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Supporting Information

Lewis Acidic Boranes, Lewis Bases, and Equilibrium Constants: A Reliable Scaffold for a Quantitative Lewis Acidity/Basicity Scale

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– Supporting Information –

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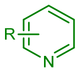
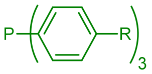
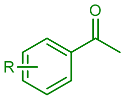
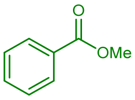
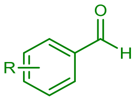
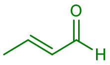
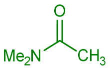
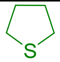
I. Additional Figures and Tables

Table S1. Equilibrium Constants K_B (M^{-1}) for the Reactions of Boranes **1** and Lewis Bases **2**–**11** in dichloromethane and comparison with the Equilibrium Constants $K_B^{eq\ 1}$ Derived by Applying Equation (1).

Lewis Base	R =		LB_B		LA_B	K_B^{exp} (M^{-1})	Method[a]	$K_B^{eq\ 1}$ (M^{-1})	$K_B^{eq\ 1}$/ K_B^{exp}
	4-NMe$_2$	**2a**	8.63	**1j**	-8.97	$(4.54 \pm 0.26) \times 10^{-1}$	NMR	4.54×10^{-1}	
	4-NMe$_2$	**2a**	8.63	**1a**	-4.28	$(3.53 \pm 0.16) \times 10^{4}$	ITC	2.20×10^{4}	0.62
	4-NMe$_2$	**2a**	8.63	**1b**	-1.92	$(3.21 \pm 1.31) \times 10^{6}$	ITC	5.15×10^{6}	1.60
	4-Morpholino	**2b**	8.13	**1a**	-4.28	$(9.35 \pm 0.22) \times 10^{3}$	ITC	7.07×10^{3}	0.76
	4-Morpholino	**2b**	8.13	**1b**	-1.92	$(1.25 \pm 0.17) \times 10^{6}$	ITC	1.65×10^{6}	1.32
	4-OMe	**2c**	7.16	**1a**	-4.28	$(1.01 \pm 0.06) \times 10^{3}$	NMR	7.52×10^{2}	0.74
	4-OMe	**2c**	7.16	**1b**	-1.92	$(1.31 \pm 0.08) \times 10^{5}$	ITC	1.76×10^{5}	1.34
	H	**2d**	6.13	**1a**	-4.28	$(7.81 \pm 0.04) \times 10^{1}$	NMR	7.05×10^{1}	0.90
	H	**2d**	6.13	**1b**	-1.92	$(2.22 \pm 0.15) \times 10^{4}$	ITC	1.65×10^{4}	0.74
	H	**2d**	6.13	**1c**	-0.57	$(3.40 \pm 0.78) \times 10^{5}$	ITC	3.68×10^{5}	1.08
	H	**2d**	6.13	**1d**	0.00	$(1.39 \pm 0.04) \times 10^{6}$	ITC	1.36×10^{6}	0.98
	H	**2d**	6.13	**1e**	0.13	$(1.30 \pm 0.04) \times 10^{6}$	ITC	1.83×10^{6}	1.41
	4-COPh	**2e**	5.42	**1a**	-4.28	9.93 ± 0.42	NMR	1.37×10^{1}	1.38
	4-COPh	**2e**	5.42	**1b**	-1.92	$(3.25 \pm 0.27) \times 10^{3}$	ITC	3.20×10^{3}	0.99
	4-COPh	**2e**	5.42	**1b**	-1.92	$(3.14 \pm 0.06) \times 10^{3}$	NMR		
	4-COPh	**2e**	5.42	**1c**	-0.57	$(7.86 \pm 1.22) \times 10^{4}$	ITC	7.14×10^{4}	0.91
	4-COPh	**2e**	5.42	**1d**	0.00	$(3.86 \pm 0.24) \times 10^{5}$	ITC	2.64×10^{5}	0.68
	4-COPh	**2e**	5.42	**1e**	0.13	$(3.01 \pm 0.41) \times 10^{5}$	ITC	3.56×10^{5}	1.18
	3-Cl	**2f**	4.83	**1a**	-4.28	1.52 ± 0.29	NMR	3.48	2.29
	3-Cl	**2f**	4.83	**1b**	-1.92	$(7.99 \pm 1.81) \times 10^{2}$	NMR	8.14×10^{2}	1.02
	3-Cl	**2f**	4.83	**1c**	-0.57	$(3.31 \pm 1.14) \times 10^{4}$	ITC	1.81×10^{4}	0.55
	3-Cl	**2f**	4.83	**1d**	0.00	$(9.33 \pm 1.05) \times 10^{4}$	ITC	6.70×10^{4}	0.72
	3-Cl	**2f**	4.83	**1e**	0.13	$(8.30 \pm 0.14) \times 10^{4}$	ITC	9.05×10^{4}	1.09
	4-CF$_3$	**2g**	4.52	**1b**	-1.92	$(4.88 \pm 0.43) \times 10^{2}$	NMR	4.07×10^{2}	0.83
	4-CF$_3$	**2g**	4.52	**1c**	-0.57	$(1.43 \pm 0.25) \times 10^{4}$	ITC	9.06×10^{3}	0.63
	4-CF$_3$	**2g**	4.52	**1d**	0.00	$(2.42 \pm 0.34) \times 10^{4}$	ITC	3.35×10^{4}	1.38
	4-CF$_3$	**2g**	4.52	**1e**	0.13	$(3.31 \pm 0.22) \times 10^{4}$	ITC	4.53×10^{4}	1.37
	4-CN	**2h**	3.92	**1b**	-1.92	$(1.68 \pm 0.04) \times 10^{2}$	NMR	9.99×10^{1}	0.59
	4-CN	**2h**	3.92	**1c**	-0.57	$(3.60 \pm 0.23) \times 10^{3}$	ITC	2.23×10^{3}	0.62
	4-CN	**2h**	3.92	**1d**	0.00	$(4.27 \pm 0.32) \times 10^{3}$	ITC	8.22×10^{3}	1.93
	4-CN	**2h**	3.92	**1e**	0.13	$(7.87 \pm 1.06) \times 10^{3}$	ITC	1.11×10^{4}	1.41
	3,5-(CF$_3$)$_2$	**2i**	1.76	**1c**	-0.57	$(1.62 \pm 0.07) \times 10^{1}$	NMR	1.57×10^{1}	0.97
	3,5-(CF$_3$)$_2$	**2i**	1.76	**1d**	0.00	$(5.04 \pm 0.71) \times 10^{1}$	NMR	5.81×10^{1}	1.15
	3,5-(CF$_3$)$_2$	**2i**	1.76	**1e**	0.13	$(6.37 \pm 0.19) \times 10^{1}$	NMR	7.85×10^{1}	1.23
	3,5-(CF$_3$)$_2$	**2i**	1.76	**1f**	1.33	$(1.71 \pm 0.75) \times 10^{3}$	NMR	1.24×10^{3}	0.73
	3,4,5-(Cl)$_3$	**2j**	2.67	**1b**	-1.92	6.06 ± 0.30	NMR	5.75	0.95
	3,4,5-(Cl)$_3$	**2j**	2.67	**1c**	-0.57	$(1.22 \pm 0.11) \times 10^{2}$	NMR	1.28×10^{2}	1.05
	3,4,5-(Cl)$_3$	**2j**	2.67	**1d**	0.00	$(4.33 \pm 0.85) \times 10^{2}$	NMR	4.73×10^{2}	1.09
	3,4,5-(Cl)$_3$	**2j**	2.67	**1e**	0.13	$(7.56 \pm 0.56) \times 10^{2}$	NMR	6.39×10^{2}	0.85
	3,4,5-(Cl)$_3$	**2j**	2.67	**1f**	1.33	$(9.29 \pm 0.22) \times 10^{3}$	NMR	1.01×10^{4}	1.09
	3,5-(F)$_2$-4-CF$_3$	**2k**	1.43	**1c**	-0.57	7.11 ± 0.61	NMR	7.24	1.02
	3,5-(F)$_2$-4-CF$_3$	**2k**	1.43	**1d**	0.00	$(5.35 \pm 1.07) \times 10^{1}$	NMR	2.68×10^{1}	0.50
	3,5-(F)$_2$-4-CF$_3$	**2k**	1.43	**1e**	0.13	$(2.96 \pm 0.13) \times 10^{1}$	NMR	3.62×10^{1}	1.22
	3,5-(F)$_2$-4-CF$_3$	**2k**	1.43	**1f**	1.33	$(3.56 \pm 0.08) \times 10^{2}$	NMR	5.72×10^{2}	1.61
	3,5-(NO$_2$)$_2$	**2l**	-0.75	**1e**	0.13	$(2.38 \pm 0.51) \times 10^{-1}$	NMR	2.43×10^{-1}	1.02
	3,5-(NO$_2$)$_2$	**2l**	-0.75	**1f**	1.33	7.91 ± 0.28	NMR	3.84	0.49
	3,5-(NO$_2$)$_2$	**2l**	-0.75	**1g**	4.08	$(4.50 \pm 1.11) \times 10^{3}$	NMR	2.18×10^{3}	0.48
	3,5-(NO$_2$)$_2$	**2l**	-0.75	**1h**	3.98	$(4.10 \pm 0.35) \times 10^{2}$	NMR	1.71×10^{3}	4.18
	4-Cl-3,5-(NO$_2$)$_2$	**2m**	-1.07	**1f**	1.33	4.87 ± 0.12	NMR	1.81	0.37
	4-Cl-3,5-(NO$_2$)$_2$	**2m**	-1.07	**1g**	4.08	$(1.60 \pm 0.22) \times 10^{3}$	NMR	1.03×10^{3}	0.64
	4-Cl-3,5-(NO$_2$)$_2$	**2m**	-1.07	**1h**	3.98	$(1.94 \pm 0.07) \times 10^{2}$	NMR	8.10×10^{2}	4.18
	2,6-(Me)$_2$	**2n**	-5.50	**1i**	7.24	$(5.47 \pm 1.02) \times 10^{1}$	NMR	5.47×10^{1}	
R-CN	Me	**3a**	-0.48	**1f**	1.33	4.93 ± 0.16	NMR	7.15	1.45
	Me	**3a**	-0.48	**1h**	3.98	$(4.63 \pm 0.25) \times 10^{3}$	NMR	3.19×10^{3}	0.69
	4-F-C$_6$H$_4$	**3b**	-0.81	**1f**	1.33	1.87 ± 0.04	NMR	3.33	1.78
	4-F-C$_6$H$_4$	**3b**	-0.81	**1g**	4.08	$(2.39 \pm 0.28) \times 10^{3}$	NMR	1.89×10^{3}	0.79
	4-F-C$_6$H$_4$	**3b**	-0.81	**1h**	3.98	$(2.10 \pm 0.38) \times 10^{3}$	NMR	1.49×10^{3}	0.71
	4-OMe	**4a**	2.43	**1e**	0.13	$(3.60 \pm 0.36) \times 10^{2}$	NMR	3.60×10^{2}	
	4-OMe	**4a**	2.43	**1f**	1.33	too high	NMR	5.69×10^{3}	
	4-OMe	**4a**	2.43	**1g**	4.08	$(8.61 \pm 0.75) \times 10^{2}$	NMR	3.23×10^{6}	
	4-OMe	**4a**	2.43	**1h**	3.98	too high	NMR	2.54×10^{6}	
	H	**4b**	0.87	**1f**	1.33	$(1.58 \pm 0.04) \times 10^{2}$	NMR	1.58×10^{2}	
	H	**4b**	0.87	**1h**	3.98	too high	NMR	7.06×10^{4}	
	4-Cl	**4c**	-0.11	**1f**	1.33	$(1.67 \pm 0.08) \times 10^{1}$	NMR	1.67×10^{1}	
	4-OMe	**5a**	-1.99	**1f**	1.33	too low	NMR	2.19×10^{-1}	
	4-OMe	**5a**	-1.99	**1g**	4.08	$(9.79 \pm 0.32) \times 10^{1}$	NMR	1.24×10^{2}	1.27

	4-OMe	**5a**	-1.99	**1h**	3.98	$(1.24 \pm 0.04) \times 10^{2}$	NMR	9.78×10^{1}	0.79
	4-Me	**5b**	-2.57	**1g**	4.08	$(2.97 \pm 0.34) \times 10^{1}$	NMR	3.24×10^{1}	1.09
	4-Me	**5b**	-2.57	**1h**	3.98	$(2.78 \pm 0.25) \times 10^{1}$	NMR	2.55×10^{1}	0.92
	4-Br	**5c**	-2.99	**1g**	4.08	6.22 ± 0.92	NMR	1.23×10^{1}	1.98
	4-Br	**5c**	-2.99	**1i**	7.24	$(3.51 \pm 1.82) \times 10^{4}$	NMR	1.77×10^{4}	0.50
	4-CF_3	**5d**	-3.29	**1g**	4.08	5.42 ± 0.58	NMR	6.17	1.14
	4-CF_3	**5d**	-3.29	**1i**	7.24	$(1.01 \pm 0.60) \times 10^{4}$	NMR	8.87×10^{3}	0.88
	4-NO_2	**5e**	-3.90	**1g**	4.08	5.02 ± 0.82	NMR	1.51	0.30
	4-NO_2	**5e**	-3.90	**1i**	7.24	$(6.53 \pm 0.92) \times 10^{2}$	NMR	2.17×10^{3}	3.33
	3,5-$(NO_2)_2$	**5f**	-6.12	**1i**	7.24	$(1.31 \pm 0.37) \times 10^{1}$	NMR	1.31×10^{1}	
		**6**	-5.38	**1i**	7.24	$(7.31 \pm 2.19) \times 10^{1}$	NMR	7.31×10^{1}	
	4-OMe	**7a**	-0.18	**1f**	1.33	6.75 ± 0.21	NMR	1.42×10^{1}	2.10
	4-OMe	**7a**	-0.18	**1g**	4.08	$(4.90 \pm 2.02) \times 10^{3}$	NMR	8.04×10^{3}	1.64
	4-OMe	**7a**	-0.18	**1h**	3.98	$(2.18 \pm 1.10) \times 10^{4}$	NMR	6.33×10^{3}	0.29
	H	**7b**	-1.78	**1g**	4.08	$(1.41 \pm 0.05) \times 10^{2}$	NMR	2.00×10^{2}	1.42
	H	**7b**	-1.78	**1h**	3.98	$(2.24 \pm 0.06) \times 10^{2}$	NMR	1.58×10^{2}	0.70
	4-Br	**7c**	-2.25	**1g**	4.08	$(5.34 \pm 0.12) \times 10^{1}$	NMR	6.78×10^{1}	1.27
	4-Br	**7c**	-2.25	**1h**	3.98	$(6.78 \pm 0.03) \times 10^{1}$	NMR	5.34×10^{1}	0.79
	4-Br	**7c**	-2.25	**1i**	7.24	too high	NMR	9.75×10^{4}	
	4-NO_2	**7d**	-3.76	**1g**	4.08	2.31 ± 0.28	NMR	2.10	0.91
	4-NO_2	**7d**	-3.76	**1h**	3.98	1.02 ± 0.13	NMR	1.66	1.62
	4-NO_2	**7d**	-3.76	**1i**	7.24	$(4.46 \pm 1.41) \times 10^{3}$	NMR	3.02×10^{3}	0.68
		**8**	-0.73	**1g**	4.08	$(1.38 \pm 0.21) \times 10^{3}$	NMR	2.23×10^{3}	1.62
		8	-0.73	**1h**	3.98	$(2.84 \pm 0.42) \times 10^{3}$	NMR	1.76×10^{3}	0.62
		**9**	0.97	**1d**	0.00	7.60 ± 0.18	NMR	9.43	1.24
		9	0.97	**1f**	1.33	$(2.50 \pm 0.19) \times 10^{2}$	NMR	2.01×10^{2}	0.81
$Et_3P=O$		**10**	2.51	**1c**	-0.57	$(1.90 \pm 0.12) \times 10^{1}$	NMR	8.68×10^{1}	4.57
		10	2.51	**1e**	0.13	$(1.98 \pm 0.33) \times 10^{3}$	NMR	4.33×10^{2}	0.22
		**11**	-0.90	**1f**	1.33	[3.54 ± 0.05][b]	NMR	2.73	0.77[b]
		11	-0.90	**1h**	3.98	[$(9.36 \pm 1.70) \times 10^{2}$][b]	NMR	1.22×10^{3}	1.33[b]

[a] ITC measurements were performed at 20 °C, NMR titrations at 22 °C. [b] Equilibrium constants K_B^{exp} for reactions of **11** were not used to determine the Lewis acidities LA_B of the boranes **1**.

Table S2. Lewis Acidity Parameters LA_B and Further Acidity Descriptors for Boranes

Borane		LA_B	σ^a	FIA (ΔH, kJ/mol)^b	ε_{LUMO} (Hartree)	GEI (eV)	FIA (ΔG, kJ/mol)	ε_{LUMO} (Hartree)	GEI (eV)
				at the BP86-D3BJ/def2-SVP level in gas-phase			at the SMD(DCM)/MN15/def2-TZVP in dichloromethane		
$B(4\text{-}Me_2N\text{-}C_6H_4)_3$	**1a**	-4.28	-0.83	-292.1	-0.06001	1.65	-96.7	-0.02941	1.10
$B(4\text{-}MeO\text{-}C_6H_4)_3$	**1b**	-1.92	-0.27	-330.0	-0.08069	2.27	-127.1	-0.04147	1.39
$B(4\text{-}Me\text{-}C_6H_4)_3$	**1c**	-0.57	-0.17	-347.3	-0.09261	2.63	-141.2	-0.04908	1.57
$B(C_6H_5)_3$	**1d**	0.00	0	-359.7	-0.10049	2.88	-147.7	-0.05429	1.69
$B(4\text{-}F\text{-}C_6H_4)_3$	**1e**	0.13	0.06	-376.7	-0.10466	3.06	-154.1	-0.05390	1.68
$B(4\text{-}Cl\text{-}C_6H_4)_3$	**1f**	1.33	0.23	-396.1	-0.11260	3.44	-163.7	-0.06249	1.84
$B(2,4,6\text{-}(F)_3\text{-}C_6H_2)_3$	**1g**	4.08		-396.5	-0.12108	3.83	-185.1	-0.07655	2.14
$B(3,4,5\text{-}(F)_3\text{-}C_6H_2)_3$	**1h**	3.98	0.74	-440.3	-0.12913	4.14	-197.2	-0.07260	2.07
$B(C_6F_5)_3$	**1i**	7.24		-458.8	-0.14437	5.31	-231.7	-0.09589	2.61
$B(2,4,6\text{-}(Me)_3\text{-}C_6H_2)_3$	**1j**	(-8.97)		-323.8	-0.09395	2.78	-87.4	-0.04968	1.54
BF_3		(8.4)		-343.9	-0.01084	1.34	-239.7	0.06314	1.09
BCl_3		(9.3)		-408.7	-0.08770	2.39	-259.6	-0.04009	1.71
BBr_3		(10.1)		-446.1	-0.10629	2.98	-263.2	-0.05910	1.90
tris(perfluoro-β-naphthyl)borane	**1k**	(6.8)		-484.6	-0.14906	6.83	-226.0	-0.10251	2.83
F_{13}-9-phenyl-9-borafluorene	**1l**	(7.35)		-475.7	-0.15295	6.49	-230.5	-0.10311	2.82

[a] Hammett σ values taken from ref S1. [b] Calculated according to the procedure outlined in ref S2 and anchored to the dissociation of fluorotrimethylsilane calculated at the G3 level in ref S3.

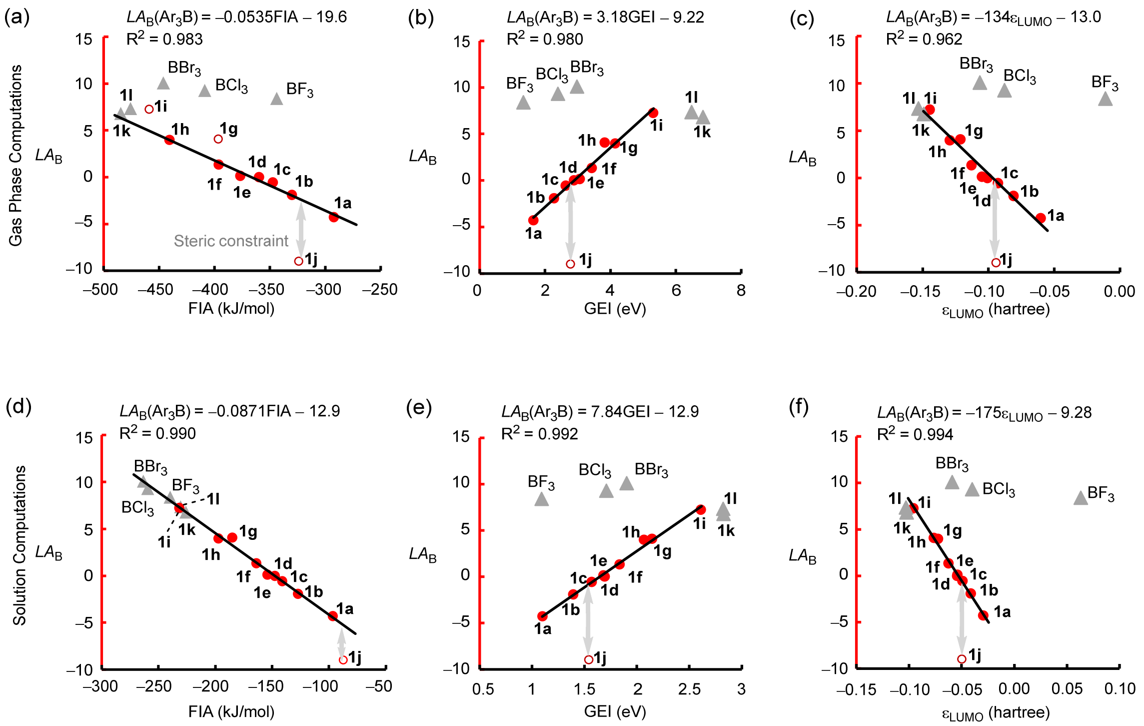
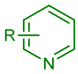
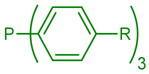
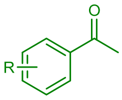
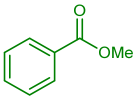
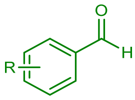
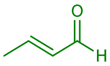
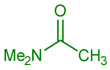
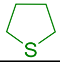


Figure S1. Correlation of LA_B with different quantum-chemically calculated acidity descriptors for boranes in gas phase and solution. (a)-(c): Correlation of LA_B with fluoride ion affinities FIA (a), global electrophilicity indices GEI (b) and LUMO energies ε_{LUMO} (c) obtained at the BP86-D3BJ/def2-SVP level of theory in gas phase (all values from Table S2). (d)-(f): Correlation of LA_B with fluoride ion affinities FIA (d), global electrophilicity indices GEI (e) and LUMO energies ε_{LUMO} (f) obtained considering dichloromethane solvation at the SMD(DCM)/MN15/def2-TZVP level of theory (all values from Table S2). The data for BF_3, BCl_3, BBr_3, **1k** and **1l** (gray triangles) were not used for the calculation of the correlation lines.

Table S3. Lewis Basicity Parameters LB_B and Further Basicity Descriptors for Pyridines, Nitriles, Phosphines, Carbonyl Compounds and Triethylphosphine Oxide

Lewis Base	R =		LB_B	Σσ[a]	LB (vs Ar_2CH^+)[b]	pK_{aH}(H_2O)	pK_{aH}(MeCN)	ΔH_{BF_3}[c]	BA[d]
	4-NMe_2	**2a**	8.63	-0.83	16.42	9.39 (ref S4)	17.95 (ref S5)	151.55	-155.3
	4-Morpholino	**2b**	8.13		15.04	8.53 (ref S4)		144.47	-152.2
	4-MeO	**2c**	7.16	-0.27	11.99	6.58 (ref S6)	14.23 (ref S5)	135.27	-146.5
	H	**2d**	6.13	0	10.02	5.21 (ref S6)	12.53 (ref S5)	128.08	-141.7
	4-COPh	**2e**	5.42	0.43	8.78	3.35 (ref S6)			-134.9
	3-Cl	**2f**	4.83	0.37	7.44	2.81 (ref S6)	9.55 (ref S5)	118.79	-131.1
	4-CF_3	**2g**	4.52	0.54	6.71	2.63 (ref S7)	8.03 (ref S5)	115.75	-130.7
	4-CN	**2h**	3.92	0.66	6.08	1.86 (ref S6)	8.50 (ref S8)	113.27	-129.3
	3,5-$(CF_3)_2$	**2i**	1.76	0.86		--			-118.8
	3,4,5-$(Cl)_3$	**2j**	2.67	0.97		--			-117.5
	3,5-$(F)_2$-4-CF_3	**2k**	1.43	1.22		--			-114.5
	3,5-$(NO_2)_2$	**2l**	-0.75	1.42		--			-106.2
	4-Cl-3,5-$(NO_2)_2$	**2m**	-1.07	1.65		--			-102.9
	2,6-$(Me)_2$	**2n**	(-5.50)	--		6.72 (ref S9)	14.41 (ref S5)	97.73	-125.5
R-CN	Me	**3a**	-0.48	--				60.39	-98.8
	4-F-C_6H_4	**3b**	-0.81	--		--			-93.4
	4-MeO	**4a**	(2.43)	-0.27	17.00	4.57 (ref S10)	10.06 (ref S11)		-145.3
	H	**4b**	(0.87)	0	14.27	2.73 (ref S12)	7.64 (ref S11)		-138.4
	4-Cl	**4c**	(-0.11)	0.23	11.65	1.03 (ref S10)			-132.7
	4-MeO	**5a**	-1.99	-0.27				83.01	-88.5
	4-Me	**5b**	-2.57	-0.17				77.82	-85.4
	4-Br	**5c**	-2.99	0.23				73.09	-79.9
	4-CF_3	**5d**	-3.29	0.54					-75.8
	4-NO_2	**5e**	-3.90	0.78				67.07	-73.9
	3,5-$(NO_2)_2$	**5f**	-6.12	1.42					-67.9
		**6**	-5.38	--				59.4	-49.4
	4-MeO	**7a**	-0.18	-0.27				84.81	-88.7
	H	**7b**	-1.78	0				74.88	-80.8
	4-Br	**7c**	-2.25	0.23					-77.7
	4-NO_2	**7d**	-3.76	0.78				62.32	-70.6
		**8**	-0.73	--					-88.9
		**9**	0.97	--				112.14	-105.7
$Et_3P=O$		**10**	2.51	--				119.28	-121.9
Et_2O			-1.0					78.77	-80.2
		**11**	-0.90					51.62	-97.3

[a] Sum of Hammett σ parameters, from ref S1. [b] Lewis basicities LB (in dichloromethane) toward diarylcarbenium ions from ref S13. [c] Experimental BF_3 affinities (in kJ/mol), from ref S14. [d] Calculated borane (BH_3) affinities BA in dichloromethane (BA = ΔG_{BH3} in kJ/mol, this work, Supporting Information).

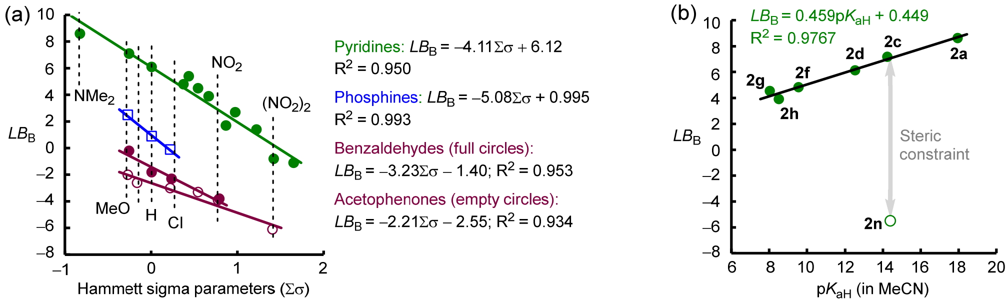


Figure S2. (a) Correlation of LB_B with the sum of Hammett substituent parameters σ[S1] for the different classes of compounds investigated in this study with data summarized in Table S3. (b) Correlation of LB_B for pyridines with their pK_{aH} in MeCN (with data from Table S3).

II. General

Solvents, Reagents, and Analytics. Triarylboranes were prepared according to the modified literature procedures as outlined below using commercialy available chemicals purchased from Sigma Aldrich, ABCR or TCI. Trimesitylborane (**1j**) was purchased from EGA-Chemie KG and used without further purification. $Ph_3B \cdot NaOH$ was purchased from TCI. All boranes were stored in an argon-filled glove box at –35 °C. Hydrazine monohydrate (purum, > 99%) was purchased from Fluka.

Dichloromethane for isothermal titration calorimetry (ITC) measurements was purchased from Merck (HPLC grade) and stirred over concentrated H_2SO_4 for 2 weeks to remove olefinic stabilizers. Subsequently, distillation over calcium hydride provided anhydrous material which was stored for 24 h over activated molecular sieves (3 Å).

Deuterated dichloromethane (CD_2Cl_2) was purchased from Eurisotop and stored for 24 h over activated molecular sieves (3 Å).

Melting points were acquired on Büchi Melting Point M-560 devices and are not corrected.

Nuclear magnetic resonance (NMR) spectra were acquired on 400 MHz spectrometers. The following abbreviations and their combinations were used in the analysis of NMR spectra: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br s = broad singlet, app = apparent. NMR signals were assigned based on information from additional 2D NMR experiments (COSY, gHSQC, gHMBC, NOESY). Chemical shifts are given in ppm. Internal reference was set to the residual solvent signals (for CD_2Cl_2: $\delta_H = 5.32$, $\delta_C = 54.00$, $CDCl_3$: $\delta_H = 7.26$, $\delta_C = 77.16$; for d_6-DMSO: $\delta_H = 2.50$, $\delta_C = 39.52$).[S15] The ^{13}C NMR spectra (101 MHz) were recorded under broad-band proton-decoupling.

High resolution (HRMS) mass spectra were recorded on a Finnigan MAT 95 sectorfield mass spectrometer where samples were vaporized on a platinum wire from 20 to 1600 °C at a rate of 120 °C/min. For ionization of the samples, electron-impact ionization (EI) was applied.

Isothermal Titration Calorimetry (ITC). The ITC measurements were performed on a Microcal VP-ITC instrument with solutions maintained under an atmosphere of dry nitrogen. The reference cell was filled with dichloromethane and the sample cell was filled with a solution of the borane in the same solvent. The syringe was filled with a solution of the Lewis base in dichloromethane, which was then gradually injected (6 µL/injection, 40 steps, 120 s spacing between injections) into the sample cell. The ITC raw data were processed and analyzed with the AFFINImeter ITC software (v.2.1710) assuming a 1:1 interaction model.[S16]

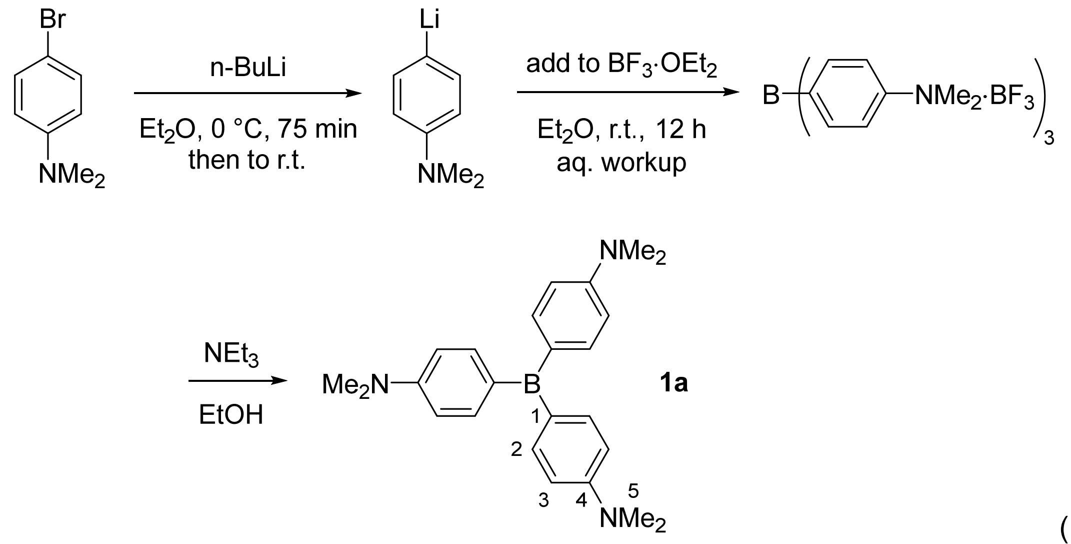
NMR Spectroscopic Titrations. NMR spectroscopic titration experiments were performed with a series of NMR tubes that were handled in an argon filled glovebox and filled with anhydrous CD_2Cl_2 solutions. In most cases, the borane was used as the minor component. Only in case of tris(pentafluorophenyl)borane (**1i**), the Lewis base was used as minor component and treated with an excess of **1i**. ^{1}H NMR measurements were performed on a 400 MHz NMR spectrometer at 22 °C. The resulting dependency of the chemical shift difference Δδ (in ppm, referenced to the residual solvent signal in d_2-dichloromethane) of the resonance of the Lewis acid (or Lewis base for reactions with **1i**) vs. the concentration of the excess component was analyzed according to the equation (S1) by non-linear fitting with the Origin software.[S17] For the detailed derivation of Eq (S1) see ref.[S18]. The only variable in Eq (S1) is K_B, all other quantities are known from the concentrations used in the titrations.

$$\Delta\delta = \frac{\Delta\delta_{\mathrm{max}}}{[\mathrm{LA}]}\left(\frac{1}{2}\left\{\left([\mathrm{LA}] + [\mathrm{LB}] + \frac{1}{K_{\mathrm{B}}}\right) - \sqrt{\left([\mathrm{LA}] + [\mathrm{LB}] + \frac{1}{K_{\mathrm{B}}}\right)^2 + 4[\mathrm{LA}][\mathrm{LB}]}\right\}\right) \quad \text{(S1)}$$

III. Synthesis

Tris(4-dimethylaminophenyl)borane (1a)

Synthesis according to the modified procedure in ref.[S19].



(RNH408)

To a flame dried 100 mL Schlenk flask under nitrogen was added diethyl ether (27 mL) and 4-(dimethylamino)bromobenzene (3.58 g, 17.9 mmol). The resulting solution was cooled to 0 °C. Under stirring *n*-BuLi (2.3 M, 7.78 mL, 17.9 mmol) was added. Then the mixture was stirred for further 75 min at 0 °C and subsequently allowed to warm to room temperature.

In a separate flame dried 100 mL Schlenk flask under nitrogen was dissolved freshly distilled $BF_3{\cdot}OEt_2$ (2.62 mL, 21.3 mmol) in diethyl ether (25 mL). Under stirring, the solution of the above prepared aryl lithium species was added dropwise causing the formation of a cloudy, yellowish precipitate. After stirring overnight, water (20 mL) was added. The organic layer was separated, and the aqueous phase placed on a rotary evaporator (40 °C, 300 mbar) to remove residual diethyl ether. The aqueous phase was filtrated, and a solution of triethylamine (1.80 g, 17.8 mmol) in ethanol (5 mL) was added. The resulting yellow precipitate was separated, washed several times with water and then methanol, and finally dried under reduced pressure (crude yield: 605 mg).

For purification, that crude material was suspended in acetone (10 mL), heated under reflux for 2.5 h and the hot mixture filtrated. The solution was concentrated to dryness and the residue recrystallized from acetone to give the borane (148 mg, 7%) as yellow, fluorescent solid.

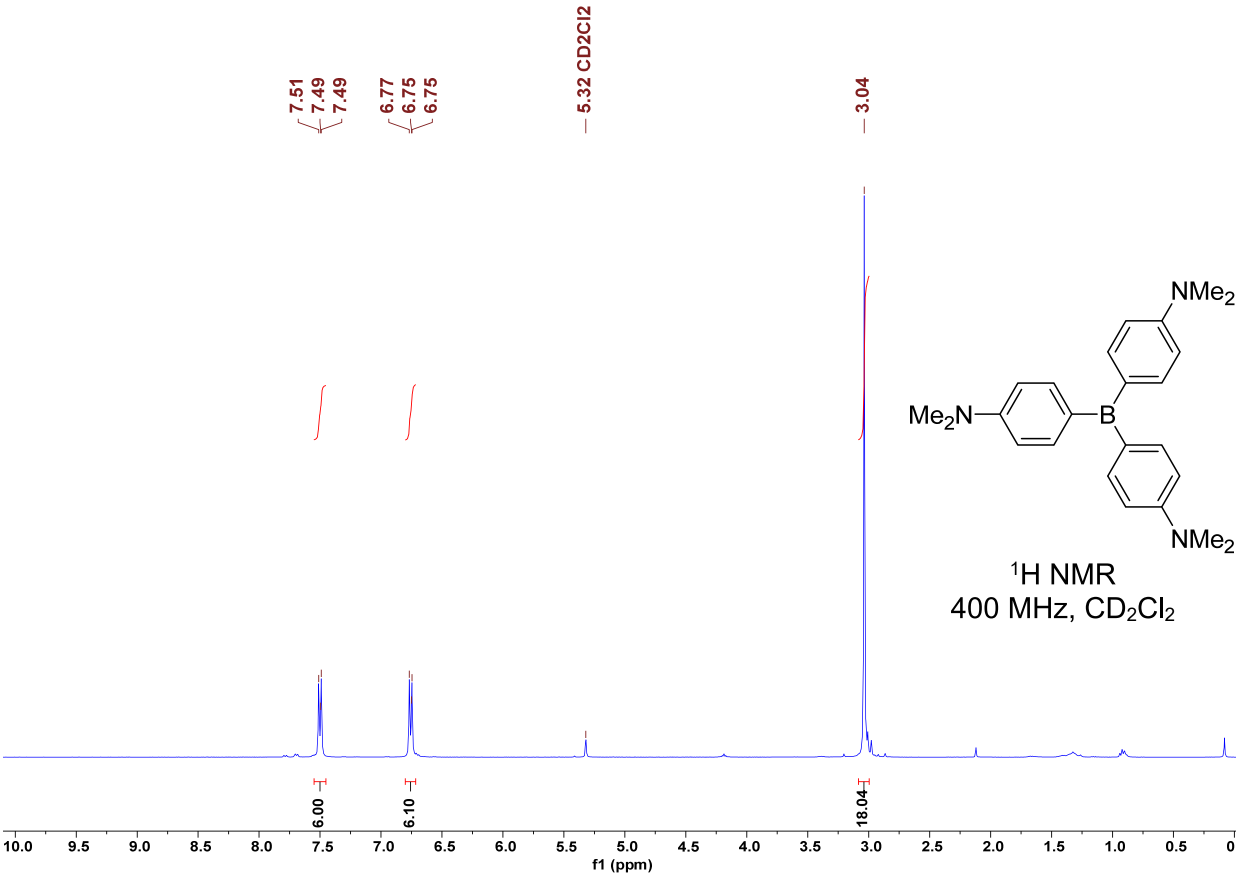
Though borane **1a** is not particularly sensitive towards moisture, we stored it in an argon filled glovebox at −35 °C. Under nitrogen, initially colorless diluted solutions of **1a** in dichloromethane turned intense yellow after exposure to light.

