Supplementary Information (SI) for ChemComm.

Supporting Information

Oxidative Decarbonylation Coupling of Anilines with Isocyanates for the Synthesis of Unsymmetric Azobenzenes

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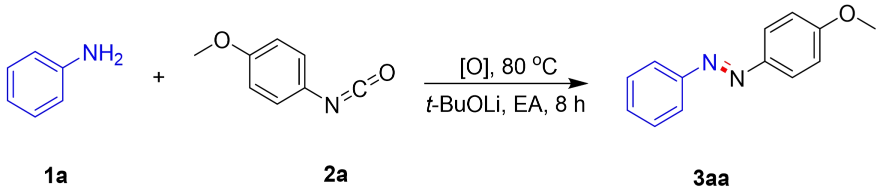
A. General information

Melting points were measured on an Electrothemal SGW-X4 microscopy digital melting point apparatus and are uncorrected; ^{1}H-NMR, ^{13}C-NMR and ^{19}F NMR spectra were obtained on Bruker-500 or Bruker-400 and referenced to 7.28 ppm and 77.16 ppm for chloroform solvent with TMS as internal standard (0 ppm). Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane. Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), multiplet (m); Column chromatography was performed on silica gel (200-300 mesh) using ethyl acetate/petroleum ether; Unless otherwise stated, all the reagents, including anilines **1** and isocyanates **2** were purchased from commercial sources (Energy Chemical, Bide Medicine, J&K Chemic, TCI, Fluka, Acros, SCRC, Macklin), used without further purification. Mass spectroscopy data of the products were collected on an HRMS-QTOF instrument.

B. The process of optimizing reaction conditions

Table S1. Screening of the oxidant ^{a}

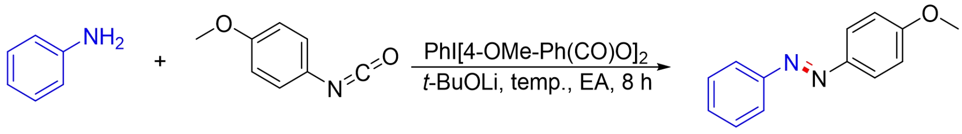


Entry	Oxidant	Yield ^{b} (%)
1	PhIO	trace
2	PIFA	trace
3	PIDA	61
4	IBX	trace
5	PhI[Ph(CO)O]$_2$	66
6	PhI[4-OMe-Ph(CO)O]$_2$	**75**

7	$PhI[4\text{-}NO_2\text{-}Ph(CO)O]_2$	24
8	$PhI[4\text{-}$*t*$\text{-}Bu\text{-}Ph(CO)O]_2$	56
9	H_2O_2	n.d.
10	Nb_2O_5 (10 %)+ H_2O_2	trace
11	Nb_2O_5 (1 eq.)+ H_2O_2	n.d.
12	TBHP	n.d.
13	DTBP	n.d.
14	*m*-CPBA	n.d.
15	K_2FeO_4	n.d.

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.15 mmol), oxidant (2 eq.), *t*-BuOLi (1 eq.), and EA (1 mL) at 80 °C under air for 8 h. [b] Isolated yield. n.d. = not detected.

Table S2. Screening of the temperature [a]

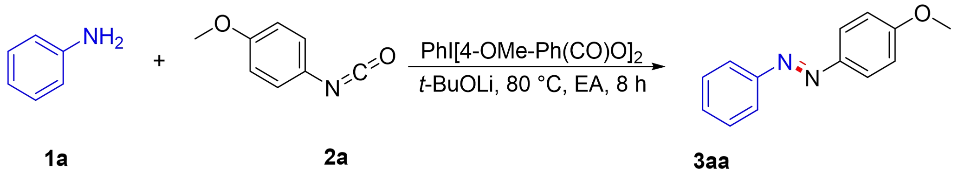


1a **2a** **3aa**

Entry	Temperature	Yield[b] (%)
1	rt	trace
2	70	60
3	**80**	**75**
5	90	65
6	100	trace

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.15 mmol), PhI[4-OMe-Ph(CO)O]$_2$ (2 eq.), *t*-BuOLi (1 eq.), and EA (1 mL) at 80 °C under air for 8 h. [b] Isolated yield.

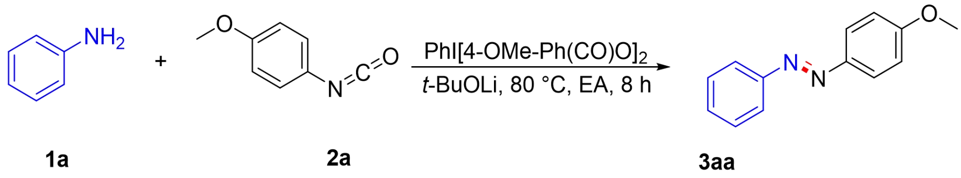
Table S3. Screening of aniline additions [a]



Entry	Aniline additions	Yield [b] (%)
1	1.0 eq.	34
2	1.5 eq.	57
3	**2.0 eq.**	**75**

[a] Reaction conditions: **1a**, **2a** (0.15 mmol), PhI[4-OMe-Ph(CO)O]$_2$ (2 eq.), *t*-BuOLi (1 eq.), and EA (1 mL) at 80 °C under air for 8 h. [b] Isolated yield.

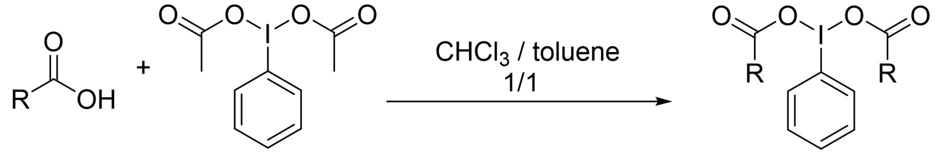
Table S4. Screening of solvent additions [a]



Entry	Solvent additions	Yield[b] (%)
1	1.0 mL	75
1	1.5 mL	70
2	2 mL	68
3	2.5 mL	60

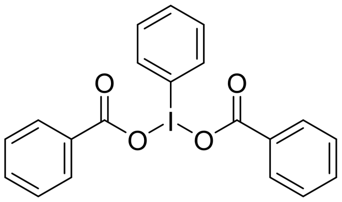
[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.15 mmol), PhI[4-OMe-Ph(CO)O]$_2$ (2 eq.), *t*-BuOLi (1 eq.), and EA at 80 °C under air for 8 h. [b] Isolated yield.

C. Preparation of hypervalent iodine (III) reagents [1]

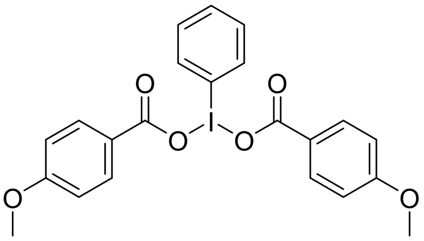


A mixture of (diacetoxyiodo) benzene (10 mmol), carboxylic acid (20 mmol) and $CHCl_3$/toluene (1:1, v/v, 100 mL) were added to a pressure-resistant tube and stirred for 30 min at 40 °C using a heating mantle. After the reaction was finished, the solvent was removed in vacuo to give crude product, which was used directly in the following reaction without any further purification.

Characterization of hypervalent iodine (III) reagents



Phenyl-λ³-iodanediyl dibenzoate[1]: white solid (3.8 g, 86% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 – 8.25 (m, 2H), 7.96 (d, J = 7.1 Hz, 4H), 7.67 – 7.63 (m, 1H), 7.57 (dd, J = 8.3, 7.0 Hz, 2H), 7.54 – 7.50 (m, 2H), 7.39 (t, J = 7.7 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.4, 134.9, 132.6, 131.7, 131.0, 130.2, 130.1, 128.2, 122.3.



Phenyl-λ³-iodanediyl bis(4-methoxybenzoate)[1]: white solid (4.0 g, 80% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, J = 7.9 Hz, 2H), 7.90 (d, J = 8.5 Hz, 4H), 7.62 (t, J = 7.2 Hz, 1H), 7.55 (t, J = 7.8 Hz, 2H), 6.86 (d, J = 8.7 Hz, 4H), 3.84 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.2, 163.1, 134.9, 132.1, 131.6, 130.9, 122.6, 122.3, 113.5, 55.4.

D. Typical procedure for the preparation of azobenzene 3

Typical procedure for preparation of 3aa-3as

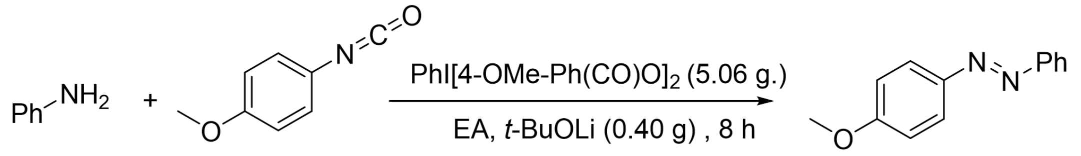
Aniline compounds **1** (0.3 mmol), 4-methoxyphenyl isocyanate **2a** (0.15 mmol, 23.4 mg, 1eq), *t*-BuOLi (0.15 mmol, 12.0 mg), PhI[4-OMe-Ph(CO)O]$_2$ (0.3 mmol, 151.8

mg) and EA (1.0 mL) were added to a 10 mL pressure-resistant tube. The reaction tube was sealed, and it was stirred for 8 h at 80 °C by heating the mantle. After the reaction was completed and cooling to room temperature, the reaction mixture was concentrated in vacuo. The crude mixture was purified by column chromatography using silica gel with eluent (petroleum ether: ethyl acetate = 50: 1) to afford the **3aa-3as**.

Typical procedure for preparation of 3ba-3bk

Aniline **1a** (0.3 mmol, 27.9 mg， 2eq), isocyanates **2** (0.15 mmol), *t*-BuOLi (0.15 mmol, 12.0 mg), PhI[4-OMe-Ph(CO)O]$_2$ (0.3 mmol, 151.8 mg) and EA (1.0 mL) were added to a 10 mL pressure-resistant tube under air. The reaction tube was sealed, and it was stirred for 8 h at 80 °C by heating the mantle. After the reaction was completed and cooling to room temperature, the reaction mixture was concentrated in vacuo. The crude mixture was purified by column chromatography using silica gel with eluent (petroleum ether: ethyl acetate = 100: 1) to afford the **3ba-3bk**.

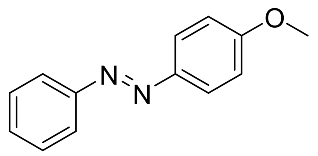
Gram reaction of 3aa



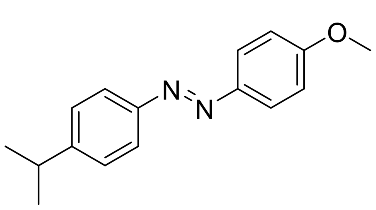
1a (0.93 g) **2a** (0.75 g) **3aa** (63% 0.67 g)

Aniline **1a** (10 mmol, 0.93 g), 4-methoxyphenyl isocyanate **2a** (5 mmol, 0.75 g), *t*-BuOLi (5 mmol, 0.40 g), PhI[4-OMe-Ph(CO)O]$_2$ (10 mmol, 5.06 g) and ethyl acetate (10.0 mL) were added to a 25 mL pressure-resistant tube under air. The reaction tube was sealed, and it was stirred for 8 h at 80 °C by heating the mantle. After the reaction was completed and cooling to room temperature, the reaction mixture was concentrated in vacuo. The crude mixture was purified by column chromatography using silica gel with eluent (petroleum ether: ethyl acetate = 50: 1) to afford the **3aa** (0.67 g, 63% yield).

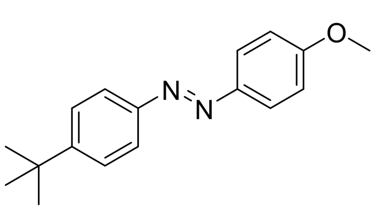
E. Spectroscopic data of azobenzene 3



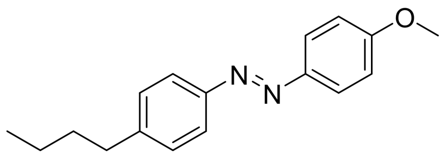
1-(4-Methoxyphenyl)-2-phenyldiazene (3aa)[2]: Orange solid (23.9 mg, 75% yield); m.p. 52-54 °C; R*f* = 0.49 (petroleum ether: ethyl acetate = 50: 1); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 9.0 Hz, 2H), 7.91 (d, *J* = 7.3 Hz, 2H), 7.53 (t, *J* = 7.5 Hz, 2H), 7.47 (t, *J* = 7.3 Hz, 1H), 7.05 (d, *J* = 9.0 Hz, 2H), 3.92 (s, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 162.1, 152.8, 147.0, 130.4, 129.1, 124.8, 122.6, 114.2, 55.6; HRMS (ESI Q-TOF) m/z: calcd for $C_{13}H_{12}N_2O$ [M]$^+$ 212.0950; found 212.0945.



1-(4-Isopropylphenyl)-2-(4-methoxyphenyl)diazene (3ab): yellow solid (21.3 mg, 56% yield); m.p. 78-80 °C; R*f* = 0.49 (petroleum ether: ethyl acetate = 50: 1); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 9.0 Hz, 2H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.04 (d, *J* = 8.9 Hz, 2H), 3.92 (s, 3H), 1.33 (s, 3H), 1.31 (s, 3H), 1.28 (s, 1H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 161.8, 151.7, 151.1, 147.1, 127.1, 124.6, 122.6, 114.2, 55.6, 34.1, 23.9; HRMS (ESI Q-TOF) m/z: calcd for $C_{16}H_{18}N_2O$ [M+H]$^+$ 255.1491; found 255.1486.

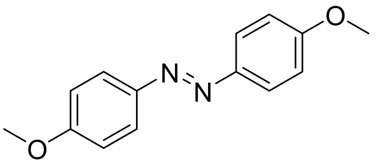


1-(4-(*tert*-Butyl)phenyl)-2-(4-methoxyphenyl)diazene (3ac): Orange solid (24.1 mg, 60% yield); m.p. 78-80 °C; R*f* = 0.50 (petroleum ether: ethyl acetate = 50: 1); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 8.9 Hz, 2H), 7.84 (d, *J* = 8.6 Hz, 2H), 7.54 (d, *J* = 8.6 Hz, 2H), 7.04 (d, *J* = 9.0 Hz, 2H), 3.92 (s, 3H), 1.40 (s, 9H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 161.8, 153.9, 150.7, 147.2, 126.0, 124.6, 122.3, 114.2, 55.6, 35.0 31.3; HRMS (ESI Q-TOF) m/z: calcd for $C_{17}H_{20}N_2O$ [M+H]$^+$ 269.1648; found 269.1642.

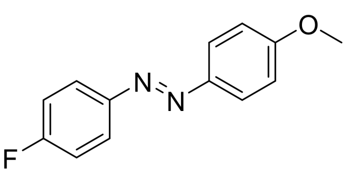


1-(4-Butylphenyl)-2-(4-methoxyphenyl)diazene (3ad): Orange solid (23.3 mg, 58% yield); m.p. 78-80 °C; R*f* = 0.45 (petroleum ether: ethyl acetate = 50: 1); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 9.0 Hz, 2H), 7.82

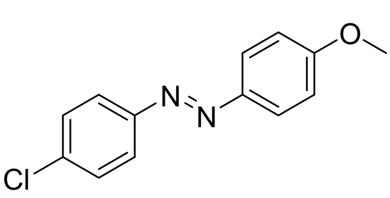
(d, J = 8.2 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 7.03 (d, J = 9.0 Hz, 2H), 3.92 (s, 3H), 2.70 (t, J = 7.7 Hz, 2H), 1.67 (t, J = 7.0 Hz, 2H), 1.43 – 1.38 (m, 2H), 0.97 (t, J = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 161.8, 151.0, 147.1, 145.9, 129.1, 124.6, 122.5, 114.2, 55.6, 35.6, 33.5, 22.4, 14.0; HRMS (ESI Q-TOF) m/z: calcd for $C_{17}H_{20}N_2O$ [M+H]$^+$ 269.1648; found 269.1641.



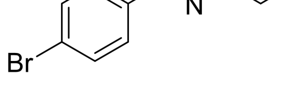
1,2-Bis(4-methoxyphenyl)diazene (3ae)[3]: Orange solid (22.9 mg, 63% yield); m.p. 160 – 162 °C; R$_f$ = 0.45 (petroleum ether: ethyl acetate = 25: 1); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.92 – 7.89 (m, 4H), 7.05 – 7.01 (m, 4H), 3.91 (s, 6H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 161.6, 147.1, 124.4, 114.2, 55.6; HRMS (ESI Q-TOF) m/z: calcd for $C_{14}H_{14}N_2O_2$ [M+H]$^+$ 243.1134; found 243.1138.



1-(4-Fluorophenyl)-2-(4-methoxyphenyl)diazene (3af)[4]: Orange solid (24.8 mg, 72% yield); m.p. 96–98 °C; R$_f$ = 0.48 (petroleum ether: ethyl acetate = 50: 1); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.94 – 7.90 (m, 4H), 7.22 – 7.19 (m, 2H), 7.04 (d, J = 9.0 Hz, 2H), 3.92 (s, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 164.0(d, J = 250.0 Hz), 162.1, 149.3 (d, J = 2.5 Hz), 146.8, 124.7, 124.5 (d, J = 8.8 Hz), 116.0(d, J = 22.5 Hz), 114.3, 55.6; ^{19}F NMR (471 MHz, Chloroform-*d*) δ -110.41 – -110.51 (m). HRMS (ESI Q-TOF) m/z: calcd for $C_{13}H_{11}FN_2O$ [M+H]$^+$ 231.0929; found 231.0928.

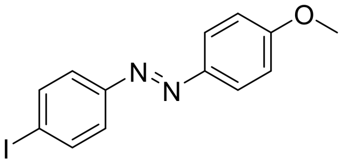


1-(4-Chlorophenyl)-2-(4-methoxyphenyl)diazene (3ag)[4]: Orange solid (22.5 mg, 61% yield); m.p. 127–129 °C; R$_f$ = 0.49 (petroleum ether: ethyl acetate = 50: 1); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.94 (d, J = 8.9 Hz, 2H), 7.85 (d, J = 8.6 Hz, 2H), 7.49 (d, J = 8.7 Hz, 2H), 7.04 (d, J = 9.0 Hz, 2H), 3.92 (s, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 162.3, 151.1, 146.9, 136.2, 129.3, 124.9, 123.8, 114.3, 55.7; HRMS (ESI Q-TOF) m/z: calcd for $C_{13}H_{11}ClN_2O$ [M+H]$^+$ 247.0633; found 247.0632.

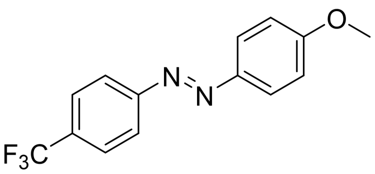


1-(4-Bromophenyl)-2-(4-methoxyphenyl)diazene

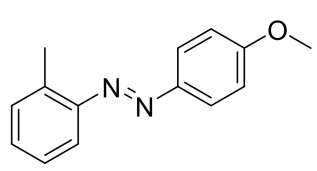
(3ah)[4]: Orange solid (28.7 mg, 66% yield); m.p. 166–168 °C; R*f* = 0.50 (petroleum ether: ethyl acetate = 50: 1); ^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 7.94 (d, *J* = 8.9 Hz, 2H), 7.78 (d, *J* = 8.6 Hz, 2H), 7.65 (d, *J* = 8.7 Hz, 2H), 7.04 (d, *J* = 9.0 Hz, 2H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) *δ* 162.4, 151.5, 146.9, 132.3, 124.9, 124.6, 124.1, 114.3, 55.6; HRMS (ESI Q-TOF) m/z: calcd for $C_{13}H_{11}BrN_2O$ [M+H]$^+$ 291.0128; found 291.0127.



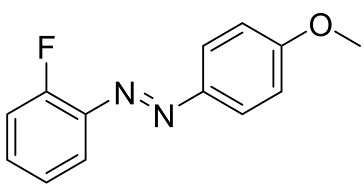
1-(4-Iodophenyl)-2-(4-methoxyphenyl)diazene (3ai): Orange solid (36.8 mg, 65% yield); m.p. 178-180 °C; R*f* = 0.50 (petroleum ether: ethyl acetate = 50: 1); ^{1}H NMR (500 MHz, Chloroform-*d*) *δ* 7.94 (d, *J* = 9.0 Hz, 2H), 7.86 (d, *J* = 8.5 Hz, 2H), 7.64 (d, *J* = 8.5 Hz, 2H), 7.04 (d, *J* = 9.0 Hz, 2H), 3.92 (s, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) *δ* 162.4, 152.1, 146.9, 138.3, 125.0, 124.3, 114.3, 96.7, 55.6; HRMS (ESI Q-TOF) m/z: calcd for $C_{13}H_{11}IN_2O$ [M+H]$^+$ 338.9988; found 338.9994.



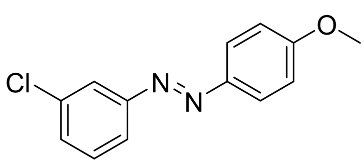
1-(4-Methoxyphenyl)-2-(4-(trifluoromethyl)phenyl) diazene (3aj)[4]: Orange solid (25.2 mg, 60% yield)**;** m.p. 133–135 °C; R*f* = 0.45 (petroleum ether: ethyl acetate = 50: 1); ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.98 (d, *J* = 8.9 Hz, 4H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.06 (d, *J* = 8.9 Hz, 2H), 3.94 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ* 162.8, 154.7, 146.9, 131.4 (q, *J* = 32.5 Hz), 126.2 (q, *J* = 3.8 Hz), 125.2, 124.2 (q, *J* = 272.3 Hz) 122.7, 114.4, 55.7; ^{19}F NMR (471 MHz, Chloroform-d) *δ* -62.43 HRMS (ESI Q-TOF) m/z: calcd for $C_{14}H_{11}F_3N_2O$ [M+H]$^+$ 281.0897; found 281.0894.



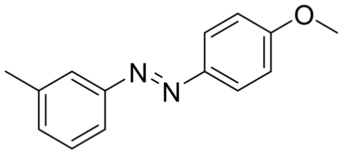
1-(4-Methoxyphenyl)-2-(o-tolyl)diazene (3ak): Orange oil (22.0 mg, 65% yield); m.p. 53–55 °C; R*f* = 0.48 (petroleum ether: ethyl acetate = 50: 1); ^{1}H NMR (500 MHz, Chloroform-*d*) *δ* 7.95 (d, *J* = 8.9 Hz, 2H), 7.64 – 7.61 (m, 1H), 7.35 (d, *J* = 5.1 Hz, 2H), 7.29 (s, 1H), 7.04 (d, *J* = 9.0 Hz, 2H), 3.92 (s, 3H), 2.73 (s, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) *δ* 161.9, 150.8, 147.5, 137.6, 131.2, 130.3, 126.4, 124.8, 115.4, 114.2, 55.6, 17.5; HRMS (ESI Q-TOF) m/z: calcd for $C_{14}H_{14}N_2O$ $[M+H]^+$ 227.1178; found 227.1171.



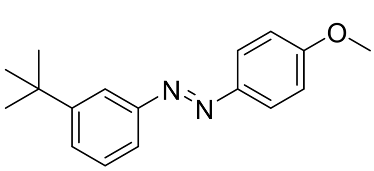
1-(2-Fluorophenyl)-2-(4-methoxyphenyl)diazene (3al): Orange solid (23.5 mg, 68% yield); m.p. 98-100 °C; R_f = 0.48 (petroleum ether: ethyl acetate = 50: 1); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.98 (d, J = 9.0 Hz, 2H), 7.76 (t, J = 7.8 Hz, 1H), 7.47 – 7.40 (m, 1H), 7.28 – 7.20 (m, 2H), 7.04 (d, J = 9.0 Hz, 2H), 3.93 (s, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 162.5, 159.9(d, J = 262.5 Hz)， 147.3, 140.8(d, J = 6.3 Hz), 131.7 (d, J = 8.8 Hz), 125.2, 124.3(d, J = 3.8 Hz), 117.8, 117.0 (d, J = 18.8 Hz), 114.3, 55.6; ^{19}F NMR (471 MHz, Chloroform-*d*) δ -125.03 – -125.13 (m); HRMS (ESI Q-TOF) m/z: calcd for $C_{13}H_{11}FN_2O$ $[M+H]^+$ 231.0929; found 231.0927.



1-(3-Chlorophenyl)-2-(4-methoxyphenyl)diazene (3am): Orange solid (25.8 mg, 70% yield); m.p. 128-130 °C; R_f = 0.48 (petroleum ether: ethyl acetate = 50: 1); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.95 (d, J = 9.0 Hz, 2H), 7.89 (t, J = 1.9 Hz, 1H), 7.81 (d, J = 7.6 Hz, 1H), 7.48 – 7.42 (m, 2H), 7.05 (d, J = 9.0 Hz, 2H), 3.93 (s, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 162.5, 153.6, 146.8, 135.1, 130.08, 130.1, 125.1, 122.1, 121.5, 114.3, 55.7; HRMS (ESI Q-TOF) m/z: calcd for $C_{13}H_{11}ClN_2O$ $[M+H]^+$ 247.0632; found 247.0629.

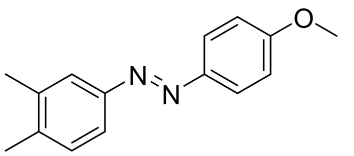


1-(4-Methoxyphenyl)-2-(m-tolyl)diazene (3an): Orange solid (20.7 mg, 61% yield); m.p. 78-80 °C R_f = 0.48 (petroleum ether: ethyl acetate = 50: 1); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.94 (d, J = 9.0 Hz, 2H), 7.72 (d, J = 1.8 Hz, 2H), 7.42 (dd, J = 8.4, 7.5 Hz, 1H), 7.29 (s, 1H), 7.04 (d, J = 9.0 Hz, 2H), 3.92 (s, 3H), 2.48 (s, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 162.0, 152.9, 147.1, 138.9, 131.2, 128.9, 124.7, 122.6, 120.2, 114.2, 55.6, 21.4; HRMS (ESI Q-TOF) m/z: calcd for $C_{14}H_{14}N_2O$ $[M+H]^+$ 227.1178; found 227.1174.

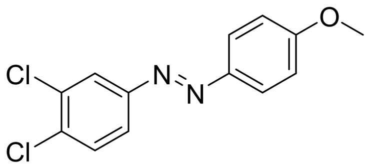


1-(3-(*tert*-Butyl)phenyl)-2-(4-methoxyphenyl)diazene (3ao): Orange solid (21.3 mg, 53% yield); m.p.

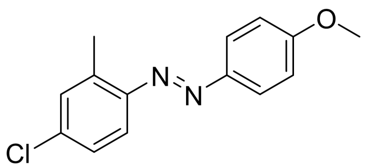
68-70 °C; R*f* = 0.48 (petroleum ether: ethyl acetate = 50: 1); ^{1}H NMR (500 MHz, Chloroform-*d*) *δ* 7.95 (d, *J* = 8.9 Hz, 3H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.51 (d, *J* = 7.0 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 1H), 7.05 (d, *J* = 8.9 Hz, 2H), 3.92 (s, 3H), 1.43 (s, 9H); ^{13}C NMR (125 MHz, Chloroform-*d*) *δ* 161.9, 152.8, 152.3, 147.1, 128.7, 127.5, 124.7, 120.7, 118.8, 114.2, 55.6, 35.0，31.4; HRMS (ESI Q-TOF) m/z: calcd for $C_{17}H_{20}N_2O$ $[M+H]^+$ 269.1648; found 269.1643.



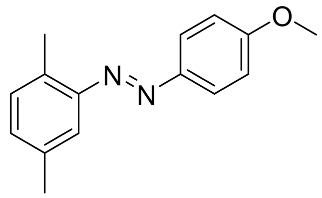
1-(3,4-Dimethylphenyl)-2-(4-methoxyphenyl)diazene (3ap): Orange solid (18.4 mg, 51% yield); m.p. 78-80 °C; R*f* = 0.49 (petroleum ether: ethyl acetate = 50: 1); ^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 7.92 (d, *J* = 9.0 Hz, 2H), 7.71 – 7.63 (m, 2H), 7.30 – 7.27 (m, 1H), 7.05 – 7.01 (m, 2H), 3.91 (s, 3H), 2.38 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) *δ* 161.8, 151.2, 147.1, 1396, 137.4, 130.2, 124.5, 123.2, 120.6, 114.2, 55.6, 19.9, 19.9; HRMS (ESI Q-TOF) m/z: calcd for $C_{15}H_{16}N_2O$ $[M+H]^+$ 241.1335; found 241.1331.



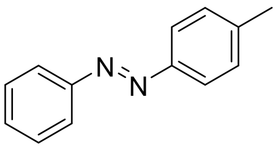
1-(3,4-Dichlorophenyl)-2-(4-methoxyphenyl)diazene (3aq): Orange solid (22.3 mg, 58% yield); m.p. 178-180 °C; R*f* = 0.48 (petroleum ether: ethyl acetate = 50: 1); ^{1}H NMR (500 MHz, Chloroform-*d*) *δ* 8.00 (s, 1H), 7.94 (d, *J* = 9.0 Hz, 2H), 7.77 (d, *J* = 8.5 Hz, 1H), 7.60 (d, *J* = 8.5 Hz, 1H), 7.04 (d, *J* = 9.0 Hz, 2H), 3.93 (s, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) *δ* 162.7, 151.7, 146.7, 134.1, 133.4, 130.8, 125.2, 123.6, 122.6, 114.4, 55.7; HRMS (ESI Q-TOF) m/z: calcd for $C_{13}H_{10}Cl_2N_2O$ $[M+H]^+$ 281.0242; found 281.0234.



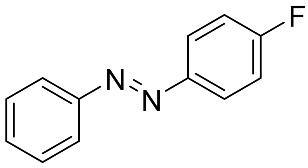
1-(4-Chloro-2-methylphenyl)-2-(4-methoxyphenyl)diazene (3ar): Orange solid (19.5 mg, 50% yield); m.p. 188-190 °C; R*f* = 0.48 (petroleum ether: ethyl acetate = 50: 1); ^{1}H NMR (500 MHz, Chloroform-*d*) *δ* 7.93 (d, *J* = 8.9 Hz, 2H), 7.60 (d, *J* = 8.6 Hz, 1H), 7.34 (s, 1H), 7.26 – 7.23 (m, 1H), 7.04 (d, *J* = 8.9 Hz, 2H), 3.92 (s, 3H), 2.70 (s, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) *δ* 162.1, 149.2, 147.3, 139.3, 135.6, 130.9, 126.7, 124.9, 116.8, 114.3, 55.6, 17.4; HRMS (ESI Q-TOF) m/z: calcd for $C_{14}H_{13}ClN_2O$ $[M+H]^+$ 261.0789; found 261.0786.



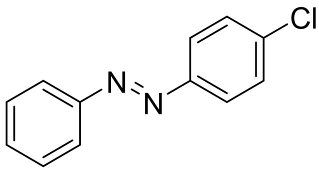
1-(2,5-Dimethylphenyl)-2-(4-methoxyphenyl)diazene (3as): Orange solid (19.8 mg, 55% yield); m.p. 80.0 – 82.0 ºC; R$_f$ = 0.48 (petroleum ether: ethyl acetate = 50: 1); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.96 – 7.92 (m, 2H), 7.44 (d, J = 1.9 Hz, 1H), 7.24 (d, J = 7.7 Hz, 1H), 7.18 (dd, J = 7.7, 1.9 Hz, 1H), 7.04 (d, J = 9.0 Hz, 2H), 3.92 (s, 3H), 2.68 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 161.8, 150.6, 147.5, 136.1, 134.6, 131.2, 131.0, 124.7, 115.7, 114.2, 55.6, 21.1, 17.1; HRMS (ESI Q-TOF) m/z: calcd for $C_{15}H_{16}N_2O$ [M+H]$^+$ 241.1335; found 241.1325.



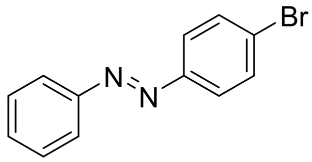
1-Phenyl-2-(p-tolyl)diazene (3ba)[2]: Orange solid (18.5 mg, 63% yield); m.p. 65-67 °C; R$_f$ = 0.52 (petroleum ether: ethyl acetate = 100: 1); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.95 – 7.91 (m, 2H), 7.86 (d, J = 8.2 Hz, 2H), 7.54 (t, J = 7.4 Hz, 2H), 7.49 (d, J = 7.0 Hz, 1H), 7.34 (d, J = 8.0 Hz, 2H), 2.47 (s, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 152.7, 150.8, 141.6, 130.7, 129.8, 129.1, 122.9, 122.7, 21.5; HRMS (ESI Q-TOF) m/z: calcd for $C_{13}H_{12}N_2$ [M]$^+$ 196.1000; found 196.0997.



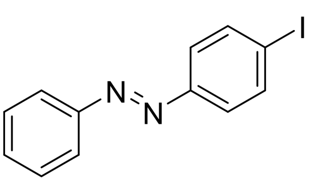
1-(4-Fluorophenyl)-2-phenyldiazene (3bb)[2]: Orange solid (19.2 mg, 64% yield); m.p. 76-78 °C; R$_f$ = 0.50 (petroleum ether: ethyl acetate = 100: 1); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.03 – 7.94 (m, 4H), 7.59 – 7.50 (m, 3H), 7.24 (t, J = 8.6 Hz, 2H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 164.4 (d, J = 250.0 Hz), 152.5, 149.2 (d, J = 2.5 Hz), 131.1, 129.2, 124.9 (d, J = 8.8 Hz), 122.9, 116.1 (d, J = 22.5 Hz); ^{19}F NMR (471 MHz, Chloroform-*d*) δ -109.28. HRMS (ESI Q-TOF) m/z: calcd for $C_{12}H_9FN_2$ [M]$^+$ 200.0750; found 200.0754.



