Azo Synthesis meets Molecular Iodine Catalysis

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SUPPORTING INFORMATION

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General Experimental Methods

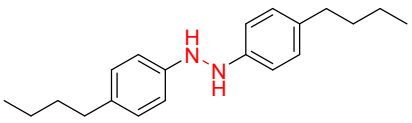
All chemicals were used as received unless otherwise stated. Syringes were used in all protocols requiring the transfer of a liquid reactant or solvent. All solvents were dried by distillation under nitrogen atmosphere prior to use. All reactions were conducted in oven-dried round-bottom flasks and were monitored by thin-layer chromatography (TLC) using TLC silica gel 60 F254, EMD Merck. Column chromatography was performed on silica gel 60 (70-260 mesh). Yields are reported as isolated yields considered to be ≥98% pure by ^{1}H NMR. All compounds were characterized by ^{1}H and ^{13}C NMR spectra obtained with a Bruker DPX-300 spectrometer (^{1}H 300 MHz, ^{13}C 75.5 MHz) in $CDCl_3$. The chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane (δ = 0 ppm) in $CDCl_3$ as an internal standard. Mass spectra was recorded using chemical ionization (CI).

General Procedure A: Aniline Coupling Reaction

To a solution of CuBr (0.04 mmol) and aniline (1 mmol) in toluene (10 mL) was added pyridine (0.08 mmol) under air (1 atm). The reaction mixture was vigorously stirred at 60 °C for 20 h. The reaction was then cooled to room temperature and concentrated under reduced pressure rotary evaporation. The resulting residue was purified by flash chromatography on silica gel (Hexane: EtOAc) to afford the corresponded azo derivative. The overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.[1]

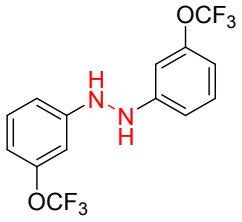
General Procedure B: Arylhydrazine Preparation

To a solution of azo compound (1 mmol) and activated Pd/C (5 mol%) in ethyl acetate (15 mL) was added pyridine (10 mol%).The reaction mixture was degassed three times using N_2 (g) and three times with H_2 (g) (1 atm) and vigorously stirred for 1-2 h at room temperature under H_2 (g). The reaction was completed after the solution turned colorless and no starting azo compound was visible by TLC. The reaction mixture was filtered, and the solvent removed under vacuum to afford a quantitative yield of pure arylhydrazine.[2] The overall spectroscopic data were in complete agreement with assigned structures and consistent with literature.[3-4]



1,2-bis(4-butylphenyl)hydrazine (1d) Synthesized according to known general procedures A using 4-butylaniline (149.2 mg, 1 mmol) to afford (*E*)-1,2-bis(4-butylphenyl)diazene **2d** (241.4 mg, 0.82 mmol). **2d** (294.4 mg, 1 mmol) was then used in known general procedure B to afford **1a** (266.8 mg, 0.9 mmol) as a yellow liquid; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.06 (d, *J* = 8.1 Hz, 4H), 6.69 (d, *J* = 8.4 Hz, 4H), 3.58 (br, 2H), 2.60 (t, *J* = 7.5 Hz, 4H),1.60-1.70 (m, 4H), 1.38-1.50

(m, J = 2.8 Hz, 4H), 1.04 (t, J = 7.2 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ = 144.1, 133.0, 129.2, 115.3, 34.8, 34.1, 22.4, 14.1; m/z calcd for $C_{20}H_{28}N_2$ (M+): 296.2252, found: 296.2173.

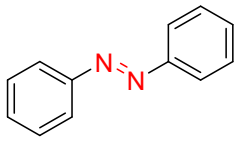


1,2-bis(3-(trifluoromethoxy)phenyl)hydrazine (1t)

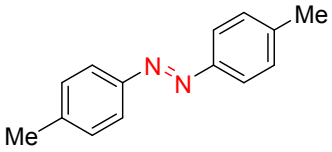
Synthesized according to known general procedures A using 3-(trimethoxy)aniline (177.0 mg, 1 mmol) to afford (*E*)-1,2-bis(3-(trifluoromethoxy)phenyl)diazene **2t** (213.5mg, 0.61 mmol). **2t** (350.0 mg, 1 mmol) was then used in known general procedure B to afford **1t** (316.8 mg, 0.9 mmol) as a dark yellow liquid; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.27 (dd, J = 1.8, 7.8 Hz, 2H), 6.79 (dd, J = 1.8, 6.3 Hz, 6H), 5.75 (s, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ = 150.58, 149.95, 112.06, 110.46, 104.90; m/z calcd for $C_{14}H_{10}F_6N_2O_2$ (M+): 352.0646, found: 352.0640.

General Procedure C: Iodine-Catalyzed Oxidation of Arylhydrazine Derivatives

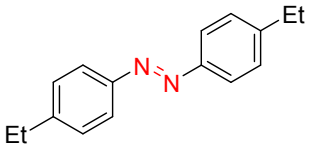
A mixture of diphenylhydrazine derivate (1 mmol) with iodine (2 mol%) in a flame dried flask covered in foil was dissolved in distilled DCM (5 mL), and allowed to stir vigorously under dry air (1 atm) and at room temperature for 20 min. the solvent was removed under vacuum to afford the pure corresponding azo compound. Products **2i**, **2q**, and **2t** were purified by flash chromatography on silica gel using a solvent system of Hexane:EtOAc (100:1). The overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.



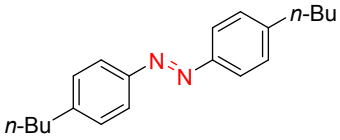
1,2-diphenyldiazene (2a) Synthesized according to general procedure C starting from **1a** (184.2 mg, 1 mmol) to obtain an orange solid (178.5 mg, 0.98 mmol); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.00-8.03 (m, 4H), 7.55-7.59 (m, 6H).[1]



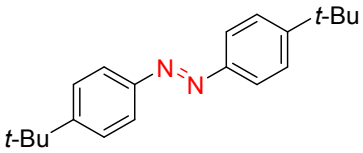
1,2-di-*p*-tolyldiazene (2b) Synthesized according to general procedure C starting from **1b** (212.3 mg, 1 mmol) to obtain a light orange solid (206.06 mg, 0.98 mmol); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.84 (d, *J* = 8.4 Hz, 4H), 7.28-7.35 (m, 4H), 2.46 (s, 6H).[1]



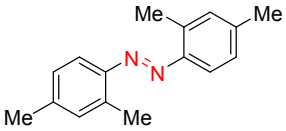
1,2-bis(4-ethylphenyl)diazene (2c) Synthesized according to general procedure C starting from **1c** (240.3 mg, 1 mmol) to obtain light yellow solid (233.6 mg, 0.98 mmol); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.92 (d, *J* = 8.4 Hz, 4H), 7.39 (d, *J* = 8.1 Hz, 4H), 2.78 (q, *J* = 7.5, 7.5 Hz, 4H), 1.35 (t, *J* = 7.5, 6H).[5]



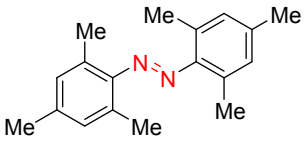
1,2-bis(4-butylphenyl)diazene (2d) Synthesized according to general procedure C starting from **1d** (296.4 mg, 1 mmol) to obtain a dark red liquid (285.6 mg, 0.97 mmol); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.97 (d, *J* = 8.1 Hz, 4H), 7.41 (d, *J* = 8.1 Hz, 4H), 2.78 (t, *J* = 7.5 Hz, 4H), 1.70-1.80 (m, 4H), 1.43-1.55 (m, 4H), 1.06 (t, *J* = 7.5 Hz, 6H).[6]



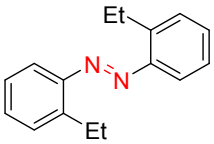
1,2-bis(4-(*tert*-butyl)phenyl)diazene (2e) Synthesized according to general procedure C starting from **1e** (296.4 mg, 1 mmol) to obtain an orange solid (276.8, 0.96 mmol); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.89 (d, *J* = 8.7 Hz, 4H), 7.56 (d, *J* = 8.7 Hz, 4H), 1.42 (s, 18H).[7]



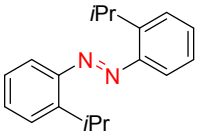
1,2-bis(2,4-dimethylphenyl)diazene (2f) Synthesized according to general procedure C starting from **1f** (240.3 mg, 1 mmol) to obtain a dark orange solid (233.6 mg, 0.98 mmol); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.60 (d, *J* = 8.4 Hz, 2H), 7.28 (s, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 2.75 (s, 6H), 2.43 (s, 6H).[8]



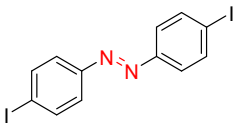
1,2-dimesityldiazene (2g) Synthesized according to general procedure C starting from **1g** (268.4 mg, 1 mmol) to obtain an orange solid (253.1 mg, 0.95 mmol); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.07 (s, 4H), 2.54 (s, 12H), 2.44 (s, 6H).[12]



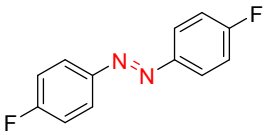
1,2-bis(2-ethylphenyl)diazene (2h) Synthesized according to general procedure C starting from **1h** (240.3 mg, 1 mmol) to obtain a light orange solid (219.3 mg, 0.92 mmol); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.76 (d, *J* = 7.8 Hz, 2H), 7.47-7.49 (m, 4H), 7.35-7.41 (m, 2H), 3.31 (q, *J* = 7.5, 7.5 Hz, 4H), 1.44 (t, *J* = 7.5 Hz, 6H).[9]



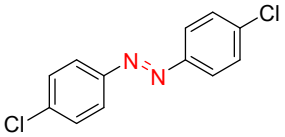
1,2-bis(2-isopropylphenyl)diazene (2i) Synthesized according to general procedure C starting from **1a** (268.4 mg, 1 mmol) to obtain a dark orange solid (218.4 mg, 0.82 mmol); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.83 (d, *J* = 7.8 Hz, 2H), 7.56-7.65 (m, 4H), 7.41-7.45 (m, 2H), 4.37-4.44 (m, 2H), 1.56 (dd, *J* = 5.1, 1.8 Hz, 12H).[10]



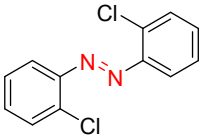
1,2-bis(4-iodophenyl)diazene (2j) Synthesized according to general procedure C starting from **1j** (436.0 mg, 1 mmol) to obtain a dark orange solid (416.6 mg, 0.96 mmol); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.88 (d, J = 8.7 Hz, 4H), 7.51 (d, J = 8.4 Hz, 4H).[1]



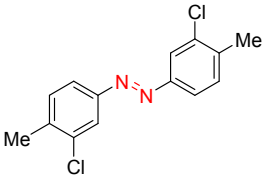
1,2-bis(4-fluorophenyl)diazene (2k) Synthesized according to general procedure C starting from **1k** (220.2 mg, 1 mmol) to obtain an orange solid (211.6 mg, 0.97 mmol); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.92-7.97 (m, 4H), 7.19-7.28 (m, 4H).[1]



1,2-bis(4-chlorophenyl)diazene (2l) Synthesized according to general procedure C starting from **1l** (253.1 mg, 1 mmol) to obtain a light orange solid (233.5 mg, 0.93 mmol); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.88 (d, J = 8.7 Hz, 4H), 7.50 (d, J = 8.7 Hz, 4H).[1]

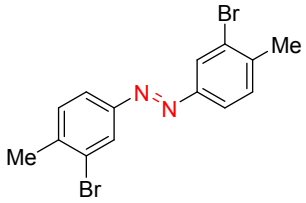


1,2-bis(2-chlorophenyl)diazene (2m) Synthesized according to general procedure C starting from **1m** (253.1 mg, 1 mmol) to obtain an orange solid (238.5 mg, 0.95 mmol); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.80 (dd, J = 6.0, 1.8 Hz, 2H), 7.59 (dd, J = 6.3, 1.5 Hz, 2H), 7.35-7.47 (m, 4H).[13]

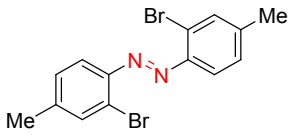


1,2-bis(3-chloro-4-methylphenyl)diazene (2n) Synthesized according to general procedure C starting from **1o** (281.2 mg, 1 mmol) to obtain an orange solid (265.2 mg, 0.95 mmol); ^{1}H NMR

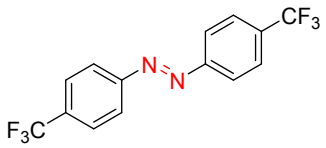
($CDCl_3$, 300 MHz): δ 7.91 (d, *J* = 1.8 Hz, 2H), 7.74 (dd, *J* = 6.3, 1.8 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H).[11]



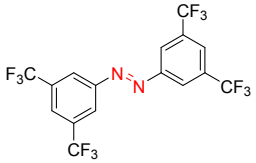
1,2-bis(3-bromo-4-methylphenyl)diazene (2o) Synthesized according to general procedure C starting from **1p** (370.1 mg, 1 mmol) to obtain an orange solid (342.3 mg, 0.93 mmol); ^1H NMR ($CDCl_3$, 300 MHz): δ 8.09 (d, *J* = 1.5 Hz, 2H), 7.78 (dd, *J* = 6.6, 1.5 Hz, 2H), 7.28-7.40 (m, 2H), 2.49 (s, 6H).[11]



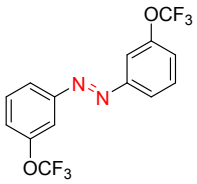
1,2-bis(2-bromo-4-methylphenyl)diazene (2p) Synthesized according to general procedure C starting from **1q** (370.1 mg, 1 mmol) to obtain a dark orange solid (287.1 mg, 0.78 mmol); ^1H NMR ($CDCl_3$, 300 MHz): δ 7.71 (d, *J* = 8.1 Hz, 2H), 7.59 (s, 2H), 7.21 (dd, *J* = 7.2, 0.9 Hz, 2H), 2.43 (s, 6H).[12]



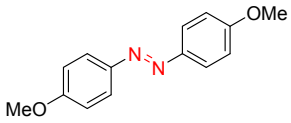
1,2-bis(4-(trifluoromethyl)phenyl)diazene (2q) Synthesized according to general procedure C starting from **1r** (320.2 mg, 1 mmol) to obtain a light orange solid (305.5 mg, 0.96 mmol); ^1H NMR ($CDCl_3$, 300 MHz): δ 8.05 (d, *J* = 8.4 Hz, 4H), 7.82 (d, *J* = 8.4 Hz, 4H).[11]



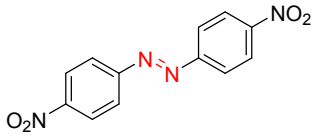
1,2-bis(3,5-bis(trifluoromethyl)phenyl)diazene (2r) Synthesized according to general procedure C starting from **1s** (456.2 mg, 1 mmol) to obtain a dark orange solid (404.2 mg, 0.89 mmol); ^1H NMR ($CDCl_3$, 300 MHz): δ 8.47 (s, 4H), 8.09 (s, 2H).[1]



(E)-1,2-bis(3-(trifluoromethoxy)phenyl)diazene (2s) Synthesized according to general procedure C starting from **1t** (350.2 mg, 1 mmol) to obtain a light orange solid (219.6 mg, 0.72 mmol); mp 38-41 ^{0}C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.91 (d, *J* = 7.8 Hz, 2H), 7.83 (s, 2H), 7.56 (t, *J* = 8.1 Hz, 2H), 7.37-7.40 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ = 153.3, 150.0, 149.9, 123.5, 122.6, 114.3; m/z calcd for $C_{20}H_{28}N_2$ (M+): 350.05, found: 350.486.

