Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

SUPPORTING INFORMATION

Controllable redox reaction cycle enabled by multifunctional Ru-containing polyoxometalates-based catalysts

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Experimental

Materials

All reagents were purchased from Sigma-Aldrich and TCI without any further purification.

Characterization

The compounds **1–3** powder was characterized by inductively coupled plasma optical emission spectrometry (ICP-OES, PerkinElmer Optima 2100 DV inductively coupled plasma), Fouriertransform infrared spectroscopy (FTIR, Bruker VERTEX 70), Powder X-ray diffraction (XRD, Bruker D8 Advance diffractometer), Ultraviolet-visible spectrophotometry (UV-vis, Hitachi U-4100 spectrophotometer), Thermogravimetric analysis (TGA, NETZSCH STA449F5/QMS403D), X-ray photoelectron spectra (XPS, Kratos, Manchester, UK), and EPR spectra (Bruker EMX580 spectrometer). Ultraviolet photoemission spectroscopy (UPS, ESCALAB 250Xi, Thermo Fisher Scientifc) was performed to evaluate the energy band structure using the He I UPS spectrum from the excitation energy (21.22 eV). The reaction mixture was stirred and heated at the prescribed conditions on the parallel reactor of WATTCAS-1020 H. The photocatalytic reactions were performed on WATTCAS Parallel Light Reactor (WP-TEC-1020HSL) with 10 W COB LED. GC analyses were performed on a Bruker 450-GC with a flame ionization detector equipped with a 30 m column (GsBP-1, 0.25 mm internal diameter and 0.25 μm film thickness) with nitrogen as the carrier gas. ^{1}H NMR and ^{13}C NMR spectra were taken on Bruker 500 MHz Liquid State NMR Spectrometer (^{1}H 500 MHz, ^{13}C 126 MHz). Chemical shifts of ^{1}H NMR spectra and ^{13}C NMR spectra were reported using residual solvent signal of $CDCl_3$ (δ = 7.26 ppm) and $CDCl_3$ (δ = 77.0 ppm) as internal standard, respectively.

Preparation of 2

Compound **2** was synthesized by using $Na_2WO_4 \cdot 2H_2O$ (4.0 g, 12 mmol) and Sb_2O_3 (0.35 g, 1.2 mmol) to 10 mL H_2O with stirring. After dissolution the pH was adjusted to 6.0 by adding 4 M HCl dropwise. $RuCl_3$ (0.25 g, 1.2 mmol) was added successively, followed by the adjustment pH = 4.5 with 4.0 M HCl (aq). This mixture was stirred until a black solution was formed. Then, CsCl (0.2 g, 1.2 mmol) was dissolved in above solution with stirred for 2 h at room temperature. The black solution was sealed in a Teflon-lined autoclave and heated at 200 °C for 72 h. After cooling down to room temperature, the filtrate was kept in a 25 mL beaker to allow slow evaporation at room temperature. After 2 weeks, black block crystals suitable for X-ray crystallography were isolated, filtrated, and air-dried to give 256 mg of **2** (7.8 % yield, based on W). Anal. Calcd (%) for **2**: Na, 0.89; Cs, 1.29; Ru, 0.98; W, 63.52; Sb, 3.56. Found: Na, 1.04; Cs, 1.11; Ru, 0.94; W, 64.14; Sb, 3.50. IR (KBr pellet) for **2**: λ = 3477 (s), 1620 (m), 972 (s), 906 (s), 840 (m) and 681 (m) cm^{-1}.

Preparation of 3

Compound **3** was synthesized by using $Na_2WO_4 \cdot 2H_2O$ (4.0 g, 12 mmol) and Sb_2O_3 (0.35 g, 1.2 mmol) to 10 mL H_2O with stirring. After dissolution the pH of the mixture was adjusted to 4.2 with 4.0 M HCl (aq) under stirring continuously. The yellow solution was sealed in a Teflon-lined autoclave and heated at 200 °C for 72 h. After cooling down to room temperature, the filtrate was kept in a 25 mL beaker to allow slow evaporation at room temperature. After 2 weeks, yellow block crystals suitable for X-ray crystallography were isolated, filtrated, and air-dried to give 528 mg of **3** (16.6 % yield, based on W). Anal. Calcd (%) for **3**: Na, 1.28; W, 68.72; Sb, 4.08. Found: Na, 1.42; W, 69.98; Sb, 4.24. IR (KBr pellet) for **3**: λ = 3477 (s), 1620 (m), 971 (s), 906 (s), 840 (m) and 685 (m) cm^{-1}.

X-ray crystallography

Suitable quality crystals of **1–3** were directly mounted in a cooled nitrogen gas stream on a Bruker D8 VENTURE PHOTON II CCD diffractometer with graphite-monochromated Mo Kα radiation (the value of λ is 0.71073 Å). The structure was solved with the ShelXT structure solution program using intrinsic phasing and further refined by the full-matrix least-squares method on F^2 using the ShelXL refinement package within Olex-2. During the refinement, the command 'omit −3 50.2' was used for compounds **1–3** to remove the weak reflections above 50 degrees. In the last refinement cycles, all the atoms of the polyoxoanions **1–3** (Sb, Ru, W, Na, Cs, Cl and O) were refined anisotropically. All lattice water molecules were positioned using Fourier maps and established by TG analyses. The crystallographic data and structural determination of **1–3** are listed in Table S1. Further details on the crystal structure investigations quoting the depository numbers CCDC 2172137-2172139.

Heat treatment experiments

Compounds **1** and **3** (1.0 g) was transferred to a temperature-programmed tube furnace under N_2 flow (40–60 mL min^{-1}) and subsequently heat treated at 325 °C for 4 h with a heating rate of 5 °C min^{-1}. The sample was then cooled to room temperature naturally under Ar flow to obtain **1-HT** and **3-HT**.

Recycling experiments

The products of AOB, AB, NSB, NB and AN are soluble in the corresponding reaction system, but can successfully be separated by extraction with normal hexane without interfering with the catalyst. The experimental procedure was as follows: After the reaction is completed, an excess of normal hexane is added to the reaction system. After the intense shock stratification, the catalyst is retained in the solvent phase, and the product is retained in the normal hexane system. The two phases are separated, and the recovered catalyst was obtained by rotary evaporation in the solvent phase. The reusability was tested by three consecutive times for model substrates after the initial reaction (Figure 5).

Analysis of data

Compounds **1–3** were synthesized through a simple control composition strategy and characterized by FTIR, XRD, UV-vis, TGA, ICP and XPS analyses. The phase purity of compounds **1–3** are identified by the conformity between the experimental PXRD pattern and the simulated pattern on the strength of structural analyses (Figure 2a).[1] The characteristic vibration patterns of the lacunary Keggin-type POM framework dominate the IR spectra of **1–3** (Figure 2b). Several same characteristic bands were observed at 976, 906, 840 and 685 cm^{-1} which are assigned to the characteristic $v_{as}(Sb–O_a)$, $v_{as}(W–O_t)$, $v_{as}(W–O_b)$, and $v_{as}(W–O_c)$.[2] The ultraviolet-visible (UV-vis) spectra in Figure S3 show that **1** and **2** exhibited one main absorption band with maxima at 400 nm, which could be assigned to the charge-transfer transition of O→Ru.[3,4] The determined number of crystal water molecules in **1–3** was 43, 113 and 56, respectively, as determined by the weight loss of TGA between 30-500 °C (Figures 4a, S1 and S2). Besides, the weight loss between 200 and 400 °C indicates the coordination of 18, 13 and 9 water molecules in **1–3**, which is agreement with the result by bond valence sum calculations. Elemental analyses were conducted by ICP-OES, confirming that the atomic ratio of W:Ru was 96.9:3.1 and 98.5:1.5 for **1** and **2**, respectively.

Supporting results

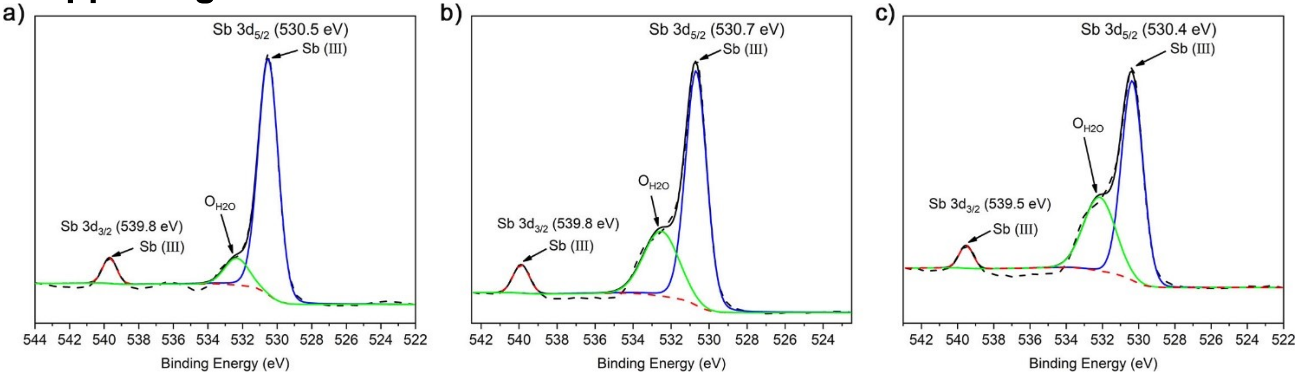


Figure S1. The XPS for Sb 3d for a) **1**; b) **2**; c) **3**.

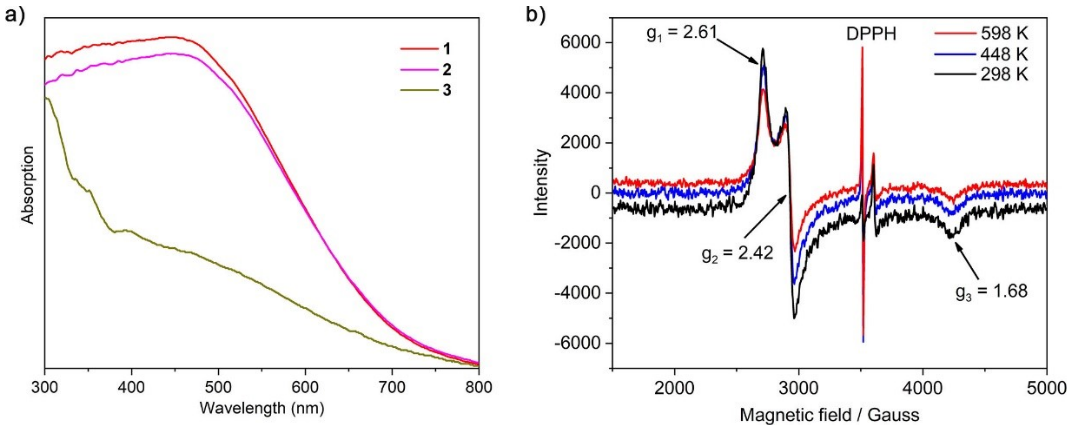


Figure S2. a) UV-vis DRS of compounds **1-3**;b) the EPR spectra of heat treatment of **1**. DPPH = di(phenyl)-(2,4,6-trinitrophenyl)iminoazanium radical was used as a standard.

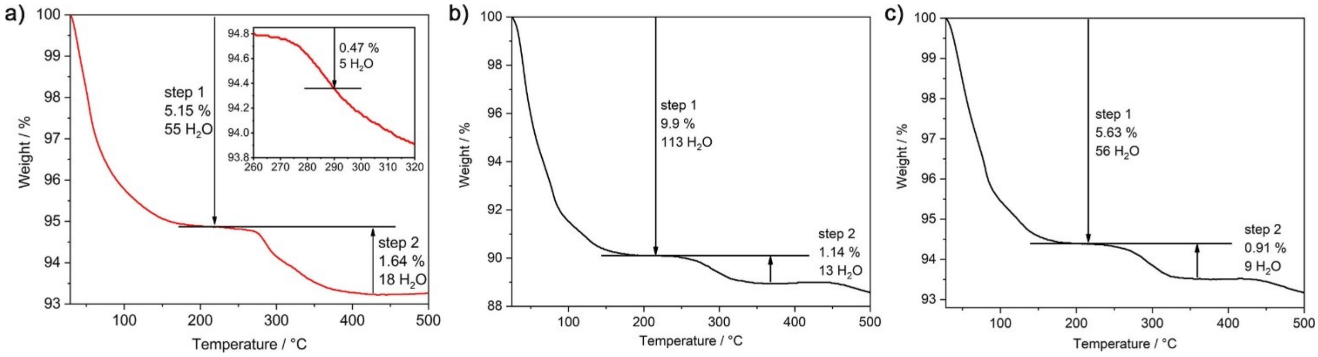


Figure S3. Thermogravimetric analysis curve for a) **1**; b) **2**; c) **3**.

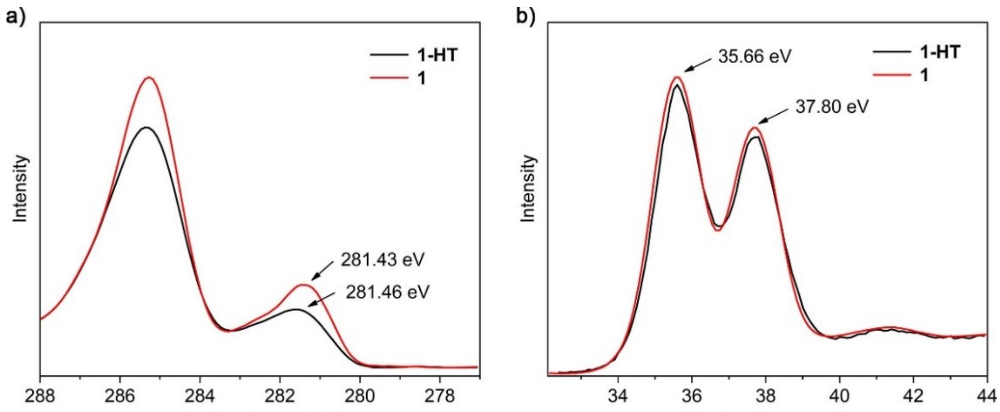
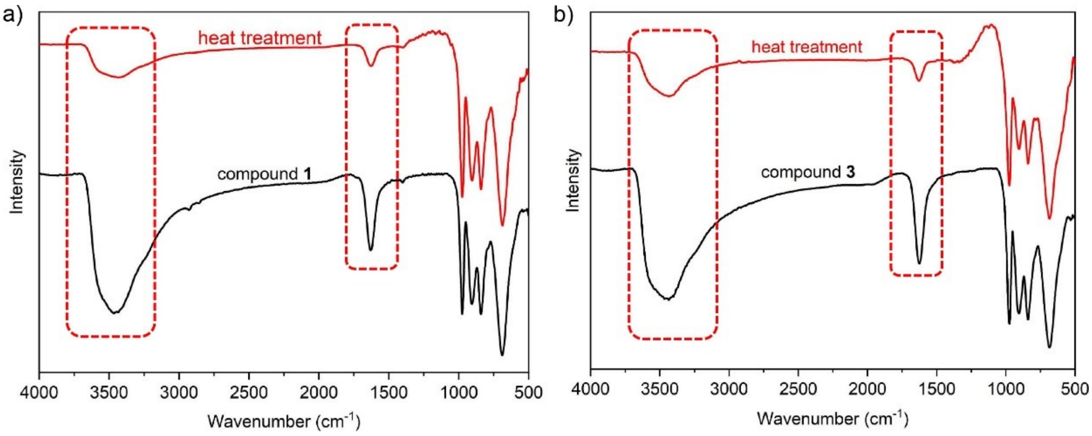


Figure S4. XPS spectra of a) Ru3d; b) W4f.



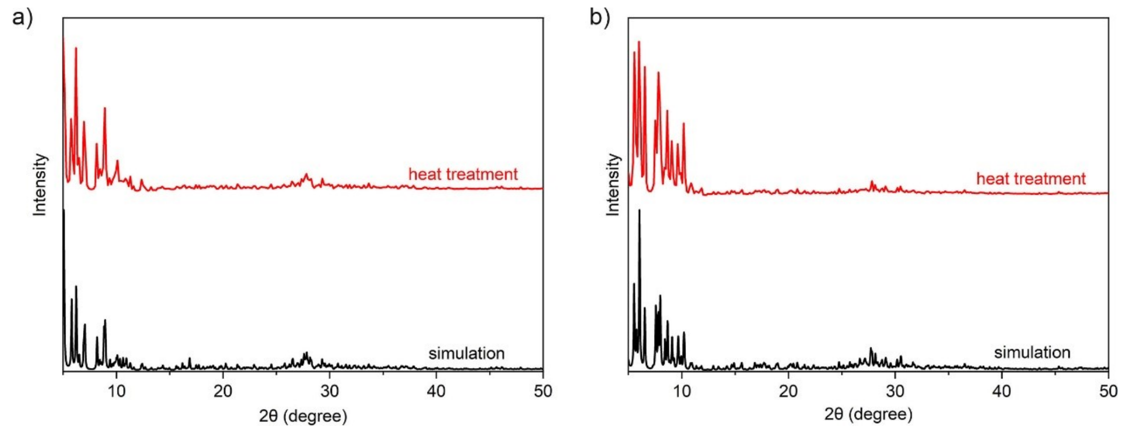
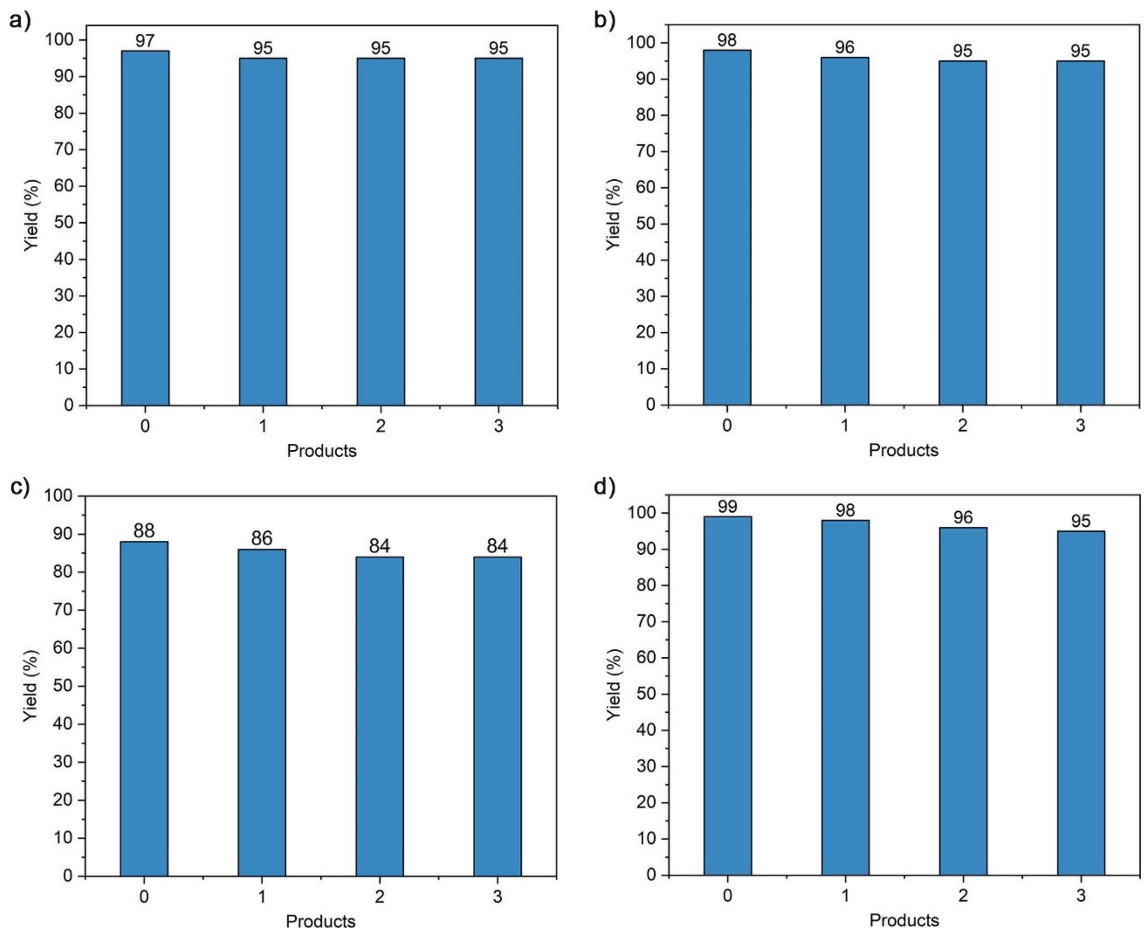


Figure S5. IR spectra after heat treatment of a) **1** and b) **3**.

Figure S6. XRD spectra after heat treatment of a) **1**, and b) **3**.

Figure S7. Recyclability tests for oxidation of AN to AOB, AB, NSB, NB in three consecutive runs, respectively.



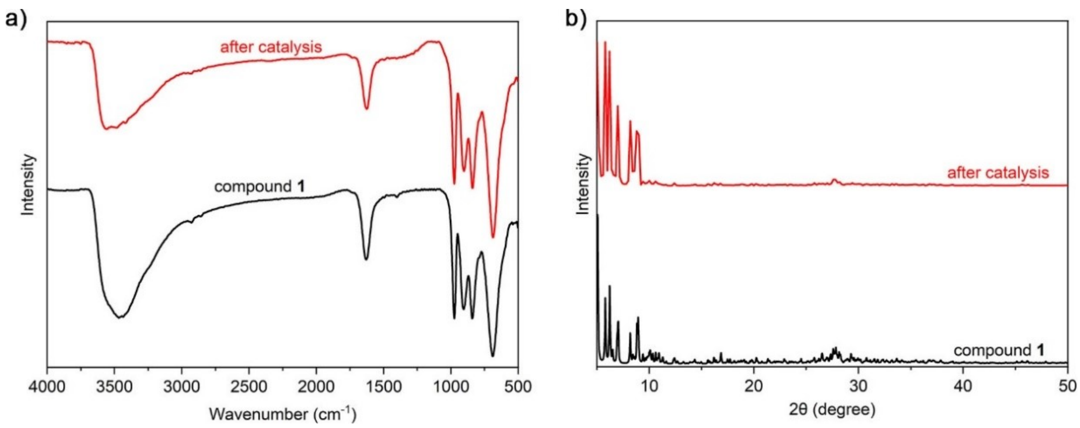


Figure S8. a) The IR spectra of **1** after catalysis; b) The XRD spectra of **1** after catalysis.

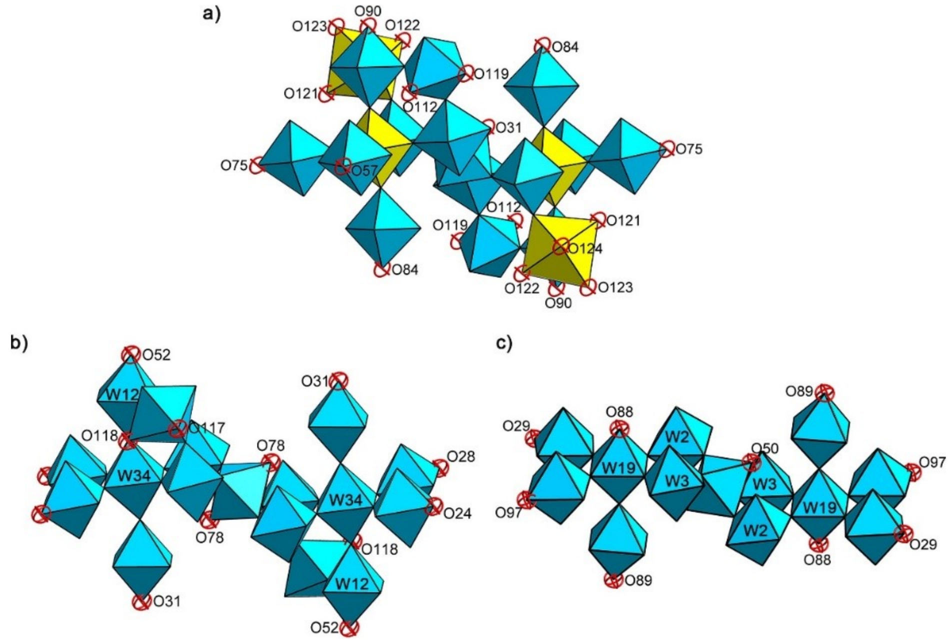


Figure S9. a) The position of water molecules for **1**; b) The position of water molecules for **2**; b) The position of water molecules for **3**. (RuO_6, yellow polytope; WO_6, sky blue polytope)

The structural differences of the three compounds are mainly reflected in the intermediate metallic oxygen clusters. Two WO_6 hexahedrons connect two W19 and W3 polyhedra in compound **3**, respectively, then, the anion carries two ruthenium atoms on the structure outside to form compound **2.** Four W12 and W34 atoms in compound **2** are replaced by Ru atoms to form compound **1.** In addition, the detail explanation of structural differences about three compounds also should be provide in the revised supplement information.

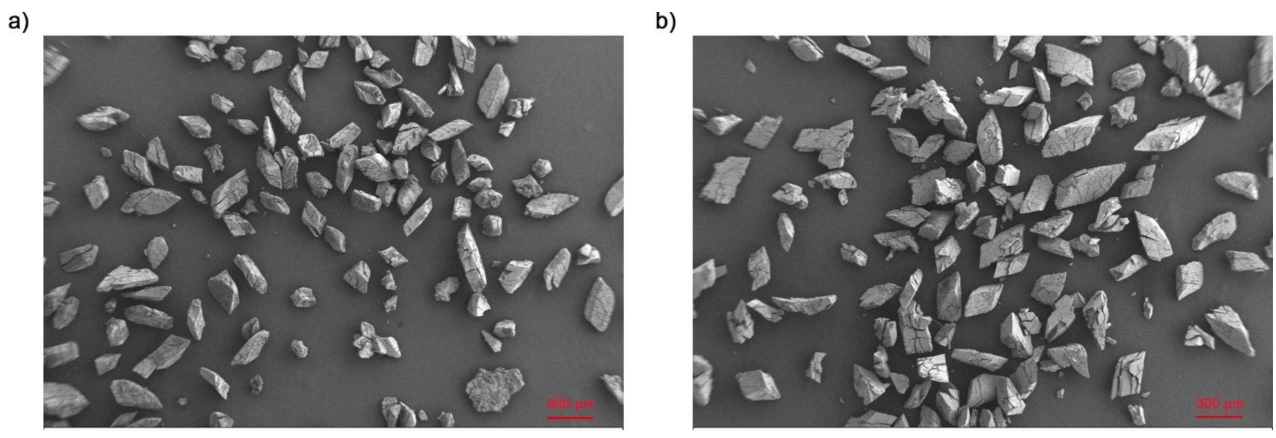
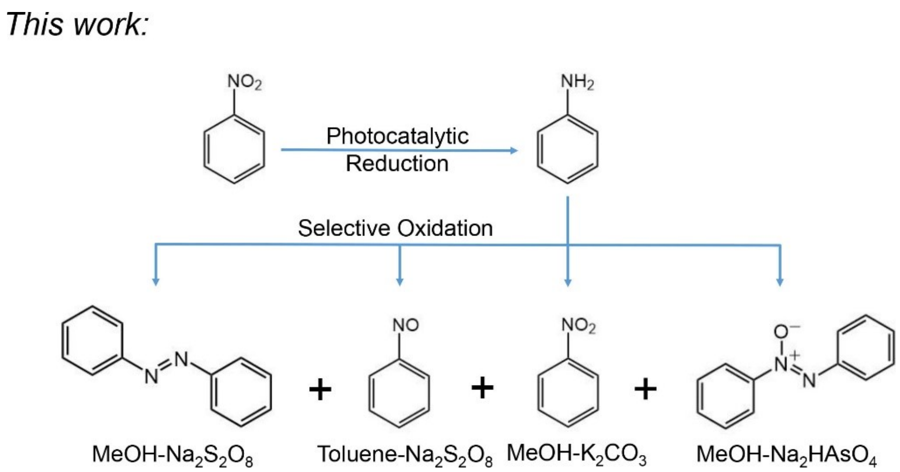
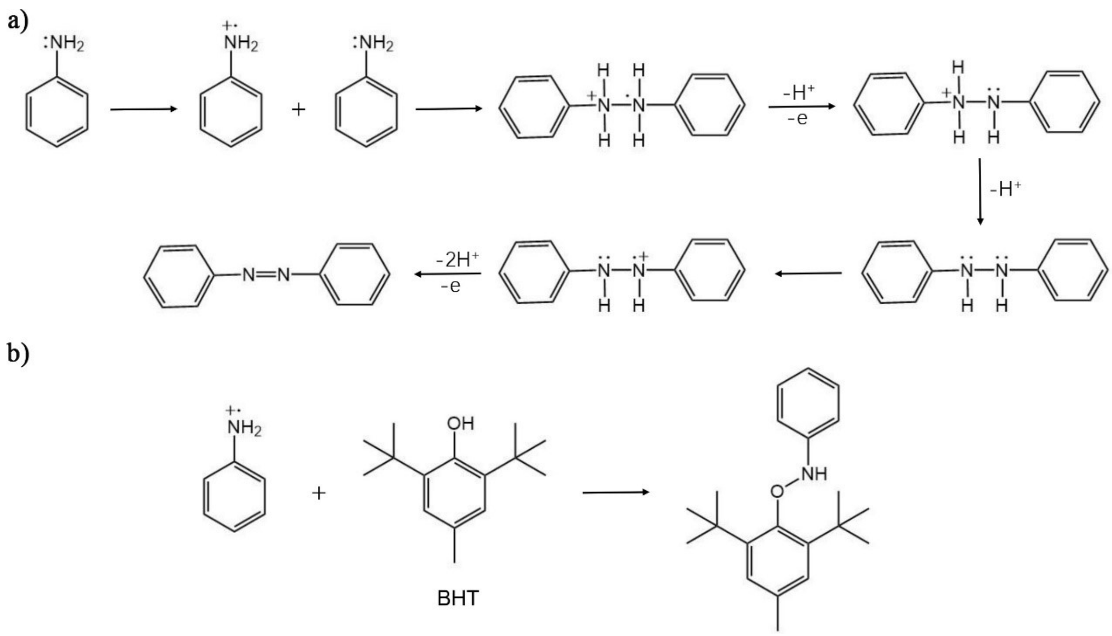


Figure S10. SEM images of a) **1** and b) **2**.



Scheme S1. The reaction systems of photocatalytic reduction of NB to anilines and selective oxidation of anilines to AOB, AB,



NSB and NB.

Scheme S2. a) The synthesis mechanism of azobenzene from aniline in oxygen atmosphere proposed by Corma; b) Spin trapping mechanism of aniline radical with BHT. The reaction mixture was analyzed by GC-MS after cooling to room temperature.

Scheme S3. Reaction mechanism of NB reduction to anilines proposed by Haber.

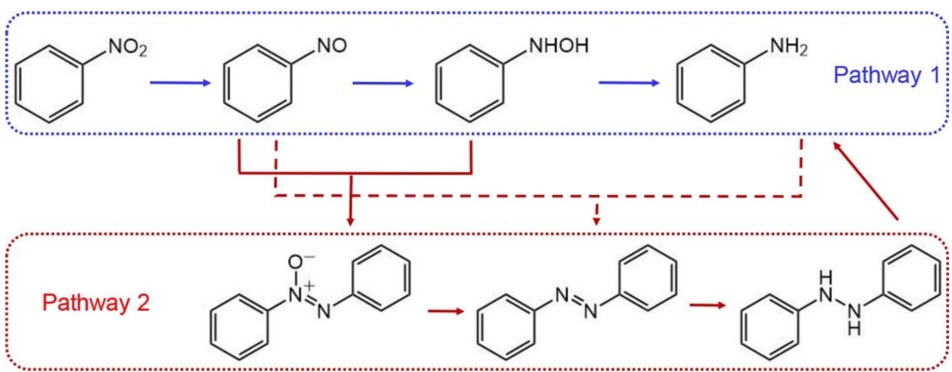


Table S1. Crystal data and structure refinement for compounds **1-3**.

Compound	**1**	**2**	**3**
Formula	$Na_4Cs_2Sb_6O_{273}Ru_4W_{69}Cl_3$	$Na_8Cs_2Sb_6O_{296}Ru_2W_{71}Cl_6$	$Na_{10}Sb_6O_{278}W_{67}$
M	18652.56	19384.43	17726.35
λ/Å	0.71073	0.71073	0.71073
T/K	150	150	150
Crystal dimensions/mm	0.11 × 0.08 × 0.07	0.18 × 0.16 × 0.12	0.1 × 0.05 × 0.04
Crystal system	triclinic	triclinic	triclinic
Space group	P-1	P-1	P-1
a/Å	20.0315 (5)	20.3555 (7)	18.065 (9)
b/Å	20.3566 (4)	20.4304 (6)	20.373 (9)
c/Å	21.2690 (5)	23.8990 (10)	24.517 (13)
α (°)	98.9870 (10)	79.8480 (10)	76.462 (14)
β (º)	115.7630 (10)	64.8990 (10)	73.843 (13)
γ (º)	92.0170 (10)	63.0760 (10)	64.497 (15)
V/Å^3	7663.0 (3)	8023.2 (5)	7754 (7)
Z	1	1	1
D_c/Mg m^{-3}	4.042	4.012	3.796
μ/mm^{-1}	26.844	26.301	25.356
F(000)	7977.0	8316.0	7598.0
2*θ* Range/°	4.332 to 50.198	4.342 to 50.2	4.386 to 50.198
Data/restraints/parameters	27229/47/1666	28494/79/1765	27614/87/1639
$R_1(I > 2\sigma(I))^a$	R_1 = 0.0463	R_1 = 0.0535	R_1 = 0.0527
wR_2 (all data)^b	wR_2 = 0.1365	wR_2 = 0.1611	wR_2 = 0.1617
Goodness-of-fit on F^2	1.025	1.038	1.021

[a] $R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $wR_2=\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

Table S2. Selected bond distances of compound **1**.

Bond	Bond length	Bond	Bond length	Bond	Bond length
Ru1–O3	2.043 (11)	Ru1–O11	1.893 (11)	Ru1–O12	1.926 (11)
Ru1–O22	2.072 (11)	Ru1–O24	1.905 (11)	Ru1–O41	2.043 (10)
Ru2–O92	2.068 (10)	Ru2–O121	2.430 (13)	Ru2–O122	2.18 (3)
Ru2–O123	2.21 (3)	Ru2–O124	2.25 (3)	Ru2–O108	2.114 (11)
Ru3–Cl1	2.363 (10)	Ru3–Cl2	2.348 (12)	Ru3–Cl3	2.361 (11)
Ru3–O89	2.032 (12)	Ru3–O96	1.991 (13)	Ru3–O97	2.017 (12)
Sb1–O4	1.994 (10)	Sb1–O13	2.011 (9)	Sb1–O40	2.003 (10)
Sb2–O59	1.990 (9)	Sb2–O66	1.985 (10)	Sb2–O27	1.994 (9)
Sb3–O53	2.020 (10)	Sb3–O55	1.972 (10)	Sb3–O46	2.001 (10)
W1–O1	2.074 (10)	W1–O2	1.897 (9)	W1–O3	1.755 (10)
W1–O10	1.920 (9)	W1–O19	2.220 (10)	W1–O47	1.781 (10)
W2–O5	2.116 (10)	W2–O6	1.941 (9)	W2–O92	1.771 (10)
W2–O41	1.764 (10)	W2–O17	1.911 (9)	W2–O52	2.231 (9)
W3–O52	1.739 (10)	W3–O1	1.839 (10)	W3–O70	1.975 (10)
W3–O13	2.203 (9)	W3–O30	1.915 (10)	W3–O36	1.959 (10)
W4–O5	1.818 (9)	W4–O14	1.983 (10)	W4–O18	1.901 (10)
W4–O19	1.769 (10)	W4–O25	1.949 (10)	W4–O27	2.225 (10)
W5–O59	2.276 (10)	W5–O61	1.960 (11)	W5–O6	1.900 (10)
W5–O18	1.925 (10)	W5–O26	1.916 (10)	W5–O99	1.708 (11)
W6–O20	2.088 (10)	W6–O22	1.755 (11)	W6–O87	1.851 (10)
W6–O90	2.264 (11)	W6–O34	2.002 (10)	W6–O108	1.766 (10)
W7–O50	1.964 (10)	W7–O59	2.284 (10)	W7–O61	1.920 (10)
W7–O21	1.882 (10)	W7–O28	1.935 (10)	W7–O105	1.722 (11)
W8–O7	1.904 (10)	W8–O13	2.291 (11)	W8–O16	1.910 (10)
W8–O80	1.924 (10)	W8–O36	1.896 (10)	W8–O106	1.715 (11)
W9–O48	1.950 (11)	W9–O4	2.295 (10)	W9–O10	1.927 (10)
W9–O91	1.704 (12)	W9–O30	1.906 (10)	W9–O38	1.913 (9)
W10–O55	2.256 (11)	W10–O81	1.991 (11)	W10–O29	1.910 (9)
W10–O93	1.722 (11)	W10–O33	1.947 (10)	W10–O42	1.897 (11)
W11–O14	1.884 (11)	W11–O27	2.280 (10)	W11–O35	1.951 (11)
W11–O98	1.728 (11)	W11–O39	1.902 (10)	W11–O43	1.916 (10)
W12–O63	1.996 (11)	W12–O64	1.961 (10)	W12–O74	1.935 (10)
W12–O20	1.831 (10)	W12–O88	1.734 (11)	W12–O46	2.275 (10)
W13–O55	2.305 (11)	W13–O74	1.903 (11)	W13–O32	1.951 (10)
W13–O34	1.856 (10)	W13–O100	1.713 (12)	W13–O42	1.990 (11)
W14–O62	1.951 (11)	W14–O64	1.913 (12)	W14–O8	1.919 (9)
W14–O85	1.927 (11)	W14–O103	1.709 (11)	W14–O46	2.260 (10)
W15–O51	1.915 (11)	W15–O70	1.902 (10)	W15–O13	2.314 (9)
W15–O80	1.937 (11)	W15–O86	1.921 (11)	W15–O111	1.707 (12)
W16–O56	1.913 (11)	W16–O68	1.900 (11)	W16–O25	1.924 (11)
W16–O27	2.320 (9)	W16–O39	1.945 (10)	W16–O113	1.704 (11)
W17–O66	2.229 (10)	W17–O69	1.937 (11)	W17–O76	1.945 (12)
W17–O23	1.907 (9)	W17–O97	1.724 (12)	W17–O45	1.882 (10)
W18–O56	1.891 (11)	W18–O59	2.315 (10)	W18–O78	1.912 (11)
W18–O26	1.919 (11)	W18–O28	1.952 (10)	W18–O107	1.702 (11)
W19–O53	2.319 (10)	W19–O67	1.949 (11)	W19–O81	1.879 (10)
W19–O82	1.939 (11)	W19–O83	1.920 (10)	W19–O104	1.707 (12)
W20–O53	2.232 (11)	W20–O54	1.889 (10)	W20–O77	1.926 (11)
W20–O83	1.938 (10)	W20–O89	1.714 (11)	W20–O37	1.902 (10)
W21–O67	1.885 (11)	W21–O55	2.338 (10)	W21–O79	1.907 (10)

W21–O32	1.945 (11)	W21–O33	1.902 (10)	W21–O101	1.726 (11)
W22–O48	1.898 (11)	W22–O49	1.944 (10)	W22–O4	2.276 (10)
W22–O71	1.964 (12)	W22–O15	1.926 (10)	W22–O102	1.699 (12)
W23–O49	1.922 (11)	W23–O51	1.893 (11)	W23–O4	2.295 (9)
W23–O73	1.858 (11)	W23–O38	1.956 (11)	W23–O226	1.728 (11)
W24–O50	1.884 (10)	W24–O58	1.914 (12)	W24–O66	2.333 (10)
W24–O76	1.922 (11)	W24–O78	1.938 (11)	W24–O120	1.721 (10)
W25–O58	1.958 (11)	W25–O66	2.346 (11)	W25–O68	1.935 (11)
W25–O69	1.919 (11)	W25–O95	1.687 (11)	W25–O35	1.913 (11)
W26–O63	1.901 (12)	W26–O79	1.902 (10)	W26–O85	1.942 (11)
W26–O94	1.900 (12)	W26–O115	1.717 (12)	W26–O46	2.317 (10)
W27–O53	2.300 (10)	W27–O62	1.894 (11)	W27–O77	1.966 (11)
W27–O82	1.917 (11)	W27–O94	1.931 (13)	W27–O110	1.712 (10)
W28–O54	1.900 (10)	W28–O75	2.173 (11)	W28–O21	1.979 (10)
W28–O23	1.876 (9)	W28–O24	1.809 (11)	W28–O29	1.952 (10)
W29–O60	1.935 (11)	W29–O65	1.946 (11)	W29–O9	1.897 (10)
W29–O96	1.765 (13)	W29–O40	2.235 (11)	W29–O44	1.895 (10)
W30–O60	1.913 (12)	W30–O72	1.928 (11)	W30–O16	1.922 (10)
W30–O86	1.923 (11)	W30–O40	2.332 (11)	W30–O109	1.729 (12)
W31–O7	1.925 (10)	W31–O9	1.886 (10)	W31–O12	1.816 (11)
W31–O84	2.169 (12)	W31–O43	1.930 (10)	W31–O45	1.896 (9)
W32–O57	2.159 (11)	W32–O8	1.930 (10)	W32–O11	1.829 (11)
W32–O15	1.933 (11)	W32–O37	1.891 (10)	W32–O44	1.882 (10)
W33–O65	1.894 (12)	W33–O71	1.878 (12)	W33–O72	1.949 (11)
W33–O73	1.984 (12)	W33–O40	2.313 (10)	W33–O114	1.706 (12)
W34–O87	1.936 (11)	W34–O112	2.424 (16)	W34–O117	1.746 (16)
W34–O118	1.741 (16)	W34–O119	2.097 (11)	W34–O47	2.128 (10)
W35–O2	1.908 (9)	W35–O17	1.892 (9)		

Table S3. Selected bond distances of compound **2**.

Bond	Bond length	Bond	Bond length	Bond	Bond length
Ru1–Cl1	2.335 (13)	Ru1–Cl2	2.309 (9)	Ru1–Cl3	2.322 (16)
Ru1–O54	2.013 (14)	Ru1–O87	1.987 (13)	Ru1–O94	2.002 (13)
Sb1–O50	1.956 (12)	Sb1–O63	2.020 (12)	Sb1–O64	1.994 (11)
Sb2–O61	2.000 (13)	Sb2–O25	2.021 (12)	Sb2–O34	2.008 (11)
Sb3–O62	1.993 (12)	Sb3–O69	1.997 (11)	Sb3–O19	1.992 (12)
W1–O55	1.793 (11)	W1–O3	2.072 (11)	W1–O4	1.851 (11)
W1–O13	2.226 (11)	W1–O20	1.946 (10)	W1–O21	1.756 (11)
W2–O71	1.918 (11)	W2–O13	1.757 (11)	W2–O79	1.994 (12)
W2–O25	2.205 (12)	W2–O44	1.931 (12)	W2–O45	1.809 (11)
W3–O27	1.767 (12)	W3–O32	1.717 (12)	W3–O33	1.901 (11)
W3–O37	1.884 (11)	W3–O42	2.214 (13)	W3–O45	2.120 (12)
W4–O63	2.193 (12)	W4–O3	1.826 (11)	W4–O15	1.942 (11)
W4–O42	1.767 (13)	W4–O46	1.917 (12)	W4–O43	1.987 (11)
W5–O63	2.290 (12)	W5–O8	1.948 (11)	W5–O72	1.912 (12)
W5–O12	1.898 (11)	W5–O109	1.701 (13)	W5–O43	1.907 (12)
W6–O68	1.975 (13)	W6–O71	1.912 (12)	W6–O89	1.909 (12)
W6–O33	1.940 (11)	W6–O34	2.246 (12)	W6–O98	1.741 (14)
W7–O51	1.938 (12)	W7–O67	1.942 (14)	W7–O18	1.915 (11)
W7–O25	2.289 (12)	W7–O108	1.719 (13)	W7–O44	1.888 (12)
W8–O1	1.959 (12)	W8–O64	2.282 (12)	W8–O11	1.879 (12)
W8–O75	1.691 (12)	W8–O20	1.909 (11)	W8–O46	1.896 (12)
W9–O50	2.239 (12)	W9–O16	1.893 (13)	W9–O23	1.856 (13)
W9–O87	1.751 (13)	W9–O91	1.952 (12)	W9–O92	1.982 (12)
W10–O58	1.851 (13)	W10–O64	2.310 (11)	W10–O11	2.008 (12)
W10–O17	1.928 (13)	W10–O82	1.912 (13)	W10–O107	1.728 (12)
W11–O69	2.258 (12)	W11–O14	1.843 (11)	W11–O90	1.958 (13)
W11–O35	1.942 (12)	W11–O39	1.990 (14)	W11–O106	1.699 (14)
W12–O52	2.256 (12)	W12–O2	1.732 (14)	W12–O66	1.783 (11)
W12–O14	2.073 (12)	W12–O22	1.964 (11)	W12–O115	1.871 (14)
W13–O54	1.750 (14)	W13–O59	1.878 (12)	W13–O61	2.210 (14)
W13–O73	1.974 (13)	W13–O77	1.899 (13)	W13–O83	1.949 (13)
W14–O63	2.300 (12)	W14–O72	1.937 (12)	W14–O15	1.924 (11)
W14–O82	1.907 (12)	W14–O30	1.879 (12)	W14–O102	1.716 (12)
W15–O53	1.947 (12)	W15–O60	1.857 (12)	W15–O9	1.887 (12)
W15–O19	2.222 (13)	W15–O94	1.731 (13)	W15–O38	1.949 (12)
W16–O62	2.275 (12)	W16–O5	1.896 (12)	W16–O6	1.977 (13)
W16–O86	1.875 (14)	W16–O97	1.939 (12)	W16–O111	1.702 (13)
W17–O62	2.275 (13)	W17–O7	1.921 (14)	W17–O22	1.889 (11)
W17–O86	2.007 (12)	W17–O90	1.876 (13)	W17–O100	1.697 (14)
W18–O50	2.361 (12)	W18–O8	1.904 (12)	W18–O92	1.902 (12)
W18–O30	1.973 (12)	W18–O96	1.708 (13)	W18–O41	1.932 (12)
W19–O57	1.967 (12)	W19–O68	1.904 (12)	W19–O81	1.938 (13)
W19–O34	2.272 (12)	W19–O104	1.712 (14)	W19–O47	1.876 (11)
W20–O69	2.272 (11)	W20–O70	1.911 (13)	W20–O35	1.919 (11)
W20–O105	1.718 (13)	W20–O40	1.913 (13)	W20–O48	1.946 (12)
W21–O49	1.867 (12)	W21–O50	2.360 (11)	W21–O58	1.973 (12)
W21–O91	1.891 (14)	W21–O99	1.716 (13)	W21–O41	1.928 (12)
W22–O49	1.992 (12)	W22–O1	1.924 (12)	W22–O64	2.281 (12)
W22–O17	1.983 (12)	W22–O85	1.730 (13)	W22–O29	1.864 (11)
W23–O74	1.880 (14)	W23–O76	1.878 (13)	W23–O81	1.928 (14)

W23–O89	1.939 (14)	W23–O34	2.320 (11)	W23–O119	1.729 (12)
W24–O65	1.940 (13)	W24–O6	1.871 (13)	W24–O80	1.913 (13)
W24–O19	2.325 (12)	W24–O38	1.909 (13)	W24–O112	1.723 (14)
W25–O53	1.933 (12)	W25–O80	1.960 (13)	W25–O19	2.336 (12)
W25–O93	1.928 (15)	W25–O95	1.701 (15)	W25–O40	1.912 (13)
W26–O51	1.935 (12)	W26–O56	1.924 (14)	W26–O76	1.916 (13)
W26–O79	1.897 (13)	W26–O25	2.305 (11)	W26–O114	1.727 (13)
W27–O69	2.324 (12)	W27–O93	1.895 (15)	W27–O101	1.707 (13)
W27–O103	1.889 (13)	W27–O39	1.911 (14)	W27–O48	1.935 (12)
W28–O62	2.317 (12)	W28–O65	1.873 (13)	W28–O7	1.971 (13)
W28–O97	1.939 (13)	W28–O103	1.920 (13)	W28–O113	1.709 (13)
W29–O57	1.862 (12)	W29–O61	2.329 (12)	W29–O73	1.888 (15)
W29–O74	1.964 (15)	W29–O88	1.917 (14)	W29–O120	1.732 (14)
W30–O56	1.924 (14)	W30–O61	2.329 (13)	W30–O67	1.896 (13)
W30–O83	1.929 (15)	W30–O88	1.941 (13)	W30–O116	1.721 (14)
W31–O12	1.936 (12)	W31–O16	1.879 (13)	W31–O77	1.876 (12)
W31–O18	1.920 (12)	W31–O26	1.969 (12)	W31–O31	2.037 (11)
W32–O59	1.899 (12)	W32–O5	1.944 (12)	W32–O9	1.889 (12)
W32–O84	1.939 (12)	W32–O24	2.064 (11)	W32–O47	1.965 (12)
W33–O60	1.906 (12)	W33–O10	1.897 (13)	W33–O70	1.932 (13)
W33–O23	1.915 (13)	W33–O28	2.128 (13)	W33–O29	1.984 (12)
W34–O66	2.089 (11)	W34–O10	1.836 (13)	W34–O21	2.108 (11)
W34–O84	1.828 (13)	W34–O26	1.864 (12)	W34–O27	2.087 (12)
W35–O55	2.112 (11)	W35–O115	1.907 (14)	W35–O117	2.102 (12)
W35–O118	2.393 (16)	W35–O121	1.734 (17)	W35–O122	1.730 (19)
W36–O4	1.925 (12)	W36–O78	1.700 (13)	W36–O37	1.923 (12)

Table S4. Selected bond distances of compound **3**.

Bond	Bond length	Bond	Bond length	Bond	Bond length
Sb1–O66	2.016 (12)	Sb1–O40	1.996 (13)	Sb1–O48	1.994 (12)
Sb2–O14	2.019 (12)	Sb2–O20	1.996 (12)	Sb2–O34	1.980 (11)
Sb3–O9	2.010 (15)	Sb3–O83	1.994 (14)	Sb3–O109	1.990 (13)
W1–O2	1.815 (13)	W1–O14	2.208 (11)	W1–O18	1.985 (12)
W1–O22	1.946 (12)	W1–O30	1.743 (12)	W1–O32	1.957 (11)
W2–O26	1.930 (11)	W2–O28	1.799 (11)	W2–O93	1.734 (13)
W2–O6	1.877 (10)	W2–O62	2.217 (13)	W2–O2	2.177 (11)
W3–O4	2.165 (11)	W3–O8	1.925 (12)	W3–O12	1.878 (12)
W3–O102	1.737 (11)	W3–O42	1.758 (11)	W3–O30	2.224 (12)
W4–O62	1.765 (12)	W4–O64	1.942 (13)	W4–O66	2.210 (11)
W4–O4	1.805 (11)	W4–O16	1.922 (14)	W4–O38	1.980 (11)
W5–O52	1.890 (14)	W5–O20	2.275 (12)	W5–O22	1.887 (12)
W5–O26	1.918 (13)	W5–O94	1.971 (13)	W5–O103	1.714 (14)
W6–O74	1.957 (11)	W6–O76	1.939 (14)	W6–O77	1.709 (13)
W6–O14	2.283 (11)	W6–O24	1.898 (13)	W6–O32	1.894 (12)
W7–O8	1.928 (11)	W7–O16	1.895 (14)	W7–O82	1.966 (14)
W7–O90	1.739 (13)	W7–O36	1.893 (13)	W7–O40	2.265 (12)
W8–O54	1.928 (12)	W8–O76	1.932 (13)	W8–O14	2.309 (13)
W8–O18	1.904 (11)	W8–O110	1.739 (14)	W8–O46	1.896 (13)
W9–O70	1.874 (12)	W9–O98	1.987 (13)	W9–O34	2.279 (13)
W9–O100	1.872 (13)	W9–O101	1.922 (15)	W9–O107	1.669 (16)
W10–O67	1.975 (15)	W10–O72	1.870 (13)	W10–O11	1.971 (13)
W10–O43	1.720 (14)	W10–O44	1.879 (13)	W10–O48	2.260 (12)
W11–O66	2.307 (12)	W11–O13	1.899 (16)	W11–O91	1.912 (18)
W11–O38	1.902 (12)	W11–O108	1.894 (13)	W11–O47	1.747 (13)
W12–O61	1.679 (16)	W12–O64	1.905 (12)	W12–O66	2.284 (13)
W12–O68	1.944 (14)	W12–O10	1.892 (11)	W12–O91	1.957 (14)
W13–O52	1.996 (12)	W13–O54	1.896 (12)	W13–O81	1.716 (15)
W13–O20	2.312 (13)	W13–O96	1.845 (14)	W13–O112	1.918 (13)
W14–O60	1.849 (13)	W14–O82	1.902 (15)	W14–O86	1.983 (13)
W14–O87	1.704 (16)	W14–O40	2.251 (14)	W14–O111	1.979 (13)
W15–O58	1.845 (15)	W15–O7	1.981 (13)	W15–O20	2.274 (12)
W15–O27	1.692 (14)	W15–O94	1.914 (13)	W15–O112	1.975 (14)
W16–O63	1.943 (13)	W16–O71	1.917 (15)	W16–O78	1.912 (12)
W16–O84	1.903 (15)	W16–O85	1.720 (14)	W16–O109	2.283 (13)
W17–O74	1.880 (11)	W17–O34	2.328 (12)	W17–O101	1.889 (17)
W17–O104	1.942 (13)	W17–O45	1.728 (14)	W17–O46	1.941 (14)
W18–O13	1.911 (16)	W18–O86	1.871 (16)	W18–O31	1.695 (14)
W18–O36	1.972 (12)	W18–O106	1.854 (13)	W18–O40	2.339 (12)
W19–O56	1.763 (13)	W19–O88	2.205 (12)	W19–O92	1.754 (15)
W19–O28	2.070 (11)	W19–O42	2.122 (11)	W19–O113	1.764 (12)
W20–O3	1.715 (14)	W20–O7	1.896 (14)	W20–O96	1.971 (15)
W20–O98	1.872 (14)	W20–O34	2.332 (12)	W20–O104	1.934 (14)
W21–O68	1.886 (15)	W21–O11	1.923 (12)	W21–O79	1.932 (17)
W21–O25	1.716 (15)	W21–O108	1.949 (13)	W21–O48	2.285 (13)
W22–O65	1.956 (14)	W22–O9	2.257 (14)	W22–O95	1.864 (14)
W22–O99	1.865 (13)	W22–O35	1.698 (18)	W22–O39	1.908 (15)
W23–O55	1.939 (12)	W23–O59	1.981 (15)	W23–O83	2.314 (17)
W23–O37	1.704 (18)	W23–O105	1.889 (12)	W23–O41	1.867 (14)
W24–O48	2.345 (15)	W24–O5	1.702 (18)	W24–O67	1.891 (13)

W24–O79	1.909 (16)	W24–O106	1.970 (12)	W24–O111	1.866 (14)
W25–O53	1.922 (16)	W25–O57	1.894 (14)	W25–O1	1.735 (19)
W25–O65	1.887 (15)	W25–O71	1.932 (15)	W25–O109	2.275 (15)
W26–O53	1.930 (17)	W26–O59	1.861 (16)	W26–O63	1.896 (14)
W26–O73	1.930 (15)	W26–O21	1.742 (16)	W26–O109	2.307 (14)
W27–O55	1.938 (16)	W27–O69	1.831 (13)	W27–O73	1.939 (14)
W27–O75	1.883 (19)	W27–O17	1.686 (16)	W27–O83	2.335 (14)
W28–O49	1.758 (14)	W28–O51	1.94 (2)	W28–O9	2.241 (13)
W28–O80	2.052 (13)	W28–O23	1.730 (15)	W28–O95	2.001 (14)
W29–O57	1.961 (14)	W29–O9	2.323 (15)	W29–O75	1.908 (18)
W29–O80	1.847 (13)	W29–O33	1.672 (18)	W29–O39	1.934 (15)
W30–O51	1.90 (2)	W30–O69	2.079 (14)	W30–O15	1.732 (15)
W30–O19	1.792 (16)	W30–O83	2.223 (13)	W30–O41	2.010 (17)
W31–O56	2.204 (13)	W31–O70	1.901 (12)	W31–O10	1.962 (11)
W31–O24	1.950 (13)	W31–O89	1.769 (13)	W31–O44	1.904 (13)
W32–O56	1.612 (15)	W32–O70	1.969 (17)	W32–O10	1.962 (15)
W32–O24	1.989 (19)	W32–O89	2.358 (15)	W32–O44	1.922 (18)
W33–O60	2.007 (13)	W33–O72	1.916 (13)	W33–O78	1.895 (12)
W33–O92	2.120 (15)	W33–O97	2.052 (13)	W33–O99	1.954 (13)
W34–O58	1.996 (15)	W34–O84	1.878 (15)	W34–O29	2.035 (12)
W34–O100	1.903 (13)	W34–O105	1.964 (13)	W34–O113	2.098 (12)
W35–O50	1.726 (11)	W35–O6	1.921 (10)	W35–O12	1.930 (12)

Table S5. BVS values of selected O atoms of compound **1**.

Atom	BVS	Atom	BVS	Atom	BVS	Atom	BVS
O1	1.89	O2	1.69	O3	2.03	O4	2.16
O5	1.89	O6	1.98	O7	2.01	O8	1.96
O9	2.14	O10	1.97	O11	1.99	O12	1.97
O13	2.07	O14	1.93	O15	1.93	O16	2.01
O17	2.05	O18	2.02	O19	1.93	O20	1.89
O21	1.94	O22	1.99	O23	1.81	O24	2.03
O25	2.05	O26	1.90	O27	2.20	O28	1.86
O29	1.93	O30	2.04	O31	**0.32**	O32	1.54
O33	1.96	O34	1.97	O35	1.92	O36	1.95
O37	2.11	O38	1.91	O39	2.14	O40	2.01
O41	1.99	O42	1.88	O43	1.97	O44	2.16
O45	2.16	O46	2.04	O47	2.01	O48	1.97
O49	1.92	O50	1.97	O51	2.07	O52	2.05
O53	2.00	O54	2.13	O55	2.07	O56	2.08
O57	**0.52**	O58	1.90	O59	20.4	O60	1.96
O61	1.88	O62	1.98	O63	1.85	O64	1.90
O65	1.99	O66	2.04	O67	2.01	O68	2.00
O69	1.94	O70	1.90	O71	1.99	O72	1.89
O73	2.01	O74	1.99	O75	**0.50**	O76	1.91
O77	1.85	O78	1.96	O79	2.07	O80	1.93
O81	1.93	O82	1.94	O83	1.94	O84	**0.51**
O85	1.91	O86	1.97	O87	2.15	O88	1.64
O89	2.22	O90	**0.39**	O91	1.78	O92	1.96
O93	1.69	O94	2.01	O95	1.86	O96	2.06
O97	2.20	O98	1.67	O99	1.76	O100	1.74
O101	1.68	O102	1.80	O103	1.75	O104	1.76
O105	1.69	O106	1.73	O107	1.79	O108	1.88
O109	1.66	O110	1.74	O111	1.76	O112	**0.25**
O113	1.78	O114	1.77	O115	1.72	O116	1.67
O117	1.59	O118	1.61	O119	**0.61**	O120	1.70
O121	**0.15**	O122	**0.25**	O123	**0.17**	O124	**0.16**

Table S6. BVS values of selected O atoms of compound **2**.

Atom	BVS	Atom	BVS	Atom	BVS	Atom	BVS
O1	1.87	O2	1.65	O3	1.94	O4	2.11
O5	1.99	O6	1.98	O7	1.85	O8	1.96
O9	2.16	O10	2.30	O11	1.89	O12	2.00
O13	1.97	O14	1.88	O15	1.92	O16	2.18
O17	1.81	O18	2.00	O19	2.04	O20	1.95
O21	2.14	O22	1.96	O23	2.18	O24	**0.67**
O25	2.05	O26	2.02	O27	2.13	O28	**0.57**
O29	1.99	O30	1.97	O31	**0.72**	O32	1.72
O33	1.98	O34	2.04	O35	1.93	O37	2.12
O38	1.94	O39	1.84	O40	2.02	O41	1.93
O42	1.95	O43	1.88	O44	2.04	O45	1.92
O46	2.06	O47	2.00	O48	1.88	O49	1.96
O50	2.07	O51	1.90	O52	**0.40**	O53	1.88
O54	2.09	O55	1.99	O56	1.96	O57	2.03
O58	2.05	O59	2.16	O60	2.21	O61	2.04
O62	2.05	O63	2.08	O64	2.04	O65	2.07
O66	2.06	O67	1.99	O68	1.89	O69	2.05
O70	1.98	O71	2.01	O72	1.96	O73	1.94
O74	1.99	O75	1.84	O76	2.11	O77	2.17
O78	**0.36**	O79	1.87	O80	1.90	O81	1.92
O82	2.04	O83	1.89	O84	2.21	O85	1.66
O86	1.90	O87	2.12	O88	1.94	O89	1.96
O90	2.01	O91	1.98	O92	1.88	O93	2.03
O94	2.19	O95	1.79	O96	1.76	O97	1.88
O98	1.61	O99	1.72	O100	1.81	O101	1.76
O102	1.72	O103	2.07	O104	1.74	O105	1.71
O106	1.80	O107	1.67	O108	1.71	O109	1.79
O111	1.79	O112	1.69	O113	1.75	O114	1.67
O115	2.16	O116	1.70	O117	**0.60**	O118	**0.28**
O119	1.66	O120	1.65	O121	1.64	O122	1.66

Table S7. BVS values of selected O atoms of compound **3**.

