Bi(I)-Catalyzed Transfer-Hydrogenation with Ammonia-Borane

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Supporting Information

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1. General Experimental Notes

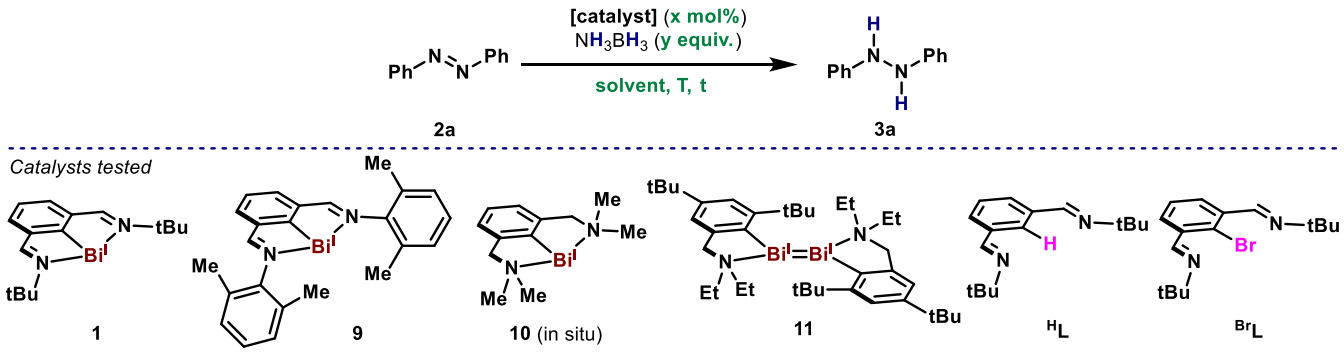
Unless otherwise stated, all manipulations were performed using standard Schlenk techniques under dry argon in flame-dried glassware. Compounds **2b-i**,[1] NH_2MeBH_3,[2] NH_3BEt_3,[3] ND_3BH_3,[4] NH_3BD_3,[4] ND_3BD_3[4], **8**[5], **9**,[6] **10** (formed in situ),[7] and **11**[6] were synthesized according to previous reports. Anhydrous solvents were distilled from appropriate drying agents and were transferred under Argon: THF, DCE (CaH_2), CH_3CN (CaH_2), acetone, toluene (Na/K), 1,4-dioxane (MS). Commercially available 1,2-diphenyldiazene (**2a**), NH_3BH_3, $NHMe_2BH_3$, NMe_3BH_3, nitroarenes (**4a-i**) and celite® 545 were obtained from Sigma Aldrich. Flash chromatography: Merck silica gel 60 (40-63 µm). MS (EI): Finnigan MAT 8200 (70 eV), ESI-MS: ESQ 3000 (Bruker). High-resolution mass determinations: Bruker APEX III FT-MS (7 T magnet) or MAT 95 (Finnigan). NMR spectra were recorded using a Bruker Avance VIII-300, Bruker Avance III HD 400 MHz spectrometer. ^{1}H NMR spectra (300.13 MHz, 400.1 MHz) were referenced to the residual protons of the deuterated solvent used. ^{13}C{1H} NMR spectra (75.47 MHz. 101 MHz) were referenced internally to the D-coupled ^{13}C resonances of the NMR solvent. ^{19}F NMR spectra (225 MHz) were referenced externally to the ^{19}F resonances of $CFCl_3$. ^{11}B NMR spectra (96 MHz) were referenced externally to the ^{11}B resonances of BF_3OEt_2. Chemical shifts (δ) are given in ppm, relative to deuterated solvent residual peak, and coupling constants (*J*) provided in Hz.

2. Optimization Studies

2.1 General Procedure for Optimization Using 1,2-Diphenyldiazene (**2a**) as standard substrate

A culture tube equipped with a stir bar was charged with 1,2-diphenyldiazene (**2a**, 36.4 mg, 0.2 mmol, 1.0 equiv.) and ammonia-borane (1.0-2.0 equiv.). A teflon cap was fitted, and the tube was evacuated and refilled with argon (3 cycles). The tube was transferred to a glove box, and catalyst (1-4 mol%) was added. The tube was removed from the glove box and subjected to a positive pressure of argon. The corresponding solvent was added (1.0 mL) and the reaction was then stirred at the desired temperature (35 to 50 °C). After the indicated time, the yield was calculated by ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standard.

Table S1. Optimization of reaction conditions for the transfer hydrogenation of **2a.**



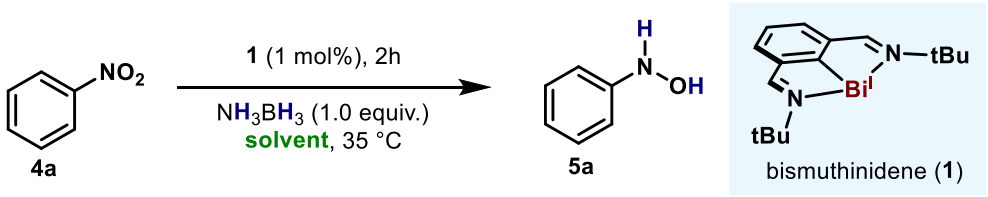
entry	catalyst	X	Y	solvent	T (°C)	t (h)	Yield (%)[a]
1	**1**	4.0	1	THF	50	24	99
2	**1**	1.0	1	THF	50	16	57[b]
3	**1**	1.0	1.5	THF	50	16	85[c]
4	**1**	1.0	2.0	THF	50	16	86[d]
5	**1**	1.0	2.0	THF	35	16	53[e]
6	**1**	1.0	2.0	DCE	50	16	76[f]
7	**1**	1.0	2.0	1,4-dioxane	50	16	87[g]
8	**1**	1.0	2.0	acetone	50	16	45[h]
9	**1**	1.0	1.0	THF (1.0 equiv. H_2O)	50	2	99
10	**1**	1.0	1.0	THF (2.0 equiv. H_2O)	50	3	99
11	**1**	**1.0**	**1.0**	**THF (1.0 equiv. H_2O)**	**35**	**3**	**99**
12	-	-	1.0	THF (1.0 equiv. H_2O)	35	16	trace
13	**1**	1.0	-	THF (1.0 equiv. H_2O)	35	16	trace
14	**9**	1.0	1.0	THF (1.0 equiv. H_2O)	35	3	41%
15	**10**	1.0	1.0	THF (1.0 equiv. H_2O)	35	3	trace
16	**11**	1.0	1.0	THF (1.0 equiv. H_2O)	35	3	7%
17	^{H}**L**	1.0	1.0	THF (1.0 equiv. H_2O)	35	3	trace
18	^{Br}**L**	1.0	1.0	THF (1.0 equiv. H_2O)	35	3	trace

[a] ^{1}H NMR yield using 1,3,5-trimethoxybenzene as internal standard.; [b] starting material recovery 41%; [c] starting material recovery 14%; [d] starting material recovery 11%; [e] starting material recovery 42%; [f] starting material recovery 5%; [g] starting material recovery 12%; [h] starting material recovery 53%.

2.2 General Procedure for Optimization Using Nitrobenzene (**4a**) as standard substrate

A culture tube equipped with a stir bar was charged with ammonia-borane (6.2 mg, 0.2 mmol, 1.0 equiv.). A teflon cap was fitted, and the tube was evacuated and refilled with argon (3 cycles). The tube was transferred to a glove box, and Bi(I) catalyst (**1**, 0.9 mg, 1 mol%) was added. The tube was removed from the glove box, and placed under a positive pressure of argon. The corresponding solvent was added (1.0 mL) together with nitrobenzene (20.6 uL, 0.2 mmol). The reaction was stirred at 35 °C. After 2h, the reaction was judged complete by TLC, the yield was calculated by ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standard.

Table S2. Optimization of reaction conditions for the transfer hydrogenation of **4a.**



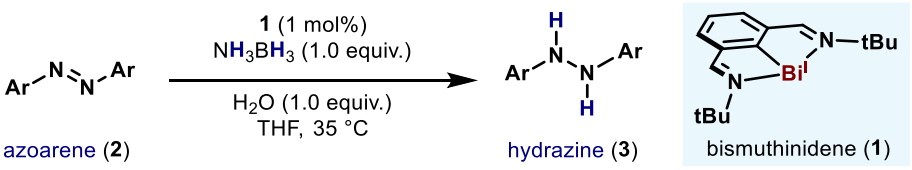
entry	solvent	yield (%)[a]
1	THF	65
2	**1,4-dioxane**	**89**
3	DCE	60
4	toluene	61
5	CH_3CN	64
6[b]	1,4-dioxane	n.r
7[c]	1,4-dioxane (1.0 equiv. H_2O)	57%

[a] ^{1}H NMR yield using 1,3,5-trimethoxybenzene as internal standard.; [b] without Bi(I) catalyst; [c] several byproducts were also detected in the crude mixture.

3. General Procedures

3.1 General Procedure A: azoarenes as substrates

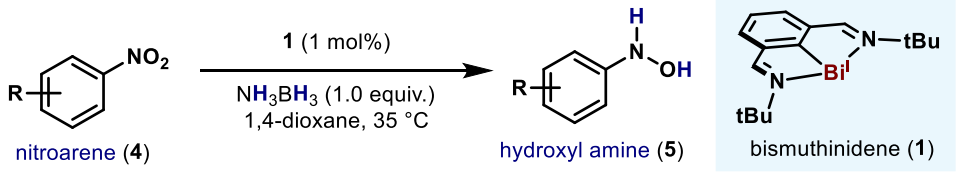
Scheme S1. General transfer hydrogenation of azoarenes with ammonia-borane.



A culture tube equipped with a stir bar was charged with azoarene (**2**, 0.3 mmol, 1.0 equiv.) and ammonia-borane (9.3 mg, 0.3 mmol, 1.0 equiv.). A teflon cap was fitted, and the tube was evacuated and refilled with argon (3 cycles). The tube was transferred to a glove box, and Bi(I) catalyst (**1**, 1.4 mg, 1 mol%) was added. The tube was removed from the glove box and placed under a positive pressure of argon. Firstly, degassed H_2O (5.4 uL, 1.0 equiv.) was added together with THF (1.0 mL) and the mixture was stirred at 35 °C. After reaction completion (monitored by TLC), the mixture was filtered through a glass funnel with a thin layer (20 mm) of celite and eluted with DCM and ethyl acetate. The filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography (hexane/ethyl acetate=10/1 to 5/1) under argon to afford product **3**.

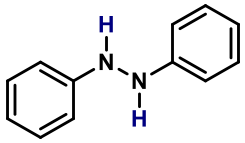
3.2 General Procedure B: nitroarenes as substrates

Scheme S2. General transfer hydrogenation of nitroarenes with ammonia-borane.



A culture tube equipped with a stir bar was charged with nitroarene (**4**, 0.5 mmol, 1.0 equiv., *if solid*), ammonia-borane (15.4mg, 0.5 mmol, 1.0 equiv.). A teflon cap was fitted, and the tube was evacuated and refilled with argon (3 cycles). The tube was transferred to a glove box, and Bi(I) catalyst (**1**, 2.3 mg, 1 mol%) was added. The tube was removed from the glove box, and placed under a positive pressure of argon. 1,4-dioxane was added (2.0 mL) together with the corresponding nitroarene (**4**, 0.5 mmol, 1.0 equiv., *if liquid*). The reaction was stirred at 35 °C. After reaction completion (monitored by TLC), the mixture was filtered through a glass funnel with a thin layer (20 mm) of celite and eluted with DCM and ethyl acetate. The filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography (hexane/ethyl acetate=5/1 to 2/1) under argon to afford product **5**.

4. Characterization Data



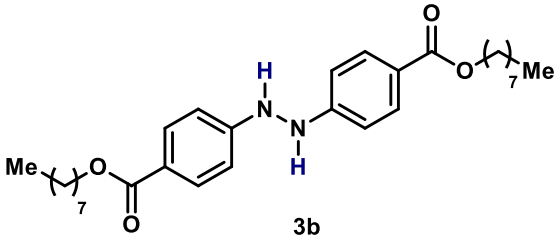
3a

1,2-Diphenylhydrazine (3a)

Following the general procedure A, **3a** was prepared from **2a** (54.7 mg, 0.3 mmol, 1.0 equiv.) in 2 h as a white solid (54.9 mg, 0.298 mmol, 99%). Spectroscopic data match those reported in the literature.[8]

^{1}H NMR - (400 MHz, $CDCl_3$): δ 7.23-7.18 (m, 4H), 6.85-6.80 (m, 6H), 5.56 (2H).

^{13}C NMR - (101 MHz, $CDCl_3$): δ 147.8, 128.3, 118.8, 111.3.



3b

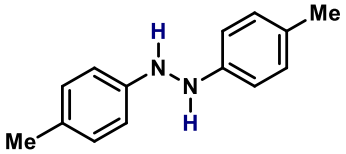
Dioctyl 4,4'-(hydrazine-1,2-diyl)dibenzoate (3b)

Following the general procedure A, **3b** was prepared from **2b** (98.9 mg, 0.2 mmol, 1.0 equiv.) in 10 h as a colorless oil (98.5 mg, 0.198 mmol, 99%).

^{1}H NMR - (400 MHz, $CDCl_3$): δ 7.90 (dt, *J* = 8.0, 4.0 Hz, 4H), 6.80 (dt, *J* = 8.0, 4.0 Hz, 4H), 6.17 (s, 2H), 4.24 (t, *J* = 6.8 Hz, 4H), 1.76-1.67 (m, 4H), 1.45-1.20 (m, 20H), 0.88 (t, *J* = 6.8 Hz, 6H).

^{13}C NMR - (101 MHz, $CDCl_3$): δ 165.6, 151.0, 130.5, 120.9, 110.2, 63.7, 30.8, 28.2, 28.2, 27.8, 25.0, 21.6, 13.1.

HRMS (ESI, m/z): calc'd for $C_{30}H_{45}N_2O_4$ $[M+H]^+$ 497.337382; found 497.338030



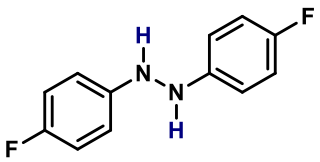
3c

1,2-Di-*p*-tolylhydrazine (3c)

Following the general procedure A, **3c** was prepared from **2c** (63.1 mg, 0.3 mmol, 1.0 equiv.) in 50 h as a off-white solid (61.5 mg, 0.289 mmol, 97%). Spectroscopic data match those reported.[9]

^{1}H NMR - (400 MHz, $CDCl_3$): δ 7.00 (d, *J* = 8.0 Hz, 4H), 6.74 (dt, *J* = 12.0, 2.0 Hz, 4H), 5.45 (s, 2H), 2.24 (s, 6H).

^{13}C NMR - (101 MHz, $CDCl_3$): δ 145.7, 128.8, 128.0, 111.4, 19.5



3d

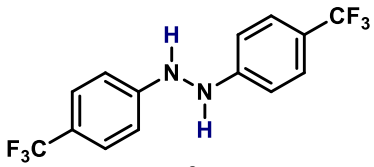
1,2-Bis(4-fluorophenyl)hydrazine (3d)

Following the general procedure A, **3d** was prepared from **2d** (65.5 mg, 0.3 mmol, 1.0 equiv.) in 10 h as a white solid (63.0 mg, 0.286 mmol, 95%). Spectroscopic data match those reported in the literature.[9]

^{1}H NMR - (300 MHz, $CDCl_3$): δ 6.94-6.86 (m, 4H), 6.79-6.71 (m, 4H), 5.50 (s, 2H).

^{13}C NMR - (75.5 MHz, $CDCl_3$): δ 157.1 (d, *J* = 237.8 Hz), 144.8 (d, *J* =1.5 Hz), 115.8 (d, *J* = 22.7 Hz), 113.3 (d, *J* = 7.5 Hz).

^{19}F NMR - (225 MHz, $CDCl_3$): δ -124.9 (s, 2F).



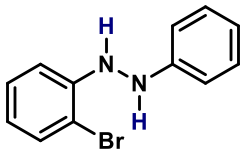
3e

1,2-Bis(4-(trifluoromethyl)phenyl)hydrazine (3e)

Following the general procedure A, **3e** was prepared from **2e** (95.5 mg, 0.3 mmol, 1.0 equiv.) in 5 min as a white solid (95.4 mg, 0.298 mmol, 99%). Spectroscopic data match those reported in the literature.[10]

^{1}H NMR - (300 MHz, $CDCl_3$): δ 7.47 (d, *J* = 8.4 Hz, 4H), 6.87 (d, *J* = 8.4 Hz, 4H), 5.92 (s, 2H).

^{13}C NMR - (75.5 MHz, $CDCl_3$): δ 150.7 (d, *J* = 1.0 Hz), 126.8 (q, *J* = 3.7 Hz), 124.6 (q, *J* = 271.0 Hz), 122.1 (q, *J* = 32.5 Hz), 111.6. **^{19}F NMR** - (225 MHz, $CDCl_3$): δ -61.4 (s, 6F)



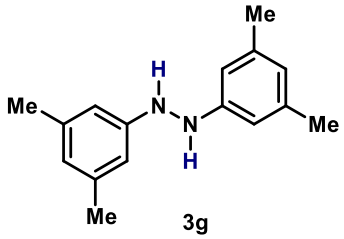
3f

1-(2-Bromophenyl)-2-phenylhydrazine (3f)

Following the general procedure A, **3f** was prepared from **2f** (83.8 mg, 0.32 mmol, 1.0 equiv.) in 16 h as a white solid (82.7 mg, 0.315 mmol, 98%). Spectroscopic data match those reported in the literature.[9]

^{1}H NMR - (400 MHz, $CDCl_3$): δ 7.45 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.25-7.20 (m, 2H), 7.18-7.13 (m, 1H), 7.02 (dd, *J* = 8.0, 1.4 Hz, 1H), 6.86 (tt, *J* = 7.4, 1.2 Hz, 1H), 6.83-6.79 (m, 2H), 6.72-6.67 (m, 1H), 6.17 (s, 1H), 5.66 (s, 1H).

^{13}C NMR - (101 MHz, $CDCl_3$): δ 147.2, 144.2, 131.4, 128.4, 127.5, 119.4, 119.2, 112.3, 111.3, 106.2.



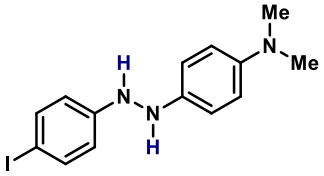
3g

1,2-Bis(3,5-dimethylphenyl)hydrazine (3g)

Following the general procedure A, **3g** was prepared from **2g** (71.5 mg, 0.3 mmol, 1.0 equiv.) in 16 h as a white solid (70.9 mg, 0.295 mmol, 98%). Spectroscopic data match those reported in the literature.[9]

^{1}H NMR - (400 MHz, $CDCl_3$): δ 6.48 (s, 2H), 6.46 (s, 4H), 5.38 (s, 2H), 2.22 (s, 12H).

^{13}C NMR - (101 MHz, $CDCl_3$): δ 148.2, 138.0, 120.7, 109.0, 20.4.



3h

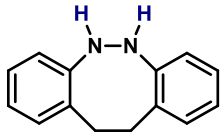
4-(2-(4-Iodophenyl)hydrazinyl)-*N*,*N*-dimethylaniline (3h)

Because of the instability of compound **3h** in air, the yield was calculated by crude ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standard, without further purification. Following the general procedure A (THF-d_8), **3h** was prepared from **2h** (105.4 mg, 0.3 mmol, 1.0 equiv.) in 40 h (99%).

^{1}H NMR - (400 MHz, THF-d_8): δ 7.29 (dt, J = 8.8, 2.0 Hz, 2H), 6.59 (dt, J = 8.8, 2.0 Hz, 2H), 6.51 (dt, J = 8.8, 2.0 Hz, 2H), 6.39 (dt, J = 8.8, 2.0 Hz, 2H), 4.60 (s, 2H), 2.74 (s, 6H).

^{13}C NMR - (101 MHz, THF-d_8): δ 148.7, 144.2, 140.4, 137.8, 116.8, 115.8, 115.7, 76.5, 41.9.

HRMS (ESI negative mode, m/z): calc'd for $C_{14}H_{15}IN_3$ $[M\text{-}H^+]^-$ 352.031618; found 352.031770.



3i

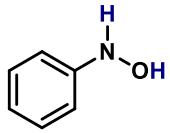
5,6,11,12-Tetrahydrodibenzo[*c*,*g*][1,2]diazocine (3i)

Following the general procedure procedure A, **3i** was prepared from **2i** (62.5 mg, 0.3 mmol, 1.0 equiv.) in 20 h as a white solid (62.7 mg, 0.298 mmol, 99%).

^{1}H NMR - (400 MHz, $CDCl_3$): δ 7.10 (dd, J = 7.4, 1.6 Hz, 2H), 7.05 (td, J = 7.4, 1.6 Hz, 2H), 6.89 (td, J = 7.4, 1.6 Hz, 2H), 6.67 (dd, J = 7.4, 1.6 Hz, 2H), 5.47 (s, 2H), 3.20 (s, 4H).

^{13}C NMR - (101 MHz, $CDCl_3$): δ 145.4, 132.3, 130.0, 125.5, 121.3, 116.6, 30.4.

HRMS (ESI, m/z): calc'd for $C_{14}H_{15}N_2$ $[M+H]^+$ 211.122973; found 211.123220.



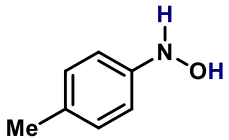
5a

***N*-Phenylhydroxylamine (5a)**

Following the general procedure B, **5a** was prepared from **4a** (51.5 uL, 0.5 mmol, 1.0 equiv.) in 2 h as a white solid (48.8 mg, 0.447 mmol, 89%). Spectroscopic data match those reported in the literature.[11]

^{1}H NMR - (400 MHz, DMSO-d_6): δ 8.27 (d, J = 2.2 Hz, 1H), 8.21 (s, 1H), 7.15 (t, J = 8.0 Hz, 2H), 6.83 (d, J = 8.0 Hz, 2H), 6.73 (t, J = 8.0 Hz, 1H).

^{13}C NMR - (101 MHz, DMSO-d_6): δ 152.5, 128.8, 119.7, 113.4.



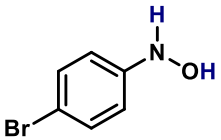
5b

***N*-(*p*-Tolyl)hydroxylamine (5b)**

Following the general procedure B, **5b** was prepared from **4b** (68.6 mg, 0.5 mmol, 1.0 equiv.) in 2 h as a white solid (58.1 mg, 0.47 mmol, 94%). Spectroscopic data match those reported in the literature.[11]

^{1}H NMR - (400 MHz, DMSO-d_6): δ 8.21 (bs, 1H), 8.07 (bs, 1H), 6.98 (d, J = 7.2 Hz, 2H), 6.75 (d, J = 7.1 Hz, 2H), 2.20 (s, 3H).

^{13}C NMR - (101 MHz, DMSO-d_6): δ 149.7, 128.8, 127.8, 113.3, 20.3.



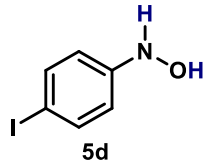
5c

***N*-(4-Bromophenyl)hydroxylamine (5c)**

Following the general procedure B, **5c** was prepared from **4c** (101.0 mg, 0.5 mmol, 1.0 equiv.) in 2 h as a white solid (85.2 mg, 0.426 mmol, 85%). Spectroscopic data match those reported in the literature.[11]

^{1}H NMR - (400 MHz, DMSO-d_6): δ 8.42 (s, 1H), 8.40 (bs, 1H), 7.31 (dt, J = 8.0, 2.1 Hz, 2H), 6.78 (dt, J = 8.0, 2.1 Hz, 2H).

^{13}C NMR - (101 MHz, DMSO-d_6): δ 151.8, 131.5, 115.3, 110.5.



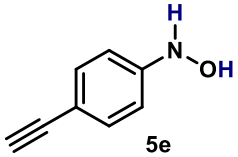
5d

***N*-(4-Iodophenyl)hydroxylamine (5d)**

Following the general procedure B, **5d** was prepared from **4d** (124.5 mg, 0.5 mmol, 1.0 equiv.) in 2 h as a white solid (103.4 mg, 0.44 mmol, 88%). Spectroscopic data match those reported in the literature.[11]

^{1}H NMR - (400 MHz, DMSO-d_6): δ 8.41 (bs, 2H), 7.46 (d, J = 7.2 Hz, 2H), 6.68 (d, J = 7.1 Hz, 2H).

^{13}C NMR - (101 MHz, DMSO-d_6): δ 151.9, 136.8, 115.4, 80.7.



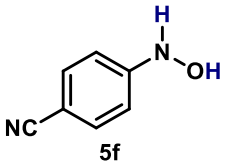
5e

***N*-(4-Ethynylphenyl)hydroxylamine (5e)**

Following the general procedure B, **5e** was prepared from **4e** (75.8 mg, 0.5 mmol, 1.0 equiv.) in 2 h as a white solid (44.8 mg, 0.337 mmol, 67%). Spectroscopic data match those reported in the literature.[11]

^{1}H NMR - (400 MHz, DMSO-d_6): δ 8.57 (s, 1H), 8.46 (s, 1H), 7.27 (d, J = 8.0 Hz, 2H), 6.79 (d, J = 8.0 Hz, 2H), 3.87 (s, 1H).

^{13}C NMR - (101 MHz, DMSO-d_6): δ 153.0, 132.7, 112.9, 111.9, 85.0, 78.5.



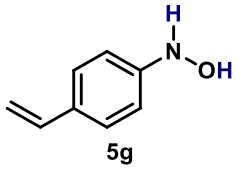
5f

4-(Hydroxyamino)benzonitrile (5f)

Following the general procedure B, **5f** was prepared from **4f** (74.1 mg, 0.5 mmol, 1.0 equiv.) in 2 h as a white solid (61.1 mg, 0.46 mmol, 91%). Spectroscopic data match those reported in the literature.[11]

^{1}H NMR - (400 MHz, DMSO-d_6): δ 9.10 (bs, 1H), 8.74 (bs, 1H), 7.54 (d, J = 7.4 Hz, 2H), 6.85 (d, J = 7.1 Hz, 2H).

