Supporting Information

Syntheses of Aporphine and Homoaporphine Alkaloids by Intramolecular *ortho*-Arylation of Phenols with Aryl Halides via S_{RN}1 Reactions in Liquid Ammonia

Silvia M. Barolo,^a Xin Teng,^b Gregory D. Cuny^{*b} and Roberto A. Rossi^{*a}

^aINFIQC, Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba. Ciudad Universitaria, 5000 Córdoba, Argentina. ^bLaboratory for Drug Discovery in Neurodegeneration, Brigham & Women's Hospital and Harvard Medical School, 65 Landsdowne St., Cambridge, MA 02139, USA

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General Method.

¹H NMR and ¹³C NMR spectra were recorded on a 200 and 500 nuclear magnetic resonance spectrometers with CDCl₃, CD₃SOCD₃, or acetone-*d*₆ as solvent. Coupling constants (*J*) are given Hz units. Mass spectra were obtained with a CG/MS. Melting points were uncorrected. Gas chromatographic analyses were performed with a flame ionization detector using a HP1 column (0.53 mm x 5 m) and a data system. Liquid chromatographic analyses were performed with a gradient pump with a variable wavelength monitor (programmable detector, covering the 190 nm to 600 nm UV range) using a Spherisorb ODS 2 column (4.0 mm x 250 mm). Irradiation was conducted in a reactor equipped with two 400-W lamps emitting maximally at 350 nm (air and water refrigerated). Potentiometric titration of halide ions was performed in a pHmeter using a Ag/Ag⁺ electrode

¹H NMR spectrum of **10b** in CDCl₃

LDN-84-15/CDCl₃
7/6/2006

exp3 s2pu1

SAMPLE		SPECIAL	
date	Jul 6 2006	temp	# not used
solvent	cdcl3	gain	not used
file	/export/home/~	spin	20
service/data/LDN/~		hst	0.008
LDN-84-15.fid		pw90	9.500
ACQUISITION		alfa	6.600
sw	8999.9	FLAGS	
at	3.001	il	n
np	54016	in	n
fb	5000	dp	y
bs	2	hs	nn
d1	1.000	PROCESSING	
nt	512	lb	0.80
ct	58	fn	not used
TRANSMITTER		DISPLAY	
tn	H1	sp	-200.1
sfrq	399.758	wp	4197.4
tof	991.9	rfl	1501.7
tpwr	58	rfp	0
pw	10.000	rp	186.0
DECOUPLER		lp	-22.8
dn	H1	PLOT	
dof	1289.7	wc	250
dm	nnn	sc	0
dmm	c	vs	1005
dpwr	35	th	12
dmf	17094	ai	ph

^{13}C NMR spectrum of **10b** in CDCl_3

^1H NMR spectrum of **10d** in CDCl_3

¹³C NMR spectrum of **10d** in CDCl₃

LDN-127-35
13C OBSERVE

exp1 s2pu1

SAMPLE # 2006
date Jul 6 2006 temp 24.0
solvent cdc13 gain not used
file /export/home/~ spin 20
service/data/audio ~ hst 0.008
2006-06-28/LDN-127~ pw90 13.000
-3501 alfa 20.000

ACQUISITION
sw 25133.5 il n
at 1.304 in n
np 65536 dp y
fb 14000 hs nn

bs 8
d1 1.000 lb 1.00
nt 25000 fn not used
ct 25000

TRANSMITTER
tn C13 sp -0.2
sfrq 100.529 wp 20103.3
tof 1545.2 rfl 9273.5
tpwr 60 rp 108.3
pw 6.500 lp -271.4

DECOUPLER
dn H1 wc 250
dof 0 sc 0
dm nyv vs 17442
dmm w th 8
dpwr 38 ai no ph
dmf 9524

INDEX	FREQUENCY	PPM	HEIGHT
1	14634.154	145.587	24.3
2	14427.821	143.534	35.5
3	13957.627	138.857	18.8
4	13357.087	132.882	41.7
5	13321.753	132.531	39.9
6	12975.052	129.081	9.2
7	12884.541	128.181	38.5
8	12794.798	127.288	42.0
9	12583.096	125.182	23.7
10	12563.153	124.984	21.4
11	11477.027	114.178	23.8
12	11134.929	110.775	27.2
13	7795.247	77.550	534.0
14	7783.741	77.436	21.1
15	7763.031	77.230	543.9
16	7731.583	76.917	502.4
17	6276.512	62.441	27.0
18	5634.502	56.054	20.9
19	4604.370	45.806	27.1
20	4243.096	42.212	24.4
21	4190.170	41.686	30.4
22	2434.421	24.219	27.4

