Experimental section

Walking Imidazolium Cations: Unexpected Rearrangements in the Synthesis of Unsymmetrical Tridentate Dianionic *N*-Heterocyclic Carbene

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1. Experimental details:

2,4-Di-*tert*-butyl-6-nitrophenol was obtained according to already reported procedure.[1] NMR spectra were recorded on Varian Mercury 300, Varian INOVA 500 or Varian INOVA 600 spectrometers and referenced to the solvent residual peak. High resolution mass spectra (HRMS) were obtained at the California Institute of Technology Mass Spectral Facility using a JEOL JMS-600H magnetic sector mass spectrometer. Elemental analyses were performed by Midwest Microlab LLC, Indianapolis, IN 46250.

2-(N-mesitylamino)nitrobenzene: The compound was obtained through an adaptation of the procedure of J. J. Kulagowski *et al.*.[2] 2-Fluoronitrobenzene (5 mL, 47.4 mmol) and 2,4,6-trimethylaniline (26.6 mL, 189.4 mmol) were heated at 180ºC during 60h. The mixture was purified by column chromatography (eluent: hexane/EtOAc: 9:1). After recrystallization in methanol, the product was obtained as an orange powder (7.9 g, 30.8 mmol, 65 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): 9.11 (br.s, 1H, NH), 8.22 (dd, J = 8.6 Hz, J = 1.6 Hz, 1H, CH_{Ph}), 7.35-7.21 (m, 1H, CH_{Ph}), 6.99 (s, 2H, CH_{Mes}), 6.74-6.61 (m, 1H, CH_{Ph}), 6.38 (dd, J = 8.6 Hz, J = 1.2 Hz, 1H, CH_{Ph}), 2.33 (s, 3H, CH_3), 2.14 (s, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): 144.8, 137.4, 136.3, 136.1, 132.7, 132.0, 129.5, 126.7, 116.3, 115.1, 21.0, 18.1. HR-MS (FAB+): *m/z*: *calcd* for $C_{15}H_{16}O_2N_2$: 256.1212; *found*: 256.1211.

2-Amino-4,6-di-tert-butylphenol: To a solution of 2,4-di-*tert*-butyl-6-nitrophenol (3.70 g, 14.7 mmol) in absolute ethanol and aqueous hydrochloric acid (3 M, 50 mL) was added tin powder (8.7 g, 73.5 mmol). After heating at reflux during one hour, the solution was neutralized with NaOH (to pH = 7). The mixture was filtrate and the precipitate was several times washed with ethyl acetate. The organic layer was extracted and dried over $MgSO_4$. After recrystallization in hexane, 2-Amino-4,6-di-*tert*-butylphenol was obtained as a white powder (2.15 g, 9.7 mmol,

[1] Vinsova, J.; Cermakova, K.; Tomeckova, A.; Ceckova, M.; Jampilek, J.; Cermak, P.; Kunes, J.; Dolezal, M.; Staud F. *Bioorg. Med. Chem*. **2006**, *14*, 5850-5865.
[2] Kulagowski, J. J.; Moody, C. J.; Rees, C. W. *J. Chem. Soc. Perkin Trans 1* **1985**, 2725.

66% yield). ^{1}H NMR (300 MHz, CDCl3): 6.91 (d, *J* = 1.5 Hz, 1H, CH_{Ph}), 6.82 (d, J = 1.5 Hz, 1H, CH_{Ph}), 5.82 (br.s, 1H, NH), 3.21 (br.s, 2H, NH), 1.42 (s, 9H, CH_3), 1.28 (s, 9H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): 144.2, 142.6, 135.8, 132.5, 117.2, 116.0, 34.8, 34.4, 31.8, 30.0. HR-MS (FAB+): *m/z*: *calcd* for $C_{14}H_{23}ON$: 221.1780; *found*: 221.1773.

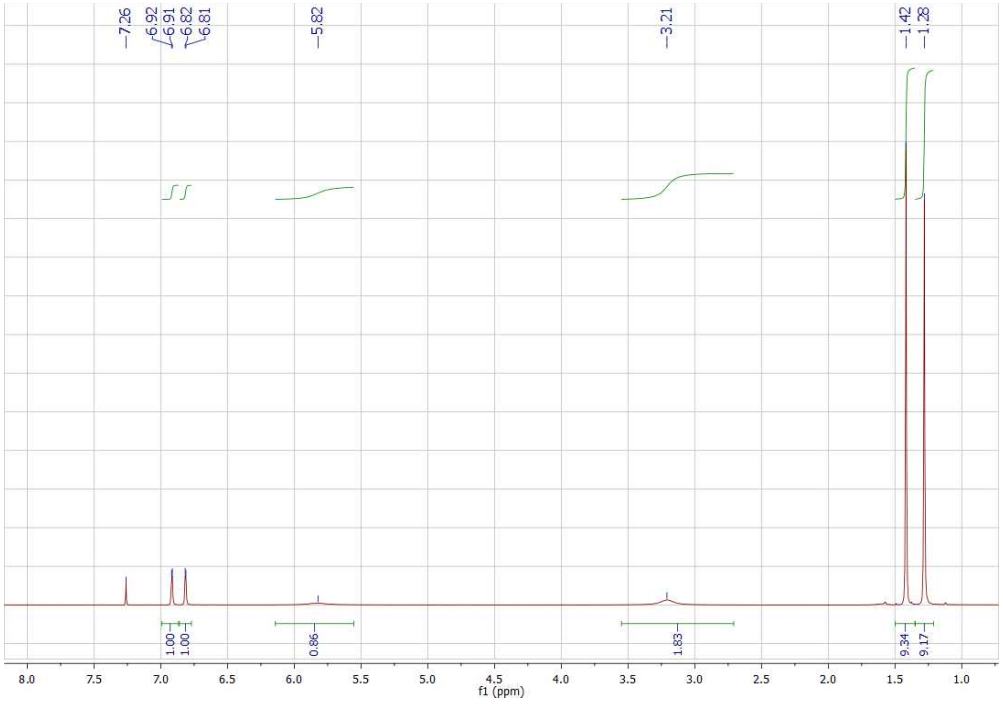


Figure S3: ^{1}H NMR of 2-amino-4,6-di-tert-butylphenol in $CDCl_3$.

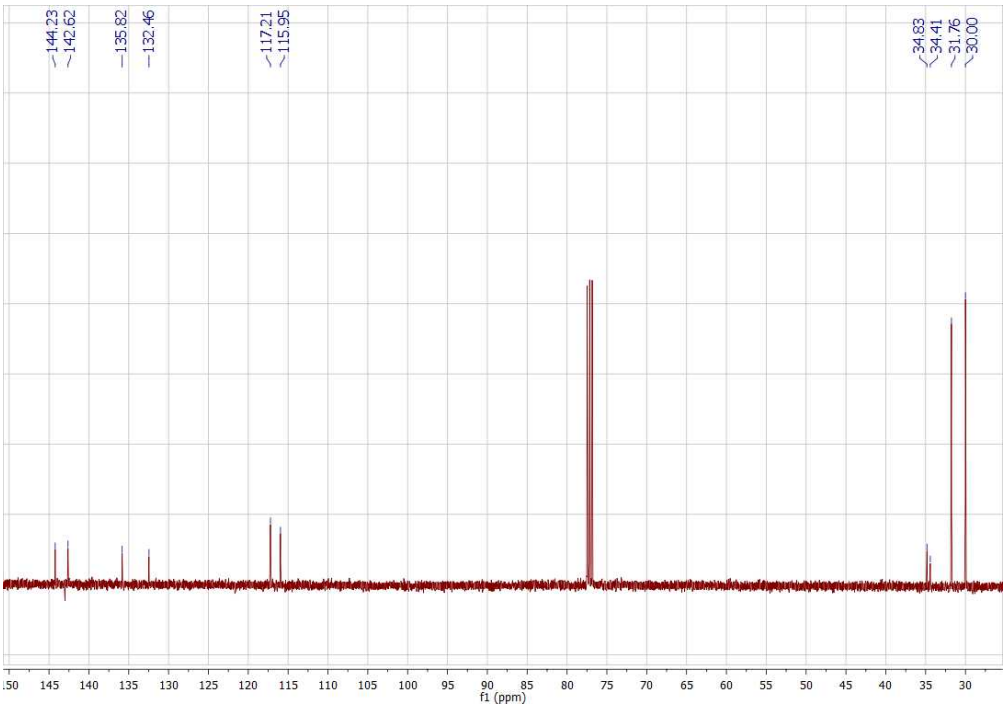


Figure S4: ^{13}C NMR of 2-amino-4,6-di-tert-butylphenol in $CDCl_3$.

2-(N-mesitylamino)aniline: To a solution of 2-(N-mesitylamino)nitrobenzene (3g, 11.7 mmol) in absolute ethanol and aqueous hydrochloric acid (3 M, 50 mL) is added tin powder (6.9 g, 58.5 mmol). After heating at reflux during one hour, the solution is neutralized with NaOH. The mixture was filtrate and the precipitate was several times washed with ethyl acetate. The organic layer was extracted and dried over $MgSO_4$. After recrystallization in a mixture ethylacetate-hexane, 2-(N-mesitylamino)aniline was obtained as a white powder (2.28 g, 10.1 mmol, 75% yield). ^{1}H NMR (300 MHz, $CDCl_3$): 6.94 (s, 2H, CH_{Mes}), 6.83-6.71 (m, 2H, CH_{Ph}), 6.67 (td, J = 1.9 Hz, J = 1.4 Hz, 1H, CH_{Ph}), 6.25 (dd, J = 7.7 Hz, J = 1.4 Hz, 1H, CH_{Ph}), 4.77 (br.s, NH), 3.62 (br.s, NH), 2.32 (s, 3H, CH_3), 2.14 (br.s, 6H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): 137.0, 135.7, 134.9, 134.1, 133.5, 129.4, 120.4, 120.2, 116.4, 115.1, 21.0, 18.2. HR-MS (FAB+): *m/z*: *calcd* for $C_{15}H_{18}N_2$: 226.1470; *found*: 226.1472.

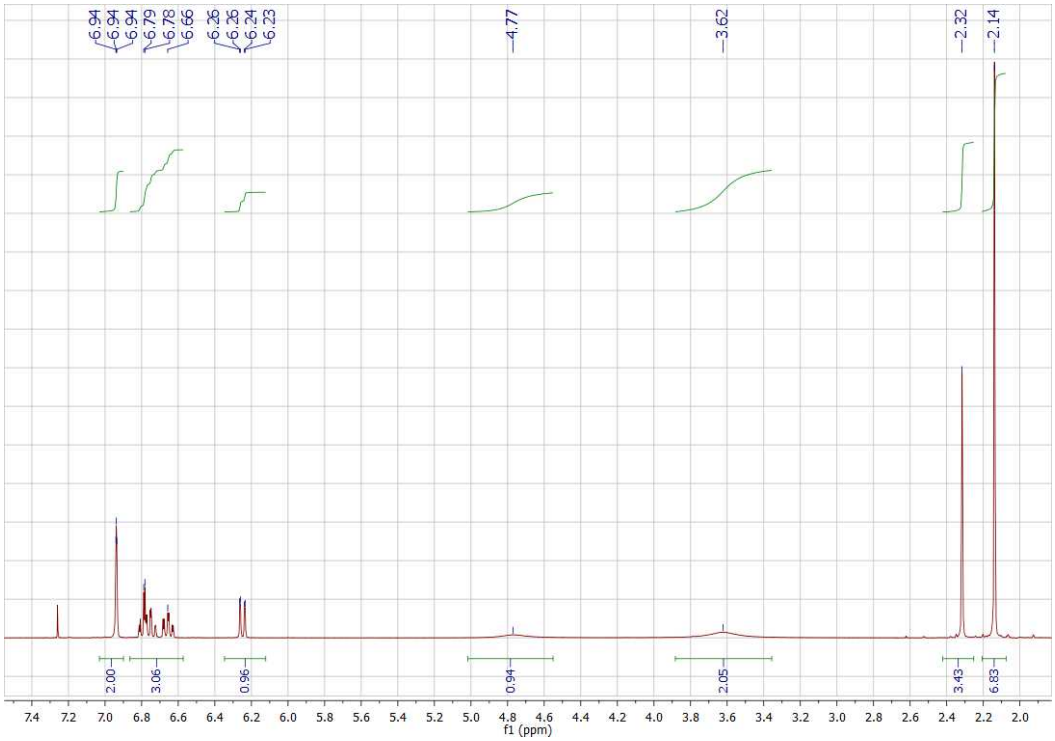


Figure S5: ^{1}H NMR of 2-(N-mesitylamino)aniline in $CDCl_3$.

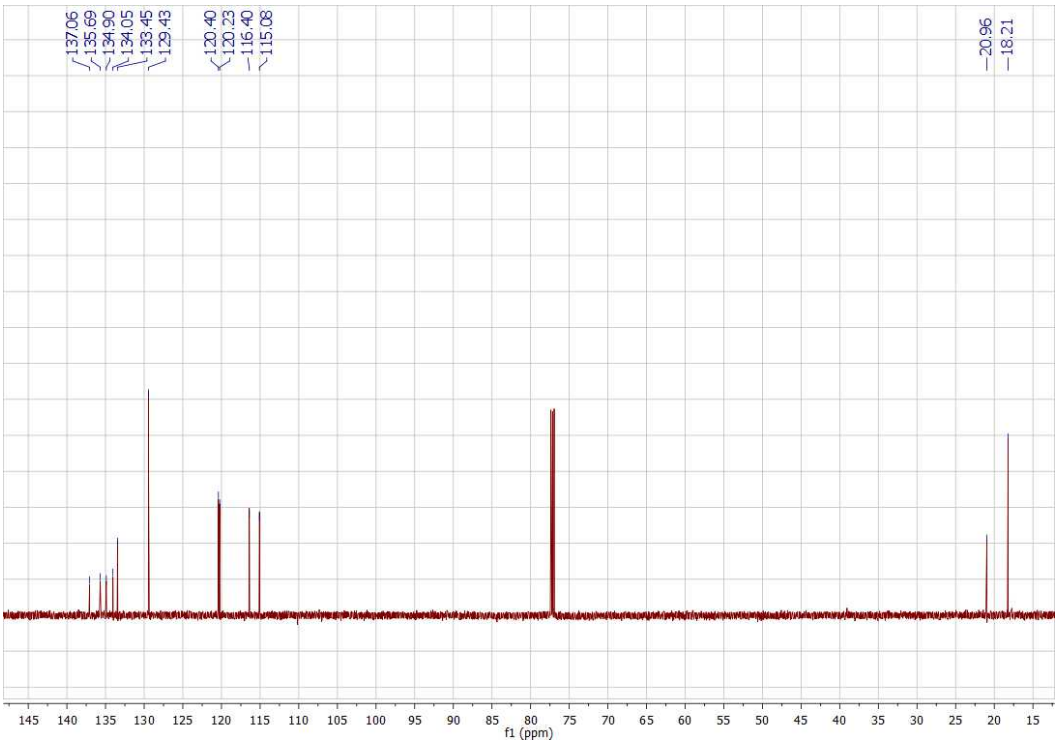


Figure S6: ^{13}C NMR of 2-(N-mesitylamino)aniline in $CDCl_3$.

N-(2-mesitylaminophenyl)-oxanilic acid ethyl ester (1): To a solution of 2-(N-mesitylamino)aniline (2.82 g, 12.46 mmol) in THF (50 mL) was added triethylamine (1.74 mL, 12.46 mmol) and ethyl chlorooxoacetate (1.38 mL, 12.46 mmol) at 0ºC. Precipitation of a white solid occurred immediately upon addition. After one night at room temperature, the mixture was filtered and the volatiles were removed under reduced pressure yielding a yellowish solid. This product was used without further purification.

^{1}H NMR (300 MHz, $CDCl_3$): 9.07 (br.s, 1H, NH), 7.50 (dd, J = 7.8 Hz, J = 1.5 Hz, 1H, CH_{Ph}), 7.09-6.96 (m, 1H, CH_{Ph}), 6.91 (s, 2H, CH_{Mes}), 6.95-6.80 (m, 1H, CH_{Ph}), 6.38 (dd, J = 8.1 Hz, J = 1.4 Hz, 1H, CH_{Ph}), 5,42 (br.s, 1H, NH), 4.45 (q, J = 7.2 Hz, 2H, OEt), 2.30 (s, CH_3), 2.12 (s, CH_3), 1.45 (t, J = 7.2 Hz, 3H, OEt). ^{13}C NMR (75 MHz, $CDCl_3$): 160.9 (CO), 154.7 (CO), 139.9, 136.1, 134.7, 134.0, 129.4, 127.7, 124.0, 123.9, 119.9, 116.5, 63.9, 21.0, 18.3, 14.2. HR-MS (EI+): *m/z*: *calcd* for $C_{19}H_{22}O_3N_2$: 326.1630; *found*: 326.1620.