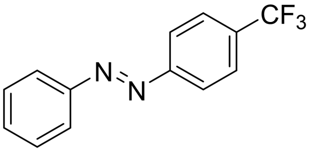
1-(4-Chlorophenyl)-2-phenyldiazene (3bc)[2]: Orange solid (19.4 mg, 60% yield); m.p. 81-83 °C; R$_f$ = 0.50 (petroleum ether: ethyl acetate = 100: 1); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.96 (d, J = 7.3 Hz, 2H), 7.92 (d, J = 8.7 Hz, 2H), 7.58 – 7.51 (m, 5H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 152.5, 151.0, 137.0, 131.3, 129.4, 129.2, 124.2, 123.0; HRMS (ESI Q-TOF) m/z: calcd for $C_{12}H_9ClN_2$ $[M]^+$ 216.0454; found 216.0452.



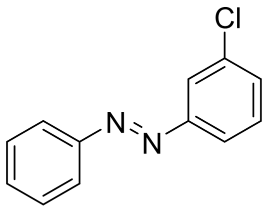
1-(4-Bromophenyl)-2-phenyldiazene (3bd)[2]: Orange solid (22.6 mg, 58% yield); m.p. 90-92 °C; R_f = 0.50 (petroleum ether: ethyl acetate = 100: 1); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 6.9 Hz, 2H), 7.83 (d, *J* = 8.6 Hz, 2H), 7.68 (d, *J* = 8.7 Hz, 2H), 7.53 (dd, *J* = 10.6, 7.2 Hz, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 152.5, 151.4, 132.4, 131.4, 129.2, 125.4, 124.4, 123.0; HRMS (ESI Q-TOF) m/z: calcd for $C_{12}H_9BrN_2$ $[M]^+$ 259.9949; found 259.9945.



1-(4-Iodophenyl)-2-phenyldiazene (3be)[2]: Orange solid (25.3 mg, 55% yield); m.p. 91-93 °C; R_f = 0.52 (petroleum ether: ethyl acetate = 100: 1); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 6.8 Hz, 2H), 7.89 (d, *J* = 8.7 Hz, 2H), 7.68 (d, *J* = 8.7 Hz, 2H), 7.57-7.51 (m, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 152.5, 152.0, 138.4, 131.4, 129.2, 124.5, 123.0; HRMS (ESI Q-TOF) m/z: calcd for $C_{12}H_9IN_2$ $[M]^+$ 307.9810; found 307.9805.

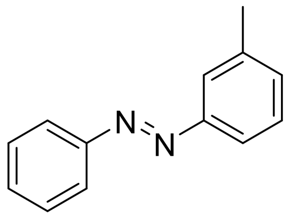


1-Phenyl-2-(4-(trifluoromethyl)phenyl)diazene (3bf)[2]: Orange solid 19.9 mg, 53% yield); m.p. 81-83 °C; R_f = 0.52 (petroleum ether: ethyl acetate = 100: 1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 8.2 Hz, 2H), 7.99 (dd, *J* = 7.8, 1.9 Hz, 2H), 7.81 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 154.4, 152.4, 132.2 (q, *J* = 40.0 Hz), 131.8, 129.2, 126.3 (q, *J* = 5 Hz), 124.0 (q, *J* = 337.5 Hz), 123.2, 123.0; ^{19}F NMR (377 MHz, Chloroform-*d*) δ -62.53. HRMS (ESI Q-TOF) m/z: calcd for $C_{13}H_9F_3N_2$ $[M]^+$ 250.0718; found 250.0715.

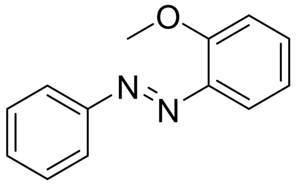


1-(3,4-Dimethylphenyl)-2-phenyldiazene (3bg): Orange solid (18.8 mg, 58% yield); m.p. 82-84 °C; R_f = 0.48 (petroleum ether: ethyl acetate = 100: 1); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.98 – 7.92 (m, 3H), 7.87 (d, *J* = 6.1 Hz, 1H), 7.55 (dd, *J* = 10.1, 7.3 Hz, 3H), 7.49 (d, *J* = 6.1 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$)

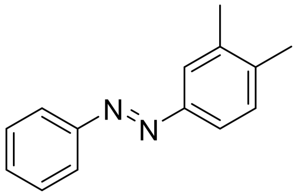
δ 153.5, 152.4, 135.2, 131.6, 130.7, 130.2, 129.2, 123.1, 122.4, 121.8; HRMS (ESI Q-TOF) m/z: calcd for $C_{12}H_9ClN_2$ $[M+H]^+$ 217.0527; found 217.0523.



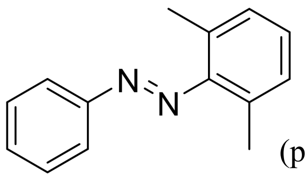
1-Phenyl-2-(m-tolyl)diazene (3bh)[2]: Orange solid (17.1 mg, 58% yield); m.p. 65-67 °C; R_f = 0.48 (petroleum ether: ethyl acetate = 100: 1); ^{1}H NMR (500 MHz, Chloroform-*d*) *δ* 7.98 – 7.94 (m, 2H), 7.77 (s, 2H), 7.56 (t, *J* = 7.4 Hz, 2H), 7.50 (t, *J* = 7.2 Hz, 1H), 7.47 – 7.42 (m, 1H), 7.33 (d, *J* = 7.4 Hz, 1H), 2.50 (s, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) *δ* 152.8, 152.7, 139.0, 131.8, 130.9, 129.1, 128.9, 123.0, 122.8, 120.5, 21.4; HRMS (ESI Q-TOF) m/z: calcd for $C_{13}H_{12}N_2$ $[M]^+$ 196.1000; found 196.0995.



1-(3-Chlorophenyl)-2-phenyldiazene (3bi)[3]: Orange solid (22.3 mg, 70% yield); m.p. 56-58 °C; R_f = 0.48 (petroleum ether: ethyl acetate = 50: 1); ^{1}H NMR (500 MHz, Chloroform-*d*) *δ* 7.99 – 7.94 (m, 2H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 2H), 7.51 – 7.45 (m, 2H), 7.15 – 7.11 (m, 1H), 7.08 – 7.03 (m, 1H), 4.05 (s, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) *δ* 157.0, 153.2, 142.3, 132.5, 130.8, 129.1, 123.0, 120.8, 117.0, 112.8, 56.4; HRMS (ESI Q-TOF) m/z: calcd for $C_{13}H_{12}N_2O$ $[M+H]^+$ 213.1028; found 213.1022.

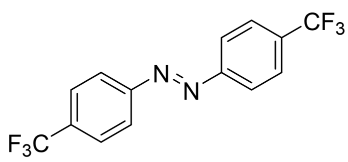


1-(3,4-Dimethylphenyl)-2-phenyldiazene (3bj)[3]: Orange solid (17.6 mg, 56% yield); mp 78-80 °C; R_f = 0.48 (petroleum ether: ethyl acetate = 100: 1); ^{1}H NMR (500 MHz, Chloroform-*d*) *δ* 7.92 (d, *J* = 8.2 Hz, 2H), 7.74 (s, 1H), 7.72 – 7.69 (m, 1H), 7.53 (t, *J* = 7.5 Hz, 2H), 7.48 (t, *J* = 7.2 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 2.39 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) *δ* 152.8, 151.2, 140.3, 137.5, 130.7, 130.4, 129.1, 123.6, 122.8, 121.0, 20.0; HRMS (ESI Q-TOF) m/z: calcd for $C_{14}H_{14}N_2$ $[M+H]^+$ 211.1229; found 211.1231.

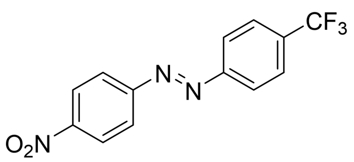


1-(2,6-Dimethylphenyl)-2-phenyldiazene (3bk): Orange solid (22.3 mg, 54% yield); mp 76-78 °C; R_f = 0.48 (petroleum ether: ethyl acetate = 100: 1); ^{1}H NMR (500 MHz, Chloroform-*d*) *δ* 7.97 – 7.92 (m, 2H), 7.60 – 7.53 (m, 3H), 7.17 (t, *J* = 4.6 Hz, 3H), 2.39 (s, 6H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 152.8, 151.5, 131.1, 130.6, 129.1, 128.1, 122.5, 18.8; HRMS (ESI Q-TOF) m/z: calcd for $C_{14}H_{14}N_2$ [M+H]$^+$ 211.1229; found 211.1226.

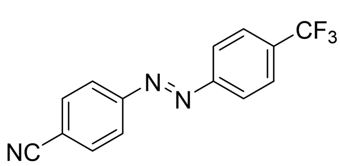
1,2-Bis(4-(trifluoromethyl)phenyl)diazene (3ca): Orange solid (25.3 mg, 53% yield); R_f = 0.48 (petroleum ether: ethyl acetate = 100: 1); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.06 (d, J = 8.2 Hz, 4H), 7.83 (d, J = 8.3 Hz, 4H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 154.1, 133.0 (q, J = 32.5 Hz), 126.4 (q, J = 3.8 Hz), 123.8 (q, J = 270.0 Hz), 123.4; ^{19}F NMR (471 MHz, Chloroform-*d*) δ -62.67.



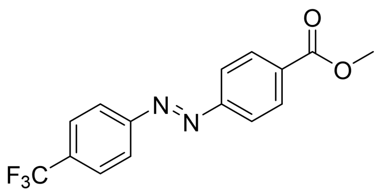
1-(4-Nitrophenyl)-2-(4-(trifluoromethyl)phenyl)diazene (3cb): Orange solid (19.9 mg, 45% yield); R_f = 0.40 (petroleum ether: ethyl acetate = 50: 1); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.44 (d, J = 9.0 Hz, 2H), 8.13 – 8.07 (m, 4H), 7.85 (d, J = 8.3 Hz, 2H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 155.3, 154.0, 149.2, 133.5 (q, J = 32.5 Hz), 126.5(q, J = 3.8 Hz), 124.8, 123.8, 123.7 (q, J = 271.3 Hz), 123.6, ; ^{19}F NMR (471 MHz, Chloroform-*d*) δ -62.71.



4-((4-(Trifluoromethyl)phenyl)diazenyl)benzonitrile (3cc): Orange solid (19.8 mg, 48% yield); R_f = 0.48 (petroleum ether: ethyl acetate = 50: 1); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.06 (d, J = 15.8 Hz, 4H), 7.85 (dd, J = 16.5, 8.4 Hz, 4H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 154.1, 154.0, 133.3 (q, J = 32.5 Hz), 133.3, 126.5(q, J = 3.8 Hz), 123.7(q, J = 271.3 Hz), 123.7, 123.5, 118.3, 114.8; ^{19}F NMR (471 MHz, Chloroform-*d*) δ -62.69.



Methyl -4-((4-(trifluoromethyl)phenyl)diazenyl)benzoate (3cd): Orange solid (23.1 mg, 50% yield); R_f = 0.47 (petroleum ether: ethyl acetate = 50: 1); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.24 (d, J = 8.5 Hz, 2H), 8.06 (d, J = 8.2 Hz, 2H), 8.01 (d, J = 8.5 Hz, 2H), 7.83 (d, J = 8.3 Hz, 2H), 4.00 (s, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 166.4, 154.8, 154.2, 133.3 (q, J = 32.5



Hz), 133.3, 130.7, 126.4(q, *J* = 3.8 Hz), 123.8(q, *J* = 271.3 Hz), 123.3, 122.7, 52.5; ^{19}F NMR (471 MHz, Chloroform-*d*) δ -62.62.

F. Potential application of this method

Typical procedure for preparation of 4aa: **3ae** (0.2 mmol), vinylene carbonate (0.4 mmol), $[RhCp^*Cl_2]_2$ (5 mol%), $AgSbF_6$ (30 mol%), NaOAc (30 mol%), DCE (1 mL) were stirred at 80 °C for 14 h. After the reaction was completed and cooled to room temperature, the reaction mixture was concentrated in vacuo. The crude residue was purified by column chromatography using silica gel and eluent (petroleum ether: ethyl acetate =5:1) to obtain **4aa** in 65% yield.

(5-Methoxy-2-(4-methoxyphenyl)-2*H*-indazol-3-yl)methanol (4aa): orange liquid (37.1 mg, 65% yield); R_f = 0.45 (petroleum ether: ethyl acetate = 5: 1); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 9.2 Hz, 1H), 7.58 (d, *J* = 8.9 Hz, 2H), 7.07 – 7.03 (m, 1H), 7.00 (d, *J* = 9.0 Hz, 2H), 6.90 (d, *J* = 2.3 Hz, 1H), 4.92 (s, 2H), 3.88 (s, 3H), 3.85 (s, 3H), 2.43 (s, 1H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 159.7, 155.4, 145.1, 132.9, 132.6, 126.6, 121.8, 121.7, 119.1, 114.3, 95.6, 55.6, 55.4, 54.2.

G. Control experiments

To investigate the reaction mechanism, we reacted phenylhydroxylamine **6a** (1 mmol, 109 mg) with 4-methoxyphenyl isocyanate **2a** (0.5 mmol, 74.5 mg), *t*-BuOLi (0.5 mmol, 40 mg), $PhI[4\text{-}OMe\text{-}Ph(CO)O]_2$ (0.1 mmol, 53.8 mg), and EA (4 mL) for 0.5 hours, as illustrated in Fig. 1. The reaction intermediates were identified using high-resolution mass spectrometry (HRMS), and their molecular weights were determined accordingly.

HRMS (ESI) of 4-methoxy-*N*-(((phenylamino)oxy)carbonyl)aniline **A**: calcd for $C_{14}H_{14}N_{2}O_{3}$ $[M+H]^+$ 259.1077; found 259.1072.

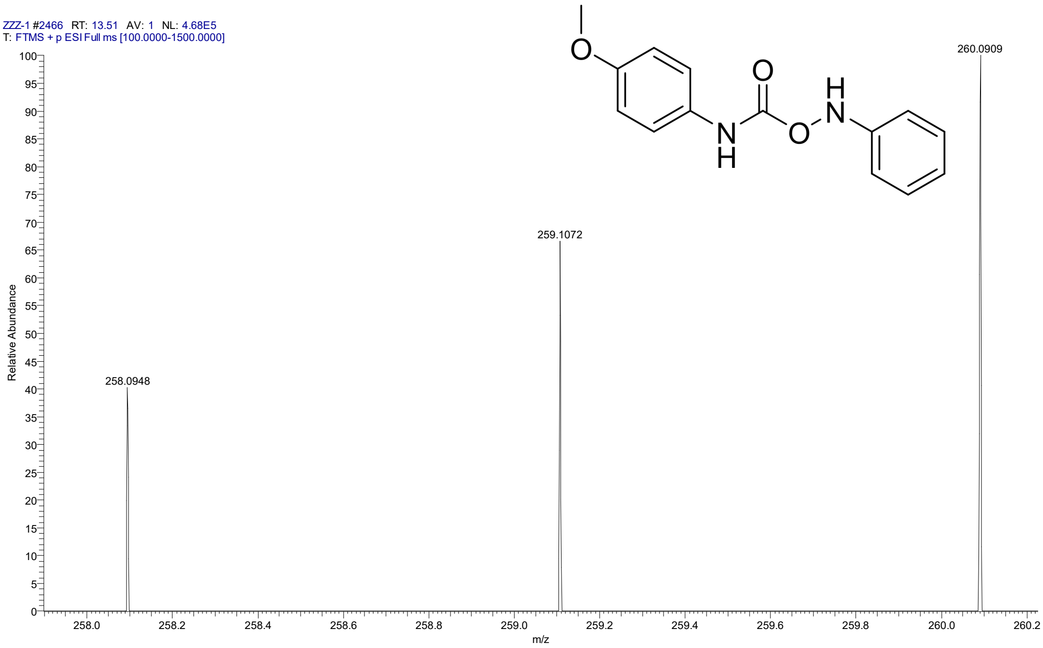
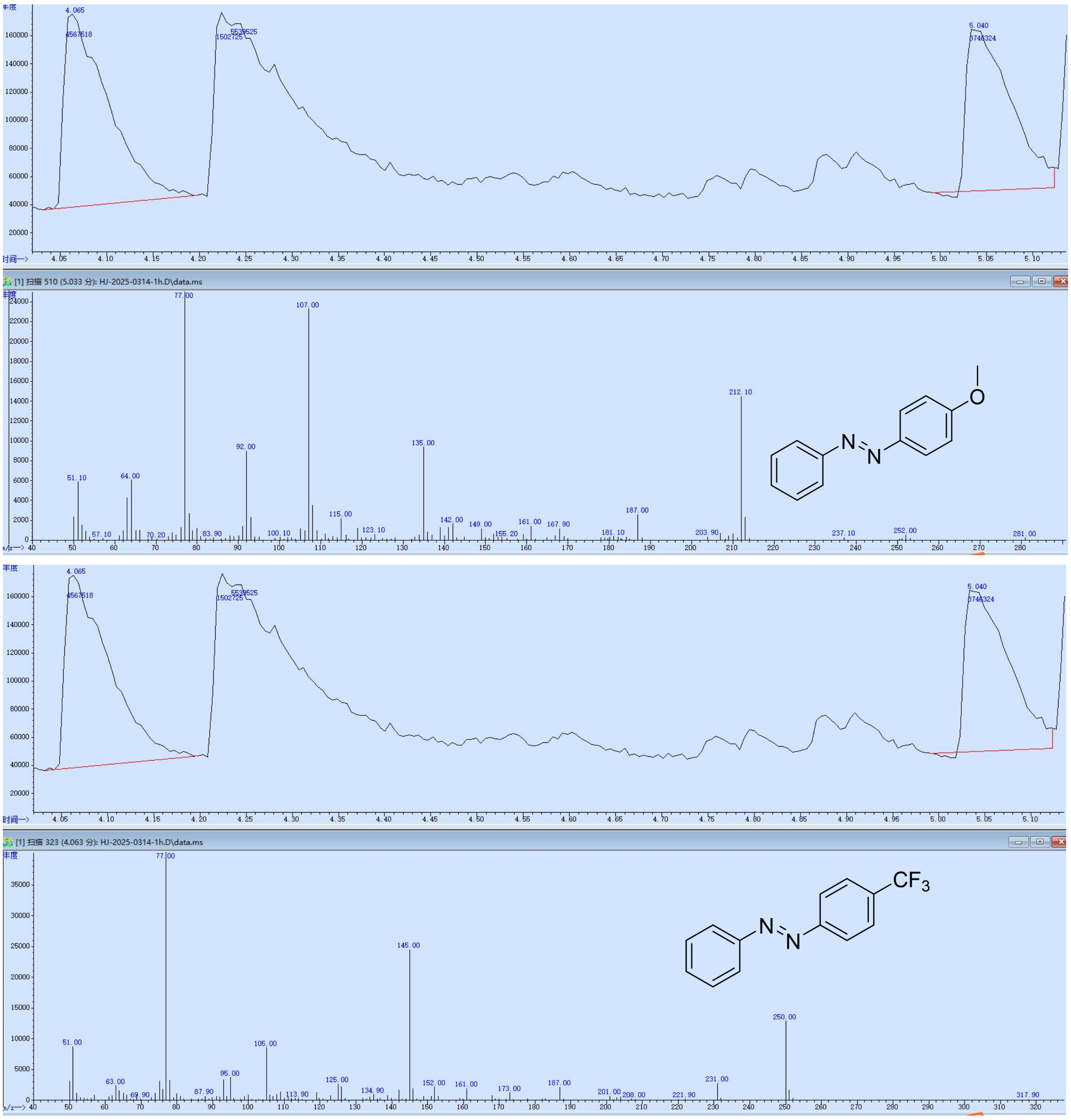


Figure 1. HRMS of Intermediates **A**

Experiment of competition experiment between 2a and 2f.

To a solution of aniline **1a** (0.3 mmol, 27.9 mg), 4-methoxyphenyl isocyanate **2a** (0.15 mmol, 22.4 mg), 4-trifluoromethylphenyl isocyanate **2f** (0.15 mmol, 28.1 mg), *t*-BuOLi (0.15 mmol, 0.12 g), and PhI[4-OMe-Ph(CO)O]$_2$ (0.3 mmol, 161.4 mg) in 2 mL of ethyl acetate, the reaction mixture was stirred at 80 °C for 1 hours. After completion, the mixture was cooled to room temperature. The ratio of peak areas of **3aa** and **3bg** was obtained as 1:1.2 by GC-MS.



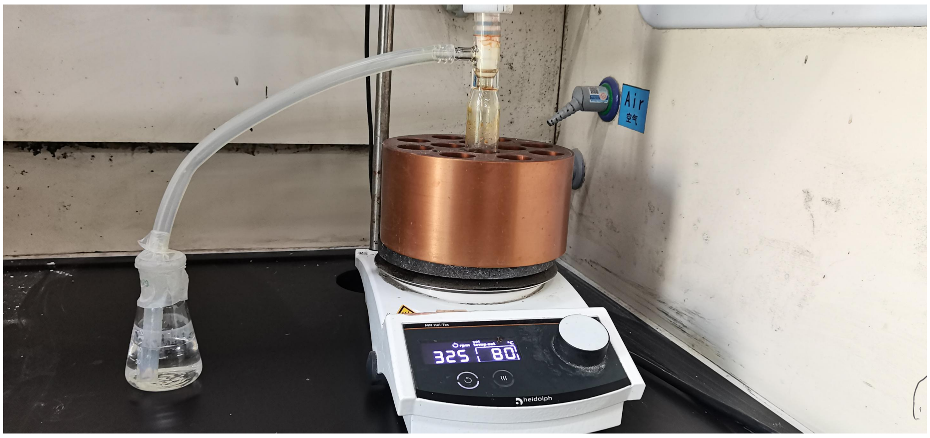
No	Peak Time	Peak Area	Peak Area Ratio
3aa	5.033 min	3746234	**3aa**：**3bf** 1：1.2
3bf	4.063 min	4567518	

Table 1. 3aa to **3bf** yield ratio

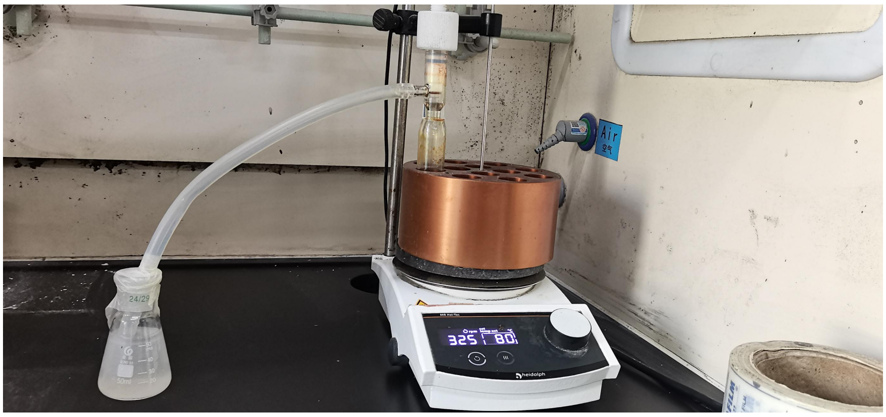
CO_2 verification experiment

To a solution of aniline **1a** (4 mmol, 0.37 g), 4-methoxyphenyl isocyanate **2a** (2 mmol, 0.30 g), *t*-BuOLi (2 mmol, 0.16 g), PhI[4-OMe-Ph(CO)O]$_2$ (4 mmol, 2.02 g) in EA (10 mL). The reaction mixture was reacted at 80 °C for 8 h and cooled to room temperature. The branch port of the closed tube was introduced into a pre-prepared clarified saturated clear Ca(OH)$_2$ solution using arubber hose. Slowly twist the cork and stop twisting the cork when there are stable and continuous bubbles, and the clarified $Ca(OH)_2$ solution graduallybecomes turbid after a continuous passage of the reacted gas mixture, which proves that CO_2 is produced during the reaction.

The diagram below shows the experimental setup:



Upon introduction of the gas mixture



References

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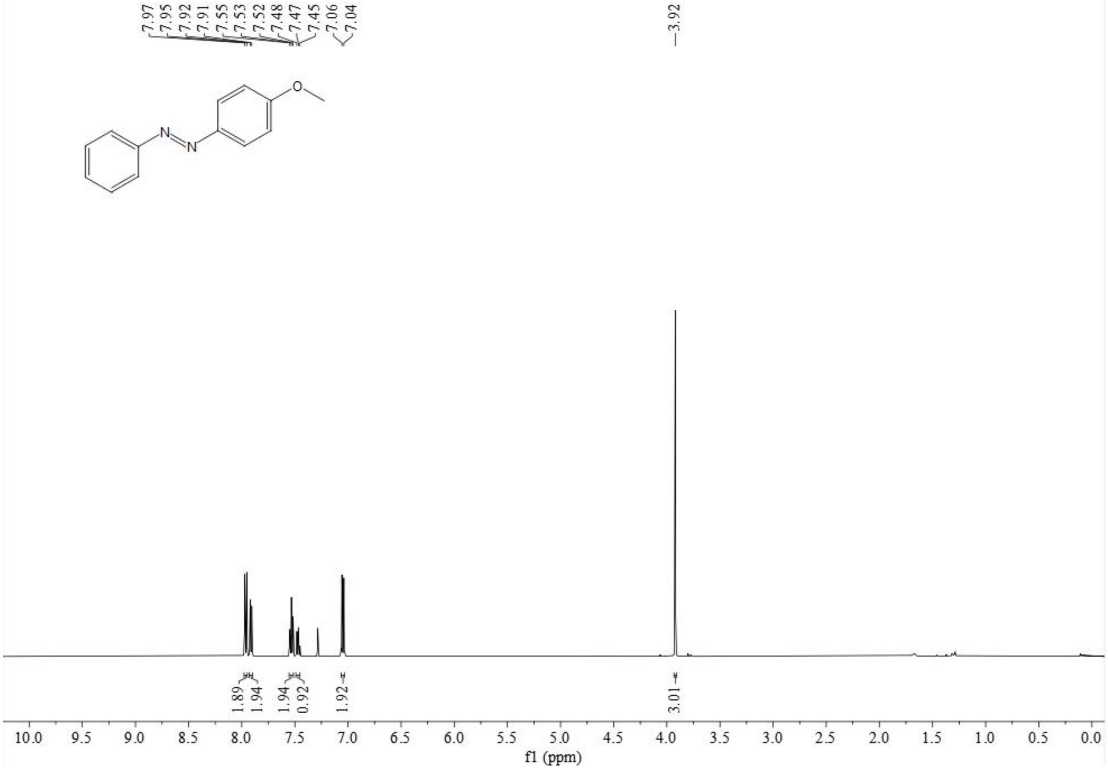
[2] Haiping Lv, Ronibala Devi Laishram, Jiayan Li, Photocatalyzed Oxidative Dehydrogenation of Hydrazobenzenes to Azobenzenes. *Green Chem.* 2019, **21**, 4055-4061.

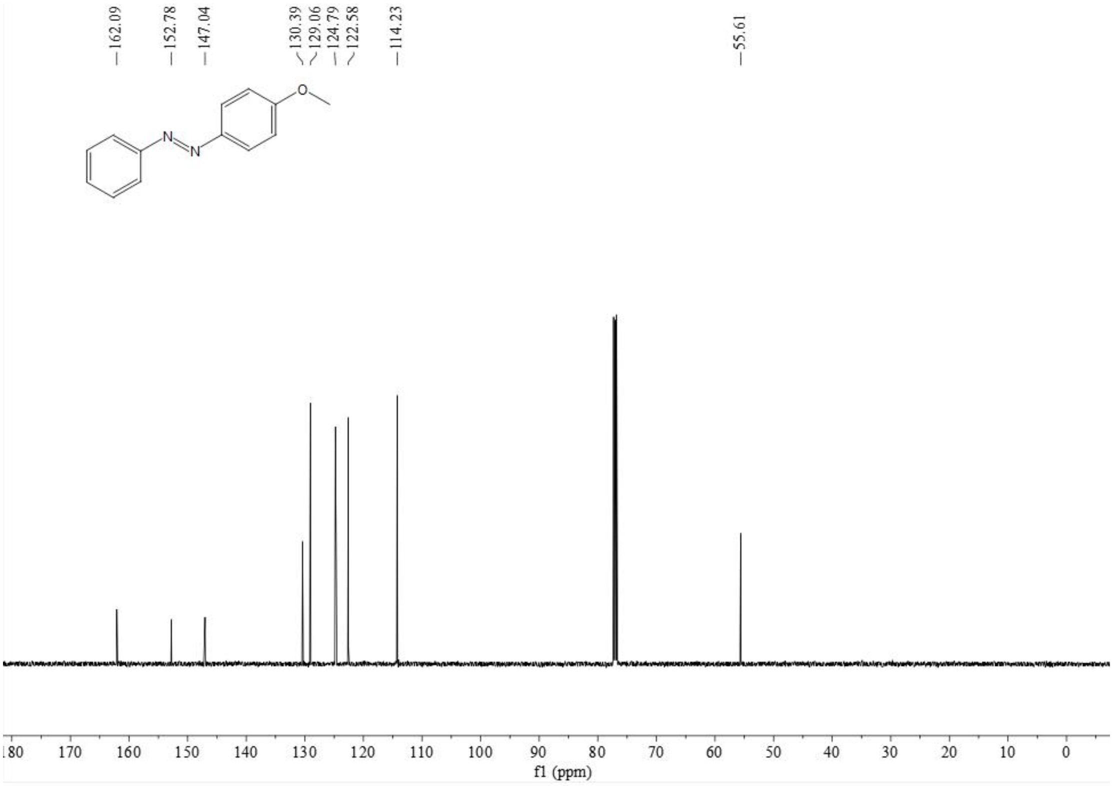
[3] Van Hieu Tran, Hee-Kwon Kim, Visible-Light-Driven SAQS-Catalyzed Aerobic Oxidative Dehydrogenation of Alkyl 2- Phenylhydrazinecarboxylates. *RSC Adv.* 2022, **12**, 30304-30309.

[4] L. Finck, M, Oestreich, Synthesis of Non-Symmetric Azoarenes by Palladium-Catalyzed Cross-Coupling of Silicon-Masked Diazenyl Anions and (Hetero)Aryl Halides. *Angew. Chem. Int. Ed*. 2022, **61**, e202210907.

