Supporting Information

The modular synthesis of heterocyclic carbene (NHC) precursors

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Table of contents

General experimental methods	S2
ORTEP drawing of 6o	S3
Crystal data and structure refinement for (6o).	S4
Packing diagramm of 6o	S5
¹ H and ¹³ C NMR spectra of compounds 3a-f	S6 – S17
¹ H and ¹³ C NMR spectra of compounds 4a-c	S18 - S23
¹ H and ¹³ C NMR spectra of compounds 5a-f	S24 - S35
¹ H and ¹³ C NMR spectra of compounds 6a-s	S36 - S73
¹ H and ¹³ C NMR spectra of compounds 7a-f	S74 - S85
¹ H and ¹³ C NMR spectra of compounds 8a-f	S86 - S97
¹ H and ¹³ C NMR spectra of compounds 9a-f	S98 - S109
¹ H and ¹³ C NMR spectra of compounds 10d	S110 - S111
¹ H and ¹³ C NMR spectra of compounds 11a-d	S112 - S119

General experimental methods

Unless otherwise indicated, all starting materials were obtained from commercial suppliers (Aldrich, Fisher, Merck) and were used without further purification. 1-Iodo-2-methoxynaphthalene,¹ 2-(3'-chloropropoxy)-benzaldehyde (**10a**),² 2-(4'-bromobutoxy)-benzaldehyde (**10b**),³ and 2-(5'-bromopentoxy)-benzaldehyde (**10c**)⁴ were prepared according to literature procedures. Abs. THF was distilled from potassium/benzophenone. Analytical thin-layer chromatography (TLC) was performed on Polygram SIL G/ UV 254 pre-coated plastic TLC plates with 0.25mm silica gel from Macherey-Nagel + Co. Visualization was performed with a 254 nm ultraviolet lamp. Silica gel column chromatography was carried out with 0.040–0.063 mm Flash silica gel. All melting point values are reported as the midpoint of the thermal transition. The ¹H and ¹³C NMR spectra were recorded in CDCl₃ or dms^o-d₆. Chemical shifts are expressed in parts per million (ppm) using residual solvent protons as internal standards: chloroform (δ : 7.26 for ¹H and 77.0 for ¹³C), dimethylsulfoxide (2,50 for ¹H and 39.43 for ¹³C). Coupling constants (*J*) are reported in Hertz (Hz). Splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br s (broad singlet). Optical rotations were measured at 20 °C. Gas chromatographic measurements were performed using a 30 m x 0.25 mm column with 0.25 μ m RH-5 MS+ coating and H₂ carrier gas. Single Crystal X-ray: X-ray quality crystal of **6o** was fixed onto the tip of glass fiber with epoxy glue. Data were collected at 293(1) K using Mo K α radiation λ = 0.71073 Å, ω –2 θ motion. The structure was solved using direct methods⁵ and refined on F² using SHELX–

¹ Iskra, J.; Stavber, S.; Zupan, M. *Synthesis* **2004**, *11*, 1869-1873.

² Osuka, A.; Kobayashi, F.; Maruyama, K. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 1213-1225.

³ Sanders, G. M.; van Dijk, M.; van Veldhuizen, A.; van der Plas, H. C.; Hofstra, U.; Schaafsma, T. J. *J. Org. Chem.* **1988**, *53*, 5272-5281.

⁴ Perchonock, C. D.; Uzinskas, I.; McCarthy, M. E.; Erhard, K. F.; Gleason, J. G.; et al. *J. Med. Chem.* **1986**, *29*, 1442-1452.

⁵ A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, *J. Appl. Cryst.* **1993**, *26*, 343–350.

97 program,⁶ publication material was prepared with the WINGX-97 suite.⁷ Other details of X-ray structure determination including the ORTEP plot and crystal packing diagram are summarized in the Supplementary Information. Residual electron density peaks were close to iodine atom. Hydrogen atoms were placed into geometric position. Empirical absorption correction was made⁸ using the psi scan method. Although two unit cell angle data are close to 90°, no additional crystallographic symmetry element can be found in the structure.

