni catalyst. The tube was evacuated in vacuo and then backfilled with CO in a balloon for three times. NMP solvent and TMSCl were transferred into the tube via a syringe. The resulting mixture was stirred under a CO atmosphere under positive balloon pressure in a preheated heat block for 18 h. At this point, the reaction mixture was cooled down to room temperature. The reaction mixture was diluted with $CH_2Cl_2$ and then washed with dilute aqueous HCl solution and saturated brine, dried with anhydrous $Na_2SO_4$, and finally concentrated in vacuo. The residue was purified by flash chromatography on silica gel using petroleum ether (PE) and ethyl acetate (EtOAc) as the eluent to give the heterocycle product **2a**.

**Table S1.** Optimization of reductive aminocarbonylation to access fused heterocycle.[a]



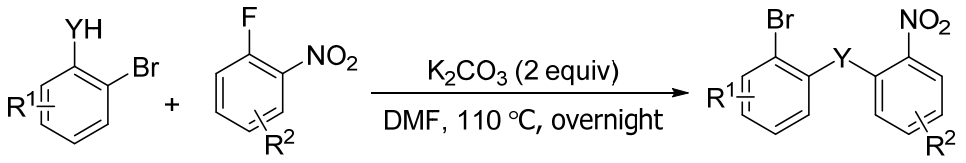




| Entry | Ni salt (mol %) | Ligand (mol %) | Mn (equiv) | Solvent | Yield of **2a** / %[b] |
|---|---|---|---|---|---|
| 1 | $NiCl_2$ (30) | **L1** (30) | 5 | MeCN | trace |
| 2 | $NiCl_2$ (30) | **L1** (30) | 5 | 1,4-dioxane | trace |
| 3 | $NiCl_2$ (30) | **L1** (30) | 5 | DMA | 30 |
| 4 | $NiCl_2$ (30) | **L1** (30) | 5 | NMP | 32 |
| 5 | $NiBr_2$ (30) | **L1** (30) | 5 | NMP | trace |
| 6 | $Ni(acac)_2$ (30) | **L1** (30) | 5 | NMP | trace |
| 7 | $Ni(dme)Cl_2$ (30) | **L1** (30) | 5 | NMP | 46 |
| 8 | $Ni(dme)Br_2$ (30) | **L1** (30) | 5 | NMP | 30 |
| 9 | $Ni(dme)Cl_2$ (30) | **L2** (30) | 5 | NMP | 40 |
| 10 | $Ni(dme)Cl_2$ (30) | **L3** (30) | 5 | NMP | 40 |
| 11 | $Ni(dme)Cl_2$ (30) | **L4** (30) | 5 | NMP | 60 |
| 12 | $Ni(dme)Cl_2$ (30) | **L5** (30) | 5 | NMP | 80 |
| 13 | $Ni(dme)Cl_2$ (30) | **L6** (30) | 5 | NMP | 30 |
| 14 | $Ni(dme)Cl_2$ (15) | **L5** (15) | 5 | NMP | 82 |
| 15 | $Ni(dme)Cl_2$ (15) | **L5** (20) | 5 | NMP | 64 |
| 16 | $Ni(dme)Cl_2$ (10) | **L5** (20) | 5 | NMP | 38 |
| 17 | $Ni(dme)Cl_2$ (10) | **L5** (10) | 5 | NMP | 48 |
| 18 | $Ni(dme)Cl_2$ (15) | **L5** (15) | 4 | NMP | 82 |
| 19 | $Ni(dme)Cl_2$ (15) | **L5** (15) | 3 | NMP | 75 |
| 20 | $Ni(dme)Cl_2$ (15) | **L5** (15) | 2 | NMP | 38 |
| 21 | $Ni(dme)Cl_2$ (15) | **L5** (15) | 4 | NMP | 39[c] |

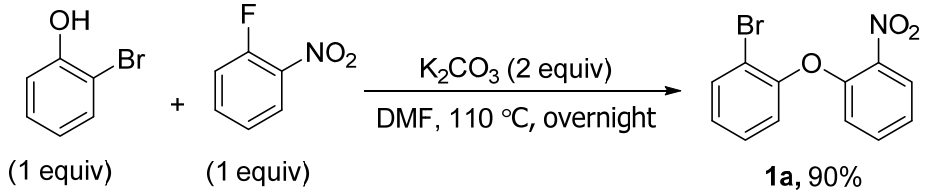
[a] Reaction conditions: **1a** (0.25 mmol), CO (baloon), Ni salt (10-30 mol %), ligand (10-30 mol %),solvent (2 mL), Mn (2-5 equiv.), TMSCl (3 equiv.), 140 °C, 18 h.[b] Isolated yield. [c] TMSCl (2 equiv.) was used.

## Experimental Section

### General Procedures for the Synthesis of haloaryl-tethered 2-nitroarenes (General Procedures A).[1]



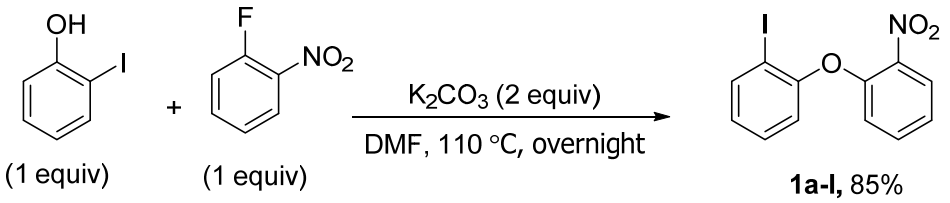

To a 100 mL round bottom flask equipped with a magnetic stir bar was charged with the 2-bromophenol/2-bromothiophenol (1 equiv, 10 mmol), $K_2CO_3$ (2 equiv, 20 mmol) and DMF (15 mL) under an air atmosphere. A solution of 2-fluoronitroarene (1 equiv, 10 mmol) in DMF (5 mL) was added into the solution. The resulting reaction mixture was then stirred at 110 °C overnight. At this point, the reaction mixture was cooled down to room temperature. $CH_2Cl_2$ (100 mL) was added to the reaction mixture and the organic fraction was washed successively with an aqueous solution of NaOH (~1 M, ~30 mL), water (3 × ~100 mL), and brine (30 mL). The organic fraction was concentrated in vacuo with the aid of rotary evaporator. The residue was recrystallized with $CH_2Cl_2$ and petroleum ether to afford the haloaryl-tethered 2-nitroarene as the starting material.




**1-Bromo-2-(2-nitrophenoxy)benzene (1a).**

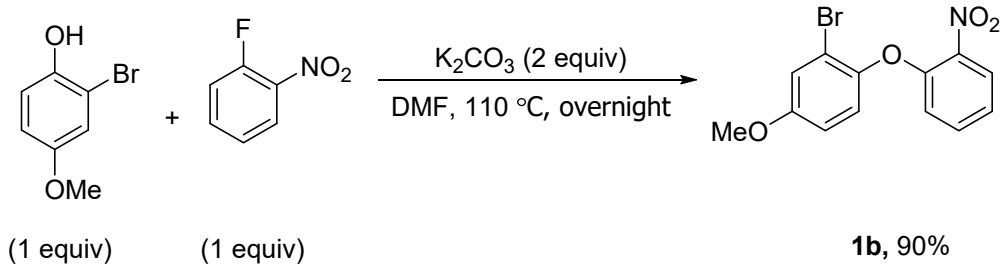
Following the general procedure A, the title compound was prepared from 2-bromophenol (20 mmol, 2.32 mL), 1-fluoro-2-nitrobenzene (20 mmol, 2.12 mL), $K_2CO_3$ (40 mmol, 5.53 g), and DMF (40 mL) to obtain the title compound as a white solid (5.29 g, 90%). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.00 – 7.97 (m, 1H), 7.67 – 7.64 (m, *J* = 8.0, 1.5 Hz, 1H), 7.51-7.47 (m, 1H), 7.35-7.31 (m, 1H), 7.23-7.19 (m, 1H), 7.14-7.10 (m, 1H), 7.07-7.04 (m, 1H), 6.85 (d, *J* = 8.3 Hz, 1H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 152.1, 150.2, 140.6, 134.3, 134.2, 129.1, 126.5, 126.0,

123.3, 121.3, 119.1, 115.2. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_9BrNO_3^+$ 293.9766; Found 293.9766.




**1-Iodo-2-(2-nitrophenoxy)benzene (1a-I).**

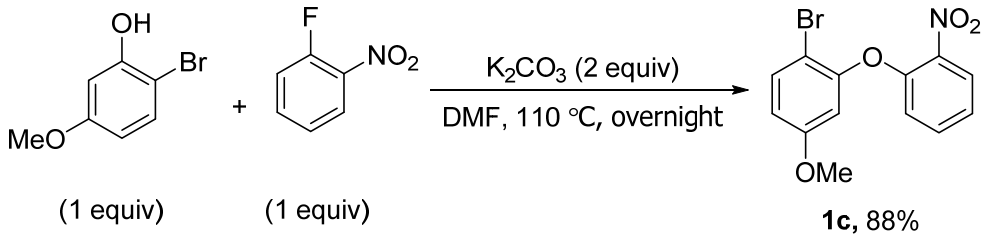
Following the general procedure A, the title compound was prepared from 2-iodophenol (20 mmol, 2.26 mL), 1-fluoro-2-nitrobenzene (20 mmol, 2.11 mL), $K_2CO_3$ (40 mmol, 5.53 g), and DMF (40 mL) to obtain the title compound as a grey solid (5.80 g, 85%). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.1 Hz, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.50 (td, *J* = 8.7, 1.7 Hz, 1H), 7.35 (t, *J* = 7.8 Hz, 1H), 7.21 (t, *J* = 7.8 Hz, 1H), 6.98 – 6.94 (m, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.3 Hz, 1H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 155.1, 150.1, 140.8, 140.3, 134.4, 130.6, 126.7, 126.0, 123.4, 120.1, 119.5, 88.9. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_9INO_3^+$ 341.9630; Found 341.9627.




**2-Bromo-4-methoxy-1-(2-nitrophenoxy)benzene (1b).**

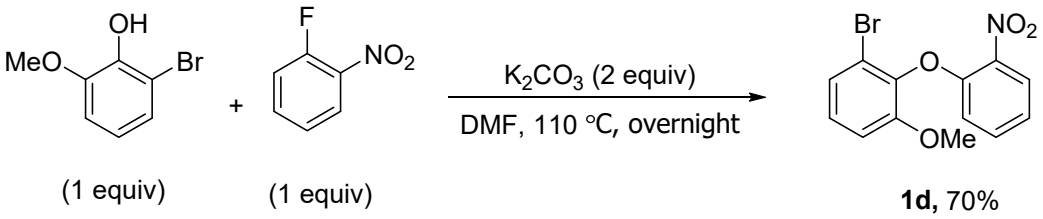
Following the general procedure A, the title compound was prepared from 2-bromo-4-methoxyphenol (20 mmol, 2.56 mL), 1-fluoro-2-nitrobenzene (20 mmol, 2.12 mL), $K_2CO_3$ (40 mmol, 5.53 g), and DMF (40 mL) to obtain the title compound as a yellow solid (5.80 g, 90%). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.42 – 7.37 (m, 1H), 7.23 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.15 – 7.10 (m, 2H), 6.95 (dd, *J* = 8.3, 1.5 Hz, 1H), 6.66 (dd, *J* = 8.4, 1.2 Hz, 1H), 3.75 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 153.4, 150.9, 140.0, 139.4, 134.1, 127.4,

125.9, 125.2, 122.0, 117.9, 116.2, 112.1, 56.4. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{11}NO_4Br^+$ 323.9871; Found: 323.9877.




**1-Bromo-4-methoxy-2-(2-nitrophenoxy)benzene (1c).**

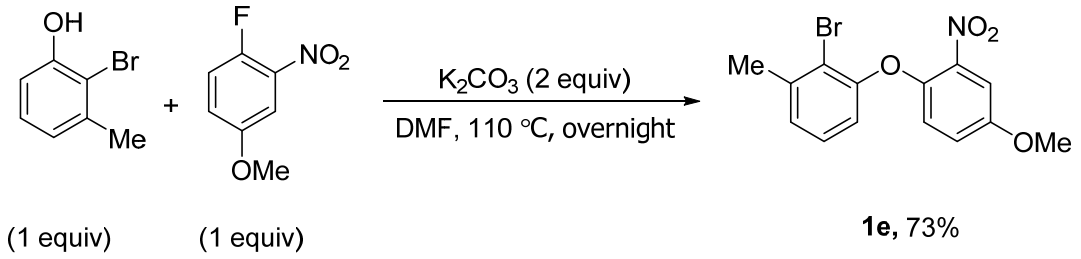
Following the general procedure A, the title compound was prepared from 2-bromo-5-methoxyphenol (1 equiv, 20 mmol, 2.56 mL), 1-fluoro-2-nitrobenzene (20 mmol, 2.12 mL), $K_2CO_3$ (40 mmol, 5.53 g), and DMF (40 mL) to obtain the title compound as a yellow solid (5.70 g, 88%). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.52 – 7.48 (m, *J* = 8.2 Hz, 2H), 7.23 – 7.17 (m, 1H), 6.87 (dd, *J* = 8.4, 1.3 Hz, 1H), 6.68 (dd, *J* = 8.9, 2.9 Hz, 1H), 6.60 (d, *J* = 2.8 Hz, 1H), 3.75 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 160.3, 152.6, 150.1, 140.5, 134.4, 134.1, 126.0, 123.3, 119.2, 112.3, 107.6, 105.5, 55.8. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{11}NO_4Br^+$ 323.9871; Found: 323.9874.




**1-Bromo-3-methoxy-2-(2-nitrophenoxy)benzene (1d).**

Following the general procedure A, the title compound was prepared from 2-bromo-6-methoxyphenol (20 mmol, 2.56 mL), 1-fluoro-2-nitrobenzene (20 mmol, 2.12 mL), $K_2CO_3$ (40 mmol, 5.53 g), and DMF (40 mL) to obtain the title compound as a yellow solid (4.54 g, 70%). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.46 – 7.42 (m, 1H), 7.17 (d, *J* = 2.9 Hz, 1H), 7.16 – 7.11 (m, 1H), 7.06 (d, *J* = 8.9 Hz, 1H), 6.88 (dd, *J* = 8.9, 2.9 Hz, 1H), 6.75 (dd, *J* = 8.4, 1.2 Hz, 1H), 3.81 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 157.6, 151.2, 145.1, 140.0, 134.2, 125.9, 123.0, 122.4, 118.9, 117.7, 116.2, 114.8, 55.9. **HRMS** (ESI) m/z: $[M+H]^+$

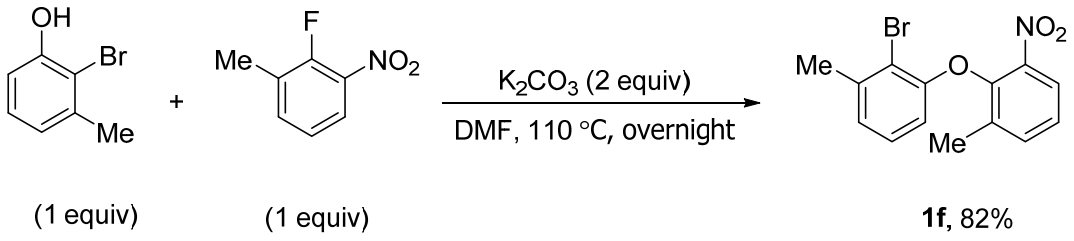
Calcd for $C_{13}H_{11}NO_4Br^+$ 323.9871; Found: 323.9874.




(1 equiv) (1 equiv) **1e,** 73%

**1-Bromo-3-methoxy-2-(2-nitrophenoxy)benzene (1e).**

Following the general procedure A, the title compound was prepared from 2-bromo-3-methylphenol (10 mmol, 1.87 g), 1-fluoro-4-methoxy-2-nitrobenzene (10 mmol, 1.71 g) $K_2CO_3$ (20 mmol, 2.76 g) and DMF (20 mL) to obtain the title compound as a yellow solid (2.47g, 73%). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 3.1 Hz, 1H), 7.12 (t, *J* = 7.8 Hz, 1H), 7.06 (dd, *J* = 9.2, 3.1 Hz, 1H), 7.01 (d, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 9.2 Hz, 1H), 6.69 (d, *J* = 8.1 Hz, 1H), 3.82 (s, 3H), 2.43 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 155.4, 153.5, 143.4, 141.2, 140.7, 127.9, 126.3, 122.1, 121.1, 116.6, 116.5, 109.8, 56.1, 23.2. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{13}NO_4Br$ 338.0028; Found: 338.0028.

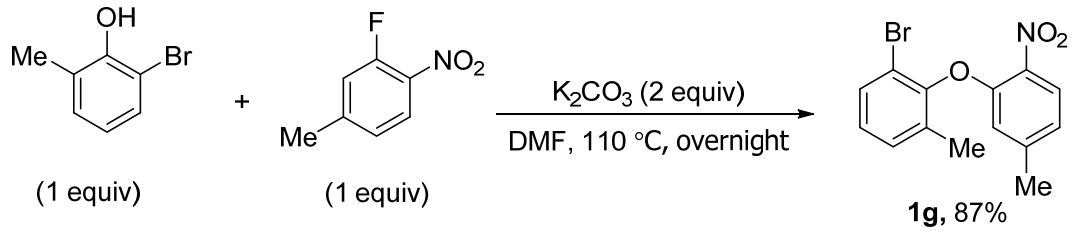



(1 equiv) (1 equiv) **1f**, 82%

**2-Bromo-1-methyl-3-(2-methyl-6-nitrophenoxy)benzene (1f).**

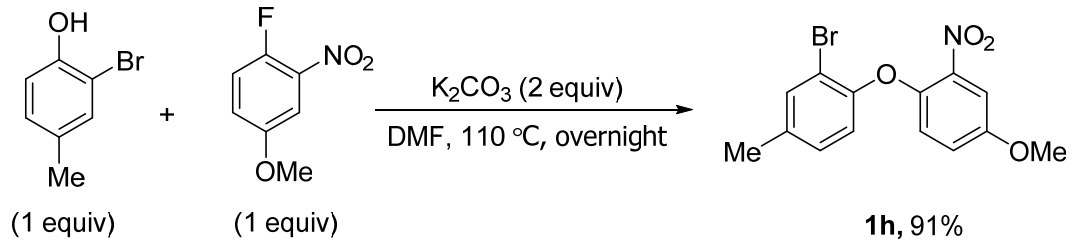
Following the general procedure A, the title compound was prepared from 2-bromo-3-methylphenol (10 mmol, 1.87 g), 2-fluoro-1-methyl-3-nitrobenzene (10 mmol, 1.55 g), $K_2CO_3$ (20 mmol, 2.76 g), and DMF (20 mL) to obtain the title compound as a brown solid (2.64g, 82%). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.28 (t, *J* = 7.9 Hz, 1H), 7.01 (t, *J* = 7.8 Hz, 1H), 6.93 (dd, *J* = 7.6, 1.7 Hz, 1H), 6.26 (dd, *J* = 8.1, 1.7 Hz, 1H), 2.46 (s, 3H), 2.17 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 153.9, 145.8, 143.8,

140.5, 136.4, 134.9, 127.5, 125.6, 124.7, 123.4, 113.9, 111.4, 23.3, 16.4. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{13}BrNO_3^+$ 322.0079; Found: 322.0074.




**1-Bromo-3-methyl-2-(5-methyl-2-nitrophenoxy)benzene (1g).**

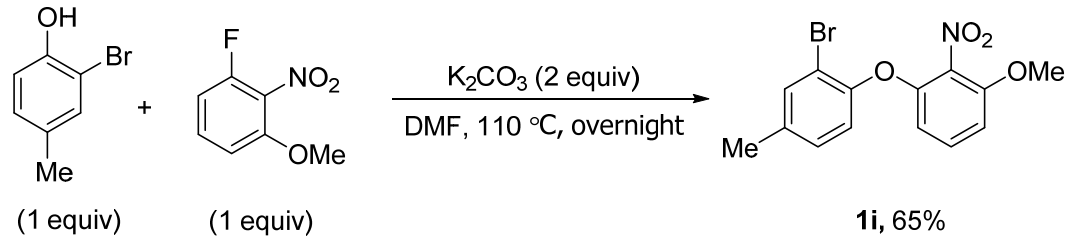
Following the general procedure A, the title compound was prepared from 2-bromo-6-methylphenol (10 mmol, 1.87 g), 2-fluoro-4-methyl-1-nitrobenzene (10 mmol, 1.55 g), $K_2CO_3$ (20 mmol, 2.76 g), and DMF (20 mL) to obtain the title compound as a brown solid (2.80 g, 87%). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.3 Hz, 1H), 7.49 (dd, *J* = 7.9, 2.0 Hz, 1H), 7.25 (d, *J* = 7.7 Hz, 1H), 7.09 (t, *J* = 7.8 Hz, 1H), 6.90 (dd, *J* = 8.3, 1.1 Hz, 1H), 6.31 (d, *J* = 1.2 Hz, 1H), 2.28 (s, 3H), 2.23 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 150.4, 148.8, 146.1, 136.7, 133.7, 131.6, 130.8, 127.2, 126.3, 122.7, 117.1, 115.6, 21.8, 16.8. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{13}BrNO_3^+$ 322.0079; Found: 322.0081.




**2-Bromo-1-(4-methoxy-2-nitrophenoxy)-4-methylbenzene (1h).**

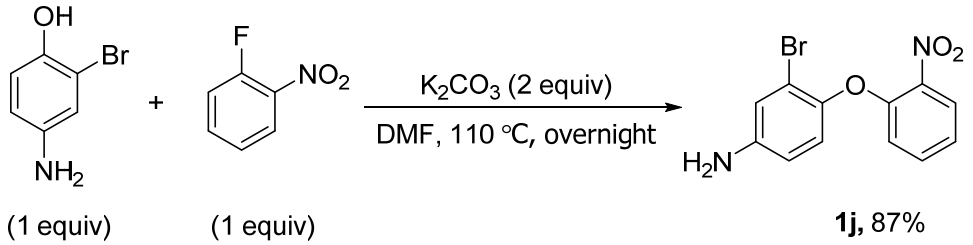
Following the general procedure A, the title compound was prepared from 2-bromo-4-methylphenol (20 mmol, 3.74 g), 1-fluoro-4-methoxy-2-nitrobenzene (20 mmol, 3.42 g), $K_2CO_3$ (40 mmol, 5.53 g), and DMF (40 mL) to obtain the title compound as a yellow solid (6.15 g, 91%). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 3.1 Hz, 1H), 7.44 (d, *J* = 1.3 Hz, 1H), 7.08 – 7.04 (m, 2H), 6.86 (d, *J* = 9.2 Hz, 1H), 6.81 (d, *J* = 8.3 Hz, 1H), 3.85 (s, 3H), 2.32 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 155.1, 151.0, 143.9, 141.2, 135.7, 134.3, 129.4, 121.5,

121.2, 119.6, 114.0, 109.6, 56.1, 20.5. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{13}BrNO_4^+$ 338.0028; Found: 338.0026.




**1-(2-Bromo-4-methylphenoxy)-3-methoxy-2-nitrobenzene (1i).**

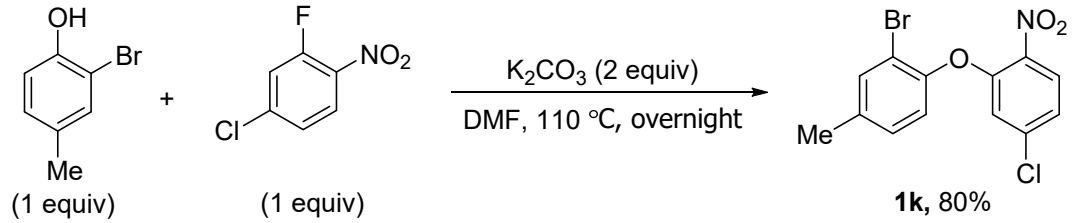
Following the general procedure A, the title compound was prepared from 2-bromo-4-methylphenol (20 mmol, 3.74 g), 1-fluoro-3-methoxy-2-nitrobenzene (20 mmol, 3.42 g), $K_2CO_3$ (40 mmol, 5.53 g), and DMF (40 mL) to obtain the title compound as a yellow solid (4.40 g, 65%). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 2.0 Hz, 1H), 7.23 (t, *J* = 8.6 Hz, 1H), 7.11 (dd, *J* = 8.3, 2.6 Hz, 1H), 7.01 (d, *J* = 8.3 Hz, 1H), 6.71 (d, *J* = 8.6 Hz, 1H), 6.29 (dd, *J* = 8.5, 0.9 Hz, 1H), 3.92 (s, 3H), 2.34 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 152.2, 150.0, 149.3, 137.1, 134.3, 132.8, 131.1, 129.7, 122.1, 115.3, 108.5, 106.3, 56.7, 20.6. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{13}BrNO_4^+$ 338.0028; Found: 338.0031.




**3-bromo-4-(2-nitrophenoxy)aniline (1j).**

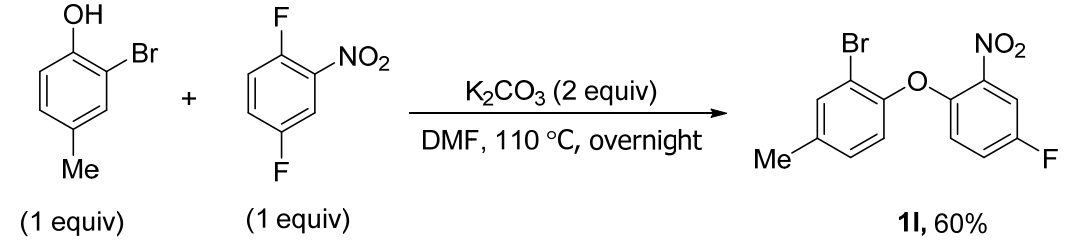
Following the general procedure A, the title compound was prepared from 4-amino-2-bromophenol (20 mmol, 3.76 g), 1-fluoro-2-nitrobenzene (20 mmol, 2.12 mL), $K_2CO_3$ (40 mmol, 5.53 g), and DMF (40 mL) to obtain the title compound as a brown solid (5.38 g, 87%). **$^1$H NMR** (400 MHz, DMSO) δ 7.99 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.61 – 7.57 (m, 1H), 7.24 – 7.20 (m, 1H), 7.00 (d, *J* = 8.7 Hz, 1H), 6.90 (d, *J* = 2.6 Hz, 1H), 6.75 (dd, *J* = 8.4, 1.2 Hz, 1H), 6.63 (dd, *J* = 8.7, 2.6 Hz, 1H), 5.46 (s, 2H). **$^{13}$C NMR** (101 MHz, DMSO) δ 151.4, 148.8, 140.1,

139.7, 135.2, 126.0, 124.0, 122.7, 117.8, 117.1, 115.7, 114.8. **HRMS** (ESI) m/z: $[M-H]^-$ Calcd for $C_{12}H_8BrN_2O_3^-$ 306.9718; Found: 306.9719.




**2-Bromo-1-(5-chloro-2-nitrophenoxy)-4-methylbenzene (1k).**

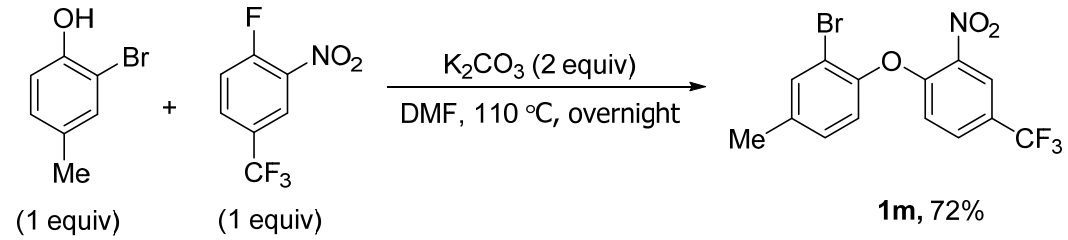
Following the general procedure A, the title compound was prepared from 2-bromo-4-methylphenol (20 mmol, 2.41 mL), 4-chloro-2-fluoro-1-nitrobenzene (20 mmol, 2.35 mL), $K_2CO_3$ (40 mmol, 5.53 g), and DMF (40 mL) to obtain the title compound as a yellow solid (5.48 g, 80 %). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.8 Hz, 1H), 7.51 (d, *J* = 2.1 Hz, 1H), 7.20 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.15 (dd, *J* = 8.8, 2.1 Hz, 1H), 7.05 (d, *J* = 8.2 Hz, 1H), 6.75 (d, *J* = 2.1 Hz, 1H), 2.37 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 151.7, 148.7, 140.3, 138.0, 137.7, 134.7, 130.0, 127.1, 122.8, 122.1, 118.0, 115.2, 20.7. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{10}NO_3ClBr$ 341.9533; Found: 341.9529.




**2-Bromo-1-(4-fluoro-2-nitrophenoxy)-4-methylbenzene (1l).**

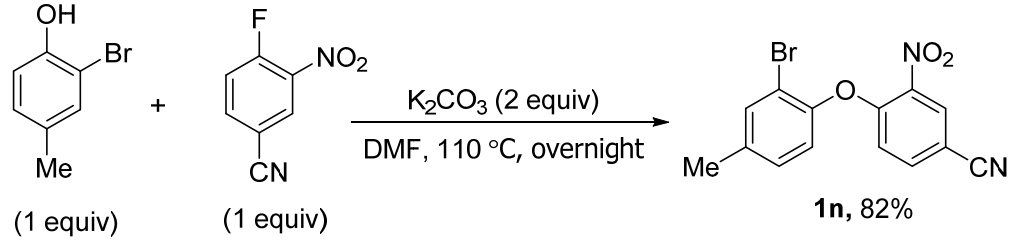
Following the general procedure A, the title compound was prepared from 2-bromo-4-methylphenol (20 mmol, 2.41 mL), 1,4-difluoro-2-nitrobenzene (20 mmol, 2.17 mL), $K_2CO_3$ (40 mmol, 5.53 g), and DMF (40 mL) to obtain the title compound as a yellow solid (3.91 g, 60%). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 7.7, 3.1 Hz, 1H), 7.47 (d, *J* = 2.8 Hz, 1H), 7.23 – 7.19 (m, 1H), 7.14 − 7.11 (m, 1H), 6.93 (d, *J* = 8.3 Hz, 1H), 6.83 (dd, *J* = 9.2, 4.5 Hz, 1H), 2.35 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 156.8 (d, $J_{C-F}$ = 246.8 Hz), 149.8, 147.0 (d, $J_{C-F}$ = 3.1 Hz), 140.1 (d, $J_{C-F}$ = 8.4 Hz), 136.9, 134.5, 129.8, 121.5 (d, $J_{C-F}$ = 23.1 Hz), 121.0,

120.4 (d, $J_{C\text{-}F}$ = 7.9 Hz), 114.7, 113.0 (d, $J_{C\text{-}F}$ = 27.6 Hz), 20.6. **$^{19}$F NMR** (376 MHz, $CDCl_3$) δ -117.12. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{10}NO_3BrF$ 325.9828; Found: 325.9830.




**2-Bromo-4-methyl-1-(2-nitro-4-(trifluoromethyl)phenoxy)benzene (1m).**

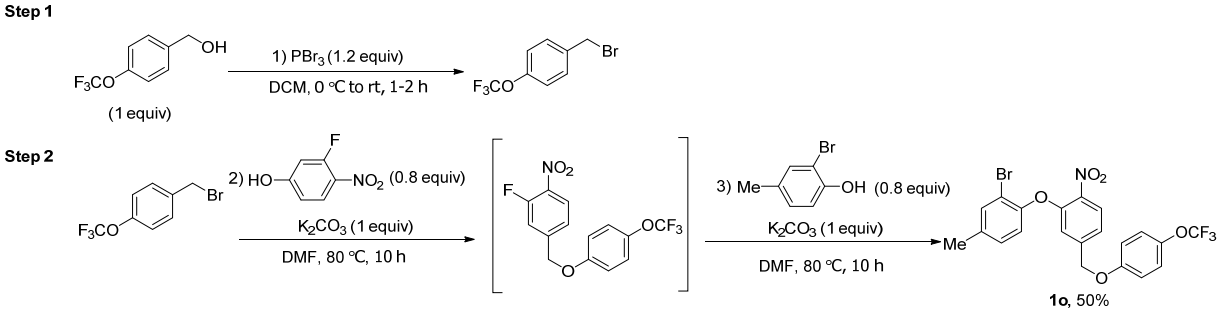
Following the general procedure A, the title compound was prepared from 2-bromo-4-methylphenol (20 mmol, 2.41 mL), 1-fluoro-2-nitro-4-(trifluoromethyl)benzene (20 mmol, 2.55 mL) $K_2CO_3$ (40 mmol, 5.53 g), and DMF (40 mL) to obtain the title compound as a yellow solid (5.42 g, 72%). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.25 (d, $J$ = 2.7 Hz, 1H), 7.67 (dd, $J$ = 8.9, 2.6 Hz, 1H), 7.50 (d, $J$ = 2.8 Hz, 1H), 7.20 (dd, $J$ = 8.3, 2.9 Hz, 1H), 7.07 (d, $J$ = 8.2 Hz, 1H), 6.84 (d, $J$ = 8.8 Hz, 1H), 2.38 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 153.4, 148.3, 139.4, 138.2, 134.7, 130.9 (q, $J_{C\text{-}F}$ = 3.4 Hz), 130.1, 122.88 (q, $J_{C\text{-}F}$ = 272.1 Hz), 124.7 (q, $J_{C\text{-}F}$ = 34.3 Hz), 123.7 (q, $J_{C\text{-}F}$ = 3.9 Hz), 122.4, 117.9, 115.4, 20.7. **$^{19}$F NMR** (376 MHz, $CDCl_3$) δ -62.19. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{10}NO_3BrF_3$ 375.9796; Found: 375.9801.




**4-(2-Bromo-4-methylphenoxy)-3-nitrobenzonitrile (1n).**

Following the general procedure A, the title compound was prepared from 2-bromo-4-methylphenol (20 mmol, 2.41 mL), 4-fluoro-3-nitrobenzonitrile (20 mmol, 3.32 g), $K_2CO_3$ (40 mmol, 5.53 g), and DMF (40 mL) to obtain the title compound as a gray solid (5.46 g, 82%). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.27 (d, $J$ = 2.1 Hz, 1H), 7.69 (dd, $J$ = 8.7, 2.1 Hz, 1H), 7.50 (d, $J$ = 2.1 Hz, 1H), 7.21 (dd, $J$ = 8.6, 2.5 Hz, 1H), 7.09 (d, $J$ = 8.2 Hz, 1H), 6.81 (d, $J$ = 8.7 Hz,

1H), 2.39 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 154.2, 147.7, 139.5, 138.6, 137.3, 134.8, 130.2, 130.1, 122.6, 118.0, 116.6, 115.4, 106.2, 20.7. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{14}H_9N_2O_3BrNa^+$ 354.9694; Found 354.9695.



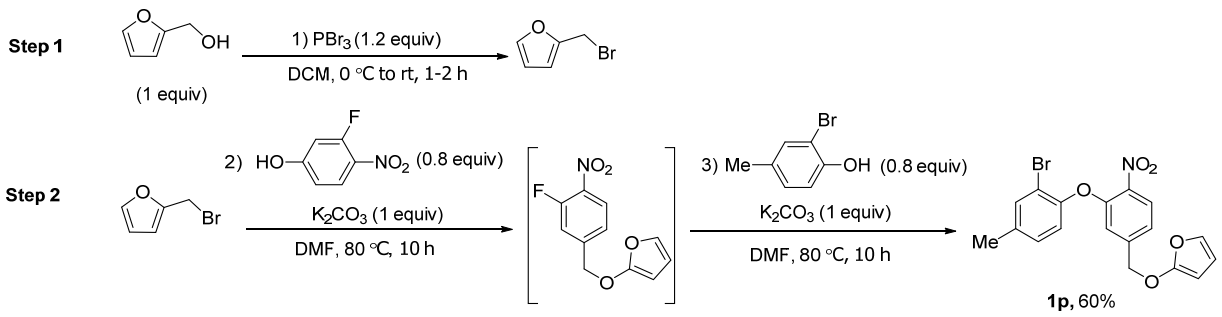

**2-Bromo-4-methyl-1-(2-nitro-5-((4-(trifluoromethoxy)phenoxy)methyl)phenoxy)benzene (1o).**

Steps **1** and **2** are performed according to the literature procedures.[2,3]

**Step 1:** In an oven-dried 250 mL round bottom flask equipped with a magnetic stir bar was charged with (4-(trifluoromethoxy)phenyl)methanol (1 equiv, 20 mmol, 2.90 mL) and dry DCM (100 mL, 0.2 M) under argon atmosphere. The reaction mixture was cooled to 0 °C, and $PBr_3$ (1.2 equiv, 24 mmol, 2.26 mL) was added dropwise. The resulting reaction mixture was warmed to room temperature and was stirred until the consumption of substrate as judged by TLC. The reaction was then quenched with ice-cold water, and the organic fraction was separated and washed with saturated $NaHCO_3$ solution and dried over anhydrous $Na_2SO_4$. The organic fraction concentrated under reduced pressure with the aid of rotary evaporator to give 4-trifluoromethoxybenzyl bromide which was used for the step 2 without further purification.

**Step 2:** In an oven-dried 250 mL round bottom flask equipped with a magnetic stir bar was charged with 3-fluoro-4-nitrophenol (0.8 equiv, 16 mmol, 2.51 g), $K_2CO_3$ (1 equiv, 20 mmol, 2.76 g), and DMF (30 mL). After stirring for 10 min at room temperature, 4-trifluoromethoxybenzyl bromide (~1 equiv, from **step 1**) was added, and the resulting mixture was stirred continued at 80 °C under air atmosphere for 10 h until the consumption of substrate as judged by TLC. 2-bromo-4-methylphenol (0.8 equiv, 16 mmol, 1.93 mL) and $K_2CO_3$ (1 equiv, 20 mmol, 2.76 g) were then added, and the resulting mixture was further stirred under air atmosphere at 80 °C for 10 h. the reaction mixture was cooled down to room temperature.

At this point, $CH_2Cl_2$ (100 mL) was added to the reaction mixture and the organic fraction was washed successively with an aqueous solution of NaOH (~1 M, ~100 mL), water (3 × ~100 mL), and brine (100 mL). The organic fraction was concentrated in vacuo with the aid of rotary evaporator. The residue was recrystallized with $CH_2Cl_2$ and petroleum ether to afford the title compound as a white solid (3.99 g, 50%). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.58 (d, $J$ = 3.2 Hz, 1H), 7.47 (s, 1H), 7.45 (s, 2H), 7.26 (d, $J$ = 7.8 Hz, 2H), 7.11 (dd, $J$ = 9.1, 3.1 Hz, 1H), 7.07 (dd, $J$ = 8.3, 2.8 Hz, 1H), 6.87 – 6.83 (m, 2H), 5.08 (s, 2H), 2.33 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 153.8, 150.7, 149.2 (d, $J_{C\text{-}F}$ = 2.2 Hz), 144.5, 140.8, 136.0, 134.5, 134.4, 129.5, 129.1, 128.3, 121.8, 121.3, 120.5 (q, $J_{C\text{-}F}$ = 255.9 Hz), 120.0, 114.2, 110.8, 70.1, 20.5. **$^{19}$F NMR** (376 MHz, $CDCl_3$) δ -57.84. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{21}H_{16}BrF_3NO_5^+$ 498.0164; Found: 498.0170.

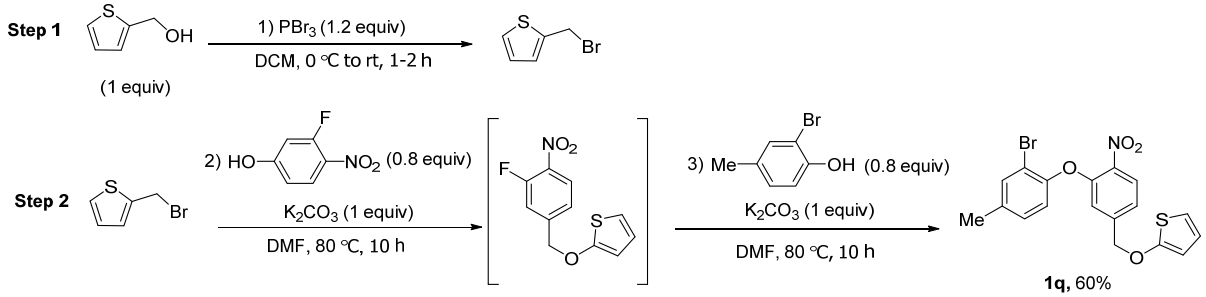



**2-((3-(2-Bromo-4-methylphenoxy)-4-nitrobenzyl)oxy)furan (1p).**

**Step 1:** In an oven-dried 250 mL round bottom flask equipped with a magnetic stir bar was charged with furan-2-ylmethanol (1 equiv, 20 mmol, 1.73 mL) and dry DCM (100 mL, 0.2 M) under argon atmosphere. The reaction mixture was cooled to 0 °C, and $PBr_3$ (1.2 equiv, 24 mmol, 2.26 mL) was added dropwise. The resulting reaction mixture was warmed to room temperature and was stirred until the consumption of substrate as judged by TLC. The reaction was then quenched with ice-cold water, and the organic fraction was separated and washed with saturated $NaHCO_3$ solution and dried over anhydrous $Na_2SO_4$. The organic fraction concentrated under reduced pressure with the aid of rotary evaporator to give 2-(bromomethyl)furan which was used for the step 2 without further purification.

**Step 2:** In an oven-dried 250 mL round bottom flask equipped with a magnetic stir bar was charged with 3-fluoro-4-nitrophenol (0.8 equiv, 16 mmol, 2.51 g), $K_2CO_3$ (1 equiv, 20 mmol,

2.76 g), and DMF (30 mL). After stirring for 10 min at room temperature, 2-(bromomethyl)furan (~1 equiv, from **step 1**) was added, and the resulting mixture was stirred continued at 80 °C under air atmosphere for 10 h until the consumption of substrate as judged by TLC. 2-bromo-4-methylphenol (0.8 equiv, 16 mmol, 1.93 mL) and $K_2CO_3$ (1 equiv, 20 mmol, 2.76 g) were then added, and the resulting mixture was further stirred under air atmosphere at 80 °C for 10 h. the reaction mixture was cooled down to room temperature. At this point, $CH_2Cl_2$ (100 mL) was added to the reaction mixture and the organic fraction was washed successively with an aqueous solution of NaOH (~1 M, ~100 mL), water (3 × ~100 mL), and brine (100 mL). The organic fraction was concentrated in vacuo with the aid of rotary evaporator. The residue was recrystallized with $CH_2Cl_2$ and petroleum ether to afford the title compound as a red solid (3.88 g, 60%). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 3.1 Hz, 1H), 7.40 – 7.37 (m, 2H), 7.13 (dd, *J* = 9.2, 3.1 Hz, 1H), 7.09 – 7.05 (m, 1H), 6.86 – 6.82 (m, 2H), 6.47 (dd, *J* = 3.2, 0.7 Hz, 1H), 6.41 – 6.38 (m, 1H), 5.03 (s, 2H), 2.33 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 153.7, 151.0, 149.1, 144.5, 143.6, 141.1, 135.9, 134.4, 129.5, 122.2, 121.2, 119.9, 114.2, 111.0, 110.8, 110.7, 63.2, 20.5. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{18}H_{15}BrNO_5^+$ 404.0127; Found: 404.0134.

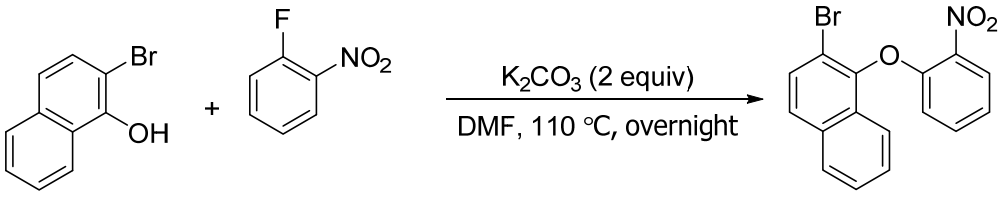



**2-((3-(2-Bromo-4-methylphenoxy)-4-nitrobenzyl)oxy)thiophene (1q).**

**Step 1:** In an oven-dried 250 mL round bottom flask equipped with a magnetic stir bar was charged with thiophen-2-ylmethanol (1 equiv, 20 mmol, 1.88 mL) and dry DCM (100 mL, 0.2 M) under argon atmosphere. The reaction mixture was cooled to 0 °C, and $PBr_3$ (1.2 equiv, 24 mmol, 2.26 mL) was added dropwise. The resulting reaction mixture was warmed to room temperature and was stirred until the consumption of substrate as judged by TLC. The reaction was then quenched with ice-cold water, and the organic fraction was separated and washed with saturated $NaHCO_3$ solution and dried over anhydrous $Na_2SO_4$. The organic fraction

concentrated under reduced pressure with the aid of rotary evaporator to give 2-(bromomethyl)thiophene which was used for the step 2 without further purification.

**Step 2:** In an oven-dried 250 mL round bottom flask equipped with a magnetic stir bar was charged with 3-fluoro-4-nitrophenol (0.8 equiv, 16 mmol, 2.51 g), $K_2CO_3$ (1 equiv, 20 mmol, 2.76 g), and DMF (30 mL). After stirring for 10 min at room temperature, 2-(bromomethyl)thiophene (~1 equiv, from **step 1**) was added, and the resulting mixture was stirred continued at 80 ℃ under air atmosphere for 10 h until the consumption of substrate as judged by TLC. 2-bromo-4-methylphenol (0.8 equiv, 16 mmol, 1.93 mL) and $K_2CO_3$ (1 equiv, 20 mmol, 2.76 g) were then added, and the resulting mixture was further stirred under air atmosphere at 80 ℃ for 10 h. the reaction mixture was cooled down to room temperature. At this point, $CH_2Cl_2$ (100 mL) was added to the reaction mixture and the organic fraction was washed successively with an aqueous solution of NaOH (~1 M, ~100 mL), water (3 × ~100 mL), and brine (100 mL). The organic fraction was concentrated in vacuo with the aid of rotary evaporator. The residue was recrystallized with $CH_2Cl_2$ and petroleum ether to afford the title compound as a red solid (4.03 g, 60%). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 3.1 Hz, 1H), 7.45 (d, *J* = 2.2 Hz, 1H), 7.36 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.14 – 7.11 (m, 2H), 7.07 (dd, *J* = 8.3, 2.2 Hz, 1H), 7.04 – 7.00 (m, 1H), 6.86 – 6.82 (m, 2H), 5.25 (s, 2H), 2.33 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 153.6, 150.7, 144.5, 140.7, 137.8, 135.9, 134.4, 129.5, 127.6, 127.0, 126.9, 122.1, 121.3, 119.9, 114.2, 111.1, 65.9, 20.5. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{15}BrNO_4S^+$ 419.9905; Found: 419.9910.

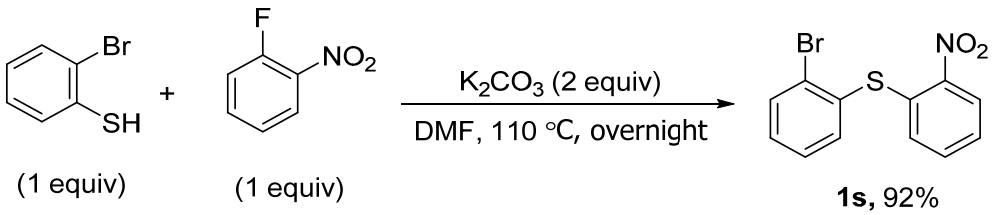



(1 equiv) (1 equiv) **1r,** 90%

**2-Bromo-1-(2-nitrophenoxy)naphthalene (1r).**

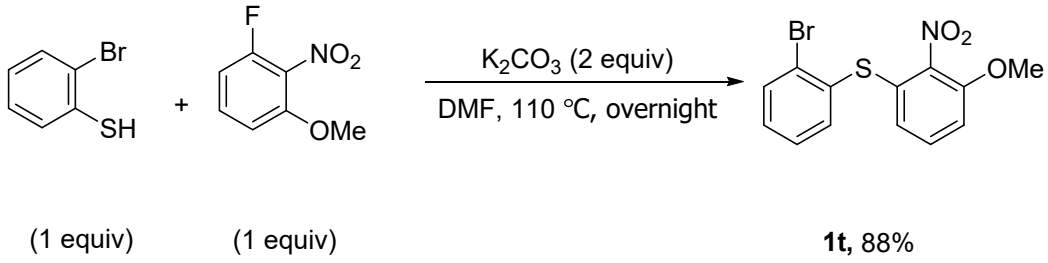
Following the general procedure A, the title compound was prepared from 2-bromonaphthalen-1-ol (5 mmol, 1.12 g), 1-fluoro-2-nitrobenzene (5 mmol, 0.53 mL), $K_2CO_3$ (10 mmol, 1.38 g), and DMF (10 mL) to obtain the title compound as a yellow solid (1.55 g, 90%). **$^1$H NMR** (400

MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.96 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.75 – 7.66 (m, 1H), 7.66 – 7.58 (m, 1H), 7.48 – 7.36 (m, 3H), 7.33 (s, 1H), 7.22 – 7.10 (m, 1H), 6.87 (dd, *J* = 8.4, 1.3 Hz, 1H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 150.4, 149.8, 134.4, 133.3, 133.0, 131.7, 127.3, 127.2, 126.9, 126.5, 126.1, 123.6, 119.8, 117.3, 116.1, 114.3. **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd for $C_{16}H_{10}BrNO_3Na^+$ 365.9742; Found: 365.9742.




**(2-Bromophenyl)(2-nitrophenyl)sulfane (1s).**

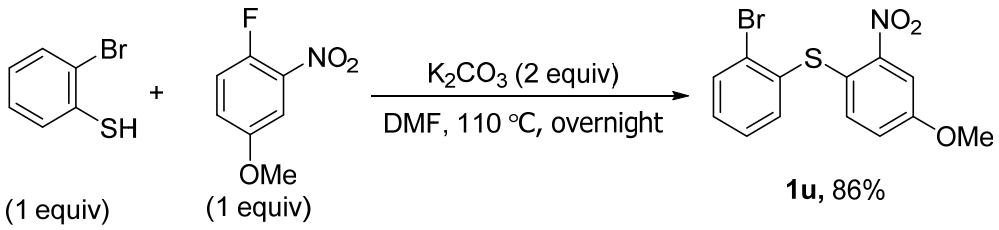
Following the general procedure A, the title compound was prepared from 2-bromobenzenethiol (20 mmol, 2.40 mL), 1-fluoro-2-nitrobenzene (20 mmol, 2.12 mL), $K_2CO_3$ (40 mmol, 5.53 g), and DMF (40 mL) to obtain the title compound as a yellow solid (5.71 g, 92%). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.69 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.64 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.35 (td, *J* = 7.5, 1.5 Hz, 1H), 7.33 – 7.25 (m, 2H), 7.20 – 7.16 (m, 1H), 6.68 (dd, *J* = 8.2, 1.3 Hz, 1H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 145.1, 138.1, 137.3, 134.3, 133.7, 132.3, 131.8, 131.1, 128.9, 128.0, 126.0, 125.4. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_9BrNO_2S^+$ 309.9537; Found 309.9535.




**(2-Bromophenyl)(3-methoxy-2-nitrophenyl)sulfane (1t).**

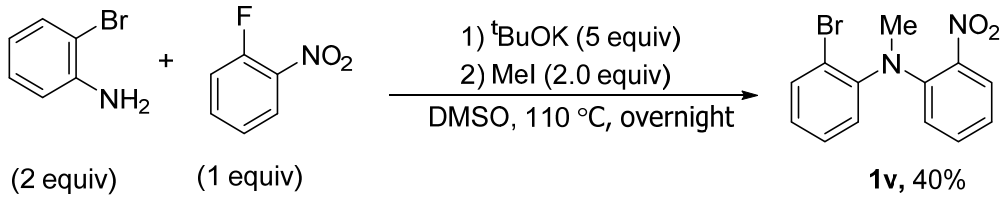
Following the general procedure A, the title compound was prepared from 2-bromobenzenethiol (20 mmol, 2.40 mL), 1-fluoro-3-methoxy-2-nitrobenzene (20 mmol, 2.60 mL), $K_2CO_3$ (40 mmol, 5.53 g), and DMF (40 mL) to obtain the title compound as a yellow solid (5.99 g, 88%). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.61 – 7.57 (m, 1H), 7.33 (t, *J* = 8.3 Hz,

1H), 7.27 – 7.20 (m, 2H), 7.17 – 7.12 (m, 1H), 6.98 (dd, $J$ = 8.5, 1.2 Hz, 1H), 6.83 (dd, $J$ = 8.0, 1.0 Hz, 1H), 3.92 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 151.7, 135.1, 133.6, 133.0, 131.4, 129.3, 129.0, 128.2, 126.0, 124.6, 111.9, 56.6. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{11}BrNO_3S^+$ 339.9643; Found 339.9646.




**(2-Bromophenyl)(5-methoxy-2-nitrophenyl)sulfane (1u).**

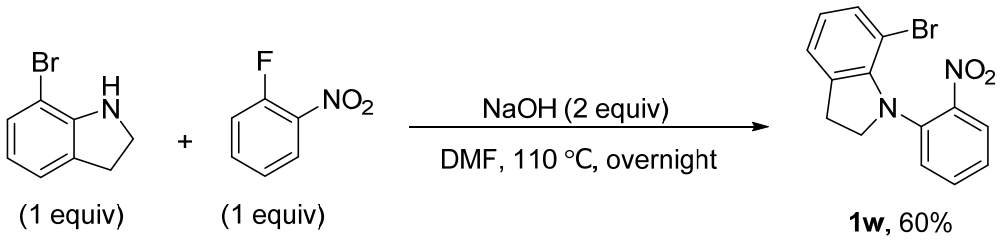
Following the general procedure A, the title compound was prepared from 2-bromobenzenethiol (20 mmol, 2.40 mL), 2-fluoro-4-methoxy-1-nitrobenzene (20 mmol, 2.60 mL), $K_2CO_3$ (40 mmol, 2 equiv, 5.53 g), and DMF (40 mL) to obtain the title compound as a green solid (5.85 g, 86%). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.27 (d, $J$ = 9.2 Hz, 1H), 7.78 (dd, $J$ = 7.9, 1.5 Hz, 1H), 7.73 (dd, $J$ = 7.5, 1.8 Hz, 1H), 7.43 (td, $J$ = 7.6, 1.6 Hz, 1H), 7.37 (td, $J$ = 7.6, 1.8 Hz, 1H), 6.71 (dd, $J$ = 9.2, 2.6 Hz, 1H), 6.10 (s, 1H), 3.64 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 163.6, 140.6, 138.4, 138.3, 134.3, 132.2, 132.0, 131.4, 129.0, 128.5, 111.9, 111.0, 55.7. **HRMS** (ESI) m/z: [M+H]+ Calcd for $C_{13}H_{11}BrNO_3S^+$ 339.9643; Found 339.9647.




**2-Bromo-N-methyl-N-(2-nitrophenyl)aniline (1v).**

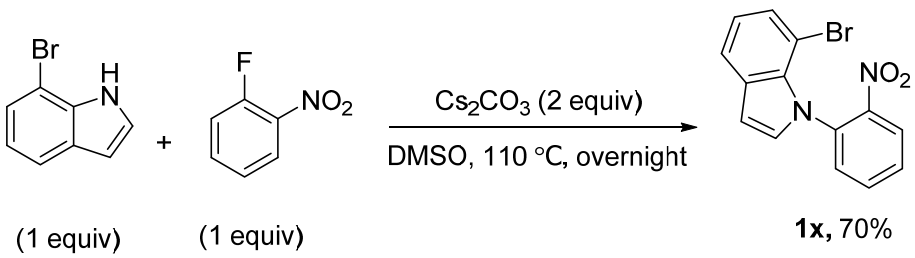
The known title compound was prepared according to the reported literature procedure.[4] The title compound was prepared using 1-fluoro-2-nitrobenzene (20 mmol) and 2-bromoaniline (20 mmol) to afford the title compound as a red solid (2.46 g, 40%). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.67 (dd, $J$ = 8.1, 1.7 Hz, 1H), 7.61 (dd, $J$ = 8.0, 1.5 Hz, 1H), 7.48 – 7.43 (m, 1H), 7.27 – 7.23 (m, 1H), 7.10 – 7.05 (m, 3H), 7.01 – 6.94 (m, 1H), 3.29 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$)

δ 146.5, 142.9, 141.3, 134.6, 133.2, 128.7, 127.3, 126.6, 126.2, 121.5, 120.7, 120.4, 41.5. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{12}BrN_2O_2^+$ 307.0082; Found 307.0083.



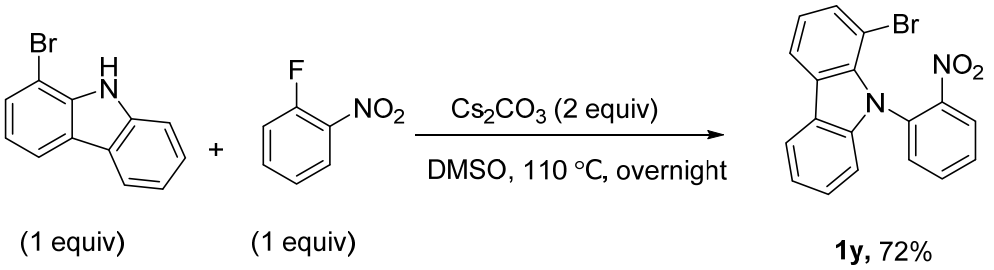

**7-Bromo-1-(2-nitrophenyl)indoline (1w).**

The title compound was prepared according to the similar literature procedure.[5] To a 25 mL round bottom flask equipped with a magnetic stirrer bar was charged with the a 7-bromoindoline (1 equiv, 1 mmol, 198 mg), NaOH (2 equiv, 2 mmol, 80 mg) and DMF (5 mL) under an argon atmosphere. A solution of 1-fluoro-2-nitrobenzene (1 equiv, 1 mmol, 106 $\mu$L) in DMF (5 mL) was added into the solution. The resulting reaction mixture was then stirred at 110 °C overnight. At this point, the reaction mixture was cooled down to room temperature. $CH_2Cl_2$ (100 mL) was added to the reaction mixture and the organic fraction was washed successively with an aqueous solution of NaOH (~1 M, ~30 mL), water (3 × ~100 mL), and brine (30 mL). The residue was purified by flash chromatography on silica gel using a mixture of ethyl acetate and petroleum ether (1:100) as eluent to obtain the title compound as a red liquid (191.4 mg, 60%). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.95 (dd, $J$ = 8.2, 1.6 Hz, 1H), 7.50 – 7.47 (m, 1H), 7.26 – 7.17 (m, 4H), 6.77 (t, $J$ = 7.6 Hz, 1H), 4.30 (q, $J$ = 9.9 Hz, 1H), 3.65 – 3.58 (m, 1H), 3.35 – 3.27 (m, 1H), 3.15 – 3.08 (m, 1H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 145.8, 142.6, 141.0, 135.5, 133.1, 132.2, 126.7, 125.5, 124.5, 124.0, 123.1, 107.2, 57.4, 30.0. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{12}BrN_2O_2^+$ 319.0082; Found 319.0086.



**Bromo-1-(2-nitrophenyl)-1H-indole (1x).**

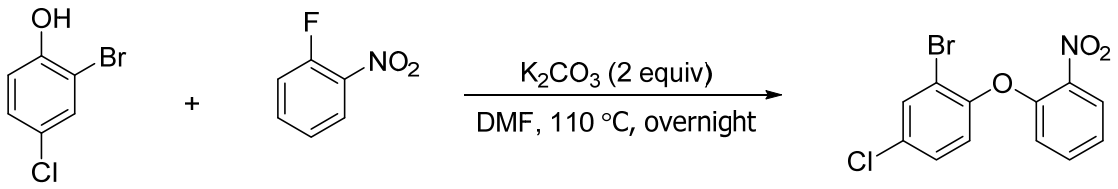
The title compound was prepared according to the similar literature procedure.[5] To a 25 mL round bottom flask equipped with a magnetic stirrer bar was charged with the 7-bromo-1H-indole (1 equiv, 10 mmol, 1.96 g), $Cs_2CO_3$ (2 equiv, 20 mmol, 6.52 g) and DMSO (15 mL). A solution of 1-fluoro-2-nitrobenzene (1 equiv, 10 mmol, 1.06 mL) in DMSO (5 mL) was added into the solution. The resulting reaction mixture was then stirred at 110 ℃ overnight. At this point, the reaction mixture was cooled down to room temperature. $CH_2Cl_2$ (100 mL) was added to the reaction mixture and the organic fraction was washed successively with an aqueous solution of NaOH (~1 M, ~100 mL), water (3 × ~100 mL), and brine (100 mL). The residue was purified by flash chromatography on silica gel using a mixture of ethyl acetate and petroleum ether (1:20) as eluent to obtain the title compound as a a yellow solid (2.22 g, 70%). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.74 – 7.59 (m, 3H), 7.53 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.35 (d, *J* = 7.7 Hz, 1H), 7.17 (d, *J* = 3.3 Hz, 1H), 7.03 (t, *J* = 7.8 Hz, 1H), 6.74 (d, *J* = 3.3 Hz, 1H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 147.8, 134.0, 133.7, 133.2, 132.4, 131.4, 131.2, 129.9, 127.5, 124.8, 121.8, 120.8, 104.4, 103.9. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{10}BrN_2O_2^+$ 316.9926; Found 316.9928.




**1-Bromo-9-(2-nitrophenyl)-9H-carbazole (1y).**

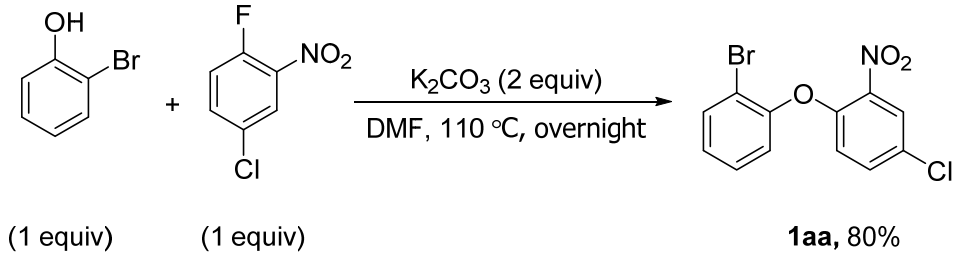
The title compound was prepared according to the similar literature procedure.[5] To a 25 mL round bottom flask equipped with a magnetic stirrer bar was charged with the 1-bromo-9H-carbazole (1 equiv, 50 mmol, 12.31 g), $Cs_2CO_3$ (2 equiv, 100 mmol, 32.58 g) and DMSO (70 mL). A solution of 1-fluoro-2-nitrobenzene (1 equiv, 50 mmol, 5.30 mL) in DMSO (10 mL) was added into the solution. The resulting reaction mixture was then stirred at 110 ℃ overnight. At this point, the reaction mixture was cooled down to room temperature. $CH_2Cl_2$ (100 mL) was added to the reaction mixture and the organic fraction was washed successively with an aqueous solution of NaOH (~1 M, ~100 mL), water (3 × ~100 mL), and brine (100 mL). The residue was purified by flash chromatography on silica gel using a mixture of ethyl acetate and

petroleum ether (1:20) as eluent to obtain the title compound as a yellow solid (13.22 g, 72%). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 8.1, 1.7 Hz, 1H), 8.14 – 8.07 (m, 2H), 7.85 – 7.69 (m, 2H), 7.65 – 7.50 (m, 2H), 7.44 – 7.28 (m, 2H), 7.16 (t, *J* = 7.8 Hz, 1H), 6.97 – 6.90 (m, 1H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 148.5, 142.5, 137.6, 133.8, 133.5, 132.2, 130.9, 130.2, 127.0, 126.7, 125.5, 123.0, 121.5, 121.1, 120.5, 119.8, 110.0, 103.4. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{12}BrN_2O_2^+$ 367.0082; Found 367.0086.




**2-Bromo-4-chloro-1-(2-nitrophenoxy)benzene (1z).**

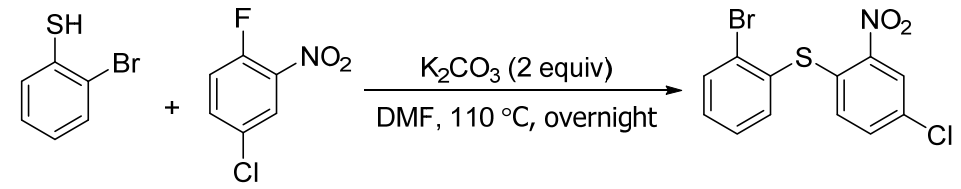
Following the general procedure A, the title compound was prepared from 2-bromo-4-chlorophenol (20 mmol, 2.59 mL), 1-fluoro-2-nitrobenzene (20 mmol, 2.1mL), $K_2CO_3$ (40 mmol, 5.53 g), and DMF (40 mL) to obtain the title compound as a white solid (5.72 g, 87%). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.64 (d, *J* = 2.4 Hz, 1H), 7.55 – 7.50 (m, 1H), 7.35 – 7.15 (m, 2H), 6.96 (d, *J* = 8.7 Hz, 1H), 6.88 (dd, *J* = 8.3, 1.3 Hz, 1H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 151.2, 149.7, 140.7, 134.5, 133.7, 130.9, 129.1, 126.1, 123.9, 121.5, 119.5, 115.6. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_8NO_3ClBr^+$ 327.9376; Found 327.9370.




**(2-Bromophenoxy)-4-chloro-2-nitrobenzene (1aa).**

Following the general procedure A, the title compound was prepared from 2-bromophenol (20 mmol, 2.32 mL), 4-chloro-1-fluoro-2-nitrobenzene (20 mmol, 2.36 mL), $K_2CO_3$ (40 mmol, 5.53 g), and DMF (40 mL) to obtain the title compound as a yellow solid (5.26 g, 80%). **$^1$H**

**NMR** (400 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.65 (d, *J* = 2.4 Hz, 1H), 7.55 – 7.51 (m, 1H), 7.30 – 7.23 (m, 2H), 6.96 (d, *J* = 8.7 Hz, 1H), 6.88 (dd, *J* = 8.4, 1.3 Hz, 1H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 151.2, 149.7, 140.7, 134.5, 133.7, 130.9, 129.1, 126.1, 123.9, 121.5, 119.5, 115.6. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_8NO_3ClBr^+$ 327.9376; Found 327.9370.




(1 equiv) (1 equiv) **1ab,** 90%

**(2-Bromophenyl)(4-chloro-2-nitrophenyl)sulfane (1ab).**

Following the general procedure A, the title compound was prepared from 2-bromobenzenethiol (20 mmol, 2.40 mL), 4-chloro-1-fluoro-2-nitrobenzene (20 mmol, 2.36 mL), $K_2CO_3$ (40 mmol, 5.53 g), and DMF (40 mL). to obtain the title compound as a yellow solid (6.20 g, 90 %). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 2.3 Hz, 1H), 7.78 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.72 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.44 (td, *J* = 7.5, 1.5 Hz, 1H), 7.38 (td, *J* = 7.6, 1.8 Hz, 1H), 7.33 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.68 (d, *J* = 8.7 Hz, 1H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 145.2, 138.1, 136.1, 134.5, 133.8, 132.1, 131.8, 131.2, 131.1, 129.02, 129.01, 125.8. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_8NO_2SClBr^+$ 343.9148; Found 343.9141.

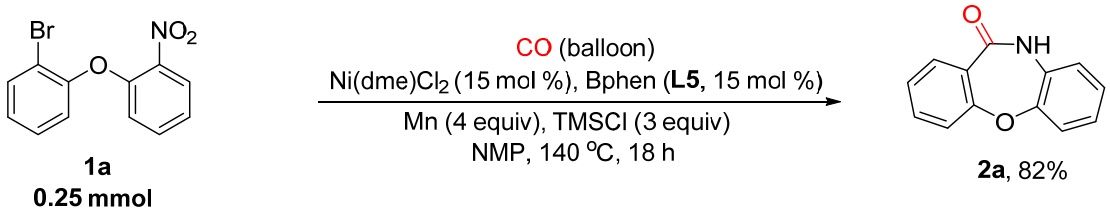
## Synthesis of dibenzo-azepinone-based heterocycles via Ni-catalyzed intramolecular aminocarbonylation (General Procedure B).