Atom	BVS	Atom	BVS	Atom	BVS	Atom	BVS
O1	1.64	O2	1.81	O3	1.73	O4	1.87
O5	1.79	O6	2.10	O7	1.90	O8	1.95
O9	2.05	O10	2.84	O11	1.85	O12	2.14
O13	2.07	O14	2.06	O15	1.65	O16	2.05
O17	1.87	O18	1.87	O19	1.41	O20	2.04
O21	1.60	O22	2.01	O23	1.66	O24	1.88
O25	1.72	O26	1.96	O27	1.84	O28	2.04
O29	**0.73**	O30	2.04	O31	1.82	O32	1.96
O33	1.94	O34	2.01	O35	1.81	O36	1.93
O37	1.78	O38	1.88	O39	1.98	O40	2.06
O41	1.92	O42	2.11	O43	1.70	O44	2.09
O45	1.67	O46	2.00	O47	1.58	O48	2.02
O49	1.54	O50	**0.33**	O51	1.99	O52	1.88
O53	1.95	O54	2.03	O55	1.89	O56	1.98
O57	1.95	O58	2.02	O59	2.00	O60	1.99
O61	1.90	O62	1.95	O63	1.99	O64	1.97
O65	1.98	O66	2.06	O67	1.93	O68	2.01
O69	1.91	O70	1.99	O71	1.96	O72	2.14
O73	1.91	O74	2.00	O75	2.12	O76	1.90
O77	1.75	O78	2.07	O79	1.98	O80	1.90
O81	1.72	O82	1.92	O83	2.05	O84	2.15
O85	1.70	O86	1.97	O87	1.78	O88	**0.46**
O89	**0.30**	O90	1.62	O91	1.91	O92	2.13
O93	1.64	O94	1.87	O95	1.95	O96	2.08
O97	**0.69**	O98	1.96	O99	2.06	O100	2.17
O101	1.90	O102	1.63	O103	1.73	O104	1.89
O105	1.96	O106	2.05	O107	1.95	O108	1.98
O109	2.06	O110	1.62	O111	1.99	O112	1.85
O113	2.13						

Table S8. Screening of solvents for aniline oxidation over **1** in H_2O_2 system.[a]

Entry	Solvent	Conv. %	Sel. of AOB %[b]	Sel. of AB %[b]	Sel. of NSB %[b]	Sel. of NB %[b]
1	Methanol	86	63	35	2	0
2	Ethanol	83	62	31	1	5
3	Acetonitrile	82	51	43	2	4
4	Acetone	79	60	33	5	2
5	Acetic acid	76	57	42	1	0
6	Diethyl ether	79	51	44	4	1
7	Petroleum ether	86	63	36	1	0
8	N-hexane	78	52	42	5	1
9	Cyclohexane	71	56	48	1	1
10	Toluene	64	34	31	31	3
11	Dichloromethane	77	49	46	3	1
12	Mesitylene	58	26	40	31	3

[a] Reaction conditions: aniline (1 mmol), catalyst (0.1 mol%), solvent (1 mL), H_2O_2 (30%, w/w, 2.0 equiv.), 30 ºC, 12 h. [b] Determined by GC and naphthalene as internal standard.

Table S9. Screening of additives for aniline oxidation over **1** in H_2O_2 system.[a]

Entry	Additive (equiv)	Conv. %	Sel. of AOB %[c]	Sel. of AB %[c]	Sel. of NSB %[c]	Sel. of NB %[c]
1	As_2O_3	88	76	22	2	0
2	$NaAsO_2$	93	73	26	1	0
3	Na_2HAsO_4	95	**96**	3	1	0
4	K_3PO_4	90	67	28	4	1
5	Na_2SO_3	74	52	47	1	0
6	Na_2HSO_3	82	53	43	4	0
7	Na_2SO_4	88	41	58	1	0
8	$Na_2S_2O_3$	74	58	37	5	0
9	$Na_2S_2O_4$	76	51	45	4	0
10	$Na_2S_2O_8$	99	20	**79**	1	0
11[b]	$Na_2S_2O_8$	99	0	12	**88**	0
12	K_2CO_3	82	14	32	3	**51**
13	Na_2CO_3	71	28	36	6	31
14	$NaHCO_3$	71	25	46	3	27

[a] Reaction conditions: aniline (1 mmol), catalyst (0.1 mol%), methanol (1 mL), H_2O_2 (30%, w/w, 2.0 equiv.), 30 ºC, 12 h. [b] Toluene (1 mL). [c] Determined by GC and naphthalene as internal standard.

Table S10. Optimization of the reaction conditions for oxidation of anline to AOB over **1** in H_2O_2 system.[a]

Entry	Catalyst (mol%)	T/ ºC	Time (h)	H_2O_2 (equiv)	Solvent (mL)	Additive (equiv)	Conv. %	Sel. of AOB % [b]
1	0.1	40	12	2.0	1	Na_2HAsO_4 (0.075)	99	98
2	0.1	40	12	2.0	1	Na_2HAsO_4 (0.05)	99	97
3	0.1	40	12	2.0	1	Na_2HAsO_4 (0.025)	99	96
4	0.15	40	12	2.0	1	Na_2HAsO_4 (0.05)	99	97
5	0.05	40	12	2.0	1	Na_2HAsO_4 (0.05)	99	96
6	0.1	30	12	2.0	1	Na_2HAsO_4 (0.05)	98	95
7	0.1	50	12	2.0	1	Na_2HAsO_4 (0.05)	99	95
8	0.1	40	12	2.5	1	Na_2HAsO_4 (0.05)	99	89
9	0.1	40	12	1.5	1	Na_2HAsO_4 (0.05)	98	91
10	0.1	40	24	2.0	1	Na_2HAsO_4 (0.05)	99	97
11	0.1	40	6	2.0	1	Na_2HAsO_4 (0.05)	98	91
12	0.1	40	12	2.0	2	Na_2HAsO_4 (0.05)	97	80
13	0.1	40	12	2.0	0.5	Na_2HAsO_4 (0.05)	99	74

[a] Reaction conditions: aniline (1 mmol), solvent (methanol). [b] Determined by GC and naphthalene as internal standard.

Table S11. Optimization of the reaction conditions for oxidation of anline to AB over **1** in H_2O_2 system.[a]

Entry	Catalyst (mol%)	T/ ºC	Time (h)	H_2O_2 (equiv)	Solvent (mL)	Additive (equiv)	Conv. %	Sel. of AB %[b]
1	0.1	40	24	1.6	3	$Na_2S_2O_8$ (0.075)	99	98
2	0.1	40	24	1.6	3	$Na_2S_2O_8$ (0.05)	99	97
3	0.1	40	24	1.6	3	$Na_2S_2O_8$ (0.025)	95	96
4	0.15	40	24	1.6	3	$Na_2S_2O_8$ (0.05)	99	97
5	0.05	40	24	1.6	3	$Na_2S_2O_8$ (0.05)	90	94
6	0.1	30	24	1.6	3	$Na_2S_2O_8$ (0.05)	79	87
7	0.1	50	24	1.6	3	$Na_2S_2O_8$ (0.05)	98	98
8	0.1	40	24	1.8	3	$Na_2S_2O_8$ (0.05)	99	91
9	0.1	40	24	1.4	3	$Na_2S_2O_8$ (0.05)	84	98
10	0.1	40	36	1.6	3	$Na_2S_2O_8$ (0.05)	99	99
11	0.1	40	18	1.6	3	$Na_2S_2O_8$ (0.05)	88	93
12	0.1	40	24	1.6	4	$Na_2S_2O_8$ (0.05)	84	98
13	0.1	40	24	1.6	2	$Na_2S_2O_8$ (0.05)	99	82

[a] Reaction conditions: aniline (1 mmol), solvent (methanol). [b] Determined by GC and naphthalene as internal standard.

Table S12. Optimization of the reaction conditions for oxidation of anline to NSB over **1** in H_2O_2 system.[a]

Entry	Catalyst (mol%)	T/ ºC	Time (h)	H_2O_2 (equiv)	Solvent (mL)	Additive (equiv)	Conv. %	Sel. of NSB %[b]
1	0.025	30	6	1.4	1	$Na_2S_2O_8$ (0.075)	99	87
2	0.025	30	6	1.4	1	$Na_2S_2O_8$ (0.05)	99	88
3	0.025	30	6	1.4	1	$Na_2S_2O_8$ (0.025)	91	89
4	0.03	30	6	1.4	1	$Na_2S_2O_8$ (0.05)	99	91
5	0.02	30	6	1.4	1	$Na_2S_2O_8$ (0.05)	89	86
6	0.025	25	6	1.4	1	$Na_2S_2O_8$ (0.05)	81	89
7	0.025	40	6	1.4	1	$Na_2S_2O_8$ (0.05)	99	73
8	0.025	30	6	1.6	1	$Na_2S_2O_8$ (0.05)	99	73
9	0.025	30	6	1.2	1	$Na_2S_2O_8$ (0.05)	72	89
10	0.025	30	8	1.4	1	$Na_2S_2O_8$ (0.05)	99	63
11	0.025	30	4	1.4	1	$Na_2S_2O_8$ (0.05)	83	70
12	0.025	30	6	1.4	2	$Na_2S_2O_8$ (0.05)	67	51
13	0.025	30	6	1.4	0.5	$Na_2S_2O_8$ (0.05)	98	43

[a] Reaction conditions: aniline (1 mmol), solvent (toluene). [b] Determined by GC and naphthalene as internal standard.

Table S13. Optimization of the reaction conditions for oxidation of anline to NB over **1** in H_2O_2 system.[a]

Entry	Catalyst (mol%)	T/ ºC	Time (h)	H_2O_2 (equiv)	Solvent (mL)	Additive (equiv)	Conv. %	Sel. of NB %[b]
1	0.05	40	2	5.0	1	K_2CO_3 (0.075)	99	99
2	0.05	40	2	5.0	1	K_2CO_3 (0.05)	99	99
3	0.05	40	2	5.0	1	K_2CO_3 (0.025)	92	93
4	0.06	40	2	5.0	1	K_2CO_3 (0.05)	99	99
5	0.03	40	2	5.0	1	K_2CO_3 (0.05)	91	96
6	0.05	30	2	5.0	1	K_2CO_3 (0.05)	74	89
7	0.05	50	2	5.0	1	K_2CO_3 (0.05)	99	99
8	0.05	40	2	6.0	1	K_2CO_3 (0.05)	99	97
9	0.05	40	2	4.0	1	K_2CO_3 (0.05)	92	93
10	0.05	40	3	5.0	1	K_2CO_3 (0.05)	99	99
11	0.05	40	1	5.0	1	K_2CO_3 (0.05)	86	94
12	0.05	40	2	5.0	2	K_2CO_3 (0.05)	84	89
13	0.05	40	2	5.0	0.5	K_2CO_3 (0.05)	99	83

[a] Reaction conditions: aniline (1 mmol), solvent (methanol). [b] Determined by GC and naphthalene as internal standard.

Table S14. The catalytic results of anilines oxidation reaction in Methanol-Na_2HAsO_4 system using different catalysts.[a]

Eentry	Catalyst	Conv. %	Sel of AOB %[b]	Sel. of AB %[b]	Sel. of NSB %[b]	Sel. of NB %[b]
1	none	0	0	0	0	0
2	Na_2WO_4	18	58	42	0	0
3	Sb_2O_3	0	0	0	0	0
4	$RuCl_3$	0	0	0	0	0
5	**1**	99	96	2	2	0
6	**1-HT**	92	95	1	1	0
7	**2**	87	91	9	0	0
8	**3**	49	85	15	0	0
9	**3-HT**	50	84	16	0	0

[a] Catalyst (0.1 mol%), **2a** (1.0 mmol), methanol (1.0 mL), 30% H_2O_2 (2.0 equiv), $Na_2S_2O_8$ (0.05 equiv), 40 °C, 12 h. [b] Determined by GC and naphthalene as internal standard.

Table S15. The catalytic results of anilines oxidation reaction in Methanol-$Na_2S_2O_8$ system using different catalysts.[a]

Eentry	Catalyst	Conv. %	Sel of AOB %[b]	Sel. of AB %[b]	Sel. of NSB %[b]	Sel. of NB %[b]
1	none	0	0	0	0	0
2	Na_2WO_4	29	23	77	0	0
3	Sb_2O_3	0	0	0	0	0
4	$RuCl_3$	0	0	0	0	0
5	**1**	99	0	98	2	0
6	**1-HT**	92	3	95	2	0
7	**2**	90	7	93	0	0
8	**3**	56	6	94	2	0
9	**3-HT**	57	18	82	0	0

[a] Catalyst (0.1 mol%), **2a** (1.0 mmol), methanol (3.0 mL), 30% H_2O_2 (1.5 equiv), $Na_2S_2O_8$ (0.05 equiv), 40 °C, 24 h. [b] Determined by GC and naphthalene as internal standard.

Table S16. The catalytic results of anilines oxidation reaction in Toluene-$Na_2S_2O_8$ system using different catalysts.[a]

Eentry	Catalyst	Conv. %	Sel of AOB %[b]	Sel. of AB %[b]	Sel. of NSB %[b]	Sel. of NB %[b]
1	none	0	0	0	0	0
2	Na_2WO_4	24	11	38	51	0
3	Sb_2O_3	0	0	0	0	0
4	$RuCl_3$	0	0	0	0	0
5	**1**	99	0	12	88	0
6	**1-HT**	93	12	13	75	0
7	**2**	94	9	9	82	0
8	**3**	44	32	14	54	0
9	**3-HT**	44	30	11	59	0

[a] Catalyst (0.025 mol%), **2a** (1.0 mmol), Toluene (1.0 mL), 30% H_2O_2 (1.5 equiv), $Na_2S_2O_8$ (0.05 equiv), 30 °C, 1 h. [b] Determined by GC and naphthalene as internal standard.

Table S17. The catalytic results of anilines oxidation reaction in Methanol-K_2CO_3 system using different catalysts.[a]

Eentry	Catalyst	Conv. %	Sel of AOB %[b]	Sel. of AB %[b]	Sel. of NSB %[b]	Sel. of NB %[b]
1	none	0	0	0	0	0
2	Na_2WO_4	26	6	42	0	53
3	Sb_2O_3	0	0	0	0	0
4	$RuCl_3$	0	0	0	0	0
5	**1**	99	0	0	0	99
6	**1-HT**	92	0	0	0	99
7	**2**	92	0	0	0	99
8	**3**	36	16	33	4	47
9	**3-HT**	37	19	31	4	46

[a] Catalyst (0.05 mol%), **2a** (1.0 mmol), methanol (1.0 mL), 30% H_2O_2 (5.0 equiv), K_2CO_3 (0.05 equiv), 40 °C, 2 h. [b] Determined by GC and naphthalene as internal standard.

Table S18. Experiments on investigating the reaction mechanism over **1** in H_2O_2 system.

Entry	Substrate	Solvent/mL	H_2O_2 Equiv.	Additive	Conv%	Sel. of AOB %[a]	Sel. of AB %[a]	Sel. of NSB %[a]	Sel. of NB %[a]
1[b]	Ph-NH_2+BHT	CH_3OH/1 mL	2.0	$NaHAsO_4$	99	96	0	4	0
2[c]	Ph-NH_2+BHT	CH_3OH/3 mL	1.6	$Na_2S_2O_8$	99	1	97	2	0
3[d]	Ph-NH_2+BHT	Toulene/1 mL	1.4	$Na_2S_2O_8$	95	16	3	81	0
4[e]	Ph-NH_2+BHT	CH_3OH/1 mL	5.0	K_2CO_3	99	2	0	0	98
5[f]	Ph-NHOH	CH_3OH/1 mL	2.0	no	99	98	0	2	0
6[g]	Ph-NHOH	CH_3OH/3 mL	1.6	$Na_2S_2O_8$	86	0	0	99	0
7[h]	Ph-NHOH	CH_3OH/3 mL	1.6	no	43	90	2	8	0
8[i]	Ph-NHOH	Toulene/1 mL	1.4	$Na_2S_2O_8$	99	18	0	82	0
9[j]	Ph-NHOH	Toulene/1 mL	1.4	no	46	16	1	83	0
10[k]	Ph-NHOH	CH_3OH/1 mL	5.0	K_2CO_3	99	2	0	1	97
11[l]	Ph-NHOH+Ph-NO	CH_3OH/1 mL	0	no	99	99	0	1	0
12[m]	Ph-NHOH+Ph-NO	CH_3OH/3 mL	0	$Na_2S_2O_8$	36	3	1	96	0
13[n]	Ph-NHOH+Ph-NO	CH_3OH/3 mL	0	no	99	99	0	1	0
14[o]	Ph-NHOH+Ph-NO	Toulene/1 mL	0	$Na_2S_2O_8$	21	20	2	78	0
15[p]	Ph-NHOH+Ph-NO	CH_3OH/1 mL	0	K_2CO_3	25	80	3	17	0
16[q]	Ph-NH_2+Ph-NO	CH_3OH/1 mL	0	$NaHAsO_4$	33	0	78	22	0
17[r]	Ph-NH_2+Ph-NO	CH_3OH/3 mL	0	$Na_2S_2O_8$	99	1	96	2	0
18[s]	Ph-NH_2+Ph-NO	Toulene/1 mL	0	$Na_2S_2O_8$	15	0	77	23	0
19[t]	Ph-NH_2+Ph-NO	CH_3OH/1 mL	0	K_2CO_3	22	0	89	11	0
20[u]	Ph-NH_2+Ph-NO	CH_3OH/1 mL	0	no	97	0	91	9	0
21[v]	Ph-NO	CH_3OH/1 mL	2.0	K_2CO_3	99	0	0	0	99
22[w]	Ph-NO	CH_3OH/1 mL	2.0	no	99	0	0	0	99

[a] Determined by GC and naphthalene as internal standard. [b] Reaction conditions: Ph-NH_2 (1 mmol), BHT (1.2 mmol), catalyst (0.1 mol% based on Ph-NH_2), additive (0.05 equiv.), 40°C, 12 h. [c] Reaction conditions: Ph-NH_2 (1 mmol), BHT (1.2 mmol), catalyst (0.1 mol% based on Ph-NH_2), additive (0.05 equiv.), 40°C, 24 h. [d] Reaction conditions: Ph-NH_2 (1 mmol), BHT (1.2 mmol), catalyst (0.025 mol% based on Ph-NH_2), additive (0.05 equiv.), 30°C, 1 h. [e] Reaction conditions: Ph-NH_2 (1 mmol), BHT (1.2 mmol), catalyst (0.05 mol% based on Ph-NH_2), additive (0.05 equiv.), 40°C, 2 h. [f] Reaction conditions: Ph-NHOH (1 mmol), catalyst (0.1 mol% based on Ph-NHOH), 40°C, 30 min. [g] Reaction conditions: Ph-NHOH (1 mmol), catalyst (0.1 mol% based on Ph-NHOH), additive (0.5 equiv.), 40°C, 24 h. [h] Reaction conditions: Ph-NHOH (1 mmol), catalyst (0.1 mol% based on Ph-NHOH), 40°C, 24 h. [i] Reaction conditions: Ph-NHOH (1 mmol), catalyst (0.025 mol% based on Ph-NHOH), additive (0.05 equiv.), 30°C, 1 h. [j] Reaction conditions: Ph-NHOH (1 mmol), catalyst (0.025 mol% based on Ph-NHOH), 30°C, 1 h. [k] Reaction conditions: Ph-NHOH (1 mmol), catalyst (0.05 mol% based on Ph-NHOH), additive (0.05 equiv.), 40°C, 2 h. [l] Reaction conditions: Ph-NHOH (0.5 mmol), Ph-NO (0.5 mmol), catalyst (0.1 mol% based on Ph-NHOH+Ph-NO), 40°C, 30 min. [m] Reaction conditions: Ph-NHOH (0.5 mmol), Ph-NO (0.5 mmol), catalyst (0.1 mol% based on Ph-NHOH+Ph-NO), additive (0.05 equiv.), 40°C, 24 h. [n] Reaction conditions: Ph-NHOH (0.5 mmol), Ph-NO (0.5 mmol), catalyst (0.1 mol% based on Ph-NHOH+Ph-NO), 40°C, 30 min. [o] Reaction conditions: Ph-NHOH (0.5 mmol), Ph-NO (0.5 mmol), additive (0.05 equiv.), catalyst (0.025 mol% based on Ph-NHOH+Ph-NO), 30°C, 1 h. [p] Reaction conditions: Ph-NHOH (0.5 mmol), Ph-NO (0.5 mmol), additive (0.05 equiv.), catalyst (0.05 mol% based on Ph-NHOH+Ph-NO), 40°C, 2 h. [q] Reaction conditions: Ph-NH_2 (0.5 mmol), Ph-NO (0.5 mmol), additive (0.05 equiv.), catalyst (0.1 mol% based on Ph-NH_2+Ph-NO), 40°C, 12 h. [r] Reaction conditions: Ph-NH_2 (0.5 mmol), Ph-NO (0.5 mmol), additive (0.05 equiv.), catalyst (0.1 mol% based on Ph-NH_2+Ph-NO), 40°C, 30 min. [s] Reaction conditions: aniline (0.5 mmol), Ph-NO (0.5 mmol), additive (0.05 equiv.), catalyst (0.025 mol% based on Ph-NH_2+Ph-NO) 30°C, 1 h. [t] Reaction conditions: Ph-NH_2 (0.5 mmol), Ph-NO (0.5 mmol), additive (0.05 equiv.), catalyst (0.05 mol% based on Ph-NH_2+Ph-NO), 40°C, 2 h. [u] Reaction conditions: Ph-NH_2 (0.5 mmol), Ph-NO (0.5 mmol), catalyst (0.05 mol% based on Ph-NH_2+Ph-NO), 40°C, 2 h. [v] Reaction conditions: Ph-NO (1 mmol), additive (0.05 equiv.), catalyst (0.05 mol% based on Ph-NO), 40°C, 30 min. [w] Reaction conditions: Ph-NO (1 mmol), (0.05 mol% based on Ph-NO), 40°C, 30min.

Table S19. Photocatalytic activity with different catalysts and control experiment.[a]

Entry	Catalyst	t(h)	Conv. %[c]	Sel. %[c]
1	**1**	4	99	99
2	**2**	6	99	99
3	**3**	6	43	99
4	Na_2WO_4	6	24	99
5	Sb_2O_3	6	24	99
6	$RuCl_3$	6	31	99
7	$RuCl_3$/**3**	6	40	99
8	**1**[b]	6	trace	trace
9	None	6	trace	trace

[a] Reaction conditions: substrate (0.5 mmol), catalyst (0.05 mol%), methanol (0.5 mL), $N_2H_4{\cdot}H_2O$ (2 mmol), 10 W LED lamp, rt. [b] Dark. [c] Determined by GC and naphthalene as internal standard.

Table S20. Photocatalytic activity of photocatalyst **1** with different solvents.[a]

Entry	Solvent	Conv. %[b]	Sel. %[b]
1	CH_3CN	45	98
2	CH_3CH_2OH	56	99
3	CH_2Cl	57	99
4	DMF	58	99
5	Toluene	46	99
6	Hexane	75	99
7	CH_3OH	99	99

[a] Reaction conditions: substrate (0.5 mmol), catalyst (0.05 mol%), solvent (0.5 mL), $N_2H_4{\cdot}H_2O$ (2 mmol), 10 W LED lamp, rt. [b] Determined by GC and naphthalene as internal standard.

Table S21. Photocatalytic activity of photocatalyst **1** with different substrates for reaction pathway study.[a]

Entry	Substrate	t(h)	Conv. %[c]	Sel. %[e]
1	Nitrobenzene	4	99	99
2	Nitrosobenzene	1	99	99
3	Hydroxylamine	0.5	99	99
4	Azobenzene	4	0	0
5	Azoxybenzene	4	25	0
6	Nitrobenzene+CCl_4[b]	4	11	99
7	Nitrobenzene[c]	4	0	0
8	Nitrobenzene+BHT[d]	4	99	99

[a] Reaction conditions: substrate (0.5 mmol), catalyst (0.05 mol%), methanol (0.5 mL), $N_2H_4{\cdot}H_2O$ (2 mmol), 10 W LED lamp, rt. [b] CCl_4 (0.5 mmol). [c] H_2 (2 atm) replace $N_2H_4{\cdot}H_2O$. [d] BHT (0.6 mmol). [e] Determined by GC and naphthalene as internal standard.

Table S22. The summary of aniline oxidation reaction.

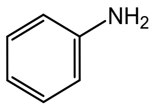
Catalyst	Solvent	Oxidizing agent	t	T	Conversion (%)	Yield				Ref
						AB	AOB	NSB	NB	
Material catalysts										
Au/TiO_2	toluene	O_2 (5 bars)	22 h	100 °C	100	98	0.5	1.5	--	5
Ti superoxide	MeOH	H_2O_2	0.5 h	25 °C	100	--	--	1.82	98.18	6
CuBr	toluene	air	20 h	60 °C	n.p	96	--	--	--	7
Meso-Mn_2O_3	toluene	air	8 h	110 °C	99	99	--	--	--	8
Na_{12}[-Ln_4]	$C_2H_4Cl_2$	H_2O_2	9 h	RT	100	--	100	--	--	9
Au/CeO_2	toluene	O_2 (5 bars)	10 h	100 °C	100	93	--	--	--	10
RuO_2/Cu_2O NPS	MeCN	air	16 h	85 °C	n.p	94	--	--	--	11
Ag/C-KOH	DMSO	air (1 atm)	24 h	60 °C	n.p	97	--	--	--	12
Ag/WO_3	CH_3CN	H_2O_2	24 h	25 °C	87	--	79	--	--	13
Nb_2O_5/FeOOH	propanol	H_2O_2	24 h	25 °C	100	--	70	--	--	14
$Zr(OH)_4$	methanol	H_2O_2	2 h	25 °C	98	--	96	3	--	15
$Zr(OH)_4$	acetic acid	TBHP	24 h	40 °C	96	90	3	1	--	15
$Zr(OH)_4$	mesitylene	H_2O_2	4 h	25 °C	96	0	12	84	--	15
WO_xMCN_x	CH_3CN	H_2O_2	12 h	90 °C	89.7	71.3	13	6.3	--	16
$CuCr_2O_4$	1,4-dioxane	H_2O_2	10 h	70 °C	78	--	71.8	--	--	17
AuPd@C	DMSO	O_2	12 h	25 °C	55	54	--	--	--	18
CuCl	CH_3CN	air	48 h	25 °C	n.p	33	--	--	--	19
$Ag_{1-x}Ni_x$	DMSO	air	24 h	60 °C	94.4	94	--	--	--	20
POM catalysts										
Mo_6	methanol	H_2O_2	24 h	60 °C	99	99	--	--	--	21
Mo_6	MTBE	H_2O_2	24 h	50 °C	99	--	93	--	--	21
Ru-POM	CH_3OH	H_2O_2	48 h	25 °C	n.p	--	94	--	--	22
Rh-POM	CH_3OH	H_2O_2	48 h	60 °C	n.p	--	95	--	--	23
1	methanol	H_2O_2	12	40 °C	99	--	97	--	--	This work
1	methanol	H_2O_2	24	40 °C	99	98	--	--	--	This work
1	toluene	H_2O_2	1	60 °C	99	--	--	88	--	This work
1	methanol	H_2O_2	2	60 °C	99	--	--	--	99	This work

Note: n.p = not provided

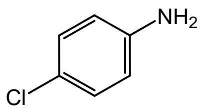
Table S23. Summary of the yield of the reduction of nitrobenzene with different catalysts.

Catalyst	T/°C	Light source	Hydrogen source	t/h	Yield/%	Ref.
Material catalysts						
Pd-Au NRs	25	λ> 320nm	HCOOH/HCOONa	5	>99	24
$PbBiO_2Br$	RT	440 nm	TEOA	6	>99	25
Cu-$CoFe_2O_4$	RT	Visible light	H_2O	1.5	99	26
Ag-rGO/g-C_3N_4	RT	λ> 400 nm	methanol	4	98	27
EY	RT	LED (525 nm)	TEOA	24	>99	28
3.0 wt% CQDs/$ZnIn_2S_4$	/	LED irradiation	TEOA/MeOH (1:1)	16	>99	29
Co@CN/SiO_2-500	70	/	N_2H_4•H_2O	1.2	>99.5	30
Pd/C	80	/	N_2H_4•H_2O	4	100	31
MMC-Fe_2O_3	80	/	N_2H_4•H_2O	2	100	32
Rh-Fe_2O_3	80	/	N_2H_4•H_2O	1	99	33
NC-90	90	/	N_2H_4•H_2O	1	100	34
Zr_{12}-TPDC-Co	110	/	$NaBEt_3H/H_2$	72	100	35
POM catalysts						
ZnW-TPT	RT	LED irradiation	N_2H_4•H_2O	6	99	36
Rh-POM	RT	10 W LED lamp	N_2H_4•H_2O	6	96	23
CoW-TPT	RT	365 nm	TEOA	12	95	37
1	RT	Visible light	N_2H_4•H_2O	6	97	This work

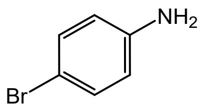
NMR data of products



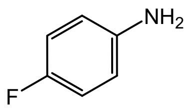
Aniline (2a) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.06 (t, *J*=8.36 Hz, 2H), 6.67 (t, *J*=7.36 Hz, 1H), 6.55–6.52 (dd, *J*=1.04, 0.92 Hz, 2H), 3.47 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.73, 129.48, 118.60, 115.29 ppm.



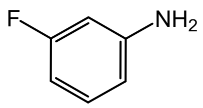
4-chloroaniline (2b) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 (d, *J*=8.72 Hz, 2H), 6.60 (d, *J*=8.72 Hz, 2H), 3.64 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.13, 129.15, 123.02, 116.31 ppm.



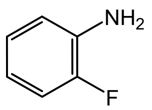
4-bromoaniline (2c) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (d, *J*=8.55 Hz, 2H), 6.62 (d, *J*=8.70 Hz, 2H), 3.64 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.46, 132.04, 116.74, 110.21 ppm.



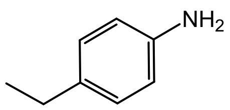
4-fluoroaniline (2d) ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.93 (t, *J*=8.73 Hz, 2H), 6.67 (dd, *J*=4.5, 4.5 Hz, 2H), 3.60 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.96, 154.85, 142.71, 115.84 ppm.



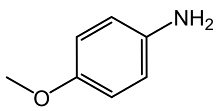
3-fluoroaniline (2e) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 (t, *J*=7.98 Hz, 1H), 6.83 (d, *J*=7.98 Hz, 1H), 6.71 (t, *J*=2.07 Hz, 1H), 6.61 (dd, *J*=2.16, 1.5 Hz, 1H), 3.76 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.89, 134.83, 130.49, 118.43, 114.99, 113.38 ppm.



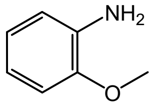
2-fluoroaniline (2f) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13–7.01 (m, 2H), 6.87–6.76 (m, 2H), 3.79 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.43, 150.27, 134.78, 134.61, 124.60, 118.73, 117.11, 115.43, 115.18 ppm.



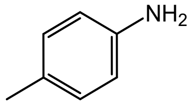
4-ethylaniline (2g) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (d, *J*=8.1 Hz, 2H), 6.79 (d, *J*=8.31 Hz, 2H), 3.65 (s, 2H), 2.78 (dd, *J*=7.56, 7.59 Hz, 2H), 1.42 (t, *J*=7.56 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.37, 134.45, 128.75, 115.45, 28.19, 16.17 ppm.



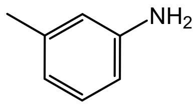
4-methoxyaniline (2h) ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.82 (d, *J*=8.85 Hz, 2H), 6.71 (d, *J*=8.85 Hz, 2H), 3.79 (s, 3H), 3.42 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.83, 140.02, 116.48, 114.86, 55.78 ppm.



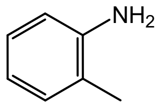
2-methoxyaniline (2i) ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.94–6.82 (m, 4H), 3.95 (s, 3H), 3.89 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.45, 136.44, 121.25, 118.49, 115.14, 110.63, 55.52 ppm.



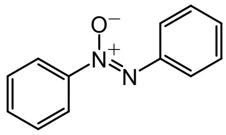
***p*-toluidine (2j)** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13 (d, *J*=8.07 Hz, 2H), 6.74 (d, *J*=8.28 Hz, 2H), 3.61 (s, 2H), 2.40 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.08, 129.89, 127.76, 115.40, 20.60 ppm.



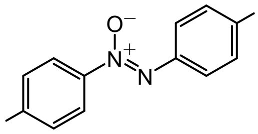
***m*-toluidine (2k)** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (t, *J*=7.71 Hz, 1H), 6.78 (d, *J*=7.59 Hz, 1H), 6.65 (d, *J*=6.42 Hz, 2H), 3.70 (s, 2H), 2.44 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.66, 139.21, 129.32, 119.52, 116.09, 112.43, 21.60 ppm.



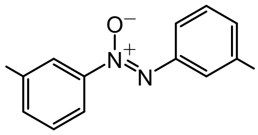
***o*-toluidine (2l)** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (t, *J*=7.32 Hz, 2H), 6.94 (t, *J*=7.35 Hz, 1H), 6.85 (d, *J*=7.86 Hz, 1H), 3.71 (s, 2H), 2.35 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.90, 130.65, 127.18, 122.49, 118.75, 115.14, 17.52 ppm.



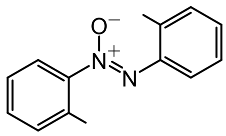
(*Z*)-Diphenyldiazene N-oxide (3a) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, *J*=8.7 Hz, 2H), 8.22 (d, *J*=8.3 Hz, 2H), 7.56–7.41 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.26, 143.94, 131.50, 129.54, 128.71, 125.47, 122.27 ppm.



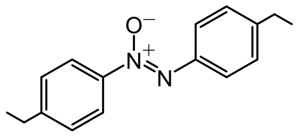
(*Z*)-1,2-Di-*p*-tolyldiazene 1-oxide (3b). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.25 Hz, 2H), 8.14 (d, *J* = 7.1 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 4H), 2.44 (d, *J* = 11.0 Hz, 6H). 13C NMR (126 MHz, $CDCl_3$) δ 146.21, 141.87, 139.95, 129.25, 125.61, 122.10, 21.50, 21.24 ppm.



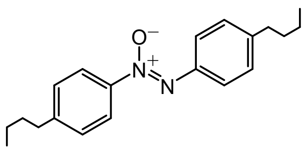
(*Z*)-1,2-Di-*m*-tolyldiazene 1-oxide (3c). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (t, *J* = 15.2 Hz, 2H), 8.00 (d, *J*=8.35 Hz, 2H), 7.39 (t, *J* = 19.85 Hz, 3H), 7.23 (d, *J* = 7.1 Hz, 1H), 2.48 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.40, 144.03, 138.95, 138.42, 132.25, 130.33, 128.56, 128.47, 125.98, 122.76, 122.48, 119.48, 21.45, 21.37 ppm.



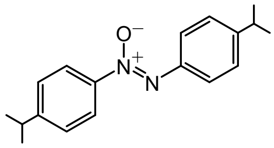
(*Z*)-1,2-Bis(2-methylphenyl)diazene 1-oxide (3d). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.75 Hz, 1H), 7.94 (d, *J* = 8.65 Hz, 1H), 7.70 (d, *J* = 7.75 Hz, 1H), 7.38–7.30 (m, 5H), 2.53 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.79, 134.10, 131.77, 130.77, 130.00, 128.56, 126.58, 126.04, 125.66, 123.58, 121.53, 18.42, 17.22 ppm.



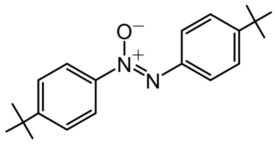
(*Z*)-1,2-bis(4-ethylphenyl)diazene 1-oxide (3e) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.7 Hz, 2H), 8.15 (d, *J* = 8.5 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 4H), 2.71–2.75 (m, 4H), 1.30–1.27 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.14, 146.21, 142.05, 128.06, 125.71, 122.25, 28.61, 15.28 ppm.



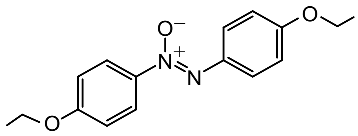
(*Z*)-1,2-bis(4-butylphenyl)diazene 1-oxide (3f) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.5 Hz, 2H), 8.15 (d, *J* = 12.6 Hz, 2H), 7.30 (d, *J* = 8.6 Hz, 4H), 2.72–2.66 (m, 4H), 1.65 (t, *J* = 5.9 Hz, 4H), 1.39 (d, *J* = 7.6 Hz, 4H), 0.95 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.84, 144.94, 142.01, 128.60, 125.62, 122.15, 35.59, 33.30, 22.23, 13.89 ppm.



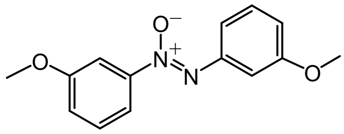
(*Z*)-1,2-bis(4-isopropylphenyl)diazene 1-oxide (3g) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22–8.20 (d, *J* = 8.75 Hz, 2H), 8.15–8.14 (d, *J* = 8.6 Hz, 2H), 7.34 (m, 4H), 3.01 (m, 2H), 1.29 (m, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.73, 149.77, 145.43, 141.13, 125.71, 124.71, 121.28, 32.98, 22.78 ppm.



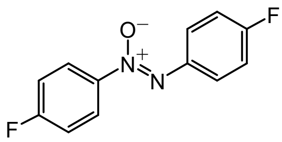
(*Z*)-1,2-bis(4-tert-butylphenyl)diazene 1-oxide (3h) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.95 Hz, 2H), 8.16 (d, *J* = 8.85 Hz, 2H), 7.52–7.50 (m, 4H), 1.38 (d, *J* = 2.8 Hz, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.00, 152.96, 146.06, 141.75, 125.53, 121.95, 34.94, 31.17 ppm.



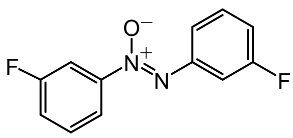
(Z)-1,2-bis(3-methoxyphenyl)diazene 1-oxide (3i) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (dd, *J* = 9.25, 9.2 Hz, 4H), 6.92 (dd, *J* = 9.2, 9.2 Hz, 4H), 4.08 (dd, *J* = 4.25, 4.25 Hz, 4H), 1.44 (dd, *J* = 7.0, 7.0 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.18, 159.55, 141.48, 137.82, 127.75, 123.66, 114.13, 63.63, 14.70 ppm.



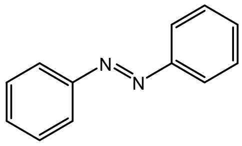
(Z)-1,2-bis(3-methoxyphenyl)diazene 1-oxide (3j) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* =8.15 Hz, 1H), 7.84 (t, *J* =2.3 Hz, 1H), 7.80 (t, *J* =2.05 Hz, 1H), 7.74 (d, *J* =7.95 Hz, 1H), 7.42 (dd, *J* =8.2, 8.15 Hz, 2H), 7.12 (d, *J* =11.35 Hz, 1H),6.98 (d, *J* =10.85 Hz, 1H), 3.91 (d, *J* =16.75 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.95, 149.56, 145.05, 129.49, 118.40, 116.32, 114.69, 110.06, 107.55, 55.45 ppm.



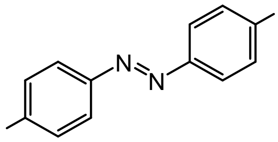
(*Z*)-1,2-bis(4-fluorophenyl)diazene 1-oxide (3k) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (dd, *J* = 4.8, 4.8 Hz, 2H), 7.26 (dd, *J* = 5.35, 5.35 Hz, 2H), 7.20–7.15 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.48, 143.24, 139.25, 127.00, 123.55, 114.78, 114.55 ppm.



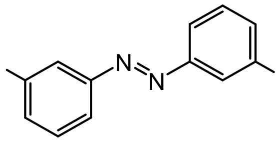
(Z)-1,2-bis(3-fluorophenyl)diazene 1-oxide (3l) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (dd, *J* = 1.55, 1.55 Hz, 1H), 8.08–8.03 (m, 2H), 7.86 (d, *J* = 8.15 Hz, 1H), 7.50–7.45 (m, 2H), 7.31–7.28 (m, 1H), 7.15–7.11 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.42, 161.40, 149.31, 144.83, 130.07, 129.72, 122.10, 119.08, 118.13, 116.76, 112.14, 110.20 ppm.



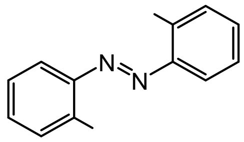
(E)-1,2-Diphenyldiazene (4a) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.35 Hz, 4H), 7.60–7.53 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.79, 131.10, 129.20, 123.01 ppm.



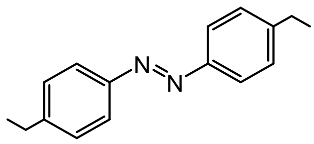
(E)-1,2-Di-p-tolyldiazene (4b) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.3 Hz, 4H), 7.31 (d, *J* = 8.05 Hz, 4H), 2.43 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.83, 141.19, 129.69, 122.71, 21.47 ppm.



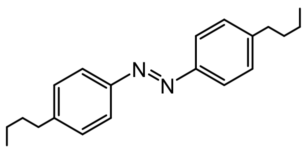
(E)-1,2-Di-m-tolyldiazene (4c) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (s, 4H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.30 (d, *J* = 7.5 Hz, 2H), 2.47 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.83, 138.98, 131.70, 128.91, 122.88, 120.48, 21.38 ppm.



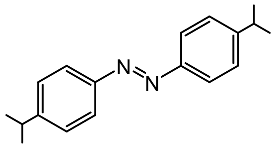
(E)-1,2-Di-o-tolyldiazene (4d) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.9 Hz, 2H), 7.37 (d, *J* = 7.35 Hz, 4H), 7.29 (d, *J* = 11.7 Hz, 2H), 2.75 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.10, 137.99, 131.25, 130.66, 126.35, 115.84, 17.60 ppm.



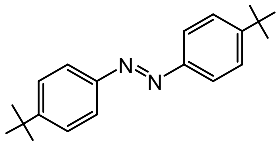
(E)-1,2-bis(4-ethylphenyl)diazene (4e) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.2 Hz, 4H), 7.39 (d, *J* = 8.1 Hz, 4H), 2.78 (d, *J* = 7.65 Hz, 4H), 1.33 (t, *J* = 7.6 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.14, 147.50, 128.57, 122.91, 28.89, 15.50 ppm.



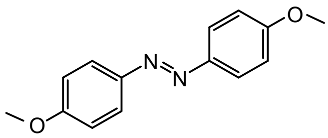
(E)-1,2-bis(4-butylphenyl)diazene (4f) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.35 Hz, 4H), 7.32 (d, *J* = 8.4 Hz, 4H), 2.69 (t, *J* = 7.65 Hz, 4H), 1.68–1.62 (m, 4H), 1.41–1.36 (m, 4H), 0.95 (t, *J* = 7.35 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.04, 146.17, 129.05, 122.69, 35.56, 33.45, 22.33, 13.93 ppm.



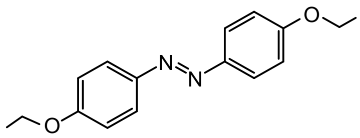
(E)-1,2-bis(4-isopropylphenyl)diazene (4g) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, J = 8.4 Hz, 4H), 7.38 (d, J = 8.3 Hz, 4H), 1.31 (d, J = 6.95 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.99, 151.17, 127.05, 122.78, 34.12, 23.86 ppm.



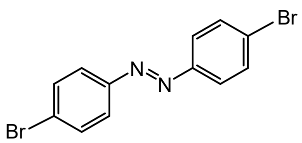
(E)-1,2-bis(4-tert-butylphenyl)diazene (4h) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, J = 8.65 Hz, 4H), 7.54 (d, J = 8.65 Hz, 4H), 1.38 (s, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.22, 150.76, 125.96, 122.43, 34.97, 31.28 ppm.



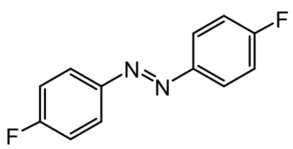
(E)-1,2-bis(4-methoxyphenyl)diazene (4i) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, J = 8.95 Hz, 4H), 7.01 (d, J = 8.95 Hz, 4H), 3.89 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.57, 147.11, 124.35, 114.17, 55.57 ppm.



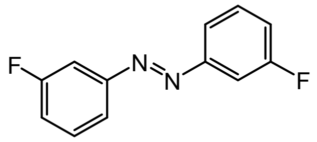
(E)-1,2-bis(4-ethoxyphenyl)diazene (4j) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, J = 9 Hz, 4H), 7.00 (d, J = 9 Hz, 4H), 4.13 (dd, J = 7, 6.95 Hz, 4H), 1.45 (t, J = 7 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.97, 147.00, 124.32, 114.65, 63.78, 14.80 ppm.



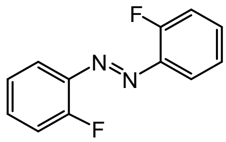
(E)-1,2-bis(4-bromophenyl)diazene (4k) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, J = 8.7 Hz, 4H), 7.66 (d, J = 8.75 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.15, 132.40, 124.41 ppm.



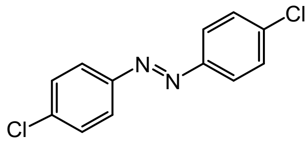
(E)-1,2-bis(4-fluorophenyl)diazene (4l) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94–7.91 (m, 4H), 7.21–7.18 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.36, 148.96, 124.75, 116.08 ppm.



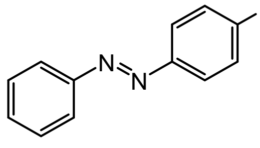
(E)-1,2-bis(3-fluorophenyl)diazene (4m) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (dt, *J* = 1.7, 1 Hz, 2H), 7.62 (dt, *J* = 4.35, 4.35 Hz, 2H), 7.53 (dt, *J* = 8.1, 8.05 Hz, 2H), 7.21–7.19 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.29, 153.76, 130.30, 120.79, 118.29, 108.23 ppm.



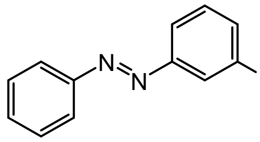
(E)-1,2-bis(2-fluorophenyl)phenyl (4n) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (t, *J* = 6.15 Hz, 2H), 7.55–7.50 (m, 2H), 7.34–7.28 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.39, 159.34, 140.83, 133.02, 124.34, 117.90 ppm.



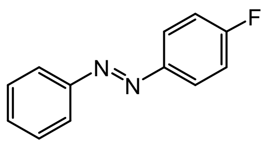
(E)-1,2-bis(4-chlorophenyl)diazene (4o) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.7 Hz, 4H), 7.50 (d, *J* = 8.7 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.80, 137.23, 129.40, 124.18 ppm.



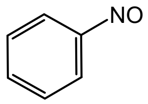
(E)-1-(4-methylphenyl)-2-phenyldiazene (4p) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (t, *J* = 11.25 Hz, 2H), 7.84 (t, *J* = 11.15 Hz, 2H), 7.54–7.51 (m, 3H), 7.33 (t, *J* = 6 Hz, 2H), 2.46 (d, *J* = 3.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.73, 150.83, 141.16, 130.66, 129.68, 129.02, 122.84, 122.70, 21.45 ppm.



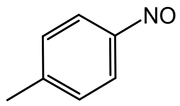
(E)-1-(3-methylphenyl)-2-phenyldiazene (4q) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (t, *J* = 5.85 Hz, 2H), 7.73 (d, *J* = 5.55 Hz, 2H), 7.53–7.51 (m, 2H), 7.48–7.40 (m, 2H), 2.47 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.74, 139.00, 131.69, 130.99, 129.10, 122.86, 120.47, 21.38 ppm.



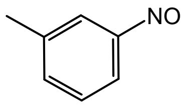
(E)-1-(4-fluorophenyl)-2-phenyldiazene (4r) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97–7.91 (m, 4H), 7.53–7.48 (m, 3H), 7.22–7.19 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.34, 151.45, 148.12, 130.00, 128.07, 123.79, 121.78, 114.91 ppm.



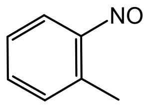
Nitrosobenzene (5a) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.9 Hz, 2H), 7.61 (t, *J* = 7.3 Hz, 1H), 7.52 (d, *J* = 2.9 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.77, 134.54, 128.21, 119.76 ppm.



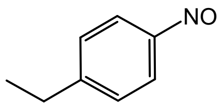
4-Methylnitrosobenzene (5b) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (dd, *J* = 8.6, 8.45 Hz, 2H), 7.29 (d, *J* = 8.25 Hz, 2H), 2.44 (d, *J* = 13.25 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.56, 146.23, 129.28, 122.13, 21.52 ppm.



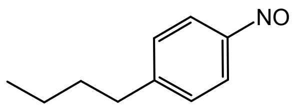
3-Methylnitrosobenzene (5c) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11–7.96 (m, 1H), 7.78 (d, *J* = 7.25 Hz, 1H), 7.64–7.52 (m, 1H), 7.50–7.36 (m, 1H), 2.50 (d, *J* = 17.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.25, 139.44, 136.21, 129.08, 120.66, 119.01, 21.14 ppm.



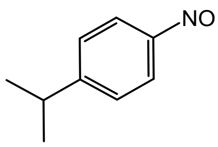
2-Methylnitrosobenzene (5d) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.2 Hz, 1H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.15 (t, *J* = 7.95 Hz, 1H), 6.29 (d, *J* = 8.15 Hz, 1H), 3.35 (s, 3H),. ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.97, 141.28, 135.22, 131.91, 124.64, 106.31, 16.19 ppm.



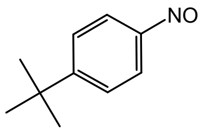
4-ethylphenylnitrosobenzene (5e) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8 Hz, 2H), 7.42 (d, *J* = 8.05 Hz, 2H), 2.76 (dd, *J* = 7.6, 7.55 Hz, 2H), 1.29 (t, *J* = 7.65 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.69, 153.14, 128.53, 121.35, 29.16, 14.84 ppm.



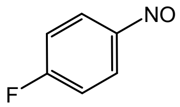
4-butylphenylnitrosobenzene (5f) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.2 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 2.70 (t, *J* = 7.7 Hz, 2H), 1.65 (t, *J* = 7.75 Hz, 2H), 1.38 (t, *J* = 7.45 Hz, 2H), 0.96 (d, *J* = 7.35 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.70, 152.02, 129.08, 121.31, 35.92, 32.95, 22.31, 13.84 ppm.



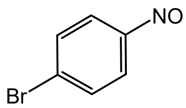
4-isopropylphenylnitrosobenzene (5g) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.25 Hz, 2H), 7.46 (d, *J* = 8.35 Hz, 2H), 3.01 (t, *J* = 6.9 Hz, 1H), 1.31 (d, *J* = 6.85 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.78, 157.60, 127.16, 121.43, 34.56, 23.44 ppm.



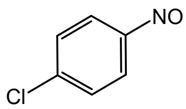
4-tert-butylphenylnitrosobenzene (5h) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.5 Hz, 2H), 7.63 (d, *J* = 8.8 Hz, 2H), 1.38 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.21, 158.76, 125.05, 119.99, 34.60, 29.94 ppm.



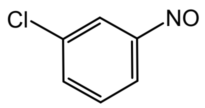
4-fluorophenylnitrosobenzene (5i) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 5.25, 5.2 Hz, 2H), 7.33 (t, *J* = 8 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.89, 162.59, 122.97, 115.25 ppm.



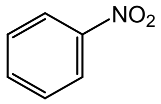
1-Bromo-4-nitrosobenzene (5j) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 1.9 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.82, 132.69, 131.69, 122.12 ppm.



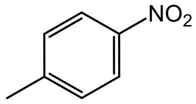
4-chlorophenylnitrosobenzene (5k) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.65 Hz, 2H), 7.60 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.72, 142.26, 129.66, 122.15 ppm.



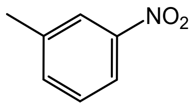
3-chlorophenylnitrosobenzene (5l) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.75 Hz, 1H), 7.70 (d, *J* = 7.4 Hz, 1H), 7.65 (t, *J* = 7.9, 7.75 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.03, 136.02, 134.96, 130.72 , 121.44, 118.72 ppm.



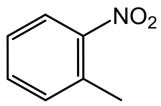
Nitrobenzene (6a) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.8 Hz, 2H), 7.59 (t, *J* = 7.55 Hz, 1H), 7.42 (t, *J* = 9.1 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.91, 134.57, 129.21, 123.09 ppm.



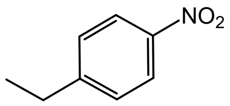
4-methylnitrobenzene (6b) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.85 Hz, 2H), 7.18 (d, *J* = 8.8 Hz, 2H), 2.31 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.04, 144.96, 128.71, 122.24, 20.27 ppm.



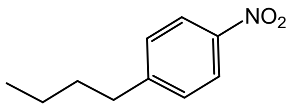
3-methylnitrobenzene (6c) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.85 Hz, 2H), 7.46 (d, *J* = 7.65 Hz, 1H), 7.38 (d, *J* = 8 Hz, 1H), 2.42 (d, *J* = 6.75 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.15, 138.75, 134.30, 128.00, 122.69, 119.52, 20.08 ppm.



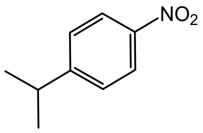
2-methylnitrobenzene (6d) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.25 Hz, 1H), 7.49 (d, *J* = 8.75 Hz, 1H), 7.33 (t, *J* = 4.95 Hz, 2H), 2.60 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.28, 131.95, 131.71, 125.85, 123.59, 19.34 ppm.



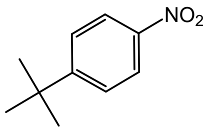
4-ethylphenylnitrobenzene (6e) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.8 Hz, 2H), 7.29 (d, *J* = 8.85 Hz, 2H), 2.71 (d, *J* = 7.7 Hz, 2H), 1.25 (d, *J* = 7.65 Hz, 3H),. ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.02, 145.16, 127.58, 122.49, 27.77, 13.92 ppm.



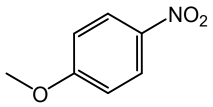
4-butylphenyllnitrobenzene (6f) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 8.55, 8.6 Hz, 2H), 7.30 (t, *J* = 8.05 Hz, 2H), 2.71 (d, *J* = 7.55 Hz, 2H), 1.64 (d, *J* = 8.1 Hz, 2H), 1.37 (t, *J* = 7.45 Hz, 2H), 0.95 (t, *J* = 7.35 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.75, 145.85, 128.09, 122.48, 34.50, 32.03, 21.22, 12.79 ppm.



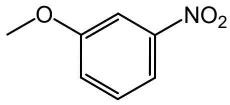
4-isopropylphenylnitrobenzene (6g) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.85 Hz, 2H), 7.17 (d, *J* = 8.9 Hz, 2H), 2.81 (t, *J* = 6.95 Hz, 1H), 1.09 (t, *J* = 5.35 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.50, 145.13, 126.18, 122.46, 33.13, 22.37 ppm.



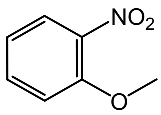
4-tert-butylphenylnitrobenzene (6h) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.85 Hz, 2H), 7.34 (d, *J* = 8.9 Hz, 2H), 1.19 (d, *J* = 11.7 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.71, 144.75, 125.12, 122.11, 34.17, 29.82 ppm.



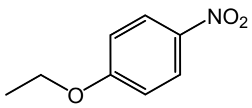
4-methoxyphenylnitrobenzene (6i) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 9.3 Hz, 2H), 6.93 (d, *J* = 9.3 Hz, 2H), 3.87 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.61, 140.46, 124.83, 112.99, 54.93 ppm.



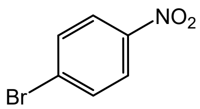
3-methoxyphenylnitrobenzene (6j) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.1 Hz, 1H), 7.72 (s, 1H), 7.42 (t, *J* = 8.25 Hz, 1H), 7.23 (d, *J* = 8.3 Hz, 1H), 3.89 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.12, 149.23, 129.88, 121.24, 115.71, 108.10, 55.79 ppm.



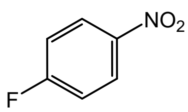
2-methoxyphenylnitrobenzene (6k) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.1 Hz, 1H), 7.39 (t, *J* = 8.65 Hz, 1H), 6.97 (d, *J* = 8.5 Hz, 1H), 6.87 (t, *J* = 7.2 Hz, 1H), 3.79 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.86, 139.59, 134.34, 125.44, 120.23, 113.59, 56.40 ppm.



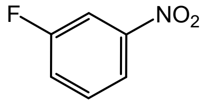
4-ethoxyphenylnitrobenzene (6l) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 9.25 Hz, 2H), 6.90 (d, *J* = 9.25 Hz, 2H), 4.10 (dd, *J* = 7, 7 Hz, 2H), 1.41 (t, *J* = 7.05 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.07, 140.24, 124.81, 113.36, 63.43, 13.49 ppm.



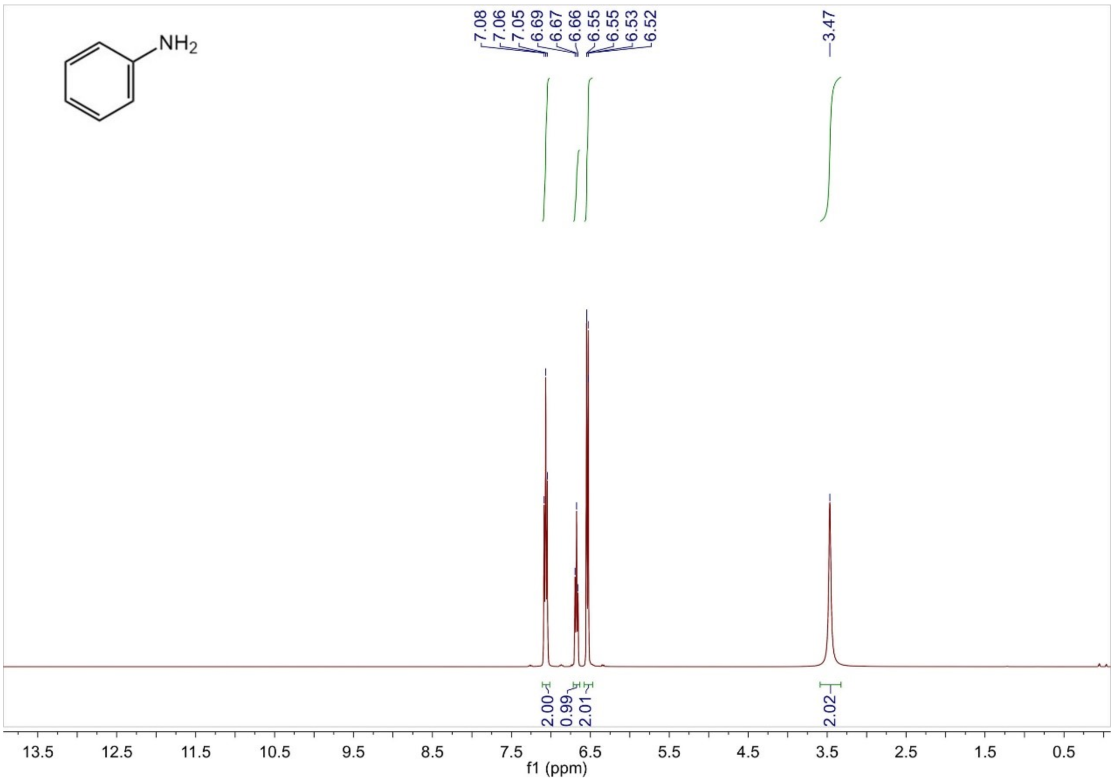
1-Bromo-4-nitrobenzene (6m) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 11.25 Hz, 2H), 7.70 (d, *J* = 11.25 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.03, 132.64, 130.00, 125.02 ppm.

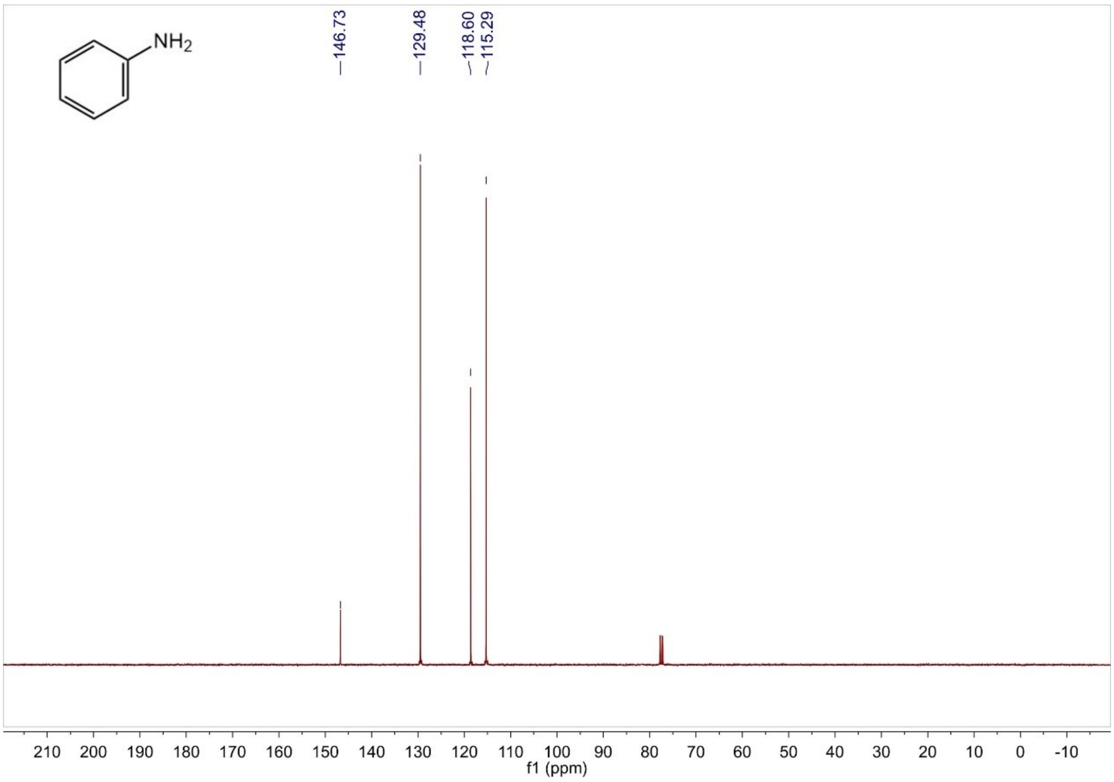


4-Fluoronitrobenzene (6n) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 11.25 Hz, 2H), 7.52 (d, *J* = 11.25 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.52, 141.39, 129.60, 124.95 ppm.



3-Fluoronitrobenzene (6o) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 10.25 Hz, 1H), 7.89–7.86 (m, 1H) , 7.57–7.52 (m, 1H) , 7.43–7.39 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.58, 149.15, 130.83, 121.79, 119.28, 111.33 ppm.

