Supporting Information

Amidinoquinoxaline *N*-oxides as novel spin traps

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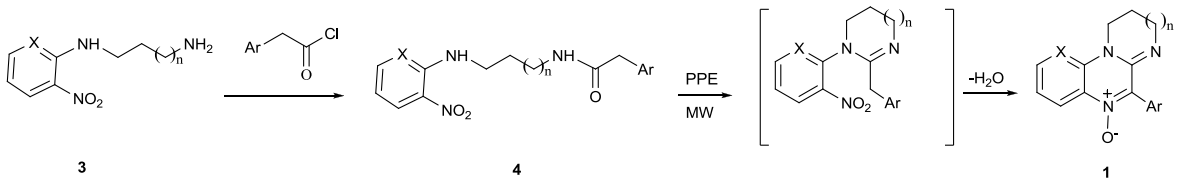
Contents

1. Scheme. Synthesis of nitrones **1**



2. Synthesis of *N*-(2-nitroaryl)-1, 3-propanediamines 3

N-(2-Nitrophenyl)-1,3-propanediamine was described in the literature.[1]

N-(3-Nitropyridin-2-yl)-1,3-propanediamine[2] was obtained as a yellow solid (0,175 g, 89%). ^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC, TMS): δ= 8.44 (1H, bs, ex), 8.39-8.41 (2H, m), 6.61-6.64 (1H, m), 3.72-3.75 (2H, m), 2.84 (2H, t, *J*=6.7), 1.83 (2H, p, *J*=6.7). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC): δ= 155.7, 152.7, 135.3, 111.5, 39.6, 38.9, 32.9. Anal. Calcd for $C_8H_{12}N_4O_2$: C, 49.0; H, 6.2; N, 28.6. Found: C, 48.4; H, 6.3; N, 28.3%.

3. Synthesis of *N*-arylacetyl-*N´*-(2-nitroaryl)-1,3-propanediamines 4. Geneneral Procedure.

The acyl chloride (1 mmol) was added to a chloroformic solution of the corresponding *N*-(*o*-nitrophenyl)-1,*n*-diamine **3** (1 mmol), followed by aq 4% NaOH (1 mL). The mixture was shaken for 15 min, after which the organic layer was separated, washed with H_2O, dried (Na_2SO_4) and filtered. The solvent was removed in vacuo. The crude product was purified by flash chromatography on silica gel using mixtures of chloroform:ethyl acetate as eluent. Yields and analytical data of new compounds are as follows.

N-(2-Methoxyphenyl)acetyl-*N´*-(2-nitrophenyl)-1,3-propanediamine **4e**
This compound was obtained as a yellow solid (0.343 g, 100%), mp 125-127ºC (from ethanol/water). ^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC, TMS): δ= 8.17 (1H, dd, *J*=8.6, 1.5), 8.00 (1H, bs ex), 7.40-7.44 (1H, m), 7.22-7.31 (2H, m), 6.86-6.98 (2H, m), 6.77 (1H, d, *J*=8.5), 6.64-6.67 (1H, m), 5.90 (1H, bs ex), 3.85 (3H, s), 3.60 (2H, s), 3.34-3.38 (2H, m), 3.27-3.30 (2H, m), 1.86 (2H, p, *J*=6.9). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC): δ=171.8, 157.1, 145.3, 136.2, 131.9, 131.3, 128.9, 126.9, 123.5, 121.2, 115.3, 113.6, 110.8, 55.5, 40.3, 38.7, 37.1, 29.1. Anal. Calcd for $C_{18}H_{21}N_3O_4$: C, 63.0; H, 6.2; N, 12.2. Found: C, 63.2; H, 6.3; N, 12.0%.

N-(2-Iodophenyl)acetyl-*N´*-(2-nitrophenyl)-1,3-propanediamine **4g**
This compound was obtained as a yellow solid (0.422 g, 96%), mp 126-128 °C (from hexane/chloroform). ^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC, TMS): δ= 8.18 (1H, dd, *J* = 8.5, 1.5), 8.06 (1H, bs ex), 7.87-7.89 (1H, m), 7.44 (1H, ddd, *J*= 8.7, 7.0, 1.5), 7.37–7.38 (2H,

m), 7.00-7.04 (1H, m), 6.82 (1H, dd, *J* = 8.7, 1.1), 6.67 (1H, dd, *J* = 8.5, 7.0), 5.61 (1H, sa., ex.), 3.76 (2H, s), 3.39-3.43 (2H, m), 3.34–3.38 (2H, m), 1.93 (2H, p, *J*= 6.9). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC): δ= 169.87, 145.29, 139.89, 138.15, 136.23, 131.97, 131.00, 129.30, 129.00, 126.92, 115.37, 113.66, 101.11, 48.59, 40.57, 37.43, 29.02. Anal. Calcd for $C_{17}H_{18}IN_3O_3$: C, 46.5; H, 4.1; N, 9.6. Found: C, 46.3; H, 4.3; N, 9.5%.