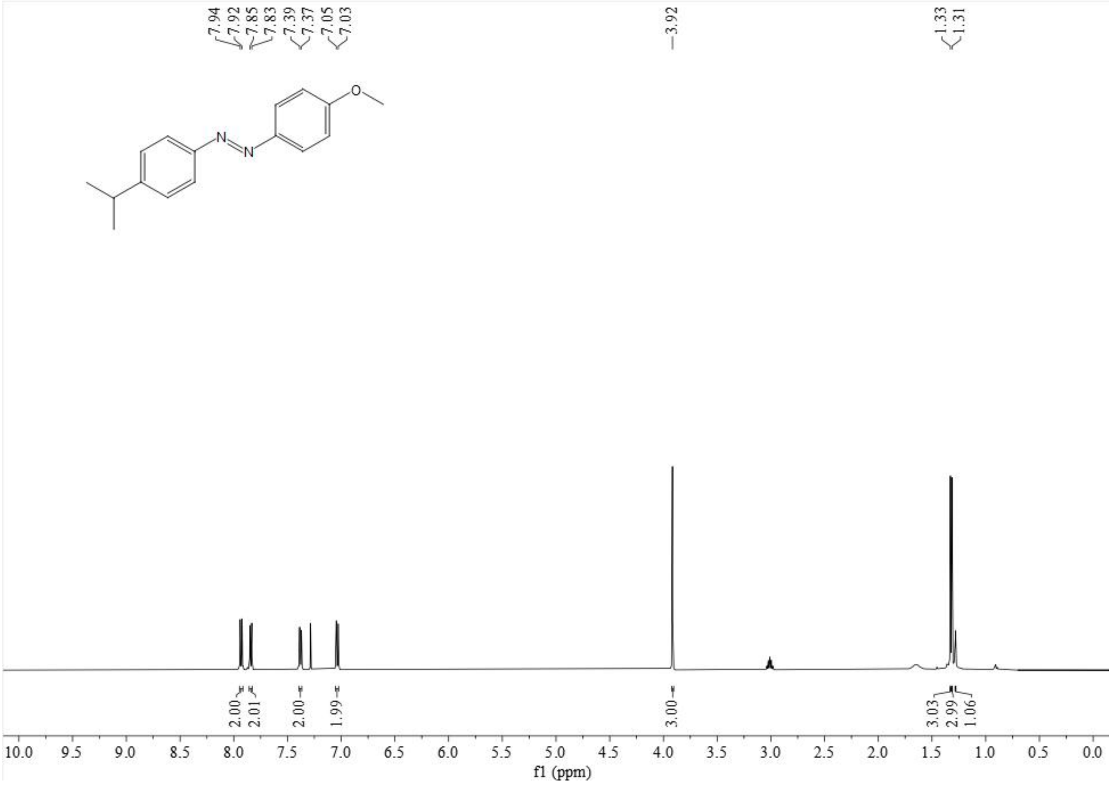
H. Copies of ^{1}H, ^{13}C and ^{19}F NMR spectra

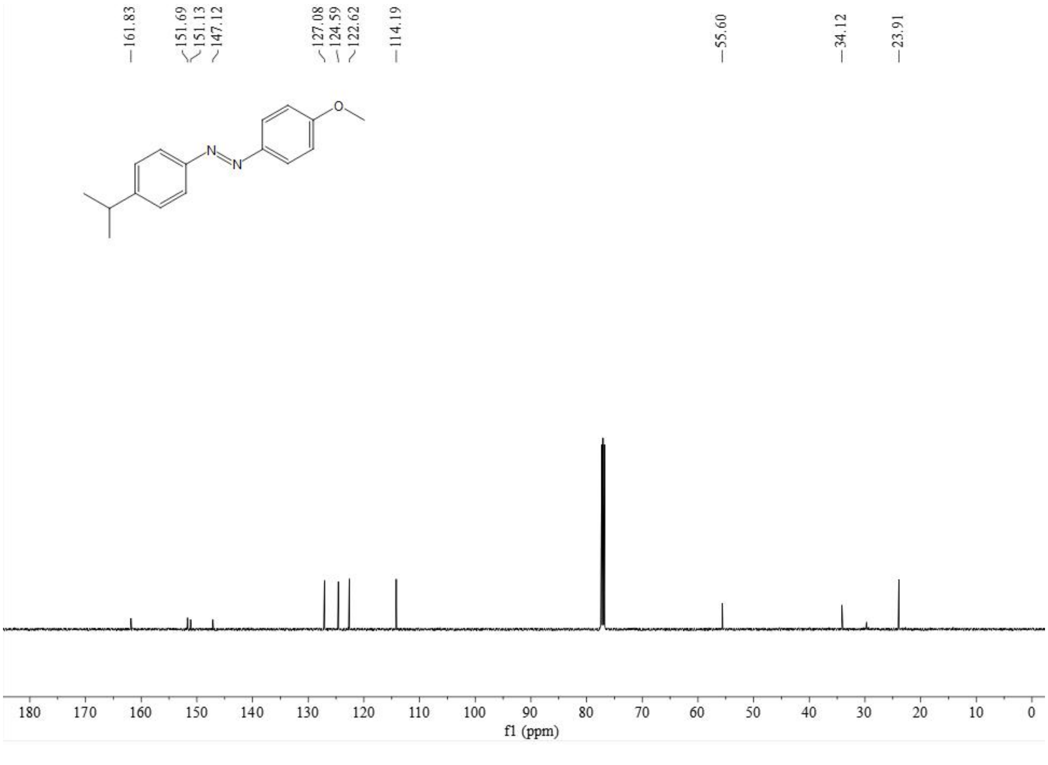
^{1}H NMR and ^{13}C NMR of 1-(4-Methoxyphenyl)-2-phenyldiazene 3aa (500 MHz, CDCl$_3$)



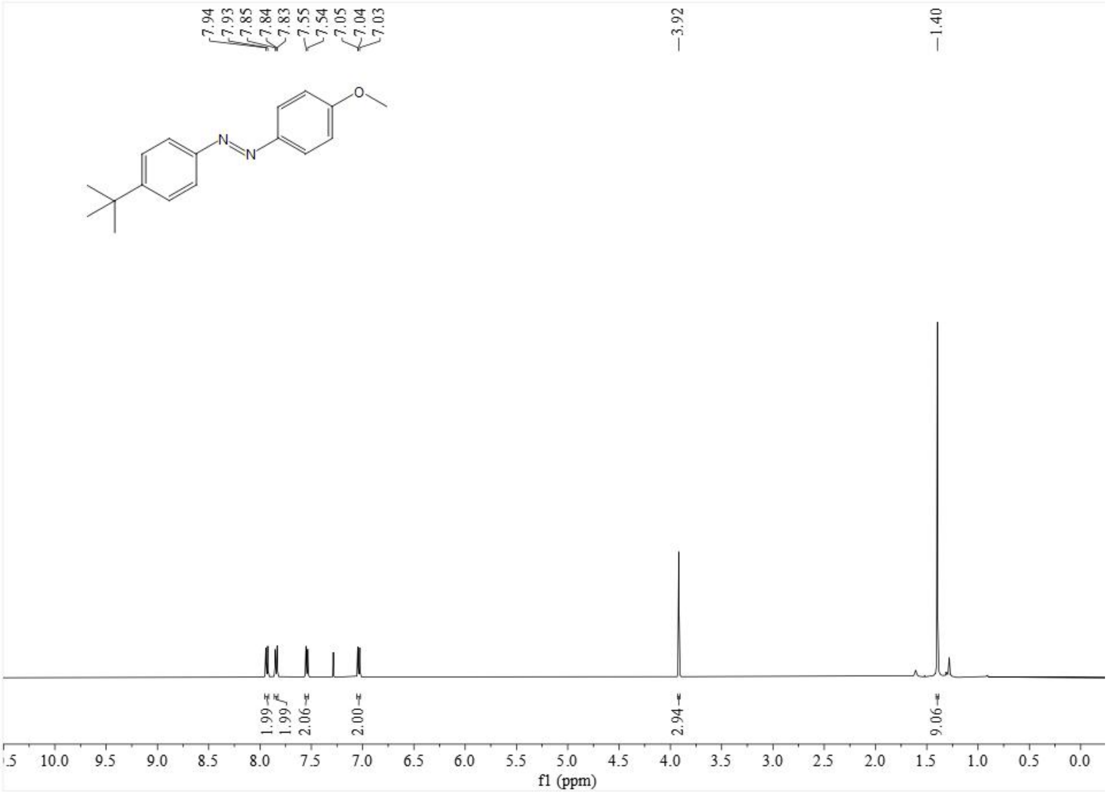


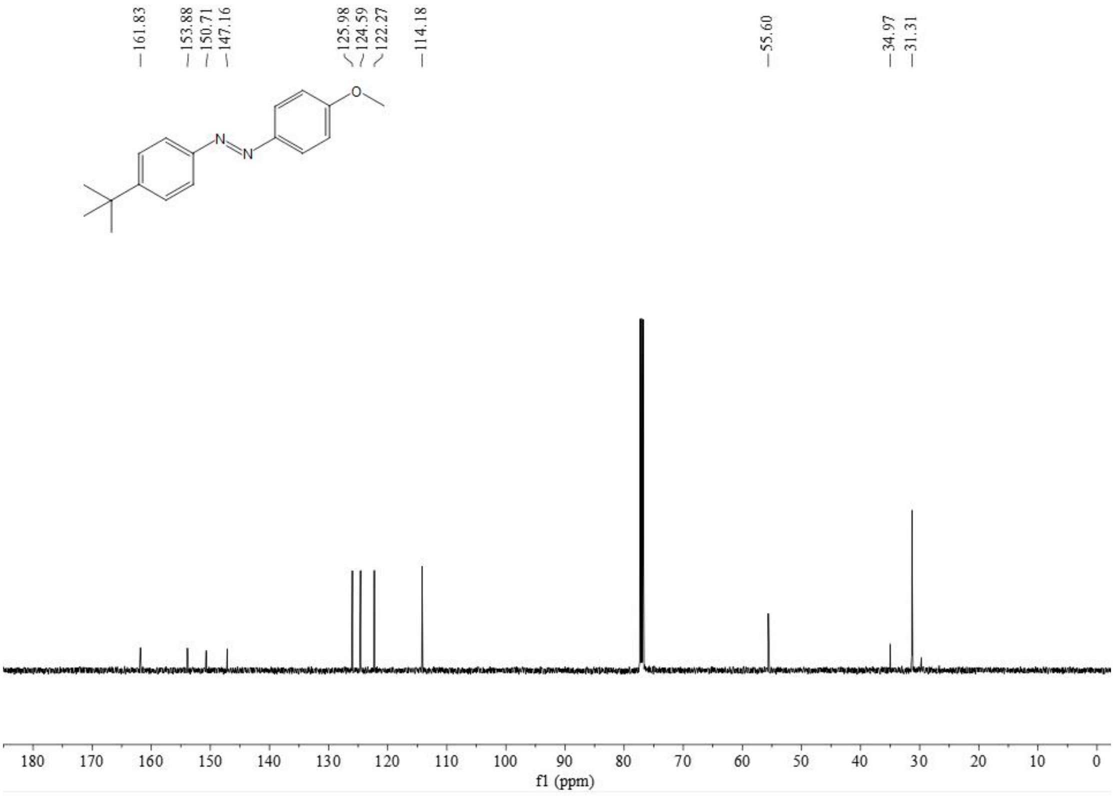
^1H NMR and ^{13}C NMR of 1-(4-Isopropylphenyl)-2-(4-methoxyphenyl) diazene 3ab (500 MHz, $CDCl_3$)



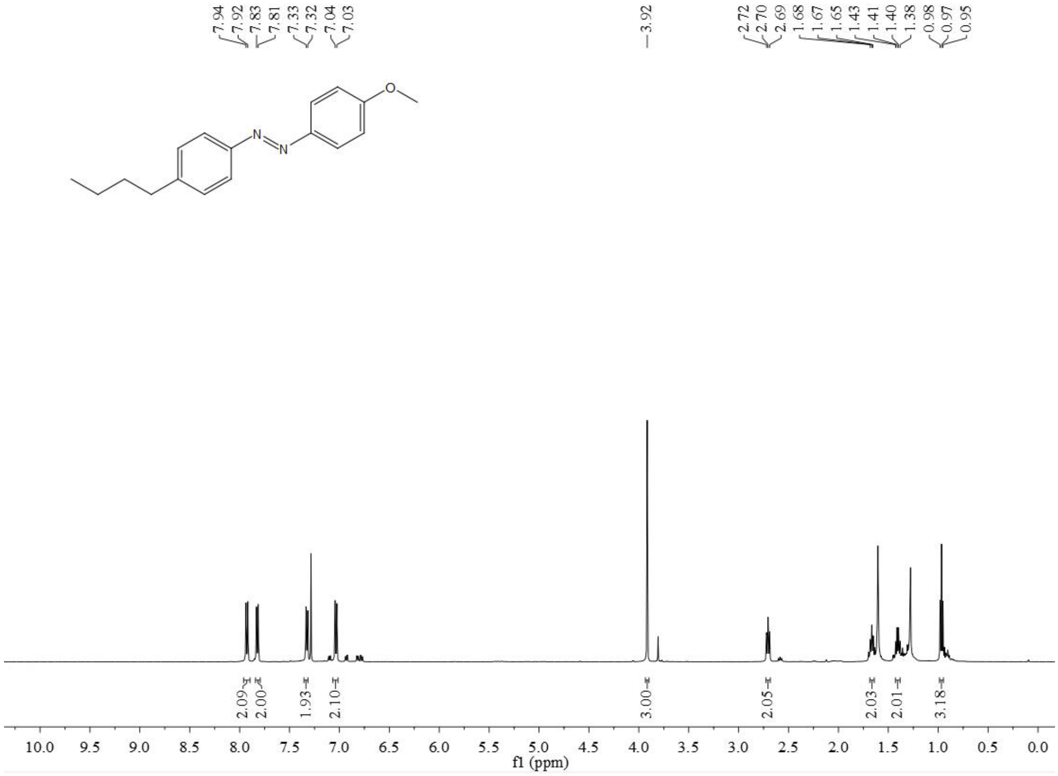


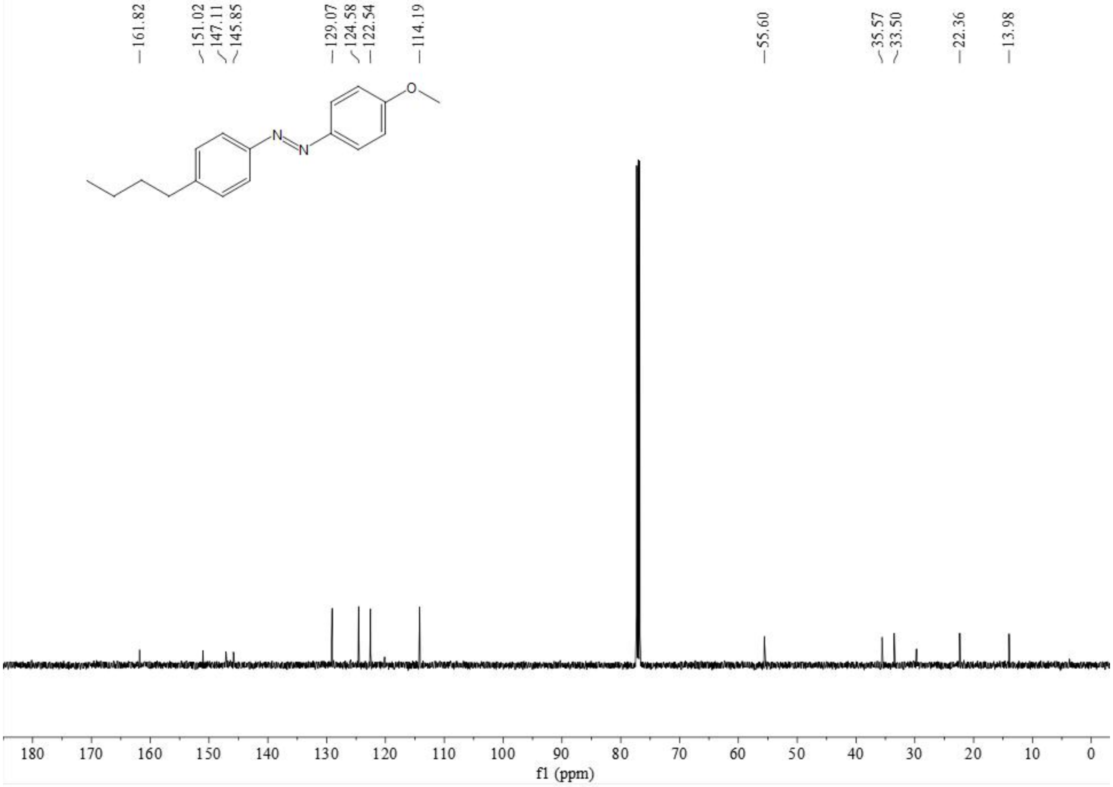
^{1}H NMR and ^{13}C NMR of 1-(4-(*tert*-Butyl)phenyl)-2-(4-methoxyphenyl)diazene 3ac (500 MHz, $CDCl_3$)



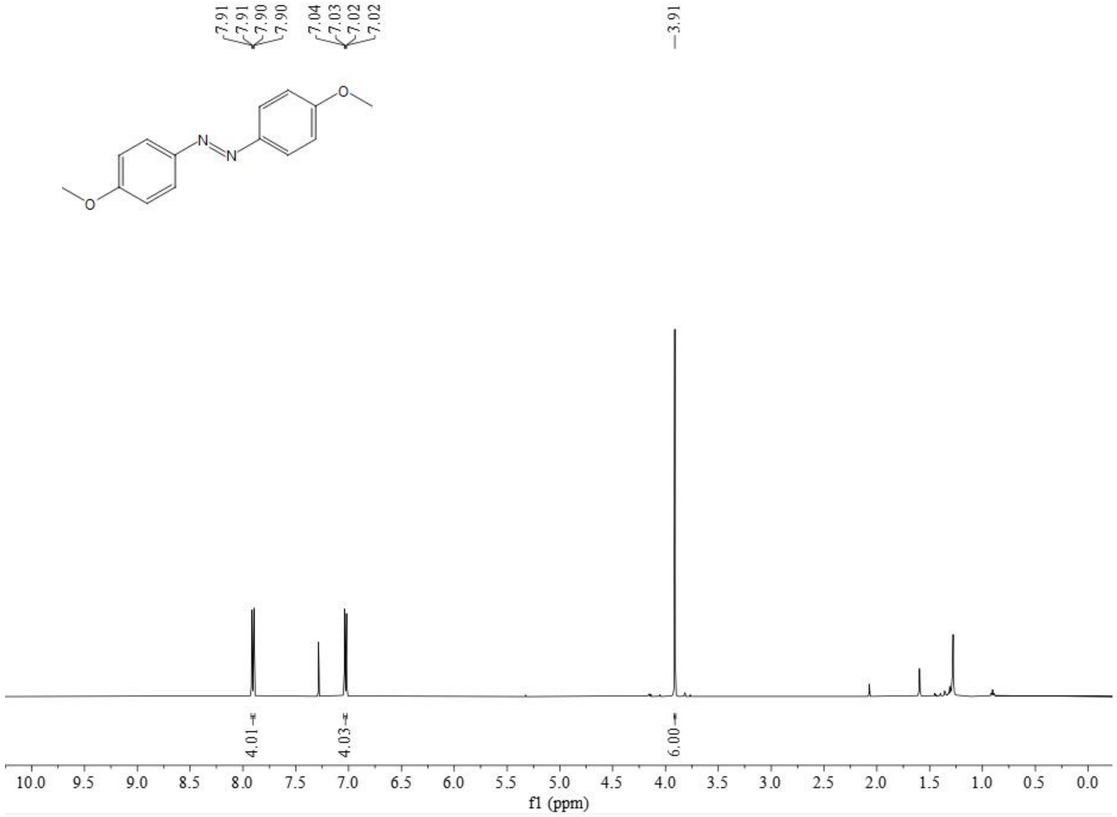


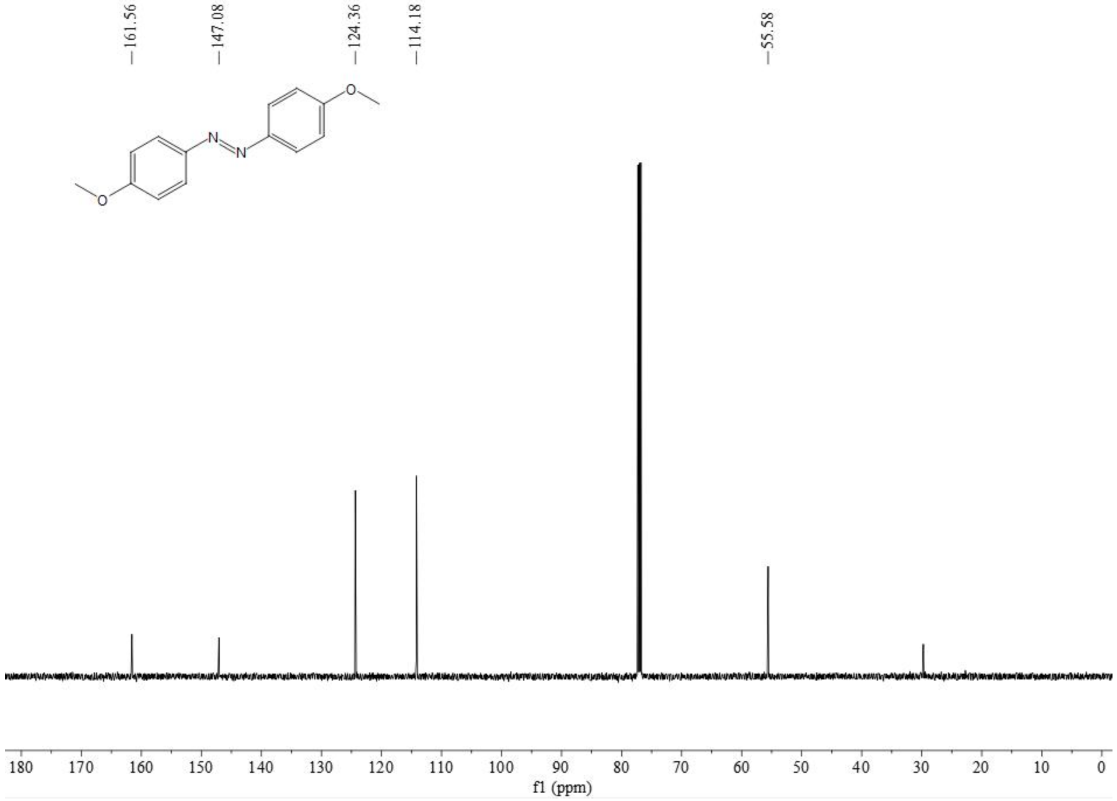
^{1}H NMR and ^{13}C NMR of 1-(4-Butylphenyl)-2-(4-methoxyphenyl)diazene 3ad (500 MHz, $CDCl_3$)



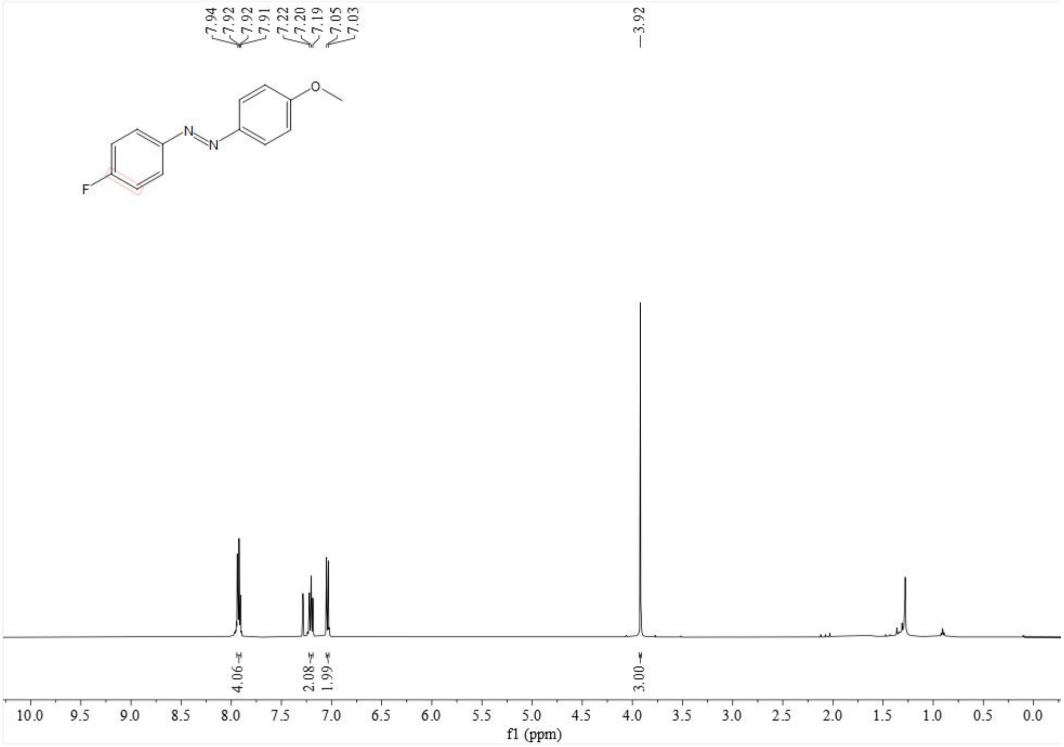


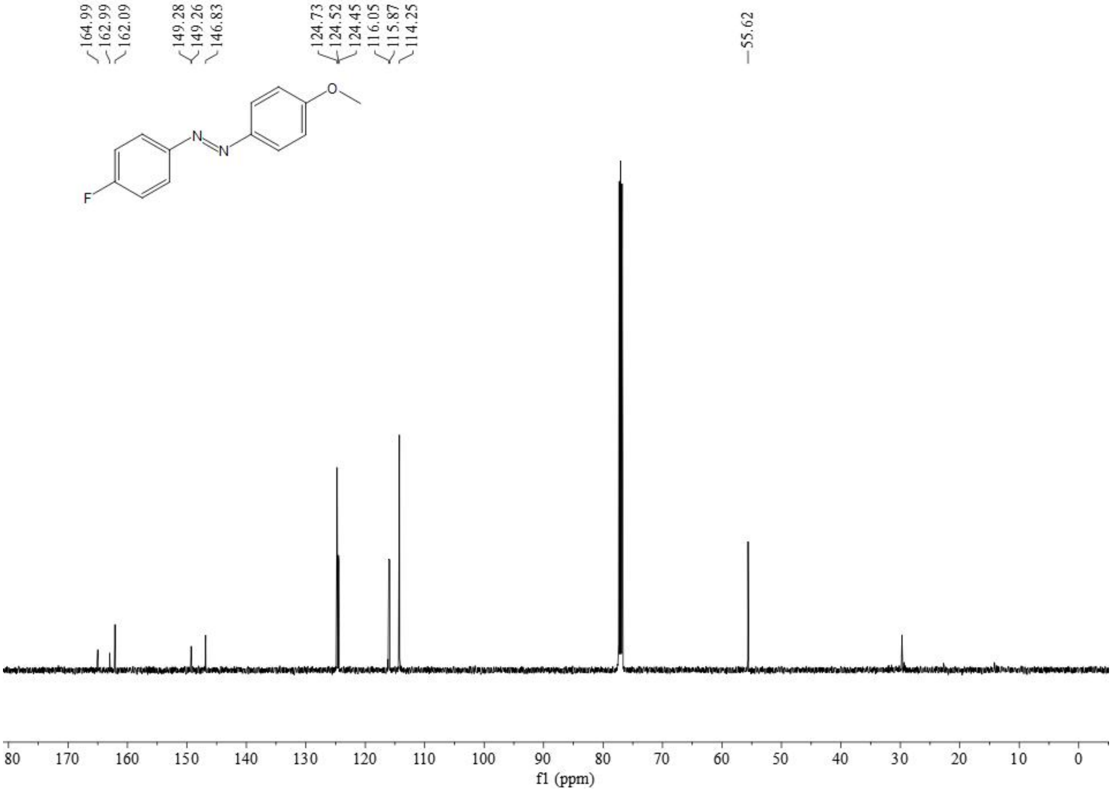
^{1}H NMR and ^{13}C NMR of 1,2-Bis(4-methoxyphenyl)diazene 3ae (500 MHz, CDCl$_3$)

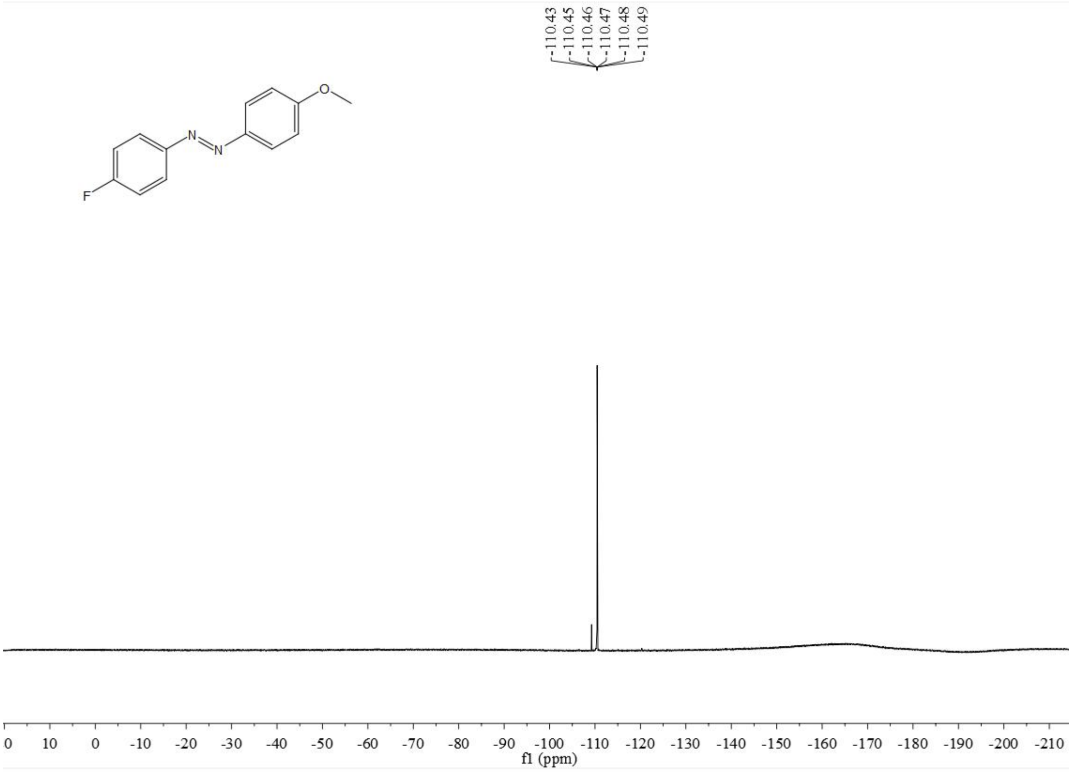




^{1}H NMR and ^{13}C NMR and 19F NMR of 1-(4-Fluorophenyl)-2-(4-methoxyphenyl) diazene 3af (500 MHz, CDCl$_3$)



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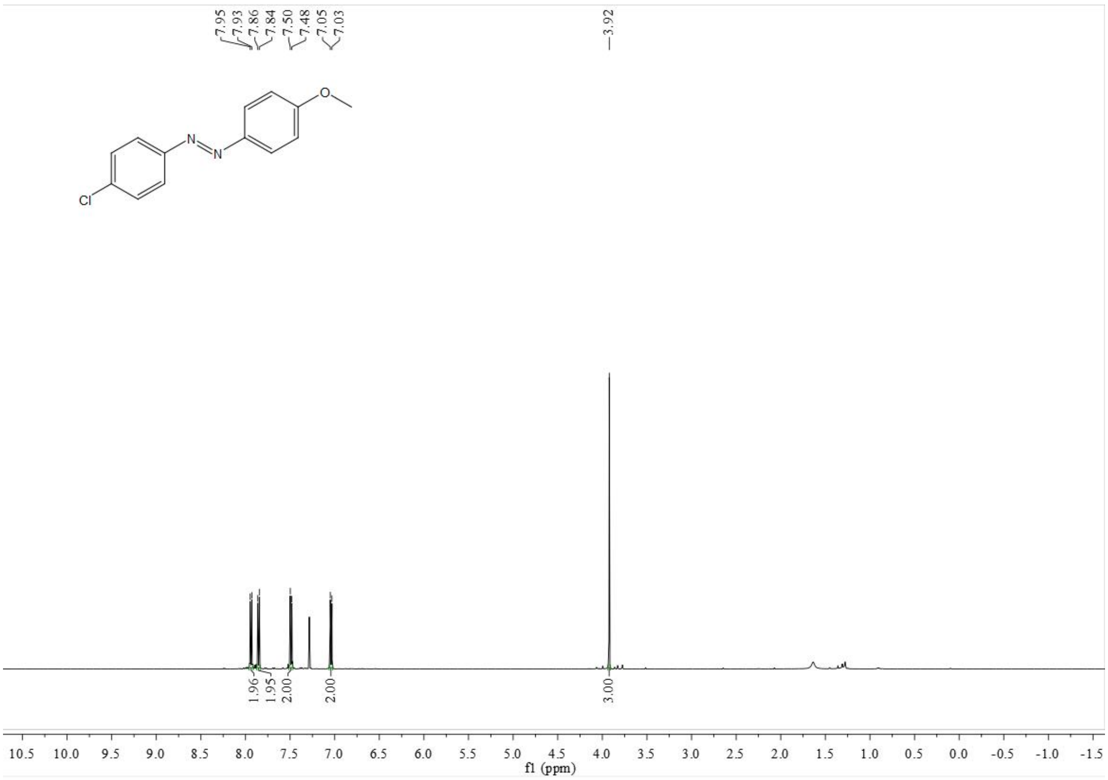
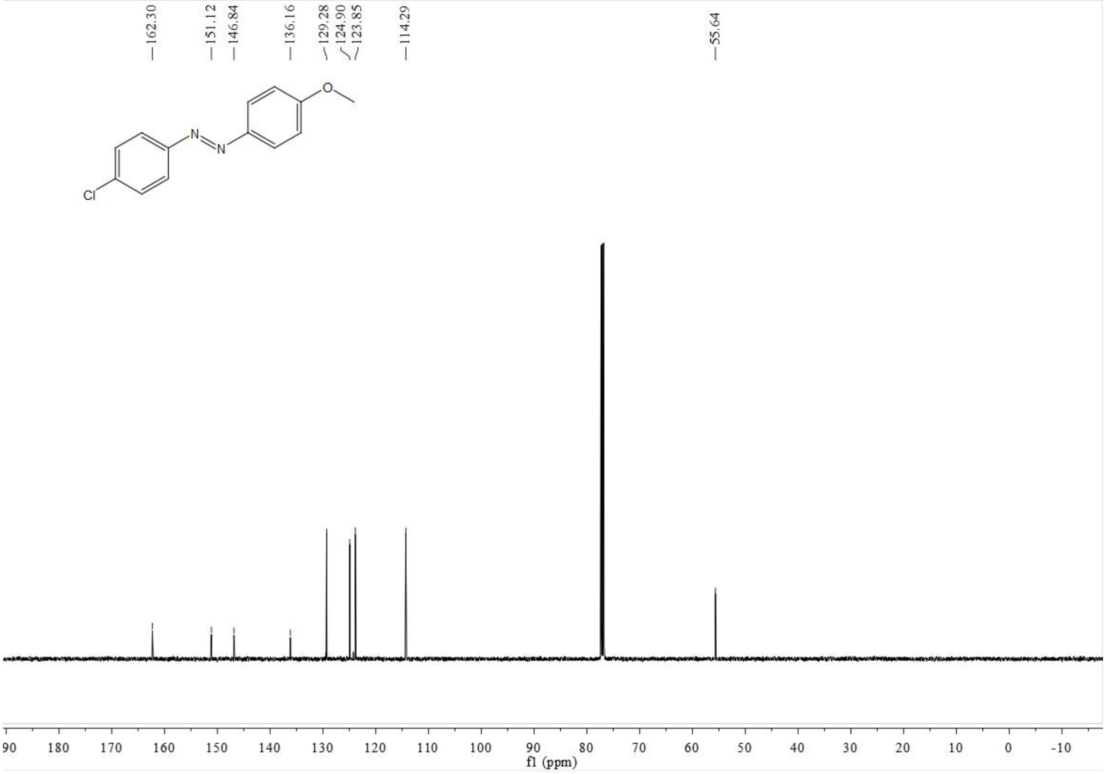
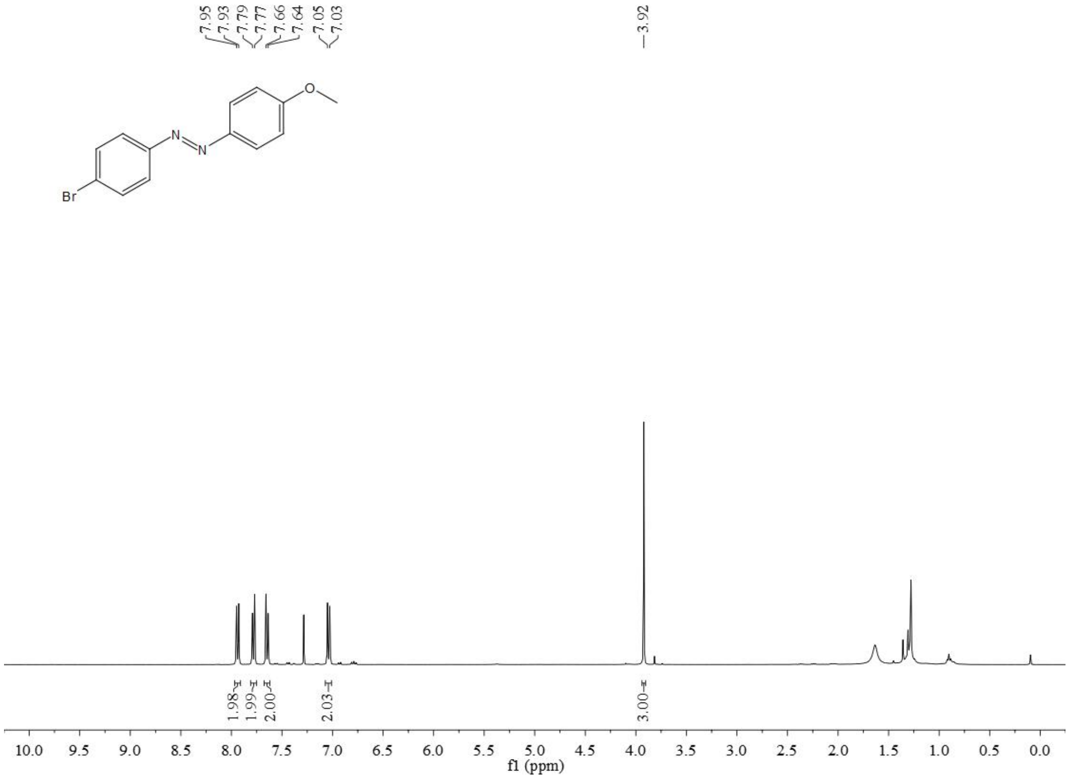
f1 (ppm)