An oven-dried 10 mL Schlenk tube equipped with a stir bar was sequentially charged with 2-haloaryl-tethered nitroarene (1 equiv, 0.25 mmol), $Ni(dme)Cl_2$ (0.15 equiv, 0.0375 mmol, 9.0 mg), Bphen (**L5**, 0.15 equiv, 0.0375 mmol, 13 mg), and Mn powder (4 equiv, 1 mmol, 55 mg). The tube was evacuated in vacuo and then backfilled with CO using a CO balloon for three times. NMP solvent (2 mL) and TMSCl (3 equiv, 0.75 mmol, 95 $\mu$L) were transferred into the tube via a syringe. The resulting mixture was stirred under an CO balloon pressure in a preheated heat block at 140 °C for 18 h. At this point, the reaction mixture was cooled down to

room temperature. The reaction mixture was diluted with $CH_2Cl_2$ and then washed with dilute aqueous HCl solution (~0.1 M, 2 x 30 mL) and saturated brine (~30 mL), dried with anhydrous $Na_2SO_4$, and concentrated in vacuo with the aid of a rotary evaporator. The residue was purified by flash chromatography on silica gel using a mixture of petroleum ether (PE) and ethyl acetate (EtOAc) as the eluent to give the dibenzo-azepinone-based heterocycle product. (**Note:** water was used for washing instead of HCl (aq) for products containing the amino groups.)

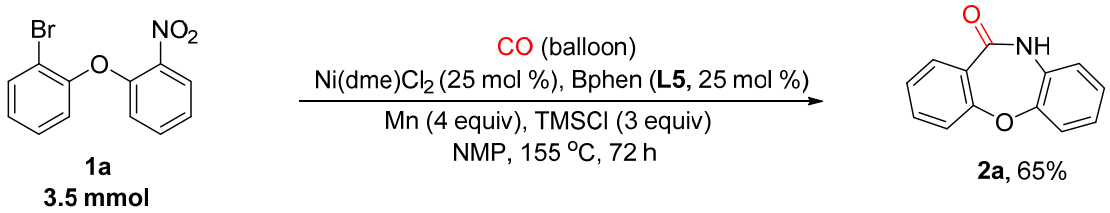
**Dibenzo[b,f][1,4]oxazepin-11(10H)-one (2a).**

**(i) 0.25 mmol scale:**




Following the general procedure B, the title compound was prepared from **1a** (0.25 mmol, 74 mg) using PE/EtOAc (10:1) as an eluent to afford the title compound as an orange amorphous solid (43 mg, 82%). **$^1$H NMR** (400 MHz, DMSO) δ 10.54 (s, 1H), 7.77 (dd, $J$ = 7.8, 1.8 Hz, 1H), 7.60 (td, $J$ = 7.5, 1.8 Hz, 1H), 7.36 – 7.30 (m, 3H), 7.20 – 7.11 (m, 3H). **$^{13}$C NMR** (101 MHz, DMSO) δ 166.3, 159.4, 150.9, 134.9, 131.9, 131.6, 126.4, 126.2, 125.9, 125.7, 122.1, 121.8, 121.1. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{10}NO_2^+$ 212.0712; Found 212.0715.

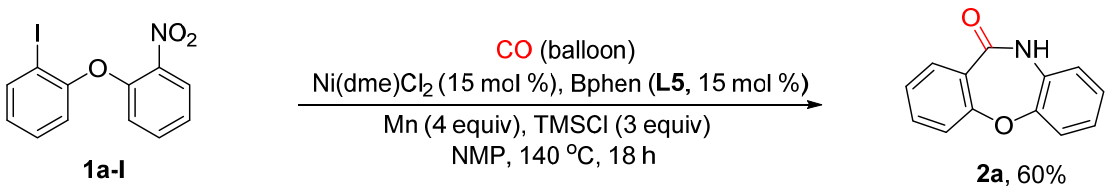
**(ii) 3.5 mmol scale:**




**Dibenzo[b,f][1,4]oxazepin-11(10H)-one (2a).**

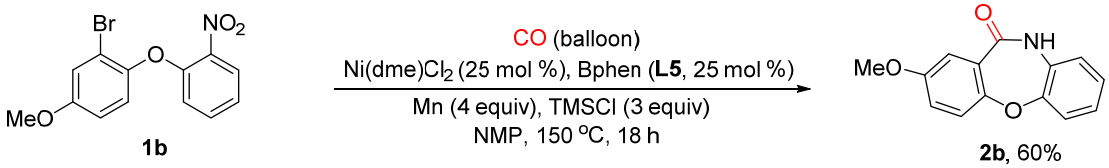
Following the general procedure B, the title compound was obtained using **1a** (1 equiv, 3.5 mmol, 1.03 g), $Ni(dme)Cl_2$ (0.875 mmol, 195 mg), Bphen (0.875 mmol, 294 mg), Mn (14 mmol, 769 mg), TMSCl (10.5 mmol, 1.33 mL), and NMP (30 mL) at 155 °C using a mixture

of PE/EtOAc (10:1) as an eluent to afford the amide product as an orange amorphous solid (480 mg, 65%). The $^{1}$H NMR spectra was in agreement with the identical compound from **(i)**.



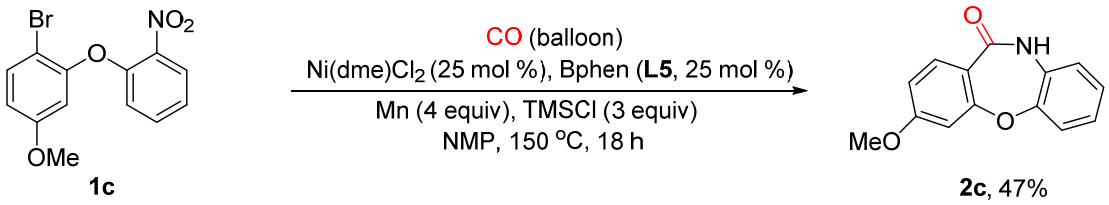

**Dibenzo[b,f][1,4]oxazepin-11(10H)-one (2a).**

Following the general procedure B, the title compound was prepared from **1a-I** (1 equiv, 0.25 mmol, 85 mg) using PE/EtOAc (10:1) as an eluent to afford the title compound as an orange amorphous solid (32 mg, 60%).



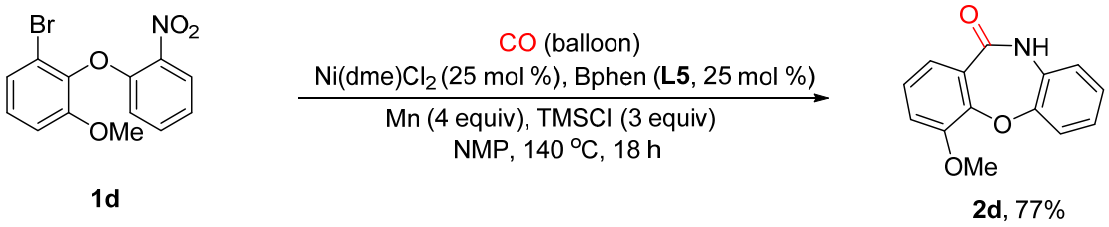

**2-Methoxydibenzo[b,f][1,4]oxazepin-11(10H)-one (2b).**

Following the general procedure B, the title compound was prepared from **1b** (1 equiv, 0.25 mmol, 81 mg), $Ni(dme)Cl_2$ (0.25 equiv, 0.0625 mmol, 14 mg), and Bphen (0.25 equiv, 0.0625 mmol, 21 mg) at 150 °C using PE/EtOAc (10:1) as an eluent to afford the title compound as a white amorphous solid (37 mg, 60%). **$^{1}$H NMR** (400 MHz, DMSO) δ 10.53 (s, 1H), 7.31 (dd, *J* = 7.8, 2.0 Hz, 1H), 7.29 – 7.22 (m, 3H), 7.19 – 7.09 (m, 3H), 3.90 (s, 3H). **$^{13}$C NMR** (101 MHz, DMSO) δ 166.3, 151.14, 151.08, 148.1, 132.0, 127.6, 126.3, 126.0, 125.6, 122.1, 122.0, 121.9, 117.1, 56.8. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{12}NO_3^+$ 242.0817; Found 242.0823.



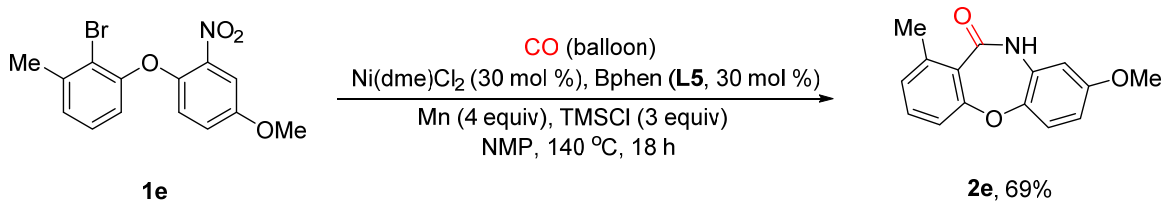

**3-Methoxydibenzo[b,f][1,4]oxazepin-11(10H)-one (2c).**

Following the general procedure B, $Ni(dme)Cl_2$ (0.25 equiv, 0.0625 mmol, 14 mg), and Bphen (0.25 equiv, 0.0625 mmol, 21 mg) at 150 °C using PE/EtOAc (10:1) as an eluent to afford the title compound as a white amorphous solid (29 mg, 47%). **$^1$H NMR** (400 MHz, DMSO) δ 10.35 (s, 1H), 7.71 (d, $J$ = 8.7 Hz, 1H), 7.32 (d, $J$ = 7.6 Hz, 1H), 7.20 – 7.09 (m, 3H), 6.93 – 6.84 (m, 2H), 3.84 (s, 3H). **$^{13}$C NMR** (101 MHz, DMSO) δ 165.9, 164.5, 160.7, 150.4, 133.2, 131.8, 126.4, 125.5, 121.9, 121.8, 118.2, 112.3, 105.8, 56.3. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{12}NO_3^+$ 242.0817; Found 242.0812.




**4-Methoxydibenzo[b,f][1,4]oxazepin-11(10H)-one (2d).**

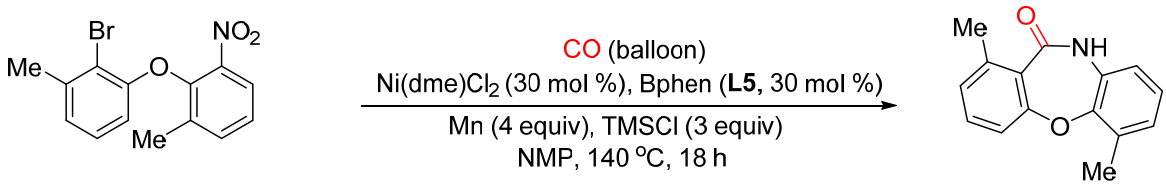
Following the general procedure B, the title compound was prepared from **1d** (1 equiv, 0.25 mmol, 81 mg), $Ni(dme)Cl_2$ (0.25 equiv, 0.0625 mmol, 14 mg), and Bphen (0.25 equiv, 0.0625 mmol, 21 mg) using PE/EtOAc (10:1) as an eluent to afford the title compound as a white amorphous solid (47 mg, 77%). **$^1$H NMR** (400 MHz, DMSO) δ 10.55 (s, 1H), 7.29 (m, 2H), 7.22 (d, $J$ = 3.2 Hz, 1H), 7.20 – 7.08 (m, 4H), 3.76 (s, 3H). **$^{13}$C NMR** (101 MHz, DMSO) δ 166.1, 156.7, 153.1, 151.3, 131.6, 126.8, 126.3 125.8, 122.2, 122.1, 121.6, 120.9, 114.9, 56.1. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{12}NO_3^+$ 242.0817; Found 242.0822.




**1e** **2e**, 69%

**8-Methoxy-4-methyldibenzo[b,f][1,4]oxazepin-11(10H)-one (2e).**

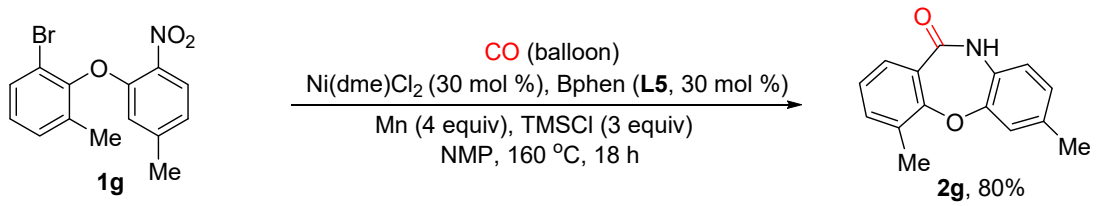
Following the general procedure B, the title compound was prepared from **1e** (1 equiv, 0.25 mmol, 85 mg), Ni(dme)$Cl_2$ (0.3 equiv, 0.0750 mmol, 17 mg), and Bphen (0.3 equiv, 0.0750 mmol, 25 mg) using PE/EtOAc (10:1) as an eluent to afford the title compound as a yellow amorphous solid (44 mg, 69%). **$^1$H NMR** (400 MHz, DMSO) δ 10.30 (s, 1H), 7.39 (t, $J$ = 7.9 Hz, 1H), 7.18 (d, $J$ = 8.0 Hz, 1H), 7.13 (d, $J$ = 7.6 Hz, 1H), 7.02 (d, $J$ = 8.8 Hz, 1H), 6.95 (d, $J$ = 2.8 Hz, 1H), 6.75 (dd, $J$ = 8.8, 2.8 Hz, 1H), 3.73 (s, 3H), 2.40 (s, 3H). **$^{13}$C NMR** (101 MHz, DMSO) δ 166.4, 160.5, 157.4, 153.3, 141.0, 132.3, 128.8, 126.1, 124.7, 122.9, 118.6, 112.0, 106.9, 56.1, 20.8. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{14}NO_3^+$ 256.0974; Found 256.0971.




**1f** **2f**, 60%

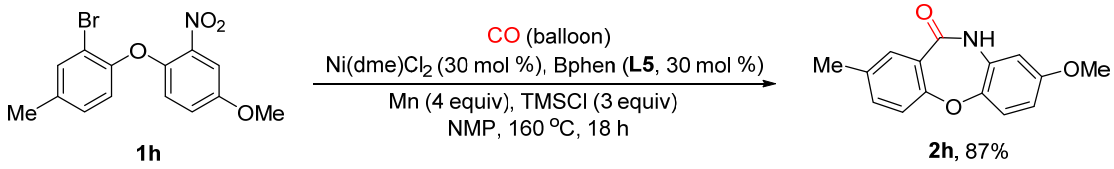
**1,6-Dimethyldibenzo[b,f][1,4]oxazepin-11(10H)-one (2f).**

Following the general procedure B, the title compound was prepared from **1f** (1 equiv, 0.25 mmol, 81 mg), Ni(dme)$Cl_2$ (0.3 equiv, 0.0750 mmol, 17 mg), and Bphen (0.3 equiv, 0.0750 mmol, 25 mg) using PE/EtOAc (10:1) as an eluent to afford the title compound as a yellow amorphous solid (42 mg, 60%). **$^1$H NMR** (400 MHz, DMSO) δ 10.47 (s, 1H), 7.40 (t, $J$ = 7.8 Hz, 1H), 7.23 (d, $J$ = 8.1 Hz, 1H), 7.14 (d, $J$ = 7.5 Hz, 1H), 7.09 – 6.96 (m, 2H), 6.94 (dd, $J$ = 7.5, 2.1 Hz, 1H), 2.43 (s, 3H), 2.41 (s, 3H). **$^{13}$C NMR** (101 MHz, DMSO) δ 166.7, 160.5, 150.5, 141.2, 132.4, 131.8, 130.5, 128.6, 126.9, 126.3, 125.6, 119.9, 118.8, 20.8, 16.4. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{14}NO_2^+$ 240.1025; Found 240.1024.



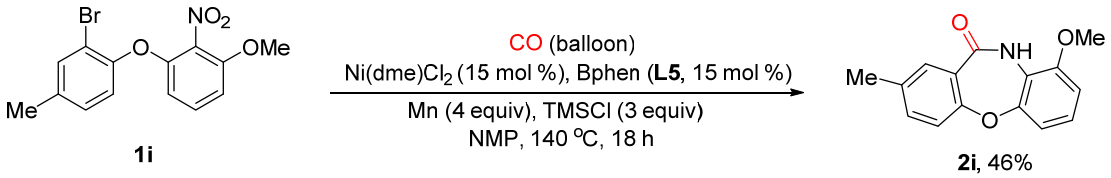

**4,8-Dimethyldibenzo[b,f][1,4]oxazepin-11(10H)-one (2g).**

Following the general procedure B, the title compound was prepared from **1g** (1 equiv, 0.25 mmol, 81 mg), Ni(dme)$Cl_2$ (0.3 equiv, 0.0750 mmol, 17 mg), and Bphen (0.3 equiv, 0.0750 mmol, 25 mg) at 160 °C using PE/EtOAc (10:1) as an eluent to afford the title compound as a white amorphous solid (48 mg, 80%). **$^1$H NMR** (400 MHz, DMSO) δ 10.42 (s, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.48 (d, *J* = 8.1 Hz, 1H), 7.22 – 7.13 (m, 2H), 7.07 – 6.94 (m, 2H), 2.48 (s, 3H), 2.27 (s, 3H). **$^{13}$C NMR** (101 MHz, DMSO) δ 166.6, 157.4, 150.7, 135.5, 135.3, 129.9, 129.5, 129.3, 126.8, 126.5, 125.30, 122.4, 121.8, 20.6, 16.4. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{13}NO_2Na^+$ 262.0844; Found 262.0852.



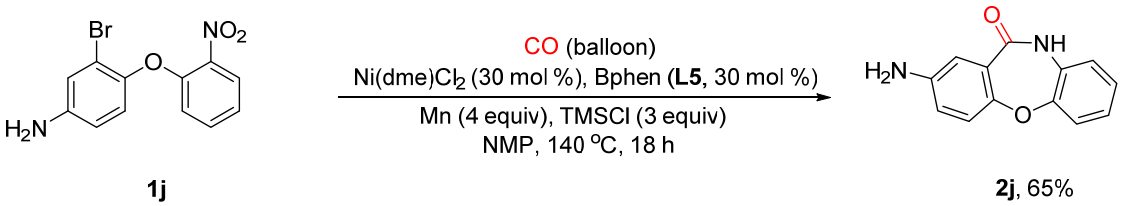

**8-Methoxy-2-methyldibenzo[b,f][1,4]oxazepin-11(10H)-one (2h).**

Following the general procedure B, the title compound was prepared from **1h** (1 equiv, 0.25 mmol, 85 mg), Ni(dme)$Cl_2$ (0.3 equiv, 0.0750 mmol, 17 mg), and Bphen (0.3 equiv, 0.0750 mmol, 25 mg) at 160 °C using PE/EtOAc (10:1) as an eluent to afford the title compound as a white amorphous solid (56 mg, 87%). **$^1$H NMR** (400 MHz, DMSO) δ 10.41 (s, 1H), 7.55 (d, *J* = 2.3 Hz, 1H), 7.39 (dd, *J* = 8.2, 2.3 Hz, 1H), 7.20 (t, *J* = 8.5 Hz, 2H), 6.73 – 6.64 (m, 2H), 3.70 (s, 3H), 2.30 (s, 3H). **$^{13}$C NMR** (101 MHz, DMSO) δ 166.5, 157.6, 157.1, 144.8, 135.3, 135.0, 132.3, 131.8, 125.7, 122.1, 120.7, 110.4, 107.1, 56.0, 20.6. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{14}NO_3^+$ 256.0974; Found 256.0977.



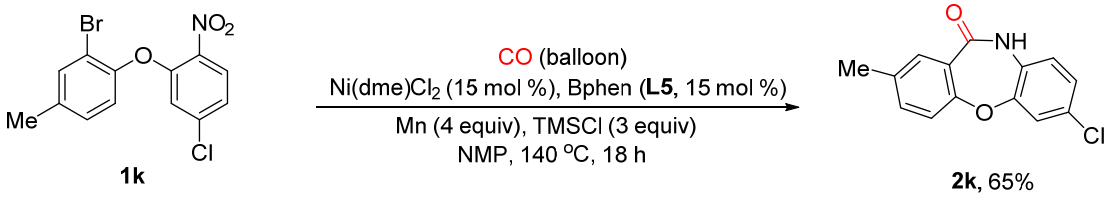

**9-Methoxy-2-methyldibenzo[b,f][1,4]oxazepin-11(10H)-one (2i).**

Following the general procedure B, **1i** (1 equiv, 0.25 mmol, 85 mg) using PE/EtOAc (10:1) as an eluent to afford the title compound as a white amorphous solid (30 mg, 46%). **$^1$H NMR** (400 MHz, DMSO) δ 9.52 (s, 1H), 7.53 (d, $J$ = 2.3 Hz, 1H), 7.39 (dd, $J$ = 8.3, 2.4 Hz, 1H), 7.21 (d, $J$ = 8.2 Hz, 1H), 7.11 (t, $J$ = 8.3 Hz, 1H), 6.93 – 6.89 (m, 2H), 3.82 (s, 3H), 2.30 (s, 3H). **$^{13}$C NMR** (101 MHz, DMSO) δ 166.0, 157.7, 152.9, 151.6, 135.3, 135.1, 131.7, 125.93, 125.90, 120.8, 120.6, 113.4, 109.0, 56.7, 20.6. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{14}NO_3^+$ 256.0974; Found 256.0977.



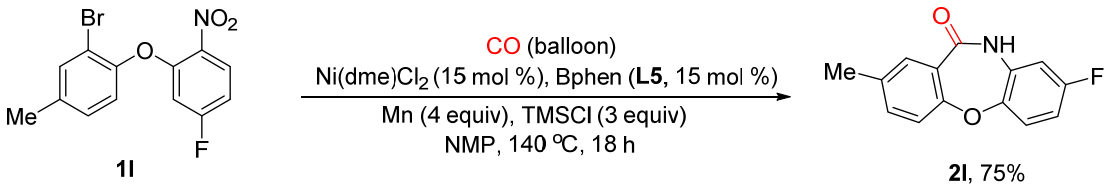

**2-Aminodibenzo[b,f][1,4]oxazepin-11(10H)-one (2j).**

Following the general procedure B, **1j** (1 equiv, 0.25 mmol, 78 mg), $Ni(dme)Cl_2$ (0.3 equiv, 0.0750 mmol, 17 mg), and Bphen (0.3 equiv, 0.0750 mmol, 25 mg) using PE/EtOAc (10:1) as an eluent to afford the title compound as a brown amorphous solid (37 mg, 65%). **$^1$H NMR** (400 MHz, DMSO) δ 10.32 (s, 1H), 7.25 – 7.20 (m, 1H), 7.19 – 7.04 (m, 3H), 6.99 (d, $J$ = 8.6 Hz, 1H), 6.93 (d, $J$ = 2.9 Hz, 1H), 6.73 (dd, $J$ = 8.6, 3.0 Hz, 1H), 5.22 (s, 2H). **$^{13}$C NMR** (101 MHz, DMSO) δ 166.8, 151.7, 149.8, 146.6, 131.9, 126.2, 125.8, 125.5, 121.9, 121.4, 121.3, 119.5, 115.0. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{11}N_2O_2^+$ 227.0821; Found 227.0819.



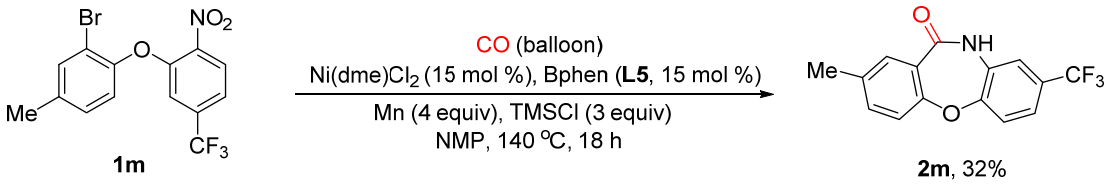
**7-Chloro-2-methyldibenzo[b,f][1,4]oxazepin-11(10H)-one (2k).**

Following the general procedure B, **1k** (1 equiv, 0.25 mmol, 86 mg) using PE/EtOAc (10:1) as an eluent to afford the title compound as a yellow amorphous solid (42 mg, 65%). **$^1$H NMR** (400 MHz, DMSO) δ 10.59 (s, 1H), 7.57 (d, $J$ = 2.3 Hz, 1H), 7.48 (d, $J$ = 2.4 Hz, 1H), 7.43 (dd, $J$ = 8.2, 2.4 Hz, 1H), 7.28 – 7.24 (m, 2H), 7.17 (d, $J$ = 8.6 Hz, 1H), 2.31 (s, 3H). **$^{13}$C NMR** (101 MHz, DMSO) δ 166.0, 156.8, 151.3, 135.6, 135.5, 131.8, 131.0, 128.8, 126.4, 125.5, 123.1, 121.9, 120.9, 20.6. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{11}NO_2Cl^+$ 260.0478; Found 260.0481.




**8-Fluoro-2-methyldibenzo[b,f][1,4]oxazepin-11(10H)-one (2l).**

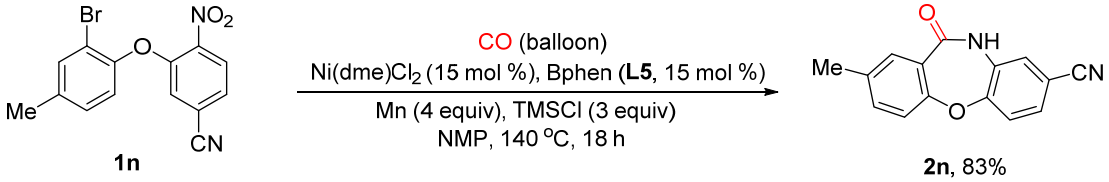
Following the general procedure B, **1l** (1 equiv, 0.25 mmol, 82 mg) using PE/EtOAc (10:1) as an eluent to afford the title compound as a white amorphous solid (46 mg, 75%). **$^1$H NMR** (400 MHz, DMSO) δ 10.58 (s, 1H), 7.57 (s, 1H), 7.42 (d, $J$ = 8.3 Hz, 1H), 7.37 – 7.33 (m, 1H), 7.23 (d, $J$ = 8.2 Hz, 1H), 7.01 – 6.93 (m, 2H), 2.31 (s, 3H). **$^{13}$C NMR** (101 MHz, DMSO) δ 166.2, 159.4 (d, $J_{C-F}$ = 241.0 Hz), 157.1, 147.2, 135.5, 135.4, 133.1 (d, $J_{C-F}$ = 11.2 Hz), 131.8, 125.5, 123.0 (d, $J_{C-F}$ = 9.9 Hz), 120.8, 111.8 (d, $J_{C-F}$ = 23.4 Hz), 108.5 (d, $J_{C-F}$ = 26.4 Hz), 20.6. **$^{19}$F NMR** (376 MHz, DMSO) δ -116.62. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{11}NO_2F^+$ 244.0774; Found 244.0774.




**2-Methyl-8-(trifluoromethyl)dibenzo[b,f][1,4]oxazepin-11(10H)-one (2m).**

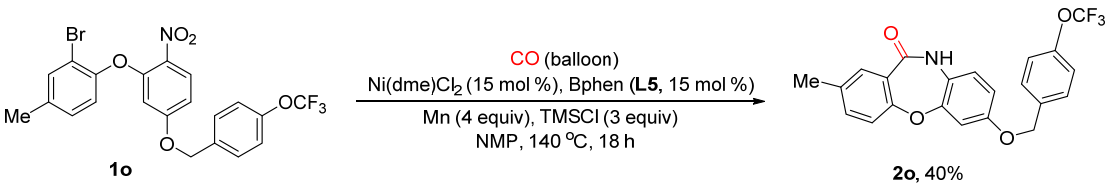
Following the general procedure B, **1m** (1 equiv, 0.25 mmol, 94 mg) using PE/EtOAc (10:1) as an eluent to afford the title compound as a white amorphous solid (23 mg, 32%)**. $^1$H NMR**

(400 MHz, DMSO) δ 10.70 (s, 1H), 7.60 (d, $J$ = 2.3 Hz, 1H), 7.57 – 7.50 (m, 3H), 7.45 (dd, $J$ = 8.3, 2.4 Hz, 1H), 7.29 (d, $J$ = 8.2 Hz, 1H), 2.32 (s, 3H). **$^{13}$C NMR** (101 MHz, DMSO) δ 166.0, 156.5, 153.4, 135.71, 135.68, 132.7, 131.9, 127.0 (q, $J_{C-F}$ = 32.4 Hz), 125.2, 124.1 (q, $J_{C-F}$ = 270.4 Hz), 123.0, 122.6 (q, $J_{C-F}$ = 4.2 Hz), 121.0, 118.93(q, $J_{C-F}$ = 3.6 Hz), 20.57. **$^{19}$F NMR** (376 MHz, DMSO) δ -60.83. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{11}NO_3F_3^+$ 294.0742; Found 294.0740.




**2-Methyl-11-oxo-10,11-dihydrodibenzo[b,f][1,4]oxazepine-8-carbonitrile (2n).**

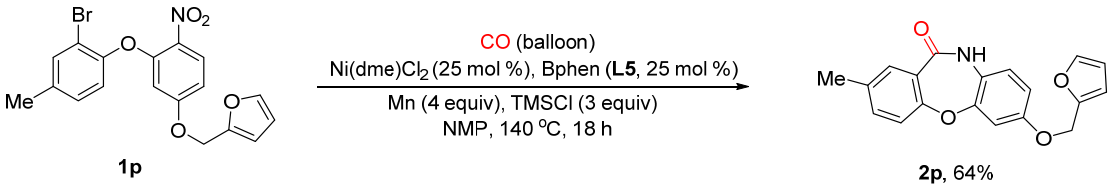
Following the general procedure B, **1n** (1 equiv, 0.25 mmol, 84 mg) using PE/EtOAc (10:1) as an eluent to afford the title compound as a yellow amorphous solid (52 mg, 83%). **$^1$H NMR** (400 MHz, DMSO) δ 10.69 (s, 1H), 7.63 (dd, $J$ = 8.3, 2.0 Hz, 1H), 7.58 (d, $J$ = 2.3 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.44 (dd, $J$ = 8.3, 2.3 Hz, 1H), 7.27 (d, $J$ = 8.3 Hz, 1H), 2.31 (s, 3H). **$^{13}$C NMR** (101 MHz, DMSO) δ 165.9, 156.3, 154.2, 135.9, 135.8, 133.0, 131.9, 130.0, 125.7, 125.1, 123.4, 121.05, 118.4, 109.1, 20.6. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{11}N_2O_2^+$ 251.0821; Found 251.0818.




**2-Methyl-7-((4-methylbenzyl)oxy)dibenzo[b,f][1,4]oxazepin-11(10H)-one (2o).**

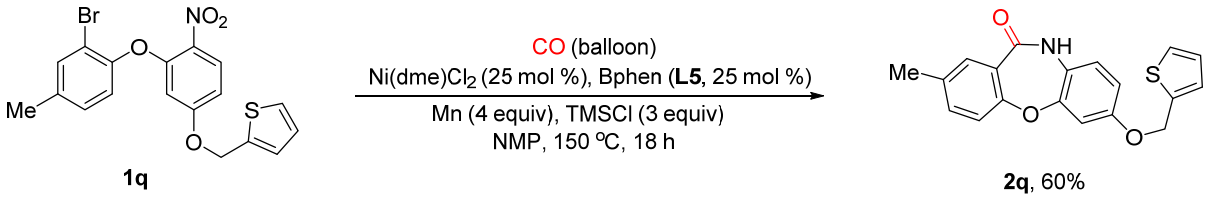
Following the general procedure B, **1o** (1 equiv, 0.25 mmol, 125 mg) using PE/EtOAc (10:1) as an eluent to afford the title compound as a yellow amorphous solid (35 mg, 40%). **$^1$H NMR** (400 MHz, DMSO) δ 10.44 (s, 1H), 7.57 – 7.53 (m, 3H), 7.40 – 7.37 (m, 3H), 7.24 – 7.17 (m, 2H), 6.81 – 6.74 (m, 2H), 5.08 (s, 2H), 2.29 (s, 3H). **$^{13}$C NMR** (101 MHz, DMSO) δ 166.4, 157.5, 156.0, 148.4, 145.0, 136.8, 135.3, 135.0, 132.4, 131.8, 130.0, 125.7, 122.2, 121.5, 120.7,

120.5 (q, $J_{C\text{-}F}$ = 254.8 Hz), 111.1, 108.2, 69.2, 20.6. **$^{19}$F NMR** (376 MHz, DMSO) δ -56.80. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{17}NO_4F_3^+$ 416.1110; Found 416.1112.




**7-(Furan-2-ylmethoxy)-2-methyldibenzo[b,f][1,4]oxazepin-11(10H)-one (2p).**

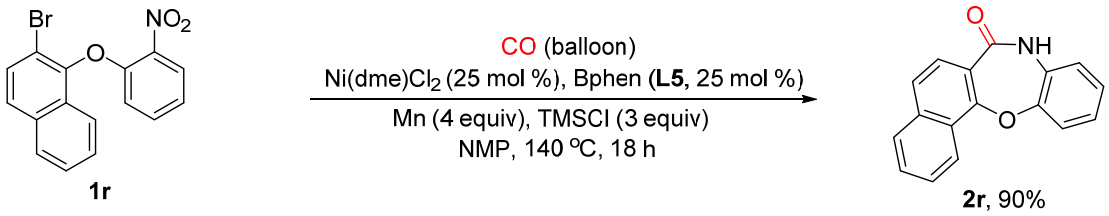
Following the general procedure B, the title compound was prepared from **1p** (1 equiv, 0.25 mmol, 102 mg), $Ni(dme)Cl_2$ (0.25 equiv, 0.0625 mmol, 14 mg), and Bphen (0.25 equiv, 0.0625 mmol, 21 mg) using PE/EtOAc (10:1) as an eluent to afford the title compound as a white amorphous solid (51 mg, 64%). **$^1$H NMR** (400 MHz, DMSO) δ 10.42 (s, 1H), 7.68 (d, $J$ = 1.8 Hz, 1H), 7.55 (d, $J$ = 2.3 Hz, 1H), 7.39 (dd, $J$ = 8.2, 2.4 Hz, 1H), 7.23 – 7.18 (m, 2H), 6.79 – 6.76 (m, 1H), 6.58 (d, $J$ = 3.3 Hz, 1H), 6.46 – 6.45 (m, 1H), 4.99 (s, 2H), 2.30 (s, 3H). **$^{13}$C NMR** (101 MHz, DMSO) δ 166.4, 157.5, 155.7, 150.2, 145.1, 144.1, 135.3, 135.0, 132.3, 131.8, 125.7, 122.1, 120.7, 111.23, 111.15, 111.12, 108.3, 62.4, 20.6. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{16}NO_4^+$ 322.1078; Found 322.1083.




**2-Methyl-7-(thiophen-2-ylmethoxy)dibenzo[b,f][1,4]oxazepin-11(10H)-one (2q).**

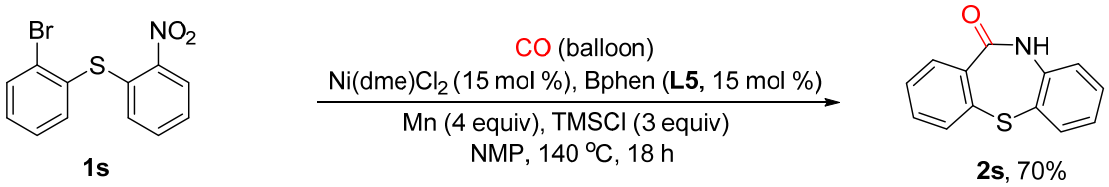
Following the general procedure B, the title compound was prepared from the title compound was prepared from **1q** (1 equiv, 0.25 mmol, 106 mg), $Ni(dme)Cl_2$ (0.25 equiv, 0.0625 mmol, 14 mg), and Bphen (0.25 equiv, 0.0625 mmol, 21 mg) at 150 °C using PE/EtOAc (10:1) as an eluent to afford the title compound as a white amorphous solid (51 mg, 60%). **$^1$H NMR** (400 MHz, DMSO) δ 10.43 (s, 1H), 7.56 – 7.53 (m, 2H), 7.39 (dd, $J$ = 8.3, 2.3 Hz, 1H), 7.24 – 7.18 (m, 3H), 7.03 – 7.01 (m, 1H), 6.80 – 6.77 (m, 2H), 5.23 (s, 2H), 2.30 (s, 3H). **$^{13}$C NMR** (101 MHz, DMSO) δ 166.5, 157.5, 155.6, 145.1, 139.3, 135.3, 135.0, 132.3, 131.8, 128.2, 127.4,

127.3, 125.7, 122.2, 120.7, 111.3, 108.4, 65.1, 20.6. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{16}NO_3S^+$ 338.0815; Found 338.0853.



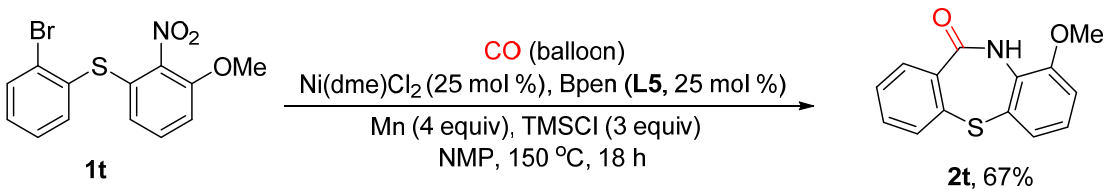

**Benzo[b]naphtho[2,1-f][1,4]oxazepin-7(8H)-one (2r).**

Following the general procedure B, the title compound was prepared from **1r** (1 equiv, 0.25 mmol, 87 mg), $Ni(dme)Cl_2$ (0.25 equiv, 0.0625 mmol, 14 mg), and Bphen (0.25 equiv, 0.0625 mmol, 21 mg) using PE/EtOAc (10:1) as an eluent to afford the title compound as a white amorphous solid (59 mg, 90%). **$^1$H NMR** (400 MHz, DMSO) δ 10.63 (s, 1H), 8.48 (s, 1H), 8.09 (d, $J$ = 8.2 Hz, 1H), 7.97 (d, $J$ = 8.3 Hz, 1H), 7.88 (s, 1H), 7.66 – 7.62 (m, 1H), 7.56 – 7.52 (m, 1H), 7.44 – 7.38 (m, 1H), 7.25 – 7.12 (m, 3H). **$^{13}$C NMR** (101 MHz, DMSO) δ 166.2, 156.0, 150.7, 136.1, 133.5, 131.6, 130.5, 129.5, 129.2, 127.5, 126.7, 126.5, 126.1, 125.8, 122.1, 122.0, 117.3. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{12}NO_2^+$ 262.0868; Found 262.0864.



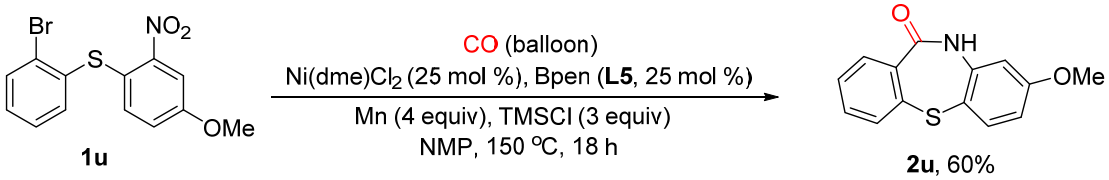

**Dibenzo[b,f][1,4]thiazepin-11(10H)-one (2s).**

Following the general procedure B, **1s** (1 equiv, 0.25 mmol, 78 mg) using PE/EtOAc (10:1) as an eluent to afford the title compound as a yellow amorphous solid (35 mg, 40%). **$^1$H NMR** (400 MHz, DMSO) δ 10.71 (s, 1H), 7.68 (d, $J$ = 7.0 Hz, 1H), 7.57 -7.52 (m, 2H), 7.52 – 7.41 (m, 2H), 7.37 (t, $J$ = 7.7 Hz, 1H), 7.23 (d, $J$ = 7.9 Hz, 1H), 7.15 (t, $J$ = 7.5 Hz, 1H). **$^{13}$C NMR** (101 MHz, DMSO) δ 168.9, 140.4, 138.3, 136.8, 133.0, 132.5, 131.9, 131.8, 130.3, 129.4, 125.9, 123.7. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{10}NOS^+$ 228.0843; Found 228.0489.



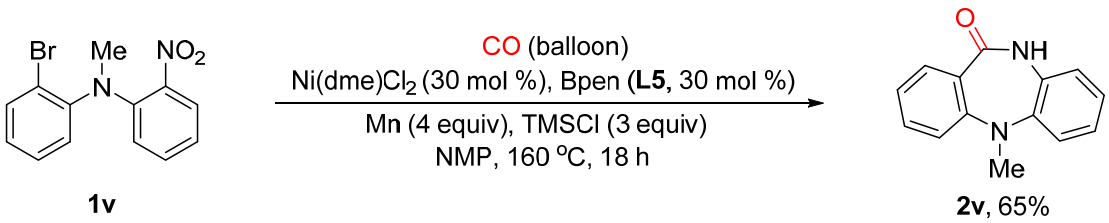

**9-Methoxydibenzo[b,f][1,4]thiazepin-11(10H)-one (2t).**

Following the general procedure B, the title compound was prepared from the title compound was prepared from **1t** (1 equiv, 0.25 mmol, 85 mg), $Ni(dme)Cl_2$ (0.25 equiv, 0.0625 mmol, 14 mg), and Bphen (0.25 equiv, 0.0625 mmol, 21 mg) at 150 °C using PE/EtOAc (10:1) as an eluent to afford the title compound as a white amorphous solid (43 mg, 67 %). **$^1$H NMR** (400 MHz, DMSO) δ 9.83 (s, 1H), 7.66 (dd, *J* = 7.0, 2.2 Hz, 1H), 7.52 (dd, *J* = 7.1, 1.9 Hz, 1H), 7.49 – 7.41 (m, 2H), 7.19 – 7.11 (m, 2H), 7.09 – 7.05 (m, 1H), 3.82 (s, 3H). **$^{13}$C NMR** (101 MHz, DMSO) δ 168.5, 152.8, 138.3, 137.2, 132.3, 132.0, 131.9, 131.6, 129.5, 128.9, 126.7, 124.3, 112.8, 56.5. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{12}NO_2S^+$ 258.0589; Found 258.0593.



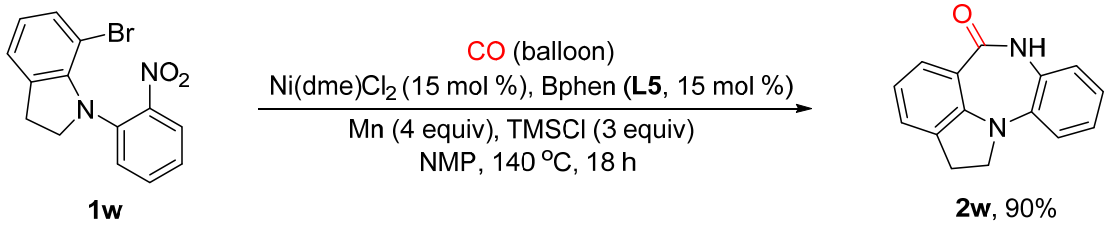

**8-Methoxydibenzo[b,f][1,4]thiazepin-11(10H)-one (2u).**

Following the general procedure B, the title compound was prepared from the title compound was prepared from **1u** (1 equiv, 0.25 mmol, 85 mg), $Ni(dme)Cl_2$ (0.25 equiv, 0.0625 mmol, 14 mg), and Bphen (0.25 equiv, 0.0625 mmol, 21 mg) at 150 °C using PE/EtOAc (10:1) as an eluent to afford the title compound as a white amorphous solid (39 mg, 60%). **$^1$H NMR** (400 MHz, DMSO) δ 10.51 (s, 1H), 7.67 (dd, *J* = 7.0, 2.2 Hz, 1H), 7.53 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.50 – 7.42 (m, 2H), 7.17 – 7.09 (m, 2H), 6.94 (dd, *J* = 8.7, 2.9 Hz, 1H), 3.73 (s, 3H). **$^{13}$C NMR** (101 MHz, DMSO) δ 168.7, 156.9, 138.4, 136.7, 133.3, 132.3, 132.0, 131.7, 131.0, 129.5, 124.8, 117.1, 116.4, 56.1. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{12}NO_2S^+$ 258.0589; Found 258.0591.



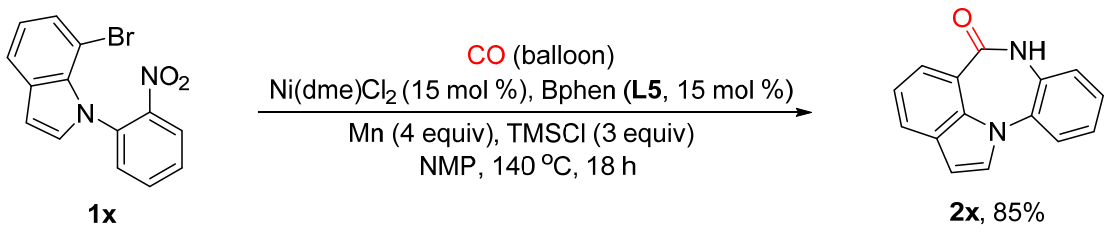

**5-Methyl-5,10-dihydro-11H-dibenzo[b,e][1,4]diazepin-11-one (2v).**

Following the general procedure B, the title compound was prepared from **1v** (1 equiv, 0.25 mmol, 77 mg), $Ni(dme)Cl_2$ (0.3 equiv, 0.0750 mmol, 17 mg), and Bphen (0.3 equiv, 0.0750 mmol, 25 mg) at 160 °C using PE/EtOAc (10:1) as an eluent to afford the title compound as a yellow amorphous solid (37 mg, 65%). **$^1$H NMR** (400 MHz, DMSO) δ 10.21 (s, 1H), 7.63 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.50 – 7.46 (m, 1H), 7.21 – 7.15 (m, 2H), 7.13 – 7.07 (m, 2H), 7.07 – 7.01 (m, 2H), 3.26 (s, 3H). **$^{13}$C NMR** (101 MHz, DMSO) δ 168.8, 153.4, 144.9, 133.2, 132.8, 131.4, 127.4, 125.1, 124.3, 123.1, 121.8, 119.6, 118.0, 38.1. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{13}N_2O^+$ 225.1028; Found 225.1027.




**11,12-Dihydrobenzo[2,3][1,4]diazepino[6,7,1-hi]indol-4(5H)-one (2w).**

Following the general procedure B, **1w** (1 equiv, 0.25 mmol, 80 mg) using PE/EtOAc (8:1) as an eluent to afford the title compound as a yellow amorphous solid (53 mg, 90%). **$^1$H NMR** (400 MHz, DMSO) δ 9.42 (s, 1H), 7.58 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.22 (dd, *J* = 7.1, 1.3 Hz, 1H), 7.00 – 6.91 (m, 2H), 6.91 – 6.84 (m, 2H), 6.75 – 6.68 (m, 1H), 3.80 (t, *J* = 8.6 Hz, 2H), 3.04 (t, *J* = 8.5 Hz, 2H). **$^{13}$C NMR** (101 MHz, DMSO) δ 167.3, 151.1, 138.2, 132.1, 130.4, 129.1, 125.0, 123.0, 122.2, 120.0, 116.4, 116.2, 116.1, 50.7, 27.13. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{13}N_2O^+$ 237.1028; Found 237.1030.

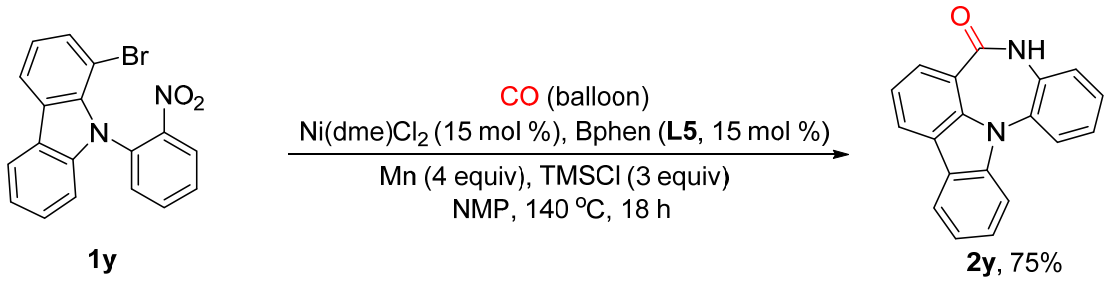



**1x** **2x**, 85%

**Benzo[2,3][1,4]diazepino[6,7,1-hi]indol-4(5H)-one (2x).**

Following the general procedure B, the title compound was prepared from **1x** (1 equiv, 0.25 mmol, 80 mg) using PE/EtOAc (8:1) as an eluent to afford the title compound as a yellow amorphous solid (50 mg, 90%). **$^1$H NMR** (400 MHz, DMSO) δ 10.01 (s, 1H), 8.12 (d, *J* = 3.5 Hz, 1H), 7.87 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.78 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.48 (dd, *J* = 7.5, 2.0 Hz, 1H), 7.26 (dd, *J* = 7.5, 2.0 Hz, 1H), 7.22 – 7.04 (m, 3H), 6.87 (d, *J* = 3.5 Hz, 1H). **$^{13}$C NMR** (101 MHz, DMSO) δ 165.9, 137.7, 131.3, 131.1, 129.5, 127.4, 126.4, 126.2, 125.4, 123.0, 122.1, 121.4, 117.6, 107.0. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{11}N_2O^+$ 235.0871; Found 235.0876.

**(i) 0.25 mmol scale:**

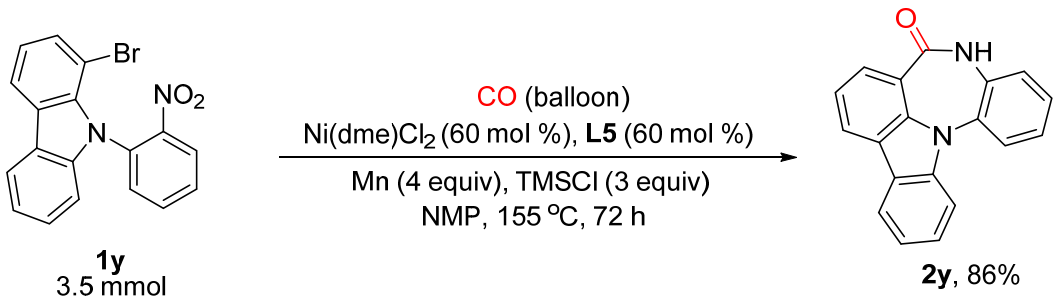



**1y** **2y**, 75%

**Benzo[2,3][1,4]diazepino[6,7,1-jk]carbazol-4(5H)-one (2y).**

Following the general procedure B, the title compound was prepared from **1y** (1 equiv, 0.25 mmol, 92 mg) using PE/EtOAc (8:1) as an eluent to afford the title compound as a purple amorphous solid (53 mg, 75%). **$^1$H NMR** (400 MHz, DMSO) δ 10.17 (s, 1H), 8.36 (dd, *J* = 7.7, 1.3 Hz, 1H), 8.29 (d, *J* = 7.5 Hz, 1H), 8.04 (dd, *J* = 7.7 Hz, 1.2 Hz, 1H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.62 – 7.54 (m, 2H), 7.45 – 7.40 (m, 2H), 7.36 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.25 (td, *J* = 7.6, 1.4 Hz, 1H), 7.17 (td, *J* = 7.7, 1.6 Hz, 1H). **$^{13}$C NMR** (101 MHz, DMSO) δ 167.2, 145.1, 139.9, 133.5, 131.2, 129.7, 127.3, 126.7, 126.0, 125.8, 125.6, 125.1, 124.3, 123.0, 122.4, 121.7, 121.0, 118.8, 115.6. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{13}N_2O^+$ 285.1028; Found 285.1026.

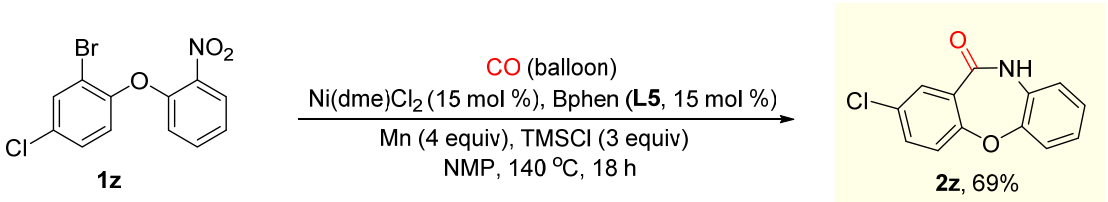
**(ii) 3.5 mmol scale:**




**Benzo[2,3][1,4]diazepino[6,7,1-jk]carbazol-4(5H)-one (2y).**

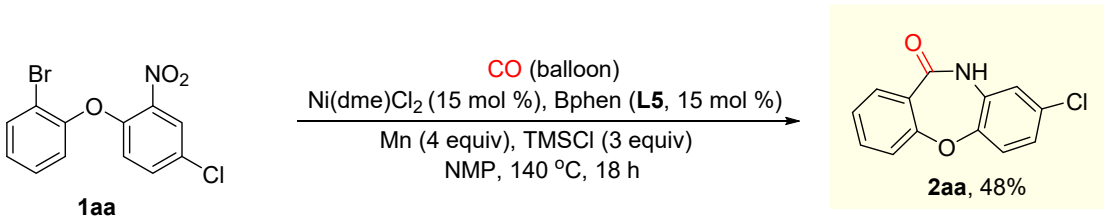
Following the general procedure B, the title compound was prepared from **1y** (1 equiv, 3.5 mmol, 1.29 g), Ni(dme)$Cl_2$ (2.1 mmol, 467 mg), Bphen (2.1 mmol, 705 mg), Mn (14 mmol, 769 mg), TMSCl (10.5 mmol, 1.33 mL), and NMP (30 mL) at 155 °C using a mixture of PE/EtOAc (10:1) as eluents to afford the amide product as a purple amorphous solid (856 mg, 86%).

## Synthesis of drug intermediates 2z, 2aa, and 2ab



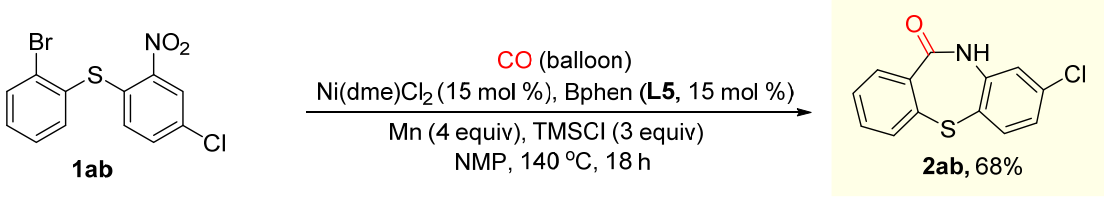

**2-Chlorodibenzo[b,f][1,4]oxazepin-11(10H)-one (2z).**

Following the general procedure B, the title compound was prepared from **1z** (1 equiv, 0.25 mmol, 83 mg) using PE/EtOAc (10:1) as an eluent to afford the title compound as a white amorphous solid (42 mg, 69%). **$^1$H NMR** (400 MHz, DMSO) δ 10.65 (s, 1H), 7.79 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.65 (td, *J* = 7.7, 1.8 Hz, 1H), 7.52 (d, *J* = 2.3 Hz, 1H), 7.41 – 7.33 (m, 2H), 7.28 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.19 (d, *J* = 8.6 Hz, 1H). **$^{13}$C NMR** (101 MHz, DMSO) δ 166.0, 158.9, 151.1, 135.1, 131.9, 130.9, 128.8, 126.5, 126.3, 125.9, 123.2, 122.0, 121.2. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_9NO_2Cl^+$ 246.0322; Found 246.0328.




**8-Chlorodibenzo[b,f][1,4]oxazepin-11(10H)-one (2aa).**

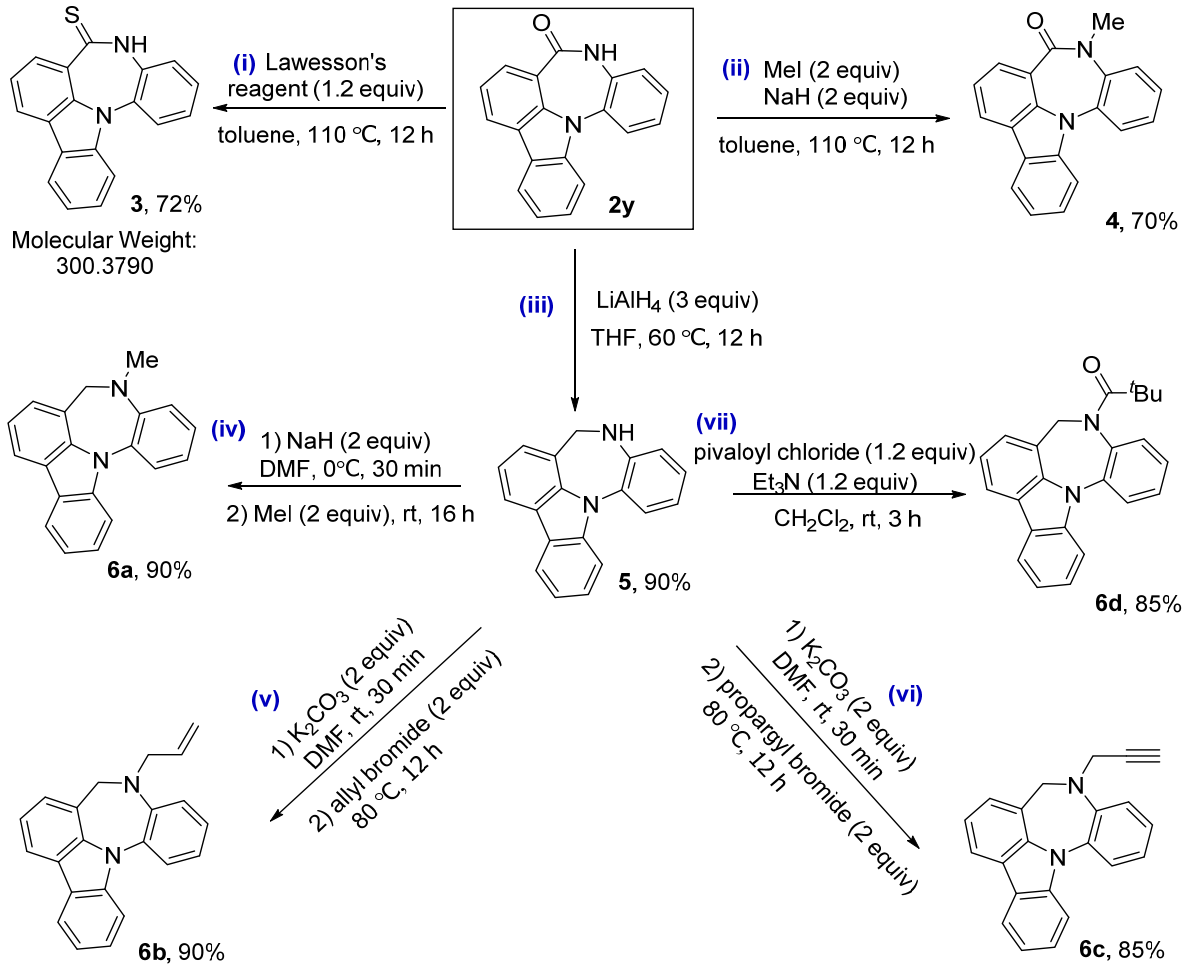
Following the general procedure B, the title compound was prepared from **1aa** (1 equiv, 0.25 mmol, 82 mg) using PE/EtOAc (10:1) as an eluent to afford the title compound as a white amorphous solid (30 mg, 48%). **$^1$H NMR** (400 MHz, DMSO) δ 10.62 (s, 1H), 7.78 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.64 (td, *J* = 7.8, 1.8 Hz, 1H), 7.51 (d, *J* = 2.4 Hz, 1H), 7.40 – 7.31 (m, 2H), 7.28 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.17 (d, *J* = 8.6 Hz, 1H). **$^{13}$C NMR** (101 MHz, DMSO) δ 165.9, 158.9, 151.2, 135.1, 131.9, 130.9, 128.8, 126.5, 126.3, 125.9, 123.2, 122.0, 121.2. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_9NO_2Cl^+$ 246.0322; Found 246.0318.




**8-Chlorodibenzo[b,f][1,4]thiazepin-11(10H)-one (2ab).**

Following the general procedure B, the title compound was prepared from **1ab** (1 equiv, 0.25 mmol, 86 mg) using PE/EtOAc (10:1) as an eluent to afford the title compound as a white amorphous solid (45 mg, 68%). **$^1$H NMR** (400 MHz, DMSO) δ 10.79 (s, 1H), 7.69 (dd, *J* = 7.2, 1.9 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.56 – 7.44 (m, 3H), 7.29 (d, *J* = 2.3 Hz, 1H), 7.22 (dd, *J* = 8.3, 2.3 Hz, 1H). **$^{13}$C NMR** (101 MHz, DMSO) δ 168.7, 141.8, 138.1, 136.1, 134.4, 132.8, 131.9, 130.9, 129.7, 128.2, 125.6, 123.1. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_9NOSCl^+$ 262.0093; Found 262.0098.

## Chemical transformations of 2y:




**(i) Thiolation of amide group: Synthesis of benzo[2,3][1,4]diazepino[6,7,1-jk]carbazole-4(5H)-thione (3).**

**3** was prepared according to the typical literature procedure.[6] To a 10 mL Schlenk tube equipped with a magnetic stir bar was charged with the **2y** (1 equiv, 0.2 mmol, 57 mg), Lawesson's reagent (1.2 equiv, 0.24 mmol, 97 mg), and toluene (3 mL) under an air atmosphere. The resulting reaction mixture was then stirred at 110 °C for 12 h. The crude reaction residue was purified by column chromatography using PE/EtOAc (12:1) as an eluent to afford the title compound **3** as yellow amorphous solid (43 mg, 72% yield). **$^1$H NMR** (400 MHz, DMSO) δ 12.23 (s, 1H), 8.33 – 8.29 (m, 2H), 8.25 (d, $J$ = 7.7 Hz, 1H), 7.90 (d, $J$ = 8.2 Hz, 1H), 7.63 – 7.53 (m, 1H), 7.45 – 7.35 (m, 4H), 7.27 – 7.20 (m, 2H). **$^{13}$C NMR** (101 MHz,

DMSO) δ 198.8, 144.7, 140.3, 136.8, 133.8, 131.4, 127.49, 127.47, 126.5, 126.4, 126.3, 125.2, 125.1, 124.7, 123.6, 122.9, 121.8, 120.3, 116.4. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{13}N_2S^+$ 301.0799; Found 301.0805.

**(ii) *N*-methylation of amide group: Synthesis of 5-methylbenzo[2,3][1,4]diazepino[6,7,1-jk]carbazol-4(5H)-one (4).**

**4** was prepared according to the typical literature procedure.[7] To a 10 mL Schlenk tube equipped with a magnetic stir bar was charged with **2y** (1 equiv, 0.2 mmol, 57 mg) and dried THF (3 mL) under an air atmosphere. The reaction mixture was cooled at 0 ºC, and NaH (60% in oil, 2 equiv 0.4 mmol, 16 mg) was then slowly added. The resulting reaction mixture was warmed to room temperature and was stirred for 30 min, after which time $CH_3I$ (2 equiv, 0.4 mmol, 25 $\mu$L) was added. The resulting mixture was further stirred at 40 °C for 8 hours. The crude reaction residue was purified by column chromatography using PE/EtOAc (20:1) to afford the title compound **4** (54 mg, 90% yield) as a white solid. **$^1$H NMR** (400 MHz, DMSO) δ 8.34 (dd, *J* = 7.6, 1.2 Hz, 1H), 8.29 (d, *J* = 7.7 Hz, 1H), 8.03 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.64 – 7.56 (m, 2H), 7.50 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.47 – 7.40 (m, 2H), 7.40 – 7.31 (m, 1H), 7.28 – 7.20 (m, 1H), 3.49 (s, 3H). **$^{13}$C NMR** (101 MHz, DMSO) δ 167.3, 146.4, 140.3, 137.2, 135.2, 129.9, 127.5, 126.91, 126.88, 126.5, 126.0, 125.6, 124.9, 123.4, 122.8, 121.9, 120.2, 119.6, 116.1, 38.5. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{15}N_2O$ 299.1184; Found 299.1191.

**(iii) Reduction of carbonyl group: Synthesis of 4,5-dihydrobenzo[2,3][1,4]diazepino[6,7,1-jk]carbazole (5).**

**5** was prepared according to the typical literature procedure.[8] An oven-dried 10 mL Teflon screw-capped Schlenk tube equipped with a Teflon-coated magnetic stir bar was sequentially charged with **2y** (1 equiv, 0.2 mmol, 57 mg), dried THF (2 mL), and $LiAlH_4$ (3 equiv, 0.6 mmol, 32 mg) under air atmosphere. The resulting reaction mixture was then heated at 60 ºC for 12 hours. The crude reaction residue was purified by column chromatography using PE/EtOAc (10:1) to afford **5** (49 mg, 90 % yield) as a white solid. **$^1$H NMR** (400 MHz, DMSO) δ 8.24 (dd, *J* = 7.8, 1.4 Hz, 1H), 8.08 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.87 (d, *J* = 8.3 Hz, 1H), 7.77 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.49 – 7.44 (m, 1H), 7.33 – 7.25 (m, 3H), 7.23 – 7.08 (m, 3H), 5.92 (t, *J* = 3.1

Hz, 1H), 4.35 (d, *J* = 3.0 Hz, 2H). **$^{13}$C NMR** (101 MHz, DMSO) δ 145.7, 139.5, 138.3, 131.7, 126.4, 125.8, 125.7, 125.1, 124.6, 123.9, 123.8, 123.4, 122.5, 121.2, 121.0, 120.2, 118.7, 112.7, 52.5. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{15}N_2^+$ 271.1235; Found 271.1236.

**(iv) *N*-methylation of amine group: Synthesis of 5-methyl-4,5-dihydrobenzo[2,3][1,4]diazepino[6,7,1-jk]carbazole (6a).**

**6a** was prepared according to the typical literature procedure.[9] To a 10 mL Schlenk tube equipped with a magnetic stir bar was charged with **5** (1 equiv, 0.2 mmol, 54 mg) and dried DMF (3 mL) under an air atmosphere. The reaction mixture was cooled to 0 ºC, and NaH (60% in oil, 2 equiv 0.4 mmol, 16 mg) was then slowly added. The reaction mixture was stirred at room temperature for 30 min. At this point, $CH_3I$ (2 equiv, 0.4 mmol, 25 $\mu$L) was added, and the resulting mixture was stirred at room temperature for 16 hours. The crude reaction residue was purified by column chromatography using PE/EtOAc (10:1) to afford the title compound **6a** (51 mg, 90 % yield) as a white solid. **$^1$H NMR** (400 MHz, DMSO) δ 8.27 – 8.20 (m, 1H), 8.11 – 8.03 (m, 1H), 7.84 – 7.77 (m, 1H), 7.72 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.52 – 7.39 (m, 2H), 7.36 – 7.25 (m, 2H), 7.25 – 7.15 (m, 3H), 4.27 (s, 2H), 3.00 (s, 3H). **$^{13}$C NMR** (101 MHz, DMSO) δ 147.4, 139.6, 138.2, 132.9, 126.5, 126.3, 125.1, 124.7, 124.4, 123.8, 123.7, 123.6, 121.3, 121.1, 120.4, 120.0, 118.9, 112.8, 60.7, 42.7. **HRMS** (ESI) m:z: $[M+H]^+$ Calcd for $C_{20}H_{17}N_2^+$ 285.1329; Found 285.1387.