N-(3-Thienyl)acetyl-*N´*-(2-nitrophenyl)-1,3-propanediamine **4h**

This compound was obtained as a yellow solid (0.238 g, 87%), mp 104-106ºC. (from hexane/chloroform). ^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC, TMS): δ= 8.14 (1H, dd, *J*=8.5, 1.5), 8.05 (1H, bs ex), 7.42 (1H, ddd, *J*=8.6, 7.0, 1.5), 7.32 (1H, dd, *J*=4.8, 3.0), 7.14-7.15 (1H, m), 7.00 (1H, dd, *J*=4.8, 1.1), 6.78 (1H, d, *J*=8.6), 6.64 (1H, ddd, *J*=8.6, 7.0, 1.0), 3.61 (2H, s), 5.85 (1H, bs ex), 3.37 (2H, q, *J*=6.7), 3.28-3.32 (2H, m), 1.88 (2H, p, *J*=6.7). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC): δ= 170.9, 145.2, 136.2, 134.7, 131.8, 128.3, 126.9, 126.7, 123.4, 115.4, 113.6, 40.5, 38.1, 37.3, 29.0. *Anal*. Calcd for $C_{15}H_{18}N_2OS$: C, 65.7; H, 6.6; N, 10.2. Found: C, 65.5; H, 6.7; N, 10.2%.

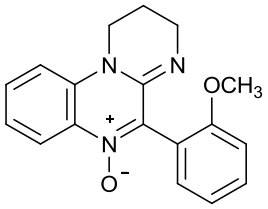
N-Phenylacetyl-*N´*-(3-Nitropyridine-2-yl)-1,3-propanediamine **4i**

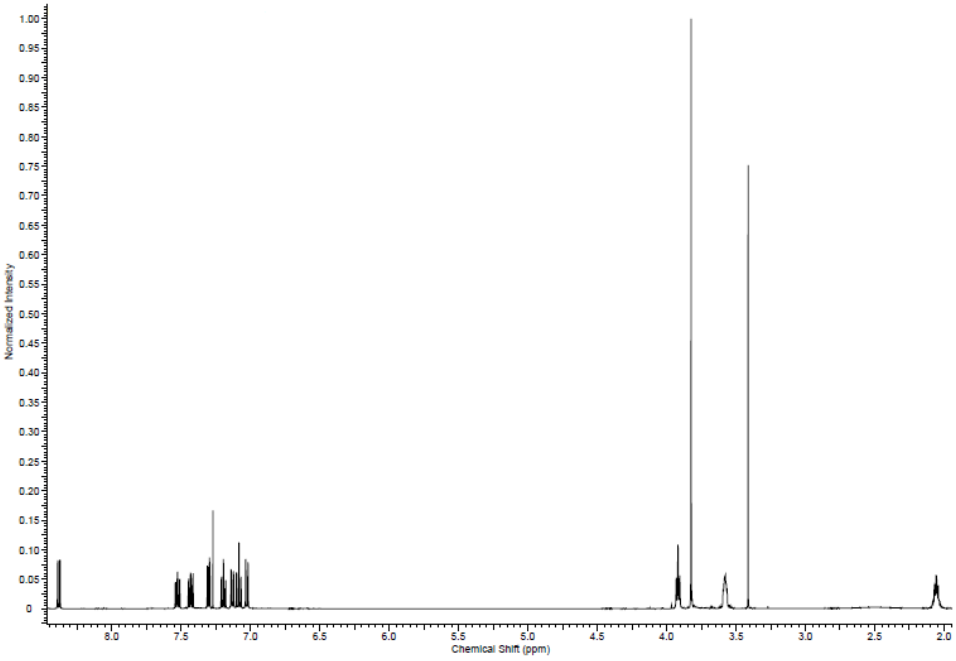
This compound was obtained as a yellow solid (0.292 g, 93%), mp 116-118ºC (from hexane/chloroform). ^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC, TMS): δ= 8.39 (1H, dd, *J*=8.4, 1.7), 8.35 (1H, bs ex), 8.04 (1H, dd, *J*=4.5, 1.7), 7.36-7.39 (2H, m), 7.29-7.33 (3H, m), 6.59 (1H, dd, *J*=8.4, 4.5), 6.08 (1H, bs ex), 3.63 (2H, q, *J*=6.4), 3.63 (2H, s), 3.29 (2H, q, *J*=6.4), 1.79 (2H, p, *J*=6.4). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC): δ= 171.3, 155.5, 152.8, 135.4, 135.0, 129.6, 129.0, 128.0, 127.3, 111.6, 44.0, 38.0, 36.5, 30.0. *Anal*. Calcd for $C_{16}H_{18}N_4O_3$: C, 61.1; H, 5.8; N, 17.8. Found: C, 60.9; H, 5.9; N, 17.6%.

