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Supporting Information For:

Efficient and Versatile Catalysis of *N*-alkylation of Heterocyclic Amines with Alcohols and One-pot Synthesis of 2-aryl Substituted Benzazoles with Newly Designed Ruthenium(II) Complexes of PNS Thiosemicarbazones

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1. Spectra for all the ligands and complexes:

1.1 ¹H NMR spectra for ligands and complexes:

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Figure S1: ¹H NMR for ligand **PNS-H**



Figure S2: ¹H NMR for ligand **PNS-Me**



Figure S3: ¹H NMR for ligand **PNS-Ph**



Figure S4: ¹HNMR for Ru(II) complex 1



Figure S5: ¹H NMR for Ru(II) complex **2**



Figure S6: ¹H NMR for Ru(II) complex **3**



Figure S7: 1 H NMR for Ru(II) complex 4



Figure S8: 1 H NMR for Ru(II) complex **5**

Figure S9: ¹H NMR for Ru(II) complex 6

1.2¹³C NMR spectra for ligands and complexes:

Figure S10: ¹³C NMR for ligand PNS-H

Figure S11: ¹³C NMR for ligand **PNS-Me**

Figure S12: ¹³C NMR for ligand **PNS-Ph**

Figure S14: ¹³C NMR for Ru(II) complex 2

Figure S15: ¹³C NMR for Ru(II) complex **3**

Figure S16: ¹³C NMR for Ru(II) complex 4

Figure S17: ¹³C NMR for Ru(II) complex 5

Figure S18: ¹³C NMR for Ru(II) complex 6

1.3 ³¹P NMR spectra for complexes:

Figure S19: ³¹P NMR for Ru(II) complex 1

Figure S20: ³¹P NMR for Ru(II) complex **2**

Figure S21: ³¹P NMR for Ru(II) complex **3**

Figure S22: ³¹P NMR for Ru(II) complex 4

Figure S23: ³¹P NMR for Ru(II) complex **5**

Figure S24: ³¹P NMR for Ru(II) complex **5**

1.4 ESI-MASS spectra for complexes

Figure S25: ESI-MS for Ru(II) complex 1

Figure S26: ESI-MS for Ru(II) complex 2

Figure S27: ESI-MS for Ru(II) complex **3**

Figure S28: ESI-MS for Ru(II) complex 4

Figure S29: ESI-MS for Ru(II) complex 5

Figure S30: ESI-MS for Ru(II) complex 6

2 Calalysis:

2.1 General Information:

Thin-layer chromatography (TLC) was performed on Merck 1.05554 aluminum sheets precoated with silica gel 60 F254, and the spots were visualized with UV light at 254 nm or under iodine. Column chromatography purifications were performed by using Merck silica gel 60 (0.063-0.200 mm). ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were taken in CDCl₃ at room temperature with a Bruker AV400 instrument with chemical shifts relative to tetramethylsilane. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. GC-Mass was performed using a JEOL GCMATE II GC-MS system. Unless otherwise stated, all reagents and solvents were purchased from commercial suppliers and used without further purification.

2.2 General experimental procedure for alkylation of (hetero)aromatic amines and amide with alcohols

A typical procedure is as follows. To a stirred suspension of ruthenium(II) catalyst (0.5 mol %) and KOH (4 mmol) in toluene (5 mL) were added alcohol (2.0 mmol), amine/amide (2.0 mmol) at room temperature and then temperature was raised to 100 °C for 12 h. Upon completion (as monitored by TLC), the reaction mixture was cooled at ambient temperature, H₂O (3 mL) was added and the organic layer was extracted with CH₂Cl₂ (3 × 10 mL). The combined organic layers were dried with magnesium sulphate and concentrated. The crude product was analyzed by GC-MS or purified by Column chromatography (n-hexane/ EtOAc). Reported isolated yields are an average of two runs.

2.3 Direct amination of 2-nitropyridine with benzyl alcohol

To a stirred suspension of ruthenium(II) catalyst (0.5 mol %) and KOH (4 mmol) in toluene (5 mL) were added benzyl alcohol (12.0 mmol), 2-nitropyridine (2.0 mmol) at room temperature and then temperature was raised to 100 °C for 12 h. Upon completion (as monitored by TLC), the reaction mixture was cooled at ambient temperature, H_2O (3 mL) was added and the organic layer was

extracted with CH_2Cl_2 (3 × 10 mL). The The combined organic layers were dried with magnesium sulphate and concentrated. The crude product was analyzed by GC-MS or purified by Column chromatography (n-hexane/ EtOAc). Reported isolated yields are an average of two runs.

2.4 General experimental procedure for alkylation of hetero aromatic diamine with alcohols

To a stirred suspension of ruthenium(II) catalyst (0.1 mol %) and KOH (4 mmol) in toluene (5 mL) were added alcohol (4 mmol), diamine (2.0 mmol) at room temperature and then temperature was raised to 120 °C for 12 h. Upon completion (as monitored by TLC), the reaction mixture was cooled at ambient temperature, H₂O (3 mL) was added and the organic layer was extracted with CH₂Cl₂ (3 × 10 mL). The combined organic layers were concentrated *in vacuo* and the crude product was analyzed by GC-MS or purified by Column chromatography over silica-gel (n-hexane/ethyl acetate). Reported isolated yields are an average of two runs.

2.5 General experimental procedure for the one-pot synthesis of 2-substituted benzazoles

To a stirred suspension of ruthenium catalyst (0.5 mol %) and KOH (4 mmol) in toluene (5 mL) were added alcohol (3 mmol), *o*-substituted aniline (2.0 mmol) at room temperature and then temperature was raised to 120 °C for 24 h. Upon completion (as monitored by TLC), the reaction mixture was cooled at ambient temperature, H₂O (3 mL) was added and the organic layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were concentrated *in vacuo* and the crude product was analyzed by GC-MS or purified by Column chromatography (n-hexane/EtOAc). Reported isolated yields are an average of two runs.