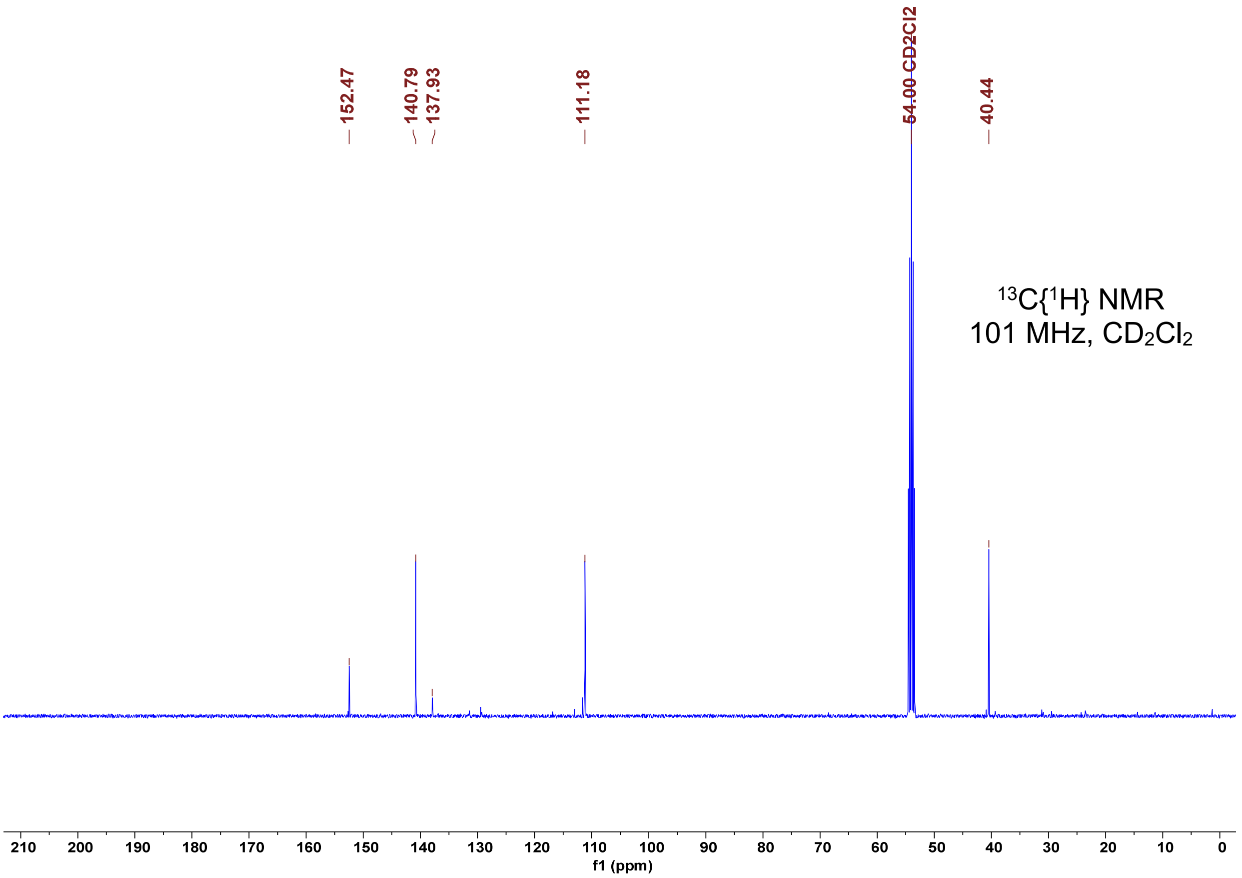
Mp.: 199-221 °C (ref.[S19]: mp 209-212 °C)

^{1}H NMR (400 MHz, CD_2Cl_2) δ = 7.51–7.49 (m, 6 H), 6.77–6.75 (m, 6 H), 3.04 (s, 18 H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2) δ = 152.5 (C_q, C-4), 140.8 (CH, C-2), 137.9 (C_q, C-1), 111.2 (CH, C-3), 40.4 (CH_3, C-5).

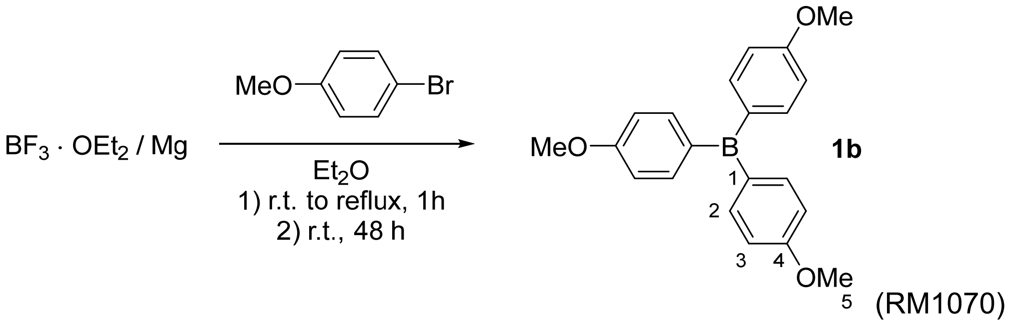
HRMS (EI^+) calcd *m*/*z* for $C_{24}H_{30}BN_3^{\bullet +}$ ($M^{\bullet +}$) 371.2527; found 371.2538.


7.51
7.49
7.49
6.77
6.75
6.75
5.32 CD2Cl2
3.04
NMe$_2$
Me$_2$N
B
NMe$_2$
^{1}H NMR
400 MHz, CD$_2$Cl$_2$
6.00
6.10
18.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)


152.47
140.79
137.93
111.18
54.00 CD2Cl2
40.44
^{13}C{^{1}H} NMR
101 MHz, CD$_2$Cl$_2$
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Tris(4-methoxyphenyl)borane (1b)

Synthesis according to the modified procedure in ref.[S20].



A 100 mL Schlenk flask with reflux condenser was charged with magnesium turnings (854 mg, 35.1 mmol), flame dried under vacuum, and filled with dry nitrogen. Diethyl ether (20 mL) and freshly distilled $BF_3{\cdot}OEt_2$ (1.26 mL, 10.0 mmol) were added. To the vigourously stirred mixture, a solution of 4-bromoanisole (3.78 mL, 30.2 mmol) in diethyl ether (20 mL) was added. The Grignard reaction was initiated by the addition of 2 drops of iodomethane and careful heating to reflux causing the suspension to turn yellow. The mixture was heated to reflux for 3 h, allowed to cool to room temperature, and then stirred for another 64 h. All volatiles were subsequently removed under reduced pressure. The residue was suspended in *n*-hexane (50 mL) and filtered through a Schlenk-frit. The resulting yellow solution was concentrated under reduced pressure to leave a yellow solid residue, which was recrystallized from *n*-hexane to afford the product (1.22 g, 37%) as yellowish, crystalline solid.

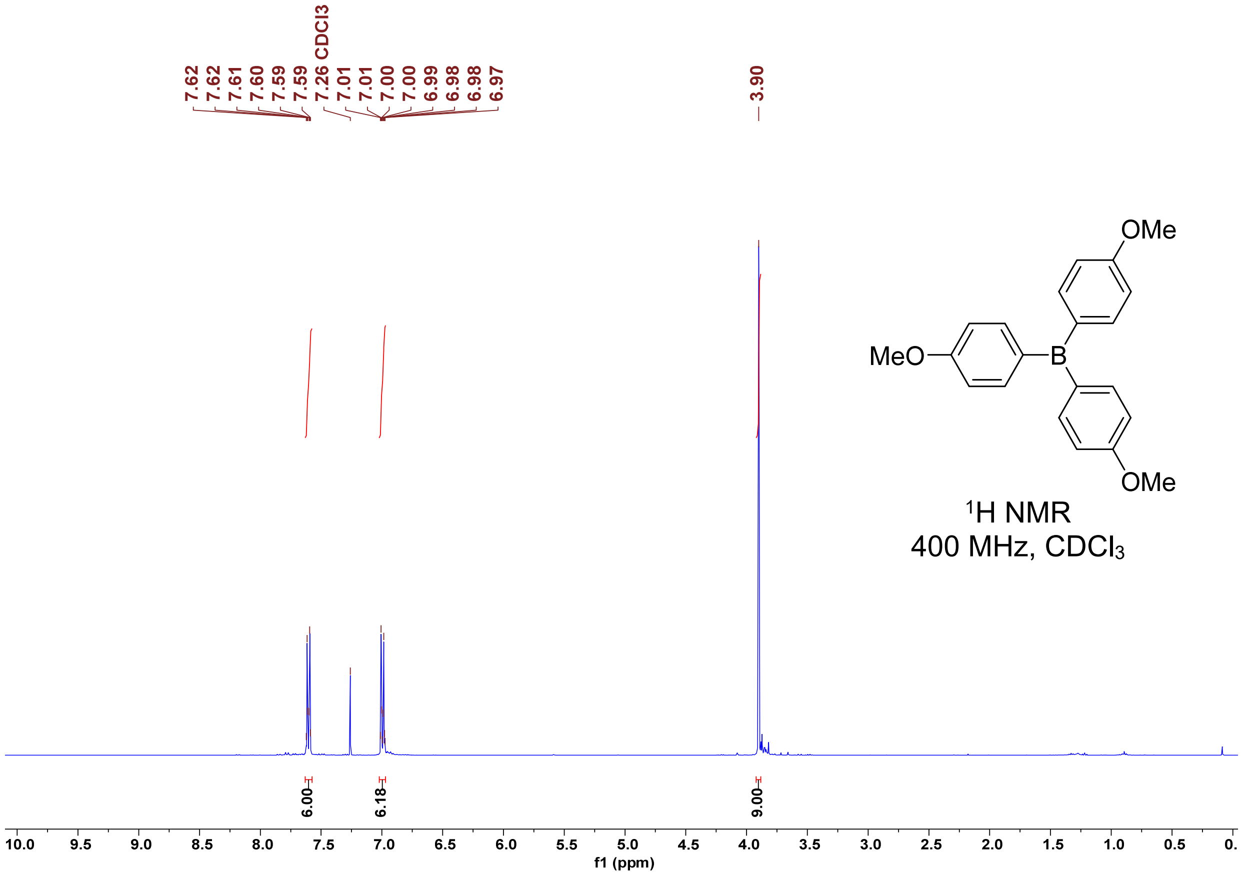
Mp.: 80-95 °C (ref.[S21]: mp 128 °C)

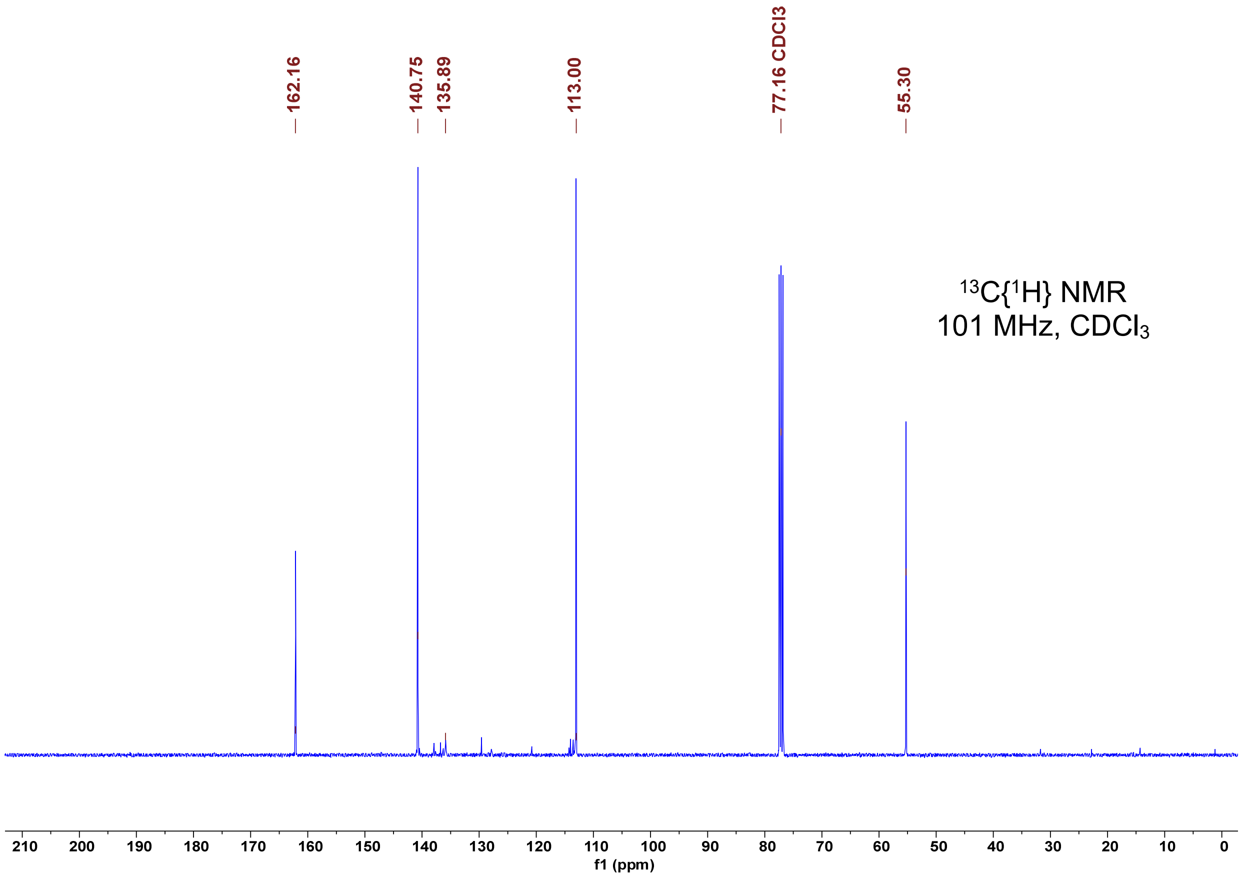
^1H NMR (400 MHz, $CDCl_3$) δ = 7.62–7.59 (m, 6 H, 2-H), 7.01–6.97 (m, 6 H, 3-H), 3.90 (s, 9 H, 5-H).

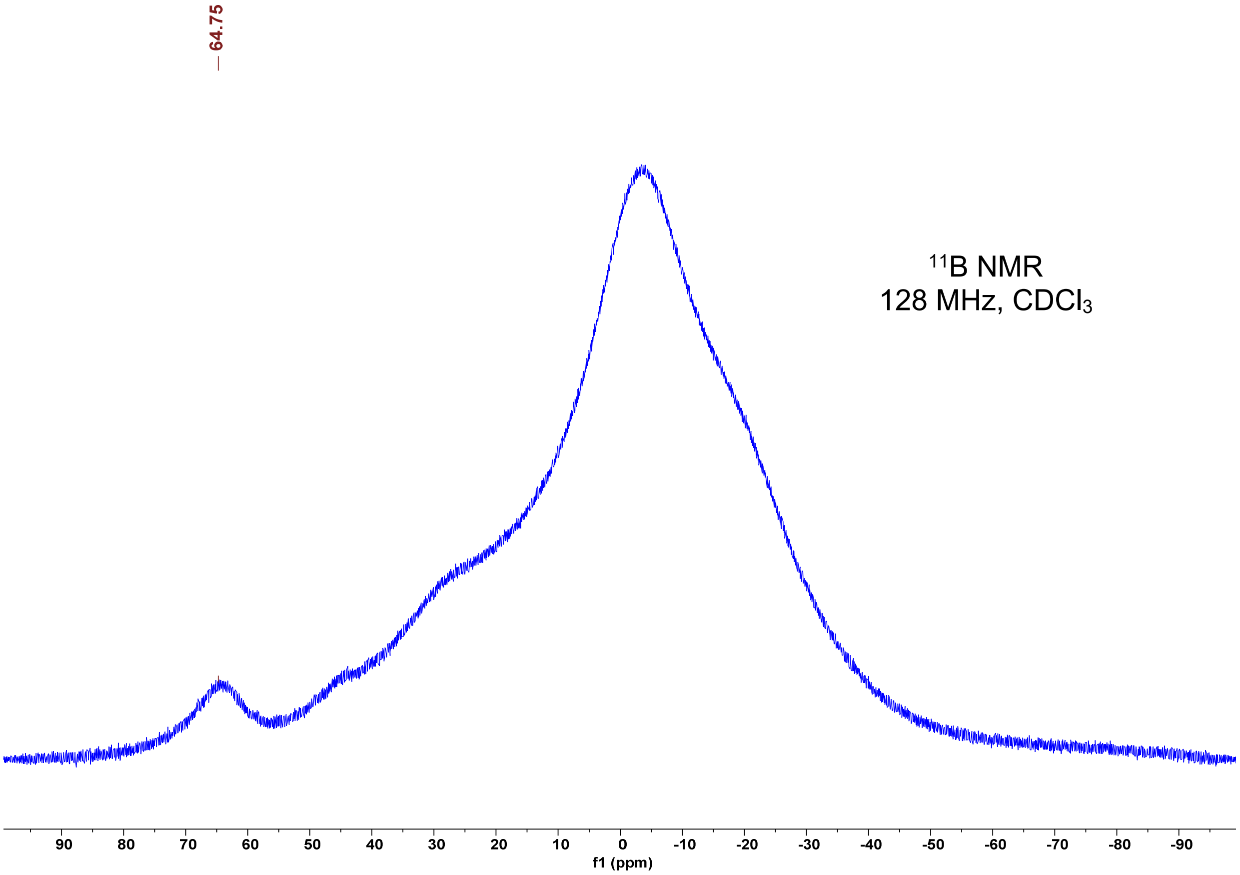
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ = 162.2 (C_q, C-4), 140.7 (CH, C-2), 135.9 (br, C_q, C-1), 113.0 (CH, C-3), 55.3 (CH_3, C-5).

^{11}B NMR (128 MHz, $CDCl_3$) δ = 64.8.

HRMS (EI^+) calcd *m/z* for $C_{21}H_{21}BO_3^{\bullet +}$ ($M^{\bullet +}$) 332.1578; found 332.1571.

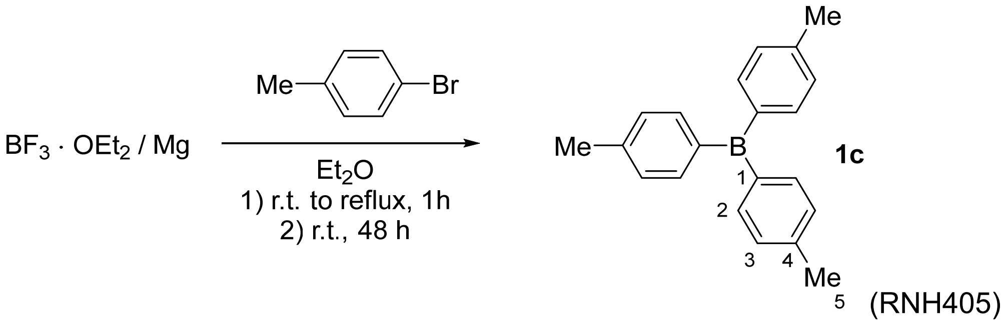

7.62
7.62
7.61
7.60
7.59
7.59
7.26 CDCl3
7.01
7.01
7.00
7.00
6.99
6.98
6.98
6.97
3.90
OMe
MeO
B
OMe
^{1}H NMR
400 MHz, $CDCl_3$
6.00
6.18
9.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)


162.16
140.75
135.89
113.00
77.16 CDCl3
55.30
$^{13}C\{^1H\}$ NMR
101 MHz, $CDCl_3$
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


64.75
11B NMR
128 MHz, CDCl3
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

Tris(4-methylphenyl)borane (1c)

Synthesis according to the modified procedure in ref.[S20].



1c

(RNH405)

A 100 mL Schlenk flask with reflux condenser was charged with magnesium turnings (853 mg, 35.1 mmol), flame dried under vaccum, and filled with dry nitrogen. Diethyl ether (20 mL), a crystal of iodine and freshly distilled $BF_3{\cdot}OEt_2$ (1.26 mL, 10.0 mmol) were added. To the vigourously stirred mixture, a solution of 4-bromotoluene (3.74 mL, 30.2 mmol) in diethyl ether (20 mL) was added. The Grignard reaction was initiated by careful heating causing the suspension to turn yellow. The mixture was stirred for another 12 h. Volatiles were removed under reduced pressure. The residue was suspended in *n*-hexane (40 mL) and stirred for 30 minutes or until the residue was finely suspended. The suspension was filtered through a Schlenk-frit. The solid was washed with *n*-hexane (10 mL), and the clear filtrate concentrated to dryness. The crude product was recrystallized from *n*-hexane to give the borane (646 mg, 23%) as colorless, crystalline solid. Further concentration of the mother liquor afforded additional material of lower quality, which was not used in our experiments.

Mp.: 150 °C (ref.[S19]: mp 142-144 °C)

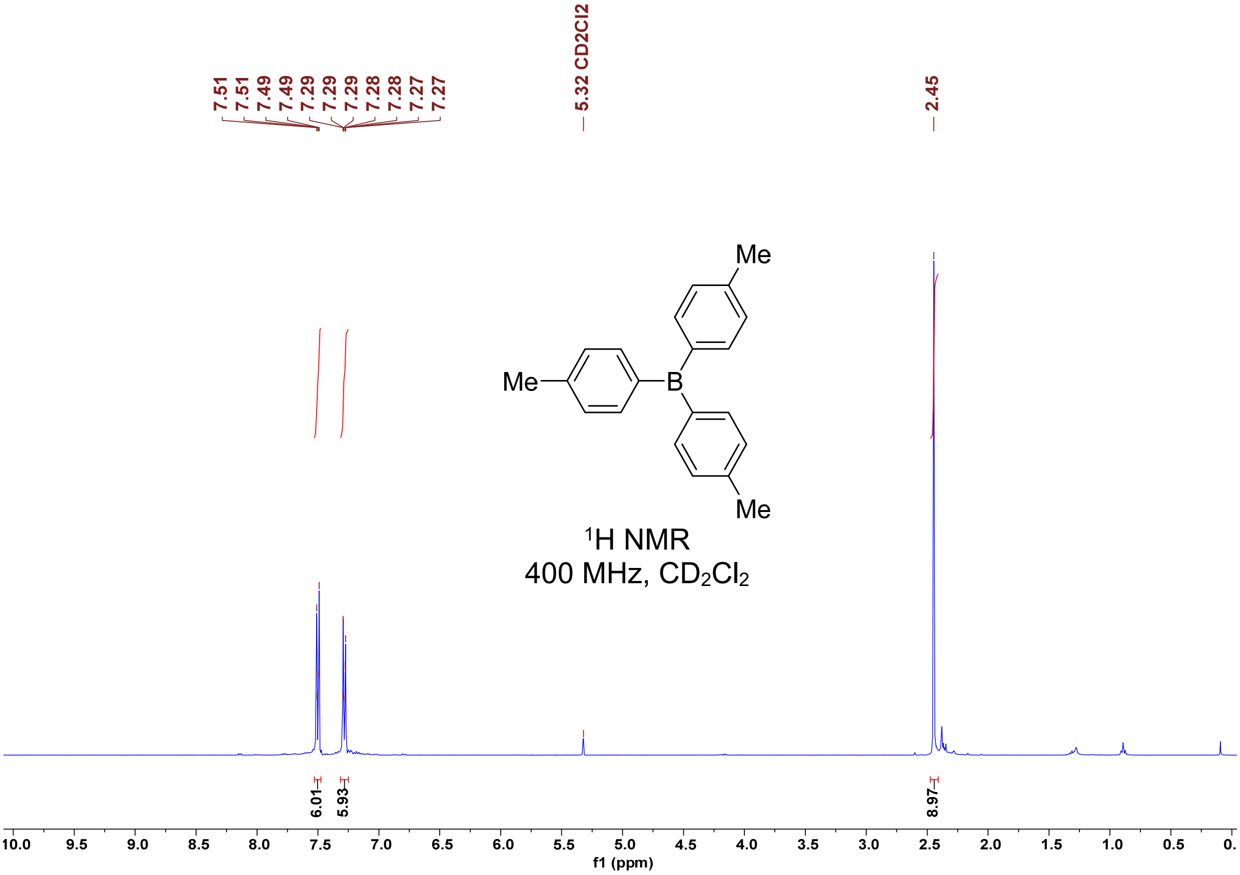
^{1}H NMR (400 MHz, CD_2Cl_2) δ = 7.51–7.49 (m, 6 H, 2-H), 7.29–7.27 (m, 6 H, 3-H), 2.45 (s, 9 H, 5-H).

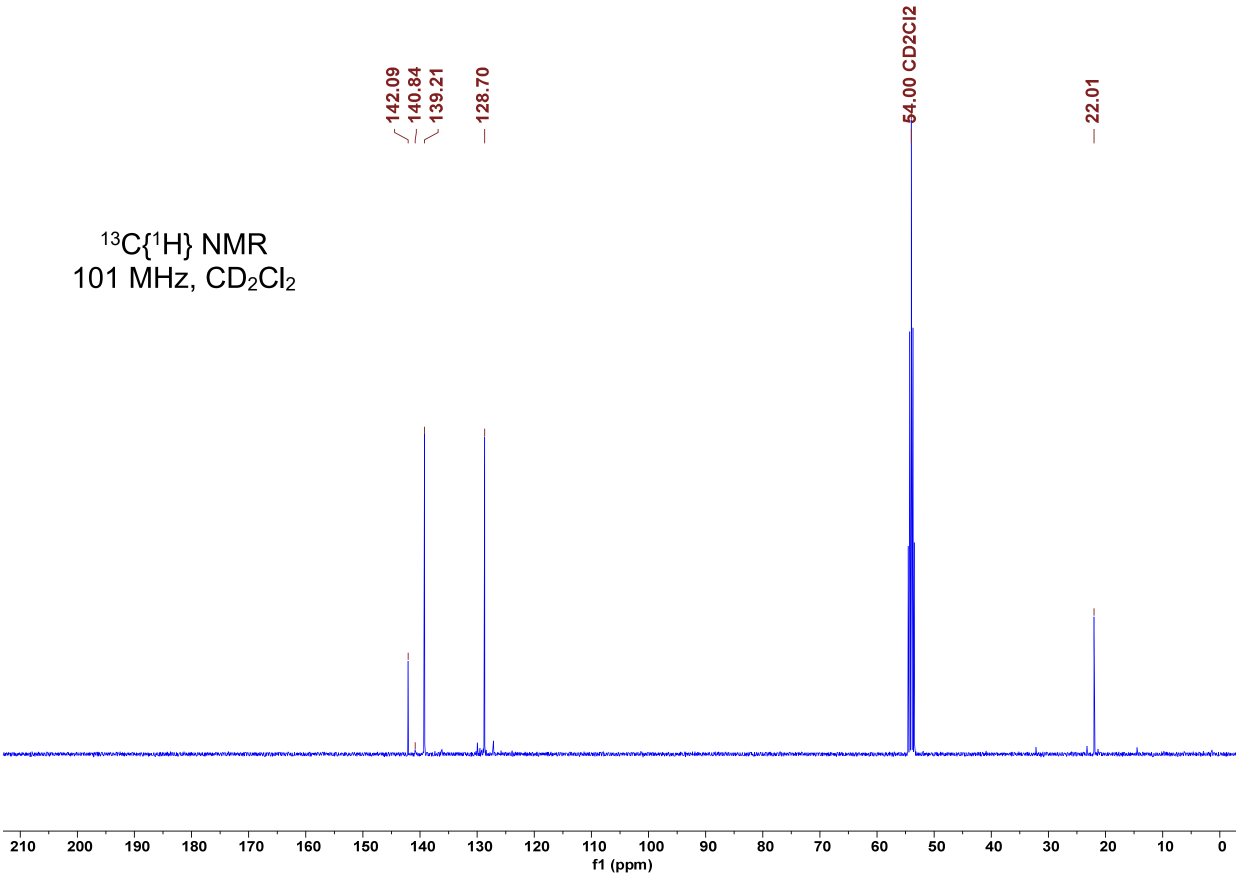
^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ = 142.1 (C_q, C-4), 140.8 (br, C_q, C-1), 139.2 (CH, C-2), 128.7 (CH, C-3), 22.0 (CH_3, C-5).

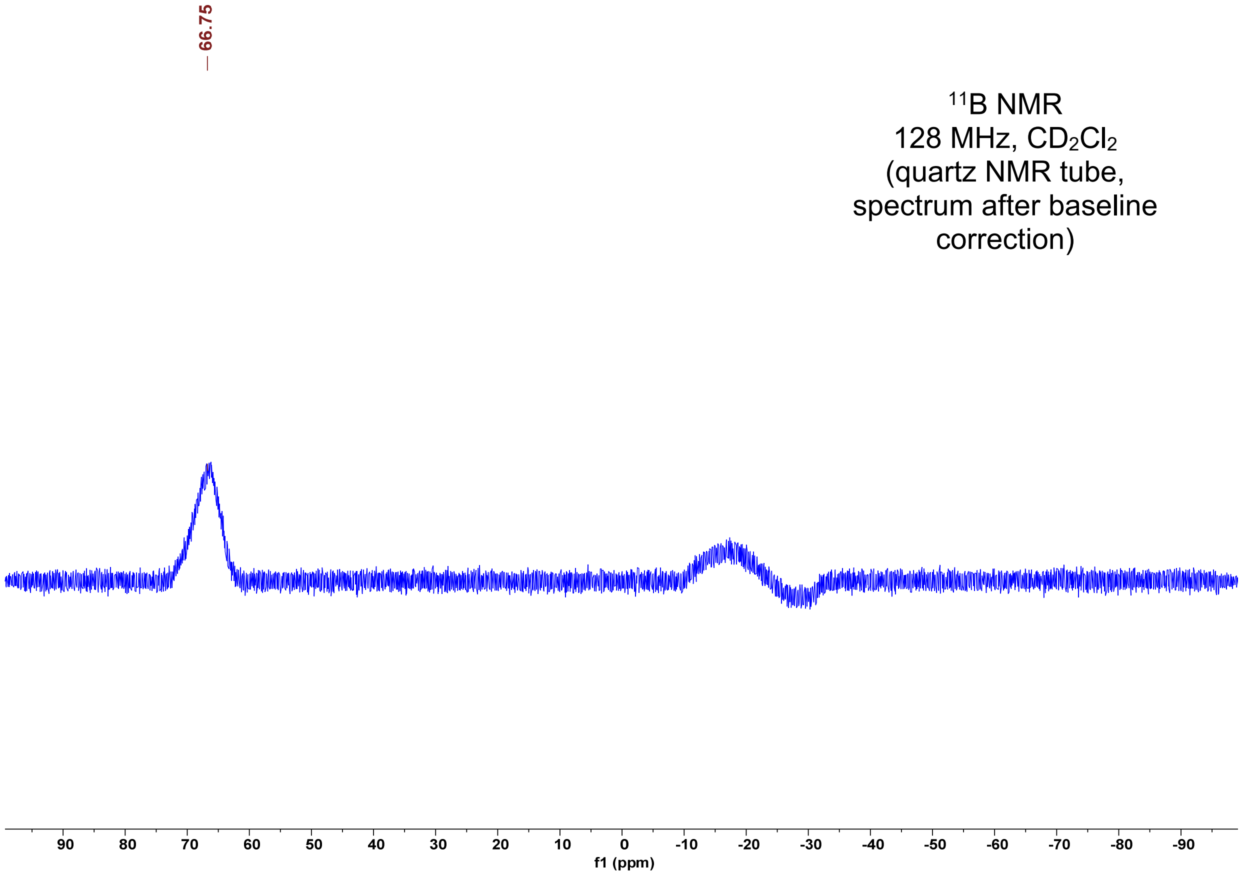
^{11}B NMR (128 MHz, CD_2Cl_2) δ = 66.8.

HRMS (EI^+) calcd *m/z* for $C_{21}H_{21}B^{\bullet+}$ ($M^{\bullet+}$) 284.1731; found 284.1717.

NMR data agree with those reported in ref.[S22].


7.51
7.51
7.49
7.49
7.29
7.29
7.29
7.28
7.28
7.27
7.27
5.32 CD2Cl2
2.45
Me
Me
B
Me
^{1}H NMR
400 MHz, CD_2Cl_2
6.01
5.93
8.97
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

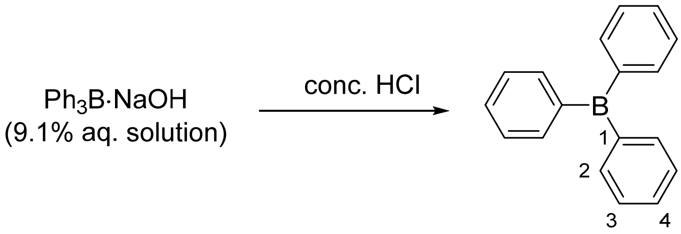

142.09
140.84
139.21
128.70
54.00 CD2Cl2
22.01
$^{13}C\{^1H\}$ NMR
101 MHz, CD_2Cl_2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



^{11}B NMR
128 MHz, CD_2Cl_2
(quartz NMR tube,
spectrum after baseline
correction)

Triphenylborane (1d)

Triphenylborane from various commercial sources was not of sufficient quality for our experiments. Starting from a aqueous solution of the adduct $Ph_3B{\cdot}NaOH$ and following the procedure described in ref.[S23] yielded pure **1d**.



1d

(AB014/AB023/AB026)

In a 100 mL Schlenk flask under nitrogen was placed a commercial solution of 9.1 w% aq $Ph_3B{\cdot}NaOH$ (25 g, 8.1 mmol). Careful addition of conc. hydrochloric acid (ca. 3 mL in total, pH 1) caused the formation of a colorless precipitate, which was isolated immediately by filtration through a Schlenk-frit under nitrogen (according to the literature, the freshly formed Ph_3B is highly oxgen sensitive and decomposes rapidly in acidic aq solution[S23b]). The solid material was washed with water and dried under reduced pressure. The crude product was recrystallized from *n*-heptane (7 mL) to give **1d** (1.65 g, 84%) as colorless, crystalline needles which were further purified by sublimation (120 °C, 1×10^{-2} mbar).

Ph_3B was found to be highly air and moisture sensitive. Already during the time needed for NMR characterization small amounts of decomposed material were observed.

Mp.: 128-133 °C (ref.[S24]: mp 142 °C)

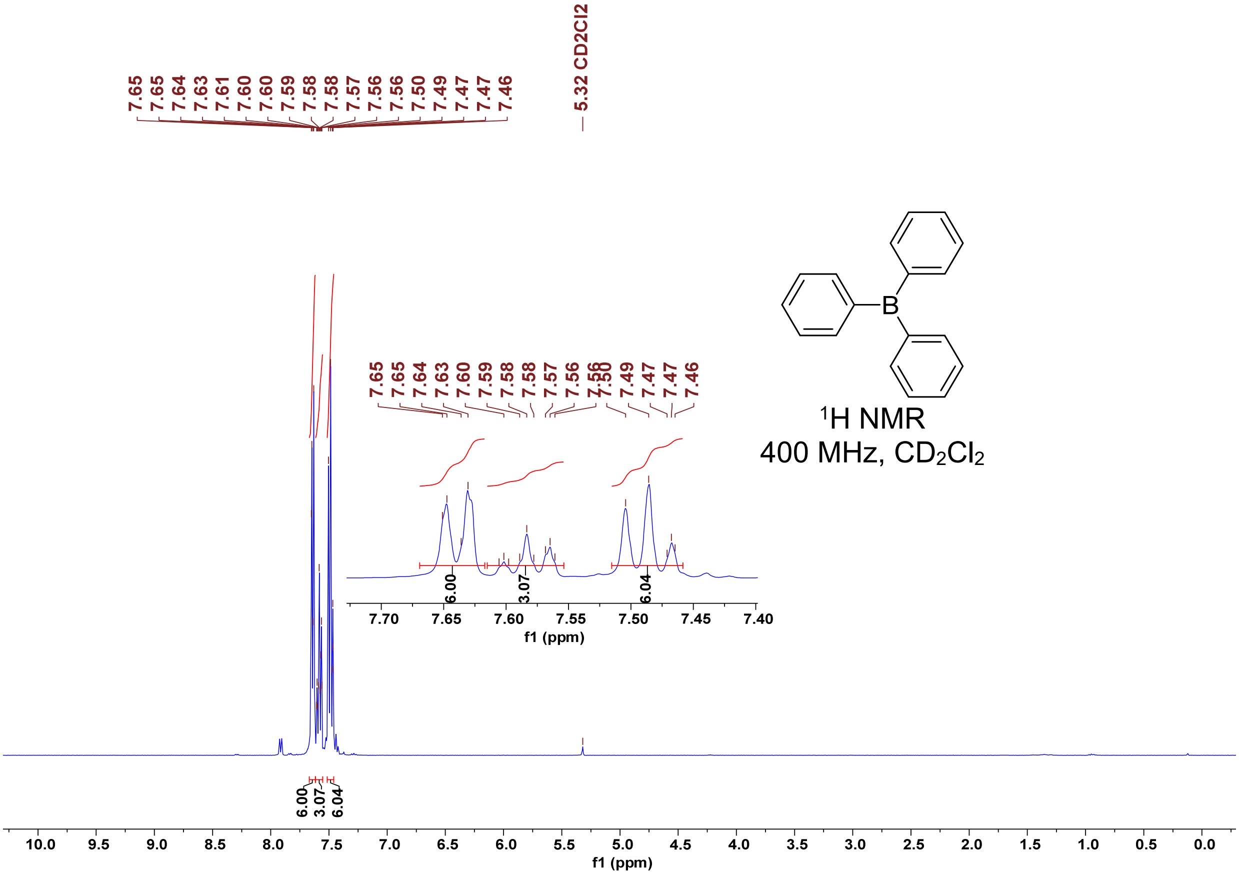
^{1}H NMR (400 MHz, CD_2Cl_2) δ = 7.65–7.63 (m, 2 H, 2-H), 7.60–7.56 (m, 1 H, 4-H), 7.50–7.46 (m, 2 H, 3-H).

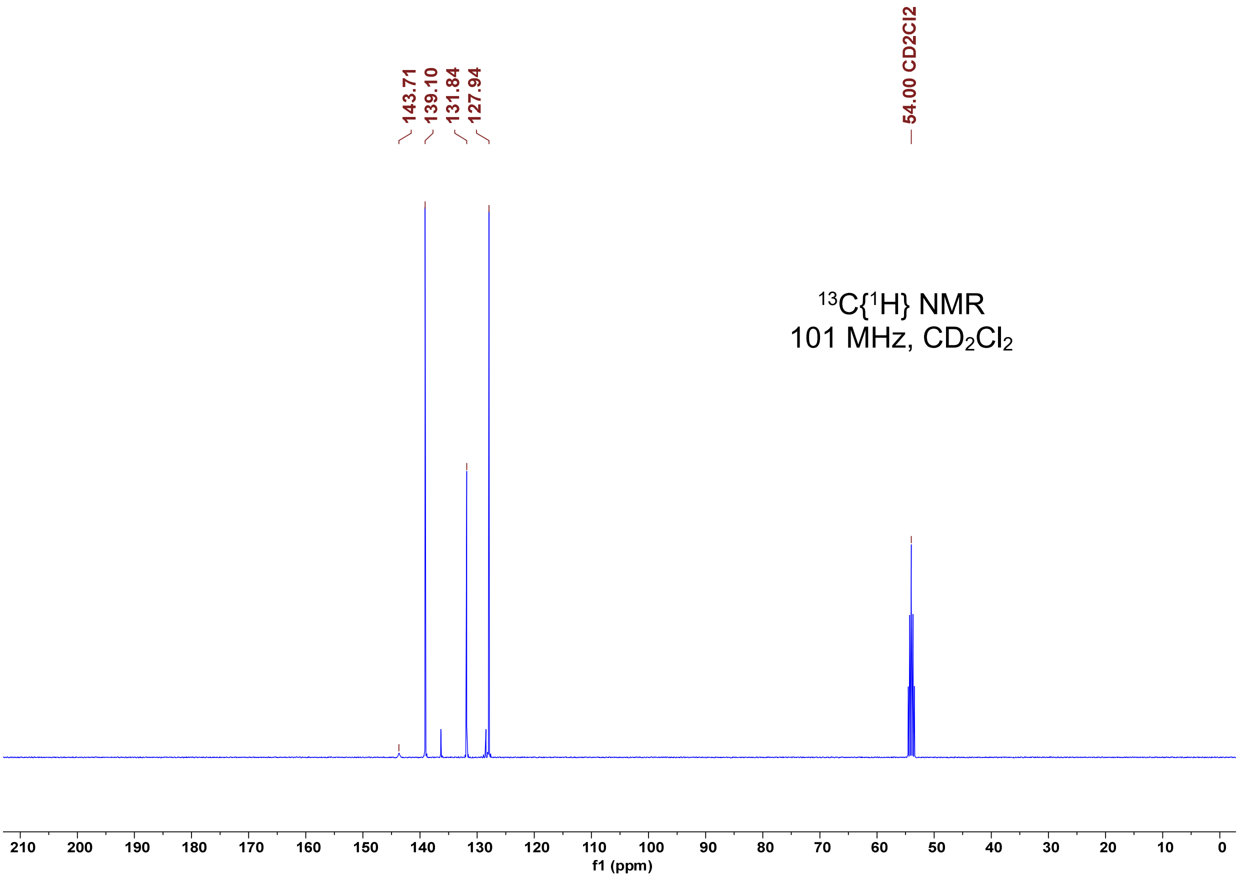
^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ = 143.7 (br, C_q, C-1), 139.1 (CH, C-2), 131.8 (CH, C-4), 127.9 (CH, C-3).

