Electronic Supplementary Material (ESI) for Green Chemistry

Supporting Information for

Mechanosynthesis of nitrosobenzenes: a proof-of-principle study in combining solvent-free synthesis with solvent-free separations

Igor Huskić, Ivan Halasz, Tomislav Friščić and Hrvoj Vančik

Department of Chemistry, Faculty of Science, University of Zagreb
Horvatovac 102a, 10002 Zagreb (Croatia)
Fax: (+) 385 1 460 6401
E-mail: ihalasz@chem.pmf.hr

T. Friščić
Department of Chemistry, McGill University,
801 Sherbrooke St. W., H3A 2K6 Montréal (Canada)

Table S1. Synthesis results depending upon experimental conditions (neat, LAG or $NaHCO_3$) and milling time. Green background highlights the optimal conditions. Different synthesis outcomes when the synthesis is performed in the same conditions is the consequence of relatively small reagent quantities resulting in large relative errors during manipulation. Also, as is well known, syntheses may not be strictly reproducible.

derivative	yield	purity	Method	time/min
p-Br	0.10	0.16	LAG, MeOH	10
p-Br	0.10	0.78	LAG, CH3CN	10
p-Br	0.03	0.15	LAG, CHCl3	10
p-Br	0.05	0.19	LAG, CHCl3	5
p-Br	0.06	0.29	LAG, hexane	20
p-Br	0.06	0.18	LAG, hexane	30
p-Br	0.45	0.69	neat, $NaHCO_3$	20
p-Br	0.62	0.74	neat, $NaHCO_3$	20
p-Br	0.80	0.90	neat, $NaHCO_3$	20
p-Br	0.11	0.73	neat	10
p-Br	0.16	0.62	neat	10
p-Br	0.17	0.82	neat	5
p-Br	0.12	0.31	neat	20
p-Br	0.13	0.42	neat	30
p-I	0.85	0.92	$NaHCO_3$	20
p-I	0.11	0.73	neat	20
p-I	0.13	0.89	neat	10
p-I	0.20	0.84	LAG, MeOH	20
p-I	0.18	0.88	LAG, MeOH	10
p-I	0.13	0.87	LAG, MeCN	20
p-I	0.16	0.81	LAG, MeCN	10
p-I	0.07	0.29	LAG, $CHCl_3$	20
p-I	0.16	0.86	LAG, $CHCl_3$	10
p-Cl	0.28	0.50	neat, $NaHCO_3$	20
p-Cl	0.44	0.53	neat, $NaHCO_3$	20
p-Cl	0.70	0.80	neat, $NaHCO_3$	20
p-Cl	0.48	0.59	neat, $NaHCO_3$	20
p-Cl	0.06	0.81	LAG, MeCN	5
p-Cl	0.09	0.69	neat	5
p-Cl	0.07	0.61	neat	10
p-Me	0.52	0.69	neat, $NaHCO_3$	20
p-Me	0.31	0.34	neat, $NaHCO_3$	20
p-NO2	N/A	0.88	LAG, MeCN	35
p-NO2	0.26	0.90	neat	30
p-NO2	0.29	0.84	neat	60

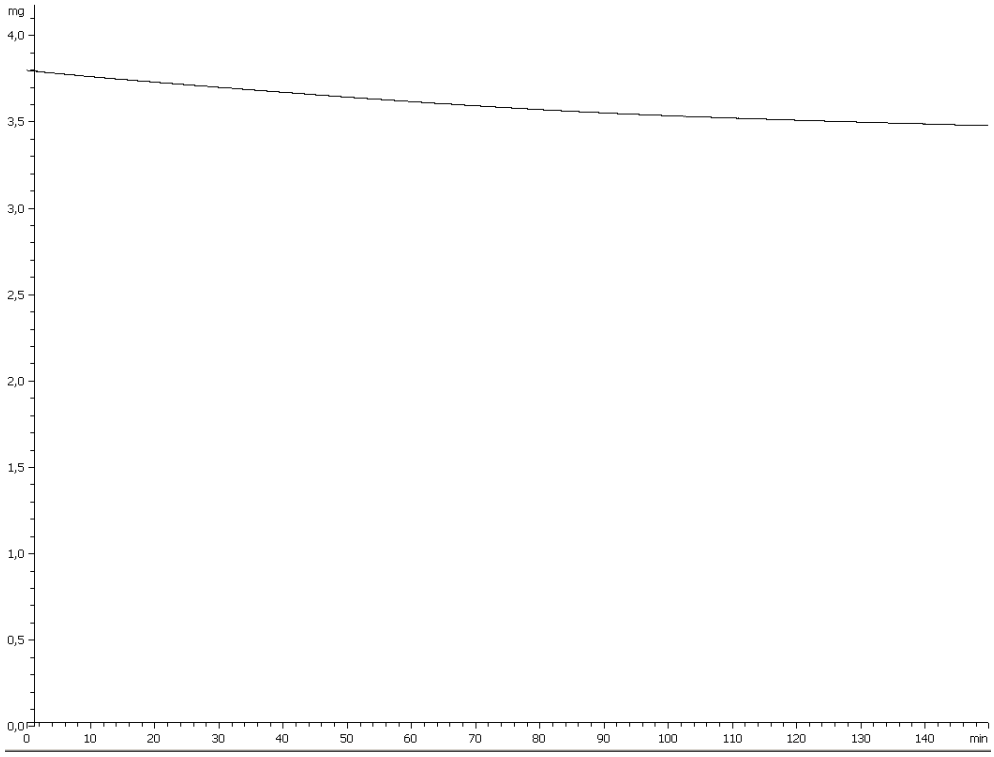

Figure S1. Isothermal (25 °C) mass loss during dimerisation of *p*-bromonitrosobenzene showing sublimation of the material.