^{13}C NMR - (101 MHz, DMSO-d_6): δ 155.4, 133.1, 120.1, 111.8, 99.1.



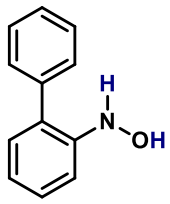
5g

***N*-(4-Vinylphenyl)hydroxylamine (5g)**

Following the general procedure B, **5g** was prepared from **4g** (74.6 mg, 0.5 mmol, 1.0 equiv.) in 2 h as a white solid (55.4 mg, 0.410 mmol, 82%). Spectroscopic data match those reported in the literature.[12]

^{1}H NMR - (400 MHz, DMSO-d_6): δ 8.35 (t, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 7.3 Hz, 2H), 6.80 (d, *J* = 7.0 Hz, 2H), 6.60 (dd, *J* = 6.6 Hz, 1H), 5.58 (dd, *J* = 5.6 Hz, 1H), 5.0 (dd, *J* = 5.4 Hz, 1H).

^{13}C NMR - (101 MHz, DMSO-d_6): δ 151.9, 136.7, 128.4, 126.6, 112.8, 110.2.



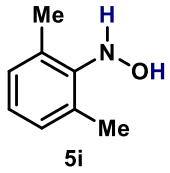
5h

***N*-([1,1'-Biphenyl]-2-yl)hydroxylamine (5h)**

Following the general procedure B, **5h** was prepared from **4h** (99.5 mg, 0.5 mmol, 1.0 equiv.) in 2 h as a white solid (69.5 mg, 0.375 mmol, 75%). Spectroscopic data match those reported in the literature.[13]

^{1}H NMR - (400 MHz, DMSO-d_6): δ 8.38 (bs, 1H), 7.49-7.39 (m, 5H), 7.38-7.31 (m, 1H), 7.29-7.23 (m, 2H), 7.12-7.05 (m, 1H), 6.93-6.85 (m, 1H).

^{13}C NMR - (101 MHz, DMSO-d_6): δ 148.3, 138.6, 129.6, 128.8, 128.5, 128.1, 127.2, 126.8, 120.0, 113.8.



5i

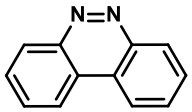
***N*-(2,6-Dimethylphenyl)hydroxylamine (5i)**

Following the general procedure B, **5h** was prepared from **4h** (75.6 mg, 0.5 mmol, 1.0 equiv.) in 2 h reaction time as a white solid (15.3 mg, 0.112 mmol, 22%). Spectroscopic data match those reported in the literature.[14]

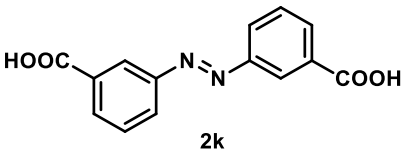
^{1}H NMR - (400 MHz, DMSO-d_6): δ 8.06 (s, 1H), 7.15 (bs, 1H), 6.92 (d, *J* = 7.4 Hz, 2H), 6.83 (dd, *J* = 8.8, 8.4 Hz, 1H), 2.28 (s, 6H).

^{13}C NMR - (101 MHz, DMSO-d_6): δ 146.4, 131.0 128.7, 124.1, 18.6.

Scheme S3. Unsuccessful azoarenes for the transfer hydrogenation with ammonia-borane.



2j

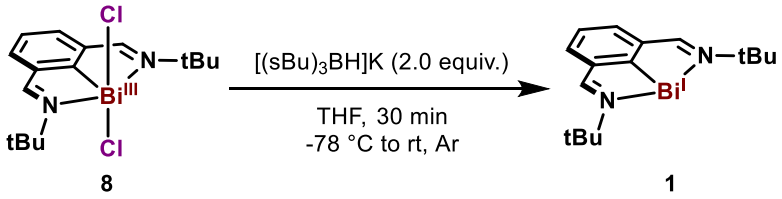


2k

Probably due to the aromatic system in **2j**, reaction under the optimal conditions did not result in the corresponding *N,N'*-arylhydrazine. Indeed, no product was obtained even at higher temperatures (50 °C). Substrate containing acidic functionalities (**2k**) was also not successful, showing bad solubility in THF and hence low reactivity. Another possibility for its low conversion to the hydrogenated product might be the catalyst deactivation due to the acidic carboxylate groups.

5. Synthesis of bismuthinidene 1[6]

Scheme S4. Reduction of chlorobismuthine **8** to bismuthinidene **1** with K-Selectride.



8 **1**

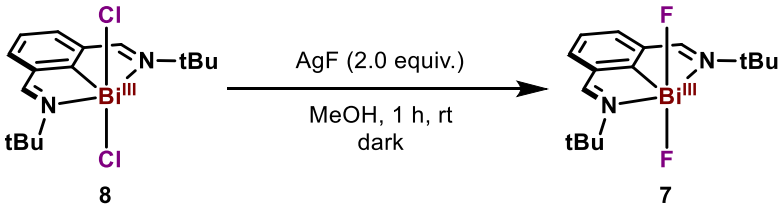
Bismuthinidene **1** was synthesized following a reported protocol.[6] A schlenk flask equipped with a stir bar was charged with **8** (522 mg, 1 mmol, 1.0 equiv.) and THF (10 ml) under an argon atmosphere and cooled to -78 °C in a dry ice/acetone bath. Then, a 1 M solultion of K-Selectride (2 ml, 2 mmol, 2.0 equiv.) was added and the mixture was stirred over 30 min. After reaction completion, the solvent was removed. The crude was redissolved in pentane and filtered through a glass funnel with a thin layer (20 mm) of celite under argon. The volume of the filtrate was reduced to 5 ml and cooled to -20 °C overnight. After this time, **1** was obtained as dark crystalline solid in 61% yield (275 mg, 0.61 mmol).

^{1}H NMR - (400 MHz, THF-d_8): δ 9.82 (s, 2H), 7.95 (d, J = 7.9 Hz, 2H), 7.09 (t, J = 7.2 Hz, 1H), 1.58 (s, 18H).
^{13}C NMR - (101 MHz, THF-d_8): δ 164.9, 147.6, 134.2, 122.7, 60.5, 33.7.
HRMS (ESI, m/z): calc'd for $C_{16}H_{23}N_2Bi$ $[M]^+$ 452.16651; found 452.16730.

Note: The carbon corresponding to the C–Bi bond is also not observable by ^{13}C NMR due to the high quadrupole moment of the ^{209}Bi nucleus (100%, I = 9/2, quadrupole moment -0.4 x 10^{-28} m^{-2}), which broaden the peaks corresponding to atoms bonded to the Bi center to such an extent that they are not observable under standard conditions.

6. Synthesis of fluorobismuthine 7

Scheme S5. Anion metathesis of **8** with AgF for the synthesis of fluorobismuthine **7**.



8 7

A schlenk flask equipped with a stir bar was charged with **8** (261 mg, 0.5 mmol, 1.0 equiv.) and AgF (127 mg, 1 mmol, 2.0 equiv.) and MeOH (10 ml). The mixture was stirred over 1 h, and after reaction completion, the solvent was removed. The crude was redissolved in DCM and filtered through a glass funnel with a thin layer (20 mm) of celite to remove precipitated AgCl. After evaporating the solvent, **7** was obtained as a pure white solid in 89% yield (218 mg, 0.44 mmol).

^{1}H NMR - (400 MHz, $CDCl_3$): δ 9.62 (s, 2H), 8.17 (d, *J* = 8.17 Hz, 2H), 7.84 (t, *J* = 7.9 Hz, 1H), 1.60 (s, 18H).
^{13}C NMR - (101 MHz, $CDCl_3$): δ 166.8, 148.5, 136.1, 129.6, 61.7, 30.67.
^{19}F NMR - (101 MHz, $CDCl_3$): δ -133.45 (2F).
HRMS (EI, m/z): calc'd for $C_{16}H_{23}N_2BiF_2$ [M] 490.16304; found 490.16335.

Note: ^{19}F NMR shown a low intensity broad peak, probably due to the high quadrupole moment of the ^{209}Bi nucleus (100%, I = 9/2, quadrupole moment -0.4 x 10^{-28} m^{-2}), which broaden the peaks corresponding to atoms bonded to the Bi center to such an extent that they are not observable under standard conditions. Similarly, the carbon corresponding to the C−Bi bond is also not observable by ^{13}C NMR spectroscopy.

7. Mechanistic studies

7.1 Dehydrogenation of ammonia-borane with **1**

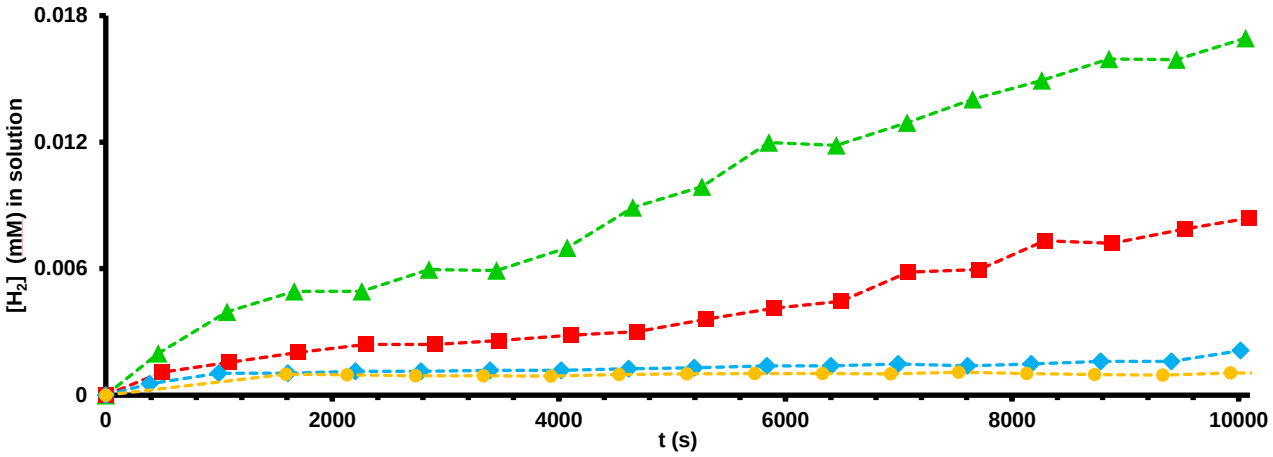
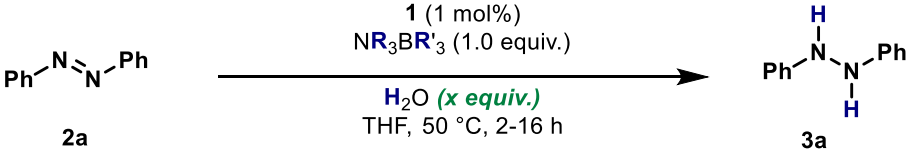


Figure S1. H_2 evolution (in solution) in absence of bismuthinidene **1** (**blue**), with H_2O and in absence of **1** (**yellow**), in presence of **1** without H_2O (**red**) and in presence of **1** with H_2O (**green**).

Representative protocol: A J-Young NMR tube was charged with ammonia-borane complex (3.1 mg, 0.1 mmol), **1** (36.4 mg, 0.02 mmol, 20 mol%), H_2O (1.8 µL, 1.0 equiv.) and 1 mL of THF-d_8. A teflon cap was fitted, and the tube was inserted into the NMR machine. ^{1}H NMR was measured every 10 min over a period of 10000 min at 50 °C. The concentration of H_2 (4.55 ppm) was calculated by ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standard. Data is shown in Figure S1.

7.2 Reaction with amino-borane complexes

Table S3. Transfer hydrogenation of azoarenes using differently substituted amino-borane complexes.[a]



	NH_3BH_3	NH_2MeBH_3	$NHMe_2BH_3$	NMe_3BH_3	NH_3BEt_3
without H_2O	57% (16h)	55% (16h)	36% (16h)	10% (16h)	- (16h)
with 1.0 equiv. H_2O	99% (2h)	97% (7h)	90% (16h)	31% (16h)	- (16h)

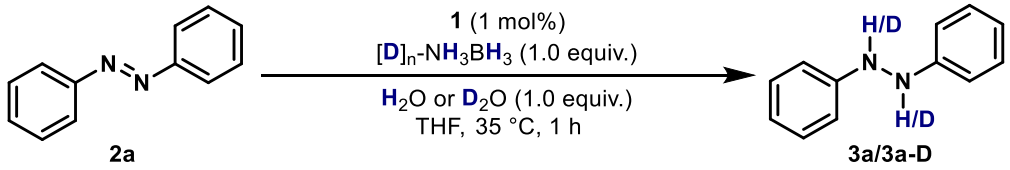
[a] ^{1}H NMR yield using 1,3,5-trimethoxybenzene as internal standard.

A culture tube equipped with a stir bar was charged with **2a** (36.4 mg, 0.2 mmol, 1.0 equiv.), **amino-borane derivative** (0.2 mmol, 1.0 equiv.) and **H_2O** (0 or 1.0 equiv.). A teflon cap was fitted, and the tube was evacuated and refilled with argon (3 cycles). The tube was transferred to a glove box, and Bi(I)

catalyst (**1**, 0.9 mg, 1 mol%) was added. The tube was removed from the glove box, and placed under a positive pressure of argon. THF was added (1.0 mL) and the reaction was stirred at 50 °C and followed by TLC. After reaction completion, the mixture was quenched by filtering it through a glass funnel with a thin layer (20 mm) of celite and eluted with DCM and ethyl acetate. The filtrate was concentrated under reduced pressure. The yield was calculated by ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standard (1.0 equiv.).

7.3 Kinetic Isotope Effects

Scheme S6. Transfer hydrogenation of azoarenes using labeled ammonia-borane complexes.



A culture tube equipped with a stir bar was charged with **2a** (36.4 mg, 0.2 mmol, 1.0 equiv.), $[D]_n$-**ammonia-borane** (0.2 mmol, 1.0 equiv.). A teflon cap was fitted, and the tube was evacuated and refilled with argon (3 cycles). The tube was transferred to a glove box, and Bi(I) catalyst (**1**, 0.9 mg, 1 mol%) was added. The tube was removed from the glove box, and placed under a positive pressure of argon. $[D]_n$-H_2O (0 or 1.0 equiv.) (D_2O was added when the reaction was performed with ND_3 labeled compounds, while H_2O was used with NH_3 compounds) and THF were added (1.0 mL) and the reaction was stirred at 35 °C for 1h. After this time, the mixture was quenched by filtering it through a glass funnel with a thin layer (20 mm) of celite and eluted with DCM and ethyl acetate. The filtrate was concentrated under reduced pressure. The yield was calculated by ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standard (1.0 equiv.). KIE were calculated by comparing the yield of independent reactions using labeled ammonia-borane complexes at the same reaction time (1 h) [KIE = Yield(NH_3BH_3)/Yield(D_n-NH_3BH_3)] . Data obtained is shown in Table S4.

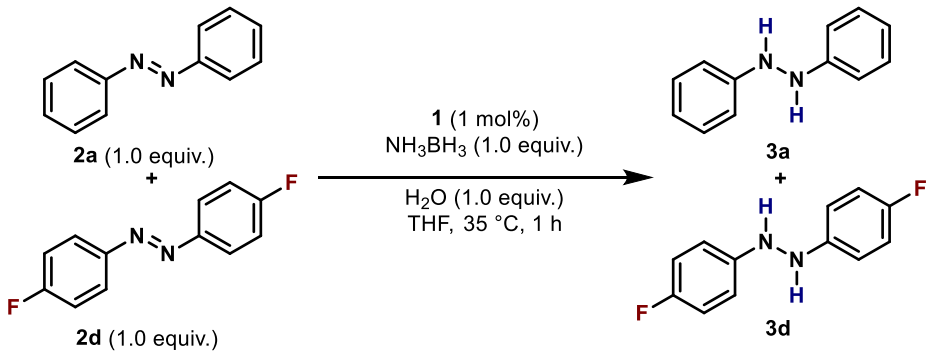
Table S4. Yields obtained with differently labeled ammonia-borane complexes after 1 h and KIE obtained.[a]

entry	Derivative	**3a**, yield (%)	***KIE***
1	NH_3BH_3	27.0%	-
2	ND_3BH_3	16.5%	1.63
3	NH_3BD_3	6.9%	3.94
4	ND_3BD_3	3.8%	7.05

[a] ^{1}H NMR yield using 1,3,5-trimethoxybenzene as internal standard.

7.4 Competition experiment

Scheme S7. Competition experiment between electronically different azoarenes.



A culture tube equipped with a stir bar was charged with **2a** (36.4 mg, 0.2 mmol, 1.0 equiv.), **2d** (43.6 mg, 0.2 mmol, 1.0 equiv.) and ammonia-borane (6.2 mg, 0.2 mmol, 1.0 equiv.). A teflon cap was fitted, and the tube was evacuated and refilled with argon (3 cycles). The tube was transferred to a glove box, and Bi(I) catalyst (**1**, 0.9 mg, 1 mol%) was added. The tube was removed from the glove box, and placed under a positive pressure of argon. At first, degassed H_2O (3.6 uL, 1.0 equiv.) was added, followed by THF (1.0 mL) and stirred at 35 °C. After 1 h, the reaction was quenched by filtering it through a glass funnel with a thin layer (20 mm) of celite and eluted with DCM and ethyl acetate. The filtrate was concentrated under reduced pressure. The yield was calculated by ^1H NMR using 1,3,5-trimethoxybenzene as internal standard (1.0 equiv.), obtaining an 8% of **3a** and an 8% of **3d** (1:1 ratio, Figure S2).

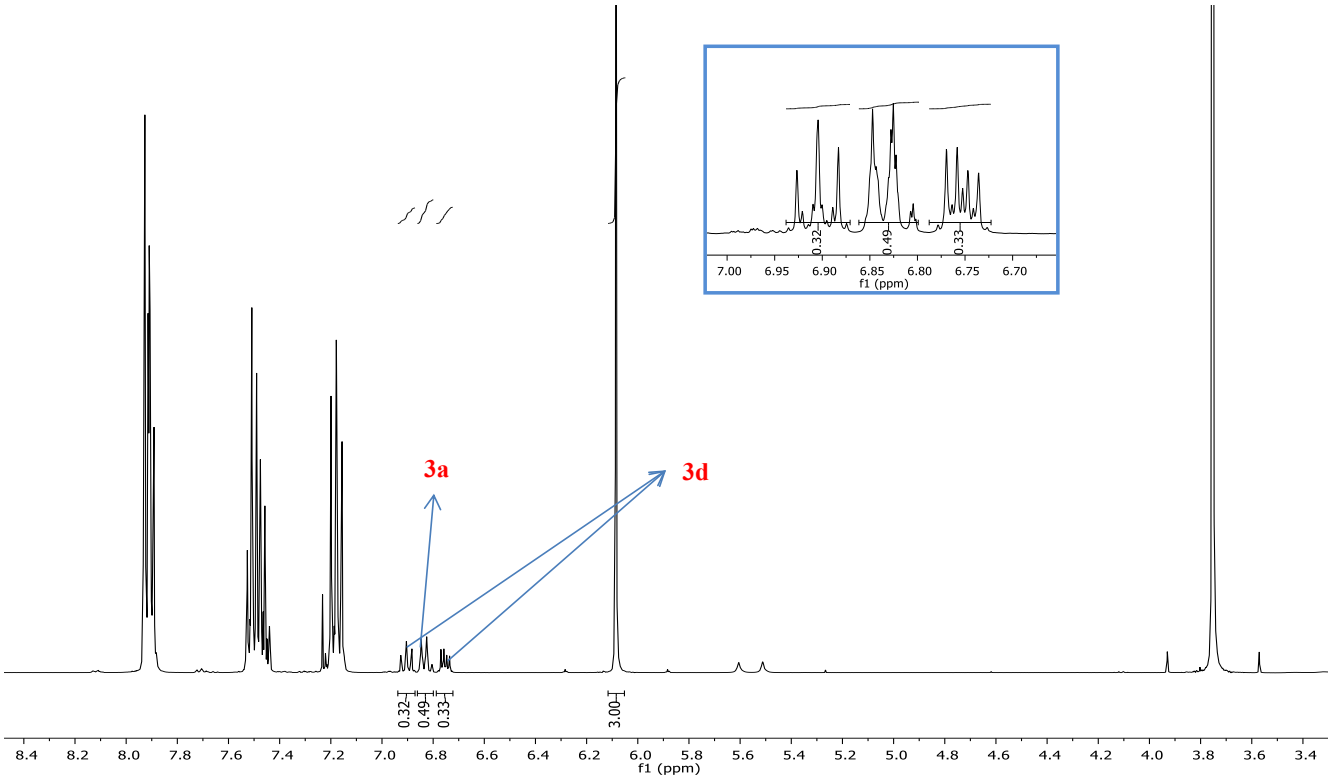
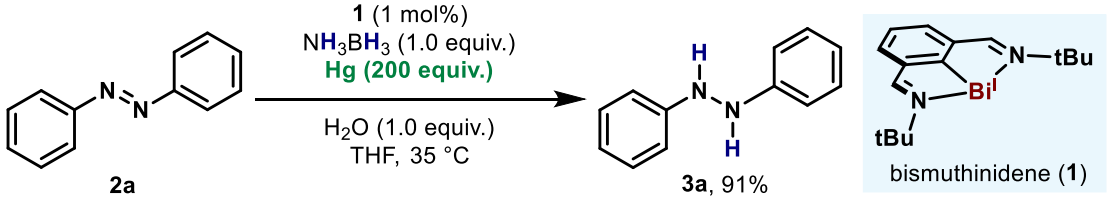


Figure S2. ^{1}H NMR of crude mixture of the competition experiment after 1 h showing the formation of **3a** and **3d**. 1,3,5-trimethoxybenzene (TMB) used as internal standard.

7.5 Homogeneity test

Scheme S8. Transfer hydrogenation of **2a** in presence of Hg.



A culture tube equipped with a stir bar was charged with **2a** (36.4 mg, 0.2 mmol, 1.0 equiv.) and ammonia-borane (6.2 mg, 0.2 mmol, 1.0 equiv.). A teflon cap was fitted, and the tube was evacuated and refilled with argon (3 cycles). The tube was transferred to a glove box, and Bi(I) catalyst (**1**, 0.9 mg, 1 mol%) was added. The tube was removed from the glove box, and placed under a positive pressure of argon. Firstly, degassed H_2O (3.6 uL, 1.0 equiv.) was added together with Hg (85 mg, 200 equiv. respect to Bi(I) catalyst). Then, THF was added (1.0 mL) and the mixture was stirred at 35 °C for 3h. After this time, the reaction was quenched by filtering through a glass funnel with a thin layer (20 mm) of celite and eluted with DCM and ethyl acetate. The filtrate was concentrated under reduced pressure. The yield

was calculated by ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standard (TMB, 1.0 equiv.), obtaining a 91% yield of **3a**.

Further proof of the homogeneity of this reaction was obtained when the concentration of **1** was analyzed before and after the reaction, obtaining the same values (0.002 mmol in 1 mL of THF-d_8, 0.002 mM; see Figure S3).

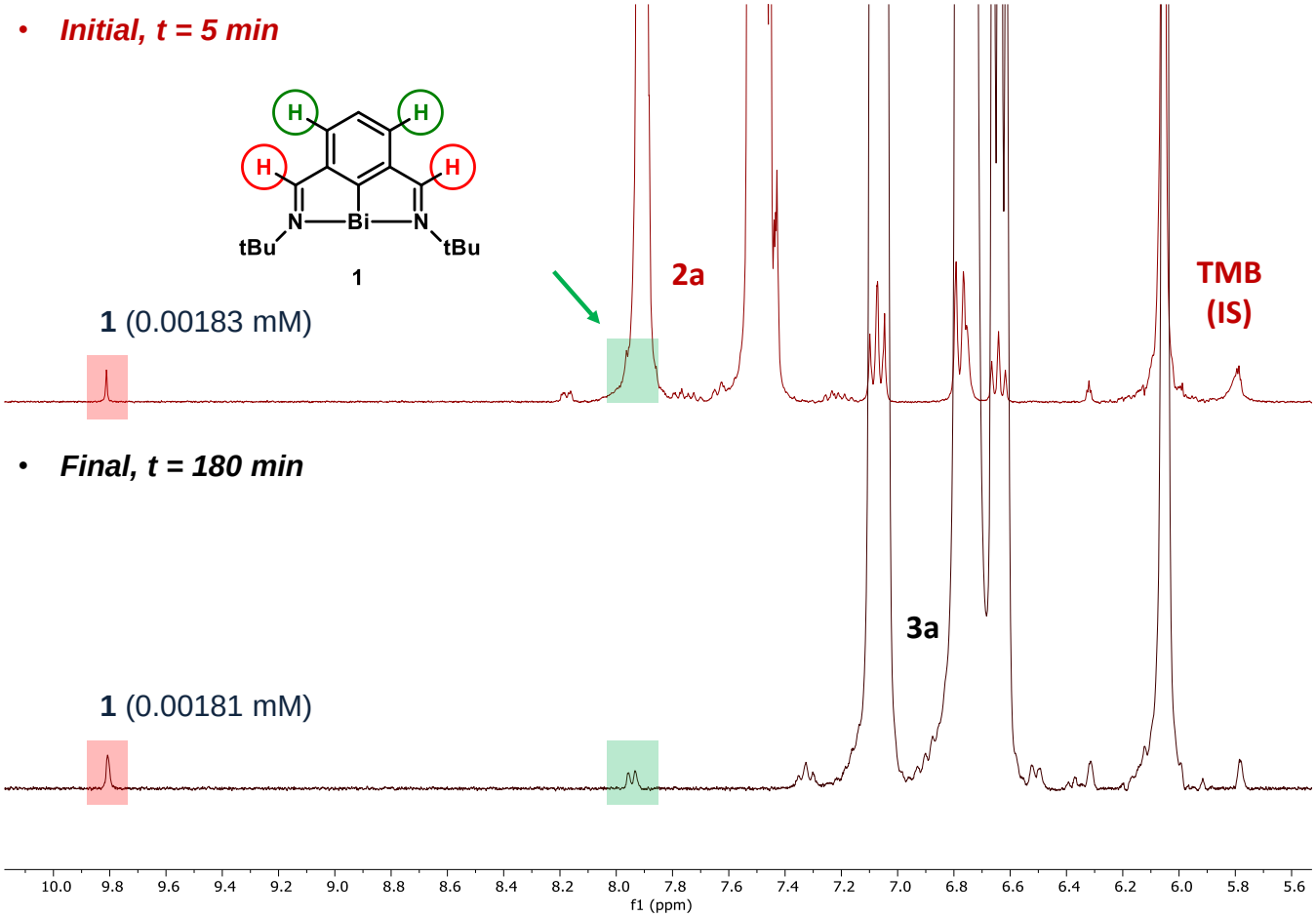
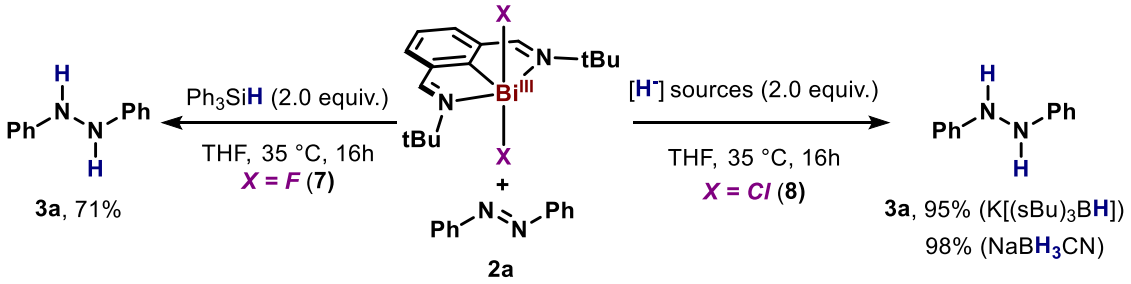


Figure S3. ^{1}H NMR of initial mixture (t = 5 min) and after reaction completion (t = 180 min). As shown, concentration of **1** remains constant. 1,3,5-trimethoxybenzene (TMB, 1.0 equiv.) was used as internal standard.