ORTEP drawing of **6o** at 50% probability level with numbering scheme.

Selected bond length (Å) and angles (deg): I1-C2 3.251(4); N1-C2 1.314(4); N1-C6 1.487(17); N3-C2 1.304(4); N3-C4 1.53(3); C5-C6 1.52(2); O31-C31 1.382(6); C32-C37 1.430(11); C37-C38 1.298(10); C38-C39 1.297(12); N3-C2-N1 123.8(3); C2-N1-C6 120.2(6); C6-C5-C4 109.0(2); C39-C38-C37 138.5(14); C32-C37-C38 123.2(10).

⁶ Sheldrick, G. M. (1997) *SHELXS97 and SHELXL97*. University of Göttingen, Germany.

⁷ Farrugia, L. J.: WINGX-97 system, University of Glasgow, U.K, 1996.

⁸ North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Cryst.* **1968**, A24, 351-359.

Crystal data and structure refinement for **(6o)**.

Empirical formula	C ₂₈ H ₃₉ N ₂ OI (6o)
Formula weight	546.51
Temperature (K)	293
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P-1 (No. 2)
Unit cell dimensions	
a (Å)	8.7553(10)
b (Å)	11.861(2)
c (Å)	14.220(2)
$\alpha(^{\circ})$	90.41(1)
$\beta(^{\circ})$	90.47(1)
$\gamma(^{\circ})$	111.54(1)
V (Å ³)	1373.5(3)
Z	2
D _{calc} (Mg m ⁻³)	1.321
Absorption coefficient (mm ⁻¹)	1.186
F (000)	564
Crystal size (mm ³)	0.35 x 0.3 x 0.26
Crystal color	colorless
Habit	block
Theta range for data collection	2.46 – 25.5
Index ranges	0 ≤ h ≤ 10 -14 ≤ k ≤ 13 -17 ≤ l ≤ 17
Reflections collected	5032
Independent reflections	5032 [R _{int} = 0.00]
Completeness of data	98.3 %
Absorption correction	Empirical (psi scan)
Max/min transmission	0.5365 / 0.6697
Decay (%)	5
Refinement method	Full matrix least-squares on F^2
Data/restraints/parameters	5032 / 1 / 317
Final R indices [all data]	R1 = 0.0496, wR2 = 0.1416
Goodness of fit on F2	1.015
Largest difference peak and hole	0.898 / - 1.064 (e Å ⁻³)

Packing diagram of **60**, view normal to (100).