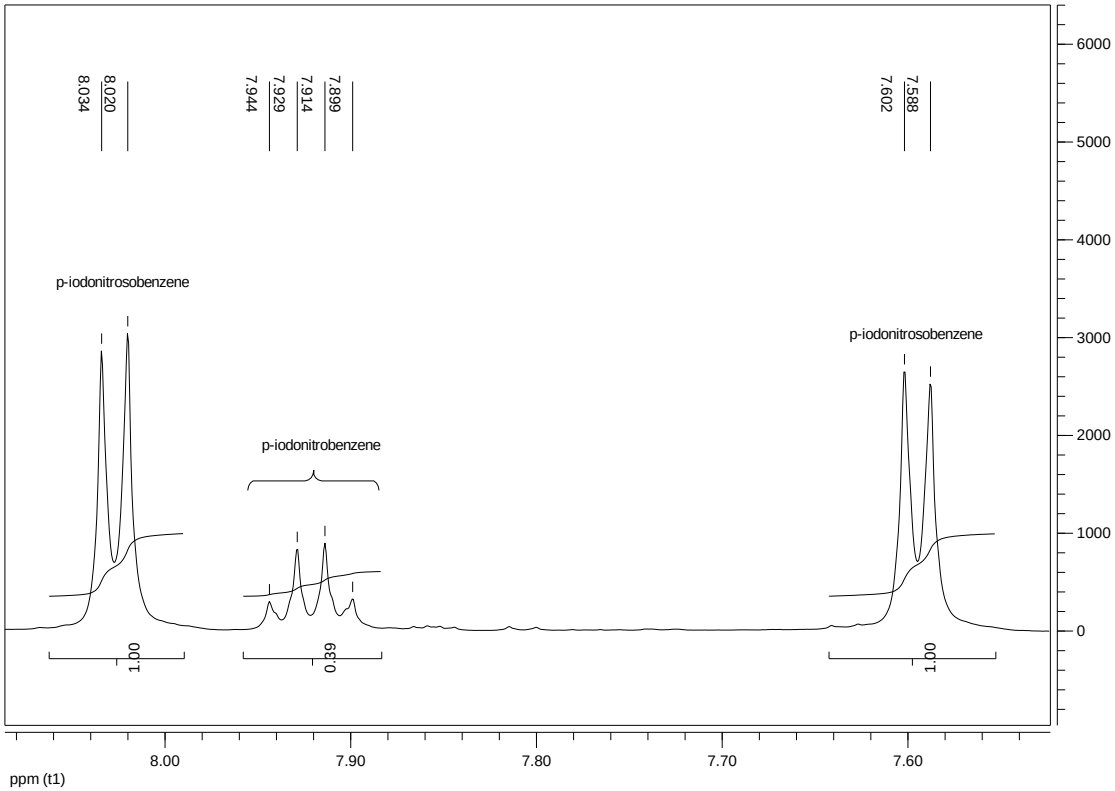

Figure S2. ^{1}H NMR spectra of the reaction mixture of *p*-iodoaniline and *Oxone* prior to sublimation.

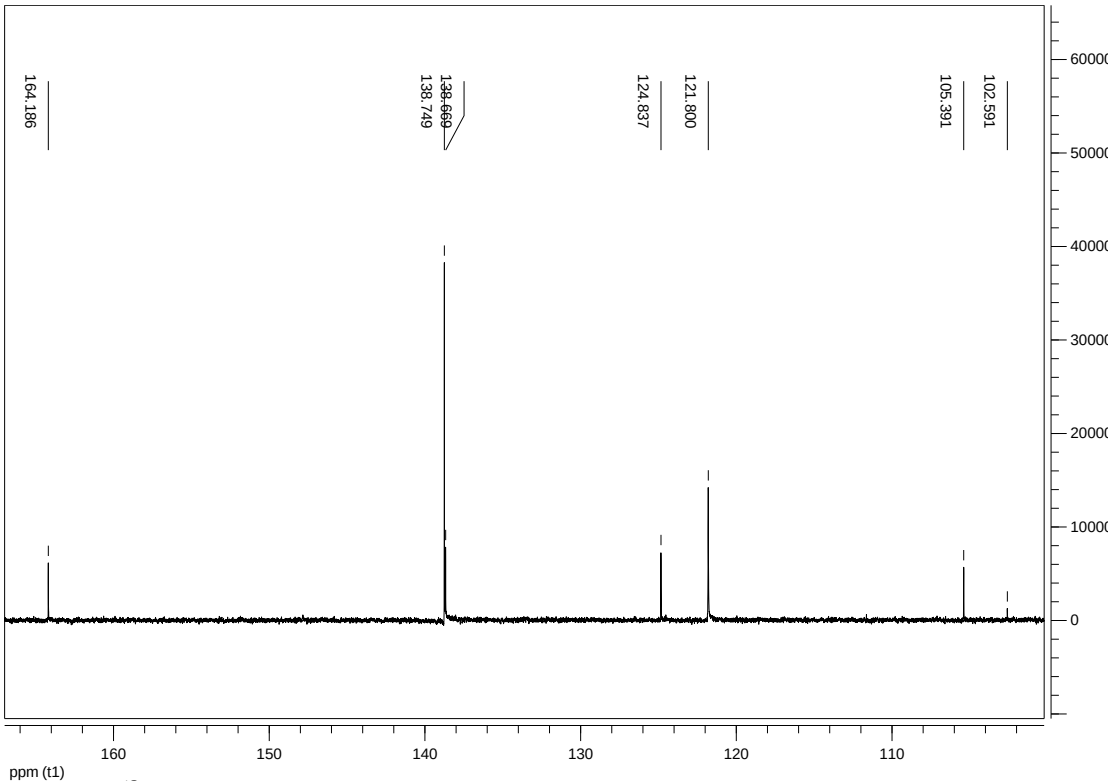

Figure S3. ^{13}C NMR spectra of reaction mixture of *p*-iodoaniline and *Oxone* prior to sublimation.

Table S2. ^{13}C NMR shifts according to Fig S4.

Atom	Shift	Atom	Shift
a	102.65	a’	105.39
b	138.69	b’	138.74
c	124.87	c’	121.80
d	147.85	d’	164.17

