Insertion of CO_2 and CS_2 into Bi–N Bonds Enables Catalyzed CH-Activation and Light-Induced Bismuthinidene Transfer

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Experimental

General considerations

All air and moisture-sensitive manipulations were carried out using standard Schlenk techniques or in a glovebox containing purified argon. Solvents were purified by distillation using the appropriate drying agents, degassed and stored over molecular sieves (4 Å) prior to use. Deuterated solvents used for NMR spectroscopy were dried, degassed and stored over molecular sieves (4 Å) under dry argon prior to use. $BiCl_3$ was sublimed prior to use. CS_2 was degassed by three freeze-pump-thaw cycles and stored over molecular sieves (4 Å) under dry argon. Compounds **1-H**[1] and **1-Me**[2] were prepared according to the literature.

All NMR spectra were acquired either on a Bruker Avance 400 spectrometer or on Bruker Avance I/III 500 spectrometer. ^{1}H and ^{13}C chemical shifts are reported relative to $SiMe_4$ using the residual solvent peak of the solvent as a secondary standard. ^{19}F chemical shifts are reported relative to $CFCl_3$ as an external standard. Elemental analyses (C, H, N, S) were conducted on Vario Micro Cube intruments by Elementar Analysesysteme GmbH. Mass spectrometric analyses were conducted using either an AccuTOF GCv by JEOL (LIFDI) or a LTQ-FT Ultra by Thermo Fischer Scientific (APCI). UV-vis spectra were recorded on a Specord S600 diode array spectrometer by AnalytikJena. Photochemical experiments were performed using a low-pressure mercury-vapor lamp by Peschl Ultraviolet (P = 2.7 W, λ = 254 nm) and regular borosilicate glassware.

Single-crystals suitable for X-ray diffraction analysis were coated with perfluorinated polyether oil in a glovebox, transferred to a nylon loop and then transferred to the goniometer of a diffractometer (Bruker D8 Quest or Bruker X8-Apex II) equipped with a molybdenum X-ray tube (λ = 0.71073 Å).

[Bi(N(C$_6$H$_5$)(C$_6$H$_4$)(C(O)O))(OTf)] (2-H). [Bi$_2$(N(C$_6$H$_5$)(C$_6$H$_4$))$_2$(OTf)$_2$(thf)$_3$] (**1-H**) (217 mg, 0.17 mmol) was dispersed in THF (1 mL) and the atmosphere was exchanged for CO_2 (1 atm) in three freeze-pump-thaw cycles.[3] A white solid started to precipitate immediately. After 30 h, when all orange solid was consumed and the reaction mixture was colorless, the solid was isolated by filtration, washed with THF and pentane and dried *in vacuo*. The product contains 0.5 equiv. THF which could not be removed under reduced pressure.
Yield: 180 mg (0.30 mmol, 87%)

^{1}H NMR: (298 K, 500 MHz, Acetonitrile-*d$_3$*): δ = 1.77 – 1.83 (m, 2H, β-thf), 3.63 – 3.67 (m, 2H, α-thf), 6.38 (s, br, 2H, 2,6-C$_6$H$_5$), 7.16 – 7.23 (m, 3H, 3-C$_6$H$_4$, 3,5-C$_6$H$_5$), 7.34 (d, $^3J_{HH}$ = 8.2 Hz, 1H, 5-C$_6$H$_4$), 7.38 (tt, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.1 Hz, 1H, 4-C$_6$H$_5$), 7.67 (ddd, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, 4-C$_6$H$_4$), 8.83 (dd, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.2 Hz, 2-C$_6$H$_4$) ppm.
^{13}C NMR: (298 K, 126 MHz, Acetonitrile-*d$_3$*): δ = 26.2 (s, β-thf), 68.4 (s, α-thf), 121.3 (q, $^1J_{CF}$ = 320 Hz, OTf), 127.4 (s, 2-C$_6$H$_4$), 128.9 (s, 4-C$_6$H$_5$), 129.3 (s, 2,6-C$_6$H$_5$), 129.8 (s, 4-C$_6$H$_4$), 130.7 (s, 3,5-C$_6$H$_5$), 131.2 (s, 3-C$_6$H$_5$), 137.7 (s, 5-C$_6$H$_4$), 141.9 (s, 1-C$_6$H$_5$), 149.4 (s, 1-C$_6$H$_4$), 160.4 (s, C=O), 223.4 (s, 6-C$_6$H$_4$) ppm.
^{19}F NMR: (298 K, 471 MHz, Acetonitrile-*d$_3$*): δ = –78.96 (s, OTf) ppm.
ESI-MS (Pyridine): positive mode, found *m/z* 376.0529, calcd. for $C_{12}H_9BiN^+$ *m/z* 376.0539. *The detected fragment represents the monomeric species after elimination of CO_2 and $[OTf]^-$ during the ionization process.*
ESI-MS (Pyridine): negative mode, found *m/z* 673.9568, calcd. for $C_{14}H_9BiF_6NO_6S_2^-$ *m/z* 673.9584. *The detected fragment represents the monomeric species after elimination of CO_2 and association with $[OTf]^-$ during the ionization process.*
Elemental analysis. Anal. calc. for $C_{14}H_9BiF_3NO_5S \times 0.5\ [C_4H_8O]$ (605.32 g/mol): C, 31.75; H, 2.16.; N, 2.31; S, 5.30; found: C, 31.90; H, 2.20; N, 2.26; S, 5.30.

[Bi(N(C$_6$H$_4$Me)(C$_6$H$_3$Me)(C(O)O))(OTf)] (2-Me). [Bi$_2$(N(C$_6$H$_4$Me)(C$_6$H$_3$Me))$_2$(OTf)$_2$(thf)] (**1-Me**) (120 mg, 0.11 mmol) was dissolved in THF (3 mL) and the atmosphere was exchanged for CO_2 (1 atm) in three freeze-pump-thaw cycles. The reaction mixture was stirred at ambient temperature overnight and the color changed to pale yellow. The solvent was removed under reduced pressure, and the residue was washed with pentane (3 x 5 mL). The product was obtained as white powder after drying *in vacuo* for 5 h.
Yield: 105 mg (0.18 mmol, 92%)

^{1}H NMR: (298 K, 500 MHz, Acetonitrile-*d$_3$*): δ = 2.36 (s, 3H, C$_6$H$_3$*Me*), 2.41 (s, 3H, C$_6$H$_4$*Me*), 6.36 (s, br, 2H, 2,6-C$_6$H$_4$Me), 6.98 – 7.02 (m, 3H, 3,5-C$_6$H$_4$Me, 3-C$_6$H$_3$Me), 7.32 (d, 1H, $^3J_{HH}$ = 8.5 Hz, 2-C$_6$H$_3$Me), 8.62 (s, 1H, 5-C$_6$H$_3$Me) ppm.
^{13}C NMR: (298 K, 126 MHz, Acetonitrile-*d$_3$*): δ = 21.2 (s, C$_6$H$_3$*Me*), 21.3 (s, C$_6$H$_4$*Me*), 121.1 (q, $^1J_{CF}$ = 319 Hz, OTf), 127.1 (s, 2-C$_6$H$_3$Me), 129.2 (s, 2,6-C$_6$H$_4$Me), 131.0 (s, 3,5-C$_6$H$_4$Me), 131.8 (s, 3-C$_6$H$_3$Me), 138.0 (s, 5-C$_6$H$_3$Me), 138.9 (s, 5-C$_6$H$_4$Me), 139.3 (s, 1-C$_6$H$_4$Me), 139.6 (s, 4-C$_6$H$_3$Me), 146.9 (s, 1-C$_6$H$_3$Me), 160.5 (s, C=O), 222.7 (s, 6-C$_6$H$_3$Me) ppm.
^{19}F NMR: (298 K, 471 MHz, Acetonitrile-*d$_3$*): δ = – 78.89 (s, OTf) ppm.
Elemental analysis. Anal. calc. for $C_{16}H_{13}BiF_3NO_5S$ (597.32 g/mol): C, 32.17; H, 2.19; N, 2.34; S, 5.37; found: C, 32.31; H, 2.37; N, 2.15; S, 5.14.

[Bi(N(C_6H_5)(C_6H_4)(C(S)S))(OTf)(diglyme)] (3-H). [Bi_2(N(C_6H_5)(C_6H_4))$_2$(OTf)$_2$(thf)$_3$] (**1-H**) (630 mg, 0.50 mmol) was dissolved in diglyme (5 mL), cooled to 0 °C and CS_2 (3.5 mL) was added. The reaction mixture was stirred at 0 °C for 1.5 h and a yellow solid started to precipitate. The reaction mixture was layered with *n*-hexane (5 mL) and the reaction vessel was stored at –30 °C for 3 d, and a yellow solid precipitated. It was isolated by filtration and washed with *n*-hexane (15 mL). The obtained product was dried for 2 h *in vacuo*. The number of diglyme ligands *n* in the bulk material ranges from 1.0 to 2.0 and must be determined for every batch individually.
Yield (*n* = 1): 654 mg (0.88 mmol, 89%)

^{1}H NMR: (298 K, 500 MHz, Pyridine-d_5): δ = 3.26 (s, 6H, CH_3, diglyme) 3.49 – 3.54 (m, 4H, CH_2, diglyme), 3.61 – 3.65 (m, 4H, CH_2, diglyme), 7.33 (dd, 1H, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 8.5 Hz, 3-C_6H_4), 7.50 (dd, 1H, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 8.5 Hz, 4-C_6H_4), 7.96 (d, 1H, $^3J_{HH}$ = 8.2 Hz, 5-C_6H_4), 8.36 (d, br, 1H, $^3J_{HH}$ = 8.5 Hz, 2-C_6H_4) ppm. *The resonances of the phenyl group show chemical shifts between 7.10 and 7.55 ppm and could not to be assigned to individual positions due to severe signal broadening. When the number of solvent protons and the number of the protons of the phenylene unit are subtracted from the sum of the integrals of the relevant section of the spectrum (isolated doublet as calibration signal), the expected value of five is obtained, corresponding to the five protons of the phenyl group.*
^{13}C NMR: (298 K, 126 MHz, Pyridine-d_5): δ = 58.9(s, CH_3, diglyme), 71.0 (s, CH_2, diglyme), 72.6 (s, CH_2, diglyme),122.8 (s, $^1J_{CF}$ = 322 Hz, OTf), 129.8 (s, C_6H_5), 130.0 (s, 3-C_6H_4, 130.4 (s, C_6H_5), 130.6 (3-C_6H_4), 131.3 (s, C_6H_5), 131.9 (s, 4-C_6H_4), 138.1 (s, 2-C_6H_4), 146.4 (s, 1-C_6H_5), 152.5 (s, 6-C_6H_4), 201.0 (s, *C*S_2), 210.0 (s, 1-C_6H_4) ppm. *Due to the signal broadening of the signals of the phenyl group in the ^{1}H NMR spectrum, the assignment of the exact position of the carbon atoms of the phenyl group at 129.8, 130.4 and 131.3 ppm was not possible.*
^{19}F NMR: (298 K, 471 MHz, Pyridine-d_5): δ = – 77.29(s, OTf) ppm.
ESI-MS (THF): positive mode, found *m/z* 451.9970; 903.9970, 1052.9474 calcd. for $C_{13}H_9BiNS_2^+$ *m/z* 451.9980; for $C_{26}H_{18}Bi_2N_2S_4^+$ *m/z* 903.9960; for $C_{27}H_{18}Bi_2F_3N_2O_3S_5^+$ *m/z* 1052.9475. *The three signals correspond to the monomeric fragment without [OTf]$^-$, the dimeric fragment without [OTf]$^-$, and the dimeric fragment with one [OTf]$^-$ anion.*
Elemental analysis. Anal. calc. for $C_{14}H_9Bi_1F_3NO_3S_3 \times [C_6H_{14}O_3]$ (735.56 g/mol): C, 32.66; H, 3.15; N, 1.90; S, 13.08; found: C, 32.50; H, 3.52; N, 1.95; S, 13.01.

[Bi(N(C_6H_4Me)(C_6H_3Me)(C(S)S))(OTf)(diglyme)$_2$] (3-Me). [Bi_2(N(C_6H_4Me)(C_6H_3Me))$_2$(OTf)$_2$(thf)] (**1-Me**) (550 mg, 0.47 mmol) was dissolved in diglyme (6 mL) and CS_2 (3.00 mL) was added. The reaction mixture was stirred at room temperature for 45 min and layered with *n*-hexane (6 mL). The reaction vessel was stored at –30 °C for 3 d, and yellow crystals formed. These were isolated by filtration and washed with *n*-hexanes (3 x 15 mL). The obtained product was dried under exclusion of light for 4 h *in vacuo*. The number of diglyme ligands *n* in the bulk material ranges from 1.0 to 2.0 and must be determined for every batch individually.
Yield (*n* = 2): 603 mg (0.68 mmol, 72%)

^{1}H NMR: (298 K, 500 MHz, Pyridine-d_5): δ = 2.11 (s, 3H, C_6H_3*Me*), 2.21 (s, 3H, C_6H_4*Me*), 3.27 (s, 12H, CH_3, diglyme) 3.50 – 3.54 (m, 8H, CH_2, diglyme), 3.62 – 3.65 (m, 8H, CH_2, diglyme), 6.95 (s, br, 2H, 3,5-C_6H_4Me), 7.18 (d, $^3J_{HH}$ = 8.4 Hz, 1H, 3-C_6H_3Me), 7.20 – 7.36 (s, br, 2H, 2,6-C_6H_4Me) 7.97 (d, $^3J_{HH}$ = 8.4 Hz, 1H, 2-C_6H_3Me), 8.21 (s, 1H, 5-C_6H_3Me) ppm.

^{13}C NMR: (298 K, 126 MHz, Pyridine-d_5): δ = 21.0 (s, C_6H_3*Me*) 21.3 (s, C_6H_4*Me*) 59.0 (s, CH_3, diglyme), 71.1 (s, CH_2, diglyme), 72.6 (s, CH_2, diglyme), 122.8 (s, $^1J_{CF}$ = 320 Hz, OTf), 129.1 (s, 2,6-C_6H_4Me) 130.9 (s, 3,5-C_6H_4Me, 2-C_6H_3Me), 132.1 (s, 3-C_6H_3Me), 138.5 (s, 5-C_6H_3Me), 139.8 (s, 4-C_6H_4Me), 142.2 (s, 4-C_6H_3Me), 143.9 (s, 1-C_6H_4Me), 150.3 (s, 1-C_6H_3Me), 200.2 (s, *C*S_2), 208.1 (s, 6-C_6H_3Me) ppm.
The singal at 150.3 ppm overlaps with the residual solvent signal of pyridine-d_5 and was assigned on the basis of the ^{1}H/^{13}C HMBC spectrum.
^{19}F NMR: (298 K, 471 MHz, Pyridine-d_5): δ = – 77.29 (s, OTf) ppm.
Elemental analysis. Anal. calc. for $C_{16}H_{18}BiF_3NO_3S_3 \times 2$ [$C_6H_{14}O_3$] (897.79 g/mol): C, 37.46; H, 4.60; N, 1.56; S, 10.71; found: C, 37.64; H, 4.15; N, 1.64; S, 11.05.

UV-vis spectra of 3-R:

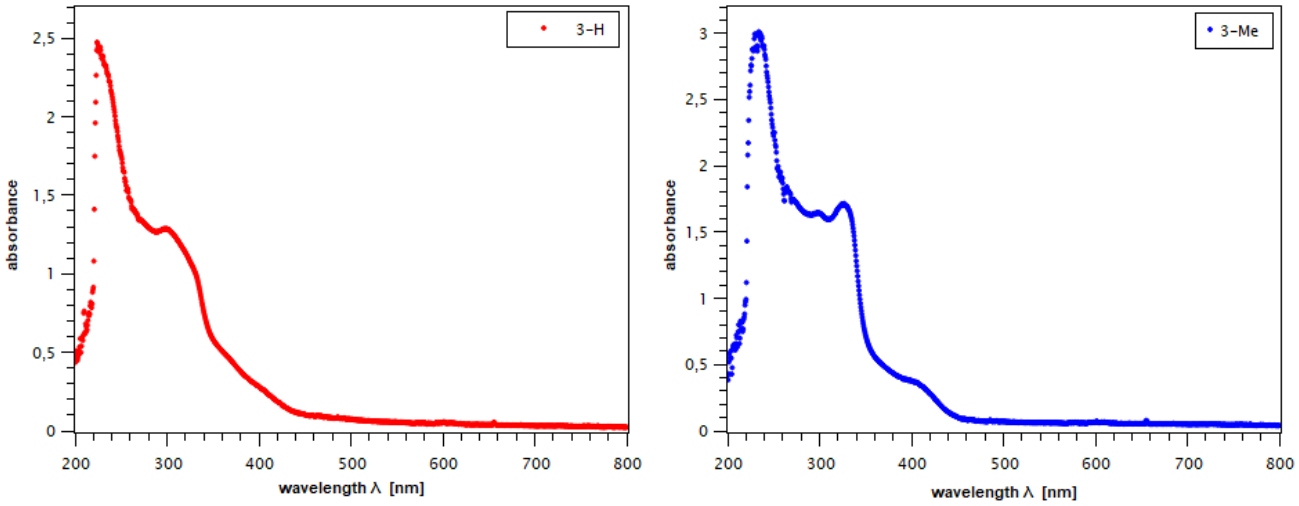


Figure S1. UV-vis spectra of compounds **3-R** in THF.

Preparation of 3-phenylbenzo[d]thiazole-2(3H)-thione (5-H):
[Bi(N(C_6H_5)(C_6H_4)(C(S)S))(OTf)(diglyme)] (**3-H**) (270 mg, 0.37 mmol) was dissolved in THF (8 mL) and irradiated at 254 nm with a low-pressure Hg lamp for 5 h. The yellow reaction mixture turned orange and a black solid precipitated. The solvent was removed under reduced pressure, and the residue was extracted with dichloromethane. The combined organic phases were washed with water (3 x 15 mL) and dried over Mg(SO_4). The solvent was removed under reduced pressure and the crude product purified by column chromatography (DCM, 8% ethanol). After removal of the solvent, pure benzothiazolethione **5-H** was obtained as a yellow oil.
Yield: 58.4 mg (0.24 mmol, 65%)

^{1}H NMR: (298 K, 400 MHz, $CDCl_3$): δ = 6.73 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 7.28-7.33 (m, 2H), 7.39 (d, $^3J_{HH}$ = 8.4 Hz, 2H), 7.51 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.59 (d, $^3J_{HH}$ = 7.2 Hz, 1H), 7.62-7.67 (m, 2H) ppm.[4]
APCI-MS: positive mode, found *m/z* 244.0248, calcd. for $C_{13}H_{10}NS_2^+$ *m/z* 244.0255.

Preparation of 3-(4-methylphenyl)-6-methylbenzo[d]thiazole-2(3H)-thione (5-Me):
[Bi(N(C_6H_4Me)(C_6H_3Me)(C(S)S))(OTf)(diglyme)$_2$] (**3-Me**) (300 mg, 0.34 mmol) was dissolved in THF (8 mL) and irradiated at 254 nm for 5 h. The yellow reaction mixture turned orange and a black solid precipitated. The solvent was removed under reduced pressure and the residue was extracted with dichloromethane and washed with water (3 x 15 mL). After drying over Mg(SO_4), the solvent was removed and the crude product purified by column chromatography (DCM, 5% ethanol). After removal of the solvent, pure benzothiazolethione **5-Me** was obtained as yellow powder.
Yield: 73.4 mg (0.27 mmol, 81%)

^{1}H NMR: (298 K, 500 MHz, Benzene-d_6): δ = 1.95 (s, 3H, C_6H_3*Me*), 2.02 (s, 3H, C_6H_4*Me*), 6.32 (d, $^3J_{HH}$ = 8.4 Hz, 1H, 6-C_6H_3Me), 6.44 (s, 1H, 3-C_6H_3Me), 6.59 (d, $^3J_{HH}$ = 8.4 Hz, 1H, 5-C_6H_3Me), 6.87 (d, $^3J_{HH}$ = 8.4 Hz, 2H, 2,6-C_6H_4Me), 6.90 (d, $^3J_{HH}$ = 8.4 Hz, 2H, 3,5-C_6H_4Me) ppm.
^{13}C NMR: (298 K, 126 MHz, Benzene-d_6): δ = 20.8 (s, C_6H_3*Me*), 21.1 (s, C_6H_4*Me*), 113.0 (s, 6-C_6H_3Me), 121.4 (s, 3-C_6H_3Me), 127.5 (s, 5-C_6H_3Me), 128.0 (s, 2-C_6H_3Me), 128.5 (s, 2,6-C_6H_4Me), 130.7 (s, 3,5-C_6H_4Me), 134.4 (s, 4-C_6H_3Me), 134.9 (s, 1-C_6H_4Me), 139.3 (s, 4-C_6H_4Me), 142,1 (s, 1-C_6H_3Me), 190.1 (s, C=S) ppm.
APCI-MS: positive mode, found *m/z* 272.0564, calcd for $C_{15}H_{14}NS_2^+$ *m/z* 272.0567.

