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I. General Information

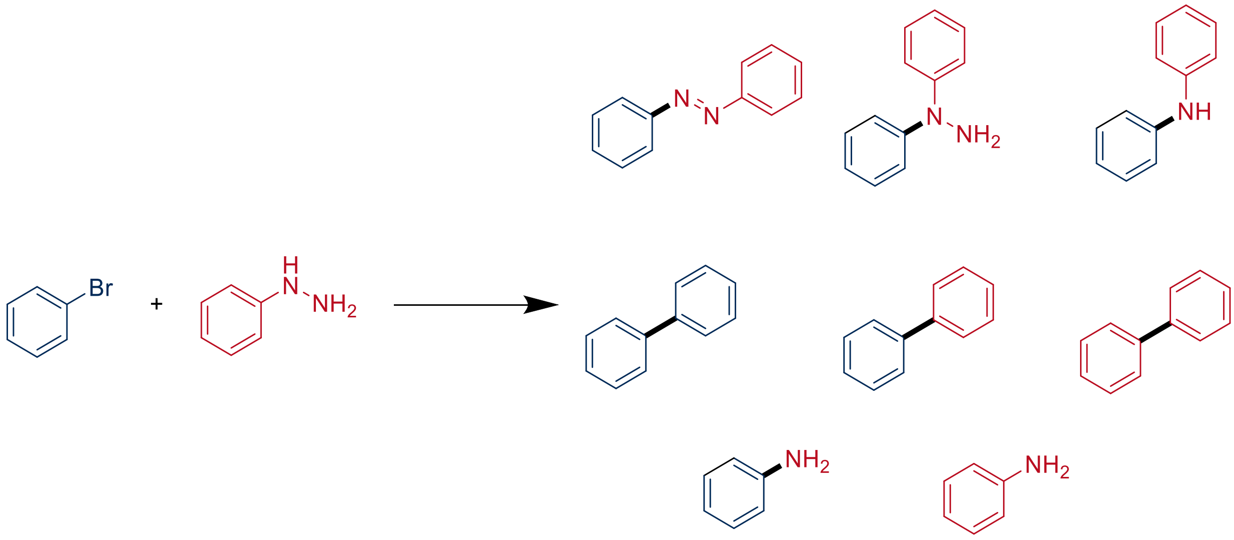
Air-sensitive synthesis were performed under argon atmosphere, air- and moisture-sensitive synthesis were performed under argon atmosphere in heating gun vacuum dried glassware. Chemicals were purchased from Aldrich, TCI, BLDpharm, ABCR, enamine, activate scientific and Strem chemicals. Ar, was provided by Linde Europe Solvents under argon conditions were degassed prior to use.

The products were characterized by ^{1}H NMR, ^{13}C and ^{19}F spectroscopy. 1H, 13C and 19F NMR spectra were recorded on Bruker Avance 300 (300 MHz), 400 (400 MHz) Fourier-300 (300 MHz) NMR spectrometers. Chemical shifts δ (ppm) are given relative to solvent : references for $CDCl_3$ were 7.26 ppm (^{1}H NMR) and 77.16 ppm (^{13}C NMR); references for MeOH-d_4 were 3.31 ppm (^{1}H NMR) and 49.00 ppm (^{13}C NMR) ; references for DMSO-d_6 were 2.50 ppm (^{1}H NMR) and 39.52 (^{13}C).^{13}C-NMR spectra were acquired on a broad band decoupled mode. Multiplets were assigned as s (singlet), d (doublet), t (triplet), q (quadruplet) and m (multiplet).

GC-MS analyses were performed using an Agilent 8890 GC instrument and a 5977B GC/MSD instrument using an Agilent HP-5MS column. The oven program used was the following: 50 °C for 0 min, then 8 °C/min to 120 °C, then 15 °C/min to 200 °C, then 25 °C/min to 300 °C, then 15 min at 300 °C.

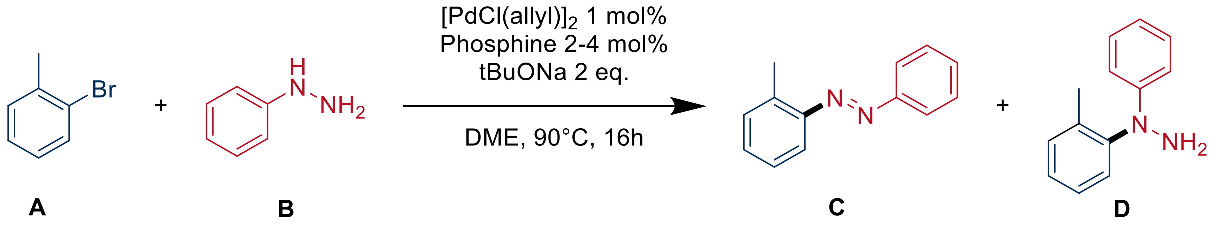
GC/FID and GC/MS yields for optimization are calculated considering that all azo-compounds have the same answer factor than azobenzene using tetradecane as an internal standard.

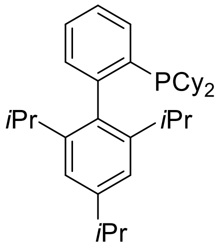
According to GC/MS analysis, the following products are formed but in trace amount in most of the reactions even if not reported:



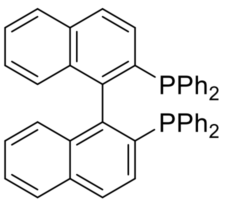
II. Additional experiments on reaction optimization

Table S1. Choice of phosphines (1)

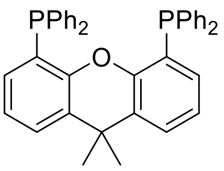




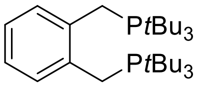
XPhos



BINAP



XanthPhos

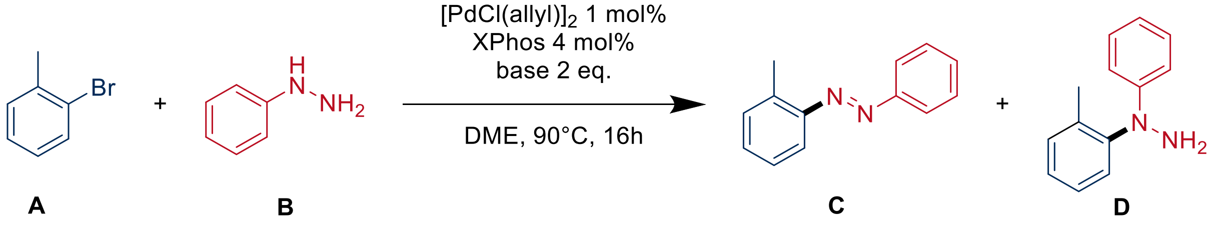


dtbpx

Entry	Phosphine	A azobenzene / A dodecane (internal standard), GC/MS
1	**XPhos 4 mol%**	**0.67 / 1**
2	**BINAP 2 mol%**	**0.66 / 1**
3	XanthPhos	0.24 / 1
4	dtbpx	0.14 / 1

Reaction conditions : 2-bromotoluene (0.5 mmol, 60 µL), phenylhydrazine (0,5 mmol (49 µL), $[PdCl(allyl)]_2$ (5 µmol, 1.9 mg), phosphine (20-40 µmol), tBuONa (1 mmol), DME (1 mL), 90°C, 16h

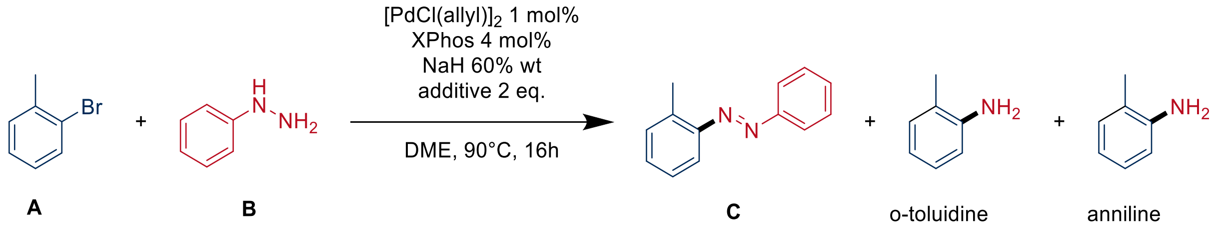
Table S2. Choice of base (1)



Entry	Base	GC/MS yield of C	Area of C(GC/MS)/ Area of D (GC/MS)
5	tBuONa	50	0042
6	K_2CO_3	0	Not determined
7	KOH	0	Not determined
8	K_3PO_4	25	Not determined
9	**NaH 60%wt**	**62**	**0.068**
10	KOAc	1	Not determined
11	AgOAc	0	Not determined

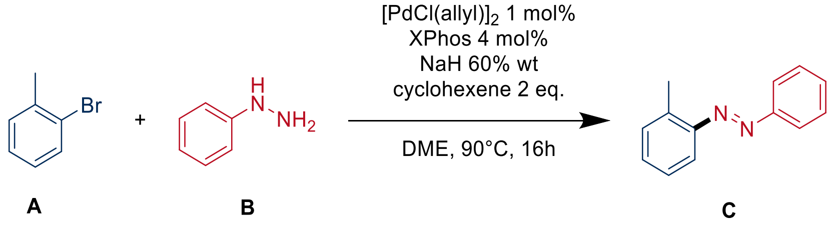
Reaction conditions : 2-bromotoluene (0 .5 mmol, 60 µL), phenylhydrazine (0,5 mmol) (49 µL), $[PdCl(allyl)]_2$ (5 µmol, 1.9 mg), XPhos (20 µmol, 9.5 mg), base (1 mmol), DME (1 mL), 90°C, 16h

Table S3. Test of additives



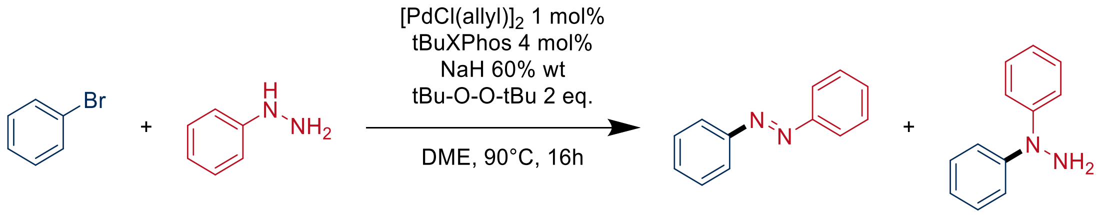
Entry	Additive	GC/FID yield of C	GC/FID yield of *o*-toluidine	GC/FID yield of anniline
12	No additive	31	34	44
13	Cyclohexene	52	45	46
14	***t*Bu-O-O-*t*Bu**	**65**	**2**	**3**
15	**DCC**	**65**	**8**	**5**
16	Ph-CO_2-O-*t*Bu	30	24	26
Reaction conditions : 2-bromotoluene (0 .5 mmol, 60 µL), phenylhydrazine (0,5 mmol (49 µL), $[PdCl(allyl)]_2$ (5 µmol, 1.9 mg), XPhos (20 µmol, 9.5 mg), tBuONa (1 mmol, 96 mg), additive (1mmol) DME (1 mL), 90°C, 16h				

Table S4. Importance of all reagents

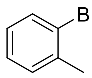


Entry	$[PdCl(allyl)]_2$	XPhos	NaH 60% wt	Cyclohexene	Yield of C
17	✓	✓	✓	✓	**46**
18	✗	✓	✓	✓	1
19	✗	✗	✓	✓	2
20	✓	✓	✗	✓	0
21	✓	✓	✗	✓	0
22	✗	✗	✓	✗	0
Reaction conditions : 2-bromotoluene (0 .5 mmol, 60 µL), phenylhydrazine (0,5 mmol(49 µL), $[PdCl(allyl)]_2$ (5 µmol, 1.9 mg), XPhos (20 µmol, 9.5 mg), tBuONa (1 mmol, 96 mg), cyclohexene (1mmol) DME (1 mL), 90°C, 16h					

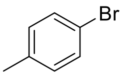
Table S5. Optimization of phosphine (2), comparison with different aryl bromides



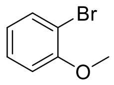
A **B** **C** **D**



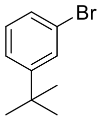
2-bromotoluene



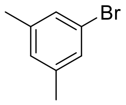
4-bromotoluene



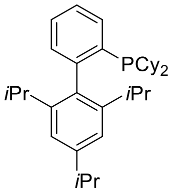
2-bromoanisole



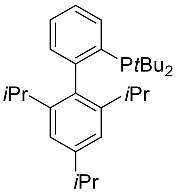
3-bromotertbutylbenzene



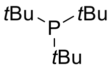
3,5-dimethylbromobenzene



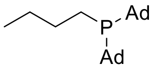
XPhos



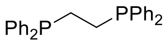
*t*BuXPhos



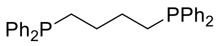
P*t*Bu$_3$



Cataxcium



dppe

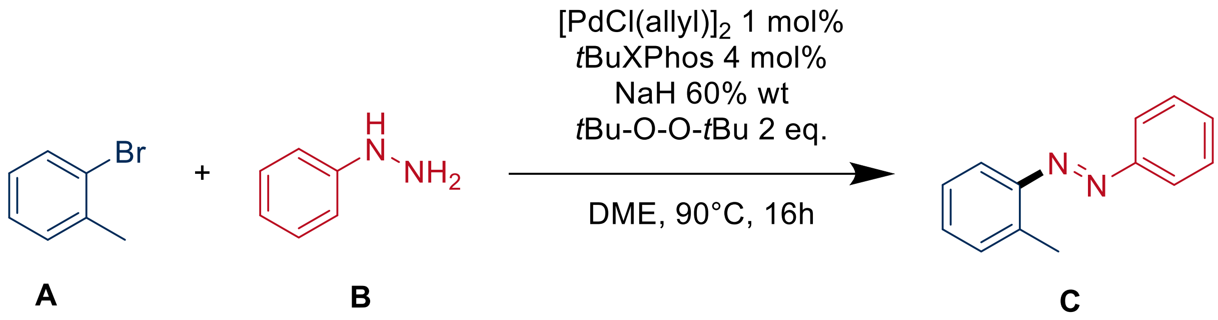


dppb

Entry	Aryl bromide	Phosphine	GC/FID yield of azobenzene
23	**2-bromotoluene**	**XPhos**	**54**
24	2-bromotoluene	*t*BuXPhos	27
25	**2-bromotoluene**	**P*t*Bu$_3$** 10%wt in hexane	**51**
26	4-bromotoluene	XPhos	**0**
27	**4-bromotoluene**	***t*BuXPhos**	**26**
28	4-bromotoluene	CatacXium	0
29	4-bromotoluene	Dppb	0
30	4-bromotoluene	Dppe	0
31	4-bromotoluene	P*t*Bu$_3$ 10%wt in hexane	19
32	2-bromoanisole	XPhos	0
33	**2-bromoanisole**	***t*BuXPhos**	**64**
34	2-bromoanisole	P*t*Bu$_3$ 10%wt in hexane	33
35	3-bromotertbutylbenzene	XPhos	0
36	**3-bromotertbutylbenzene**	***t*BuXPhos**	**45**
37	3-bromotertbutylbenzene	P*t*Bu$_3$ 10%wt in hexane	28
38	3,5-dimethylbromobenzene	XPhos	0
39	**3,5-dimethylbromobenzene**	***t*BuXPhos**	**25**
40	3,5-dimethylbromobenzene	P*t*Bu$_3$ 10%wt in hexane	24

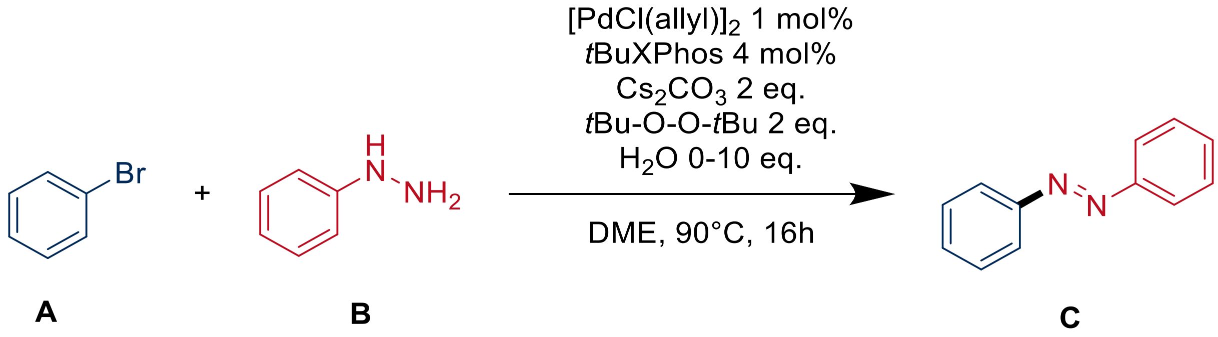
Reaction conditions : aryl bromide (0.5 mmol, 60 µL), phenylhydrazine (0,5 mmol) (49 µL), [PdCl(allyl)]$_2$ (5 µmol, 1.9 mg), phosphine (20 µmol, 9.5 mg), NaH 60% wt (0.5 mmol, 40 mg), *t*Bu-O-O-*t*Bu (1mmol, 184 µL) DME (1 mL), 90°C, 16h

Table S6. Scope of base (2)



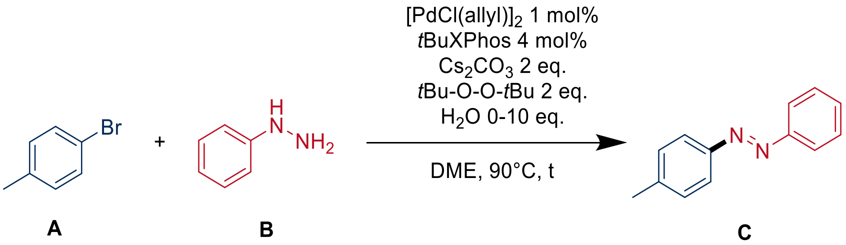
Entry	Base	GC/MS yield of C
41	NaH 60%wt	38
42	*t*BuONa	9
43	*t*BuOK	10
44	AcONa	0
45	K_2CO_3	7
46	**Cs_2CO_3**	**62**
47	K_3PO_4	43
Reaction conditions : 2-bromotoluene (0 .5 mmol, 60 µL), phenylhydrazine (0,5 mmol (49 µL), $[PdCl(allyl)]_2$ (5 µmol, 1.9 mg), *t*BuXPhos (20 µmol, 8.5 mg), base (1 mmol), DME (1 mL), 90°C, 16h		

Table S7 Role of water



Entry	Aryl bromide	Amount of H_2O	GC/FID yield of azobenzene
48	2-bromotoluene	0	64
49	2-bromotoluene	0.5	70
50	**2-bromotoluene**	**1**	**74**
51	**2-bromotoluene**	**2**	**71**
52	2-bromotoluene	10	13
53	1-bromo-2(trifluoromethoxy)benzene	0	4
54	1-bromo-2(trifluoromethoxy)benzene	0.5	28
55	1-bromo-2(trifluoromethoxy)benzene	1	51
56	**1-bromo-2(trifluoromethoxy)benzene**	**2**	**69**
57	1-bromo-2(trifluoromethoxy)benzene	10	10
Reaction conditions : aryl bromide (1 mmol, 120 µL), phenylhydrazine (1 mmol (98 µL), $[PdCl(allyl)]_2$ (10 µmol, 3.7 mg), *t*BuXPhos (20 µmol, 17 mg), Cs_2CO_3 (2 mmol, 652mg), *t*Bu-O-O-*t*Bu (2 mmol, 368 µL), H_2O (0-10 mmol) DME (1 mL), 90°C, 16h			

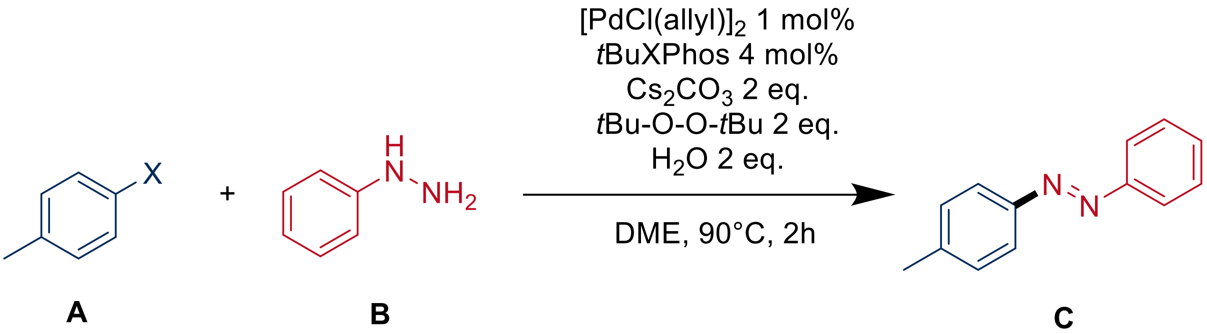
Table S8. Shorter reaction time



Entry	Time	GC/FID yield of azobenzene
58	2 minutes	11
59	5 minutes	13
60	2 hours	42
61	16 hours	46

Reaction conditions : 2-bromotoluene (1 mmol, 120 µL), phenylhydrazine (1 mmol (98 µL), $[PdCl(allyl)]_2$ (10 µmol, 3.7 mg), *t*BuXPhos (20 µmol, 17 mg), Cs_2CO_3 (2 mmol, 652mg), *t*Bu-O-O-*t*Bu (2 mmol, 368 µL), H_2O (2 mmol, 36 µL), DME (1 mL), 90°C, t

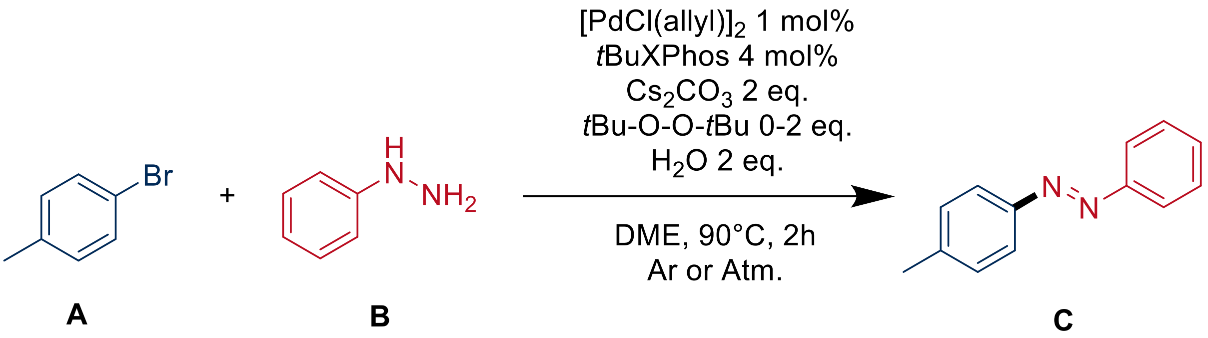
Table S9. Comparison of aryl halides



Entry	X	GC/FID yield of azobenzene
62	Cl	26
63	**Br**	**52**
64	I	22

Reaction conditions : 2-halogenotoluene (1 mmol, 120 µL), phenylhydrazine (1 mmol (98 µL), $[PdCl(allyl)]_2$ (10 µmol, 3.7 mg), *t*BuXPhos (20 µmol, 17 mg), Cs_2CO_3 (2 mmol, 652mg), *t*Bu-O-O-*t*Bu (2 mmol, 368 µL), H_2O (2 mmol, 36 µL), DME (1 mL), 90°C, 2h

Table S10. Role of dioxygen in the reaction, no influence of additive in presence of O_2



Entry	tBu-O-O-tBu ?	Atmosphere	Volume of the Schlenk (mL)	Amount of 02 (considering 25°C, 1 atm.)	GC/FID yield of azobenzene
65	Yes	Ar	25	0.21	13
66	Yes	Atm	25	0.21	47
67	No	Ar	25	0.21	43
68	No	Atm	25	0.21	43
69	**No**	**Atm**	**50**	**0.42**	**53-78**
70	**No**	**Atm**	**100**	**0.84**	**69-77**

Reaction conditions : 2-bromotoluene (1 mmol, 120 µL), phenylhydrazine (1 mmol (98 µL), $[PdCl(allyl)]_2$ (10 µmol, 3.7 mg), tBuXPhos (20 µmol, 17 mg), Cs_2CO_3 (2 mmol, 652mg), *t*Bu-O-O-*t*Bu (0-2 mmol), H_2O (0-10 mmol) DME (1 mL), 90°C, 16h

III. Experimental procedures and characterization data

General procedure for the synthesis of azo compounds :

In a 100 mL Schlenk (filled with Atm) equipped with a magnetic stirring bar, are added 3.7 mg of $[PdCl(allyl)]_2$ (0.01 mmol), 17 mg of *t*BuXPhos (0.04 mmol), 652 mg of Cs_2CO_3. 1 mL of 1,2-dimethoxyethane, 36 µL of water (2 mmol), 1 mmol of aryl bromide and 1 mmol of phenylhydrazine derivatives are added. The Schlenk is then closed and stir for 2 hours in an oil bath at 90°C. After cooling down to rt, water is added and the organic phase is extracted with ethyl acetate. Organic phase is then dried with $MgSO_4$, concentrated in vacuo and the crude product is purified on flash chromatographic column (12 g SiO_2, “gold” quality, pentane/AcOEt) to afford the desired azo-compound.

In some case the “Z azobenzene isomer is present and observed in NMR analysis.

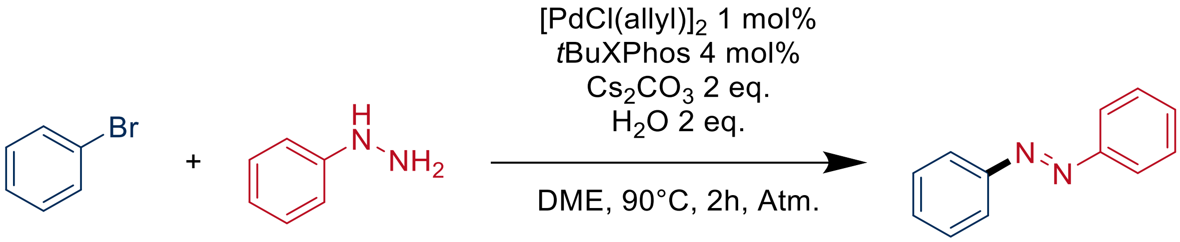
All compounds are analyzed by ^{1}H and ^{13}C NMR (^{19}F NMR analysis has also been performed for fluorine containing molecules) and GC/MS.

HRMS were performed for the non-described compounds.

Purification of phenylhydrazine

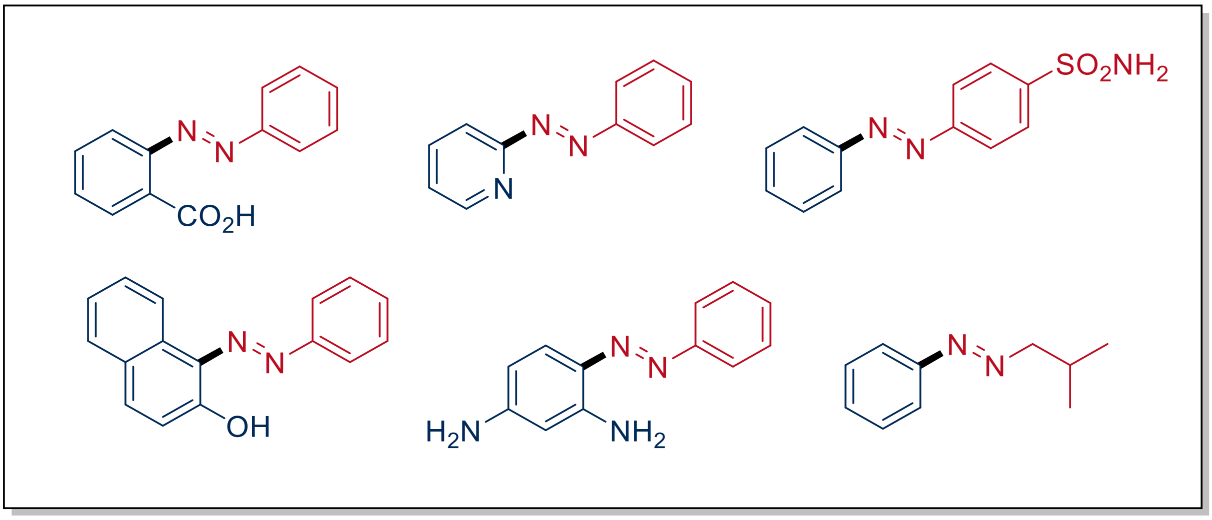
In a 250 mL Erlenmeyer are added 29 mmol of phenylhydrazine hydrochloride derivative. 58 mmol of potassium hydroxide, 30 mL of dichloromethane and 30 mL of water are added and the solution is stirred for 15 minutes. Organic phase is recovered, dry over $MgSO_4$ and concentrated in vacuo to afford the pure phenylhydrazine derivative.

Figure S1 : failed experiments

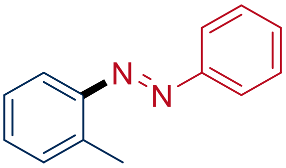


A **B** **C (not identified)**

Failed reactions, azobenzenes not identified



(*E*)-1-Phenyl-2-(*o*-tolyl)diazene (3a)



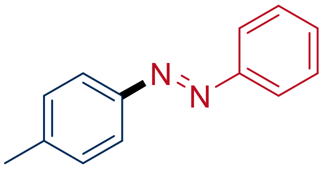
Prepared according to general procedure from phenylhydrazine (108.1 mg, 1 mmol, 1 equiv.) and 2-bromotoluene (171.0 mg, 1 mmol, 1 equiv.). After purification, 148 mg of **3a** are obtained (0.75 mmol, 75%). Around 5% of the *Z* isomer are observed according to ^{1}H NMR.

^{1}H NMR (300 MHz, MeOD) δ 7.87 – 7.76 (m, 2H), 7.59 – 7.50 (m, 1H), 7.48 – 7.32 (m, 3H), 7.32 – 7.19 (m, 2H), 7.19 – 7.09 (m, 1H), 2.61 (s, 3H).

{^{1}H}^{13}C NMR (75 MHz, MeOD) δ 154.2, 151.7, 139.2, 132.2, 132.0, 131.9, 130.1, 127.3, 123.8, 116.2, 17.6.

The NMR data are consistent with those reported for the known compound (CAS 6676-90-0).

(*E*)-1-Phenyl-2-(*p*-tolyl)diazene (3b)



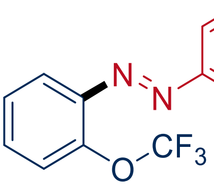
Prepared according to general procedure from phenylhydrazine (108.1 mg, 1 mmol, 1 equiv.) and 4-bromotoluene (171.0 mg, 1 mmol, 1 equiv.). After purification, 99 mg of **3b** was obtained (0.50 mmol, 50%). An additional 41 mg of **3b** (0.28 mmol, 28%) was recovered in a fraction containing biphenyl as an impurity. Around 5% of the *Z* isomer are observed according to ^{1}H NMR.

^{1}H NMR (300 MHz, MeOD) δ 7.91 – 7.83 (m, 2H), 7.83 – 7.76 (m, 2H), 7.56 – 7.45 (m, 3H), 7.37 – 7.27 (m, 2H), 2.40 (s, 3H).

{^{1}H}^{13}C NMR (75 MHz, MeOD) δ 154.0, 152.0, 143.1, 131.9, 130.8, 130.2, 123.8, 123.6, 21.5.

The NMR data are consistent with those reported for the known compound (CAS 949-87-1).

(*E*)-1-Phenyl-2-(2-(trifluoromethoxy)phenyl)diazene (3c)



Prepared according to general procedure from phenylhydrazine (108.1 mg, 1 mmol, 1 equiv.) and 2-trifluoromethoxybromobenzene (241.0 mg, 1 mmol, 1 equiv.). After purification, 184 mg of **3c** are obtained (0.69 mmol, 69%). Around 10% of the *Z* isomer are observed according to ^{1}H NMR.

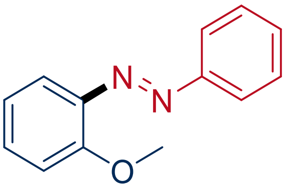
^{1}H NMR (300 MHz, MeOD) δ 7.97 – 7.83 (m, 2H), 7.75 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.59 – 7.37 (m, 6H).

{^{1}H, ^{19}F}^{13}C NMR (75 MHz, MeOD) δ 154.1, 148.0, 148.0, 146.2, 133.4, 132.9, 130.3, 129.1, 124.2, 124.1, 118.4.

