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Supporting Information

Perfect Polar Alignment of Parallel Beloamphiphile Monolayers: Synthesis, Characterization, and Crystal Architectures of Unsymmetrical Phenoxy-Substituted Acetophenone Azines

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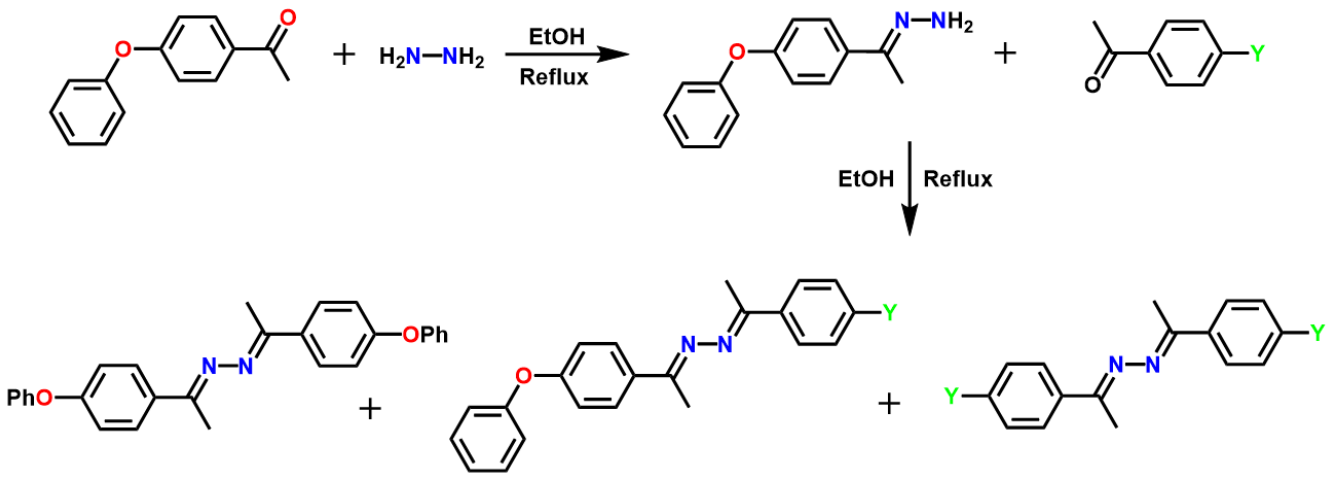
Acetophenone Azine Synthesis and Characterization



Scheme S1. Synthesis of unsymmetrical phenoxy series of (PhO, Y)-azines with Y = F, Cl, Br and I.

Table S1. GC retention times and molecular ion peaks for (PhO, Y)-azines.

	(PhO, F)[a]	(PhO, Cl)[b]	(PhO, Br)[a]	(PhO, I)[a]
Retention time (min)	8.561	24.625	10.829	10.966
m/z (a.u., spectra)	346	362 & 364 (~3:1)	406 & 408 (~1:1)	454
m/z (a.u., calculated)	346.40	362.85	407.30	454.30

[a]Parameters listed in **Table S5** [b]Parameters listed in **Table S6**

Table S2. ^{1}H-NMR chemical shifts (in ppm relative to TMS) for (PhO, Y)-azines.[a]

	H_0	H_m	CH_3	$'CH_3$	H_m'	H_0'	H_0''	H_m''	H_p''
(PhO, F)	7.04	7.87	2.31	2.31	7.90	7.07	7.01	7.35	7.13
(PhO, Cl)	7.05	7.88	2.30	2.30	7.83	7.35	7.01	7.35	7.13
(PhO, Br)	7.04	7.87	2.30	2.28	7.76	7.52	7.01	7.35	7.13
(PhO, I)	7.04	7.88	2.29	2.29	7.62	7.74	7.01	7.35	7.14

[a]Cf. Supporting Information in The Azine Bridge as a Conjugation Stopper: An NMR Spectroscopic Study of Electron Delocalization in Acetophenone Azines, M. Lewis, R. Glaser, *J. Org. Chem.* **2002**, *67*, 7168.

Table S3. ^{13}C-NMR chemical shifts (in ppm relative to TMS) for (PhO, Y)-azines.[a],[b]

	C_i	C_o	C_m	C_p	C_{az}	CH_3	$'CH_3$	C_{az}'	C_p'	C_m'	C_o'	C_i'
(PhO, F)	158.9	119.4	129.8	133.3	157.9	14.9	14.9	157.3	134.6	128.5	115.3	163.8
(PhO, Cl)	158.9	119.4	129.8	133.2	157.8	14.8	15.0	157.2	136.9	127.9	128.5	135.6
(PhO, Br)	158.9	119.4	129.8	133.1	157.8	14.8	14.9	157.2	137.3	128.1	131.4	124.0
(PhO, I)	158.9	119.4	129.9	133.1	157.7	14.7	15.0	157.4	138.0	128.3	137.5	96.0

[a]PhO group (in ppm for C_i", C_o", C_m", and C_p") in (PhO, F): 156.6, 118.1, 128.2, 123.8; (PhO, Cl): 156.5, 118.1, 128.3, 123.8; (PhO, Br): 156.5, 118.1, 128.2, 123.7; (PhO, I): 156.6, 118.1, 128.3, 123.8. [b]Cf. Supporting Information in The Azine Bridge as a Conjugation Stopper: An NMR Spectroscopic Study of Electron Delocalization in Acetophenone Azines, M. Lewis, R. Glaser, *J. Org. Chem*. **2002**, *67*, 7168.

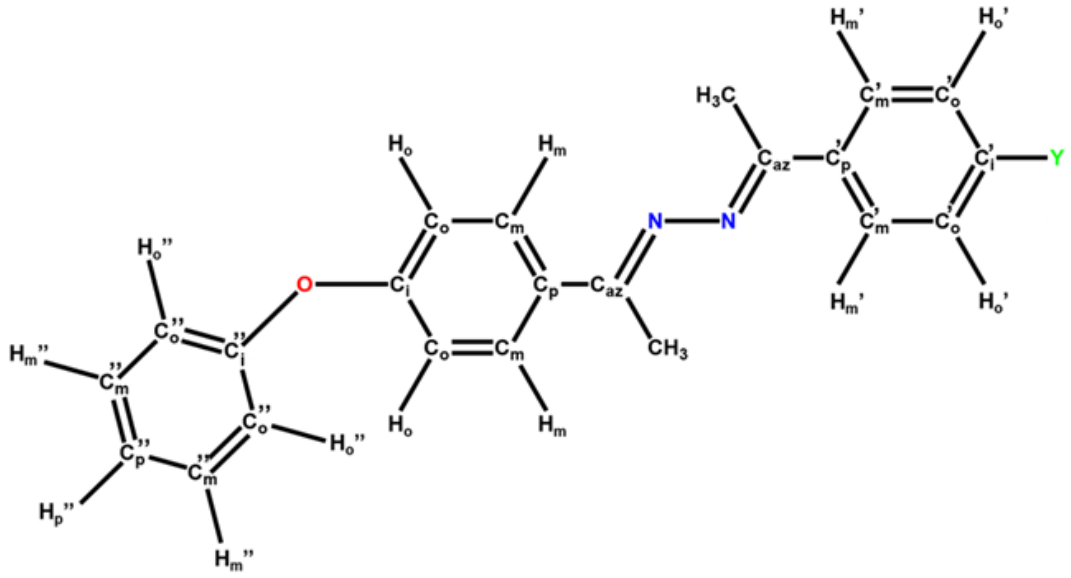


Table S4. Characteristic IR frequencies (in cm^{-1}) for (PhO, Y)-azines.

Assignment	(PhO, F)	(PhO, Cl)	(PhO, Br)	(PhO, I)
CH_3 asym. str.	2963	2964	2962	2962
CH_3 asym. str.	2924	2923	2923	2923
CH_3 sym. str.	2584	2583	2583	2583
C=N–N=C asym. str.	1653	1660	1645	1645
Comb. Ph w/ C=N str.	1590	1584	1586	1600
Comb. Ph w/ C=N str.	1550	1561	1560	1580
C–O str.	1257	1255	1253	1257

Table S5. Energies, thermochemical data, and molecular properties of (PhO, Y)-azines, p-nitroaniline (PNA) and (MeO, Y)-azines.

	Total Energy (Hartree)	ZPVE (kcal mol^{-1})	Thermal Energy, TE (kcal mol^{-1})	Entropy, *S* (cal K^{-1} mol^{-1})	Dipole Moment, μ_m (Debye)	Van der Waals Vol., V_{vdW} ($Å^3$)[a]	μ_m/V_{vdW} (x10^{-3} Debye $Å^{-3}$)
(PhO, F)	-1133.632434	224.84	239.05	168.441	2.7779	347.77	7.9878
(PhO, Cl)	-1493.941589	223.96	238.42	171.147	3.3609	356.91	9.4166
(PhO, Br)	-3607.783932	223.54	238.17	174.060	3.3343	360.99	9.2367
(PhO, I)	-7953.153558	223.30	238.04	176.228	3.4377	366.98	9.3676
PNA	-491.831618	75.66	80.85	89.647	7.2152	118.10	61.0919
(MeO, F)	-942.012153	192.01	204.21	148.682	2.8952	271.83	10.6506
(MeO, Cl)	-1302.321343	191.14	203.59	151.432	3.5252	280.98	12.5462
(MeO, Br)	-3416.163689	190.71	203.34	154.262	3.4856	285.05	12.2280
(MeO, I)	-7761.533321	190.48	203.21	156.352	3.5960	291.04	12.3555

[a]Cf. *J. Org. Chem.* **2003**, *68*, 7368-7373.

Table S6. First-order hyperpolarizability tensor components of (PhO, Y)-azines, p-nitroaniline (PNA) and (MeO, Y)-azines.

Param.[a]	(PhO, F)	(PhO, Cl)	(PhO, Br)	(PhO, I)	PNA	(MeO, F)	(MeO, Cl)	(MeO, Br)	(MeO, I)
β_{xxx}	-10.499	-3.687	-1.053	-2.148	4.011	-43.308	-36.150	-33.655	-34.555
β_{xxy}	64.382	61.113	60.516	57.725	0.000	69.821	66.656	66.099	63.339
β_{xyy}	28.714	30.312	30.022	27.868	3.790	-2.943	-0.365	-0.429	-2.850
β_{yyy}	104.494	107.270	108.576	105.887	0.000	-3.273	-0.138	0.926	-1.663
β_{xxz}	53.635	58.233	51.297	63.201	-17.426	17.839	15.729	8.263	19.386
β_{xyz}	-193.321	-182.325	-176.571	-165.619	0.000	-196.553	-191.621	-186.572	-177.236
β_{yyz}	-118.080	-141.032	-149.333	-143.223	-148.896	-18.276	-40.718	-48.241	-39.628
β_{xzz}	-300.231	-432.201	-438.605	-471.596	34.056	-310.956	-421.372	-428.564	-466.966
β_{yzz}	289.656	302.312	317.472	335.517	0.000	384.061	424.975	442.550	465.935
β_{zzz}	1720.581	2133.114	2079.402	2143.034	1396.314	1671.720	2051.102	2013.060	2115.184
β_x[b]	-282.016	-405.576	-409.637	-445.877	41.858	-357.206	-457.887	-462.648	-504.371
β_y[b]	458.533	470.694	486.564	499.128	0.000	450.609	491.493	509.575	527.612
β_z[b]	1656.136	2050.315	1981.366	2063.013	1229.992	1671.283	2026.112	1973.083	2094.942
β_o[b]	1741.428	2142.390	2080.951	2168.860	1230.704	1767.436	2134.562	2089.681	2218.456
β_o[c]	15.045	18.509	17.978	18.737	10.632	15.269	18.441	18.053	19.166
β_o/V_{vdW}[d]	43.261	51.859	49.803	51.058	90.022	56.170	65.631	63.333	65.853

[a]In a.u. unless otherwise noted.

[b]$\beta_x = (\beta_{xxx} + \beta_{xyy} + \beta_{xzz})$, $\beta_y = (\beta_{yyy} + \beta_{xxy} + \beta_{yzz})$, $\beta_z = (\beta_{zzz} + \beta_{xxz} + \beta_{yyz})$, $\beta_o = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$.

[c]In units of $x10^{-30}$ esu,1 a.u. = 8.3693×10^{-33} esu.

[d]In units of $x10^{-33}$ esu $Å^{-3}$.