7.6 Stoichiometric reactions with hydride sources

7.6.1 Reduction of **2a** with hydride sources

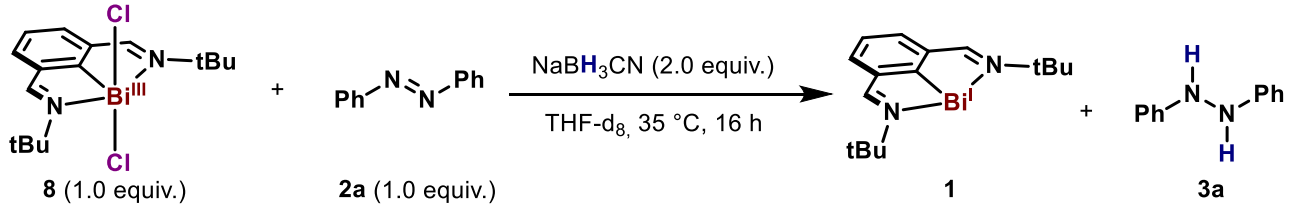
Scheme S9. Stoichiometric experiments with Bi(III) halides and hydride donors.



When the hydride donor is a solid: A culture tube equipped with a stir bar was charged with halobismuthine **7** or **8** (0.1 mmol, 1.0 equiv.) and the hydride source (0.2 mmol, 2.0 equiv.). Then, THF (1 mL) was added and the reaction mixture was stirred at 35 °C over 16 h. *When the hydride donor is a solution:* A culture tube equipped with a stir bar was charged with halobismuthine **8** (0.1 mmol, 1.0 equiv.) and THF (1 mL). Then, the hydride source was added (0.2 mmol, 1M solution, 2.0 equiv.) and the reaction mixture was stirred at 35 °C over 16 h. The reaction was then quenched by filtering it through a glass funnel with a thin layer (20 mm) of celite and eluted with DCM and ethyl acetate. The filtrate was concentrated under reduced pressure. The yield was calculated by ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standard (1.0 equiv.). *Note:* Reactions with hydride sources conducted in the absence of halobismuthines **7** and **8** did not yield any hydrogenated product (**3a**).

7.6.2 Detection of **1** in the stoichiometric reactions with hydride sources

Scheme S10. Stoichiometric experiments with Bi(III) halides and hydride donors.



A culture tube equipped with a stir bar was charged with chlorobismuthine **8** (0.1 mmol, 1.0 equiv.), $NaBH_3CN$ (0.2 mmol, 2.0 equiv.) and **2a** (0.1 mmol, 1.0 equiv.). Then, THF (1 mL) was added and the reaction mixture was stirred at 35 °C over 16 h. After this time, the crude mixture was transferred to an NMR tube under an argon atmosphere and analyzed by ^{1}H NMR.

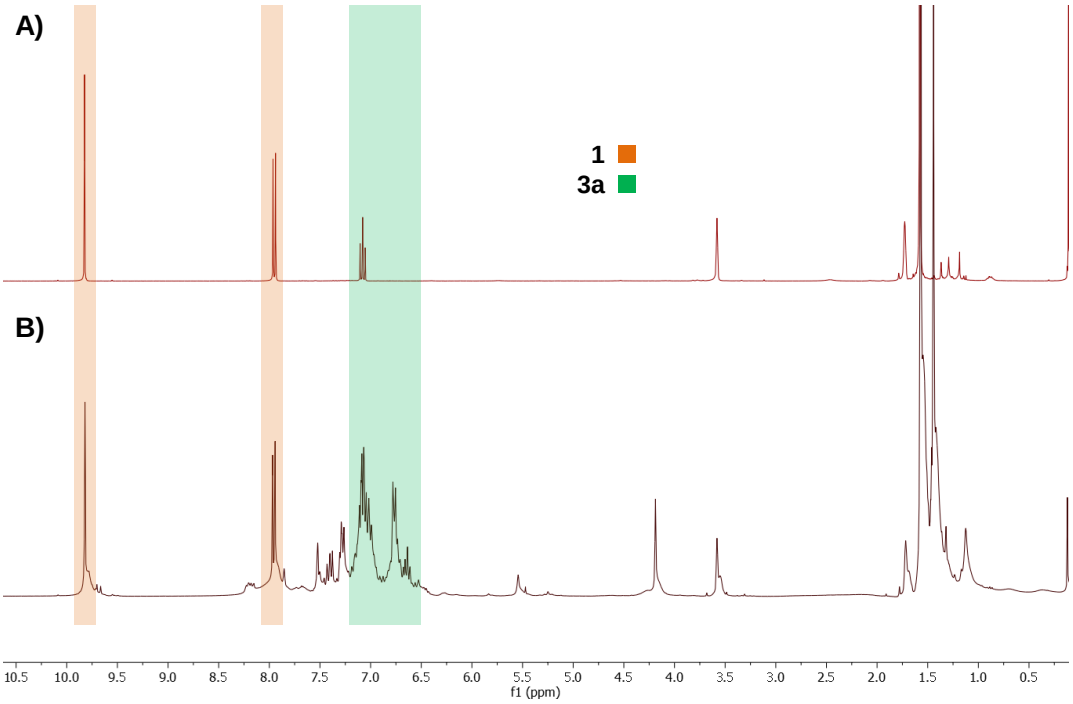
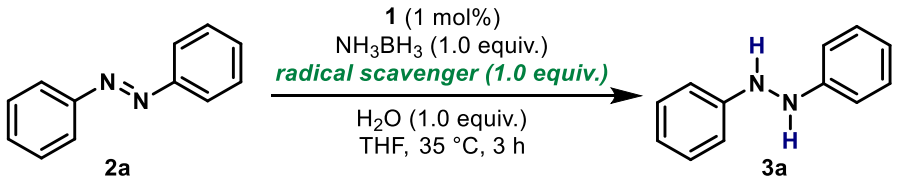


Figure S4. Stoichiometric reaction of **8** and **2a** in the presence of $NaBH_3CN$ showing the formation of bismuthinidene **1** as well as hydrogenated product **3a**.

7.7 Radical trap experiments

Scheme S11. Transfer hydrogenation of **2a** in the presence of 1.0 equiv of radical scavenger.



A culture tube equipped with a stir bar was charged with **2a** (36.4 mg, 0.2 mmol, 1.0 equiv.), ammonia-borane (6.2 mg, 0.2 mmol, 1.0 equiv.) and **radical scavenger** (1.0 equiv.). A teflon cap was fitted, and the tube was evacuated and refilled with argon (3 cycles). The tube was transferred to a glove box, and Bi(I) catalyst (**1**, 0.9 mg, 1 mol%) was added. The tube was removed from the glove box, and placed under a positive pressure of argon. Firstly, degassed H_2O (3.6 uL, 1.0 equiv.) was added together with THF (1.0 mL) and the mixture was stirred at 35 °C for 3h. After this time, the reaction was quenched by filtering through a glass funnel with a thin layer (20 mm) of celite and eluted with DCM and ethyl acetate. The filtrate was concentrated under reduced pressure. The yield was calculated by ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standard (1.0 equiv.). Results are shown in Table S5.

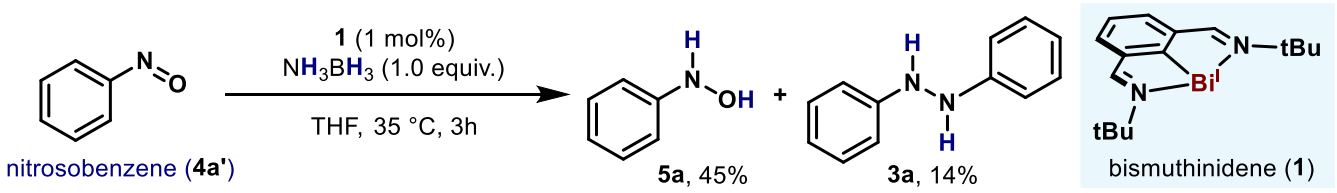
Table S5. Yields obtained in presence of 1.0 equiv of radical scavengers.[a]

Radical scavenger	**3a**, yield (%)
none	99
Butylated hydroxytoluene	87
2,2′-Azobis(2-methylpropionitrile)	89
1,1-Diphenylethylene	97

[a] ^{1}H NMR yield using 1,3,5-trimethoxybenzene as internal standard.

7.8 Reaction with nitrosobenzene (**4a'**)

Scheme S12. Transfer hydrogenation of nitrosobenzene (**4a'**).

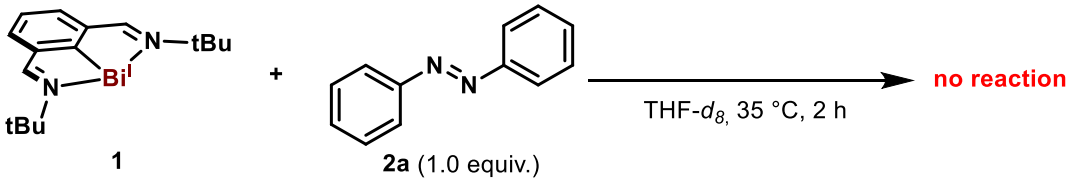


A culture tube equipped with a stir bar was charged with **4a'** (21.4 mg, 0.2 mmol, 1.0 equiv.) and ammonia-borane (6.2 mg, 0.2 mmol, 1.0 equiv.). A teflon cap was fitted, and the tube was evacuated and refilled with argon (3 cycles). The tube was transferred to a glove box, and Bi(I) catalyst (**1**, 0.9 mg, 1 mol%) was added. The tube was removed from the glove box, and placed under a positive pressure of argon. THF (1.0 mL) was added and the mixture was stirred at 35 °C for 3h. After this time, the reaction was quenched by filtering through a glass funnel with a thin layer (20 mm) of celite and eluted with DCM and ethyl acetate. The filtrate was concentrated under reduced pressure. The yield was calculated by ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standard (1.0 equiv.). As shown in Scheme S11, **5a** (45%) was obtained together with **3a** (14%), as a consequence of a dimerization of nitrosobenzene (**4a'**) with hydroxyl amines and its further reduction to hydrazine.

7.9 Reaction of **1** with each reaction component individually

7.9.1 Reaction of **1** with azobenzene **2a**

Scheme S13. Equimolar reaction of 1 with azobenzene (**2a**).



Under an argon atmosphere, an NMR tube was charged with **2a** (18.4 mg, 0.1 mmol, 1.0 equiv.) and **1** (45 mg, 0.1 mmol, 1.0 equiv.). A septum was fitted, and the tube was evacuated and refilled with argon (3 cycles) in an argon line. THF-d_8 (1.0 mL) was added and a ^{1}H-NMR was recorded. Then, the mixture was stirred at 35 °C for 2h. After this time, the crude mixture was analyzed by ^{1}H-NMR again. No noticeable changes were observed.

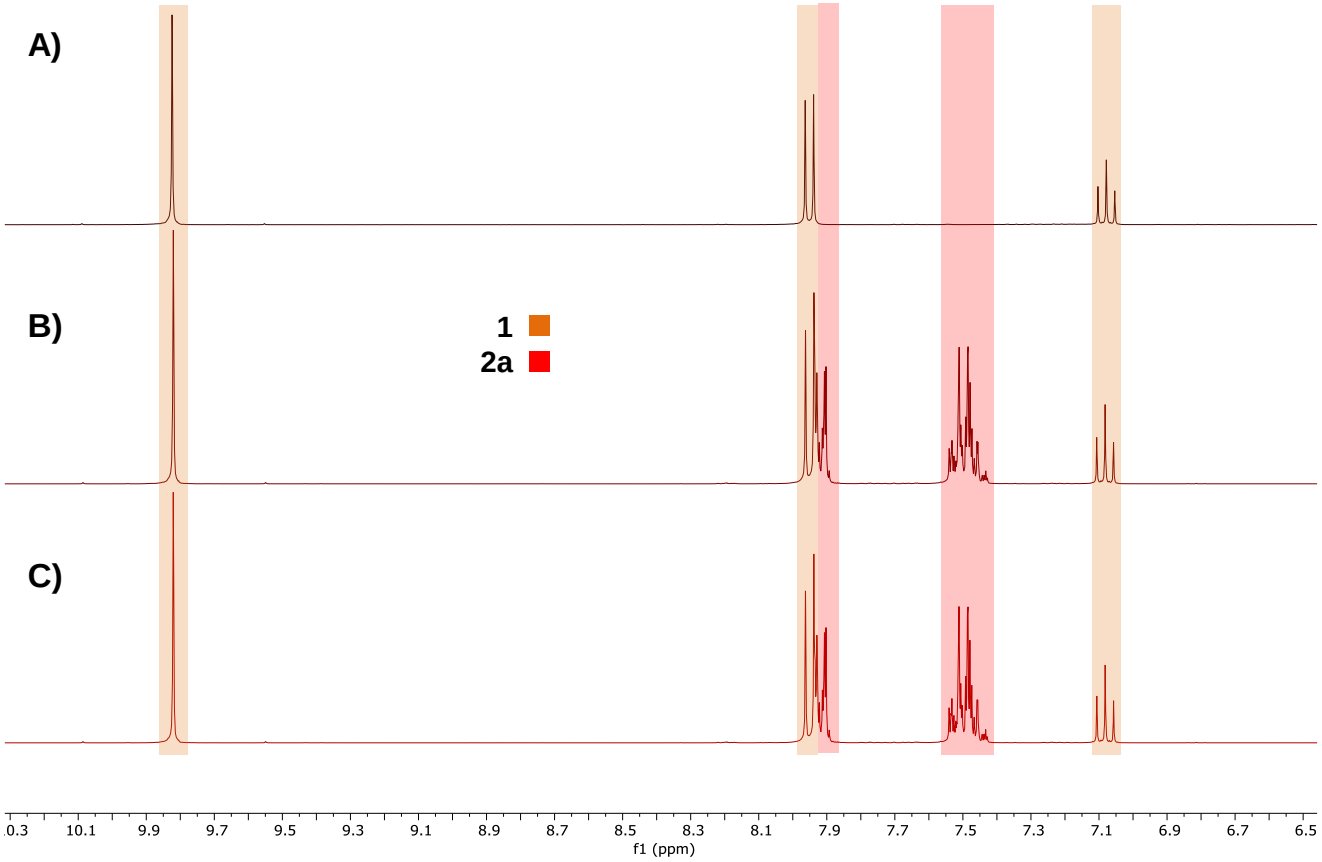
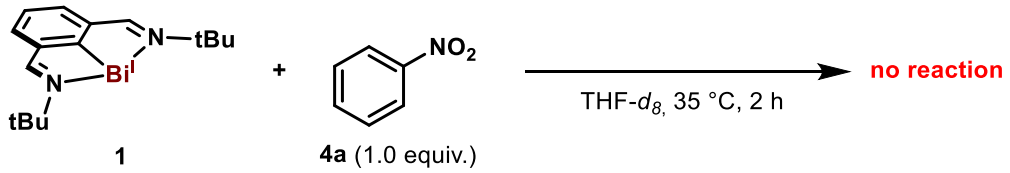


Figure S5. Reactivity experiments of **1** with azobenzene **2a**. (**A**) ^{1}H NMR spectrum of **1** in THF-d_8. (**B**) ^{1}H NMR spectrum of 1:1 mixture of **2a** and **1** in THF-d_8 at rt. (**C**) ^{1}H NMR spectrum of 1:1 mixture of **2a** and **1** in THF-d_8 at 35 ºC for 2 h.

7.9.2 Reaction of **1** with nitrobenzene **4a**

Scheme S14. Equimolar reaction of **1** with nitrobenzene (**4a**).



Under an argon atmosphere, an NMR tube was charged with **4a** (12.3 mg, 0.1 mmol, 1.0 equiv.) and **1** (45 mg, 0.1 mmol, 1.0 equiv.). A septum was fitted, and the tube was evacuated and refilled with argon (3 cycles) in an argon line. THF-d_8 (1.0 mL) was added and a ^{1}H-NMR was recorded. Then, the mixture was stirred at 35 °C for 2h. After this time, the crude mixture was analyzed by ^{1}H-NMR again. No noticeable changes were observed.

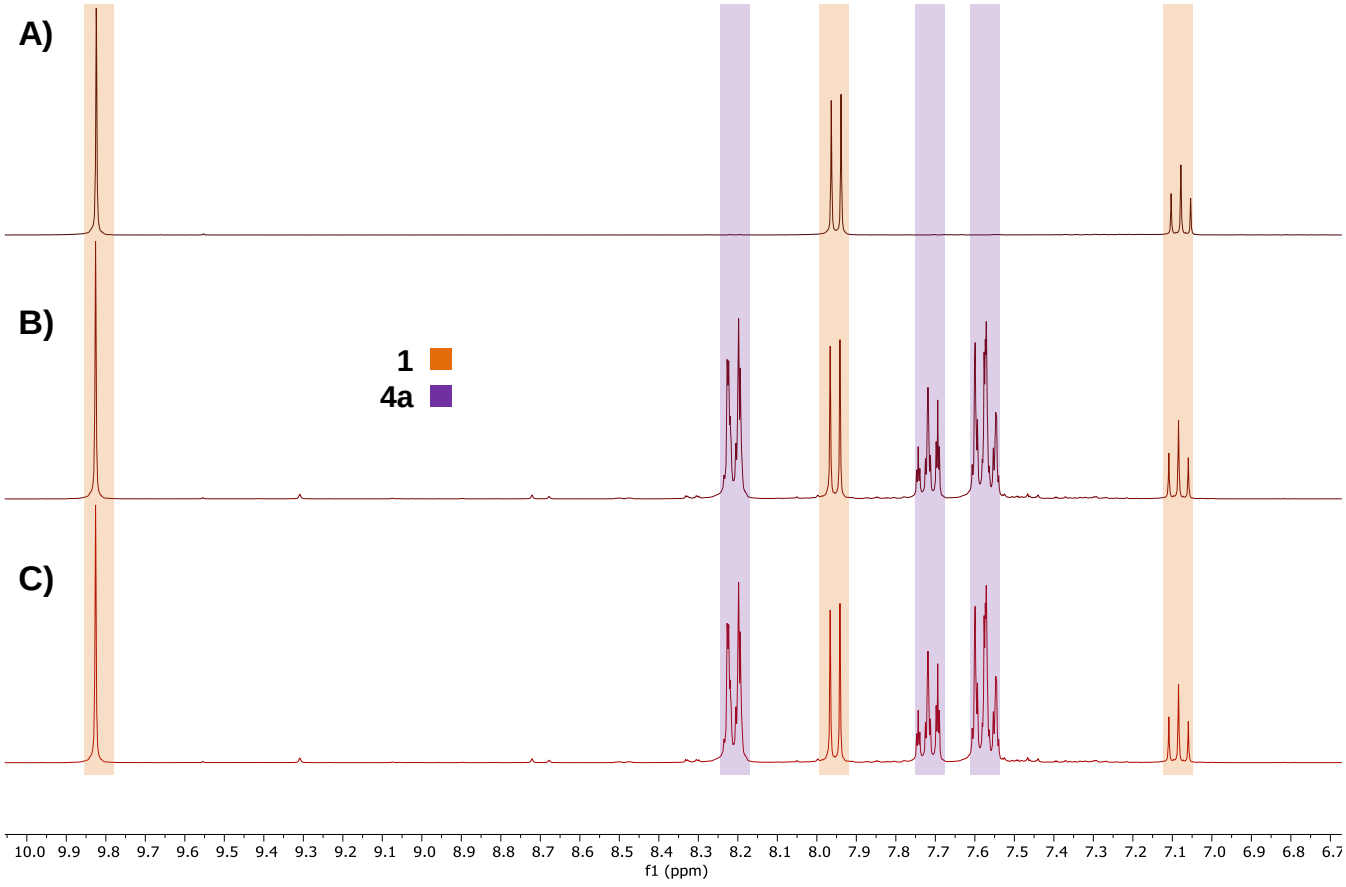
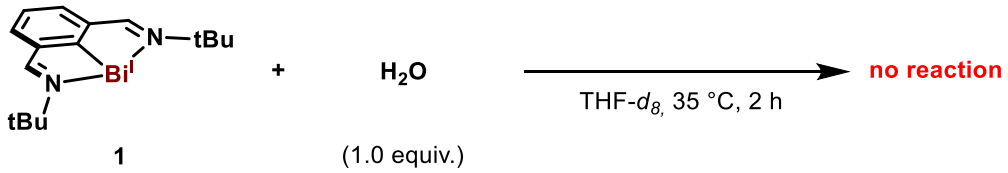


Figure S6. Reactivity experiments of **1** with nitrobenzene **4a**. (**A**) ^{1}H NMR spectrum of **1** in THF-d_8. (**B**) ^{1}H NMR spectrum of 1:1 mixture of **4a** and **1** in THF-d_8 at rt. (**C**) ^{1}H NMR spectrum of 1:1 mixture of **4a** and **1** in THF-d_8 at 35 ºC for 2 h.

7.9.3 Reaction of **1** with H_2O

Scheme S15. Equimolar reaction of **1** with H_2O.



Under an argon atmosphere, an NMR tube was charged with H_2O (2 µL, 0.1 mmol, 1.0 equiv.) and **1** (45 mg, 0.1 mmol, 1.0 equiv.). A septum was fitted, and the tube was evacuated and refilled with argon (3 cycles) in an argon line. THF-d_8 (1.0 mL) was added and a ^{1}H-NMR was recorded. Then, the mixture was stirred at 35 °C for 2 h. After this time, the crude mixture was analyzed by ^{1}H-NMR again. No noticeable changes were observed.

