Supporting Information

Carbon Monoxide Insertion at a Heavy p-Block Element: Unprecedented Formation of a Cationic Bismuth Carbamoyl

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Experimental

General considerations. All air- and moisture-sensitive manipulations were carried out using standard vacuum line Schlenk techniques or in gloveboxes containing an atmosphere of purified argon. Solvents were degassed and purified according to standard laboratory procedures. NMR spectra were recorded on Bruker instruments operating at 300, 400, or 500 MHz with respect to ^{1}H. ^{1}H and ^{13}C NMR chemical shifts are reported relative to $SiMe_4$ using the residual ^{1}H and ^{13}C chemical shifts of the solvent as a secondary standard. ^{19}F NMR chemical shifts are reported relative to $CFCl_3$ as an external standard. NMR spectra were recorded at 25 °C, if not otherwise noted. Infrared spectra were collected on a Bruker ATR-IR-Alpha or a JASCO FT/IR-4100 spectrometer. Elemental analyses were performed on a Leco or a Carlo Erba instrument. Cyclic voltammograms were recorded using a Gamry Instruments Reference 600 potentiostat. A standard three-electrode cell configuration was employed using a platinum disk working electrode, a platinum wire counter electrode, and a silver wire, separated by a *Vycor* tip, serving as the reference electrode. Formal redox potentials are referenced to the ferrocene/ferrocenium redox couple. UV/vis spectra were recorded with a Jasco V-660 UV/vis spectrometer. Single crystals suitable for X-ray diffraction were coated with polyisobutylene or perfluorinated polyether oil in a glovebox, transferred to a nylon loop and then transferred to the goniometer of a diffractometer equipped with a molybdenum X-ray tube (λ = 0.71073 Å). The structures were solved using direct methods (SHELXS) completed by Fourier synthesis and refined by full-matrix least-squares procedures. CCDC 1875340-1875343 contain the crystallographic information for this work.

All DFT calculations were performed with the Amsterdam Density Functional (ADF) program[1] using relativistic, dispersion-corrected density functional theory (DFT) at the ZORA-BLYP-D3BJ/TZ2P level of theory for geometry optimizations and energy calculations, with the full electron model for all atoms (no frozen core).[2,3] Solvation in tetrahydrofuran (THF) was simulated by using the conductor-like screening model (COSMO).[4] All stationary points were verified to be minima on the potential energy surface through vibrational analysis.
The bonding mode in **2**, with special emphasis on Bi–(CONR) interactions, was analyzed within the framework of quantitative Kohn-Sham molecular orbital theory[5] in combination with a quantitative energy decomposition analysis (EDA)[5] in the gas phase. The electronic bond energy ΔE can be decomposed into the strain energy ΔE_{strain} associated with deforming two fragments (in triplet state) from their equilibrium structure to the geometry they adopt in **2** plus the interaction energy ΔE_{int} between these deformed fragments. The latter is further decomposed into the classical electrostatic attraction ΔV_{elstat}, Pauli repulsion ΔE_{Pauli} between occupied orbitals, stabilizing orbital interactions ΔE_{oi}, and dispersion interactions ΔE_{disp}.[2] Atomic charges were computed with the Voronoi deformation density (VDD) method.[6] TD-DFT calculations were carried out at the CAMY-B3LYP/TZ2P level of theory.

Synthesis of compounds 2-5.

Bi(CONPh(C$_6$H$_4$))(NC$_5$H$_5$)$_2$][OTf] (2). A suspension of **1** (250 mg, 197 µmol) in THF (2 mL) was degassed in two freeze/pump/thaw cycles and pressurized with CO (1.5 bar). After 3 d, the solid was filtered off and recrystallized from pyridine (2 mL) by layering with Et_2O / pentane (3 mL, 2:1) and storage at –30 °C. After 1 d, a pale yellow crystalline material had formed, which was isolated by filtration and dried in vacuo. Yield: 160 mg, 240 µmol, 61%.

^{1}H NMR (500 MHz, NC_5D_5): δ = 7.13-7.18 (m, 2H, *o*-Ph), 7.21-7.24 (m, 4H, 3,5-NC_5H_5), 7.26

(dd, 1H, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.1 Hz, 6-(1-NPh,2-Bi-C_6H_4)), 7.32 (ddd, 1H, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.2 Hz, 5-(1-NPh,2-Bi-C_6H_4)), 7.45 (ddd, 1H, $^3J_{HH}$ = 6.6 Hz, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.6 Hz, *p*-Ph), 7.50 (ddd, 1H, $^3J_{HH}$ = 7.3 Hz, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.2 Hz, 4-(1-NPh,2-Bi-C_6H_4); overlapping with signal due to *m*-Ph), 7.50-7.54 (m, 2H, *m*-Ph; overlapping with signal due to 4-(1-NPh,2-Bi-C_6H_4)), 7.57-7.61 (m, 2H, 4-NC_5H_5), 8.73-8.74 (m, 4H, 2,6-NC_5H_5), 9.19 (br d, 1H, $^3J_{HH}$ = 7.3 Hz, 3-(1-NPh,2-Bi-C_6H_4)) ppm.

^{1}H NMR (500 MHz, THF-d_8): δ = 7.06 (d, 2H, $^3J_{HH}$ = 7.6 Hz, *o*-Ph), 7.14 (m, 1H, 6-(1-NPh,2-Bi-C_6H_4)), 7.21 (m, 1H, 5-(1-NPh,2-Bi-C_6H_4)), 7.33 (m, 1H, 4-(1-NPh,2-Bi-C_6H_4)), 7.41 (m, 5H, *p*-Ph, 3,5-NC_5H_5), 7.48 (m, 2H, *m*-Ph), 7.85 (m, 2H, 4-NC_5H_5), 8.67 (m, 4H, 2,6-NC_5H_5), 8.95 (m, 1H, 3-(1-NPh,2-Bi-C_6H_4)) ppm.

^{13}C NMR (126 MHz, NC_5D_5): δ = 116.01 (s, 6-(1-NPh,2-Bi-C_6H_4)), 122.90 (quart, $^1J_{CF}$ = 322.6 Hz, CF_3), 124.54 (s, 4-NC_5H_5), 127.51 (s, 4-(1-NPh,2-Bi-C_6H_4)), 129.56 (s, *o*-Ph), 129.58 (s, *p*-Ph), 131.12 (s, *m*-Ph), 133.20 (s, 5-(1-NPh,2-Bi-C_6H_4)), 136.51 (s, 3,5-NC_5H_5), 137.70 (br s, 3-(1-NPh,2-Bi-C_6H_4)), 142.22 (*ipso*-Ph), 150.76 (s, 2,6-NC_5H_5), 156.58 (s, 1-(1-NPh,2-Bi-C_6H_4)), 187.23 (s, 2-(1-NPh,2-Bi-C_6H_4)), 251.30 (s, CO) ppm.

^{13}C NMR (126 MHz, THF-d_8): δ = 114.98 (s, 6-(1-NPh,2-Bi-C_6H_4)), 121.44 (quart., $^1J_{CF}$ = 321.0 Hz, CF_3), 125.47 (s, 3,5-NC_5H_5), 126.68 (s, 4-(1-NPh,2-Bi-C_6H_4)), 128.90 (s, *p*-Ph), 129.59 (s, *o*-Ph), 130.54 (s, *m*-Ph), 132.42 (s, 5-(1-NPh,2-Bi-C_6H_4)), 137.90 (s, 3-(1-NPh,2-Bi-C_6H_4)), 138.39 (s, 4-NC_5H_5), 142.77 (s, *ipso*-Ph), 150.07 (s, 2,6-NC_5H_5), 157.08 (s, 1-(1-NPh,2-Bi-C_6H_4)), 192.02 (s, 2-(1-NPh,2-Bi-C_6H_4)), 259.41 (s, CO) ppm.

^{19}F NMR (376 MHz, NC_5D_5) δ = –76.2 (s) ppm.

Elemental analysis. When dried in vacuo at 23 °C, the compound contained residual amounts of lattice-bound pyridine according to elemental analysis: Anal. calc. for $C_{24}H_{19}BiF_3N_3O_4S \cdot (NC_5H_5)_{0.10}$ (719.38 g/mol): C, 40.91; H, 2.73; N, 6.04; S, 4.46; found: C, 41.23; H, 2.37; N, 6.12; S, 4.24. When dried in vacuo at 80 °C, the bismuth-bound pyridine ligands could partially be removed according to elemental analysis: Anal. calc. for $C_{14}H_9BiF_3NO_4S \cdot (NC_5H_5)_{0.30}$ (576.00 g/mol): C, 32.26; H, 1.83; N, 3.16; S, 5.56; found: C, 32.26; H, 1.47; N, 3.34; S, 5.37.

IR (neat): $\bar{\nu}$ = 3061 (w), 1637 (m), 1598 (m), 1564 (m), 1486 (m), 1445 (m), 1256 (s), 1221 (s), 1152 (s), 1121 (m), 1094 (m), 1064 (m), 1023 (s), 1005 (m) cm^{-1}.

[Bi(CNMeNPh(C_6H_4))(NC_5H_5)$_2$][OTf] (3). A 0.1 M solution of methyl-isonitrile in 1,2-difluorobenzene (860 µL, 86 µmol) was added to a stirred suspension of **1** (52 mg, 41 µmol) in THF (1 mL). Yellow starting material **1** was consumed and an off-white solid precipitated. After 1 h, the reaction mixture was filtered. The solid was dissolved in pyridine (1 mL) and layered with Et_2O (2 mL). A pale yellow crystalline material had precipitated after 14 h, which was isolated by filtration and dried in vacuo. Yield: 45 mg, 62 µmol, 76%.

^{1}H NMR (500 MHz, NC_5D_5): δ = 3.93 (s, 3H, Me), 7.18 (m, 1H, 6-(1-NPh,2-Bi-C_6H_4); overlapping with resonances due to 3,5-NC_5H_5), 7.21-7.24 (m, 4H, 3,5-NC_5H_5; overlapping with resonances due to 6-(1-NPh,2-Bi-C_6H_4) and *o*-Ph), 7.24-7.27 (m, 2H, *o*-Ph; overlapping with resonances due to 3,5-NC_5H_5 and 4-(1-NPh,2-Bi-C_6H_4)), 7.25-7.29 (m, 1H, 4-(1-NPh,2-Bi-C_6H_4); overlapping with resonances due to *o*-Ph), 7.32 (ddd, 1H, $^3J_{HH}$ = 7.3 Hz, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.7 Hz, 5-(1-NPh,2-Bi-C_6H_4)), 7.43 (ddd, 1H, $^3J_{HH}$ = 6.9 Hz, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 1.2 Hz, *p*-Ph), 7.51-7.55 (m, 2H, *m*-Ph), 7.56-7.61 (m, 2H, 4-NC_5H_5), 8.73-8.74 (m, 4H, 2,6-NC_5H_5), 8.94 (br d, 1H, $^3J_{HH}$ = 7.1 Hz, 3-(1-NPh,2-Bi-C_6H_4)) ppm.

^{13}C NMR (126 MHz, NC_5D_5): δ = 53.33 (s, Me), 115.33 (s, 6-(1-NPh,2-Bi-C_6H_4), 123.05 (quart, $^1J_{CF}$ = 322.6 Hz, CF_3), 123.42 (s, 4-(1-NPh,2-Bi-C_6H_4)), 124.51 (s, 4-NC_5H_5), 128.82 (s, *p*-Ph), 130.31 (s, *o*-Ph), 131.05 (s, *m*-Ph), 133.24 (s, 5-(1-NPh,2-Bi-C_6H_4)), 136.46 (s, 3,5-

NC_5H_5), 138.03 (s, 3-(1-NPh,2-Bi-C_6H_4)), 145.53 (s, *ipso*-Ph), 150.76 (s, 2,6-NC_5H_5), 161.00 (s, 1-(1-NPh,2-Bi-C_6H_4)), 173.21 (s, 2-(1-NPh,2-Bi-C_6H_4)), 219.53 (s, *C*NMe) ppm.

^{19}F NMR (376 MHz, NC_5D_5) δ = –76.2 (s) ppm.

Elemental analysis. When dried in vacuo at 23 °C, the compound contained residual amounts of lattice-bound pyridine according to elemental analysis: Anal. calc. for $C_{25}H_{22}BiF_3N_4O_3S \cdot (NC_5H_5)_{0.375}$ (754.17 g/mol): C, 42.80; H, 3.19; N, 8.13; S, 4.25; found: C, 43.13; H, 3.37; N, 7.74; S, 4.12.

IR (neat): $\bar{\nu}$ = 3050 (w), 2932 (w), 2909 (w), 2879 (w), 1623 (m), 1572 (m), 1568 (m), 1468 (m), 1433 (m), 1404 (m), 1274 (m), 1249 (m), 1219 (m), 1143 (m), 1105 (w), 1062 (m), 1025 (s), 1005 (s) cm^{-1}.

[Bi(CN*t*BuNPh(C_6H_4))(NC_5H_5)$_2$][OTf] (4). Neat *t*-butyl-isonitrile (10 mg, 120 µmol) was added to a stirred of **1** (50 mg, 39 µmol) in pyridine (1 mL). After 2 h, the solution was layered with diethylether (5 mL) and cooled to –30 °C. After 2 d, yellow crystals had formed, which were isolated by filtration and dried in vacuo. Yield: 38 mg, 50 µmol, 64%.

^{1}H NMR (500 MHz, NC_5D_5): δ = 1.17 (s, 9H, *t*Bu), 7.18 (ddd, 1H, $^3J_{HH}$ = 7.1 Hz, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.2 Hz, 4-(1-NPh,2-Bi-C_6H_4)), 7.21-7.24 (m, 4H, 3,5-NC_5H_5), 7.26 (ddd, 1H, $^3J_{HH}$ = 7.1 Hz, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 1.2 Hz, 5-(1-NPh,2-Bi-C_6H_4)), 7.31 (dd, 1H, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 1.2 Hz, 6-(1-NPh,2-Bi-C_6H_4)), 7.38-7.40 (m, 2H, *o*-Ph), 7.43 (tt, 1H, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.2 Hz, *p*-Ph), 7.57-7.59 (m, 2H, *m*-Ph; overlapping with signals due to pyridine), 7.58-7.61 (m, 2H, 4-NC_5H_5), 8.73-8.74 (m, 4H, 2,6-NC_5H_5), 8.91 (br d, 1H, $^3J_{HH}$ = 7.3 Hz, 3-(1-NPh,2-Bi-C_6H_4)) ppm. Resonances due to lattice bound Et_2O were also detected.

^{13}C NMR (126 MHz, NC_5D_5): δ = 32.13, (s, C*Me*$_3$), 56.89 (s, *C*Me$_3$), 115.37 (s, 6-(1-NPh,2-Bi-C_6H_4)), 123.62, (s, 4-(1-NPh,2-Bi-C_6H_4)), 122.90 (quart, $^1J_{CF}$ = 320.1 Hz, CF_3), 124.54 (s, 4-NC_5H_5), 128.47 (s, *p*-Ph), 130.61 (s, *o*-Ph), 130.94 (s, *m*-Ph), 133.26 (s, 5-(1-NPh,2-Bi-C_6H_4)), 136.51 (s, 3,5-NC_5H_5), 137.82 (br s, 3-(1-NPh,2-Bi-C_6H_4)), 146.08 (*ipso*-Ph), 150.78 (s, 2,6-NC_5H_5), 158.06 (s, 1-(1-NPh,2-Bi-C_6H_4)), 179.05 (br s, 2-(1-NPh,2-Bi-C_6H_4)), 210.08 (s, *C*N*t*Bu) ppm. Resonances due to lattice bound Et_2O were also detected.

^{19}F NMR (376 MHz, NC_5D_5) δ = –77.3 (s) ppm.

Elemental analysis. The exact amount of pyridine ligands n and lattice-bound Et_2O m has to be determined for every batch individually. Typical values were n = 1-2 and m = 0.2-0.8 after drying the sample at ambient temperature *in vacuo* for several hours. $C_{18}H_{18}BiF_3N_2O_3S \cdot (C_5H_5N)_{1.7} \cdot (C_4H_{10}O)_{0.6}$ (787.33 g/mol): C, 44.09; H, 4.16; N, 6.58; S, 4.07; found: C, 44.03; H, 3.80; N, 6.56; S, 3.79.

IR (neat) $\bar{\nu}$ = 3075 (w), 3036 (w), 2970 (m), 2930 (w), 1618 (w), 1600 (s), 1589 (m), 1573 (s), 1554 (m), 1490 (m), 1450 (m), 1439 (s), 1388 (w), 1360 (m), 1311 (m), 1281 (s), 1253 (s), 1218 (s), 1194 (s), 1157 (s), 1122 (m), 1095 (m), 1064 (m), 1024 (s), 1005 (s) cm^{-1}.

[Bi(CN*t*BuNPh(C_6H_4))(thf)][OTf] (4-thf). Neat *t*-butyl-isonitrile (10 mg, 120 µmol) was added to a stirred suspension of **1** (50 mg, 39 µmol) in THF (1 mL). Yellow starting material **1** was consumed to give a yellow solution. After 2 h, the solution was layered with pentane (5 mL) and cooled to –30 °C. After 1 d, an orange oil had precipitated, which solidified upon standing at low temperature. The supernatant was decanted. The orange solid turned into an oil at ambient temperature and was dried in vacuo. Yield: 42 mg, 62 µmol, 79%.

^{1}H NMR (400 MHz, THF-d_8) δ = 1.27 (s, 9H, *t*Bu), 1.76-1.79 (m, 4H, β-THF), 3.60-3.63 (m, 4H, α-THF), 7.11 (ddd, 1H, $^3J_{HH}$ = 7.1 Hz, $^3J_{HH}$ = 7.1 Hz, $^4J_{HH}$ = 1.4 Hz, 4-(1-NPh,2-Bi-C_6H_4)), 7.18 (ddd, 1H, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 8.2Hz, $^4J_{HH}$ = 1.6 Hz, 5-(1-NPh,2-Bi-C_6H_4)), 7.19-7.23

(m, 3H, *o*-Ph, 6-(1-NPh,2-Bi-C_6H_4) (overlapping)), 7.35 (t, 1H, $^3J_{HH}$ = 7.5 Hz, *p*-Ph), 7.49 (m, 2H, *m*-Ph), 8.76 (dd, 1H, $^3J_{HH}$ = 7.2 Hz, $^3J_{HH}$ = 1.5 Hz, 3-(1-NPh,2-Bi-C_6H_4)) ppm.