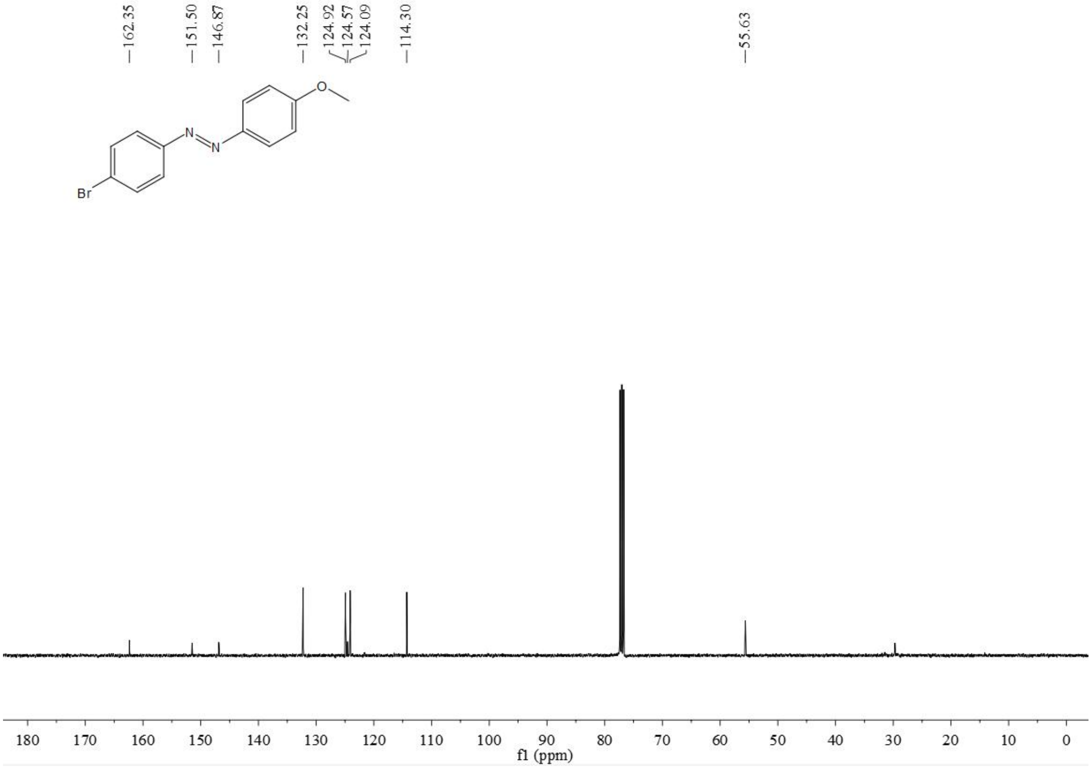
^{1}H NMR and ^{13}C NMR of 1-(4-Chlorophenyl)-2-(4-methoxyphenyl)diazene 3ag (500 MHz, CDCl$_3$)



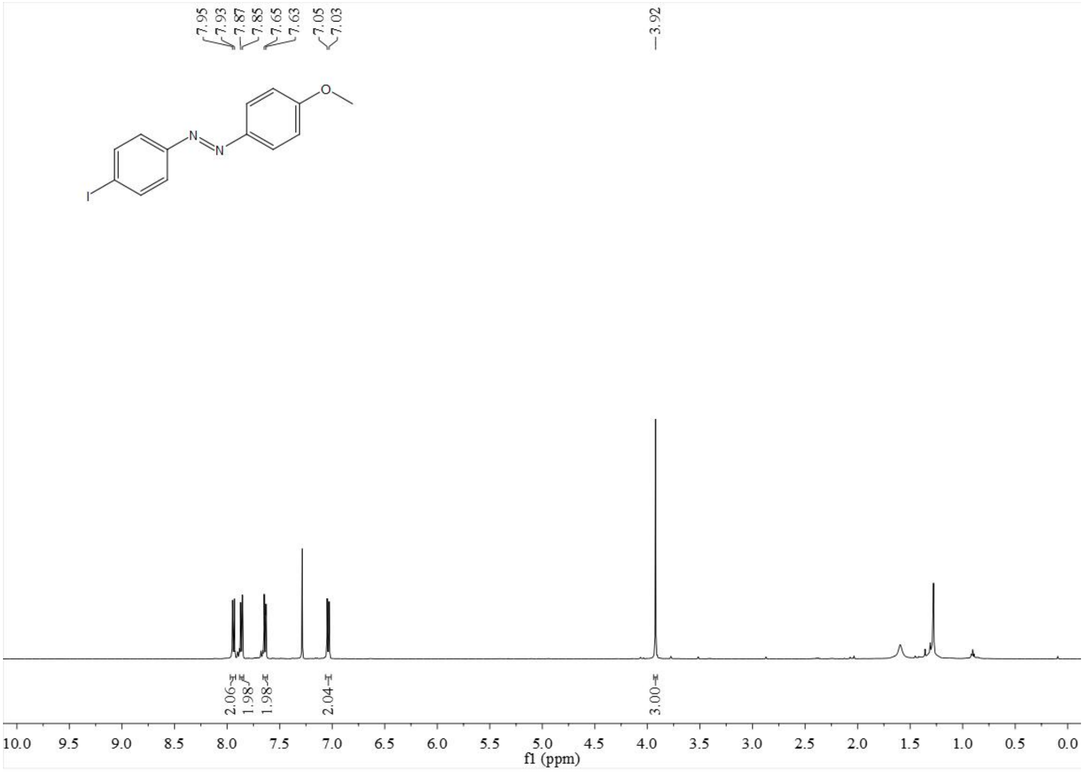


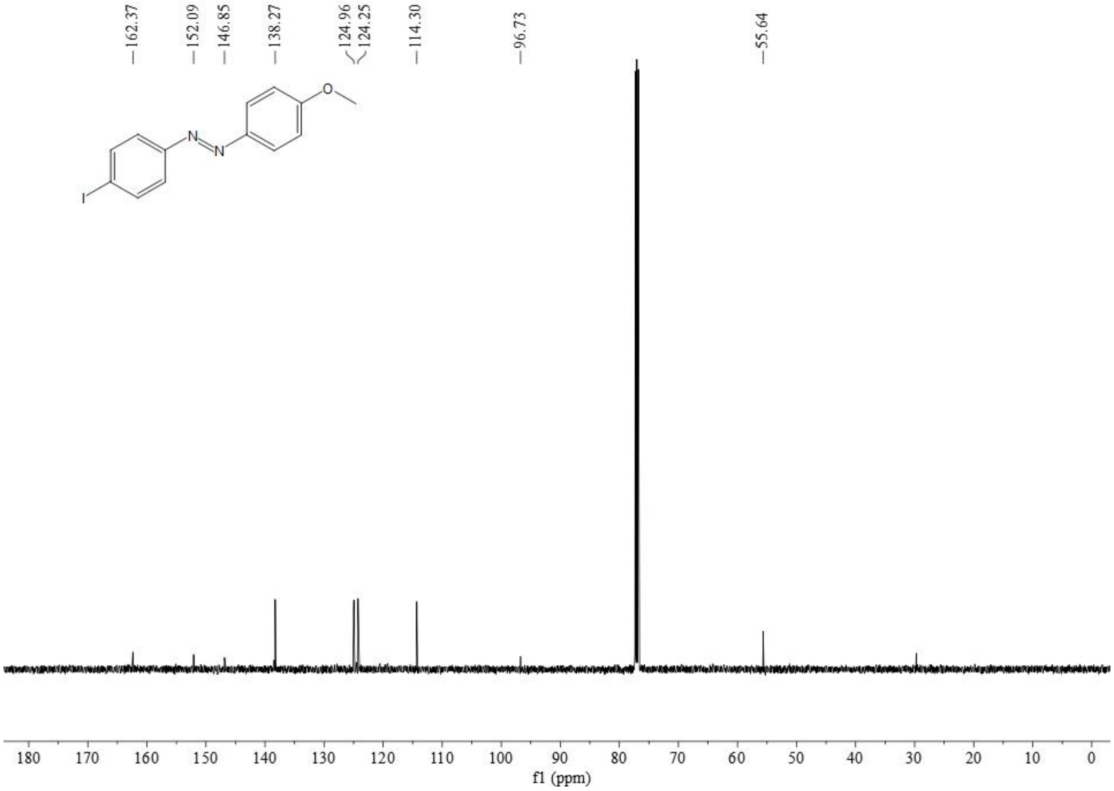
^{1}H NMR and ^{13}C NMR of 1-(4-Bromophenyl)-2-(4-methoxyphenyl)diazene 3ah (400 MHz, $CDCl_3$)



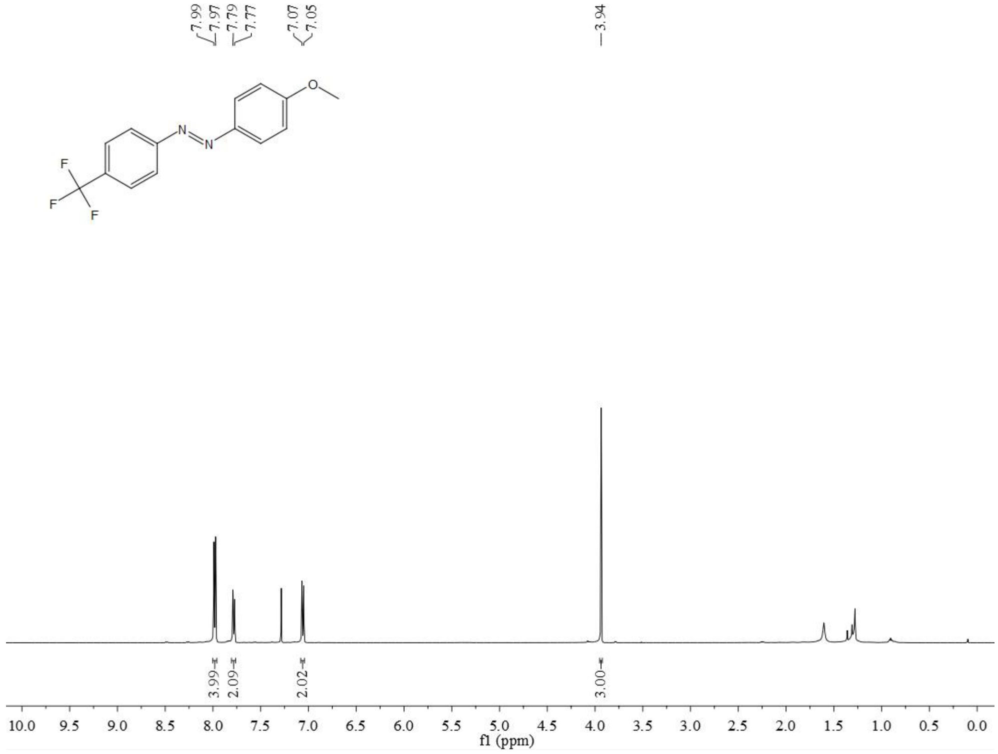


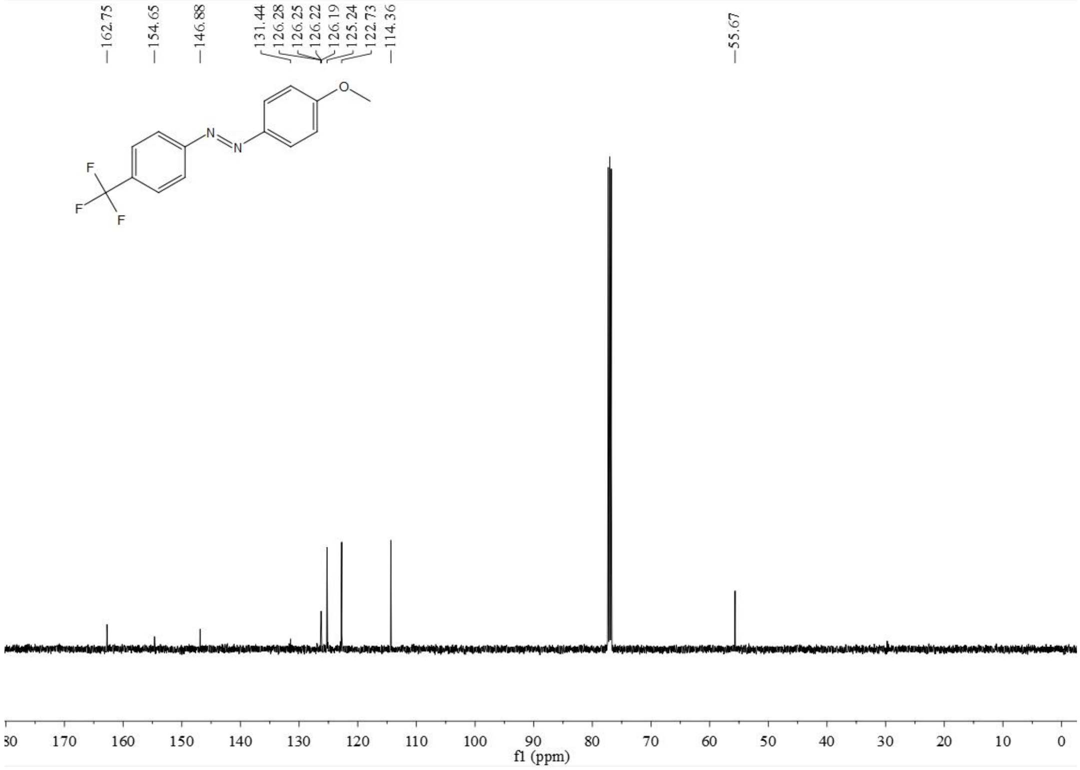
^{1}H NMR and ^{13}C NMR of 1-(4-Iodophenyl)-2-(4-methoxyphenyl)diazene 3ai (500 MHz, CDCl$_3$)

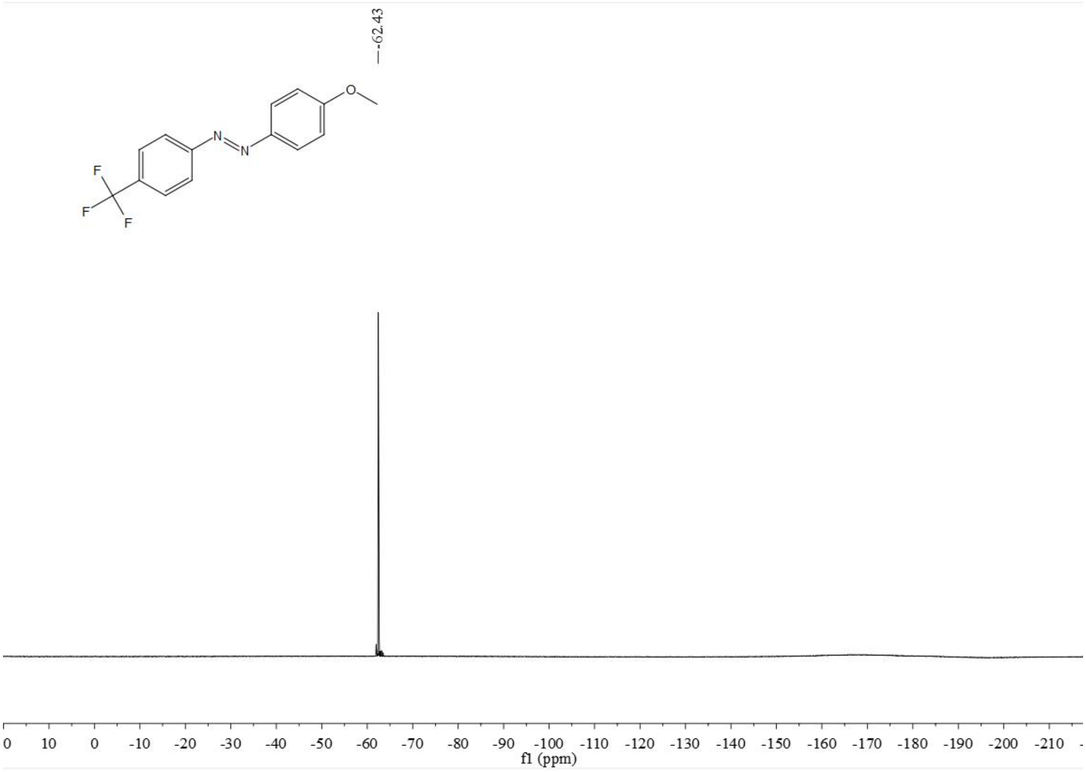




1H NMR and 13C NMR and 19F NMR 1-(4-Methoxyphenyl)-2-(4-(trifluoro methyl)phenyl) diazene 3aj (500 MHz, $CDCl_3$)



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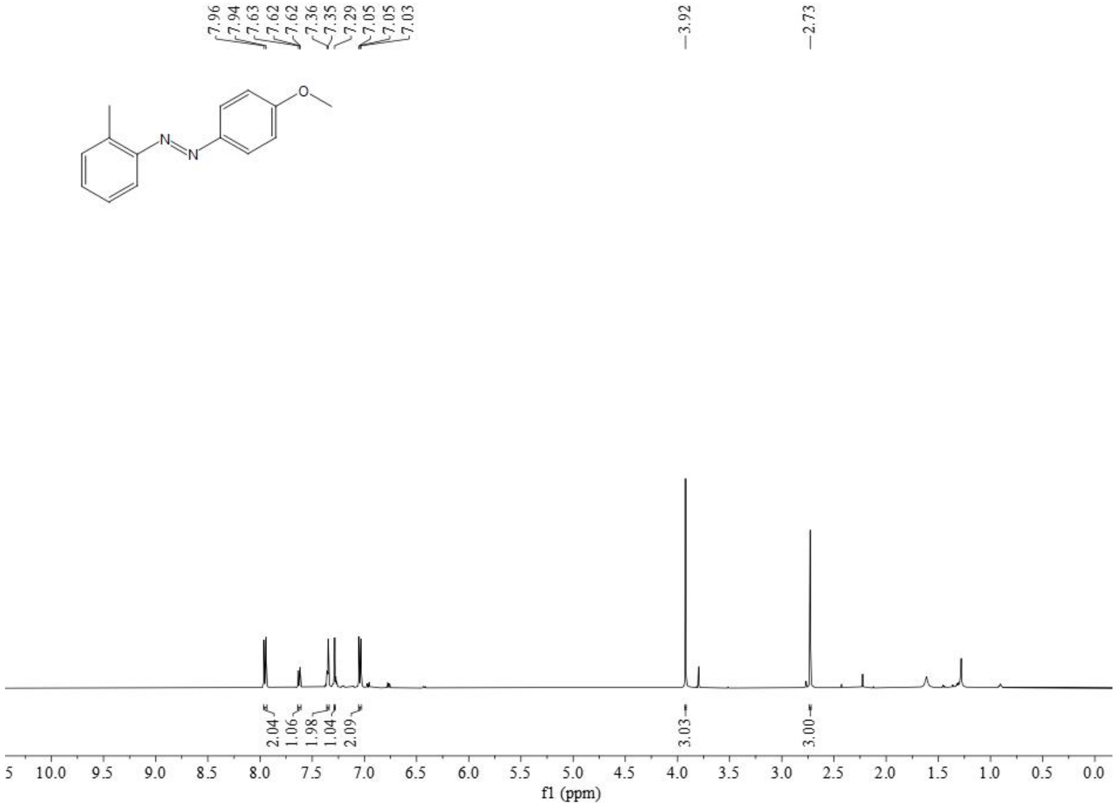
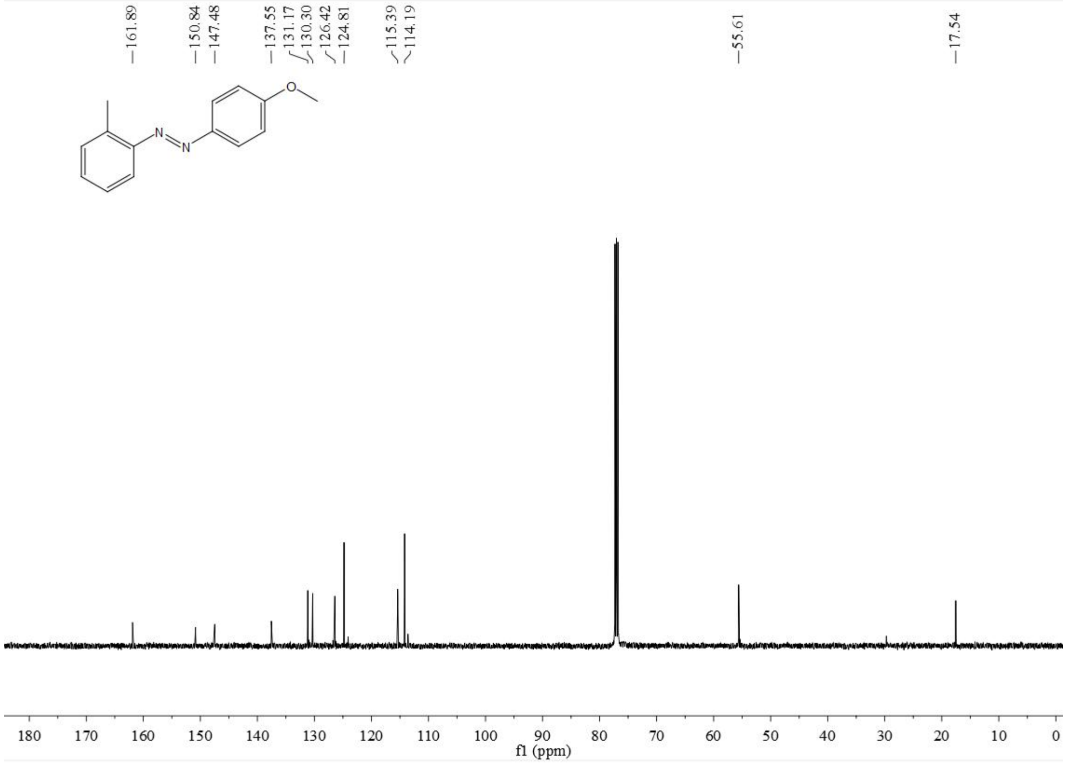
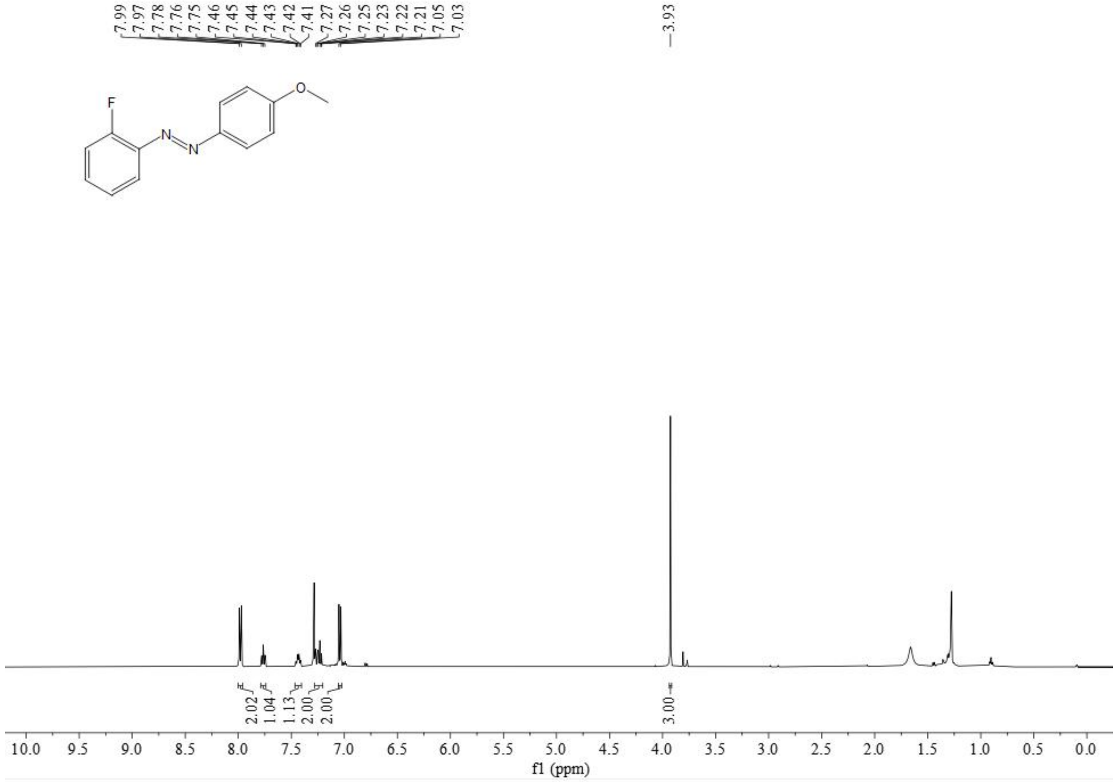
f1 (ppm)

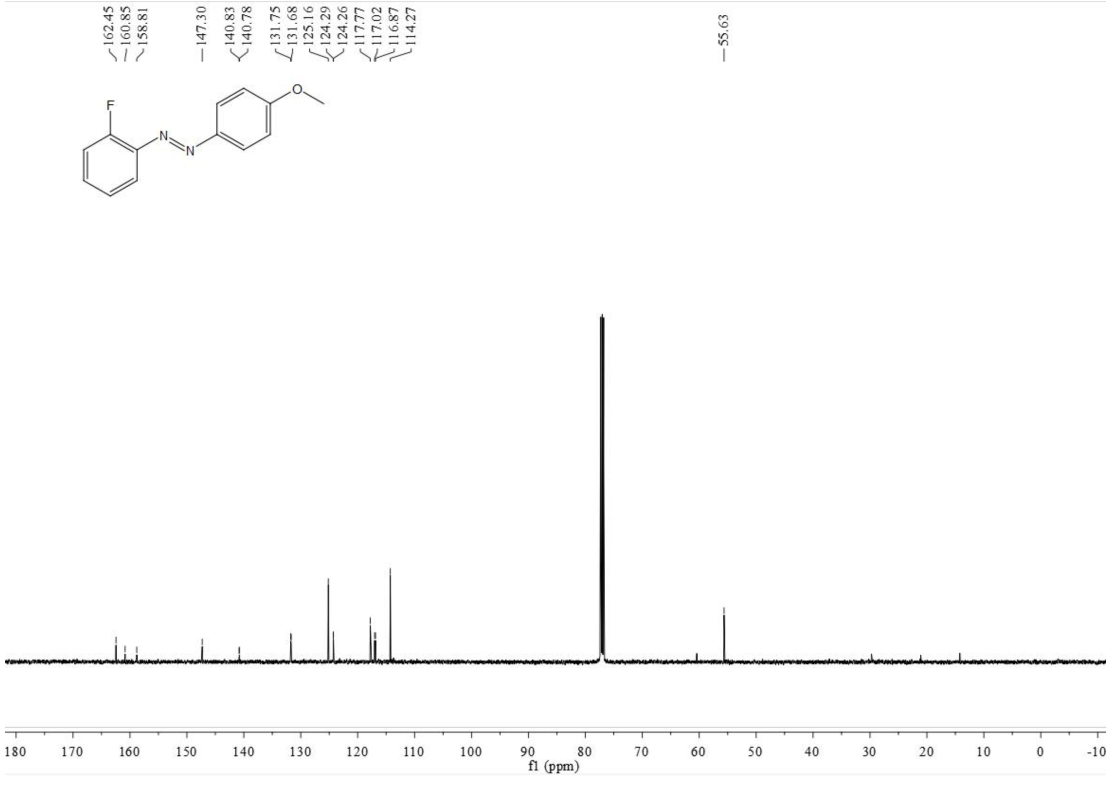
^{1}H NMR and ^{13}C NMR of 1-(4-Methoxyphenyl)-2-(o-tolyl)diazene 3ak (500 MHz, $CDCl_3$)

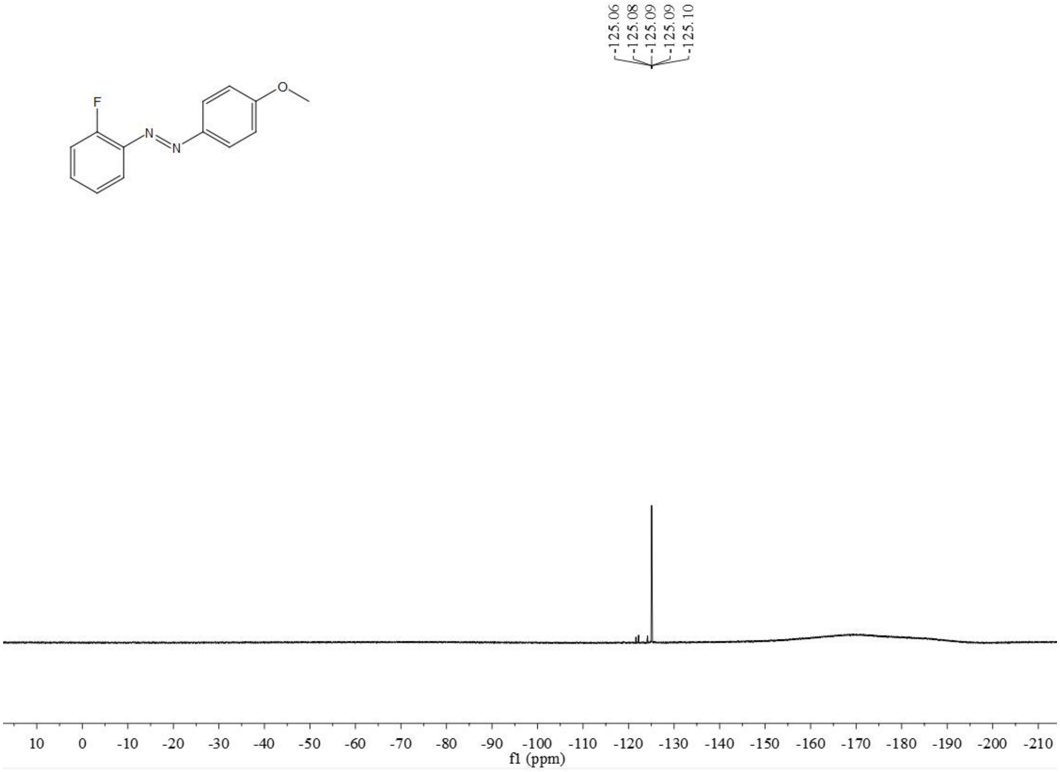




^{1}H NMR and ^{13}C NMR and ^{19}F NMR of 1-(2-Fluorophenyl)-2-(4-methoxyphenyl) diazene 3al (500 MHz, CDCl$_3$)