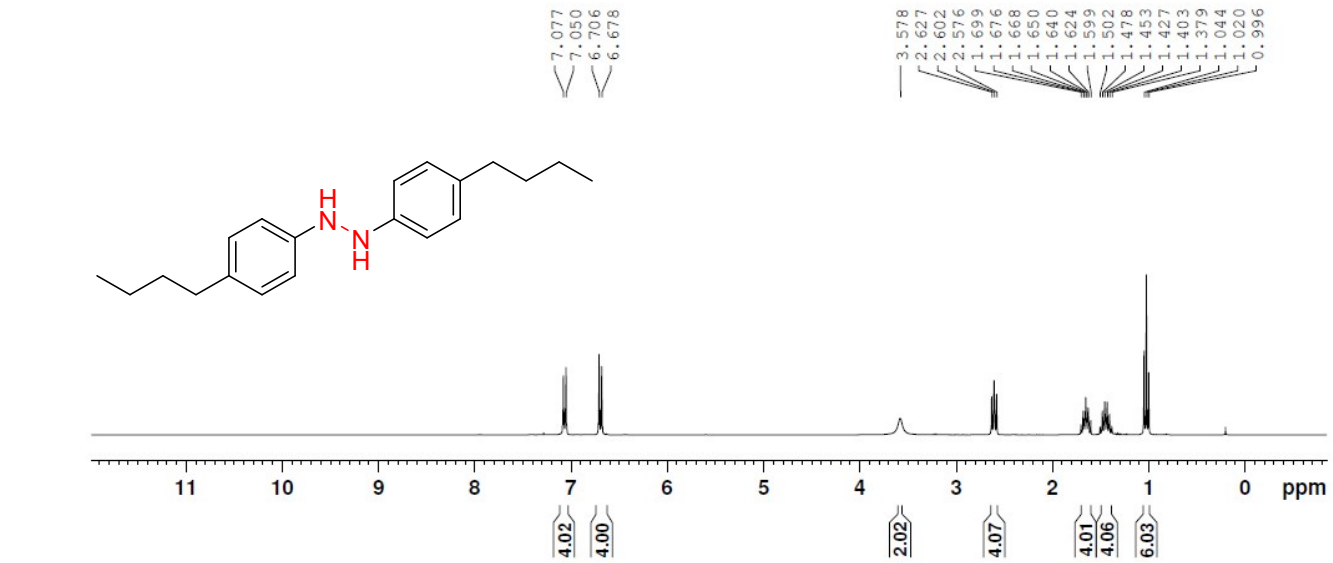


1,2-bis(4-methoxyphenyl)hydrazine (2t) Synthesized according to general procedure C starting from **1u** (244.1 mg, 1 mmol) to obtain a yellow solid (120.6 mg, 0.87 mmol); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.88-7.93 (m, 4H), 7.00-7.05 (m, 4H), 3.91 (s, 6H).[13]

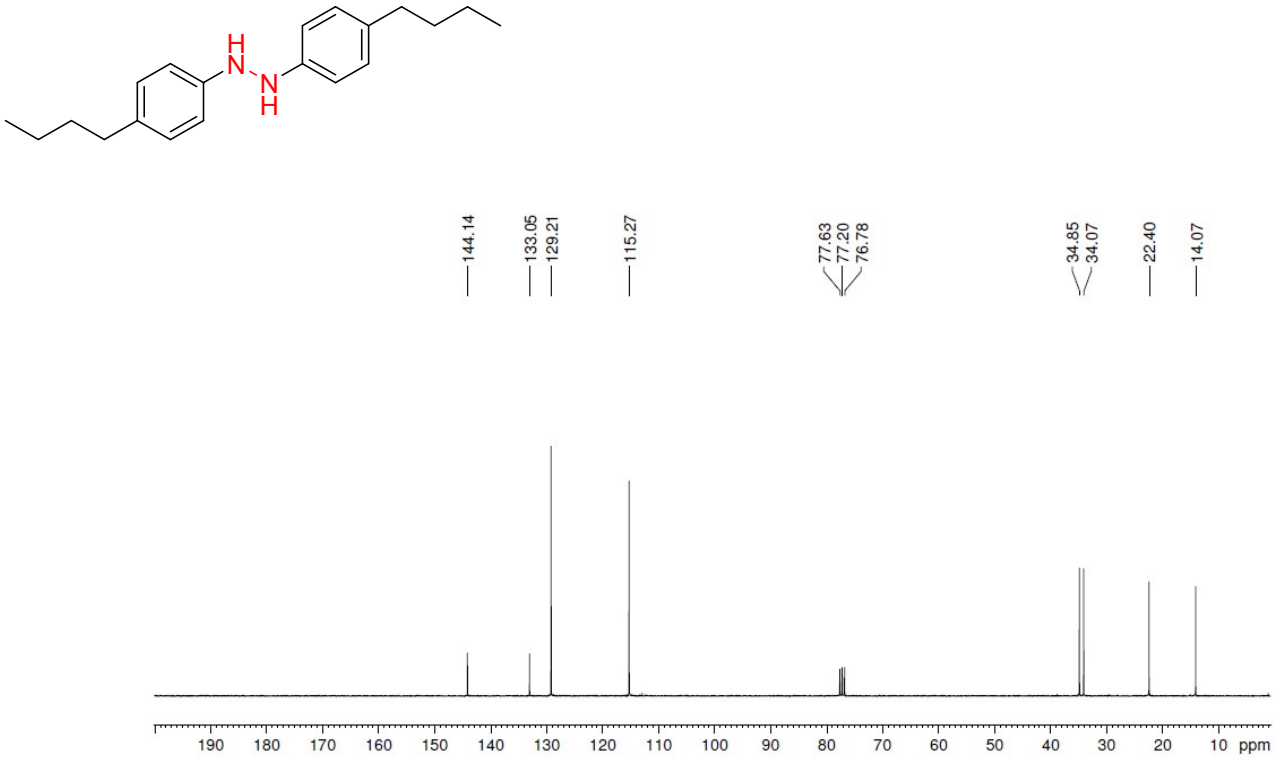


1,2-bis(4-nitrophenyl)diazene (2u) Synthesized according to general procedure C starting from **1v** (272.2 mg, 1 mmol) to obtain a light orange solid (266.8 mg, 0.98 mmol); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.02 (dd, *J* = 7.5, 1.2 Hz, 2H), 7.27-7.32 (m, 2H), 6.82 (dd, *J* = 7.5, 0.9 Hz, 2H), 6.59-6.65 (m, 2H).[1]