{^{1}H}^{19}F NMR (282 MHz, MeOD) δ -59.0.

HRMS (ESI) theoretical mass for [M+H]: 267.0740; found: 267.0746.

(*E*)-1-(2-Methoxyphenyl)-2-phenyldiazene (3d)



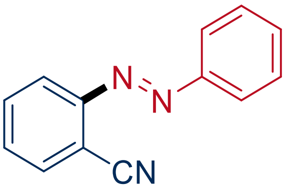
Prepared according to general procedure from phenylhydrazine (108.1 mg, 1 mmol, 1 equiv.) and 2-bromoanisole (187.0 mg, 1 mmol, 1 equiv.). After purification, 163 mg of **3d** was obtained (0.77 mmol, 77%). An additional 50 mg of **3d** (0.23 mmol, 23%) was recovered in a fraction containing biphenyl as an impurity. Around 5% of the *Z* isomer are observed according to ^{1}H NMR.

^{1}H NMR (300 MHz, MeOD) δ 7.92 – 7.82 (m, 2H), 7.61 (ddd, *J* = 8.0, 1.7, 0.4 Hz, 1H), 7.57 – 7.39 (m, 4H), 7.21 – 7.16 (m, 1H), 7.00 (ddd, *J* = 8.0, 7.3, 1.2 Hz, 1H), 3.98 (s, 3H).

{^{1}H}^{13}C NMR (75 MHz, MeOD) δ 157.1, 153.1, 142.0, 132.5, 130.6, 128.8, 122.5, 120.4, 116.3, 112.9, 55.4.

The NMR data are consistent with those reported for the known compound (CAS 6319-21-7).

(*E*)-2-(Phenyldiazenyl) benzonitrile (3e)



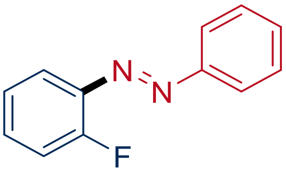
Prepared according to general procedure from phenylhydrazine (108.1 mg, 1 mmol, 1 equiv.) and 2-bromobenzonitrile (182.0 mg, 1 mmol, 1 equiv.). After purification, 167 mg of **3e** are obtained (0.81 mmol, 81%).

^{1}H NMR (400 MHz, MeOD) δ 7.97 – 7.91 (m, 2H), 7.86 (dddd, *J* = 15.6, 8.2, 1.3, 0.6 Hz, 2H), 7.73 (ddd, *J* = 8.2, 7.4, 1.4 Hz, 1H), 7.60 (td, *J* = 7.5, 1.2 Hz, 1H), 7.57 – 7.48 (m, 3H).

{^{1}H}^{13}C NMR (101 MHz, MeOD) δ 154.3, 153.6, 134.9, 134.9, 133.7, 132.5, 130.4, 124.5, 118.1, 117.6, 113.8.

The NMR data are consistent with those reported for the known compound (CAS 38302-59-9).

(*E*)-1-(2-Fluorophenyl)-2-phenyldiazene () (3f)



Prepared according to general procedure form phenyl hydrazine (108.1 mg, 1 mmol, 1 equiv.) and 1-bromo-2-fluorobenzene (175.0 mg, 1 mmol, 1 equiv.). After purification, 173 mg of **3f** was obtained (0.86 mmol, 86%). Traces of 2-fluoro-*N*-phenylaniline were still detected, as confirmed by GC/MS and NMR analysis. Around 10% of the *Z* isomer are observed according to ^{1}H NMR.

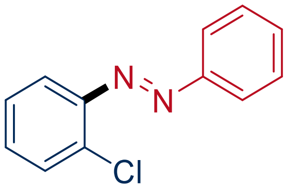
^{1}H NMR (400 MHz, MeOD) δ 7.91 (dd, *J* = 7.1, 1.6 Hz, 2H), 7.74 (t, *J* = 7.9 Hz, 1H), 7.58 – 7.45 (m, 4H), 7.31 (dd, *J* = 10.5, 9.0 Hz, 1H), 7.24 (t, *J* = 8.1 Hz, 1H).

{^{1}H}^{13}C NMR (101 MHz, MeOD) δ 161.4 (d, *J* =256 Hz), 154.1, 141.8 (d, *J* = 7.9 Hz), 134.0 (d, *J* = 8.1 Hz), 132.7, 130.3, 125.6 (d, J = 4.0Hz), 124.0, 118.6, 118.1 (d, *J* = 20.1 Hz).

{^{1}H}^{19}F NMR (376 MHz, MeOD) δ -126.5.

The NMR data are consistent with those reported for the known compound (CAS 68196-71-4).

(*E*)-1-(2-Chlorophenyl)-2-phenyldiazene (3g)



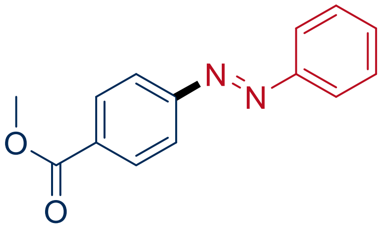
Prepared according to general procedure form phenyl hydrazine (108.1 mg, 1 mmol, 1 equiv.) and 1-bromo-2-chlorobenzene (191.4 mg, 1 mmol, 1 equiv.). After purification, 144 mg of **3g** are obtained (0.66 mmol, 66%). Around 13% of the *Z* isomer are observed according to ^{1}H NMR.

^{1}H NMR (400 MHz, MeOD) δ 7.93 – 7.83 (m, 2H), 7.60 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.51 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.49 – 7.41 (m, 3H), 7.38 – 7.32 (m, 1H), 7.28 (ddd, *J* = 7.9, 7.3, 1.4 Hz, 1H).

{^{1}H}^{13}C NMR (101 MHz, MeOD) δ 153.9, 149.7, 136.3, 133.0, 132.7, 131.7, 130.2, 128.5, 124.2, 118.4.

The NMR data are consistent with those reported for the known compound (CAS 18264-99-8).

(*E*)-Methyl-4-(phenyldiazenyl)benzoate (3h)



Prepared according to general procedure from phenylhydrazine (108.1 mg, 1 mmol, 1 equiv.) and methyl 4-bromobenzoate (215.0 mg, 1 mmol, 1 equiv.). After purification, 177 mg of **3h** are obtained (0.74 mmol 74%).

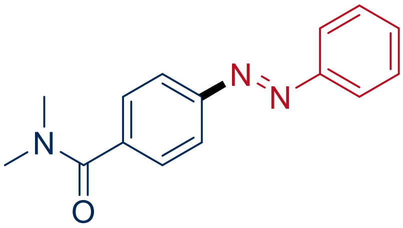
According to ^{1}H NMR analysis, this compound was isolated and observed in solution as a mixture of *Z*/*E* isomers in a 25:75 ratio.

^{1}H NMR (400 MHz, MeOD) δ 8.24 – 8.16 (m, 2.1H), 8.02 – 7.88 (m, 4.9H), 7.62 – 7.51 (m, 3H), 7.33 – 7.15 (m, 1.4H), 6.96 – 6.80 (m, 1.7H), 3.95 (s, 3H), 3.87 (s, 1.3H).

{^{1}H}^{13}C NMR (101 MHz, MeOD) δ 133.1, 131.7, 131.4, 130.4, 130.00, 124.1, 123.7, 121.7, 121.1, 52.9.

The NMR data are consistent with those reported for the known compound (CAS 2918-88-9).

N,N-dimethyl-4-(phenyldiazenyl)benzamide (3i)



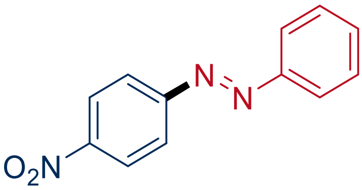
Prepared according to general procedure from phenylhydrazine (108.1 mg, 1 mmol, 1 equiv.) and 4-bromo-*N*,*N*-dimethylbenzamide (228.1 mg, 1 mmol, 1 equiv.). After purification, 184 mg of **3i** are obtained (0.73 mmol, 73%).

^{1}H NMR (400 MHz, MeOD) δ 8.02 – 7.96 (m, 2H), 7.96 – 7.91 (m, 2H), 7.65 – 7.59 (m, 2H), 7.59 – 7.50 (m, 3H), 3.09 (d, *J* = 37.6 Hz, 6H).

{^{1}H}^{13}C NMR (101 MHz, MeOD) δ 172.9, 154.4, 153.9, 139.7, 132.8, 130.4, 129.1, 124.0, 123.9, 40.00, 35.67.

HRMS (EI) theoretical mass for [M+H]: 254.1288; found: 254.1295.

(*E*)-1-(4-Nitrophenyl)-2-phenyldiazene (3j)



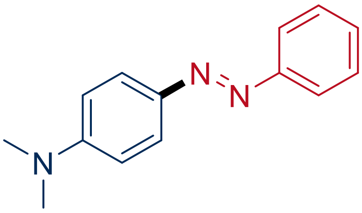
Prepared according to general procedure from phenylhydrazine (108.1 mg, 1 mmol, 1 equiv.) and 1-bromo-4-nitrobenzene (202.0 mg, 1 mmol, 1 equiv.). After purification, 79 mg of **3j** are obtained (0.35 mmol, 35%).

^{1}H NMR (400 MHz, MeOD) δ 8.47 – 8.40 (m, 2H), 8.13 – 8.05 (m, 2H), 8.03 – 7.95 (m, 2H), 7.63 – 7.56 (m, 3H).

{^{1}H}^{13}C NMR (101 MHz, MeOD) δ 157.2, 153.9, 150.3, 133.6, 130.5, 125.9, 124.5, 124.4.

The NMR data are consistent with those reported for the known compound (CAS 2491-52-3).

(*E*)-*N*,*N*-Dimethyl-4-(phenyldiazenyl)aniline () (3k)



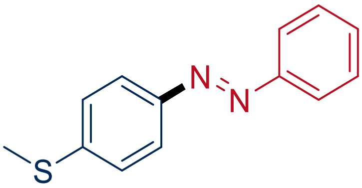
Prepared according to general procedure from phenylhydrazine (108.1 mg, 1 mmol, 1 equiv.) and 4-bromo-*N',N'*-dimethylaniline (200.1 mg, 1 mmol, 1 equiv.). After purification, 124 mg of **3k** are obtained (0.55 mmol, 55%).

^{1}H NMR (400 MHz, MeOD) δ 7.85 – 7.80 (m, 2H), 7.80 – 7.76 (m, 2H), 7.52 – 7.43 (m, 2H), 7.43 – 7.35 (m, 1H), 6.86 – 6.79 (m, 2H), 3.09 (s, 6H).

{^{1}H}^{13}C NMR (101 MHz, MeOD) δ 154.5, 154.3, 144.8, 130.5, 130.1, 125.9, 123.1, 112.7, 40.4.

The NMR data are consistent with those reported for the known compound (CAS 60-11-7).

(*E*)-1-(4-(Methylthio)phenyl)-2-phenyldiazene (3l)



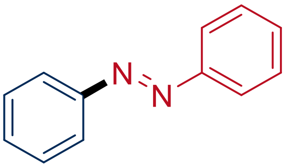
Prepared according to general procedure from phenylhydrazine (108.1 mg, 1 mmol, 1 equiv.) and 4-bromothioanisole (203.1 mg, 1 mmol, 1 equiv.). After purification 161 mg of **3l** are obtained (0.71 mmol, 71%).

^{1}H NMR (400 MHz, MeOD) δ 7.92 – 7.82 (m, 4H), 7.56 – 7.46 (m, 3H), 7.43 – 7.36 (m, 2H), 2.56 (s, 3H).

{^{1}H}^{13}C NMR (101 MHz, MeOD) δ 154.1, 151.2, 145.1, 132.0, 130.2, 127.0, 124.3, 123.7, 15.1.

HRMS (EI) theoretical mass for [M+H]: 229.0794; found: 229.0799.

(*E*)-Azobenzene (3m)



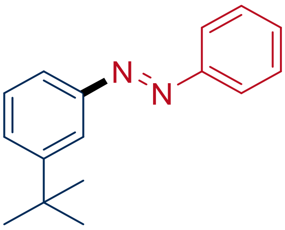
Prepared according to general procedure from phenylhydrazine (108.1 mg, 1 mmol, 1 equiv.) and bromobenzene (157.0 mg, 1 mmol, 1 equiv.) After purification, 78 mg of **3m** are obtained (0.43 mmol, 43%). Around 5% of the *Z* isomer are observed according to ^{1}H NMR.

^{1}H NMR (300 MHz, MeOD) δ 7.95 – 7.84 (m, 4H), 7.59 – 7.42 (m, 6H).

{^{1}H}^{13}C NMR (75 MHz, MeOD) δ 153.9, 132.2, 130.2, 123.8.

The NMR data are consistent with those reported for the known compound (CAS 103-33-3).

(*E*)-1-(3(*Tert*-butyl)phenyl)-2-phenyldiazene (3n)



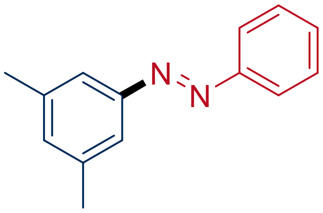
Prepared according to general procedure from phenylhydrazine (108.1 mg, 1 mmol, 1 equiv.) and 1-bromo-3-*tert*-butylbenzene (213.1 mg, 1 mmol, 1 equiv.). After purification, 201 mg of **3n** are obtained (0.84 mmol, 84%).

^{1}H NMR (400 MHz, MeOD) δ 7.94 (t, *J* = 2.0 Hz, 1H), 7.89 – 7.83 (m, 2H), 7.66 (ddd, *J* = 7.7, 1.9, 1.1 Hz, 1H), 7.48 – 7.31 (m, 5H), 1.29 (s, 9H).

{^{1}H}^{13}C NMR (101 MHz, MeOD) δ 153.8, 153.7, 153.4, 132.0, 130.1, 129.8, 129.2, 123.7, 121.3, 120.6, 35.6, 31.7.

HRMS (EI) theoretical mass for [M+H]: 239.1543; found: 239.1547.

(*E*)-1-(3,5-Dimethylphenyl)-2-phenyldiazene (3o)



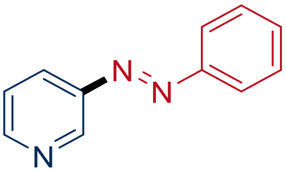
Prepared according to general procedure from phenylhydrazine (108.1 mg, 1 mmol, 1 equiv.) and 3,5-dimethylbromobenzene (185.1 mg, 1 mmol, 1 equiv.). After purification, 163 mg of **3o** are obtained (0.78 mmol, 78%). Around 10% of the *Z* isomer are observed according to ^{1}H NMR.

^{1}H NMR (300 MHz, MeOD) δ 7.87 – 7.77 (m, 2H), 7.50 – 7.33 (m, 5H), 7.03 – 6.95 (m, 1H), 2.29 – 2.26 (m, 6H).

{^{1}H}^{13}C NMR (75 MHz, MeOD) δ 153.9, 153.9, 139.8, 133.6, 131.9, 130.1, 123.1, 121.6, 21.4.

The NMR data are consistent with those reported for the known compound (CAS 77775-95-2).

(*E*)-3-(Phenyldiazenyl)pyridine (3p)



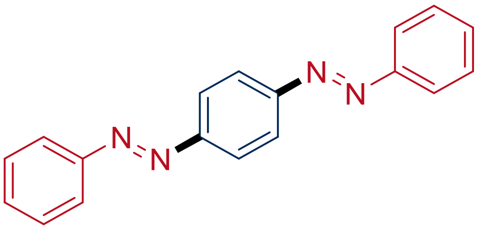
Prepared according to general procedure from phenylhydrazine (108.1 mg, 1 mmol, 1 equiv.) and 2-bromopyridine (158.0 mg, 1 mmol, 1 equiv.). After purification, 129 mg of **3p** are obtained (0.70 mmol, 70%).

^{1}H NMR (400 MHz, MeOD) δ 8.96 (dd, *J* = 2.4, 0.8 Hz, 1H), 8.56 (dd, *J* = 4.8, 1.6 Hz, 1H), 8.08 (ddd, *J* = 8.2, 2.4, 1.5 Hz, 1H), 7.82 (tddd, *J* = 5.9, 4.2, 2.6, 1.4 Hz, 2H), 7.51 – 7.41 (m, 4H).

{^{1}H}^{13}C NMR (101 MHz, MeOD) δ 153.5, 152.1, 149.2, 147.1, 133.1, 130.3, 128.9, 125.7, 124.1.

The NMR data are consistent with those reported for the known compound (CAS 2569-55-3).

(*E*)-1,4-*bis*-Phenyldiazenyl)benzene (1161-45-1) (3q)



Prepared according to a modified procedure from phenylhydrazine (108.1 mg, 1 mmol, 2 equiv.) and 1,4-dibromobenzene (167.9 mg, 0.5 mmol, 1 equiv.). 95 mg of **3q** are obtained (0.33 mmol, 66%).

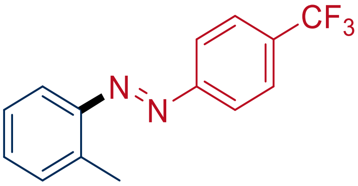
Ethyl acetate present in the NMR spectrums.

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.93 (s, 4H), 7.86 – 7.79 (m, 4H), 7.45 – 7.32 (m, 6H).

{^{1}H}^{13}C NMR (75 MHz, CDCl$_3$) δ 153.6, 152.6, 131.3, 129.0, 123.6, 122.9.

The NMR data are consistent with those reported for the known compound (CAS 1161-45-1).

(*E*)-1-(*o*-Tolyl)-2-(4-trifluoromethyl)phenyl)diazene (4a)



Prepared according to general procedure from 4-trifluoromethylphenylhydrazine (176.1 mg, 1 mmol, 1 equiv.) and 2-bromotoluene (171.0 mg, 1 mmol, 1 equiv.). After purification, 207 mg of **4a** are obtained (0.78 mmol, 78%).

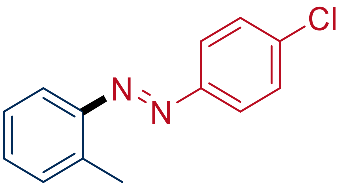
^{1}H NMR (300 MHz, MeOD) δ 7.87 – 7.76 (m, 2H), 7.70 – 7.59 (m, 2H), 7.50 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.33 – 7.19 (m, 2H), 7.13 (dddd, *J* = 8.1, 7.0, 1.8, 0.5 Hz, 1H), 2.57 (s, 3H).

{^{1}H, ^{19}F}^{13}C NMR (75 MHz, MeOD) δ 155.9, 151.4, 140.1, 133.0, 132.4, 127.4, 127.2 (q, *J* = 3.7 Hz), 124.1, 116.2, 17.6.

{^{1}H}^{19}F NMR (282 MHz, MeOD) δ -63.8.

HRMS (EI) theoretical mass for [M]: 264.08688; found: 264.08649.

(*E*)-1-(4-Chlorophenyl)-2-(*o*-tolyl)diazene (4b)



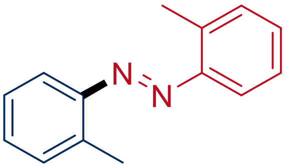
Prepared according to general procedure from (4-chlorophenyl)hydrazine (142.6 mg, 1 mmol, 1 equiv.) and 2-bromotoluene (171.0 mg, 1 mmol, 1 equiv.). After purification, 80 mg of **4b** are obtained (0.37 mmol, 37%).

^{1}**H NMR** (400 MHz, MeOD) δ 7.90 – 7.82 (m, 2H), 7.60 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.44 – 7.32 (m, 2H), 7.29 – 7.21 (m, 1H), 2.69 (s, 3H).

{^{1}H}^{13}C NMR (101 MHz, MeOD) δ 152.8, 151.7, 139.6 137.8, 132.5, 132.4, 130.4, 127.5, 125.3, 116.2, 17.6.

The NMR data are consistent with those reported for the known compound (CAS 1992832-16-2).

(*E*)-1,2-Di-o-tolyldiazene (4c)



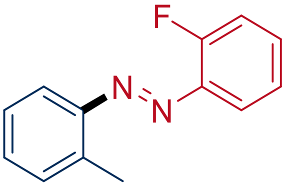
Prepared according to general procedure from (2-methylphenyl)hydrazine (122.2 mg, 1 mmol, 1 equiv.) and 2-bromotoluene (171.0 mg, 1 mmol, 1 equiv.). After purification, 132 mg of **4c** are obtained (0.63 mmol, 63%).

^{1}**H NMR** (400 MHz, MeOD) ^{1}H NMR (400 MHz, MeOD) δ 7.58 (d, *J* = 7.7 Hz, 2H), 7.40 – 7.31 (m, 4H), 7.30 – 7.20 (m, 2H), 2.71 (s, 6H).

{^{1}H}^{13}C NMR (101 MHz, MeOD) δ 152.3, 139.1, 132.4, 132.0, 127.5, 116.6, 17.7.

The NMR data are consistent with those reported for the known compound (CAS 584-90-7).

(*E*)-1-(2-Fluorophenyl)-2-(*o*-tolyl)diazene (4d)



Prepared according to general procedure from (2-fluorophenyl)hydrazine (126.1 mg, 1 mmol, 1 equiv.) and 2-bromotoluene (171.0 mg, 1 mmol, 1 equiv.). After purification of **4d** are obtained, 110 mg (0.55 mmol, 55%).

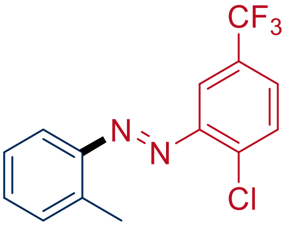
^{1}H NMR (400 MHz, MeOD) δ 7.71 (td, *J* = 7.8, 1.7 Hz, 1H), 7.61 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.50 (dddd, *J* = 8.3, 7.3, 5.0, 1.8 Hz, 1H), 7.43 – 7.20 (m, 5H), 2.70 (d, *J* = 1.1 Hz, 3H).

{^{1}H}^{13}C NMR (101 MHz, MeOD) δ 161.4 (d, *J* = 256.6 Hz), 160.1, 152.1, 142.2 (d, *J* = 6.9 Hz), 139.8, 133.7 (d, *J* = 8.4 Hz), 132.6 (d, *J* = 25.6 Hz), 127.5, 125.6 (d, *J* = 3.9 Hz), 118.9, 118.0 (d, *J* = 19.9 Hz), 116.5, 17.6.

{^{1}H}^{19}F NMR (376 MHz, MeOD) δ -126.8 – -126.9 (m).

The NMR data are consistent with those reported for the known compound (CAS 2479972-17-1).

(*E*)-1-(2-Chloro-5-(trifluoromethyl)phenyl)-2-(*o*-tolyl)diazene (4e)



Prepared according to general procedure from [2-chloro-5-(trifluoromethyl)phenyl]hydrazine (210.6 mg, 1 mmol, 1 equiv.) and 2-bromotoluene (171.0 mg, 1 mmol, 1 equiv.). After purification, 96 mg of **4e** (0.32 mmol, 32%).

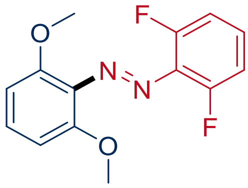
^{1}H NMR (300 MHz, MeOD) δ 7.88 (dt, *J* = 2.1, 0.7 Hz, 1H), 7.85 – 7.73 (m, 2H), 7.69 (ddd, *J* = 8.1, 0.9, 0.5 Hz, 1H), 7.51 – 7.35 (m, 2H), 7.35 – 7.23 (m, 1H), 2.74 (s, 3H).

{^{1}H, ^{19}F}^{13}C NMR (75 MHz, MeOD) δ 151.9, 150.3, 140.5, 139.7, 133.7, 133.0, 132.7, 128.9, 128.9, 127.7, 117.2, 115.7, 115.6, 17.7.

{^{1}H}^{19}F NMR (282 MHz, MeOD) δ -64.3.

HRMS (EI) theoretical mass for [M]: 298.04791; found: 298.04882.

(*E*)-1-(2,6-Difluorophenyl)-2-(2,6-dimethoxyphenyldiazene) (5a)



Prepared according to general procedure from (2,6-difluorophenyl)hydrazine (144.1 mg, 1 mmol, 1 equiv.) and 2,6-dimethoxybromobenzene (217.1 mg, 1 mmol, 1 equiv.). After purification, 174 mg (0.63 mmol, 63%) of **5a** are obtained.

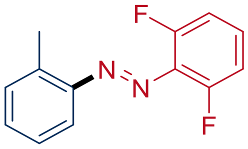
^{1}H NMR (300 MHz, DMSO) δ 7.58 – 7.46 (m, 1H), 7.38 (t, *J* = 8.5 Hz, 1H), 7.34 – 7.24 (m, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 3.78 (s, 6H).

{^{1}H, ^{19}F}^{13}C NMR (75 MHz, DMSO) δ 155.9 (d, *J* = 4.6 Hz), 152.5 (d, *J* = 4.7 Hz), 151.9, 133.1, 131.3, 131.1 (t, *J* = 10.3 Hz), 113.2 – 112.7 (m), 105.3, 56.3.

{^{1}H}^{19}F NMR (282 MHz, DMSO) δ -123.8 (dd, *J* = 9.1, 6.1 Hz).

The NMR data are consistent with those reported for the known compound (CAS 2972643-51-7).

(*E*)-1-(2,6-Difluorophenyl)-2-(*o*-tolyl)diazene (5b)



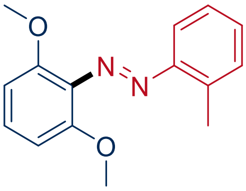
Prepared according to general procedure from (2,6-difluorophenyl)hydrazine (144.1 mg, 1 mmol, 1 equiv.) and 2-bromotoluene (171.0 mg, 1 mmol, 1 equiv.). After purification, 93 mg of **5b** was obtained (0.40 mmol, 40%). An additional 98 mg of **5b** (0.42 mmol, 42%) was recovered in a second fraction containing approximately 5% biphenyls, which could not be fully separated during purification.

^{1}H NMR (300 MHz, MeOD) δ 7.56 (d, *J* = 7.9 Hz, 1H), 7.46 – 7.34 (m, 3H), 7.26 (dddd, *J* = 8.1, 6.6, 2.2, 0.6 Hz, 1H), 7.17 – 7.06 (m, 2H), 2.65 (s, 3H).

{^{1}H, ^{19}F}^{13}C NMR (75 MHz, MeOD) δ 158.8 (d, *J* = 4.4 Hz), 155.4 (d, *J* = 4.4 Hz), 152.7, 140.1, 133.2, 132.5, 131.8 (t, *J* = 10.4 Hz), 127.5, 115.7, 113.8 – 113.4 (m), 17.4.

{^{1}H}^{19}F NMR (282 MHz, MeOD) δ -124.2 (dd, *J* = 9.4, 5.9 Hz).

(*E*)-1-(2,6-Dimethoxyphenyl)-2-(o-tolyl)diazene (5c)



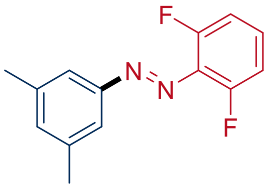
Prepared according to general procedure from 2-methylphenylhydrazine (122.2 mg, 1 mmol, 1 equiv.) and 2,6-dimethoxybromonenzene (217.1 mg, 1 mmol, 1 equiv.). After purification, 120mg of **5d** are obtained (0.47 mmol, 47%). According to NMR analysis, this compound was isolated and observed in solution as a mixture of *Z*/*E* isomers in a 25:75 ratio. The ^{1}H NMR peaks correspond exclusively to the *E* isomer, while the ^{13}C NMR signals include contributions from both the *Z* and *E* isomers.

^{1}H NMR (300 MHz, DMSO) δ 7.49 – 7.20 (m, 6H), 6.82 (d, *J* = 8.5 Hz, 2H), 3.77 (s, 6H), 2.56 (s, 3H).

{^{1}H}^{13}C NMR (75 MHz, DMSO) δ 151.7, 151.1, 148.1, 136.6, 133.4, 131.2, 130.9, 130.5, 129.5, 128.1, 127.9, 126.5, 125.1, 115.0, 113.8, 105.4, 104.4, 56.3, 55.6, 17.0, 16.6.

HRMS (EI) theoretical mass for [M+H]: 257.1290; found: 257.1292.

(*E*)-1-(2,6-difluorophenyl)-2-(3,5-dimethylphenyl)diazene (5d)



Prepared according to general procedure from (2.6-difluorophenyl)hydrazine (144.1 mg, 1 mmol, 1 equiv.) and 3,5-dimethylbromobenzene (185.1 mg, 1 mmol, 1 equiv.). After purification, 197 mg of **5c** are obtained (0.80 mmol, 80%) are obtained. According to NMR analysis, this compound was isolated and observed in solution as a mixture of *Z*/*E* isomers in a 20:80 ratio. The ^{1}H NMR peaks correspond exclusively to the *E* isomer, while the ^{13}C NMR signals include contributions from both the *Z* and *E* isomers.

^{1}H NMR (300 MHz, DMSO) δ 7.61 – 7.51 (m, 1H), 7.49 (dq, *J* = 1.9, 0.6 Hz, 2H), 7.39 – 7.23 (m, 3H), 2.38 (q, *J* = 0.7 Hz, 6H).

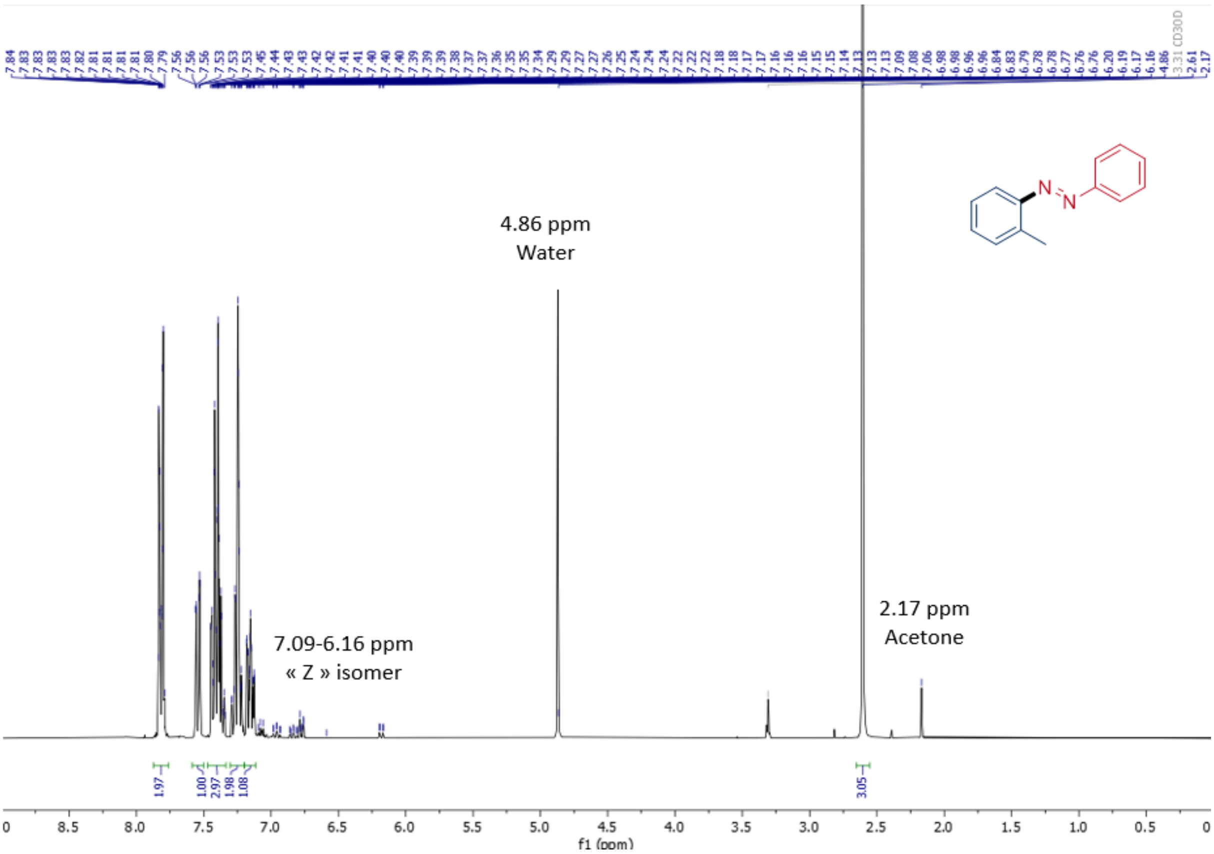
{^{1}H}^{13}C NMR (75 MHz, DMSO) δ 156.5 (d, *J* = 4.1 Hz), 153.1 (d, *J* = 4.5 Hz), 152.7, 138.9, 138.4, 137.9, 133.9, 131.4 (t, *J* = 10.6 Hz), 130.4, 120.3, 115.8, 114.7, 113.0 (dd, *J* = 20.9, 2.8 Hz), 20.7.

