RSC Advances

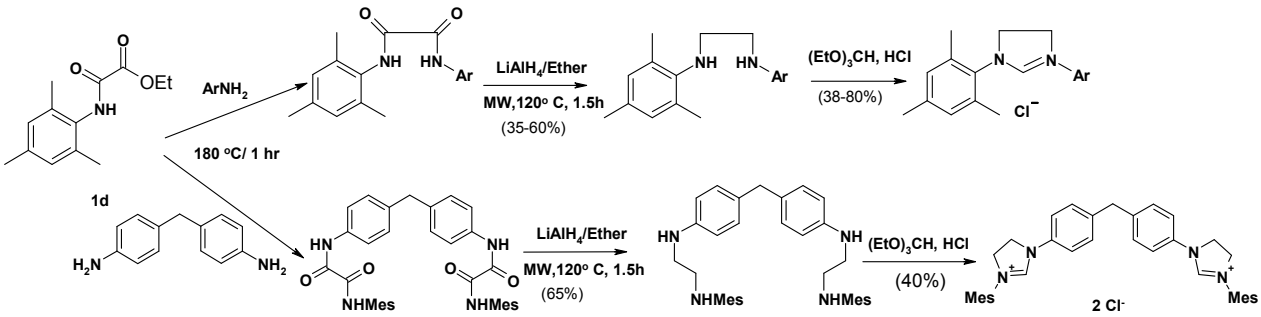
ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Graphical Abstract

Improved microwaves synthesis of unsymmetrical *N,N'*-diaryl-1,2-aminoethane and imidazolidinium salts as precursors of *N*-heterocyclic carbenes

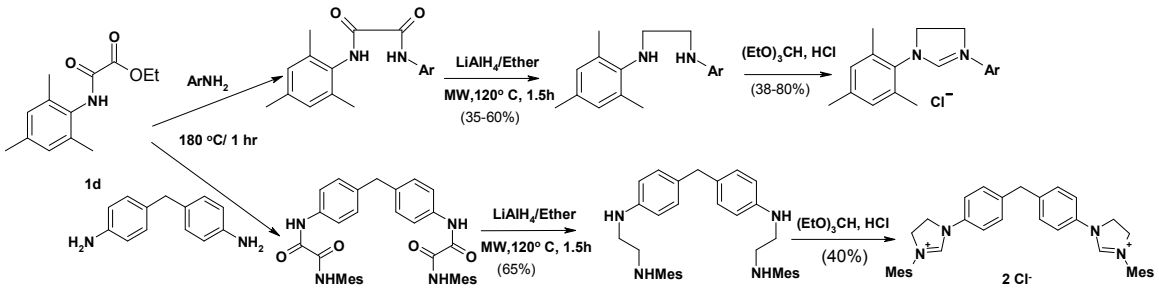
Yehia A. Ibrahim,* Nouria A. Al-Awadi, Talal F. Al-Azemi and Elizabeth John



Graphical Abstract

Improved microwaves synthesis of unsymmetrical *N,N'*-diaryl-1,2-aminoethane and imidazolidinium salts as precursors of *N*-heterocyclic carbenes

Yehia A. Ibrahim,* Nouria A. Al-Awadi, Talal F. Al-Azemi and Elizabeth John



Improved microwaves synthesis of unsymmetrical *N,N′*-diaryl-1,2-aminoethane and imidazolidinium salts as precursors of *N*-heterocyclic carbenes

Yehia A. Ibrahim,* Nouria A. Al-Awadi, Talal F. Al-Azemi and Elizabeth John

Address: Chemistry Department, Faculty of Science, Kuwait University, P.O. Box 5969, Safat 13060, Kuwait

Email: Yehia A. Ibrahim - yehia.ibrahim@ku.edu.kw

Abstract

Lithium aluminium hydride reduction of *bis*-unsymmetric-diaryloxamides **3** is difficult to accomplish especially for the sterically hindered mesityl derivative. Using microwaves LAH reduction of **3a,d** was successful in short time however, with cleavage of the ether linkage to give compounds **11a,d**. Extension of this method enabled the reduction of bis-oxamide derivatives **13** to the corresponding tetraamine derivative **14** which was then converted to the bis-imidazolidinium salt **15**. Application of this method led to rapid reduction of unsymmetric *N*,*N′*-diaryloxamides **16** to the corresponding *N*,*N′*-diarylethylenediamines **17** which were converted to their corresponding imidazolidinium salts **18**.

Keywords

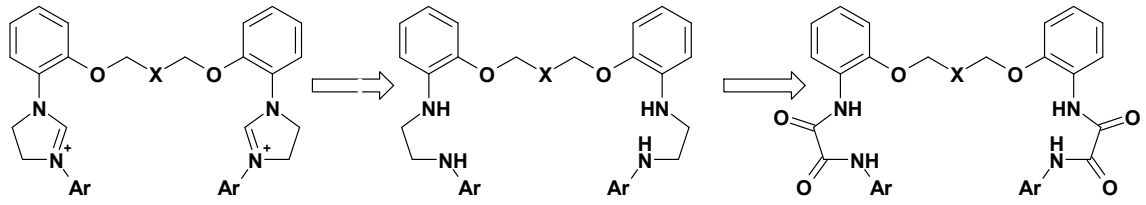
LAH reduction; microwaves; *N*,*N′*-diarylethylenediamines; imidazolidinium salts; bis-imidazolidinium salts

Introduction

Since their discovery, *N*-heterocyclic carbenes (NHCs) have attracted considerable attention due to their extensive applications as organocatalysts, ligands in

organometallic chemistry and in transition metal catalysis.[1-3] Increasing interests in the synthesis and applications of *N*-heterocyclic carbenes derived from imidazolium ions and related heterocyclic derivatives have been the subject of many recent papers and reviews.[1-10] Of important significance is their use as an alternative ligands to phosphines in the design of new organometallic catalysts of attractive important applications in metathesis and coupling reactions. The remarkable stability of transition metal complexes of NHC compared to their phosphine counterparts contributed considerably to the racent advances in the developments of these ligands and the design of new organometallic catalysts with wider application in organic chemistry. NHC act as excellent ligands forming complexes with palladium, ruthenium, nickel, rhodium, iridium, gold, copper and silver yielding useful organometallic catalysts. These organometallic catalysts were efficiently used in many catalytic reactions including olefin metathesis, transfer hydrogenation, Heck, Suzuki and Sonogashira coupling reactions, as well as many other homogeneous catalytic reactions.[1,7-10]

In this work we report our attempts to synthesize bis-imidazolidinium salts **1** to study their possible catalytic application as well as their potentialities in preparing bis-NHC for possible ligation with different metals. Scheme 1 illustrate the proposed reterosynthetic strategy for the synthesis of **1**.