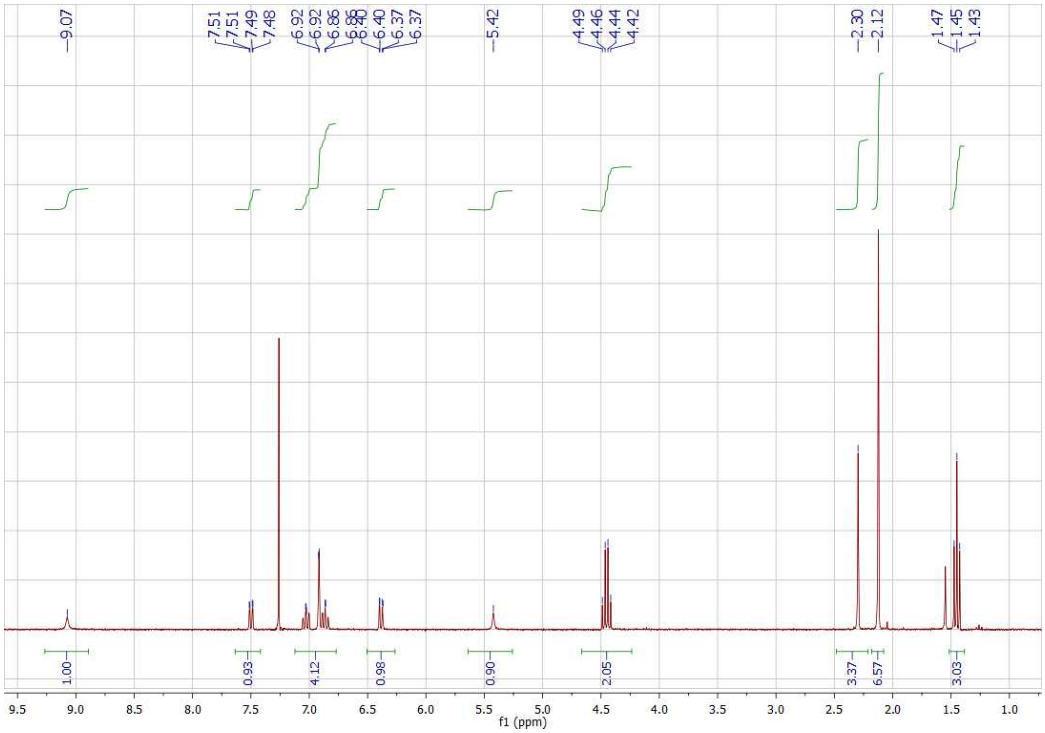


Figure S7: ^{1}H NMR of N-(2-mesitylaminophenyl)-oxanilic acid ethyl ester (**1**) in $CDCl_3$.

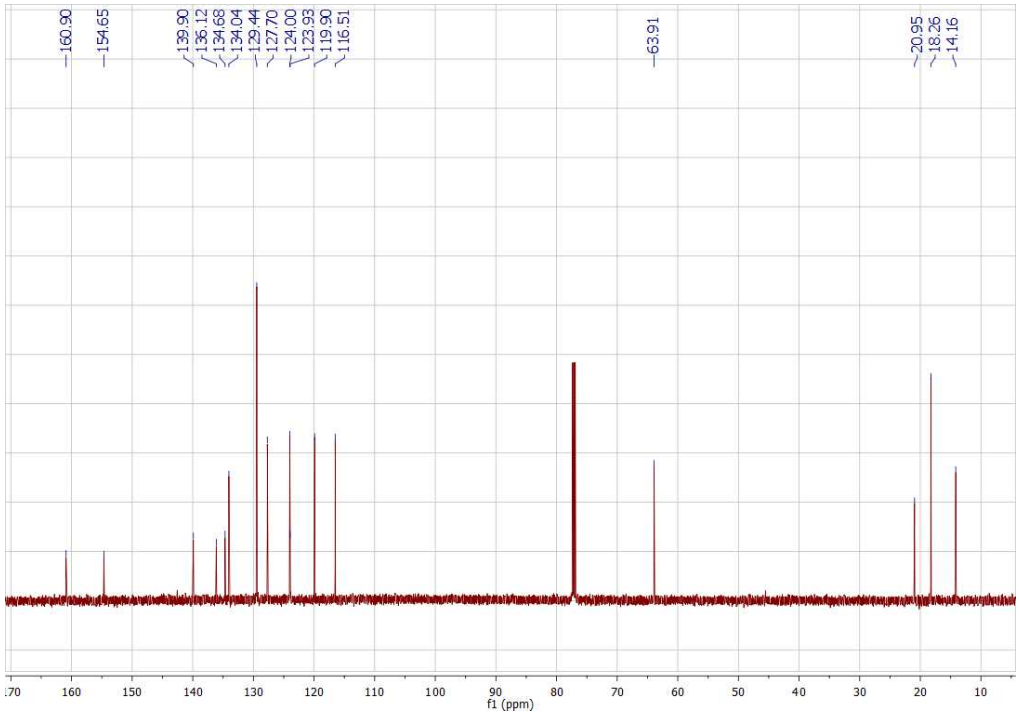


Figure S8: ^{13}C NMR of N-(2-mesitylaminophenyl)-oxanilic acid ethyl ester (**1**) in $CDCl_3$.

N-(2-mesitylaminophenyl)-N'-(3,5-di-tert-butyl-2-hydroxyphenyl)-oxalamide (2): N-(2-mesitylaminophenyl)-oxanilic acid ethyl ester (3.7 g, 11.34 mmol) and 2,4-di-*tert*-butyl-6-aminophenol (2.5g, 11.34 mmol) were dissolved in toluene (35 mL) and triethylamine (3.2 mL, 22.68 mmol) was added. After refluxing overnight, all the volatiles were removed under reduced pressure yielding the desired oxalamide **2** as a yellow solid (quantitative). This product was used without further purification.

^{1}H NMR (300 MHz, $CDCl_3$): 9.56 (br.s, 1H, NH), 9.48 (br.s, 1H, NH), 7.85 (br.s, 1H, OH), 7.60 (dd, J = 7.9 Hz, J = 1.4 Hz, 1H, CH_{Ph}), 7.30 (d, J = 2.3 Hz, 1H, CH_{Ph}), 7.08 (d, J = 2.3 Hz, 1H, CH_{Ph}), 7.08-7.02 (m, 1H, CH_{Ph}), 6.93 (s, 2H, CH_{Mes}), 6.93-6.87 (m, 1H, CH), 6.42 (dd, J = 8.1 Hz, J = 1.3 Hz, 1H, CH), 5.36 (br.s, 1H, NH), 2.31 (s, 3H, CH_{3Mes}), 2.14 (s, 6H, CH_{3Mes}), 1.46 (s, 9H, *t*Bu), 1.31 (s, 9H, *t*Bu). ^{13}C NMR (75 MHz, $CDCl_3$): 158.3 (CO), 157.2 (CO), 146.1, 143.3, 140.1, 139.7, 134.9, 134.1, 129.5, 129.4, 129.2, 128.4, 127.8, 123.8, 123.2, 120.1, 117.9, 116.6,

35.6, 34.6, 31.6, 30.0, 21.0, 18.3. HR-MS (FAB+): *m/z*: *calcd* for $C_{31}H_{39}O_3N_3$: 501.2991; *found*: 501.3000.

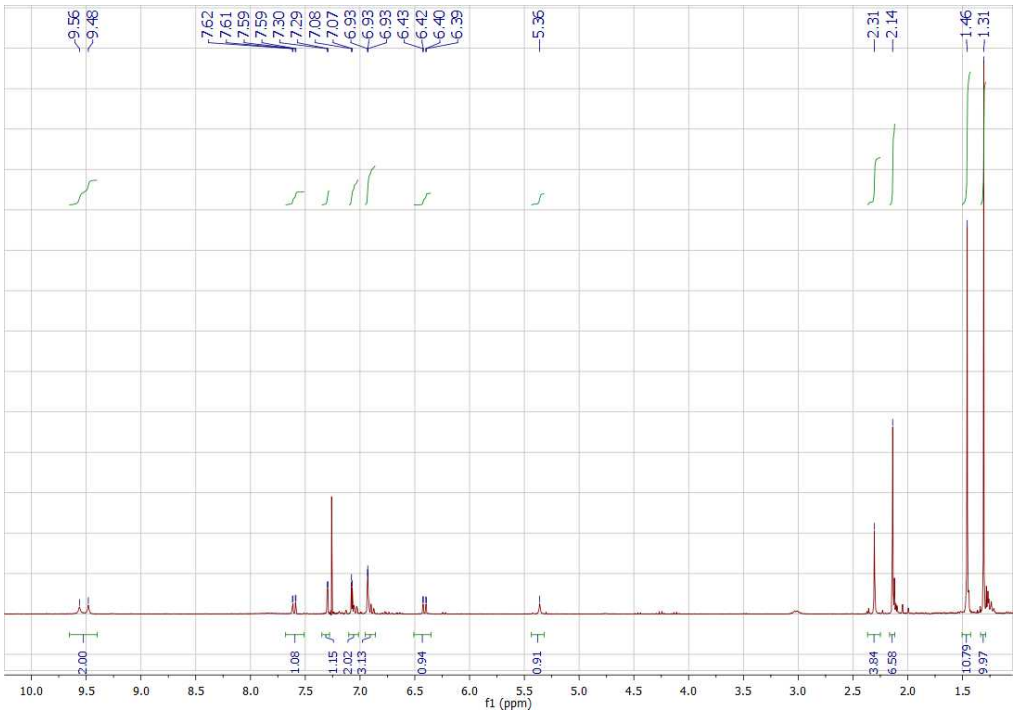


Figure S9: ^{1}H NMR of N-(2-mesitylaminophenyl)-N'-(3,5-di-tert-butyl-2-hydroxyphenyl)-oxalamide (**2**) in $CDCl_3$.

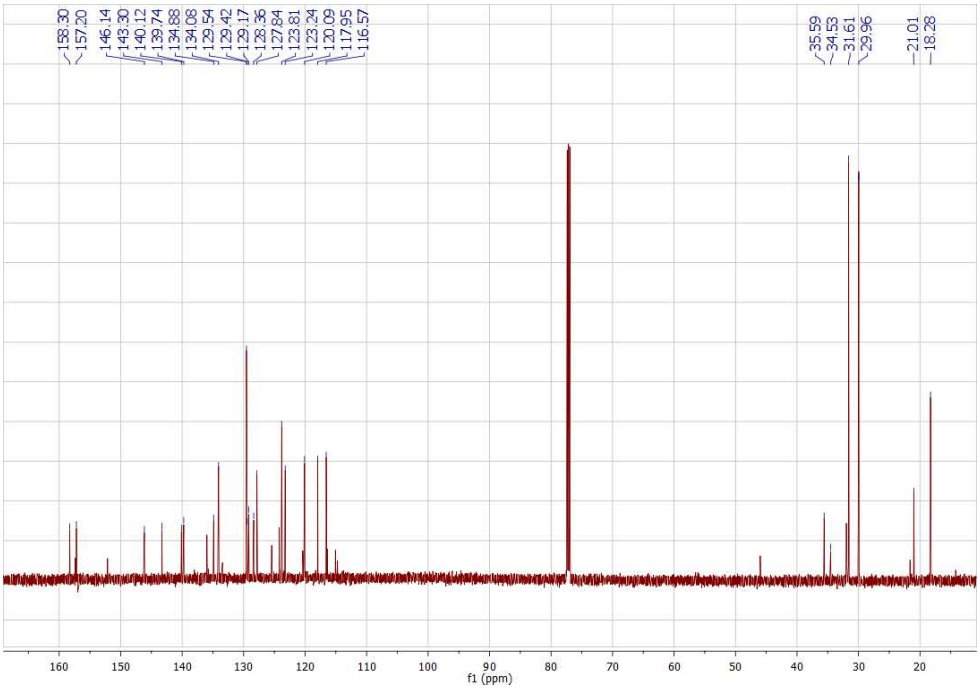


Figure S10: ^{13}C NMR of N-(2-mesitylaminophenyl)-N'-(3,5-di-tert-butyl-2-hydroxyphenyl)-oxalamide (**2**) in $CDCl_3$.

N-(2-mesitylaminophenyl)-N'-(3,5-di-tert-butyl-2-hydroxyphenyl)-ethylenediamine (3): The reduction can be achieved following two procedures:

1) *By borane reduction:* Borane THF adduct (56 mL, 56 mmol) was added to oxalamide **2** (5.6 g, 11.2 mmol) at room temperature and the solution was allowed to reflux overnight. Then the mixture was quenched by slowly adding methanol until the bubbling ceases. The volatiles were removed under reduce pressure, water was added to the residue and the product was extracted with ether and dried over $MgSO_4$. After purification with a column chromatography (eluent: hexane/EtOAc: 9:1), the diamine was obtained as a yellow powder (2.3 g, 4.9 mmol, 43%). The purity of the product was not perfect but it was used as it for the next step.

2) *By LAH reduction:* A solution of oxalamide (4.7 g, 9.5 mmol) in THF (20 mL) was added to a suspension of LAH (1.8 g, 47.5 mmol) in THF (30 mL). The reaction mixture was refluxed overnight, and then quenched carefully with water. The product was extracted with ether and

dried over $MgSO_4$. After purification with a column chromatography (eluent: hexane/EtOAc: 9:1), the diamine was obtained as a yellow/brownish powder (3.9, 8.2 mmol, 88%). The purity of the product was not perfect but it was used as is for the next step.

^{1}H NMR (400 MHz, $CDCl_3$): 7.07 (s, 2H, CH), 7.00-6.95 (m, 4H, CH), 6.96 (m, 1H, CH), 6.44 (m, 1H, CH), 5.13 (br.s, 1H, NH or OH), 3.57 (m, 4H, NCH_2), 2.45 (s, 3H, CH_{3Mes}), 2.26 (s, 6H, CH_{3Mes}), 1.56 (br.s, 9H, *t*Bu), 1.46 (br.s, 9H, *t*Bu). ^{13}C NMR (100 MHz, $CDCl_3$): 144.7 (C), 137.7 (C), 137.0 (C), 135.4 (C), 135.3 (C), 134.9(C), 133.7(C), 133.3 (CH), 129.3 (CH), 129.2 (C), 120.5 (CH), 119.3 (CH), 117.1 (C), 114.6 (C), 113.6 (CH), 112.3 (C), 46.7 (NCH_2), 44.2 (NCH_2), 34.7 (*t*Bu), 34.4 (*t*Bu), 31.8 (br, *t*Bu), 29.8 (*t*Bu), 20.8 (CH_3), 18.0 (CH_3). HR-MS (FAB+): *m/z*: *calcd* for $C_{31}H_{44}ON_3$: 474.3484; *found*: 474.3500.

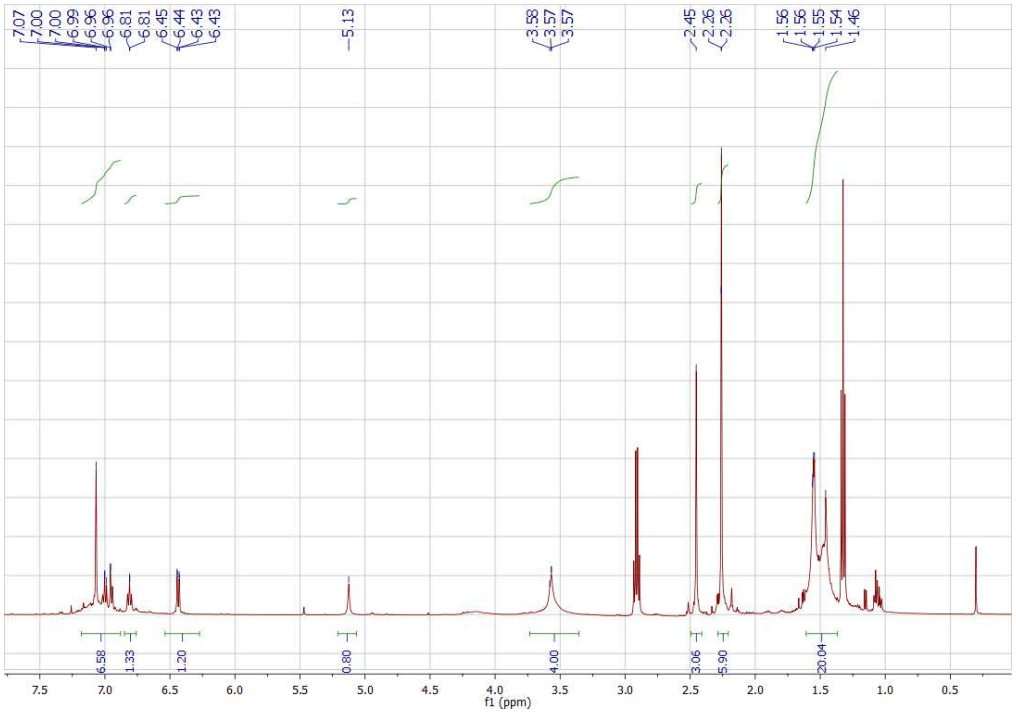


Figure S11: ^{1}H NMR of N-(2-mesitylaminophenyl)-N'-(3,5-di-tert-butyl-2-hydroxyphenyl)-ethylenediamine (**3**) in $CDCl_3$ (with trace of ethanol).