**(v) *N*-allylation of amine group: Synthesis of 5-allyl-4,5-dihydrobenzo[2,3][1,4]diazepino[6,7,1-jk]carbazole (6b).**

**6b** was prepared according to the typical literature procedure.[10] To a 10 mL Schlenk tube equipped with a magnetic stir bar was charged with **5** (1 equiv, 0.2 mmol, 54 mg), $K_2CO_3$ (2 equiv, 0.4 mmol, 56 mg), and MeCN (3 mL) under an argon atmosphere. The reaction mixture was stirred for 30 min at room temperature, and 3-bromopropene (2 equiv, 0.4 mmol, 35$\mu$L) was then added. The resulting reaction mixture was stirred at 80 ℃ for 12 h. The crude reaction residue was purified by column chromatography using PE/EtOAc (20:1) to afford the desired product **6b** (56 mg, 90% yield) as a white solid. **$^1$H NMR** (400 MHz, DMSO) δ 8.24 (dd, *J* = 7.8, 1.3 Hz, 1H), 8.07 (dd, *J* = 6.5, 2.5 Hz, 1H), 7.82 (d, *J* = 8.3 Hz, 1H), 7.74 (dd, *J* = 7.9, 1.7

Hz, 1H), 7.51 – 7.45 (m, 1H), 7.45 – 7.38 (m, 1H), 7.35 – 7.27 (m, 2H), 7.27 – 7.21 (m, 1H), 7.21 – 7.12 (m, 2H), 5.87 – 5.77 (m, 1H), 5.23 (dd, *J* = 17.3, 1.9 Hz, 1H), 5.14 (dd, *J* = 10.3, 1.8 Hz, 1H), 4.28 (s, 2H), 3.93 (d, *J* = 5.9 Hz, 2H). **$^{13}$C NMR** (101 MHz, DMSO) δ 139.5, 138.4, 136.1, 133.7, 131.6, 129.1, 126.5, 126.3, 125.0, 124.8, 124.2, 123.9, 123.7, 122.1, 121.4, 121.1, 120.5, 118.9, 118.4, 112.8, 57.7, 56.4. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{19}N_2^+$ 311.1548; Found 311.1550.

**(vi) *N*-propargylation of amine: Synthesis of 5-(prop-2-yn-1-yl)-4,5-dihydrobenzo[2,3][1,4]diazepino[6,7,1-jk]carbazole (6c).**

**6c** was prepared according to the typical literature procedure.[10] To a 10 mL Schlenk tube equipped with a magnetic stir bar was charged with the **5** (1 equiv, 0.2 mmol, 54 mg), $K_2CO_3$ (2 equiv, 0.4 mmol, 56 mg), MeCN (3 mL) under an argon atmosphere. The reaction mixture was stirred for 30 min at room temperature, and propargyl bromide (2 equiv, 0.4 mmol, 32 $\mu$L) was then added. The resulting reaction mixture was stirred at 80 °C for 12 h. The crude reaction residue was purified by column chromatography using PE/EtOAc (20:1) to afford the desired product **6c** (52 mg, 85% yield) as a white solid. **$^1$H NMR** (400 MHz, DMSO) δ 8.24 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.08 (dd, *J* = 7.3, 1.6 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.75 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.60 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.50 – 7.45 (m, 1H), 7.36 – 7.28 (m, 2H), 7.28 – 7.17 (m, 3H), 4.39 (s, 2H), 4.16 (d, *J* = 2.5 Hz, 2H), 3.34 (s, 1H). **$^{13}$C NMR** (101 MHz, DMSO) δ 145.6, 139.5, 138.2, 133.2, 126.6, 126.2, 125.2, 124.7, 124.4, 124.1, 124.0, 123.7, 121.4, 121.2, 121.1, 120.5, 119.0, 112.8, 81.1, 76.4, 57.9, 43.5. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{17}N_2^+$ 309.1392; Found 309.1397.

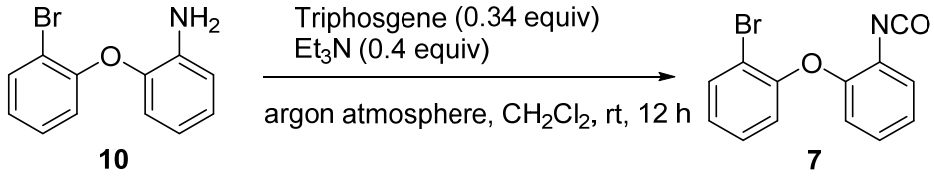
**(vii) *N*-acylation of amine: Synthesis of 1-(benzo[2,3][1,4]diazepino[6,7,1-jk]carbazol-5(4H)-yl)-2,2-dimethylpropan-1-one (6d).**

An oven-dried 10 mL Schlenk tube equipped with a Teflon-coated magnetic stir bar was sequentially charged with **5** (1 equiv, 0.2 mmol, 54 mg), $CH_2Cl_2$ (3 mL), $Et_3N$ (1.2 equiv, 0.24 mmol, 33 $\mu$L), and pivaloyl chloride (1.2 equiv, 0.24 mmol, 30 $\mu$L) under air atmosphere. The resulting reaction mixture was stirred at room temperature for 3 h. The crude reaction residue was purified by silica gel column chromatography PE/EtOAc (20:1) to afford the pure product

**6d** as a purple solid (63 mg, 90%). **$^1$H NMR** (400 MHz, DMSO) δ 8.25 (d, *J* = 7.7 Hz, 1H), 8.10 (d, *J* = 7.6 Hz, 1H), 7.94 – 7.76 (m, 2H), 7.71 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.57 (td, *J* = 7.8, 1.6 Hz, 1H), 7.53 – 7.49 (m, 1H), 7.44 (td, *J* = 7.6, 1.4 Hz, 1H), 7.37 – 7.33 (m, 2H), 7.25 (t, *J* = 7.5 Hz, 1H), 5.63 (d, *J* = 15.6 Hz, 1H), 4.28 (d, *J* = 15.5 Hz, 1H), 0.89 (s, 9H). **$^{13}$C NMR** (101 MHz, DMSO) δ 175.7, 139.0, 138.0, 137.0, 131.8, 129.9, 127.0, 126.6, 126.5, 125.2, 125.1, 124.6, 123.8, 121.9, 121.3, 121.0, 119.4, 112.5, 53.5, 28.75. (The *α*-carbon signal of $^t$Bu group was not observed due to overlapping with the residual carbon signals of DMSO-$d_6$.) **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{23}N_2O^+$ 355.1810; Found 355.1810.

## Mechanistic study of Ni-catalyzed intramolecular aminocarbonylation

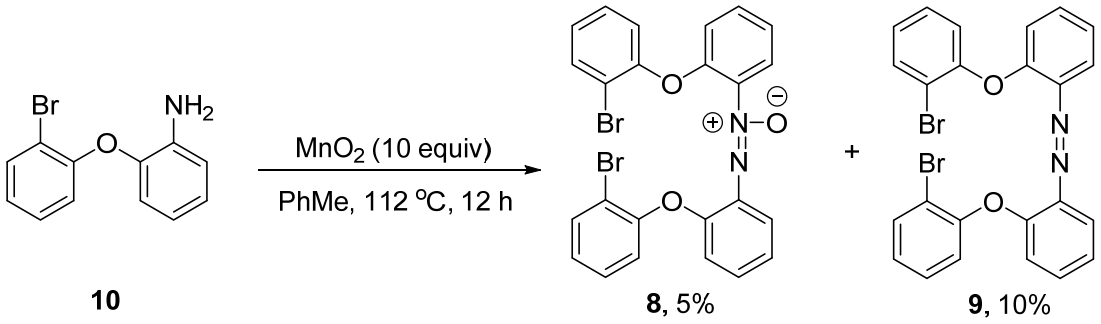
**Synthesis of 1-bromo-2-(2-isocyanatophenoxy)benzene (7):**




**10** **7**

**7** was prepared according to the typical literature procedure.[11] To a 10 mL Schlenk tube equipped with a magnetic stir bar was charged with triphosgene (0.34 equiv, 0.085 mmol, 26 mg) and $CH_2Cl_2$ (1 mL) under an argon atmosphere. Aniline **10** (1 equiv, 0.25 mmol, 66 mg) in $CH_2Cl_2$ (1 mL) was then slowly added into the reaction mixture, followed by the dropwise addition of triethylamine (0.4 equiv, 0.1 mmol, 14 $\mu$L) in $CH_2Cl_2$ (1 mL). The resulting mixture was further stirred for 2 h. At this point, the reaction mixture was concentrated in vacuo with the aid of a rotary evaporator and further dried in vacuo to obtain the crude **7** as a white amorphous solid. The product was unstable and it was subjected to the reaction without further purification.

**Synthesis of 1,2-bis(2-(2-bromophenoxy)phenyl)diazene 1-oxide (8) and 1,2-bis(2-(2-bromophenoxy)phenyl)diazene (9):**




**10** **8**, 5% **9**, 10%

The title compounds were prepared according to the literature procedure.[12] In an oven-dried 250 mL pressure round-bottom flask equipped with a Teflon-coated magnetic stir bar was charged with aniline **10** (1 equiv, 10 mmol, 2.64 g) and toluene (50 mL) under an air atmosphere. Activated $MnO_2$ (10 equiv, 100 mmol, 8.69 g) was then added, and the resulting mixture was heated at 112 °C for 12 h. At this point, **10** was consumed as determined by TLC. The reaction mixture was filtered through a pad of Celite and washed with toluene. The mixture was further extracted with EtOAc (3 x 60 mL). The combined organic fraction was washed with saturated NaCl (aq), dried with anhydrous $Na_2SO_4$, filtered, and concentrated in vacuo with the aid of rotary evaporator. The residue was purified by column chromatography using PE/EtOAc (20:1) as an eluent to afford **8** and **9**.

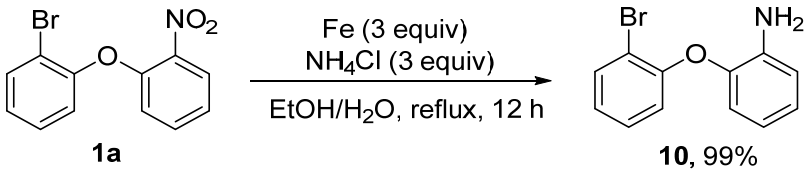
**Characterization of 1,2-Bis(2-(2-bromophenoxy)phenyl)diazene 1-oxide (8).**

**8** was obtained as an orange amorphous solid (270 mg, 5% yield). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.64 – 7.60 (m, 2H), 7.44 – 7.38 (m, 2H), 7.26 – 7.21 (m, 1H), 7.19 – 7.11 (m, 2H), 7.11 – 7.06 (m, 2H), 7.05 – 7.00 (m, 1H), 6.98 – 6.92 (m, 3H), 6.88 (dd, *J* = 8.1, 1.5 Hz, 1H), 6.84 (dd, *J* = 8.2, 1.5 Hz, 1H), 6.67 (dd, *J* = 8.1, 1.0 Hz, 1H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 155.6, 154.3, 152.7, 146.7, 145.5, 143.8, 133.8, 133.6, 132.5, 128.8, 128.6, 125.5, 124.6, 124.3, 123.5, 121.0, 120.8, 119.8, 119.3, 117.8, 117.6, 115.0, 113.5. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{17}N_2O_3Br_2^+$ 538.9606; Found 538.9597.

**Characterization of 1,2-Bis(2-(2-bromophenoxy)phenyl)diazene (9):**

**9** was obtained as an as a red amorphous solid (524 mg, 10% yield). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 7.9, 1.7 Hz, 2H), 7.48 – 7.31 (m, 4H), 7.23 – 7.06 (m, 6H), 6.97 – 6.93 (m, 2H), 6.83 (dd, *J* = 8.2, 1.5 Hz, 2H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 155.6, 154.3, 143.8, 133.6, 132.5, 128.6, 124.6, 124.3, 120.8, 119.3, 117.8, 113.5. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{17}N_2O_2Br_2^+$ 522.9657; Found 522.9651.

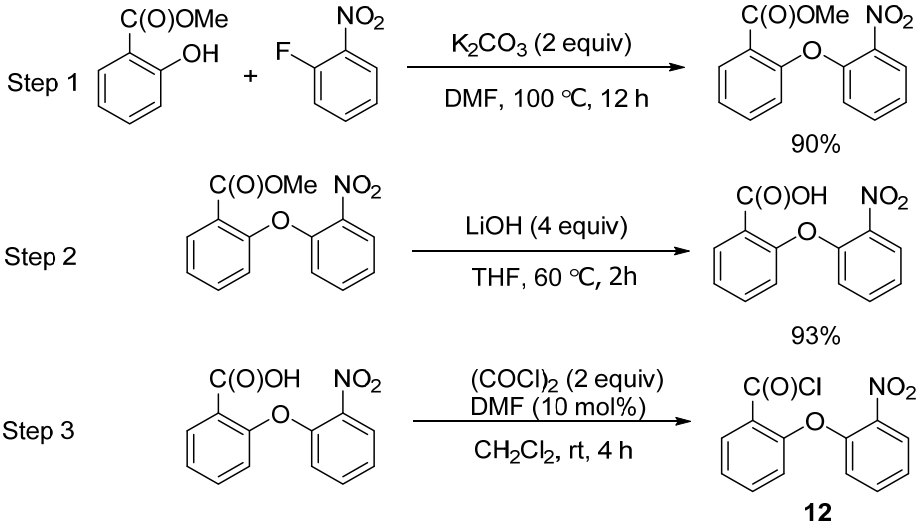
**Synthesis of 2-(2-bromophenoxy)aniline (10):**




**1a** **10**, 99%

**10** was prepared according to the typical literature procedure.[13] An oven-dried 300 mL round-bottom flask equipped with a stir bar was sequentially charged with 1-bromo-2-(2-nitrophenoxy)benzene (1 equiv, 45 mmol, 13.23 g), EtOH (50 mL), $H_2O$ (50 mL), Fe powder (3 equiv, 135 mmol, 7.56 g), and $NH_4Cl$ (3 equiv, 135 mmol, 7.22 g). The resulting reaction mixture was refluxed under air atmosphere for 12 h. At this point, the reaction was cooled down to room temperature. The crude mixture was filtered through a pad of Celite and concentrated in vacuo with the aid of rotary evaporator. The residue was further extracted with EtOAc (3×80 mL), and the combined organic fraction was washed with brine (200 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo to afford the title compound as a brown solid (12 g, 99%). **$^1$H NMR** (400 MHz, DMSO) δ 7.73 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.35 (td, *J* = 8.2, 7.7, 1.5 Hz, 1H), 7.07 (td, *J* = 7.6, 1.5 Hz, 1H), 6.98 (td, *J* = 7.6, 1.5 Hz, 1H), 6.88 (dd, *J* = 8.0, 1.7 Hz, 1H), 6.81 (dd, *J* = 8.2, 1.5 Hz, 1H), 6.74 (dd, *J* = 8.0, 1.4 Hz, 1H), 6.59 (td, *J* = 7.6, 1.7 Hz, 1H), 4.98 (s, 2H). **$^{13}$C NMR** (101 MHz, DMSO) δ 154.3, 142.0, 140.5, 133.9, 129.6, 125.7, 124.7, 120.0, 118.2, 116.9, 116.4, 112.9.

**Synthesis of 2-(2-nitrophenoxy)benzoyl chloride (12):**



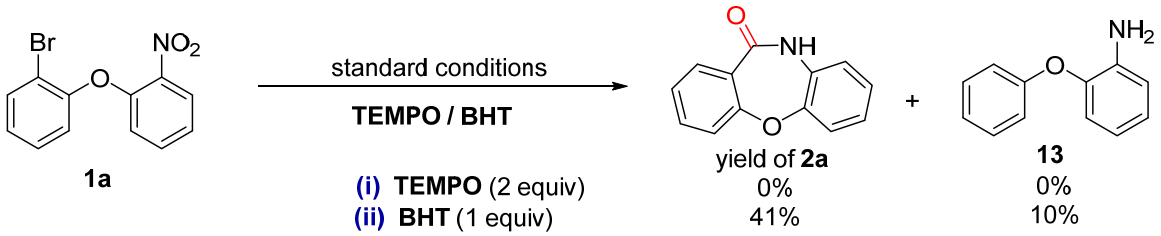
Steps **1, 2, 3** were performed according to the literature procedures.[1,14,15]

**Step 1**: The title compound were prepared according to the literature procedure.[1] Following the general procedure A, the title compound was prepared using methyl 2-hydroxybenzoate (1 equiv, 20 mmol, 2.74 mL), 1-fluoro-2-nitrobenzene (1 equiv, 20 mmol, 2.12 mL), $K_2CO_3$ (2 equiv, 40 mmol, 5.53 g), and DMF (40 mL). The crude residue was recrystallized with $CH_2Cl_2$ and petroleum ether to afford methyl 2-(2-nitrophenoxy)benzoate as a yellow solid (5.00 g, 90 %).

**Step 2:** Methyl 2-(2-nitrophenoxy)benzoate (from **step 1**, 1 equiv, 5 mmol, 1.38 g) was dissolved in THF (10 mL), and LiOH (aq, 2 M, 5 equiv, 25 mmol, 12.5 mL) was then added. The resulting mixture was stirred at 60 ℃ for 2 hours. At this point, the reaction mixture was cooled to room temperature. The reaction mixture was concentrated in vacuo and was then acidified with HCl (2 M) until ~pH 2 was obtained. The precipitate was filtered, washed with diluted NaOH (aq, ~0.1 M), and dried in vacuo to obtain 2-(2-nitrophenoxy)benzoic acid (1.2 g, 93%).

**Step 3:** An oven-dried 100 mL round-bottom flask equipped with a stir bar was sequentially charged with 2-(2-nitrophenoxy)benzoic acid (from **step 2**, 1 equiv, 2 mmol, 0.55 g), dry $CH_2Cl_2$ (10 mL), and a catalytic amount of DMF (~15 $\mu$L). The reaction mixture was cooled to 0 ℃ and stirred for 5 min. $(COCl)_2$ (2 equiv, 4 mmol, 0.34 mL) was then added dropwise into the reaction mixture, and the resulting mixture was further stirred at room temperature for 4 h. The reaction mixture was concentrated in vacuo to afford **12** quantitatively. **12** was used directly for study according to the general procedure B without further purification.

## Probing the radical mechanism using TEMPO or BHT:




The reactions were set up according to the the general procedure B, except that TEMPO (2 equiv, 0.5 mmol, 78 mg) and BHT (1 equiv, 0.25 mmol, 55 mg) were added respectively. In

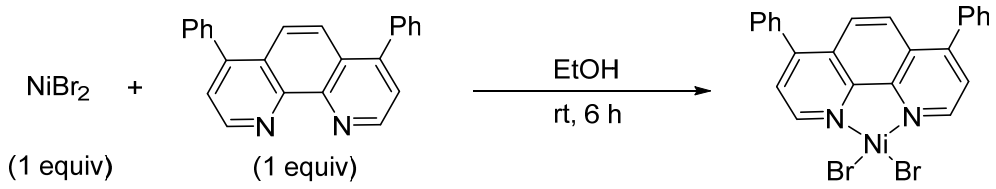
the reaction with BHT, 2-phenoxyaniline (**13**) was also isolated as the co-product (4.6 mg, 10%), the yield of **2a** decreased from 82% to 41%. In the reaction with TEMPO, the reaction was quenched, product **2a** and co-product **13** were not detected.

**Characterization of 2-phenoxyaniline (13):**

**$^1$H NMR** (400 MHz, DMSO) δ 7.33 (t, *J* = 7.7 Hz, 2H), 7.05 (t, *J* = 7.4 Hz, 1H), 6.96 (d, *J* = 7.9 Hz, 3H), 6.91 (d, *J* = 7.8 Hz, 1H), 6.84 (d, *J* = 7.9 Hz, 1H), 6.60 (t, *J* = 7.6 Hz, 1H), 4.94 (s, 2H). **$^{13}$C NMR** (101 MHz, DMSO) δ 158.1, 142.0, 141.1, 130.1, 125.6, 122.7, 121.0, 117.1, 117.0, 116.4. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{12}NO^+$ 186.0919; Found 186.0925.

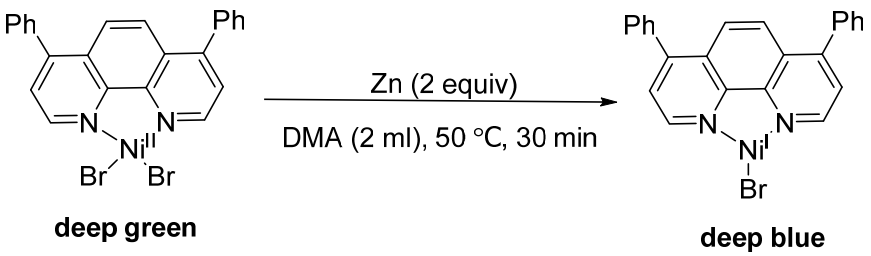
**Reactivity study of (L5)Ni$^I$Br (14):**

**(i) Synthesis of (L5)Ni$^{II}$Br$_2$:**



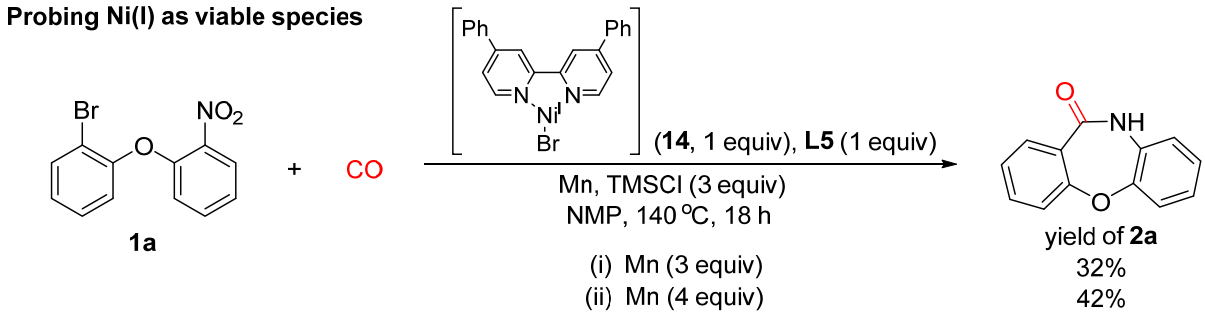

The title compound was prepared according to the literature procedure.[16] An oven-dried 200 mL round-bottom flask equipped with a stir bar was charged with Bphen (**L5**, 1 equiv, 20 mmol, 6.65 g) and EtOH (20 mL). A solution of $NiBr_2$ (1 equiv, 20 mmol, 4.37 g) in EtOH (30 mL) was then added, and the resulting mixture was stirred at room temperature for 6 h. The pale green precipitate was filtered, washed with EtOH (3 × 30 mL), and dried in vacuo to afford **(L5)NiBr$_2$** as a pale green solid (8.8 g, 80%). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{17}Br_2N_2Ni^+$ 548.9112; Found 548.9113.

**(ii) *In-situ* reduction of (L5)Ni$^{II}$Br$_2$ to (L5)Ni$^I$Br (14):**



(**L5**)$Ni^{I}Br$ was formed *in situ* according to the analogous procedure.[17] An oven-dried 10 mL Schlenk tube equipped with a stir bar was charged with (**L5**)$NiBr_2$ (from **step (i)**, 1 equiv, 0.2 mmol, 110 mg), Zn (2 equiv, 0.4 mmol, 26 mg) and DMA (2 mL) under argon atmosphere. The resulting mixture was stirred at 50 °C for 30 min, at which time the color of the reaction mixture changed from deep green to deep blue. The deep blue color indicated the conversion of (**L5**)$Ni^{II}Br_2$ to (**L5**)$Ni^{I}Br$ (**14**), in line with the color change of analogous Ni complexes.[17] The tube containing the *in-situ* formed **14** was used directly for the reaction study according to the general procedure B.

**(iii) Probing (L5)$Ni^{I}Br$ (14) as viable species:**




The *in situ* formed $Ni^{I}$(**L5**)Br (**14**, from **step (ii)**) was used directly for reactivity study based on the general procedure B. In the presence of Mn (3 equiv, 0.75 mmol, 41 mg), the yield of **2a** was 32%. In the presence of Mn (4 equiv, 1.00 mmol, 55 mg), the yield of **2a** was 42%.

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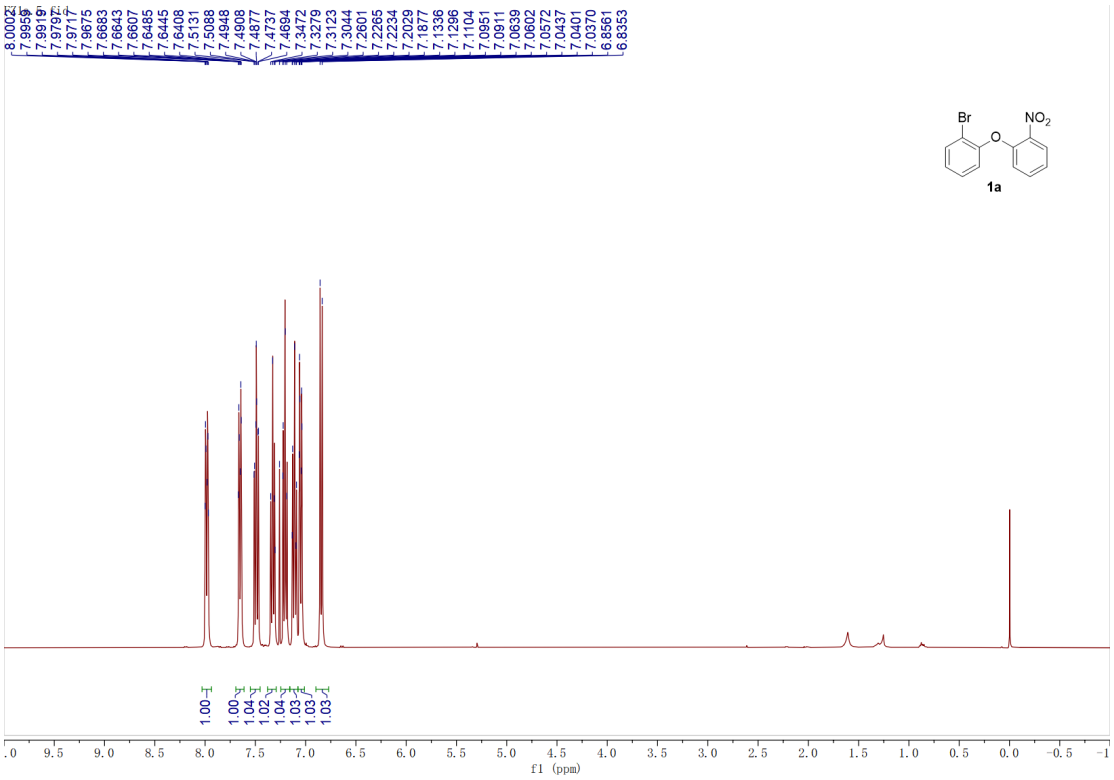
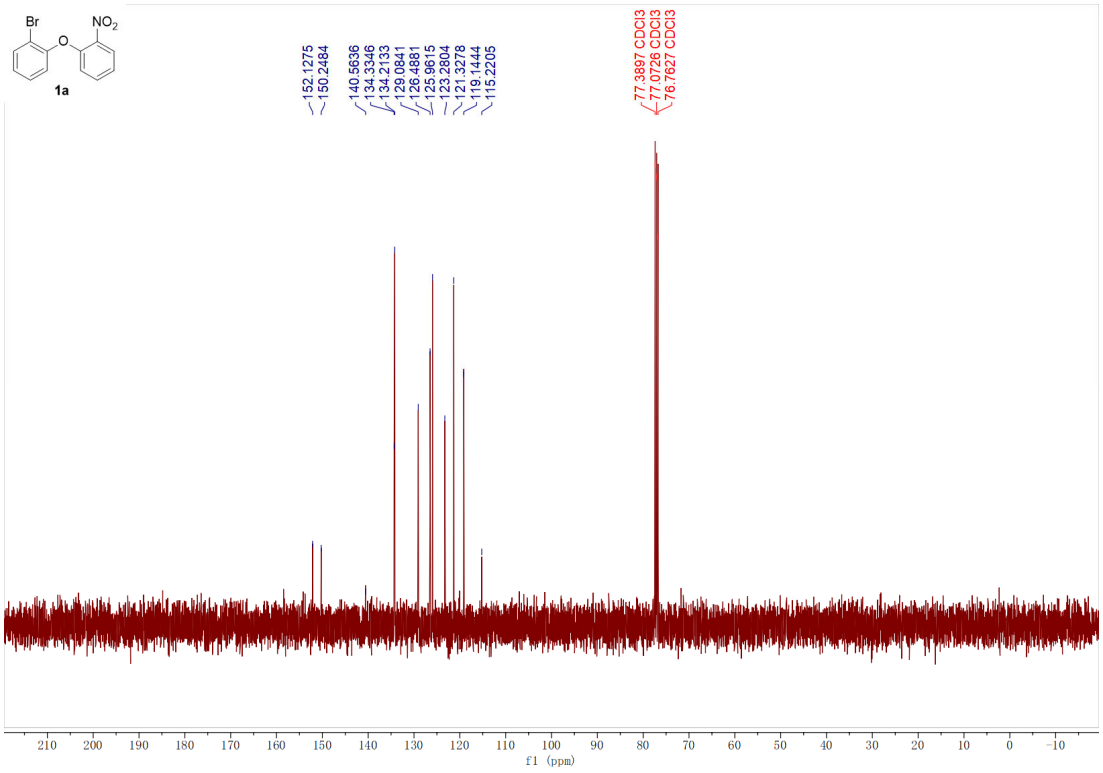
## NMR spectra




$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **1a**

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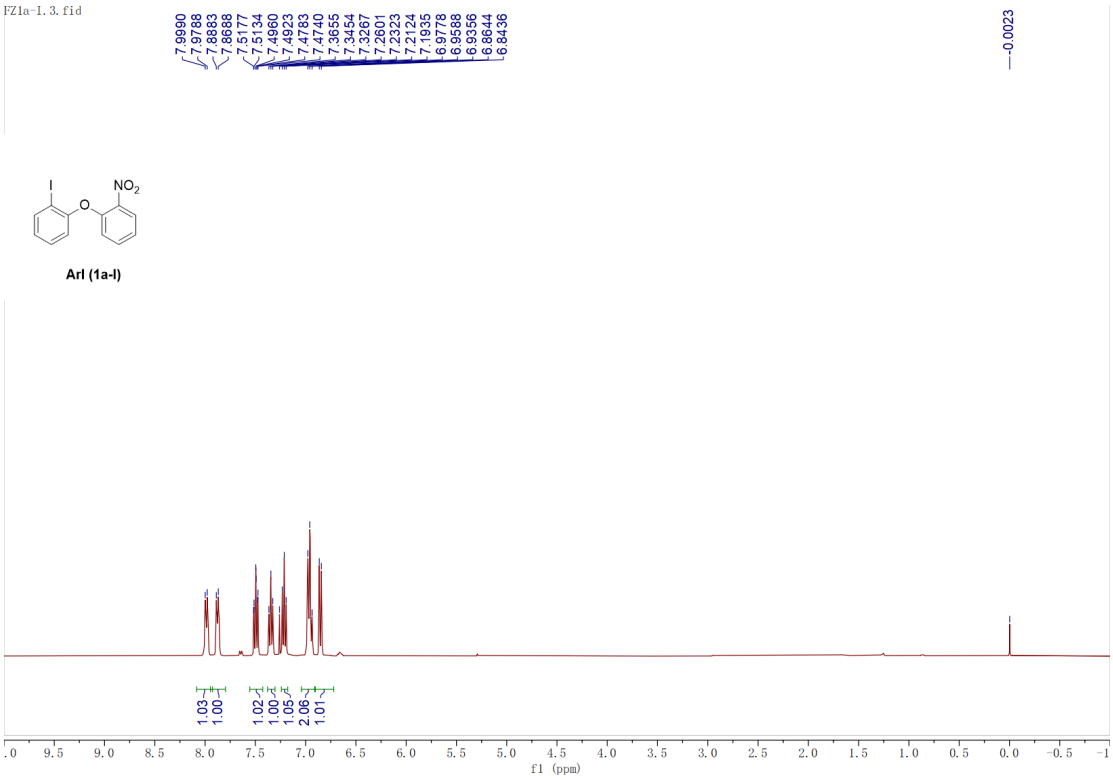


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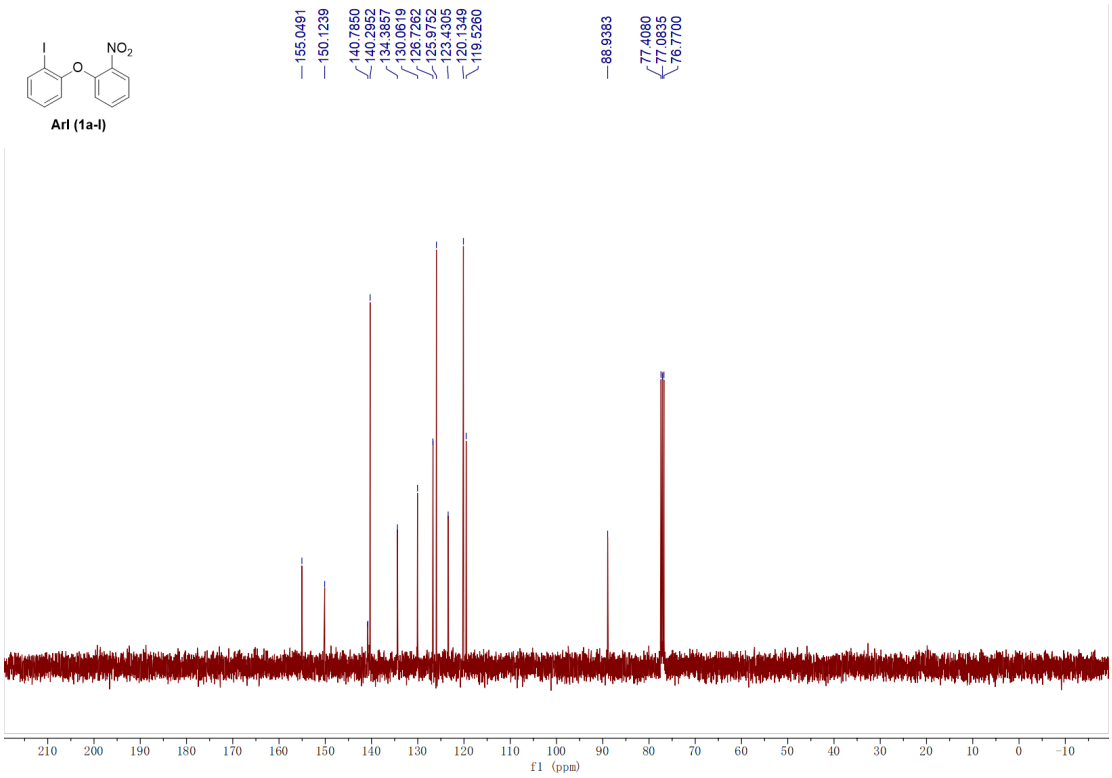


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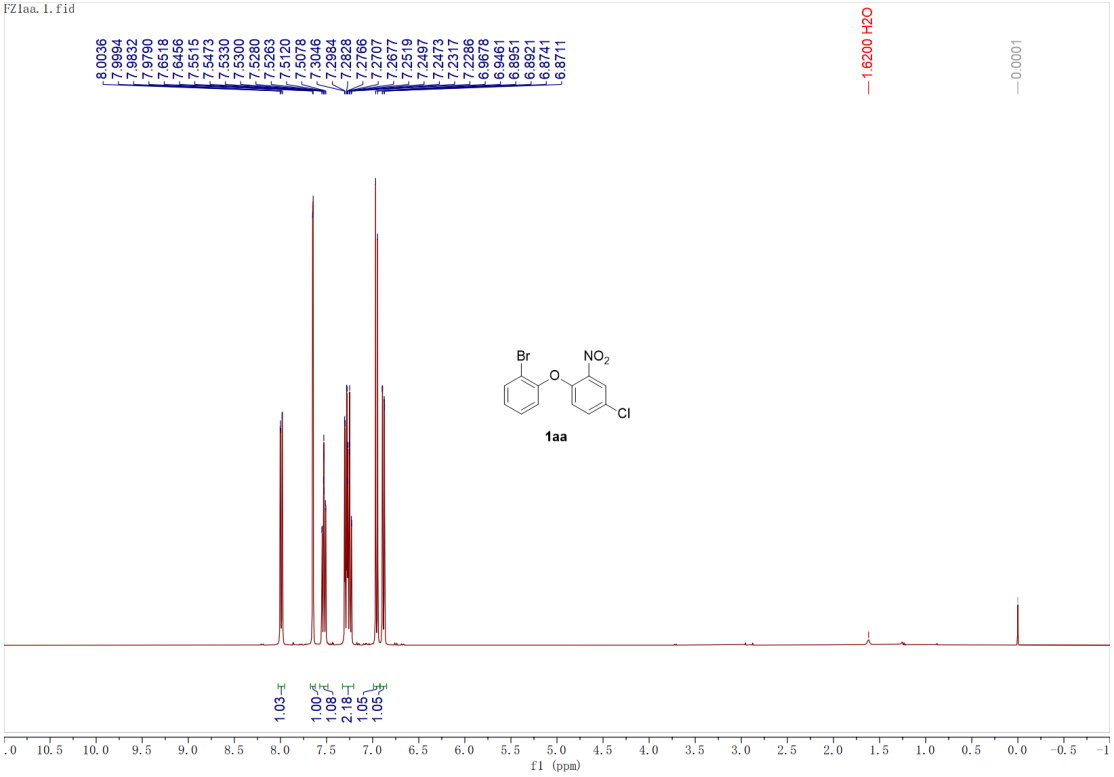
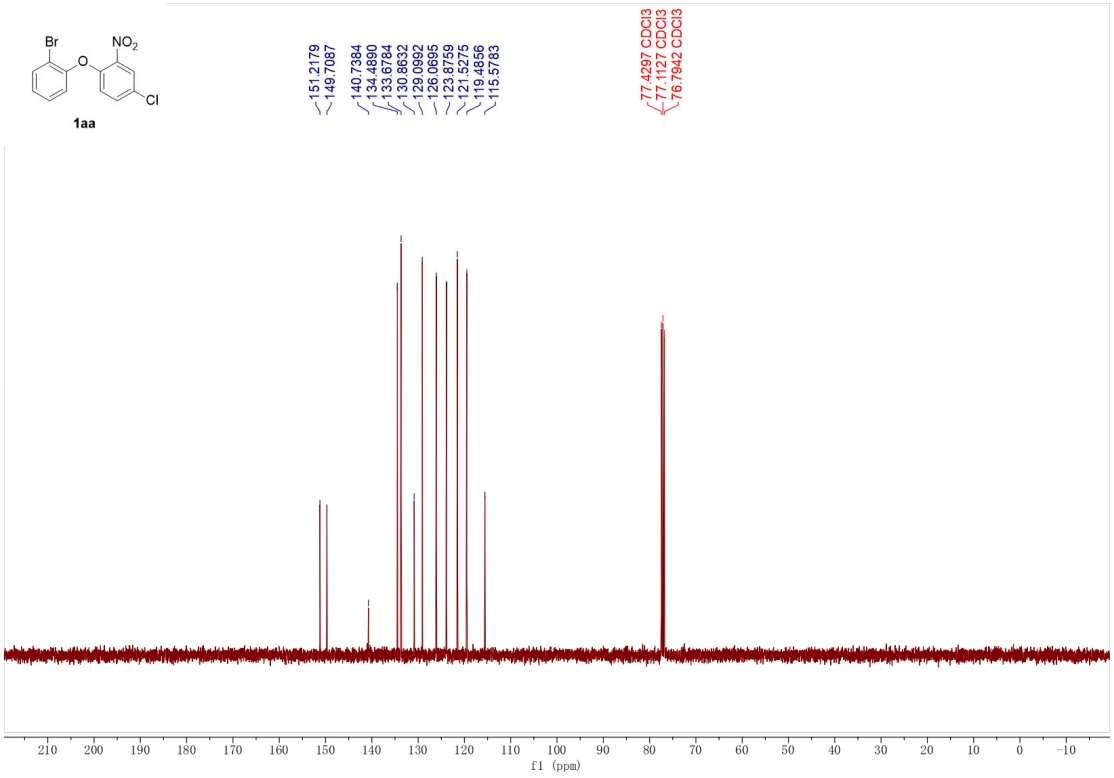
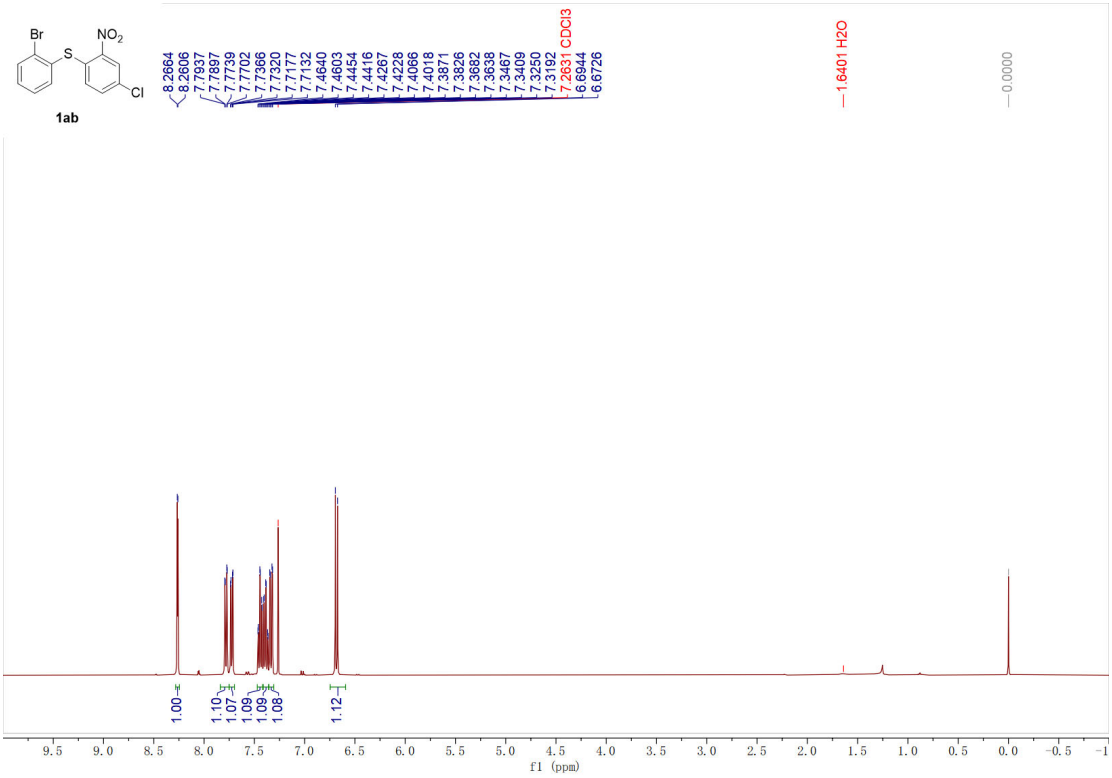


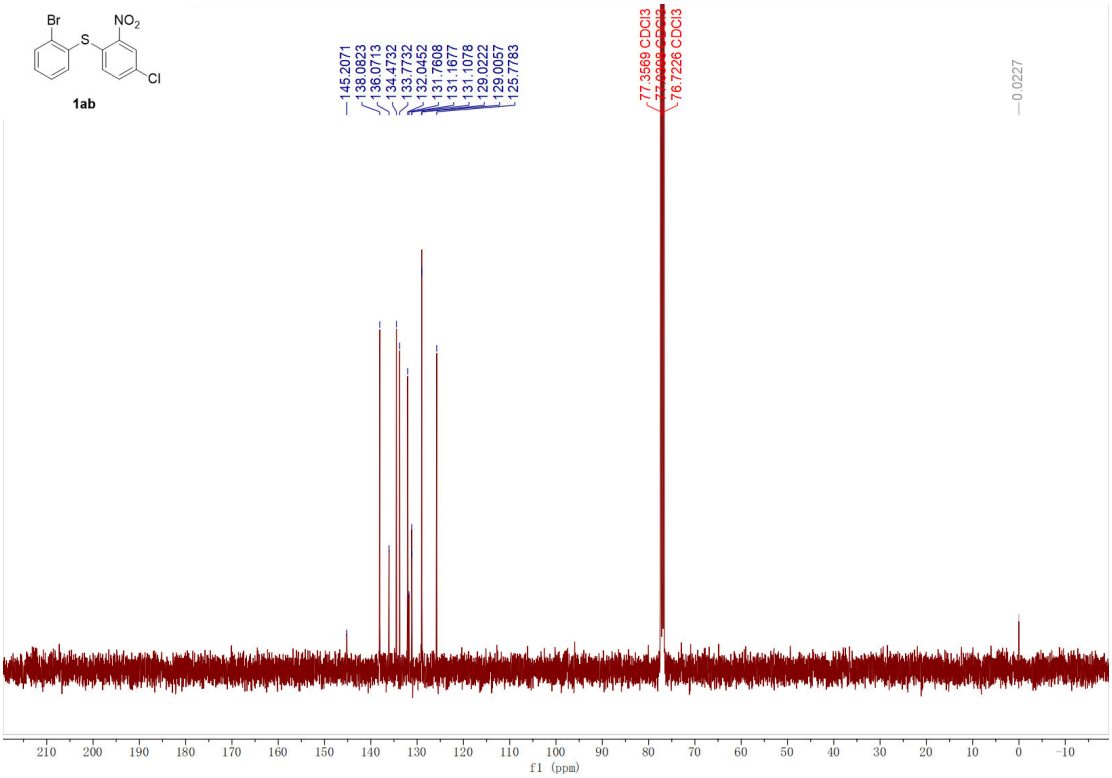

$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **1aa**




$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **1aa**




$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **1ab**



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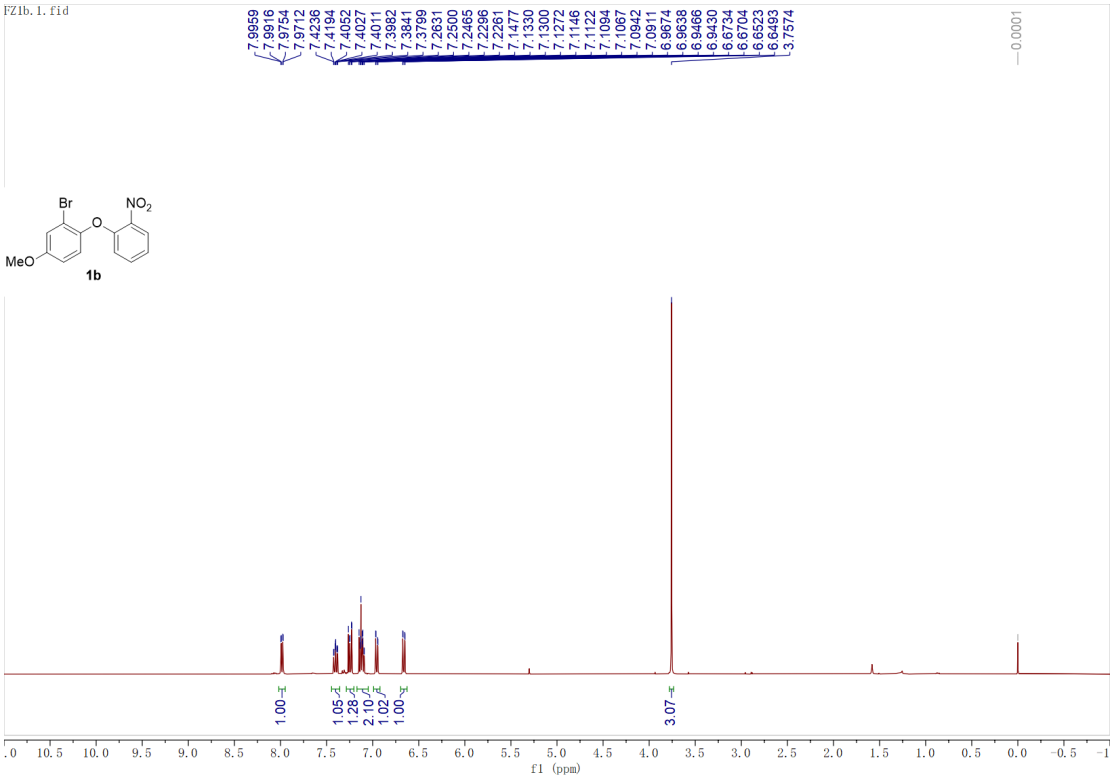
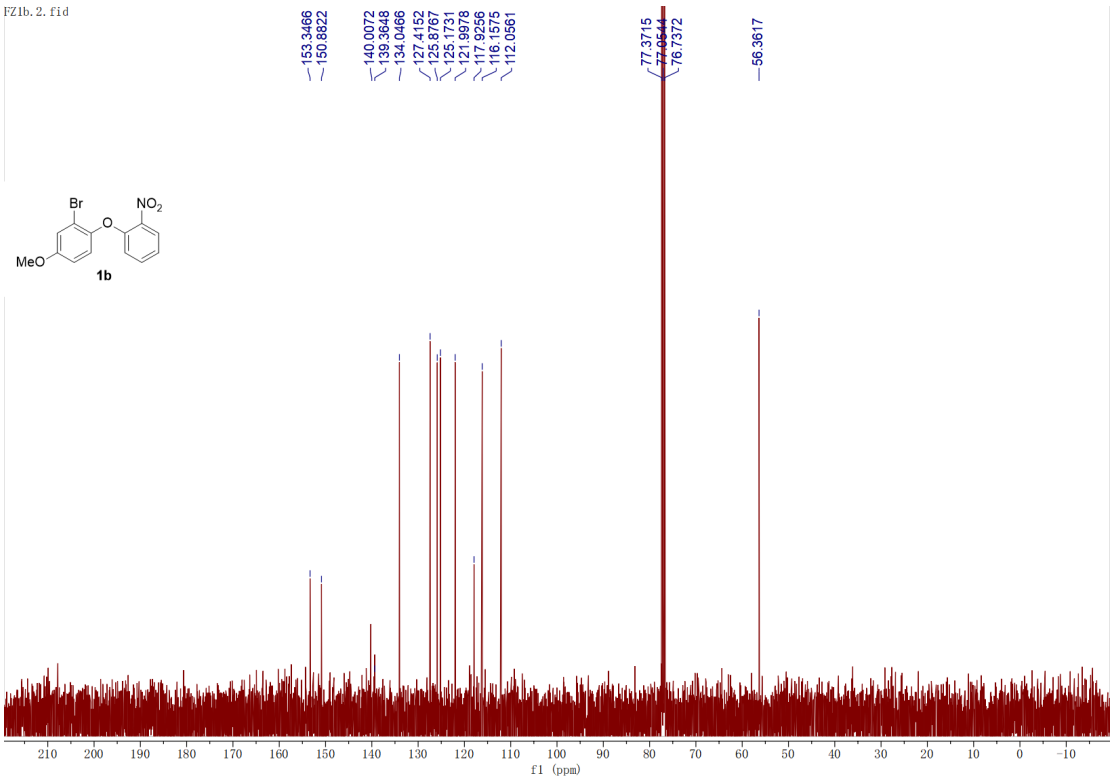



$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **1b**

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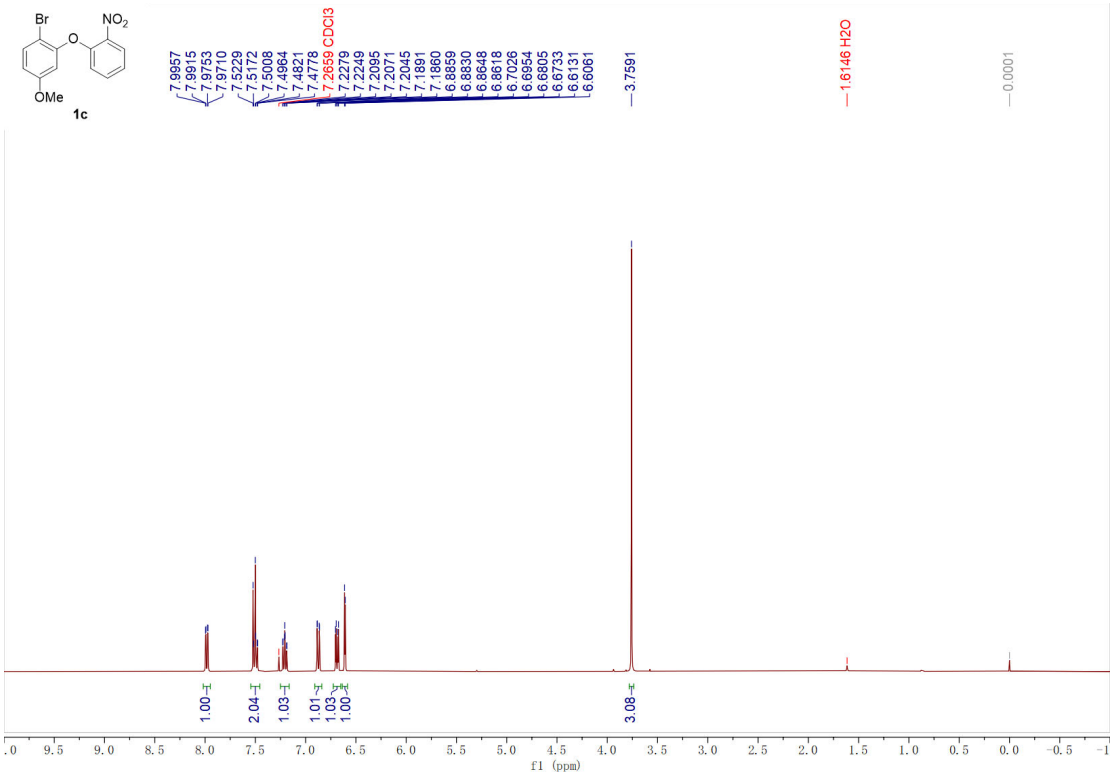


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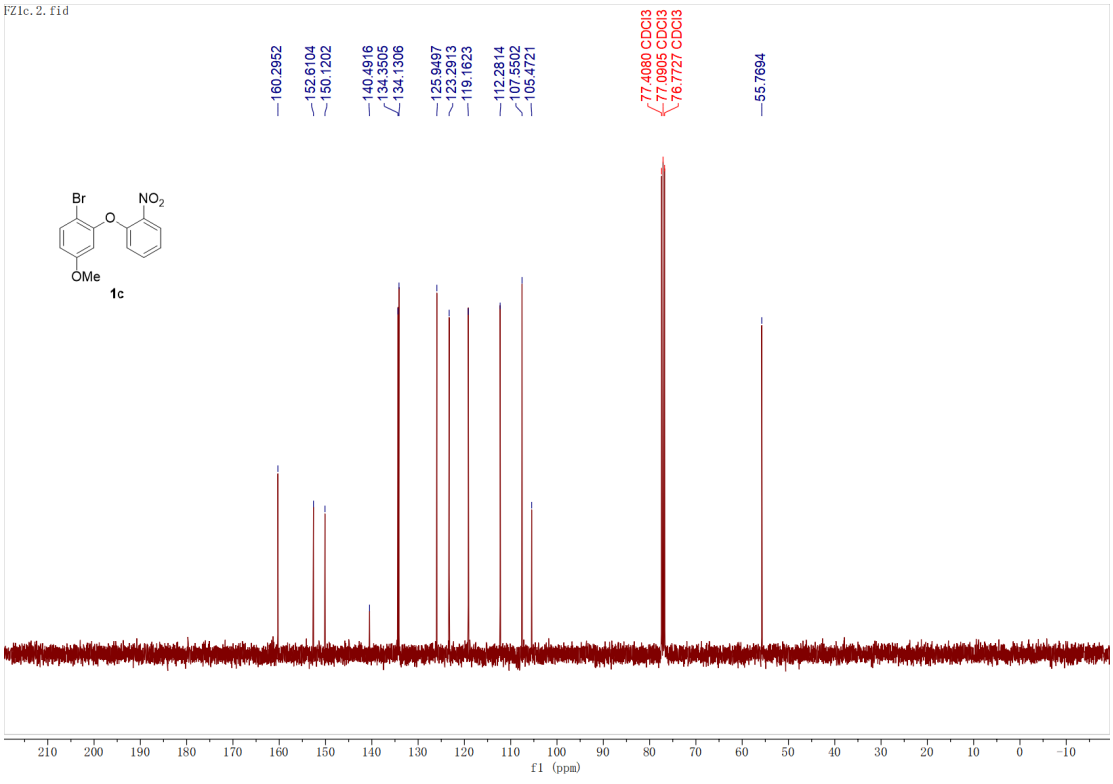


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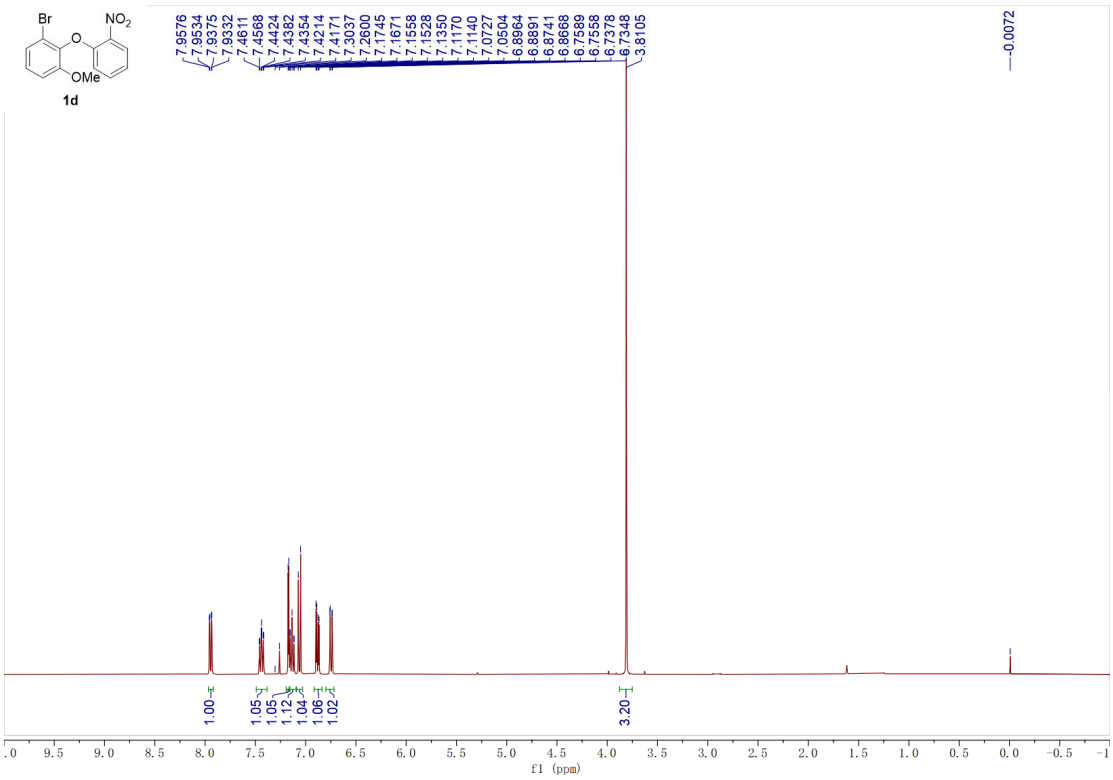


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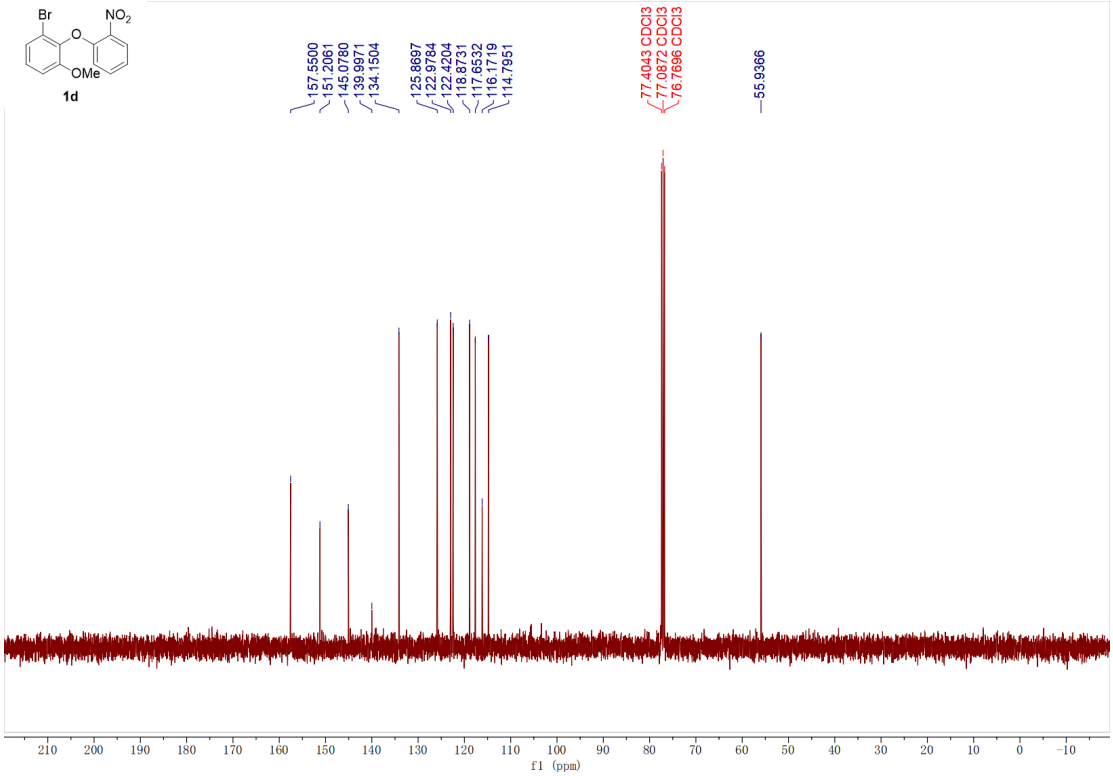


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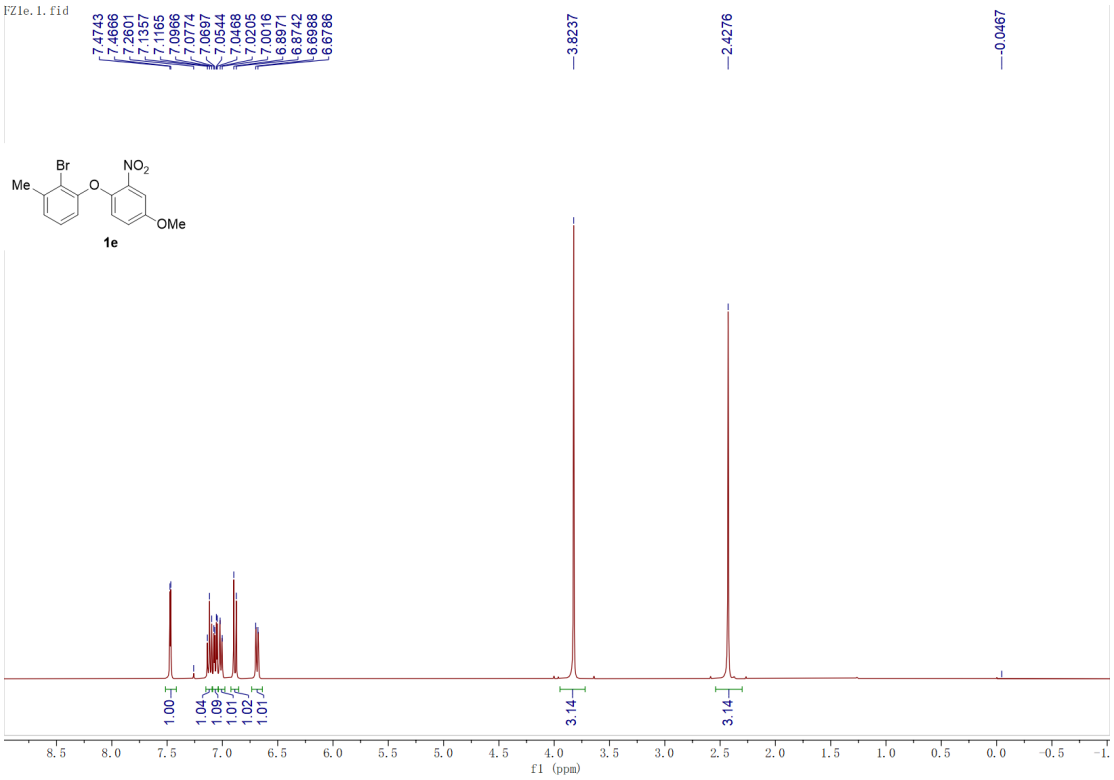


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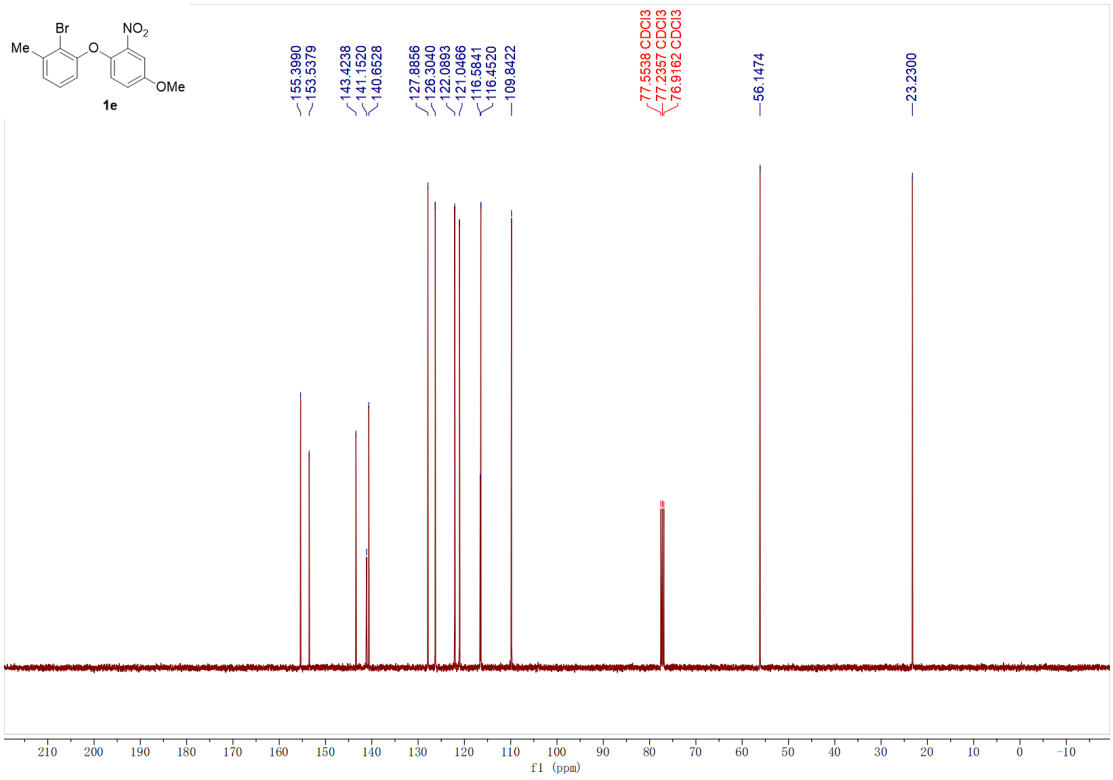


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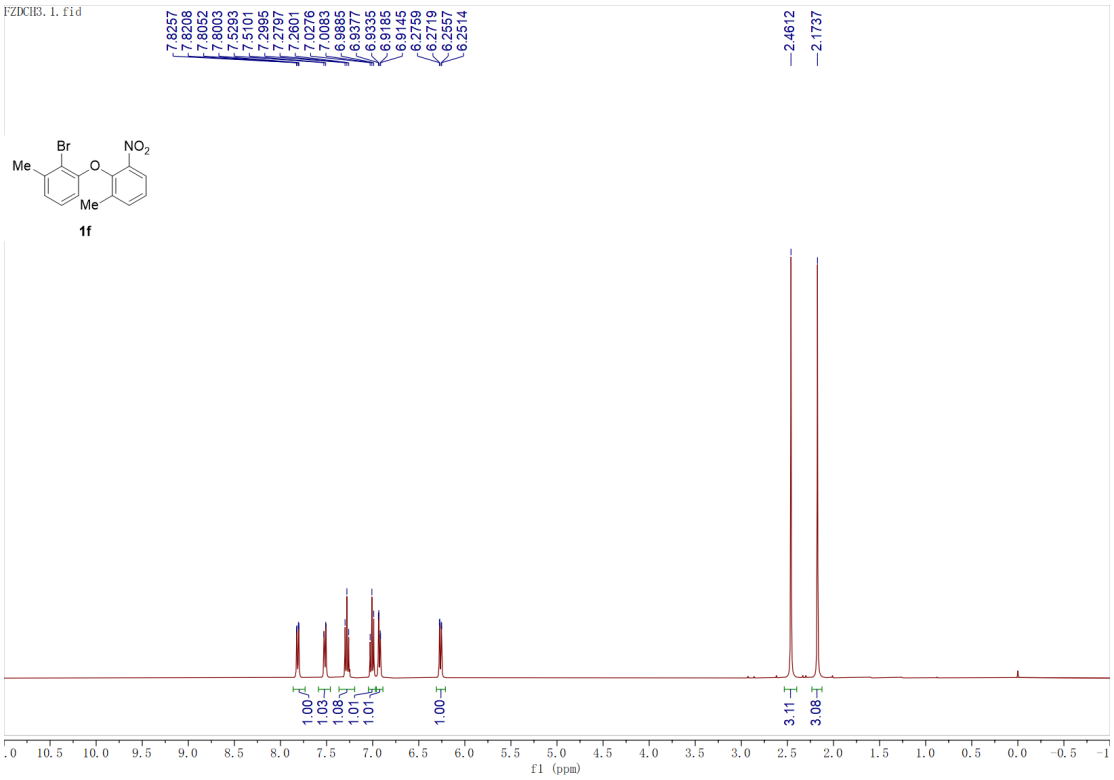