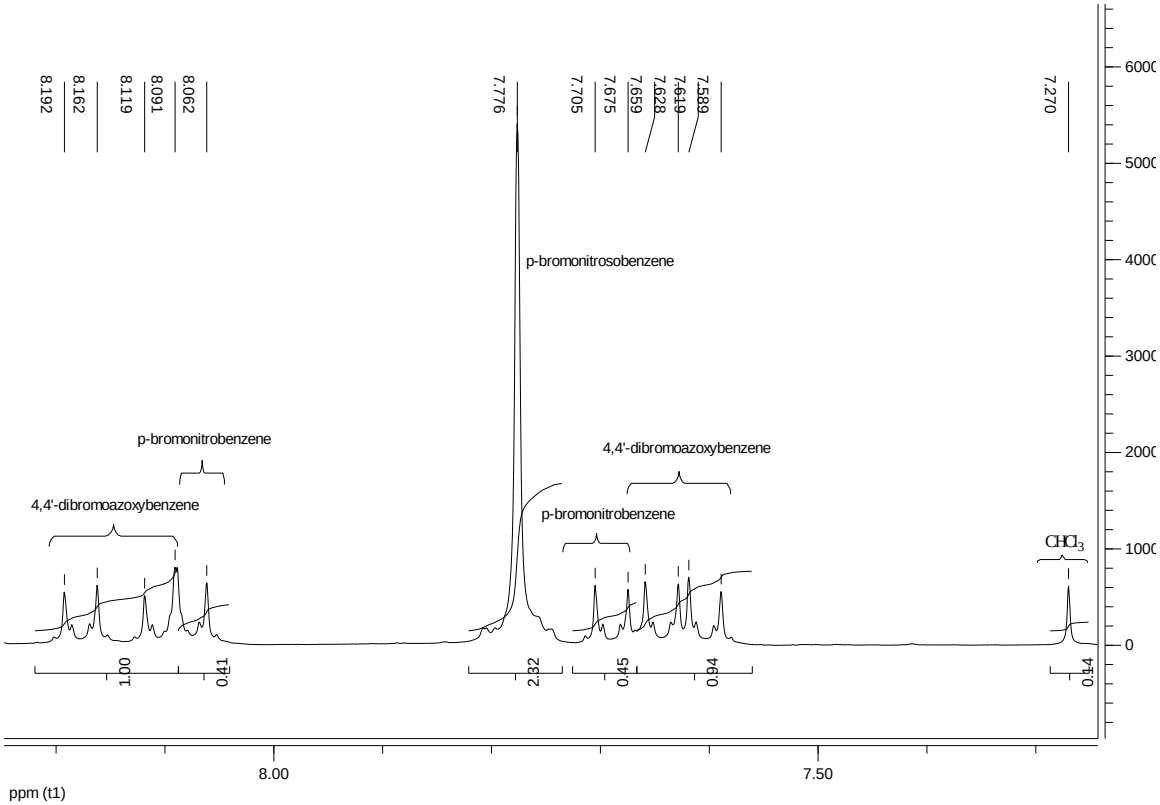

Figure S4. ^{1}H NMR spectra of the reaction mixture of *p*-bromoaniline and *Oxone* prior to sublimation.

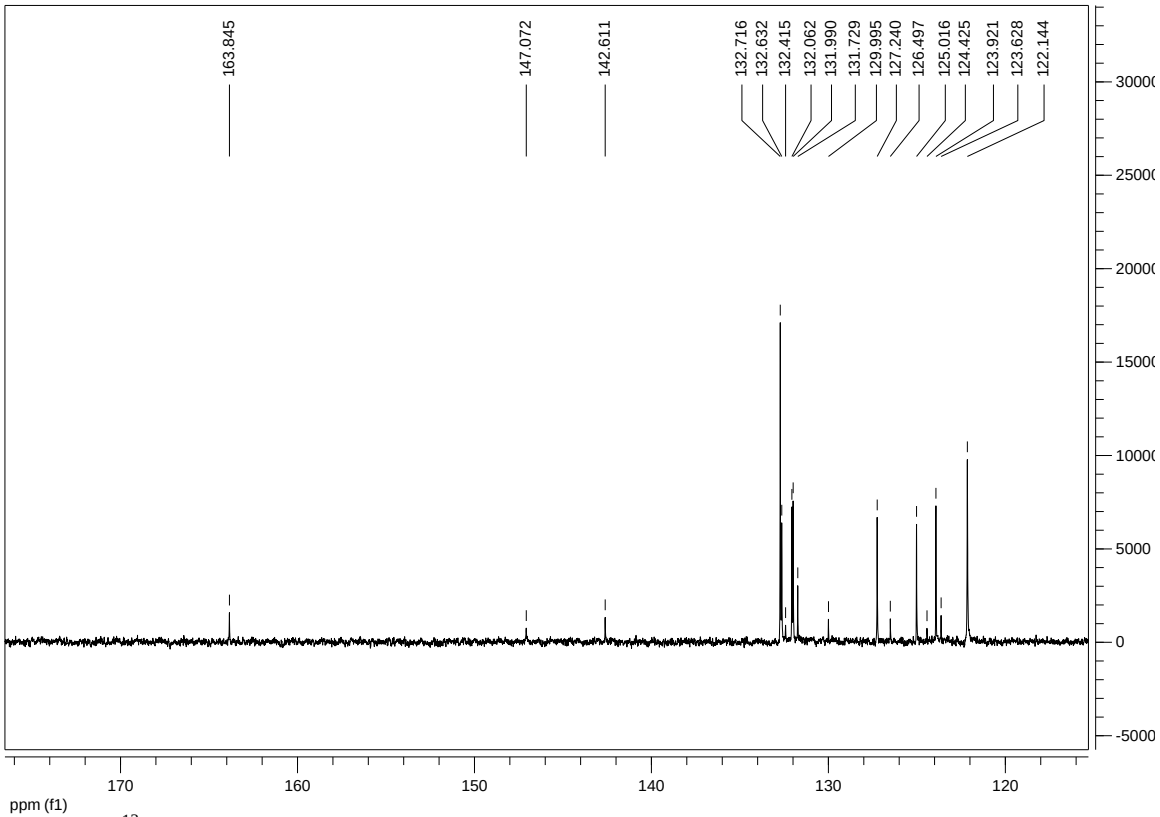

Figure S5. ^{13}C NMR spectra of reaction mixture of *p*-bromoaniline and *Oxone* prior to sublimation.

Table S3. ^{13}C NMR shifts according to Fig. S6.

Atom	Shift	Atom	Shift
a	129.99	e	132.06
b	132.63	f	132.41
c	125.02	g	127.24
d	147.07	h	/
a’	131.73	i	142.61
b’	132.71	j	126.50
c’	122.14	k	/
d’	163.84	l	131.99