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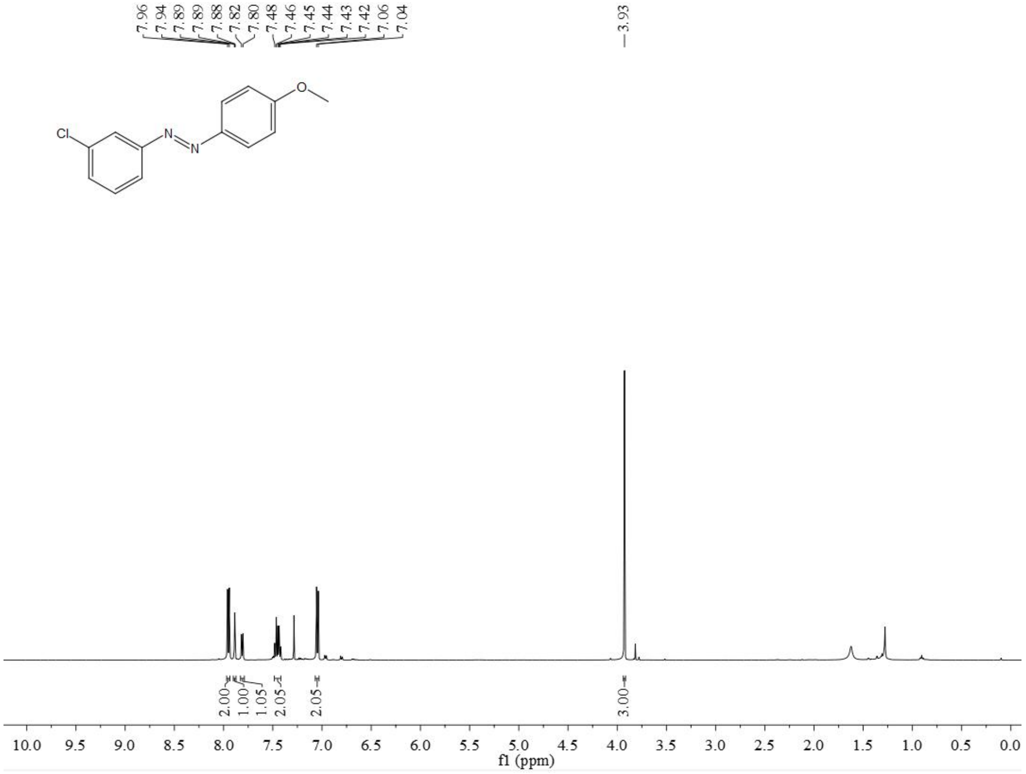
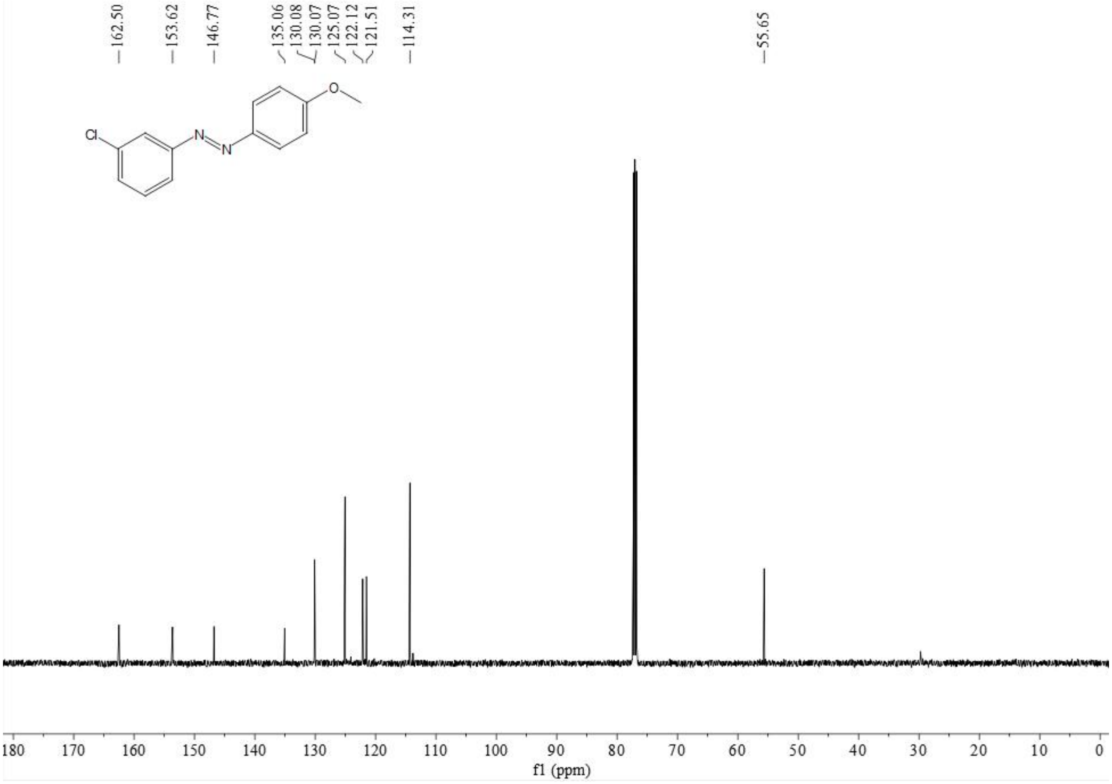
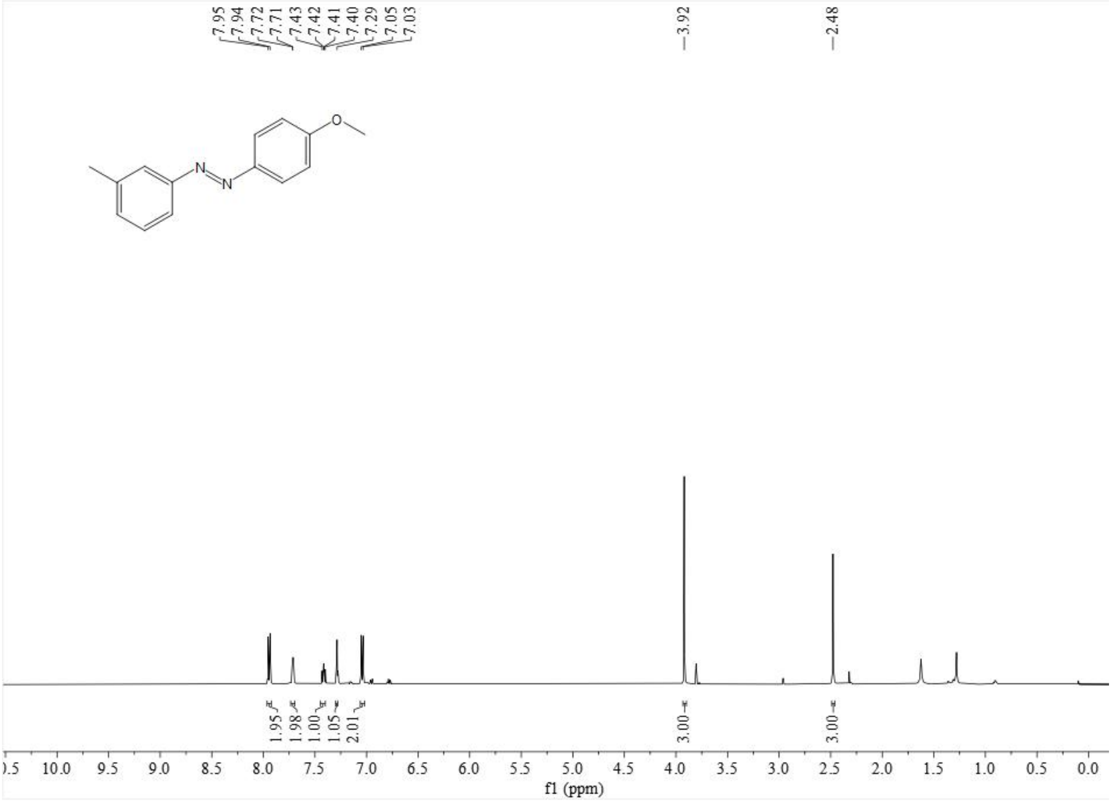
f1 (ppm)

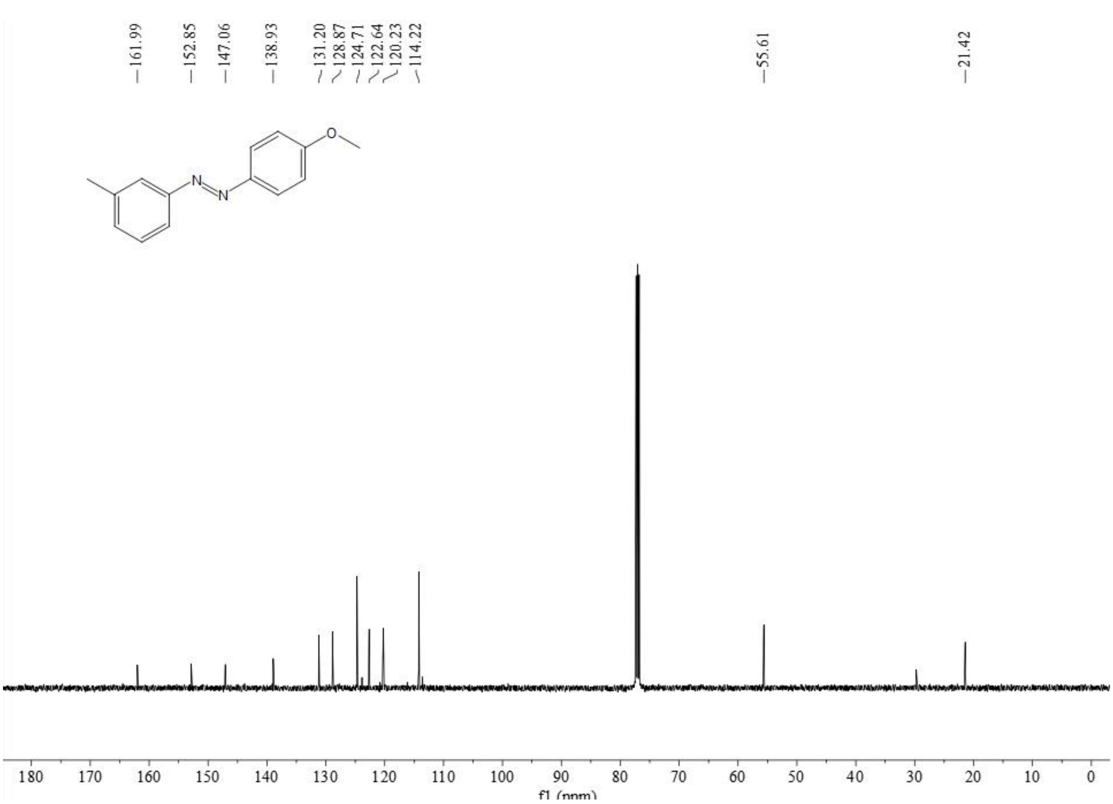
^{1}H NMR and ^{13}C NMR of 1-(3-Chlorophenyl)-2-(4-methoxyphenyl)diazene 3am (500 MHz, $CDCl_3$)



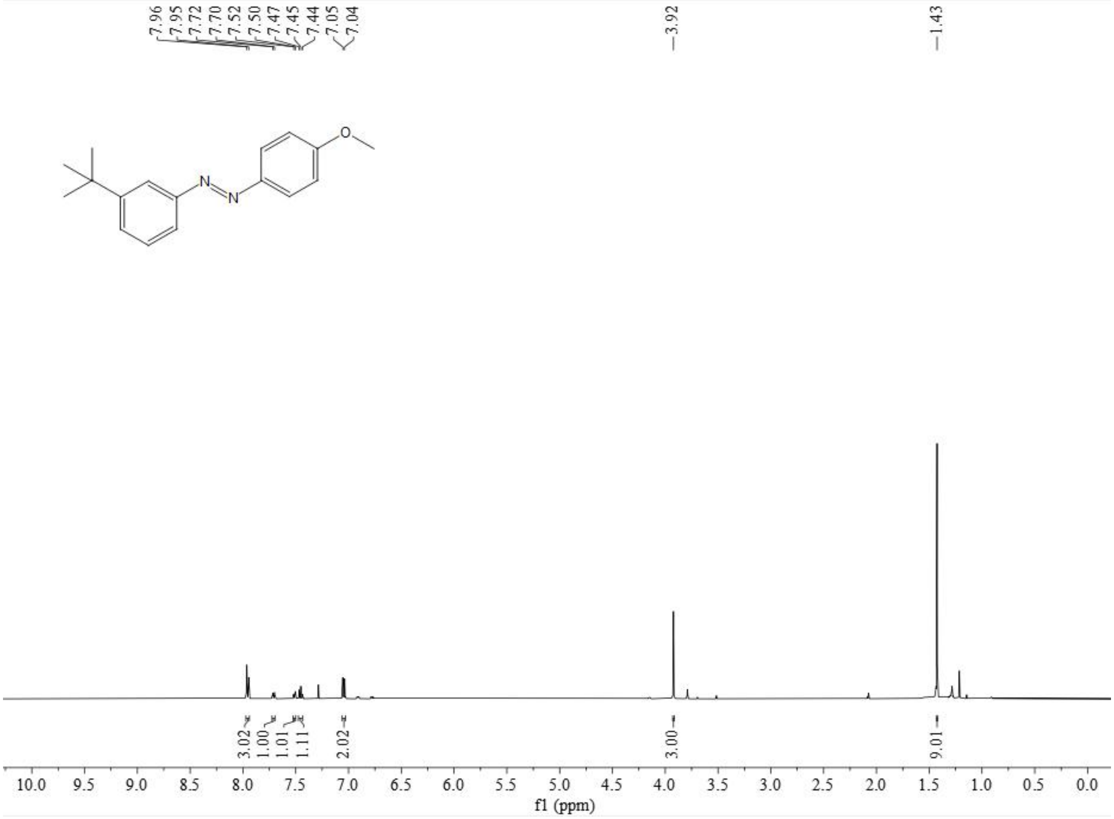


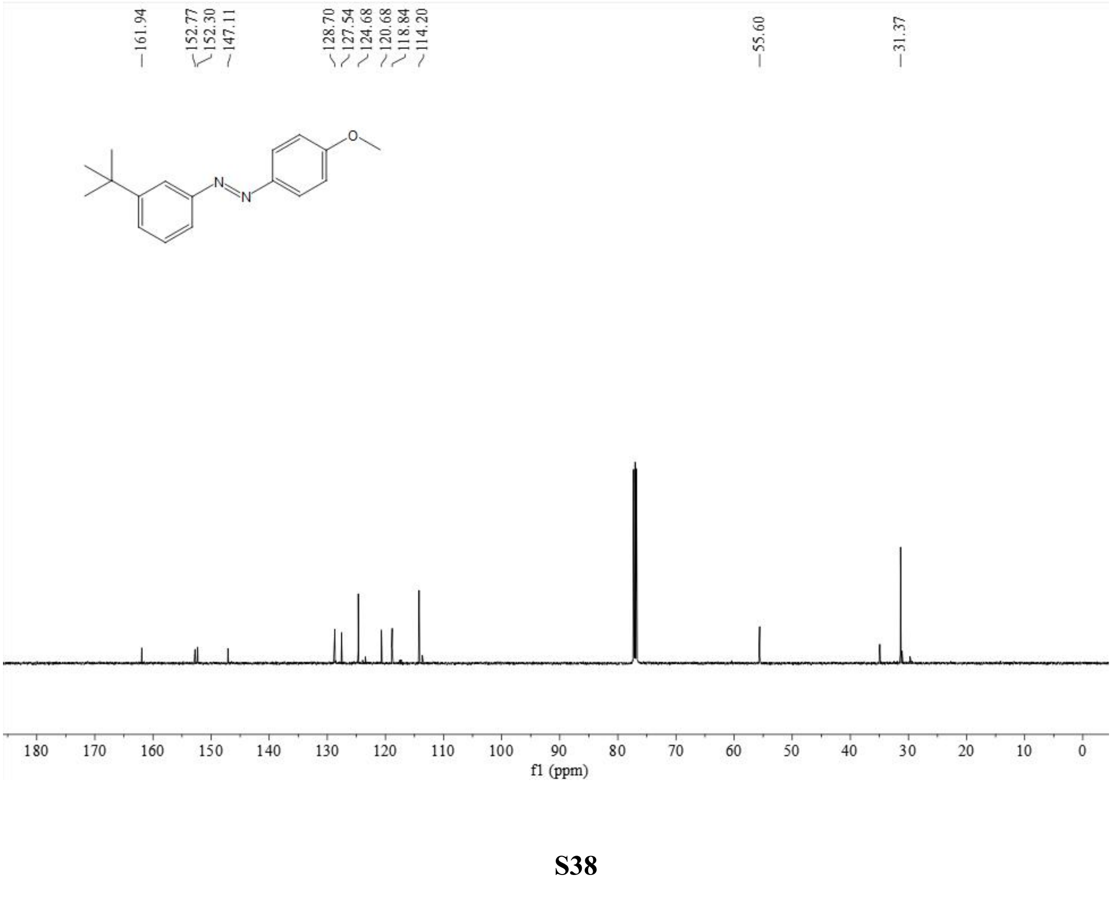
^1H NMR and ^{13}C NMR of 1-(4-Methoxyphenyl)-2-(m-tolyl)diazene 3an (500 MHz, $CDCl_3$)



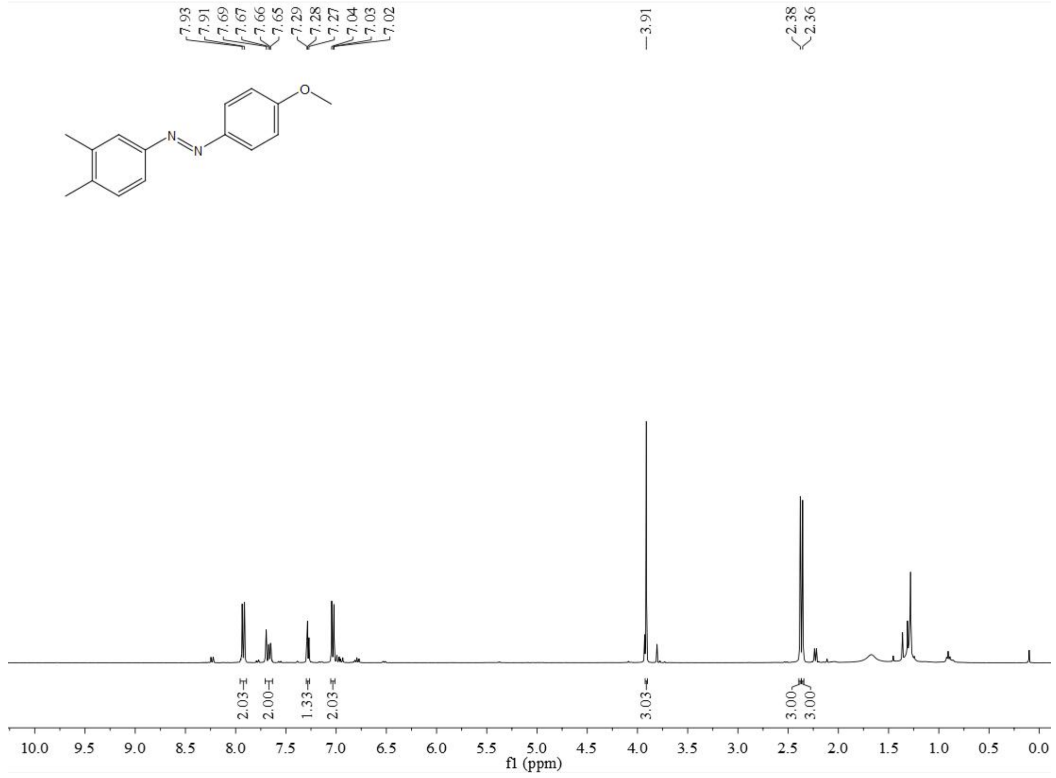


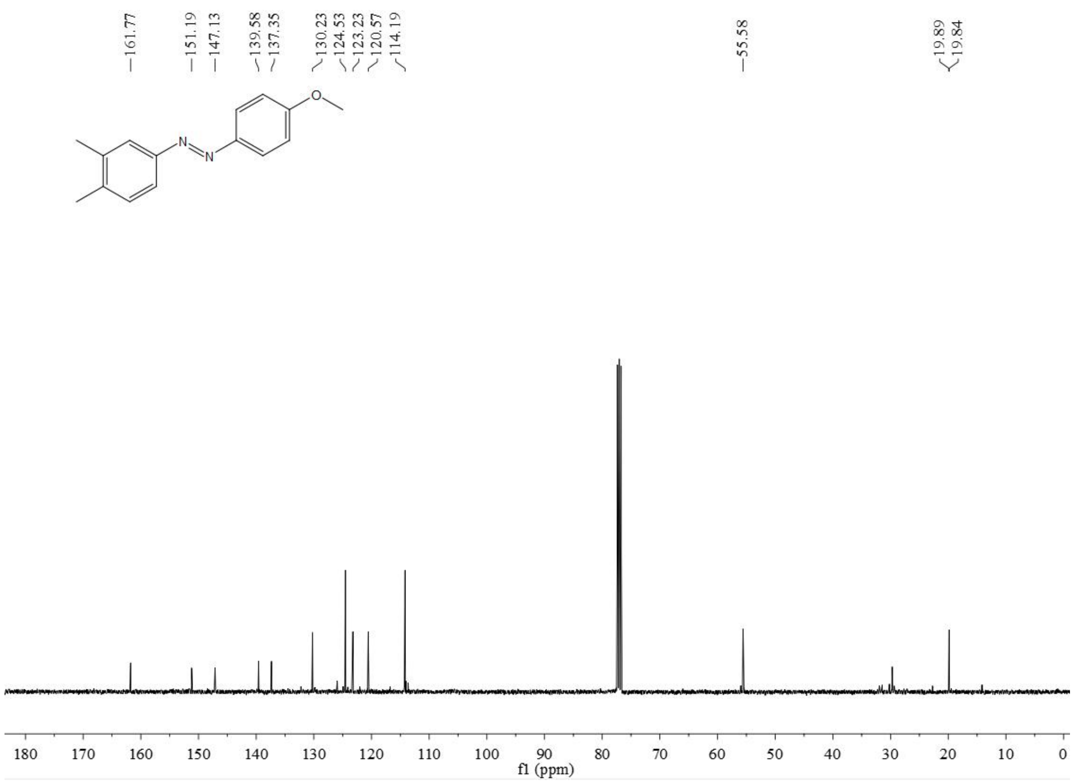
^{1}H NMR and ^{13}C NMR of 1-(3-(*tert*-Butyl)phenyl)-2-(4-methoxyphenyl)diazene 3ao (500 MHz, CDCl$_3$)



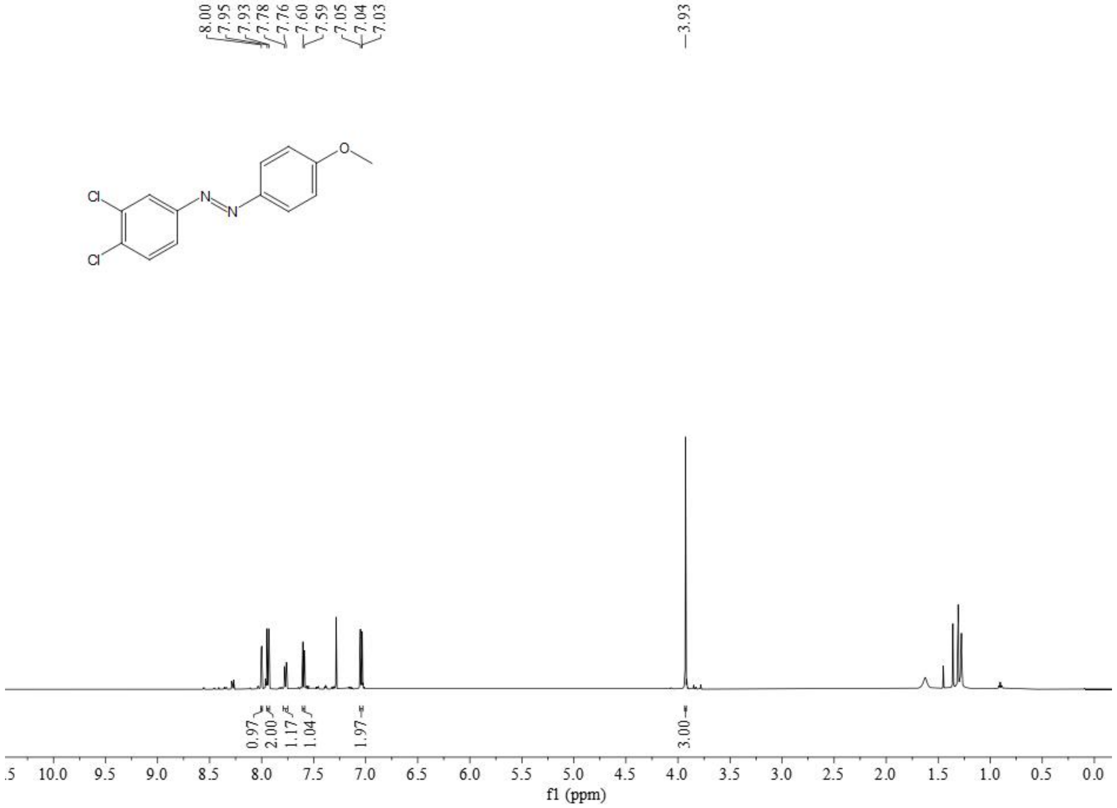


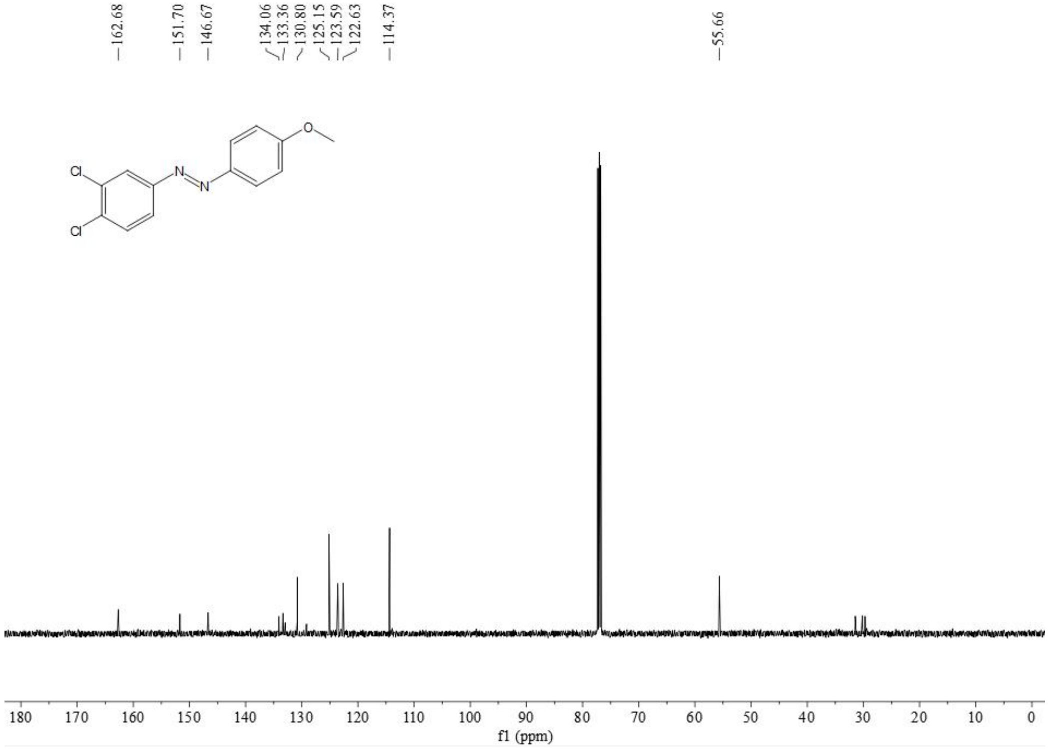
^{1}H NMR and ^{13}C NMR of 1-(3,4-Dimethylphenyl)-2-(4-methoxyphenyl)diazene 3ap (500 MHz, $CDCl_3$)



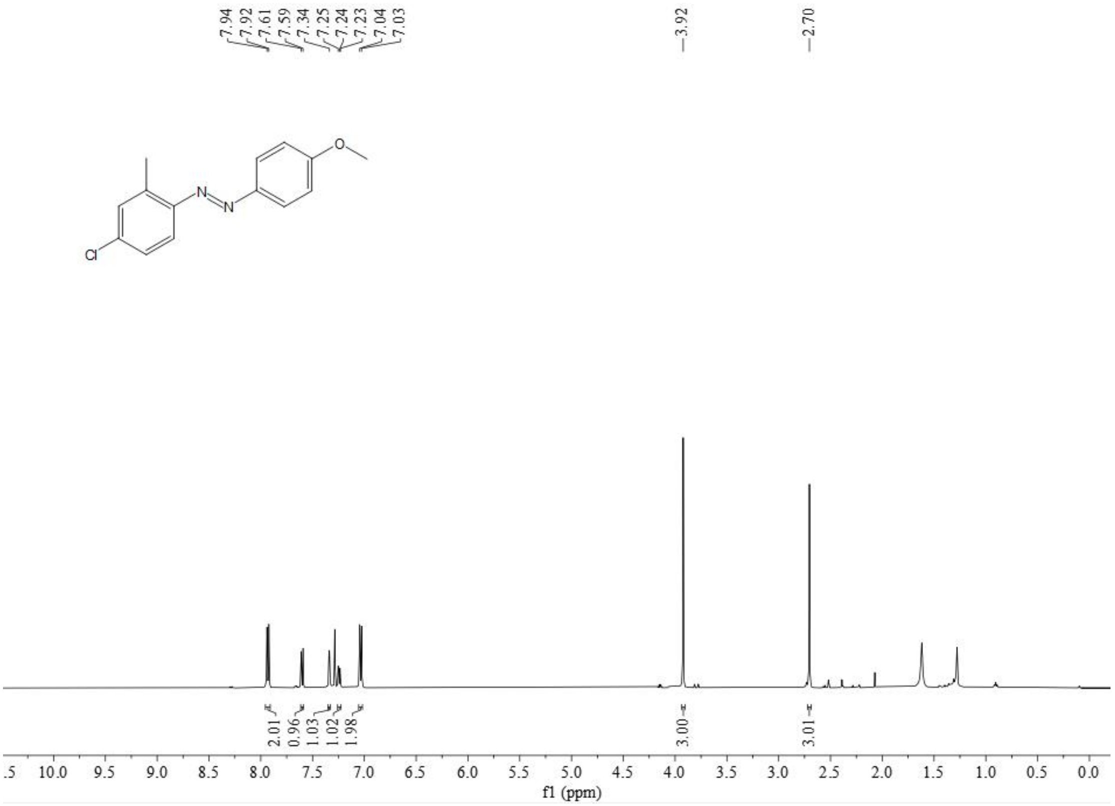


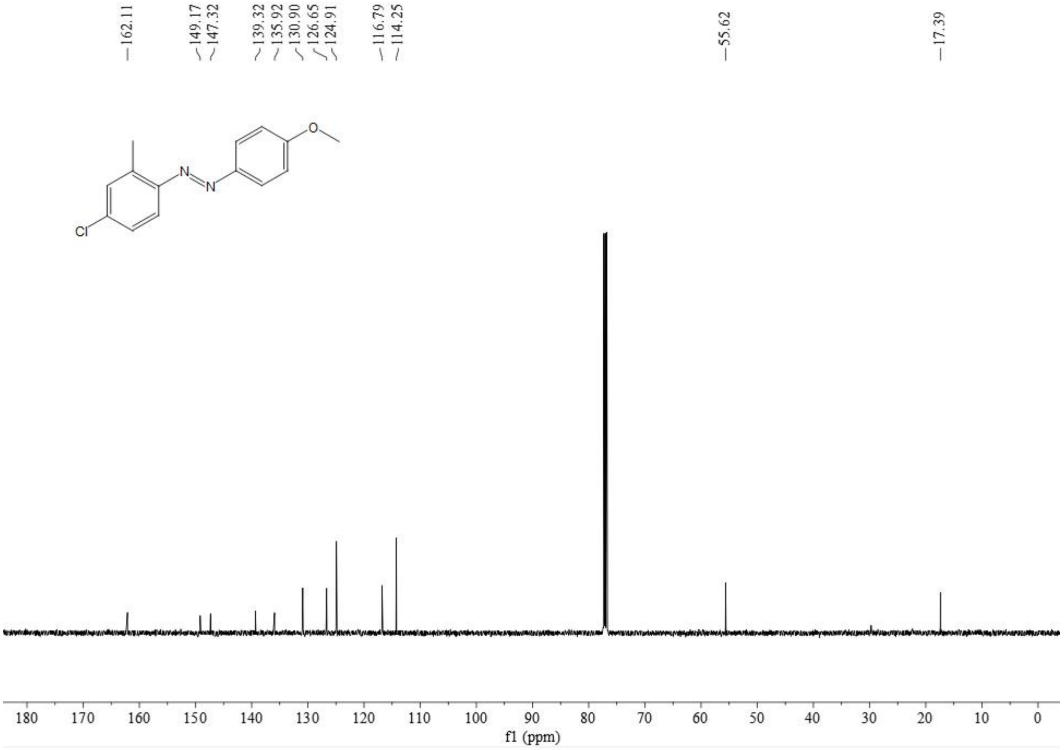
^{1}H NMR and ^{13}C NMR of 1-(3,4-Dichlorophenyl)-2-(4-methoxyphenyl)diazene 3aq (500 MHz, CDCl$_3$)



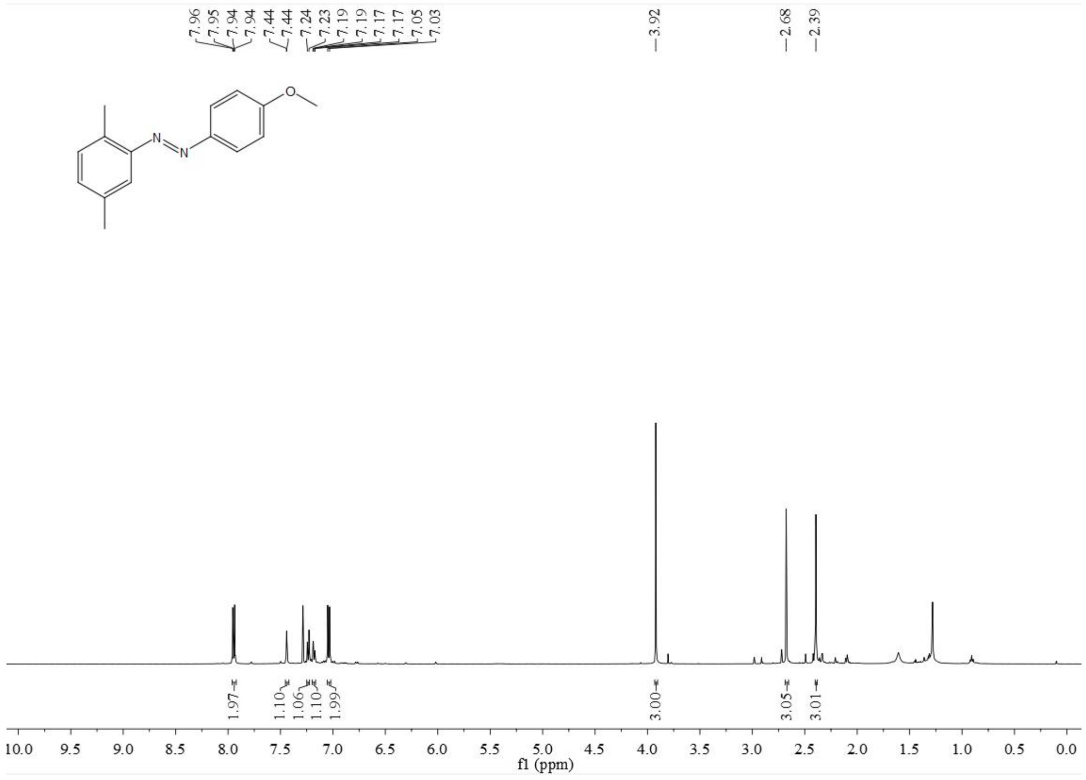


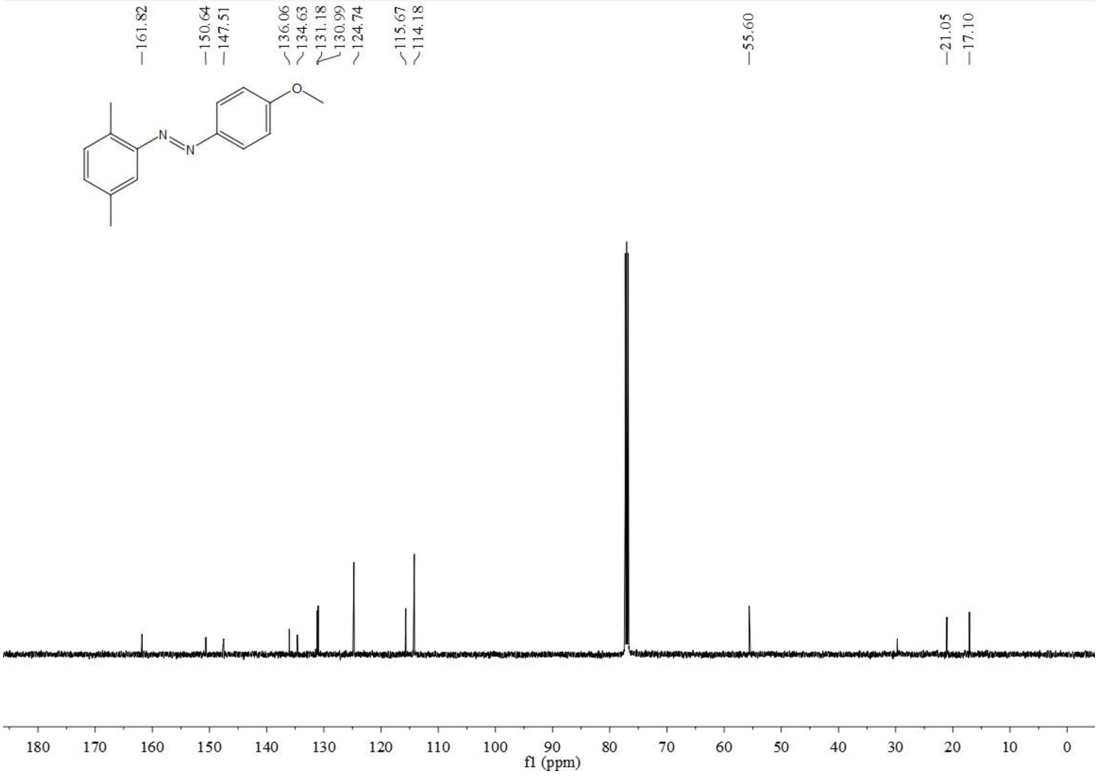
^{1}H NMR and ^{13}C NMR of 1-(4-Chloro-2-methylphenyl)-2-(4-methoxyphenyl) diazene 3ar (500 MHz, $CDCl_3$)



