Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supplementary Information

Organozincs for Direct and Versatile Synthesis of Non-Symmetric Azoarenes

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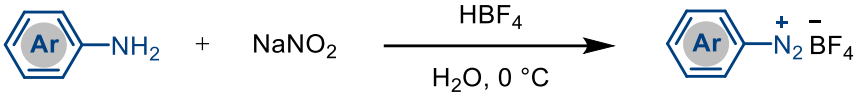
Contents

1. General Remarks

Unless otherwise indicated, all reactions were carried out with magnetic stirring and in flame-dried glassware under nitrogen. Syringes used to transfer reagents and solvents were purged with N_2 prior to use. Commercial solvents and reagents were used as received with the following exceptions. Aryl diazonium tetrafluoroborates,[1] $Zn(OPiv)_2$,[2] arylzinc pivalates reagents,[2] diarylzinc reagents[3]were prepared according to published procedures. Reactions were monitored by thin layer chromatography (TLC). TLC were performed using aluminum plates covered with SiO_2 (Merck 60, F-254) and visualized by UV detection. Purification *via* column chromatography was performed using Merck silica gel 60 (40–63 mm 230–400 mesh ASTM from Merck). THF was continuously refluxed and freshly distilled from sodium benzophenone ketyl under nitrogen. NMR spectra were recorded in $CDCl_3$ and chemical shifts (δ) are reported in parts per million (ppm). Mass spectra and highresolution mass spectra (HR-MS) were recorded using electro ionization (EI) except where otherwise noted.

2. Representative Procedures

2.1 Typical procedure 1 (TP1) for the synthesis of aryl diazonium tetrafluoroborates:



Scheme S1. Preparation of aryl diazonium tetrafluoroborates

The appropriate aniline (10 mmol) was dissolved in a mixture of 4 mL of distilled water and 3.4 mL of 50% hydrofluoroboric acid. After cooling the reaction mixture to 0 ℃ using the ice bath, sodium nitrite (0.69 g in 1.5 mL of distilled water) was added dropwise in 5 min. The resulting mixture was stirred for 30 min and the precipitate was collected by filtration and re-dissolved in minimum amount of acetone. Diethyl ether was added until precipitate of diazonium tetrafluoroborates, which is filtered, washed several times with diethyl ether and dried under vacuum.[1]

2.2 Typical procedure 2 (TP2) for the preparation of $Zn(OPiv)_2$:

Pivalic acid (20.4 g, 22.6 mL, 200 mmol) was placed in a dry and argon-flushed 500 mL three-necked roundbottom flask, equipped with a magnetic stirring bar, a septum and a pressure equalizer, and was dissolved in dry THF (120 mL). The mixture was cooled to 0 ℃, and a solution of Et_2Zn (13.0 g, 10.8 mL, 105 mmol) in dry THF (120 mL) was added over a period of 30 min under vigorous stirring. Then, the ice-bath was removed and stirring was continued at 23 ℃ for one additional hour at which point bubbling has ceased (a thick slurry was formed). The solvent was removed in vacuo and the solid residue was dried for at least 4 h longer. $Zn(OPiv)_2$ was obtained in quantitative yield, as a puffy amorphous white solid.[2]

2.3 Typical procedure 3 (TP3) for the preparation of organozinc reagents:

2.3.1 preparation of diarylzinc reagents:

Method A:

An oven-dried Schlenk tube equipped with magnetic stir bar was charged with magnesium turnings (6.00 mmol, 1.20 equiv), LiCl (6.00 mmol, 1.20 equiv) and THF (5.00 mL). The aromatic halide (5.00 mmol, 1.00 equiv) was added dropwise and the reaction mixture was stirred at 23 ℃ for 1 hour. If necessary, the Schlenk-flask was placed in a water bath for cooling

during the initial heat evolution of the insertion reaction. for 1 hour. The resulting solution of Grignard reagent was titrated with I_2 according to Knochel's method to afford Grignard reagents with concentration typically ranging 0.6-0.8 M in THF. A solution of $ZnCl_2$ (2.50 mL, 0.50 equiv, 1.00 M in THF) was added in one portion and the reaction mixture was stirred at 23 ℃ for 5 minutes, and the diarylzinc reagents was prepared.[2]

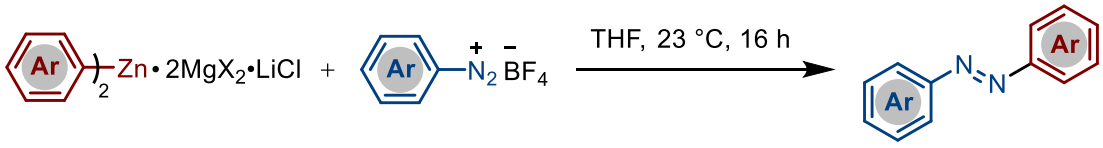
Method B:

An oven-dried Schlenk tube equipped with magnetic stir bar was charged with the aryl iodide (5.00 mmol, 1.00 equiv), THF (5.00 mL), and the solution was cooled to -40 ℃. A solution of *i*PrMgBr·LiCl (5.00 mL, 1.00 equiv, 1.00 M in THF) was slowly added along the edges of Schlenk tube and the reaction mixture was stirred at -40 ℃ for 1 hour. The resulting solution of Grignard reagent was titrated with I_2 according to Knochel's method to afford Grignard reagents with concentration typically ranging 0.6-0.8 M in THF.A solution of $ZnCl_2$ (2.50 mL, 0.50 equiv, 1.00 M in THF) was slowly added along the edges of Schlenk tube and the reaction mixture was stirred at 23 ℃ for 10 minutes.[2]

2.3.2 preparation of arylzinc pivalates:

An oven-dried Schlenk tube equipped with magnetic stir bar was charged with magnesium turnings (6.00 mmol, 1.20 equiv), LiCl (6.00 mmol, 1.20 equiv) and THF (5.00 mL). The aromatic halide (5.00 mmol, 1.00 equiv) was added dropwise and the reaction mixture was stirred at 23 ℃ for 1 hour. If necessary, the Schlenk-flask was placed in a water bath for cooling during the initial heat evolution of the insertion reaction. for 1 hour. The resulting solution of Grignard reagent was titrated with I_2 according to Knochel's method to afford Grignard reagents with concentration typically ranging 0.6-0.8 M in THF. Solid $Zn(OPiv)_2$ (1.2 equiv) was added in one portion and the reaction mixture was stirred at 23 ℃ for 15 minutes, and the arylzinc pivalates reagents was prepared.[3]

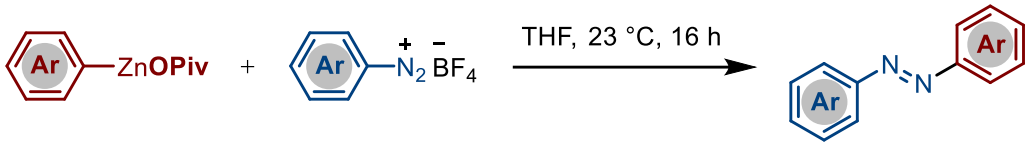
2.4 Typical Procedure 4 (TP4) for the azo compounds:



Scheme S2. Preparation of azo compounds

A oven-dried Schlenk tube equipped with magnetic stir bar was charged with the aryl diazonium tetrafluoroborates (0.50 mmol, 1.0 equiv) and THF (2.50 mL). The diarylzinc reagent (0.38 mmol, 0.75 equiv) prepared according to **TP3** were added to this Schlenk tube and the reaction mixture was stirred at 23 ℃ for 16 hours. Upon the reaction is completed. The reaction mixture was diluted with ethyl acetate (2 mL). The solvent was evaporated in vacuo and the remaining residue was purified by column chromatography on silica gel (PE/EA) to yield products **3-44**.

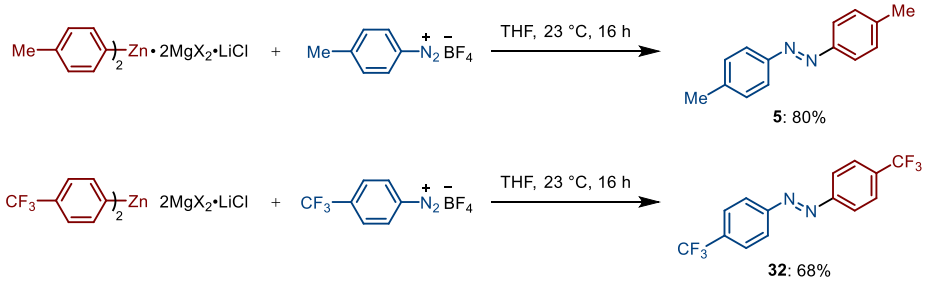
2.5 Typical Procedure 5 (TP5) for the reaction of OPiv-supported arylzinc reagents in this transition-metal-free direct arylation of diazonium salts



Scheme S3. OPiv-supported arylzinc reagents for the synthesis of non-symmetric azoarenes

A oven-dried Schlenk tube equipped with magnetic stir bar was charged with the aryl diazonium tetrafluoroborates (0.50 mmol, 1.0 equiv) and THF (2.50 mL). The arylzinc pivalates reagent (0.75 mmol, 1.5 equiv) prepared according to **TP3** were added to this Schlenk tube and the reaction mixture was stirred at 23 ℃ for 16 hours. Upon the reaction is completed. The reaction mixture was diluted with ethyl acetate (2 mL).The solvent was evaporated in vacuo and the remaining residue was purified by column chromatography on silica gel (PE/EA) to yield products.

2.6 Gram-scale experiments



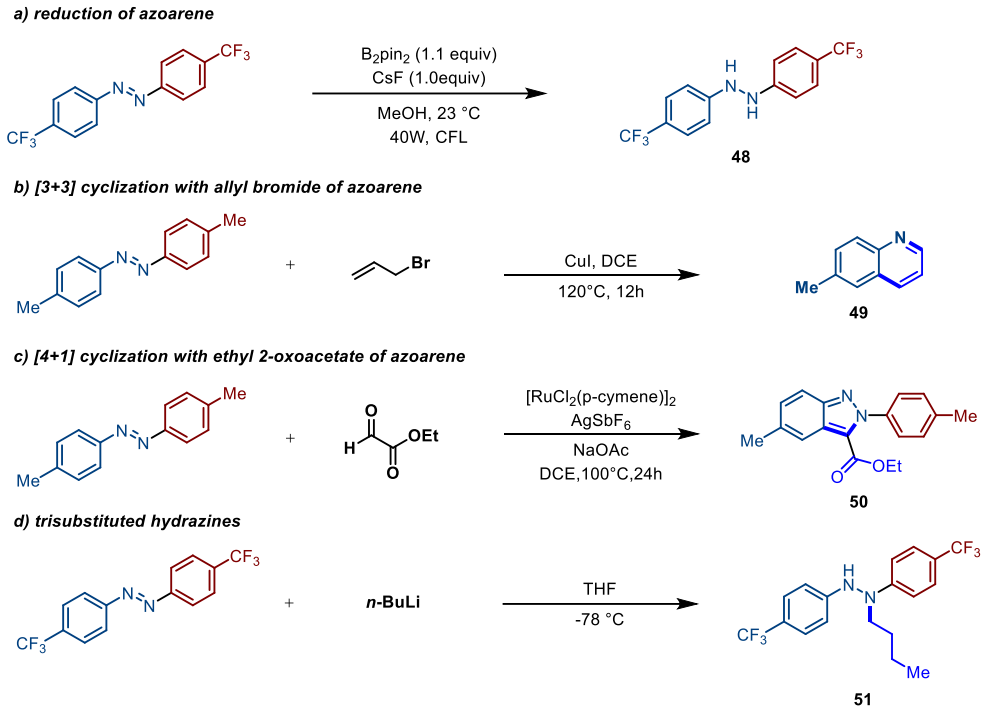
Scheme S4. Gram-scale experiments

A oven-dried Schlenk tube equipped with magnetic stir bar was charged with the aryl diazonium tetrafluoroborates (7.00 mmol, 1.0 equiv) and THF (25.00 mL). The diarylzinc reagent (0.75

equiv) prepared according to **TP3** were added to this Schlenk tube and the reaction mixture was stirred at 23 ℃ for 16 hours. Upon the reaction is completed. The reaction mixture was diluted with ethyl acetate. The solvent was evaporated in vacuo and the remaining residue was purified by column chromatography on silica gel (PE/EA) to yield products **5**.

A oven-dried Schlenk tube equipped with magnetic stir bar was charged with the aryl diazonium tetrafluoroborates (5.00 mmol, 1.0 equiv) and THF (20.00 mL). The diarylzinc reagent (0.75 equiv) prepared according to **TP3** were added to this Schlenk tube and the reaction mixture was stirred at 23 ℃ for 16 hours. Upon the reaction is completed. The reaction mixture was diluted with ethyl acetate. The solvent was evaporated in vacuo and the remaining residue was purified by column chromatography on silica gel (PE/EA) to yield products **32**.

2.7 Facile derivatizations of azoarenes



Scheme S5. Late-stage modifications of aryl azo compounds.

Procedure for Scheme S5a:

Azobenzenes (0.2 mmol), CsF (30.4 mg, 0.2 mmol, 1.0 equiv), B_2pin_2 (55.9 mg, 0.22 mmol, 1.1 equiv), and MeOH (3 mL) were added into a 10 mL Pyrex glass tube equipped with a magnetic stirring bar. Then, the reaction mixture was stirred under irradiation of a 23 W CFL at 23 ℃. Upon completion of the reaction (monitored by TLC), the mixture was concentrated

under vacuum and the residue was purified by column chromatography (PE/EA) to give the pure product **48**.[4]

Procedure for Scheme S5b:

A sealed tube was charged with the mixture of azobenzenes (0.2 mmol), CuI (0.2 mmol, 38.2 mg), allyl bromide (0.4 mmol), then stirred in 1,2-dichloroethane (DCE, 2 mL) at given temperature under nitrogen atmosphere for a given reaction time. When the reaction completed, water (2 mL) and ammonia (0.5 mL, 25% weight) were added and sufficiently mixed with the organic phase. Then, the mixture was extracted with dichloromethane (2 mL × 3). After being dried over Na_2SO_4, the organic phase was evaporated, and the residue was purified by column chromatography (PE/EA) to give the pure product **49**.[5]

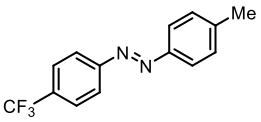
Procedure for Scheme S5c:

A second oven-dried Schlenk tube was charged with azobenzenes (0.2 mmol), [Ru(*p*-cymene)Cl_2] (5 mol%), $AgSbF_6$ (20 mol%), NaOAc (50 mol%) and DCE (1.5 mL) under N_2 atmosphere. Then ethyl glyoxalate (0.4 mmol) in DCE (0.5 mL) was added in one-pot under N_2 and the mixture was stirred at 100 ℃ for 24 h. The corresponding reaction mixture was filtered through a pad of Celite, washed with DCE and concetrated under reduced pressure. The residue was purified by column chromatography (PE/EA) to give the pure product **50**.[6]

Procedure for Scheme S5d:

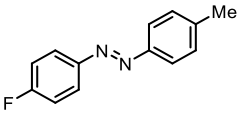
A solution of alkyllithium (0.22 mmol) in hexane was added dropwise to a stirred solution of azobenzene (0.20 mmol) in 0.60 mL THF at - 78 ℃ under N_2. The mixture was stirred at this temperature for 2 h, allowed to warm up to 23 ℃. and stirred for another 10 h. The mixture was poured into H_2O (2.00 mL), extracted with EA (4.00 mL), washed with H_2O (2.00 mL), dried (Mg_2SO_4), concentrated and purified by column chromatography (PE/EA) to give the pure product **51**.[7]

3. Characterization Data



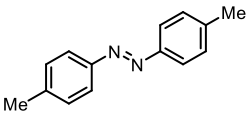
***(E)*-1-(*p*-Tolyl)-2-[4-(trifluoromethyl)phenyl]diazene (3)**

The general procedure **TP4** was followed using **4-(trifluoromethyl)benzenediazonium tetrafluoroborate** and **bis(4-methylphenyl)zinc**. Purification by column chromatography (PE) yielded **3** (103 mg, 78%) as an orange needle crystal. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.97 (d, J = 8.2 Hz, 2H), 7.86 (dt, J = 8.2, 1.6 Hz, 2H), 7.76 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 7.9 Hz, 2H), 2.45 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 154.7 (d, $^{4}J_{C-F}$ = 1.5 Hz), 150.7, 142.7, 132.1 (q, $^{2}J_{C-F}$ = 32.5 Hz), 130.0, 126.4 (q, $^{3}J_{C-F}$ = 3.8 Hz), 124.1, (q, $^{1}J_{C-F}$ = 271.0 Hz), 123.4, 123.0, 21.7. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -62.46 (s). HR-MS (EI) m/z calcd for $C_{14}H_{11}F_3N_2$ [M+H$^+$] 265.0947, found 265.0949.



***(E)*-1-(4-Fluorophenyl)-2-(*p*-tolyl)diazene (4)**

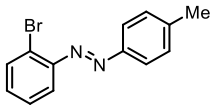
The general procedure **TP4** was followed using **4-fluorobenzenediazonium tetrafluoroborate** and **bis(4-methylphenyl)zinc**. Purification by column chromatography (PE) yielded **4** (77 mg, 72%) as an orange crystal. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.92 (dd, *J* = 8.9, 5.3 Hz, 2H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.18 (t, *J* = 8.6 Hz, 2H), 2.44 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 164.3 (d, $^{1}J_{C-F}$ = 251.3 Hz), 150.7, 149.4 (d, $^{4}J_{C-F}$ = 3.0 Hz), 141.8, 129.9, 124.8 (d, $^{3}J_{C-F}$ = 8.8 Hz), 123.0, 116.1 (d, $^{2}J_{C-F}$ = 22.8 Hz), 21.7. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -109.93 (s). HR-MS (EI) m/z calcd for $C_{13}H_{11}FN_2$ [M+H$^+$] 215.0979, found 215.0977.



***(E)*-1,2-Di-*p*-tolyldiazene (5)**

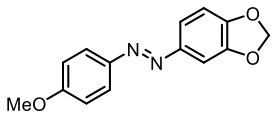
The general procedure **TP4** was followed using **4-methylbenzenediazonium tetrafluoroborate** and **bis(4-methylphenyl)zinc**. Purification by column chromatography (PE) yielded **5** (84 mg, 80%) as an orange needle crystal. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.81 (d,

J = 8.3 Hz, 4H), 7.29 (d, *J* = 8.2 Hz, 4H), 2.42 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 151.0, 141.3, 129.8, 122.9, 21.6. HR-MS (EI) m/z calcd for $C_{14}H_{14}N_2$ [M+H$^+$] 211.1230, found 211.1233.



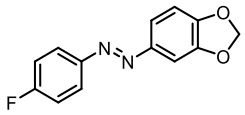
***(E)*-1-(2-Bromophenyl)-2-(*p*-tolyl)diazene (6)**

The general procedure **TP4** was followed using **2-bromobenzenediazonium tetrafluoroborate** and **bis(4-methylphenyl)zinc**. Purification by column chromatography (PE) yielded **6** (85 mg, 62%) as an orange needle crystal. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.89 (d, *J* = 8.3 Hz, 2H), 7.74 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.66 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.38 (td, *J* = 7.7, 1.4 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.28 (dd, *J* = 7.7, 1.7 Hz, 1H), 2.44 (s, 3H).^{13}C-NMR (100 MHz, $CDCl_3$): δ = 151.0, 149.9, 142.4, 133.8, 131.7, 130.0, 128.1, 125.6, 123.6, 118.0, 21.7. HR-MS (EI) m/z calcd for $C_{13}H_{11}BrN_2$ [M+H$^+$] 275.0178, found 275.0179.



***(E)*-1-[Benzo(*d*) (1,3)dioxol-5-yl]-2-(4-methoxyphenyl)diazene (7)**

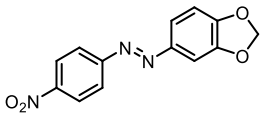
The general procedure **TP4** was followed using **4-methoxybenzenediazonium tetrafluoroborate** and **bis(benzo[*d*][1,3]dioxol-5-yl)zinc**. Purification by column chromatography (PE: EA = 20:1) yielded **7** (83 mg, 64%) as an orange needle crystal. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.88 (s, 1H), 7.86 (s, 1H), 7.53 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.41 (d, *J* = 1.9 Hz, 1H), 7.01 (s, 1H), 6.99 (s, 1H), 6.93 (d, *J* = 8.2 Hz, 1H), 6.05 (s, 2H), 3.89 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 161.8, 149.9, 148.8, 148.8, 147.0, 124.6, 122.9, 114.3, 108.1, 101.9, 99.2, 55.7. HR-MS (EI) m/z calcd for $C_{14}H_{12}N_2O_3$ [M+H$^+$] 257.0921, found 257.0923.



***(E)*-1-[Benzo(*d*)(1,3)dioxol-5-yl]-2-(4-fluorophenyl)diazene (8)**

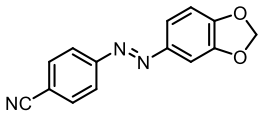
The general procedure **TP4** was followed using **4-fluorobenzenediazonium tetrafluoroborate** and **bis(benzo[*d*][1,3]dioxol-5-yl)zinc**. Purification by column chromatography (PE: EA = 20:1) yielded **8** (85 mg, 70%) as an orange needle crystal. ^{1}H-NMR

(400 MHz, $CDCl_3$): δ = ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.93 – 7.83 (m, 2H), 7.56 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.41 (d, *J* = 2.0 Hz, 1H), 7.22 – 7.12 (m, 2H), 6.94 (d, *J* = 8.2 Hz, 1H), 6.06 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 164.2 (d, $^1J_{C\text{-}F}$ = 251.2 Hz), 150.5, 149.2 (d, $^4J_{C\text{-}F}$ = 3.0 Hz), 148.9, 148.5, 124.7 (d, $^3J_{C\text{-}F}$ = 8.8 Hz), 123.9, 116.1 (d, $^2J_{C\text{-}F}$ = 22.9 Hz), 108.1, 102.1, 99.1. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -110.18 (s). HR-MS (EI) m/z calcd for $C_{13}H_9FN_2O_2$ [M+H$^+$] 245.0721, found 245.0722.



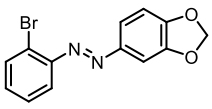
***(E)*-1-[Benzo(*d*)(1,3)dioxol-5-yl]-2-(4-nitrophenyl)diazene (9)**

The general procedure **TP4** was followed using **4-nitrobenzenediazonium tetrafluoroborate** and **bis(benzo[*d*][1,3]dioxol-5-yl)zinc**. Purification by column chromatography (PE: EA = 20:1) yielded **9** (123 mg, 90%) as an orange needle crystal. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.38 – 8.34 (m, 2H), 8.00 – 7.96 (m, 2H), 7.68 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.45 (d, *J* = 1.9 Hz, 1H), 6.99 (d, *J* = 8.2 Hz, 1H), 6.10 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 156.0, 151.8, 149.2, 148.7, 148.5, 126.1, 124.9, 123.4, 108.3, 102.4, 98.8. HR-MS (EI) m/z calcd for $C_{13}H_9N_3O_4$ [M+H$^+$] 272.0666, found 272.0665.



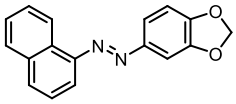
***(E)*-4-[Benzo(*d*)(1,3)dioxol-5-yldiazenyl]benzonitrile (10)**

The general procedure **TP4** was followed using **4-cyanobenzenediazonium tetrafluoroborate** and **bis(benzo[*d*][1,3]dioxol-5-yl)zinc**. Purification by column chromatography (PE: EA = 20:1) yielded **10** (62.5 mg, 50%) as an orange needle crystal. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 8.2 Hz, 2H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.65 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.43 (d, *J* = 2.0 Hz, 1H), 6.98 (d, *J* = 8.2 Hz, 1H), 6.09 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 154.7, 151.6, 149.2, 148.6, 133.3, 125.7, 123.3, 118.8, 113.5, 108.3, 102.3, 98.8. HR-MS (EI) m/z calcd for $C_{14}H_9N_3O_2$ [M+H$^+$] 252.0768, found 252.0766.



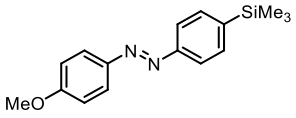
***(E)*-1-[Benzo(*d*)(1,3)dioxol-5-yl]-2-(2-bromophenyl)diazene (11)**

The general procedure **TP4** was followed using **2-bromobenzenediazonium tetrafluoroborate** and **bis(benzo[*d*][1,3]dioxol-5-yl)zinc**. Purification by column chromatography (PE: EA = 20:1) yielded **11** (103 mg, 67%) as an orange needle crystal. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.73 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.66 (dd, *J* = 3.1, 1.8 Hz, 1H), 7.64 (dd, *J* = 3.3, 1.8 Hz, 1H), 7.49 (d, *J* = 1.9 Hz, 1H), 7.37 (ddd, *J* = 8.1, 7.2, 1.4 Hz, 1H), 7.31 – 7.27 (m, 1H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.08 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 151.0, 149.6, 149.0, 148.9, 133.8, 131.5, 128.1, 125.6, 125.0, 117.9, 108.1, 102.1, 99.4. HR-MS (EI) m/z calcd for $C_{13}H_9BrN_2O_2$ [M+H$^+$] 304.9920, found 304.9922.



***(E)*-1-[Benzo(*d*)(1,3)dioxol-5-yl]-2-(naphthalen-1-yl)diazene (12)**

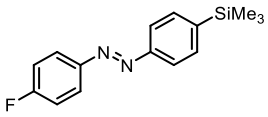
The general procedure **TP4** was followed using **naphthalene-1-diazonium tetrafluoroborate** and **bis(benzo[*d*][1,3]dioxol-5-yl)zinc**. Purification by column chromatography (PE: EA = 20:1) yielded **12** (105 mg, 76%) as an orange needle crystal. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.91 – 8.87 (m, 1H), 7.98 – 7.88 (m, 2H), 7.79 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.70 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.66 – 7.60 (m, 1H), 7.60 – 7.52 (m, 3H), 6.98 (d, *J* = 8.1 Hz, 1H), 6.08 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 150.5, 149.4, 149.0, 147.8, 134.4, 131.4, 130.9, 128.1, 126.8, 126.5, 125.8, 124.4, 123.6, 111.9, 108.2, 102.1, 99.2. HR-MS (EI) m/z calcd for $C_{17}H_{12}N_2O_2$ [M+H$^+$] 277.0972, found 277.0970.



***(E)*-1-(4-Methoxyphenyl)-2-[4-(trimethylsilyl)phenyl]diazene (13)**

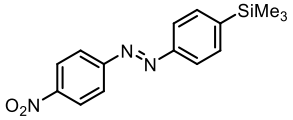
The general procedure **TP4** was followed using **4-methoxybenzenediazonium tetrafluoroborate** and **bis[4-(trimethylsilyl)phenyl]zinc**. Purification by column chromatography (PE: EA = 50:1) yielded **13** (119 mg, 84%) as an orange needle crystal. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.94 – 7.90 (m, 2H), 7.85 – 7.81 (m, 2H), 7.68 – 7.62 (m, 2H), 7.05 – 6.96 (m, 2H), 3.87 (s, 3H), 0.31 (s, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 162.2, 153.2,

147.3, 143.8, 134.2, 124.9, 121.8, 114.3, 55.7, -1.00. HR-MS (EI) m/z calcd for $C_{16}H_{20}N_2OSi$ [M+H$^+$] 285.1418, found 285.1415.



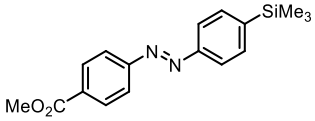
***(E)*-1-(4-Fluorophenyl)-2-[4-(trimethylsilyl)phenyl]diazene** (**14**)

The general procedure **TP4** was followed using **4-fluorobenzenediazonium tetrafluoroborate** and **bis(4-(trimethylsilyl)phenyl)zinc**. Purification by column chromatography (PE: EA = 50:1) yielded **14** (109 mg, 80%) as an orange needle crystal. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.96 – 7.91 (m, 2H), 7.87 – 7.84 (m, 2H), 7.70 – 7.63 (m, 2H), 7.23 – 7.14 (m, 2H), 0.31 (s, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 164.5 (d, $^1J_{C–F}$ = 252.0 Hz), 152.9, 149.4 (d, $^4J_{C–F}$ = 3.0 Hz), 144.7, 134.3, 125.0 (d, $^3J_{C–F}$ = 8.8 Hz), 122.0, 116.2 (d, $^2J_{C–F}$ = 23.0 Hz), -1.0. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -109.39 (s). HR-MS (EI) m/z calcd for $C_{15}H_{17}FN_2Si$ [M+H$^+$] 273.1218, found 273.1216.



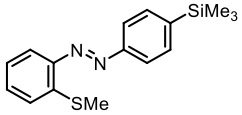
***(E)*-1-(4-Nitrophenyl)-2-[4-(trimethylsilyl)phenyl]diazene** (**15**)

The general procedure **TP4** was followed using **4-nitrobenzenediazonium tetrafluoroborate** and **bis[4-(trimethylsilyl)phenyl]zinc**. Purification by column chromatography (PE: EA = 50:1) yielded **15** (120 mg, 80%) as an orange needle crystal. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.36 (dd, J = 9.0, 2.0 Hz, 2H), 8.04 – 7.99 (m, 2H), 7.92 (d, J = 8.2 Hz, 2H), 7.73 – 7.68 (m, 2H), 0.33 (s, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 155.9, 152.7, 146.8, 134.4, 129.4, 124.8, 123.6, 122.5, -1.1. HR-MS (EI) m/z calcd for $C_{15}H_{17}N_3O_2Si$ [M+H$^+$] 300.1163, found 300.1165.



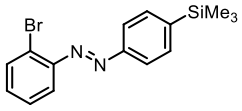
Methyl *(E)*-4-{[4-(trimethylsilyl)phenyl]diazinyl}benzoate (**16**)

The general procedure **TP4** was followed using **4-(methoxycarbonyl)benzenediazonium tetrafluoroborate** and **bis[4-(trimethylsilyl)phenyl]zinc**. Purification by column chromatography (PE: EA = 50:1) yielded **16** (83 mg, 53%) as an orange needle crystal. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.23 – 8.16 (m, 2H), 7.98 – 7.93 (m, 2H), 7.92 – 7.89 (m, 2H), 7.72 – 7.66 (m, 2H), 3.96 (s, 3H), 0.32 (s, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 166.7, 155.4, 153.0, 145.7, 134.3, 131.9, 130.8, 122.8, 122.3, 52.5, -1.1. HR-MS (EI) m/z calcd for $C_{17}H_{20}N_2O_2Si$ [M+H$^+$] 313.1367, found 313.1366.



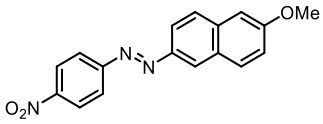
***(E)*-1-[2-(Methylthio)phenyl]-2-[4-(trimethylsilyl)phenyl]diazene (17)**

The general procedure **TP4** was followed using **2-(methylthio)benzenediazonium tetrafluoroborate** and **bis[4-(trimethylsilyl)phenyl]zinc**. Purification by column chromatography (PE) yielded **17** (116 mg, 77%) as an orange needle crystal. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.89 (dd, J = 8.8, 5.0 Hz, 2H), 7.68 – 7.64 (m, 3H), 7.40 – 7.36 (m, 1H), 7.31 (dt, J = 7.7, 3.4 Hz, 1H), 7.18 (dd, J = 7.5, 3.6 Hz, 1H), 2.49 (q, J = 6.2, 4.8 Hz, 3H), 0.30 (dt, J = 6.2, 3.6 Hz, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 153.2, 149.0, 144.7, 141.0, 134.2, 131.5, 124.9, 124.7, 122.3, 117.0, 14.9, -1.1. HR-MS (EI) m/z calcd for $C_{16}H_{20}N_2SSi$ [M+H$^+$] 301.1189, found 301.1190.



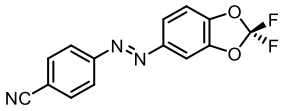
***(E)*-1-(2-Bromophenyl)-2-[4-(trimethylsilyl)phenyl]diazene** (**18**)

The general procedure **TP4** was followed using **2-bromobenzenediazonium tetrafluoroborate** and **bis(4-(trimethylsilyl)phenyl)zinc**. Purification by column chromatography (PE) yielded **18** (135 mg, 81%) as an orange needle crystal. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.96 – 7.92 (m, 2H), 7.73 (dd, J = 7.9, 1.4 Hz, 1H), 7.70 – 7.64 (m, 3H), 7.37 (td, J = 7.7, 1.4 Hz, 1H), 7.31 – 7.26 (m, 1H), 0.31 (s, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 153.0, 149.9, 145.5, 134.3, 133.9, 132.0, 128.1, 125.9, 122.6, 117.9, -1.0. HR-MS (EI) m/z calcd for $C_{15}H_{17}BrN_2Si$ [M+H$^+$] 333.0417, found 333.0415.



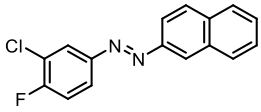
***(E)*-1-(6-Methoxynaphthalen-2-yl)-2-(4-nitrophenyl)diazene** (**19**)

The general procedure **TP4** was followed using **4-nitrobenzenediazonium tetrafluoroborate** and **bis(6-methoxynaphthalen-2-yl)zinc**. Purification by column chromatography (PE: EA = 20:1) yielded **19** (91 mg, 59%) as an orange needle crystal. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.47 (d, J = 1.9 Hz, 1H), 8.43 – 8.35 (m, 2H), 8.09 – 8.01 (m, 3H), 7.94 (d, J = 8.9 Hz, 1H), 7.81 (dd, J = 8.6, 5.4 Hz, 1H), 7.24 (dd, J = 8.9, 2.6 Hz, 1H), 7.21 (d, J = 2.5 Hz, 1H), 3.97 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 160.0, 156.2, 149.0, 137.3, 131.4, 130.3, 128.8, 128.2, 124.9, 123.4, 119.9, 117.2, 106.5, 55.6. HR-MS (EI) m/z calcd for $C_{17}H_{13}N_3O_3$ [M+H$^+$] 308.1030, found 308.1031.



***(E)*-4-{[2,2-Difluorobenzo (*d*)(1,3)dioxol-5-yl]diazinyl}benzonitrile (20)**

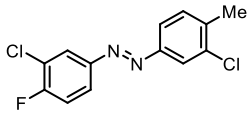
The general procedure **TP4** was followed using **4-cyanobenzenediazonium tetrafluoroborate** and **bis(2,2-difluorobenzo[*d*][1,3]dioxol-5-yl)zinc**. Purification by column chromatography (PE: EA = 20:1) yielded **39** (95 mg, 66%) as an orange needle crystal. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.00 – 7.94 (m, 2H), 7.87 (d, J = 8.5, Hz, 1H), 7.84 – 7.79 (m, 2H), 7.66 (d, J = 2.0 Hz, 1H), 7.24 (d, J = 8.5 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 154.1, 149.1, 146.5, 144.9, 133.3, 131.9 (t, $^{1}J_{C-F}$ = 256 Hz), 125.0, 123.5, 118.4, 114.4, 109.6, 100.9. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -49.8 (s). HR-MS (EI) m/z calcd for $C_{14}H_7F_2N_3O_2$ [M+H$^+$] 288.0579, found 288.0577.



***(E)*-1-(3-Chloro-4-fluorophenyl)-2-(naphthalen-2-yl)diazene** (**21**)

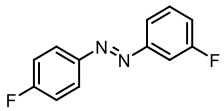
The general procedure **TP4** was followed using **3-chloro-4-fluorobenzenediazonium tetrafluoroborate** and **di(naphthalen-2-yl)zinc**. Purification by column chromatography (PE:

EA = 50:1) yielded **21** (109 mg, 69%) as an orange needle crystal. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.45 (d, J = 1.9 Hz, 1H), 8.05 (dd, J = 7.0, 2.4 Hz, 1H), 8.03 (d, J = 1.9 Hz, 1H), 8.01 (d, J = 2.0 Hz, 1H), 7.91 (s, 1H), 7.89 (t, J = 4.5 Hz, 2H), 7.60 – 7.53 (m, 2H), 7.30 (t, J = 8.6 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 159.5 (d, $^{1}J_{C-F}$ = 254.3 Hz), 149.9, 149.3 (d, $^{4}J_{C-F}$ = 3.5 Hz), 135.1, 133.5, 129.5, 129.3, 128.8, 128.0 (d, $^{3}J_{C-F}$ = 8.1 Hz), 126.9, 124.2 (d, $^{3}J_{C-F}$ = 7.7 Hz), 124.0, 122.2 (d, $^{2}J_{C-F}$ = 19.2 Hz), 117.1, 116.8, 116.7. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -111.8 (s). HR-MS (EI) m/z calcd for $C_{16}H_{10}ClFN_2$ [M+H$^+$] 285.0589, found 285.0588.



***(E)*-1-(3-Chloro-4-fluorophenyl)-2-(3-chloro-4-methylphenyl)diazene** (**22**)

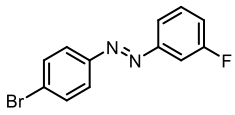
The general procedure **TP4** was followed using **3-chloro-4-fluorobenzenediazonium tetrafluoroborate** and **bis(3-chloro-4-methylphenyl)zinc**. Purification by column chromatography (PE) yielded **22** (92 mg, 65%) as an orange needle crystal. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.97 (dd, J = 6.9, 2.4 Hz, 1H), 7.89 (d, J = 2.0 Hz, 1H), 7.83 (ddd, J = 8.8, 4.5, 2.4 Hz, 1H), 7.72 (dd, J = 8.1, 2.0 Hz, 1H), 7.37 (d, J = 8.1 Hz, 1H), 7.28 (t, J = 8.6 Hz, 1H), 2.45 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 159.8 (d, $^{1}J_{C-F}$ = 254.8 Hz), 151.4, 149.1 (d, $^{4}J_{C-F}$ = 3.4 Hz), 139.9, 135.4, 131.5, 124.4 (d, $^{3}J_{C-F}$ = 7.7 Hz), 124.2, 122.7, 122.5, 122.3, 117.1 (d, $^{2}J_{C-F}$ = 22.4 Hz), 20.4. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -111.3 (s). HR-MS (EI) m/z calcd for $C_{13}H_9Cl_2FN_2$ [M+H$^+$] 283.0200, found 283.0202.



***(E)*-1-(3-Fluorophenyl)-2-(4-fluorophenyl)diazene** (**23**)

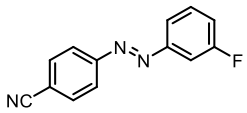
The general procedure **TP4** was followed using **4-fluorobenzenediazonium tetrafluoroborate** and **bis(3-fluorophenyl)zinc**. Purification by column chromatography (PE) yielded **23** (57 mg, 52%) as an orange needle crystal. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.94 (dd, J = 8.7, 5.3 Hz, 2H), 7.72 (t, J = 6.7 Hz, 1H), 7.59 – 7.55 (m, 1H), 7.47 (ddd, J = 13.7, 8.0, 5.8 Hz, 1H), 7.18 (q, J = 7.5, 6.5 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 164.8 (d, $^{1}J_{C-F}$ = 251.0 Hz), 163.4 (d, $^{1}J_{C-F}$ = 246.0 Hz), 154.1 (d, $^{3}J_{C-F}$ = 7.0 Hz), 149.0 (d, $^{4}J_{C-F}$ = 3.0 Hz), 130.4 (d,

$^{3}J_{C-F}$ = 8.5 Hz), 125.2 (d, $^{3}J_{C-F}$ = 9.1 Hz), 120.6 (d, $^{4}J_{C-F}$ = 2.9 Hz), 117.9 (d, $^{2}J_{C-F}$ = 22.0 Hz), 116.3 (d, $^{2}J_{C-F}$ = 23.0 Hz), 108.1 (d, $^{2}J_{C-F}$ = 22.9 Hz). ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -108.5, -112.0. HR-MS (EI) m/z calcd for $C_{12}H_8F_2N_2$ [M+H$^+$] 219.0728, found 219.0727.



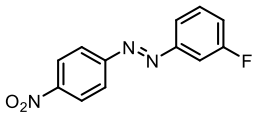
***(E)*-1-(4-Bromophenyl)-2-(3-fluorophenyl)diazene (24)**

The general procedure **TP4** was followed using **4-bromobenzenediazonium tetrafluoroborate** and **bis(3-fluorophenyl)zinc**. Purification by column chromatography (PE) yielded **24** (104 mg, 75%) as an orange needle crystal. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 2.0 Hz, 1H), 7.75 (d, *J* = 2.0 Hz, 1H), 7.71 (dt, *J* = 7.9, 1.3 Hz, 1H), 7.62 (d, *J* = 2.1 Hz, 1H), 7.61 (d, *J* = 2.0 Hz, 1H), 7.56 (dt, *J* = 9.7, 2.2 Hz, 1H), 7.45 (td, *J* = 8.1, 5.8 Hz, 1H), 7.16 (tdd, *J* = 8.1, 2.6, 1.0 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 163.4 (d, $^{1}J_{C-F}$ = 247.9 Hz), 154.0 (d, $^{3}J_{C-F}$ = 7.0 Hz), 151.1, 132.5, 130.4 (d, $^{3}J_{C-F}$ = 8.4 Hz), 126.1, 124.6, 120.8 (d, $^{4}J_{C-F}$ = 2.9 Hz), 118.2 (d, $^{2}J_{C-F}$ = 22.0 Hz), 108.2 (d, $^{2}J_{C-F}$ = 22.9 Hz). ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -111.8 (s). HR-MS (EI) m/z calcd for $C_{12}H_8BrFN_2$ [M+H$^+$] 278.9928, found 278.9926.



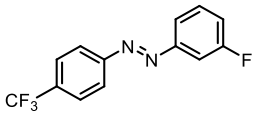
***(E)*-4-[(3-Fluorophenyl) diazinyl] benzonitrile (25)**

The general procedure **TP4** was followed using **4-cyanobenzenediazonium tetrafluoroborate** and **bis(3-fluorophenyl)zinc**. Purification by column chromatography (PE) yielded **25** (86 mg, 76%) as an orange needle crystal. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.92 – 7.86 (m, 2H), 7.76 – 7.67 (m, 3H), 7.52 (dt, *J* = 9.7, 2.1 Hz, 1H), 7.43 (td, *J* = 8.1, 7.7, 6.1 Hz, 1H), 7.15 (td, *J* = 8.2, 2.6 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 163.3 (d, $^{1}J_{C-F}$ = 248.6 Hz), 154.2, 153.8 (d, $^{3}J_{C-F}$ = 7.0 Hz), 123.6, 121.3 (d, $^{4}J_{C-F}$ = 3.0 Hz), 119.2, 119.0, 118.4, 114.5, 108.3 (d, $^{2}J_{C-F}$ = 23.0 Hz). ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -111.4 (td, *J* = 8.8, 5.9 Hz). HR-MS (EI) m/z calcd for $C_{13}H_8FN_3$ [M+H$^+$] 226.0775, found 226.0777.



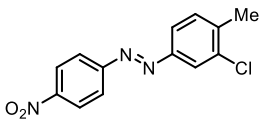
***(E)*-1-(3-Fluorophenyl)-2-(4-nitrophenyl)diazene (26)**

The general procedure **TP4** was followed using **4-nitrobenzenediazonium tetrafluoroborate** and **bis(3-fluorophenyl)zinc**. Purification by column chromatography (PE: EA = 50:1) yielded **26** (91 mg, 74%) as an orange needle crystal. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.31 (d, J = 8.5 Hz, 2H), 7.96 (d, J = 8.5 Hz, 2H), 7.75 (d, J = 7.7 Hz, 1H), 7.56 (dt, J = 9.7, 2.2 Hz, 1H), 7.47 (td, J = 8.1, 5.9 Hz, 1H), 7.23 – 7.14 (m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 163.4 (d, $^{1}J_{C–F}$ = 248.6 Hz), 155.5, 153.9 (d, $^{3}J_{C–F}$ = 7.2 Hz), 149.1, 130.7 (d, $^{3}J_{C–F}$ = 8.4 Hz), 124.9, 123.8, 121.5 (d, $^{4}J_{C–F}$ = 2.9 Hz), 119.3 (d, $^{2}J_{C–F}$ = 22.1 Hz), 108.4 (d, $^{2}J_{C–F}$ = 22.9 Hz). ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -111.4 (s). HR-MS (EI) m/z calcd for $C_{12}H_8FN_3O_2$ [M+H$^+$] 273.1218, found 273.1216.



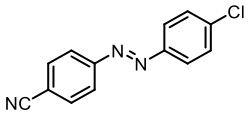
***(E)*-1-(3-Fluorophenyl)-2-[4-(trifluoromethyl)phenyl]diazene** (**27**)

The general procedure **TP4** was followed using **4-(trifluoromethyl)benzenediazonium tetrafluoroborate** and **bis(3-fluorophenyl)zinc**. Purification by column chromatography (PE: EA = 50:1) yielded **27** (71 mg, 53%) as an orange needle crystal. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.31 (d, J = 8.1 Hz, 2H), 8.12 – 8.06 (m, 3H), 7.93 (dt, J = 9.6, 2.2 Hz, 1H), 7.82 (td, J = 8.0, 5.8 Hz, 1H), 7.53 (td, J = 9.0, 8.1, 3.5 Hz, 1H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 163.4 (d, $^{1}J_{C–F}$ = 248.3 Hz), 154.2, 154.0 (d, $^{3}J_{C–F}$ = 7.1 Hz), 133.0, 132.6, 130.6 (d, $^{3}J_{C–F}$ = 8.4 Hz), 126.5 (q, $^{4}J_{C–F}$ = 3.8 Hz), 124.0 (q, $^{1}J_{C–F}$ = 271.0 Hz), 123.3, 121.1 (d, $^{4}J_{C–F}$ = 3.0 Hz), 118.7 (d, $^{2}J_{C–F}$ = 22.0 Hz). ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -62.6 (s), -111.7 (s). HR-MS (EI) m/z calcd for $C_{13}H_8F_4N_2$ [M+H$^+$] 269.0696, found 269.0699.



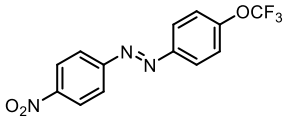
***(E)*-1-(3-Chloro-4-methylphenyl)-2-(4-nitrophenyl)diazene** (**28**)

The general procedure **TP4** was followed using **4-nitrobenzenediazonium tetrafluoroborate** and **bis(3-chloro-4-methylphenyl)zinc**. Purification by column chromatography (PE: EA = 20:1) yielded **28** (128 mg, 93%) as an orange needle crystal. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.40 – 8.33 (m, 2H), 8.01 (d, J = 8.9 Hz, 2H), 7.95 (d, J = 2.0 Hz, 1H), 7.80 (dd, J = 8.1, 2.0 Hz, 1H), 7.41 (d, J = 8.1 Hz, 1H), 2.47 (s, 3H). ^{13}C-NMR (100 Hz, $CDCl_3$): δ = 155.6, 151.5, 148.9, 141.0, 135.6, 131.6, 124.9, 123.6, 123.0, 122.9, 20.5. HR-MS (EI) m/z calcd for $C_{13}H_{10}ClN_3O_2$ [M+H$^+$] 276.0534, found 276.0533.



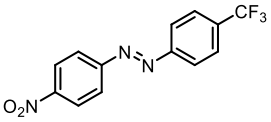
***(E)*-4-[(4-Chlorophenyl)diazinyl]benzonitrile** (**29**)

The general procedure **TP4** was followed using **4-cyanobenzenediazonium tetrafluoroborate** and **bis(4-chlorophenyl)zinc**. Purification by column chromatography (PE: EA = 50:1) yielded **29** (92 mg, 76%) as an orange needle crystal. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.99 – 7.96 (m, 2H), 7.92 – 7.88 (m, 2H), 7.83 – 7.80 (m, 2H), 7.53 – 7.49 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 154.4, 150.8, 138.4, 133.4, 129.7, 124.7, 123.5, 118.5, 114.4. HR-MS (EI) m/z calcd for $C_{13}H_8ClN_3$ [M+H$^+$] 242.0480, found 242.0480.



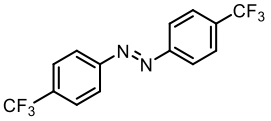
***(E)*-1-(4-Nitrophenyl)-2-[4-(trifluoromethoxy)phenyl]diazene** (**30**)

The general procedure **TP4** was followed using **4-cyanobenzenediazonium tetrafluoroborate** and **bis(4-(trifluoromethoxy)phenyl)zinc**. Purification by column chromatography (PE: EA = 20:1) yielded **30** (101 mg, 65%) as an orange needle crystal. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.40 – 8.36 (m, 2H), 8.03 (dq, J = 7.9, 3.0 Hz, 4H), 7.39 (d, J = 8.5 Hz, 2H) ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 155.5, 152.0 (d, $^{4}J_{C-F}$ = 1.9 Hz), 150.5, 149.1, 125.2, 124.9, 123.7, 121.5. 120.5 (q, $^{1}J_{C-F}$ = 257.0 Hz). ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -57.7 (s). HR-MS (EI) m/z calcd for $C_{13}H_8F_3N_3O_3$ [M+H$^+$] 312.0591, found 312.0590.



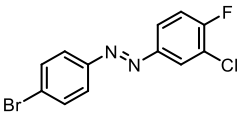
***(E)*-1-(4-Nitrophenyl)-2-[4-(trifluoromethyl)phenyl]diazene** (**31**)

The general procedure **TP4** was followed using **4-nitrobenzenediazonium tetrafluoroborate** and **bis(4-(trifluoromethyl)phenyl)zinc**. Purification by column chromatography (PE: EA = 50:1) yielded **31** (80 mg, 54%) as an orange needle crystal. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.42 – 8.38 (m, 2H), 8.09 – 8.05 (m, 4H), 7.82 (d, J = 8.3 Hz, 2H).^{13}C-NMR (100 MHz, $CDCl_3$): δ = 155.4, 154.1 (d, $^{4}J_{C-F}$ = 1.6 Hz), 149.3, 133.5 (q, $^{2}J_{C-F}$ = 32.6 Hz), 126.6 (q, $^{3}J_{C-F}$ = 3.7 Hz), 124.9, 123.9, 123.8 (q, $^{1}J_{C-F}$ = 272.5 Hz), 123.7. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -62.7 (s). HR-MS (EI) m/z calcd for $C_{13}H_8F_3N_3O_2$ [M+H$^+$] 296.0641, found 296.0640.



***(E)*-1,2-Bis[4-(trifluoromethyl)phenyl]diazene** (**32**)

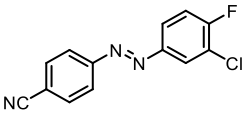
The general procedure **TP4** was followed using **4-(trifluoromethyl)benzenediazonium tetrafluoroborate** and **bis(4-(trifluoromethyl)phenyl)zinc**. Purification by column chromatography (PE) yielded **32** (97 mg, 61%) as an orange needle crystal. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.05 – 8.01 (m, 4H), 7.80 (d, J = 8.3 Hz, 4H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 154.2 (d, $^{4}J_{C-F}$ = 1.6 Hz), 133.1 (q, $^{2}J_{C-F}$ = 32.6 Hz), 126.6 (q, $^{3}J_{C-F}$ = 3.8 Hz), 124.0 (q, $^{1}J_{C-F}$ = 271.0 Hz), 123.5. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -62.7 (d, J = 5.9 Hz). HR-MS (EI) m/z calcd for $C_{14}H_8F_6N_2$ [M+H$^+$] 319.0664, found 319.0660.