^1H NMR spectrum of **11b** in CD_3SOCD_3

^1H NMR spectrum of **11b** in CD_3SOCD_3

¹H NMR spectrum of **11b** in CD₃SOCD₃

^{13}C NMR spectrum of **11b** in CD_3SOCD_3

^{13}C NMR spectrum of **11b** in CD_3SOCD_3

¹H NMR spectrum of **11d** in CD₃COCD₃

^1H NMR spectrum of **11d** in CD_3COCD_3

^1H NMR spectrum of **11d** in CD_3COCD_3

^{13}C NMR spectrum of **11d** in CD_3COCD_3

^{13}C NMR spectrum of **11d** in CD_3COCD_3

^{13}C NMR spectrum of **11d** in CD_3COCD_3

¹H NMR spectrum of **15** in CD₃COCD₃

^1H NMR spectrum of **15** in CD_3COCD_3

^{13}C NMR spectrum of **15** in CD_3COCD_3

^{13}C NMR spectrum of **15** in CD_3COCD_3

^1H NMR spectrum of **16** in CD_3SOCD_3

^1H NMR spectrum of **16** in CD_3SOCD_3

^{13}C NMR spectrum of **16** in CD_3SOCD_3

^{13}C NMR spectrum of **16** in CD_3SOCD_3

¹H NMR spectrum of **19a** in CDCl₃

LDN-84-59d/CDCl₃
7/6/2006

exp3 - s2pu1

SAMPLE		SPECIAL	
date	Jul 6 2006	temp	not used
solvent	cdcl3	gain	not used
file	/export/home/~	spin	20
service/data/LDN/~		hst	0.008
LDN-84-59d.fid		pw90	9.500
ACQUISITION		alfa	6.600
sw	8999.9	FLAGS	
at	3.001	il	n
np	54016	in	n
fb	5000	dp	y
bs	2	hs	nn
d1	1.000	PROCESSING	
nt	512	lb	0.80
ct	160	fn	not used
TRANSMITTER		DISPLAY	
tn	H1	sp	-200.1
sfrq	399.758	wp	4197.4
tof	991.9	rfl	1501.7
tpwr	58	rfl	0
pw	10.000	rp	180.9
DECOUPLER		lp	-20.5
dn	H1	PLOT	
dof	1289.7	wc	250
dm	nnn	sc	0
dmm	c	vs	799
dpwr	35	th	12
dmf	17094	ai	ph

¹³C NMR spectrum of **19a** in CDCl₃

¹H NMR spectrum of **19b** in CDCl₃LDN-84-59b/CDCl₃
7/6/2006

exp3 s2pu1

SAMPLE		SPECIAL	
date	Jul 6 2006	temp	not used
solvent	cdc13	gain	not used
file	/export/home/~	spin	20
service/data/LDN/~	hst	0.008	
LDN-84-59b.fid	pw90	9.500	
ACQUISITION	alfa	6.600	

ACQUISITION		FLAGS	
sw	8999.9		
at	3.001	il	n
np	54016	in	n
fb	5000	dp	y
bs	2	hs	nn

PROCESSING	
nt	1.000
ct	512
	218

TRANSMITTER		DISPLAY	
tn	H1	sp	-200.1
sfrq	399.758	wp	4197.4
tof	991.9	rf1	1501.7
tpwr	58	rfp	0
pw	10.000	rp	186.0
DECOUPLER	lp		-30.2

PLOT	
dn	H1
dof	1289.7
dm	nnn
dmm	c
dpwr	35
dmf	17094

¹³C NMR spectrum of **19b** in CDCl₃

LDDN/LDN-84-59b
13C OBSERVE

exp1 s2pu1

SAMPLE 1
date Aug 15 2008

solvent cdc13
file /export/home/~
service/data/auto/~
2006-08-15/LDDN/LD-
N-84-59b01

ACQUISITION
sw 25133.5
at 1.304
np 65536
fb 14000
bs 8
dl 1.000
nt 10000
ct 10000