2.6 Characterization data of compounds 1a-e, 2a-e, 3a-e, 4a-e, 5a-e, 6a-f, 7a-n.

N-Benzylpyridin-2-amine (1a):

The title compound (1a) was synthesized according to the general procedure, using 2-aminopyridine (2.0 mmol) and benzyl alcohol (2.0 mmol). 1a was isolated by column chromatography (SiO₂; hexane/EtOAc, 80:20) as a colorless solid (92 %). ¹H NMR (400MHz, CDCl₃): $\delta = 8.08$ (d, J = 5.1 Hz, 1H), 7.44–7.24 (m, 6H), 6.57 (t, J = 5.9 Hz, 1H), 6.37 (d, J = 8.4 Hz, 1H), 4.78 (bs, 1H), 4.43 (d, J = 5.8 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): $\delta = 158.7$, 148.6, 139.5, 137.6, 128.6, 127.5, 127.4, 113.4, 107.2, 46.7. Data agrees with literature values.¹

N-(4-Methylbenzyl)pyridin-2-amine (1b):

The title compound (**1b**) was synthesized according to the general procedure, using 2-aminopyridine (2.0 mmol) and 4-methylbenzyl alcohol (2.0 mmol). **1b** was isolated by column chromatography (SiO₂; hexane/EtOAc, 60:40) as a colorless solid (92 %). ¹H NMR (400MHz, CDCl₃): $\delta = 8.07$ (d, J = 5.0 Hz, 1H), 7.39 (t, J = 7.9 Hz, 1H), 7.24 (d, J = 5.9 Hz, 2H), 7.17 (d, J = 7.9 Hz, 2H), 6.57 (t, J = 6.4 Hz, 1H), 6.38 (d, J = 8.4 Hz, 1H), 4.84 (bs, 1H), 4.43, (d, J = 5.2 Hz, 2H)2.34 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): $\delta = 158.8$, 148.4, 137.2, 136.3, 129.5, 127.5, 113.4, 107.0, 46.4, 21.3. Data agrees with literature values.²

N-(4-Methoxybenzyl)pyridin-2-amine (1c):

The title compound (1c) was synthesized according to the general procedure, using 2-aminopyridine (2.0 mmol) and 4-methoxybenzyl alcohol (2.0 mmol). 1c was isolated by column chromatography (SiO₂; hexane/EtOAc, 50:50) as a colorless solid (81 %). ¹H NMR (400MHz, CDCl₃): δ = 8.08 (d, *J* = 5.5 Hz, 1H), 7.37 (t, *J* = 8 Hz, 1H), 7.28 (d, *J* = 7.9 Hz, 1H), 7.23 (t, *J* = 8.1 Hz, 2H), 6.87 (t, *J* = 6.1 Hz, 1H), 6.54 (t, *J* = 6.1 Hz, 1H) 6.38 (d, *J* = 8.4 Hz, 1H), 4.94 (bs, 1H), 4.47 (d, *J* = 6.3 Hz 2H), 3.85 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ = 159.2, 157.9, 148.2, 137.5, 128.9, 129.6, 127.4, 120.6, 113.1, 110.3, 106.8, 55.6, 41.8. Data agrees with literature values.²

N-(4-Chlorobenzyl)pyridin-2-amine (1d):

The title compound (1d) was synthesized according to the general procedure, using 2-aminopyridine (2.0 mmol) and 4-chlorobenzyl alcohol (2.0 mmol). 1d was isolated by column chromatography (SiO₂; hexane/EtOAc, 50:50) as a colorless solid (96 %). ¹H NMR (400MHz, CDCl₃): $\delta = 8.09$ (d, J = 4.9 Hz, 1H), 7.41–7.24 (m, 5H), 6.57 (d, J = 7.1 Hz, 1H), 6.32 (d, J = 8.4 Hz, 1H), 4.86 (s, 1H), 4.45 (d, J = 4.1 Hz 2H). ¹³C NMR (100 MHz, CDCl₃): $\delta = 158.5$, 148.7, 138.1, 137.6, 133.0, 129.0, 128.8, 113.3, 107.0, 45.8. Data agrees with literature values.²

N-(4-Bromobenzyl)pyridin-2-amine (1e):

The title compound (1e) was synthesized according to the general procedure, using 2-aminopyridine (2.0 mmol) and 4-bromobenzyl alcohol (2.0 mmol). 1e was isolated by column chromatography (SiO₂; hexane/EtOAc, 60:40) as a colorless solid (93 %). ¹H NMR (400MHz, CDCl₃): $\delta = 8.10$ (d, J = 4.5 Hz, 1H), 7.40–7.26 (m, 5H), 6.57 (d, J = 7.3 Hz, 1H), 6.38 (d, J = 8.4 Hz, 1H), 4.72 (bs, 1H), 4.55 (d, J = 4.4 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): $\delta = 157.1$, 148.4, 138.1, 137.9, 133.9, 129.4, 128.5, 111.7, 113.1, 107.8, 46.9. Data agrees with literature values.²

N-Benzylpyrimidin-2-amine (2a):

The title compound (**2a**) was synthesized according to the general procedure, using 2-aminopyrimidine (2.0 mmol) and benzyl alcohol (2.0 mmol). **2a** was isolated by column chromatography (SiO₂; hexane/EtOAc, 90:10); Yield 97 %; ¹H NMR (400MHz, CDCl₃): $\delta = 8.22-8.10$ (m, 2H), 7.48 (m, 1H), 7.41–7.32 (m, 2H), 7.21 (d, J = 7.9 Hz, 1H), 6.61 (m, 2H), 5.24 (bs, 1H), 4.69 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): $\delta = 167.6$, 162.9, 158.9, 128.9, 127.9, 127.6, 113.7, 110.4, 107.8, 46.9.