^{13}C NMR (101 MHz, THF-d_8) δ = 26.55 (s, β-THF), 32.41 (s, C*Me*$_3$), 58.01 (s, *C*Me$_3$), 68.39 (s, α-THF), 114.67 (s, 6-(1-NPh,2-Bi-C_6H_4)), 120.84 (quart $^1J_{CF}$ = 320.4 Hz, CF_3), 123.28 (s, 4-(1-NPh,2-Bi-C_6H_4)), 128.09 (s, *p*-Ph), 130.61 (s, *m*-Ph), 131.17 (s, *o*-Ph), 133.39 (s, 5-(1-NPh,2-Bi-C_6H_4)), 138.12 (s, 3-(1-NPh,2-Bi-C_6H_4)), 147.36 (s, *ipso*-Ph), 159.96 (s, 1-(1-NPh,2-Bi-C_6H_4)), 191.87 (s, 2-(1-NPh,2-Bi-C_6H_4)), 221.19 (s, *C*NtBu) ppm.

^{19}F NMR (376 MHz, THF-d_8) δ = –78.9 (s) ppm.

Elemental analysis. When dried in vacuo at 23 °C for prolonged periods of time, the bismuth-bound THF ligands could partially be removed according to elemental analysis: Anal. calc. for $C_{18}H_{18}BiF_3N_2O_3S \cdot (C_4H_8O)_{0.66}$ (655.98 g/mol): C, 37.81; H, 3.58; N, 4.27; S, 4.88; found: C, 37.92; H, 3.45; N, 4.38; S, 4.84.

ESI-MS (THF), positive mode: m/z (%) found: 609.086 (2); 628.215 (100); 711.288 (42); 1085.215 (4); 1235.175 (1); calculated: m/z = 609.087 ($C_{18}H_{19}BiF_3N_2O_3^+$); 628.216 ($C_{29}H_{29}BiN_3^+$); 711.290 ($C_{34}H_{38}BiN_4^+$); 1085.217 ($C_{35}H_{38}Bi_2F_3N_4O_4S^+$); 1235.177 ($C_{36}H_{39}Bi_2F_6N_4O_7S_2^+$). ESI-MS (THF), negative mode: m/z (%) found: 148.951 (100); calculated for $CF_3SO_3^-$: m/z = 148.952.

[Bi(CN(2,6-Me$_2$-C$_6$H$_3$)NPh(C$_6$H$_4$))(NC$_5$H$_5$)$_2$)][OTf] (5). Neat CN(2,6-Me$_2$-C_6H_3) (12 mg, 91 µmol) was added to a suspension of **1** (60 mg, 47 µmol) in THF (3 mL) to give an orange solution. After 15 min, all volatiles were removed under reduced pressure to give an orange solid. Addition of pyridine (0.4 mL) gave an orange solution, which was layered with Et_2O (4 mL) and cooled to 0 °C. After 1 d, a light yellow solid had precipitated, which was isolated by filtration, washed with pentane (3 × 2 mL) and dried in vacuo. Yield: 45 mg, 55 µmol, 60%.

^{1}H NMR (500 MHz, THF-d_8): δ = 1.65 (s, 6H, 2,6-*Me*$_2$-C_6H_3), 6.80 (t, 1H, $^3J_{HH}$ = 7.5 Hz, 4-(2,6-Me$_2$-C_6H_3)), 6.91 (d, 2H, $^3J_{HH}$ = 7.5 Hz, 3,5-(2,6-Me$_2$-C_6H_3)), 7.19 (t, 1H, $^3J_{HH}$ = 7.2 Hz, 4-(1-NPh,2-Bi-C_6H_4)), 7.23 (d, 1H, $^3J_{HH}$ = 7.2 Hz, 6-(1-NPh,2-Bi-C_6H_4)), 7.31 (t, 1H, $^3J_{HH}$ = 7.2 Hz, 5-(1-NPh,2-Bi-C_6H_4)), 7.39 (dd, 4H, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 7.4 Hz, 3,5-NC_5H_5), 7.42 (d, 2H, $^3J_{HH}$ = 6.4 Hz, *o*-Ph), 7.43 (t, 1H, $^3J_{HH}$ = 6.4 Hz, *p*-Ph), 7.57 (m, 2H, *m*-Ph), 7.85 (t, 2H, $^3J_{HH}$ = 7.7 Hz, 4-NC_5H_5), 8.48 (m, 4H, 2,6-NC_5H_5), 8.65 (d, 1H, $^3J_{HH}$ = 7.2 Hz, 3-(1-NPh,2-Bi-C_6H_4)) ppm.

^{13}C NMR (125 MHz, THF-d_8): δ = 18.1 (s, 2,6-*Me*$_2$-C_6H_3), 115.7 (s, *m*-Ph), 121.2 (q, $^2J_{CF}$ = 321.1 Hz, *C*F$_3$), 124.3 (s, *p*-Ph), 124.5 (s, 4-(1-NPh,2-Bi-C_6H_4)), 126.0 (s, 3,5-NC_5H_5), 128.5 (s, 6-(1-NPh,2-Bi-C_6H_4)), 128.8 (s, *p*-Ph), 129.8 (s, 2,6-(2,6-Me$_2$-C_6H_3)), 130.3 (s, *o*-Ph), 131.0 (s, *m*-Ph), 132.6 (s, 5-(1-NPh,2-Bi-C_6H_4)), 138.6 (s, 3-(1-NPh,2-Bi-C_6H_4)), 138.7 (s, 4-NC_5H_5), 145.3 (s, *ipso*-Ph), 150.7 (s, 2,6-NC_5H_5), 155.2 (s, 1-(2,6-Me$_2$-C_6H_3)), 161.5 (s, 1-(1-NPh,2-Bi-C_6H_4)), 180.8 (s, 2-(1-NPh,2-Bi-C_6H_4)), 222.7 (s, *C*N(2,6-Me$_2$-C_6H_3) ppm.

^{19}F NMR (500 MHz, THF-d_8): δ = –79.2 (s) ppm.

Elemental analysis. When dried in vacuo at 23 °C, the compound contained residual amounts of lattice-bound Et_2O according to elemental analysis: Anal. calc. for $C_{32}H_{28}BiF_3N_4O_3S \cdot (C_2H_{10}O)_{0.15}$ (825.75 g/mol): C, 47.42; H, 3.60; N, 6.78; S, 3.88; found: C, 47.57; H, 3.42; N, 6.95; S, 3.55.

IR (neat): $\tilde{\nu}$ = 3058 (w), 2920 (w), 2850 (w), 1606 (m), 1598 (m), 1584 (m), 1570 (m), 1559 (m), 1488 (m), 1437 (s), 1281 (s), 1242 (s), 1219 (s), 1191 (s), 1154 (s), 1128 (s), 1109 (m), 1089 (m), 1064 (m), 1024 (s), 1005 (s) cm^{-1}.

Single-Crystal X-ray Analyses

Compounds **4** and **5** were investigated by single crystal X-ray analysis as mentioned in the main text. The bonding parameters are highly similar to those observed for compound **3**. Larger graphic representations and details are given in Figures S1 and S2.

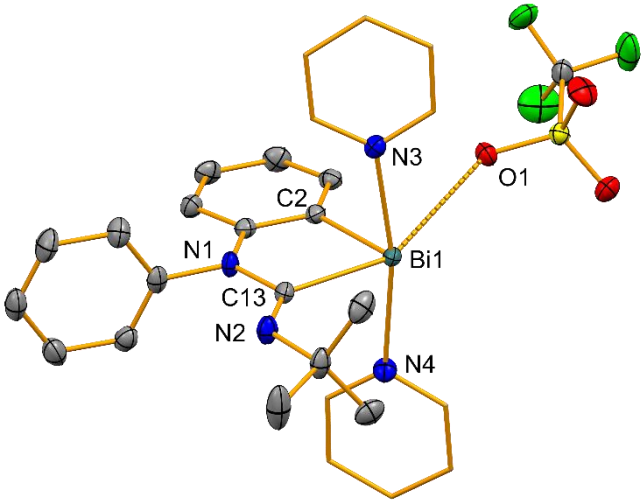


Figure S1. Molecular structure of [Bi(CN*t*BuNPh(C_6H_4))(NC_5H_5)$_2$][OTf] (**4**) in the solid state. Displacement ellipsoids are shown at the 50% probability level; carbon atoms of pyridine ligands are shown as wireframe. Hydrogen atoms and lattice-bound solvent molecules (0.5 equiv. of OEt_2 and 0.5 equiv of pyridine) are omitted for clarity. Selected bond lengths (Å) and angles (°): Bi1–C2, 2.225(3); Bi1–C13, 2.331(3); Bi1–N3, 2.485(3); Bi1–N4, 2.525(3); Bi1···O1, 2.997(2); C13–N1, 1.415(4); C13–N2, 1.261(4); C2–Bi1–C13, 77.35(12); C2–Bi1–N3, 87.63(11); C2–Bi1···O1, 80.94(10); N3–Bi1–N4, 169.39(9); C13–Bi1···O1, 153.18(9); τ_5 = 0.27.

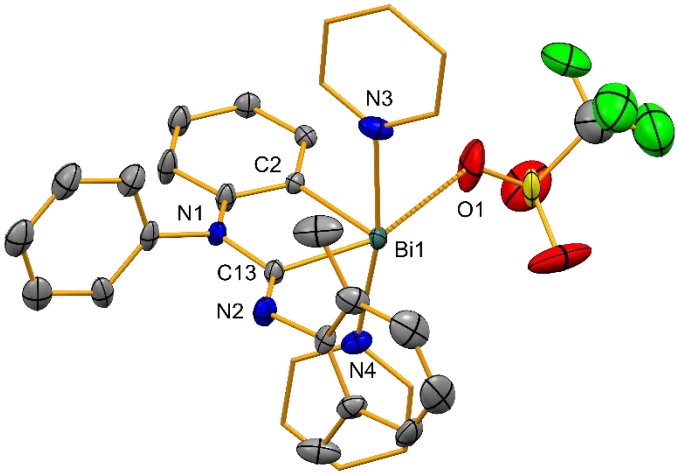
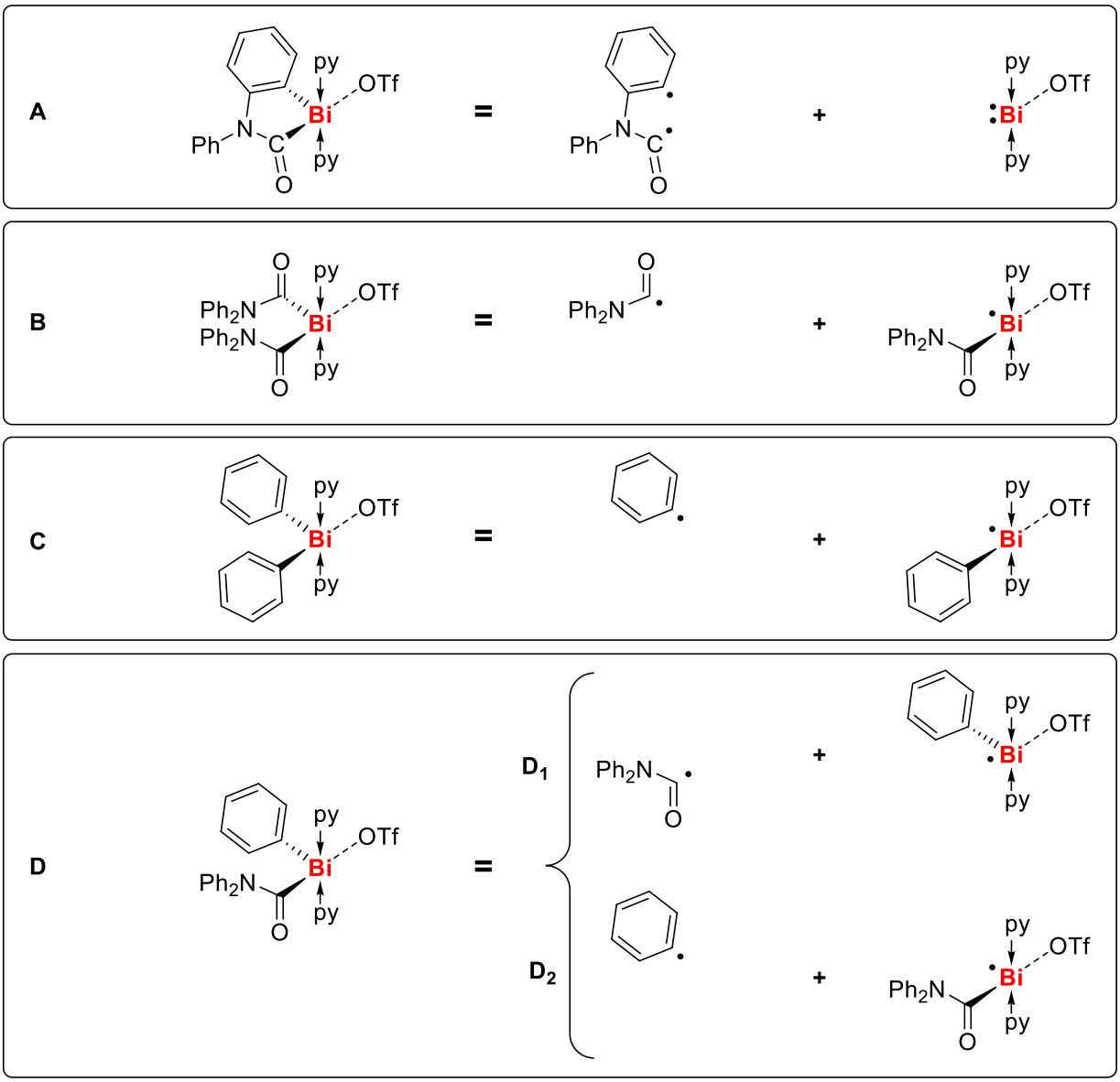


Figure S2. Molecular structure of [Bi(CN(2,6-Me_2-C_6H_3)NPh(C_6H_4))(NC_5H_5)$_2$][OTf] (**5**) in the solid state. Displacement ellipsoids are shown at the 50% probability level; carbon atoms of pyridine ligands are shown as wireframe for clarity. Hydrogen atoms, a lattice-bound molecule of pyridine, and split positions of disordered NPh and OTf groups are omitted for clarity. Selected bond lengths (Å) and angles (°): Bi1–C2, 2.202(4); Bi1–C13, 2.299(4); Bi1–N3, 2.510(4); Bi1–N4, 2.488(4); Bi1···O1, 2.907(15); C13–N1, 1.43(2); C13–N2, 1.269(6); C2–Bi1–C13, 76.89(15); C2–Bi1–N3, 84.96(14); C2–Bi1···O1, 82.0(3); N3–Bi1–N4, 169.41(13); C13–Bi1···O1, 158.8(3); τ_5 = 0.18.

Energy Decomposition Analysis

Nature of the Bi–(CONR) bond in compound 2.

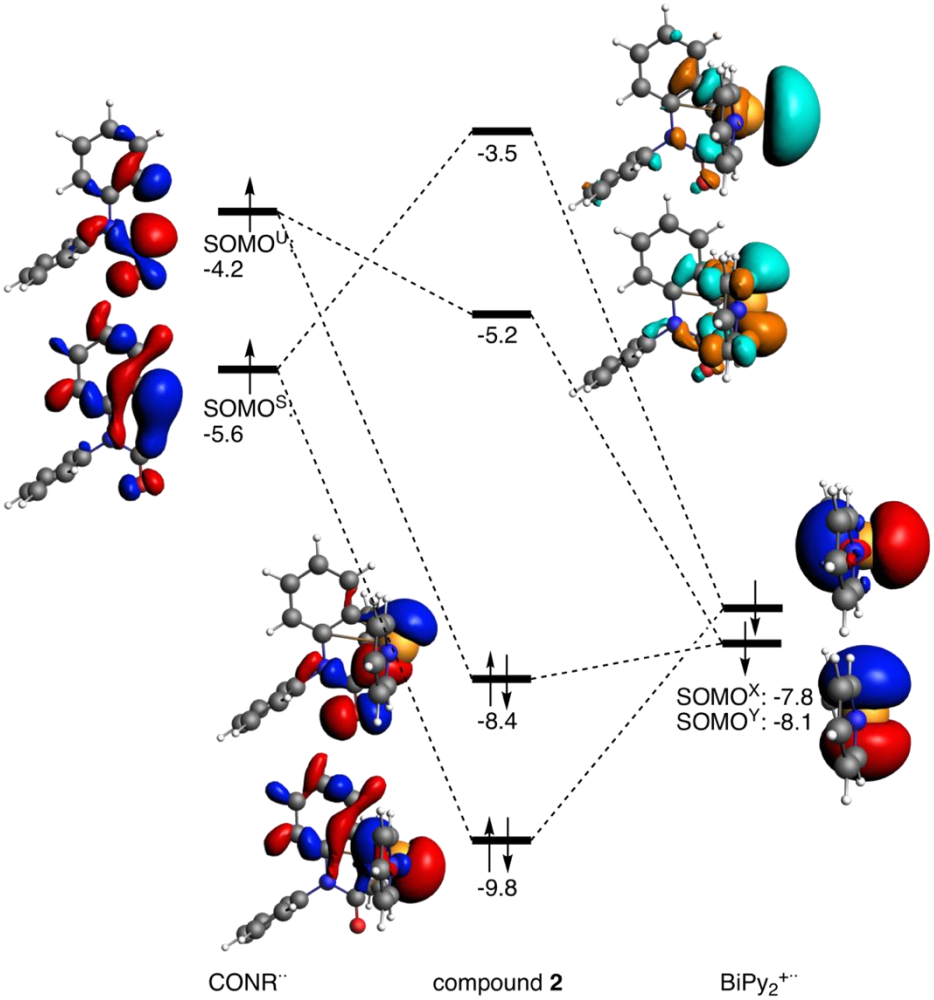
The nature of Bi−(CONRR') bond in compound **2** was investigated by means of a quantitative Kohn-Sham MO analysis with an energy decomposition analysis (EDA) at the same the ZORA-BLYP-D3BJ/TZ2P level of theory in vacuo at the relaxed geometry in THF.
For the EDA, the two Bi−C bonds of **2** were cleaved homolytically to give two fragments in their triplet states (Scheme S1, **A**). This interaction, which involves the formation of two Bi−C bonds as primary bonding interactions, presents a total bonding energy of −119.0 kcal·mol^{-1} (**A** in Table S1), from which only +9.6 kcal·mol^{-1} correspond to the strain energy (ΔE_{strain}, deformation of the two fragments from their equilibrium geometries to those in the complex). The rest is the interaction energy (ΔE_{int} = −128.6 kcal·mol^{-1}). ΔE_{int} can be further decomposed into ΔE_{Pauli} = +270.3 kcal·mol^{-1}, ΔV_{elstat} = −181.7 kcal·mol^{-1}, ΔE_{oi} = −195.3 kcal·mol^{-1}, and ΔE_{disp} = −21.8 kcal·mol^{-1}. The repulsive Pauli term is largely compensated by attractive electrostatic and orbital interaction terms. According to this analysis, the interactions of disconnection approach **A** show a highly similar electrostatic and covalent character (46% electrostatic vs. 49% covalent).