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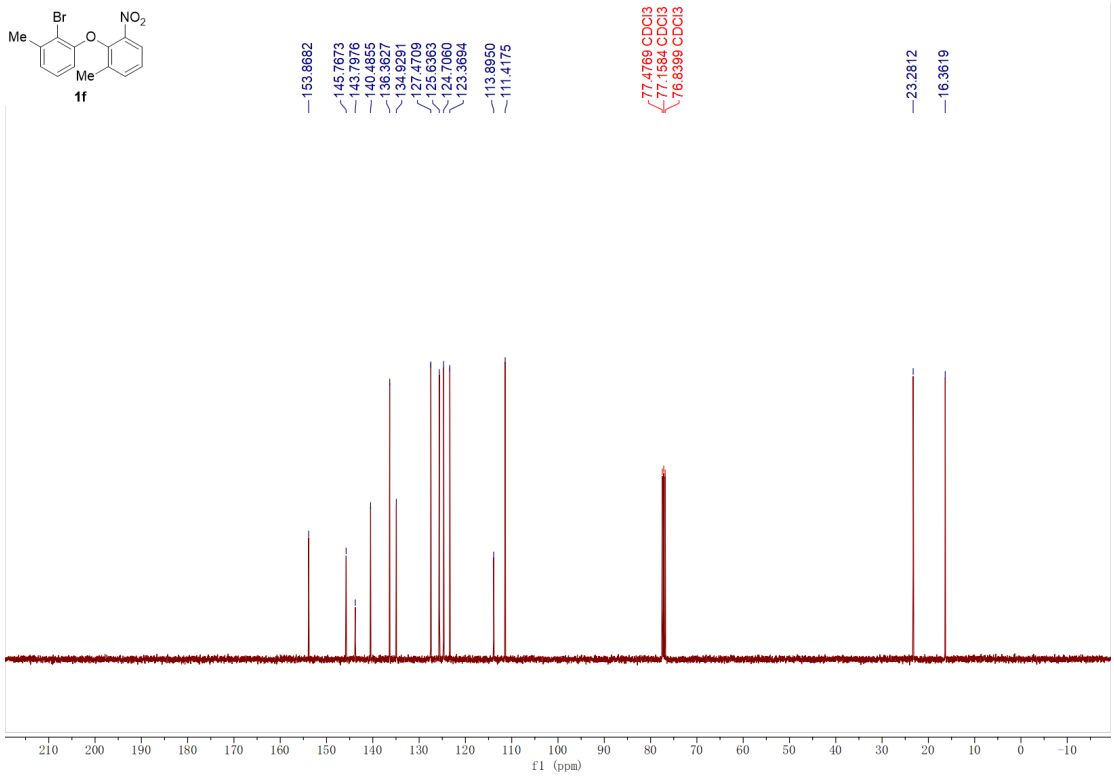


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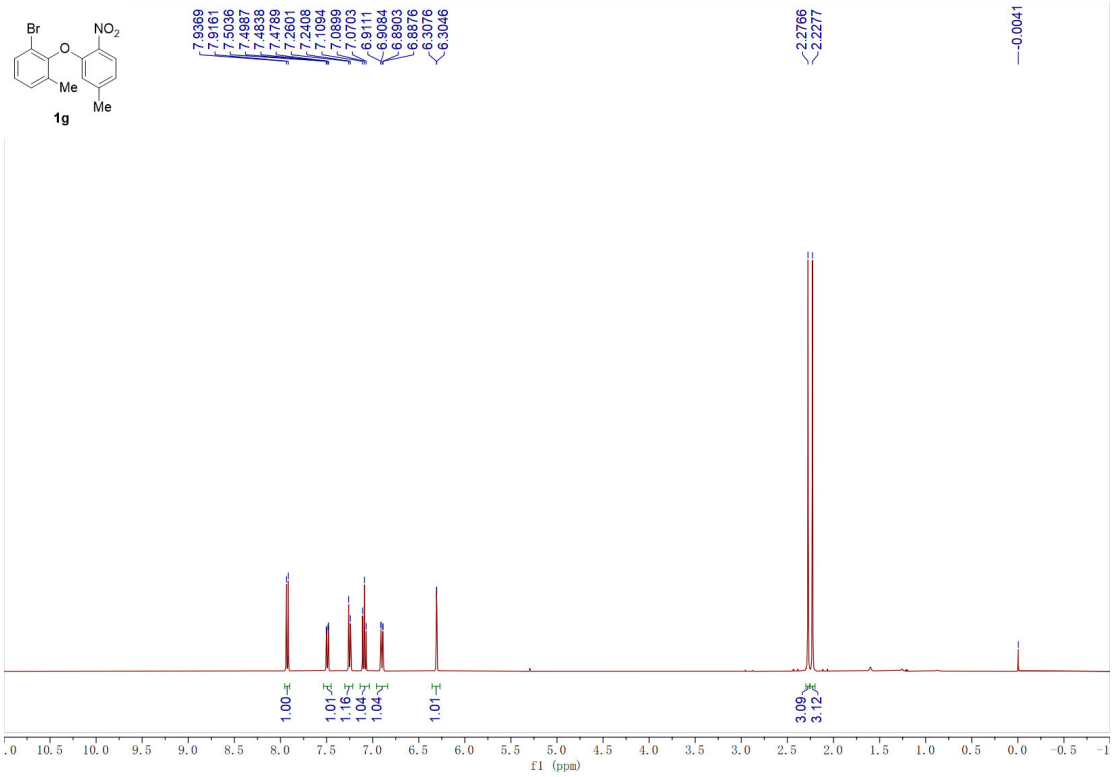


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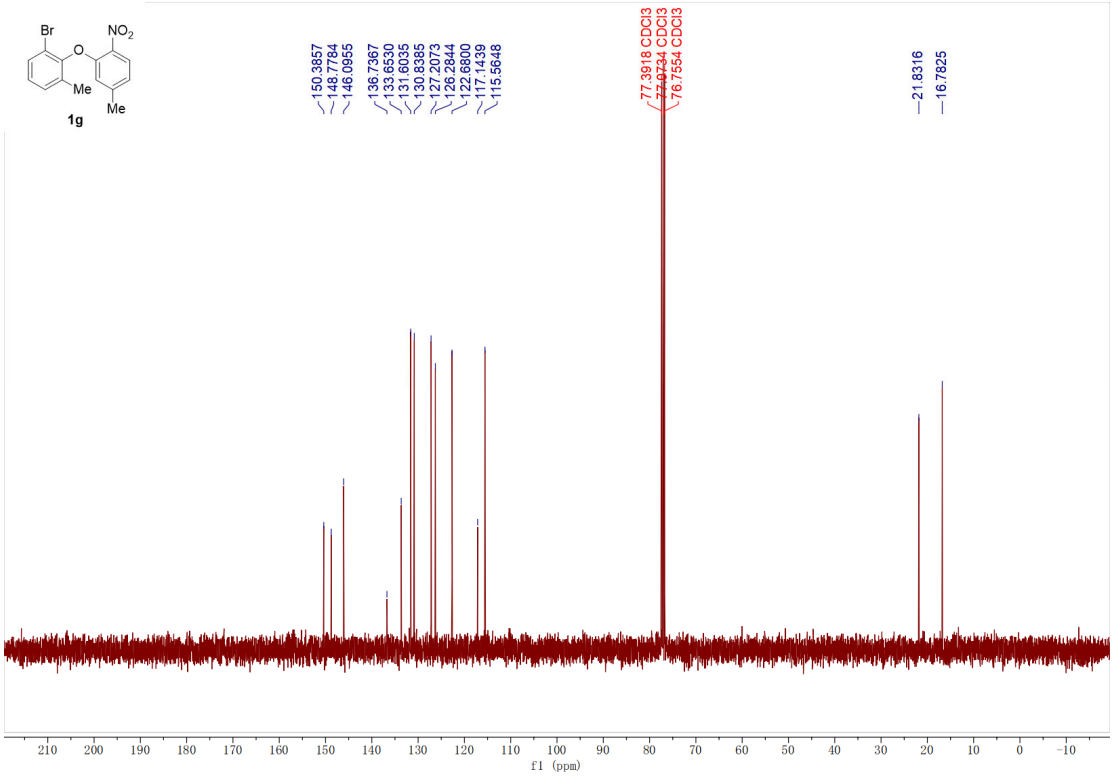
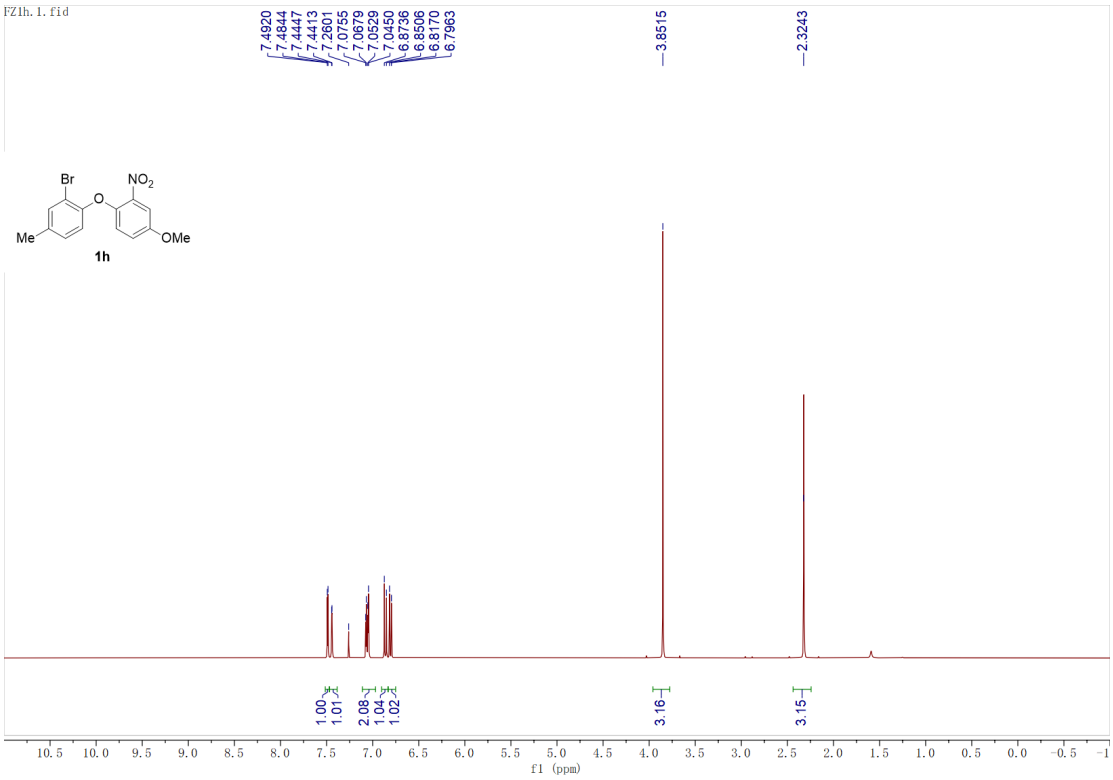
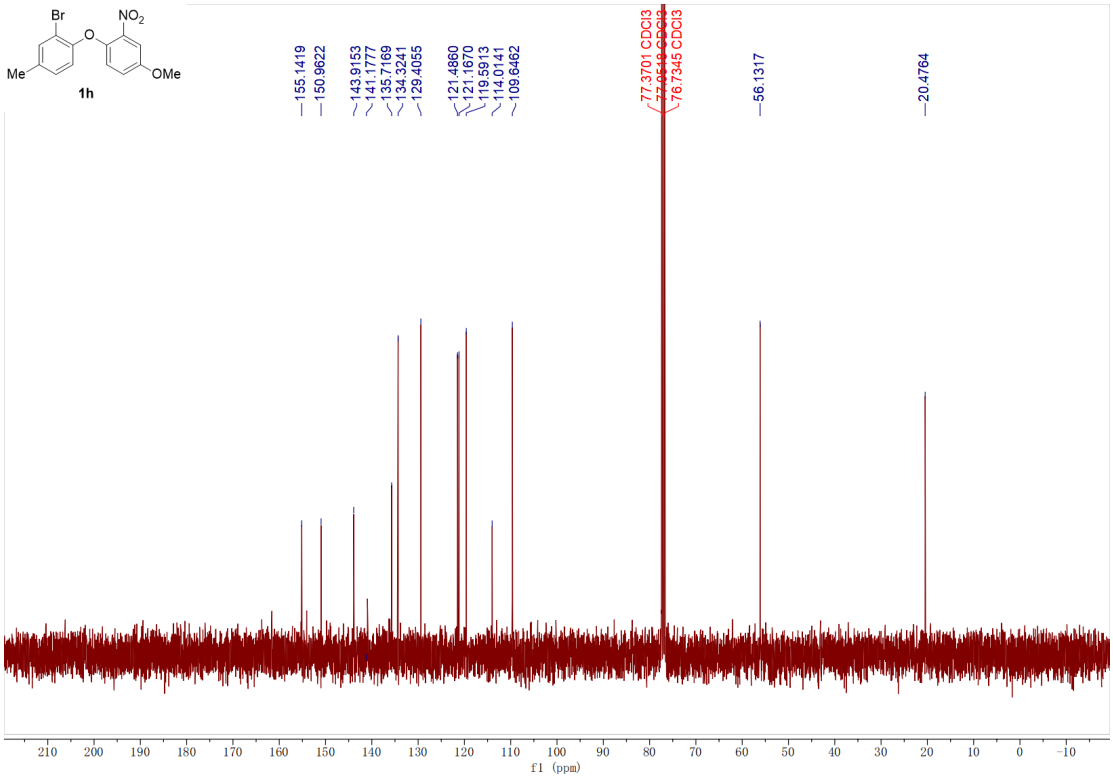