***(E)*-1-(4-Bromophenyl)-2-(3-chloro-4-fluorophenyl)diazene** (**33**)

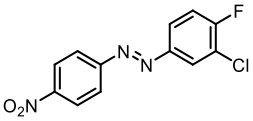
The general procedure **TP4** was followed using **4-bromobenzenediazonium tetrafluoroborate** and **bis(3-chloro-4-fluorophenyl)zinc**. Purification by column chromatography (PE) yielded **33** (90 mg, 57%) as an orange needle crystal. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.97 (dd, J = 6.9, 2.4 Hz, 1H), 7.83 (ddd, J = 8.8, 4.6, 2.4 Hz, 1H), 7.77 – 7.73 (m, 2H), 7.65 – 7.61 (m, 2H), 7.30 – 7.23 (m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 159.8 (d, ^{1}J

= 254.9 Hz), 151.0, 149.1 (d, $^{4}J_{C-F}$ = 3.6 Hz), 132.6, 126.2, 124.6, 124.4 (d, $^{3}J_{C-F}$ = 7.7 Hz), 124.2, 122.4 (d, $^{2}J_{C-F}$ = 19.4 Hz), 117.1 (d, $^{2}J_{C-F}$ = 22.5 Hz). ^{19}F-NMR (376 MHz, $CDCl_3$): δ = 111.0 (s). HR-MS (EI) m/z calcd for $C_{12}H_7BrClFN_2$ [M+H$^+$] 312.9538, found 312.9537.



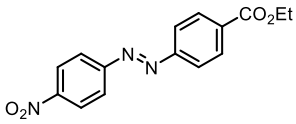
***(E)*-4-[(3-Chloro-4-fluorophenyl)diazinyl]benzonitrile** (**34**)

The general procedure **TP4** was followed using **4-cyanobenzenediazonium tetrafluoroborate** and **bis(3-chloro-4-fluorophenyl)zinc**. Purification by column chromatography (PE) yielded **34** (87 mg, 67%) as an orange needle crystal. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.00 (dd, *J* = 6.9, 2.4 Hz, 1H), 7.96 – 7.92 (m, 2H), 7.87 (ddd, *J* = 8.8, 4.5, 2.4 Hz, 1H), 7.82 – 7.75 (m, 2H), 7.29 (t, *J* = 8.6 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 160.4 (d, $^{1}J_{C-F}$ = 256.4 Hz), 154.1, 149.0 (d, $^{4}J_{C-F}$ = 3.6 Hz), 133.4, 124.9 (d, $^{3}J_{C-F}$ = 7.9 Hz), 124.6, 123.6, 122.6 (d, $^{2}J_{C-F}$ = 19.4 Hz), 118.4, 117.3 (d, $^{2}J_{C-F}$ = 22.5 Hz), 114.6. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -109.29 (s). HR-MS (EI) m/z calcd for $C_{13}H_7ClFN_3$ [M+H$^+$] 260.0385, found 260.0388.



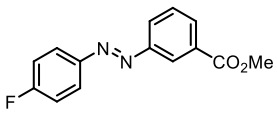
***(E)*-1-(3-Chloro-4-fluorophenyl)-2-(4-nitrophenyl)diazene** (**35**)

The general procedure **TP4** was followed using **4-nitrobenzenediazonium tetrafluoroborate** and **bis(3-chloro-4-fluorophenyl)zinc**. Purification by column chromatography (PE: EA = 50:1) yielded **35** (94 mg, 67%) as an orange needle crystal. ^{1}H-NMR (400 MHz, $CDCl_3$) δ = 8.41 (s, 1H), 8.39 (s, 1H), 8.07 (dd, *J* = 6.9, 2.4 Hz, 1H), 8.04 (d, *J* = 8.9 Hz, 2H), 7.96 – 7.92 (m, 1H), 7.34 (t, J = 8.5 Hz, 1H). ^{13}C-NMR (400 MHz, $CDCl_3$): δ = 160.5 (d, $^{1}J_{C-F}$ =256.8), 155.3 (s), 149.1 (s), 149.0 (d, $^{4}J_{C-F}$ =3.3), 125.1 (d, $^{3}J_{C-F}$ =8.0), 124.9 (s), 124.6 (s), 123.7 (s), 122.7 (d, $^{2}J_{C-F}$ =19.7), 117.3 (d, $^{2}J_{C-F}$ =22.6). ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -108.93 (s). HR-MS (EI) m/z calcd for $C_{12}H_7ClFN_3O_2$ [M+H$^+$] 280.0284, found 280.0283.



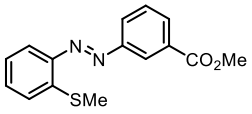
Ethyl *(E)*-4-[(4-nitrophenyl)diazinyl]benzoate (**36**)

The general procedure **TP4** was followed using **4-nitrobenzenediazonium tetrafluoroborate** and **bis(4-(ethoxycarbonyl)phenyl)zinc**. Purification by column chromatography (PE:EA = 20:1) yielded **36** (74 mg, 50%) as an orange needle crystal. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.41 – 8.36 (m, 2H), 8.25 – 8.20 (m, 2H), 8.08 – 8.03 (m, 2H), 8.01 – 7.98 (m, 2H), 4.43 (q, J = 7.1 Hz, 2H), 1.44 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 165.9, 155.5, 154.7, 149.2, 133.5, 130.8, 124.9, 123.8, 123.2, 61.6, 14.4. HR-MS (EI) m/z calcd for $C_{15}H_{13}N_3O_4$ [M+H$^+$] 300.0979, found 300.0979.



Methyl *(E)*-3-[(4-fluorophenyl)diazinyl]benzoate (**37**)

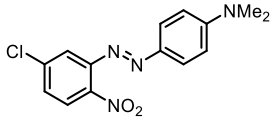
The general procedure **TP4** was followed using **4-fluorobenzenediazonium tetrafluoroborate** and **bis(3-(methoxycarbonyl)phenyl)zinc**. Purification by column chromatography (PE:EA = 20:1) yielded **37** (108 mg, 84%) as an orange needle crystal. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.57 (t, J = 1.9 Hz, 1H), 8.17 (dt, J = 7.7, 1.5 Hz, 1H), 8.10 (ddd, J = 8.0, 2.0, 1.2 Hz, 1H), 8.02 – 7.96 (m, 2H), 7.61 (t, J = 7.8 Hz, 1H), 7.26 – 7.19 (m, 2H), 3.99 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 166.7, 164.8 (d, $^{1}J_{C-F}$ = 252.7 Hz), 152.6, 149.1 (d, $^{4}J_{C-F}$ = 3.0 Hz), 131.8, 131.5, 129.4, 127.1, 125.2 (d, $^{3}J_{C-F}$ = 8.9 Hz), 124.1, 116.3 (d, $^{2}J_{C-F}$ = 22.9 Hz), 52.5. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -108.6 (s). HR-MS (EI) m/z calcd for $C_{14}H_{11}FN_2O_2$ [M+H$^+$] 259.0877, found 259.0873.



Methyl *(E)*-3-{[2-(methylthio)phenyl]diazenyl}benzoate (**38**)

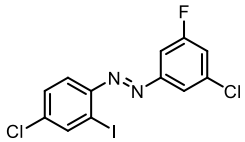
The general procedure **TP4** was followed using **2-(methylthio)benzenediazonium tetrafluoroborate** and **bis(3-(methoxycarbonyl)phenyl)zinc**. Purification by column chromatography (PE: EA = 20:1) yielded **38** (107 mg, 68%) as an orange needle crystal. ^{1}H-

NMR (400 MHz, $CDCl_3$): δ = 8.64 – 8.57 (m, 1H), 8.19 – 8.08 (m, 2H), 7.77 – 7.71 (m, 1H), 7.60 (dt, *J* = 7.7 Hz, 1H), 7.47 – 7.40 (m, 1H), 7.38 – 7.32 (m, 1H), 7.27 – 7.20 (m, 1H), 4.01 – 3.96 (m, 3H), 2.57 – 2.51 (m, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 166.7, 152.9, 148.8, 141.3, 131.9, 131.9, 131.5, 129.4, 126.3, 125.5, 124.9, 124.7, 117.6, 52.5, 15.0. HR-MS (EI) m/z calcd for $C_{15}H_{14}N_2O_2S$ [M+H$^+$] 287.0849, found 287.0844.



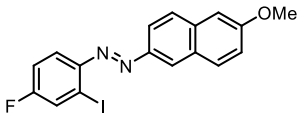
***(E)*-4-[(5-Chloro-2-nitrophenyl)diazinyl]-N,N-dimethylaniline** (**39**)

The general procedure **TP4** was followed using **4-chloro-2-nitrobenzenediazonium tetrafluoroborate** and **bis(4-(dimethylamino)phenyl)zinc**. Purification by column chromatography (PE: EA = 40:1) yielded **41** (77 mg, 57%) as an orange needle crystal. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.91 – 7.84 (m, 2H), 7.80 (d, *J* = 8.6 Hz, 1H), 7.71 (d, *J* = 2.3 Hz, 1H), 7.38 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.77 – 6.70 (m, 2H), 3.13 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 153.8, 147.0, 145.6, 143.8, 139.1, 128.2, 126.7, 125.3, 118.6, 111.6, 40.4. HR-MS (EI) m/z calcd for $C_{14}H_{13}ClN_4O_2$ [M+H$^+$] 305.0800, found 305.0803.



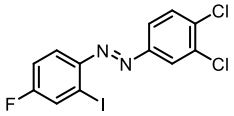
***(E)*-1-(4-Chloro-2-iodophenyl)-2-(3-chloro-5-fluorophenyl)diazene** (**40**)

The general procedure **TP4** was followed using **4-chloro-2-iodobenzenediazonium tetrafluoroborate** and **bis(3-chloro-5-fluorophenyl)zinc**. Purification by column chromatography (PE: EA = 50:1) yielded **40** (144 mg, 73%) as an orange needle crystal. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, *J* = 2.2 Hz, 1H), 7.79 (d, *J* = 1.8 Hz, 1H), 7.62 – 7.54 (m, 2H), 7.42 (dd, *J* = 2.0 Hz, 1H), 7.28 – 7.20 (m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 163.1 (d, $^1J_{C-F}$ = 251.4 Hz), 153.8 (d, $^3J_{C-F}$ = 8.2 Hz), 149.5, 139.6, 138.8, 135.9 (d, $^3J_{C-F}$ = 11.1 Hz), 129.5, 120.9 (d, $^4J_{C-F}$ = 3.3 Hz), 119.0 (d, $^2J_{C-F}$ = 25.6 Hz), 118.0, 108.5 (d, $^2J_{C-F}$ = 23.2 Hz), 103.9. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -109.5 (s). HR-MS (EI) m/z calcd for $C_{12}H_6Cl_2FIN_2$ [M+H$^+$] 394.9010, found 394.9012.



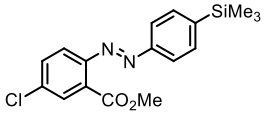
***(E)*-1-(4-Fluoro-2-iodophenyl)-2-(6-methoxynaphthalen-2-yl)diazene** (**41**)

The general procedure **TP4** was followed using **4-fluoro-2-iodobenzenediazonium tetrafluoroborate** and **bis(6-methoxynaphthalen-2-yl)zinc**. Purification by column chromatography (PE: EA = 40:1) yielded **41** (113 mg, 56%) as an orange needle crystal. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.42 (d, J = 1.9 Hz, 1H), 8.10 (dd, J = 8.9, 2.0 Hz, 1H), 7.92 (d, J = 8.7 Hz, 1H), 7.80 (d, J = 8.9 Hz, 1H), 7.75 (ddd, J = 10.4, 7.6, 4.2 Hz, 2H), 7.24 – 7.15 (m, 3H), 3.97 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 163.6 (d, $^{1}J_{C-F}$ = 256.4 Hz), 159.6, 148.8, 148.2 (d, $^{4}J_{C-F}$ = 3.3 Hz), 136.8, 131.2, 129.6, 128.8, 128.2, 126.6 (d, $^{2}J_{C-F}$ = 24.5 Hz), 119.7, 118.3 (d, $^{3}J_{C-F}$ = 8.8 Hz), 117.8, 116.4, 116.3 (d, $^{2}J_{C-F}$ = 22.7 Hz), 116.2, 106.5, 55.6. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -109.3 (s). HR-MS (EI) m/z calcd for $C_{17}H_{12}FIN_2O$ [M+H$^+$] 407.0051, found 407.0055.



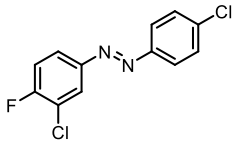
***(E)*-1-(3,4-Dichlorophenyl)-2-(4-fluoro-2-iodophenyl)diazene (42)**

The general procedure **TP4** was followed using **4-fluoro-2-iodobenzenediazonium tetrafluoroborate** and **bis(3,4-dichlorophenyl)zinc**. Purification by column chromatography (PE) yielded **42** (63 mg, 32%) as an orange needle crystal. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.03 (d, J = 2.2 Hz, 1H), 7.81 (dd, J = 8.5, 2.3 Hz, 1H), 7.75 (dd, J = 7.7, 2.6 Hz, 1H), 7.66 (dd, J = 9.0, 5.6 Hz, 1H), 7.59 (d, J = 8.5 Hz, 1H), 7.16 (ddd, J = 8.9, 7.5, 2.7 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 164.3 (d, $^{1}J_{C-F}$ = 258.5 Hz), 151.1, 147.6 (d, $^{4}J_{C-F}$ = 3.3 Hz), 135.7, 133.7, 131.1, 126.9 (d, $^{2}J_{C-F}$ = 24.6 Hz), 125.0, 123.1, 118.4 (d, $^{3}J_{C-F}$ = 9.0 Hz), 116.4 (d, $^{2}J_{C-F}$ = 22.9 Hz), 104.1 (d, $^{3}J_{C-F}$ = 8.8 Hz). ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -107.1 (s). HR-MS (EI) m/z calcd for $C_{12}H_6Cl_2FIN_2$ [M+H$^+$] 394.9010, found 394.9015.



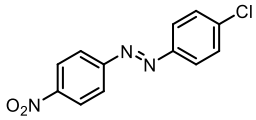
***(E)*-Methyl-5-chloro-2-{[4-(trimethylsilyl)phenyl]diazenyl}benzoate (43)**

The general procedure **TP4** was followed using **4-chloro-2-(methoxycarbonyl)benzenediazonium tetrafluoroborate** and **bis(4-(trimethylsilyl)phenyl)zinc**. Purification by column chromatography (PE: EA = 20:1) yielded **43** (67 mg, 39%) as an orange needle crystal. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.86 (d, J = 8.2 Hz, 2H), 7.79 (d, J = 2.3 Hz, 1H), 7.67 (d, J = 8.3 Hz, 2H), 7.62 (d, J = 8.6 Hz, 1H), 7.54 (dd, J = 8.6, 2.3 Hz, 1H), 3.92 (s, 3H), 0.32 (s, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 166.9, 152.9, 150.2, 145.8, 136.0, 134.3, 132.1, 130.5, 129.8, 122.4, 120.3, 52.8, -1.1. HR-MS (EI) m/z calcd for $C_{17}H_{19}ClN_2O_2Si$ [M+H$^+$] 347.0977, found 347.0977.



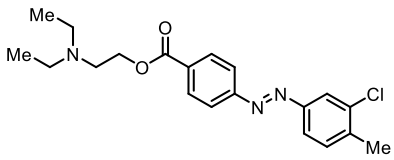
(*E*)-1-(3-Chloro-4-fluorophenyl)-2-(4-chlorophenyl)diazene (44)

The general procedure **TP4** was followed using **1-(3-chloro-4-fluorophenyl)benzenediazonium tetrafluoroborate** and **bis(4-chlorophenyl)zinc**. Purification by column chromatography (PE: EA = 50:1) yielded **44** (50 mg, 37%) as an orange needle crystal. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.99 (dd, J = 6.9, 2.4 Hz, 1H), 7.85 (m, J = 8.8, 2.4 Hz, 3H), 7.51 – 7.46 (m, 2H), 7.31 – 7.25 (m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 159.82, (d, $^{1}J_{C-F}$ = 247.0 Hz), 150.68, 149.14 (d, $^{4}J_{C-F}$ = 4.2 Hz), 137.66, 129.61, 124.4 (d, $^{3}J_{C-F}$ = 8,0 Hz) 124.22, 122.5, 117.12 (d, $^{2}J_{C-F}$ = 22.5 Hz). ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -111.10 (s). HR-MS (EI) m/z calcd for $C_{12}H_6Cl_2FN_2$ [M+H$^+$] 269.0043, found 269.0044.



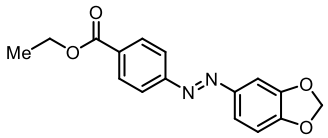
***(E)*-1-(4-Chlorophenyl)-2-(4-nitrophenyl)diazene (45)**

The general procedure **TP4** was followed using **4-nitrobenzenediazonium tetrafluoroborate** and **bis(4-chlorophenyl)zinc**. Purification by column chromatography (PE: EA = 40:1) yielded **45** (80 mg, 61%) as an orange needle crystal. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.43 – 8.36 (m, 2H), 8.07 – 8.00 (m, 2H), 7.97 – 7.90 (m, 2H), 7.57 – 7.50 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 155.6, 150.9, 149.0, 138.7, 129.8, 124.9, 124.8, 123.7. HR-MS (EI) m/z calcd for $C_{12}H_8ClN_3O_2$ [M+H$^+$] 262.0378, found 262.0377.



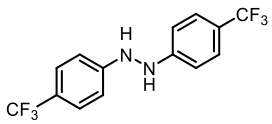
2-(Diethylamino)ethyl (*E*)-4-[(3-chloro-4-methylphenyl)diazenyl]benzoate (46)

The general procedure **TP4** was followed using **procaine derivative** and **bis(3-chloro-4-methylphenyl)zinc**. Purification by column chromatography (PE: EA = 10:1) yielded **46** (80 mg, 61%) as an orange needle crystal. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.22 – 8.15 (m, 2H), 7.93 (dd, *J* = 8.7, 1.9 Hz, 3H), 7.78 (dd, *J* = 8.1, 2.0 Hz, 1H), 7.40 (dd, *J* = 8.1, 0.9 Hz, 1H), 4.43 (t, *J* = 6.2 Hz, 2H), 2.88 (t, *J* = 6.2 Hz, 2H), 2.65 (q, *J* = 7.2 Hz, 4H), 2.47 (s, 3H), 1.09 (t, *J* = 7.1 Hz, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 166.1, 155.0, 151.7, 140.1, 135.4, 132.3, 131.5, 130.8, 122.8, 122.8, 122.6, 63.8, 51.1, 47.9, 20.4, 12.1. HR-MS (EI) m/z calcd for $C_{20}H_{24}ClN_3O_2$ [M+H$^+$] 374.1630, found 374.1633.



Ethyl (*E*)-4-{benzo[*d*][1,3]dioxol-5-yldiazenyl}benzoate (47)

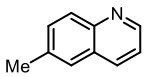
The general procedure **TP4** was followed using **benzocaine derivative** and **bis(benzo[*d*][1,3]dioxol-5-yl)zinc**. Purification by column chromatography (PE: EA = 20:1) yielded **47** (80 mg, 61%) as an orange needle crystal. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.17 (d, *J* = 8.6 Hz, 2H), 7.90 (d, *J* = 8.6 Hz, 2H), 7.64 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.45 (d, *J* = 1.9 Hz, 1H), 6.97 (d, *J* = 8.2 Hz, 1H), 6.08 (s, 2H), 4.41 (q, *J* = 7.1 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 166.3, 155.2, 151.1, 149.0, 148.7, 131.8, 130.7, 125.0, 122.5, 108.2, 102.2, 98.9, 61.3, 14.5. HR-MS (EI) m/z calcd for $C_{16}H_{14}N_2O_4$ [M+H$^+$] 299.1026, found 299.1027.



1,2-Bis[4-(trifluoromethyl)phenyl]hydrazine (48)

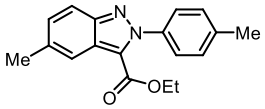
The general procedure **Procedure for Scheme S5a** was followed, using **(*E*)-1,2-bis(4-(trifluoromethyl)phenyl)diazene**. Purification by column chromatography (PE: EA = 20:1)

yielded **48** (51 mg, 80%) as an white solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.47 (d, J = 8.5 Hz, 4H), 6.88 (d, J = 8.5 Hz, 4H), 5.95 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 150.9, 127.0 (q, $^{4}J_{C-F}$ = 3.8 Hz), 124.7 (q, $^{1}J_{C-F}$ = 269.0 Hz), 122.3 (q, $^{2}J_{C-F}$ = 32.0 Hz), 111.80. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -61.39. (s). HR-MS (EI) m/z calcd for $C_{14}H_{10}F_6N_2$ [M+H$^+$] 321.0821, found 321.0822.



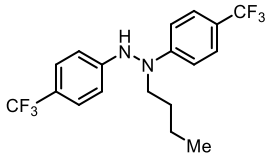
6-Methylquinoline (49)

The general procedure **Procedure for Scheme S5b** was followed, using **(*E*)-1,2-di-p-tolyldiazene** and **allyl bromide**. Purification by column chromatography (PE: EA = 10:1) yielded **49** (37 mg, 65%) as an colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.84 (dd, J = 4.2, 1.7 Hz, 1H), 8.06 (dd, J = 8.4, 1.8 Hz, 1H), 8.00 (d, J = 8.5 Hz, 1H), 7.59 – 7.52 (m, 2H), 7.35 (dd, J = 8.3, 4.2 Hz, 1H), 2.53 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 149.7, 147.0, 136.5, 135.5, 131.9, 129.3, 128.5, 126.7, 121.2, 21.7. HR-MS (EI) m/z calcd for $C_{10}H_9N$ [M+H$^+$] 144.0808, found 144.0806.



Ethyl 5-methyl-2-(*p*-tolyl)-2H-indazole-3-carboxylate (50)

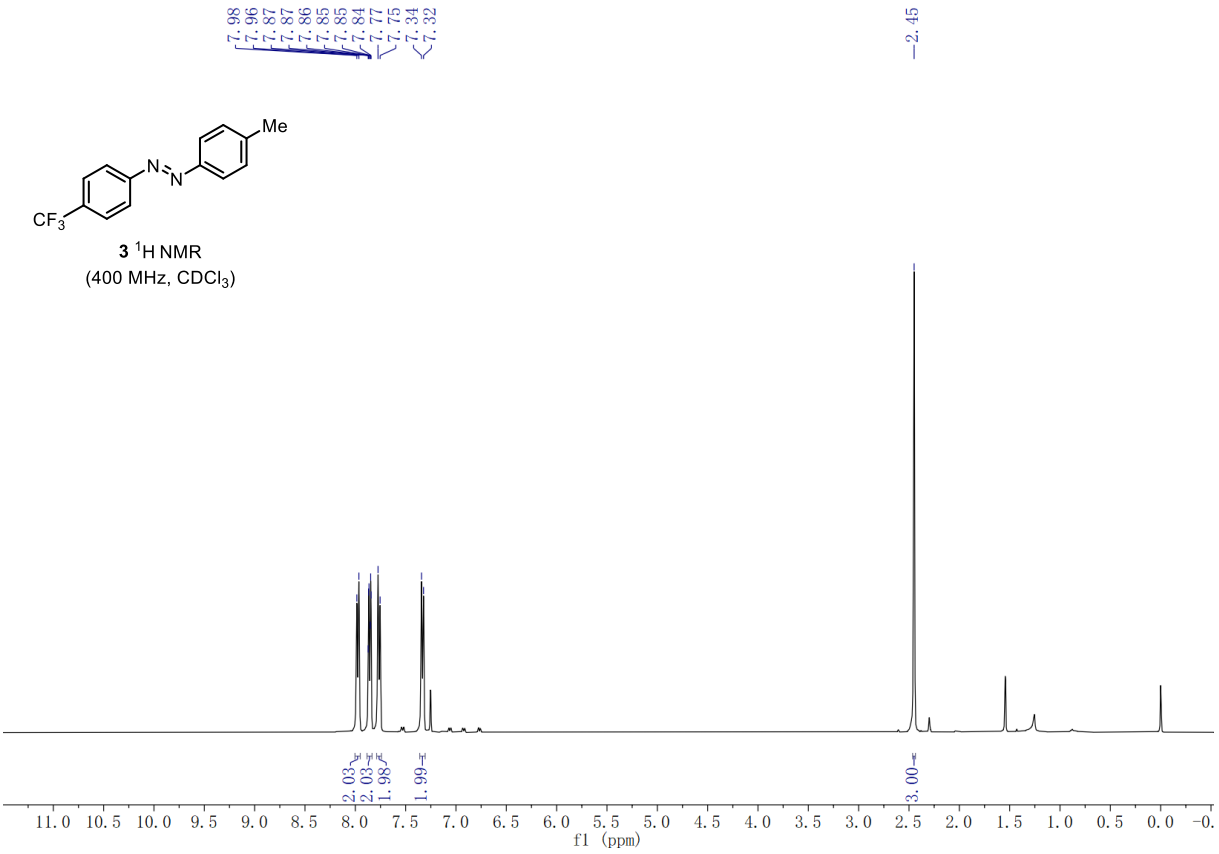
The general procedure **Procedure for Scheme S5c** was followed, using **(*E*)-1,2-di-p-tolyldiazene** and **ethyl glyoxalate**. Purification by column chromatography (PE: EA = 10:1) yielded **50** (36 mg, 61%) as an brown solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.85 (dt, J = 2.0, 1.0 Hz, 1H), 7.74 (dd, J = 8.8, 0.9 Hz, 1H), 7.41 – 7.37 (m, 2H), 7.32 – 7.28 (m, 2H), 7.27 – 7.22 (m, 1H), 4.36 (q, J = 7.1 Hz, 2H), 2.51 (d, J = 1.1 Hz, 3H), 2.45 (s, 3H), 1.35 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 159.8, 147.5, 139.4, 138.8, 135.4, 130.0, 129.3, 126.2, 124.5, 124.3, 119.8, 118.3, 61.1, 22.3, 21.5, 14.4. HR-MS (EI) m/z calcd for $C_{18}H_{18}N_2O_2$ [M+H$^+$] 295.1441, found 295.1444.



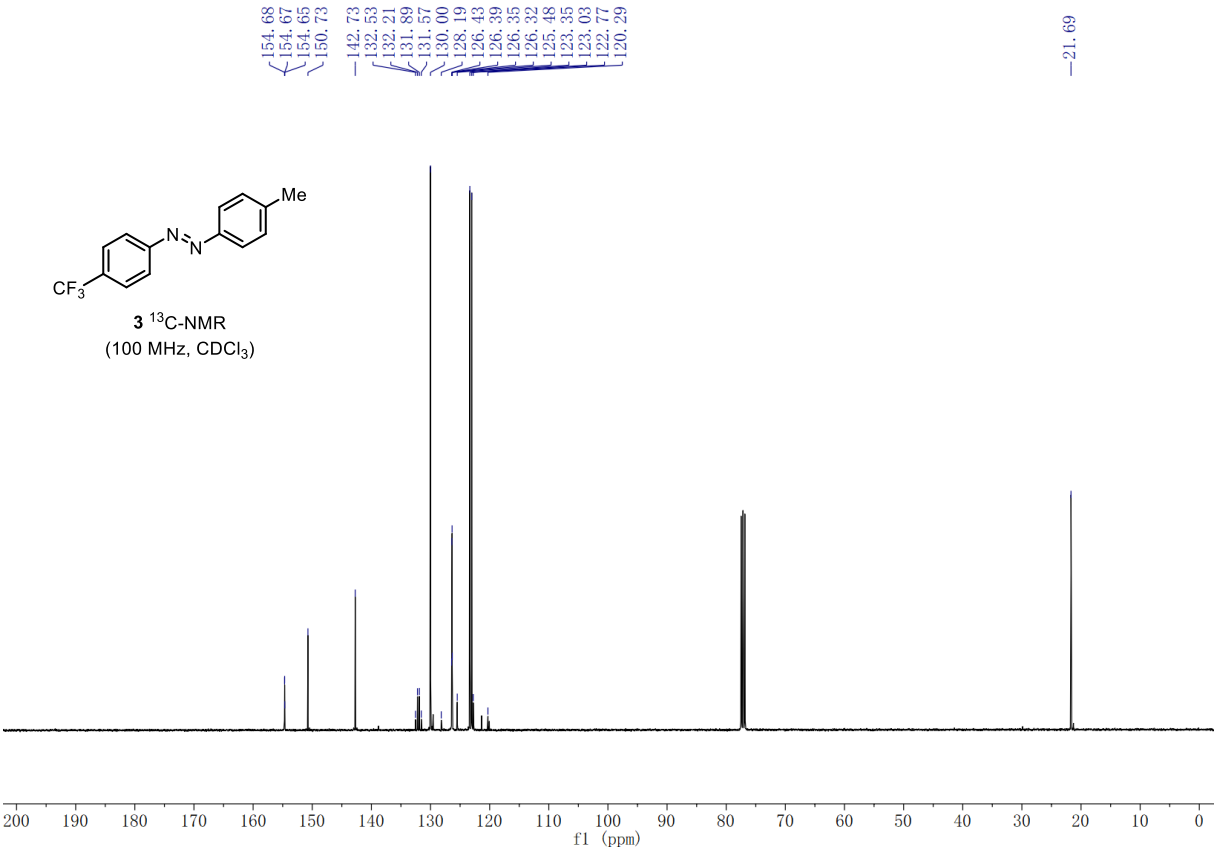
3,8-Bis(trifluoromethyl)indazolo[2,3-a]quinoline (51)

The general procedure **Procedure for Scheme S5d** was followed, using **(*E*)-1,2-bis(4-(trifluoromethyl)phenyl)diazene** and ***n*-Butyllithium**. Purification by column chromatography (PE: EA = 100:1) yielded **51** (50 mg, 66%) as a white solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = δ 7.50 – 7.43 (m, 4H), 6.90 (d, J = 8.6 Hz, 2H), 6.79 (d, J = 8.4 Hz, 2H), 5.95 (s, 1H), 3.55 (s, 2H), 1.67 (p, J = 7.5 Hz, 2H), 1.39 (h, J = 7.3 Hz, 2H), 0.96 (t, J = 7.4 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 151.6 (d, $^{5}J_{C-F}$ = 1.2 Hz), 149.7 (d, $^{5}J_{C-F}$ = 1.1 Hz), 127.1 (q, $^{4}J_{C-F}$ = 3.8 Hz), 126.9 (q, $^{4}J_{C-F}$ = 3.8 Hz), 126.1 (d, $^{3}J_{C-F}$ = 14.7 Hz), 123.4 (d, $^{3}J_{C-F}$ = 15.0 Hz), 122.1 (d, $^{2}J_{C-F}$ = 32.6 Hz), 120.7 (d, $^{2}J_{C-F}$ = 32.7 Hz), 112.1, 111.7, 51.6, 28.3, 20.5, 14.0. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -61.30 (s), -61.40. (s). HR-MS (EI) m/z calcd for $C_{18}H_{18}F_6N_2$ [M+H$^+$] 377.1447, found 377.1445.

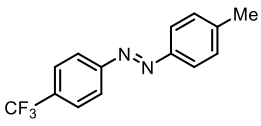
4. NMR spectra



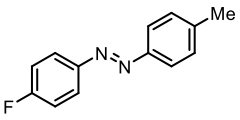
3 ^{1}H NMR
(400 MHz, $CDCl_3$)



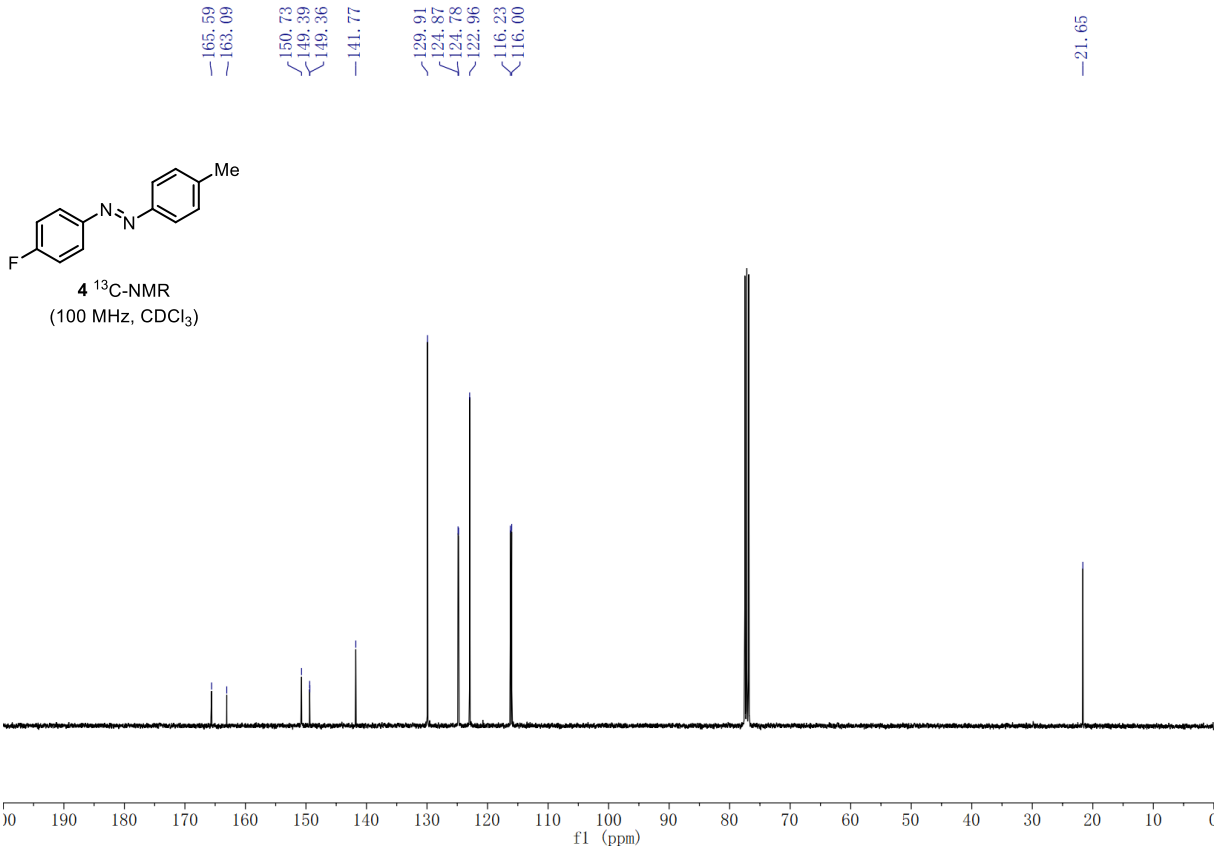
3 ^{13}C-NMR
(100 MHz, $CDCl_3$)



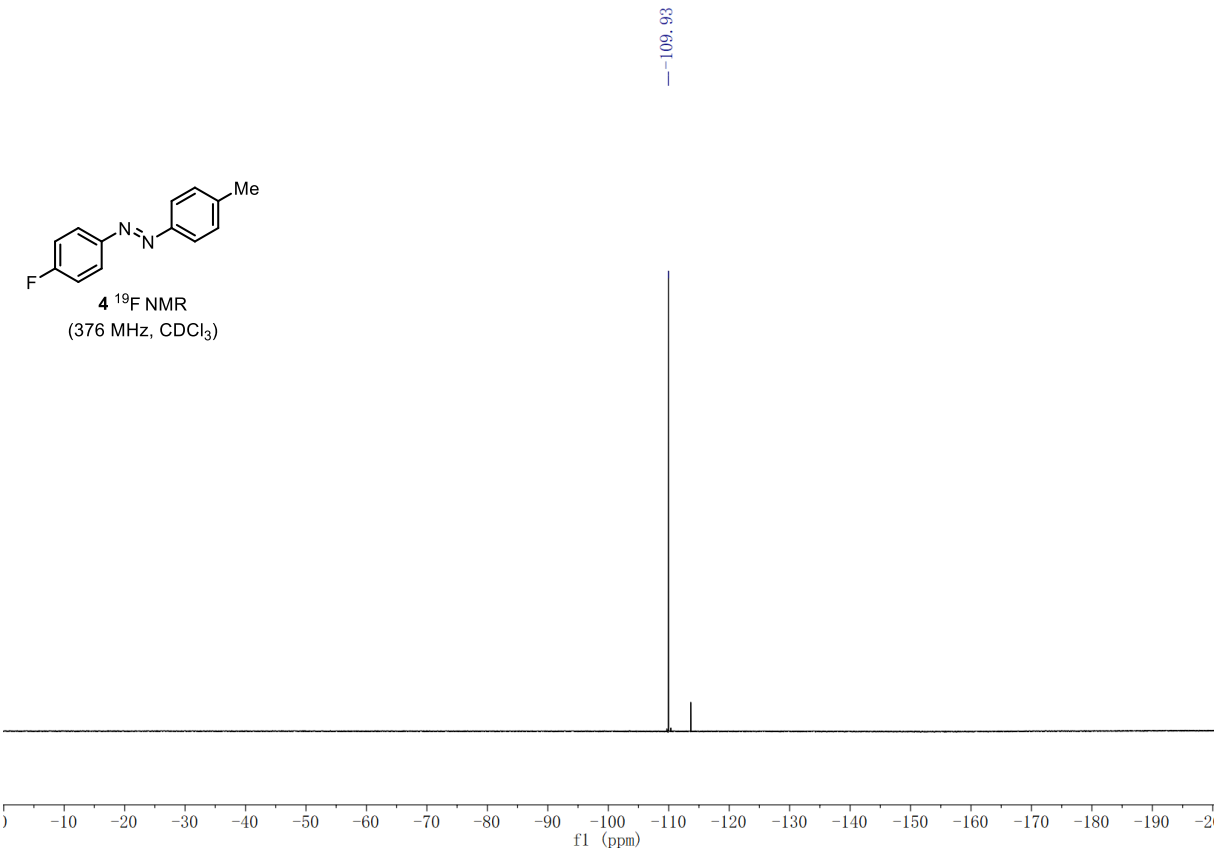
3 ^{19}F NMR
(376 MHz, $CDCl_3$)



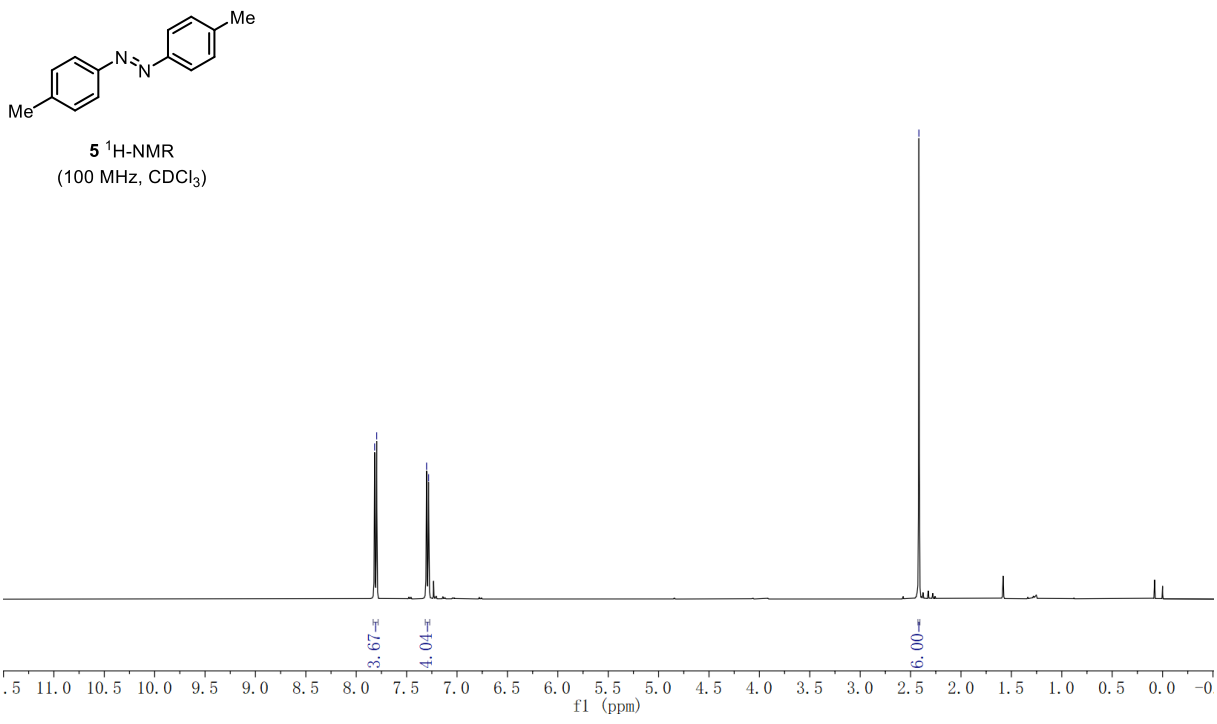
4 ^{1}H NMR
(100 MHz, $CDCl_3$)



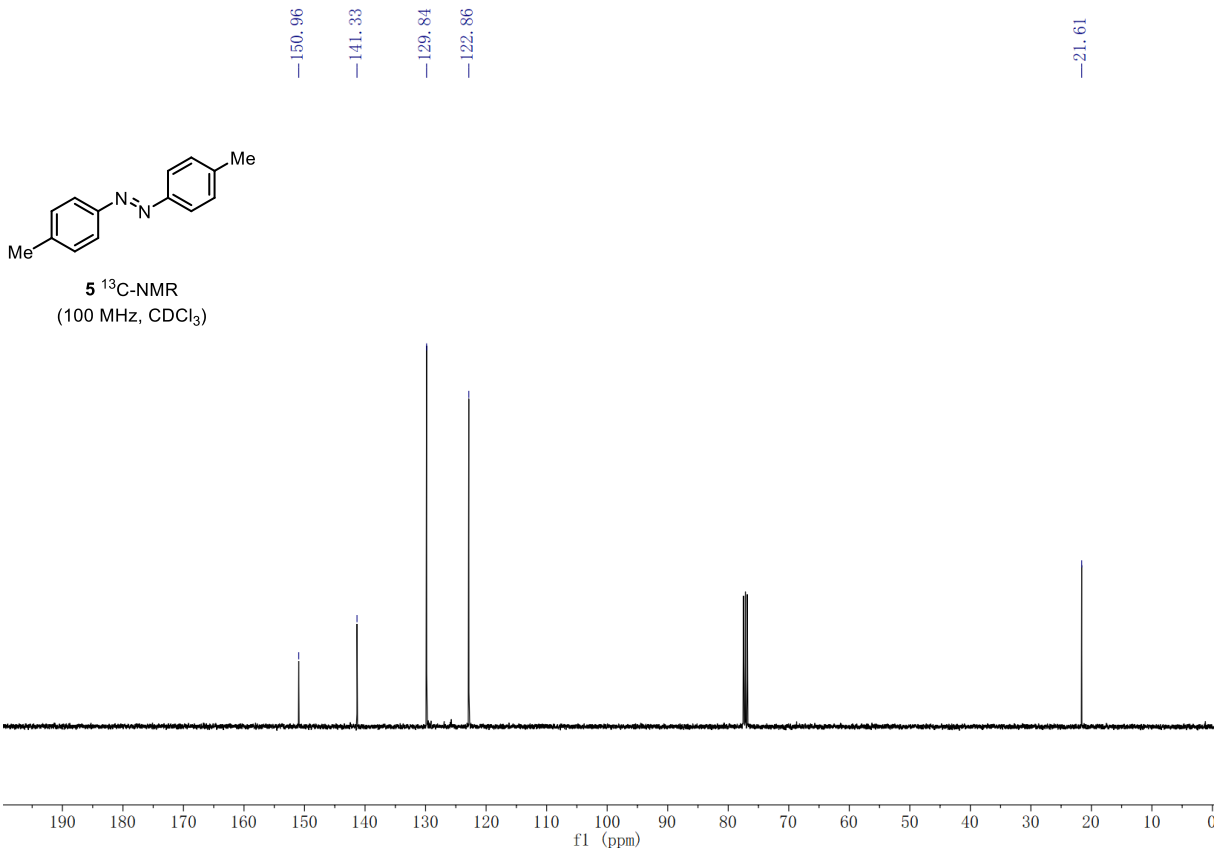
4 ^{13}C-NMR
(100 MHz, $CDCl_3$)



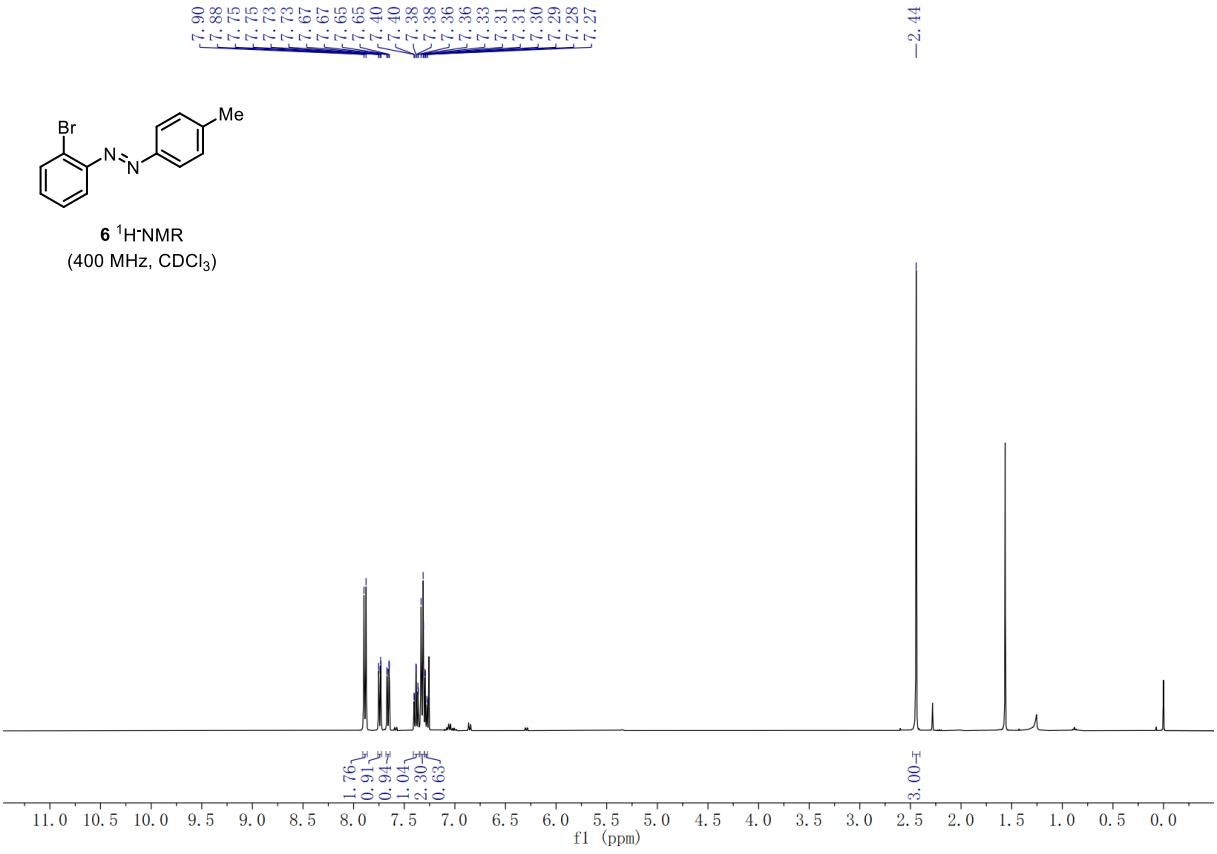
4 ^{19}F NMR
(376 MHz, $CDCl_3$)



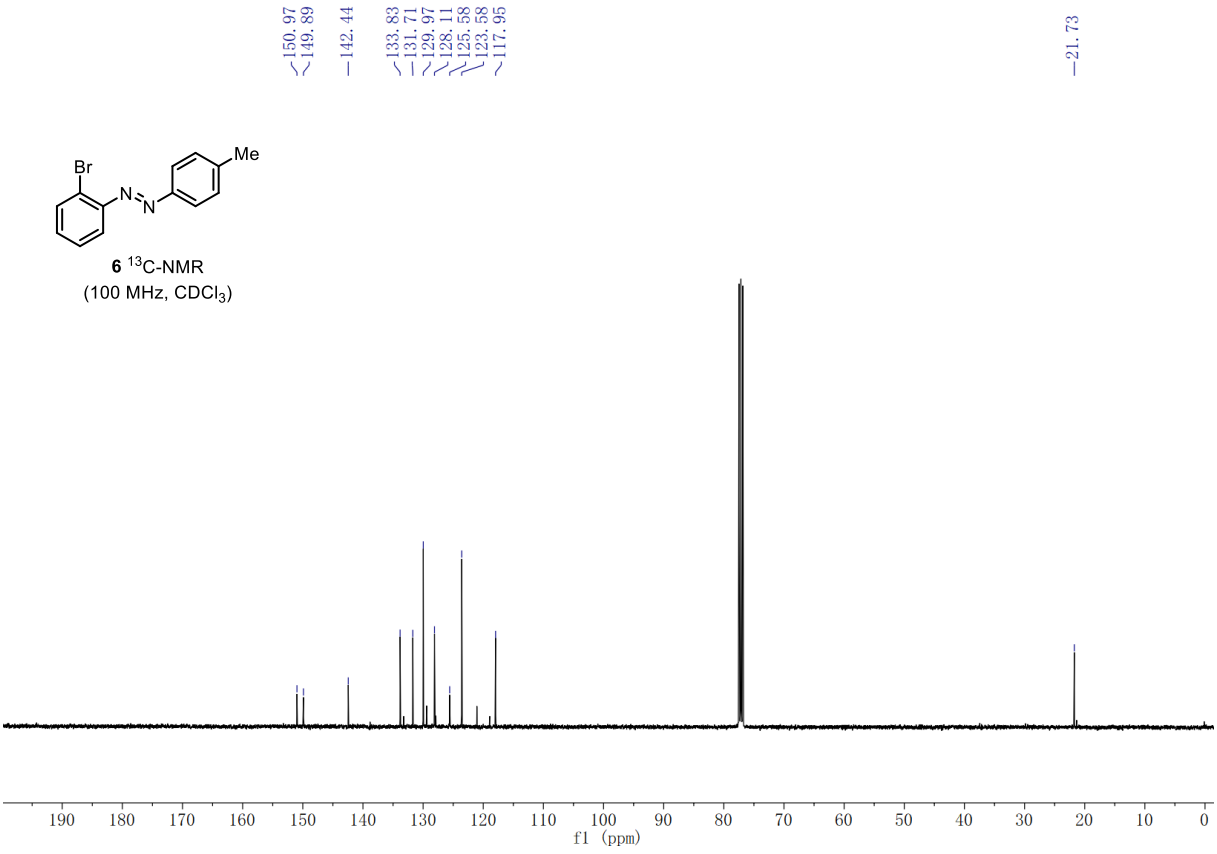
5 ^{1}H-NMR
(100 MHz, $CDCl_3$)