GC/MS Analysis

Table S7. Parameters used for the GC/MS analyses of (PhO, Y)-azines with Y = F, Br, and I.

```
═══ Analytical Line 1 ═══

[GC-2010]
Column Oven Temp.              :60.0 °C
Injection Temp.                :320.00 °C
Injection Mode                 :Split
Flow Control Mode              :Pressure
Pressure                       :100.0 kPa
Total Flow                     :20.7 mL/min
Column Flow                    :1.61 mL/min
Linear Velocity                :46.3 cm/sec
Purge Flow                     :3.0 mL/min
Split Ratio                    :10.0
High Pressure Injection        :OFF
Carrier Gas Saver              :ON
Carrier Gas Saver Split Ratio  :1.0
Carrier Gas Saver Time         :1.00 min
Splitter Hold                  :OFF
Oven Temp. Program
  Rate                         Temperature(°C)          Hold Time(min)
   -                           60.0                     2.00
  10.00                        180.0                    3.00

< Ready Check Heat Unit >
    Column Oven                : Yes
    SPL                        : Yes
    MS                         : Yes
< Ready Check Detector(FTD/BID) >
< Ready Check Baseline Drift >
< Ready Check Injection Flow >
    SPL Carrier                : Yes

    SPL Purge                  : Yes
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 < Ready Check Detector APC Flow >
 External Wait                 :No
 Equilibrium Time              :0.1 min

 [GC Program]

 [GCMS-QP2020]
 IonSourceTemp                                  :200.00 °C
 Interface Temp.                                :320.00 °C
 Solvent Cut Time                               :2.00 min
 Detector Gain Mode                             :Relative to the Tuning Result
 Detector Gain                                  :0.75 kV +0.00 kV
 Threshold                                      :0

 [MS Table]
  --Group  1 - Event  1--
 Start Time                                     :2.10min
 End Time                                       :17.00min
 ACQ Mode                                       :Scan
 Event Time                                     :0.05sec
 Scan Speed                                     :5000
 Start m/z                                      :10.00
 End m/z                                        :200.00

 Sample Inlet Unit                              :GC

 [MS Program]
 Use MS Program          :OFF
```

Table S8. Parameters used for the GC/MS analysis of (PhO, Cl)-azine.

═══ Analytical Line 1 ═══

[GC-2010]

Column Oven Temp.	:120.0 °C
Injection Temp.	:300.00 °C
Injection Mode	:Split
Flow Control Mode	:Pressure
Pressure	:100.0 kPa
Total Flow	:28.7 mL/min
Column Flow	:1.22 mL/min
Linear Velocity	:41.5 cm/sec
Purge Flow	:3.0 mL/min
Split Ratio	:20.0
High Pressure Injection	:OFF
Carrier Gas Saver	:ON
Carrier Gas Saver Split Ratio	:1.0
Carrier Gas Saver Time	:1.00 min
Splitter Hold	:OFF

Oven Temp. Program

Rate	Temperature(°C)	Hold Time(min)
-	120.0	2.00
18.00	300.0	3.00

< Ready Check Heat Unit >

Column Oven	: Yes
SPL	: Yes
MS	: Yes

< Ready Check Detector(FTD/BID) >
< Ready Check Baseline Drift >
< Ready Check Injection Flow >

SPL Carrier	: Yes

< Ready Check Detector(FTD/BID) >
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< Ready Check Injection Flow >

SPL Carrier	: Yes
SPL Purge	: Yes

< Ready Check APC Flow >
< Ready Check Detector APC Flow >

External Wait	:No
Equilibrium Time	:3.0 min

[GC Program]

[GCMS-QP2020]

IonSourceTemp	:200.00 °C
Interface Temp.	:300.00 °C
Solvent Cut Time	:2.90 min
Detector Gain Mode	:Relative to the Tuning Result
Detector Gain	:0.80 kV +0.00 kV
Threshold	:0

[MS Table]

--Group 1 - Event 1--

Start Time	:3.00min
End Time	:12.00min
ACQ Mode	:Scan
Event Time	:0.10sec
Scan Speed	:10000
Start m/z	:10.00
End m/z	:500.00

Sample Inlet Unit :GC

Peak Report TIC

R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H
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			4795962	100.00	2651422	100.00	

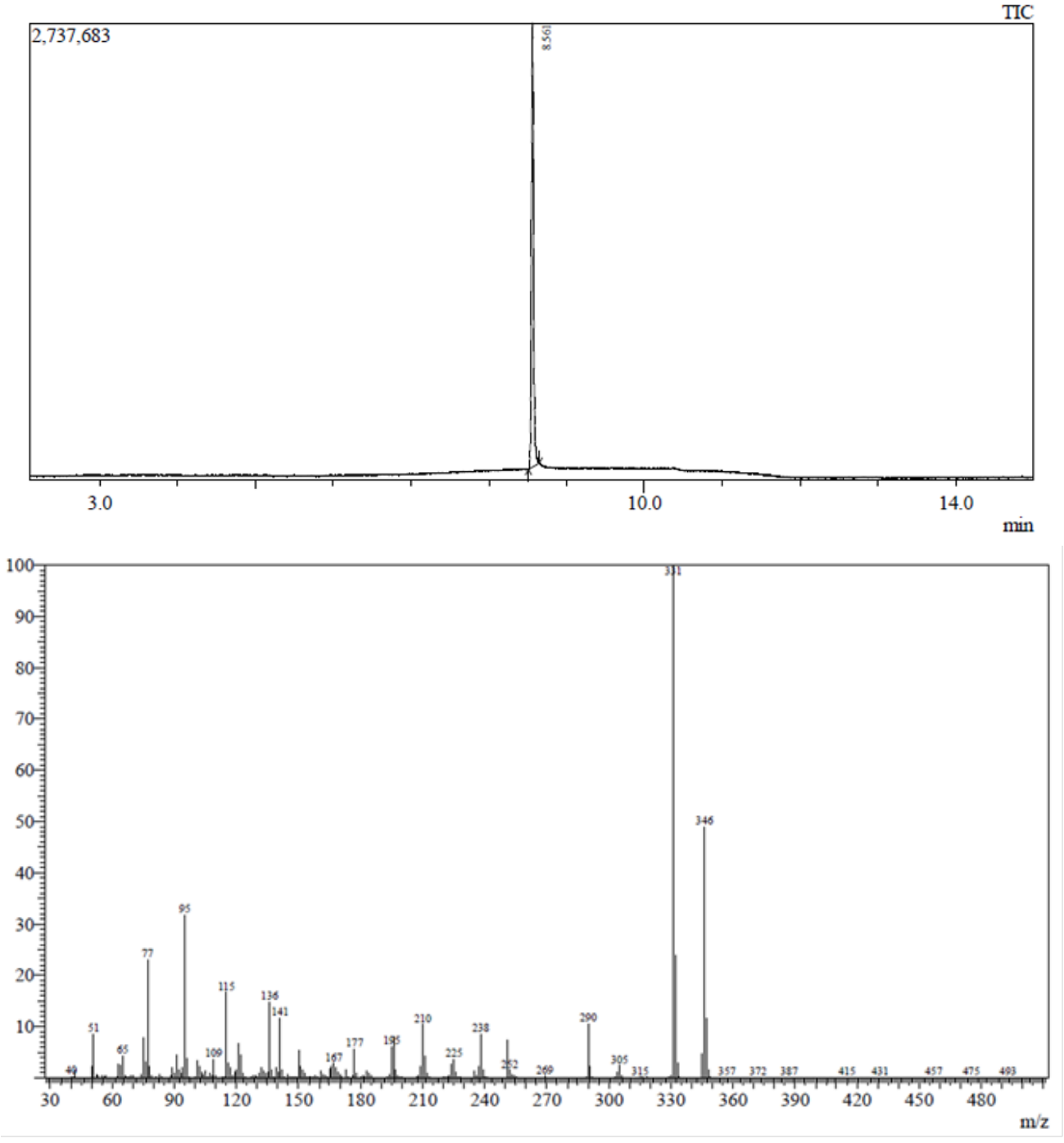

Figure S1. GC trace (top) and mass spectrum (bottom) of pure (PhO, F)-azine (molecular mass = 346.40 a.u.).

Peak#	R.Time	Area%	Height	Height%
1	10.020	6.67	144901	7.76
2	19.793	5.46	113897	6.10
3	24.625	82.34	1505934	80.63
4	26.520	5.54	102864	5.51
		100.00	1867596	100.00

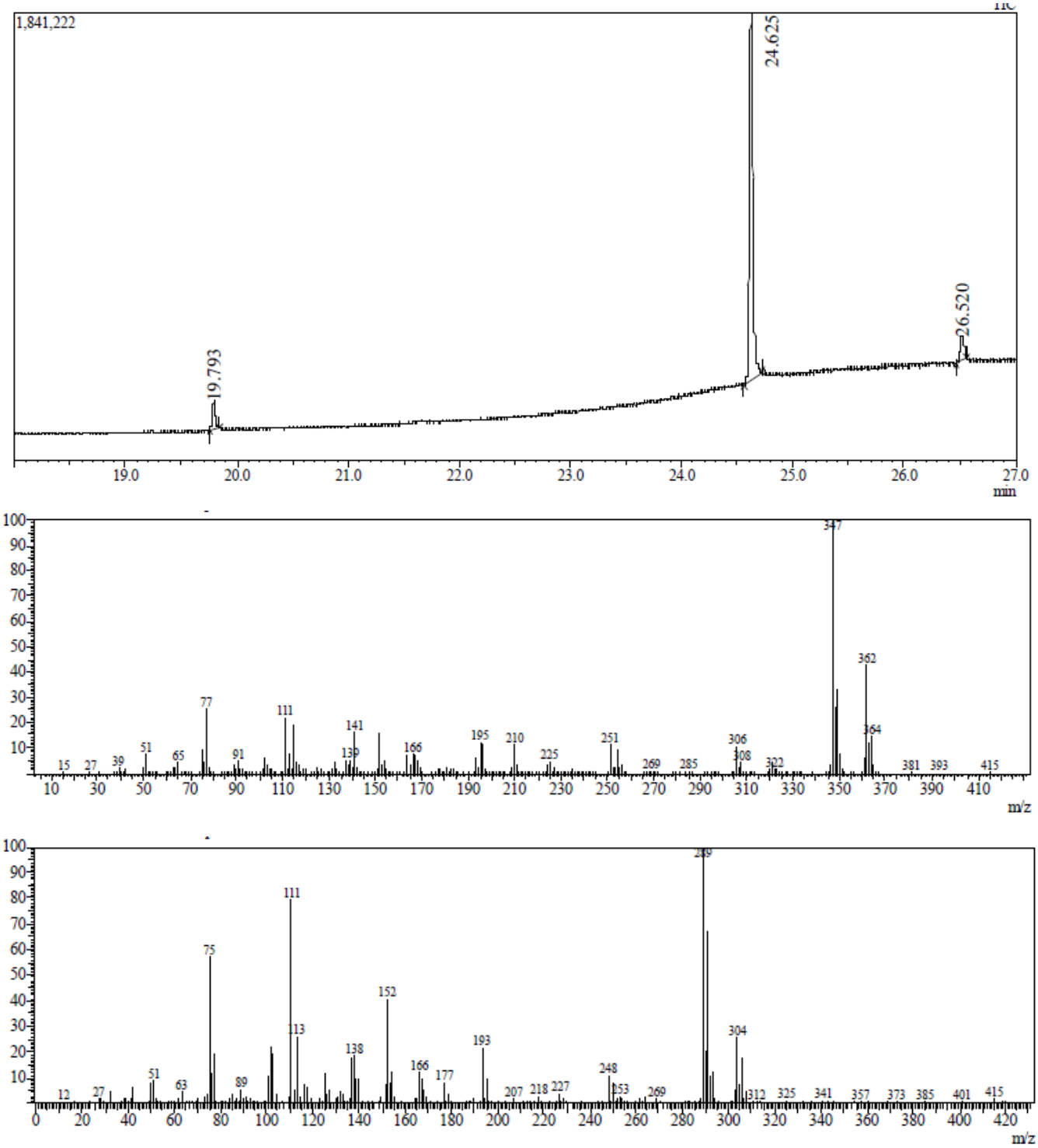

Figure S2. GC trace (top) and mass spectrum (centre) of (PhO, Cl)-azine (molecular mass = 362.85 a.u.). The peaks at retention times 10.02 min and 26.52 min originate from impurities in the column and not from the (PhO, Cl)-azine reaction. The peak at 19.79 min is due to small remaining amounts of (Cl, Cl)-azine (molecular mass = 305.20 a.u.) and its mass spectrum is shown at the bottom.