Trapping of Bi^I(OTf) to yield compound 7
[Bi(N(C_6H_5)(C_6H_4)(C(S)S))(OTf)(diglyme)] (**3-H**) (220 mg, 0.15 mmol) and 3,5-di-*tert*-butyl-*o*-benzoquinone (**6**) (62 mg, 0.28 mmol) were dissolved in THF (5 mL) and irradiated at 254 nm for 16 h. Traces of a black precipitate formed and the reaction mixture turned orange. The solvent was removed and the residue was washed with pentane (3 x 8 mL). THF (1.5 mL) was added, the suspension containing minor amounts of a dark solid was filtered, and the filtrate was layered with *n*-hexanes (0.5 mL) and stored at –30 °C for two weeks. Crystals had formed, were isolated by filtration, washed with pentane (3 x 5 mL), dried *in vacuo* for 3 h to give compound **7** with two equiv. thf per bismuth atom, which could not be removed under reduced pressure.
Yield: 91 mg (0.13 mmol, 42%)
^{1}H NMR spectroscopic reaction monitoring indicated the formation of **7** in quantitative spectroscopic yield after 16 h reaction time.
^{1}H NMR: (298 K, 500 MHz, THF-d_8): δ = 1.28 (s, 9H, 3-*t*Bu), 1.45 (s, 9H, 5-*t*Bu), 1.75 – 1.81 (m, 8H, β-THF), 3.60 – 3.66 (m, 8H, α-THF), 6.53 (d, $^4J_{HH}$ = 2.23 Hz, 1H, 6-C*H*), 6.58 (d, $^4J_{HH}$ = 2.23 Hz, 1H, 4-C*H*) ppm.
^{13}C NMR: (298 K, 126 MHz, THF-d_8): δ = 26.4 (s, β-THF), 30.3 (s, CH_3 (5-*t*Bu)), 32.5 (s, CH_3 (3-*t*Bu), 34.6 (s, C_q (3-*t*Bu)), 35.1 (C_q (5-*t*Bu), 68.3 (s, α-THF), 114.0 (s, 4-C_6H_2(*t*Bu)$_2$) 119.2 (s, 6-C_6H_2(*t*Bu)$_2$), 121.4 (q, $^1J_{CF}$ = 320 Hz, OTf), 141.8 (s, 3-C_6H_2(*t*Bu)$_2$), 142.3 (s, 5-C_6H_2(*t*Bu)$_2$), 153.8 (s, 2-C_6H_2(*t*Bu)$_2$), 157.8 (s, 1-C_6H_2(*t*Bu)$_2$) ppm.
^{19}F NMR: (298 K, 282 MHz, THF-d_8): δ = –79.26 (s, OTf) ppm.
LIFDI-MS: positive mode, found *m/z* 578.0791, calcd. for $C_{15}H_{20}BiF_3O_5S^+$ *m/z* 578.0787.
Elemental analysis (the sample was dried in a stream of argon). Anal. calc. for $C_{15}H_{20}BiF_3O_5S \times 3$ [C_4H_8O] (794.68 g/mol): C, 40.81; H, 5.58; S, 4.03; found: C, 40.56; H, 5.51; S, 3.64.

Reaction monitoring: formation of 5-H from 3-H

General procedure: a defined amount of **3-H** was dissolved in THF-d_8 (0.5 mL) and the progress of the reaction was monitored by ^{1}H NMR spectroscopy. The reaction conditions are summarized in Table S1.

Table S1. Overview of the conducted reactions to assess the different factors of the transformation of **3-H** to yield **5-H**.

#	Conditions	Concentration	Full Conversion to **5-H**
1	**THF, rt**	$4.08 \cdot 10^{-3}$ mmol/mL	5d
2	**THF, rt**	$13.6 \cdot 10^{-3}$ mmol/mL	5d
3	**THF, rt**	$47.6 \cdot 10^{-3}$ mmol/mL	5d
4	**THF, rt, dark**	$13.6 \cdot 10^{-3}$ mmol/mL	Stable
5	**THF, 60 °C, dark**	$13.6 \cdot 10^{-3}$ mmol/mL	Stable
6	**THF, hv**	$13.6 \cdot 10^{-3}$ mmol/mL	45 min

NMR spectroscopic data of **5-H** has been previously described.[4]

Test reactions of 4-H with 6:

NMR spectroscopic monitoring of reactions of equimolar amounts of **4-H** and **6** in THF indicated coordination of **6** in the dark. After irradiation of the reaction mixture with a low-pressure Hg lamp for up to 16 h, no reaction could be observed, except for minor decomposition reactions. The formation of **7** and carbozole (as the corresponding C–C coupling product) could not be detected. This is in line with Bi–S bonds showing a higher tendency towards photochemical activation than Bi–C bonds.[5]

Investigations of Reactions under Catalytic Conditions: Transformation of 1-R to 4-R

Blind measurement:
In a J. Young-type NMR tube, **1-H** (20.0 mg, 15.8 µmol) was dissolved in THF-d_8 (0.5 mL) and was heated to 60 °C for 4 d. The ^{1}H NMR spectrum revealed that **1-H** is stable under these conditions and the formation of **4-H** was not observed.

Blind measurement:
In a J. Young-type NMR tube, **2-H** (13.0 mg, 0.02 mmol) was dispersed in THF-d_8 (0.5 mL) and was heated to 60 °C for 14 d. A yellow reaction solution was formed and **4-H** was identified by ^{1}H NMR spectroscopy with near-quantitative yield.

Reaction under catalytic conditions:
In a J. Young-type NMR tube, THF-d_8 (0.5 mL) was added to **1-H** (20.0 mg, 15.8 µmol) and **2-H** (0.9 mg, 1.58 µmol, 10 mol%) and the reaction mixture was heated to 60 °C for 4 d. **4-H** was spectroscopically identified with 91% yield.

To **1-H** (20.0 mg, 15.8 µmol) and **2-H** (0.09 mg, 0.16 µmol, 1 mol%) THF-d_8 (0.5 mL) was added and the reaction mixture was heated to 60 °C for 17 d. **4-H** was spectroscopically identified with 84% yield. Full conversion of **1-H** was not achieved at this point.

Single-Crystal X-ray Analyses

Deposition Numbers 2223276-2223278 contain the supplementary crystallographic information for this work. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service under www.ccdc.cam.ac.uk/structures.

Compound 2-H

Compound **2-H** crystallizes from a saturated solution in acetonitrile which was layered with diethyl ether at –30 °C in the orthorhombic space group $P2_12_12_1$ with Z = 4. Its molecular structure in the solid state is depicted in the main part Scheme 1b, and to further clarify the bonding situation also in Figure S2. The discussion of the bonding modes and parameters is presented in the main part. However, it should be noted that the distances between Bi1 and O3 (2.976(5) Å), Bi2 and O5 (2.939(5) Å), as well as Bi3 and O1 (3.029(4) Å) fulfill the distance criteria for Bi–O bond formation (, $\Sigma r_{van\ der\ Waals}$(Bi, O) = 3.59 Å),[6] which could thus be taken into account. In this case, the bismuth centers Bi1 and Bi2 would have a coordination number of six and adopt a distorted octahedral coordination geometry, while Bi3 would show a coordination number of seven (as recently reported for dihalo bismuth cations[7]) and a strongly distorted pentagonal bipyramidal coordination geometry. The CO_2 moieties would show a bridging μ_2-η^2:η^1 coordination mode. We argue that this coordination mode is less likely to be present in this compound, and the proximity of Bi1/O3, Bi2/O5, and Bi3/O1 is rather a result of geometric constraints than of tight binding interactions in this compound, because the chelating bonding mode of the CO_2 moieties would be highly unsymmetric. Thus, while a μ_2-η^2:η^1 coordination mode can formally not be ruled out, we prefer the description in terms of μ_2-η^1:η^1 coordination of the CO_2 moieties in **2-H**. All the Bi–C bonds in **2-H** are in the same range (Ø = 2.203 Å) and thus equal within limits of error to those in **1-H** (2.207(4) Å).[1] In contrast to **3-Me**, insertion of CO_2 does not result in the elongation of the Bi–C bond (*vide infra*).

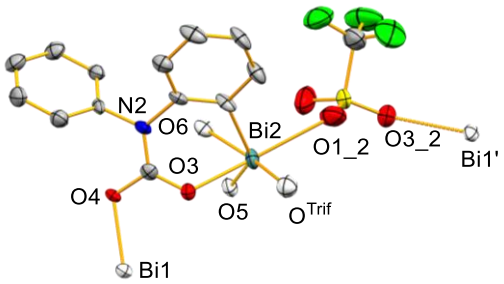


Figure S2. Representation of the mononuclear subunit **2-H** in the solid state. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity and atoms exceeding one subunit are drawn as white ellipsoids.

Compound 2-Me

Compound **2-Me** crystallizes from a saturated diglyme solution which was layered with *n*-hexanes at –30 °C in the monoclinic space group $P2_1$ with Z = 2. The unit cell parameters are: a = 10.178(4) Å, b = 27.160(8) Å, c = 13.043(4) Å, α = 90°, β = 106.577(15)°, γ = 90°, V = 3456(2) Å^3. The quality of the obtained data is not sufficient for a detailed discussion of the bonding parameters but provides a proof of connectivity. The molecular structure in the solid state is shown in Figure S3. The CO_2 moieties are probably best described in a μ_2-η^1:η^1 coordination mode, as observed and discussed for **2-H**. Compound

2-Me exists similarly to **3-H** as a dinuclear complex, but the coordination modes of the CE_2 units differ ((μ_2-η^1:η^1 in **2-H** and **2-Me**, but terminal η^1:η^1 in **3-H**). Due to one bridging triflate unit, both bismuth atoms adopt a distorted pentagonal bipyramidal coordination geometry and are coordinatively saturated by one diglyme ligand each. The second triflate unit does not interact directly with any bismuth atom and can be considered as weakly coordinating anion.

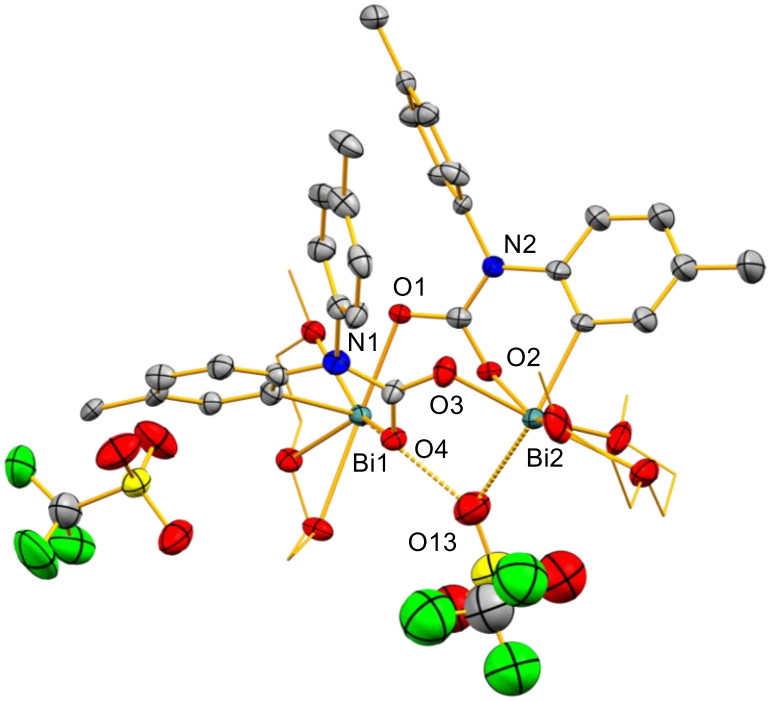


Figure S3. Molecular structure of compound **2-Me** in the solid state. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity, diglyme ligands are depicted in the wireframe model.

Compound 3-H

Compound **3-H** crystallizes from a saturated dimethoxyethane (DME) solution, which was layered with *n*-hexane at ambient temperature, in the triclinic space group $P\bar{1}$ with Z = 2. The unit cell parameters are: a = 10.2847(6) Å, b = 14.4870 (8) Å, c = 16.8468(9) Å, α = 69.701(2)°, β = 79.652(2)°, γ = 89.710(2)°, V = 2311.4(2) Å^3. The quality of the obtained data is not sufficient for detailed discussion of the bonding parameters, but provides a proof of connectivity. The molecular structure of **3-H** in the solid state is shown in Figure S4. It reveals a tetranuclear complex with bridging μ_2-η^1:η^1-coordinated CS_2 units between Bi1 and Bi2 and bridging triflate ligands between Bi1 and Bi1' as well as Bi2 and Bi2'. All bismuth centers adopt a square pyramidal coordination geometry.

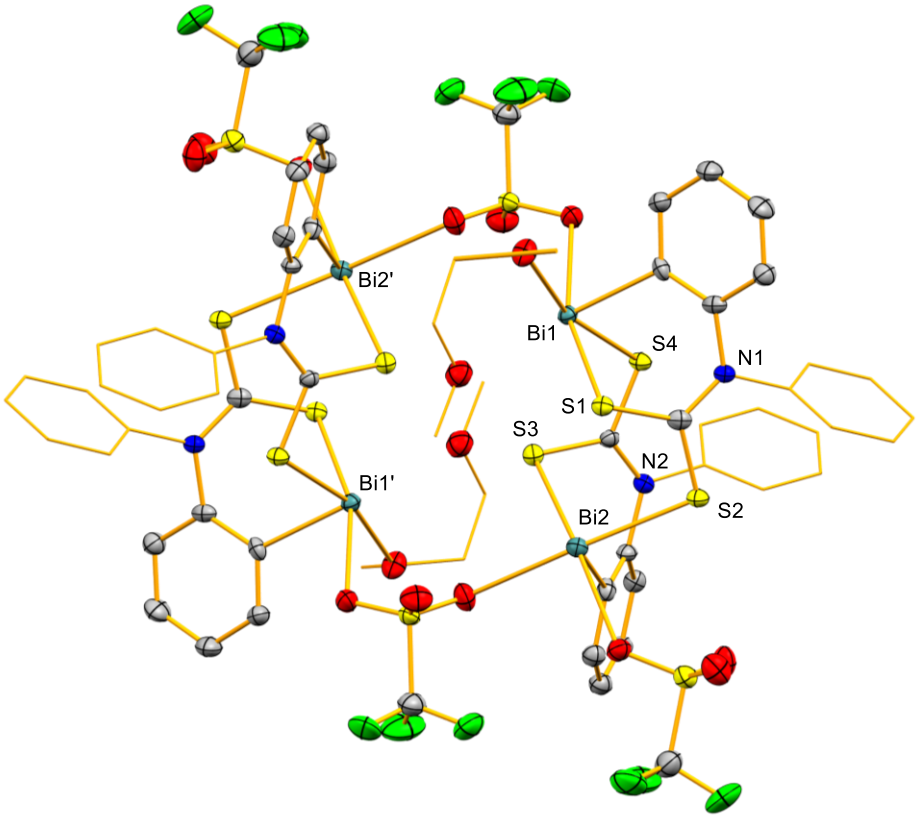


Figure S4. Molecular structure of **3-H** in the solid state. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity, DME ligands and phenyl groups are depicted as wireframe.

Compound 3-Me

Compound **3-Me** crystallizes from a saturated diglyme solution, which was layered with *n*-hexane at –30 °C, in the orthorhombic space group *Pnna* with $Z = 4$, and its molecular structure in the solid state is shown in the main part (Scheme 1c). The unit cell contains multiple disordered molecules of diglyme and *n*-hexane (in superposition) which have been treated as a diffuse contribution to the overall scattering without specific atom positions by Squeeze/Platon. A detailed discussion of the structural parameters is presented in the main part.

Compound 7

Compound **7** crystallizes from a THF solution, which was layered with *n*-hexane at –30 °C, over the period of two weeks in the monoclinic space group $P2_1/c$ with $Z = 2$. The unit cell parameters are: a = 10.2720(19) Å, b = 17.948(3) Å, c = 16.609(3) Å, α = 90°, β = 105.482(7)°, γ = 90°, V = 2950.9(9) Å^3. The quality of the obtained data is not sufficient for detailed discussion of the bonding parameters, but provides a proof of connectivity. The molecular structure in the solid state is shown in Figure S5 and reveals a dinuclear complex. The bismuth atom Bi1 adopts a distorted octahedral coordination geometry. The hydroquinolate moieties act as bridging ligands and appear to be in plane with the two bismuth atoms and the oxygen atoms of two thf ligands. A second thf ligand and a triflate unit bound in the axial positions saturate the coordination sphere of each bismuth atom.

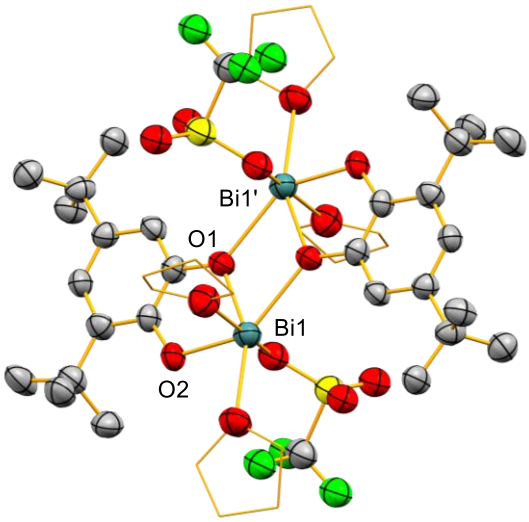


Figure S5. Molecular structure of compound **7** in the solid state. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms and lattice bound THF are omitted for clarity, THF ligands are depicted in the wireframe model.

Compound 4-Me

4-Me crystallized from a THF solution layered with *n*-hexane at –30 °C in the monoclinic space group $P2_1/c$ with Z = 4. The molecular structure of a compound closely related to **4-Me** has previously been described: in the previous example, two pyridine ligands were bound to the bismuth center instead of the two thf ligands that are observed in **4-Me**.[2] This has no significant effect on the bonding parameter and the coordination geometry around bismuth: Bi1 adopts a bisphenoidal coordination geometry with the two thf ligands in the axial positions (O4–Bi1–O5, 167.61(10)°) and the triflate anion forms a hydrogen bond with the NH moiety, while showing a weak interaction with the bismuth center of an adjacent formula unit (not displayed in Figure S6).

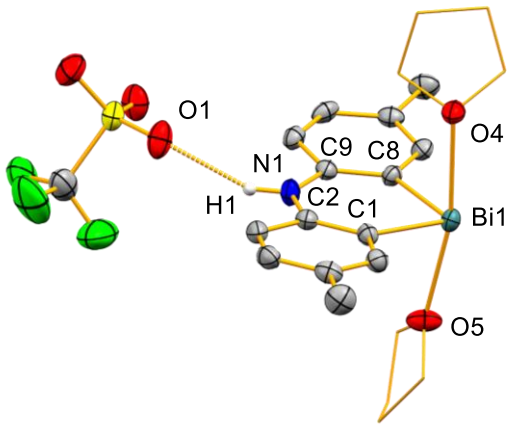


Figure S6. Molecular structure of compound **4-Me** in the solid state. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms but H1 are omitted for clarity, THF ligands are depicted as wireframe. Selected bond lengths [Å] and angles [°]: Bi1–C1, 2.207(4); Bi1–C8, 2.190(4); C1–C2, 1.397(6); C8–C9, 1.408(5); H1···O1, 2.190; C1–Bi1–C8, 90.21(15); C1–Bi1–O4, 84.25(12); C1–Bi1–O5, 85.23(13); O4–Bi1–O5, 167.61(10).

NMR Spectra of Isolated Compounds

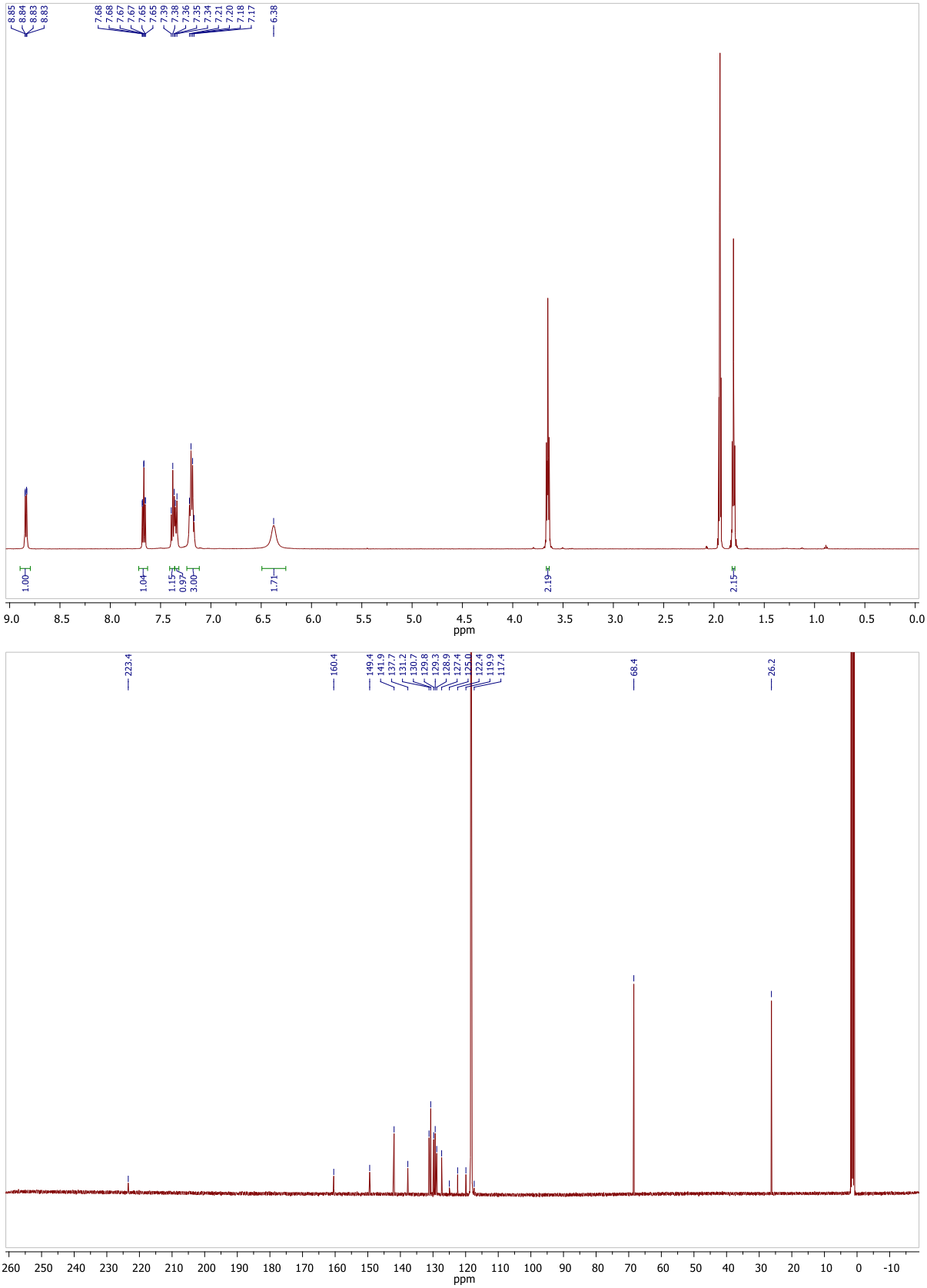


Figure S7. ^{1}H and ^{13}C NMR spectra of [Bi(N(C_6H_5)(C_6H_4)(C(O)O))(OTf)] (**2-H**) in acetonitrile-d_3.