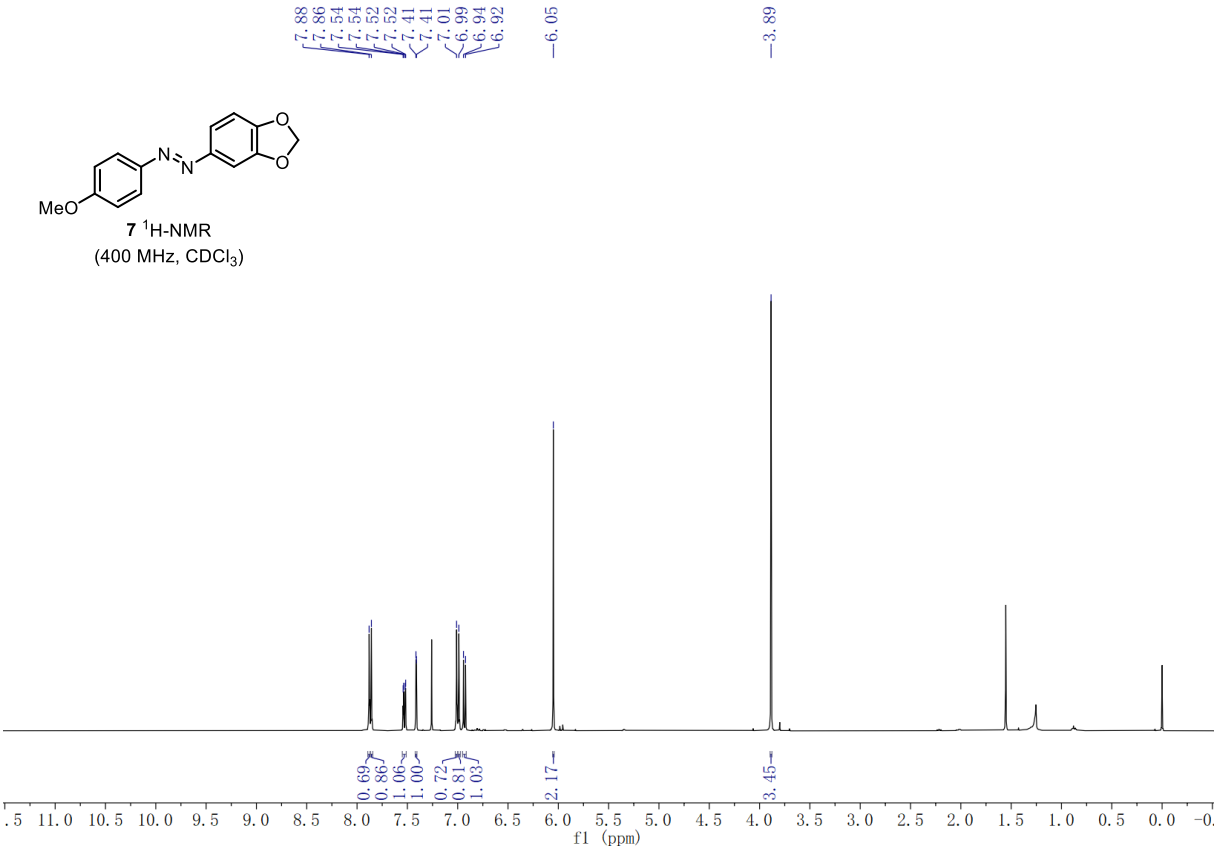
5 ^{13}C-NMR
(100 MHz, $CDCl_3$)



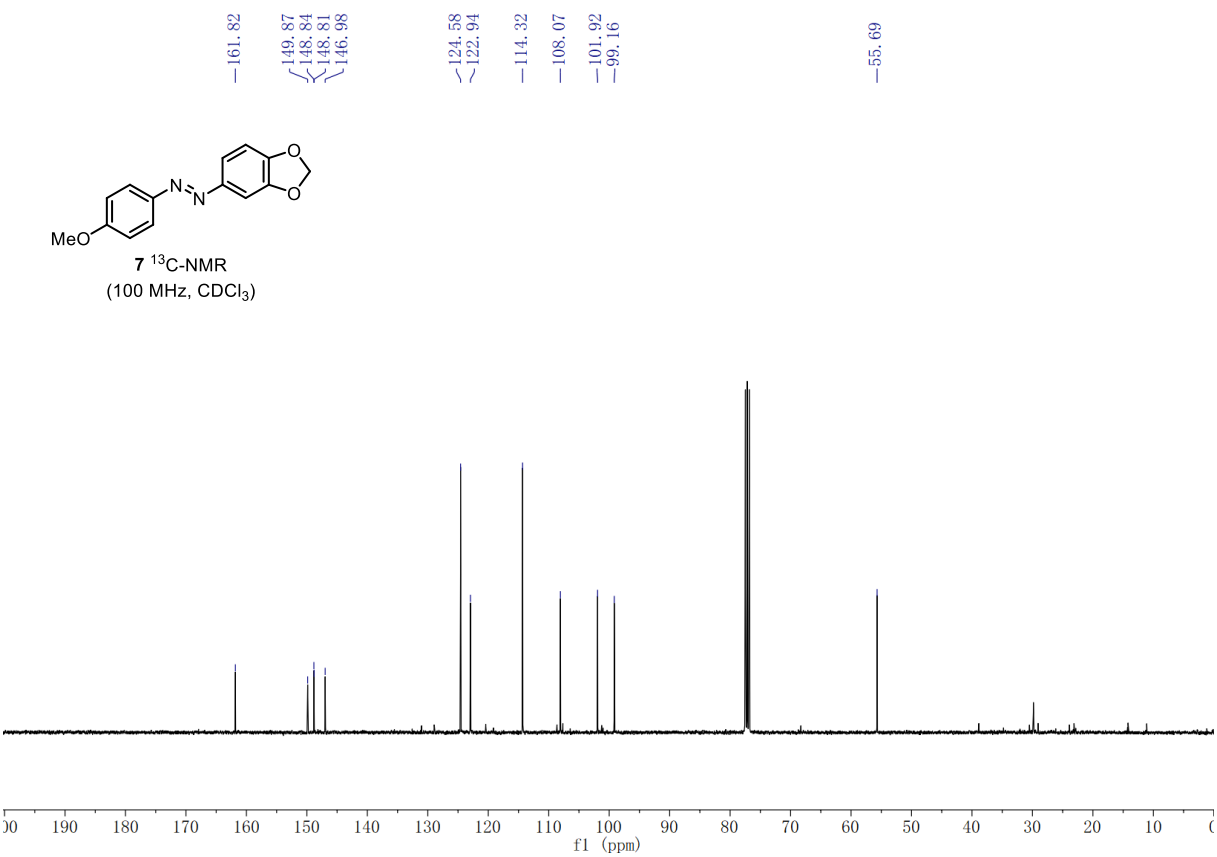
6 ^{1}H-NMR
(400 MHz, $CDCl_3$)



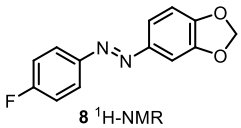
6 ^{13}C-NMR
(100 MHz, $CDCl_3$)



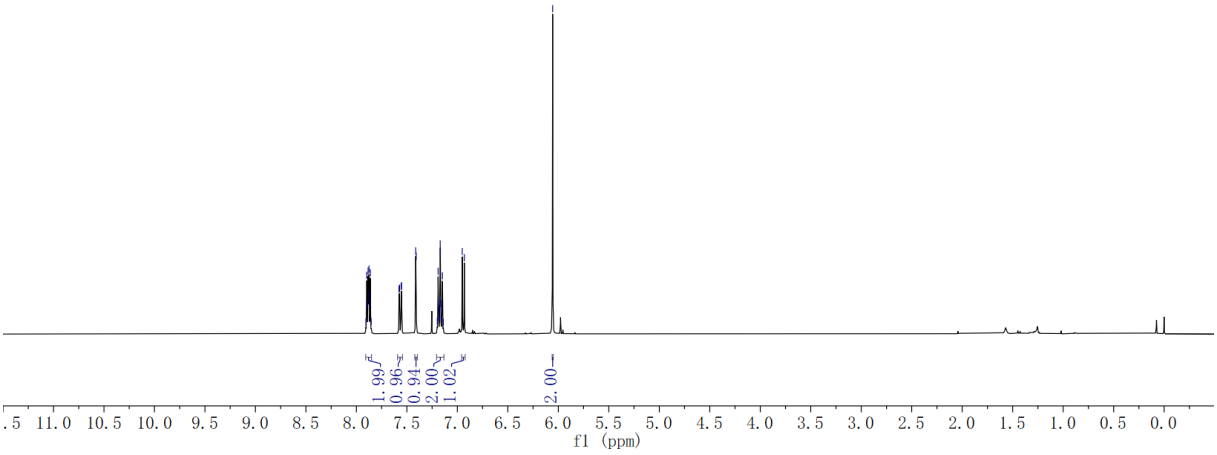
7 ^{1}H-NMR
(400 MHz, $CDCl_3$)

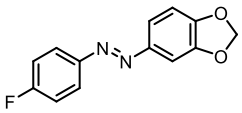


7 ^{13}C-NMR
(100 MHz, $CDCl_3$)

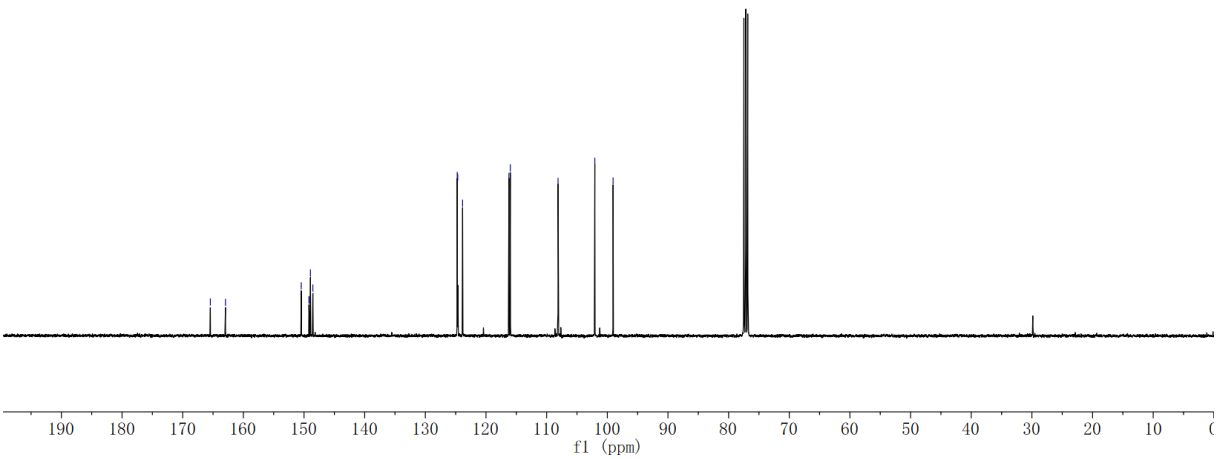


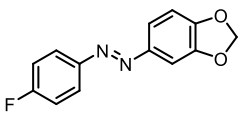
8 ^{1}H-NMR
(400 MHz, $CDCl_3$)



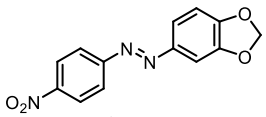


8 ^{13}C-NMR
(100 MHz, $CDCl_3$)

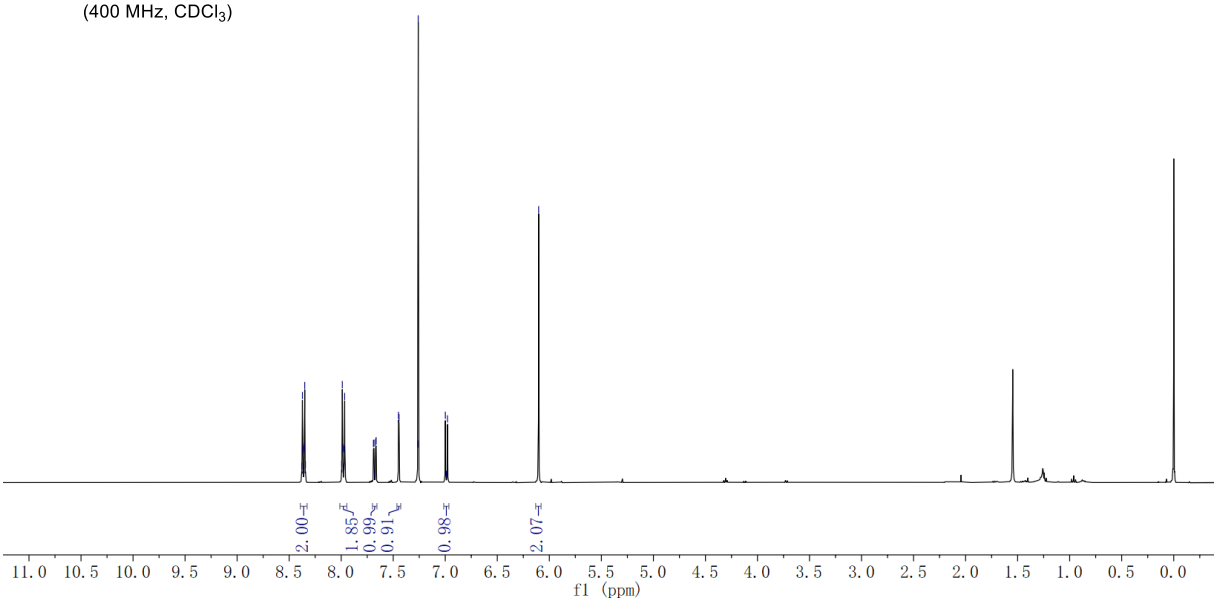


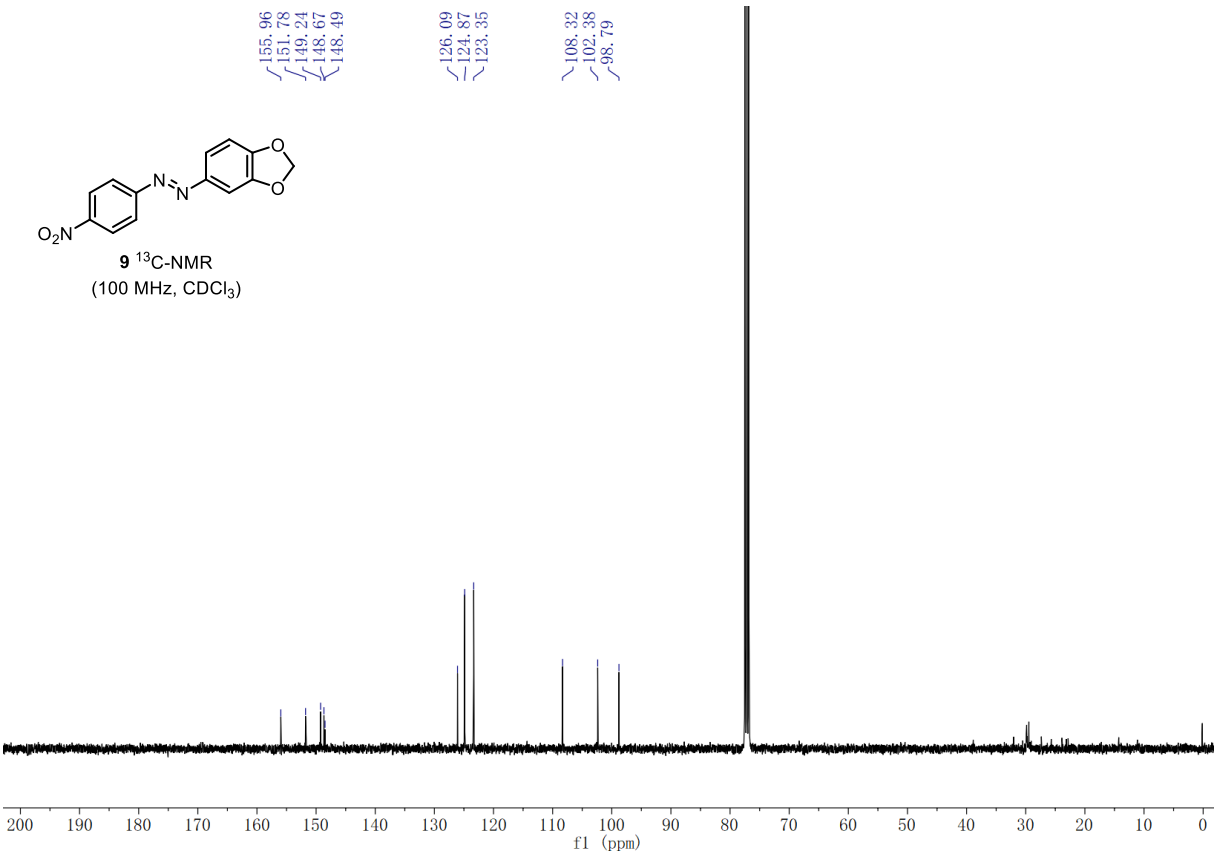


8 ^{19}F-NMR
(376 MHz, $CDCl_3$)

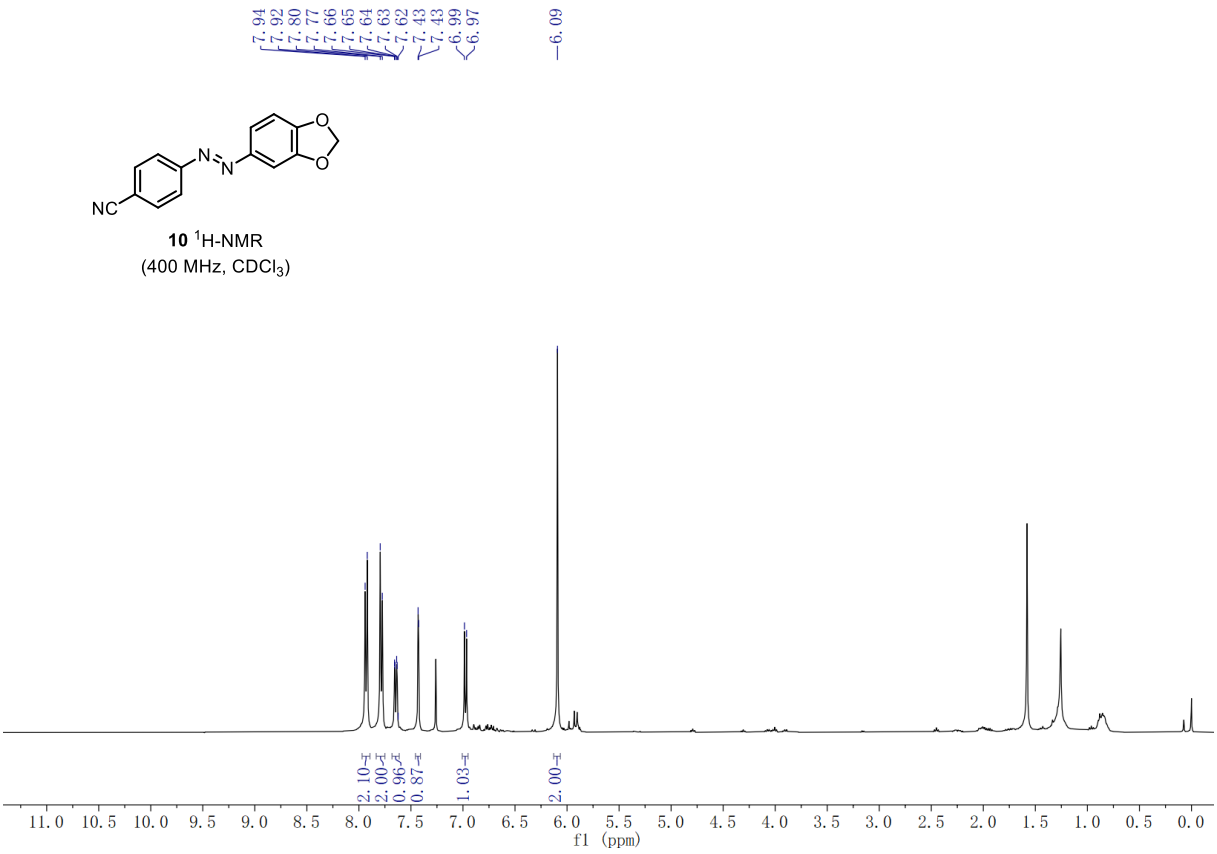


9 ^{1}H-NMR
(400 MHz, $CDCl_3$)

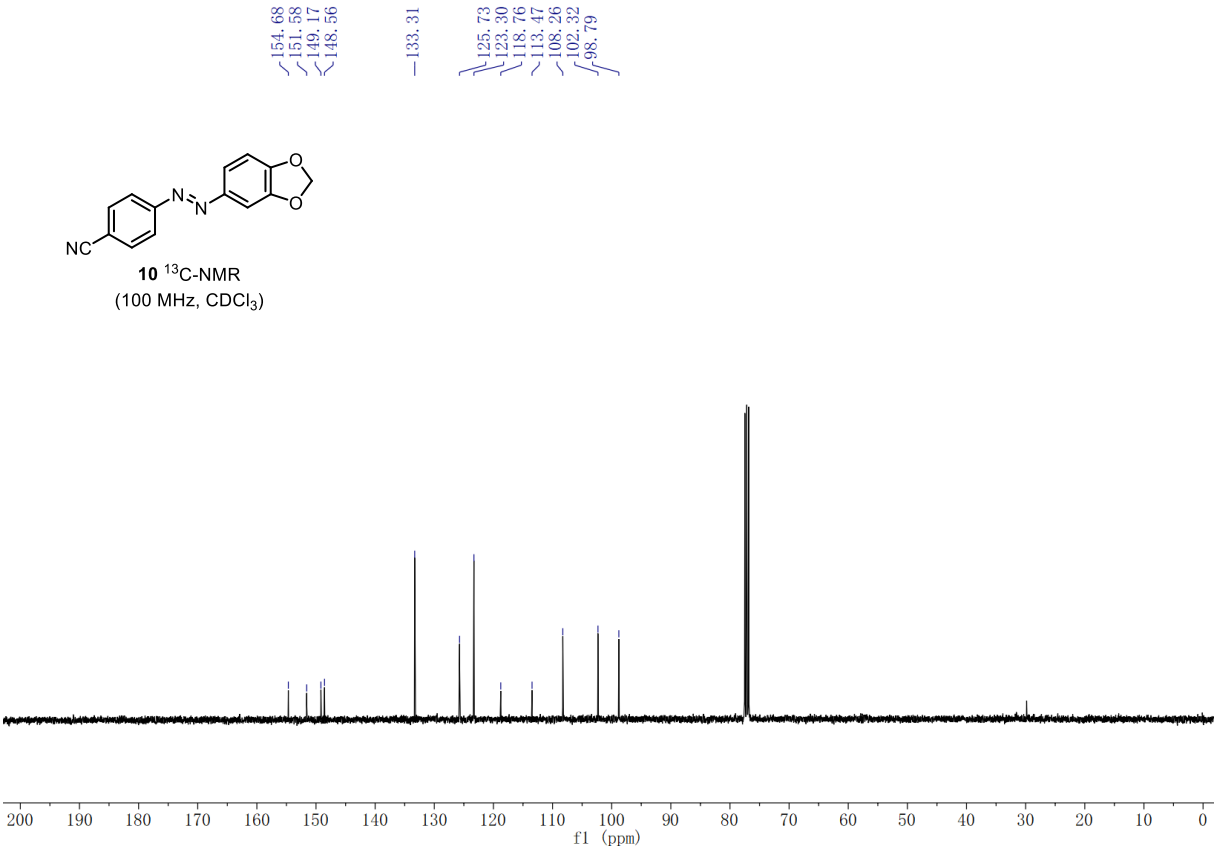




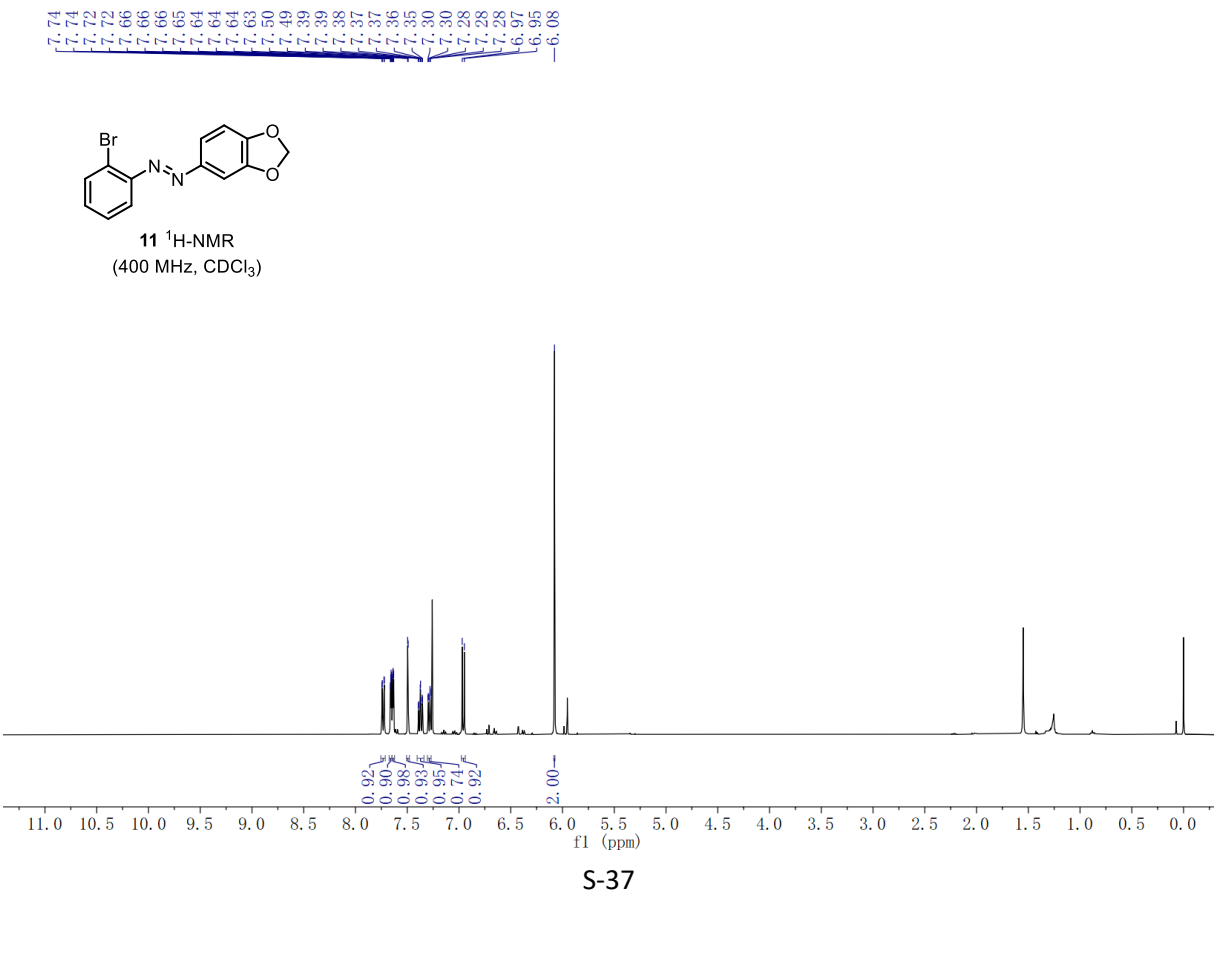
9 ^{13}C-NMR
(100 MHz, $CDCl_3$)



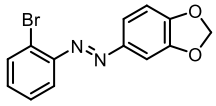
10 ^{1}H-NMR
(400 MHz, $CDCl_3$)



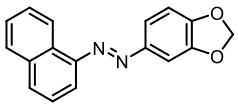
10 ^{13}C-NMR
(100 MHz, $CDCl_3$)



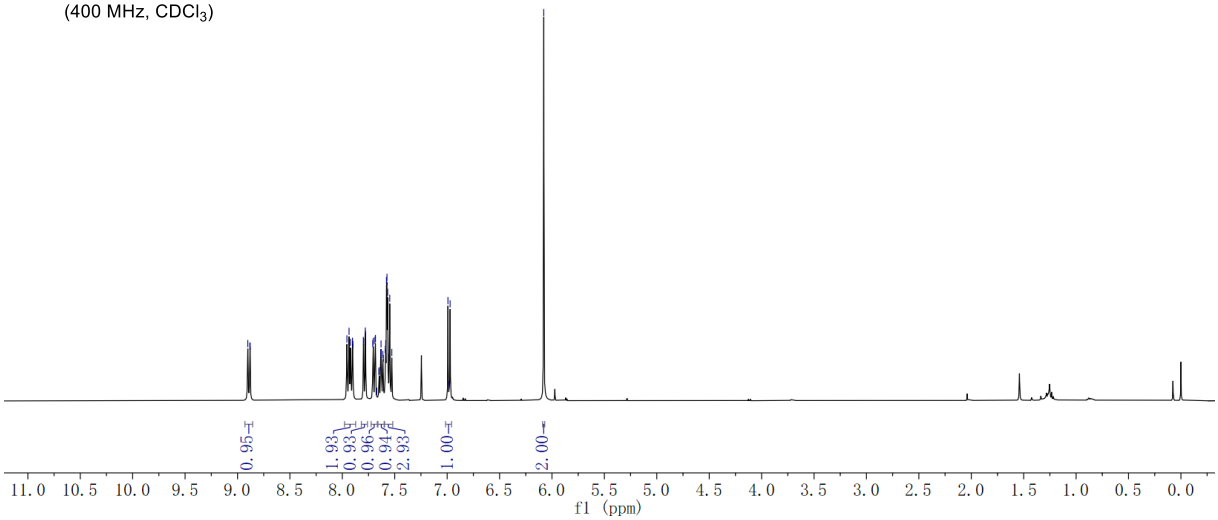
11 ^{1}H-NMR
(400 MHz, $CDCl_3$)

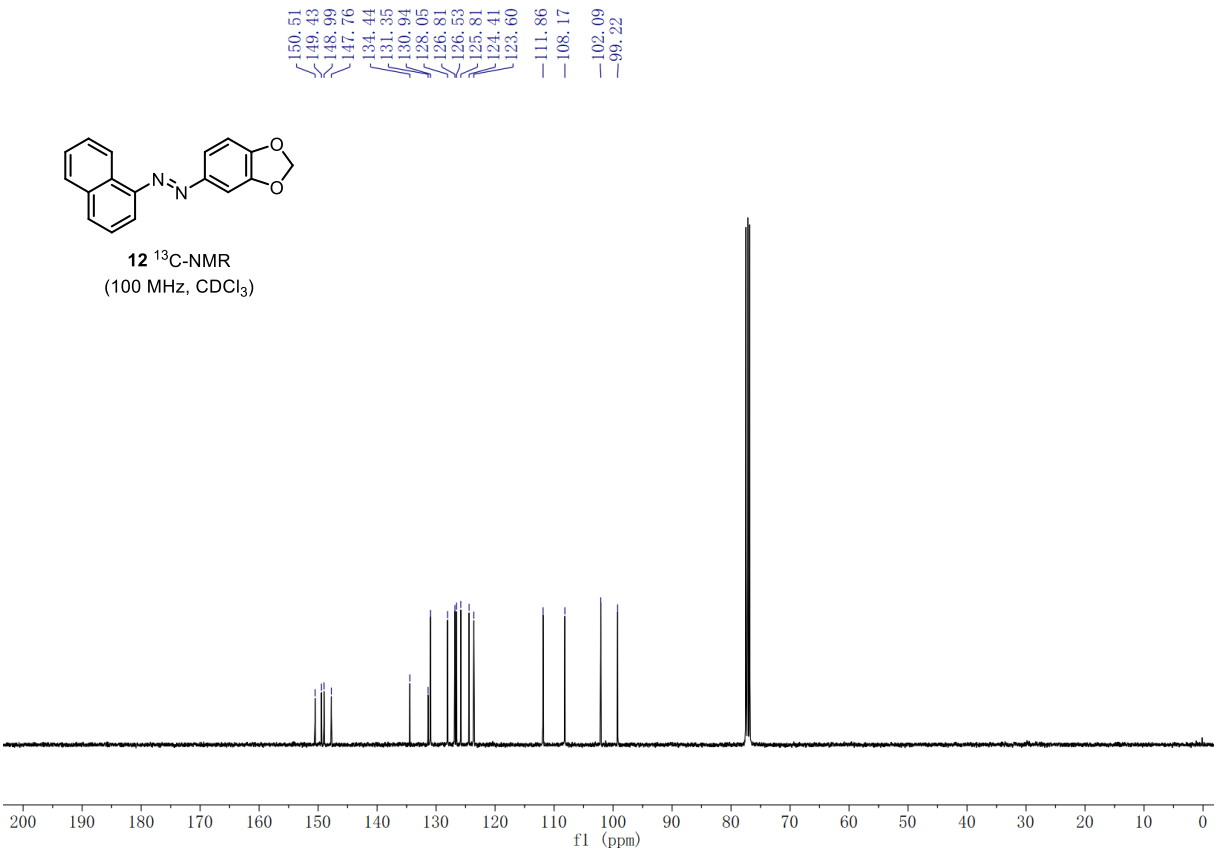


11 ^{13}C-NMR
(100 MHz, $CDCl_3$)

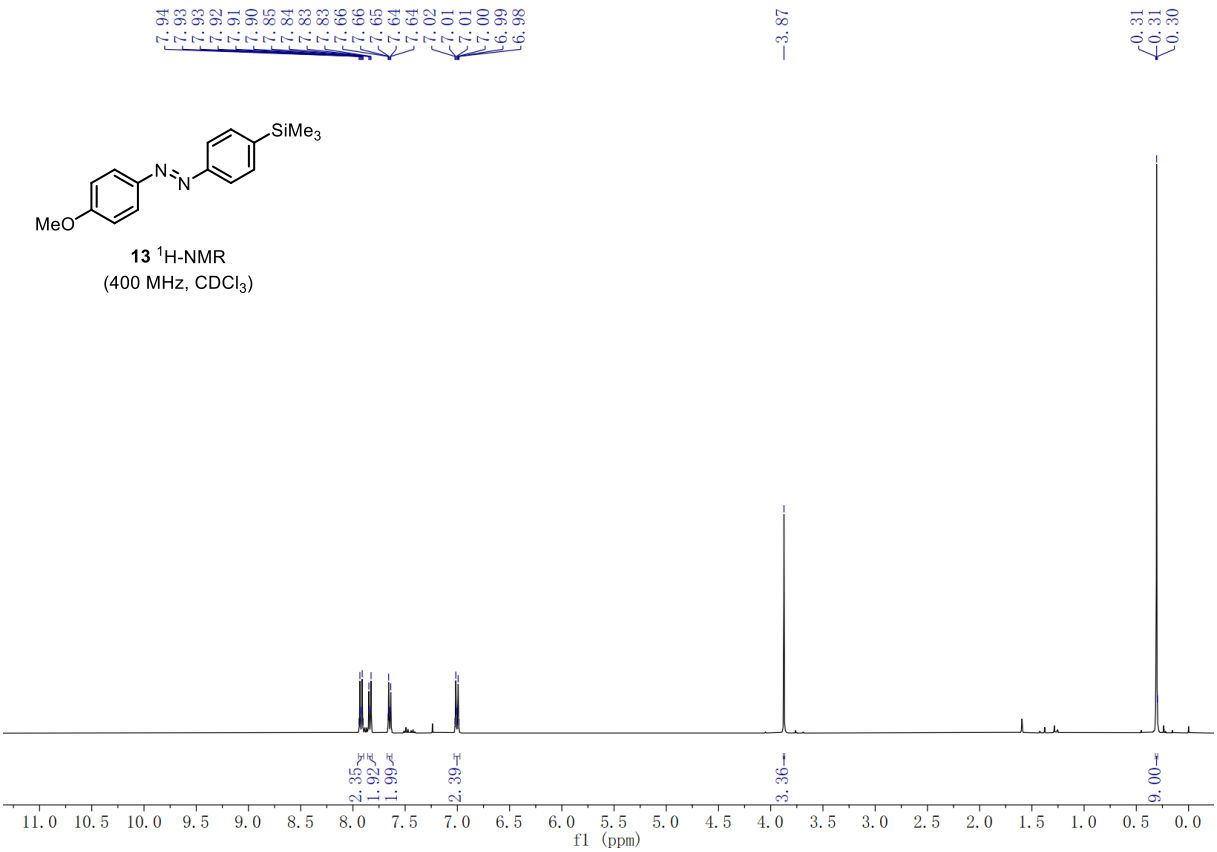


12 ^{1}H-NMR
(400 MHz, $CDCl_3$)

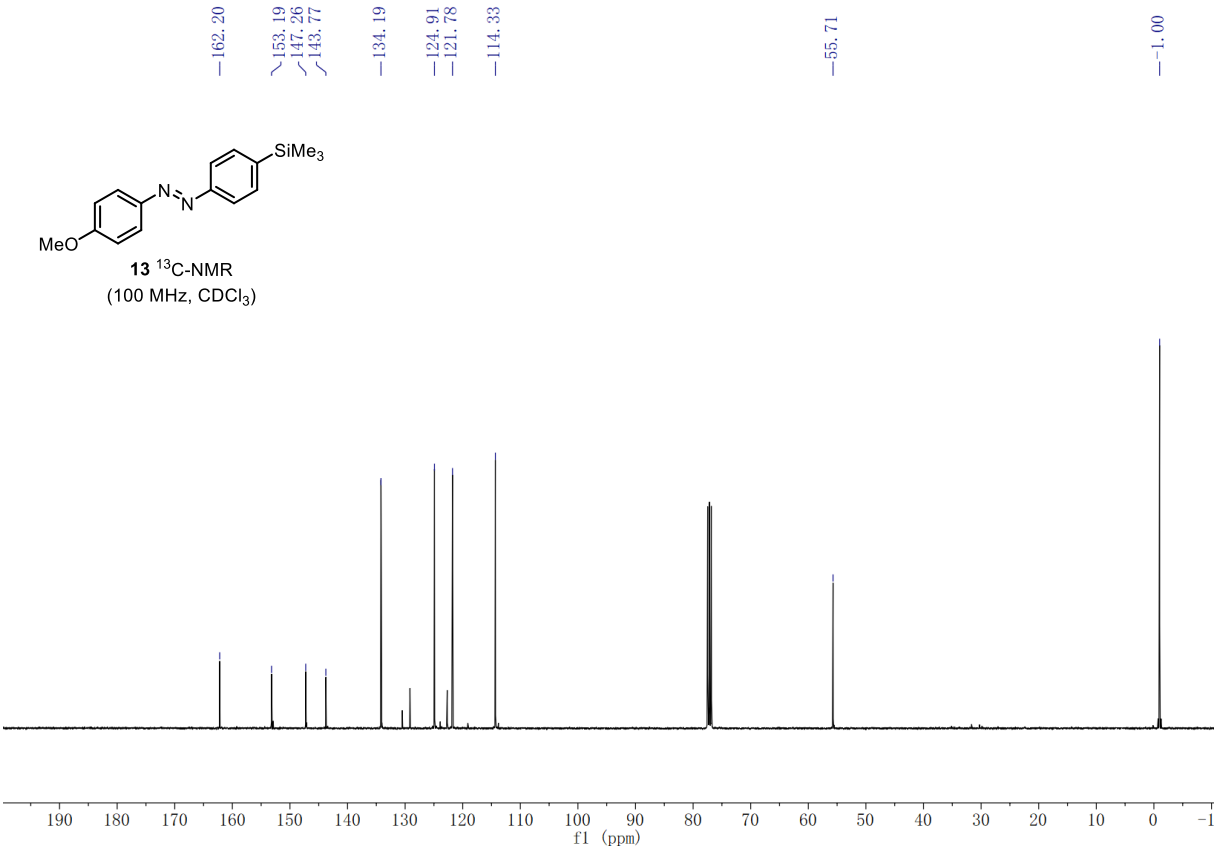




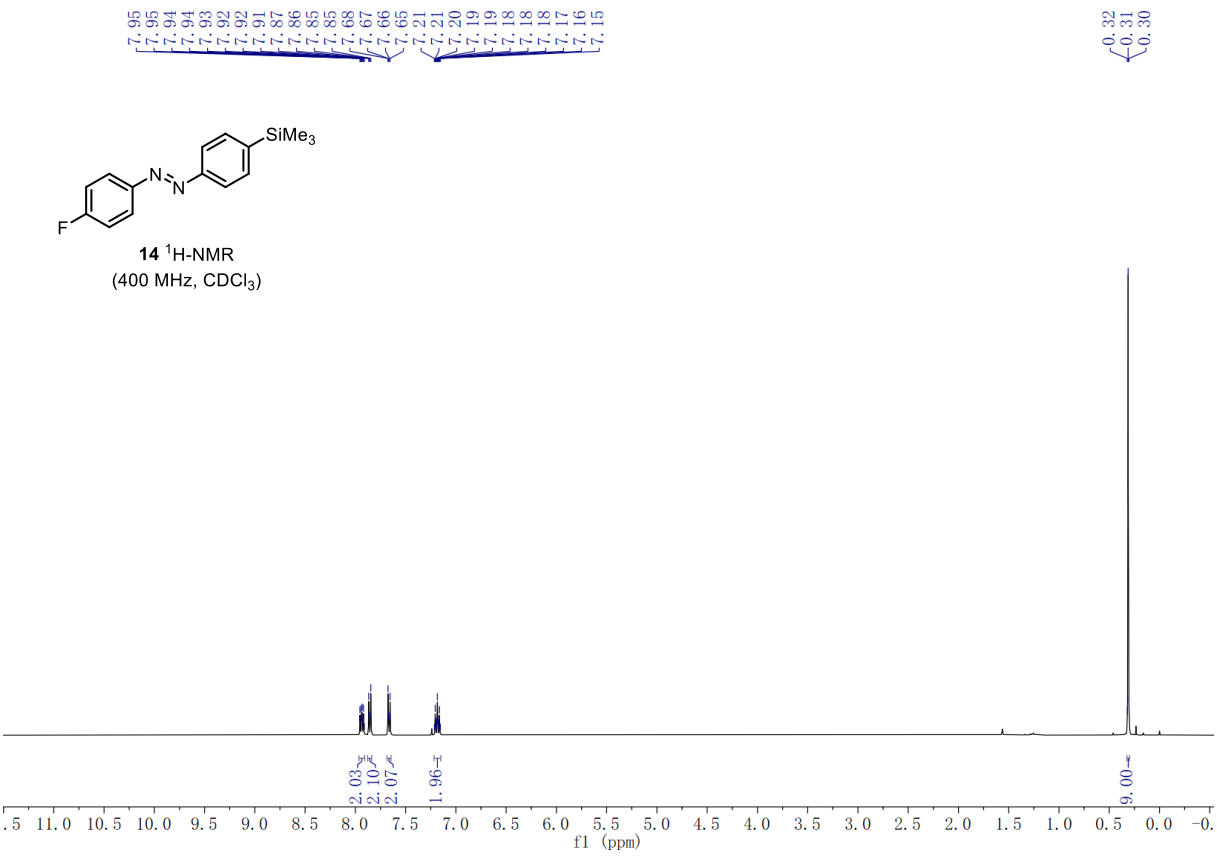
12 ^{13}C-NMR
(100 MHz, $CDCl_3$)



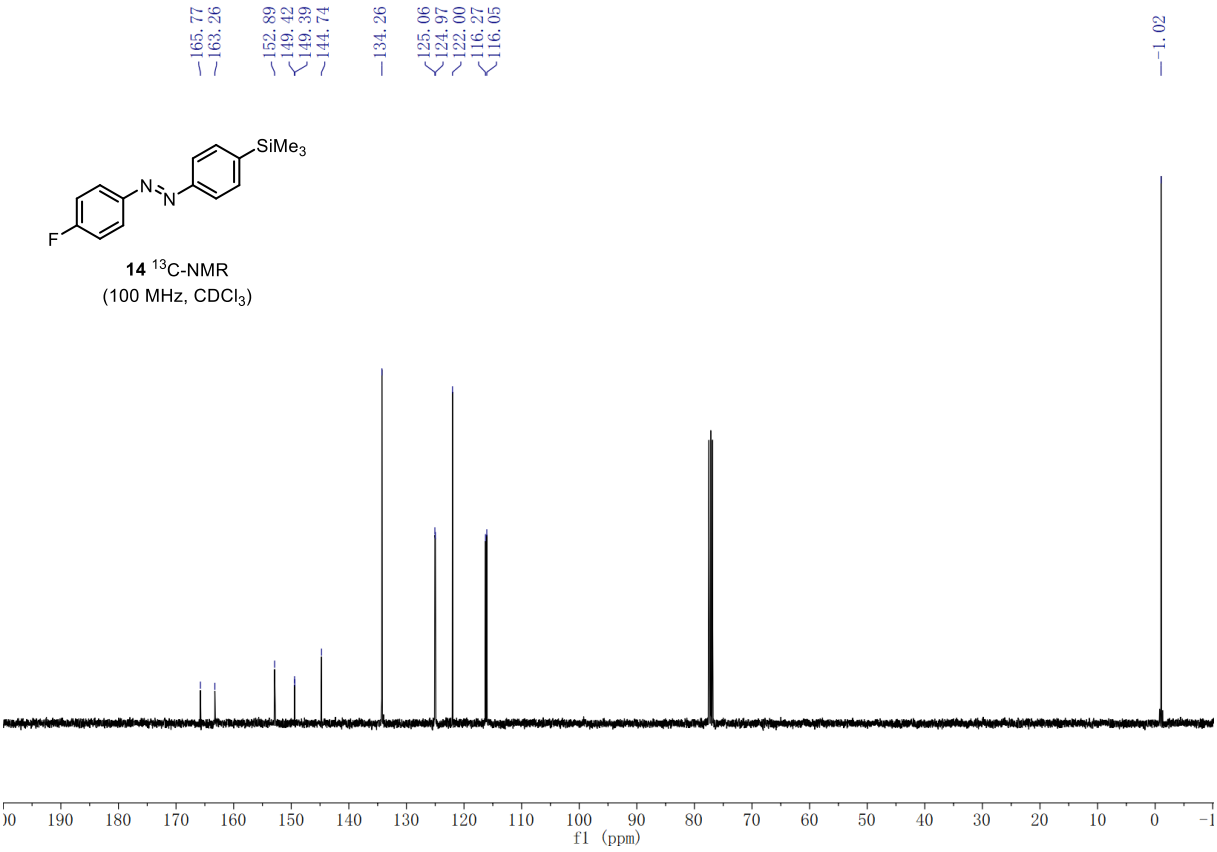
13 ^{1}H-NMR
(400 MHz, $CDCl_3$)



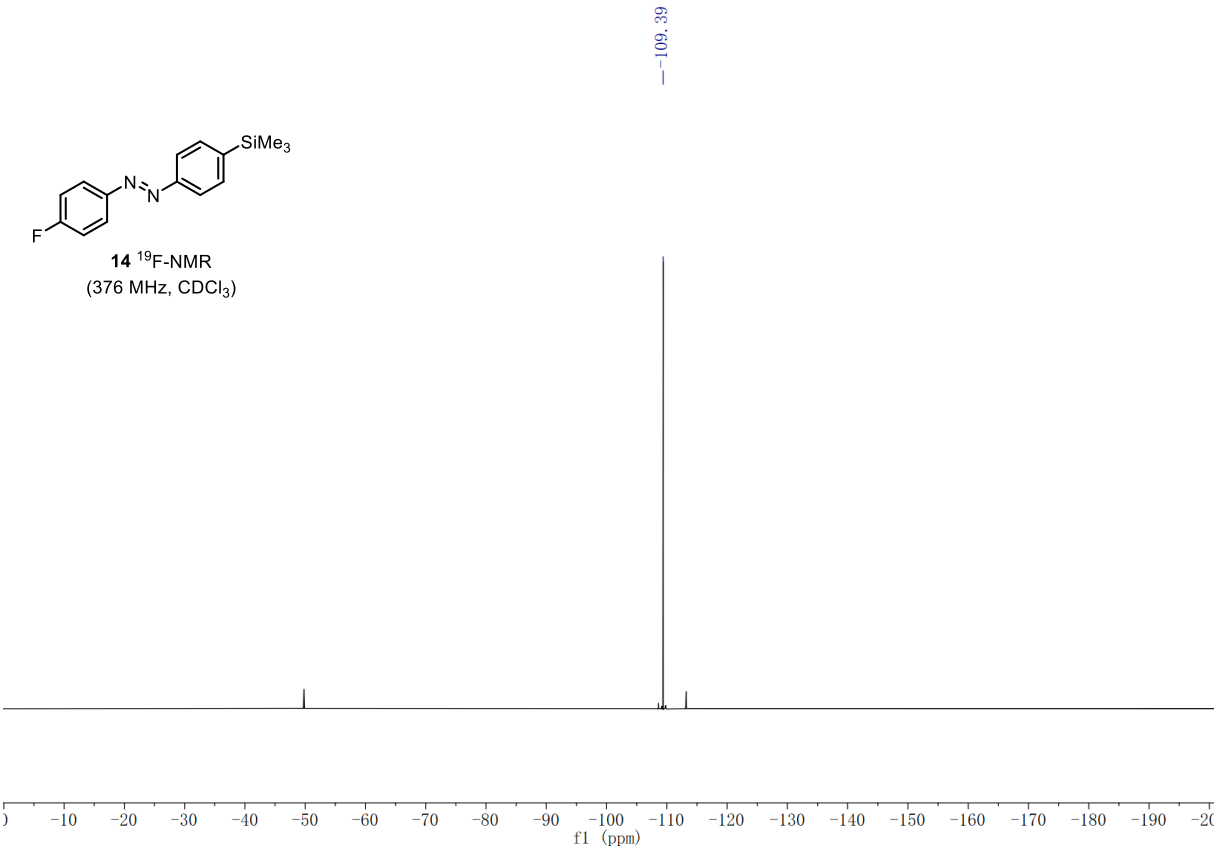
13 ^{13}C-NMR
(100 MHz, $CDCl_3$)



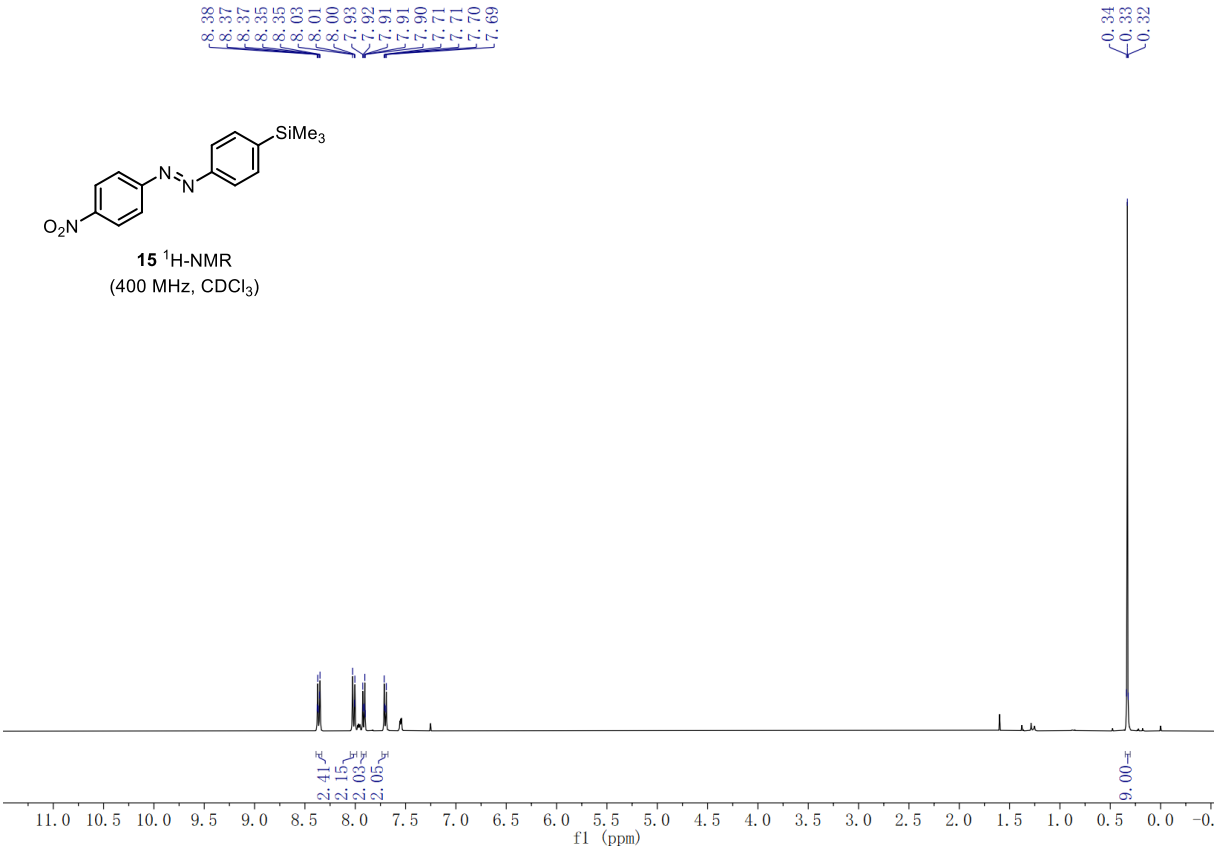
14 ^{1}H-NMR
(400 MHz, $CDCl_3$)