References

1. I. A. Perillo and S. Lamdan, *J. Heterocycl. Chem.*, 1973, **10**, 915.
2. P. Gharagozloo, *WO 035500*, 2005.

^{1}H and ^{13}C NMR (500 MHz, $CDCl_3$) of compound **1e**





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1	2.05	0.0565
2	2.06	0.0577
3	2.07	0.0412
4	3.41	0.7518
5	3.57	0.0429
6	3.57	0.0468
7	3.58	0.0571
8	3.58	0.0556
9	3.58	0.0514
10	3.82	1.0000
11	3.91	0.0566

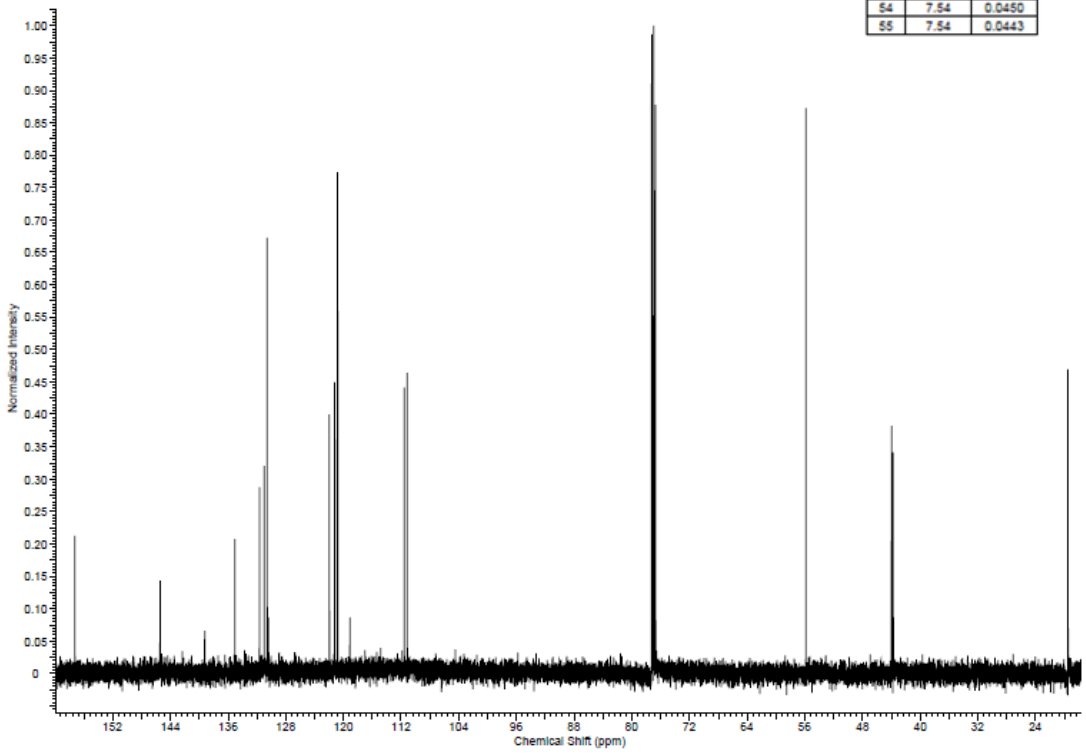
No.	(ppm)	Height
12	3.92	0.1089
13	3.93	0.0525
14	7.02	0.0726
15	7.02	0.0790
16	7.03	0.0803
17	7.04	0.0845
18	7.07	0.0543
19	7.07	0.0518
20	7.08	0.1113
21	7.08	0.1124
22	7.10	0.0597

No.	(ppm)	Height
23	7.10	0.0618
24	7.12	0.0590
25	7.12	0.0641
26	7.14	0.0660
27	7.14	0.0673
28	7.18	0.0483
29	7.18	0.0479
30	7.19	0.0586
31	7.19	0.0842
32	7.20	0.0547
33	7.21	0.0544

No.	(ppm)	Height
34	7.21	0.0504
35	7.27	0.1666
36	7.29	0.0803
37	7.29	0.0870
38	7.31	0.0712
39	7.31	0.0732
40	7.41	0.0601
41	7.42	0.0515
42	7.43	0.0550
43	7.43	0.0598
44	7.43	0.0611