Peak Report TIC

R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H
10.829	10.758	10.945	905381	100.00	228325	100.00	3.97
			905381	100.00	228325	100.00	

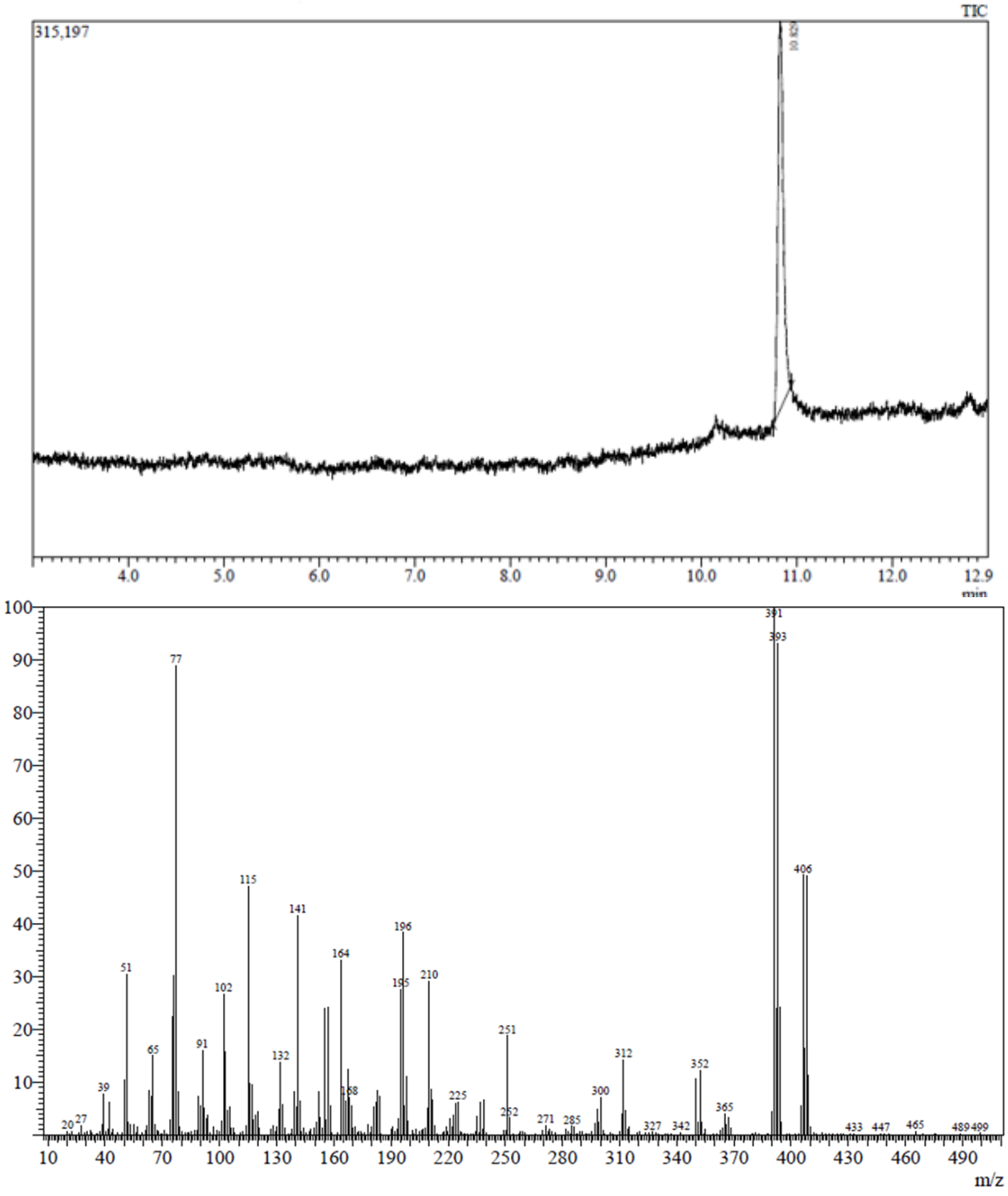

Figure S3. GC trace (top) and mass spectrum (bottom) of pure (PhO, Br)-azine (molecular mass = 407.30 a.u.).

Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H
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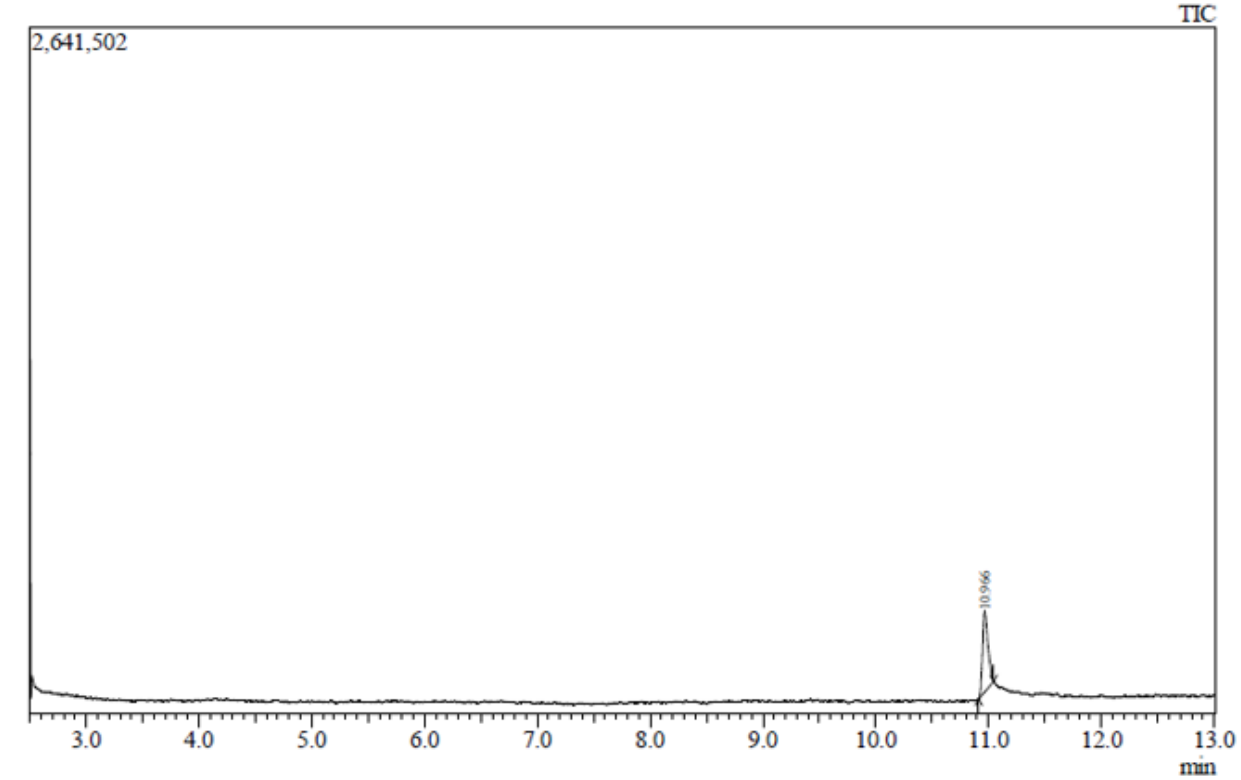
				1050317	100.00	312614	100.00	



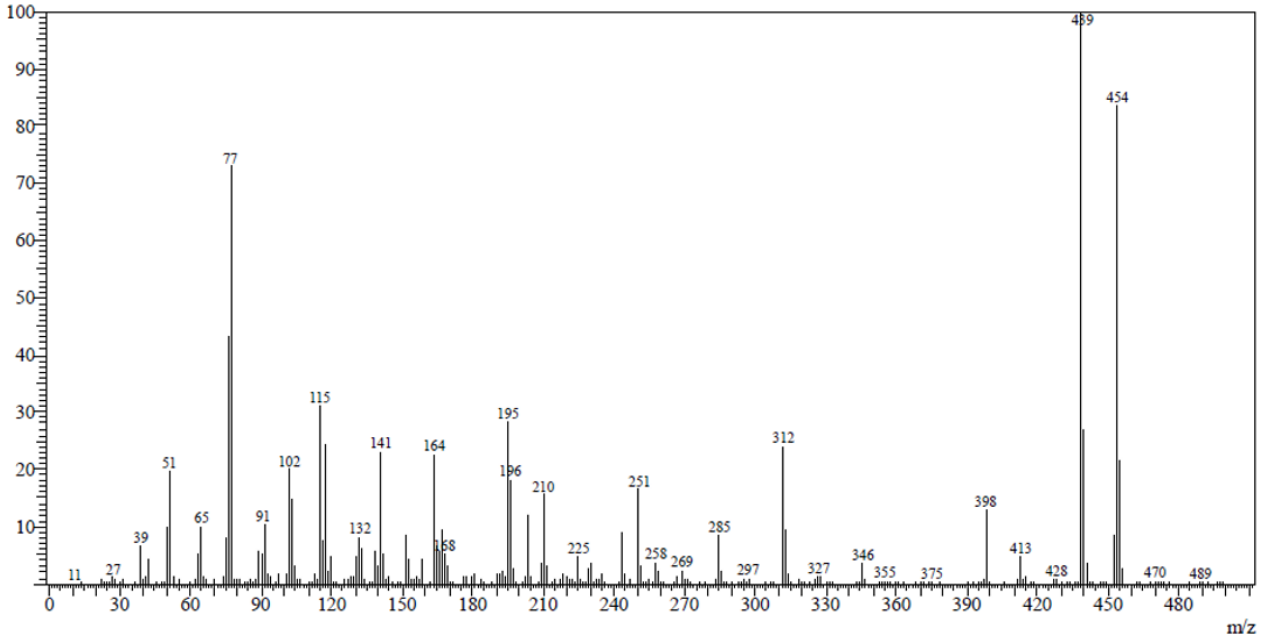


Figure S4. GC trace (top) and mass spectrum (bottom) of pure (PhO, I)-azine (molecular mass = 454.30 a.u.).

^{1}H-NMR Spectroscopy

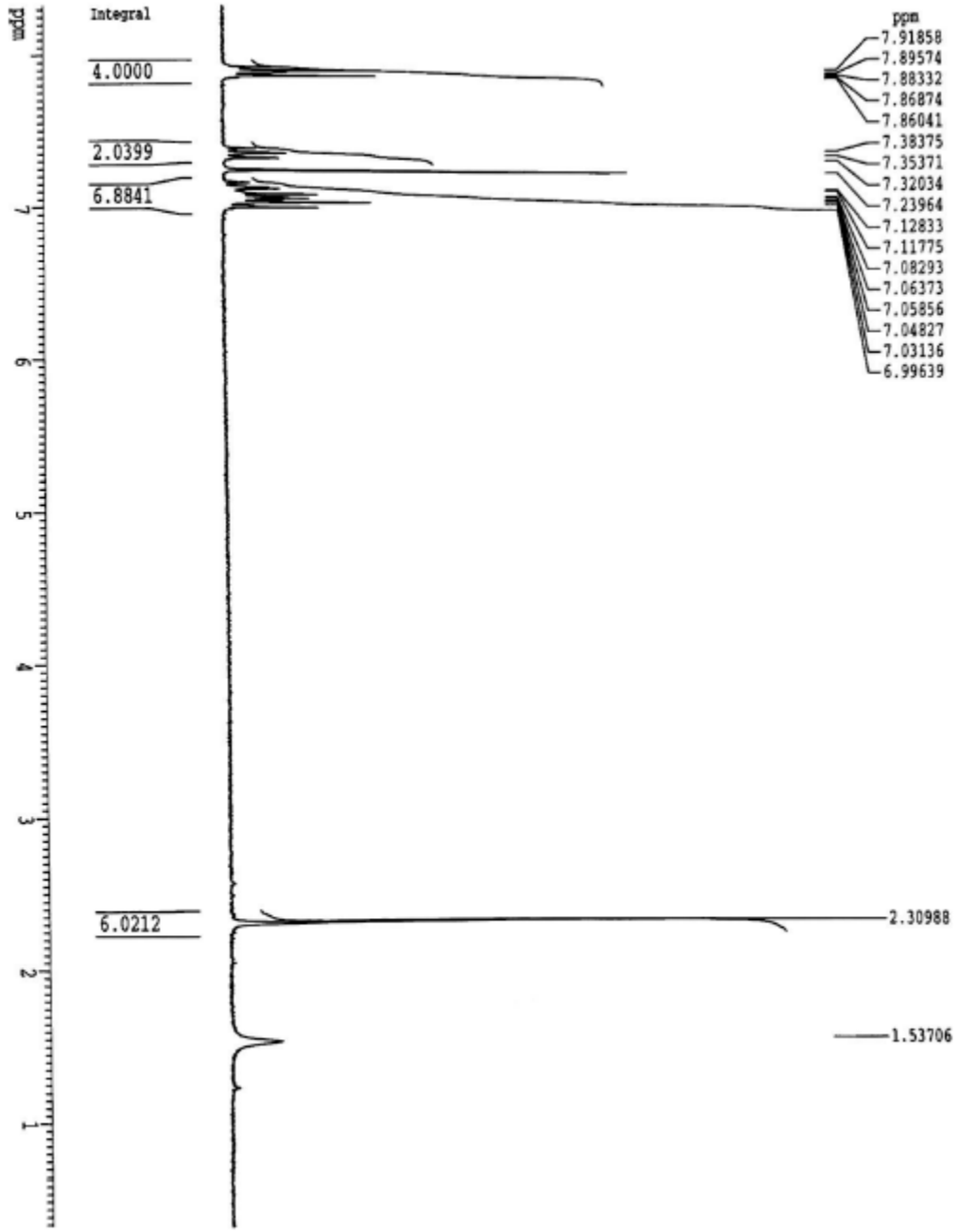


Figure S5. ^{1}H-NMR spectrum of pure (PhO, F)-azine in $CDCl_3$.