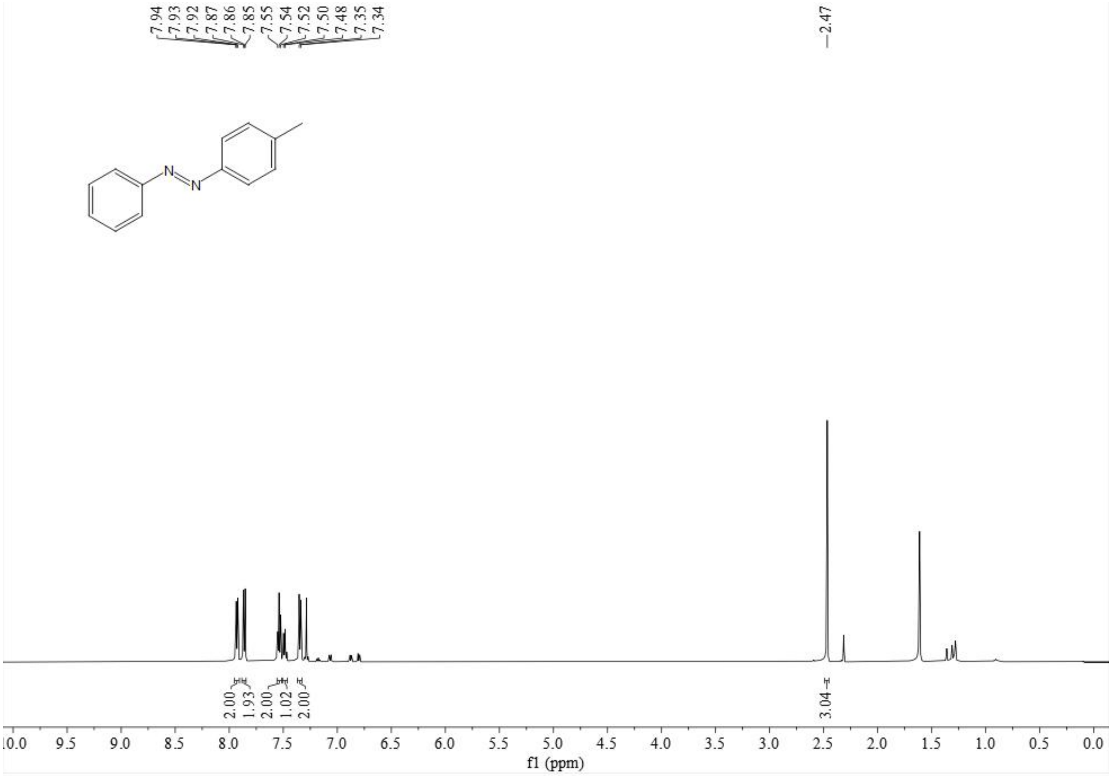


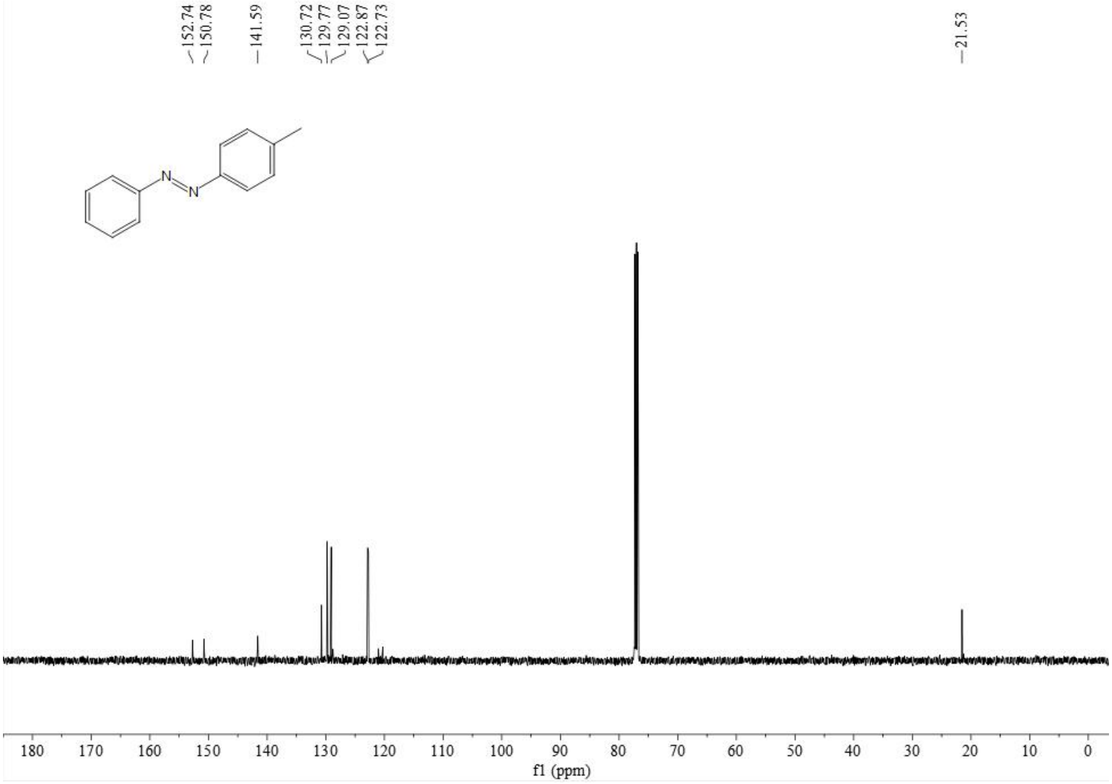
^{1}H NMR and ^{13}C NMR of 1-(2,5-Dimethylphenyl)-2-(4-methoxyphenyl)diazene 3as (500 MHz, CDCl$_3$)



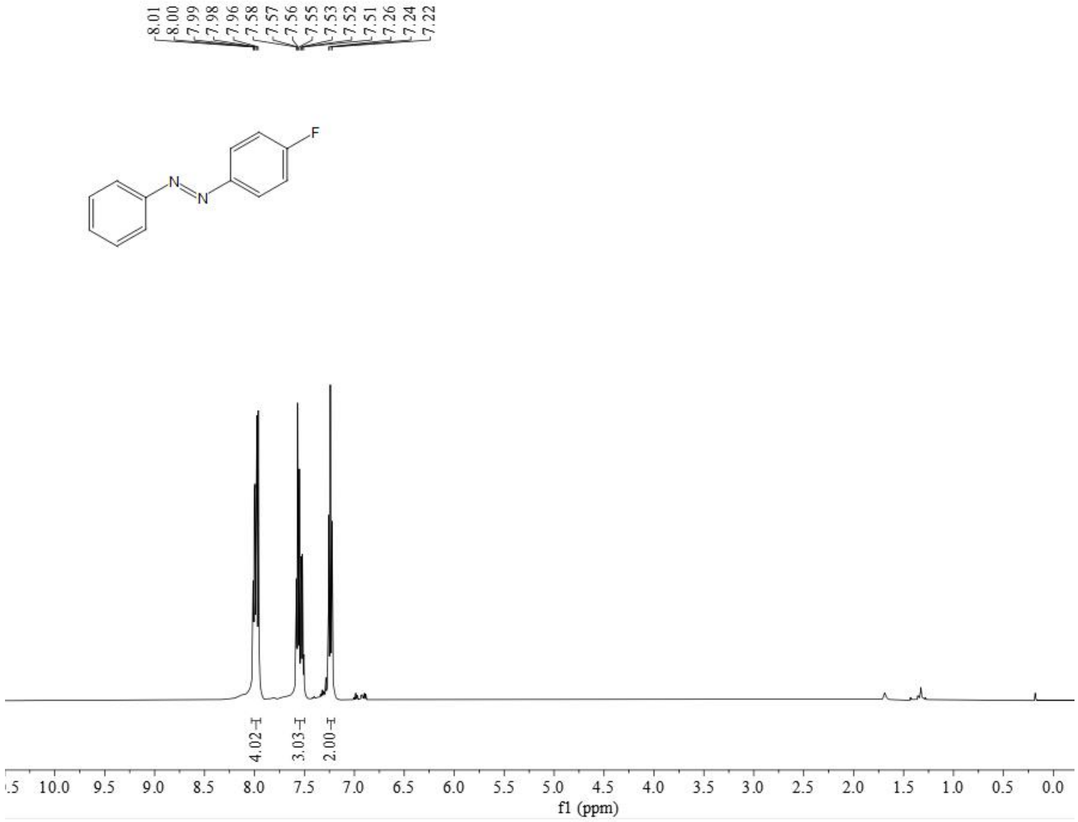


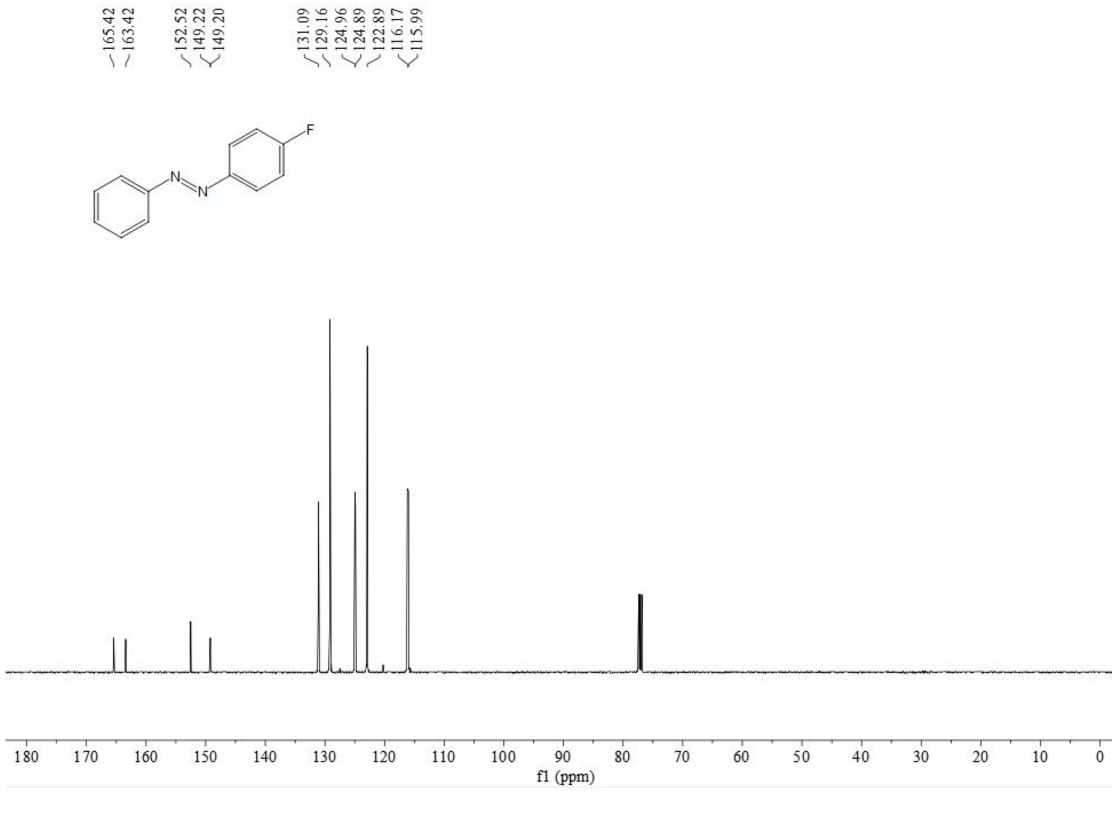
^{1}H NMR and ^{13}C NMR of 1-Phenyl-2-(p-tolyl)diazene 3ba (500 MHz, $CDCl_3$)

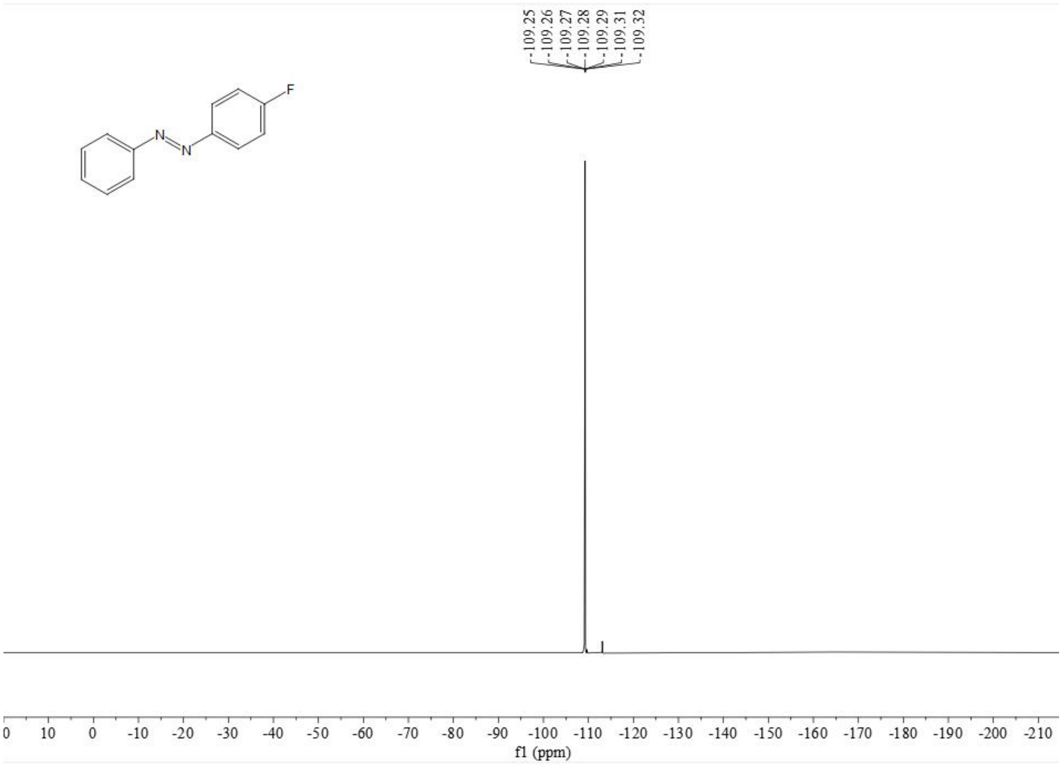




^{1}H NMR, ^{13}C NMR and ^{19}F NMR of 1-(4-Fluorophenyl)-2-phenyldiazene 3bb (500 MHz, $CDCl_3$)







-109.25
-109.26
-109.27
-109.28
-109.29
-109.31
-109.32
F
N
N
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10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
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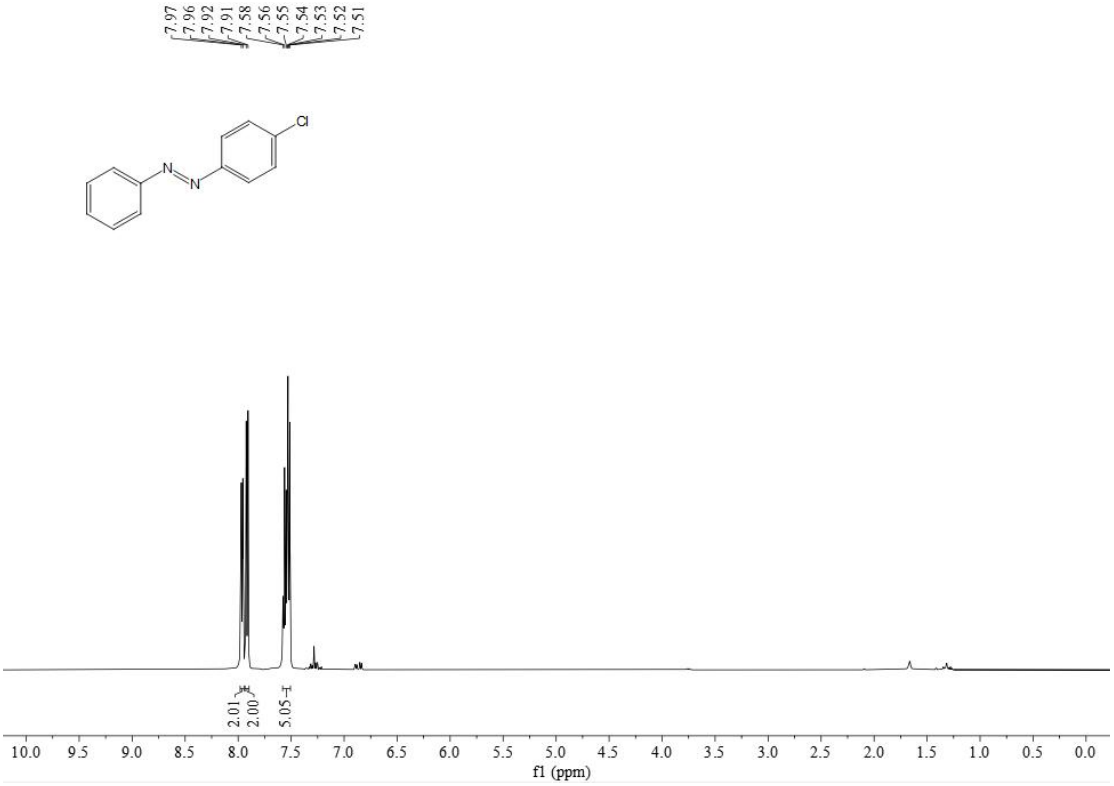
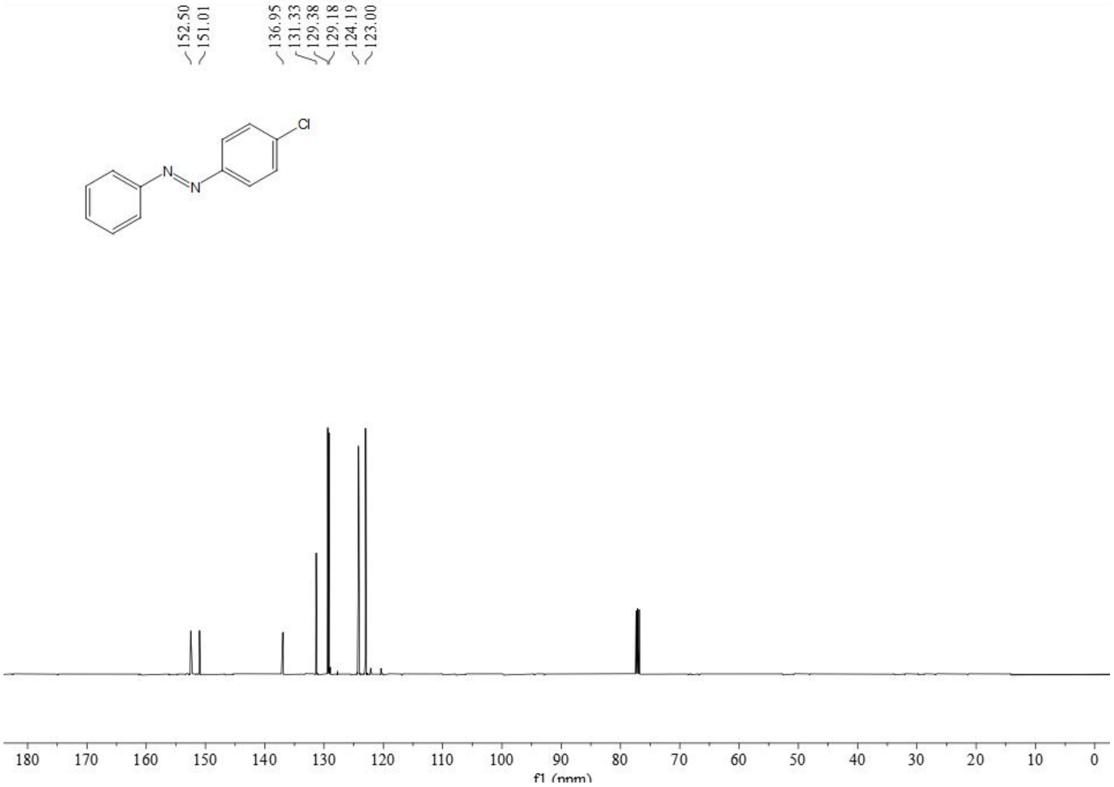
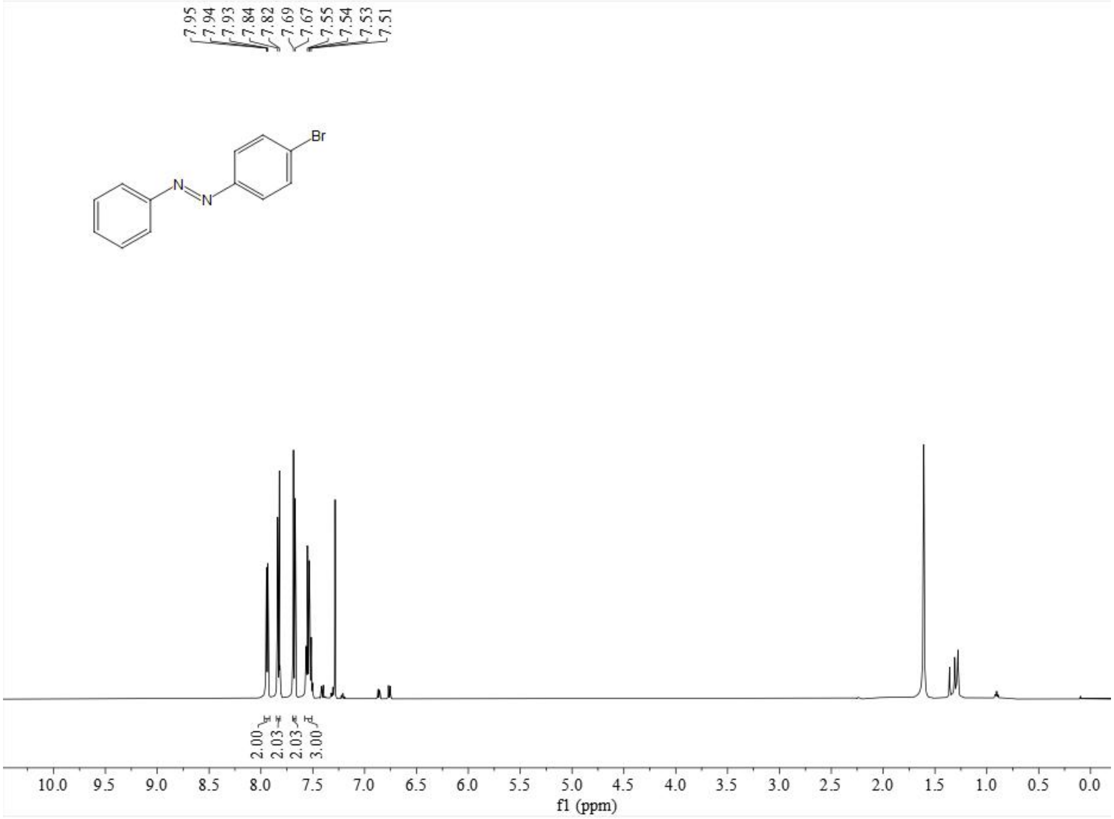
-200
-210
f1 (ppm)

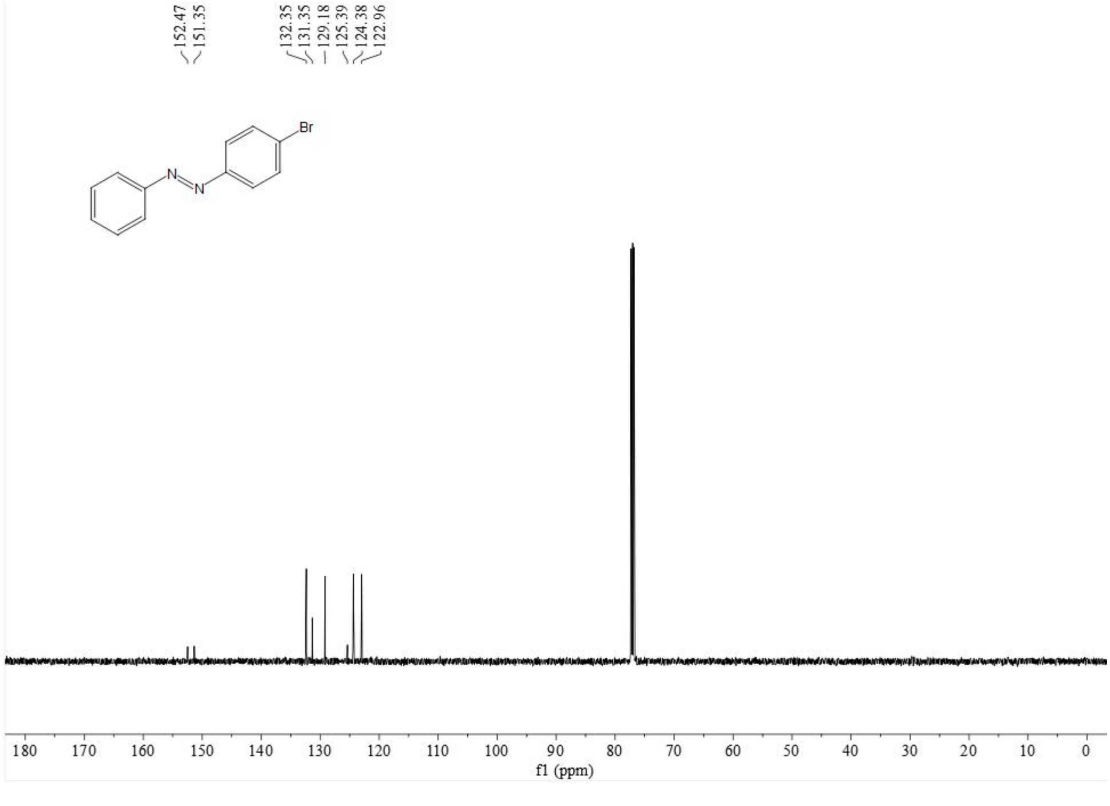
^{1}H NMR and ^{13}C NMR of 1-(4-Chlorophenyl)-2-phenyldiazene 3bc (500 MHz, CDCl$_3$)



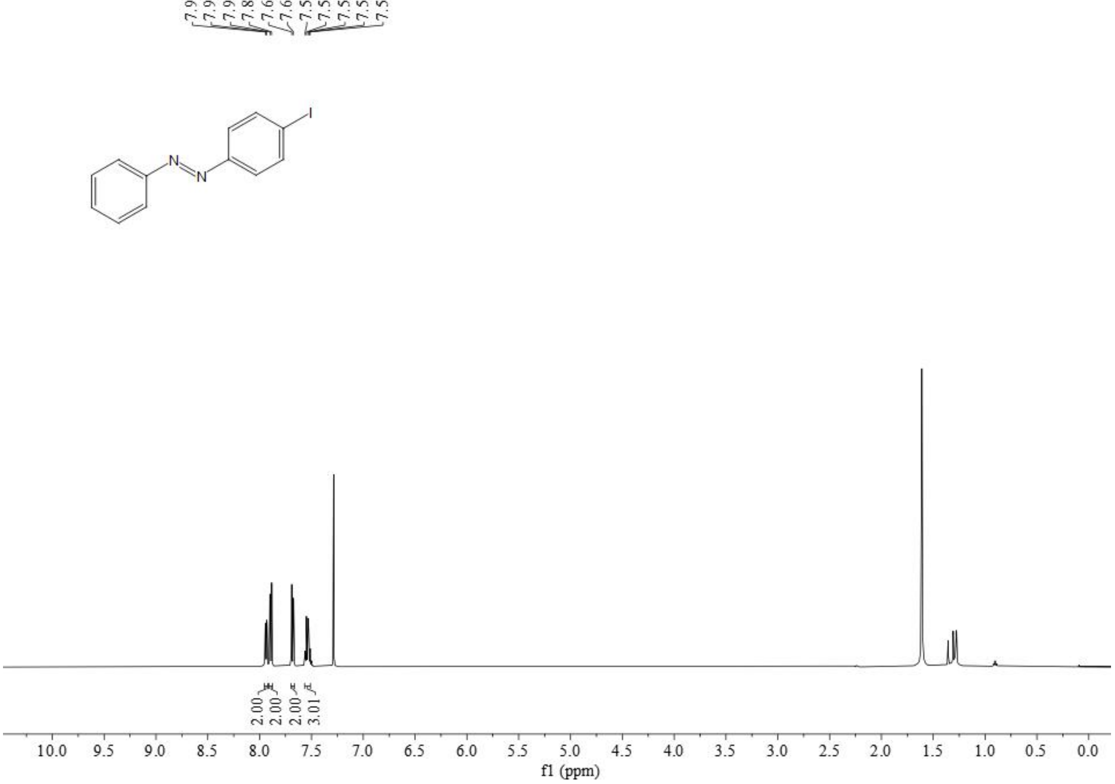


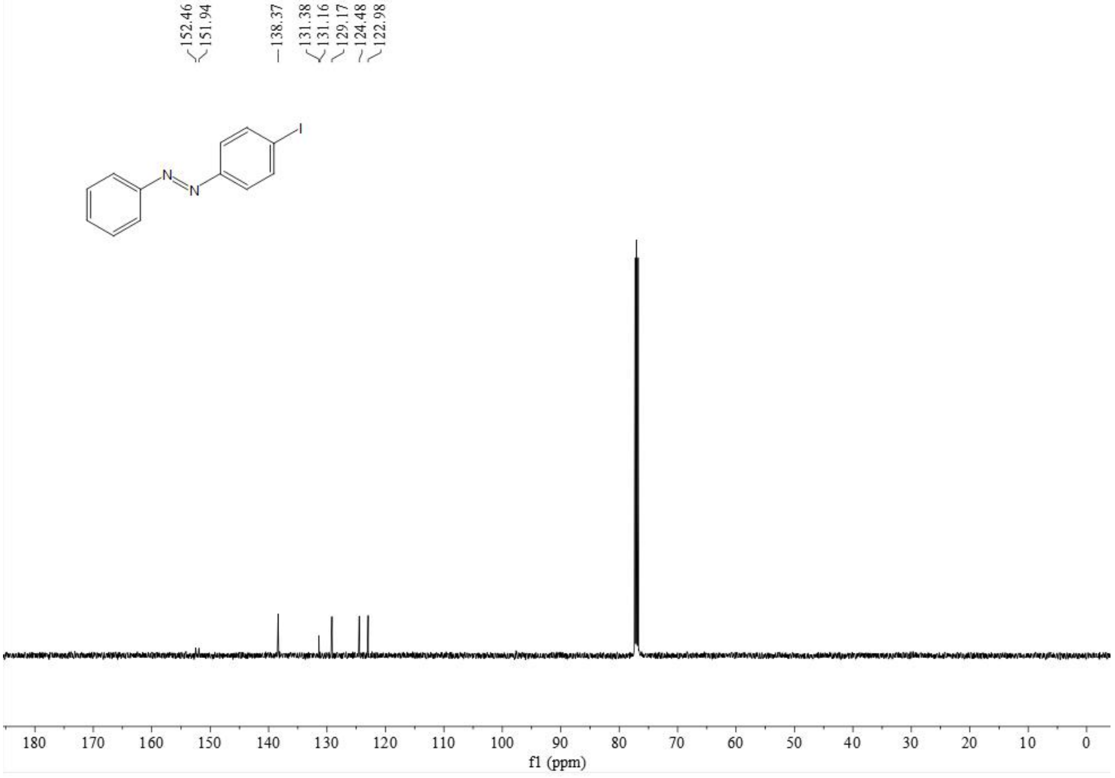
^1H NMR and ^{13}C NMR of 1-(4-Bromophenyl)-2-phenyldiazene 3bd (500 MHz, $CDCl_3$)