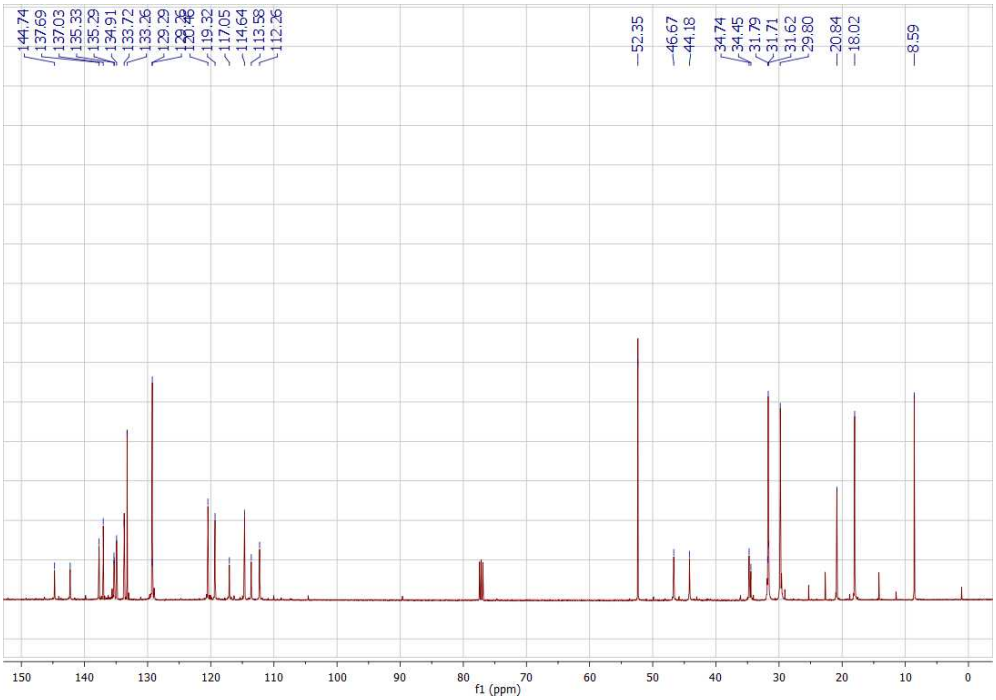


Figure S12: ^{13}C NMR of N-(2-mesitylaminophenyl)-N'-(3,5-di-tert-butyl-2-hydroxyphenyl)-ethylenediamine (**3**) in $CDCl_3$ (with trace of ethanol).

3-(3,5-di-tert-butyl-2-hydroxyphenyl)-1-(2-(mesitylamino)phenyl)-4,5-dihydro-1H-imidazol-3-ium chloride (4): To a solution of diamine **3** (0.5 g, 1.06 mmol) in methanol (20 mL) was added 1N HCl solution (2.1 mL, 2.12 mmol). After stirring during 30 minutes, the solution was evaporated under vacuum yielding the dihydrochloride salt of the diamine. To this solid was then added triethylorthoformate (20 mL) and the mixture was heated at 40 ºC. After 15 minutes, a white solid precipitated, which was filtrated and washed several times with hexane. The desired dihydro-1*H*-imidazolium **4** was obtained as a white powder (0.32 g, 0.63 mmol, 59 %). ^1H NMR (400 MHz, $CDCl_3$): 9.74 (s, 1H, OH), 8.18 (s, 1H, NCHN), 8.11 (s, 1H, NH), 7.35 (s, 1H, CH_{Ph}), 7.13 (m, 1H, CH_{Ph}), 7.11 (m, 1H, CH_{Ph}), 6.99 (s, 1H, CH_{Ph}), 6.89 (s, 2H, CH_{Mes}), 6.67 (m, 1H, CH_{Ph}), 6.28 (m, 1H, CH_{Ph}), 4.77 (s, 4H, NCH_2), 2.28 (s, 3H, CH_{3Mes}), 2.22 (s, 6H, CH_{3Mes}), 1.41 (s, 9H, *t*Bu), 1.30 (s, 9H, *t*Bu).^1H NMR (500 MHz, MeOH-d4, -40ºC): 7.43-7.40 (m, 3H, CH), 7.17 (pt, *J* = 7.2 Hz, 1H, CH), 7.00 (s, 2H, CH), 6.78 (pt, J = 7.2 Hz, 1H, CH), 6.16 (d, J = 8.3

Hz, 1H, CH), 4.56 (m, 2H, NCH_2), 4.45 (m, 2H, NCH_2), 2.32 (s, 3H, CH_{3Mes}), 2.18 (s, 6H, CH_{3Mes}), 1.45 (s, 9H, tBu), 1.33 (s, 9H, tBu). ^{13}C NMR (100 MHz, $CDCl_3$): 158.1 (NCHN), 148.5 (C), 143.9 (C), 143.3 (C), 142.0 (C), 136.4 (C), 135.7 (C), 134.7 (C), 131.3 (CH), 129.4 (CH), 126.6 (CH), 125.3 (C), 125.2 (CH), 120.9 (C), 118.6 (CH), 117.1 (CH), 114.7 (CH), 52.1 (NCH_2), 50.2 (NCH_2), 35.8 (*t*Bu), 34.6 (*t*Bu), 31.6 (*t*Bu), 29.9 (*t*Bu), 21.1 (CH_{3Mes}), 18.7 (CH_{3Mes}). Anal. Calcd. for $C_{32}H_{42}ClN_3O$: C, 73.89; H, 8.14; N, 8.08. Found: C, 73.78; H, 8.23; N, 7.88.

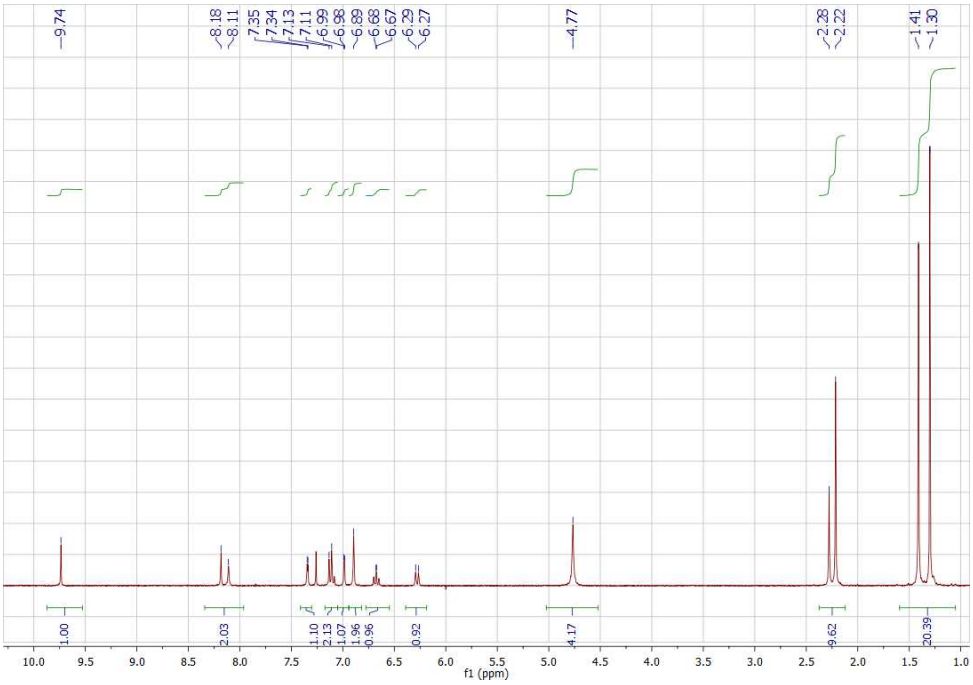


Figure S13: ^1H NMR of 3-(3,5-di-tert-butyl-2-hydroxyphenyl)-1-(2-(mesitylamino)phenyl)-4,5-dihydro-1H-imidazol-3-ium chloride (**4**) in $CDCl_3$.

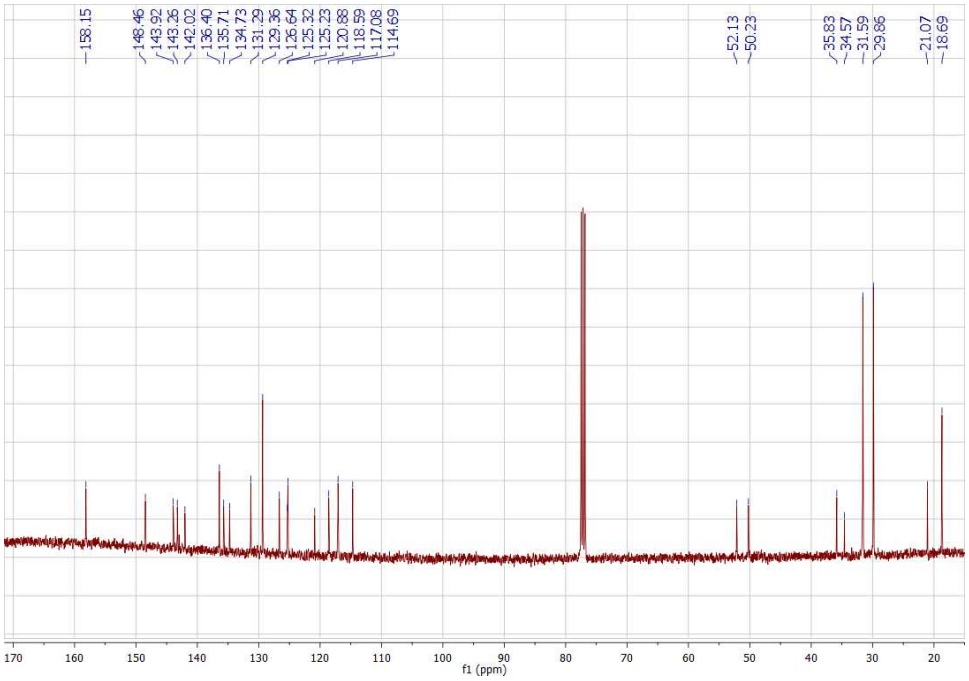


Figure S14: ^{13}C NMR of 3-(3,5-di-tert-butyl-2-hydroxyphenyl)-1-(2-(mesitylamino)phenyl)-4,5-dihydro-1H-imidazol-3-ium chloride (**4**) in $CDCl_3$.

3-(2-((3,5-di-tert-butyl-2-hydroxyphenyl)amino)ethyl)-1-mesityl-1H-benzo[d]imidazole-3-ium chloride (5): A solution of dihydroimidazolium **4** (0.5 g, 0.96 mmol) in toluene (20 mL) was heated at 90 ºC, the solid slowly dissolved. After 20 minutes at 90 ºC, the solution was evaporated to yield the desired product as a white powder (0.5 g, 0.96 mmol, 100 %). ^1H NMR (400 MHz, toluene d_8): 11.65 (s, 1H, NCHN), 8.66 (s, 1H, OH), 7.64 (d, J = 8.2 Hz, 1H, CH_{Ph}), 7.13 (t, J = 7.8 Hz, 1H, CH_{Ph}), 6.88 (t, J = 7.8 Hz, 1H, CH_{Ph}), 6.82 (m, 1H, CH_{Ph}), 6.66 (s, 2H, CH_{Mes}), 6.44 (d, J = 8.2 Hz, 1H, CH_{Ph}), 6.33 (br.s, 1H, NH), 6.21 (s, 1H, CH_{Ph}), 5.13 (m, 2H, NCH_2), 3.57 (m, 2H, NCH_2), 2.07 (s, 3H, CH_3), 1.83 (s, 6H, CH_3), 1.65 (s, 9H, *t*Bu), 1.12 (s, 9H, *t*Bu). ^{13}C NMR (100 MHz, toluene d_8): 147.1 (NCHN), 142.3 (C), 141.6 (C), 140.7 (C), 138.6 (C), 137.2 (C), 136.5 (C), 131.8 (C), 131.3 (C), 129.9 (CH), 126.7 (CH), 126.6 (CH), 125.2 (C), 114.2 (CH), 112.7 (CH), 112.3 (CH), 105.7 (CH), 48.7 (NCH_2), 42.2 (NCH_2), 35.5 (*t*Bu), 34.5 (*t*Bu), 31.9 (*t*Bu), 30.6 (*t*Bu), 21.1 (CH_3), 17.7 (CH_3). Anal. Calcd. for $C_{32}H_{42}ClN_3O$: C, 73.89; H, 8.14; N, 8.08. Found: C, 73.50; H, 8.52; N, 8.13.

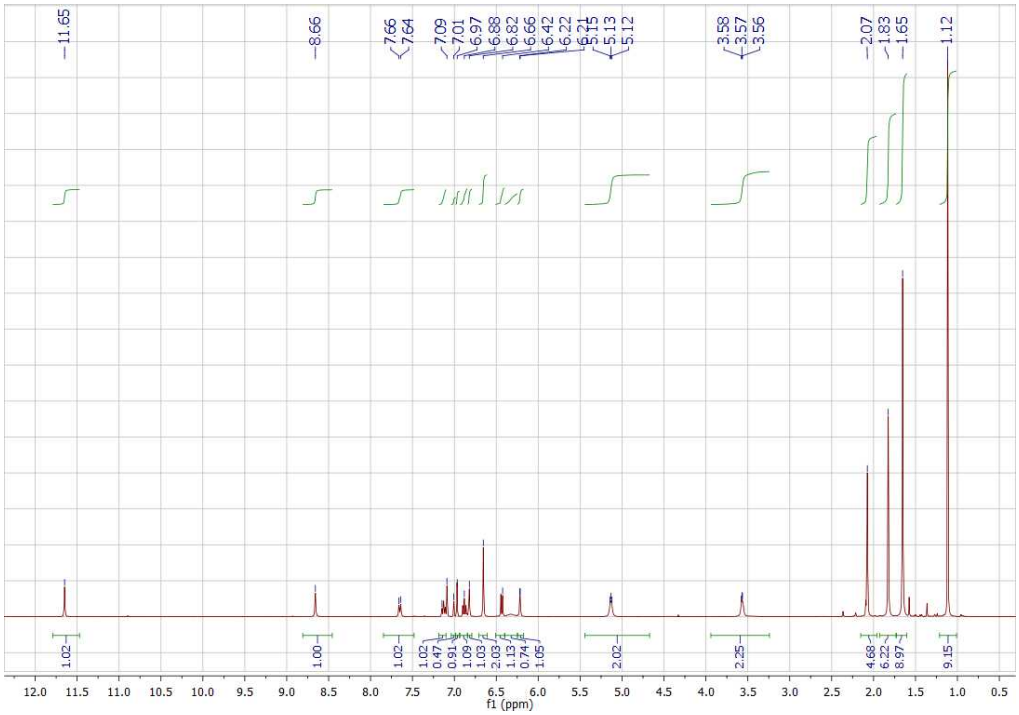


Figure S15: ^{1}H NMR of 3-(2-((3,5-di-tert-butyl-2-hydroxyphenyl)amino)ethyl)-1-mesityl-1H-benzo[d]imidazole-3-ium chloride (**5**) in toluene d_8.

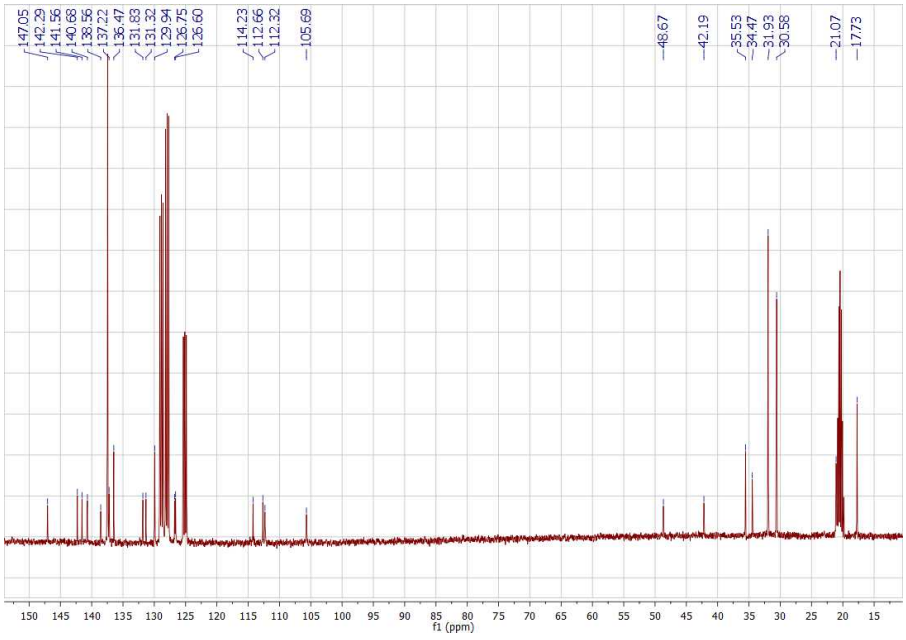


Figure S16: ^{13}C NMR of 3-(2-((3,5-di-tert-butyl-2-hydroxyphenyl)amino)ethyl)-1-mesityl-1H-benzo[d]imidazole-3-ium chloride (**5**) in toluene d_8.