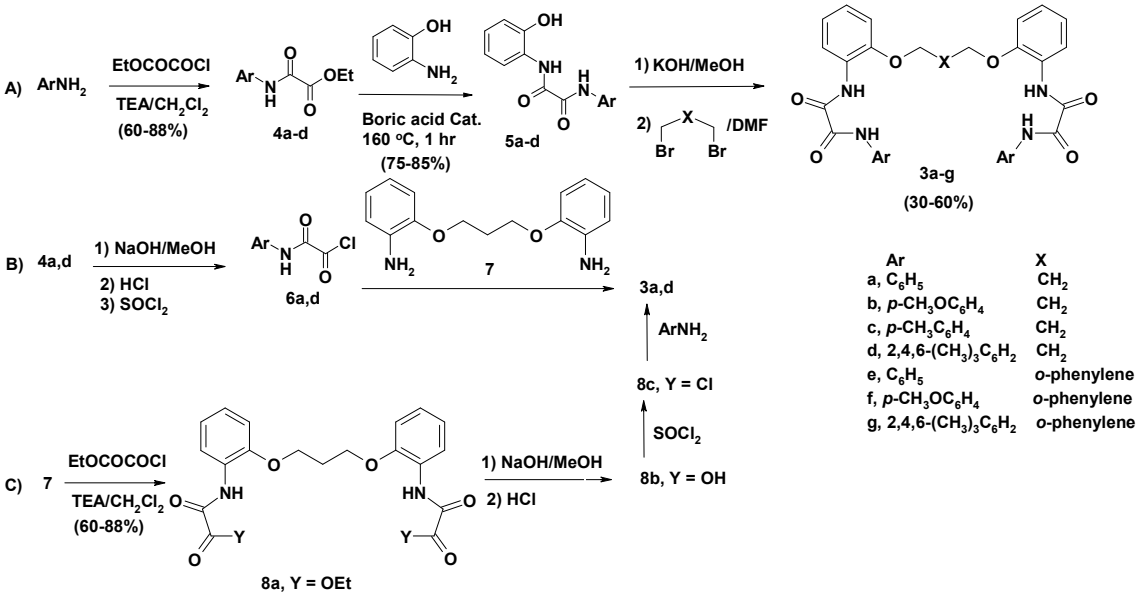


1 **2** **3**

Scheme 1

Results and Discussion

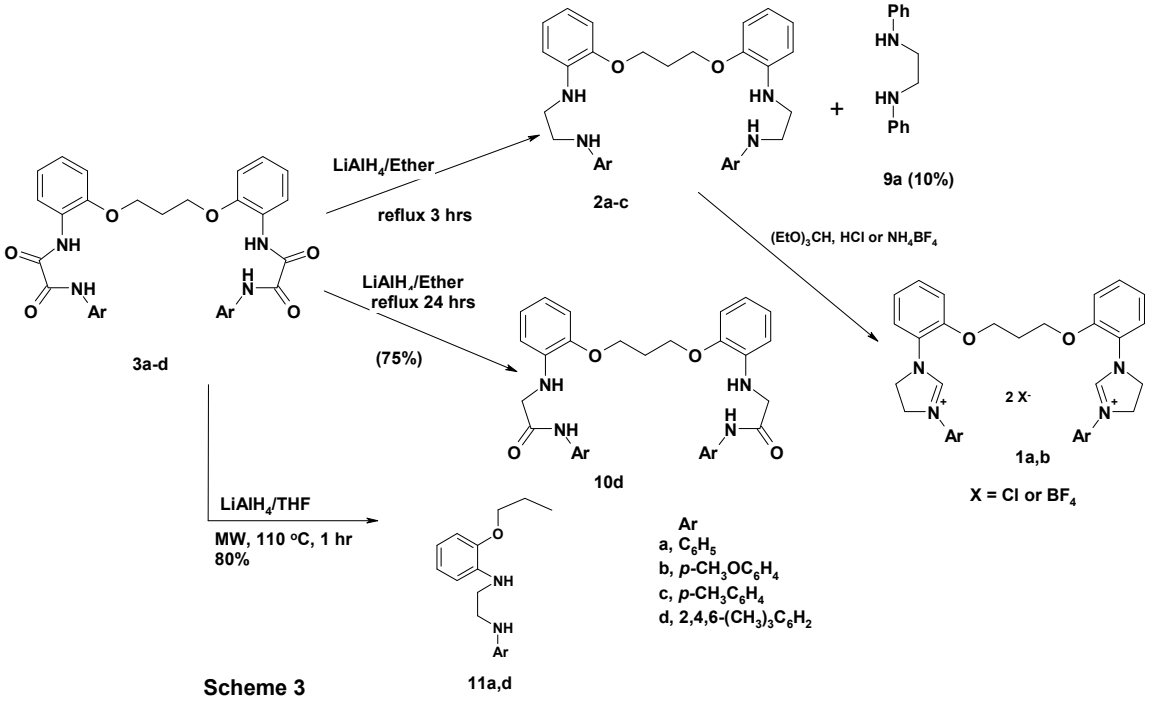
Scheme 2 illustrates the synthesis of the starting bis-oxamide derivatives **3**. Three different routes have been used for the synthesis of compounds **3** utilizing bis-alkylation of phenolic compounds (routes A) and traditional amidation methods (route B, C).



Scheme 2: Synthetic approaches of the tetra-amides 3a-g

Reduction of the tetraamides **3** has now been investigated in an attempt to synthesize the corresponding tetraamines **2** which are the precursors of target imidazolinium salts **1**. Scheme 3 illustrates the products **2, 9, 10, 11** obtained by lithium aluminum hydride reduction of bis-oxamide derivatives **3**. Thus, LAH reduction of **3a** in dry ether afforded the corresponding tetramine **2a**; which crystallized out from the ethereal solution; together with 1,2-dianilinoethane **9a** as minor by-product. Similar LAH reduction of **3b,c** yielded **2b,c**. On the other hand, LAH reduction of compound **3d** in refluxing ether gave only the bis-amide **10d** after 24 hrs. The high insolubility of the other bis-oxamides **3e-g** in refluxing ether or even THF led upon LAH reduction to the formation of complex mixture containing mainly unreacted starting materials.

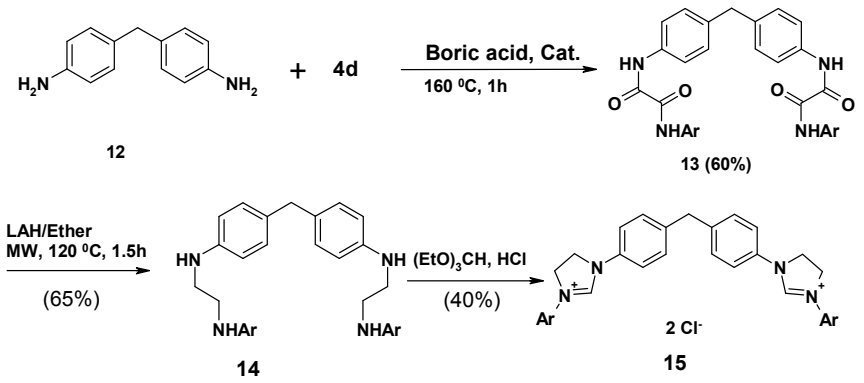
the conversion of **2a,b** into the target bis-imidazolinium salts **1a,b** has been readily achieved upon heating the hydrochloride salt **2a** with triethyl orthoformate at 110 ^{o}C for 24 h or by heating **2a,b** under reflux for 24 h in toluene with ammonium tetrafluoroborate and triethyl orthoformate with catalytic amount of formic acid.



Scheme 3

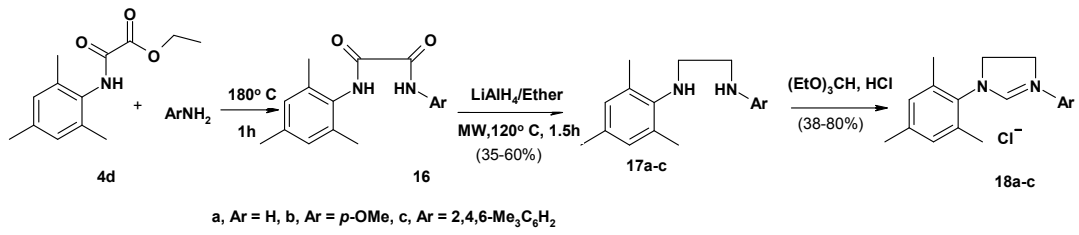
To overcome the difficulties in the LAH reduction of compounds **3c-g** we investigated the use of microwave reactors for achieving this reduction at higher temperature. Thus, heating each of **3a,d** with LAH in ether at 110 ^{o}C in microwave gave compounds **11a,d**. Although under this conditions all amide groups were successfully reduced to the corresponding amines, the compounds have also been reduced at the ether linkage. This method appears to be a short good method for sterically hindered oxamide derivatives. We therefore investigated the application of this microwaves LAH reduction procedure for the synthesis of many important imidazolium salts.

Scheme 4 illustrate the successful synthesis of the bis-imidazolium **15** starting with bis(4-aminophenyl)methane**12** using microwaves LAH reduction as the key step for obtaining the tetraamine **14**.



Scheme 4: Synthesis of bis-imidazolidinium salt 15. Ar = 2,4,6-$(CH_3)_3C_6H_2$

The same method has also been applied for the synthesis of many other simple imidazolinium salts **18a-c** (Scheme 5). The microwaves LAH reduction of asymmetric oxamides **16** give reasonable yield of the corresponding substituted 1,2-diaminoethane **17a-c** in short time compared to other reported conditions which requires very long refluxing time in high boiling solvent (DME).[12] Compounds **17a-c** were readily converted to the corresponding imidazolinium salts **18a-c**.



Scheme 5

Conclusion

In this work during our attempt to prepare bis-imidazolidinium salts we discovered an improved rapid application of microwaves in lithium aluminum hydride reduction of sterically hindered unsymmetric *N*,*N*′-diaryloxamides to the corresponding *N*,*N*′-diarylethylenediamines. This provides an expedient method to synthesize the

stericaly hindered *N,N'*-diaryl-1,2-diaminoethane thus facilitates the synthesis of many important imidazolidinium and bis-imidazolidinium salts which have many important applications specially as precursors of *N*-heterocyclic carbenes.

Experimental

General: All melting points are uncorrected. The microwave oven used was a single mode cavity explorer microwave (CEM Corporation, NC, USA) and irradiation was conducted in heavy-walled pyrex tubes (capacity 10 mL). IR spectra were recorded in KBr disks on a Perkin Elmer System 2000 FT-IR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 400, 400 MHz, Avance^{II} 600, 600 MHz super-conducting NMR spectrometers. Mass spectra were measured on GCMSDFS-Thermo and with LCMS using Agilent 1100 series LC/MSD with an API-ES/APCI ionization mode. Microanalyses were performed on LECO CH NS-932 Elemental Analyzer.

Synthesis of oxalamic acid ethyl ester: General procedure

To an ice cold (0-5 ^{o}C) stirred solution of substituted aniline (10 mmol) or compound **7** (5 mmol), and triethylamine (1 mL, 10 mmol) in DCM (30 mL) was added ethyl chlorooxoacetate (1.1 mL, 10 mmol) in DCM (10 mL). The reaction mixture was stirred for 1 h in ice and stirring was continued overnight at room temperature. The solvent was then removed in vacuo and the remaining precipitate was washed with water. The solid obtained was crystallized from ethanol to give the corresponding oxalamic esters **4a-d and 8a**.

N-Phenyloxalamic acid ethyl ester **4a.** Colorless crystals; yield 0.16 g (83%); mp 66 ^{o}C (lit. [13] mp 64-66 ^{o}C); δ_H(400 MHz, $CDCl_3$) 1.44 (t, 3H, *J* 7.2), 4.43 (q, 2H, *J* 7.2), 7.20 (t, 1H, *J* 7.6), 7.39 (t, 2H, *J* 8.0), 7.66 (d, 2H, *J* 8.0), 8.96 (s, 1H); δ_C($CDCl_3$, 100 MHz) 14.2, 64.0, 120.0, 125.7, 129.4, 136.5, 154.1, 161.2.

N-4-Methoxyphenyloxalamic acid ethyl ester **4b.** Colorless crystals; yield 0.19 g (85%); mp 100 ^{o}C (lit. [17] mp 100-104 ^{o}C); δ_H(400 MHz, $CDCl_3$) 1.42 (t, 3H, *J* 7.2), 3.80 (s, 3H), 4.41 (q, 2H, *J* 7.2), 6.90 (d, 2H, *J* 8.8), 7.56 (d, 2H, *J* 8.8), 8.80 (s, 1H); δ_C($CDCl_3$, 100 MHz) 14.2, 55.6, 63.8, 114.5, 121.6, 129.7, 153.9, 157.3, 161.3.