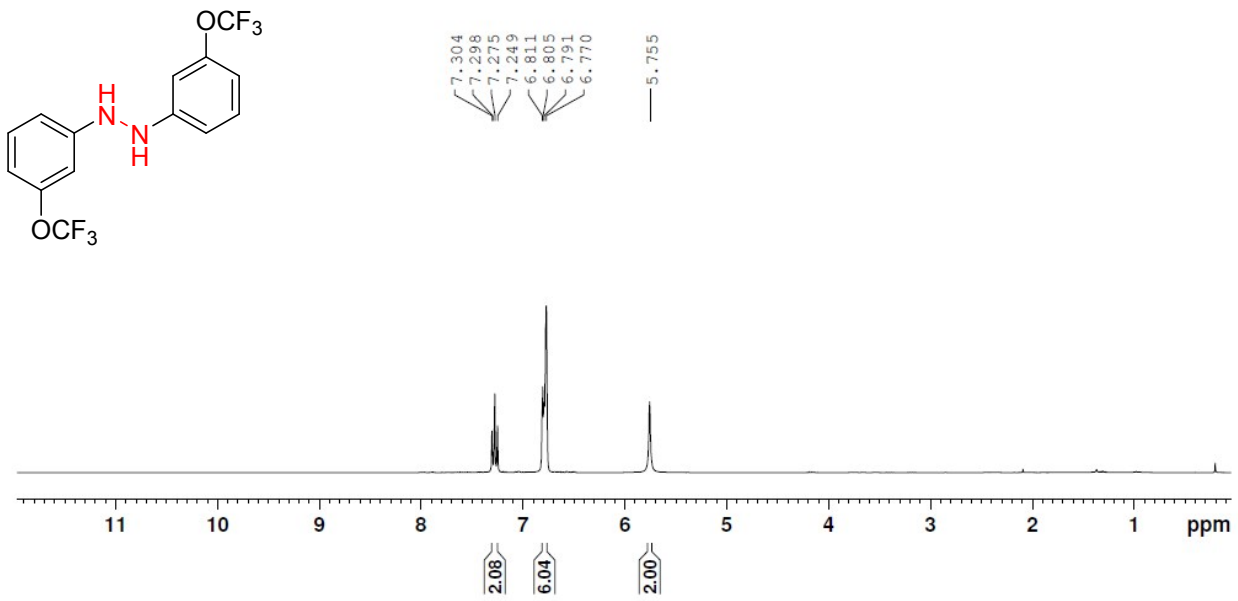
Spectra



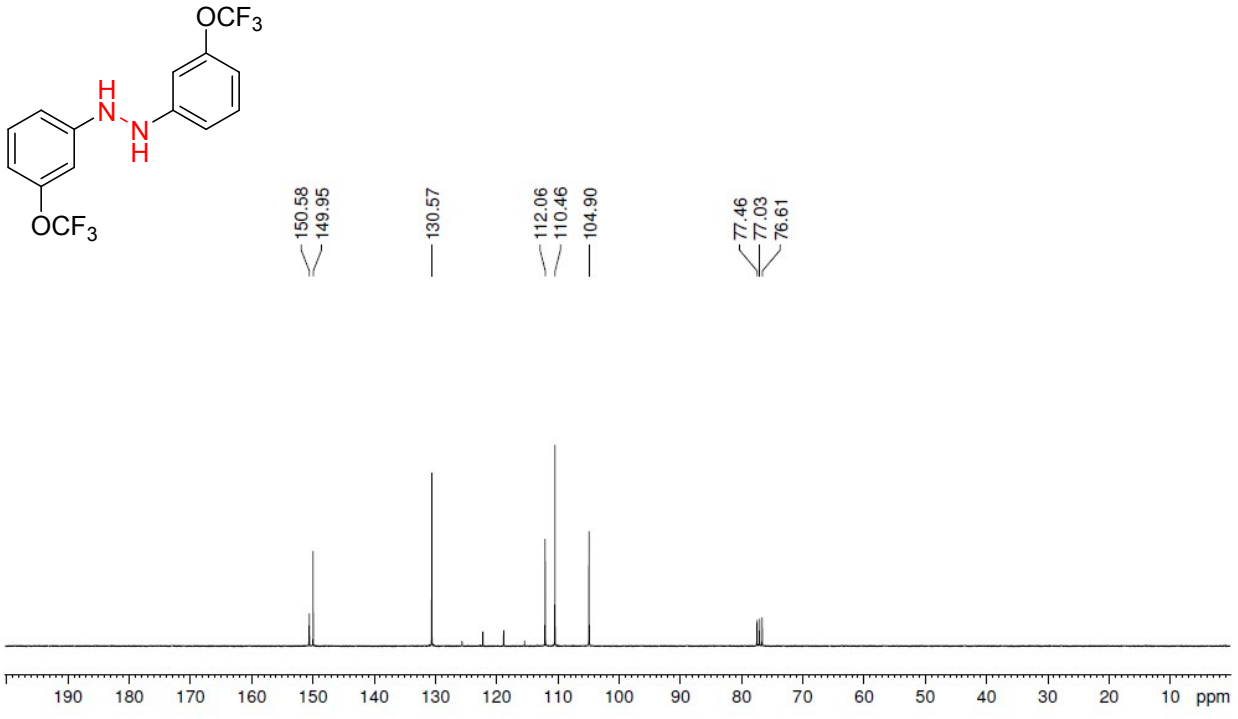
^{1}H NMR of compound 1d in $CDCl_3$



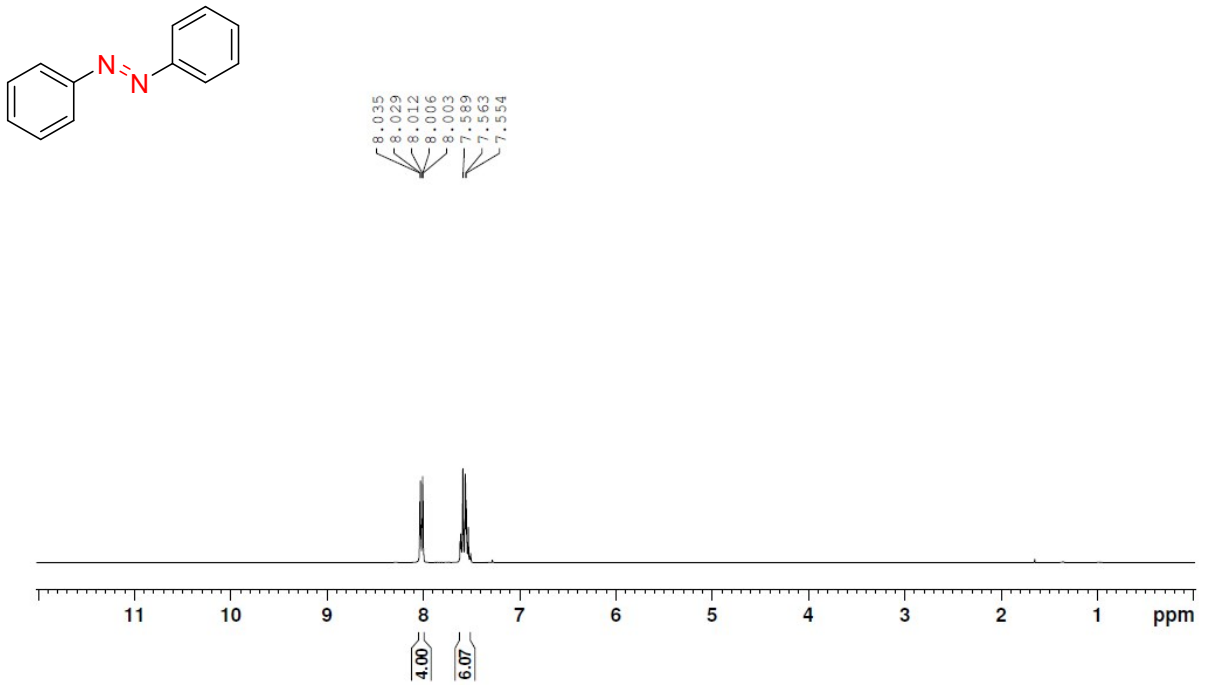
^{13}C NMR of compound 1d in $CDCl_3$



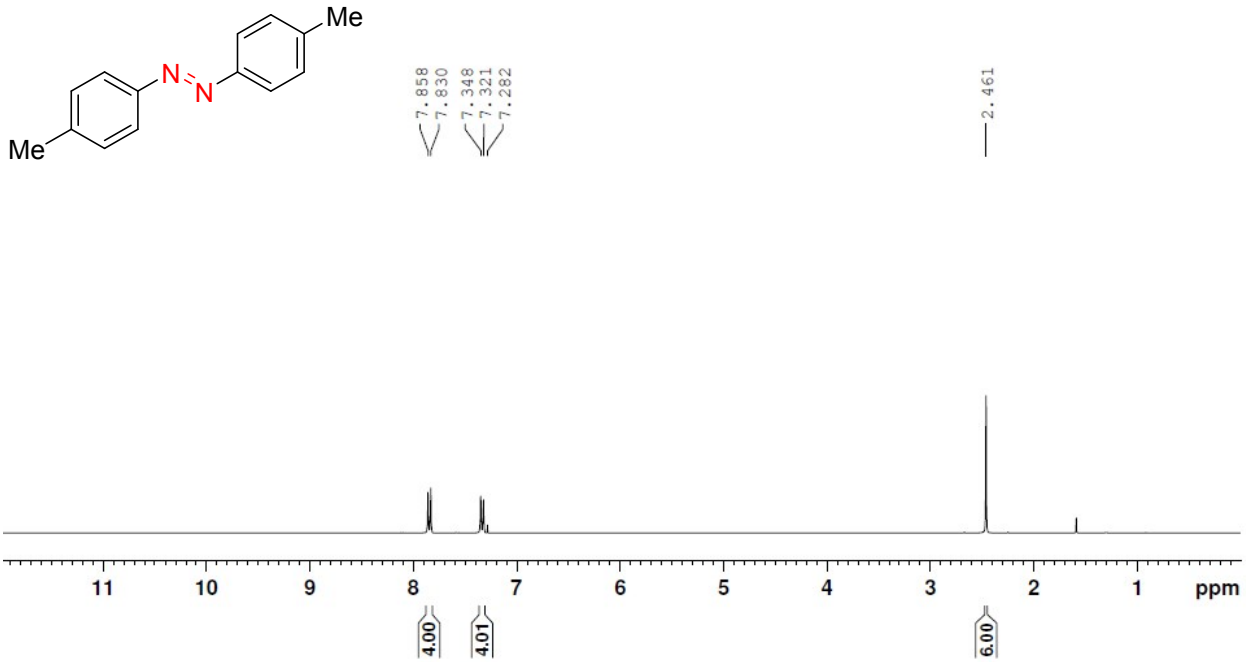
^{1}H NMR of compound 1t in $CDCl_3$



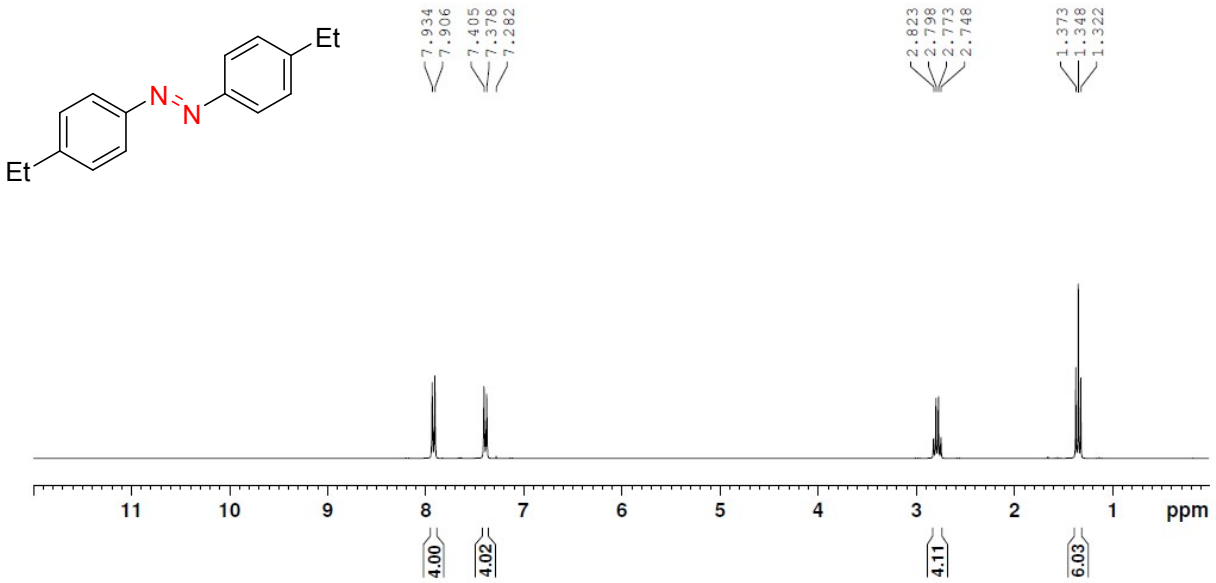
^{13}C NMR of compound 1t in $CDCl_3$



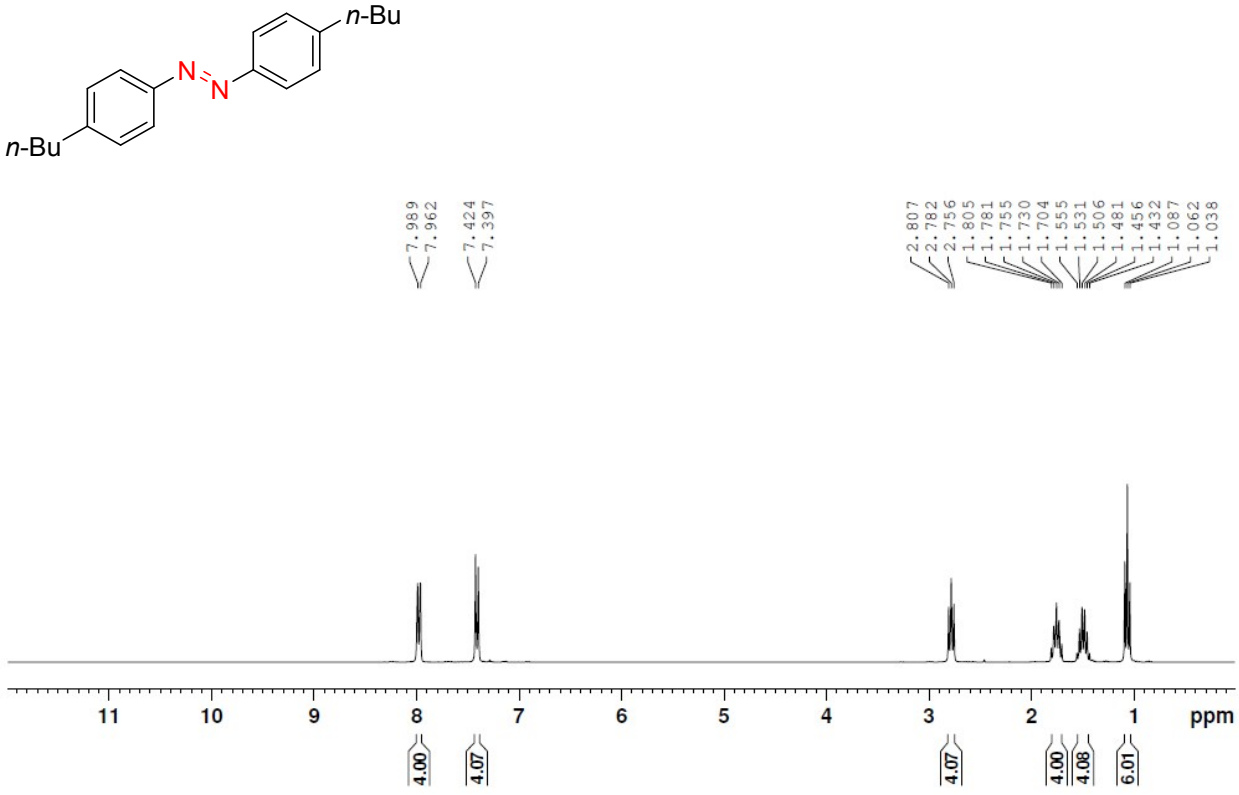
^{1}H NMR of compound 2a in $CDCl_3$



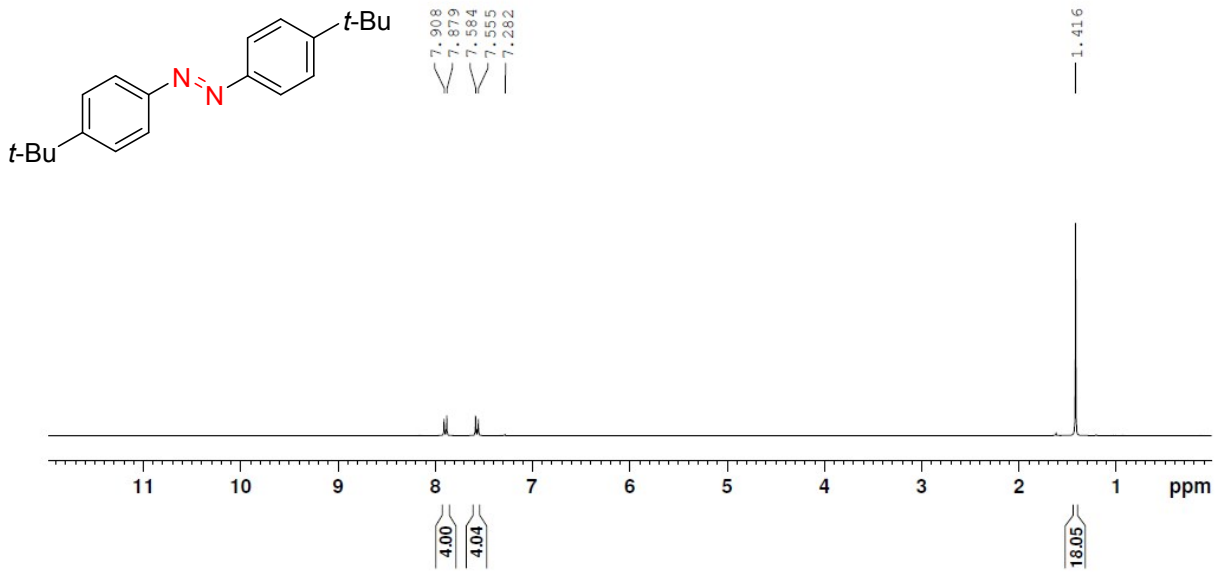
^{1}H NMR of compound 2b in $CDCl_3$



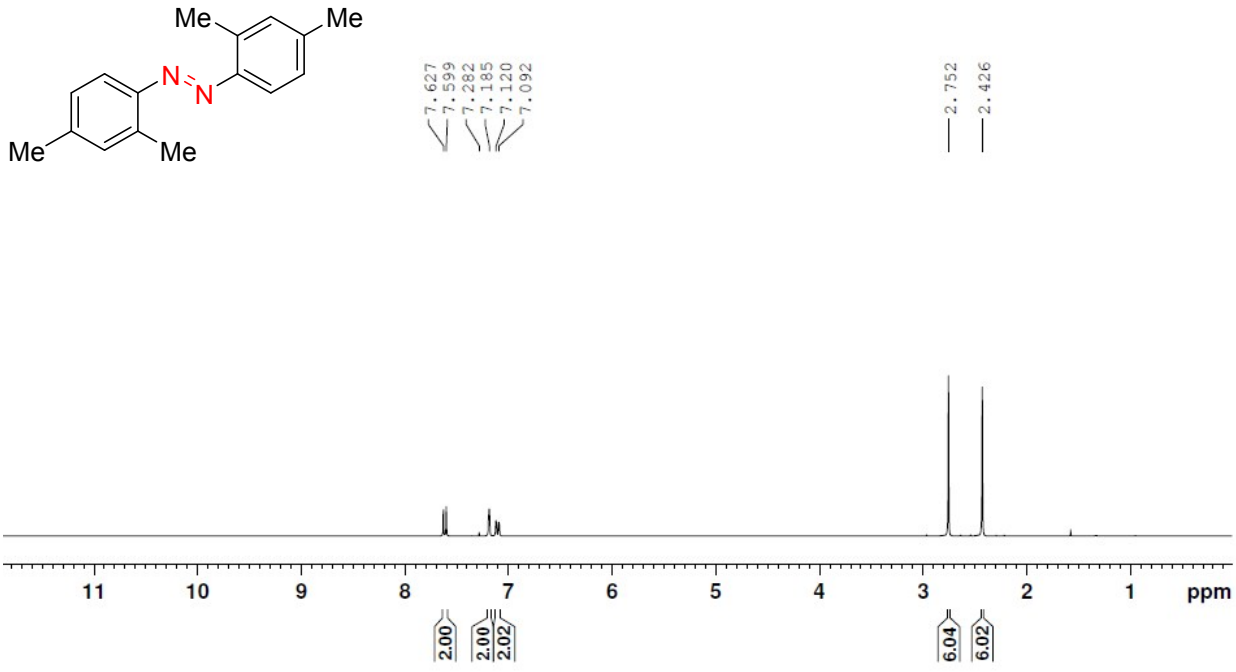
^{1}H NMR of compound 2c in $CDCl_3$



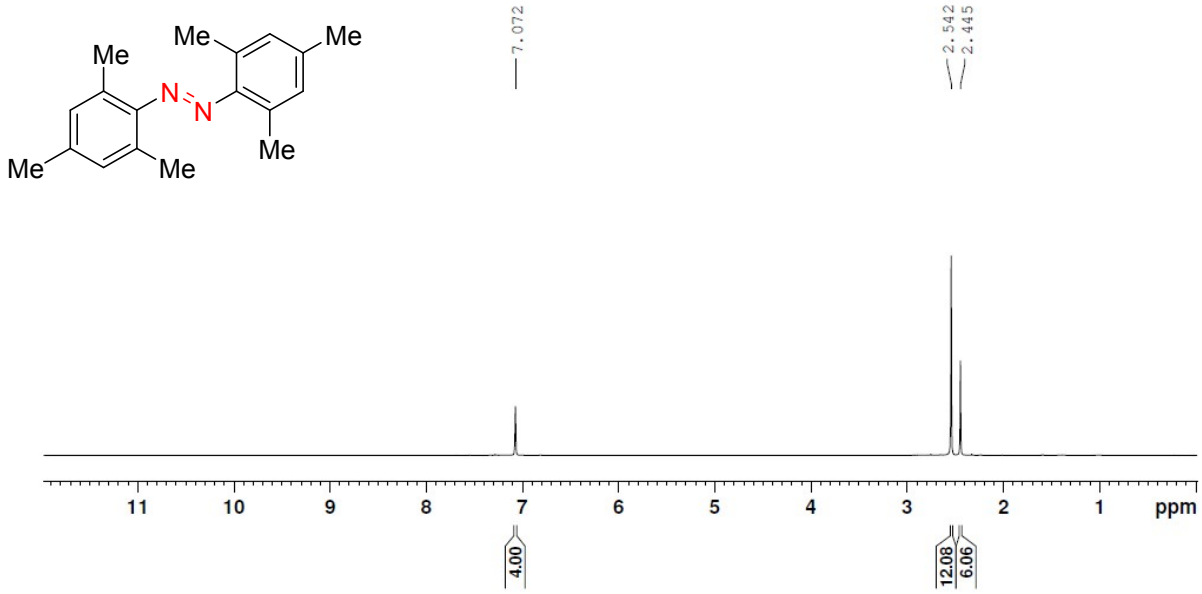
^{1}H NMR of compound 2d in $CDCl_3$



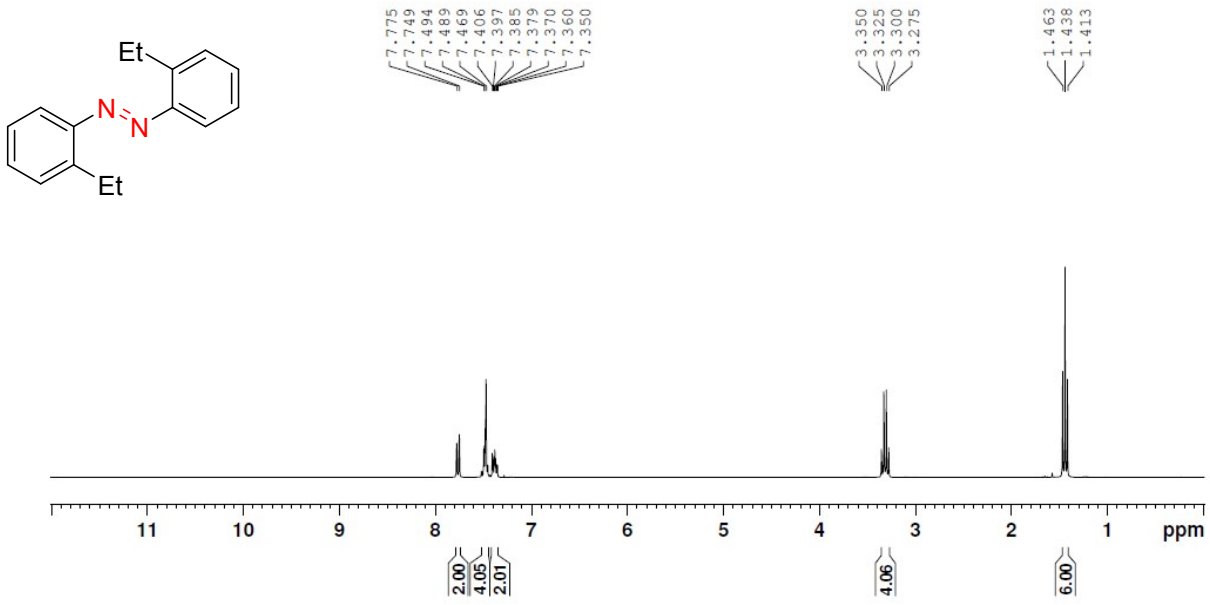
^{1}H NMR of compound 2e in $CDCl_3$



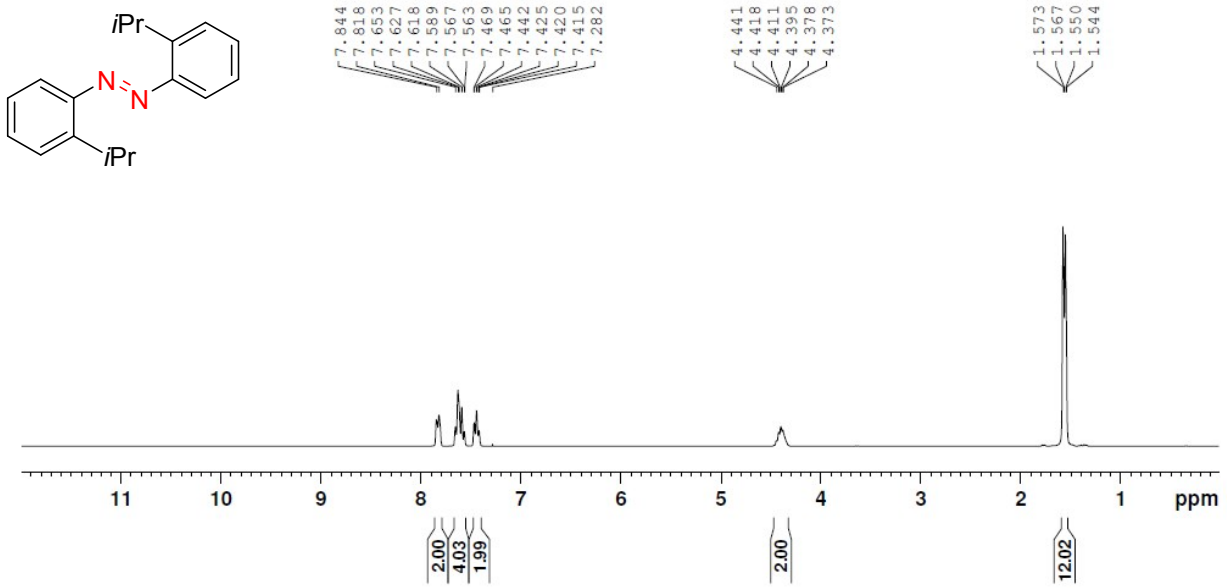
^{1}H NMR of compound 2f in $CDCl_3$



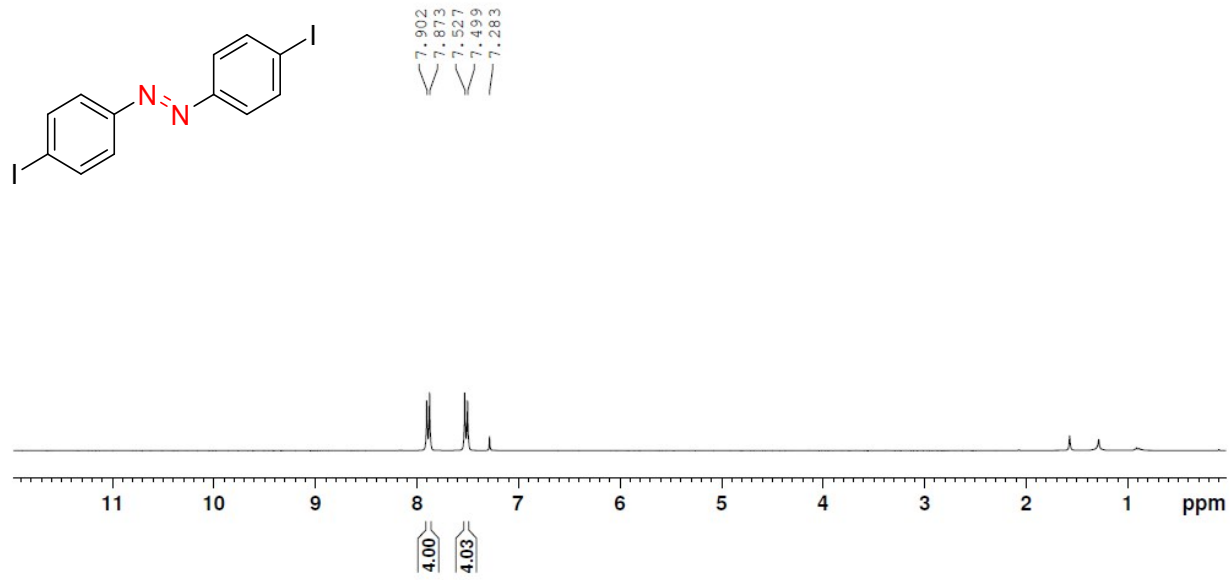
^{1}H NMR of compound 2g in $CDCl_3$



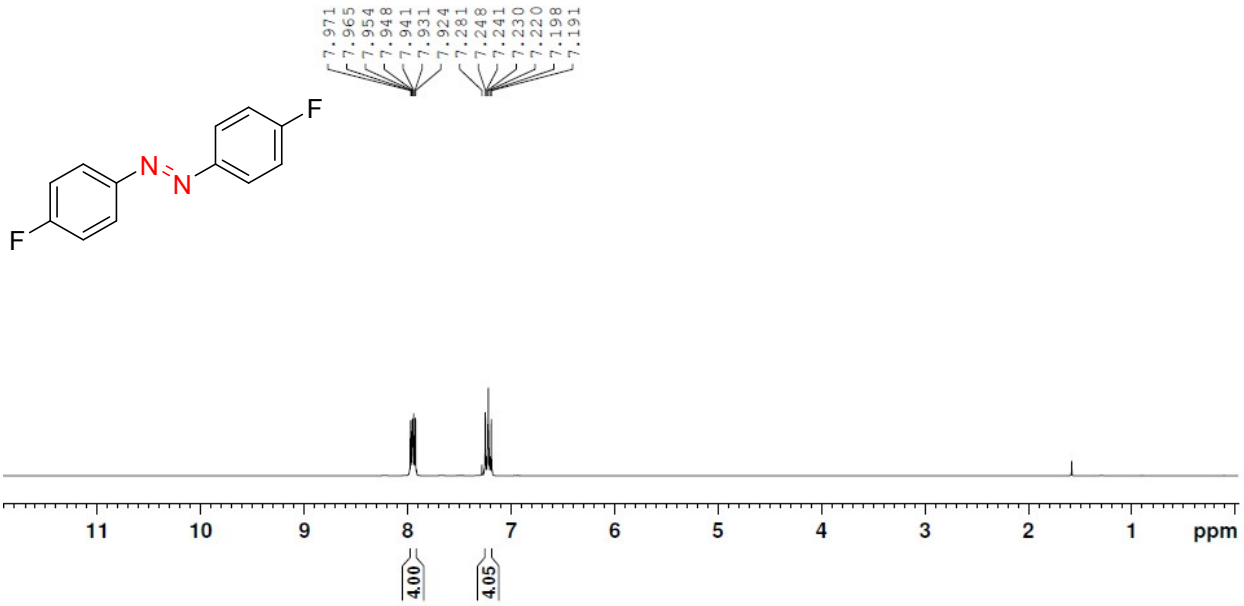
^{1}H NMR of compound 2h in $CDCl_3$



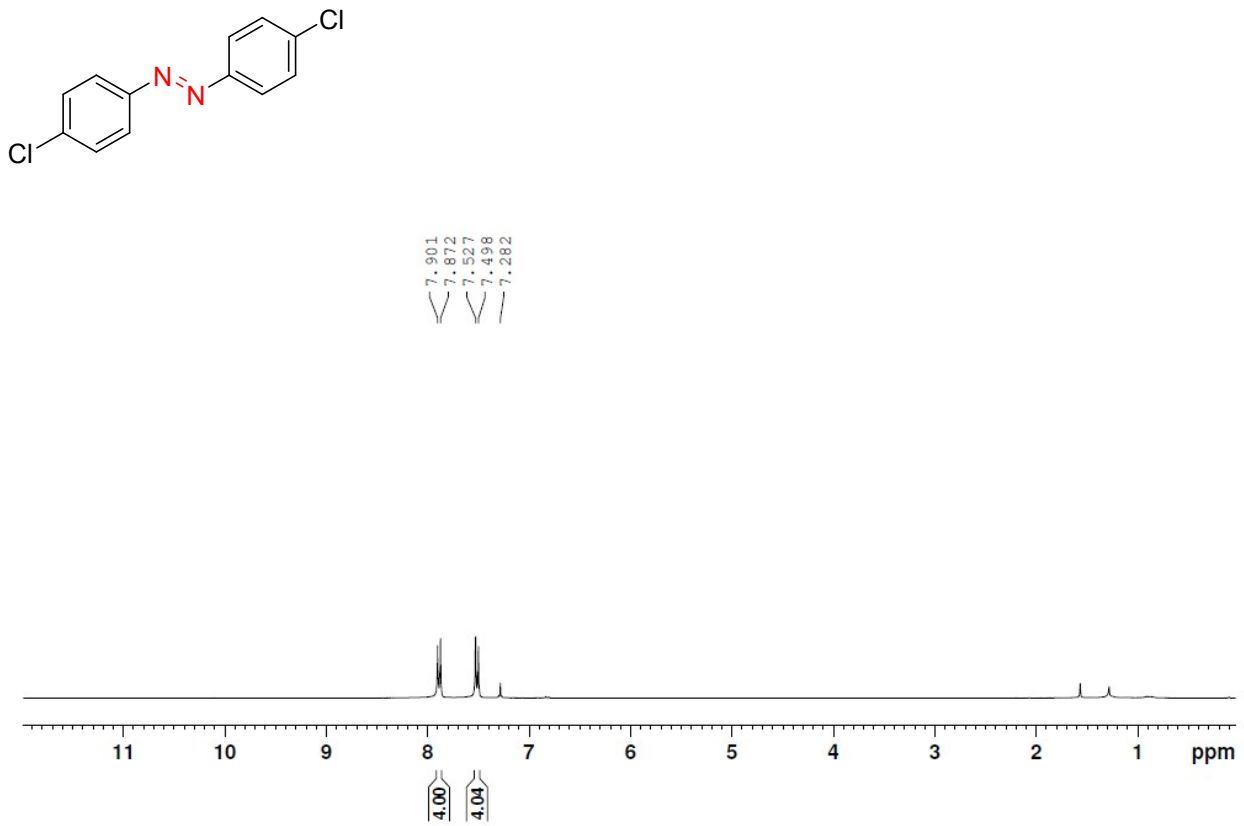
^{1}H NMR of compound 2i in $CDCl_3$



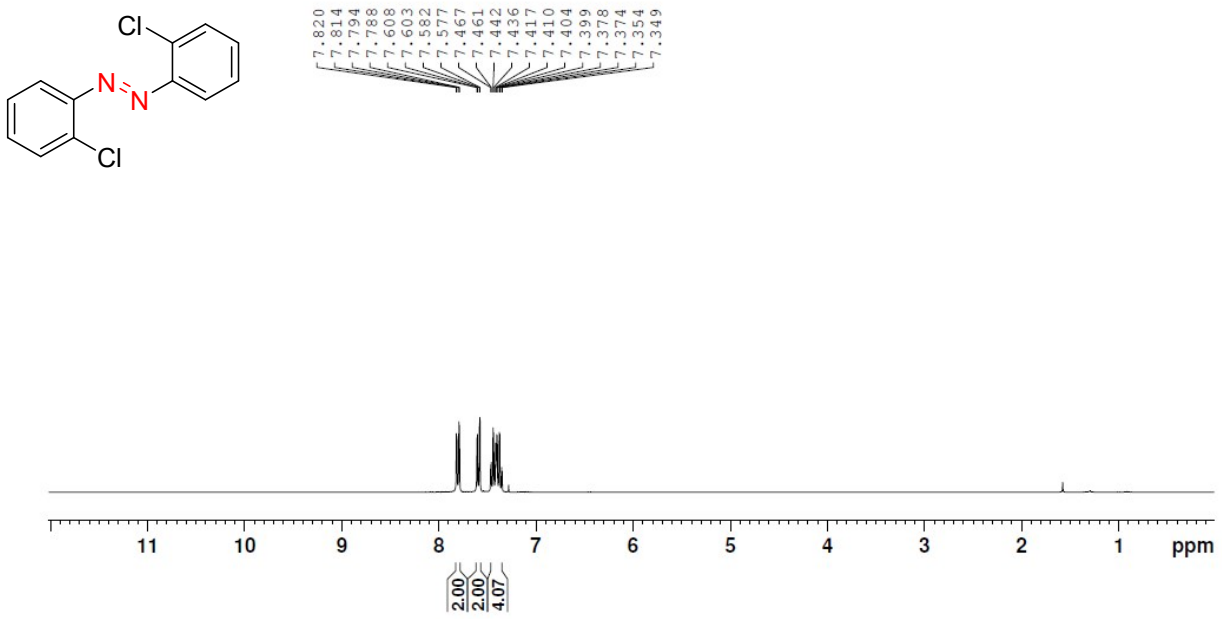
^{1}H NMR of compound 2j in $CDCl_3$



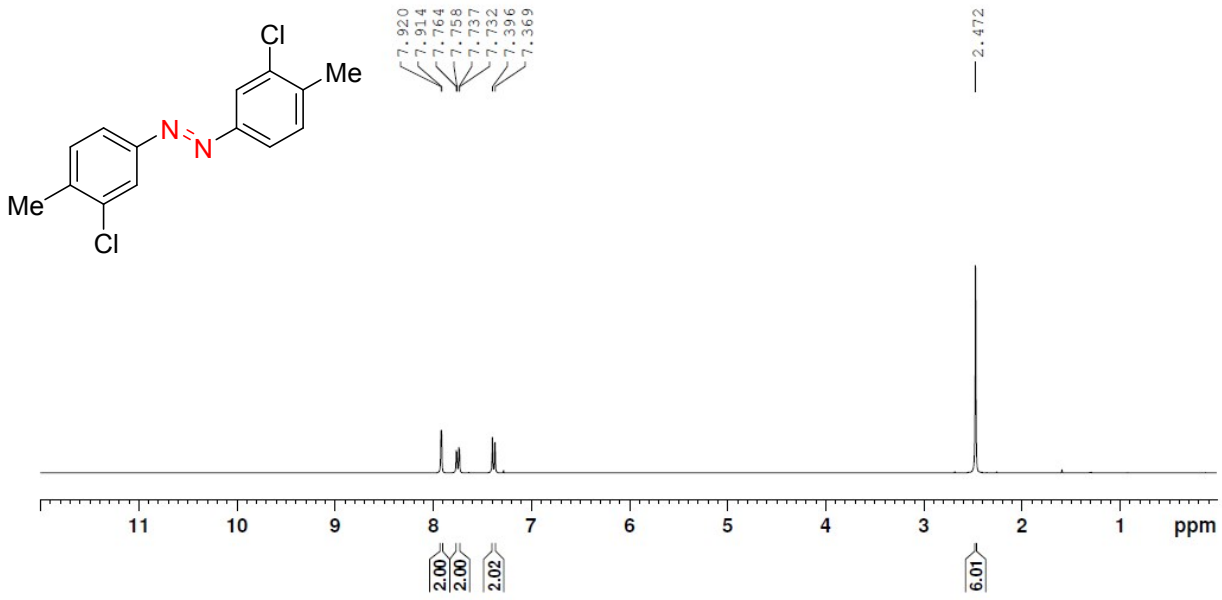
^{1}H NMR of compound 2k in $CDCl_3$



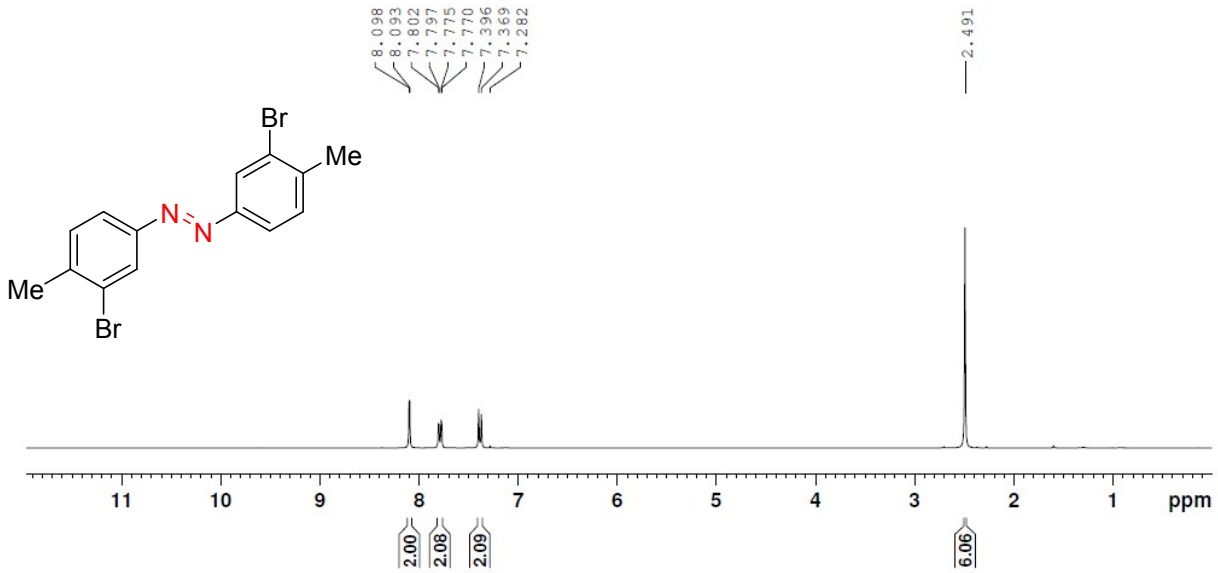
^{1}H NMR of compound 2l in $CDCl_3$



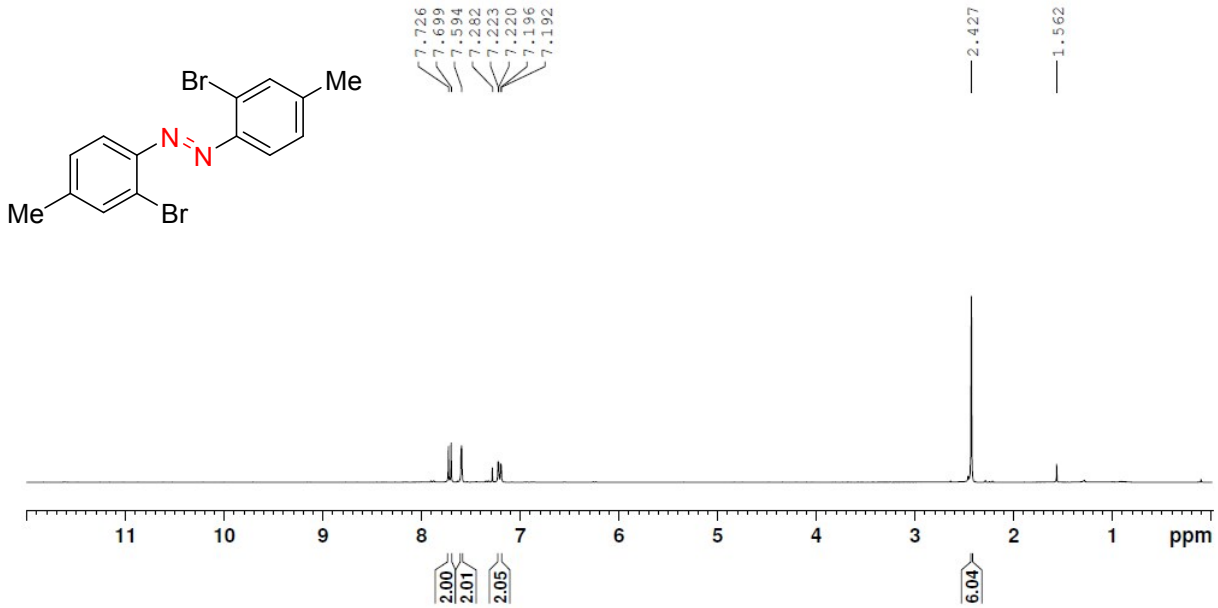
^{1}H NMR of compound 2m in $CDCl_3$



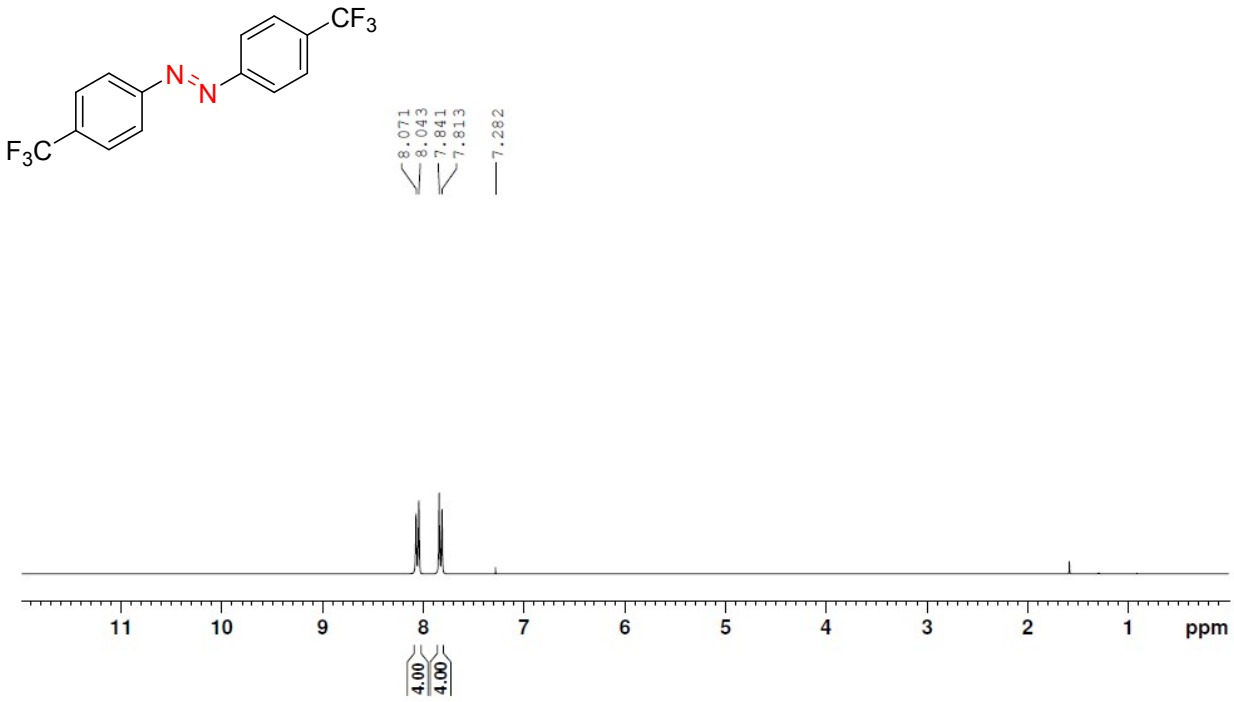
^{1}H NMR of compound 2n in $CDCl_3$



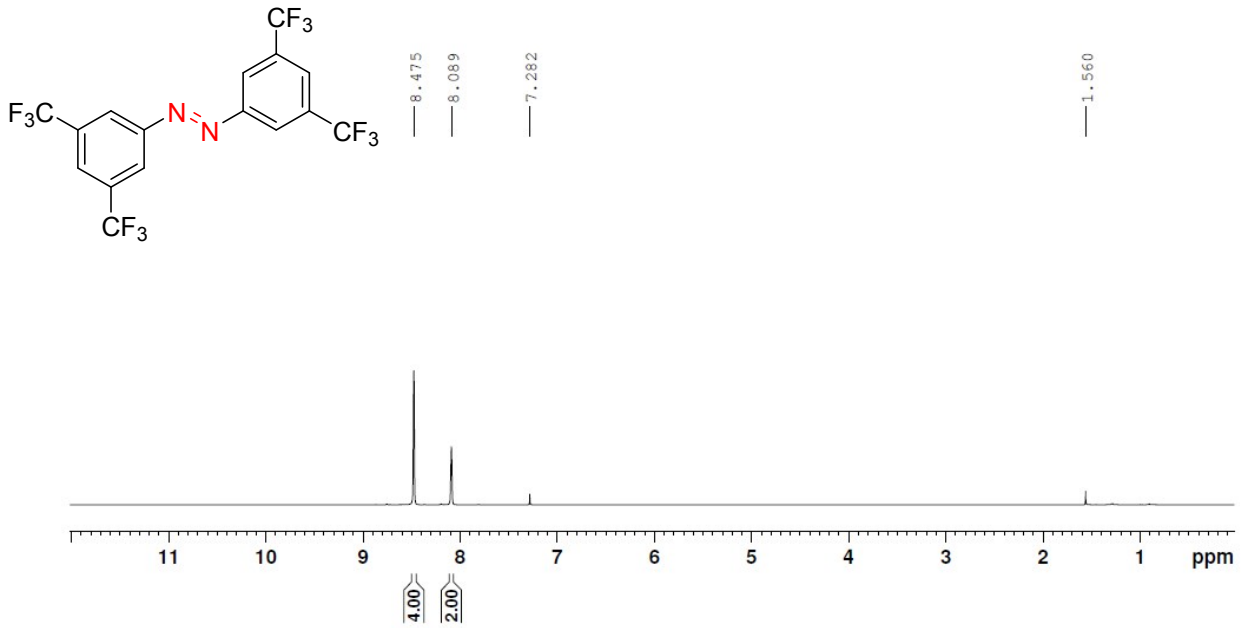
^{1}H NMR of compound 2o in $CDCl_3$



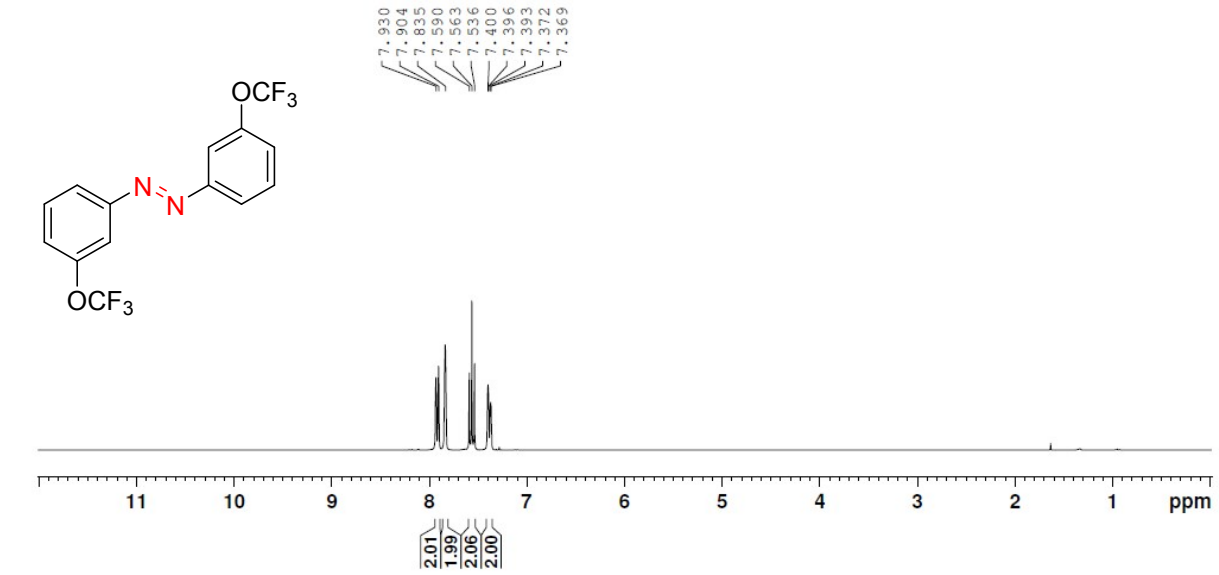
^{1}H NMR of compound 2p in $CDCl_3$



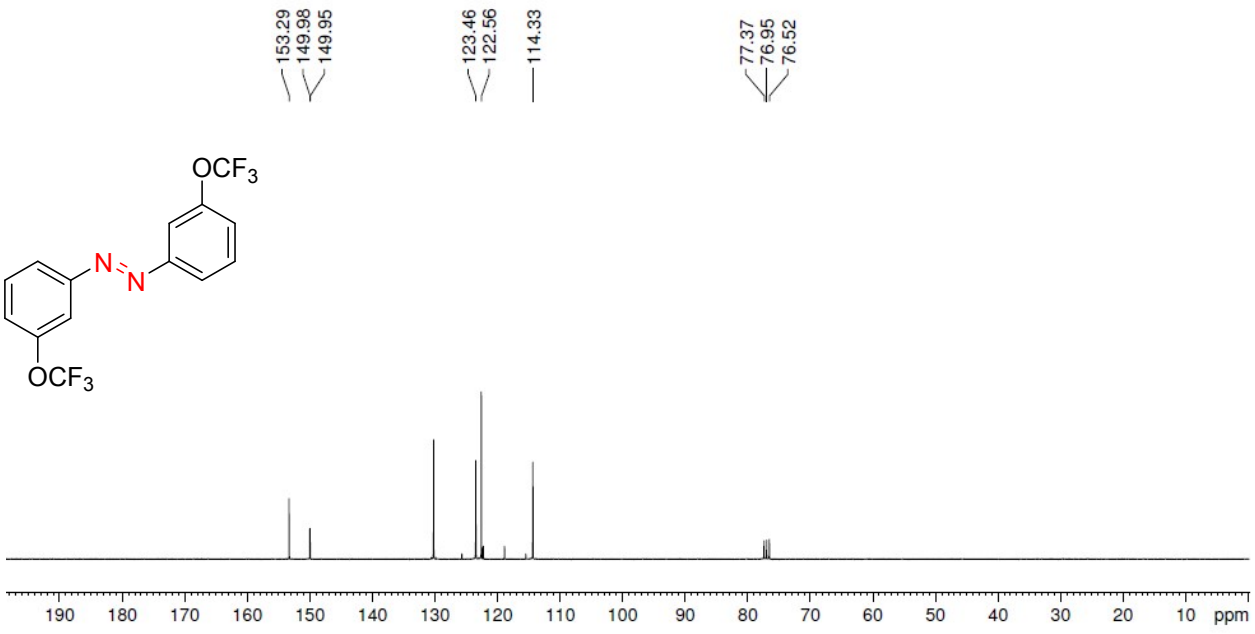
^{1}H NMR of compound 2q in $CDCl_3$



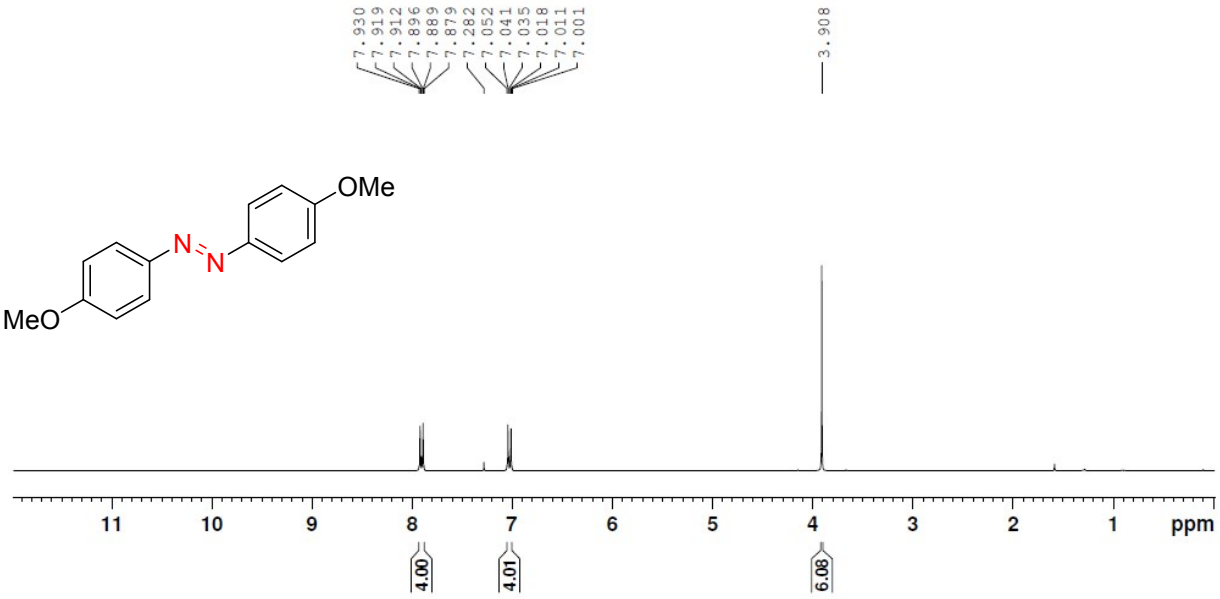
^{1}H NMR of compound 2r in $CDCl_3$



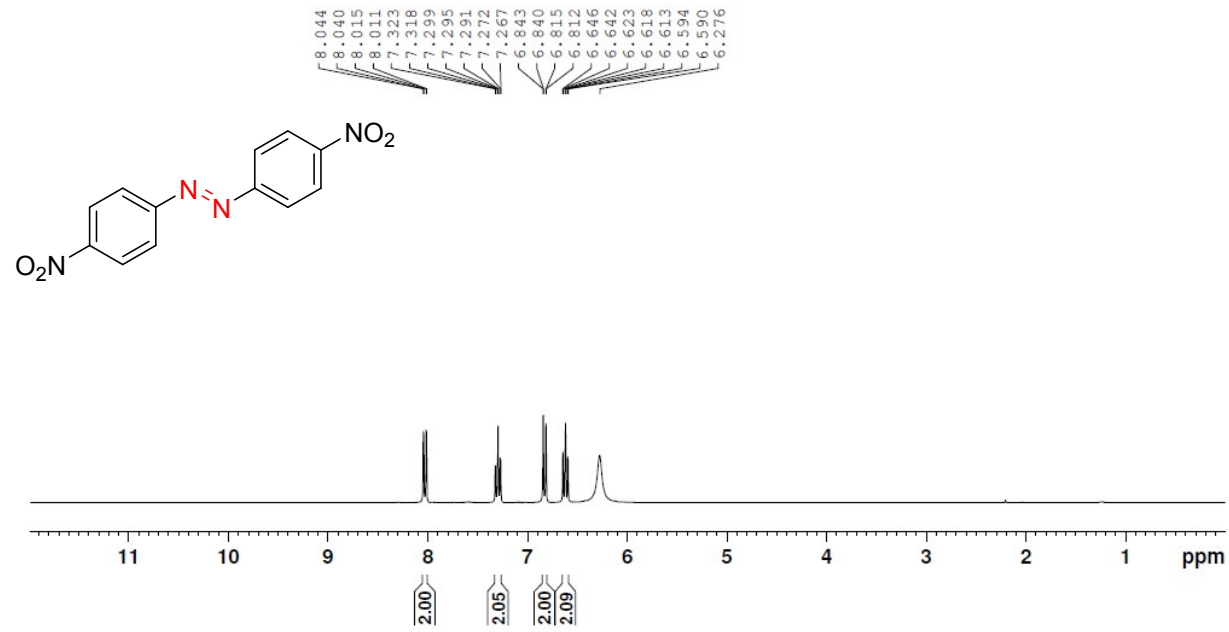
^{1}H NMR of compound 2s in $CDCl_3$



^{13}C NMR of compound 2s in $CDCl_3$



^{1}H NMR of compound 2t in $CDCl_3$



^{1}H NMR of compound 2u in $CDCl_3$