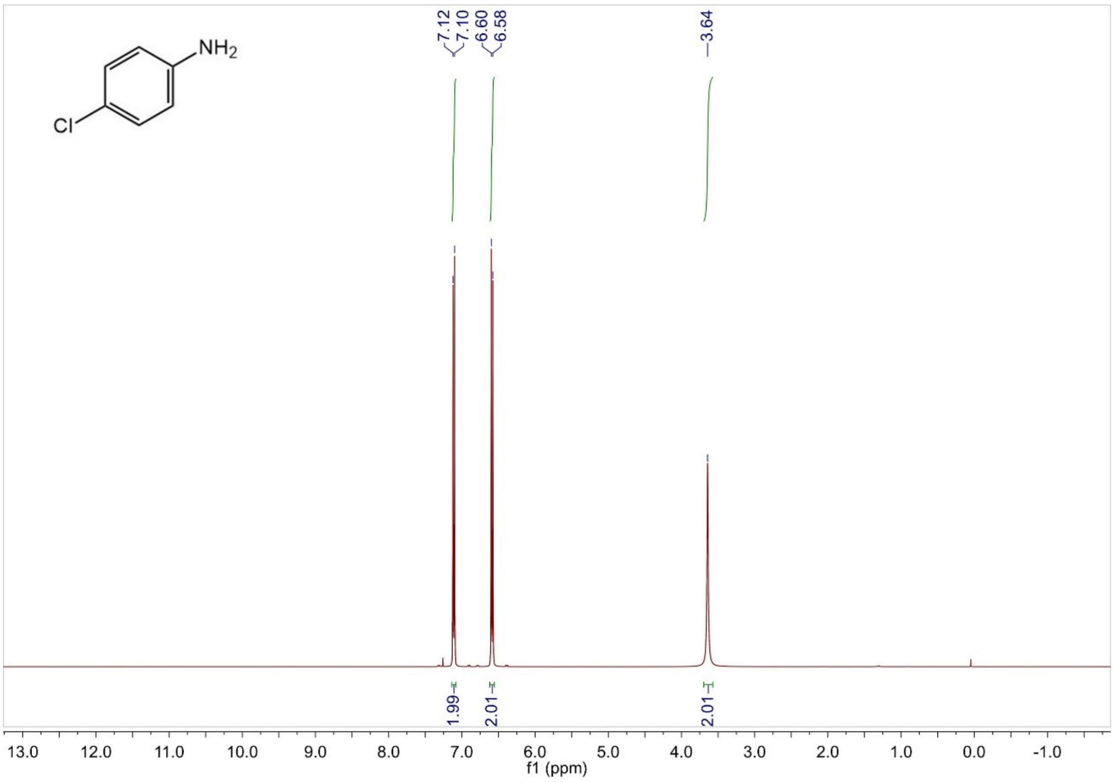


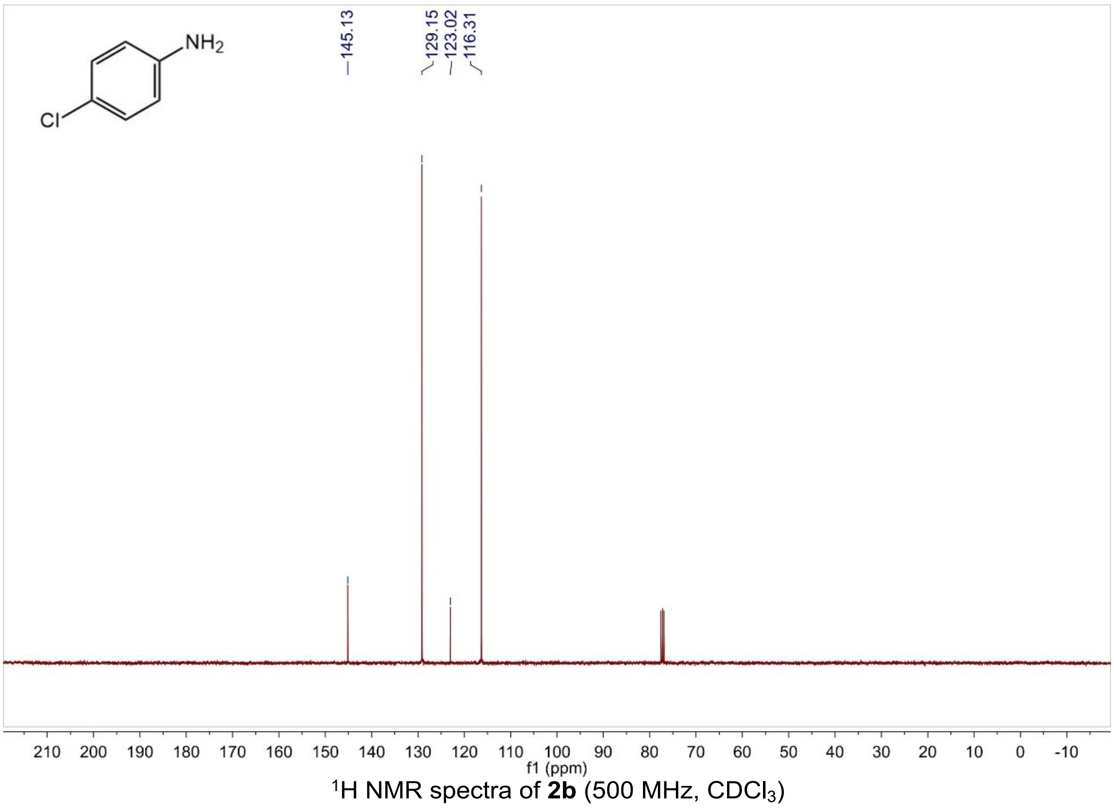


[1]H NMR and [13]C NMR spectra of spectra

^{1}H NMR spectra of **2a** (500 MHz, $CDCl_3$)

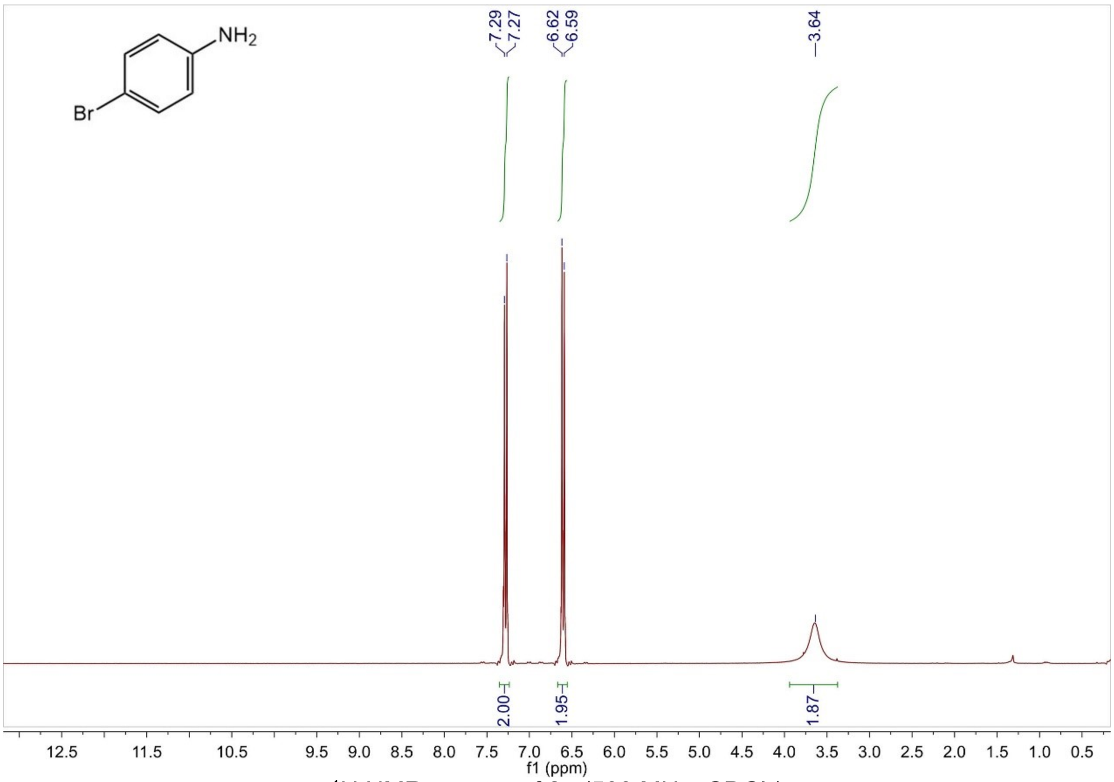
^{13}C NMR spectra of **2a** (126 MHz, $CDCl_3$)



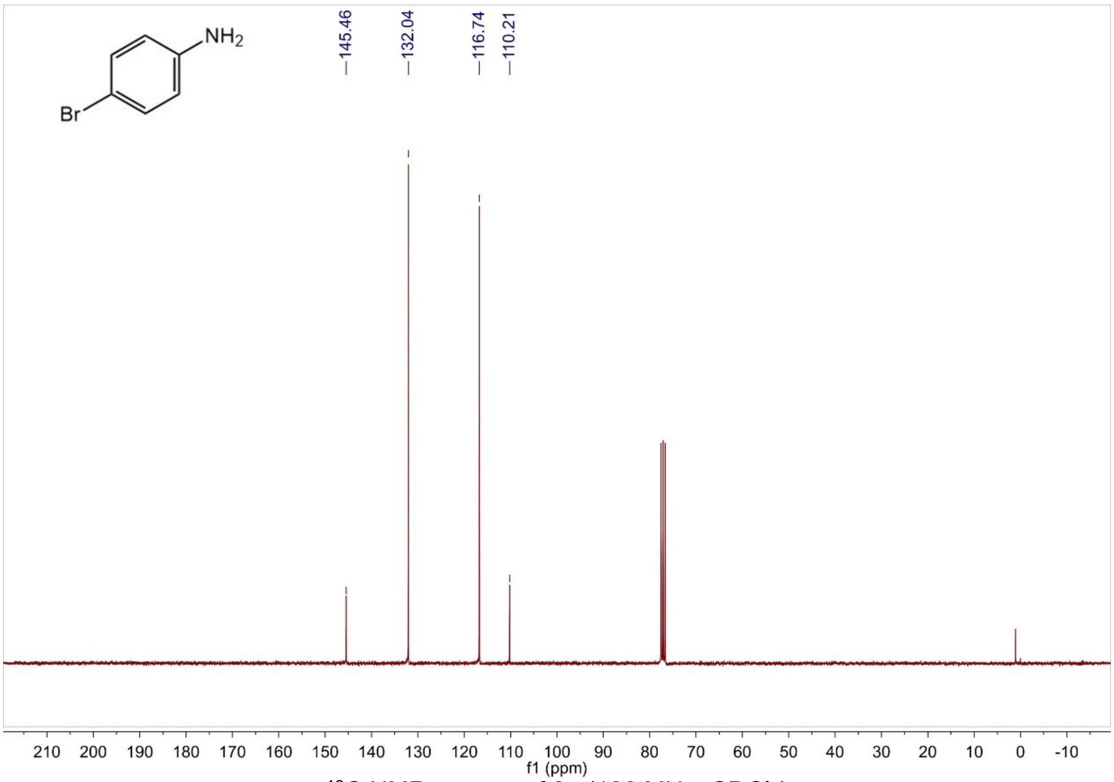


^{1}H NMR spectra of **2b** (500 MHz, $CDCl_3$)

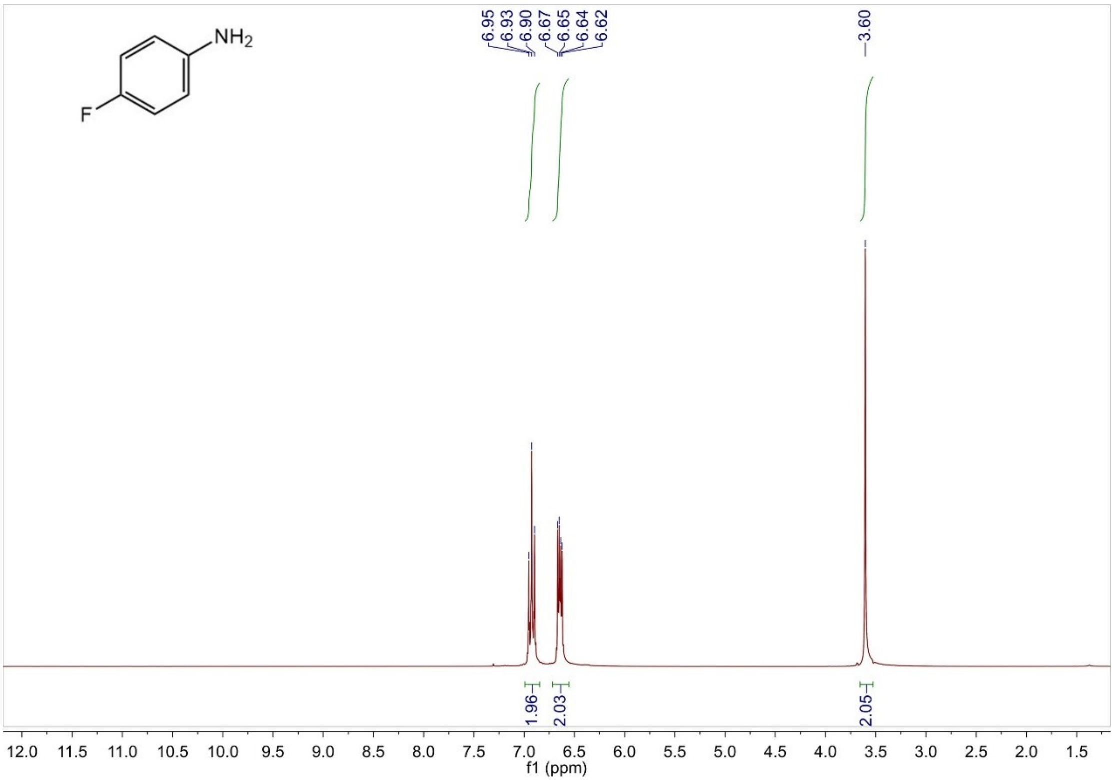
^{13}C NMR spectra of **2b** (126 MHz, $CDCl_3$)

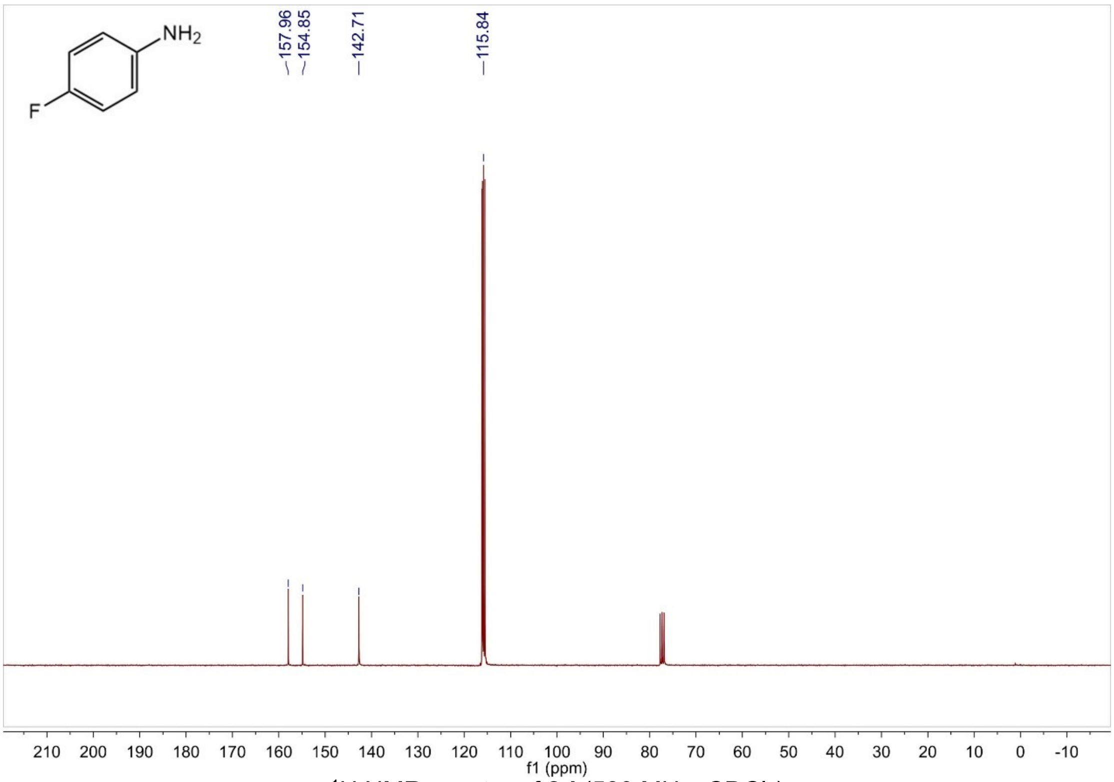


^{1}H NMR spectra of **2c** (500 MHz, $CDCl_3$)



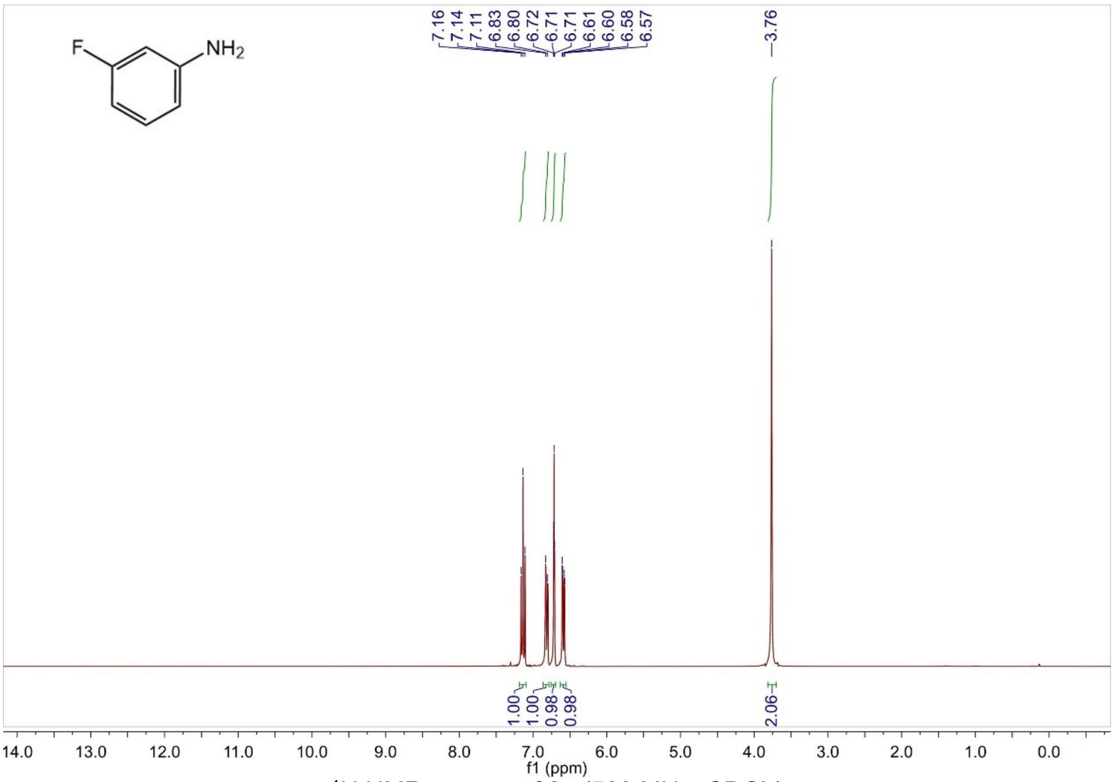
^{13}C NMR spectra of **2c** (126 MHz, $CDCl_3$)



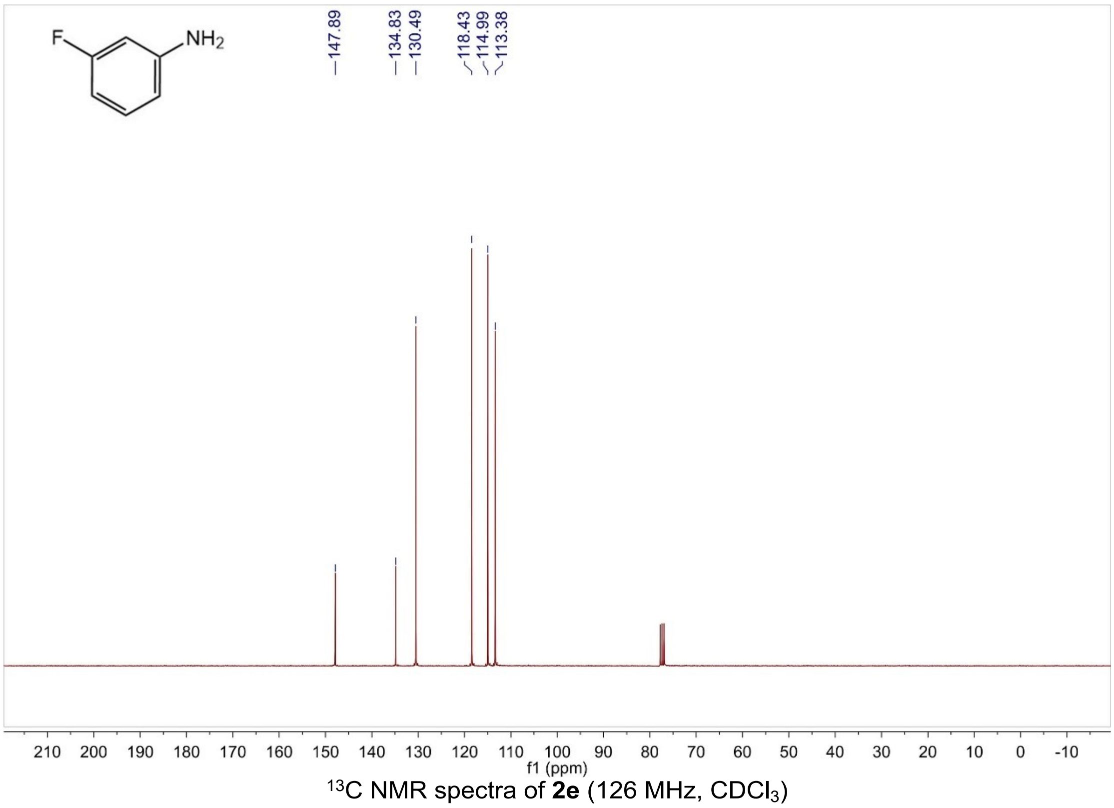


^{1}H NMR spectra of **2d** (500 MHz, $CDCl_3$)

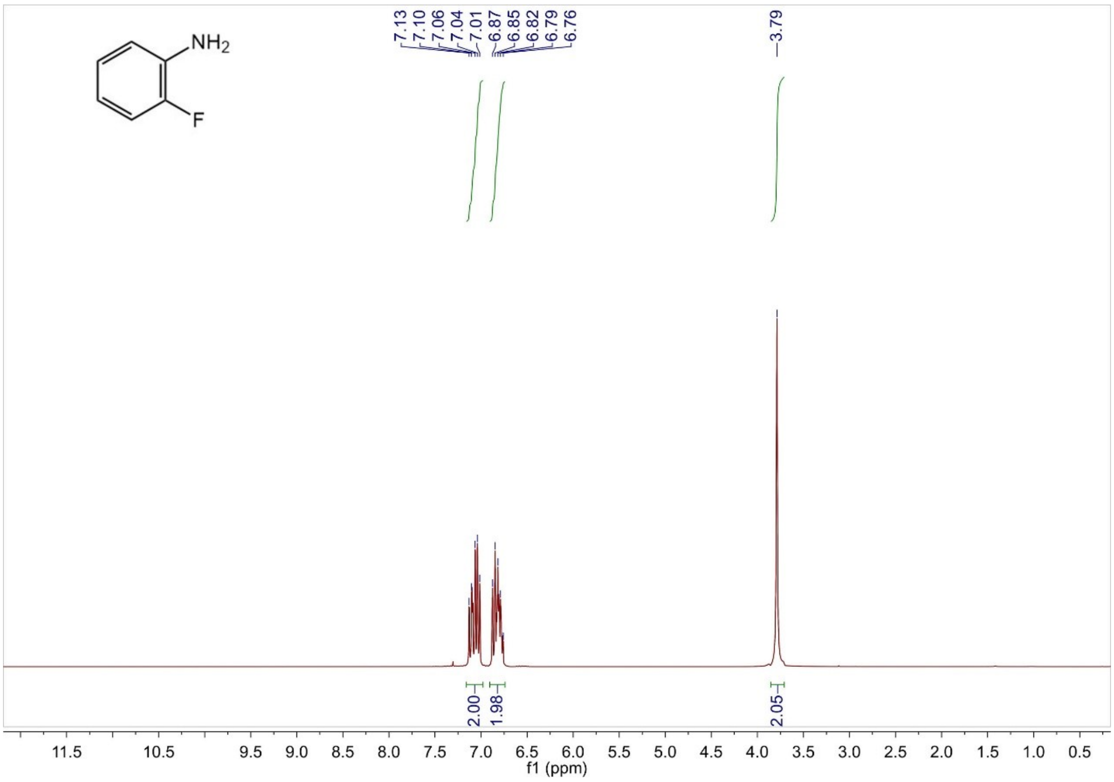
^{13}C NMR spectra of **2d** (126 MHz, $CDCl_3$)

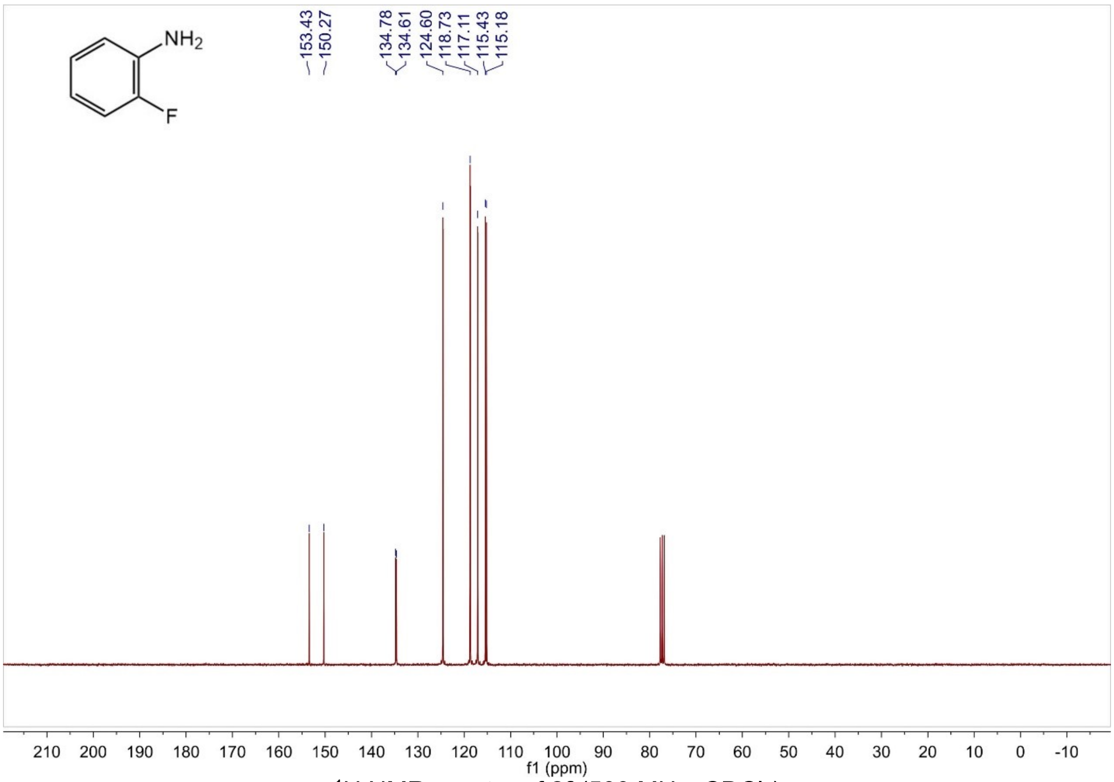


^{1}H NMR spectra of **2e** (500 MHz, $CDCl_3$)



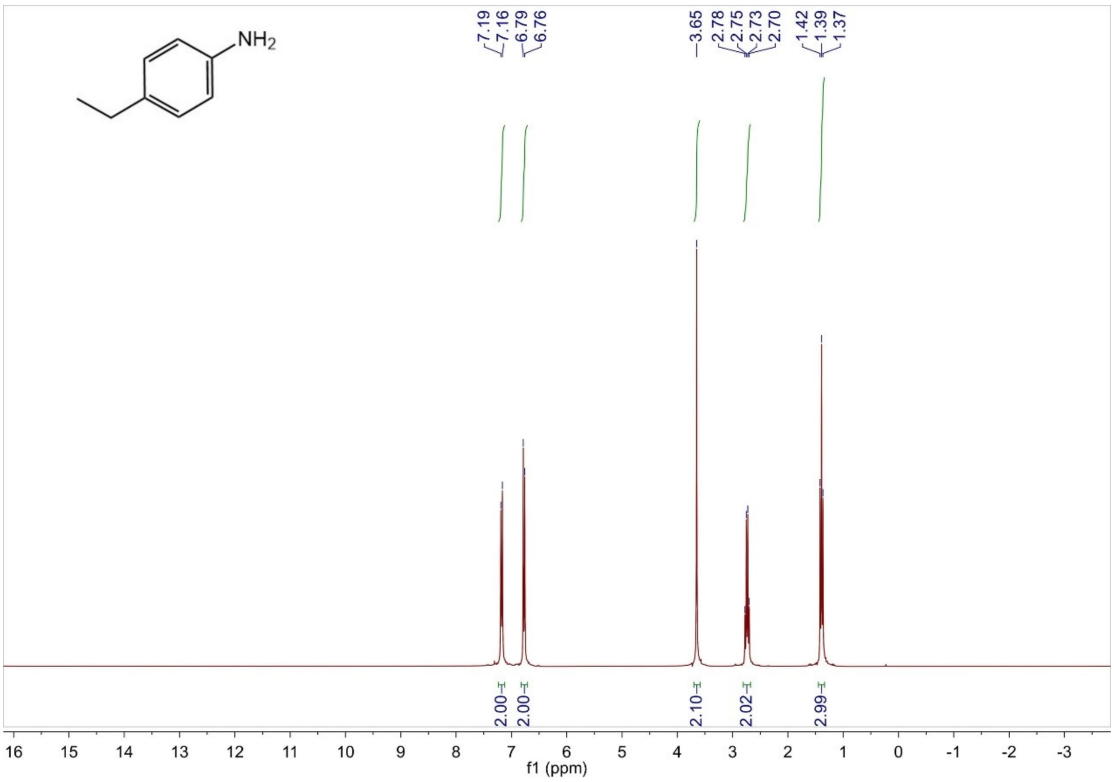
^{13}C NMR spectra of **2e** (126 MHz, $CDCl_3$)

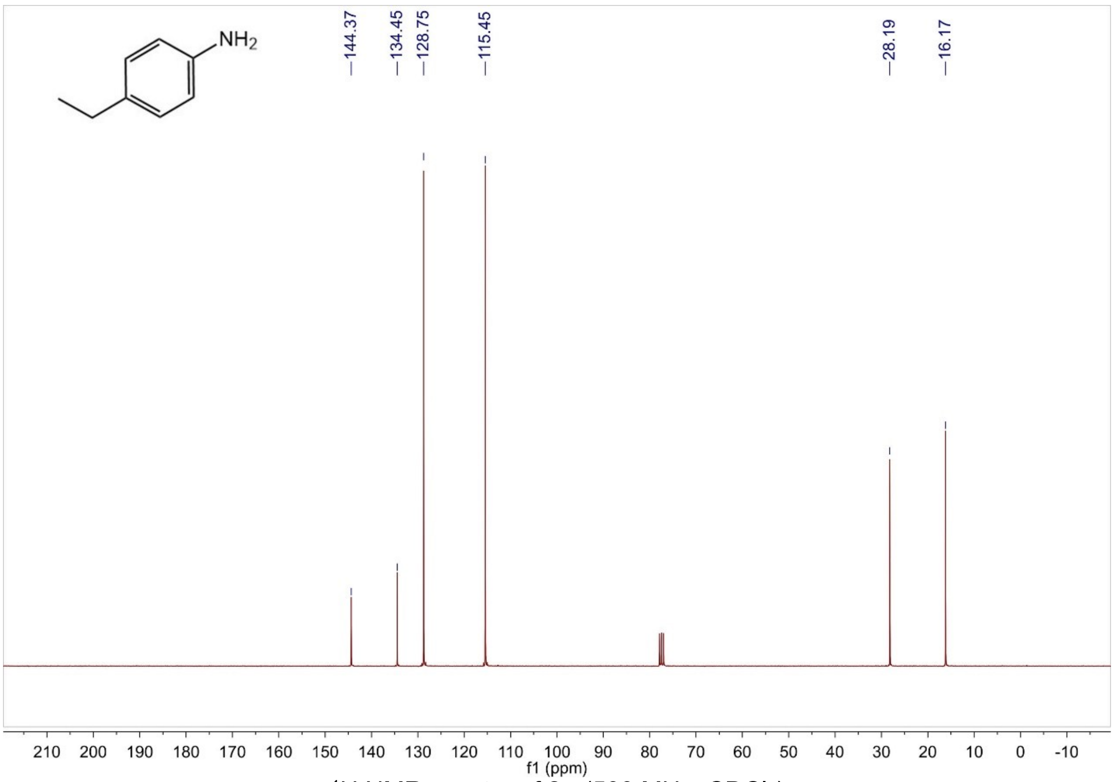




[1]H NMR spectra of **2f** (500 MHz, $CDCl_3$)

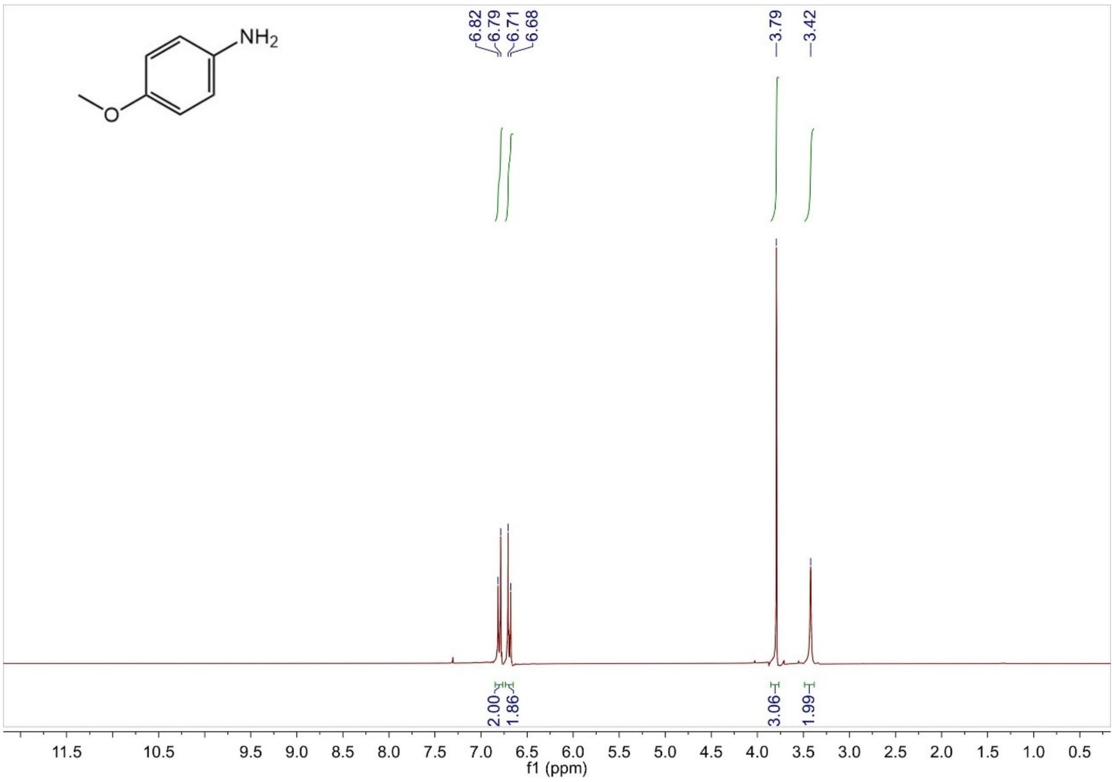
[13]C NMR spectra of **2f** (126 MHz, $CDCl_3$)

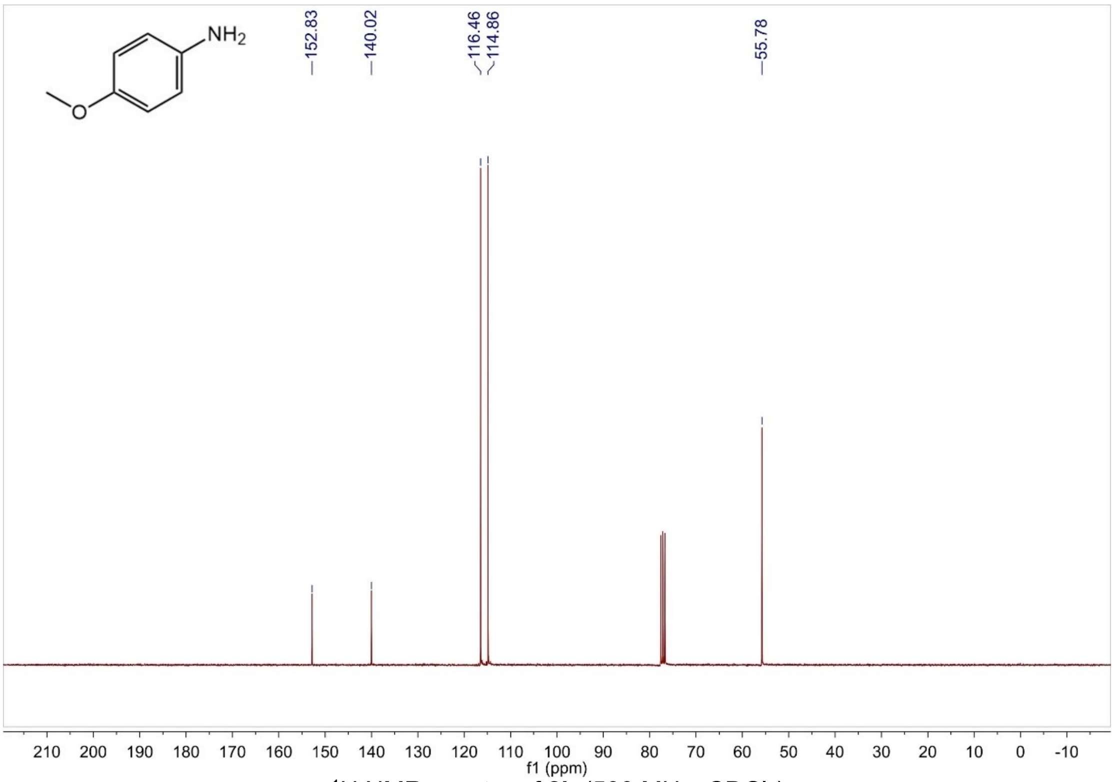




^{1}H NMR spectra of **2g** (500 MHz, $CDCl_3$)

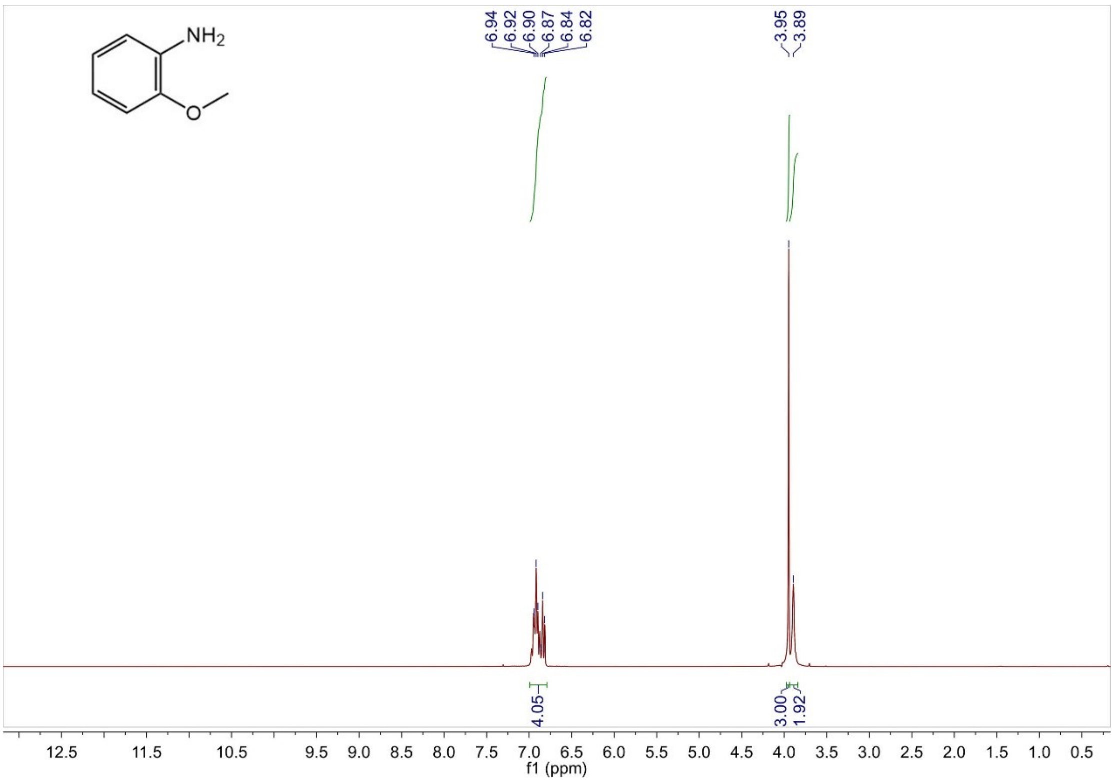
^{13}C NMR spectra of **2g** (126 MHz, $CDCl_3$)

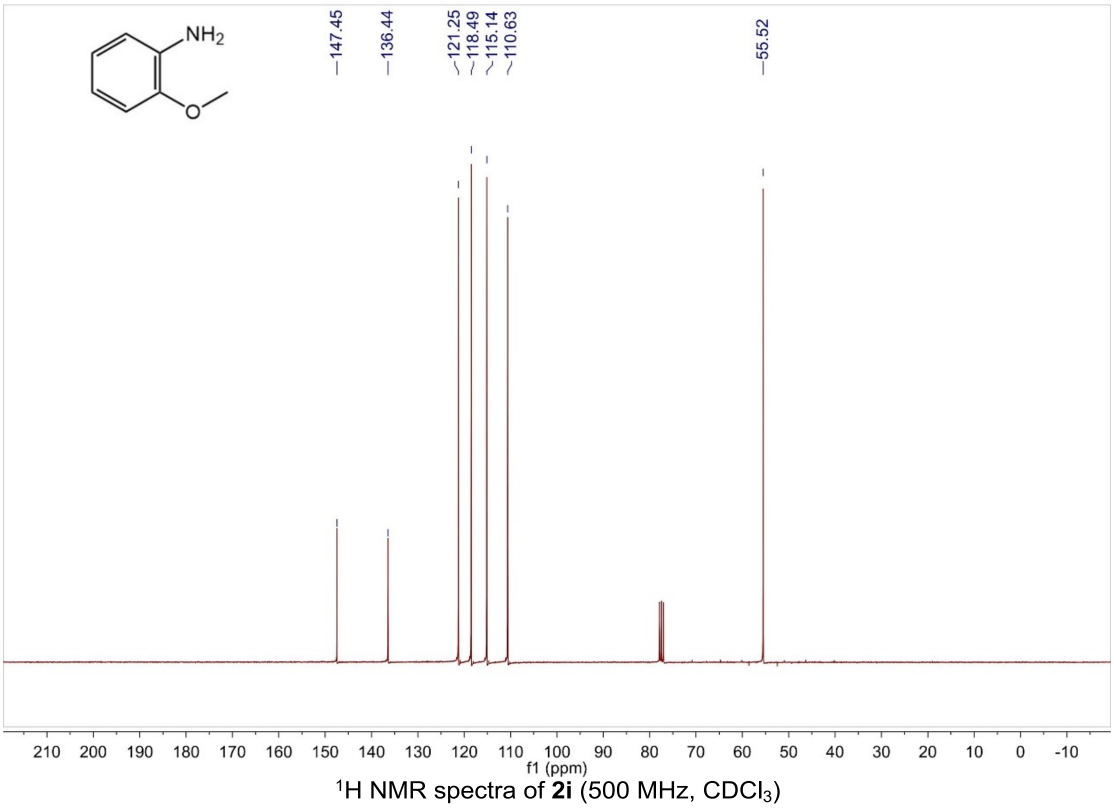




^{1}H NMR spectra of **2h** (500 MHz, $CDCl_3$)

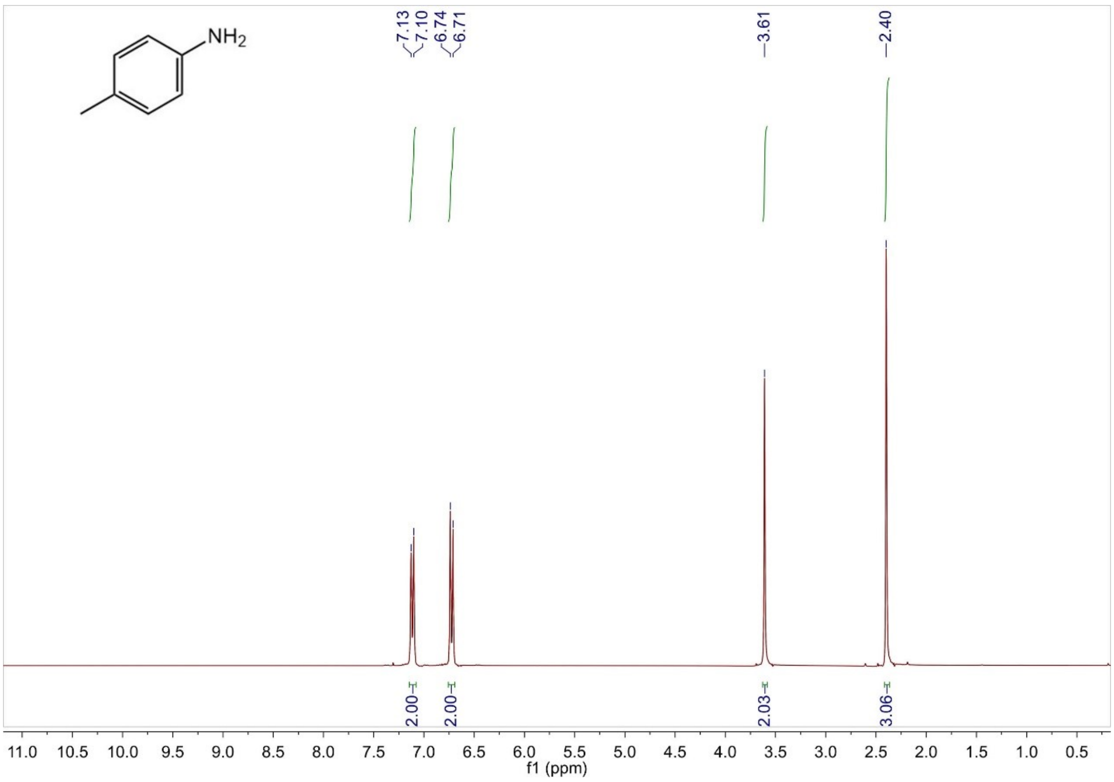
^{13}C NMR spectra of **2h** (126 MHz, $CDCl_3$)

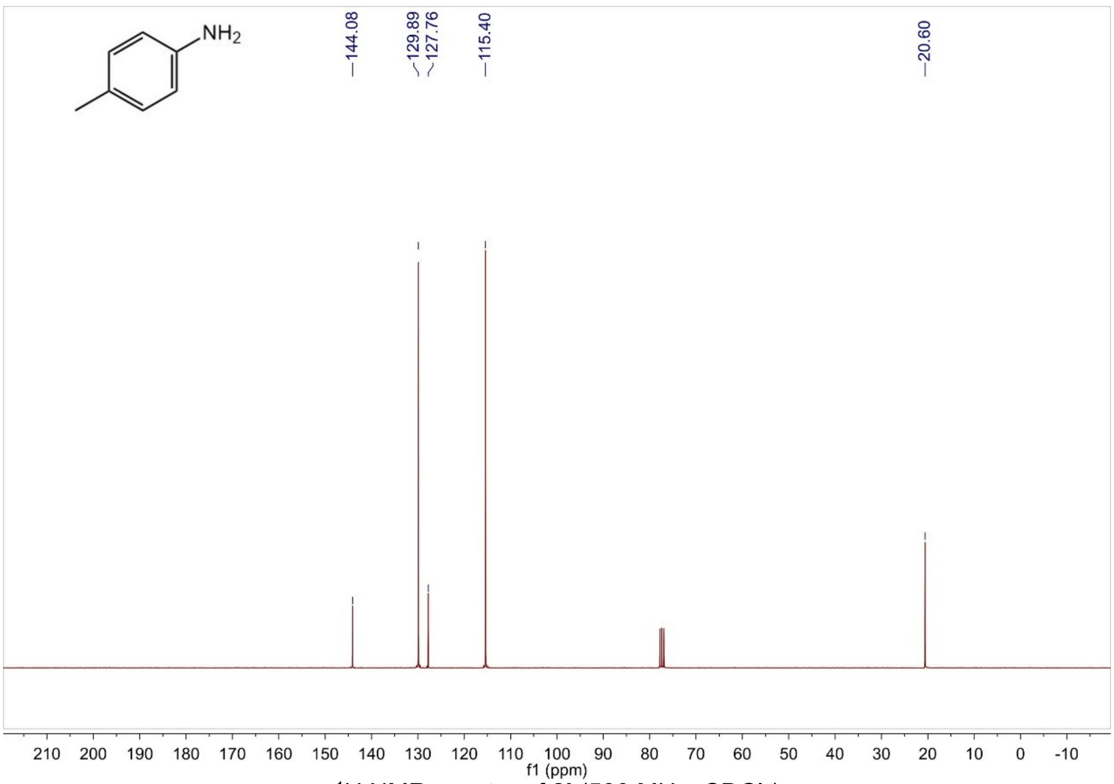




^{1}H NMR spectra of **2i** (500 MHz, $CDCl_3$)

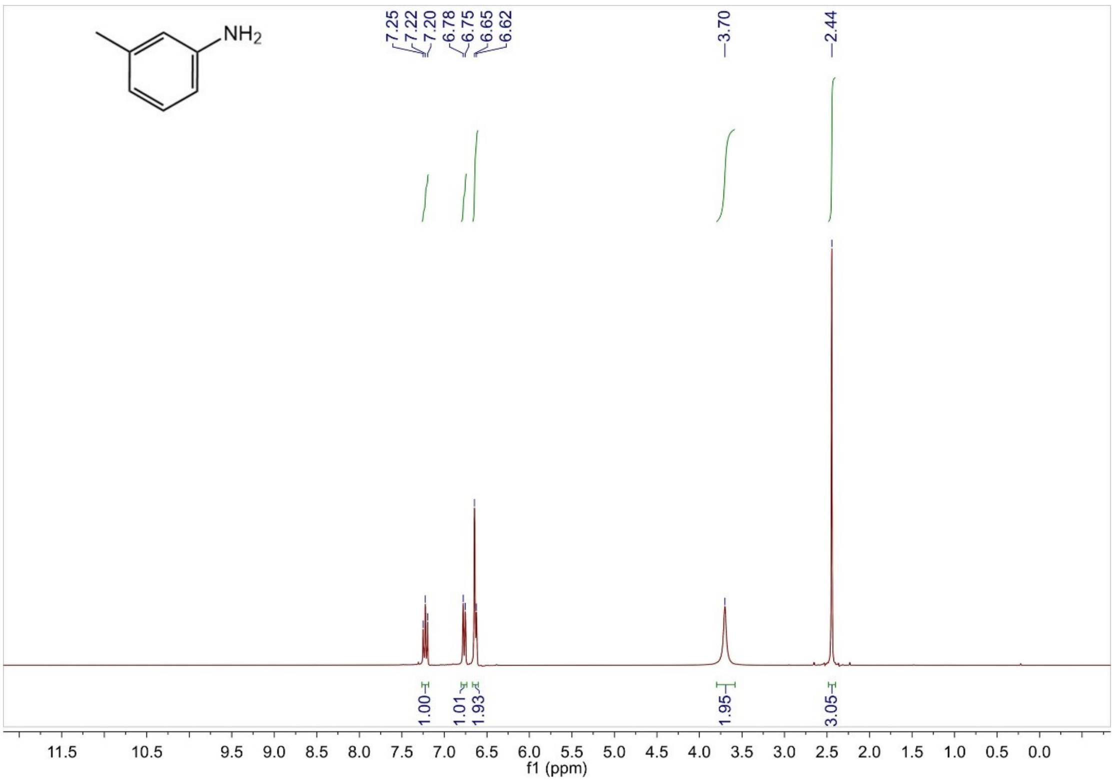
^{13}C NMR spectra of **2i** (126 MHz, $CDCl_3$)

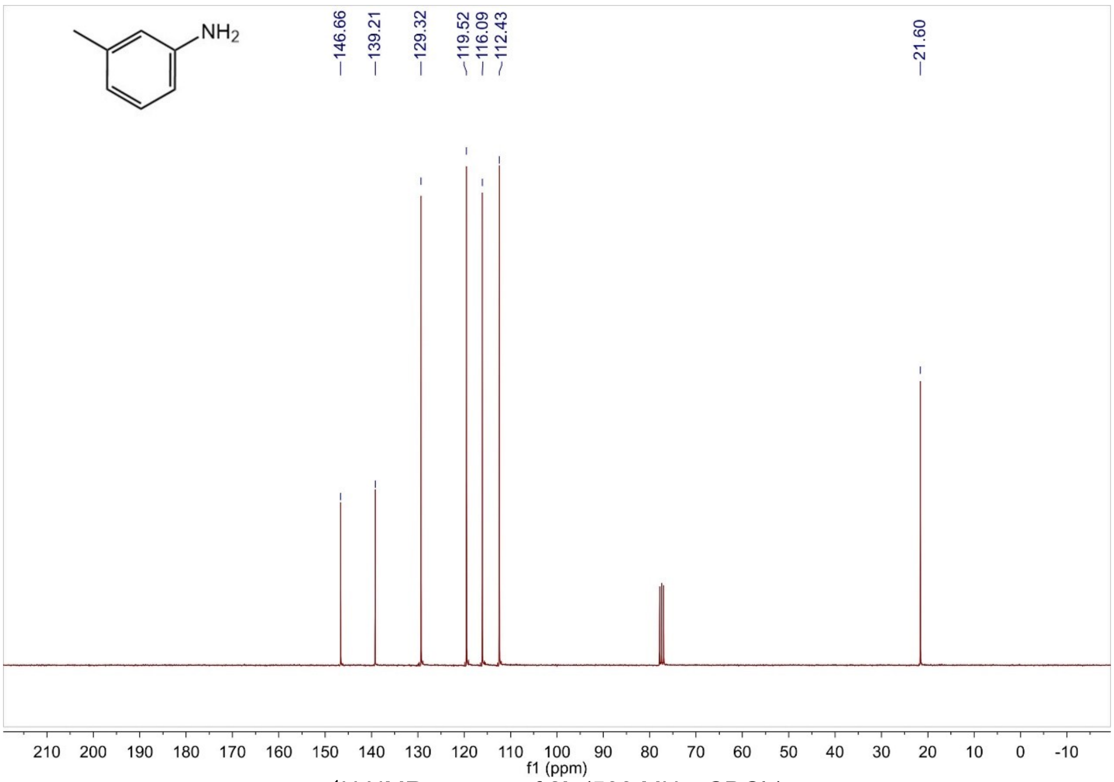




[1]H NMR spectra of **2j** (500 MHz, $CDCl_3$)

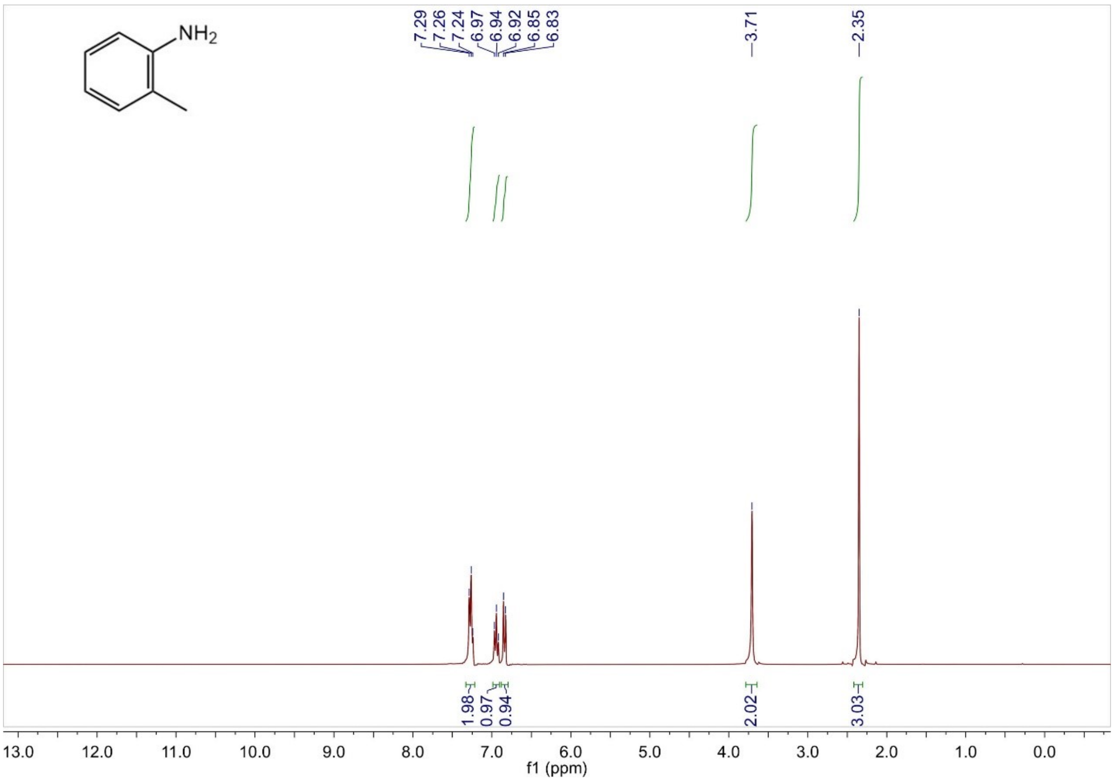
[13]C NMR spectra of **2j** (126 MHz, $CDCl_3$)

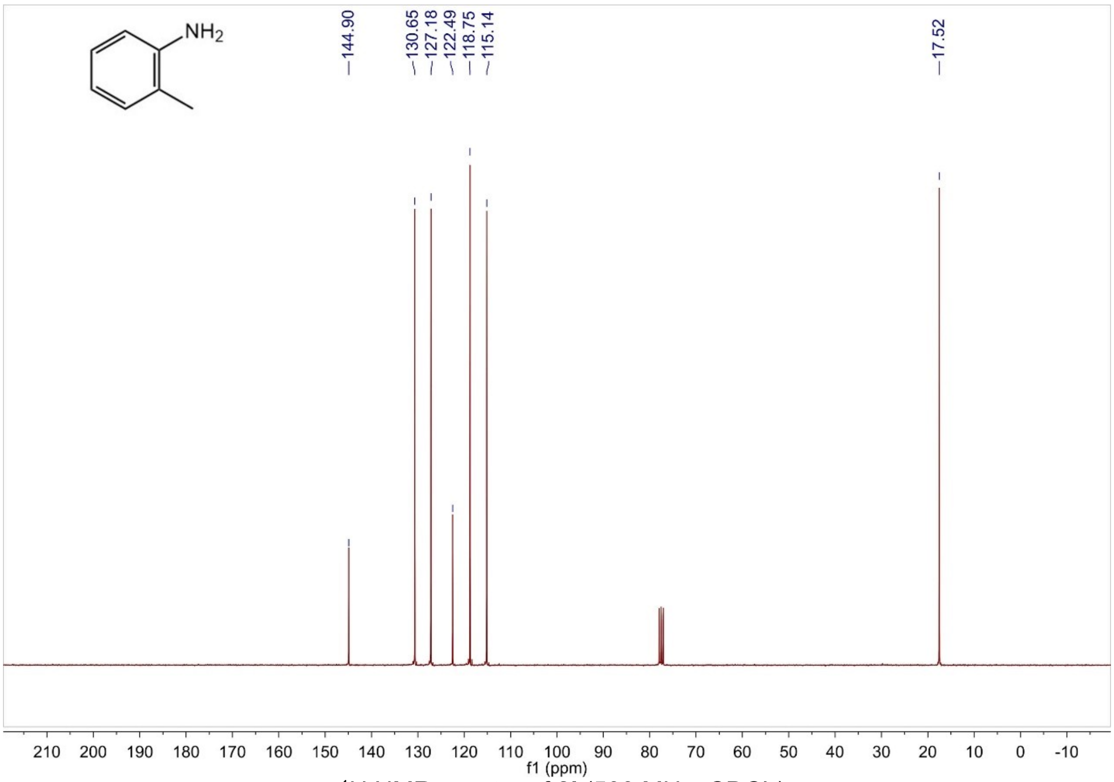




^{1}H NMR spectra of **2k** (500 MHz, $CDCl_3$)

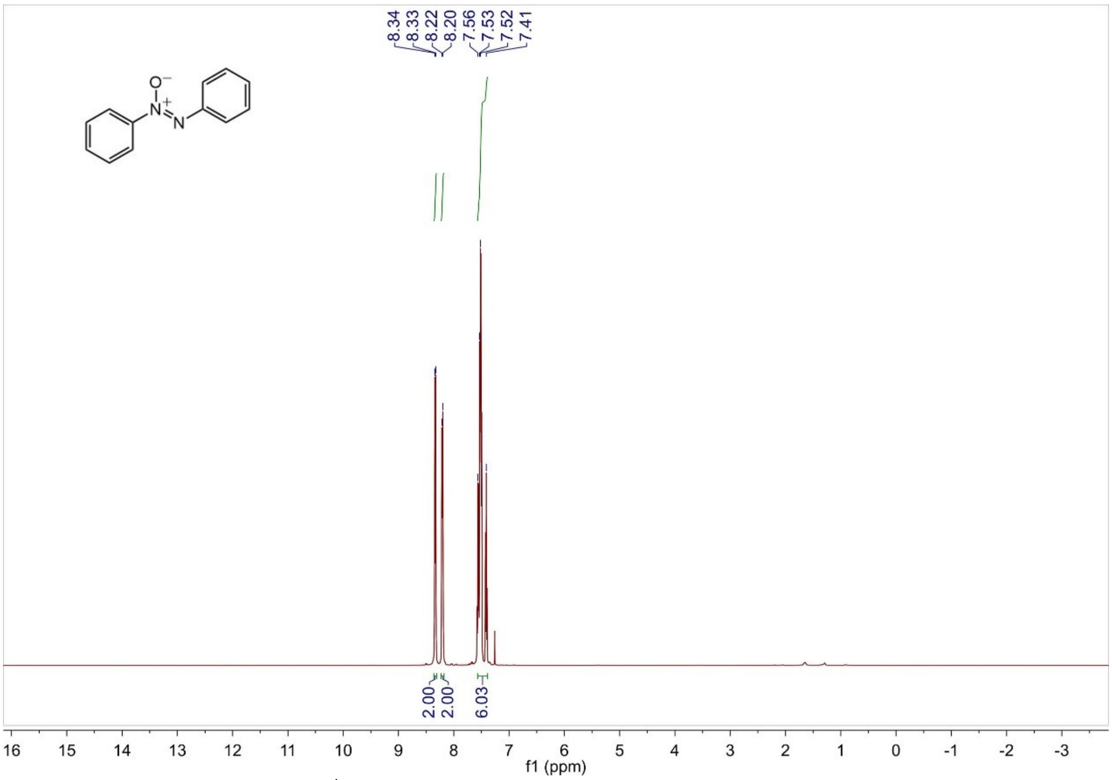
^{13}C NMR spectra of **2k** (126 MHz, $CDCl_3$)