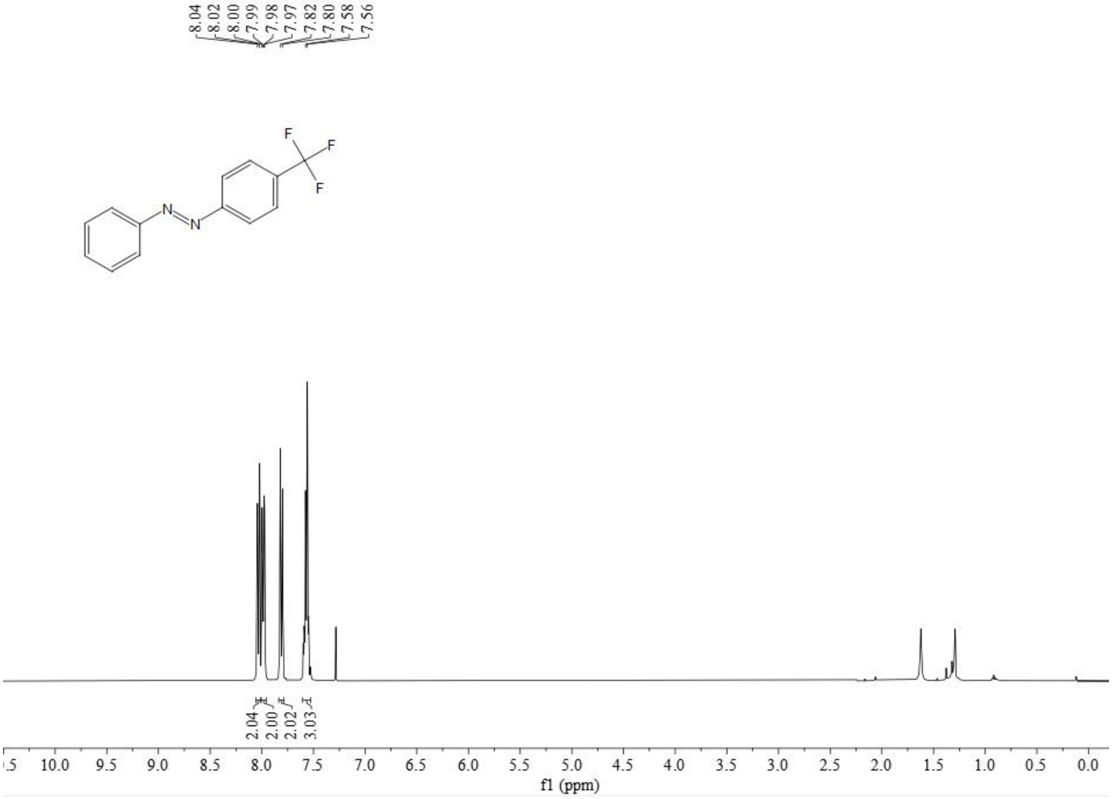


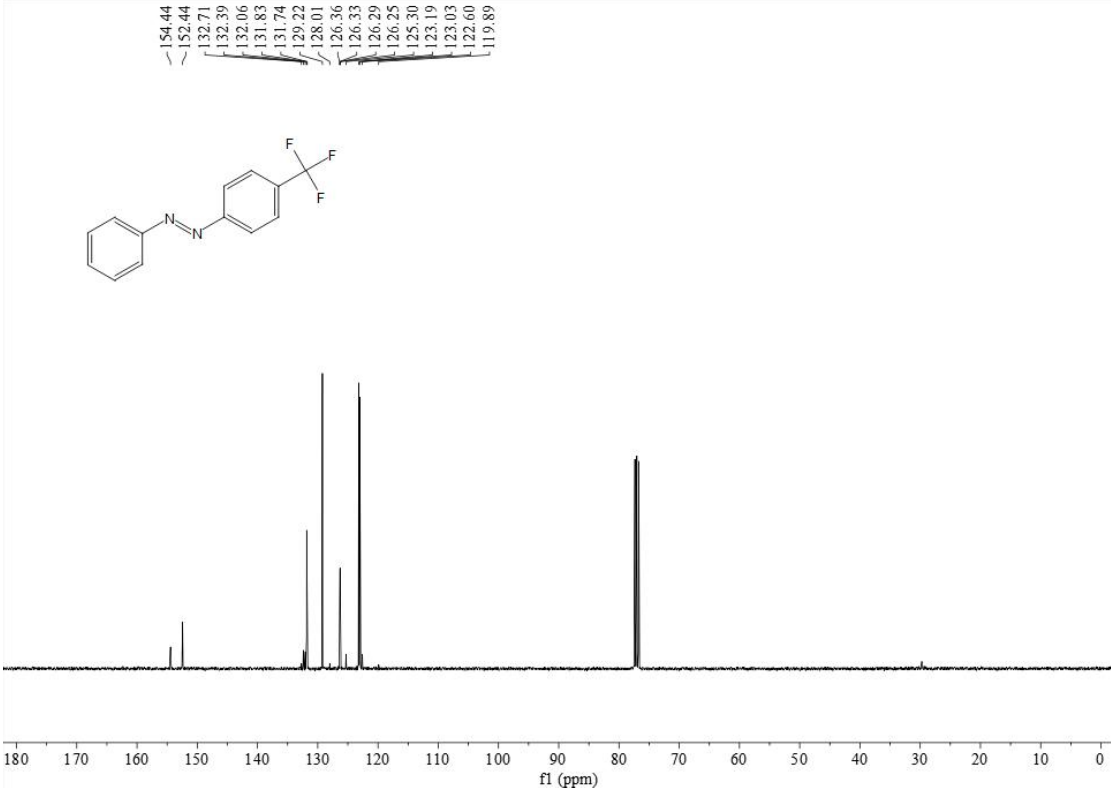
^{1}H NMR and ^{13}C NMR of 1-(4-Iodophenyl)-2-phenyldiazene 3be (500 MHz, CDCl$_3$)

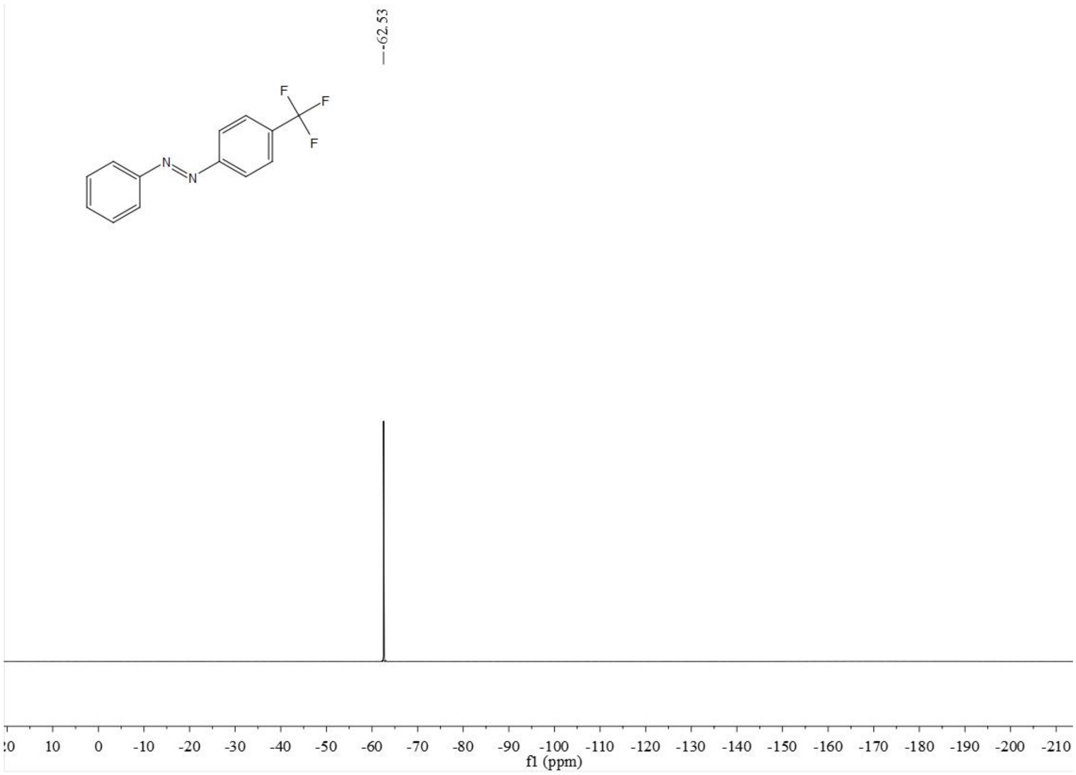




^{1}H NMR, ^{13}C NMR and ^{19}F NMR of 1-Phenyl-2-(4-(trifluoromethyl)phenyl) diazene 3bf (500 MHz, CDCl$_3$)



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N
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0
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-100
-110
-120
-130
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-150
-160
-170
-180
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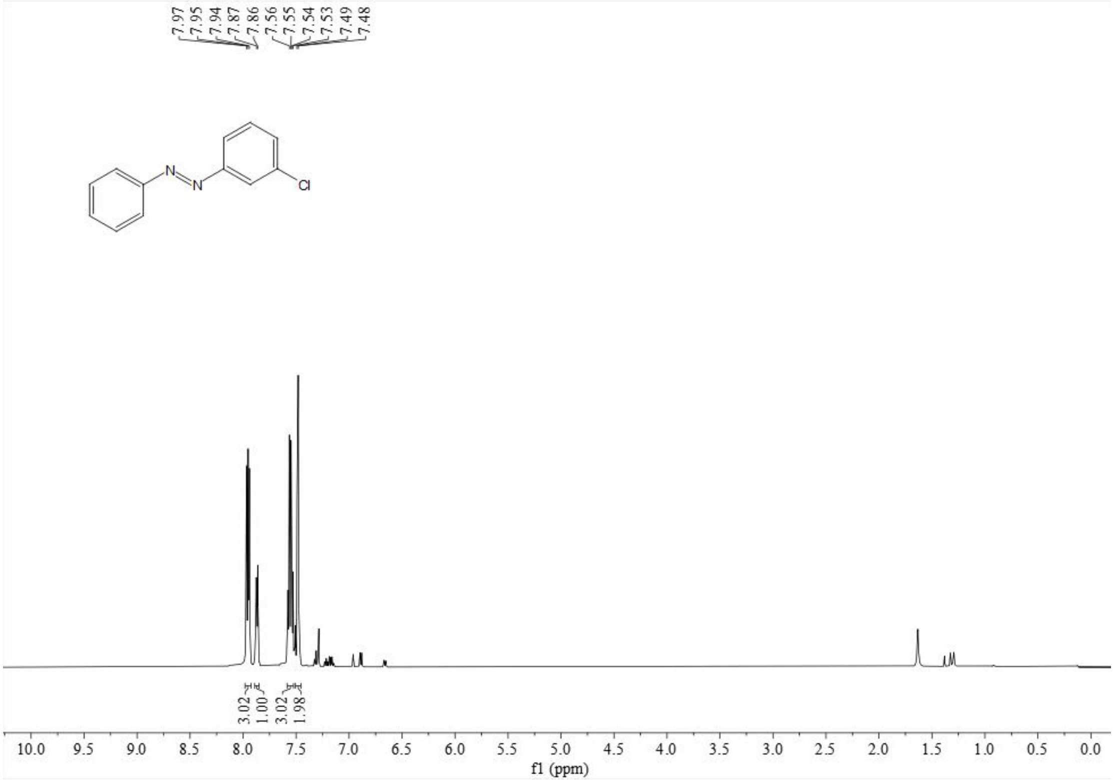
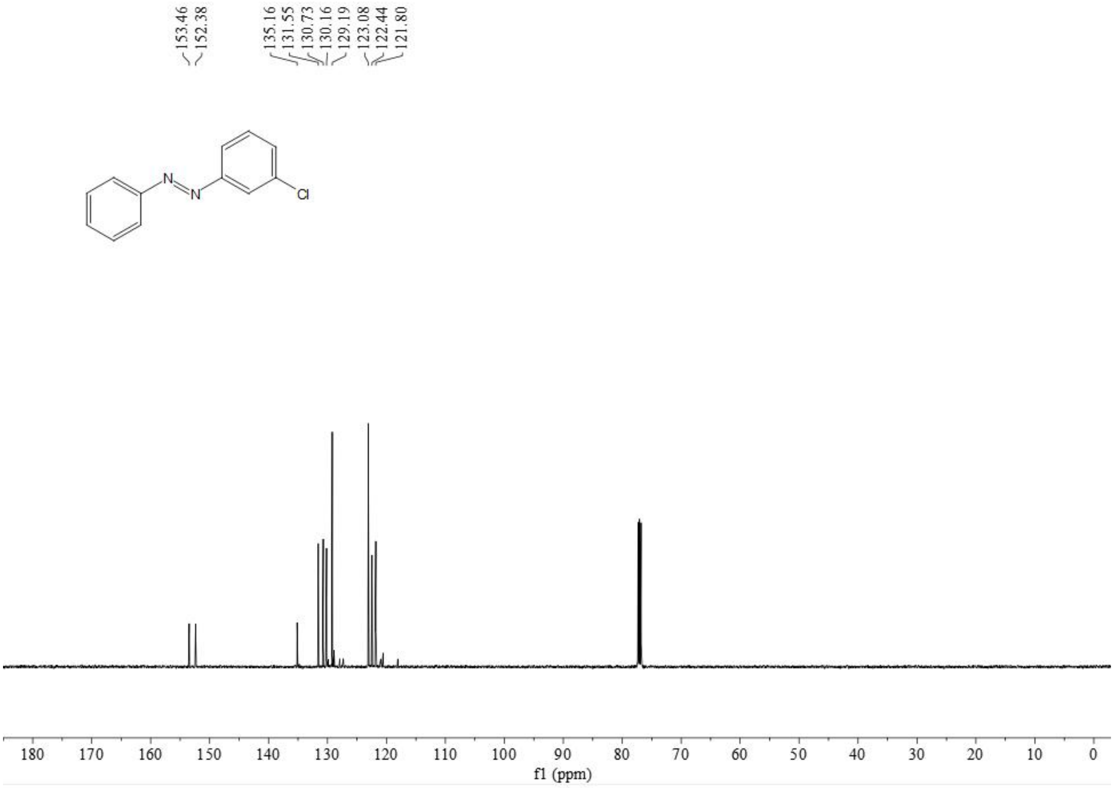
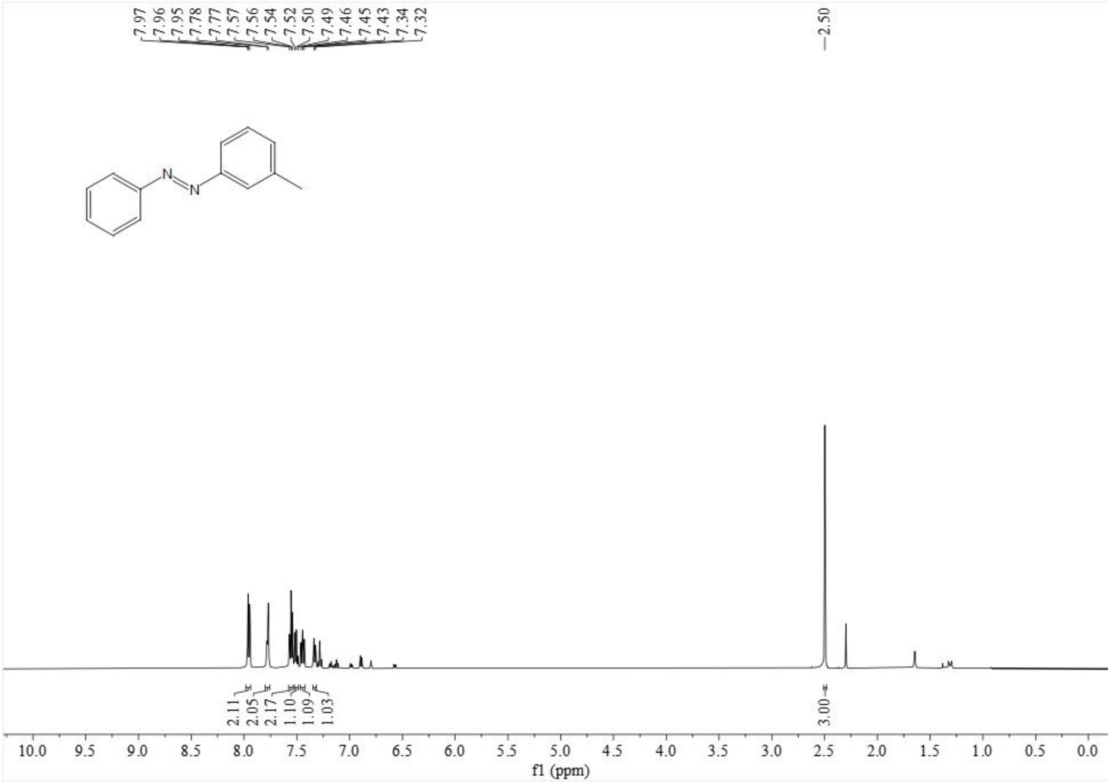
f1 (ppm)

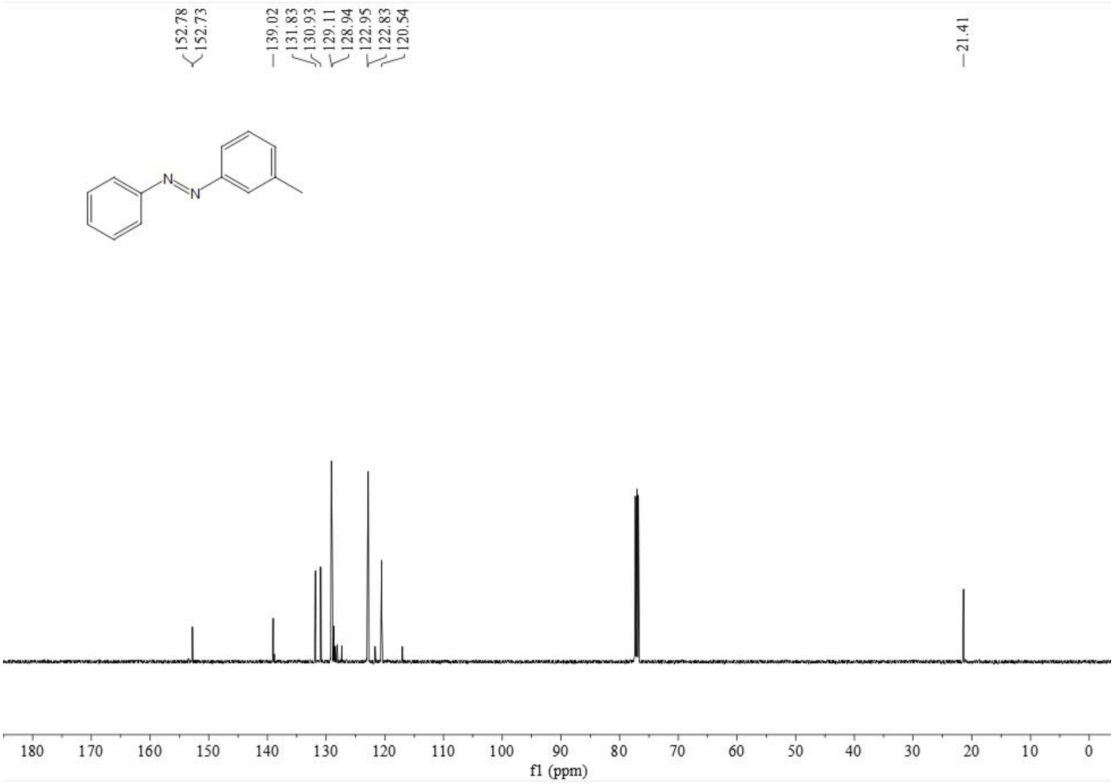
^{1}H NMR and ^{13}C NMR of 1-(3-Chlorophenyl)-2-phenyldiazene 3bg (500 MHz, CDCl$_3$)



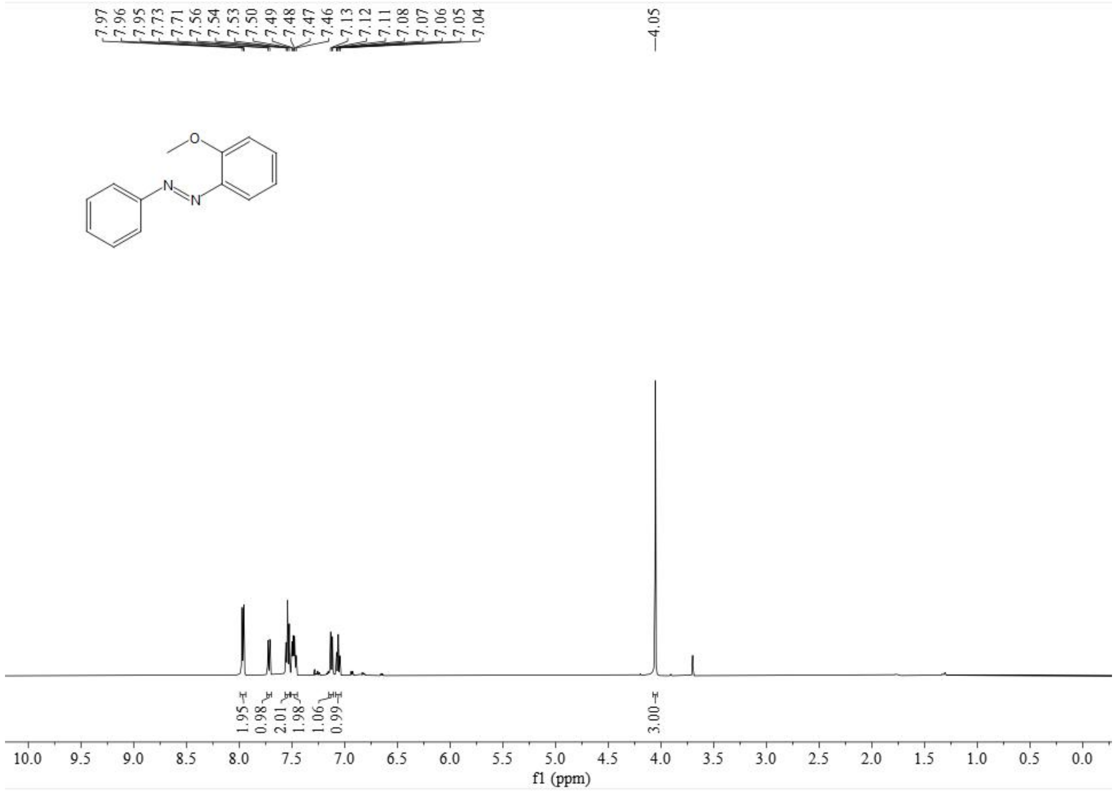


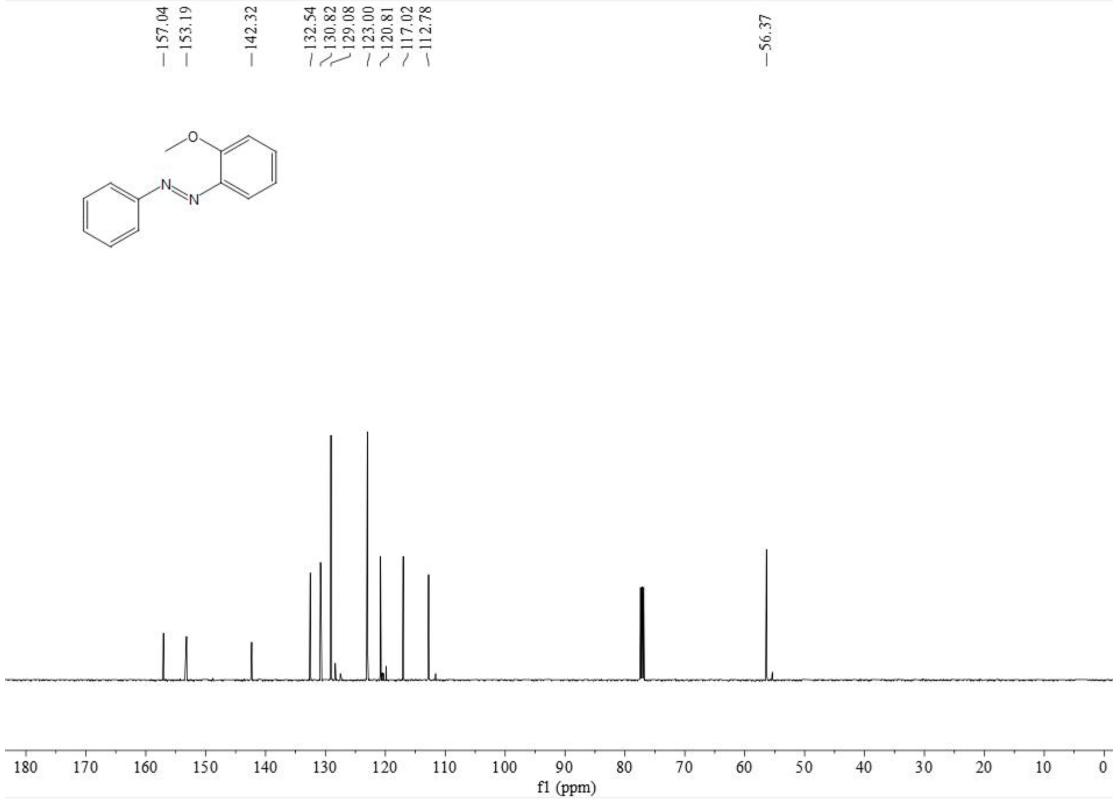
^{1}H NMR and ^{13}C NMR of 1-Phenyl-2-(m-tolyl)diazene 3bh (500 MHz, $CDCl_3$)



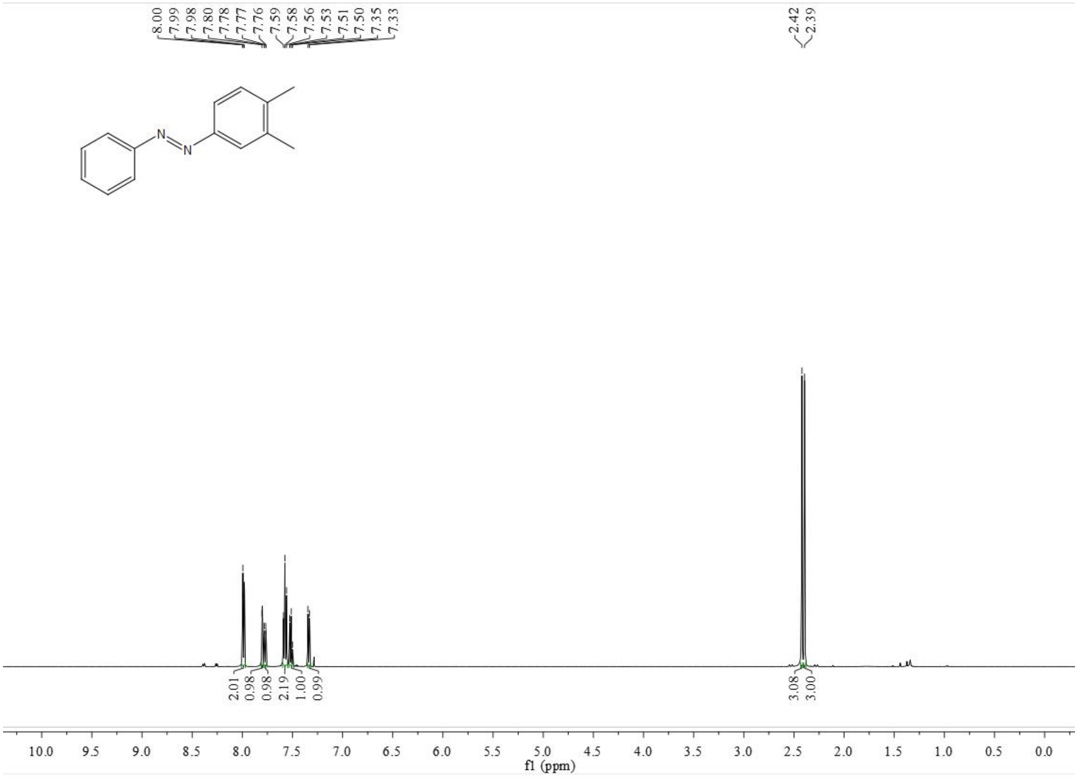


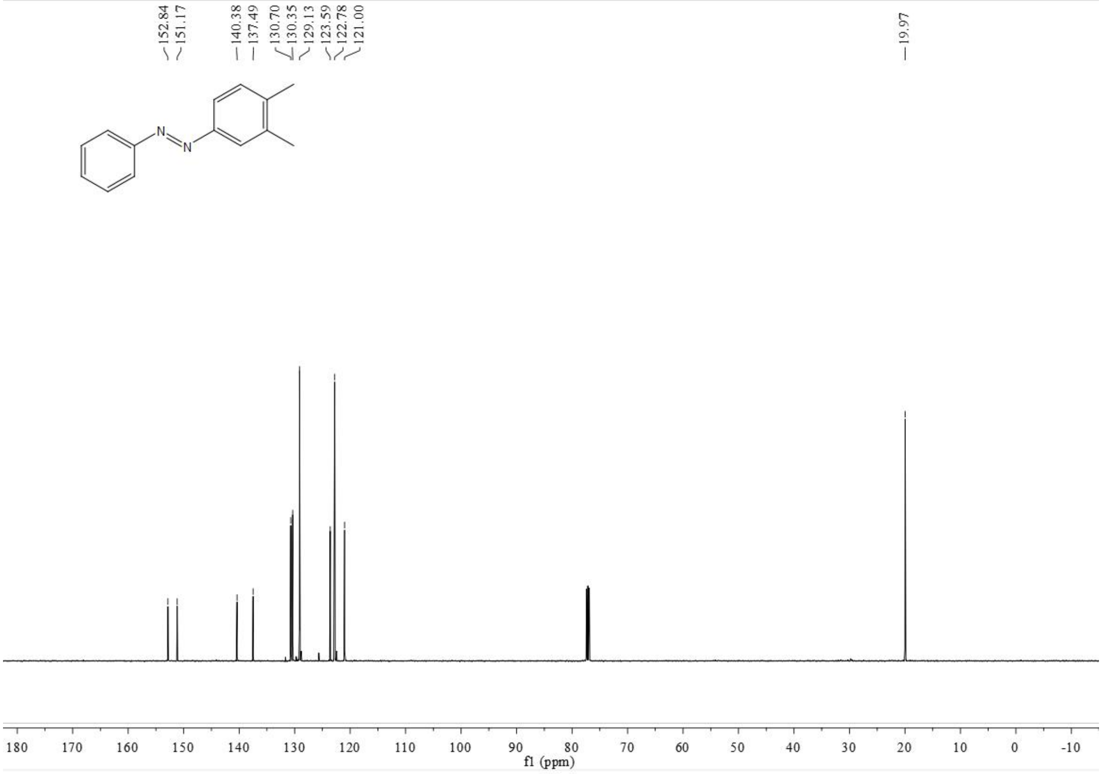
^{1}H NMR and ^{13}C NMR of 1-(2-Methoxyphenyl)-2-phenyldiazene 3bi (500 MHz, CDCl$_3$)



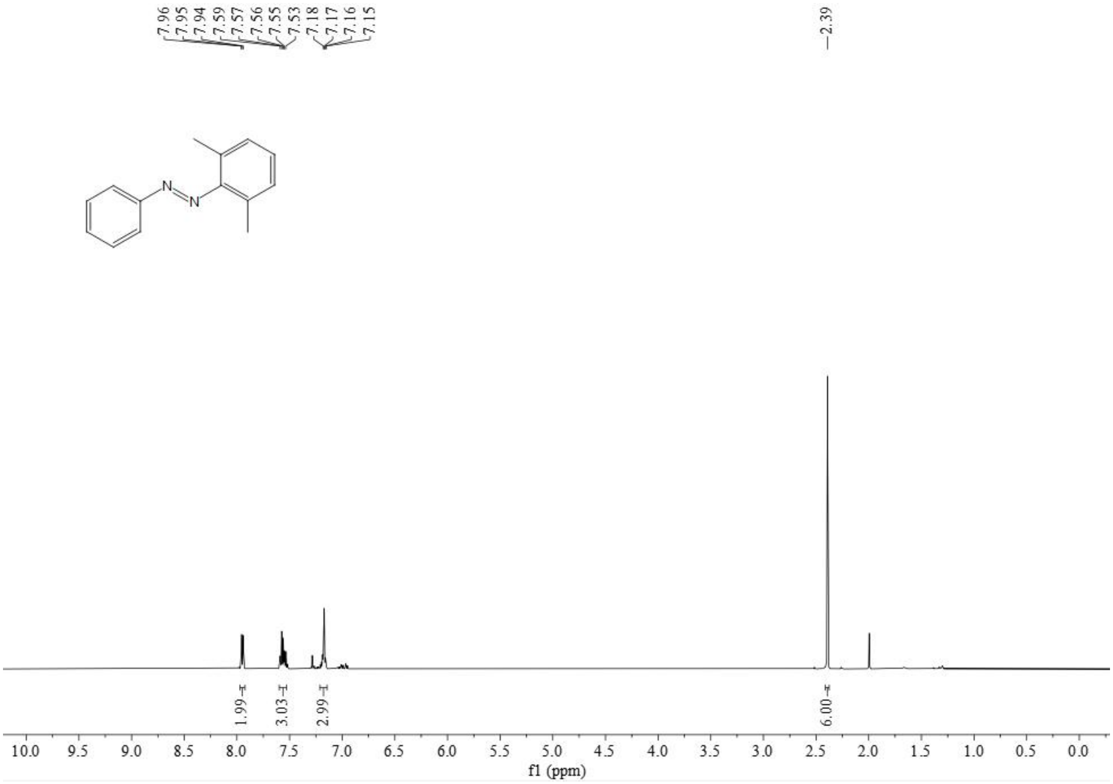


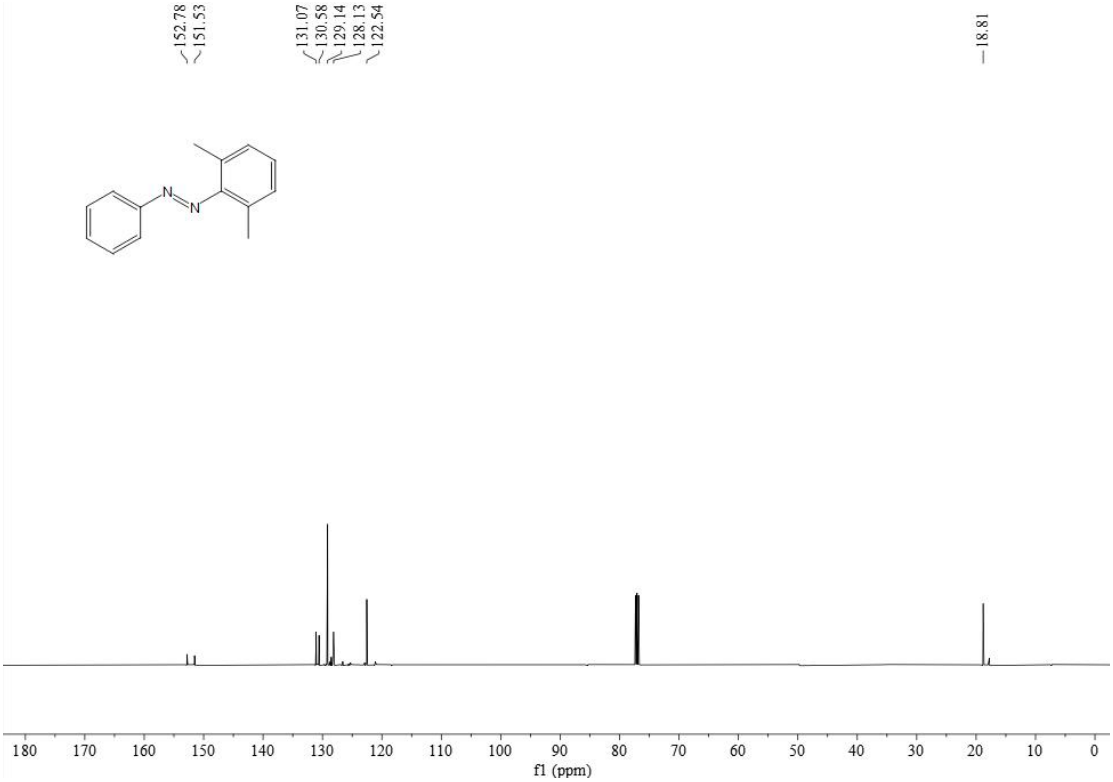
^{1}H NMR and ^{13}C NMR of 1-(3,4-Dimethylphenyl)-2-phenyldiazene 3bj (500 MHz, $CDCl_3$)