5,7-di-tert-butyl-3-(2-(1-mesityl-1H-benzo[d]imidazole-3-ium-3-yl)ethyl)benzo[d]oxazol-3-ium bis-tetrafluoroborate (6): To a solution of diamine **3** (1.8 g, 3.80 mmol) in methanol (40 mL) was added a solution of HBF_4 in ether (2.1 mL, 54% wt, 7.60 mmol). After stirring during 30 minutes, the solution was evaporated under vacuum yielding the dihydrotetrafluoroborate salt of the diamine. To this solid was then added triethylorthoformate (30 mL) and the mixture was heated at 40 ºC. After 15 minutes, a white solid precipitated, which was filtrated and washed several times with hexane. The benzimidazolium-benzoxazolium was obtained as a white powder (2.2 g, 62 %). ^{1}H NMR (400 MHz, acetone-d_6): 10.56 (s, 1H, NCH), 9.58 (s, 1H, NCH), 8.64 (m, 1H, CH_{Ph}), 7.99 (m, 1H, CH_{Ph}), 7.88 (m, 1H, CH_{Ph}), 7.77 (s, 1H, CH_{Ph}), 7.55 (m, 2H, CH_{Mes}), 7.15 (s, 2H, CH_{Ph}), 5.80 (pt, J = 6.1 Hz, 2H, NCH_2), 5.66 (pt, J = 6.1 Hz, 2H, NCH_2), 2.36 (s, 3H, CH_3), 1.71 (s, 6H, CH_3), 1.54 (s, 9H, *t*Bu), 1.16 (s, 9H, *t*Bu). ^{13}C NMR (100 MHz, acetone-d_6): 159.5 (NCH), 154.1 (C), 146.8 (C), 144.9 (NCH), 142.6 (C), 138.3 (C), 136.4 (C),132.9 (C), 132.2 (C), 130.8 (CH), 130.1 (CH), 129.7 (CH), 129.4 (C), 128.9 (CH), 125.8 (CH), 115.6 (CH), 114.8 (CH), 108.9 (CH), 48.0 (NCH_2), 46.2 (NCH_2), 36.5 (*t*Bu), 35.6 (*t*Bu), 31.5 (*t*Bu), 30.1 (*t*Bu), 21.2 (CH_3), 17.1 (CH_3). Anal. Calcd. for $C_{33}H_{41}B_2F_8N_3O$: C, 59.22; H, 6.17; N, 6.28. Found: C, 58.83; H, 6.10; N, 6.01.

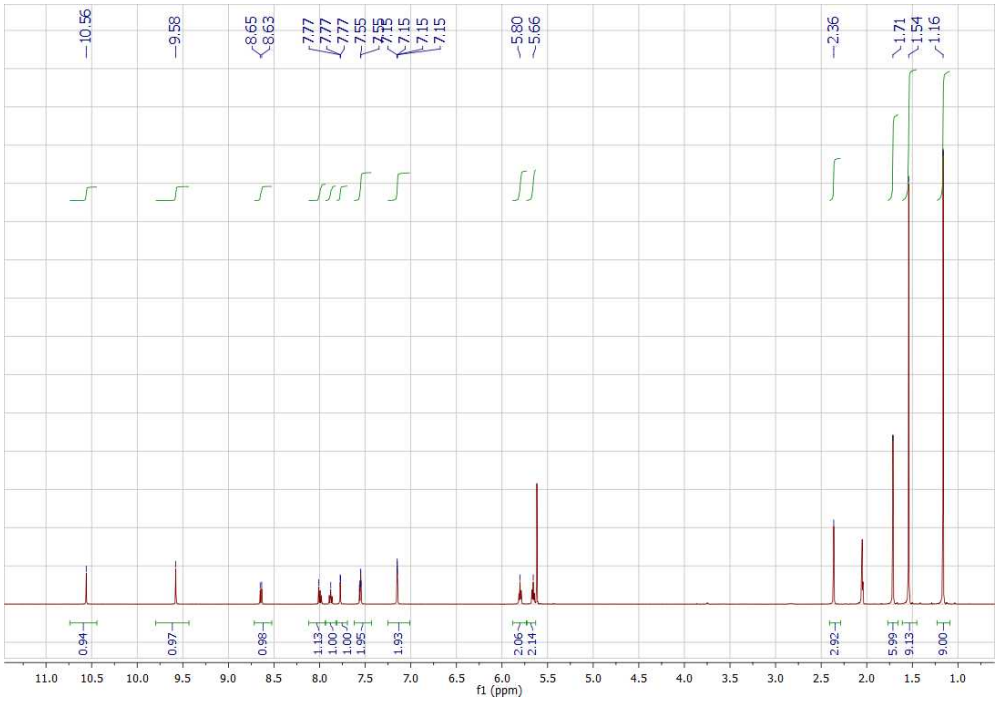


Figure S17: ^{1}H NMR of 5,7-di-tert-butyl-3-(2-(1-mesityl-1H-benzo[d]imidazole-3-ium-3-yl)ethyl)benzo[d]oxazol-3-ium bis-tetrafluoroborate (**6**) in acetone d_6 (with trace of CH_2Cl_2).

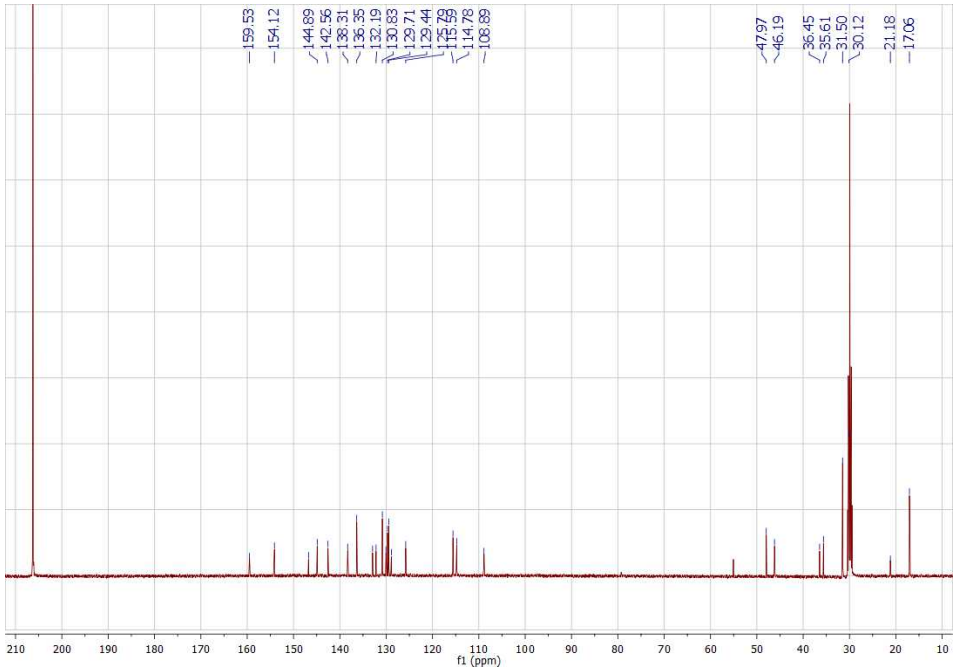


Figure S18: ^{13}C NMR of 5,7-di-tert-butyl-3-(2-(1-mesityl-1H-benzo[d]imidazole-3-ium-3-yl)ethyl)benzo[d]oxazol-3-ium bis-tetrafluoroborate (**6**) in acetone d_6 (with trace of CH_2Cl_2).

Bis-[3-(2-((3,5-di-tert-butyl-2-hydroxyphenyl)amino)ethyl)-1-mesityl-1H-benzo[d]imidazoly-3-dene zirconium complex (7): To a solution of imidazolium **4** (40.0 mg, 0.076 mmol) in toluene (4 mL) was added a solution of KHMDS (46 mg, 0.23 mmol) in toluene (2 mL). After 30 minutes at room temperature, a solution of $ZrCl_4$ (9.0 mg, 0.038 mmol) in toluene (2 mL) was added. After stirring during 30 minutes, the solution was filtrated through a plug a celite and evaporated. The product was recrystallized from toluene/pentane at low temperature (-20°C) to give **7** as red crystals (21 mg, 52 %).

^{1}H NMR (400 MHz, C_6D_6): 6.97 (s, 2H, CH), 6.96 (s, 2H, CH), 6.86 (d, J = 2.1 Hz, 2H, CH), 6.79 (s, 2H, CH), 6.74 (m, 2H, CH), 6.53 (s, 2H, CH), 6.30 (d, J = 8.2 Hz, 2H, CH), 6.06 (d, J = 2.1 Hz, 2H, CH), 4.20 (m, 2H, NCH_2), 3.62 (m, 2H, NCH_2), 3.40 (m, 2H, NCH_2), 2.75 (m, 2H, NCH_2), 2.29 (s, 6H, CH_3), 1.66 (s, 36H, *t*Bu), 1.30 (s, 6H, CH_3), 0.86 (s, 6H, CH_3). ^{13}C NMR (151 MHz, C_6D_6): 200.1 (C_{carb}), 153.6 (C), 152.3 (C), 139.7 (C), 139.5(C), 138.1 (C), 135.1 (C), 134.4 (C), 133.7 (C), 133.4 (C), 131.4 (CH), 130.9 (C), 128.3 (CH), 124.4 (CH), 124.1 (CH), 111.7 (CH), 111.1 (CH), 110.5 (CH), 104.7 (CH), 50.5 (NCH_2), 47.4 (NCH_2), 35.1 (*t*Bu), 35.0 (*t*Bu), 33.0 (*t*Bu), 30.4 (*t*Bu), 21.3 (CH_3), 17.7 (CH_3), 16.9 (CH_3). Anal. Calcd. for $C_{64}H_{80}N_6O_2Zr$: C, 72.75; H, 7.63; N, 7.95. Found: C, 70.30; H, 6.88; N, 7.32. The poor purity observed with the elemental analysis is probably due to the sensitivity of the compound.

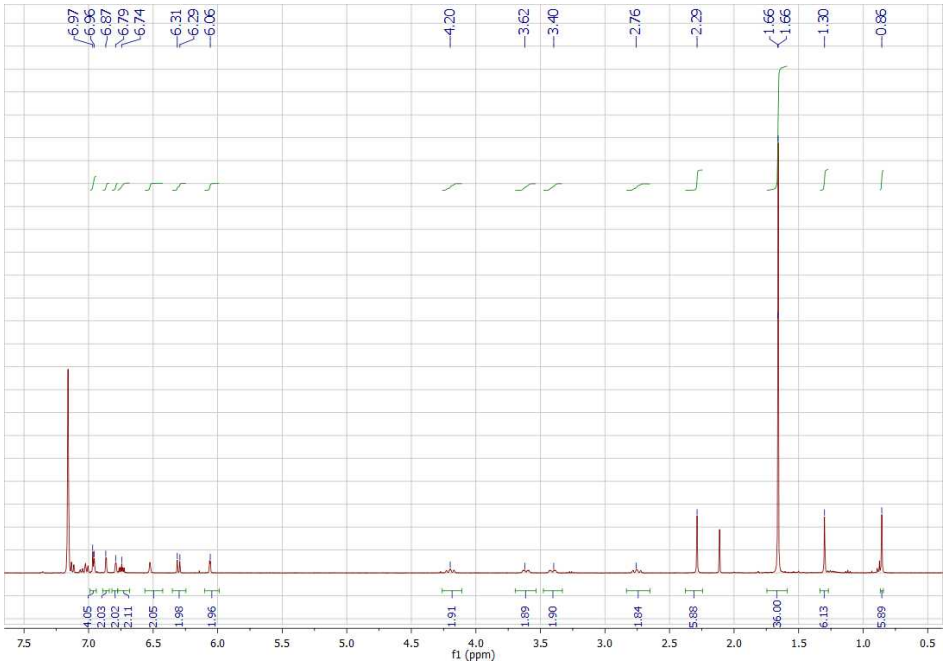


Figure S19: ^{1}H NMR of Bis-[3-(2-((3,5-di-tert-butyl-2-hydroxyphenyl)amino)ethyl)-1-mesityl-1H-benzo[d]imidazoly-3-dene zirconium complex (**7**) in C_6D_6 (with trace of toluene).

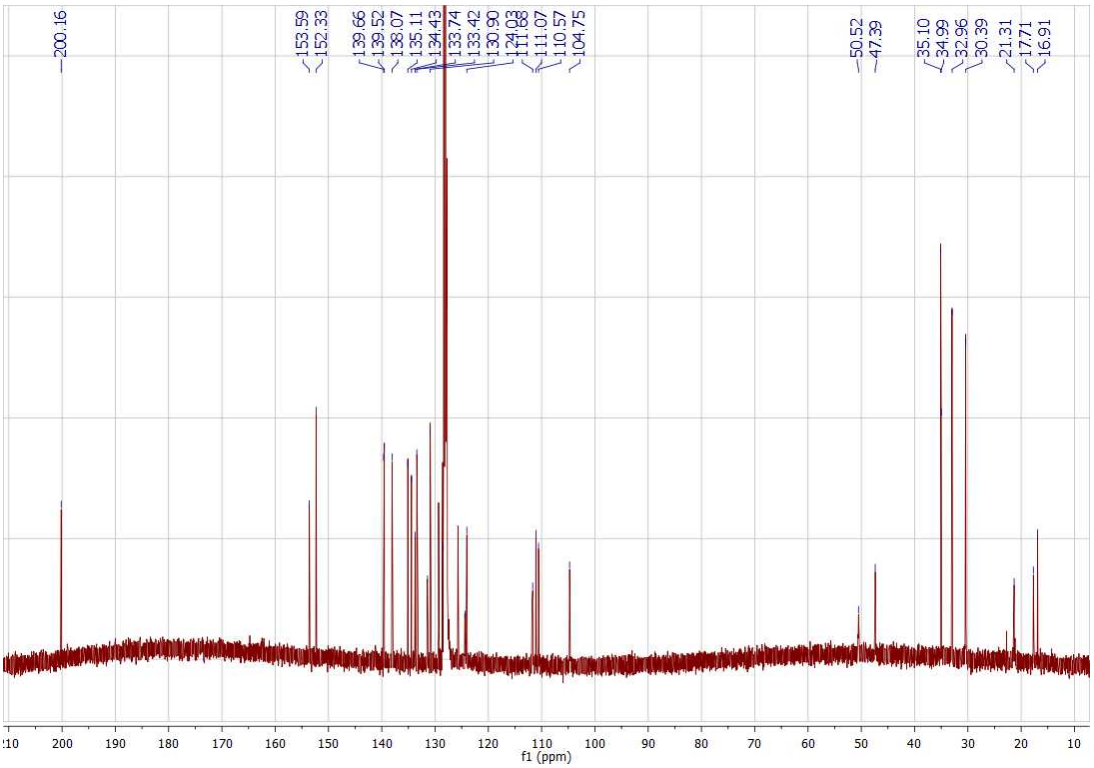


Figure S20: ^{13}C NMR of Bis-[3-(2-((3,5-di-tert-butyl-2-hydroxyphenyl)amino)ethyl)-1-mesityl-1H-benzo[d]imidazoly-3-dene zirconium complex (**7**) in C_6D_6 (with trace of toluene).

2. Crystallographic data:

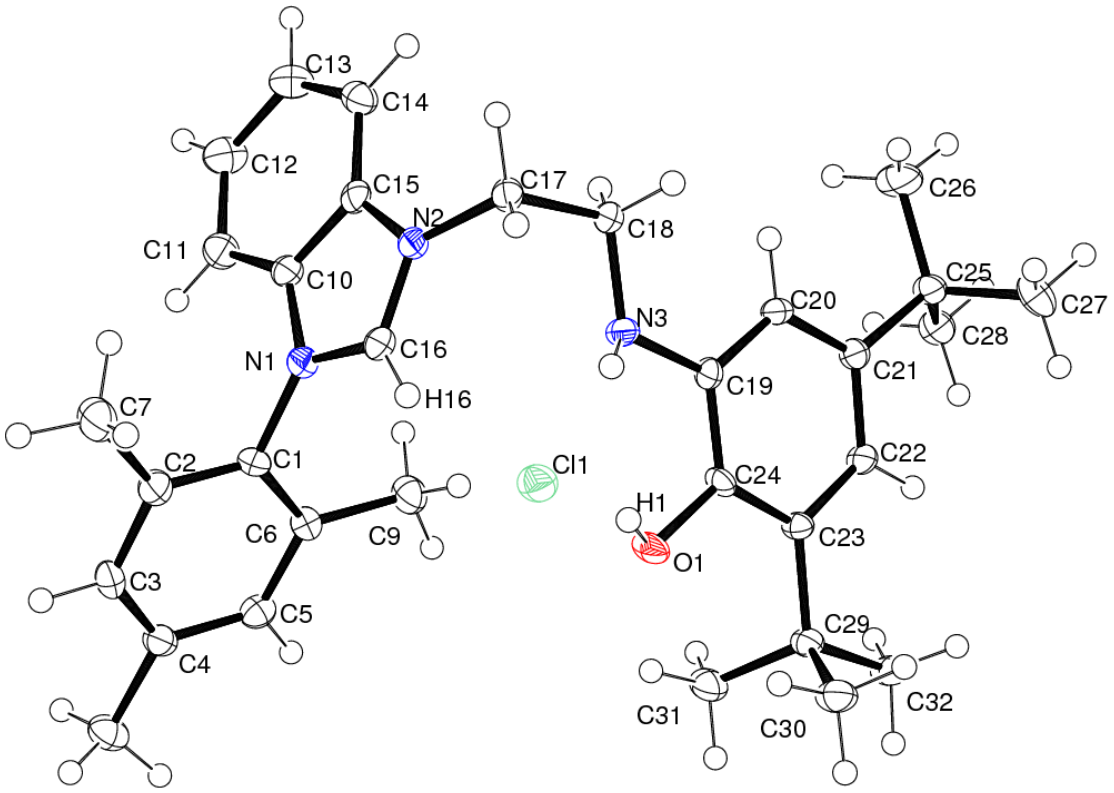


Figure 1. Molecular structure of benzoimidazolium **5** (CCDC 857560).