Scheme S1. Fragments for the EDA of the Bi−(CONRR') interaction.

Furthermore, pyridine ligands do not affect this interaction, which was shown by carrying out the same EDA analysis in the absence of the two pyridine ligands.

With respect to the orbital interactions, each fragment presents two unpaired electrons (Scheme S2). In the case of the $(Bi(Py)_2)^{+\bullet\bullet}$ fragment, the two SOMOs correspond to the p_x and p_y orbitals of the Bi atom, which interact with the two SOMOs of the $(CONRR')^{\bullet\bullet}$ fragment (symmetric S and unsymmetric U). Charge transfer is observed from $(Bi(Py)_2)^{+\bullet\bullet}$ to $(CONRR')^{\bullet\bullet}$. The Mulliken populations amount to 0.88 and 0.79 electrons for $SOMO^X$ and $SOMO^Y$, respectively, whereas $SOMO^U$ and $SOMO^S$ amount to 1.17 and 1.23, respectively. Furthermore, the FMO overlap integrals amount to $\langle SOMO^X|SOMO^S\rangle$ = 0.293 and $\langle SOMO^Y|SOMO^U\rangle$ = 0.287, which are relevant values that support the orbital interactions under analysis.



Scheme S2. MO diagram for the formation of compound **2** from two triplet-state fragments.

In the above EDA analysis, two Bi−C bonds are broken at the same time (Scheme S1, **A**), so the interactions discussed till now cannot differentiate between these two bonds. With this in mind, further analyses were performed with the aim to individually evaluate Bi−aryl and Bi−CONRR' interactions.

First of all, it is necessary to convert the five-membered ring into two individual substituents. This is not a problem based on the fact that the ΔE_{strain} is quite small (9.6 kcal·mol^{-1} as compared to interaction energy of −128.6 kcal·mol^{-1}). Scheme S1 and Table S1 enclose the new bonding analyses performed: **A** corresponds to compound **2** analyzed above; **B**, **C** and **D** correspond to the breaking of only one bond (two doublet fragments), either Bi−Ph or Bi−$CONPh_2$; whereas

the corresponding approaches **B'**, **C'** and **D'** involve the cleavage of two bonds (two triplet fragments, not depicted in Scheme S1).

First, **A** and **D'** show similar EDA values with the main differences in dispersion and strain energies, which proves the viability of substituting the ring by Ph and $CONPh_2$ moieties. Next, approaches **B** and **D_1** correspond to the cleavage of a Bi−$CONPh_2$ bond into two doublet fragments, whereas **C** and **D_2** correspond to the cleavage of a Bi−Ph bond into two doublet fragments. In fact, **B** should be compared to **C**, whereas **D_1** should be compared to **D_2**. In both cases the Bi−C bond appears to be stronger in Bi−Ph than in Bi−$CONPh_2$ by 10.1 and 17.9 kcal·mol^{-1} ($\Delta\Delta E_{int}$), respectively. This difference comes from more favorable electrostatic and orbital interactions in the case of Bi−Ph. In addition, both bonds present very similar electrostatic and covalent character. In the case of the ΔE_{oi} term, its stronger interaction in Bi−Ph is also supported by the larger overlap between the SOMO orbital of each fragment (0.290 vs. 0.331 for **B** and **C**, respectively, and 0.280 vs. 0.333 for **D_1** and **D_2**, respectively).

Table S1. Energy decomposition analysis (EDA) of the approaches enclosed in Scheme S1. Energy values are given in kcal·mol^{-1}.

	ΔE_{Pauli}	**ΔV_{elstat}**	**ΔE_{oi}**	**ΔE_{disp}**	**ΔE_{int}**	**ΔE_{strain}**	**ΔE**	Bonds broken
A	270.3	−181.7	−195.3	−21.8	−128.6	9.6	−119.0	Bi−CONRR' & Bi−Ph
One bond broken:								
B	154.4	−96.4	−96.2	−25.4	−63.6	10.6	−53.0	Bi−CONRR'
C	156.7	−109.2	−107.2	−14.0	−73.7	5.2	−68.6	Bi−Ph
D_1	142.1	−86.5	−90.1	−22.4	−56.9	10.2	−46.7	Bi−CONRR'
D_2	153.9	−104.5	−104.6	−19.5	−74.8	19.8	−54.9	Bi−Ph
Two bonds broken:								
B'	273.8	−170.5	−178.9	−40.7	−116.2	8.5	−107.8	2 × Bi−CONRR'
C'	278.6	−191.3	−204.9	−24.5	−142.0	7.9	−134.2	2 × Bi−Ph
D'	269.2	−176.5	−188.7	−28.7	−124.7	10.6	−114.0	Bi−CONRR' & Bi−Ph

IR Spectroscopy

The CO insertion reaction was monitored using IR spectroscopy. The reaction was set up in analogy with the procedure described in the experimental part. However, the liquid phase of the reaction mixture was peristaltically pumped through a flow-through cell (using tubing equipped with a filter at the inlet) and the spectra were recorded at different time intervals. After having passed the IR cell, the solution was fed back into the reaction vessel. During the IR spectroscopic reaction monitoring, five signals at 1573, 1592, 1602, 1655 and 1669 cm^{-1} were detected during the period of the measurement. The spectra were normalized to a major solvent signal, baseline corrected and eventually the solvent background was subtracted (see Figure S3). Subsequently, the experimental IR data were compared to the IR resonances obtained by DFT calculations at the ZORA-BLYP-D3BJ/TZ2P level of theory (see Figure S4). Please note, that the displayed calculations are harmonic and unscaled, therefore adequate deviations in absolute IR frequencies between experiment and theory are expected.

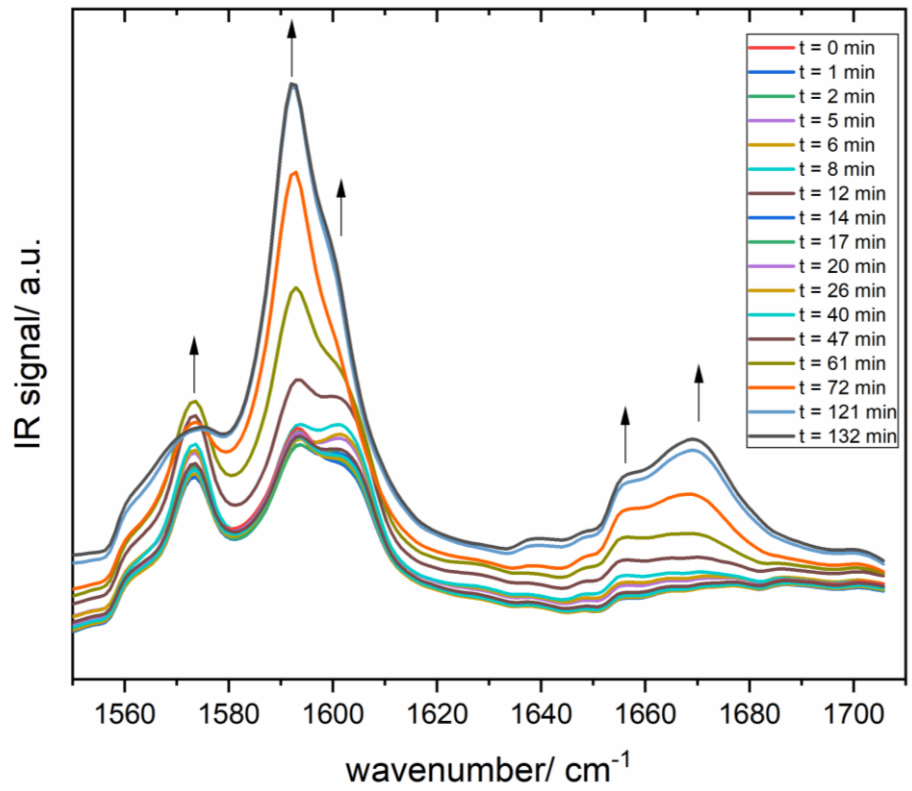


Figure S3. IR spectra of the CO insertion reaction at different time intervals over 132 min. The spectra were normalized, baseline-corrected and background-subtracted.

We assign the major peak at 1592 cm^{-1} to the product formation of **I-5**. The signal increases rapidly after the 47 min mark until it stays constant after approximately 2 h, presumably due to **I-5** reaching the solubility limit. This is in good agreement with the calculations showing only one major vibrational mode at 1595 cm^{-1} for **I-5**. The signal at a slightly larger wavenumber of 1602 cm^{-1} shows a small increase at earlier time until it starts rising more rapidly forming a right shoulder to the major peak of the spectrum. This resonance is suggested to originate from

I-2 and/or **I-3**, which can be expected to be formed at early stages of the reaction (before their concentration rises until an equilibrium state is reached). The calculations overestimate the modes only slightly by 14 cm^{-1} (**I-2**) and 19 cm^{-1} (**I-3**). The lowest wavenumber signal at 1573 cm^{-1} corresponds well with bands expected for **1**. The signal also increases over time, which is due to all other intermediates (**I-1**, **I-2**, **I-3**, **I-4**, and **I-5**) also showing small IR activity in this region. The signal broadening in the region of 1550-1580 cm^{-1} at later stages of the reaction is

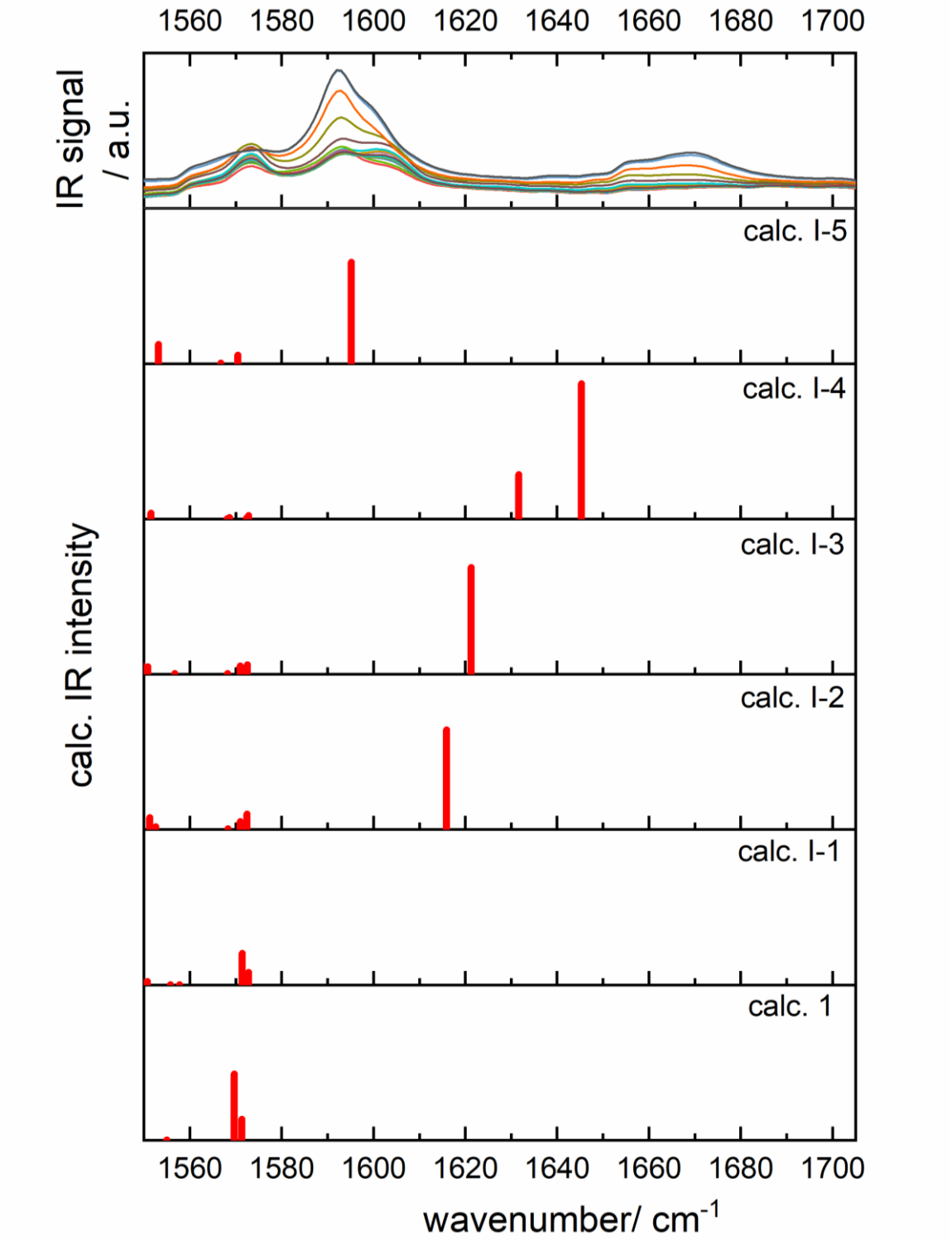


Figure S4. Comparison of the experimental spectra with vibrational calculations of **1**, **I-1**, **I-2**, **I-3**, **I-4** and **I-5**. From the bottom to the top, the wavenumbers of calculated resonances are displayed in the order of appearance as proposed in Scheme 3 (main part).

explained by accumulation of the aforementioned intermediates (**I-1** to **I-5**) in the reaction mixture. Lastly, we tentatively assign the two signals at 1655 cm^{-1} and 1669 cm^{-1} to **I-4**. The motif and relative distance of those signals (14 cm^{-1} spacing for experimental and calculated peaks and similar relative intensity of the signals in calculated and experimental spectra) is in reasonable agreement with DFT calculations, albeit the calculation underestimates the wavenumbers by up to 24 cm^{-1} (i. e. by up to 1.5%). CO stretching frequencies of intermediates **I-1** and **I-3** could not be detected unambiguously due to low relative signal intensities (confirmed by DFT calculations), resonance frequencies close to those of free CO (confirmed by DFT calculations), absorption features of the solvent THF in this region, and possibly also by a relatively low concentration and/or short-lived character of these intermediates.

UV/vis Spectroscopy

UV/vis spectra of **I-5** and **2** in THF are shown in Figures S5 and S6.

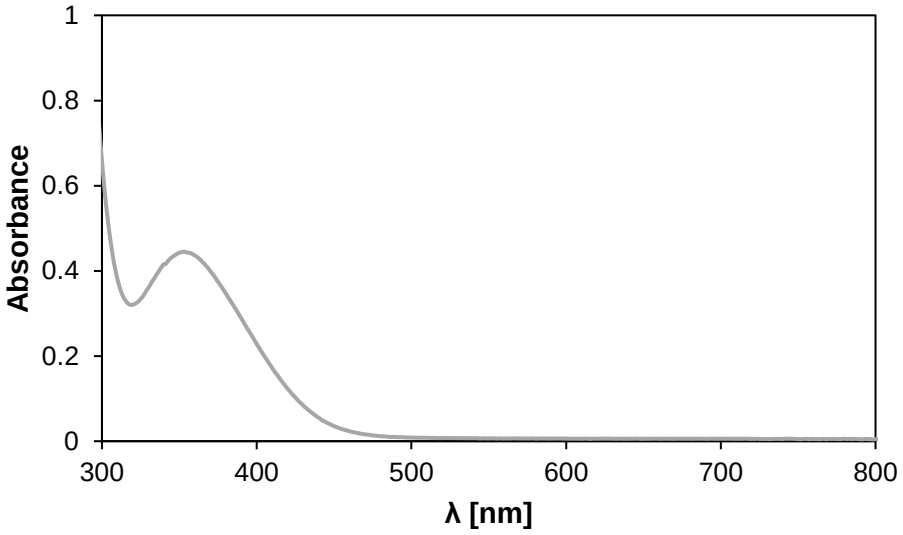


Figure S5. UV/vis spectrum of **2** (0.4(1) mM solution in THF).