N-(4-Methylbenzyl)pyrimidin-2-amine (2b):

The title compound (**2b**) was synthesized according to the general procedure, using 2-aminopyrimidine (2.0 mmol) and 4methylbenzyl alcohol (2.0 mmol). **2b** was isolated by column chromatography (SiO₂; hexane/EtOAc, 90:10); Yield 86 %; ¹H NMR (400MHz, CDCl₃): $\delta = 8.32-8.10$ (m, 2H), 7.43–7.31 (m, 2H), 7.27–7.11 (m, 1H), 6.43-6.31 (m, 1H), 6.22 (d, J = 7.9 Hz, 1H), 5.32 (bs, 1H), 4.61 (s, 2H), 2.24 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): $\delta = 168.0$, 162.9, 158.4, 138.5, 133.2, 130.3, 129.2, 127.6, 124.6, 124.2, 45.4, 24.5.

N-(4-Methoxybenzyl)pyrimidin-2-amine (2c):

The title compound (**2c**) was synthesized according to the general procedure, using 2-aminopyrimidine (2.0 mmol) and 4methoxybenzyl alcohol (2.0 mmol). **2c** was isolated by column chromatography (SiO₂; hexane/EtOAc, 90:10); Yield 83 %; ¹H NMR (400MHz, CDCl₃): $\delta = 8.34-8.26$ (m, 2H), 7.45–7.34 (m, 2H), 7.26–7.14 (m, 1H), 6.91-6.93 (m, 1H), 6.41-6.32 (m, 1H), 5.32 (bs, 1H), 4.61 (s, 2H), 2.24 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): $\delta = 167.5$, 162.3, 159.1, 143.1, 130.9, 119.6, 113.6, 112.7, 110.6, 45.6, 22.5. *N*-(4-Chlorobenzyl)pyrimidin-2-amine (2d):

The title compound (**2d**) was synthesized according to the general procedure, using 2-aminopyrimidine (2.0 mmol) and 4chlorobenzyl alcohol (2.0 mmol). **2d** was isolated by column chromatography (SiO₂; hexane/EtOAc, 90:10); Yield 98 %; ¹H NMR (400MHz, CDCl₃): $\delta = 8.34-8.12$ (m, 2H), 7.45–7.30 (m, 1H), 7.31–7.22 (m, 1H), 7.18 (d, J = 7.9 Hz, 1H), 6.67–6.59 (m, 1H), 6.34 (m. 1H), 5.53 (bs, 1H), 4.71 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): $\delta = 167.8$, 162.3, 139.1, 133.3, 130.1, 127.6, 124.8, 124.2, 110.4, 45.6.

N-(4-Bromobenzyl)pyrimidin-2-amine (2e):

The title compound (**2e**) was synthesized according to the general procedure, using 2-aminopyrimidine (2.0 mmol) and 4-bromobenzyl alcohol (2.0 mmol). **2e** was isolated by column chromatography (SiO₂; hexane/EtOAc, 90:10); Yield 98 %; ¹H NMR (400MHz, CDCl₃): $\delta = 8.34-8.12$ (m, 2H), 7.45–7.30 (m, 1H), 7.31–7.22 (m, 1H), 7.18 (d, J = 7.9 Hz, 1H), 6.67–6.59 (m, 1H), 6.34 (m. 1H), 5.53 (bs, 1H), 4.71 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): $\delta = 167.6$, 162.3, 139.2, 133.0, 130.5, 129.0, 127.8, 124.6, 110.6, 45.8.

N-Benzylbenzo[d]thiazol-2-amine (3a):

The title compound (**3a**) was synthesized according to the general procedure, using 2-aminobenzothiazole (2.0 mmol) and benzyl alcohol (2.0 mmol). **3a** was isolated by column chromatography (SiO₂; hexane/EtOAc, 80:20) as a colorless solid (92 %). ¹H NMR (400MHz, CDCl₃): δ = 7.60 (d, *J* = 7.9 Hz, 1H), 7.53 (d, *J* = 7.9, 2H), 7.4–7.34 (m, 5H), 7.32–7.24 (m, 1H), 7.16–7.11 (m, 1H), 4.56 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): δ = 167.7, 152.8, 137.6, 130.7, 129.6, 128.6, 128.1, 126.2, 122.6, 121.6, 119.4, 49.4. Data agrees with literature values.³

N-(4-Methylbenzyl)benzo[d]thiazol-2-amine (3b):

The title compound (**3b**) was synthesized according to the general procedure, using 2-aminobenzothiazole (2.0 mmol) and 4methylbenzyl alcohol (2.0 mmol). **3b** was isolated by column chromatography (SiO₂; hexane/EtOAc, 80:20) as a colorless solid (81 %). ¹H NMR (400MHz, CDCl₃): δ = 7.53 (d, *J* = 8 Hz, 1H), 7.43 (d, *J* = 7.9 Hz, 1H), 7.29–7.26 (m, 4H), 7.15 (d, *J* = 8 Hz, 2H), 7.06 (t, *J* = 7.9, 1H), 6.36 (bs, 1H), 4.56 (s, 2H), 2.32 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): δ = 167.4, 152.4, 137.3, 134.8, 130.6, 126.9, 123.4, 122.2, 121.6, 121.1, 119.3, 21.4. Data agrees with literature values.⁴

N-(4-Methoxybenzyl)benzo[d]thiazol-2-amine (3c):

The title compound (**3c**) was synthesized according to the general procedure, using 2-aminobenzothiazole (2.0 mmol) and 4methoxybenzyl alcohol (2.0 mmol). **3c** was isolated by column chromatography (SiO₂; hexane/EtOAc, 80:20) as a colorless solid (79 %). ¹H NMR (400MHz, CDCl₃): δ = 7.57 (d, *J* = 7.9 Hz, 1H), 7.53 (d, *J* = 8 Hz, 1H), 7.31–7.27 (m, 3H), 7.05 (t, *J* = 8 Hz, 1H), 6.96–6.87 (m, 2H), 5.86 (bs, 1H), 4.58 (s, 2H), 3.82 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ = 167.5, 159.4, 152.5, 130.5, 129.9, 129.3, 126.1, 120.6, 118.7, 114.3, 55.2, 48.8. Data agrees with literature values.⁵

