Transforming Atmospheric CO₂ into Alternative Fuels: a Metal-Free Approach under Ambient Conditions

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Experimental Section

Experimental Materials and Instrumentation

Compounds 1 and 2 were prepared under a dry and oxygen-free atmosphere (argon) using standard Schlenk techniques or inside a glovebox maintained below 0.1 ppm of O₂ and H₂O levels. Glasswares were dried for overnight at 130 °C before use. THF, toluene, hexane and benzene were dried over a sodium/benzophenone mixture and distilled before use. Apart from compounds 1 and 2, other compounds were prepared in open atmosphere. Carbon dioxide was purchased from Praxair in a 5.5 purity gas cylinder with 99.995% purity. The ¹H and ¹³C NMR spectra were recorded on 400 and 500 MHz NMR spectrometers with residual undeuterated solvent as an internal standard. ¹¹B NMR spectra were obtained by using a Bruker Avance 500 MHz NMR spectrometer. Chemical shifts for ¹¹B NMR spectra were referenced using Et₂O·BF₃ as an external standard. Chemical shifts (δ) are given in ppm, and J values are given in Hz. Elemental analyses were performed in a Perkin–Elmer 2400, Series II, CHNS/O analyzer. The HRMS was measured in Bruker Daltonics Micro TOF-Q-II with electro spray ionization (ESI). Thermogravimetry was carried out on NETSZCH TGA-DTA system. All solid reagents or substrates were purchased (Sigma-Aldrich, Merck and Spectrochem) and used as received. Unless otherwise noted, liquid chemicals were purchased from commercial suppliers (Sigma-Aldrich, Merck and Spectrochem) and dried over molecular sieves (4 Å) prior to use. The molecular sieves (4 Å, Merck) were dried under a dynamic vacuum at 250 °C for 48 h prior to use. Isolated abnormal N-heterocyclic carbene (aNHC), 1 was prepared according to the literature procedure.¹ Capture of carbon dioxide from air and its reduction into methoxyborane or sodium formate was performed in open atmosphere using a glass vial. During catalysis, we performed freeze-pump-thaw
cycle using J. Young tube and we waited until the temperature of J. Young tube reached to room temperature. Then the reaction mixture was exposed to atmospheric pressure of CO₂ gas and the J. Young tube was sealed to perform the reaction.

**Synthesis of 1,3-bis(2,6-diisopropylphenyl)-2,4-diphenylimidazolidine-9-borabicyclo[3.3.1]nonane (2)**

A 25 mL Schlenk flask equipped with a stirring bar was charged with \( \text{1} \) (272.0 mg, 0.50 mmol, 1 equiv), 9-BBN (0.25 mmol, 1 equiv) and toluene (10 mL) at 40 °C for 2 h. During this period, reaction mixture becomes transparent from initial green color. After 2 h, the solvent was dried under reduced pressure and the final off white solid product was washed with hexane for three times to afford the title compound \( \text{2} \) (255 mg, 0.375 mmol, 75%). This reaction protocol represents an improvement over the previously reported procedure by Crudden and co-workers using aNHC salt. \(^2\) However the X-ray structure of adduct \( \text{2} \) was not known previously. In this study X-ray quality crystals of compound \( \text{2} \) was successfully grown from toluene/hexane mixture under inert atmosphere. \(^1\)H NMR (500 MHz, \( \text{C}_6\text{D}_6 \), 25 °C, TMS): \( \delta = 7.32 \) (d, \( J = 7.0 \) Hz, 2H), 7.29-7.26 (m, 1H), 7.14 (s, 2H), 7.02-6.88 (m, 4H), 6.81-6.78 (m, 4H), 6.55-6.46 (m, 3H), 3.41 (sept, \( J = 6.5 \) Hz, 2H), 2.85 (sept, \( J = 6.5 \) Hz, 2H), 2.46-2.32 (m, 5H), 2.19-2.17 (m, 2H), 2.06-2.03 (m, 1H), 1.89-1.80 (m, 5H), 1.61 (d, \( J = 6.5 \) Hz, 6H), 0.94 (d, \( J = 7.0 \) Hz, 6H), 0.77 (d, \( J = 6.5 \) Hz, 6H), 0.72 (d, \( J = 7.0 \) Hz, 6H) ppm; \(^{13}\)C NMR (125 MHz, \( \text{C}_6\text{D}_6 \), 25 °C, TMS): \( \delta = 146.1, 145.7, 140.9, 136.7, 135.7, 132.8, 131.9, 131.3, 131.1, 130.5, 129.8, 129.3, 128.8, 127.4, 125.0, 124.9, 124.9, 38.1, 32.5, 29.4, 29.1, 26.9, 26.7, 24.6, 24.1, 23.8, 23.7 ppm; \(^{11}\)B NMR (160 MHz, \( \text{C}_6\text{D}_6 \), 25 °C, TMS): \( \delta = -15.9 \) ppm.
Synthesis of 1,3-bis(2,6-diisopropylphenyl)-2,4-diphenylimidazolidineformate boric acid (3)

A 5 mL glass vial was charged with 2 (20.0 mg, 0.029 mmol) with 2 mL benzene in open atmosphere at room temperature for 12 h. During this period we observed a sharp color change from light yellow to green with the evaporation of little amount solvent. The same observation was found in presence of C₆D₆ and toluene also. After 12 h, solvent was dried under reduced pressure and the final product was washed with hexane for three times to afford compound 3. An X-ray quality crystal of compound 3 (08 mg, 0.012 mmol, 40%) was successfully grown from benzene/n-hexane mixture as colorless crystals in open atmosphere.¹H NMR (500 MHz, CDCl₃, 25 °C, TMS): δ = 8.55 (s, 1H), 8.53 (s, 1H), 7.65-7.57 (m, 2H), 7.44-7.31 (m, 9H), 7.25-7.21 (m, 3H), 6.94 (d, J = 7.5 Hz, 2H), 2.54-2.41 (m, 4H), 1.32 (d, J = 7.0 Hz, 6H), 1.01 (d, J = 6.5 Hz, 6H), 0.87-0.85 (m, 12H) ppm; ¹³C NMR (125 MHz, CDCl₃, 25 °C, TMS): δ = 169.2, 145.3, 144.9, 144.5, 137.2, 132.9, 132.8, 132.5, 130.9, 130.1, 129.6, 129.5, 129.2, 128.4, 126.1, 125.4, 124.3, 123.2, 120.7, 36.4, 29.5, 29.2, 25.4, 23.8, 23.3, 22.5, 20.0 ppm; ¹¹B NMR (160 MHz, CDCl₃, 25 °C, TMS): δ = 20.8 ppm. Elemental analysis: Calcd. for C₄₀H₅₂BN₂O₅: C 73.72, H 8.04, N 4.30; found: C 71.72, H 7.29, N 4.34.

Methoxyborane formation with compound 3

In a glovebox, borane (0.07 mmol, 10 equiv) was added in a 5 mL glass vial containing compound 3 (5.0 mg, 0.007 mmol) and finally the vial was closed with proper cap and taken outside. To this glass vial, 2 mL C₆D₆ was added after quickly opening the vial in air and then closed with the cap and kept it at RT. Immediately, we observed a gas evolution (please see video clip), which was confirmed as hydrogen gas by ¹H NMR spectroscopy (δ =
4.46 ppm). The reaction was continued for 6 h and we observed a sharp color change from light yellow to deep yellow. The formation of methoxyborane with full consumption of starting compound 3 was confirmed by $^1$H NMR spectroscopy. During this reaction, we observed that 10 equivalents borane were necessary to consume the starting compound 3. It may be attributed to the fact that some amount of borane might be decomposing on exposure to air before it can react with 3.