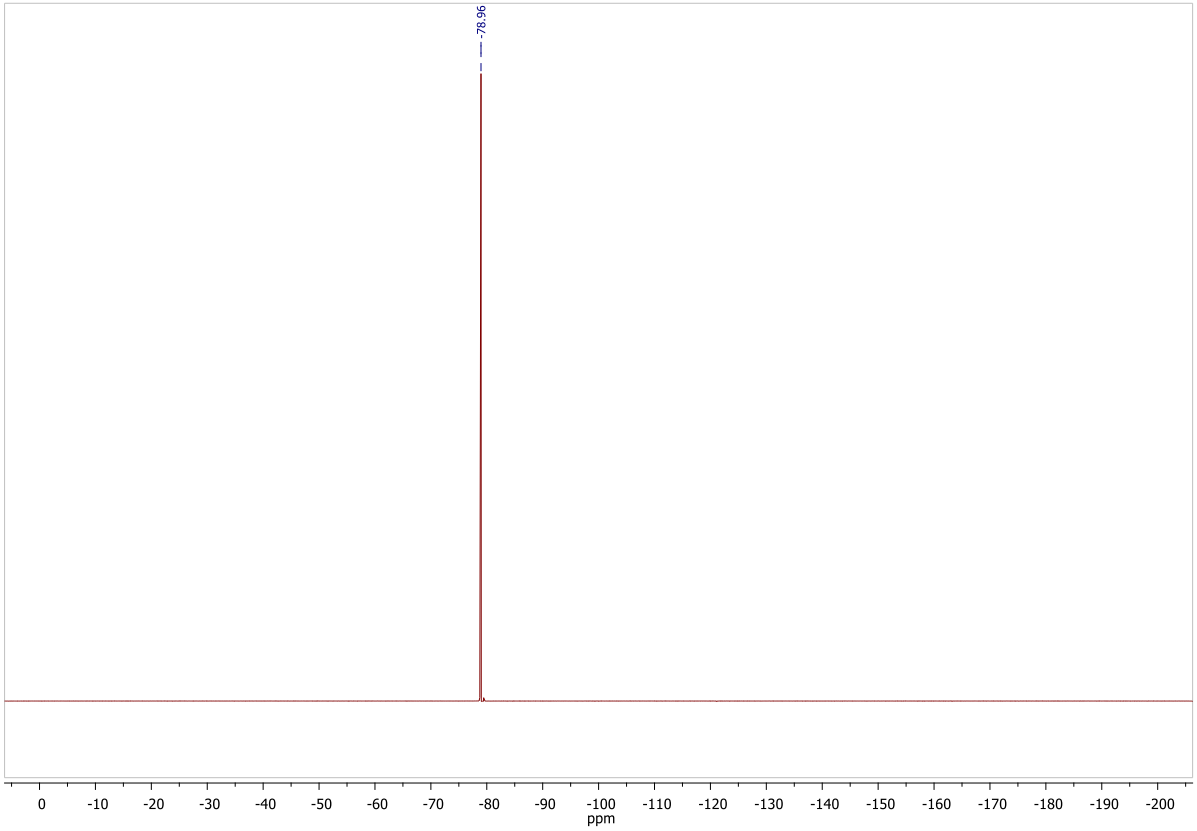


Figure S8. ^{19}F NMR spectrum of [Bi(N(C_6H_5)(C_6H_4)(C(O)O))(OTf)] (**2-H**) in acetonitrile-d_3.

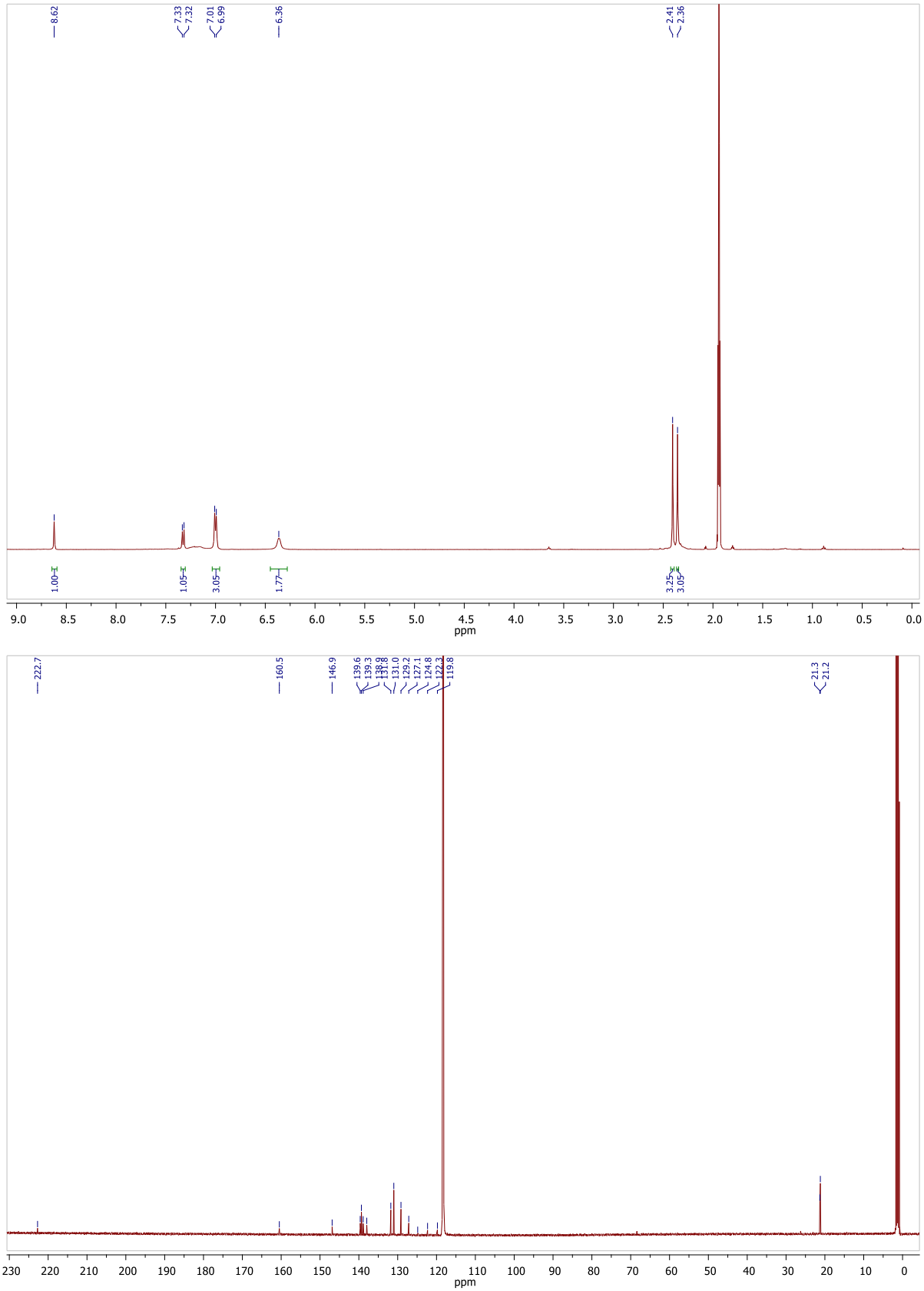


Figure S9. ^{1}H and ^{13}C NMR spectra of [Bi(N(C_6H_4Me)(C_6H_3Me)(C(O)O))(OTf)] (**2-Me**) in acetonitrile-d_3.

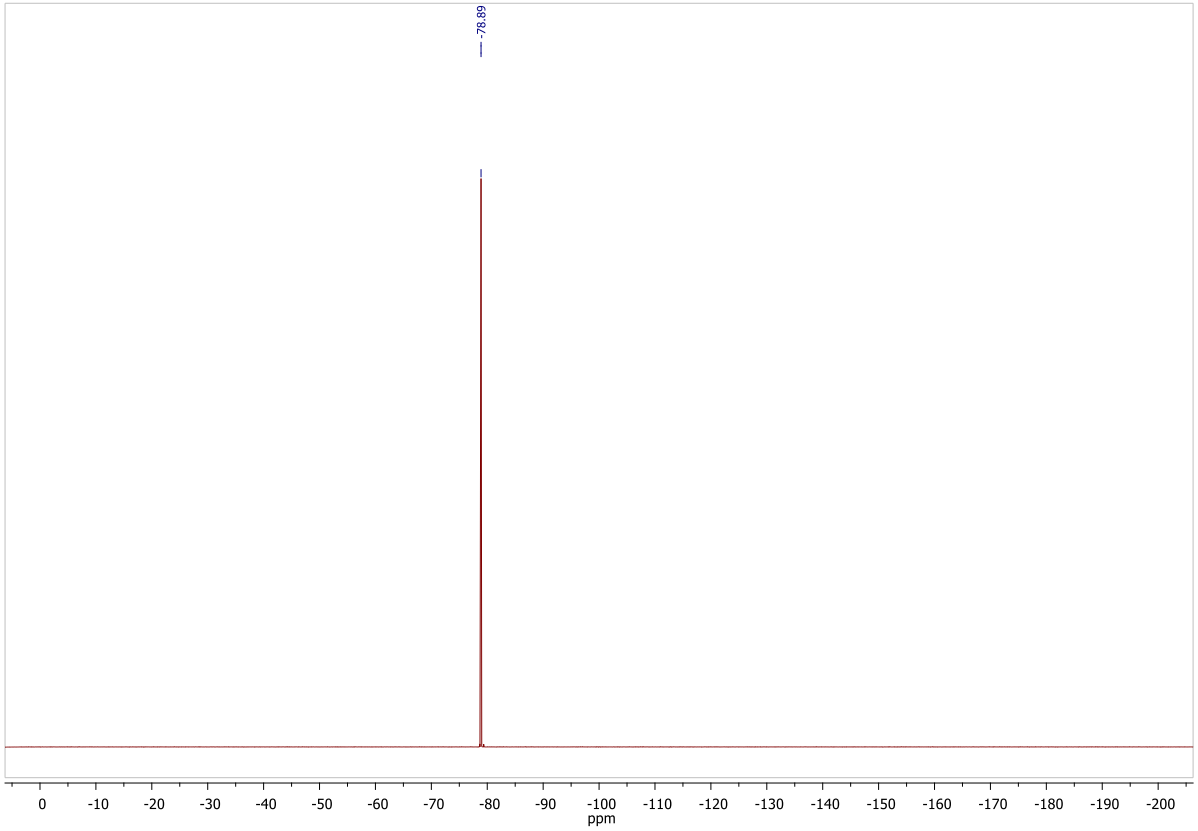
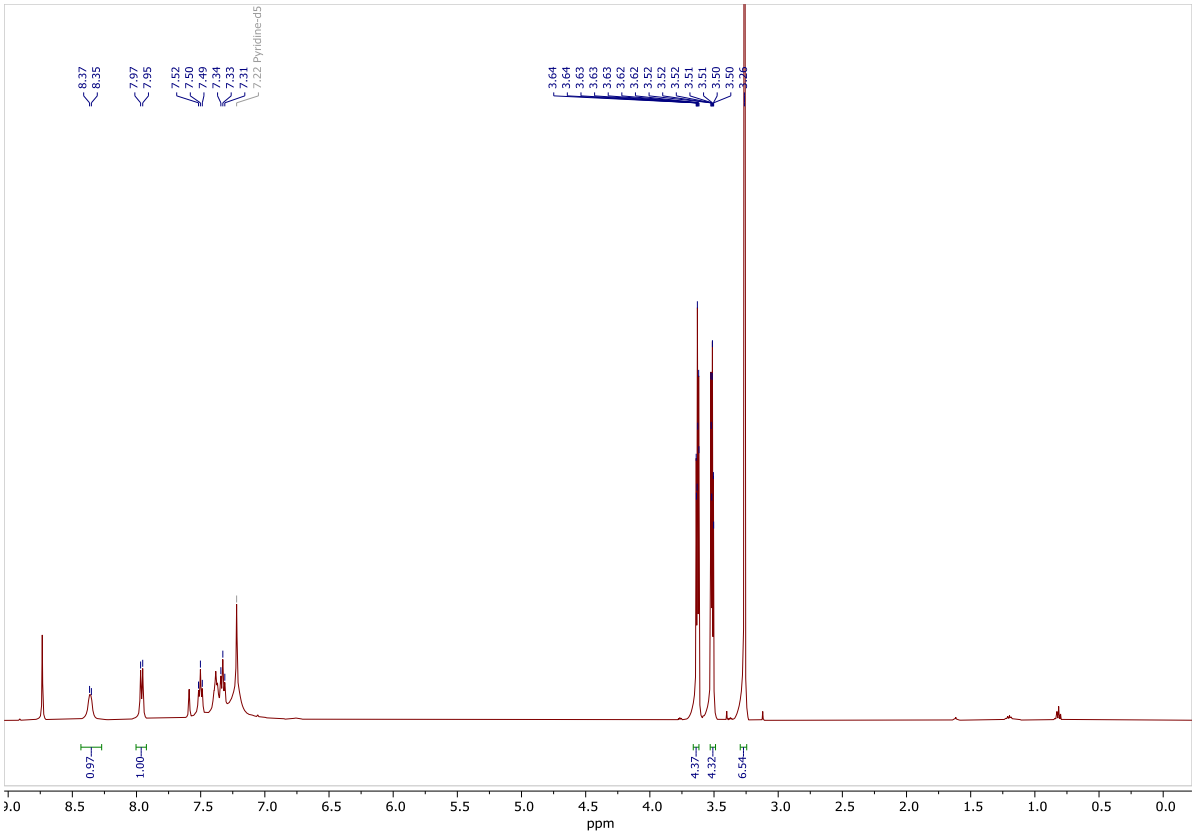


Figure S10. ^{19}F NMR spectrum of [Bi(N(C_6H_4Me)(C_6H_3Me)(C(O)O))(OTf)] (**2-Me**) in acetonitrile-d_3.



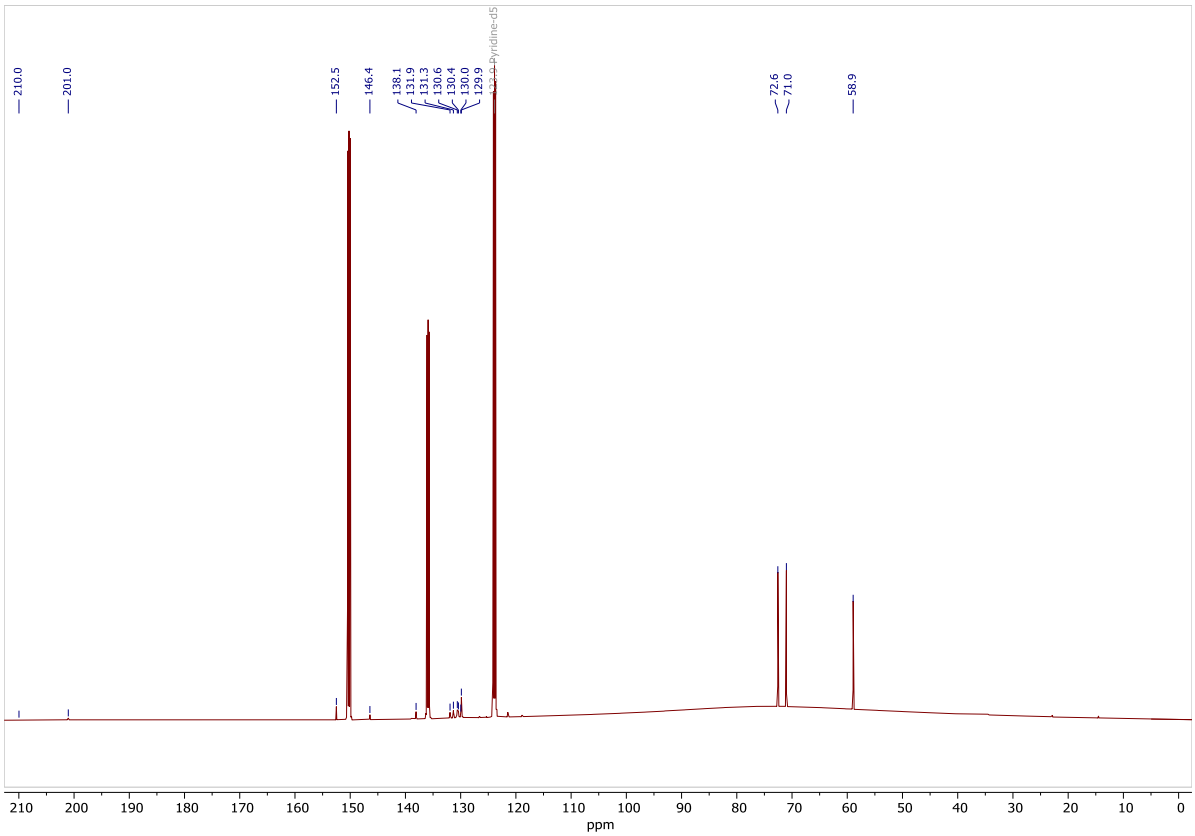


Figure S11. ^{1}H and ^{13}C NMR spectra of [Bi(N(C_6H_5)(C_6H_4)(C(S)S))(OTf)(diglyme)] (**3-H**) in pyridine-d_5.

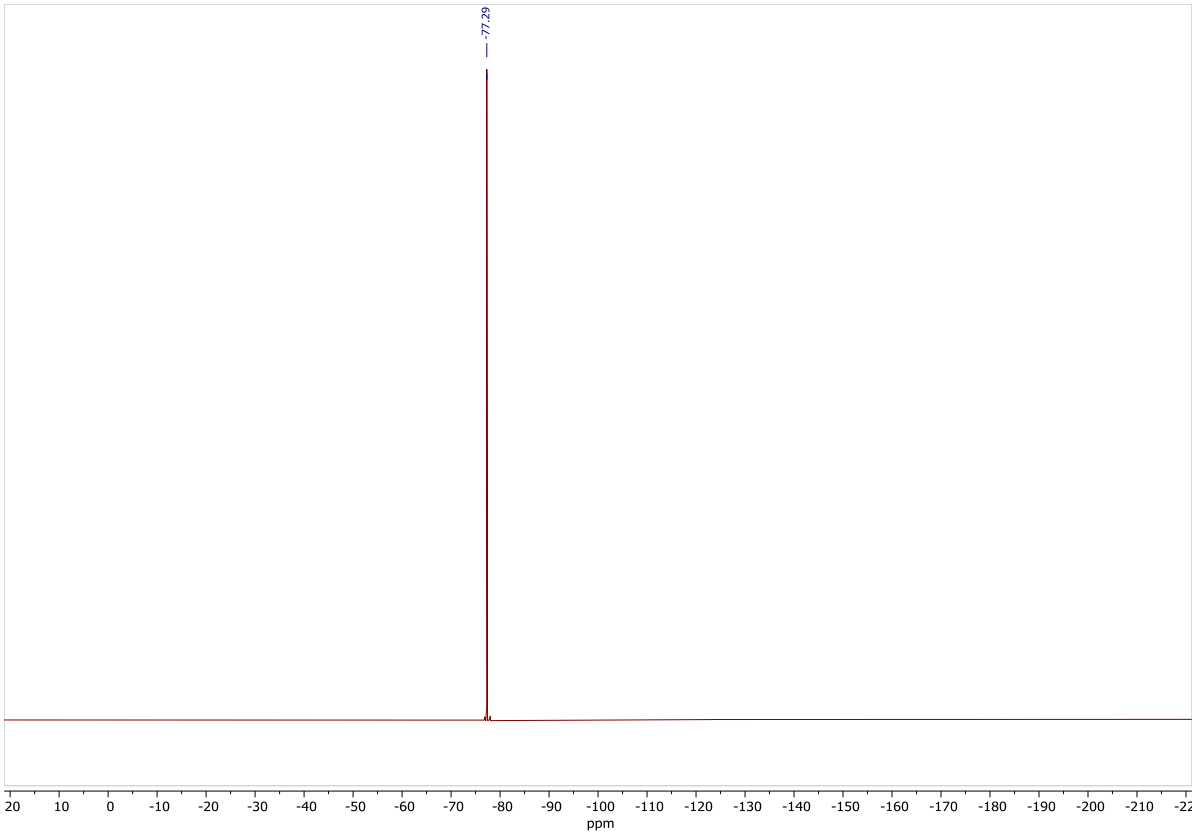


Figure S12. ^{19}F NMR spectrum of [Bi(N(C_6H_5)(C_6H_4)(C(S)S))(OTf)(diglyme)] (**3-H**) in pyridine-d_5.