N-4-Tolyloxalamic acid ethyl ester **4c***.* Colorless crystals; yield 0.16 g (80%); mp 65-67 ^{o}C (lit. [17] mp 65-67 ^{o}C); δ_H(400 MHz, $CDCl_3$) 1.42 (t, 3H, *J* 7.2), 2.33 (s, 3H), 4.40 (q, 2H, *J* 7.2), 7.17 (d, 2H, *J* 8.4), 7.52 (d, 2H, *J* 8.4), 8.83 (s, 1H) ; δ_C($CDCl_3$, 100 MHz) 14.1, 21.1, 63.8, 120.0, 129.9, 134.0, 135.5, 154.0, 161.3.

N-(2,4,6-Trimethylphenyl)oxalamic acid ethyl ester **4d.** Colorless crystals; yield 0.14 g (90%); mp 77-78 ^{o}C (lit. [14] mp 76-78 ^{o}C); δ_H(400 MHz, $CDCl_3$) 1.44 (t, 3H, *J* 7.2), 2.20 (s, 6H), 2.28 (s, 3H), 4.43 (q, 2H, *J* 7.2), 6.92 (s, 2H), 8.35 (s, 1H); δ_C($CDCl_3$, 100 MHz) 14.2, 18.5, 21.1, 63.8, 129.3, 129.6, 134.9, 137.9, 155.0, 161.2.

N-(2-{3-[2-(Ethoxyoxalylamino)-phenoxy]-propoxy}-phenyl)oxalamic acid ethyl ester **8a.** Colorless crystals; yield 0.36 g (80%); mp 106 ^{o}C; ν_{max}(KBr)/cm^{-1} 3385, 3370, 2990, 2970, 2927, 2890, 1702, 1602, 1541, 1489, 1455, 1413, 1368, 1336, 1291,

1250, 1208, 1176, 1113, 1044, 1028, 1012, 748; 668; δ_H(400 MHz, $CDCl_3$) 1.42 (t, 6H, *J* 7.2), 2.45 (quint, 2H, *J* 6.0), 4.32-4.42 (m, 8H), 6.97-7.03 (m, 4H), 7.12 (dt, 2H, *J* 8.0, 1.2), 8.39 (dd, 2H, *J* 8.0, 1.2), 9.56 (s, 2H); δ_C($CDCl_3$, 100 MHz) 14.2, 29.4, 63.8, 65.2, 111.5, 120.1, 121.7, 125.5, 126.5, 147.7, 153.7, 161.2; *m/z* (EI) 455 (M^+); *m/z* (EI) 458.1683 (M^+, $C_{23}H_{26}N_2O_8$ requires 458.1683).

Synthesis of oxamides 5a-d: General procedure

A mixture of each of compounds **4a-d** (1 mmol), *o*-aminophenol (0.109 g, 1 mmol) and boric acid (0.005 g) was heated at 170 ^oC for 1 h. The solid obtained was boiled in ethanol and the insoluble solid was collected to give products **5a-d**.

N-2-Hydroxyphenyl-N'-phenyloxalamide **5a**. Brown powder; yield 0.19 g (75%); mp 263-264 ^oC (lit. [15] mp 261-262 ^oC); δ_H(400 MHz, DMSO) 6.89 (t, 1H, *J* 7.6), 6.95 (d, 1H, *J* 7.6), 7.02-7.04 (m, 1H), 7.18 (t, 1H, *J* 7.6), 7.39 (t, 2H, *J* 8.0), 7.87 (d, 2H, *J* 8.0), 8.16 (d, 1H, *J* 8.0), 8.12 (d, 1H, *J* 8.0), 9.88 (s, 1H), 9.89 (s, 1H) 10.41 (s, 1H), 10.42 (s, 1H), 10.86 (s, 1H), 10.95 (s, 1H); δ_C(DMSO, 100 MHz) 115.0, 115.1, 119.3, 119.7, 119.9, 120.5, 120.7, 124.65, 124.72, 124.8, 125.0, 125.3, 125.5, 128.8, 137.5, 137.7, 147.1, 147.3, 157.1, 157.2, 158.4, 158.6; *m/z* (EI) 256 (M^+); *m/z* (EI) 256.0842 (M^+, $C_{14}H_{12}N_2O_3$ requires 256.0842).

N-2-Hydroxyphenyl-N'-4-methoxyphenyloxalamide **5b**. Colorless powder; yield 0.23 g (80%); mp 216-217 ^oC; δ_H(400 MHz, DMSO) 3.75 (s, 3H), 6.88 (dt, 1H, *J* 6.8, 1.2), 6.95 (d, 2H, *J* 8.8), 7.03 (dt, 1H, *J* 7.2, 1.6), 7.77-7.80 (m, 2H), 8.17 (dd, 2H, *J* 8.0, 1.6), 9.89 (s, 1H), 10.41 (s, 1H), 10.86 (s, 1H); δ_C(DMSO, 100 MHz) 20.5, 115.1, 115.1, 119.3, 119.6, 119.9, 120.4, 120.5, 124.7, 125.0, 125.2, 125.6, 129.1, 133.7,

133.9, 134.9, 135.2, 147.1, 147.3, 157.1, 157.2, 158.1, 158.5; *m/z* (EI) 286 (M^+); *m/z* (EI) 286.0948 (M^+, $C_{15}H_{14}N_2O_4$ requires 286.0948).

N-2-Hydroxyphenyl-N'-4-tolyloxalamide **5c.** Brown powder; yield 0.14 g (52%); mp 228-229 ^oC (lit. [15] mp 221-222 ^oC); ν_{max}(KBr)/cm^{-1} 3339, 3243, 3220, 3126, 3036, 1658, 1610, 1593, 1534, 1458, 1375, 1283, 1228, 1195, 1100, 814, 745; δ_H(400 MHz, DMSO) 2.28 (s, 3H), 6.88 (dt, 1H, *J* 6.8, 1.2), 6.95 (d, 2H, *J* 8.8), 7.03 (dt, 1H, *J* 7.2, 1.6), 7.77-7.80 (m, 2H), 8.17 (dd, 2H, *J* 8.0, 1.6), 9.90 (s, 1H) 10.42 (s, 1H), 10.88 (s, 1H); δ_C(DMSO, 100 MHz) 20.5, 115.0, 115.1, 119.3, 119.6, 119.9, 120.4, 120.5, 124.7, 125.0, 125.2, 125.6, 129.1, 133.7, 133.9, 134.9, 135.2, 147.1, 147.3, 157.1, 157.2, 158.1, 158.5; *m/z* (EI) 270 (M^+); *m/z* (EI) 270.0999 (M^+, $C_{15}H_{14}N_2O_3$ requires 270.0999).

N-2-Hydroxyphenyl-N'-mesityloxalamide **5d**. Colorless crystals; yield 0.2 g (70%); mp 196 ^oC (lit. [14] mp 196 ^oC); ν_{max}(KBr)/cm^{-1} 3371, 3262, 2953, 2921, 2860, 1668, 1601, 1518, 1457, 1358, 1283, 1225, 1102, 1039, 853, 752, 736, 710; δ_H(400 MHz, DMSO) 2.12 (s, 6H), 2.25 (s, 3H), 6.89 (dt, 1H, *J* 1.2, 8.0), 6.92 (s, 2H), 6.96 (dd, 1H, *J* 8.0, 1.6), 7.03 (dt, 1H, *J* 1.6, 8.0), 8.21 (dd, 1H, *J* 8.0, 1.6), 9.84 (s, 1H), 10.41 (s, 1H), 10.45 (s, 1H); δ_C(DMSO, 100 MHz) 18.0, 20.5, 115.0, 119.4, 125.0, 128.4, 131.4, 134.8, 136.2, 146.9, 157.1, 158.7. *m/z* (EI) 298 (M^+); *m/z* (EI) 298.1312 (M^+, $C_{17}H_{18}N_2O_3$ requires 298.1312).

Synthesis of oxalamic acids: General procedures

To a solution of NaOH (0.12g, 3.0 mmol) in EtOH was added each of **4a,d** and **8a** (1 mmol). The mixture was stirred overnight. The solvent was then removed in vacuo

and the remaining mixture was acidified with drops of dilute HCl. The solid obtained was filtered to give the oxalamic acid.

Phenyloxalamic acid. Colorless crystals; yield 0.12 g (70%); mp 149-150 ^{o}C; ν_{max}(KBr)/cm^{-1} 3445, 3408, 3303, 1767, 1686, 1602, 1547, 1497, 1448, 1352, 1312, 1244, 1214, 1181, 1167, 1028, 938, 897, 754, 740, 721, 687; δ_H(400 MHz, $CDCl_3$) 7.12 (t, 1H, *J* 7.2), 7.34 (t, 2H, *J* 8.0), 7.76 (d, 2H, *J* 8.0), 8.17 (br, 1H), 10.67 (s, 1H); δ_C($CDCl_3$, 100 MHz) 120.1, 126.6, 129.7, 135.6, 155.1, 160.2; *m/z* (EI) 165 (M^+); *m/z* (EI) 165.0421 (M^+, $C_8H_7NO_3$ requires 165.0420).