TRANSMITTER
tn C13
sfrq 100.529
tof 1545.2
tpwr 60
pw 6.500

DECOUPLER
dn H1
dof 0
dm nyy
dmm w
dpwr 38
dmf 9524

INDEX	FREQUENCY	PPM	HEIGHT	INDEX
1	15688.064	156.072	8.2	38
2	15677.326	155.965	21.3	39
3	14591.933	145.823	22.3	
4	14581.029	145.755	11.9	
5	14500.690	144.259	28.8	
6	14494.554	144.198	13.4	
7	14058.876	139.864	27.0	
8	14047.371	139.749	13.0	
9	13449.848	133.805	11.8	
10	13429.905	133.607	27.1	
11	13390.786	133.217	22.4	
12	13363.940	132.950	10.3	
13	13215.902	131.478	29.9	
14	13196.726	131.287	13.6	
15	12976.586	129.097	10.5	
16	12961.245	128.944	26.1	
17	12902.951	128.364	30.4	
18	12658.266	125.930	28.0	
19	12642.925	125.777	12.5	
20	12402.842	123.389	9.2	
21	12375.996	123.122	20.3	
22	11366.574	113.080	9.8	
23	11328.989	112.706	31.2	
24	11154.872	110.973	17.0	
25	11130.327	110.729	10.4	
26	7795.247	77.550	364.9	
27	7763.031	77.230	377.6	
28	7730.816	76.910	349.5	
29	5644.473	56.154	22.5	
30	5450.413	54.223	9.2	
31	5408.226	53.803	18.2	
32	5309.278	52.819	8.2	
33	5267.091	52.399	26.6	
34	4302.158	42.800	19.8	
35	4243.863	42.220	9.0	
36	3889.491	38.694	6.5	
37	3792.078	37.725	20.4

^1H NMR spectrum of **19c** in CDCl_3

¹³C NMR spectrum of **19c** in CDCl₃

LDDN/LDN-84-61
13C OBSERVE

exp1 s2pul

SAMPLE SPECIAL
date Aug 17 2006 temp 24.0
solvent cdc13 gain not used
file /export/home/~ spin 20
service/data/auto/~ hst 0.008
2006-08-15/LDDN/LD~ pw90 13.000
N-84-6101 alfa 20.000

ACQUISITION FLAGS
sw 25133.5 il n
at 1.304 in n
np 65536 dp y
fb 14000 hs nn
bs 8
d1 1.000 lb PROCESSING 1.00
nt 15000 fn not used
ct 15000 DISPLAY

TRANSMITTER sp -0.2
tn C13 wp 20103.3
sfrq 100.529 rfl 9275.8
tof 1545.2 rfp 7763.0
tpwr 60 rp 199.8
pw 6.500 lp -278.5

DECOUPLER H1 wc 250
dn 0 sc 0
dof 0
dm nyy vs 14678
dmm w th 6
dpwr 38 ai no ph
dmf 9524

INDEX	FREQUENCY	PPM	HEIGHT	INDEX
1	15696.502	156.156	19.5	
2	14912.589	148.357	18.4	
3	14901.084	148.242	10.0	
4	14894.180	148.174	20.0	
5	14879.607	148.029	9.5	
6	14644.893	145.694	20.1	
7	14639.524	145.640	13.4	
8	14491.485	144.168	29.5	
9	14484.582	144.099	15.4	
10	13067.097	129.997	22.1	
11	13040.250	129.730	10.8	
12	12988.859	129.219	23.7	
13	12661.334	125.960	38.9	
14	11598.987	115.392	21.2	
15	11587.481	115.277	12.6	
16	11568.305	115.087	19.7	
17	11475.494	114.163	14.2	
18	11446.346	113.873	7.5	
19	11385.750	113.270	11.5	
20	11349.699	112.912	23.4	
21	11144.900	110.874	19.1	
22	11121.122	110.638	10.9	
23	7795.247	77.550	367.4	
24	7763.031	77.230	389.5	
25	7730.816	76.910	379.6	
26	5667.485	56.383	17.7	
27	5654.445	56.253	18.7	
28	5642.172	56.131	28.9	
29	5499.503	54.711	8.5	
30	5463.453	54.353	14.8	
31	5305.443	52.781	6.1	
32	5272.460	52.453	22.6	
33	4247.698	42.258	14.1	
34	4166.392	41.449	8.0	
35	3916.338	38.961	8.1	
36	3796.680	37.771	14.9	
37	2853.224	28.385	19.3