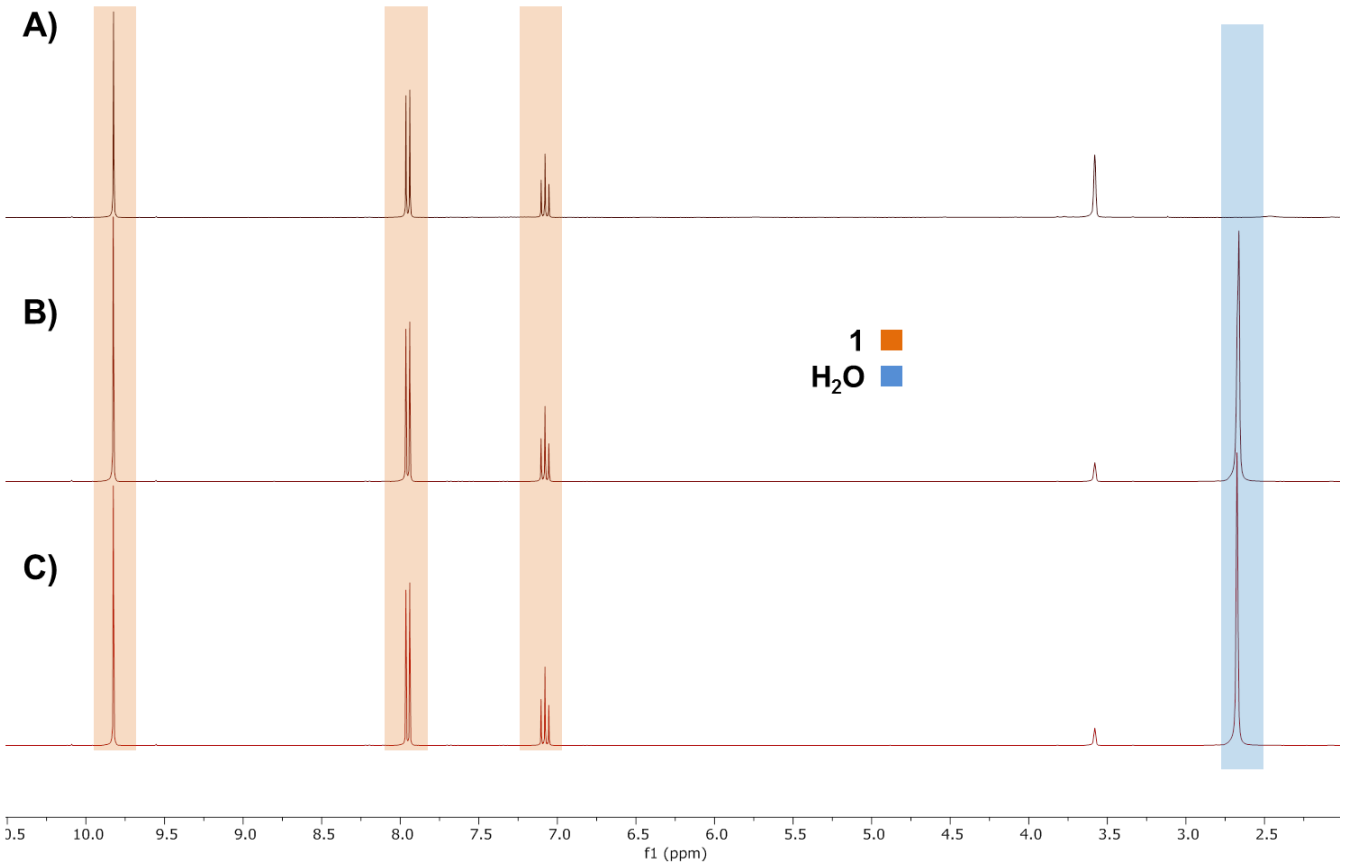
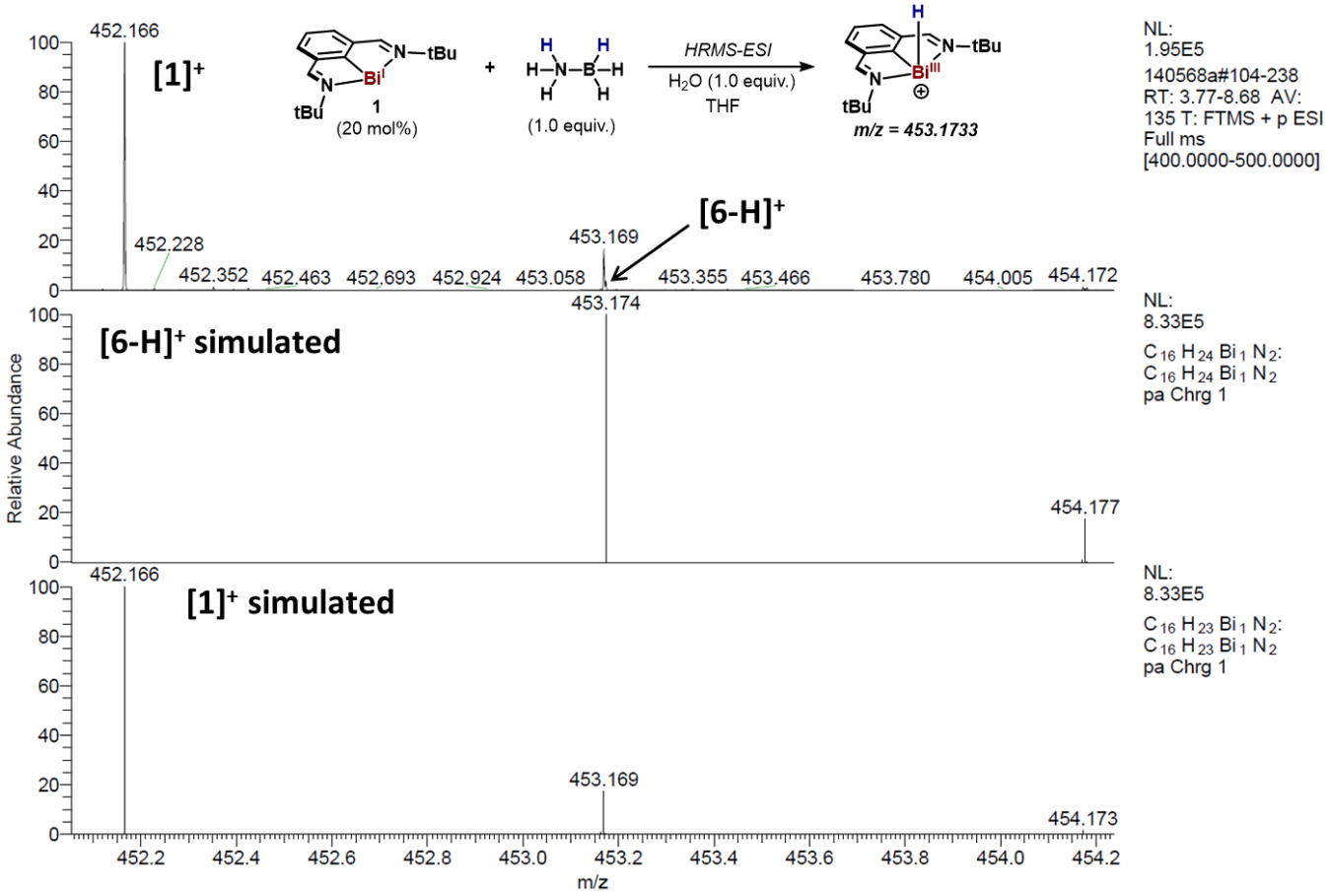


Figure S7. (**A**) ^{1}H NMR of **1** in THF-d_8.(**B**) ^{1}H-NMR of a mixture of **1** and H_2O at room temperature in THF-d_8. (**C**) Mixture of **1** and H_2O after heating at 35 °C for 2 h in THF-d_8.

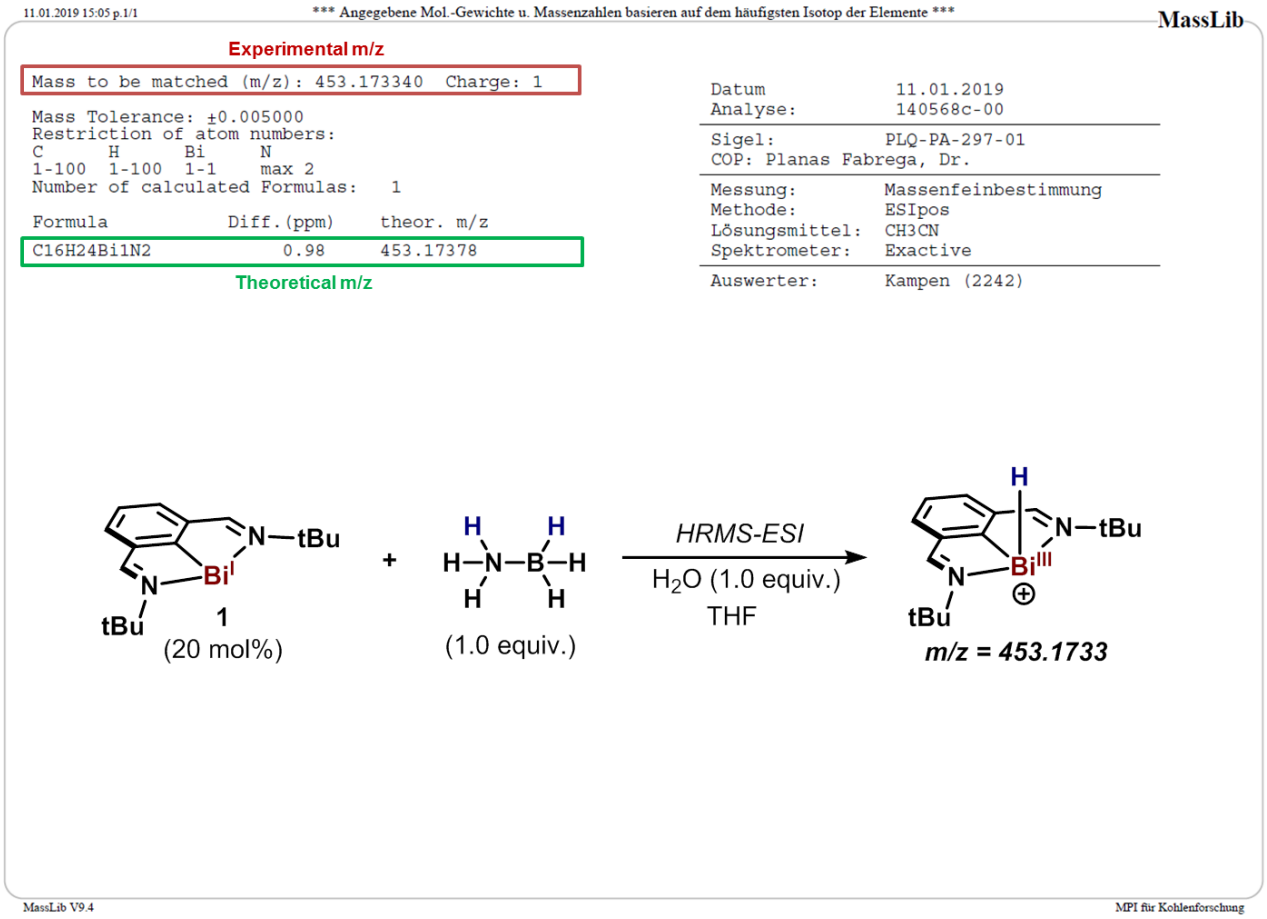
7.10 High-Resolution Mass Spectrometry studies

7.10.1 Studies with ammonia-borane (NH_3BH_3) and H_2O

Under an argon atmosphere, a culture tube was charged with **1** (0.1 mmol, 1.0 equiv.) and NH_3BH_3 (15.4 mg, 0.5 mmol, 5.0 equiv.). A teflon cap was fitted, and the tube was evacuated and refilled with argon (3 cycles) in an argon line. THF (1.0 mL) was added together with H_2O (0.5 mmol, 5.0 equiv.) and the reaction was stirred at 35 °C over a period of 1 h. After this time, the crude was analyzed by High-Resolution Mass Spectrometry, which showed a peak corresponding to [**6**-H]$^+$ (*m/z* = 453.1733, see below) .



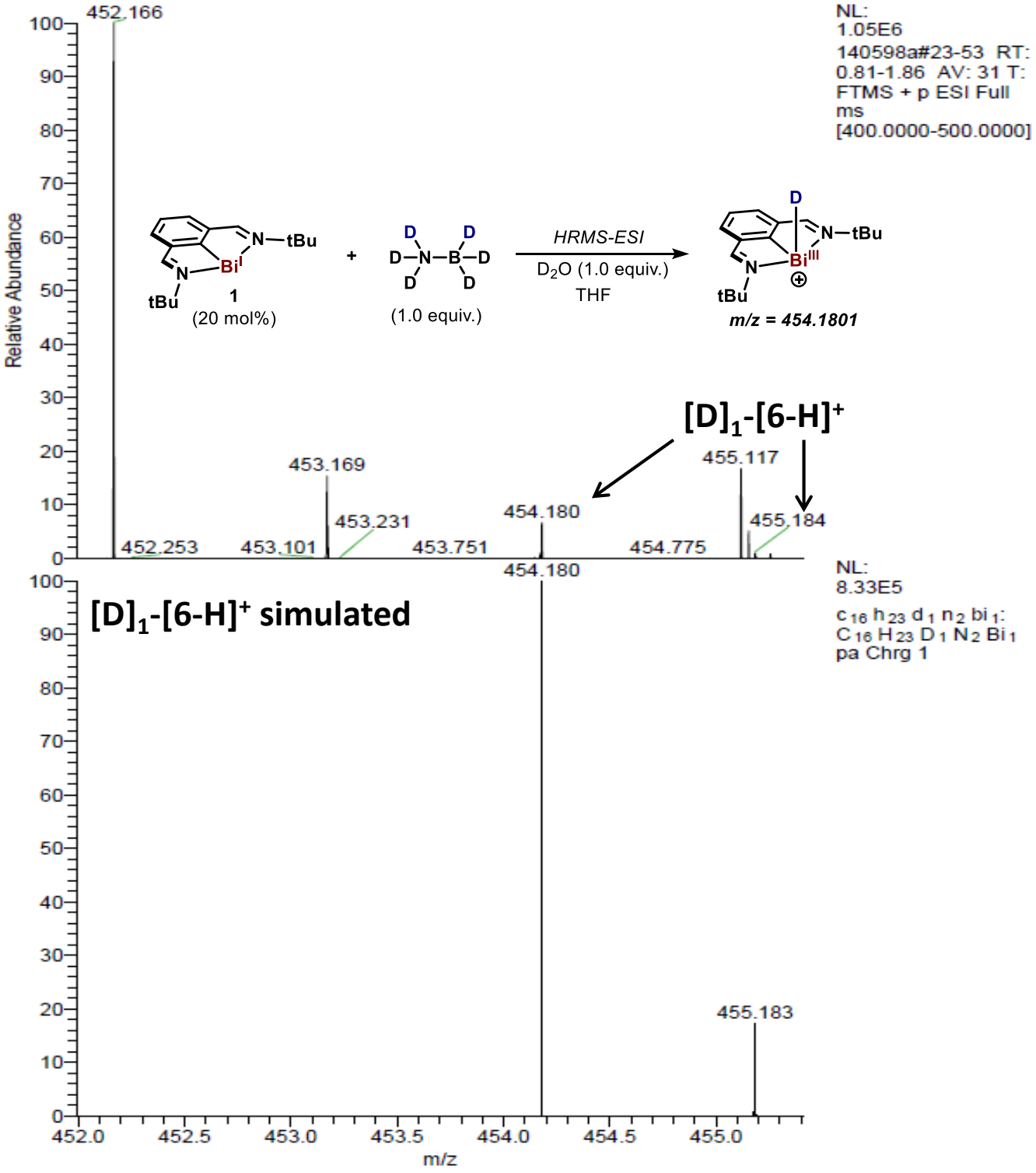
Scheme S16. High-Resolution Mass Spectrum of the crude reaction of **1** and NH_3BH_3 (up), showing a peak corresponding to [**6**-H]$^+$; theoretical *m/z* of the peak corresponding to [**6**-H]$^+$ (middle); theoretical *m/z* of the peak corresponding to [**1**]$^+$ (bottom).



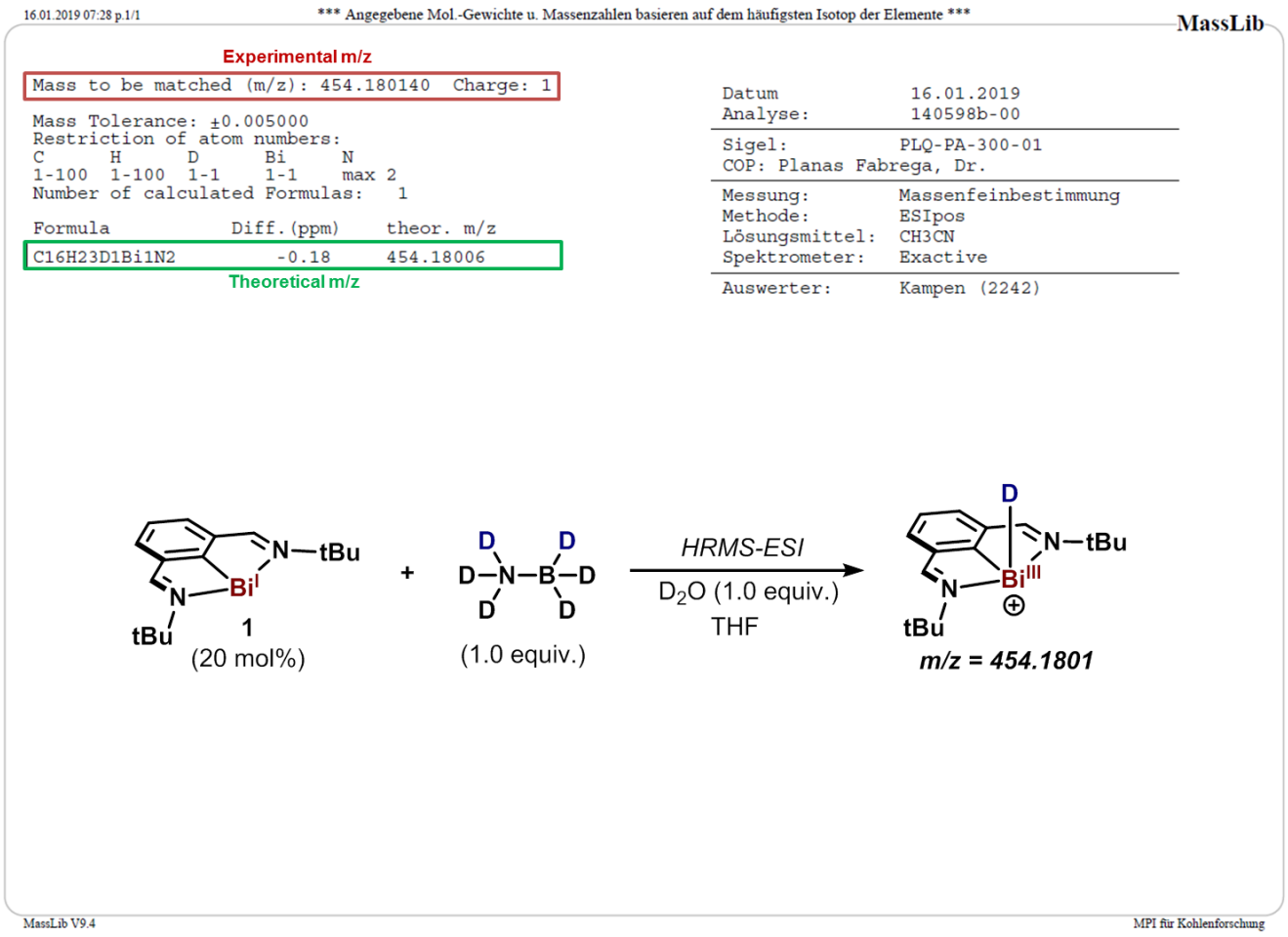
Scheme S17. Detection of [**6**–H]$^+$ in the HRMS.

7.10.2 Studies with *d*$_6$-labeled ammonia-borane (ND_3BD_3) and D_2O

Under an argon atmosphere, a culture tube was charged with **1** (0.1 mmol, 1.0 equiv.) and ND_3BD_3 (15.4 mg, 0.5 mmol, 5.0 equiv.). A teflon cap was fitted, and the tube was evacuated and refilled with argon (3 cycles) in an argon line. THF (1.0 mL) was added together with D_2O (0.5 mmol, 5.0 equiv.) and the reaction was stirred at 35 °C over a period of 1 h. After this time, the crude was analyzed by High-Resolution Mass Spectrometry, which showed a peak corresponding to $[D]_1$-[**6**-H]$^+$ (*m/z* = 454.1801, see below) .



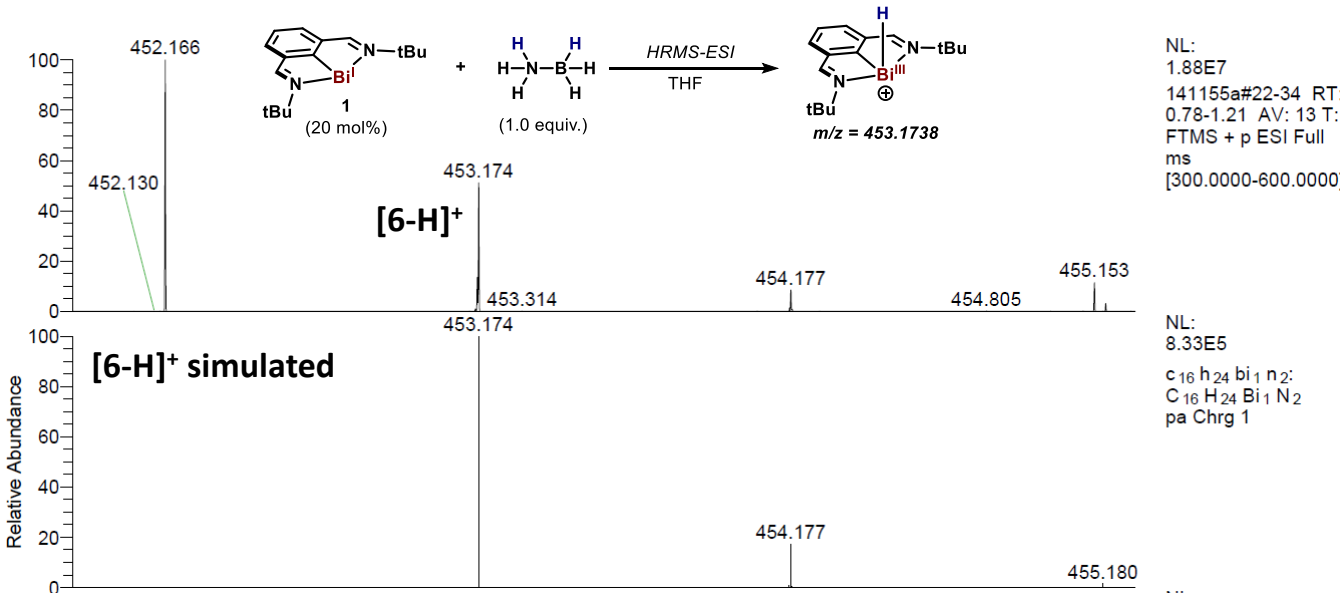
Scheme S18. High-Resolution Mass Spectrum of the crude reaction of **1** and ND_3BD_3 (up), showing a peak corresponding to $[D]_1$-[**6**-H]$^+$; theoretical *m/z* of the peak corresponding to $[D]_1$-[**6**-H]$^+$ (bottom).



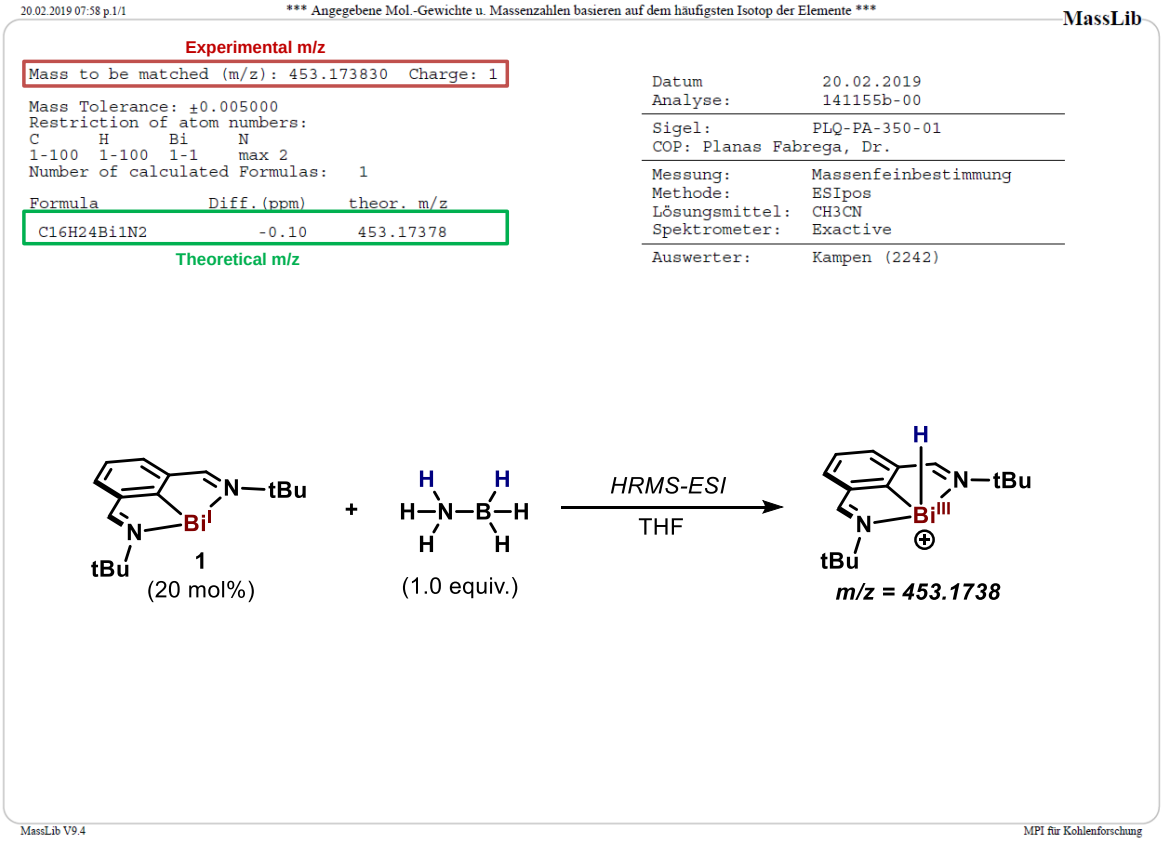
Scheme S19. Detection of $[D]_1$-[**6**-H]$^+$ in the HRMS.

7.10.3 Studies with ammonia-borane (NH_3BH_3) without H_2O

Under an argon atmosphere, a culture tube was charged with **1** (0.1 mmol, 1.0 equiv.) and NH_3BH_3 (15.4 mg, 0.5 mmol, 5.0 equiv.). A teflon cap was fitted, and the tube was evacuated and refilled with argon (3 cycles) in an argon line. THF (1.0 mL) was added and the reaction was stirred at 35 °C over a period of 4 h. After this time, the crude was analyzed by High-Resolution Mass Spectrometry, which showed a peak corresponding to [**6**-H]$^+$ (*m/z* = 453.1738, see below) .



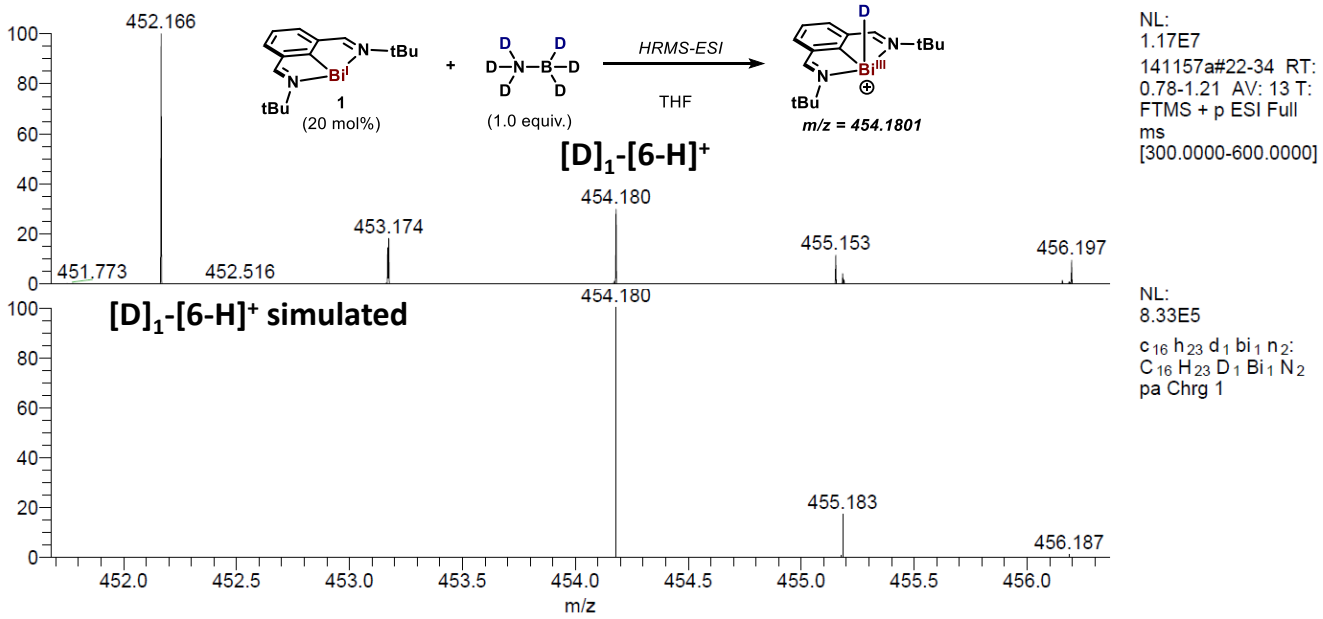
Scheme S20. High-Resolution Mass Spectrum of the crude reaction of **1** and NH_3BH_3 (up), showing a peak corresponding to [**6**-H]$^+$; theoretical *m/z* of the peak corresponding to [**6**-H]$^+$ (bottom).