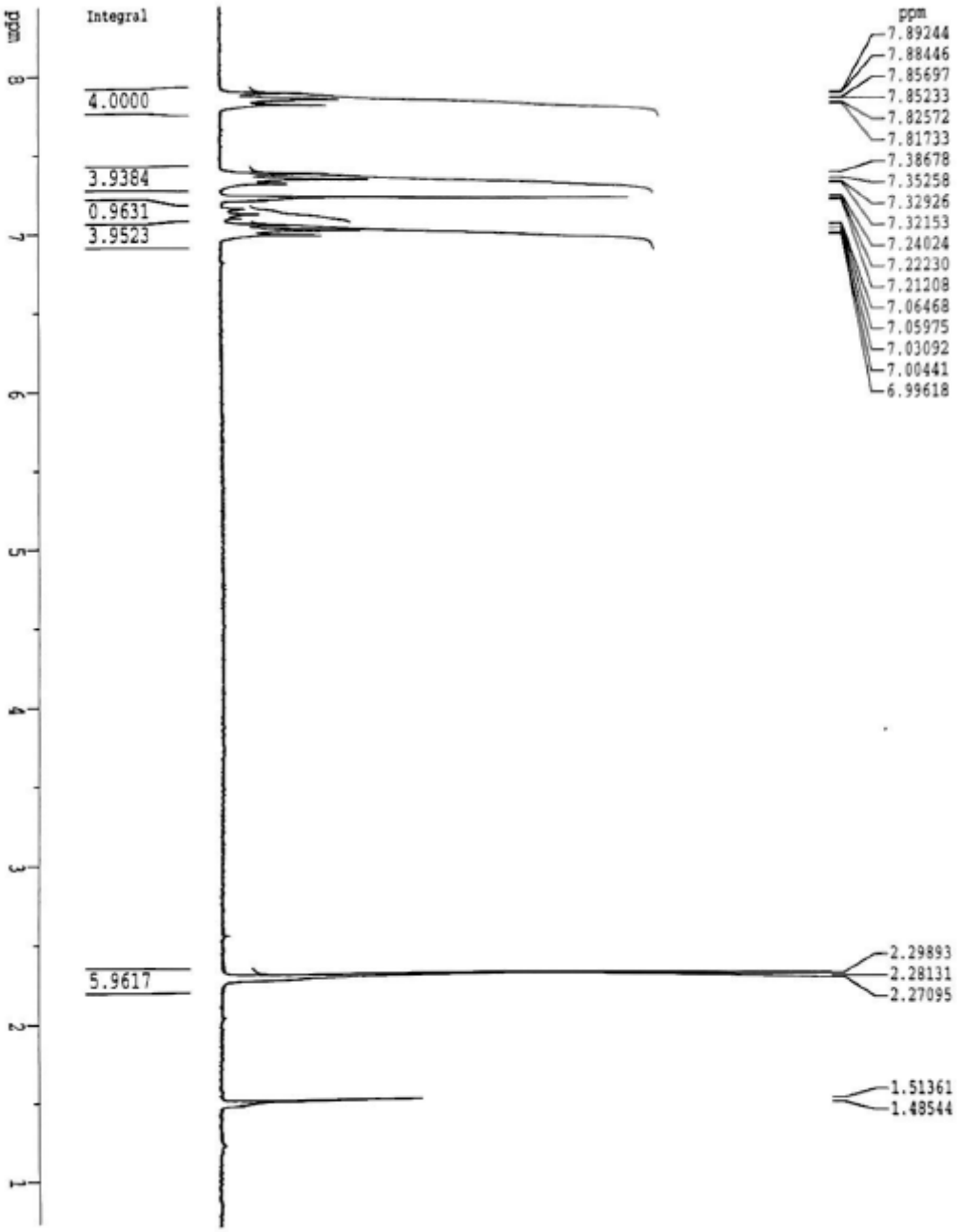


Figure S6. ^{1}H-NMR spectrum of pure (PhO, Cl)-azine in $CDCl_3$.

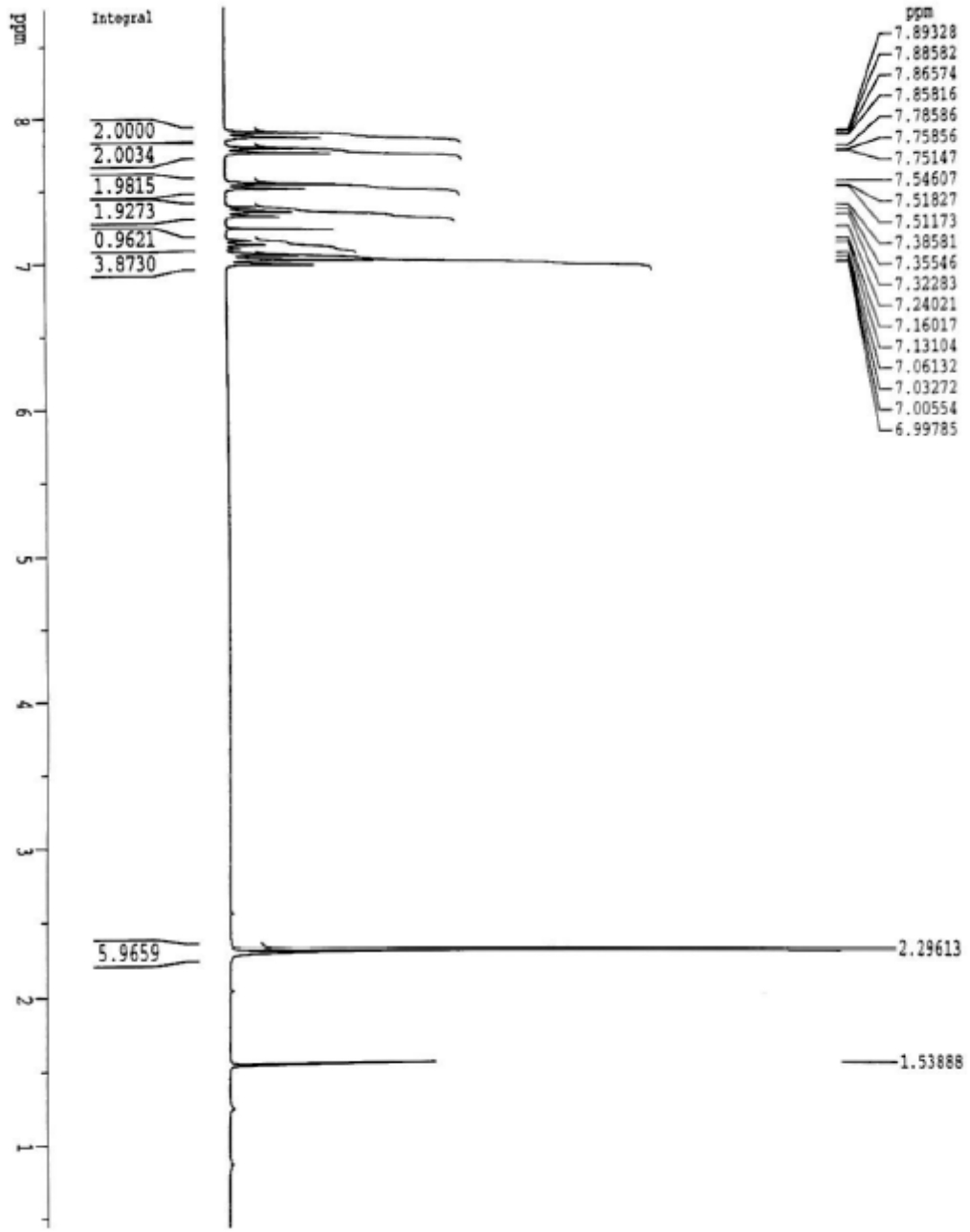


Figure S7. ^{1}H-NMR spectrum of pure (PhO, Br)-azine in $CDCl_3$.

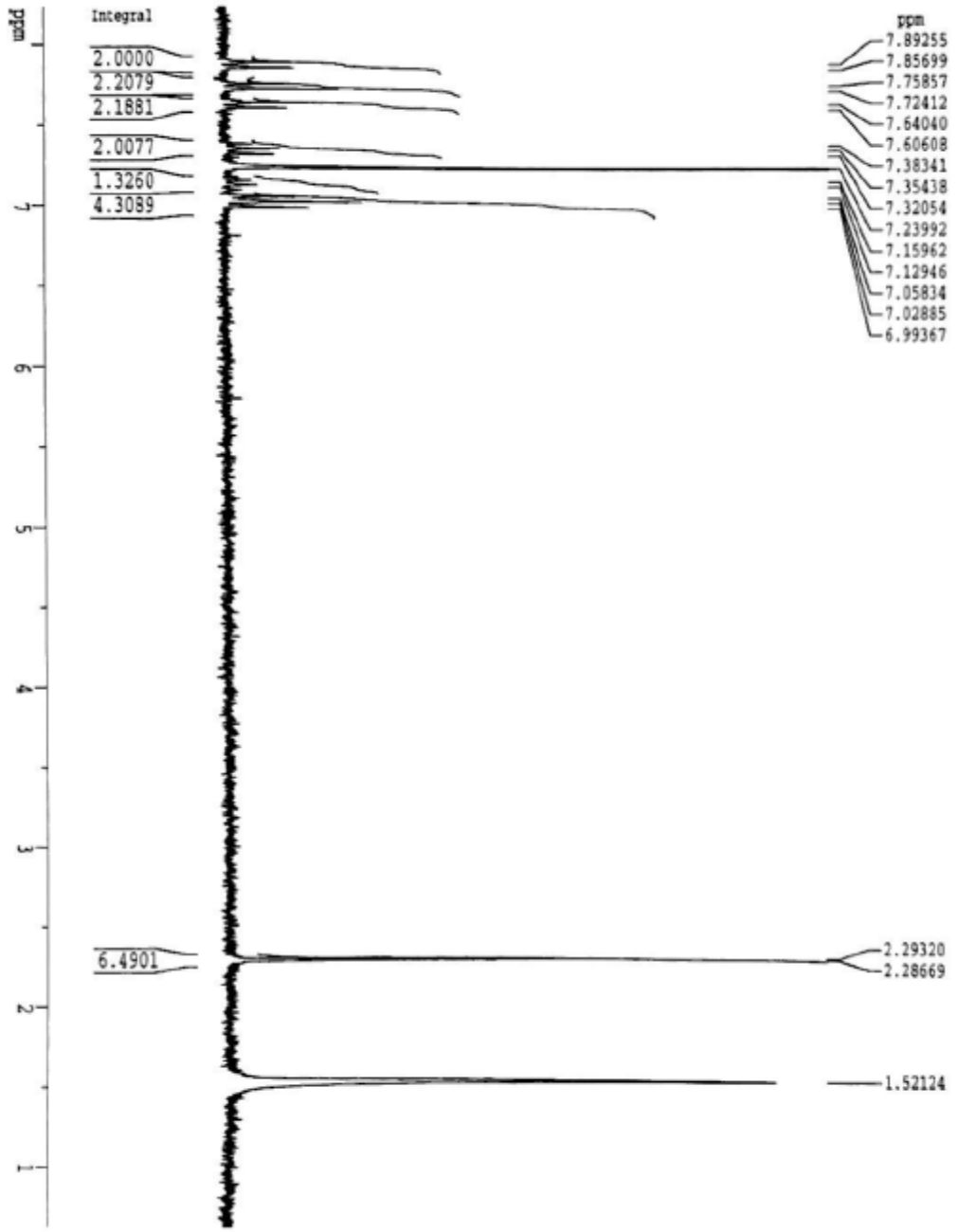


Figure S8. ^{1}H-NMR spectrum of pure (PhO, I)-azine in $CDCl_3$.