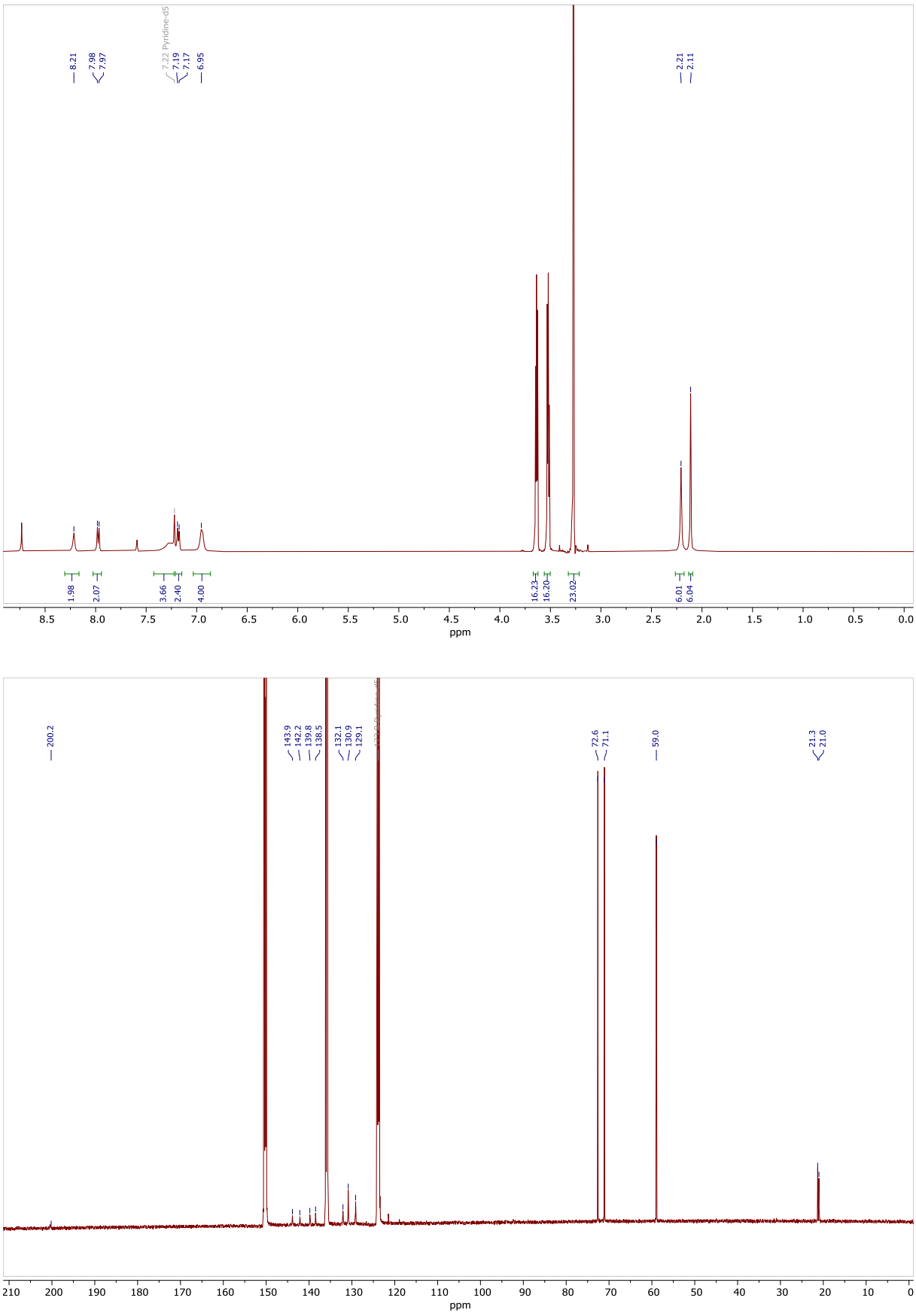


Figure S13. ^{1}H and ^{13}C NMR spectra of [Bi(N(C_6H_4Me)(C_6H_3Me)(C(S)S))(OTf)(diglyme)$_2$] (**3-Me**) in pyridine-d_5.

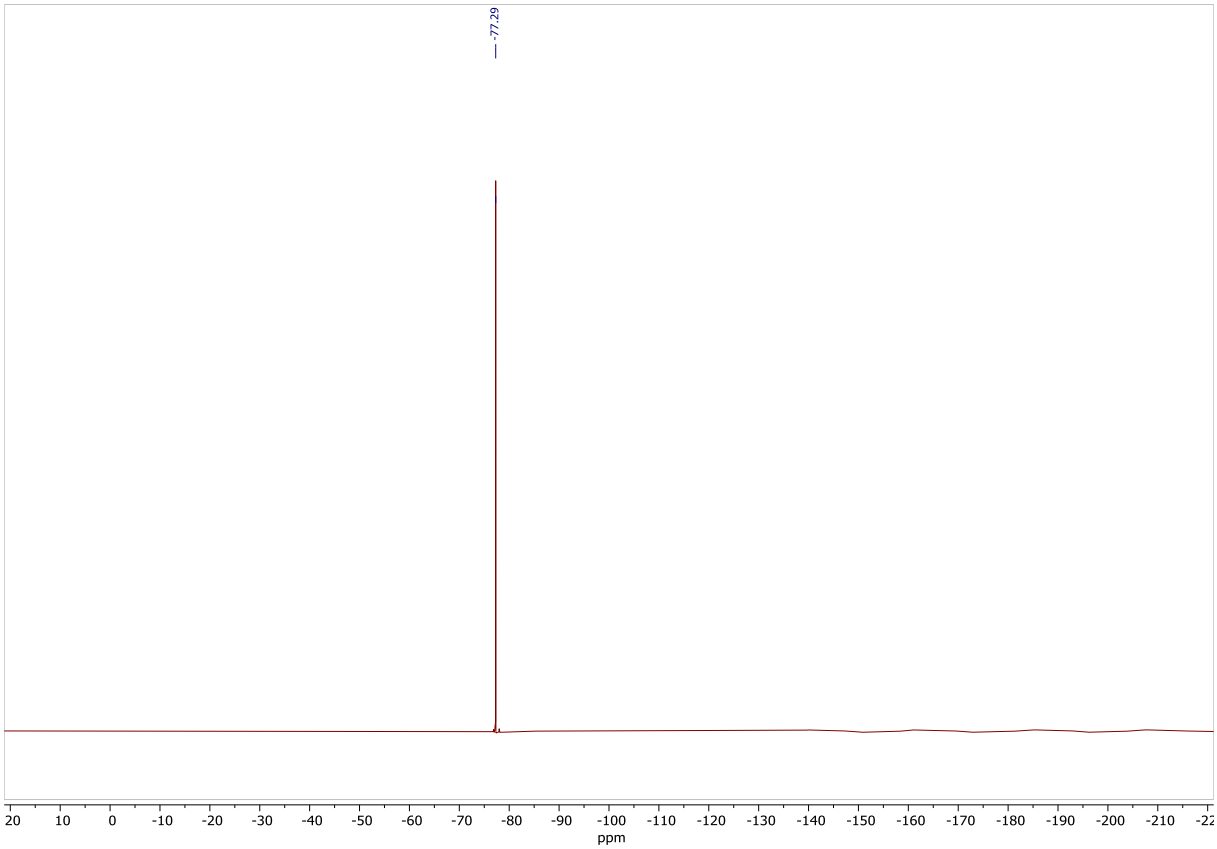


Figure S14. ^{19}F NMR spectrum of [Bi(N(C_6H_4Me)(C_6H_3Me)(C(S)S))(OTf)(diglyme)$_2$] (**3-Me**) in pyridine-d_5.

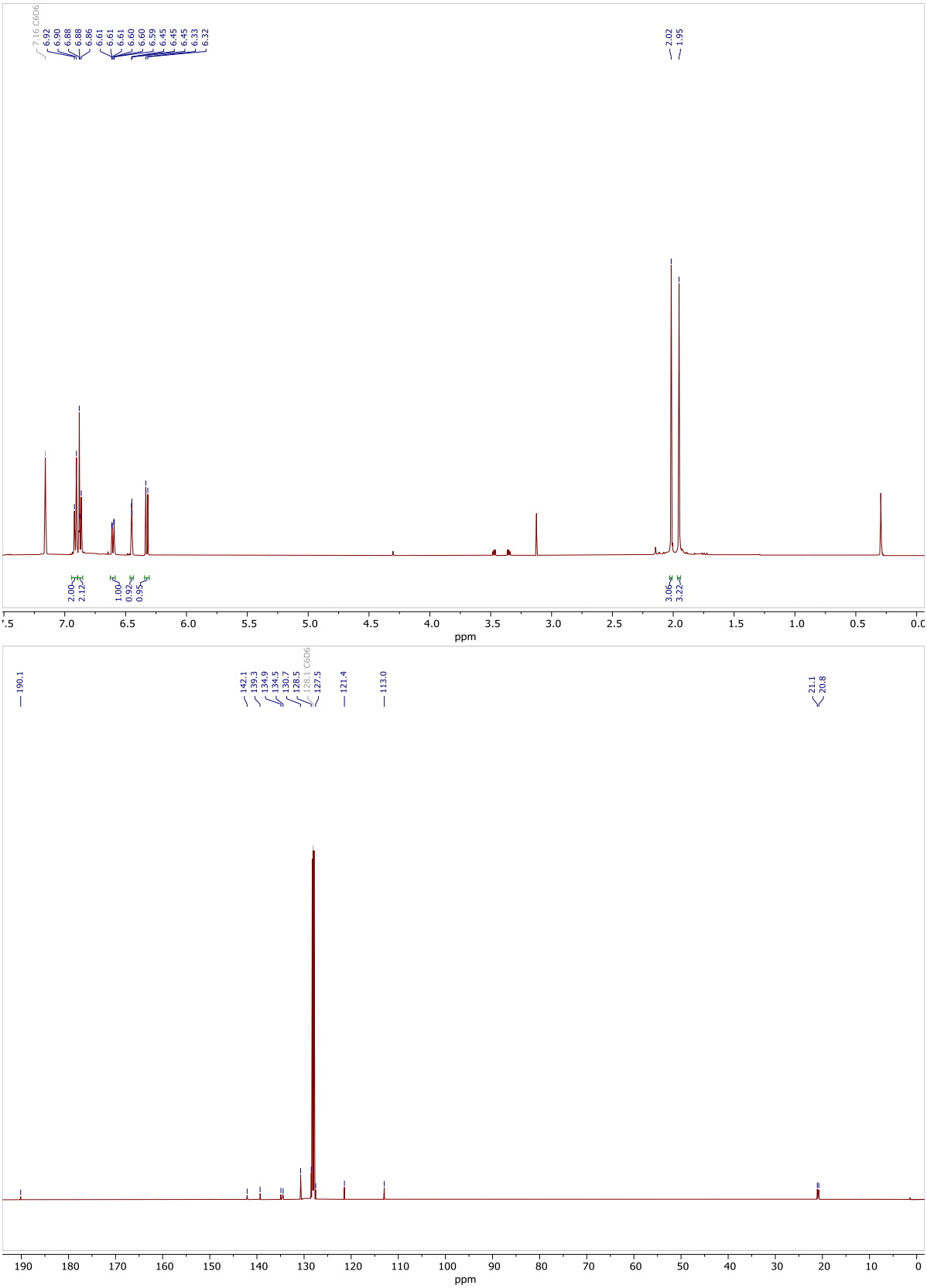


Figure S15. ^{1}H and ^{13}C NMR spectra of the benzothiazolethione **5-Me** in benzene-d_6.

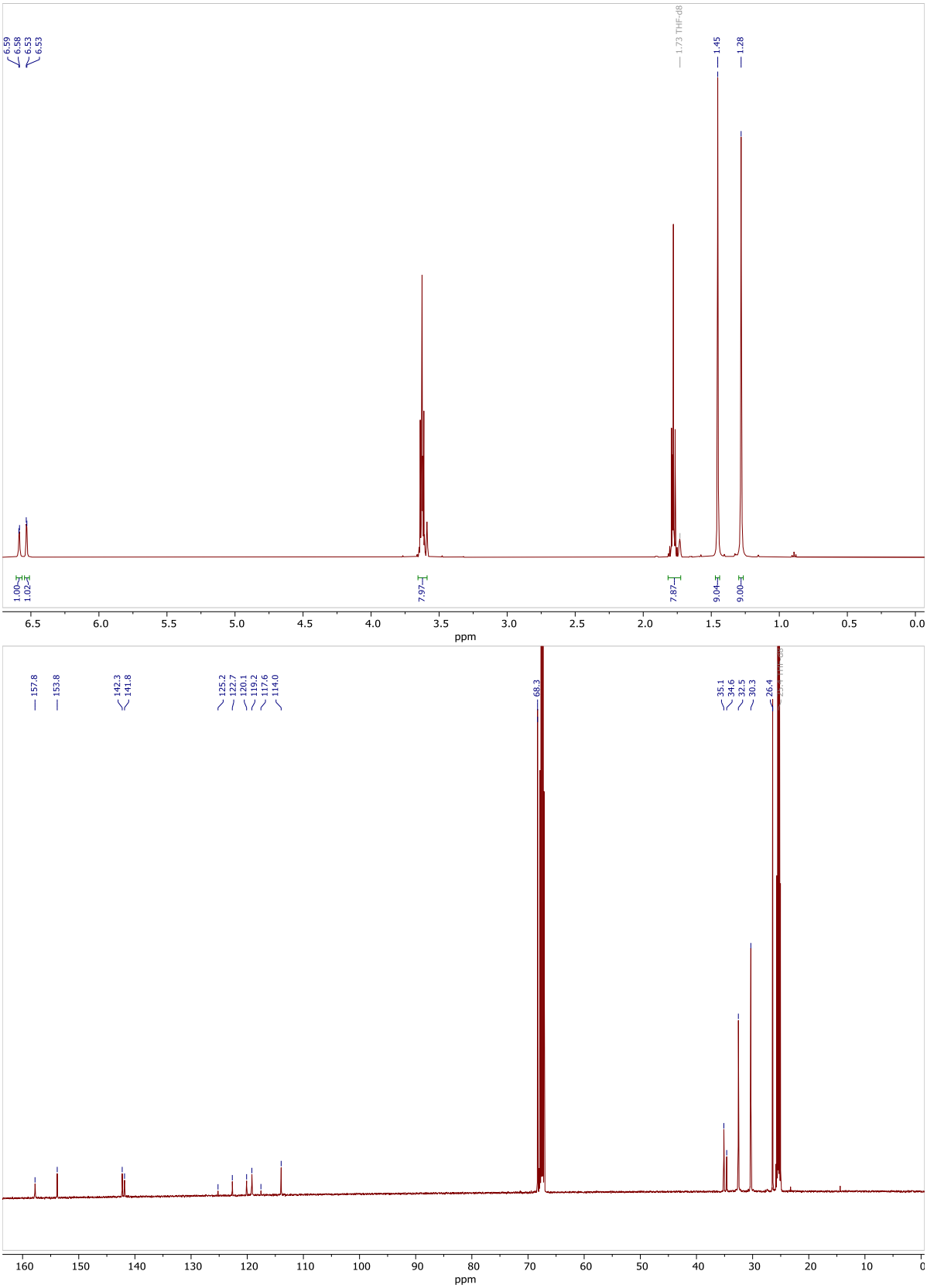


Figure S16. ^{1}H and ^{13}C NMR spectra of compound **7** in THF-d_8.

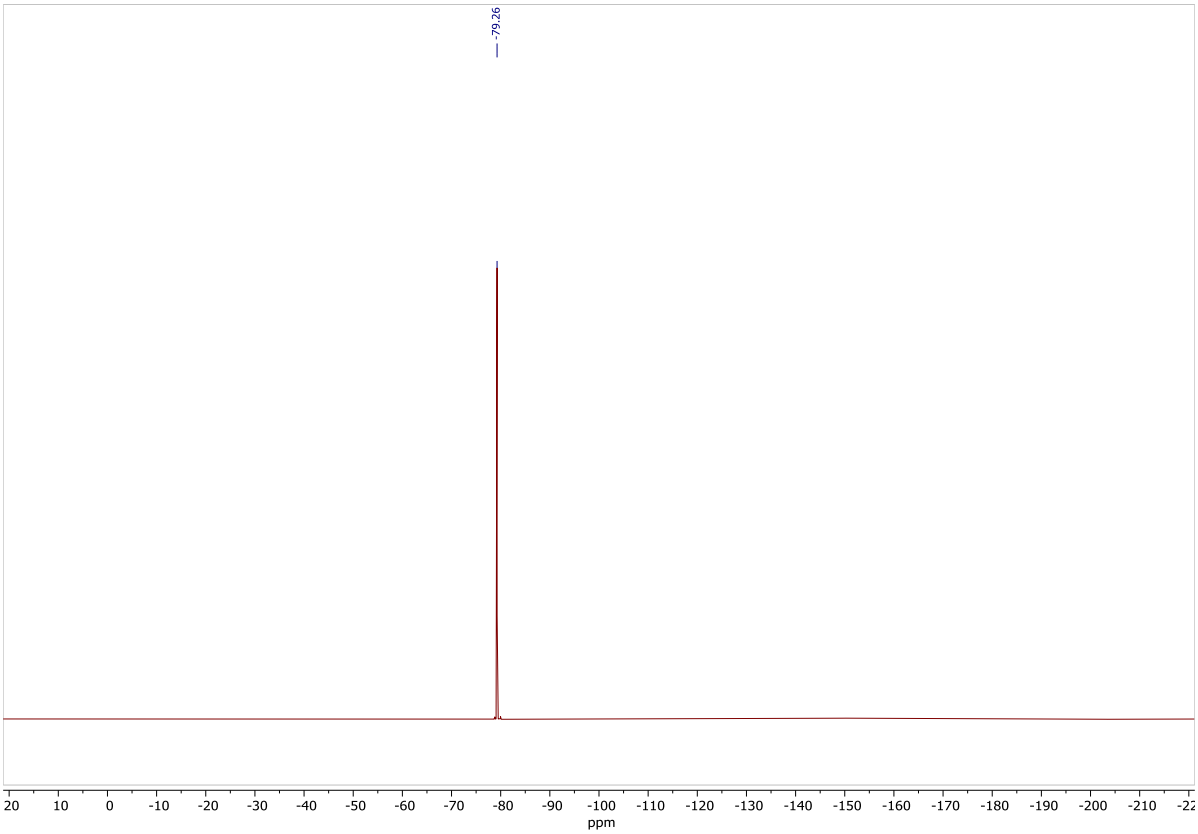


Figure S17. ^{19}F NMR spectrum of compound **7** in THF-d_8.

Diffusion-Ordered NMR Spectroscopy

Samples for DOSY measurements were prepared by dissolving 4 mg of the compounds of interest (**2-H** or **3-H**) in 0.5 mL of a deuterated solvent (see Table S2). NMR spectroscopic measurements were performed on a Bruker AVIII 500 instrument with a cryo probe Prodigy BB-H&F with z-gradient at 298 K. The temperature was calibrated with a Bruker standard (4% methanol in methanol-d_4). DOSY experiments were done using pulse sequences with a long delay for the recovery of the eddy current and bipolar gradients, and with the method of double stimulated echo for compensating the effect of thermal convection on diffusion.[8] Pulse sequences were ledbpgp2s and dstegp3s from the Bruker pulse program library. The gradient shape used was smoothed square SMSQ10.100 and the gradient length was between 2 and 3 ms. The optimized diffusion delays (Δ) were between 30 and 50 ms. Diffusion attenuation was realized with 9 steps in gradient ramp. The DOSY 2D spectra were recorded with 9 experiments and each with 16 to 32 transients. Relaxation delays were 3 s.

Based on the experimentally determined diffusion coefficients, the hydrodynamic radii of **2-H** and **3-H** were calculated. Through a comparison between the experimentally determined hydrodynamic radii and those obtained by the method of hard-sphere increments,[9] the nuclearity of the compounds was estimated. Mononuclear model compounds were used as a starting point and the results are summarized in Table S2.

Table S2. Diffusion coefficients, hydrodynamic radii and extent of aggregation of **2-H** and **3-H** 298 K.

Compound	Solvent	Monomer (model species)	D [$\times 10^{-9}$ $m^2 \cdot s^{-1}$]	R_H [Å]	R_H^{HSI} [Å]	Oligmer (*n*)
2-H	Acetonitrile	$[Bi(NC_6H_4Ph)CO_2(MeCN)_2(O_3SCF_3)]$	0.85	6.9	4.7	trimer(3.2)
3-H	THF	$[Bi(NC_6H_4Ph)CS_2(THF)_2(O_3SCF_3)]$	0.65	7.0	4.9	trimer (2.8)

a: When pyridine was used as the solvent, two species were detected in the ^{1}H NMR spectrum, which were also separated in the diffusion dimension.

Quantum Chemical Analyses

All DFT calculations were performed with the Amsterdam Density Functional (ADF) program[10] 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).[11] Solvation in THF and pyridine was simulated by using the conductor-like screening model (COSMO).[12] All stationary points were verified to be minima on the potential energy surface through vibrational analysis.

Table S3. Cartesian coordinates and ADF total electronic energy (in parentheses and in kcal mol^{-1}) of compounds **2-H** and **3-H** and their dimeric species under analysis computed at the ZORA-BLYP-D3(BJ)/TZ2P level of theory in pyridine.