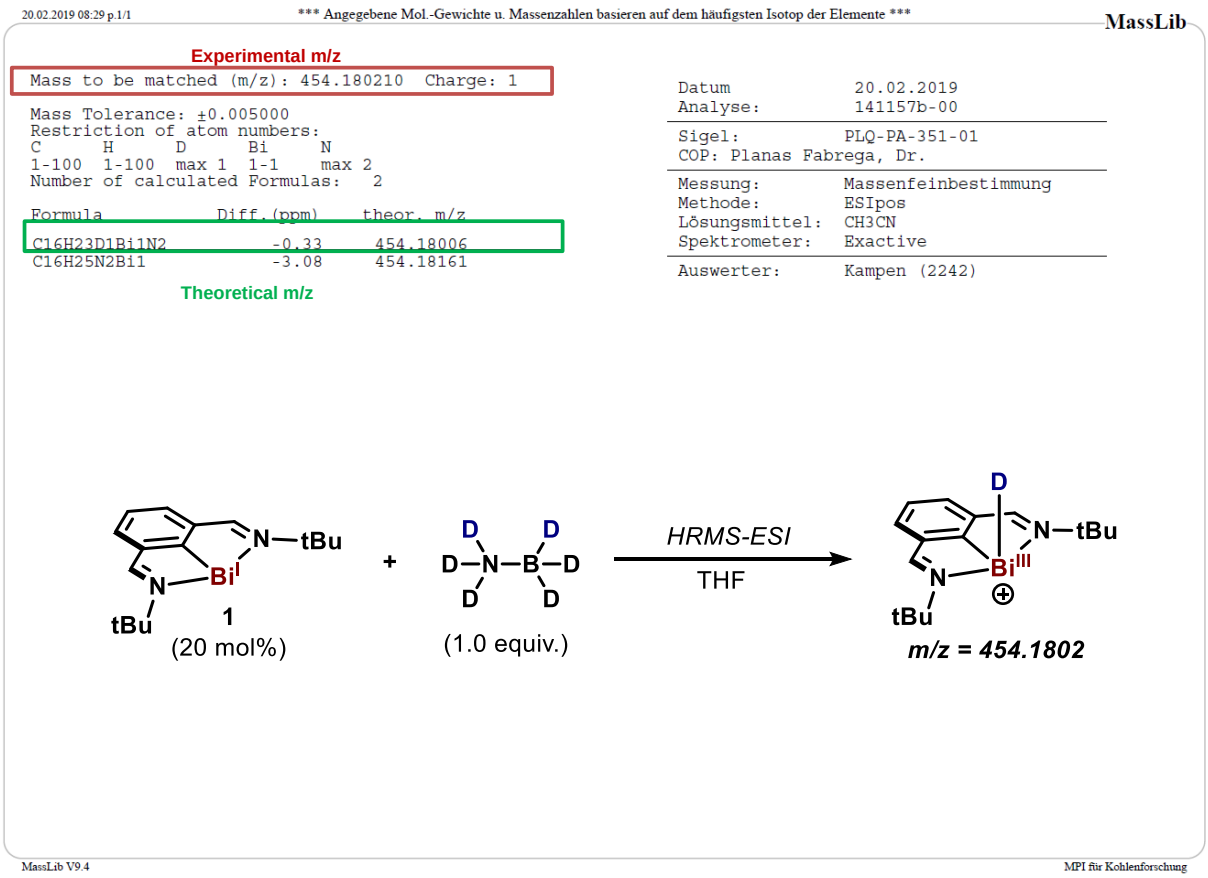
Scheme S21. Detection of [**6**-H]$^+$ in the HRMS.

7.10.4 Studies with ammonia-borane (ND_3BD_3) without D_2O

Under an argon atmosphere, a culture tube was charged with **1** (0.1 mmol, 1.0 equiv.) and ND_3BD_3 (15.4 mg, 0.5 mmol, 5.0 equiv.). A teflon cap was fitted, and the tube was evacuated and refilled with argon (3 cycles) in an argon line. THF (1.0 mL) was added and the reaction was stirred at 35 °C over a period of 4 h. After this time, the crude was analyzed by High-Resolution Mass Spectrometry, which showed a peak corresponding to $[D]_1$-[**6**-H]$^+$ (*m/z* = 454.1801, see below) .



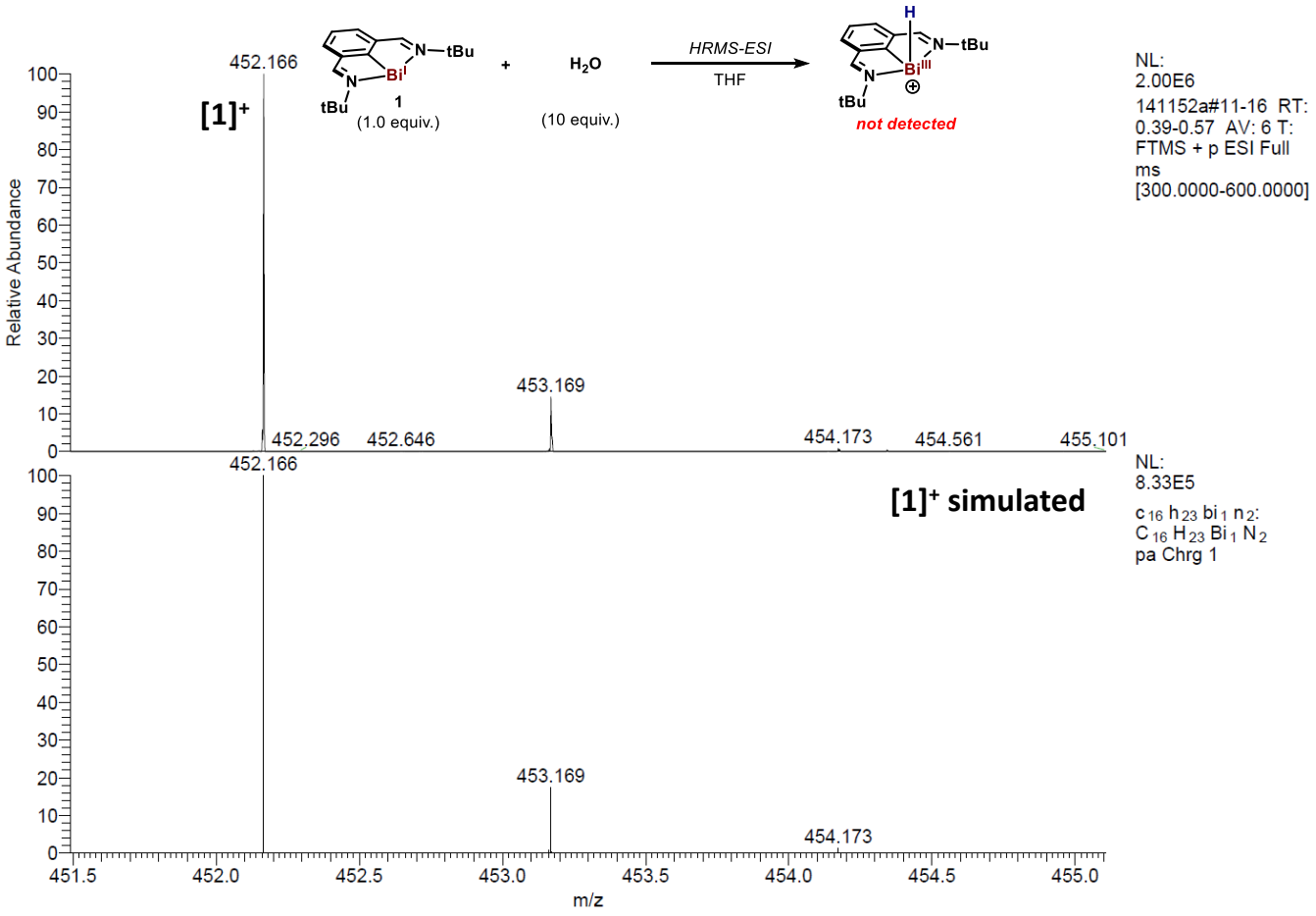
Scheme S22. High-Resolution Mass Spectrum of the crude reaction of **1** and ND_3BD_3 (up), showing a peak corresponding to $[D]_1$-[**6**-H]$^+$; theoretical *m/z* of the peak corresponding to $[D]_1$-[**6**-H]$^+$ (bottom).



Scheme S23. Detection of $[D]_1$-[**6**-H]$^+$ in the HRMS.

7.10.5 Studies with H_2O

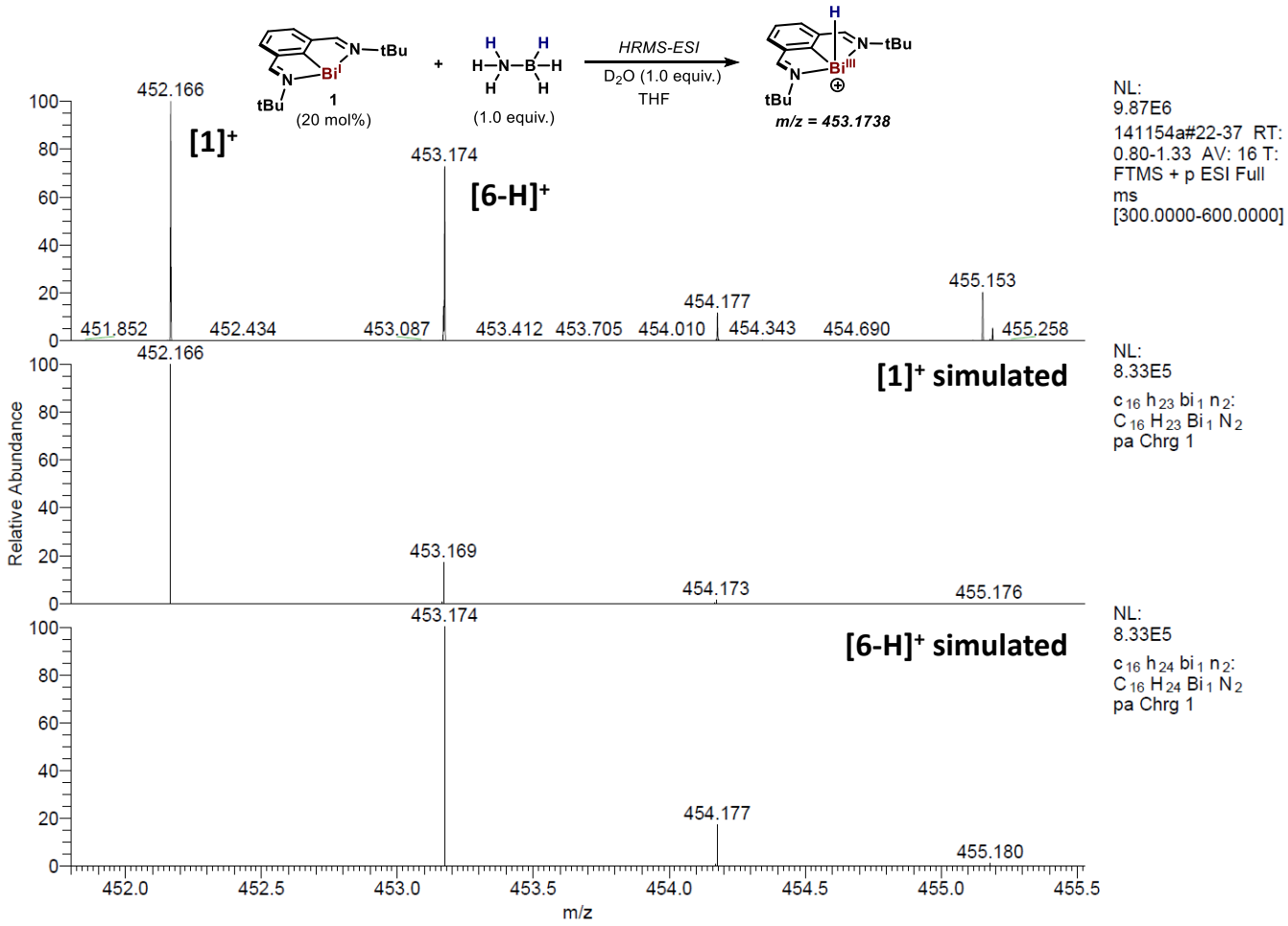
Under an argon atmosphere, a culture tube was charged with **1** (0.1 mmol, 1.0 equiv.). A teflon cap was fitted, and the tube was evacuated and refilled with argon (3 cycles) in an argon line. THF (1.0 mL) was added together with H_2O (10 equiv.) and the reaction was stirred at 35 °C over a period of 2 h. After this time, the crude was analyzed by High-Resolution Mass Spectrometry, which did not show any peak corresponding to [**6**-H]$^+$ (see below).



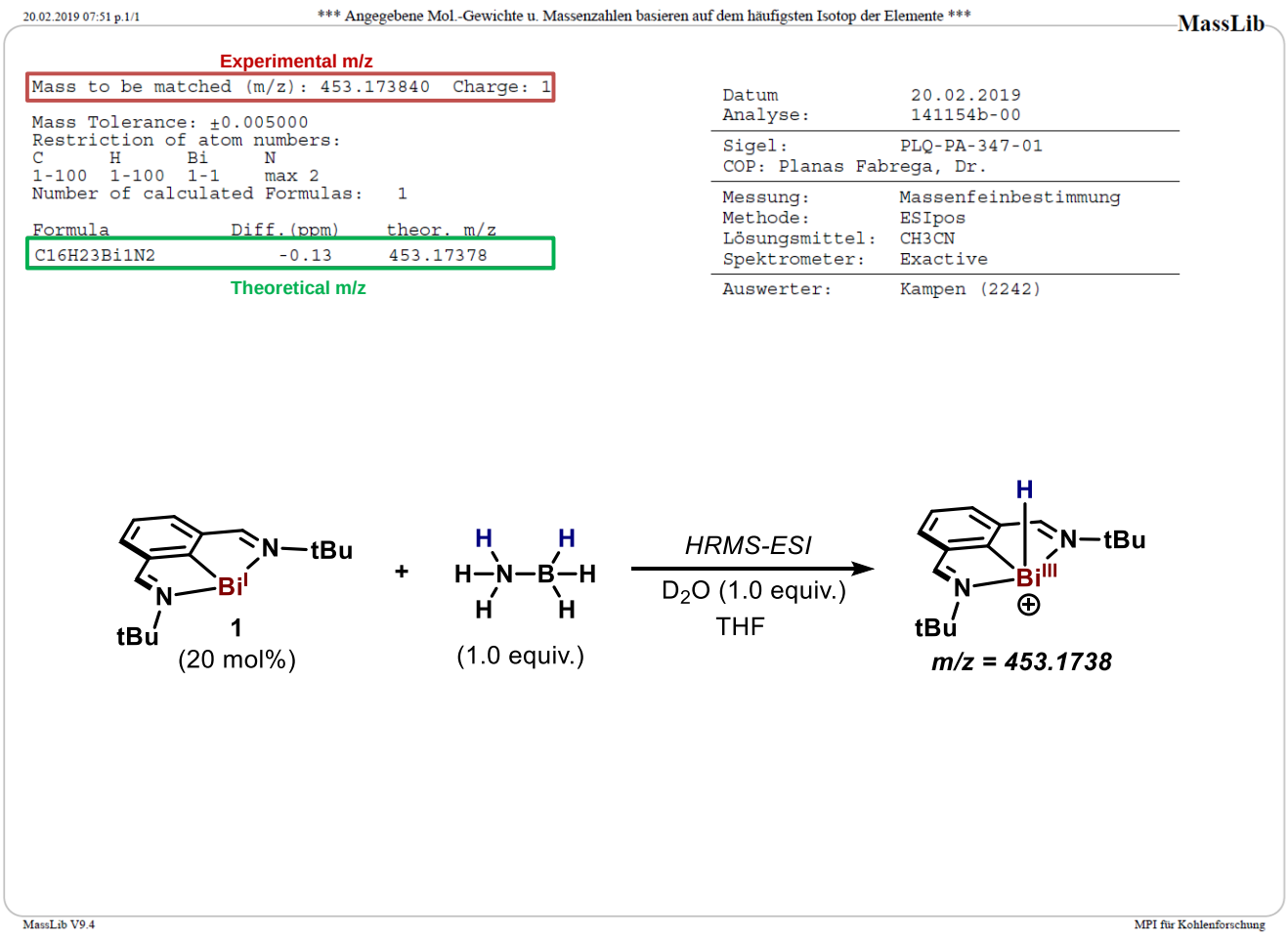
Scheme S24. High-Resolution Mass Spectrum of the crude reaction of **1** and H_2O (up), showing no formation of peak [**6**-H]$^+$. **1** was the sole peak detected.

7.10.6 Studies with with ammonia-borane (NH_3BH_3) and D_2O

Under an argon atmosphere, a culture tube was charged with **1** (0.1 mmol, 1.0 equiv.) and NH_3BH_3 (15.4 mg, 0.5 mmol, 5.0 equiv.). A teflon cap was fitted, and the tube was evacuated and refilled with argon (3 cycles) in an argon line. THF (1.0 mL) was added together with D_2O (10 equiv.) and the reaction was stirred at 35 °C over a period of 2 h. After this time, the crude was analyzed by High-Resolution Mass Spectrometry, which showed a peak corresponding to [**6**-H]$^+$ (*m/z* = 453.1738, see below) .



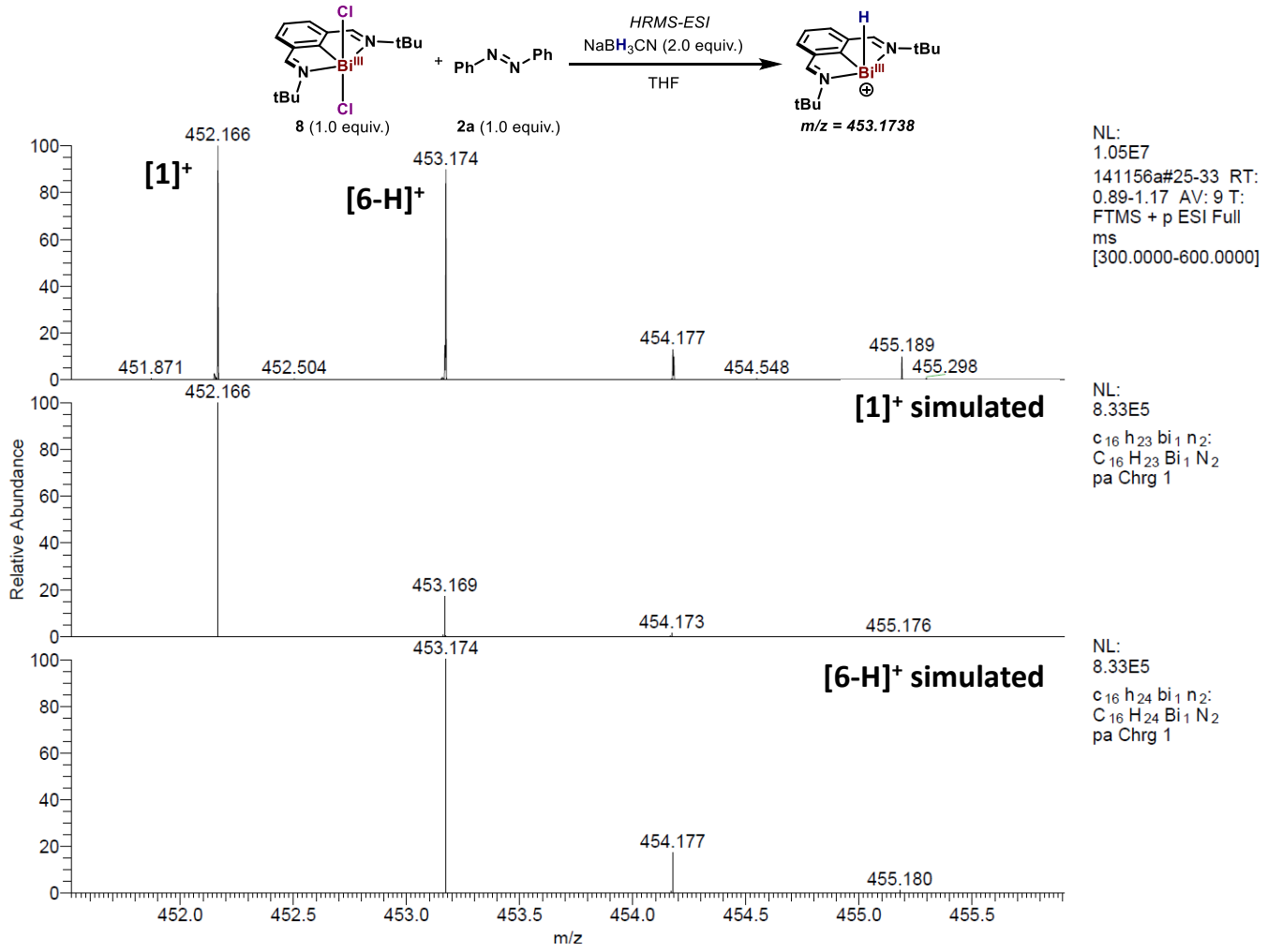
Scheme S25. High-Resolution Mass Spectrum of the crude reaction of **1** and NH_3BH_3 in presence of D_2O (up), showing a peak corresponding to [**6**-H]$^+$; theoretical *m/z* of the peak corresponding to [**6**-H]$^+$ (bottom).



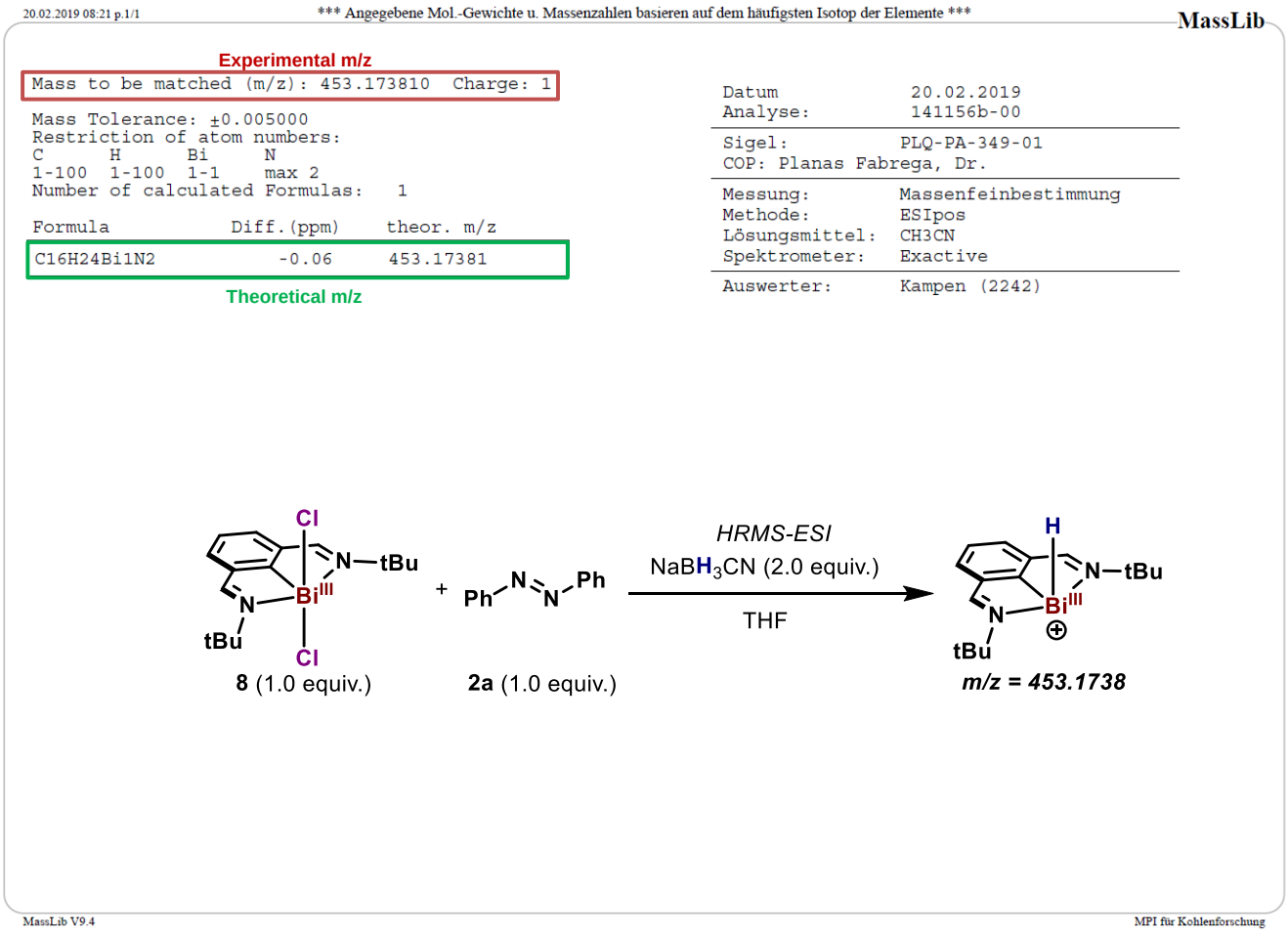
Scheme S26. Detection of [**6**-H]$^+$ in the HRMS

7.10.7 Studies with with stoichiometric amounts of **8**, $NaBH_3CN$ and **2a**

A culture tube equipped with a stir bar was charged with chlorobismuthine **8** (0.1 mmol, 1.0 equiv.), $NaBH_3CN$ (0.2 mmol, 2.0 equiv.) and **2a** (0.1 mmol, 1.0 equiv.). Then, THF (1 mL) was added and the reaction mixture was stirred at 35 °C over 4 h. After this time, the crude was analyzed by High-Resolution Mass Spectrometry, which showed a peak corresponding to [**6**-H]$^+$ (*m/z* = 453.1738, see below) .