General Computational Methods

Density functional theory calculations were performed using the software package Gaussian 16, Revision C.01.[13] All optimizations were performed applying the APFD functional[14] along with the DGDZVP basis set. The optimized geometries were verified as transition state structures (one imaginary frequency) or minima (zero imaginary frequencies) by frequency calculations. Intrinsic reaction coordinate (IRC)[15,16] calculations were performed to confirm that all transition state structures were linked to relevant minima. The energies of the UAPFD/DGDZVP optimized structures were further refined by single-point calculations performed at the UAPFD/def2-TZVP level of theory using the integral equation formalism polarizable continuum model (IEFPCM) with the default parameters of dichloromethane (ε = 8.93) to account for solvent.[17] The thermal corrections to the Gibbs free energies (temperature = 298.15 K, pressure = 1 atm) computed at the lower level of theory (UAPFD/DGDZVP) were added to the electronic energies obtained from the single-point calculations to provide the final reported Gibbs free energies. The keyword (integral=grid=ultrafine) was used for all calculations. The 3D images of all optimized geometries were generated using the program CYLview.[18] GaussView6[19] was used to construct all structures prior to optimization and to visualize the output from the Gaussian 09 calculations. Electrostatic potential energy (ESP) surfaces were computed using the Jaguar program of the Schrödinger software package.[20]

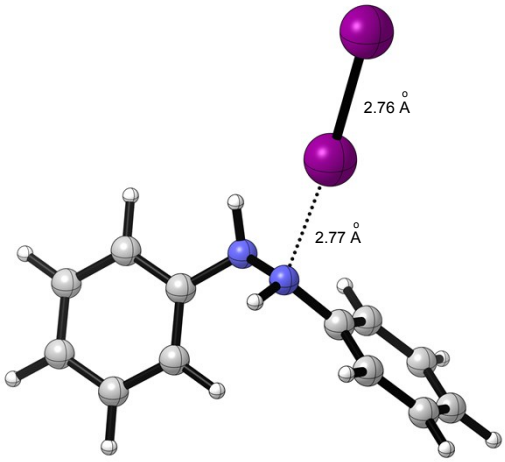
Energies of Calculated Structures and Cartesian Coordinates

Table S1. Single point energies of all structures calculated at the $IEFPCM_{(DCM)}$ UAPFD/def2-TZVP level of theory and thermal correction to Gibbs Free Energy and Gibbs Free Energy calculated at the UAPFD/DGDZVP level of theory. All energies are reported in Hartrees.