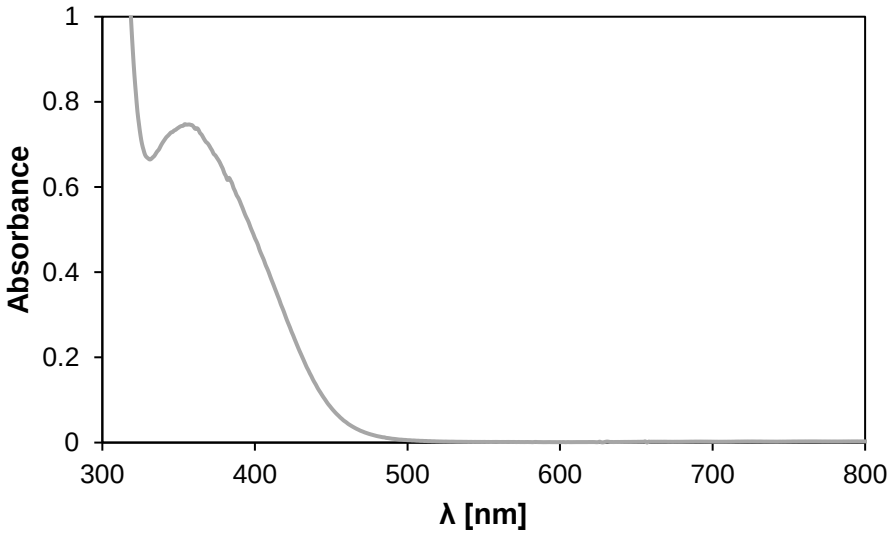
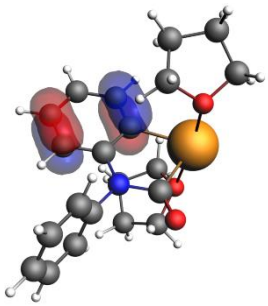
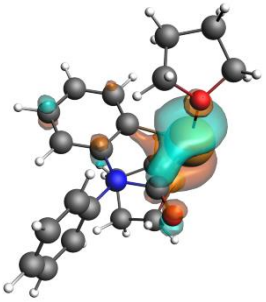
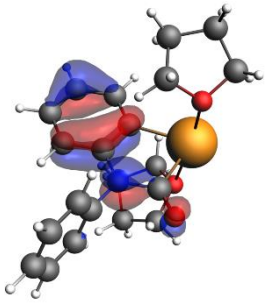
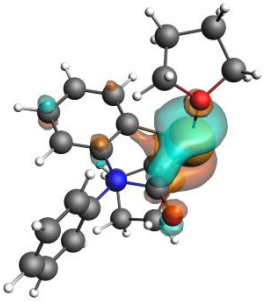
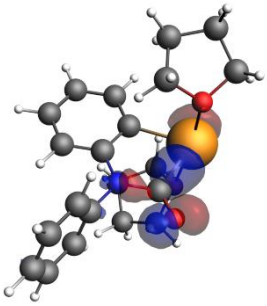
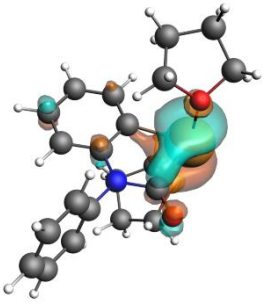


Figure S6. UV/vis spectrum of **I-5** (0.4(1) mM solution in THF).

As the UV/vis spectrum was experimentally obtained in THF, it was also computed at the same CAMY-B3LYP level of theory for $[Bi(CONPh(C_6H_4))(thf)_2]^+$, which corresponds to the cationic part of **2**, but with two THF ligands instead of two pyridines (it also corresponds to [**I-5**]$^+$). A perturbation approach was used to account for spin-orbit coupling. The results are summarized in Table S2.

Table S2. Transitions in the UV/vis spectrum calculated for $[Bi(CONPh(C_6H_4)(thf)_2]^+$ computed at the CAMY-B3LYP level of theory using a perturbation approach to account for spin-orbit coupling. All calculated transitions are singlet-singlet transitions.

E [eV]	λ [nm]	Oscillator Strength	Occupied Orbital	Virtual Orbital
4.78	260	0.036	 **HOMO-4**	 **LUMO**
3.77	329	0.018	 **HOMO**	 **LUMO**
3.50	354	0.0013	 **HOMO-1**	 **LUMO**

The transition at 354 nm matches the experimental findings. It corresponds to the singlet-singlet excitation from HOMO−1 to LUMO. The former involves a bismuth- and an oxygen-centered p-orbital in the plane of the carbamoyl group, whereas the latter involves a bismuth-centered p-orbital and π*-orbital of CO, which are orthogonal to the carbamoyl plane.
It is hypothesized that in an excess of THF, the pyridine ligands of $[Bi(CONPh(C_6H_4))(py)_2]^+$ can be exchanged for THF ligands to give $[Bi(CONPh(C_6H_4))(thf)_2]^+$. This hypothesis is possible because ΔΔG for THF versus Py coordination is only 3.5 kcal mol^{-1}. The calculation is based on the last step of the proposed mechanism: From **I-5** to compound **2**, ΔG = −7.1 kcal mol^{-1}, which corresponds to 3.5 kcal mol^{-1} per ligand. The results are in congruency with experimental findings.

Cyclic Voltammetry and DFT Calculations on $[Bi(NPh(C_6H_4(CO))]^{\bullet}$ (2red)

Cyclic voltammograms of **2** were recorded in THF/0.1 M $[N(nBu)_4][PF_6]$ at 23 °C at scan rates in the range of 0.1-2.0 $V \cdot s^{-1}$ (range of 0.1-0.5 $V \cdot s^{-1}$ depicted in Figure S7). A chemically reversible redox event was detected at a potential of –1.66 V vs Fc/Fc^+ ($Fc = Fe(C_5H_5)_2$).

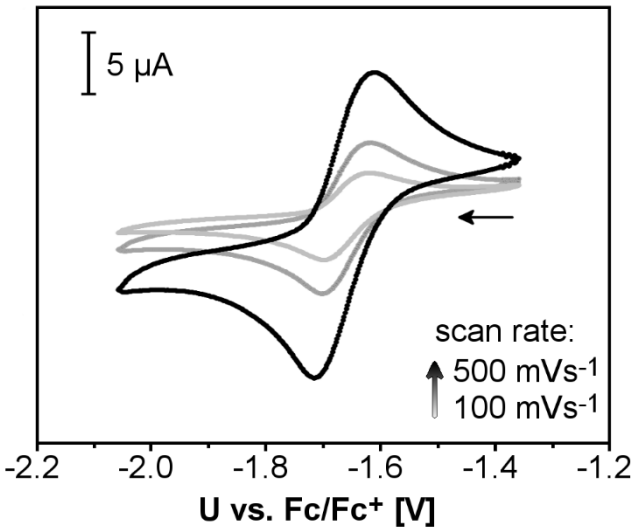
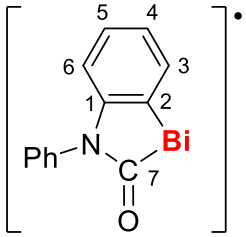


Figure S7. Cyclic voltammogram of $[Bi(CONPh(C_6H_4))(NC_5H_5)_2][OTf]$ (**2**) in THF/0.1 M $[N(nBu)_4][PF_6]$ at 23 °C and scan rates in the range of 0.1-0.5 $V \cdot s^{-1}$ ($Fc = Fe(C_5H_5)_2$).

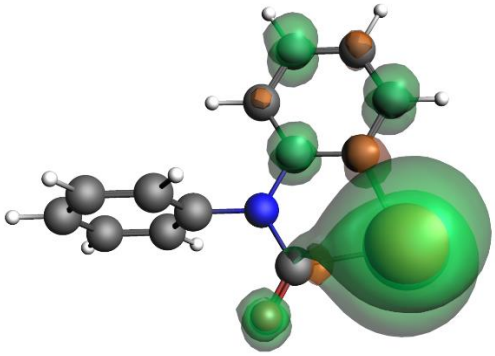
It may be expected that compound $[Bi(CONPh(C_6H_4))(NC_5H_5)_2]^{\bullet}$ (**2red-py**) is formed upon reduction of **2**. The thermochemistry of ligand dissociation from **2red-py** to give **2red** was investigated by DFT calculations, according to which this reaction is endothermic (ΔH = +13.1 $kcal \cdot mol^{-1}$) and exergonic (ΔG = –6.9 $kcal \cdot mol^{-1}$). Thus, **2red** can be considered to be the relevant species present in solution after reduction of **2**.

The Mulliken spin densities that were calculated for **2red** are summarized in Table S3 along with percentage spin densities at individual positions based on absolute values of spin density at all atoms.

Table S3. Mulliken spin densities of **2red** as determined by DFT calculations (spin densities with absolute values greater than 0.003 and that for C7 are listed).



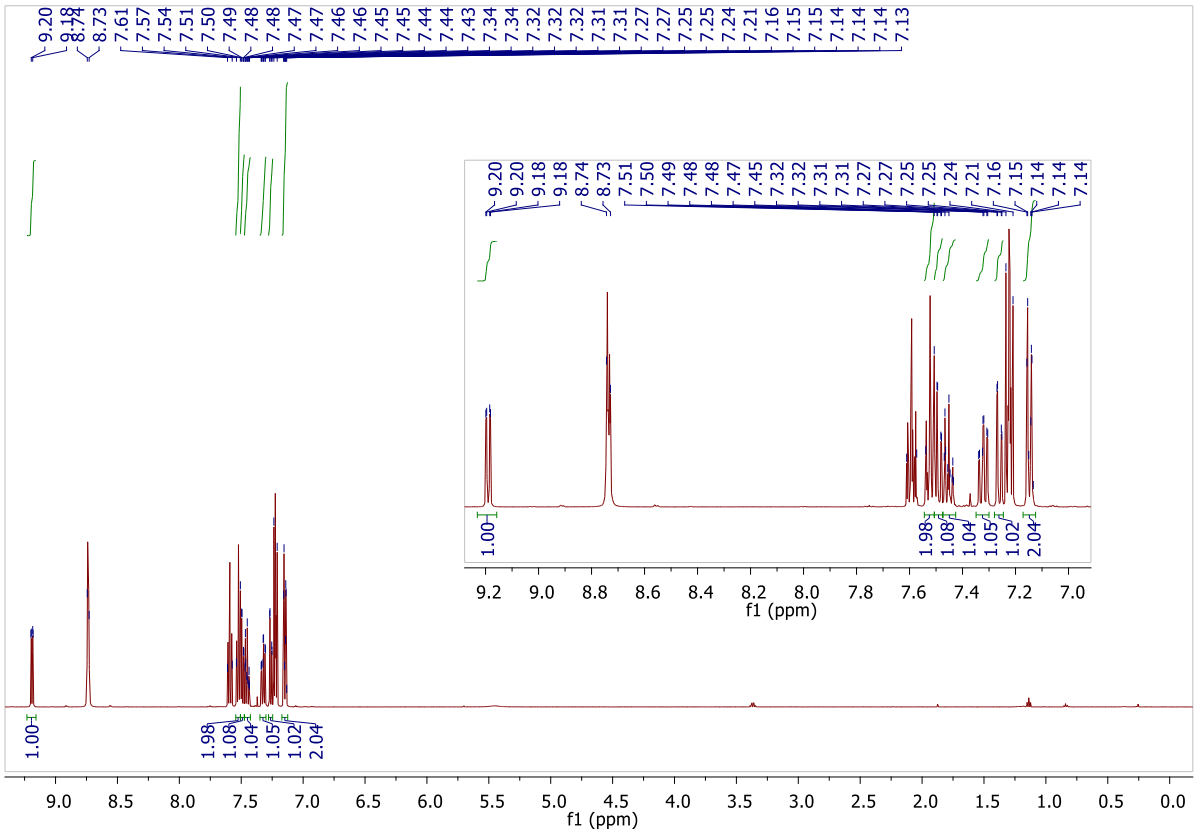
2-red



Atom	Spin density (α- and β-spin differentiated)	Spin density [%] (α- and β-spin not differentiated)
Bi	0.92	74
N	−0.01	1
O	0.05	4
C1	0.04	3
C2	−0.07	5
C3	0.05	4
C4	−0.02	2
C5	0.06	5
C6	−0.02	2
C7	0.00	0

Attempts to detect **2red** (generated *in situ*, for instance from the reaction of **2** with elemental sodium) by EPR spectroscopy were unsuccessful so far. Possible reasons include (i) the reaction conditions being potentially unsuitable for an efficient generation of **2red** in sufficient quantities, (ii) a short lifetime of **2red**, and (iii) very fast relaxation as a result of large spin-orbit coupling, as discussed in previous work.[7]

NMR Spectra



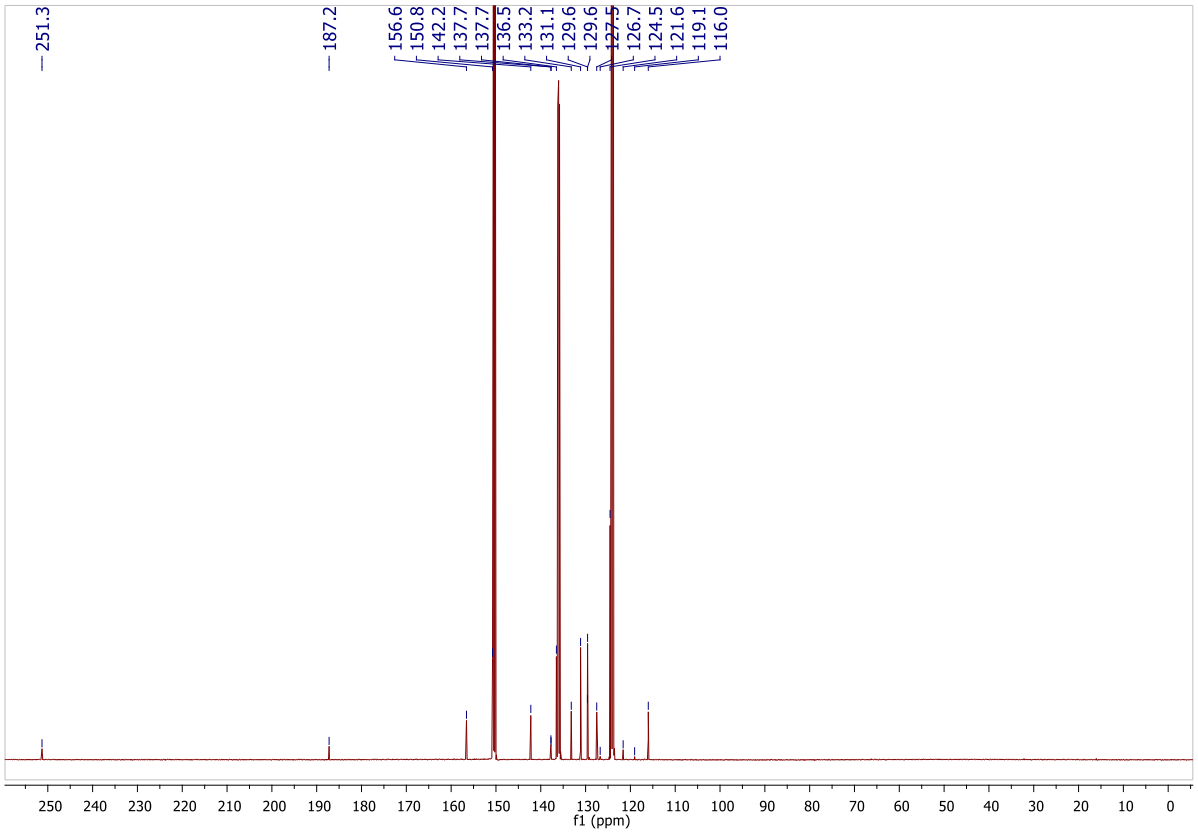


Figure S8. ^{1}H and ^{13}C NMR spectra of [Bi(CONPh(C_6H_4))(NC_5H_5)$_2$][OTf] (**2**) in NC_5D_5.

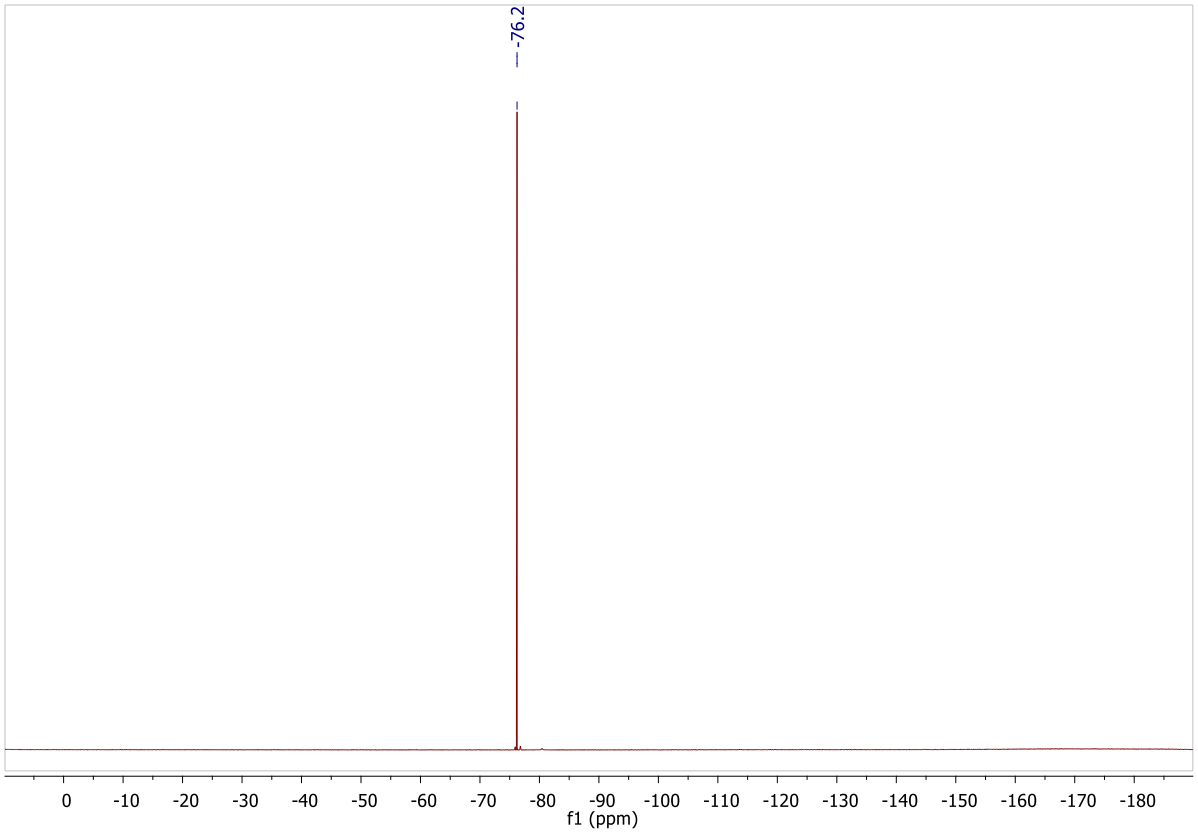


Figure S9. ^{19}F spectrum of $[Bi(CONPh(C_6H_4))(NC_5H_5)_2][OTf]$ (**2**) in NC_5D_5.