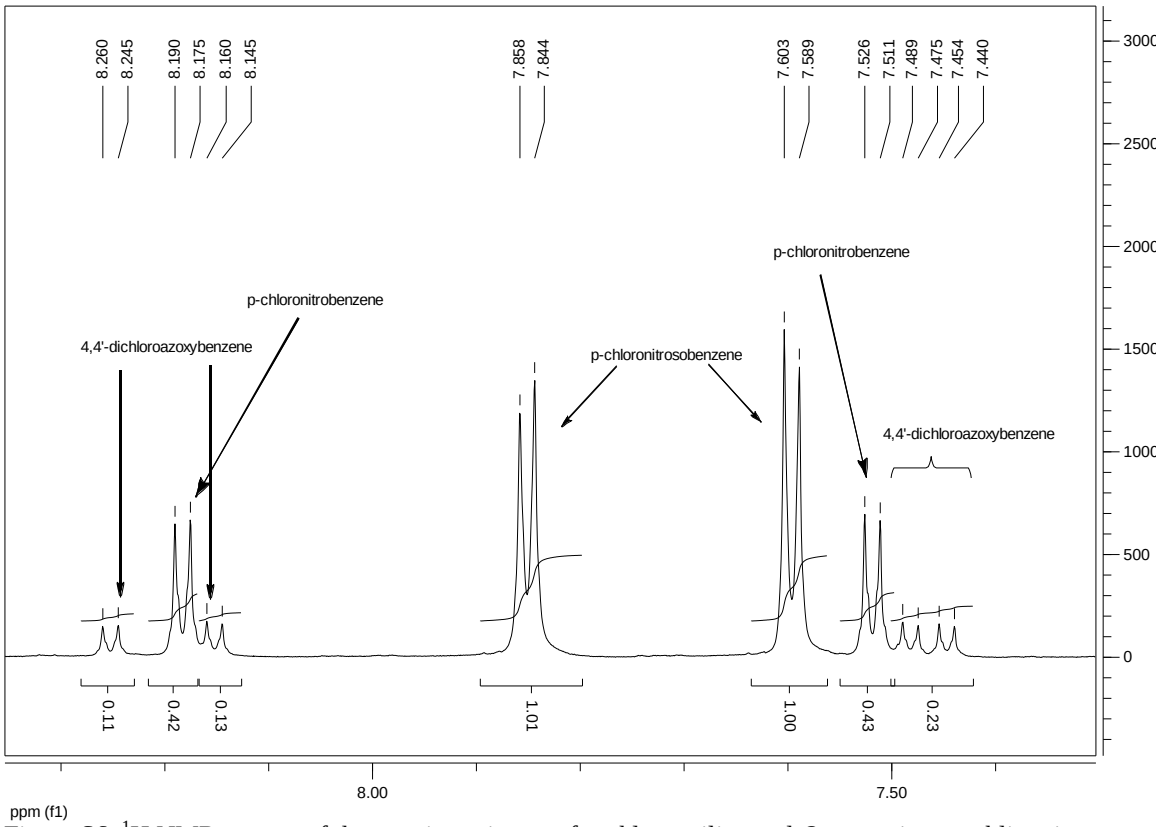

Figure S6. ^{1}H NMR spectra of the reaction mixture of *p*-chloroaniline and *Oxone* prior to sublimation.

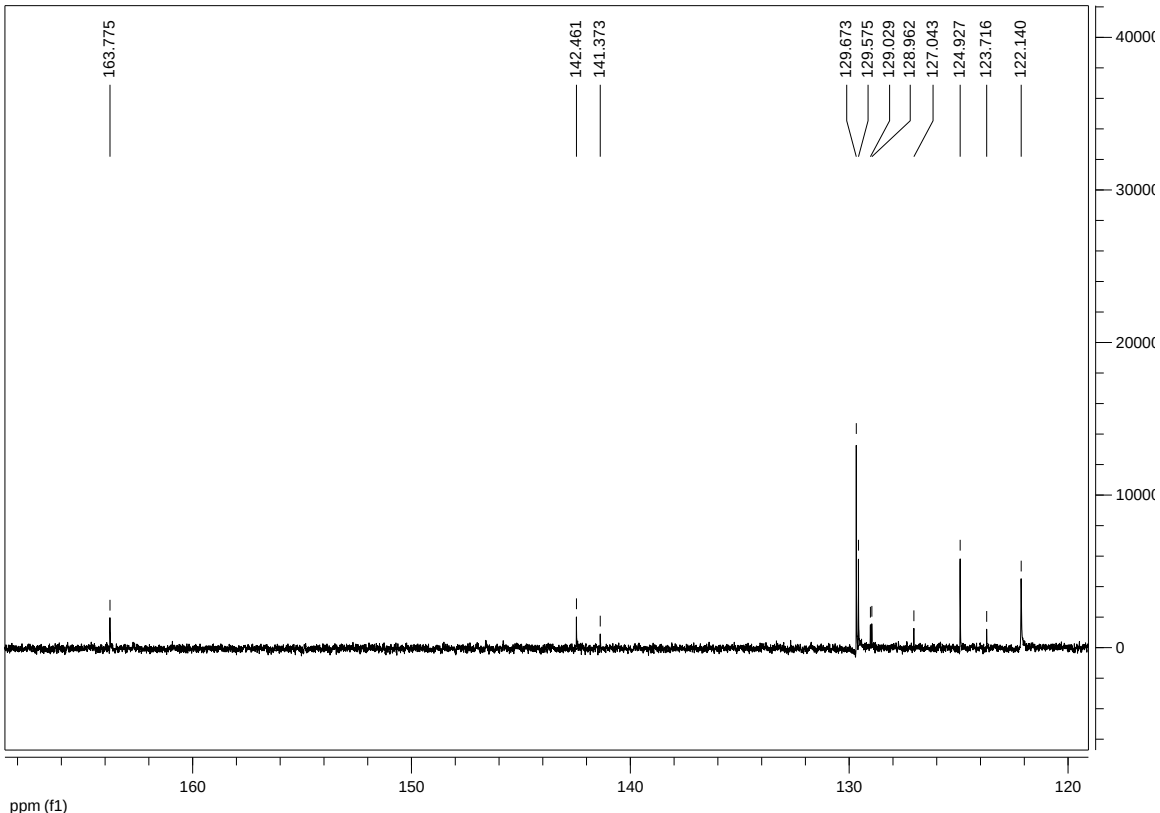

Figure S7. ^{13}C NMR spectra of reaction mixture of *p*-chloroaniline and *Oxone* prior to sublimation.

Table S4. ^{13}C NMR shifts according to Fig. S8.

Atom	Shift	Atom	Shift
a	141.40	e	/
b	129.59	f	129.04
c	124.95	g	123.71
d	/	h	/
a’	142.50	i	/
b’	129.69	j	127.08
c’	122.19	k	128.98
d’	163.74	l	/