Structure	Single point Energies (E) $IEFPCM_{(DCM)}$ UAPFD/ def2-TZVP	Thermal Corrections to Gibbs Free Energies (G) UAPFD /DGDZVP	Gibbs Free Energies (G) UAPFD /DGDZVP	Gibbs Free Energies (G) $IEFPCM_{(DCM)}$ UAPFD / def2-TZVP// UAPFD /DGDZVP
Complex XB	-1169.292237	0.168287	-14412.696631	-1169.12395
TS1	-1169.263012	0.16118	-14412.667277	-1169.101832
TS2	-1169.236404	0.153849	-14412.649744	-1169.082555
2a-H^+	-870.887869	0.160839	-7492.419248	-870.72703

O_2	-150.274212	-0.016129	-150.248182	-150.290341
I_2	-595.564508	-0.025232	-13839.340318	-595.58974
H_2O	-76.406635	0.00386	-76.367628	-76.402775
HI	-298.372406	-0.014908	-6920.257659	-298.387314
1a	-574.129304	0.177873	-573.353643	-573.534427
2a	-572.485543	0.152985	-572.160585	-572.332558
I^-	-297.949462	-0.016848	-6919.76161	-297.96631

Complex XB:



- Thermochemistry -

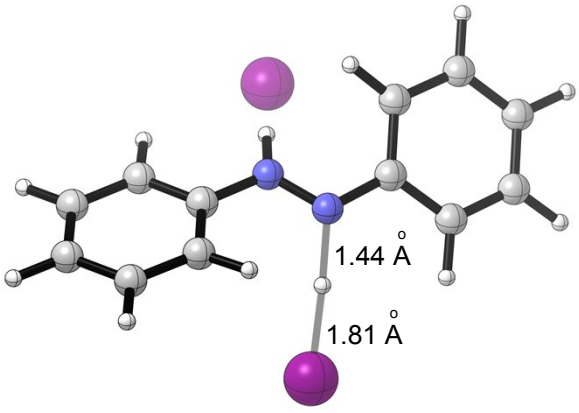
Zero-point correction=	0.218242 (Hartree/Particle)
Thermal correction to Energy=	0.234001
Thermal correction to Enthalpy=	0.234945
Thermal correction to Gibbs Free Energy=	0.168287
Sum of electronic and zero-point Energies=	-14412.646675
Sum of electronic and thermal Energies=	-14412.630916
Sum of electronic and thermal Enthalpies=	-14412.629972
Sum of electronic and thermal Free Energies=	-14412.696631

Number of Imaginary Frequencies = 0

E (Single Point Energy) [IEFPCM$_{(DCM)}$ UAPFD/ def2-TZVP] = -1169.292237

C	-5.54903200	-2.62955500	-0.34328700
C	-5.29340400	-1.33895200	-0.80331300
C	-4.08076300	-0.70610700	-0.52687300
C	-3.10185800	-1.37699200	0.21742900
C	-3.35508000	-2.67567000	0.68159600
C	-4.57134700	-3.29112400	0.40424400
H	-6.49642400	-3.11484700	-0.56174600
H	-6.04703400	-0.80763100	-1.37977100
H	-3.91594400	0.31350000	-0.86397000
H	-2.59680500	-3.20160400	1.25939100
H	-4.75280800	-4.29953100	0.76839900
N	-1.88083000	-0.76132900	0.55206600
N	-1.37533200	0.20299100	-0.32453500
C	-1.75313900	1.55102100	-0.06755600
C	-1.62079900	2.48425400	-1.10019800
C	-2.19104200	1.95179100	1.19494900
C	-1.93321600	3.82076300	-0.86619900
H	-1.26512000	2.16912700	-2.07985000