C₁₁H₁₄ClNO
Mol. Wt.: 211,69

3a

7.835

7.260

6.905

4.211

2.277

2.184

0.013

1.0

2.0

2.0

3.0

6.0

CDCl₃

S6

κ¹

$\text{C}_{11}\text{H}_{14}\text{ClNO}$
Mol. Wt.: 211,69

3a

164.497

137.467

134.953

129.991

128.974

77.502

76.995

76.487

42.675

20.855

18.056

C₁₄H₂₀ClNO
Mol. Wt.: 253,77

3b

C₁₄H₂₀ClNO
Mol. Wt.: 253,77

3b

$C_{10}H_{12}ClNO$
Mol. Wt.: 197.661

3c

$\text{C}_{10}\text{H}_{12}\text{ClNO}$
Mol. Wt.: 197,661

3c

164.899

142.253

128.704

127.549

126.009

77.509

76.995

76.493

49.163

42.558

21.592

$\text{C}_{12}\text{H}_{18}\text{ClNO}$
Mol. Wt.: 227,73

3d

7.259

6.222

3.905

2.072

1.999

1.988

1.676

1.664

1.653

2.20 2.15 2.10 2.05 2.00 1.95 1.90 1.85

0.9

2.0

3.0

6.0

6.0

S12

C₁₂H₁₈ClNO
Mol. Wt.: 227,73

3d

164.504

77.500
76.997
76.486

52.269

42.821
41.139
36.117

29.266

200 175 150 125 100 75 50 25 0

S13

λ

C₈H₁₆ClNO
Mol. Wt.: 177,67

3e

7.260

6.463

4.036

3.905

3.877

3.866

3.849

3.838

3.823

3.811

3.783

1.086

1.059

0.891

CDCl₃

0.9

2.0

1.0

3.0

9.0

S14

C₈H₁₆ClNO
Mol. Wt.: 177,67

3e

3f

7.644

7.260

6.938

6.768

3.785

3.760

3.749

3.734

3.723

3.697

2.702

2.677

2.651

2.384

2.359

2.333

2.300

2.220

2.202

2.058

9.0

0.8

2.0

2.0

1.7

0.2

S16

C₁₂H₁₆ClNO
Mol. Wt.: 225,71

3f

172.067
168.520

138.213
136.626
136.239
134.972
131.146
130.971
129.297
128.573

77.508
76.998
76.484

40.300
39.057
38.977
34.921

20.840
20.804
18.253
18.100

4a

C₁₉H₂₄N₂O
Mol. Wt.: 296,41

4a

C₁₇H₂₈N₂O₂
Mol. Wt.: 292,416

4b

C₁₉H₂₄N₂O₂
Mol. Wt.: 312,406

4c

8.218
8.185

7.346
7.338
7.324
7.313
7.296
7.245
7.229
7.212
7.196
7.176

5.008
4.980
4.951
4.919
4.892
4.461

3.502
3.481
3.458
3.135
2.694
2.673
2.650
2.499

1.355
1.327

$C_{19}H_{24}N_2O_2$
Mol. Wt.: 312,406

4c

$C_{19}H_{26}N_2$
Mol. Wt.: 282,42

5a

$C_{19}H_{26}N_2$
Mol. Wt.: 282,42

5a

145.717
143.781

129.370
128.421
126.868
126.491

77.509
76.997
76.492

58.160

48.599
47.870

24.333
20.488
18.400

C₁₇H₃₀N₂O
Mol. Wt.: 278,43

5b

7.333
7.328
7.314
7.292
7.282
7.273
7.258
7.251
7.236

4.463

3.507
3.485
3.462

2.768
2.747
2.724
2.705
2.683
2.661
2.588
2.582
2.567
2.558
2.543
2.538
2.499
2.464
2.442
2.420
2.398
2.377
2.139
2.114
2.088
2.062
0.907
0.881
0.822