^{13}C-NMR Spectroscopy

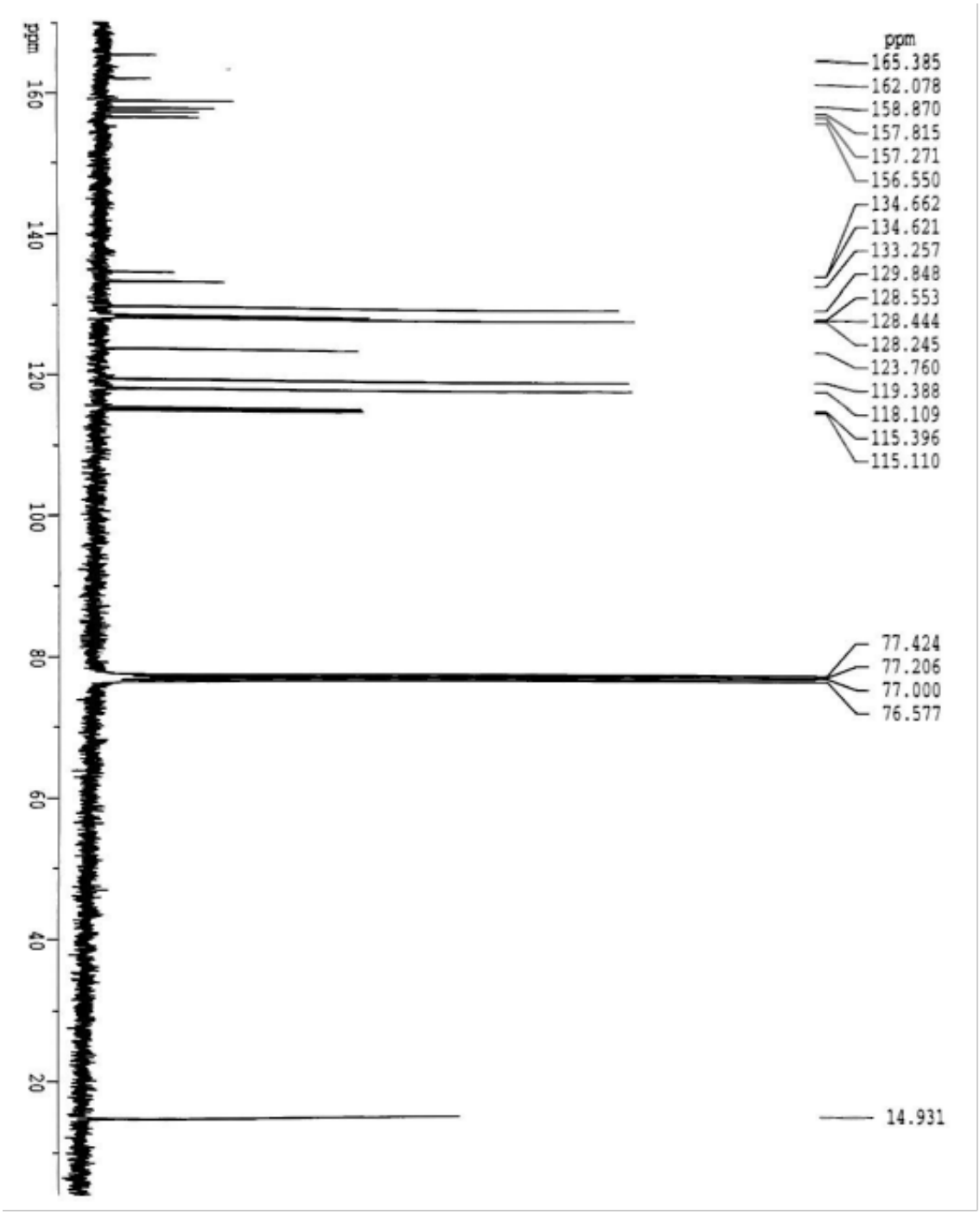


Figure S9. ^{13}C-NMR spectrum of pure (PhO, F)-azine in $CDCl_3$.

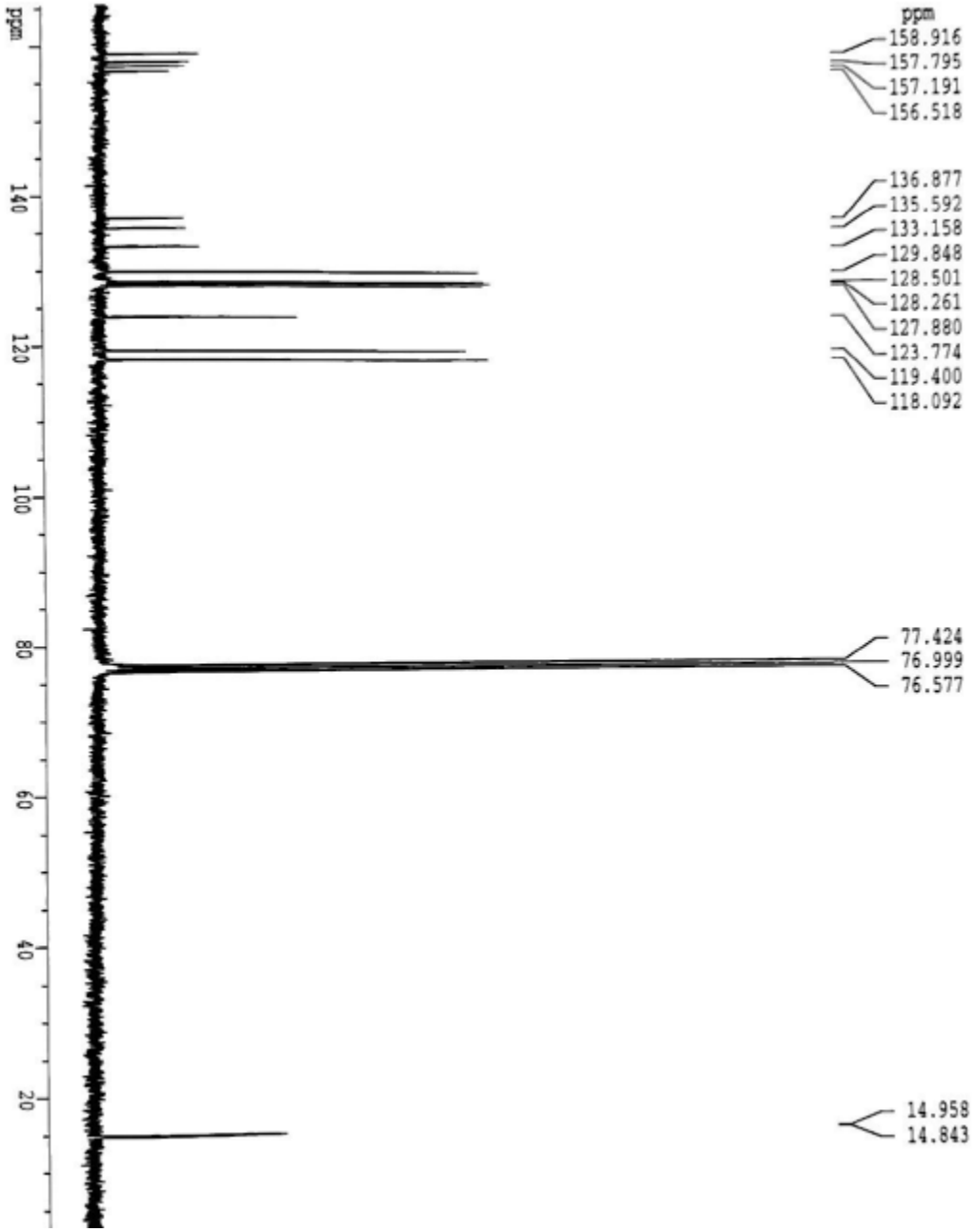


Figure S10. ^{13}C-NMR spectrum of pure (PhO, Cl)-azine in $CDCl_3$.

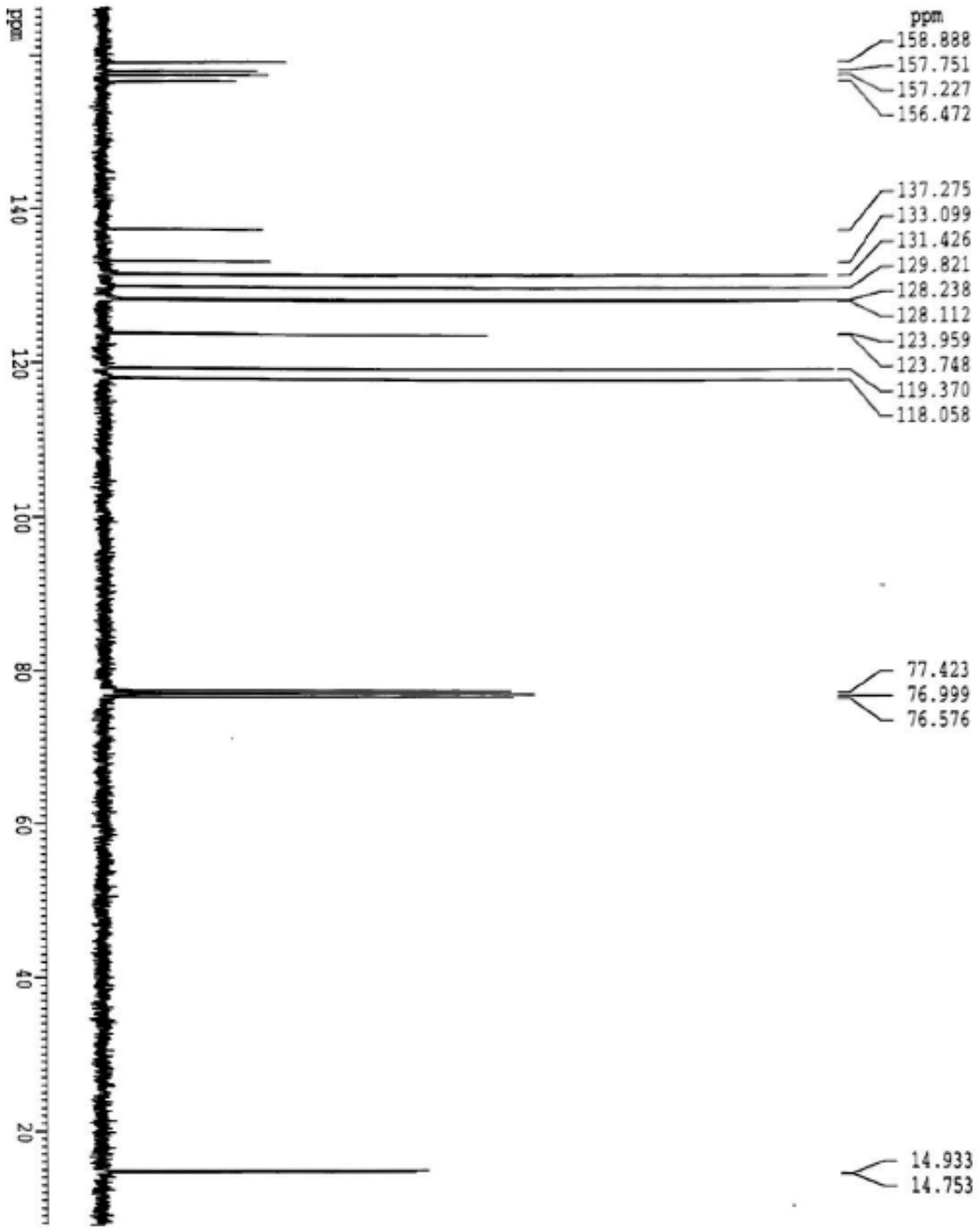


Figure S11. ^{13}C-NMR spectrum of pure (PhO, Br)-azine in $CDCl_3$.

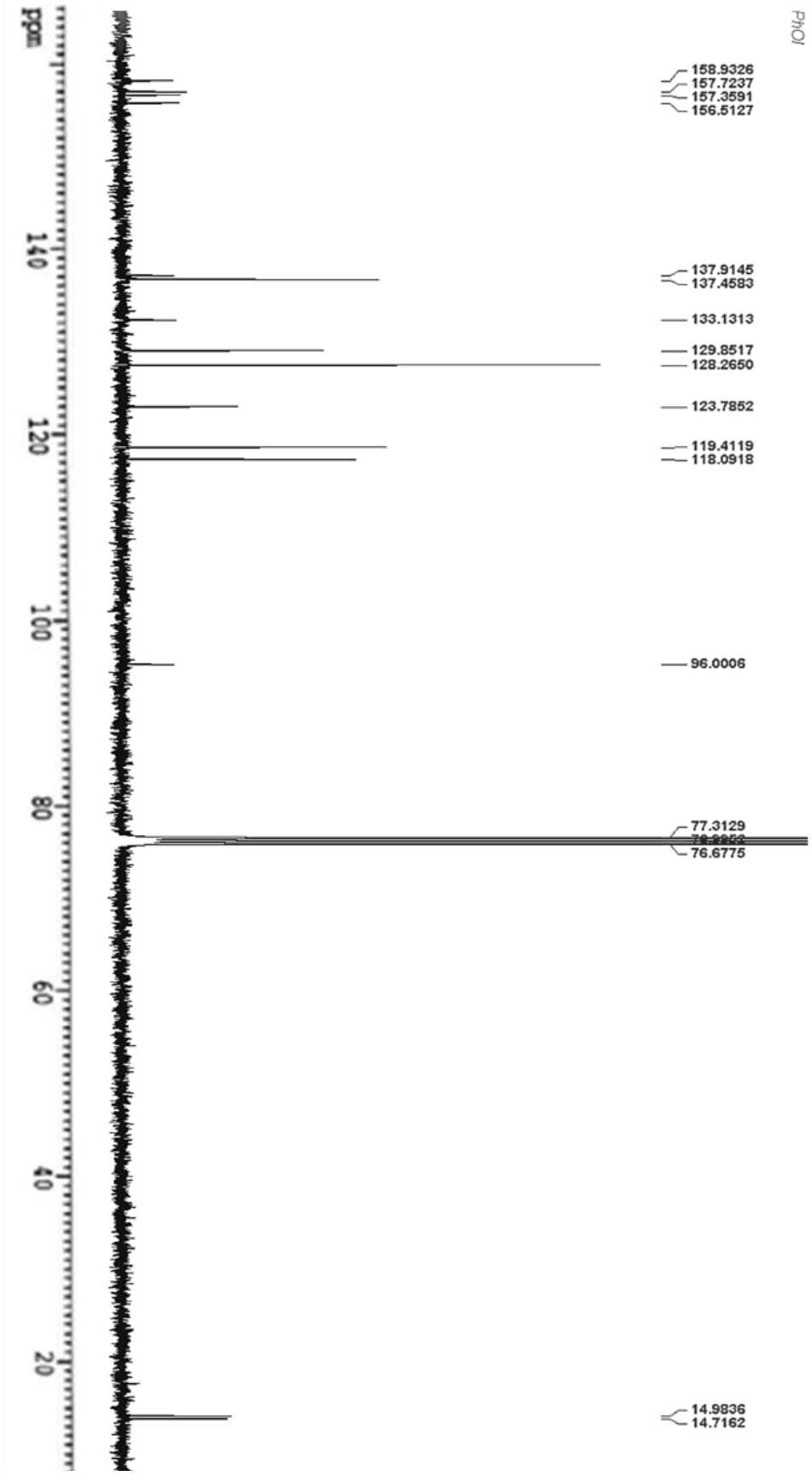


Figure S12. ^{13}C-NMR spectrum of pure (PhO, I)-azine in $CDCl_3$.