C	-2.50114300	3.29273300	1.41564900
H	-2.29285600	1.21209100	1.98254500
C	-2.37531200	4.23289500	0.39252100
H	-1.82851900	4.54293600	-1.67209300
H	-2.84670300	3.60262000	2.39894400
H	-2.61869400	5.27661600	0.57284300
I	1.38042400	-0.07232500	-0.15906100
I	4.09292800	-0.53542100	0.06248100
H	-1.52937200	-0.05149800	-1.30261900
H	-1.14740800	-1.41323600	0.81020700

TS1:



- Thermochemistry -

Zero-point correction=	0.209325 (Hartree/Particle)
Thermal correction to Energy=	0.224471
Thermal correction to Enthalpy=	0.225415
Thermal correction to Gibbs Free Energy=	0.161180
Sum of electronic and zero-point Energies=	-14412.619132
Sum of electronic and thermal Energies=	-14412.603986
Sum of electronic and thermal Enthalpies=	-14412.603042
Sum of electronic and thermal Free Energies=	-14412.667277

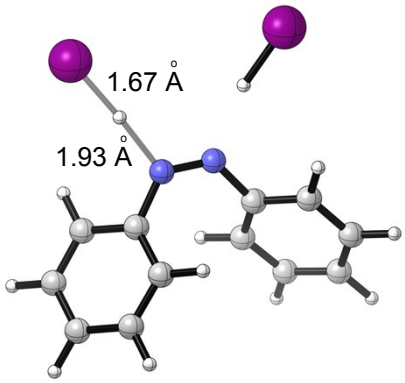
Number of Imaginary Frequencies = 1

E (Single Point Energy) [IEFPCM$_{(DCM)}$UAPFD/def2-TZVP] = -1169.263012

C	-1.78075900	3.76248100	0.41671900
C	-0.75119200	2.83206000	0.39997700
C	-0.98758300	1.55507800	0.93469700
C	-2.22519000	1.21457000	1.50395700
C	-3.24046200	2.16070500	1.50874700
C	-3.02384200	3.43006500	0.96454000
H	-1.61714300	4.74898300	-0.00777500
H	0.21281300	3.05962300	-0.04929500
H	-2.36971200	0.23912300	1.95715500
H	-4.20398400	1.90950200	1.94284800
H	-3.82465000	4.16491800	0.97363800
C	0.92183200	-1.46134200	1.02913300
C	2.19957700	-1.01295200	1.43382700
C	0.71497500	-2.80778000	0.65371800
C	3.26387300	-1.90830300	1.42374500
H	2.33199600	-0.01487800	1.83834500
C	1.78821100	-3.67783600	0.64786200
C	3.06364500	-3.22854200	1.02704700
H	4.24881800	-1.56946200	1.73052500
H	1.64391300	-4.70968600	0.34052800
H	3.90042900	-3.92243500	1.02433000
N	0.06158800	0.63936600	0.90641100
N	-0.16769300	-0.62174200	0.96941300
H	-0.27185000	-3.13015500	0.33406600
H	1.00990100	0.96872000	0.47984200
I	-2.66222800	-1.50028000	-0.90101000
H	-1.32174000	-1.05749700	0.23046900

I	2.68761400	1.38784000	-0.90256100

TS2:



- Thermochemistry -