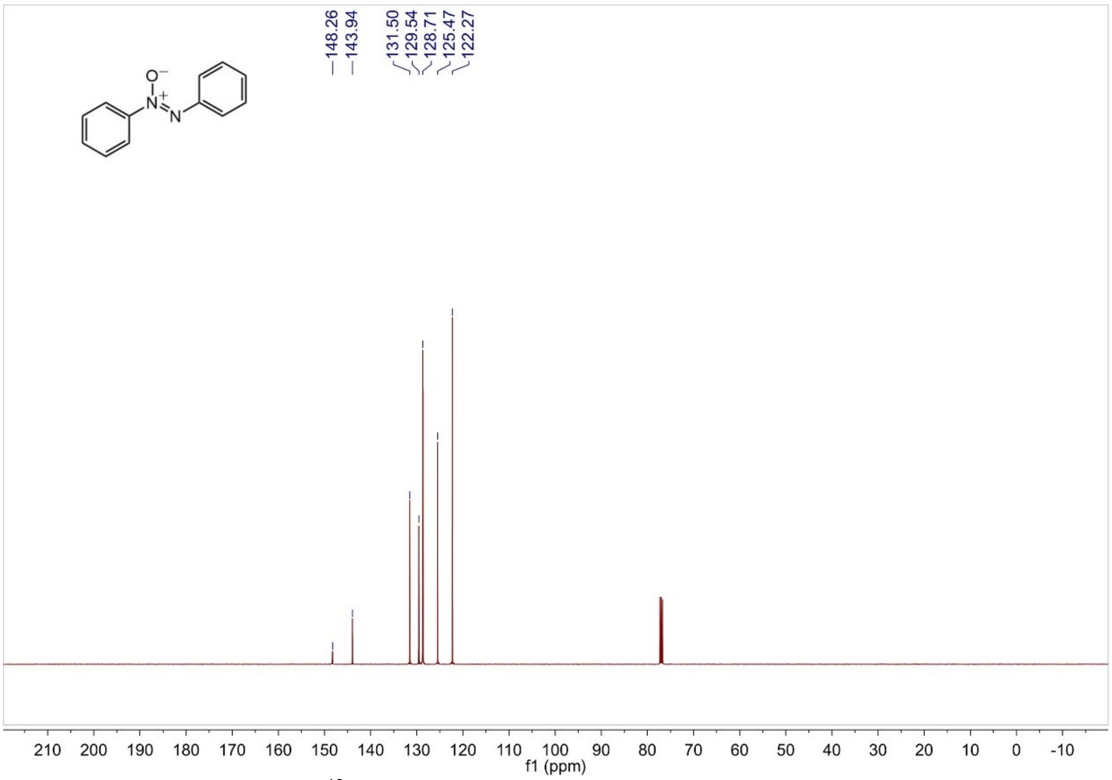


^{1}H NMR spectra of **2l** (500 MHz, $CDCl_3$)

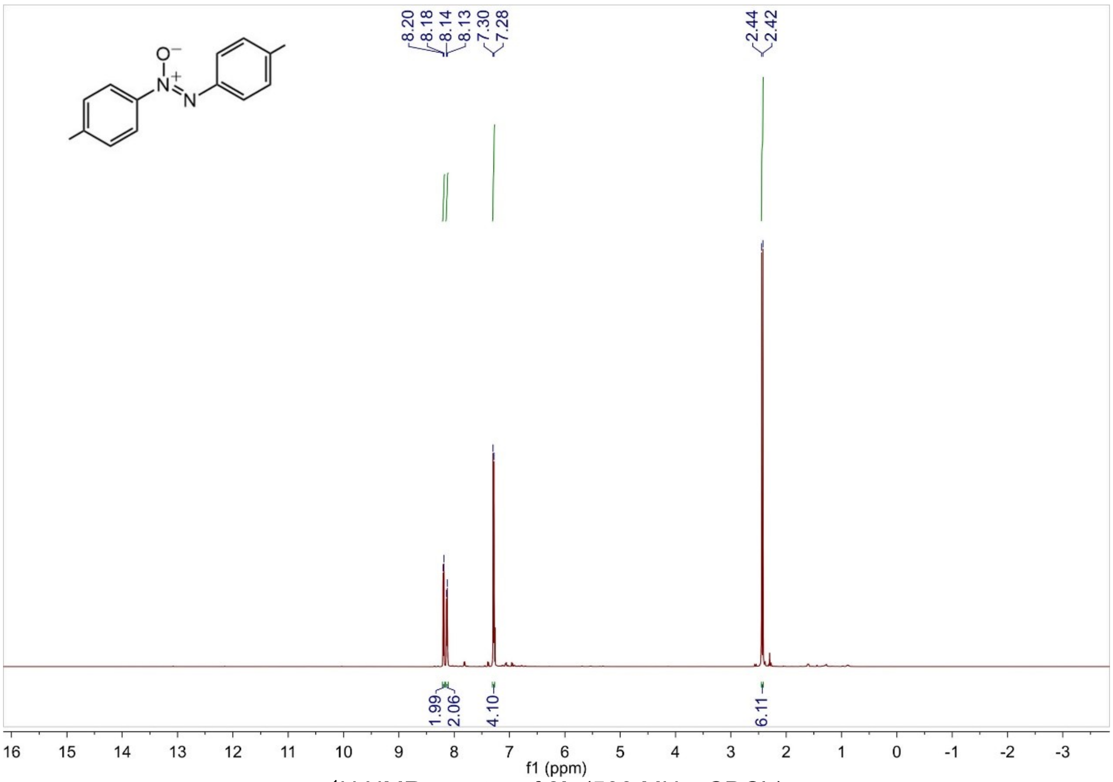
^{13}C NMR spectra of **2l** (126 MHz, $CDCl_3$)



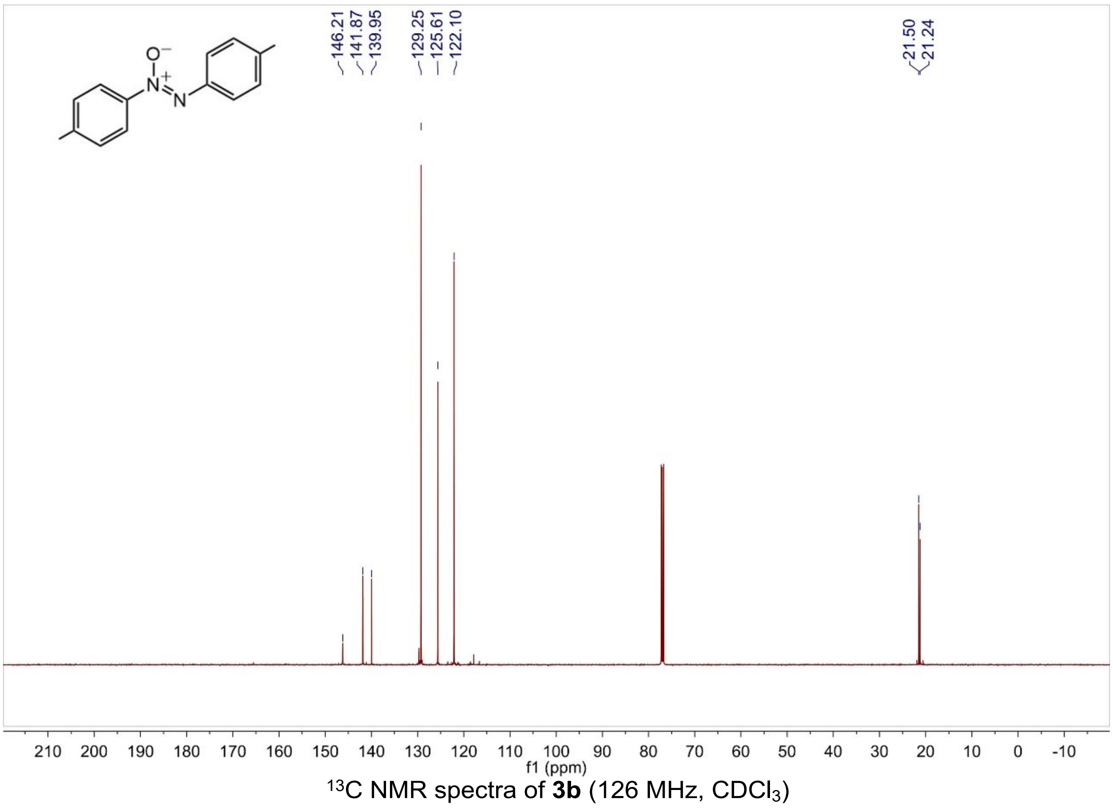
^{1}H NMR spectra of **3a** (500 MHz, $CDCl_3$)



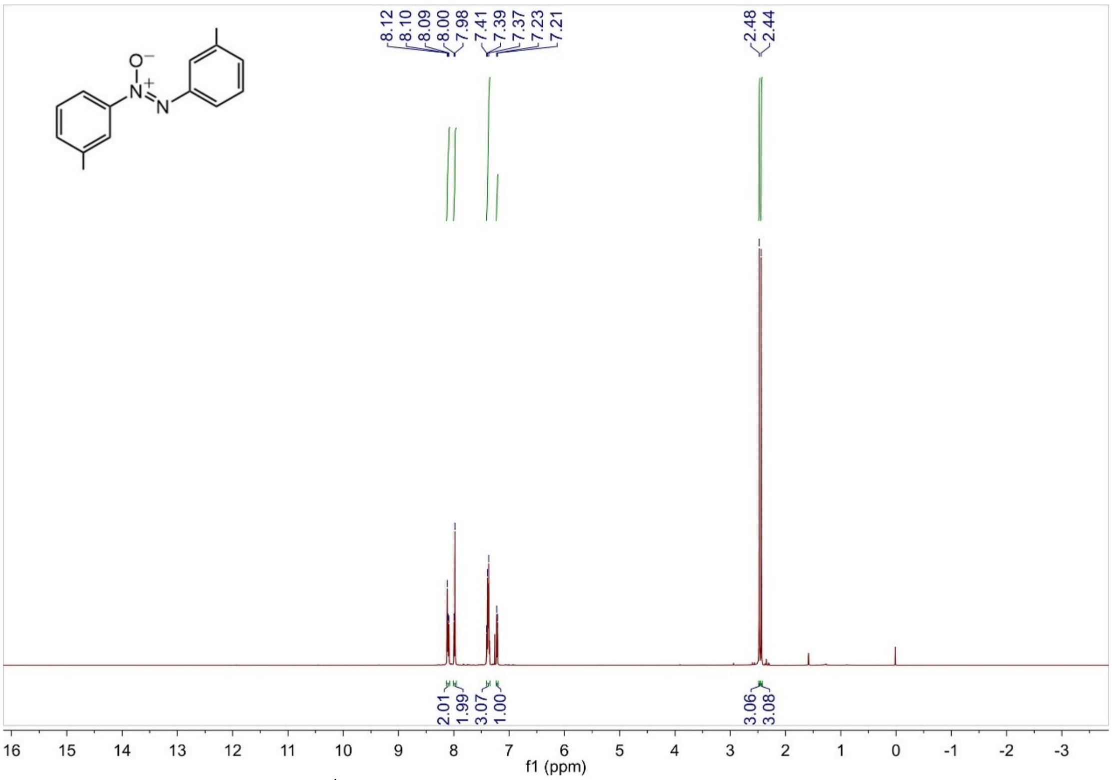
^{13}C NMR spectra of **3a** (126 MHz, $CDCl_3$)



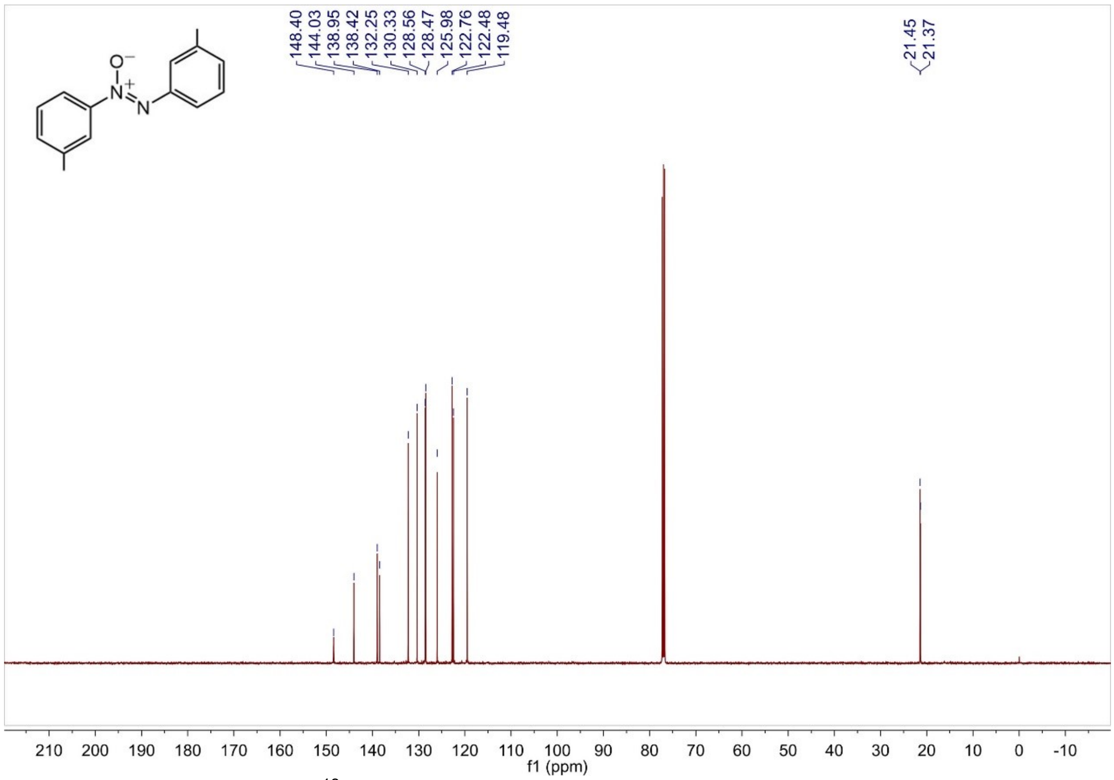
^{1}H NMR spectra of **3b** (500 MHz, $CDCl_3$)



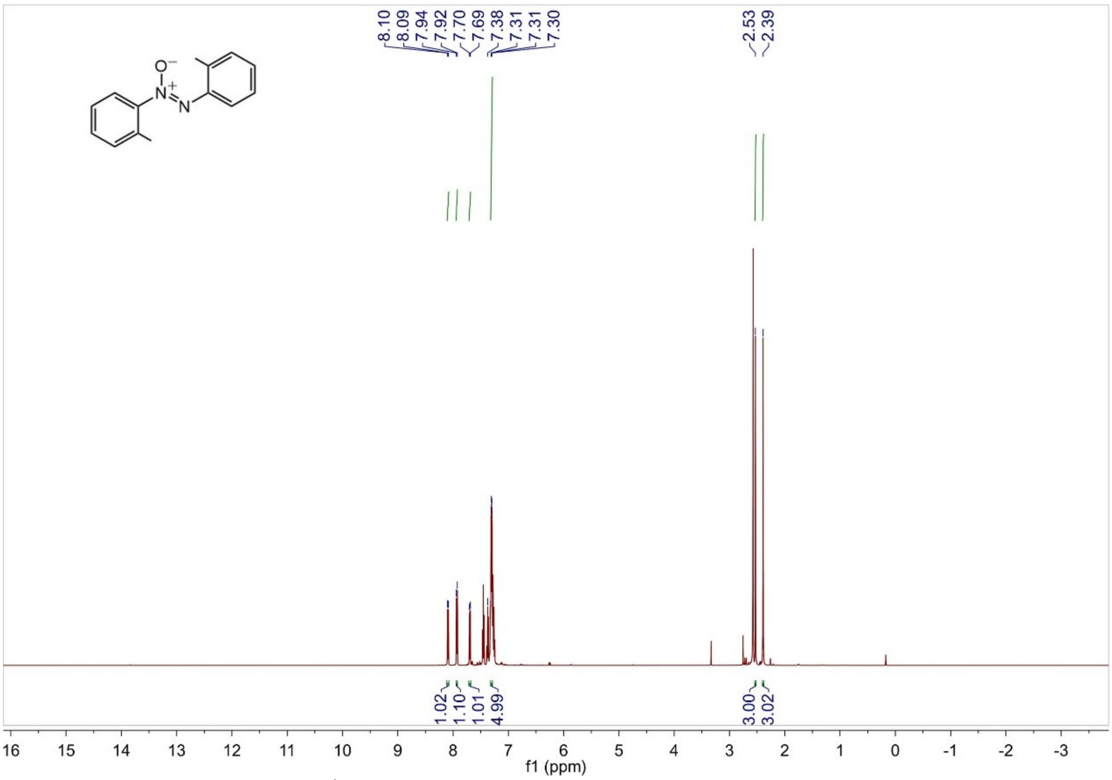
^{13}C NMR spectra of **3b** (126 MHz, $CDCl_3$)



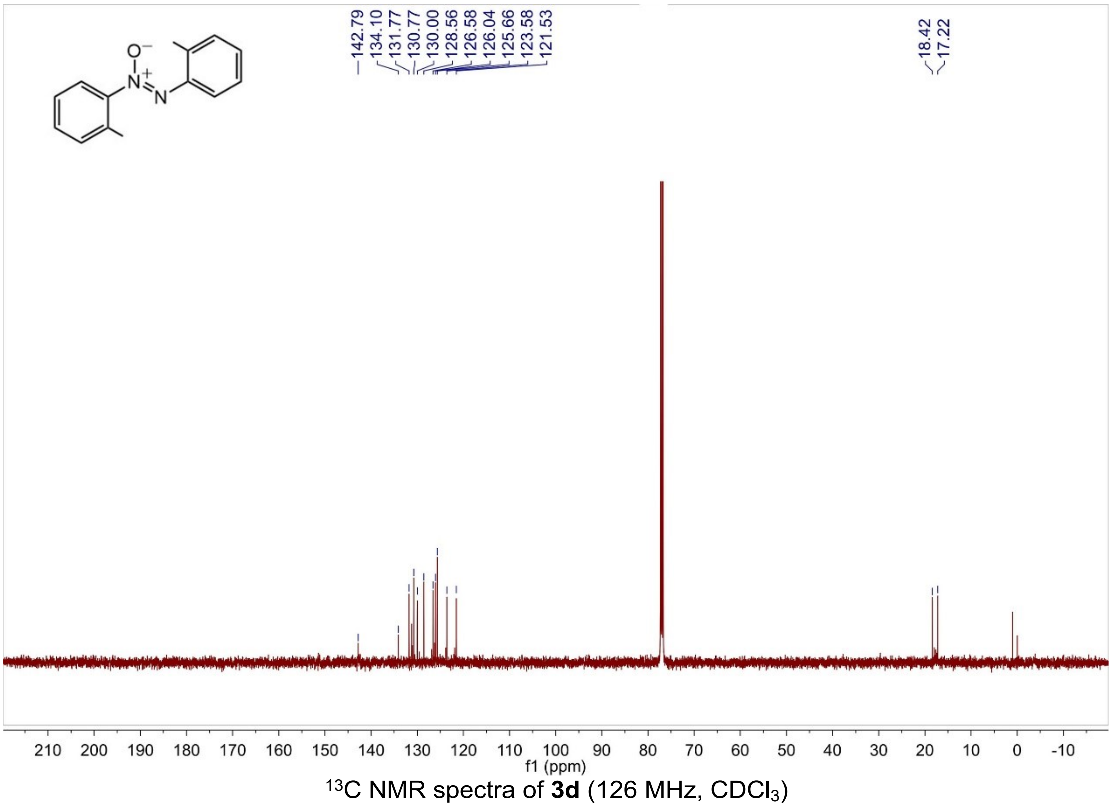
^{1}H NMR spectra of **3c** (500 MHz, $CDCl_3$)



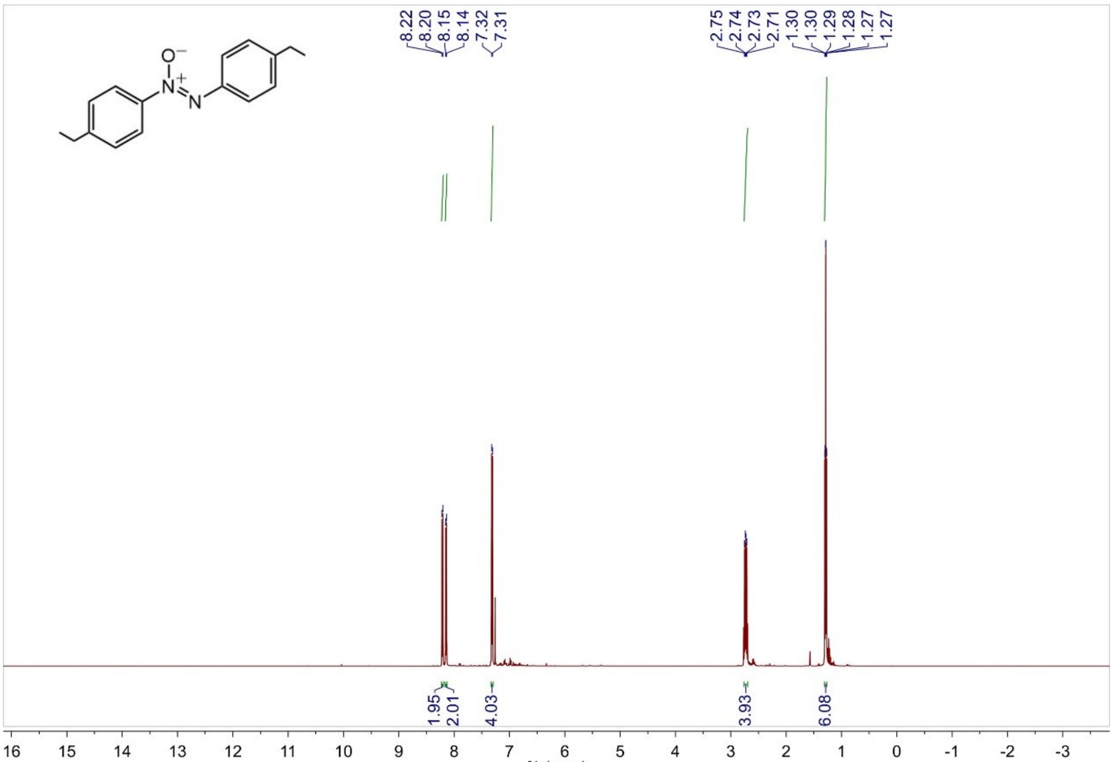
^{13}C NMR spectra of **3c** (126 MHz, $CDCl_3$)



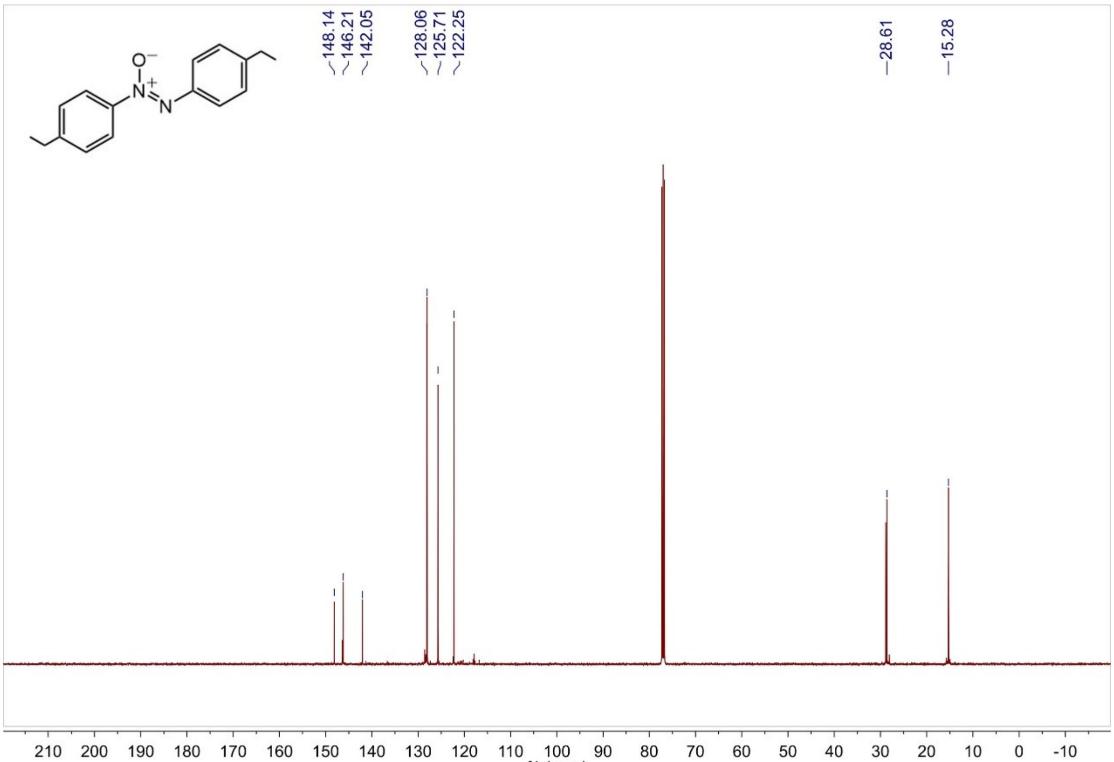
^{1}H NMR spectra of **3d** (500 MHz, $CDCl_3$)



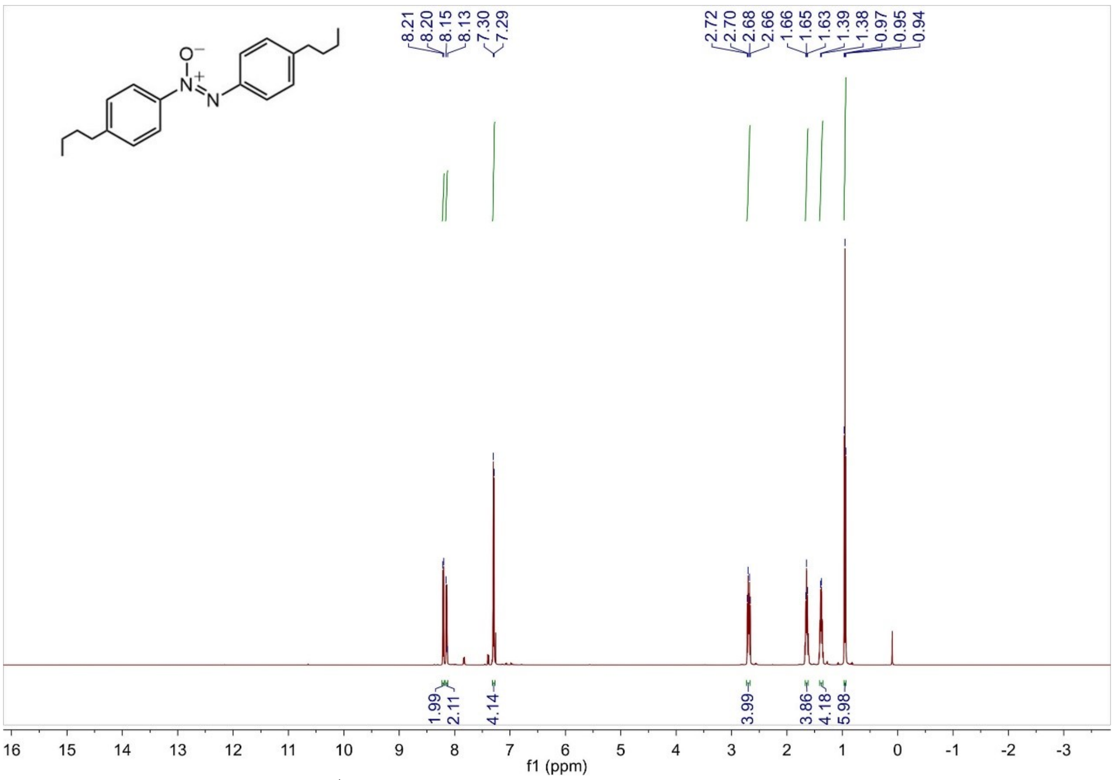
^{13}C NMR spectra of **3d** (126 MHz, $CDCl_3$)



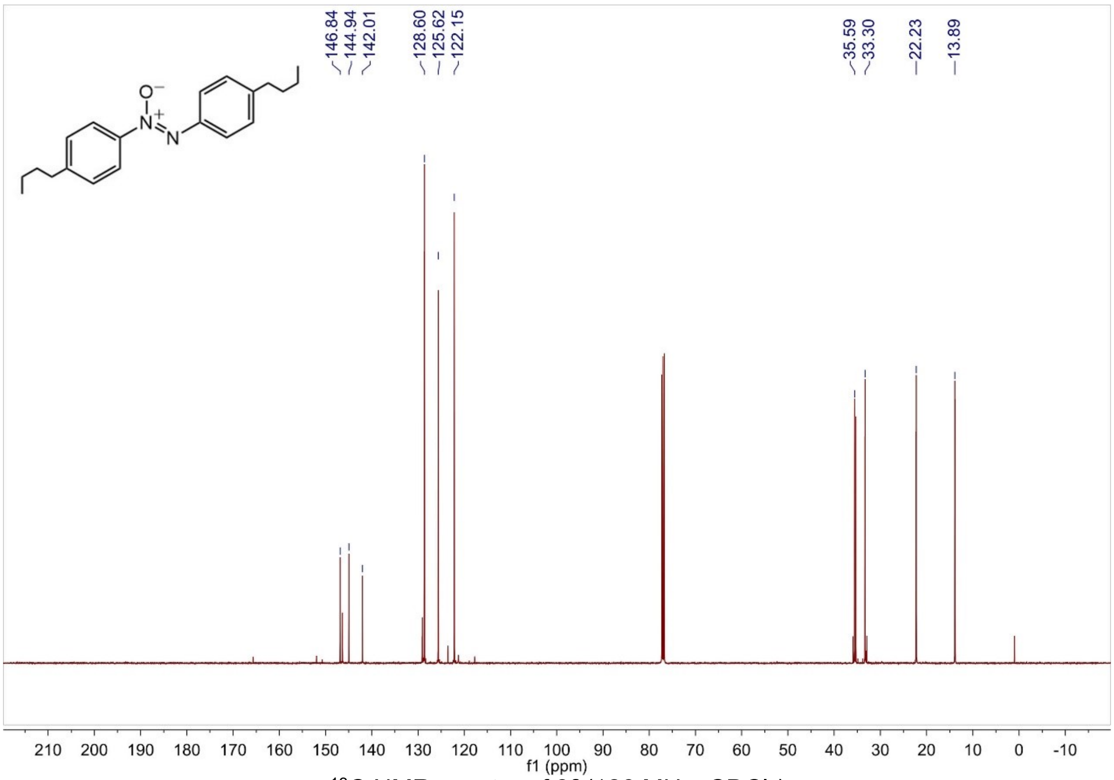
^{1}H NMR spectra of **3e** (500 MHz, $CDCl_3$)



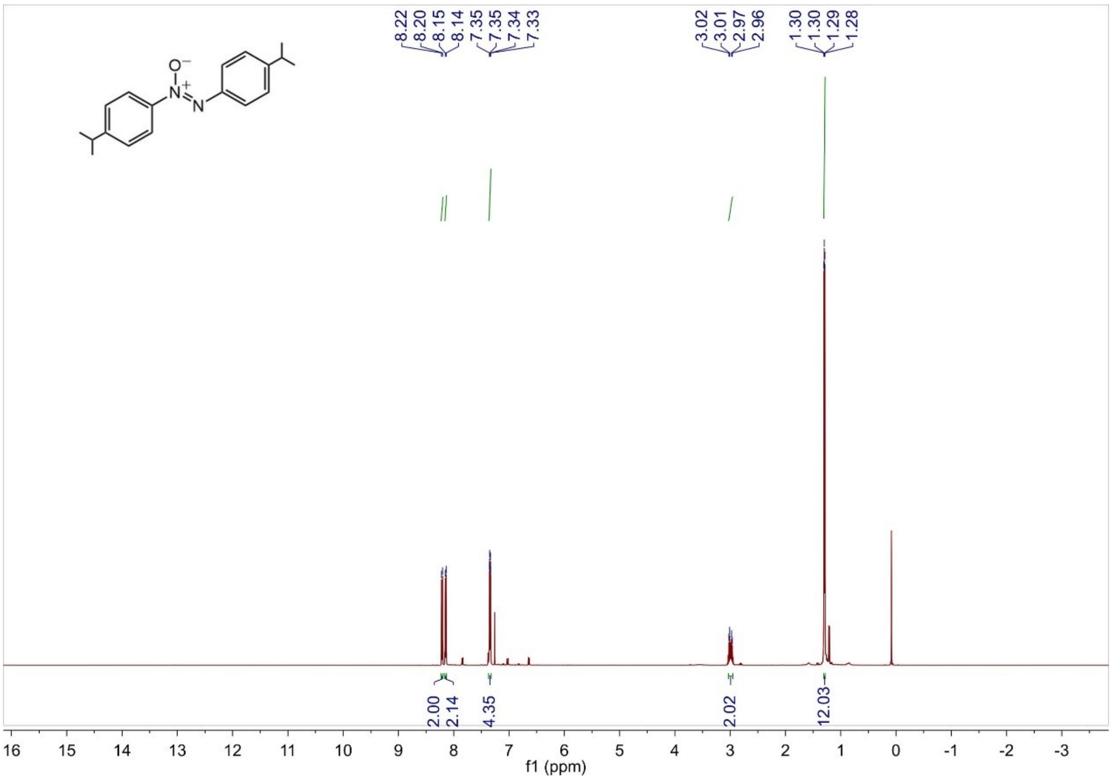
^{13}C NMR spectra of **3e** (126 MHz, $CDCl_3$)

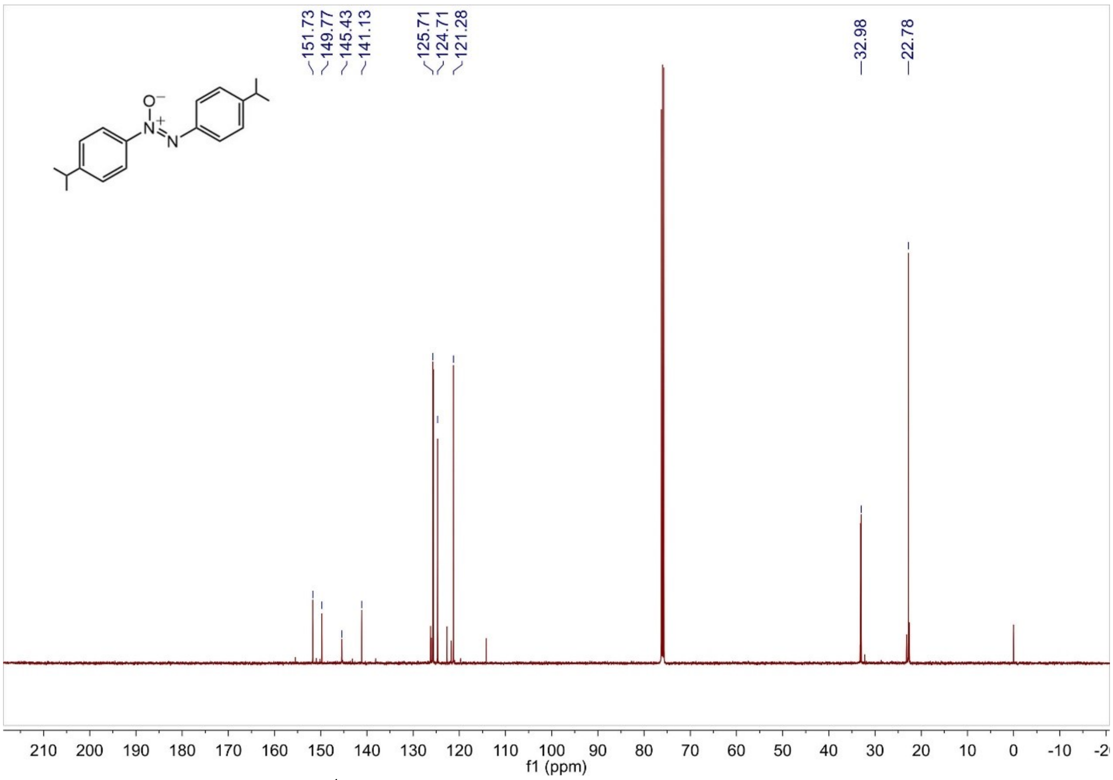


^{1}H NMR spectra of **3f** (500 MHz, $CDCl_3$)



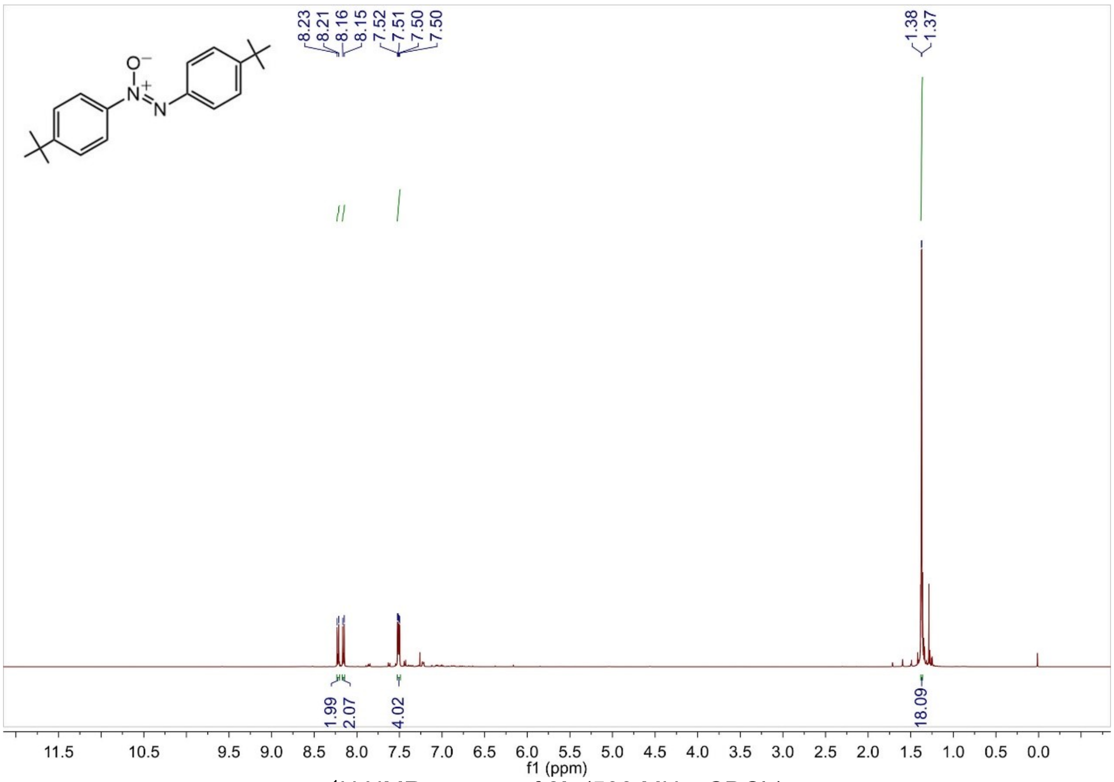
^{13}C NMR spectra of **3f** (126 MHz, $CDCl_3$)



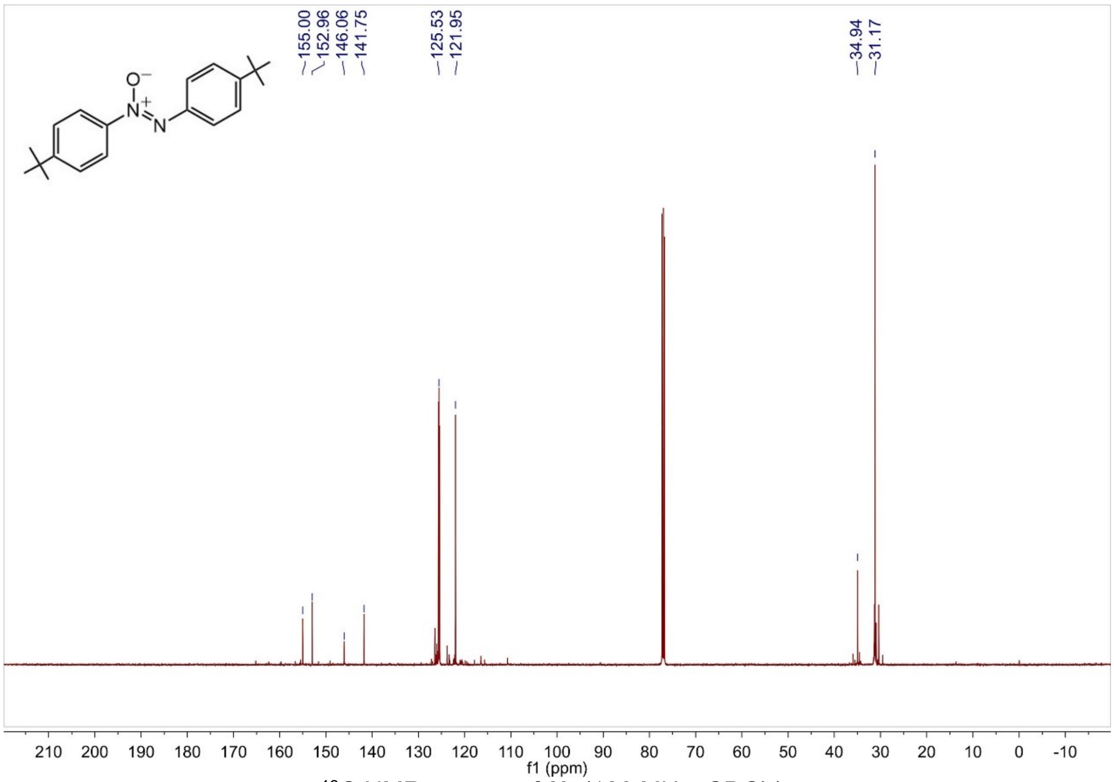


^{1}H NMR spectra of **3g** (500 MHz, $CDCl_3$)

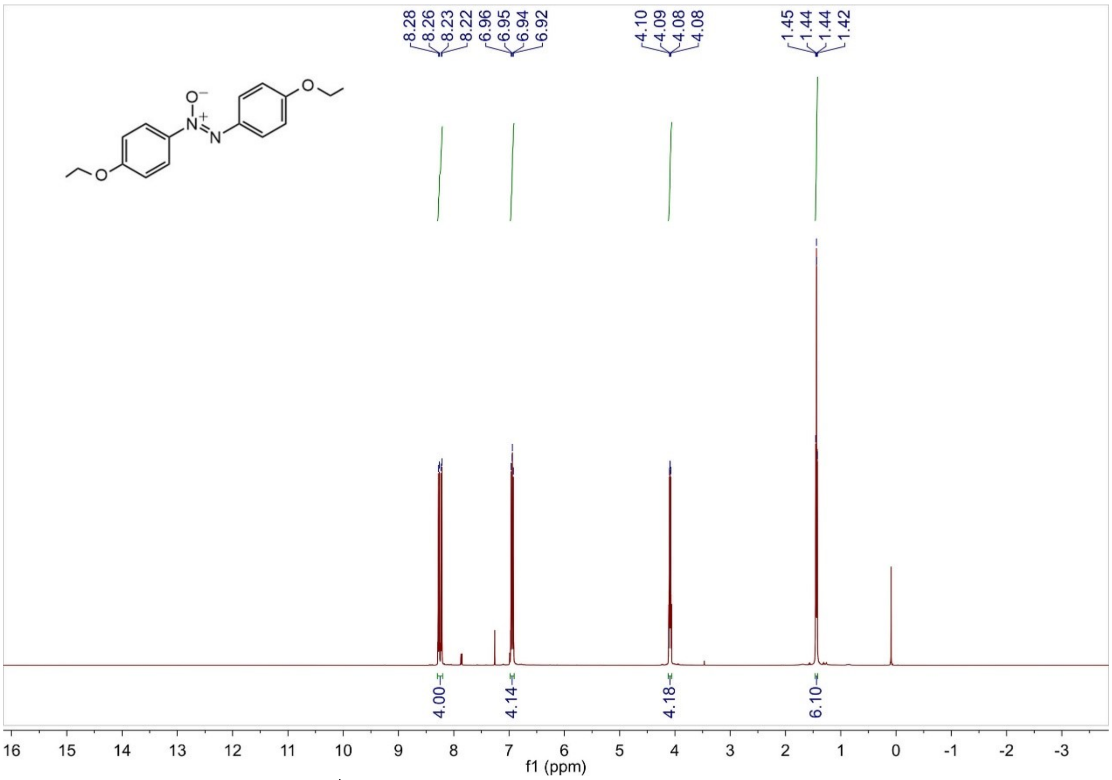
^{13}C NMR spectra of **3g** (126 MHz, $CDCl_3$)



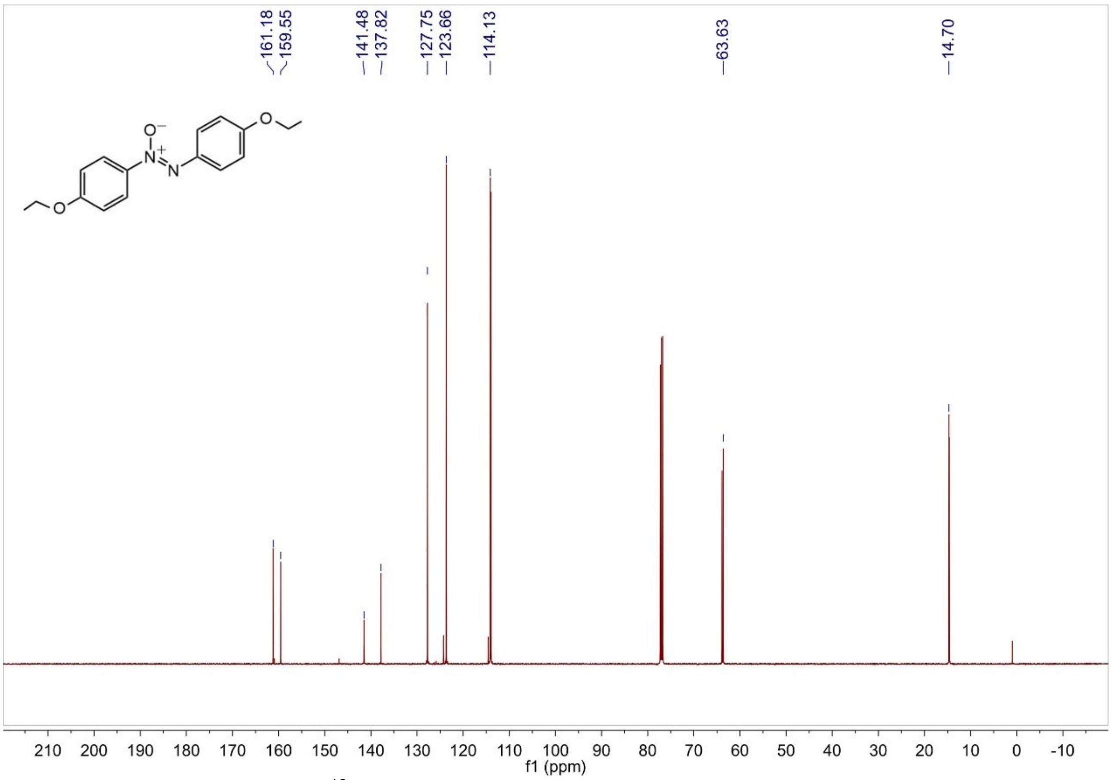
[1]H NMR spectra of **3h** (500 MHz, $CDCl_3$)



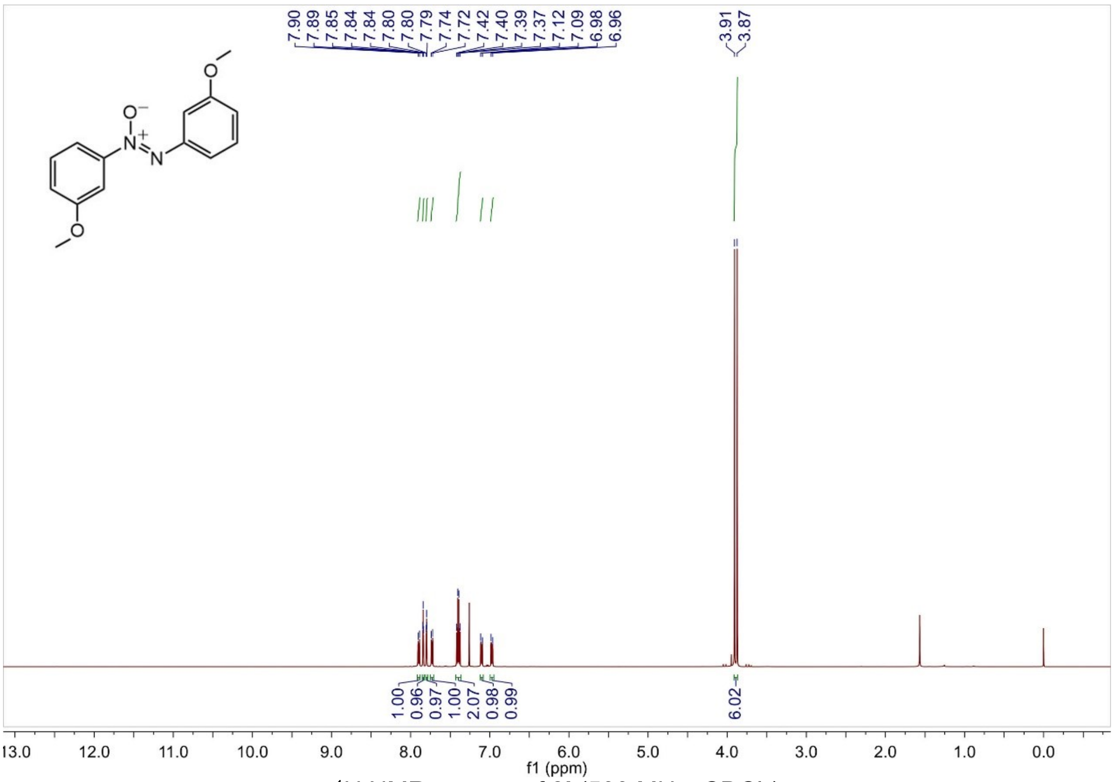
[13]C NMR spectra of **3h** (126 MHz, $CDCl_3$)



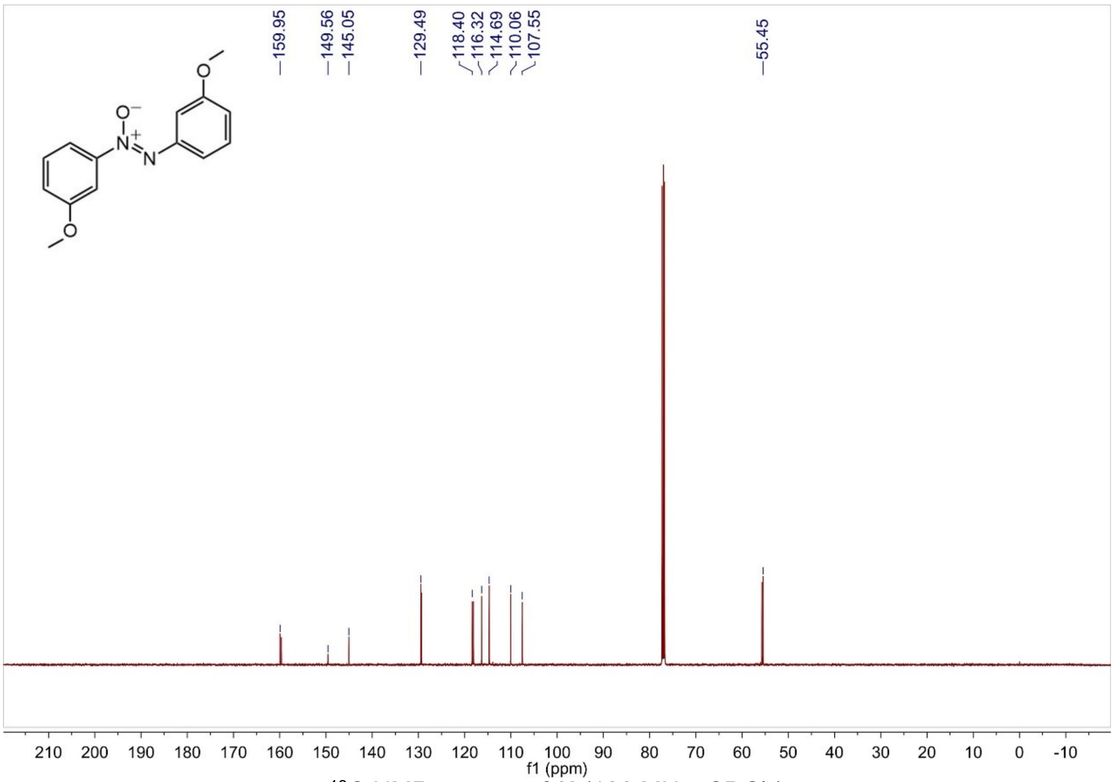
^{1}H NMR spectra of **3i** (500 MHz, $CDCl_3$)



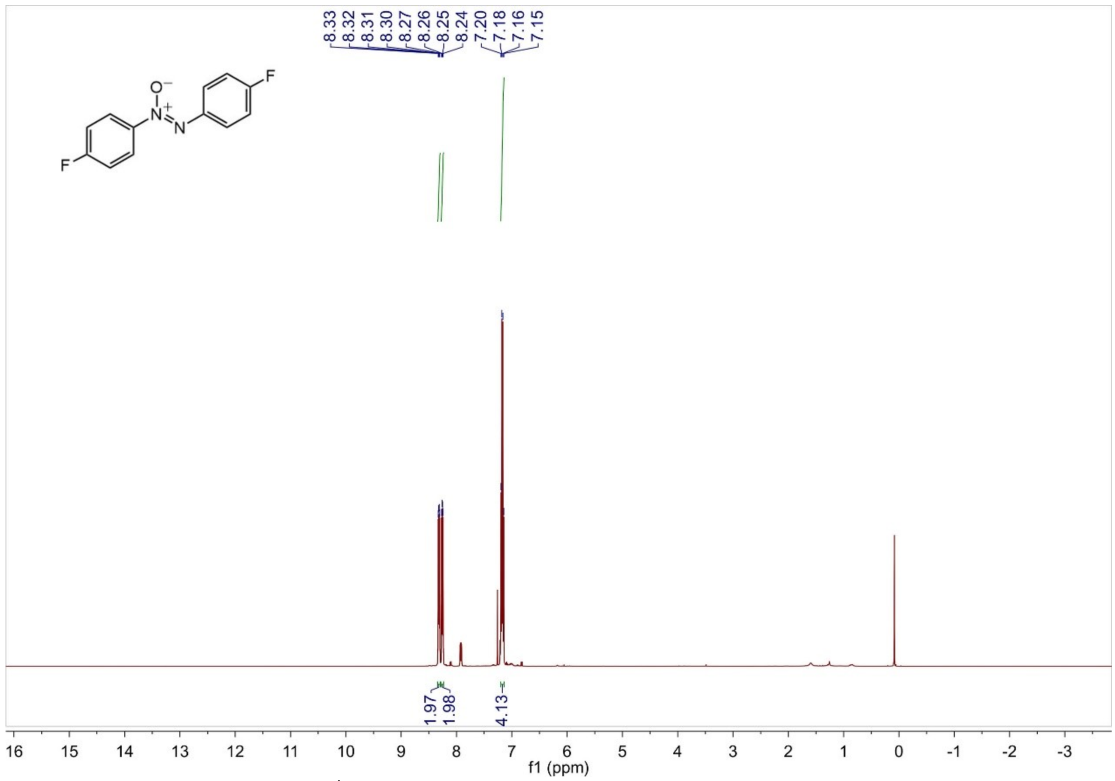
^{13}C NMR spectra of **3i** (126 MHz, $CDCl_3$)



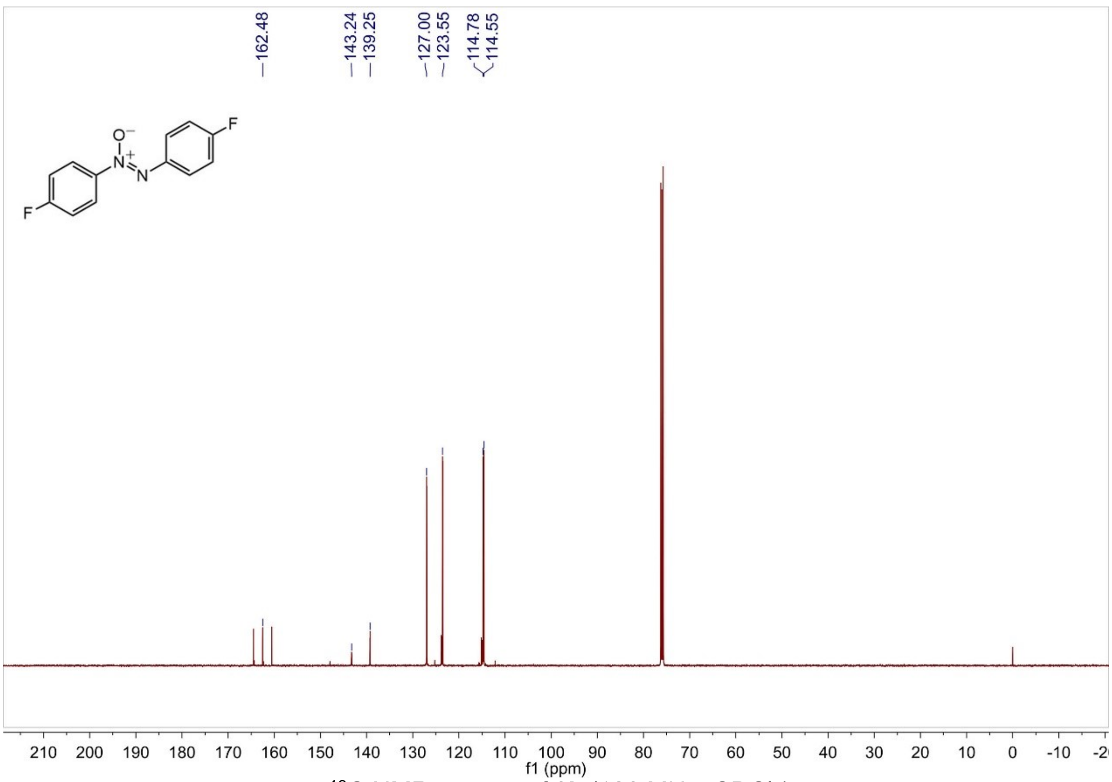
^{1}H NMR spectra of **3j** (500 MHz, $CDCl_3$)



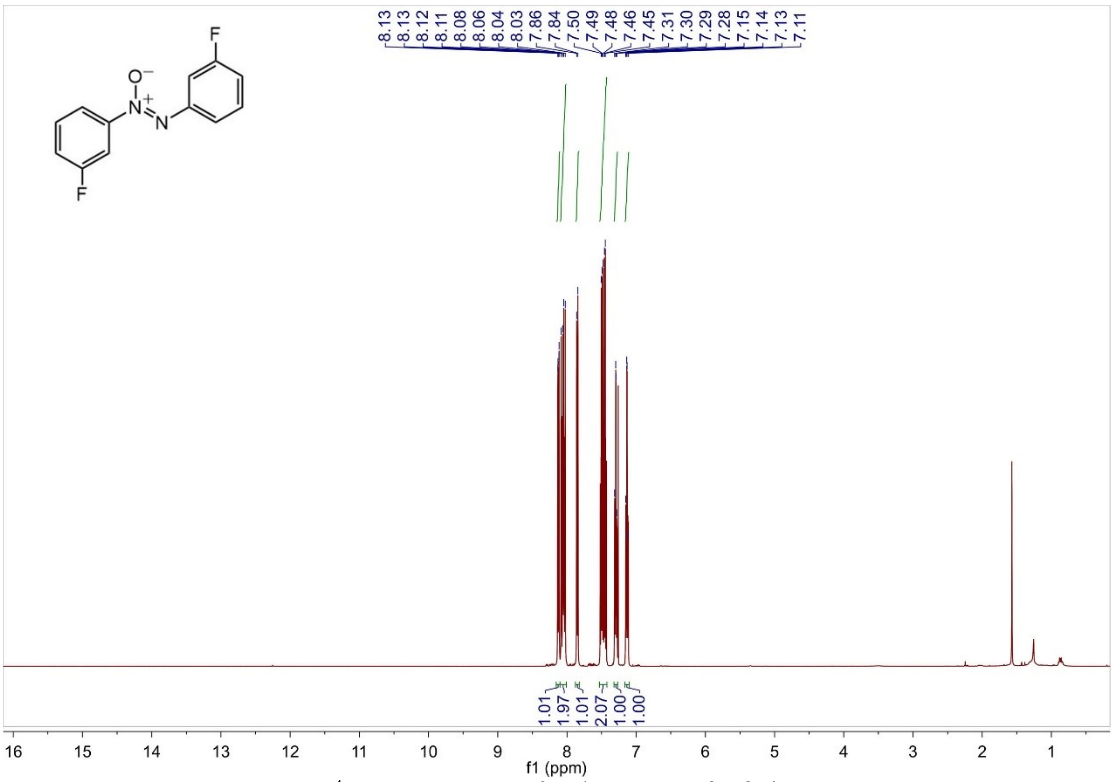
^{13}C NMR spectra of **3j** (126 MHz, $CDCl_3$)



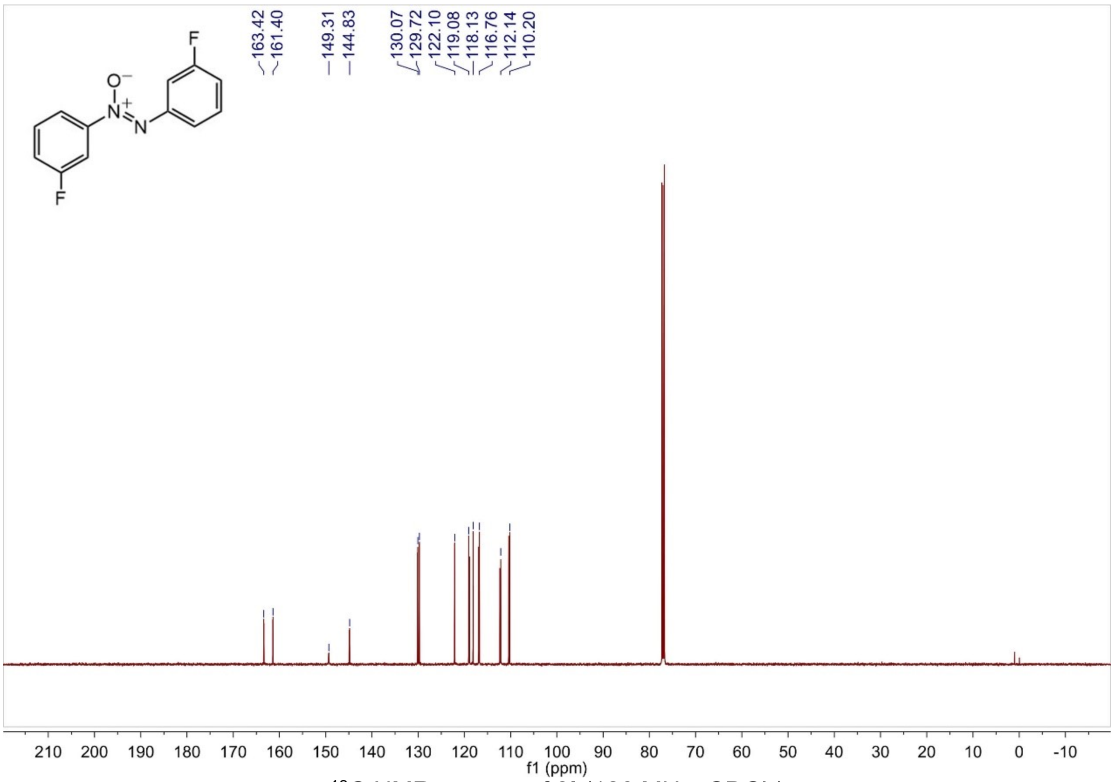
^{1}H NMR spectra of **3k** (500 MHz, $CDCl_3$)