FTIR Spectroscopy

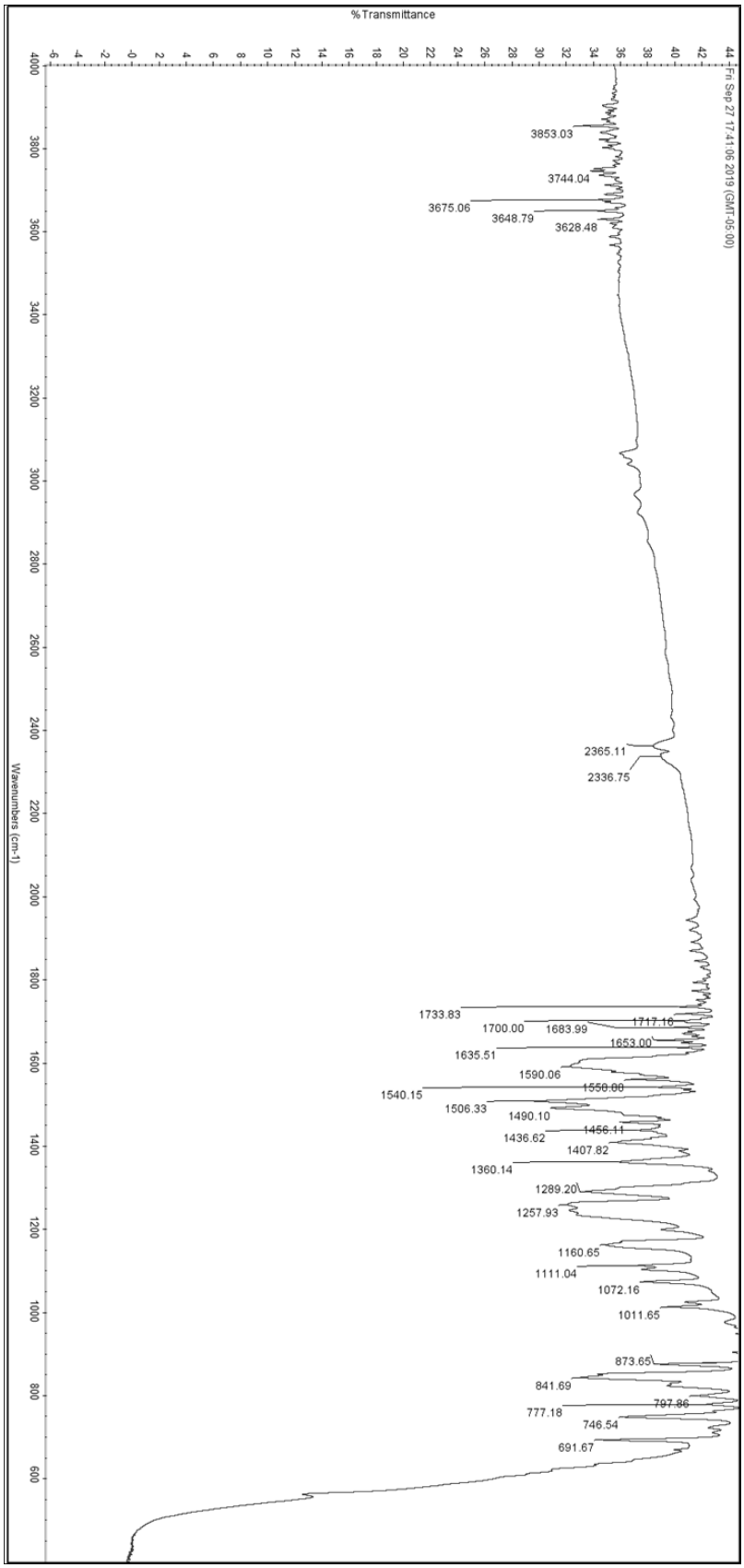


Figure S13. FTIR spectrum of pure (PhO, F)-azine.

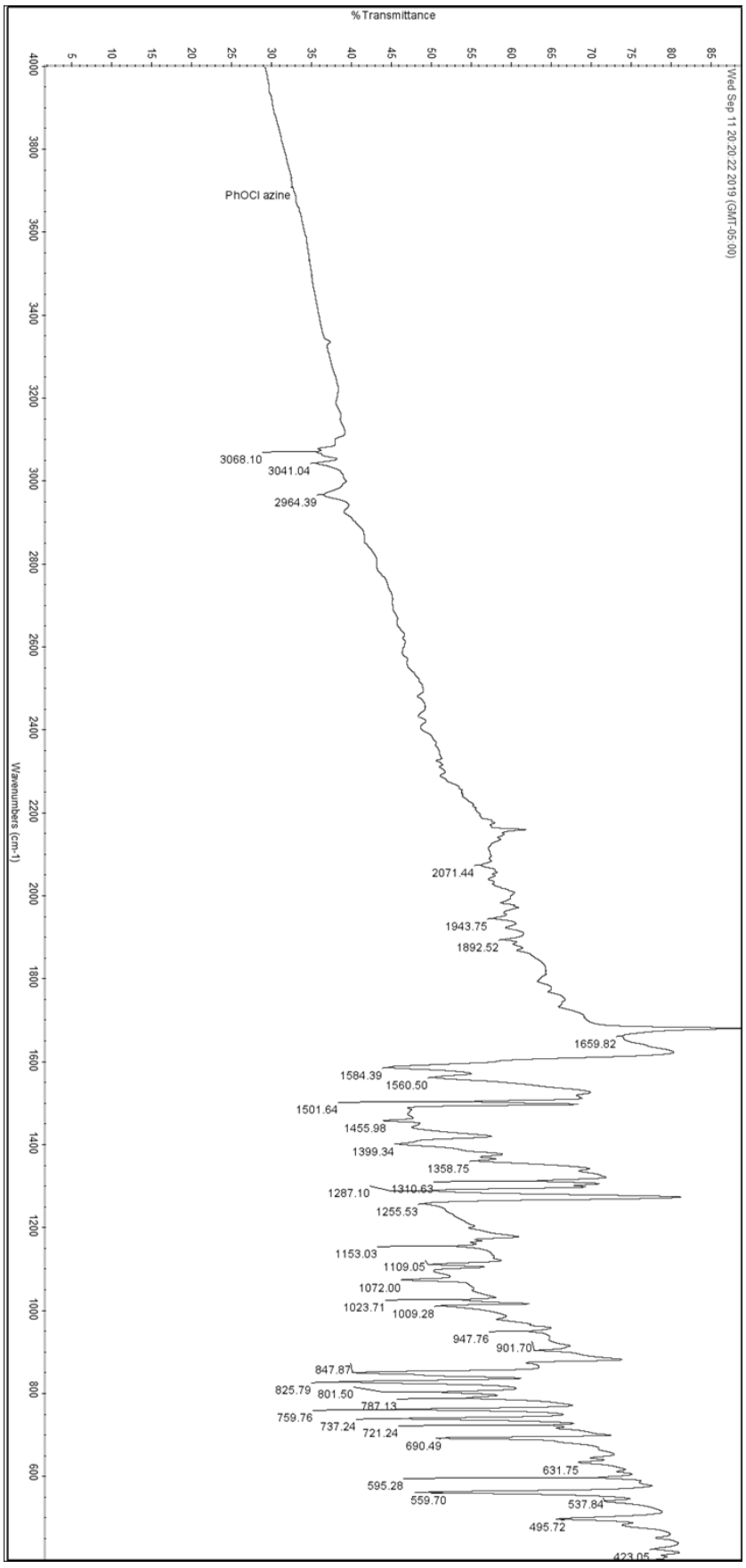


Figure S14. FTIR spectrum of pure (PhO, Cl)-azine.

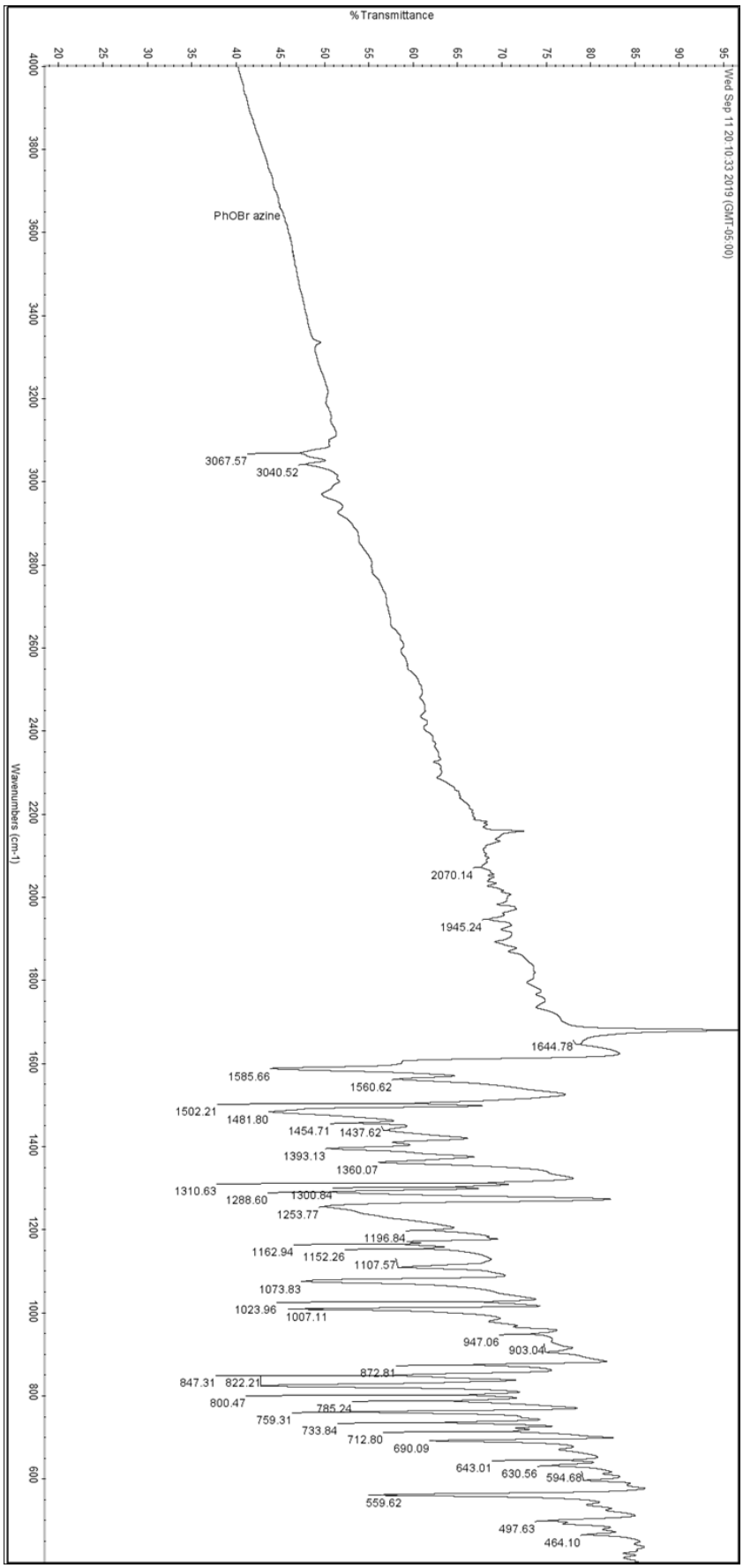


Figure S15. FTIR spectrum of pure (PhO, Br)-azine.