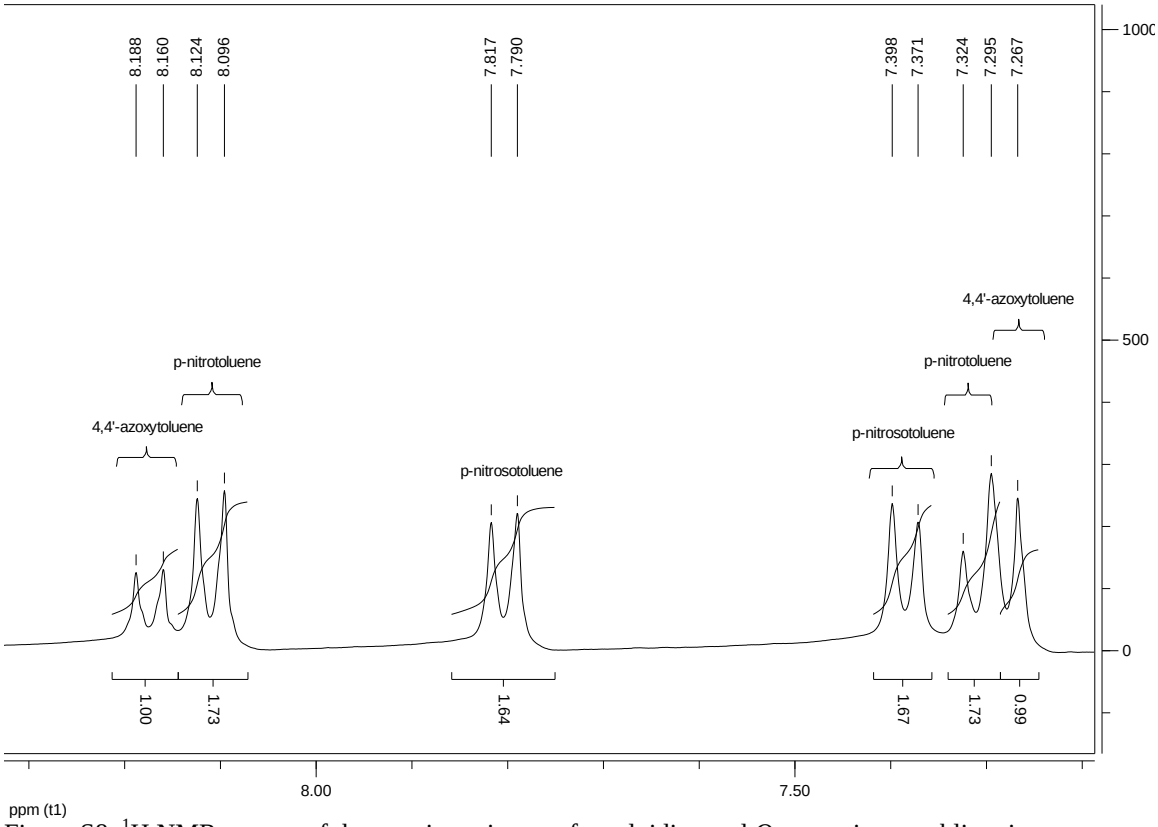

Figure S8. ^{1}H NMR spectra of the reaction mixture of *p*-toluidine and *Oxone* prior to sublimation.

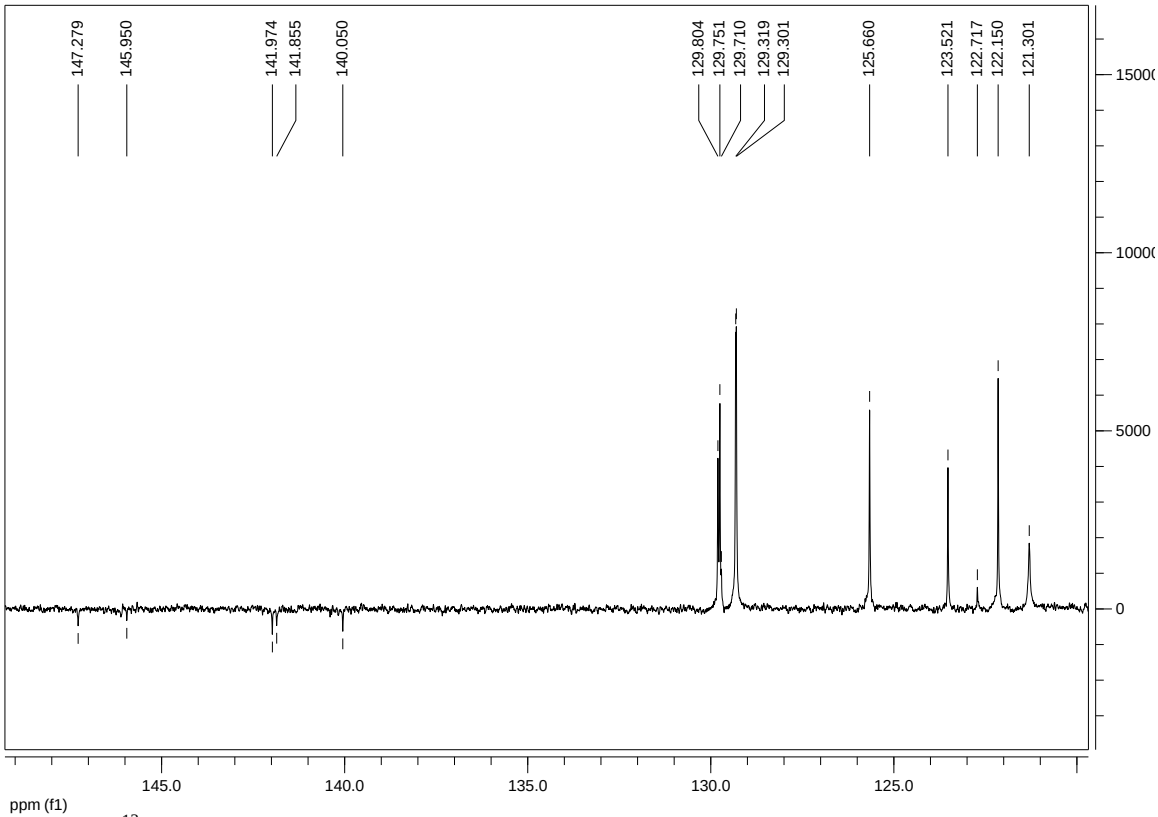

Figure S9. ^{13}C NMR spectra of reaction mixture of *p*-toluidine and *Oxone* prior to sublimation.

Table S5. ^{13}C NMR shifts according to Fig. S10.

Atom	Shift	Atom	Shift
a	145.95	e	141.97
b	129.80	f	129.32
c	123.52	g	122.15
d	/	h	/
a’	147.28	i	/
b’	/	j	125.66
c’	121.301	k	129.30
d’	/	l	141.86