No.	(ppm)	Height
45	7.43	0.0576
46	7.44	0.0510
47	7.45	0.0470
48	7.51	0.0508
49	7.51	0.0503
50	7.52	0.0518
51	7.52	0.0607
52	7.53	0.0627
53	7.53	0.0546
54	7.54	0.0450
55	7.54	0.0443

No.	(ppm)	Height
56	8.37	0.0830
57	8.37	0.0831
58	8.39	0.0824
59	8.39	0.0780



No.	(ppm)	Height
1	19.53	0.4695
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No.	(ppm)	Height
4	55.85	0.8724
5	111.16	0.4642
6	111.56	0.4414

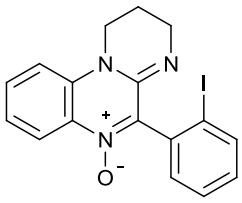
No.	(ppm)	Height
7	119.09	0.0859
8	120.80	0.7738
9	121.19	0.4497

No.	(ppm)	Height
10	121.94	0.3998
11	130.36	0.0862
12	130.55	0.6722

No.	(ppm)	Height
13	130.96	0.3203
14	131.61	0.2878
15	135.02	0.2074

No.	(ppm)	Height
16	139.24	0.0661
17	145.41	0.1434
18	157.21	0.2125

^{1}H and ^{13}C NMR (500 MHz, $CDCl_3$) of compound **1g**



No.	(ppm)	Height