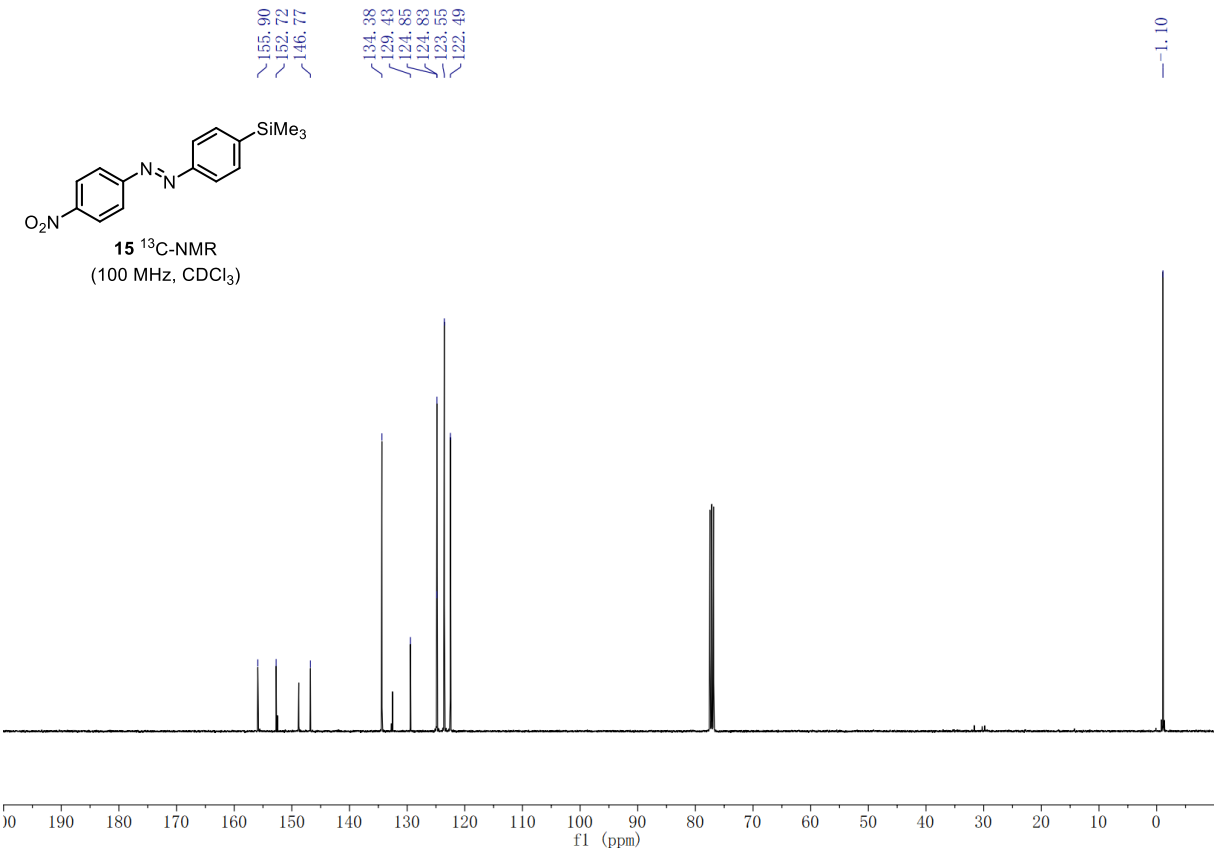
14 ^{13}C-NMR
(100 MHz, $CDCl_3$)



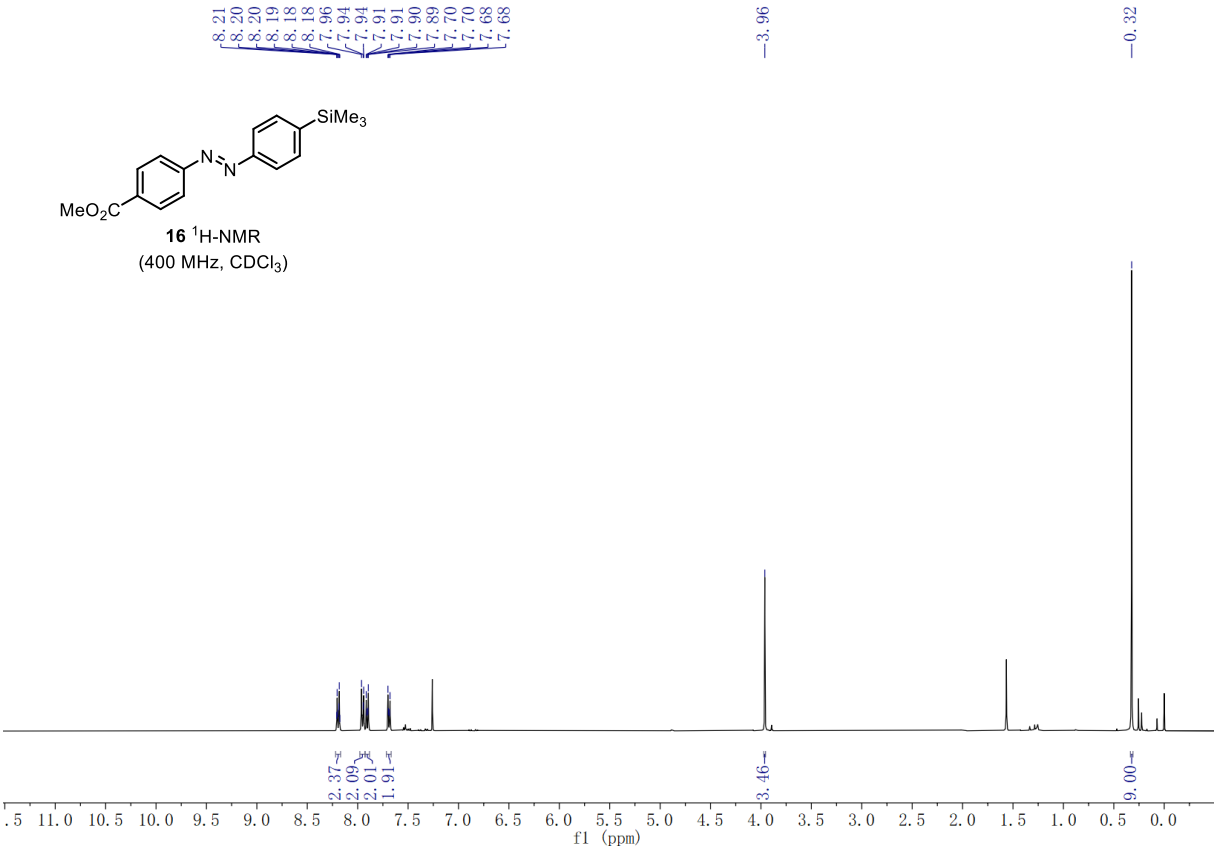
14 ^{19}F-NMR
(376 MHz, $CDCl_3$)



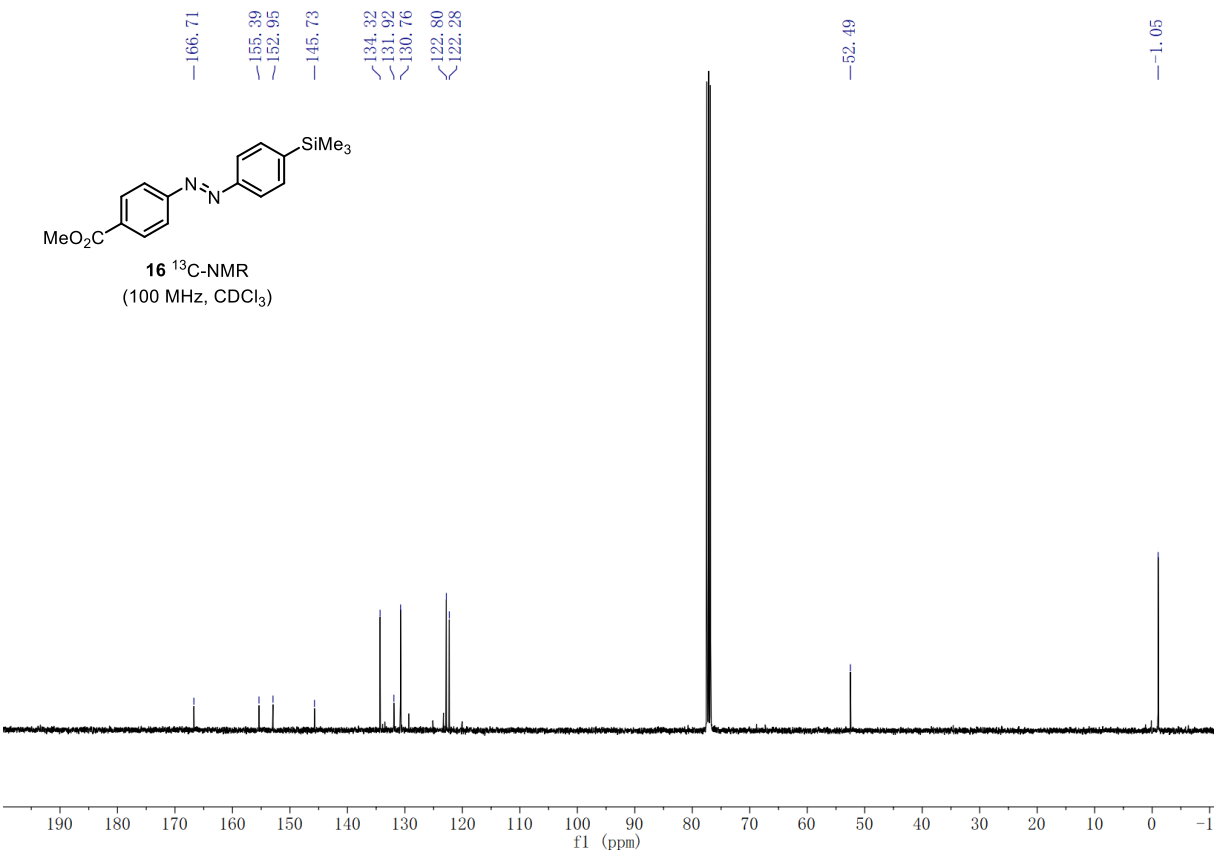
15 ^{1}H-NMR
(400 MHz, $CDCl_3$)



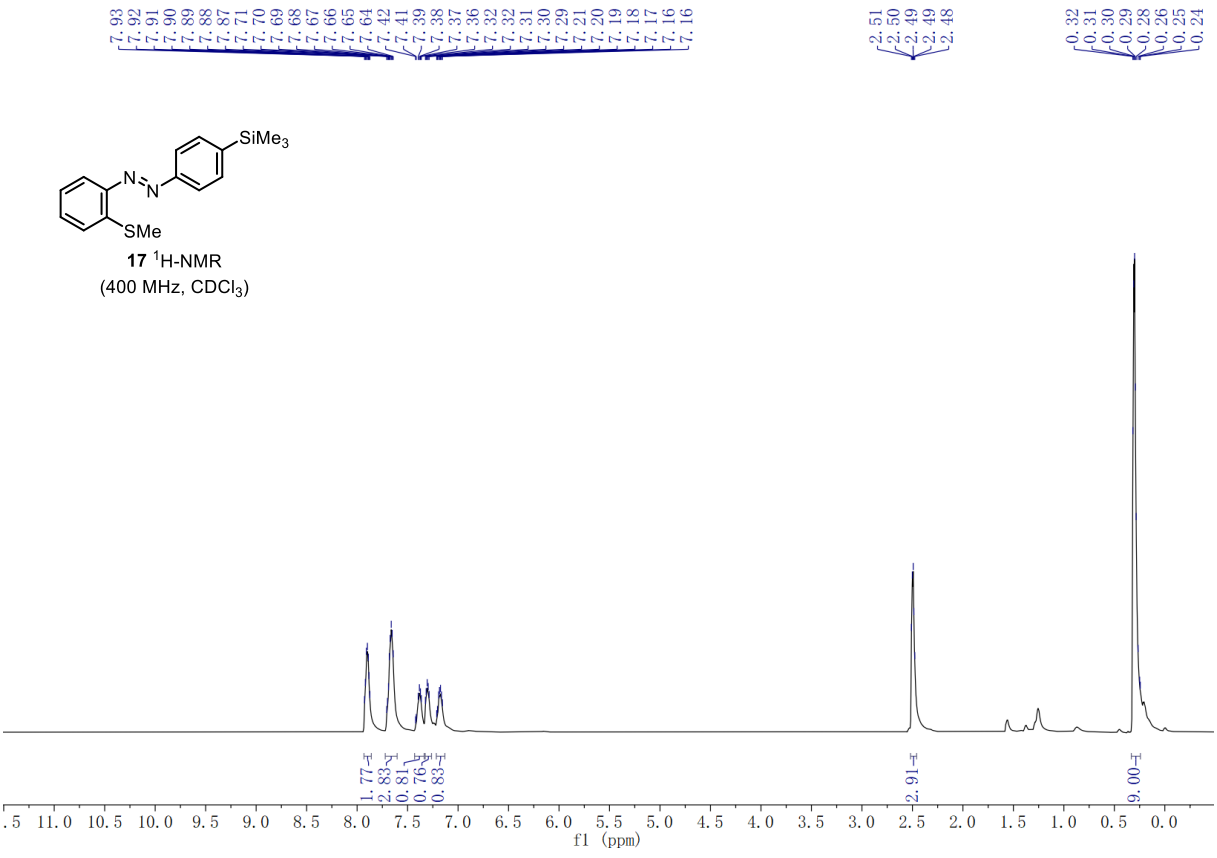
15 ^{13}C-NMR
(100 MHz, $CDCl_3$)



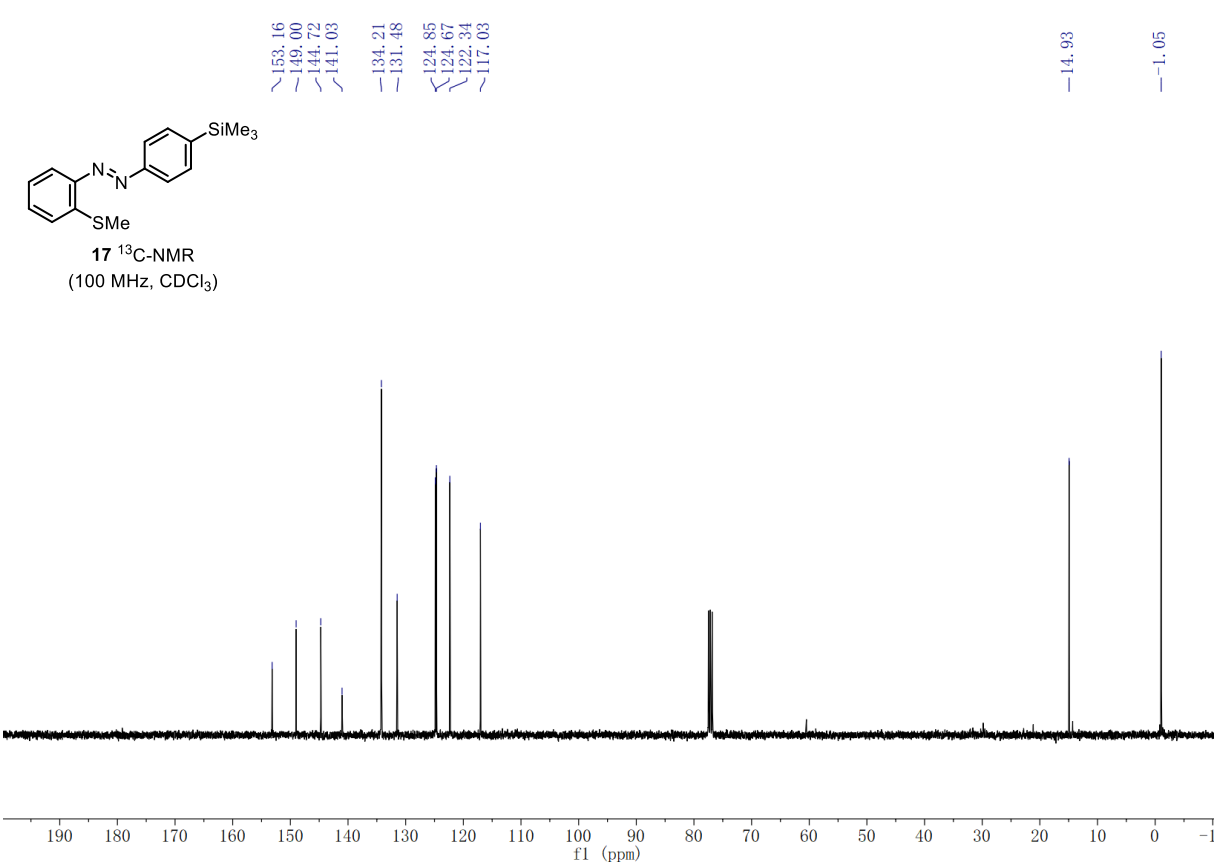
16 ^{1}H-NMR
(400 MHz, $CDCl_3$)



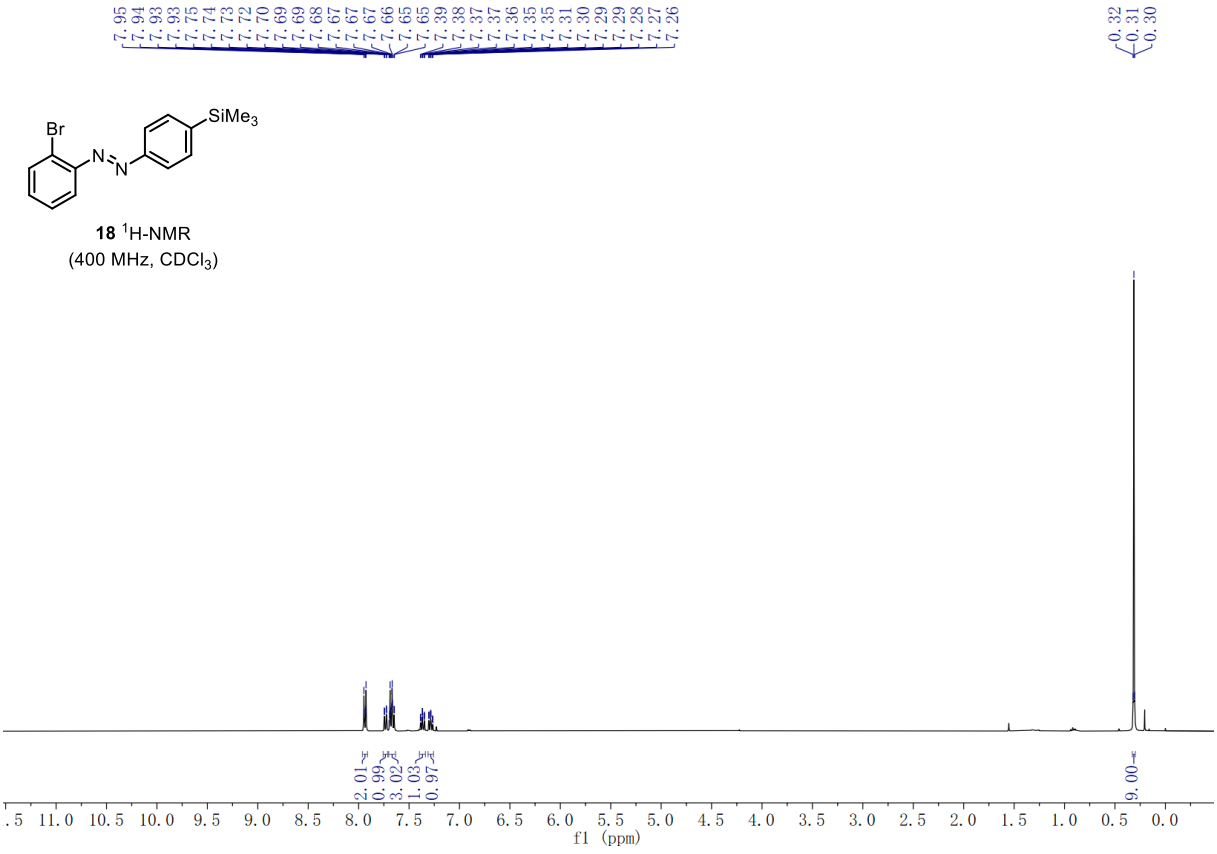
16 ^{13}C-NMR
(100 MHz, $CDCl_3$)

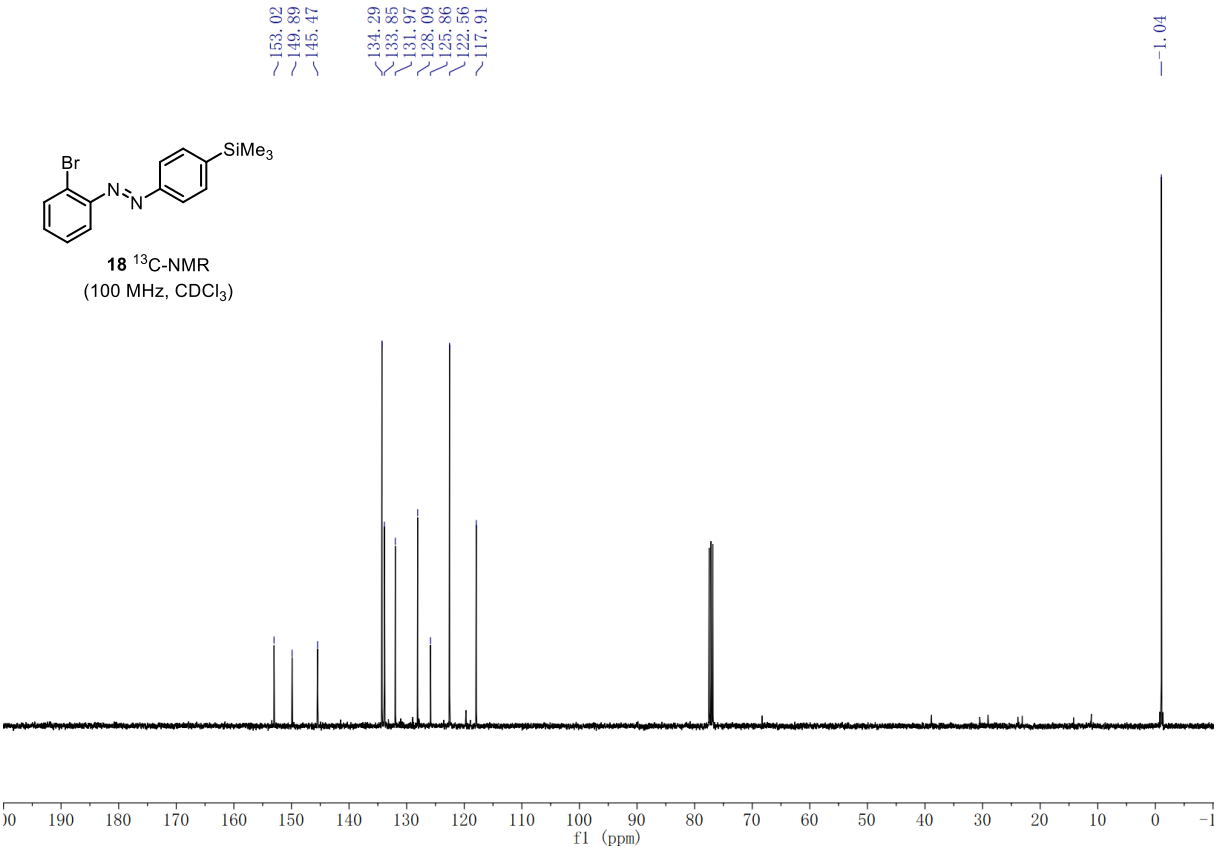


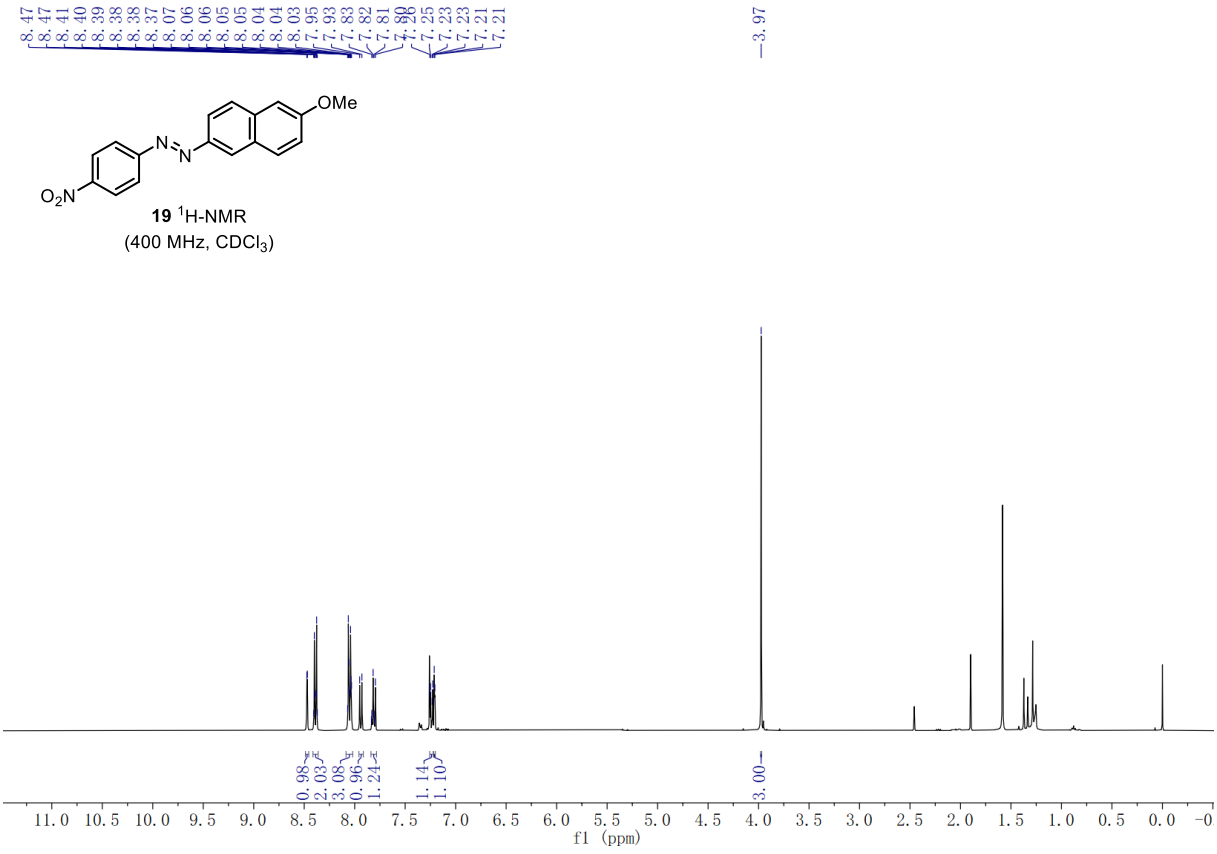
17 ^{1}H-NMR
(400 MHz, $CDCl_3$)



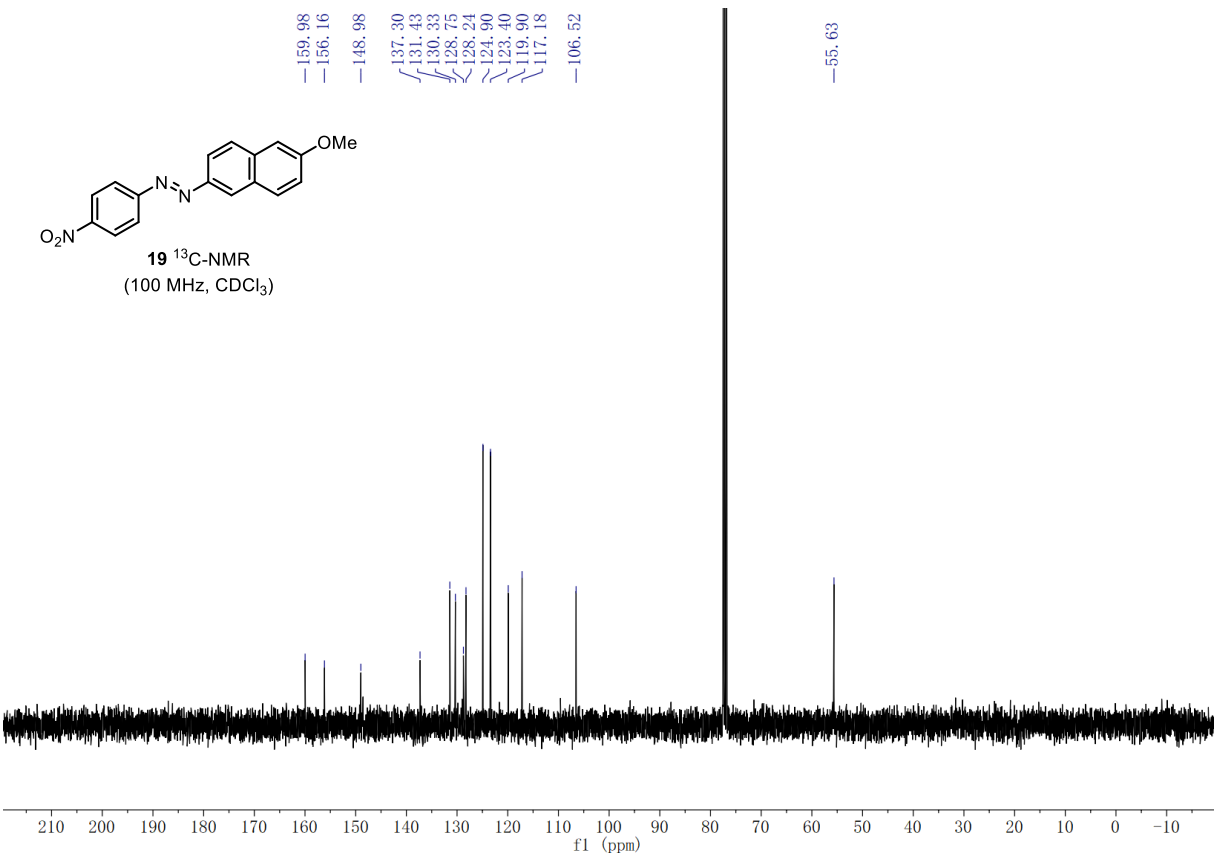
17 ^{13}C-NMR
(100 MHz, $CDCl_3$)


7.95
7.94
7.93
7.93
7.75
7.74
7.73
7.72
7.70
7.69
7.69
7.68
7.67
7.67
7.67
7.66
7.65
7.65
7.39
7.38
7.37
7.37
7.36
7.35
7.31
7.30
7.29
7.29
7.28
7.27
7.26
0.32
0.31
0.30
Br
N
N
SiMe3
18 1H-NMR
(400 MHz, CDCl3)
2.01
0.99
3.02
1.03
0.97
9.00
f1 (ppm)

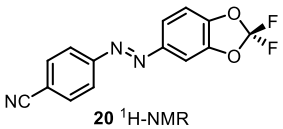

153.02
149.89
145.47
134.29
133.85
131.97
128.09
125.86
122.56
117.91
1.04
Br
N
N
SiMe3
18 13C-NMR
(100 MHz, CDCl3)
f1 (ppm)



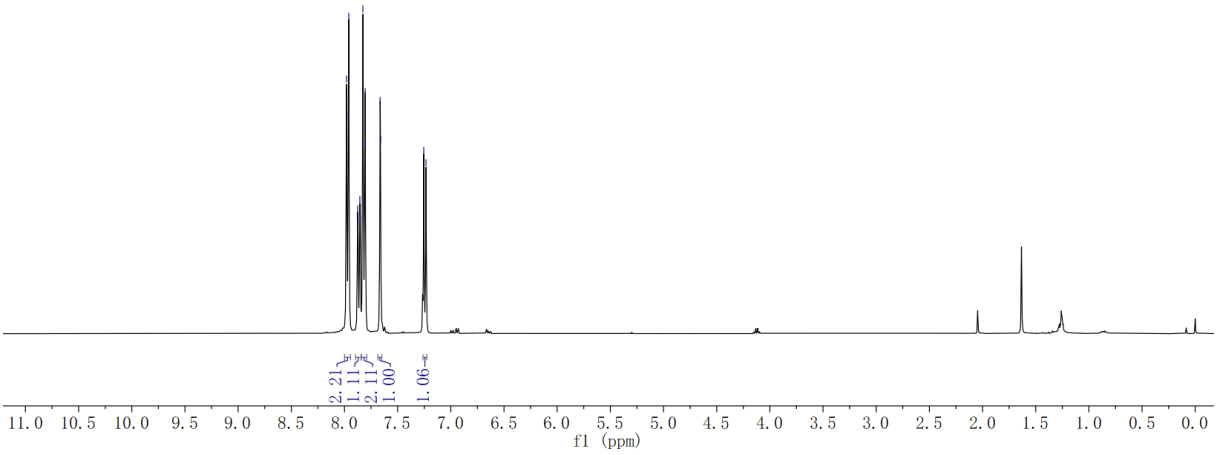
19 ^{1}H-NMR
(400 MHz, $CDCl_3$)

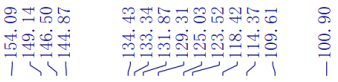


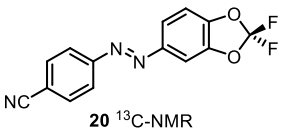
19 ^{13}C-NMR
(100 MHz, $CDCl_3$)



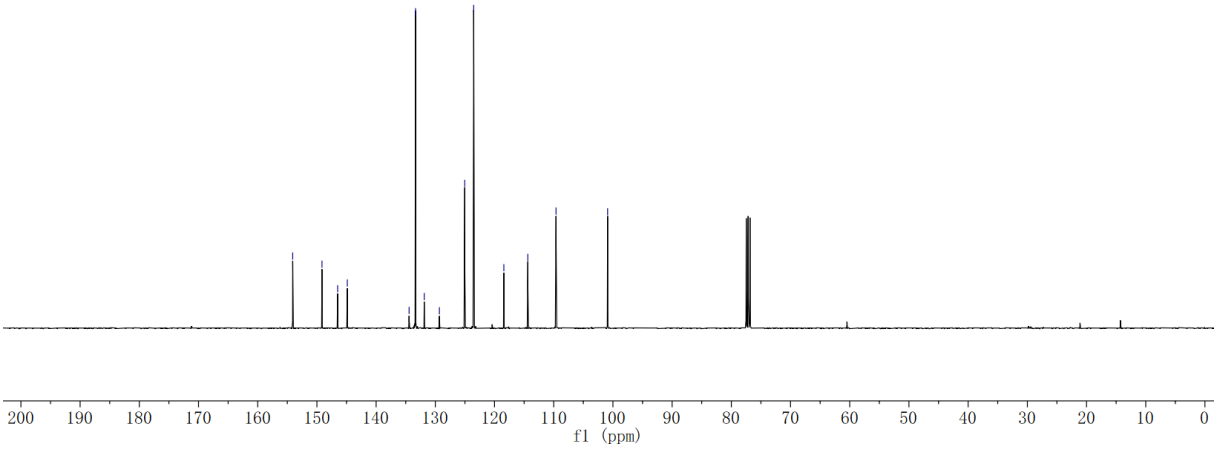
20 ^{1}H-NMR
(400 MHz, $CDCl_3$)

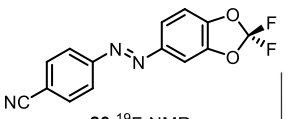




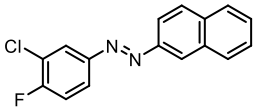


20 ^{13}C-NMR
(100 MHz, $CDCl_3$)

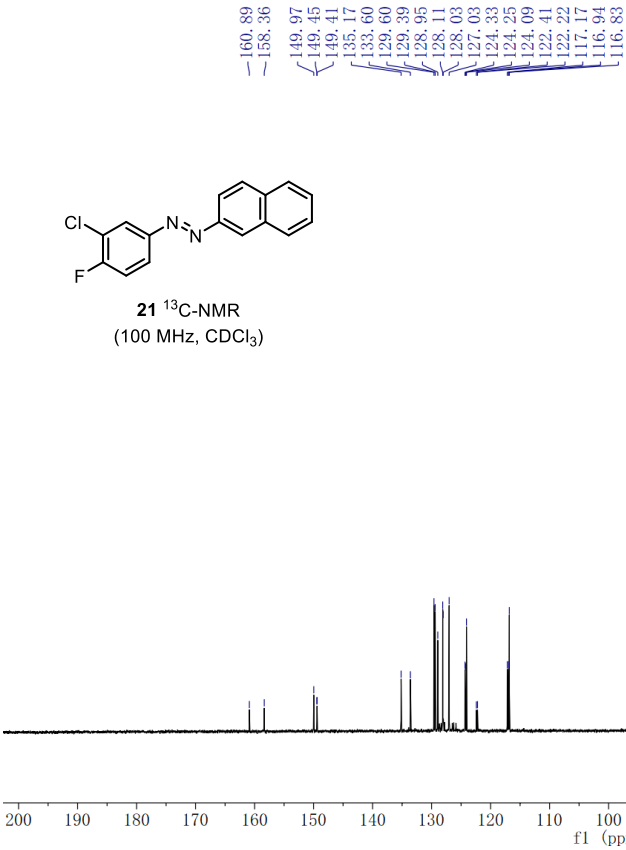




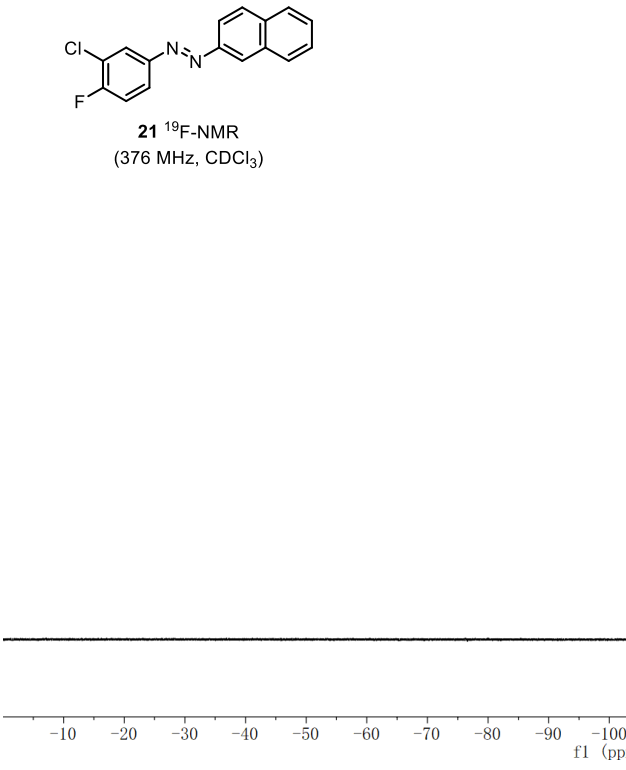
20 ^{19}F-NMR
(376 MHz, $CDCl_3$)



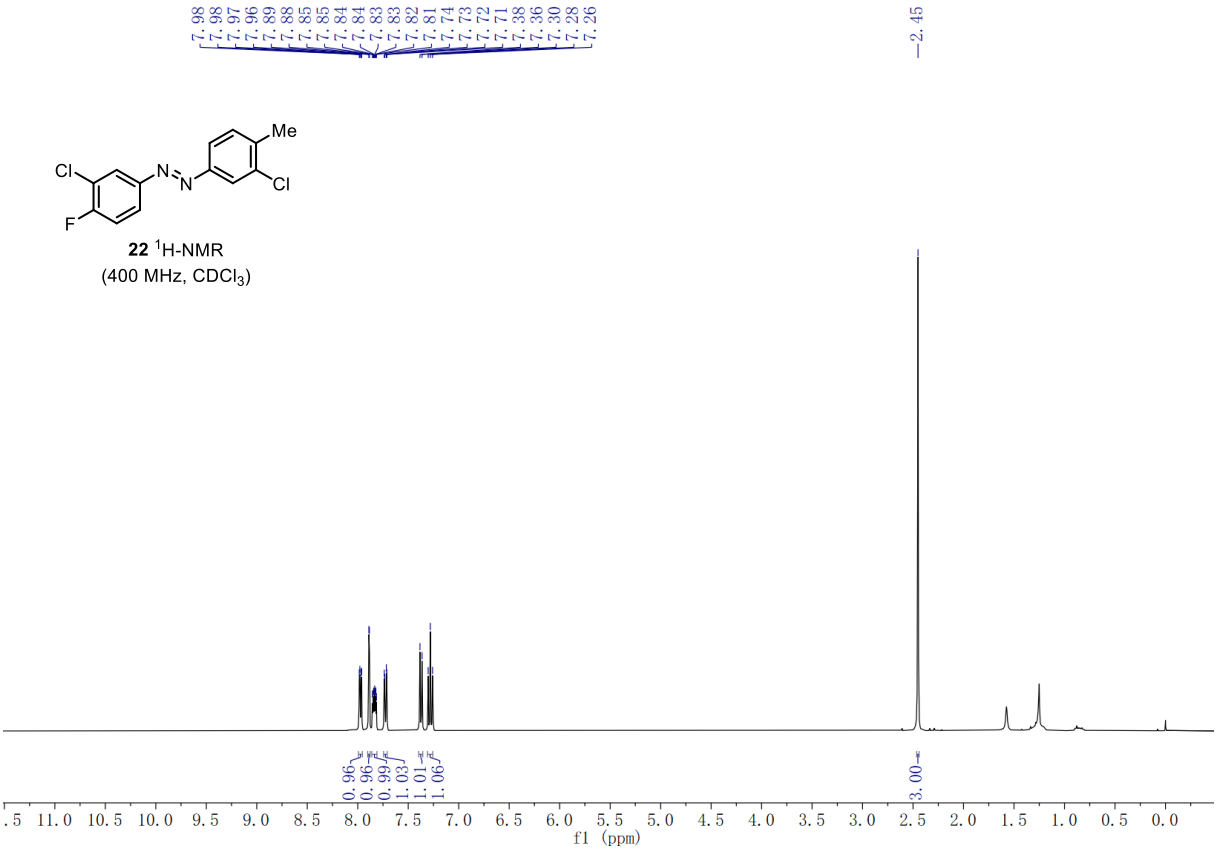
21 ^{1}H-NMR
(400 MHz, $CDCl_3$)



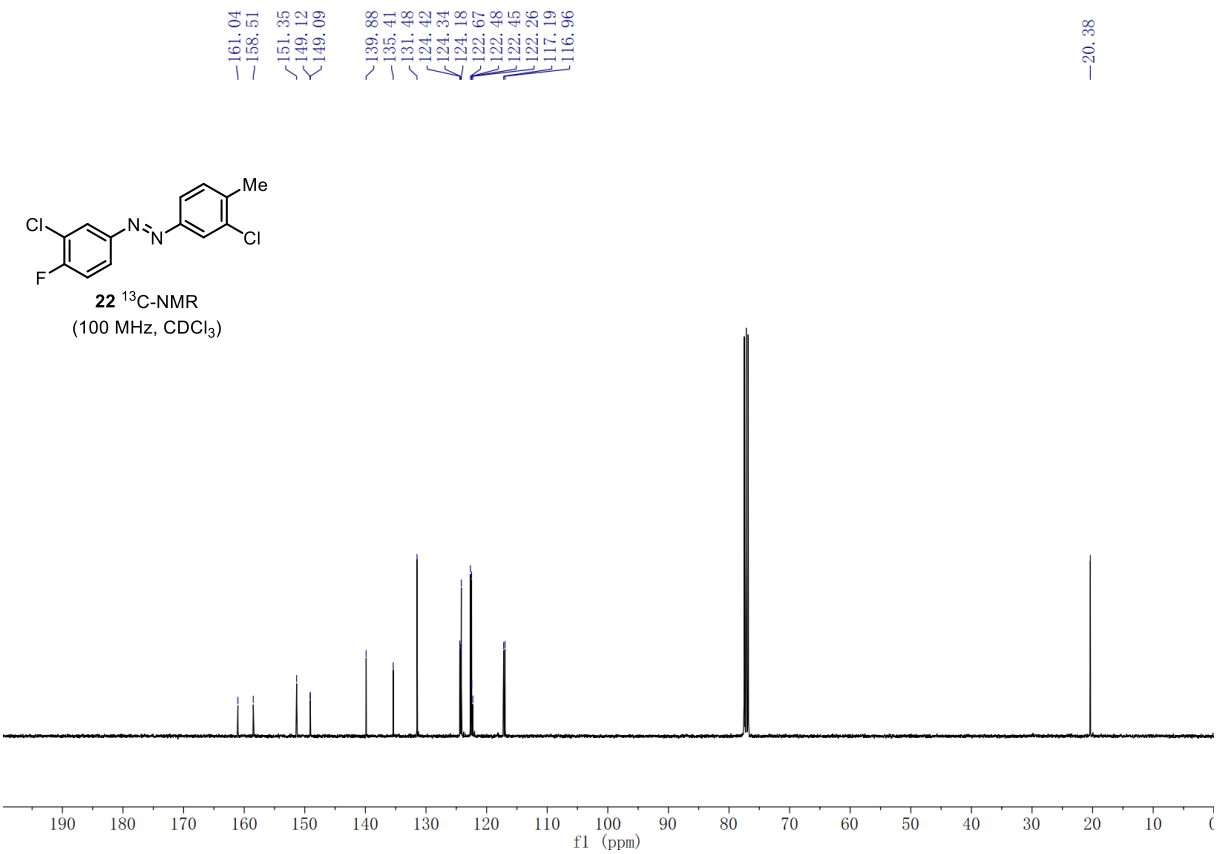
21 ^{13}C-NMR
(100 MHz, $CDCl_3$)



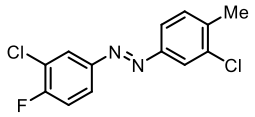
21 ^{19}F-NMR
(376 MHz, $CDCl_3$)



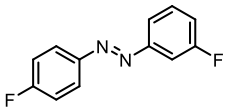
22 ^{1}H-NMR
(400 MHz, $CDCl_3$)



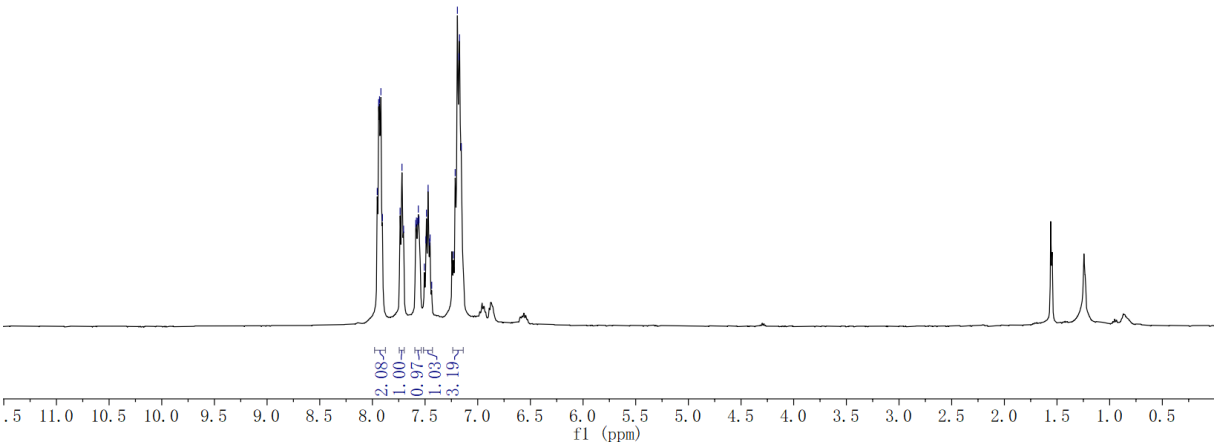
22 ^{13}C-NMR
(100 MHz, $CDCl_3$)

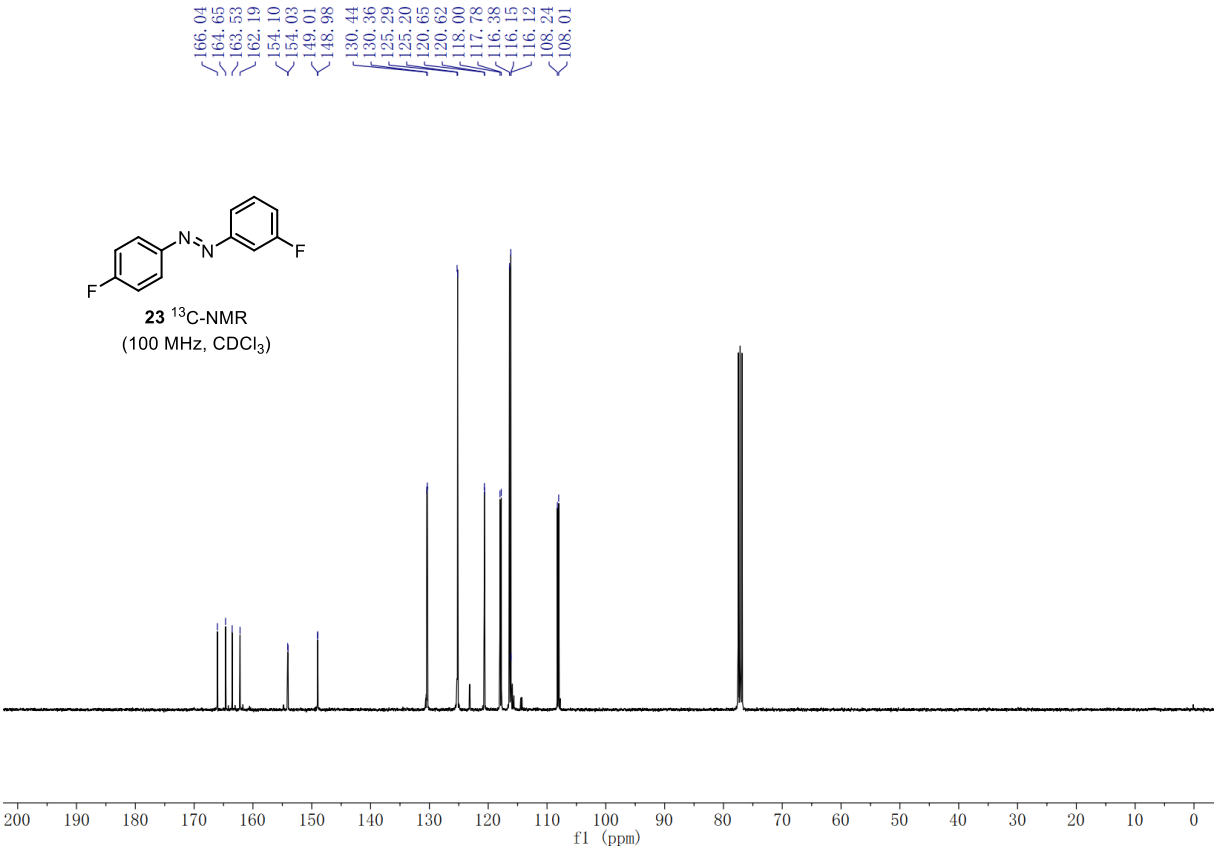


22 ^{19}F-NMR
(376 MHz, $CDCl_3$)