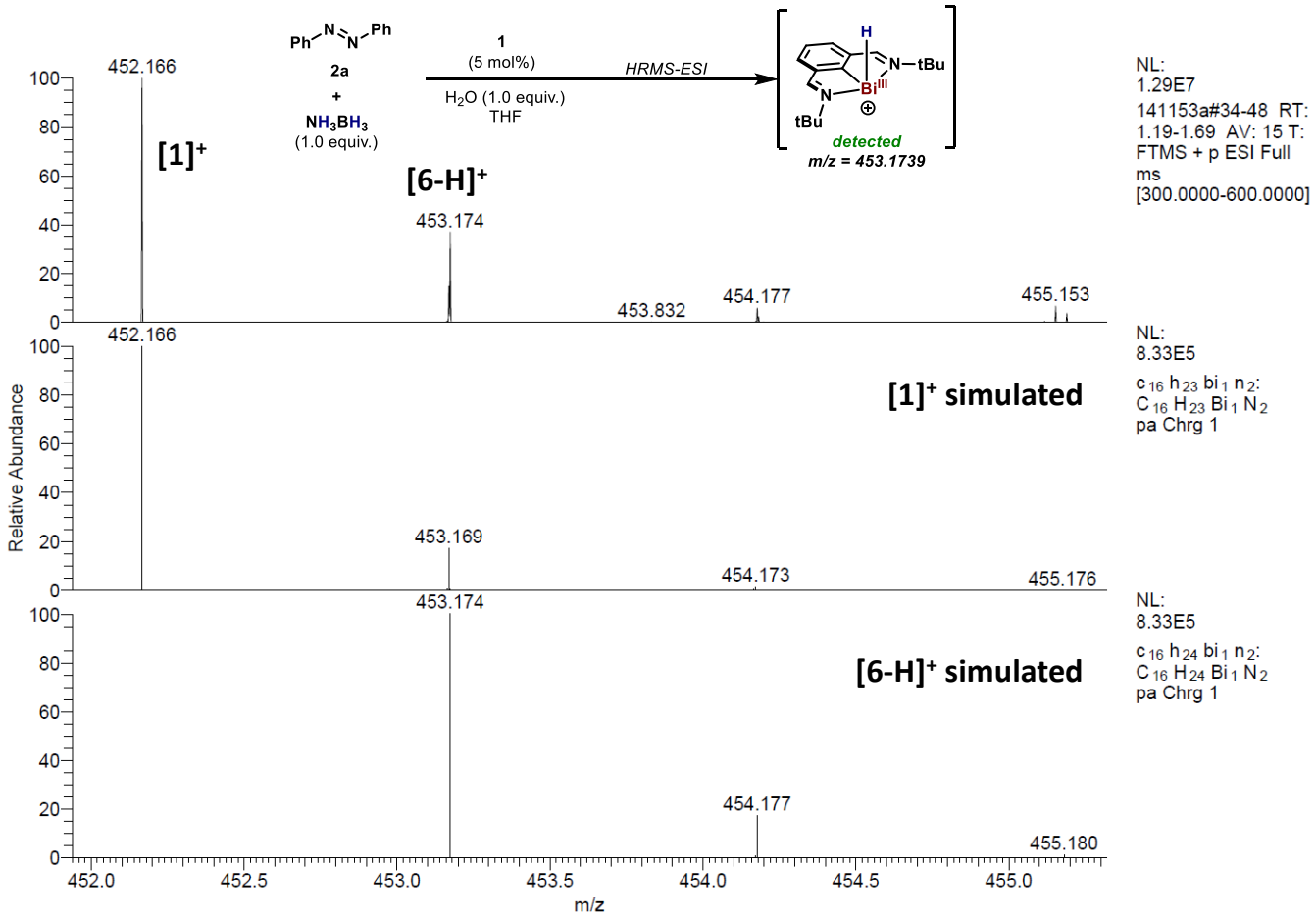
Scheme S27. High-Resolution Mass Spectrum of the crude reaction of **8** and $NaBH_3CN$ in presence of **2a** (up), showing a peak corresponding to [**6**-H]$^+$; theoretical *m/z* of the peak corresponding to [**6**-H]$^+$ (bottom).



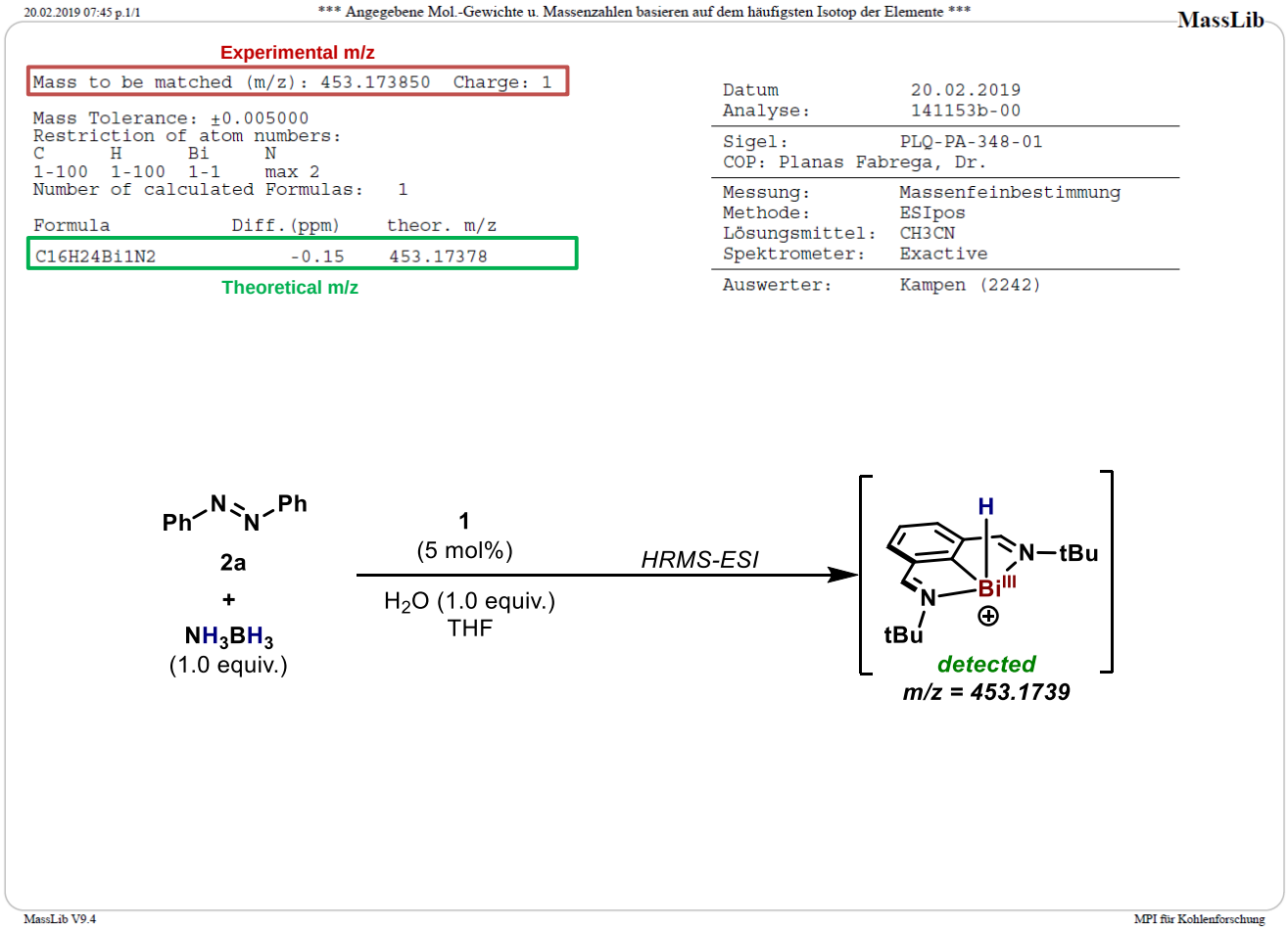
Scheme S28. Detection of [**6**-H]$^+$ in the HRMS

7.10.8 Studies under catalytic conditions

A culture tube equipped with a stir bar was charged with **2a** (36.4 mg, 0.2 mmol, 1.0 equiv.) and ammonia-borane (6.2 mg, 0.2 mmol, 1.0 equiv.). A teflon cap was fitted, and the tube was evacuated and refilled with argon (3 cycles). The tube was transferred to a glove box, and Bi(I) catalyst (**1**, 4.5 mg, 5 mol%) was added. The tube was removed from the glove box, and placed under a positive pressure of argon. Firstly, degassed H_2O (3.6 uL, 1.0 equiv.) was added together with THF (1.0 mL) and the mixture was stirred at 35 °C for 30 min. After this time, a small amount was taken for High-Resolution Mass Spectrometric analysis, which showed a peak corresponding to [**6**-H]$^+$ (*m/z* = 453.1739, see below) .



Scheme S29. High-Resolution Mass Spectrum of the crude reaction of **2a** and NH3BH3 catalyzed by 1 (5 mol%) in presence of H_2O (up), showing a peak corresponding to [**6**-H]$^+$; theoretical *m/z* of the peak corresponding to [**6**-H]$^+$ (bottom).

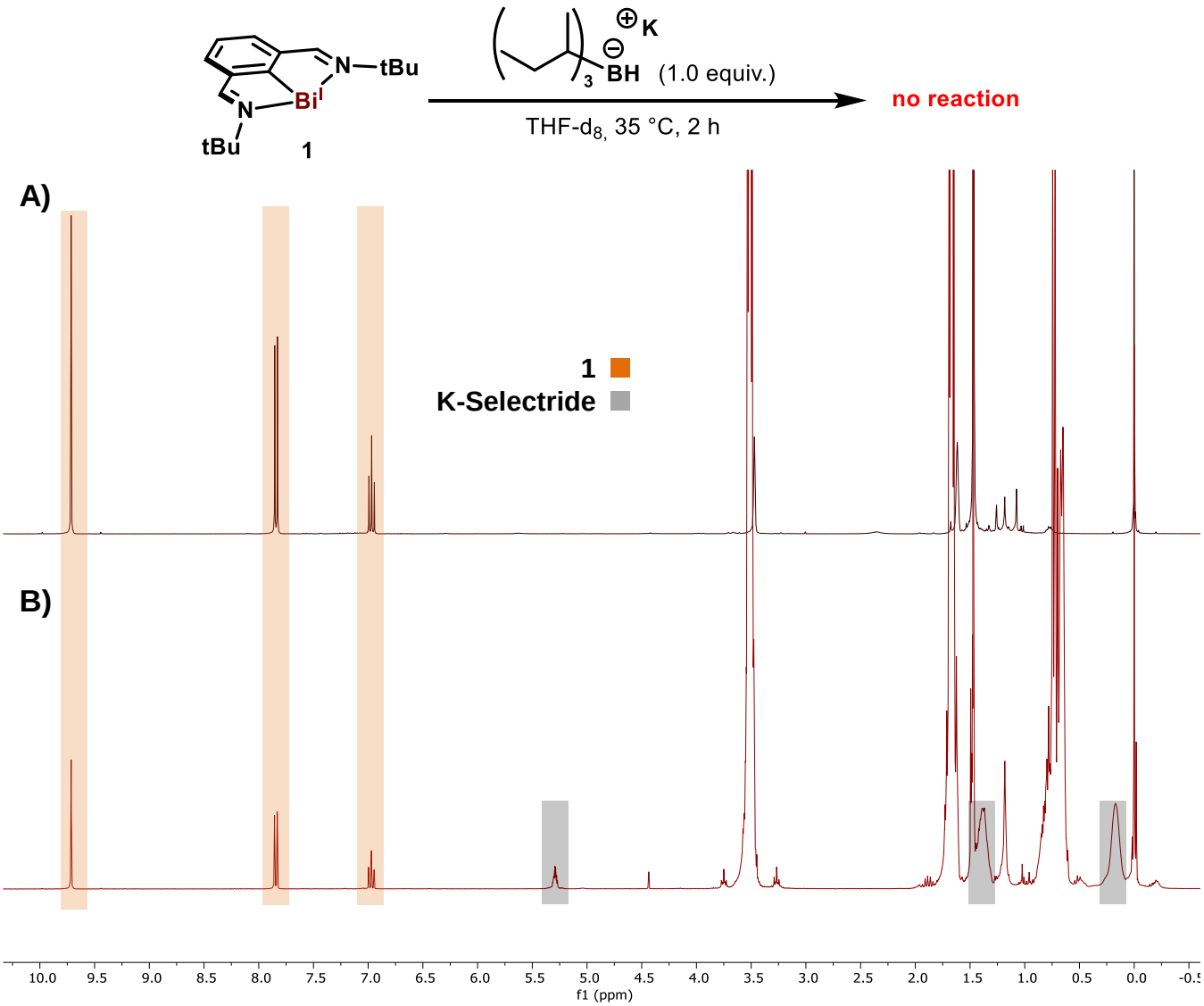


Scheme S30. Detection of [**6**-H]$^+$ in the HRMS

Then, the reaction was quenched by filtering through a glass funnel with a thin layer (20 mm) of celite and eluted with DCM and ethyl acetate. The filtrate was concentrated under reduced pressure. The yield (81% of **3a**) was calculated by ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standard (1.0 equiv.).

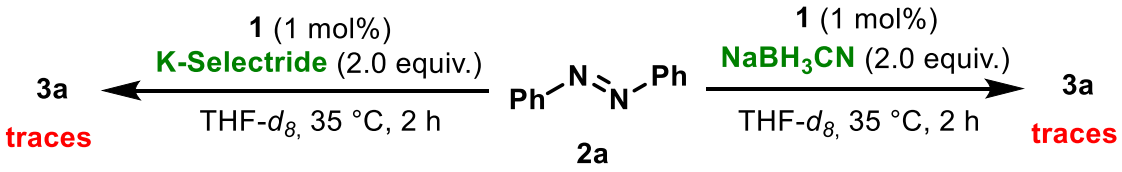
7.11 Reactivity of Bi(I) with different hydride sources

To have a deeper mechanistic insight into the actual catalytically active species, we studied the putative formation of Bi(I)-H species under reductive conditions. Initially, we sought to explore the stoichiometric reaction of **1** with a strong hydride donor such as K-Selectride. Thus, under an argon atmosphere, a culture tube was charged with **1** (0.1 mmol, 1.0 equiv.) and THF-d_8 (1.0 mL). Then, K-Selectride (0.1 mmol, 1 M solution in THF) was added and the reaction was stirred at 35 °C over a period of 2 h. After this time, the crude reaction mixture was analyzed by ^{1}H NMR, which showed no change (see below).



Scheme S31. Reactivity of **1** towards strong hydride sources such as K-Selectride. (**A**). ^{1}H NMR spectrum of **1** in THF-d_8. (**B**) ^{1}H NMR spectrum of 1:1 mixture of **1** with K-Selectride in THF-d_8.

To further explore the involvement of Bi(I) hydrides, we have carried out catalytic experiments using hydrides as H sources under catalytic conditions (Scheme S32). To do so, we followed two different protocols depending on the physical state of the hydride source:



Scheme S32. Attempts of reduction of azobenzene (**2a**) using hydride sources and **1** as catalyst.

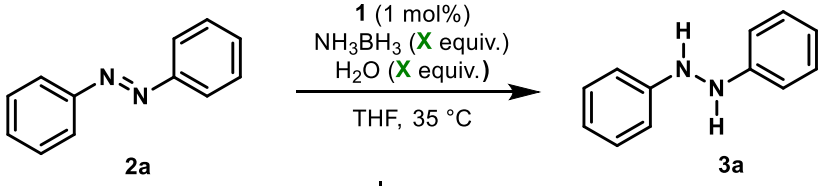
Solid hydride ($NaBH_3CN$): Under an argon atmosphere, a culture tube was charged with **1** (0.002 mmol, 1 mol%), **2a** (35.5 mg, 0.2 mmol, 1.0 equiv.) and $NaBH_3CN$ (24.8 mg, 0.4 mmol, 2.0 equiv.). Then THF (1.0 mL) was added and the reaction was stirred at 35 °C over a period of 2 h. After this time, the crude was analyzed by ^{1}H NMR, which showed traces of product **3a**.

Liquid hydride (1 M solution of K-Selectride in THF): Under an argon atmosphere, a culture tube was charged with **1** (0.002 mmol, 1 mol%), **2a** (35.5 mg, 0.2 mmol, 1.0 equiv.) and THF (1.0 mL). Then K-Selectride (0.4 mmol, 1 M solution in THF) was added and the reaction was stirred at 35 °C over a period of 2 h. After this time, the crude was analyzed by ^{1}H NMR, which showed traces of product **3a**.

7.12 Product generated per mole of ammonia-borane and identification of reaction byproducts

7.12.1 Substoichiometric experiments with ammonia-borane

Although the optimal conditions for hydrogenation of azoarenes were set with 1.0 equiv. of ammonia-borane, we have carried out further experiments to elucidate how many equivalents of H are integrated in the final product **3a**. Theoretically, if all 6 hydrogen atoms would be transferred, a minimum of 0.33 equiv. should suffice for full hydrogen transfer. Indeed, when two differently substituted azoarenes are subjected to the Bi(I)-catalyzed transfer hydrogenation using 0.5 equiv. and 0.33 equiv. of ammonia-borane, full conversion to **3a** was obtained, albeit longer reaction times were required (Scheme S33). On the other hand, when only 0.1 equiv. of ammonia-borane are used, the reaction only reached 25% conversion even after prolonged times (20% in 12 h; 25% in 24 h), thus highlighting the need of formally 3.0 equiv of H_2 to achieve full conversion.



X (equiv)	yield **3a**
1.0	99% (2 h)
0.5	99% (16 h)
0.33	98% (48 h)
0.1	20% (12 h)
0.1	25% (24 h)

Scheme S33. Reaction of **2a** with different equivalents of ammonia-borane (limiting reagent) under catalytic amounts of **1**.

Protocol: A culture tube equipped with a stir bar was charged with 1,2-diphenyldiazene (**2a**, 36.4 mg, 0.2 mmol, 1.0 equiv.) and ammonia-borane (0.1 mmol, 0.33, 0.5 or 1.0 equiv.). A teflon cap was fitted, and the tube was evacuated and refilled with argon (3 cycles). The tube was transferred to a glove box, and Bi(I) catalyst (**1**, 1 mol%) was added. The tube was removed from the glove box and subjected to a positive pressure of argon. Then, THF was added (1.0 mL) together with water (0.1, 0.33, 0.5 or 1.0 equiv.) and the reaction was then stirred at 35 °C. After the indicated time, the yield was calculated by ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standard.

7.12.2 Identification of ammonia-borane byproducts

We have analyzed the fate of the ammonia-borane reagent by NMR spectroscopy. When the reaction has reached completion (>95% conversion of **2e** to **3e**, simplified ^{1}H NMR signals), a highly insoluble material was observed. Despite its insolubility, it could be detected by ^{1}H NMR and ^{11}B NMR spectroscopy. Based on the physical properties, width of the signal by ^{11}B NMR and chemical shift, we attributed this byproduct to a polymeric B-containing material. Based on literature precedents for mixed N/O boranes (Scheme S34),[15] we believe this compound contains N–B and O–B bonds in its structure. A comparison between several reported O/N boranes reported supports the hypothesis of a mixed O/N boron byproduct.

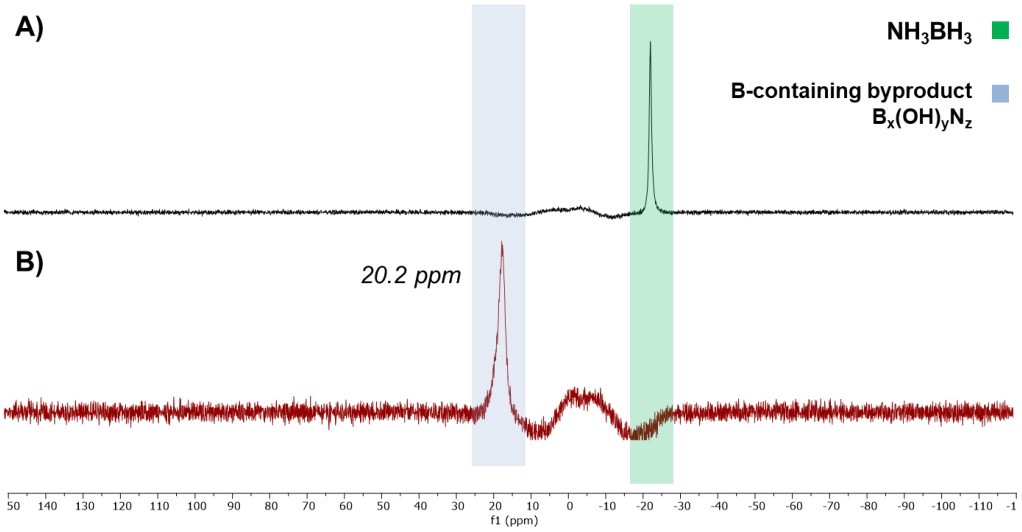
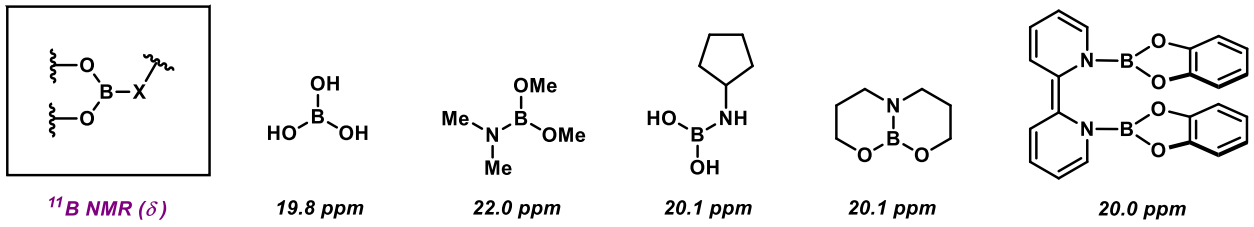


Figure S8. (**A**) ^{11}B {^{1}H} NMR of a reference sample of ammonia-borane adduct in THF-d_8. (**B**) ^{11}B-NMR of the crude reaction mixture at >95% conversion in THF-d_8.



Scheme S34. Different ^{11}B {^{1}H} NMR chemical shift of reported B–O/N compounds.

Additionally, the ^{1}H-NMR also provided information about this byproduct observed. As shown in Figure S9A, a complex signal at around 5.7 ppm was detected, which correspond to the region of $B(OH)_x$. This has been confirmed by a reference sample of boric acid (Figure S9B). These results suggest that the polymeric byproduct structure obtained contains free OH groups attached to the B atom.

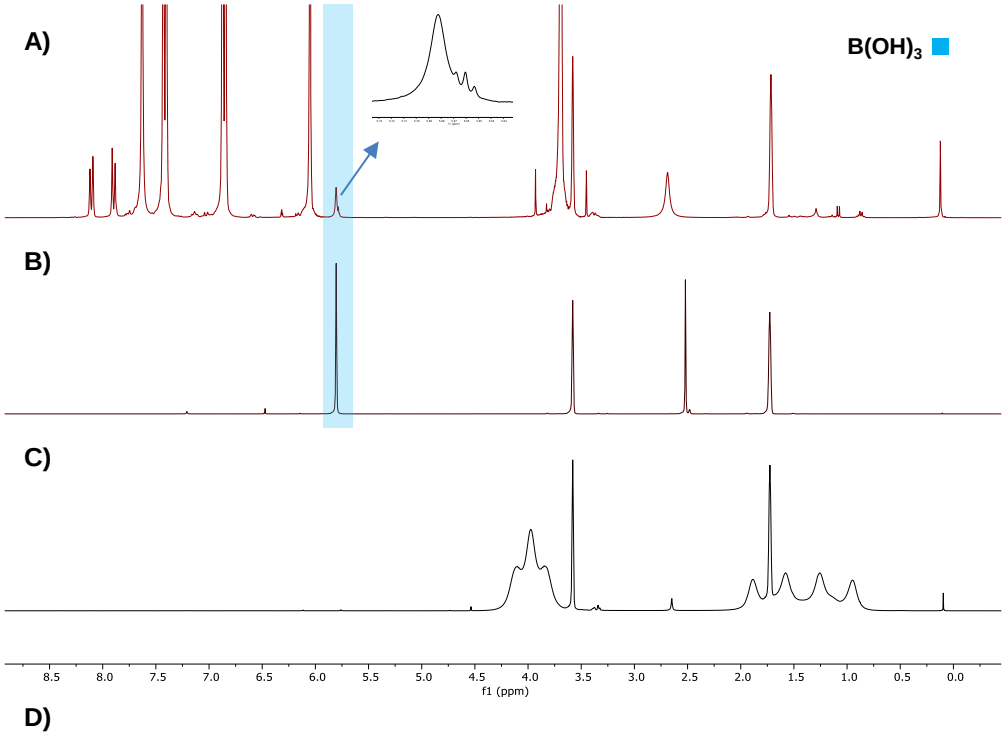


Figure S9. (**A**) ^{1}H NMR of a crude mixture of the reaction at >95% conversion in THF-d_8. (**B**) ^{1}H NMR of a reference sample of boric acid in THF-d_8. (**C**) ^{1}H NMR of a reference sample of ammonia-borane adduct in THF-d_8. (**D**) Picture of the white precipitate detected in the catalytic transfer hydrogenation reactions in a MeOH solution.