5.0

2.0

2.0

3.0

2.0

1.0

1.0

2.0

3.0

9.0

3.0

2.0

1.0

DMSO

2.80 2.70 2.60 2.50 2.40

S26

$\text{C}_{17}\text{H}_{30}\text{N}_2\text{O}$
Mol. Wt.: 278,43

5b

$C_{19}H_{26}N_2O$
Mol. Wt.: 298,42

5c

$C_{19}H_{26}N_2O$
Mol. Wt.: 298,42

5c

$C_{25}H_{32}N_2O$
Mol. Wt.: 376,53

5d

$\text{C}_{25}\text{H}_{32}\text{N}_2\text{O}$
Mol. Wt.: 376,53

5d

5e

$\text{C}_{26}\text{H}_{36}\text{FeN}_2$
Mol. Wt.: 432,42

5f

$\text{C}_{26}\text{H}_{36}\text{FeN}_2$
Mol. Wt.: 432,42

5f

$C_{20}H_{25}BF_4N_2$
Mol. Wt.: 380,23

6a

6a

$\text{C}_{18}\text{H}_{29}\text{BF}_4\text{N}_2\text{O}$
Mol. Wt.: 376,24

6b

C₁₈H₂₉BF₄N₂O
Mol. Wt.: 376,24

6b

6c

6c

C₂₅H₃₃IN₂O
Mol. Wt.: 504,45

6d
Λ

$C_{25}H_{33}IN_2O$
Mol. Wt.: 504,45

6d

$\text{C}_{19}\text{H}_{23}\text{BF}_4\text{N}_2$
Mol. Wt.: 366,2

6g

$\text{C}_{19}\text{H}_{23}\text{BF}_4\text{N}_2$
Mol. Wt.: 366,2

6g

$\text{C}_{15}\text{H}_{23}\text{BF}_4\text{N}_2\text{O}$
Mol. Wt.: 334,16

6h

8.279

7.260

6.917

5.034

4.318

4.292

4.259

4.246

4.227

4.214

4.195

4.181

4.150

4.124

3.632

3.604

3.575

3.548

2.285

2.235

1.260

1.232

1.204

-0.008

C₁₅H₂₃N₂O
Mol. Wt.: 334,16

6h

158.847

140.426

135.209

130.145

129.917

77.507

76.998

76.484

64.926

78.072

51.283

46.994

20.979

17.311

14.818

6i

C₂₂H₂₉BF₄N₂
Mol. Wt.: 408,28

6j

8.215

7.435
7.418
7.395
7.371
7.355
7.343
7.260
7.195
7.165

4.820

4.180
4.151
4.127
4.105
4.074

2.921
2.894
2.868
2.840
2.814
2.786
2.759

1.224
1.196
1.175
1.148

-0.012

12.0

6.0

2.0

4.0

2.0

2.0

1.0

2.0

6.0

CDCl₃

S54

$C_{22}H_{29}BF_4N_2$
Mol. Wt.: 408,284

6j

C₂₃H₂₉IN₂O
Mol. Wt.: 476,39

C₁₄H₂₃IN₂
Mol. Wt.: 346,25

6l

154.695

C₁₄H₂₃IN₂

Mol. Wt.: 346,25

6l

77.509
76.998
76.487

56.420

50.070

43.908

40.329

35.017

34.767

28.343

C₁₆H₂₅BF₄N₂
Mol. Wt.: 332,19

6m

C₁₆H₂₅BF₄N₂
Mol. Wt.: 332,19

6m

$C_{28}H_{39}IN_2O$
Mol. Wt.: 546,53

156.063	139.586	127.586	120.242	77.500	55.666	28.700
155.186	136.078	127.434	119.533	76.996	45.744	28.667
152.841	134.259	126.628	111.736	76.486	43.484	27.169
	129.682	126.087	111.407	67.651		25.496
	127.586	126.030		67.570		25.458
	127.434	125.914				25.290
	126.628	125.758				20.662
	126.087	125.306				18.953
	126.030	124.847				18.696
	125.914	120.242				17.929
	125.758	119.533				14.394
	125.306	111.736				
	124.847	111.407				
	120.242					
	119.533					
	111.736					
	111.407