**Formation of sodium formate from compound 3**

A 15 mL glass vial was charged with 3 (10.0 mg, 0.014 mmol), 5 mL 2(M) NaOH solution and 0.5 mL tetrahydrofuran (THF). The reaction was continued for 12 h by closing the vial with a cap. During this period, we observed a sharp color change of reaction mixture from light yellow to colorless. The formation of sodium formate with full consumption of starting compound 3 was confirmed by $^1$H NMR spectroscopy using D$_2$O.

**Catalytic hydroboration of CO$_2$ with compound 3**

Under an argon atmosphere, a 25 mL Schlenk tube equipped with a J. Young valve was charged with 3 (5.0 mg, 0.007 mmol), BH$_3$SMe$_2$ (0.14 mmol, 20 equiv.) and C$_6$D$_6$ (2 mL). To this solution, hexamethylbenzene was added as an internal standard. The mixture was degassed by a freeze-pump-thaw cycle and placed under 1 atm. of CO$_2$ (99.995% pure CO$_2$ from a CO$_2$ cylinder) at room temperature. The progress of the reaction was monitored by $^1$H NMR spectroscopy and the conversion was calculated based on the integration of methoxy group of (CH$_3$OBO)$_3$ with respect to internal standard. All reported conversion of product was an average of at least two runs.
Synthesis of \{1,3-bis(2,6-diisopropylphenyl)-2,4-diphenyl-imidazolium (Cl\textsuperscript{-})\} (4)

In the open atmosphere, compound 3 (20.0 mg, 0.028 mmol) was passed through a column containing DOWEX chloride ion-exchange resin. The eluent was methanol (MeOH). After column chromatography, the title compound was isolated under reduced pressure as a white solid (08 mg, 0.014 mmol, 50%). Finally compound 4 \{1,3-bis(2,6-diisopropylphenyl)-2,4-diphenyl-imidazolium (Cl\textsuperscript{-})\} was obtained as colorless crystals from methanol upon crystallization.\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, 25 °C, TMS): $\delta = 8.84$ (s, 1H), 7.63 (t, $J = 7.6$ Hz, 1H), 7.57 (t, $J = 8.4$ Hz, 1H), 7.36-7.29 (m, 9H), 7.22 (t, $J = 7.6$ Hz, 3H), 6.91 (d, $J = 7.6$ Hz, 2H), 2.53-2.40 (m, 4H), 1.35 (d, $J = 6.8$ Hz, 6H), 1.00 (d, $J = 6.8$ Hz, 6H), 0.85-0.83 (m, 12 H) ppm; \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}, 25 °C, TMS): $\delta = 145.1, 144.8, 144.4, 137.0, 132.9, 132.8, 132.4, 130.8, 130.0, 129.6, 129.4, 129.2, 128.6, 126.1, 125.4, 124.3, 123.5, 120.6, 36.3, 29.4, 29.1, 25.6, 23.7, 23.3, 22.5, 21.9, 20.0 ppm. HRMS $m/z$ (ESI) calc. for C\textsubscript{39}H\textsubscript{49}ClN\textsubscript{2} \[M+H\]^+ 545.3879, found 545.3862.

Expulsion of carbon dioxide from compound 3 under heating

In the open atmosphere, solid compound 3 (10.0 mg, 0.014 mmol) was heated at 150 °C for 12 h in a glass vial. During this process, we observed a sharp color change from colorless to chocolate color. After 12 h, the final compound was washed with hexane for three times.\textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}, 25 °C, TMS): $\delta = 8.36$ (s, 1H), 7.98-7.92 (m, 2H), 7.64-7.57 (m, 2H), 7.43-7.40 (m, 2H), 7.37-7.29 (m, 7H), 7.24-7.21 (m, 7H), 6.93 (d, $J = 7.5$ Hz, 2H), 3.14 (sept, $J = 6.5$ Hz, 1H), 2.52-2.39 (m, 4H), 1.88-1.83 (m, 7H), 1.64-1.56 (m, 6H), 1.29 (d, $J = 7.0$ Hz, 6H), 1.22 (d, $J = 7.0$ Hz, 3H), 1.00 (d, $J = 6.5$ Hz, 6H), 0.85-0.84 (m, 12H) ppm; \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}, 25 °C, TMS): $\delta = 144.8, 144.4, 132.8, 132.5, 129.6, 129.5, 129.2, 128.5, 128.0,
127.8, 127.5, 127.1, 126.1, 125.4, 71.6, 36.3, 29.5, 29.4, 29.2, 25.4, 23.8, 23.5, 23.3, 22.5, 20.0 ppm. \(^{11}\)B NMR (160 MHz, CDCl\(_3\), 25 °C, TMS): \(\delta = 20.9\) ppm

**Synthesis of \{1,3-bis(2,6-diisopropylphenyl)-2,4-diphenylimidazolidine bicarbonate boric acid\} (5)**

The compound \(2\) (20.0 mg, 0.029 mmol) was exposed as a fine powder in a petridish for 3 days in an open atmosphere at room temperature. From this air-exposed solid, colorless crystals of compound \(5\) \{1,3-bis(2,6-diisopropylphenyl)-2,4-diphenylimidazolidine bicarbonate boric acid\} (9.5 mg, 0.0145 mmol, 50%) were grown using a benzene/\(n\)-hexane solvent mixture. \(^1\)H NMR (500 MHz, CDCl\(_3\), 25 °C, TMS): \(\delta = 8.77\) (s, 1H), 8.58 (s, 0.5H), 7.41-7.29 (m, 11H), 7.24-7.20 (m, 2H), 6.94 (d, \(J = 7.5\) Hz, 2H), 2.55-2.42 (m, 4H), 1.34 (d, \(J = 6.5\) Hz, 6H), 1.01 (d, \(J = 7.0\) Hz, 6H), 0.87-0.85 (m, 12H) ppm; \(^{13}\)C NMR (125 MHz, CDCl\(_3\), 25 °C, TMS): \(\delta = 169.0, 144.9, 144.5, 137.1, 132.7, 132.4, 132.2, 130.9, 129.7, 129.5, 129.2, 129.1, 128.6, 127.8, 127.1, 126.1, 125.4, 124.8, 124.6, 123.7, 120.8, 29.5, 29.2, 25.4, 23.8, 23.4, 22.6 ppm; \(^{11}\)B NMR (160 MHz, CDCl\(_3\), 25 °C, TMS): \(\delta = 21.0\) ppm. Elemental analysis: Calcd. for\(C_{40}H_{53}BN_2O_6\): C 71.85, H 7.99, N 4.19; found: C 73.72, H 8.19, N 4.24.

**Details of TGA study**

In order to have a clear picture on expulsion of \(CO_2\) molecule from the compound \(3\), we have performed thermogravimetric experiment using NETSZCH TGA-DTA system upon heating from 27 to 550 °C ramp at 4°C/min. According to the thermal gravimetric curve (black) in Fig. 3d, it is seen that first significant weight loss starts from 95.5 °C continue up to 160.2°C. This corresponds to the weight loss of 7.22% (M.W. 651.4 to 603.9). This is
slightly high to the mass loss of CO\textsubscript{2} per mole or per formula unit (theoretical value 6.76% for M.W. 651.4 to 607.4). Differential Thermal Analysis (DTA) curve (blue) in Fig. 3d also shows the complete exothermic loss of CO\textsubscript{2} molecule in this particular region. From the DTA curve, it is convincing that complete weight loss of CO\textsubscript{2} lasts up to around 160 °C assuming that decomposing volatiles obey first order kinetics. So, it is concluded from the gravimetric analysis that heating the compound at 150 °C can result in the release of carbon dioxide from 3.