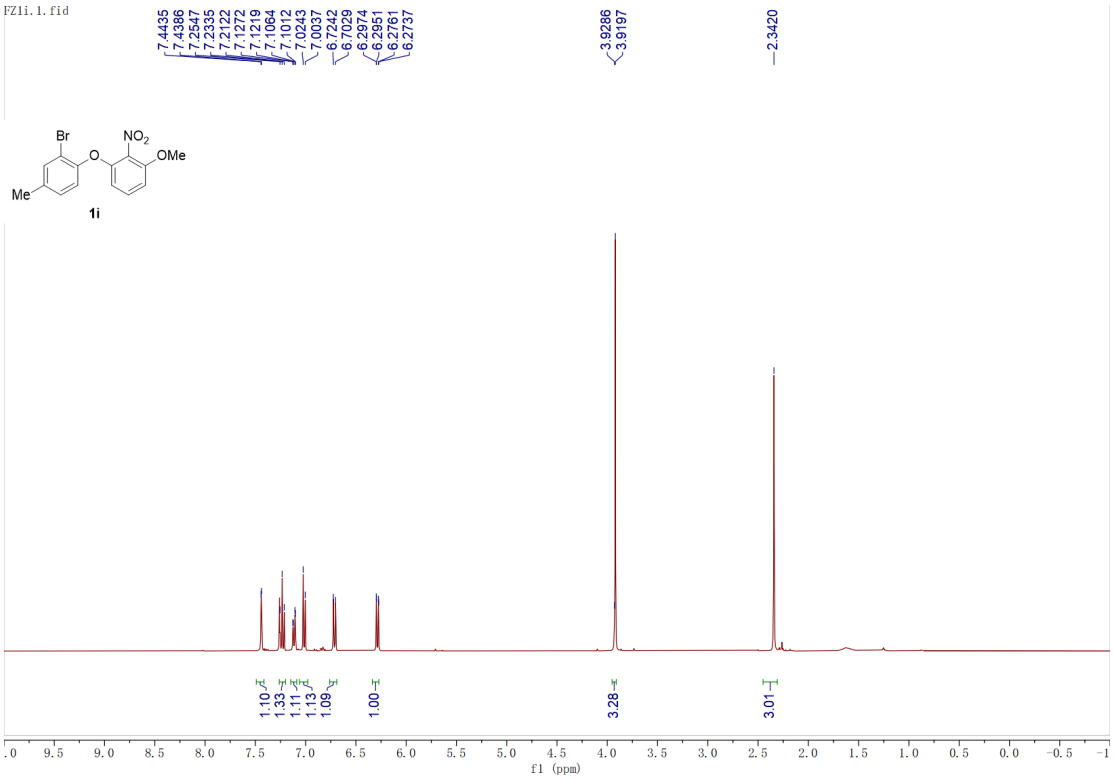

$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **1g**



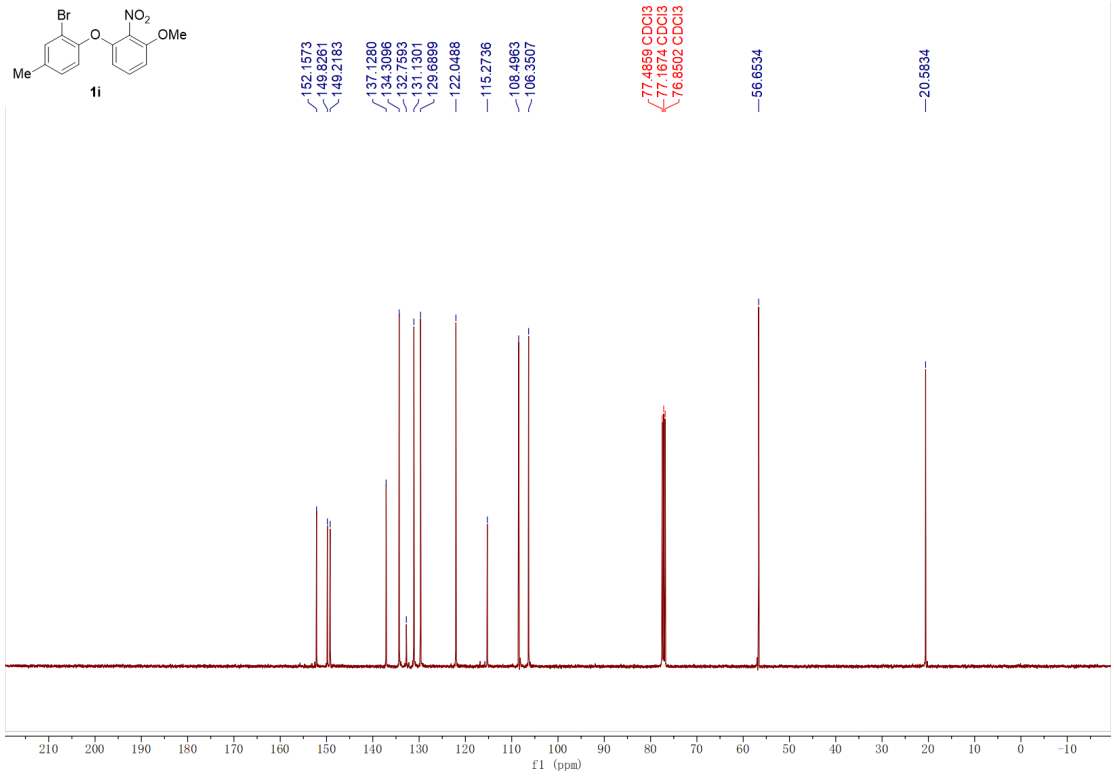

$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **1h**



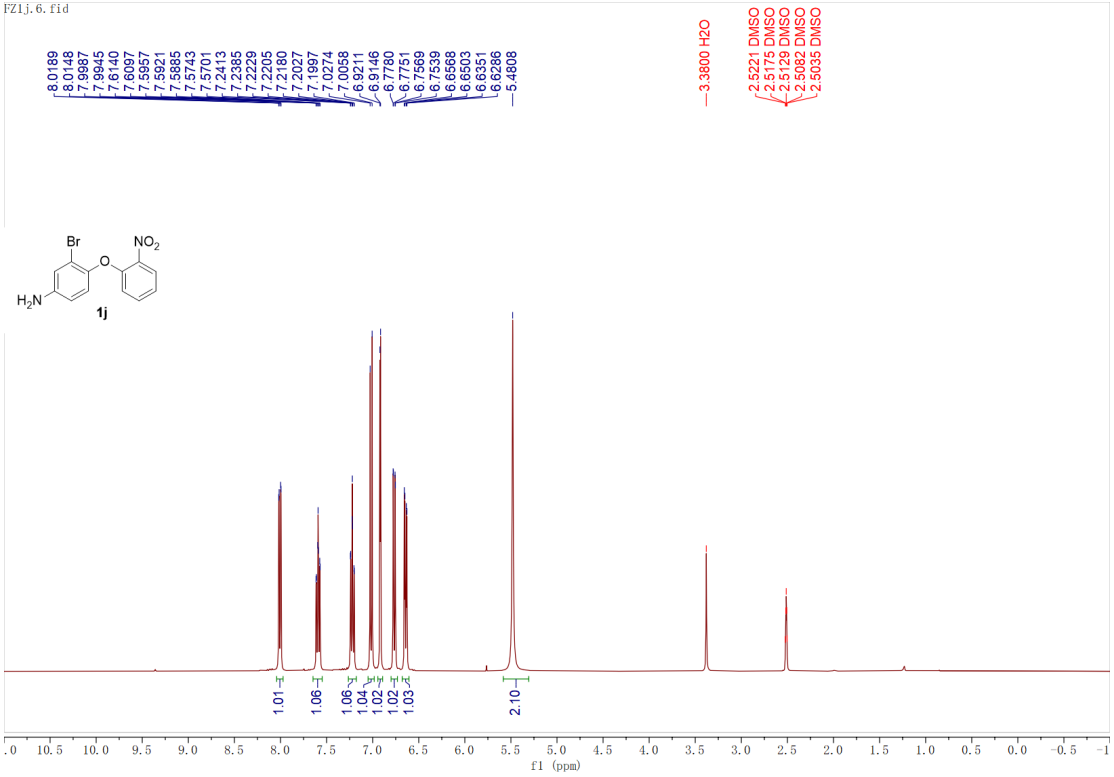

$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **1h**



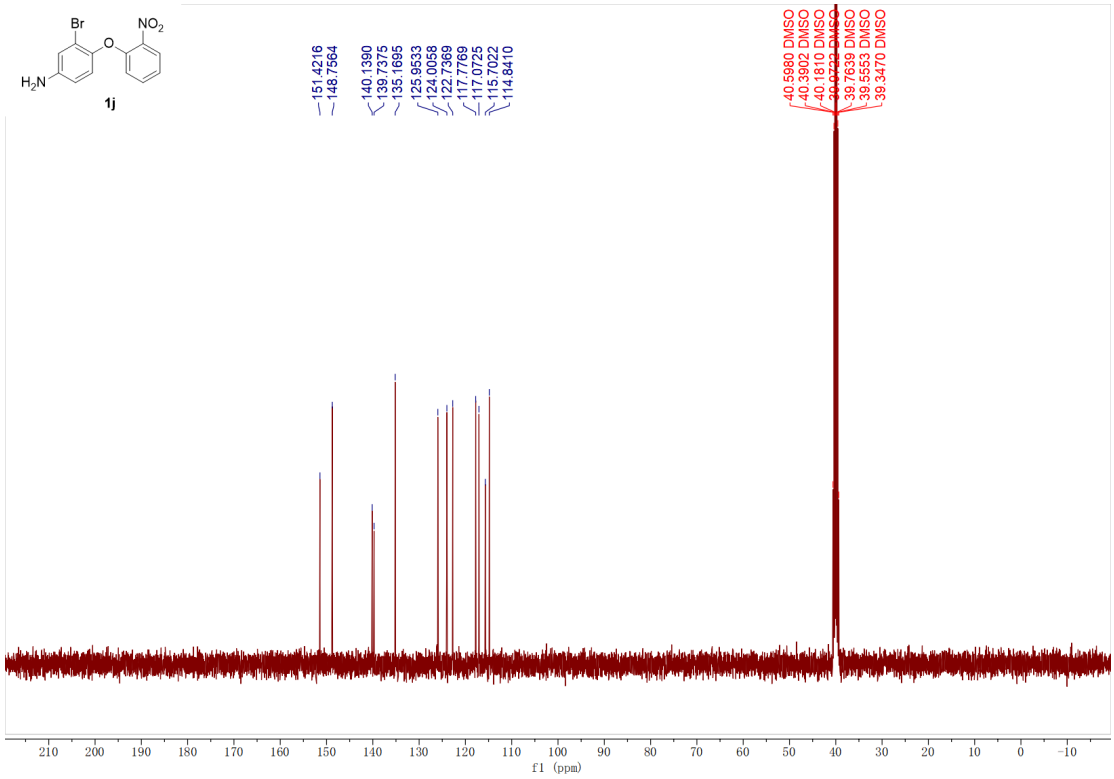

$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **1i**



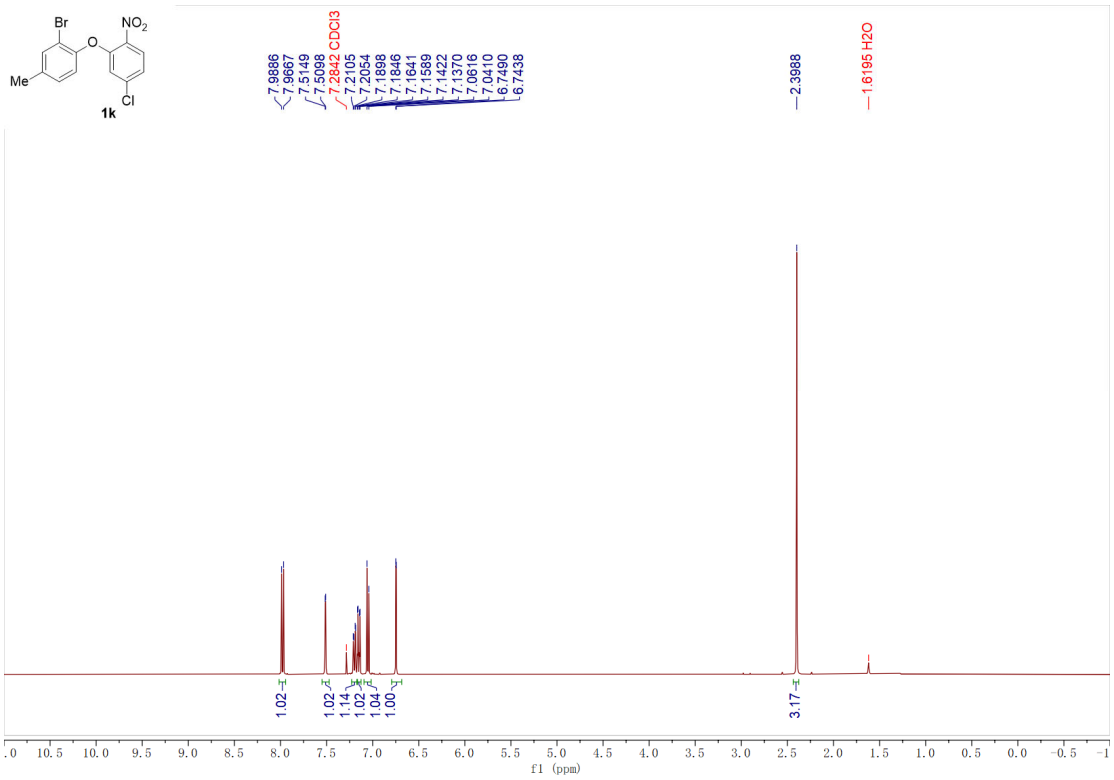

$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **1i**



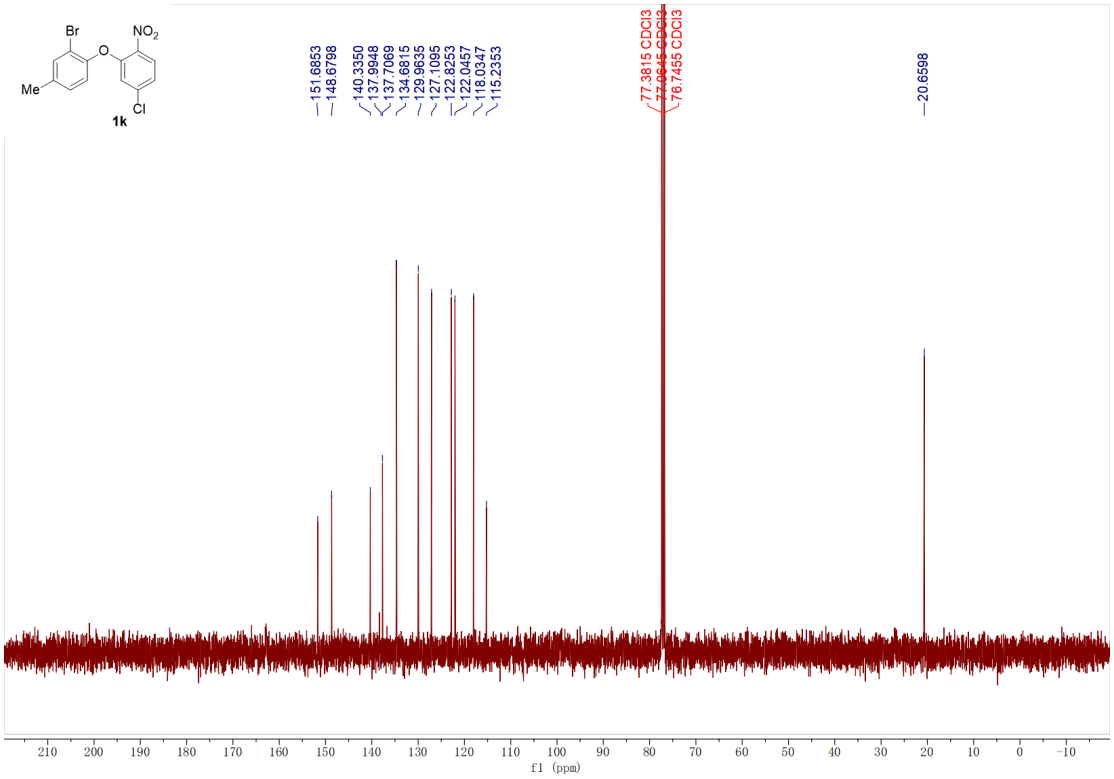

$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **1j**



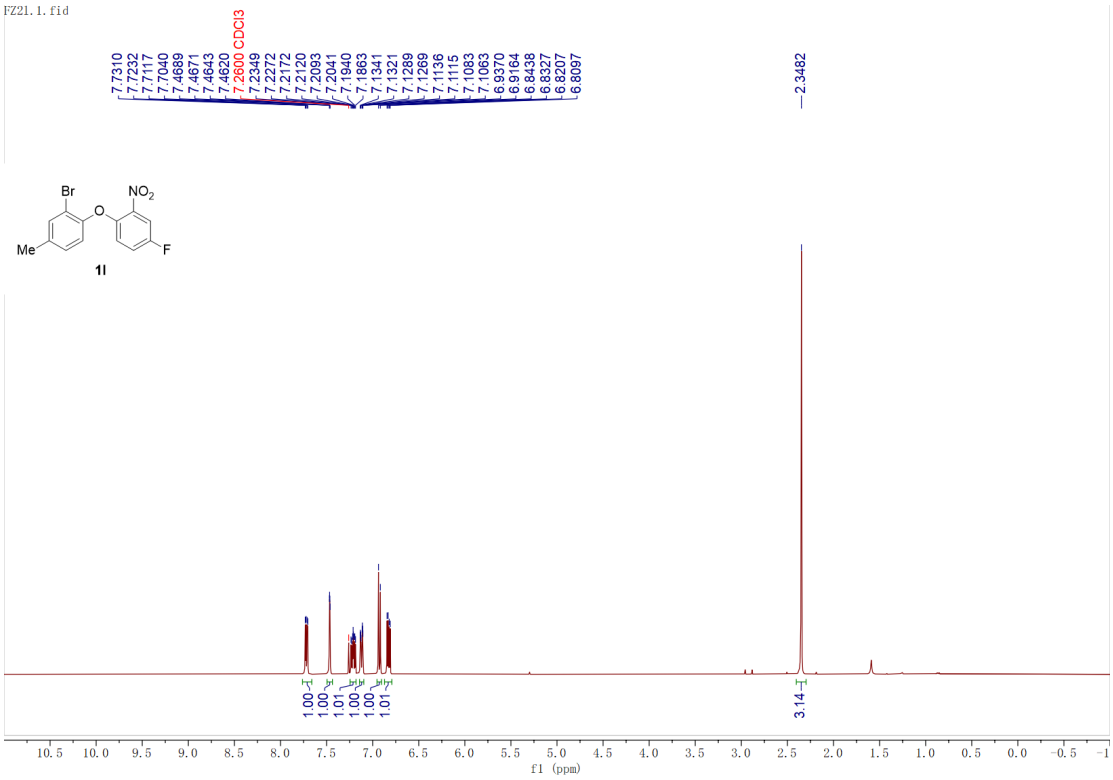

$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **1j**



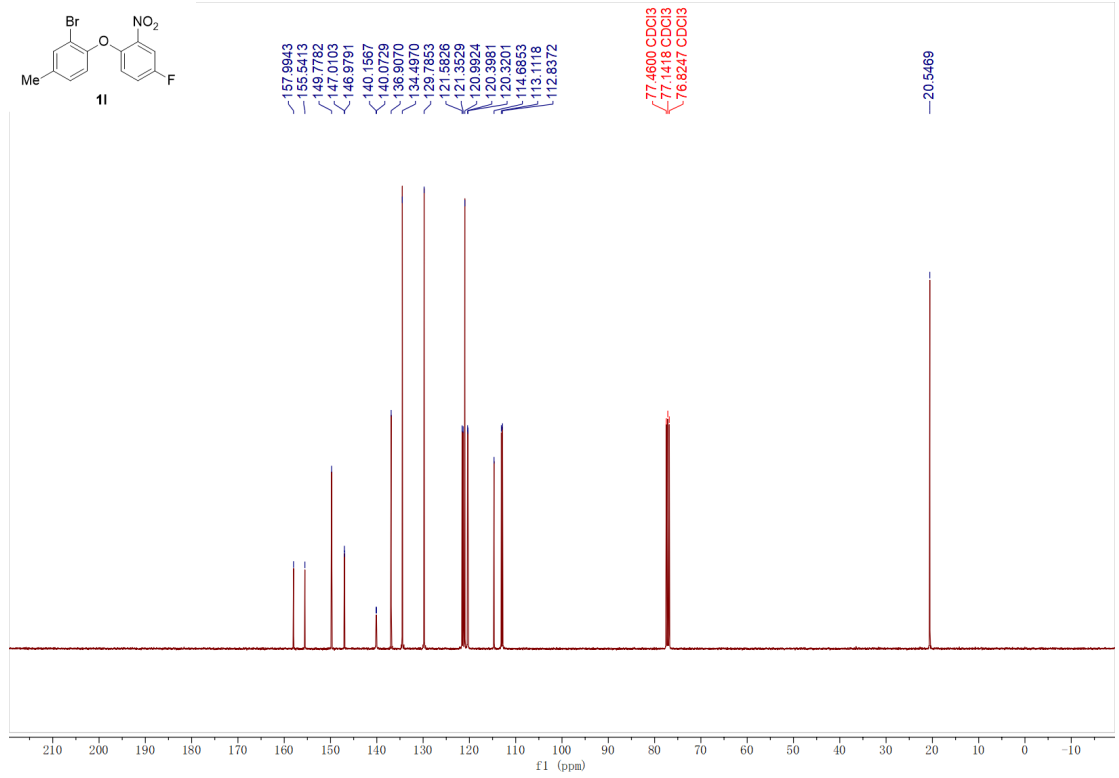

$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **1k**



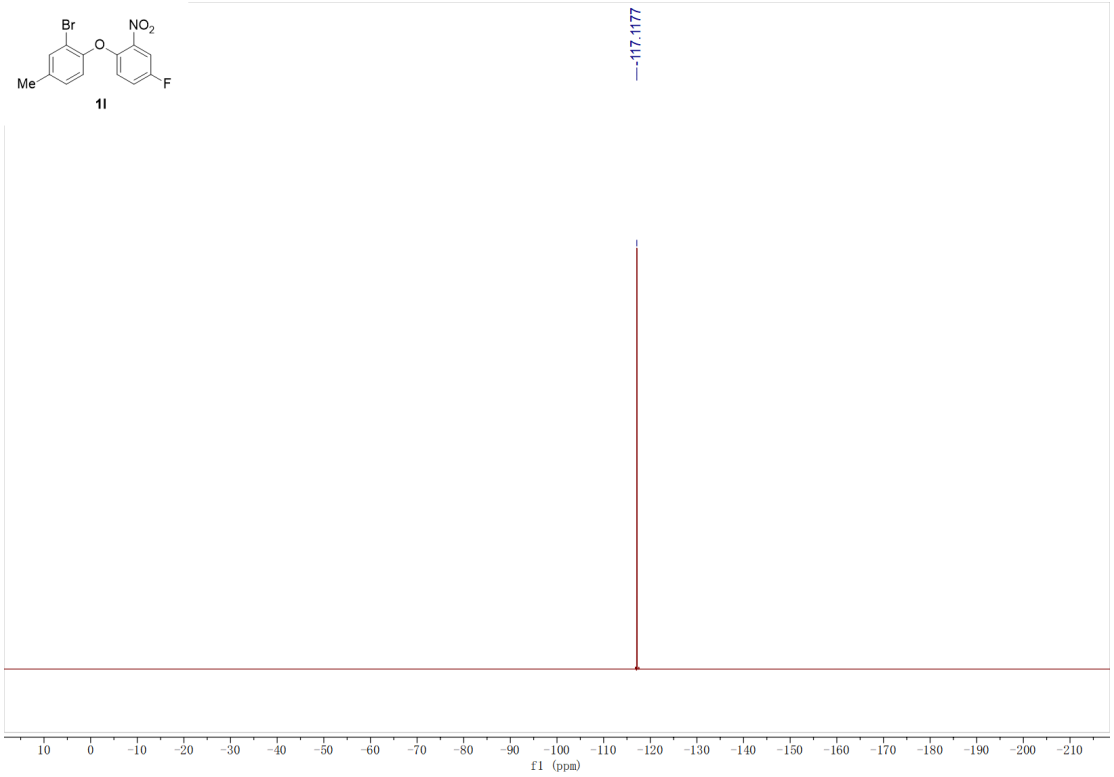

$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **1k**



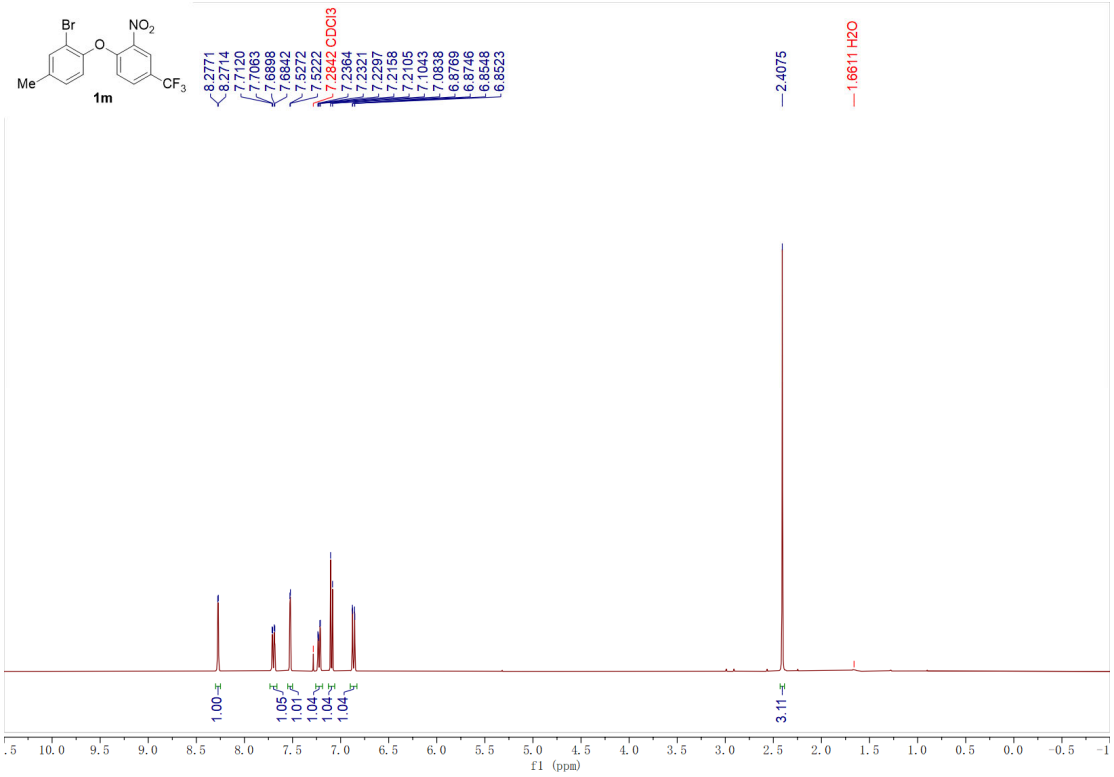

$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **1l**



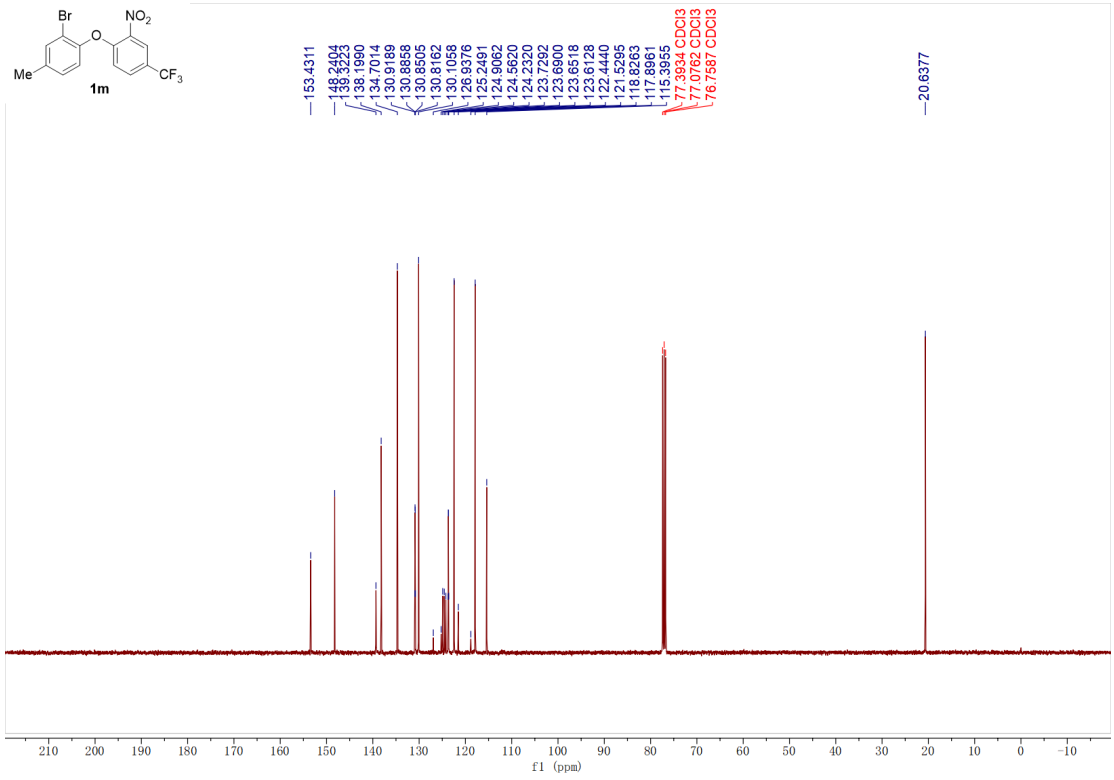

$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **1l**



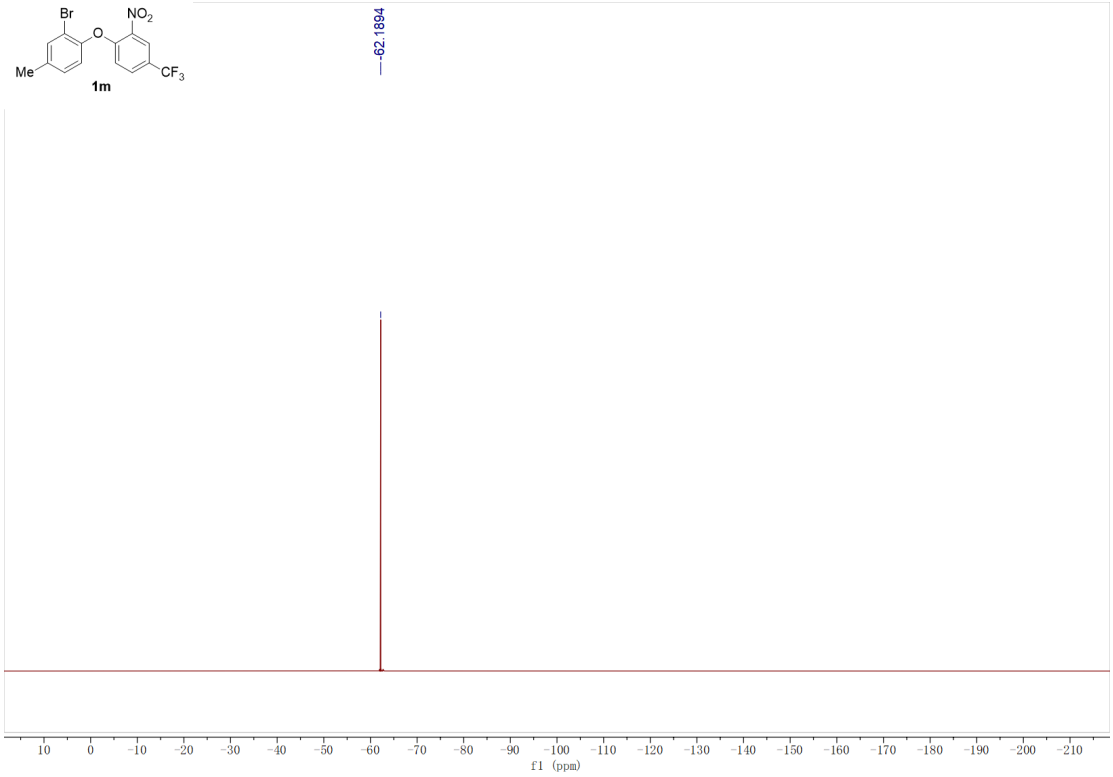

$^{19}$F NMR spectra (376 MHz, Chloroform-*d*) of **1l**



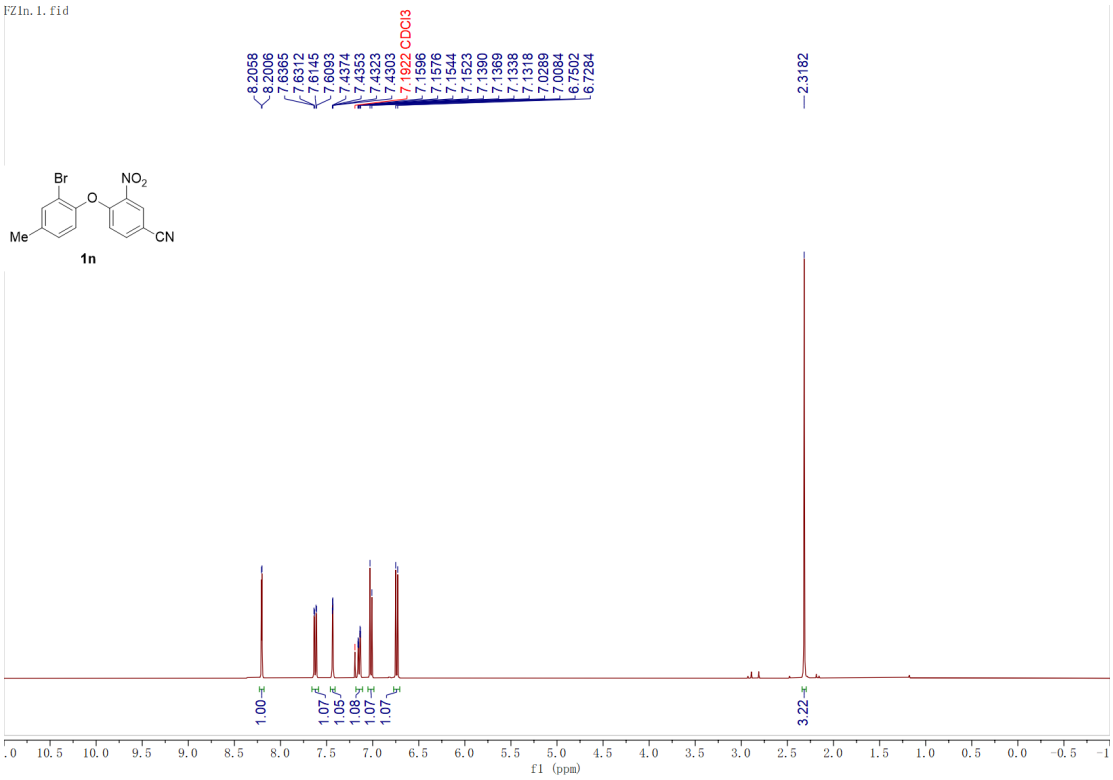

$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **1m**



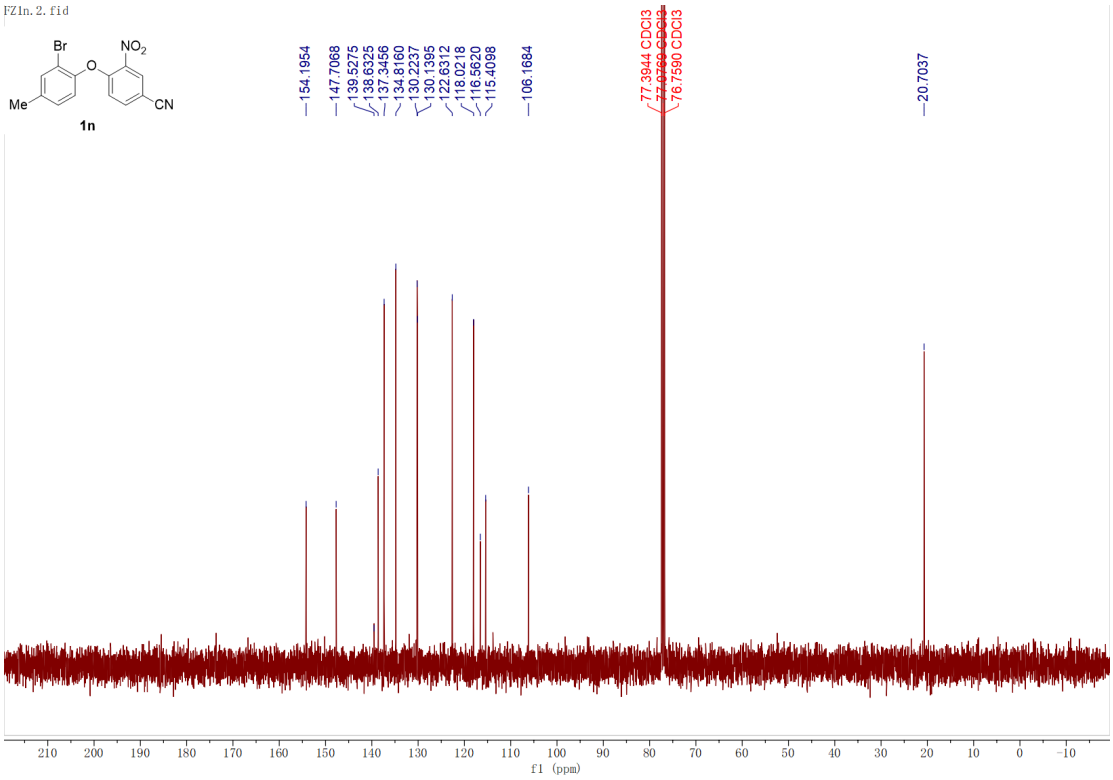

$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **1m**



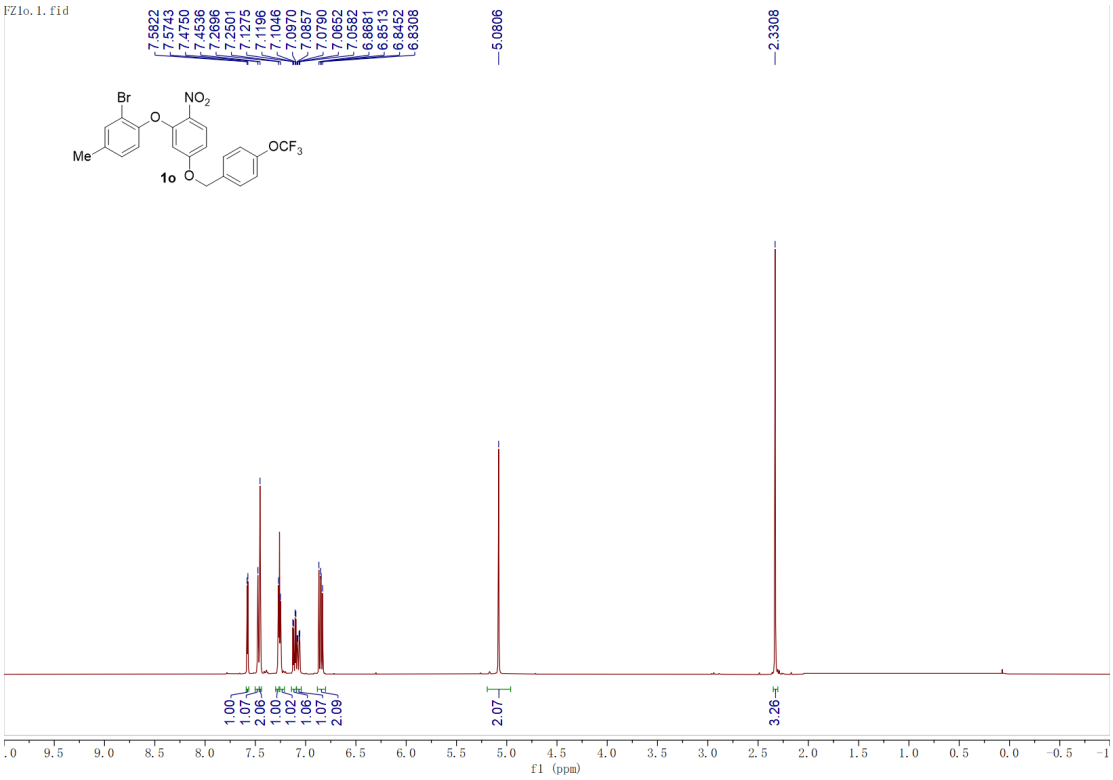

$^{19}$F NMR spectra (376 MHz, Chloroform-*d*) of **1m**



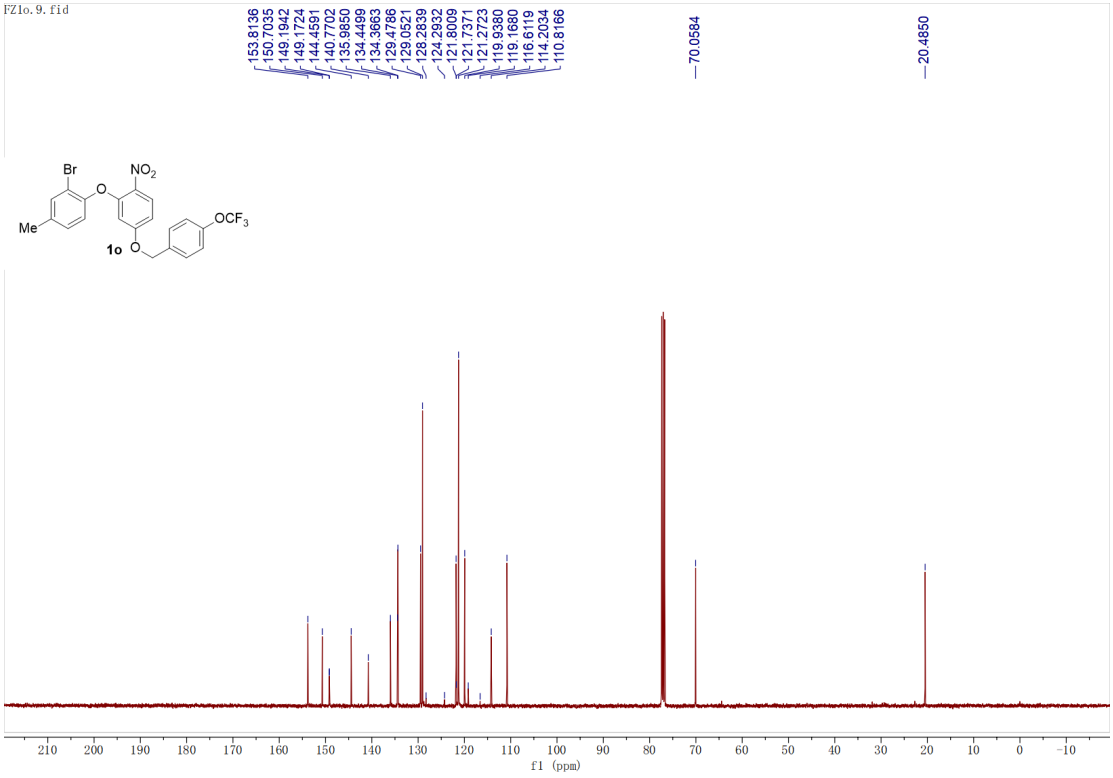

$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **1n**



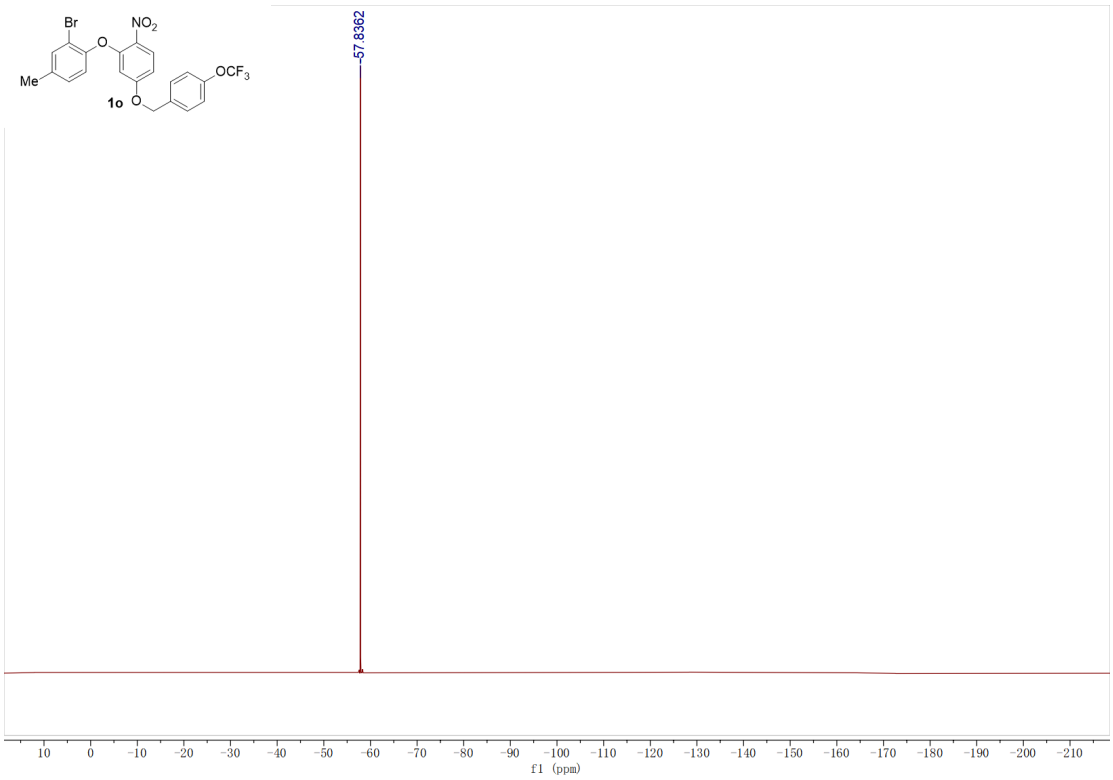

$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **1n**



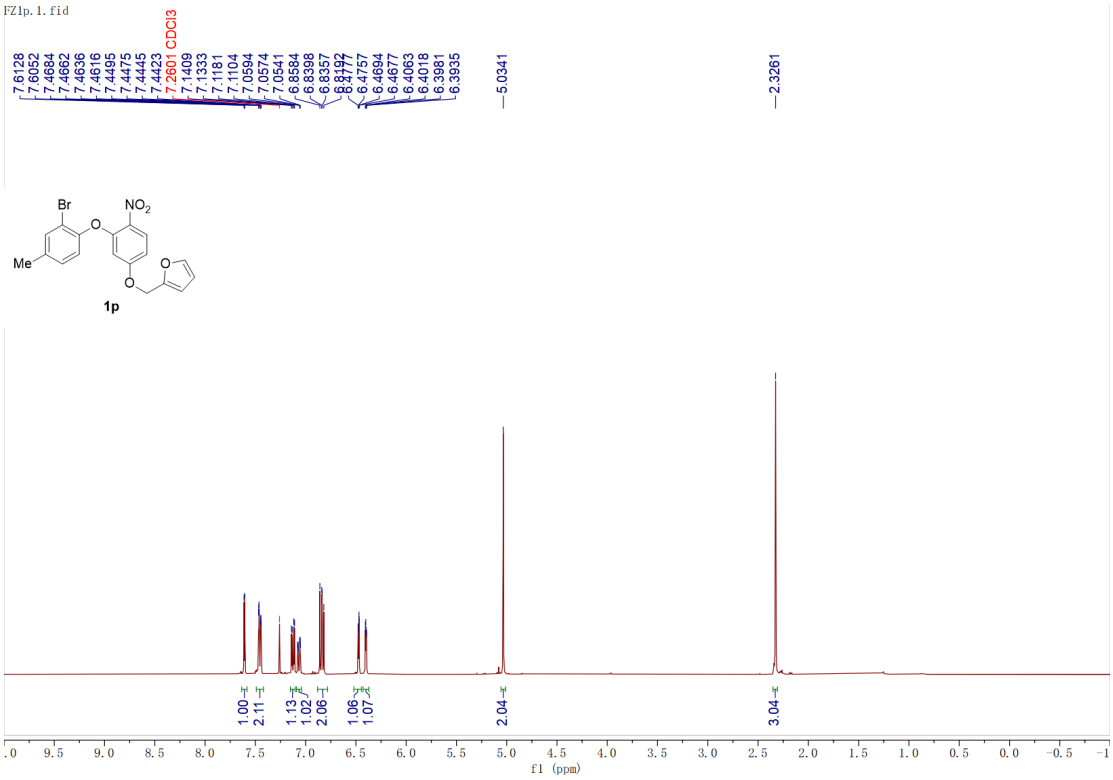

$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **1o**



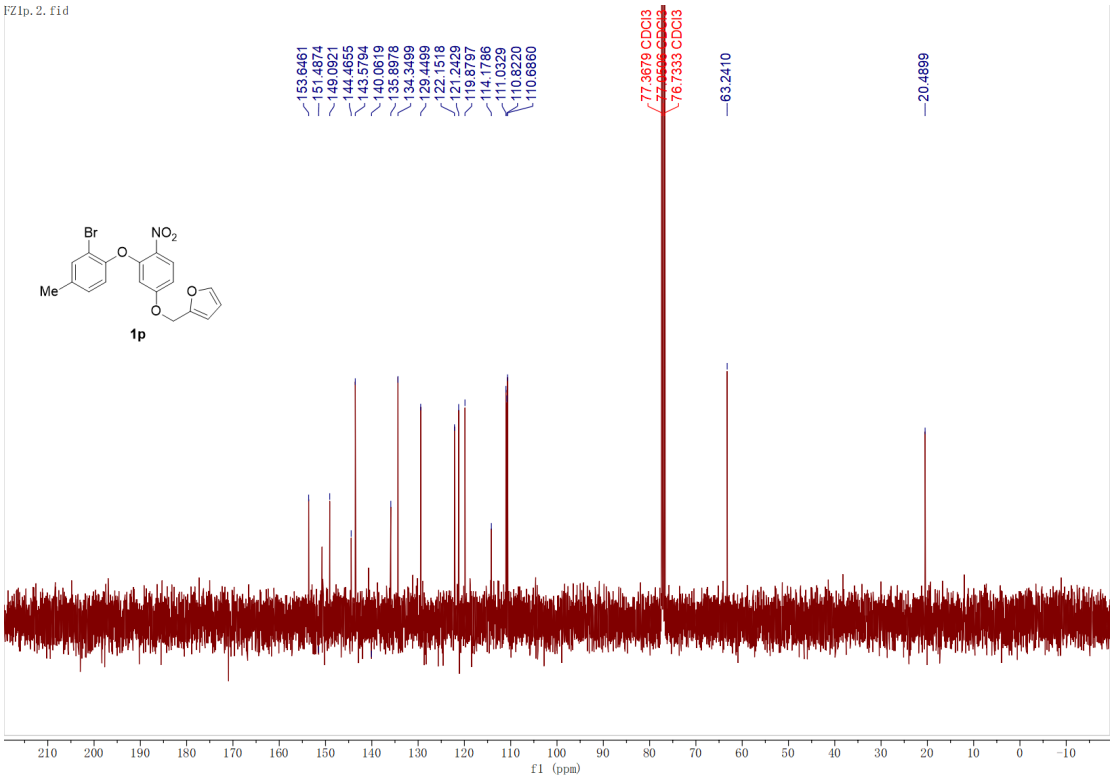

$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **1o**



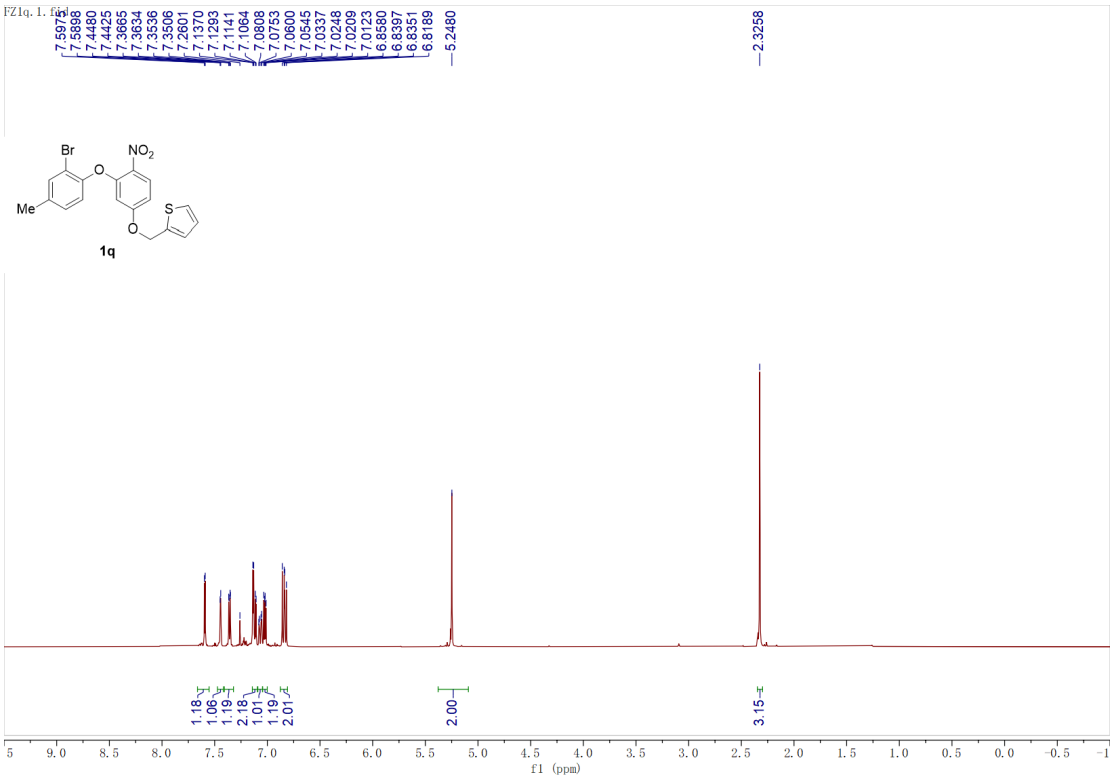

$^{19}$F NMR spectra (376 MHz, Chloroform-*d*) of **1o**



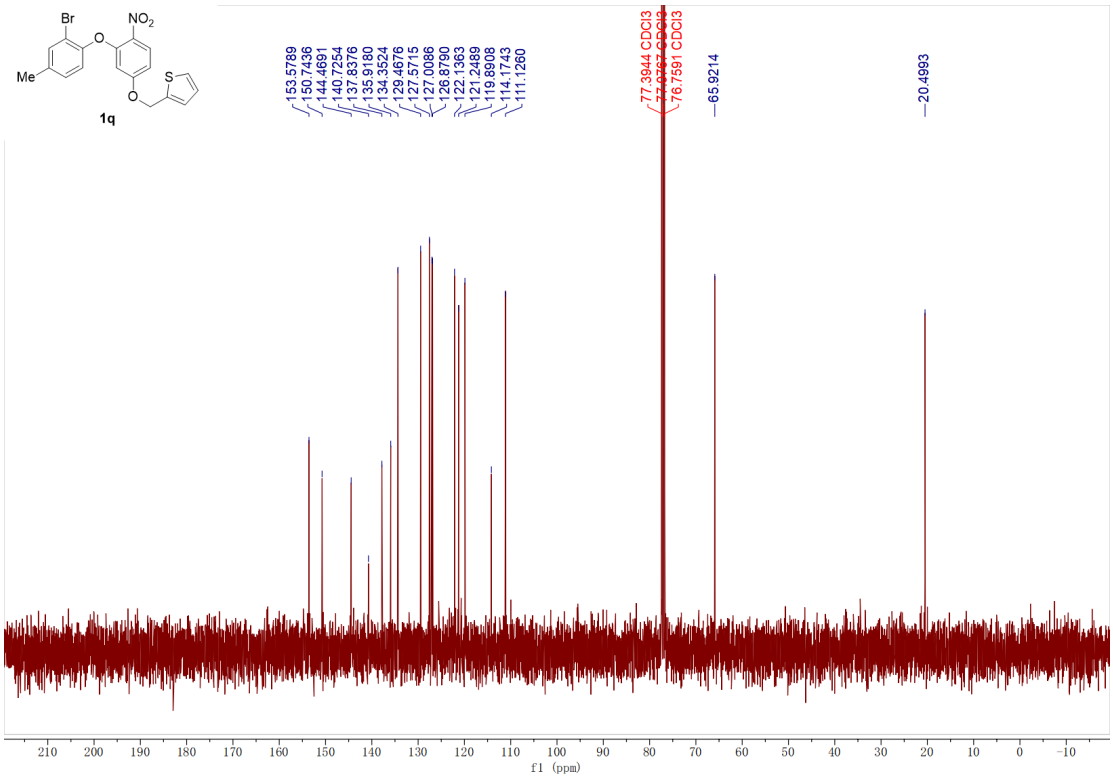

$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **1p**



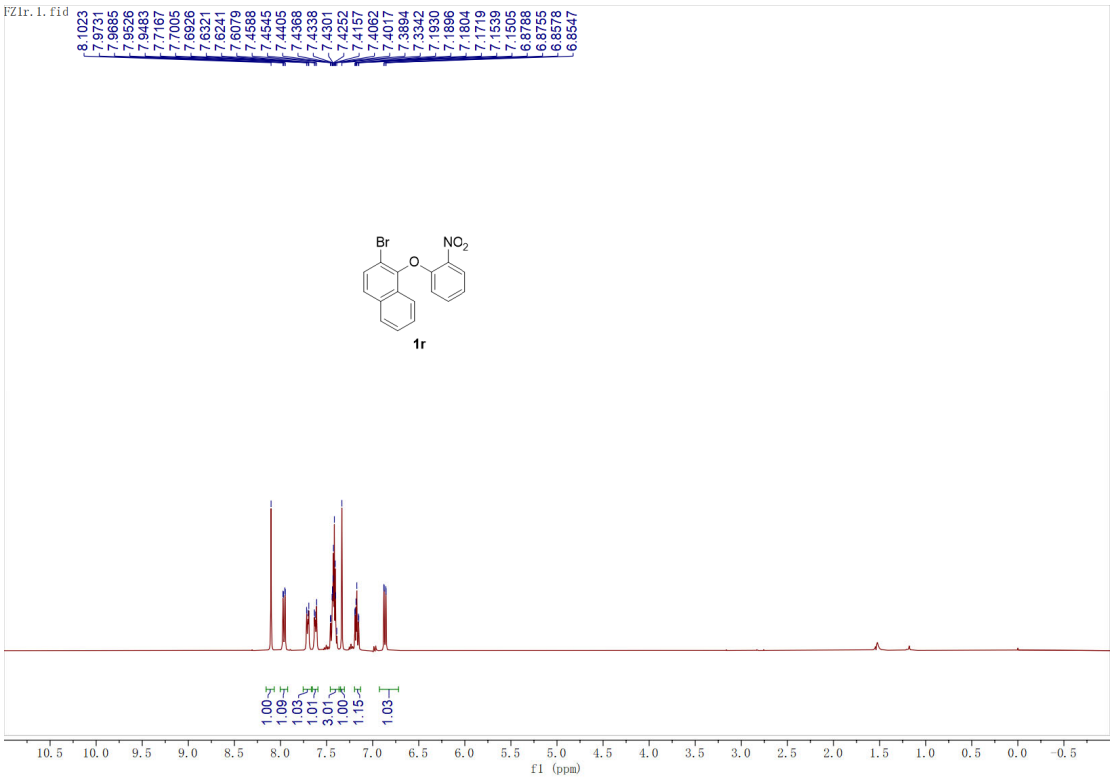

$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **1p**



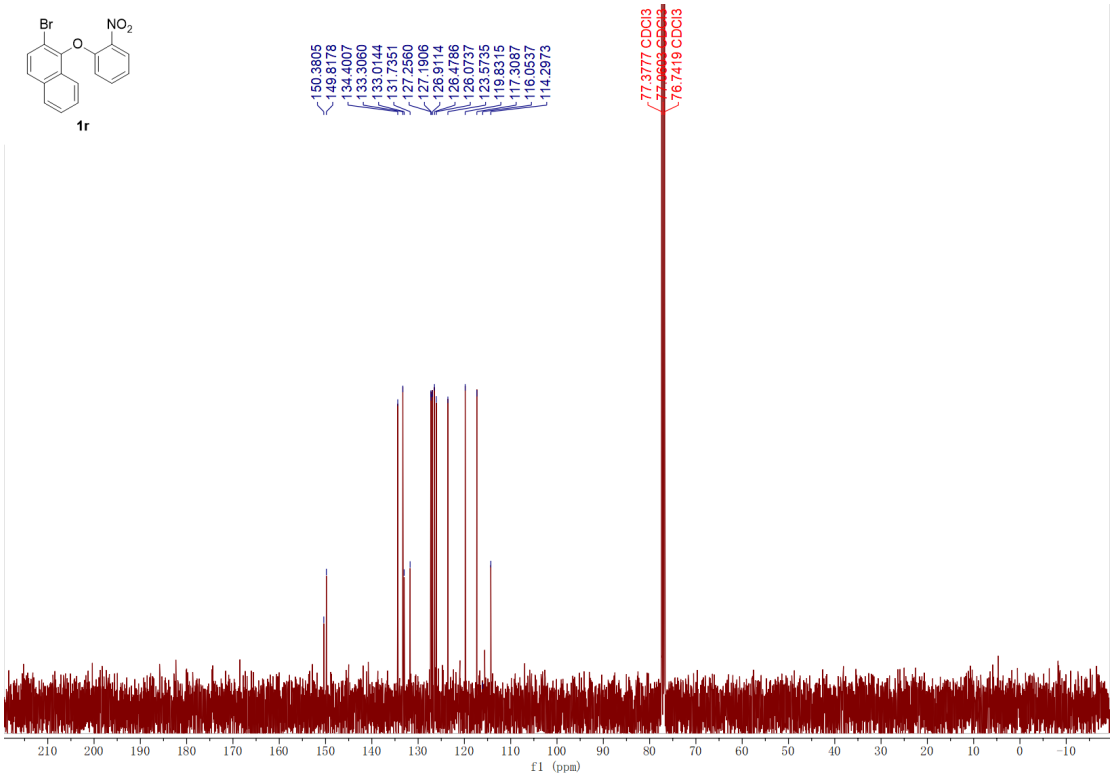

$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **1q**



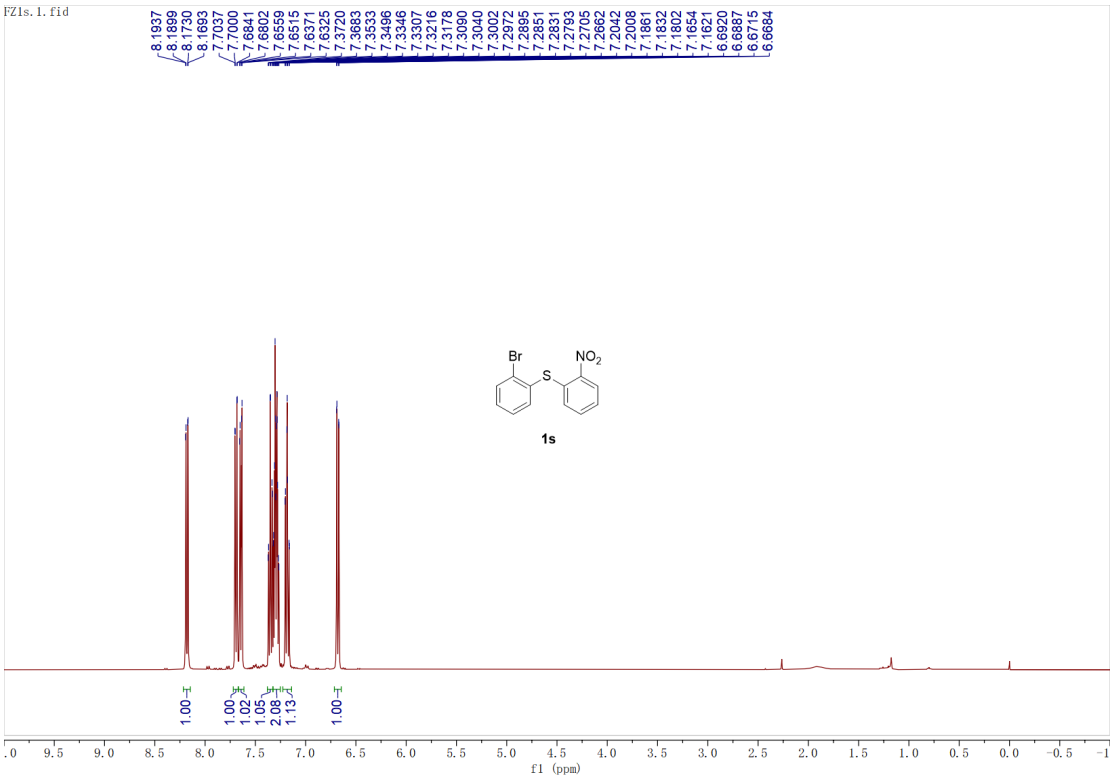

$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **1q**



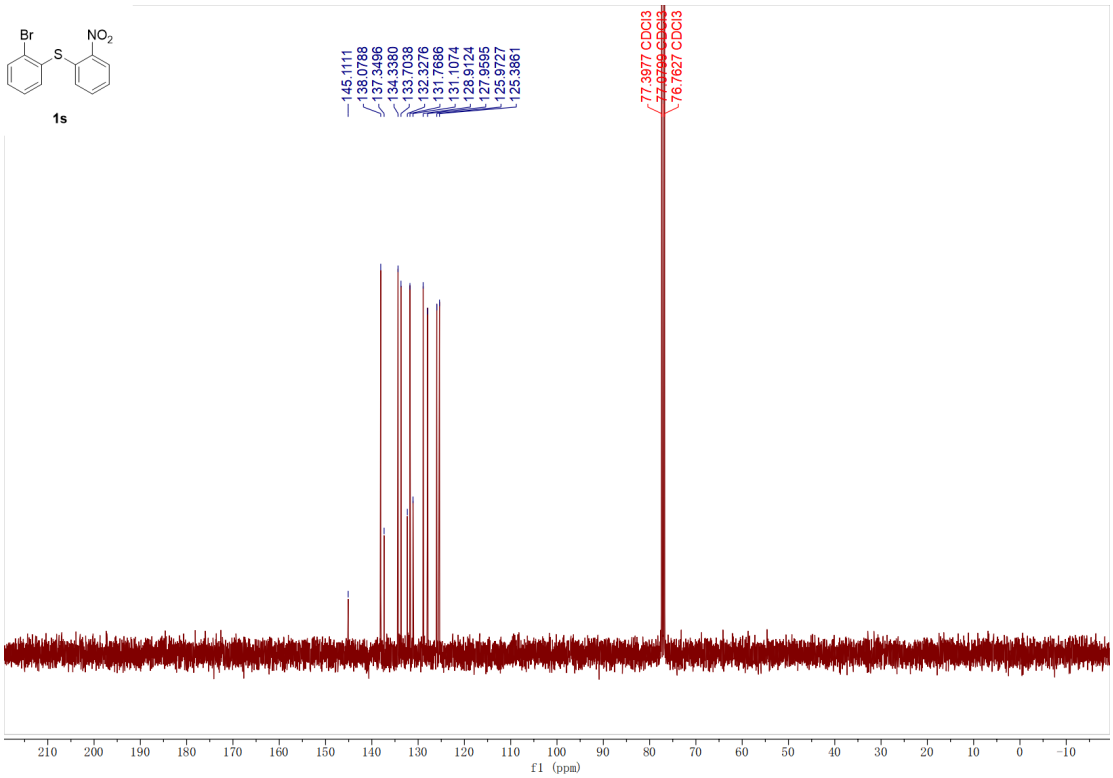

$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **1r**



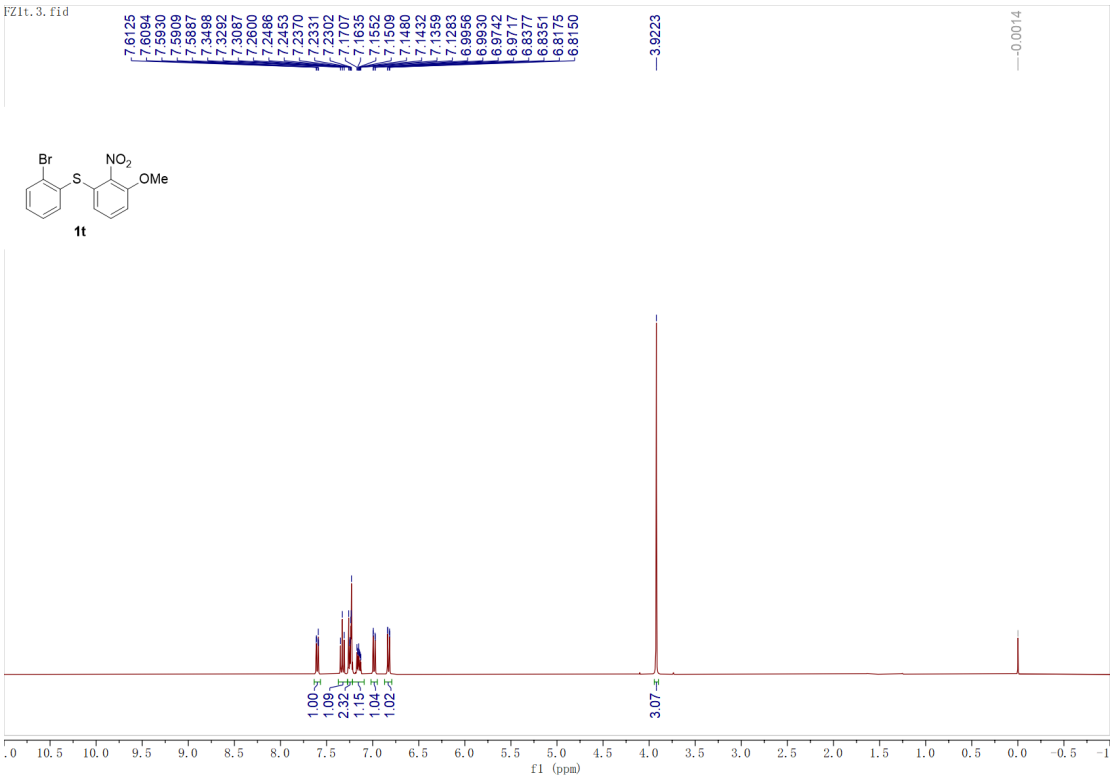

$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **1r**



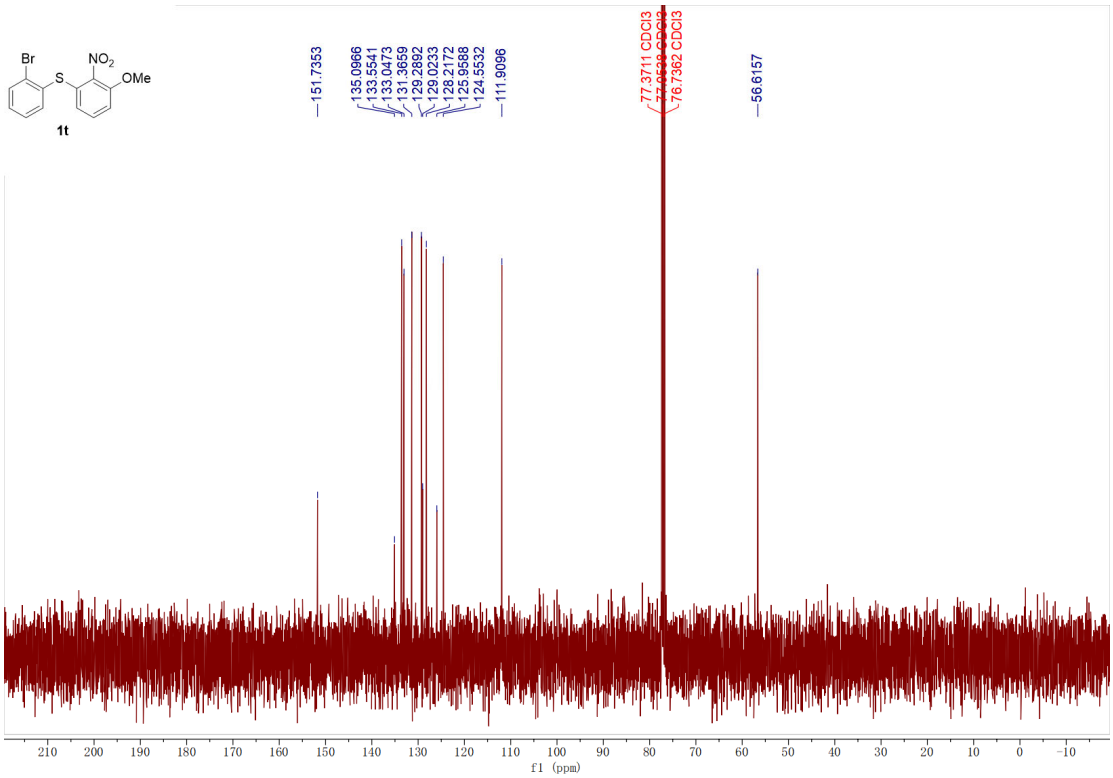

$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **1s**



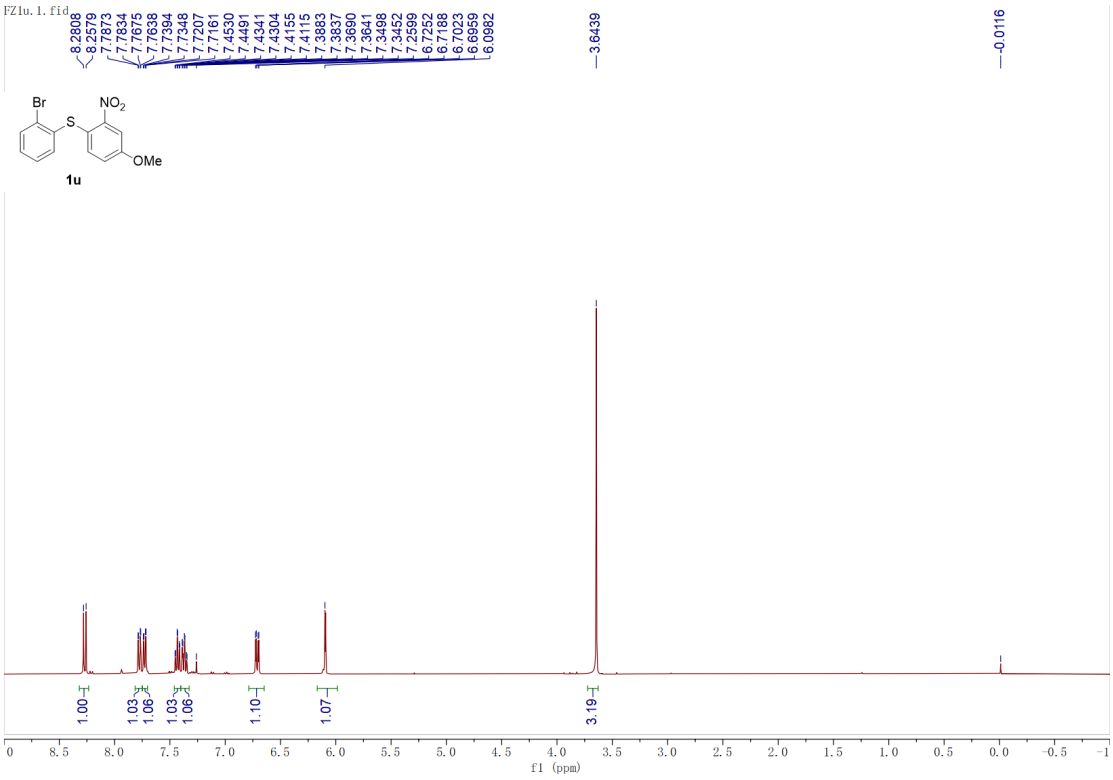

$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **1s**



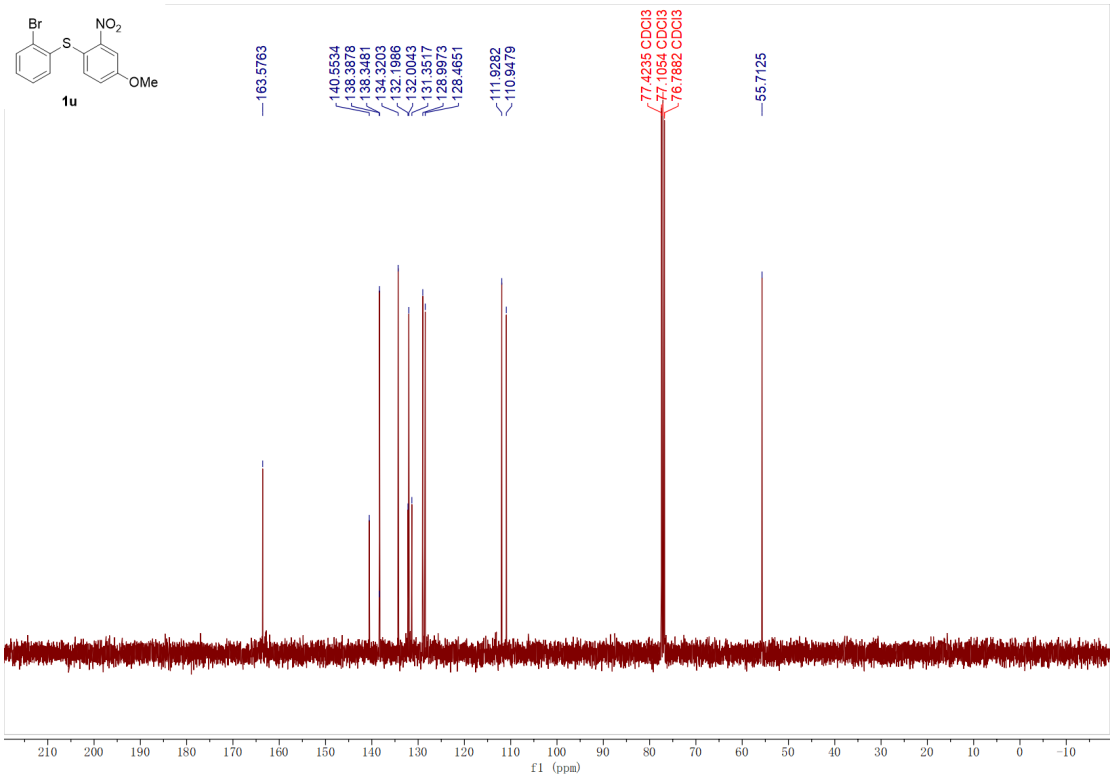

$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **1t**



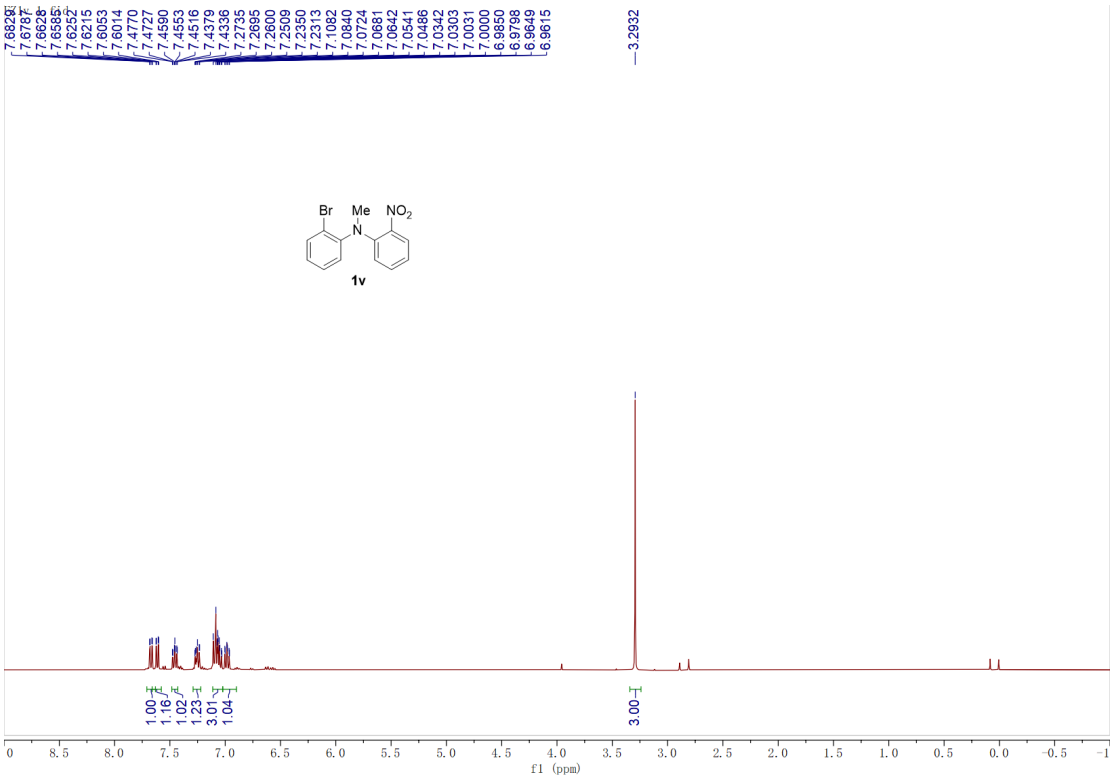

$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **1t**



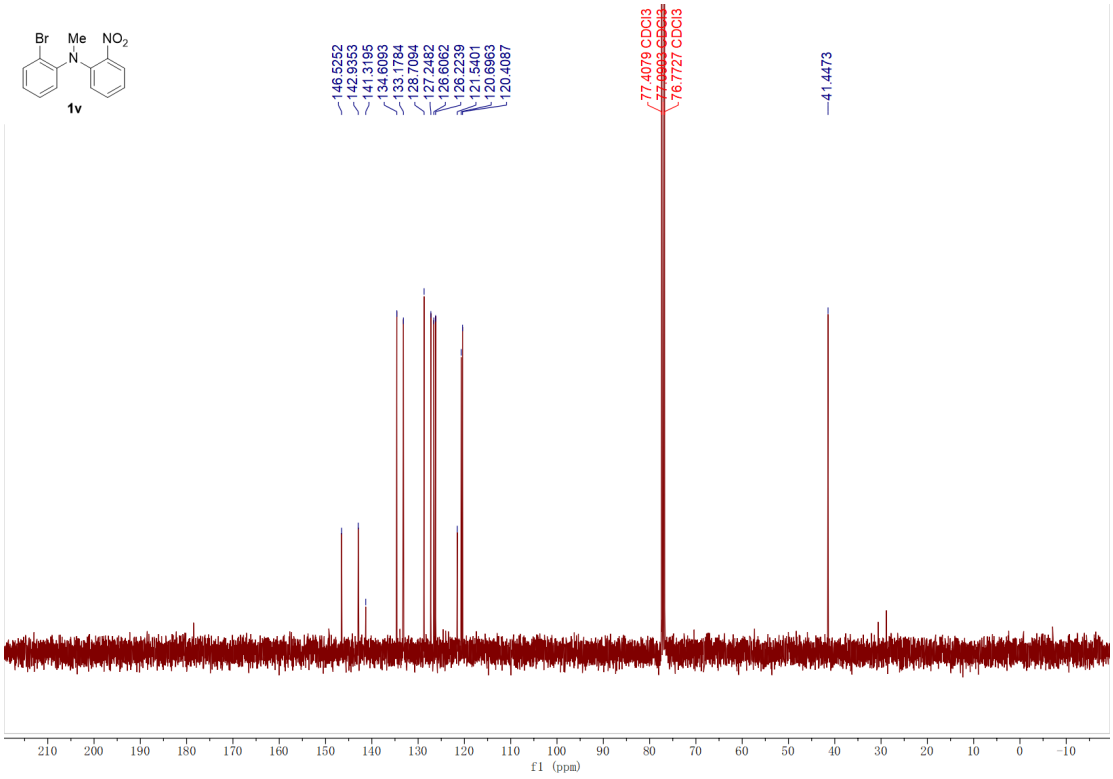

$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **1u**



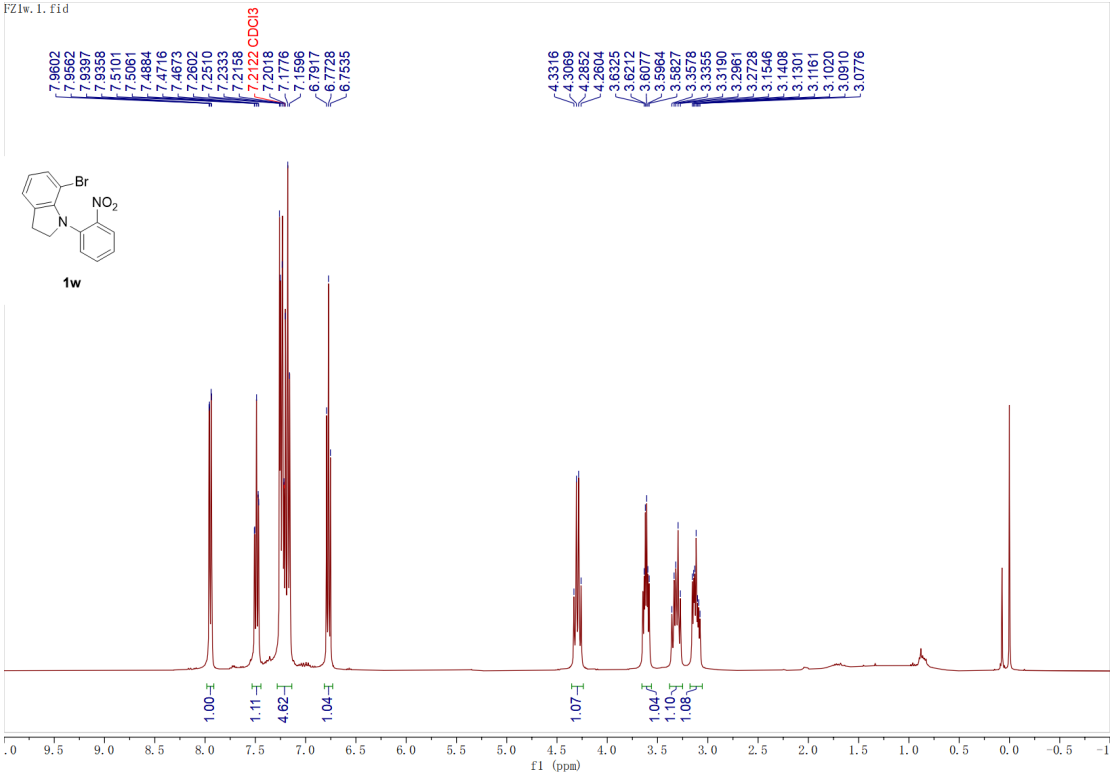

$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **1u**




$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **1v**




$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **1v**

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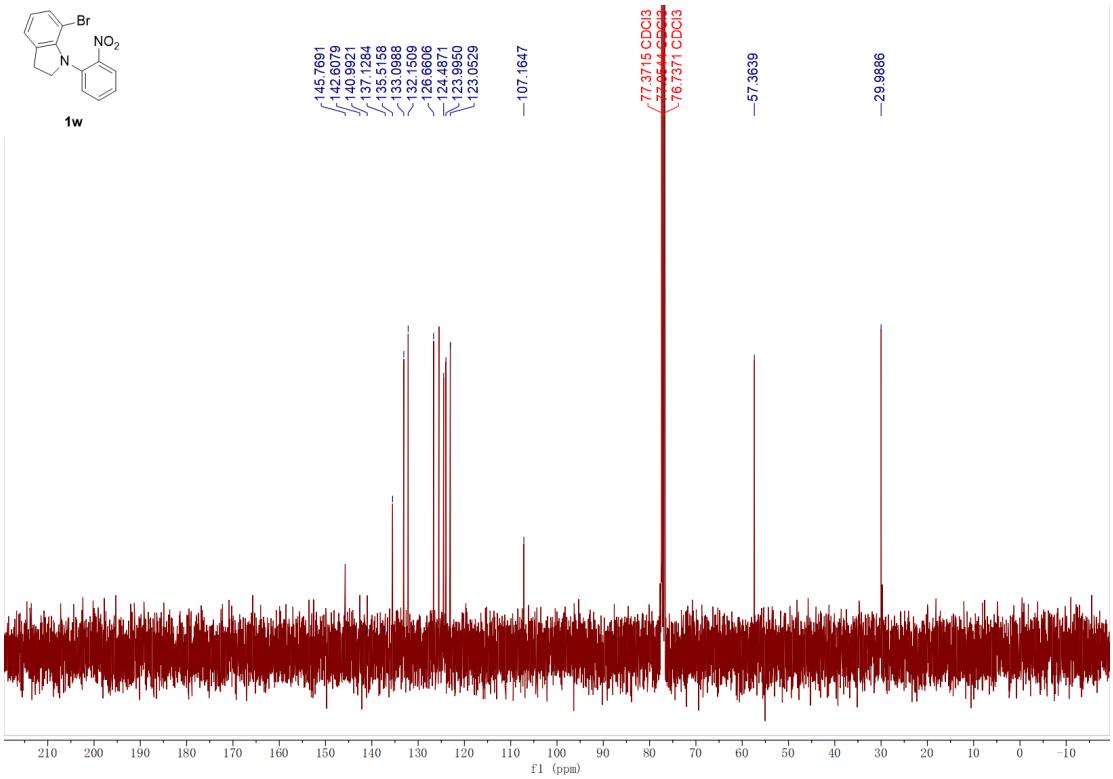
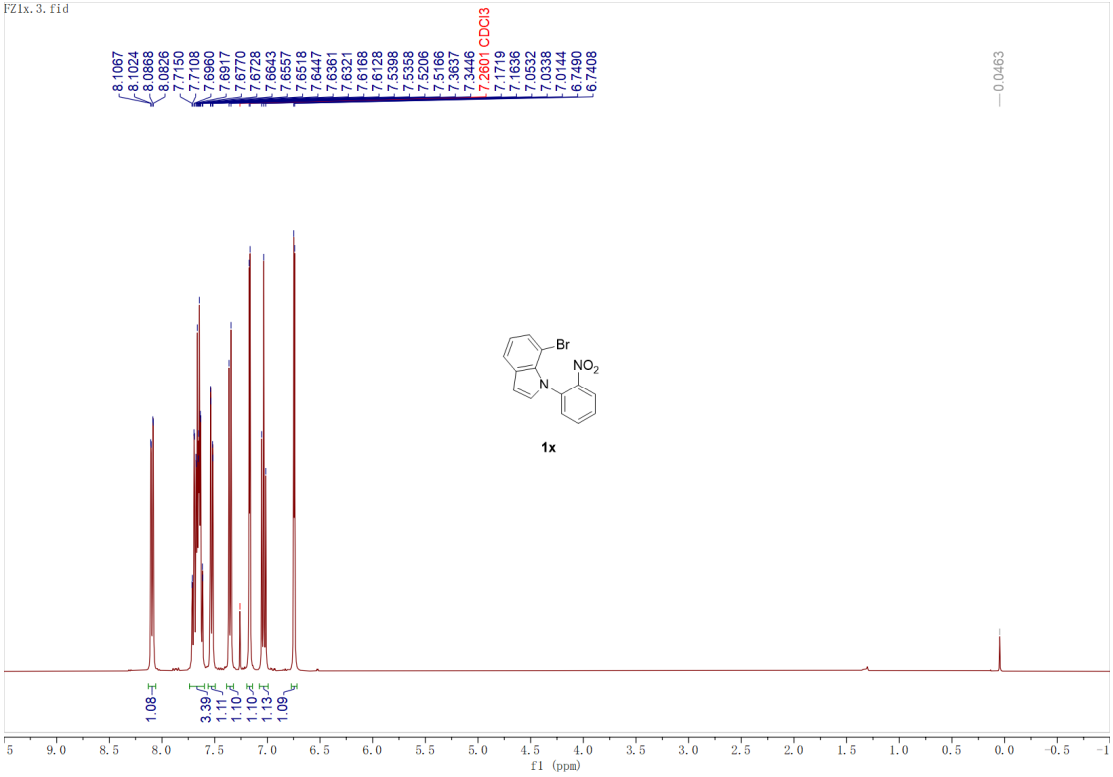
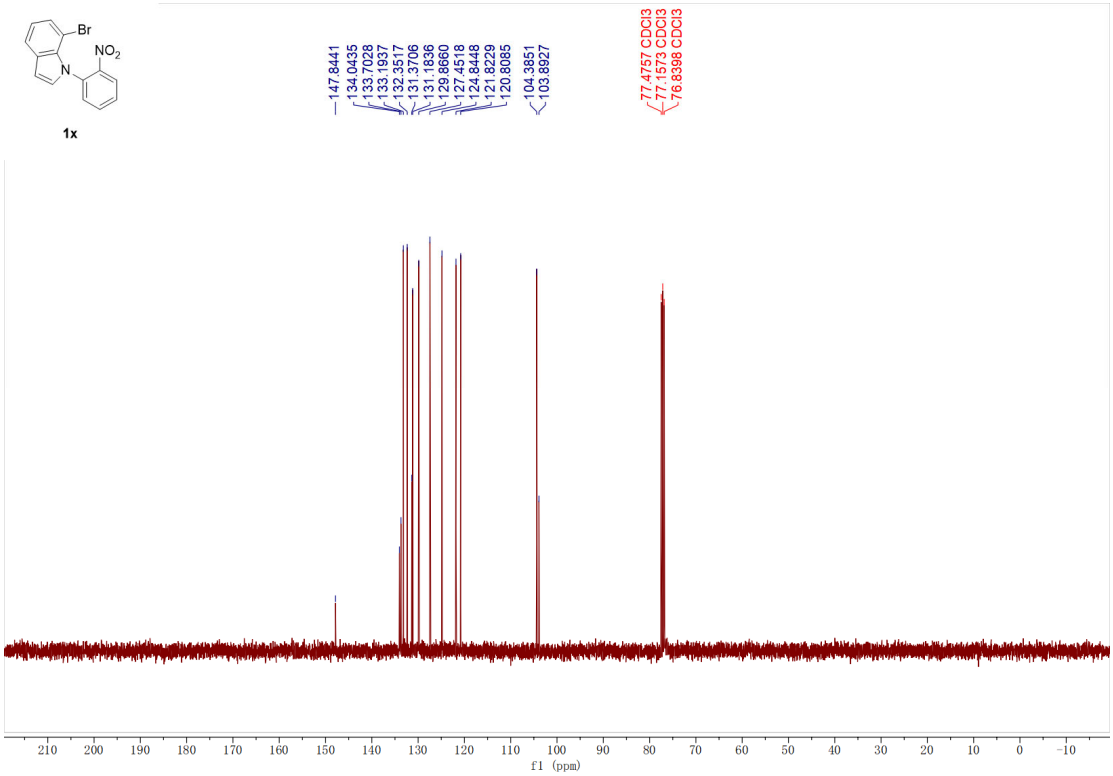