N-(4-Chlorobenzyl)benzo[d]thiazol-2-amine (3d):

The title compound (**3d**) was synthesized according to the general procedure, using 2-aminobenzothiazole (2.0 mmol) and 4chlorobenzyl alcohol (2.0 mmol). **3d** was isolated by column chromatography (SiO₂; hexane/EtOAc, 80:20) as a colorless solid (97 %). ¹H NMR (400MHz, CDCl₃): $\delta = 8.57$ (t, J = 6 Hz, 1H), 7.63 (d, J = 7.8 Hz, 1H), 7.41–7.36 (m, 5H), 7.25 (t, J = 7.6 Hz, 1H), 7.07 (t, J = 7.9 Hz, 1H), 4.56 (d, J = 7.8 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): $\delta = 166.2$, 153.4, 138.1, 131.5, 130.5, 129.2, 128.2, 125.6, 121.5, 118.6, 47.9. Data agrees with literature values.³

N-(4-Bromobenzyl)benzo[d]thiazol-2-amine (3e):

The title compound (**3e**) was synthesized according to the general procedure, using 2-aminobenzothiazole (2.0 mmol) and 4bromobenzyl alcohol (2.0 mmol). **3e** was isolated by column chromatography (SiO₂; hexane/EtOAc, 80:20) as a colorless solid (94 %). ¹H NMR (400MHz, CDCl₃): δ = 8.56 (s, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.53 (d, *J* = 7.9 Hz, 2H), 7.39–7.32 (m, 3H), 7.25 (t, *J* = 7.9 Hz, 1H), 7.06 (t, *J* = 7.8 Hz, 1H), 4.57 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): δ = 166.0, 152.4, 138.3, 131.2, 130.5, 129.5, 125.2, 121.1, 120.9, 120.1, 117.2, 46.4. Data agrees with literature values.⁶

N-Benzyl-4-methybenzenesulfonamide (4a):

The title compound (**4a**) was synthesized according to the general procedure, using *p*-toluenesulfonamide (2.0 mmol) and benzyl alcohol (2.0 mmol). **4a** was isolated by column chromatography (SiO₂; hexane/EtOAc, 80:20) as a colorless solid (82 %). ¹H NMR (400MHz, CDCl₃): δ = 7.71 (d, *J* = 7.9 Hz, 2H), 7.31–7.16 (m, 7H), 4.92 (br, 1H), 4.11 (d, *J* = 5.8 Hz, 2H), 2.46 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ = 143.5, 136.8, 136.1, 129.7, 128.8, 127.8, 127.7, 127.3, 47.9, 21.4. Data agrees with literature values.⁷

N-(4-Methylbenzyl)-4-methybenzenesulfonamide (4b):

The title compound (**4b**) was synthesized according to the general procedure, using *p*-toluenesulfonamide (2.0 mmol) and 4methylbenzyl alcohol (2.0 mmol). **4b** was isolated by column chromatography (SiO₂; hexane/EtOAc, 80:20) as a colorless solid (88 %). ¹H NMR (400MHz, CDCl₃): δ = 7.75 (d, *J* = 7.9 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 7.06 (s, 4H), 4.56 (bs, 1H), 4.11 (d, *J* = 5.8 Hz, 2H), 2.46 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ = 143.5, 136.8, 136.1, 129.7, 128.8, 127.8, 127.7, 127.3, 47.9, 21.4. Data agrees with literature values.⁷

N-(4-Methoxybenzyl)-4-methybenzenesulfonamide (4c):

The title compound (**5c**) was synthesized according to the general procedure, using *p*-toluenesulfonamide (2.0 mmol) and 4methoxybenzyl alcohol (2.0 mmol). **5c** was isolated by column chromatography (SiO₂; hexane/EtOAc, 80:20) as a colorless solid (76 %). ¹H NMR (400MHz, CDCl₃): δ = 7.72 (d, *J* = 7.9 Hz, 2H), 7.35 (d, *J* = 7.9 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 6.75, (d, *J* = 7.9 Hz, 2H), 4.59 (bs, 2H), 4.05 (d, *J* = 5.9 Hz, 2H), 3.76 (s, 3H), 2.43 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ = 156.6, 143.8, 139.8, 129.4, 129.1, 128.7, 127.7, 114.3, 55.5, 46.5, 21.4. Data agrees with literature values.⁸

N-(2-Chlorobenzyl)-4-methybenzenesulfonamide (4d):

The title compound (**4d**) was synthesized according to the general procedure, using *p*-toluenesulfonamide (2.0 mmol) and 4chlorobenzyl alcohol (2.0 mmol). **4d** was isolated by column chromatography (SiO₂; hexane/EtOAc, 80:20) as a colorless solid (91 %). ¹H NMR (400MHz, CDCl₃): δ = 7.78 (d, *J* = 7.9 Hz, 2H), 7.15–7.35 (m, *J* = 7.9 Hz, 6H), 4.75 (t, *J* = 5.9 Hz, 1H), 4.26 (d, *J* = 5.9 Hz, 2H), 2.46 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ = 143.2, 136.8, 134.2, 133.6, 129.7, 129.5, 129.2, 127.1, 126.8, 45.5, 21.2. Data agrees with literature values.⁷

N-(2-Bromobenzyl)-4-methybenzenesulfonamide (4e):

The title compound (4e) was synthesized according to the general procedure, using *p*-toluenesulfonamide (2.0 mmol) and 4chlorobenzyl alcohol (2.0 mmol). 4e was isolated by column chromatography (SiO₂; hexane/EtOAc, 80:20) as a colorless solid (86 %). ¹H NMR (400MHz, CDCl₃): δ = 7.78 (d, *J* = 7.9 Hz, 2H), 7.15–7.35 (m, *J* = 7.9 Hz, 4H), 4.75 (t, *J* = 5.9 Hz, 1H), 4.26 (d, *J* = 5.9 Hz, 2H), 2.46 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ = 143.8, 137.0, 135.4, 132.6, 130.3, 129.5, 129.2, 127.1, 127.2, 123.4, 47.5, 21.3. Data agrees with literature values.⁹