**Computational details**

All optimization were performed using M062X\textsuperscript{3-4}/6-31+G(d,p)\textsuperscript{5} level of theory as M062X is reported to be highly efficient for main group elements. Gaussian 09\textsuperscript{6} suit of programs is employed for all calculation. As reported earlier, the ground state of αNHCcarbene (1) is singlet and the first triplet state is 49.8 kcal/mol higher in energy.\textsuperscript{7} ΔE\textsubscript{ST} were calculated using B3LYP\textsuperscript{8-9}DFT functional along with same basis set. All the ground state minima are characterized by absence of imaginary frequency while the transition states are confirmed by presence of one unique imaginary frequency that connects pertinent reactant and products. For the incorporation of solvent effect, a polarizable continuum model based on SMD has been used. All the free energy energies are obtained using SMD/M062X/6-31+G(d,p)//M062X/6-31+G(d,p) level of theory. Few structures are optimized utilizing two layer ONIOM\textsuperscript{10-12} method where M062X/6-31+G(d,p) is used for high layer and AM1\textsuperscript{13} is used for low layer. Layer specification for the ONIOM method is shown below.
**Fig. S1** Theoretical investigation of compound 2. a) Optimized geometry of 2. b) Electrostatic potential surface of 2. c) Highest Occupied Molecular Orbital (HOMO) (iso=0.04) of 2.

**Fig. S2** A tube model is used to describe the high LEVEL layer, which has been treated quantum mechanically and the LOW LEVEL layer (shown with a wireframe model) has been treated with a semi-empirical method.
Fig. S3 Structural drawings of compounds involving the proposed mechanism depicted in Figures 6 and 7 of the main manuscript.

**Fate of intermediate 10 in presence of moisture**

In step 6 (Fig.6, manuscript), during hydride transfer from 2 to 7, the intermediate 10 is released. Since this is an open atmosphere reaction, water reacts with 10 to form a weak reactant complex 13 that undergoes O-H bond cleavage of water *via* TS6(Figure S3) and generates 9BBN-OH (14) along with the release of the carbene salt (15). The activation energy for the decomposition is computed to be 25.6 kcal/mol and it goes through a
transition state namely **TS6**. The overall exergonicity of the process is 28.7 kcal/mol (ΔG = -28.7 kcal/mol). All the free energies in the bracket are given in kcal/mol. Relevant bond distances are shown in Å.

**Fig. S4** Optimized structures for conversion of compound 10 to 14 and 15 via TS6.

**Details for preparation of video clipping of the carbon dioxide reduction from air with compound 3**

With the help of a glovebox, 9-BBN (0.035 mmol, 10 equiv) was added in a 5 mL glass vial containing compound 3 (5.0 mg, 0.007 mmol) and the vial was taken out of the glovebox. To the vial, quickly 2 mL C₆D₆ was added in open air and the cap of the vial was closed and kept. Immediately, we observed a gas evolution, which was confirmed as hydrogen by ¹H
NMR spectroscopy ($\delta = 4.46$ ppm). Although the total time of the reaction to consume the substrates is about 6 h, we have presented the edited video file capturing visual gas evaluation during the reaction initial thirty seconds when gas evolution rate was very high. In this video, especially we have captured the gas evolution first few seconds after addition of 9-BBN, when the rate of gas evolution was very high and the rate becomes slow with time (after 30 min. the rate of evolution becomes very slow).

**X-ray crystal structure measurements**

Suitable single crystals of 2, 3 and 5 were selected and mounted under nitrogen atmosphere using the X-TEMP2 and intensity data were collected on a Super Nova, Dual, Cu at zero, Eos diffractometer. The crystal was kept at 100.00(10) K during data collection. Using Olex2, the structure was solved with the Superflip structure solution program using Charge Flipping and refined with the ShelXL refinement package using Least Squares minimization. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model. Disordered moieties were refined using bond lengths restraints and isotropic displacement parameters restraints. Crystallographic data (excluding structure factors) for the structures have been deposited with the Cambridge Crystallographic Data Centre. Single-crystal X-ray structural studies of compound 4 were performed on an Oxford Diffraction XCALIBUR-EOS CCD equipped diffractometer with an Oxford Instruments low temperature attachment. Crystal data were collected at 293(2) K using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073 \text{ Å}$). The strategy for the data collection was evaluated by using the CrysAlisPro CCD software. The data were collected by the standard
'\psi-\omega' scan method and were scaled and reduced using CrysAlisPro RED software. The structures were solved by direct methods (SHELXS) and refined by full-matrix least-squares calculations on F^2 (SHELXL).\textsuperscript{18} Copies of the data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. CCDC 1583077, 1583079, 1583078 and 1583080 contains the supplementary crystallographic data of compounds 2, 3, 4 and 5 respectively for this paper.

**Table S1.** Crystallographic and data collection parameters for compounds 2-5.

|                      | C_{47}H_{59}BN_2, 2 | C_{43}H_{52}BN_2O_5, 3 | C_{39}H_{47}N_2ClO, 4 | C_{40}H_{48}BN_2O, 5 |
|----------------------|---------------------|------------------------|-----------------------|----------------------|
| Formula weight       | 662.77              | 687.68                 | 595.24                | 633.75               |
| Temperature          | 100.00 K            | 293.00 K               | 295                   | 100 K                |
| Crystal system       | Monoclinic          | Monoclinic             | orthorhombic          | orthorhombic         |
| Space group          | P21/n               | P21/n                  | Pna21                 | P21212               |
| a (Å)                | 11.2461(3)          | 12.6081(5)             | 18.4291(7)            | 19.3779(19)          |
| b (Å)                | 23.0691(6)          | 14.3388(6)             | 13.1243(4)            | 14.5134(16)          |
| c (Å)                | 15.3687(3)          | 22.0714(7)             | 14.5076(6)            | 13.085(2)            |
| \(\alpha\) (°)      | 90.000              | 90.00                  | 90.00                 | 90.00                |
| \(\beta\) (°)       | 98.7643(19)         | 98.028(4)              | 90.00                 | 90.00                |
| \(\gamma\) (°)      | 90.000              | 90.00                  | 90.00                 | 90.00                |
| V(Å³)                | 3940.66(17)         | 3951.1(3)              | 3508.9(2)             | 3680.0(8)            |
Table S2. Selected bond distances (Å) and angles (°) for compounds 2-5.

| Compound 2 | Bond distances (Å) | Bond angles (°) |
|------------|-------------------|-----------------|
|            |                   |                 |
| C5 -B1     | 1.636(2)          | C5 -B1 -C42     | 111.13(13) |
| B1 -H1     | 0.9800            | C5 -B1 -C46     | 116.74(14) |
| C46 -B1    | 1.631(2)          | C42 -B1 -C46    | 104.07(13) |
| C42 -B1    | 1.639(2)          | N1 -C5 -B1      | 121.94(13) |
| N1 -C5     | 1.415(2)          | C4 -C5 -B1      | 134.35(14) |
| C4 -C5     | 1.368(2)          | N1 -C5 -C4      | 103.71(13) |
|            |                   | C5 -B1 -H1      | 108.00     |
|            |                   | C42 -B1 -H1     | 108.00     |
|            |                   | C46 -B1 -H1     | 108.00     |