$C_{20}H_{25}BF_4N_2$
Mol. Wt.: 380,23

6p

11.0

4.0

2.0

2.0

1.0

5.0

$\text{C}_{20}\text{H}_{25}\text{BF}_4\text{N}_2$
Mol. Wt.: 380,23

6p

S67

$\text{C}_{26}\text{H}_{31}\text{BF}_4\text{N}_2\text{O}$
Mol. Wt.: 474,34

6q

$C_{26}H_{31}BF_4N_2O$
Mol. Wt.: 474,34

6q

160.740

152.386

146.235

132.264

131.203

129.784

129.442

129.012

128.565

128.396

129.784

129.442

129.012

128.565

128.396

124.759

120.256

116.179

112.643

77.509

76.998

76.484

56.844

54.225

52.378

28.556

24.727

23.819

S69

$\text{C}_{20}\text{H}_{25}\text{BF}_4\text{N}_2$
Mol. Wt.: 380,23

6r

7.552
7.386
7.361
7.329
7.307
7.260
6.948

4.044
4.023
4.001
3.897
3.876
3.855

2.570
2.570
2.548
2.526
2.505
2.366
2.326
2.281

0.008

6r

$\text{C}_{27}\text{H}_{35}\text{BF}_4\text{FeN}_2$
Mol. Wt.: 530,23

6s

7a

7.612

7.259

6.891

4.123

2.270

2.161

0.010

7a

$C_{14}H_{20}N_4O$
Mol. Wt.: 260,33

7b

7.625
7.358
7.330
7.324
7.296
7.260
7.212
7.184

7.260

4.189

3.089
3.062
3.033
3.007
2.979
2.952
2.923

1.225
1.197

0.011

C₁₄H₂₀N₄O
Mol. Wt.: 260,33

7b

165.937

145.937

129.922

128.691

123.560

77.502

76.995

76.487

52.722

28.806

23.506

C₁₀H₁₂N₄O
Mol. Wt.: 204,23

7c

7.382
7.354
7.345
7.325
6.655
7.312
7.285
7.272
7.257
7.247
7.239

5.178
5.150
5.121
5.091
5.063

4.002
3.936
3.927
3.861

1.519
1.491

-0.000

5.0

1.0

1.0

2.0

3.0

TMS

C₁₀H₁₂N₄O
Mol. Wt.: 204,23

7c

C₁₂H₁₈N₄O
Mol. Wt.: 234,3

7d

7.260

5.960

3.797

2.037

1.961

1.950

1.633

1.644

1.621

CDCl₃

1.0

2.0

3.1

6.0

5.9

S80

C₁₂H₁₈N₄O
Mol. Wt.: 234,3

7d

165.228

77.510

76.996

76.492

52.839

52.034

41.242

36.039

29.193

200

175

150

125

100

S81

75

50

25

0

$C_8H_{16}N_4O$
Mol. Wt.: 184,239

7e

7.260

6.208

3.940

3.928

3.890

3.864

3.852

3.836

3.824

3.809

3.796

3.769

1.044

1.017

0.857

9.0

1.0

1.8

1.0

3.0

C₈H₁₆N₄O
Mol. Wt.: 184,239

7e

165.571

77.501
76.995
76.486

52.774
52.628

33.978

25.962

15.835

C₁₂H₁₆N₄O
Mol. Wt.: 232,28

7f

7.383
7.260

6.936
6.816

3.651
3.625
3.599
3.558
3.533
3.507

2.553
2.528
2.502
2.295
2.235
2.205
2.184
2.149
2.123
2.105
2.079
2.070

C₁₂H₁₆N₄O
Mol. Wt.: 232,28

7f

172.586
168.801

138.242
136.880
136.276
135.019
131.300
130.941
129.334
128.711

77.499
76.998
76.485

47.600
46.612

35.499
31.478

20.818
18.049

C₁₁H₁₈N₂
Mol. Wt.: 178,27

8a

7.260

6.837

3.015
3.007
2.995
2.988
2.982
2.968
2.965
2.927
2.924
2.910
2.904
2.897
2.884
2.877
2.291
2.242

0.020

9.2

3.9

2.0

2.4

C₁₁H₁₈N₂
Mol. Wt.: 178,27

8a

143.459

131.146

129.677

129.334

77.510

76.995

76.493

51.210

42.507

20.461

18.268

$C_{14}H_{24}N_2$
Mol. Wt.: 220,35

8b

7.260
7.142
7.125
7.104
7.089
7.070
7.051
7.032

3.421
3.394
3.366
3.339
3.311
3.284
3.257
3.003
2.993
2.987
2.965
2.955
2.950
2.941
2.918
2.912
2.902
1.275
1.247

0.018

C₁₄H₂₄N₂
Mol. Wt.: 220,35

8b

C₁₀H₁₆N₂
Mol. Wt.: 164,25

8c

7.357
7.323
7.307
7.276
7.257
7.239
7.223
7.213
7.204
7.189

3.797
3.770
3.743
3.717

2.613
2.592
2.568
2.545
2.522
2.506
2.483
2.456
2.436
2.410
2.771
2.744
2.721
1.389
1.373
1.346
-0.000