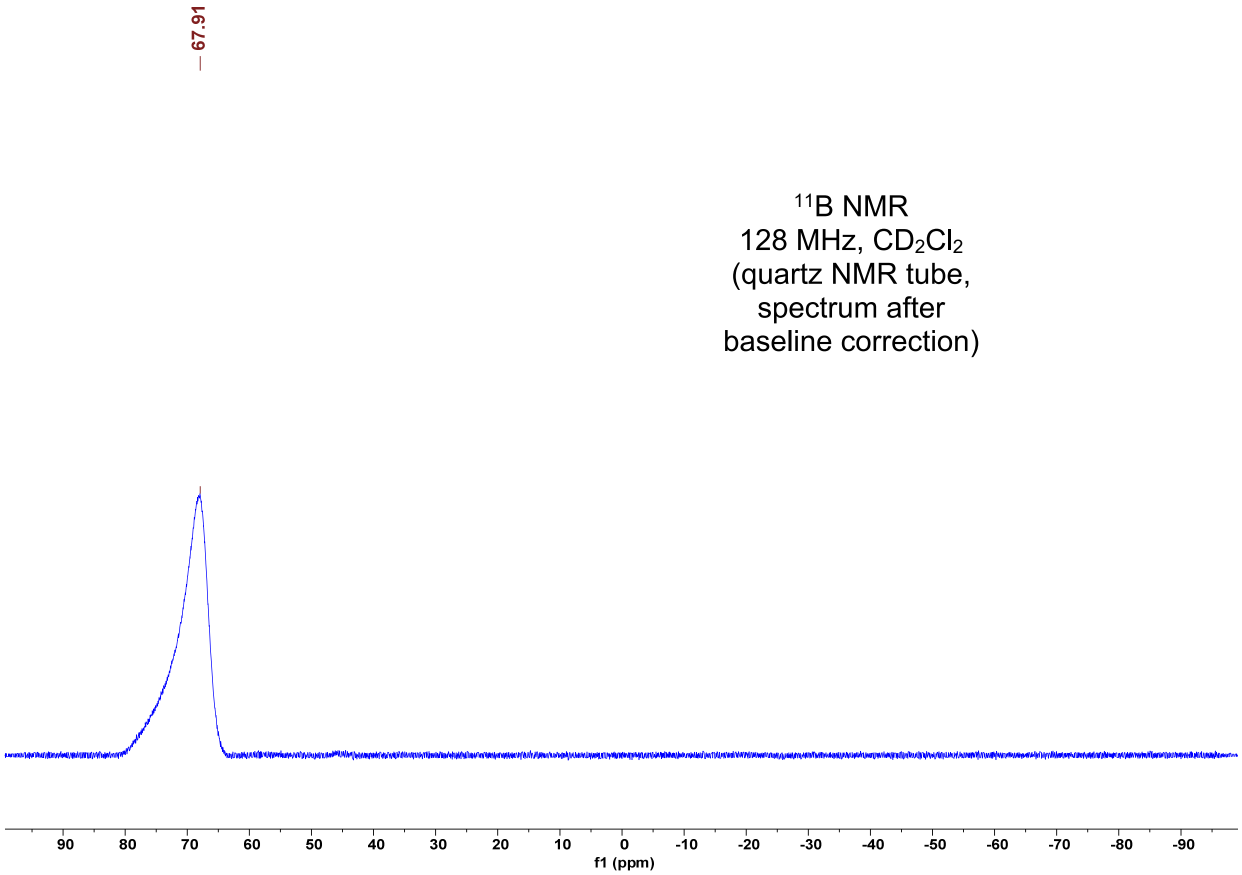
^{11}B NMR (128 MHz, CD_2Cl_2) δ = 67.9.

HRMS (EI$^+$) calcd *m/z* for $C_{18}H_{15}B^{\bullet+}$ ($M^{\bullet+}$) 242.1261; found 242.1249.

NMR data agree with those reported in ref.[S25].

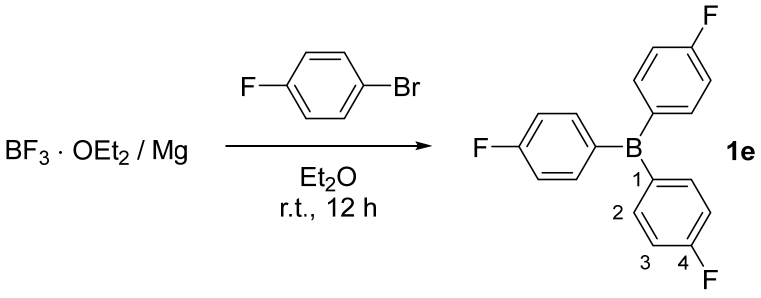

7.65
7.65
7.64
7.63
7.61
7.60
7.60
7.59
7.58
7.58
7.57
7.56
7.56
7.50
7.49
7.47
7.47
7.46
5.32 CD2Cl2
B
^{1}H NMR
400 MHz, CD_2Cl_2
6.00
3.07
6.04
7.70
7.65
7.60
7.55
7.50
7.45
7.40
f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


143.71
139.10
131.84
127.94
54.00 CD2Cl2
$^{13}C\{^1H\}$ NMR
101 MHz, CD_2Cl_2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


67.91
^{11}B NMR
128 MHz, CD_2Cl_2
(quartz NMR tube,
spectrum after
baseline correction)
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

Tris(4-fluorophenyl)borane (1e)

Synthesis according to the modified procedure in ref.[S20].



1e

(RM1069)

A 100 mL Schlenk flask with reflux condenser was charged with magnesium turnings (854 mg, 35.1 mmol), flame dried under vacuum, and filled with dry nitrogen. Diethyl ether (20 mL) and freshly distilled $BF_3 \cdot OEt_2$ (1.26 mL, 10.0 mmol) were added. To the vigorously stirred mixture, a solution of 4-bromo-1-fluorobenzene (3.30 mL, 30.2 mmol) in diethyl ether (20 mL) was added. The Grignard reaction was initiated by heating causing the suspension to turn brownish. The mixture was stirred for another 12 h to give a mixture of liquid two phases, whereupon all volatiles were removed under reduced pressure to form a solid. The residue was suspended in *n*-hexane (40 mL) and filtered through a Schlenk-frit and washed with *n*-hexane(10 mL) to give a clear filtrate, which was concentrated to dryness to give a solid residue. The crude product was recrystallized from *n*-hexane to give the borane **1e** (955 mg, 32%) as a soft yellow, crystalline solid.

Mp.: 99-113 °C

^{1}H NMR (400 MHz, CD_2Cl_2) δ = 7.63–7.59 (m, 6 H, 2-H), 7.21–7.15 (m, 6 H, 3-H).

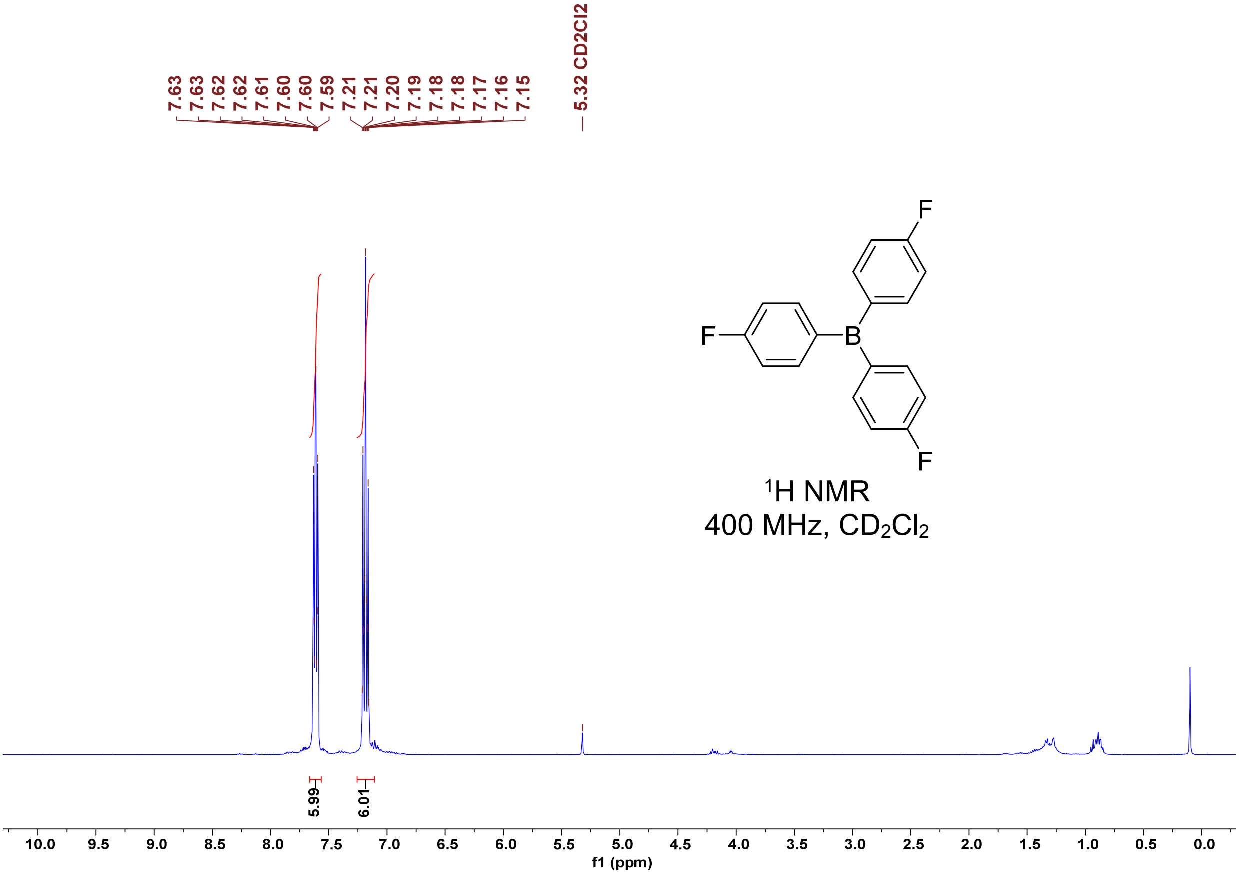
$^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2) δ = 165.9 (d, C_q, $J_{C,F}$ = 252.0 Hz, C-4), 141.5 (d, CH, $J_{C,F}$ = 8.4 Hz, C-2), 139.4 (br, C_q, C-1), 115.2 (d, CH, $J_{C,F}$ = 20.0 Hz, C-3).

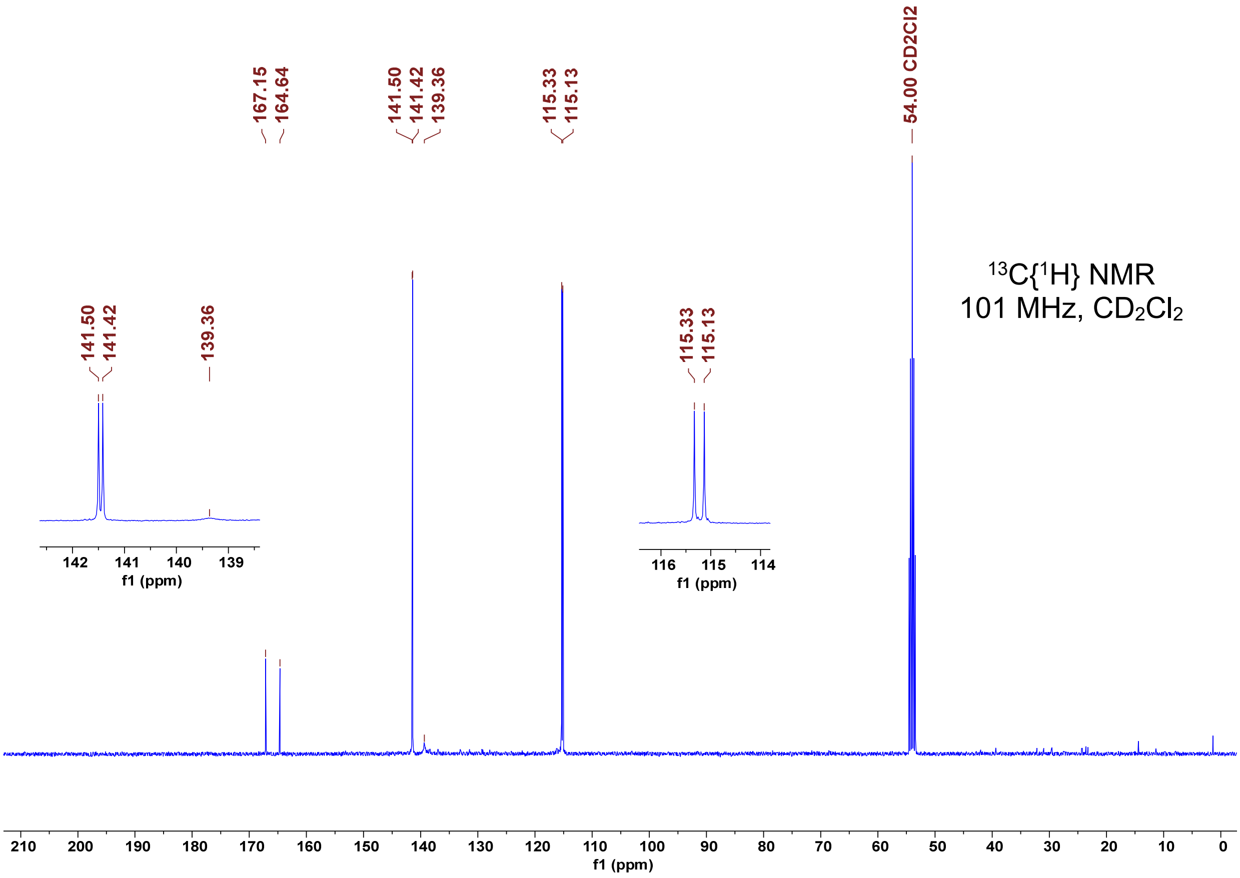
^{11}B NMR (128 MHz, CD_2Cl_2) δ = 63.2.

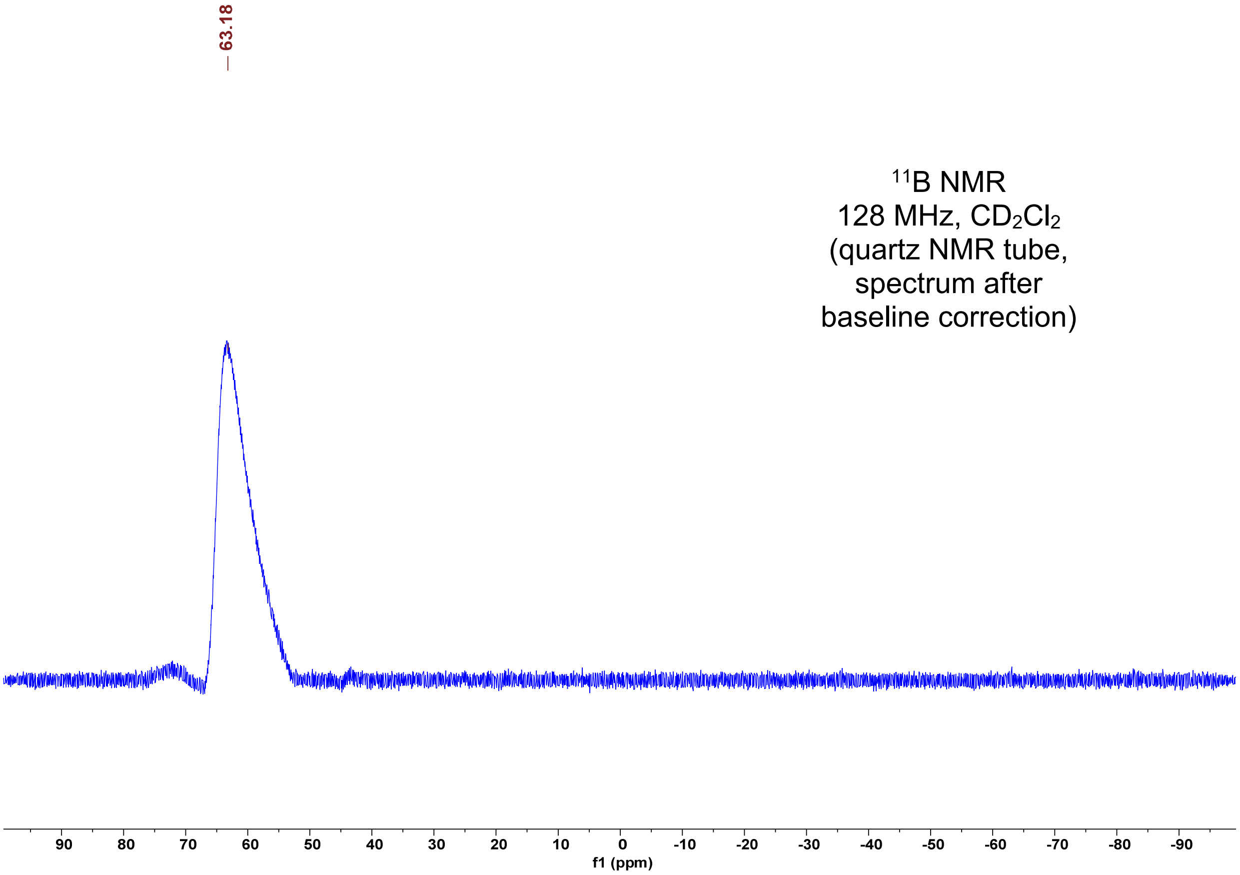
^{19}F NMR (377 MHz, CD_2Cl_2) δ = -108.75 (tt, *J* = 9.3, 6.3 Hz)

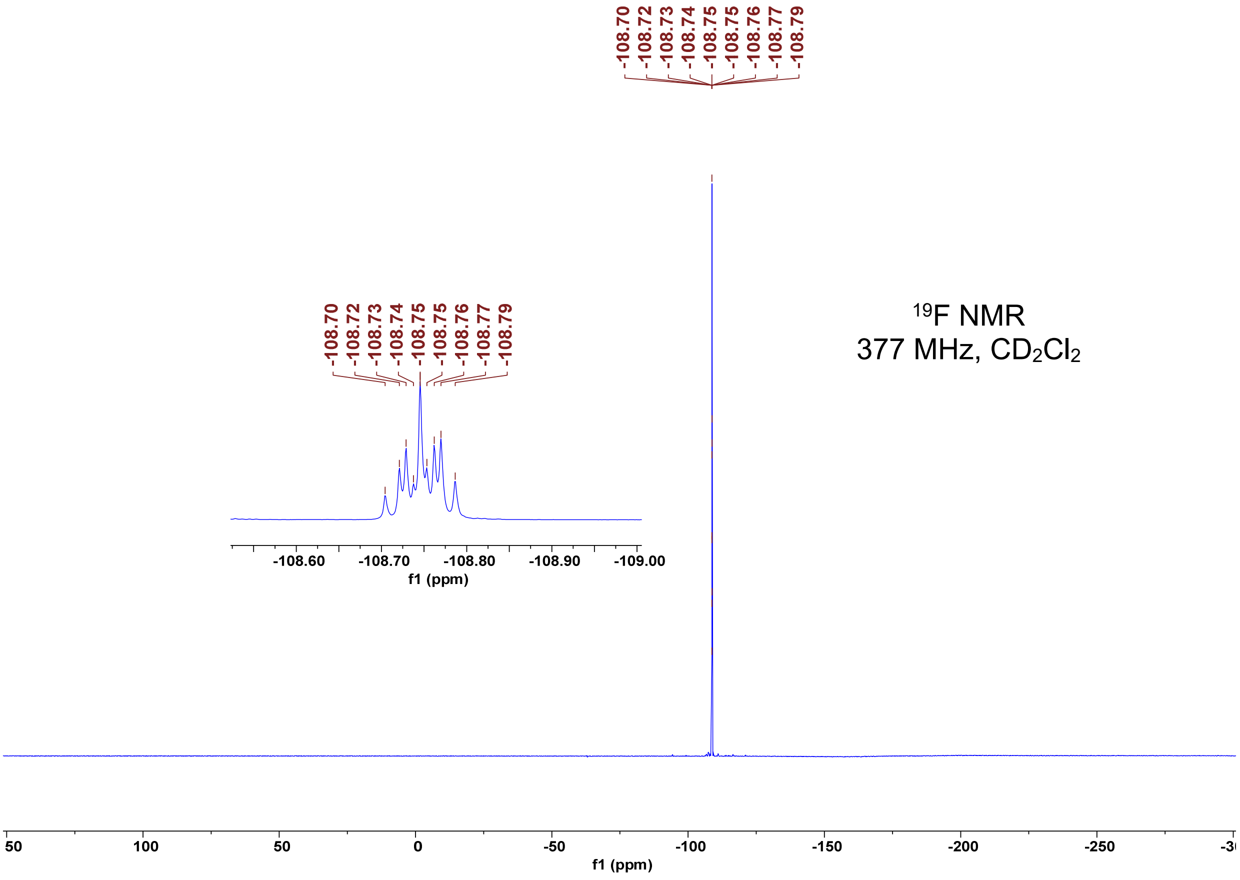
HRMS (EI^+) calcd *m/z* for $C_{18}H_{12}F_3B^{\bullet+}$ ($M^{\bullet+}$) 296.0979; found 296.0984.

NMR data agree with those reported in ref.[S26].


7.63
7.63
7.62
7.62
7.61
7.60
7.60
7.59
7.21
7.21
7.20
7.19
7.18
7.18
7.17
7.16
7.15
5.32 CD2Cl2
F
F
B
F
1H NMR
400 MHz, CD2Cl2
5.99
6.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

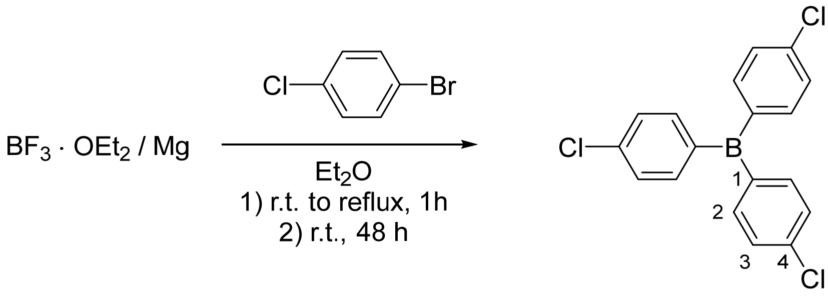

167.15
164.64
141.50
141.42
139.36
115.33
115.13
54.00 CD2Cl2
13C{1H} NMR
101 MHz, CD2Cl2
141.50
141.42
139.36
142
141
140
139
f1 (ppm)
115.33
115.13
116
115
114
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


63.18
^{11}B NMR
128 MHz, CD_2Cl_2
(quartz NMR tube,
spectrum after
baseline correction)
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)


-108.70
-108.72
-108.73
-108.74
-108.75
-108.75
-108.76
-108.77
-108.79
^{19}F NMR
377 MHz, CD_2Cl_2
-108.60
-108.70
-108.80
-108.90
-109.00
f1 (ppm)
150
100
50
0
-50
-100
-150
-200
-250
-3
f1 (ppm)

Tris(4-chlorophenyl)borane (1f)

Synthesis according to the modified procedure in ref.[S20].



1f

(RNH407)

A 100 mL Schlenk flask with reflux condenser was charged with magnesium turnings (853 mg, 35.1 mmol), flame dried under vacuum, and filled with dry nitrogen. Diethyl ether (20 mL) and freshly distilled $BF_3{\cdot}OEt_2$ (1.26 mL, 10.0 mmol) were added. To the vigourously stirred mixture, a solution of 4-bromo-1-chlorobenzene (5.78 g, 30.2 mmol) in diethyl ether (20 mL) was added. After about 10 mL of the bromoarene solution was added, heat was applied to initiate the Grignard reaction. Then the remaining 4-bromo-1-chlorobenzene solution was added. The mixture was stirred for another 12 h. Then volatiles were removed under reduced pressure. The residue was suspended in dichloromethane (40 mL) and filtrated through a Schlenk-frit. The clear solution was concentrated to dryness and the residue purified by sublimation (191 °C, 1.6×10^{-2} mbar) to give **1e** (885 mg, 26%) as colorless to pale yellow crystals.

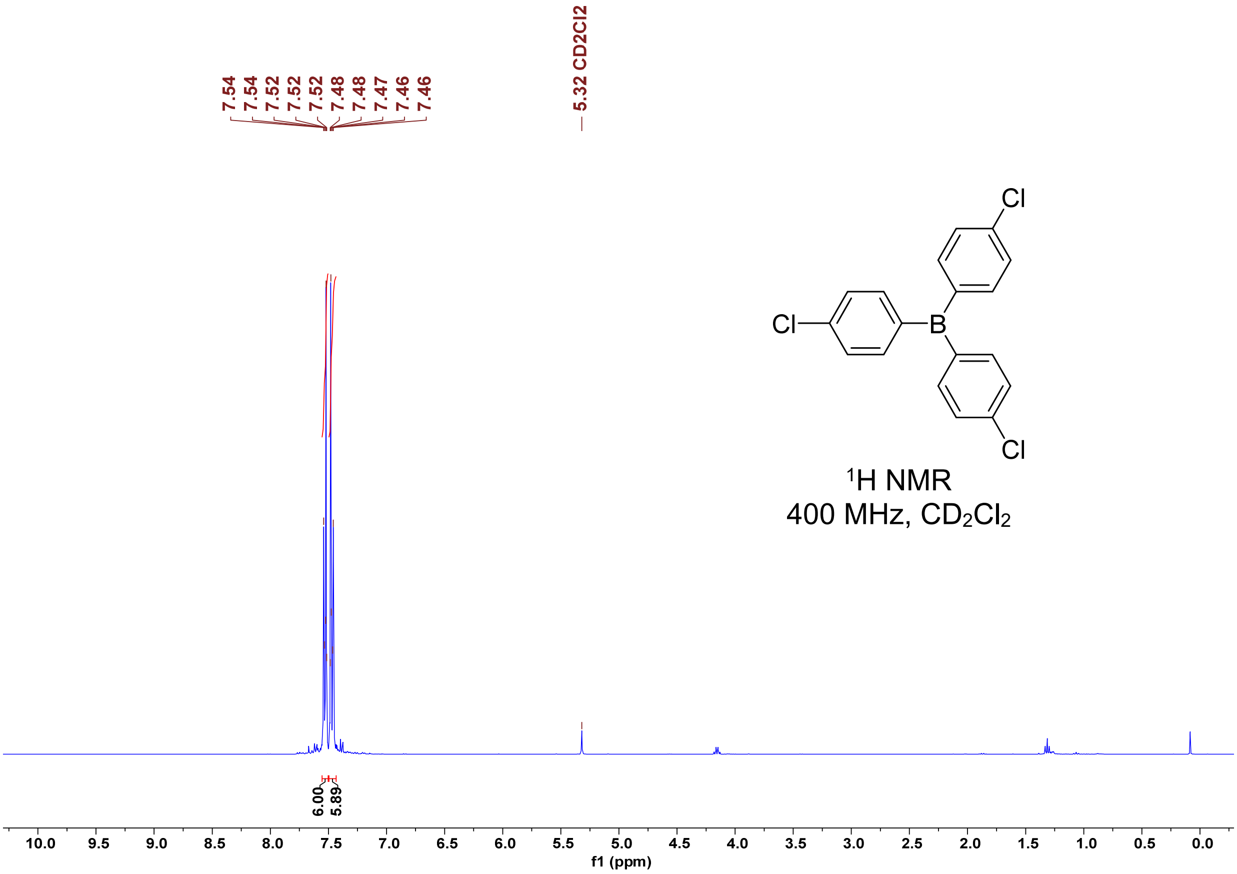
Mp.: 166 °C (ref.[S27]: mp 197-202 °C)

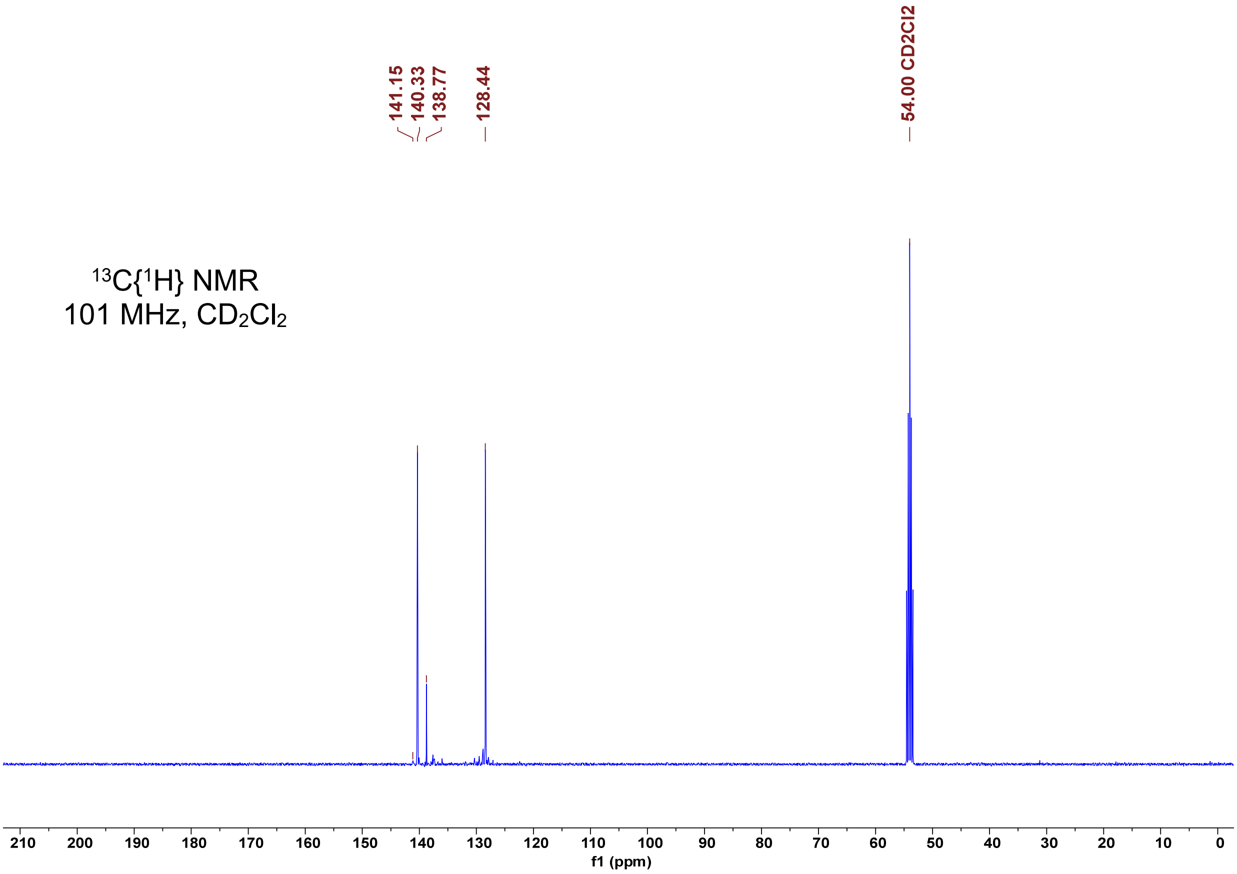
^{1}H NMR (400 MHz, CD_2Cl_2) δ = 7.54–7.52 (m, 6 H), 7.48–7.46 (m, 6 H).

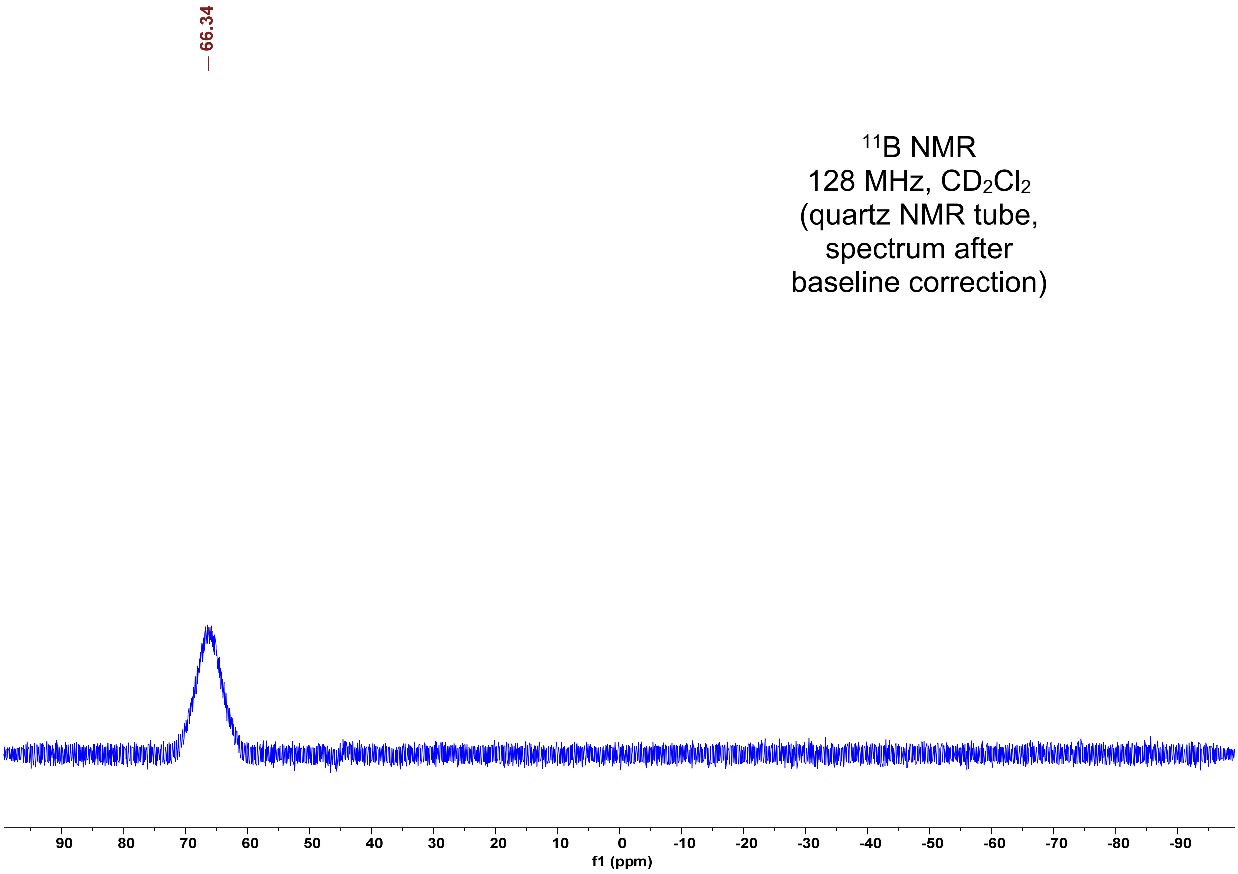
$^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2) δ = 141.2 (br, C_q, C-4), 140.3 (CH), 138.8 (C_q, C-1), 128.4 (CH).

^{11}B NMR (128 MHz, $CDCl_3$) δ = 66.3.

HRMS (EI^+) calcd *m/z* for $C_{18}H_{12}BCl_3^{\bullet+}$ ($M^{\bullet+}$) 344.0092; found 344.0093.


7.54
7.54
7.52
7.52
7.52
7.48
7.48
7.47
7.46
7.46
5.32 CD2Cl2
Cl
Cl
B
Cl
^{1}H NMR
400 MHz, CD_2Cl_2
6.00
5.89
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

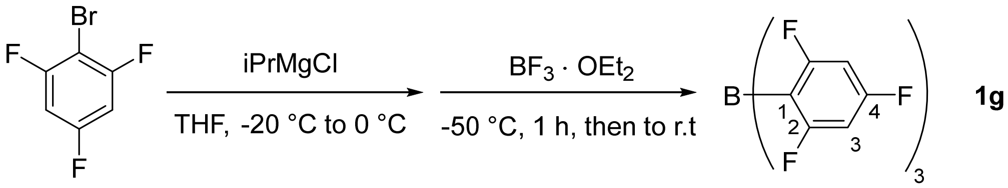

141.15
140.33
138.77
128.44
54.00 CD2Cl2
$^{13}C\{^1H\}$ NMR
101 MHz, CD_2Cl_2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



^{11}B NMR
128 MHz, CD_2Cl_2
(quartz NMR tube,
spectrum after
baseline correction)

Tris(2,4,6-trifluorophenyl)borane (1g)

Synthesis according to the modified procedure in ref.[S28].



(RM1072)

In a 100 mL flame dried Schlenk flask under nitrogen was dissolved 1-bromo-2,4,6-trifluorobenzene (3.50 mL, 30 mmol) in THF (100 mL). The solution was cooled to -20 °C and isopropylmagnesium chloride (2.0 M solution in THF, 15 mL, 30 mmol) was added in portions. The solution was allowed to warm to 0 °C over a period of 1 h and subsequently cooled to -50 °C. At -50 °C, freshly distilled $BF_3{\cdot}OEt_2$ (1.26 mL, 10.0 mmol) was added. The solution was stirred at -50°C for another 60 min. The solution was subsequently allowed to warm up to room temperature within 2 d. Next, all volatiles were removed. The residue was suspended in *n*-hexane (40 mL) and filtered through a Schlenk-frit. After washing of the solid with *n*-hexane (20 mL) and concentration of the filtrate the crude product was furnished as a colorless solid. Purification by sublimation (120 °C, 1×10^{-3} mbar) afforded **1g** (524 mg, 13%) as colorless, crystalline solid.