2-H (-8065.7)

1	Bi	18.84409025	6.19393414	1.89301515
2	C	16.04388166	5.89853035	3.44226236
3	N	15.46404218	5.51442978	2.18267131
4	C	15.17360476	6.00010893	4.54916128
5	H	14.11197627	5.82550567	4.41199328
6	O	15.14755653	5.65473763	-0.08460620
7	C	15.65399074	6.32253327	5.81778577
8	H	14.95420613	6.39295482	6.64718354
9	O	16.97013173	6.63460925	0.77333461
10	C	17.01664398	6.56331378	6.01800651
11	H	17.39786584	6.81635394	7.00427896
12	C	17.88474867	6.48029580	4.92627113
13	H	18.94054498	6.68852149	5.07349971
14	C	17.42102898	6.13970656	3.64800109
15	C	15.85320232	5.93674031	0.89605412
16	C	19.87027077	9.42664602	1.99119752
17	H	20.78103316	8.87355113	1.78086219
18	N	18.74454913	8.69901015	2.14278759
19	C	19.87179774	10.81469967	2.11118522
20	H	20.79860769	11.36531708	1.98289313
21	C	18.67054440	11.46721019	2.39989562
22	H	18.64136717	12.54845902	2.50165579
23	C	17.50678496	10.70864977	2.55712604
24	H	16.55332405	11.17628302	2.78286096
25	C	17.58249657	9.32493676	2.42042074
26	H	16.70894500	8.69067494	2.53162320
27	C	17.67109222	3.35796617	0.31304825
28	N	18.08997703	3.77943677	1.52432363
29	C	17.27477810	2.04164528	0.08521783
30	C	17.32380598	1.13022223	1.14255797
31	C	17.76333924	1.56870109	2.39488107
32	H	17.81409424	0.89452644	3.24428277
33	C	18.13517988	2.90203162	2.54923740
34	H	18.47596533	3.29156748	3.50265565
35	C	23.06407651	5.56504935	2.87341167
36	F	23.92246018	6.54413020	3.25795173
37	O	20.92075364	6.94691634	3.64250619
38	F	23.69156126	4.36760021	2.99283838
39	O	21.96607301	5.39595729	5.30441469
40	F	22.75009775	5.75891785	1.56366588
41	S	21.49257873	5.60300241	3.93319017

42	O	20.66015726	4.51675512	3.35612418
43	H	17.02241987	0.09706121	0.99449434
44	H	16.93559050	1.74481084	-0.90232969
45	H	17.64373816	4.10160685	-0.47812870
46	C	14.27627780	4.68178369	2.24263664
47	C	14.41684201	3.33913745	2.60228133
48	C	13.01137779	5.21416592	1.97380167
49	C	13.28629287	2.52017792	2.69021533
50	C	11.88328734	4.39308420	2.05913517
51	C	12.01766632	3.04510324	2.41777764
52	H	15.40427278	2.94332161	2.81521399
53	H	12.91787456	6.26057406	1.69825857
54	H	13.39810345	1.47462725	2.96756125
55	H	10.89956400	4.80637453	1.84924503
56	H	11.13822956	2.40902300	2.48466212

3-H (-7913.7)

1	Bi	18.74377831	6.19870811	1.81934179
2	C	15.78187177	6.10580854	3.21224047
3	N	15.21617513	5.49297291	2.01832754
4	C	14.86207013	6.45123126	4.22143824
5	H	13.80052251	6.31967379	4.04542941
6	S	14.57138155	5.14921062	-0.57237840
7	C	15.29460136	6.95468265	5.44756100
8	H	14.56047764	7.21667725	6.20525398
9	S	16.76502116	6.91677234	0.24908004
10	C	16.66021683	7.11713550	5.69430067
11	H	17.00988644	7.49573868	6.65167128
12	C	17.57677155	6.79832859	4.68923674
13	H	18.63634626	6.95528662	4.86831724
14	C	17.15815375	6.29292008	3.44826289
15	C	15.46936300	5.79719148	0.70538456
16	C	20.16078624	9.27811908	2.02659784
17	H	20.98200935	8.61082082	1.78201030
18	N	18.94217387	8.71441736	2.15078820
19	C	20.36531302	10.64323882	2.21673433
20	H	21.36192826	11.05961753	2.10574620
21	C	19.27337470	11.44681559	2.55422752
22	H	19.40268108	12.51377966	2.71368338
23	C	18.01212867	10.85779217	2.68470864
24	H	17.13785069	11.44605718	2.94657388
25	C	17.88486137	9.48739861	2.47166372
26	H	16.92691352	8.98269078	2.55262695
27	C	17.61531950	3.38920052	0.16961992
28	N	18.03156965	3.79331730	1.38790378
29	C	17.28488835	2.06126696	-0.09397754
30	C	17.39945084	1.11999861	0.93060564
31	C	17.83965235	1.54020981	2.18940870
32	H	17.94218770	0.84261781	3.01501929
33	C	18.14377995	2.88495988	2.38265446
34	H	18.48967592	3.25874735	3.34039947
35	C	22.87717864	5.50175886	3.02346247
36	F	23.76188912	6.47357033	3.37133222
37	O	20.78650947	6.88744163	3.89367882
38	F	23.50764022	4.30061554	3.09934443
39	O	21.89902544	5.33120430	5.50119151
40	F	22.50838077	5.70856969	1.72667982
41	S	21.35373200	5.54078265	4.15306211
42	O	20.50942765	4.44718402	3.61787455
43	H	17.14889587	0.07781466	0.75343792
44	H	16.94251908	1.78090375	-1.08524924
45	H	17.53672382	4.15499995	-0.59540200
46	C	14.17782478	4.50290564	2.30310099

47	C	14.57057699	3.24818527	2.76597238
48	C	12.82503533	4.82664857	2.16428820
49	C	13.59737344	2.29214073	3.07841024
50	C	11.85697576	3.87279656	2.48535721
51	C	12.24075316	2.60241133	2.93801767
52	H	15.62422777	3.02264586	2.88083855
53	H	12.54019975	5.80994005	1.80348219
54	H	13.90198656	1.31066793	3.43347451
55	H	10.80347406	4.12021165	2.38100976
56	H	11.48394011	1.86153815	3.18396338

2-H dimer (-16136.7)

1	Bi	14.70193168	6.68406917	6.31129773
2	N	13.86940686	8.21496637	3.07033400
3	C	14.49039960	7.22640569	2.36135365
4	O	15.76429863	7.10857244	2.35221912
5	O	13.76171810	6.38144214	1.68939830
6	C	12.46302447	8.49066170	2.93099810
7	C	11.86829724	8.54584780	1.66316851
8	H	12.47056922	8.39277458	0.77600080
9	C	10.49748877	8.78675271	1.55146148
10	H	10.03872746	8.81920224	0.56607058
11	C	9.72032839	8.99506480	2.69744001
12	C	10.32768215	8.97001419	3.95852157
13	H	9.73398407	9.13392147	4.85459062
14	C	11.69691671	8.71776303	4.08046250
15	H	12.15720508	8.67724397	5.06127430
16	H	8.65284670	9.18088616	2.60788824
17	C	14.68298455	9.08281281	3.90036277
18	C	14.95990292	10.36555415	3.41180210
19	H	14.54072864	10.67060567	2.45625724
20	C	15.77647418	11.22832122	4.14506369
21	H	15.99606968	12.22296798	3.76483067
22	C	16.31832668	10.79835938	5.36170850
23	C	16.01705244	9.52144122	5.84636968
24	H	16.42697804	9.22389492	6.80936393
25	C	15.18547533	8.64437960	5.12970380
26	H	16.96308316	11.45838958	5.93769410
27	O	12.29869800	8.55862667	9.80156779
28	F	11.39745171	10.79388131	8.03527869
29	S	13.01331072	8.70281432	8.52712973
30	O	14.48887768	8.56221674	8.59565826
31	O	12.42527306	7.96335370	7.37693567
32	C	12.73047470	10.52186234	8.05792762
33	F	13.24190027	10.79847261	6.83416836
34	F	13.32060405	11.34245011	8.96798714
35	Bi	15.50862413	5.24447365	0.76225593
36	N	13.27261919	4.07991207	3.44421054
37	C	13.62288355	5.06144056	4.34497466
38	O	14.89762696	5.23605155	4.54693704
39	O	12.77759384	5.77135347	4.98630638
40	C	11.97886598	3.95417207	2.84540809
41	C	11.06923164	5.02845168	2.81976366
42	H	11.33324420	5.97458080	3.26790655
43	C	9.82691305	4.87721464	2.20215386
44	H	9.14520375	5.72426991	2.18828837
45	C	9.46681456	3.67037743	1.59231490
46	C	10.38081061	2.61295093	1.59484537
47	H	10.13357791	1.67337653	1.10656736
48	C	11.62726834	2.74869924	2.21066123
49	H	12.32577490	1.92085006	2.18757007
50	H	8.49948494	3.56266708	1.10808277
51	C	14.31607894	3.11553131	3.11411066

52	C	14.33955734	1.93314203	3.86022509
53	H	13.60876556	1.79200217	4.65249564
54	C	15.29313798	0.94925214	3.58750477
55	H	15.30696719	0.03246123	4.17076582
56	C	16.22918603	1.15978670	2.57253199
57	C	16.21698381	2.36166797	1.85267729
58	H	16.97247076	2.51282451	1.08475166
59	C	15.26305605	3.36055359	2.11135959
60	H	16.97705940	0.40218104	2.34860114
61	O	18.08984650	5.19928770	1.70345736
62	S	18.92398640	4.71308374	0.57228458
63	O	20.15833726	4.01963331	0.95819463
64	F	20.25850583	7.05237157	0.65746208
65	C	19.52128015	6.32722814	-0.22438923
66	O	18.12032715	4.07539503	-0.49743082
67	F	18.45591347	7.08302291	-0.61211277
68	F	20.28587632	6.07448330	-1.31854632
69	N	17.13036041	6.38016958	6.15006312
70	C	17.86731867	6.19560663	7.26653390
71	C	17.71182913	6.27870663	4.93263761
72	C	19.22712337	5.90542473	7.20515224
73	C	19.06388703	5.97297413	4.80059905
74	C	19.83447192	5.78634880	5.95116207
75	H	17.34432602	6.27365598	8.21575291
76	H	17.07466663	6.43789396	4.06892381
77	H	19.79001231	5.76826335	8.12304764
78	H	19.48321257	5.87500688	3.80485247
79	H	20.89154156	5.54763465	5.87390494
80	N	15.21024829	3.90325955	7.20409490
81	C	14.17312663	3.29429174	7.81035200
82	C	16.20205863	3.13198361	6.71951111
83	C	14.08879056	1.90770018	7.96180390
84	C	16.20885167	1.74196372	6.83805980
85	C	15.13097102	1.11689587	7.47082441
86	H	13.38217527	3.94307563	8.18465516
87	H	17.00934007	3.64866907	6.20678573
88	H	13.22702211	1.46547197	8.45400086
89	H	17.03389615	1.16642779	6.42872542
90	H	15.09982481	0.03514824	7.57220695
91	N	14.83219730	7.72084131	-0.89068251
92	C	15.26066498	8.87490341	-0.33988811
93	C	13.78800338	7.78049690	-1.74078935
94	C	14.66314695	10.11035697	-0.59997626
95	C	13.12691509	8.97004123	-2.05594126
96	C	13.57098184	10.15895383	-1.47014302
97	H	16.09986508	8.79592739	0.34755500
98	H	13.46875320	6.83735196	-2.17916601
99	H	15.04694554	11.01013543	-0.12727062
100	H	12.28467605	8.95940223	-2.74227554
101	H	13.07654007	11.10202493	-1.68730098
102	N	13.54133595	4.29603831	-0.43809733
103	C	13.71778703	3.12995626	-1.09458202
104	C	12.33758615	4.90769455	-0.48062915
105	C	12.69631806	2.53735965	-1.83151027
106	C	11.27367389	4.37504282	-1.20273085
107	C	11.45395532	3.17398262	-1.89175672
108	H	14.69896934	2.66801999	-1.01728647
109	H	12.24426188	5.82099571	0.09395931
110	H	12.87775131	1.59842340	-2.34505546
111	H	10.31940858	4.89072570	-1.20814115
112	H	10.63770313	2.73586333	-2.45910329

3-H dimer (-15850.5)

1	Bi	15.03688894	6.68716158	6.05151478
2	N	13.47346211	8.36989280	3.00165572
3	C	13.95511269	7.45379576	2.13353547
4	S	15.65433061	7.33305291	1.88777046
5	S	12.87451530	6.38388884	1.27276546
6	C	12.06912442	8.68403802	3.13812071
7	C	11.31182089	9.04348884	2.01698020
8	H	11.77422333	9.06699684	1.03654815
9	C	9.96307384	9.37304494	2.17518261
10	H	9.37393821	9.65231908	1.30524250
11	C	9.37910084	9.35847639	3.44783957
12	C	10.15244184	9.02162295	4.56553176
13	H	9.70927102	9.01902370	5.55809936
14	C	11.50031725	8.68643891	4.41623306
15	H	12.09907929	8.43440692	5.28342326
16	H	8.33037349	9.61867811	3.56830756
17	C	14.39713227	9.20826610	3.76185924
18	C	14.51011336	10.53641701	3.33259661
19	H	13.92395097	10.87056246	2.48176647
20	C	15.37376367	11.41207503	3.99040539
21	H	15.46554620	12.44108113	3.65213095
22	C	16.11582118	10.95144594	5.08219931
23	C	15.97828046	9.62652649	5.50807660
24	H	16.54923726	9.30552638	6.37610291
25	C	15.11881567	8.72095565	4.86018472
26	H	16.79148153	11.62176088	5.60876950
27	O	12.62927645	8.22696619	9.81269895
28	F	11.32935971	10.29260850	8.03768931
29	S	13.26827147	8.48639001	8.51439499
30	O	14.74350727	8.58379456	8.52529444
31	O	12.74414444	7.66819601	7.38644980
32	C	12.68949894	10.23937754	8.07255307
33	F	13.16093065	10.62111498	6.86011917
34	F	13.12779614	11.13116886	9.00306803
35	Bi	15.05998188	5.34998060	0.09111263
36	N	13.62185356	3.58465595	3.13734719
37	C	14.01178323	4.55931910	3.99444988
38	S	15.70947256	4.82203175	4.23885376
39	S	12.85584192	5.54325794	4.81340314
40	C	12.25215972	3.12093056	3.07818696
41	C	11.64127160	2.60499671	4.22691565
42	H	12.18693097	2.58061318	5.16362833
43	C	10.33010089	2.13001746	4.15244653
44	H	9.85299231	1.72914042	5.04332593
45	C	9.63647882	2.16130760	2.93536570
46	C	10.26111762	2.66740618	1.78949319
47	H	9.73013622	2.69240500	0.84129925
48	C	11.57148325	3.14830318	1.85932736
49	H	12.06288866	3.54525684	0.98213991
50	H	8.61659733	1.78894564	2.88061896
51	C	14.61472308	2.82247836	2.39200338
52	C	14.83770711	1.50680510	2.81927159
53	H	14.26232062	1.11508651	3.65417509
54	C	15.79813182	0.71718596	2.18487307
55	H	15.97100752	-0.30159147	2.52209379
56	C	16.54141686	1.25312256	1.12879597
57	C	16.30342386	2.56575506	0.70553564
58	H	16.89936046	2.96409919	-0.11324735
59	C	15.32974030	3.37485511	1.31763115
60	H	17.30285131	0.65442094	0.63427905
61	O	17.74162126	5.41050225	-0.15630988
62	S	18.70583804	5.71445149	0.94654861
63	O	18.83085451	7.14500069	1.25874845

64	F	20.56305519	6.05076405	-0.99283583
65	C	20.35616364	5.28674494	0.11578277
66	O	18.63289683	4.79935944	2.08962585
67	F	20.39105953	3.97830182	-0.26095428
68	F	21.39107136	5.50467445	0.97639118
69	N	17.63095943	6.86103819	5.88200140
70	C	18.37906180	6.69343567	6.99219741
71	C	18.24465540	7.05782858	4.69589011
72	C	19.77205062	6.72332742	6.95731013
73	C	19.63250427	7.09096794	4.57988083
74	C	20.40962693	6.92461241	5.72906350
75	H	17.83974683	6.53611049	7.92358268
76	H	17.60474063	7.18575862	3.82878860
77	H	20.33852897	6.58967354	7.87409392
78	H	20.07496667	7.23660513	3.60004866
79	H	21.49455804	6.94821957	5.67015547
80	N	14.37184966	4.11367665	7.60293751
81	C	13.14022863	4.17959012	8.14649898
82	C	14.79491622	2.91900429	7.14606151
83	C	12.29626277	3.07192769	8.25907273
84	C	14.01882952	1.75912374	7.21210503
85	C	12.74388034	1.83731998	7.78073892
86	H	12.81646030	5.16222819	8.48457962
87	H	15.78534958	2.89942910	6.69661087
88	H	11.31072449	3.18127305	8.70341329
89	H	14.40674876	0.82085760	6.82458060
90	H	12.11111863	0.95567260	7.84449957
91	N	15.07825950	8.10751024	-1.55544498
92	C	16.35664510	8.47720085	-1.32871927
93	C	14.10602811	8.92372657	-1.09901963
94	C	16.70809155	9.64905460	-0.65543917
95	C	14.36306641	10.11185639	-0.41301370
96	C	15.69130471	10.48156162	-0.18493933
97	H	17.12529924	7.78929080	-1.67530759
98	H	13.08273007	8.60132138	-1.28349011
99	H	17.75505678	9.88264477	-0.48556229
100	H	13.53893416	10.72907020	-0.06564298
101	H	15.92708754	11.39217329	0.35904088
102	N	13.15873159	3.95195235	-1.15738366
103	C	13.21621340	2.60942315	-1.27610948
104	C	12.11351472	4.61120683	-1.69945853
105	C	12.22466711	1.87791011	-1.92765205
106	C	11.07866780	3.95122380	-2.36026881
107	C	11.13363596	2.55921851	-2.47410711
108	H	14.07217036	2.12133318	-0.81834774
109	H	12.10978128	5.69220623	-1.58380221
110	H	12.30781299	0.79739292	-1.99601050
111	H	10.25059591	4.52032404	-2.77183498
112	H	10.34046121	2.01542613	-2.97971371

Table S4. Thermodynamic data (in kcal mol^{-1}) of the dimerization of **2-H** and **3-H** computed at the ZORA-BLYP-D3(BJ)/TZ2P level of theory in pyridine and in vacuo.

	pyridine		***vacuo***	
	Δ*E*	**Δ*G***	**Δ*E***	**Δ*G***
2-H dimer	-5.3	10.9	-15.8	-4.5
3-H dimer	-23.1	-8.8	-29.6	-20.4

When using a pyridine solvent model (COSMO), a monomeric species is **2-H** is favored, while a dinuclear species of **3-H** is slightly preferred. Since a higher reactivity of mononuclear species has been suggested for closely related systems based on combined experimental and theoretical approaches,[1,13] the following mechanistic investigations were performed with mononuclear species not only for **2-H** (and related compounds), but also for **3-H** (and related compounds).

Table S5. Cartesian coordinates and ADF total electronic energy (in parentheses and in kcal mol^{-1}) of compounds involved in the mechanism for the extrusion of CE_2 (E = O, S) from **2-H** and **3-H** to give **4-H**, computed at the ZORA-BLYP-D3(BJ)/TZ2P level of theory in THF.