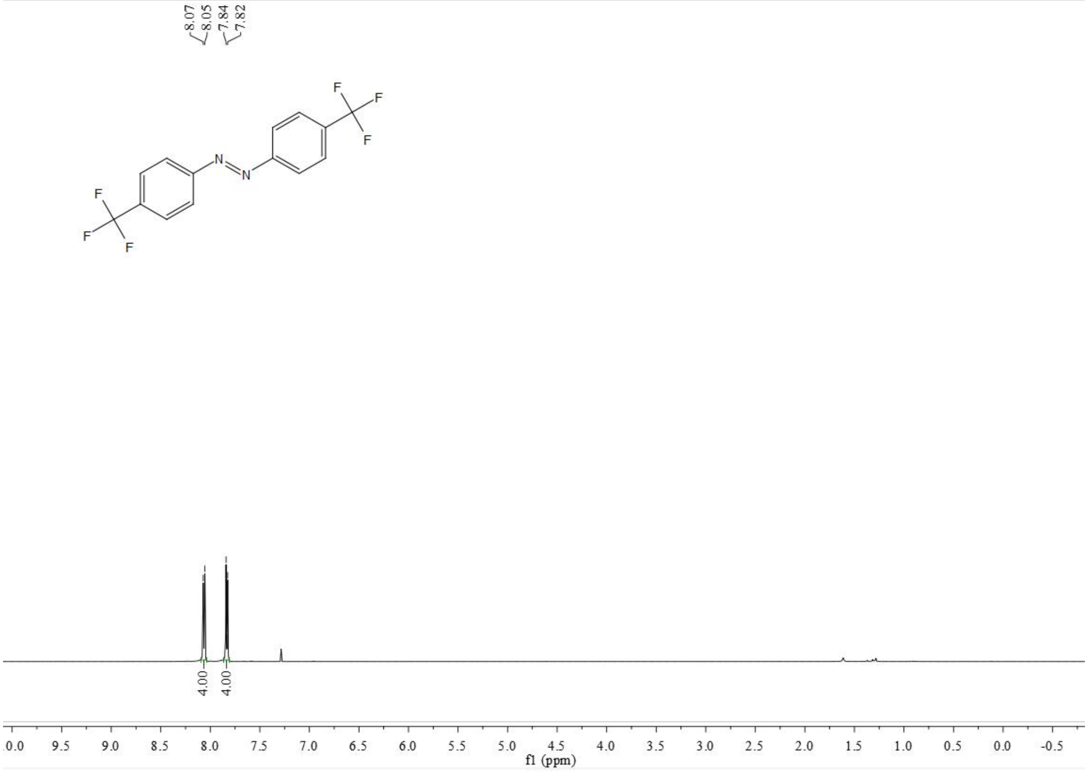


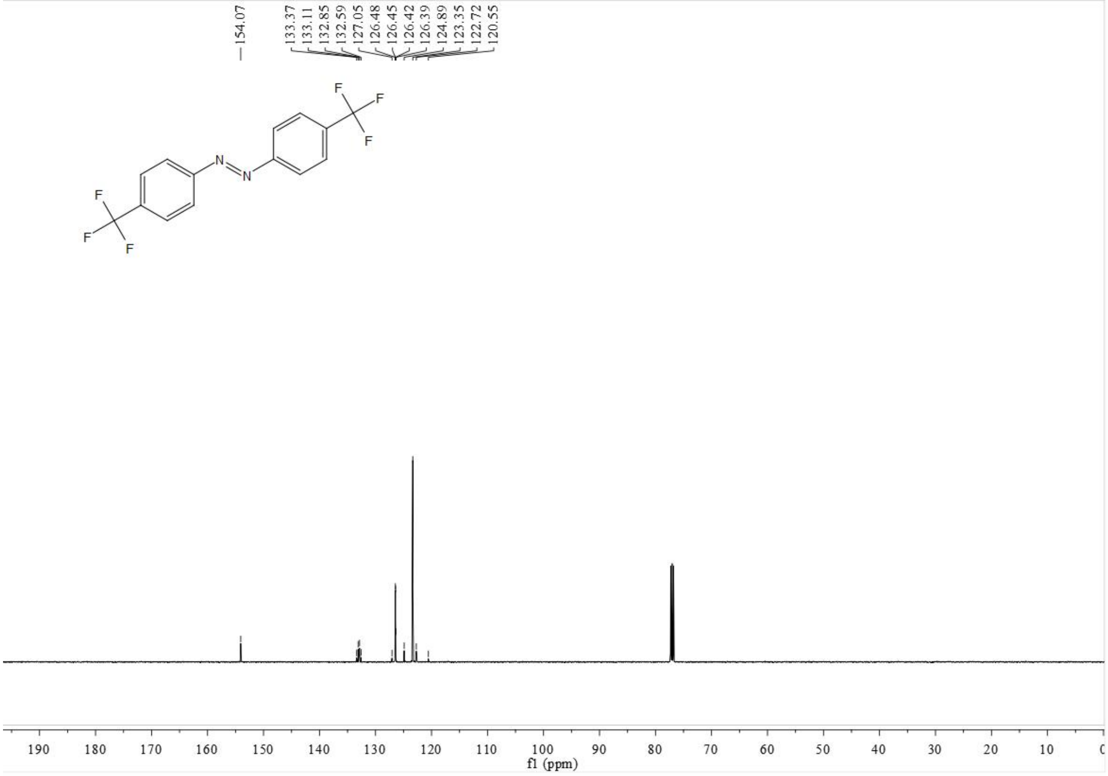
^{1}H NMR and ^{13}C NMR of 1-(2,6-Dimethylphenyl)-2-phenyldiazene 3bk (500 MHz, $CDCl_3$)

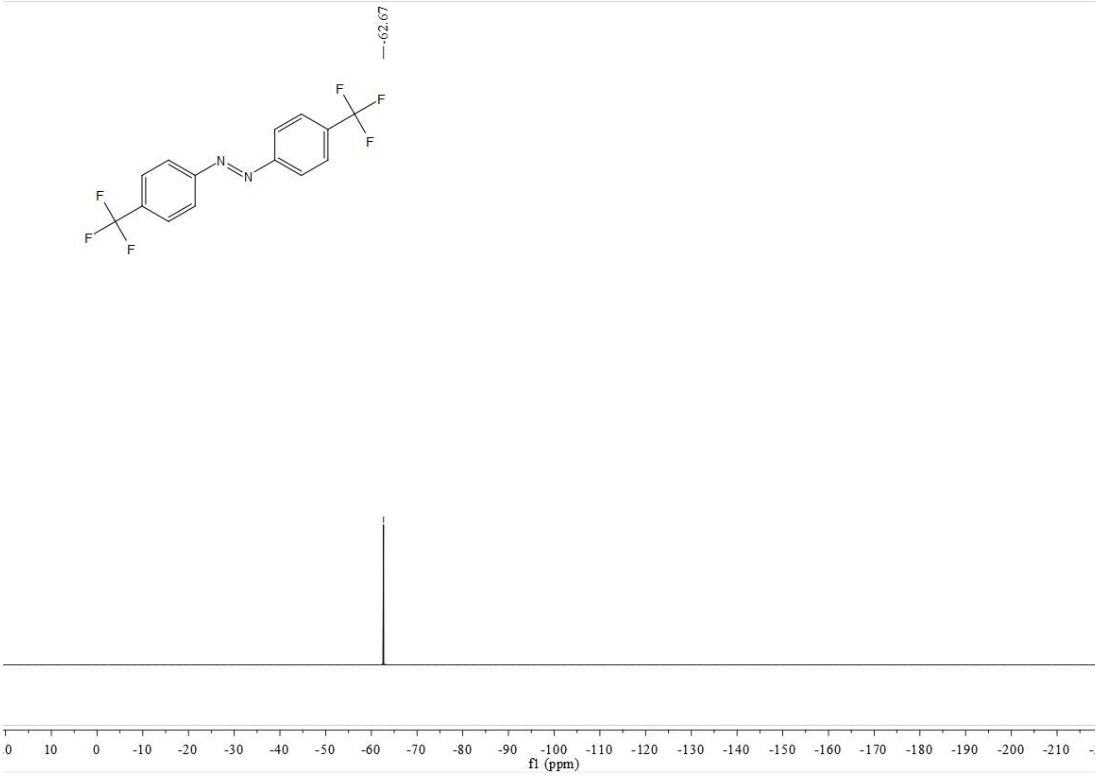




^{1}H NMR, ^{13}C NMR and ^{19}F NMR of 1,2-Bis(4-(trifluoromethyl)phenyl)diazene 3ca (500 MHz, $CDCl_3$)



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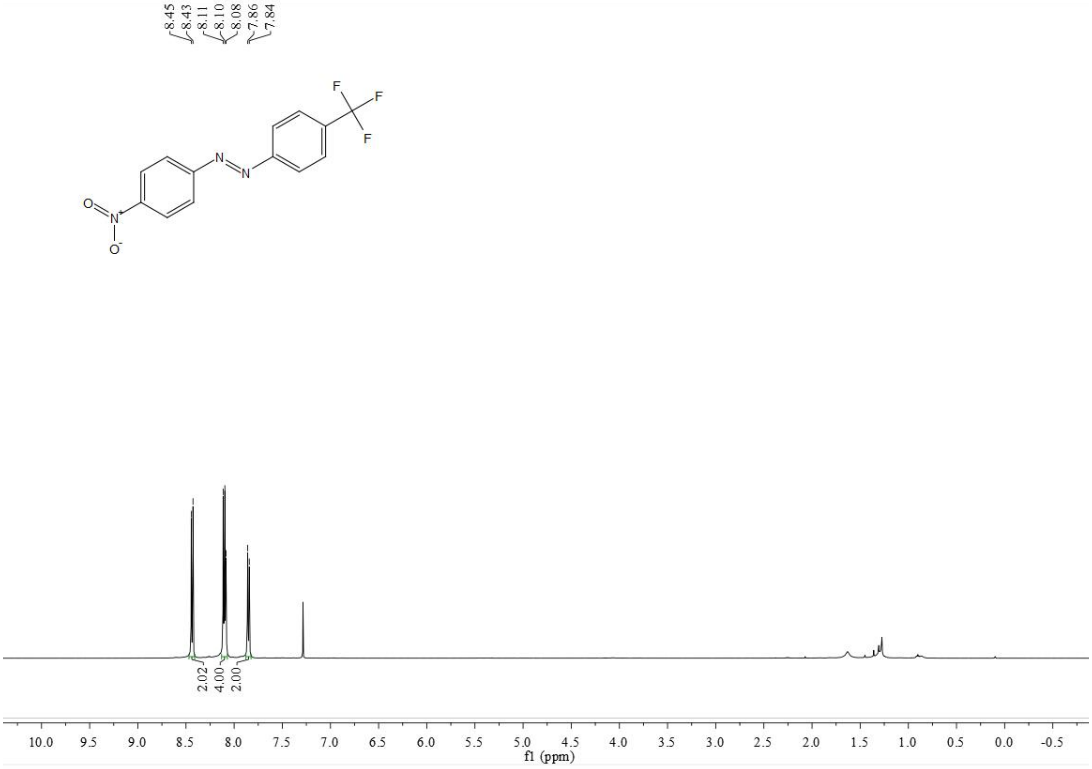
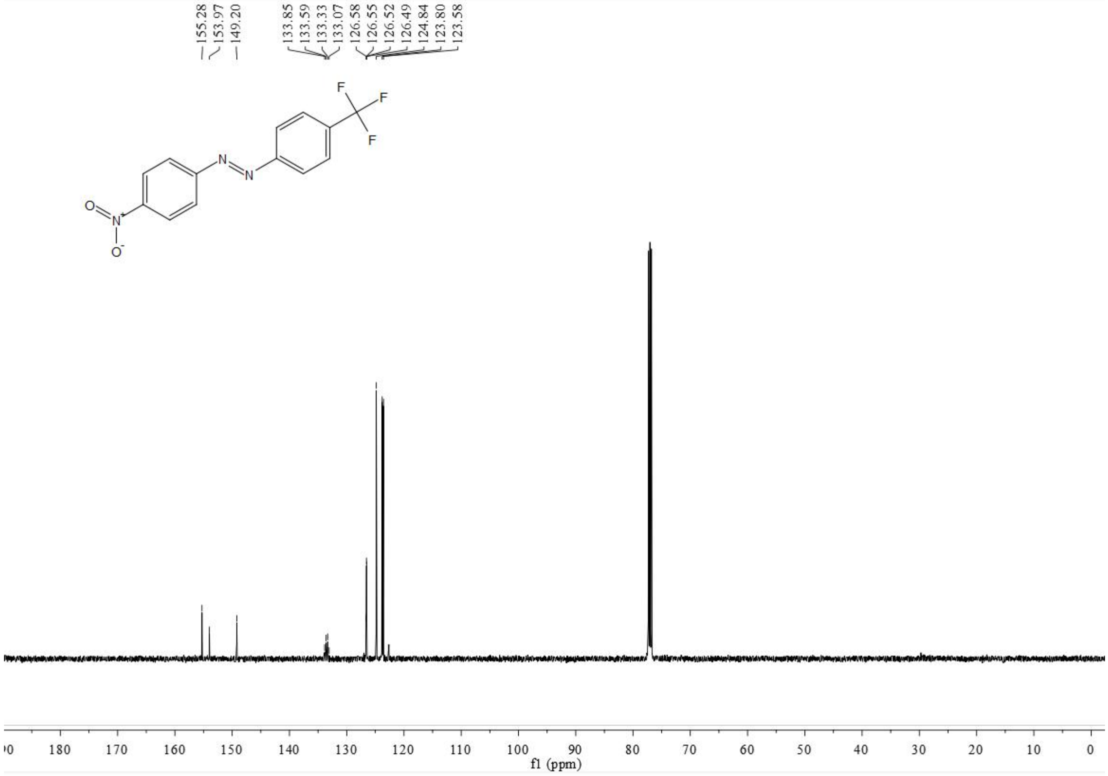
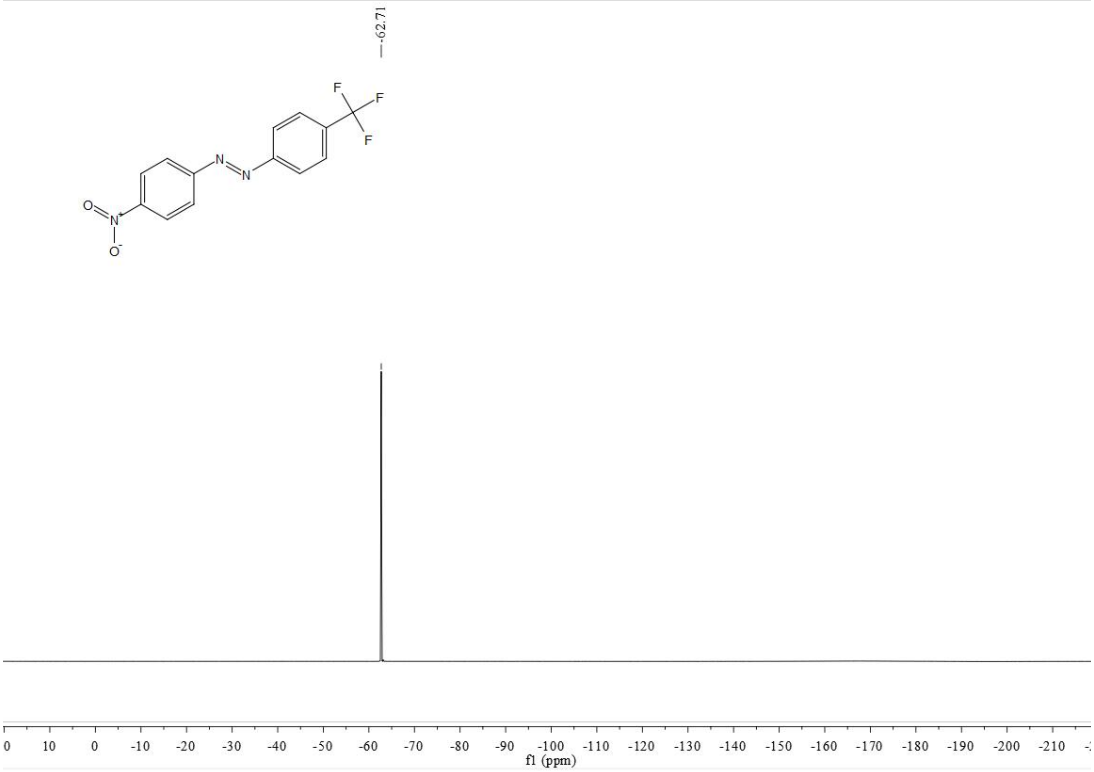
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

^1H NMR, ^{13}C NMR and ^{19}F NMR of 1-(4-Nitrophenyl)-2-(4-(trifluoromethyl)phenyl)diazene 3cb (500 MHz, $CDCl_3$)



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N
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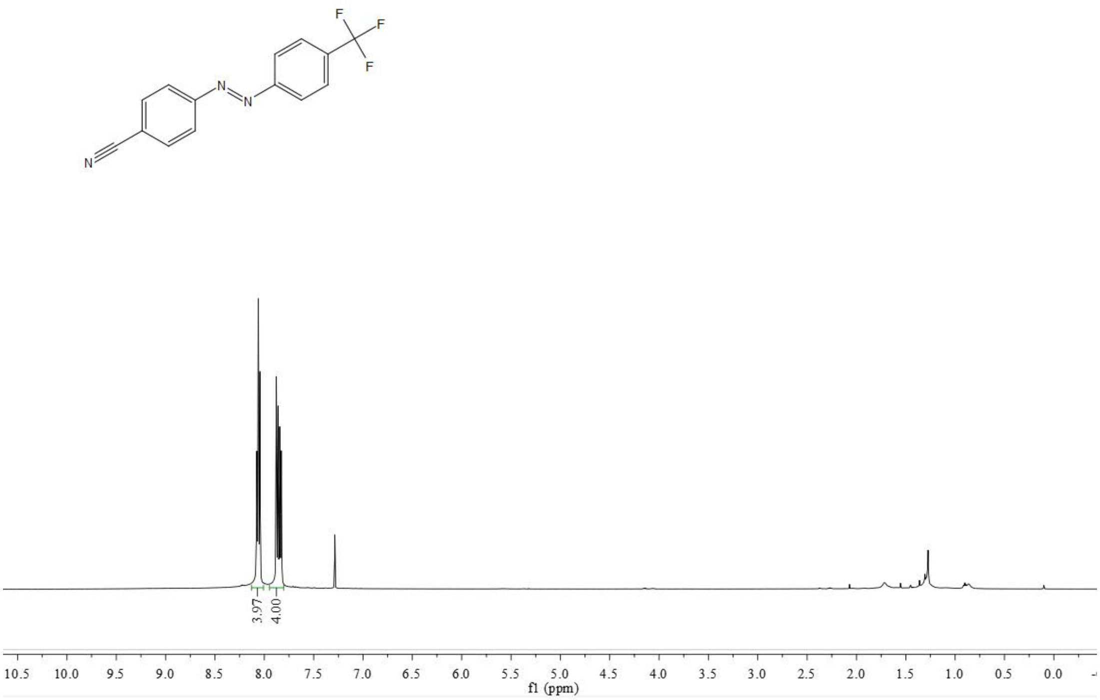
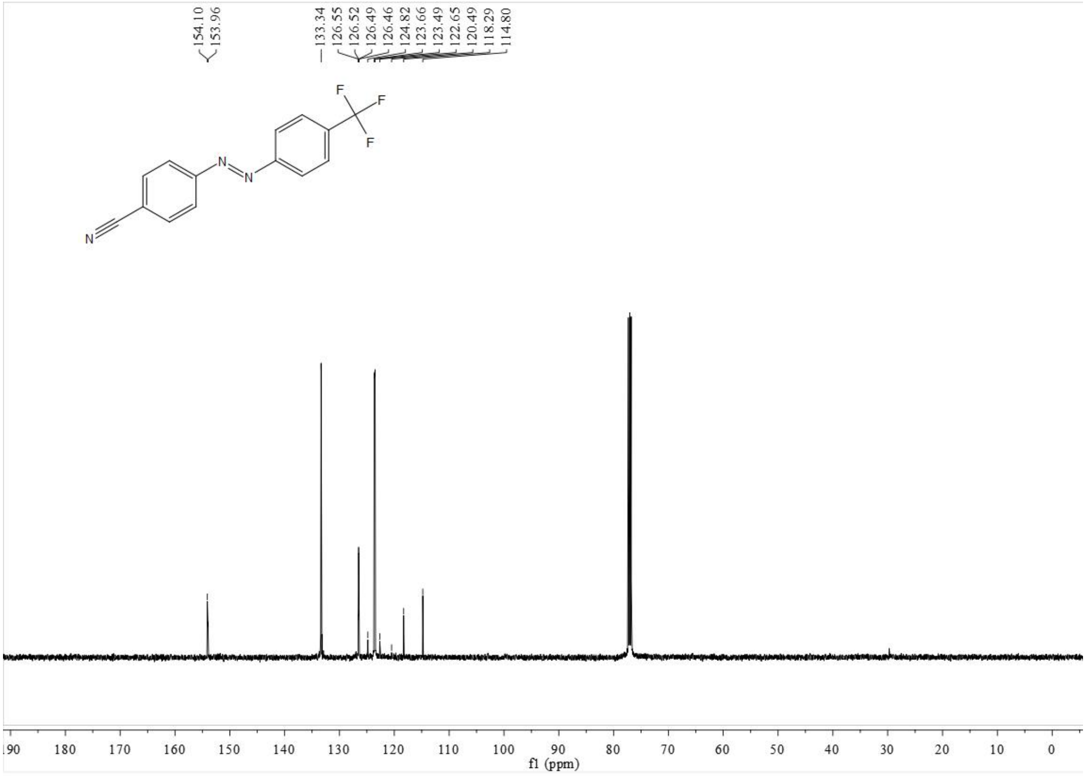
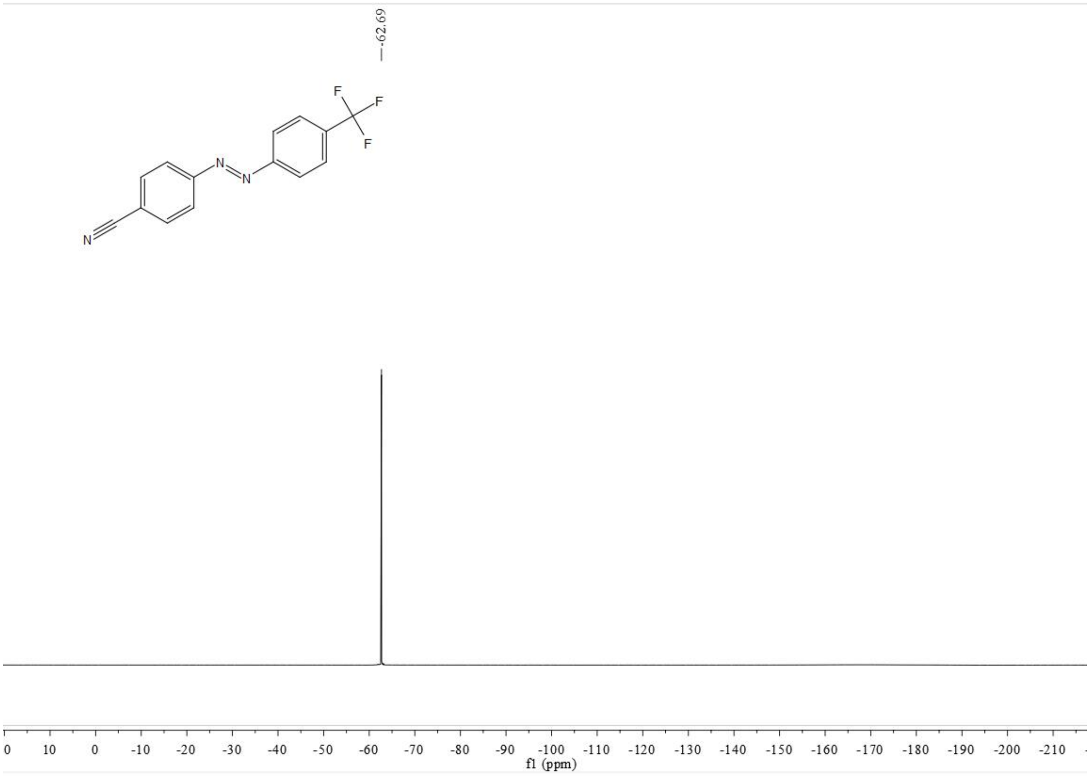
N+
O-
0 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

^{1}H NMR, ^{13}C NMR and ^{19}F NMR of 4-((4-(Trifluoromethyl)phenyl)diazenyl)benzonitrile 3cc (500 MHz, $CDCl_3$)






—-62.69
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-80
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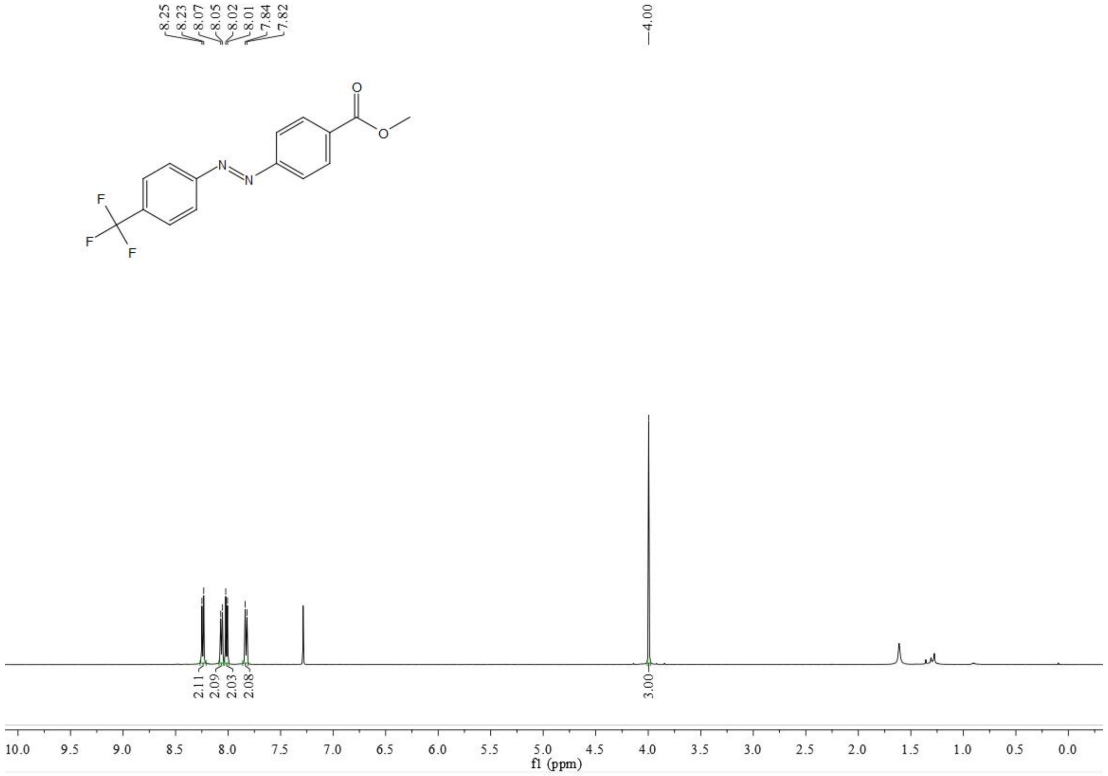
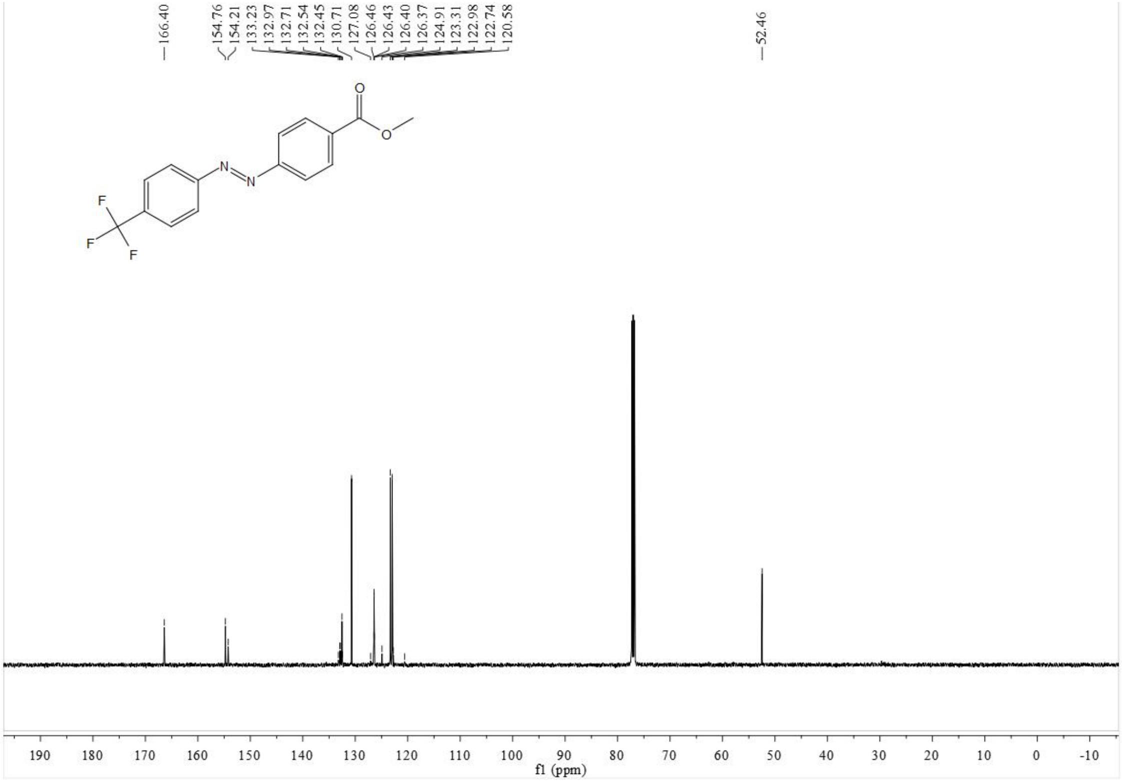
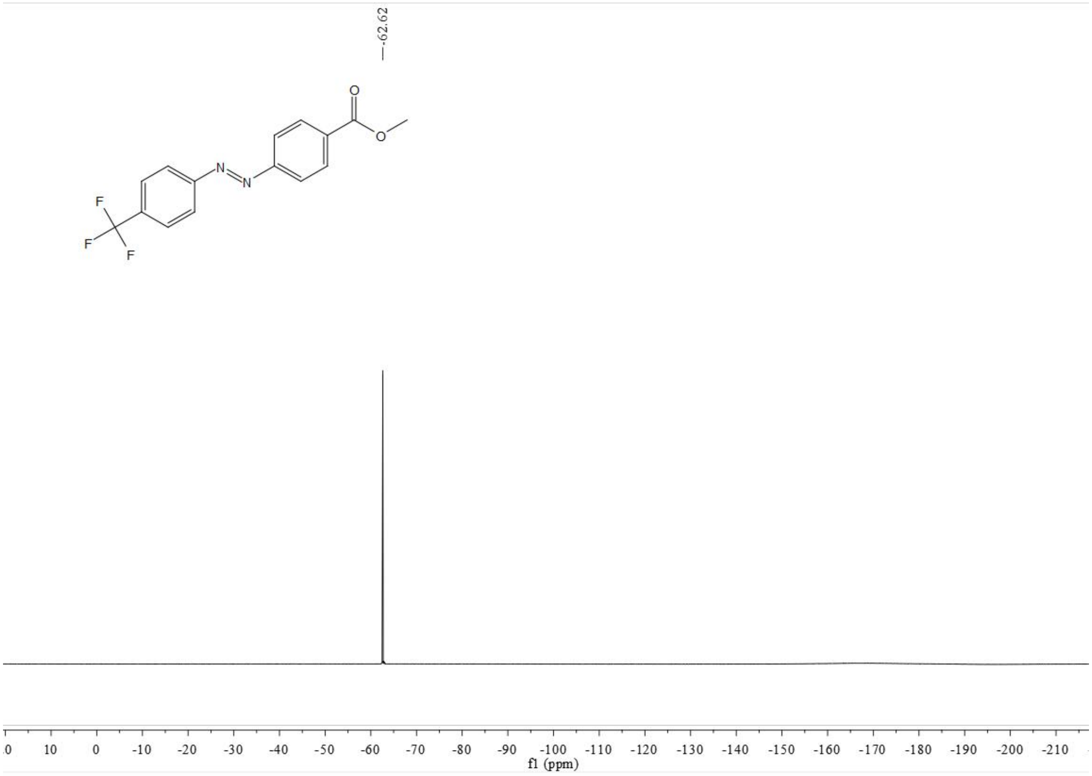
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

^{1}H NMR, ^{13}C NMR and ^{19}F NMR of Methyl -4-((4-(trifluoromethyl)phenyl)diazenyl)benzoate 3cd (500 MHz, CDCl$_3$)



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-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

^1H NMR and ^{13}C NMR of (5-Methoxy-2-(4-methoxyphenyl)-2H-indazol-3-yl) methanol (4aa) (500 MHz, $CDCl_3$)