8. References

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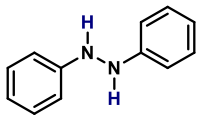
9. Experimental Spectra

^{1}H NMR Spectra



3a

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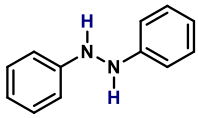

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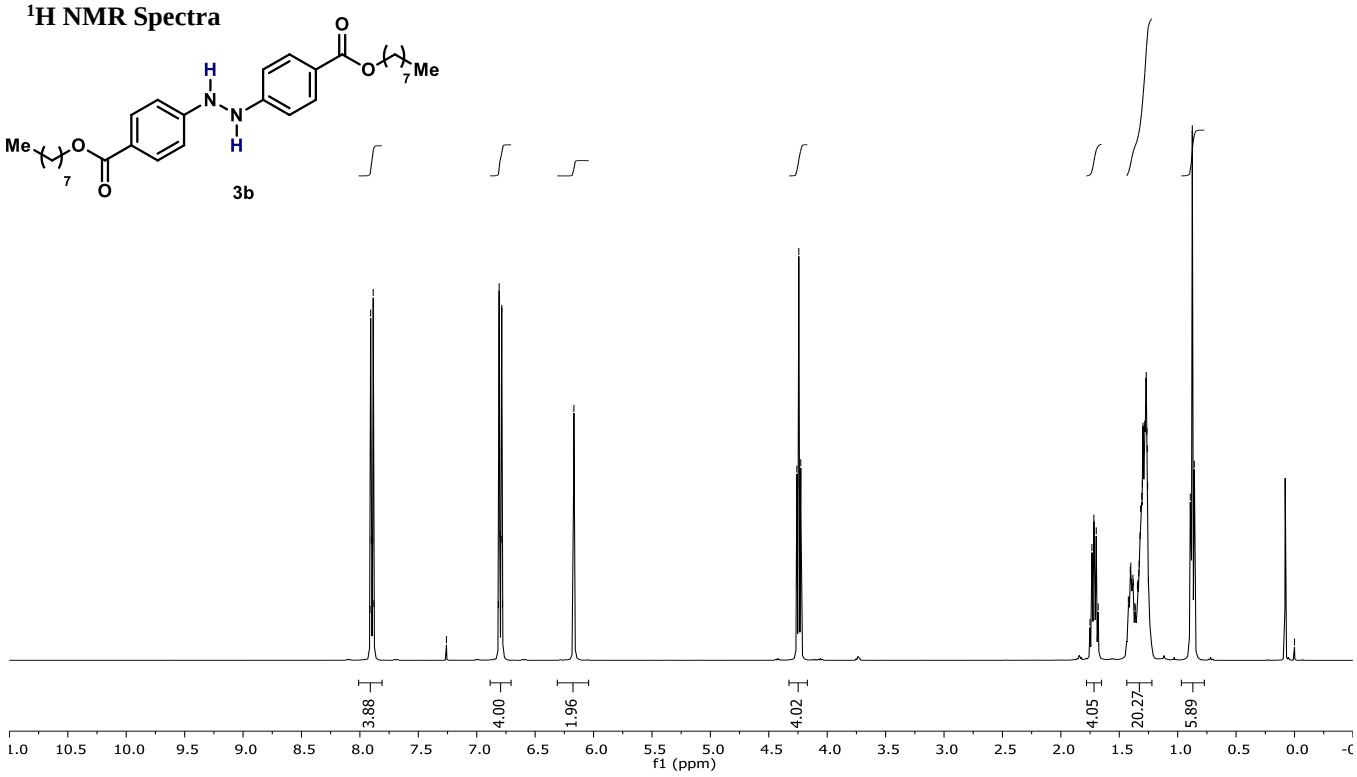

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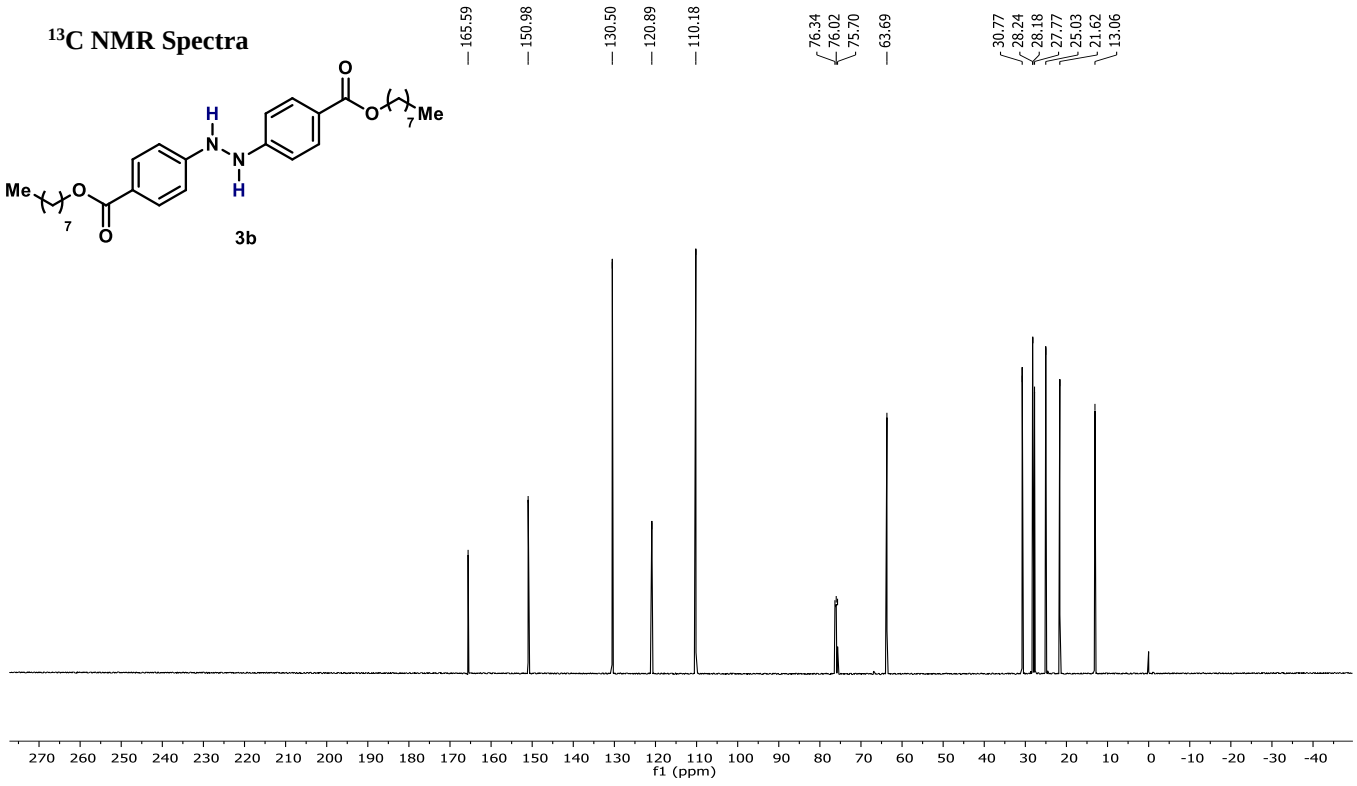

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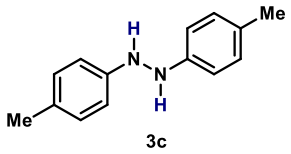

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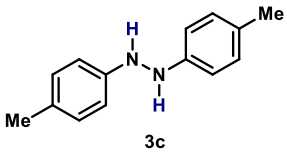

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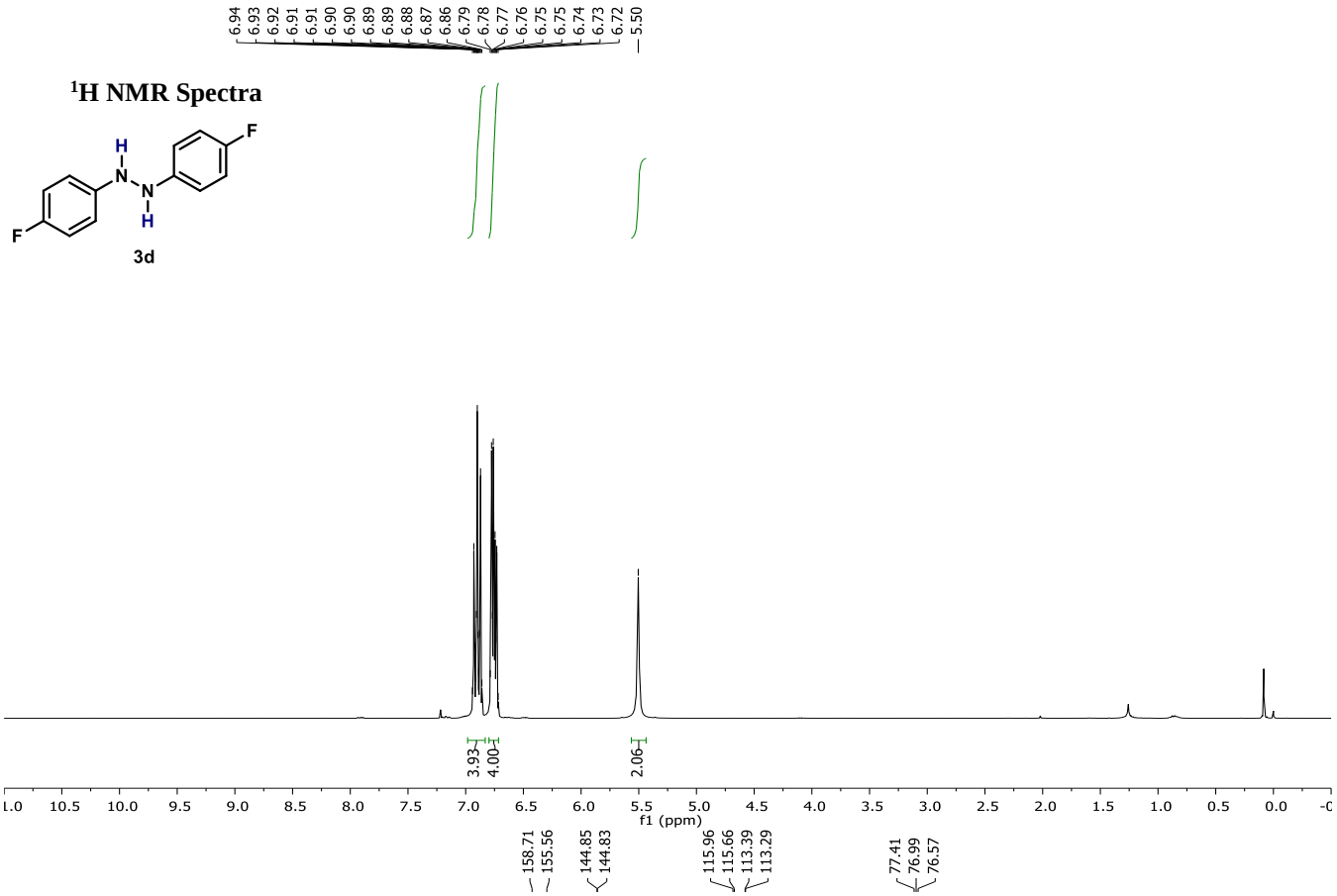

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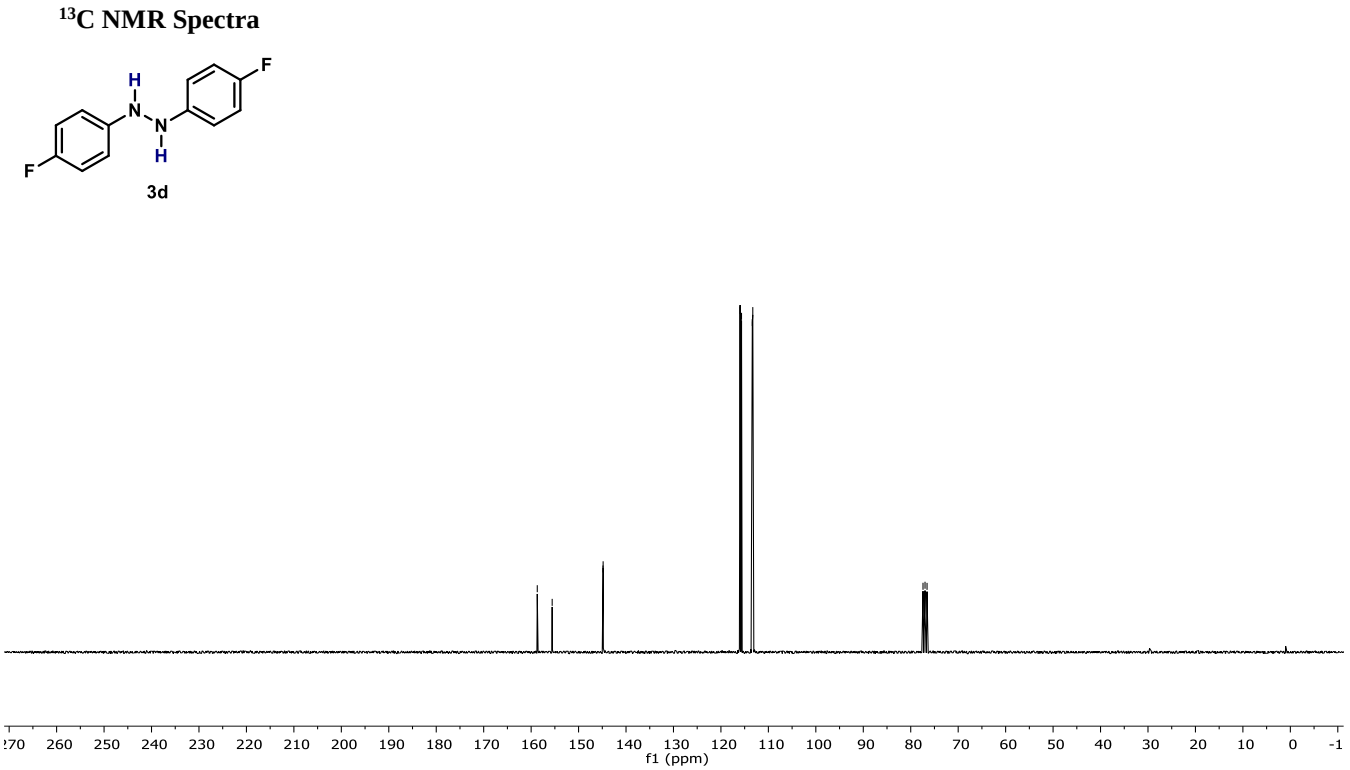

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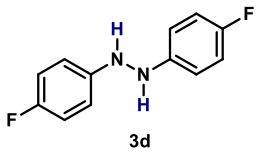
3d

^{19}F NMR Spectra



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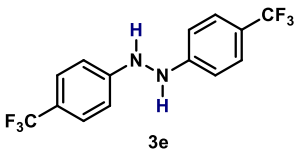

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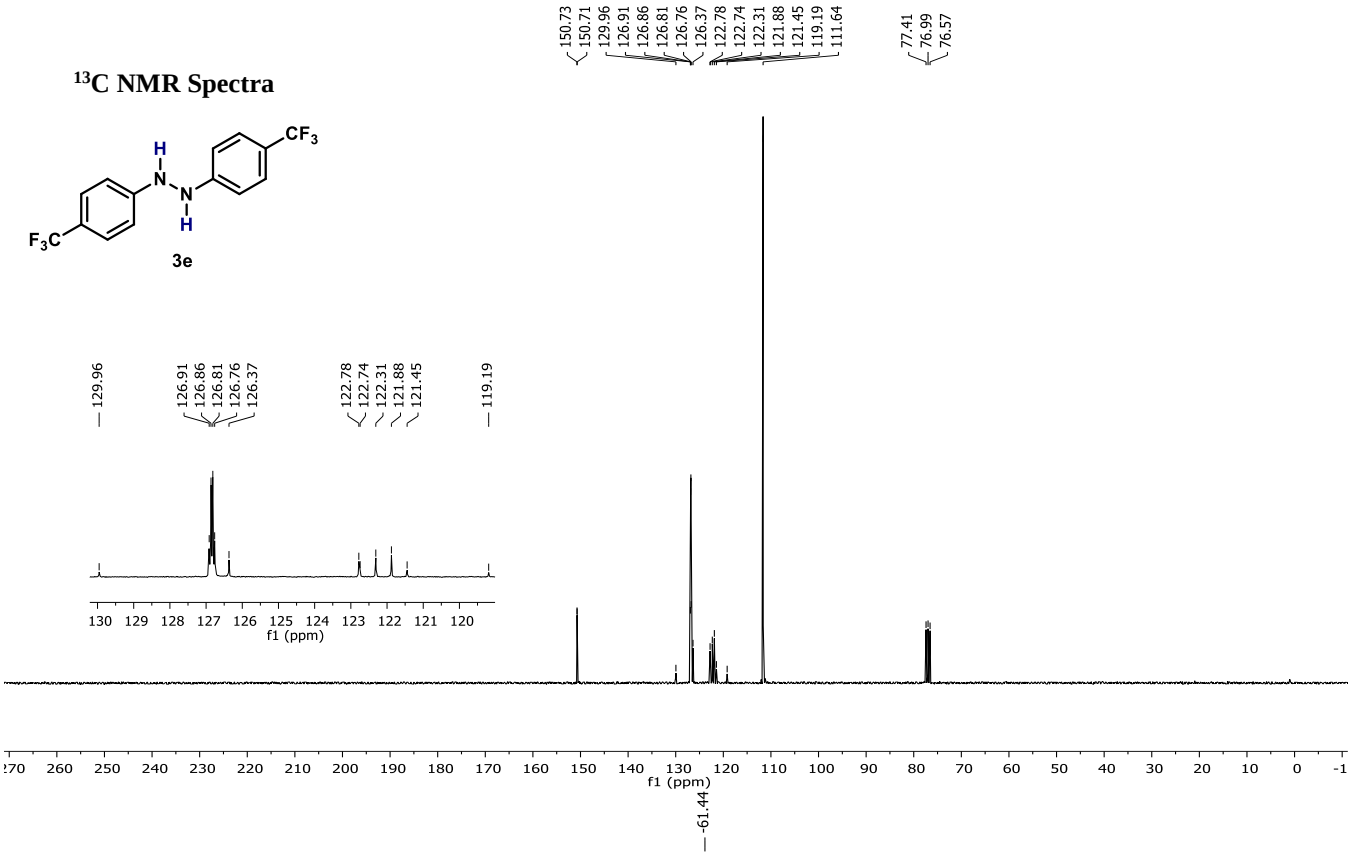

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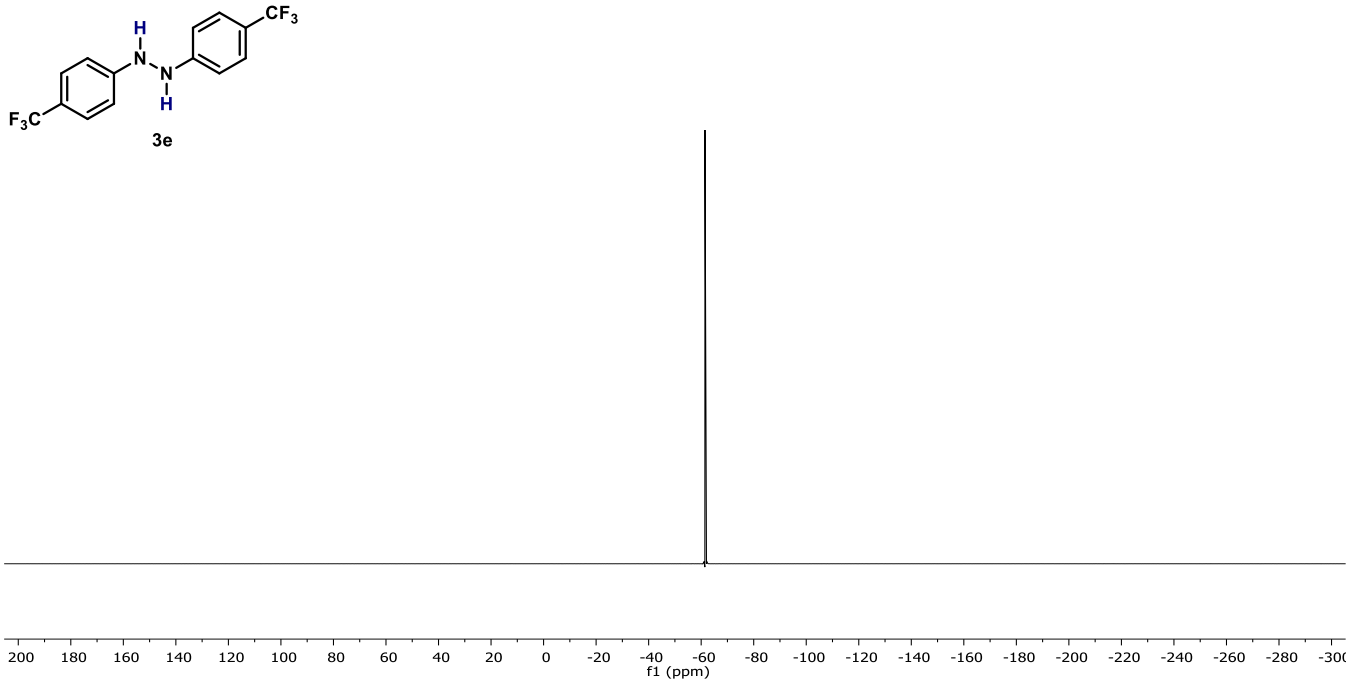

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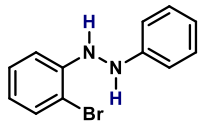

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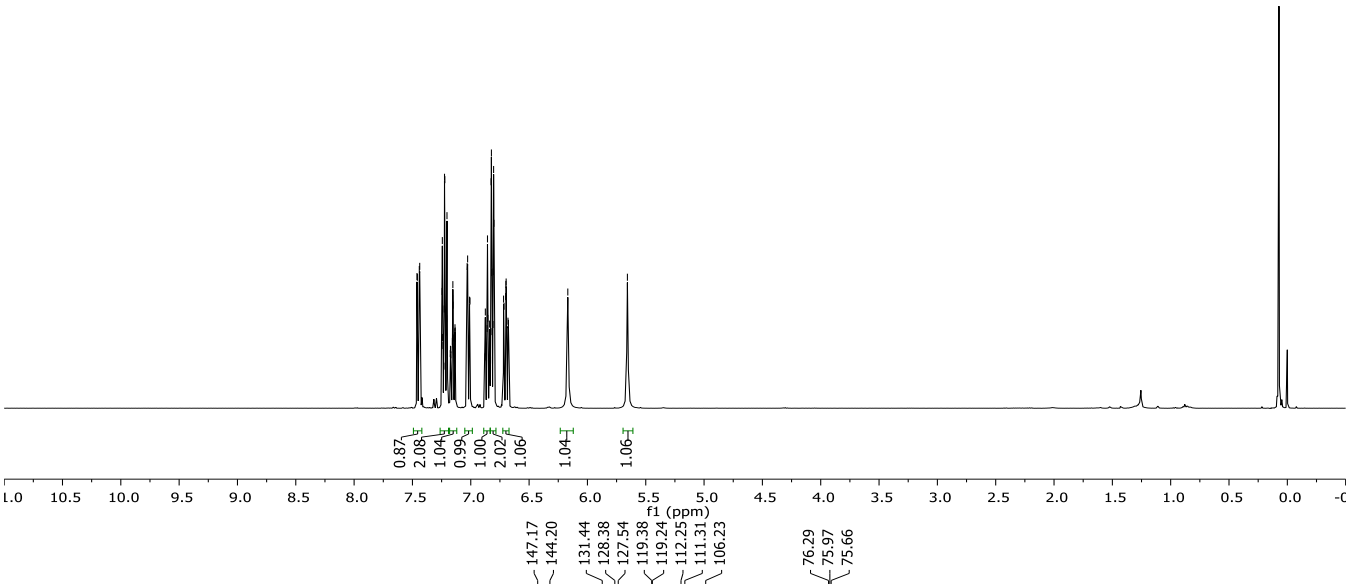

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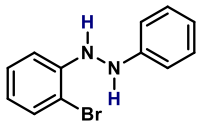

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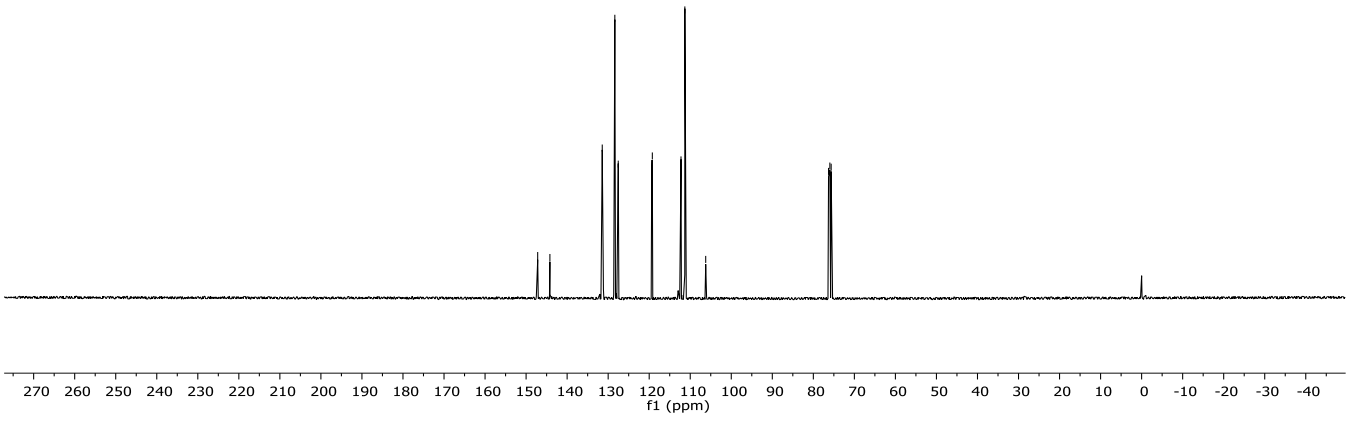