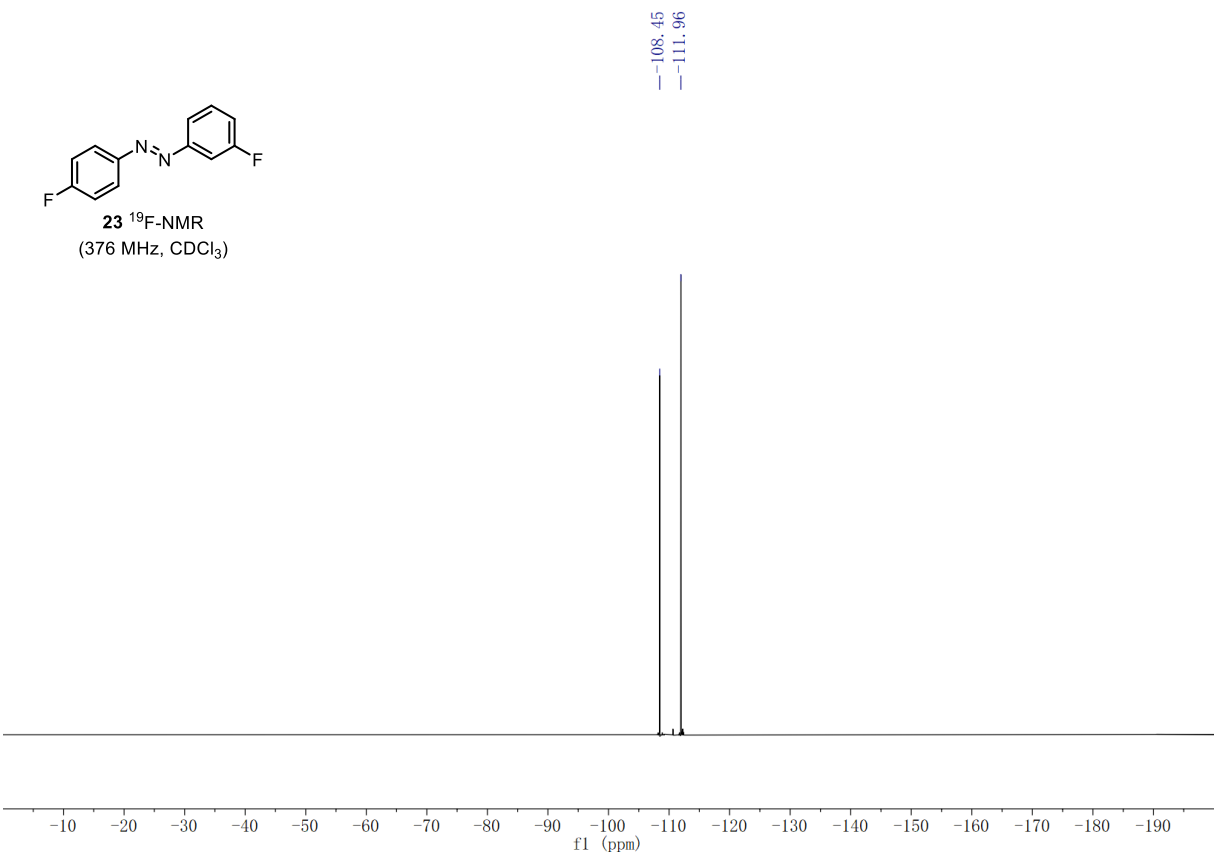


23 ^{1}H-NMR
(400 MHz, $CDCl_3$)

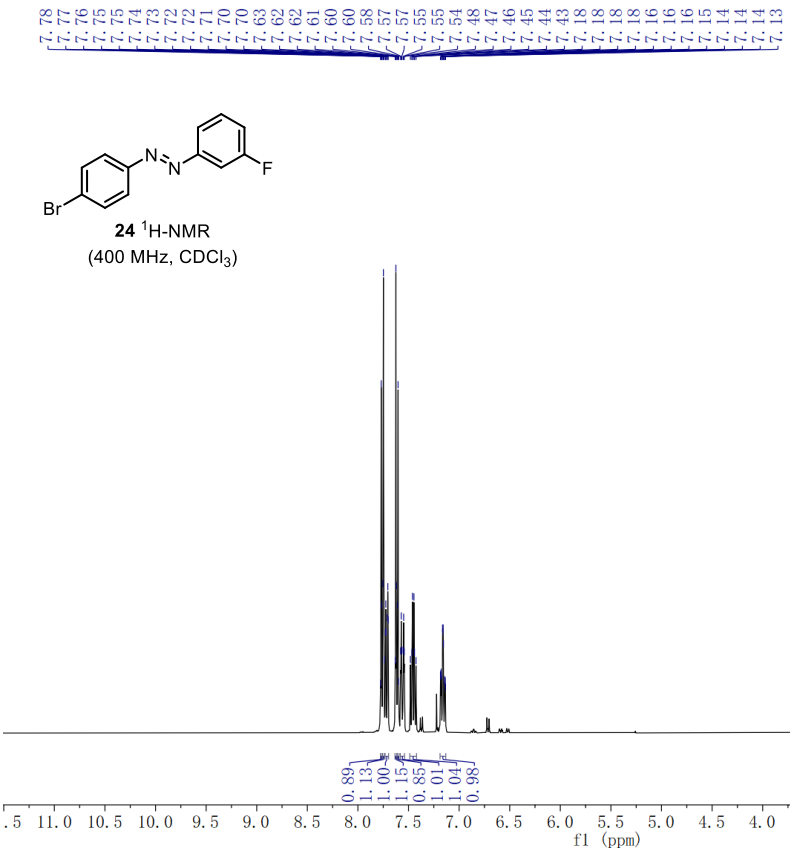




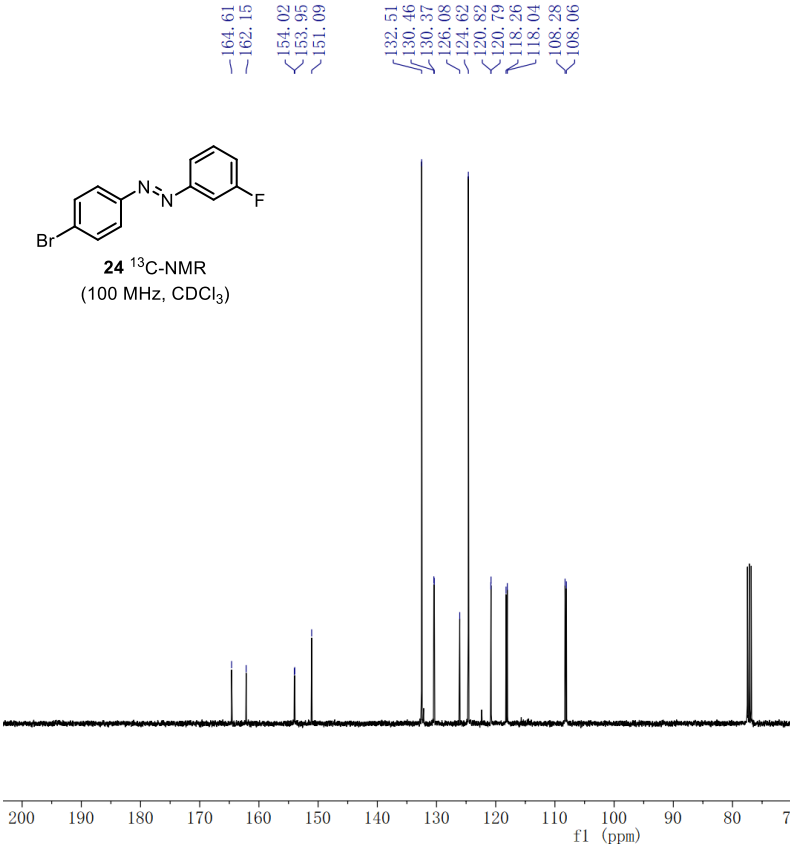
23 ^{13}C-NMR
(100 MHz, $CDCl_3$)



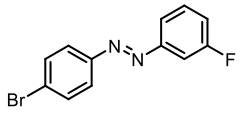
23 ^{19}F-NMR
(376 MHz, $CDCl_3$)



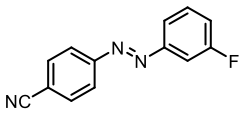
24 ^{1}H-NMR
(400 MHz, $CDCl_3$)



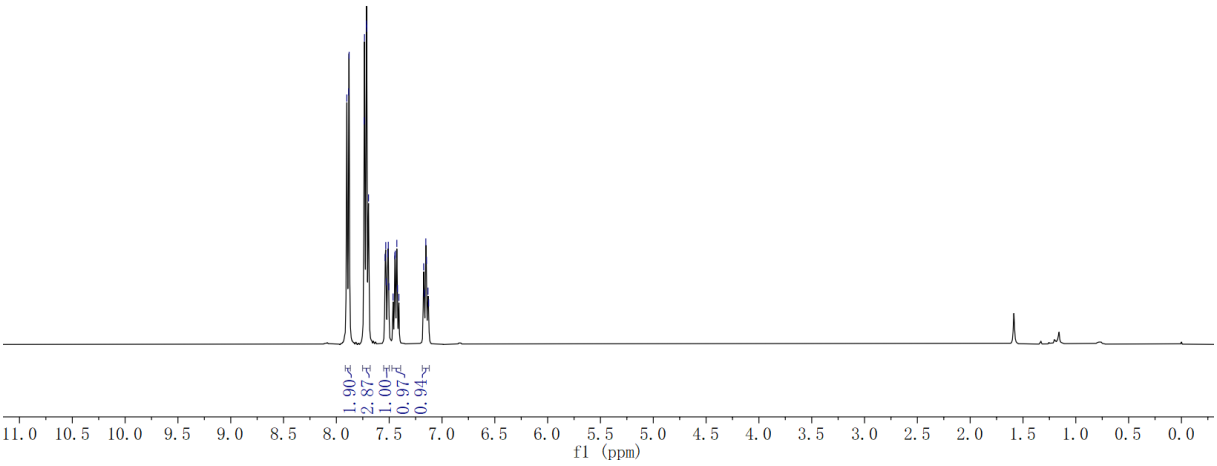
24 ^{13}C-NMR
(100 MHz, $CDCl_3$)

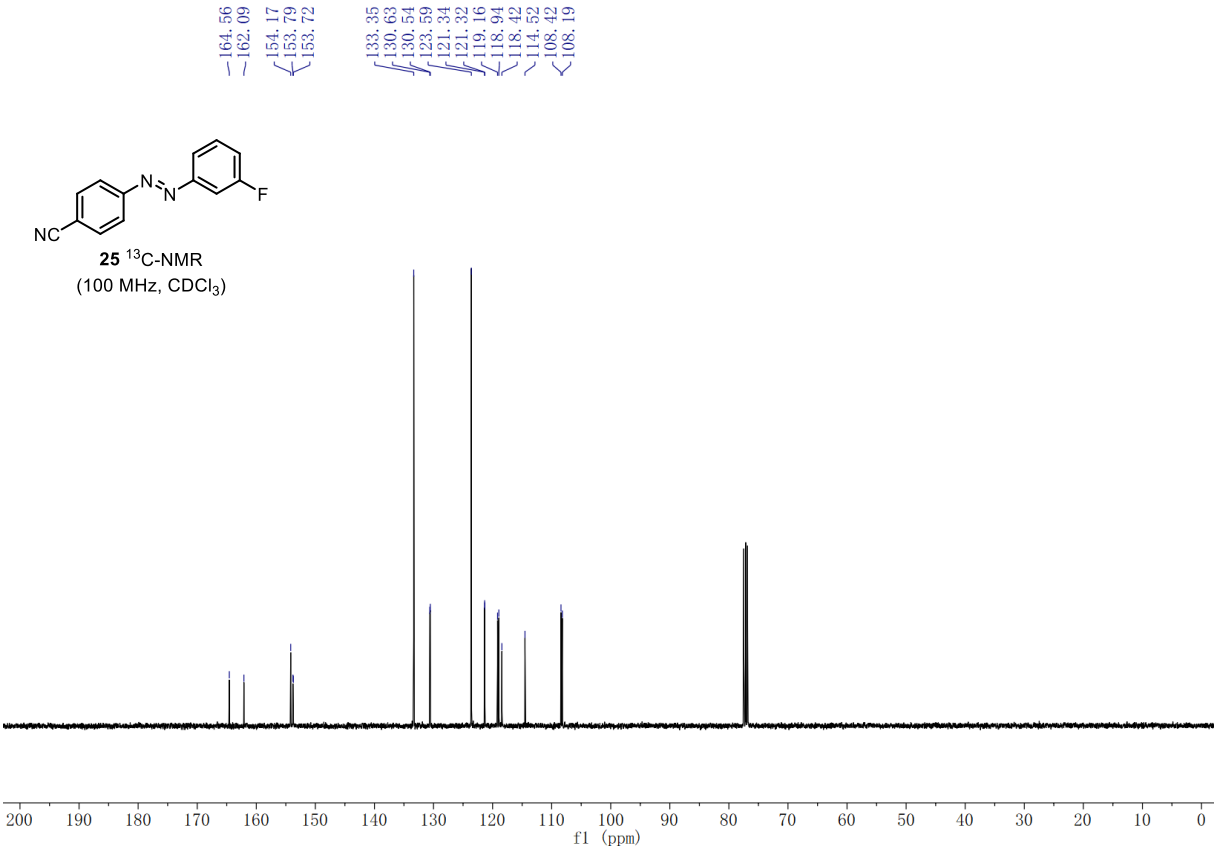


24 ^{19}F-NMR
(376 MHz, $CDCl_3$)

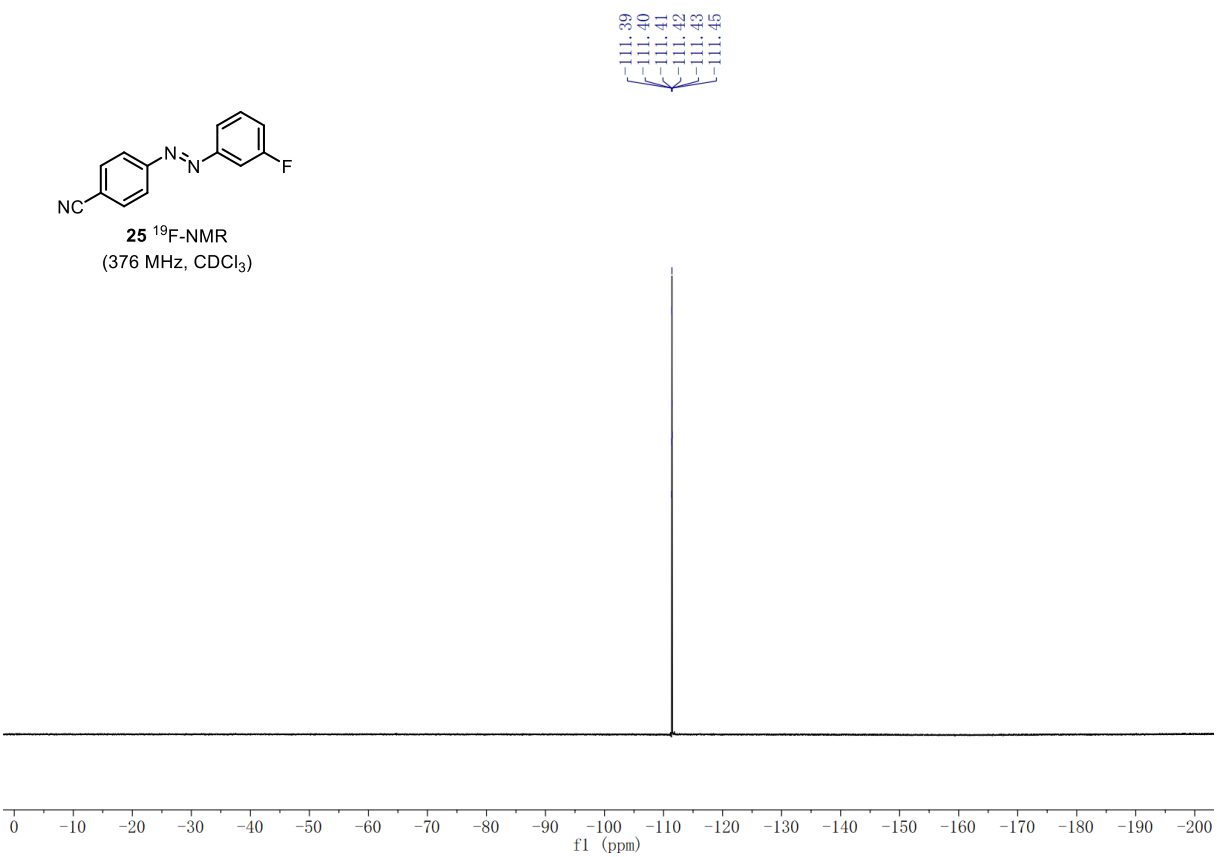


25 ^{1}H-NMR
(400 MHz, $CDCl_3$)

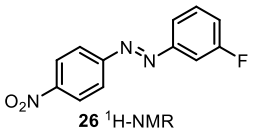




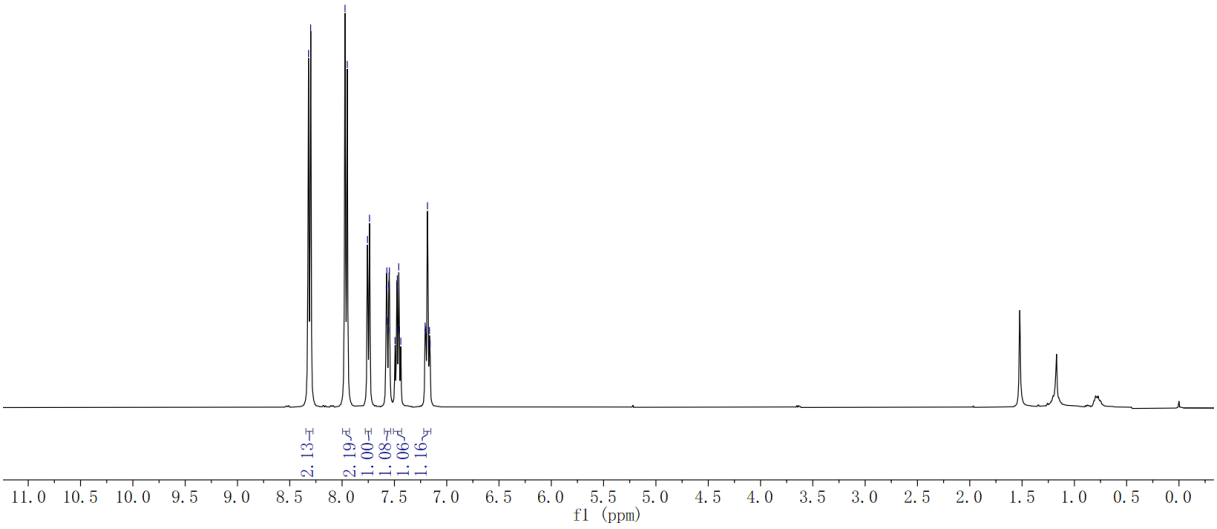
25 ^{13}C-NMR
(100 MHz, $CDCl_3$)

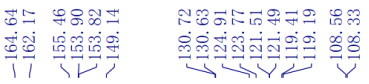


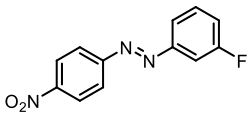
25 ^{19}F-NMR
(376 MHz, $CDCl_3$)



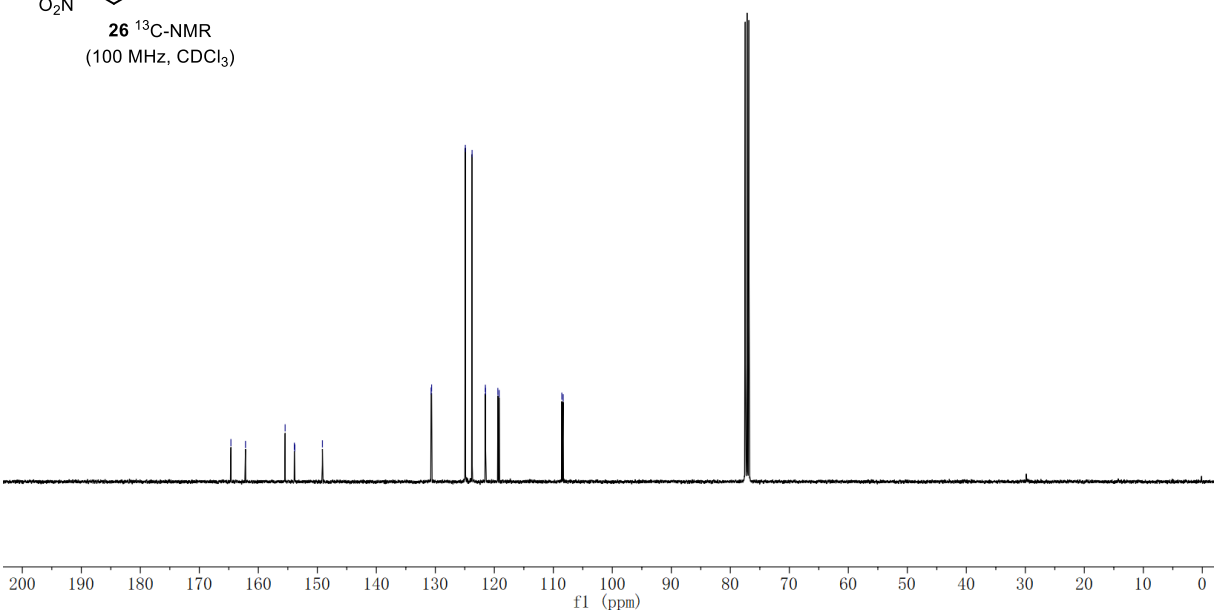
26 ^{1}H-NMR
(400 MHz, $CDCl_3$)

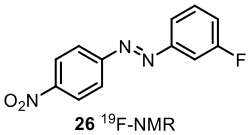




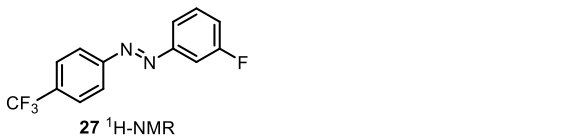


26 ^{13}C-NMR
(100 MHz, $CDCl_3$)

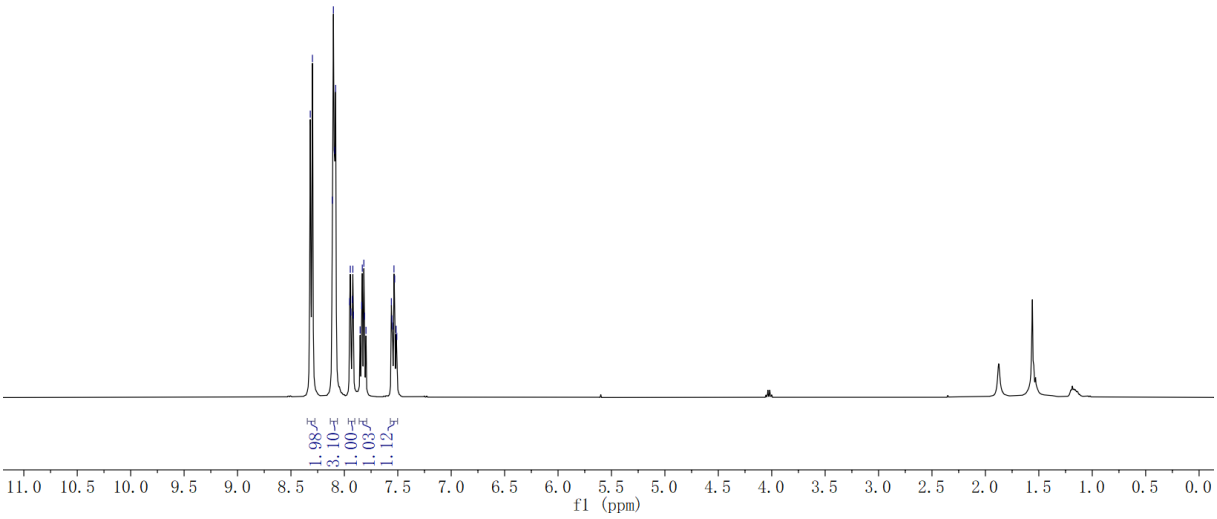


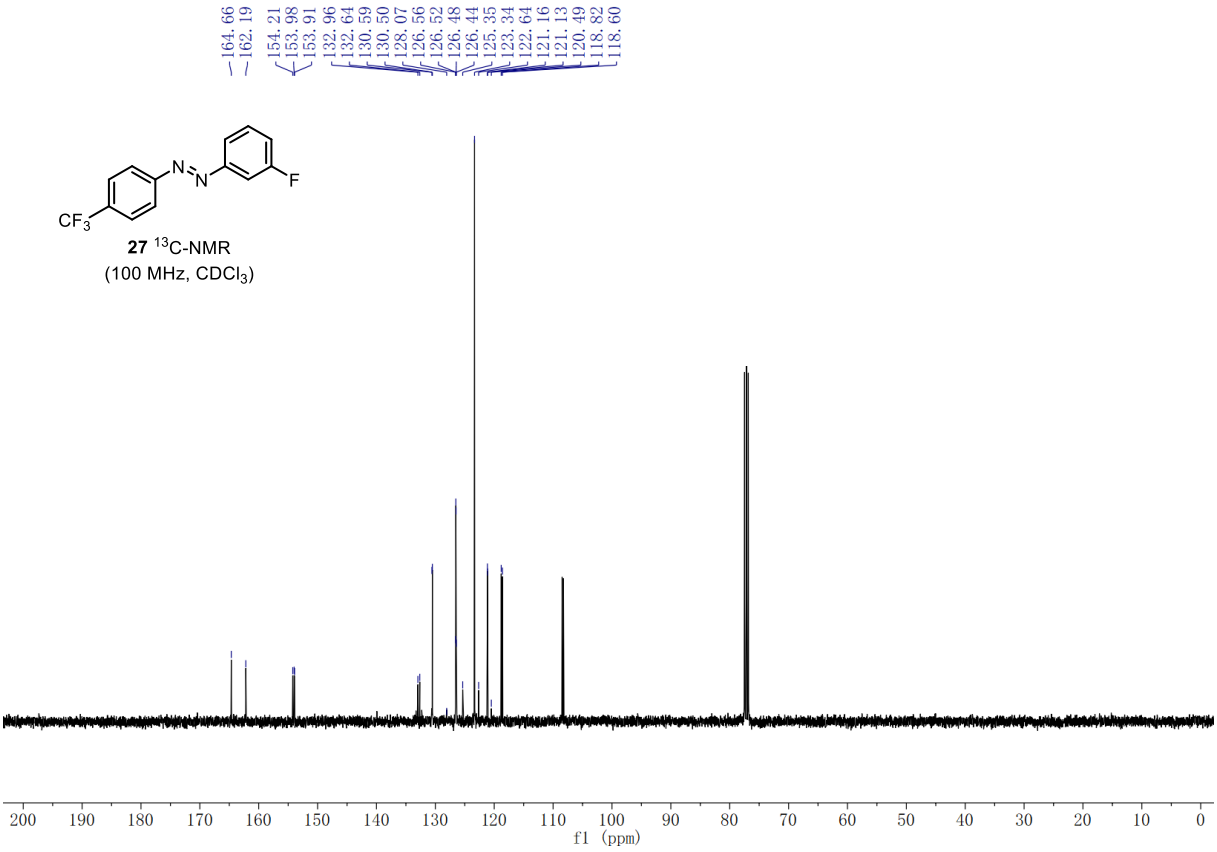


26 ^{19}F-NMR
(376 MHz, $CDCl_3$)

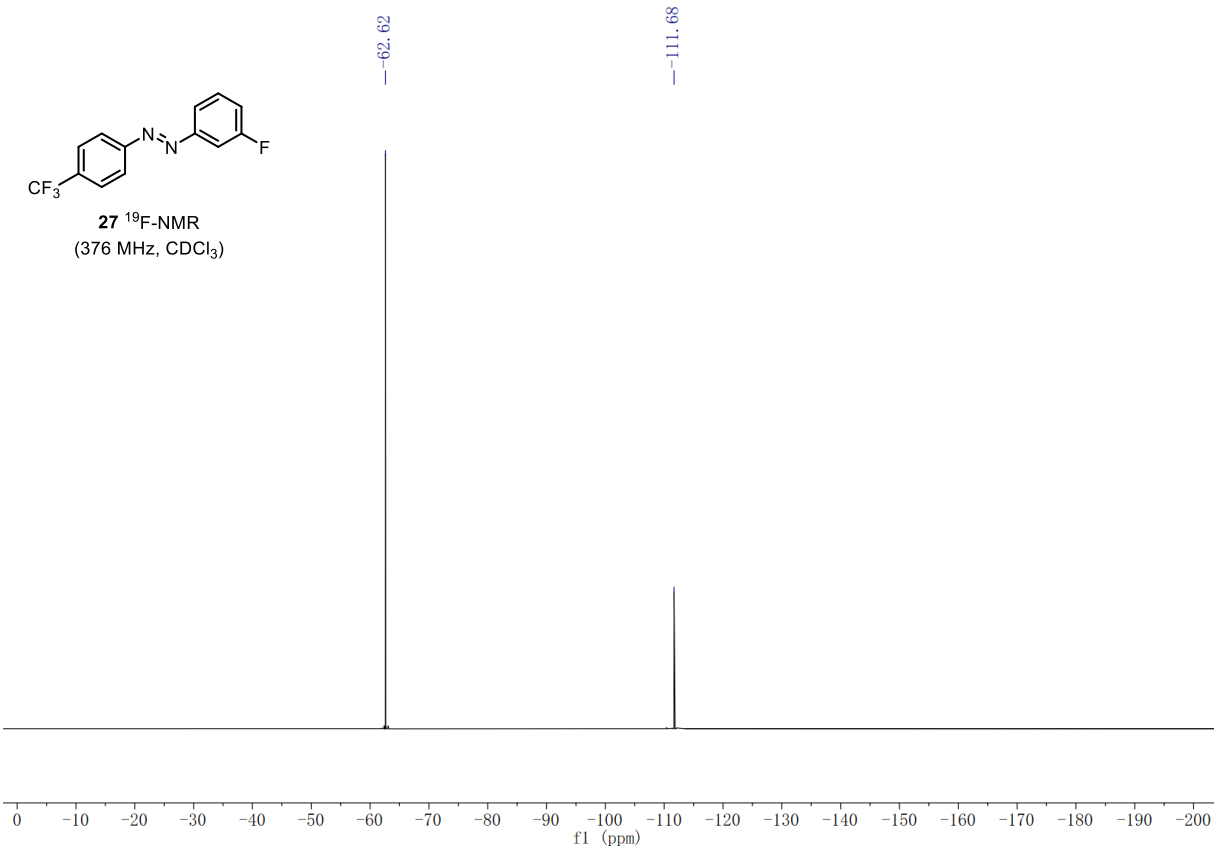


27 ^{1}H-NMR
(400 MHz, $CDCl_3$)

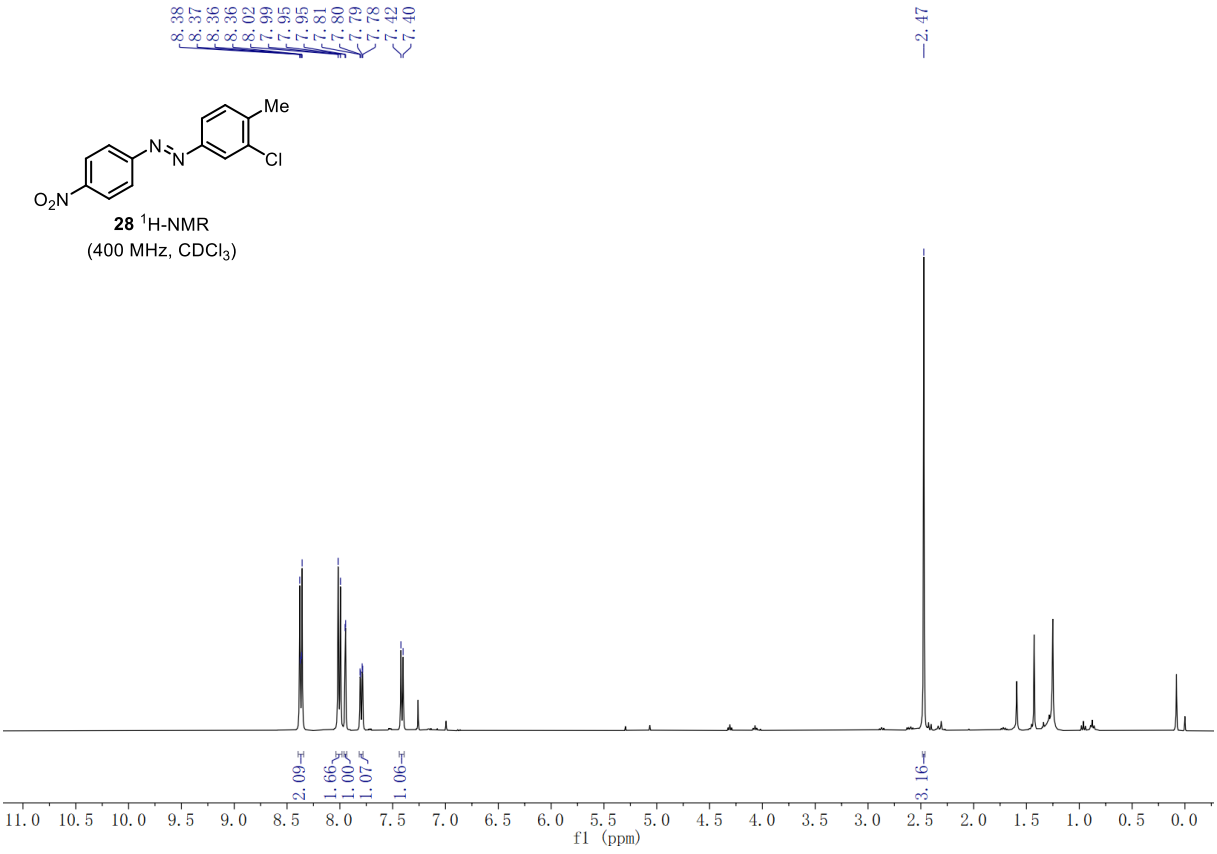




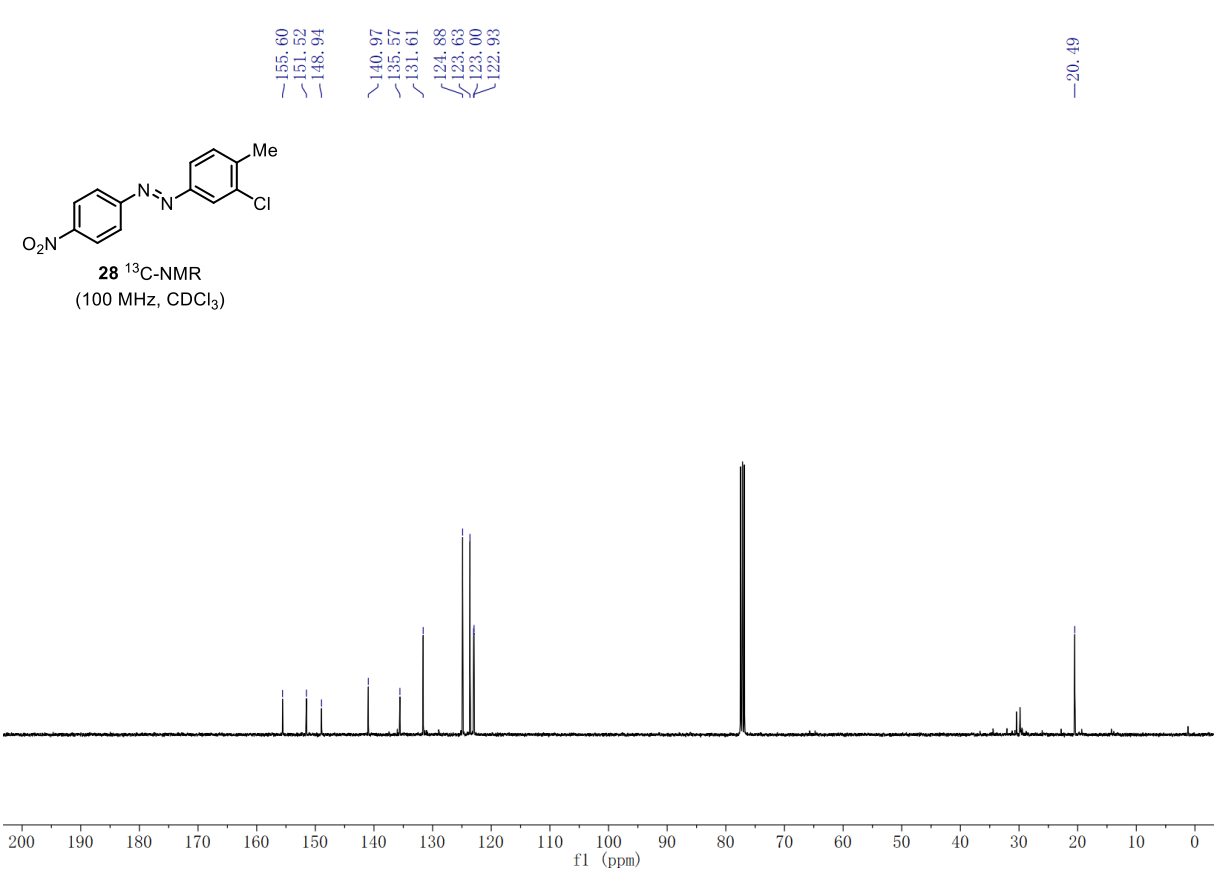
27 ^{13}C-NMR
(100 MHz, $CDCl_3$)



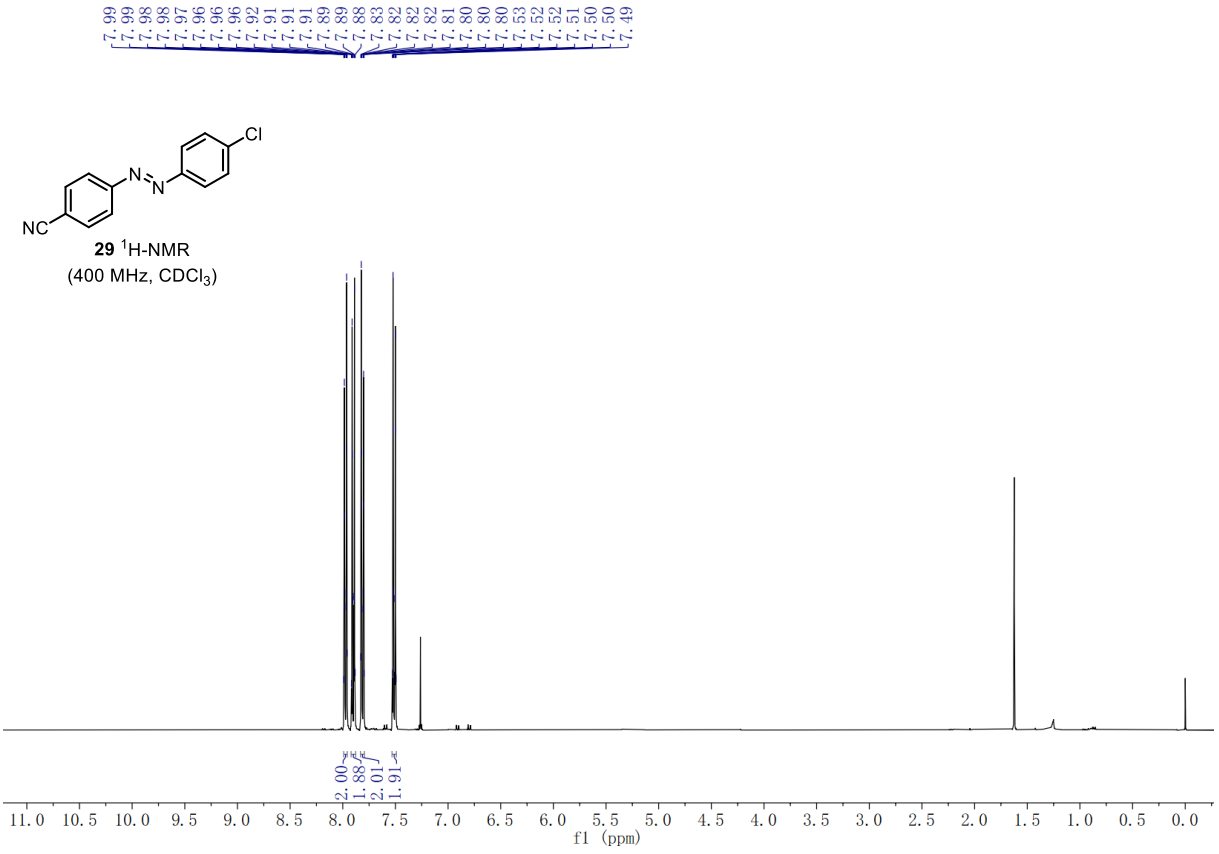
27 ^{19}F-NMR
(376 MHz, $CDCl_3$)

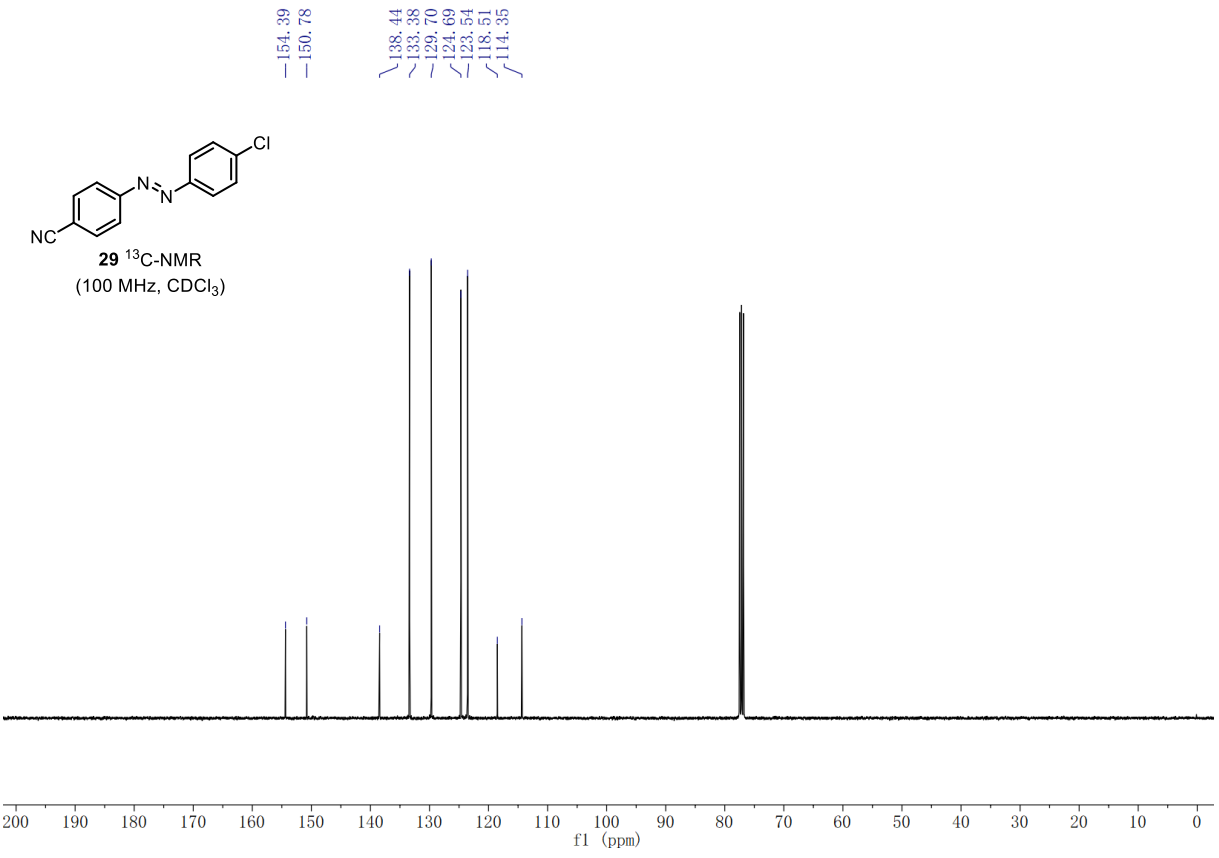


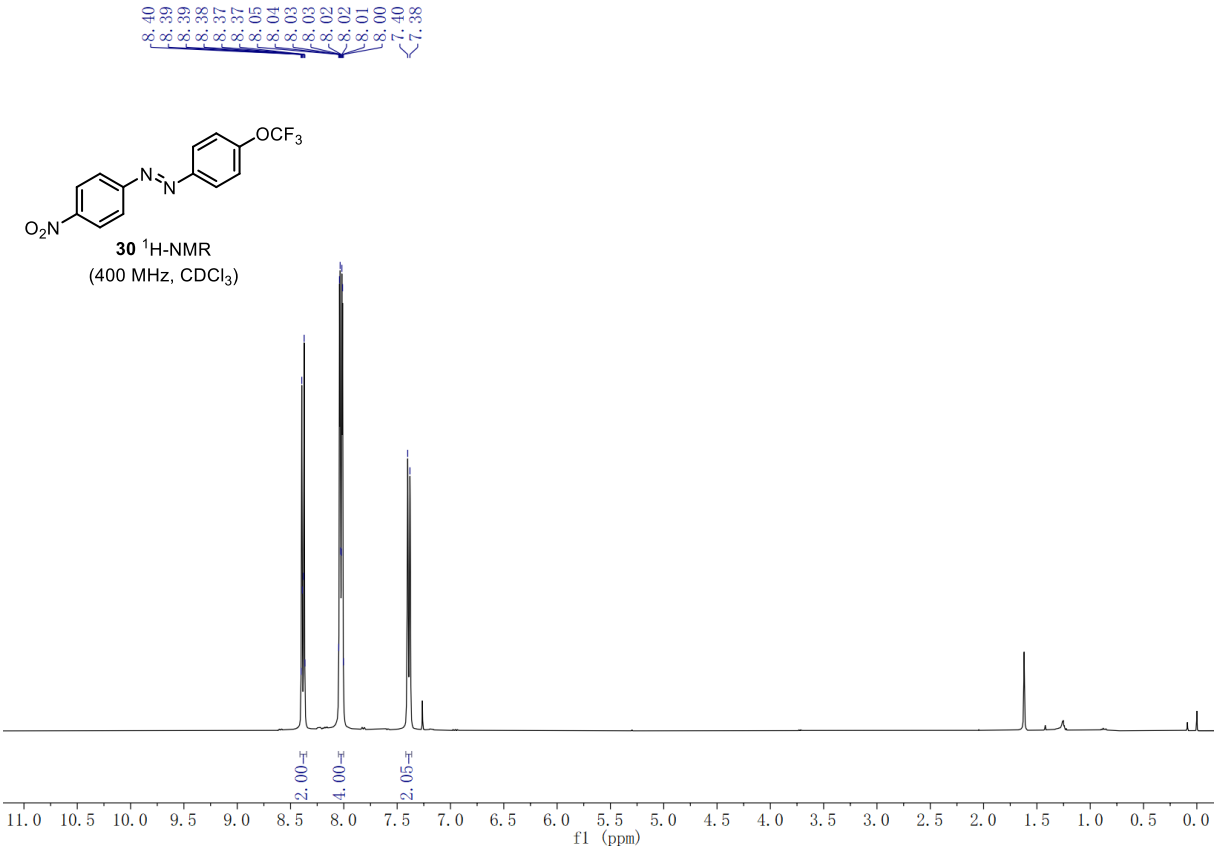
28 ^{1}H-NMR
(400 MHz, $CDCl_3$)

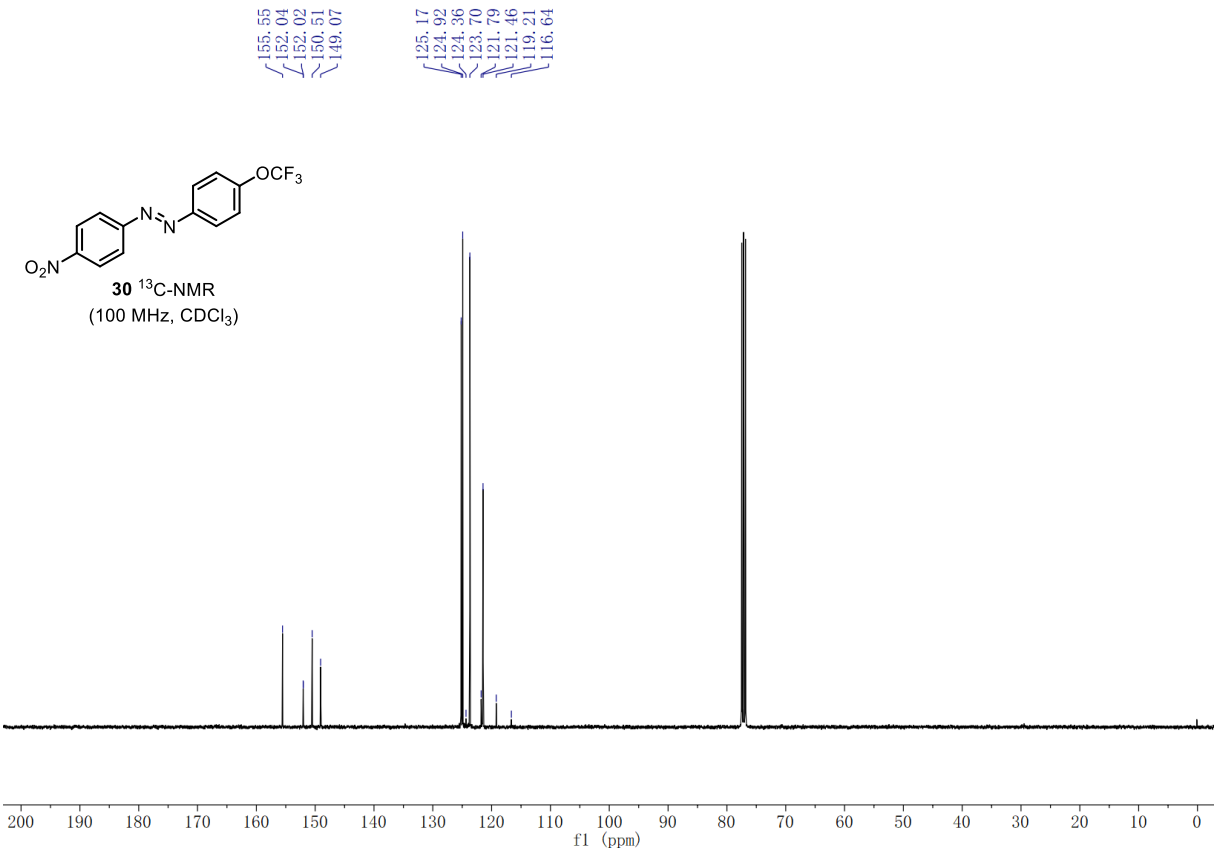


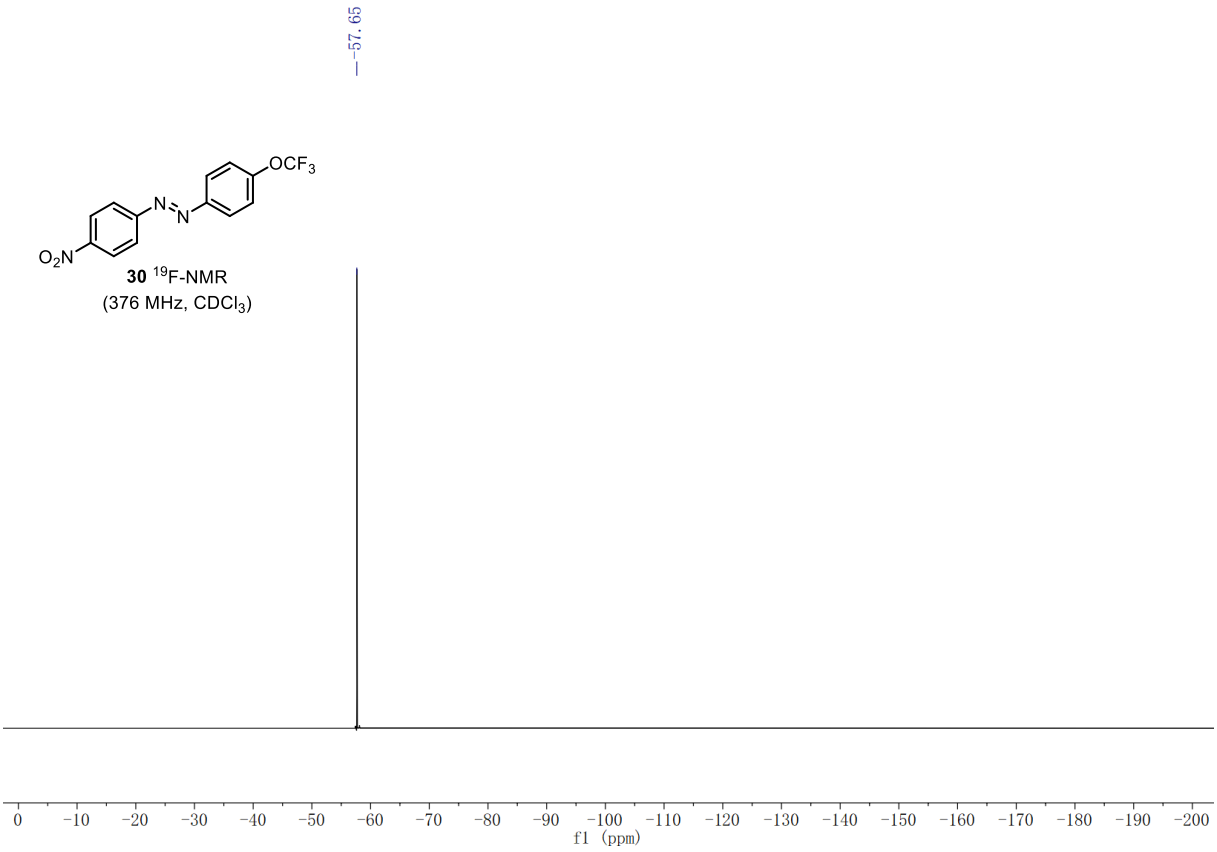
28 ^{13}C-NMR
(100 MHz, $CDCl_3$)