Mp.: 106-111 °C

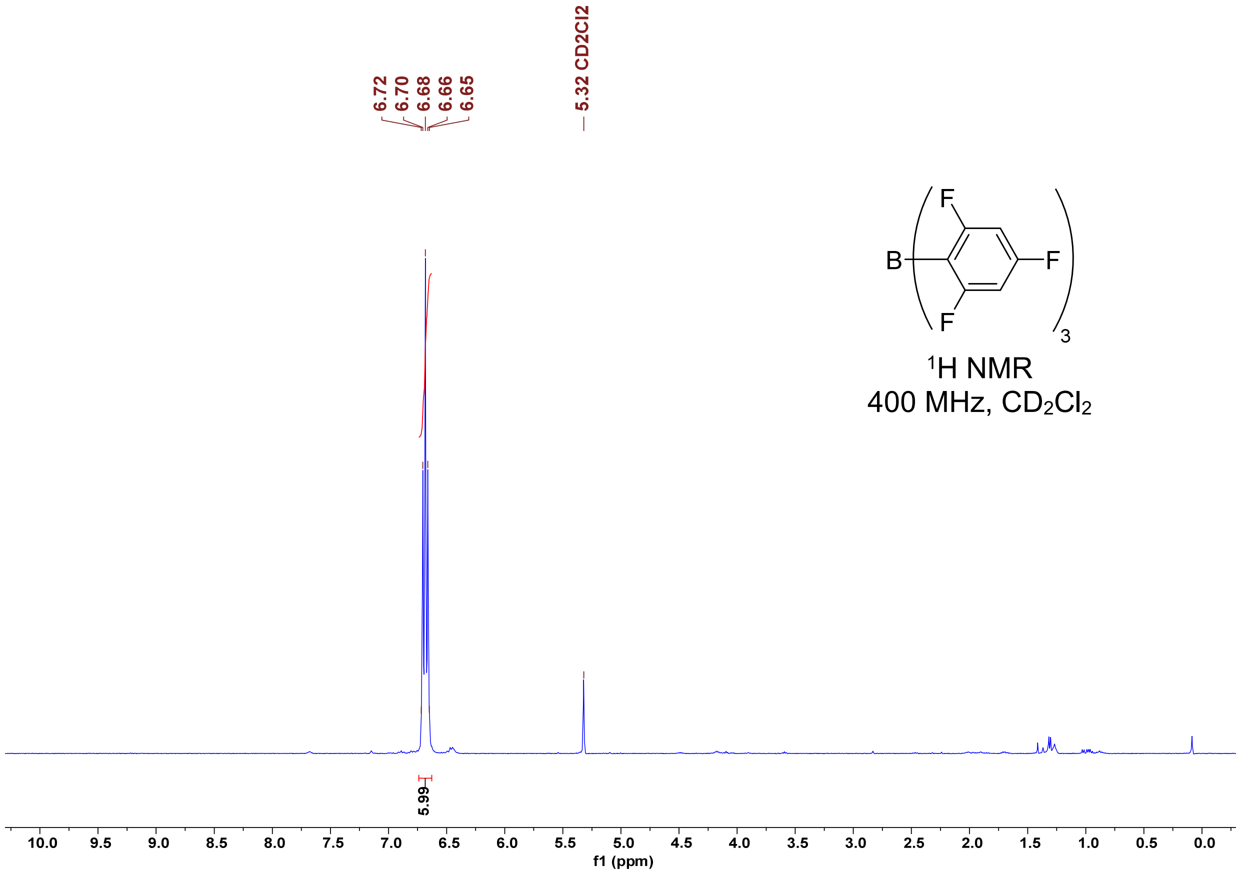
^{1}H NMR (400 MHz, CD_2Cl_2) δ = 6.72–6.65 (m, 6 H).

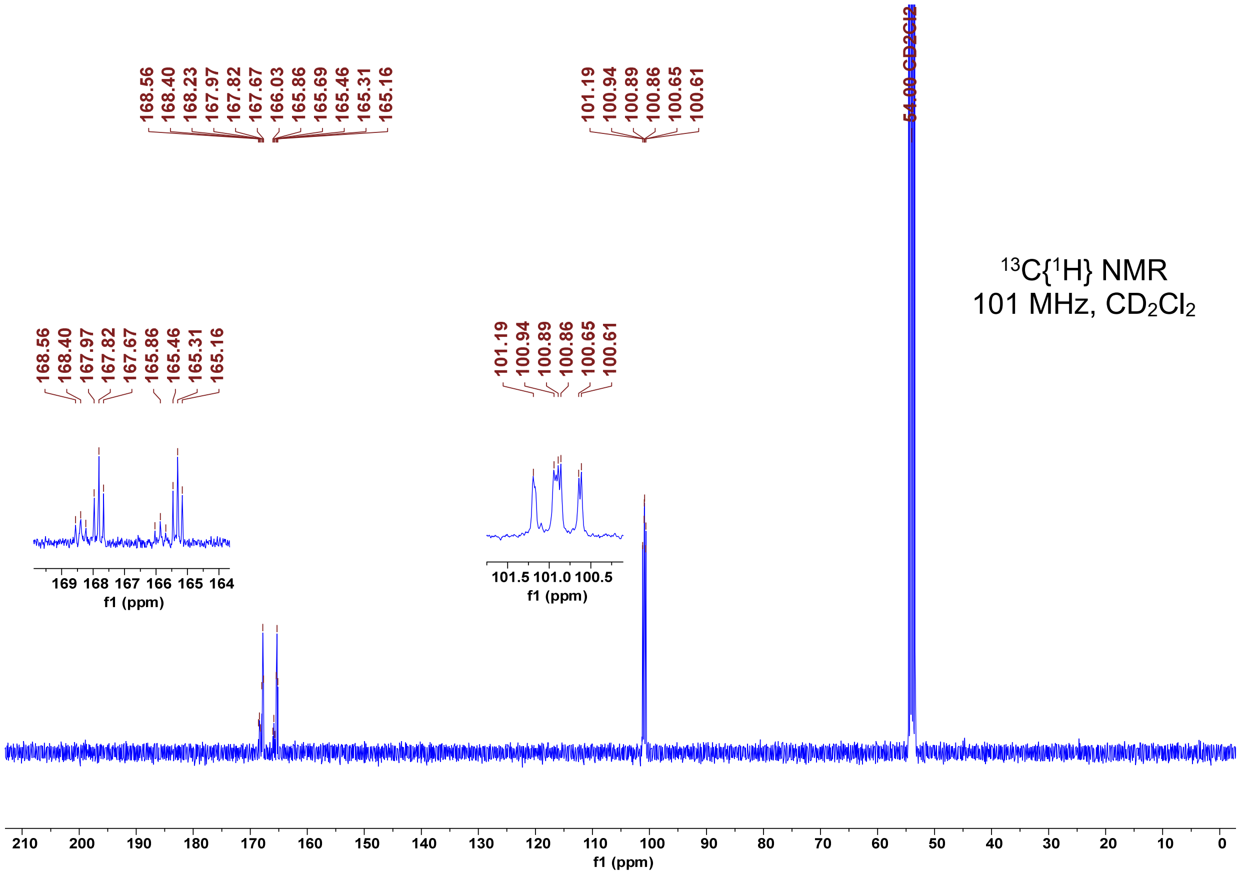
^{13}C NMR (101 MHz, CD_2Cl_2) δ = 167.1 (C_q, dt, J = 256.0 Hz, 16.6 Hz, C-4), 166.6 (C_q, dt, $J_{C,F}$ = 252.2 Hz, J = 14.9 Hz, C-2), 101.3–100.5 (m, CH, C-3). The resonance for C-1 was not detected.

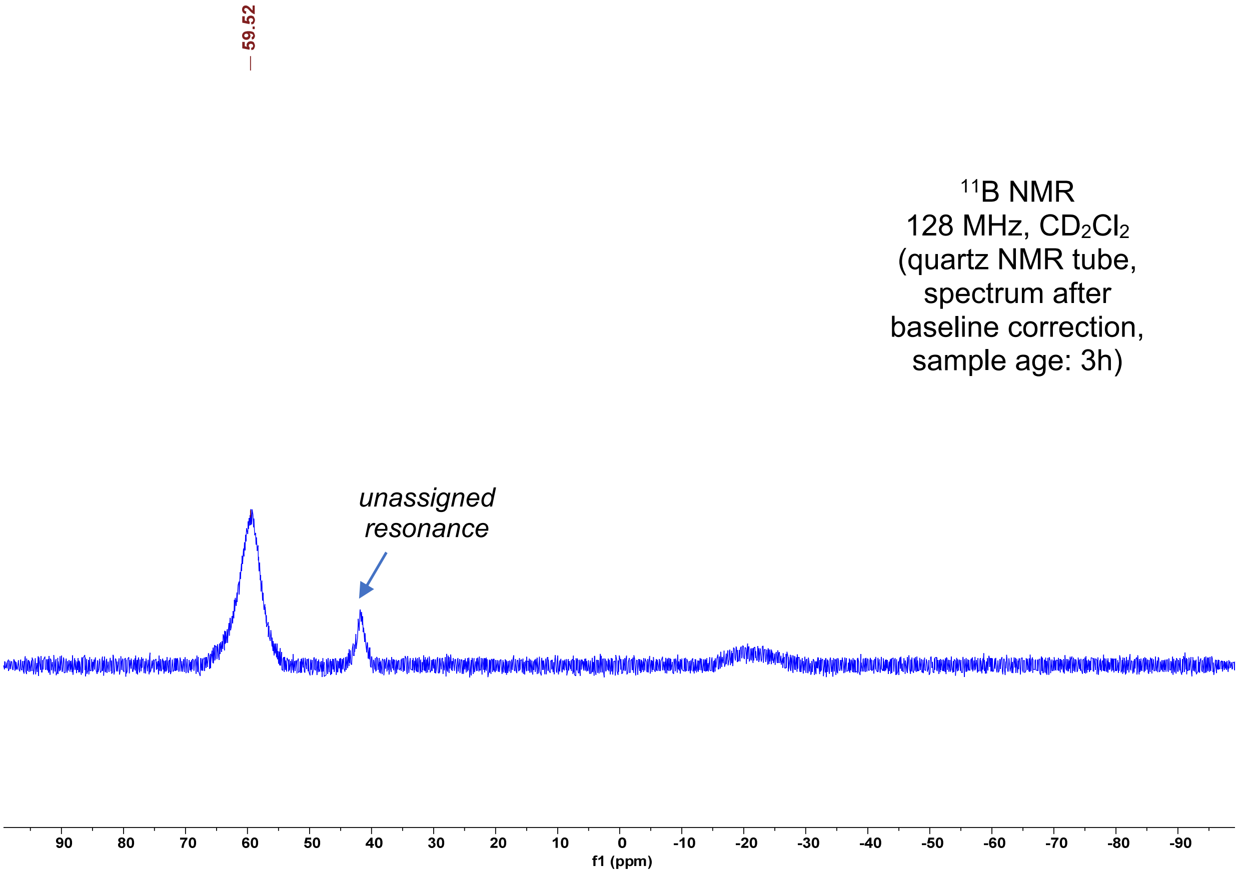
^{11}B NMR (128 MHz, $CDCl_3$) δ = 59.5.

^{19}F NMR (377 MHz, CD_2Cl_2) δ = -96.4 (app t, J = 8.2 Hz, 6 F, 2-F), -100.9 (app pent, J = 9.8 Hz, 3 F, 4-F).

HRMS (EI$^+$) calcd *m/z* for $C_{18}H_6BF_9^{\bullet+}$ ($M^{\bullet+}$) 404.0413; found 404.0398.

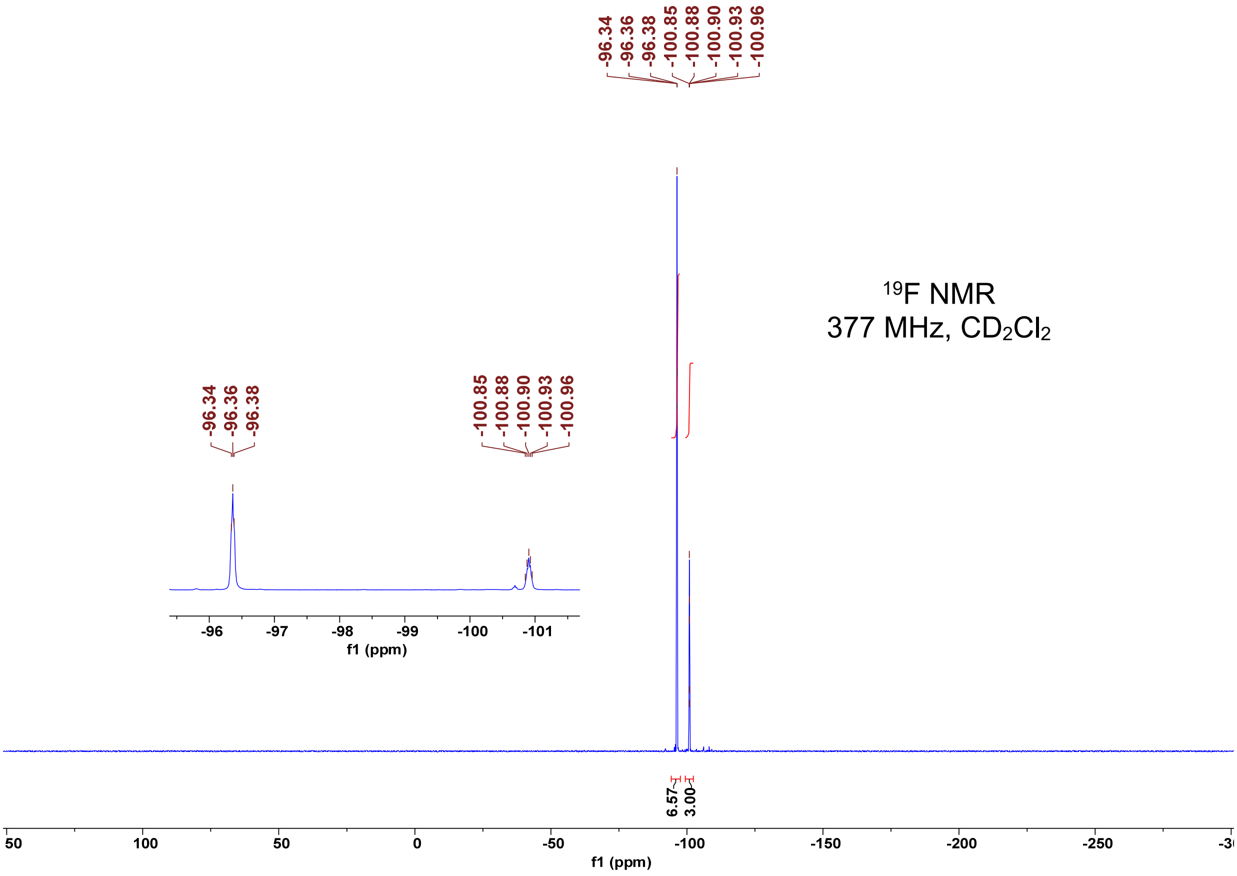

6.72
6.70
6.68
6.66
6.65
5.32 CD2Cl2
B
F
F
F
3
^{1}H NMR
400 MHz, CD$_2$Cl$_2$
5.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


168.56
168.40
168.23
167.97
167.82
167.67
166.03
165.86
165.69
165.46
165.31
165.16
101.19
100.94
100.89
100.86
100.65
100.61
54.00 CD2Cl2
^{13}C{^{1}H} NMR
101 MHz, CD$_2$Cl$_2$
168.56
168.40
167.97
167.82
167.67
165.86
165.46
165.31
165.16
169 168 167 166 165 164
f1 (ppm)
101.19
100.94
100.89
100.86
100.65
100.61
101.5 101.0 100.5
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



^{11}B NMR
128 MHz, CD_2Cl_2
(quartz NMR tube,
spectrum after
baseline correction,
sample age: 3h)

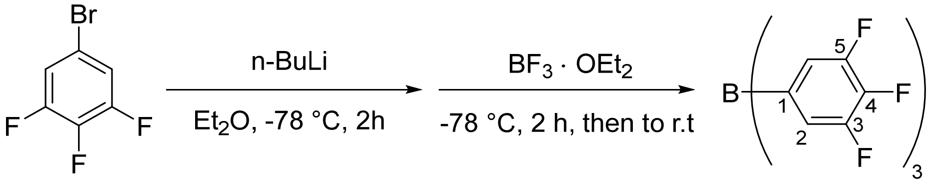
unassigned resonance



^{19}F NMR
377 MHz, CD_2Cl_2

Tris(3,4,5-trifluorophenyl)borane (1h)

Synthesis according to the modified procedure in ref.[S28].



(RNH415)

In a 250 mL flame dried Schlenk flask under nitrogen was added 1-bromo-3,4,5-fluorobenzene (7.02 mL, 58.8 mmol) and diethyl ether (100 mL). The solution was cooled to -78 °C and *n*-BuLi (2.3 M, 25.6 mL, 58.8 mmol) was added slowly to give a milky suspension. Stirring was continued for 2 h at -78 °C whereupon freshly distilled $BF_3 \cdot OEt_2$ (2.39 mL, 19.4 mmol) was added and the mixture stirred for an additional 2 h at -78 °C. The mixture was allowed to warm up to room temperature overnight and all voilatiles were removed under reduced pressure. The residue was suspended in pentane, the solvent again removed and the crude product purified by sublimation (150 °C, 8 × 10^{-3} mbar) to give the borane as yellowish, oily crystals. The sublimated material was suspended in *n*-hexane (5 mL) and the solvent removed with a Pasteur pipett (repeated two more times) to give the borane as colorless solid (2.20 g, 28%).

Mp.: 160-177 °C

^1H NMR (400 MHz, CD_2Cl_2) δ = 7.24–7.16 (m, 6 H, 2-H).

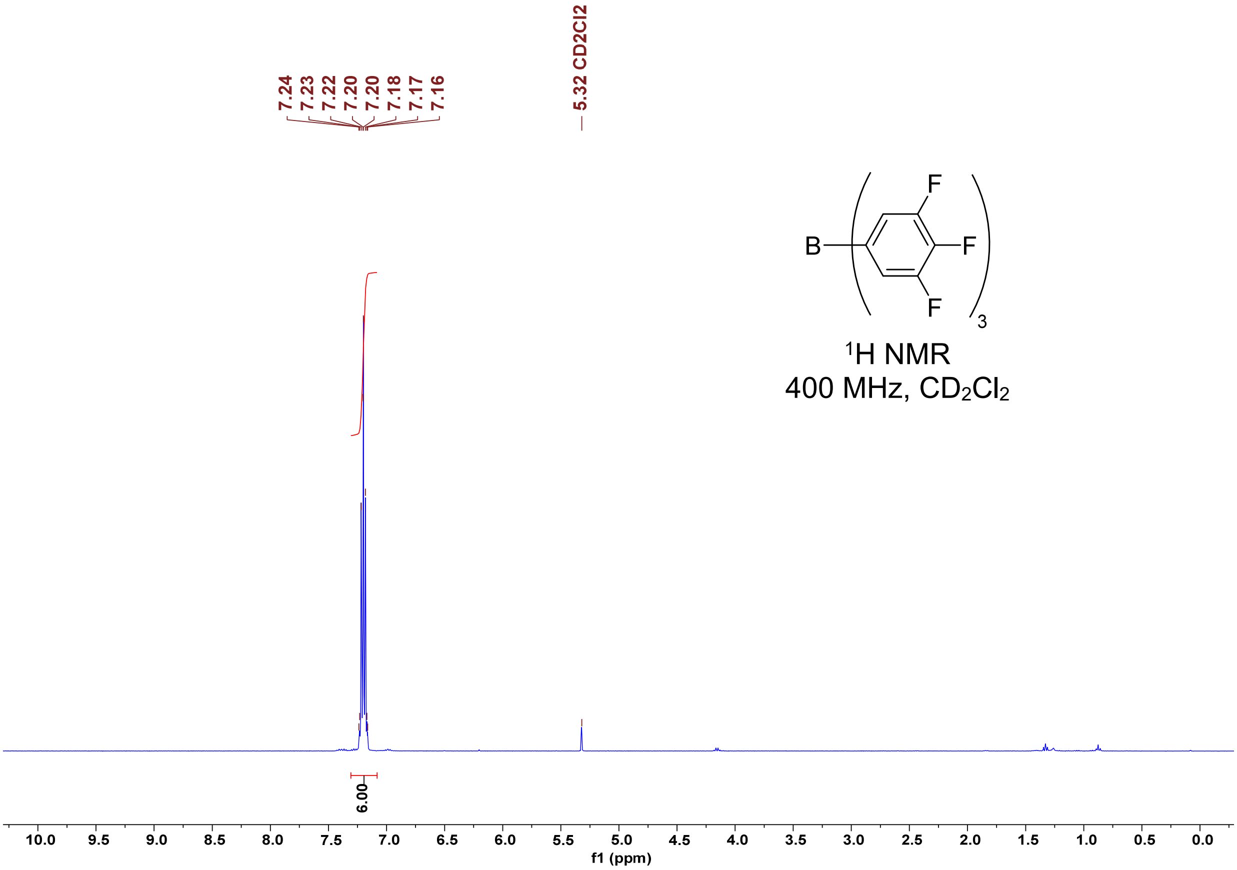
$^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2) δ = 151.5 (C_q, ddd, *J* = 252.8 Hz, 9.6 Hz, 2.9 Hz, C-3), 143.2 (C_q, dt, *J* = 259.0 Hz, 15.2 Hz, C-4), 137.0–136.8 (C_q, m, C-1), 122.5 (CH, dd, *J* = 13.7 Hz, 5.0 Hz, C-2).

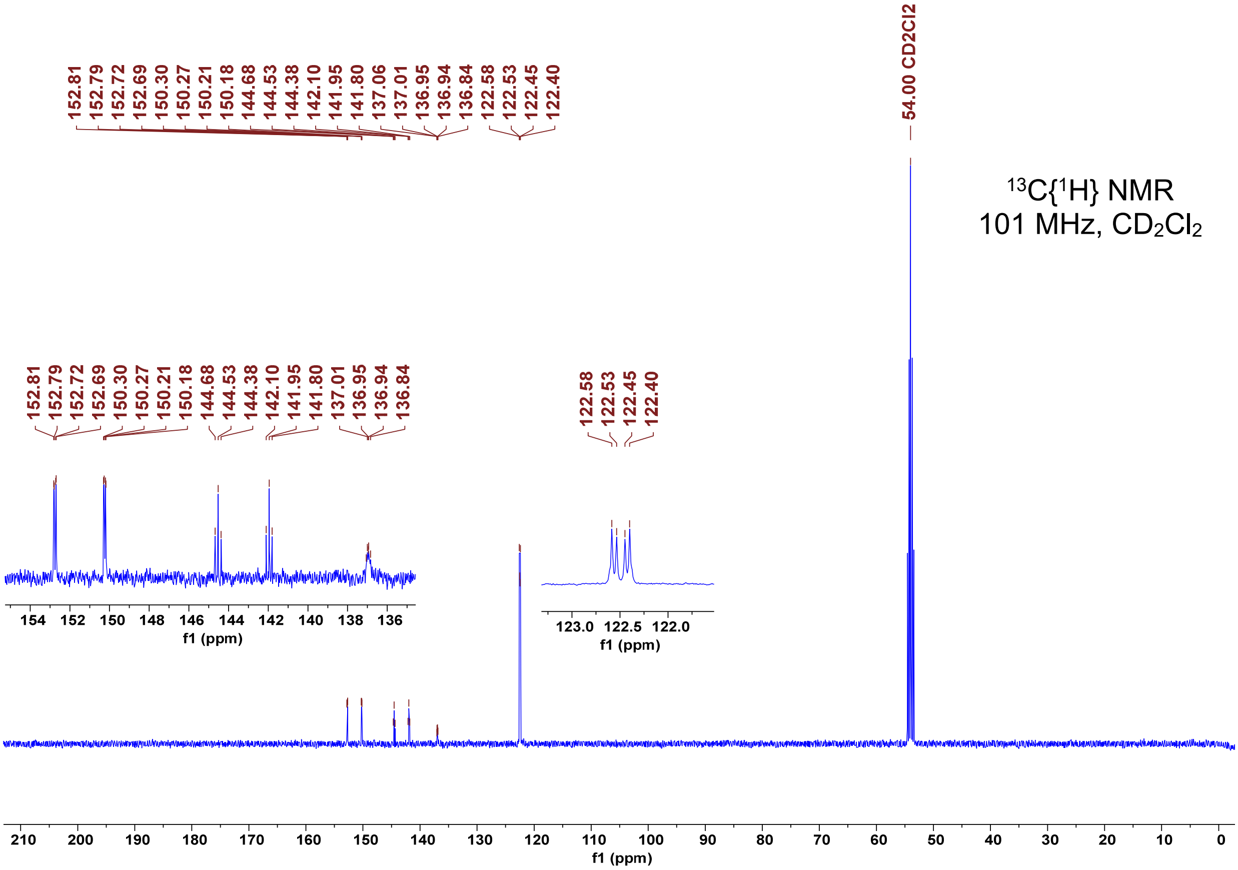
^{11}B NMR (128 MHz, CD_2Cl_2) δ = 64.7.

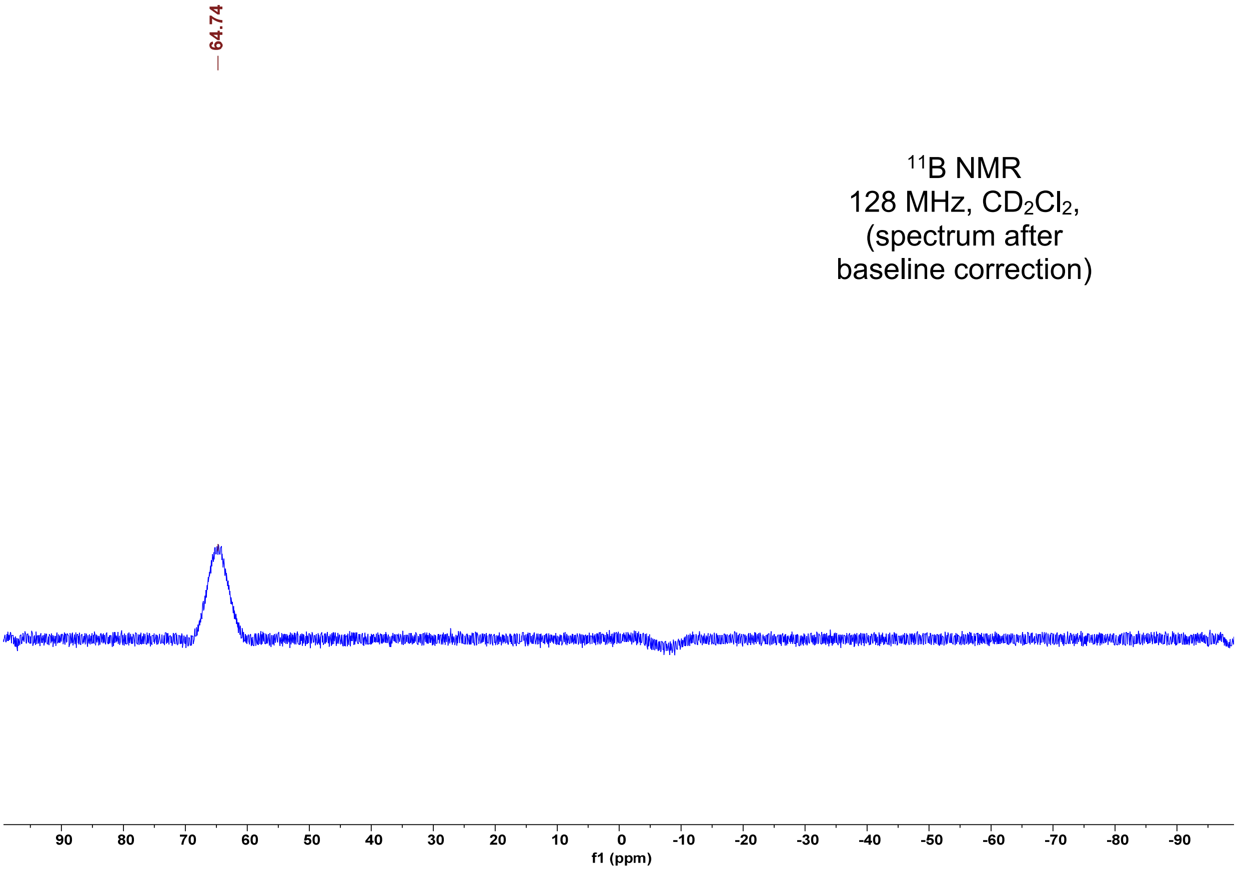
^{19}F NMR (377 MHz, CD_2Cl_2) δ = (-134.6) – (-134.7) (m, 6 F, 3-F and 5-F), (-154.1) – (-154.2) (m, 3 F, 4-F).

HRMS (EI^+) calcd *m/z* for $C_{18}H_6BF_9^{\bullet+}$ ($M^{\bullet+}$) 404.0413; found 404.0409.

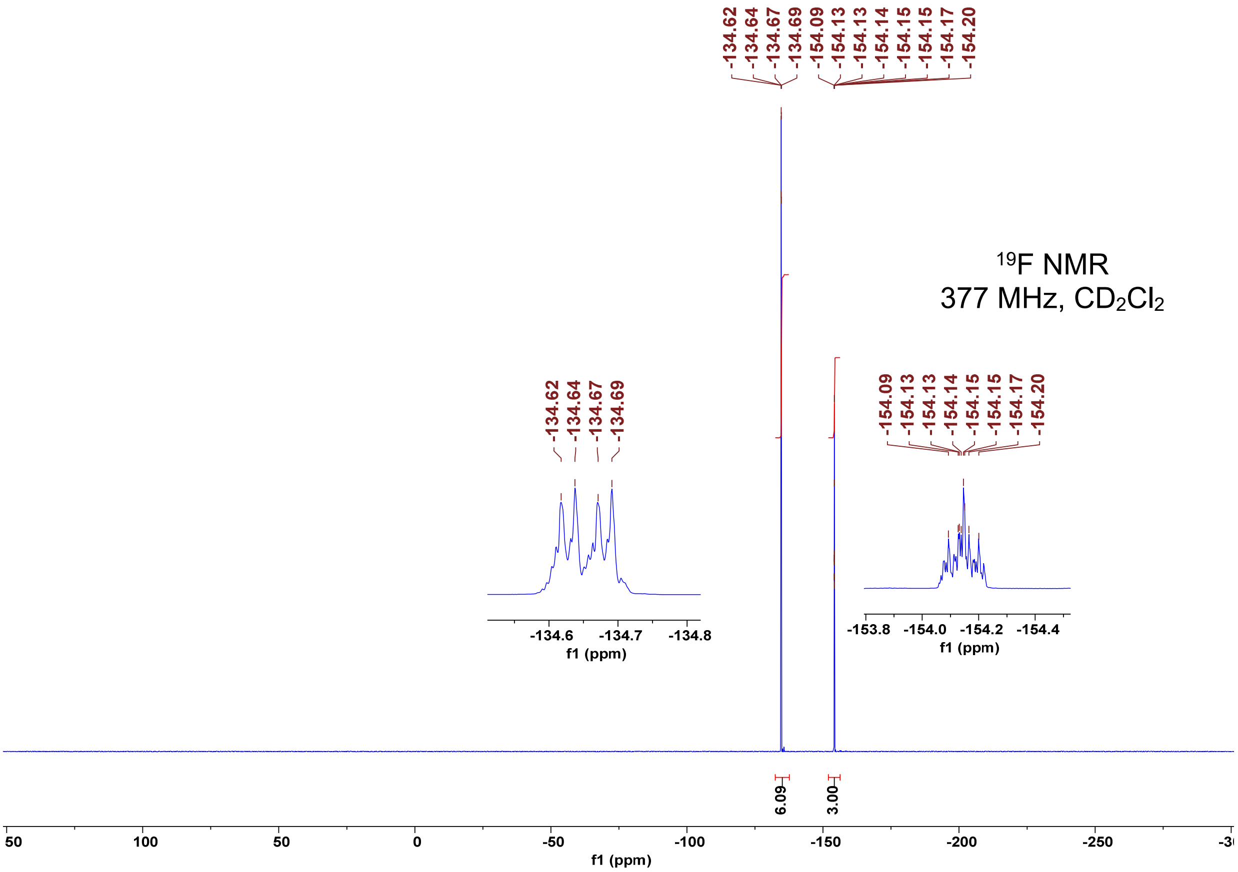
NMR data agree with those reported in ref.[S28].


7.24
7.23
7.22
7.20
7.20
7.18
7.17
7.16
5.32 CD2Cl2
B
F
F
F
3
^{1}H NMR
400 MHz, CD_2Cl_2
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


152.81
152.79
152.72
152.69
150.30
150.27
150.21
150.18
144.68
144.53
144.38
142.10
141.95
141.80
137.06
137.01
136.95
136.94
136.84
122.58
122.53
122.45
122.40
54.00 CD2Cl2
^{13}C{^{1}H} NMR
101 MHz, CD_2Cl_2
152.81
152.79
152.72
152.69
150.30
150.27
150.21
150.18
144.68
144.53
144.38
142.10
141.95
141.80
137.01
136.95
136.94
136.84
154 152 150 148 146 144 142 140 138 136
f1 (ppm)
122.58
122.53
122.45
122.40
123.0 122.5 122.0
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



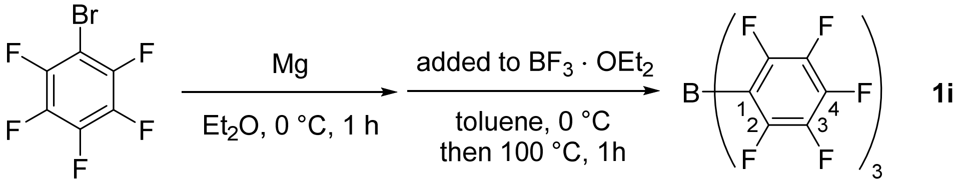
^{11}B NMR
128 MHz, CD_2Cl_2,
(spectrum after
baseline correction)



^{19}F NMR
377 MHz, CD_2Cl_2

Tris(pentafluorophenyl)borane (1i)

Synthesis according to the modified procedure in ref.[S29].



(RNH344)

In a flame dried 500 mL three necked round bottom flask with nitrogen inlet and reflux condenser under nitrogen was added magnesium turnings (2.43 g, 0.100 mol) and diethyl ether (167 mL). Bromopentafluorobenzene (12.5 mL, 0.100 mol) was added dropwise under stirring. After the initiation of the Grignard reaction the reaction mixture was cooled with an ice-bath. After stirring for another 60 min at 0 °C, the Grignard solution was transferred via syringe techniques into a separate flame dried flask containing a solution of $BF_3{\cdot}OEt_2$ (4.10 mL, 0.033 mol) in toluene (67 mL) at 0 °C. After the transfer of the Grignard reagent was complete, the reaction mixture was allowed to warm at room temperature while diethyl ether was removed under reduced pressure. The remaining toluene solution was heated to 100 °C for 1 h. Then concentration to dryness yielded a beige solid residue. *n*-Hexane (200 mL) was added and the mixture was heated to 45 °C under vigorous stirring. The suspension was filtrated through a pre-heated Schlenk frit. The clear filtrate was cooled to 5 °C causing the formation of feathery, colorless crystals. Filtration through a Schlenk frit, washing with *n*-hexane (20 mL) and drying gave pure **1i** (8.74 g, 52%).

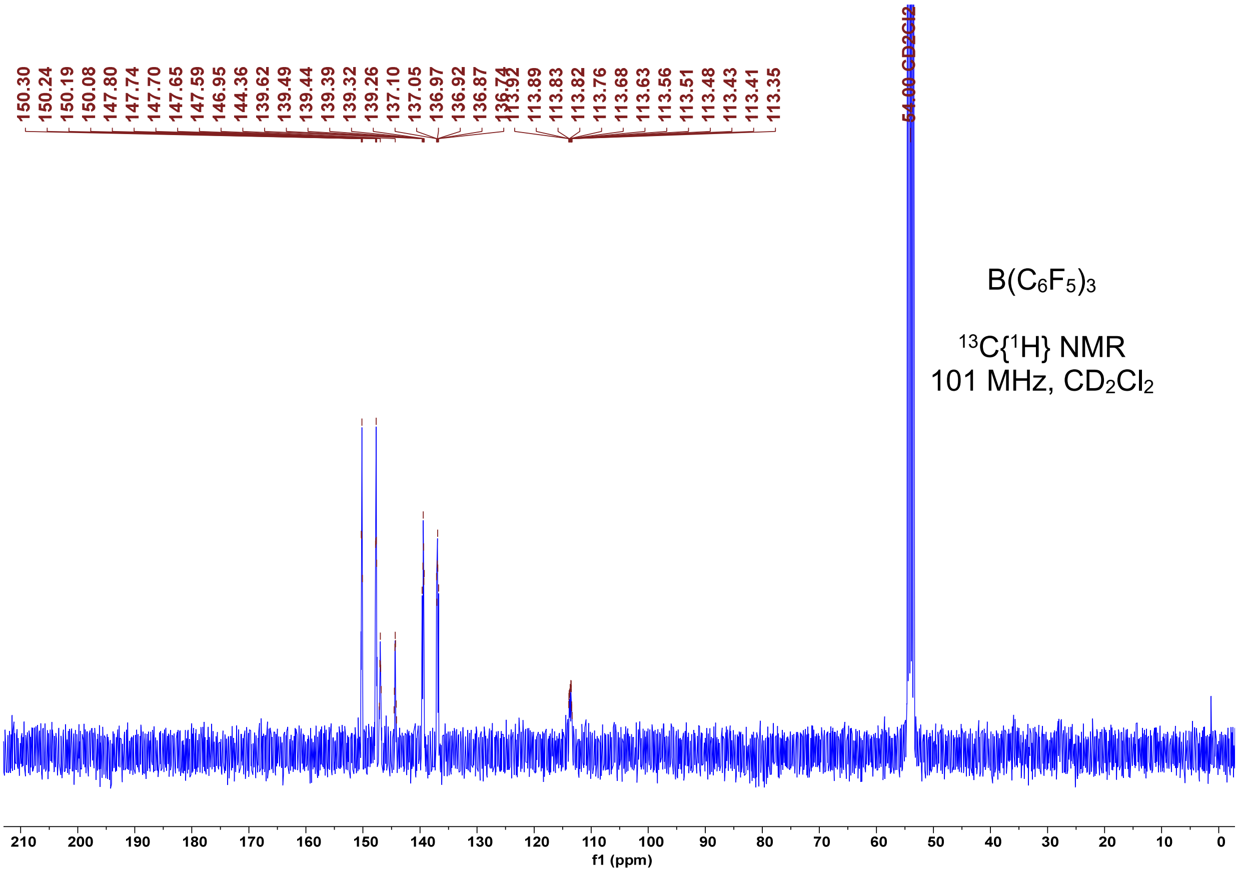
Mp.: 133-134 °C (ref.[S30]: mp 132-134 °C)

$^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2) δ = 150.3–147.6 (m), 147.1–144.1 (m), 139.6–136.7 (m), 113.9–113.3 (m, C_q, C-1).

^{11}B NMR (128 MHz, CD_2Cl_2) δ = 58.8.

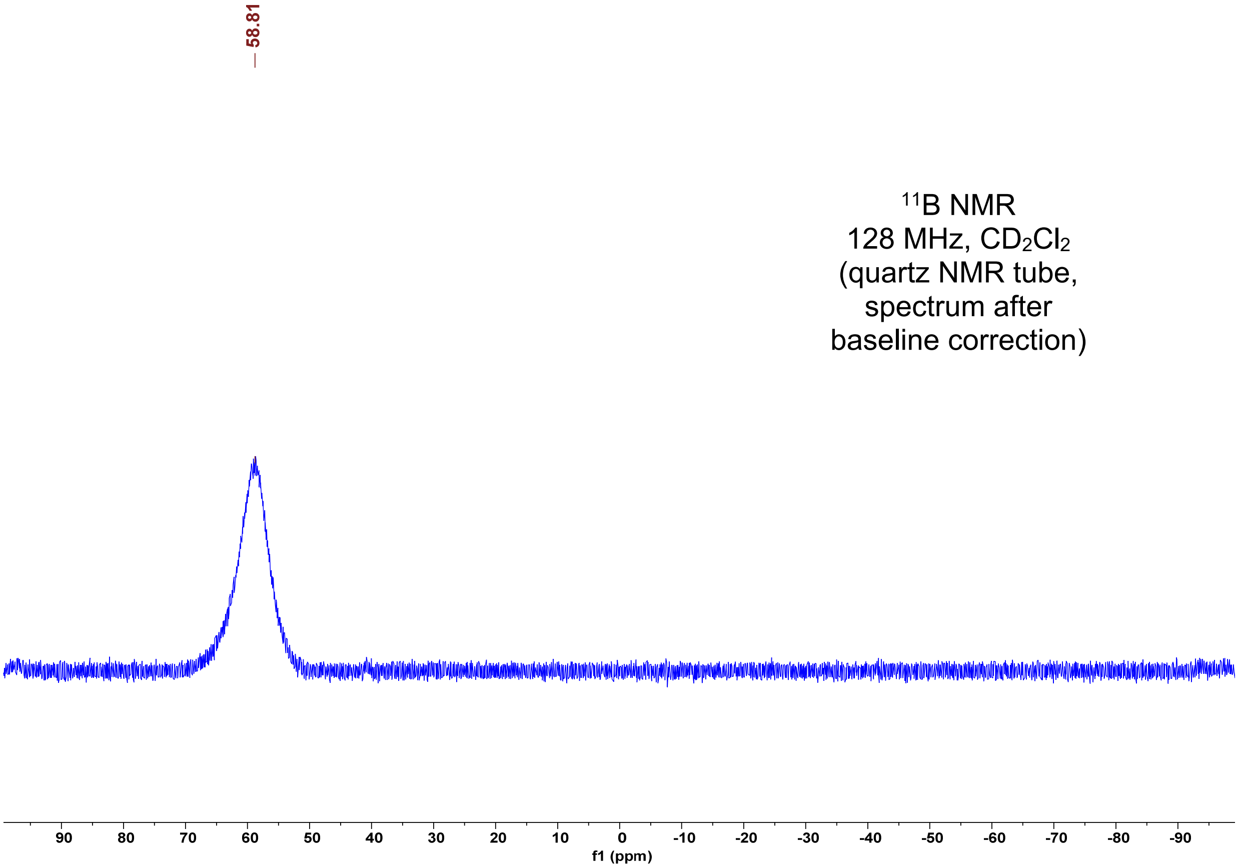
^{19}F NMR (377 MHz, CD_2Cl_2) δ = -128.2 (s, 2 F, 2-F), -143.9 (s, 1 F, 4-F), (-161.0) – (-161.1) (m, 2 F, 3-F).