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7	2.09	0.4860
8	2.09	0.2459
9	2.10	0.4041
10	2.10	0.0853
11	2.11	0.1189
12	2.11	0.1200
13	2.11	0.0470
14	3.52	0.0810
15	3.52	0.0830
16	3.53	0.0974
17	3.53	0.1138
18	3.53	0.1041
19	3.54	0.0867
20	3.54	0.0851
21	3.55	0.1544
22	3.55	0.1525
23	3.56	0.1757
24	3.56	0.2534
25	3.57	0.1493
26	3.62	0.1308
27	3.62	0.1503
28	3.63	0.2712
29	3.63	0.2264
30	3.64	0.1419
31	3.64	0.1382
32	3.65	0.0796
33	3.66	0.0858
34	3.66	0.1573
35	3.67	0.1180
36	3.67	0.0790
37	3.68	0.0738
38	3.86	0.0738
39	3.86	0.0746
40	3.87	0.0955
41	3.88	0.1474
42	3.89	0.1956
43	3.90	0.1907
44	3.90	0.3082
45	3.91	0.1534
46	3.93	0.1848
47	3.94	0.2624
48	3.94	0.2481
49	3.95	0.1893
50	3.95	0.1846
51	3.96	0.1294
52	3.97	0.1185
53	3.97	0.0599
54	3.98	0.0565
55	7.12	0.4934
56	7.12	0.5173
57	7.13	0.5426
58	7.14	0.5485