2-H (-8089.1)

1	C	-2.59996800	-0.17561305	-3.48615642
2	C	-4.12966884	5.46602302	-2.32706667
3	H	-3.26231860	-0.27921828	-4.34233698
4	C	-4.29149996	3.57052792	-0.81993405
5	H	-4.58118284	6.33757903	-2.79479366
6	Bi	0.22332603	0.07593138	0.70706340
7	S	3.14381444	-1.15536502	-0.56177091
8	N	-2.35442747	2.05771357	-0.51698022
9	C	3.39395046	-0.93697660	-2.43070318
10	O	3.10508165	0.23447560	-0.05171832
11	C	-4.86799399	4.69252527	-1.42195712
12	C	-2.04093683	0.97039791	-1.40179801
13	C	-0.93266171	0.10411611	-1.24346805
14	H	-5.89547613	4.95998656	-1.18703900
15	O	4.27612290	-1.98369608	-0.14182538
16	O	1.80604876	-1.81685217	-0.46922161
17	C	-2.96890212	3.22660687	-1.11742748
18	F	4.60388661	-0.37304285	-2.67724772
19	C	-2.22948166	3.99252315	-2.02407078
20	H	-1.21126713	3.70448112	-2.26353349
21	H	-4.85771878	2.96450565	-0.11903989
22	C	-2.80995266	5.11118004	-2.62952353
23	H	-2.23058024	5.70438985	-3.33291277
24	F	3.33673893	-2.13588400	-3.06485487
25	C	-2.87192739	0.80085509	-2.52918011
26	H	-3.73568376	1.44536346	-2.65435752
27	C	-0.67906365	-0.87571245	-2.21474567
28	H	0.16941236	-1.53921211	-2.08635821
29	C	-1.49212994	-1.01610295	-3.34162360
30	H	-1.26961888	-1.77586483	-4.08675345
31	F	2.43097168	-0.12934596	-2.94968262
32	C	0.91578442	3.48735914	1.12614495
33	C	-0.45979154	-3.25955060	1.30262553
34	C	1.46380862	4.34492373	-1.04941268
35	H	2.25745052	2.29574089	-1.32202335
36	H	0.57964647	2.48799743	-1.89637536
37	C	0.72087888	4.72330749	0.25662535
38	H	0.14592469	3.33968499	1.88496408
39	H	1.91477166	3.44103786	1.57673939
40	H	1.04496240	4.85143103	-1.92311023
41	H	2.52225795	4.61284822	-0.97650563
42	H	1.13041640	5.62364672	0.72292969
43	C	-2.41138377	-3.22945290	-0.16276095
44	H	-3.07092849	-2.38534231	1.76653044
45	H	-2.80589381	-1.14158261	0.51377513
46	C	-0.99689716	-3.86641701	0.00433375
47	H	0.62063067	-3.11573873	1.32310640
48	H	-0.78562536	-3.81423220	2.19048252
49	H	-2.53633299	-2.82456375	-1.16928056
50	H	-3.20521883	-3.95999708	0.01541574
51	H	-1.03578751	-4.95772314	0.06153147
52	H	-0.34828770	-3.58867875	-0.83048090
53	H	-0.34699170	4.87598328	0.07036685
54	O	-2.53481406	3.08887143	1.52540490
55	C	-2.17115972	2.09718194	0.87963262

56	O	-1.62112852	1.04032697	1.46425403
57	O	0.78011749	2.38302789	0.15950698
58	C	1.31123093	2.81423523	-1.15415539
59	O	-1.08338682	-1.92327222	1.36858583
60	C	-2.47201886	-2.10623048	0.89332244

3-H (-7937.1)

1	C	-3.05124202	-0.26693723	-3.19826219
2	C	-3.66260695	5.55185759	-2.91239796
3	H	-3.77834391	-0.43836633	-3.98788084
4	C	-4.27803277	3.83895334	-1.30803465
5	H	-3.94073623	6.39350183	-3.54192911
6	Bi	0.05654282	0.10023800	0.77621814
7	S	3.04890059	-1.08808933	-0.72621630
8	N	-2.56701394	2.24090251	-0.48662570
9	C	3.12484760	-0.60129441	-2.55860412
10	O	3.12040681	0.20825067	-0.01842266
11	C	-4.63090597	4.91781891	-2.12113986
12	C	-2.32960857	1.03923670	-1.26799013
13	C	-1.21503444	0.18783787	-1.11408903
14	H	-5.66127759	5.26424749	-2.13691358
15	O	4.19216656	-1.99112717	-0.55086319
16	O	1.71205648	-1.73550792	-0.61647852
17	C	-2.95207693	3.39704300	-1.29281856
18	F	4.28981076	0.04155761	-2.83538408
19	C	-1.98490850	4.00975333	-2.08878645
20	H	-0.96815696	3.63587023	-2.07934264
21	H	-5.01693524	3.34557066	-0.68429342
22	C	-2.34057045	5.09528869	-2.89670331
23	H	-1.58630892	5.57749127	-3.51352744
24	F	3.04086237	-1.70059820	-3.35298769
25	C	-3.24383214	0.78977218	-2.30836955
26	H	-4.10850248	1.43408931	-2.42432035
27	C	-1.02959950	-0.86089238	-2.02904495
28	H	-0.16692126	-1.51026147	-1.92022090
29	C	-1.92823197	-1.08807595	-3.07477499
30	H	-1.75535693	-1.90096711	-3.77577446
31	F	2.09382242	0.23111122	-2.87534469
32	C	0.85185951	3.43408913	1.34121177
33	C	-0.21980183	-3.34188800	1.29407065
34	C	1.52565331	4.37133168	-0.78701034
35	H	2.31907190	2.31004978	-0.88085005
36	H	0.78539532	2.50243153	-1.76713852
37	C	0.84846605	4.74474235	0.56250022
38	H	0.04805483	3.33781039	2.07222873
39	H	1.82406447	3.21458473	1.80014450
40	H	1.05595523	4.89305477	-1.62462330
41	H	2.58730960	4.63305550	-0.77895505
42	H	1.38508113	5.53671062	1.09205983
43	C	-2.15924162	-3.71806319	-0.10913623
44	H	-2.99234223	-2.66237803	1.64408239
45	H	-2.73923470	-1.59576595	0.23792849
46	C	-0.64925011	-4.06925201	0.02326138
47	H	0.83056030	-3.05149178	1.31551734
48	H	-0.48201023	-3.89543326	2.20418074
49	H	-2.42891694	-3.51617344	-1.14855100
50	H	-2.78640705	-4.53687758	0.25466591
51	H	-0.47616554	-5.14691372	0.09296087
52	H	-0.08206542	-3.68100230	-0.82675757
53	H	-0.18603461	5.06410073	0.40325704
54	S	-2.86073218	3.85921590	1.63911799
55	C	-2.50851646	2.39688323	0.87303113
56	S	-2.09592511	1.03127790	1.93715051

57	O	0.58554461	2.43790734	0.28804089
58	C	1.36402213	2.83860310	-0.90472561
59	O	-1.01780797	-2.10100306	1.28321137
60	C	-2.35898299	-2.46479658	0.77375510

Int-1-O (-8071.4)

1	C	-3.56421815	1.91100499	-3.07127428
2	C	-1.38230151	1.99770620	3.87945981
3	H	-4.21062476	2.30960999	-3.84965090
4	C	-2.29786264	2.54292625	1.69123862
5	H	-0.75090458	2.25516162	4.72494104
6	Bi	-0.58314972	0.14122601	0.61559009
7	S	1.61729013	-2.01705286	-0.65797611
8	N	-3.80706807	0.99258398	0.53832872
9	C	3.26521441	-1.21590742	-1.15132775
10	O	1.67816045	-2.18138328	0.79845071
11	C	-1.48177148	2.86160304	2.77996559
12	C	-3.25546896	1.22937816	-0.75800748
13	C	-1.91080919	0.90840646	-1.05336891
14	H	-0.93596643	3.80123392	2.77381410
15	O	1.48623368	-3.20118752	-1.49683554
16	O	0.62837591	-0.91720171	-1.05798032
17	C	-3.03712461	1.32899588	1.66782190
18	F	4.28156648	-2.05850899	-0.86032861
19	C	-2.90803201	0.45216058	2.77924850
20	H	-3.45791900	-0.48033821	2.77848203
21	H	-2.38486129	3.22804534	0.85340103
22	C	-2.10338562	0.79879115	3.87024258
23	H	-2.02884242	0.11203494	4.70950350
24	F	3.27701460	-0.94596622	-2.47627827
25	C	-4.06809351	1.74440582	-1.78013224
26	H	-5.09850499	1.99996818	-1.55313092
27	C	-1.41339566	1.07352994	-2.35150392
28	H	-0.38916434	0.79662624	-2.58460156
29	C	-2.23841442	1.57071642	-3.36639042
30	H	-1.84789802	1.69207780	-4.37379452
31	F	3.44080341	-0.05884166	-0.46572933
32	C	1.83268288	2.42635057	1.35689885
33	C	-2.52838122	-2.33553933	-0.74264886
34	H	2.90187333	4.30692041	1.62538295
35	H	1.13644263	4.44042287	1.76008603
36	C	0.74724988	3.15550892	-0.69888660
37	H	1.51932800	5.18736654	-0.54820288
38	H	2.76256224	3.94290530	-0.80255628
39	O	0.93730904	2.01605165	0.23961299
40	H	1.37124509	2.09499795	2.29023309
41	H	2.78613760	1.91197604	1.20901618
42	H	0.85590640	2.75883740	-1.70858179
43	H	-2.73395454	-4.39718145	-1.40752424
44	H	-3.77079077	-3.96181950	-0.03130177
45	C	-1.60606932	-2.98577486	1.43079323
46	H	-1.90420363	-5.11470837	1.07988963
47	H	-0.71573570	-4.34538249	0.00288593
48	O	-1.91039126	-1.83580960	0.53192223
49	H	-3.42727848	-1.73837624	-0.90222270
50	H	-1.79793613	-2.16611233	-1.53797172
51	H	-0.62464005	-2.80573327	1.87364131
52	H	-2.37839347	-2.99517772	2.20603532
53	H	-0.26895412	3.53560414	-0.55768586
54	O	-5.57465303	0.14514122	1.80112936
55	C	-5.03772073	0.13093307	0.66618338
56	O	-5.36604243	-0.47951472	-0.37846869
57	C	1.95237616	3.94182882	1.22549038

58	C	1.81711292	4.16605056	-0.29616279
59	C	-2.78260430	-3.81762367	-0.48157831
60	C	-1.67136752	-4.20500825	0.51979749

Int-1-S (-7915.5)

1	C	-3.52878780	1.99028077	-3.06393894
2	C	-1.36403805	2.01832524	3.84349749
3	H	-4.14401438	2.44611215	-3.83573150
4	C	-2.34937126	2.62750007	1.70444934
5	H	-0.71945850	2.26127075	4.68333749
6	Bi	-0.60245409	0.07469965	0.60489058
7	S	1.62094075	-2.03788127	-0.67141343
8	N	-3.84317616	1.05752008	0.53511957
9	C	3.27640277	-1.23306406	-1.13296561
10	O	1.65756324	-2.21314388	0.78467429
11	C	-1.51829753	2.92728045	2.78790530
12	C	-3.27003017	1.24335421	-0.76832185
13	C	-1.94321023	0.85809418	-1.05156244
14	H	-1.00072446	3.88206151	2.81186686
15	O	1.49801370	-3.21416812	-1.52163978
16	O	0.63983764	-0.93038130	-1.07574230
17	C	-3.04361513	1.39977953	1.66308266
18	F	4.28812316	-2.07123285	-0.81747255
19	C	-2.86603385	0.47386657	2.72134856
20	H	-3.39299583	-0.47290984	2.68599759
21	H	-2.47850940	3.33703208	0.89297730
22	C	-2.04137787	0.79379559	3.80568047
23	H	-1.92044390	0.07623722	4.61254276
24	F	3.31457560	-0.96673366	-2.45756340
25	C	-4.04729705	1.82889025	-1.77983055
26	H	-5.05904500	2.14663861	-1.54896868
27	C	-1.43475315	1.01340487	-2.34925185
28	H	-0.42355033	0.69222238	-2.58110361
29	C	-2.22525113	1.57055381	-3.35864733
30	H	-1.82266319	1.68440061	-4.36208895
31	F	3.43202934	-0.07329676	-0.44657448
32	C	1.78458429	2.39646993	1.36222723
33	C	-2.40680345	-2.45942494	-0.80022190
34	H	2.88863364	4.25980965	1.60759962
35	H	1.12783832	4.42092958	1.77410424
36	C	0.67346586	3.13938742	-0.67642762
37	H	1.48160559	5.15861895	-0.54229788
38	H	2.69927485	3.89309487	-0.81641859
39	O	0.85364147	2.00323964	0.26870476
40	H	1.34006784	2.07321137	2.30644496
41	H	2.72573457	1.86631841	1.19204118
42	H	0.76241240	2.73482272	-1.68487599
43	H	-2.59261061	-4.53747192	-1.41303770
44	H	-3.69603119	-4.05256166	-0.10543675
45	C	-1.60059353	-3.04845289	1.43903234
46	H	-1.89310301	-5.18430188	1.13164154
47	H	-0.64832035	-4.44994827	0.09387728
48	O	-1.87644006	-1.92223963	0.49911548
49	H	-3.29214135	-1.86432901	-1.03343943
50	H	-1.62403561	-2.31680027	-1.54956262
51	H	-0.63596715	-2.85400043	1.91199167
52	H	-2.40171910	-3.03905691	2.18418389
53	H	-0.33414266	3.53757908	-0.52412589
54	S	-5.99895249	0.89100617	2.12092776
55	C	-5.12263463	0.44827549	0.71513872
56	S	-5.66520014	-0.65971013	-0.46599904
57	C	1.92630249	3.90926740	1.22572435

58	C	1.76692009	4.13292693	-0.29364852
59	C	-2.68475914	-3.92971051	-0.50867049
60	C	-1.62771389	-4.29188681	0.55843272

TS-1-O (-8063.7)

1	C	-3.20030588	1.81236808	-3.16937050
2	C	-2.04362744	1.60049363	4.24661131
3	H	-3.77813606	2.18272362	-4.01363700
4	C	-2.03061550	2.06637317	1.85312469
5	H	-1.62423509	1.72137587	5.24105371
6	Bi	-0.46292271	0.22593376	0.78759032
7	S	2.08090636	-1.71150317	-0.53743070
8	N	-3.77976010	1.09859421	0.41812318
9	C	3.11659381	-0.79034689	-1.83313249
10	O	2.54483895	-1.18095021	0.75357414
11	C	-1.50222120	2.26031160	3.15986024
12	C	-3.08550461	1.28226014	-0.77863540
13	C	-1.72768011	0.88544275	-0.97614248
14	H	-0.65537737	2.93216543	3.28302365
15	O	2.31068559	-3.13014669	-0.81142801
16	O	0.68502270	-1.25388057	-0.88397626
17	C	-3.21140337	1.25444584	1.63109766
18	F	4.43458305	-1.04462011	-1.64323198
19	C	-3.73021430	0.58124993	2.78885712
20	H	-4.58854350	-0.07045179	2.66988008
21	H	-1.73054162	2.75111739	1.06323664
22	C	-3.16268490	0.75309259	4.03676443
23	H	-3.58610423	0.21564611	4.88294807
24	F	2.77204058	-1.18026346	-3.08483165
25	C	-3.79195773	1.75780731	-1.90749052
26	H	-4.82452195	2.07198104	-1.77573885
27	C	-1.15379464	0.92284523	-2.25057340
28	H	-0.13265180	0.57957441	-2.39426273
29	C	-1.87969142	1.38707862	-3.35571579
30	H	-1.41912380	1.41507722	-4.34014721
31	F	2.91641582	0.55186764	-1.73033612
32	C	2.24143328	2.26786377	1.20537740
33	C	-1.26038474	-2.87172651	1.71318011
34	C	2.22667239	3.95776861	-0.50572861
35	H	0.57809544	2.87980121	-1.52409371
36	H	0.06772303	3.89004072	-0.14001824
37	C	2.69833825	3.70218712	0.94297556
38	H	1.94580214	2.07588890	2.24000927
39	H	2.96856931	1.51856407	0.88299069
40	H	2.14221851	5.02216490	-0.74142495
41	H	2.91310364	3.49347434	-1.22209162
42	H	3.78021537	3.80616649	1.06110283
43	C	-2.54369975	-3.79261466	-0.08163826
44	H	-3.49919560	-1.80176515	-0.34276370
45	H	-1.90868321	-1.98927554	-1.14260478
46	C	-1.26552183	-4.05045120	0.74653526
47	H	-0.26431067	-2.56435140	2.04362217
48	H	-1.90312281	-3.03483407	2.58384098
49	H	-2.53994329	-4.32346692	-1.03778025
50	H	-3.43361279	-4.09450972	0.48214819
51	H	-1.28678807	-5.00712071	1.27571497
52	H	-0.37788307	-4.02087735	0.10547904
53	H	2.20443417	4.39543901	1.63296842
54	O	-6.33144152	0.84922043	1.04964787
55	C	-5.66171101	0.26296031	0.24462436
56	O	-5.54565446	-0.56245449	-0.61777334
57	O	-1.85630018	-1.74284063	0.94425116
58	C	-2.52202187	-2.28062856	-0.28672354

59	O	1.03158636	2.09466862	0.35376295
60	C	0.86942827	3.26316805	-0.54653903

TS-1-S (-7899.7)

1	C	-2.99835870	1.91918356	-3.18244732
2	C	-2.16241523	1.01552963	4.29021502
3	H	-3.55350140	2.34380155	-4.01604153
4	C	-1.92559656	1.69516883	1.95680107
5	H	-1.81062099	0.99954135	5.31750511
6	Bi	-0.27627910	0.15921974	0.71831309
7	S	2.36569687	-1.55296306	-0.83229399
8	N	-3.65907063	1.05999742	0.34670173
9	C	3.11050242	-0.44988149	-2.18450573
10	O	2.85182792	-0.95581636	0.42273283
11	C	-1.48460507	1.71598619	3.31856987
12	C	-2.92942889	1.27879547	-0.81795471
13	C	-1.57923223	0.85075138	-1.00940366
14	H	-0.59218438	2.28809605	3.56311533
15	O	2.82795669	-2.90278744	-1.16080050
16	O	0.89124457	-1.34641756	-1.04545554
17	C	-3.16391529	1.03085404	1.59014388
18	F	4.46458200	-0.47155158	-2.12207749
19	C	-3.83911592	0.32026496	2.63993104
20	H	-4.74679067	-0.22123127	2.40022066
21	H	-1.57800195	2.48940578	1.29827808
22	C	-3.34774212	0.31526300	3.92741839
23	H	-3.88331539	-0.24602470	4.69038552
24	F	2.72401593	-0.86658494	-3.41558719
25	C	-3.60757356	1.82678414	-1.93292112
26	H	-4.63093264	2.16458841	-1.79758481
27	C	-0.99275494	0.92820704	-2.27823564
28	H	0.02291011	0.57232312	-2.42440404
29	C	-1.68992638	1.45900287	-3.37067413
30	H	-1.21496365	1.51491599	-4.34694969
31	F	2.69403753	0.83918202	-2.01985123
32	C	2.34085558	2.38732205	1.09689744
33	C	-1.65094596	-2.66101528	2.05388369
34	C	2.09477148	4.05785988	-0.62007394
35	H	0.23209800	3.05970861	-1.29003739
36	H	0.04503579	4.10495263	0.14979013
37	C	2.81834657	3.78990115	0.71840396
38	H	2.22613167	2.23123069	2.17251702
39	H	2.96071683	1.59467347	0.67123632
40	H	2.01987286	5.12366064	-0.85302688
41	H	2.60924472	3.55436442	-1.44555331
42	H	3.90714991	3.83083580	0.62670648
43	C	-2.76168533	-3.77067402	0.23077425
44	H	-2.83531829	-1.85225921	-0.86585456
45	H	-1.24647725	-2.69519399	-0.93374248
46	C	-1.89369733	-4.05558136	1.47747344
47	H	-0.67206953	-2.53668106	2.52525662
48	H	-2.43858951	-2.33851304	2.73994297
49	H	-2.73519752	-4.58847264	-0.49481154
50	H	-3.80317273	-3.58525576	0.51649685
51	H	-2.39077876	-4.70757267	2.20085282
52	H	-0.94542333	-4.51906198	1.18393057
53	H	2.50499971	4.51964386	1.47319663
54	S	-6.53157268	1.58516743	0.66535920
55	C	-5.57020548	0.42455051	0.07050022
56	S	-5.50347089	-1.01482798	-0.66631464
57	O	-1.71483278	-1.74582089	0.88172272
58	C	-2.13989742	-2.50096669	-0.33364357
59	O	0.98797201	2.26654288	0.48550400

60	C	0.72207599	3.43363694	-0.39082396

Int-2-O (-8068.9)

1	C	1.06265112	-2.03734631	-3.70386293
2	C	4.10516914	0.07480807	2.89622316
3	H	1.13155988	-2.64329235	-4.60520317
4	C	2.63987619	-0.88093257	1.17799028
5	H	4.34768477	0.28077552	3.93518095
6	Bi	0.58302343	0.40003221	0.68901476
7	S	-2.20034078	2.60723407	0.11811661
8	N	3.38089723	-0.67170504	-1.18495800
9	C	-3.64862860	1.62036632	-0.60733240
10	O	-2.15635964	2.17147801	1.52653949
11	C	2.99830123	-0.65505542	2.56336175
12	C	2.16946737	-1.03400862	-1.75551224
13	C	0.89551715	-0.52198791	-1.34975317
14	H	2.34885029	-1.06573672	3.33418584
15	O	-2.55642938	4.00971089	-0.12590044
16	O	-1.04777060	2.11378412	-0.69274595
17	C	3.55866204	-0.45454052	0.10868503
18	F	-4.80469212	1.90977824	0.04203522
19	C	4.72955255	0.28007234	0.53279018
20	H	5.41467287	0.61666689	-0.24102264
21	H	2.08250581	-1.79812084	0.97629438
22	C	4.97433963	0.54520507	1.85389802
23	H	5.85977450	1.11591039	2.12762423
24	F	-3.81337105	1.89592178	-1.92647017
25	C	2.20522401	-1.81572125	-2.93874480
26	H	3.16423690	-2.22507527	-3.24976945
27	C	-0.23180567	-0.70614251	-2.16213543
28	H	-1.18226262	-0.26526145	-1.87277306
29	C	-0.16355710	-1.46378522	-3.33684747
30	H	-1.05057262	-1.60872334	-3.94869646
31	F	-3.41540893	0.27917852	-0.48146617
32	C	-1.88029061	-1.53100735	2.04600162
33	C	2.21939733	2.61069765	-1.31573215
34	H	-3.81375167	-2.10837204	1.19629443
35	H	-2.98201766	-3.40766698	2.07022780
36	C	-0.63981546	-2.94051263	0.53478204
37	H	-2.40104394	-3.99713875	-0.21043490
38	H	-2.28345794	-2.29331978	-0.70268461
39	O	-0.55478864	-1.74221805	1.39555832
40	H	-1.74401762	-1.68077268	3.12001281
41	H	-2.17017718	-0.49420911	1.85611582
42	H	0.06120480	-2.79603330	-0.28832079
43	C	1.43709279	4.62162539	-0.26626206
44	H	0.70831634	3.40212564	1.42588623
45	H	2.45271156	3.79311973	1.49731491
46	C	2.40468945	4.12355237	-1.36270563
47	H	3.09396497	2.02119901	-1.58881031
48	H	1.35201445	2.28231412	-1.89353682
49	H	1.68050137	5.62627481	0.09024515
50	H	0.40612379	4.61635749	-0.63361455
51	H	2.16229873	4.52529046	-2.35073926
52	H	3.43812066	4.39537721	-1.11900195
53	H	-0.34267343	-3.80733331	1.13672210
54	C	-2.10363587	-2.99692958	0.11719118
55	O	1.94699899	2.31327429	0.12090590
56	C	1.60988889	3.57760081	0.83349582
57	C	-2.83638230	-2.55168449	1.40339084
58	C	5.08990203	0.21261527	-3.30714019
59	O	4.26753652	0.96349846	-3.67516664
60	O	5.95615968	-0.51391393	-2.99409761

Int-2-S (-7913.7)