| Compound 3 |
|------------|
|            |
| O1 -C1     | 1.242(3)          | O1 -C1 -O2      | 127.6(2)  |
| O2 -C1     | 1.260(3)          | O3 -B1 -O4      | 118.4(2)  |
| O3 -B1     | 1.363(4)          | O3 -B1 -O5      | 117.9(3)  |
| O4 -B1     | 1.375(4)          | O4 -B1 -O5      | 123.7(3)  |
| O5 -B1     | 1.358(4)          | N1 -C5 -C4      | 108.8(2)  |
| C4 -C5     | 1.355(3)          |                 |           |
| Compound 4 | N1 - C5 | 1.376(3) | N1 - C5 - C4 | 107.94(16) |
| Compound 4 | C4 - C5 | 1.356(3) | N3 - C4 - C5 | 105.77(16) |
| Compound 4 | N3 - C2 | 1.348(2) | N1 - C2 - N3 | 106.88(16) |
| Compound 4 | N1 - C2 | 1.344(2) | C2 - N3 - C4 | 109.66(14) |
| Compound 4 | N3 - C4 | 1.402(2) | N1 - C5 - H5 | 126.00 |
| Compound 4 | C5 - H5 | 0.9300 | C4 - C5 - H5 | 126.00 |

| Compound 5 | O1 - C42 | 1.323(11) | O1 - C42 - O3 | 111.4(7) |
| Compound 5 | O2 - C42 | 1.340(9) | O2 - C42 - O3 | 124.3(7) |
| Compound 5 | O3 - C42 | 1.338(10) | O1 - C42 - O2 | 124.3(8) |
| Compound 5 | O4 - B1 | 1.356(7) | O4 - B1 - O5 | 121.9(4) |
| Compound 5 | O5 - B1 | 1.329(12) | O4 - B1 - O6 | 116.3(8) |
| Compound 5 | N1 - C5 | 1.371(6) | N1 - C5 - C4 | 109.1(4) |
| Compound 5 | C4 - C5 | 1.326(7) | | | |

**Table S3.** Final coordinates and equivalent isotropic displacement parameters of the non-hydrogen atoms for compound 2.

| Atom  | x       | y       | Z       | U(eq)   |
|-------|---------|---------|---------|---------|
| N3    | 8247.0(11) | 1221.2(5) | 2478.5(8) | 13.8(3) |
| N1    | 10015.4(11) | 1486.7(6) | 2261.5(8) | 13.8(3) |
| C31   | 11345.3(15) | 1434.6(7) | 1155.2(11) | 19.6(3) |
| C30   | 11228.8(14) | 1445.9(7) | 2053.8(11) | 16.2(3) |
| C17   | 6623.6(14) | 528.5(7)  | 2047.8(11) | 16.9(3) |
| C6    | 7005.2(14) | 2106.4(7) | 2037.8(10) | 14.9(3) |
| C12   | 7242.9(13) | 887.9(7)  | 2691.4(10) | 14.8(3) |
| C13   | 6976.1(14) | 934.8(7)  | 3551.4(10) | 16.2(3) |
|   |       |       |       |       |
|---|-------|-------|-------|-------|
| C2 | 9368.5(14) | 1021.2(7) | 2456.4(10) | 14.6(3) |
| C5 | 9310.5(14) | 1997.1(7) | 2149.2(10) | 14.8(3) |
| C15 | 5398.6(15) | 230.9(7) | 3130.4(12) | 22.3(4) |
| C24 | 9759.9(14) | 408.9(7) | 2571.7(10) | 16.6(3) |
| C29 | 10684.8(15) | 187.0(7) | 2147.9(11) | 19.8(3) |
| C35 | 12199.5(15) | 1393.7(7) | 2736.4(11) | 19.2(3) |
| C11 | 6243.4(15) | 2240.5(7) | 2644.9(11) | 18.7(3) |
| C21 | 7701.1(15) | 1320.3(7) | 4243.6(10) | 18.9(3) |
| C4 | 8188.1(14) | 1813.2(6) | 2263.1(10) | 14.2(3) |
| C18 | 6948.6(15) | 477.8(7) | 1124.5(11) | 20.1(4) |
| C49 | 11677.0(14) | 3318.4(7) | 2382.0(11) | 20.0(3) |
| C10 | 5149.5(15) | 2511.2(7) | 2378.6(11) | 20.9(4) |
| C26 | 9542.9(16) | -552.0(7) | 3171.7(12) | 24.2(4) |
| C32 | 12502.2(17) | 1363.4(8) | 956.3(12) | 25.8(4) |
| C43 | 10558.0(16) | 2904.4(8) | 3584.8(11) | 23.1(4) |
| C19 | 5942.8(16) | 706.1(8) | 427.0(11) | 25.8(4) |
| C16 | 5685.0(15) | 200.8(7) | 2290.7(12) | 21.1(4) |
| C42 | 11008.3(14) | 2798.4(7) | 2704.1(10) | 17.4(3) |
| C28 | 11027.9(16) | -390.1(8) | 2246.5(12) | 24.5(4) |
| C46 | 8989.8(15) | 3183.3(7) | 1888.2(11) | 18.5(3) |
| C45 | 8583.1(15) | 3327.4(8) | 2777.9(12) | 23.9(4) |
| C48 | 10890.2(15) | 3843.0(7) | 2063.8(12) | 20.8(4) |
| C7 | 6640.1(15) | 2256.6(7) | 1156.8(11) | 19.0(3) |
|   |       |       |       |       |
|---|-------|-------|-------|-------|
| C44 | 9593.5(16) | 3372.9(8) | 3567.0(11) | 25.5(4) |
| C14 | 6036.6(15) | 593.7(7)  | 3755.5(11) | 20.5(4) |
| C9  | 4797.6(15) | 2655.4(7) | 1502.0(11) | 22.5(4) |
| C25 | 9202.9(15) | 25.7(7)   | 3093.2(11) | 20.9(4) |
| C47 | 9660.6(15) | 3690.5(7) | 1524.7(12) | 21.8(4) |
| C8  | 5543.8(16) | 2530.9(8) | 893.5(11)  | 24.2(4) |
| C36 | 12079.3(16)| 1408.9(8) | 3708.4(11) | 24.0(4) |
| C33 | 13481.1(17)| 1305.1(8) | 1613.9(14) | 29.9(4) |
| C23 | 6922.8(17) | 1574.4(8) | 4884.9(12) | 27.3(4) |
| C27 | 10460.6(17)| -762.2(8) | 2753.8(12) | 27.0(4) |
| C34 | 13332.0(16)| 1321.3(8) | 2487.2(13) | 26.6(4) |
| B1  | 9884.7(16) | 2623.9(8) | 1939.8(12) | 16.2(4) |
| C41 | 9844.2(17) | 861.9(8)  | 97.8(12)   | 27.9(4) |
| C22 | 8779.8(17) | 1002.4(9) | 4762.4(12) | 29.1(4) |
| C20 | 7269.1(17) | -148.8(8) | 920.8(12)  | 26.6(4) |
| C37 | 12952.9(18)| 1845.7(9) | 4220.8(13) | 33.3(5) |
| C38 | 12293.6(18)| 810.7(9)  | 4138.0(13) | 32.1(4) |
| C40 | 10514(2)   | 1831.3(9) | -358.5(13) | 41.4(5) |
| C39 | 10269.7(17)| 1464.4(8) | 423.5(11)  | 23.6(4) |
Table S4. Hydrogen atom positions and isotropic displacement parameters for compound 2.