59	7.14	0.3803
60	7.15	0.4463
61	7.16	0.4975
62	7.16	0.4763
63	7.16	0.5194
64	7.16	0.5342
65	7.17	0.4333
66	7.18	0.4203
67	7.19	0.3820
68	7.19	0.3670
69	7.20	0.4697
70	7.20	0.6787
71	7.21	0.4060
72	7.22	0.4270
73	7.22	0.3816
74	7.29	1.0000
75	7.31	0.5392
76	7.31	0.5618
77	7.33	0.6186
78	7.33	0.6482
79	7.33	0.5930
80	7.50	0.4753
81	7.50	0.4705
82	7.51	0.0310
83	7.51	0.7687
84	7.52	0.7406
85	7.53	0.3564
86	7.53	0.3442
87	7.54	0.3897
88	7.54	0.3785
89	7.55	0.4054
90	7.56	0.4886
91	7.56	0.4731
92	7.56	0.4253
93	7.57	0.3578
94	7.57	0.3466
95	7.94	0.6447
96	7.94	0.6158
97	7.95	0.0329
98	7.95	0.0337
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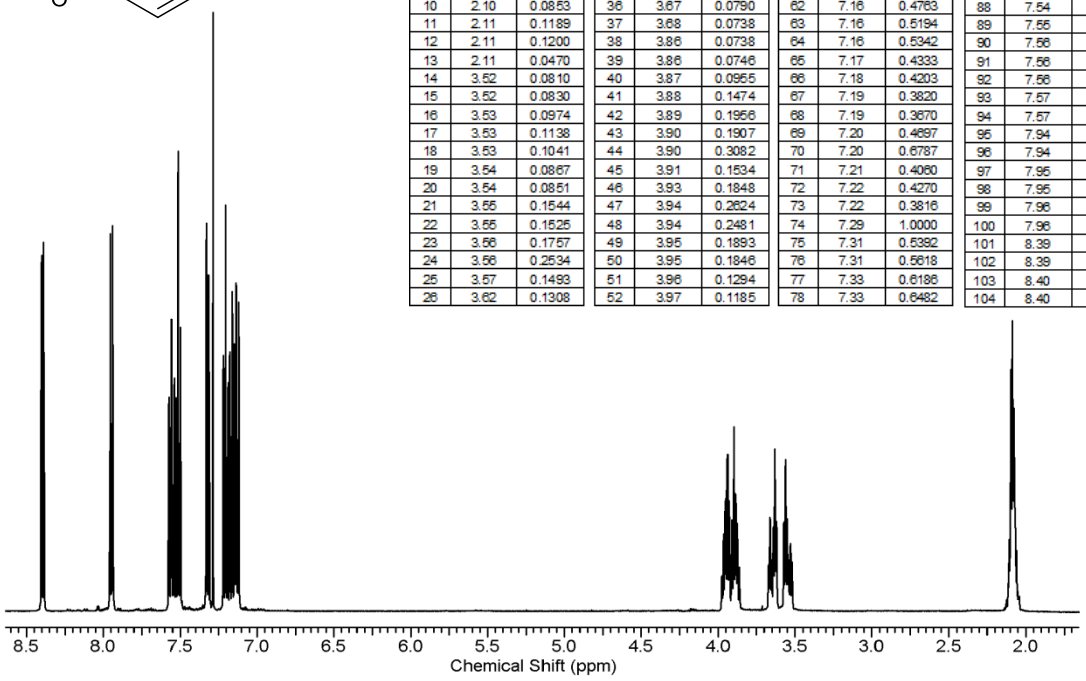
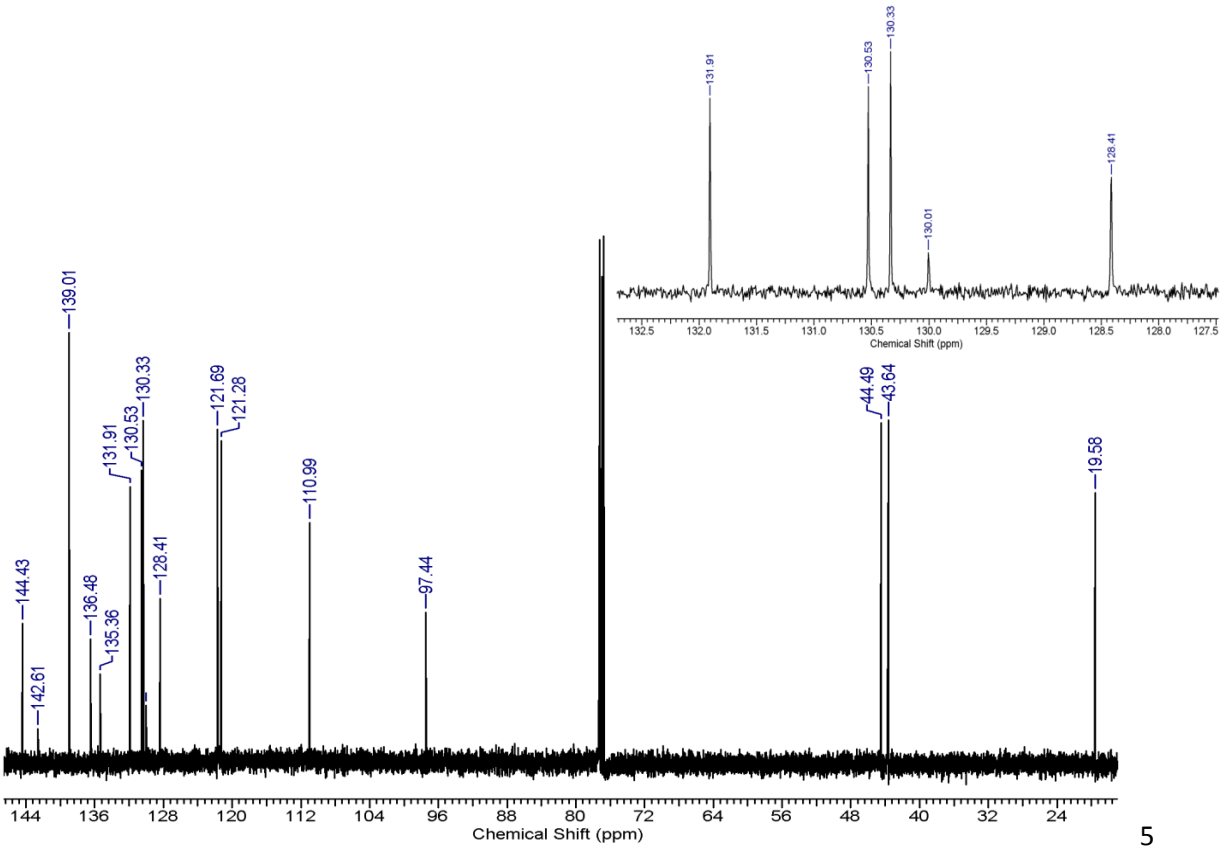
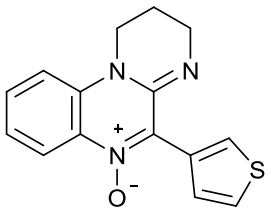
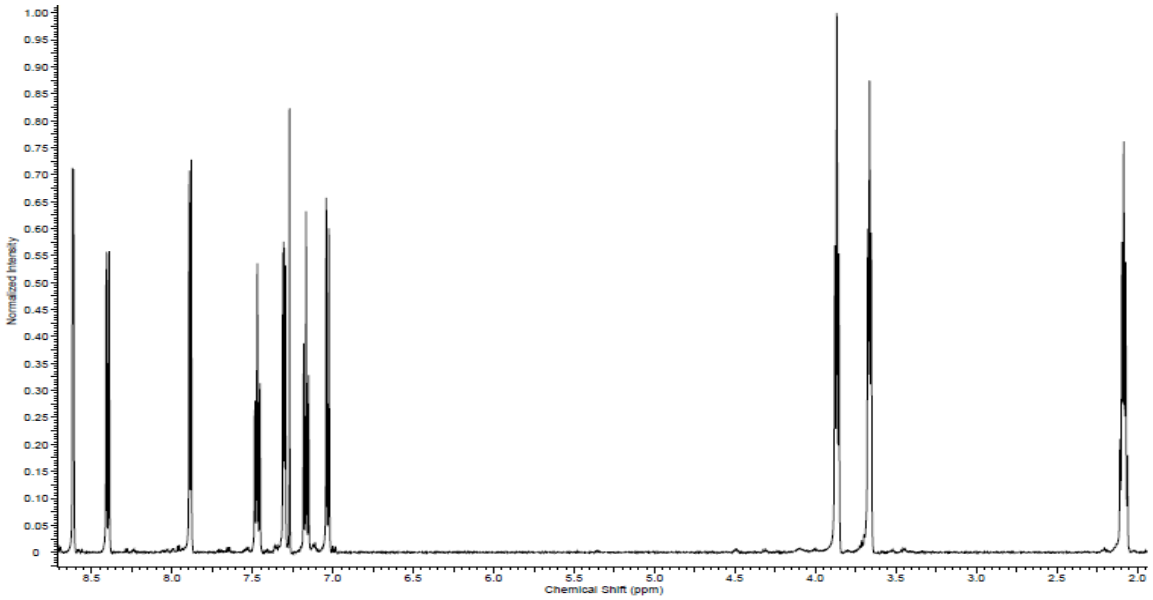