N-(2-Pyridyl)aminomethylferrocene (5a):

The title compound (**5a**) was synthesized according to the general procedure, using 2-aminopyridine (2.0 mmol) and ferrocenemethanol (2.0 mmol). **5a** was isolated by column chromatography (SiO₂; hexane/EtOAc, 80:20) as a yellow solid (82 %). ¹H NMR (400MHz, CDCl₃): δ = 8.42 (m, 1H), 7.42 (m, 1H), 6.63 (m, 1H), 6.61 (d, *J* = 8.5 Hz, 1H), 4.75 (bs, 1H), 4.27 (t, *J* = 1.9 Hz, 2H), 4.19 (s, 5H), 4.16–4.14 (m, 4H). ¹³C NMR (100 MHz, CDCl₃): δ = 158.9, 139.1, 136.0, 135.4, 129.8, 127.9, 95.3, 46.3, 20.9. Data agrees with literature values.¹⁰

N-(Phenyl)aminomethylferrocene (5b):

The title compound (**5b**) was synthesized according to the general procedure, using aniline (2.0 mmol) and ferrocenemethanol (2.0 mmol). **5b** was isolated by column chromatography (SiO₂; hexane/EtOAc, 70:30) as a yellow solid (77 %). ¹H NMR (400MHz, CDCl₃): δ = 7.26-7.22 (m, 2H), 6.78 (m, 1H), 6.73-6.64 (m, 2H), 4.26 (t, *J* = 1.9 Hz, 2H), 4.22 (s, 5H), 4.18 (t, *J* = 1.9 Hz, 2H), 3.98 (s, 2H), 3.91 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ = 148.5, 129.5, 116.9, 112.7, 86.4, 68.5, 68.3, 66.9, 43.7. Data agrees with literature values.¹¹

N-(4-Methylphenyl)aminomethylferrocene (5c):

The title compound (**5c**) was synthesized according to the general procedure, using 4-methylaniline (2.0 mmol) and ferrocenemethanol (2.0 mmol). **5c** was isolated by column chromatography (SiO₂; hexane/EtOAc, 80:20) as a yellow solid (68 %). ¹H NMR (400 MHz, CDCl₃): δ = 7.14 (d, *J* = 8.4 Hz, 2H), 6.64 (d, *J* = 8.4 Hz, 2H), 4.30 (t, *J* = 1.7 Hz, 2H), 4.19 (s, 5H), 4.12 (t, *J* = 1.7 Hz, 2H), 3.96 (s, 2H), 3.81 (br s, 1H), 2.24 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ = 146.3, 129.7, 126.5, 113.1, 86.7, 86.3, 67.9, 43.6, 21.0. Data agrees with literature values.¹¹

N-(4-Chlorobenzyl)aminomethylferrocene (5d):

The title compound (**5d**) was synthesized according to the general procedure, using 4-chloroaniline (2.0 mmol) and ferrocenemethanol (2.0 mmol). **5d** was isolated by column chromatography (SiO₂; hexane/EtOAc, 80:20) as a yellow solid (91 %). ¹H NMR (400 MHz, CDCl₃): δ = 7.16 (d, *J* = 8.6 Hz, 2H), 6.61 (d, *J* = 8.9 Hz, 2H), 4.27 (t, *J* = 1.8 Hz, 2H), 4.21 (s, 5H), 4.17 (t, *J* = 1.8 Hz, 2H), 3.94 (s, 2H), 3.87 (br s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ = 146.9, 129.4, 126.5, 122.3, 113.9, 86.4, 68.3, 68.0, 43.7. Data agrees with literature values.¹¹

N-(4-Bromobenzyl)aminomethylferrocene (5e):

The title compound (**5e**) was synthesized according to the general procedure, using 4-bromoaniline (2.0 mmol) and ferrocenemethanol (2.0 mmol). **5e** was isolated by column chromatography (SiO₂; hexane/EtOAc, 80:20) as a yellow solid (86 %).¹H NMR (400 MHz, CDCl₃): δ = 7.18 (d, *J* = 8.9 Hz, 2H), 6.61 (d, *J* = 8.9 Hz, 2H), 4.28 (t, *J* = 1.8 Hz, 2H), 4.22 (s, 5H), 4.16 (t, *J* = 1.7 Hz, 2H), 3.94 (s, 2H), 3.87 (br s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ = 146.7, 129.4, 122.1, 113.9, 86.1, 68.6, 68.3, 68.1, 43.5. Data agrees with literature values.¹¹

N,N'-Dibenzylpyridine-2,6-diamine (6a):

The title compound (**6a**) was synthesized according to the general procedure, using 2,6-diaminopyridine (2.0 mmol) and benzyl alcohol (4.0 mmol). **6a** was isolated by column chromatography (SiO₂; hexane/EtOAc, 80:20) as a colorless solid (87 %). ¹H NMR (400MHz, CDCl₃): δ = 7.36–7.15 (m, 11H), 5.74 (d, J = 7.6 Hz, 2H), 4.63 (bs, 2H), 4.43 (d, J = 5.7 Hz, 4H); ¹³C NMR (100 MHz, CDCl₃): δ = 158.2, 139.5, 139., 128.8, 127.3, 127.2, 95.0, 46.4. Data agrees with literature values.¹²

N,*N*'-Bis(4-methylbenzyl)pyridine-2,6-diamine (6b):

The title compound (**6b**) was synthesized according to the general procedure, using 2,6-diaminopyridine (2.0 mmol) and benzyl alcohol (4.0 mmol). **6b** was isolated by column chromatography (SiO₂; hexane/EtOAc, 80:20) as a colorless solid (62 %). ¹H NMR (400MHz, CDCl₃): δ = 7.31 (s, 4H), 7.22 (t, *J* = 7.8 Hz, 1H), 7.12 (d, J = 7.6 Hz, 4 H), 5.69 (t, *J* = 8.05 Hz, 2H), 4.65 (t, *J* = 5.4 Hz, 2H), 4.43 (d, *J* = 5.9 Hz, 4H), 2.38 ppm (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ = 158.9, 139.1, 136.0, 135.4, 129.8, 127.9, 95.3, 46.3, 20.9. Data agrees with literature values.¹²