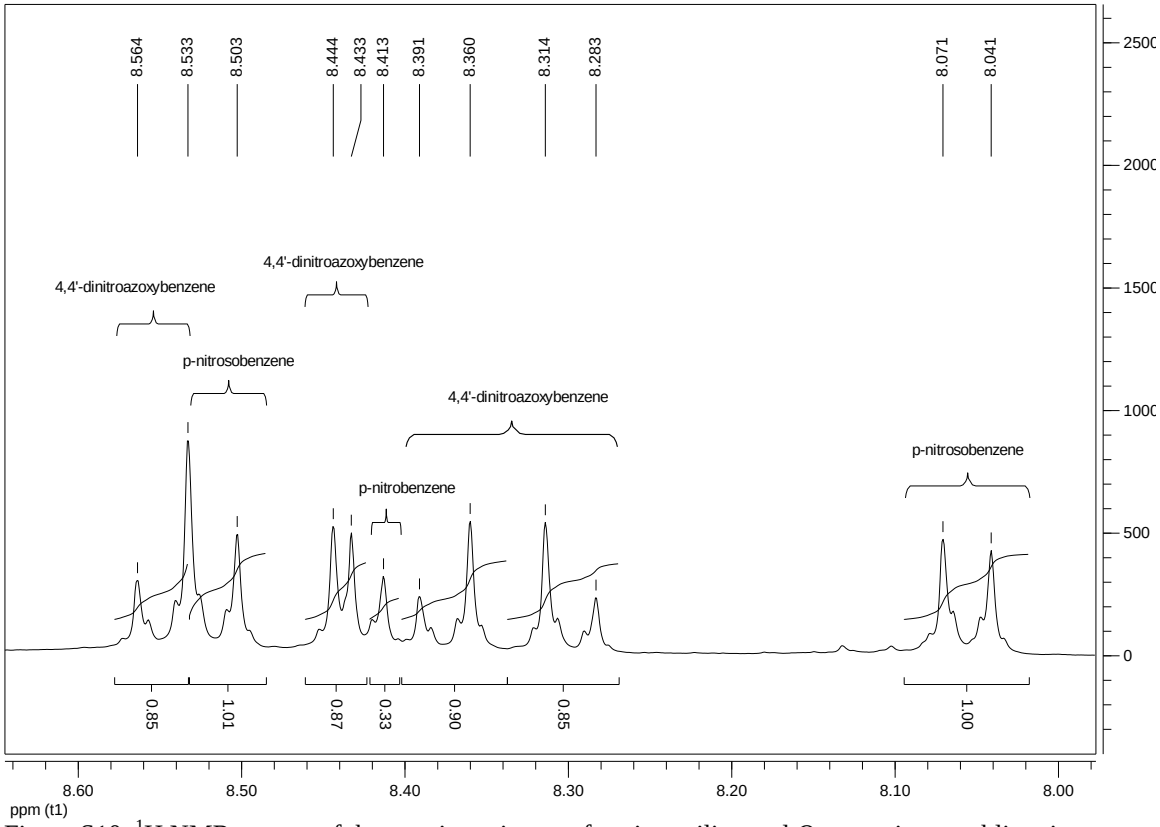

Figure S10. ^{1}H NMR spectra of the reaction mixture of *p*-nitroaniline and *Oxone* prior to sublimation.

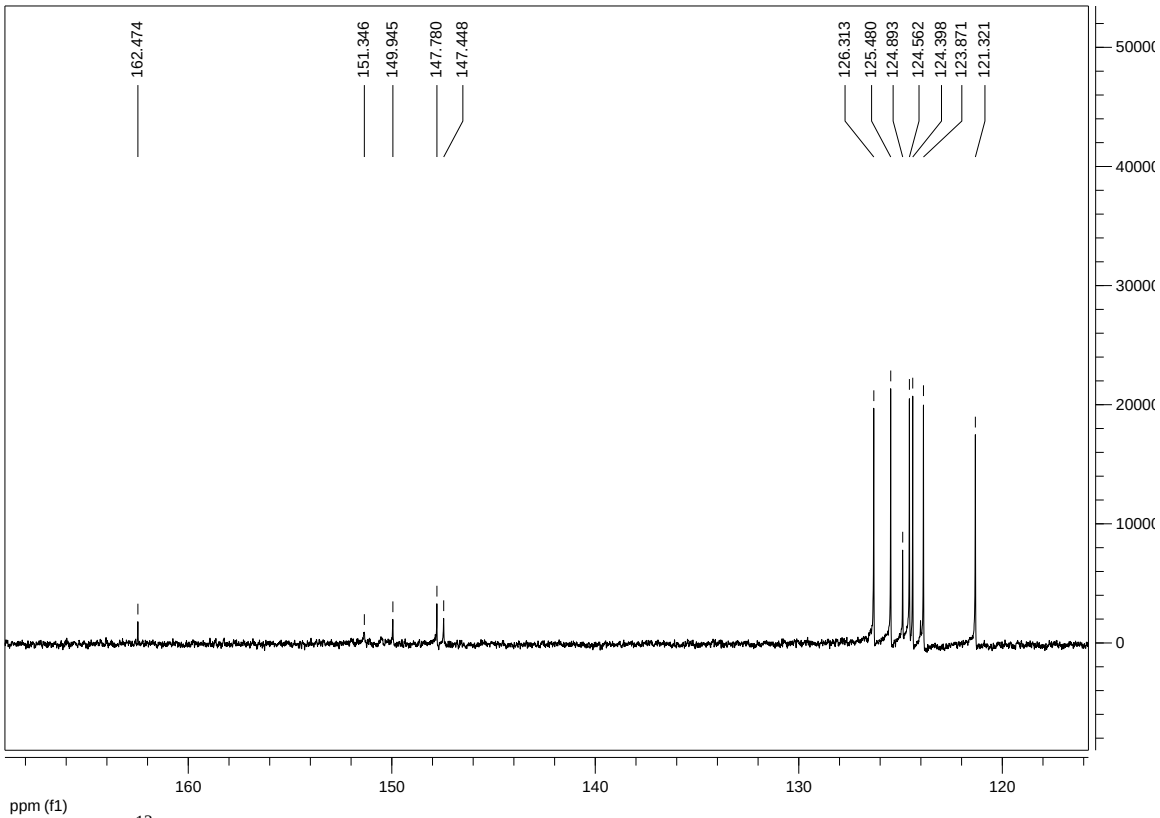

Figure S11. ^{13}C NMR spectra of reaction mixture of *p*-nitroaniline and *Oxone* prior to sublimation.

Table S6. ^{13}C NMR shifts according to Fig. S12.

Atom	Shift	Atom	Shift
a	147.45	e	149.95
b	126.31	f	124.56
a’	147.78	g	123.87
b’	125.48	h	/
c’	121.32	i	/
d’	162.47	j	124.89
		k	124.40
		l	151.35