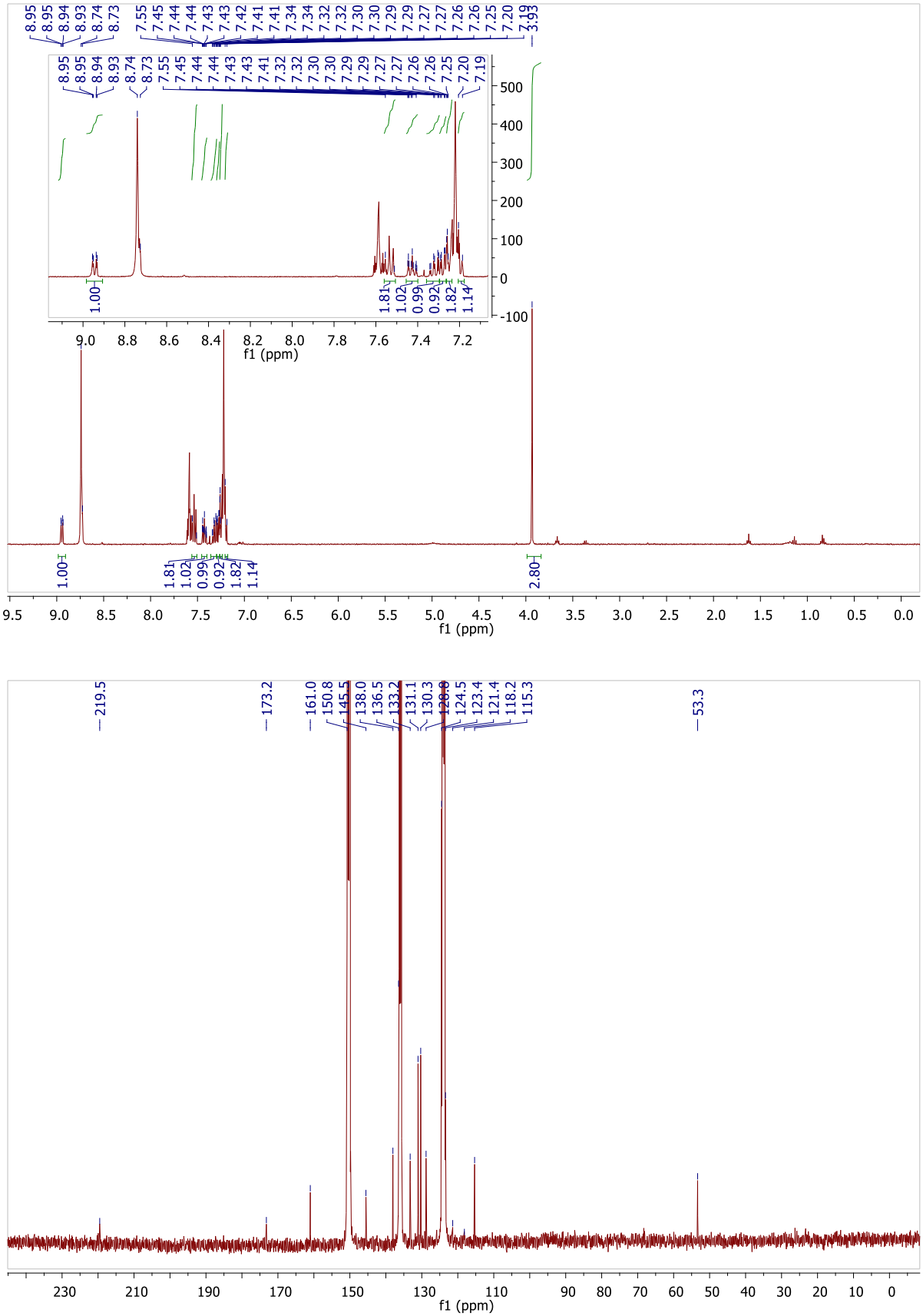


Figure S10. ^{1}H and ^{13}C NMR spectra of [Bi(CNMeNPh(C_6H_4))(NC_5H_5)$_2$][OTf] (**3**) in NC_5D_5.

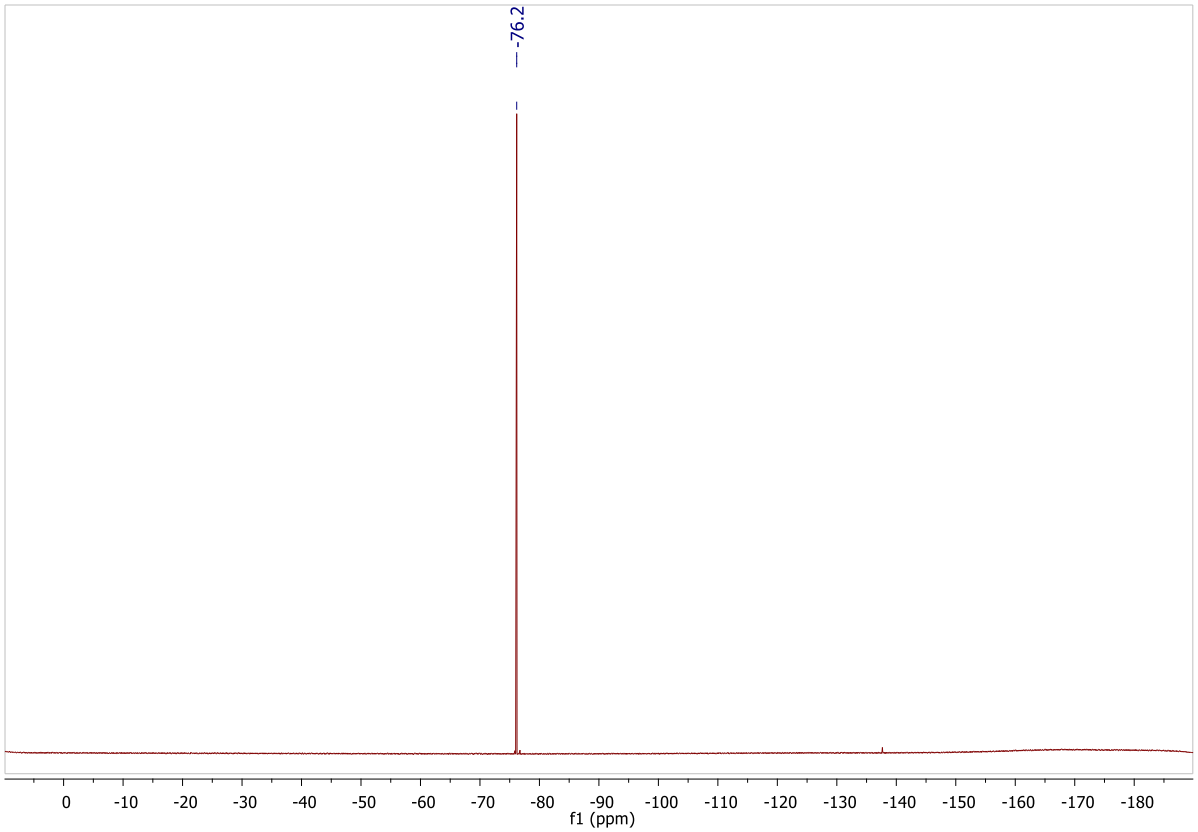


Figure S11. ^{19}F spectrum of [Bi(CNMeNPh(C_6H_4))(NC_5H_5)$_2$][OTf] (**3**) in NC_5D_5.

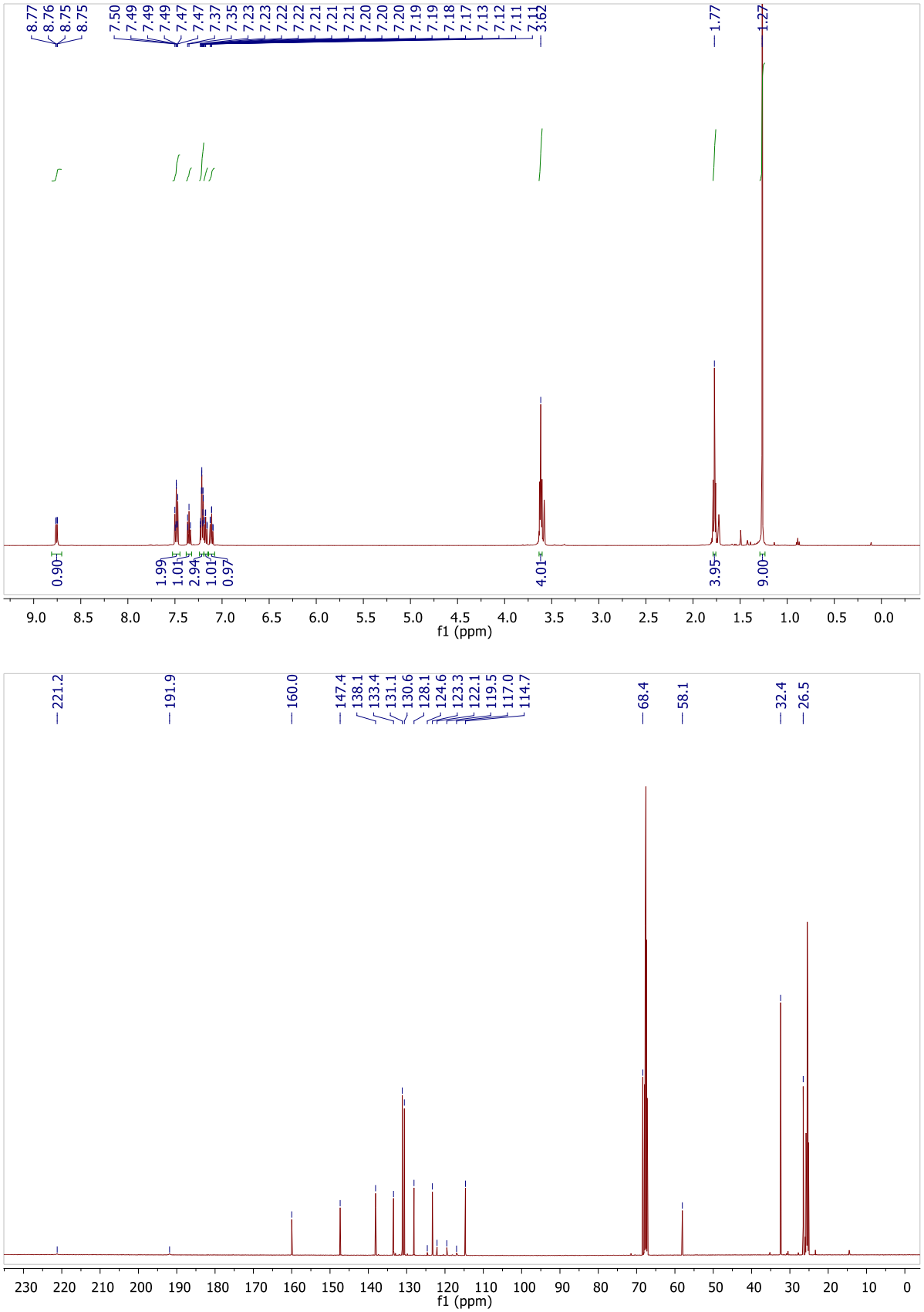


Figure S12. ^{1}H and ^{13}C NMR spectra of [Bi(CN*t*BuNPh(C_6H_4))(thf)][OTf] (**4-thf**) in THF-d_8.

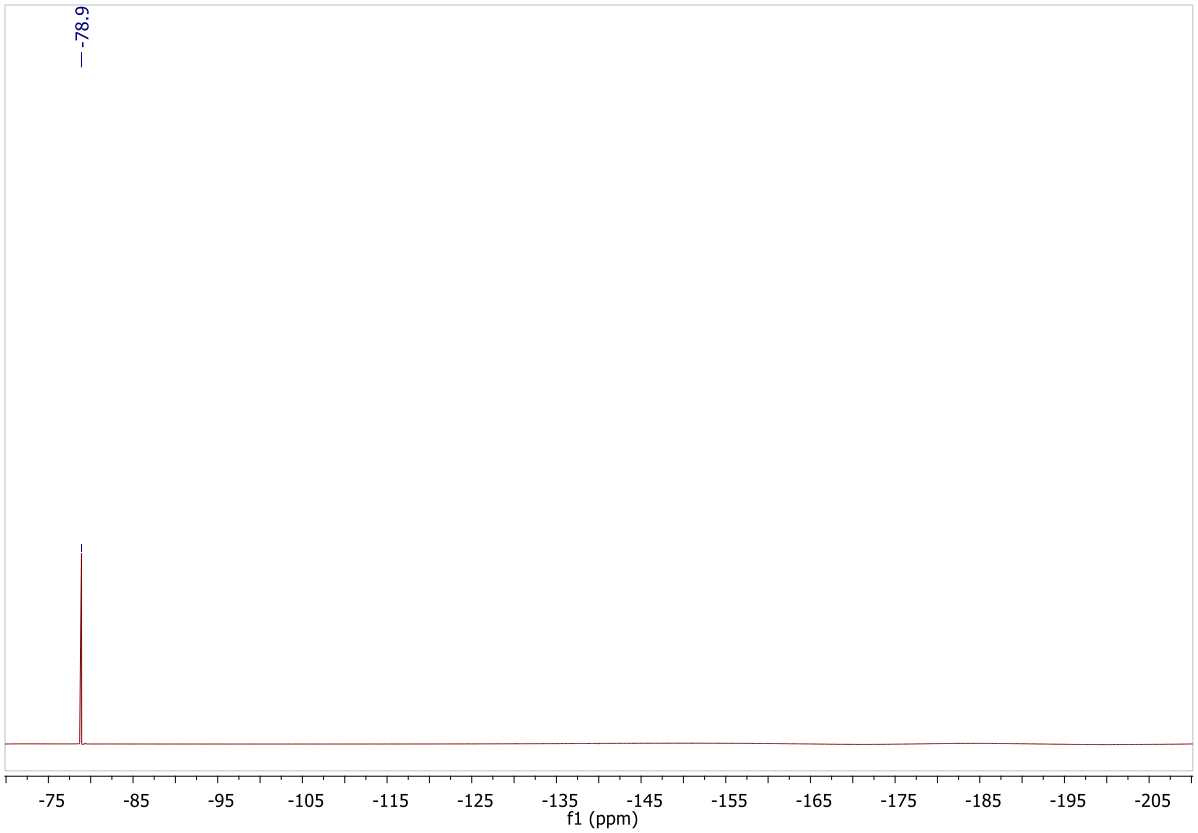


Figure S13. ^{19}F spectrum of [Bi(CN*t*BuNPh(C_6H_4))(thf)][OTf] (**4-thf**) in THF-d_8.

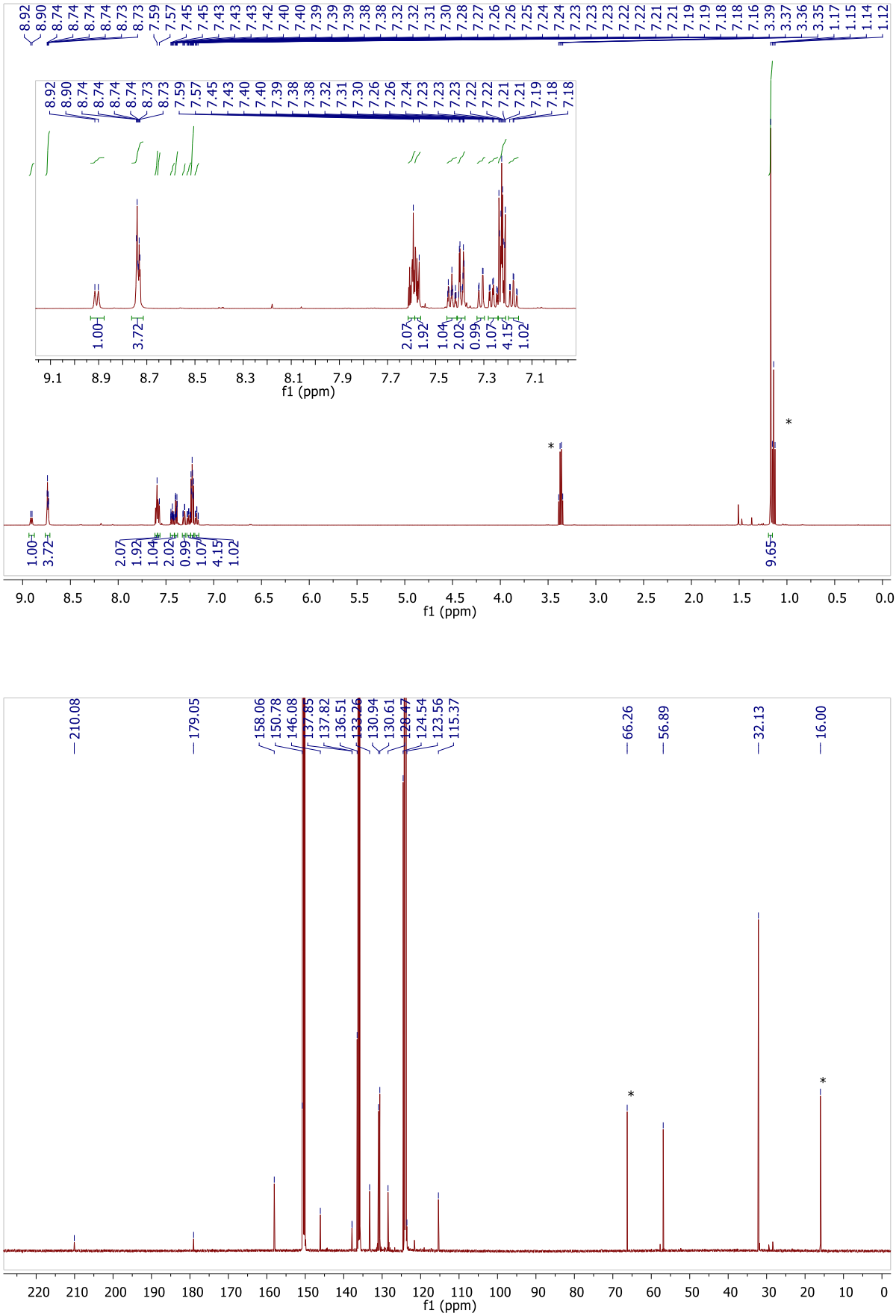


Figure S14. ^{1}H and ^{13}C NMR spectra of [Bi(CN*t*BuNPh(C_6H_4))(NC_5H_5)$_2$][OTf] (**4**) in NC_5D_5; asterisks indicate resonances of lattice-bound Et_2O.