N,*N*'-Bis(4-methoxybenzyl)pyridine-2,6-diamine (6c):

The title compound (**6b**) was synthesized according to the general procedure, using 2,6-diaminopyridine (2.0 mmol) and 4methoxybenzyl alcohol (4.0 mmol). **6b** was isolated by column chromatography (SiO₂; hexane/EtOAc, 90:10) as a colorless solid (76 %). ¹H NMR (400MHz, CDCl₃): δ = 7.32–7.27 (m, 4H), 7.24 (t, *J* = 7.8 Hz, 1H), 6.86 (d, *J* = 8.6 Hz, 4 H), 5.71 (d, *J* = 7.6 Hz, 2H), 4.57 (t, *J* = 5.4 Hz, 2H), 4.36 (d, *J* = 5.4 Hz, 4H), 3.78 ppm (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ = 158.3, 157.7, 139.1, 132.0, 129.8, 128.6, 95.4, 56.0, 45.7. Data agrees with literature values¹².

N,N'-Bis(4-chlorobenzyl)pyridine-2,6-diamine (6d):

The title compound (6d) was synthesized according to the general procedure, using 2,6-diaminopyridine (2.0 mmol) and 4chlorobenzyl alcohol (4.0 mmol). 6d was isolated by column chromatography (SiO₂; hexane/EtOAc, 60:40) as a colorless solid (93 %). ¹H NMR (400MHz, CDCl₃): δ = 7.32 (m, 8H), 7.19 (t, *J* = 8.4 Hz, 1H), 5.72 (d, *J* = 7.6 Hz, 2H), 4.65 (t, *J* = 5.6 Hz, 2H), 4.45 (d, *J* = 5.7 Hz, 4H). ¹³C NMR (100 MHz, CDCl₃): δ = 157.7, 139.5, 138.3, 129.8, 128.6, 95.6, 45.2. Data agrees with literature values.¹²

N,*N*'-Bis(4-bromobenzyl)pyridine-2,6-diamine (6e):

The title compound (**6e**) was synthesized according to the general procedure, using 2,6-diaminopyridine (2.0 mmol) and 4bromobenzyl alcohol (4.0 mmol). **6e** was isolated by column chromatography (SiO₂; hexane/EtOAc, 60:40) as a colorless solid (82 %). ¹H NMR (400MHz, CDCl₃): δ = 7.31 (m, 8H), 7.16 (t, *J* = 8.5 Hz, 1H), 5.70 (d, *J* = 7.5 Hz, 2H), 4.63 (t, *J* = 5.4 Hz, 2H), 4.43 (d, *J* = 5.6 Hz, 4H). ¹³C NMR (100 MHz, CDCl₃): δ = 158.0, 139.6, 139.1, 138.5, 128.6, ,128. 3, 123.9, 95.0, 46.2, 21.2. Data agrees with literature values.¹²

N,*N*'-Bis (ferrocenylmethyl)pyridine-2,6-diamine (6f):

The title compound (**6e**) was synthesized according to the general procedure, using 2,6-diaminopyridine (2.0 mmol) and ferrocenemethanol (4.0 mmol). **6e** was isolated by column chromatography (SiO₂; hexane/EtOAc, 80:20) as a yellow solid (82 %). ¹H NMR (400MHz, CDCl₃): δ = 7.31–7.26 (m, 8H), 7.16 (t, *J* = 8.5 Hz, 1H), 5.70 (d, *J* = 7.5 Hz, 2H), 4.63 (t, *J* = 5.4 Hz, 2H), 4.43 (d, *J* = 5.6 Hz, 4H). ¹³C NMR (100 MHz, CDCl₃): δ = 158.0, 139.6, 139.1, 138.5, 128.6, 128. 3, 123.9, 95.0, 46.2, 21.2. Data agrees with literature values.¹³

2-Phenyl-1H-benzimidazole (7a):

The title compound (7a) was synthesized according to the general procedure, using *o*-phenylenediamine (2.0 mmol) and benzyl alcohol (3.0 mmol). 7a was isolated by column chromatography (SiO₂; hexane/EtOAc, 60:40) as a colorless solid (93 %). ¹H NMR (400MHz, CDCl₃): $\delta = 12.87$ (br, s, 1H), 8.21 (d, J = 6.7 Hz, 2H), 7.68–7.59 (m, 1H), 7.56–7.45 (m, 4H), 7.24–7.19 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 151.5$, 144.3, 133.5, 129.5, 128.8, 126.3, 122.2, 120.9, 118.2. (EI): *m/z* 194 [M]⁺, 166, 91, 78, 63, 58. Data agrees with literature values.¹⁴

2-(4-Methoxyphenyl)-1H-benzimidazole (7b):

The title compound (**7b**) was synthesized according to the general procedure, using *o*-phenylenediamine (2.0 mmol) and 4methoxybenzyl alcohol (3.0 mmol). **7b** was isolated by column chromatography (SiO₂; hexane/EtOAc, 60:40) as a colorless solid (81 %). ¹H NMR (400MHz, CDCl₃): δ = 8.16 (d, *J* = 9.8 Hz, 2H), 7.56 (s, 2H), 7.19–7.04 (m, 4H), 3.82 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ = 163.1, 152.5, 132.4, 129.1, 128.8, 122.2, 116.3, 48. Data agrees with literature values.¹⁴

2-(4-Chlorophenyl)-1H-benzimidazole (7c):