Mesityloxalamic acid. Colorless crystals; yield 0.19 g (90%); mp 106 ^{o}C; ν_{max}(KBr)/cm^{-1} 3527, 3395, 3364, 3316, 3275, 1713, 1657, 1606, 1531, 1484, 1377, 1313, 1234, 847, 736, 707; δ_H(400 MHz, $CDCl_3$) 1.42 (t, 6H, *J* 7.2), 2.45 (quint, 2H, *J* 6.0), 4.32-4.42 (m, 8H), 6.97-7.03 (m, 4H), 2.18 (s, 6H), 2.29 (s, 3H), 6.92 (s, 2H), 8.51 (s, 1H); δ_C($CDCl_3$, 100 MHz) 18.3, 20.9, 129.1, 129.2, 134.5, 138.1, 156.8, 160.8; *m/z* (EI) 207 (M^+); *m/z* (EI) 207.0888 (M^+, $C_{11}H_{13}NO_3$ requires 207.0889).

N-(2-{3-[2-(Oxalylamino)phenoxy]-propoxy}-phenyl)-oxalamic acid **8b**. Colorless crystals; yield 0.39 g (96%); mp 214 ^{o}C; ν_{max}(KBr)/cm^{-1} 3375, 3358, 3294, 3275, 2970, 2928, 2895, 1761, 1686, 1604, 1543, 1498, 1459, 1346, 1316, 1292, 1264, 1224, 1212, 1118, 991, 781, 751, 690; δ_H(400 MHz, DMSO) 2.28 (quint, 2H, *J* 6.0), 4.31 (t, 4H, *J* 6.4), 7.00-6.96 (m, 2H), 7.14 (m, 4H), 8.06 (d, 2H, *J* 7.6), 9.73 (s, 2H), 14.39 (s, 2H); δ_C($CDCl_3$, 100 MHz) 28.5, 65.1, 112.2, 120.3, 120.7, 125.5, 126.0, 148.3, 155.6, 161.9; *m/z* (EI) 402 (M^+); *m/z* (EI) 402.1054 (M^+, $C_{19}H_{18}N_2O_8$ requires 402.1058).

Synthesis of *Arylamino-oxoacetyl chloride*: **General procedures**

A mixture of the appropriate oxalamic acid (1 mmol), thionyl chloride (2 mL) and one drop DMF was heated at 80 ^{o}C for 40 min. The excess thionyl chloride was evaporated to give the corresponding acid chlorides **6a,d and 8c**.

Anilino-oxoacetyl chloride **6a.** Colorless solid; yield 0.07 g (40%);mp 156-157 ^{o}C; ν_{max}(KBr)/cm^{-1} 3303, 3145, 3092, 3068, 3049, 1767, 1685, 1602, 1548, 1497, 1450, 1352, 1326, 1312, 1247, 1212, 1166, 938, 753, 734, 700; *m/z* (EI) 183 (M^+); *m/z* (EI) 183.0082 (M^+, $C_8H_6ClNO_2$ requires 183.0082).

Mesitylamino-oxoacetyl chloride **6d.** Colorless solid; yield 0.1 g (45%); mp 175-176 ^{o}C; ν_{max}(KBr)/cm^{-1} 3323, 3197, 2979, 2960, 2921, 2861, 1770, 1696, 1528, 1483, 1444, 1378, 1342, 1305, 1235, 1208, 1178, 1037, 945, 921, 854, 842, 803, 726, 704, 662; *m/z* (EI) 225 (M^+); *m/z* (EI) 225.0552 (M^+, $C_{11}H_{12}ClNO_2$ requires 225.0551).

(2-{3-[2-(Chlorooxalylamino)-phenoxy]propoxyphenylamino}-oxoacetyl chloride **8c.** Colorless powder; yield 0.4 g (90%); mp 272 ^{o}C; ν_{max}(KBr)/cm^{-1} 3346, 3296, 1776, 1710, 1691, 1601, 1535, 1492, 1457, 1291, 1257, 1222, 1207, 1120, 994, 981, 750, 651; δ_H(400 MHz, $CDCl_3$) 2.45 (quint, 2H, *J* 6.0), 4.33 (t, 4H, *J* 6.0), 6.98 (dd, 2H, *J* 8.0, 1.2), 7.04 (dt, 2H, *J* 1.2, 7.8), 7.18 (dt, 2H, *J* 1.6, 8.0), 8.33 (dd, 2H, *J* 8.0, 1.6), 9.15 (s, 2H); δ_C($CDCl_3$, 100 MHz) 29.2, 65.2, 111.5, 120.3, 121.8, 125.6, 126.5, 147.8, 151.1, 169.3; *m/z* (EI) 438 (M^+); *m/z* (EI) 438.0378 (M^+, $C_{19}H_{16}Cl_2N_2O_6$ requires 438.0379).

Synthesis of oxamides 3a-g: General procedures

Method A: To a solution of KOH (0.3 g, 5.4 mmol) in MeOH (15 mL) was added each of compounds **5a-d** (0.15 g, 5.9 mmol). The mixture was stirred at room temperature

for 10 min and the solvent was then removed in vacuo. To the mixture was added DMF (1 mL) and the appropriate dibromo derivatives (2.8 mmol). The reaction mixture was heated at 120 ^{o}C for 2 h. After cooling, water (20 mL) was added and the solid obtained was collected, boiled with ethanol and the insoluble solid was collected washed with cold ethanol and dried to give the corresponding oxamides **3a-g**.

Method B: To a solution of NaOH (0.12 g, 3.0 mmol) in ethanol was added each of compounds **4a,d** (1.2 mmol) or **8a** (0.6 mmol). The mixture was stirred overnight. The ethanol was evaporated and the mixture was acidified with drops of dilute HCl. The solid obtained was collected and dried to give the corresponding oxalamic acid or bis-oxalamic acid **8b**. A mixture of the latter acid (1.2 mmol), thionyl chloride (2 mL) and one drop DMF was heated at 80 ^{o}C for 40 min. The excess thionyl chloride was evaporated to give the corresponding acid chloride **6a,d** or **8c**. To an ice cold (0-5 ^{o}C) stirred solution of **7** (0.5 mmol) or the appropriate aromatic amine (1 mmol), and triethylamine (4 mmol) in DCM (30 mL) was added the the appropriate acid chloride **6a,d** (1 mmol) or **8c** (0.5 mmol) in DCM (10 mL). The reaction mixture was stirred overnight at room temperature. The solvent was removed in vacuo and remaining precipitate was washed with water and recrystallized from ethanol to give the corresponding product **3a,d**.

Anilino-oxoacetyl chloride **6a.** Colorless solid; yield 0.12 g (70%);mp 156-157 ^{o}C; ν_{max}(KBr)/cm^{-1} 3303, 3145, 3092, 3068, 3049, 1767, 1685, 1602, 1548, 1497, 1450, 1352, 1326, 1312, 1247, 1212, 1166, 938, 753, 734, 700; δ_H(400 MHz, DMSO-d_6) 7.13 (t, 1H, *J* 7.8), 7.35 (t, 2H, *J* 8.0), 7.76 (d, 2H, *J* 8.0), 10.71 (s, 1H); δ_C(DMSO-d_6, 100 MHz) 120.4, 124.6, 128.8, 137.7, 157.1, 162.2; *m/z* (EI) 183 (M^+); *m/z* (EI) 183.0082 (M^+, $C_8H_6ClNO_2$ requires 183.0082).

Oxo-(2,4,6-trimethylphenylamino)acetyl chloride **6d.** Colorless solid; yield 0.1 g (45%); mp 175-176 ^{o}C; ν_{max}(KBr)/cm^{-1} 3323, 3197, 2979, 2960, 2921, 2861, 1770, 1696, 1528, 1483, 1444, 1378, 1342, 1305, 1235, 1208, 1178, 1037, 945, 921, 854, 842, 803, 726, 704, 662; δ_H(400 MHz, DMSO-d_6) 2.09 (s, 6H), 2.23 (s, 3H), 6.90 (s, 2H), 10.12 (s, 1H); δ_C(DMSO-d_6, 100 MHz) 17.8, 20.5, 128.3, 131.3, 134.7, 136.1, 157.2, 162.2; *m/z* (EI) 225 (M^+); *m/z* (EI) 225.0552 (M^+, $C_{11}H_{12}ClNO_2$ requires 225.0551).

N-(2-{3-[2-(Oxalylamino)phenoxy]-propoxy}-phenyl)-oxalamic acid **8b**. Colorless crystals; yield 0.39 g (96%); mp 214 ^{o}C; ν_{max}(KBr)/cm^{-1} 3375, 3358, 3294, 3275, 2970, 2928, 2895, 1761, 1686, 1604, 1543, 1498, 1459, 1346, 1316, 1292, 1264, 1224, 1212, 1118, 991, 781, 751, 690; δ_H(400 MHz, DMSO-d_6) 2.28 (quint, 2H, *J* 6.0), 4.31 (t, 4H, *J* 6.4), 7.00-6.96 (m, 2H), 7.14 (m, 4H), 8.06 (d, 2H, *J* 7.6), 9.73 (s, 2H), 14.39 (s, 2H); δ_C($CDCl_3$, 100 MHz) 28.5, 65.1, 112.2, 120.3, 120.7, 125.5, 126.0, 148.3, 155.6, 161.9; *m/z* (EI) 402 (M^+); *m/z* (EI) 402.1054 (M^+, $C_{19}H_{18}N_2O_8$ requires 402.1058).