Zero-point correction=	0.205461 (Hartree/Particle)
Thermal correction to Energy=	0.221220
Thermal correction to Enthalpy=	0.222164
Thermal correction to Gibbs Free Energy=	0.153849
Sum of electronic and zero-point Energies=	-14412.598132
Sum of electronic and thermal Energies=	-14412.582372
Sum of electronic and thermal Enthalpies=	-14412.581428
Sum of electronic and thermal Free Energies=	-14412.649744

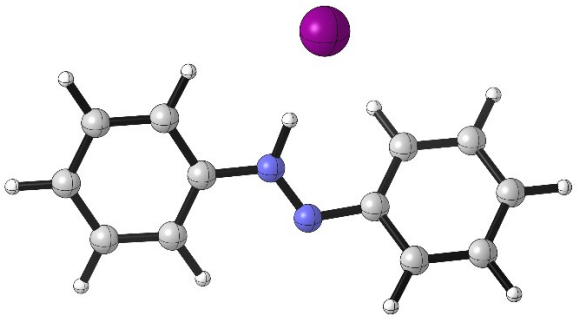
Number of Imaginary Frequencies = 1

E (Single Point Energy) [IEFPCM$_{(DCM)}$UAPFD/def2-TZVP] = -1169.236404

C	-0.98750100	4.32735500	-0.12148300
C	-0.42308200	3.07613800	-0.35819000
C	-0.96447300	1.95057000	0.27068200
C	-2.01266100	2.07625400	1.19317300
C	-2.54008100	3.33591600	1.44941000
C	-2.04358600	4.45969900	0.78092500
H	-0.58561900	5.20206500	-0.62573000
H	0.42219700	2.95976200	-1.03100200
H	-2.39338500	1.20198600	1.71270400
H	-3.34232300	3.44377600	2.17477800
H	-2.46863300	5.44011600	0.98005000
C	-2.27673400	-0.55417200	-0.30520200
C	-2.83922700	-1.67560700	0.31275100
C	-3.03085200	0.24530400	-1.17516500
C	-4.18956600	-1.95497900	0.11519500
H	-2.22102500	-2.30827200	0.94409000

C	-4.36784300	-0.06606900	-1.38898400
H	-2.57093000	1.08631200	-1.68524300
C	-4.95432000	-1.15340500	-0.73294900
H	-4.63808400	-2.81255500	0.60940900
H	-4.95699000	0.54058000	-2.07179500
H	-6.00339800	-1.38438800	-0.89914200
H	0.03153700	-1.68668100	-0.01011200
N	-0.29920600	0.71826900	0.03928600
N	-0.88019900	-0.36945900	-0.12430400
H	1.62228600	0.82840000	-0.05181200
I	3.21622100	1.28359000	-0.25945900
I	0.91849100	-3.15820800	0.26526900

Compound 2a-H$^+$:



- Thermochemistry -

Zero-point correction=	0.204103 (Hartree/Particle)
Thermal correction to Energy=	0.217166
Thermal correction to Enthalpy=	0.218110
Thermal correction to Gibbs Free Energy=	0.160839
Sum of electronic and zero-point Energies=	-7492.375984
Sum of electronic and thermal Energies=	-7492.362921
Sum of electronic and thermal Enthalpies=	-7492.361977
Sum of electronic and thermal Free Energies=	-7492.419248