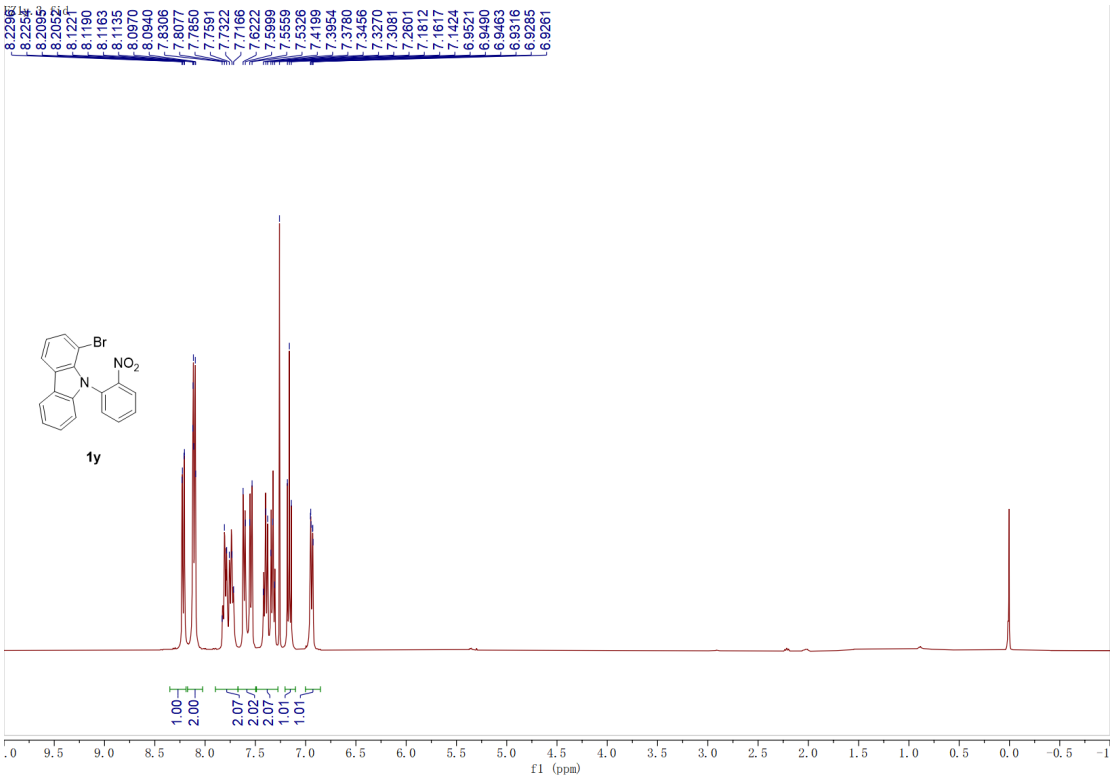

$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **1w**



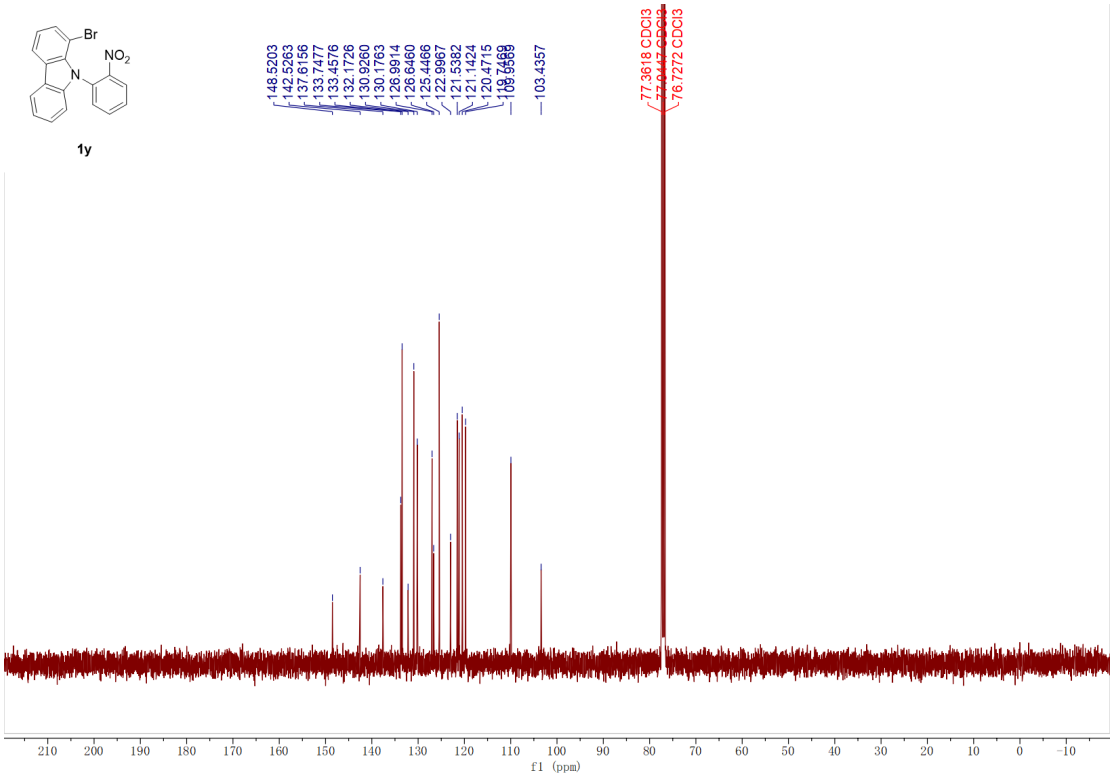

$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **1x**



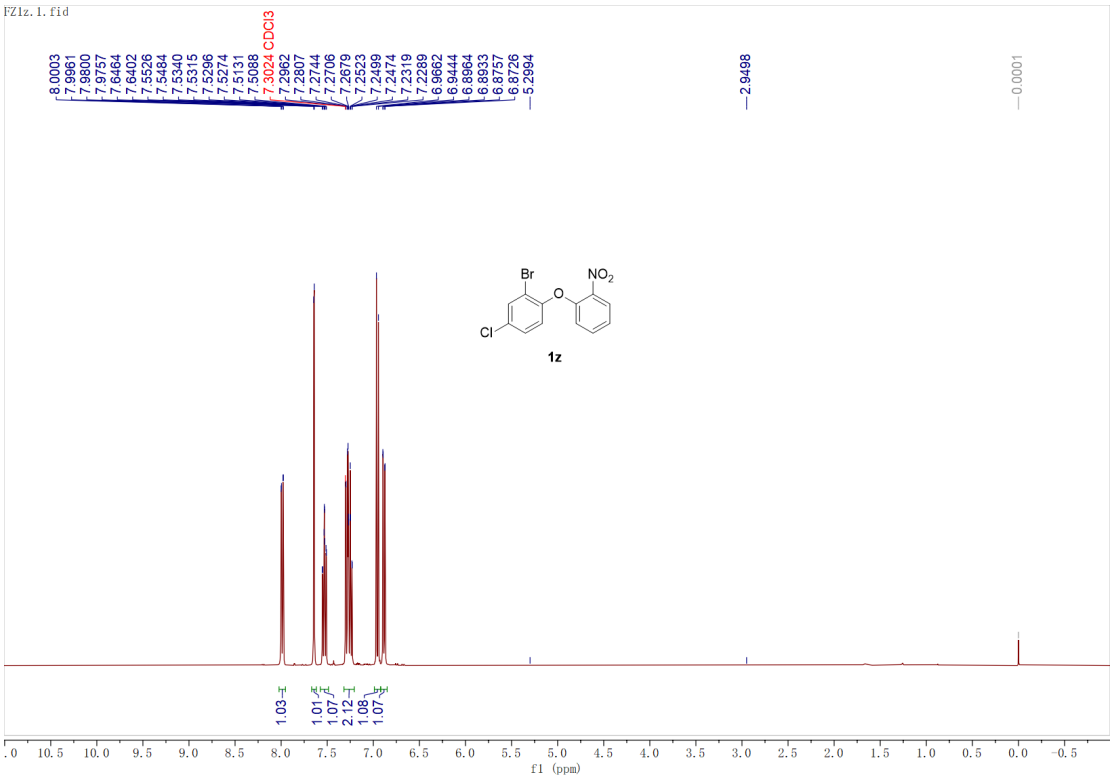

$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **1x**



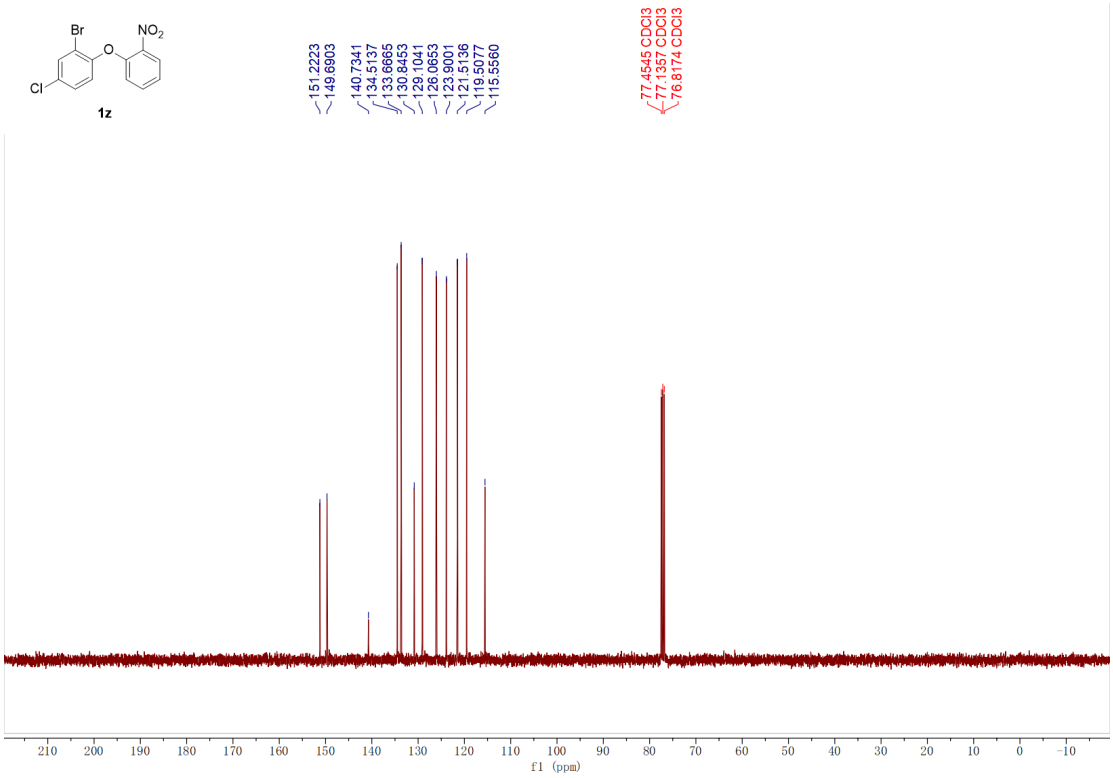

$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **1y**



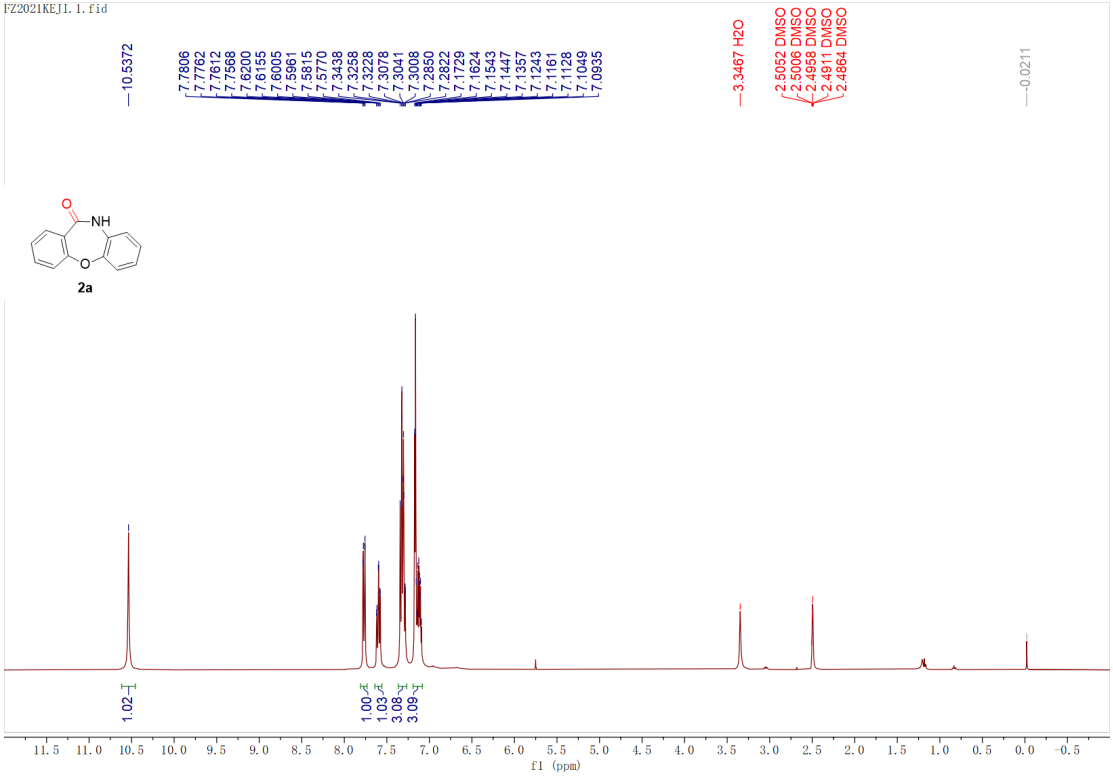

$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **1y**



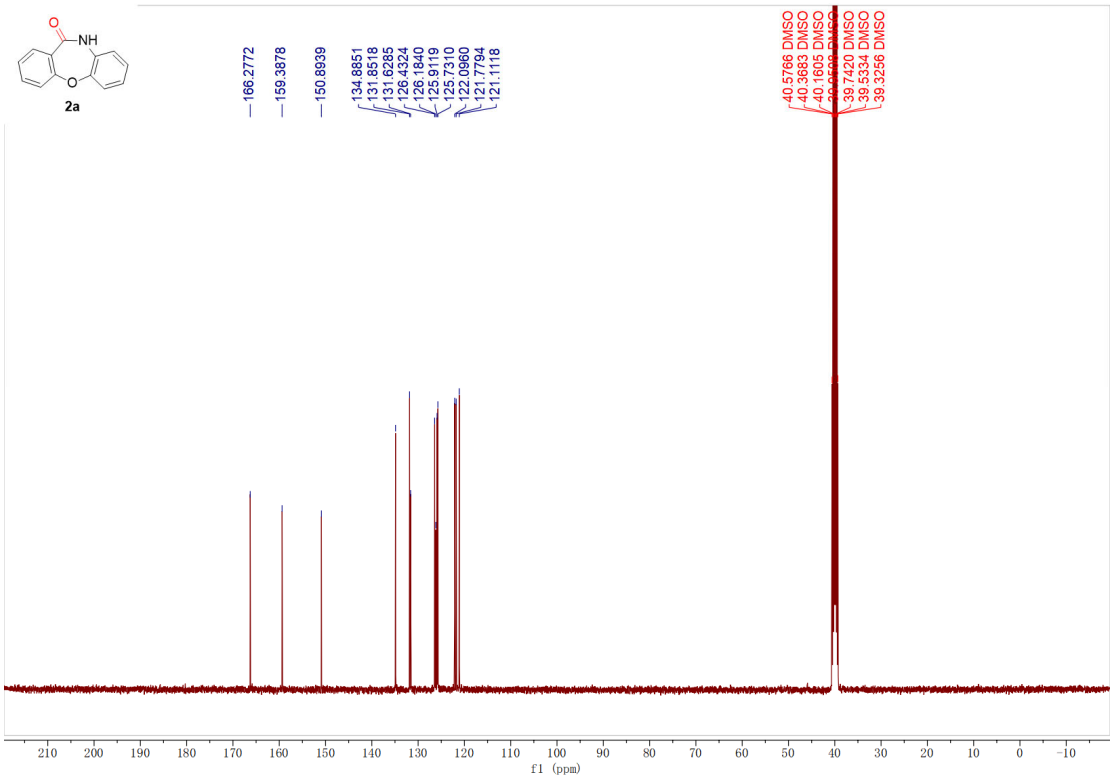

$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **1z**



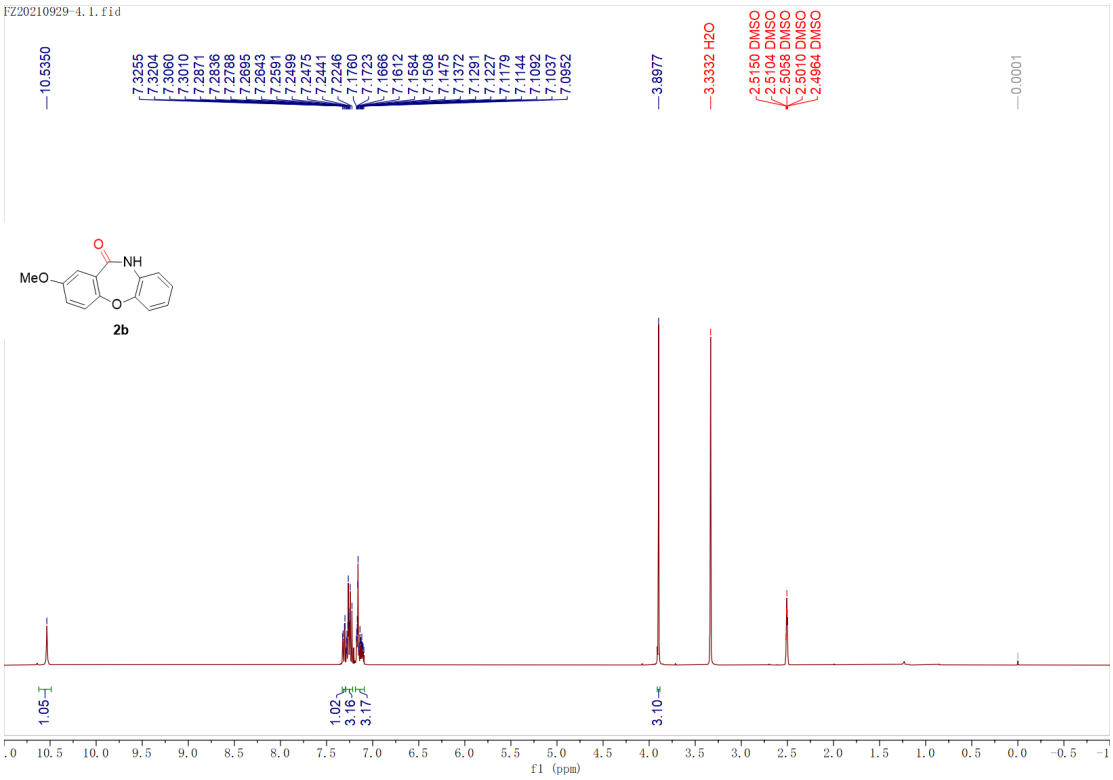

$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **1z**



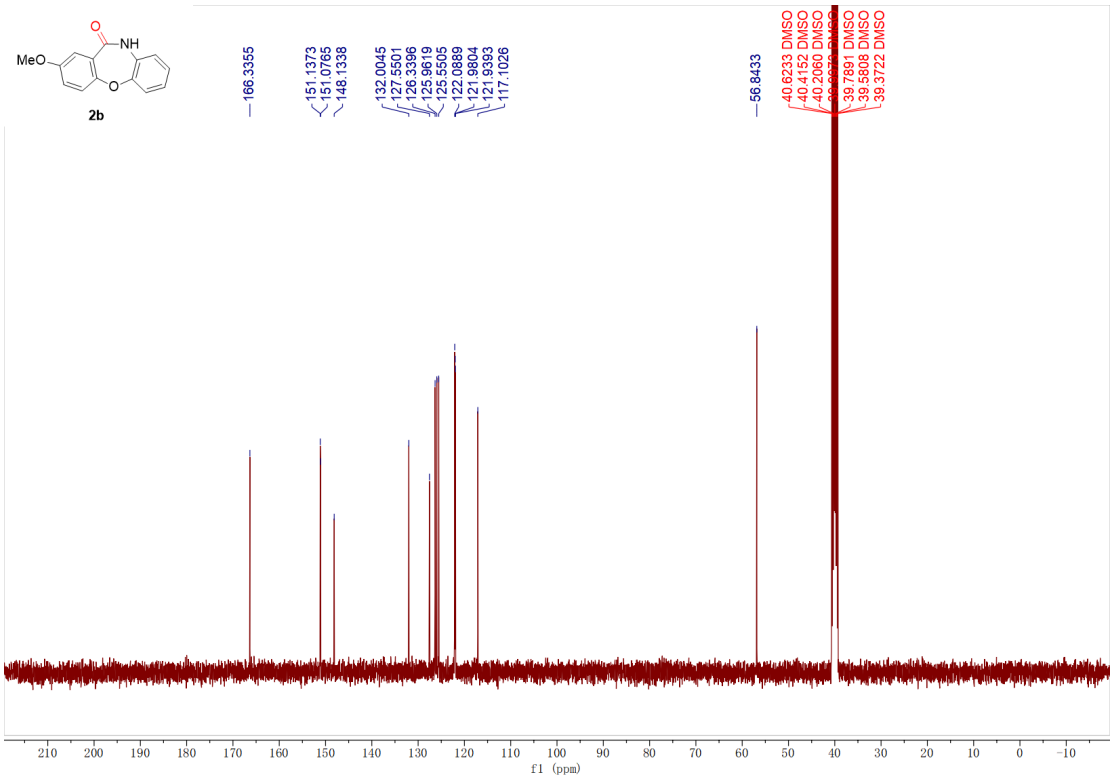

$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **2a**



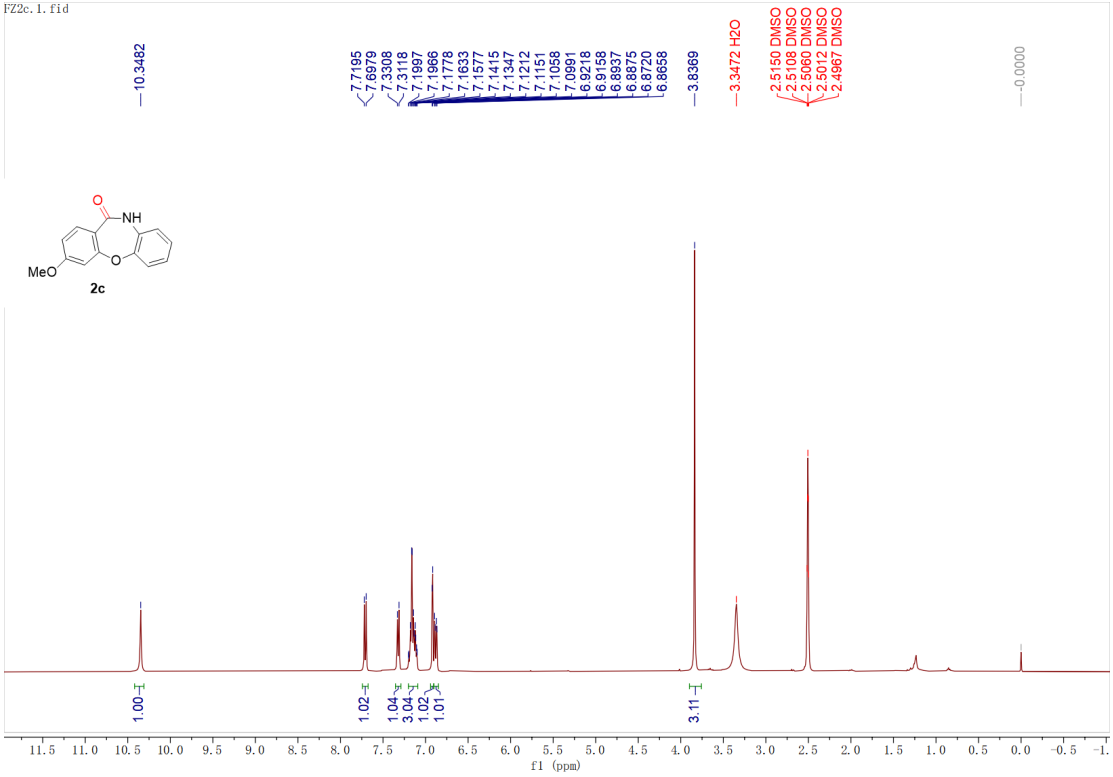

$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **2a**



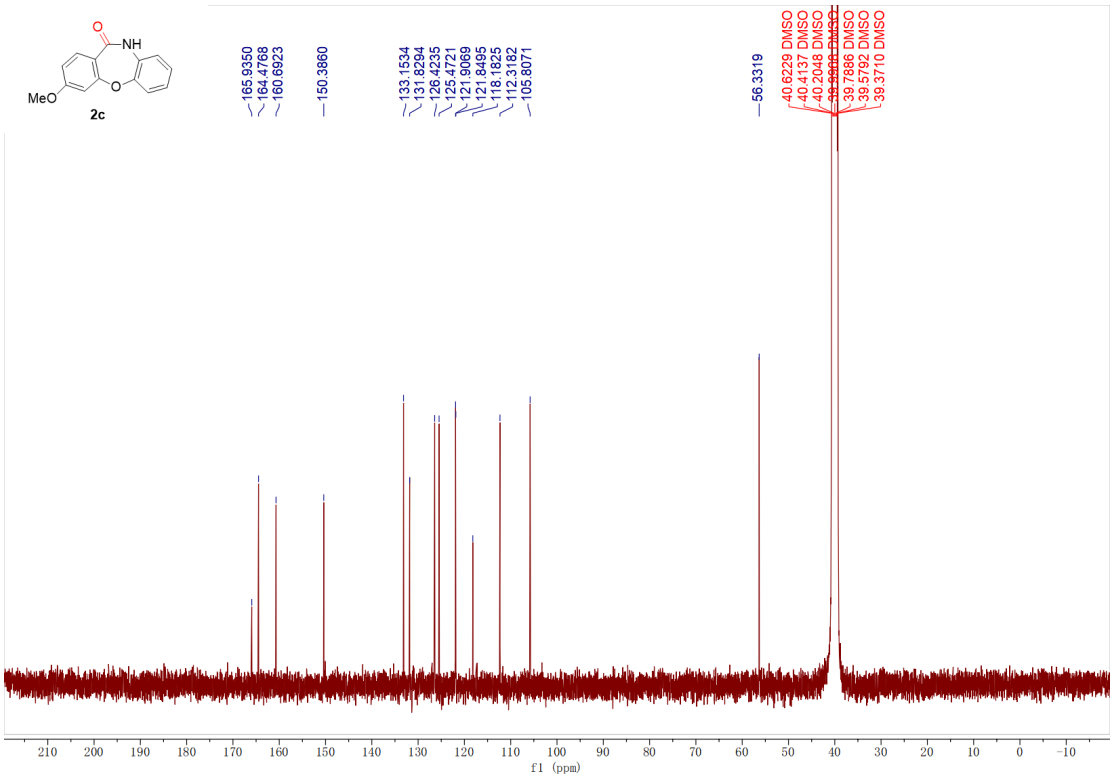

$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **2b**



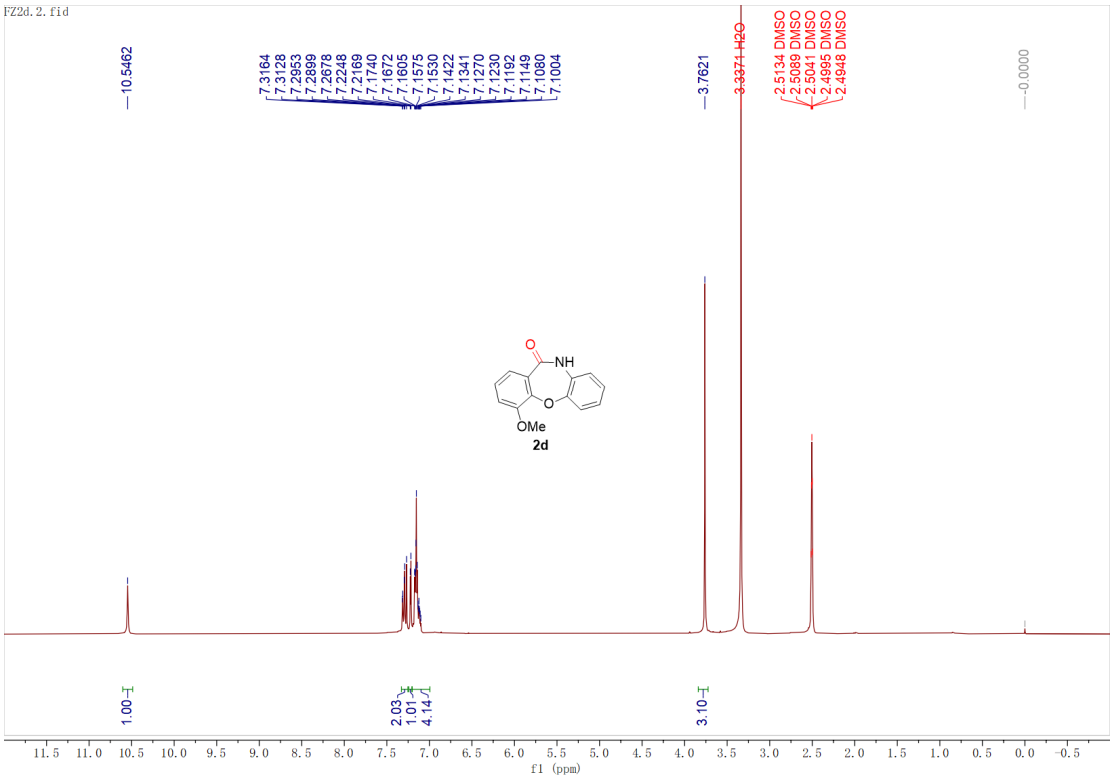

$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **2b**



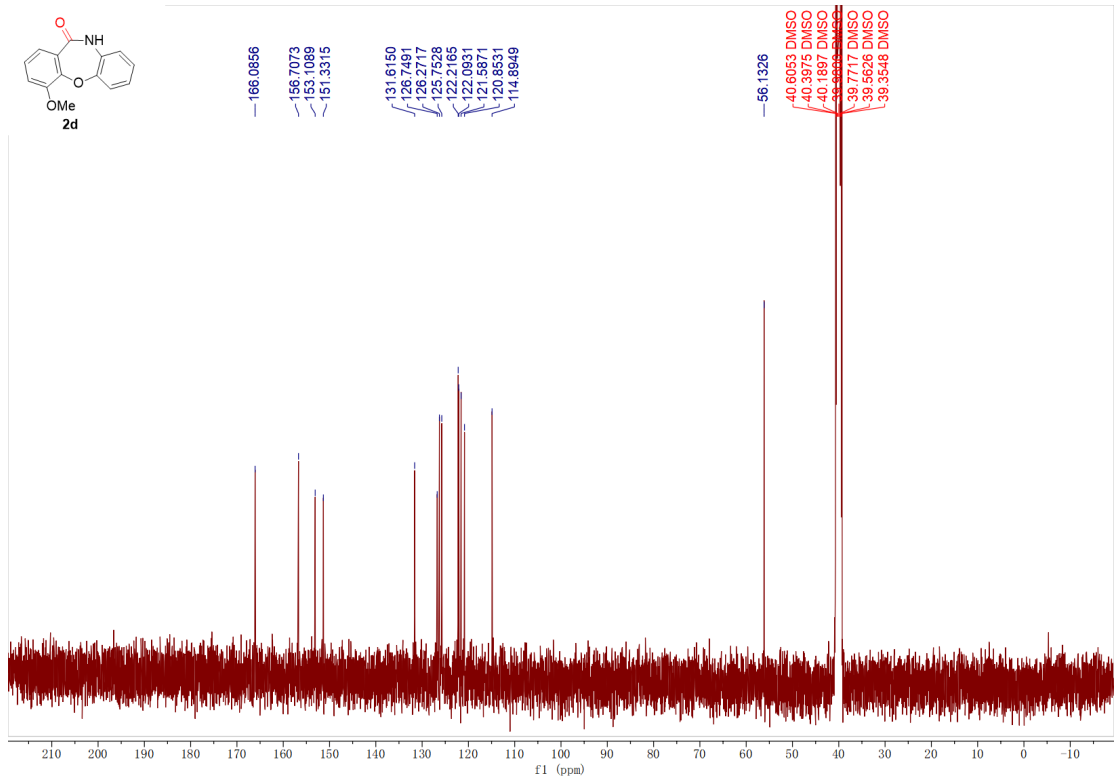

$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **2c**



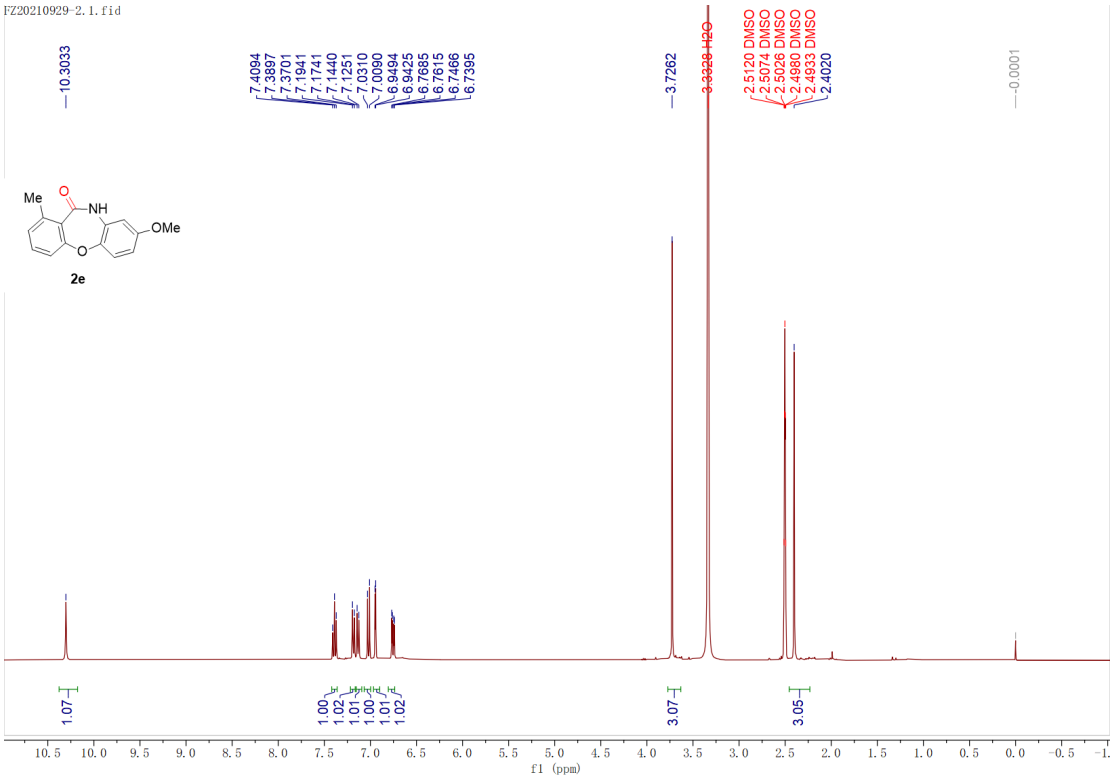

$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **2c**



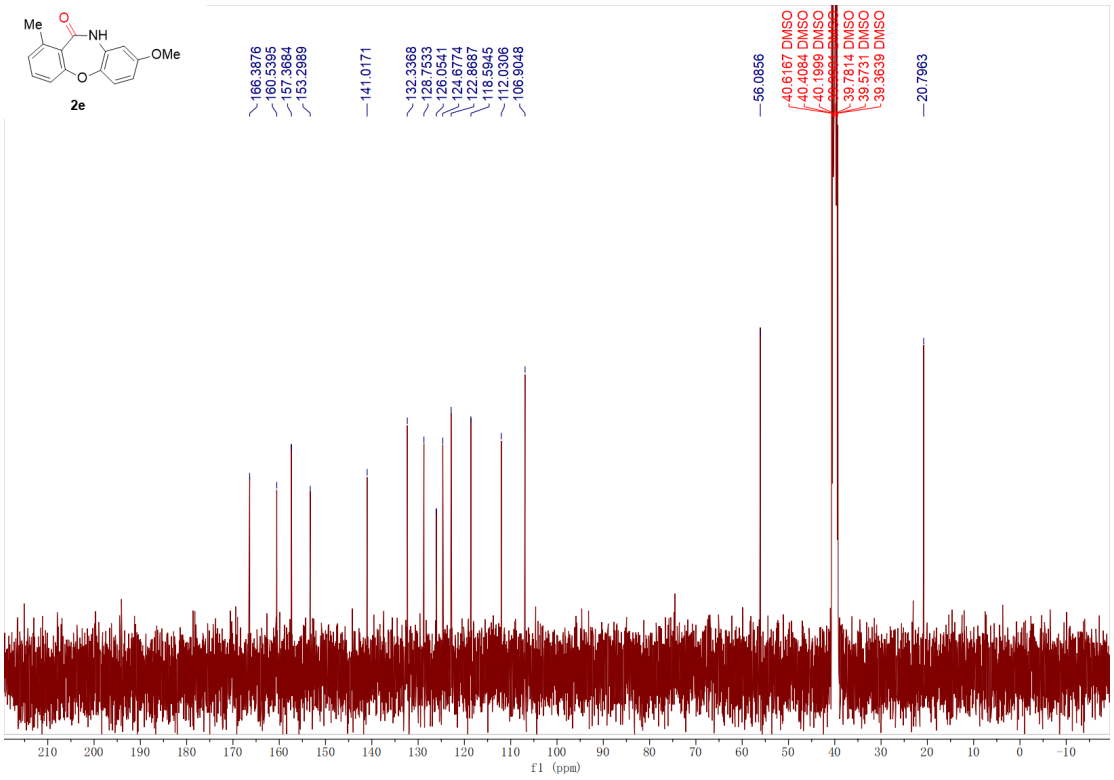

$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **2d**



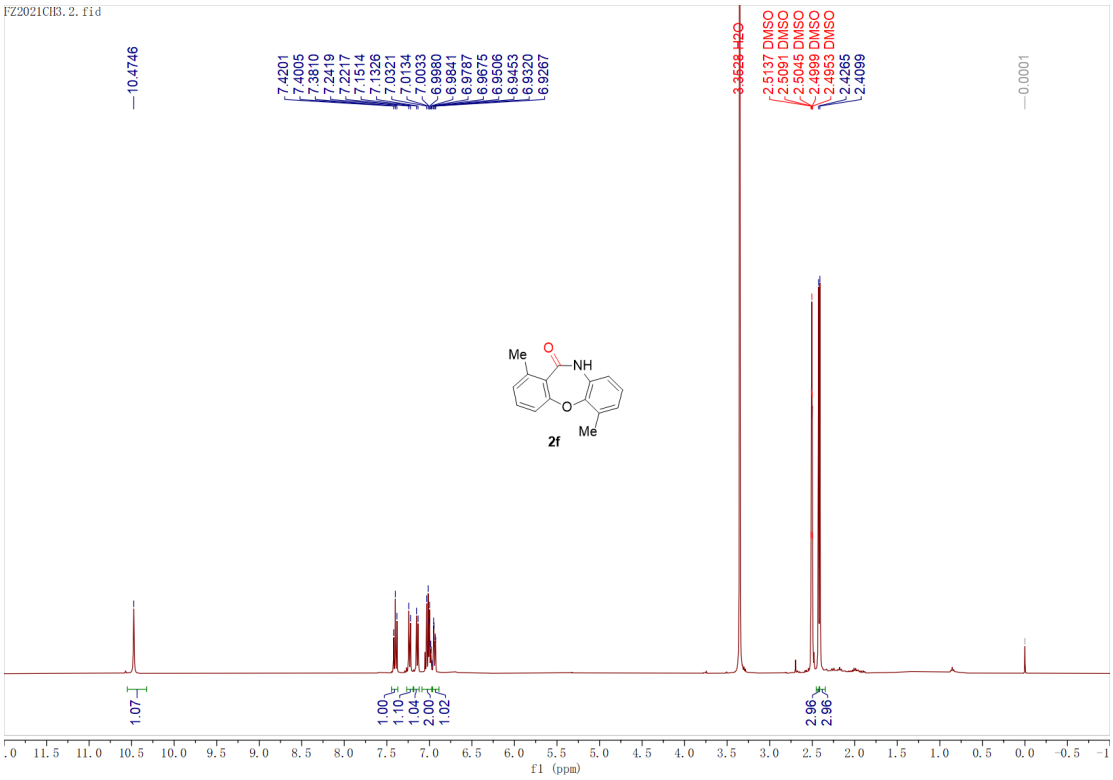

$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **2d**



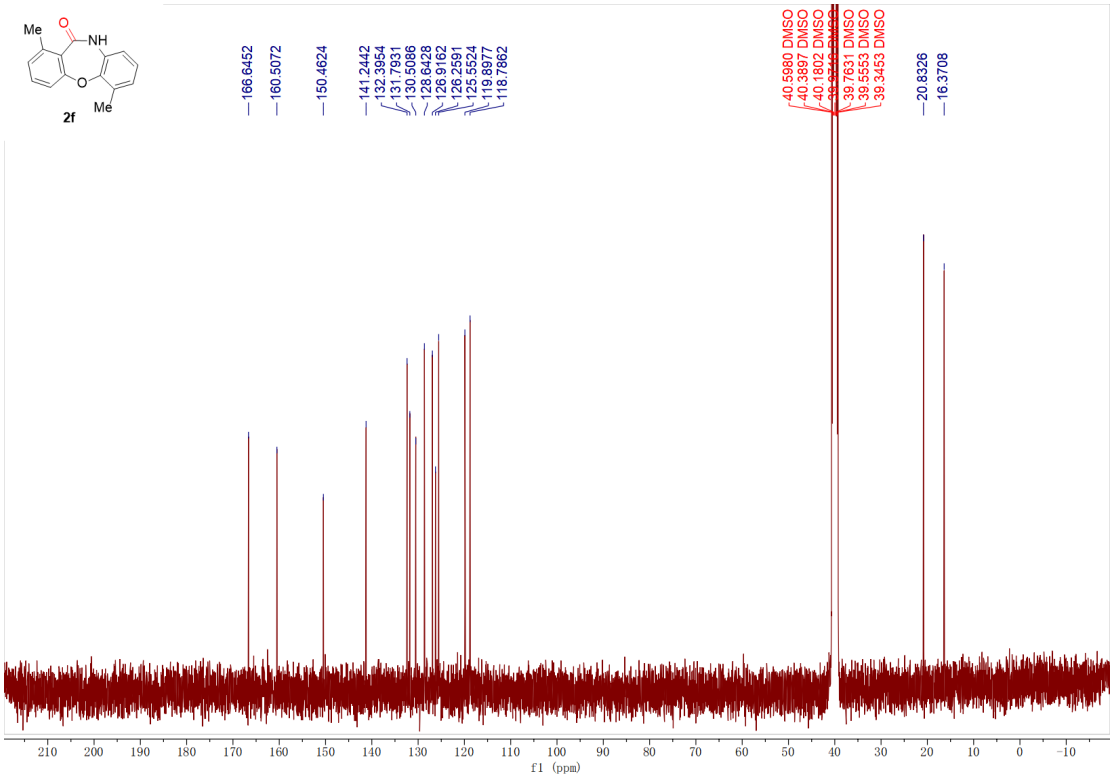

$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **2e**



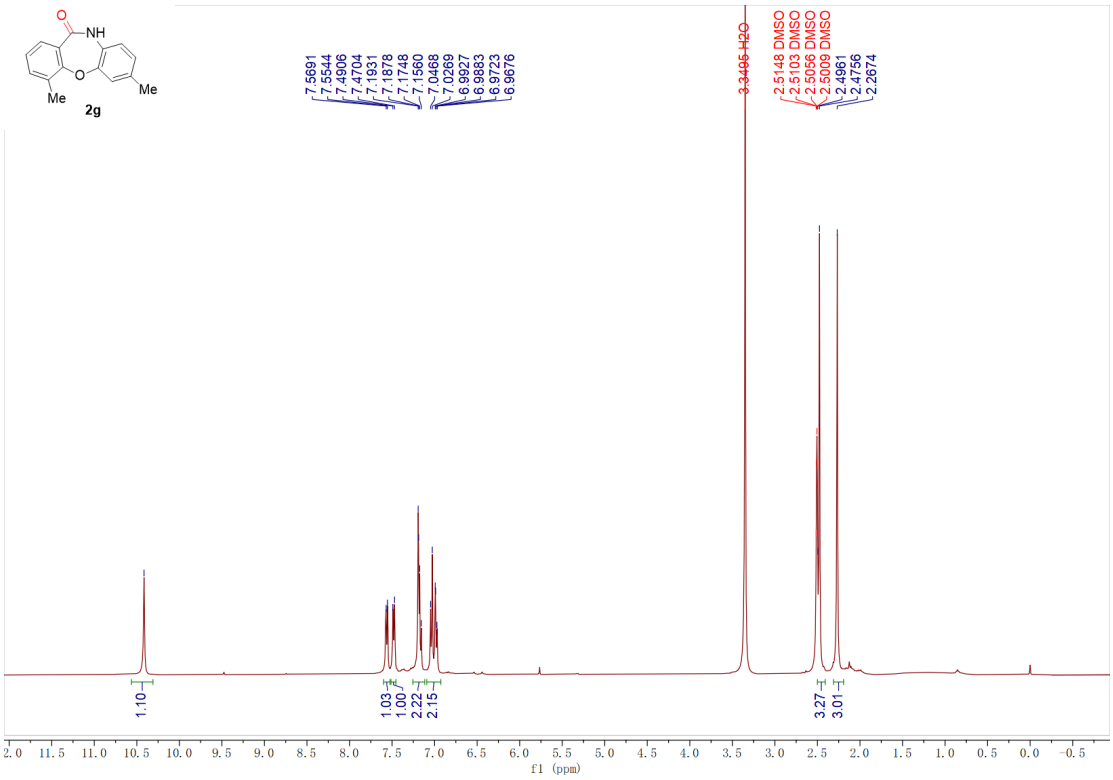

$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **2e**



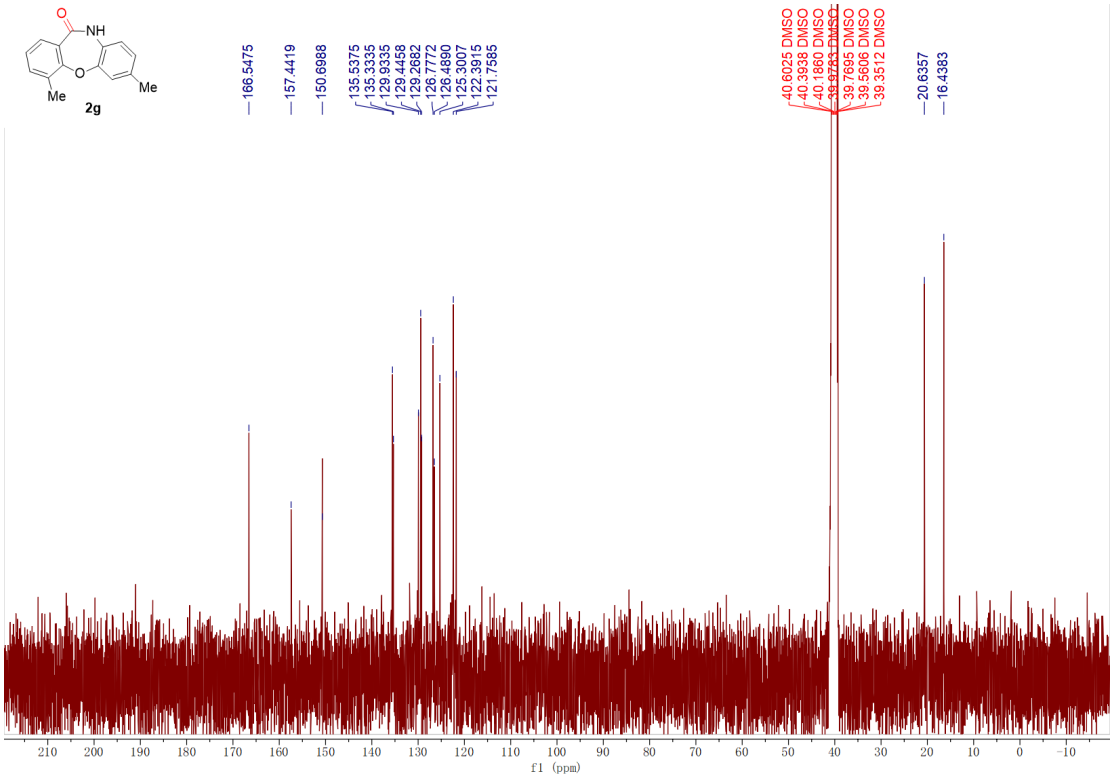

$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **2f**



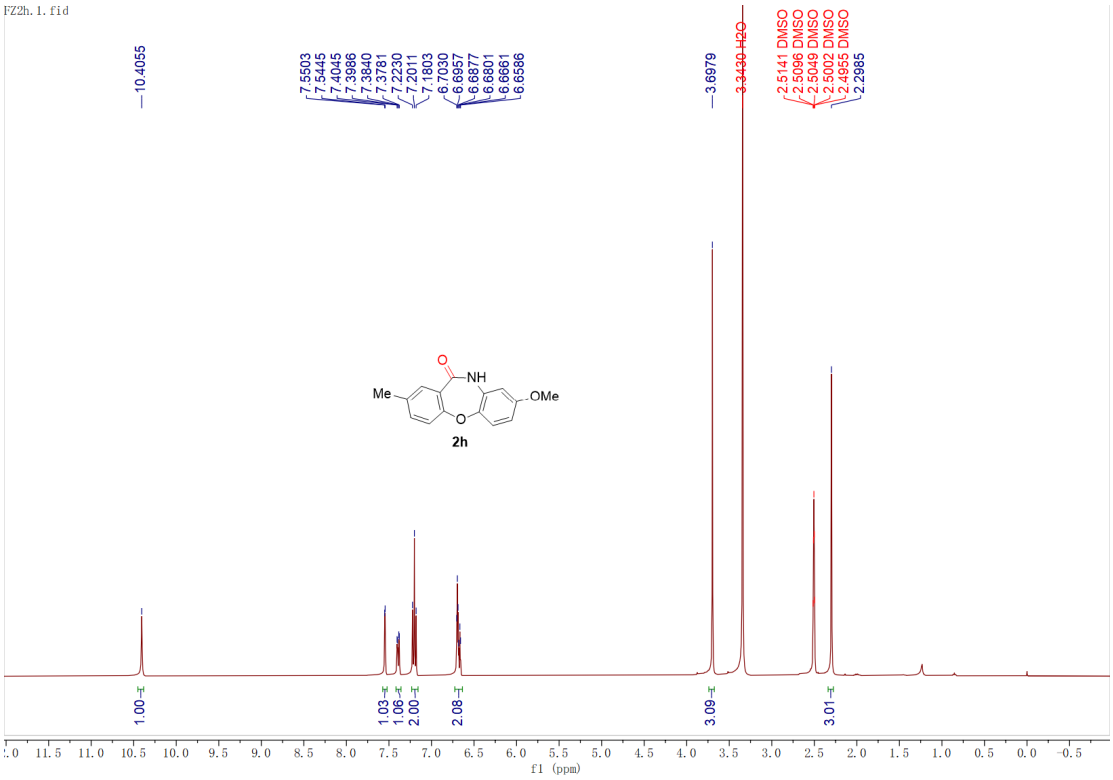

$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **2f**



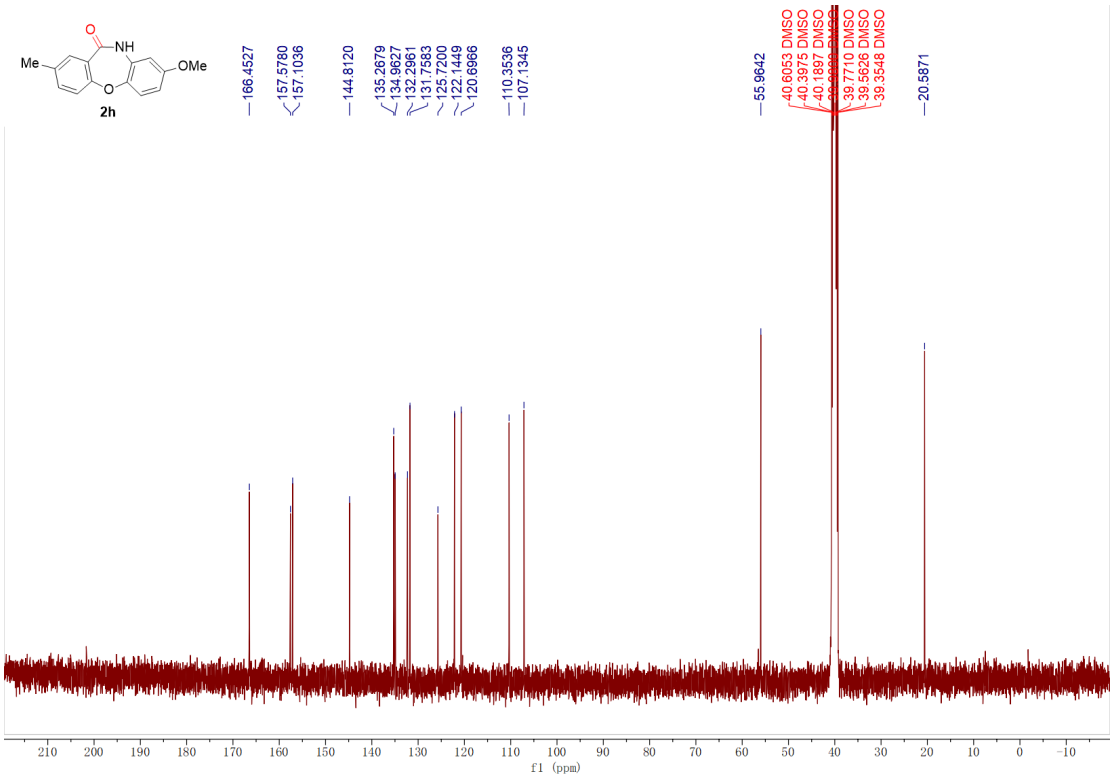

$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **2g**



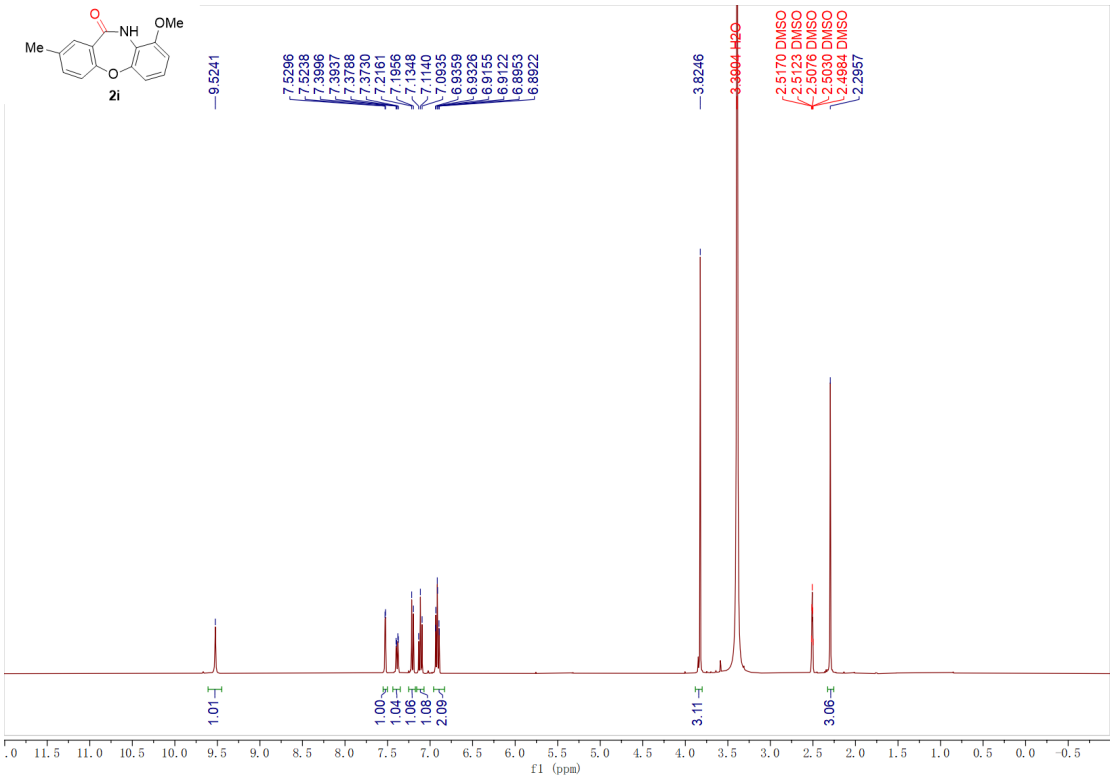

$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **2g**



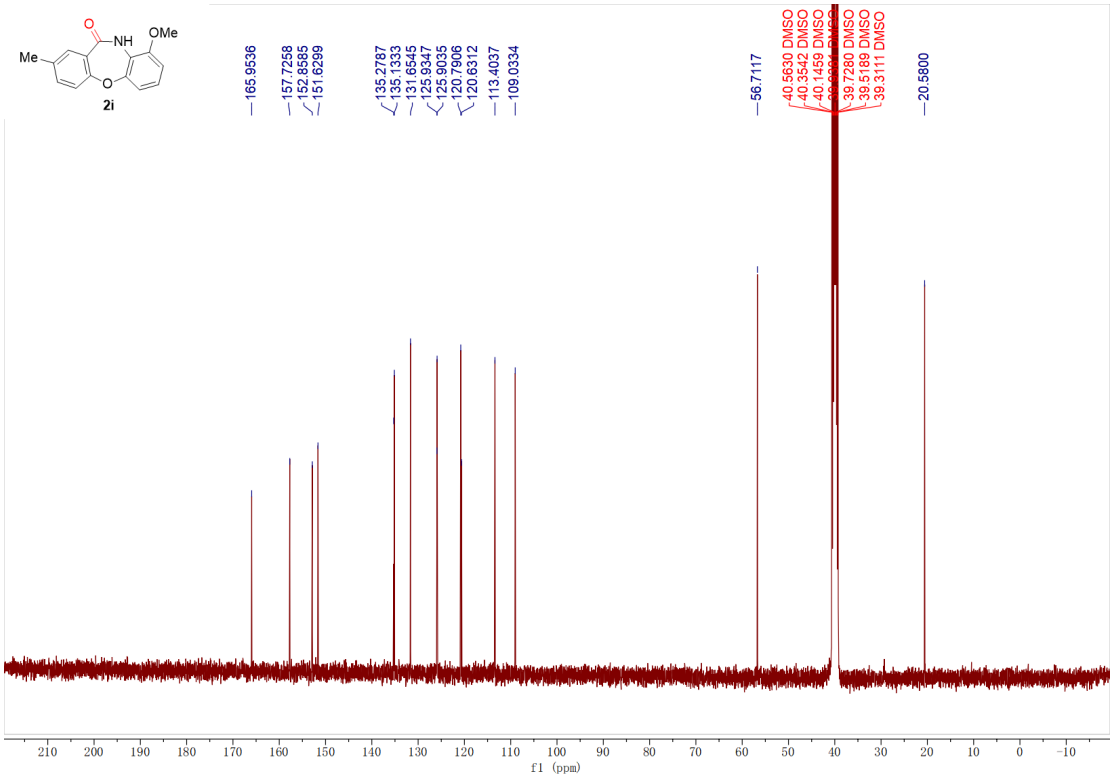

$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **2h**



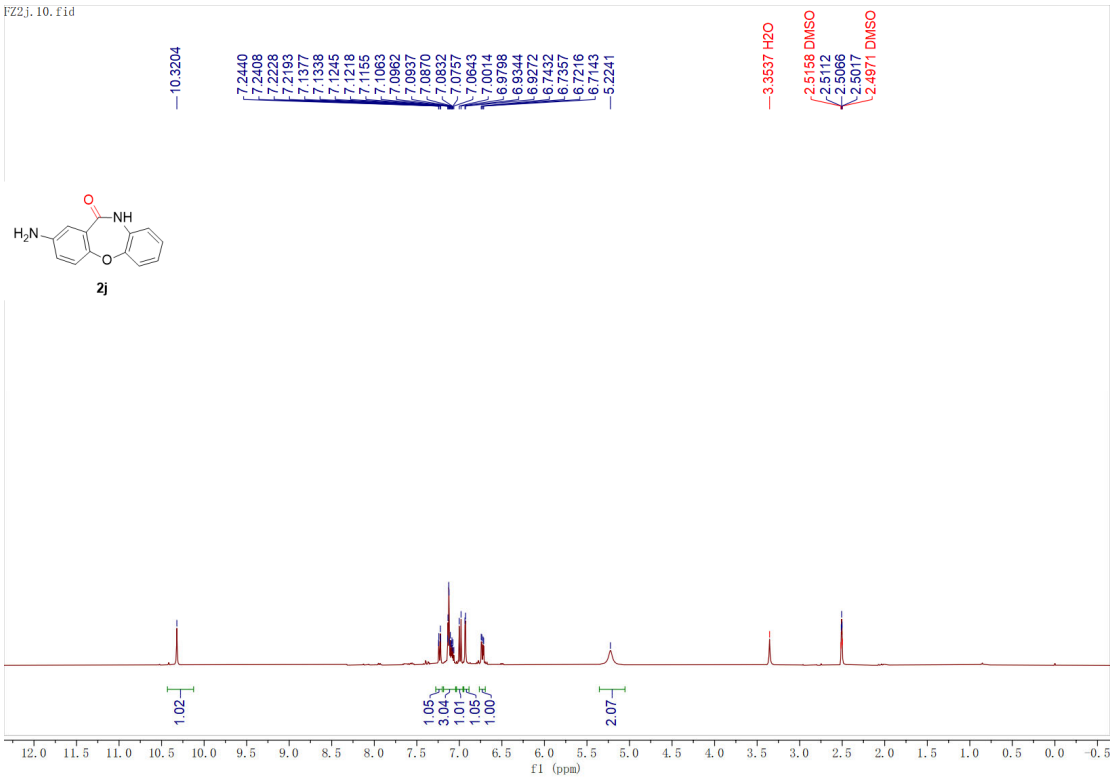

$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **2h**



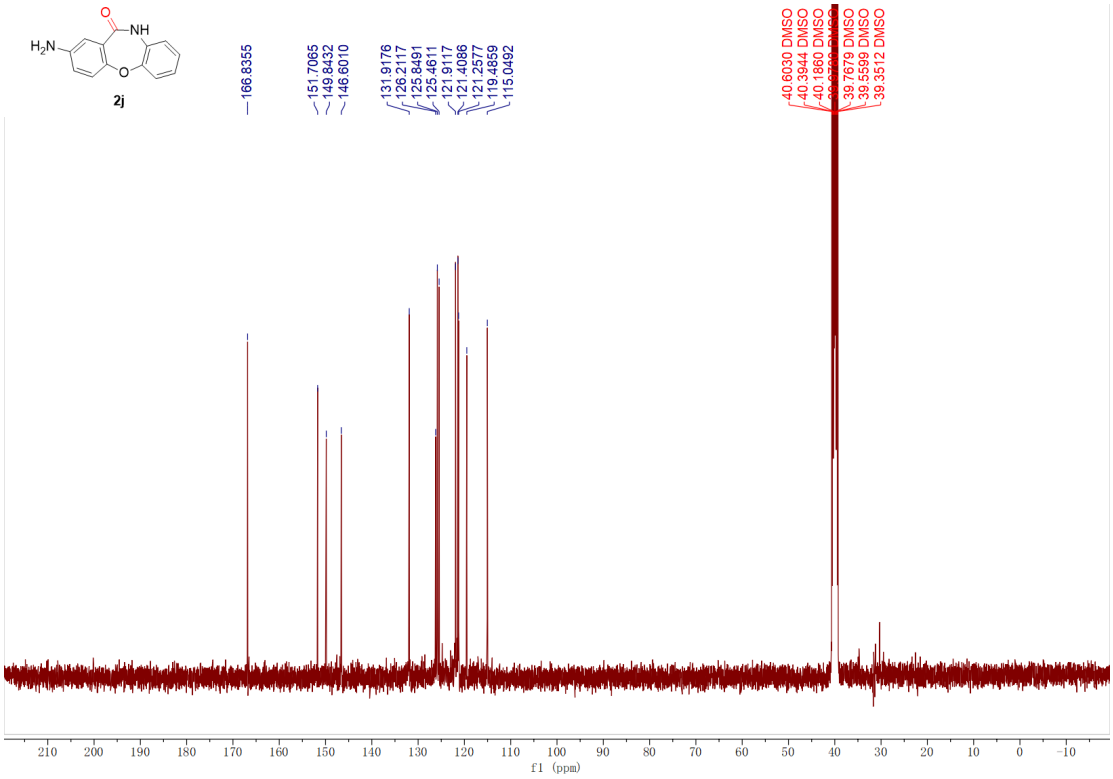

$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **2i**



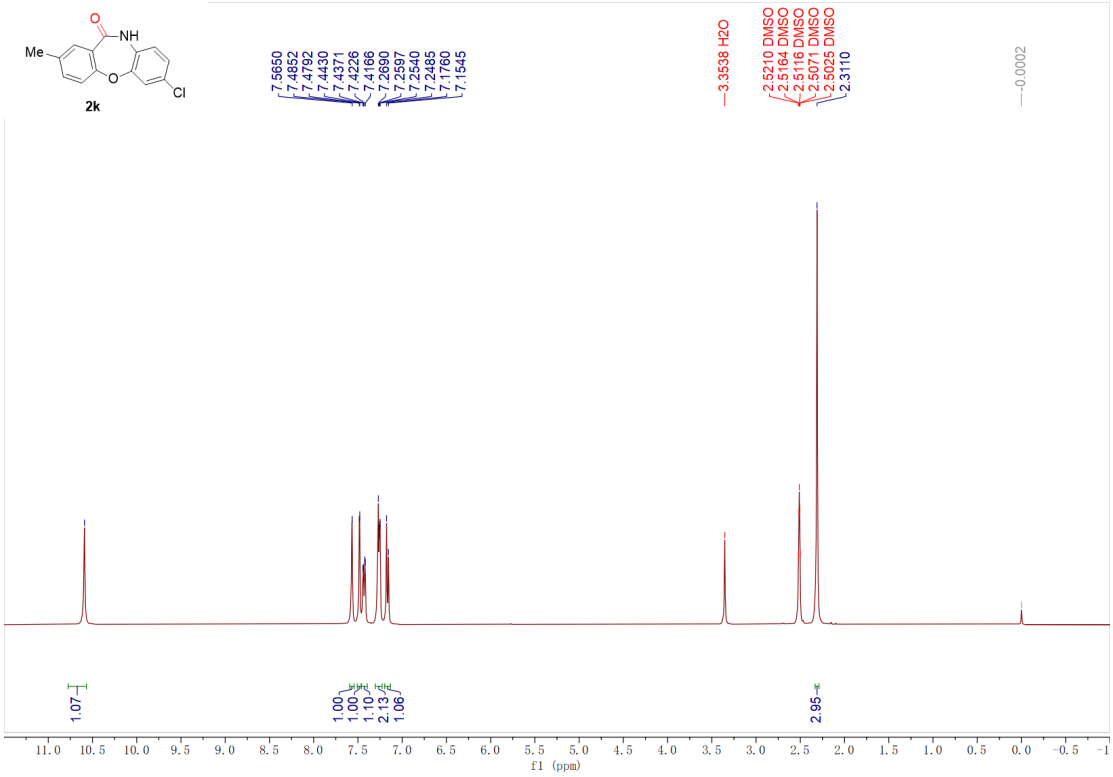

$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **2i**



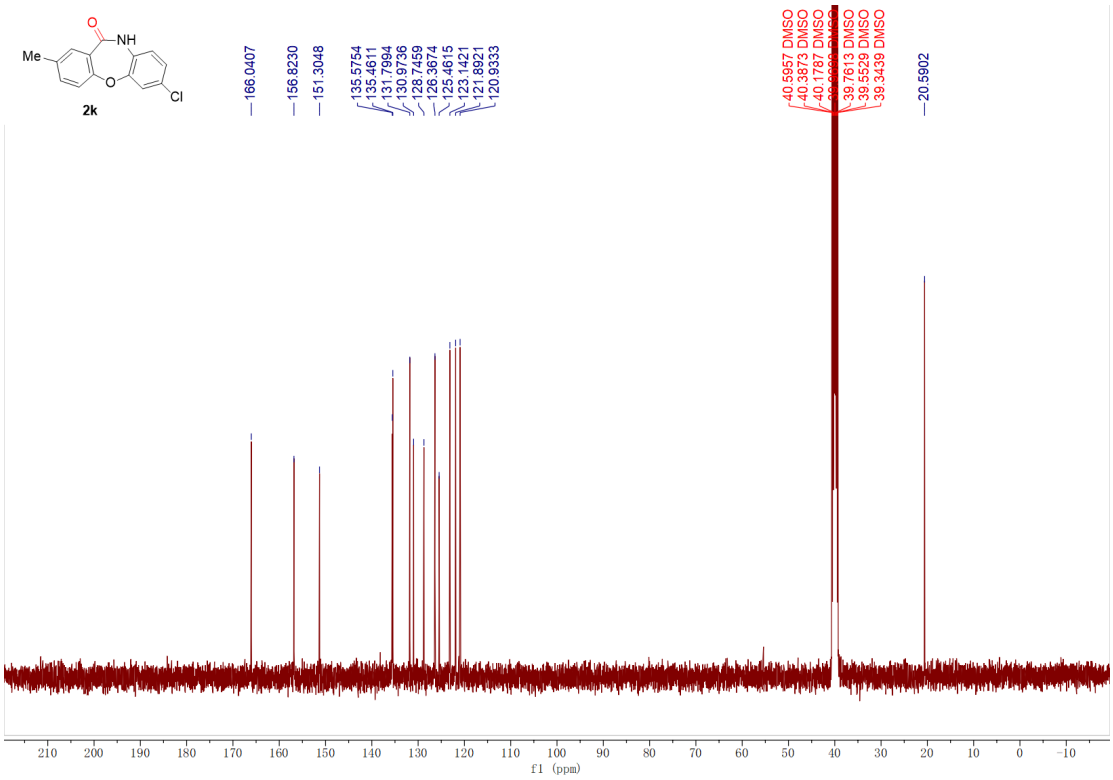

$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **2j**



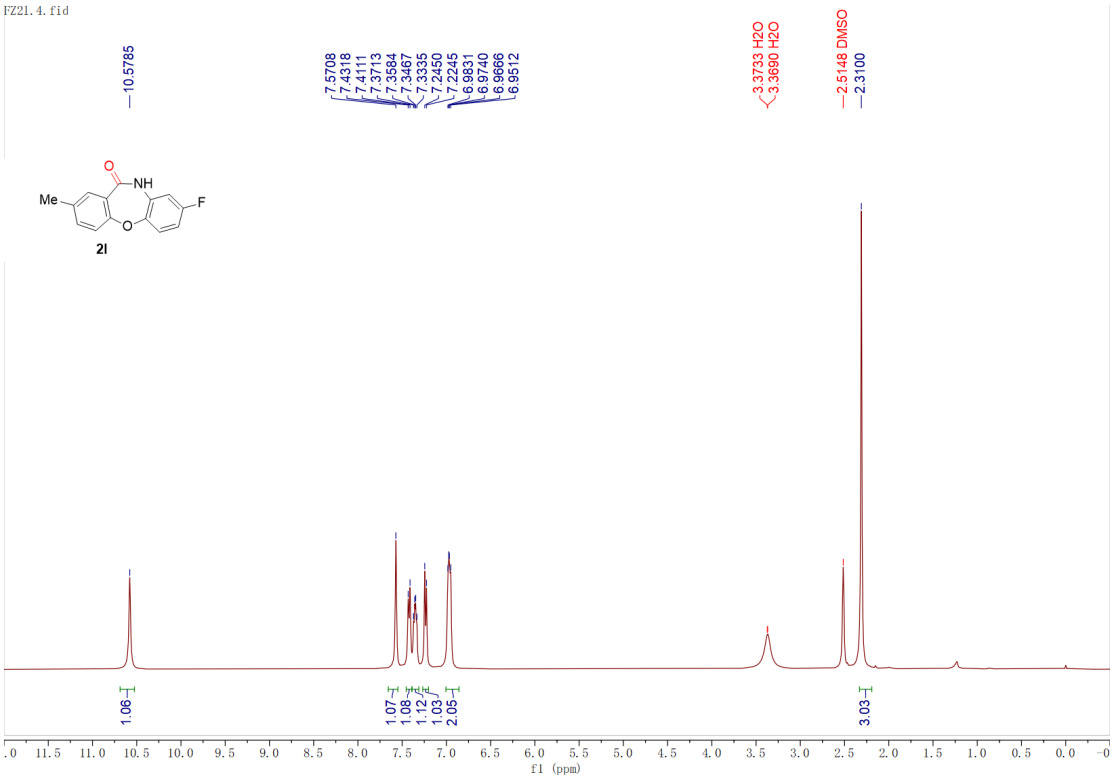

$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **2j**



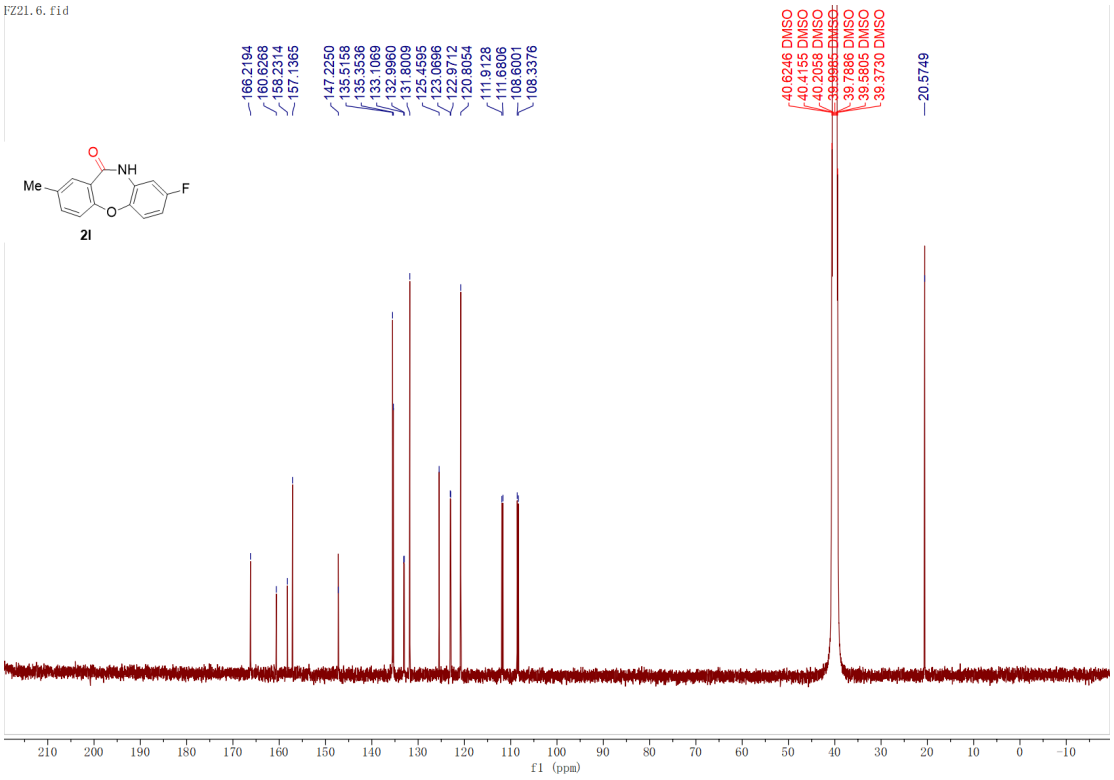

$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **2k**



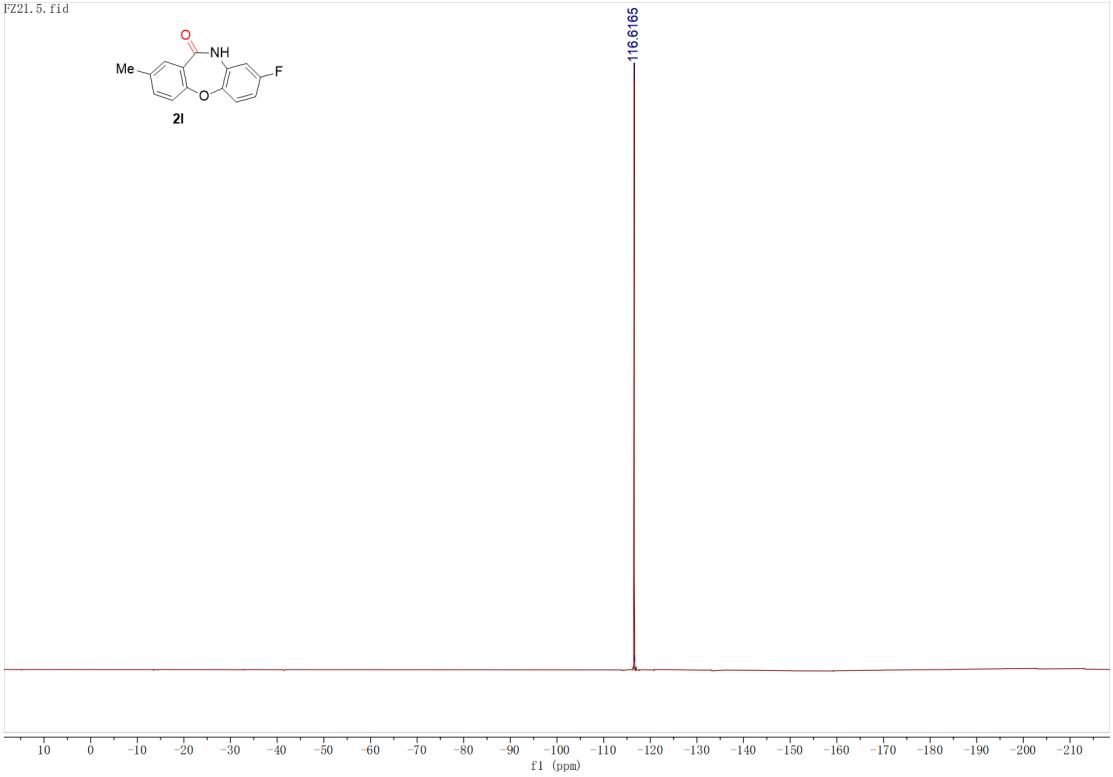

$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **2k**