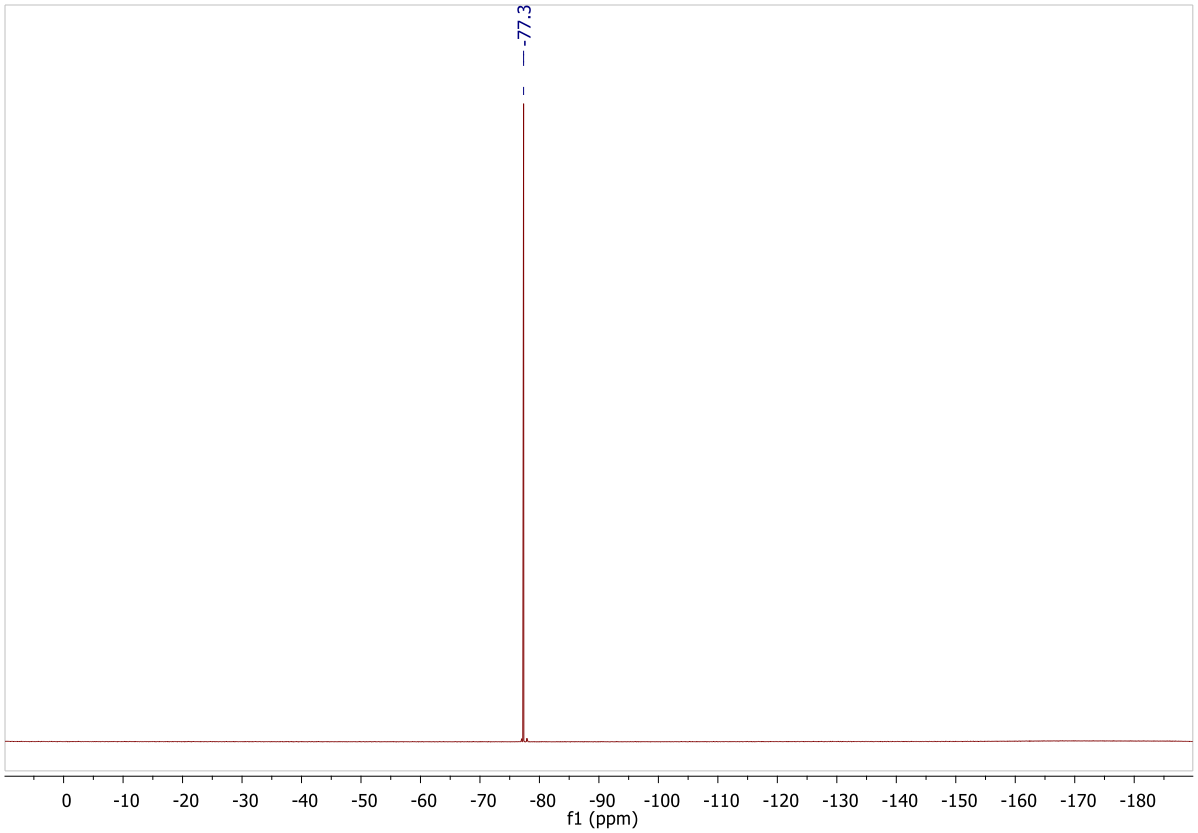


Figure S15. ^{19}F spectrum of [Bi(CN*t*BuNPh(C_6H_4))(NC_5H_5)$_2$][OTf] (**4**) in NC_5D_5.

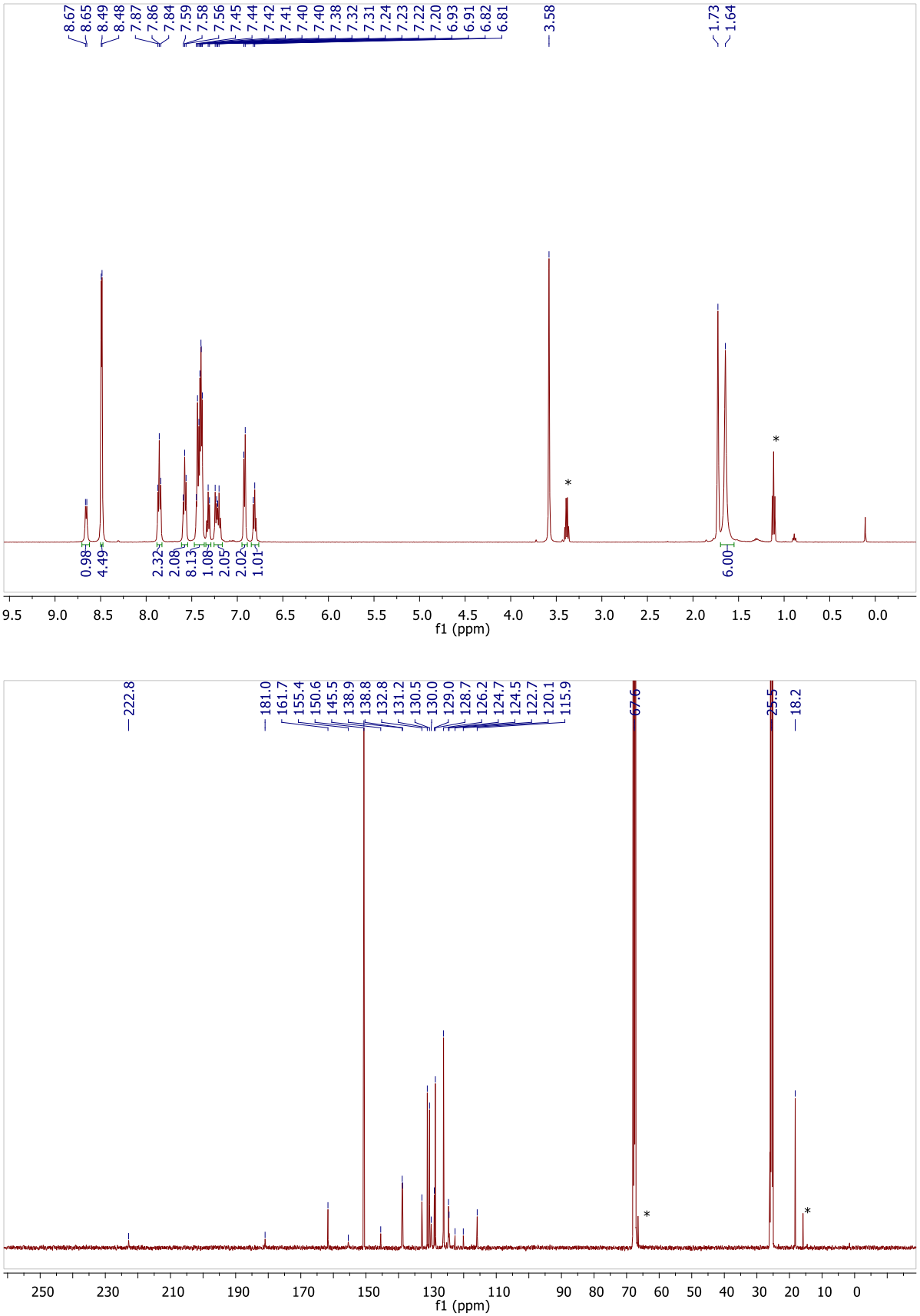


Figure S16. ^{1}H and ^{13}C NMR spectra of [Bi(CN(2,6-Me_2-C_6H_3)NPh(C_6H_4))(NC_5H_5)$_2$][OTf] (**5**) in THF-d_8; asterisks indicate resonances of lattice-bound Et_2O.

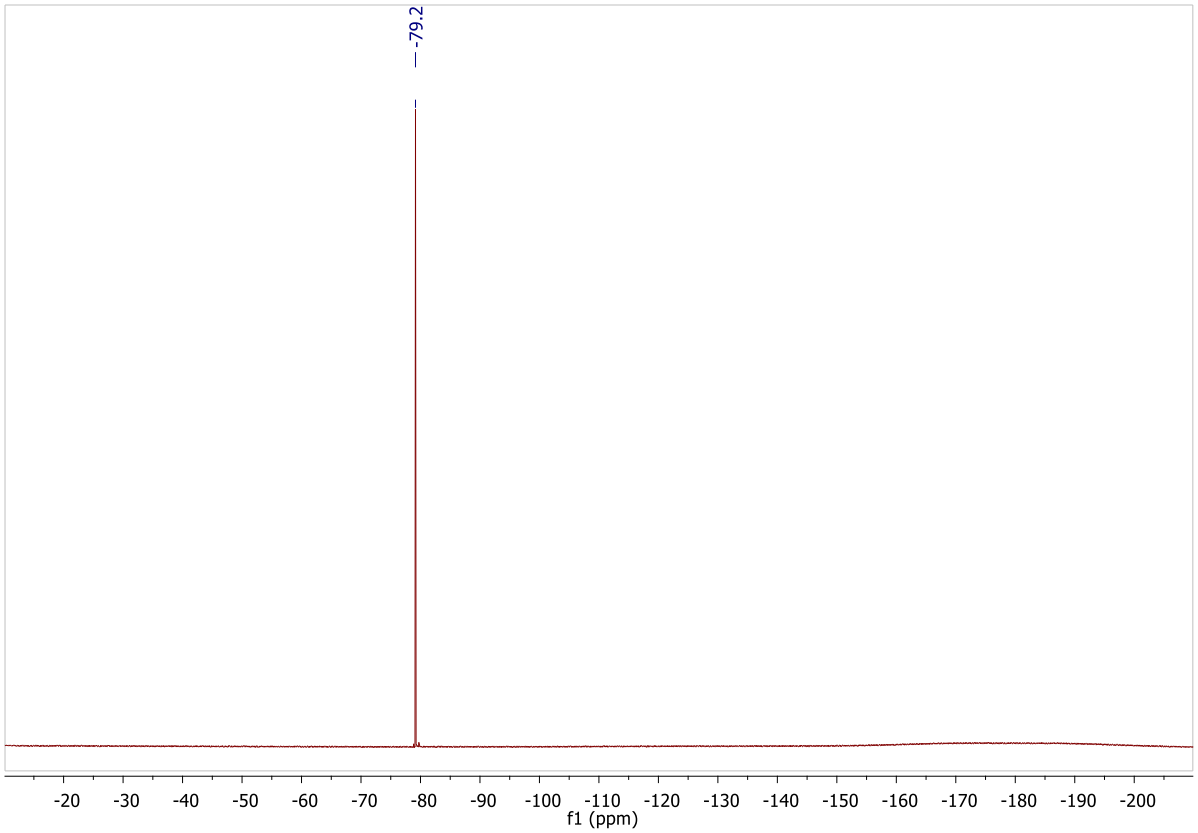


Figure S17. ^{19}F spectrum of [Bi(CN(2,6-Me_2-C_6H_3)NPh(C_6H_4))(NC_5H_5)$_2$][OTf] (**5**) in THF-d_8.

Cartesian coordinates and electronic energies relative to ADF basic atoms (in kcal · mol^{-1}) of all species analyzed in this work:

Compound 1 (−13553.2 kcal mol^{-1}):

Bi 1.741292022 -0.593345461 0.105609875
S 5.010643934 0.126718043 -0.483217183
N -0.715646194 -1.470103941 -0.158031606
O 2.843391115 -2.960614428 0.072376837
O 3.679741464 0.065355143 -1.201367255
C -0.351445219 -1.738034439 -1.526325741
C 0.910353204 -1.252935345 -1.886570931
O 4.863976988 0.041473975 0.977490195
O 6.044808385 -0.695458071 -1.110209612
C -1.104326830 -2.565640766 0.669756719
F 4.613024342 2.786641759 -0.369639448
C -0.431781726 -3.800696888 0.561399128
H 0.333903458 -3.924072745 -0.197647424
F 6.722283404 2.168978866 -0.217546958
C -1.189030344 -2.333878359 -2.474779767
H -2.170582733 -2.702850142 -2.190108629
C 1.349249825 -1.311519851 -3.206410516
H 2.321739928 -0.915129693 -3.486426436
C 0.510468891 -1.891248170 -4.167818242
H 0.829991776 -1.943515249 -5.205958108
C 3.499145407 -3.378553384 1.327577672
H 2.713836770 -3.727201202 2.003947301
H 3.998540273 -2.501906930 1.757429159
C -2.081270825 -2.418567466 1.668432636
H -2.643863084 -1.494181753 1.759135438
C -0.716484837 -4.841858638 1.445339265
H -0.178773463 -5.782634395 1.351553453
C -2.357304380 -3.462068051 2.554490155
H -3.116896130 -3.322962818 3.319684554
C -0.742123179 -2.406784895 -3.798253059
H -1.382716238 -2.854195540 -4.554576766
C -1.675415718 -4.678739539 2.453558475
H -1.891831253 -5.489787759 3.143786581
C 3.577046264 -3.517654309 -1.083260685
H 3.694789241 -2.717561059 -1.816214372
H 2.962266895 -4.318572973 -1.509516087
C 5.540772476 1.914433592 -0.831949994
C 4.498875778 -4.462427337 0.920741973
F 5.691357955 2.107242348 -2.165513037
Bi -1.696891475 0.650069554 0.176105275
S -4.960765465 -0.151834607 -0.313239410
N 0.748940130 1.527020478 -0.177876596
O -2.940955066 2.947899746 0.144469919
O -3.645939656 -0.086658129 -1.060141971
C 0.328160013 1.811476567 -1.526056559
C -0.946464317 1.328397687 -1.841004545
O -4.782365341 -0.075293980 1.144112886

O -6.007298079 0.675018470 -0.913195899
C 1.152099768 2.614894923 0.653254918
F -4.555336686 -2.811334058 -0.232079272
C 0.438524186 3.830582237 0.612036314
H -0.374798015 3.947182632 -0.097587985
F -6.660991768 -2.199282317 -0.019047058
C 1.124969172 2.421921271 -2.500261394
H 2.116228092 2.791124578 -2.250874603
C -1.438447956 1.400616940 -3.141425635
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C -0.640147551 1.993371055 -4.128789668
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H 2.781846655 1.566348635 1.626780397
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H 0.180785404 5.790619795 1.453994059
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H 2.010410122 5.516038680 3.129925854
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C -5.496368229 -1.937599912 -0.662224391
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C -4.722776758 4.391214932 -0.542797834
H -5.569995678 4.430306244 -1.233100540
H -4.346247204 5.409728130 -0.395853004
F -5.681901987 -2.119200719 -1.993053348
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H 4.013606105 -5.444856741 0.907092133
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H 5.303442981 -4.858932318 -1.100092077
H 5.633352996 -3.226019939 -0.477857599
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H -1.117777956 -1.332476861 4.737027659
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C -0.129140179 0.610245003 4.916404165
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H 0.846321007 0.977011780 5.255009514

I-1 (−12282.3 kcal mol^{-1}):

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O -2.335795492 3.173834403 -0.028136972
O -3.515293606 0.252828252 -1.224733132
C 0.741599434 1.412148413 -1.479322677
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O -4.764473535 0.566832847 0.893479982
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C 1.565265400 2.198193883 0.710171322
F -4.861086855 -2.254022082 -0.301749943
C 1.063697254 3.505272321 0.544716523
H 0.331610972 3.702754581 -0.231551364
F -6.865137029 -1.339091520 -0.279425820
C 1.686010013 1.827602137 -2.422587412
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C 1.475547603 4.531275040 1.395643254
H 1.070402622 5.531111167 1.259122712
C 2.903687638 2.987151565 2.580093073
H 3.629145563 2.776425098 3.361532475
C 1.279908482 1.944360199 -3.755639886
H 2.000027089 2.255467064 -4.508483542
C 2.392131632 4.278882460 2.424252238
H 2.707751172 5.079279263 3.088039782
C -2.943704467 3.796052612 -1.223930557
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H -2.202666356 4.480395224 -1.651948080
C -5.637682655 -1.289333311 -0.850373501
C -3.770173769 4.934687478 0.720530176
F -5.760600266 -1.531600430 -2.177804532
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N -0.881133799 -1.552720672 -0.061123580
O -0.013705574 -0.069842885 2.659856832
O 3.693310374 -0.630936267 -0.903322295
C -0.484033003 -1.955107782 -1.386673034

C 0.861115625 -1.706150321 -1.680720215
O 4.860553425 -0.586520811 1.286380004
O 5.961553922 -1.628082890 -0.714666867
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C -0.940970986 -3.855378890 0.790669446
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C -1.349048941 -2.460844928 -2.362402760
H -2.394251136 -2.647181434 -2.130955094
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H -1.473431591 1.217443069 3.440917839
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F 5.912253432 1.088576639 -2.019233775
H -4.626345537 5.128756437 1.372505418
H -3.141631319 5.831820769 0.695831453
C -4.185180734 4.523867881 -0.708791379
H -4.445331104 5.380323413 -1.336916173
H -5.037586624 3.837700471 -0.680337294
O 3.581084157 -4.700270494 -1.011277947
C 3.148809826 -3.852294240 -0.394323002

I-1_2CO (-11010.95 kcal/mol)
This potential intermediate would be obtained by substitution of the two terminal thf ligands in compound **1** for two CO ligands (ΔH: + 18.0 kcal·mol^{-1}; ΔG: + 16.2 kcal·mol^{-1}). It is suggested

not to be part of the primary reaction pathway since it is energetically less favorable than the formation of **I-2**.