TMS

S90

$C_{10}H_{16}N_2$
Mol. Wt.: 164,25

8c

145.702

128.289

126.730

126.440

77.510

76.996

76.493

58.173

50.318

41.907

24.363

S91

$C_{12}H_{22}N_2$
Mol. Wt.: 194,32

8d

7.260

12.0

3.0

2.0 2.0

3.0

$C_{12}H_{22}N_2$
Mol. Wt.: 194,32

8d

42.879

42.741

42.631

77.509

76.998

76.485

49.756

42.879

42.741

42.631

36.478

29.295

S93

$C_8H_{20}N_2$
Mol. Wt.: 144,258

8e

$\text{C}_8\text{H}_{20}\text{N}_2$
Mol. Wt.: 144,258

8e

$C_{12}H_{20}N_2$
Mol. Wt.: 192,3

8f

7.260

6.835

3.028

3.002

2.974

2.878

2.851

2.822

2.277

2.244

1.793

1.767

1.739

1.711

1.684

0.032

9.0

1.9

2.0

4.9

CDCl₃

TMS

S96

C₁₂H₂₀N₂
Mol. Wt.: 192,3

8f

9a

9a

$C_{15}H_{22}N_2$
Mol. Wt.: 230,35

9b

11.4

3.1

1.0

2.0

2.0

2.0

C₁₅H₂₂N₂

Mol. Wt.: 230,35

9b

C₁₁H₁₄N₂
Mol. Wt.: 174,24

9c

7.385
7.378
7.372
7.357
7.349
7.322
7.307
7.293
7.276
7.248
7.013

4.368
4.341
4.313
4.285
3.815
3.809
3.776
3.770
3.736
3.729
3.139
3.101
3.062
3.058

1.580
1.552

-0.000

$\text{C}_{11}\text{H}_{14}\text{N}_2$
Mol. Wt.: 174,24

9c

$C_{13}H_{20}N_2$
Mol. Wt.: 204,31

9d

$C_{13}H_{20}N_2$
Mol. Wt.: 204,31

9d

$C_9H_{18}N_2$
Mol. Wt.: 154,253

9e

7.260

6.734

3.753
3.749
3.746
3.743
3.711
3.704
3.672
3.669
3.665
3.663
3.357
3.323
3.284
3.249
3.243
3.214
3.207
3.172
3.069
3.041
3.012
2.984
1.090
1.062
0.861

S106

9e

$C_{13}H_{18}N_2$
Mol. Wt.: 202,3

9f

7.260

6.861

3.429
3.409
3.387
3.313
3.289
3.266

2.231
2.185
2.014
1.990
1.969
1.945
1.922

-0.043

8.9

3.0

2.02.0

2.1

CDCl₃

TMS

S108

C₁₃H₁₈N₂
Mol. Wt.: 202,3

9e

$\text{C}_{13}\text{H}_{17}\text{ClO}_2$
Mol. Wt.: 240,73

10d

$\text{C}_{13}\text{H}_{17}\text{ClO}_2$
Mol. Wt.: 240,73

10d

11a

11a

155.911
154.998

130.057
127.805
127.645
127.089
126.615
126.447
126.278
125.293
124.957
120.877
120.185
111.963
111.657

77.509
76.995
76.494
67.548
67.425

32.971

18.926
14.637

2.703
2.630

C₁₃H₁₇IO
Mol. Wt.: 316,18

11b

0.000

C₁₃H₁₇IO
Mol. Wt.: 316,18

11b

$C_{14}H_{19}IO$
Mol. Wt.: 330,2

11c

C₁₄H₁₉IO
Mol. Wt.: 330,2

11c

$C_{15}H_{21}IO$
Mol. Wt.: 344,23

11d

C₁₅H₂₁IO
Mol. Wt.: 344,23

11d

156.415
155.537

130.049
127.796
127.631
127.054
126.462
126.425
126.322
126.184
125.614
125.176
120.521
119.805
111.810
111.504

77.502
76.995
76.487
67.987
67.901

33.348
30.201
29.062
29.032
25.116
25.079
18.991
14.695
6.970
6.942