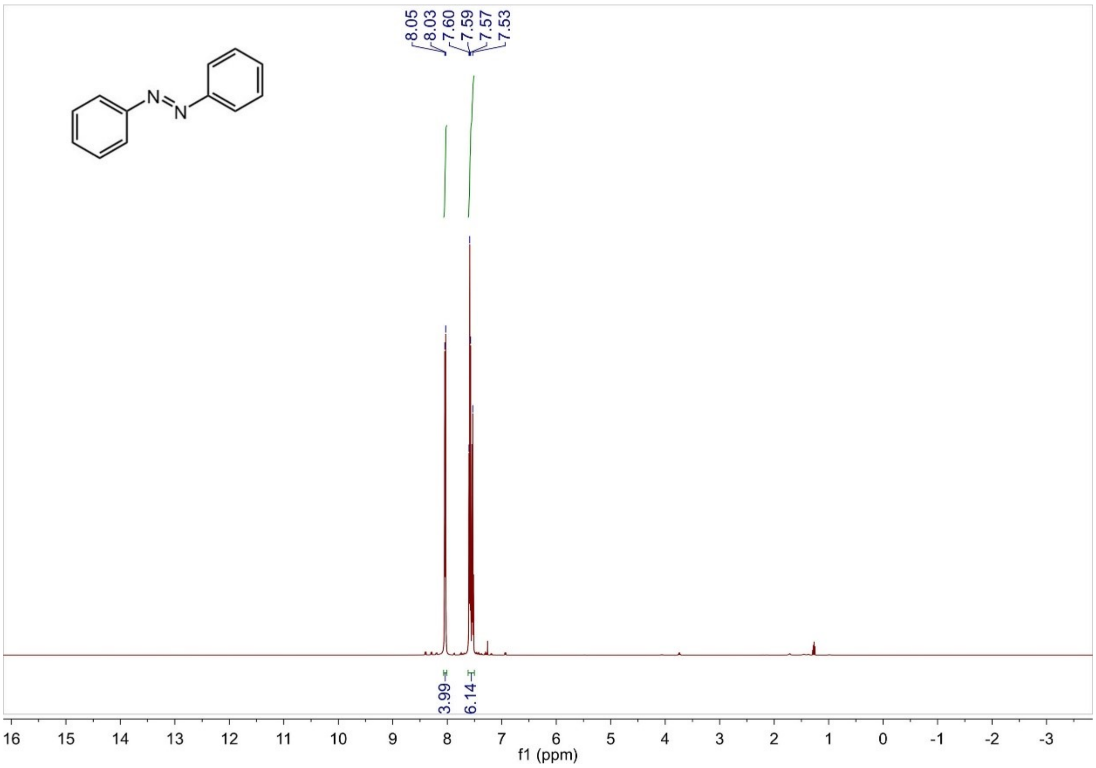
^{13}C NMR spectra of **3k** (126 MHz, $CDCl_3$)

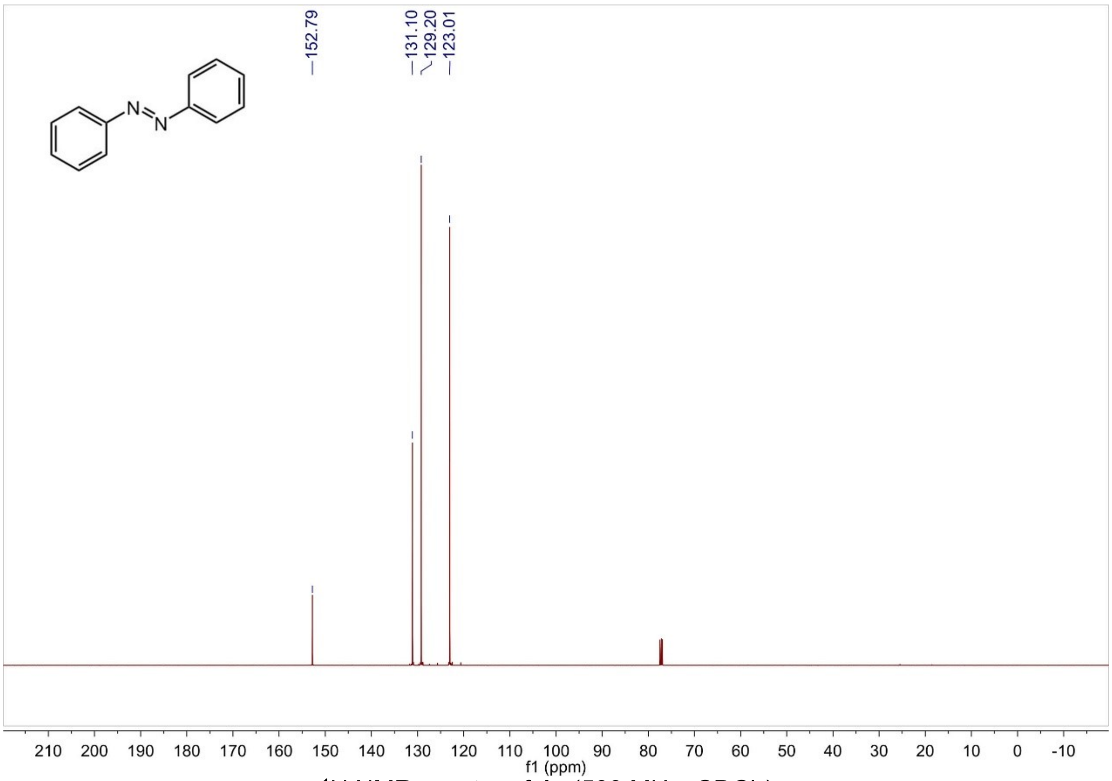


^{1}H NMR spectra of **3l** (500 MHz, $CDCl_3$)



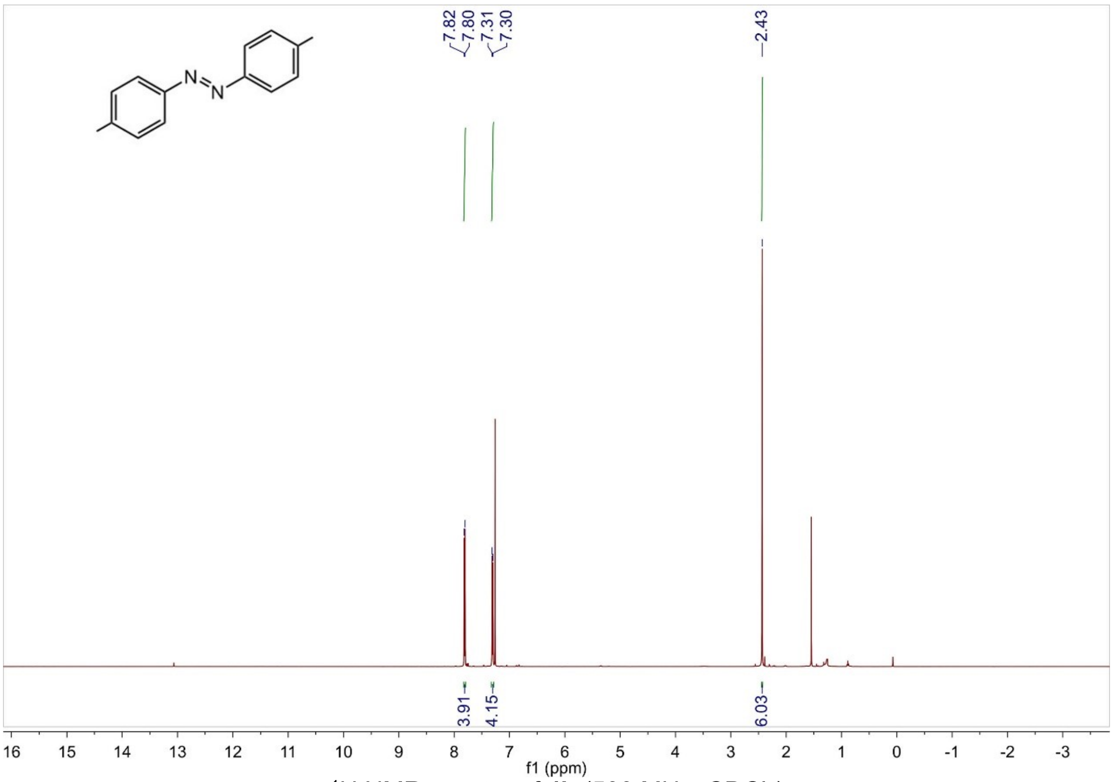
^{13}C NMR spectra of **3l** (126 MHz, $CDCl_3$)



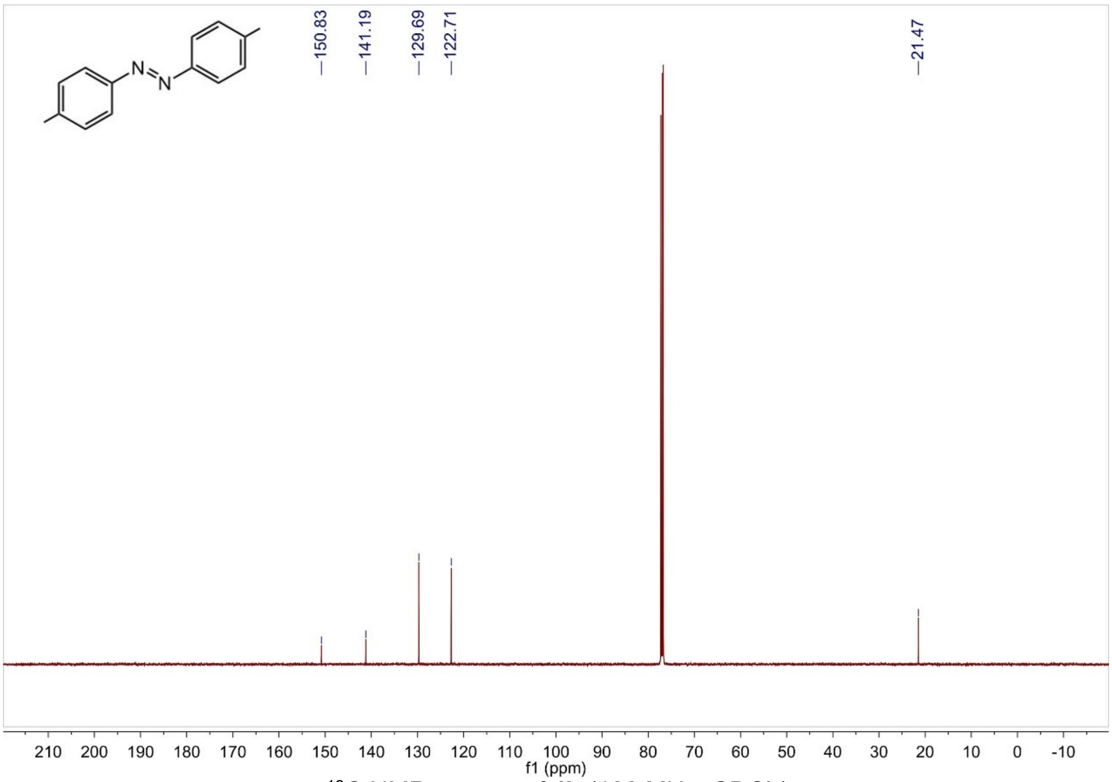


^{1}H NMR spectra of **4a** (500 MHz, $CDCl_3$)

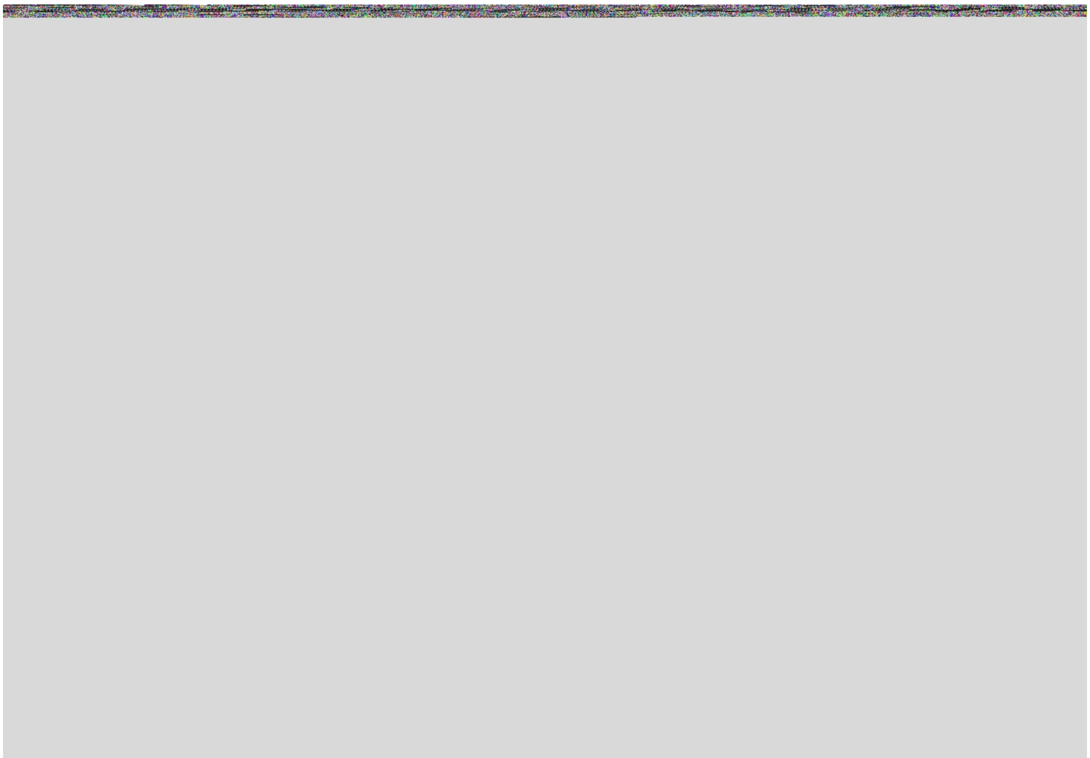
^{13}C NMR spectra of **4a** (126 MHz, $CDCl_3$)



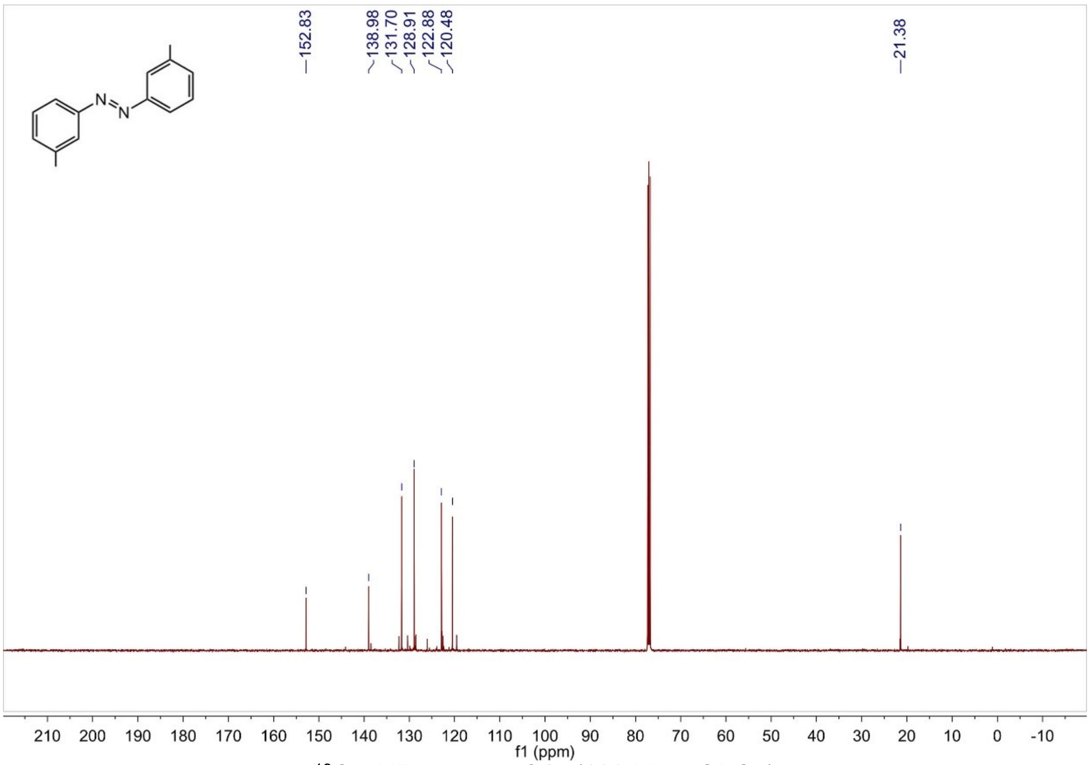
^{1}H NMR spectra of **4b** (500 MHz, $CDCl_3$)



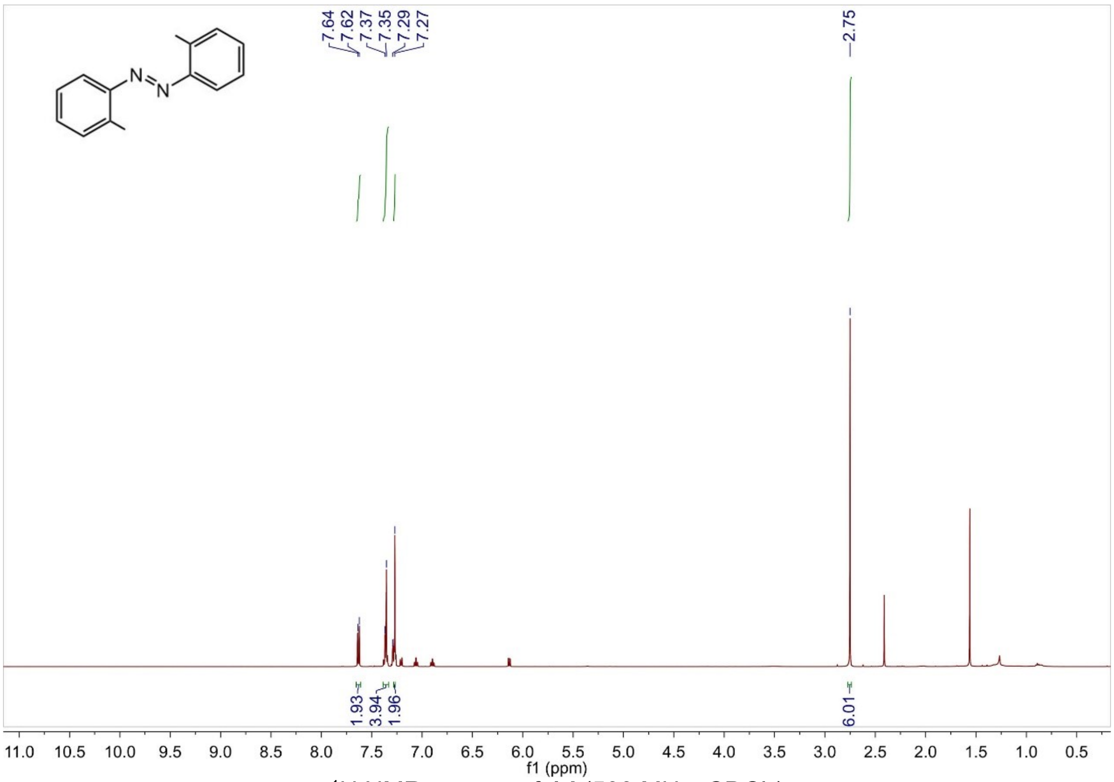
^{13}C NMR spectra of **4b** (126 MHz, $CDCl_3$)



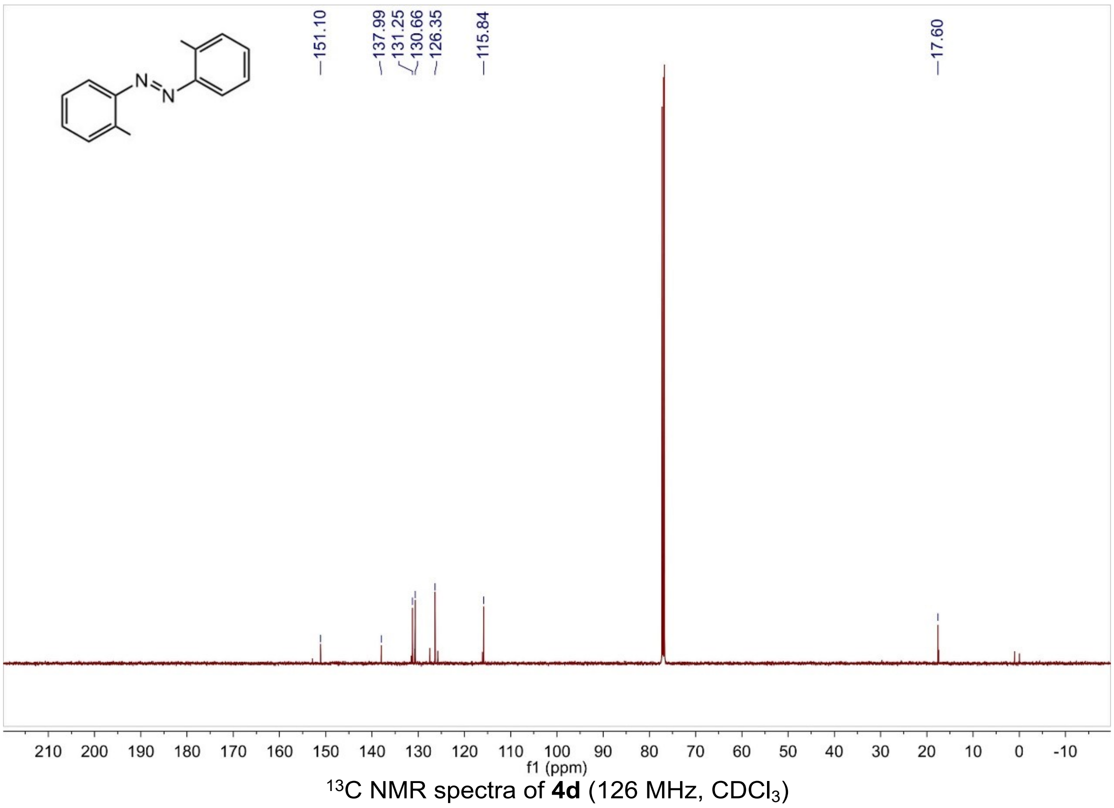
^{1}H NMR spectra of **4c** (500 MHz, $CDCl_3$)



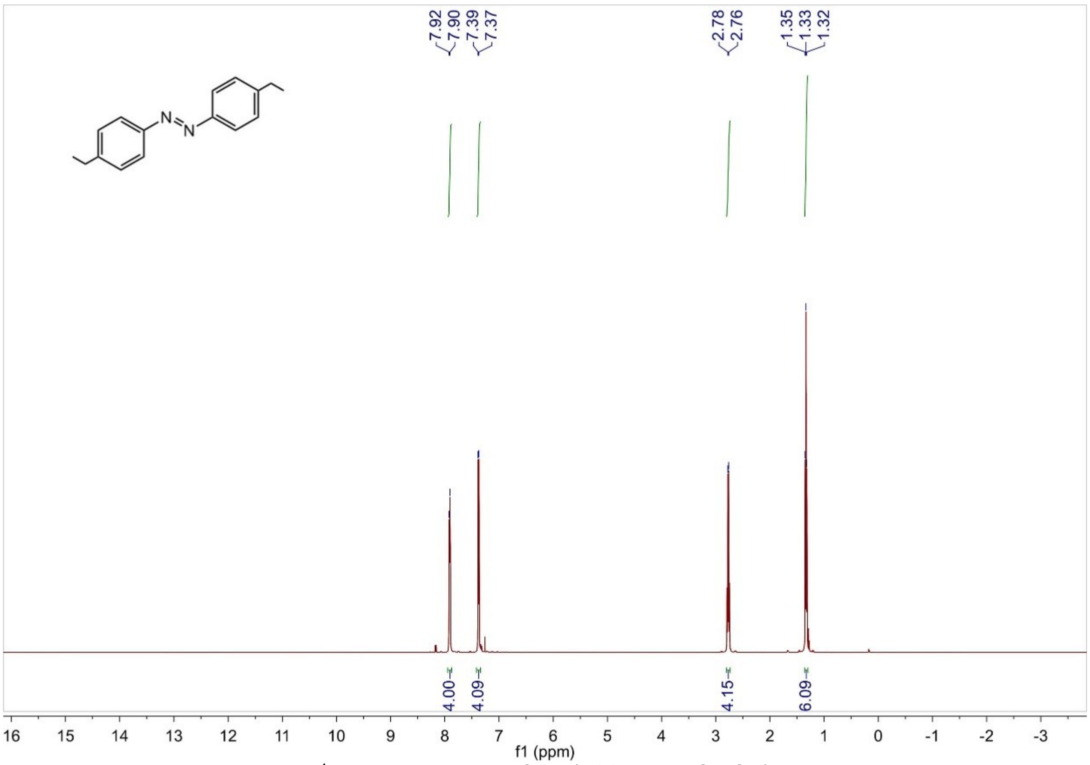
^{13}C NMR spectra of **4c** (126 MHz, $CDCl_3$)



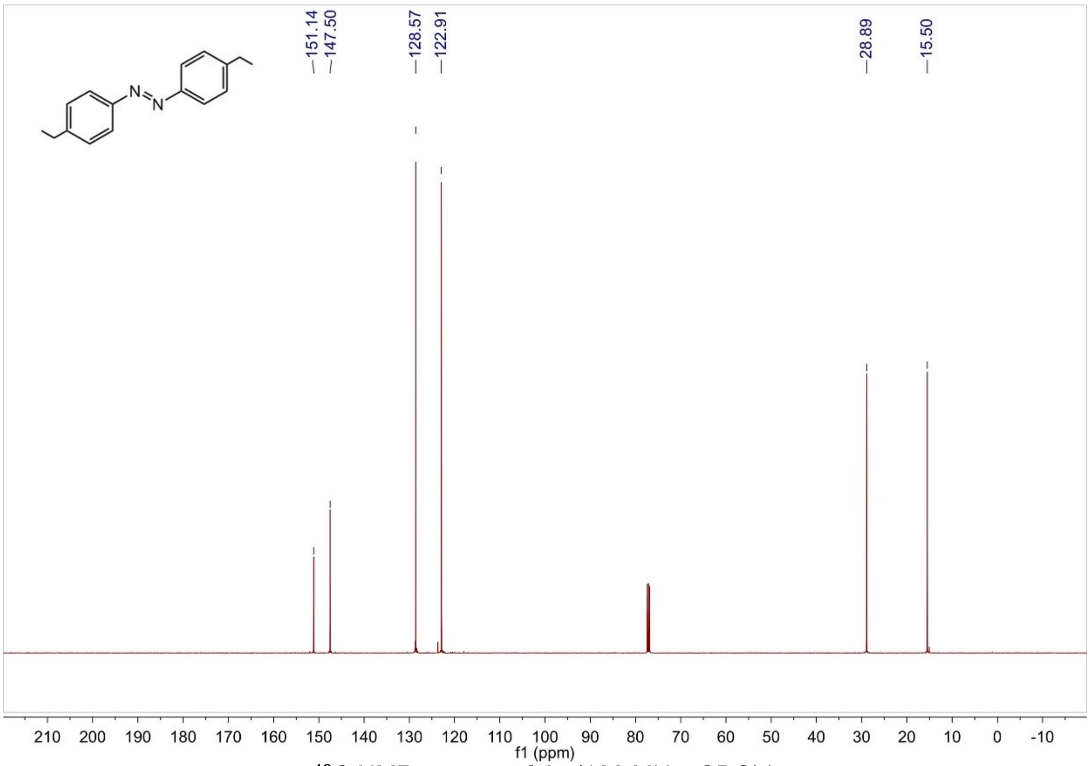
^{1}H NMR spectra of **4d** (500 MHz, $CDCl_3$)



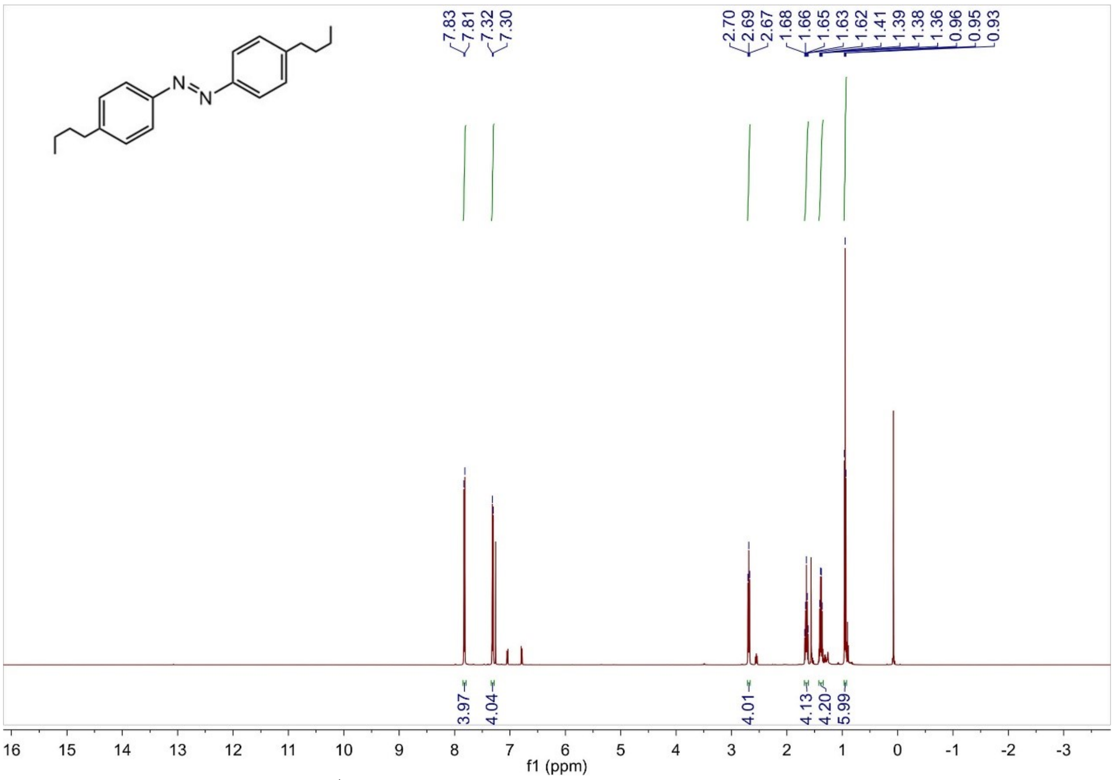
^{13}C NMR spectra of **4d** (126 MHz, $CDCl_3$)



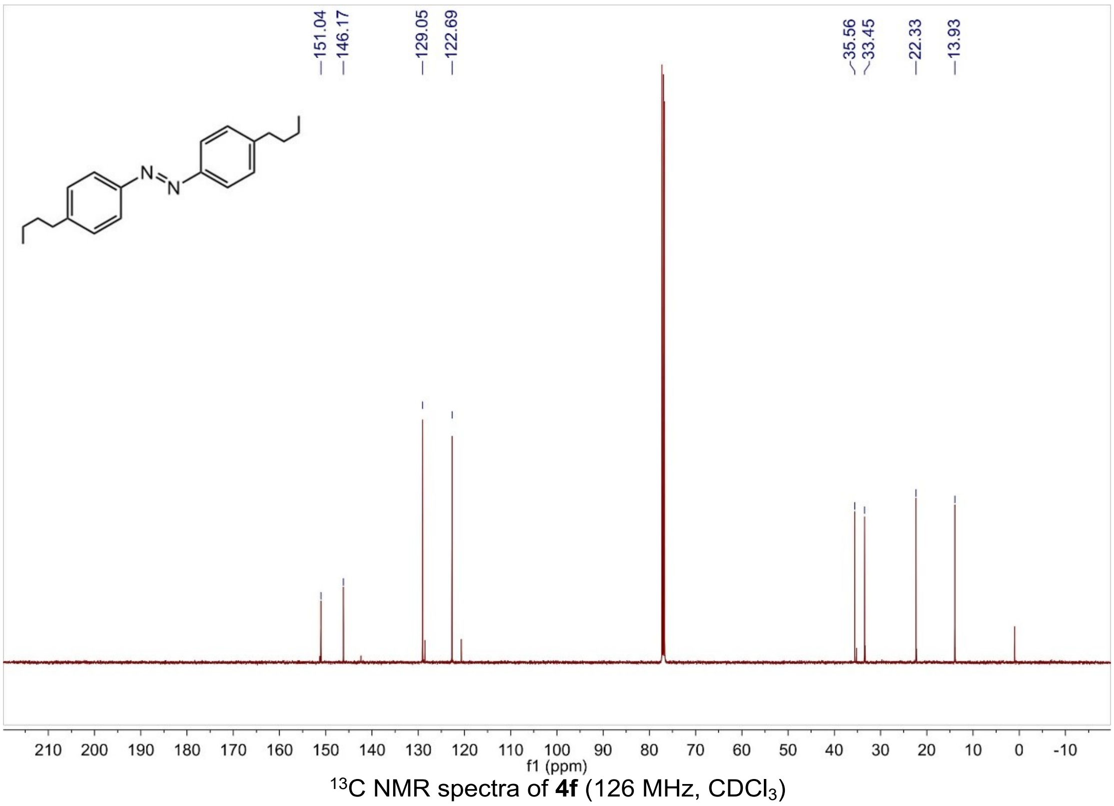
[1]H NMR spectra of **4e** (500 MHz, $CDCl_3$)



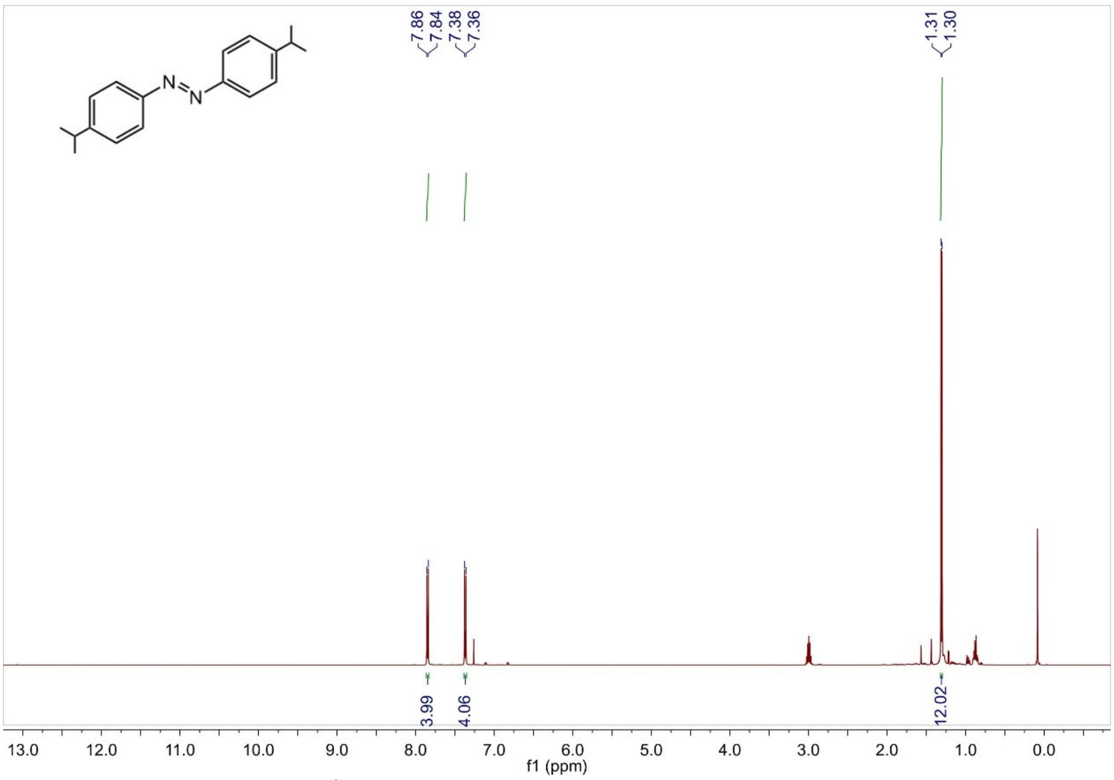
[13]C NMR spectra of **4e** (126 MHz, $CDCl_3$)



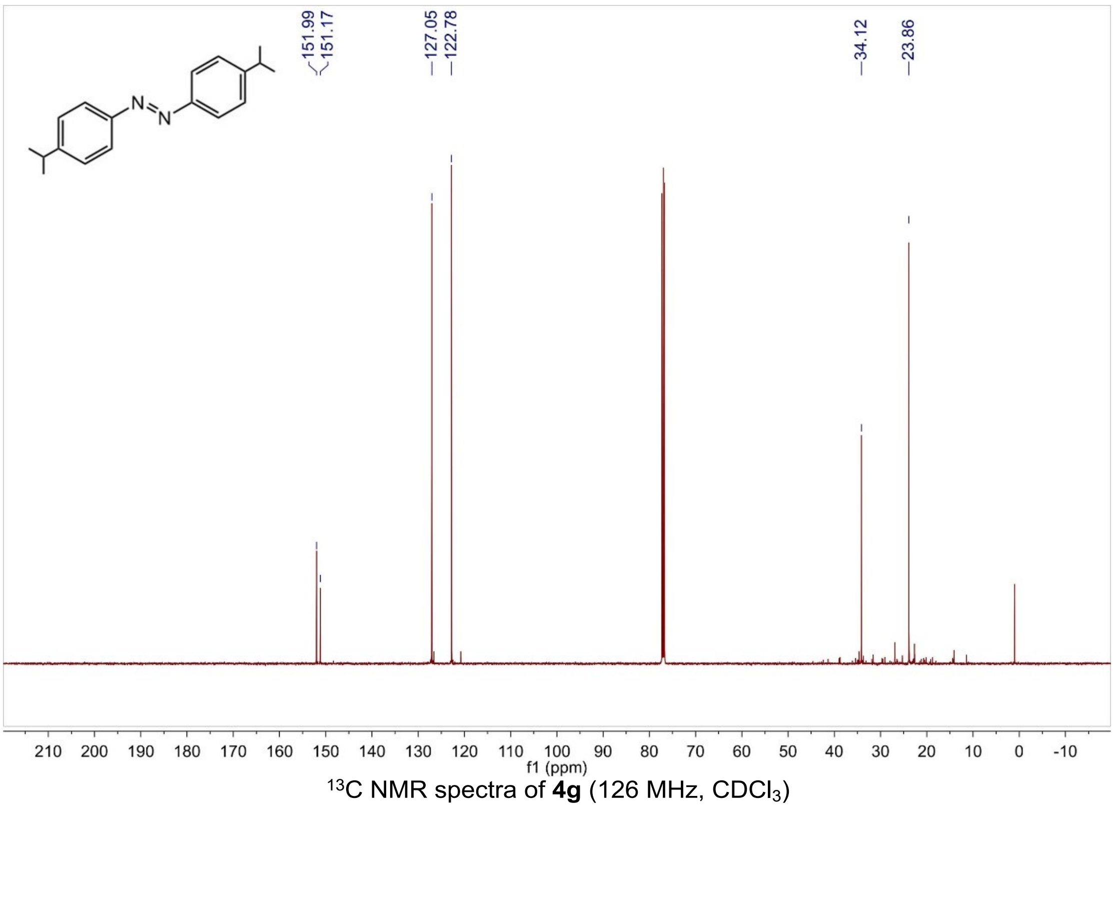
^{1}H NMR spectra of **4f** (500 MHz, $CDCl_3$)



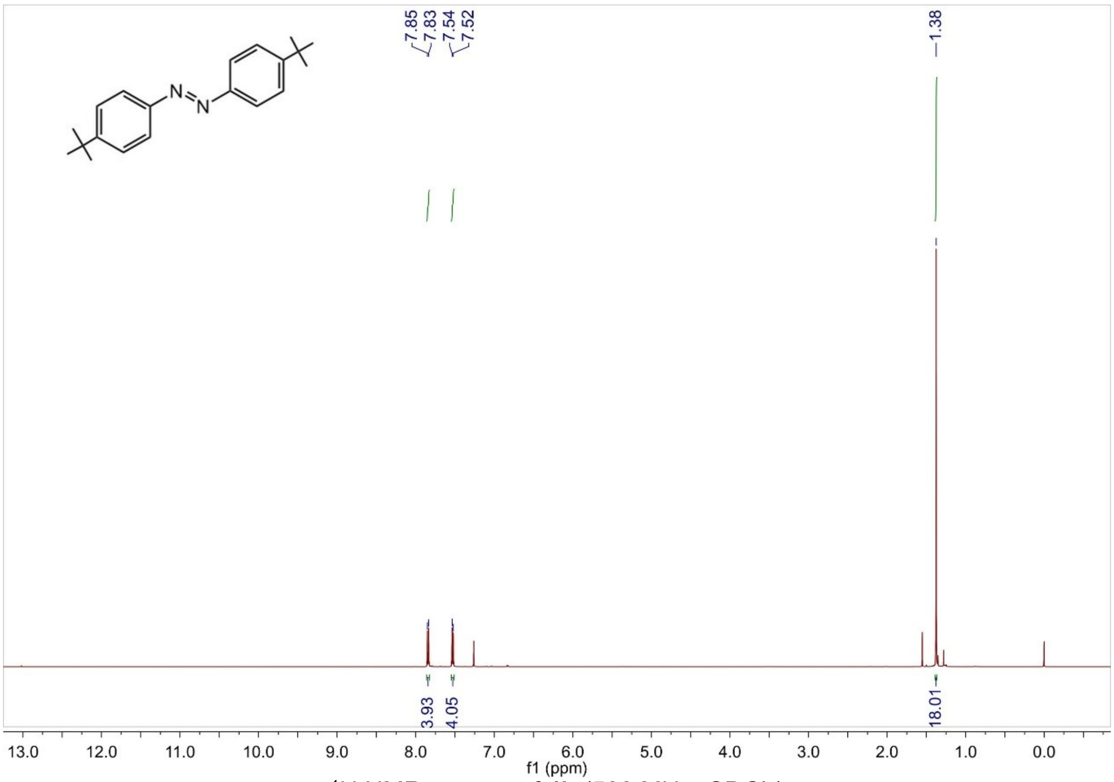
^{13}C NMR spectra of **4f** (126 MHz, $CDCl_3$)



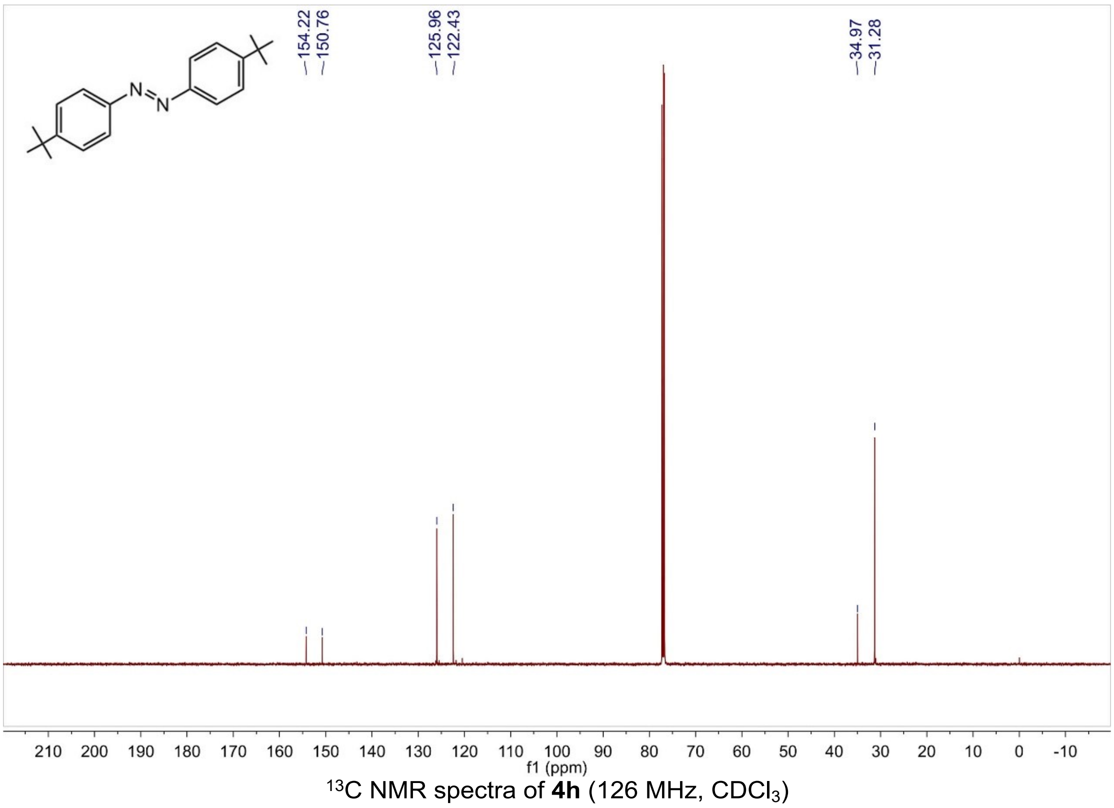
[1]H NMR spectra of **4g** (500 MHz, $CDCl_3$)



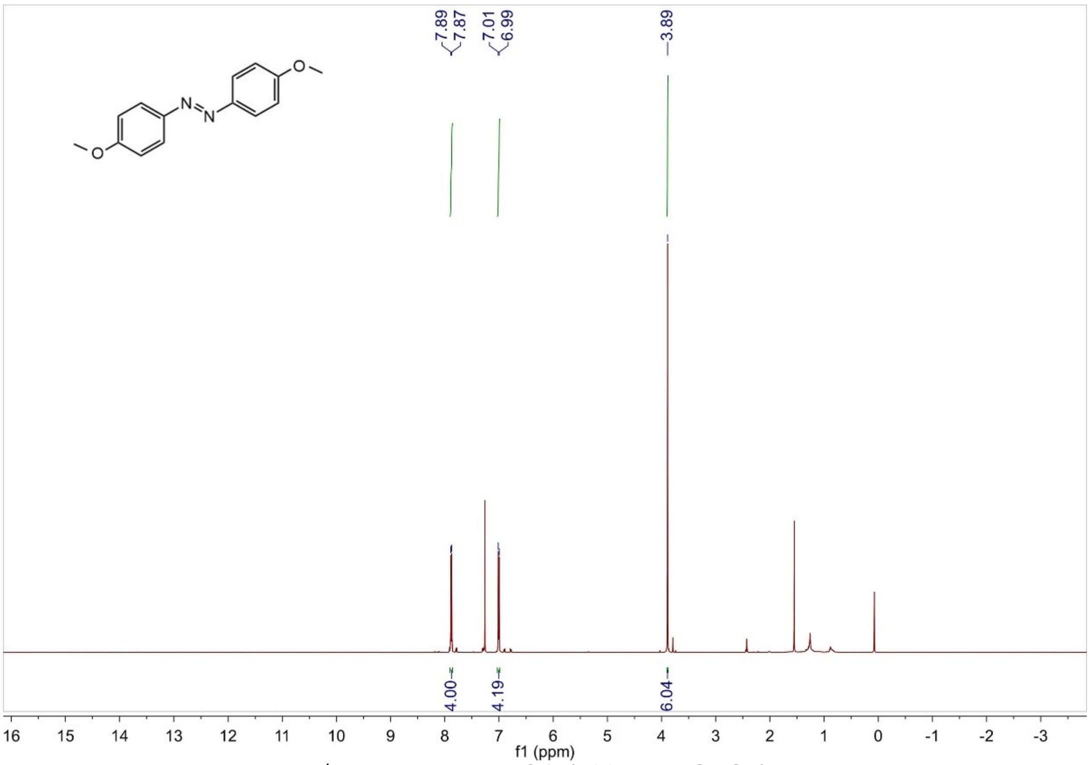
[13]C NMR spectra of **4g** (126 MHz, $CDCl_3$)



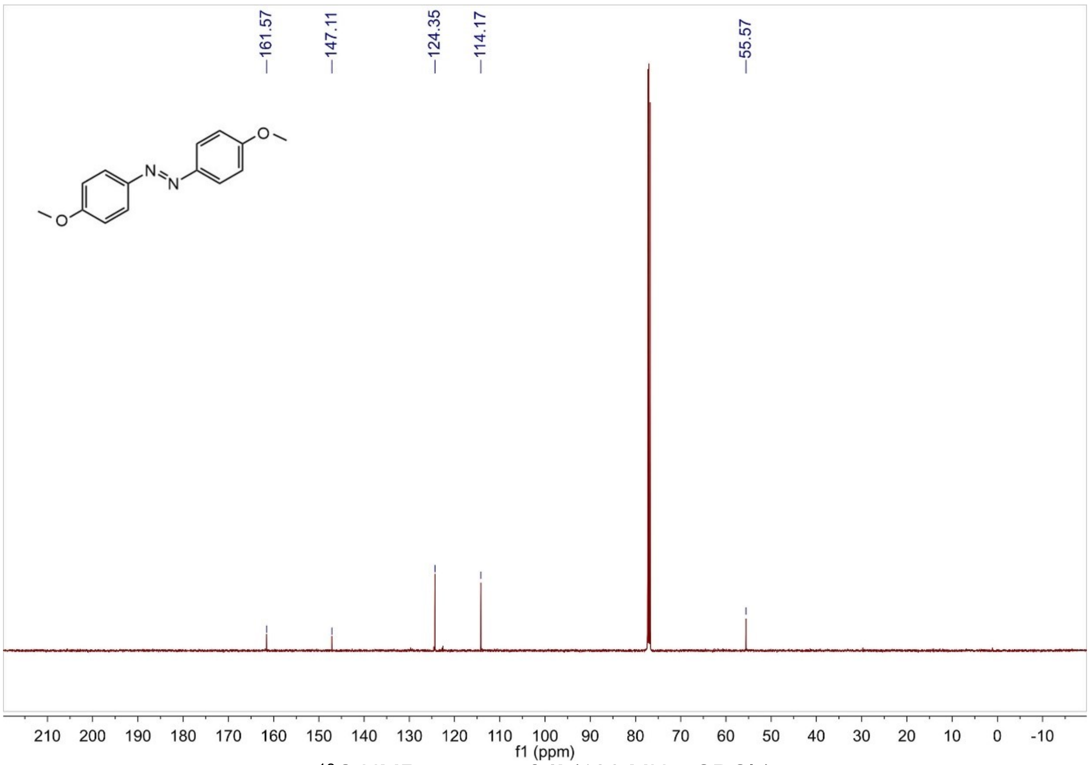
^{1}H NMR spectra of **4h** (500 MHz, $CDCl_3$)



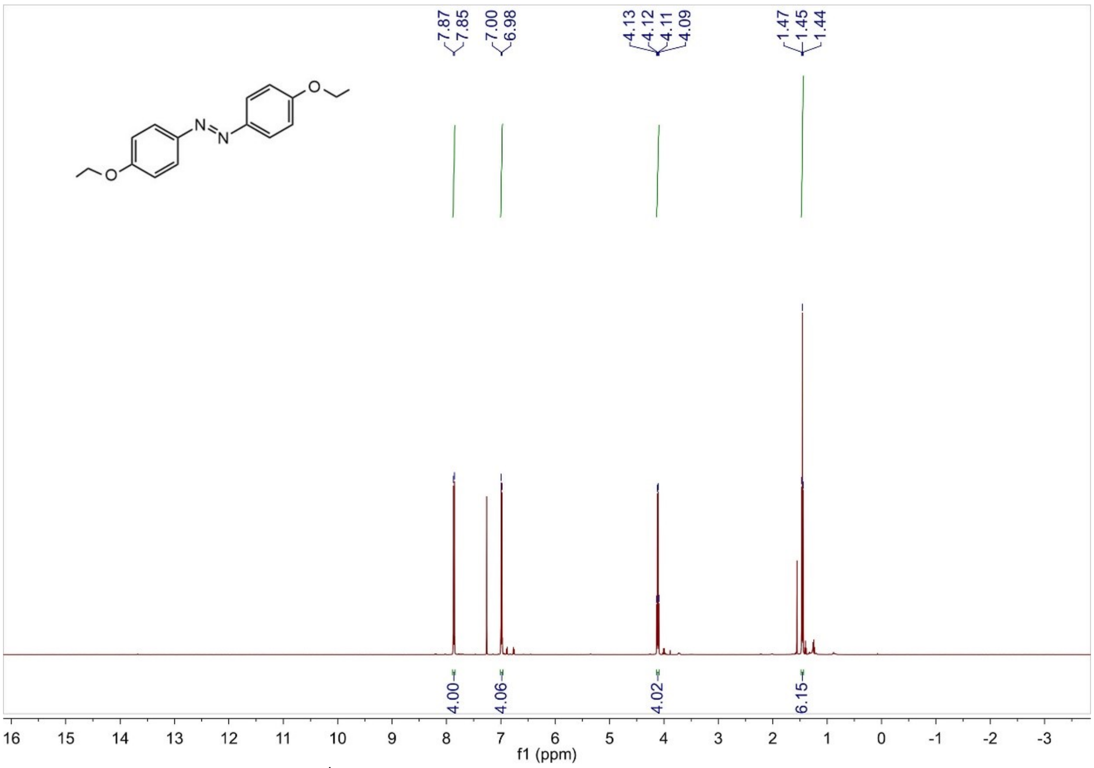
^{13}C NMR spectra of **4h** (126 MHz, $CDCl_3$)



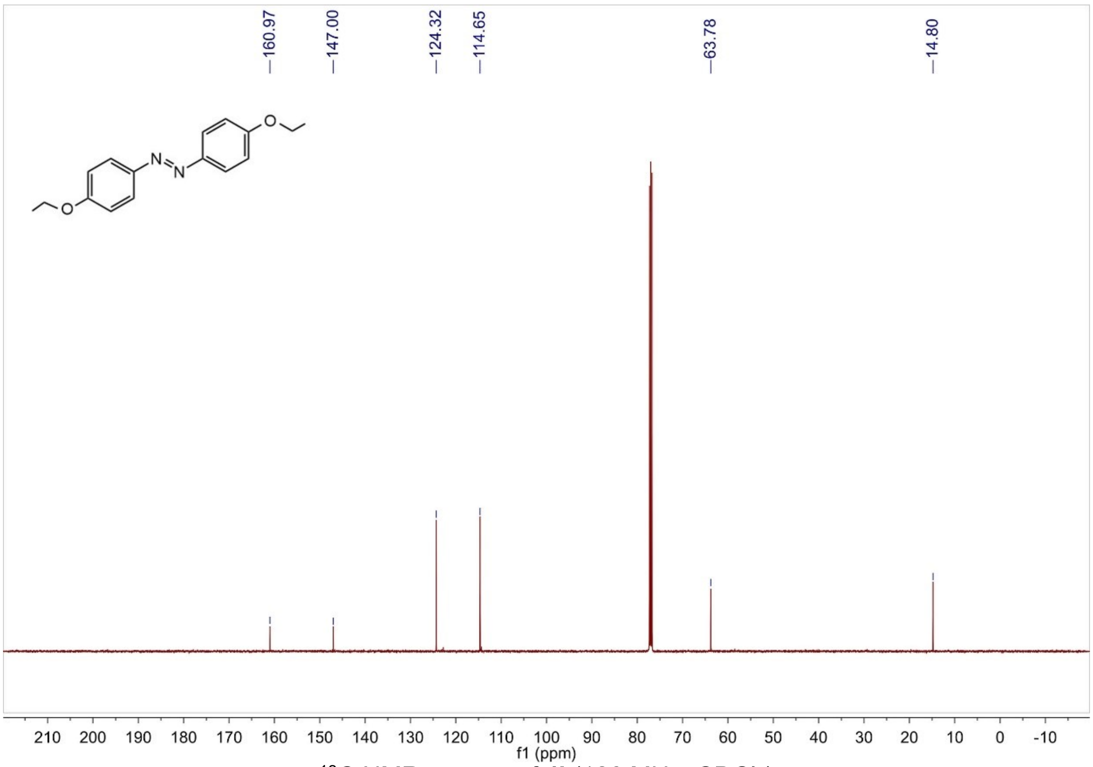
^{1}H NMR spectra of **4i** (500 MHz, $CDCl_3$)



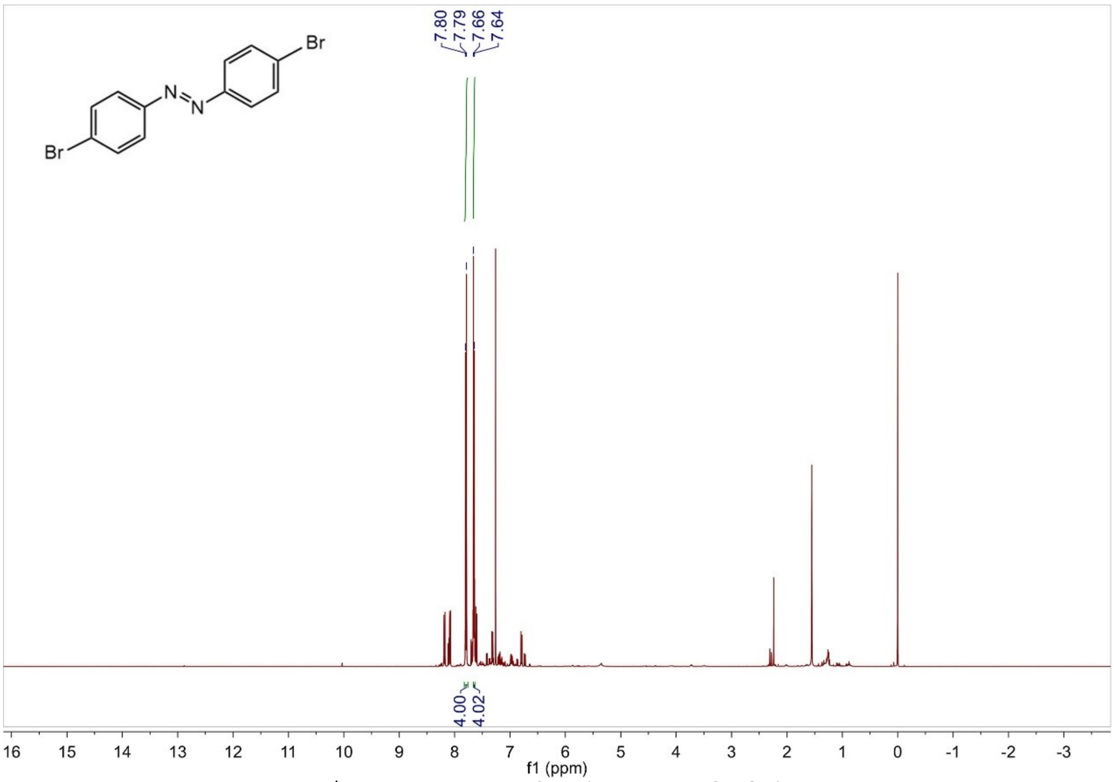
^{13}C NMR spectra of **4i** (126 MHz, $CDCl_3$)



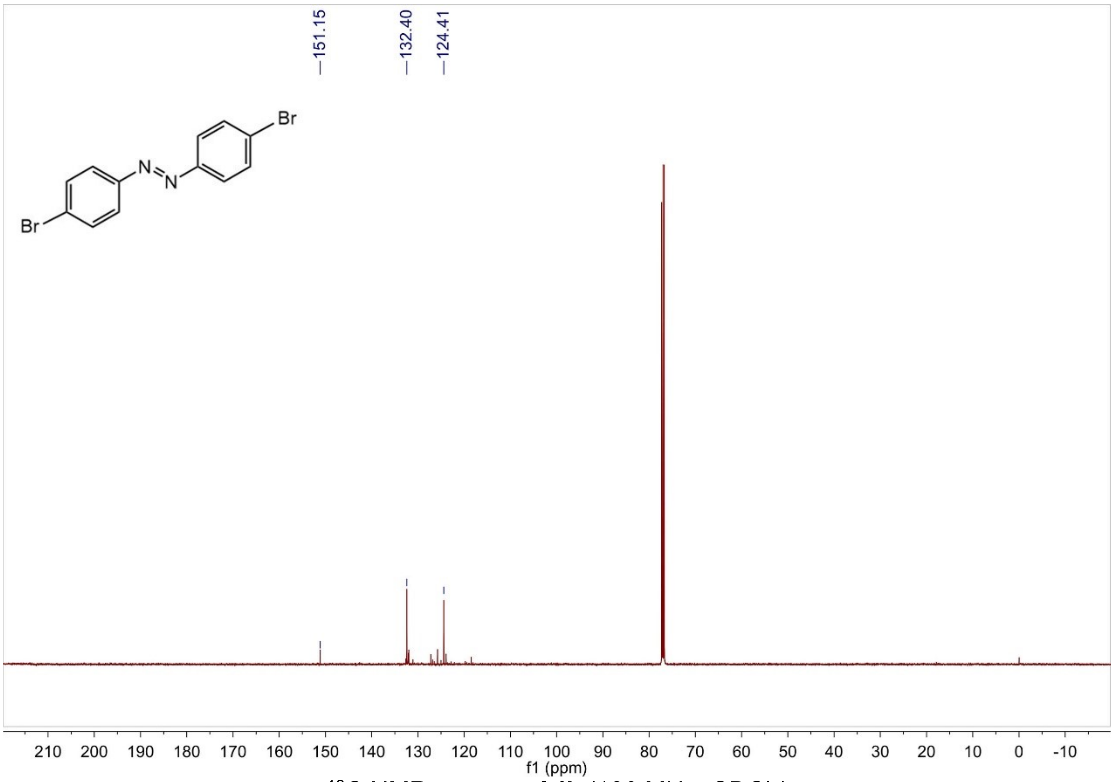
^{1}H NMR spectra of **4j** (500 MHz, $CDCl_3$)