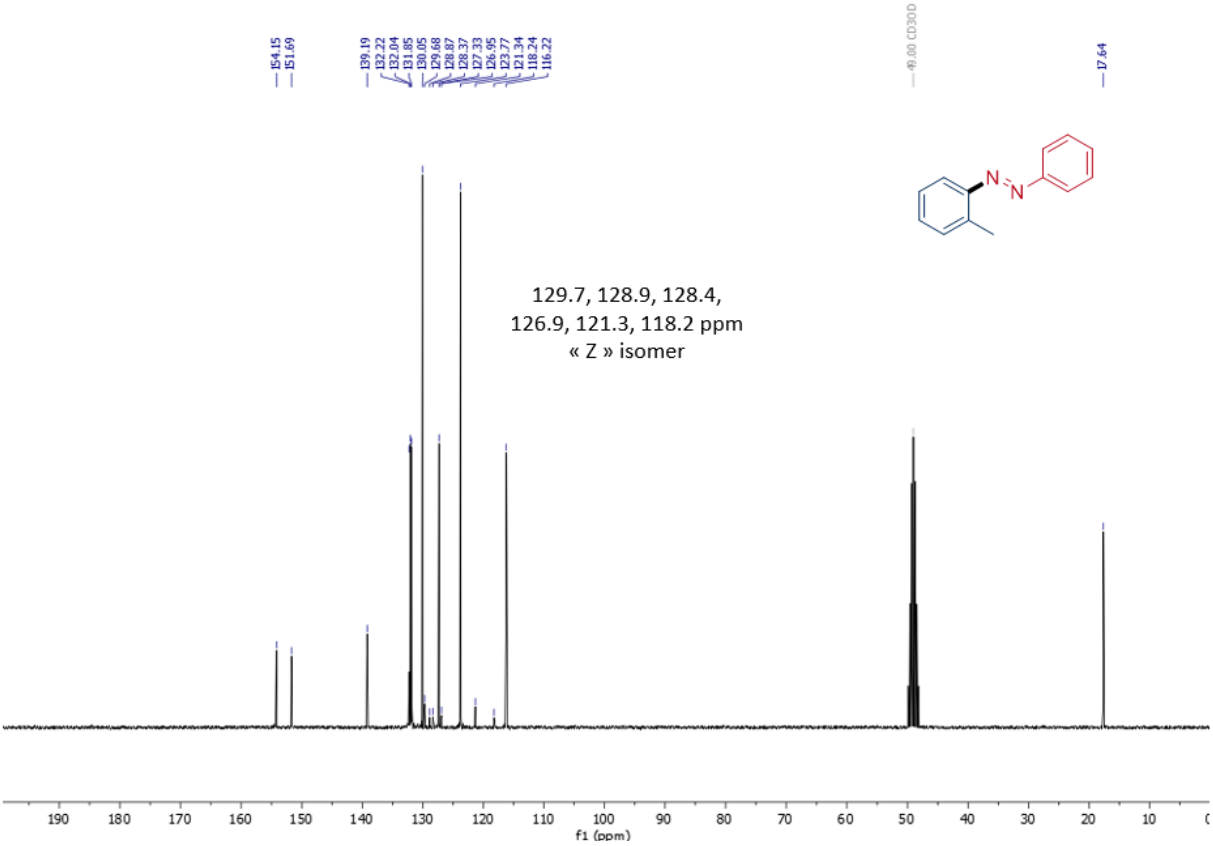
{^{1}H}^{19}F NMR (282 MHz, DMSO) δ -122.7 (dd, *J* = 9.7, 6.1 Hz).

HRMS (EI) theoretical mass for [M+H]: 247.1047; found: 247.1049.

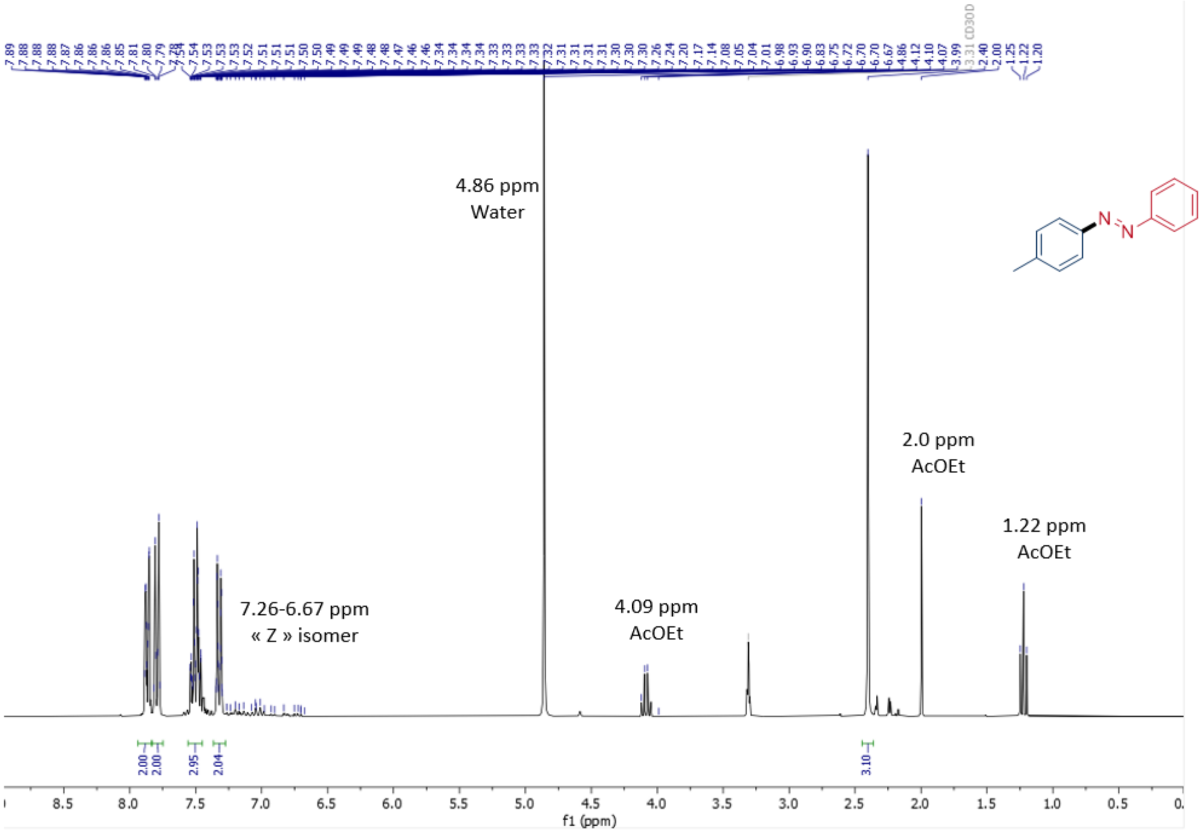
IV. 1H, 13C and 19F NMR spectrum:

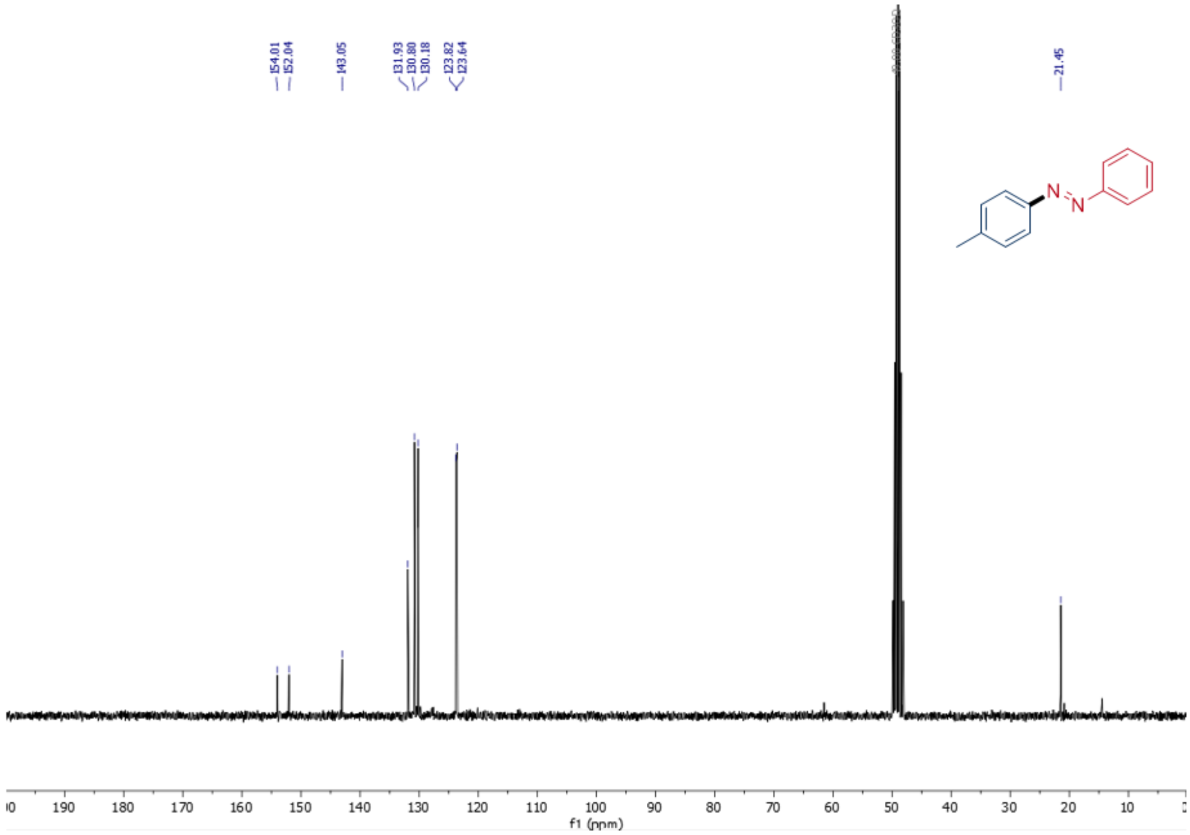
1H, 13C NMR of 3a:



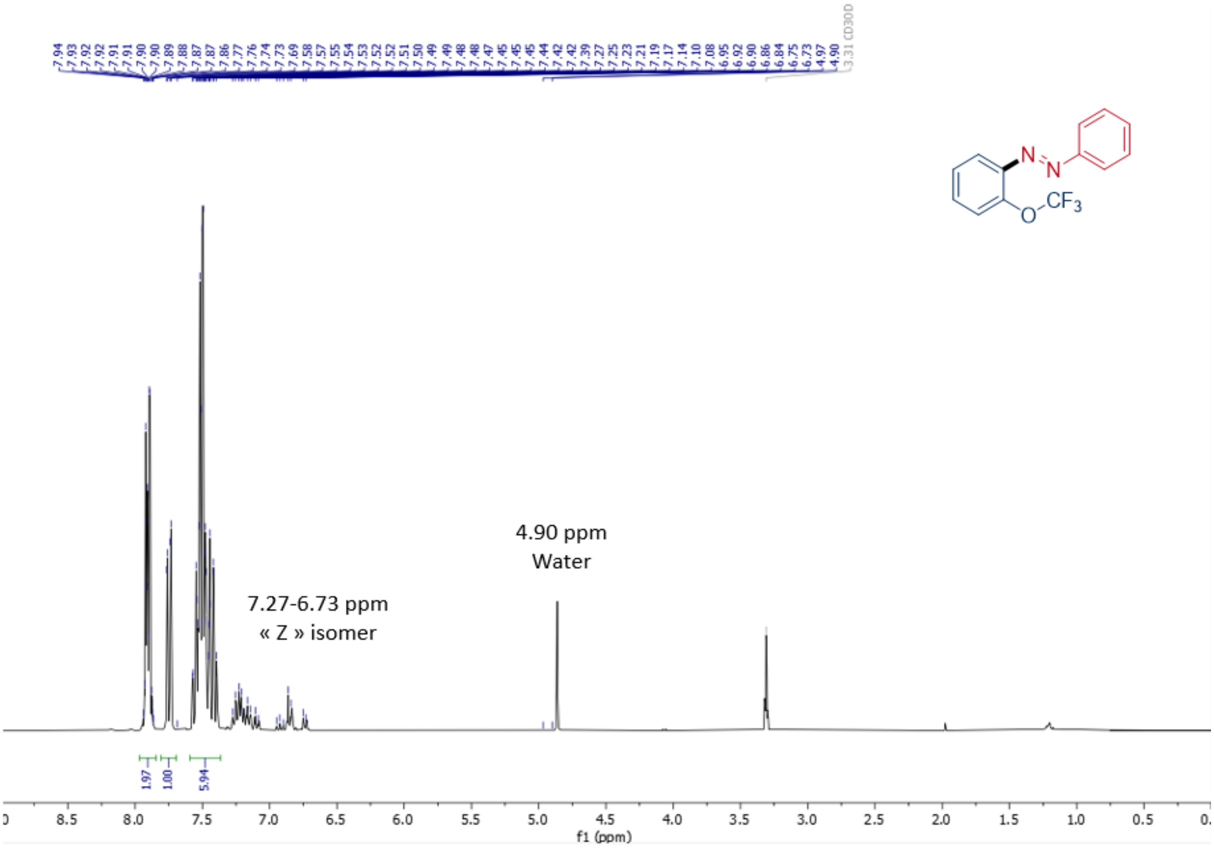


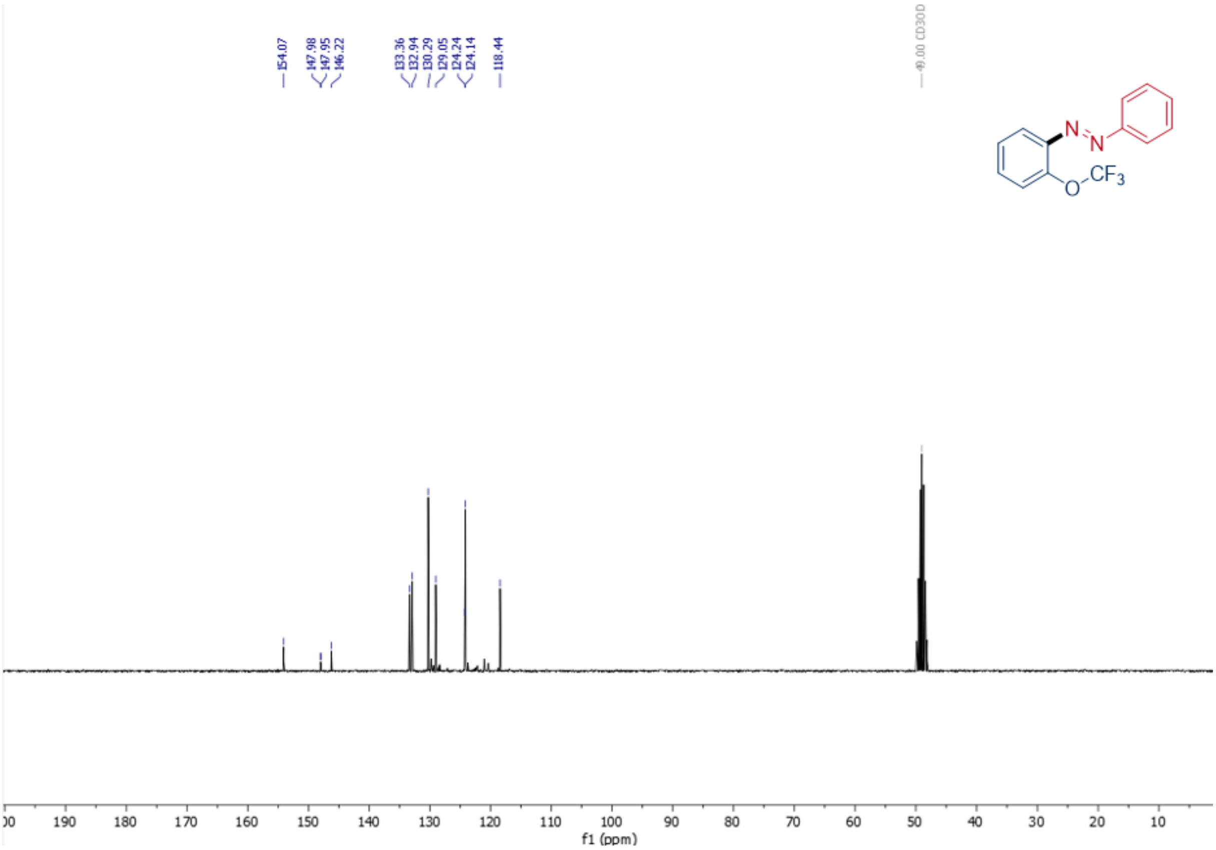
1H, 13C NMR of 3b:

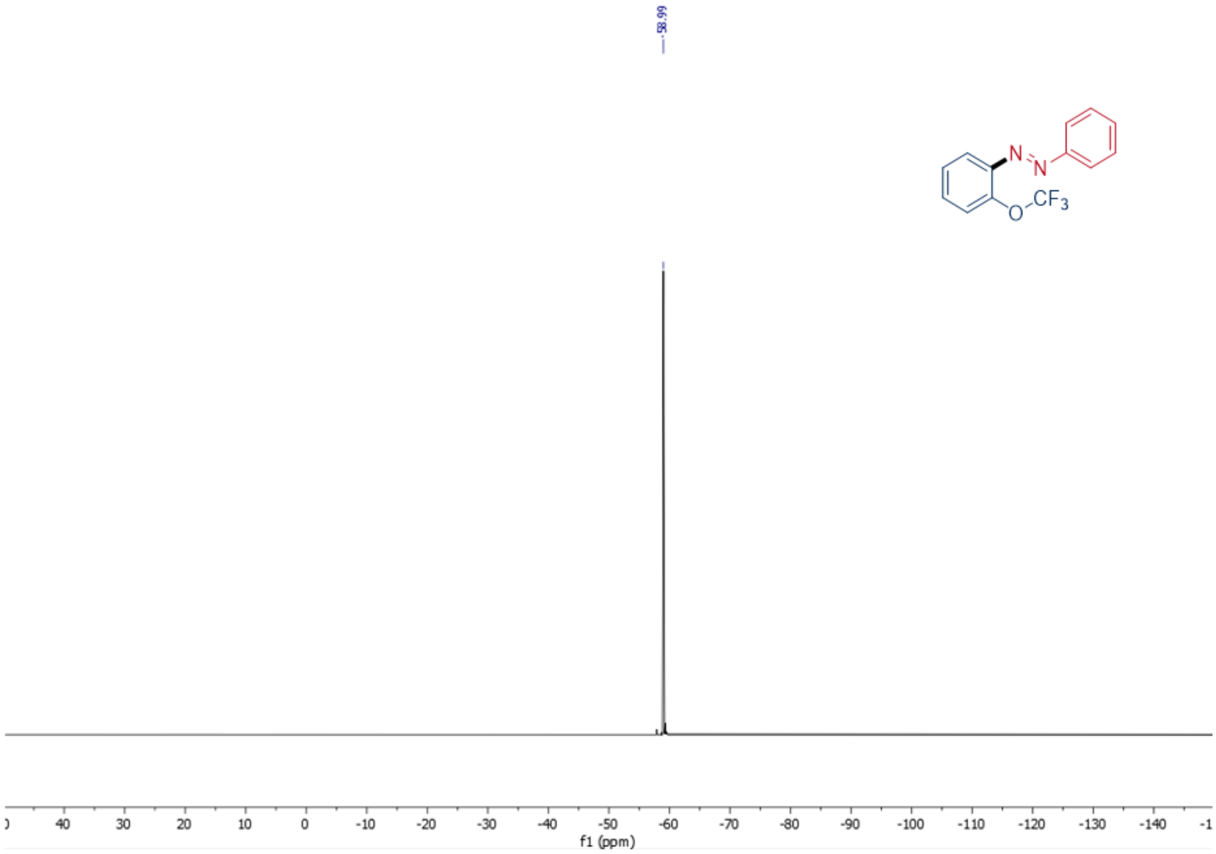




1H, 13C, 19F NMR of 3c:



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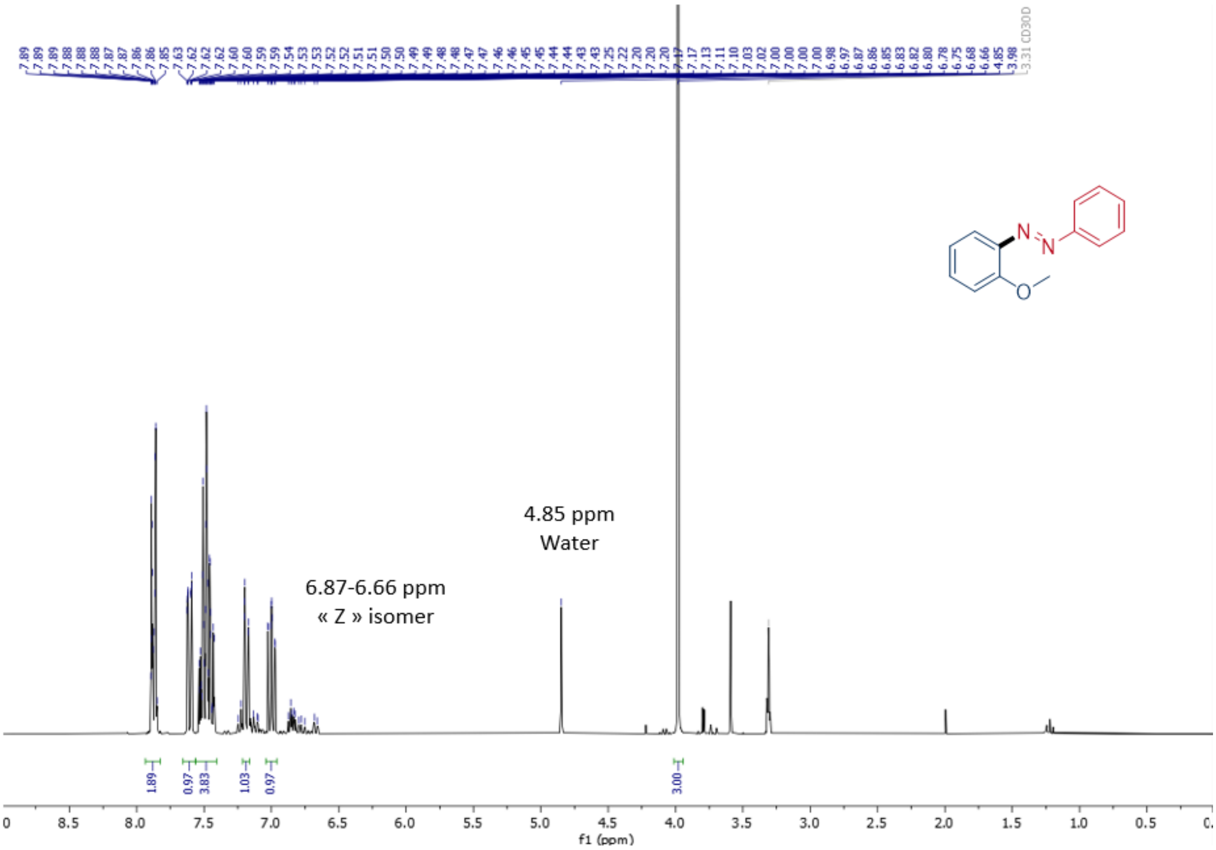
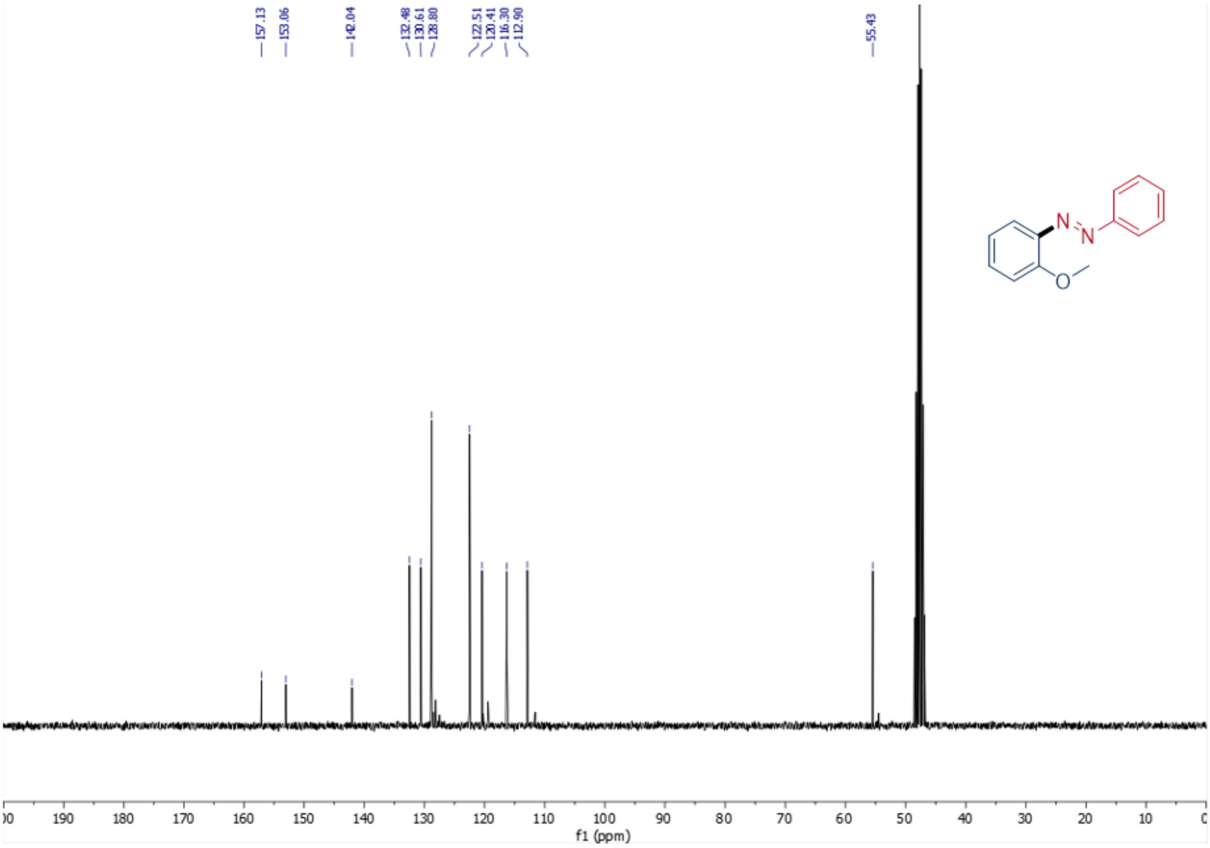
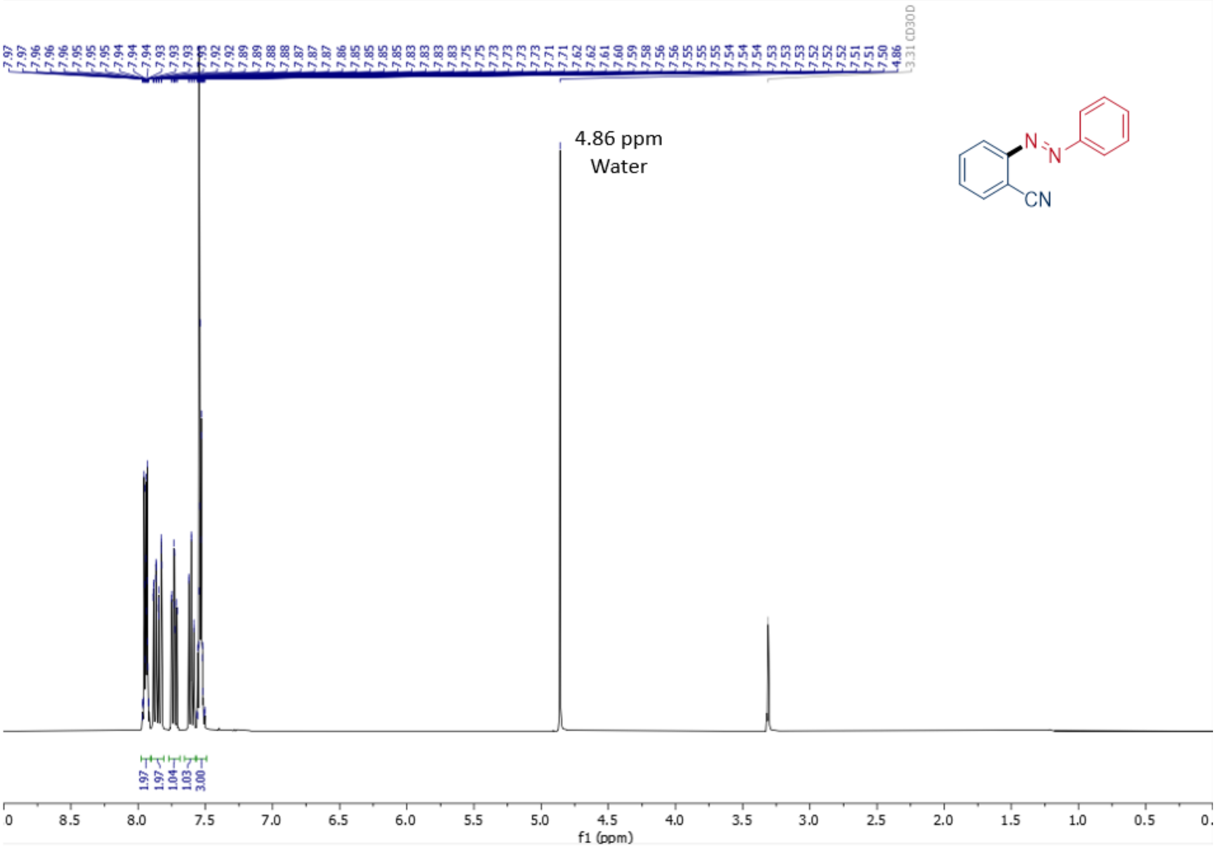
f1 (ppm)

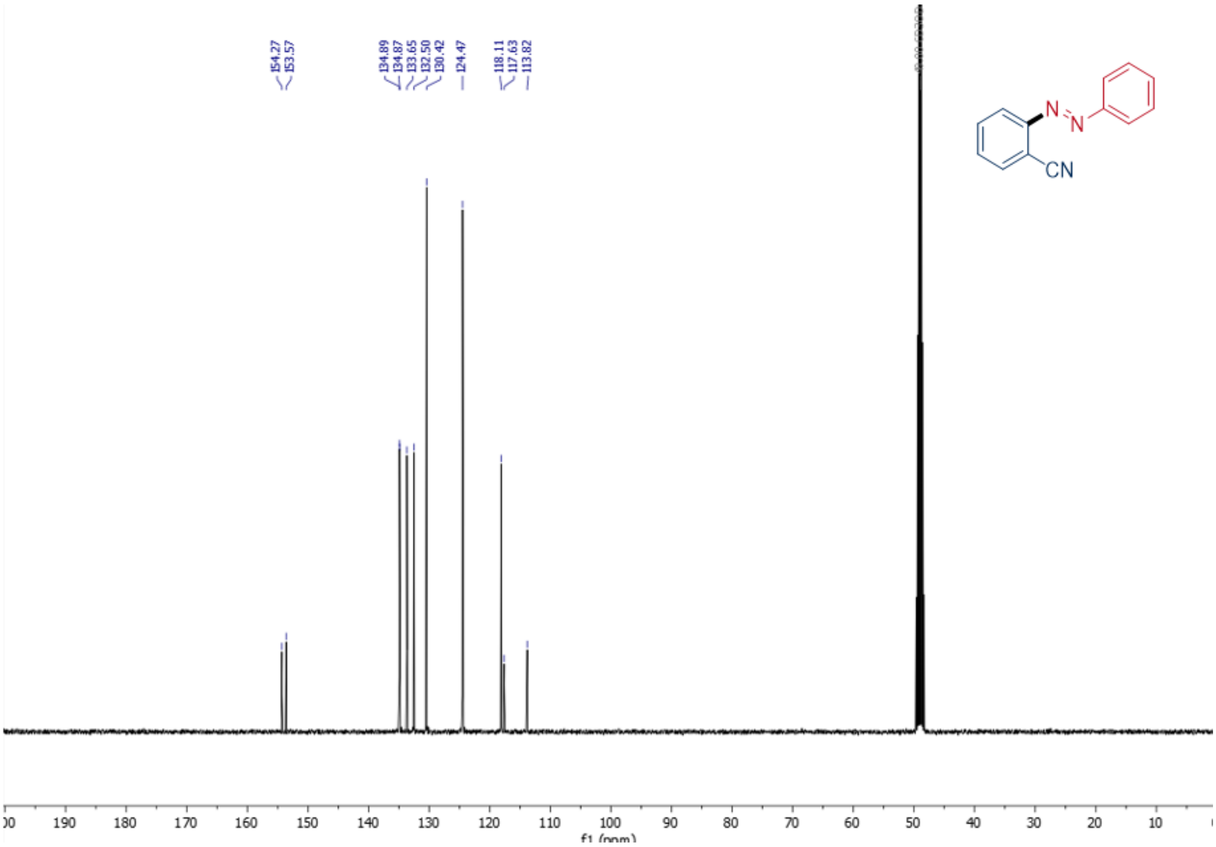
1H, 13C NMR of 3d:



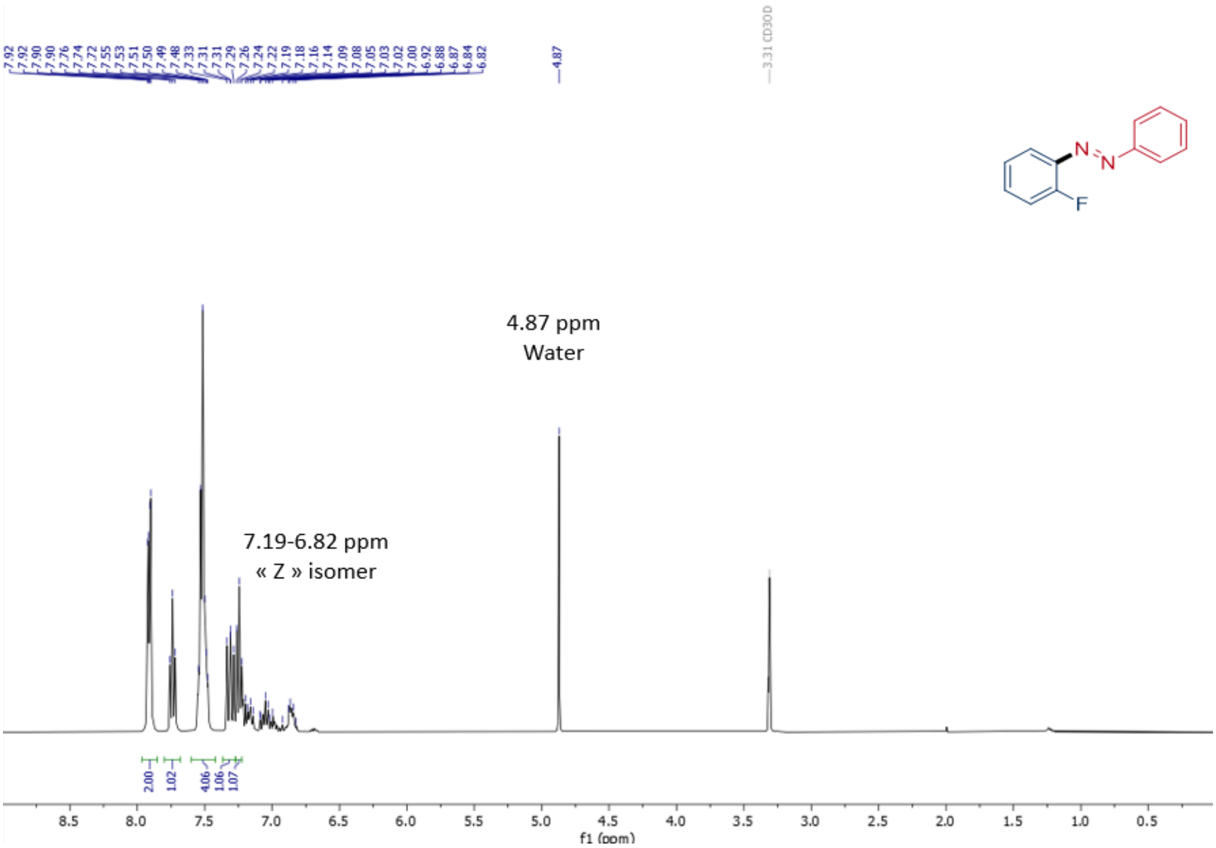


1H, 13C NMR of 3e:





1H, 13C, 19F NMR of 3f: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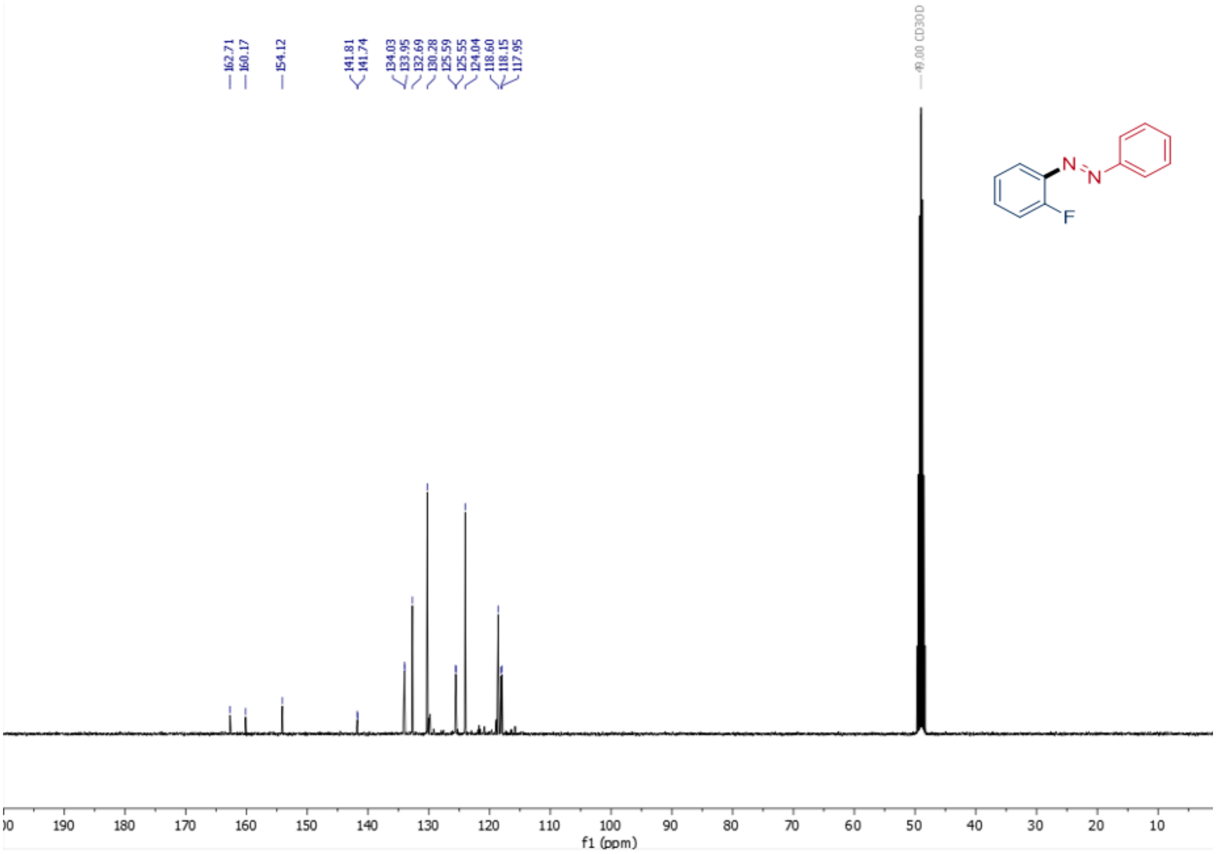
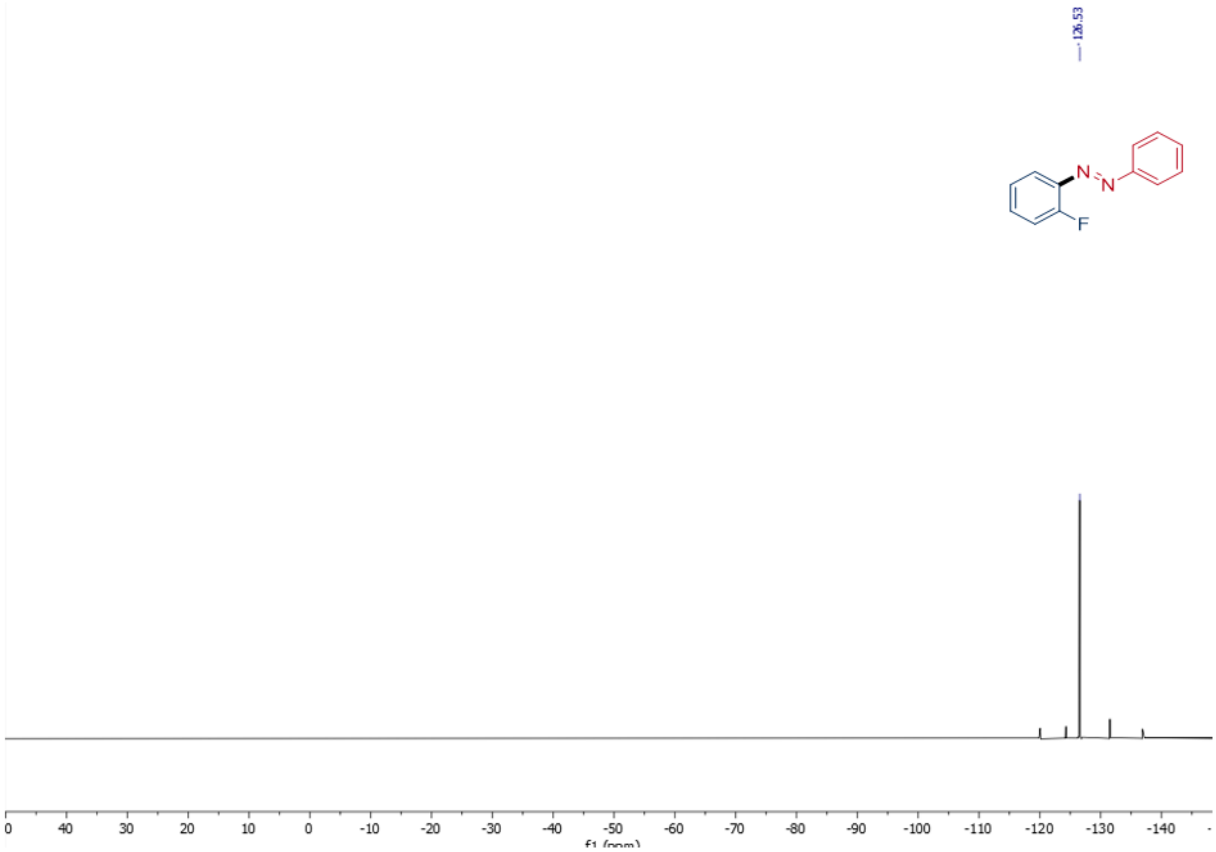
Water

7.19-6.82 ppm
« Z » isomer

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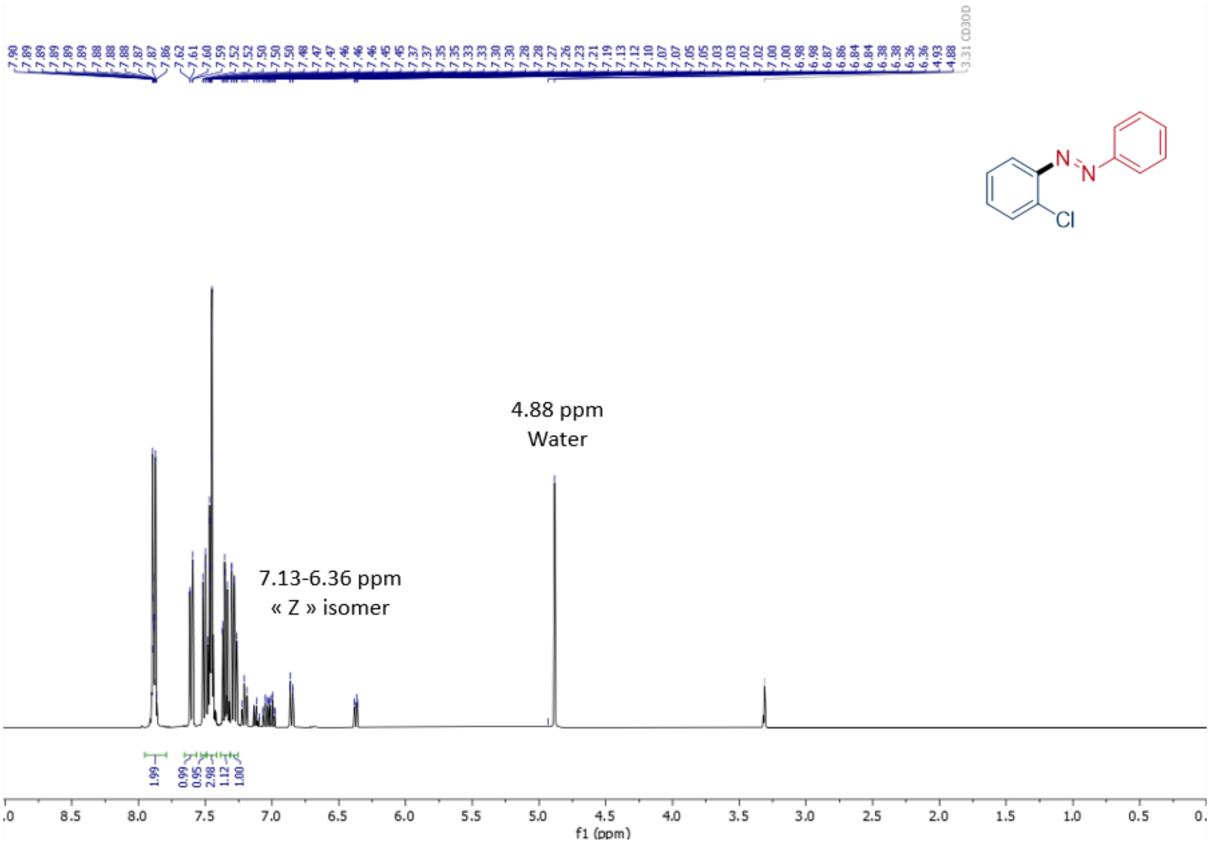
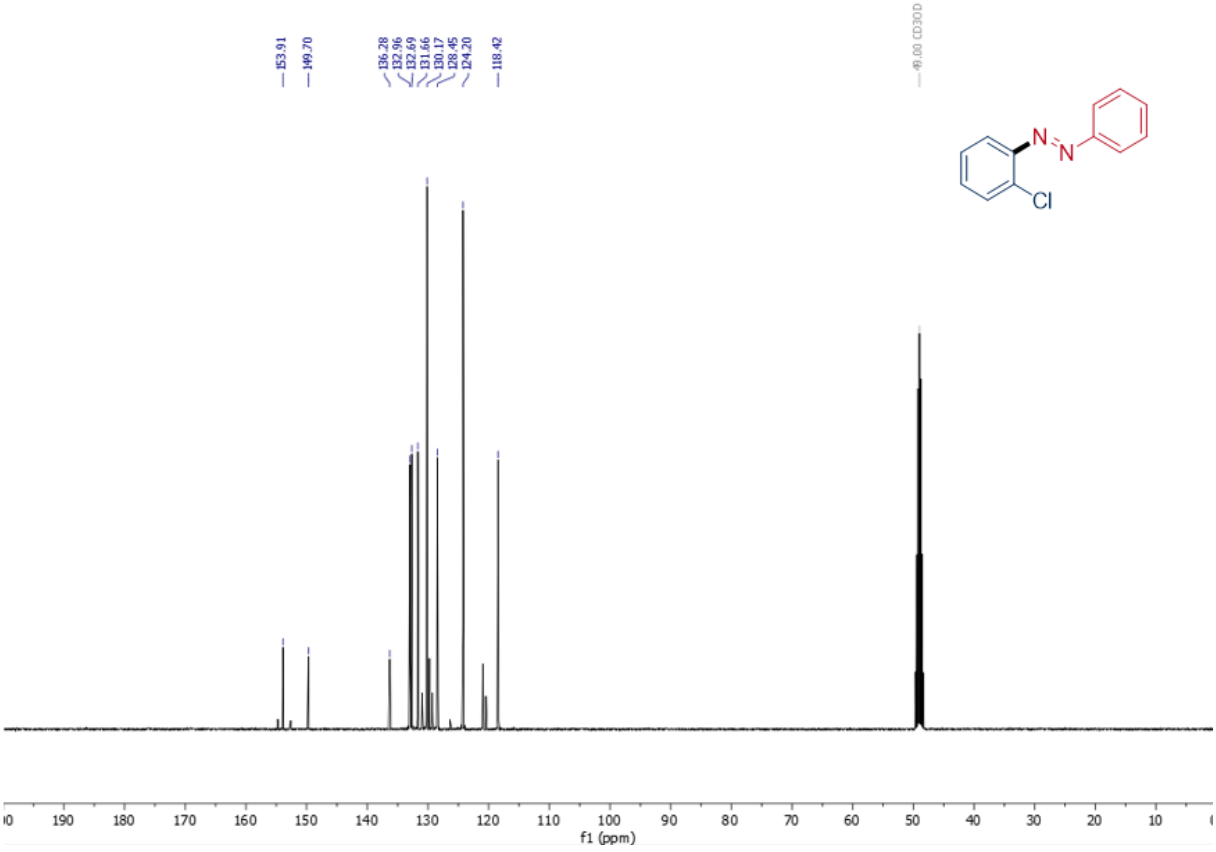
f1 (ppm)

1H, 13C NMR of 3g:

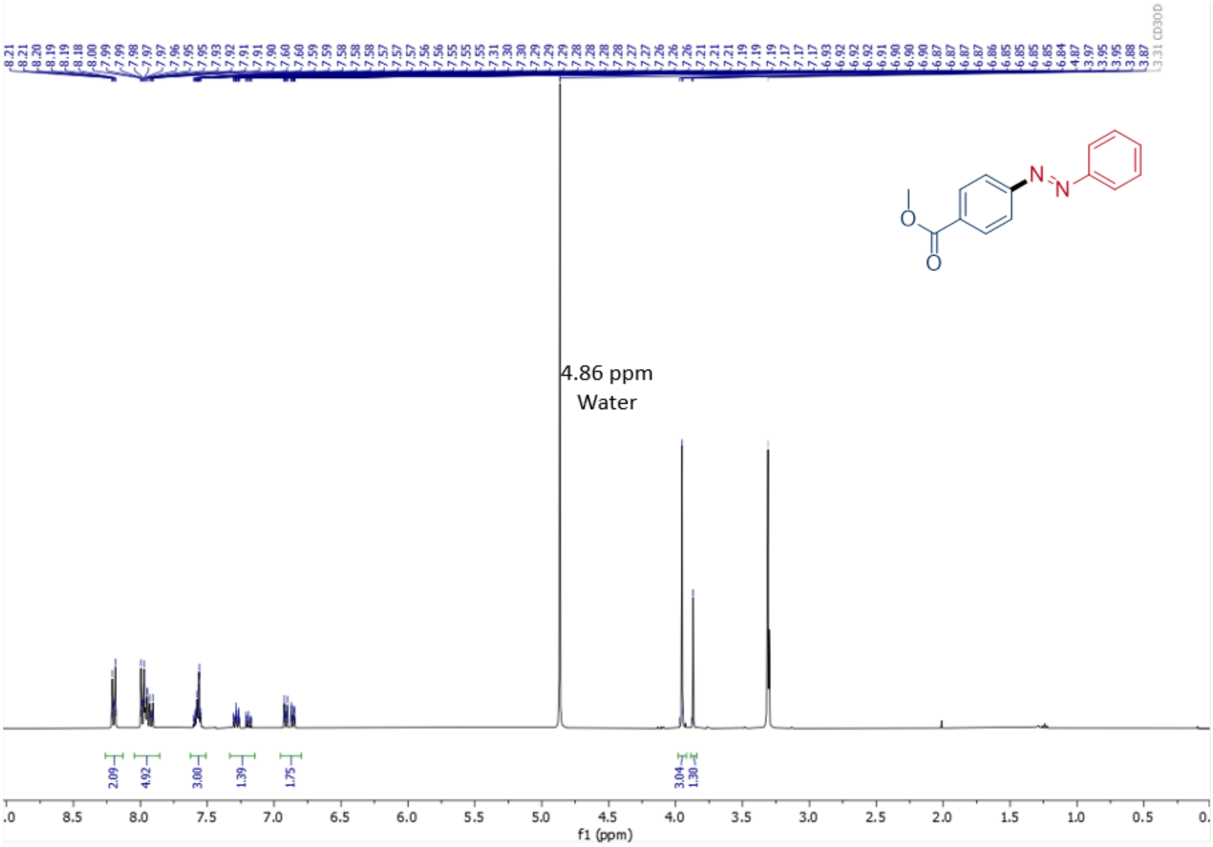


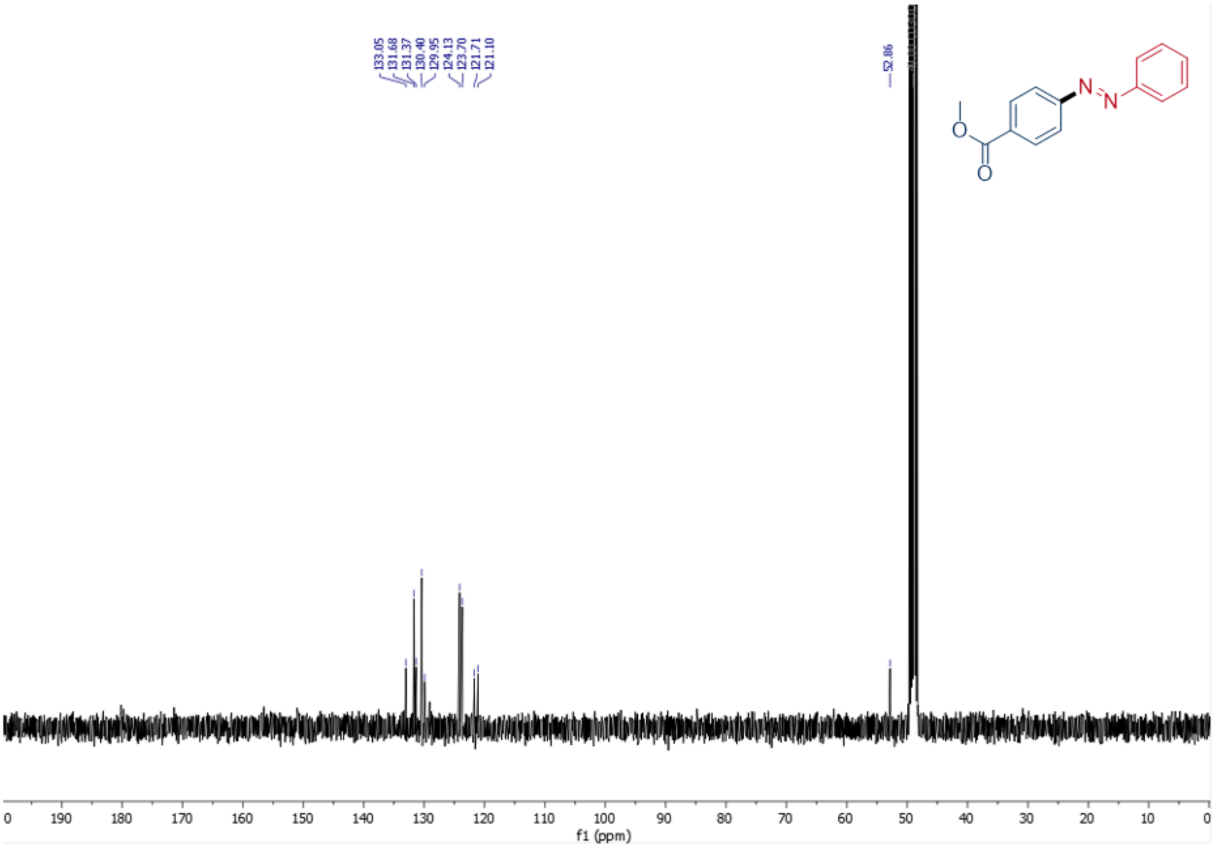
7.13-6.36 ppm « Z » isomer

4.88 ppm Water

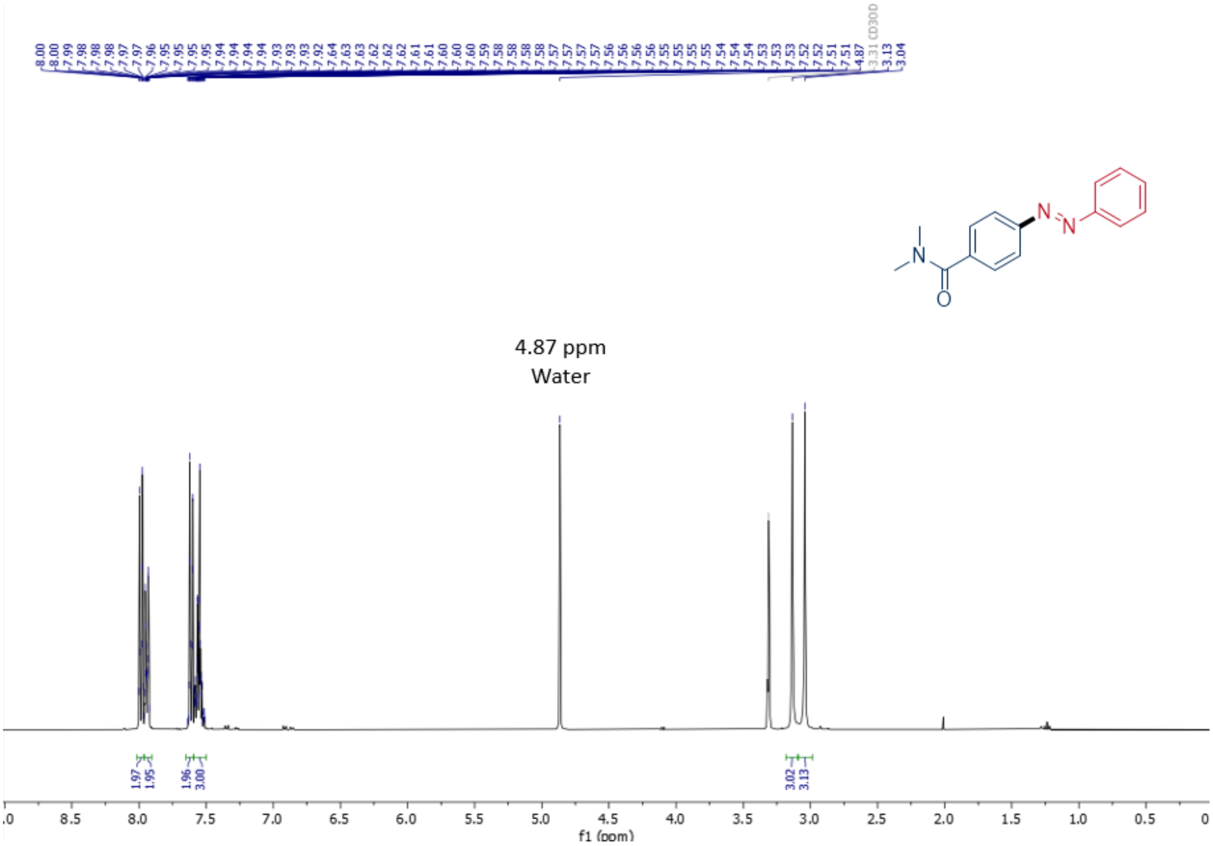


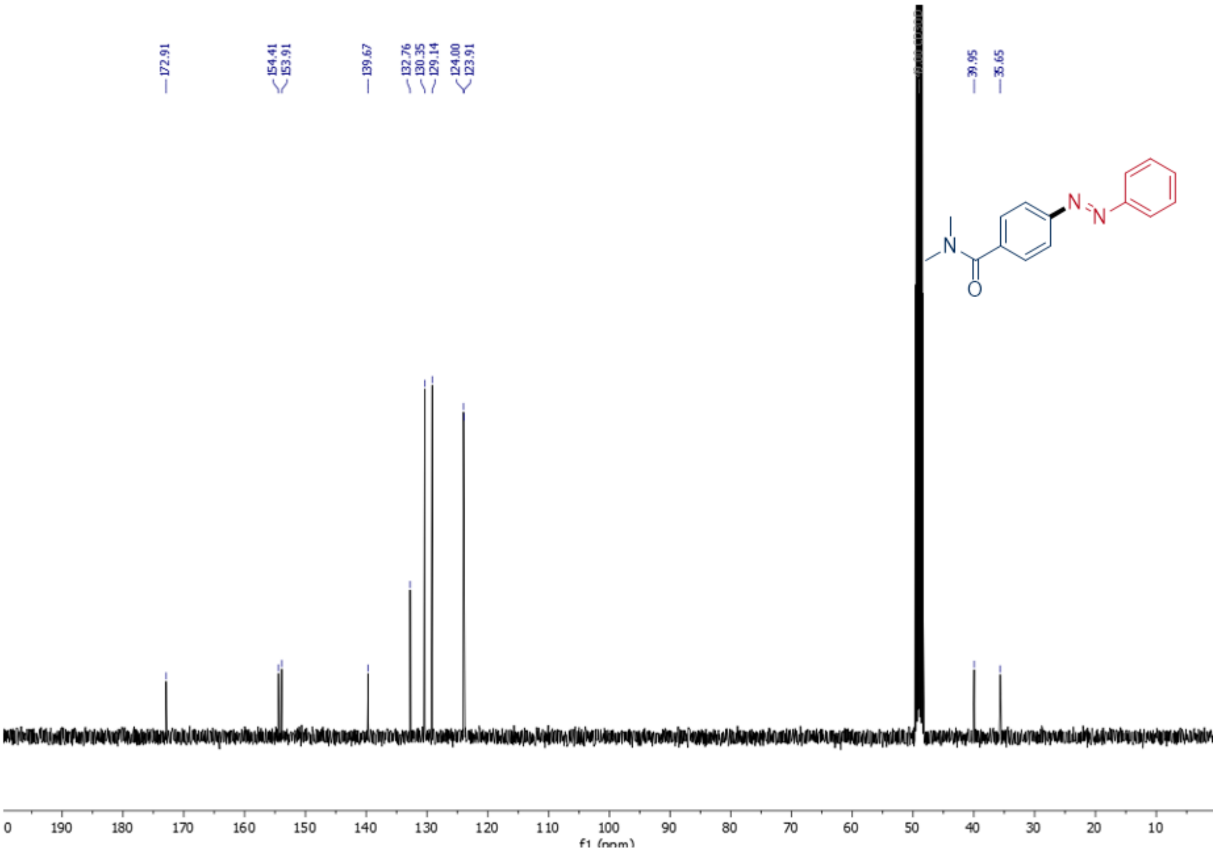
1H, 13C NMR of 3h:



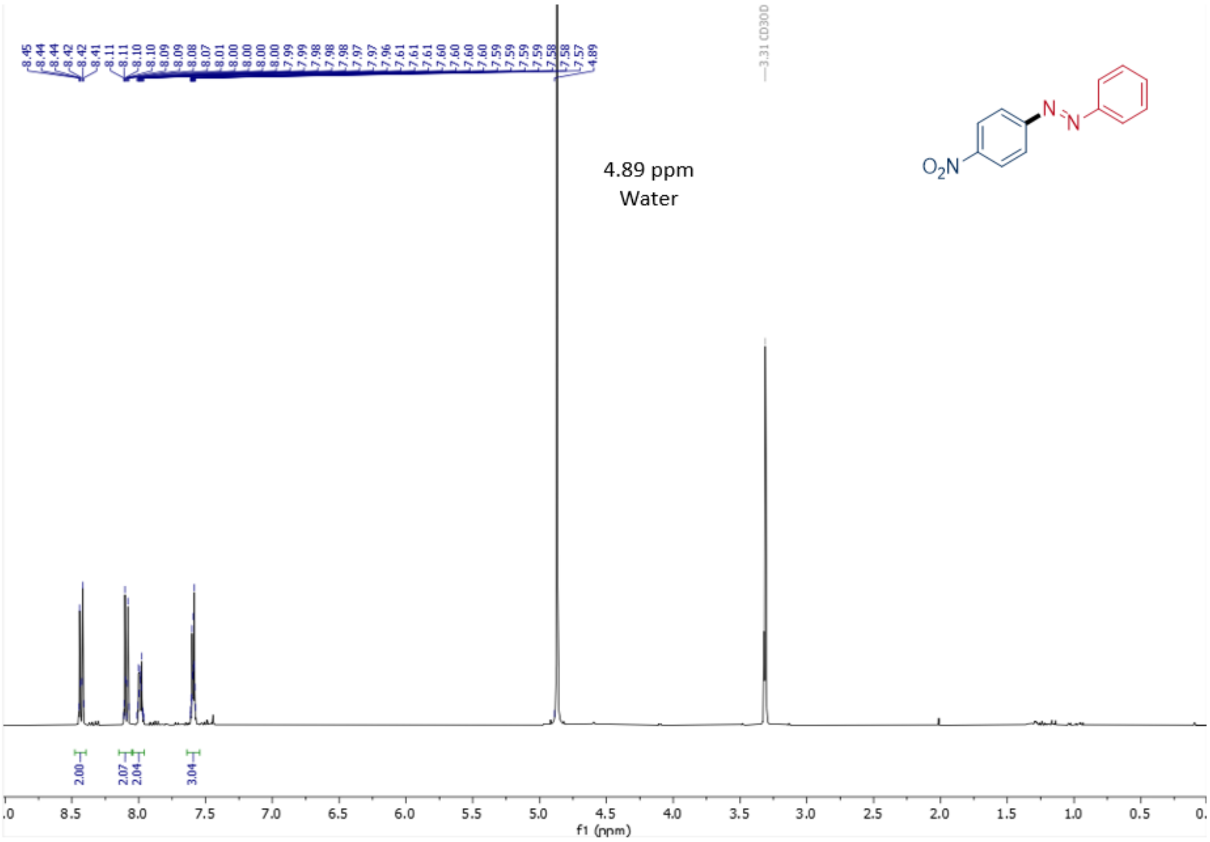


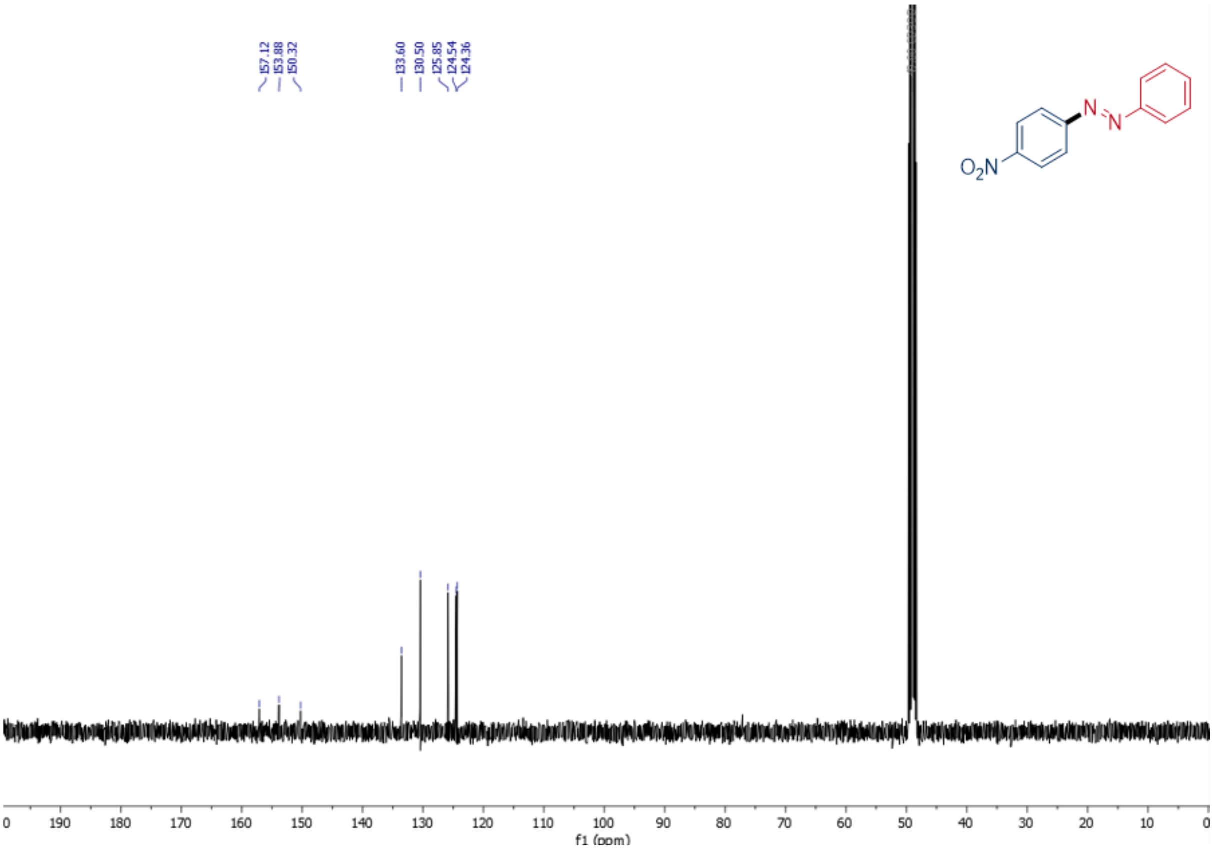
1H, 13C NMR of 3i:



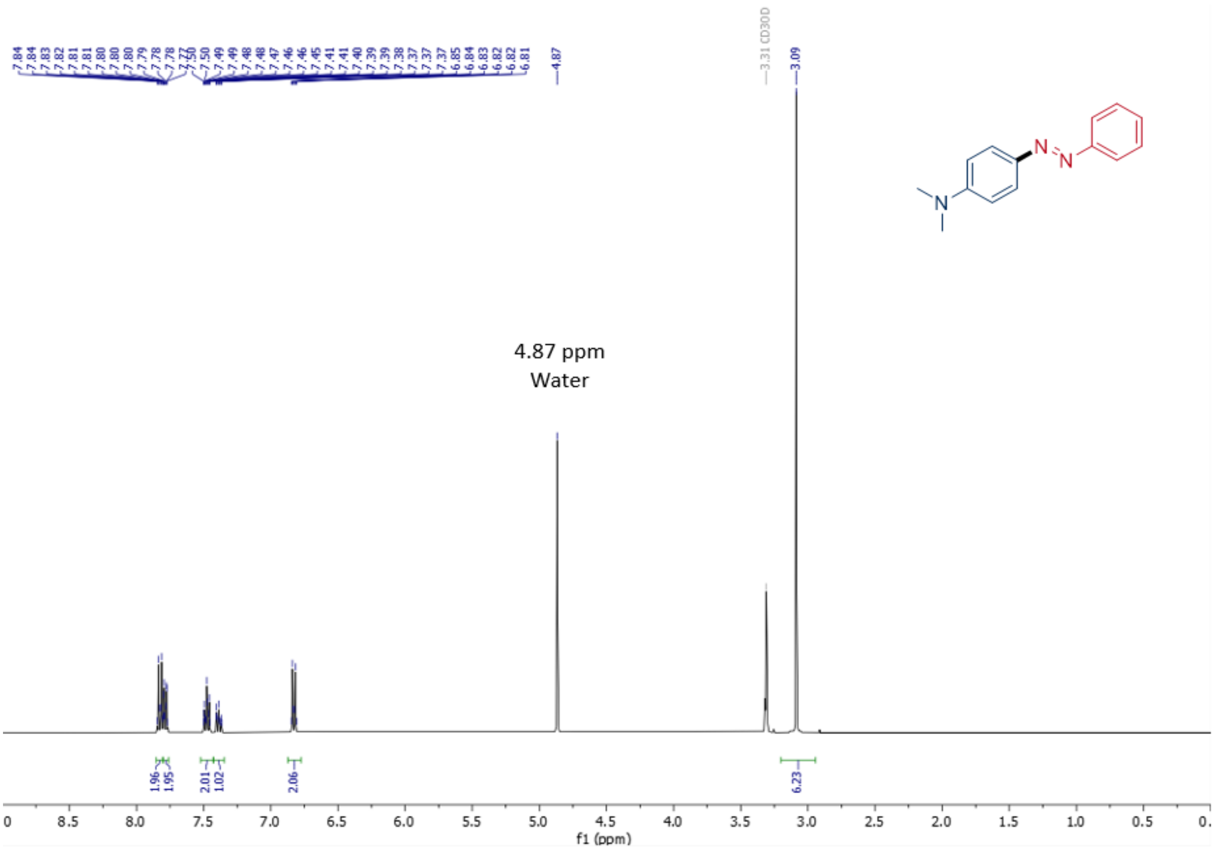


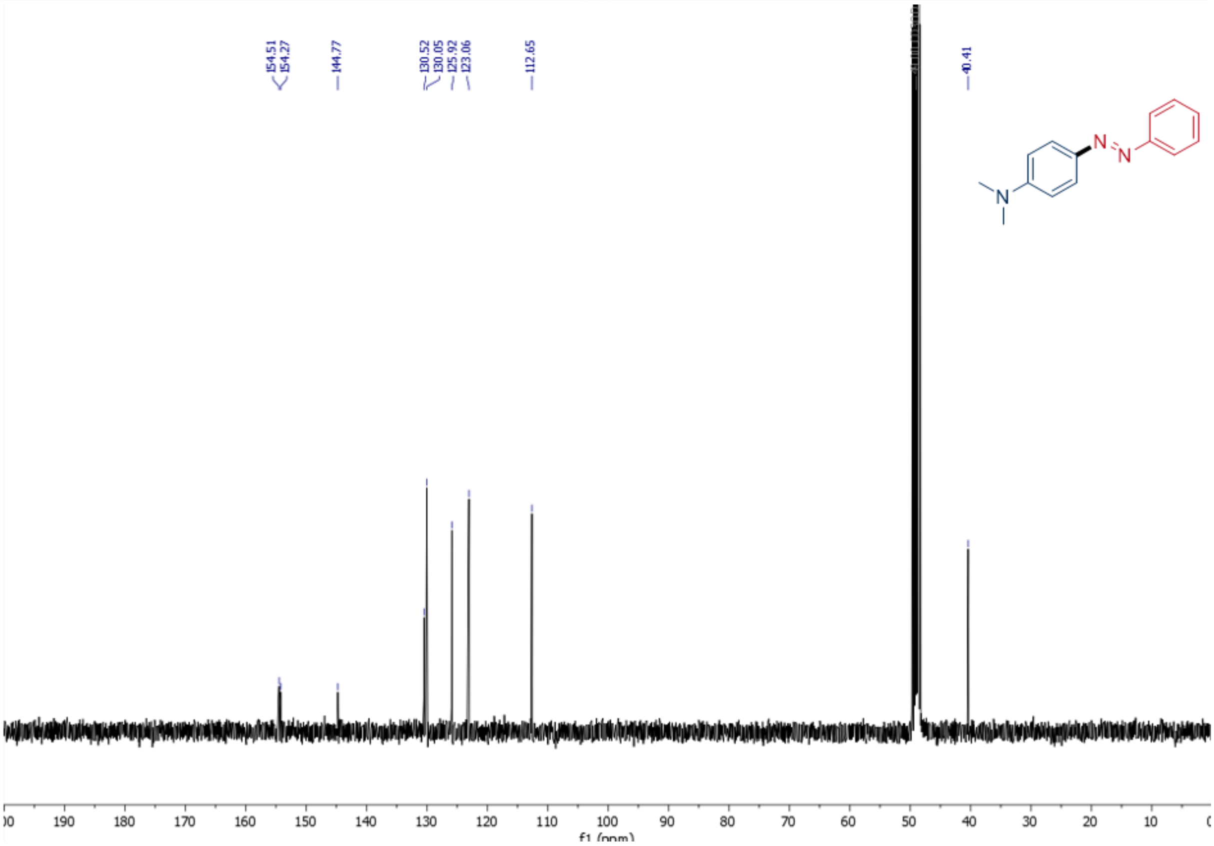
1H, 13C NMR of 3j:



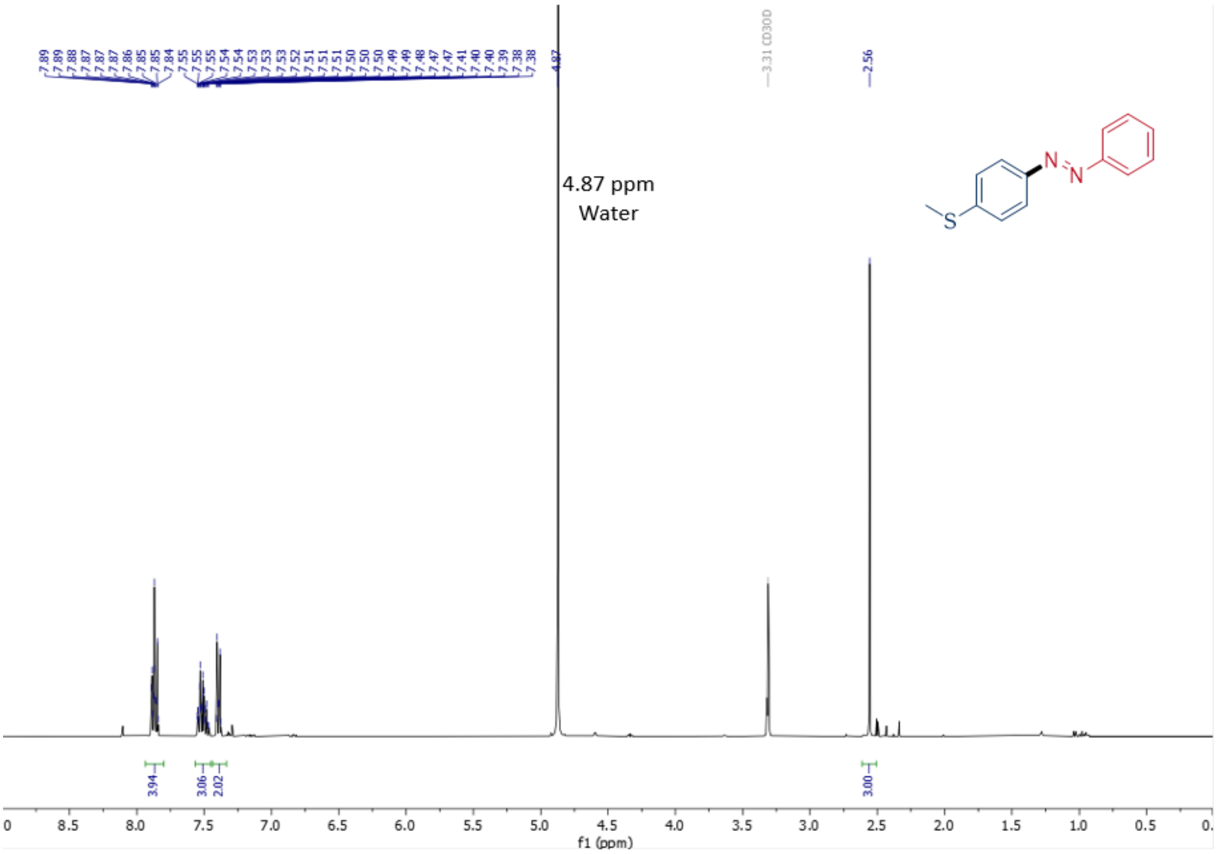


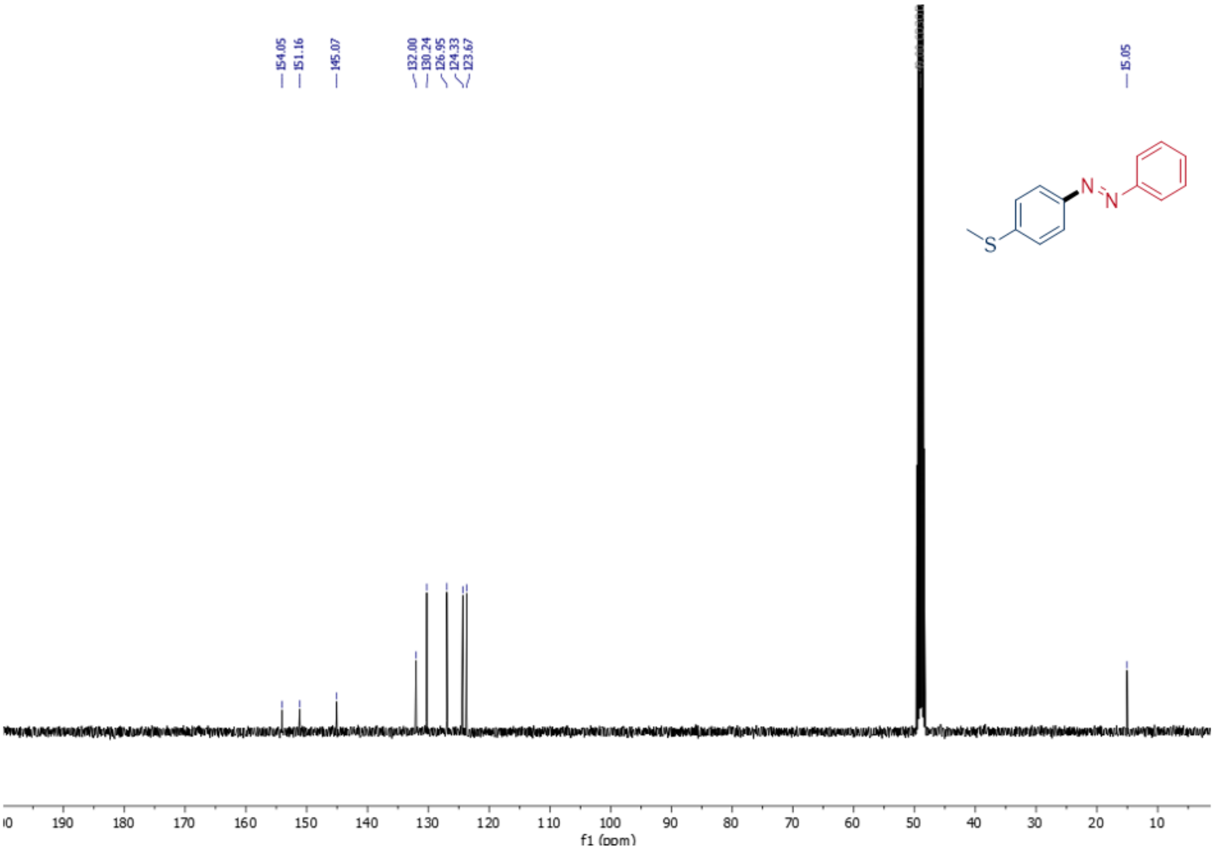
1H, 13C NMR of 3k:



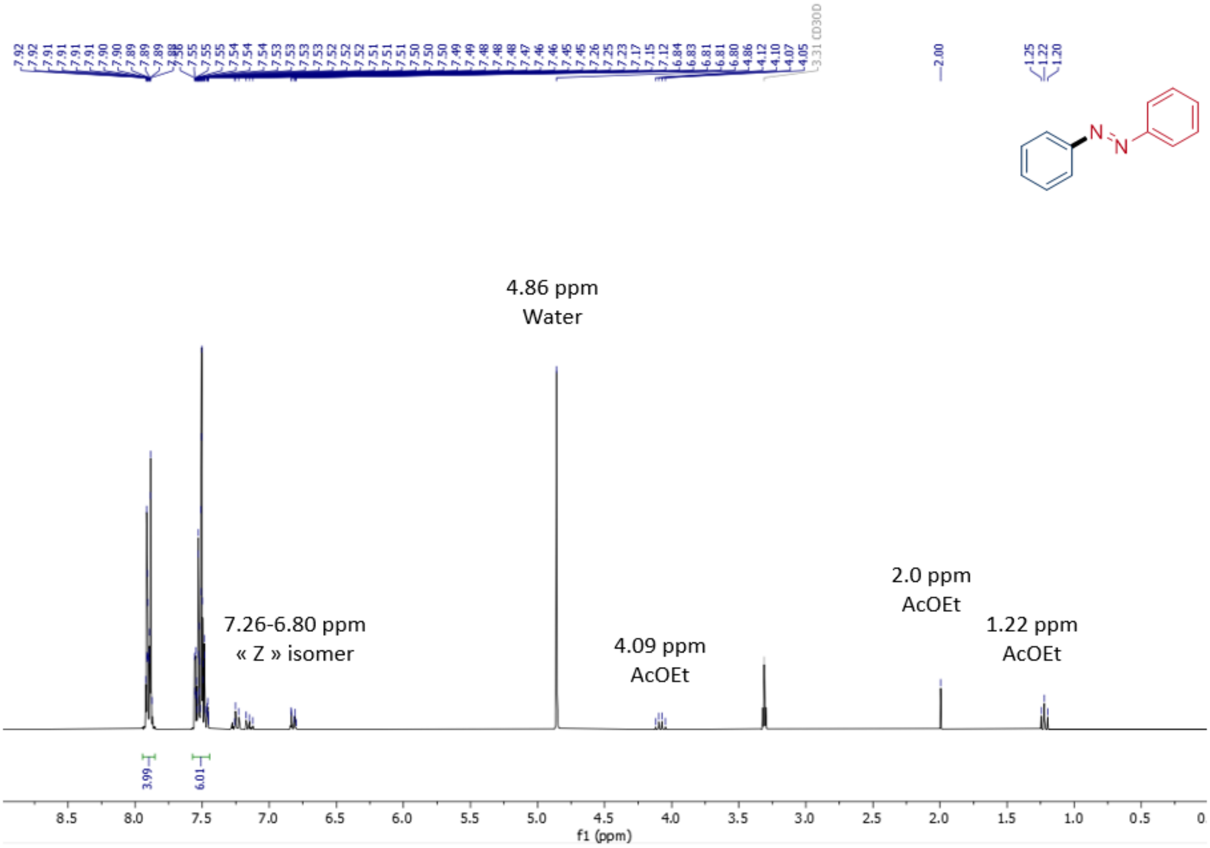


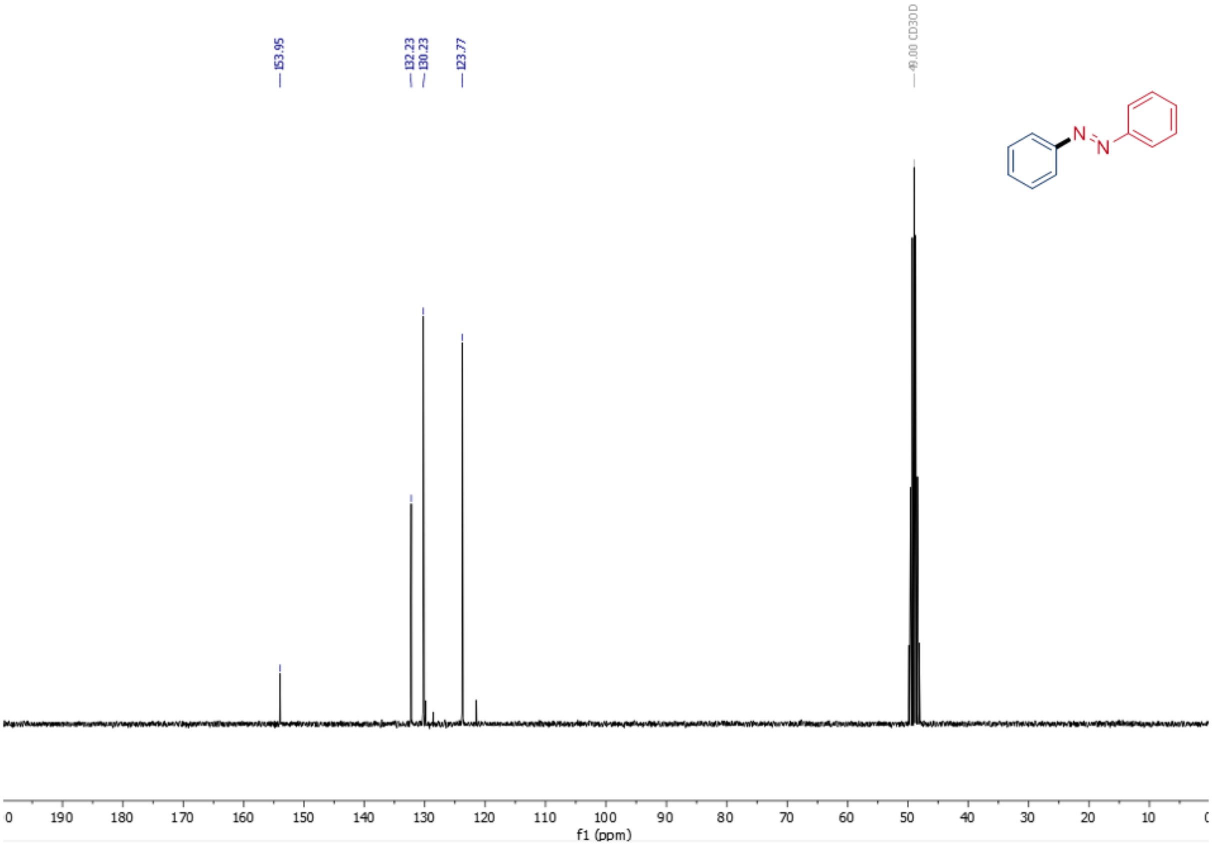
1H, 13C NMR of 3l:





1H, 13C NMR of 3m:





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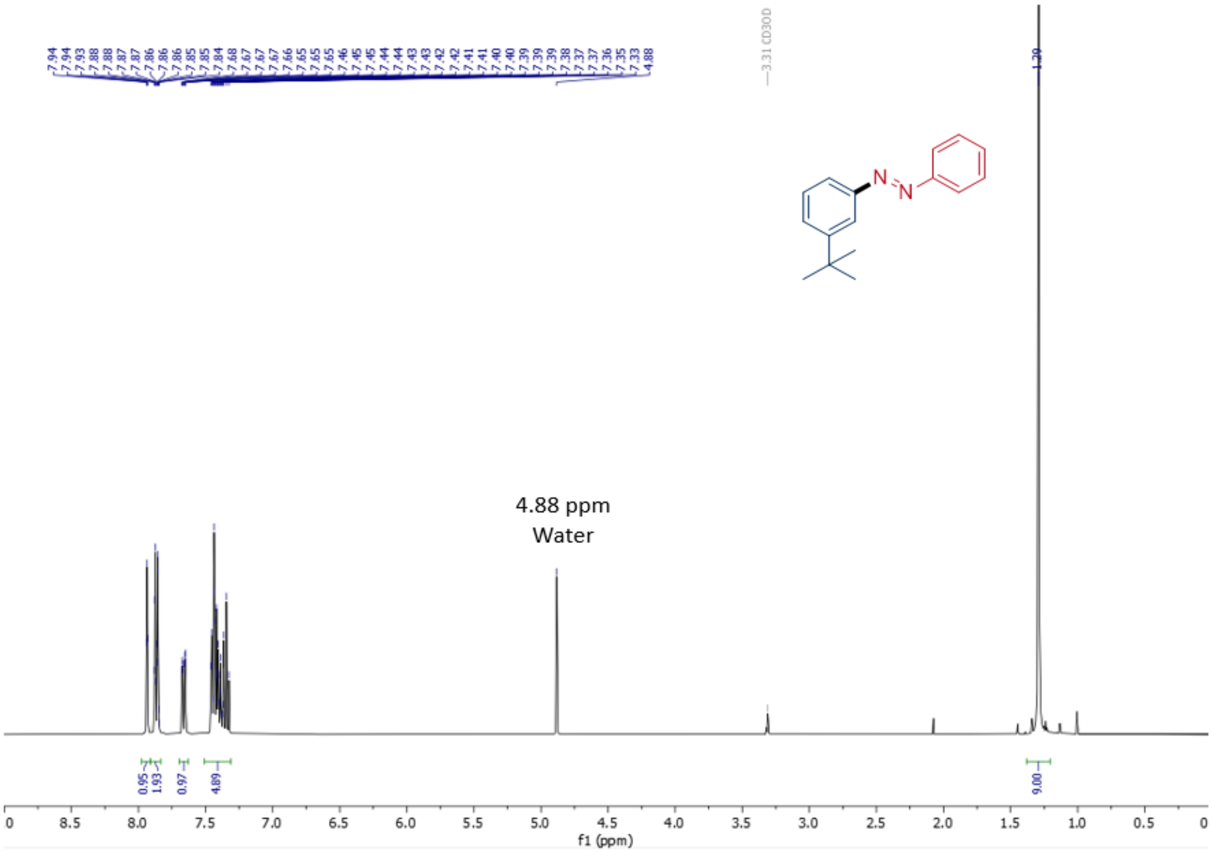
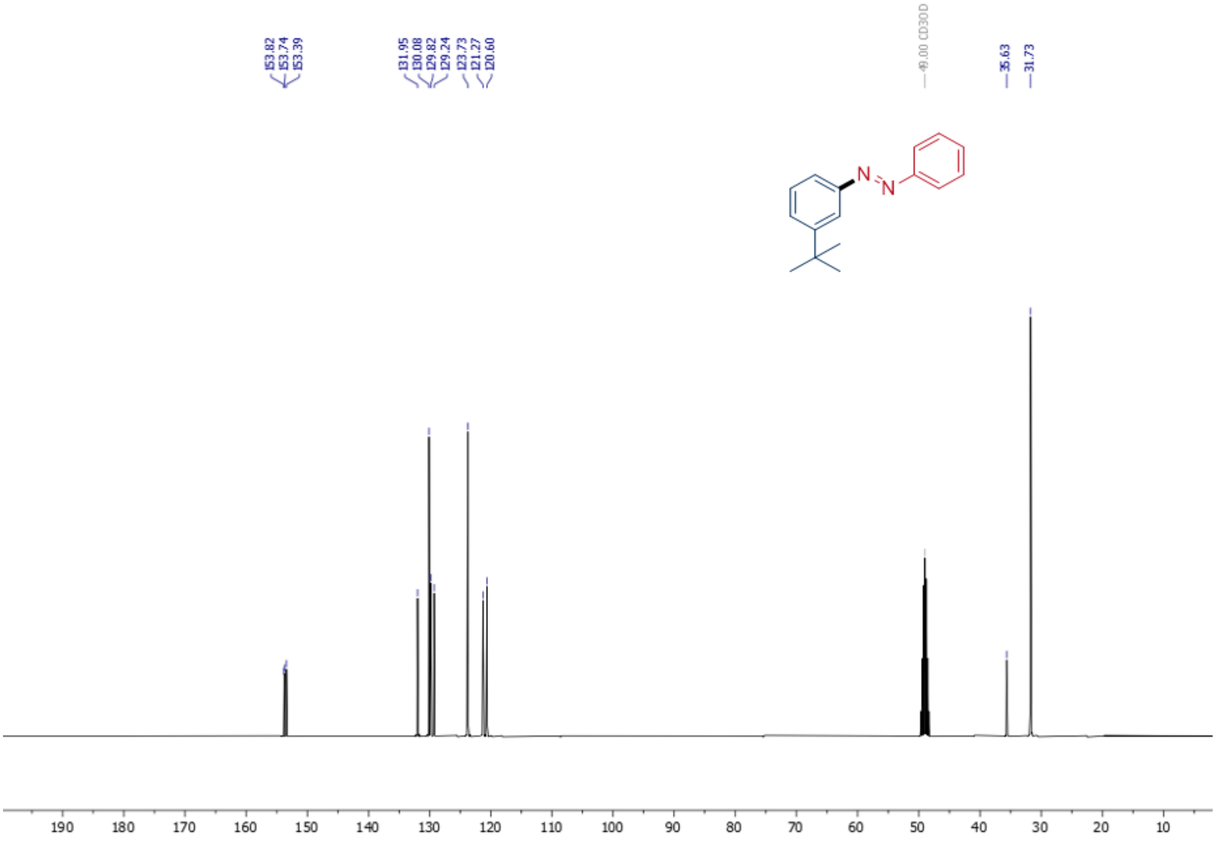
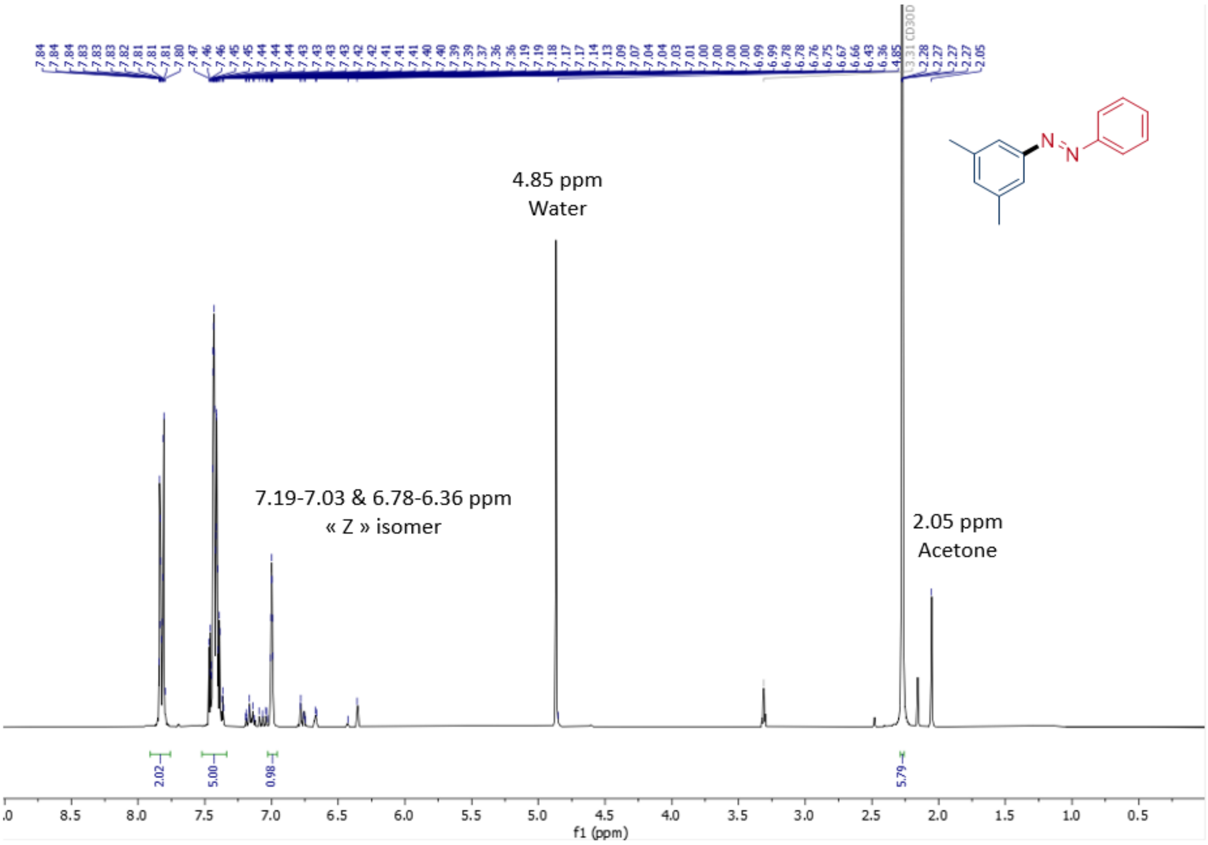
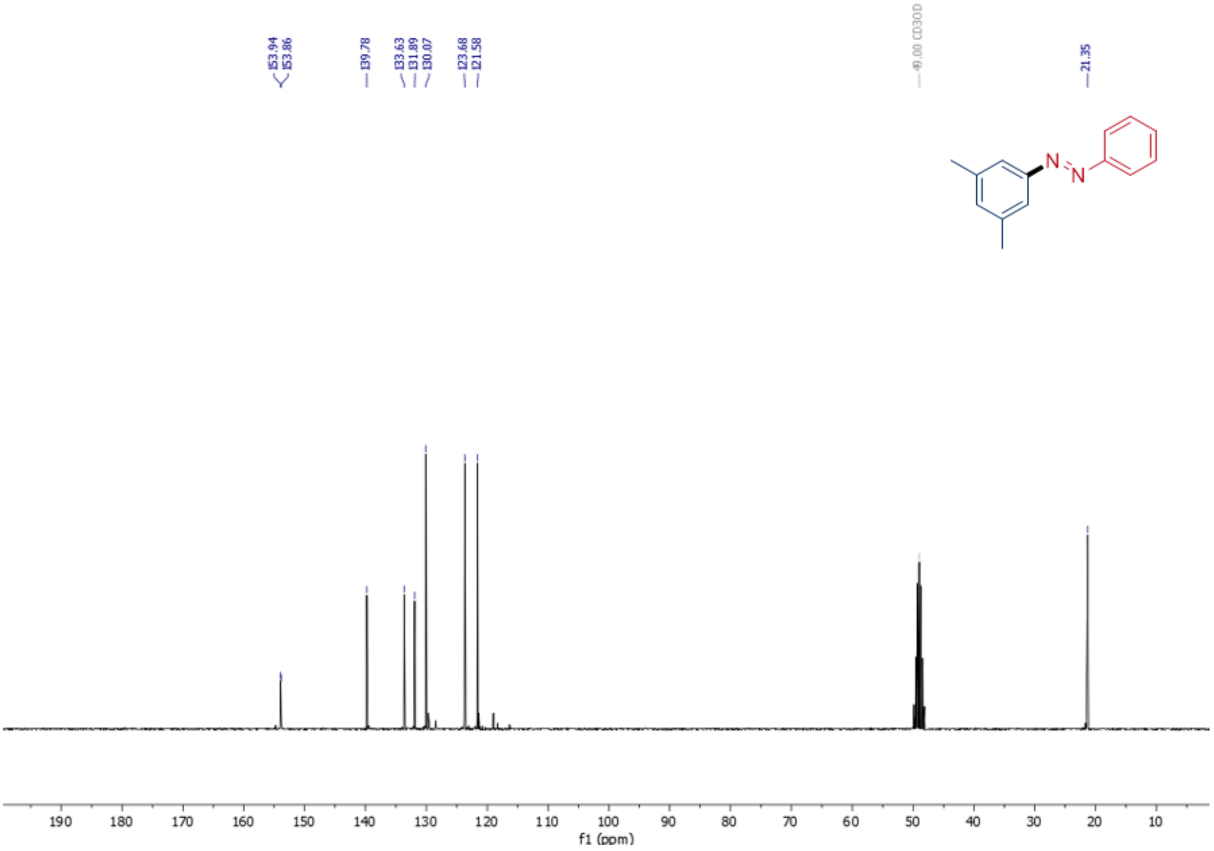