Table 1. Crystal data and structure refinement for 5 (CCDC 857560).

Empirical formula	$[C_{32}H_{42}N_3O]^+Cl^- \bullet C_3H_6O$
Formula weight	578.21
Crystallization Solvent	Acetone/pentane
Crystal Habit	Block
Crystal size	0.29 x 0.16 x 0.11 mm^3
Crystal color	Colorless
Data Collection	
Type of diffractometer	Bruker KAPPA APEX II
Wavelength	0.71073 Å MoKα
Data Collection Temperature	100(2) K
θ range for 9987 reflections used in lattice determination	2.26 to 30.51°
Unit cell dimensions	a = 10.3948(5) Å α= 90°

	b = 12.9525(6) Å β= 92.424(3)°
	c = 25.0752(13) Å γ = 90°
Volume	3373.1(3) $Å^3$
Z	4
Crystal system	Monoclinic
Space group	P $2_1/c$
Density (calculated)	1.139 Mg/m^3
F(000)	1248
Data collection program	Bruker APEX2 v2009.7-0
θ range for data collection	1.63 to 30.56°
Completeness to θ = 30.56°	99.7 %
Index ranges	$-14 \le h \le 14$, $-18 \le k \le 18$, $-35 \le l \le 35$
Data collection scan type	ω scans; 8 settings
Data reduction program	Bruker SAINT-Plus v7.68A
Reflections collected	67537
Independent reflections	10318 [R_{int}= 0.0530]
Absorption coefficient	0.146 mm^{-1}
Absorption correction	None
Max. and min. transmission	0.9841 and 0.9588

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 2008)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Difference Fourier map
Structure refinement program	SHELXL-97 (Sheldrick, 2008)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	10318 / 0 / 389
Treatment of hydrogen atoms	Mixed
Goodness-of-fit on F^2	2.400
Final R indices [I>2σ(I), 6981 reflections]	R1 = 0.0545, *w*R2 = 0.0731
R indices (all data)	R1 = 0.0844, *w*R2 = 0.0742
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.000
Average shift/error	0.000
Largest diff. peak and hole	1.226 and -1.011 $e.Å^{-3}$

Special Refinement Details:

Crystals were mounted on a glass fiber using Paratone oil then placed on the diffractometer under a nitrogen stream at 100K.

All hydrogen atoms were located in the electron density difference Fourier map then the two involved on hydrogen bonding to chloride (H1 and H3A) were refined without any restraints. Note the geometry around N3 is tetrahedral.

Table 2. Bond lengths [Å] and angles [°] for 5 (CCDC 857560).

O(1)-C(24)	1.3853(17)	C(25)-C(26)	1.529(2)
N(1)-C(16)	1.3366(19)	C(25)-C(28)	1.537(2)
N(1)-C(10)	1.4060(19)	C(25)-C(27)	1.544(2)
N(1)-C(1)	1.4528(19)	C(29)-C(32)	1.544(2)
N(2)-C(16)	1.3284(19)	C(29)-C(30)	1.541(2)
N(2)-C(15)	1.3941(19)	C(29)-C(31)	1.536(2)
N(2)-C(17)	1.4723(19)	O(2)-C(34)	1.239(3)
N(3)-C(19)	1.4068(19)	C(33)-C(34)	1.484(3)
N(3)-C(18)	1.4506(18)	C(34)-C(35)	1.524(3)
C(1)-C(2)	1.386(2)		
C(1)-C(6)	1.395(2)	C(16)-N(1)-C(10)	108.25(13)
C(2)-C(3)	1.390(2)	C(16)-N(1)-C(1)	126.87(14)
C(2)-C(7)	1.509(2)	C(10)-N(1)-C(1)	124.45(14)
C(3)-C(4)	1.384(2)	C(16)-N(2)-C(15)	108.86(14)
C(4)-C(5)	1.392(2)	C(16)-N(2)-C(17)	125.16(14)
C(4)-C(8)	1.508(2)	C(15)-N(2)-C(17)	125.54(14)
C(5)-C(6)	1.393(2)	C(19)-N(3)-C(18)	120.52(14)
C(6)-C(9)	1.517(2)	C(2)-C(1)-C(6)	123.13(15)
C(10)-C(11)	1.382(2)	C(2)-C(1)-N(1)	119.53(15)
C(10)-C(15)	1.390(2)	C(6)-C(1)-N(1)	117.26(14)
C(11)-C(12)	1.378(2)	C(3)-C(2)-C(1)	116.94(16)
C(12)-C(13)	1.403(2)	C(3)-C(2)-C(7)	120.88(16)
C(13)-C(14)	1.376(2)	C(1)-C(2)-C(7)	122.14(15)
C(14)-C(15)	1.390(2)	C(2)-C(3)-C(4)	122.74(16)
C(17)-C(18)	1.527(2)	C(3)-C(4)-C(5)	118.02(15)
C(19)-C(20)	1.388(2)	C(3)-C(4)-C(8)	121.10(15)
C(19)-C(24)	1.398(2)	C(5)-C(4)-C(8)	120.89(15)
C(20)-C(21)	1.389(2)	C(6)-C(5)-C(4)	121.88(16)
C(21)-C(22)	1.396(2)	C(5)-C(6)-C(1)	117.23(15)
C(21)-C(25)	1.538(2)	C(5)-C(6)-C(9)	120.99(15)
C(22)-C(23)	1.392(2)	C(1)-C(6)-C(9)	121.78(14)
C(23)-C(24)	1.393(2)	C(11)-C(10)-C(15)	122.38(16)
C(23)-C(29)	1.532(2)	C(11)-C(10)-N(1)	131.34(16)

C(15)-C(10)-N(1)	106.26(14)
C(12)-C(11)-C(10)	116.05(17)
C(11)-C(12)-C(13)	121.57(17)
C(14)-C(13)-C(12)	122.49(16)
C(13)-C(14)-C(15)	115.67(16)
C(10)-C(15)-C(14)	121.84(16)
C(10)-C(15)-N(2)	106.64(14)
C(14)-C(15)-N(2)	131.51(16)
N(2)-C(16)-N(1)	109.98(15)
N(2)-C(17)-C(18)	111.53(12)
N(3)-C(18)-C(17)	107.81(13)
C(20)-C(19)-N(3)	122.48(15)
C(20)-C(19)-C(24)	119.65(15)
N(3)-C(19)-C(24)	117.86(14)
C(21)-C(20)-C(19)	121.00(15)
C(20)-C(21)-C(22)	117.56(15)
C(20)-C(21)-C(25)	122.18(14)
C(22)-C(21)-C(25)	120.22(14)
C(21)-C(22)-C(23)	123.51(15)
C(24)-C(23)-C(22)	116.96(14)
C(24)-C(23)-C(29)	120.60(14)
C(22)-C(23)-C(29)	122.44(14)
O(1)-C(24)-C(23)	118.81(14)
O(1)-C(24)-C(19)	119.87(14)
C(23)-C(24)-C(19)	121.29(15)
C(26)-C(25)-C(28)	108.41(13)
C(26)-C(25)-C(21)	112.00(14)
C(28)-C(25)-C(21)	110.30(13)
C(26)-C(25)-C(27)	108.15(14)
C(28)-C(25)-C(27)	109.23(14)
C(21)-C(25)-C(27)	108.69(13)
C(32)-C(29)-C(23)	111.98(13)
C(32)-C(29)-C(30)	107.36(14)
C(23)-C(29)-C(30)	109.98(13)
C(32)-C(29)-C(31)	106.21(13)
C(23)-C(29)-C(31)	110.06(14)
C(30)-C(29)-C(31)	111.20(13)
O(2)-C(34)-C(33)	128.5(3)
O(2)-C(34)-C(35)	119.4(3)
C(33)-C(34)-C(35)	112.1(2)

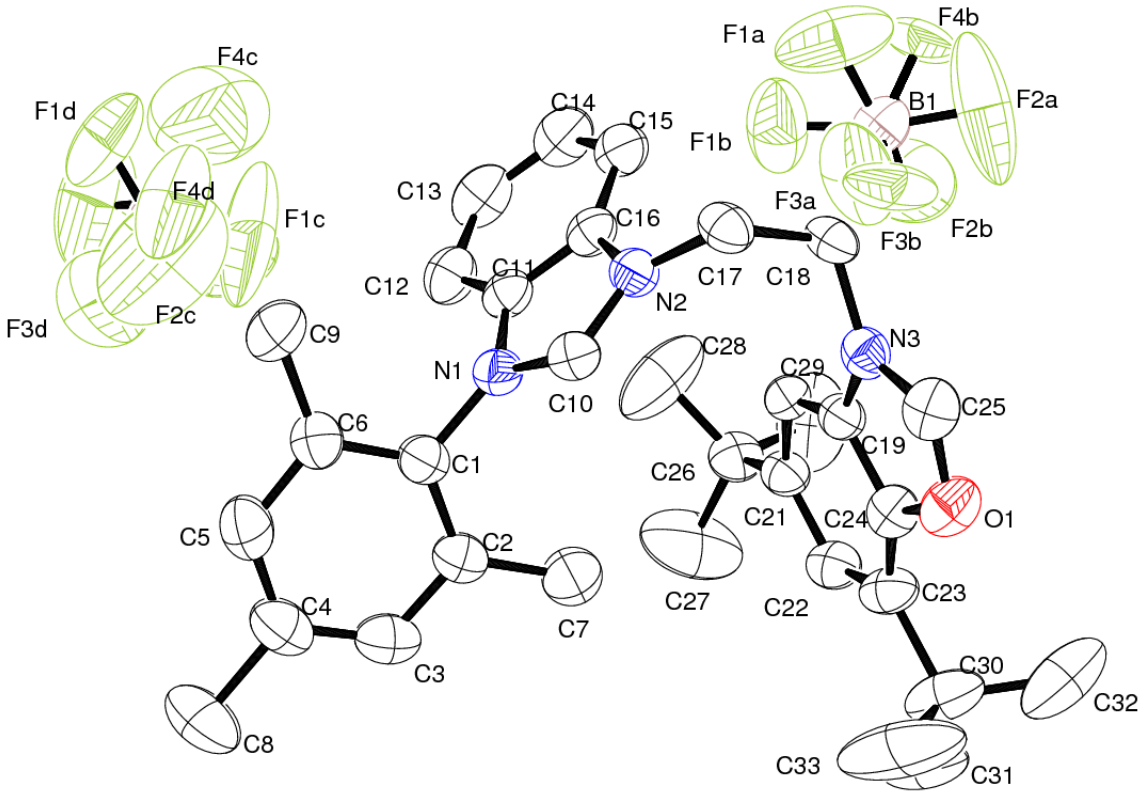


Figure 2: Molecular structure of benzoimidazolium-benzoxazolium bis-tetrafluoroborate **6**.

Table 1'. Crystal data and structure refinement for 6 (CCDC 862749).

Empirical formula	$[C_{33}H_{41}N_3O]^{+2}\ 2(BF_4)^{-} \bullet 2(C_3H_6O)$
Formula weight	785.46
Crystallization Solvent	acetone/pentane
Crystal Habit	Block
Crystal size	0.40 x 0.36 x 0.28 mm^3
Data Collection	
Type of diffractometer	Bruker KAPPA APEX II
Wavelength	0.71073 Å MoKα
Data Collection Temperature	100(2) K
θ range for 9917 reflections used in lattice determination	2.37 to 28.55°
Unit cell dimensions	a = 8.9329(3) Å α= 79.606(2)°

	b = 15.3817(5) Å β= 81.358(2)°
	c = 16.3064(6) Å γ = 75.254(2)°
Volume	2118.34(13) $Å^3$
Z	2
Crystal system	Triclinic
Space group	P-1
Density (calculated)	1.231 Mg/m^3
F(000)	828
θ range for data collection	1.74 to 30.54°
Completeness to θ = 30.54°	99.9 %
Index ranges	$-12 \le h \le 12$, $-21 \le k \le 21$, $-23 \le l \le 23$
Data collection scan type	ω scans; 11 settings
Reflections collected	58613
Independent reflections	12943 [R_{int}= 0.0310]
Absorption coefficient	0.100 mm^{-1}
Absorption correction	None
Max. and min. transmission	0.9724 and 0.9610
Structure solution and Refinement	
Structure solution program	SHELXS-97 (Sheldrick, 2008)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	SHELXL-97 (Sheldrick, 2008)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	12943 / 564 / 573
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	4.929
Final R indices [I>2σ(I), 7074 reflections]	R1 = 0.0840, *w*R2 = 0.1135
R indices (all data)	R1 = 0.1344, *w*R2 = 0.1147
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.001
Average shift/error	0.000
Largest diff. peak and hole	0.537 and -0.414 $e.Å^{-3}$

Special Refinement Details:

Crystals were mounted on a glass fiber using Paratone oil then placed on the diffractometer under a nitrogen stream at 100K.

The tetrafluoroborate anions are disordered. The B-F and F-F distances were restrained to be similar. Restraints were placed on the anisotropic displacement parameters of all atoms to approximate isotropic behavior.

Table 2'. Bond lengths [Å] and angles [°] for 6 (CCDC 862749).

O(1)-C(25)	1.305(3)	C(26)-C(27)	1.481(3)
O(1)-C(24)	1.402(3)	C(26)-C(29)	1.517(3)
N(1)-C(10)	1.327(2)	C(30)-C(31)	1.531(4)
N(1)-C(11)	1.400(2)	C(30)-C(32)	1.533(4)
N(1)-C(1)	1.447(3)	C(30)-C(33)	1.539(3)
N(2)-C(10)	1.321(2)	O(42)-C(42)	1.195(3)
N(2)-C(16)	1.397(2)	C(41)-C(42)	1.479(4)
N(2)-C(17)	1.463(2)	C(42)-C(43)	1.464(4)
N(3)-C(25)	1.304(2)	O(52)-C(52)	1.124(5)
N(3)-C(19)	1.404(3)	C(51)-C(52)	1.357(7)
N(3)-C(18)	1.473(3)	C(52)-C(53)	1.401(7)
C(1)-C(6)	1.392(3)	B(1)-F(4A)	1.278(6)
C(1)-C(2)	1.395(3)	B(1)-F(4B)	1.294(5)
C(2)-C(3)	1.383(3)	B(1)-F(3A)	1.233(7)
C(2)-C(7)	1.502(3)	B(1)-F(3B)	1.338(8)
C(3)-C(4)	1.386(3)	B(1)-F(1A)	1.380(6)
C(4)-C(5)	1.382(3)	B(1)-F(2B)	1.347(8)
C(4)-C(8)	1.523(3)	B(1)-F(2A)	1.422(6)
C(5)-C(6)	1.390(3)	B(1)-F(1B)	1.440(5)
C(6)-C(9)	1.503(3)	B(1C)-F(3C)	1.30(3)
C(11)-C(12)	1.373(3)	B(1C)-F(1C)	1.17(3)
C(11)-C(16)	1.388(3)	B(1C)-F(2C)	1.39(3)
C(12)-C(13)	1.387(3)	B(1C)-F(4C)	1.27(2)
C(13)-C(14)	1.394(3)	B(1D)-F(2D)	1.35(4)
C(14)-C(15)	1.376(3)	B(1D)-F(3D)	1.19(3)
C(15)-C(16)	1.390(3)	B(1D)-F(4D)	1.33(4)
C(17)-C(18)	1.506(3)	B(1D)-F(1D)	1.48(4)
C(19)-C(24)	1.381(3)		
C(19)-C(20)	1.390(3)	C(25)-O(1)-C(24)	106.72(18)
C(20)-C(21)	1.376(3)	C(10)-N(1)-C(11)	108.00(19)
C(21)-C(22)	1.407(3)	C(10)-N(1)-C(1)	125.19(18)
C(21)-C(26)	1.523(3)	C(11)-N(1)-C(1)	126.76(19)
C(22)-C(23)	1.384(3)	C(10)-N(2)-C(16)	108.10(18)
C(23)-C(24)	1.369(3)	C(10)-N(2)-C(17)	124.58(18)
C(23)-C(30)	1.538(3)	C(16)-N(2)-C(17)	127.12(18)
C(26)-C(28)	1.514(3)	C(25)-N(3)-C(19)	107.40(19)