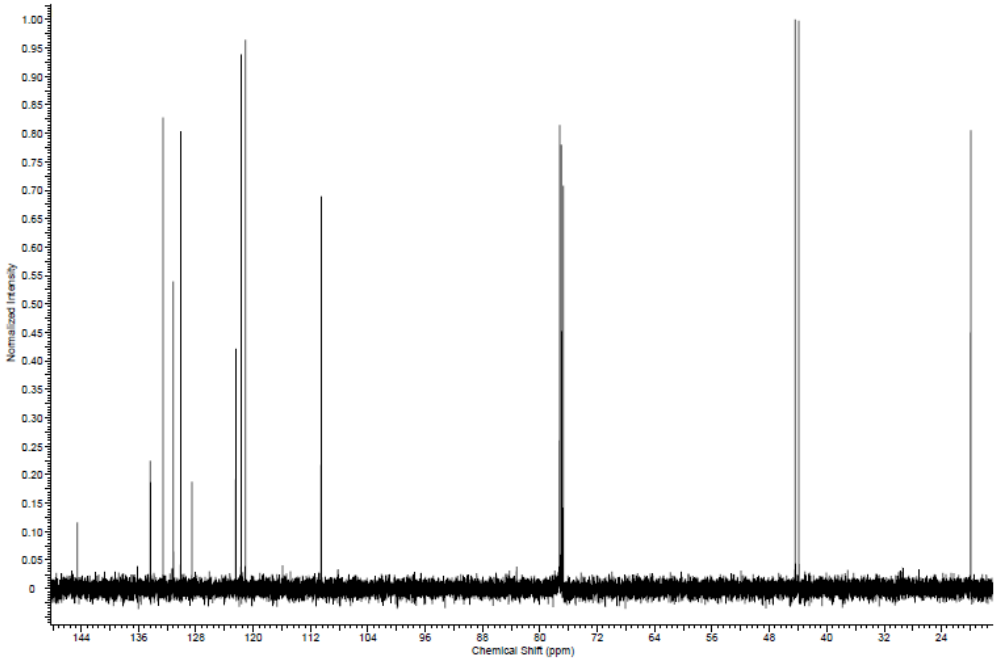


^{1}H and ^{13}C NMR (500 MHz, $CDCl_3$) of compound **1h**





No.	(ppm)	Height	No.	(ppm)	Height	No.	(ppm)	Height	No.	(ppm)	Height	No.	(ppm)	Height	No.	(ppm)	Height
1	2.06	0.1802	8	3.66	0.8746	15	7.15	0.3282	22	7.31	0.5551	29	7.88	0.6117	36	8.61	0.7101
2	2.07	0.5382	9	3.67	0.5996	16	7.17	0.6324	23	7.45	0.3132	30	7.89	0.7071	37	8.61	0.6535
3	2.08	0.7617	10	3.85	0.5534	17	7.18	0.3868	24	7.45	0.3027	31	7.89	0.6033	38	8.62	0.7125
4	2.09	0.2823	11	3.87	1.0000	18	7.27	0.8232	25	7.47	0.5355	32	8.39	0.5580	39	8.62	0.5887
5	2.09	0.5752	12	3.88	0.5688	19	7.29	0.5320	26	7.48	0.2814	33	8.39	0.5175			
6	2.11	0.2100	13	7.02	0.6003	20	7.30	0.5646	27	7.49	0.2524	34	8.41	0.5567			
7	3.65	0.5921	14	7.04	0.6571	21	7.30	0.5758	28	7.88	0.7280	35	8.41	0.5034			



No.	(ppm)	Height
1	19.91	0.8050
2	43.88	0.9974
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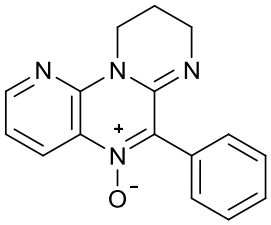
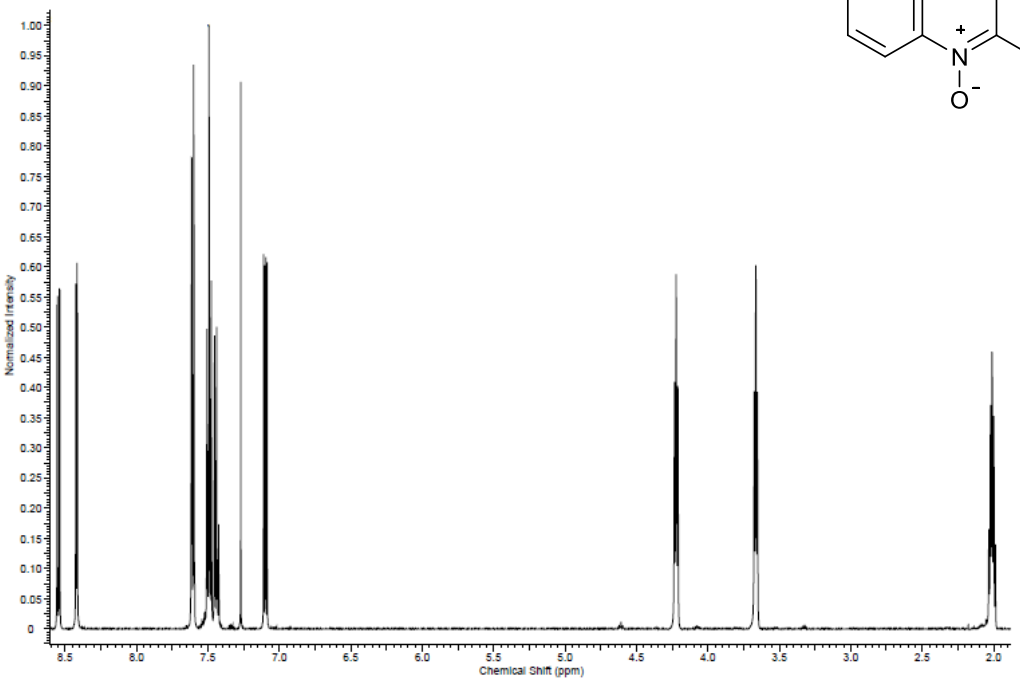
4	110.52	0.6892
5	121.08	0.9641
6	121.68	0.9384
7	122.42	0.4216
8	128.56	0.1881
9	130.13	0.8034
10	130.15	0.0836
11	131.18	0.5396
12	132.57	0.8276
13	134.35	0.2242
14	136.17	0.0397
15	144.54	0.1160