^1H NMR spectrum of **20a** in CDCl_3

¹H NMR spectrum of **20a** in CDCl₃

^1H NMR spectrum of **20a** in CDCl_3

^{13}C NMR spectrum of **20a** in CDCl_3

^{13}C NMR spectrum of **20a** in CDCl_3

^1H NMR spectrum of **20c** in CDCl_3

^1H NMR spectrum of **20c** in CDCl_3

^1H NMR spectrum of **20c** in CDCl_3

^1H NMR spectrum of **20c** in CDCl_3

^{13}C NMR spectrum of **20c** in CDCl_3

^{13}C NMR spectrum of **20c** in CDCl_3

^{13}C NMR spectrum of **20c** in CDCl_3

^1H NMR spectrum of **21** in CDCl_3

¹H NMR spectrum of **21** in CDCl₃

¹H NMR spectrum of **21** in CDCl₃

^{13}C NMR spectrum of **21** in CDCl_3

^{13}C NMR spectrum of **21** in CDCl_3

^{13}C NMR spectrum of **21** in CDCl_3

^1H NMR spectrum of **24** in CDCl_3 LDN-84-59a/CDCl₃
7/6/2006

exp3 s2pu1

SAMPLE		SPECIAL	
date	Jul 6 2006	temp	not used
solvent	cdcl3	gain	not used
file	/export/home/~	spin	20
service/data/LDDN/~		hst	0.008
LDN-84-59a.fid		pw90	9.500
ACQUISITION		alfa	6.600
sw	8999.9	FLAGS	
at	3.001	i1	n
np	54016	in	n
fb	5000	dp	y
bs	2	hs	nn
d1	1.000	PROCESSING	
nt	512	lb	0.80
ct	180	fn	not used
TRANSMITTER		DISPLAY	
tn	H1	sp	-200.1
sfrq	398.758	wp	4197.4
tof	991.9	rf1	1501.7
tpwr	58	rfp	0
pw	10.000	rp	181.4
DECOUPLER		lp	-22.8
dn	H1	PLOT	
dof	1289.7	wc	250
dm	nnn	sc	0
dmm	c	vs	1202
dpwr	35	th	12
dmf	17094	ai	ph

^{13}C NMR spectrum of **24** in CDCl_3

LDDN/LDN-84-59a
13C OBSERVE

exp1 s2pul

SAMPLE SPECIAL 24.0
date Aug 17 2006 temp
solvent cdc13 gain not used
file /export/home/~ spin 20
service/data/auto/~ hst 0.008
2006-08-15/LDDN/LD~ pw90 13.000
N-84-59a02 alfa 20.000

ACQUISITION FLAGS
sw 25133.5 il n
at 1.304 in n
np 65536 dp y
fb 14000 hs nn
bs 8
d1 1.000 lb 1.00
nt 30000 fn not used
ct 29496

TRANSMITTER sp
tn C13 wp 20103.3
sfrq 100.529 rfl 9275.8
tof 1545.2 rfp 7763.0
tpwr 60 rp -174.7
pw 6.500 lp -245.4

DECOUPLER H1 wc 250
dn 0 sc 0
dm nyy vs 19614
dmm w th 6
dpwr 38 ai ph
dmf 9524

INDEX	FREQUENCY	PPM	HEIGHT
1	15740.223	156.591	10.8
2	14631.086	145.556	12.7
3	14484.582	144.099	50.1
4	14224.556	141.512	6.5
5	14195.409	141.222	9.6
6	13378.514	133.095	8.8
7	13368.542	132.996	19.0
8	13135.363	130.676	10.1
9	13114.653	130.470	10.4
10	13099.312	130.318	14.8
11	13080.903	130.134	10.7
12	12843.889	127.777	21.4
13	12835.451	127.693	61.1
14	12626.050	125.609	9.3
15	12596.903	125.319	7.0
16	12519.432	124.549	9.1
17	11367.341	113.087	9.2
18	11333.592	112.751	11.7
19	11163.309	111.057	12.4
20	7794.480	77.543	417.9
21	7763.031	77.230	411.8
22	7730.816	76.910	420.2
23	5642.172	56.131	23.4
24	5474.191	54.460	16.7
25	5319.250	52.918	14.1
26	3851.907	38.320	7.4
27	3801.282	37.817	8.2
28	3723.044	37.038	24.2
29	3377.110	33.597	35.2
30	2815.639	28.011	8.4

data acquisition by Custom NMR Services
direct inquiries to jinhong@gis.net
or call 978-502-1244

^1H NMR spectrum of **25** in CDCl_3

^1H NMR spectrum of **25** in CDCl_3

^1H NMR spectrum of **25** in CDCl_3

^{13}C NMR spectrum of **25** in CDCl_3

^{13}C NMR spectrum of **25** in CDCl_3

^{13}C NMR spectrum of **25** in CDCl_3

DEPT spectrum of **25** in CDCl₃

DEPT spectrum of **25** in CDCl₃

DEPT spectrum of **25** in CDCl₃

^1H - ^1H COSY spectrum of **25** in CDCl_3

^1H - ^1H COSY spectrum of **25** in CDCl_3

^1H - ^1H COSY spectrum of **25** in CDCl_3

HETCOR spectrum of **25** in CDCl_3

HETCOR spectrum of **25** in CDCl_3

HETCOR spectrum of **25** in CDCl₃