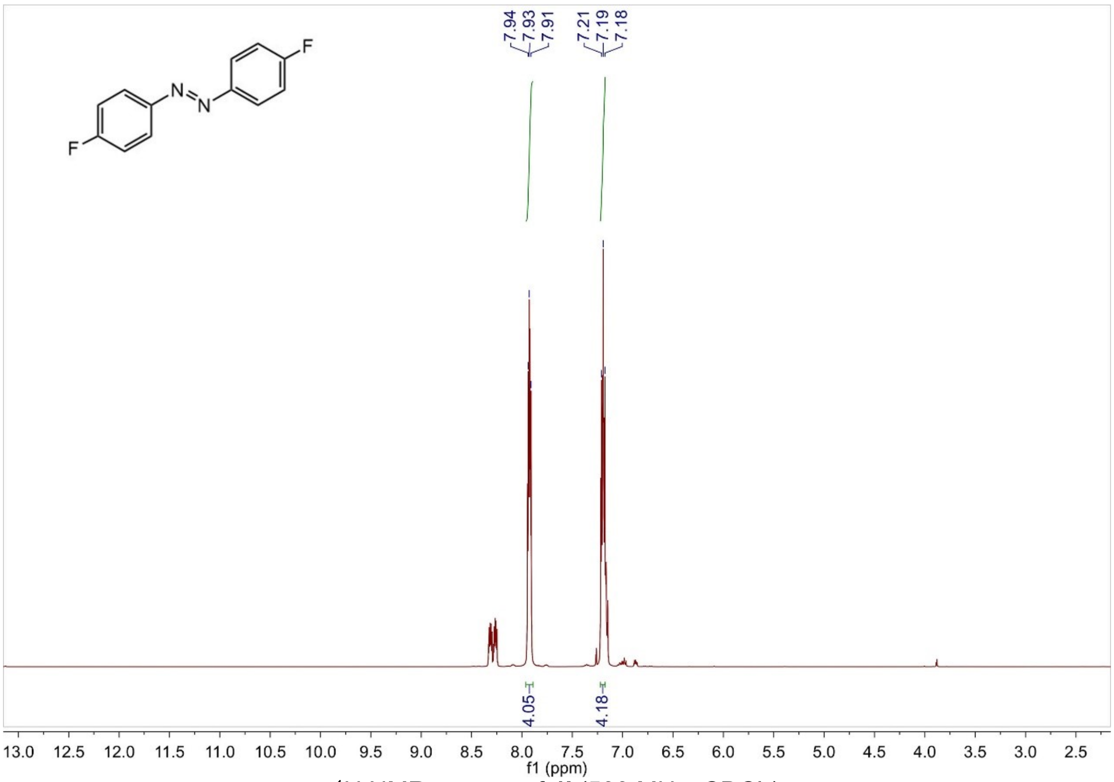
^{13}C NMR spectra of **4j** (126 MHz, $CDCl_3$)



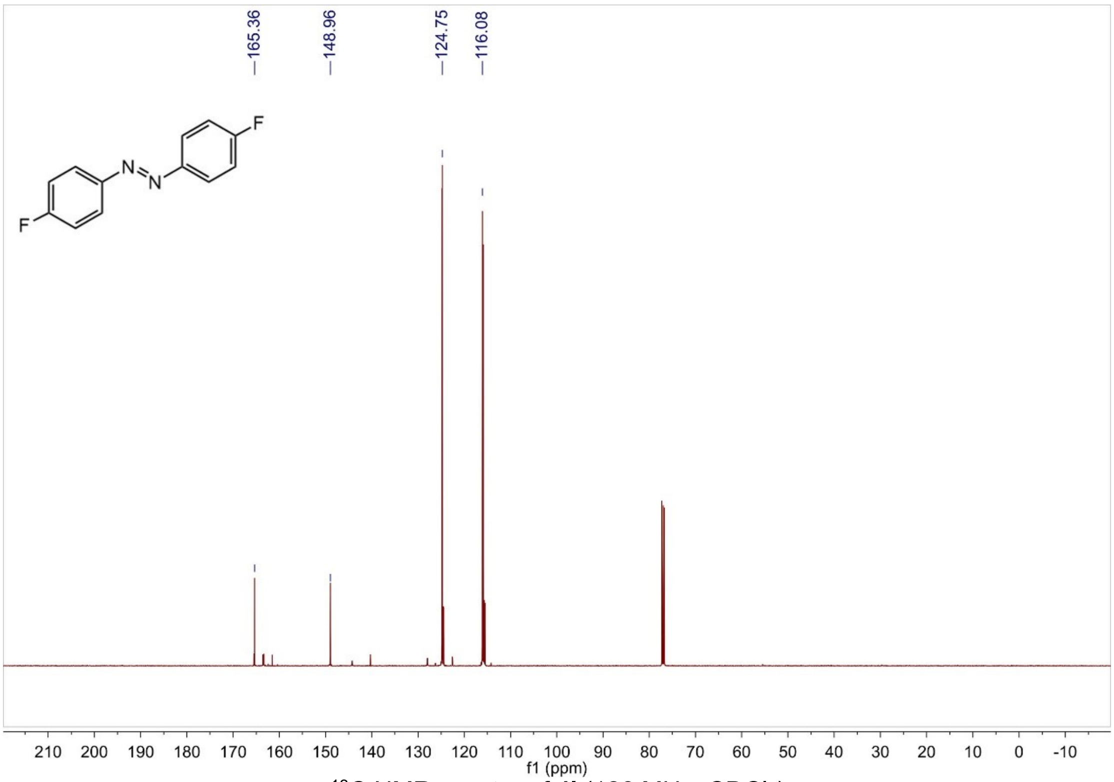
^{1}H NMR spectra of **4k** (500 MHz, $CDCl_3$)



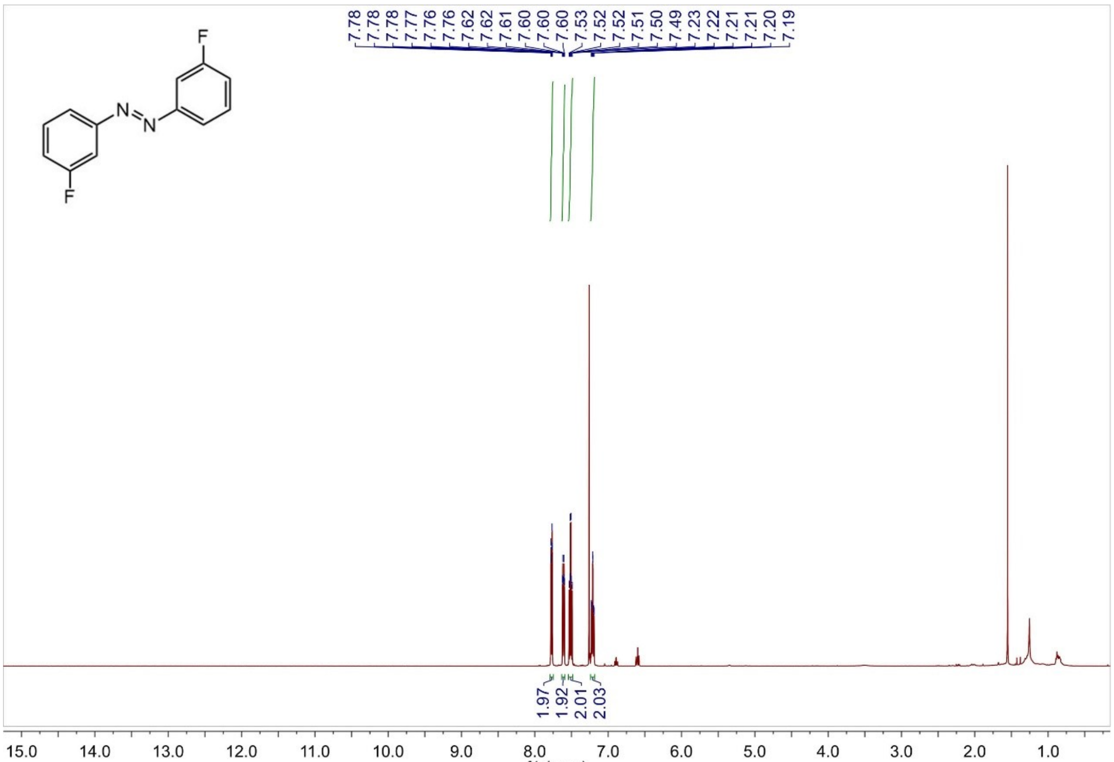
^{13}C NMR spectra of **4k** (126 MHz, $CDCl_3$)



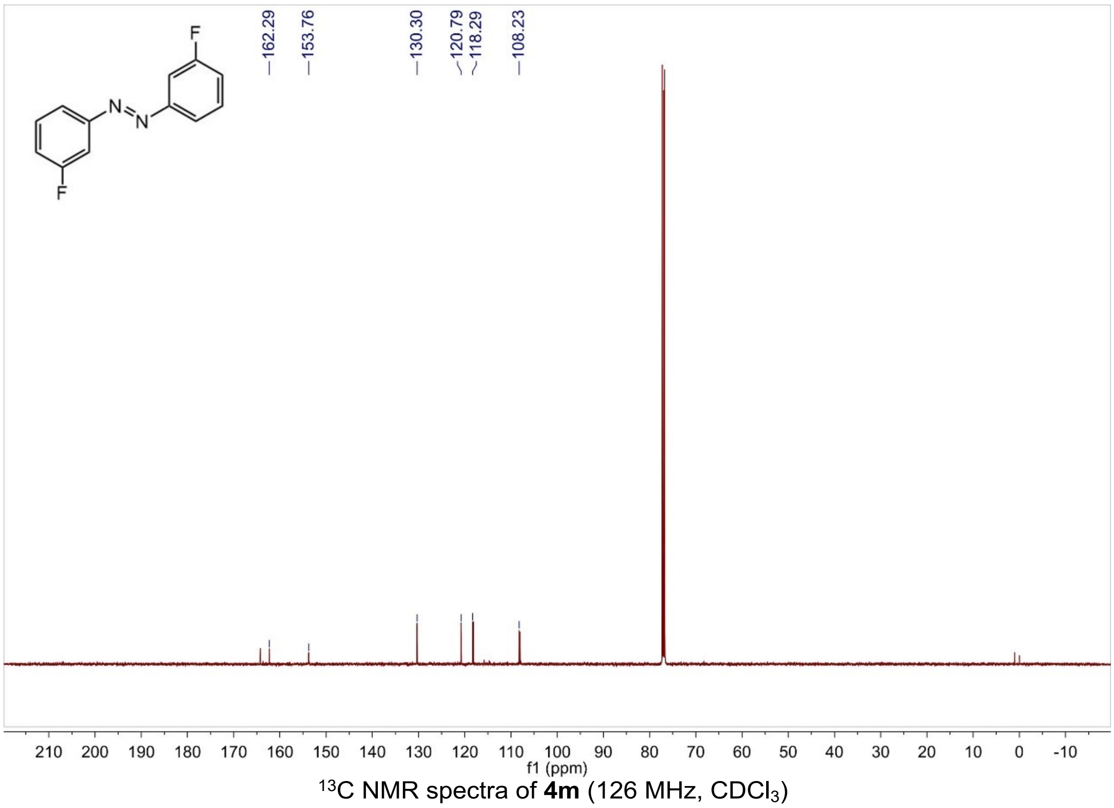
^{1}H NMR spectra of **4l** (500 MHz, $CDCl_3$)



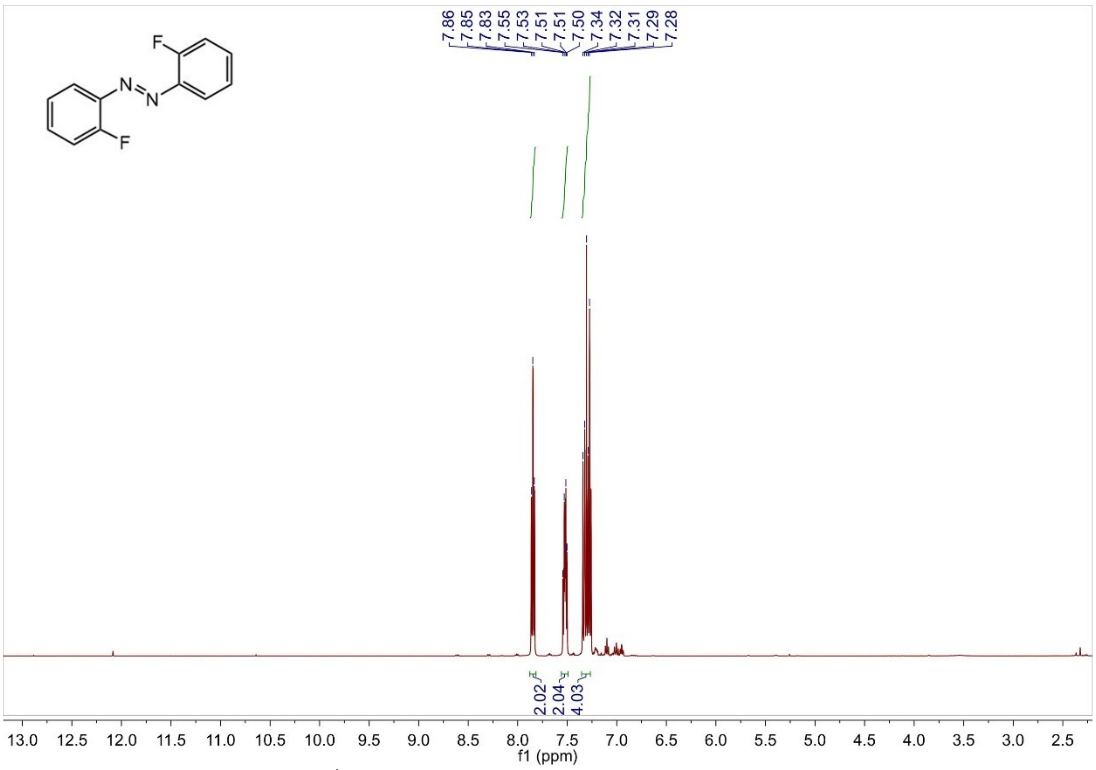
^{13}C NMR spectra of **4l** (126 MHz, $CDCl_3$)



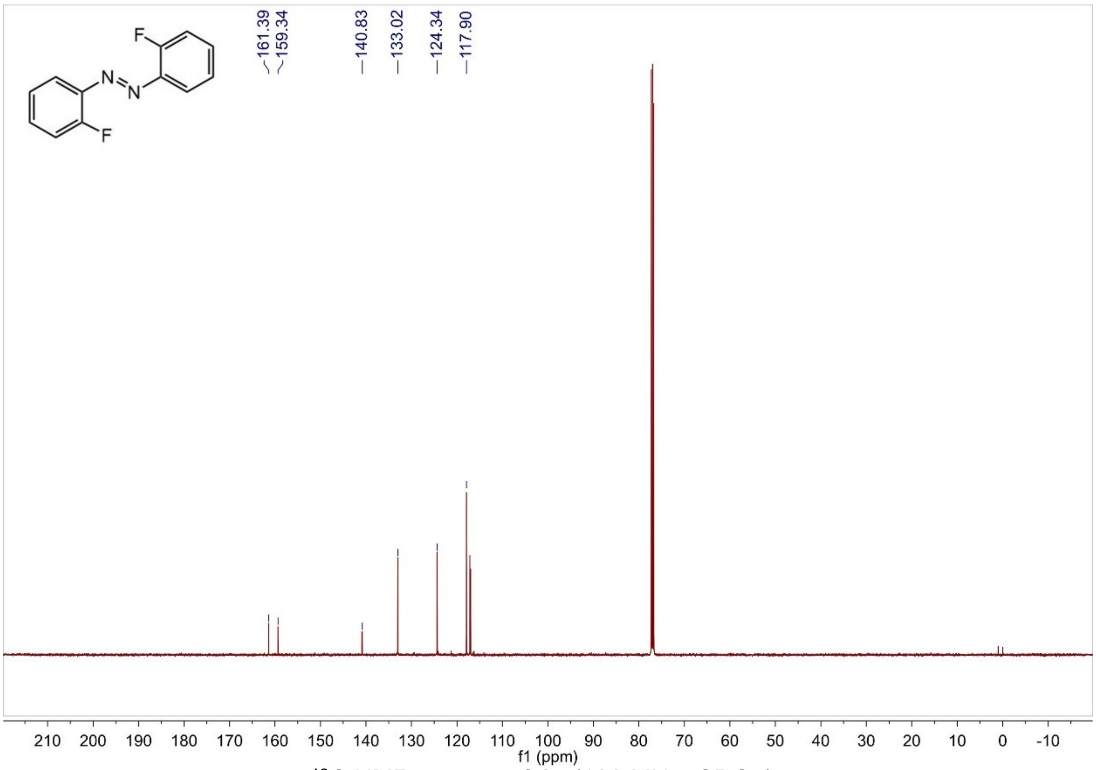
^{1}H NMR spectra of **4m** (500 MHz, $CDCl_3$)



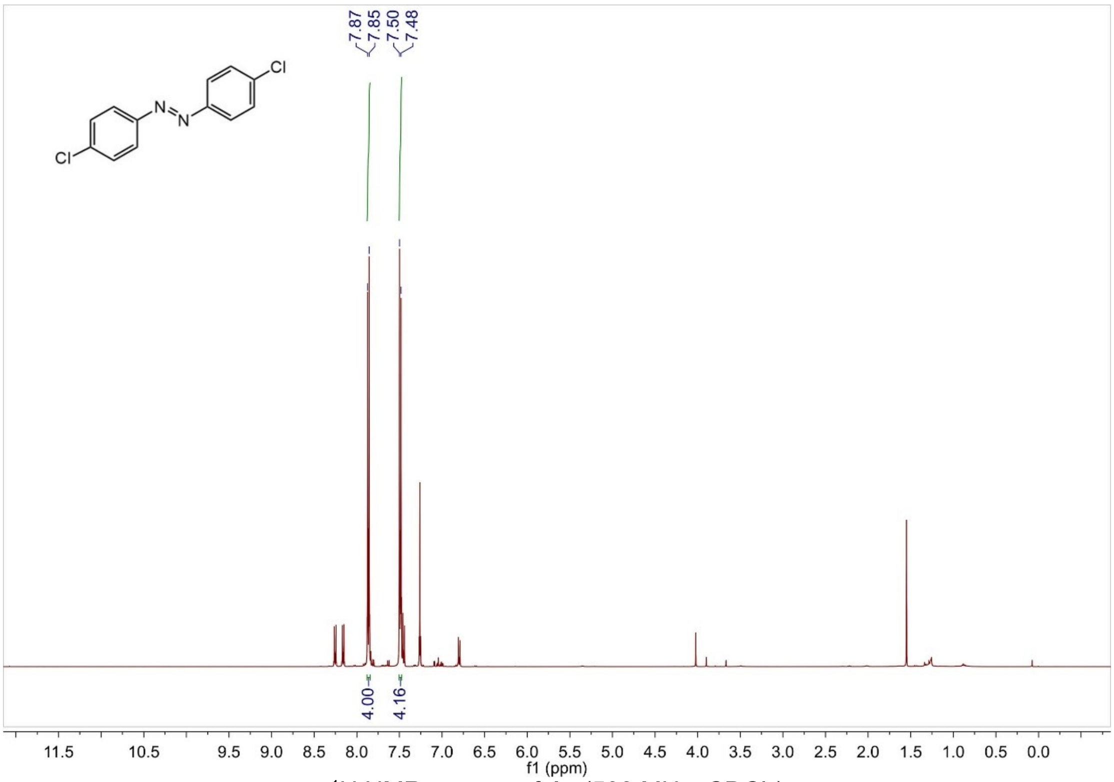
^{13}C NMR spectra of **4m** (126 MHz, $CDCl_3$)



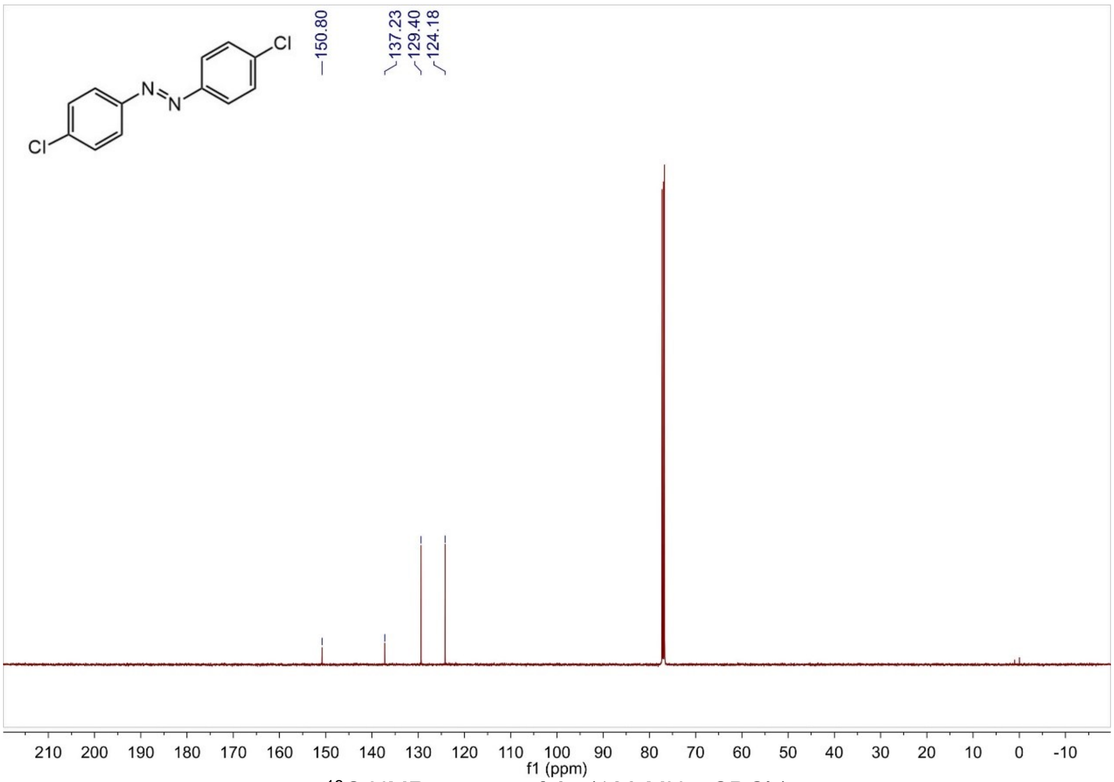
[1]H NMR spectra of **4n** (500 MHz, $CDCl_3$)



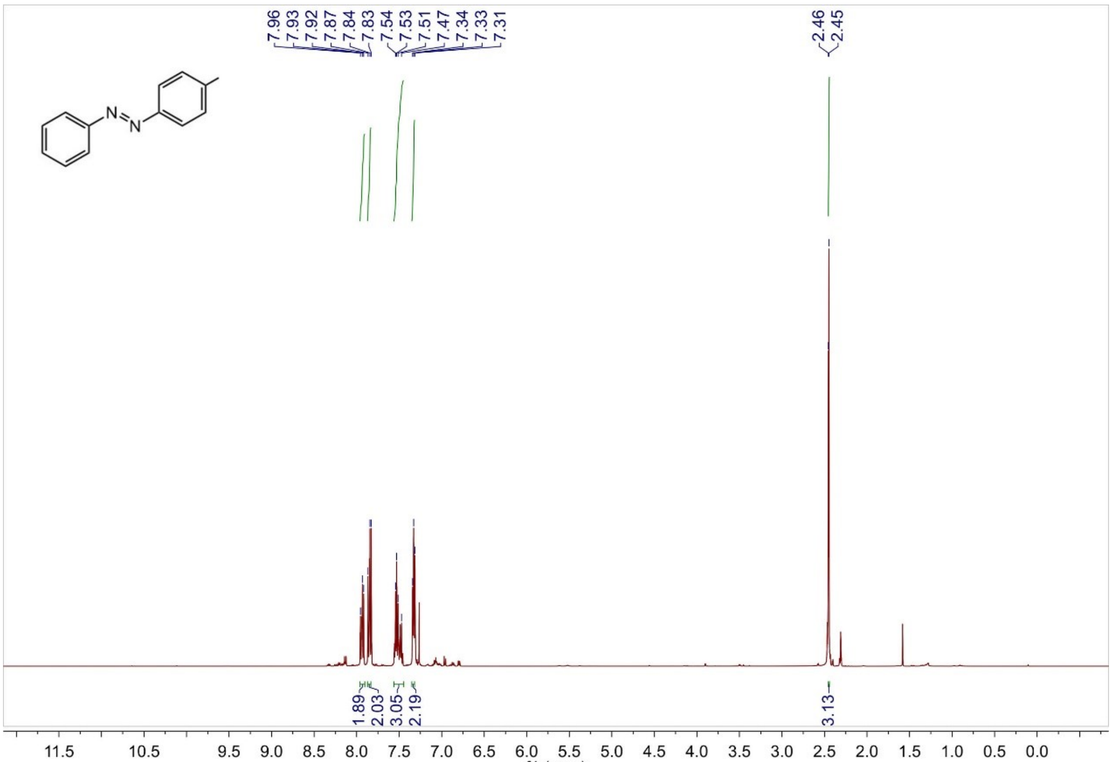
[13]C NMR spectra of **4n** (126 MHz, $CDCl_3$)



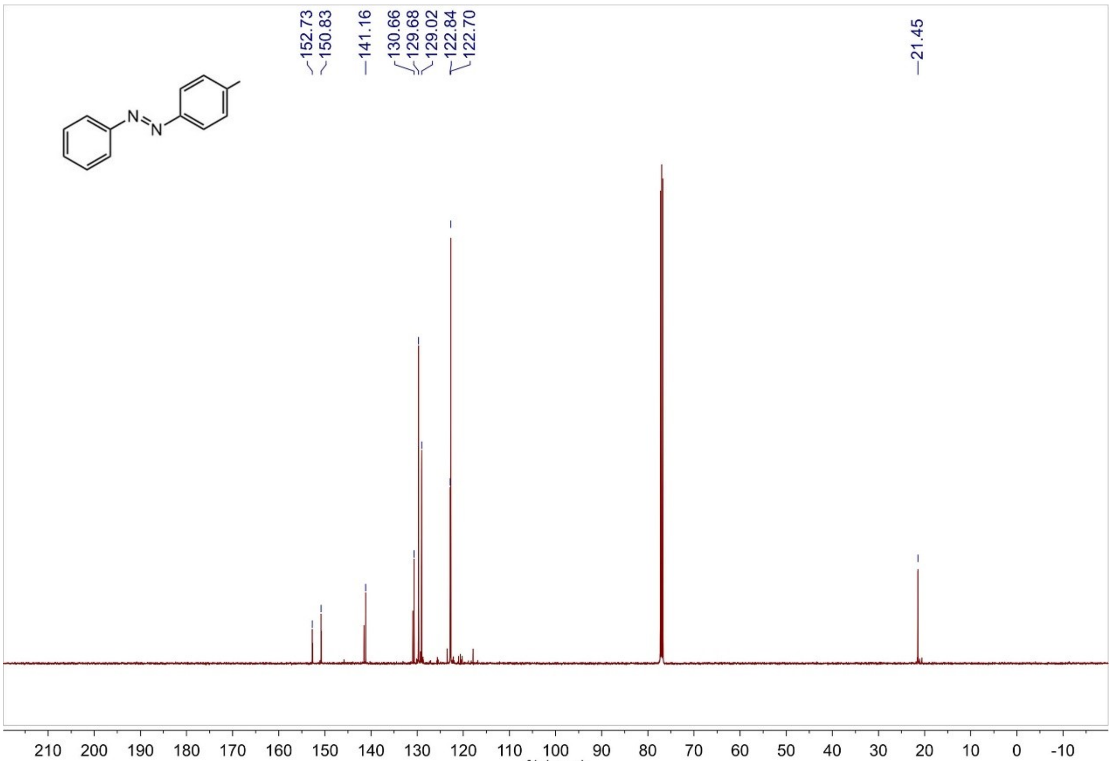
^{1}H NMR spectra of **4o** (500 MHz, $CDCl_3$)



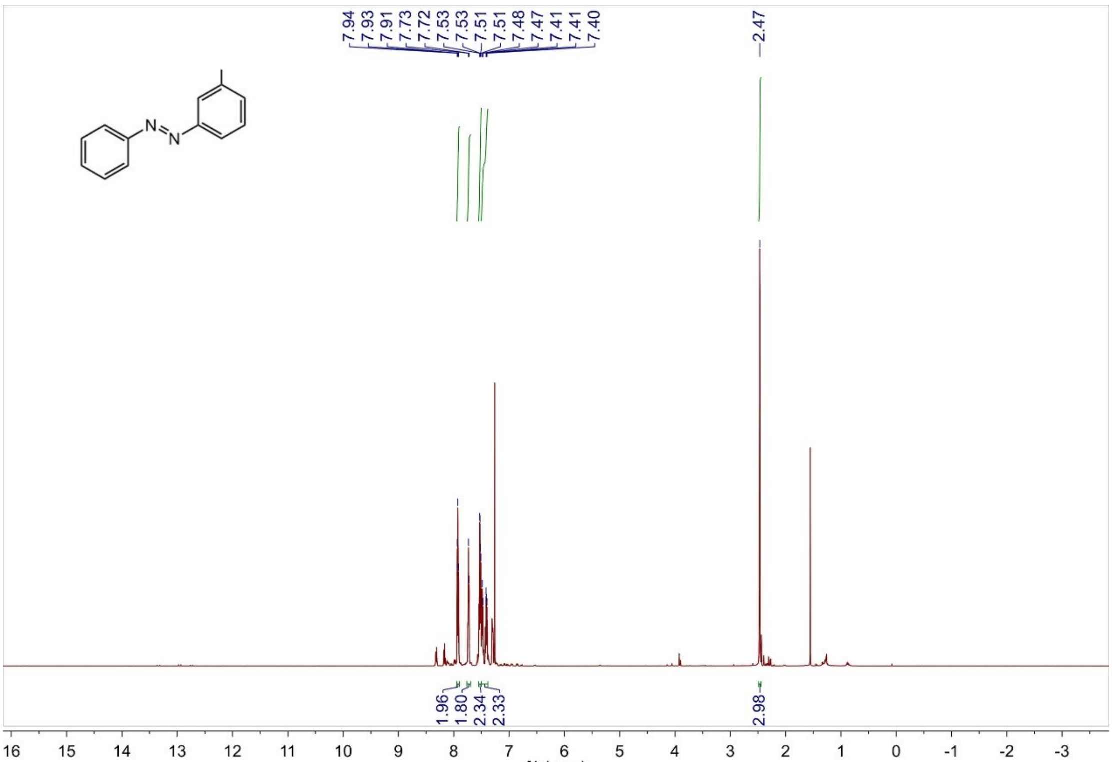
^{13}C NMR spectra of **4o** (126 MHz, $CDCl_3$)



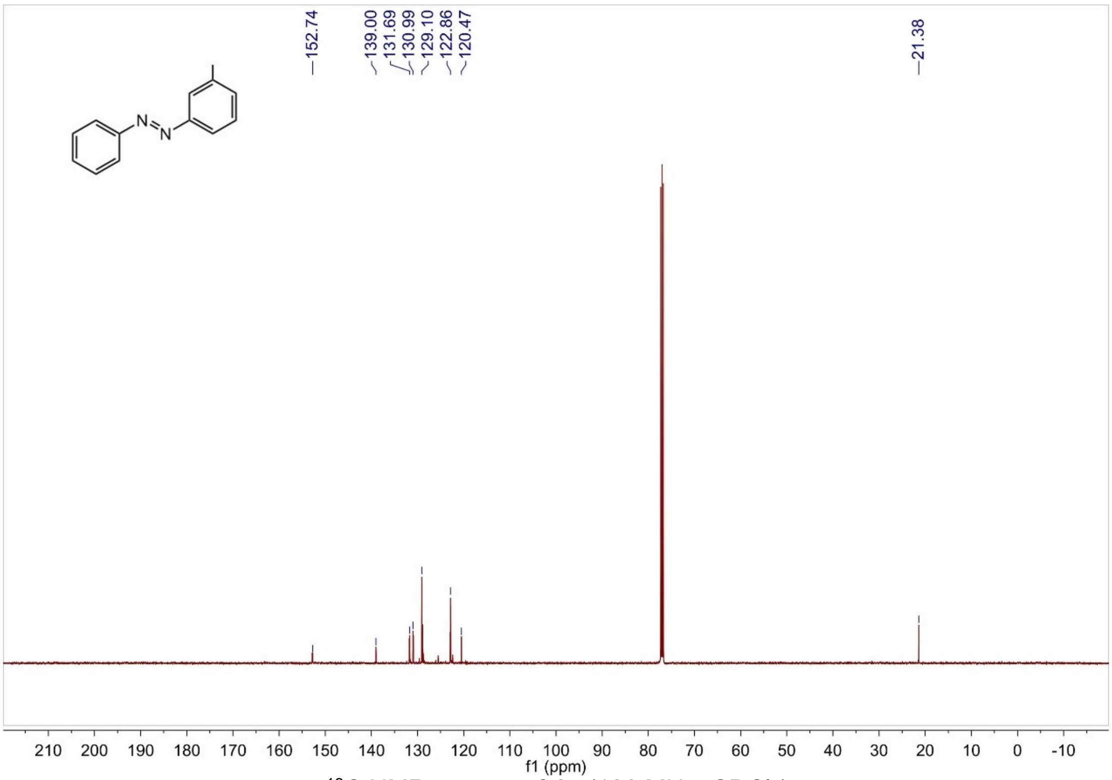
[1]H NMR spectra of **4p** (500 MHz, $CDCl_3$)



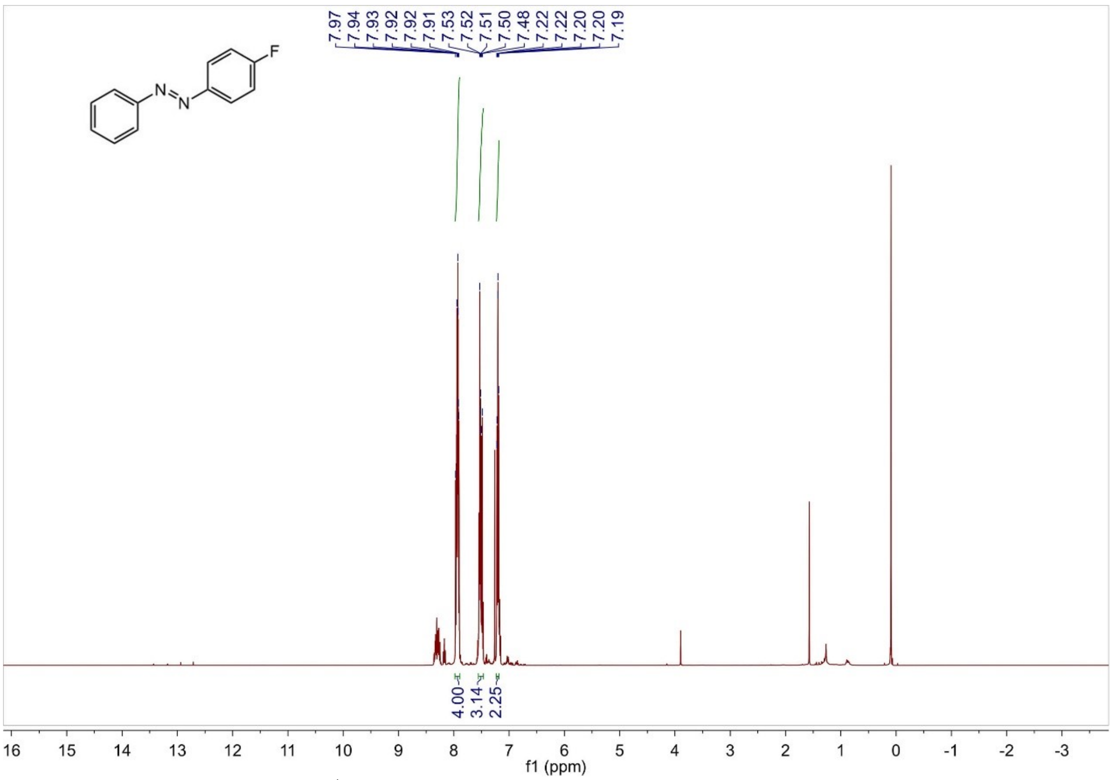
[13]C NMR spectra of **4p** (126 MHz, $CDCl_3$)



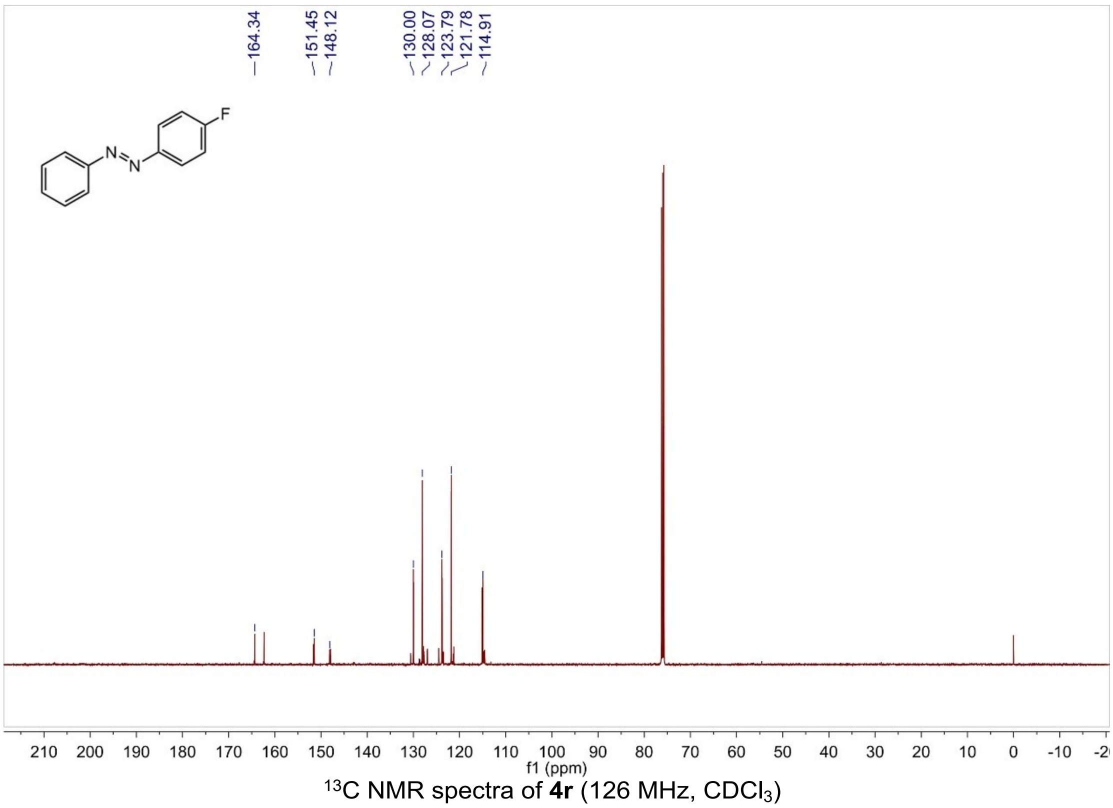
^{1}H NMR spectra of **4q** (500 MHz, $CDCl_3$)



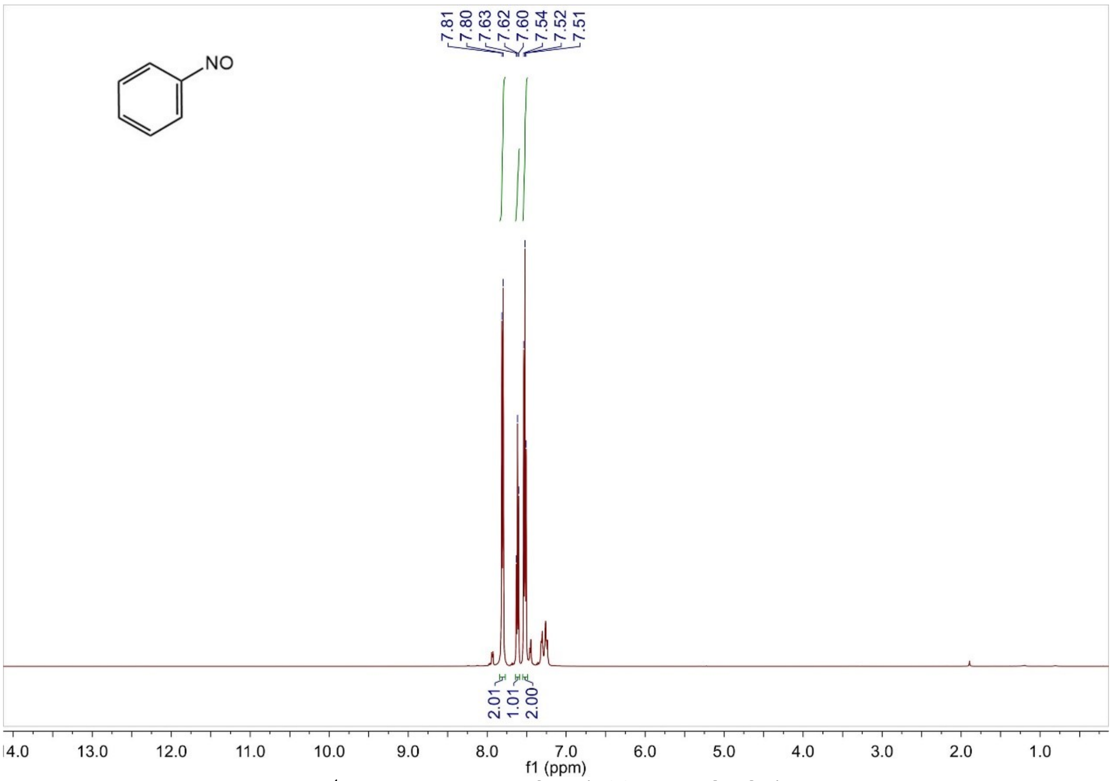
^{13}C NMR spectra of **4q** (126 MHz, $CDCl_3$)



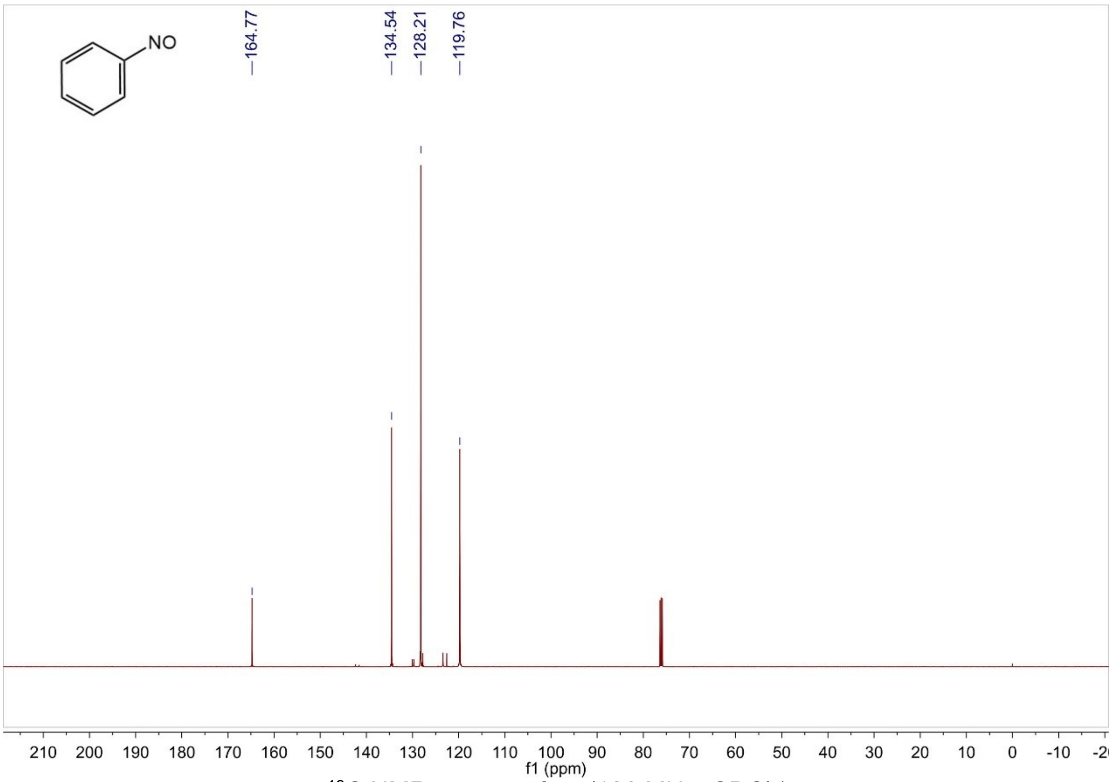
^1H NMR spectra of **4r** (500 MHz, $CDCl_3$)



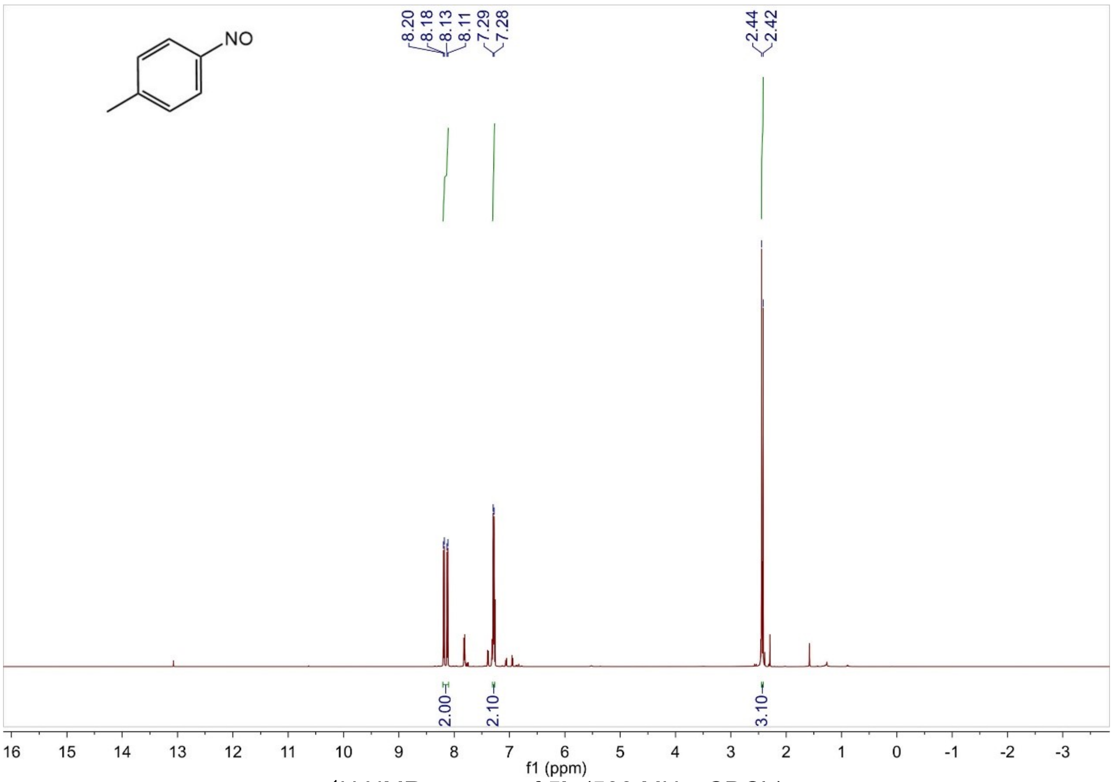
^{13}C NMR spectra of **4r** (126 MHz, $CDCl_3$)



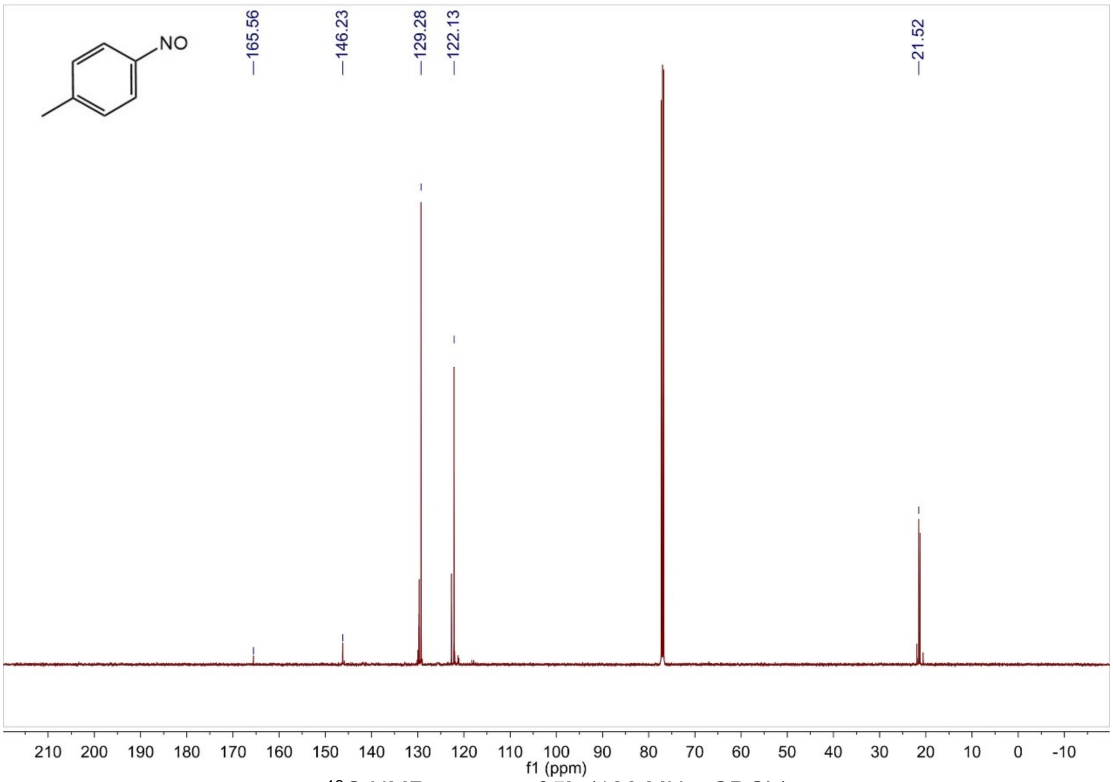
^{1}H NMR spectra of **5a** (500 MHz, $CDCl_3$)



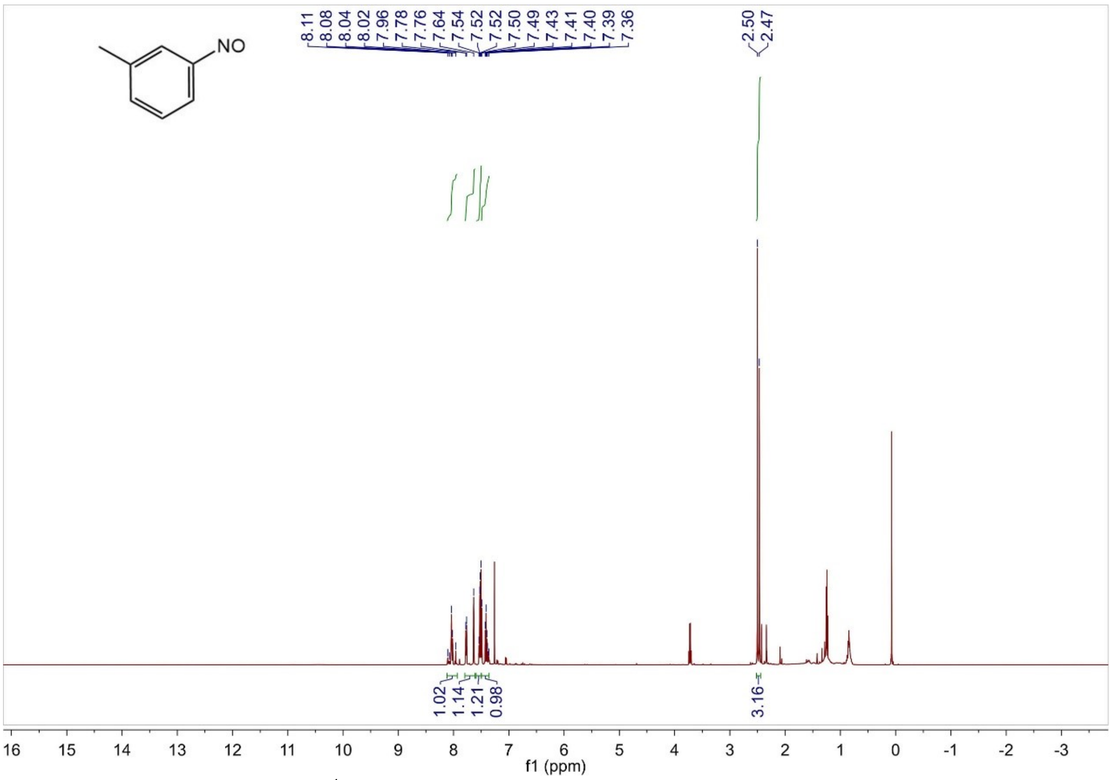
^{13}C NMR spectra of **5a** (126 MHz, $CDCl_3$)



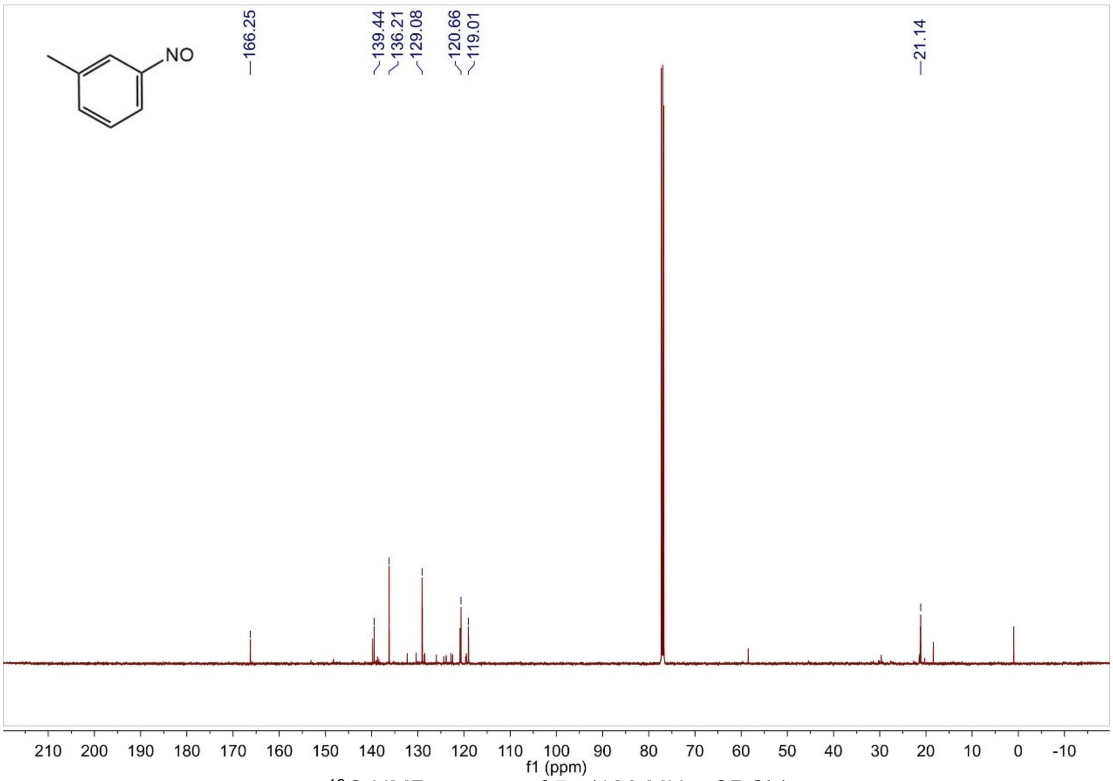
^{1}H NMR spectra of **5b** (500 MHz, $CDCl_3$)



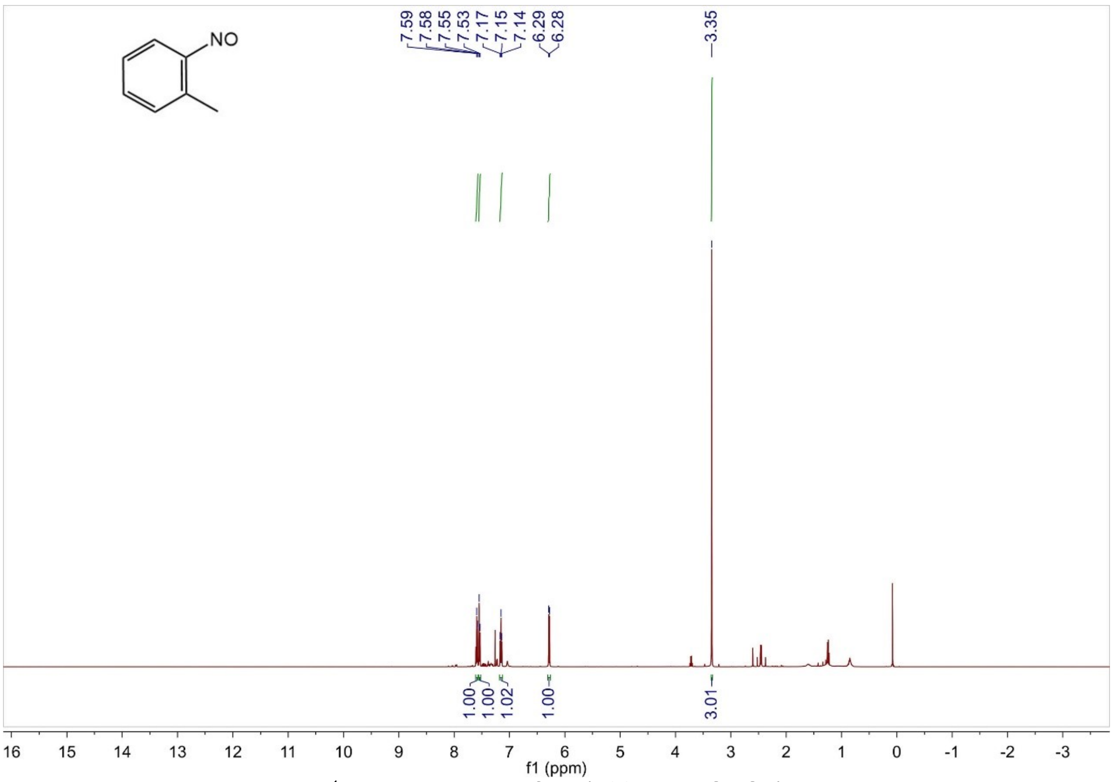
^{13}C NMR spectra of **5b** (126 MHz, $CDCl_3$)



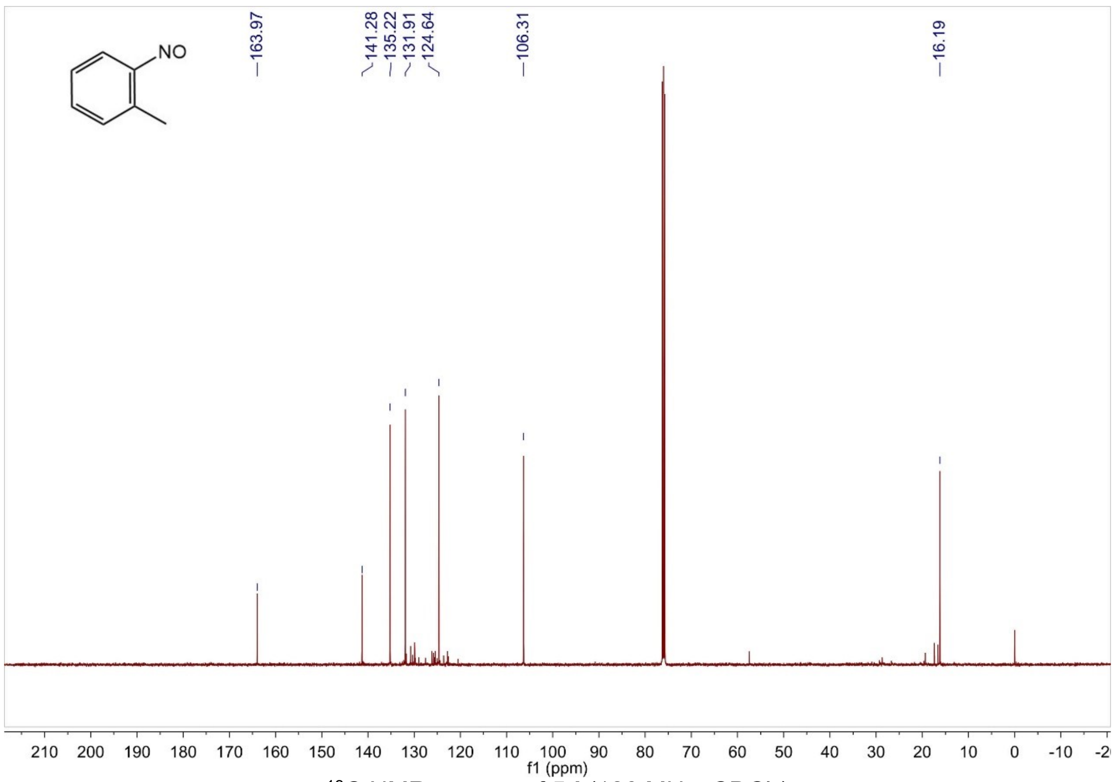
^{1}H NMR spectra of **5c** (500 MHz, $CDCl_3$)



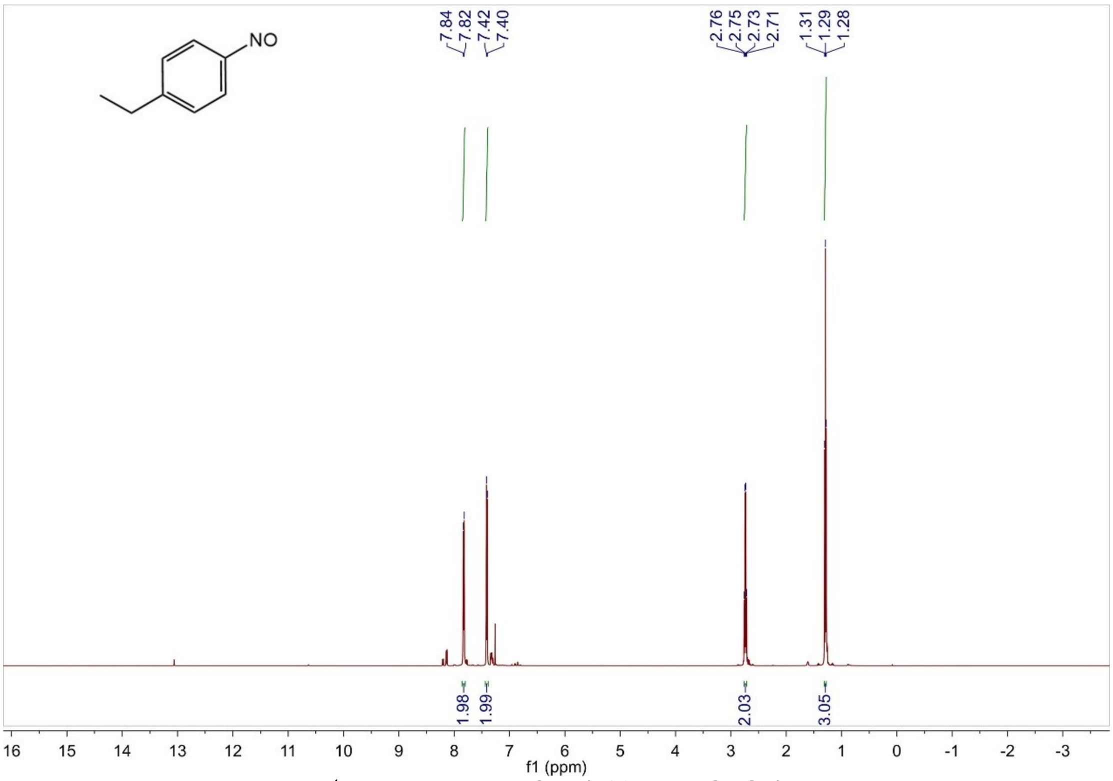
^{13}C NMR spectra of **5c** (126 MHz, $CDCl_3$)