(2-{3-[2-(Chlorooxalylamino)-phenoxy]propoxyphenylamino}-oxoacetyl chloride **8c.** Colorless powder; yield 0.4 g (90%); mp 272 ^{o}C; ν_{max}(KBr)/cm^{-1} 3346, 3296, 1776, 1710, 1691, 1601, 1535, 1492, 1457, 1291, 1257, 1222, 1207, 1120, 994, 981, 750, 651; δ_H(400 MHz, $CDCl_3$) 2.45 (quint, 2H, *J* 6.0), 4.33 (t, 4H, *J* 6.0), 6.98 (dd, 2H, *J* 8.0, 1.2), 7.04 (dt, 2H, *J* 1.2, 7.8), 7.18 (dt, 2H, *J* 1.6, 8.0), 8.33 (dd, 2H, *J* 8.0, 1.6), 9.15 (s, 2H); δ_C($CDCl_3$, 100 MHz) 29.2, 65.2, 111.5, 120.3, 121.8, 125.6, 126.5, 147.8, 151.1, 169.3; *m/z* (EI) 438 (M^+); *m/z* (EI) 438.0378 (M^+, $C_{19}H_{16}Cl_2N_2O_6$ requires 438.0379).

N-Phenyl-N'-{2-[3-o-(phenylaminooxalylaminophenoxy)propoxy]phenyl}oxamide **3a.** Colorless crystals; yield 0.22 g (40%, method A), 0.36 g (67%, method B), 0.32 g (59%, method C); mp 202 ^{o}C; ν_{max}(KBr)/cm^{-1} 3317, 3288, 3058, 2952, 2931, 1666, 1597, 1520, 1487, 1457, 1442, 1421, 1398, 1321, 1290, 1258, 992, 745, 727, 689; δ_H(400 MHz, $CDCl_3$) 2.49 (quint, 2H, *J* 6.0), 4.40 (t, 4H, *J* 6.0), 7.14-6.98 (m, 6H), 7.21 (tt, 2H, *J* 7.2, 0.8), 7.41 (t, 4H, *J* 8.4), 7.67 (dd, 4H, *J* 8.8, 1.2), 8.36 (dd, 2H, *J* 8.0, 1.6), 9.32 (s, 2H, NH), 10.01 (s, 2H, NH); δ_C($CDCl_3$, 100 MHz) 29.4, 65.3, 112.0, 119.9, 120.0, 121.6, 125.65, 125.67, 126.3, 129.5, 136.5, 148.2, 157.4, 157.8; *m/z* (EI) 552 (M^+); *m/z* (EI) 552.2003 (M^+, $C_{31}H_{28}N_4O_6$ requires 552.2003).

N-p-Methoxyphenyl-N'-{2-[3-o-(p-methoxyphenylaminooxalylaminophenoxy)propoxy]-phenyl}oxamide **3b.** Colorless crystals; yield 0.27 g (45%); mp 219-221 ^{o}C; δ_H(400 MHz, DMSO-d_6) 2.33 (quint, 2H, *J* 6.0), 3.74 (s, 6H), 4.37 (t, 4H, *J* 6.0), 6.94 (dd, 3H, *J* 9.2, 2.8), 7.01 (t, 2H, *J* 7.6), 7.12 (dd, 2H, *J* 8.0, 1.2), 7.20 (d, 2H, *J* 7.6), 7.75 (d, 3H, *J* 9.2), 8.19 (dd, 2H, *J* 7.6, 1.2), 10.00 (s, 2H), 10.68 (s, 2H), 10.82 (s, 2H); δ_C($CDCl_3$, 100 MHz) 28.6, 55.2, 65.3, 112.4, 119.4, 120.9, 121.9, 122.1, 125.3, 126.1, 130.5, 130.8, 149.0, 157.4, 158.3; *m/z* (EI) 612 (M^+); *m/z* (EI) 612.2213 (M^+, $C_{33}H_{32}N_4O_8$ requires 612.2214).

N-p-Methylphenyl-N'-{2-[3-o-(p-methylphenylaminooxalylaminophenoxy)propoxy]-phenyl}oxamide **3c.** Colorless crystals; yield 0.17 g (30%); mp 231-232 ^{o}C; ν_{max}(KBr)/cm^{-1} 3341, 3316, 2954, 2939, 2918, 2888, 1678, 1604, 1595, 1525, 1487, 1452, 1407, 1292, 1257, 1239, 1207, 1113, 1060, 1045, 995, 979, 872, 820, 744, 722; δ_H(400 MHz, DMSO-d_6) 2.29 (s, 6H), 2.35 (quint, 2H, *J* 6.0), 4.39 (t, 4H, *J* 6.4), 7.02 (dt, 2H, *J* 0.8, 8.0), 7.13 (dt, 2H, *J* 1.6, 8.0), 7.18 (d, 4H, *J* 8.0), 7.22 (dt, 2H, *J*

1.2, 8.0), 7.75 (d, 4H, *J* 8.4), 8.20 (dd, 2H, *J* 8.0, 1.6), 10.01 (s, 2H, NH), 10.88 (s, 2H, NH); δ_C(DMSO-d_6, 100 MHz) 20.6, 28.7, 65.3**,** 112.5, 119.5, 120.6, 121.0, 125.4, 126.1, 129.2, 134.0, 135.0, 148.1, 157.3, 158.1; *m/z* (EI) 580 (M^+); *m/z* (EI) 580.2315 (M^+, $C_{33}H_{32}N_4O_6$ requires 580.2316).

N-Mesityl-N'-{2-[3-o-(mesitylaminooxalylaminophenoxy)propoxy]-phenyl}oxamide **3d.** Colorless crystals; yield 0.38 g (60%, method A), 0.27 g (42%, method B), 0.22 g (35%, method C); mp 220 ^oC; ν_{max}(KBr)/cm^{-1} 3357, 3290, 2953, 2922, 2885, 2859, 1677, 1600, 1539, 1510, 1485, 1453, 1330, 1289, 1254, 1113, 1043, 789, 748, 731, 712; δ_H(400 MHz, $CDCl_3$) 2.21 (s, 12H), 2.30 (s, 6H), 2.39 (quint, 2H, *J* 6.0), 4.32 (t, 4H, *J* 6.0), 6.94 (s, 4H), 6.96-7.09 (m, 6H), 8.36 (d, 2H, *J* 8.0), 8.78 (s, 2H, NH), 10.00 (s, 2H, NH); δ_C($CDCl_3$, 100 MHz) 18.5, 21.1, 29.4, 64.7, 111.7, 119.7, 121.4, 125.5, 126.3, 129.3, 129.9, 135.0, 137.9, 148.1, 157.3, 158.7; *m/z* (EI) 636 (M^+); *m/z* (EI) 636.2942 (M^+, $C_{37}H_{40}N_4O_6$ requires 636.2942).

N-Phenyl-N'-[o-(o-phenylaminooxalylaminophenoxymethyl)benzyloxyphenyl]-oxamide **3e.** Buff powder; yield 0.43 g (70%); mp 274-275 ^oC; ν_{max}(KBr)/cm^{-1} 3362, 3063, 3034, 2920, 1687, 1600, 1526, 1481, 1445, 1383, 1330, 1295, 1251, 1204, 1113, 1041, 1013, 751, 710, 692; δ_H(400 MHz, DMSO-d_6) 5.47 (s, 4H), 7.01 (t, 2H, *J* 7.6), 7.10 (dt, 2H, *J* 8.0, 1.2), 7.16 (t, 2H, *J* 7.6), 7.28 (d, 2H, *J* 8.0), 7.37 (t, 4H, *J* 8.0), 7.44-7.46 (m, 2H), 7.66-7.68 (m, 2H), 7.83 (t, 4H, *J* 8.0), 8.18 (dd, 2H, *J* 8.0, 1.6), 10.01 (s, 2H), 10.92 (s, 2H); δ_C(DMSO-d_6, 100 MHz) 67.8, 112.7, 119.8, 120.7, 121.0, 124.8, 125.3, 126.0, 128.4, 128.66, 128.7, 134.7, 137.4, 147.9, 157.3, 158.2; *m/z* (EI) 614 (M^+); *m/z* (EI) 614.2160 (M^+, $C_{36}H_{30}N_4O_6$ requires 614.2160).

N-p-Methoxyphenyl-N'-{o-[o-(p-methoxyphenylamino)oxalylaminophenoxymethyl]-benzyloxyphenyl}-oxamide **3f.** Buff precipitate; yield 0.44 g (65%); mp 220-221 ^{o}C; ν_{max}(KBr)/cm^{-1} 3358, 3295, 2932, 2835, 1684, 1599, 1525, 1481, 1454, 1415, 1249, 1205, 1159, 1111, 1033, 827, 750; δ_H(400 MHz, $CDCl_3$) 3.81 (s, 6H), 5.35 (s, 4H), 6.90-7.00 (m, 6H), 7.03-7.07 (m, 4H), 7.42-7.44 (m, 2H), 7.56-7.61 (m, 6H), 8.35 (dd, 2H, *J* 6.0, 1.2), 9.19 (s, 2H), 9.93 (s, 2H); δ_C($CDCl_3$, 100 MHz) 55.7, 69.1, 112.2, 114.5, 120.1, 121.47, 121.54, 121.7, 125.6, 126.4, 129.2, 129.4, 129.7, 134.5, 147.9, 157.2, 157.6; *m/z* (EI) 674 (M^+); *m/z* (EI) 674.2371 (M^+, $C_{38}H_{34}N_4O_8$ requires 674.2371).