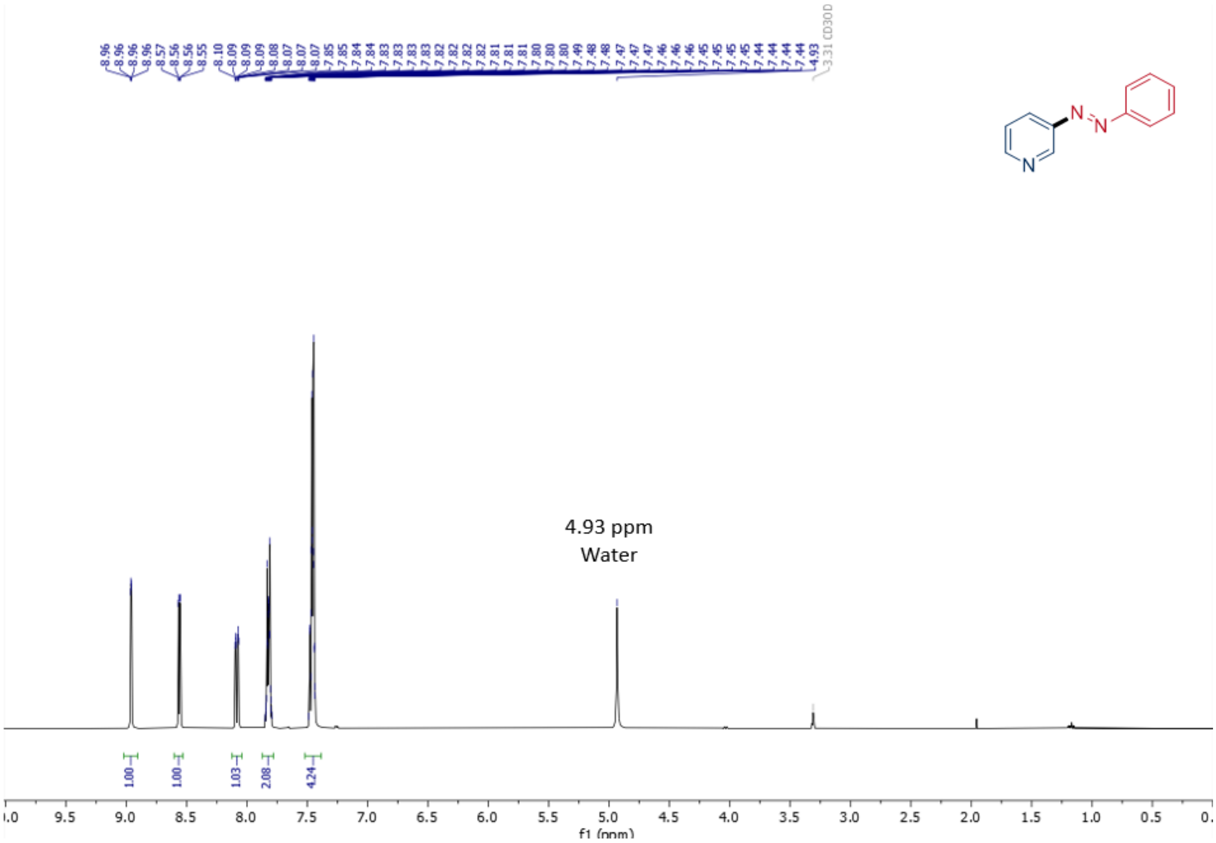


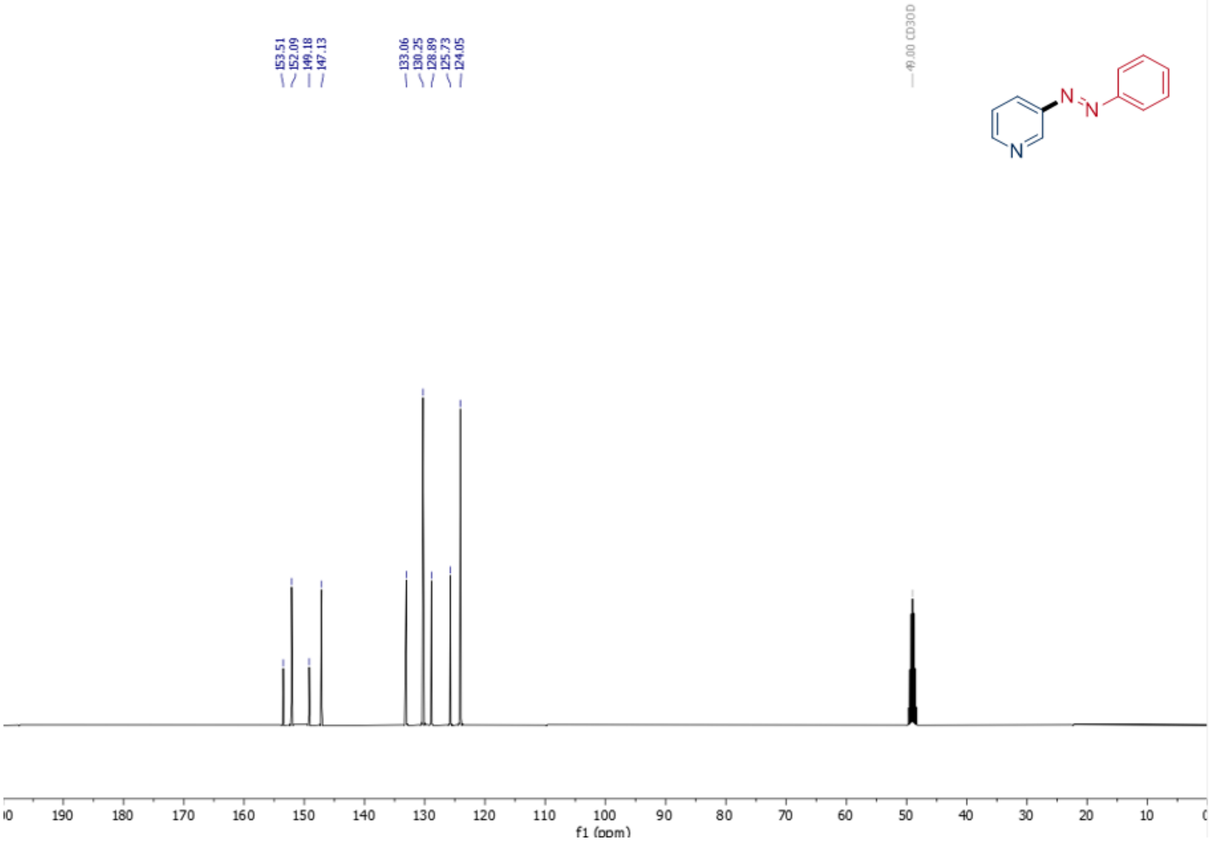
1H, 13C NMR of 3o:



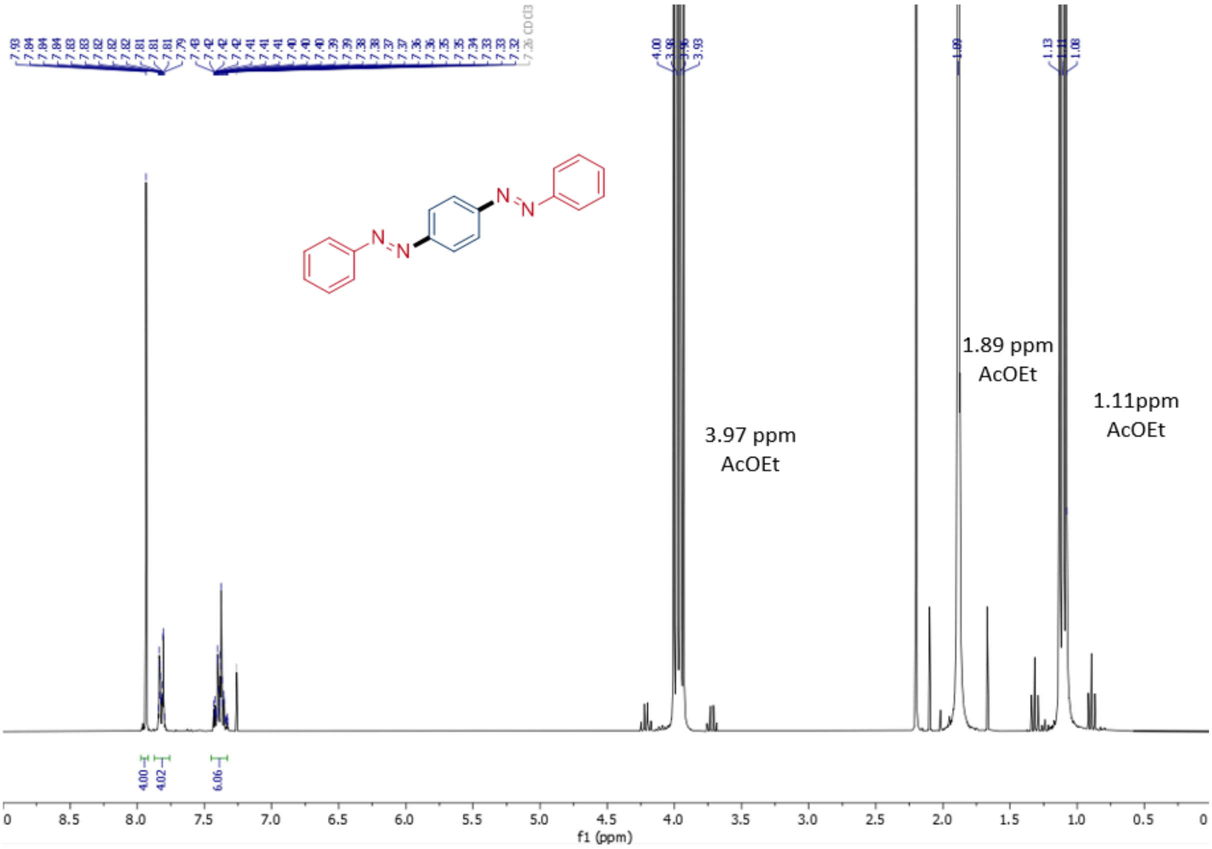


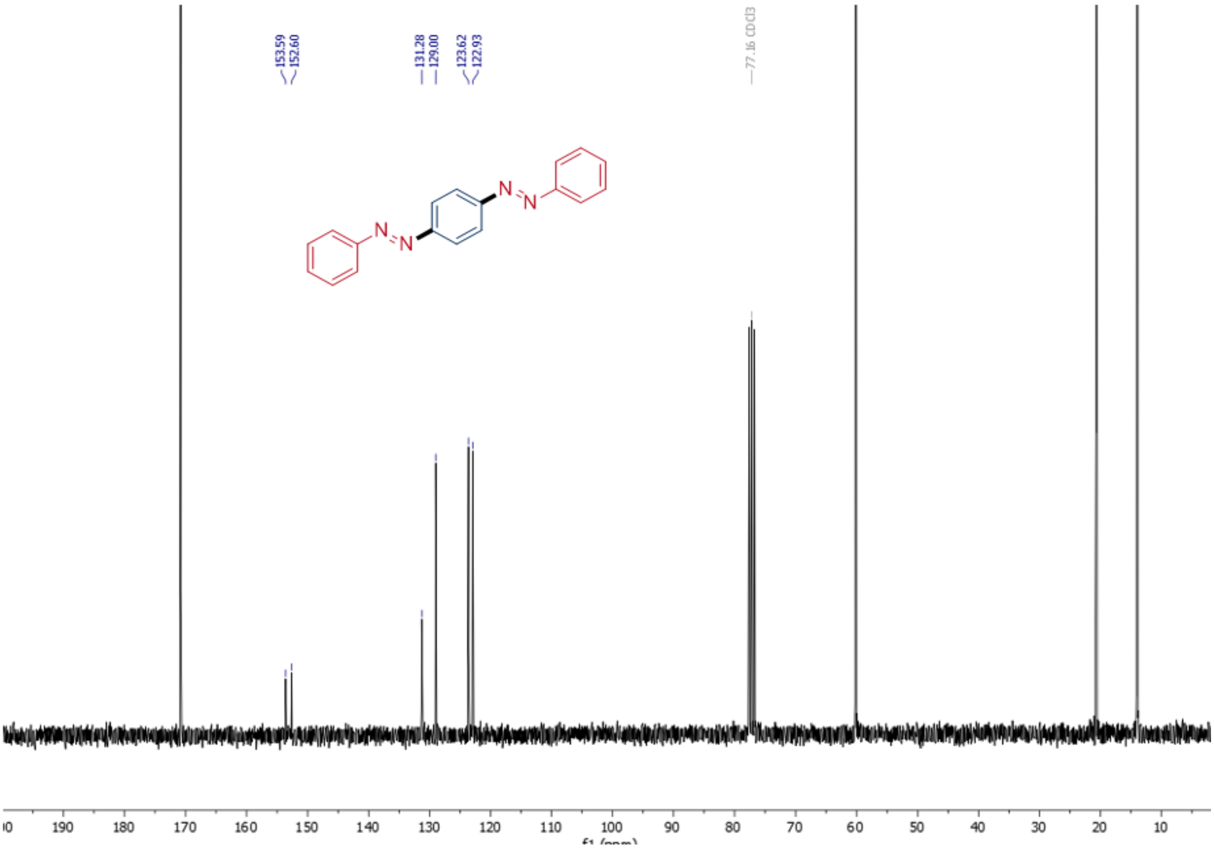
1H, 13C NMR of 3p:



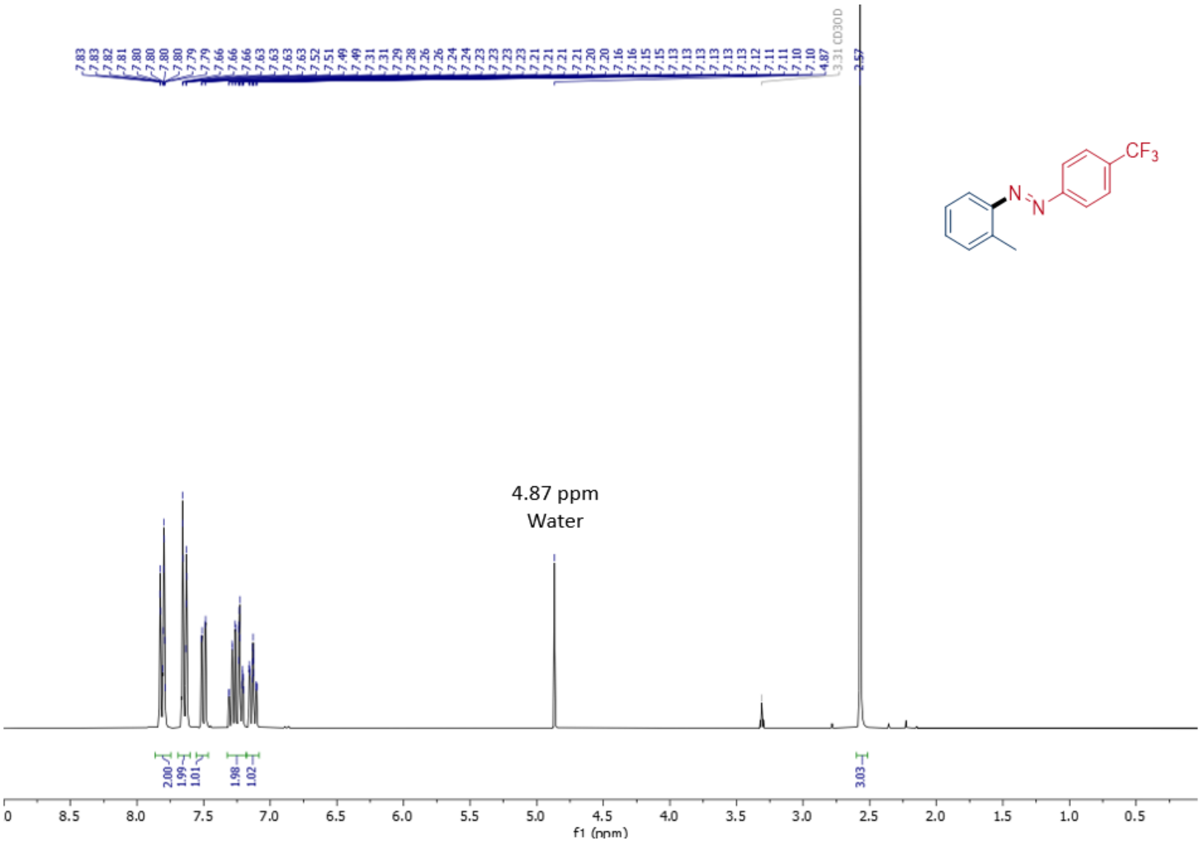


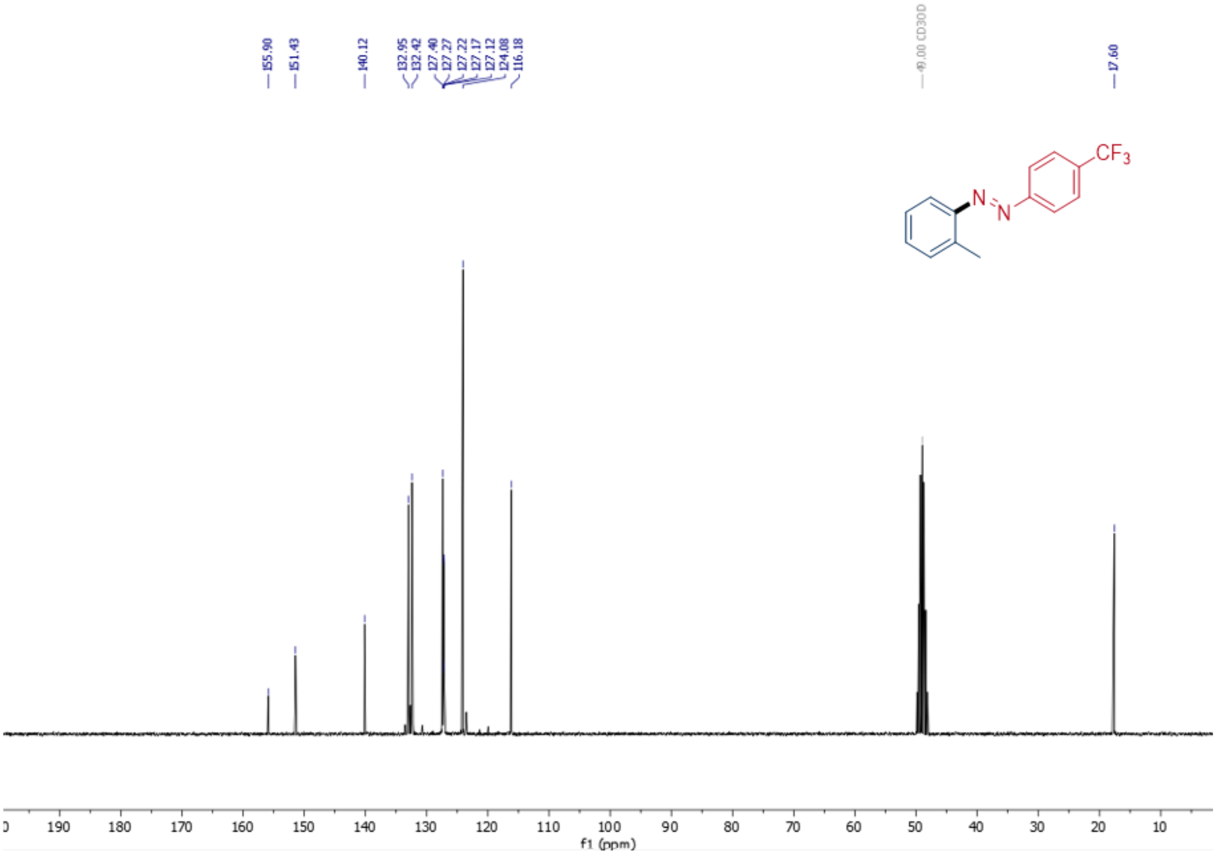
1H, 13C NMR of 3q:

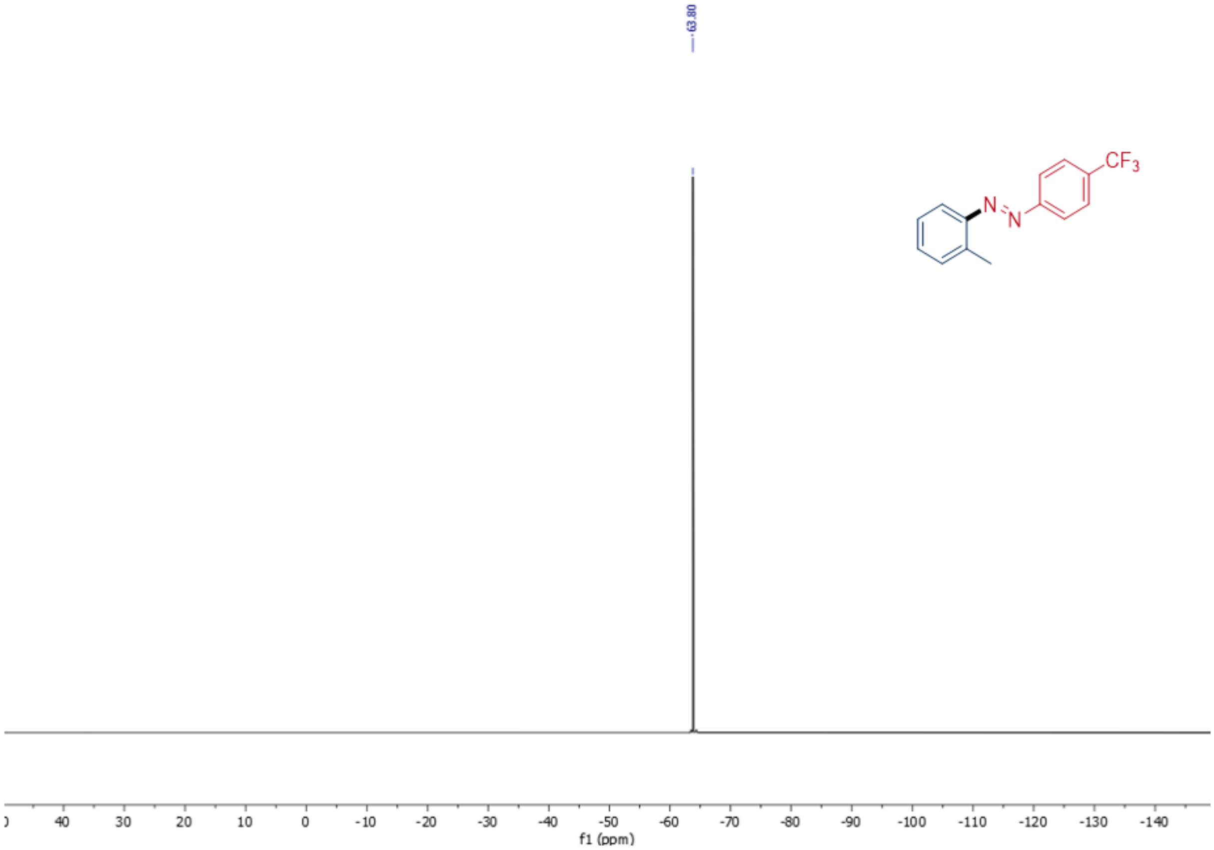




1H, 13C, 19F NMR of 4a:



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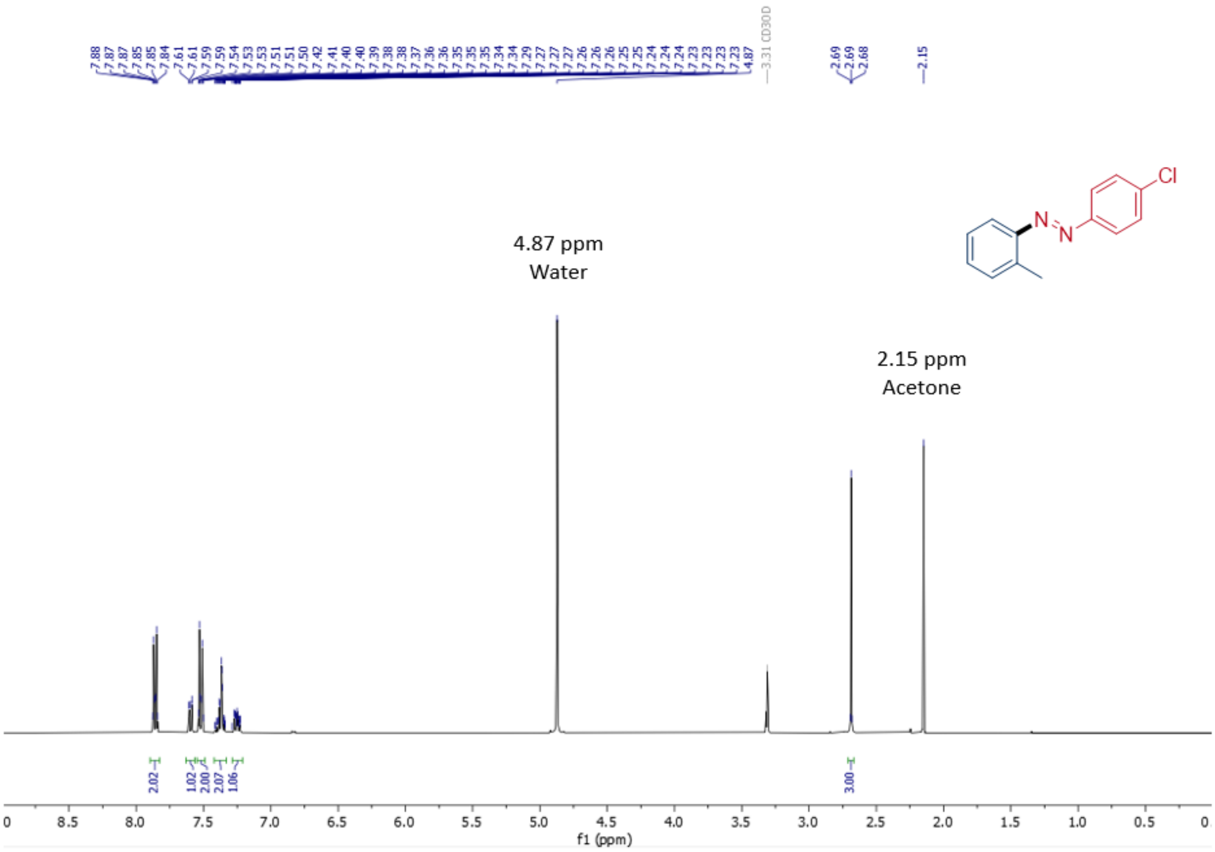
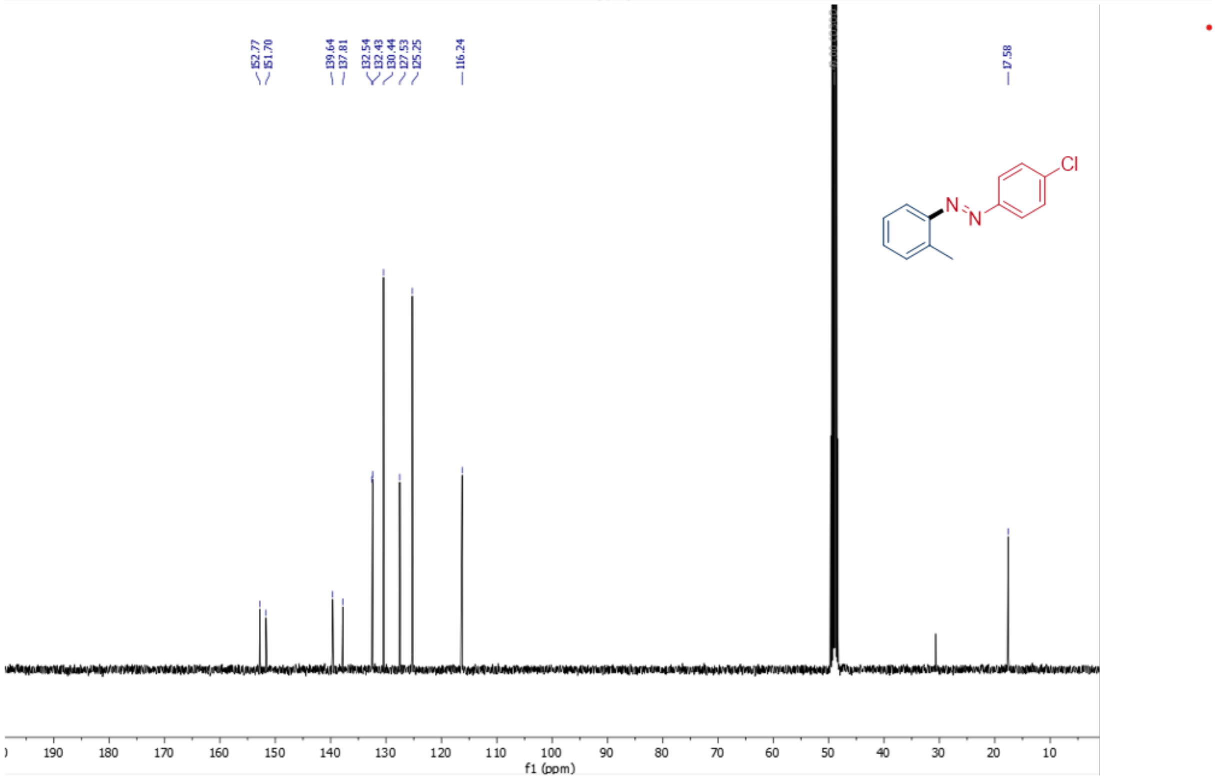
f1 (ppm)