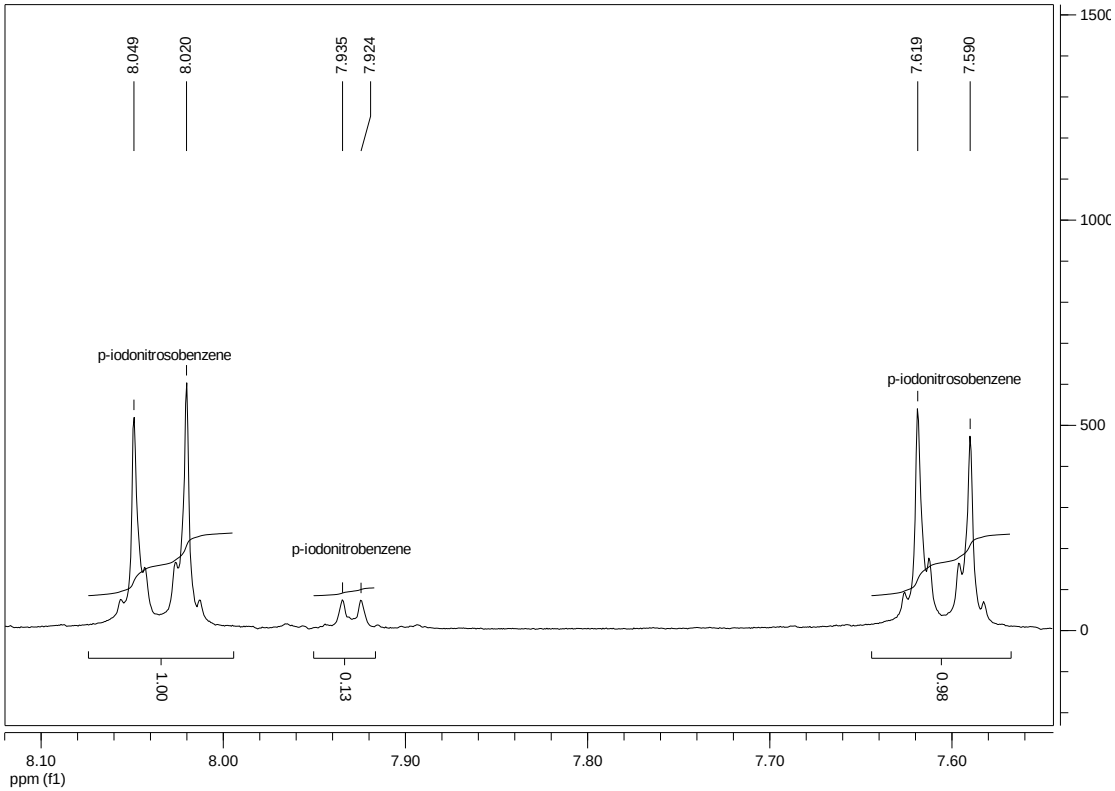

Figure S12. ^{1}H NMR spectrum of the sublimed *p*-iodonitrosobenzene.

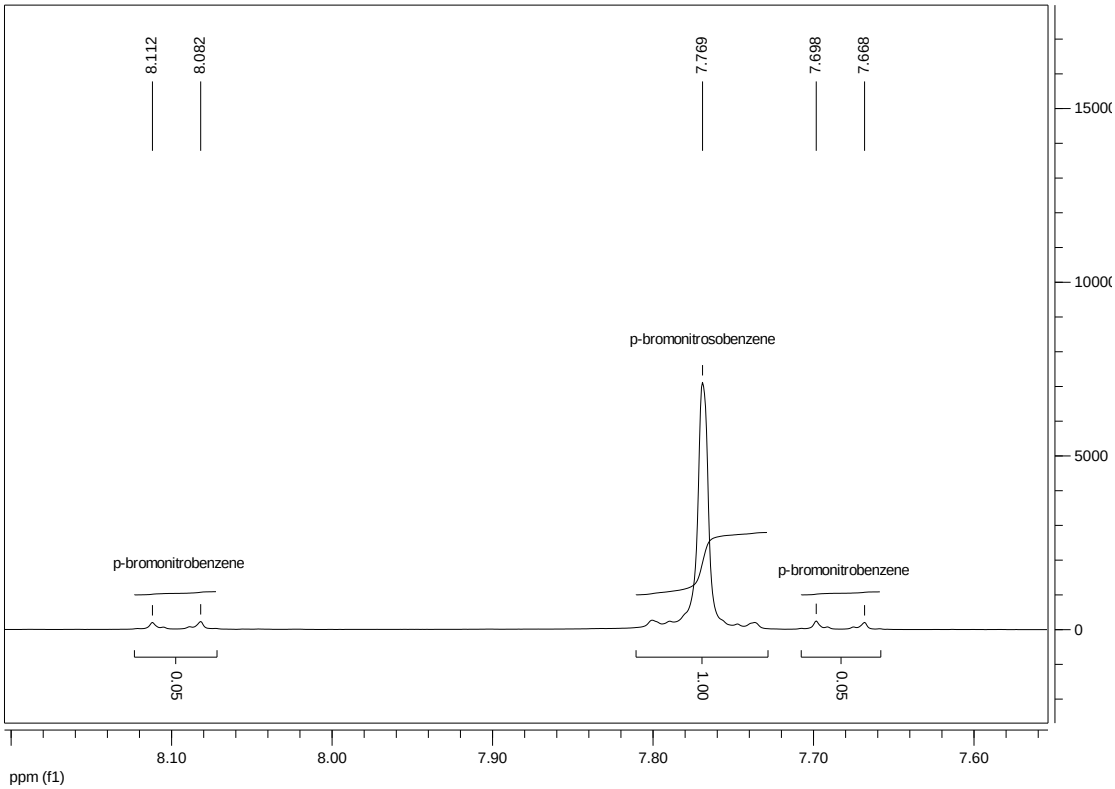

Figure S13. ^{1}H NMR spectrum of the sublimed *p*-bromonitrosobenzene.

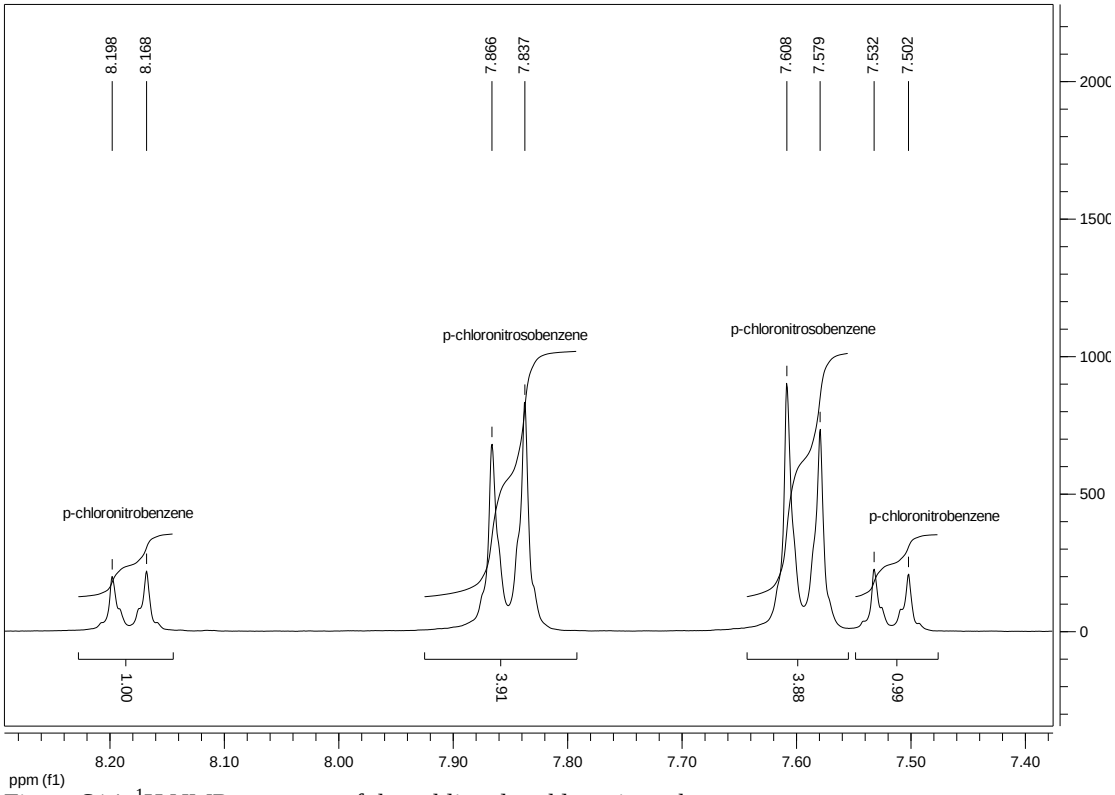

Figure S14. ^{1}H NMR spectrum of the sublimed *p*-chloronitrosobenzene.