N-Mesityl-N'-[o-(o-mesitylaminooxalylaminophenoxymethyl)benzyloxyphenyl]-oxamide **3g.** Buff crystals; yield 0.38 g (55%); mp 150-151 ^{o}C; ν_{max}(KBr)/cm^{-1} 3358, 3295, 2952, 2920, 2861, 1685, 1647, 1600, 1509, 1479, 1452, 1380, 1253, 1202, 1113, 1011, 851, 750; δ_H(400 MHz, DMSO-d_6) 2.19 (s, 12H), 2.29 (s, 6H), 5.31 (s, 4H), 6.92 (s, 4H), 6.98-7.05 (m, 6H), 7.34-7.39 (m, 2H), 7.48-7.51 (m, 2H), 8.39 (d, 2H, *J* 8.4), 8.76 (s, 2H), 9.93 (s, 2H); δ_C($CDCl_3$, 100 MHz) 18.5, 21.1, 69.1, 112.1, 119.9, 121.7, 125.6, 126.4, 129.0, 129.2, 129.3, 129.8, 134.3, 134.9, 137.8, 147.9, 157.4, 158.4; *m/z* (EI) 698 (M^+); *m/z* (EI) 698.3099 (M^+, $C_{42}H_{42}N_4O_6$ requires 698.3098).

Synthesis of diamine 2: General procedure

A solution of lithium aluminum hydride (0.5 g, 14 mmol) in dry diethyl ether (20 mL) was stirred for 5 min. Compound **3a-d** (0.9 mmol) was added and the solution was refluxed for 4-24 h. After cooling to room temperature, the reaction mixture was quenched with water (0.5 mL), 15 % aqueous NaOH (0.5 mL) and the ethereal solution was collected. After removal of the solvent in vacuo, the remaining mixture

was crystallized from ethanol to give the corresponding amine derivatives **2a-c**, **10**. The mother liquor from crystallization of **2a** was subjected to column chromatography using silca gel and elution with petroleum ether (40-60) and ethyl acetate to give compound **9**.

Bis-ethane-1,2-diamine **2a.** Colorless crystals; yield 0.38 g (78%); mp 83-85^{o}C; ν_{max}(KBr)/cm^{-1} 3049, 3021, 2951, 2925, 2876, 2854, 1601, 1509, 1468, 1442, 1323, 1255, 1211, 1135, 1054, 741, 693; δ_H(400 MHz, $CDCl_3$) 2.26 (quint, 2H, *J* 6.0), 3.38 (s, 8H), 4.16 (t, 4H, *J* 6.0), 4.19 (br, 4H, NH), 6.60 (dd, 4H, *J* 8.0, 0.8), 6.67-6.74 (m, 6H), 6.79 (d, 2H, *J* 7.6), 6.90 (dt, 2H, *J* 1.6, 8.0), 7.17 **(**t, 4H, *J* 8.0); δ_C($CDCl_3$, 100 MHz) 29.4, 43.3, 43.4, 63.4, 110.6, 111.1, 113.2, 117.3, 117.8, 121.8, 129.4, 138.2, 146.3, 148.1; *m/z* (EI) 496 (M^+); *m/z* (EI) 496.2832 (M^+, $C_{31}H_{36}N_4O_2$ requires 496.2833).

Bis-ethane-1,2-diamine **2b**. Colorless crystals; yield 0.4 g (72%); mp 132-133 ^{o}C; ν_{max}(KBr)/cm^{-1} 3372, 3350, 3046, 3021, 2947, 2937, 2876, 2882, 1601, 1508, 1468, 1442, 1323, 1258, 1211, 1133, 1054, 736, 690; δ_H(400 MHz, $CDCl_3$) 2.32 (quint, 2H, *J* 5.6), 3.36 (m, 8H), 3.74 (s, 6H), 4.18 (t, 4H, *J* 5.6), 4.67 (br, 4H, NH), 6.65 (dt, 2H, *J* 1.2, 7.6), 6.68 (d, 4H, *J* 8.8), 6.75-6.80 (m, 8H), 6.88 (dt, 2H, *J* 1.2, 7.6); δ_C($CDCl_3$, 100 MHz) 29.4, 43.2, 44.7, 56.0, 65.4, 110.5, 111.2, 115.05, 115.08, 117.1, 121.8, 138.3, 141.7, 146.3, 152.8; *m/z* (EI) 556 (M^+); *m/z* (EI) 556.3044 (M^+, $C_{33}H_{40}N_4O_4$ requires 556.3050).

Bis-ethane-1,2-diamine **2c**. Colorless crystals; yield 0.13 g (25%); mp 101-102 ^{o}C; ν_{max}(KBr)/cm^{-1} 3399, 3034, 2919, 2875, 1601, 1516, 1469, 1444, 1254, 1218, 1131, 1051, 908, 809, 772, 738; δ_H(400 MHz, $CDCl_3$) 2.25 (s, 6H), 2.33 (t, 2H, *J* 6.0), 3.37-

3.42 (m, 8H), 4.17 (t, 4H, *J* 6.0), 4.17 (br, 4H, NH), 6.63-6.71 (m, 8H), 6.79 (d, 2H, *J* 1.2, 6.8), 6.87 (dt, 2H, *J* 1.2, 7.6), 7.00 (d, 4H, *J* 8.4); δ_C(100 MHz, DMSO-d_6) 20.7, 29.5, 42.7, 45.6, 66.0, 110.7, 111.5, 115.5, 117.5, 121.8, 129.6, 130.0, 130.2, 138.0, 146.6; *m/z* (EI) 524 (M^+); *m/z* (EI) 524.3146 (M^+, $C_{33}H_{40}N_4O_2$ requires 524.3146).

N,N'-Diphenylethane-1,2-diamine **9a.** Colorless solid; yield 0.05 g (10%); mp 63-65 ^oC (lit. [16] mp 63-65 ^oC); δ_H(400 MHz, $CDCl_3$) 3.41 (s, 4H), 3.80 (br, 2H, NH), 6.68 (d, 4H, *J* 8.4), 6.76 (t, 2H, *J* 7.6), 7.22 (d, 4H, *J* 8.0); δ_C($CDCl_3$, 100 MHz) 43.4, 113.2, 118.0, 129.5, 148.2; *m/z* (EI) 212 (M^+).

N-Mesityl-2-o-{3-[o-(Mesitylcarbamoylmethylamino)phenoxy]propoxy}phenylamino-acetamide **10d**. Colorless crystals; yield (0.45 g, 75%); mp213-21^4 ^oC; ν_{max}(KBr)/cm^{-1} 3270, 3064, 3035, 2954, 2920, 2879, 1650, 1602, 1513, 1485, 1463, 1450, 1446, 1260, 1218, 1129, 1063, 1054, 854, 734; δ_H(400 MHz, $CDCl_3$) 2.11 (s, 12H), 2.24 (s, 6H), 2.42 (quint, 2H, *J* 6.0), 3.96 (s, 4H), 4.28 (t, 4H, *J* 6.0), 4.99 (br, 2H, NH), 6.70 (dd, 2H, *J* 7.6, 1.2), 6.78 (dt, 2H, *J* 8.0, 1.2), 6.85 (s, 4H), 6.86 (m, 2H), 6.92 (dt, 2H, *J* 8.0, 1.2), 8.00 (s, 2H, NH); δ_C($CDCl_3$, 100 MHz) 18.6, 21.1, 29.6, 49.1, 65.2, 110.9, 111.4, 119.0, 121.9, 129.1, 130.7, 135.2, 137.1, 137.2, 146.2, 169.4; *m/z* (EI) 608 (M^+); *m/z* (EI) 608.3357 (M^+, $C_{37}H_{44}N_4O_4$ requires 608.3357).

Synthesis of Bis-imidazolinium salts 1a,b.

Method A: HCl gas is passed for 20 min to diethylether and this solution was added to the above compound **2a** (0.1 mmol) in ether. A solid forms and to this solid, triethylorthoformate (4 mL) was added and heated at 110 ^oC for 24 h. The triethylorthoformate was decanted and the product was washed with ether.

Method B: A mixture of the bisamine **2a,b** (0.1 mmol), ammonium tetrafluoroborate (0.4 mmol), triethylorthoformate (4 mL), 2 drops of formic acid in toluene (10 mL) was heated under reflux for 24 h. The triethylorthoformate was decanted and the product was washed with ether.

Bis-imidazolinium **1a, X = Cl**. Buff solid; yield 0.045 g (85%); mp 150-151 ^{o}C; ν_{max}(KBr)/cm^{-1} 3336, 3045, 2930, 2884, 1674, 1620, 1591, 1498, 1460, 1270, 1222, 1124, 1045, 987, 958, 754; δ_H(400 MHz, DMSO-d_6) 2.35 (quint, 2H, *J* 6.0), 4.33 (t, 4H, *J* 6.0), 4.57 (s, 8H), 7.13 (t, 2H, *J* 7.6), 7.27 (d, 2H, *J* 7.6), 7.37 (t, 2H, *J* 7.2), 7.42 (t, 2H, *J* 7.6), 7.52 (t, 4H, *J* 7.6), 7.57 (d, 4H, *J* 7.6), 7.62 (dd, 4H, *J* 7.6, 1.2), 9.81 (s, 2H). δ_C(100 MHz, DMSO-d_6) 28.3, 48.3, 50.8, 65.8, 113.6, 118.1, 121.1, 124.7, 124.9, 126.9, 129.1, 130.0, 136.1, 151.5, 154.6; *m/z* (EI) 519.2754 (M^+, $C_{33}H_{36}{}^{35}Cl_2N_4O_2$ –HCl_2 requires 519.2754).