| Atom  | x     | y     | z     | U(eq) |
|-------|-------|-------|-------|-------|
| H15   | 4773  | 6     | 3279  | 27    |
| H29   | 11072 | 430   | 1797  | 24    |
| H11   | 6473  | 2147  | 3235  | 22    |
| H21   | 8015  | 1645  | 3935  | 23    |
| H18   | 7663  | 717   | 1102  | 24    |
| H49A  | 12291 | 3443  | 2858  | 24    |
| H49B  | 12084 | 3190  | 1903  | 24    |
| H10   | 4649  | 2597  | 2790  | 25    |
| H26   | 9149  | -801  | 3509  | 29    |
| H32   | 12620 | 1355  | 370   | 31    |
| H43A  | 10237 | 2544  | 3775  | 28    |
| H43B  | 11240 | 3011  | 4021  | 28    |
| H19A  | 5220  | 490   | 453   | 39    |
| H19B  | 6173  | 663   | -146  | 39    |
| H19C  | 5804  | 1108  | 536   | 39    |
| H16   | 5245  | -42   | 1879  | 25    |
| H42   | 11567 | 2470  | 2782  | 21    |
| H28   | 11649 | -528  | 1967  | 29    |
| H46   | 8271  | 3097  | 1462  | 22    |
|    |     |     |     |     |
|----|-----|-----|-----|-----|
| H45A | 8151 | 3693 | 2718 | 29 |
| H45B | 8023 | 3031 | 2905 | 29 |
| H48A | 11328 | 4086 | 1706 | 25 |
| H48B | 10756 | 4068 | 2573 | 25 |
| H7   | 7136 | 2172 | 742  | 23 |
| H44A | 9972 | 3750 | 3556 | 31 |
| H44B | 9244 | 3348 | 4105 | 31 |
| H14  | 5833 | 609  | 4319 | 25 |
| H9   | 4061 | 2835 | 1325 | 27 |
| H25  | 8597 | 161  | 3390 | 25 |
| H47A | 9780 | 3596 | 929  | 26 |
| H47B | 9152 | 4032 | 1492 | 26 |
| H8   | 5313 | 2631 | 306  | 29 |
| H36  | 11257 | 1530 | 3759 | 29 |
| H33  | 14246 | 1255 | 1466 | 36 |
| H23A | 6185 | 1719 | 4561 | 41 |
| H23B | 7348 | 1886 | 5210 | 41 |
| H23C | 6748 | 1278 | 5285 | 41 |
| H27  | 10692 | -1149 | 2814 | 32 |
| H34  | 14002 | 1283 | 2920 | 32 |
| H1   | 10192 | 2593 | 1378 | 19 |
| H41A | 10474 | 671  | -150 | 42 |
| H41B | 9146 | 898  | -344 | 42 |
| Atom   | x       | y       | Z       | U(eq)   |
|--------|---------|---------|---------|---------|
| O2     | 1958.6(16) | 8892.6(14) | 4592.5(8) | 31.9(5) |

Table S5. Final coordinates and equivalent isotropic displacement parameters of the non-hydrogen atoms for compound 3.
|   | X     | Y     | Z     | U   | V   | W   |
|---|-------|-------|-------|-----|-----|-----|
| 05 | 5638.7(17) | 2307.8(14) | 4875.6(10) | 39.4(6) |
| N1 | 5285.1(16) | 5546.8(14) | 8017.8(9) | 16.7(5) |
| 04 | 6036.7(16) | 678.2(14) | 5049.5(9) | 33.6(5) |
| 01 | 2226.6(17) | 7407.2(14) | 4896.1(9) | 40.3(6) |
| 03 | 4261.3(15) | 1217.9(14) | 4847.6(10) | 36.8(5) |
| N3 | 6162.7(16) | 5530.3(14) | 7237.9(9) | 15.3(5) |
| C36 | 8111(2) | 5519.0(18) | 7788.8(11) | 18.6(6) |
| C35 | 4929(2) | 3310(2) | 6250.8(13) | 32.3(7) |
| C4 | 6932(2) | 5525.7(17) | 7762.7(11) | 16.7(6) |
| C2 | 5175(2) | 5528.7(17) | 7396.1(11) | 16.1(6) |
| C12 | 4775(2) | 4007.5(19) | 8802.7(12) | 25.7(7) |
| C30 | 6771(2) | 7284.6(18) | 6729.5(12) | 25.3(7) |
| C29 | 6558(2) | 6401.6(19) | 6341.8(12) | 22.0(7) |
| C25 | 6167(2) | 4705.6(18) | 6265.7(11) | 20.0(6) |
| C40 | 9766(2) | 5561(2) | 7350.0(13) | 31.1(7) |
| C33 | 5955(2) | 3784.4(18) | 6565.2(12) | 23.9(6) |
| C24 | 6331.3(19) | 5544.0(18) | 6593.6(11) | 16.8(6) |
| C5 | 6366(2) | 5546.5(17) | 8241.1(11) | 18.9(6) |
| C37 | 8723(2) | 5514.5(19) | 8369.6(12) | 25.2(7) |
| C19 | 3936(2) | 5958.9(18) | 6434.2(11) | 19.2(6) |
| C15 | 4242(2) | 7349.9(19) | 7989.4(12) | 26.3(7) |
| C18 | 4130(2) | 5479.8(17) | 6995.4(11) | 17.7(6) |
| C7 | 3944(2) | 6551.4(19) | 8383.9(11) | 22.9(6) |
|   |   |   |   |   |
|---|---|---|---|---|
| C23 | 3323(2) | 4946.8(18) | 7185.1(11) | 20.0(6) |
| C28 | 6583(2) | 6410(2) | 5712.3(12) | 26.8(7) |
| C6  | 4447(2) | 5677.9(19) | 8397.9(11) | 20.3(6) |
| C20 | 2937(2) | 5903.5(18) | 6086.3(12) | 22.7(6) |
| C32 | 5802(2) | 7931.1(19) | 6675.2(13) | 30.7(7) |
| C14 | 5487(2) | 3917(2) | 9426.3(12) | 29.7(7) |
| C26 | 6221(2) | 4763(2) | 5638.6(12) | 27.2(7) |
| C41 | 8651(2) | 5527(2) | 7279.4(12) | 27.9(7) |
| C11 | 4194(2) | 4938.1(19) | 8770.1(11) | 22.4(6) |
| C27 | 6413(2) | 5603(2) | 5369.0(12) | 29.4(7) |
| C38 | 9828(2) | 5534(2) | 8433.8(13) | 29.7(7) |
| C22 | 2322(2) | 4904.0(19) | 6835.7(12) | 24.7(7) |
| C1  | 1667(2) | 8066(2) | 4669.4(12) | 30.3(7) |
| C34 | 6925(2) | 3139(2) | 6581.0(13) | 35.2(8) |
| C21 | 2129(2) | 5380.8(19) | 6283.1(12) | 25.7(7) |
| C8  | 3148(2) | 6668(2) | 8757.7(12) | 30.1(7) |
| C17 | 4768(2) | 8154(2) | 8380.7(13) | 32.5(7) |
| C31 | 7746(2) | 7824(2) | 6571.0(16) | 43.3(9) |
| C9  | 2872(2) | 5954(2) | 9125.1(12) | 32.8(8) |
| C16 | 3256(2) | 7682(2) | 7549.1(13) | 33.8(8) |
| C10 | 3388(2) | 5102(2) | 9127.9(12) | 28.5(7) |
| C13 | 4000(2) | 3176(2) | 8695.0(13) | 37.9(8) |
| C39 | 10352(2) | 5567(2) | 7925.1(13) | 30.3(7) |
**Table S6.** Hydrogen atom positions and isotropic displacement parameters for compound 3.