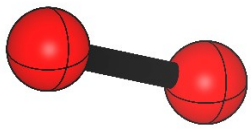
Number of Imaginary Frequencies = 0

E (Single Point Energy) [IEFPCM$_{(DCM)}$UAPFD/def2-TZVP] = -870.887869

N	-0.69307300	-0.77785300	-0.23097600
C	-2.09498700	-0.79860200	-0.13440100
C	-2.76578900	0.42039100	-0.29360200
C	-2.79147200	-1.99550000	0.07961300
C	-4.15586800	0.43485300	-0.22889600
H	-2.19703000	1.33676900	-0.43663200
C	-4.17799600	-1.95983800	0.13954500

H	-2.24379400	-2.92572600	0.19023000
C	-4.86323400	-0.74859700	-0.01344400
H	-4.68579900	1.37646700	-0.34290000
H	-4.73203200	-2.88059400	0.30222100
H	-5.94907800	-0.73154000	0.03424800
C	1.36231600	-1.69877500	-0.08564800
C	2.11854200	-2.63737200	0.64889100
C	2.00840200	-0.74546800	-0.90460100
C	3.50082400	-2.58347100	0.61577300
H	1.58963300	-3.36609400	1.25676800
C	3.39823900	-0.71099800	-0.93225900
H	1.43871600	-0.09532100	-1.55979800
C	4.14034700	-1.61425300	-0.17126800
H	4.08796700	-3.28928000	1.19669500
H	3.90043200	0.02475500	-1.55347500
H	5.22653300	-1.57811900	-0.20277800
N	-0.00083900	-1.79446400	0.08200500
H	-0.23223400	0.19885300	-0.31576700
I	0.65241700	2.22192100	0.19161800

Triplet Oxygen molecule ($^3O_2$):



- Thermochemistry -

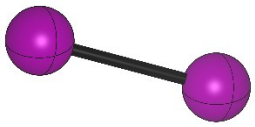
Zero-point correction=	0.003843 (Hartree/Particle)
Thermal correction to Energy=	0.006206
Thermal correction to Enthalpy=	0.007150
Thermal correction to Gibbs Free Energy=	-0.016129
Sum of electronic and zero-point Energies=	-150.228210
Sum of electronic and thermal Energies=	-150.225847
Sum of electronic and thermal Enthalpies=	-150.224903
Sum of electronic and thermal Free Energies=	-150.248182

Number of Imaginary Frequencies = 0

E (Single Point Energy) [IEFPCM$_{(DCM)}$UAPFD/def2-TZVP] = -150.274212

O	0.00000000	0.00000000	0.60520500
O	0.00000000	0.00000000	-0.60520500

Iodine molecule (I_2):



- Thermochemistry -

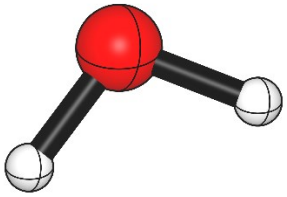
Zero-point correction=	0.000507 (Hartree/Particle)
Thermal correction to Energy=	0.003394
Thermal correction to Enthalpy=	0.004338
Thermal correction to Gibbs Free Energy=	-0.025232
Sum of electronic and zero-point Energies=	-13839.314579
Sum of electronic and thermal Energies=	-13839.311693
Sum of electronic and thermal Enthalpies=	-13839.310748
Sum of electronic and thermal Free Energies=	-13839.340318

Number of Imaginary Frequencies = 0

E (Single Point Energy) [IEFPCM$_{(DCM)}$UAPFD/def2-TZVP] = -595.564508

I	0.00000000	0.00000000	1.35380200
I	0.00000000	0.00000000	-1.35380200

Water molecule (H_2O):



- Thermochemistry -

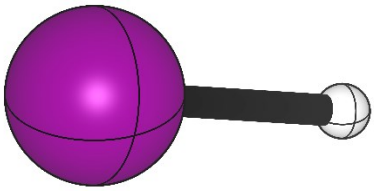
Zero-point correction=	0.021513 (Hartree/Particle)
Thermal correction to Energy=	0.024347
Thermal correction to Enthalpy=	0.025292
Thermal correction to Gibbs Free Energy=	0.003860
Sum of electronic and zero-point Energies=	-76.349976
Sum of electronic and thermal Energies=	-76.347141
Sum of electronic and thermal Enthalpies=	-76.346197
Sum of electronic and thermal Free Energies=	-76.367628

Number of Imaginary Frequencies = 0

E (Single Point Energy) [IEFPCM$_{(DCM)}$UAPFD/def2-TZVP] = -76.406635

H	0.00000000	0.76773400	-0.46871000
O	0.00000000	0.00000000	0.11717700
H	0.00000000	-0.76773400	-0.46871000

Hydrogen Iodide molecule (HI):



- Thermochemistry -

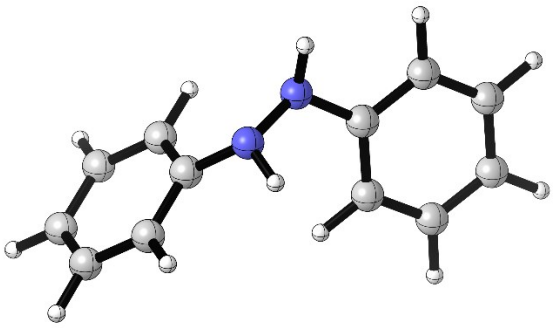
Zero-point correction=	0.005251 (Hartree/Particle)
Thermal correction to Energy=	0.007612
Thermal correction to Enthalpy=	0.008556
Thermal correction to Gibbs Free Energy=	-0.014908
Sum of electronic and zero-point Energies=	-6920.237500
Sum of electronic and thermal Energies=	-6920.235139
Sum of electronic and thermal Enthalpies=	-6920.234195
Sum of electronic and thermal Free Energies=	-6920.257659

Number of Imaginary Frequencies = 0

E (Single Point Energy) [IEFPCM$_{(DCM)}$UAPFD/def2-TZVP] = -298.372406

I	0.00000000	0.00000000	0.03031100
H	0.00000000	0.00000000	-1.60650500

Compound 1a:



- Thermochemistry -

Zero-point correction=	0.216180 (Hartree/Particle)
Thermal correction to Energy=	0.227521
Thermal correction to Enthalpy=	0.228465
Thermal correction to Gibbs Free Energy=	0.177873
Sum of electronic and zero-point Energies=	-573.315335
Sum of electronic and thermal Energies=	-573.303994
Sum of electronic and thermal Enthalpies=	-573.303050
Sum of electronic and thermal Free Energies=	-573.353643

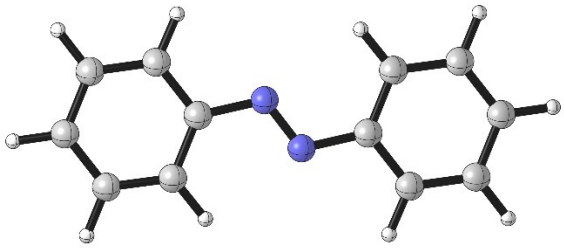
Number of Imaginary Frequencies = 0

E (Single Point Energy) [IEFPCM$_{(DCM)}$UAPFD/def2-TZVP] = -573.7123

C	2.31092700	-1.19309200	1.23191100
C	1.36639700	-0.19069800	1.01640900
C	1.53049500	0.70471800	-0.04801900
C	2.64764300	0.57609300	-0.88695100
C	3.58370800	-0.42809200	-0.65941600
C	3.42457400	-1.32216200	0.40207500
H	2.16631900	-1.88564700	2.05805200
H	0.49575900	-0.11721800	1.66119700
H	2.78365000	1.26981000	-1.71566700
H	4.44412600	-0.51297900	-1.31939400
H	4.15482300	-2.10803200	0.57563100
N	0.63327100	1.75904900	-0.27328300
H	0.65618100	2.15986300	-1.20277500
N	-0.63325400	1.75903300	0.27332100
H	-0.65618000	2.15985700	1.20280800
C	-1.53048700	0.70471900	0.04803200
C	-1.36642300	-0.19064900	-1.01644100
C	-2.64761300	0.57606100	0.88698900
C	-2.31096200	-1.19303100	-1.23196100
H	-0.49580400	-0.11714600	-1.66125200

C	-3.58368800	-0.42810900	0.65943400
H	-2.78359300	1.26974000	1.71574200
C	-3.42458700	-1.32213400	-0.40210100
H	-2.16637900	-1.88554900	-2.05813700
H	-4.44408900	-0.51302300	1.31943200
H	-4.15484300	-2.10799300	-0.57567100

Compound 2a:



- Thermochemistry -

Zero-point correction=	0.191637 (Hartree/Particle)
Thermal correction to Energy=	0.202542
Thermal correction to Enthalpy=	0.203486
Thermal correction to Gibbs Free Energy=	0.152985
Sum of electronic and zero-point Energies=	-572.121933
Sum of electronic and thermal Energies=	-572.111028
Sum of electronic and thermal Enthalpies=	-572.110084
Sum of electronic and thermal Free Energies=	-572.160585

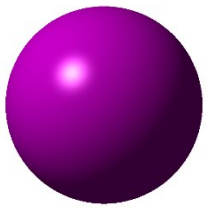
Number of Imaginary Frequencies = 0

E (Single Point Energy) [IEFPCM$_{(DCM)}$UAPFD/def2-TZVP] = -572.485543

N	0.38290400	0.49802800	-0.00000300
C	1.76048100	0.18379700	-0.00000400
C	2.62391400	1.28512000	-0.00001000
C	2.28492900	-1.11910800	0.00000100
C	4.00436900	1.09411600	-0.00001200
H	2.19074000	2.28225500	-0.00001400
C	3.66190900	-1.30239300	-0.00000100
H	1.60229000	-1.96349500	0.00000600
C	4.52568600	-0.19980600	-0.00000700
H	4.67186800	1.95228100	-0.00001700
H	4.07259000	-2.30950700	0.00000200

H	5.60221500	-0.35367300	-0.00000900
C	-1.76048100	-0.18379700	0.00000400
C	-2.62391400	-1.28512000	0.00001100
C	-2.28492900	1.11910800	-0.00000100
C	-4.00436900	-1.09411600	0.00001300
H	-2.19074000	-2.28225500	0.00001500
C	-3.66190900	1.30239300	0.00000000
H	-1.60229000	1.96349500	-0.00000600
C	-4.52568600	0.19980600	0.00000700
H	-4.67186800	-1.95228100	0.00001800
H	-4.07259000	2.30950700	-0.00000400
H	-5.60221500	0.35367300	0.00000900
N	-0.38290400	-0.49802800	0.00000300

Iodine anion (I^-):



- Thermochemistry -

Zero-point correction=	0.000000 (Hartree/Particle)
Thermal correction to Energy=	0.001416
Thermal correction to Enthalpy=	0.002360
Thermal correction to Gibbs Free Energy=	-0.016848
Sum of electronic and zero-point Energies=	-6919.744762
Sum of electronic and thermal Energies=	-6919.743346
Sum of electronic and thermal Enthalpies=	-6919.742402
Sum of electronic and thermal Free Energies=	-6919.761610

Number of Imaginary Frequencies = 0

E (Single Point Energy) [IEFPCM$_{(DCM)}$UAPFD/def2-TZVP] = -297.949462

I	0.00000000	0.00000000	0.00000000

References

[1] S. Okumura, C. H. Lin, Y. Takeda, and S. Minakata, *J. Org. Chem*., 2013, **78**, 12090.
[2] M. K., Sahoo, K. Saravanakumar, G. Jaiswal, E. Balaraman, *ACS. Catal*. 2018, ***8***, 7727.
[3] X. Wang, X., Wang, C. Xia, and L. Wu, *Green. Chem*., 2019, **21**, 4189.
[4] M. A. Chacon-Teran, , R. E. Rodriguez-Lugo, R. Wolf, V. R. Landaeta, *Eur. J. Inorg. Chem*. 2019, 4336.
[5] X. Wang, X., Wang, C. Xia, and L. Wu, *Green. Chem*., 2019, **21**, 4189.
[6] N. A. Noureldin, J. W. Bellegarde, Synthesis, 1999, **6**, 939.
[7] K. Nozawa-Kumada, E. Abe, S. Ito, M. Shigeno, and Y. Kondo, *Org. Biomol. Chem*, 2018, **16**, 3095.
[8] C. Zhang, N. Jiao, *Angew. Chem. Int. Ed*. 2010, ***49***, 6174.
[9] E. Paris, F. Bigi, D. A. Cauzzi, R. Maggi, and G. Maestri, *Green Chem.*, 2018, **20**, 382.
[10] Z. W. Davis-Gilbert, X. Wen, J. D. Goodpaster, I. A. Tonks, *J. Am. Chem. Soc*., 2018, **140**, 7267.
[11] X. Liu, H.-Q. Li, S.Ye, Y.-M. Liu, H.-Y. He, Y. Cao, *Angew. Chem. Int. Ed.* 2014, **53**, 7624.
[12] Z. Yan, X. Xie, Q. Song, F. Ma, X.Sui, Z. Huo, M. Ma, *Green Chem.*2020, **22**, 1301.
[13] Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.
[14] A. Austin, G. A. Petersson, M. J. Frisch, F. J. Dobek, G. Scalmani, and K. Throssell, *J. Chem. Theory Comput*.**,** 2012, **8**, 4989.
[15] F. Weigend, and R. Ahlrichs, *Phys. Chem. Chem. Phys*., 2005, **7**, 3297.
[16] C. González, and H. B. Schlegel, *J. Phys. Chem*., 1990, **94**, 5523.
[17] E. Cancès, B. Mennucci, and J. Tomasi, *J. Chem. Phys.,* 1997, **107**, 3032.
[18] C. Y. Legault, CYLview, version 1.0b; Universitéde Sherbrooke: Quebec, Canada, 2009; http://www.cylview.org.
[19] GaussView, Version 6.1, Roy Dennington, Todd A. Keith, and John M. Millam, Semichem Inc., Shawnee Mission, KS, 2016.
[20] **Schrödinger Release 2018-4**: Jaguar, Schrödinger, LLC, New York, NY, 2018**.**