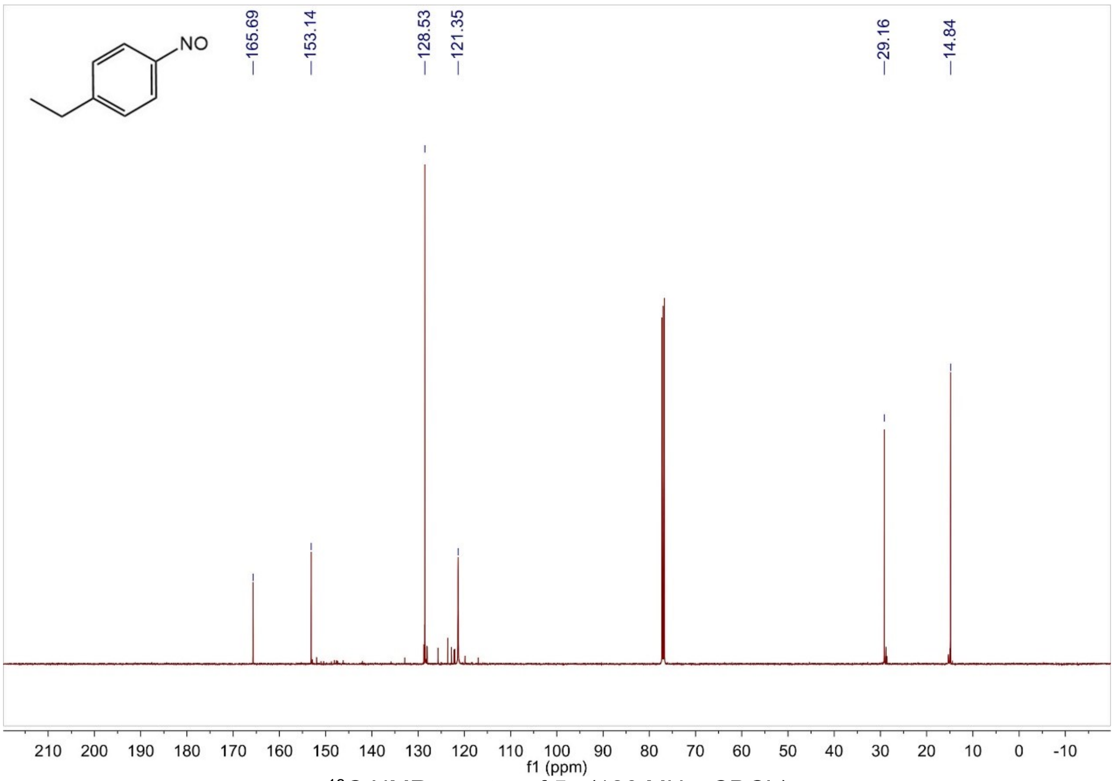
^{1}H NMR spectra of **5d** (500 MHz, $CDCl_3$)



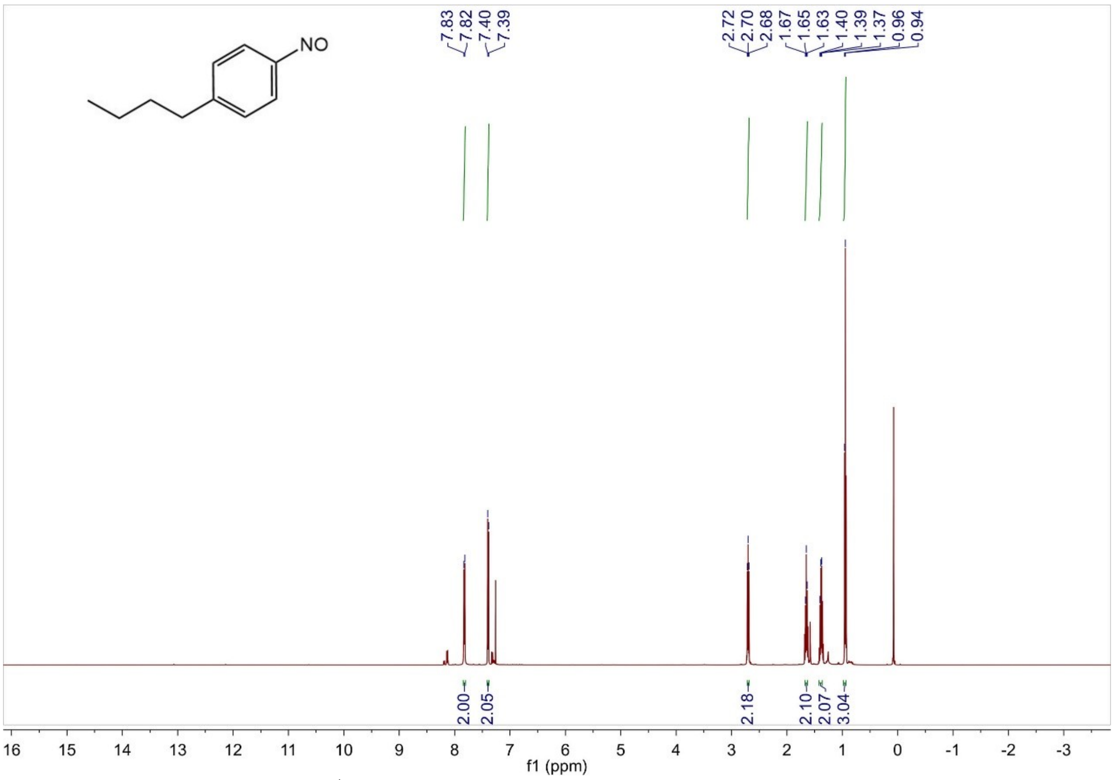
^{13}C NMR spectra of **5d** (126 MHz, $CDCl_3$)



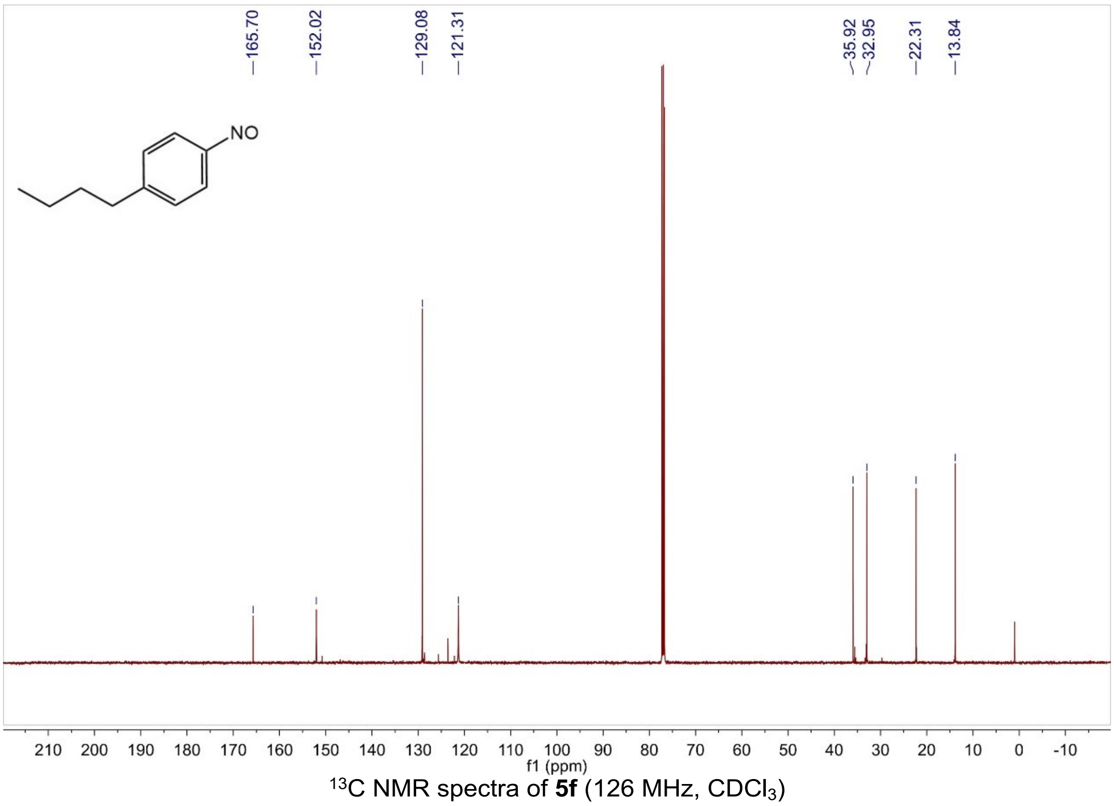
^1H NMR spectra of **5e** (500 MHz, $CDCl_3$)



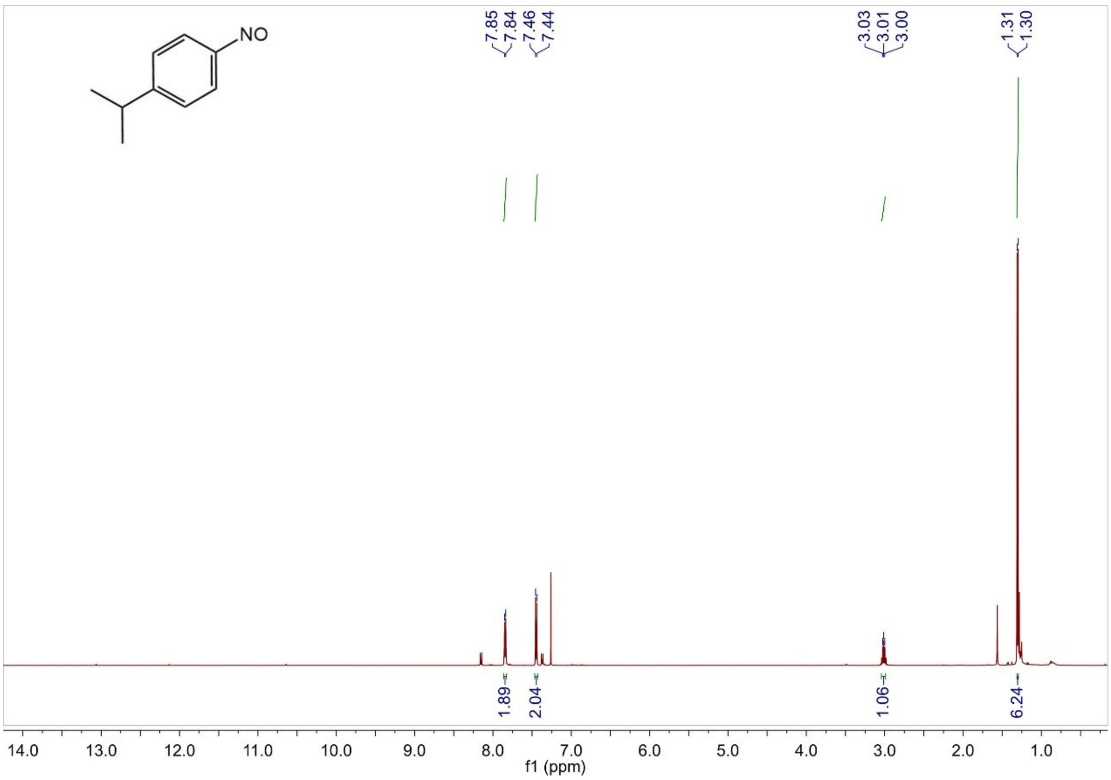
^{13}C NMR spectra of **5e** (126 MHz, $CDCl_3$)



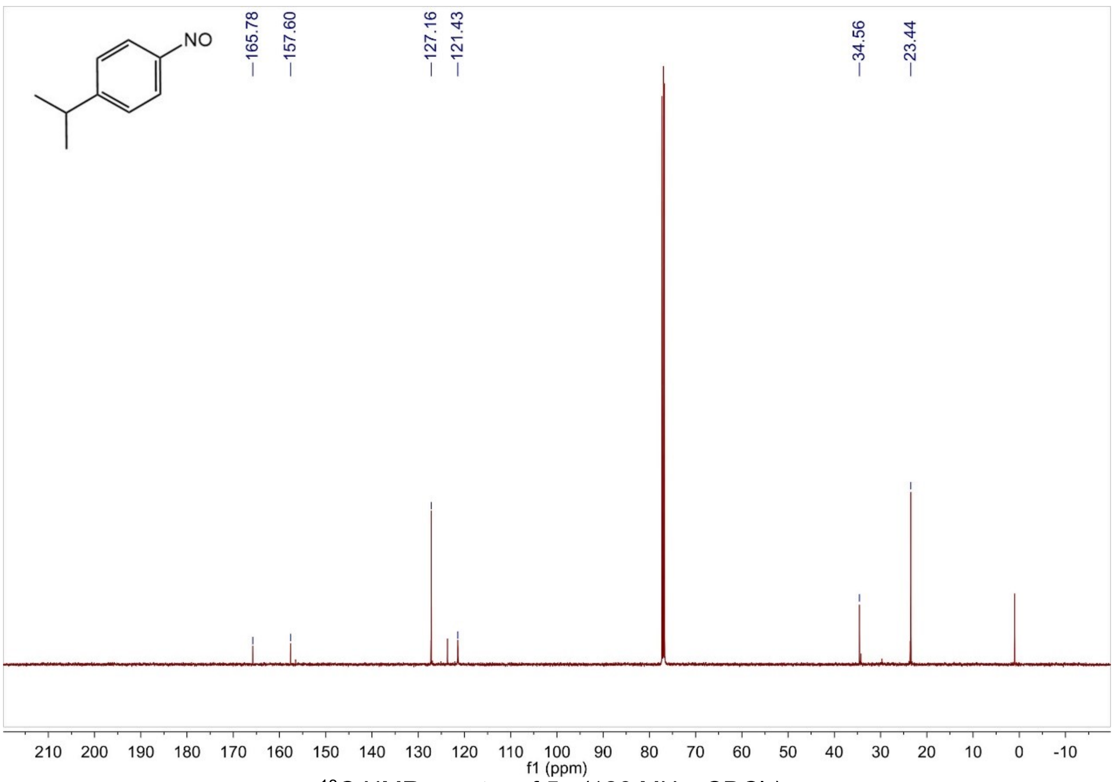
^{1}H NMR spectra of **5f** (500 MHz, $CDCl_3$)



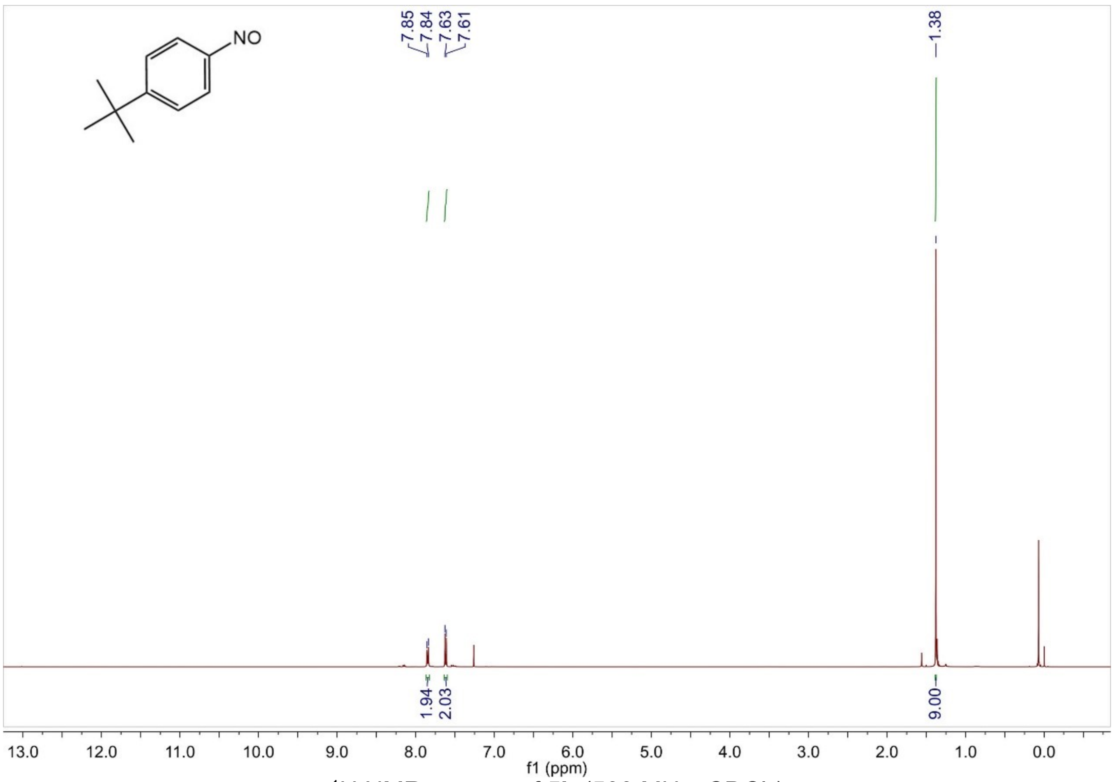
^{13}C NMR spectra of **5f** (126 MHz, $CDCl_3$)



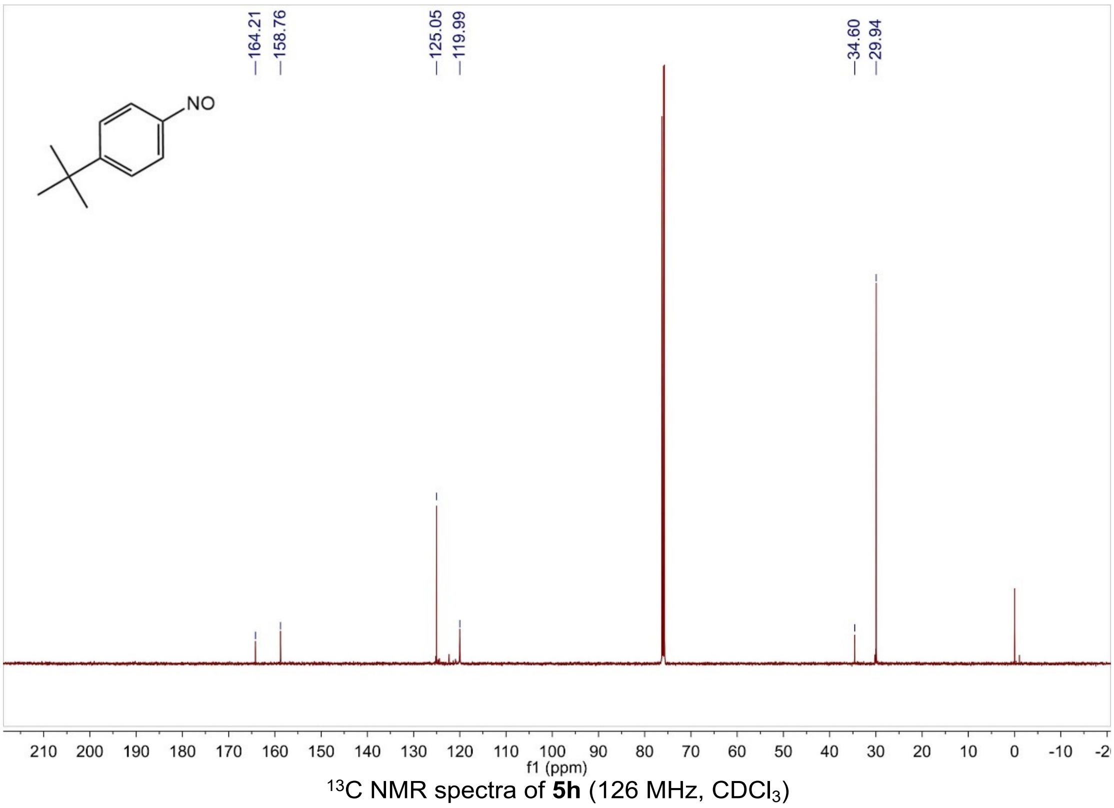
^{1}H NMR spectra of **5g** (500 MHz, $CDCl_3$)



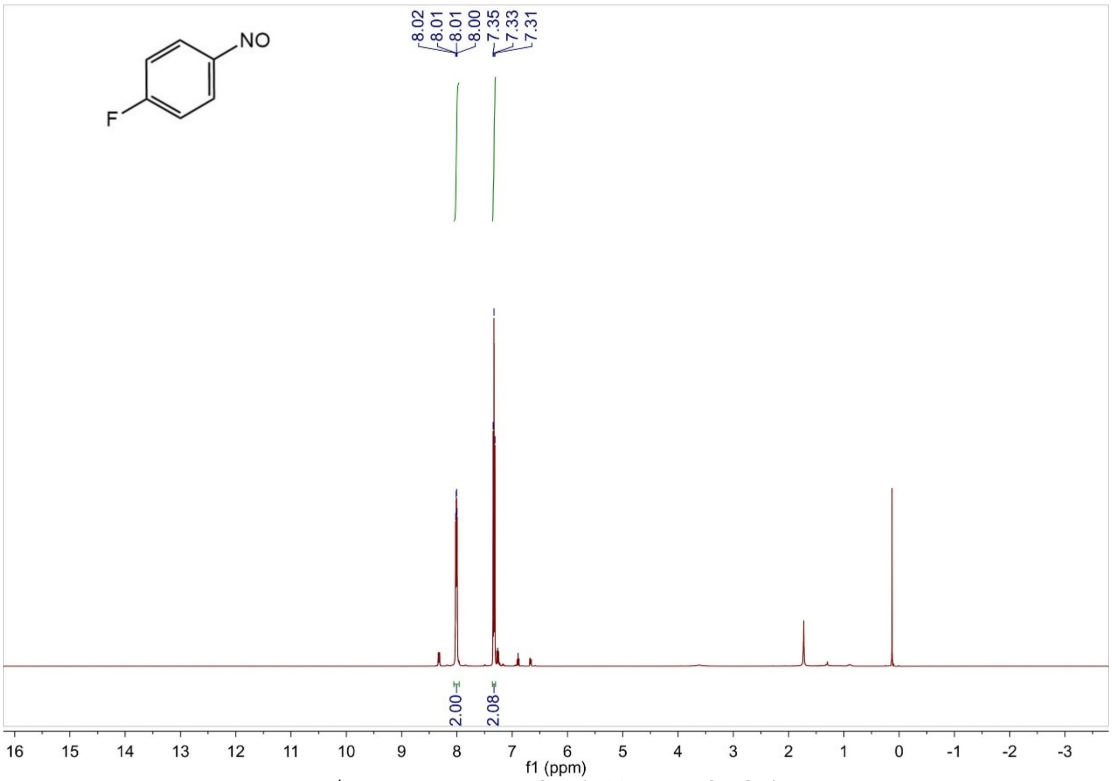
^{13}C NMR spectra of **5g** (126 MHz, $CDCl_3$)



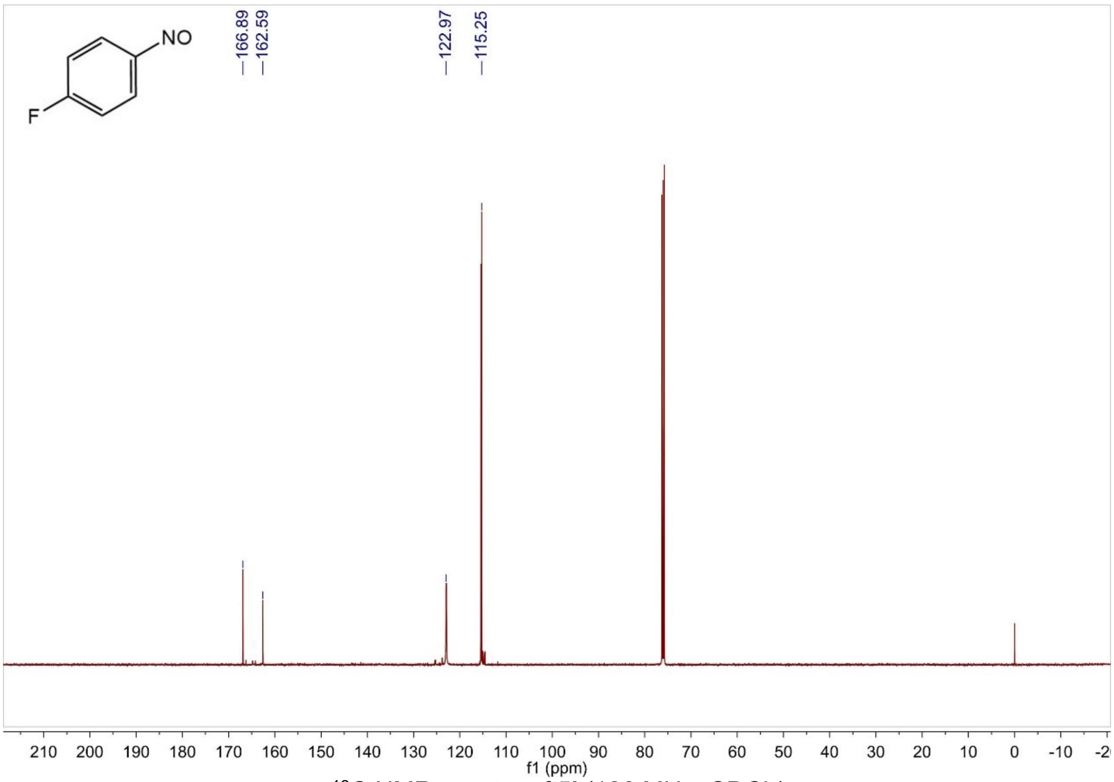
^{1}H NMR spectra of **5h** (500 MHz, $CDCl_3$)



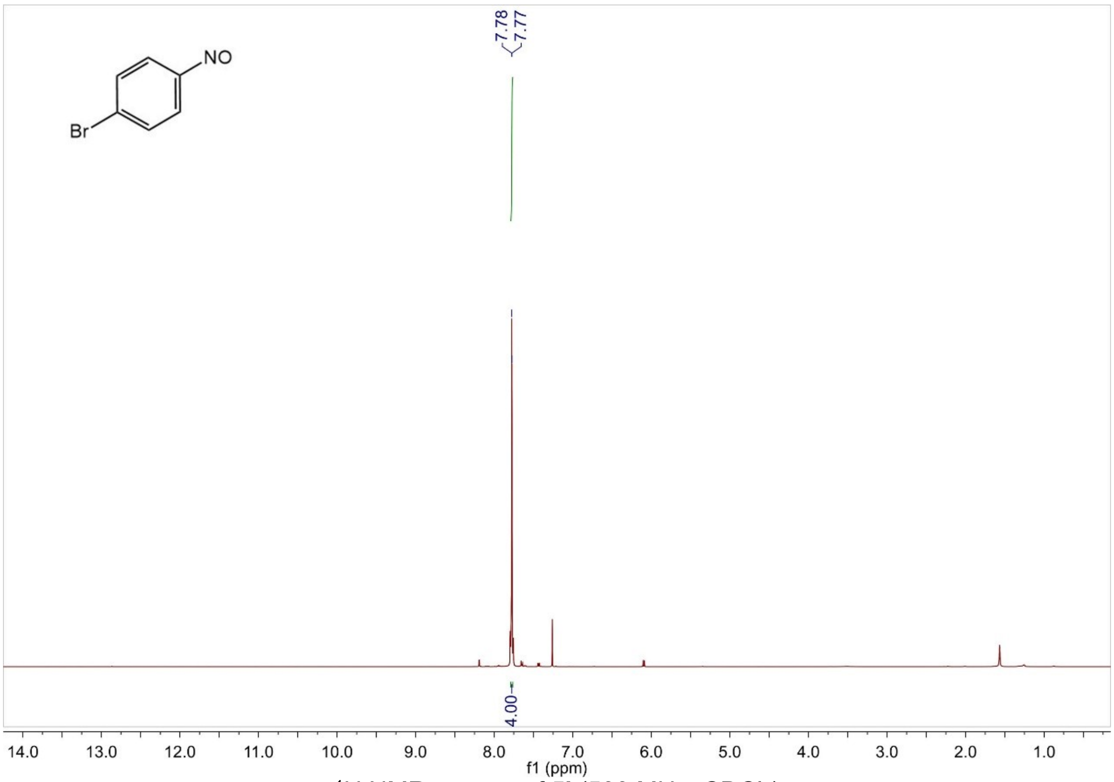
^{13}C NMR spectra of **5h** (126 MHz, $CDCl_3$)



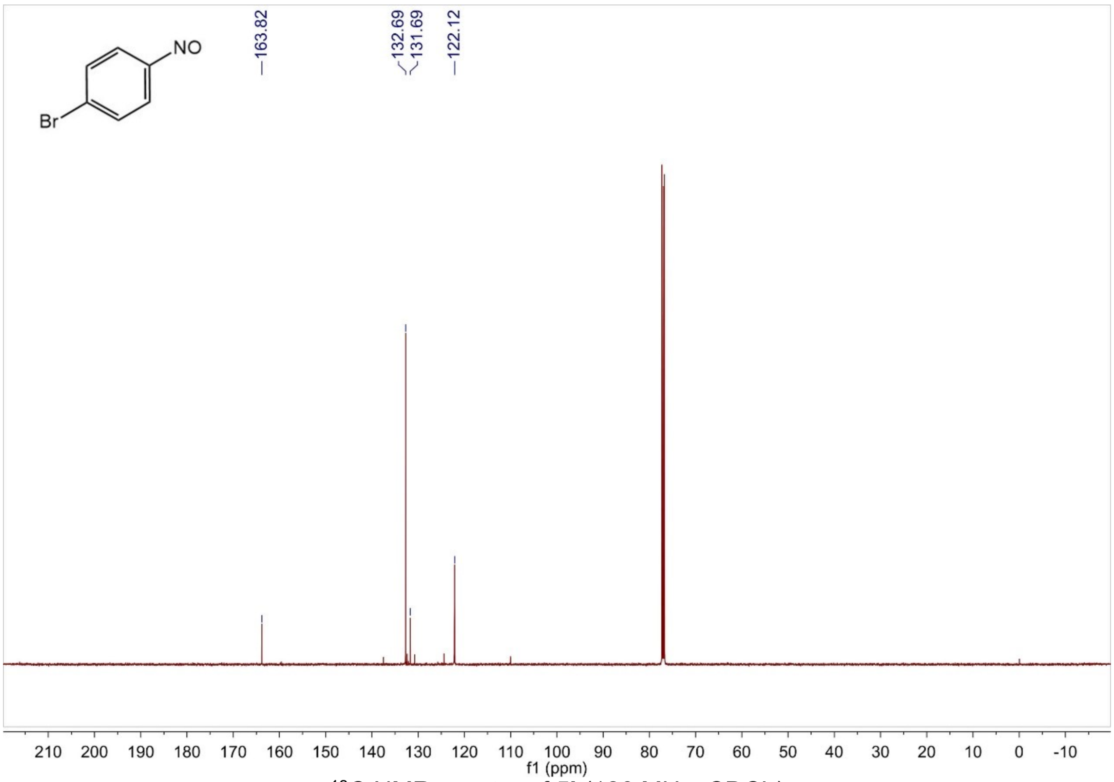
^{1}H NMR spectra of **5i** (500 MHz, $CDCl_3$)



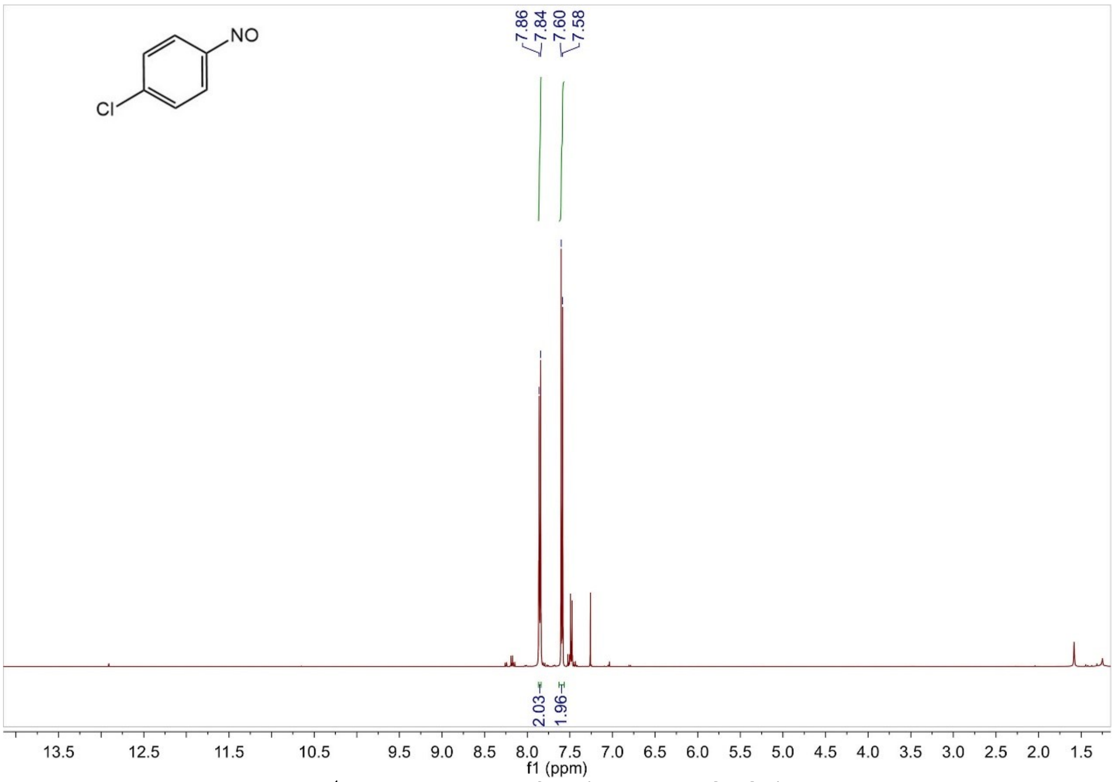
^{13}C NMR spectra of **5i** (126 MHz, $CDCl_3$)



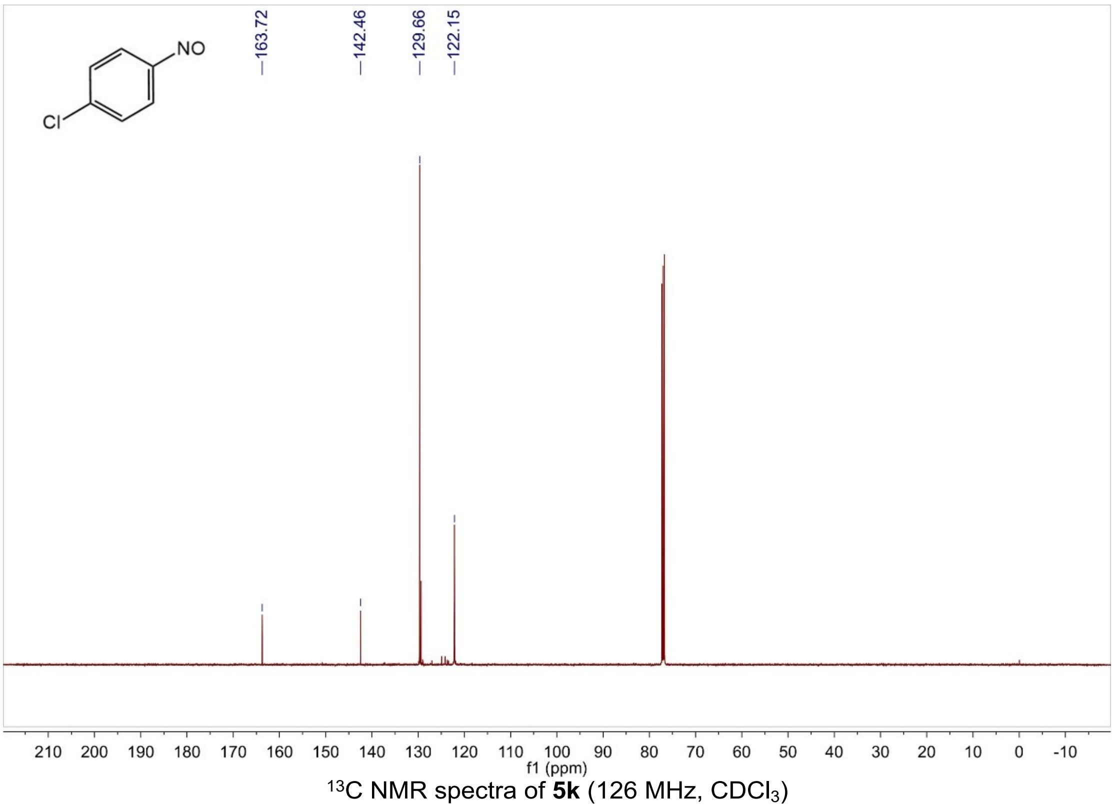
^{1}H NMR spectra of **5j** (500 MHz, $CDCl_3$)



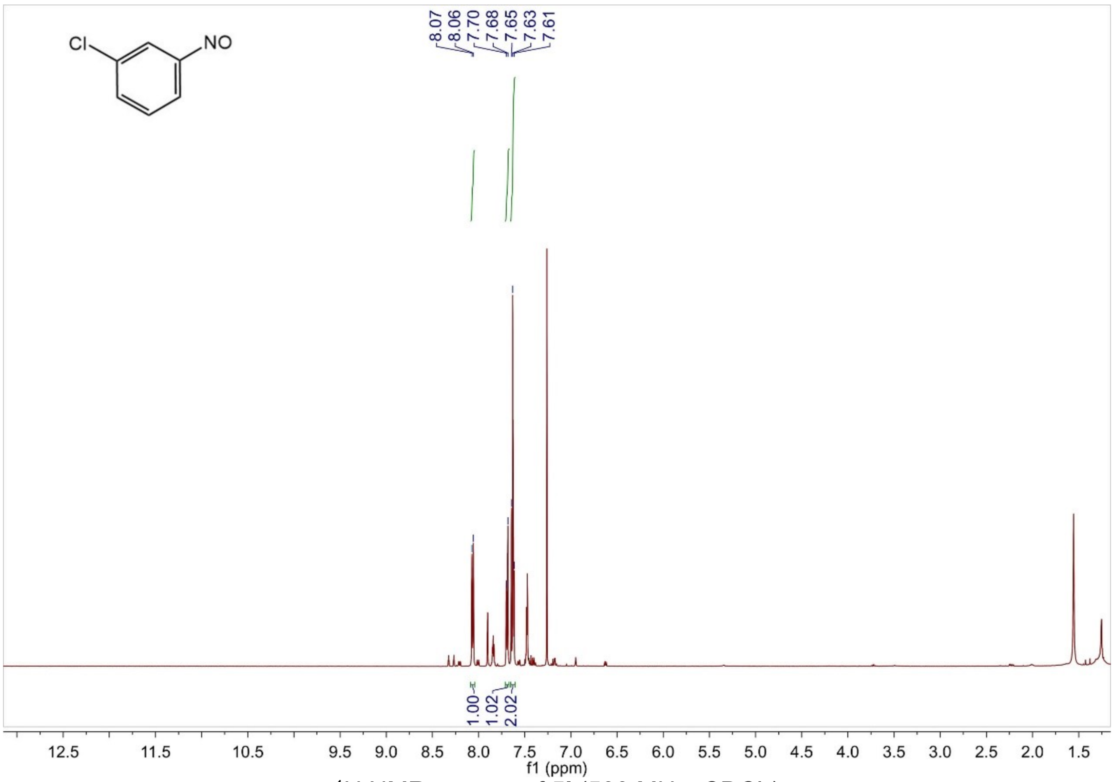
^{13}C NMR spectra of **5j** (126 MHz, $CDCl_3$)



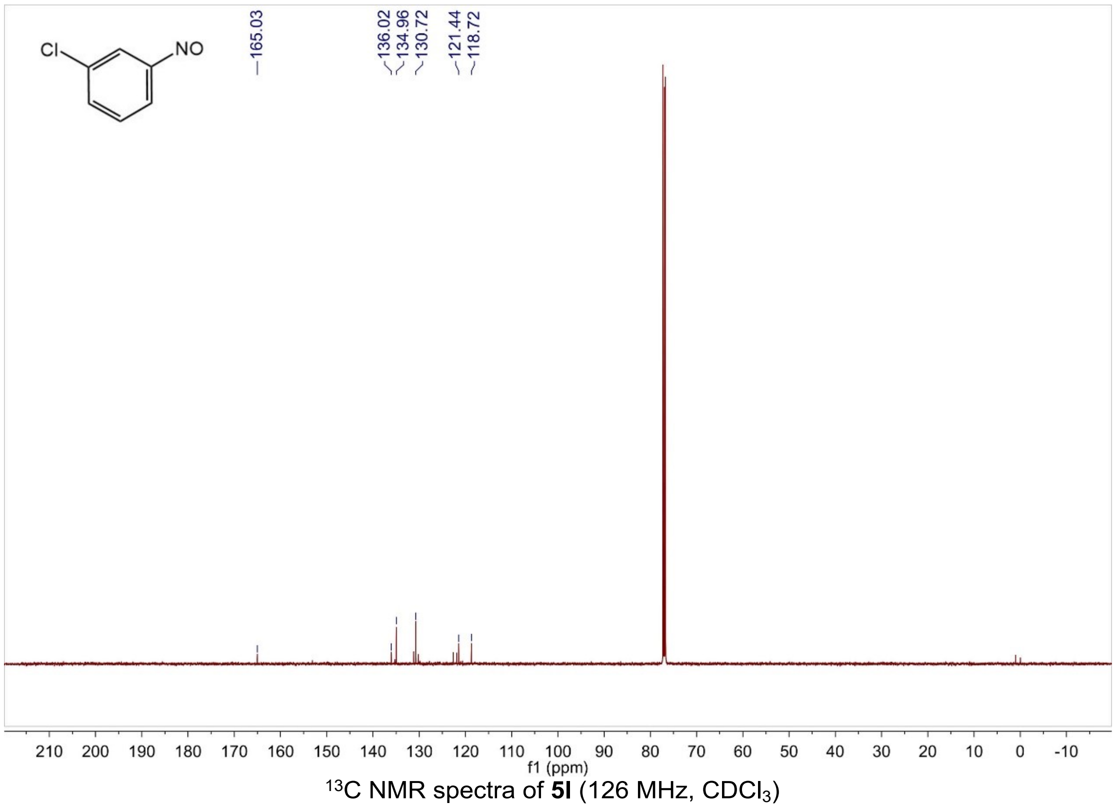
^{1}H NMR spectra of **5k** (500 MHz, $CDCl_3$)



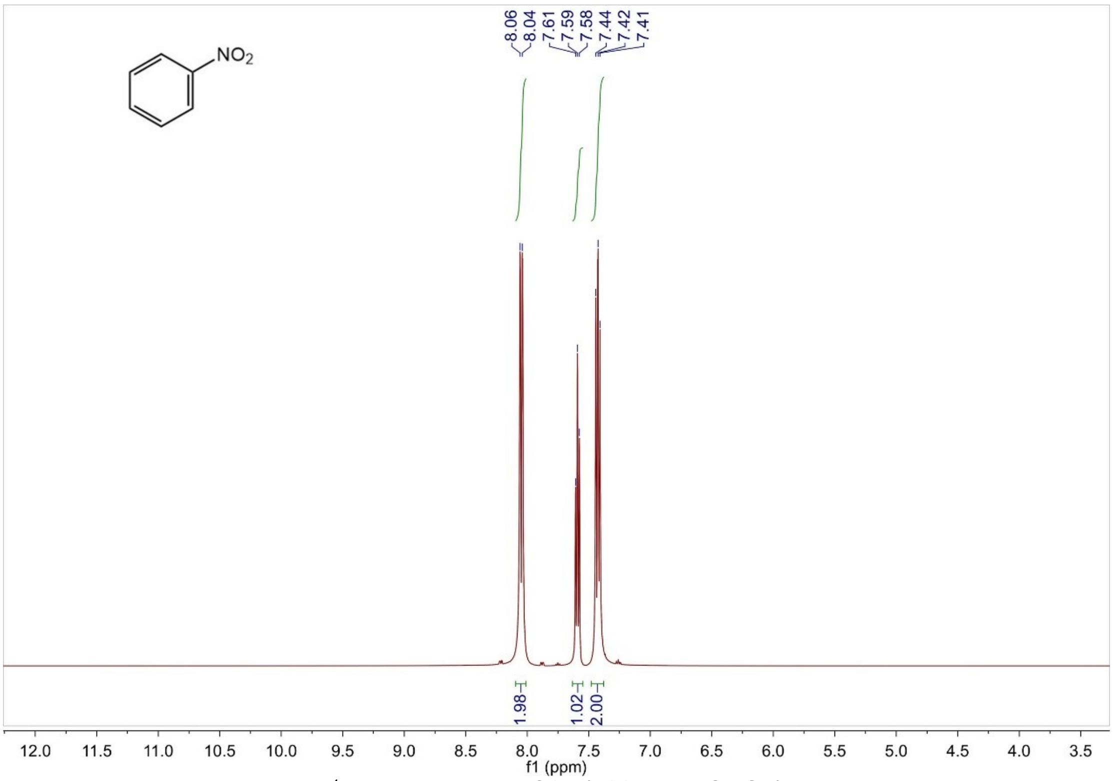
^{13}C NMR spectra of **5k** (126 MHz, $CDCl_3$)



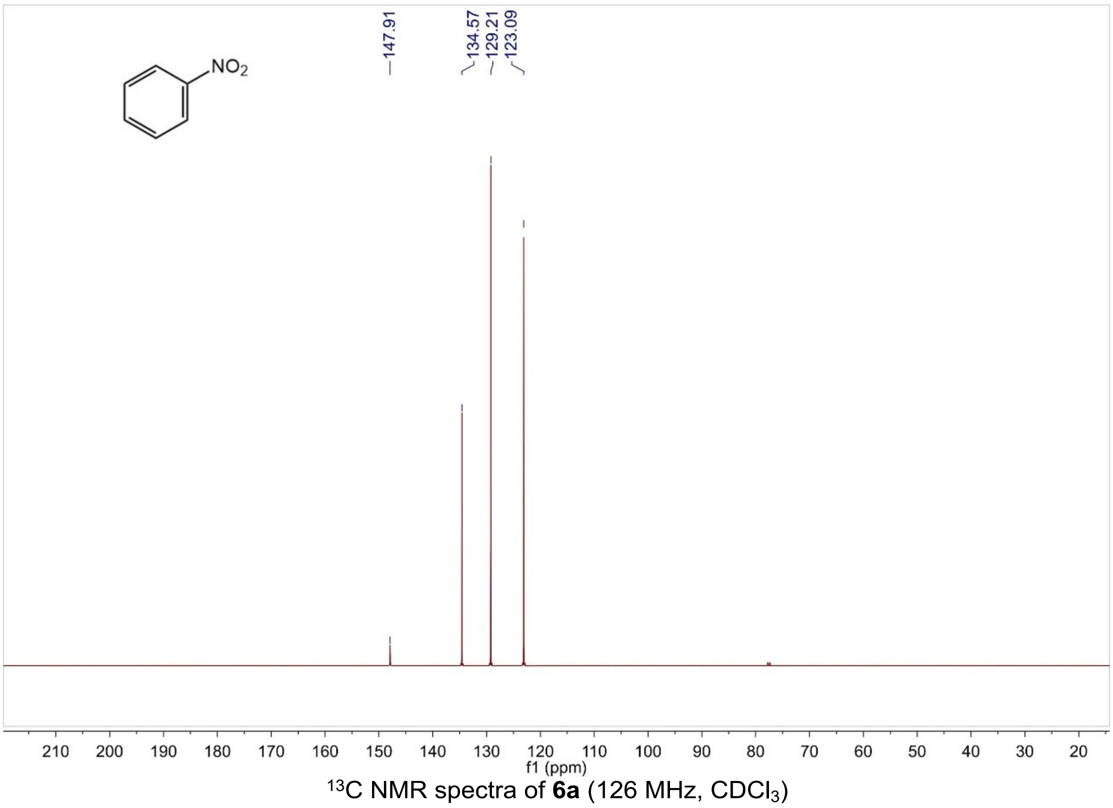
^{1}H NMR spectra of **5l** (500 MHz, $CDCl_3$)



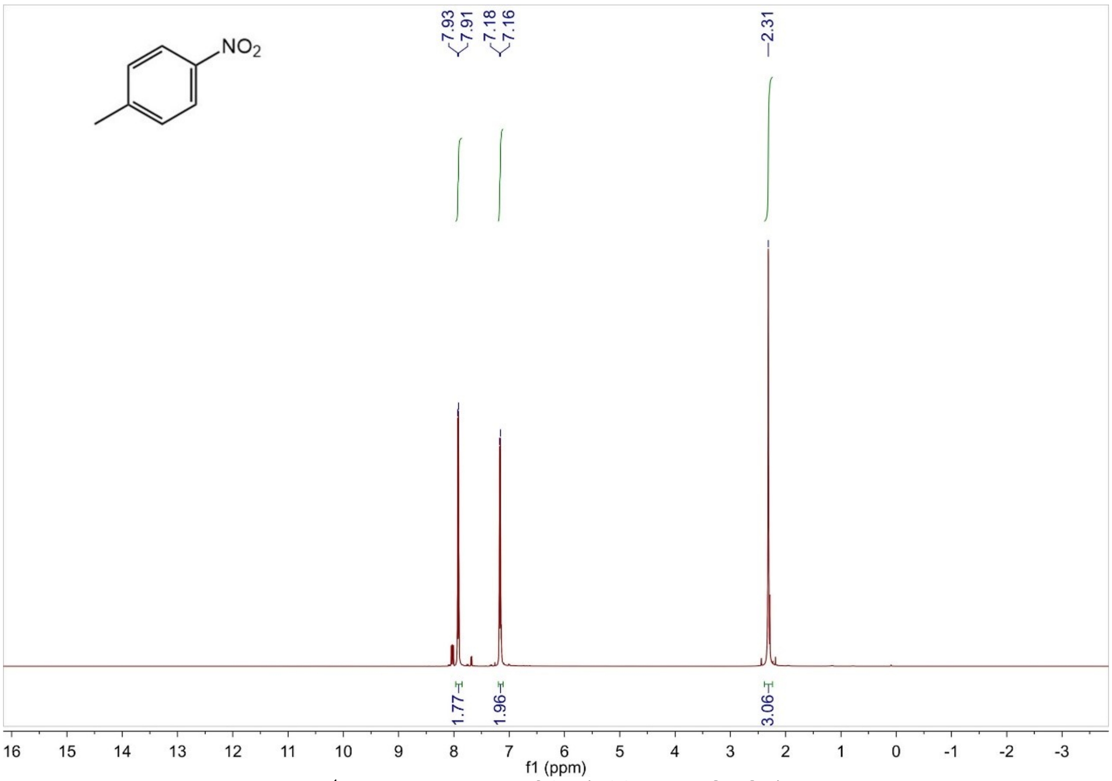
^{13}C NMR spectra of **5l** (126 MHz, $CDCl_3$)



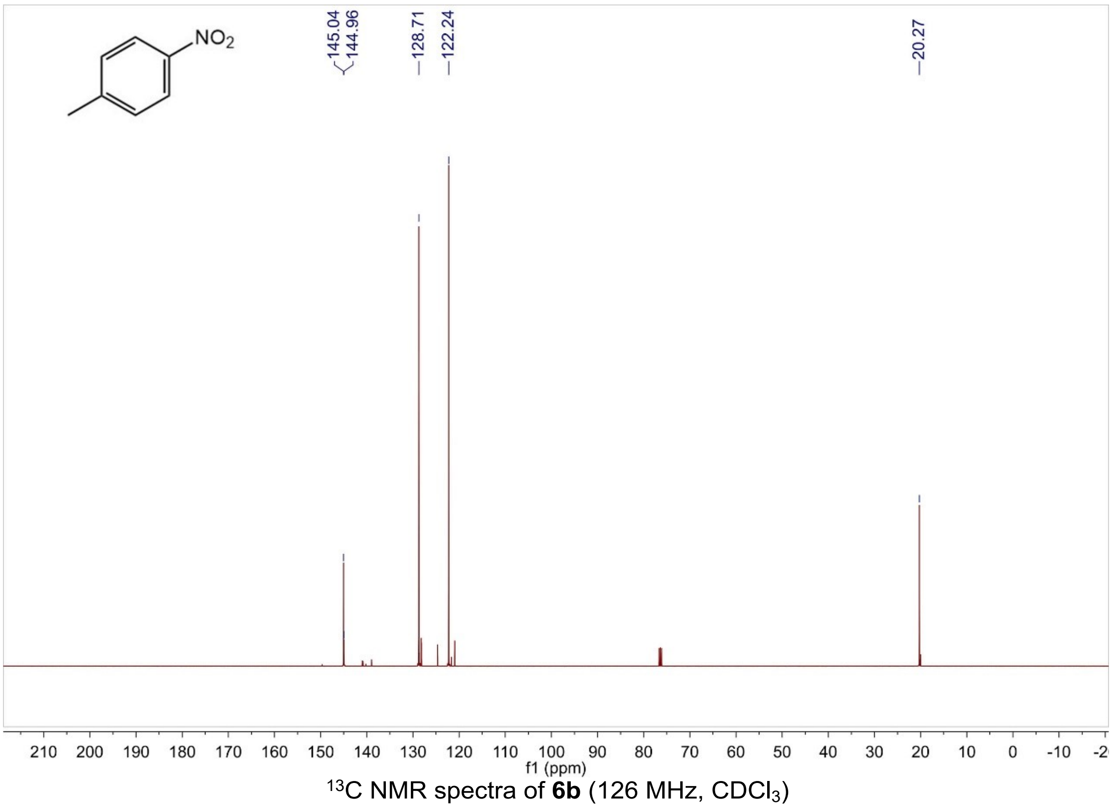
^1H NMR spectra of **6a** (500 MHz, $CDCl_3$)



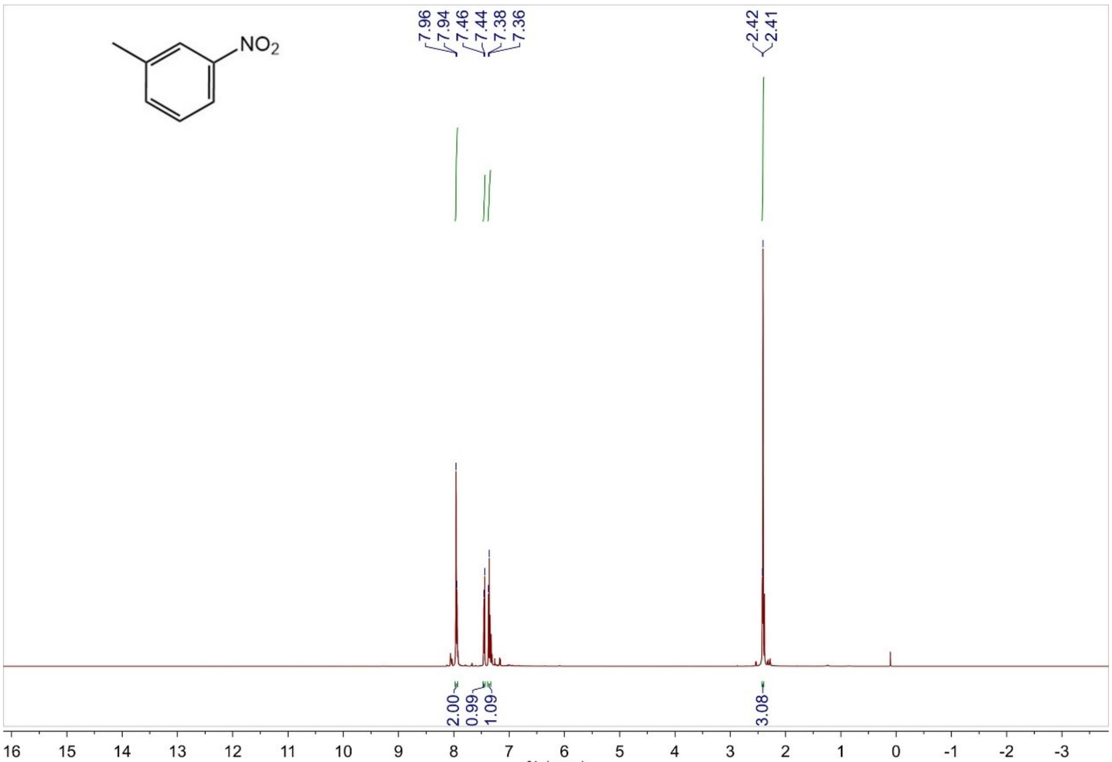
^{13}C NMR spectra of **6a** (126 MHz, $CDCl_3$)



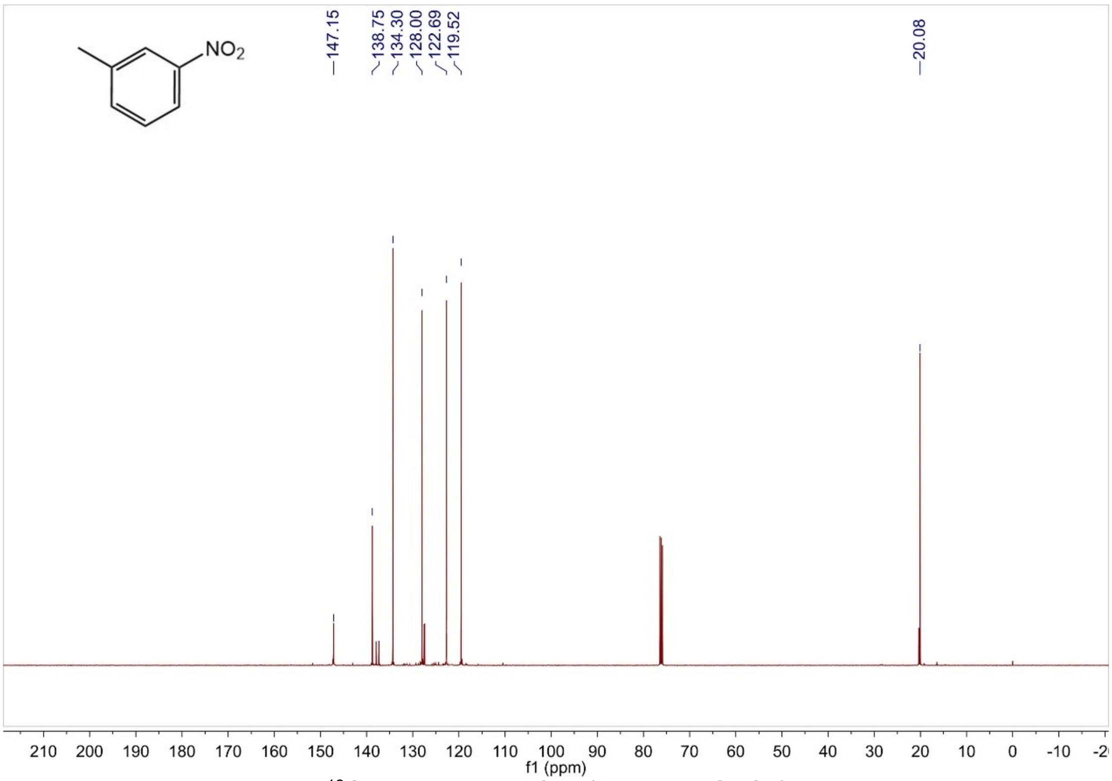
[1]H NMR spectra of **6b** (500 MHz, $CDCl_3$)



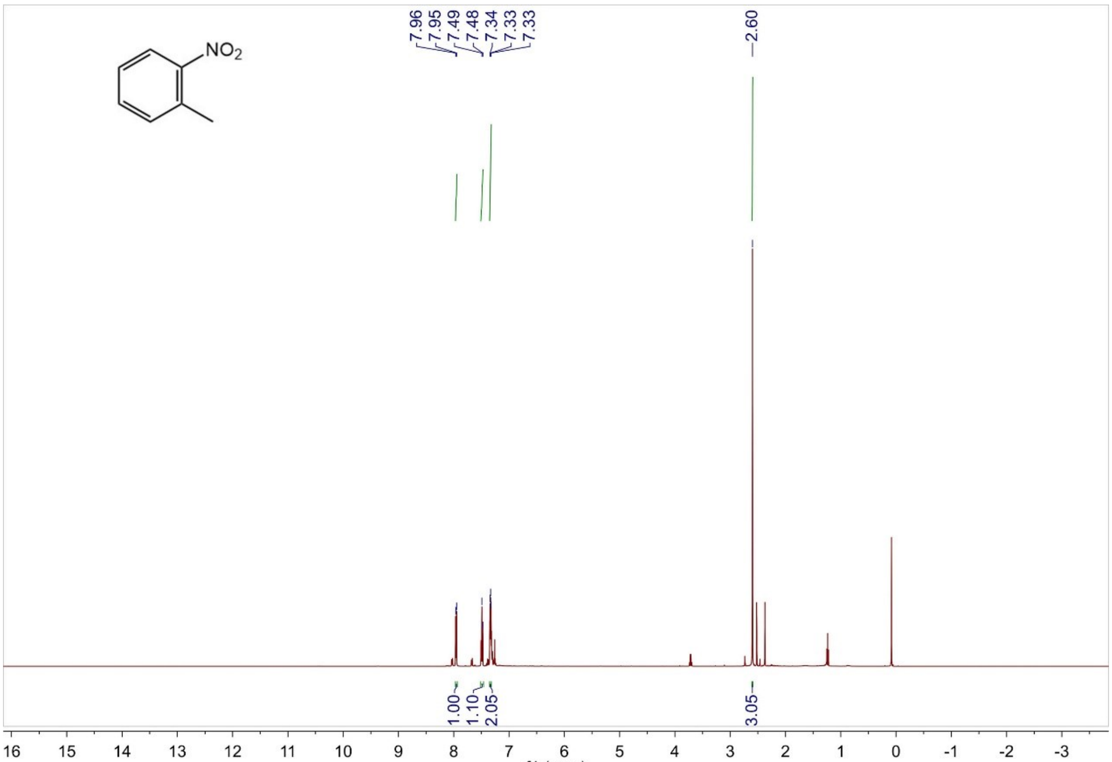
[13]C NMR spectra of **6b** (126 MHz, $CDCl_3$)