| Atom | x     | y     | z     | U(eq) |
|------|-------|-------|-------|-------|
| H5A  | 6292  | 2344  | 4955  | 59    |
| H3   | 4170  | 652   | 4859  | 55    |
| H35A | 4332  | 3726  | 6252  | 48    |
| H35B | 4802  | 2750  | 6468  | 48    |
| H35C | 5012  | 3158  | 5836  | 48    |
| H12  | 5241  | 3999  | 8482  | 31    |
| H30  | 6930  | 7091  | 7158  | 30    |
| H40  | 10117 | 5580  | 7006  | 37    |
| H33  | 5855  | 3915  | 6989  | 29    |
| H5   | 6657  | 5559  | 8652  | 23    |
| H37  | 8381  | 5498  | 8716  | 30    |
| H19  | 4476  | 6310  | 6298  | 23    |
| H15  | 4769  | 7113  | 7740  | 32    |
| H23  | 3454  | 4615  | 7550  | 24    |
|   |   |   |   |   |
|---|---|---|---|---|
| H28 | 6717 | 6966 | 5520 | 32 |
| H20 | 2807 | 6221 | 5716 | 27 |
| H32A | 5628 | 8135 | 6259 | 46 |
| H32B | 5965 | 8463 | 6936 | 46 |
| H32C | 5202 | 7603 | 6797 | 46 |
| H14A | 6009 | 4409 | 9470 | 45 |
| H14B | 5847 | 3325 | 9449 | 45 |
| H14C | 5051 | 3960 | 9748 | 45 |
| H26 | 6127 | 4228 | 5400 | 33 |
| H41 | 8264 | 5508 | 6889 | 33 |
| H27 | 6427 | 5627 | 4949 | 35 |
| H38 | 10222 | 5525 | 8823 | 36 |
| H22 | 1779 | 4556 | 6971 | 30 |
| H1 | 948 | 7934 | 4541 | 36 |
| H34A | 6791 | 2568 | 6784 | 53 |
| H34B | 7546 | 3439 | 6798 | 53 |
| H34C | 7048 | 3005 | 6170 | 53 |
| H21 | 1458 | 5348 | 6047 | 31 |
| H8 | 2796 | 7237 | 8759 | 36 |
| H17A | 4293 | 8364 | 8656 | 49 |
| H17B | 4915 | 8659 | 8119 | 49 |
| H17C | 5426 | 7941 | 8611 | 49 |
| H31A | 8354 | 7416 | 6602 | 65 |
Table S7. Final coordinates and equivalent isotropic displacement parameters of the non-hydrogen atoms for compound 4.

| Atom | x        | y        | z        | U(eq)    |
|------|----------|----------|----------|----------|
| N3   | -4539.0(8) | -2222.1(10) | -4022.4(11) | 37.0(3)  |
| N1   | -4355.9(8) | -3714.8(11) | -3436.6(12) | 40.9(4)  |
| C29  | -4264.1(13) | -415.4(15)  | -3816.7(14) | 50.6(5)  |
| Atom | X         | Y         | Z         | U           |
|------|-----------|-----------|-----------|-------------|
| C4   | -4111.2(10) | -2763.1(13) | -4654.3(13) | 37.9(4)     |
| C5   | -3998.4(10) | -3691.5(14) | -4269.3(14) | 42.4(4)     |
| C18  | -5138.3(11) | -2568.9(15) | -2483.9(13) | 44.2(5)     |
| C24  | -4767.7(11) | -1156.7(13) | -4070.2(13) | 40.9(4)     |
| C2   | -4686.2(10) | -2816.8(14) | -3288.5(13) | 38.5(4)     |
| C25  | -5482.9(12) | -951.4(15)  | -4329.6(13) | 46.5(5)     |
| C6   | -4341.9(12) | -4557.7(15) | -2780.3(15) | 49.6(5)     |
| C15  | -5308.3(14) | -5423.9(19) | -3768.8(19) | 65.4(7)     |
| C36  | -3847.3(10) | -2385.0(14) | -5548.8(13) | 40.0(4)     |
| C38  | -3892.5(14) | -1273.8(19) | -6867.8(16) | 61.5(6)     |
| C7   | -4831.8(14) | -5360.4(16) | -2922.2(18) | 59.2(6)     |
| C22  | -6083.0(14) | -3041(2)   | -1422.5(18) | 66.6(7)     |
| C23  | -5670.2(12) | -3247.0(17) | -2190.1(16) | 53.0(5)     |
| C19  | -5044.4(15) | -1667.8(18) | -1995.6(15) | 59.5(6)     |
| C30  | -3478.5(15) | -651(2)    | -3590.3(19) | 68.3(7)     |
| C37  | -4168.7(13) | -1586.6(16) | -6022.3(15) | 52.8(5)     |
| C33  | -5999.3(12) | -1749.1(17) | -4683.9(18) | 61.2(6)     |
| C28  | -4519.5(17) | 590.3(16)  | -3805.1(17) | 65.6(7)     |
| C41  | -3262.5(12) | -2881.9(19) | -5948.9(16) | 56.5(6)     |
| C27  | -5225.9(17) | 806.7(17)  | -4027(2)    | 72.0(8)     |
| C40  | -2998.8(14) | -2568(2)   | -6797.5(17) | 67.6(7)     |
| C8   | -4849(2)    | -6108(2)   | -2253(2)    | 83.6(9)     |
| C26  | -5704.9(14) | 69.5(16)   | -4287.8(17) | 60.4(6)     |
| Atom | x      | y      | z      | U(eq)   |
|------|--------|--------|--------|---------|
| C39  | -3309.0(15) | -1763(2) | -7246.7(17) | 65.8(6)  |
| C11  | -3855.3(14) | -4495(2)  | -2057.8(18) | 65.1(7)  |
| C9   | -4403(2)  | -6057(2)  | -1513(3)  | 99.2(11) |
| C21  | -5974.1(16) | -2155(2)  | -941.8(17) | 73.7(8)  |
| C34  | -6259.4(16) | -1485(3)  | -5655(2)  | 86.8(9)  |
| C17  | -6069.0(17) | -5846(3)  | -3569(3)  | 99.0(11) |
| C16  | -4934.2(17) | -6070(2)  | -4508(2)  | 86.7(9)  |
| C10  | -3901.6(19) | -5292(3)  | -1407(2)  | 92.6(10) |
| C20  | -5465.8(18) | -1467(2)  | -1229.2(17) | 74.8(8)  |
| C31  | -2973.7(17) | -256(3)   | -4340(2)  | 96(1)    |
| C12  | -3284.2(17) | -3686(3)  | -1975(2)  | 88.3(10) |
| C32  | -3239(2)  | -231(3)   | -2652(3)  | 114.5(14) |
| C35  | -6660.4(16) | -1890(3)  | -4054(2)  | 86.9(9)  |
| C14  | -2529(2)  | -4218(4)  | -2077(4)  | 136.7(16) |
| C13  | -3337(2)  | -3074(3)  | -1089(3)  | 114.2(12) |
| Cl1  | -2728.1(3) | -5549.7(5) | -4789.0(7) | 83.4(2)  |
| O1   | -3293(2)  | -7338(2)  | -3543(3)  | 157.8(15) |

Table S8. Hydrogen atom positions and isotropic displacement parameters for compound 4.