7.99
7.99
7.98
7.98
7.97
7.96
7.96
7.96
7.92
7.91
7.91
7.89
7.89
7.88
7.83
7.82
7.82
7.82
7.81
7.80
7.80
7.80
7.53
7.52
7.52
7.51
7.50
7.50
7.49
Cl
N
N
NC
29 1H-NMR
(400 MHz, CDCl3)
2.00
1.88
2.01
1.91
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

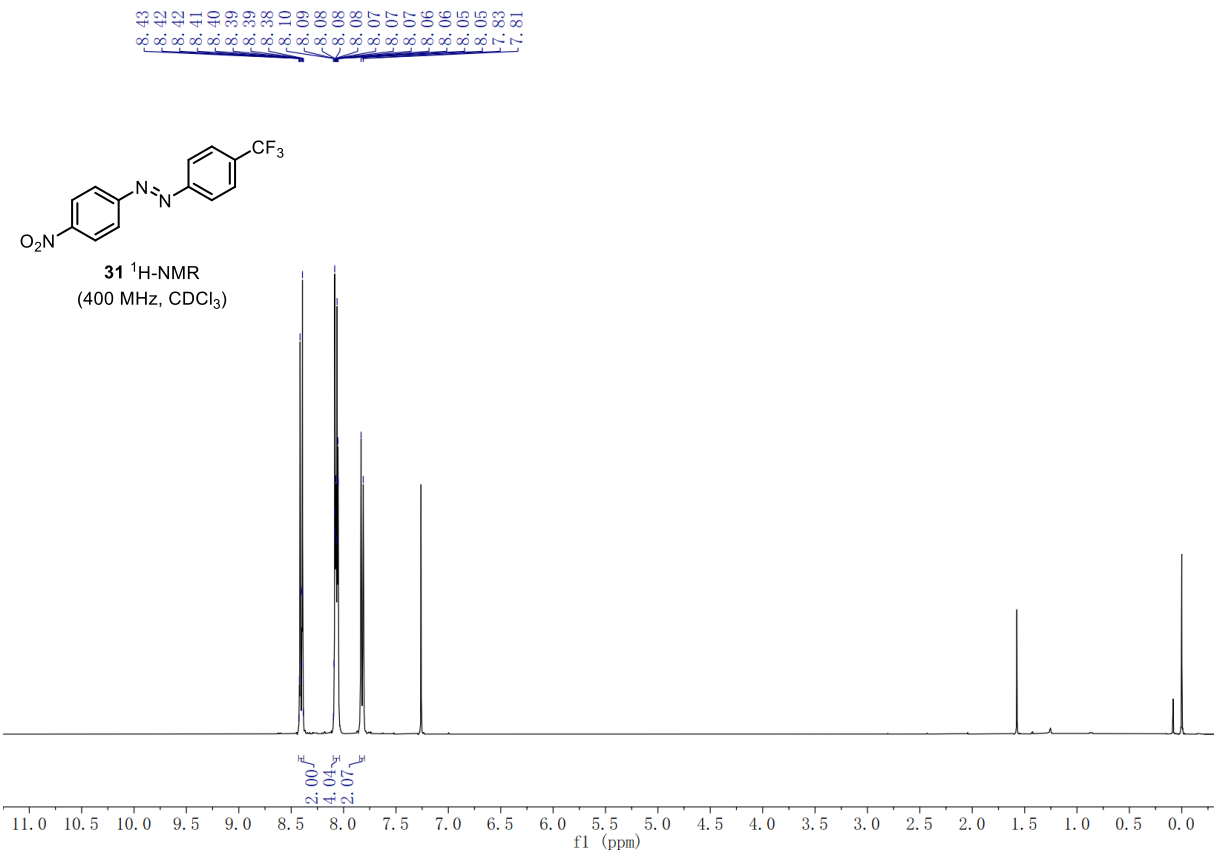

154.39
150.78
138.44
133.38
129.70
124.69
123.54
118.51
114.35
Cl
N
N
NC
29 13C-NMR
(100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.40
8.39
8.39
8.38
8.37
8.37
8.05
8.04
8.03
8.03
8.02
8.02
8.01
8.00
7.40
7.38
OCF3
N
N
O2N
30 1H-NMR
(400 MHz, CDCl3)
2.00
4.00
2.05
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

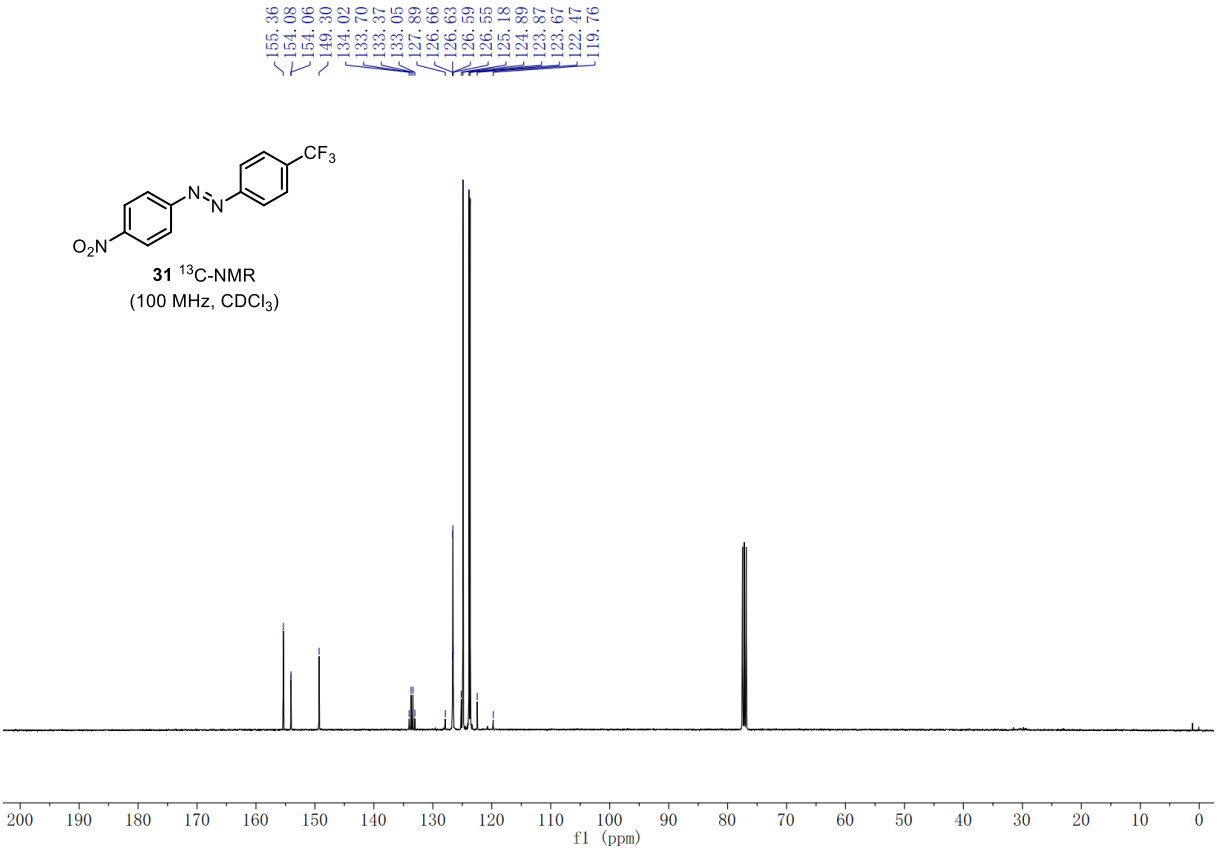

155.55
152.04
152.02
150.51
149.07
125.17
124.92
124.36
123.70
121.79
121.46
119.21
116.64
OCF3
N
N
O2N
30 13C-NMR
(100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



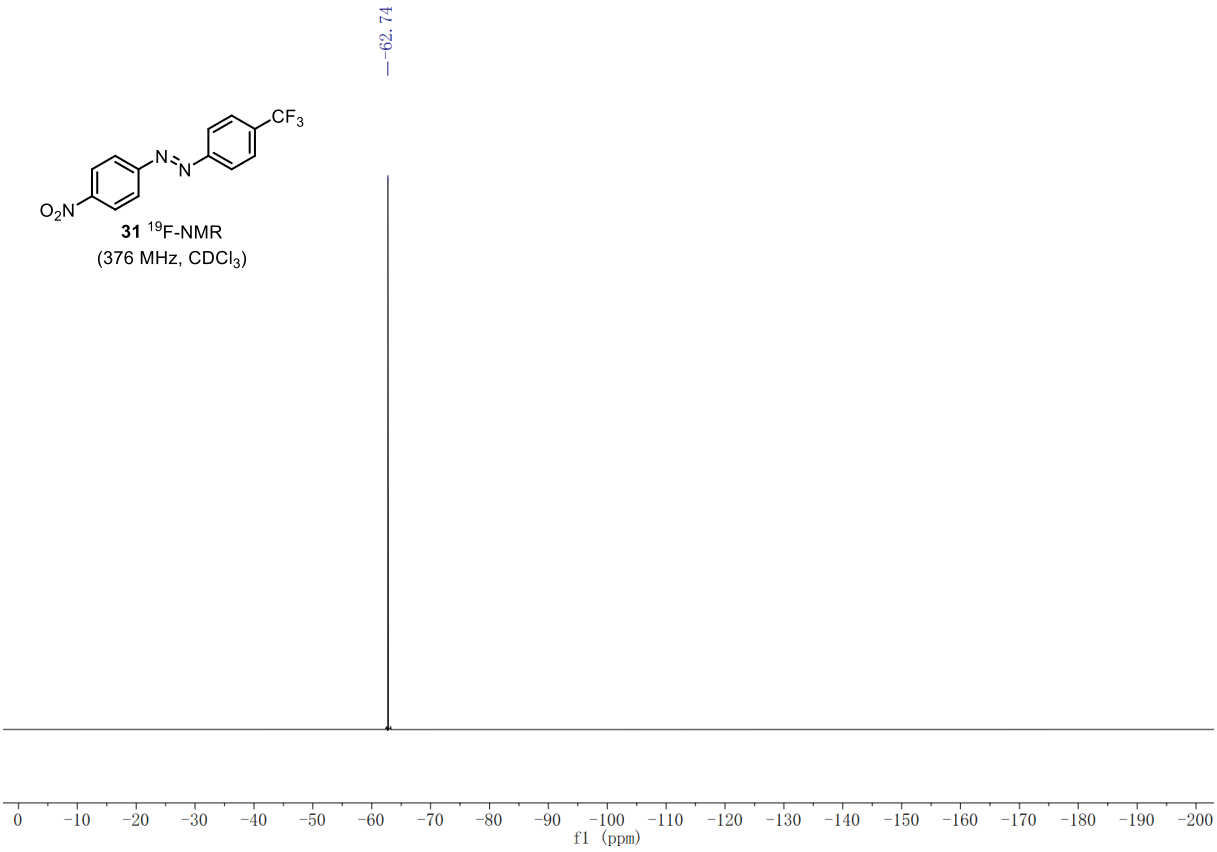
30 ^{19}F-NMR
(376 MHz, $CDCl_3$)



31 ^{1}H-NMR
(400 MHz, $CDCl_3$)

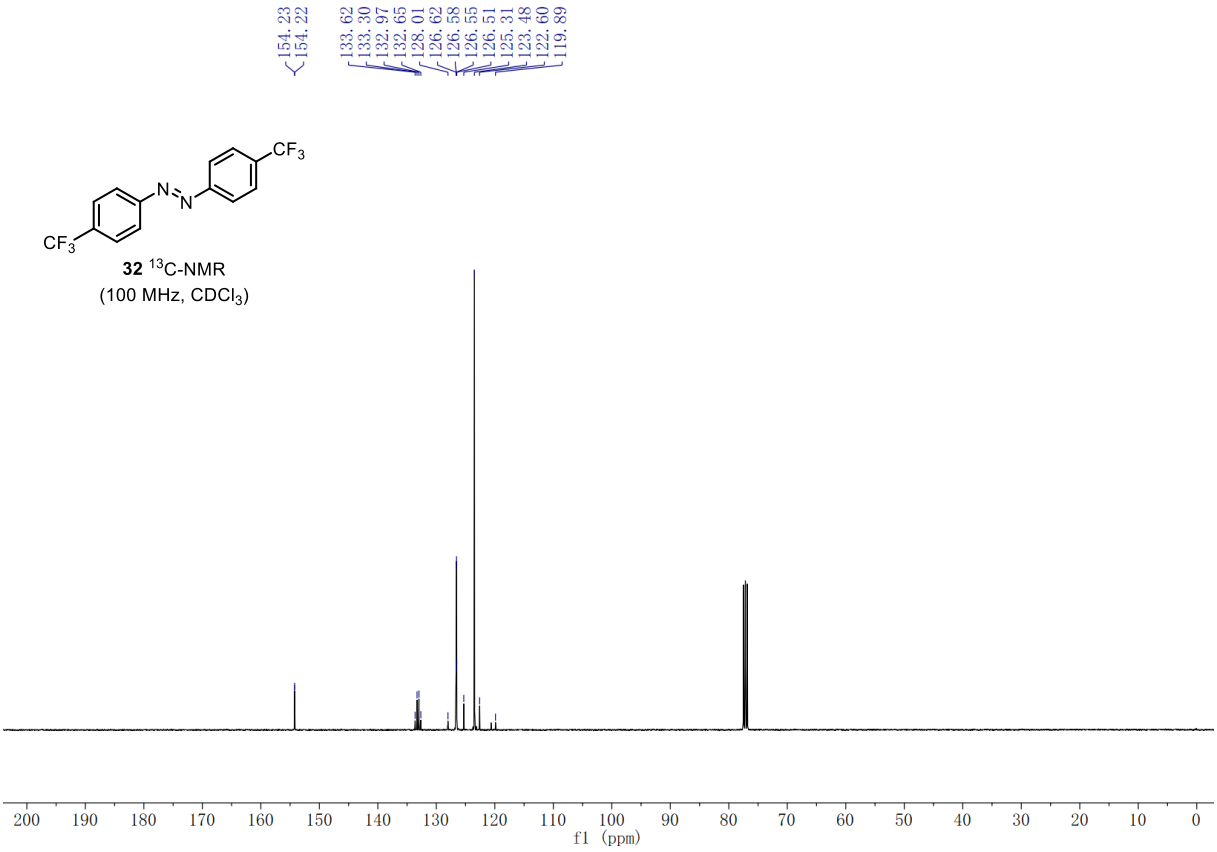


31 ^{13}C-NMR
(100 MHz, $CDCl_3$)

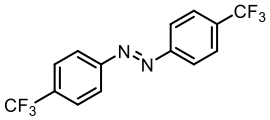


31 ^{19}F-NMR
(376 MHz, $CDCl_3$)

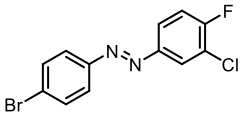
32 ^{1}H-NMR
(400 MHz, $CDCl_3$)



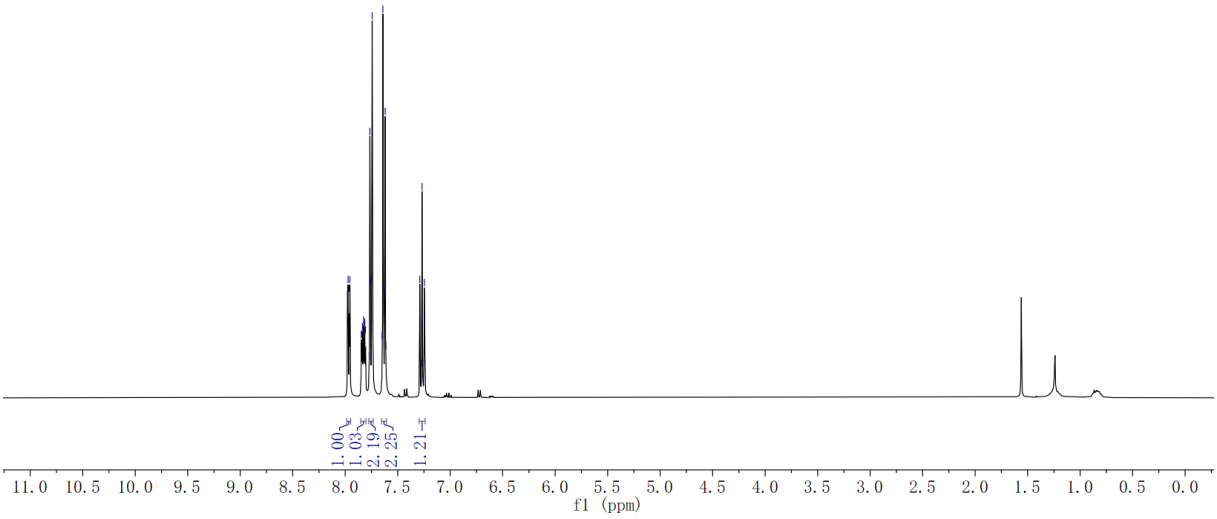
32 ^{13}C-NMR
(100 MHz, $CDCl_3$)

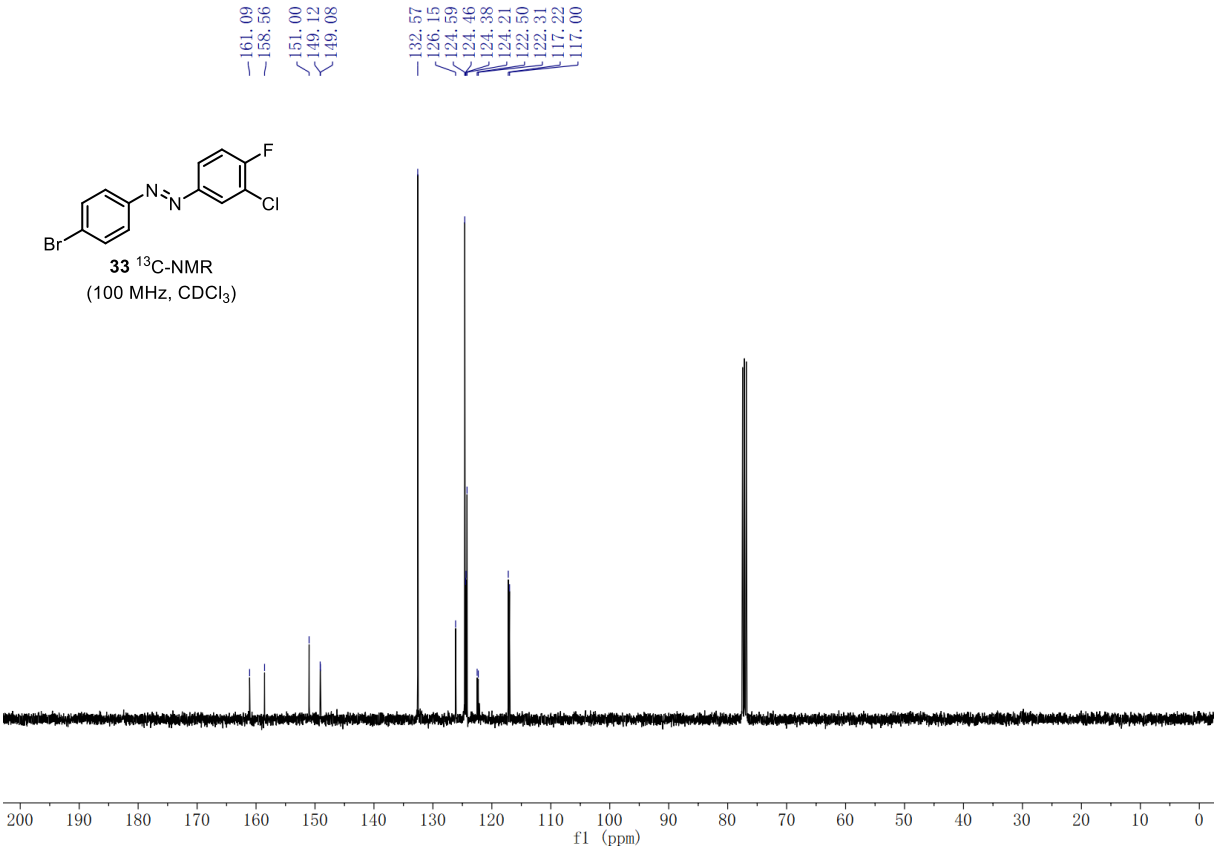


32 ^{19}F-NMR
(376 MHz, $CDCl_3$)

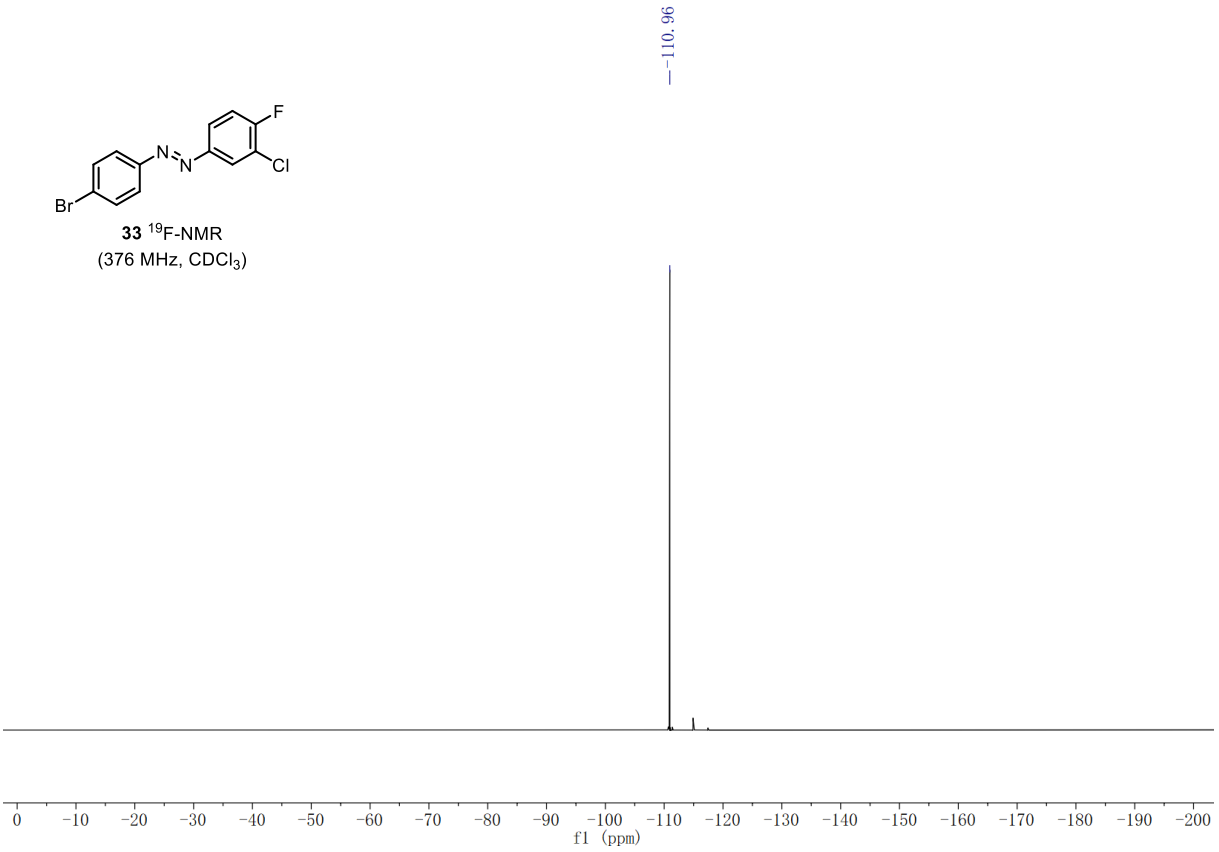


33 ^{1}H-NMR
(400 MHz, $CDCl_3$)

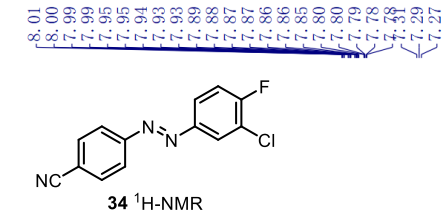




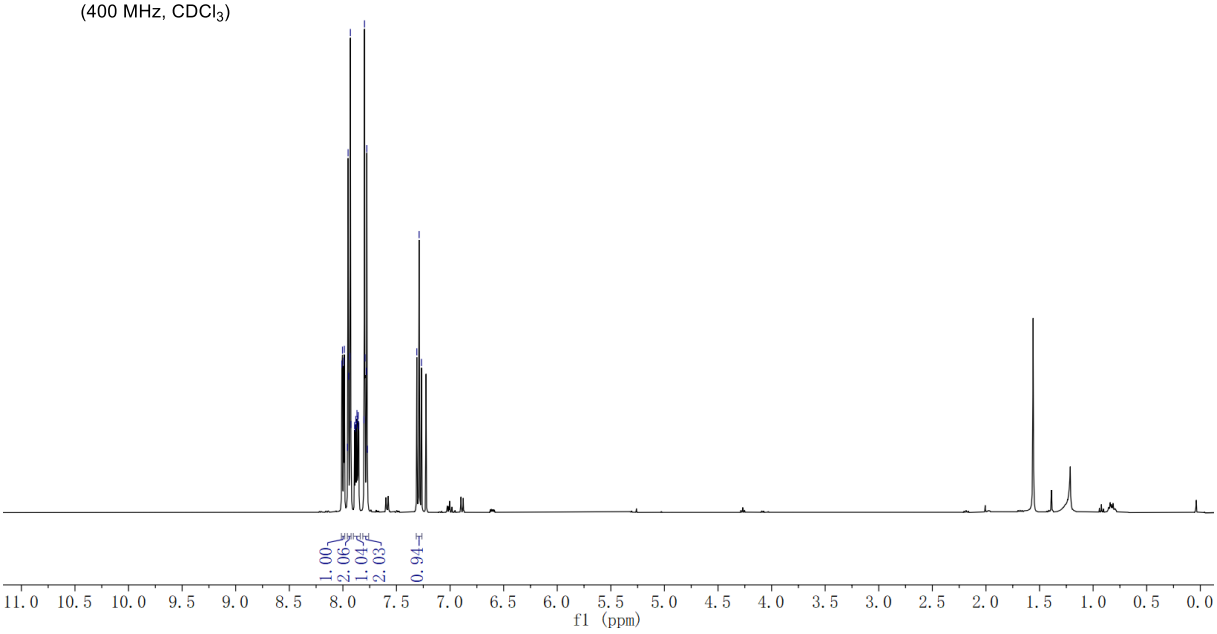
33 ^{13}C-NMR
(100 MHz, $CDCl_3$)

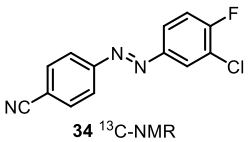


33 ^{19}F-NMR
(376 MHz, $CDCl_3$)

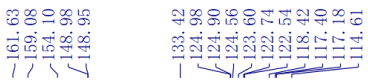


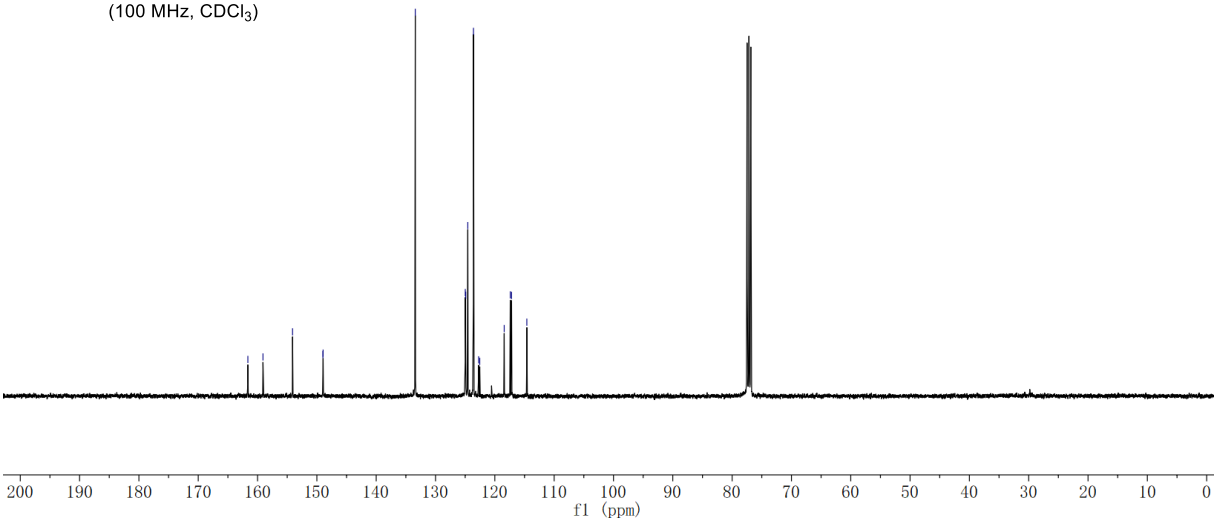
34 ^{1}H-NMR
(400 MHz, $CDCl_3$)

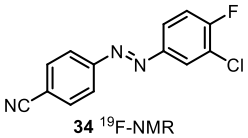




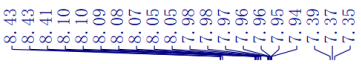
34 ^{13}C-NMR
(100 MHz, $CDCl_3$)

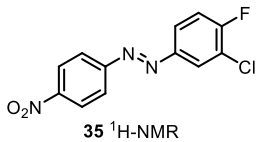




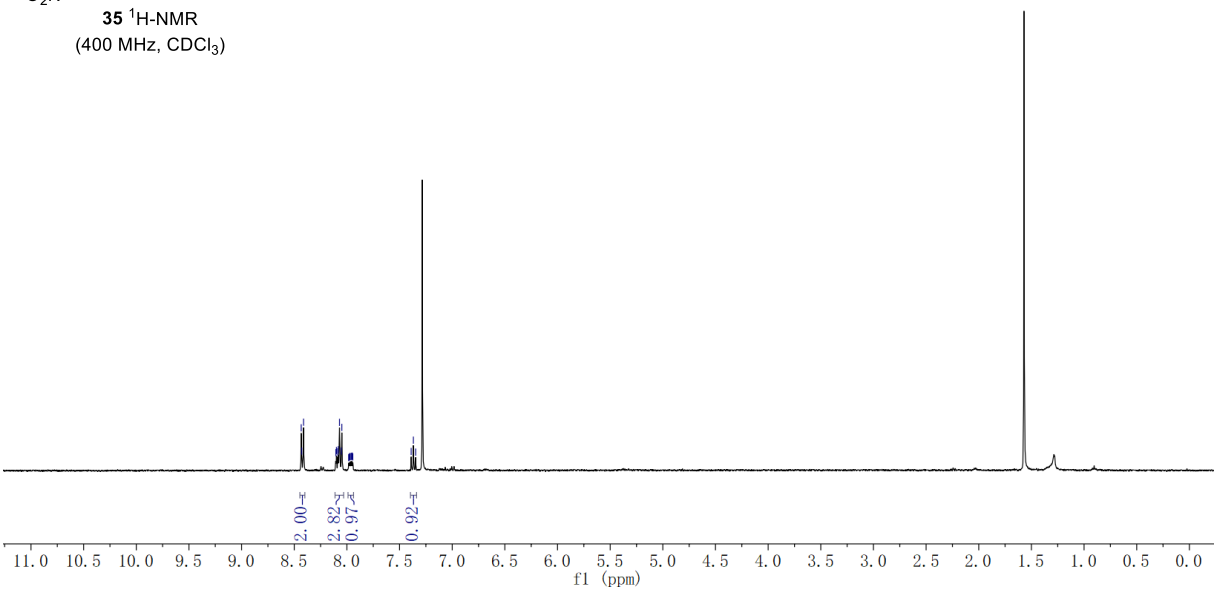


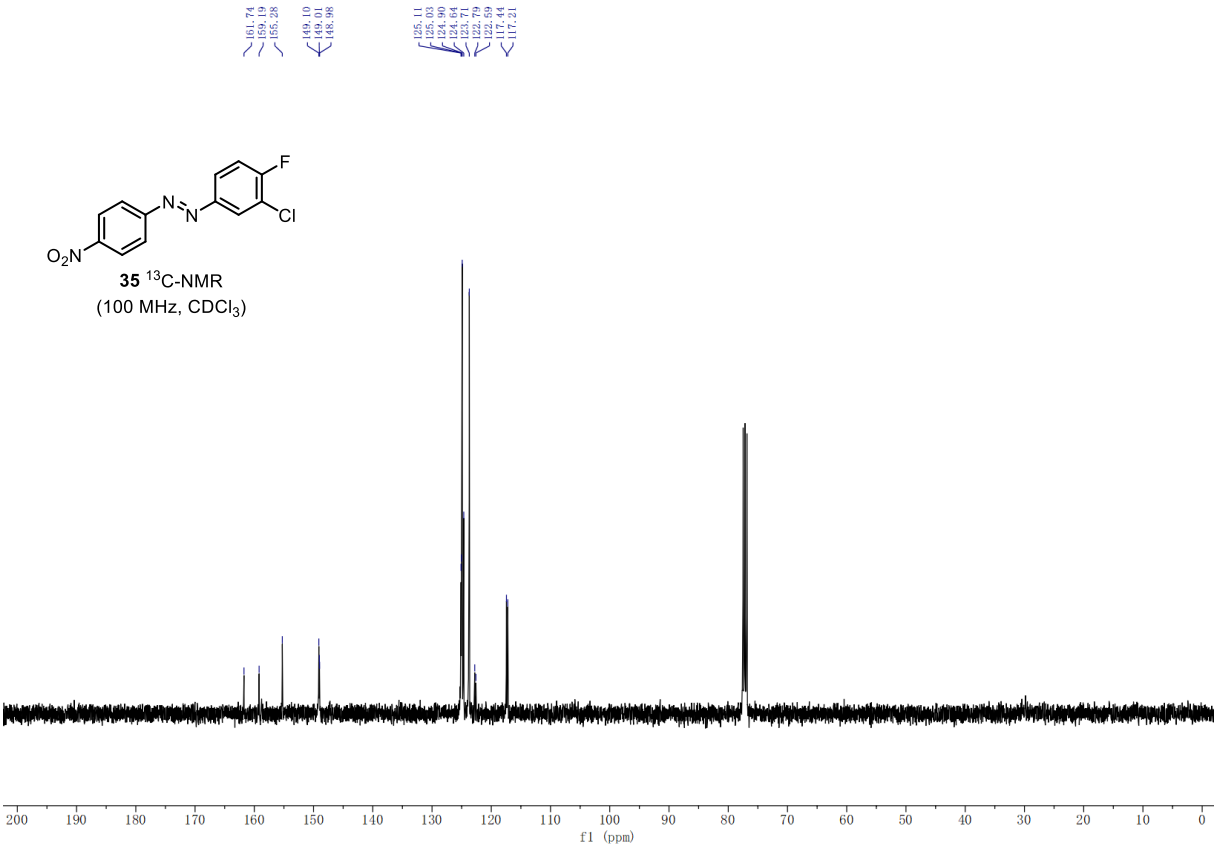
34 ^{19}F-NMR
(376 MHz, $CDCl_3$)



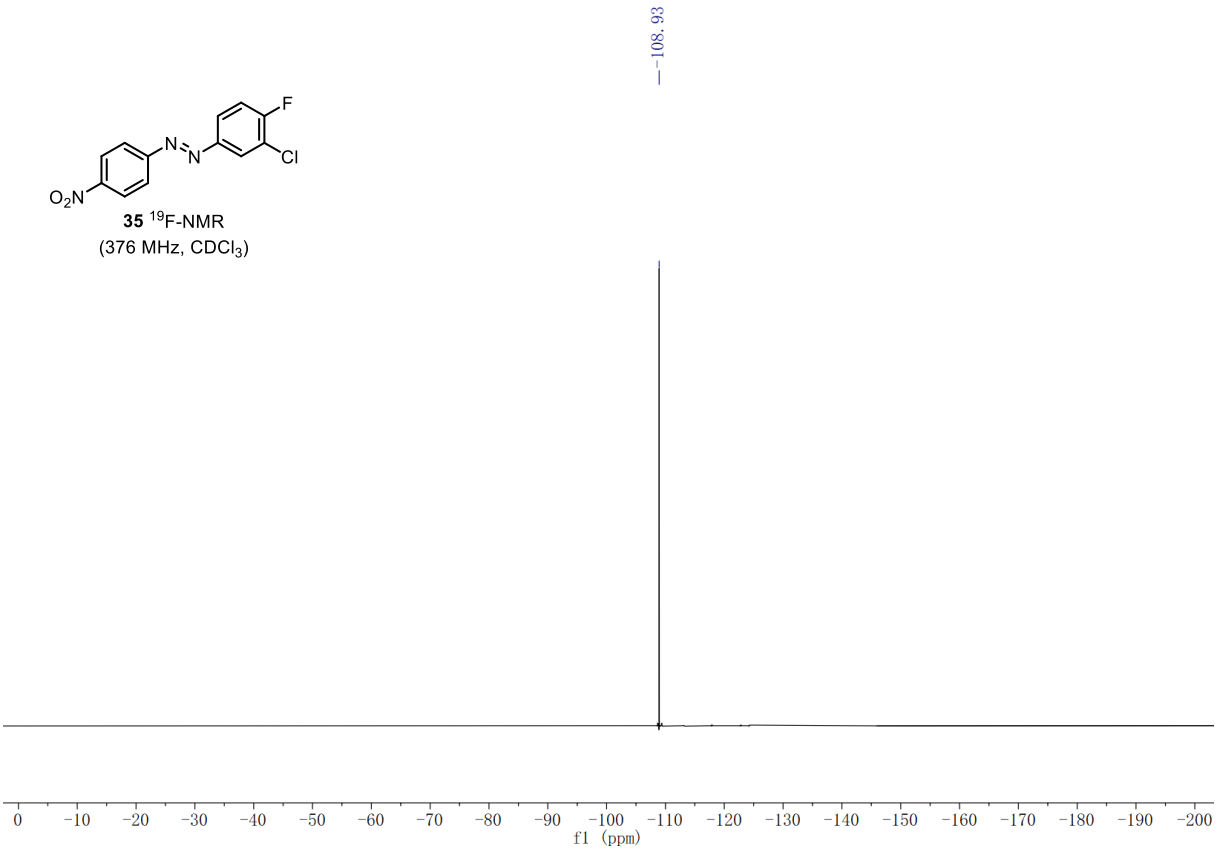


35 ^{1}H-NMR
(400 MHz, $CDCl_3$)

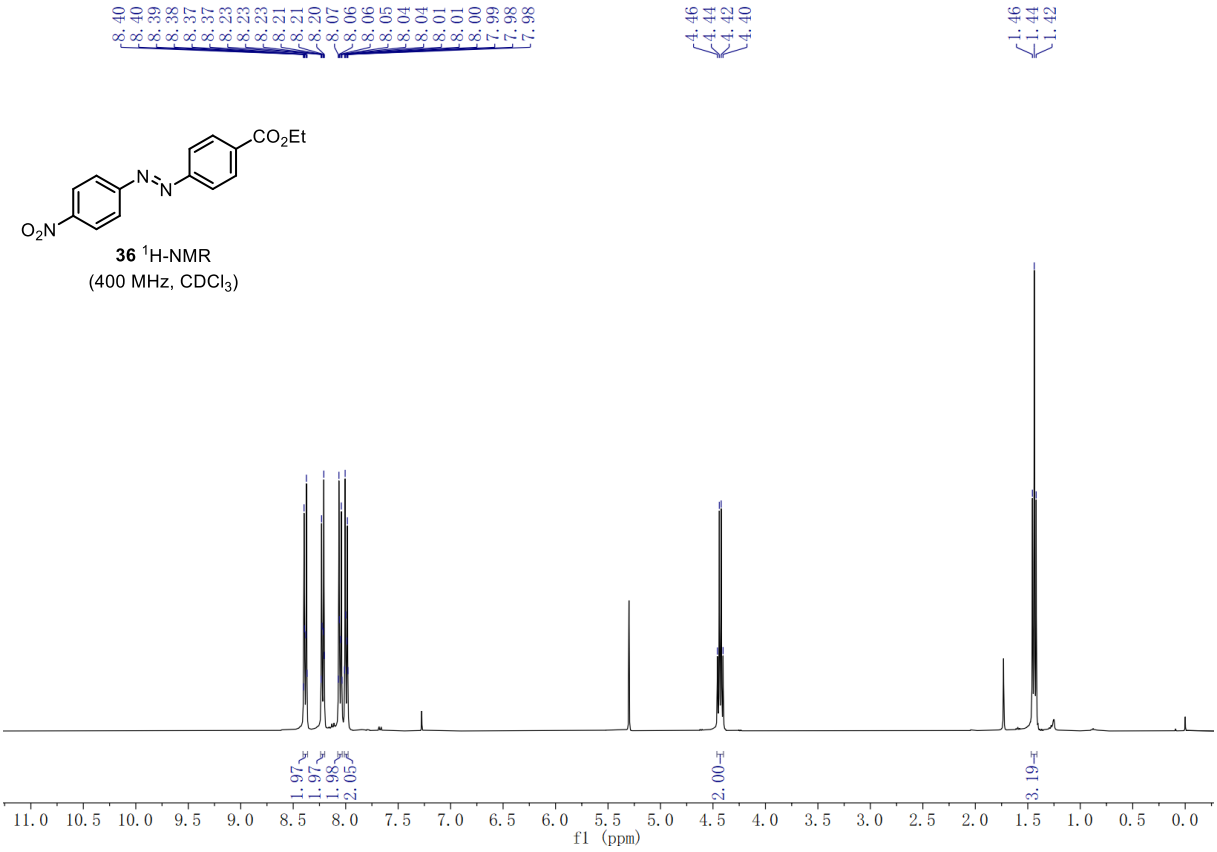




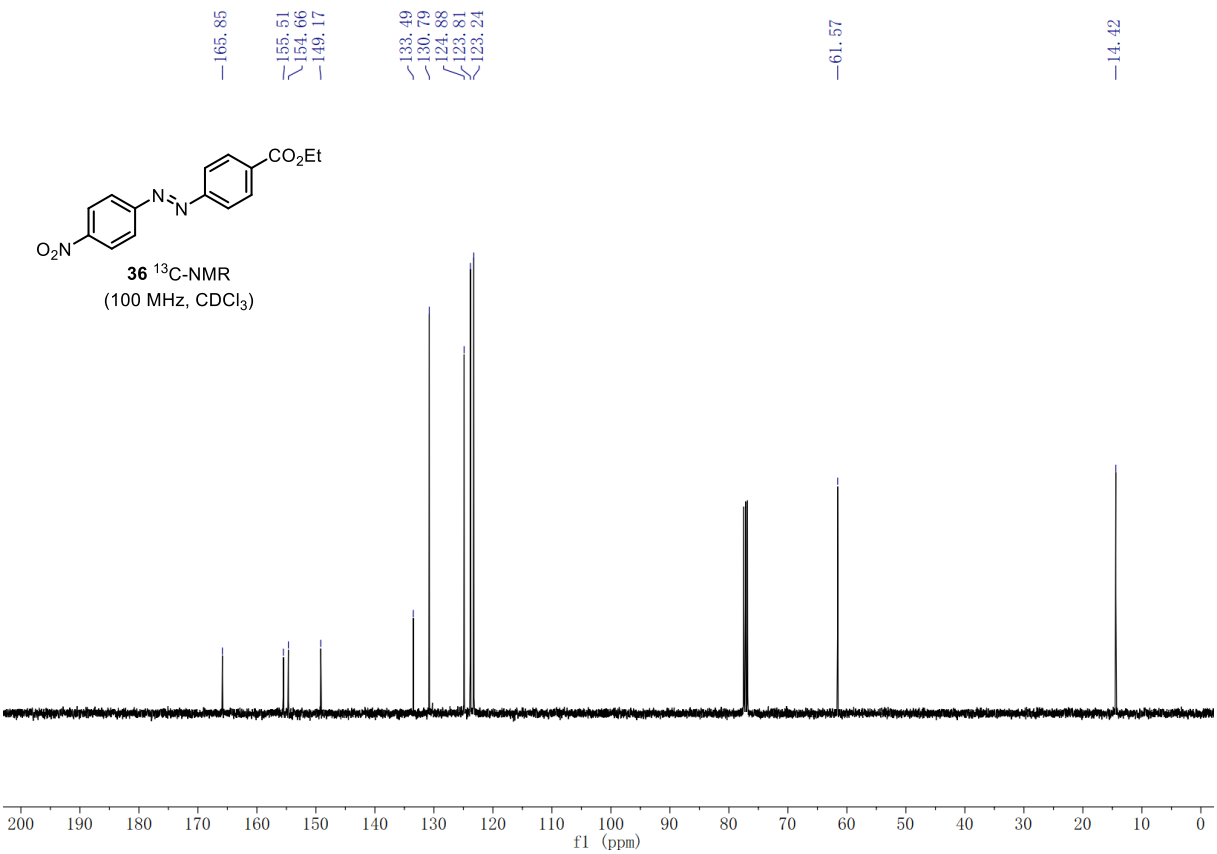
35 ^{13}C-NMR
(100 MHz, $CDCl_3$)



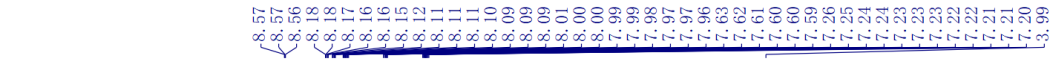
35 ^{19}F-NMR
(376 MHz, $CDCl_3$)

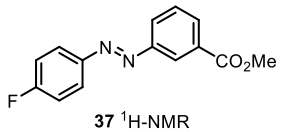


36 ^{1}H-NMR
(400 MHz, $CDCl_3$)

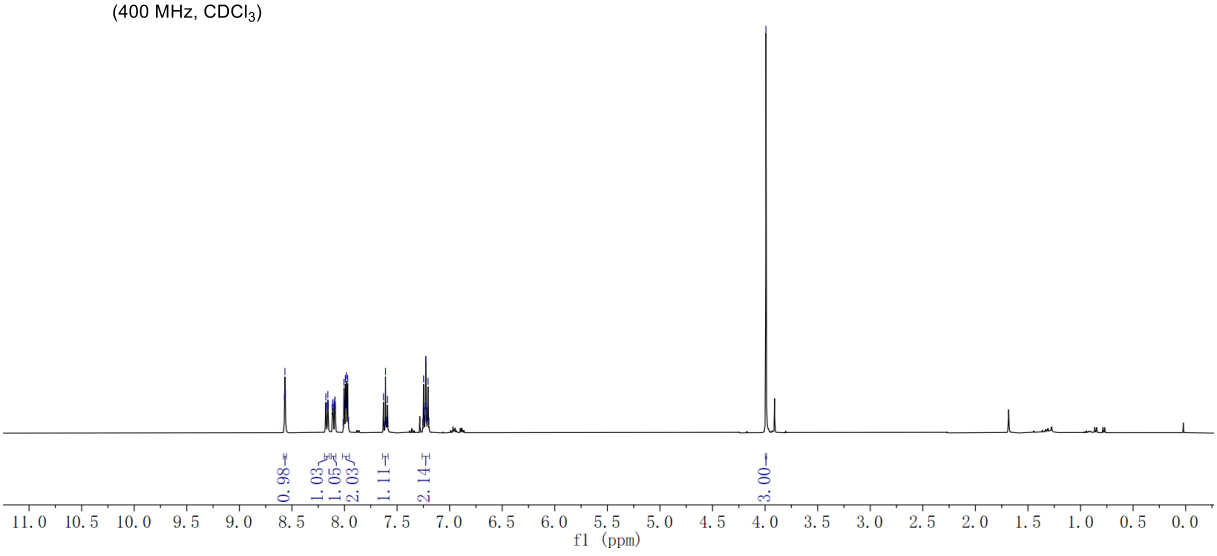


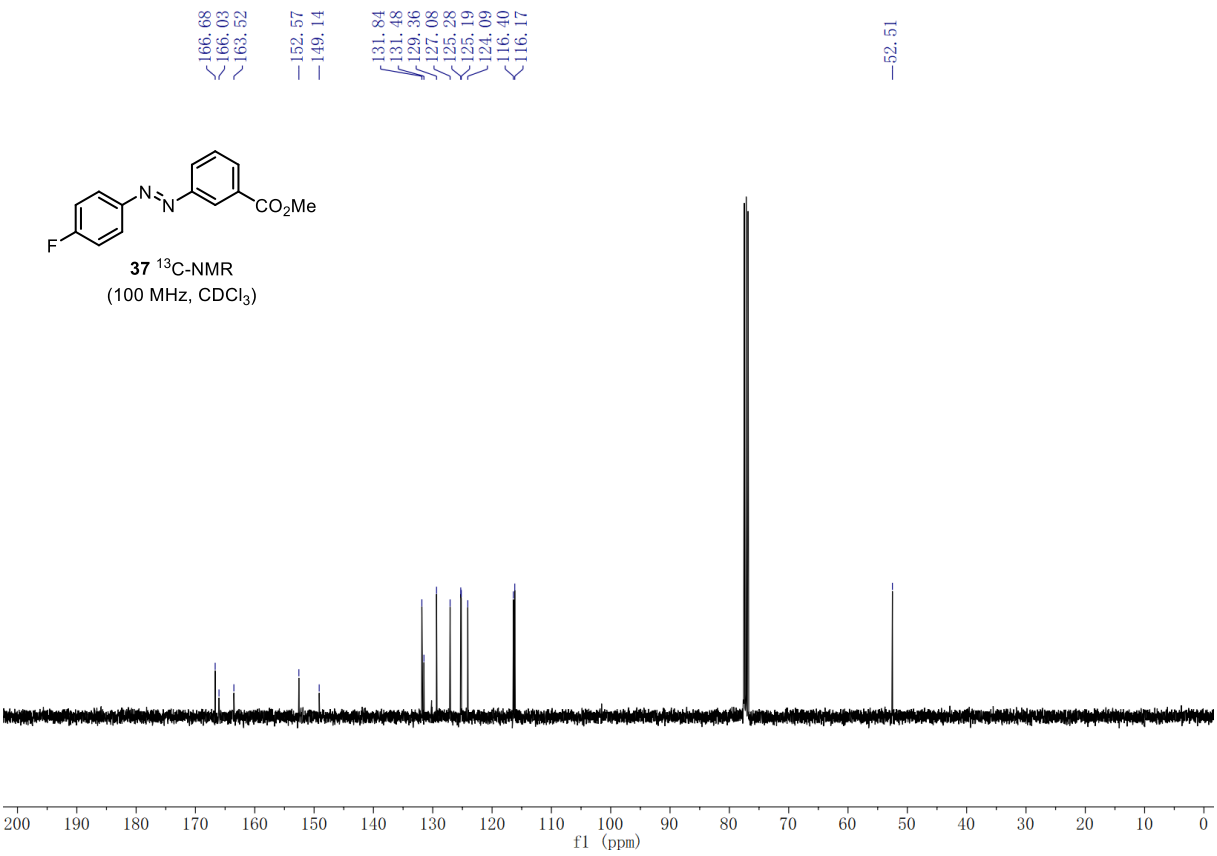
36 ^{13}C-NMR
(100 MHz, $CDCl_3$)