The title compound (7c) was synthesized according to the general procedure, using *o*-phenylenediamine (2.0 mmol) and 4chlorobenzyl alcohol (3.0 mmol). 7c was isolated by column chromatography (SiO₂; hexane/EtOAc, 60:40) as a colorless solid (98 %); ¹H NMR (400MHz, CDCl₃): δ = 12.8 (bs, 1H), 8.26 (d, *J* = 8.9 Hz, 2H), 7.66–7.54 (m, 2H), 7.41–7.15 (M, 4H). ¹³C NMR (100 MHz, CDCl₃): δ = 152.0, 136.3, 130.8, 129.3, 127.3, 122.4, 121.8, 115.3. Data agrees with literature values.¹⁴

2-(2-Pyridyl)-1H-benzimidazole (7d):

The title compound (7d) was synthesized according to the general procedure, using *o*-phenylenediamine (2.0 mmol) and 2-pyridylmethanol (3.0 mmol). 7d was isolated by column chromatography (SiO₂; hexane/EtOAc, 60:40) as a colorless solid (99 %). ¹H NMR (400MHz, CDCl₃): δ = 13.2 (bs, 1H), 8.81–8.72 (m, 1H), 8.34–8.29 (m, 1H), 7.88–7.82 (m, 1H), 7.71 (s, 2H), 7.46–7.49 (m, 1H), 7.28–7.26 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ = 152.0, 151. 8, 149. 3, 139.6, 137.8, 126.1, 123.8, 122.3. Data agrees with literature values.¹⁴

2-(3-Methylbutane)-1H-benzimidazole (7e):

The title compound (7e) was synthesized according to the general procedure, using *o*-phenylenediamine (2.0 mmol) and 3methylbutanol (3.0 mmol). 7e was isolated by column chromatography (SiO₂; hexane/EtOAc, 60:40) as a colorless solid (55 %). ¹H NMR (400MHz, CDCl₃): δ = 7.79–8.68 (m, 1H), 7.48–7.41 (m, 1H), 7.46–7.31 (m, 2H), 1.56 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): δ = 151.2, 141. 6, 143. 3, 125.2, 124. 4, 120.4, 110.1, 36.2, 32.3, 28.3. Data agrees with literature values.¹⁴

2-Phenyl-1,3-benzoxazole (7f):

The title compound (**7f**) was synthesized according to the general procedure, using 2-aminophenol (2.0 mmol) and benzyl alcohol (3.0 mmol). **7f** was isolated by column chromatography (SiO₂; *n*-hexane/EtOAc, 90:10) as a pale yellow solid (95 %). ¹H NMR (400MHz, CDCl₃): $\delta = 8.29-8.24$ (m, 2H), 7.88–7.75 (m, 1H), 7.56–7.46 (m, 4H), 7.38–7.32 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): $\delta = 162.4$, 153.2, 142.6, 131.6, 129. 3, 127.9, 127.6, 125.5, 124.6, 120.4, 110.1. Data agrees with literature values.¹⁵

2-(4-Methoxyphenyl)-1,3-benzoxazole (7g):

The title compound (**7g**) was synthesized according to the general procedure, using 2-aminophenol (2.0 mmol) and 4-methoxybenzyl alcohol (3.0 mmol). **7g** was isolated by column chromatography (SiO₂; hexane/EtOAc, 90:10) as a colourless solid (84 %). ¹H NMR (400MHz, CDCl₃): δ = 8.19 (d, J = 8.9 Hz, 2H), 7.78–7.75 (m, 1H), 7.56–7.53 (m, 1H), 7.34–7.28 (m, 2H), 7.05 (d, *J* = 9.0 Hz, 2H), 3.84 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ = 163.5, 162.6, 151.0, 142.7, 129.6, 128.9, 125.5, 124.6, 120.4, 120.1, 113.9, 110.2, 55.3. Data agrees with literature values.¹⁵

2-(4-Chlorophenyl)-1,3-benzoxazole (7h):

The title compound (**7h**) was synthesized according to the general procedure, using 2-aminophenol (2.0 mmol) and 4-chlorobenzyl alcohol (3.0 mmol). **7h** was isolated by column chromatography (SiO₂; hexane/EtOAc, 90:10) as a colourless solid (99 %).¹H NMR (400MHz, CDCl₃): $\delta = 8.14-8.11$ (m, 2H), 7.76–7.73 (m, 1H), 7.66–7.63 (m, 2H), 7.57–7.54 (m, 1H), 7.38–7.35 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): $\delta = 161.4$, 151.0, 142.2, 132.4, 128.8, 126.3, 126.5, 125.1, 124.7, 120.4, 110.8. Data agrees with literature values.¹⁵

2-pyridin-2-yl-1,3-benzoxazole (7i):

The title compound (**7i**) was synthesized according to the general procedure, using 2-aminophenol (2.0 mmol) and 2-pyridylmethanol (3.0 mmol). **7i** was isolated by column chromatography (SiO₂; hexane/EtOAc, 90:10) as a colourless solid (98 %).¹H NMR (400MHz, CDCl₃): δ = 8.93 (d, *J* = 8.9 Hz, 1H), 8.45 (d, *J* = 8.9 Hz, 1H), 8.32 (d, *J* = 8.1 Hz, 1H), 8.24 (d, *J* = 8.0 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.81 (t, *J* = 8.4 Hz, 1H), 7.53 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ = 169.6, 157.6, 152.2, 149.7, 137.0, 136.0, 126.2, 123.5, 125.5, 122.1, 120.2. Data agrees with literature values.¹⁶

2-Phenyl-1,3-benzothiazole (7j):

The title compound (**7j**) was synthesized according to the general procedure, using 2-aminothiophenol (2.0 mmol) and benzyl alcohol (3.0 mmol). **7j** was isolated by column chromatography (SiO₂; hexane/EtOAc, 90:10) as a colourless solid (93 %). ¹H NMR (400MHz, CDCl₃): $\delta = 6.82-6.85$ (m, 3H), 6.46-6.58 (m, 6H). ¹³C NMR (100 MHz, CDCl₃): $\delta = 166.8$, 155.0, 135.2, 133.4, 128.9, 127.6, 126.2, 125.0, 123.2, 121.9. Data agrees with literature values.¹⁷