| Atom | x      | y      | z      | U(eq)   |
|------|--------|--------|--------|---------|
| H5   | -3727  | -4219  | -4523  | 51      |
|     |       |       |       |     |
|-----|-------|-------|-------|-----|
| H15 | -5365 | -4733 | -4014 | 78  |
| H38 | -4105 | -730  | -7177 | 74  |
| H22 | -6435 | -3501 | -1230 | 80  |
| H23 | -5748 | -3847 | -2517 | 64  |
| H19 | -4697 | -1199 | -2185 | 71  |
| H30 | -3427 | -1394 | -3569 | 82  |
| H37 | -4571 | -1259 | -5773 | 63  |
| H33 | -5739 | -2399 | -4714 | 73  |
| H28 | -4206 | 1117  | -3645 | 79  |
| H41 | -3046 | -3428 | -5646 | 68  |
| H27 | -5384 | 1479  | -3998 | 86  |
| H40 | -2608 | -2908 | -7063 | 81  |
| H8  | -5170 | -6651 | -2311 | 100 |
| H26 | -6179 | 244   | -4439 | 72  |
| H39 | -3123 | -1547 | -7810 | 79  |
| H9  | -4438 | -6557 | -1061 | 119 |
| H21 | -6248 | -2021 | -417  | 88  |
| H34A| -6561 | -889  | -5631 | 130 |
| H34B| -6533 | -2045 | -5900 | 130 |
| H34C| -5848 | -1355 | -6043 | 130 |
| H17A| -6033 | -6548 | -3391 | 149 |
| H17B| -6363 | -5790 | -4112 | 149 |
| H17C| -6287 | -5462 | -3077 | 149 |
|    |    |    |    |    |
|----|----|----|----|----|
| H16A | -4469 | -5781 | -4649 | 130 |
| H16B | -5228 | -6082 | -5054 | 130 |
| H16C | -4871 | -6753 | -4283 | 130 |
| H10  | -3590 | -5300 | -903  | 111 |
| H20  | -5403 | -860  | -907  | 90  |
| H31A | -3121 | -527  | -4925 | 144 |
| H31B | -2485 | -465  | -4209 | 144 |
| H31C | -2997 | 475   | -4358 | 144 |
| H12  | -3343 | -3214 | -2493 | 106 |
| H32A | -3227 | 500   | -2676 | 172 |
| H32B | -2764 | -484  | -2507 | 172 |
| H32C | -3576 | -445  | -2186 | 172 |
| H35A | -6500 | -2042 | -3440 | 130 |
| H35B | -6953 | -2442 | -4280 | 130 |
| H35C | -6942 | -1275 | -4048 | 130 |
| H14A | -2434 | -4626 | -1541 | 205 |
| H14B | -2157 | -3710 | -2139 | 205 |
| H14C | -2531 | -4646 | -2614 | 205 |
| H13A | -3823 | -2826 | -1015 | 171 |
| H13B | -3007 | -2509 | -1116 | 171 |
| H13C | -3213 | -3502 | -575  | 171 |
| H1A  | -3147 | -6871 | -3182 | 237 |
| H1B  | -3723 | -7206 | -3719 | 237 |
Table S9. Final coordinates and equivalent isotropic displacement parameters of the non-hydrogen atoms for compound 5.

| Atom | x    | y    | z    | U(eq)  |
|------|------|------|------|--------|
| O4   | 123(2)| 4224(3)| 9763(3) | 45.4(11) |
| N1   | 1932(2) | 3004(3) | 8485(3) | 26.2(10) |
| N3   | 2139(2) | 3661(3) | 7033(3) | 27.5(10) |
| O2   | 5128(3) | 2279(3) | 9003(3) | 58.0(13) |
| O3   | 5639(2) | 1371(4) | 7704(4) | 54.8(12) |
| O5   | 0     | 5000 | 11326(4) | 56.5(19) |
| C24  | 2748(2) | 2142(4) | 7346(4) | 28.2(12) |
| C5   | 1584(2) | 3826(3) | 8476(4) | 27.4(11) |
| C6   | 1473(3) | 5168(4) | 7242(4) | 29.5(12) |
| C12  | 2317(3) | 3738(4) | 5941(4) | 27.3(11) |
| C2   | 2275(2) | 2913(3) | 7599(4) | 24.7(11) |
| C13  | 1797(3) | 3543(4) | 5235(4) | 29.9(12) |
| C11  | 1829(3) | 5719(4) | 6574(4) | 36.2(13) |
| C16  | 3141(3) | 3998(4) | 4624(5) | 38.0(14) |
| C30  | 1884(3) | 2289(4) | 9273(4) | 32.5(13) |
| C4   | 1711(3) | 4258(3) | 7603(4) | 29.3(12) |
| C31  | 2271(3) | 2407(4) | 10169(4) | 30.5(12) |
| C35  | 1479(3) | 1510(4) | 9059(4) | 29.4(12) |
| C18  | 1058(3) | 3290(4) | 5530(4) | 32.3(13) |
| Atom | X       | Y       | Z       | Uiso |
|------|---------|---------|---------|------|
| C17  | 3000(3) | 3963(4) | 5667(4) | 29.0(12) |
| C25  | 2692(3) | 1643(4) | 6431(4) | 31.2(12) |
| C32  | 2235(3) | 1681(4) | 10878(5) | 41.2(14) |
| C7   | 849(3)  | 5507(4) | 7673(5) | 36.0(14) |
| C29  | 3264(3) | 1946(4) | 8050(4) | 34.0(13) |
| C15  | 2645(3) | 3800(4) | 3902(5) | 36.8(13) |
| C27  | 3655(3) | 692(4)  | 6951(5) | 42.0(15) |
| C36  | 1023(3) | 1428(4) | 8136(4) | 33.5(13) |
| C33  | 1857(3) | 918(4)  | 10695(5) | 39.8(14) |
| C21  | 3573(3) | 4150(4) | 6424(5) | 38.5(14) |
| C39  | 2684(3) | 3280(4) | 10390(5) | 35.5(13) |
| C41  | 2244(3) | 3949(4) | 11024(5) | 41.4(15) |
| C28  | 3707(3) | 1216(4) | 7844(5) | 41.9(15) |
| C9   | 971(3)  | 6922(4) | 6713(5) | 40.5(14) |
| C14  | 1971(3) | 3576(4) | 4208(5) | 34.0(13) |
| C38  | 1149(3) | 544(4)  | 7544(5) | 41.1(15) |
| C26  | 3142(3) | 925(4)  | 6240(4) | 36.1(13) |
| C34  | 1471(3) | 826(4)  | 9819(5) | 41.1(14) |
| C8   | 610(3)  | 6357(4) | 7412(5) | 39.7(14) |
| C23  | 4175(3) | 3458(4) | 6273(5) | 38.7(14) |
| C40  | 3371(3) | 3051(5) | 10941(5) | 43.5(15) |
| B1   | 0       | 5000    | 10310(8) | 46(3) |
| C20  | 540(3)  | 3982(4) | 5088(5) | 42.8(15) |
| Atom | x     | y     | z     | U(eq)  |
|------|-------|-------|-------|--------|
|      | 5499(4) | 2181(6) | 8146(6) | 56(2)  |
| C42  | 246(3)  | 1501(5) | 8468(5) | 46.7(16) |
| C37  | 856(3)  | 2316(4) | 5180(5) | 42.7(15) |
| C19  | 1585(3) | 6586(4) | 6305(5) | 41.4(15) |
| C10  | 5762(4) | 2874(5) | 7618(6) | 100(2)  |
| O1   | 3854(3) | 5133(4) | 6320(6) | 54.0(18) |
| C22  | 3854(3) | 5133(4) | 6320(6) | 54.0(18) |