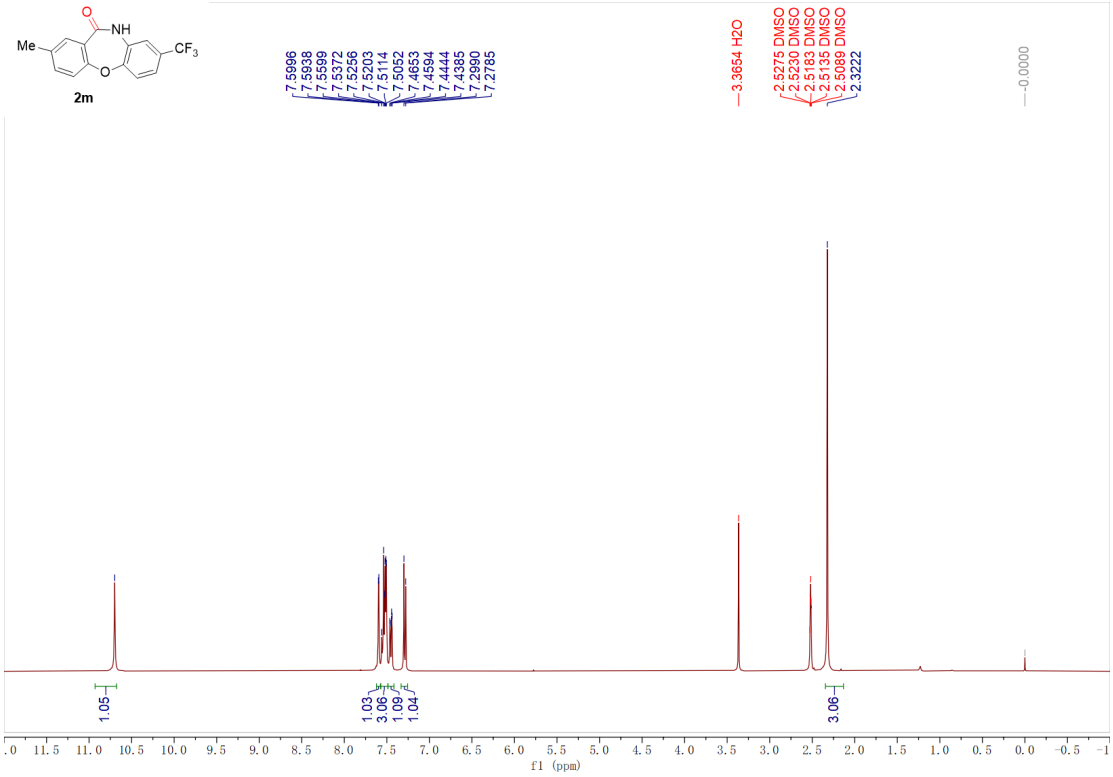

$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **2l**



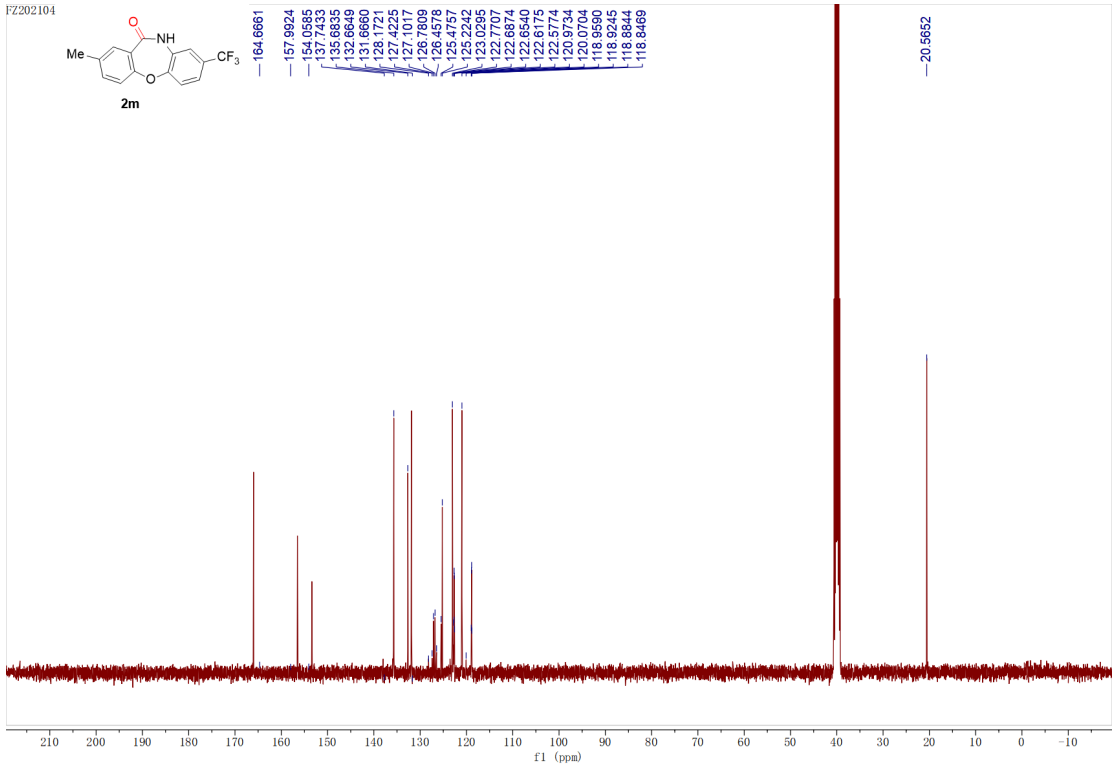

$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **2l**



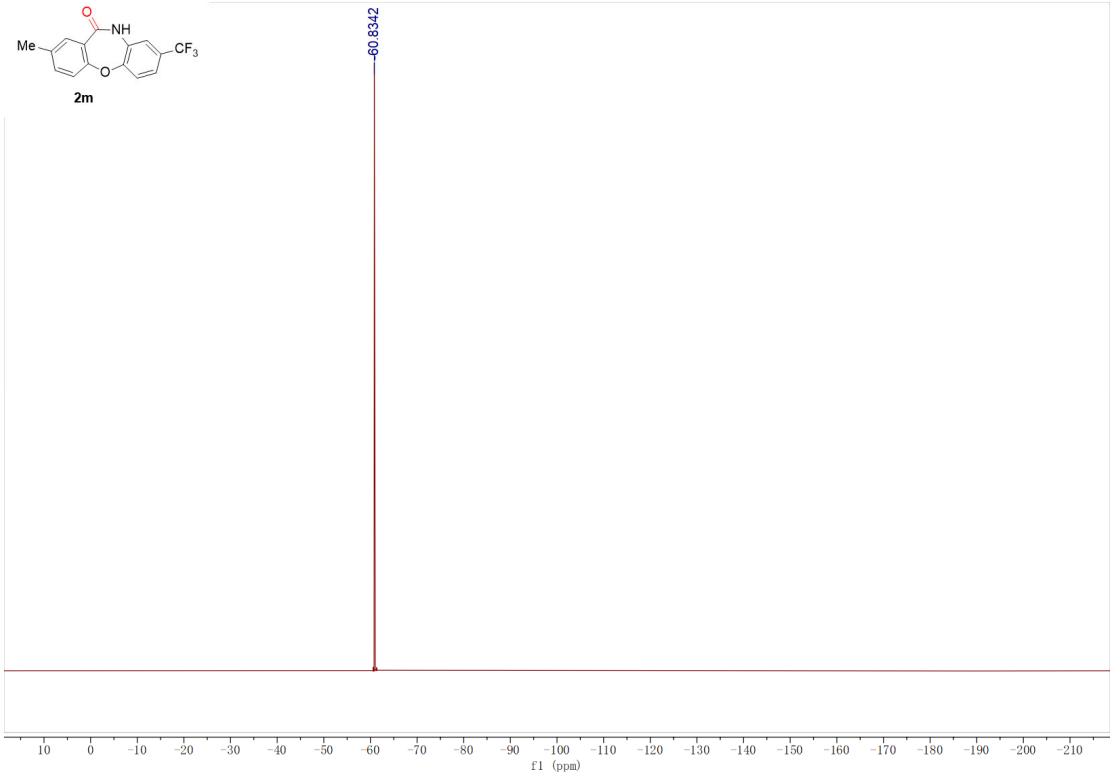

$^{19}$F NMR spectra (376 MHz, Chloroform-*d*) of **2l**



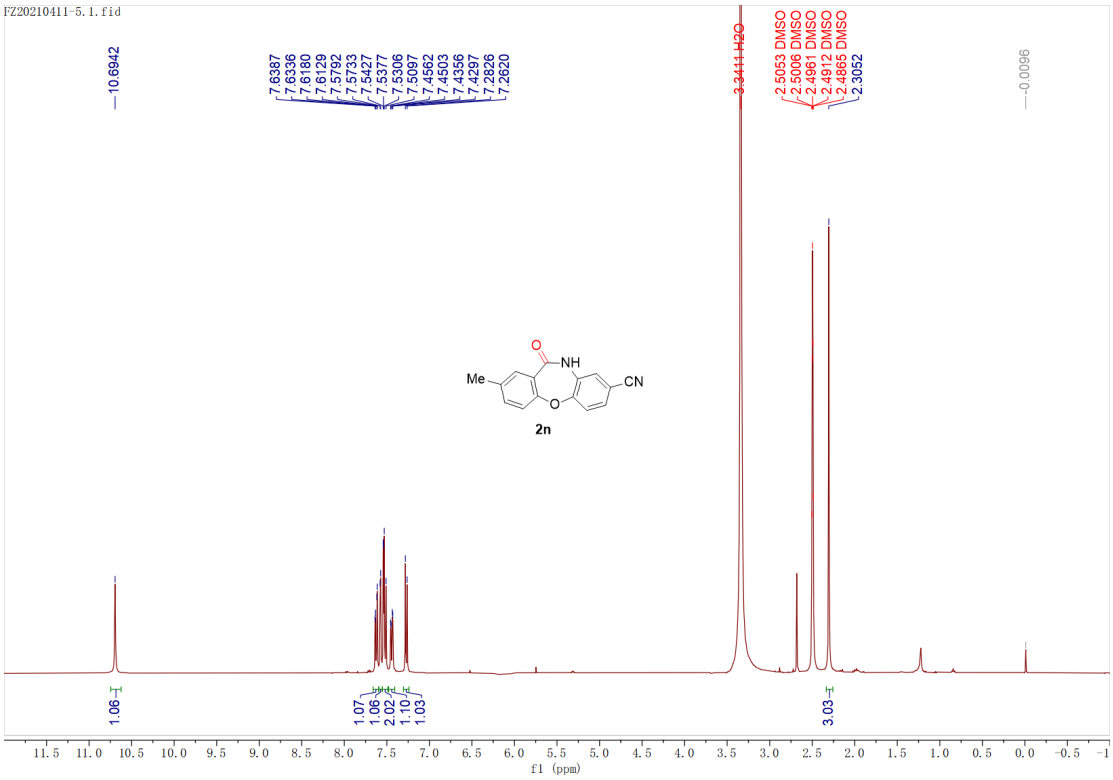

$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **2m**



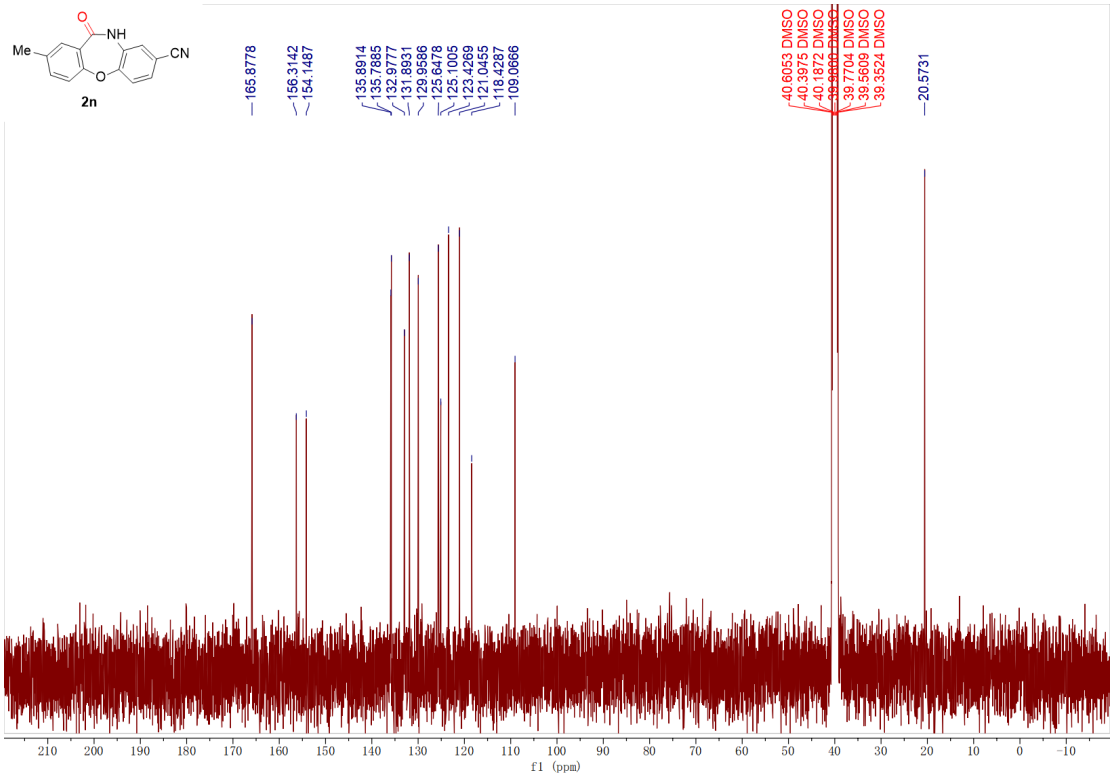

$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **2m**



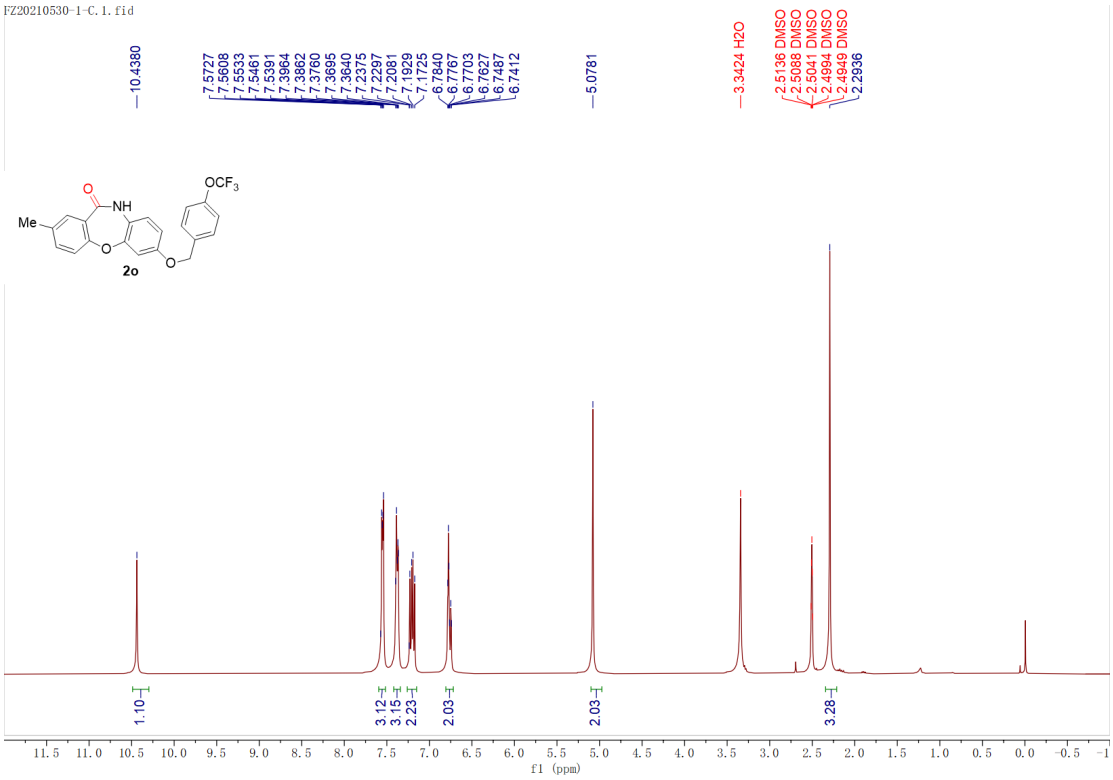

$^{19}$F NMR spectra (376 MHz, Chloroform-*d*) of **2m**



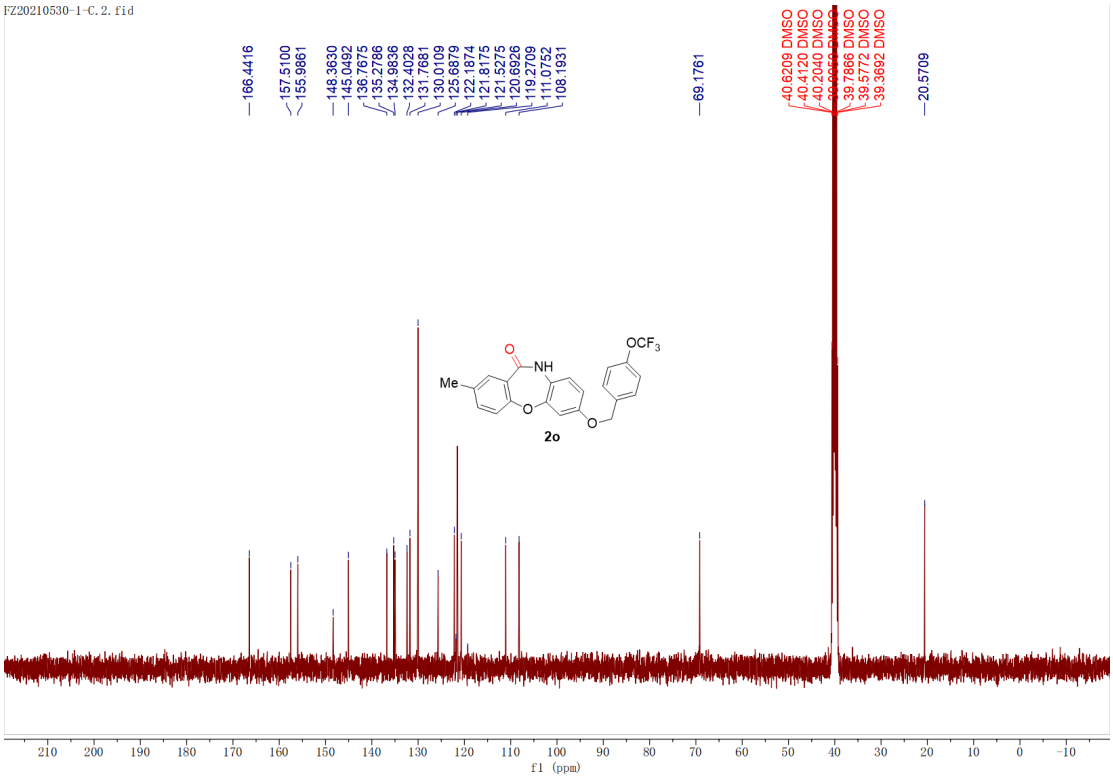

$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **2n**



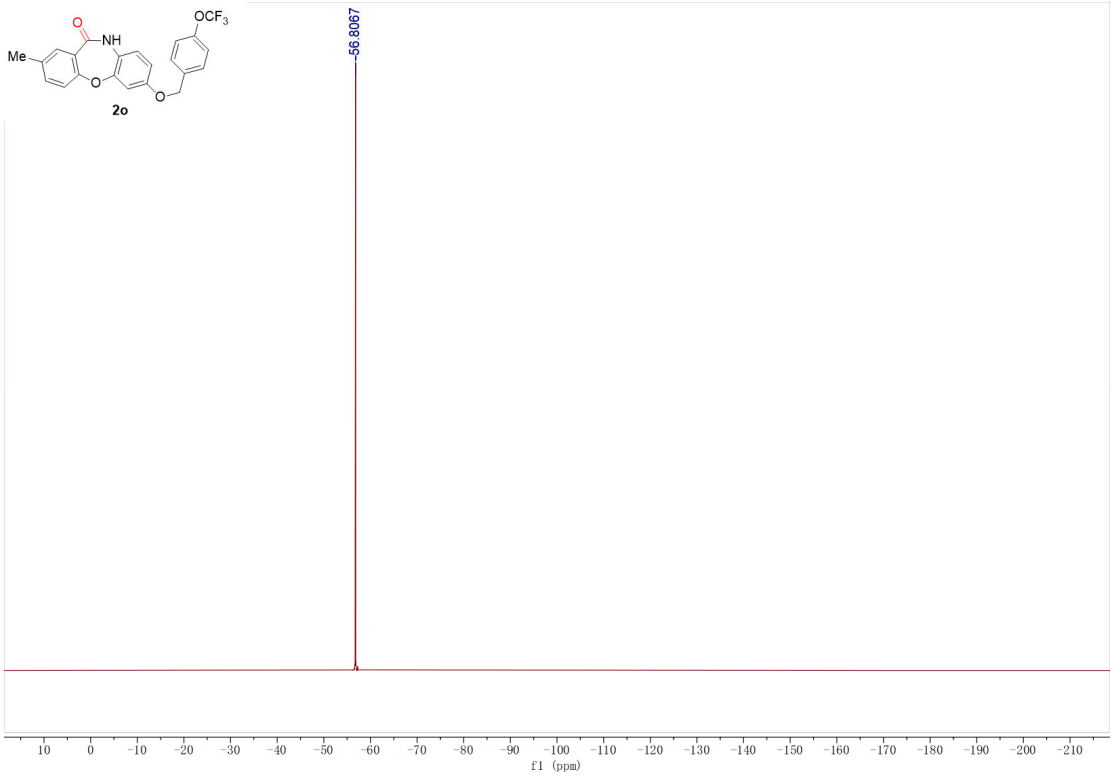

$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **2n**



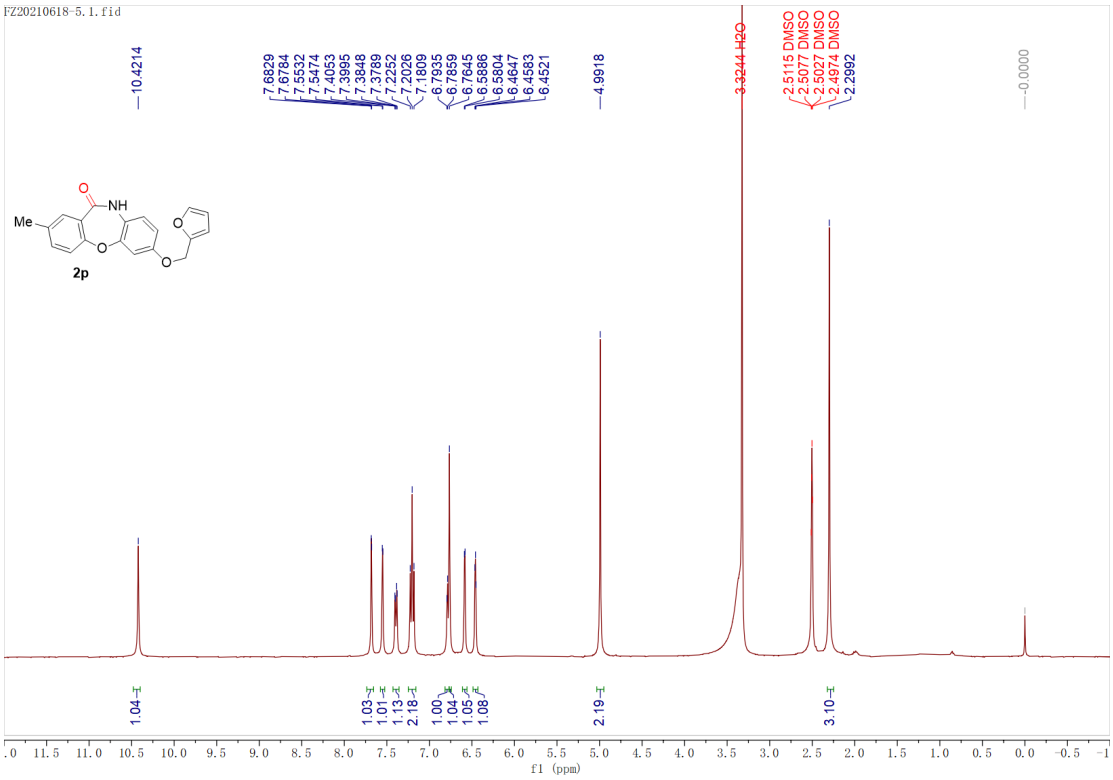

$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **2o**



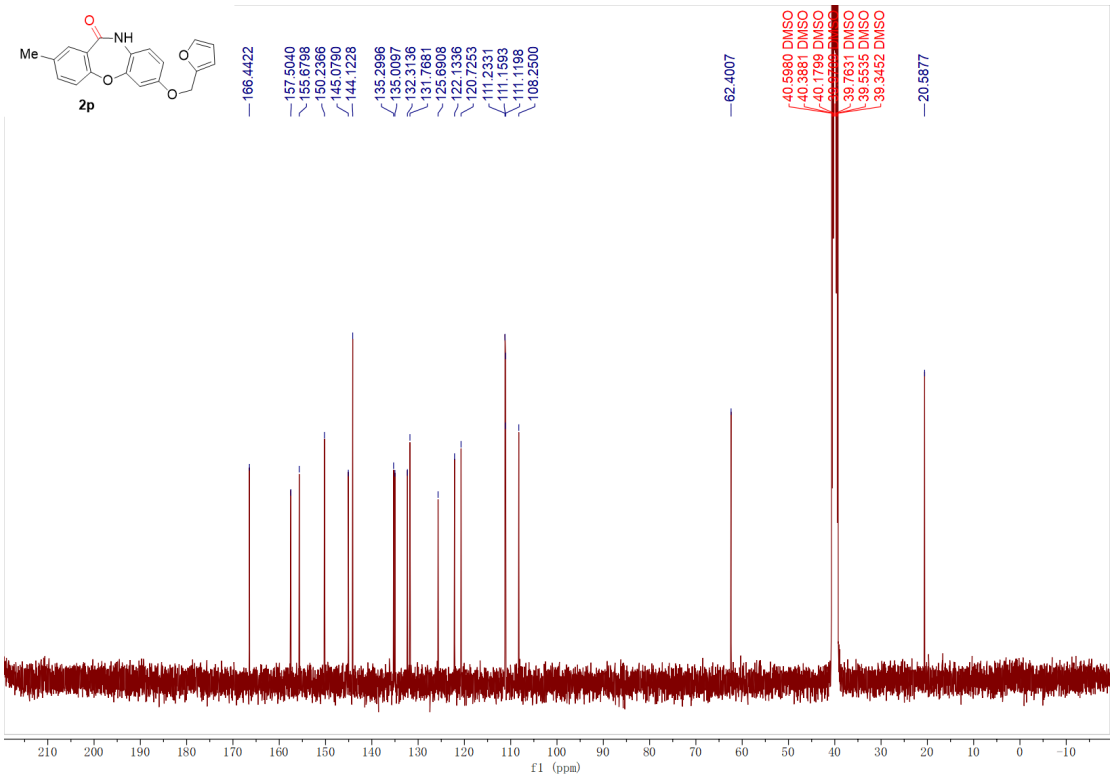

$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **2o**



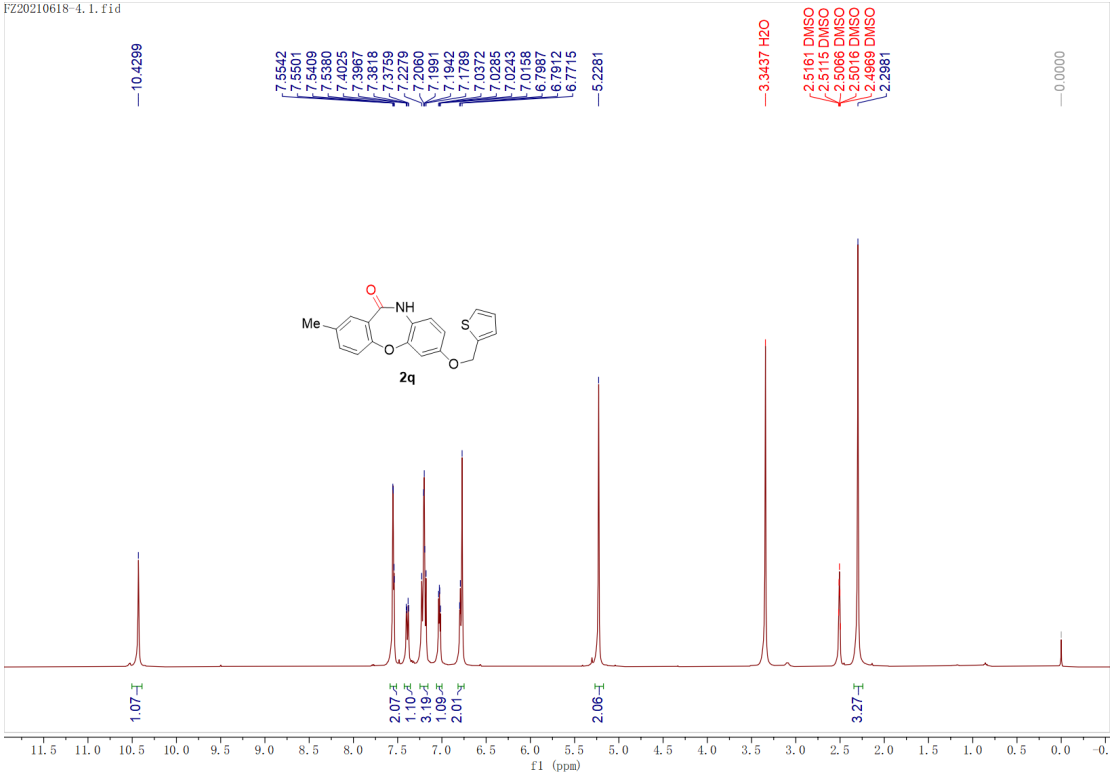

$^{19}$F NMR spectra (376 MHz, Chloroform-*d*) of **2o**



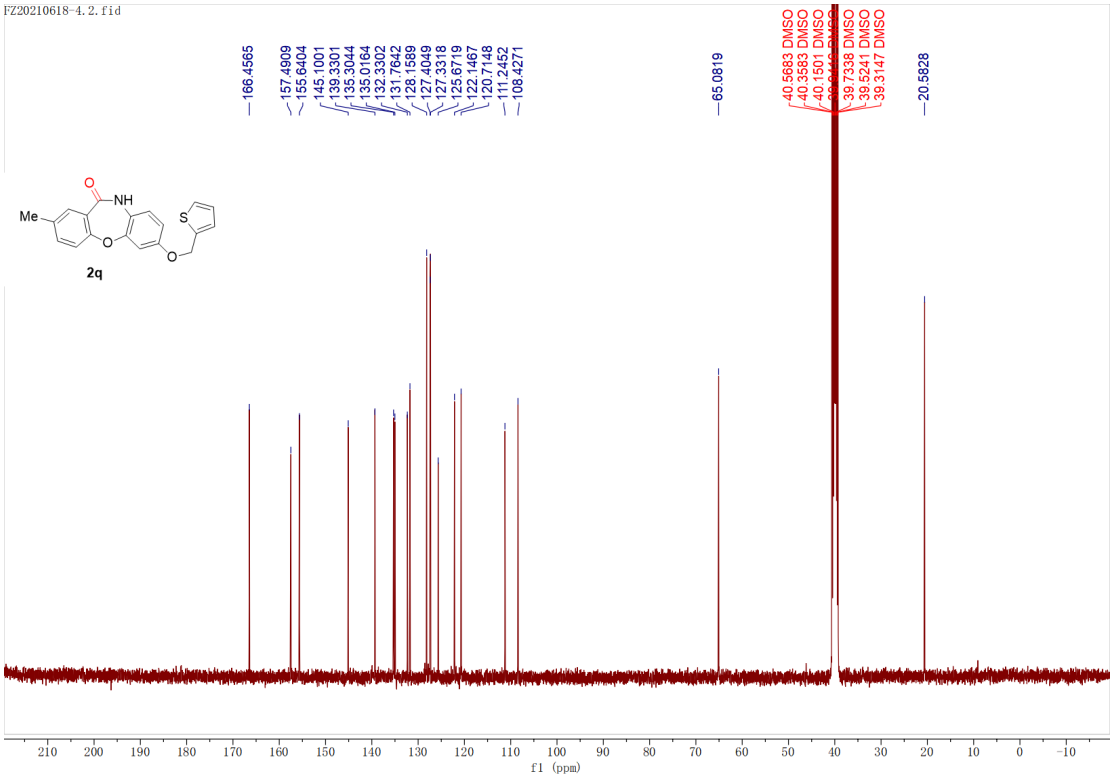

$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **2p**



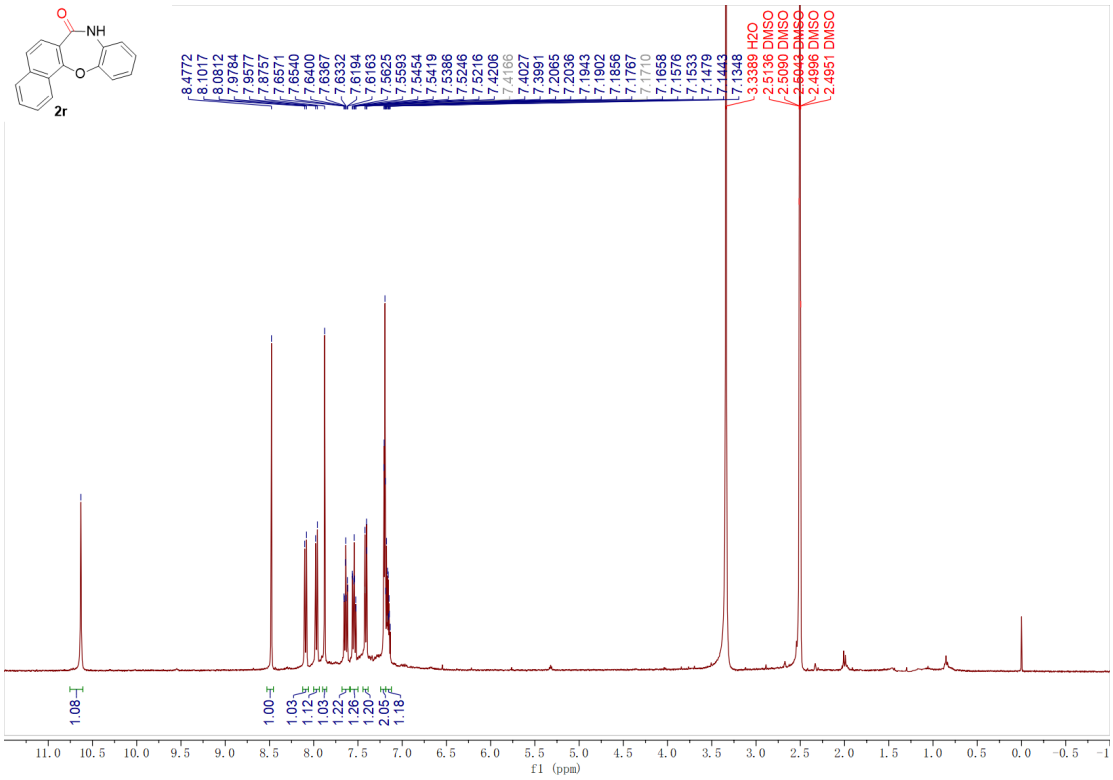

$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **2p**



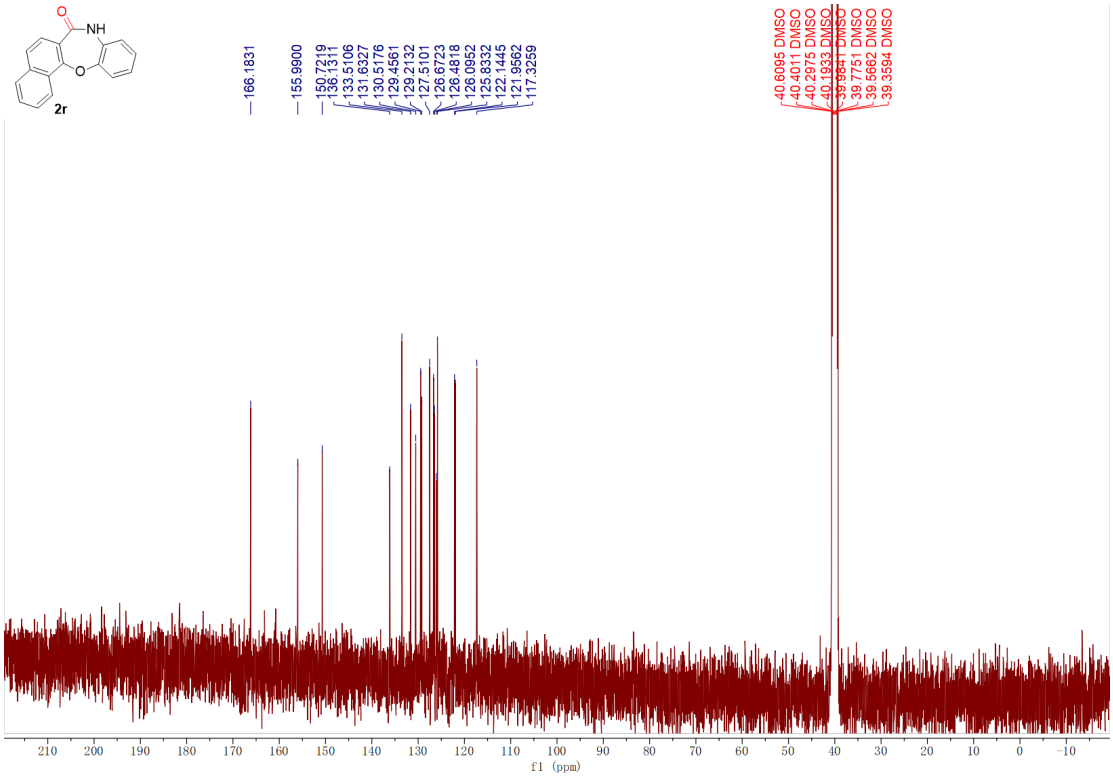

$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **2q**



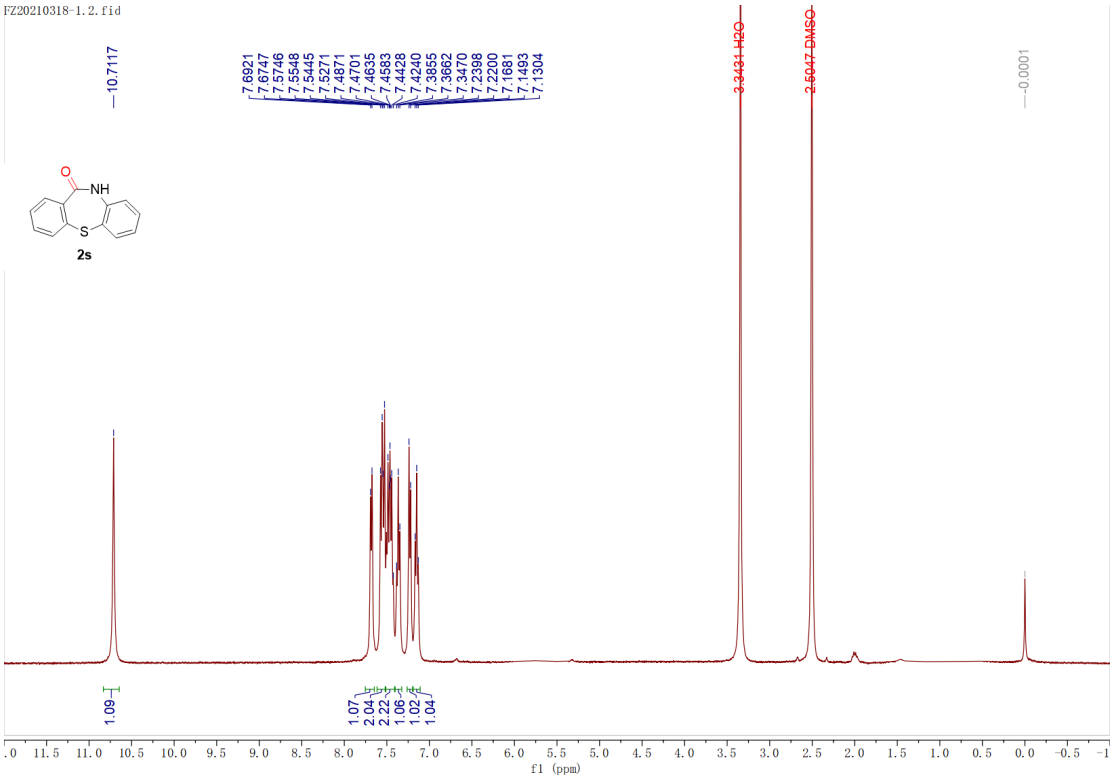

$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **2q**



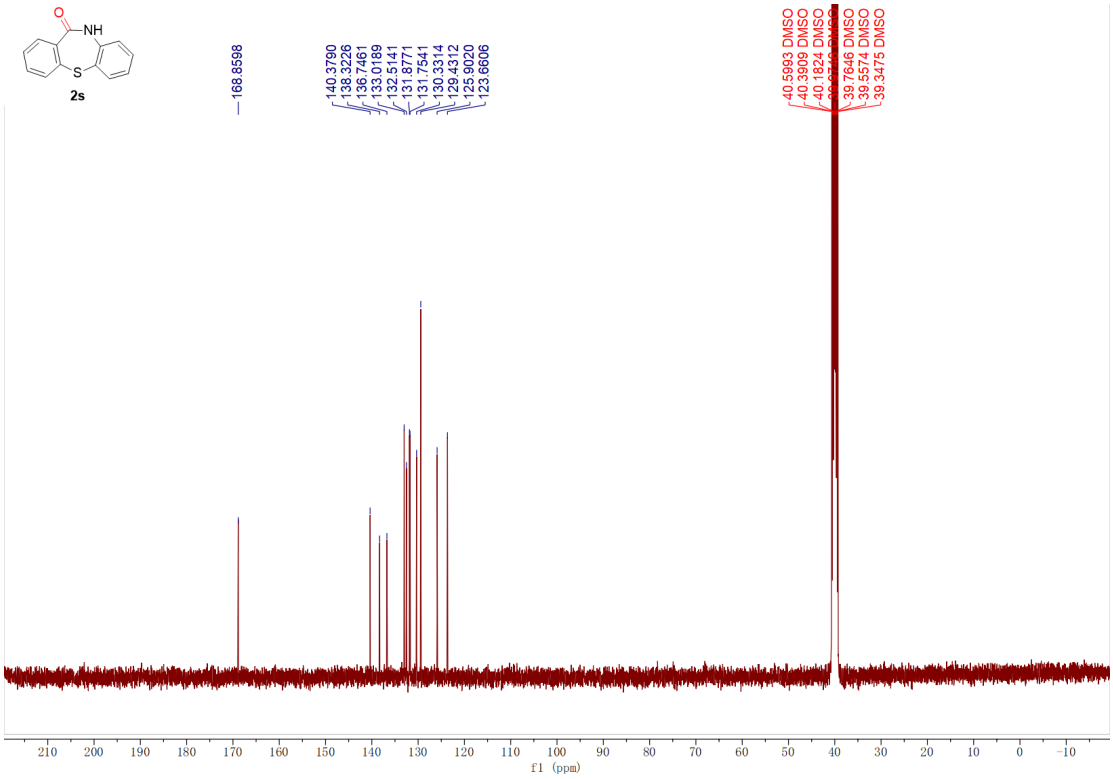

$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **2r**



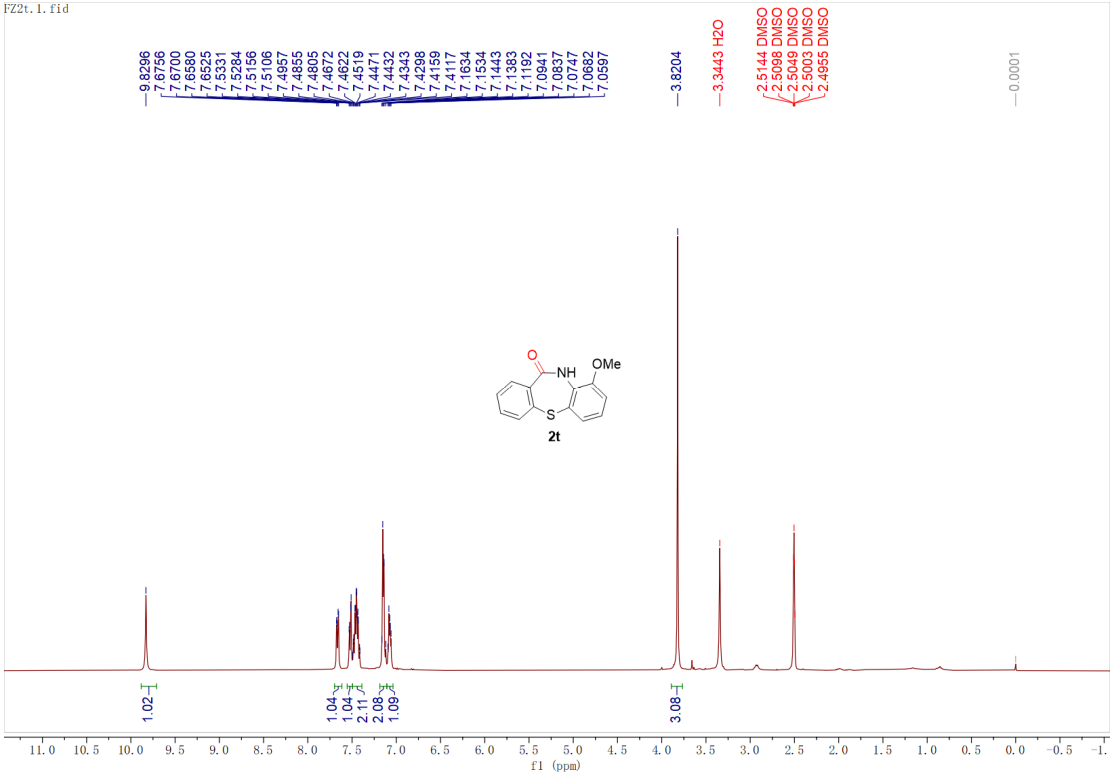

$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **2r**



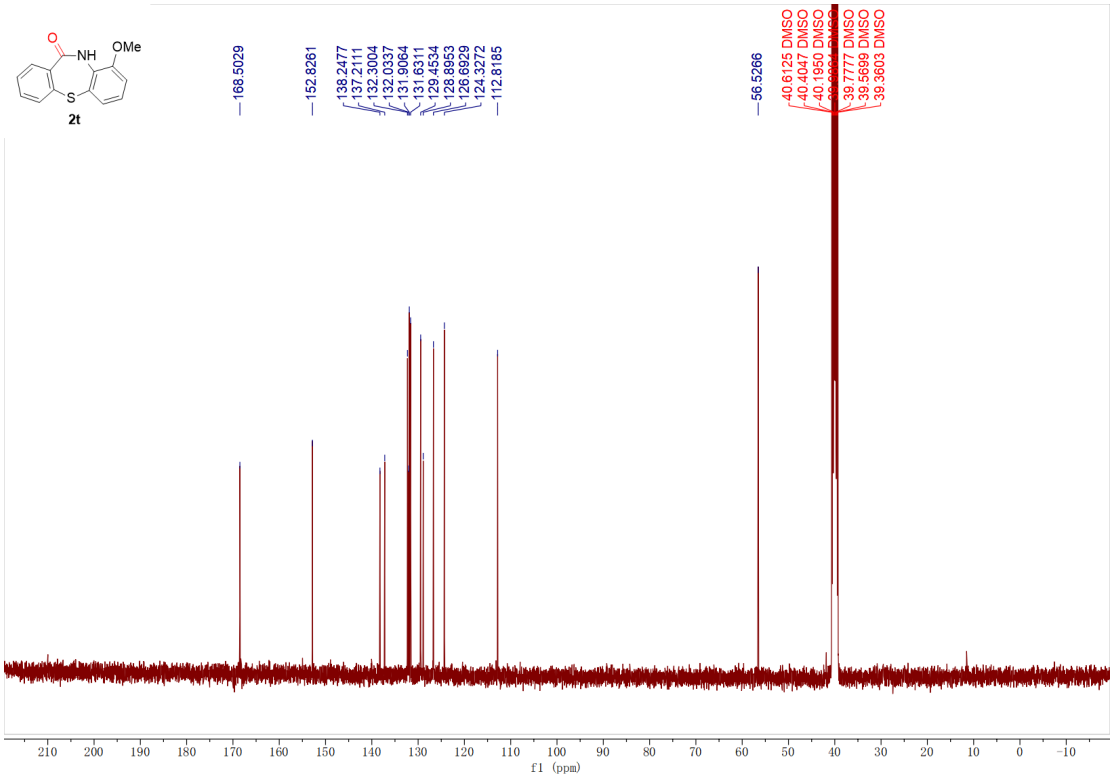

$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **2s**



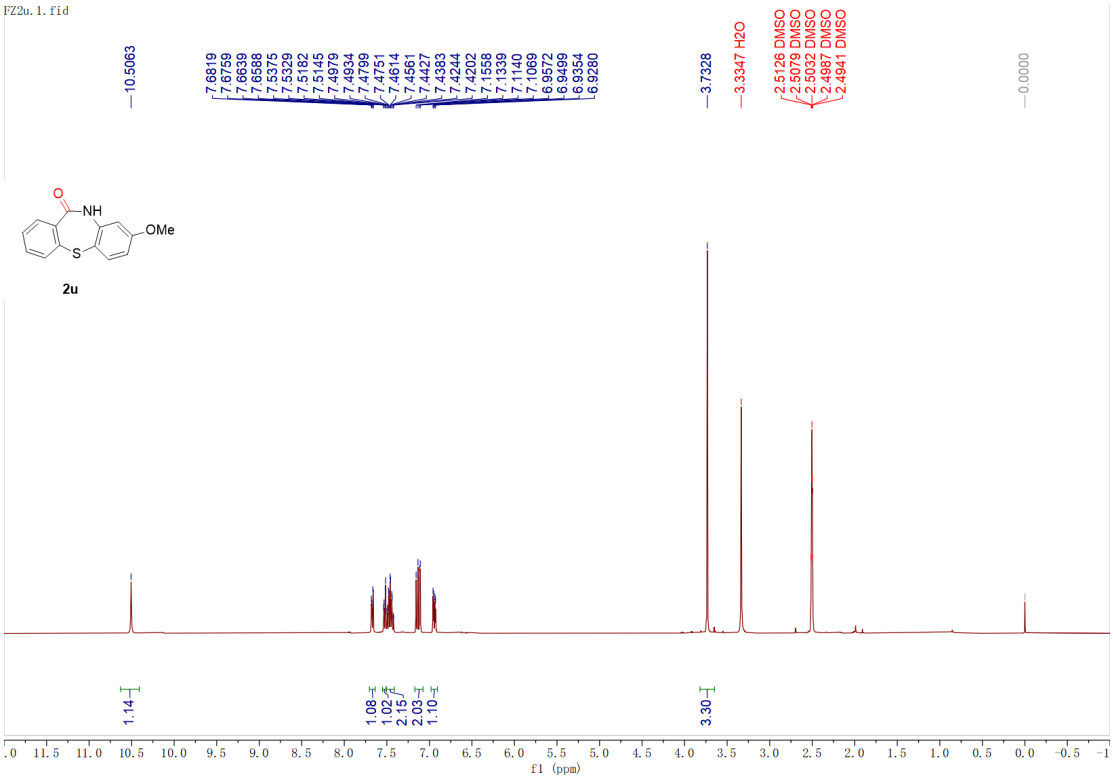

$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **2s**



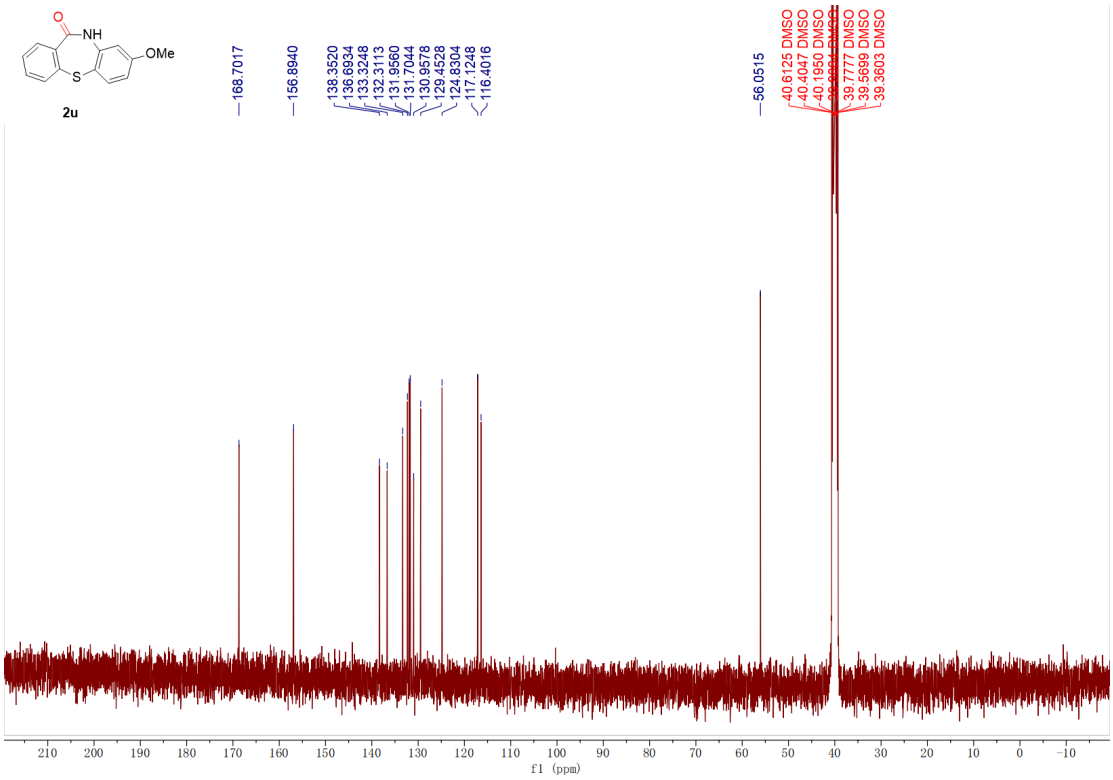

$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **2t**



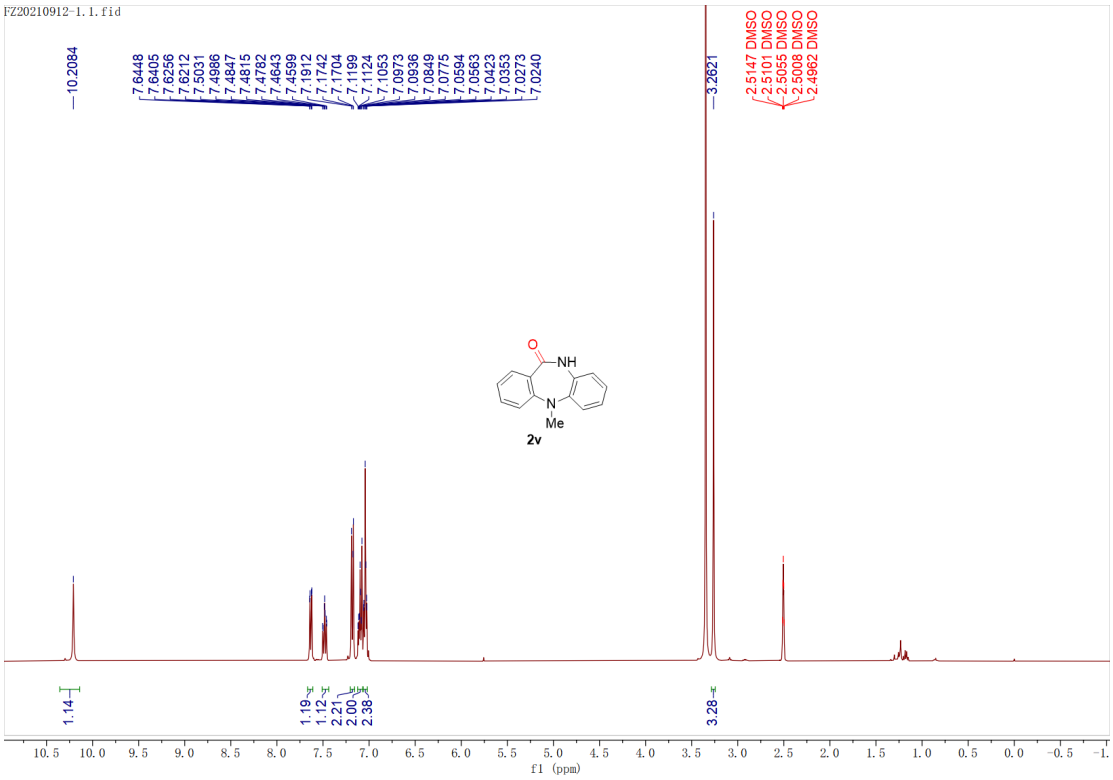

$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **2t**



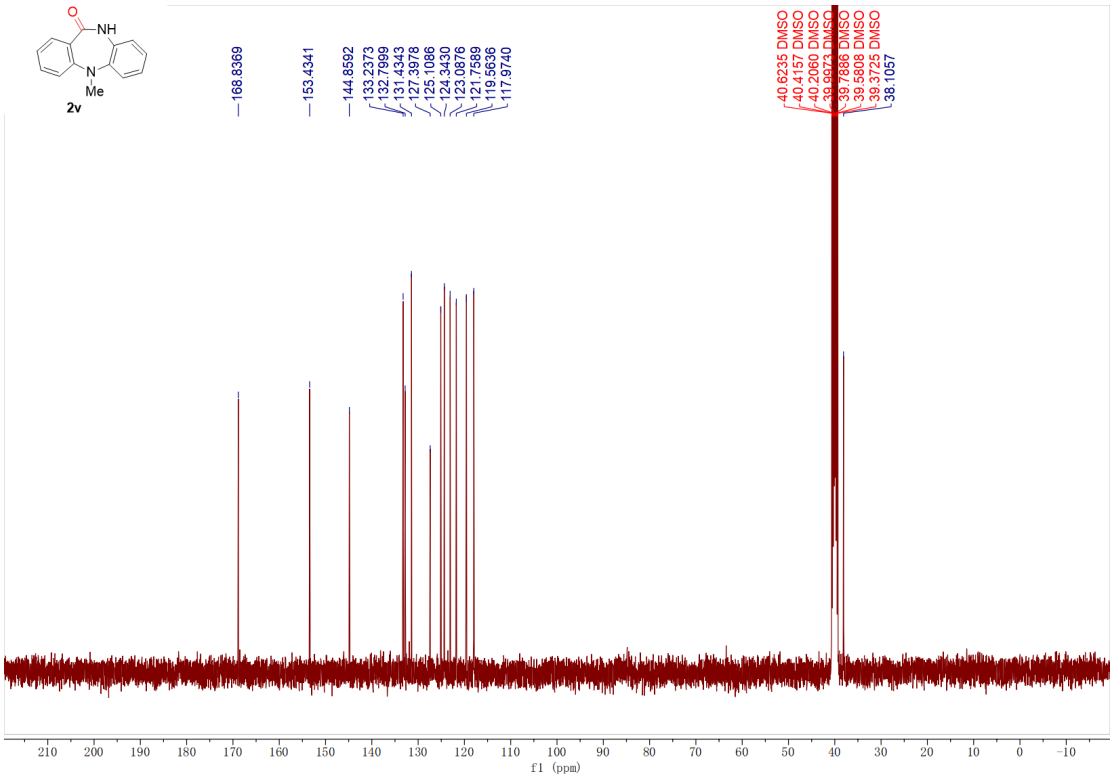

$^{1}$H NMR spectra (400 MHz, Chloroform-d) of **2u**



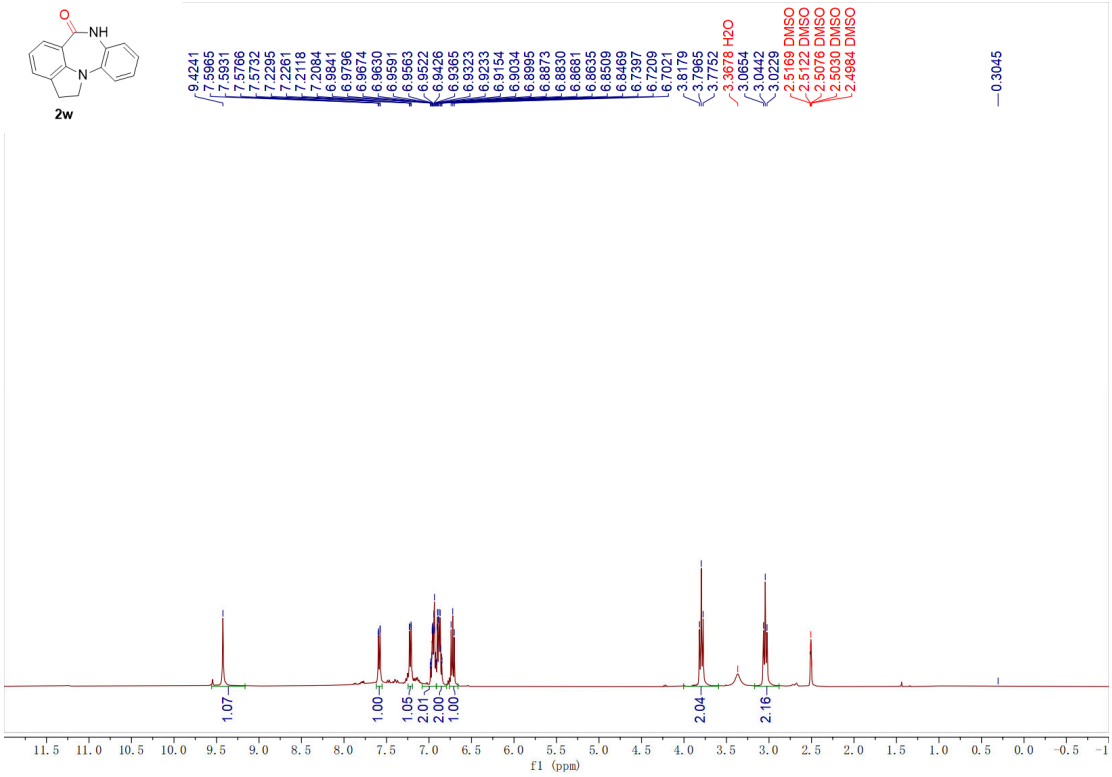

$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **2u**



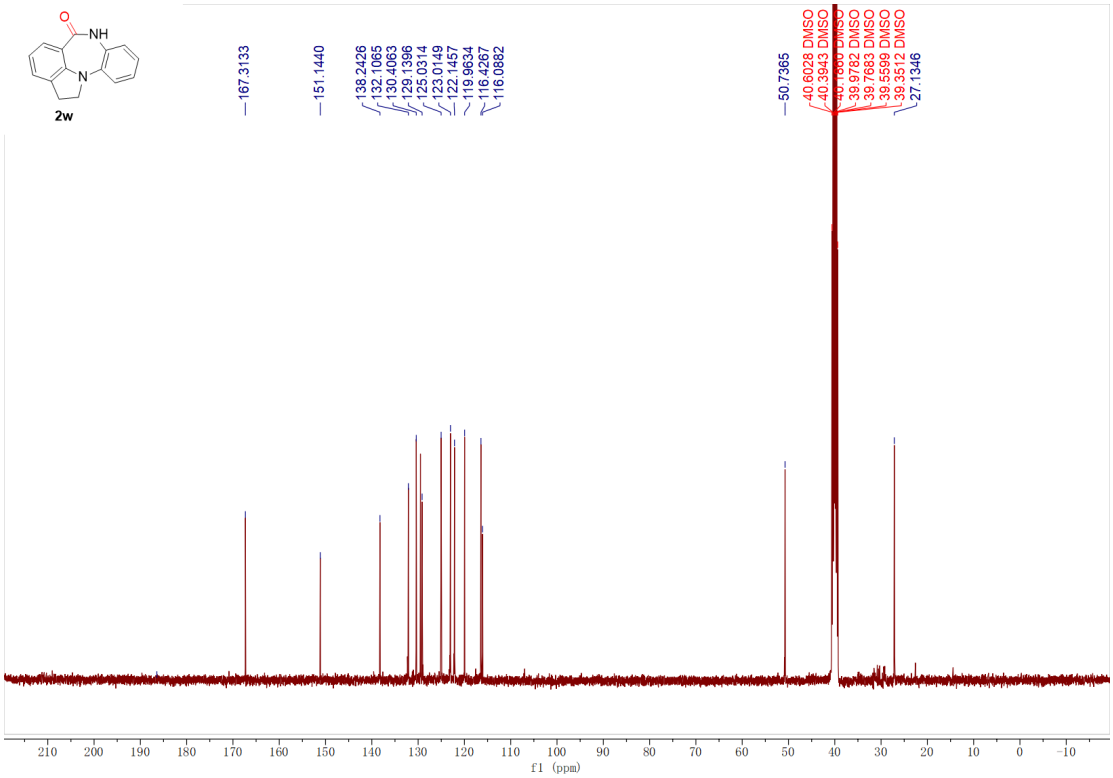

$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **2v**



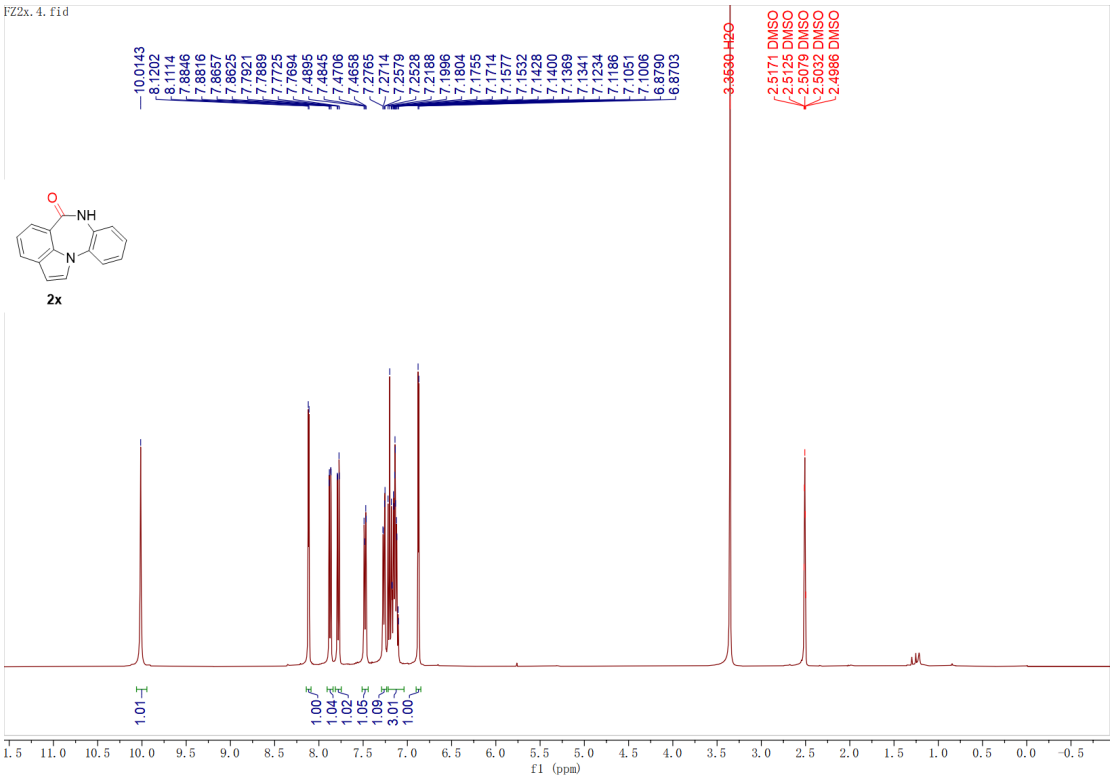

$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **2v**



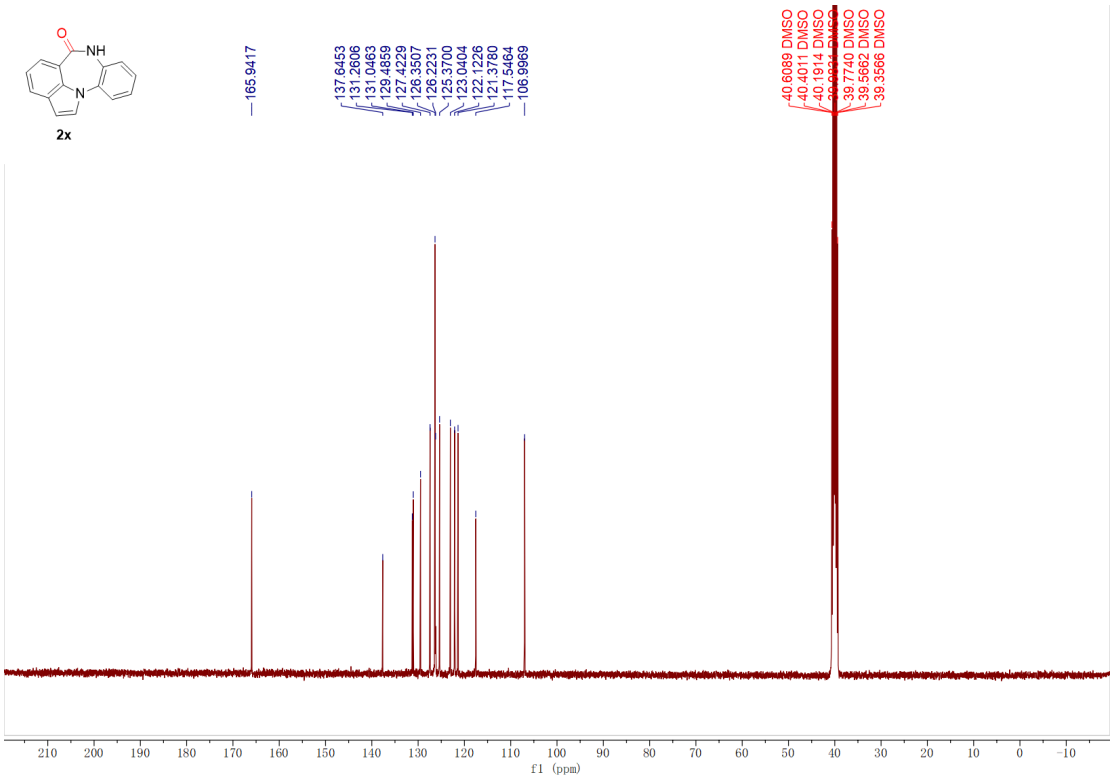

$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **2w**



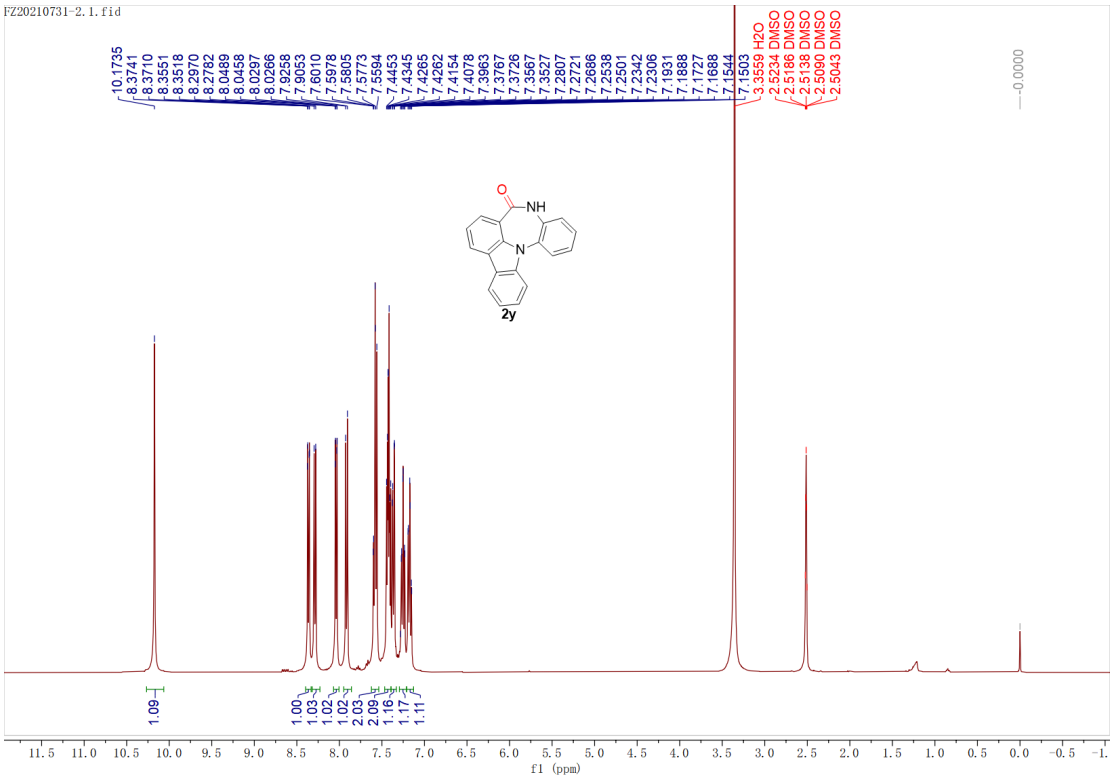

$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **2w**



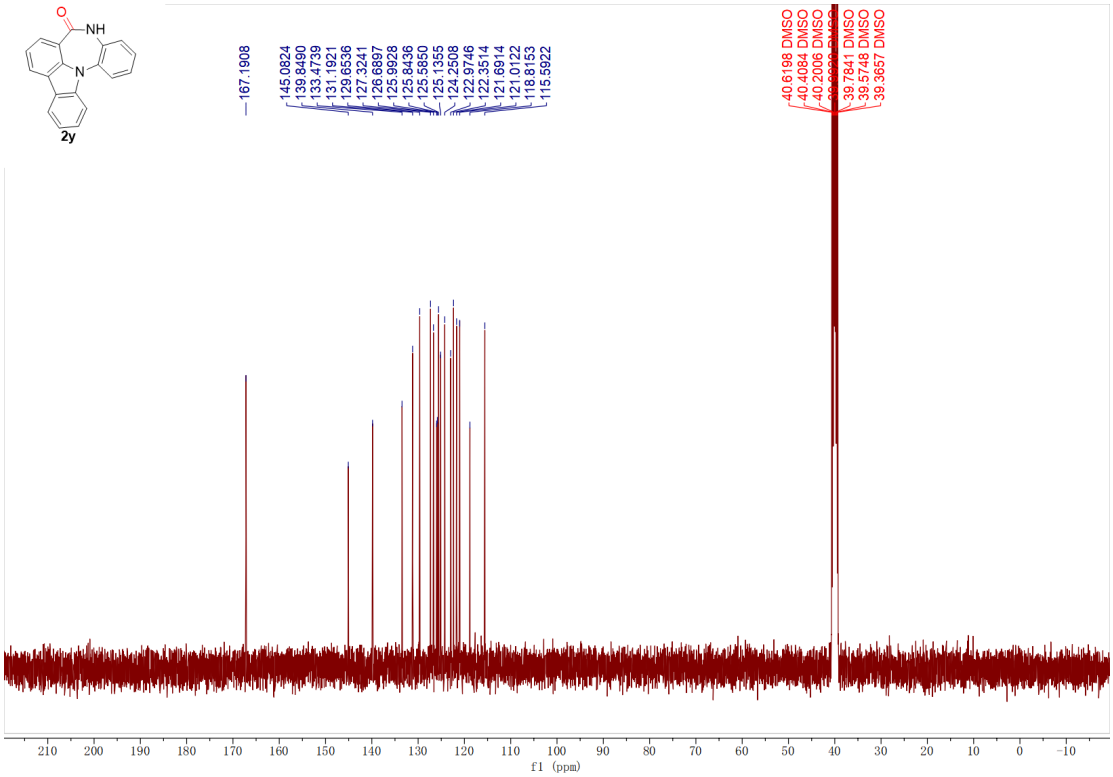

$^{1}$H NMR spectra (400 MHz, Chloroform-d) of **2x**



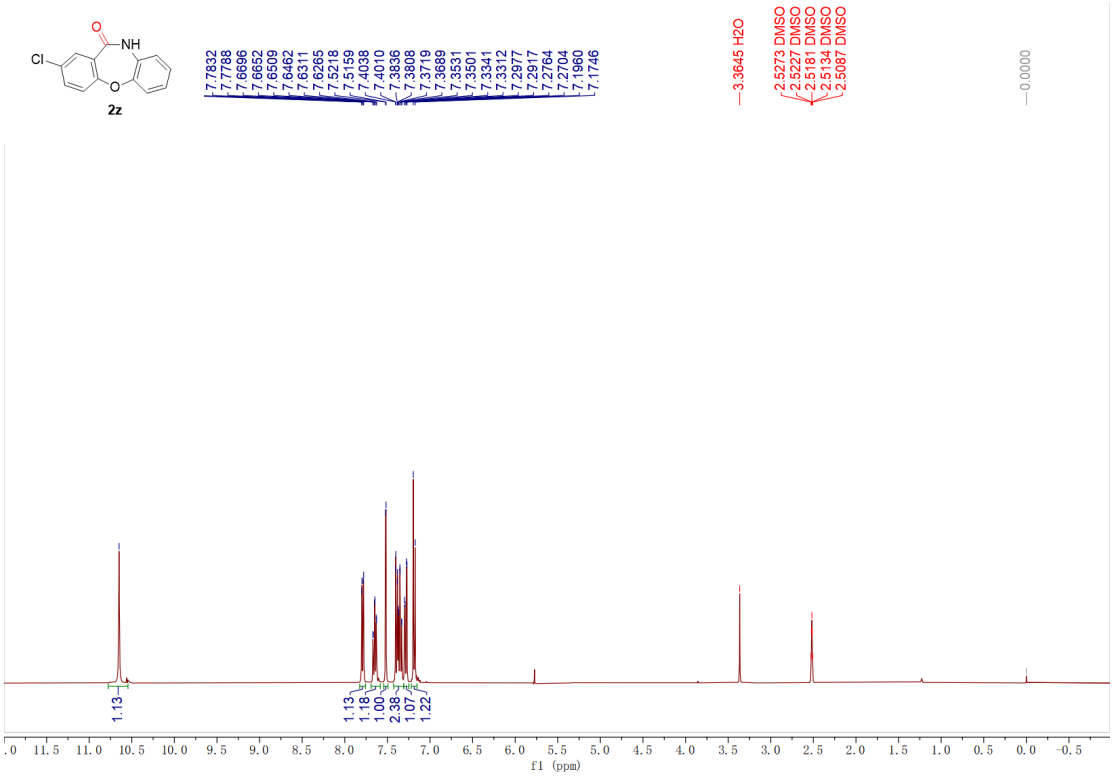

$^{13}$C NMR spectra (101 MHz, Chloroform-d) of **2x**