Bis-imidazolinium 1a, X = BF_4. Buff solid; yield 0.045 g (75%); mp 118-119 ^{o}C; ν_{max}(KBr)/cm^{-1} 3335, 3079, 2952, 1676, 1627, 1592, 1548, 1499, 1437, 1290, 1262, 1223, 1053, 758. δ_H(400 MHz, DMSO-d_6) 2.35 (quint, 2H, *J* 6.0), 4.33 (t, 4H, *J* 6.0), 4.57 (s, 8H), 7.09-7.15 (m, 2H), 7.21-7.28 (m, 2H), 7.37-7.39 (m, 2H), 7.42 (t, 2H, *J* 7.6), 7.51-7.54 (m, 8H), 7.61 (d, 2H, *J* 7.6), 9.81 (s, 2H); δ_C(100 MHz, DMSO-d_6) 28.3, 48.4, 50.8, 65.8, 113.6, 118.1, 121.2, 124.8, 124.9, 127.0, 129.8, 130.1, 136.1, 151.5, 154.6; *m/z* (FAB) 606 (M^+); *m/z* (EI) 606.2898 (M^+, $C_{33}H_{36}N_4O_2.BF_4$ requires 606.2898).

bis-imidazolinium 1b, X = BF_4. Buff powder; yield 0.05 g (82%); mp 142-143 ^{o}C; δ_H(400 MHz, DMSO-d_6) 2.35 (quint, 2H, *J* 6.0), 3.75 (s, 6H), 4.31 (t, 4H, *J* 6.0), 4.53 (s, 8H), 6.65-7.12 (m, 16H), 7.48 (d, 2H, *J* 9.2), 9.57 (s, 2H). δ_C(DMSO-d_6, 100 MHz)

28.9, 48.9, 50.6, 55.5, 65.7, 114.1, 119.9, 121.7, 123.7, 125.2, 129.1, 129.7, 138.4, 141.5, 145.8, 154.0; *m/z* (ESI) 666 (M^+, $C_{35}H_{40}N_4O_4.BF_4$ requires 666).

Synthesis of diamine 11: General procedure

To a solution of lithium aluminum hydride (0.05 g, 14 mmol) in dry diethyl ether (2 ml) was added compound **3a,d** (0.1 mmol) and the solution was heated at 110 ^oC in the microwave for 1 h. After cooling to room temperature, the reaction was quenched by adding H_2O (0.05 ml), 15 % aqueous NaOH and small amount of water. The white precipitate was filtered and the product was extracted with ether to give compound **11**.

N-Phenyl-N'-(2-propoxyphenyl)-ethane-1,2-diamine **11a.** Buff precipitate; yield 0.21 g (80%); mp 69-70 ^oC; ν_{max}(KBr)/cm^{-1} 3061, 3050, 3024, 2963, 2933, 2903, 2873, 1597, 1506, 1476, 1466, 1443, 1390, 1307, 1262, 1253, 1221, 1210, 1181, 1141, 1116, 1043, 1017, 906, 869, 745, 736, 692; δ_H(400 MHz, $CDCl_3$) 1.04 (t, 3H, *J* 7.4), 1.83 (sixtet, 2H, *J* 6.8), 3.44 (s, 4H), 3.96 (t, 2H, *J* 6.4), 4.34 (br, 2H, NH), 6.67 (dd, 2H, *J* 2.4, 8.0), 6.69-6.81 (m, 4H), 6.89 (dt, 1H, *J* 1.2, 7.6), 7.21 (tt, 2H, *J* 2.0, 8.0); δ_C($CDCl_3$, 100 MHz) 10.8, 22.8, 43.26, 43.34, 69.1, 110.3, 110.8, 113.1, 117.1, 117.8, 121.3, 129.4, 138.1, 146.5, 148.2; *m/z* (EI) 270 (M^+); *m/z* (EI) 270.1726 (M^+, $C_{17}H_{22}N_2O$ requires 270.1727).

N-Mesityl-N'-(2-propoxyphenyl)-ethane-1,2-diamine **11d.** Colorless oil; yield 0.25 g (80%); δ_H(400 MHz, $CDCl_3$) 1.05 (t, 3H, *J* 7.2), 1.83 (sixtet, 2H, *J* 7.2), 2.23 (s, 3H), 2.27 (s, 6H), 3.22 (t, 2H, *J* 6.0), 3.36 (t, 2H, *J* 6.0), 3.96 (t, 2H, *J* 6.0), 4.14 (br, 2H, NH), 6.64-6.71 (m, 2H), 6.77-6.88 (m, 4H); *m/z* (EI) 312 (M^+); *m/z* (EI) 312.2196 (M^+, $C_{20}H_{28}N_2O$ requires 312.2196).

Preparation of compound 13-18.

A mixture of compound **4d** (5.17 g, 2.2 mmol), diamine **12, substituted aniline** (1 mmol) and boric acid (0.05 g) was heated at 180 ^{o}C for 1 h. The solid obtained was recrystallised from DMF to give product **13, 16a-c**. To a solution of lithium aluminum hydride (0.05 g, 14 mmol) in dry diethyl ether (2 ml) was added compounds **13, 16a-c** (0.1 mmol) and the solution was heated at 120 ^{o}C in the microwave for 1.5 h. After cooling to room temperature, the white precipitate was filtered off and the product was extracted with ether. Removal of the solvent in vacuo gave the corresponding amino derivatives **14, 17a-c** which was used in the next step without further purification. HCl gas was passed for 20 min to ether and this ether solution was added to the above compound **14, 17a-c** (0.25 g) in ether. A solid forms and to this solid, triethylorthoformate (4 mL) was added and heated at 110 ^{o}C for 24 h. Excess triethylorthoformate was decanted and the product obtained was washed with ether to give the corresponding imidazolidinium chloride **15**, **18a-c**.

N-Mesityl-N'-(4-{4-[(mesitylaminooxalyl)-amino]-benzyl}-phenyl)-oxamide **13**. Colorless crystals; yield 0.34 g (60%); mp 294-295 ^{o}C; ν_{max}(KBr)/cm^{-1} 3260, 3036, 2918, 2855, 1668, 1641, 1593, 1512, 1497, 1462, 1435, 1412, 1377, 1313, 1238, 1178, 1117, 1018, 847, 816, 787, 739; δ_H(400 MHz, DMSO-d_6) 2.12 (s, 12H), 2.25 (s, 6H), 3.91 (s, 2H), 6.92 (s, 4H),7.23 (d, 4H, *J* 8.4), 7.78 (d, 4H, *J* 8.4),10.29 (s, 2H, NH), 10.71 (s, 2H, NH); δ_C(DMSO-d_6, 100 MHz) 17.9, 20.5, 39.9, 120.6, 128.4, 128.9, 131.5, 134.8, 135.7, 136.1, 137.6, 158.4, 158.9; *m/z* (EI) 576 (M^+); *m/z* (EI) 576.2731 (M^+, $C_{35}H_{36}N_4O_4$ requires 576.2731).

N-Mesityl-N'-(4-{4-[2-(mesitylamino)-ethylamino]-benzyl}-phenyl)-1,2-ethanediamine **14**. Colorless oil; yield 0.03 g (65%); ν_{max}(KBr)/cm^{-1} 3371, 3005, 2941, 2916, 2853, 1614, 1578, 1518, 1483, 1468, 1437, 1410, 1319, 1308, 1254, 1231, 1217, 1180, 1130, 1103, 1030, 1013, 854, 808, 756; δ_H(400 MHz, $CDCl_3$) 2.25 (s, 12H), 2.28 (s, 6H), 3.21 (s, 4H), 3.36 (s, 4H), 3.80 (s, 2H), 3.87 (br, 4H, NH), 6.60 (d, 4H, *J* 8.0),

6.84 (s, 4H), 7.01 (d, 4H, *J* 8.0); δ_C(100 MHz, $CDCl_3$) 18.5, 20.7, 40.3, 44.6, 48.2, 113.4, 129.75, 129.77, 130.2, 131.4, 132.4, 142.2, 146.3; *m/z* (EI) 520 (M^+); *m/z* (EI) 520.3560 (M^+, $C_{35}H_{44}N_4$ requires 520.3560).

Bis-imidazolidinium dichloride **15.** Green solid; yield 0.02 g (40%); mp 226-227 ^oC; ν_{max}(KBr)/cm^{-1} 3028, 2974, 2917, 2860, 1659, 1624, 1603, 1512, 1497, 1479, 1294, 1265, 1227, 1026, 989, 856, 814, 785; δ_H(400 MHz, $CDCl_3$) 2.24 (s, 6H), 2.30 (s, 12H), 3.75 (s, 4H), 4.37 (s, 4H), 4.74 (s, 2H), 6.89 (s, 4H), 7.03 (d, 4H, *J* 8.0), 7.58 (d, 4H, *J* 8.0), 10.41 (s, 2H); δ_C(100 MHz, $CDCl_3$) 18.3, 21.3, 40.7, 49.5, 51.6, 119.0, 130.1, 130.3, 130.9, 134.1, 135.1, 139.9, 140.5, 156.4; *m/z* (EI) 542 (M^+); *m/z* (EI) 541.3326 (M^+, $C_{37}H_{42}Cl_2N_4$ –HCl_2 requires 541.3325).

N-Phenyl-N'-mesityloxamide **16a.** Colorless crystals; yield 0.028 g (86%); mp 239 ^oC; ν_{max}(KBr)/cm^{-1} 3268, 3060, 3043, 3015, 2952, 2923, 2869, 1665, 1599, 1508, 1442, 1381, 1314, 1253, 1232, 1176, 1079, 1033, 877, 850, 782, 745, 711, 686. δ_H(400 MHz, $CDCl_3$) 2.22 (s, 3H), 2.30 (s, 6H), 6.94 (s, 2H), 7.22 (t, 1H, *J* 7.6), 7.39 (t, 2H, *J* 7.6), 7.68 (d, 2H, *J* 7.6), 8.86 (s, 1H), 9.38 (s, 1H); δ_C($CDCl_3$, 100 MHz) 18.5, 21.1, 120.0, 125.6, 129.3, 129.37, 129.41, 129.8, 134.9, 136.6, 137.9, 157.7, 158.6; *m/z* (EI) 282.1363 (M^+, $C_{17}H_{18}N_2O_2$ requires 282.1363).