HRMS (EI$^+$) calcd *m/z* for $C_{18}BF_{15}^{\bullet+}$ ($M^{\bullet+}$) 511.9848; found 511.9846.

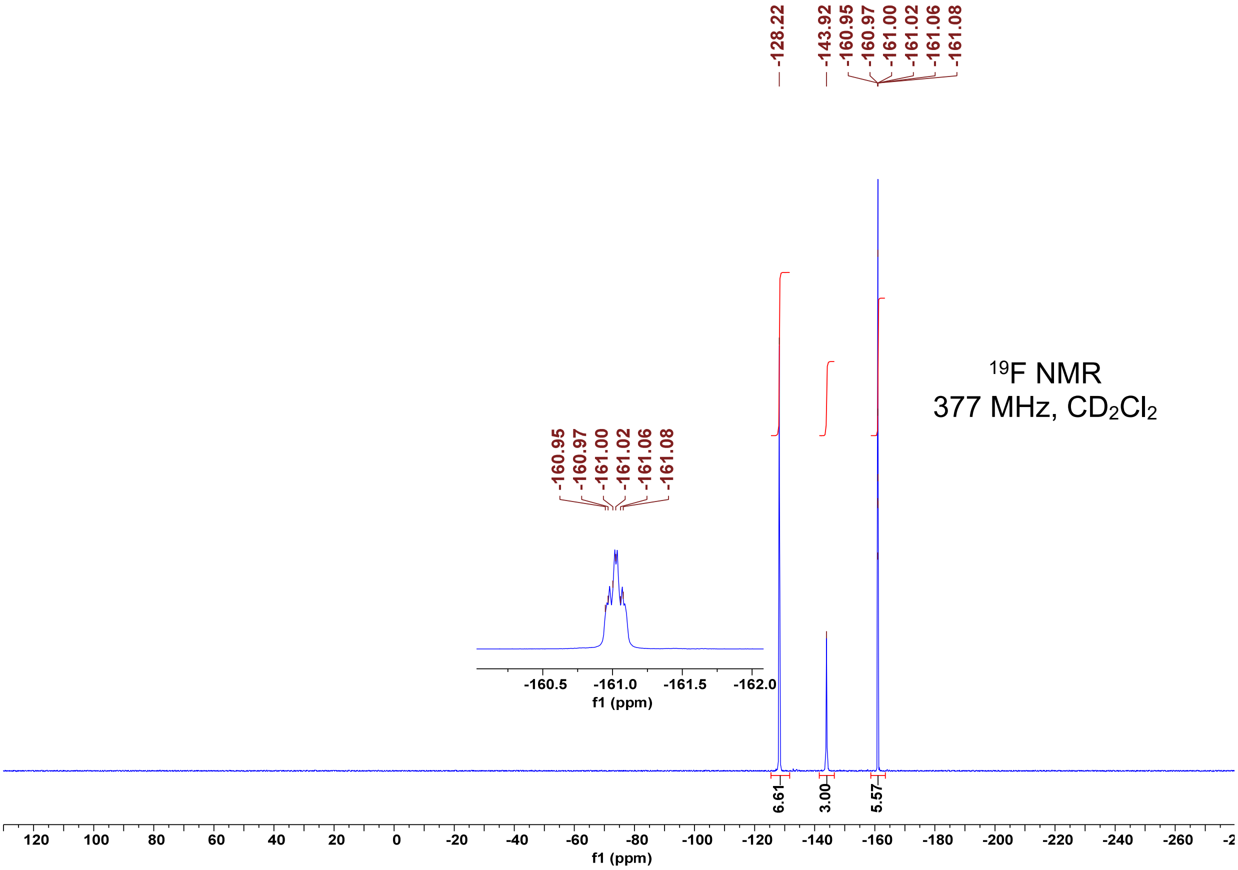


B(C_6F_5)$_3$

$^{13}C\{^1H\}$ NMR
101 MHz, CD_2Cl_2

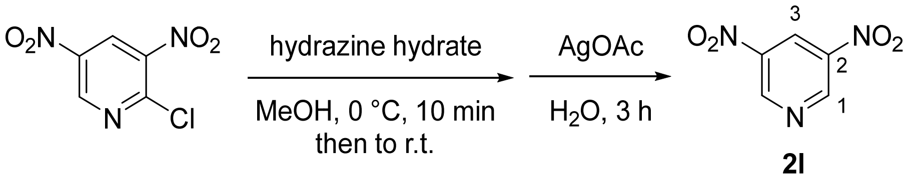


^{11}B NMR
128 MHz, CD_2Cl_2
(quartz NMR tube,
spectrum after
baseline correction)


-128.22
-143.92
-160.95
-160.97
-161.00
-161.02
-161.06
-161.08
^{19}F NMR
377 MHz, CD_2Cl_2
-160.95
-160.97
-161.00
-161.02
-161.06
-161.08
-160.5
-161.0
-161.5
-162.0
f1 (ppm)
6.61
3.00
5.57
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
f1 (ppm)

3,5-Dinitropyridine (2l)

Synthesis according to the modified procedure in ref.[S31].



2l

(RNH414)

In a 100 mL round-bottom flask was dissolved 2-chloro-3,5-dinitropyridine (2.00 g, 9.83 mmol) in methanol (20 mL). The resulting yellow solution was cooled at 0 °C and hydrazine monhydrate (0.77 mL, 15.8 mmol) was added dropwise over a period of 10 min causing the formation of a dark-brown precipitate. Stirring was continued overnight at room tempterature and gave a red suspension. The suspension was filtrated. The collected solid material was washed with MeOH (2 × 10 mL) and dried to give a red-brownish solid (1.61 g), which was used without further purification.

The solid was suspended in water (53 mL), and silver acetate (4.83 g, 28.9 mmol) was added. The brown suspension was heated for 3 h under reflux which led to decolorization. After cooling to room temperature a pH 9 was adjusted with 25% aq NaOH. Then the mixture was extracted with diethyl ether (3 x 100 mL). The combined organic phases were dried over Na_2SO_4, filtrated and concentrated under reduced pressure. The crude product was recrystallized from ethanol to yield pyridine **2l** (487 mg, 29%) as a yellow-orange crystalline solid.

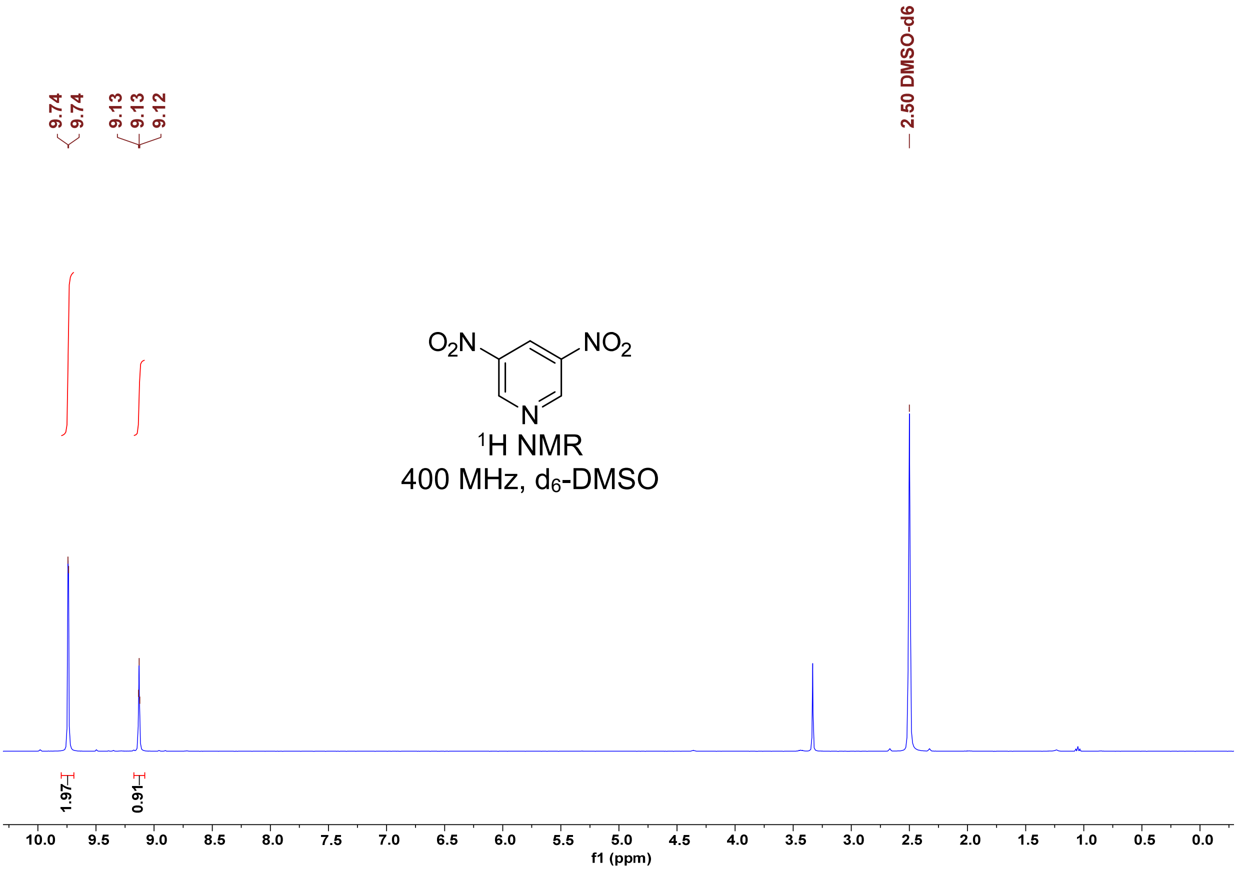
Mp.: 105-107 °C (ref.[S31]: 106 °C)

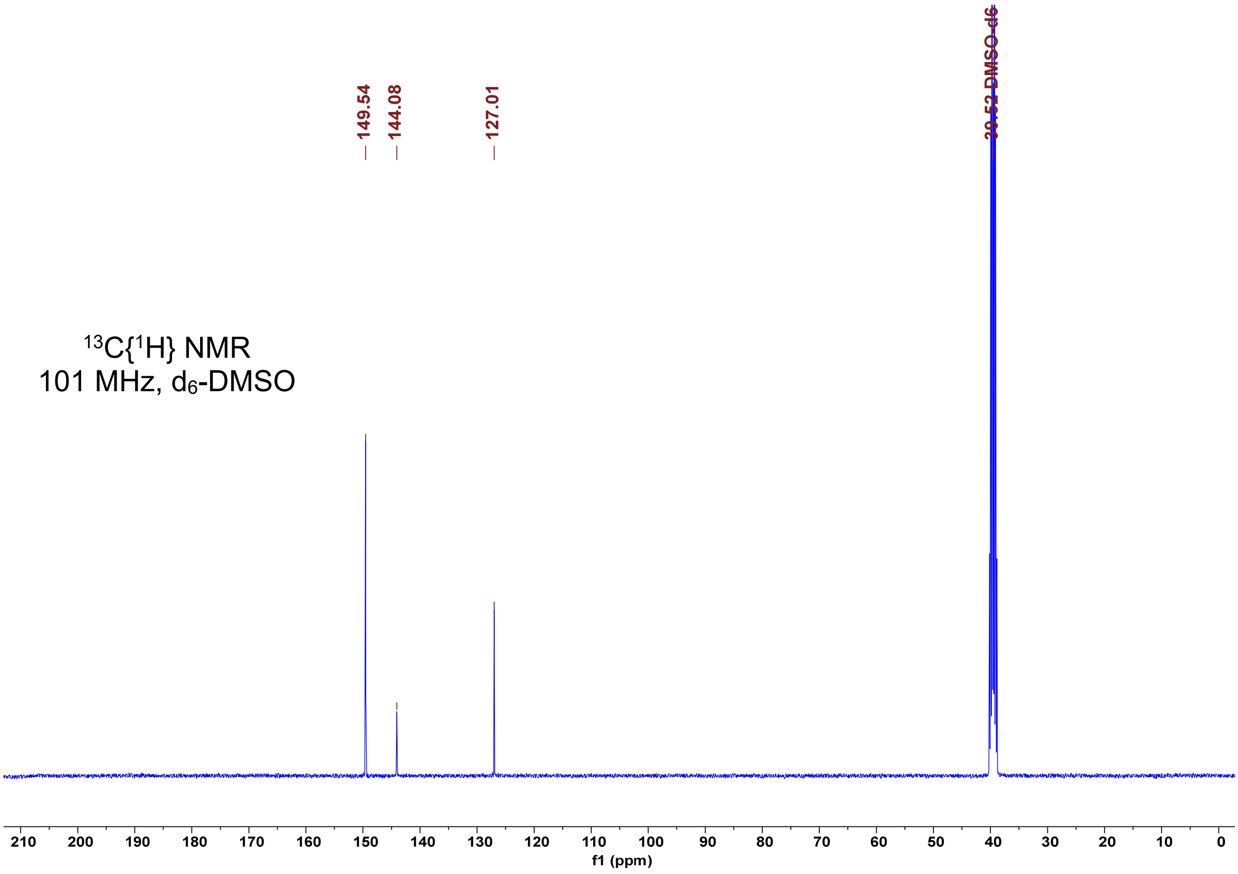
^{1}H NMR (400 MHz, DMSO-d_6) δ = 9.74 (d, J = 2.3 Hz, 2 H, 1-H), 9.13 (t, J = 2.3 Hz, 1 H, 3-H).

^{13}C{^{1}H} NMR (101 MHz, d_6-DMSO) δ = 149.5 (CH, C-1), 144.1 (C_q, C-2), 127.0 (CH, C-3).

HRMS (EI$^+$) calcd m/z for $C_5H_3N_3O_4^{\bullet+}$ ($M^{\bullet+}$) 169.0118; found 169.0120.

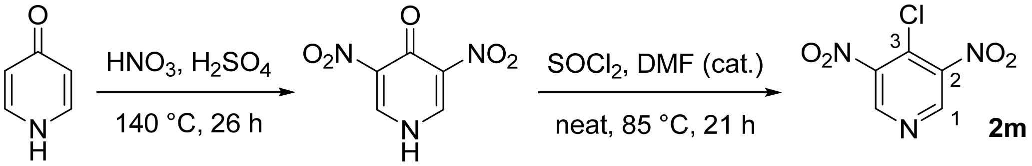
NMR data agree with those reported in ref.[S32].


9.74
9.74
9.13
9.13
9.12
2.50 DMSO-d6
O2N
NO2
N
1H NMR
400 MHz, d6-DMSO
1.97
0.91
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


149.54
144.08
127.01
39.52 DMSO-d6
13C{1H} NMR
101 MHz, d6-DMSO
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

4-Chloro-3,5-dinitropyridine (2m)

***Caution:** This reaction uses highly corrosive chemicals and produces large amounts of nitrous oxides. The reaction has to be carried out in a well ventilated fume hood.*



2m

(RM1159,RM1161)

The pyridine **2m** was prepared according to the modified procedure in ref.[S33]. A 100 mL round bottom flask with reflux condenser and drying tube ($CaCl_2$) was charged with H_2SO_4 (96%, 25 mL). 4-Pyridone (2.0 g, 21 mmol) was added, followed by HNO_3 (100%, 7 mL). The resulting solution was heated under stirring to 140 °C for 26 h (progress monitored by NMR spectroscopy). The reaction mixture was poured into ice cold water (100 mL) causing the precipitation of the product, which was collected by filtration. The crude product was recrystallized from an 1:1 mixture of acetic acid/water (100 mL) to give the product as colorless needles (2.12 g, 55%).

Synthesis according to the modified procedure in ref.[S34]. In a 20 × 1.5 cm pressure tube (Ace glassware) was added 3,5-dinitro-4-pyridone (2.12 g, 11.5 mmol), thionyl chloride (1.66 mL, 22.9 mmol) and DMF (2 drops). The pressure tube was sealed under nitrogen and heated at 85 °C overnight. The initially solid mixture slowly converted to a suspension and yielded a clear yellow solution after 21 h. After cooling to room temperature the mixture was transferred into a Schlenk flask, washed with dichloromethane (2 mL), and all volatiles were removed under reduces pressure to give a pale yellow solid. The crude product was recrystallized from cyclohexane to yield **2m** (1.02 g, 44%) as colorless crystalline solid.

Pyridine **2m** is highly moisture sensitive and was stored at -35 °C in an argon filled glovebox.

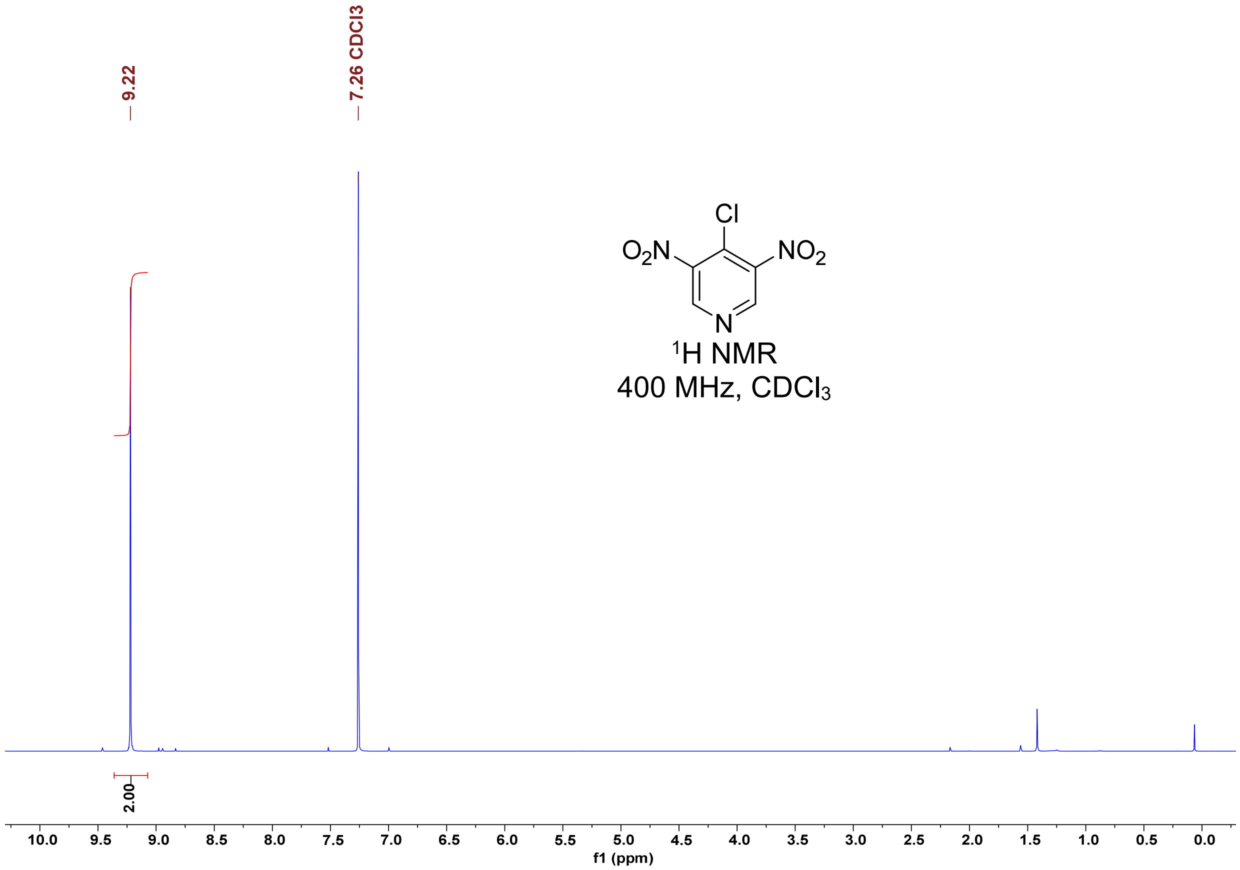
Mp.: 69-71 °C (ref.[S35]: mp 68-70 °C)

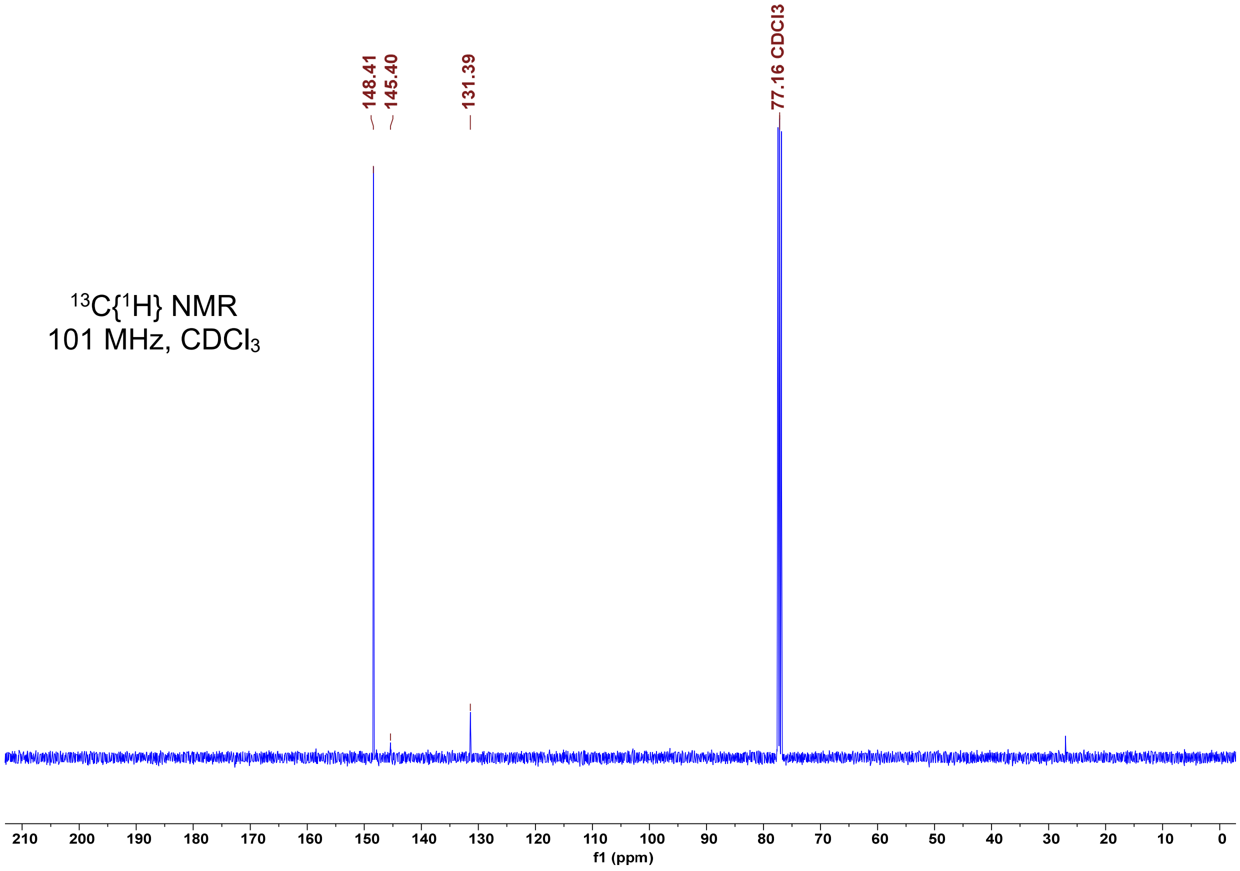
^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.22 (s, 2 H, 1-H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ =148.4 (CH, C-1), 145.4 (C_q, C-3), 131.4 (C_q, C-2).

HRMS (EI$^+$) calcd *m/z* for $C_5H_2ClN_3O_4^{\bullet+}$ ($M^{\bullet+}$) 202.9728; found 202.9725.

NMR data agree with those reported in ref.[S34].


9.22
7.26 CDCl3
Cl
O_2N
NO_2
N
^{1}H NMR
400 MHz, $CDCl_3$
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


148.41
145.40
131.39
77.16 CDCl3
^{13}C{^{1}H} NMR
101 MHz, $CDCl_3$
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

IV. Application of Lewis Acidity Parameters in Borane Catalyzed Reactions

Nazarov Cyclizations (RNH426)

Under an atmosphere of dry argon a solution of the Nazarov precursor (6.0 mg, 0.028 mmol) in CD_2Cl_2 (0.35 mL) was added to a solution of the borane (0.0028 mmol) in CD_2Cl_2 (0.35 mL). The reaction mixture was transferred into an NMR tube which was sealed with a rubber septum. The progress of the Nazarov cyclization was monitored by ^1H NMR (400 MHz) spectroscopy.

Conversion to the cyclopentenone product[S36,S37] was observed for BBr_3, BCl_3 and the triarylboranes **1i**, **1g** within 1–2 h. After 24 h reaction time partial conversion to the product was observed with **1h** but not when **1f** was used as the catalyst.

Diels-Alder Reactions of Methyl Vinyl Ketone with Cyclopentadiene

Under an atmosphere of dry argon CD_2Cl_2 solutions of methyl vinyl ketone (0.028 mmol), cyclopentadiene (freshly prepared by thermal decomposition of its dimer and subsequent distillation, 0.028 mmol), and the borane (0.0028 mmol) in CD_2Cl_2 (0.75 mL) were transferred into an NMR tube, which was sealed with a rubber septum. The reaction mixtures were analyzed by ^1H NMR spectroscopy (200 MHz) after 20 min reaction time at room temperature (25 °C).

Quantitative conversion of the educts to the Diels-Alder adduct[S38] was observed after 20 min for solutions that contained 10 mol% of the boranes **1h**, **1i** and BCl_3. With borane **1f**, traces of the product (15%) were observed after 2 h reaction time.

Michael Additions of 1-Methylindole to Methyl Vinyl Ketone

Under an atmosphere of dry argon CD_2Cl_2 solutions of methyl vinyl ketone (0.028 mmol), 1-methylindole (0.028 mmol) and the borane (0.0028 mmol) in CD_2Cl_2 (0.75 mL) were transferred into an NMR tube which was sealed with a rubber septum. The reaction mixtures were analyzed by ^1H NMR spectroscopy (200 MHz) after 20 min reaction time at room temperature (25 °C).

Quantitative conversion of the educts to the Michael adduct[S39] was observed after 20 min for solutions that contained 10 mol% of boranes **1h**, **1i**. With borane **1f**, traces of the product (24%) were observed after 24 h reaction time.

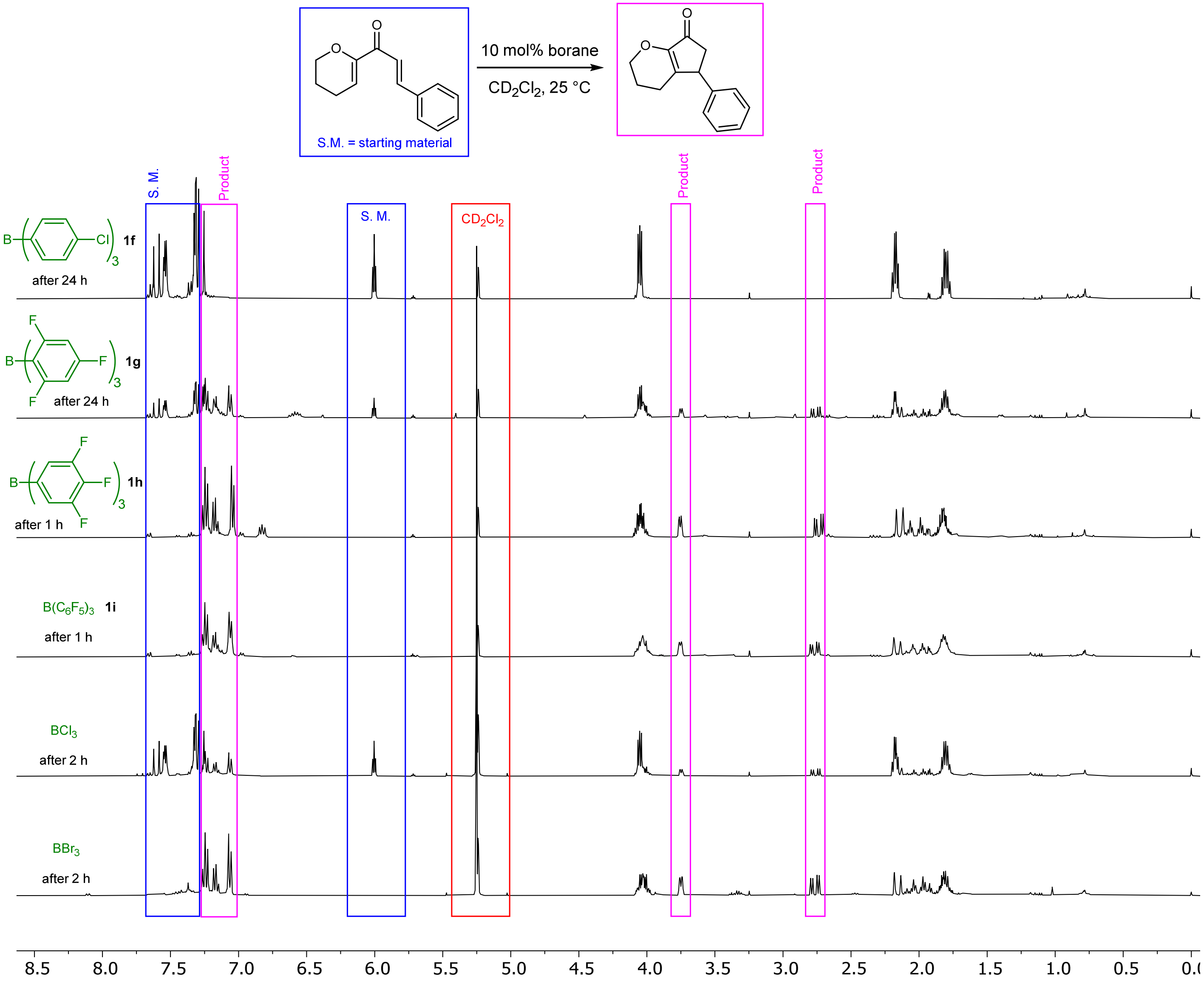


Figure S3: ^{1}H NMR spectra (400 MHz) in CD_2Cl_2 of the borane catalyzed Nazarov reaction.

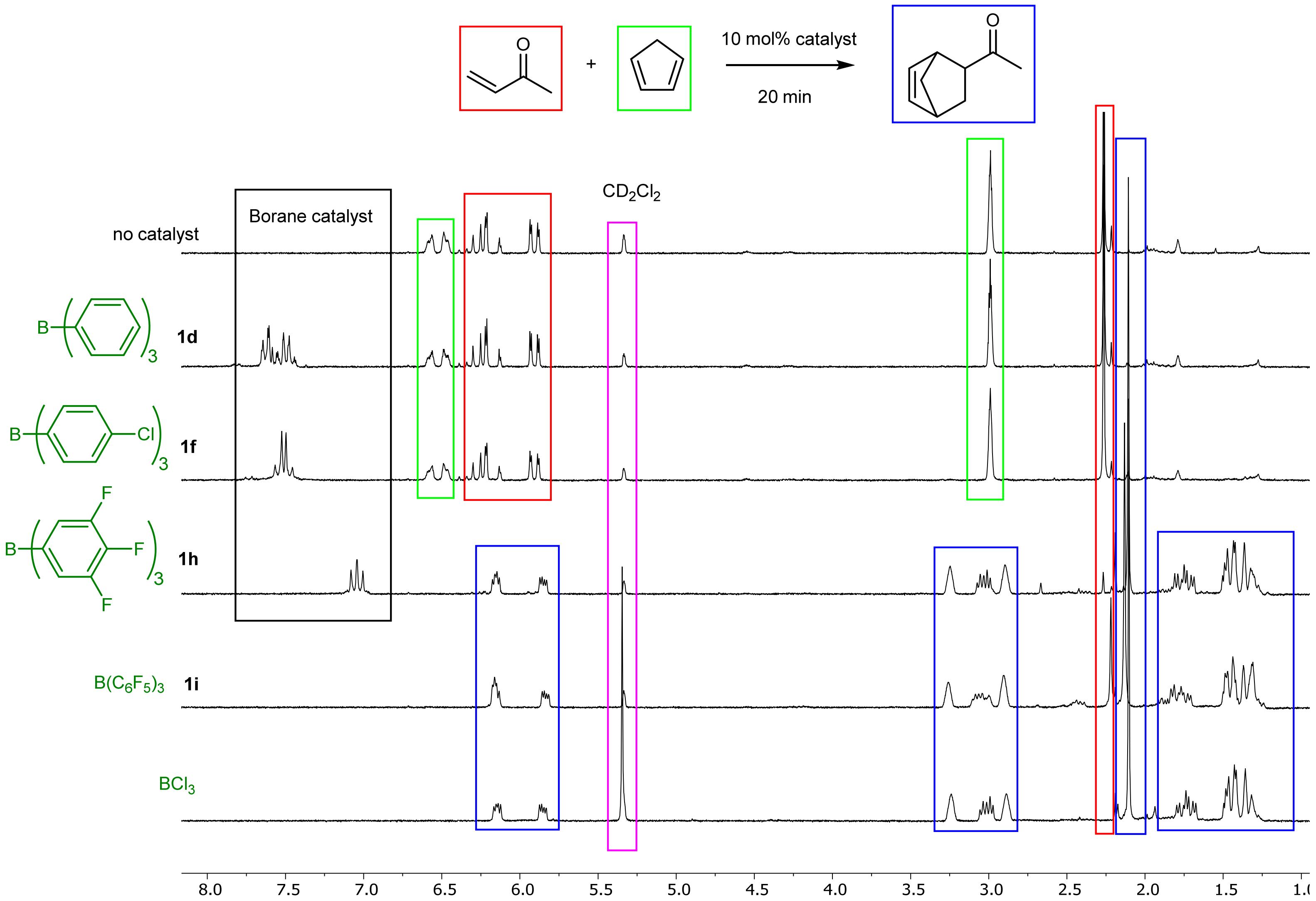


Figure S4: ^{1}H NMR spectra (200 MHz) in CD_2Cl_2 of the borane catalyzed Diels-Alder reaction of methyl vinyl ketone with cyclopentadien.

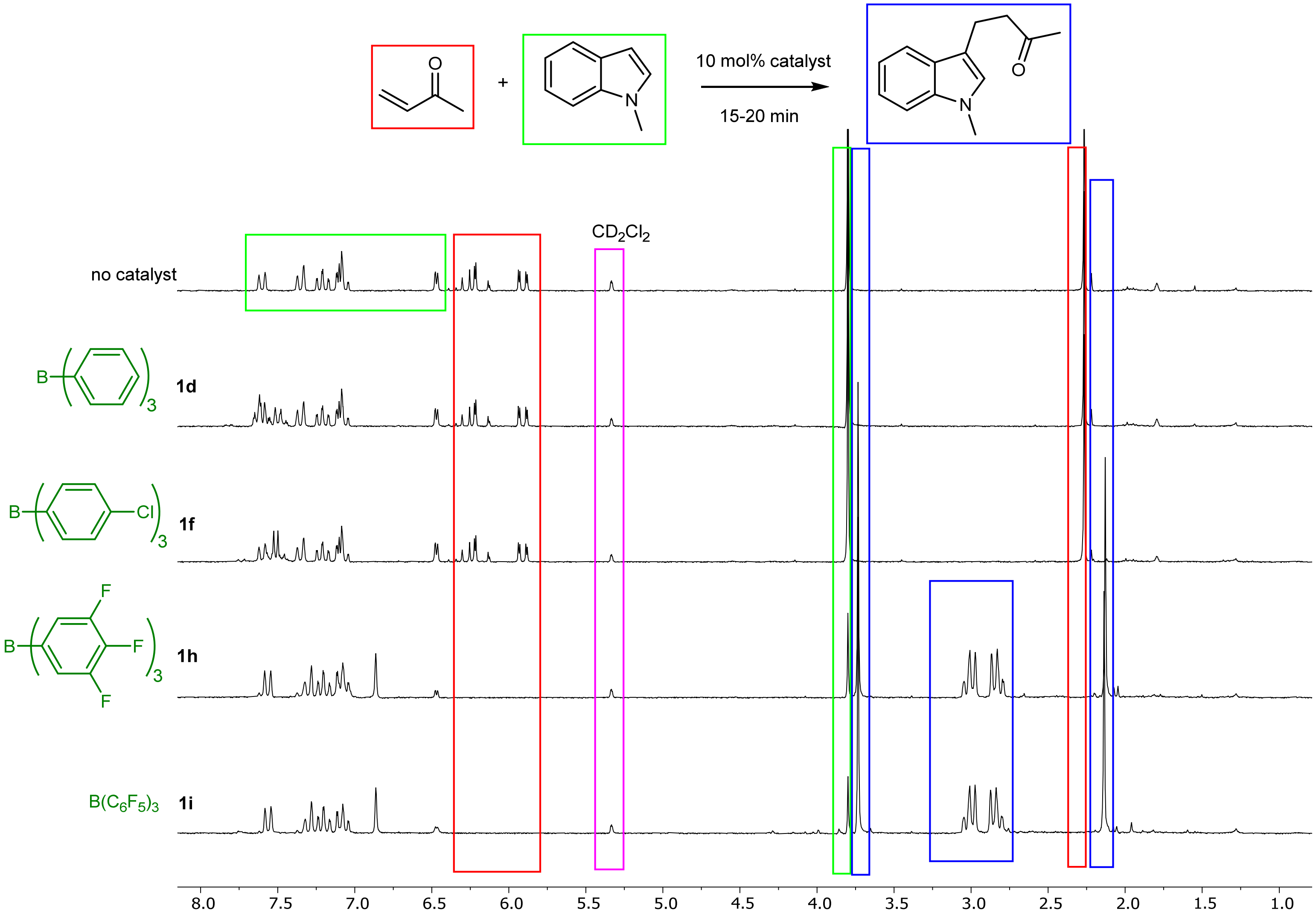


Figure S5: ^{1}H NMR spectra (200 MHz) in CD_2Cl_2 of the borane catalyzed Michael addition of 1-methylindole at methyl vinyl ketone.

V. Determination of Equilibrium Constants by Isothermal Titration Calorimetry (ITC)

Summary of ITC experiments in dichloromethane

Reported errors are standard deviations from the averaged results of three experiments under identical conditions at 20 °C.

Table S4: Summary of ITC titration experiments of boranes **1** with Lewis bases in dichloromethane at 20 °C.