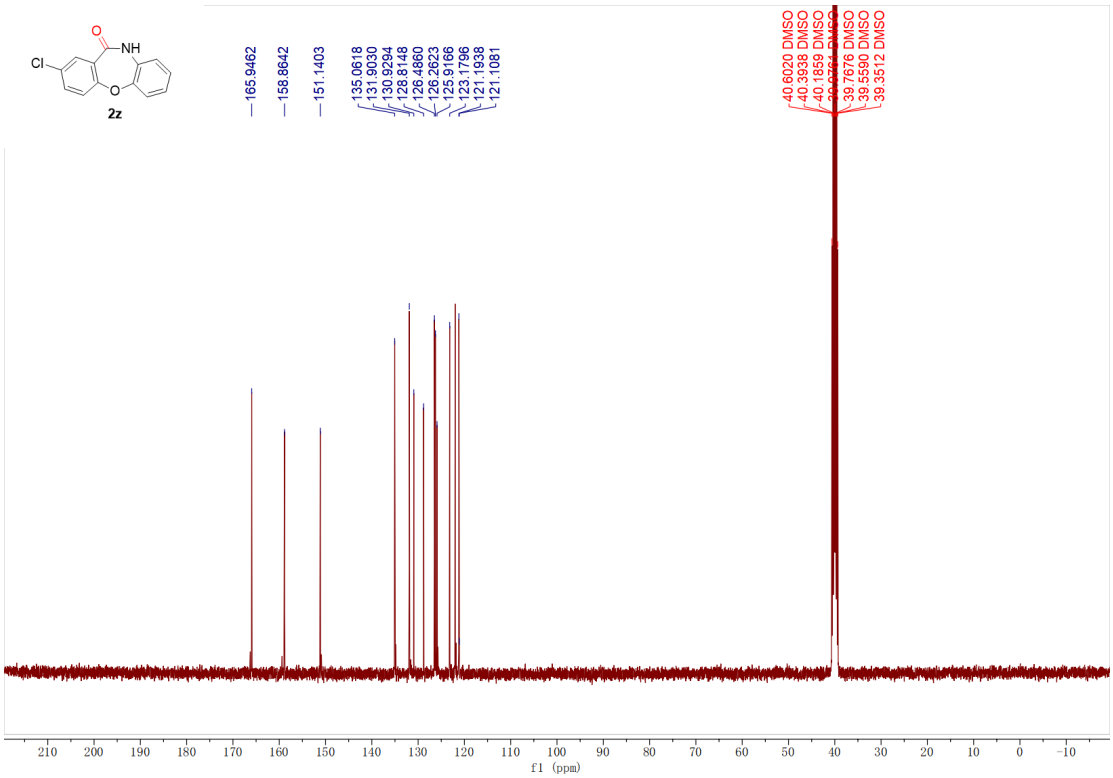

$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **2y**



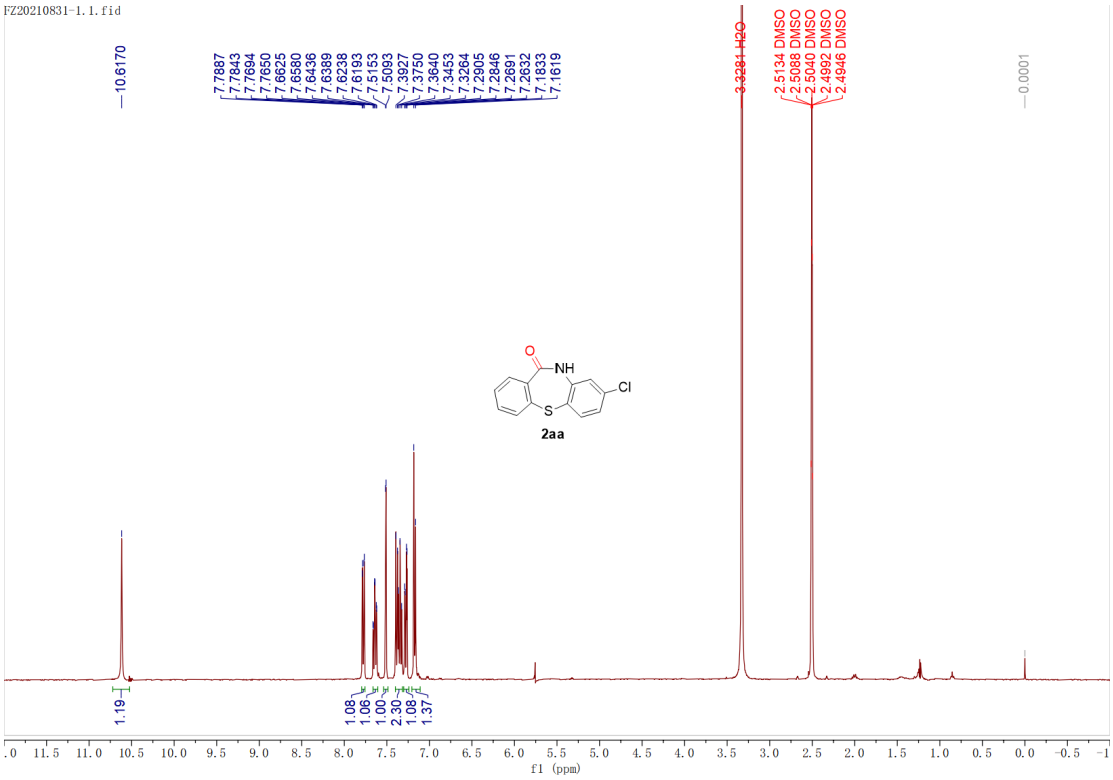

$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **2y**



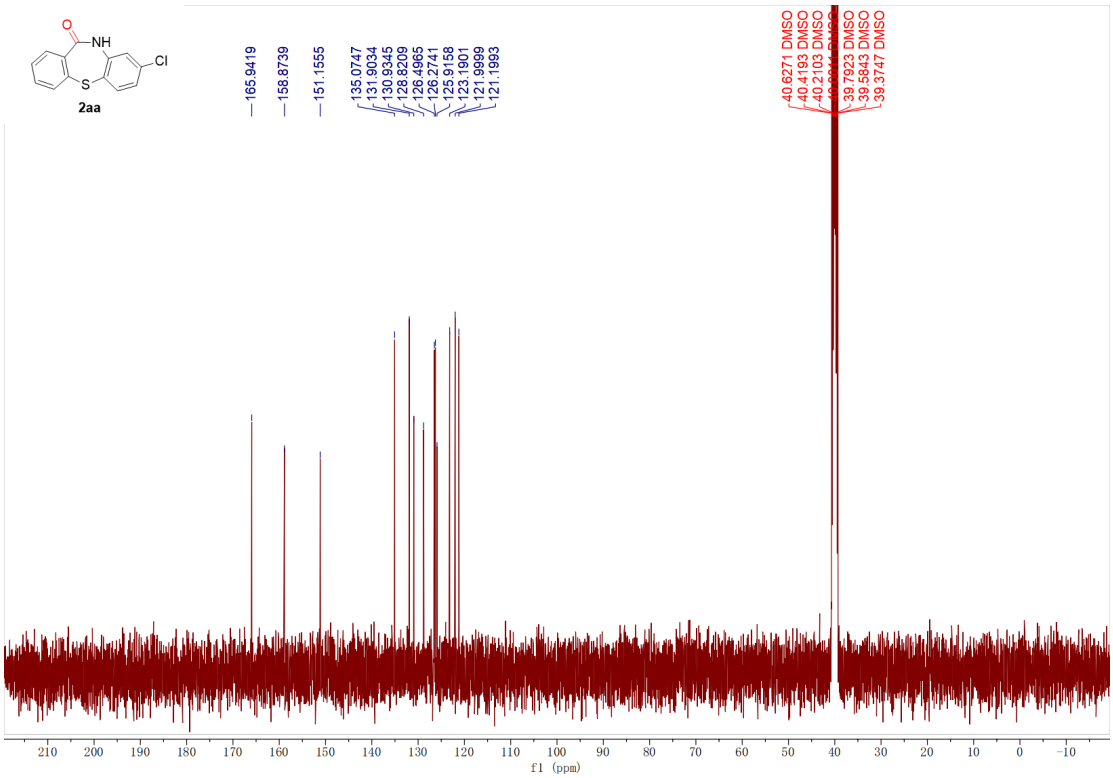

$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **2z**



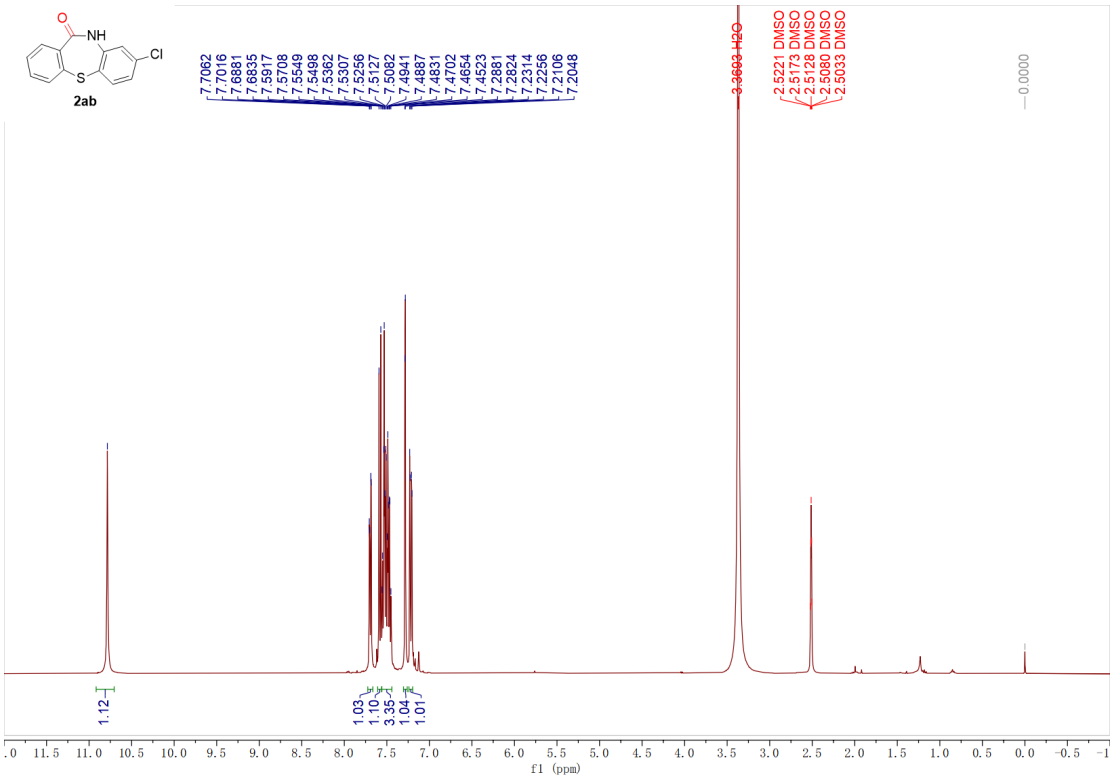

$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **2z**



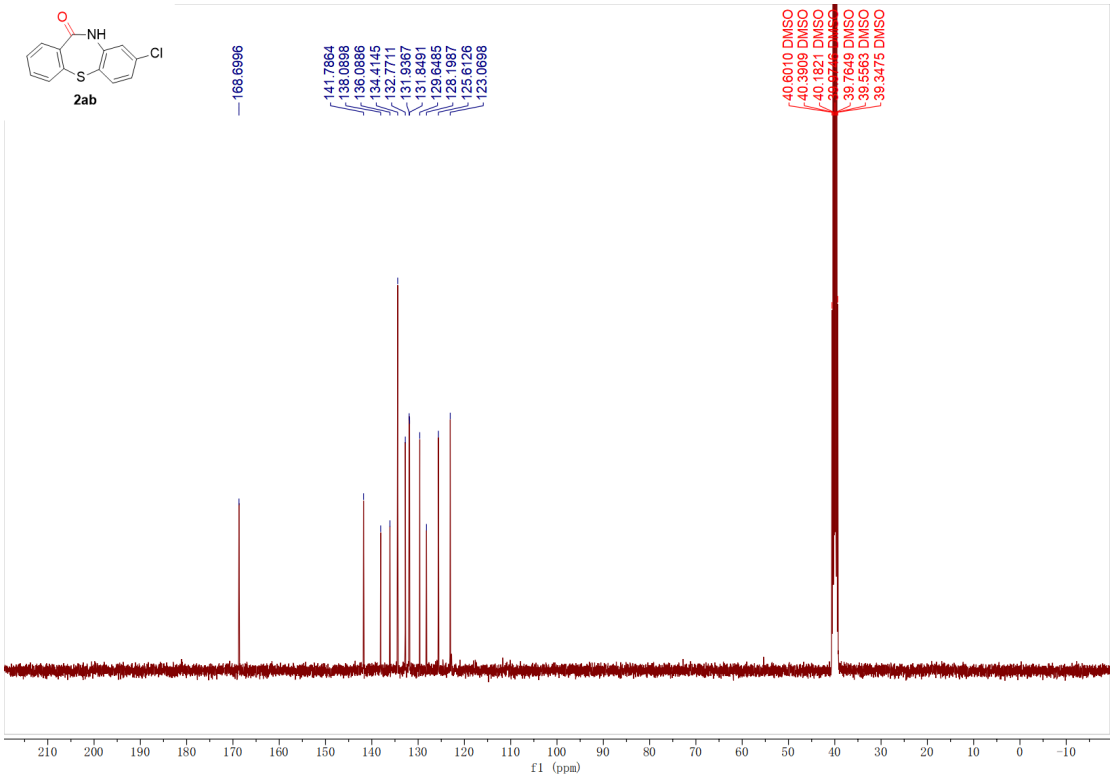

$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **2aa**



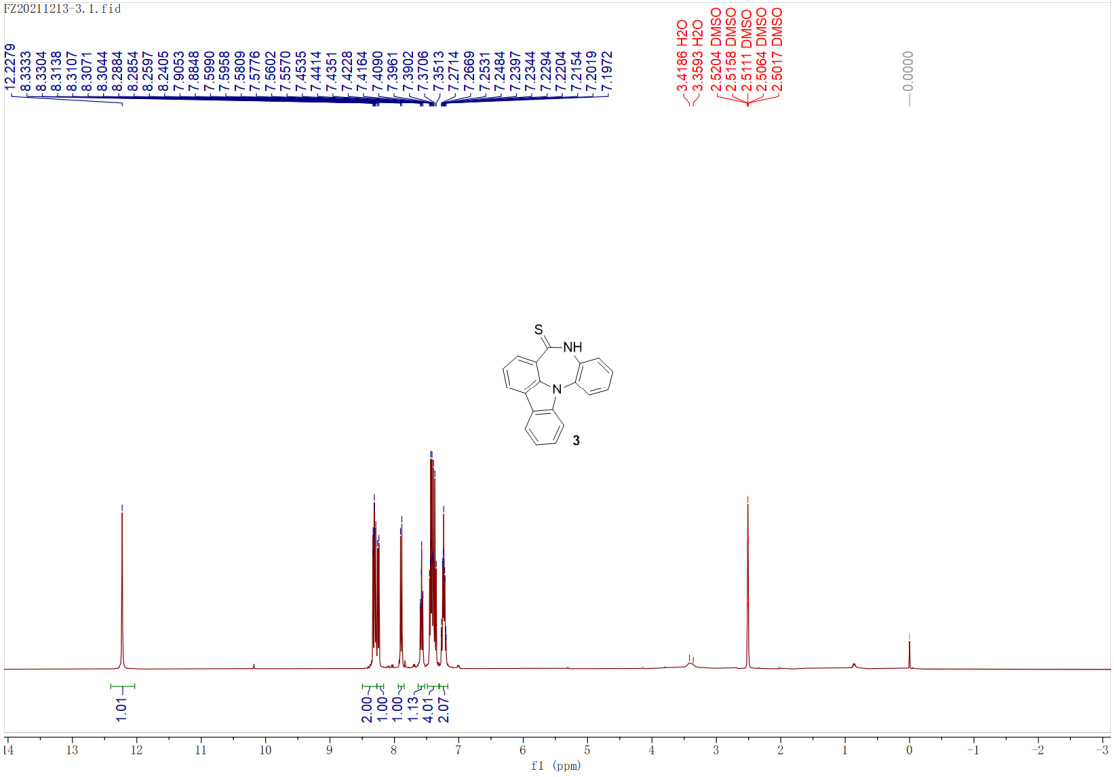

$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **2aa**



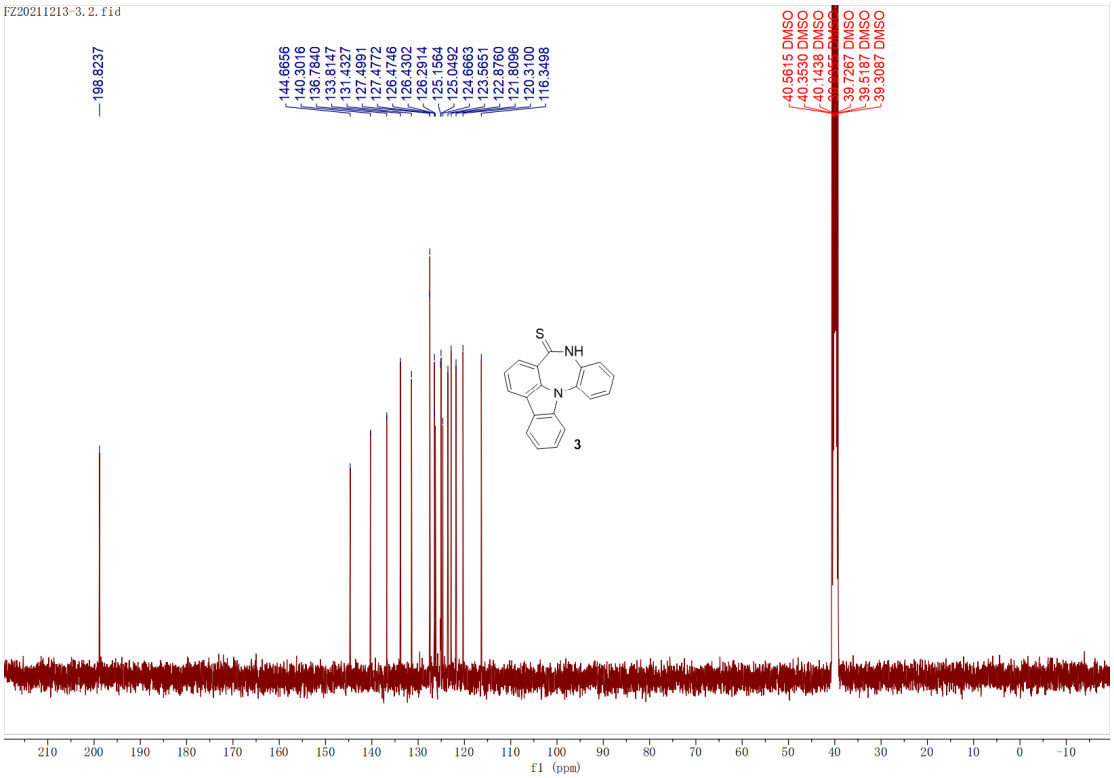

$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **2ab**



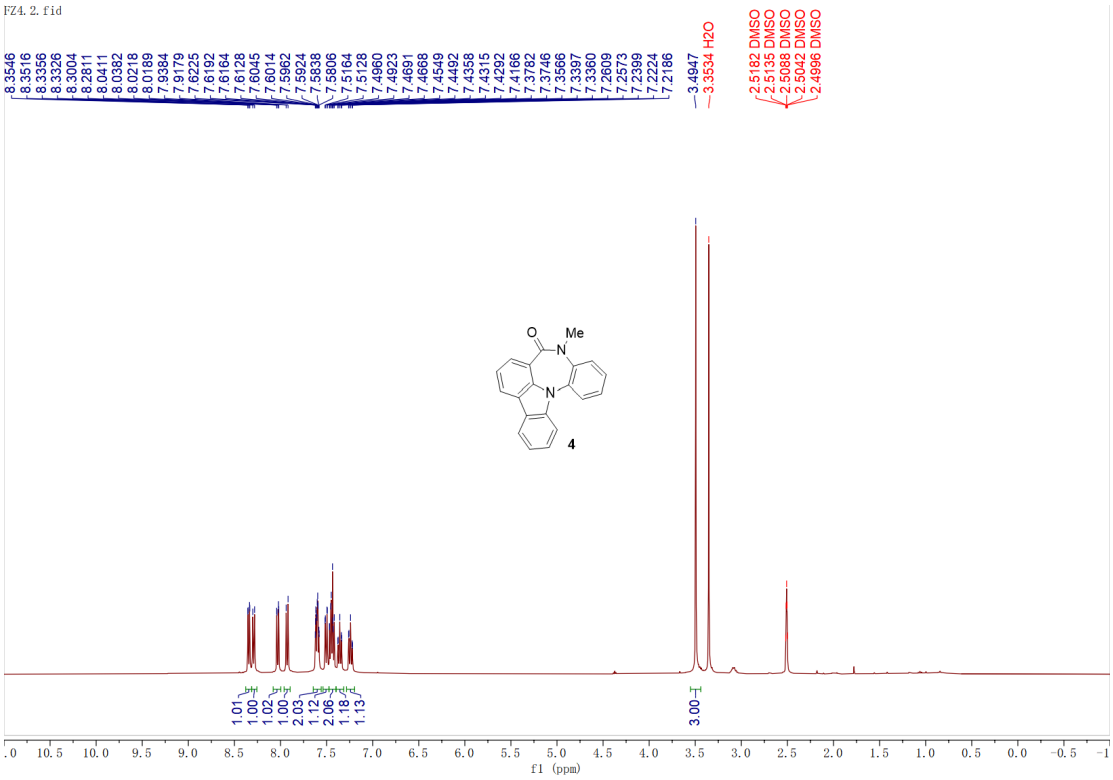

$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **2ab**



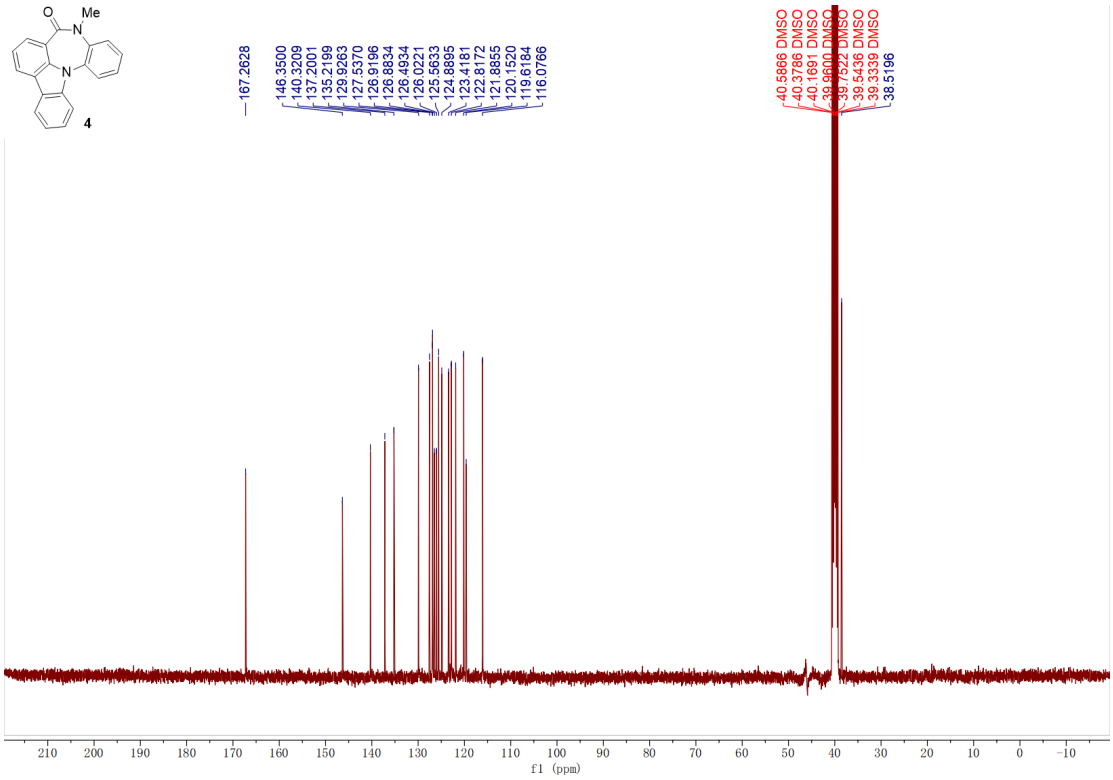

$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **3**



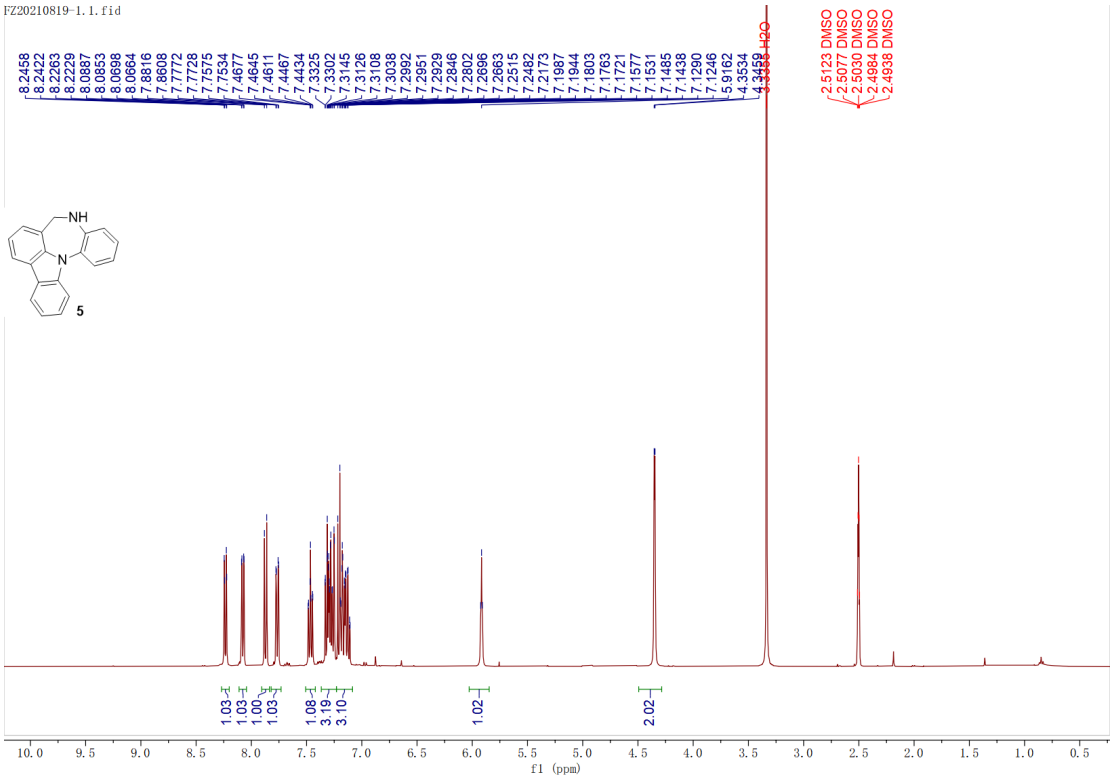

$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **3**



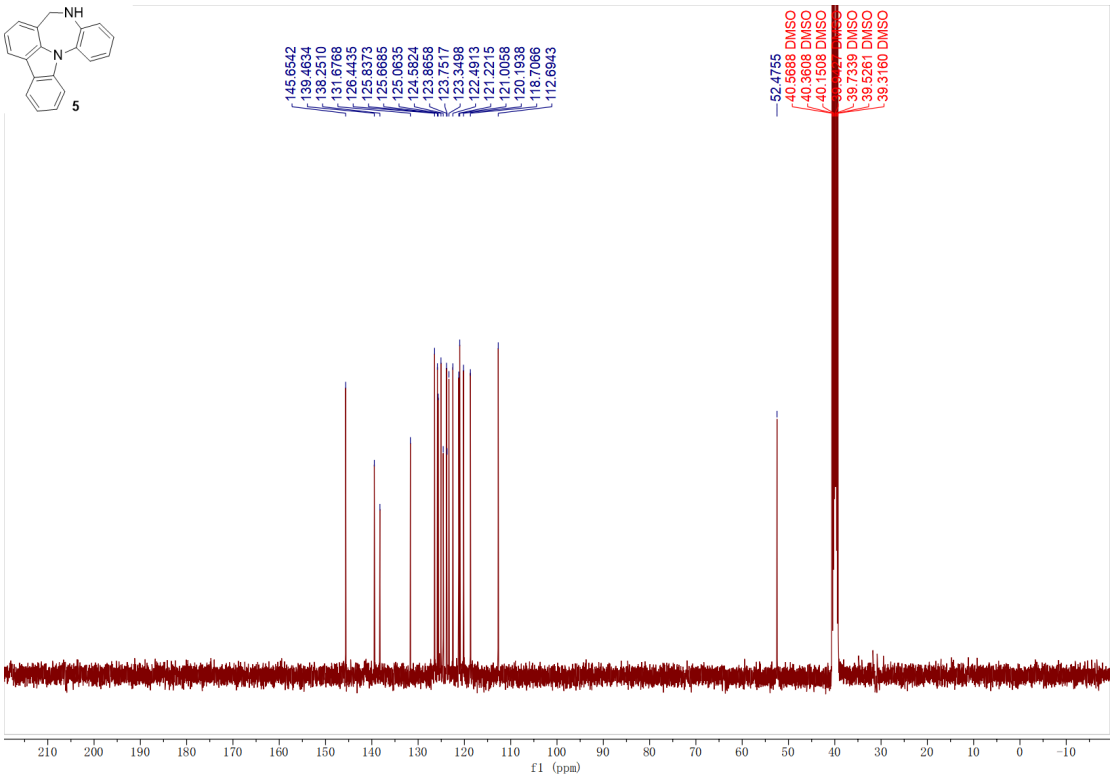

$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **4**



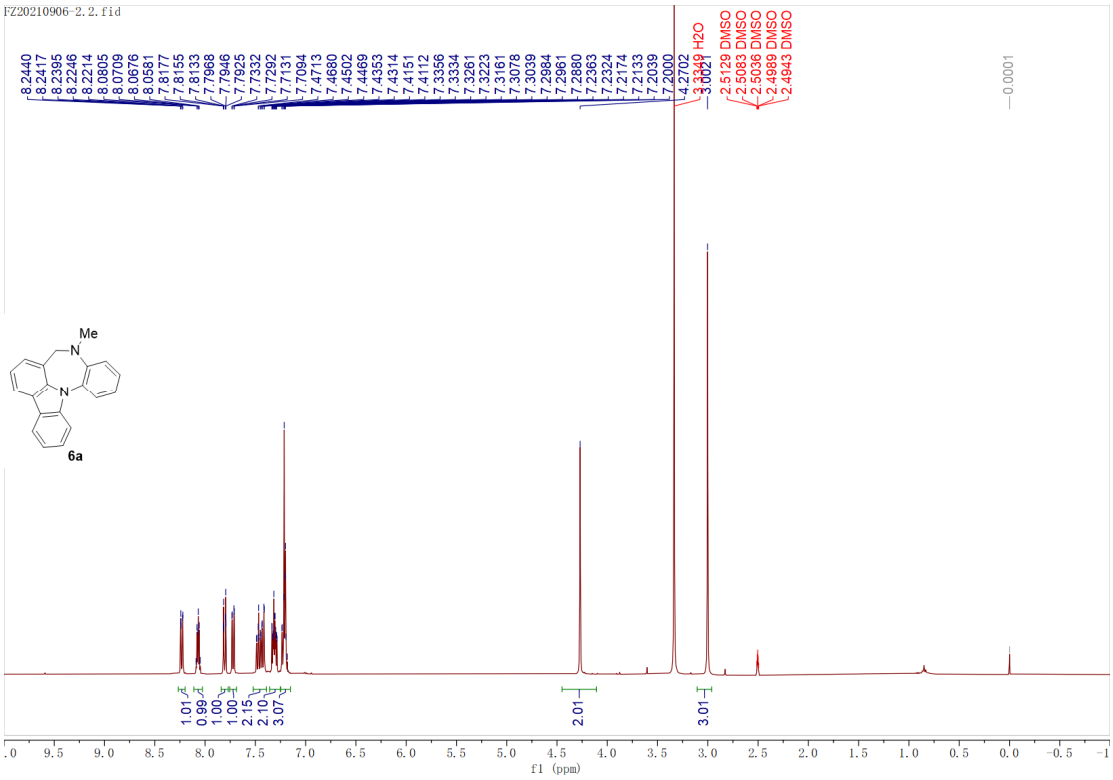

$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **4**



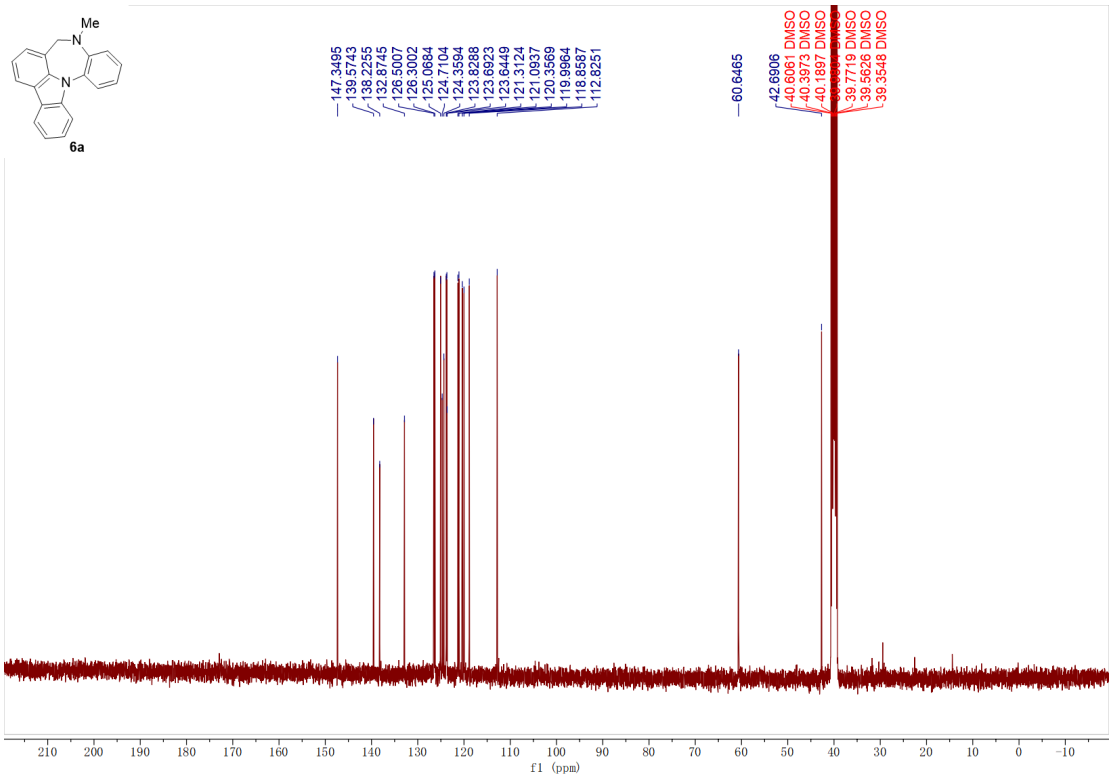

$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **5**



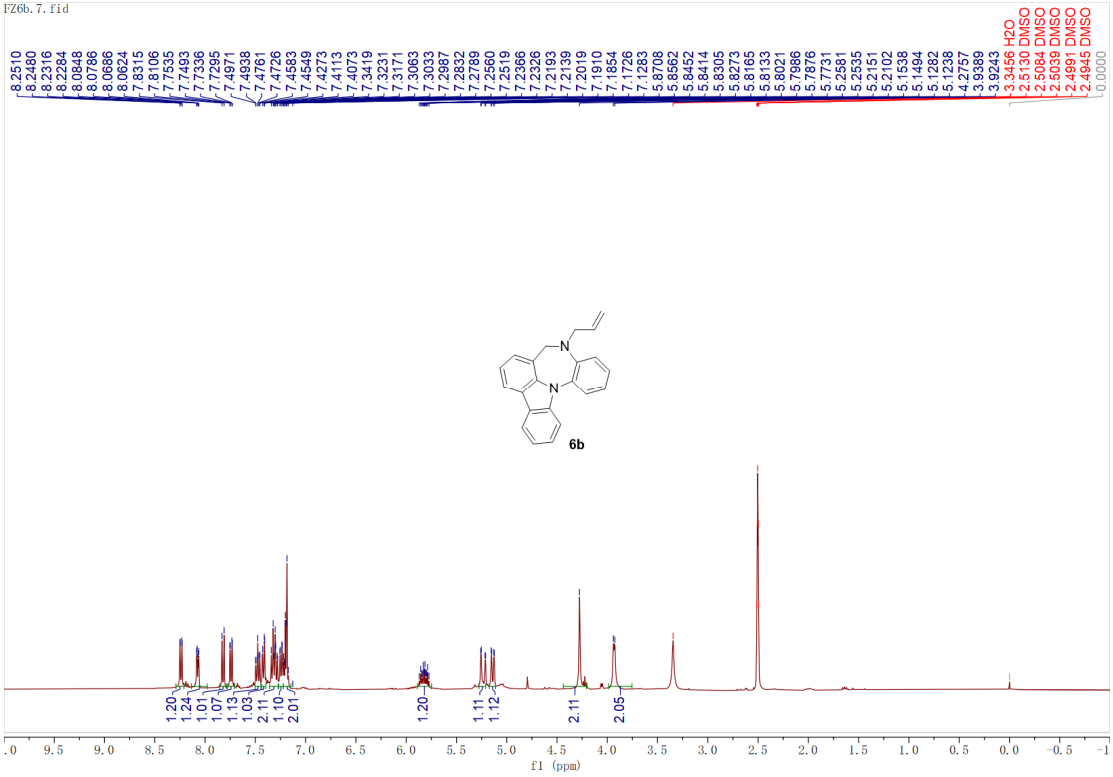

$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **5**



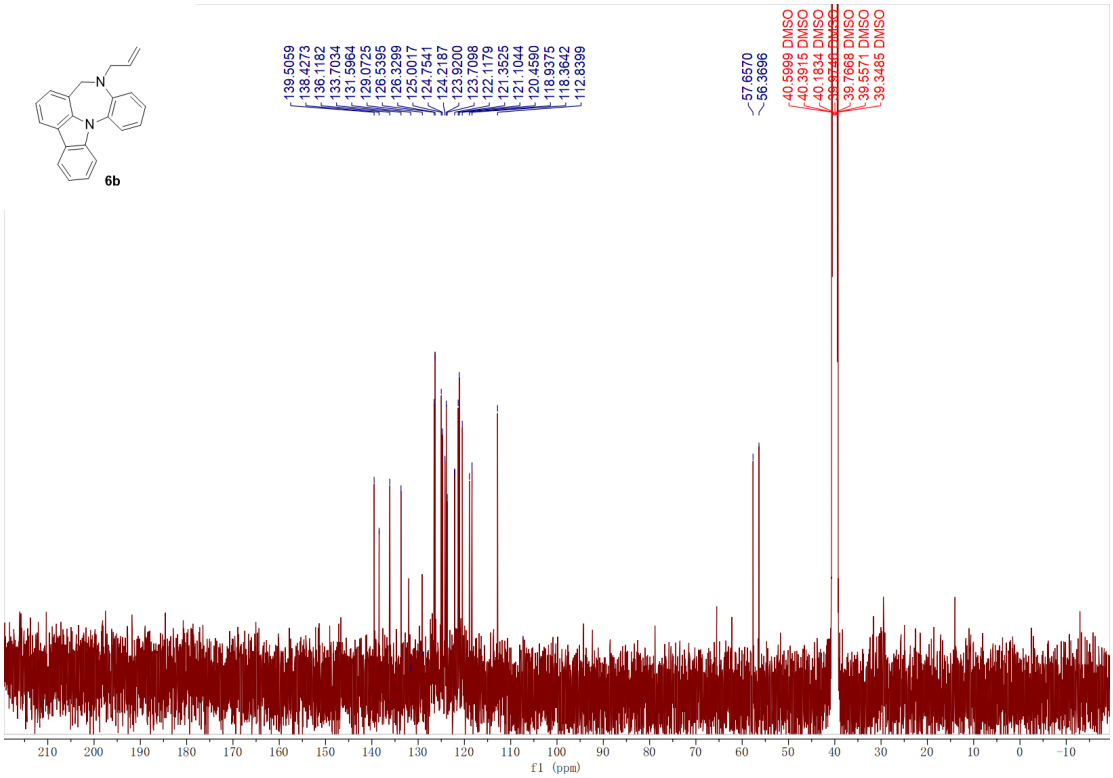

$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **6a**



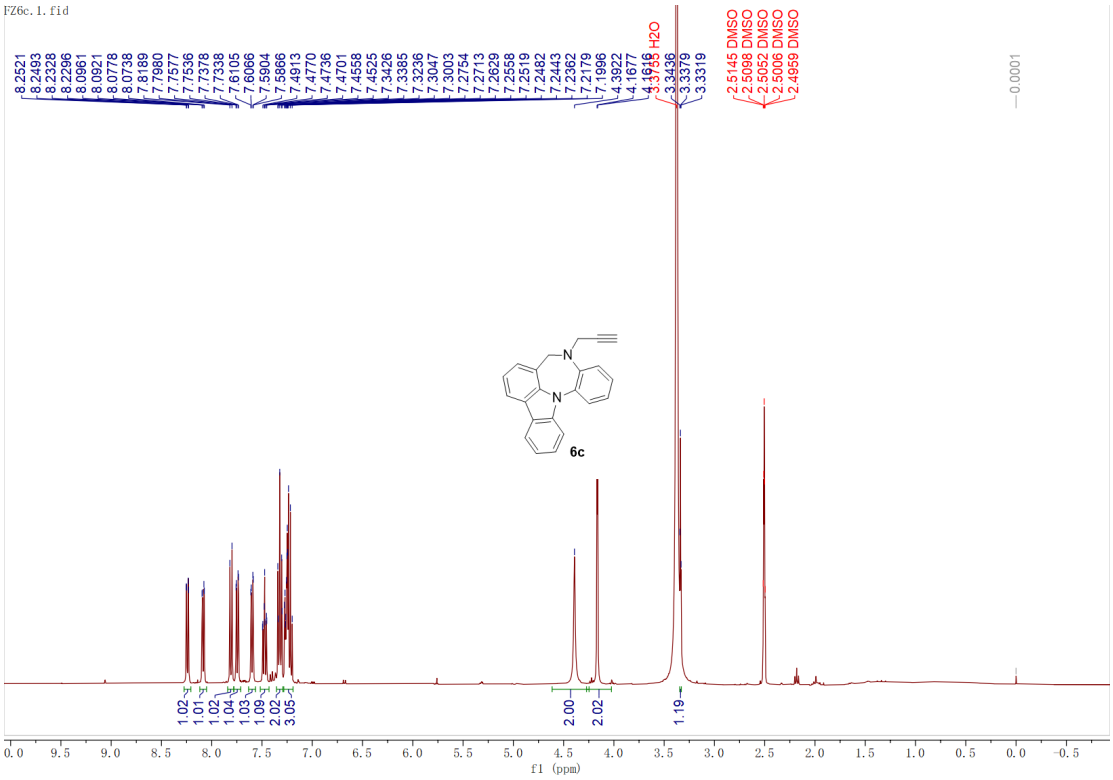

$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **6a**



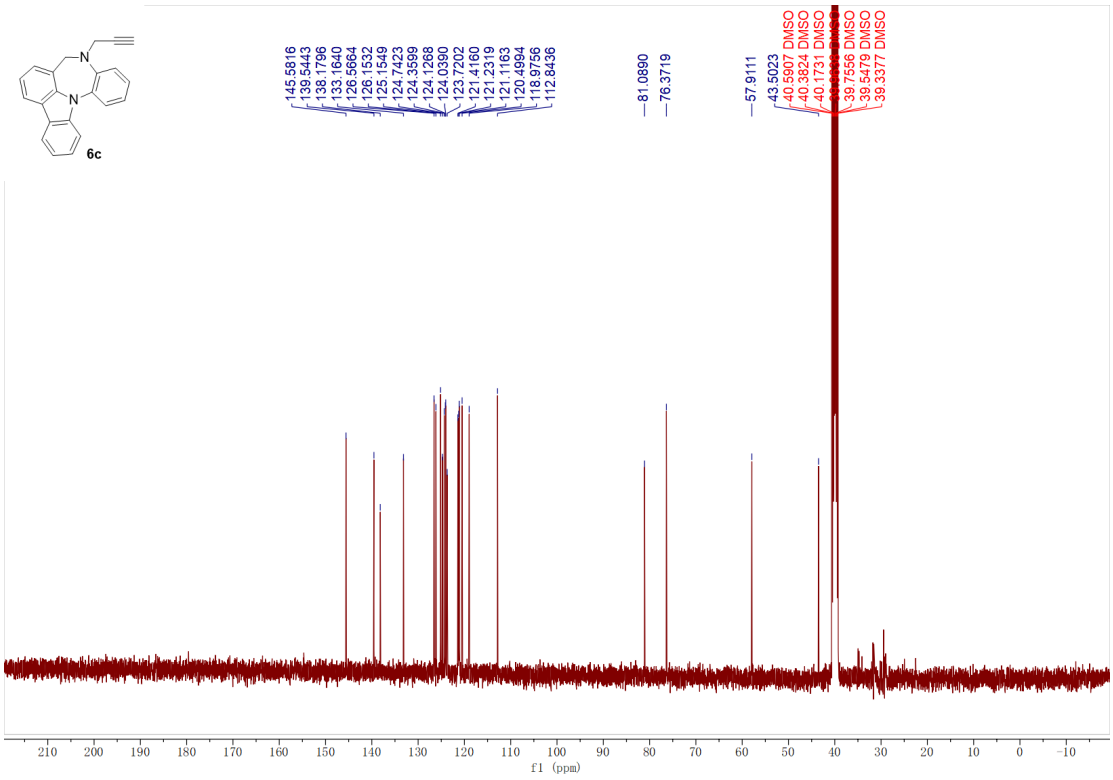

$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **6b**



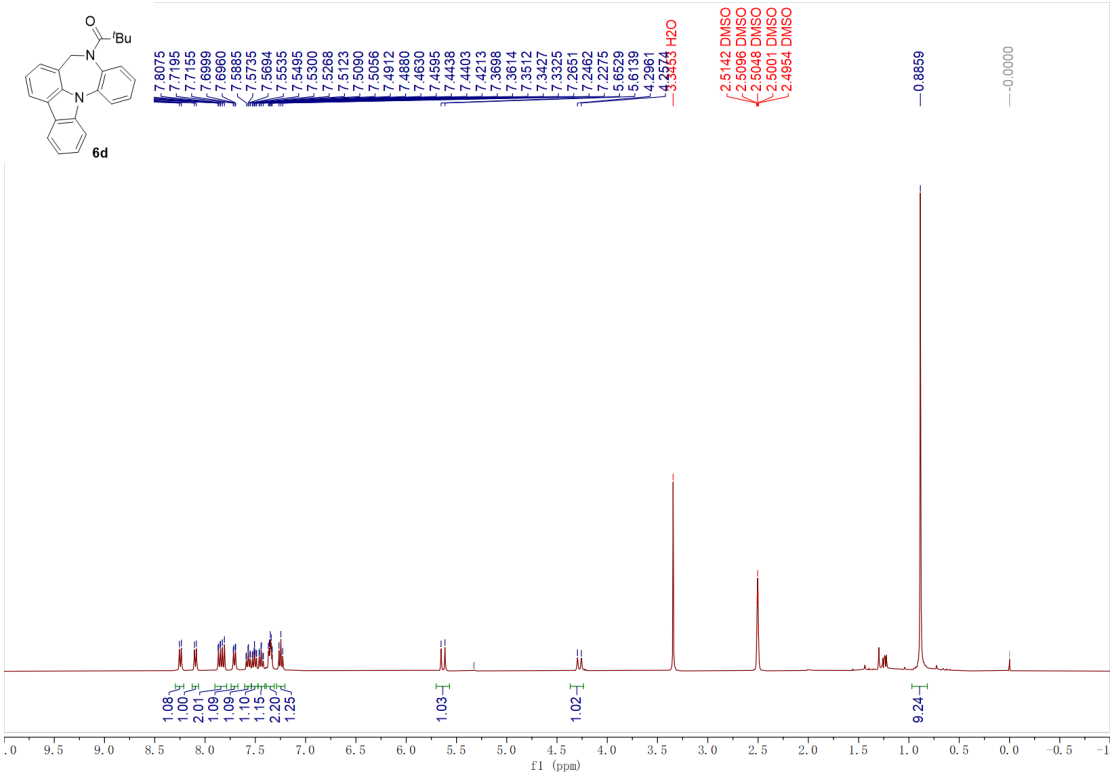

$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **6b**



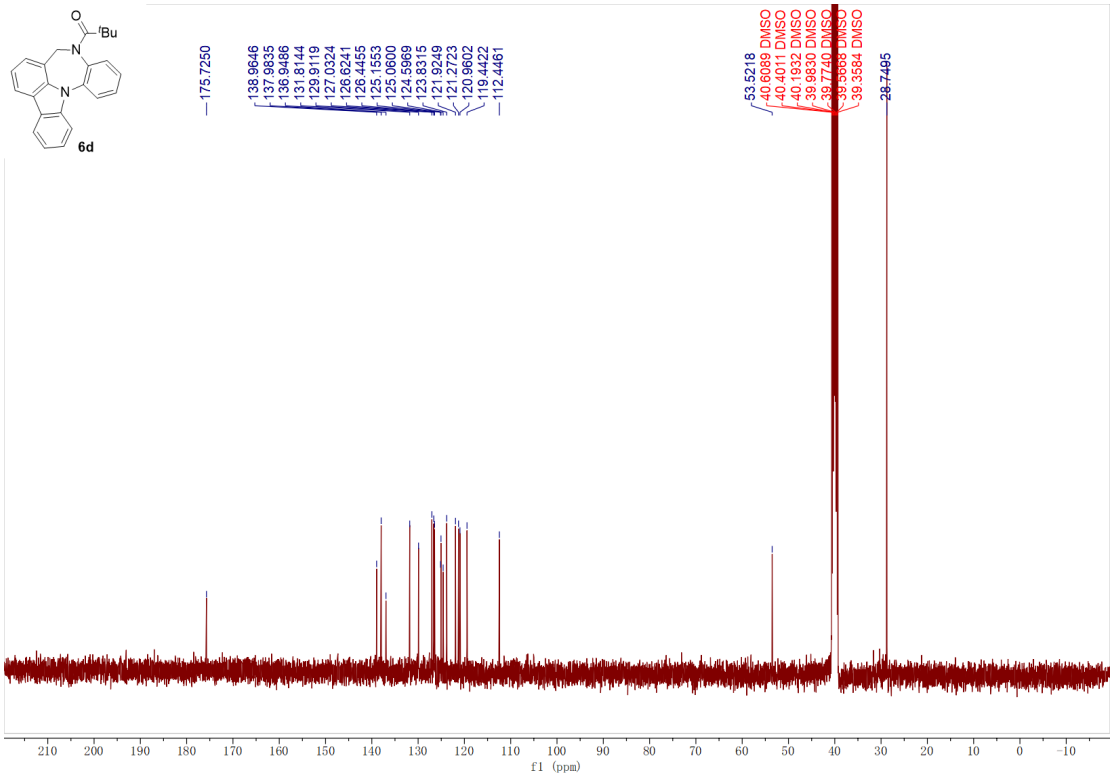

$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **6c**



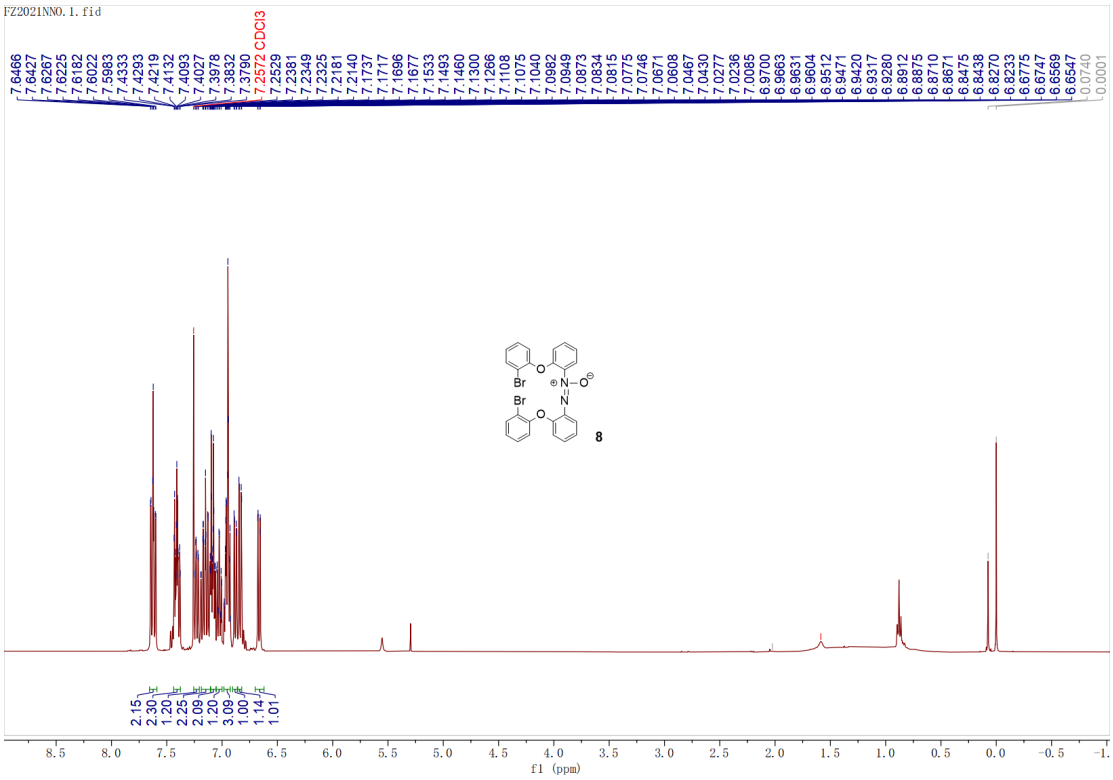

$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **6c**



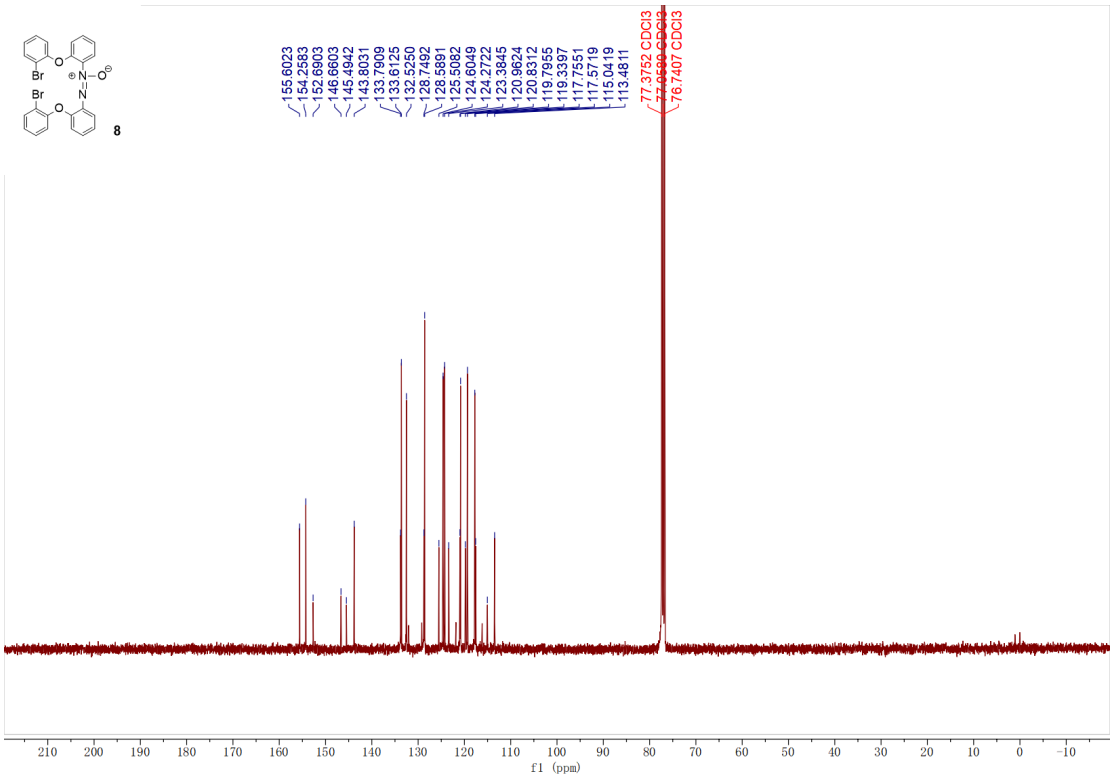

$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **6d**



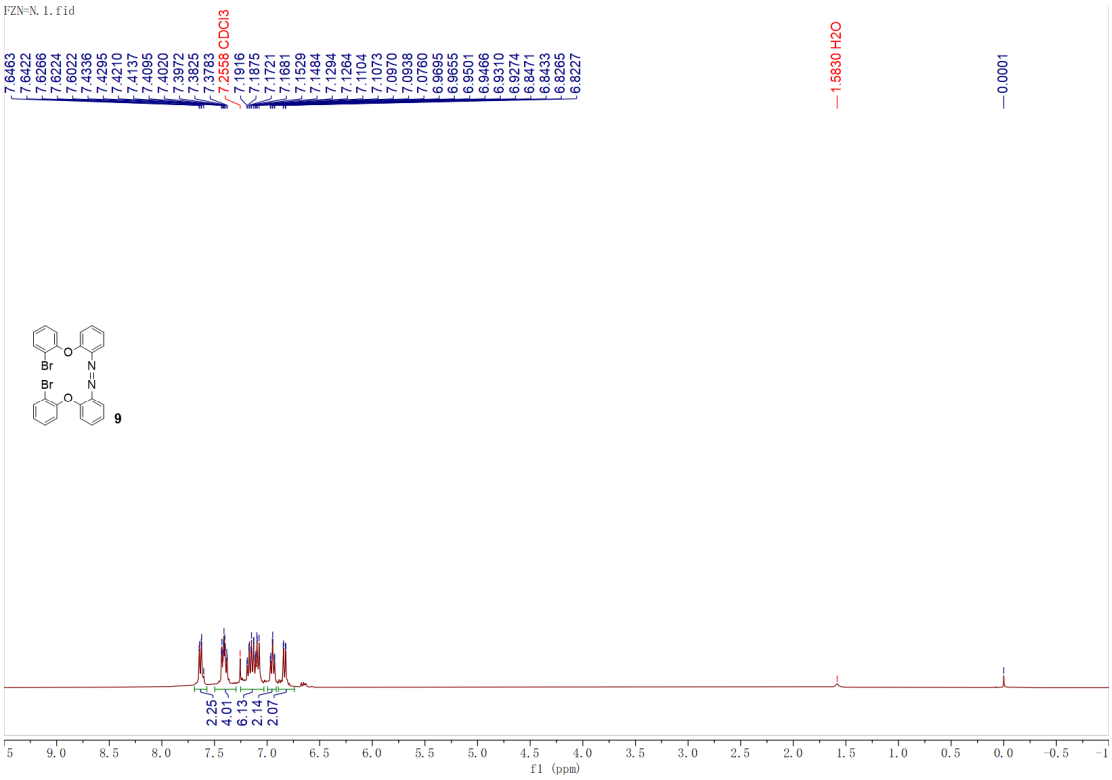

$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **6d**



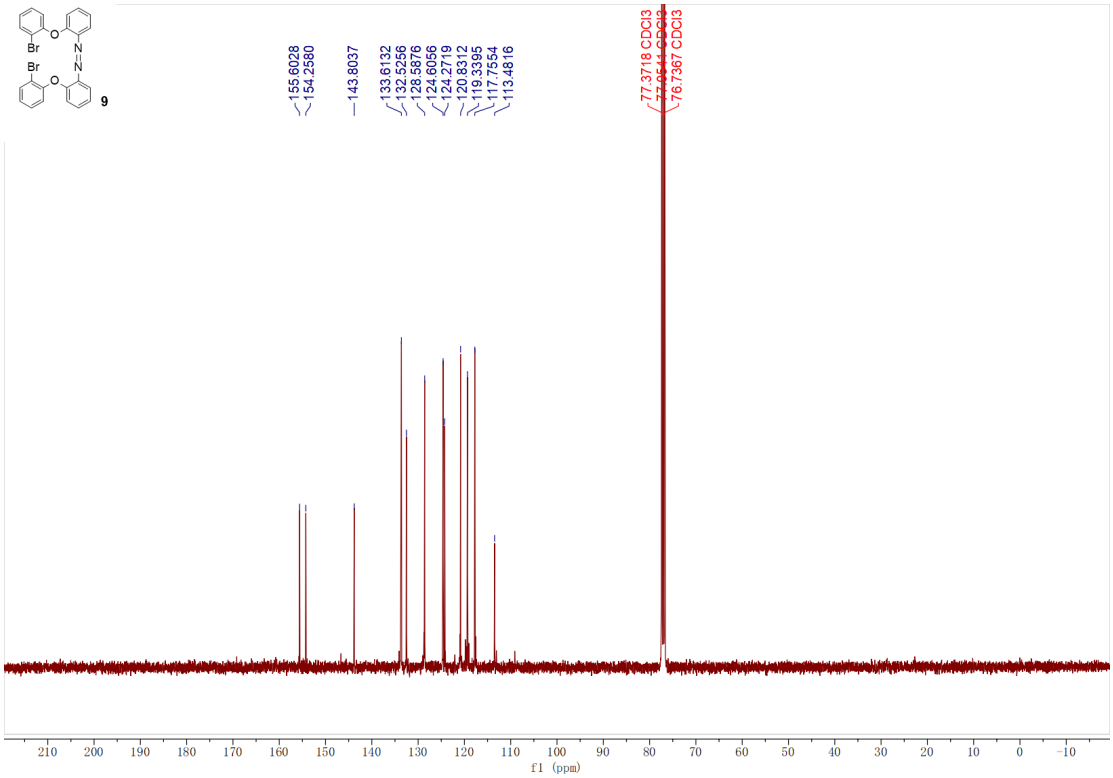

$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **8**



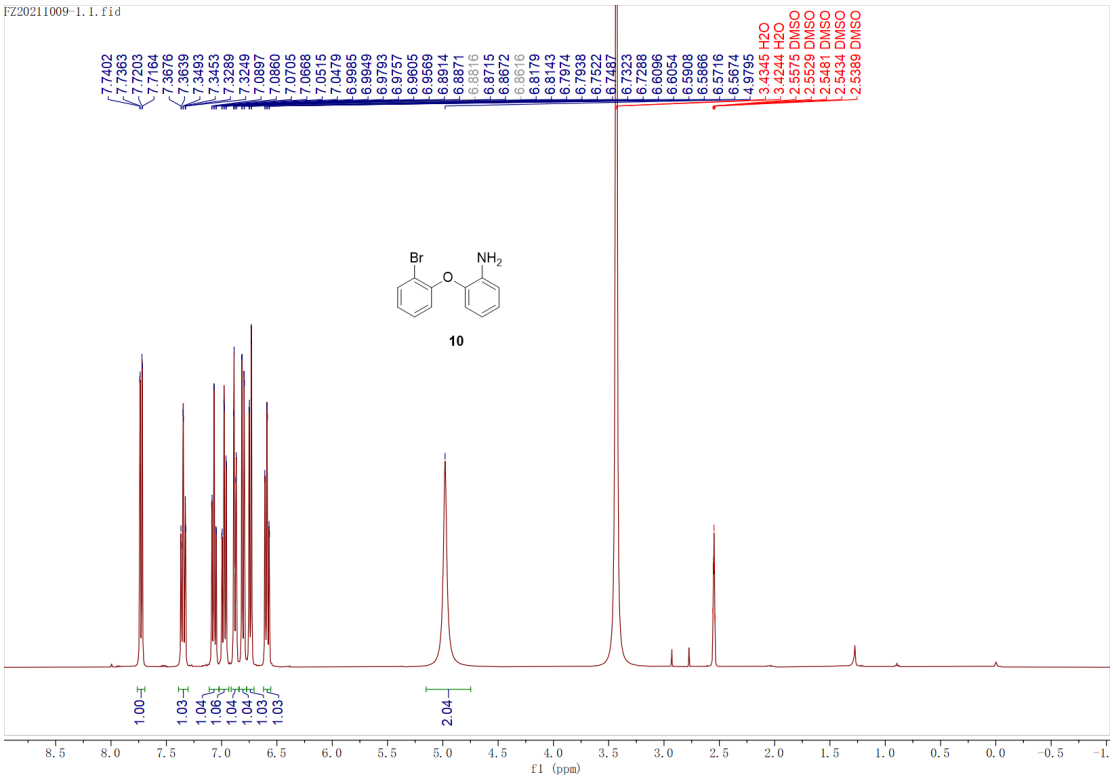

$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **8**



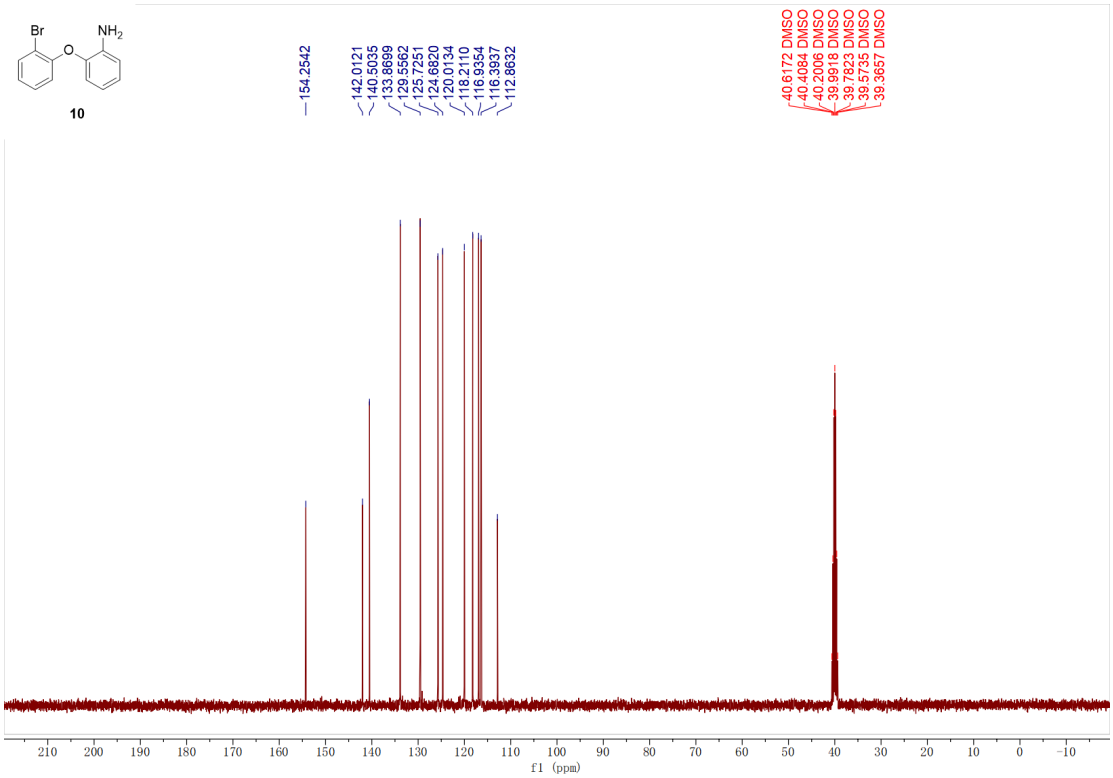

$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **9**



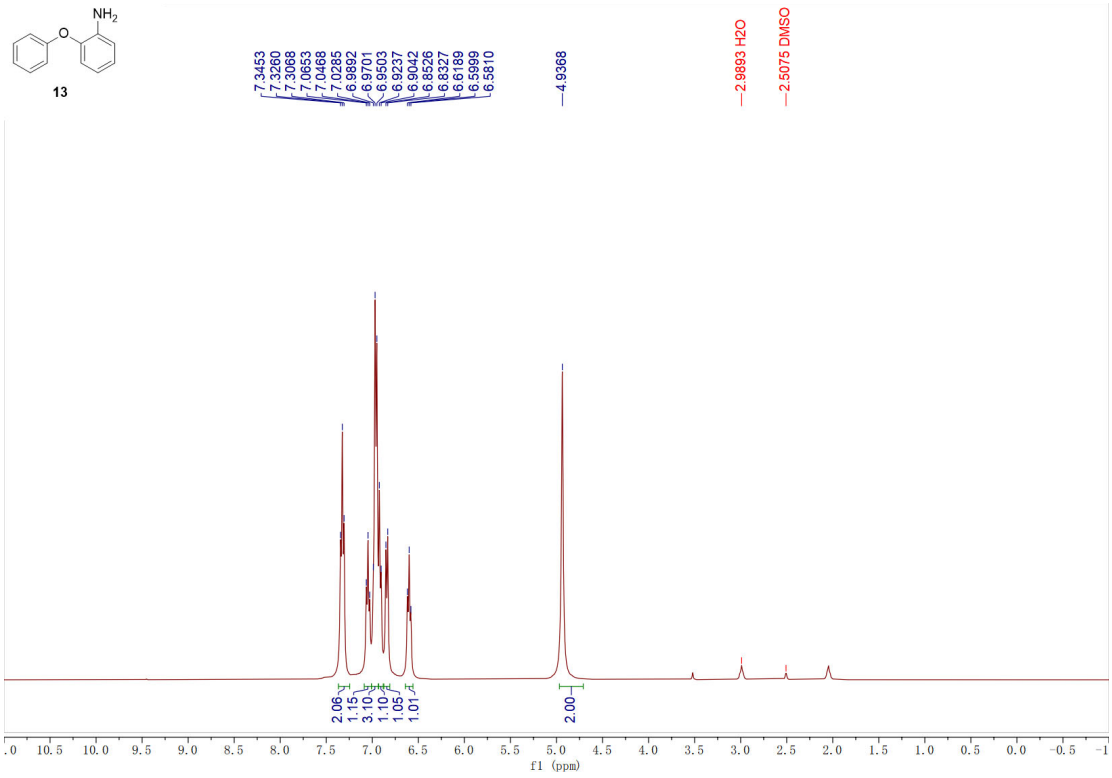

$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **9**



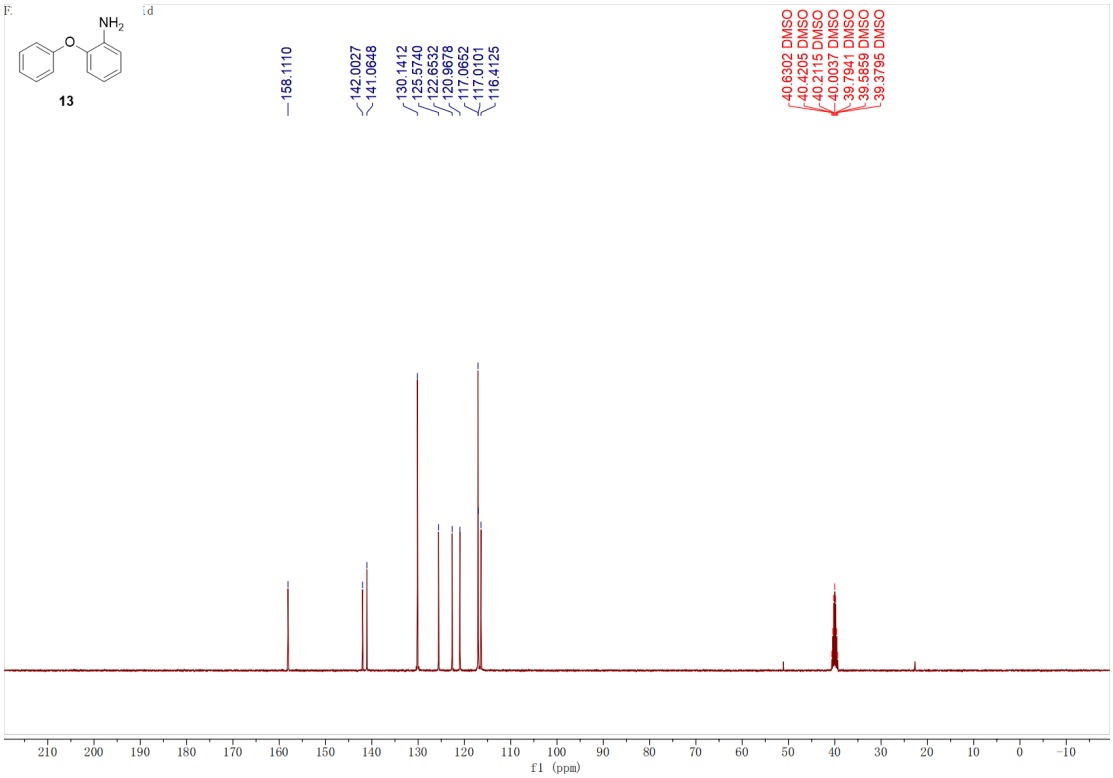

$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **10**




$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **10**




$^{1}$H NMR spectra (400 MHz, Chloroform-*d*) of **13**




$^{13}$C NMR spectra (101 MHz, Chloroform-*d*) of **13**