^{1}H and ^{13}C NMR (500 MHz, $CDCl_3$) of compound **1i**





No.	(ppm)	Height
1	1.99	0.1396
2	2.00	0.3528
3	2.01	0.4531
4	2.01	0.4595
5	2.02	0.3708
6	2.03	0.1656
7	3.65	0.3927
8	3.66	0.6030
9	3.68	0.3938

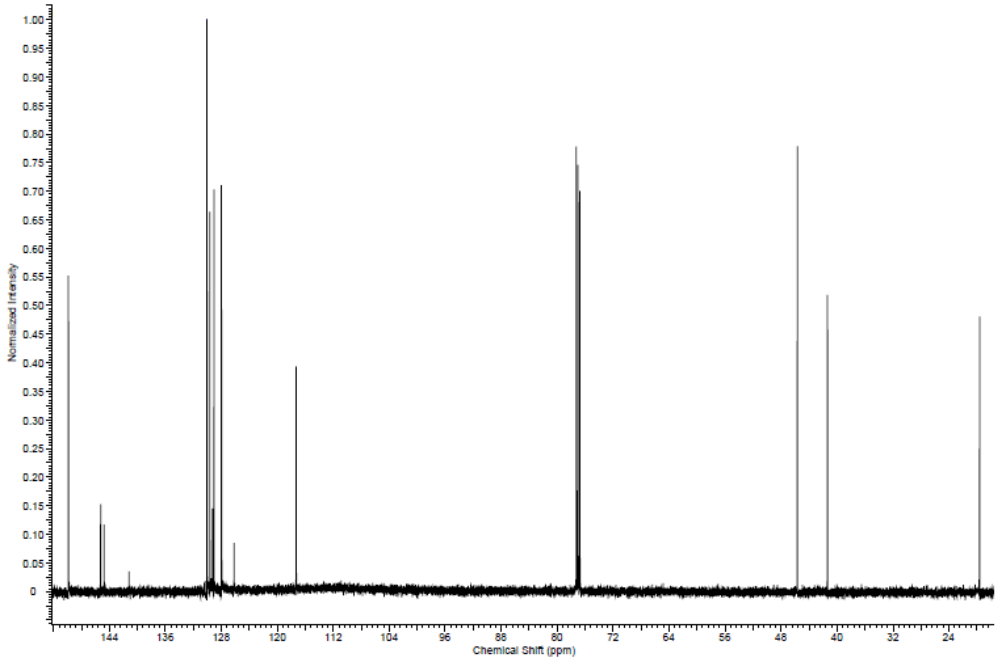
No.	(ppm)	Height
10	4.21	0.4024
11	4.22	0.5877
12	4.23	0.4094
13	7.09	0.6079
14	7.10	0.5164
15	7.10	0.6027
16	7.11	0.6214
17	7.27	0.9069
18	7.42	0.0902

No.	(ppm)	Height
19	7.43	0.1731
20	7.43	0.1044
21	7.43	0.1149
22	7.44	0.5008
23	7.44	0.1722
24	7.45	0.2795
25	7.45	0.4864
26	7.46	0.2459
27	7.47	0.1113

No.	(ppm)	Height
28	7.48	0.4586
29	7.48	0.5770
30	7.48	0.3000
31	7.49	0.5158
32	7.49	1.0000
33	7.50	0.2391
34	7.50	0.1926
35	7.51	0.4973
36	7.51	0.3060

No.	(ppm)	Height
37	7.59	0.1109
38	7.60	0.7095
39	7.60	0.9349
40	7.60	0.4219
41	7.61	0.2112
42	7.62	0.7812
43	7.62	0.5710
44	8.41	0.5235
45	8.42	0.6065

No.	(ppm)	Height
46	8.42	0.5250
47	8.43	0.5723
48	8.54	0.5623
49	8.54	0.5641
50	8.55	0.5515
51	8.56	0.5368



No.	(ppm)	Height
1	19.61	0.4812
2	41.33	0.5184
3	45.66	0.7791
4	117.30	0.3934
5	126.18	0.0846
6	127.98	0.7107
7	129.06	0.7032
8	129.26	0.1450
9	129.64	0.6640
10	130.06	1.0000
11	141.20	0.0350
12	144.77	0.1169
13	145.27	0.1528
14	149.85	0.5526