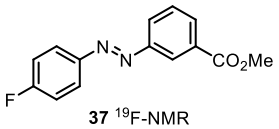


37 ^{1}H-NMR
(400 MHz, $CDCl_3$)

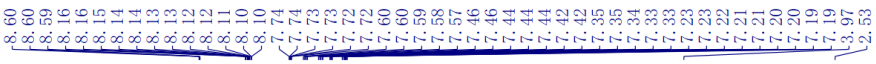


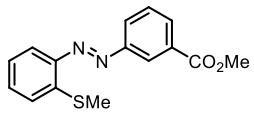


37 ^{13}C-NMR
(100 MHz, $CDCl_3$)

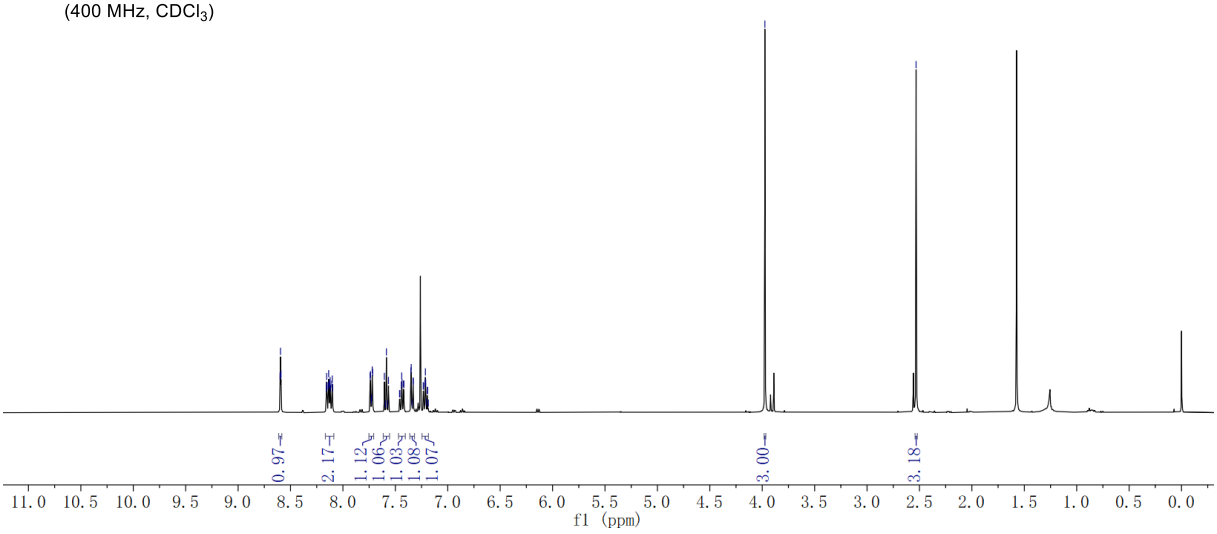


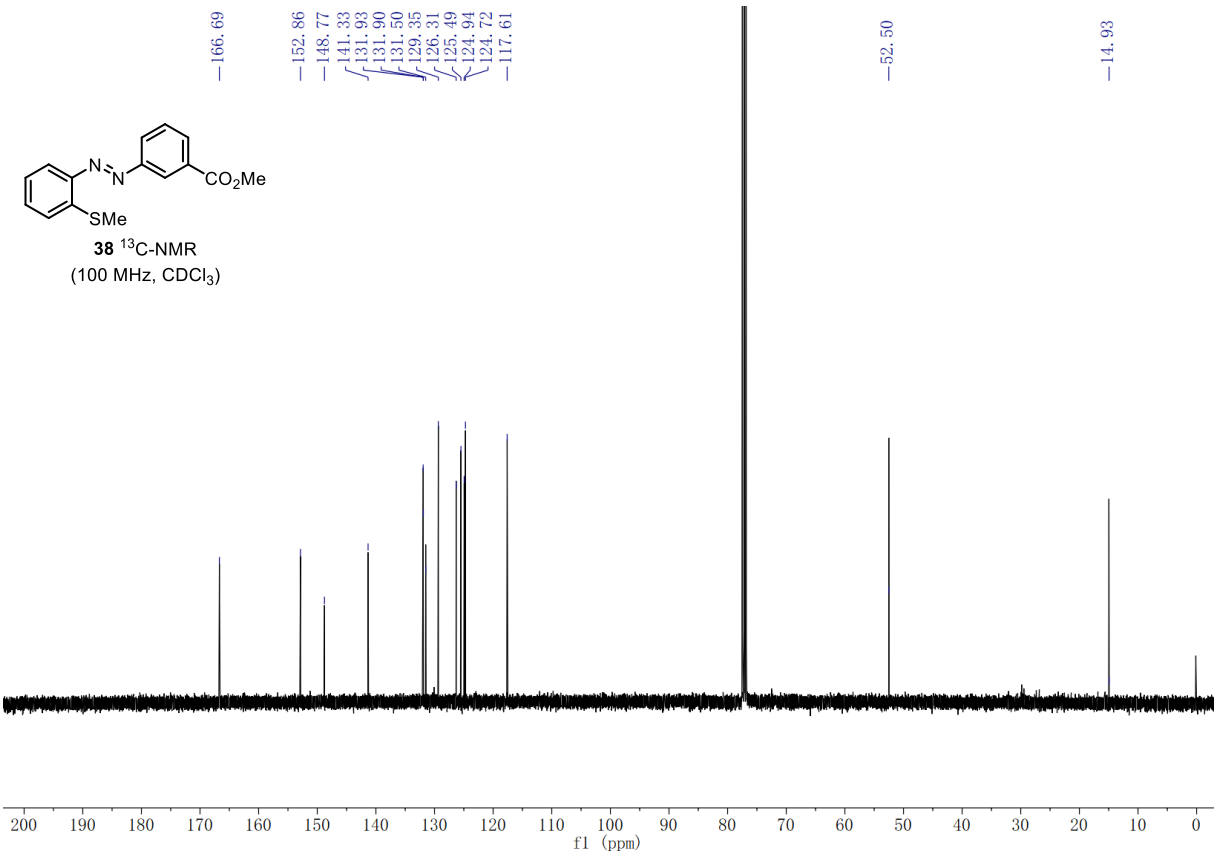
37 ^{19}F-NMR
(376 MHz, $CDCl_3$)



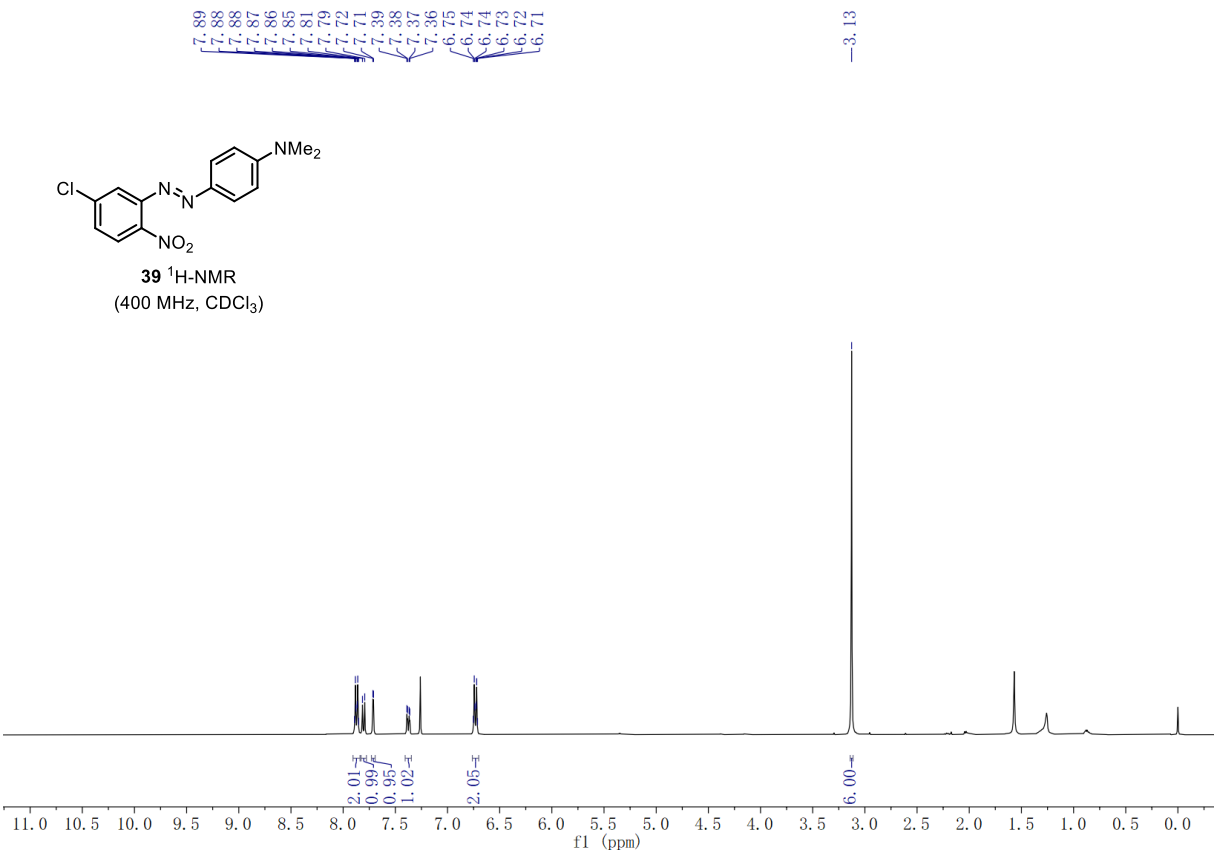


38 ^{1}H-NMR
(400 MHz, $CDCl_3$)

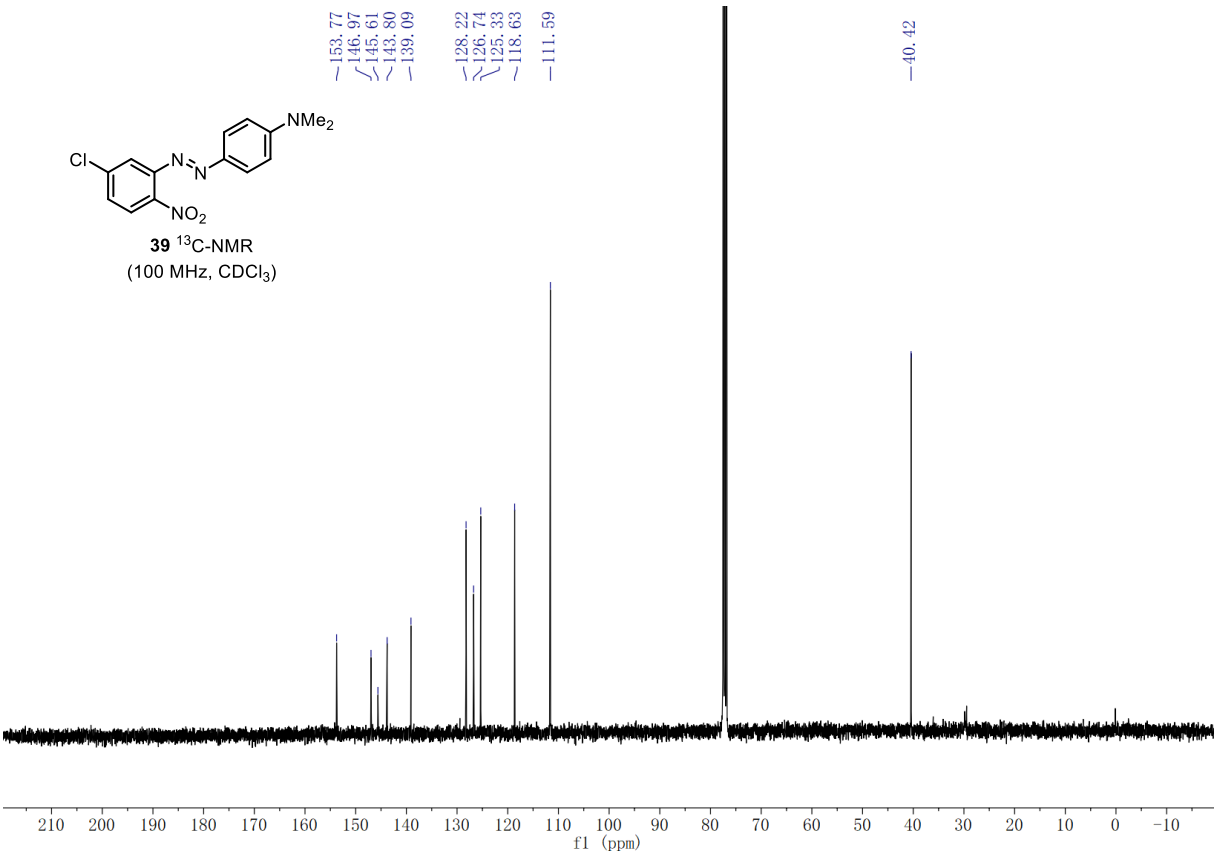




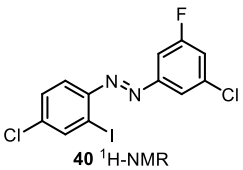
38 ^{13}C-NMR
(100 MHz, $CDCl_3$)



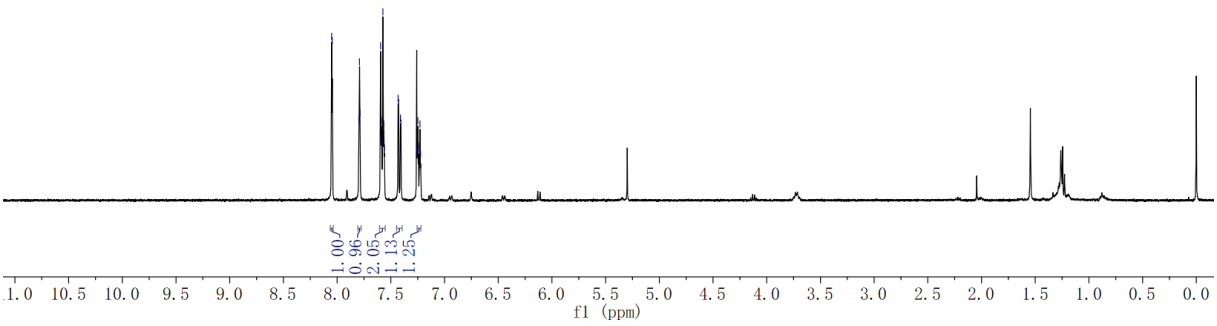
39 ^{1}H-NMR
(400 MHz, $CDCl_3$)

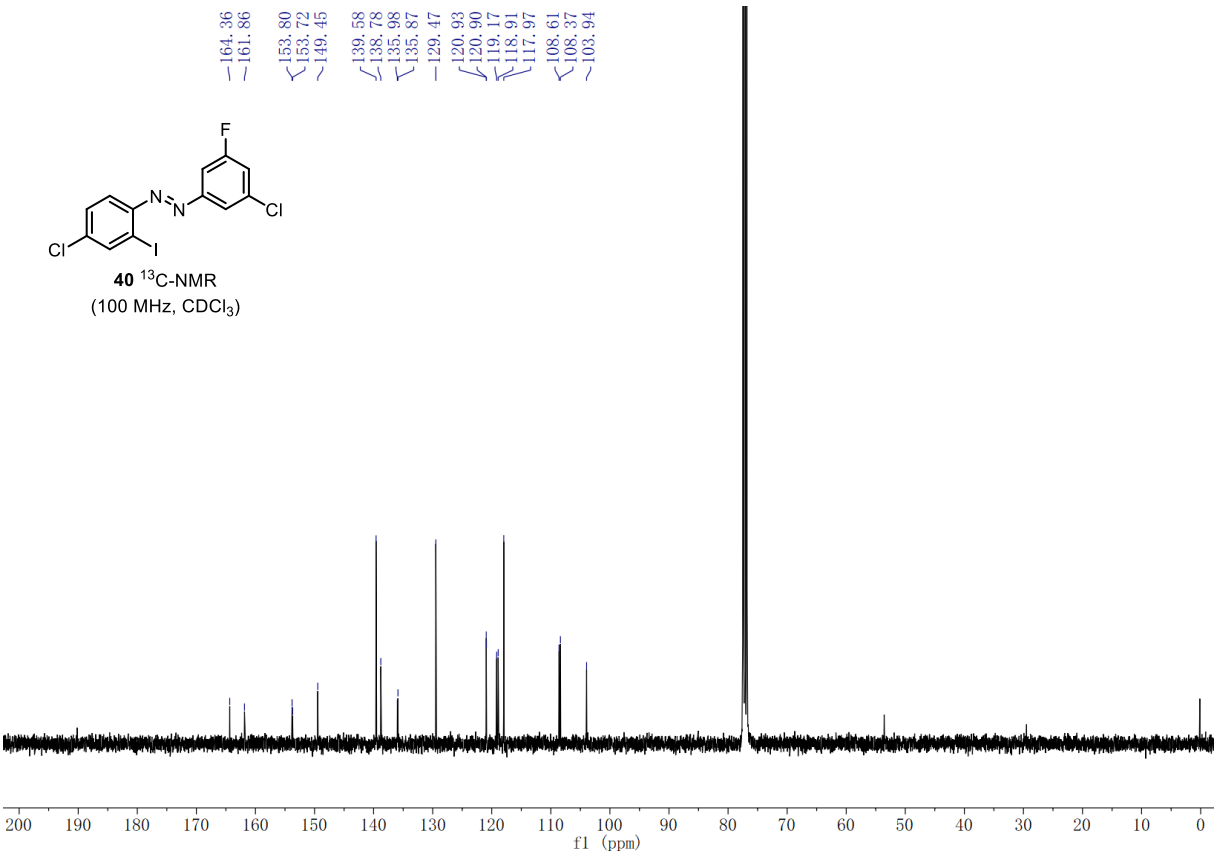


39 ^{13}C-NMR
(100 MHz, $CDCl_3$)

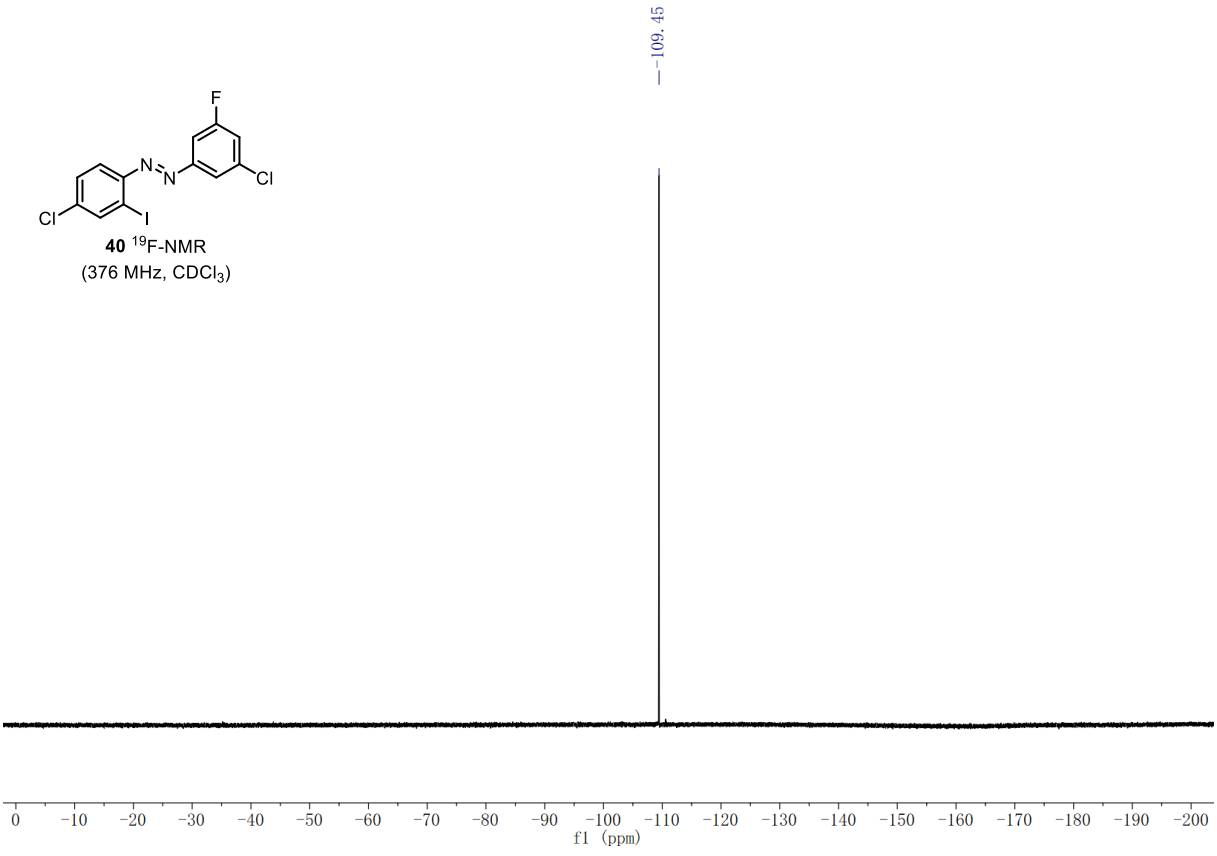


40 ^{1}H-NMR
(400 MHz, $CDCl_3$)

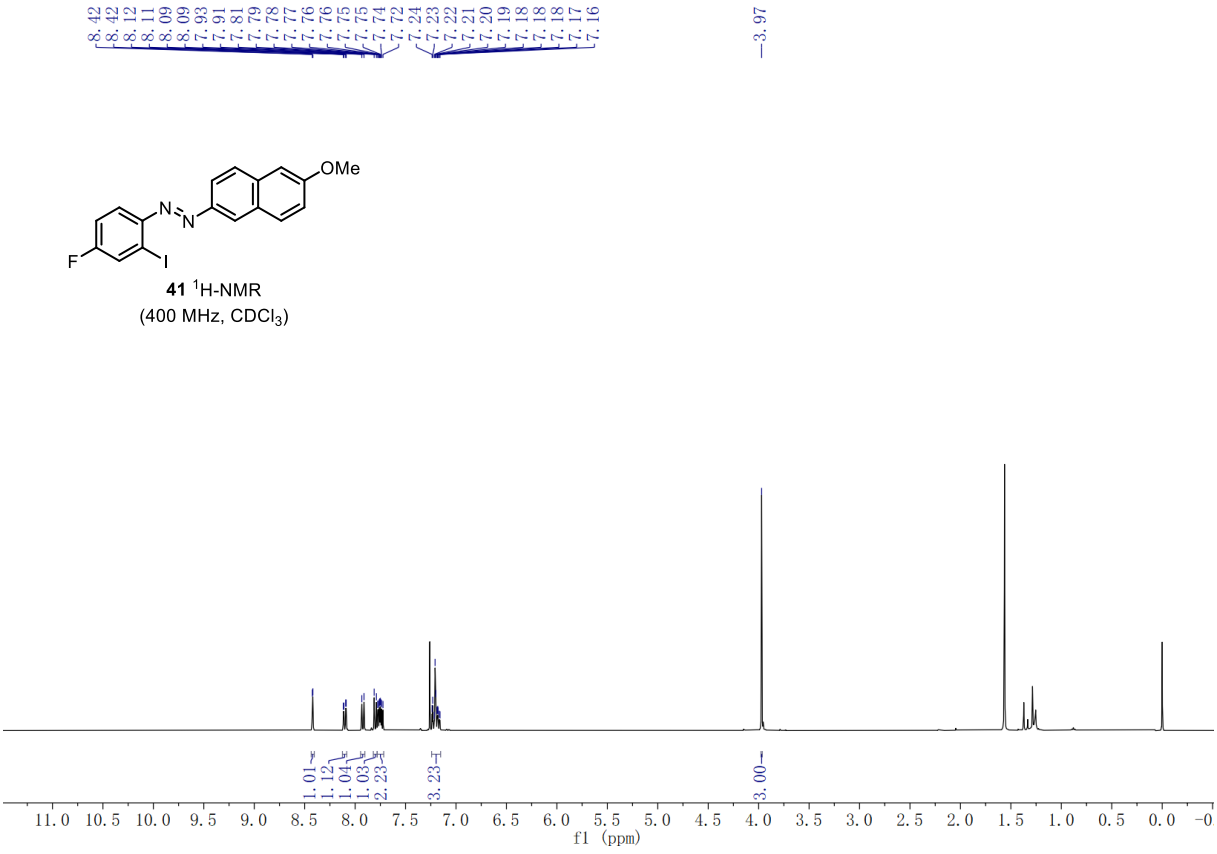




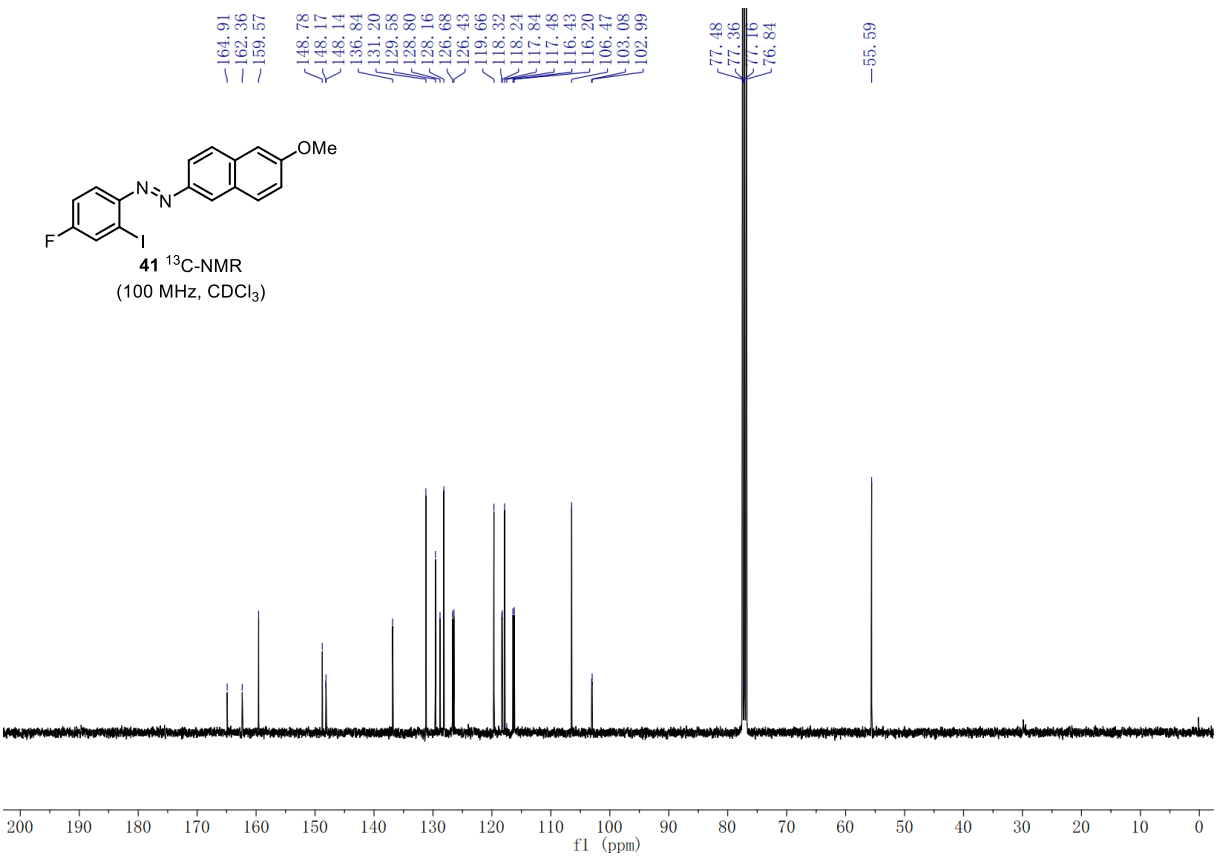
40 ^{13}C-NMR
(100 MHz, $CDCl_3$)



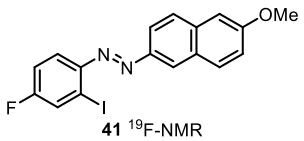
40 ^{19}F-NMR
(376 MHz, $CDCl_3$)



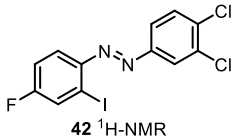
41 ^{1}H-NMR
(400 MHz, $CDCl_3$)



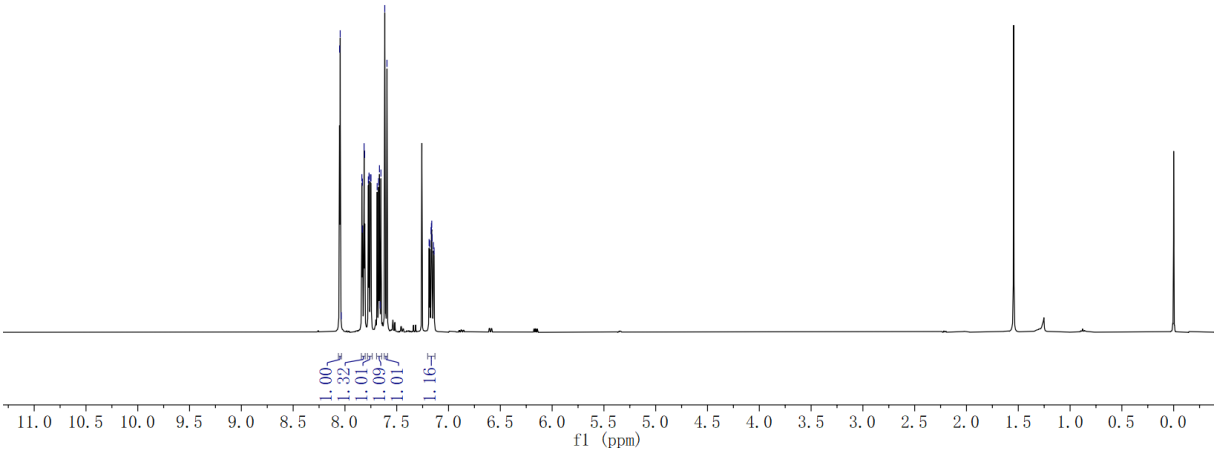
41 ^{13}C-NMR
(100 MHz, $CDCl_3$)

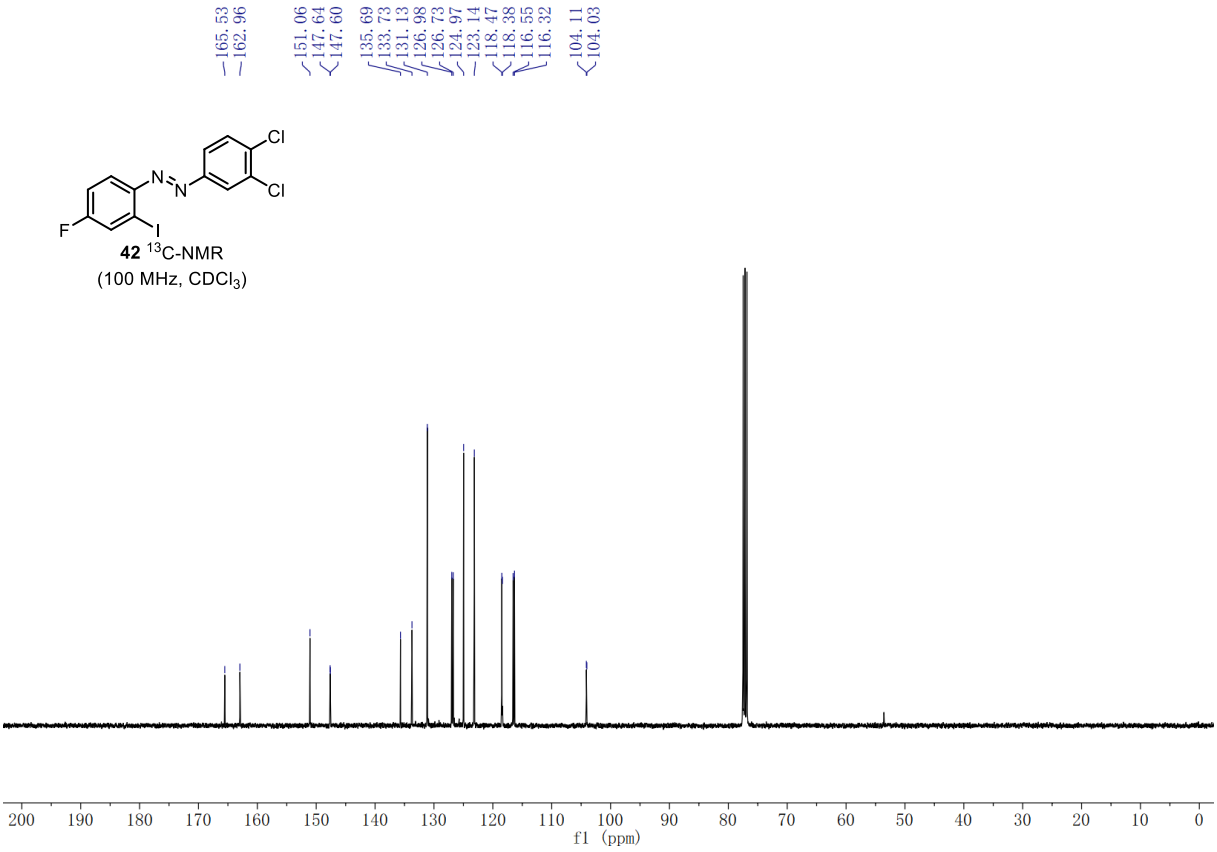


41 ^{19}F-NMR
(376 MHz, $CDCl_3$)

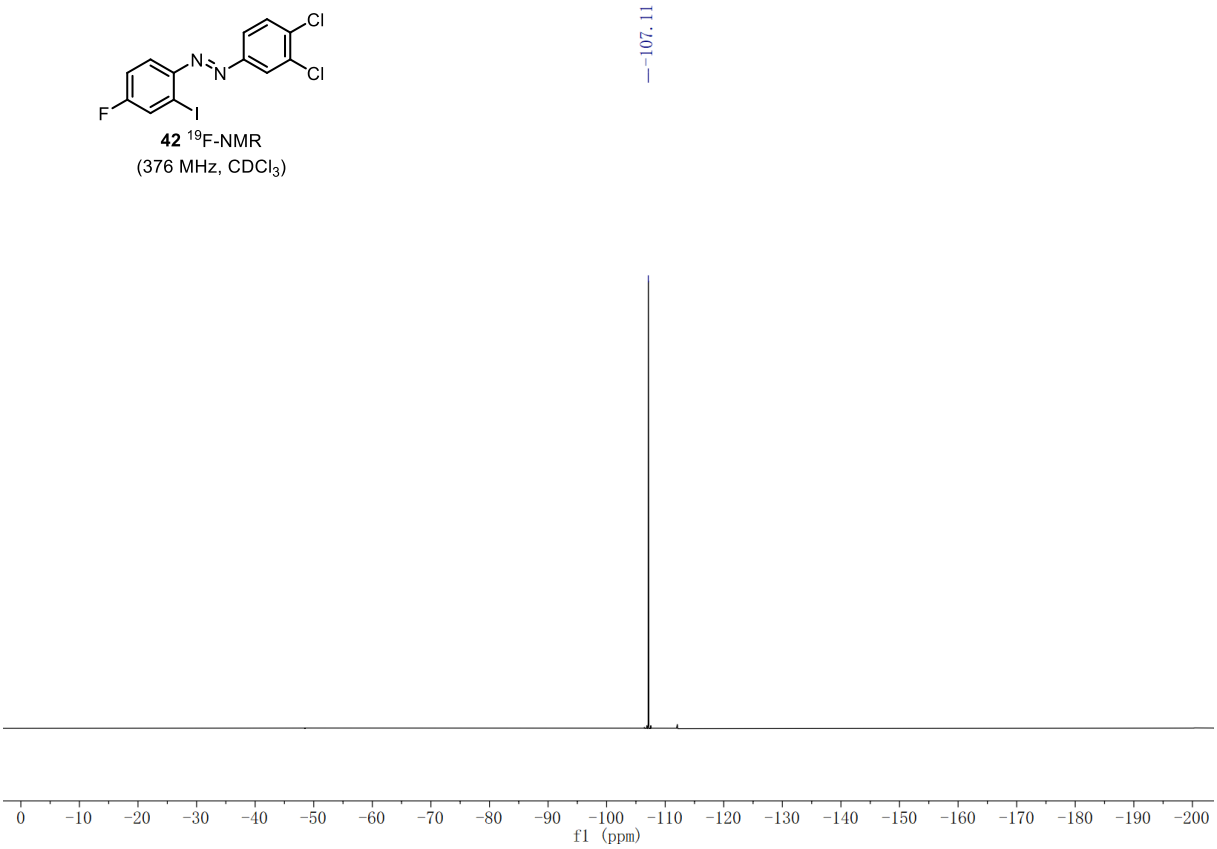


42 ^{1}H-NMR
(400 MHz, $CDCl_3$)

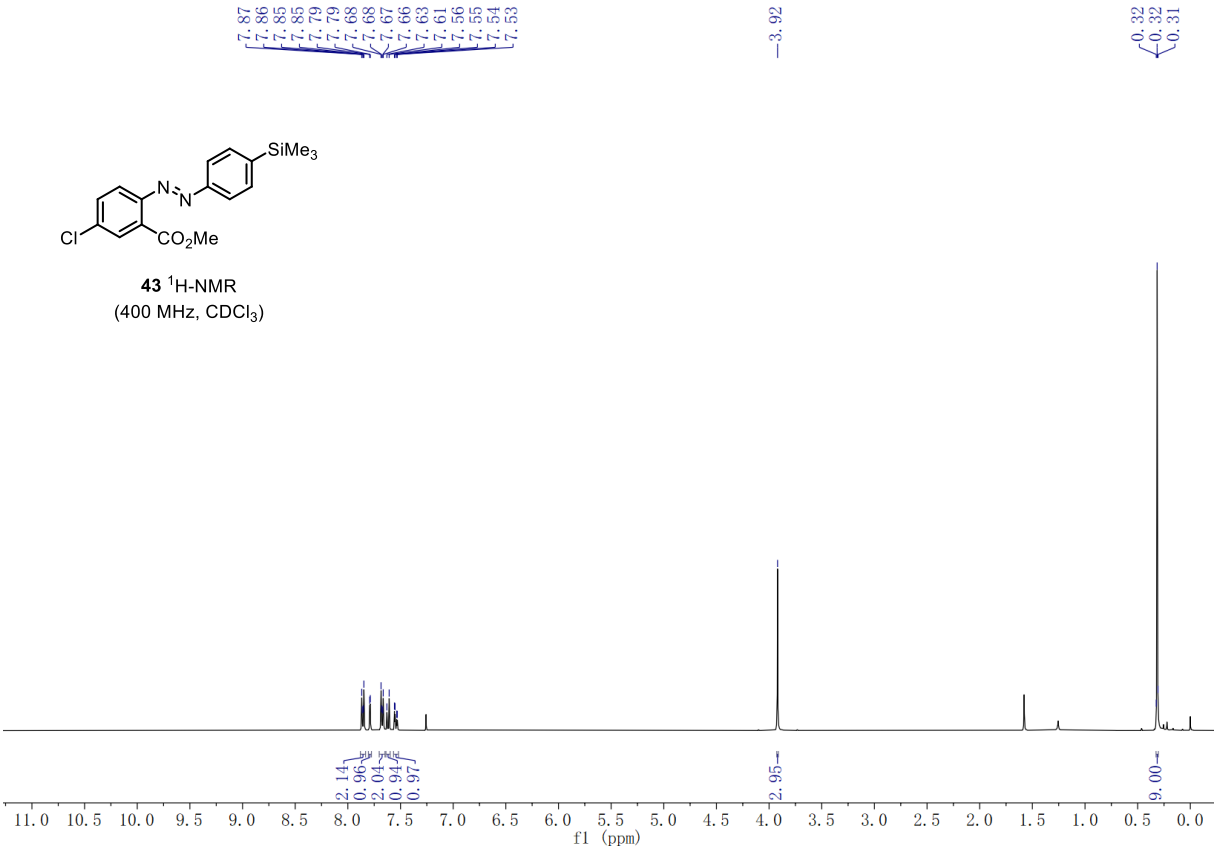




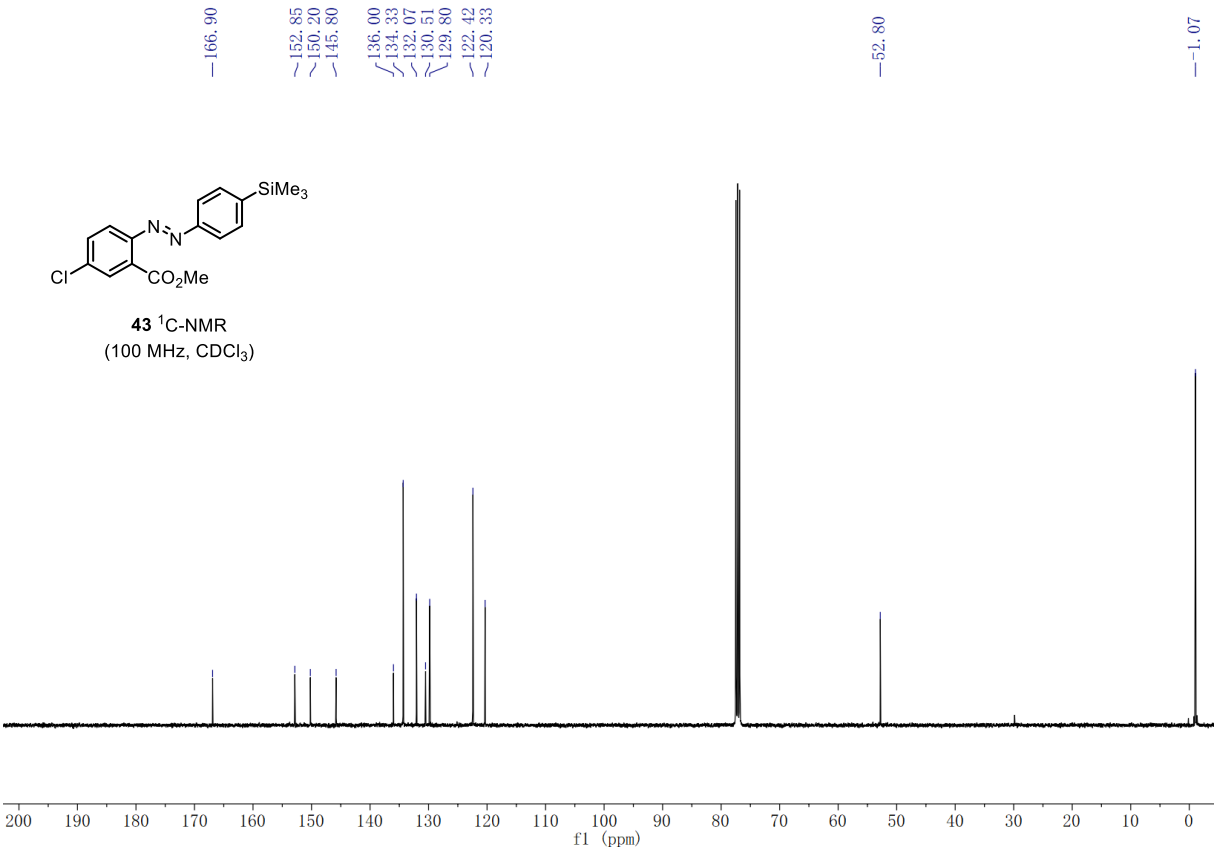
42 ^{13}C-NMR
(100 MHz, $CDCl_3$)



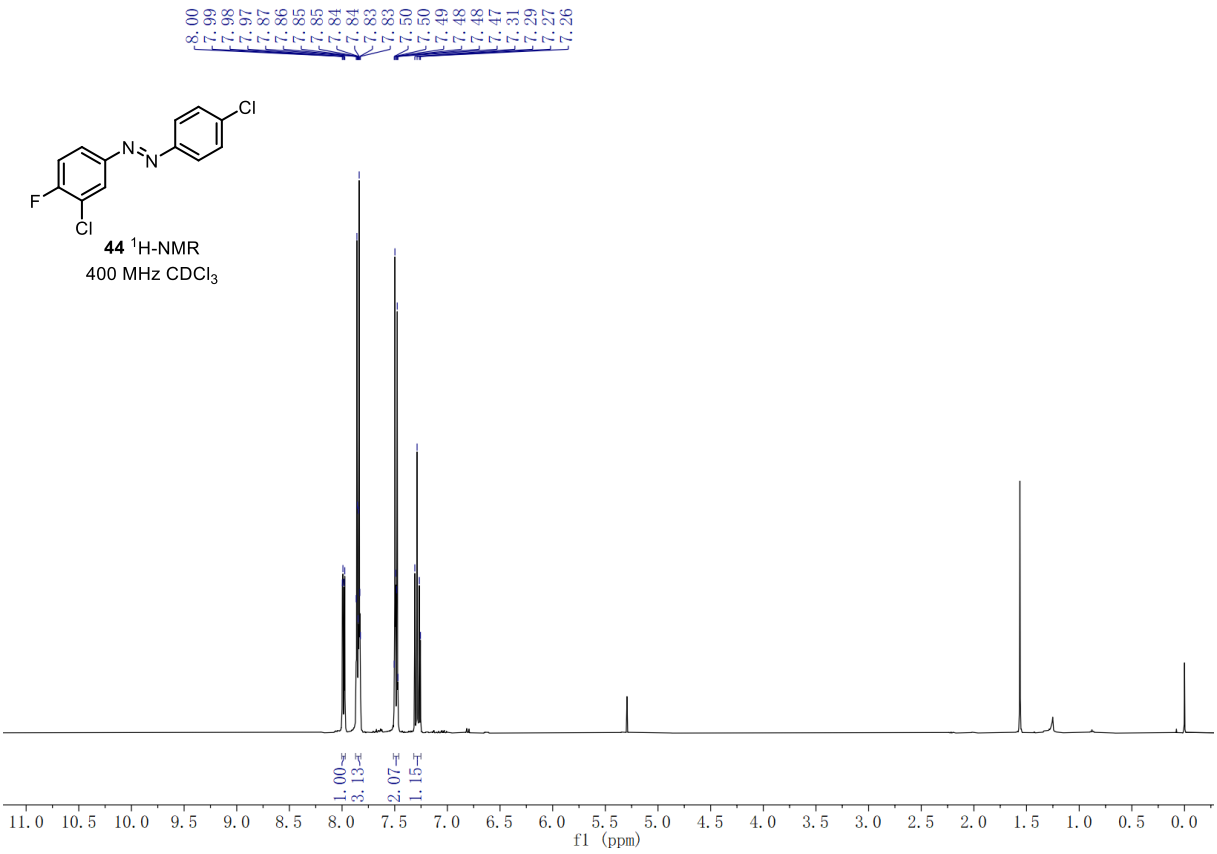
42 ^{19}F-NMR
(376 MHz, $CDCl_3$)



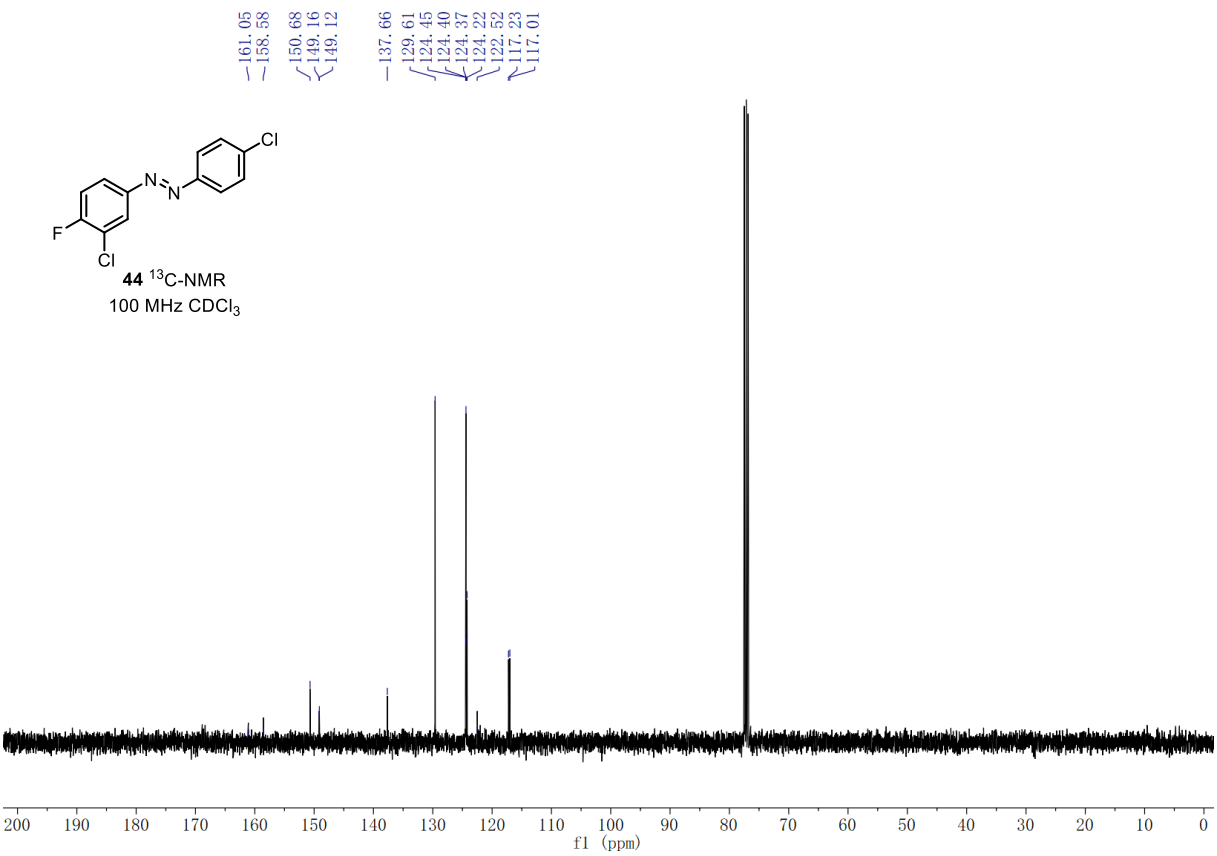
43 ^{1}H-NMR
(400 MHz, $CDCl_3$)