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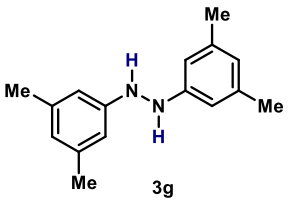

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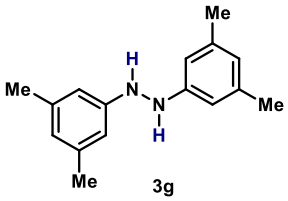

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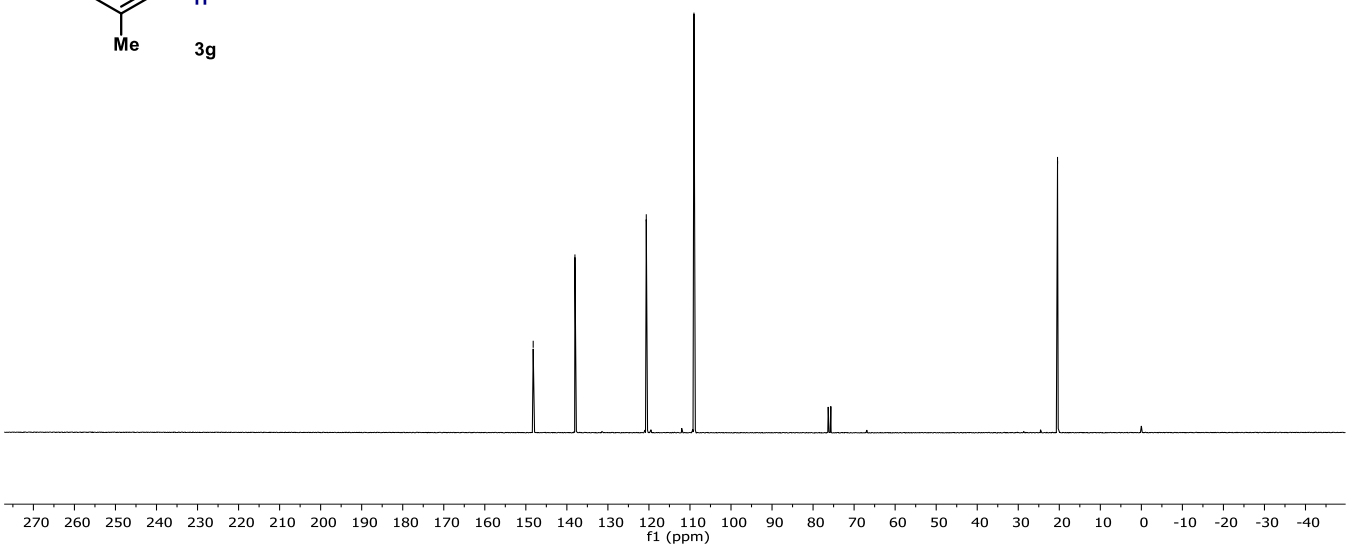

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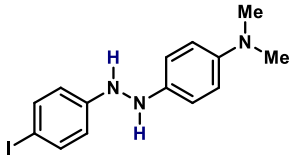

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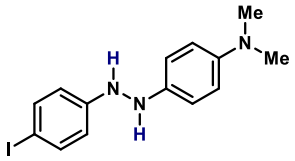

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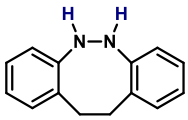

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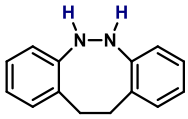

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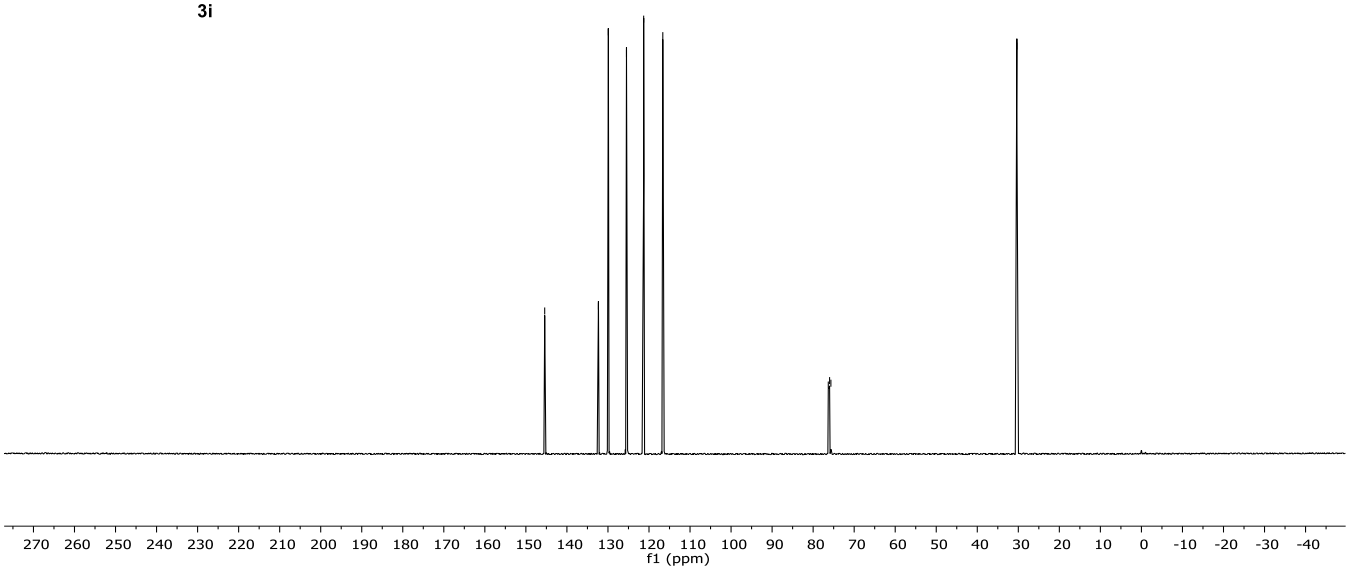

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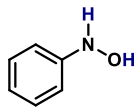

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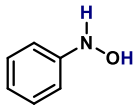

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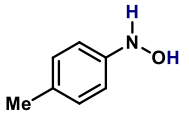

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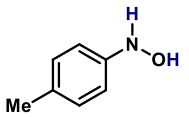

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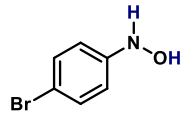

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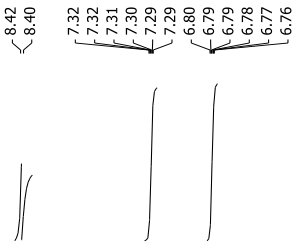

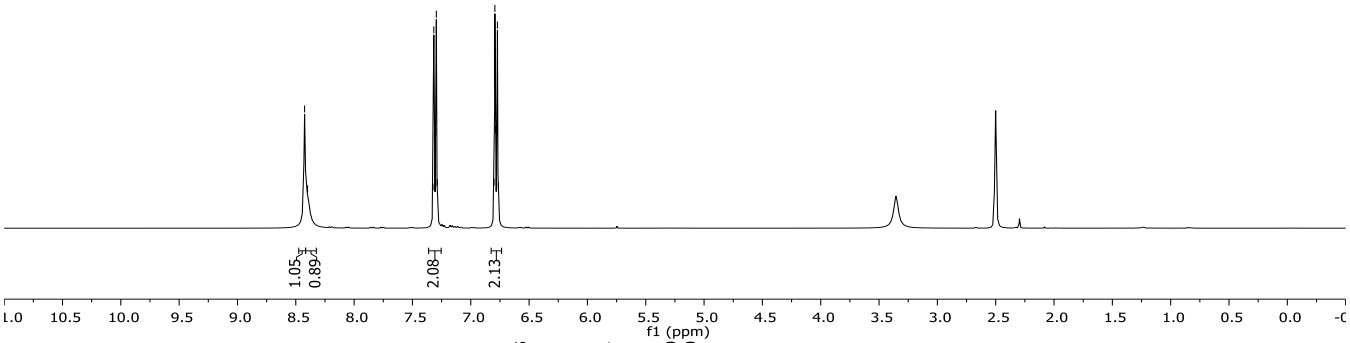

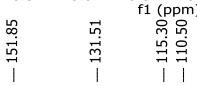

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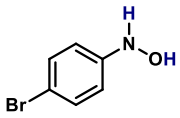

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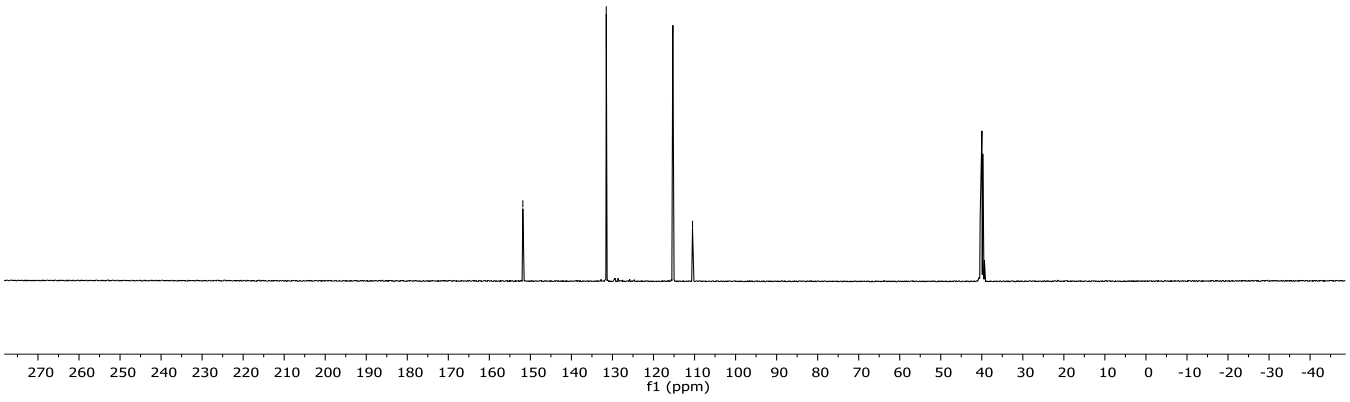

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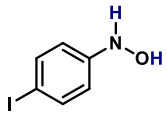

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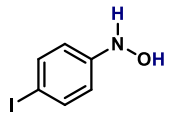

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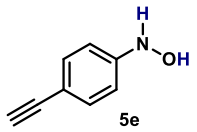

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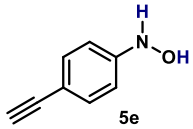

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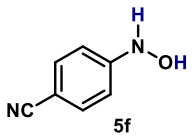

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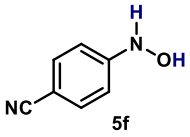

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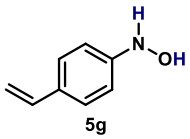

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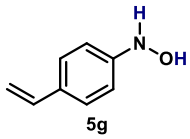

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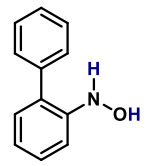

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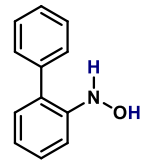

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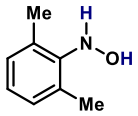

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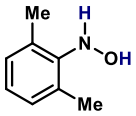

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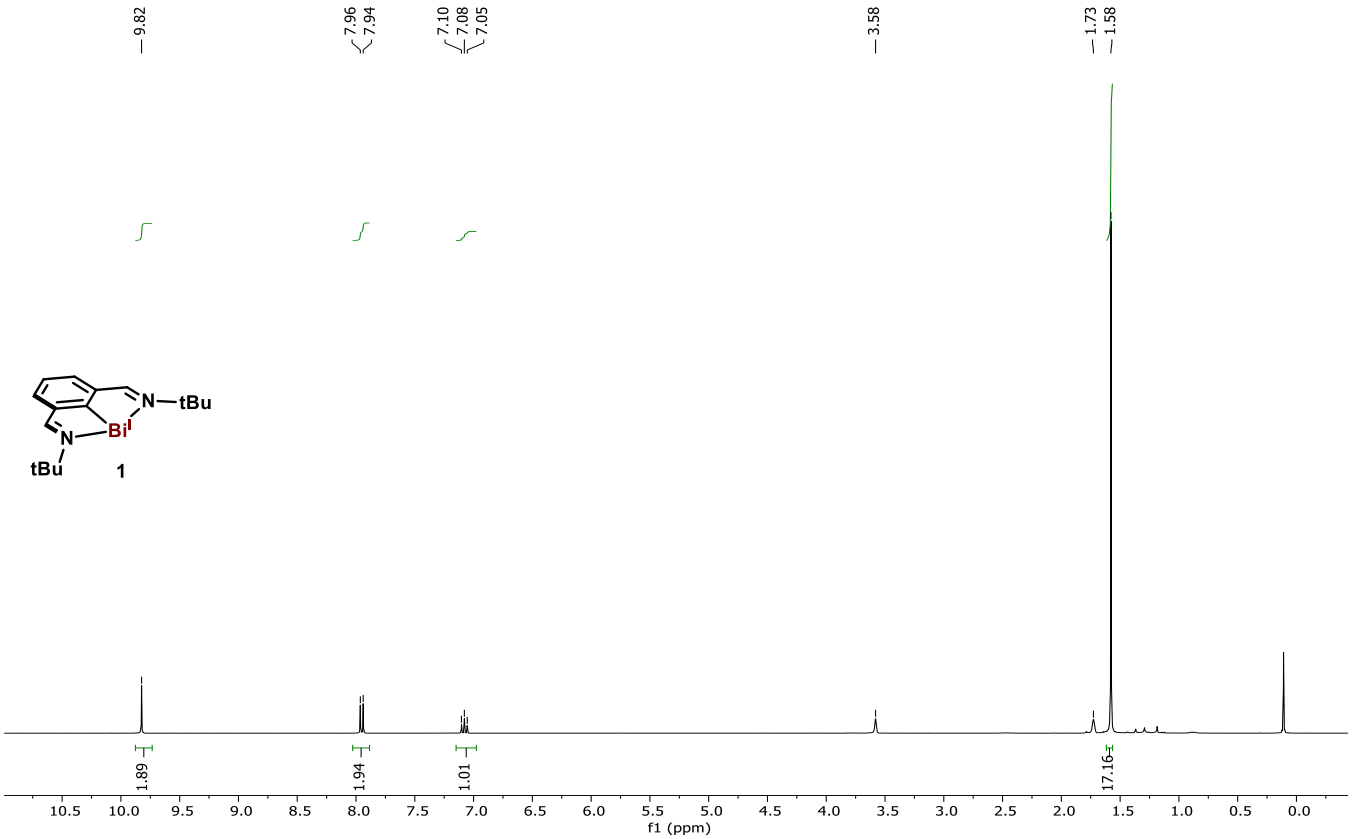

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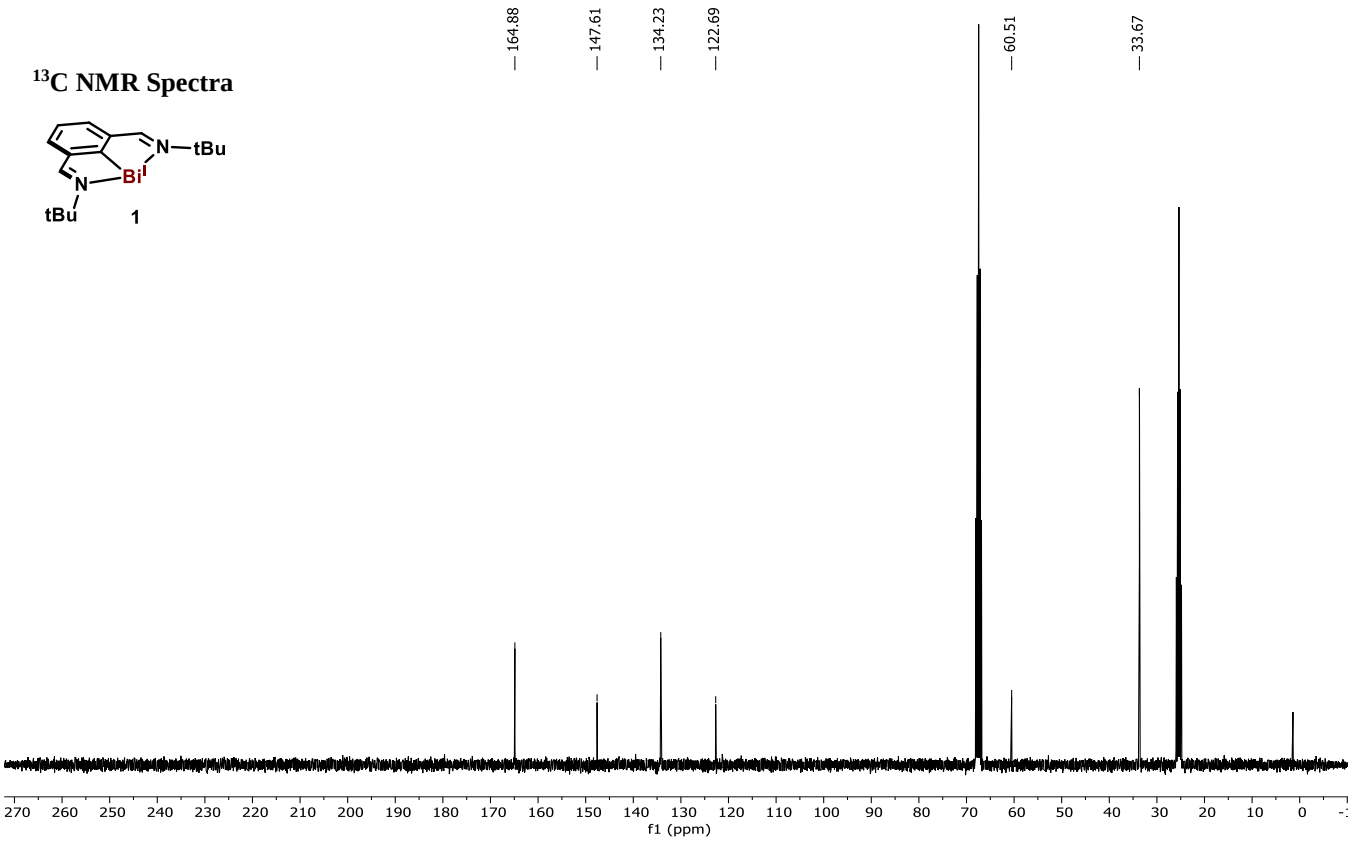
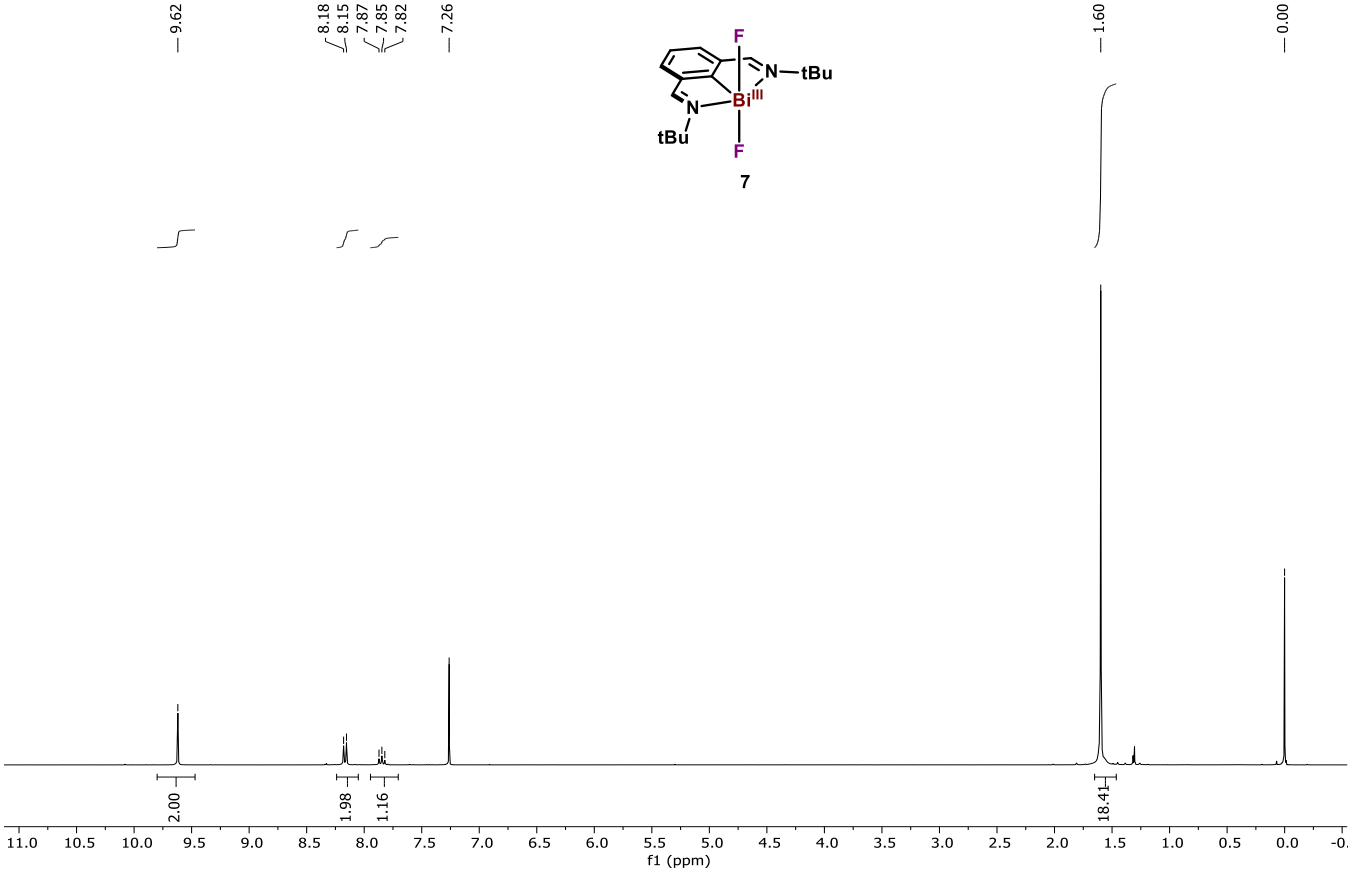
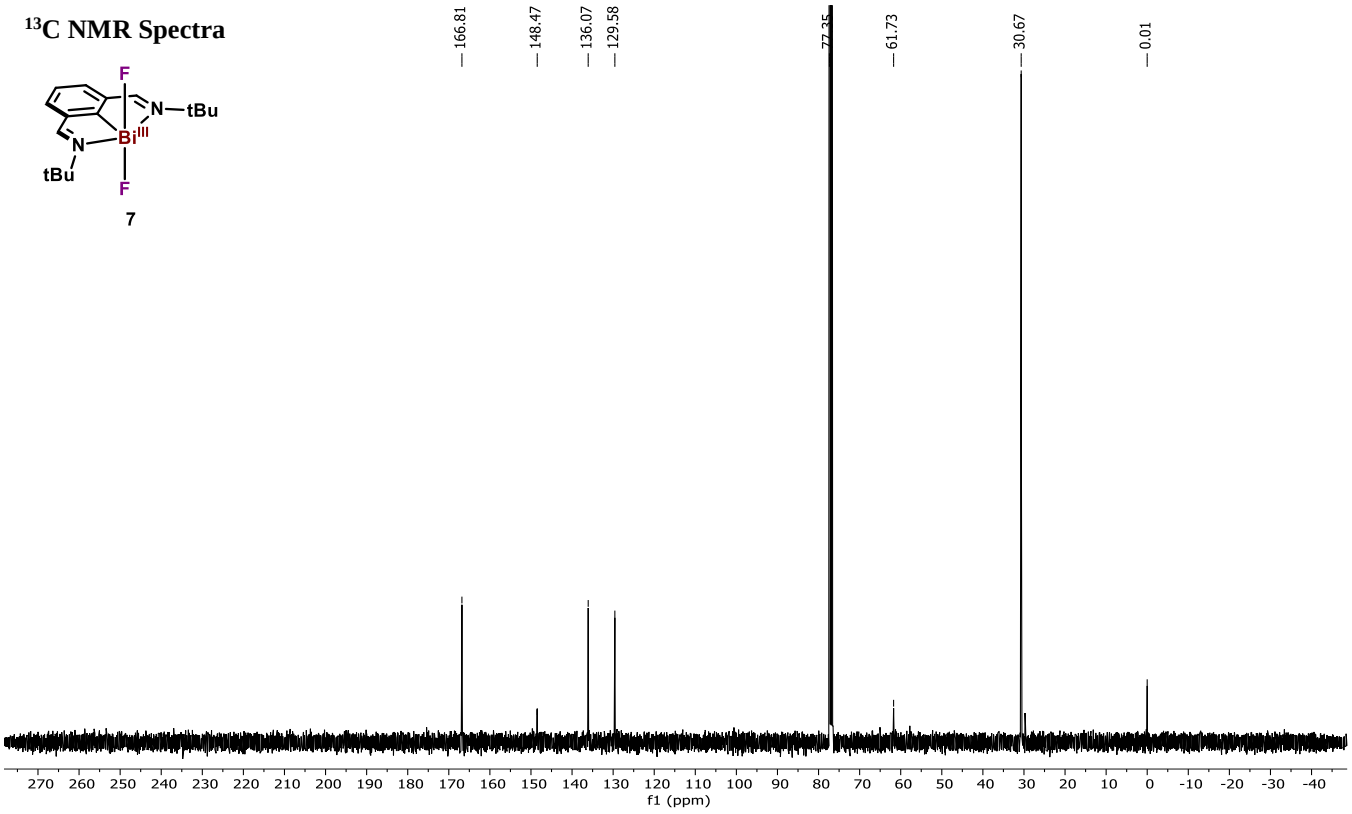


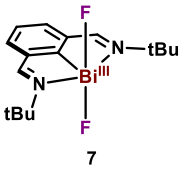
^{1}H NMR Spectra



^{13}C NMR Spectra



^{19}F NMR Spectra



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