Experiment	Ar_3B	LB	[Ar_3B] (mM)	[LB] (mM)	T (°C)	K (M^{-1})	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	$T\Delta S$ (kJ mol^{-1})	n
RM1087e1	**1a**	**2a**	0.996	11.7	20.0	3.74×10^4	-25.7	-55.2	-29.5	0.928
RM1087e2	**1a**	**2a**	0.996	11.7	20.0	3.46×10^4	-25.5	-54.8	-29.3	0.656
RM1087e3	**1a**	**2a**	0.97	11.7	20.0	3.39×10^4	-25.4	-56.8	-31.4	0.775
						$(3.53 \pm 0.16) \times 10^4$	-25.5 ± 0.1	-55.6 ± 0.9	-30.1 ± 1.0	
RM1089e1	**1a**	**2b**	1.02	11.0	20.0	9.28×10^3	-22.3	-54.8	-32.5	0.821
RM1089e2	**1a**	**2b**	0.996	10.1	20.0	9.12×10^3	-22.2	-58.1	-35.9	0.734
RM1089e3	**1a**	**2b**	0.996	10.1	20.0	9.64×10^3	-22.4	-57.3	-34.9	0.691
						$(9.35 \pm 0.22) \times 10^3$	-22.3 ± 0.1	-56.7 ± 1.4	-34.4 ± 1.4	
RM1091e1	**1b**	**2a**	0.963	11.4	20.0	2.31×10^6	-35.7	-64.8	-29.1	0.763
RM1091e2	**1b**	**2a**	0.963	11.4	20.0	5.06×10^6	-37.6	-66.5	-28.8	0.754
RM1091e3	**1b**	**2a**	0.963	11.4	20.0	2.27×10^6	-35.7	-66.5	-30.8	0.749
						$(3.21 \pm 1.31) \times 10^6$	-36.3 ± 0.9	-65.9 ± 0.8	-29.6 ± 0.9	
RM1081e1	**1b**	**2b**	0.993	10.3	20.0	1.18×10^6	-34.1	-70.2	-36.1	0.749
RM1081e2	**1b**	**2b**	0.993	10.3	20.0	1.47×10^6	-34.6	-68.6	-33.9	0.71
RM1081e3	**1b**	**2b**	0.993	10.3	20.0	1.09×10^6	-33.9	-70.2	-36.3	0.68
						$(1.25 \pm 0.17) \times 10^6$	-34.2 ± 0.3	-69.7 ± 0.8	-35.5 ± 1.1	
RM1078e1	**1b**	**2c**	1.32	14.0	20.0	1.33×10^5	-28.8	-58.1	-29.3	0.809
RM1078e2	**1b**	**2c**	1.32	14.0	20.0	1.39×10^5	-28.9	-58.1	-29.2	0.782
RM1078e3	**1b**	**2c**	1.32	14.0	20.0	1.22×10^5	-28.5	-59.8	-31.2	0.744
						$(1.31 \pm 0.08) \times 10^5$	-28.7 ± 0.1	-58.7 ± 0.8	-29.9 ± 0.9	

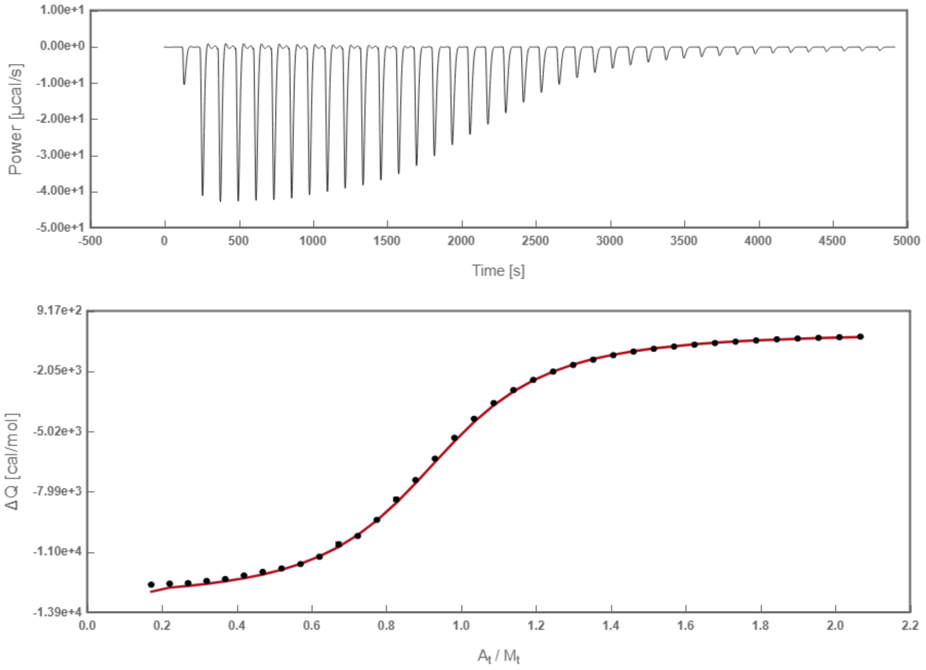
RM1075e3	**1b**	**2d**	1.50	13.2	20.0	2.02×10^{4}	-24.2	-51.8	-27.7	0.871
RM1075e4	**1b**	**2d**	1.50	13.2	20.0	2.37×10^{4}	-24.6	-51.0	-26.4	0.821
RM1075e5	**1b**	**2d**	1.50	13.2	20.0	2.27×10^{4}	-24.4	-53.9	-29.5	0.797
						$(2.22 \pm 0.15) \times 10^{4}$	-24.4 ± 0.2	-52.3 ± 1.2	-27.9 ± 1.2	
RM1077e2	**1b**	**2e**	1.50	15.0	20.0	2.89×10^{3}	-19.4	-57.7	-38.3	0.691
RM1077e3	**1b**	**2e**	1.50	15.0	20.0	3.51×10^{3}	-19.9	-52.3	-32.4	0.674
RM1077e4	**1b**	**2e**	1.50	15.0	20.0	3.34×10^{3}	-19.8	-53.1	-33.3	0.657
						$(3.25 \pm 0.27) \times 10^{3}$	-19.7 ± 0.2	-54.3 ± 2.4	-34.6 ± 2.6	
RM1079e2	**1c**	**2d**	1.06	10.8	20.0	3.18×10^{5}	-30.9	-69.0	-38.1	0.857
RM1080e1	**1c**	**2d**	1.06	10.1	20.0	2.29×10^{5}	-30.1	-74.0	-43.9	0.754
RM1116e1	**1c**	**2d**	1.02	9.62	20.0	3.69×10^{5}	-31.2	-67.7	-36.5	0.781
RM1116e2	**1c**	**2d**	1.02	9.62	20.0	4.43×10^{5}	-31.7	-69.4	-37.7	0.763
						$(3.40 \pm 0.78) \times 10^{5}$	-31.0 ± 0.6	-70.0 ± 2.4	-39.0 ± 2.9	
RM1083e1	**1c**	**2e**	1.06	9.72	20.0	9.41×10^{4}	-27.9	-76.5	-48.6	0.716
RM1086e1	**1c**	**2e**	1.09	9.95	20.0	6.42×10^{4}	-27.0	-64.4	-37.4	0.773
RM1086e2	**1c**	**2e**	1.09	9.95	20.0	7.75×10^{4}	-27.4	-69.0	-41.5	0.74
						$(7.86 \pm 1.22) \times 10^{4}$	-27.4 ± 0.4	-69.9 ± 5.0	-42.5 ± 4.6	
RM1084e1	**1c**	**2f**	1.06	10.7	20.0	2.14×10^{4}	-24.3	-79.8	-55.5	0.772
RM1084e3	**1c**	**2f**	1.06	10.7	20.0	2.94×10^{4}	-25.1	-78.2	-53.1	0.763
RM1084e4	**1c**	**2f**	1.09	10.7	20.0	4.86×10^{4}	-26.3	-76.1	-49.8	0.618
						$(3.31 \pm 1.14) \times 10^{4}$	-25.2 ± 0.4	-79.0 ± 0.8	-54.3 ± 1.2	
RM1124e1	**1c**	**2g**	1.06	10.1	20.0	1.08×10^{4}	-22.6	-71.9	-49.3	0.766
RM1124e2	**1c**	**2g**	0.985	10.1	20.0	1.58×10^{4}	-23.6	-70.6	-47.1	0.759
RM1124e3	**1c**	**2g**	1.06	9.94	20.0	1.63×10^{4}	-23.6	-71.9	-48.3	0.812
						$(1.43 \pm 0.25) \times 10^{4}$	-23.3 ± 0.5	-71.5 ± 0.6	-48.2 ± 0.9	

RM1125e2	**1c**	**2h**	1.06	10.8	20.0	3.30×10^3	-19.7	-65.2	-45.5	0.681
RM1125e3	**1c**	**2h**	0.985	10.8	20.0	3.66×10^3	-20.0	-63.5	-43.5	0.723
RM1125e4	**1c**	**2h**	1.06	10.8	20.0	3.83×10^3	-20.1	-68.6	-48.4	0.657
						$(3.60 \pm 0.23) \times 10^3$	-20.0 ± 0.2	-65.8 ± 2.1	-45.8 ± 2.0	
RM968e1	**1d**	**2d**	1.13	10.1	20.0	1.39×10^6	-34.5	-70.2	-35.7	1.1
RM968e3	**1d**	**2d**	1.13	10.1	20.0	1.43×10^6	-34.5	-74.0	-39.4	1.0
RM968e5	**1d**	**2d**	1.05	10.1	20.0	1.34×10^6	-34.4	-76.1	-41.7	1.07
						$(1.39 \pm 0.04) \times 10^6$	-34.5 ± 0.1	-73.4 ± 2.4	-39.0 ± 2.4	
RM1118e1	**1d**	**2e**	1.03	10.6	20.0	4.20×10^5	-31.6	-74.4	-42.8	0.918
RM1118e2	**1d**	**2e**	1.20	10.6	20.0	3.69×10^5	-31.2	-75.7	-44.4	0.936
RM1118e3	**1d**	**2e**	1.24	10.6	20.0	3.70×10^5	-31.3	-73.2	-41.9	0.861
						$(3.86 \pm 0.24) \times 10^5$	-31.4 ± 0.1	-74.4 ± 1.0	-43.1 ± 1.0	
AB037e2	**1d**	**2f**	1.13	10.1	20.0	8.81×10^4	-27.8	-71.9	-44.1	1.12
AB037e3	**1d**	**2f**	1.05	10.1	20.0	8.39×10^4	-27.6	-74.0	-46.4	0.84
RM1121e1	**1d**	**2f**	1.12	10.1	20.0	1.08×10^5	-28.2	-66.9	-38.6	1.01
						$(9.33 \pm 1.05) \times 10^4$	-27.9 ± 0.3	-70.9 ± 3.0	-43.0 ± 3.2	
AB035e3	**1d**	**2g**	1.13	10.1	20.0	2.82×10^4	-25.0	-67.3	-42.3	1.0
AB035e4	**1d**	**2g**	1.05	10.1	20.0	2.43×10^4	-24.6	-64.0	-39.3	1.22
AB035e5	**1d**	**2g**	1.05	10.1	20.0	2.01×10^4	-24.2	-63.1	-39.0	0.89
						$(2.42 \pm 0.34) \times 10^4$	-24.6 ± 0.3	-64.8 ± 1.8	-40.2 ± 1.5	
RM974e1	**1d**	**2h**	1.13	10.1	20.0	3.87×10^3	-20.1	-81.9	-61.8	0.95
RM974e2	**1d**	**2h**	1.13	10.1	20.0	4.64×10^3	-20.6	-80.3	-59.7	0.99
RM974e3	**1d**	**2h**	1.05	10.1	20.0	4.31×10^3	-20.4	-80.7	-60.3	0.93
						$(4.27 \pm 0.32) \times 10^3$	-20.4 ± 0.2	-81.0 ± 0.7	-60.6 ± 0.9	
RM1094e1	**1e**	**2d**	1.01	10.0	20.0	1.34×10^6	-34.4	-68.1	-33.7	0.96
RM1094e2	**1e**	**2d**	1.08	10.0	20.0	1.31×10^6	-34.3	-70.2	-35.9	0.894
RM1094e3	**1e**	**2d**	1.01	9.67	20.0	1.25×10^6	-34.2	-71.9	-37.7	0.997

						$(1.30 \pm 0.04) \times 10^6$	-34.3 ± 0.1	-70.1 ± 1.5	-35.8 ± 1.6	
RM1092e1	**1e**	**2e**	1.01	10.4	20.0	2.72×10^5	-30.5	-71.9	-41.4	0.409
RM1092e2	**1e**	**2e**	1.01	10.4	20.0	2.73×10^5	-30.5	-73.6	-43.1	0.904
RM1092e3	**1e**	**2e**	1.08	10.4	20.0	3.58×10^5	-31.2	-69.8	-38.6	0.857
						$(3.01 \pm 0.41) \times 10^5$	-30.7 ± 0.3	-71.8 ± 1.5	-41.0 ± 1.8	
RM1096e1	**1e**	**2f**	0.979	10.7	20.0	8.41×10^4	-27.6	-68.1	-40.5	0.88
RM1096e2	**1e**	**2f**	1.05	10.7	20.0	8.37×10^4	-27.6	-68.1	-40.5	0.864
RM1096e3	**1e**	**2f**	1.01	10.7	20.0	8.11×10^4	-27.6	-68.1	-40.6	0.921
						$(8.30 \pm 0.14) \times 10^4$	-27.6 ± 0.0	-68.1 ± 0.0	-40.5 ± 0.1	
RM1097e1	**1e**	**2g**	1.05	9.93	20.0	3.55×10^4	-25.5	-61.4	-35.9	0.914
RM1097e2	**1e**	**2g**	1.01	10.3	20.0	3.35×10^4	-25.4	-64.4	-39.0	0.848
RM1097e3	**1e**	**2g**	0.979	10.3	20.0	3.03×10^4	-25.2	-66.0	-40.9	1.03
						$(3.31 \pm 0.22) \times 10^4$	-25.4 ± 0.2	-64.0 ± 1.9	-38.6 ± 2.1	
RM1099e1	**1e**	**2h**	0.946	11.1	20.0	6.95×10^3	-21.6	-66.5	-44.9	0.948
RM1099e2	**1e**	**2h**	0.912	11.1	20.0	7.30×10^3	-21.7	-64.8	-43.1	0.996
RM1099e3	**1e**	**2h**	0.979	11.1	20.0	9.36×10^3	-22.3	-61.9	-39.6	0.988
						$(7.87 \pm 1.06) \times 10^3$	-21.8 ± 0.3	-64.4 ± 1.9	-42.5 ± 2.2	

Individual ITC measurements

RM1087e1



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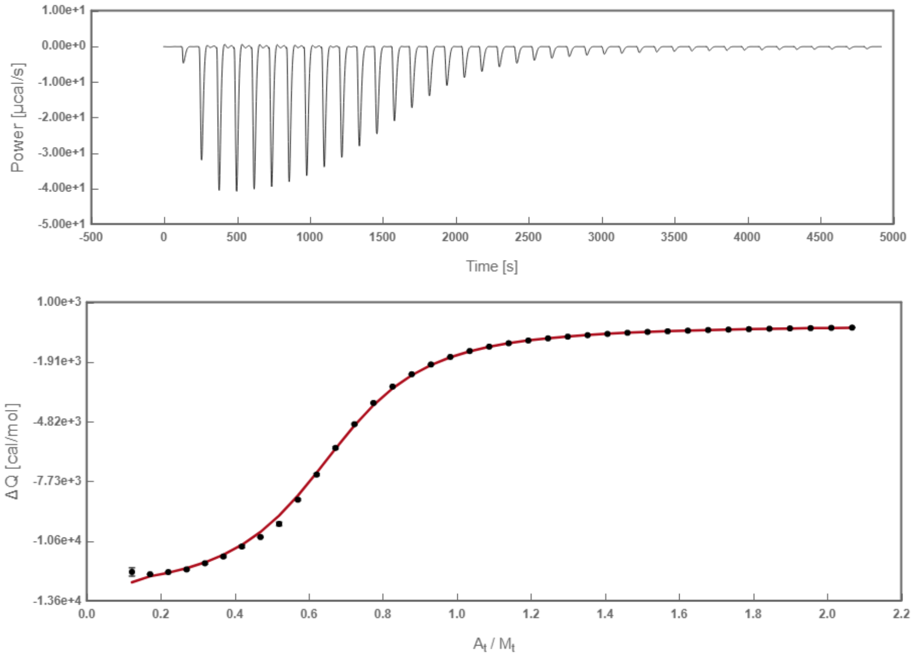

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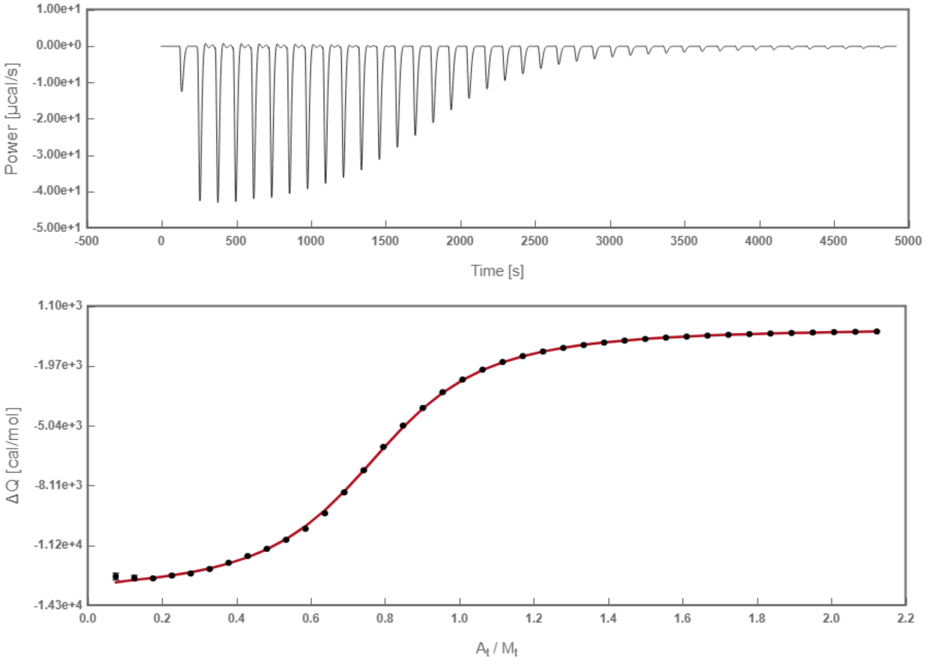

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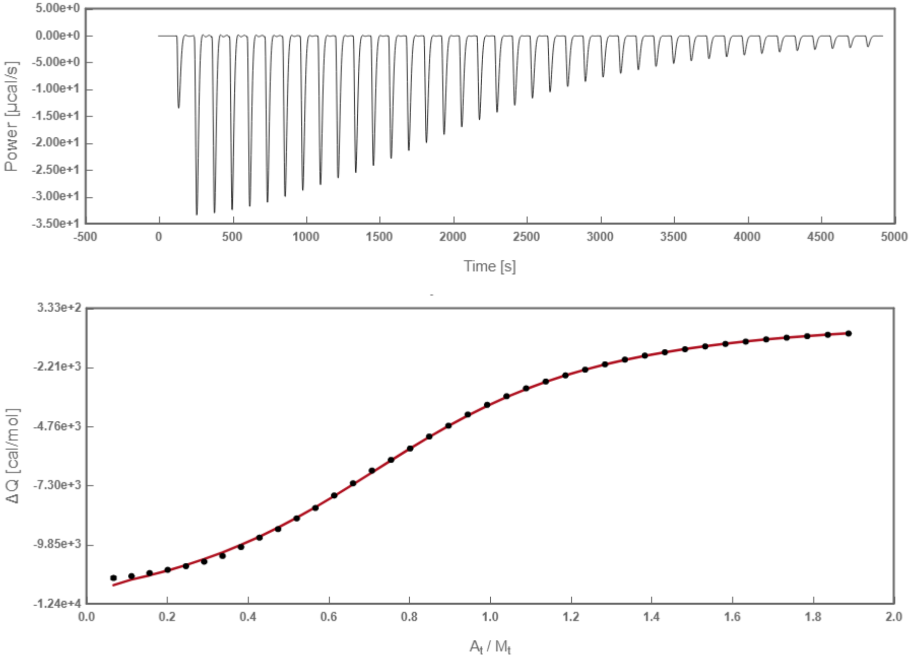

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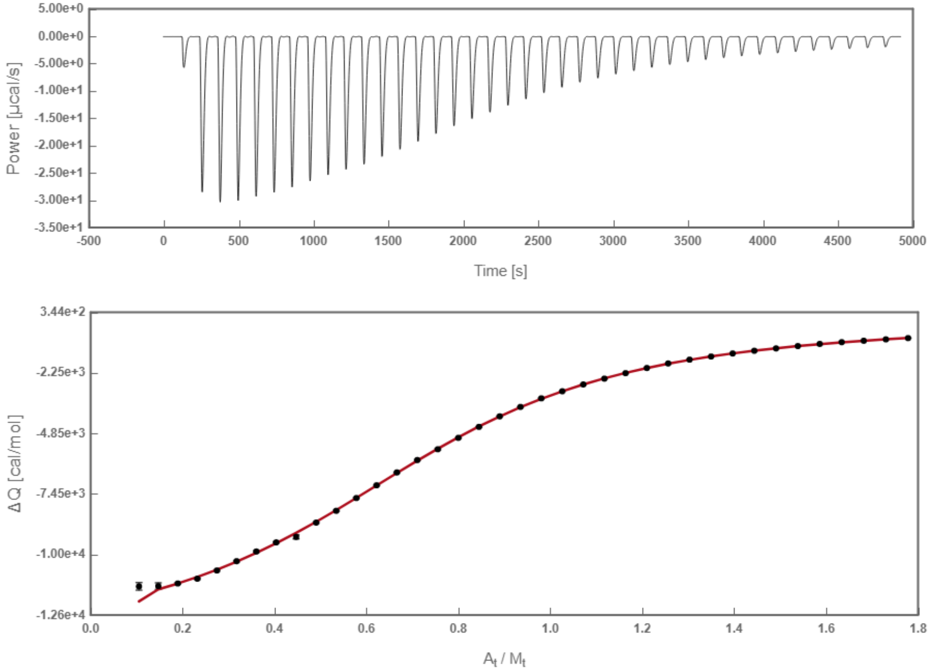

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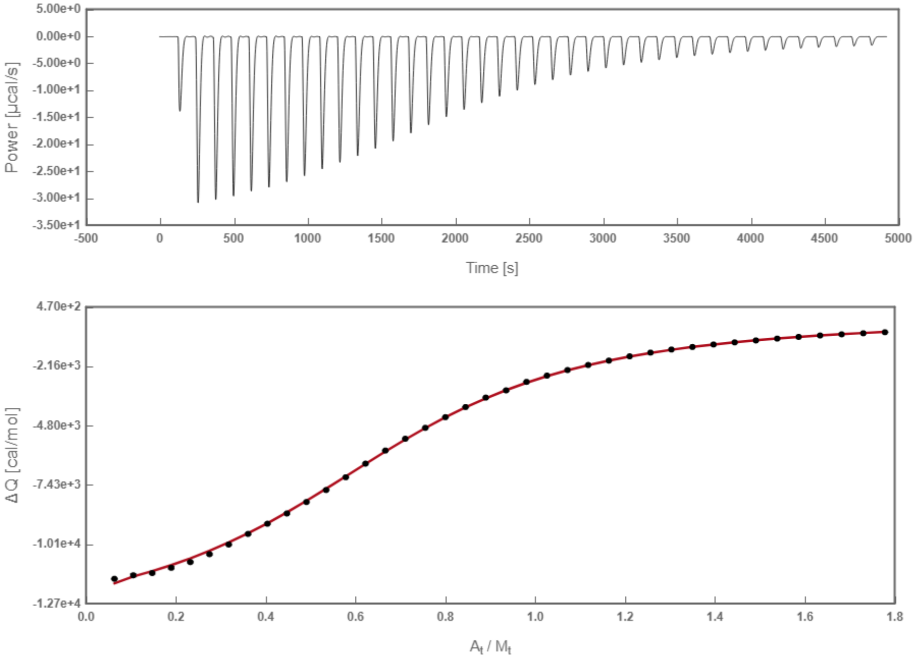

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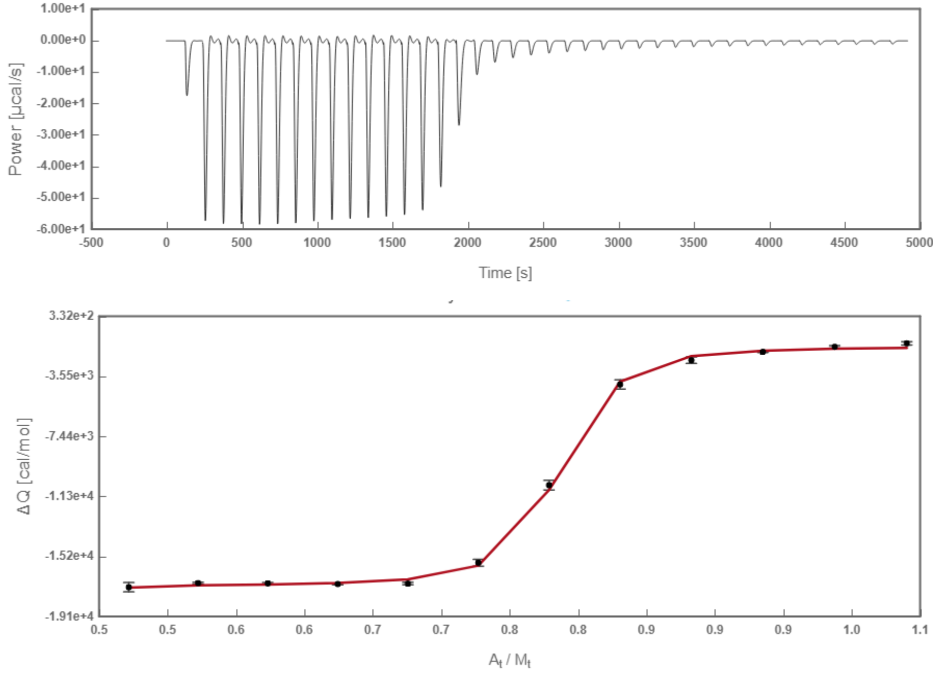

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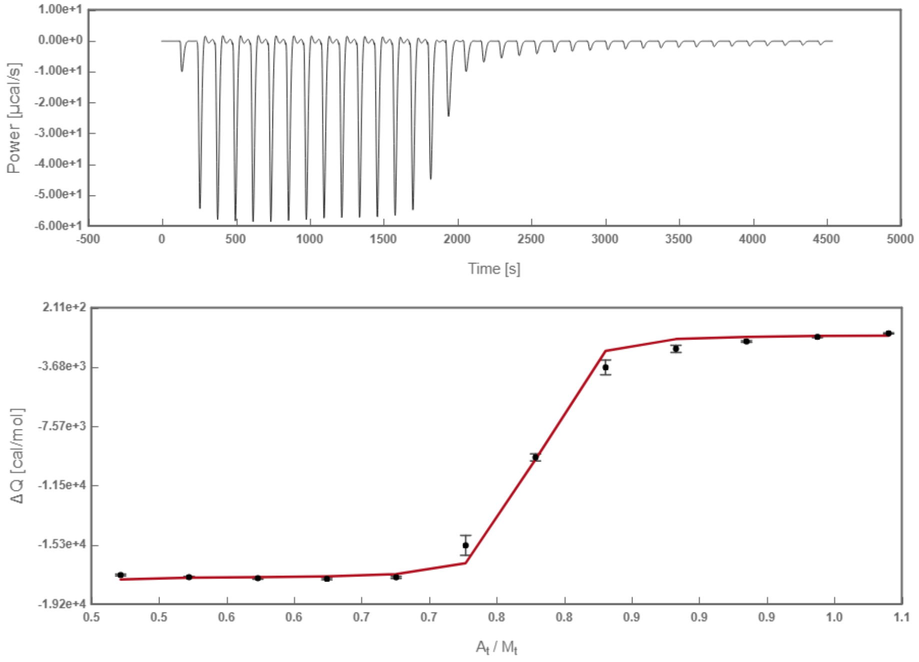

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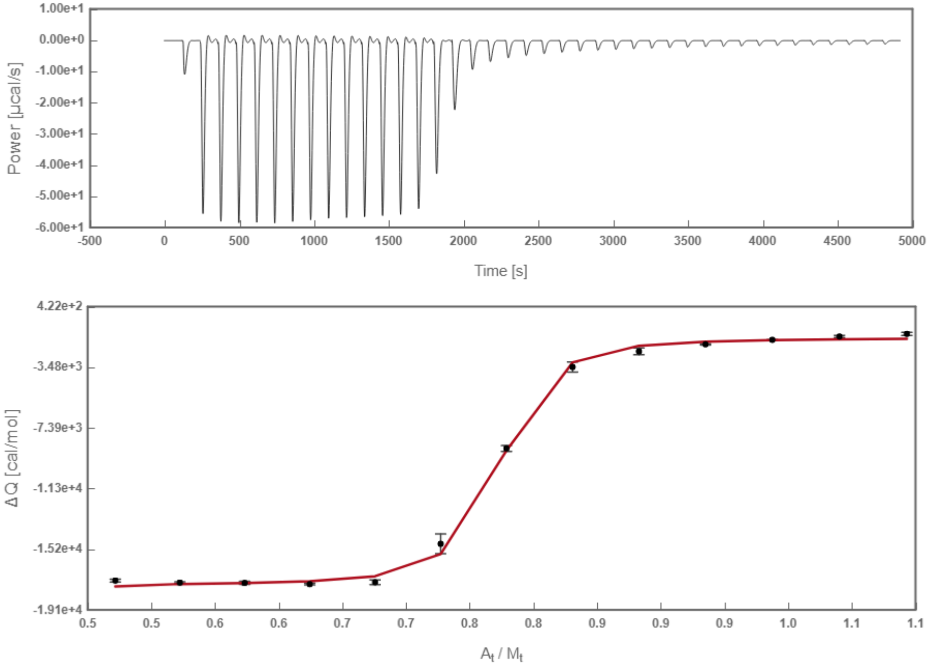

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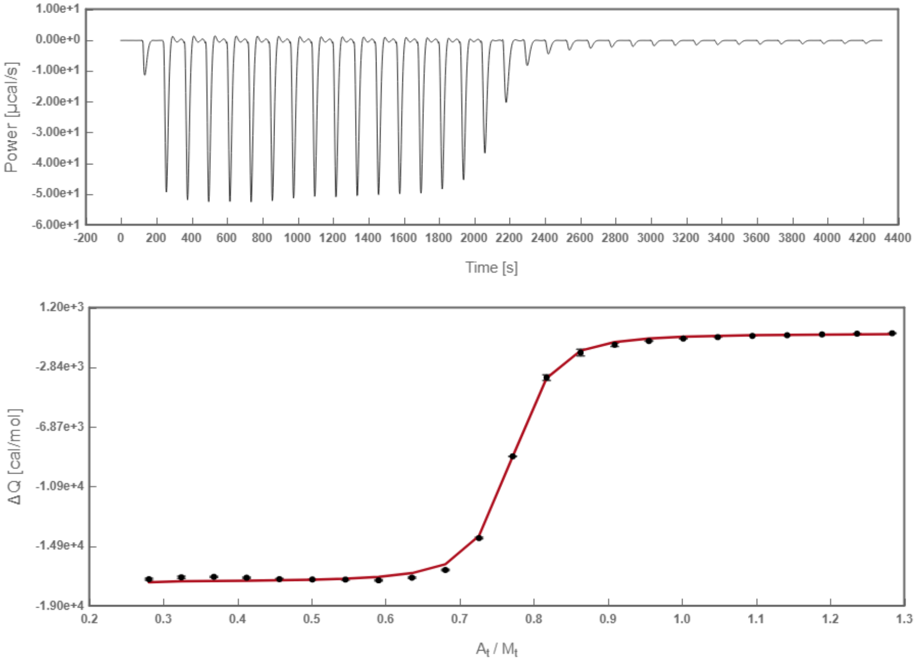

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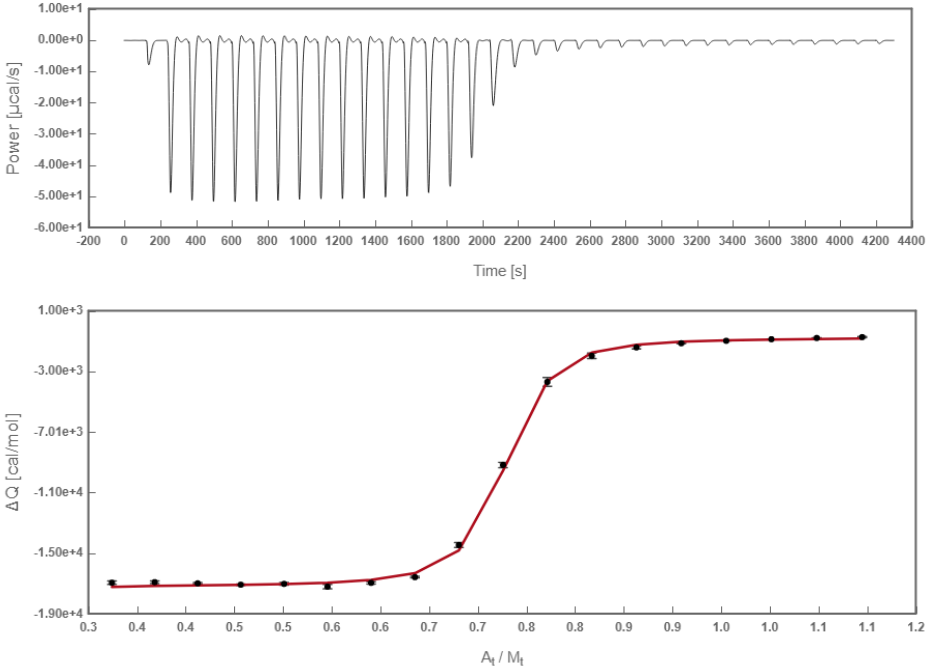

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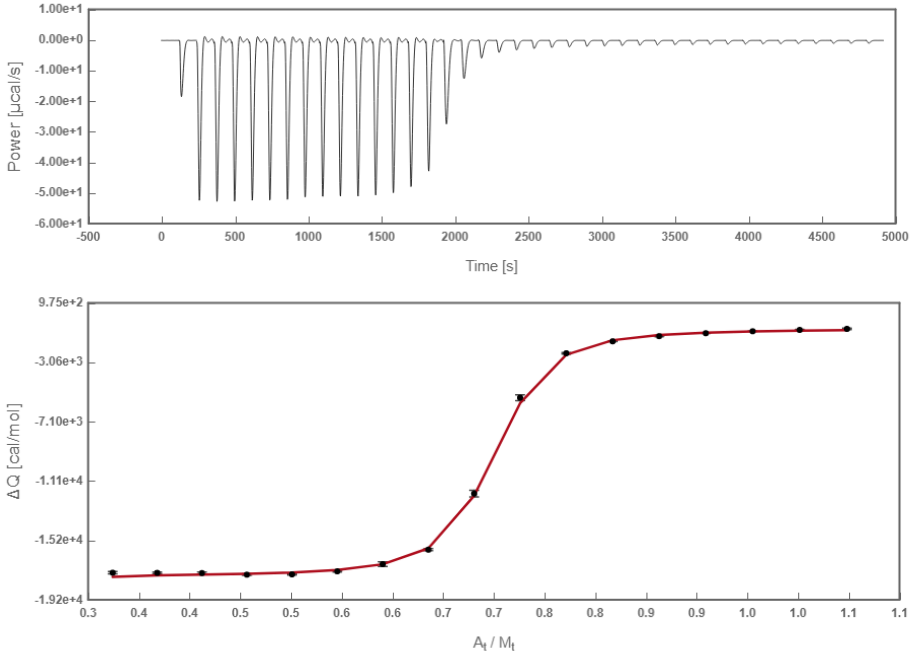

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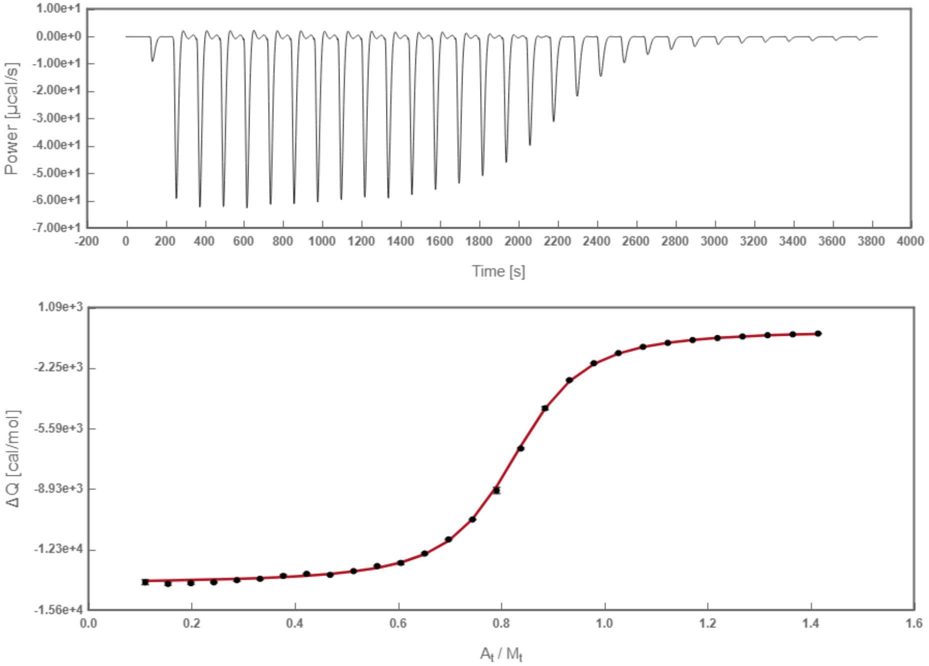

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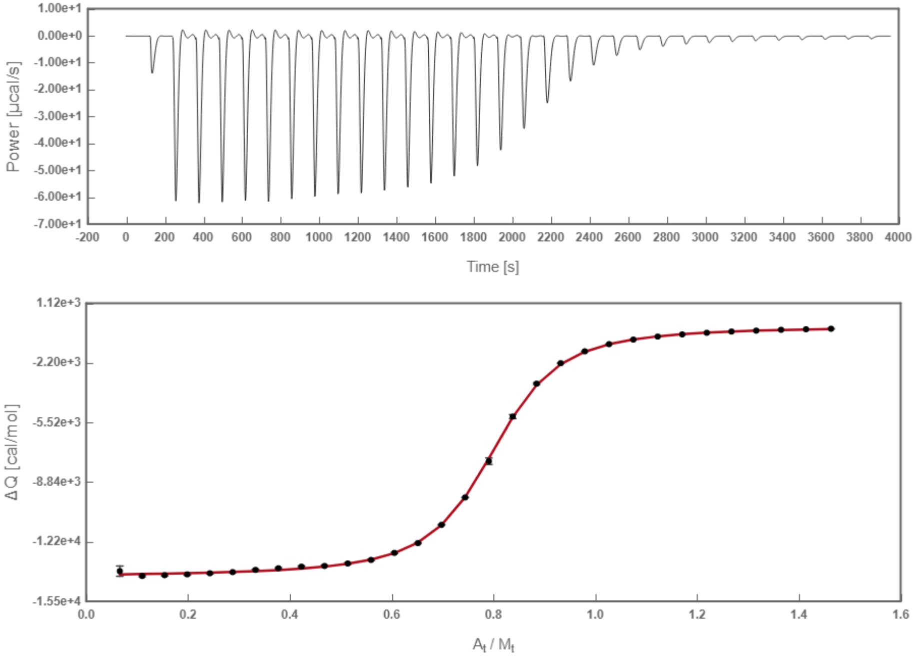