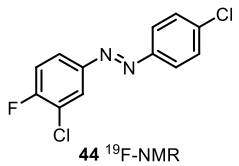
43 ^{1}C-NMR
(100 MHz, $CDCl_3$)



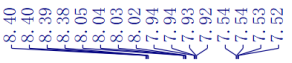
44 ^{1}H-NMR
400 MHz $CDCl_3$

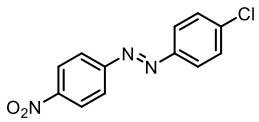


44 ^{13}C-NMR
100 MHz $CDCl_3$

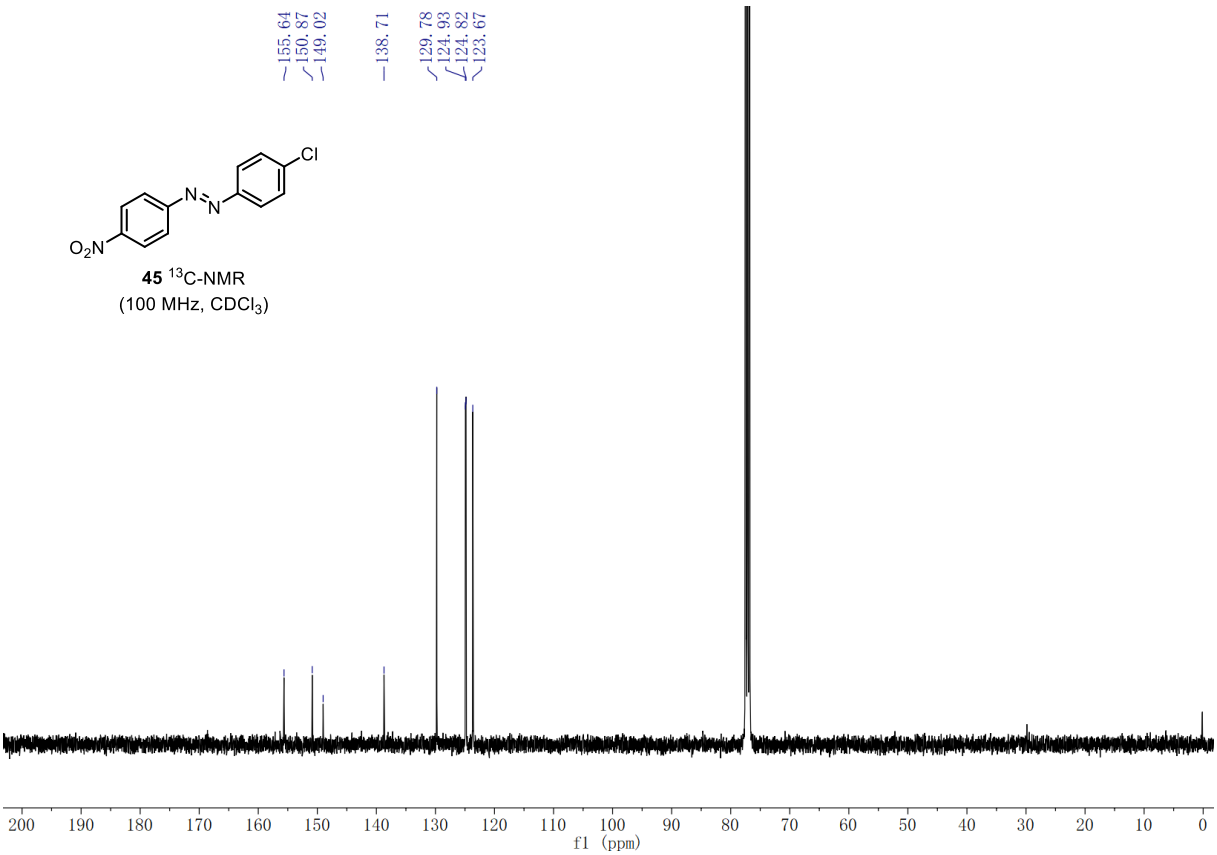


44 ^{19}F-NMR
376 MHz $CDCl_3$

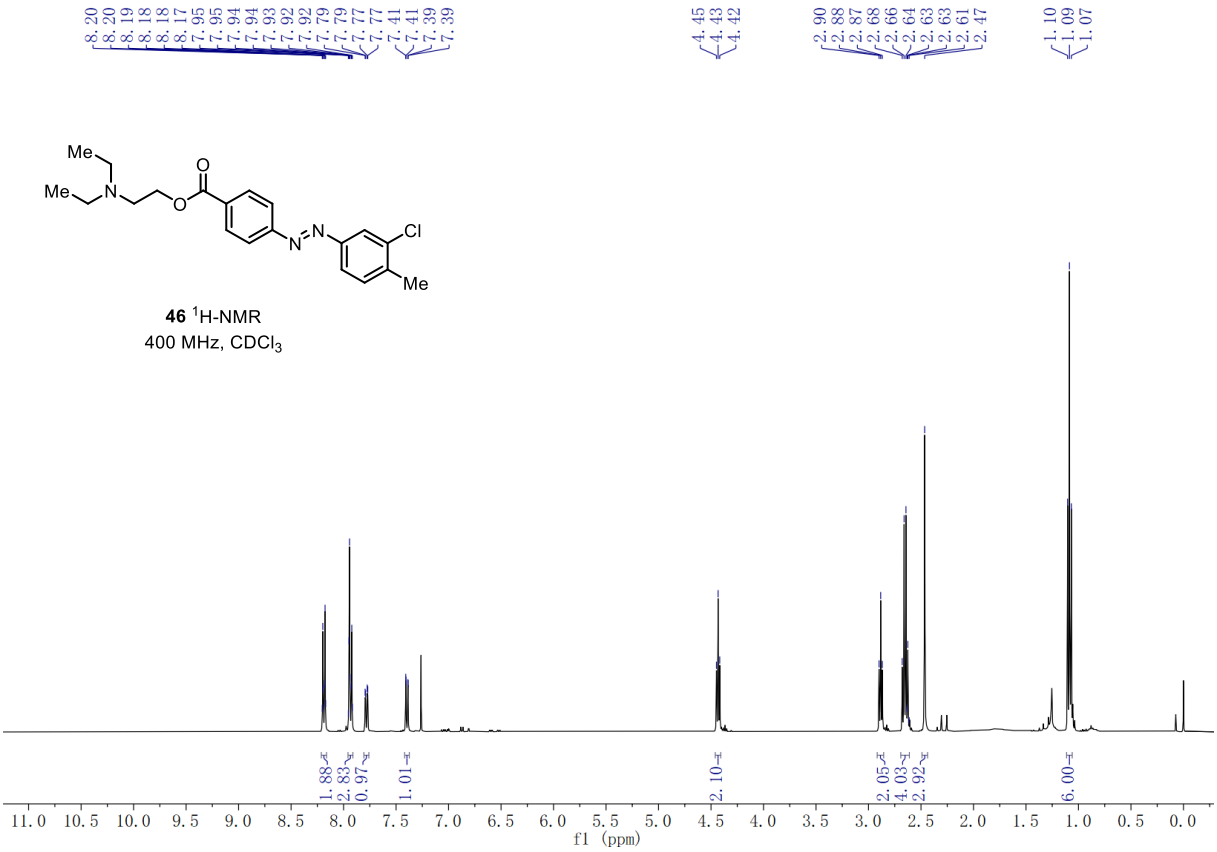




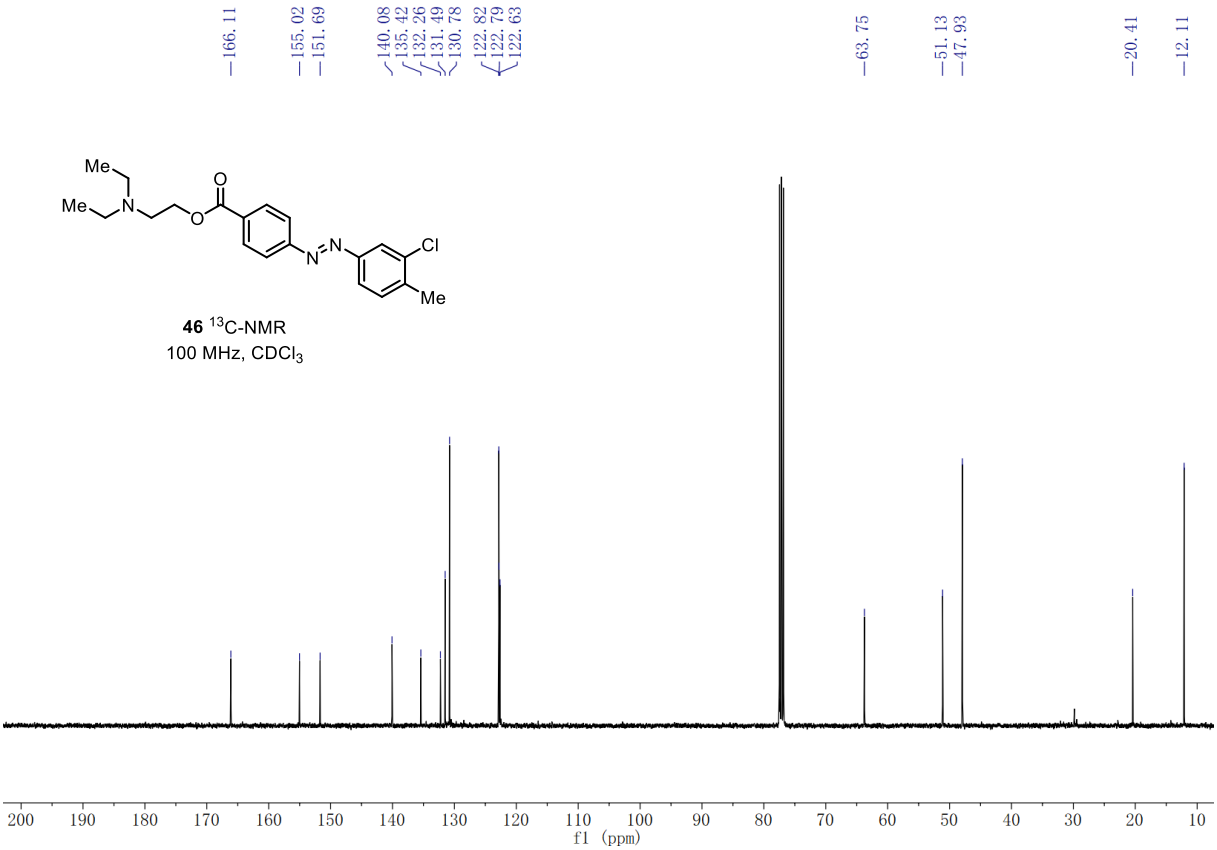
45 ^{1}H-NMR
(400 MHz, $CDCl_3$)



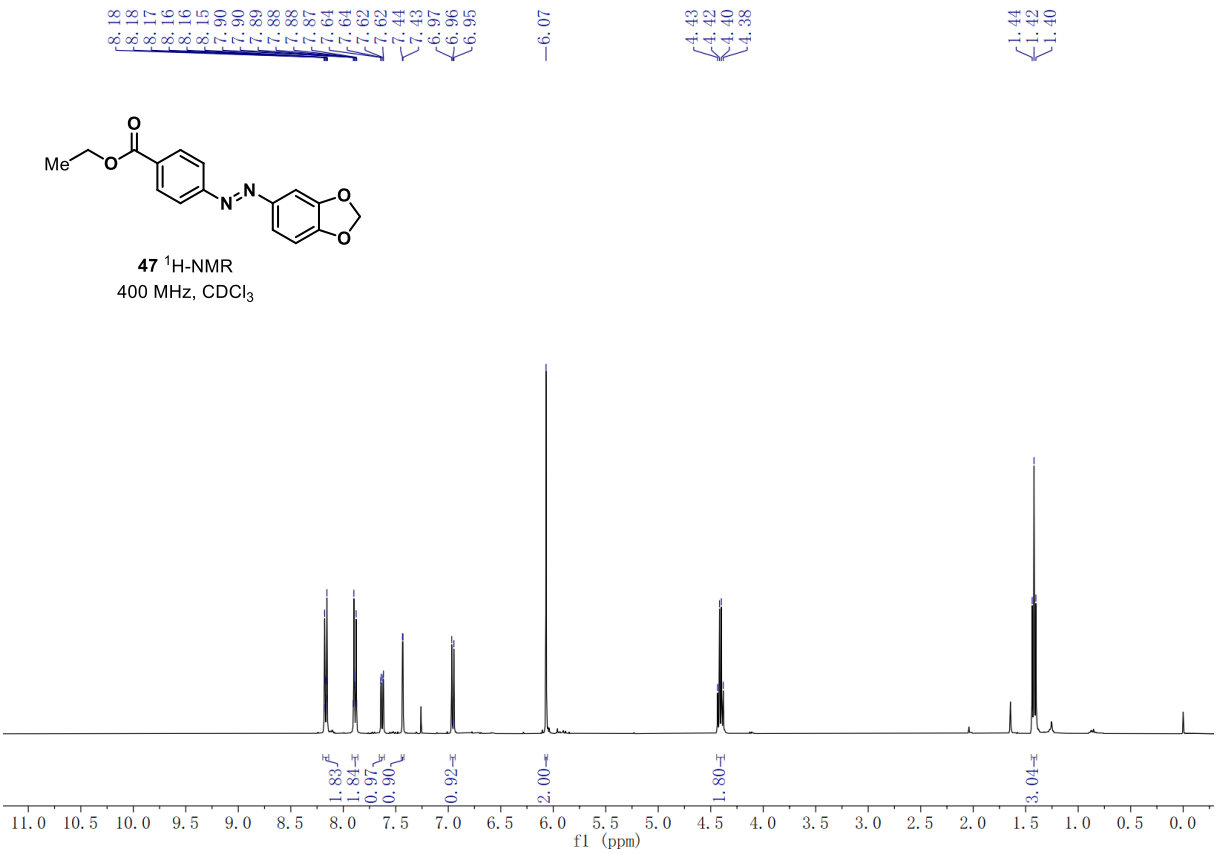
45 ^{13}C-NMR
(100 MHz, $CDCl_3$)



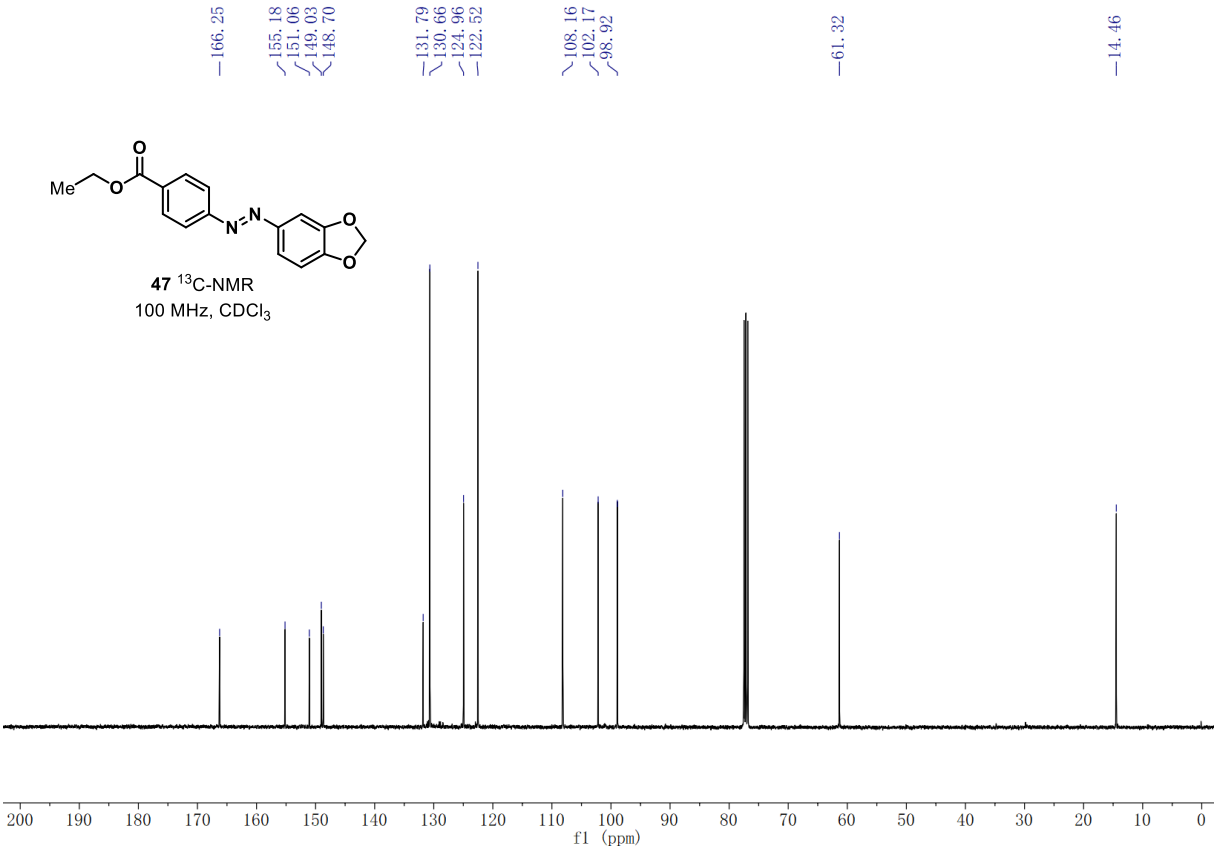
46 ^{1}H-NMR
400 MHz, $CDCl_3$

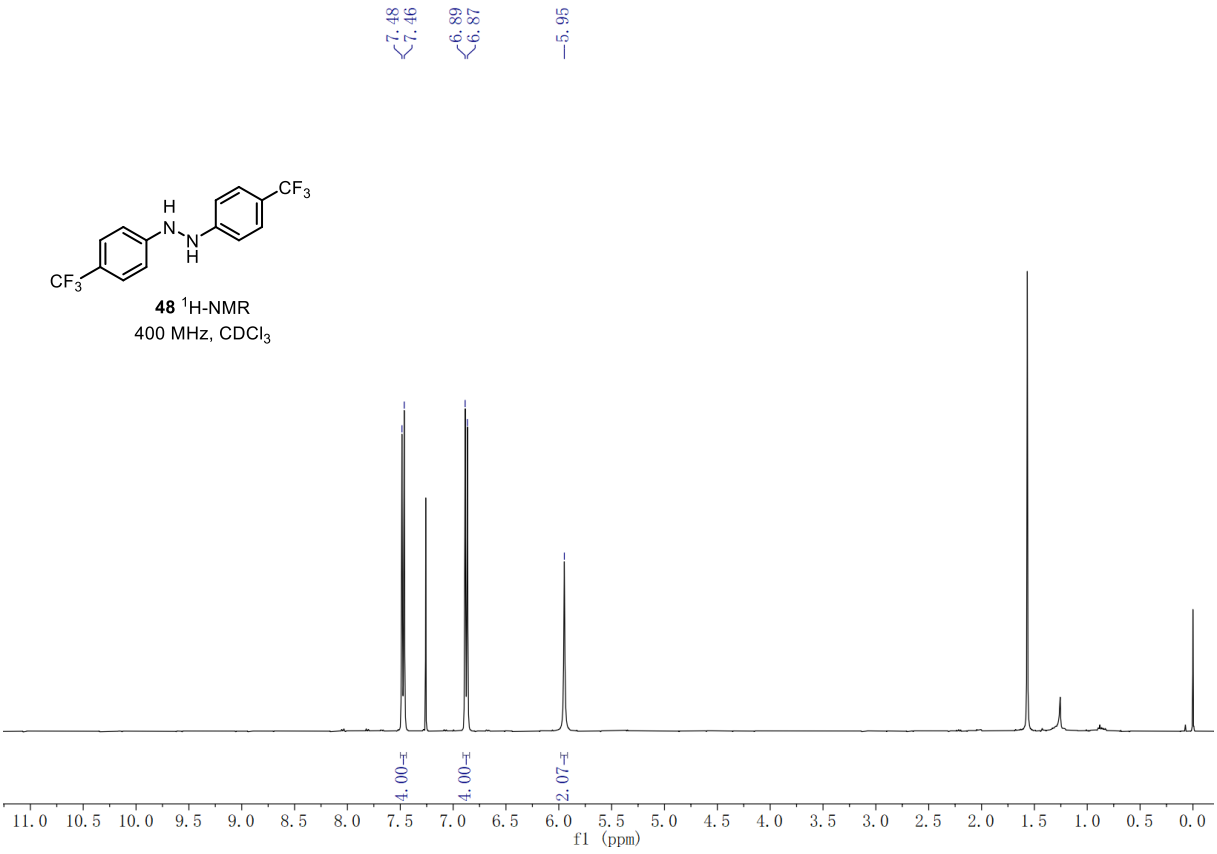


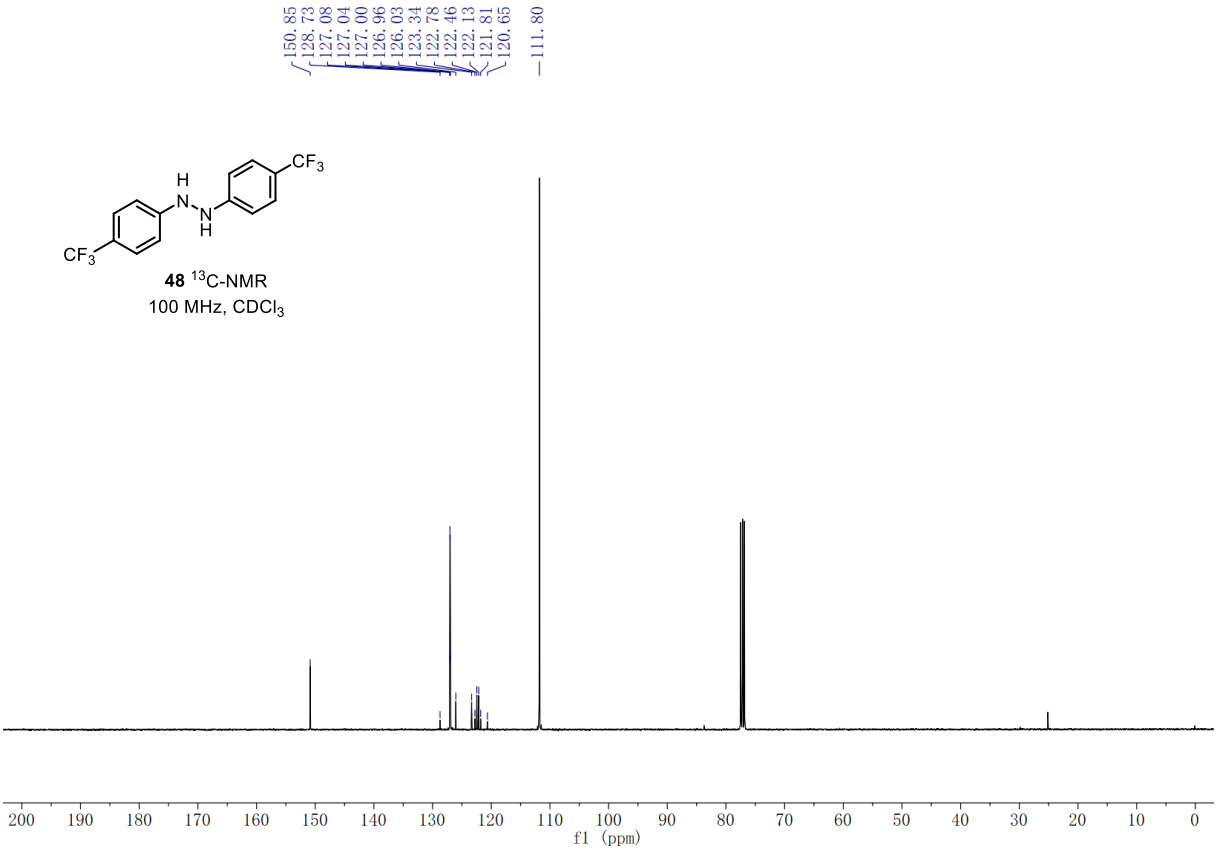
46 ^{13}C-NMR
100 MHz, $CDCl_3$



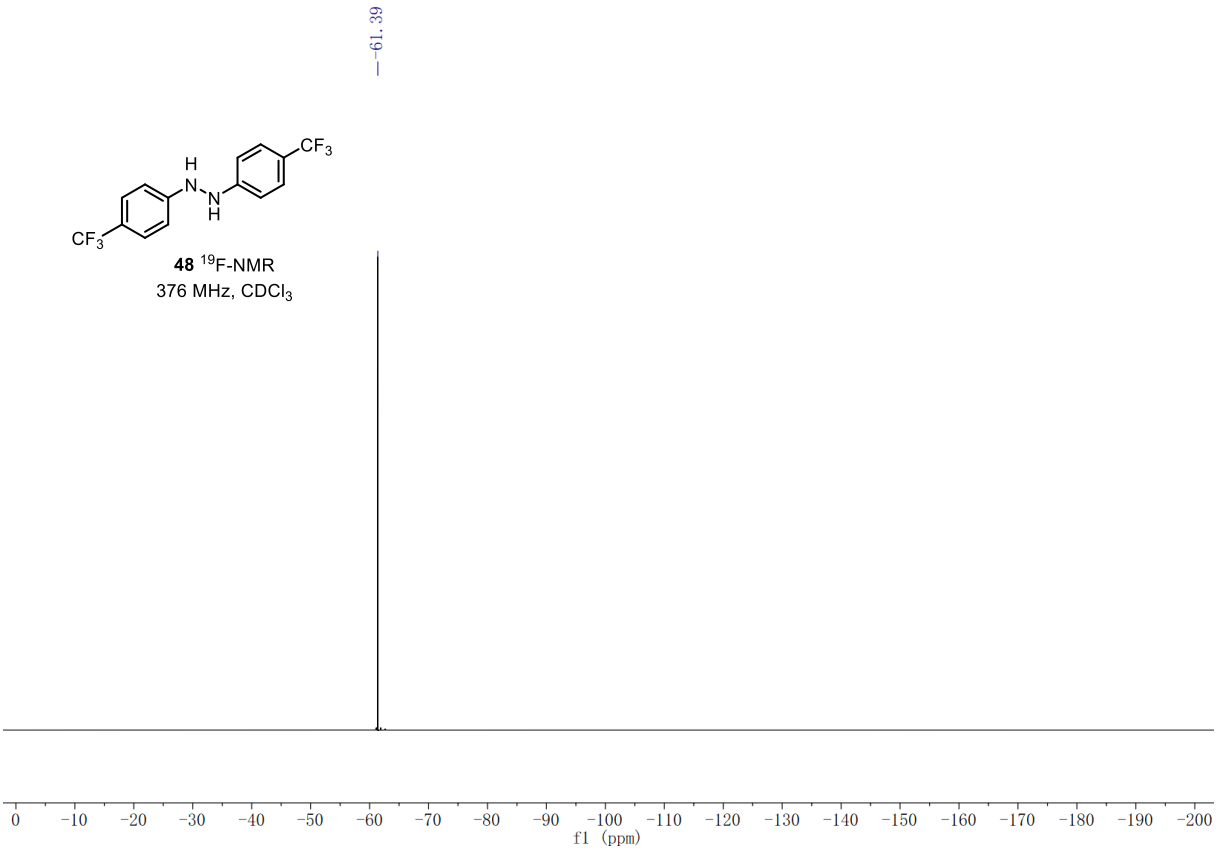
47 ^{1}H-NMR
400 MHz, $CDCl_3$


166.25
155.18
151.06
149.03
148.70
131.79
130.66
124.96
122.52
108.16
102.17
98.92
61.32
14.46
Me
O
O
N
N
O
O
47 13C-NMR
100 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

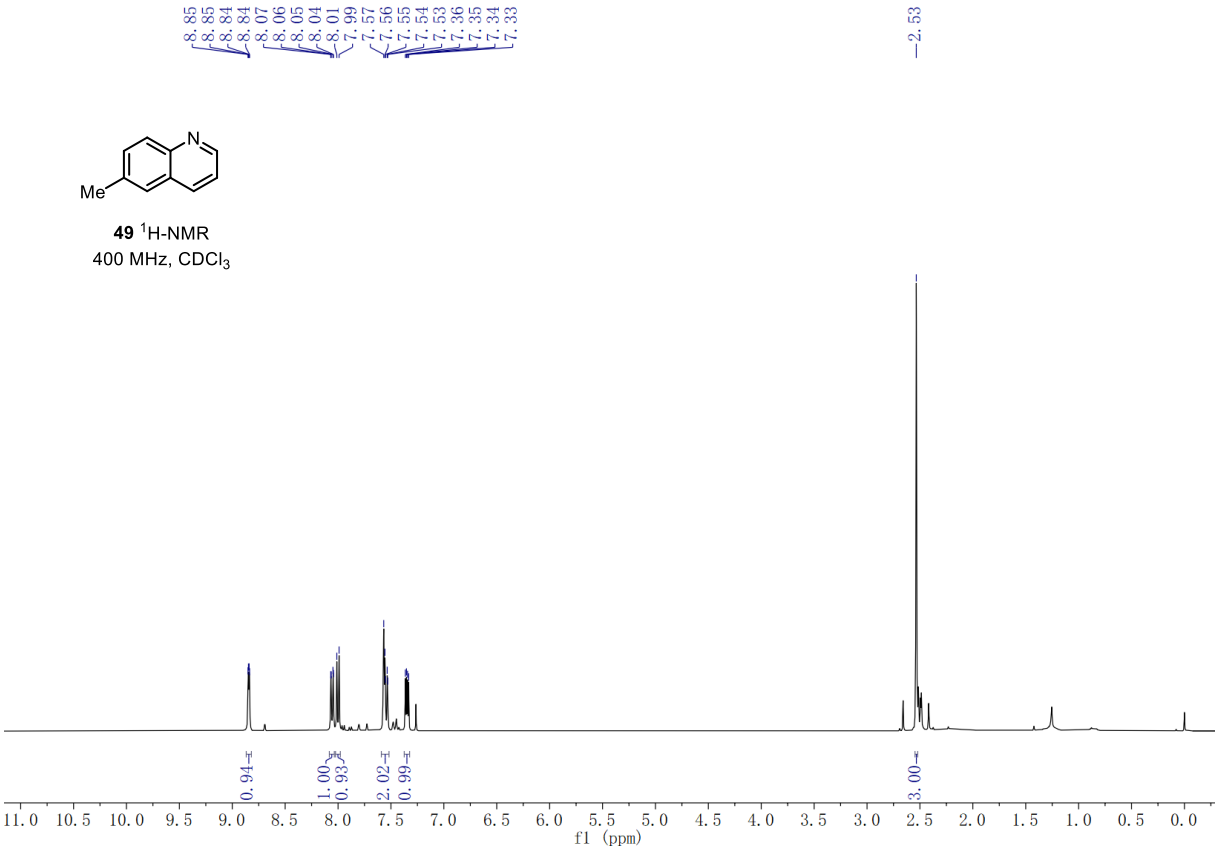

7.48
7.46
6.89
6.87
5.95
H
N
N
H
CF3
CF3
48 1H-NMR
400 MHz, CDCl3
4.00
4.00
2.07
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



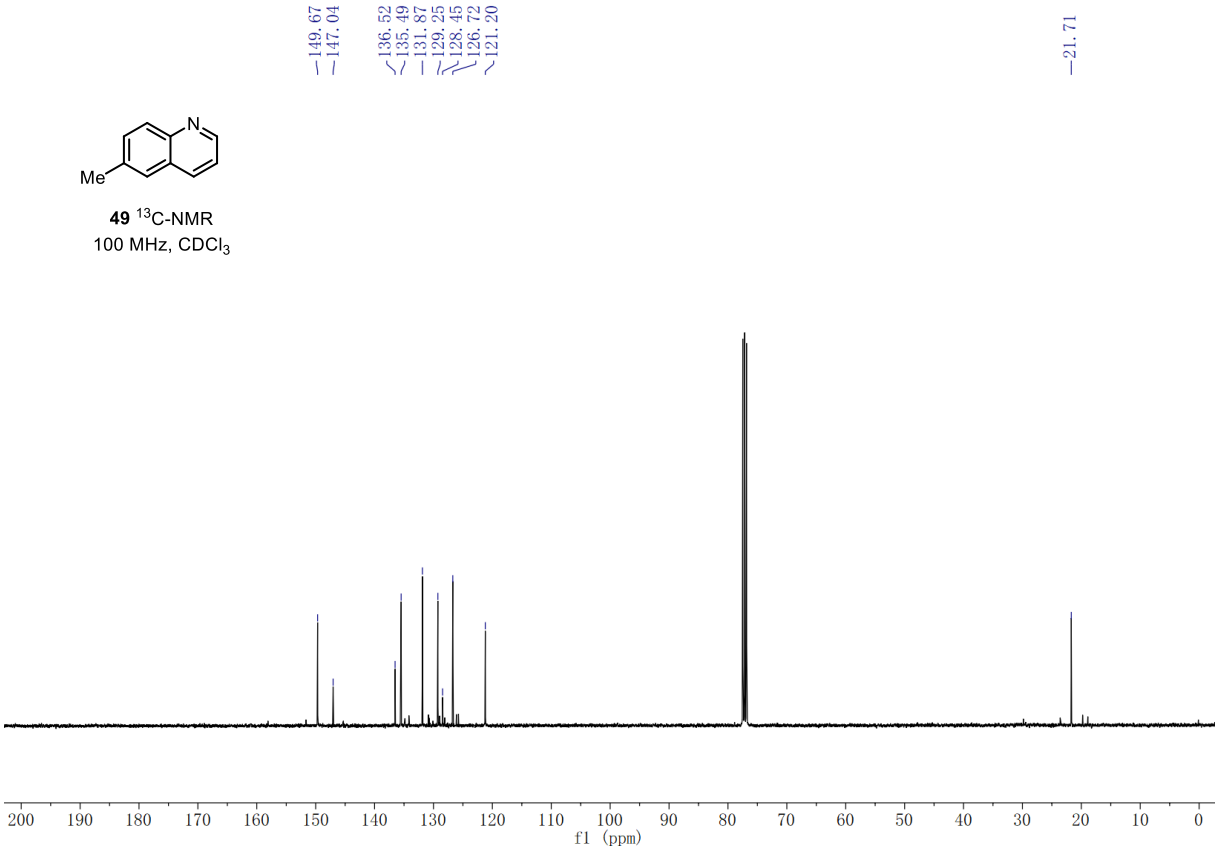
48 ^{13}C-NMR
100 MHz, $CDCl_3$



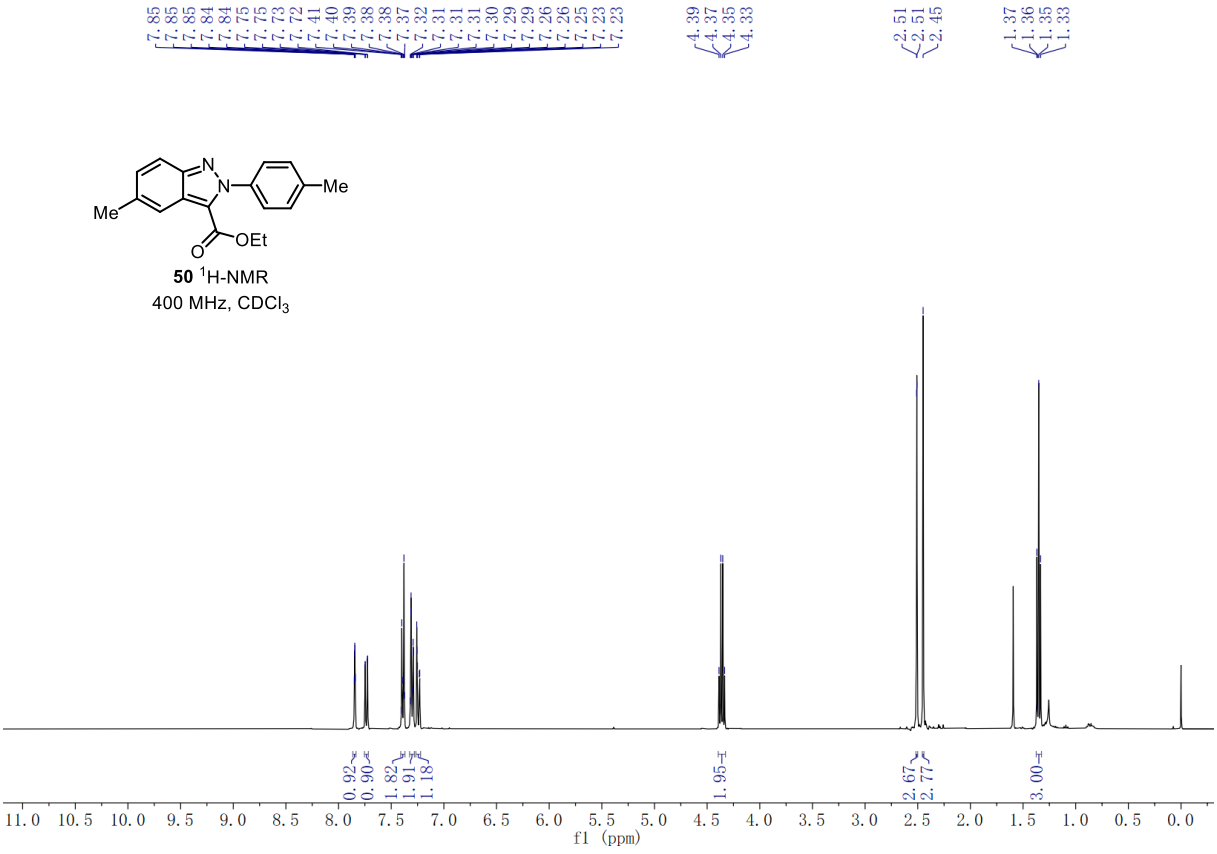
48 ^{19}F-NMR
376 MHz, $CDCl_3$



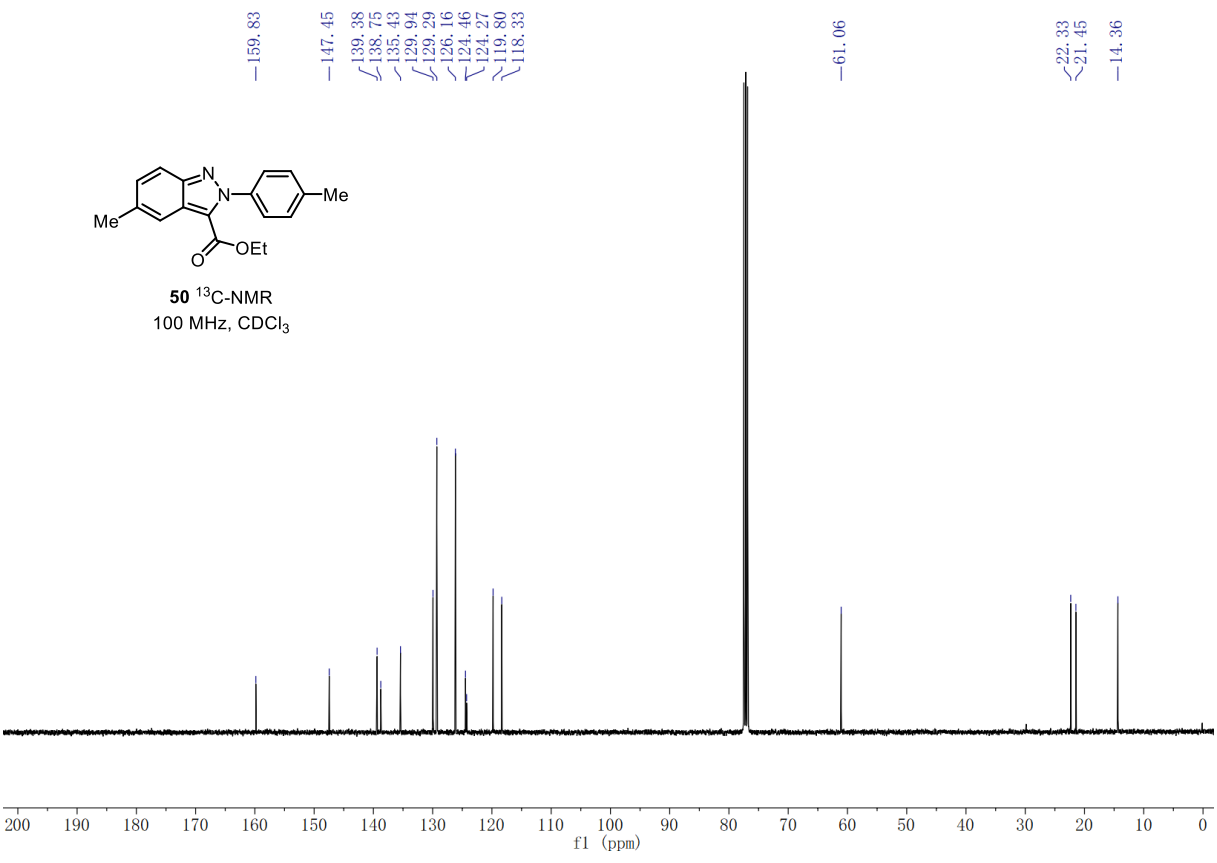
49 ^{1}H-NMR
400 MHz, $CDCl_3$



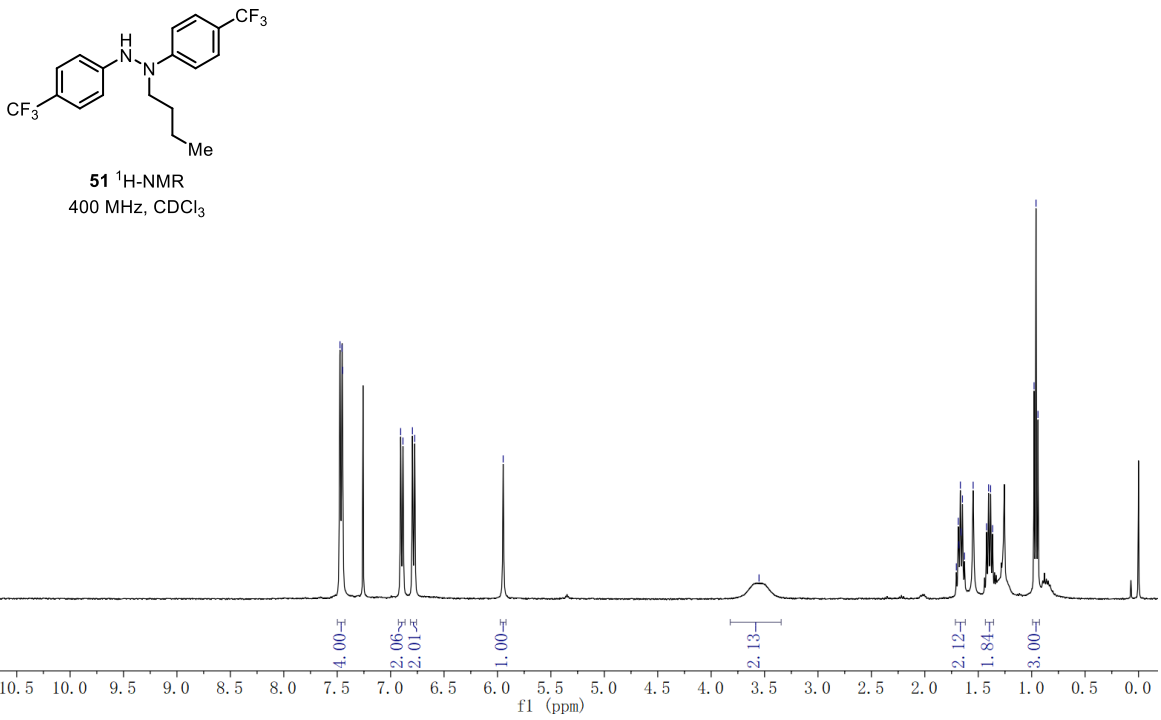
49 ^{13}C-NMR
100 MHz, $CDCl_3$



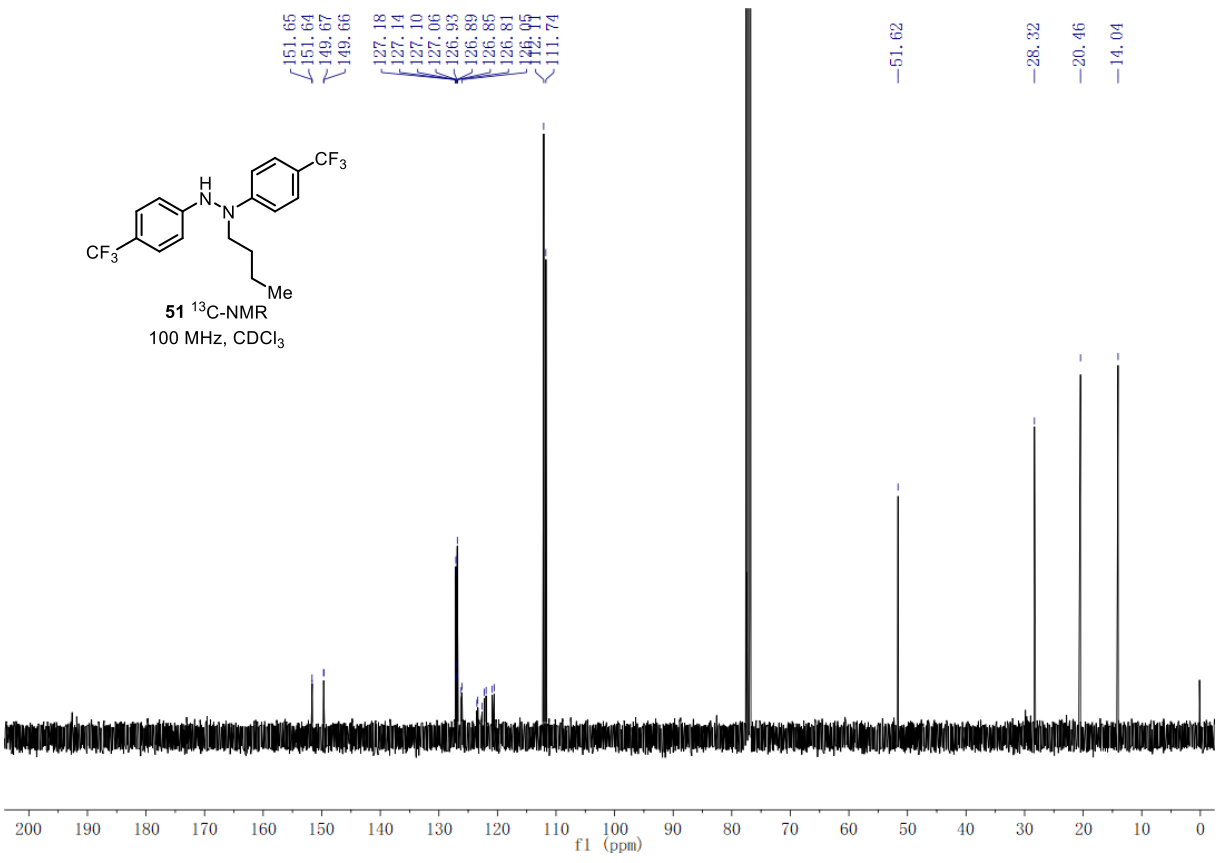
50 ^{1}H-NMR
400 MHz, $CDCl_3$



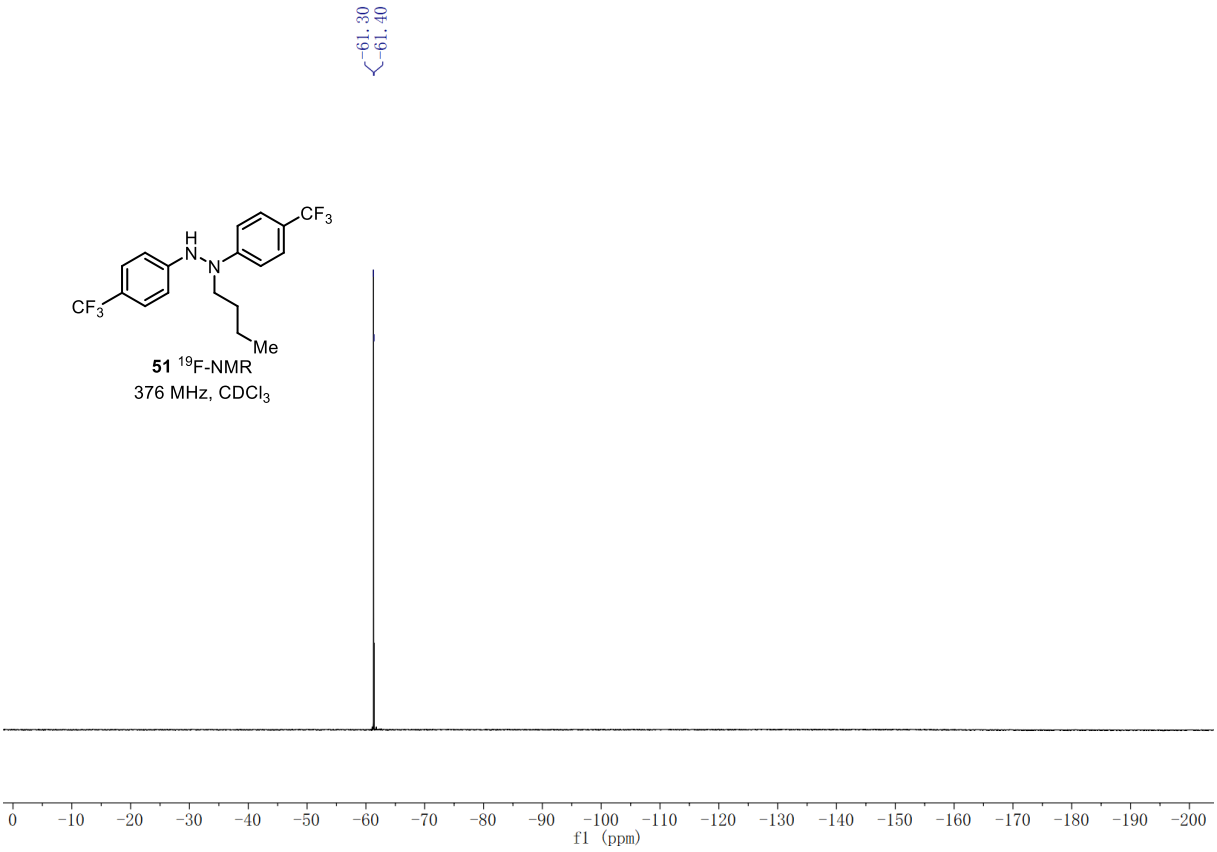
50 ^{13}C-NMR
100 MHz, $CDCl_3$



51 ^{1}H-NMR
400 MHz, $CDCl_3$



51 ^{13}C-NMR
100 MHz, $CDCl_3$



51 ^{19}F-NMR
376 MHz, $CDCl_3$

1. References:

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