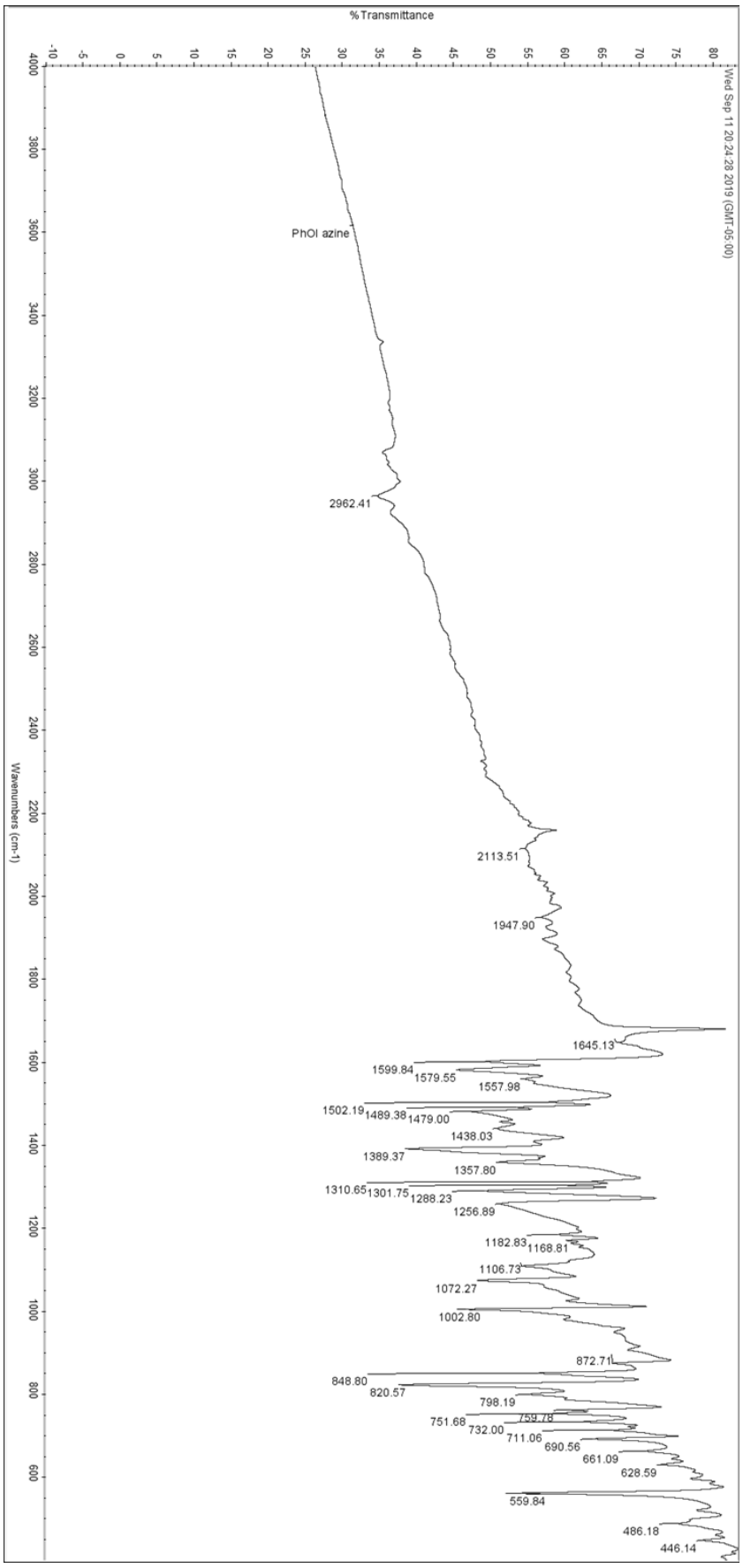


Figure S16. FTIR spectrum of pure (PhO, I)-azine.

Cartesian Coordinates and Models of Stationary Structures of Optimized Free (PhO, Y)-Azines

Table S9. (PhO, F) at APFD/6-311G*

Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.000000	0.000000	0.000000
2	7	0	0.000000	0.000000	1.355948
3	6	0	1.059917	0.421417	-0.594931
4	6	0	-1.059517	0.421259	1.949840
5	6	0	2.228271	1.026543	0.127427
6	6	0	-2.230049	1.023942	1.229691
7	6	0	1.093520	0.305170	-2.063286
8	6	0	-1.090230	0.304917	3.420381
9	6	0	2.036004	0.999289	-2.827534
10	6	0	2.062254	0.901175	-4.212915
11	6	0	1.130152	0.091973	-4.857722
12	6	0	0.184332	-0.614769	-4.114654
13	6	0	0.168295	-0.505808	-2.737517
14	1	0	2.765970	1.640136	-2.343113
15	1	0	2.801567	1.446277	-4.790018
16	8	0	1.108472	-0.109992	-6.210719
17	1	0	-0.524999	-1.246228	-4.640176
18	1	0	-0.566179	-1.049659	-2.153582
19	6	0	-2.025630	1.010729	4.183890
20	6	0	-2.047911	0.909037	5.570004
21	6	0	-1.125349	0.085907	6.191888
22	6	0	-0.182709	-0.631618	5.467045
23	6	0	-0.168964	-0.515019	4.087753
24	1	0	-2.744495	1.663823	3.699958
25	1	0	-2.766897	1.457928	6.169147
26	9	0	-1.141659	-0.023751	7.530821
27	1	0	0.520559	-1.270903	5.990881
28	1	0	0.557141	-1.064041	3.498544
29	1	0	2.184602	0.765276	1.185050
30	1	0	3.176969	0.683896	-0.292392
31	1	0	2.212052	2.119967	0.056328
32	1	0	-2.188210	0.759120	0.172849
33	1	0	-3.177842	0.682365	1.652705
34	1	0	-2.213859	2.117717	1.296674
35	6	0	1.606578	0.856843	-7.054709
36	6	0	2.480770	0.442074	-8.051105
37	6	0	2.955790	1.368506	-8.973595
38	6	0	2.567406	2.702030	-8.894713
39	6	0	1.689889	3.105731	-7.891353
40	6	0	1.201593	2.188009	-6.969638
41	1	0	2.771642	-0.602678	-8.091559
42	1	0	3.637717	1.044376	-9.754521
43	1	0	2.942550	3.423859	-9.613929
44	1	0	1.374669	4.143442	-7.828647
45	1	0	0.511677	2.490428	-6.187960

Table S10. (PhO, Cl) at APFD/6-311G*

Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.000000	0.000000	0.000000
2	7	0	0.000000	0.000000	1.354818
3	6	0	1.055421	0.429611	-0.597167
4	6	0	-1.055166	0.429508	1.950217
5	6	0	2.218235	1.046831	0.123780
6	6	0	-2.222816	1.040836	1.233216
7	6	0	1.088734	0.310970	-2.065053
8	6	0	-1.081337	0.313086	3.420985
9	6	0	2.023508	1.013062	-2.831380
10	6	0	2.049406	0.912783	-4.216586
11	6	0	1.124881	0.092947	-4.859026
12	6	0	0.186738	-0.621850	-4.113608
13	6	0	0.170745	-0.510316	-2.736819
14	1	0	2.747411	1.662210	-2.348917
15	1	0	2.782687	1.464287	-4.795226
16	8	0	1.102487	-0.111331	-6.211240
17	1	0	-0.516749	-1.261285	-4.637309
18	1	0	-0.557986	-1.060272	-2.151382
19	6	0	-2.007885	1.025362	4.188093
20	6	0	-2.025840	0.923475	5.574063
21	6	0	-1.109364	0.093533	6.202827
22	6	0	-0.175916	-0.629455	5.465174
23	6	0	-0.165311	-0.513295	4.085956
24	1	0	-2.724099	1.684457	3.708130
25	1	0	-2.744766	1.484792	6.161010
26	17	0	-1.126488	-0.047824	7.937213
27	1	0	0.530672	-1.278209	5.971790
28	1	0	0.555515	-1.068977	3.496288
29	1	0	2.179992	0.783447	1.181179
30	1	0	3.169883	0.715646	-0.298343
31	1	0	2.189414	2.140098	0.054666
32	1	0	-2.186805	0.773759	0.176678
33	1	0	-3.172110	0.707867	1.659695
34	1	0	-2.197362	2.134555	1.298067
35	6	0	1.605074	0.852501	-7.056617
36	6	0	2.494402	0.437057	-8.039056
37	6	0	2.974330	1.360706	-8.961903
38	6	0	2.575541	2.691873	-8.896780
39	6	0	1.682819	3.096214	-7.907140
40	6	0	1.189654	2.181172	-6.985372
41	1	0	2.793020	-0.605862	-8.068880
42	1	0	3.668081	1.036283	-9.732202
43	1	0	2.954410	3.411483	-9.616262
44	1	0	1.359616	4.132064	-7.855483
45	1	0	0.487918	2.483563	-6.214252

Table S11. (PhO, Br) at APFD/6-311G*

Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.000000	0.000000	0.000000
2	7	0	0.000000	0.000000	1.354629
3	6	0	1.054623	0.431071	-0.597521
4	6	0	-1.054392	0.430976	1.950281
5	6	0	2.216485	1.050307	0.123217
6	6	0	-2.221496	1.043822	1.233759
7	6	0	1.087887	0.312088	-2.065348
8	6	0	-1.079823	0.314637	3.421136
9	6	0	2.021340	1.015572	-2.831998
10	6	0	2.047188	0.914971	-4.217179
11	6	0	1.123965	0.093368	-4.859249
12	6	0	0.187142	-0.622823	-4.113477
13	6	0	0.171160	-0.510923	-2.736731
14	1	0	2.744196	1.666101	-2.349826
15	1	0	2.779439	1.467571	-4.796070
16	8	0	1.101584	-0.111281	-6.211369
17	1	0	-0.515340	-1.263588	-4.636896
18	1	0	-0.556580	-1.061937	-2.151051
19	6	0	-2.004208	1.028998	4.188589
20	6	0	-2.022128	0.927912	5.574981
21	6	0	-1.106602	0.095422	6.205052
22	6	0	-0.174675	-0.630118	5.465088
23	6	0	-0.165346	-0.513547	4.085513
24	1	0	-2.719368	1.689769	3.709165
25	1	0	-2.741128	1.492714	6.158303
26	35	0	-1.124789	-0.058563	8.100833
27	1	0	0.532597	-1.281492	5.967113
28	1	0	0.554031	-1.071079	3.495666
29	1	0	2.179118	0.786547	1.180571
30	1	0	3.168624	0.721045	-0.299277
31	1	0	2.185563	2.143536	0.054462
32	1	0	-2.186840	0.775746	0.177411
33	1	0	-3.171036	0.712978	1.661317
34	1	0	-2.193998	2.137549	1.297593
35	6	0	1.603713	0.852608	-7.057003
36	6	0	2.494680	0.437753	-8.038187
37	6	0	2.974200	1.361448	-8.961209
38	6	0	2.573360	2.692064	-8.897465
39	6	0	1.679012	3.095818	-7.909051
40	6	0	1.186254	2.180706	-6.987139
41	1	0	2.794877	-0.604742	-8.066941
42	1	0	3.669217	1.037503	-9.730565
43	1	0	2.951897	3.411705	-9.617091
44	1	0	1.354228	4.131225	-7.858490
45	1	0	0.483271	2.482596	-6.216956

Table S12. (PhO, I) at APFD/6-311G*

Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.000000	0.000000	0.000000
2	7	0	0.000000	0.000000	1.354313
3	6	0	1.053314	0.433399	-0.598163
4	6	0	-1.053178	0.433343	1.950298
5	6	0	2.213617	1.055980	0.122179
6	6	0	-2.219358	1.048607	1.234489
7	6	0	1.086464	0.313814	-2.065869
8	6	0	-1.077453	0.317177	3.421267
9	6	0	2.017795	1.019458	-2.833086
10	6	0	2.043530	0.918296	-4.218222
11	6	0	1.122370	0.093851	-4.859650
12	6	0	0.187652	-0.624513	-4.113241
13	6	0	0.171706	-0.511954	-2.736587
14	1	0	2.738996	1.672212	-2.351444
15	1	0	2.774129	1.472624	-4.797531
16	8	0	1.099784	-0.111392	-6.211568
17	1	0	-0.513244	-1.267410	-4.636166
18	1	0	-0.554451	-1.064627	-2.150495
19	6	0	-1.999044	1.034033	4.189369
20	6	0	-2.015759	0.933073	5.576098
21	6	0	-1.102498	0.098225	6.209441
22	6	0	-0.173585	-0.629373	5.464959
23	6	0	-0.164907	-0.513212	4.085004
24	1	0	-2.712964	1.696878	3.710735
25	1	0	-2.735496	1.502942	6.153563
26	53	0	-1.121671	-0.072238	8.317967
27	1	0	0.535295	-1.284459	5.959831
28	1	0	0.552656	-1.073088	3.494983
29	1	0	2.177788	0.791606	1.179458
30	1	0	3.166542	0.729931	-0.300978
31	1	0	2.179186	2.149135	0.054011
32	1	0	-2.186551	0.779365	0.178360
33	1	0	-3.169345	0.720742	1.663331
34	1	0	-2.188897	2.142323	1.297133
35	6	0	1.603102	0.851714	-7.057547
36	6	0	2.498184	0.436773	-8.034891
37	6	0	2.979013	1.359750	-8.957979
38	6	0	2.575321	2.689671	-8.897991
39	6	0	1.676846	3.093505	-7.913348
40	6	0	1.182790	2.179081	-6.991451
41	1	0	2.800508	-0.605182	-8.060745
42	1	0	3.677245	1.035797	-9.724412
43	1	0	2.954846	3.408738	-9.617668
44	1	0	1.349876	4.128364	-7.865798
45	1	0	0.476606	2.480894	-6.224165