2-(4-Methoxyphenyl)-1,3-benzothiazole (7k):

The title compound (**7k**) was synthesized according to the general procedure, using 2-aminothiophenol (2.0 mmol) and 4methoxybenzyl alcohol (3.0 mmol). **7k** was isolated by column chromatography (SiO₂; hexane/EtOAc, 90:10) as a colourless solid (93 %). ¹H NMR (400MHz, CDCl₃): $\delta = 8.06-8.03$ (m, 3H), 7.87 (d, J = 7.8 Hz, 1H), 7.43 (t, J = 7.8 Hz, 1H), 7.34 (t, J = 7.8 Hz, 1H), 6.82 (d, J = 8.4 Hz, 2H), 3.86 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 167.7, 159.5, 153.8, 135.0, 134.6, 129.8, 126.2, 125.8, 123.2, 121.7, 56.1. Data agrees with literature values.¹⁸

2-(4-Chlorophenyl)-1,3-benzothiazole (7l):

The title compound (**71**) was synthesized according to the general procedure, using 2-aminothiophenol (2.0 mmol) and 4-chlorobenzyl alcohol (3.0 mmol). **71** was isolated by column chromatography (SiO₂; hexane/EtOAc, 90:10) as a colourless solid (93 %).¹H NMR (400MHz, CDCl₃): δ = 8.07 (d, *J* = 8.1 Hz, 1H), 8.02 (d, *J* = 8.6 Hz, 2H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.45 (d, *J* = 8.6 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 2H), 3.86 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ = 167.7, 159.5, 153.8, 135.0, 134.6, 129.8, 126.2, 125.8, 123.2, 121.7, 56.1. Data agrees with literature values.¹⁸

(44) 2-pyridin-2-yl-1,3-benzothiazole (7m):

The title compound (**7m**) was synthesized according to the general procedure, using 2-aminothiophenol (2.0 mmol) and 2-pyridylmethanol (3.0 mmol). **7m** was isolated by column chromatography (SiO₂; hexane/EtOAc, 90:10) as a colourless solid (97 %). ¹H NMR (400MHz, CDCl₃): δ = 8.66 (d, *J* = 8 Hz, 1H), 8.37 (d, *J* = 7.8 Hz, 1H), 8.10 (d, *J* = 7.8 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 7.85 (t, *J* = 8.4 Hz, 1H), 7.52 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ = 169.3, 156.2, 151.3, 149.5, 137.0, 136.0, 126.2, 125.6, 125.2, 122.01, 120.1. Data agrees with literature values¹⁸.

(45) 2-(3-Methylbutane)-1-3-benzothiazole (7n):

The title compound (7n) was synthesized according to the general procedure, using 2-aminothiophenol (2.0 mmol) and 2-pyridylmethanol (3.0 mmol). 7n was isolated by column chromatography (SiO₂; hexane/EtOAc, 90:10) as a yellow solid (97 %). GC-MS (EI): m/z 191 [M]+, 176, 149, 125, 108, 71.

2.7 References

- 1. P. S. Reddy, S. Kanjilal, S. Sunitha and R. B. N. Prasad, *Tetrahedron Lett.*, 2007, 48, 8807–8810.
- 2. B. Blank, M. Madalska and R. Kempe, Adv. Synth. Catal., 2008, 350, 749-758.
- 3. L. L. Joyce, G. Evindar and R. A. Batey, Chem. Commun., 2004, 446-447.
- 4. M. B. Valentin, D. Francisca, B. Carolina, G. N. Luis, I. Luisa and A. B. Julio, Tetrahedron., 2000, 56, 2481–2490.
- 5. E. G. Feng, H. Huang, Y. Zhou, D. Ye, H. L. Jiang and H. Liu, J. Comb. Chem., 2010, 12, 422-429.
- A. Ballistrer, A. Bottino, G. Musumarra, R. Fioravanti, M. Biava, G. C. Porretta, N. Simonetti and A. Villa, J. Phys. Org. Chem., 1996, 9, 61–65.
- F. Shi, M. K. Tse, S. Zhou, M.-M. Pohl, J. Radnik, S. Hubner, K. Jahnisch, A. Bruckner and M. Beller, J. Am. Chem. Soc., 2009, 131, 1775–1779.
- 8. A. Rolfe, K. Young and P. R. Hanson, Eur. J. Org. Chem., 2008, 5254–5262.
- F. Shi, M. K. Tse, X. Cui, D. Gördes, D. Michalik, K. Thurow, Y. Deng and M. Beller, *Angew. Chem. Int. Ed.*, 2009, 48, 5912–5915.
- H. X. Wang, Y.J. Li, R. Jin, J. R. Niu, H. F. Wu, H. C. Zhou, J. Xu, R. Q. Gao and F. Y. Geng, *J. Organomet. Chem.*, 2006, 691, 987–993.
- 11. N. S. Khrushcheva, O. V. Shakhova and V. I. Sokolov, Russ. Chem. Bull., Int. Ed., 2003, 52, 2146–2148.
- 12. B. Blank, S. Michlik and R. Kempe, Chem. Eur. J. 2009, 15, 3790-3799.
- 13. S. Agrawal, M. Lenormand and B. M. Matute, Org. Lett., 2012, 14, 1456-1459.
- 14. M. Wu, X. Hu, J. Liu, Y. Liao and G. J. Deng, Org. Lett., 2012, 14, 2722-2725.
- 15. G. Evindar and R. A. Batey, J. Org. Chem., 2006, 71, 1802-1808.
- 16. H. Do and O. Daugulis, J. Am. Chem. Soc., 2007, 129, 12404–12405.
- 17. Z. Y. Duan, R. Sadananda and X. G. Liu, Org. Lett., 2010, 12, 2430-2433.

18. H. Matsushita, S. H. Lee and M. Joung, Tetrahedron Lett., 2004, 45, 313–316.