1	C	1.11601636	-2.27997048	-3.56950353
2	C	4.02710502	0.12575388	2.99563481
3	H	1.18442967	-2.93841747	-4.43330366
4	C	2.58711145	-0.91903728	1.30718365
5	H	4.24411013	0.40144569	4.02406699
6	Bi	0.56376236	0.34699643	0.69017490
7	S	-2.04216025	2.70263547	-0.11469350
8	N	3.40739785	-0.89670715	-1.04085297
9	C	-3.51083228	1.70560301	-0.78231059
10	O	-2.04524849	2.39869323	1.32830092
11	C	2.91293805	-0.60161129	2.68349440
12	C	2.20208444	-1.23276380	-1.63347053
13	C	0.94523397	-0.62597570	-1.31053379
14	H	2.23279643	-0.94037790	3.46290872
15	O	-2.33911472	4.08840619	-0.49590608
16	O	-0.89214075	2.09566031	-0.84762494
17	C	3.54894041	-0.59216704	0.23987669
18	F	-4.66914649	2.09239409	-0.19014504
19	C	4.72792741	0.13980949	0.64528184
20	H	5.43803293	0.40428595	-0.13453122
21	H	2.02134104	-1.84123811	1.15573044
22	C	4.93906633	0.49838868	1.94983278
23	H	5.82883282	1.06910844	2.20918914
24	F	-3.63777353	1.86539394	-2.12467342
25	C	2.23658449	-2.08540491	-2.76713048
26	H	3.18383015	-2.55891679	-3.01652749
27	C	-0.15407665	-0.78168518	-2.16745282
28	H	-1.08625952	-0.26847913	-1.94570624
29	C	-0.08322800	-1.60539836	-3.29604606
30	H	-0.94938795	-1.72644268	-3.94200171
31	F	-3.32923133	0.37389405	-0.53087703
32	C	-1.94877878	-1.53918550	2.01089791
33	C	2.42264661	2.47463154	-1.15327739
34	H	-3.87255944	-2.09973604	1.12785194
35	H	-3.07483679	-3.40120008	2.03093614
36	C	-0.69637822	-2.98880260	0.54939512
37	H	-2.45786718	-4.01524892	-0.23700926
38	H	-2.29484104	-2.31598488	-0.73358655
39	O	-0.60959863	-1.78836393	1.40740266
40	H	-1.85010454	-1.66689370	3.09189653
41	H	-2.21534250	-0.50154253	1.78980668
42	H	0.02987444	-2.86216326	-0.25477907
43	C	1.63879410	4.54858208	-0.24407522
44	H	0.67041510	3.40570338	1.38148652
45	H	2.41084398	3.73117913	1.64472733
46	C	2.68801908	3.97293469	-1.22278406
47	H	3.28929054	1.83788109	-1.32404779
48	H	1.59871085	2.16984762	-1.80223944
49	H	1.89550081	5.55013803	0.11175494
50	H	0.65311888	4.58387499	-0.71859890
51	H	2.56758805	4.35492755	-2.24039806
52	H	3.70410214	4.20127614	-0.88112886
53	H	-0.43341837	-3.85887450	1.16279851
54	C	-2.14946811	-3.01926148	0.09342525
55	O	2.00662352	2.23387750	0.25585319
56	C	1.64032988	3.53045927	0.89409132
57	C	-2.90532969	-2.55336596	1.35925781
58	C	4.20085411	1.29822670	-3.87767703
59	S	2.77800707	0.98899005	-4.44715638
60	S	5.62049977	1.61151587	-3.28856461

Int-3-E (-9149.2)

1	C	1.15690023	-1.75470685	-3.98223474
2	C	3.53894257	0.10815679	2.94177233
3	H	1.32459268	-2.31787586	-4.89835653
4	C	2.25765089	-0.75860713	1.03680877
5	H	3.67686490	0.25268507	4.00978433
6	Bi	0.29238265	0.64176547	0.39942345
7	S	-2.76236194	2.39769688	-0.21842284
8	N	3.21702309	-0.41096267	-1.23101037
9	C	-4.02209494	1.16036377	-0.91385282
10	O	-2.65551543	2.01609758	1.20158707
11	C	2.47607724	-0.60734217	2.45515088
12	C	2.06616467	-0.78043361	-1.91846134
13	C	0.74301966	-0.33595378	-1.59919385
14	H	1.76326431	-1.06936328	3.13642972
15	O	-3.35375313	3.71012742	-0.50673492
16	O	-1.53721087	2.08556596	-1.01512957
17	C	3.26422680	-0.26271377	0.08759584
18	F	-5.21703761	1.28223216	-0.27953756
19	C	4.37517024	0.46201402	0.66327703
20	H	5.12265440	0.85453155	-0.02251964
21	H	1.71085341	-1.65137836	0.72305831
22	C	4.49383302	0.64675330	2.01730214
23	H	5.34229085	1.20759259	2.40556888
24	F	-4.21807986	1.35930708	-2.24315229
25	C	2.22819723	-1.50144789	-3.12843454
26	H	3.22821258	-1.84849293	-3.38066333
27	C	-0.31357667	-0.55710461	-2.48979994
28	H	-1.30241852	-0.16910434	-2.25972723
29	C	-0.12384886	-1.27327051	-3.67918891
30	H	-0.95886706	-1.44718439	-4.35356469
31	F	-3.57817304	-0.11917449	-0.73865180
32	C	-1.89649729	-1.22694875	2.26611394
33	C	2.20411757	2.83957143	-1.57141548
34	H	-3.29926663	-2.70123317	3.05711799
35	H	-1.61695918	-3.26588279	2.93803155
36	C	-1.45495498	-2.48196731	0.23198704
37	H	-2.60651689	-4.21392930	0.89745769
38	H	-3.57578666	-2.75234443	0.62411120
39	O	-1.07878566	-1.28784792	1.03341379
40	H	-1.24491129	-0.86489632	3.06513100
41	H	-2.71143340	-0.51525633	2.10050686
42	H	-1.71916929	-2.14342701	-0.77010694
43	C	2.64848541	4.67213934	-0.07448114
44	H	1.27005225	3.75139135	1.39263024
45	H	2.92463709	3.05709743	1.38512496
46	C	3.21220658	3.96031690	-1.32500882
47	H	2.63645153	1.93135889	-1.99160529
48	H	1.34011149	3.16618893	-2.15845583
49	H	3.40381072	5.25793891	0.45673065
50	H	1.82107165	5.33513214	-0.35088433
51	H	3.29357834	4.62657469	-2.18836860
52	H	4.20126748	3.53956895	-1.11234207
53	H	-0.56121384	-3.10589582	0.19371744
54	C	1.30340191	-4.92985356	1.17804064
55	C	0.52448816	-5.67699581	-0.97030806
56	H	0.85967150	-3.62277687	-1.73727623
57	H	2.33118828	-4.61627162	-1.60440127
58	C	1.05312111	-6.21807859	0.37592052
59	H	2.16658651	-4.99847854	1.84922038
60	H	0.42155384	-4.64255526	1.76952608
61	H	0.65674969	-6.38182285	-1.79686730
62	H	-0.54241496	-5.43257231	-0.89412502

63	H	0.34756782	-6.88727052	0.87775410
64	H	1.99305726	-6.76105408	0.22215031
65	C	-2.38933262	-2.65835402	2.45216017
66	C	-2.61567118	-3.12462589	0.99669996
67	O	1.70731113	2.49221932	-0.21469888
68	C	2.13737276	3.50886280	0.77323747
69	O	1.56071882	-3.87440959	0.19838186
70	C	1.35348705	-4.40126664	-1.14974124

TS-2 (-9126.0)

1	C	0.61443304	-1.38009054	-4.36101537
2	C	4.17989099	-0.90462445	2.46984883
3	H	0.61783431	-1.77453905	-5.37603450
4	C	2.41756271	-0.57923928	0.78890244
5	H	4.51897540	-0.84494668	3.50123535
6	Bi	0.42749412	0.34249452	0.35740990
7	S	-2.21983261	3.18536250	0.16824467
8	N	2.97573011	-1.33302856	-1.56753374
9	C	-3.84899940	2.22387297	0.30054300
10	O	-1.64199800	3.04564435	1.51912089
11	C	2.89316146	-0.51143183	2.11915336
12	C	1.78902122	-1.07077357	-2.20621592
13	C	0.62161375	-0.38104475	-1.73122603
14	H	2.23122546	-0.12909817	2.89772800
15	O	-2.65171281	4.54609788	-0.19938953
16	O	-1.49619102	2.45270626	-0.89362151
17	C	3.27626846	-1.08029497	-0.25582512
18	F	-4.66480076	2.76228269	1.24918848
19	C	4.61195558	-1.45303259	0.14297182
20	H	5.27540534	-1.81859205	-0.63873452
21	H	2.06302603	-2.60939977	-0.04676006
22	C	5.04543254	-1.36724487	1.45175127
23	H	6.06290396	-1.66460503	1.70006323
24	F	-4.52132495	2.22734125	-0.88435287
25	C	1.72215807	-1.56512530	-3.55319575
26	H	2.59499467	-2.10032502	-3.92263098
27	C	-0.49130826	-0.19068986	-2.57990571
28	H	-1.35200522	0.35895087	-2.20421877
29	C	-0.51337222	-0.67868969	-3.88172726
30	H	-1.38101545	-0.52012553	-4.51816094
31	F	-3.61437802	0.92193921	0.64240273
32	C	-3.16985742	-2.28832397	1.33455792
33	C	1.74669227	-3.95190738	1.50706244
34	H	-1.56908393	-2.32676826	2.86323697
35	H	-1.89429750	-0.70373378	2.19633903
36	H	-3.45556473	-3.11261499	-0.69823991
37	H	-2.97248953	-1.40151114	-0.66007563
38	H	-4.00952103	-1.62178801	1.54631911
39	H	-3.41432388	-3.28233852	1.72416680
40	O	1.73863854	2.40794130	-0.27172220
41	C	1.60576342	3.60954746	0.58868232
42	C	1.73865153	2.81582853	-1.69560455
43	C	3.28381406	-5.39169241	0.33955559
44	H	2.13293777	-4.92818176	-1.50672385
45	H	3.44550708	-3.74990547	-1.15865049
46	C	3.09192966	-4.63112701	1.67445348
47	H	1.59461025	-3.02188711	2.04961203
48	H	0.89233558	-4.62069738	1.61016094
49	H	4.33566640	-5.61611724	0.14530590
50	H	2.72419336	-6.33189657	0.35162647
51	H	3.08557423	-5.30683568	2.53360974
52	H	3.87539885	-3.88160467	1.81780903
53	C	1.31749188	4.76760840	-0.36805341

54	H	0.80096977	3.42456126	1.30342344
55	H	2.55973017	3.72885875	1.11434008
56	C	2.01703372	4.31760352	-1.66965049
57	H	2.50353786	2.21682202	-2.19462538
58	H	0.75463696	2.58852845	-2.11466815
59	H	1.70302972	5.71653497	0.01612584
60	H	0.23965595	4.86874897	-0.53014058
61	H	1.61921563	4.81707396	-2.55812960
62	H	3.09500458	4.50983340	-1.61388118
63	O	1.72919626	-3.55669230	0.02845716
64	C	2.73203119	-4.45467814	-0.73164968
65	O	-0.79927223	-1.96428515	0.94838961
66	C	-1.36495713	-2.75162273	-0.15796434
67	C	-1.85994003	-1.77288473	1.96523335
68	C	-2.84137536	-2.37460851	-0.17382136
69	H	-0.81206428	-2.48157287	-1.05835529
70	H	-1.21821872	-3.81729618	0.06341884

Int-4 (-9171.4)

1	C	-3.27361233	1.56021678	-2.89296056
2	C	-1.69908533	1.51792550	4.70955073
3	H	-3.91663514	1.91417771	-3.69577385
4	C	-1.45278490	0.97123838	2.33266502
5	H	-1.35187038	1.42577578	5.73577111
6	Bi	-0.24897546	-0.14161122	0.78891484
7	S	2.57743636	-1.61663367	-1.35305843
8	N	-3.12809362	1.93451494	0.75832277
9	C	2.90385845	-0.23034522	-2.60888555
10	O	2.93414434	-0.98824159	-0.06580649
11	C	-1.02677958	0.87366964	3.67157102
12	C	-2.73661532	1.49662043	-0.50638602
13	C	-1.62409565	0.67008619	-0.79251468
14	H	-0.14824772	0.27282538	3.90660028
15	O	3.46864067	-2.70146332	-1.80199797
16	O	1.13082695	-1.88170052	-1.53111650
17	C	-2.59293870	1.75217351	2.03232369
18	F	4.21096815	0.15658349	-2.58068697
19	C	-3.27525642	2.40618903	3.09231932
20	H	-4.15374402	3.00565499	2.86341525
21	C	-1.93201717	-2.90302663	-0.30302173
22	C	-2.83472993	2.28730017	4.40417701
23	H	-3.37698499	2.79931408	5.19619107
24	F	2.61456090	-0.64073598	-3.87668900
25	C	-3.54639752	1.93859329	-1.58585926
26	H	-4.38774668	2.59352757	-1.37616862
27	C	-1.36092996	0.30920414	-2.12802415
28	H	-0.50299166	-0.32286659	-2.34180224
29	C	-2.17281293	0.73590946	-3.17808424
30	H	-1.95297394	0.43951576	-4.20070844
31	F	2.13754052	0.86271351	-2.33746380
32	C	-4.18356612	-2.64583393	0.43794388
33	H	-0.10459891	3.25764163	-0.63965231
34	H	-3.37532703	-2.05158965	2.41646639
35	H	-3.47974842	-0.72977745	1.22180547
36	C	-3.34350671	-2.73321362	-0.85406853
37	H	-1.13667995	-2.54446137	-0.95801479
38	H	-1.72457234	-3.93845657	-0.00982361
39	H	-5.16152354	-2.18385628	0.28199636
40	H	-4.33629055	-3.64470582	0.86153946
41	H	-3.63612601	-3.56828298	-1.49685814
42	H	-3.41568211	-1.80256706	-1.42835393
43	H	-0.34405773	3.30737501	1.13308885
44	C	2.45984025	3.54474458	1.50368447

45	H	2.47931511	1.36408990	1.88053244
46	H	3.13963714	1.83495375	0.29298764
47	H	1.15576364	5.21176930	0.85867803
48	H	2.03970663	4.40908834	-0.45988607
49	H	3.48187010	3.93319175	1.48089342
50	H	2.06927845	3.65332058	2.52203062
51	O	-1.90363971	-2.08054488	0.93584186
52	C	-3.29912289	-1.79938719	1.35635045
53	H	-4.03416639	2.41140659	0.76266739
54	O	1.06549548	1.92010885	0.43331486
55	C	0.39738693	3.23467381	0.32911497
56	C	2.40105781	2.08173603	1.06016025
57	C	1.52577412	4.24893049	0.49470355
58	O	-6.01501297	2.47798811	1.03594910
59	C	-6.31747825	1.08911561	1.35338679
60	C	-6.89408336	2.83516370	-0.07536369
61	C	-6.49332631	0.41445009	-0.01262097
62	H	-5.48679013	0.70325781	1.94946412
63	H	-7.24116988	1.04195063	1.94964760
64	C	-7.14341702	1.53023824	-0.88003184
65	H	-7.83118927	3.23980791	0.33000029
66	H	-6.38716685	3.61927579	-0.64456104
67	H	-7.11181773	-0.48589122	0.04591408
68	H	-5.51609740	0.13883343	-0.42078434
69	H	-6.68799902	1.57412752	-1.87294391
70	H	-8.21641780	1.36031959	-1.00837511

4-H (-7568.6)

1	C	-3.21400755	0.68166638	-2.91584283
2	C	-2.09733671	1.20946248	4.74710886
3	H	-3.87104268	0.86997841	-3.76199934
4	C	-1.59662343	0.66311392	2.41019649
5	H	-1.82811486	1.16832006	5.79969792
6	Bi	-0.11202749	-0.24782902	0.98081308
7	S	2.99074642	-1.23556077	-1.09205669
8	N	-3.23431770	1.40258768	0.68653354
9	C	2.96011502	0.18226731	-2.35585729
10	O	3.23716331	-0.53416946	0.18330036
11	C	-1.27634908	0.62827299	3.78059566
12	C	-2.75584960	0.90112186	-0.52454937
13	C	-1.53396083	0.21134323	-0.70460796
14	H	-0.35910130	0.13307400	4.09889172
15	O	4.08675536	-2.09602616	-1.57087353
16	O	1.63457715	-1.81696039	-1.22307334
17	C	-2.78822605	1.30456938	2.00555707
18	F	4.14763880	0.85020330	-2.36897307
19	C	-3.61887195	1.89922503	2.98960219
20	H	-4.53814973	2.39473508	2.67896944
21	C	-0.94994944	-3.47383877	0.24274051
22	C	-3.27759531	1.85089980	4.33538914
23	H	-3.93425127	2.31306628	5.06915507
24	F	2.72549619	-0.28604148	-3.61340928
25	C	-3.58476160	1.12672896	-1.65419765
26	H	-4.52688711	1.65693724	-1.51963323
27	C	-1.18112176	-0.22991599	-1.99468454
28	H	-0.24018857	-0.75641691	-2.12754244
29	C	-2.00225946	-0.00495275	-3.09821555
30	H	-1.70741575	-0.35487705	-4.08438314
31	F	1.97893274	1.08108899	-2.05452498
32	C	-3.33235154	-3.50254484	0.36271827
33	H	-0.41474176	2.72645262	-0.88420302
34	H	-3.11221458	-2.55354590	2.35525582
35	H	-3.15531631	-1.40982448	0.98559292

36	C	-2.17399450	-3.64635664	-0.64921967
37	H	-0.05644206	-3.10983582	-0.26677138
38	H	-0.71432318	-4.38855416	0.79933653
39	H	-4.27866973	-3.22582566	-0.11073961
40	H	-3.47910969	-4.44224146	0.90655153
41	H	-2.17634596	-4.61221627	-1.16245847
42	H	-2.21170785	-2.84730223	-1.39763091
43	H	-0.71389918	3.52615629	0.68772365
44	C	2.11097096	3.99555018	0.91345089
45	H	2.20926848	2.18886629	2.18572513
46	H	2.83663889	1.95123740	0.52946695
47	H	0.74070702	5.18918088	-0.34760133
48	H	1.65370371	3.93949922	-1.22315337
49	H	3.11874254	4.36496214	0.70359629
50	H	1.72582999	4.51845390	1.79628887
51	O	-1.35071758	-2.44142612	1.23404005
52	C	-2.83605569	-2.40268145	1.30904484
53	H	-4.12260487	1.88506759	0.59700069
54	O	0.75813226	2.04361364	0.69256220
55	C	0.05623973	3.14535323	0.00662544
56	C	2.10011064	2.48209674	1.13796926
57	C	1.14699447	4.17587706	-0.28112619

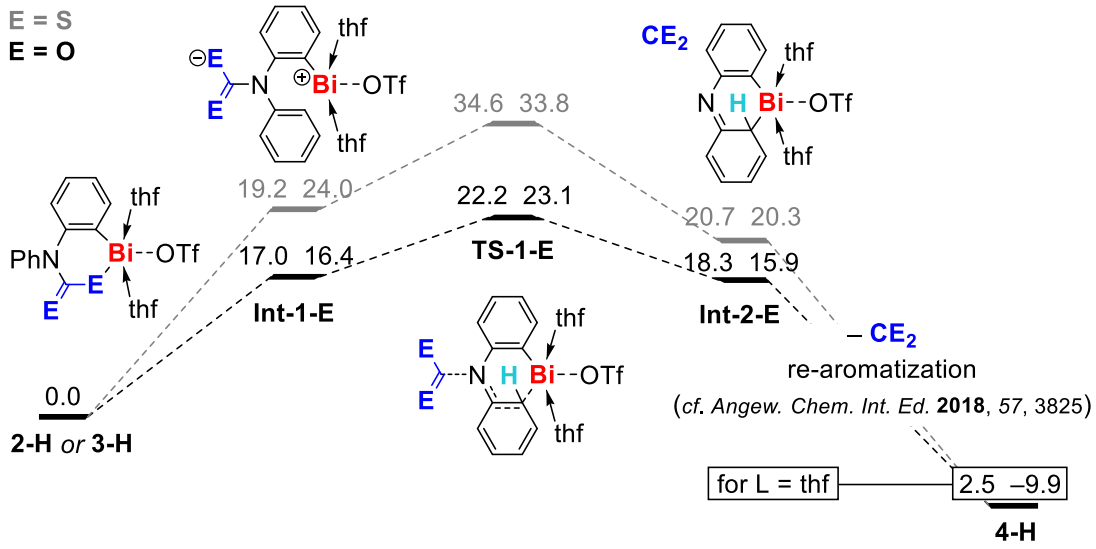


Figure S18. Thermodynamic data for the potential steps in the formation of **4-H** from **2-H** or **3-H**. Left values for ΔH and right values for ΔG (in kcal mol^{-1}).

Table S6. Cartesian coordinates and ADF total electronic energy (in parentheses and in kcal mol^{-1}) of compounds involved in the mechanism from **3-H** to **5-E** under analysis computed at the ZORA-BLYP-D3(BJ)/TZ2P level of theory in THF.