Table S13. PNA at APFD/6-311G*

Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	2.784799
3	6	0	-0.000825	-1.209867	0.717630
4	6	0	-0.000825	1.209867	0.717630
5	6	0	-0.000504	1.210076	2.098030
6	6	0	-0.000504	-1.210076	2.098030
7	1	0	-0.005906	-2.154092	0.179480
8	1	0	-0.005906	2.154092	0.179480
9	1	0	0.000583	2.137252	2.658504
10	1	0	0.000583	-2.137252	2.658504
11	7	0	-0.044203	0.000000	-1.369481
12	1	0	0.209734	-0.845413	-1.851469
13	1	0	0.209734	0.845413	-1.851469
14	7	0	0.003820	0.000000	4.238909
15	8	0	0.005361	1.081663	4.804663
16	8	0	0.005361	-1.081663	4.804663

Table S14. (MeO, F) at APFD/6-311G*

Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.435639
3	6	0	0.877562	0.703168	-0.745633
4	6	0	-0.874502	-0.700456	2.186435
5	1	0	1.620938	1.299322	-0.214732
6	1	0	-1.621276	-1.298500	1.663212
7	6	0	0.958622	0.767596	-2.195254
8	6	0	-0.944636	-0.756540	3.638946
9	6	0	1.949726	1.565527	-2.792482
10	6	0	2.074817	1.665383	-4.164510
11	6	0	1.204176	0.963369	-5.002128
12	6	0	0.208550	0.161629	-4.432961
13	6	0	0.096935	0.072701	-3.052938
14	1	0	2.636891	2.119541	-2.157446
15	1	0	2.842584	2.283541	-4.618988
16	8	0	1.406324	1.125141	-6.331029
17	1	0	-0.482788	-0.396036	-5.054879
18	1	0	-0.685165	-0.557508	-2.640102
19	6	0	-1.933758	-1.547219	4.242604
20	6	0	-2.052585	-1.642024	5.622356
21	6	0	-1.166409	-0.933491	6.416081
22	6	0	-0.172125	-0.138791	5.861681
23	6	0	-0.067667	-0.055471	4.483173
24	1	0	-2.626336	-2.100938	3.614010
25	1	0	-2.818458	-2.254202	6.087270
26	9	0	-1.268992	-1.015306	7.754105
27	1	0	0.504453	0.402077	6.515472
28	1	0	0.712484	0.567989	4.058080
29	6	0	0.556586	0.439516	-7.222352
30	1	0	0.633855	-0.646606	-7.097112
31	1	0	-0.488402	0.746117	-7.098583
32	1	0	0.892350	0.709030	-8.222169
33	1	0	-0.761346	-0.609997	-0.485400
34	1	0	0.762626	0.610951	1.918139

Table S15. (MeO, Cl) at APFD/6-311G*

Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.435157
3	6	0	-0.156784	-1.115087	-0.743770
4	6	0	0.155913	1.109411	2.186779
5	1	0	-0.289184	-2.057584	-0.210845
6	1	0	0.288964	2.057682	1.665364
7	6	0	-0.171731	-1.220675	-2.192742
8	6	0	0.167887	1.194088	3.638705
9	6	0	-0.347813	-2.482352	-2.786874
10	6	0	-0.370475	-2.643806	-4.158395
11	6	0	-0.216326	-1.537714	-4.998419
12	6	0	-0.039542	-0.270214	-4.432149
13	6	0	-0.019236	-0.125890	-3.052614
14	1	0	-0.469456	-3.355123	-2.149827
15	1	0	-0.506785	-3.620935	-4.610843
16	8	0	-0.252621	-1.796951	-6.326231
17	1	0	0.082782	0.608055	-5.056119
18	1	0	0.119520	0.869748	-2.641884
19	6	0	0.341415	2.445942	4.246748
20	6	0	0.361774	2.592132	5.626411
21	6	0	0.206273	1.469005	6.427256
22	6	0	0.031971	0.210334	5.859373
23	6	0	0.013918	0.080960	4.481022
24	1	0	0.463410	3.327146	3.622054
25	1	0	0.497098	3.568916	6.078433
26	17	0	0.229285	1.634124	8.159819
27	1	0	-0.088265	-0.659174	6.496905
28	1	0	-0.122864	-0.908237	4.055523
29	6	0	-0.101673	-0.717840	-7.220669
30	1	0	-0.901481	0.021388	-7.098005
31	1	0	0.870030	-0.226089	-7.097528
32	1	0	-0.161390	-1.147127	-8.219197
33	1	0	0.135822	0.965512	-0.486257
34	1	0	-0.136122	-0.967627	1.917556

Table S16. (MeO, Br) at APFD/6-311G*

Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.435085
3	6	0	0.704772	-0.878440	-0.743598
4	6	0	-0.700863	0.873961	2.186859
5	1	0	1.300625	-1.620465	-0.210506
6	1	0	-1.299920	1.621208	1.665795
7	6	0	0.771298	-0.962019	-2.192501
8	6	0	-0.753774	0.940059	3.638750
9	6	0	1.570905	-1.953781	-2.786546
10	6	0	1.672757	-2.081150	-4.158045
11	6	0	0.971166	-1.212274	-4.998115
12	6	0	0.167759	-0.216045	-4.431913
13	6	0	0.076814	-0.102095	-3.052415
14	1	0	2.124450	-2.639383	-2.149456
15	1	0	2.292034	-2.849187	-4.610459
16	8	0	1.134906	-1.416545	-6.325870
17	1	0	-0.389438	0.473694	-5.055965
18	1	0	-0.554500	0.680224	-2.641743
19	6	0	-0.051939	0.062117	4.480442
20	6	0	-0.132431	0.163009	5.859241
21	6	0	-0.926177	1.156061	6.429620
22	6	0	-1.634838	2.042355	5.627386
23	6	0	-1.542660	1.926835	4.247437
24	1	0	0.571456	-0.718020	4.054750
25	1	0	0.417518	-0.524963	6.492463
26	35	0	-1.039180	1.297721	8.323023
27	1	0	-2.251600	2.813895	6.075557
28	1	0	-2.098542	2.622088	3.623367
29	6	0	0.450177	-0.569001	-7.220398
30	1	0	-0.636022	-0.646945	-7.096827
31	1	0	0.756052	0.476315	-7.098200
32	1	0	0.721805	-0.906847	-8.218887
33	1	0	-0.610091	0.760493	-0.486347
34	1	0	0.611407	-0.762220	1.917506

Table S17. (MeO, I) at APFD/6-311G*

Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.434955
3	6	0	0.694667	0.886936	-0.743141
4	6	0	-0.690276	-0.882268	2.186964
5	1	0	1.281849	1.635491	-0.209567
6	1	0	-1.280469	-1.636875	1.666460
7	6	0	0.760579	0.971888	-2.191878
8	6	0	-0.741552	-0.948037	3.638752
9	6	0	1.551333	1.971140	-2.785259
10	6	0	1.652292	2.099999	-4.156644
11	6	0	0.958614	1.225209	-4.997213
12	6	0	0.163961	0.221580	-4.431624
13	6	0	0.073817	0.106198	-3.052241
14	1	0	2.098604	2.661361	-2.147746
15	1	0	2.264721	2.873739	-4.608643
16	8	0	1.120726	1.431533	-6.324713
17	1	0	-0.387053	-0.472702	-5.056116
18	1	0	-0.550791	-0.681708	-2.642008
19	6	0	-1.517664	-1.944007	4.248575
20	6	0	-1.607472	-2.059691	5.628873
21	6	0	-0.910031	-1.164953	6.434230
22	6	0	-0.129140	-0.162518	5.858815
23	6	0	-0.050450	-0.061161	4.479710
24	1	0	-2.065381	-2.646720	3.625459
25	1	0	-2.216247	-2.841080	6.070890
26	53	0	-1.032711	-1.323204	8.539452
27	1	0	0.415188	0.536103	6.485209
28	1	0	0.563087	0.726729	4.053726
29	6	0	0.443772	0.578379	-7.219927
30	1	0	0.758925	-0.464211	-7.098157
31	1	0	-0.643091	0.646664	-7.096607
32	1	0	0.712705	0.919178	-8.218130
33	1	0	-0.600906	-0.767597	-0.486558
34	1	0	0.602243	0.769468	1.917367

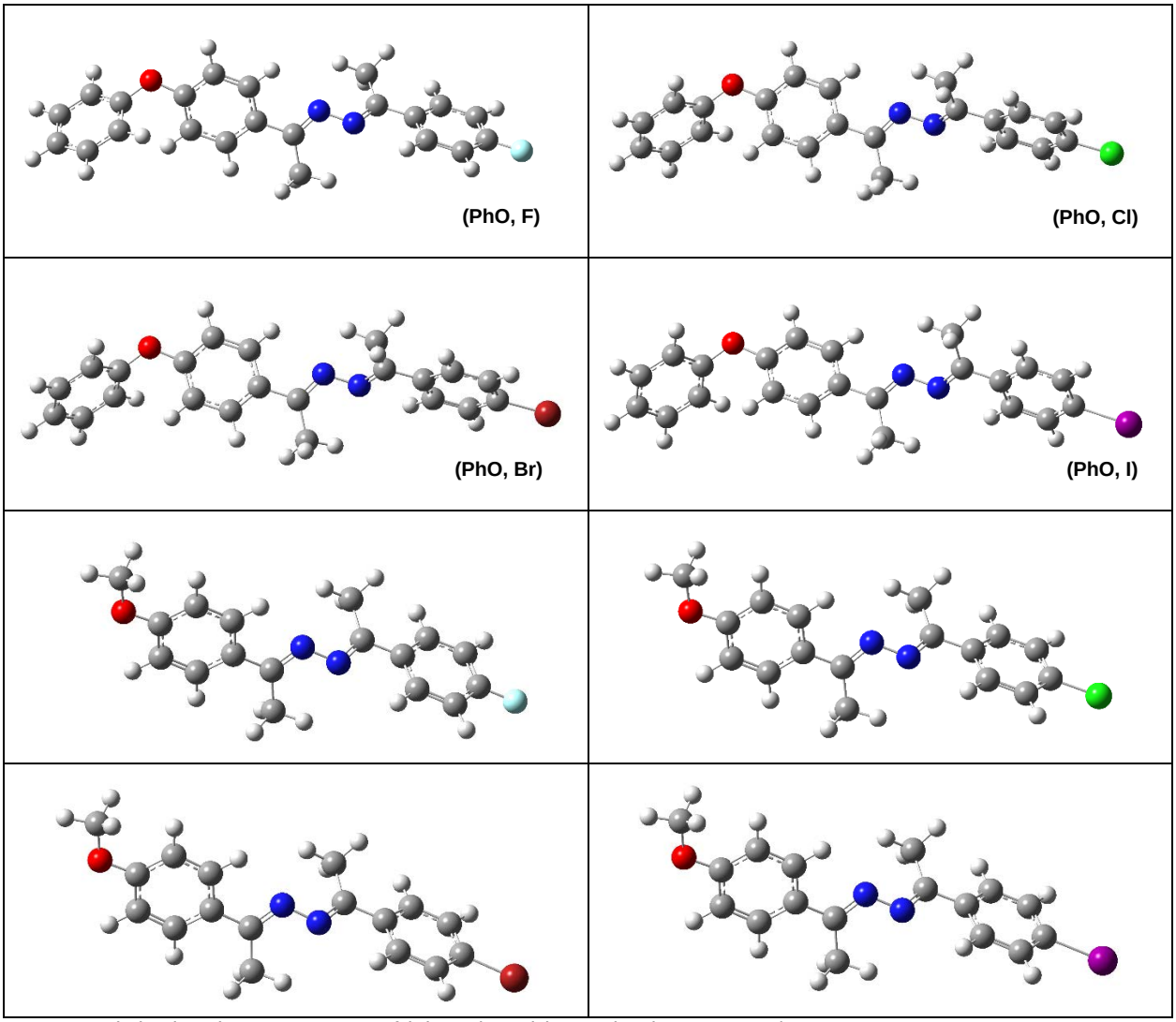


Figure S17. Optimized stationary structures of (PhO, Y)- and (MeO,Y)-azines at APFD/6-311G*.