N-(p-methoxyphenyl)-N'-mesityloxamide **16b.** Colorless crystals; yield 0.02 g (64%); mp 223-224 **^oC;** ν_{max}(KBr)/cm^{-1} 3330, 3294, 3001, 2955, 2921, 2834, 1669, 1612, 1597, 1511, 1495, 1467, 1440, 1414, 1379, 1304, 1247, 1230, 1172, 1112, 1034, 847, 825, 783, 769, 706. δ_H(400 MHz, $CDCl_3$) 2.21 (s, 3H), 2.30 (s, 6H), 3.82 (s, 3H), 6.88 (d, 2H, *J* 8.8), 6.94 (s, 2H), 7.60 (d, 2H, *J* 8.8), 8.90 (s, 1H), 9.37 (s, 1H);

δ_C($CDCl_3$, 100 MHz) 18.5, 21.1, 55.6, 114.5, 121.5, 129.3, 129.8, 129.9, 134.9, 137.8, 157.3, 157.4, 158.7; *m/z* (EI) 312.1468 (M^+, $C_{18}H_{20}N_2O_3$ requires 312.1468).

N,N'-Bis-Mesityloxamide **16c.** Colorless crystals; yield 0.020 g (61%); mp 280-281 **°C;** ν_{max}(KBr)/cm^{-1} 3197, 3006, 2975, 2919, 2876, 1671, 1535, 1489, 1459, 1443, 1389, 1258, 1035, 1019, 850, 801, 760, 703. δ_H(400 MHz, $CDCl_3$) 2.24 (s, 6H), 2.30 (s, 12H), 6.94 (s, 4H), 8.81 (s, 2H); δ_C($CDCl_3$, 100 MHz) 18.6, 21.1, 129.2, 129.8, 134.8, 137.8, 158.4; *m/z* (EI) 324.1832 (M^+, $C_{20}H_{24}N_2O_2$ requires 324.1832).

N-Mesityl-N'-phenyl-1,2-ethanediamine **17a**.[17] Colorless oil; yield 0.08 g (35%); ν_{max}(KBr)/cm^{-1} 3402, 3050, 3019, 2997, 2943, 2916, 2855, 1603, 1505, 1484, 1431, 1321, 1255, 1230, 1213, 1179, 1154, 1124, 1029, 992, 855, 749, 692; δ_H(400 MHz, $CDCl_3$) 2.23 (s, 3H), 2.28 (s, 6H), 3.22 (t, 2H, *J* 5.6), 3.39 (t, 2H, *J* 5.6), 6.66 (d, 2H, *J* 8.4), 6.73 (t, 1H, *J* 7.6), 6.83 (s, 2H), 7.19 (t, 2H, *J* 7.6); δ_C(CDCl3, 100 MHz) 18.4, 20.6, 44.7, 47.8, 113.2, 117.8, 129.4, 129.6, 130.0, 131.8, 143.1, 148.3; *m/z* (EI) 254.1777 (M^+, $C_{17}H_{22}N_2$ requires 254.1777).

N-Mesityl-N'-p-methoxyphenyl-1,2-ethanediamine **17b.** Colorless oil; yield 0.017 g (60%); δ_H(400 MHz, $CDCl_3$) 2.29 (s, 3H), 2.31 (s, 6H), 3.22 (s, 2H), 3.32 (s, 2H), 3.40 (br, 2H, NH), 3.80 (s, 3H), 6.67 (d, 2H, *J* 8.8), 6.85 (d, 2H, *J* 8.8), 6.87 (s, 2H); δ_C($CDCl_3$, 100 MHz) 18.5, 20.7, 45.5, 48.1, 55.9, 114.6, 115.0, 129.7, 130.2, 132.1, 142.4, 142.6, 152.5; *m/z* (EI) 284.1883 (M^+, $C_{18}H_{24}N_2O$ requires 284.1883).

N,N'-Dimesityl-1,2-ethanediamine **17c**.[12, 17] Colorless oil; yield 0.22 g (75%); δ_H(400 MHz, $CDCl_3$) 2.23 (s, 6H), 2.28 (s, 12H), 3.15 (s, 4H), 6.87 (s, 4H); δ_C(CDCl3, 100

MHz) 21.4, 22.9, 50.4, 132.3, 133.3, 137.9, 138.7; *m/z* (EI) 296.2247 (M^+, $C_{20}H_{28}N_2$ requires 296.2247).

1-Mesityl-3-Phenyl-4,5-dihydro-1H-imidazolidinium chloride **18a.** Colorless crystals; yield 0.014 g (55%); mp 293 ^oC; ν_{max}(KBr)/cm^{-1} 2964, 2879, 1622, 1595, 1489, 1291, 1269, 754; δ_H(400 MHz, $CDCl_3$) 2.30 (s, 3H), 2.34 (s, 6H), 4.34 (t, 2H, *J* 10.4), 4.67 (t, 2H, *J* 10.4), 7.10 (s, 2H), 7.37 (t, 1H, *J* 7.6), 7.60-7.52 (m, 4H), 9.77 (s, 1H); δ_C(DMSO-d_6, 100 MHz) 17.3, 20.6, 48.5, 50.7, 118.0, 126.6, 129.4, 129.7, 131.2, 135.5, 136.2, 139.7, 156.1; *m/z* (FAB) 265 (M, $C_{18}H_{21}N_2$ requires 265).

1-Mesityl-3-p-Methoxyphenyl-4,5-dihydro-1H-imidazolidinium chloride **18b.** Colorless crystals; yield 0.012 g (42%); mp 267 ^oC; ν_{max}(KBr)/cm^{-1} 3000, 2913, 2838, 1622, 1520, 1498, 1292, 1272, 1255, 1187, 1036, 831, 748; δ_H(400 MHz, $CDCl_3$) 2.26 (s, 3H), 2.34 (s, 6H), 3.79 (s, 3H), 4.36 (t, 2H, *J* 10.0), 4.72 (t, 2H, *J* 10.0), 6.90-6.96 (m, 4H), 7.72 (d, 2H, *J* 8.4), 10.49 (s, 1H); δ_C($CDCl_3$, 100 MHz) 17.3, 20.6, 49.0, 50.6, 55.6, 114.7, 119.8, 120.0, 129.3, 131.2, 135.5, 139.5, 155.5, 157.9; *m/z* (FAB) 295 (M + 1, $C_{19}H_{23}N_2O$ requires 295).

1,3-Bis-mesityl-4,5-dihydro-1H-imidazolidinium chloride **18c.** Colorless crystals, yield 0.027 g (70%); mp 302-303 ^oC (lit. [11] mp > 250 ^oC); δ_H(400 MHz, $CDCl_3$) 2.26 (s, 6H), 2.35 (s, 12H), 4.53 (s, 4H), 6.91 (s, 4H), 9.31 (s, 1H); δ_C($CDCl_3$, 100 MHz) 17.5, 20.8, 49.4, 50.9, 55.9, 115.1, 120.3, 129.7, 135.8, 155.7, 158.3.

Acknowledgements

Support from the University of Kuwait, received through Research Grant no. SC10/09 and facilities of GF-S (grant no. GS01/01, GS02/01, GS01/03, GS01/05) are gratefully acknowledged.

References

1. Marion, N.; Diez-Gonzalez, S.; Nolan, S. P. *Angew. Chem. Int. Ed.* **2007**, *46*, 2988-3000.
2. Enders, D.; Niemeier, O.;Henseler, A. *Chem. Rev.* **2007**, *107*, 5606.
3. Enders, D.; Balensiefer, T. *Acc. Chem. Res.* **2004**, *37*, 534.
4. Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000,** *100*, 39-91.
5. Herrmann, W. A. *Angew. Chem. Int. Ed.* **2002**, *41*, 1290-1309.
6. Peris, E., Crabtree, R. H. *Coordination Chemistry Reviews,* **2004**, *248*, 2239-2246.
7. Crudden, C. M., Allen, D. P. *Coordination Chemistry Reviews,* **2004**, *248*, 2247-2273.
8. Nolan, S. P., Ed. **2006**, N-Heterocyclic Carbenes in Transition Metal Catalysis; Wiley-VCH: Weinheim, Germany.
9. Glorius, F. Ed., **2007**, N-Heterocyclic Carbenes in Transition Metal Catalysis; Springer: Berlin.
10. Kantchev, E. A. B.; O'Brien, C. J.; Organ, M. J. *Angew. Chem. Int. Ed.* **2007,** *46*, 2768-2813.
11. Bhanu, B.A.; Prasad; Gilbertson, Scott R. *Org. Lett.* **2009,** *11*, 3710-3713.
12. Chung, C. K.; Grubbs, R. H. *Org. Lett.* **2008,** *10*, 2693-2696.

13. Kim, Yu, Mi; Kim, Sung Hwan; Kim Jae Nyoung. *Bull. Korean Chem. Soc.* **2010**, 31(6), 1765-1768.

14. Waltman, A. W; Grubbs, R. H. *Organometallics*, **2004**, 23(13), 3105-3107.

15. Fr. 1968, FR 1516276 A1 19680308.

16. Ismailov, V.M. *Russ. J. Org. Chem*. **2004**, 40(2), 284-285.

17. Vehlow, K.; Gessler, S.; Blechert, S. *Angew. Chem. Int. Ed.* **2007**, *46*, 8082-8085; Roche, S. P.; Teyssot, M. L.; Gautier, A. *Tetrahedron Lett.* **2010**, *51*, 1265-1268.