TS-3-S (-7899.6)

1	C	-4.30287198	-0.38082083	-3.24961128
2	C	-2.41758746	5.53063526	-4.27491662
3	H	-4.74633939	-0.62998140	-4.20970439
4	C	-3.81670378	4.56776050	-2.54244744
5	H	-2.25275593	6.28906513	-5.03624658
6	Bi	-0.93791041	0.13174347	0.58296366
7	S	2.56324350	0.11750680	-0.25936627
8	N	-3.04431037	2.55886326	-1.33270086
9	C	3.72418836	-1.30327910	-0.74407543
10	O	3.45355311	1.11360084	0.34890026
11	C	-3.59981969	5.53912554	-3.52417701
12	C	-3.32555239	1.24071254	-1.75702411
13	C	-3.10632086	0.23307731	-0.80263997
14	H	-4.35536126	6.29979479	-3.70326728
15	O	1.63514335	-0.55073653	0.70681568
16	O	1.91854370	0.49711256	-1.52780159
17	C	-2.83954472	3.59461899	-2.32173671
18	F	4.33072658	-1.82822052	0.35391142
19	C	-1.66100023	3.56815036	-3.07249335
20	H	-0.92421343	2.79102815	-2.89096523
21	H	-4.72703645	4.56198792	-1.95197793
22	C	-1.45012658	4.54359587	-4.05103692
23	H	-0.53388649	4.53065394	-4.63558488
24	F	3.03695671	-2.29979216	-1.36845857
25	C	-3.88543365	0.93091816	-3.00233004
26	H	-4.02081372	1.71065044	-3.74605190
27	C	-3.64000791	-1.04909372	-1.00169579
28	H	-3.54585380	-1.81593244	-0.23805070
29	C	-4.20564072	-1.35749569	-2.24298859
30	H	-4.56556025	-2.36737808	-2.42712805
31	F	4.68640533	-0.85522836	-1.59265530
32	C	0.18293479	2.94286663	2.21363124
33	C	-0.47087104	-2.71317337	-1.22573426
34	C	1.46735641	4.20105494	0.59165505
35	H	0.99472321	2.68060060	-0.94888893
36	H	-0.35079783	3.80849714	-0.55304282
37	C	0.76828585	4.33855243	1.96482236
38	H	-0.81576665	2.96258740	2.65769235
39	H	0.84805701	2.29682372	2.79423829
40	H	1.58739929	5.16366622	0.08586552
41	H	2.44879944	3.72709342	0.69729626
42	H	1.45912846	4.63050504	2.76050559
43	C	0.62957472	-4.04421895	0.44760662
44	H	-0.16454883	-2.68015928	1.99685516
45	H	-1.33239934	-3.90869968	1.41998904
46	C	0.15363037	-4.09384438	-1.02107243
47	H	-1.31916355	-2.69635105	-1.91343136
48	H	0.26954134	-1.96623102	-1.52889178
49	H	0.76241647	-5.03861703	0.88321368
50	H	1.57203501	-3.49457867	0.52626592
51	H	0.97187200	-4.27260420	-1.72394020
52	H	-0.59864468	-4.87950496	-1.15488194
53	H	-0.03625284	5.07849111	1.90822394
54	S	-2.99807514	4.36617246	0.71054867
55	C	-3.10345925	2.84417199	0.01308001
56	S	-3.33907023	1.46607612	1.10910526

57	O	0.06160715	2.32691248	0.86894946
58	C	0.52395324	3.27674714	-0.16662013
59	O	-0.99217366	-2.32101674	0.10978571
60	C	-0.49027082	-3.26781890	1.13556382

Int-5-S (triplet, -7899.1)

1	C	-3.39541168	-0.55137093	-3.20850952
2	C	-2.24528951	5.70683509	-2.60158391
3	H	-4.08768845	-0.77569615	-4.01565767
4	C	-3.56586419	4.41917136	-1.02059682
5	H	-2.04698261	6.64084208	-3.12070435
6	Bi	-0.18622515	0.24617145	0.70497989
7	S	2.95434502	-0.96823964	-1.37653398
8	N	-2.97284752	2.05162415	-0.57223199
9	C	2.55506569	-0.11392122	-3.02461787
10	O	2.98871096	0.15589248	-0.41696747
11	C	-3.30026576	5.61919203	-1.68793701
12	C	-2.72675579	0.84088699	-1.34978411
13	C	-1.60312325	0.03414126	-1.09895857
14	H	-3.93736014	6.48025613	-1.50329212
15	O	4.25924746	-1.60701751	-1.63773544
16	O	1.82208042	-1.89985344	-1.20484681
17	C	-2.74490614	3.30455788	-1.24753096
18	F	3.48597266	0.83595978	-3.32316428
19	C	-1.70600515	3.37986588	-2.18739635
20	H	-1.09965468	2.50539791	-2.38837610
21	H	-4.41519610	4.34850629	-0.35225653
22	C	-1.46018375	4.57624854	-2.85963093
23	H	-0.64978523	4.62536542	-3.58211885
24	F	2.53001293	-1.01491838	-4.04639767
25	C	-3.61570048	0.56109806	-2.39366350
26	H	-4.46782136	1.21503071	-2.56014844
27	C	-1.39200840	-1.07010372	-1.94201790
28	H	-0.51434967	-1.69308867	-1.79518308
29	C	-2.27772316	-1.36396428	-2.98494503
30	H	-2.09027091	-2.22155339	-3.62698636
31	F	1.33564581	0.49607228	-2.97814773
32	C	0.13686458	3.60675196	1.19440351
33	C	0.20765413	-3.14448594	1.30839440
34	C	1.44360369	4.58389451	-0.58359347
35	H	2.28325957	2.53492352	-0.48594487
36	H	1.07307607	2.74242319	-1.77384479
37	C	0.33516315	4.92169065	0.45113207
38	H	-0.85518867	3.46992279	1.62805922
39	H	0.91069058	3.43437590	1.95372067
40	H	1.27958261	5.10997236	-1.52724624
41	H	2.42927772	4.86470584	-0.20174361
42	H	0.62824225	5.73073695	1.12594016
43	C	-1.79162755	-4.07799603	0.31848800
44	H	-2.65067394	-2.84423475	1.94006749
45	H	-2.66812556	-2.03761911	0.34873558
46	C	-0.24219588	-4.11264492	0.21972635
47	H	1.16743416	-2.66595725	1.10968038
48	H	0.20197106	-3.60028690	2.30617409
49	H	-2.25719308	-4.15275540	-0.66794505
50	H	-2.16133807	-4.90366339	0.93343313
51	H	0.16140447	-5.11725475	0.37567205
52	H	0.09909859	-3.74796199	-0.75250995
53	H	-0.59269980	5.20468110	-0.05389913
54	S	-3.59132475	3.17685108	1.86029439
55	C	-3.41321890	1.93523240	0.70427083
56	S	-3.81658150	0.42881246	1.41679802

57	O	0.27716856	2.59765674	0.12901638
58	C	1.36494648	3.05258233	-0.77067378
59	O	-0.81908358	-2.08468434	1.28873418
60	C	-2.11903212	-2.72597269	0.99090745

TS-4-S (triplet, -7889.7)

1	C	-4.30183105	-0.75202793	-2.55017391
2	C	-1.41643690	4.53819844	-4.53461015
3	H	-4.69481249	-1.16835337	-3.47344161
4	C	-3.21780608	4.15126368	-2.95608986
5	H	-1.01901714	5.07114904	-5.39500839
6	Bi	-0.96133425	0.22660319	0.76379689
7	S	2.37431627	0.32031998	-0.78546898
8	N	-2.94277392	2.44076964	-1.19624391
9	C	3.51129976	-0.88320202	-1.71605928
10	O	3.28034381	1.40233865	-0.36944945
11	C	-2.70218005	4.83188070	-4.06310212
12	C	-3.28769611	1.07466075	-1.35231484
13	C	-3.21294388	0.28698183	-0.16349224
14	H	-3.30587546	5.58881906	-4.55750185
15	O	1.84616263	-0.51019583	0.32968061
16	O	1.35975325	0.68522168	-1.79394531
17	C	-2.43286337	3.18091015	-2.32709436
18	F	4.46309014	-1.39124595	-0.88730856
19	C	-1.15197885	2.86983236	-2.79523104
20	H	-0.55743698	2.10626373	-2.30107935
21	H	-4.21280065	4.36683063	-2.58055149
22	C	-0.64446896	3.55575230	-3.90209143
23	H	0.35306331	3.32264277	-4.26585986
24	F	2.80107425	-1.92556219	-2.23374215
25	C	-3.77665079	0.54671519	-2.54690195
26	H	-3.77937227	1.15157129	-3.44893480
27	C	-3.84042373	-0.99026941	-0.17250353
28	H	-3.84625550	-1.59564256	0.72985668
29	C	-4.36453151	-1.49876527	-1.35626364
30	H	-4.80276486	-2.49421781	-1.36511355
31	F	4.13571256	-0.24887165	-2.74437917
32	C	-0.49273166	3.20156173	2.60764526
33	C	-0.71781717	-2.26304660	-1.50651048
34	C	1.23776074	4.33970666	1.35186330
35	H	1.04250709	2.84557219	-0.26705136
36	H	-0.27914086	4.05798673	-0.19691326
37	C	0.24167402	4.54564324	2.51626297
38	H	-1.56476514	3.30188181	2.79382467
39	H	-0.04375378	2.51914823	3.33616900
40	H	1.54599315	5.28314758	0.89166364
41	H	2.13249688	3.80380834	1.68859836
42	H	0.73817759	4.79790135	3.45745504
43	C	0.65136336	-3.84698892	-0.33216705
44	H	0.45223854	-2.56930983	1.45391859
45	H	-0.90694188	-3.71480233	1.21650352
46	C	-0.19044908	-3.68964088	-1.61859052
47	H	-1.68655948	-2.09484638	-1.98042941
48	H	0.00781186	-1.52027277	-1.84987212
49	H	0.79500267	-4.89342202	-0.04894973
50	H	1.63063643	-3.37796974	-0.45877659
51	H	0.40237794	-3.82826593	-2.52704588
52	H	-1.01977626	-4.40599875	-1.62910040
53	H	-0.46735775	5.34233170	2.26935794
54	S	-3.05731696	4.67431522	0.35369064
55	C	-3.21321976	3.03600450	0.02665673
56	S	-3.77441526	1.94627801	1.27601596
57	O	-0.33159655	2.57291046	1.27348256

58	C	0.43868049	3.47292611	0.38787853
59	O	-0.92686311	-2.06213408	-0.04659335
60	C	-0.16264720	-3.08815315	0.71548436

Int-6-S (triplet, -7915.5)

1	C	15.69816682	5.62701468	2.19682131
2	C	17.22744133	5.84829100	4.97471590
3	N	16.24870448	6.65341724	4.35741431
4	C	18.14011201	4.99579017	4.34608361
5	H	18.13983615	4.88209986	3.26785890
6	S	14.21298505	8.43552847	4.80202889
7	C	19.05059733	4.29724277	5.14498325
8	H	19.76676153	3.63112260	4.67188376
9	S	15.95404109	7.09317541	6.88201974
10	C	19.06213049	4.45442195	6.54016421
11	H	19.79276291	3.91790308	7.13898216
12	C	18.14511974	5.30014266	7.17102625
13	H	18.16087309	5.43721103	8.24714562
14	C	17.22271814	5.98418557	6.37848473
15	C	15.45414499	7.39210878	5.21313430
16	C	16.41378540	8.00033729	0.88501251
17	C	15.63445929	5.70447538	0.80121634
18	C	15.99326536	6.88760638	0.14565281
19	H	16.79972877	8.78392625	2.86839664
20	H	15.41843866	4.71682900	2.71947760
21	H	16.68853192	8.92197701	0.37846182
22	H	15.30200922	4.84150404	0.23024077
23	H	15.94229845	6.94450170	-0.93876091
24	C	16.13183082	6.73959601	2.92076520
25	C	16.48409372	7.92851459	2.27754051
26	Bi	18.49013775	9.74260518	5.49031046
27	H	22.16546804	6.82092766	2.75842295
28	H	15.24804524	11.21751601	9.67168203
29	O	18.41428333	8.62007227	8.56409194
30	C	20.04052483	8.68885719	2.51633522
31	H	20.50978592	7.17050909	1.01863542
32	H	15.02503528	12.43957455	8.39765326
33	O	17.03996946	11.17427236	6.86840056
34	S	19.80725035	8.15604237	8.73577547
35	H	19.16692062	6.75970221	2.10656242
36	O	20.06939775	8.59134572	3.98603342
37	H	21.72043763	7.70427198	4.91836349
38	H	20.18738042	6.81338017	5.06380435
39	H	18.78537234	12.08969408	7.59378338
40	H	17.47333419	13.20224175	7.09568209
41	H	15.11252955	10.40367395	7.02836973
42	H	16.32067079	9.66876397	8.13426600
43	O	20.59659937	8.08605403	7.48977230
44	C	20.61182093	9.60031736	9.67004934
45	O	19.97833823	7.01870981	9.65868966
46	H	19.11130424	9.19267657	2.24427658
47	H	20.89687719	9.29449293	2.19536981
48	C	21.13327367	6.63304968	3.07153663
49	C	17.10907361	12.21815989	9.02623576
50	C	15.69279226	11.65572671	8.77335196
51	C	20.82764143	7.37449473	4.38318559
52	F	20.55734610	10.74989428	8.93264720
53	F	21.92207246	9.34343413	9.94200635
54	F	19.97532193	9.83605664	10.85267463
55	C	20.14691863	7.24314457	2.04795967
56	H	21.00116927	5.55416371	3.18468640
57	C	17.70858658	12.27117272	7.62128262
58	H	17.09860896	13.20474671	9.49788328

59	H	17.68309350	11.53138837	9.65694158
60	C	15.94778663	10.60004563	7.70408512

Int-6-S (singlet, -7916.1)

1	C	15.54930893	5.80209889	2.63722755
2	C	17.45703142	5.59518606	5.23519698
3	N	16.34214374	6.37962346	4.89068928
4	C	18.34104381	4.95906036	4.35814989
5	H	18.20388905	5.03378009	3.28505548
6	S	14.19389934	7.76823905	5.86157478
7	C	19.39641701	4.22193140	4.90253353
8	H	20.09167477	3.71870787	4.23620139
9	S	16.34412893	6.35914728	7.46812997
10	C	19.57124370	4.12553550	6.29257935
11	H	20.40600236	3.55686765	6.69370717
12	C	18.68290986	4.75375760	7.17050720
13	H	18.81931949	4.69613411	8.24487319
14	C	17.62092761	5.48165899	6.63069181
15	C	15.59799996	6.86161827	5.94668002
16	C	16.12773977	8.40953562	1.77808112
17	C	15.32768525	6.16770928	1.30450802
18	C	15.61669940	7.46819212	0.87525751
19	H	16.76446082	8.75425546	3.82838642
20	H	15.32612119	4.79821750	2.98753190
21	H	16.35283685	9.41965829	1.44505359
22	H	14.92809693	5.43666756	0.60641804
23	H	15.44220355	7.74905189	-0.16044077
24	C	16.06558748	6.74864972	3.52340399
25	C	16.35583372	8.05041547	3.10804600
26	Bi	19.17485925	9.46372425	6.11398042
27	H	22.06156371	7.12124169	2.31937159
28	H	14.83633456	11.31472379	8.17124521
29	O	18.35783163	9.14083541	8.63822111
30	C	20.01555527	8.98906291	2.78430080
31	H	19.98609054	7.60231544	1.09590019
32	H	14.99779432	12.58211071	6.93748429
33	O	17.50824871	11.23138718	6.20782852
34	S	19.30695579	8.03840467	8.96684847
35	H	18.99029203	7.10945927	2.48023606
36	O	20.63499552	8.82054346	4.12057029
37	H	22.12046380	7.48908791	4.72171160
38	H	20.44457275	6.88078396	4.91065325
39	H	18.83350996	12.39193059	7.31690993
40	H	17.61141824	13.31580180	6.38333916
41	H	15.59185750	10.71971220	5.52984340
42	H	16.18520800	9.76733684	6.91421853
43	O	20.09202239	7.64987653	7.75569268
44	C	20.59137385	8.86456650	10.09898679
45	O	18.78122162	6.93976261	9.77377874
46	H	19.03936490	9.46364769	2.92395961
47	H	20.66834409	9.65438334	2.20968251
48	C	21.13132186	6.86432296	2.83807357
49	C	16.78451921	12.36200751	8.17164660
50	C	15.53130038	11.78816636	7.47196666
51	C	21.13377016	7.42874679	4.25733654
52	F	21.17122711	9.92227304	9.48040588
53	F	21.55894400	7.97282187	10.43305479
54	F	19.99254839	9.30238954	11.23590761
55	C	19.93106430	7.58479627	2.18790280
56	H	21.02234734	5.77668807	2.83875443
57	C	17.78321756	12.44347367	7.02486272
58	H	16.60314186	13.33860322	8.62974284
59	H	17.14980185	11.67040516	8.93873172

60	C	16.11171783	10.76900920	6.48836417

5-H (-3659.5)

1	C	13.95536401	6.05830388	0.93097317
2	C	16.22377759	5.86972282	3.35863499
3	N	16.06819910	5.46075540	2.02302336
4	C	15.21932606	5.96585144	4.32680374
5	H	14.19238021	5.71255949	4.08277979
6	S	17.34246710	5.00987210	-0.35293789
7	C	15.57840004	6.39447269	5.60823187
8	H	14.81238104	6.47588388	6.37476887
9	S	18.58424705	5.97355583	2.24888239
10	C	16.91002881	6.72029405	5.91741438
11	H	17.16613576	7.05179138	6.92032070
12	C	17.91479999	6.62361471	4.94820235
13	H	18.94494333	6.87487193	5.18353991
14	C	17.56025751	6.19524650	3.66700987
15	C	17.21408989	5.44661094	1.25951141
16	C	13.11844513	3.38450232	1.07487963
17	C	12.69993754	5.68942557	0.43746871
18	C	12.28248949	4.35474340	0.50870726
19	H	15.03914256	3.00656271	2.01077281
20	H	14.29798590	7.08808905	0.88220314
21	H	12.79445017	2.34847662	1.13110981
22	H	12.05104128	6.44296971	-0.00140651
23	H	11.30567007	4.07122993	0.12459892
24	C	14.77915715	5.07928094	1.48970961
25	C	14.37527654	3.74531488	1.57064615

Table S7. Dipole moments of selected compounds as determined by experimental methods (literature) or by DFT calculations the ZORA-BLYP-D3(BJ)/TZ2P level (this work).

Compound X	CH_2Cl_2	THF	Pyridine	1,2-$C_6F_2H_4$	**1-H**	**2-H**
Dipole moment of X [D]	1.6 (exp.)[14]	1.8 (exp.)[15]	2.3 (exp.)[16]	2.6 (exp.)[17]	-	-
	-	1.8 (theo.)	2.3 (theo.)	-	4.8 (theo.)	6.1 (theo).
Reaction **1-H** → **4-H** proceeds, when X is used as solvent / catalyst	No	No	Yes	Yes	No	Yes

In the analysis of the dipole moments, it has to be taken into consideration that the solvents are present in excess, while the starting material **1-H** is present in stoichiometric amounts and compound **2-H** was present in catalytic amounts.

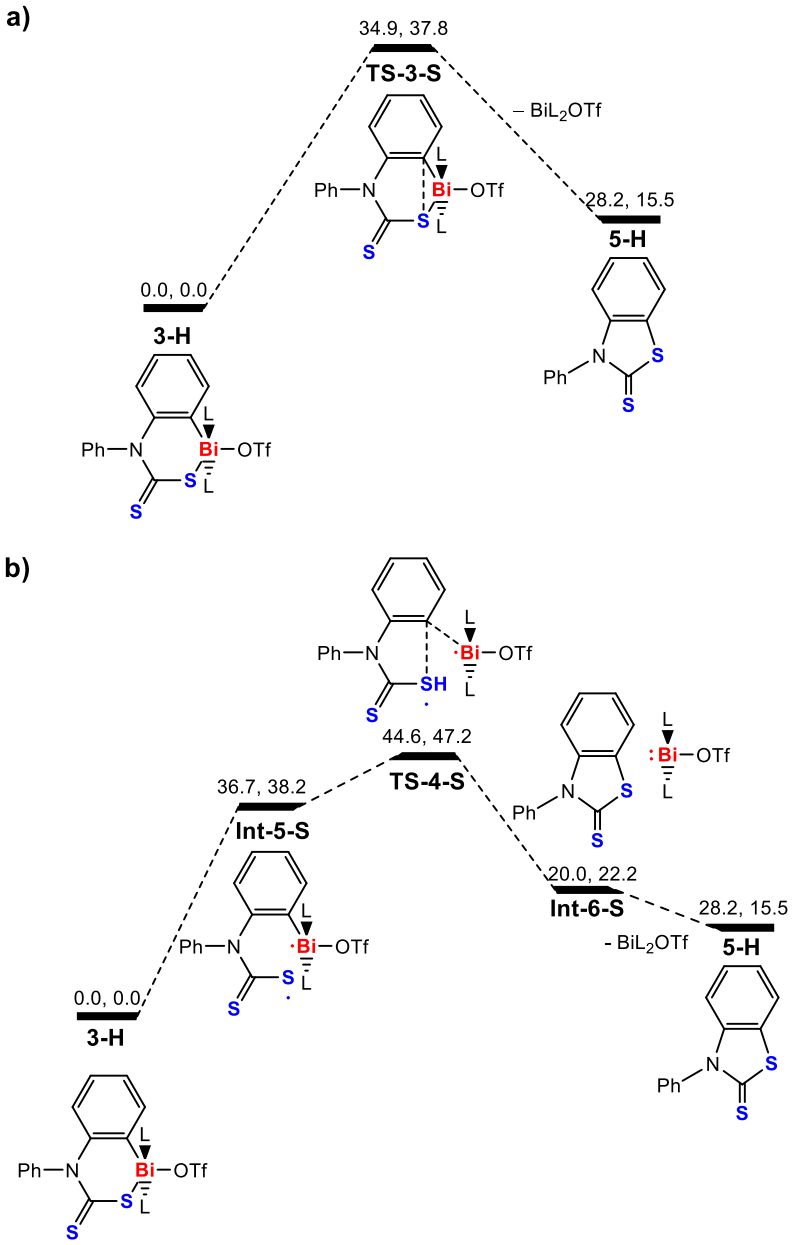


Figure S19. Thermodynamic data for the potential steps in the formation of **5-H** from **3-H**. Left values for ΔH and right values for ΔG (in kcal mol^{-1}).

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