C(25)-N(3)-C(18)	126.1(2)	C(28)-C(26)-C(27)	109.4(3)
C(19)-N(3)-C(18)	126.38(19)	C(21)-C(26)-C(29)	106.6(2)
C(6)-C(1)-C(2)	123.3(2)	C(28)-C(26)-C(29)	106.2(2)
C(6)-C(1)-N(1)	118.2(2)	C(27)-C(26)-C(29)	110.7(3)
C(2)-C(1)-N(1)	118.5(2)	C(31)-C(30)-C(32)	109.5(3)
C(3)-C(2)-C(1)	117.0(2)	C(31)-C(30)-C(23)	110.9(2)
C(3)-C(2)-C(7)	120.1(2)	C(32)-C(30)-C(23)	109.3(2)
C(1)-C(2)-C(7)	122.9(2)	C(31)-C(30)-C(33)	109.4(3)
C(4)-C(3)-C(2)	121.8(3)	C(32)-C(30)-C(33)	110.0(3)
C(5)-C(4)-C(3)	119.1(2)	C(23)-C(30)-C(33)	107.8(2)
C(5)-C(4)-C(8)	120.3(3)	O(42)-C(42)-C(43)	119.8(3)
C(3)-C(4)-C(8)	120.6(3)	O(42)-C(42)-C(41)	122.9(3)
C(4)-C(5)-C(6)	121.9(3)	C(43)-C(42)-C(41)	117.3(3)
C(5)-C(6)-C(1)	116.8(2)	O(52)-C(52)-C(51)	131.6(9)
C(5)-C(6)-C(9)	120.5(2)	O(52)-C(52)-C(53)	113.8(9)
C(1)-C(6)-C(9)	122.7(2)	C(51)-C(52)-C(53)	114.0(6)
N(2)-C(10)-N(1)	110.93(19)	F(4A)-B(1)-F(4B)	104.8(4)
C(12)-C(11)-C(16)	122.8(2)	F(4A)-B(1)-F(3A)	128.6(7)
C(12)-C(11)-N(1)	130.8(2)	F(4B)-B(1)-F(3A)	126.5(6)
C(16)-C(11)-N(1)	106.30(19)	F(4A)-B(1)-F(3B)	129.1(5)
C(11)-C(12)-C(13)	115.2(2)	F(4B)-B(1)-F(3B)	121.6(5)
C(12)-C(13)-C(14)	122.4(2)	F(3A)-B(1)-F(3B)	20.7(7)
C(15)-C(14)-C(13)	121.9(2)	F(4A)-B(1)-F(1A)	110.8(4)
C(14)-C(15)-C(16)	115.8(2)	F(4B)-B(1)-F(1A)	54.3(4)
C(11)-C(16)-C(15)	121.8(2)	F(3A)-B(1)-F(1A)	98.4(6)
C(11)-C(16)-N(2)	106.64(18)	F(3B)-B(1)-F(1A)	112.5(5)
C(15)-C(16)-N(2)	131.6(2)	F(4A)-B(1)-F(2B)	32.9(4)
N(2)-C(17)-C(18)	113.67(19)	F(4B)-B(1)-F(2B)	111.3(5)
N(3)-C(18)-C(17)	112.81(17)	F(3A)-B(1)-F(2B)	115.0(7)
C(24)-C(19)-C(20)	121.5(2)	F(3B)-B(1)-F(2B)	104.9(6)
C(24)-C(19)-N(3)	105.8(2)	F(1A)-B(1)-F(2B)	141.8(6)
C(20)-C(19)-N(3)	132.6(2)	F(4A)-B(1)-F(2A)	106.1(4)
C(21)-C(20)-C(19)	116.7(2)	F(4B)-B(1)-F(2A)	55.7(4)
C(20)-C(21)-C(22)	119.6(2)	F(3A)-B(1)-F(2A)	104.8(5)
C(20)-C(21)-C(26)	120.2(2)	F(3B)-B(1)-F(2A)	86.0(5)
C(22)-C(21)-C(26)	120.2(2)	F(1A)-B(1)-F(2A)	106.3(6)
C(23)-C(22)-C(21)	124.8(2)	F(2B)-B(1)-F(2A)	83.5(5)
C(24)-C(23)-C(22)	113.2(2)	F(4A)-B(1)-F(1B)	73.2(4)
C(24)-C(23)-C(30)	121.9(2)	F(4B)-B(1)-F(1B)	113.4(4)
C(22)-C(23)-C(30)	124.9(3)	F(3A)-B(1)-F(1B)	83.4(6)
C(23)-C(24)-C(19)	124.2(2)	F(3B)-B(1)-F(1B)	103.1(5)
C(23)-C(24)-O(1)	128.7(2)	F(1A)-B(1)-F(1B)	64.5(4)
C(19)-C(24)-O(1)	107.1(2)	F(2B)-B(1)-F(1B)	100.0(5)
N(3)-C(25)-O(1)	113.0(2)	F(2A)-B(1)-F(1B)	168.9(6)
C(21)-C(26)-C(28)	111.7(2)	F(3C)-B(1C)-F(1C)	121(2)
C(21)-C(26)-C(27)	112.1(2)	F(3C)-B(1C)-F(2C)	107.1(15)

F(1C)-B(1C)-F(2C)	102(2)	F(2D)-B(1D)-F(4D)	126(3)
F(3C)-B(1C)-F(4C)	115(2)	F(3D)-B(1D)-F(4D)	121(3)
F(1C)-B(1C)-F(4C)	96.1(14)	F(2D)-B(1D)-F(1D)	114(3)
F(2C)-B(1C)-F(4C)	116(2)	F(3D)-B(1D)-F(1D)	109(3)
F(2D)-B(1D)-F(3D)	96(3)	F(4D)-B(1D)-F(1D)	92(2)

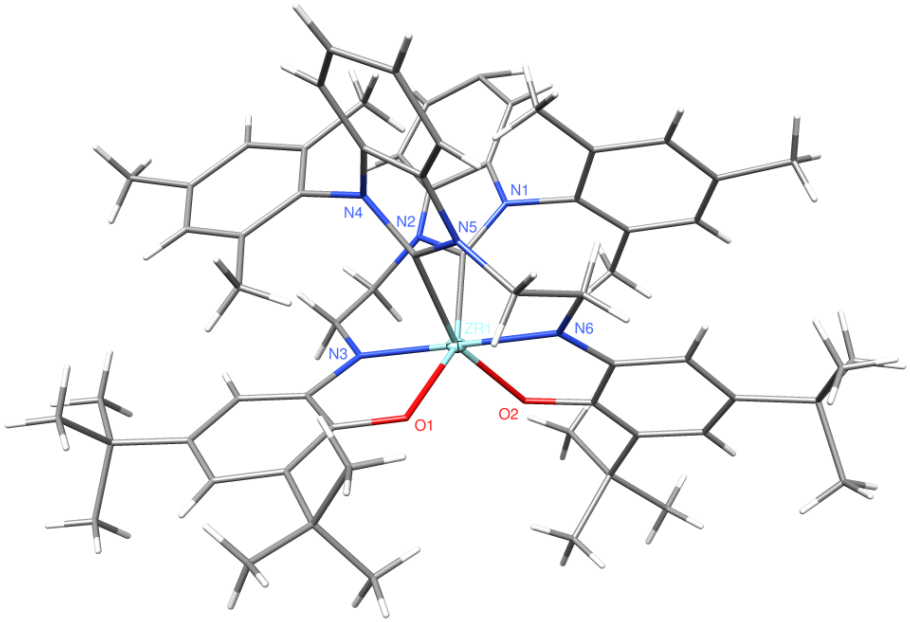


Figure 3: Molecular structure of (CNO)-carbene zirconium complex **7** (poor quality crystals).

Table 1''. Crystal data and structure refinement for 7.

Empirical formula	C85 H102 N6 O2 Zr	
Formula weight	1330.94	
Crystallization solvent	toluene/pentane	
Crystal shape	plate	
Crystal color	red	
Crystal size	0.05 x 0.13 x 0.23 mm	
Data Collection		
Preliminary photograph(s)	rotation	
Type of diffractometer	Bruker APEX-II CCD	
Wavelength	0.71073 Å MoK	
Data collection temperature	100 K	
θ range for 9964 reflections used in lattice determination	2.21 to 22.31°	
Unit cell dimensions	a = 22.077(4) Å	α= 90°
	b = 21.356(4) Å	β= 90°
	c = 31.446(5) Å	γ = 90°
Volume	14827(4) $Å^3$	
Z	8	
Crystal system	orthorhombic	
Space group	P b c a (# 61)	

Density (calculated)	1.192 g/cm^3
F(000)	5680
Theta range for data collection	1.5 to 25.0°
Completeness to theta = 25.242°	87.0%
Index ranges	$-20 \le h \le 25$, $-24 \le k \le 21$, $-36 \le l \le 35$
Data collection scan type	and scans
Reflections collected	80132
Independent reflections	11663 [R_{int}= 0.1879]
Reflections > 2σ(I)	7149
Average σ(I)/(net I)	0.1619
Absorption coefficient	0.20 mm^{-1}
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.7858

Structure Solution and Refinement

Primary solution method	dual
Hydrogen placement	geometric positions
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11663 / 0 / 434
Treatment of hydrogen atoms	constructed
Goodness-of-fit on F^2	1.06
Final R indices [I>2σ(I), 7149 reflections]	R1 = 0.2023, wR2 = 0.4486
R indices (all data)	R1 = 0.2680, wR2 = 0.4794
Type of weighting scheme used	calc
Max shift/error	0.004
Average shift/error	0.000
Extinction coefficient	0.00034(7)
Largest diff. peak and hole	2.46 and -2.91 e·Å^{-3}

Programs Used

Cell refinement	SAINT V8.27B (Bruker-AXS, 2007)
Data collection	APEX2 2011.2-3 (Bruker-AXS, 2007)
Data reduction	SAINT V8.27B (Bruker-AXS, 2007)
Structure refinement	SHELXL-2012/6 (Sheldrick, 2012)

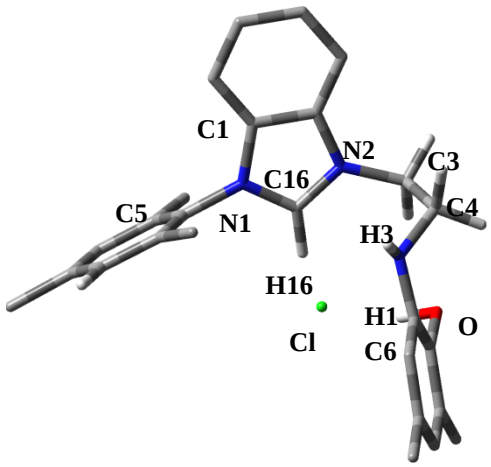
Structure **7** has a lot of absence violations; it was refined isotropically except for the Zr metal centre. The poor quality of the crystals, even after several attempts of crystallization, won't allow us to describe much in detail the different bond lengths of the structure.

3. Computational study :

Calculations were performed with the Gaussian 09 program[S1] using the Density Functional Theory method.[S2] The various structures were fully optimized at B3LYP level.[S3] This functional is built with Becke's three parameter exchange functional[S3a] and the Lee-Yang-Parr correlation functional.[S3c] The 6-31G(d,p) basis set was used. [S4] All atoms were augmented with a single set of polarization functions. The second derivatives were analytically calculated in order to determine if a minimum or a transition state (one negative eigenvalue) existed for the resulting geometry. The connection between the transition states and the corresponding minima was confirmed by IRC calculations. [S5] In the energy profile, all total energies have been calculated using the M06-2X [S6] method and the 6-31G** basis set on the geometry optimized in B3LYP/6-31G**. This method is denoted B3LYP/6-31G**//M06-2X/6-31G**. Solvent (THF) effects were taking into account by means of the single-molecule detection model (SMD) using the M06-2X/6-31G** level of theory (Single Point calculation). [S7]

Table S1. Experimental and calculated geometrical parameters for compound 5 (5") :

	with counter-anion Cl^-	
	Theo.	**RX**
compound	**5"**	**5**
C16-N1	1.344	1.336
C16-N2	1.338	1.328
C16-H16	1.101	0.950
N3-H3	1.011	0.876
O-H1	1.001	0.890
H16-Cl	2.171	2.429
H1-Cl	2.041	2.219
N1-Cl	1.400	1.406
C1-C2	1.406	1.390
N2-C2	1.396	1.394
N2-C3	1.464	1.472
C3-C4	1.545	1.527
N3-C4	1.460	1.451
N1-C5	1.446	1.453
N3-C6	1.420	1.407
C16-Cl	3.176	3.33
Cl-O	3.016	3.09
N1C16N2	109.97	109.98
ΣN3	344.0	345.19



Main bond lengths in Å and main bond angles in °.

Table S2. Theoretical geometrical parameters for compounds 4", 5", intermediate I" and transition states TS1" and TS2":

	with counter-anion Cl^-				
	4"	**5"**	**I"**	**TS1"**	**TS2"**
C16-N1	2.889	1.344	1.642	1.768	1.526
C16-N2	1.328	1.338	1.462	1.449	1.451
C16-H16	1.096	1.101	1.097	1.096	1.095
C16-N3	1.327	3.079	1.423	1.389	1.531
N3-H3	/	1.011	/	/	1.377
O-H1	1.005	1.001	1.022	1.023	1.030
H16-Cl	2.153	2.171	2.481	2.481	2.481
H1-Cl	2.010	2.041	1.912	1.910	1.880
N1-C1	1.411	1.400	1.474	1.464	1.457
C1-C2	1.417	1.406	1.395	1.397	1.395
N2-C2	1.428	1.396	1.397	1.398	1.416
N2-C3	1.327	1.464	1.478	1.481	1.476
C3-C4	1.543	1.545	1.536	1.534	1.451
N3C4	1.479	1.460	1.488	1.486	1.508
N1-C5	1.431	1.446	1.484	1.472	1.469
N3-C6	1.429	1.420	1.443	1.442	1.458
C16-Cl	3.244	3.176	3.543	3.515	3.556
Cl-O	2.989	3.016	2.910	2.910	2.884
N1C16N2	/	109.97	102.68	100.23	106.74
ΣN3	357.8	344.0	344.2	348.0	341.4

	without counter-anion Cl^-				
	4'	**5'**	**I'**	**TS1'**	**TS2'**
C16-N1	2.997	1.340	3.011	1.768	1.513
C16-N2	1.325	1.338	1.325	1.437	1.445
C16-H16	1.076	1.080	1.078	1.086	1.085
C16-N3	1.327	3.026	1.327	1.372	1.528
N3-H3	/	1.014	/	/	/
O-H1	0.967	0.967	0.967	0.966	0.967
N1-C1	1.404	1.401	1.403	1.466	1.461
C1-C2	1.415	1.405	1.415	1.395	1.393
N2-C2	1.439	1.400	1.439	1.412	1.428
N2-C3	1.482	1.468	1.482	1.488	1.478
C3-C4	1.544	1.539	1.544	1.534	1.541
N3C4	1.489	1.471	1.489	1.475	1.513
N1-C5	1.437	1.449	1.437	1.469	1.470
N3-C6	1.427	1.436	1.427	1.425	1.457
N1C16N2	/	110.66	69.51	101.05	107.83
ΣN3	360.0	334.9	360.0	360.0	340.6

Main bond lengths in Å and main bond angles in °.

The optimized geometry for **5”** (table S1) is in agreement with the crystallographic data, **5”** is found to be the thermodynamic product of the reaction (more stable than **4”** about 7.6 kcal/mol). The mechanism shows that the reaction takes place in a two steps pathway with formation of a first conformer **I”** through a transition state **TS1”** which leads to **5”** through a second transition state **TS2”** (Figure S1). The conformer **I”** is located at 22.6 kcal/mol above **4”**, its structural feature is similar to compound **4”** except the anilide nitrogen (*N*HMes) is in interaction with the C(16) carbon atom (short C(16)-N_{Mes} bond length: 1.642 Å) and the C(16) carbon is pyramidalized (ΣC(16): 338.8°). The geometrical parameters of the transition state **TS1”** indicate a rather late transition state with a C(16)-N_{Mes} bond length of 1.768 Å and a C(16) carbon (ΣC(16): 342.8°) slightly less pyramidalized than in **I”**. The activation barrier of this first step is calculated around 25 kcal/mol. It is almost the twice compared to the one calculated without Cl^- (12.6 kcal/mol : Figure 2). A second transition state **TS2”** was also found on the potential energy surface at 39.1 kcal/mol from **4”**, the energy difference between this transition state and the confromer **I”**, being smaller when including the counter-anion (16.5 kcal/mol *versus* 32.1 kcal/mol). The features of this transition state is intermediate between those of **4”** and **5”**. It presents two five-membered rings involving C(16)-N_{Mes}, C(16)-$N_{Phenolate}$ and C(16)-N_{phenyl} bond lengths respectively of 1.526 Å, 1.531 Å and 1.451 Å.

Moreover, SMD calculations show that the solvent has only a weak influence on the energy profile (first and second activation barriers almost unchanged with those of the gas phase).

For compounds **4’^{or}”** and **5’^{or}”**, the geometrical parameters are similar when including or not the counter-anion. In the conformer **I”**, when the counter-anion is taking into account, the geometrical structure looks like the compound **4”** with the nitrogen atom linked to the Mes group in interaction with the C16 carbon atom. The C16-N_{Mes} bond length is short (1.642 Å) and the carbon C16 is pyramidalized (ΣC16 : 338.8°). Without the counter-anion, the C16-N_{Mes} bond length in **I’** is longer (3.011 Å) and this corformer **I’** is more stabilized (same energy as compound **4’**). The geometrical parameters of **TS2** are relatively closed with and without Cl^-.