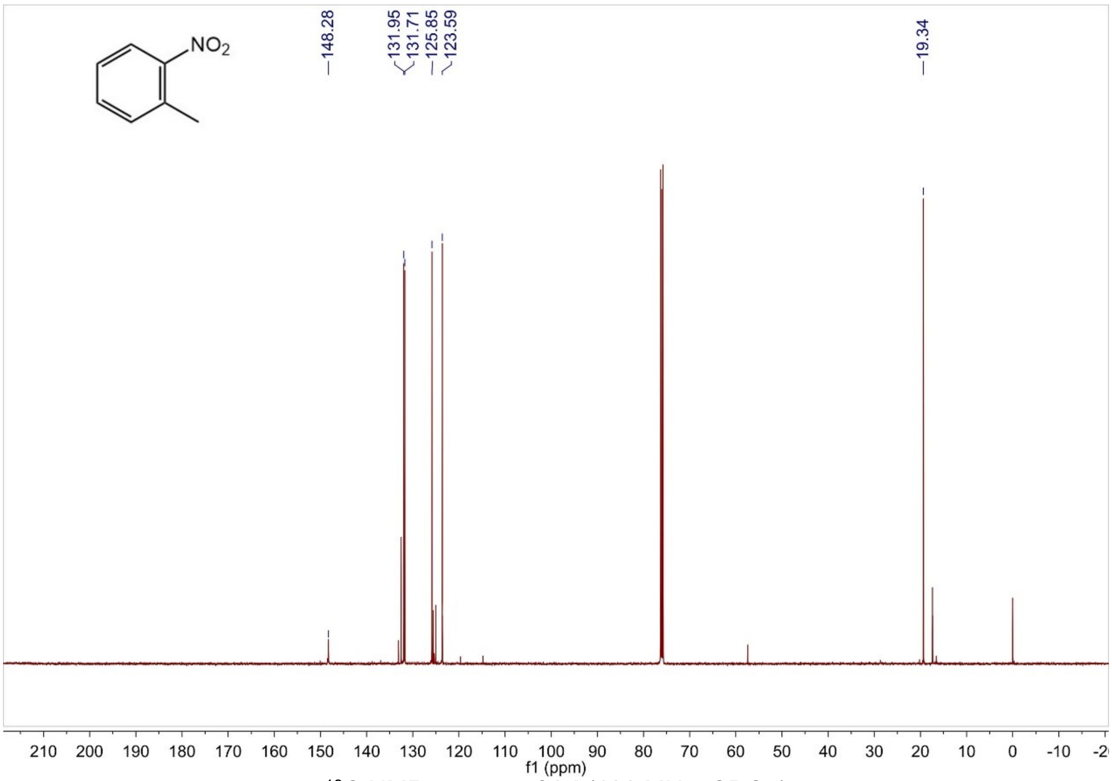
^{1}H NMR spectra of **6c** (500 MHz, $CDCl_3$)



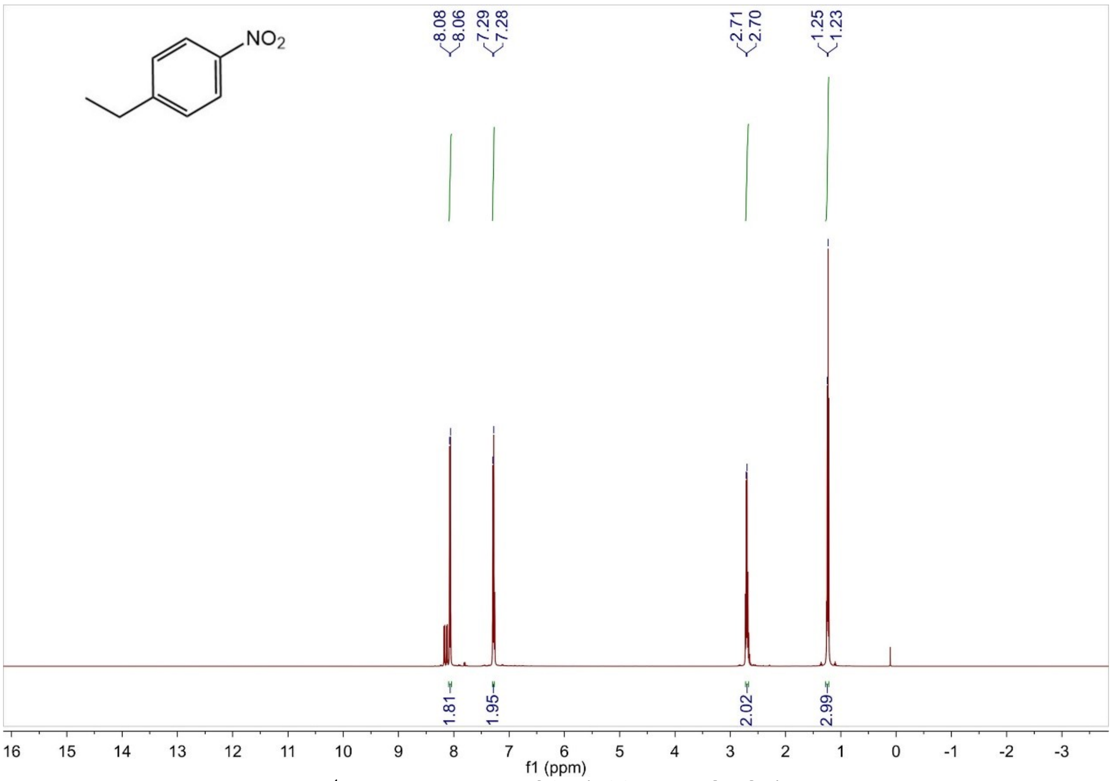
^{13}C NMR spectra of **6c** (126 MHz, $CDCl_3$)



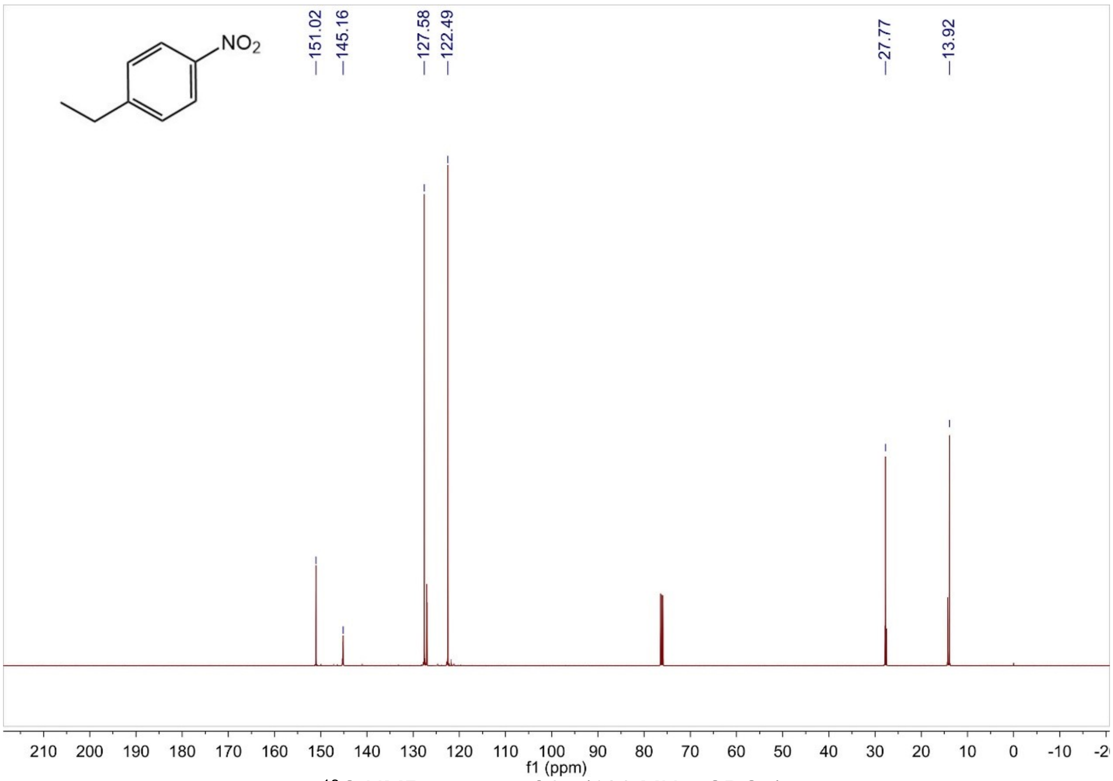
^{1}H NMR spectra of **6d** (500 MHz, $CDCl_3$)



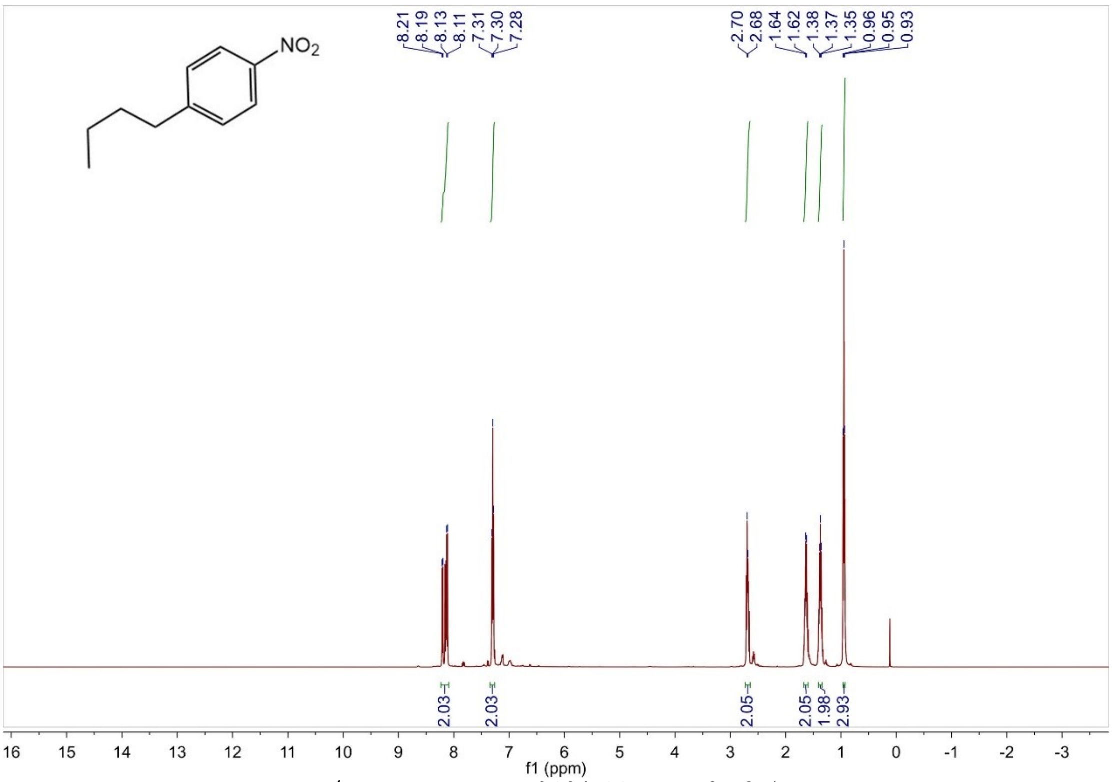
^{13}C NMR spectra of **6d** (126 MHz, $CDCl_3$)



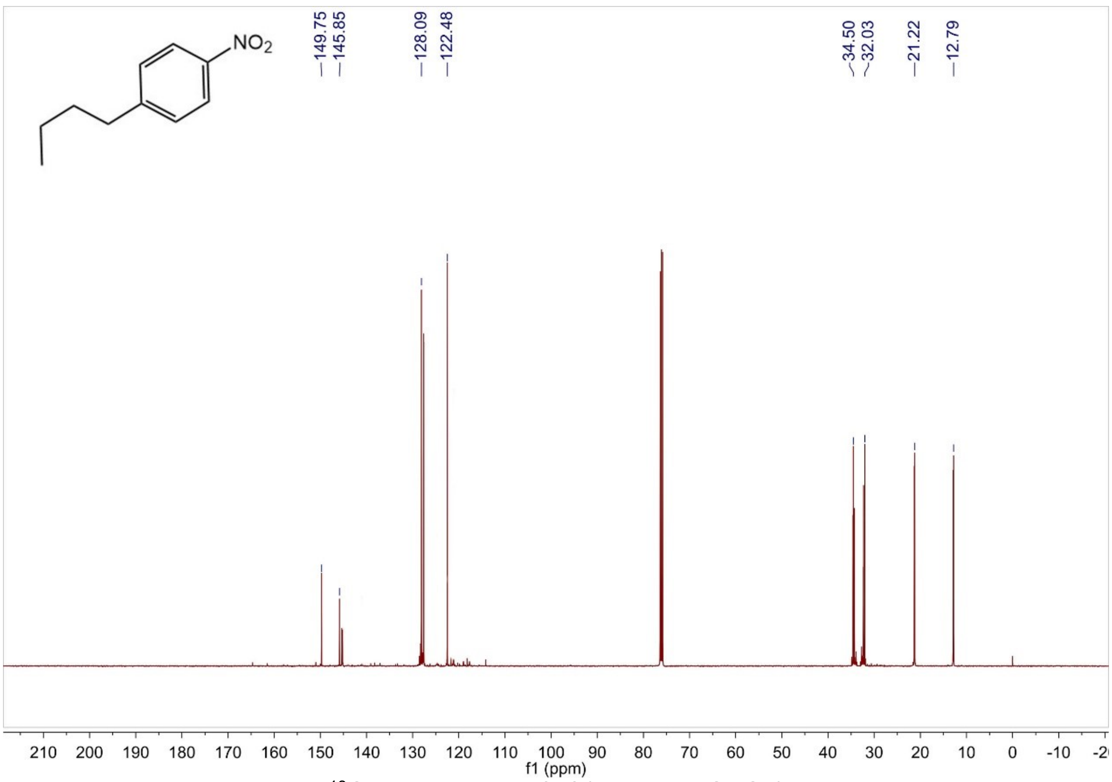
^{1}H NMR spectra of **6e** (500 MHz, $CDCl_3$)



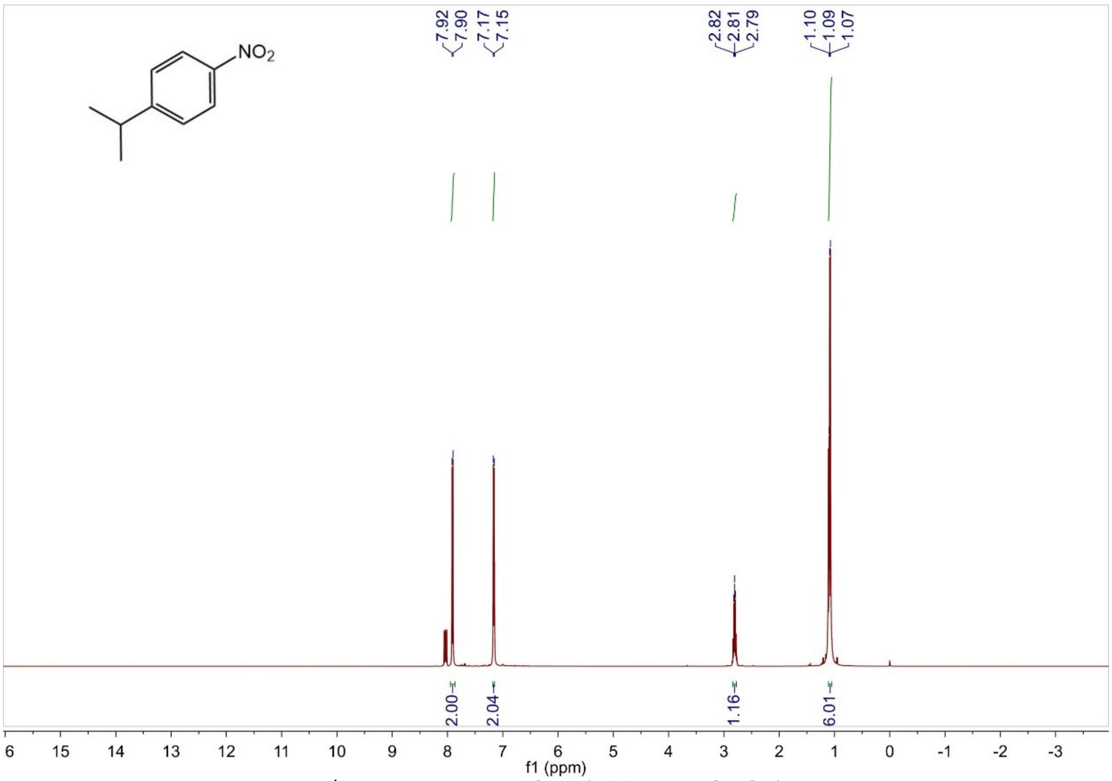
^{13}C NMR spectra of **6e** (126 MHz, $CDCl_3$)



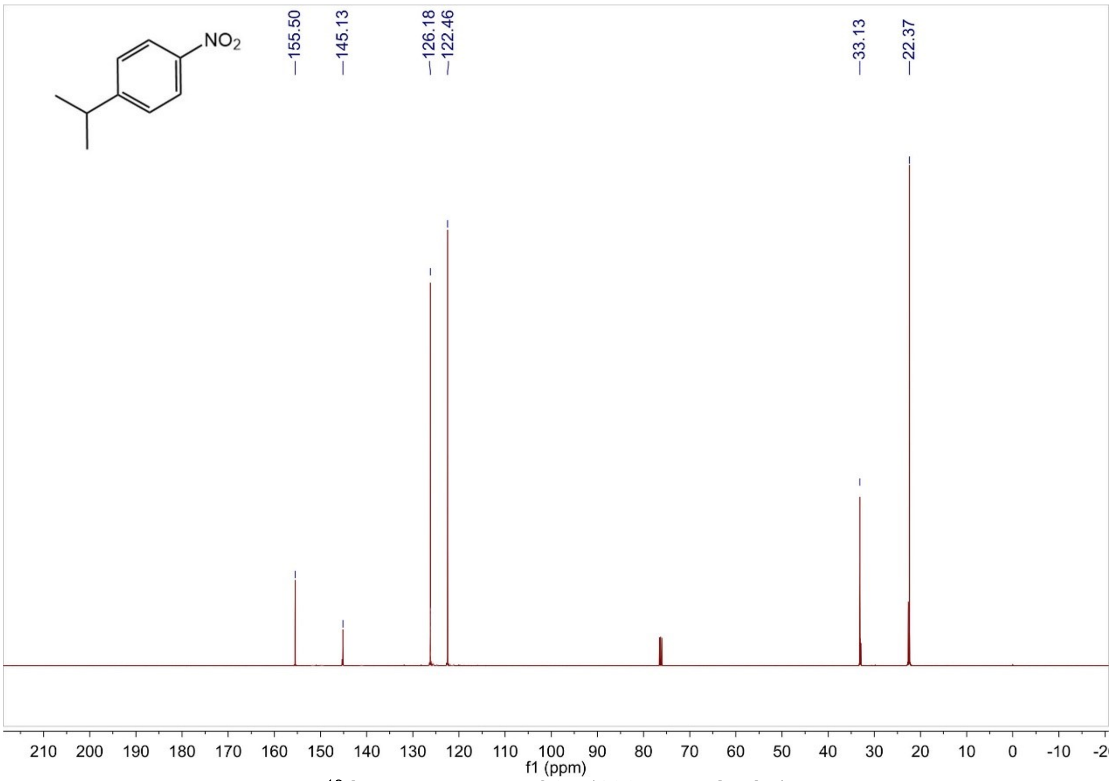
[1]H NMR spectra of **6f** (500 MHz, $CDCl_3$)



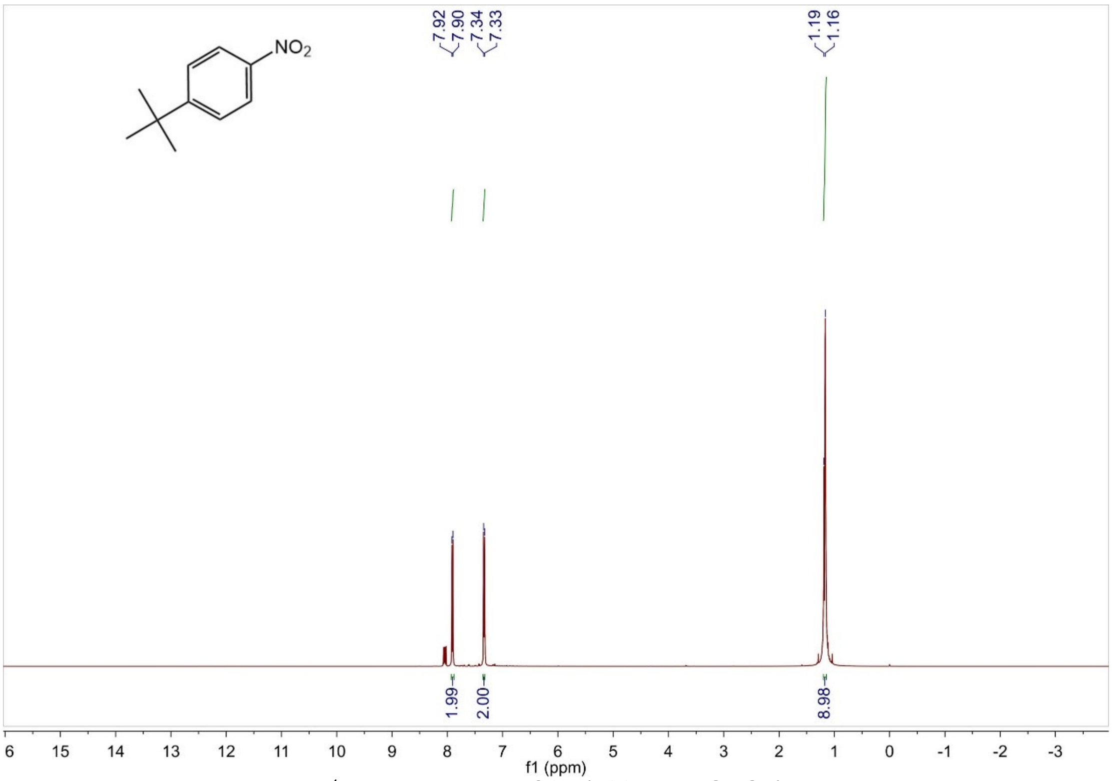
[13]C NMR spectra of **6f** (126 MHz, $CDCl_3$)



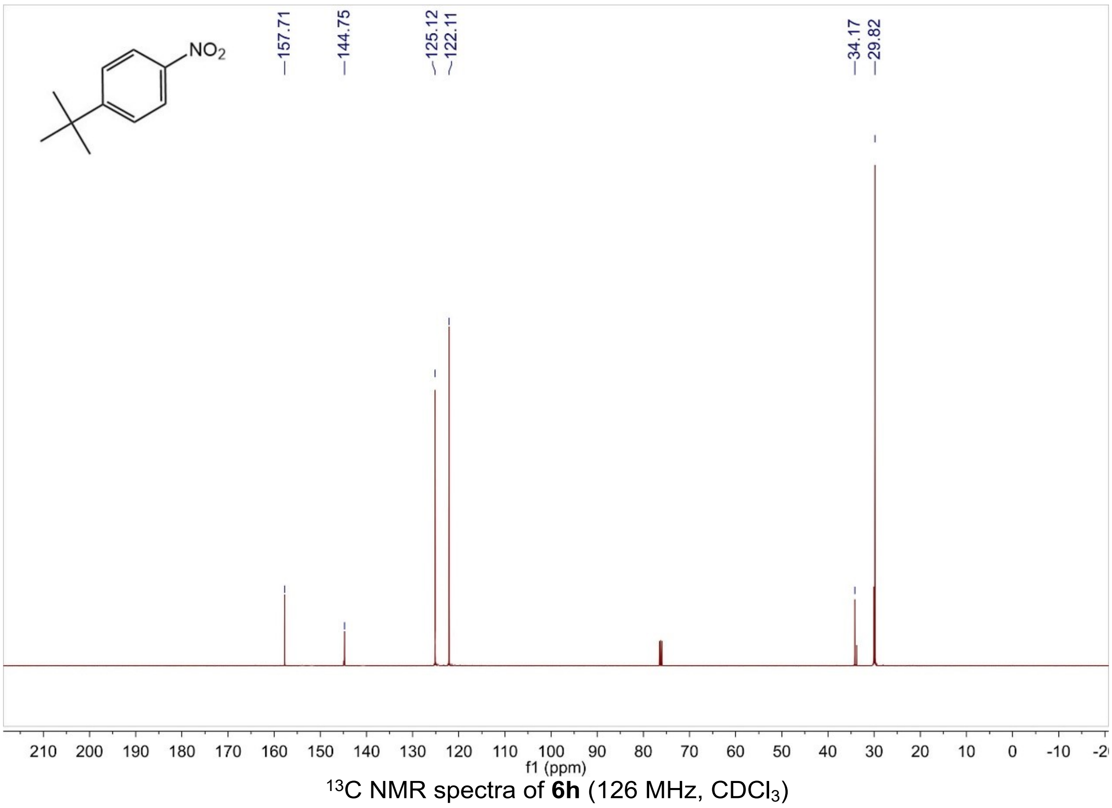
^{1}H NMR spectra of **6g** (500 MHz, $CDCl_3$)



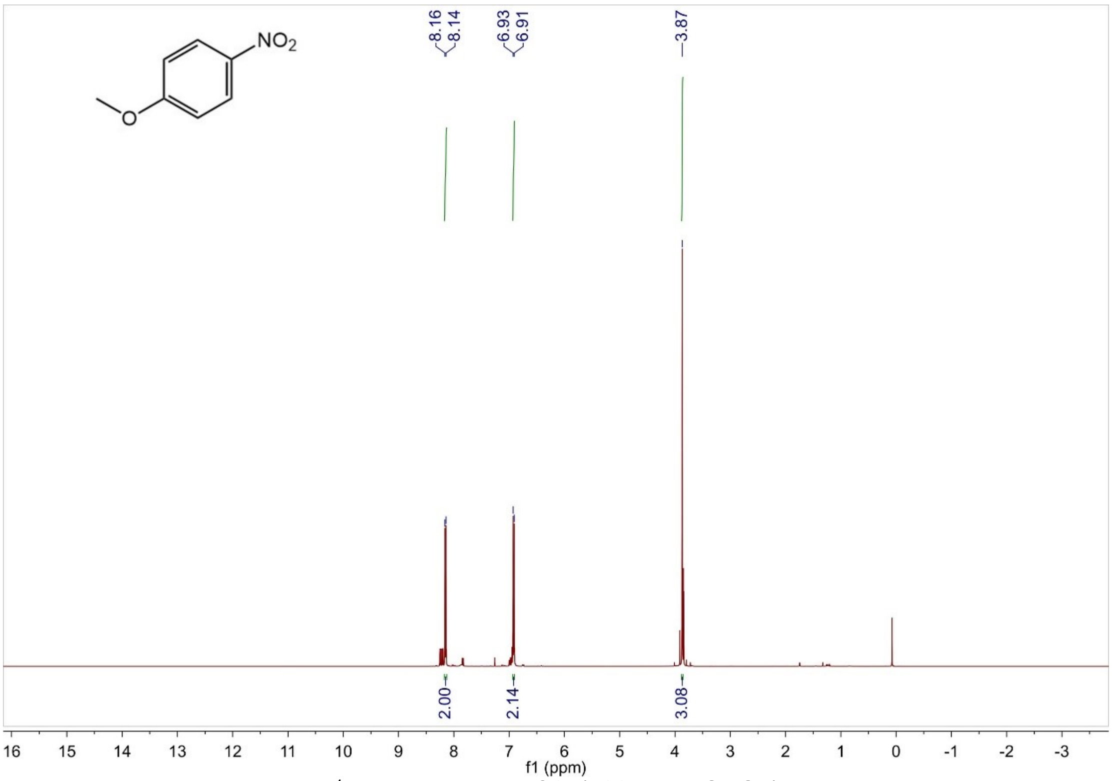
^{13}C NMR spectra of **6g** (126 MHz, $CDCl_3$)



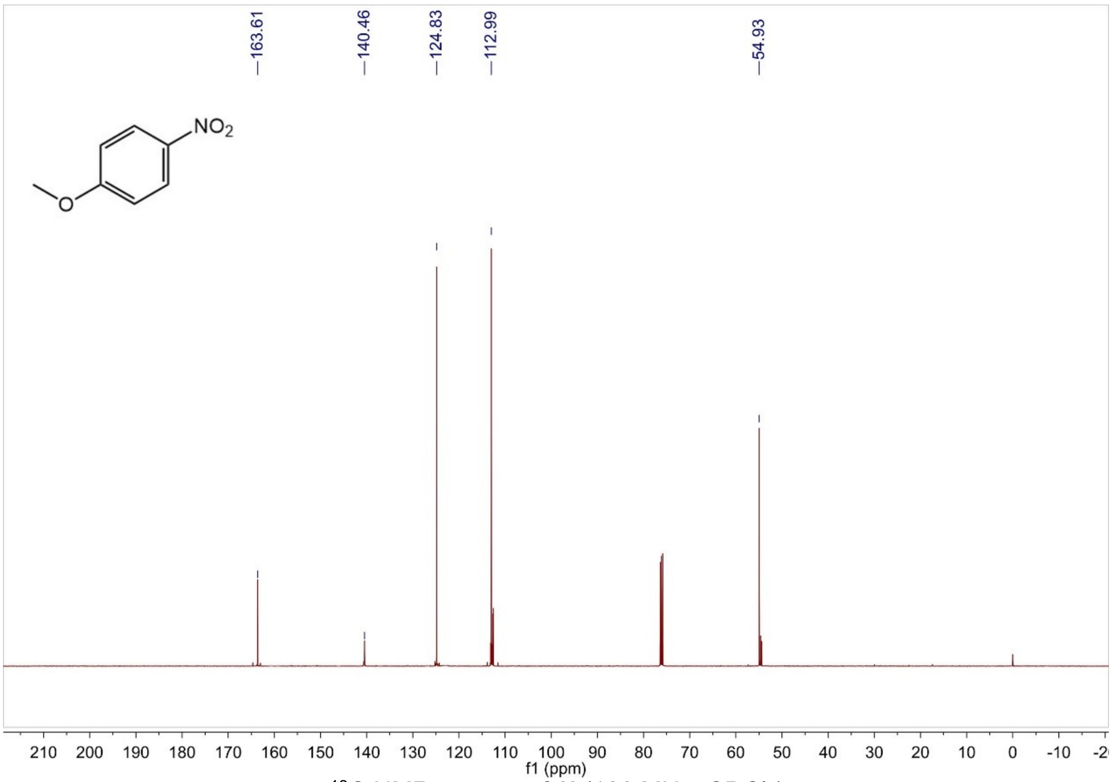
^{1}H NMR spectra of **6h** (500 MHz, $CDCl_3$)



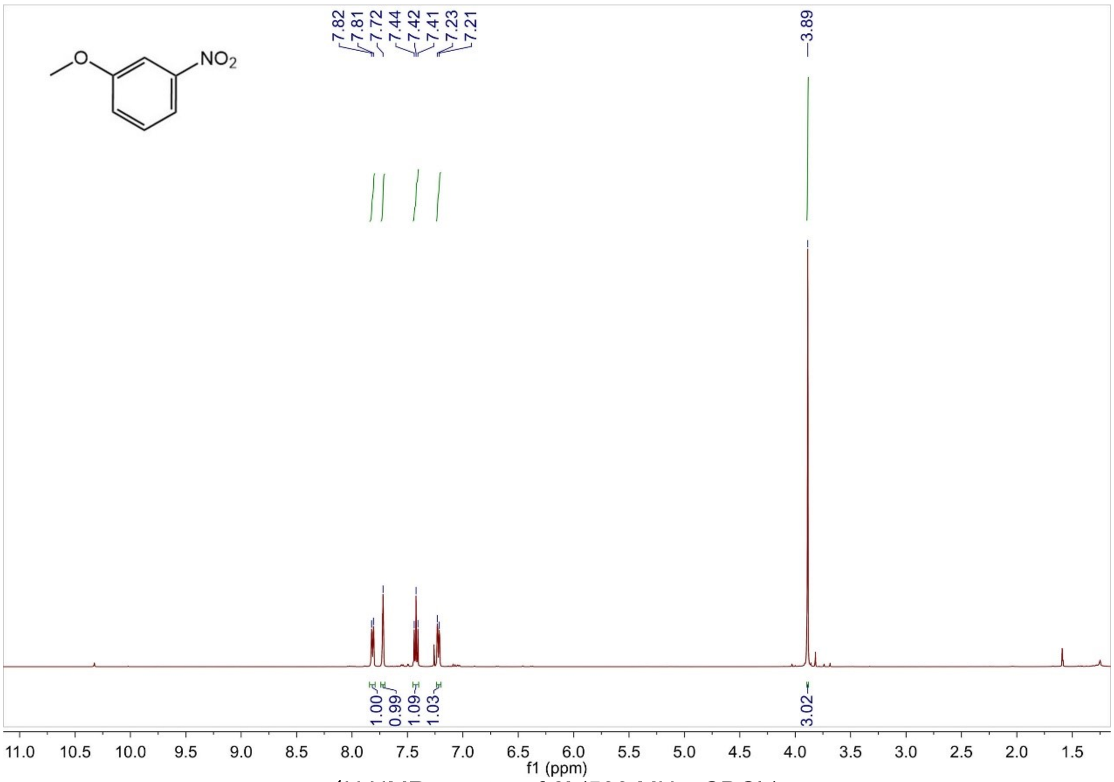
^{13}C NMR spectra of **6h** (126 MHz, $CDCl_3$)



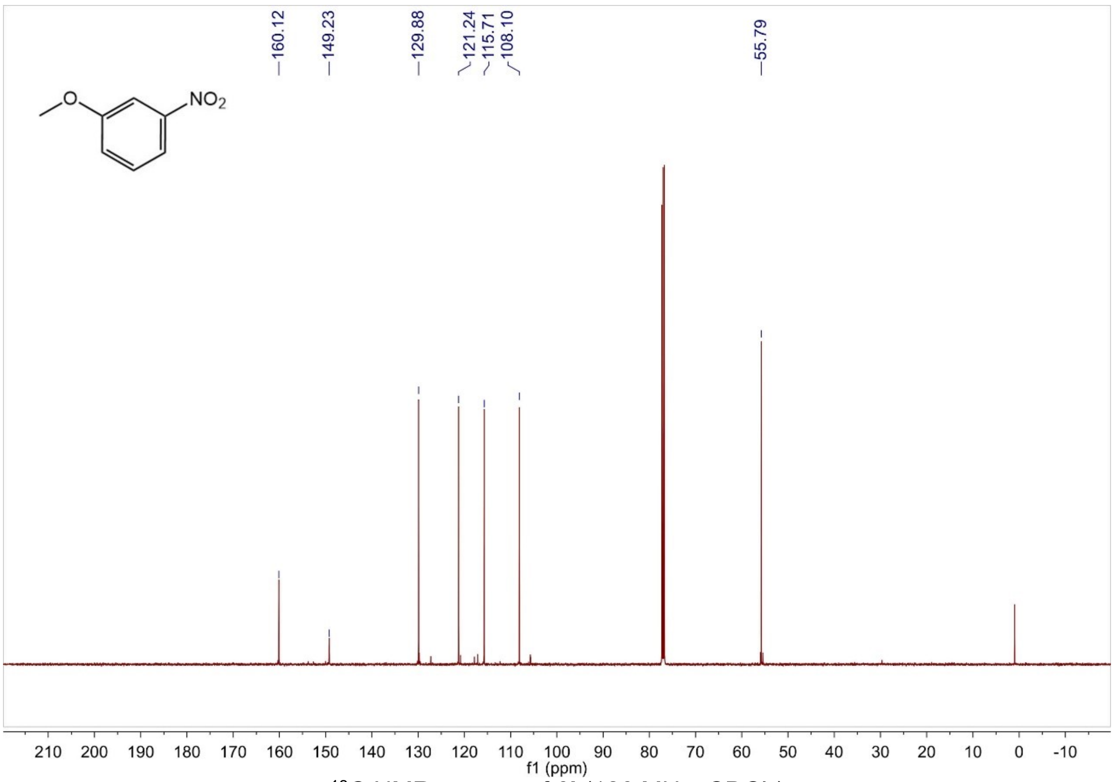
^{1}H NMR spectra of **6i** (500 MHz, $CDCl_3$)



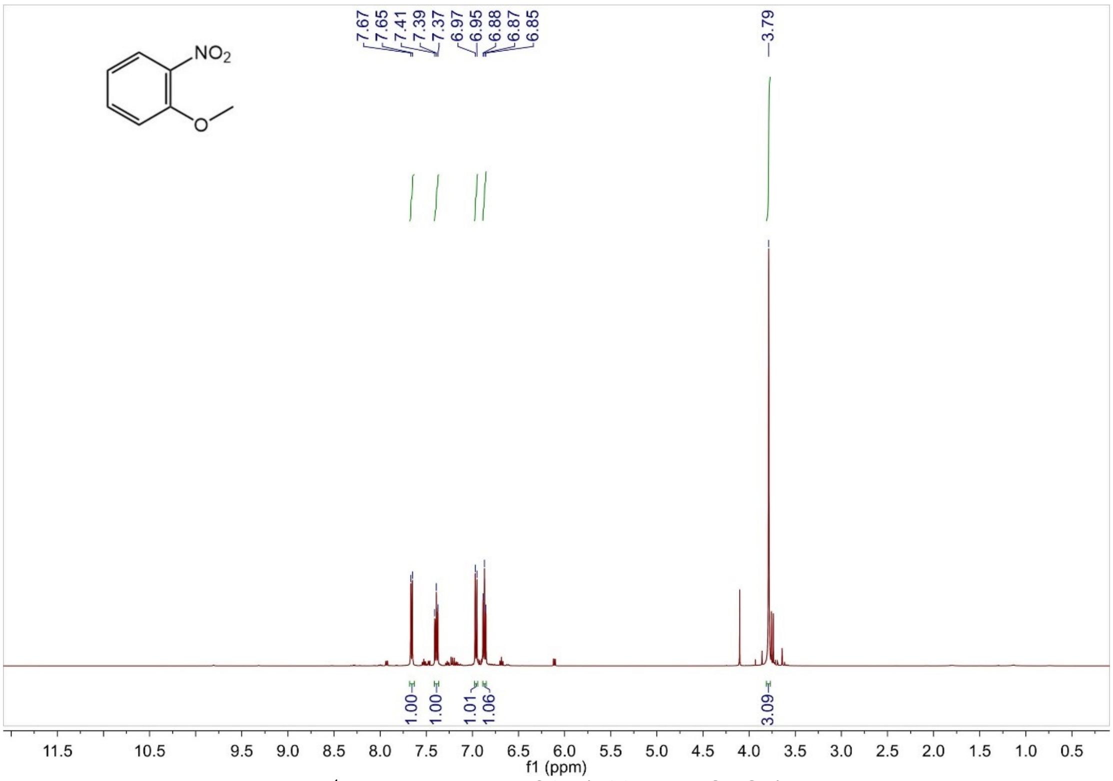
^{13}C NMR spectra of **6i** (126 MHz, $CDCl_3$)



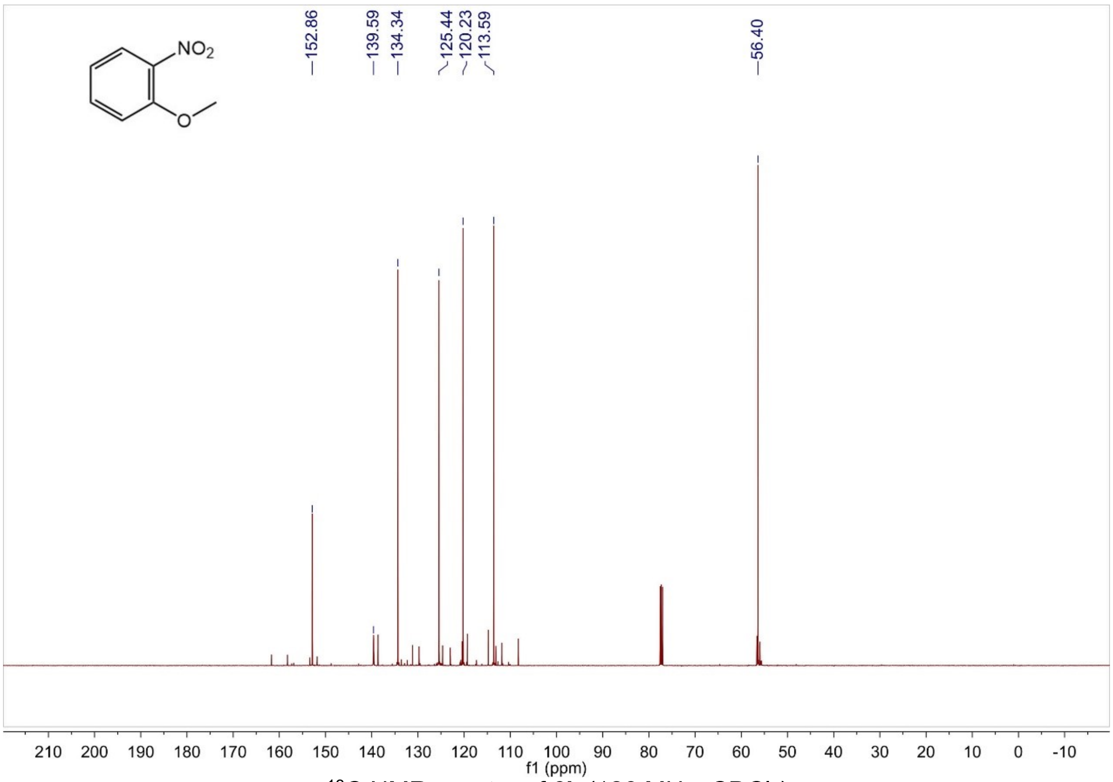
^{1}H NMR spectra of **6j** (500 MHz, $CDCl_3$)



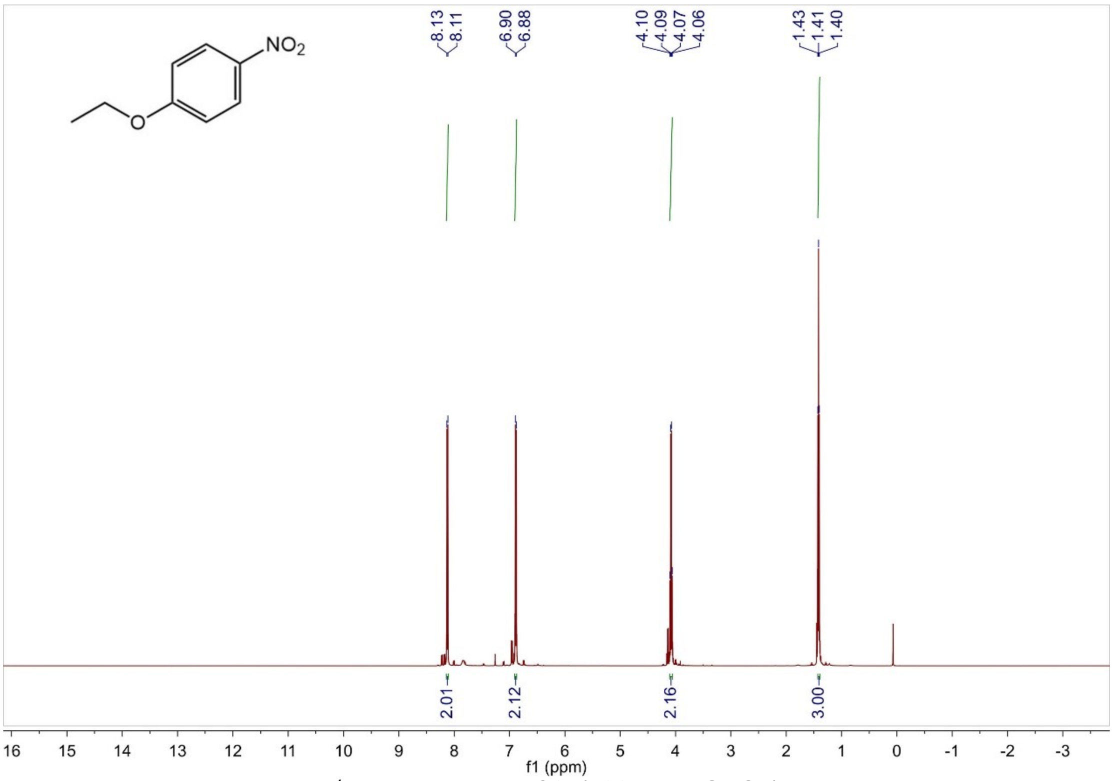
^{13}C NMR spectra of **6j** (126 MHz, $CDCl_3$)



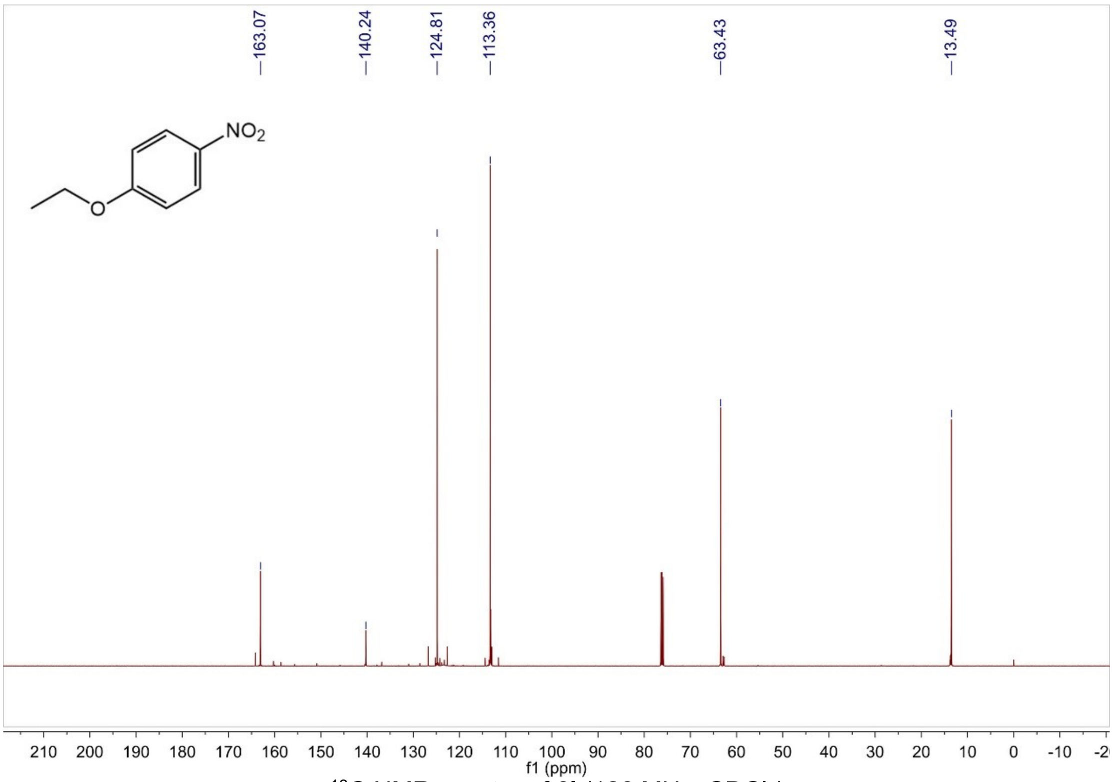
^{1}H NMR spectra of **6k** (500 MHz, $CDCl_3$)



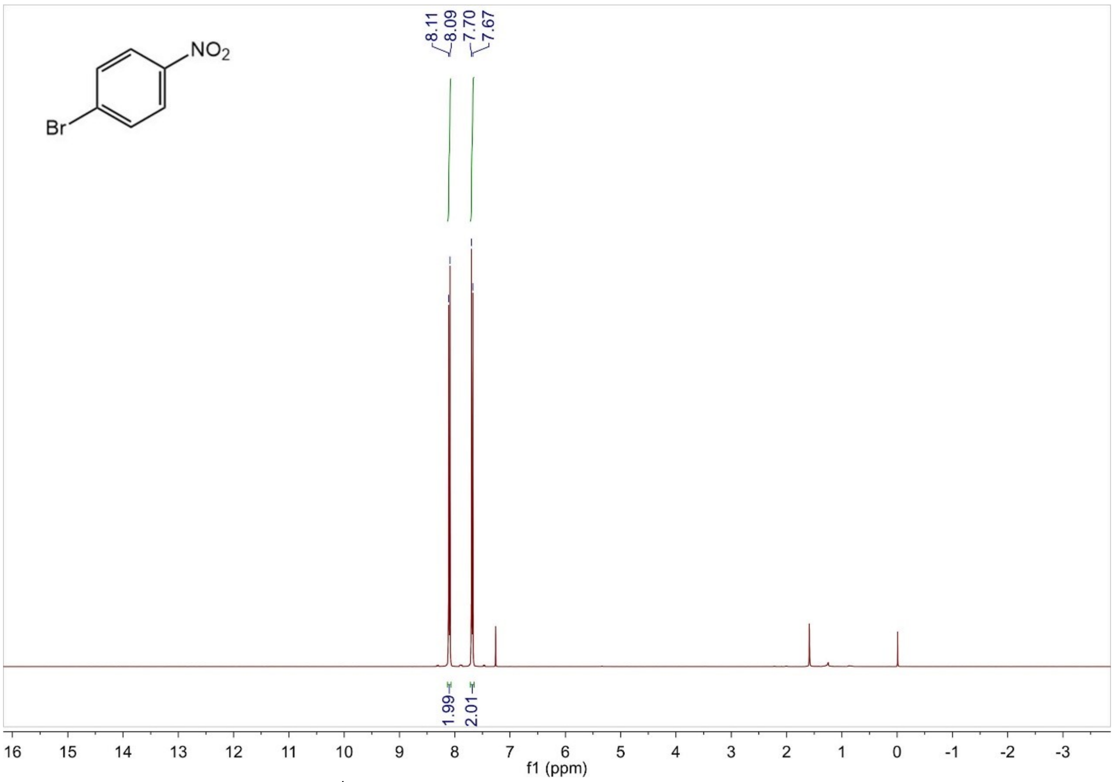
^{13}C NMR spectra of **6k** (126 MHz, $CDCl_3$)



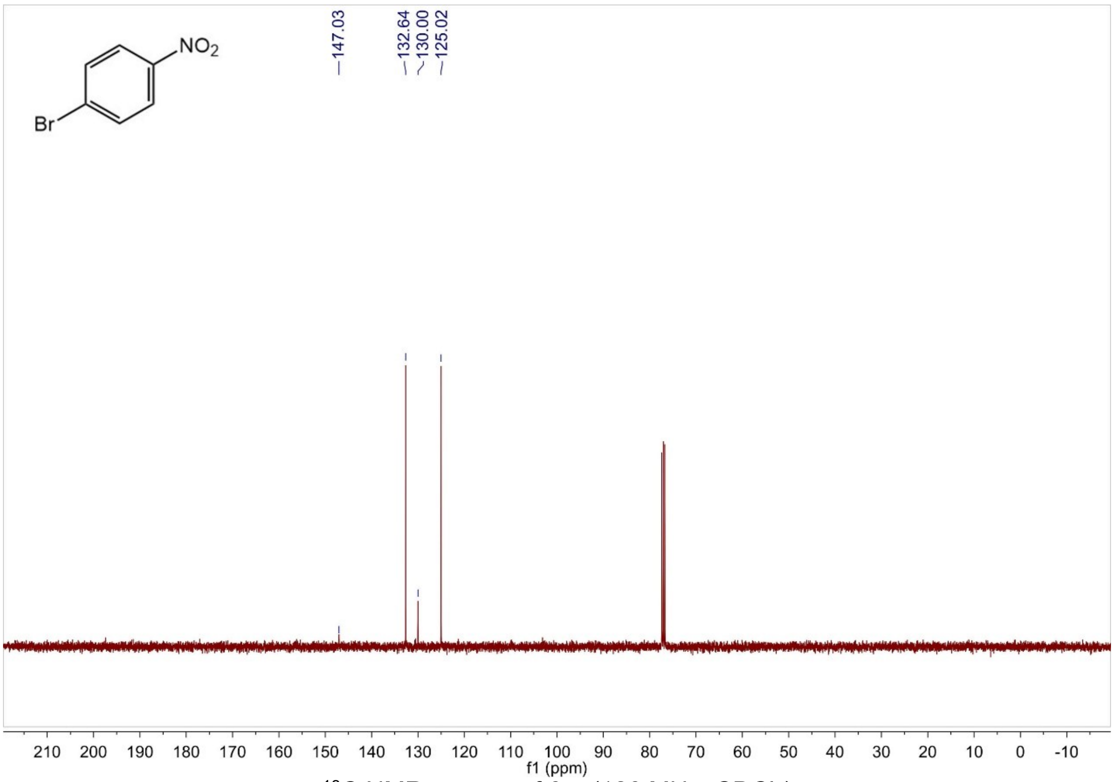
^{1}H NMR spectra of **6l** (500 MHz, $CDCl_3$)



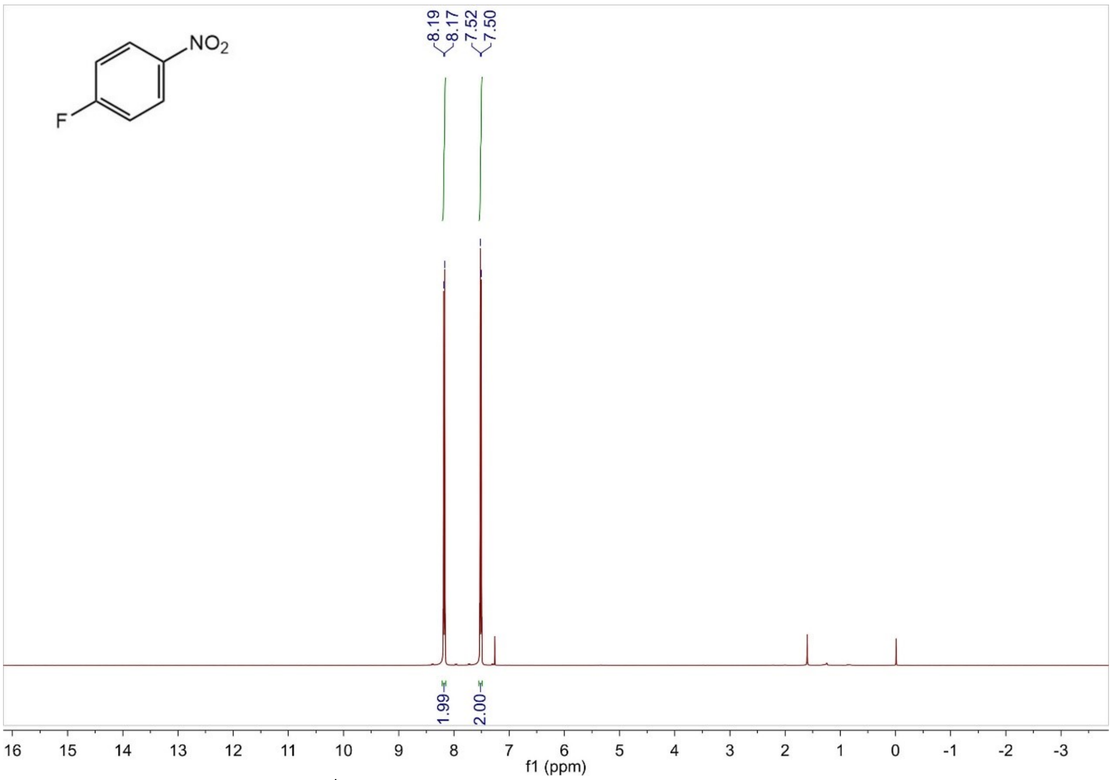
^{13}C NMR spectra of **6l** (126 MHz, $CDCl_3$)



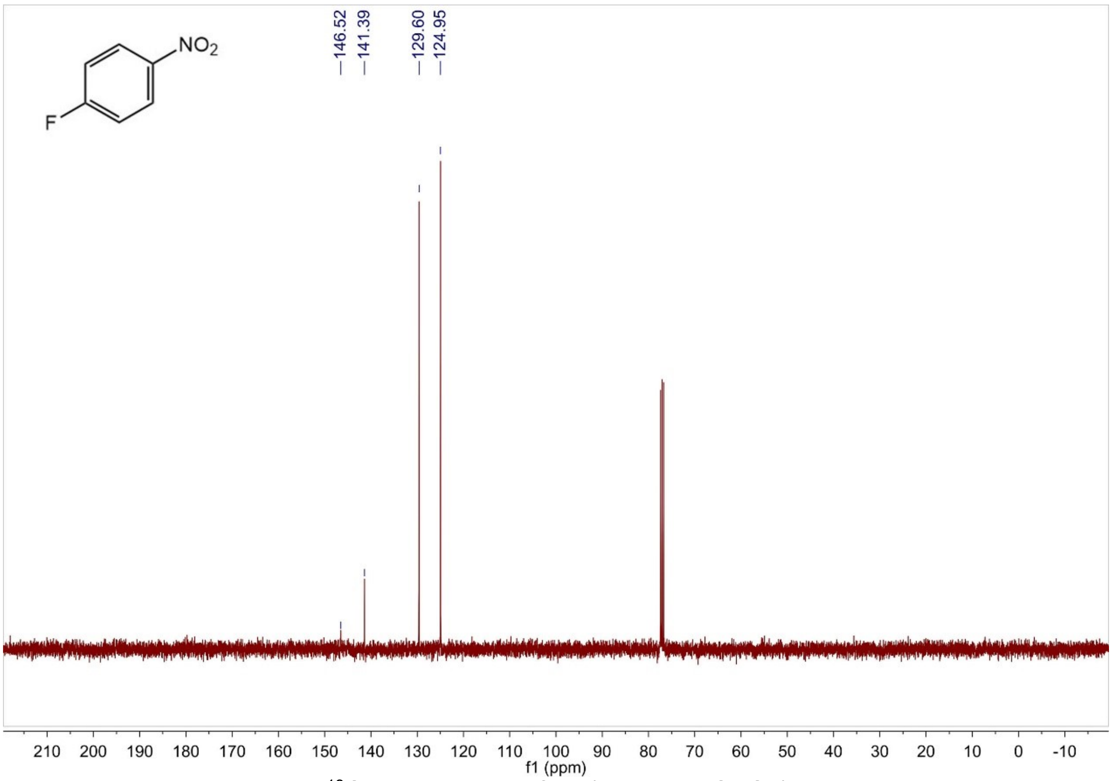
^{1}H NMR spectra of **6m** (500 MHz, $CDCl_3$)



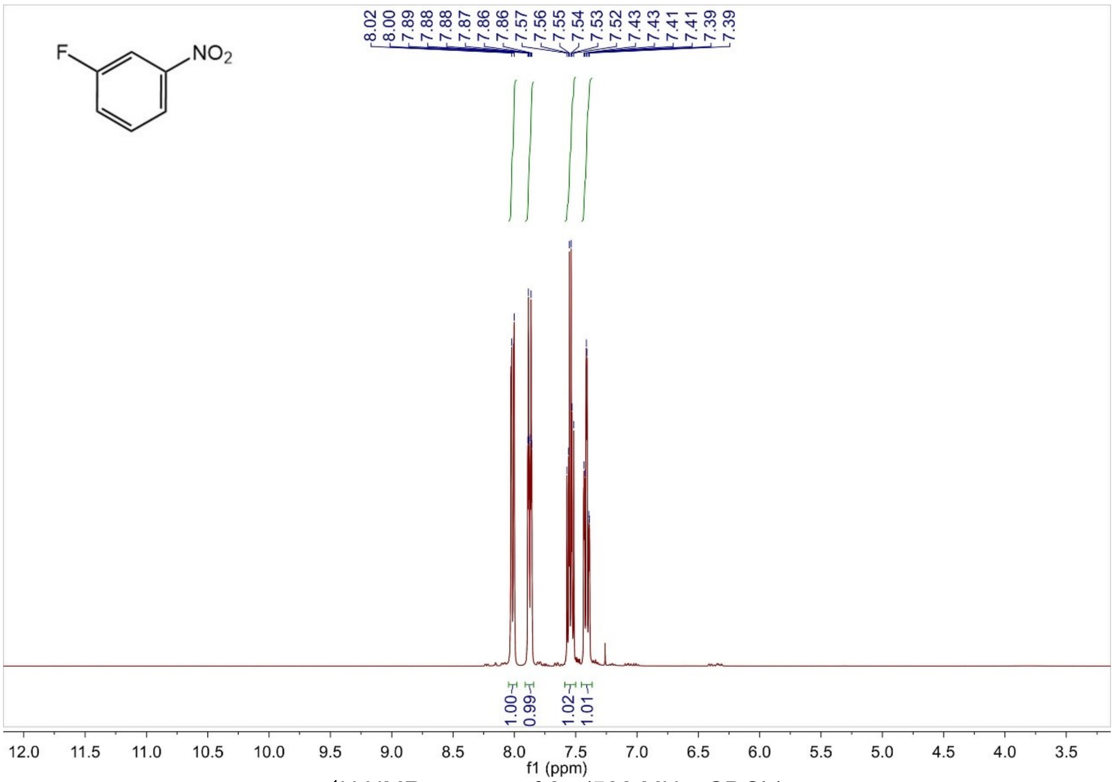
^{13}C NMR spectra of **6m** (126 MHz, $CDCl_3$)



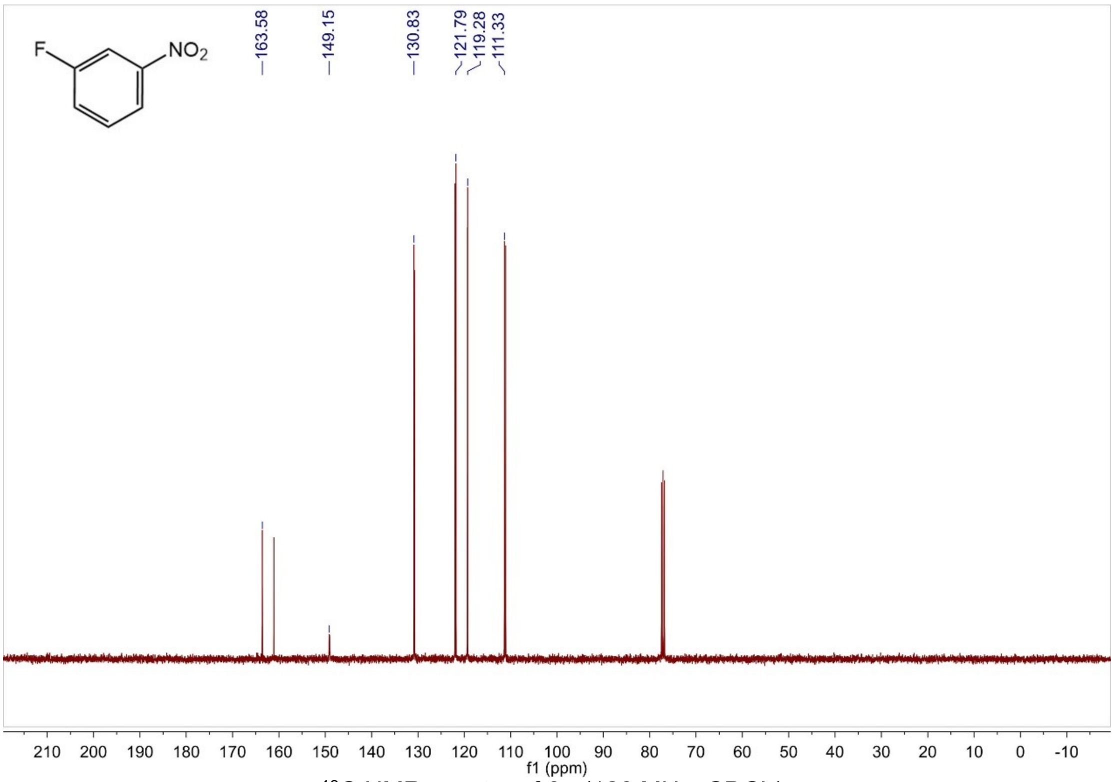
^{1}H NMR spectra of **6n** (500 MHz, $CDCl_3$)



^{13}C NMR spectra of **6n** (126 MHz, $CDCl_3$)



^{1}H NMR spectra of **6o** (500 MHz, $CDCl_3$)



^{13}C NMR spectra of **6o** (126 MHz, $CDCl_3$)

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