Table S10. Hydrogen atom positions and isotropic displacement parameters for compound 5.
| H36  | 1125(3) | 1948(4) | 7682(4) | 40.2(15) |
|------|---------|---------|---------|----------|
| H33  | 1857(3) | 444(4)  | 11173(5)| 47.8(17) |
| H21  | 3389(3) | 4073(4) | 7116(5) | 46.2(17) |
| H39  | 2794(3) | 3576(4) | 9737(5) | 42.6(16) |
| H41a | 1838(11)| 4110(20)| 10646(14)| 62(2)    |
| H41b | 2112(19)| 3657(11)| 11653(15)| 62(2)    |
| H41c | 2507(8) | 4493(13)| 11170(30)| 62(2)   |
| H28  | 4048(3) | 1071(4) | 8316(5) | 50.3(18) |
| H9   | 804(3)  | 7499(4) | 6531(5) | 48.6(17) |
| H14  | 1637(3) | 3449(4) | 3717(5) | 40.8(16) |
| H38a | 1633(4) | 479(14) | 7410(30)| 62(2)    |
| H38b | 991(19) | 28(5)   | 7940(14)| 62(2)    |
| H38c | 901(17) | 565(12) | 6909(15)| 62(2)    |
| H26  | 3104(3) | 592(4)  | 5635(4) | 43.3(16) |
| H34  | 1201(3) | 302(4)  | 9729(5) | 49.3(17) |
| H8   | 202(3)  | 6571(4) | 7699(5) | 47.6(17) |
| H23a | 4003(5) | 2840(4) | 6330(30)| 58(2)    |
| H23b | 4375(14)| 3540(20)| 5609(13)| 58(2)    |
| H23c | 4520(10)| 3560(19)| 6790(20)| 58(2)    |
| H40a | 3274(3) | 2730(30)| 11564(17)| 65(2) |
| H40b | 3652(10)| 2670(20)| 10506(14)| 65(2) |
| H40c | 3612(11)| 3612(5)| 11100(30)| 65(2) |
| H20a | 651(13) | 4591(6) | 5320(30)| 64(2)    |
|       |       |       |       |       |
|-------|-------|-------|-------|-------|
| H20b  | 560(15)| 3970(20)|4355(5) |64(2)  |
| H20c  | 82(4)  | 3823(17)|5310(30)|64(2)  |
| H37a  | 128(7) | 982(17) |8890(30)|70(2)  |
| H37b  | 177(6) | 2059(16)|8850(30)|70(2)  |
| H37c  | -42(3) | 1510(30)|7871(5)|70(2)  |
| H19a  | 920(20)| 2267(10)|4453(7)|64(2)  |
| H19b  | 1143(15)|1872(5) |5520(20)|64(2)  |
| H19c  | 382(7) | 2203(11)|5350(30)|64(2)  |
| H10   | 1834(3)| 6946(4)|5847(5)|49.7(18)|
| H1    | 5454(12)|3240(50)|7470(90)|149(3) |
| H22a  | 4000(20)|5238(12)|5628(10)|81(3)  |
| H22b  | 3500(8) | 5566(4)|6500(40)|81(3)  |
| H22c  | 4242(16)|5210(11)|6770(30)|81(3)  |
$^1$H, $^{13}$C and $^{11}$B NMR spectra

![NMR spectra](image)

**Fig. S5** $^1$H NMR (C$_6$D$_6$, RT) spectrum of 1,3-bis(2,6-diisopropylphenyl)-2,4-diphenylimidazolidine-9-borabicyclo[3.3.1]nonane (2).
**Fig. S6** $^{13}$C NMR ($\text{C}_6\text{D}_6$, RT) spectrum of 1,3-bis(2,6-diisopropylphenyl)-2,4-diphenylimidazolidine-9-borabicyclo[3.3.1]nonane (2).
Fig. S7 $^{11}$B NMR (C$_6$D$_6$, RT) spectrum of 1,3-bis(2,6-diisopropylphenyl)-2,4-diphenylimidazolidine-9-borabicyclo[3.3.1]nonane (2).
Fig. S8 $^1$H NMR (CDCl$_3$, RT) spectrum of 1,3-bis(2,6-diisopropylphenyl)-2,4-diphenylimidazolidine formate boric acid (3).
Fig. S9 $^{13}$C NMR (CDCl$_3$, RT) spectrum of 1,3-bis(2,6-diisopropylphenyl)-2,4-diphenylimidazolidine formate boric acid (3).
Fig. S10 $^{11}$B NMR (CDCl$_3$, RT) spectrum of 1,3-bis(2,6-diisopropylphenyl)-2,4-diphenylimidazolidine formate boric acid (3).
Fig. S11 $^1$H NMR (CDCl$_3$, RT) spectrum of {1,3-bis(2,6-diisopropylphenyl)-2,4-diphenyl-imidazolium (Cl$^-$)} (4).
**Fig. S12** $^{13}$C NMR (CDCl$_3$, RT) spectrum of {1,3-bis(2,6-diisopropylphenyl)-2,4-diphenyl-imidazolium (Cl$^-$)} (4).
Fig. S13  $^1$H NMR (CDCl$_3$, RT) spectrum of 1,3-bis(2,6-diisopropylphenyl)-2,4-diphenylimidazolidine bicarbonate boric acid} (5).
Fig. S14 $^{13}$C NMR (CDCl$_3$, RT) spectrum of 1,3-bis(2,6-diisopropylphenyl)-2,4-diphenylimidazolidine bicarbonate boric acid) (5).
Fig. S15  $^{11}$B NMR (CDCl$_3$, RT) spectrum of 1,3-bis(2,6-diisopropylphenyl)-2,4-diphenylimidazolidine bicarbonate boric acid) (5).
Fig. S16 ¹H NMR (CDCl₃, RT) spectrum of 1,3-bis(2,6-diisopropylphenyl)-2,4-diphenylimidazolidine formate boric acid (3) after heating at 150 °C for 12 h.
**Fig. S17** $^{13}$C NMR (CDCl$_3$, RT) spectrum of 1,3-bis(2,6-diisopropylphenyl)-2,4-diphenylimidazolidine formate boric acid (3) after heating at 150 °C for 12 h.
Fig. S18 $^{11}$B NMR (CDCl$_3$, RT) spectrum of 1,3-bis(2,6-diisopropylphenyl)-2,4-diphenylimidazolidine formate boric acid (3) after heating at 150 °C for 12 h.
**Fig. S19** Reaction mixture $^1$H NMR (C$_6$D$_6$, RT) spectrum of 1,3-bis(2,6-diisopropylphenyl)-2,4-diphenylimidazolidine-9-borabicyclo[3.3.1]nonane (2) after exposing in air for 12 h. a) Full spectrum. b) Zoom spectrum of aliphatic region.
Fig. S20 $^1$H NMR (C$_6$D$_6$, RT) spectrum of the reaction mixture after 15 min (carbon dioxide reduction from air with compound 3 in presence of 10 equivalent 9-BBN at room temperature).
Fig. S21 $^1$H NMR (C$_6$D$_6$, RT) spectrum of the reaction mixture after 6 h (carbon dioxide reduction from air with compound 3 in presence of 10 equivalents 9-BBN at room temperature).
**Fig. S22** $^{11}$B NMR ($C_6D_6$, RT) spectrum of the reaction mixture after 6 h (carbon dioxide reduction from air with compound 3 in presence of 10 equivalents 9-BBN at room temperature).
Fig. S23 $^1$H NMR (D$_2$O, RT) spectrum of the reaction mixture after 12 h (carbon dioxide reduction from air with compound 3 in presence of 2(M) NaOH solution at room temperature).
Fig. S24 $^{13}$C NMR (D$_2$O, RT) spectrum of the reaction mixture after 12 h (carbon dioxide reduction from air with compound 3 in presence of 2(M) NaOH solution at room temperature).
Fig. S25 $^{13}$C NMR (CDCl$_3$, RT) spectrum of the reaction mixture after 12 h (reaction of compound 2 with dry air in toluene for 12 h at room temperature).
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