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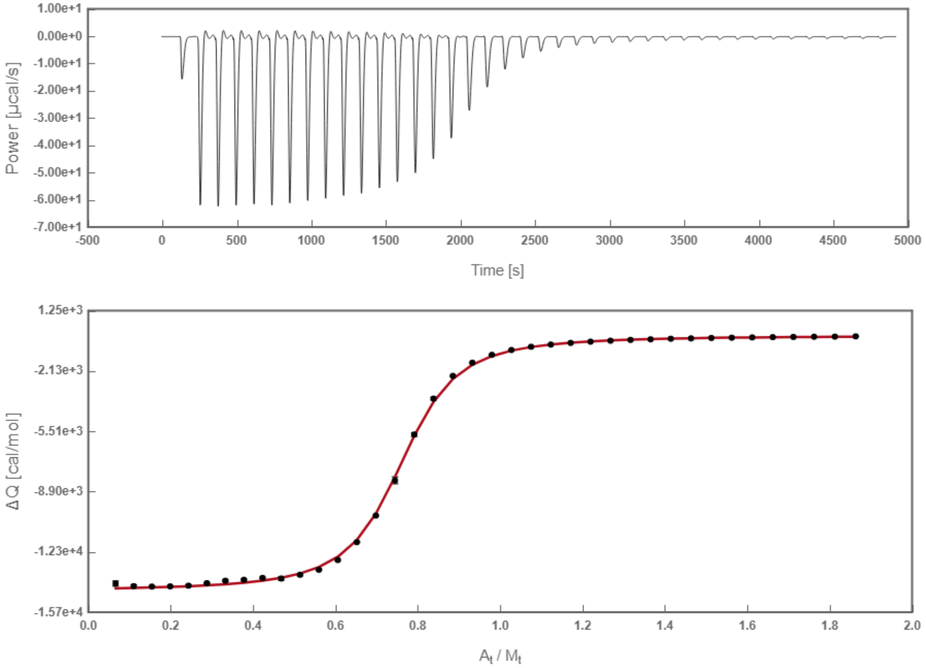

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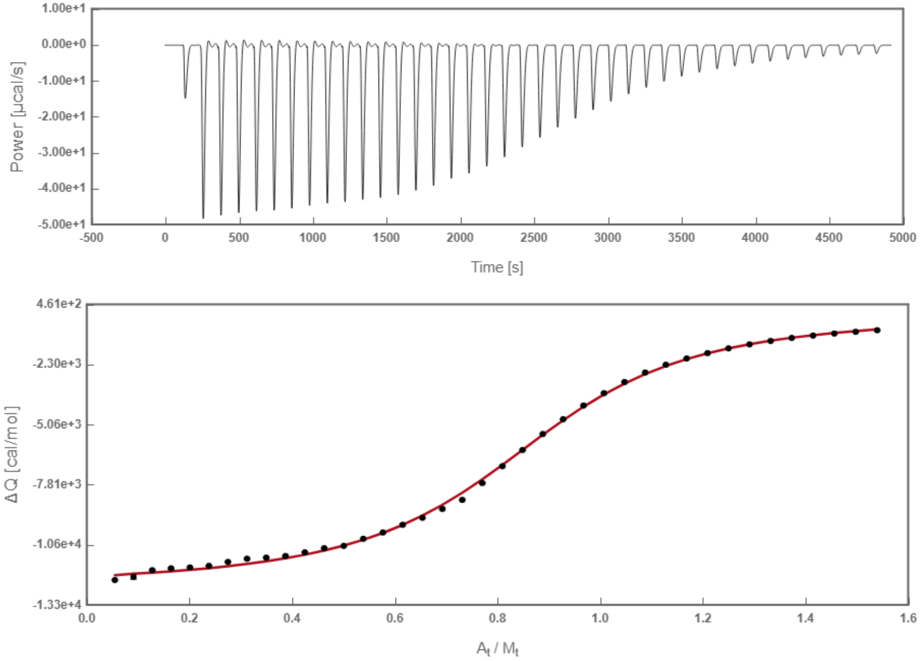

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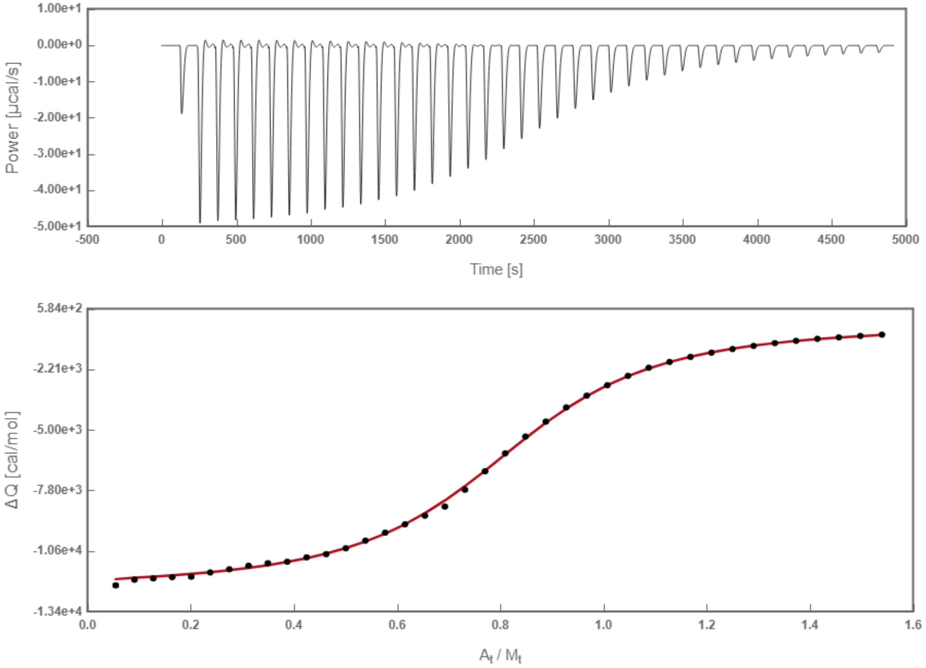

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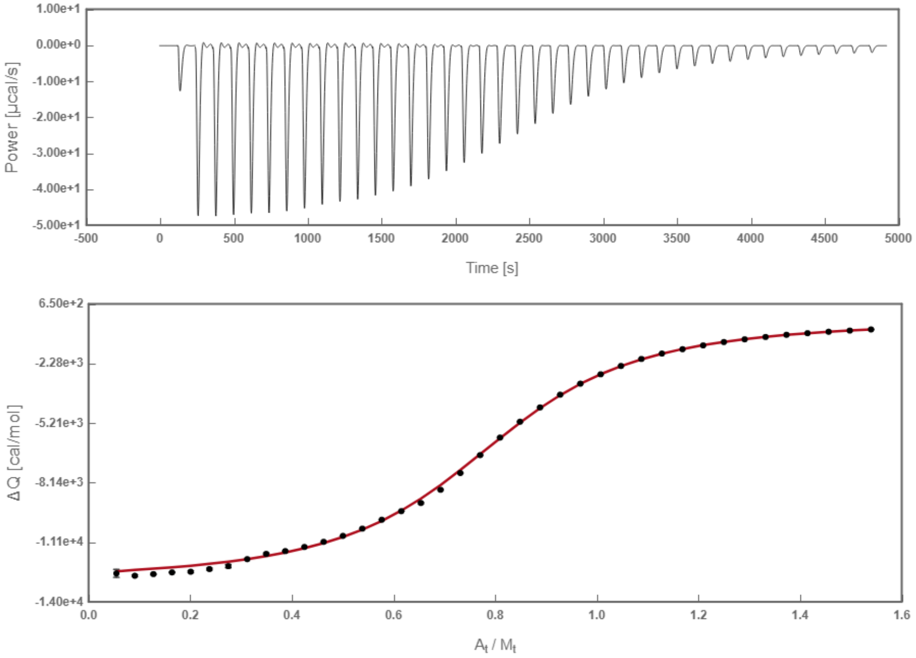

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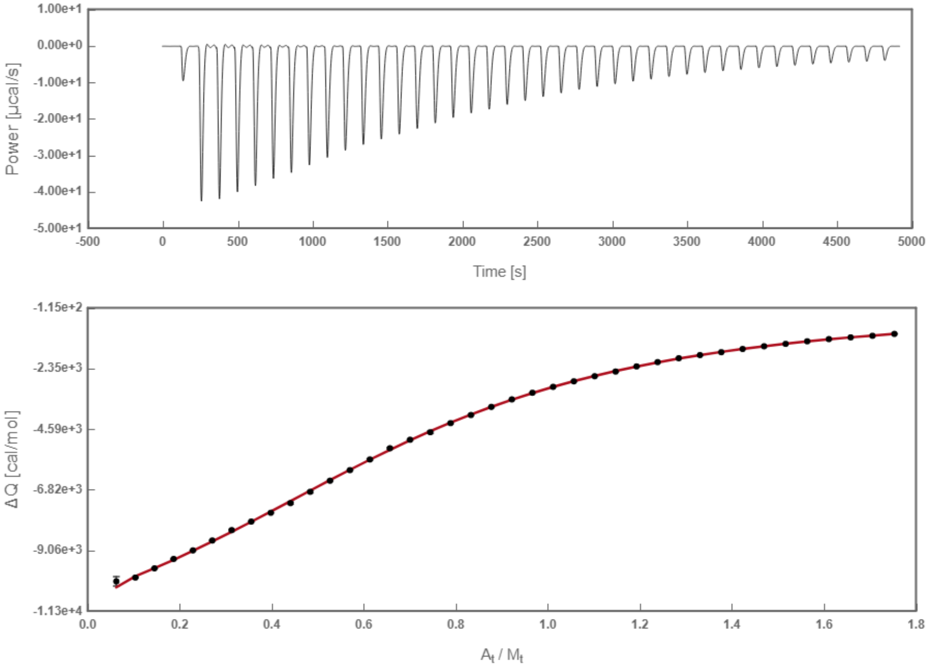

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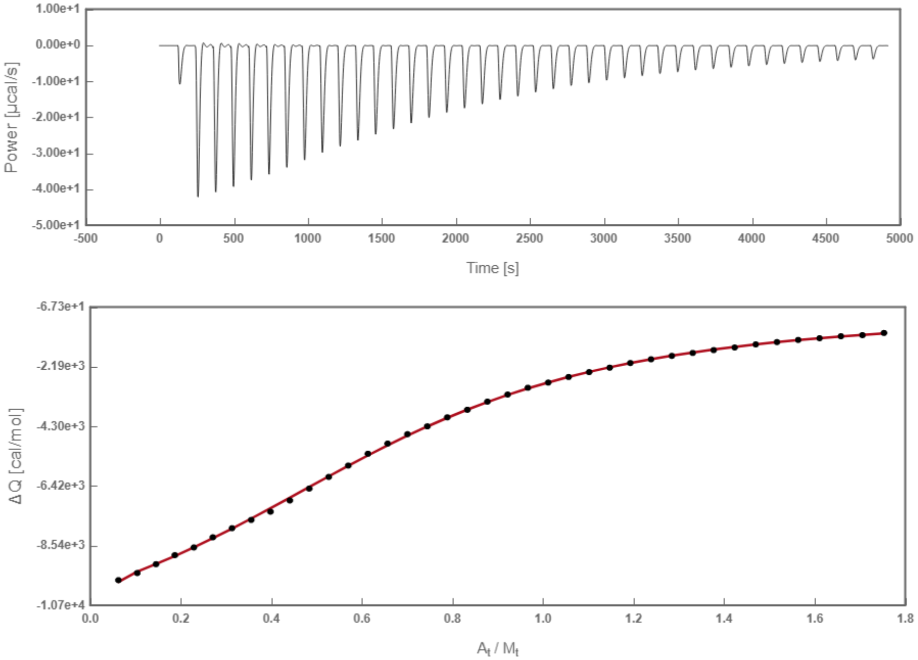

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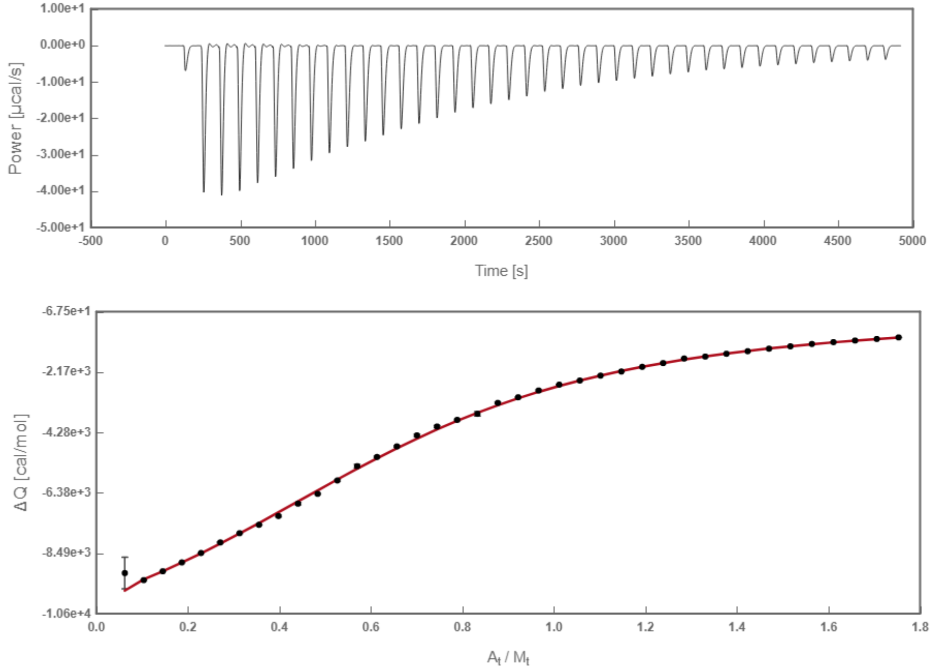
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Time [s]
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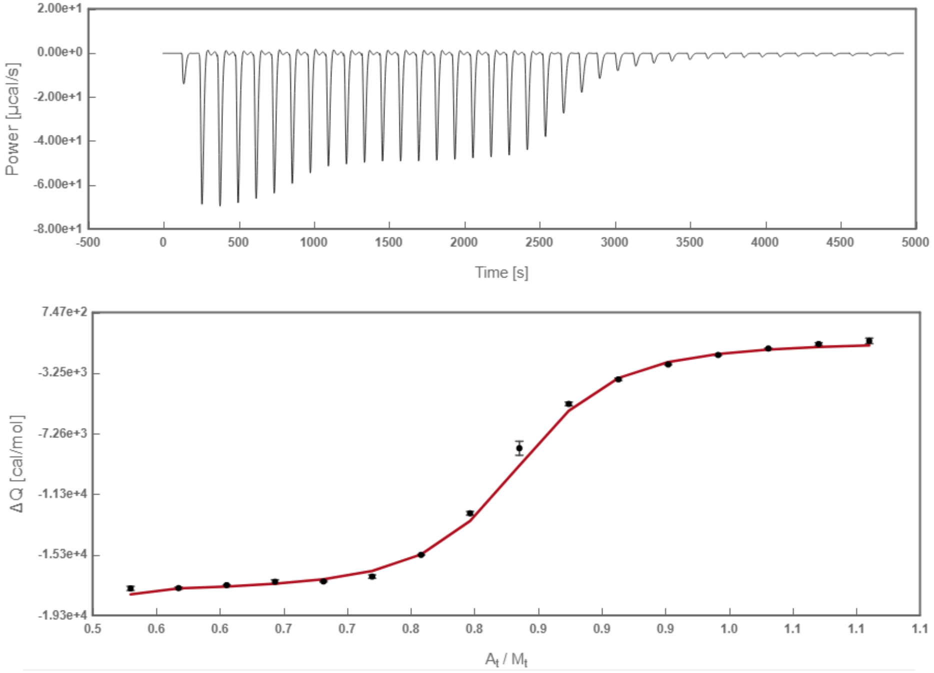
A_t / M_t

RM1085e3



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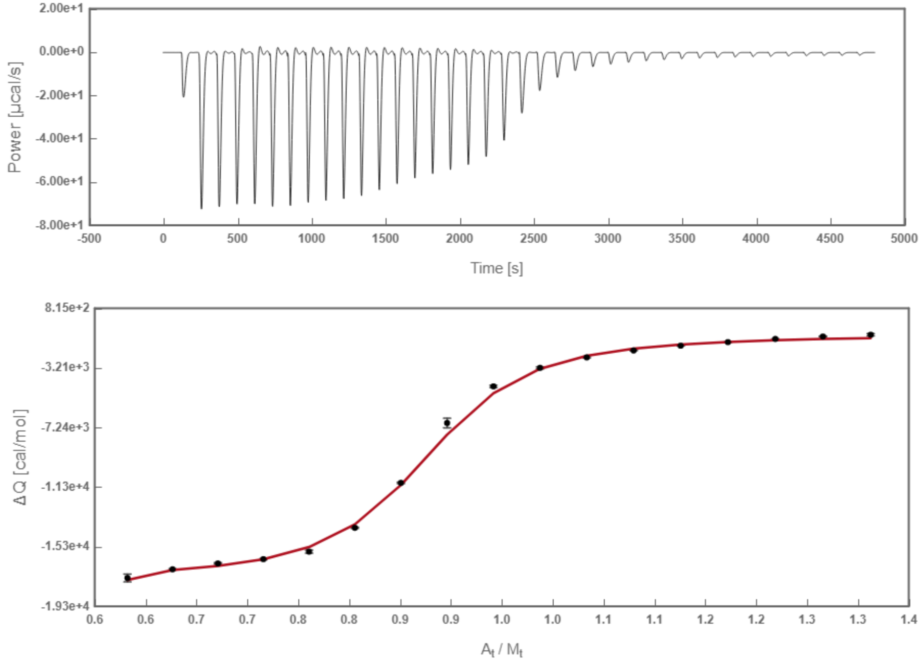

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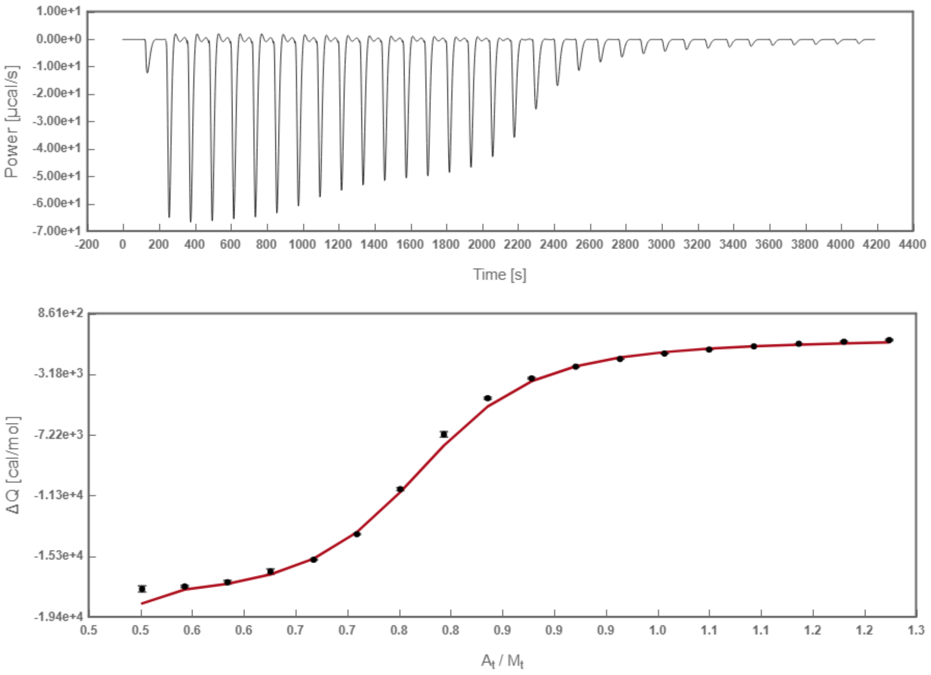

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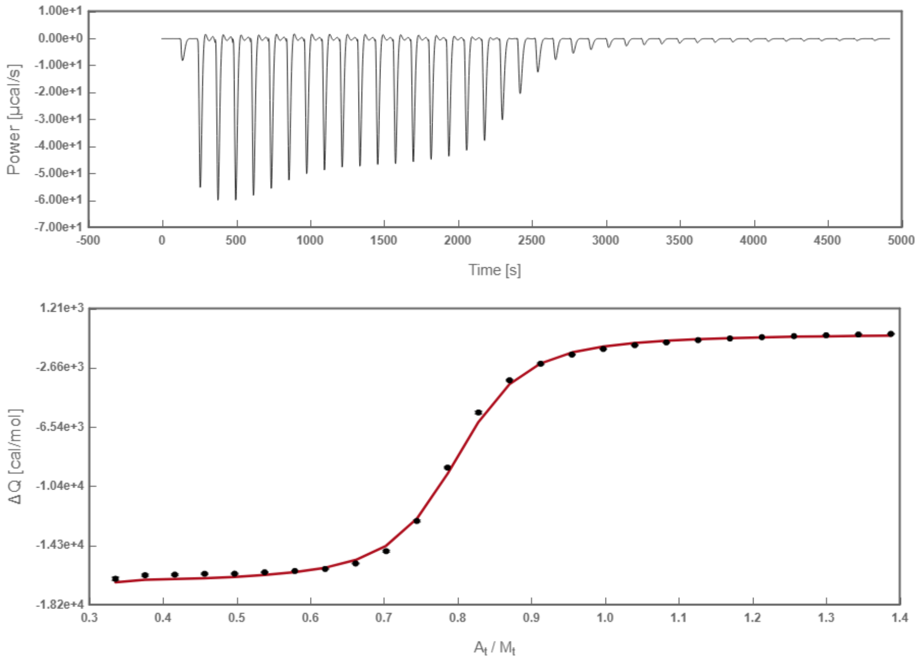

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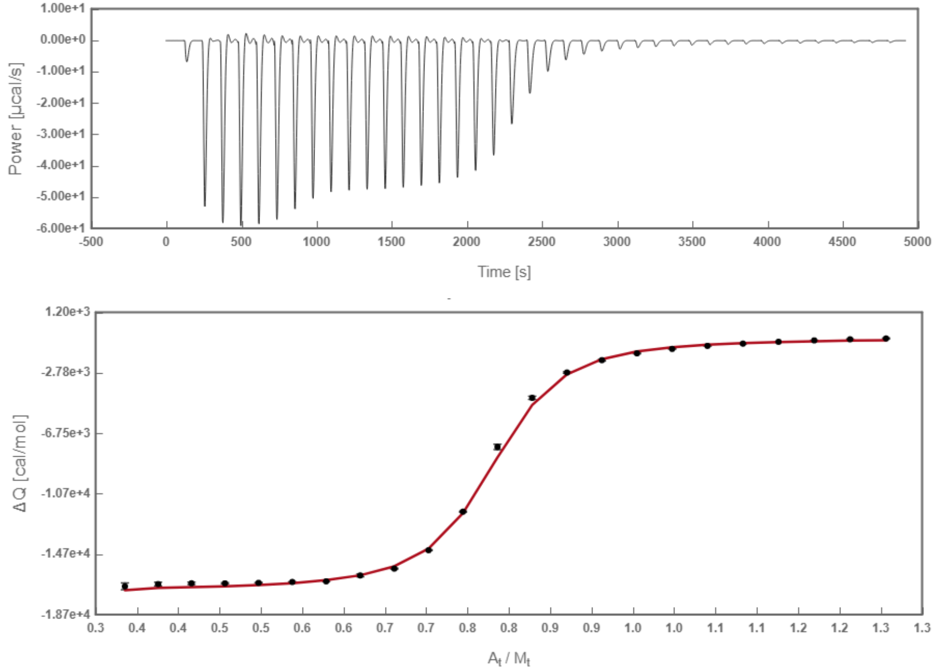

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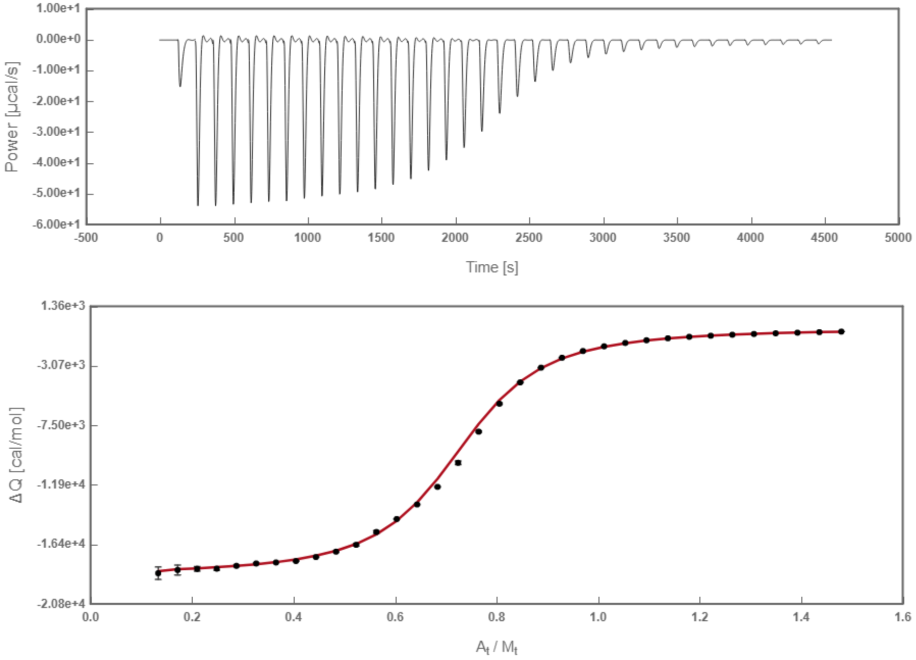

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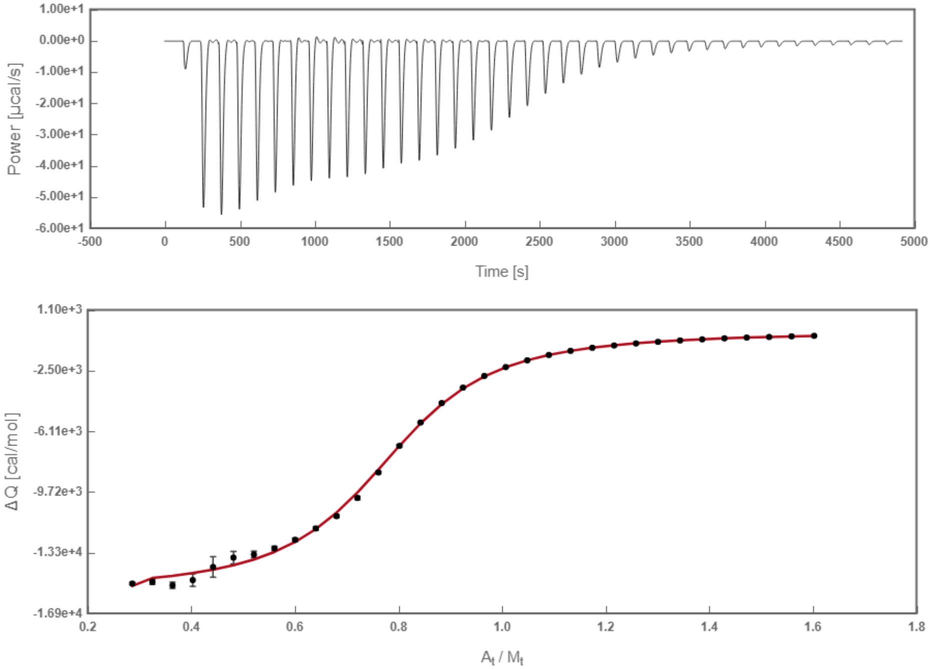

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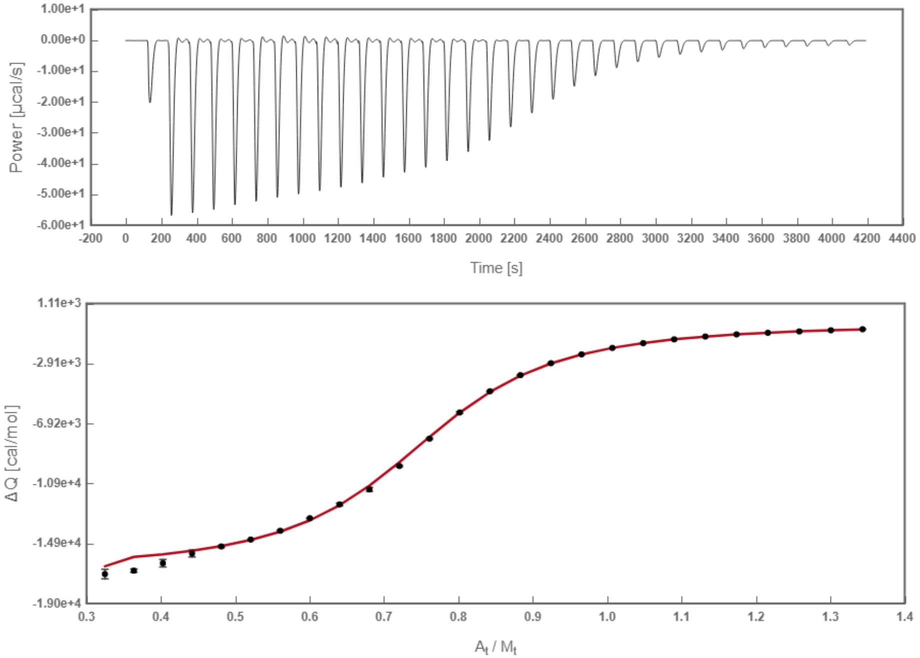

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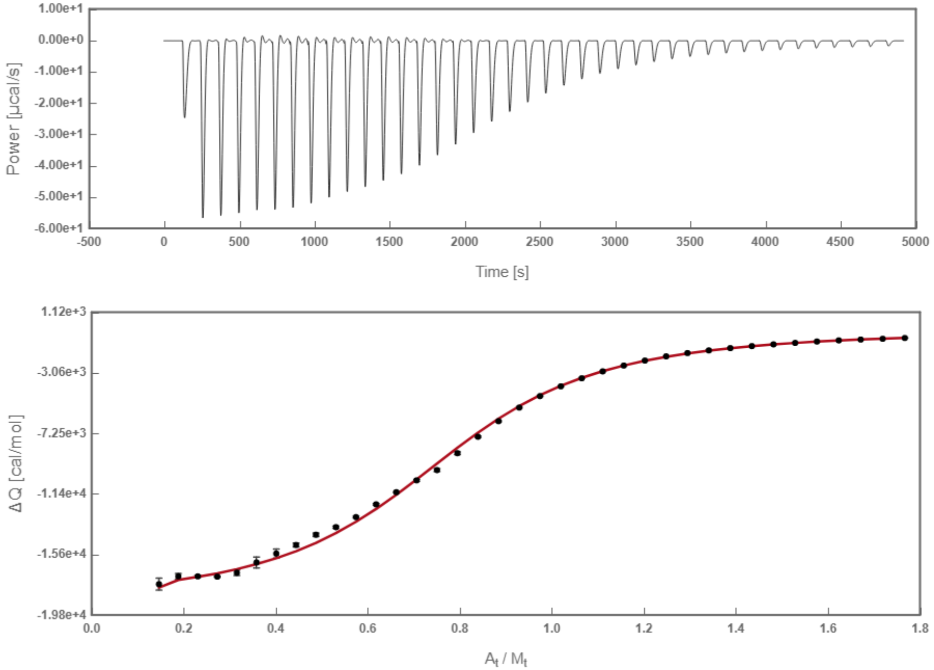

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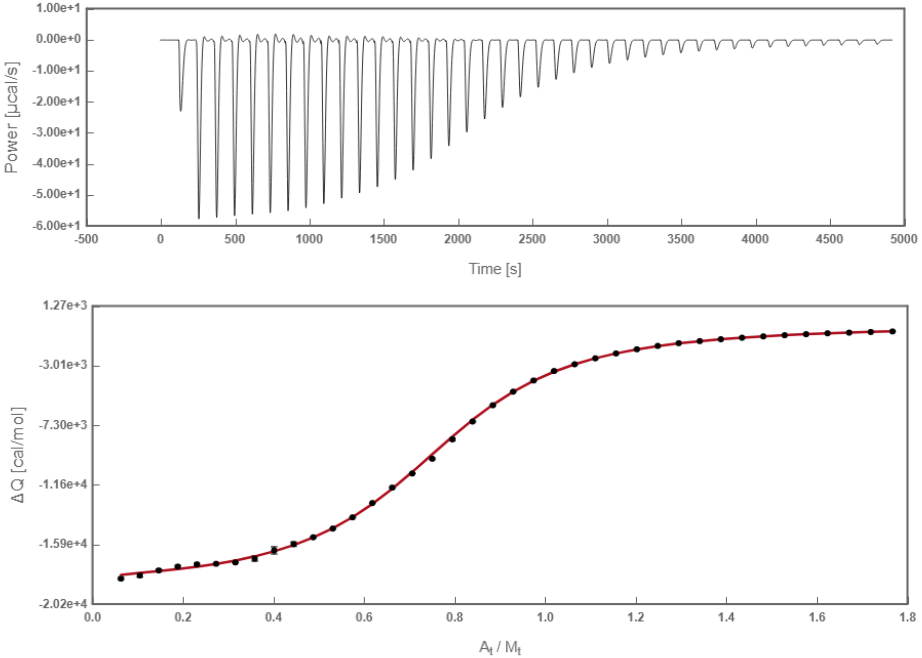

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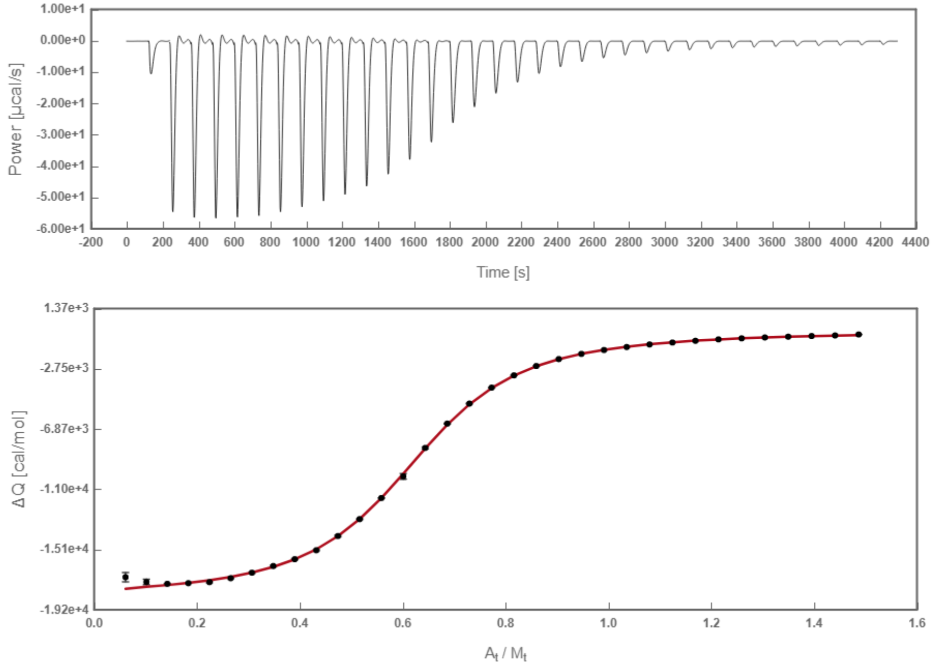

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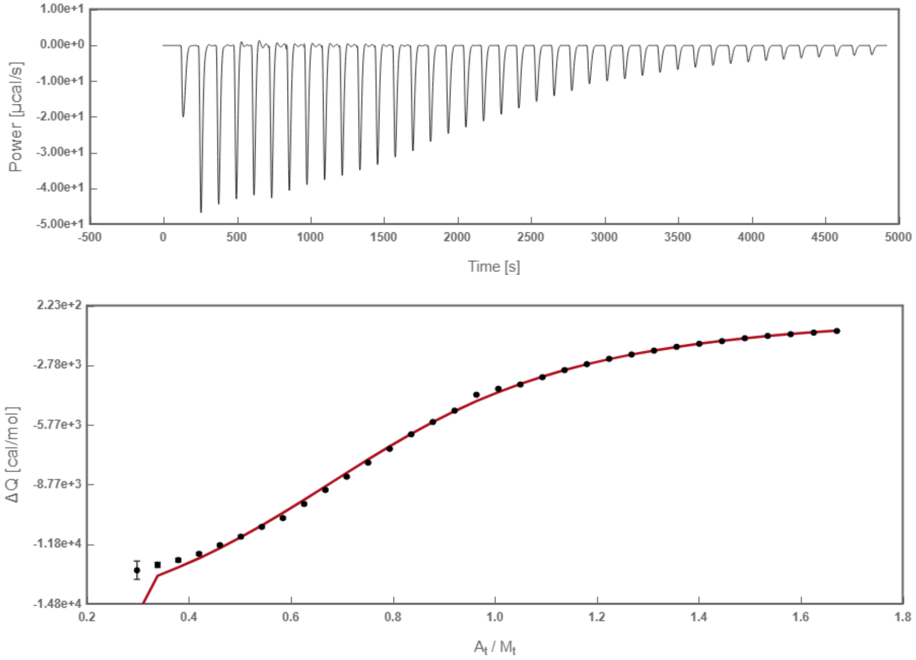

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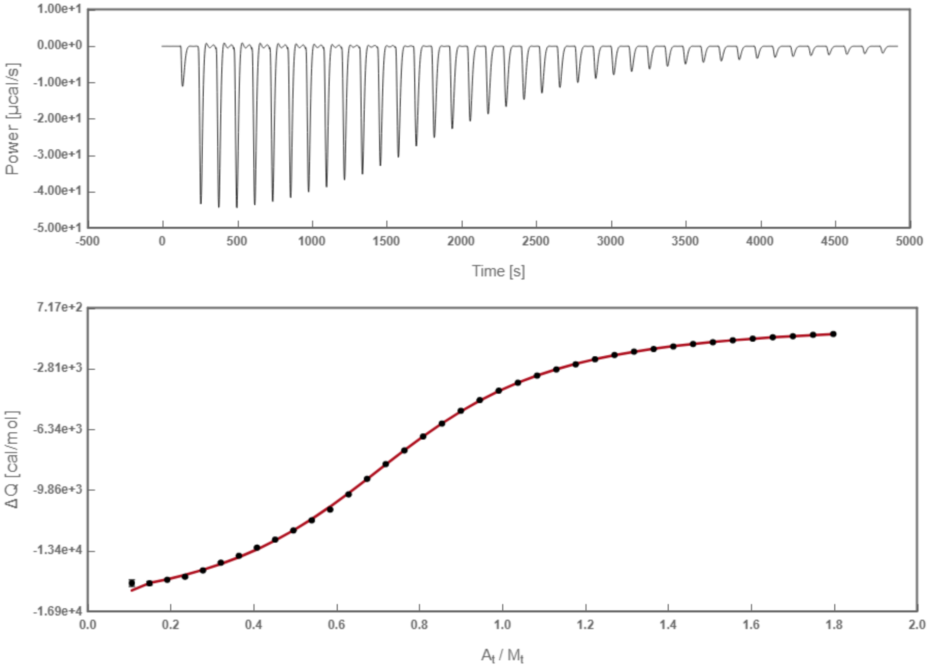

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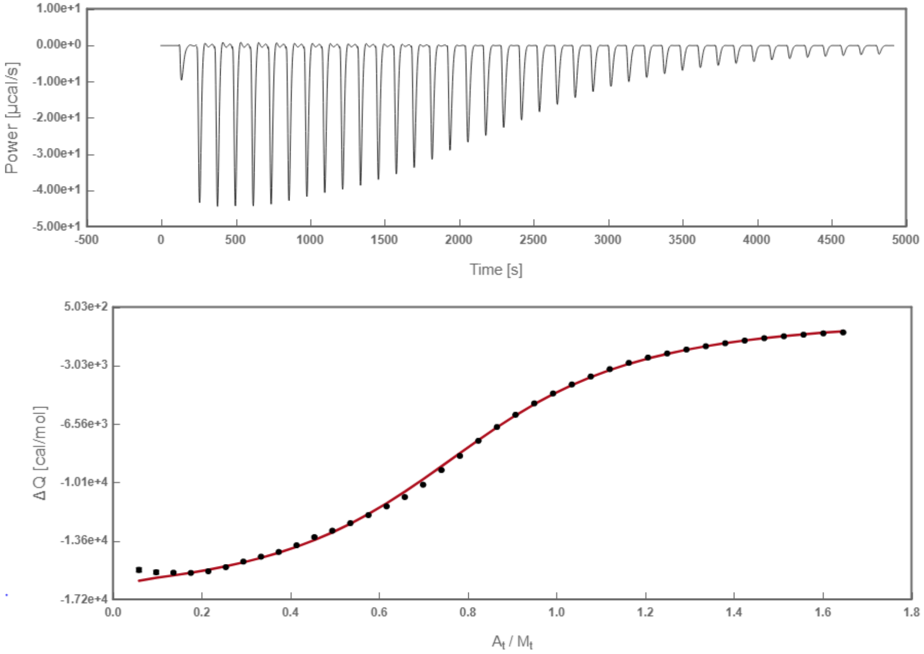