Bi 1.552786831 -0.975336743 0.087254292
S 4.875929644 -0.719565239 -0.522351335
N -1.076553952 -1.222458489 -0.222167937
C 2.879686690 -3.797969774 -0.796238580
O 3.516713145 -0.483241302 -1.162528813
C -0.763213857 -1.407262638 -1.621171532
C 0.588476081 -1.233053971 -1.934161585
O 4.774813691 -0.929874945 0.927614426
O 5.717098892 -1.631347920 -1.293330602
C -1.673849719 -2.313989667 0.483950140
F 4.921474409 1.943486143 -0.144468136
C -1.254937046 -3.630090783 0.202624412
H -0.556293822 -3.808905701 -0.609590271
F 6.905896688 0.987028588 -0.169922652
C -1.707242524 -1.656233872 -2.621400578
H -2.756022473 -1.784917855 -2.371272986
C 1.027616267 -1.268171691 -3.256460935
H 2.076094757 -1.115726634 -3.497897882
C 0.085810338 -1.498576217 -4.267289140
H 0.402731985 -1.523040599 -5.306966915
H 0.315574399 1.563775994 3.423259274
C 0.035410693 0.044285361 5.002737664
H -0.579472507 0.455075292 5.808082167
C -2.594053609 -2.105645833 1.522085232
H -2.969863086 -1.109868744 1.738430471
C -1.727644871 -4.699852524 0.964470146
H -1.387151432 -5.706892132 0.736581016
C -3.057835180 -3.179050763 2.285398740
H -3.768873799 -2.993288940 3.086111550
C -1.266445923 -1.700455789 -3.947727658
H -1.984886012 -1.879103034 -4.743690687
C -2.624700964 -4.481414634 2.016790237
H -2.987885594 -5.315145489 2.611409961
H 1.090161628 0.201573093 5.255183182
F -5.856285951 -0.721135934 -2.230071298
C -2.814150576 3.910436311 -0.139409971
C 5.677102280 0.987802167 -0.737365547
O -3.158715329 4.861579081 -0.651859589
F 5.799007814 1.284166049 -2.053345131
Bi -1.587798986 0.935671144 0.359448542
S -4.925884917 0.824622879 -0.240210828
N 1.032300851 1.261218921 0.103665286
O -0.003404756 -0.344108874 2.633608574
O -3.578289315 0.790051675 -0.944633873
C 0.708833460 1.813893335 -1.191762243
C -0.643254788 1.713932960 -1.535138242
O -4.796053991 0.643959315 1.211450777
O -5.793944926 1.893616269 -0.726849068
C 1.645970245 2.122332429 1.068608917

F -4.935034023 -1.844004466 -0.575010144
C 1.217022327 3.460933130 1.170142601
H 0.494210849 3.848525500 0.457846951
F -6.929928229 -0.945446296 -0.317561395
C 1.642263094 2.339253135 -2.089913575
H 2.691184589 2.410217049 -1.817954305
C -1.092358788 2.101393507 -2.796244228
H -2.140932144 2.007831652 -3.065819970
C -0.161330407 2.612676411 -3.709250257
H -0.486507142 2.917107136 -4.701001167
C 0.285822077 -1.618786978 3.312346501
H 1.373098688 -1.775931613 3.301111806
H -0.206347941 -2.413990014 2.748823125
C 2.595819525 1.646502671 1.984671773
H 2.979845987 0.633318874 1.910254366
C 1.710964555 4.286635771 2.181327847
H 1.362346041 5.314290241 2.247327545
C 3.081397863 2.475023321 2.998860556
H 3.816098163 2.083992184 3.697898546
C 1.190579203 2.739151448 -3.351471436
H 1.900449178 3.140303751 -4.070452473
C 2.639847868 3.797488257 3.107840688
H 3.020123295 4.440707216 3.896747957
C -0.236596188 -1.451012050 4.736207737
H 0.272942377 -2.112043757 5.442644418
H -1.311737894 -1.660746507 4.772100273
C -5.712187193 -0.778207550 -0.884402188
C -0.290673508 0.684816361 3.652175258
H -1.355072332 0.942566490 3.576591794
O 3.300256454 -4.791488120 -1.143659908

TS-1 (−12273.8 kcal mol^{-1})

Bi -1.240053679 -0.322043617 -0.272380622
S -4.575320288 -0.484682803 0.347656365
N 1.329992794 -0.875652499 -0.025547216
O -1.895785091 -2.896568900 -0.394641521
O -3.274147858 -0.168111041 1.052219339
C 0.959448702 -1.402749640 1.279971561
C -0.337667900 -1.061789142 1.666085444
O -4.444101999 -0.460385871 -1.116027085
O -5.298618406 -1.608222353 0.944113092
C 1.828454303 -1.775407719 -1.022920221
F -5.023001410 2.173609018 0.366744470
C 1.554140138 -3.153952285 -0.956396554
H 1.010621561 -3.552998087 -0.107593798
F -6.839019268 0.937890958 0.205207161
C 1.808240387 -2.104632847 2.141983508
H 2.807241101 -2.390410346 1.834011159
C -0.800382966 -1.362262658 2.944402344
H -1.807946648 -1.088328946 3.245955672

C 0.053029985 -2.031525602 3.830913157
H -0.285048002 -2.267428031 4.837233300
C -2.478869642 -3.459044185 -1.626476477
H -1.673087731 -3.545188750 -2.359199753
H -3.240218432 -2.759087567 -1.989866336
C 2.501103867 -1.273570203 -2.149824163
H 2.685120319 -0.206550068 -2.248274979
C 1.953432189 -4.001138237 -1.992804142
H 1.725121223 -5.062199049 -1.927400623
C 2.907121085 -2.126333322 -3.175697885
H 3.427901569 -1.714763464 -4.036205961
C 1.338807716 -2.415857105 3.421781785
H 1.986659673 -2.951307526 4.111226324
C 2.635100328 -3.497359469 -3.105682950
H 2.945965169 -4.160662147 -3.908131567
C -2.353313781 -3.678611251 0.771420426
H -2.664645604 -2.972799679 1.542315686
H -1.499923090 -4.263221545 1.134434463
C -5.618897284 1.036654672 0.791461964
C -3.081600295 -4.804661283 -1.218170486
F -5.788111627 1.110569109 2.136254811
Bi 2.579410979 1.069131048 0.318759763
S 5.431939915 0.133719525 1.922765908
N -0.761604088 1.911842292 0.244221140
O -0.236905361 0.133321877 -2.982380668
O 3.921498478 0.119987689 2.089039574
C -0.266363884 2.055854175 1.572823505
C 1.082008604 1.753201060 1.886321233
O 5.871220071 1.032874394 0.849149594
O 6.134078373 0.176351042 3.202033211
C -1.635961496 2.892801391 -0.286012716
F 5.017410452 -1.794795946 0.104583727
C -1.649145961 4.220127828 0.196604843
H -1.026070275 4.490627668 1.042132866
F 7.057083937 -1.764562391 0.943697529
C -1.140434143 2.381380511 2.630150411
H -2.184940108 2.571546028 2.402262740
C 1.521899553 1.792815114 3.219521526
H 2.550213987 1.539957653 3.458983587
C 0.642967501 2.126940736 4.250107668
H 0.993090869 2.145723556 5.278832847
C -0.565414847 -1.121045129 -3.669698320
H -1.646784319 -1.292516928 -3.583306273
H -0.025207019 -1.927106883 -3.166887121
C -2.421810199 2.601615542 -1.420587389
H -2.427519371 1.601015039 -1.843958281
C -2.443684357 5.194225623 -0.410318821
H -2.433609907 6.206799122 -0.012990592
C -3.209055697 3.579887455 -2.025413035
H -3.810433399 3.314910050 -2.891614649
C -0.693795230 2.415929932 3.947934480

H -1.395742385 2.650037940 4.744617041
C -3.234802975 4.885199616 -1.522251791
H -3.853576231 5.646137891 -1.990216150
C -0.147203979 -0.919223678 -5.125517994
H -0.718570423 -1.551490186 -5.810982832
H 0.917770733 -1.145341139 -5.246876262
C 5.747658591 -1.608104681 1.238302482
C 0.007934360 1.180599730 -3.981199909
H 1.078111531 1.424826903 -3.961412074
H -0.569225316 2.063175507 -3.693632724
C -0.410299525 0.586907346 -5.330214151
H 0.159287590 1.013138003 -6.160821892
H -1.476092362 0.766006049 -5.513108173
F 5.384449164 -2.550869735 2.141887294
H -3.926964807 -5.081460657 -1.854396851
H -2.326387155 -5.596451529 -1.280740952
C -3.488891323 -4.558457961 0.249571262
H -3.586158905 -5.483648982 0.824660696
H -4.435531338 -4.011452689 0.298536730
O 0.780826841 3.549621476 -1.808975001
C 1.148614259 2.660034572 -1.196614543

I-2 (−12286.8 kcal mol^{-1})

Bi 1.037339354 0.945549926 0.181031633
S 3.832921734 -0.030488580 1.850703016
N -1.382906300 1.766515701 -0.247793551
O 2.836101145 2.518396345 -0.101257118
O 2.391621590 0.300038200 2.156621434
C -1.256952896 2.481333747 1.000435804
C 0.015617214 2.396067024 1.577996633
O 4.009064467 -0.578488348 0.495645351
O 4.769796780 1.010818568 2.279054136
C -1.801395938 2.484039871 -1.401929176
F 3.606022248 -2.623781777 2.560639760
C -1.886989107 3.890539220 -1.426807043
H -1.652538179 4.463274885 -0.536247103
F 5.537427784 -1.697773466 3.051331453
C -2.305568917 3.110515247 1.685255764
H -3.297960242 3.172133488 1.245702990
C 0.265316201 2.912741430 2.849553221
H 1.240978831 2.805205994 3.315539272
C -0.774487576 3.557360755 3.530577314
H -0.599684685 3.972674882 4.519879977
C 4.006031607 2.318920704 -0.999615291
H 3.605031053 2.042465568 -1.973554564
H 4.608225193 1.501813720 -0.599037087
C -2.095421989 1.770840802 -2.582070829
H -1.998494212 0.688638374 -2.605900229
C -2.260016052 4.555703936 -2.598034224
H -2.317158981 5.641669795 -2.594519510

C -2.464826066 2.444142685 -3.746186284
H -2.680155353 1.871402039 -4.644946478
C -2.048133293 3.653928331 2.948403368
H -2.851309528 4.145616180 3.491168374
C -2.550511985 3.841728906 -3.765465690
H -2.836781116 4.363684355 -4.674427079
C 3.143942049 3.594564981 0.888117323
H 3.076932811 3.158044680 1.884369634
H 2.377175732 4.360324886 0.753879131
C 4.196680347 -1.492933202 3.009628326
C 4.724417637 3.658257273 -0.947366505
F 3.756976648 -1.232883218 4.264173654
Bi -2.675604164 -0.219824785 0.152674883
S -3.907241996 -2.866865933 2.017048186
N -0.348551549 -2.227204253 -0.531196531
O 1.114345213 1.555031716 -2.313119198
O -4.098218077 -1.561761816 2.679367812
C -0.253749079 -2.023375351 0.879837613
C -0.956338981 -0.937263352 1.465980706
O -3.431271746 -2.734955101 0.603270756
O -3.231418287 -3.909325561 2.794057016
C 0.587681105 -3.106185447 -1.203112900
F -6.409505297 -2.649062865 1.045178918
C 0.112906511 -4.241768456 -1.862964198
H -0.948825053 -4.467754836 -1.849080500
F -5.657015275 -4.718837991 1.137152019
C 0.515492156 -2.871632477 1.686665408
H 1.045479750 -3.711189942 1.251719240
C -0.859246785 -0.719178200 2.849554326
H -1.406577449 0.103603305 3.300730395
C -0.075769214 -1.551365494 3.647306385
H 0.004638473 -1.371932899 4.715465711
C 1.173077590 2.831485684 -3.059933337
H 2.060777744 3.373789914 -2.719689488
H 0.280470005 3.402671487 -2.809931233
C 1.952490690 -2.799583164 -1.196074288
H 2.324535409 -1.934203390 -0.655545496
C 1.015048010 -5.073846158 -2.532543927
H 0.649030449 -5.957729710 -3.048202828
C 2.849493407 -3.640289690 -1.859792901
H 3.910921991 -3.406959152 -1.848213674
C 0.588922815 -2.633358760 3.060336701
H 1.179337995 -3.303738672 3.677418847
C 2.382294857 -4.774980047 -2.533064296
H 3.081263341 -5.426568334 -3.051025645
C 1.259389808 2.431385147 -4.534530774
H 1.824873417 3.161396523 -5.119783863
H 0.254620287 2.346104438 -4.959473177
C -5.670897786 -3.522641124 1.781220147
C 1.324232640 0.420598813 -3.239094085
H 0.352180552 -0.040778911 -3.437331354

H 1.970508215 -0.302834582 -2.734130761
C 1.941299824 1.046860188 -4.485892838
H 1.747583376 0.447591187 -5.379495886
H 3.025803524 1.151701337 -4.368426760
F -6.279699294 -3.689841371 2.983997748
H 5.774152390 3.562553658 -1.237528835
H 4.241281043 4.382632849 -1.612440966
C 4.555366782 4.069082015 0.532607915
H 4.663904743 5.145750785 0.684920396
H 5.290173060 3.548750259 1.153395734
O -1.378239895 -1.620540738 -2.505547572
C -1.296843884 -1.531068469 -1.285112777

I-3 (−11018.7 kcal mol^{-1})

Bi 1.631834013 -0.129306106 -0.441085971
S 4.471402745 1.602089546 -0.792688609
N 0.011830085 -1.997972175 -0.425036336
O 3.212042360 -1.842648078 -0.195590204
O 3.365151264 1.081131600 -1.693011153
C 0.200430666 -2.098399500 -1.860985212
C 1.086072299 -1.140292036 -2.368558273
O 4.301895975 1.142280430 0.596480961
O 5.797847106 1.498857420 -1.392842752
C 0.301604453 -3.142856469 0.380496582
F 2.842362723 3.634293031 -0.183979743
C 1.113042496 -4.190742962 -0.093781775
H 1.474662437 -4.172733736 -1.115859278
F 4.986312748 4.089436104 0.053268382
C -0.474281703 -2.974424566 -2.717399885
H -1.162127169 -3.720227166 -2.327314902
C 1.320516330 -1.024683682 -3.736062890
H 2.002949950 -0.274759489 -4.127644855
C 0.654848250 -1.904885351 -4.600842791
H 0.822850204 -1.840764164 -5.672835472
C 3.837482929 -2.146725711 1.128414655
H 3.100072725 -2.723125049 1.688959265
H 4.046469341 -1.190843670 1.613614588
C -0.154029573 -3.185644365 1.710433575
H -0.774757638 -2.386263979 2.104122879
C 1.470992130 -5.242416459 0.751618656
H 2.105566897 -6.038363716 0.369289239
C 0.209782934 -4.240948496 2.549789806
H -0.147287150 -4.250728527 3.576427446
C -0.231450600 -2.867181453 -4.092405046
H -0.743130653 -3.538751047 -4.776817136
C 1.028316168 -5.273350555 2.079160228
H 1.313579968 -6.091234221 2.735111059
C 4.164052986 -2.184576556 -1.299785116
H 4.122264963 -1.376746200 -2.029372516
H 3.798539584 -3.114343875 -1.743127289

C 4.077766754 3.454859519 -0.721882169
C 5.107619376 -2.916868459 0.780635726
F 4.096485433 3.996622302 -1.960400434
Bi -2.144082782 -0.882361893 -0.137698064
S -4.553115876 1.400402338 -1.011668936
N -0.915510495 1.436856871 1.610776605
C -1.451365154 0.174414254 1.881442794
O -4.144015073 0.576803195 -2.164758959
C -0.808806300 1.916481037 0.275065792
C -1.065735390 1.026418115 -0.803987549
O -4.009189645 0.881327008 0.288997030
O -4.462735049 2.853741008 -1.166152826
C -0.412248982 2.237406900 2.710603382
F -6.627040020 -0.277370621 -0.653434046
C -1.307966321 2.785311265 3.630014561
H -2.374057555 2.621720789 3.505623275
F -6.915022289 1.714979740 0.244282077
C -0.436853791 3.244146574 0.011093949
H -0.243578239 3.930582437 0.827337681
C -0.955685432 1.498786179 -2.124074074
H -1.171798910 0.828397938 -2.950132872
C -0.568000413 2.814273964 -2.383057508
H -0.471836434 3.165471405 -3.406202596
C 1.502086621 -0.769212995 3.092494984
O 1.610128349 -0.981695780 4.202352342
F -7.074747812 1.456332418 -1.938513628
C 0.965468540 2.437367723 2.843150033
H 1.651811584 2.015100526 2.114956918
C -0.815519620 3.538699483 4.700020243
H -1.508371284 3.965799632 5.420028799
C 1.451190929 3.197442925 3.909725824
H 2.520801401 3.357752694 4.013894979
C -0.319319880 3.678882981 -1.310392438
H -0.030860897 4.708912349 -1.499937880
C 0.561327487 3.745393277 4.840823363
H 0.940156156 4.333706919 5.672406203
H 5.881346229 -2.767236431 1.537531823
H 4.895553176 -3.988175807 0.703434501
C 5.504590299 -2.342483156 -0.597155612
C -6.408310877 1.052859577 -0.826927938
H 6.170031566 -3.008068500 -1.152692136
H 5.993078073 -1.369143870 -0.485999311
O -1.534990950 -0.282904899 3.014201350

TS-2 (−11008.7 kcal mol^{-1})

Bi 1.969203190 0.277070919 -0.609370262
S 4.443182803 1.908868257 -2.180852925
N -0.189187346 -2.243602337 -0.100119395
O 3.873890904 -1.053276661 -0.204001044
O 3.201791617 1.057985766 -2.456869717

C 0.251559783 -2.287214391 -1.458557336
C 1.179848740 -1.350846975 -1.966519256
O 4.536639879 2.279978786 -0.763879636
O 5.630762349 1.383496882 -2.844075014
C -0.246271354 -3.474759858 0.597348827
F 2.909014708 4.077889810 -2.549901248
C 0.655934593 -4.524802918 0.305362933
H 1.357924037 -4.415243177 -0.515141208
F 5.043342768 4.370223160 -3.010057751
C -0.298802457 -3.228581055 -2.358295252
H -1.021120230 -3.948384248 -1.983202414
C 1.529740521 -1.356750029 -3.327468196
H 2.233648357 -0.625939113 -3.712289307
C 0.979484308 -2.300194075 -4.195486246
H 1.259707660 -2.300711455 -5.245420975
C 4.867897997 -0.658060867 0.846493443
H 4.389264145 -0.841716440 1.810061078
H 5.077953248 0.405662928 0.714566940
C -1.115382824 -3.639769051 1.694636522
H -1.785600786 -2.839565800 1.996050222
C 0.657050965 -5.695877929 1.060828127
H 1.361026128 -6.486847531 0.811827708
C -1.109439812 -4.817721214 2.446167344
H -1.796180570 -4.914246337 3.283637606
C 0.060458613 -3.236544765 -3.703110407
H -0.387997524 -3.966227130 -4.372582666
C -0.229719543 -5.857769431 2.134030470
H -0.226989811 -6.773410005 2.719167137
C 4.556056686 -1.845773171 -1.281139982
H 4.250273900 -1.428508680 -2.239752243
H 4.192391373 -2.870930061 -1.180108812
C 4.006701293 3.509287803 -3.102402344
C 6.077875904 -1.538870014 0.560290624
F 3.759138759 3.246339981 -4.404523723
Bi -2.191376619 -0.930301064 -0.042306891
S -4.214966970 1.809975443 -0.815800768
N -1.032328007 1.080305834 2.083819897
C -1.725268134 -0.136273106 2.146758050
O -3.838558945 1.062664192 -2.031731119
C -0.673164277 1.657800069 0.842213211
C -0.942694355 0.952930325 -0.360929702
O -3.971355374 1.038647761 0.442949059
O -3.804118081 3.216731445 -0.759179861
C -0.760843731 1.792217402 3.319142352
F -6.631041767 0.620341853 -0.925007444
C -1.761196964 2.591365580 3.875878624
H -2.724347692 2.668779815 3.379528398
F -6.607385864 2.510966951 0.207754936
C -0.046985304 2.919436152 0.788415623
H 0.161829653 3.463198028 1.702467659
C -0.608055102 1.546930602 -1.593312187