1H, 13C NMR of 4b:





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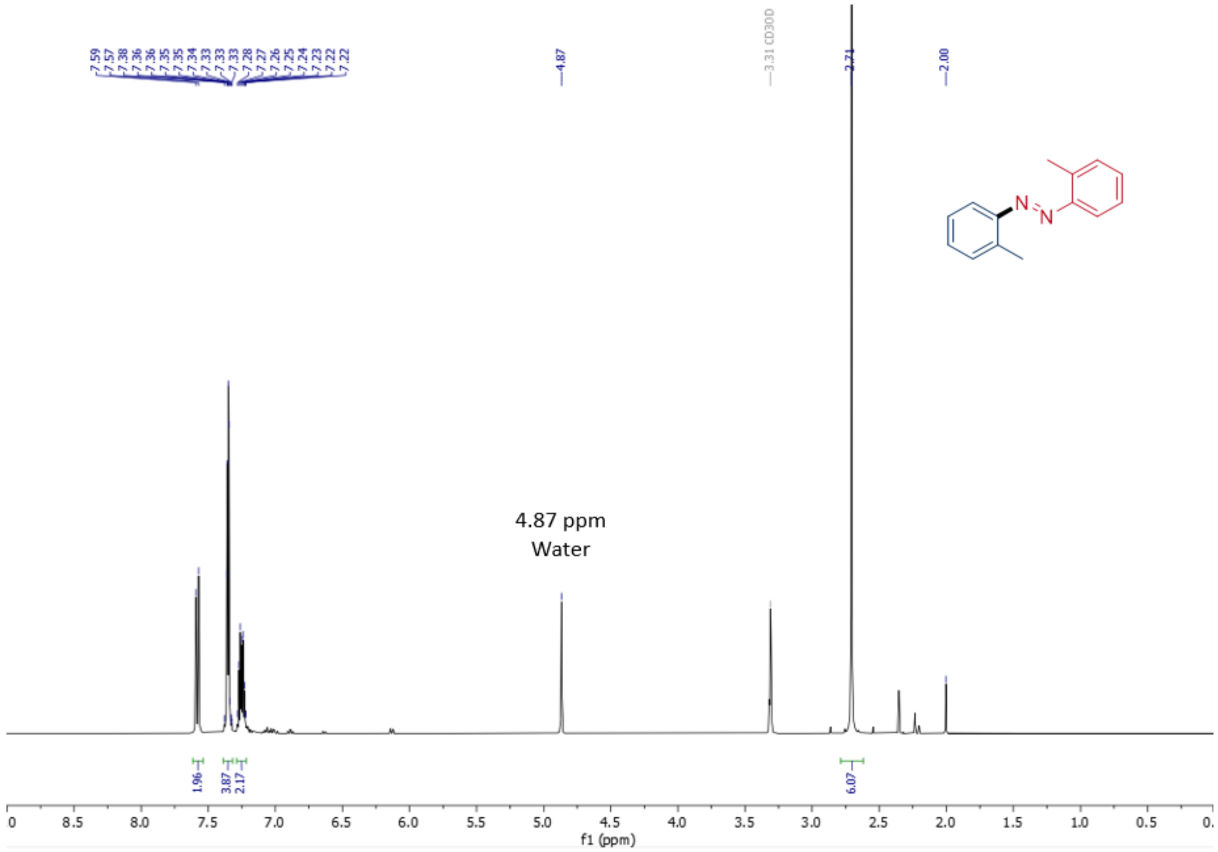
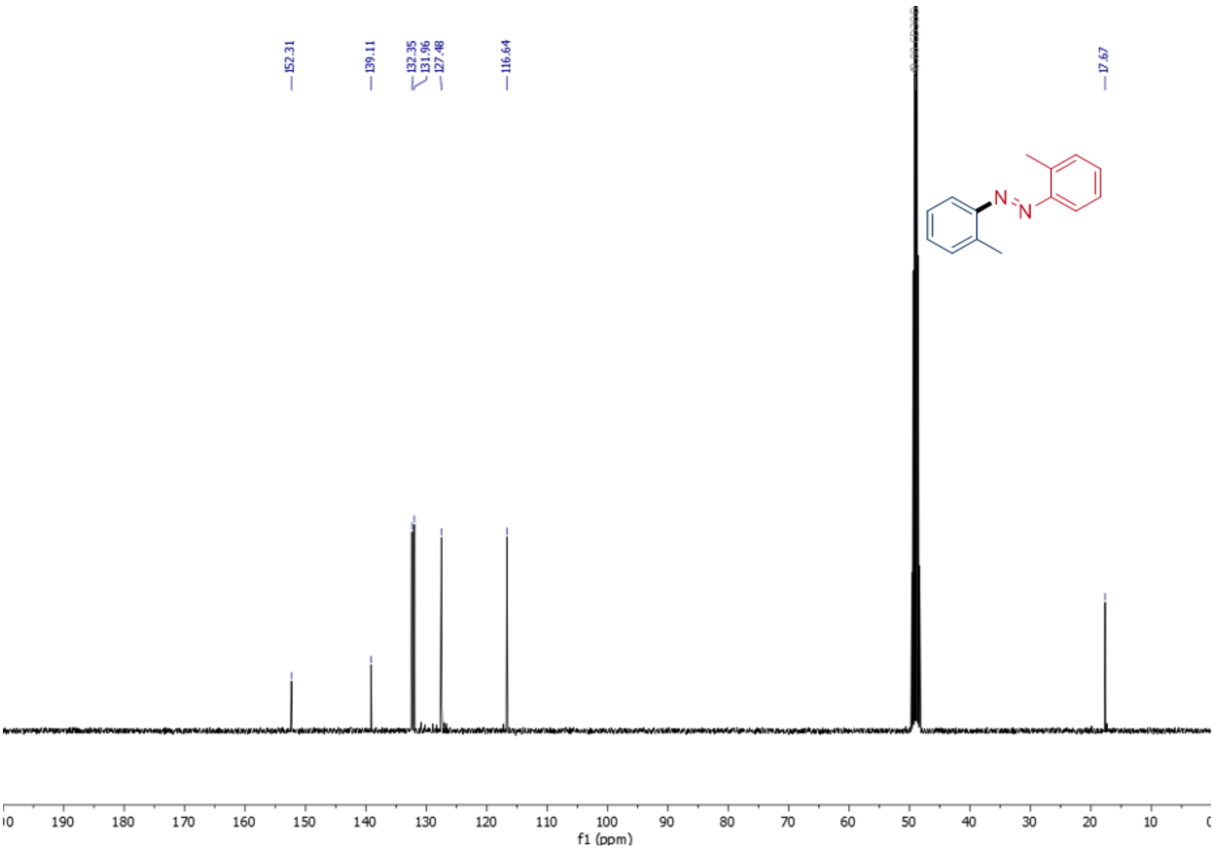
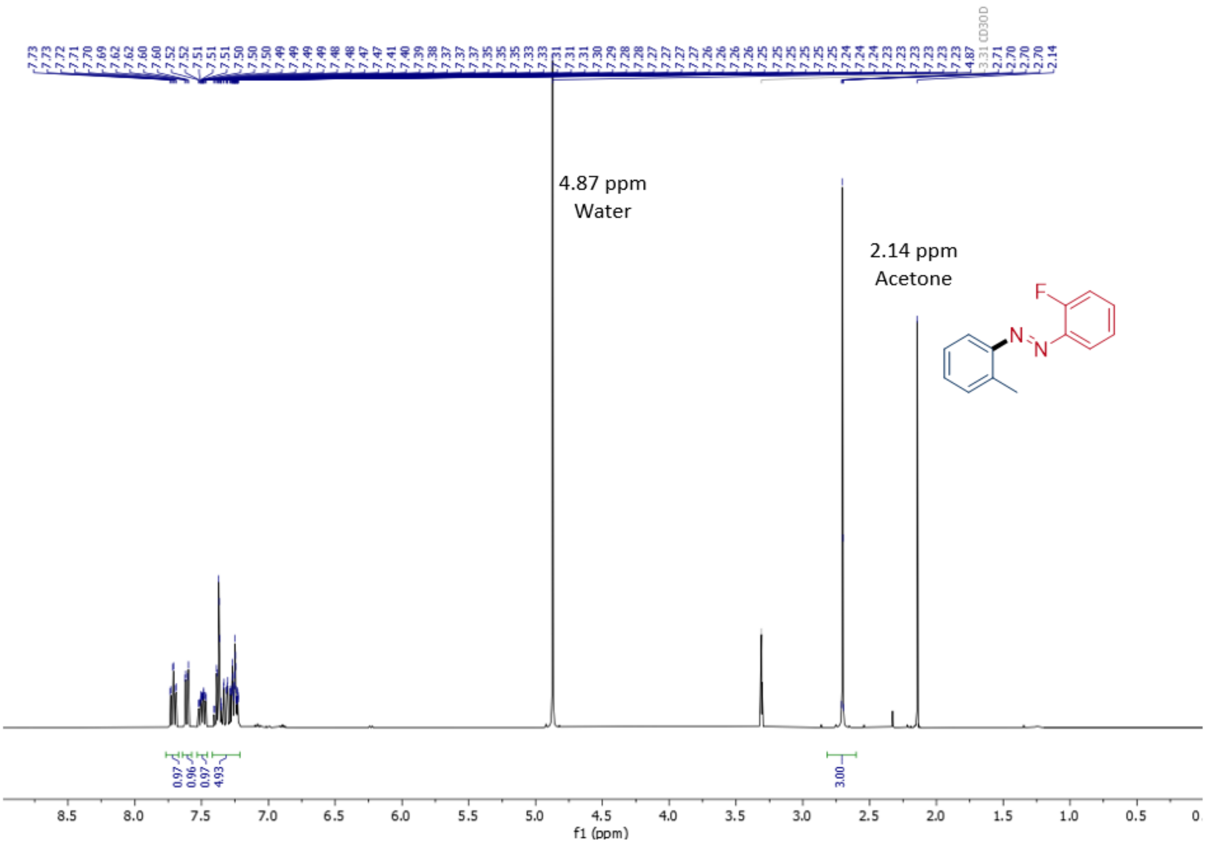
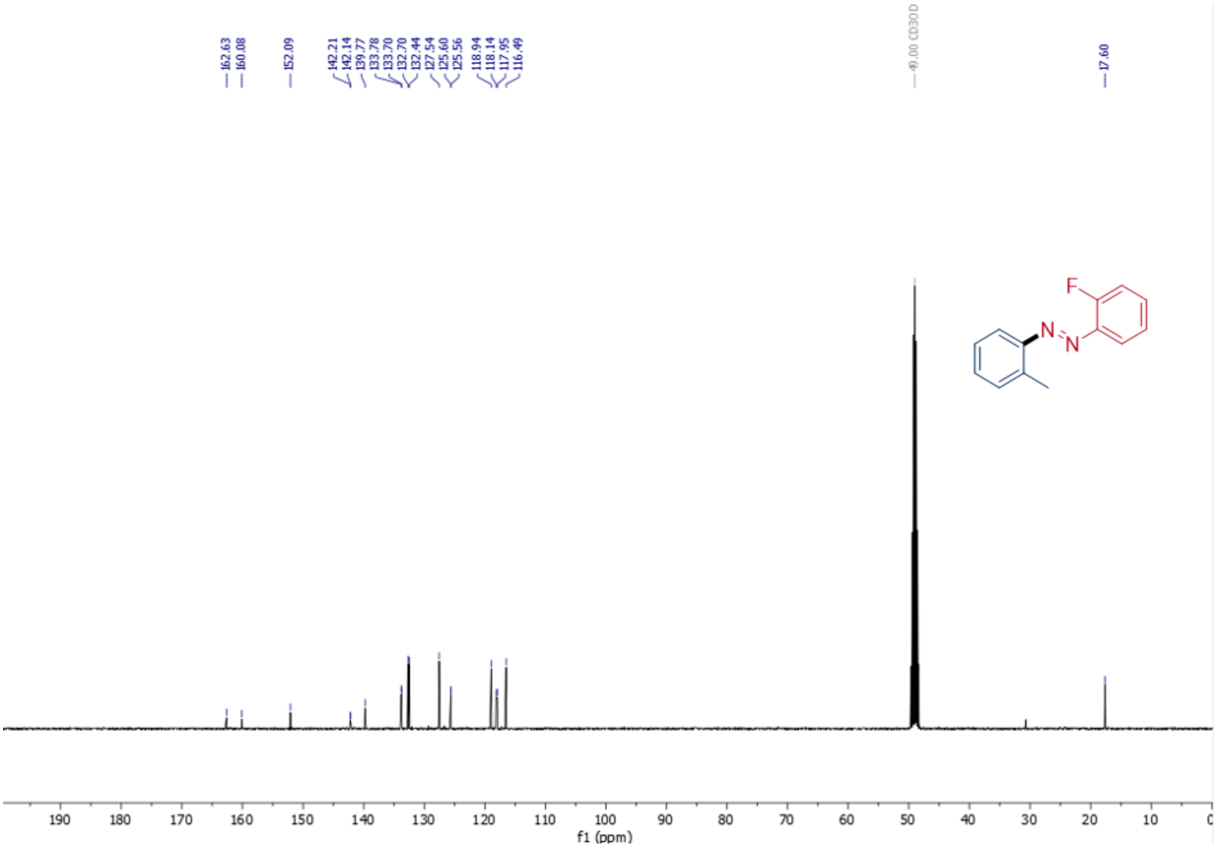
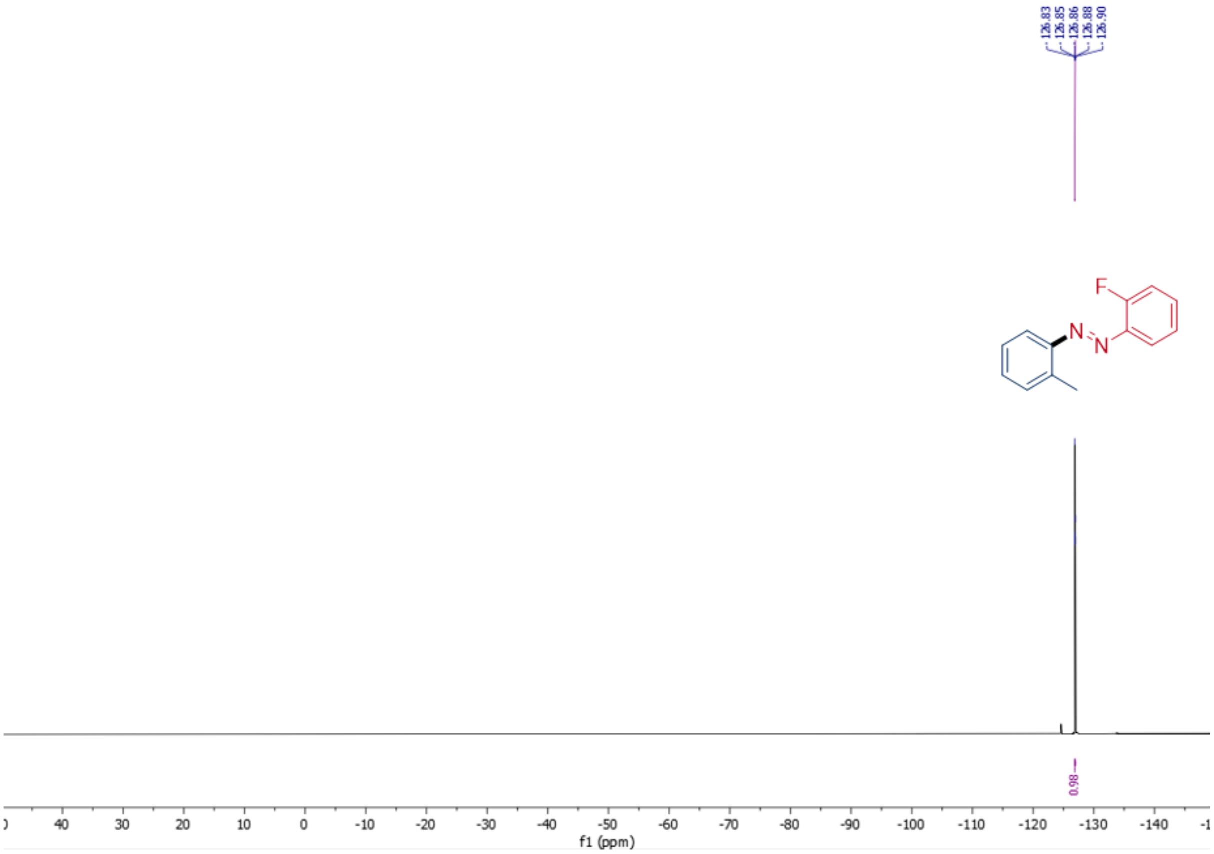




1H, 13C, 19F NMR of 4d:



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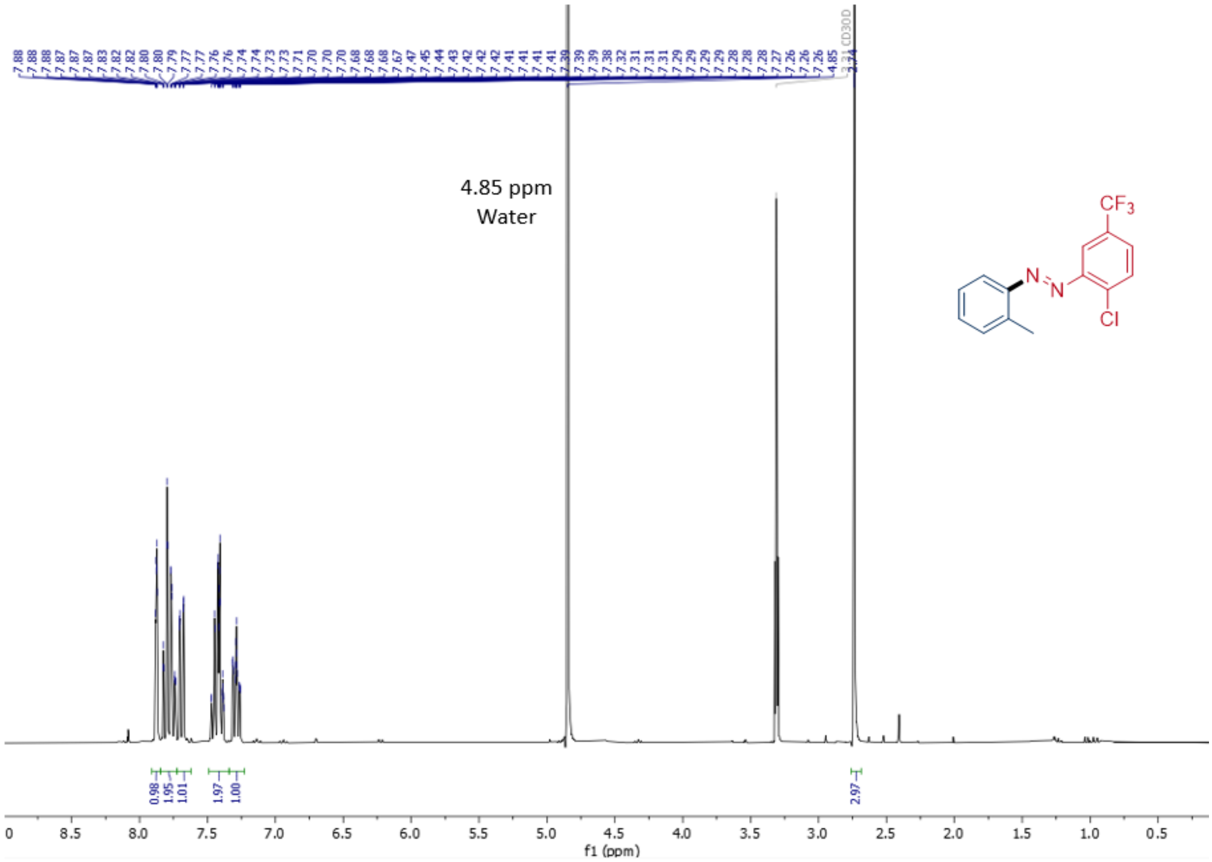
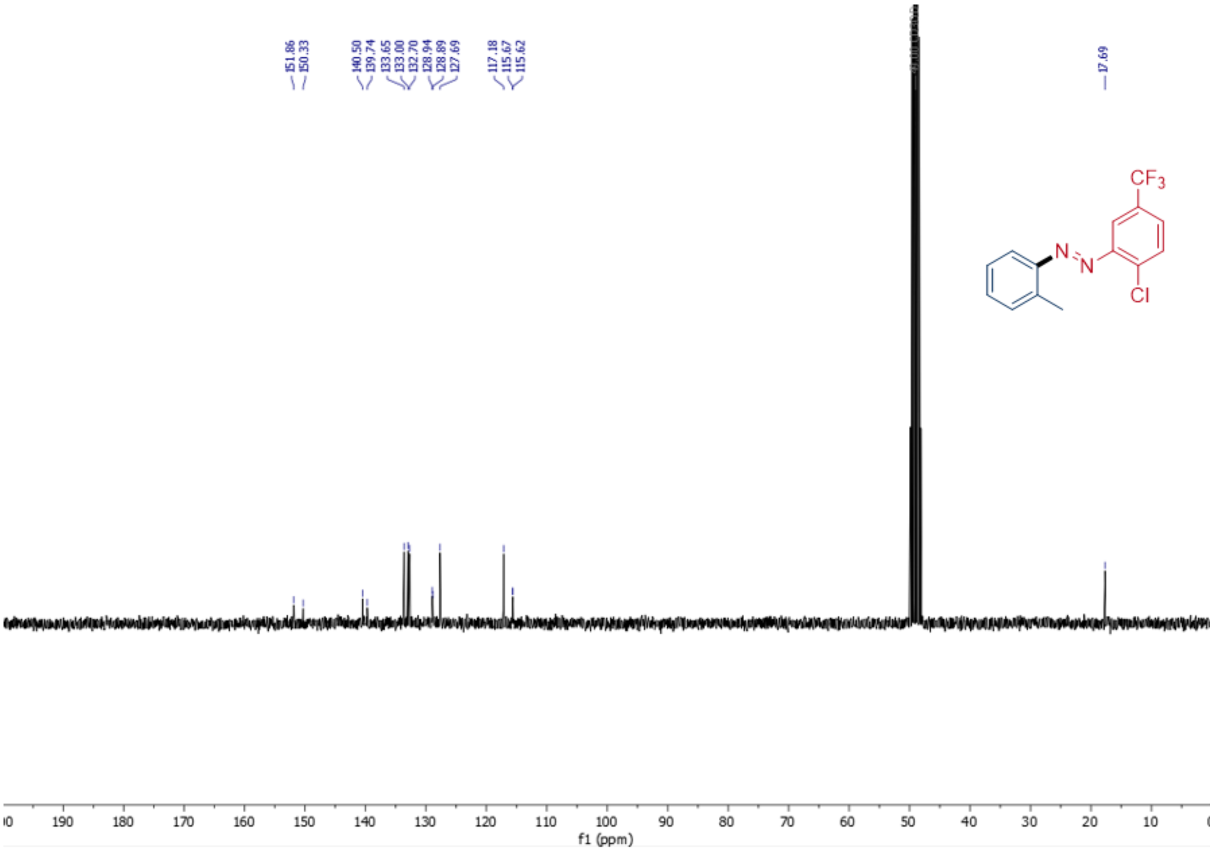
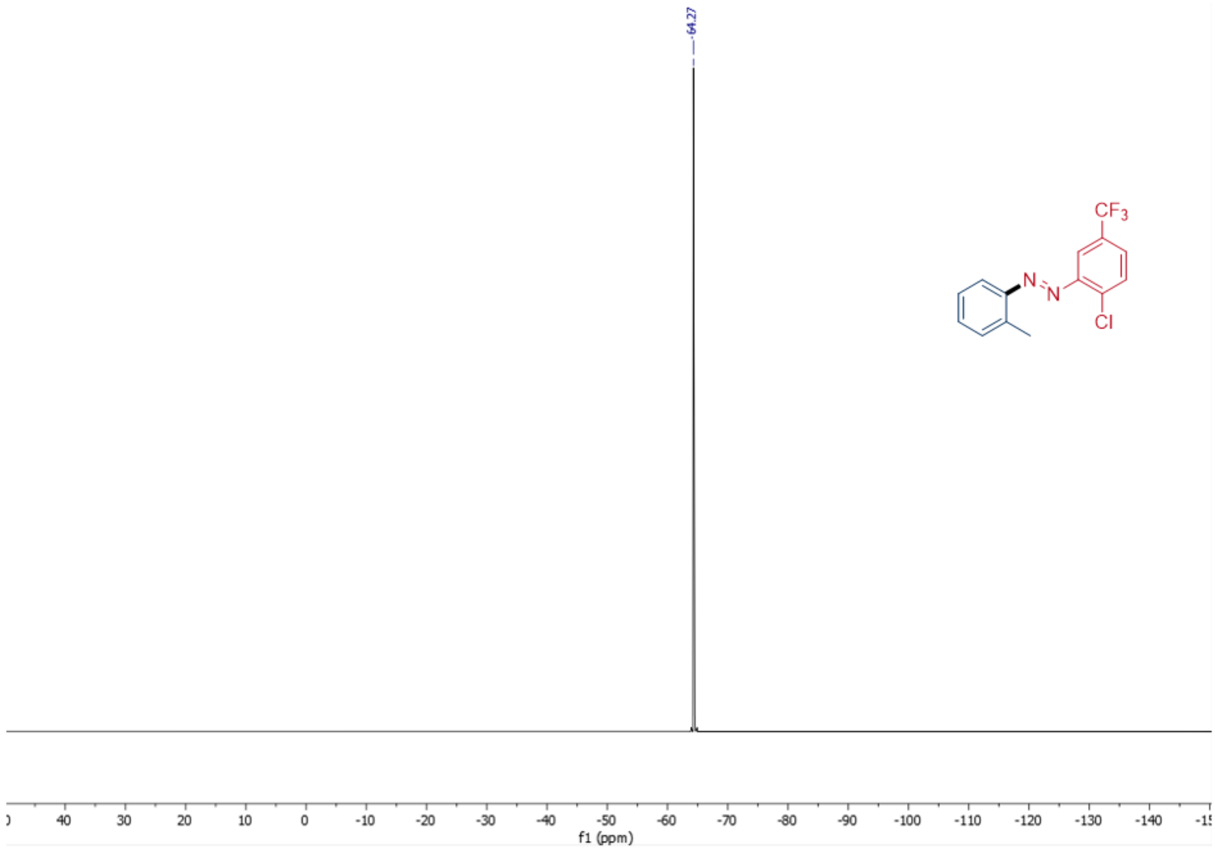
f1 (ppm)

1H, 13C, 19F NMR of 4e:



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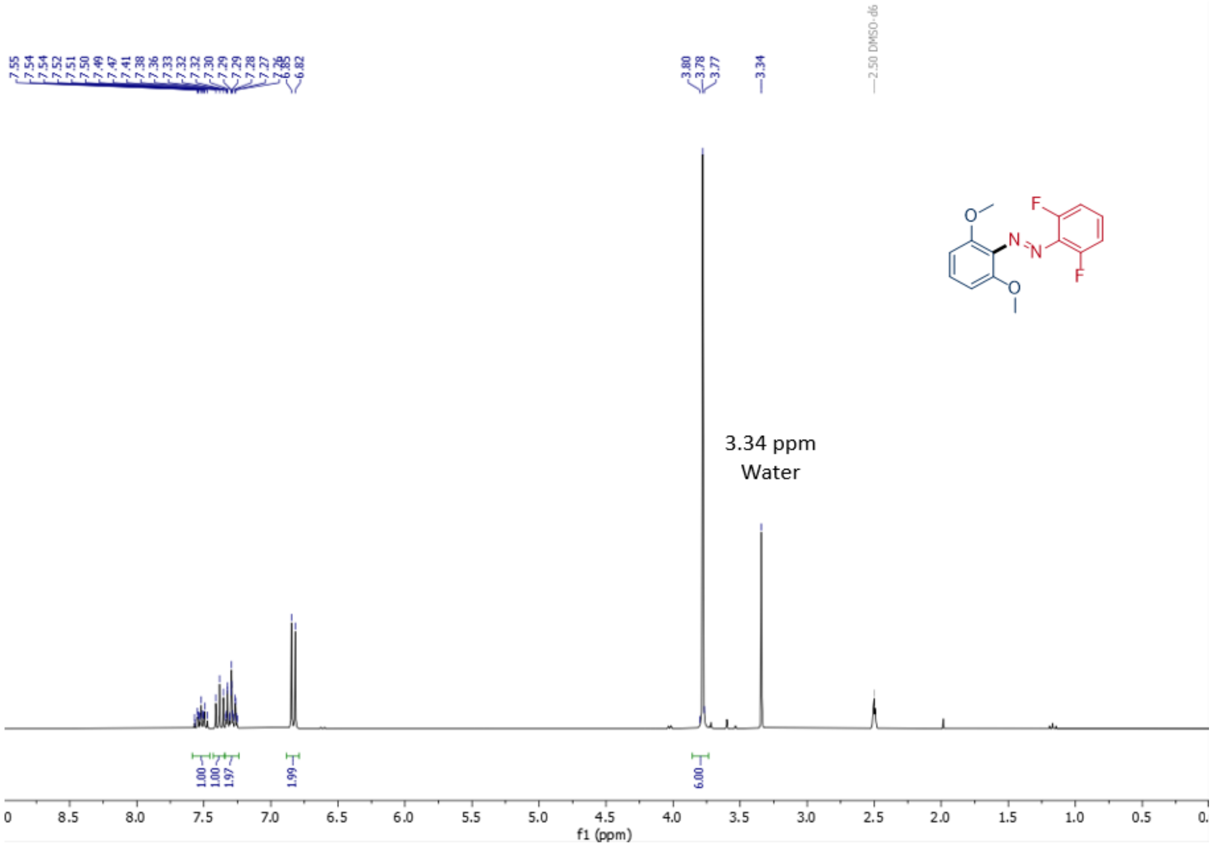
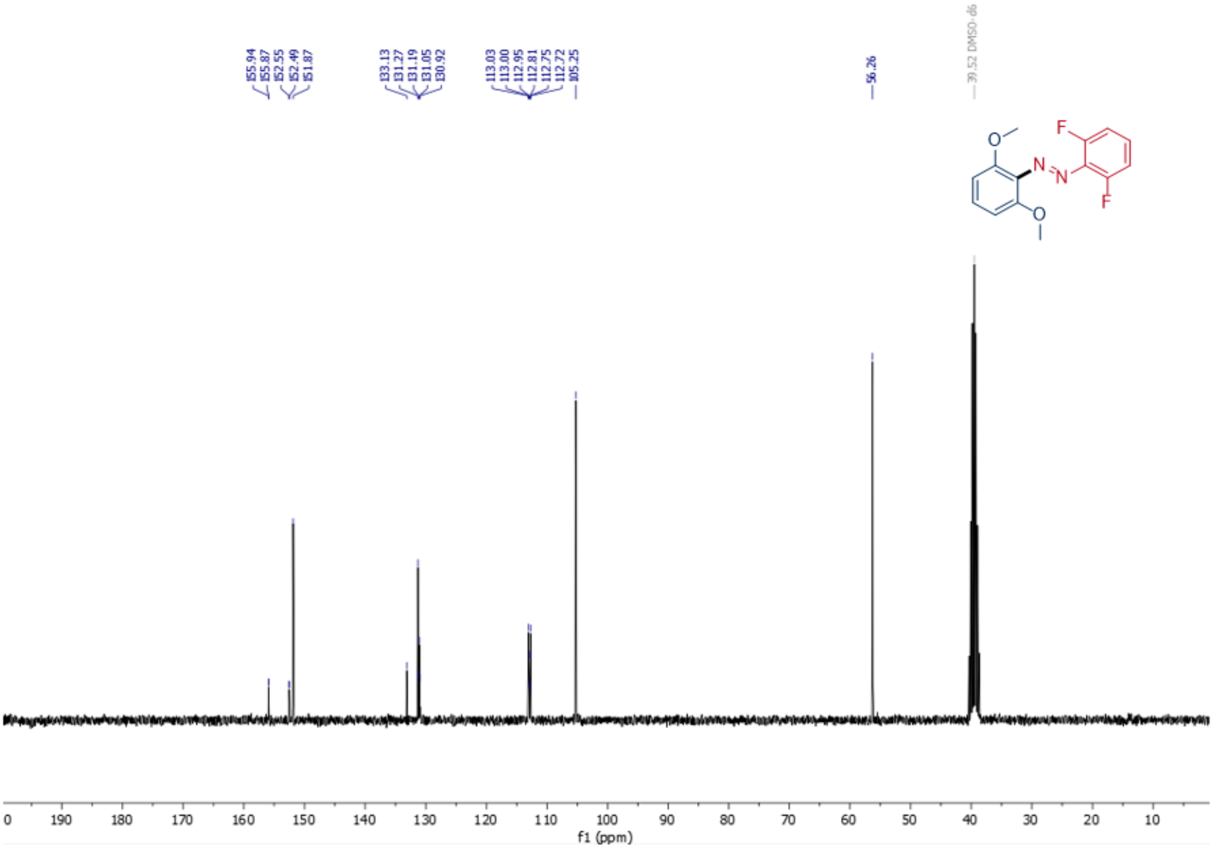
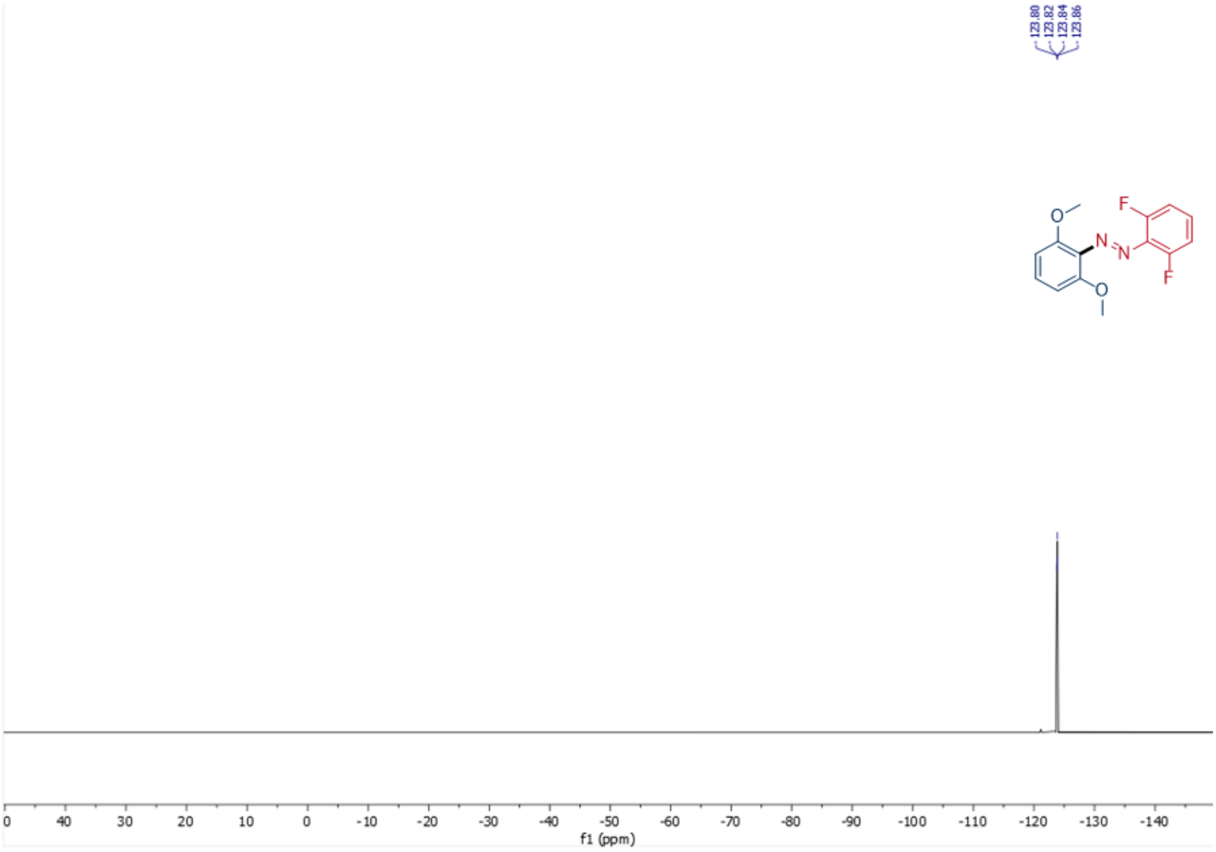
f1 (ppm)

1H, 13C, 19F NMR of 5a:



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-40
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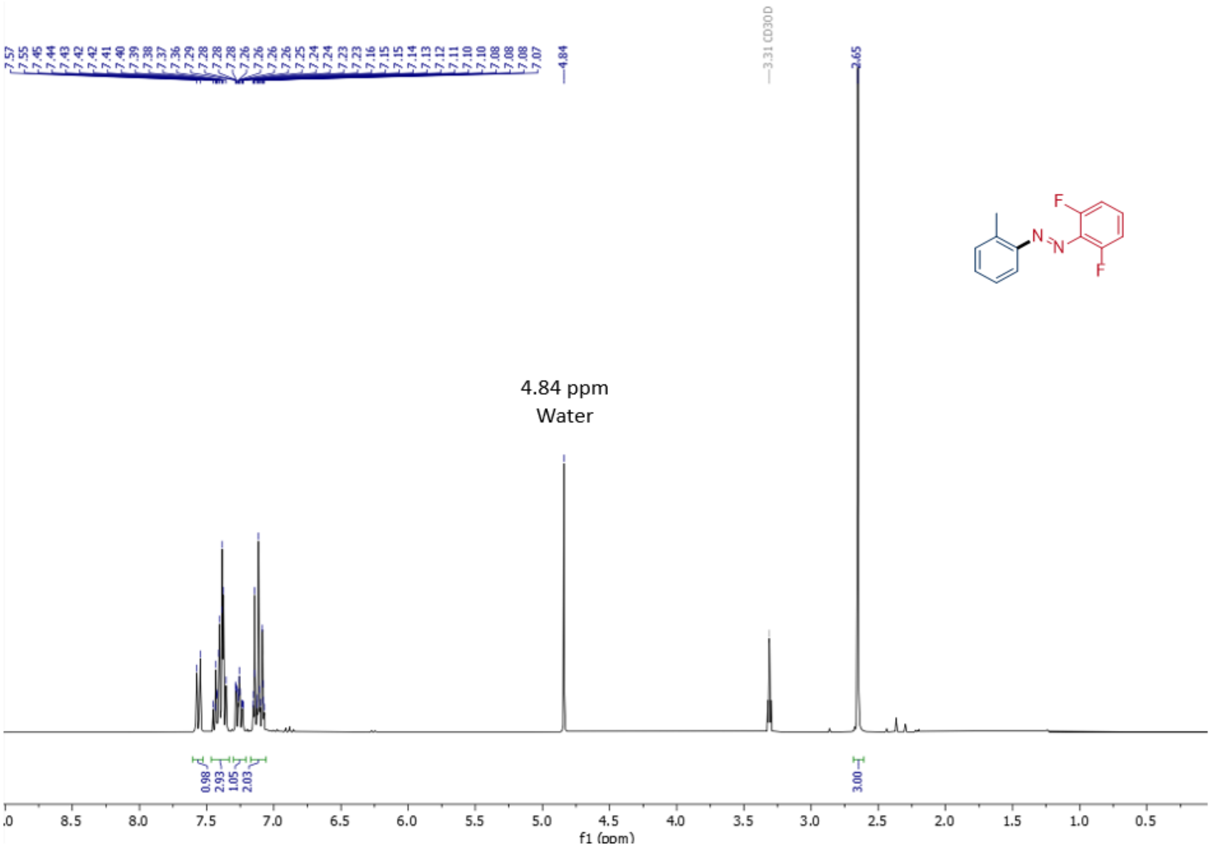
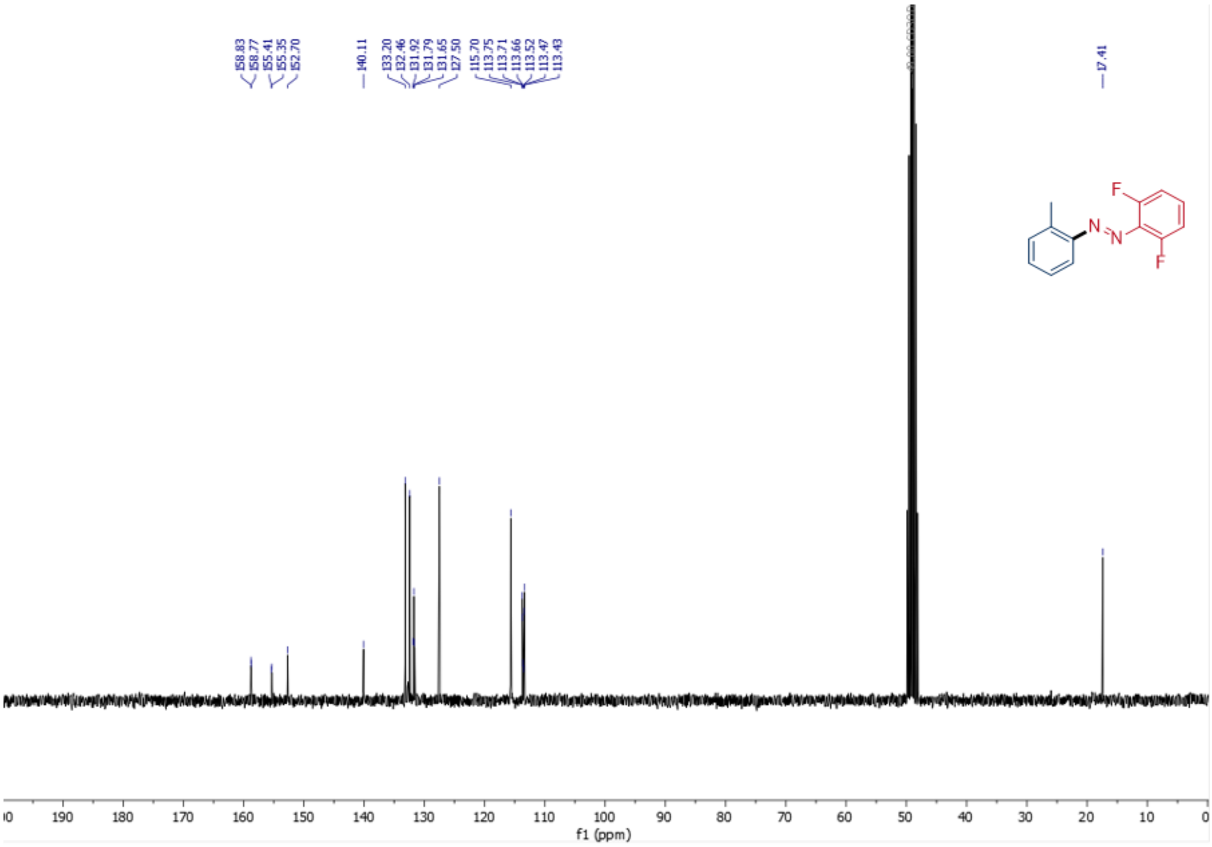
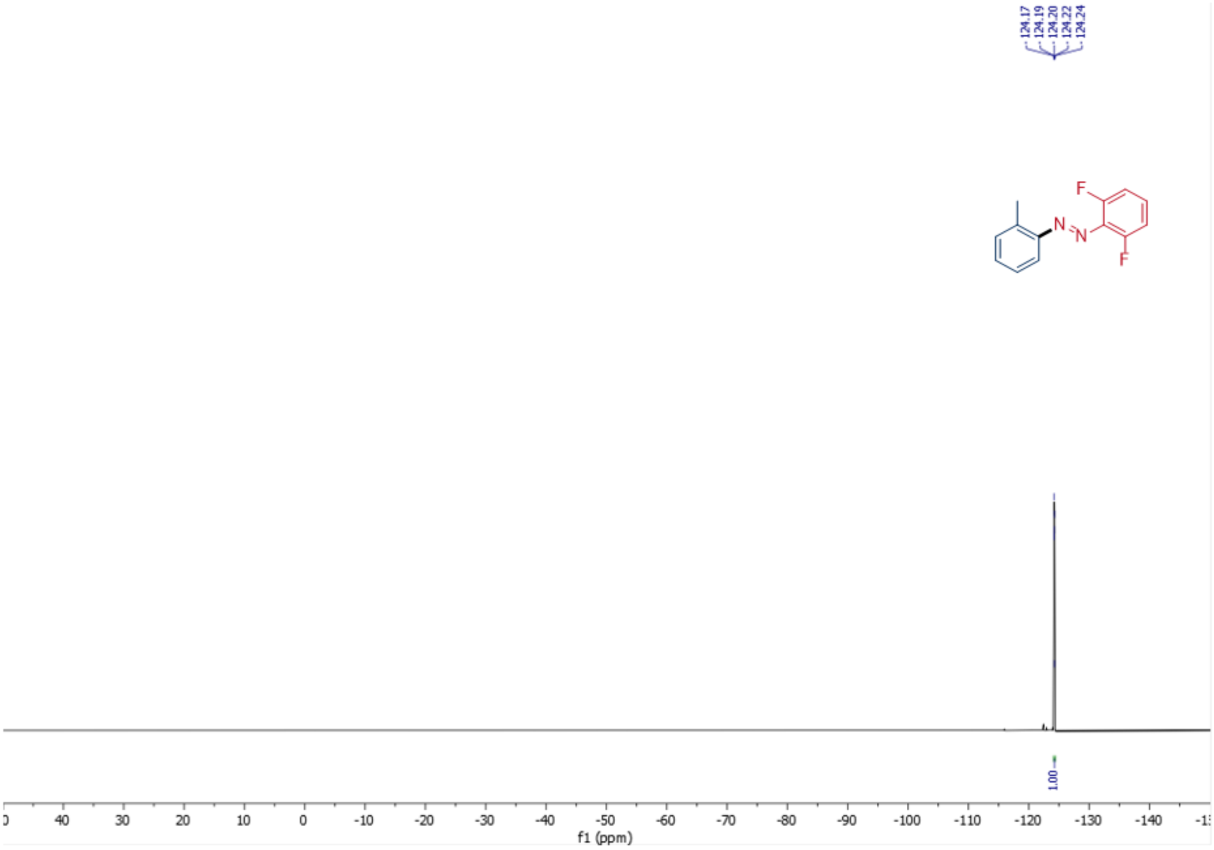
f1 (ppm)

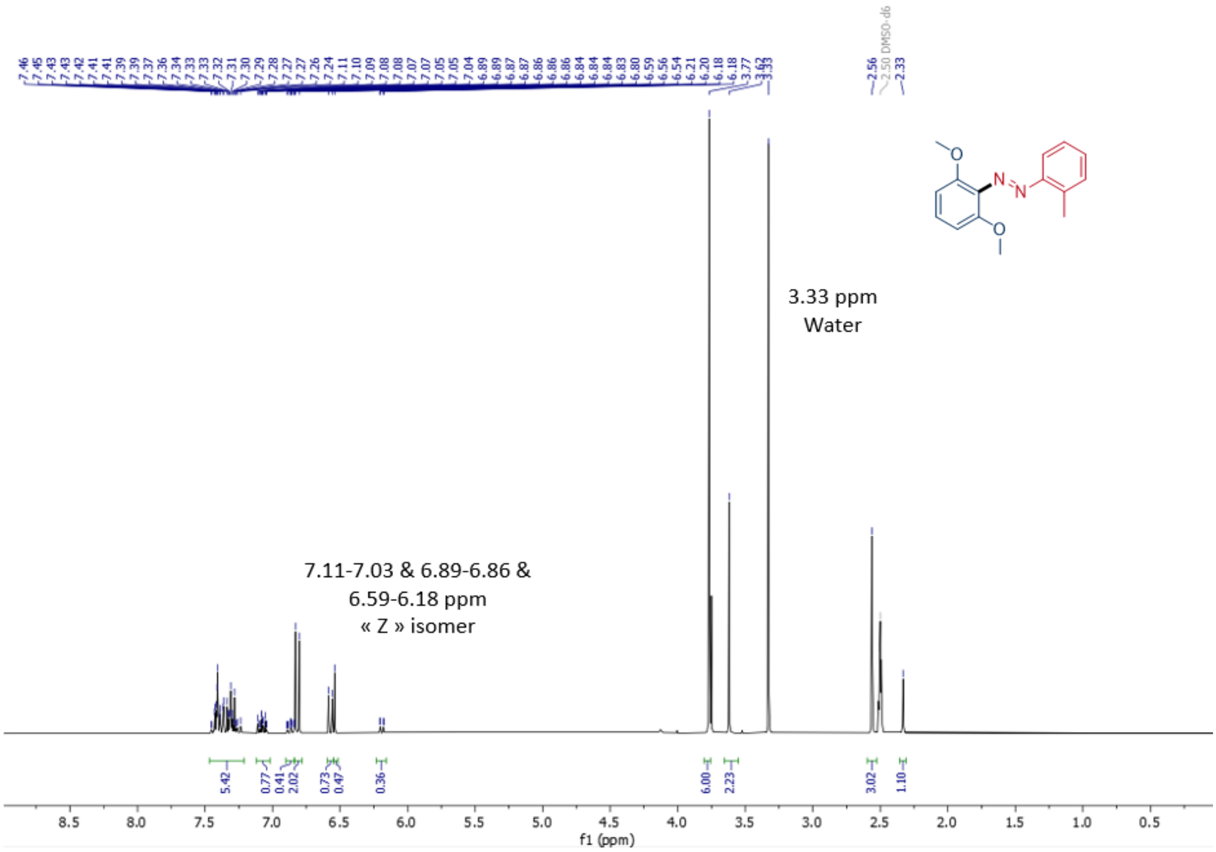
1H, 13C, 19F NMR of 5b:

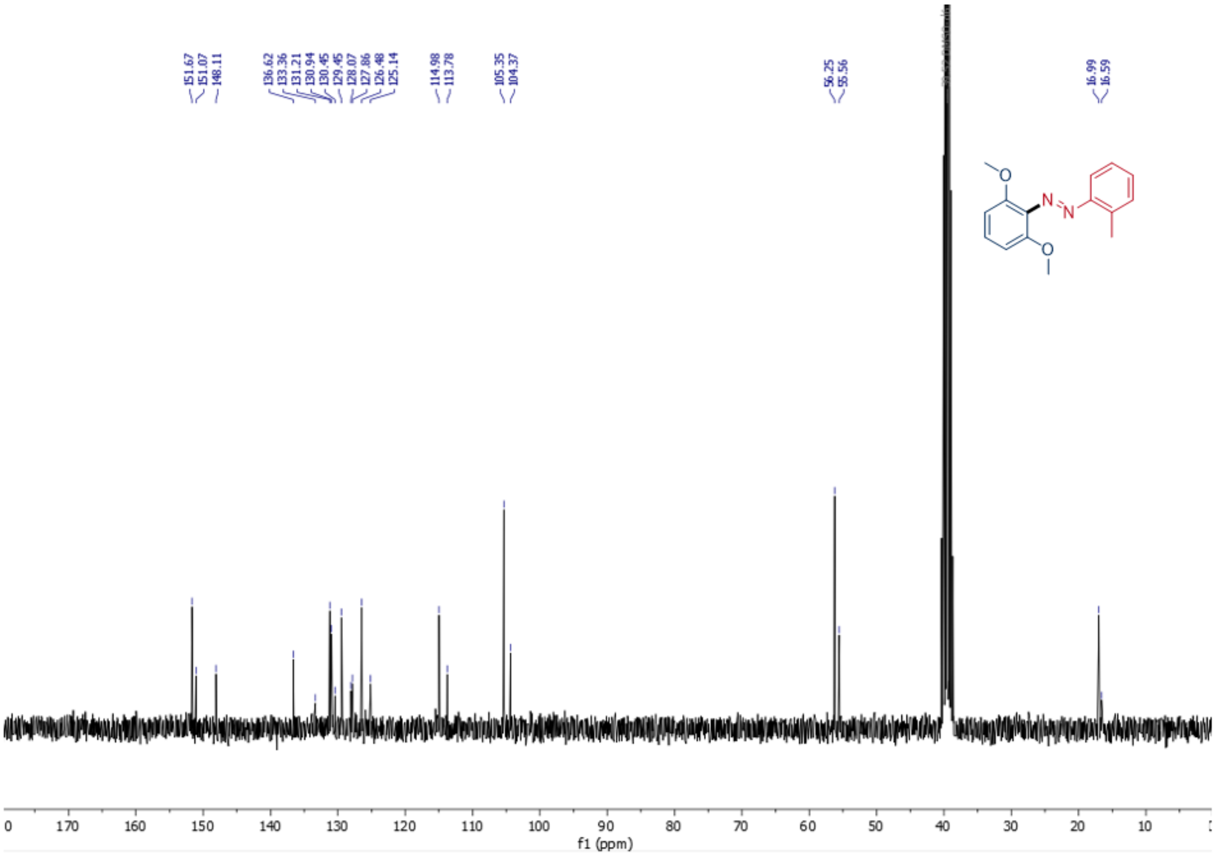




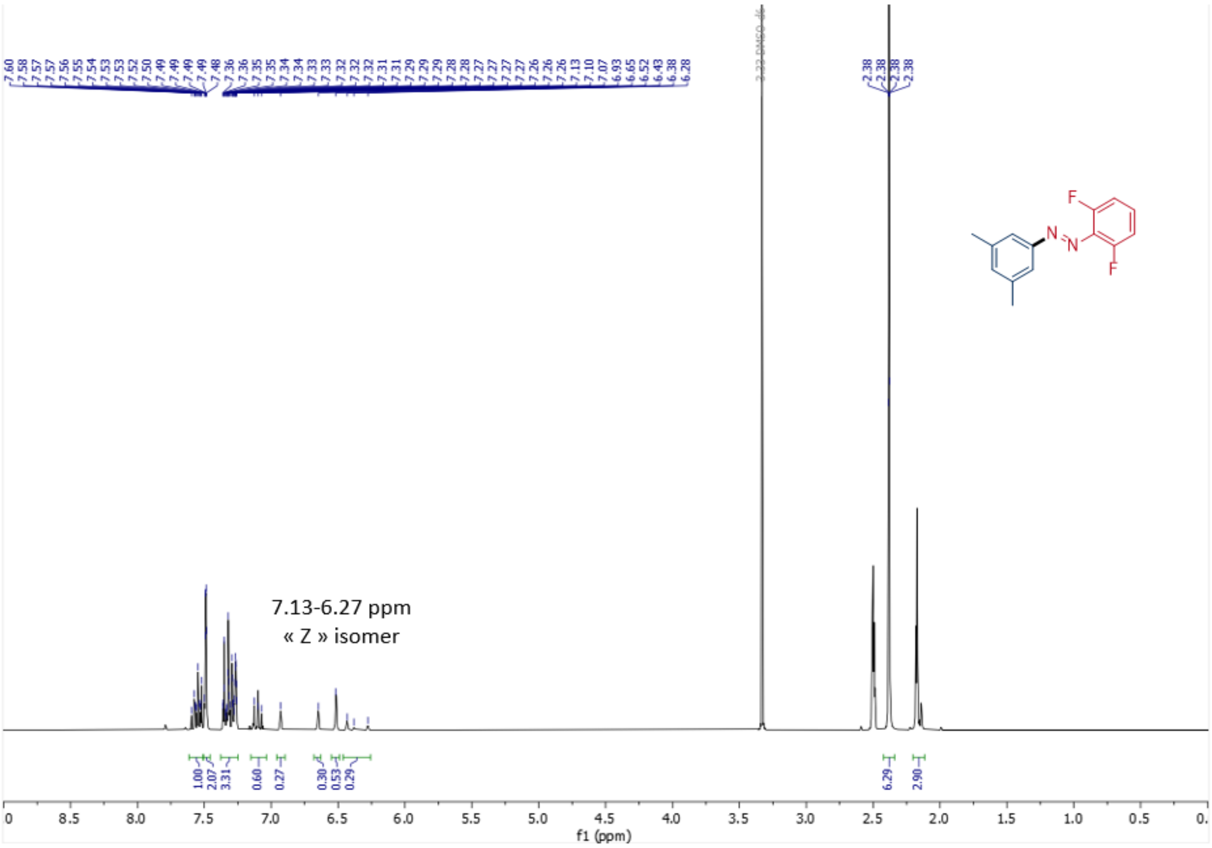

124.17
124.19
124.20
124.22
124.24
F
N
N
F
1.00
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
f1 (ppm)

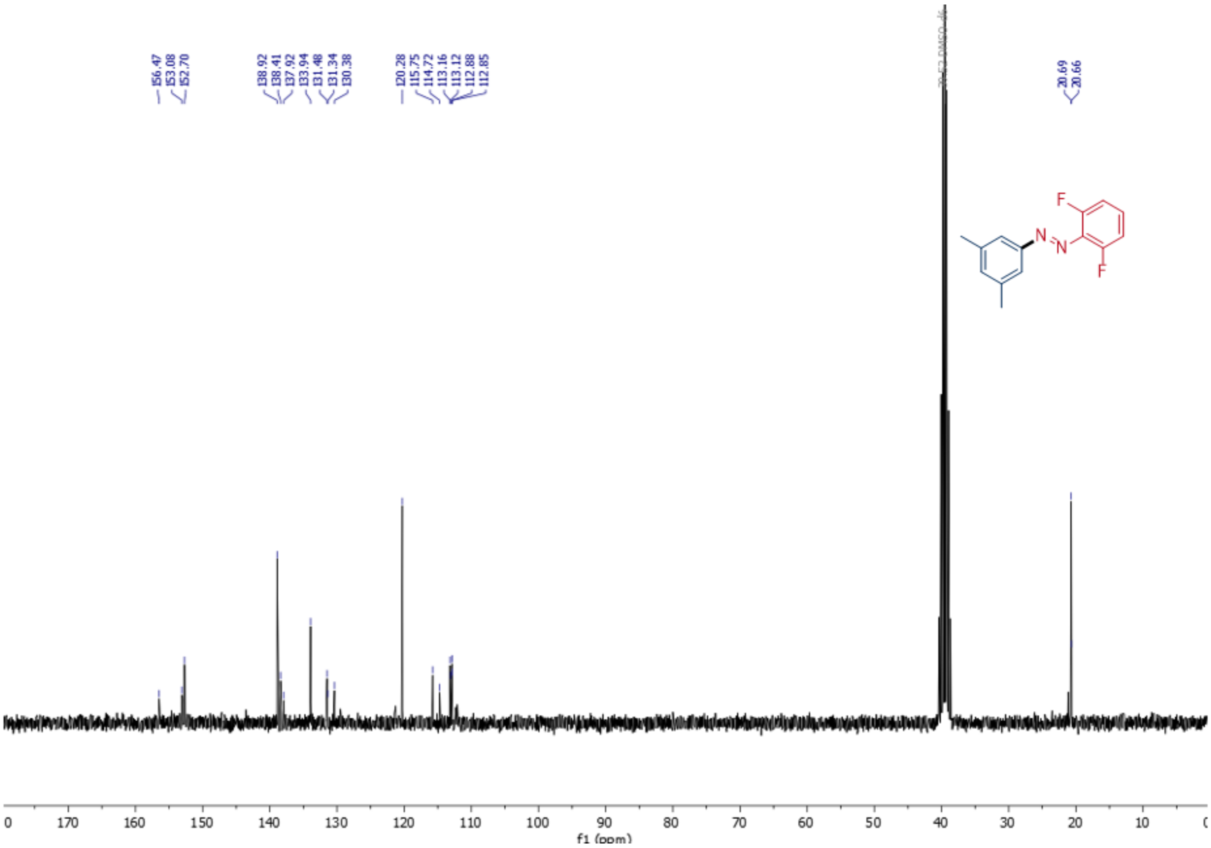
1H, 13C NMR of 5c:

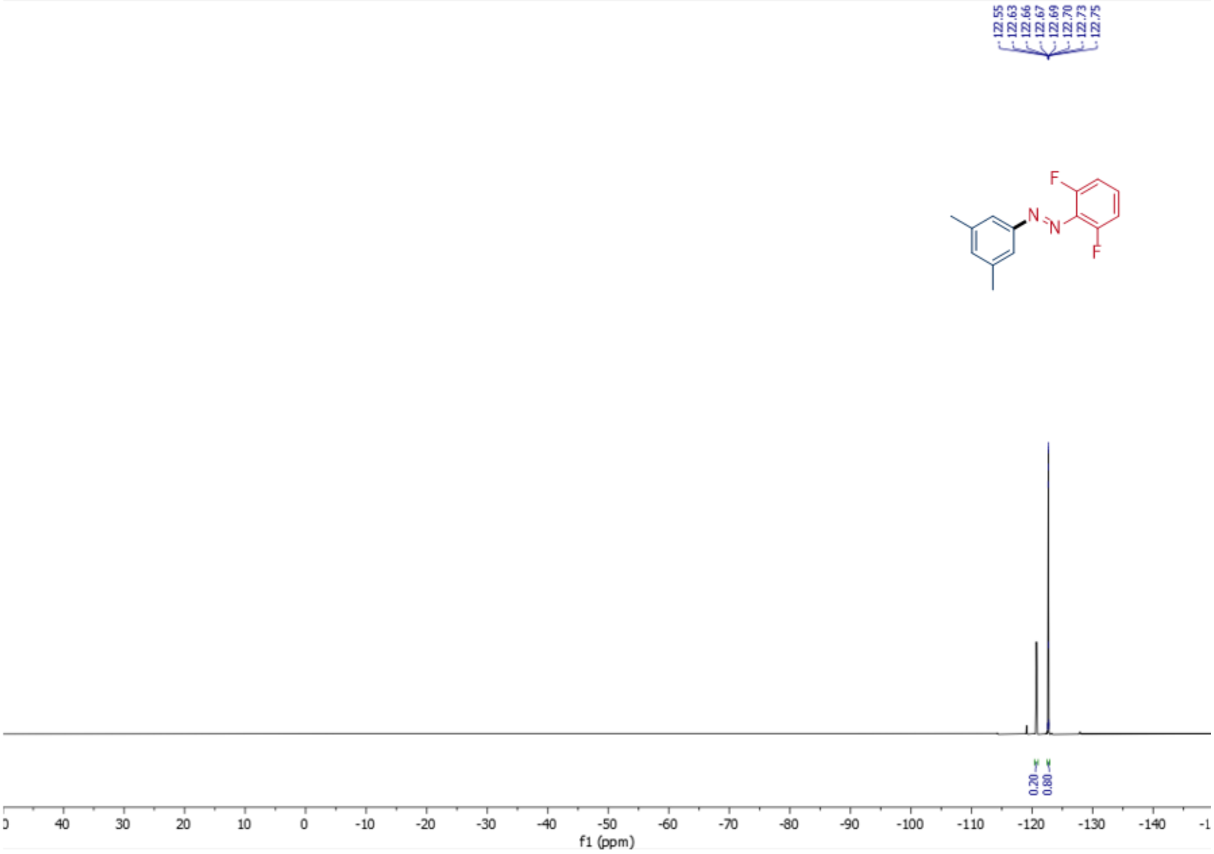




1H, 13C, 19F NMR of 5d:






122.55
122.63
122.66
122.67
122.69
122.70
122.73
122.75
F
N
N
F
0.20
0.80
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-1
f1 (ppm)