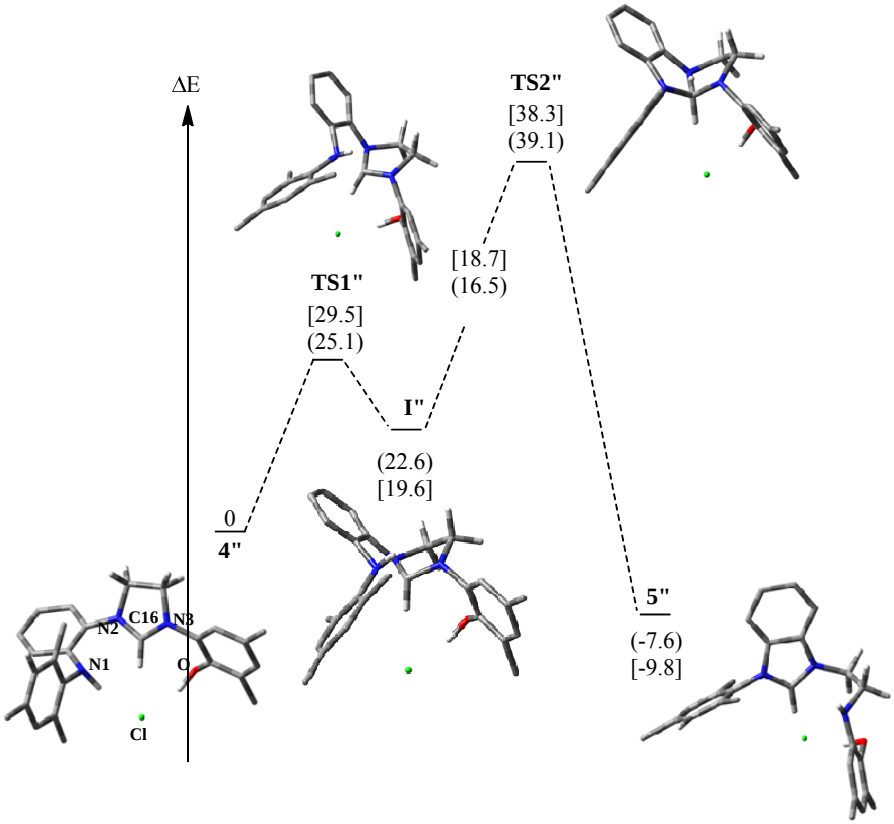


Figure S1. Energy profile (energy in kcal/mol) computed at the B3LYP/6-31G**//M06-2X/6-31G** level of theory with the counter-anion included (values in parentheses). Values in square takes into account the solvent effect (SMD calculations-THF). Some hydrogens have been omitted for clarity.

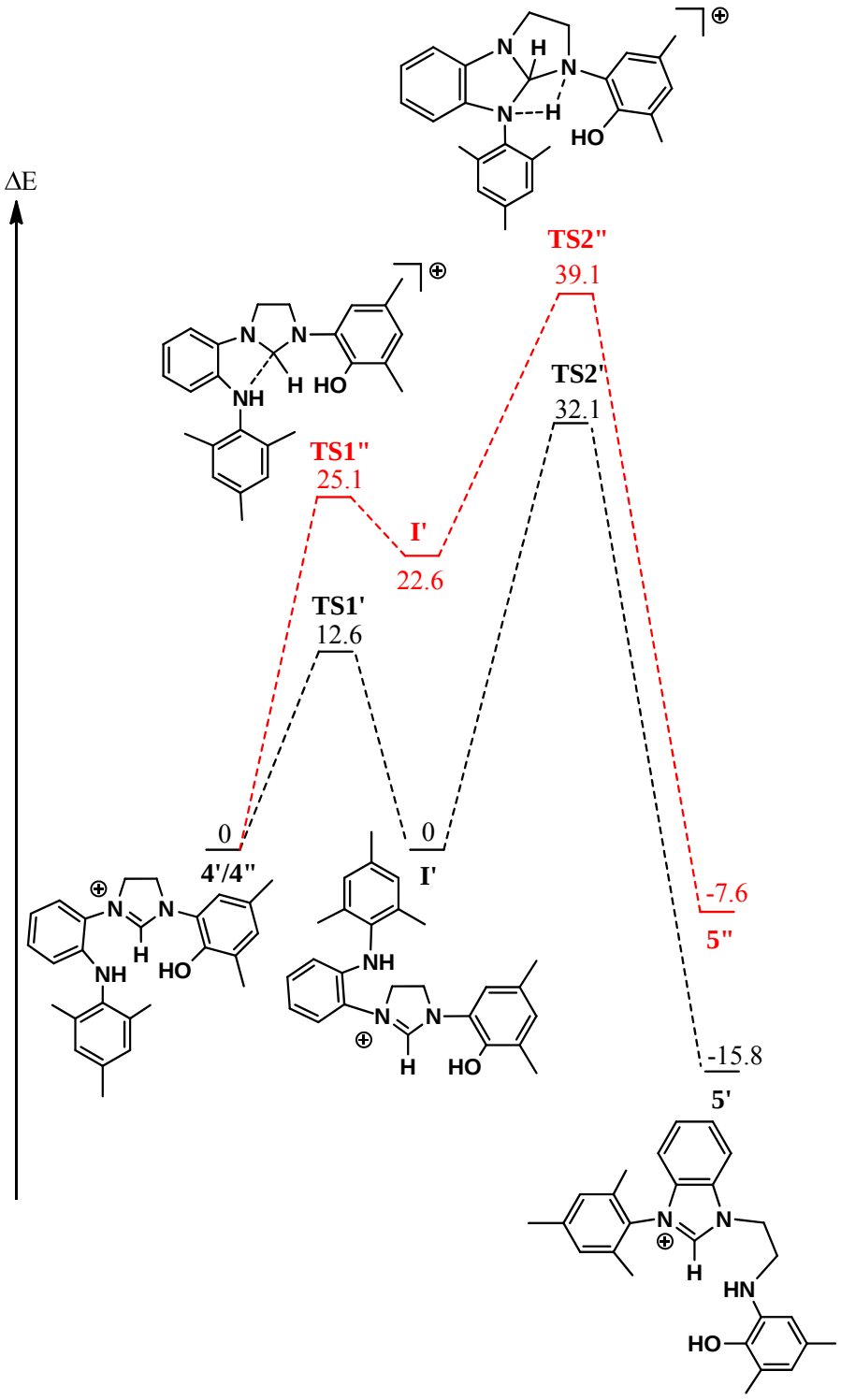


Figure S2. Same figure as Figure 2 with molecules in Chem. Draw.. Energy profile (energy in kcal/mol) computed at the B3LYP/6-31G**//M06-2X/6-31G** level of theory without the counter-anion (black) and with the counter-anion (red). Some hydrogens have been omitted for clarity.

Z-matrix :

- **With counter-anion Cl^-**

Compound 4":

C	3.28891700	1.96306600	0.54926300
C	1.98677400	1.50527700	0.27778900
C	1.02170700	2.47740000	-0.08476600
C	1.35014900	3.83898400	-0.09824500
C	2.64067800	4.26301500	0.19411200
C	3.61681100	3.31284300	0.50310600
N	1.65797200	0.13386900	0.32833200
H	1.04771200	-0.11355000	1.11651900
C	2.66978100	-0.84012800	0.05245400
C	3.21876300	-1.63058800	1.08376300
C	3.08242700	-1.02374700	-1.28393500
C	4.17202400	-2.59767600	0.74662000
C	4.04997000	-1.99144200	-1.56575400
C	4.60438200	-2.79641600	-0.56689000
H	4.36552400	-2.12945100	-2.59785700
C	2.81199400	-1.44003000	2.52549200
C	2.48092000	-0.20923900	-2.40322600
C	5.61477800	-3.86853400	-0.90091400
C	-3.15596000	-0.00748400	-0.61043500
C	-3.67525100	-0.01184400	0.69600500
C	-3.71589100	-0.80185300	-1.61746000
C	-4.76853600	-0.85351800	0.98665600
C	-4.80558700	-1.62450800	-1.34267600
C	-5.31084100	-1.63453900	-0.03300100
O	-3.17891300	0.82693800	1.64366500
H	-2.43717500	0.38451300	2.15844200
C	-5.31281100	-0.87775900	2.39082600
C	-5.42238500	-2.49275100	-2.41395600
N	-0.27712500	2.11249800	-0.55338700
N	-2.05798600	0.84835600	-0.93449400
C	-0.79317700	2.61768500	-1.85169700
H	-0.07079800	2.37570800	-2.63710100
H	-0.92927300	3.69968900	-1.82441000
C	-2.12790300	1.86013100	-2.01150400
H	-2.99890700	2.50047800	-1.84109600
H	-2.22927100	1.38599300	-2.98966100
C	-1.02572500	1.09708900	-0.13838200
H	-0.84113100	0.53905900	0.78678900
Cl	-0.68363800	-0.43324100	2.70176700

Compound 5":

C	3.69155500	1.91510600	-0.86648000
C	2.45958300	1.62208100	-0.28282200
C	1.54865500	2.63277700	0.07057400
C	1.83356100	3.97972300	-0.15963800
C	3.06076900	4.27300000	-0.74824800
C	3.97435200	3.25922400	-1.09398200

N	1.86280700	0.40784200	0.07737100
H	-1.70935000	1.57691400	-1.82776100
C	2.43687800	-0.91023800	-0.07602600
C	2.98433800	-1.54512100	1.05069300
C	2.41431800	-1.50337700	-1.34853200
C	3.54356800	-2.81218400	0.85879000
C	2.98997000	-2.76941600	-1.48021800
C	3.55725600	-3.43884900	-0.39081100
H	2.98304900	-3.24763900	-2.45628000
C	2.94065100	-0.91668500	2.42063600
C	1.77072100	-0.81940000	-2.53130200
C	4.13776100	-4.82330300	-0.55096100
C	-3.03693600	0.54123200	-0.74122300
C	-3.54457900	0.13701600	0.50549600
C	-3.58091700	-0.01211000	-1.91094700
C	-4.57420100	-0.81829200	0.57055900
C	-4.59617300	-0.96696500	-1.86614900
C	-5.08284800	-1.35786700	-0.61264100
O	-3.05839700	0.70551300	1.65679400
H	-2.46749100	0.06087400	2.14378100
C	-5.08261800	-1.24838500	1.92306200
C	-5.16460100	-1.55945900	-3.13520300
N	0.45220300	1.99209800	0.64930500
N	-1.93272000	1.42632500	-0.85356600
C	-0.81869000	2.58356600	1.07306000
H	-0.61323700	3.57582300	1.48379200
H	-1.22220300	1.94567500	1.85694700
C	-1.83001200	2.66775100	-0.09179000
H	-2.79154000	2.96046100	0.34114200
H	-1.51745300	3.46497300	-0.77713100
C	0.66201800	0.67074900	0.62140600
H	0.00611300	-0.06843100	1.10792400
Cl	-0.85702800	-0.94133500	2.89794000

Confromer (I”):

C	-3.61956000	-0.91376200	-1.34864500
C	-2.42947100	-1.10245900	-0.67010600
C	-2.14437300	-2.23725400	0.08888100
C	-3.10707000	-3.24751500	0.17489000
C	-4.31289600	-3.07815900	-0.51007700
C	-4.57827800	-1.92915900	-1.26245500
H	-3.80373400	-0.00614100	-1.91439600
H	-2.92804900	-4.13383600	0.77337900
H	-5.06647500	-3.85696900	-0.44446700
H	-5.52841800	-1.81863200	-1.77327500
N	-1.26557900	-0.19895700	-0.65421100
H	-0.83544900	-0.21397600	-1.58275500
C	-1.50967000	1.22468800	-0.31260900
C	-2.05352400	1.59108200	0.93118400
C	-1.17082400	2.16912600	-1.29849000
C	-2.24859300	2.95956800	1.15056700
C	-1.39112800	3.51806800	-1.01472200
C	-1.92263800	3.93532400	0.20771400
H	-2.65815600	3.26496500	2.10919900

H	-1.13322000	4.25782900	-1.76778700
C	-2.38355500	0.62328000	2.03879900
H	-2.98106200	1.12920500	2.80041100
H	-2.94973800	-0.24375600	1.69304700
H	-1.45767700	0.28492100	2.52511700
C	-0.56633000	1.77962900	-2.63128500
H	0.43176900	1.34012900	-2.51499200
H	-1.18896300	1.07115600	-3.19488900
H	-0.45337400	2.66244500	-3.26365200
C	-2.11022400	5.40054600	0.51548600
H	-1.24508200	5.79381000	1.06244700
H	-2.21980000	5.99290500	-0.39730100
H	-2.99210200	5.56781000	1.14065600
C	2.14910900	-0.87041500	-0.65745100
C	2.88224500	-0.80066200	0.53839900
C	2.65625000	-0.32198800	-1.84014400
C	4.10303800	-0.09499400	0.55888400
C	3.88185200	0.34611300	-1.84739100
H	2.08404900	-0.43499600	-2.75810800
C	4.57484800	0.45841500	-0.63203100
H	5.52172600	0.99484900	-0.61414400
O	2.41216000	-1.43843700	1.64096000
H	2.02713700	-0.75224800	2.29366900
C	4.84734300	0.03957600	1.86108400
H	4.24484500	0.59332200	2.58961200
H	5.04513200	-0.94351200	2.30117000
H	5.79783100	0.56151600	1.72190200
C	4.45405000	0.92823900	-3.11921700
H	4.73099600	1.98055600	-2.99025000
H	5.35996500	0.39583500	-3.43366000
H	3.73717000	0.87060200	-3.94369300
N	-0.89589300	-2.16992700	0.71164500
N	0.86341700	-1.52617800	-0.66764300
C	0.02350500	-3.32416500	0.63324800
H	-0.54073000	-4.25655200	0.57668300
H	0.65910500	-3.32094800	1.51916000
C	0.85164900	-3.01338900	-0.62200700
H	1.87534200	-3.38324900	-0.55113900
H	0.38861700	-3.42700600	-1.52664000
C	-0.13914800	-1.02445500	0.20894800
H	0.20207500	-0.31572300	0.97380200
Cl	1.01445400	0.64864400	3.11093900

TS1":

C	-3.78462500	-0.82704600	-1.16441700
C	-2.51832300	-1.05000300	-0.65146200
C	-2.15556700	-2.23944000	-0.01477400
C	-3.10857100	-3.25268700	0.12072900
C	-4.38948900	-3.04164600	-0.39545600
C	-4.73484300	-1.84506200	-1.03035100
N	-1.37525500	-0.13811500	-0.72355600
H	-1.02003900	-0.12969300	-1.68066600
C	-1.56530200	1.26354900	-0.31737400
C	-2.05712600	1.59529600	0.95991300

C	-1.21905700	2.24671700	-1.26461800
C	-2.19597200	2.95829000	1.24728900
C	-1.37908900	3.58767000	-0.91277000
C	-1.86123800	3.96619700	0.34217700
C	-2.39062400	0.59179500	2.03545000
C	-0.67187400	1.90096200	-2.63380800
C	-1.98719600	5.42122400	0.72182600
C	2.20038000	-0.77033800	-0.69970500
C	2.90738400	-0.87945400	0.50799800
C	2.73940500	-0.08442100	-1.79231900
C	4.14453500	-0.21507600	0.64106400
C	3.98003100	0.54557600	-1.68946500
C	4.65255000	0.47651100	-0.45886900
O	2.40082600	-1.64524200	1.50711500
H	1.98493200	-1.03806100	2.21750800
C	4.86370300	-0.27252800	1.96247600
C	4.58707900	1.28378600	-2.86008500
N	-0.83175200	-2.25961200	0.43350800
N	0.91111000	-1.40617500	-0.80721500
C	0.04388500	-3.40460800	0.09379100
H	-0.55673600	-4.28399300	-0.14489400
H	0.69610600	-3.61054800	0.94385300
C	0.85599900	-2.86388000	-1.08957500
H	1.87098500	-3.26074000	-1.12752300
H	0.36441800	-3.06189400	-2.05074000
C	-0.09922800	-1.06011100	0.08106700
H	0.16775200	-0.37472600	0.89329200
Cl	0.97220000	0.29070900	3.14407900

TS2”:

C	-3.61651400	-0.74768200	-1.16119800
C	-2.41282100	-1.04538300	-0.54812400
C	-2.14162100	-2.29237300	0.01498500
C	-3.09687900	-3.30261400	-0.04299400
C	-4.31664800	-3.02175900	-0.67115400
C	-4.58059300	-1.76364200	-1.21700500
N	-1.23432900	-0.19874500	-0.41750200
H	-0.33469900	-0.51574500	-1.29497800
C	-1.45700200	1.21431000	-0.08234600
C	-1.84599400	1.58795600	1.21855700
C	-1.33676600	2.15178500	-1.12284600
C	-2.05641300	2.95027200	1.45651700
C	-1.57143700	3.49716000	-0.82479300
C	-1.91523700	3.91942600	0.46121000
C	-2.02325800	0.60698900	2.34996000
C	-0.96521000	1.76308600	-2.53603600
C	-2.11869200	5.38237200	0.77211400
C	2.01665600	-0.66198900	-0.82075200
C	2.85571600	-0.85037500	0.28559100
C	2.42387700	0.09851600	-1.92014500
C	4.09502000	-0.17728200	0.32591200
C	3.66258700	0.73966900	-1.91170500
C	4.46884800	0.59837700	-0.77112300
O	2.46999600	-1.69718200	1.27128800