H -0.848830497 1.031646054 -2.518628581
C 0.039439532 2.790575623 -1.641373664
H 0.307834299 3.228655886 -2.596892954
C 1.416206677 -1.225500891 1.585238107
O 1.264568582 -1.818480680 2.547665300
F -6.518949780 2.544302222 -1.994248603
C 0.488983725 1.670511211 3.929017762
H 1.252876961 1.042721202 3.480294416
C -1.501284546 3.282968903 5.062676172
H -2.274270961 3.907737750 5.501952702
C 0.744674223 2.366969960 5.113948303
H 1.716288914 2.278791674 5.592441943
C 0.309702767 3.468266297 -0.443634925
H 0.800961295 4.436170575 -0.467816655
C -0.249954247 3.172443739 5.680201580
H -0.050128411 3.712904369 6.601740370
H 7.000259531 -1.069811595 0.911772843
H 5.969749914 -2.511739757 1.050700767
C 6.041079439 -1.693911984 -0.976075996
C -6.109260853 1.875114940 -0.884862074
H 6.607528884 -2.561968829 -1.322388041
H 6.435668709 -0.797739705 -1.464385136
O -2.049141045 -0.651595972 3.207058555

I-4 (−11018.8 kcal mol^{-1})

Bi 1.979683937 0.345444509 -0.272551492
S 4.927259402 1.686715363 -1.769599436
N 0.144385965 -2.207056174 0.243383232
O 3.665698380 -1.244173317 0.201550185
O 3.801556936 0.881352912 -2.328130179
C 0.375273260 -2.171617139 -1.188907775
C 1.165771120 -1.148020626 -1.749235575
O 4.854742225 1.841113811 -0.302378018
O 6.245957729 1.361502320 -2.325325971
C -0.214973535 -3.477491774 0.863245186
F 3.341293190 3.848934633 -1.964120115
C 0.620006749 -4.583539437 0.669567266
H 1.495470705 -4.495159790 0.032708696
F 5.497217124 4.306174644 -1.998340094
C -0.260799295 -3.101270813 -2.025155115
H -0.884057851 -3.882029224 -1.602076466
C 1.321991002 -1.073585498 -3.137048817
H 1.937642233 -0.288077907 -3.565593155
C 0.701845344 -2.009668188 -3.972024828
H 0.832096086 -1.950576421 -5.049092629
C 4.540970051 -0.987521127 1.388261555
H 3.952294779 -1.257908168 2.266610138
H 4.783848167 0.077651597 1.389623628
C -1.334087835 -3.565414737 1.691968244
H -1.953818143 -2.694910947 1.883490450

C 0.311665947 -5.795774152 1.289449145
H 0.956418920 -6.656884571 1.135663192
C -1.635957509 -4.781850302 2.313479336
H -2.507550176 -4.851135223 2.958395287
C -0.088858380 -3.016563986 -3.410152249
H -0.584261757 -3.742743854 -4.048638602
C -0.818894987 -5.897740412 2.109623511
H -1.057404231 -6.842191376 2.591405293
C 4.444701781 -1.956812316 -0.860895937
H 4.241053509 -1.456355342 -1.806247954
H 4.063212741 -2.981433564 -0.878483631
C 4.553066720 3.427242365 -2.419592384
C 5.768179057 -1.859749236 1.145363722
F 4.526078671 3.440923149 -3.777032463
Bi -2.256533032 -0.555514109 -0.272074486
S -4.290141738 1.577109715 -1.714301830
N -1.338406702 1.299293774 2.085804852
C -2.094520296 0.134153385 1.997443224
O -3.389076522 1.014608778 -2.728714209
C -0.802544480 1.923659743 0.929981543
C -0.919211264 1.281437472 -0.331640925
O -4.044992150 0.937118422 -0.341503567
O -4.450586034 3.022820718 -1.633703139
C -1.075765103 1.861536714 3.399857402
F -5.963209323 -0.465006131 -2.168002444
C -1.965164271 2.790596380 3.941957105
H -2.848072358 3.084333878 3.381258055
F -6.909659836 1.276939380 -1.204260811
C -0.163303280 3.172328186 1.013677611
H -0.052030642 3.662650257 1.974097027
C -0.444779090 1.932414347 -1.487460965
H -0.564703095 1.456777955 -2.456428058
C 0.170664550 3.188330079 -1.399002691
H 0.538924660 3.678151508 -2.294410528
C 0.834926748 -1.256467102 1.072269270
O 0.845291280 -1.360289396 2.286391297
F -6.393633037 1.348095847 -3.345129894
C 0.067406789 1.456409441 4.091523100
H 0.726198154 0.715171360 3.648280368
C -1.696500300 3.333874791 5.202238181
H -2.380990546 4.059814464 5.632751369
C 0.328781090 2.004742616 5.350812485
H 1.215122163 1.696807173 5.899159572
C 0.311180212 3.793003510 -0.145926189
H 0.795343069 4.761520881 -0.062400245
C -0.550046263 2.943580030 5.904091480
H -0.343289017 3.368782451 6.882815431
H 6.652588886 -1.444191238 1.635197724
H 5.601992541 -2.873532062 1.524602850
C 5.892384784 -1.867303977 -0.394676544
C -6.008512506 0.889086268 -2.133419473

H 6.482269576 -2.710685590 -0.762952537
H 6.349197699 -0.938616676 -0.749977320
O -2.579141220 -0.435112544 2.963509888

I-5 (−7914.6 kcal mol^{-1})

Bi	0.043746876	0.175636996	-0.978067869
O	3.158521829	-0.004565247	-1.988448318
N	2.899942746	-0.090792245	0.298142497
C	2.013660588	-0.040247317	1.416548217
C	-0.877241340	3.390093019	-1.361015831
C	-0.241602428	0.193267326	2.292359465
H	-1.304391422	0.324638582	2.117477988
C	2.418119253	0.018545473	-1.005612599
C	0.625828802	0.115916556	1.202283776
S	-3.544031633	0.033057933	-0.382924540
F	-5.173971472	-1.758798504	0.807590217
C	4.325006316	-0.244238211	0.507235461
C	5.131172397	0.890469288	0.621845841
H	4.680726951	1.877570921	0.564188833
C	6.508382480	0.739126009	0.810317077
H	7.140452927	1.618803195	0.899509778
C	1.621500996	-0.056515594	3.808736410
H	2.016784760	-0.126834545	4.819071891
H	-1.576510264	2.654824861	-1.761270295
H	-0.570172481	4.080619420	-2.151264015
C	6.253962781	-1.672503286	0.762266458
H	6.688341168	-2.667491284	0.814214810
C	4.876388536	-1.525778358	0.572445368
H	4.229740150	-2.393637951	0.476401885
C	0.847693404	3.320736804	0.269434577
H	1.434708291	4.186671941	-0.058640273
C	0.249062837	0.107193886	3.602132502
H	-0.432146972	0.167471031	4.447050469
C	2.506952522	-0.127824860	2.727370137
H	3.570314486	-0.247973634	2.905161072
H	1.488569984	2.610299332	0.791582138
C	-1.403277000	4.114460734	-0.102835917
H	-2.419543502	3.795177082	0.135043413
H	-1.402009014	5.196183517	-0.262855461
C	-0.412907816	3.720296996	1.026803399
F	-4.940766068	0.124716979	1.928269372
O	-2.628280653	1.050733493	0.183272467
C	7.069704869	-0.541221934	0.881478155
H	8.140585722	-0.657057198	1.027453342
F	-3.314779917	-1.362596090	1.920800414
O	-2.849211260	-1.088091123	-1.053522832
H	-0.227515638	4.541205612	1.724839218
H	-0.792689230	2.861744631	1.586853614
O	-4.719001900	0.566279894	-1.089905672
C	-4.289668561	-0.787570733	1.158081765
O	0.339943856	2.643946621	-0.939996255

O	0.174134801	-2.276331384	-0.831996768
C	-0.365100223	-3.017743004	-2.007967657
H	0.499077640	-3.447847701	-2.522454339
H	-0.868860118	-2.298057586	-2.657386657
C	-0.285916636	-2.938773677	0.417001267
H	-1.126029944	-2.366188492	0.818599920
H	0.553579067	-2.908889450	1.112891415
C	-1.302451625	-4.076341294	-1.427959652
H	-1.328005869	-4.975660640	-2.048786575
H	-2.315305171	-3.672906022	-1.342000367
C	-0.708194093	-4.334228063	-0.026114990
H	-1.433911392	-4.772032335	0.664933975
H	0.160962604	-4.998445915	-0.087870000

Compound 2 (−7890.0 kcal mol^{-1})

Bi -0.296525613 0.082032649 1.046693712
O 2.811785344 0.023361195 2.066285265
N 2.549567780 -0.240816711 -0.205466250
C 1.663173530 -0.354060554 -1.319800964
N 0.330895082 2.472514922 0.452176432
C -0.600039783 -0.382697171 -2.197259257
H -1.670717701 -0.319976239 -2.034373235
C 2.066328321 -0.063515997 1.087988822
C 0.269361154 -0.266207409 -1.114264576
C 1.220295722 3.161785233 1.196138207
H 1.613869631 2.657962052 2.074559271
C 3.982138255 -0.300613271 -0.407933506
C 4.642878512 -1.527515335 -0.319084969
H 4.073380185 -2.429755186 -0.113355406
C 6.028904937 -1.576440052 -0.498308293
H 6.548633192 -2.528612905 -0.429771581
C 1.277142536 -0.666003364 -3.692837284
H 1.677118511 -0.820123492 -4.692085362
C -0.748270451 -3.214084395 0.302831321
H -1.399579709 -2.696093997 -0.393468848
C 6.072683799 0.823695010 -0.846890424
H 6.626369846 1.736844724 -1.049441065
C 4.687116423 0.876830318 -0.667361861
H 4.150824126 1.819999012 -0.728424435
C 0.757048478 -3.020070694 2.070526814
H 1.289712556 -2.353768633 2.743542682
C -0.103331131 -0.583264879 -3.493636310
H -0.787524885 -0.672399731 -4.333852704
C 2.163715441 -0.554138952 -2.615662936
H 3.233171886 -0.622641776 -2.785428563
N -0.065084889 -2.440153683 1.171828307
C 0.226048244 -5.206413823 1.228594318
H 0.341621984 -6.286373543 1.248667137
C -0.627249408 -4.601732976 0.302484651
H -1.192824186 -5.190500283 -0.413111967
C -0.185553784 3.041166397 -0.656771400

H -0.901633262 2.445633344 -1.213048858
C 6.743568391 -0.402128231 -0.762677398
H 7.821046718 -0.441790915 -0.900641756
C 0.177480190 4.323011549 -1.063033996
H -0.258597067 4.745335797 -1.963142442
C 0.928678974 -4.401218374 2.128921952
H 1.601946945 -4.829695990 2.864821076
C 1.101271354 5.038848357 -0.297890868
H 1.404369994 6.039425188 -0.592940499
C 1.629616268 4.448164124 0.852894234
H 2.349438582 4.968934508 1.476658970
S -3.808029186 0.327154611 0.168187785
F -5.532172038 1.519327181 -1.531158187
F -5.737103103 -0.673045202 -1.434519824
O -3.132503914 -0.990032868 0.121743774
F -4.049534192 0.229206722 -2.526091923
O -2.887491115 1.473888990 -0.007097745
O -4.814026786 0.481630753 1.231531030
C -4.843375228 0.351781457 -1.424528978

2red (−3685.4 kcal mol^{-1})

Bi	-1.823701307	0.511959514	0.161756436
O	0.855935042	2.349355411	0.274370236
N	1.260355258	0.089587351	0.063722390
C	0.733331707	-1.227502903	-0.044374579
C	-1.193490676	-2.707960778	-0.137854323
H	-2.271373543	-2.858175896	-0.128909509
C	0.418685287	1.200031931	0.179273097
C	-0.673138560	-1.410113545	-0.031703223
C	2.693043629	0.301869720	0.056004288
C	3.403367515	0.262409449	1.258338696
H	2.874347210	0.067673519	2.187268856
C	4.786215309	0.470501642	1.248620516
H	5.342822156	0.439586678	2.181765070
C	1.039933215	-3.623283442	-0.267511354
H	1.709449448	-4.475141187	-0.358439078
C	4.729487846	0.761709283	-1.158069240
H	5.241849901	0.957538396	-2.096568116
C	3.346779433	0.552561319	-1.152892250
H	2.774218942	0.580758079	-2.075871298
C	-0.346651033	-3.816681583	-0.255589183
H	-0.762826173	-4.817921510	-0.337215374
C	1.583644834	-2.338015742	-0.163419196
H	2.660522299	-2.204298537	-0.174736356
C	5.449803101	0.719444086	0.041409343
H	6.524756148	0.881500596	0.035653657

Radical compound 2red-py (−6854.2 kcal mol^{-1})

Bi 1.143019173 1.551488477 0.675821552
O -0.533008849 -0.618670852 2.399270191

N -0.686222752 -0.881794767 0.115040182
C -0.316036474 -0.438806920 -1.181767968
N 2.755850412 -1.431303458 0.230846953
C 0.908130202 1.121736461 -2.581683589
H 1.562033680 1.985595282 -2.686876236
C -0.217038131 -0.239160749 1.267478996
C 0.534529509 0.687550516 -1.304884307
C 2.821367812 -2.265208514 1.286040264
H 2.942930633 -1.797266681 2.261855290
C -1.570571938 -2.015117828 0.269200538
C -2.952336393 -1.831334788 0.178643057
H -3.347330733 -0.839492858 -0.013206779
C -3.806238371 -2.927878886 0.332602068
H -4.882103338 -2.788469237 0.260985422
C -0.382393655 -0.653502113 -3.596371599
H -0.738839511 -1.179313896 -4.478934099
C -2.550852776 2.047140760 -1.036644018
H -1.831535082 2.187375145 -1.840578536
C -1.891174488 -4.374025248 0.676029536
H -1.477095978 -5.360119280 0.871919157
C -1.034582237 -3.279885909 0.519583808
H 0.041097238 -3.398563091 0.589141561
C -2.943128085 2.047414673 1.235486994
H -2.536654545 2.191202248 2.235314086
C 0.455331604 0.460080177 -3.730958128
H 0.753458034 0.808007344 -4.717339749
C -0.769096846 -1.105247675 -2.330457834
H -1.415452994 -1.972122320 -2.241134931
N -2.089205646 2.239683713 0.212993070
C -4.751340930 1.488639156 -0.245741223
H -5.783022748 1.196613595 -0.423672810
C -3.868767526 1.673228849 -1.313268937
H -4.189464542 1.529007971 -2.341372378
C 2.584920966 -1.976763867 -0.988325064
H 2.515751222 -1.279618746 -1.820428523
C -3.277080124 -4.200096803 0.580980687
H -3.941786928 -5.051835257 0.701831322
C 2.485045834 -3.354238926 -1.201932544
H 2.343577086 -3.740290399 -2.207664564
C -4.278153106 1.675634296 1.056062056
H -4.925151714 1.532984585 1.917271843
C 2.567734208 -4.211091238 -0.101788315
H 2.493734974 -5.287790982 -0.230314860
C 2.735763981 -3.655157755 1.169938757
H 2.796016656 -4.281499713 2.055810274

References

1 (*a*) G. te Velde, F. M. Bickelhaupt, E. J. Baerends, C. Fonseca Guerra, S. J. A. van Gisbergen, J. G. Snijders and T. Ziegler, *J. Comput. Chem.*, 2001, **22**, 931-967; (*b*) http://www.scm.com.

2 (*a*) A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098-3100; (*b*) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785-789; (*c*) B. G. Johnson, P. M. W. Gill and J. A. Pople, *J. Chem. Phys.*, 1993, **98**, 5612-5626; (*d*) T. V. Russo, R. L. Martin and P. J. Hay, *J. Chem. Phys.*, 1994, **101**, 7729-7737; (*e*) S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, 2011, **32**, 1456-1465; (*f*) S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104-1 - 154104-19.

3 (*a*) E. van Lenthe, E. J. Baerends and J. G. Snijders, *J. Chem. Phys.*, 1994, **101**, 9783-9792; (*b*) E. van Lenthe, R. van Leeuwen, E. J. Baerends and J. G. Snijders, *Int. J. Quantum. Chem.*, 1996, **57**, 281-293.

4 (*a*) A. Klamt and G. Schüürmann, *J. Chem. Soc. Perkin Trans. 2*, 1993, 799-805; (*b*) A. Klamt, *J. Phys. Chem.*, 1995, **99**, 2224-2235; (*c*) C. C. Pye and T. Ziegler, *Theor. Chem. Acc.*, 1999, **101**, 396-408.

5 (*a*) F. M. Bickelhaupt, A. Diefenbach, S. P. de Visser, L. J. de Koning and N. M. M. Nibbering, *J. Phys. Chem. A*, 1998, **102**, 9549-9553; (*b*) F. M. Bickelhaupt and E. J. Baerends in *Reviews in Computational Chemistry*, Vol. 15 (Eds.: K. B. Lipkowitz, D. B. Boyd), Wiley-VCH, New York, 2000, pp. 1-86; (*c*) L. P. Wolters and F. M. Bickelhaupt, *WIRES Comput. Mol. Sci.*, 2015, **5**, 324-343.

6 C. Fonseca Guerra, J.-W. Handgraaf, E. J. Baerends and F. M. Bickelhaupt, *J. Comput. Chem.*, 2004, **25**, 189-210.

7 S. Ishida, F. Hirakawa, K. Furukawa, K. Yoza and T. Iwamoto, *Angew. Chem. Int. Ed.*, 2014, **53**, 11172-11176.