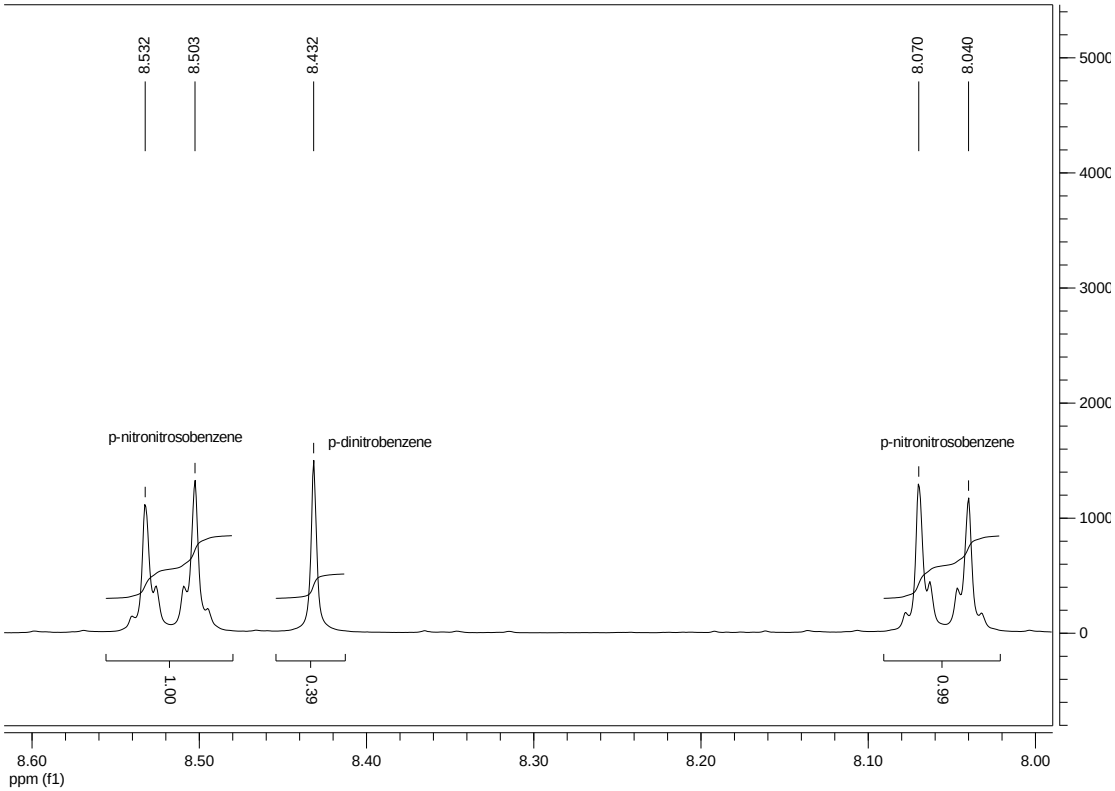

Figure S15. ^{1}H NMR spectrum of the sublimed *p*-nitronitrosobenzene.

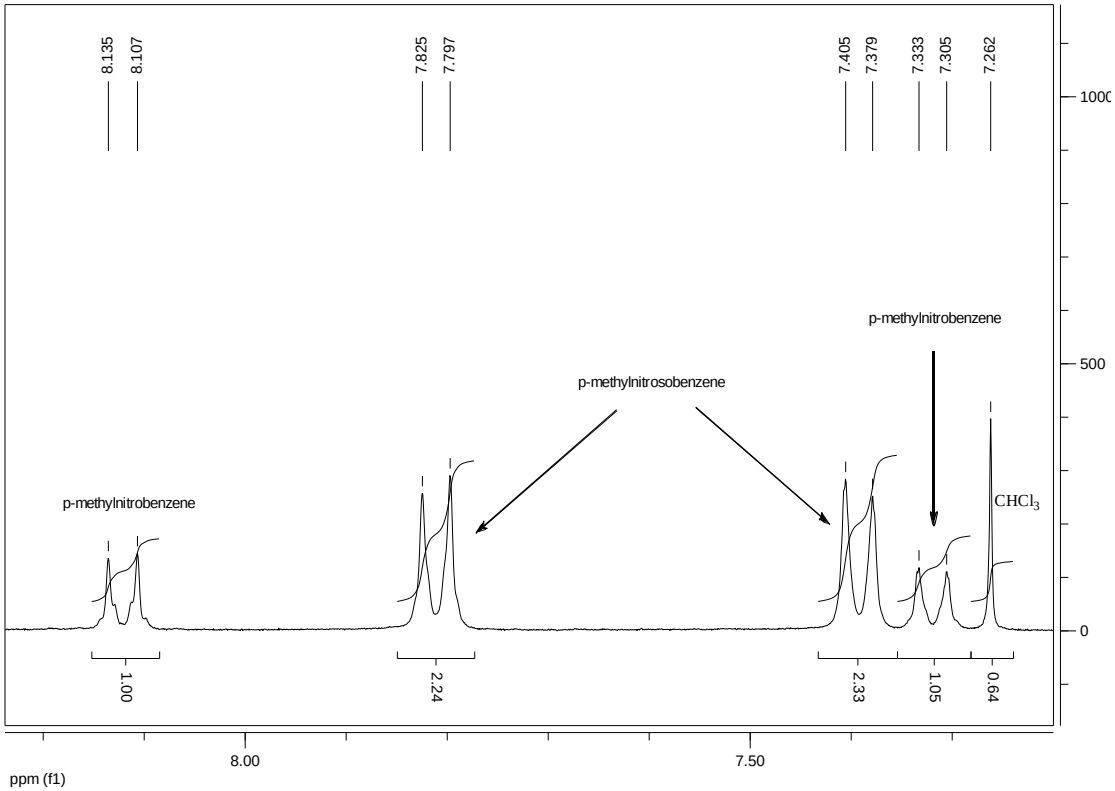

Figure S16. ^{1}H NMR spectrum of the sublimed *p*-methylnitrosobenzene.