H	2.21708300	-1.15317600	2.10819200
C	4.96298600	-0.32198600	1.54746600
C	4.12426700	1.57108000	-3.08576500
N	-0.86891100	-2.31297100	0.63550800
N	0.70458700	-1.29770200	-0.84313200
C	0.08128100	-3.36073100	0.21421900
H	-0.44418600	-4.30300300	0.05232000
H	0.83791500	-3.48094500	0.98855600
C	0.71923500	-2.78886100	-1.06730900
H	1.74519800	-3.12235500	-1.21944600
H	0.12712600	-3.02157300	-1.95666400
C	-0.22224000	-1.04546600	0.34966200
H	0.25855000	-0.54121400	1.19446000
Cl	1.42299300	0.06582800	3.29934200

- **Without counter-anion Cl^-**

Compound 4':

C	-3.18261700	1.93919000	-0.74078700
C	-1.94294400	1.54780200	-0.20885400
C	-0.89468700	2.49797100	-0.24561000
C	-1.09364400	3.78347200	-0.75284000
C	-2.33602600	4.15287600	-1.25880600
C	-3.37266000	3.21755400	-1.25754700
H	-4.00180400	1.22974700	-0.72065000
H	-0.26876900	4.48909200	-0.76806600
H	-2.48750600	5.15045800	-1.65514900
H	-4.34758600	3.48846000	-1.65016900
N	-1.71398900	0.26128700	0.30495900
H	-1.15330200	0.27122700	1.14860500
C	-2.74241900	-0.74184600	0.33112300
C	-3.02591700	-1.46231700	-0.84393900
C	-3.41581100	-1.02314700	1.53512900
C	-4.01398500	-2.45063400	-0.79254000
C	-4.38003300	-2.03426200	1.53999900
C	-4.69972200	-2.75778600	0.38642400
H	-4.24341500	-3.00521900	-1.69902400
H	-4.90347300	-2.25353200	2.46738200
C	-2.28353800	-1.19375700	-2.13031400
H	-2.53429000	-1.94289000	-2.88473100
H	-2.52335400	-0.20909400	-2.54788100
H	-1.19931700	-1.21912600	-1.97244600
C	-3.10923500	-0.25352700	2.79929200
H	-2.09892000	-0.46269400	3.17793300
H	-3.18393400	0.82888500	2.64632200
H	-3.80558500	-0.52502800	3.59543100
C	-5.73363200	-3.85725600	0.42244700
H	-5.29207100	-4.80187600	0.76248100
H	-6.55013500	-3.61641500	1.10936900
H	-6.16365400	-4.03538800	-0.56675800
C	3.32882600	0.02834300	0.19841100

C	3.36938000	-0.73082400	-0.98322600
C	4.32399000	-0.14683900	1.16978800
C	4.39947600	-1.66416300	-1.18476100
C	5.35644200	-1.06544300	0.98883300
H	4.29632400	0.43426300	2.08447500
C	5.37218700	-1.81169500	-0.19680300
H	6.16809100	-2.53376200	-0.35788200
O	2.38176900	-0.53230400	-1.91312700
H	2.58447200	-1.03080500	-2.71625000
C	4.43464200	-2.47537700	-2.45853100
H	3.53181900	-3.08737600	-2.58025400
H	4.53688200	-1.84102100	-3.34950800
H	5.28688700	-3.15693900	-2.45879800
C	6.42786000	-1.25468100	2.03533500
H	6.45772500	-2.29093700	2.38791800
H	7.41922600	-1.02189400	1.63232600
H	6.26147900	-0.61184800	2.90323000
N	0.40711800	2.14005000	0.25125500
N	2.31401700	1.00775100	0.41805100
C	1.20903400	2.96776700	1.18255100
H	0.63709800	3.17685700	2.08815400
H	1.46801200	3.91686100	0.70524300
C	2.44918300	2.08381600	1.43773900
H	3.39177800	2.61433600	1.29472800
H	2.44011200	1.63987400	2.43706800
C	1.12367600	1.10479100	-0.16127900
H	0.76607800	0.40042000	-0.89533700

Compound 5':

C	3.69952600	1.97036100	-0.52682400
C	2.43068200	1.62045800	-0.06349600
C	1.46131000	2.58767200	0.25132500
C	1.72351700	3.95286200	0.11413900
C	2.98766100	4.30252800	-0.34865800
C	3.95797900	3.32978300	-0.66370400
H	4.43983900	1.21614200	-0.76819000
H	0.98394400	4.70845500	0.35377200
H	3.23351300	5.35193900	-0.47021000
H	4.93024700	3.65093800	-1.02154600
N	1.84503200	0.37134300	0.18220300
H	-1.99118300	1.02729100	-1.82367000
C	2.45620900	-0.92657500	-0.02036700
C	3.26978700	-1.45413900	0.99518000
C	2.21603100	-1.59535400	-1.23229500
C	3.85252900	-2.70316300	0.76367500
C	2.82220100	-2.84202300	-1.40535600
C	3.64041600	-3.41308100	-0.42343400
H	4.48834300	-3.13177500	1.53334300
H	2.65353200	-3.37876800	-2.33492400
C	3.51004200	-0.71561400	2.29044800
H	4.15470700	-1.29886800	2.95041400
H	3.99282900	0.25355000	2.12529600
H	2.57474500	-0.52241400	2.82778300

C	1.35120000	-0.99539100	-2.31557600
H	0.34819000	-0.74864200	-1.95072800
H	1.78844600	-0.07168700	-2.71181800
H	1.24199400	-1.69321400	-3.14786900
C	4.25871300	-4.77347700	-0.63128200
H	3.56800600	-5.56531400	-0.31761200
H	4.49660100	-4.94793000	-1.68401600
H	5.17586900	-4.88992500	-0.04844700
C	-3.21777000	0.26320900	-0.43783100
C	-3.28339500	-0.41971600	0.78431500
C	-4.30779100	0.17447100	-1.31203500
C	-4.42314400	-1.15801700	1.14013700
C	-5.44847300	-0.56924400	-1.00295100
H	-4.25582700	0.70646700	-2.25971100
C	-5.48606800	-1.21843100	0.23633100
H	-6.36740500	-1.79265700	0.51009600
O	-2.18628300	-0.35097800	1.62972900
H	-2.37226000	-0.87898900	2.41787700
C	-4.47824300	-1.87959000	2.46715600
H	-3.69098900	-2.64060800	2.55875400
H	-4.38222000	-1.19171300	3.31808900
H	-5.43116900	-2.39839200	2.58601200
C	-6.59959800	-0.67920800	-1.97400400
H	-6.57216700	-1.63278100	-2.51463200
H	-7.56291300	-0.62821100	-1.45793300
H	-6.57392400	0.12082500	-2.71858700
N	0.32871300	1.88777600	0.68347500
N	-2.04314500	0.99990200	-0.81176500
C	-1.00496300	2.43527300	0.95928900
H	-0.88258700	3.46806100	1.29160100
H	-1.43838100	1.85442300	1.77252900
C	-1.90203400	2.36726300	-0.28941400
H	-2.87031400	2.81453800	-0.02793900
H	-1.45623400	2.98942000	-1.07260400
C	0.59311200	0.57806300	0.61230000
H	-0.12377100	-0.18901000	0.86724400

Conformer (I'):

C	-3.17629900	1.94396400	-0.74780400
C	-1.94199800	1.54238400	-0.21030500
C	-0.88900900	2.48757400	-0.23391800
C	-1.07703300	3.77685900	-0.73572700
C	-2.31372400	4.15597400	-1.24814200
C	-3.35558100	3.22627300	-1.25825600
H	-3.99977500	1.23933000	-0.73692900
H	-0.24773300	4.47753400	-0.74081600
H	-2.45715900	5.15638600	-1.64029500
H	-4.32649300	3.50485600	-1.65546300
N	-1.72310500	0.25192200	0.29575600
H	-1.15636400	0.25054500	1.13522300
C	-2.75874200	-0.74377200	0.31946500
C	-3.05018800	-1.45699800	-0.85815100
C	-3.43110000	-1.02562400	1.52383700
C	-4.04490100	-2.43865800	-0.80858300

C	-4.40240500	-2.03000400	1.52668100
C	-4.72983900	-2.74623600	0.37080700
H	-4.28046900	-2.98759200	-1.71693500
H	-4.92513400	-2.24968100	2.45435600
C	-2.30915800	-1.18774600	-2.14512000
H	-2.56466800	-1.93334900	-2.90141500
H	-2.54531400	-0.20067400	-2.55906200
H	-1.22485300	-1.21819800	-1.98927100
C	-3.11612800	-0.26372300	2.79058500
H	-2.10644800	-0.48174700	3.16594600
H	-3.18345500	0.81983800	2.64240900
H	-3.81255500	-0.53370200	3.58717600
C	-5.77097700	-3.83893600	0.40435600
H	-5.33093700	-4.79224000	0.72139000
H	-6.57509000	-3.60408900	1.10767700
H	-6.21727800	-3.99745800	-0.58101700
C	3.33561100	0.01906300	0.20890500
C	3.40169700	-0.70000500	-0.99655500
C	4.31143200	-0.18597400	1.19359700
C	4.43775300	-1.62411200	-1.20832800
C	5.35098500	-1.09474400	1.00201500
H	4.26283500	0.36361100	2.12679300
C	5.39129200	-1.80205500	-0.20646100
H	6.19121400	-2.51798900	-0.37463300
O	2.43080400	-0.47326300	-1.93749200
H	2.65055100	-0.94272600	-2.75354300
C	4.49884200	-2.39483500	-2.50597600
H	3.60029800	-3.00496400	-2.66334800
H	4.61532800	-1.73265400	-3.37468200
H	5.35315100	-3.07377700	-2.51187300
C	6.41017100	-1.30431000	2.05702700
H	6.13956100	-0.82405900	3.00067200
H	6.56683200	-2.36903600	2.25516400
H	7.37278500	-0.88959800	1.73732400
N	0.40675400	2.12050800	0.27255600
N	2.31301300	0.98760400	0.44070000
C	1.19132400	2.92525700	1.23829200
H	0.60498700	3.10680700	2.14065300
H	1.45258800	3.88847600	0.79151900
C	2.43120400	2.03911200	1.48792400
H	3.37405600	2.57532700	1.36985500
H	2.41067400	1.57137300	2.47610700
C	1.13152500	1.09698700	-0.15420800
H	0.78727100	0.41103300	-0.91187100

TS1':

C	3.70271500	-0.04206400	1.19643800
C	2.62802700	-0.55712900	0.48904200
C	2.73816700	-1.67367700	-0.33965500
C	3.97164300	-2.30805100	-0.47933800
C	5.06386300	-1.80222500	0.23139400
C	4.93926100	-0.68112500	1.05743500
H	3.58827000	0.83337100	1.82749300
H	4.08146300	-3.16567100	-1.13420400

H	6.03001700	-2.28513900	0.12759800
H	5.80363700	-0.29931000	1.58932700
N	1.24458400	-0.07300600	0.52520200
H	0.82099700	-0.35015400	1.41292400
C	0.98823900	1.36364000	0.35670200
C	1.50479900	2.06958700	-0.74724500
C	0.18127600	1.98654200	1.33014000
C	1.17814700	3.42761200	-0.84383700
C	-0.10344400	3.34415400	1.17657200
C	0.38066100	4.08582000	0.09502300
H	1.57257600	3.98867800	-1.68663700
H	-0.71730500	3.83472300	1.92682700
C	2.41976000	1.47927500	-1.80006900
H	2.46301900	2.14610600	-2.66367600
H	3.44073100	1.36463100	-1.42152900
H	2.10405100	0.49903200	-2.16437700
C	-0.37365100	1.23865800	2.52411500
H	-1.10283000	0.47161900	2.23427300
H	0.41089700	0.75976100	3.12571400
H	-0.89197800	1.92881000	3.19219000
C	0.03609900	5.54600000	-0.06193000
H	-0.92003500	5.66704600	-0.58511300
H	-0.06006200	6.04005600	0.90869300
H	0.79541400	6.07665600	-0.64183600
C	-1.94760900	-1.31684300	-0.11807200
C	-2.53576600	-0.57568100	-1.15647500
C	-2.69532900	-1.60921100	1.03012800
C	-3.85390300	-0.10647700	-1.03000900
C	-4.01637100	-1.17787000	1.16837800
H	-2.23690300	-2.19354500	1.82321500
C	-4.56767100	-0.41924200	0.12846200
H	-5.59060700	-0.06289000	0.21745600
O	-1.77768400	-0.33472000	-2.27291400
H	-2.30789300	0.13341100	-2.93124600
C	-4.47612300	0.69702700	-2.14764500
H	-3.91601700	1.61845600	-2.35426300
H	-4.53656000	0.12408900	-3.08271500
H	-5.49545200	0.99178100	-1.89201900
C	-4.83207000	-1.53182000	2.38885800
H	-4.19577100	-1.83487800	3.22471600
H	-5.44308600	-0.68663500	2.71925800
H	-5.51619700	-2.36239400	2.17913900
N	1.52412800	-2.04522400	-0.95673900
N	-0.61821400	-1.81655600	-0.23363400
C	0.98932000	-3.41623100	-0.73958500
H	1.74899700	-4.04871600	-0.27799300
H	0.69966500	-3.84921100	-1.70058100
C	-0.23465400	-3.18604500	0.15596900
H	-1.05760800	-3.87092600	-0.05467500
H	0.01633000	-3.26013000	1.22296100
C	0.46969700	-1.10932100	-0.67956500
H	0.24971400	-0.33919800	-1.41278800

TS2':

C	3.46633400	-0.70687700	1.17147300
C	2.31708100	-1.01466400	0.46475100
C	2.11509100	-2.25266500	-0.14145500
C	3.08199000	-3.24605200	-0.04357400
C	4.24685800	-2.95638900	0.67852400
C	4.44231900	-1.70712400	1.27245300
H	3.60801200	0.27022600	1.62014000
H	2.95004000	-4.20818200	-0.52708800
H	5.01730800	-3.71556100	0.76306600
H	5.35991700	-1.50358500	1.81338600
N	1.13341000	-0.18401500	0.25944400
H	0.13554100	-0.52600300	1.05776200
C	1.33842700	1.23668100	-0.05657900
C	1.81975800	1.62599700	-1.32265000
C	1.09866300	2.17005500	0.96637200
C	2.00564800	2.99215900	-1.54998800
C	1.31285400	3.52266200	0.68129500
C	1.75230000	3.95816700	-0.57067200
H	2.37624200	3.30770600	-2.52170100
H	1.13570400	4.25294500	1.46603700
C	2.15158500	0.64537600	-2.42596000
H	2.76006200	1.13549200	-3.18855500
H	2.71360200	-0.21887300	-2.06295600
H	1.25645400	0.26587400	-2.93299000
C	0.62680900	1.77023400	2.34611100
H	-0.44173900	1.52809300	2.34847900
H	1.16821800	0.90672300	2.74497000
H	0.76782100	2.59514700	3.04750400
C	1.94686300	5.42516200	-0.86319600
H	1.07180200	5.83838500	-1.37881400
H	2.08989300	6.00175200	0.05401900
H	2.81248700	5.59163100	-1.51048700
C	-2.14210700	-0.67262100	0.36471400
C	-2.88092000	-0.77840600	-0.81993100
C	-2.68499000	-0.01724300	1.47252200
C	-4.15099600	-0.18343200	-0.91485300
C	-3.95009100	0.56917700	1.41387100
H	-2.11277500	0.01270100	2.39471700
C	-4.65561600	0.47770100	0.20568100
H	-5.64039100	0.93240400	0.13483000
O	-2.31580100	-1.47877800	-1.85665600
H	-2.91167900	-1.47669100	-2.61806500
C	-4.93726500	-0.28382800	-2.20047500
H	-4.40608500	0.17469200	-3.04494600
H	-5.15887600	-1.32560700	-2.46734300
H	-5.89539100	0.23085500	-2.11023100
C	-4.54492300	1.28028500	2.60547700
H	-4.71682500	2.34045000	2.38994000
H	-5.51128900	0.84702700	2.88349300
H	-3.88913200	1.21938000	3.47747700
N	0.87732300	-2.28532500	-0.85217400
N	-0.83026100	-1.29363600	0.49482200

C	-0.08437100	-3.34870000	-0.49293400
H	0.44441900	-4.27879700	-0.28326300
H	-0.77025600	-3.50606800	-1.32644500
C	-0.83274700	-2.78775300	0.73143700
H	-1.85979400	-3.14175000	0.81577600
H	-0.30393200	-2.99740700	1.66379300
C	0.21145000	-1.02938200	-0.59148400
H	-0.20628000	-0.51304300	-1.44947200

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