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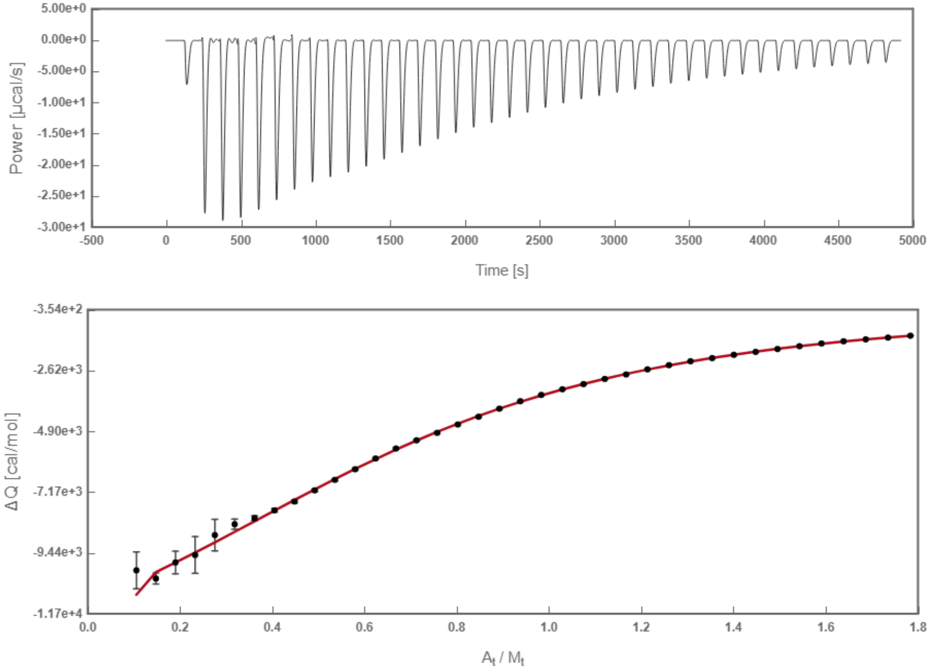

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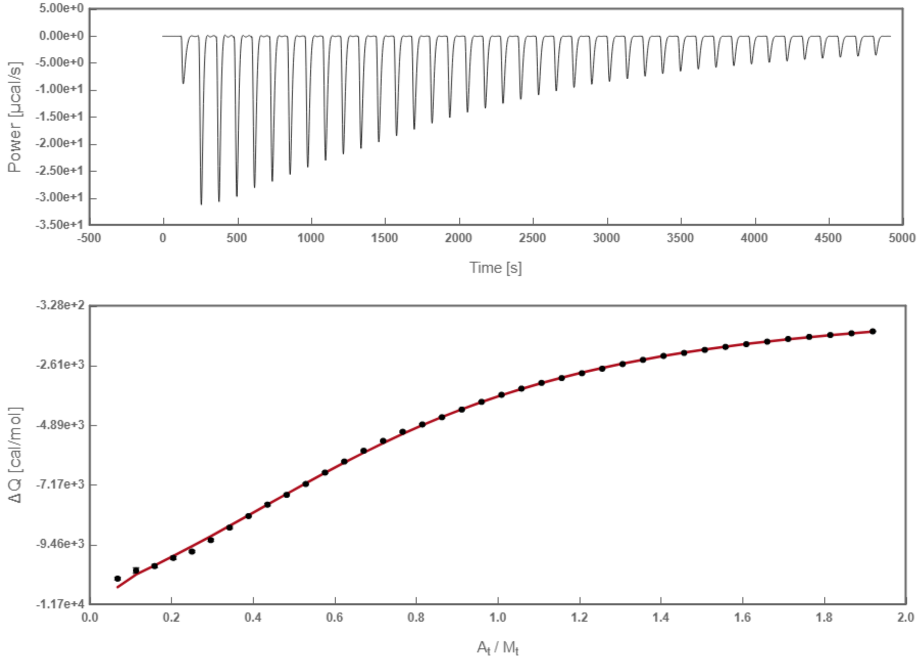

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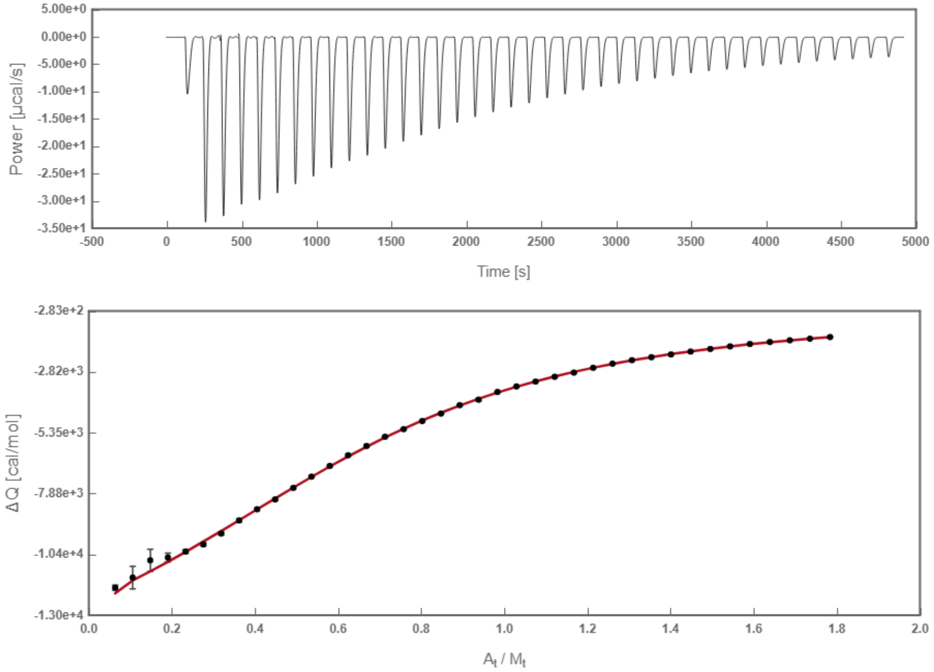

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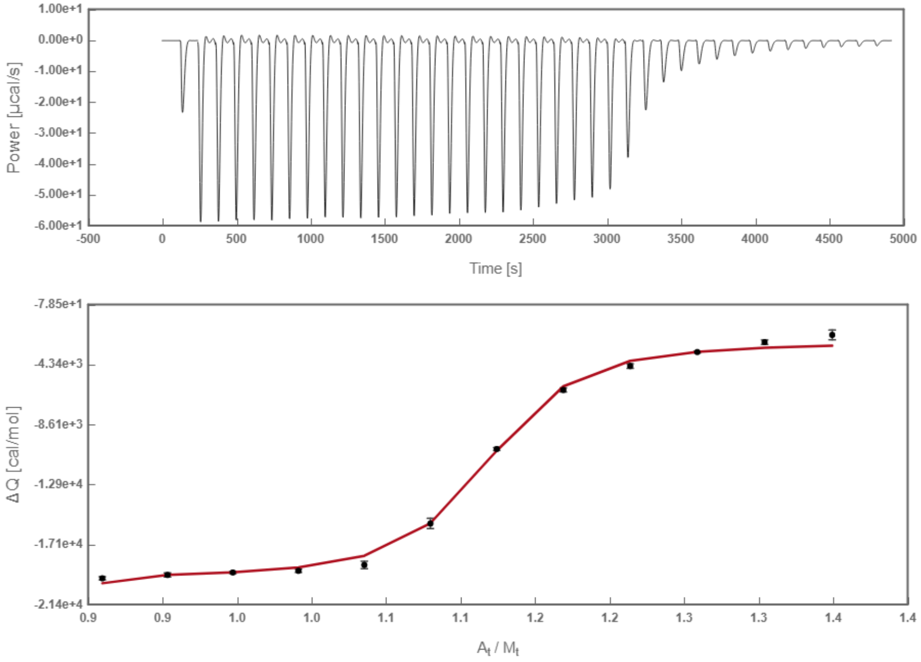

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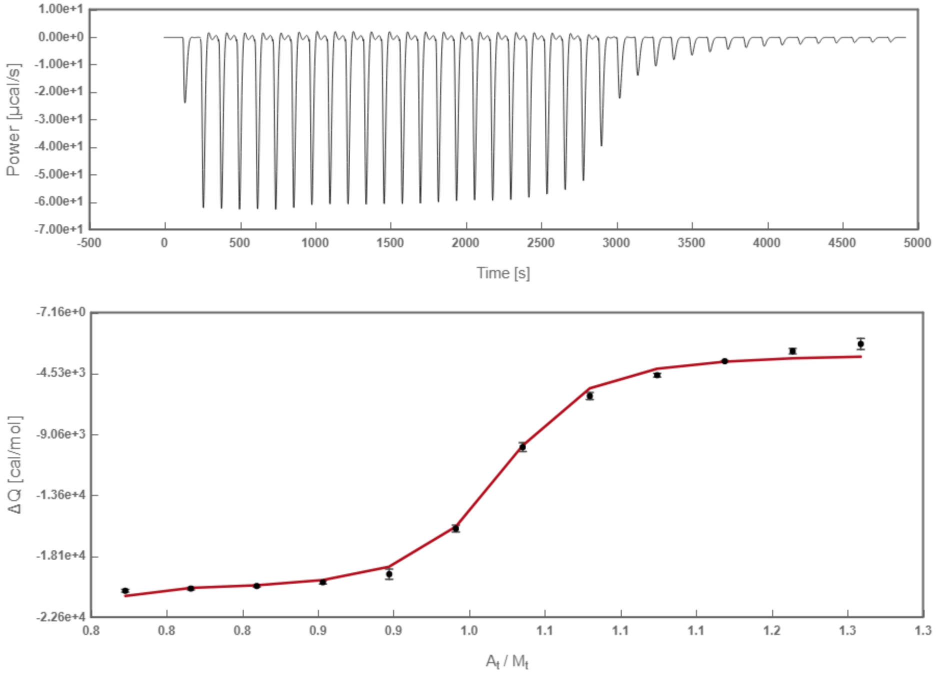

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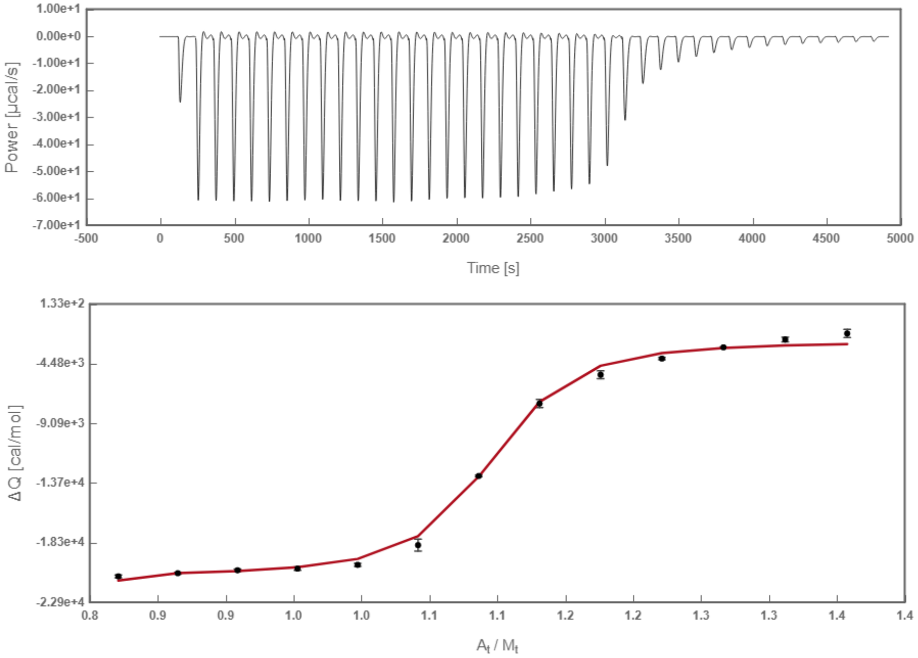

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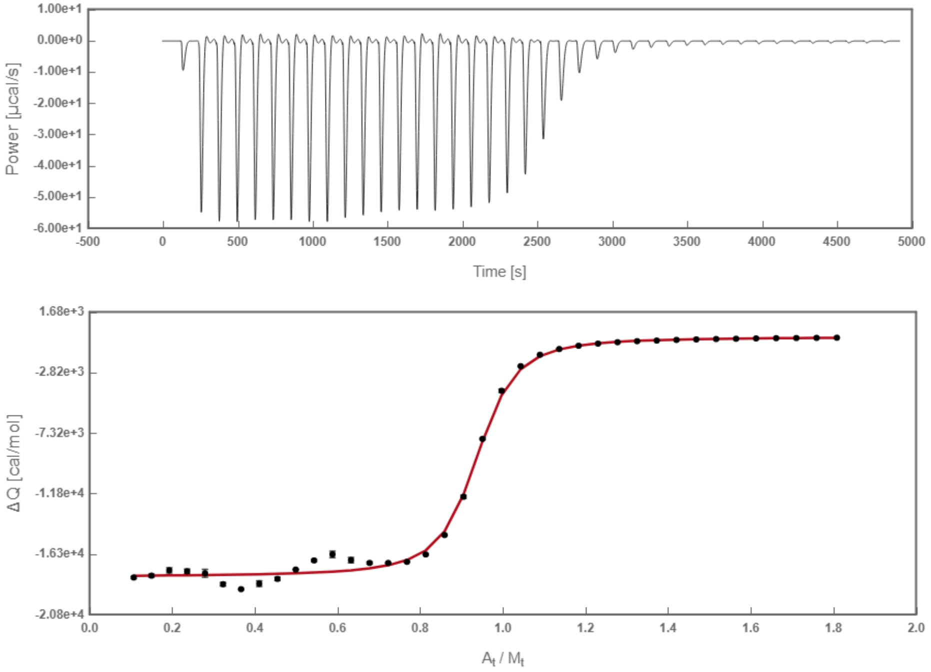

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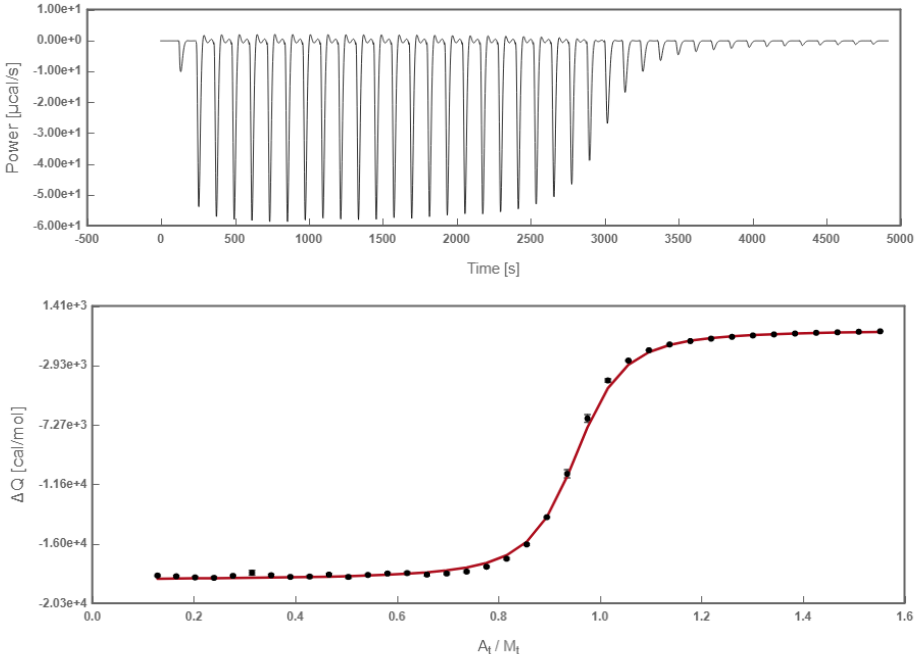

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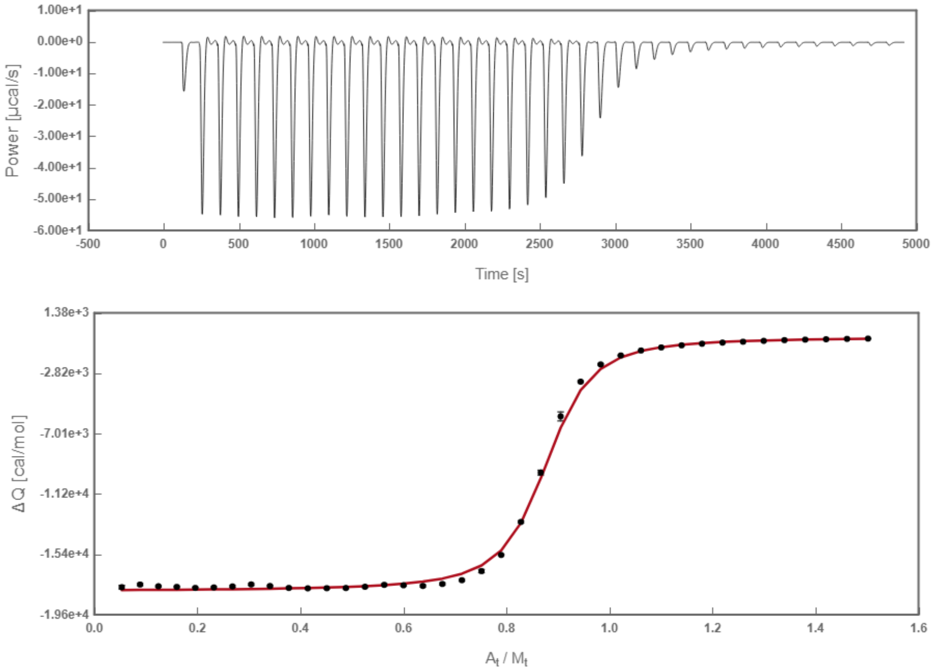

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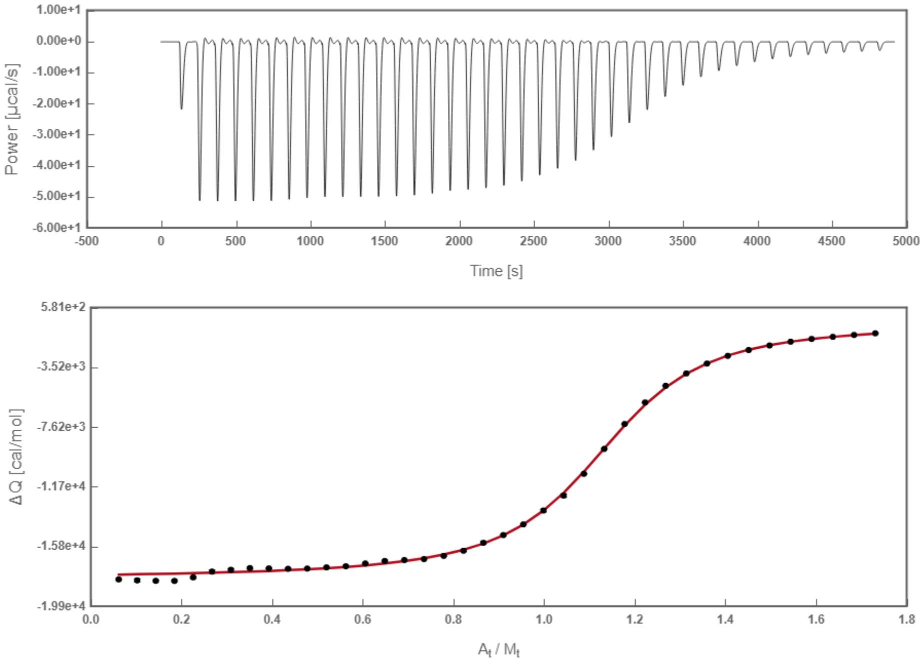

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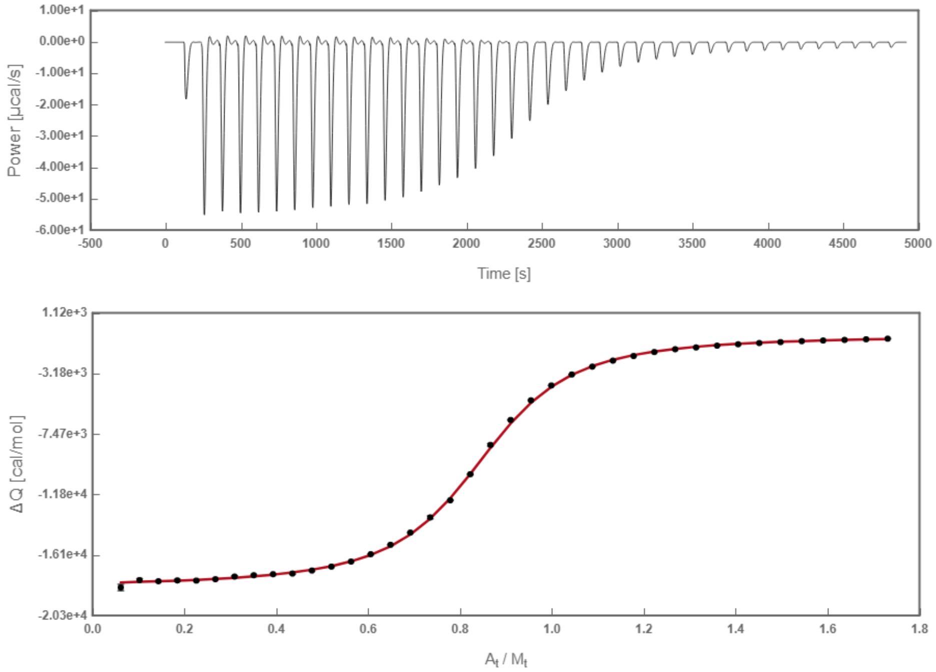

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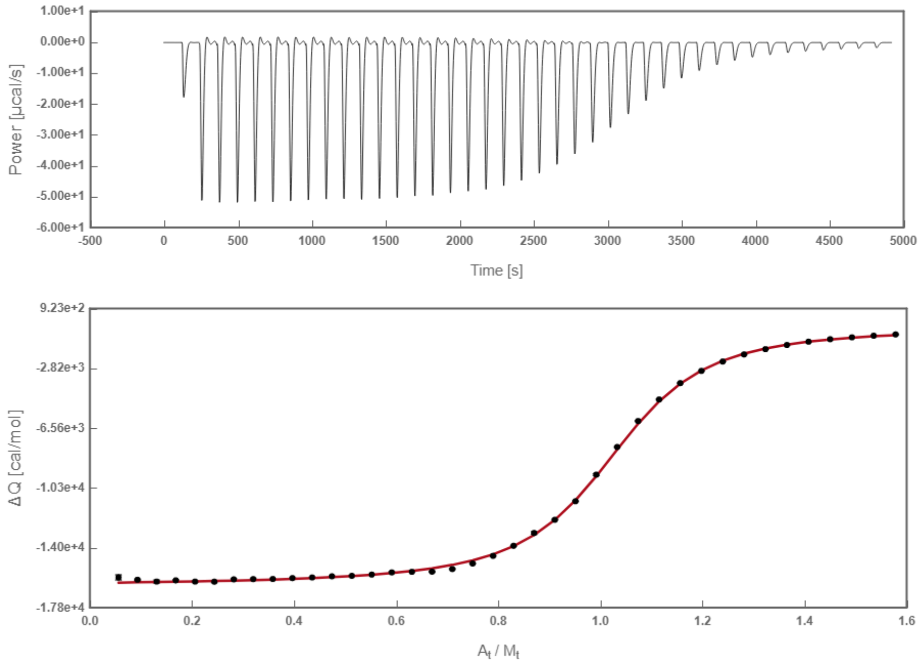

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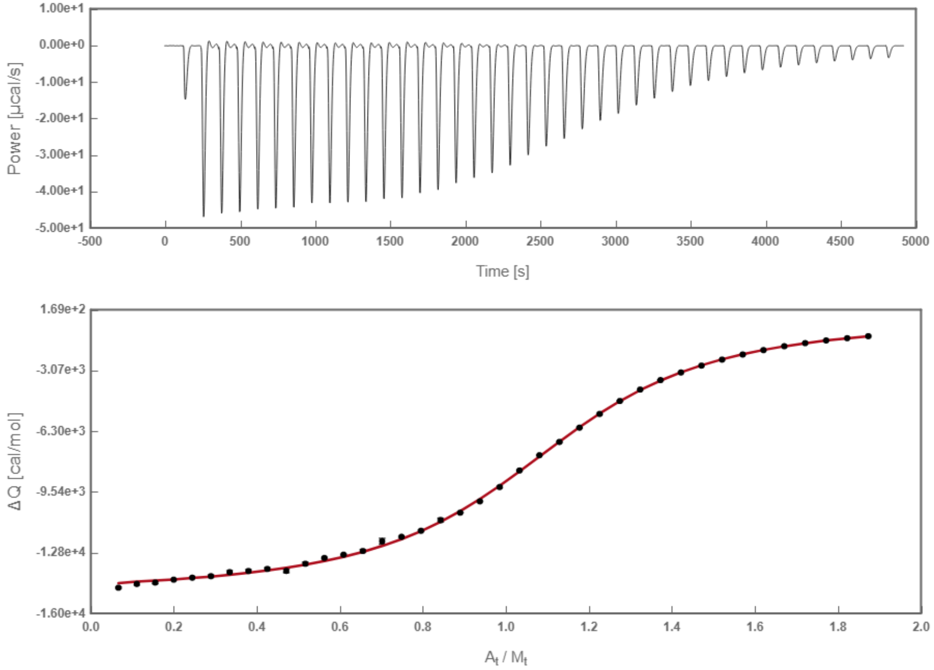

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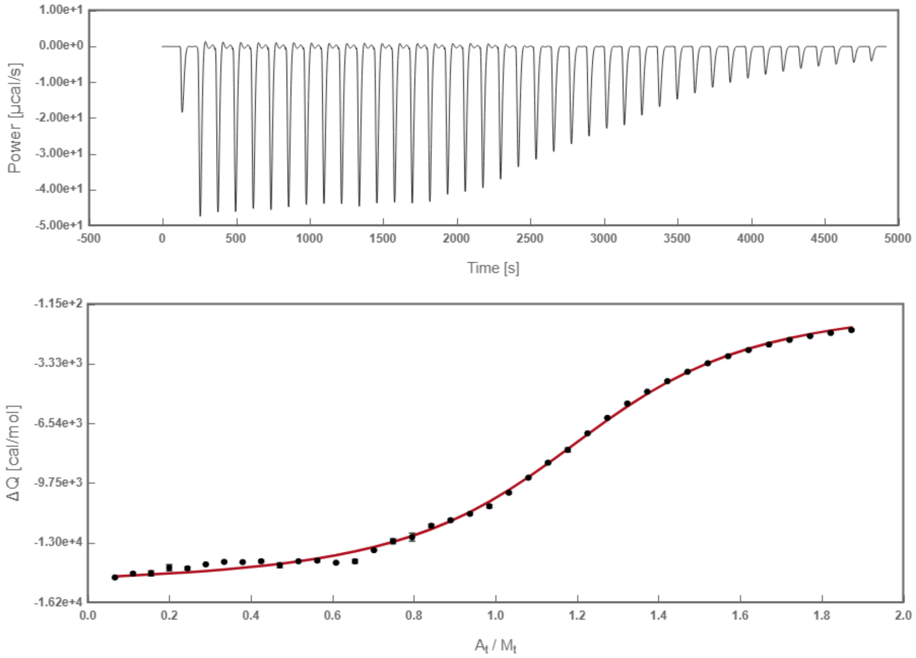

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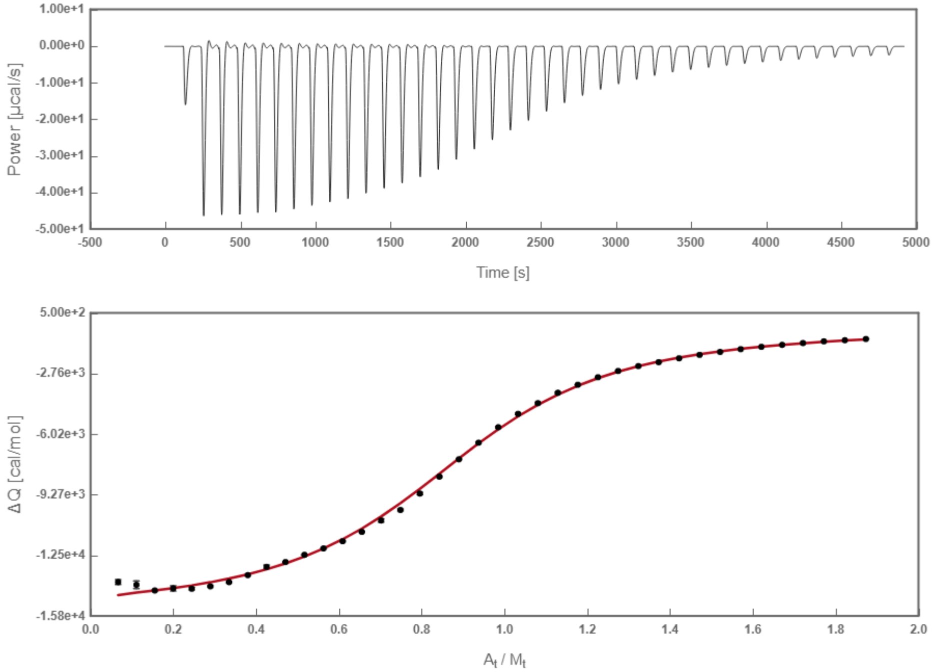

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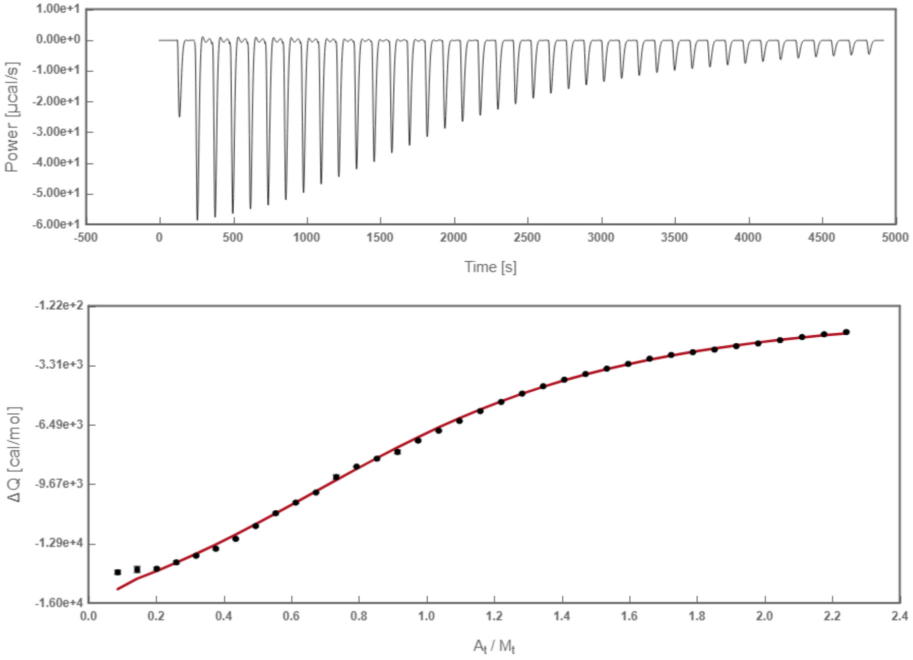

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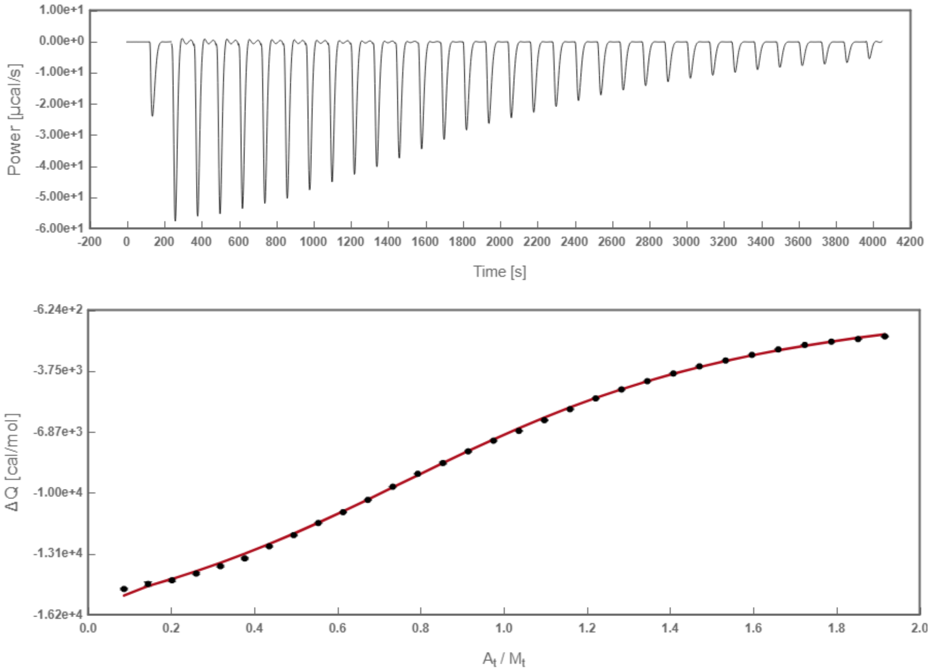

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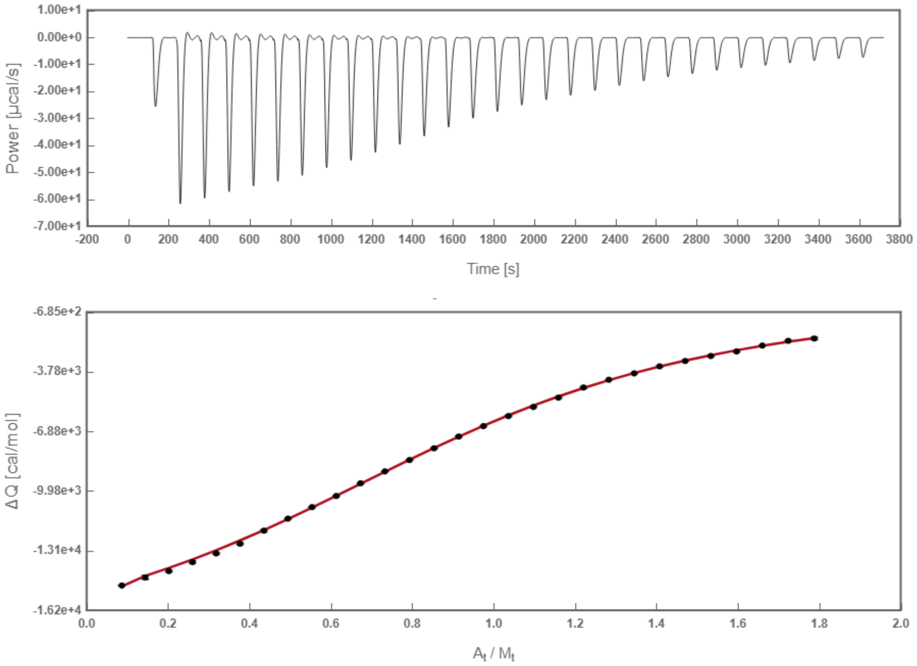

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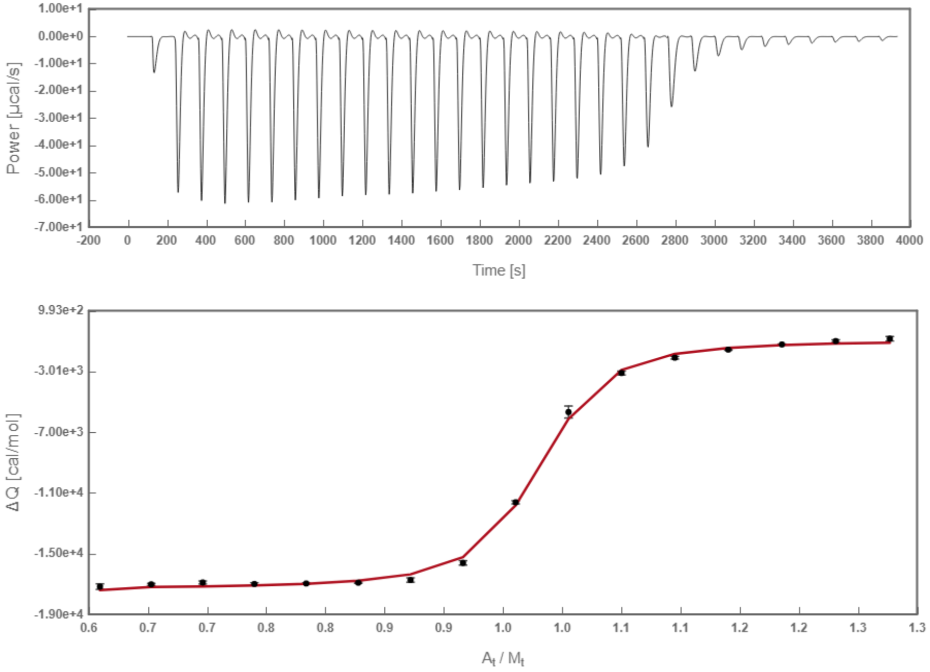

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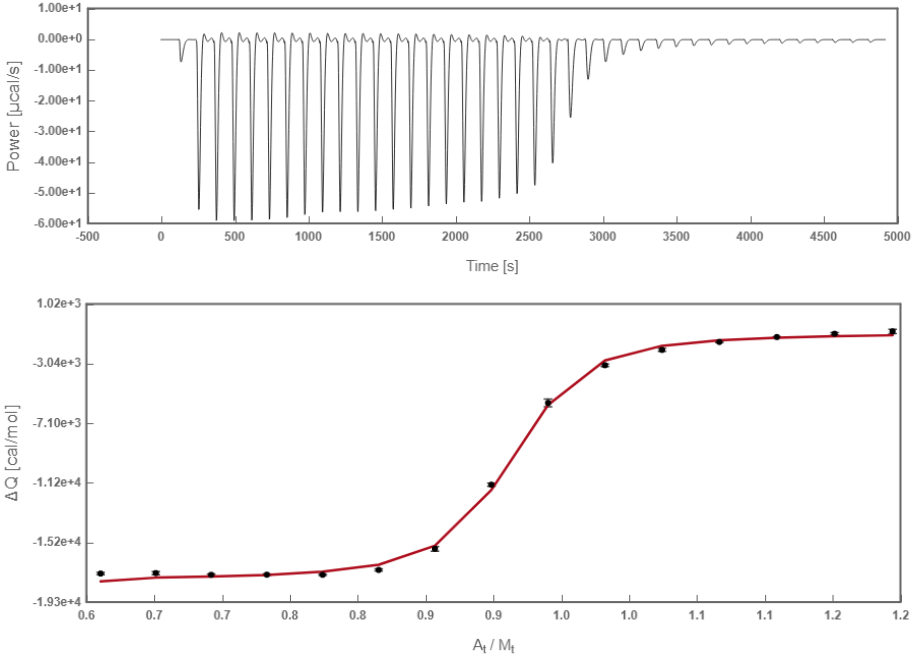

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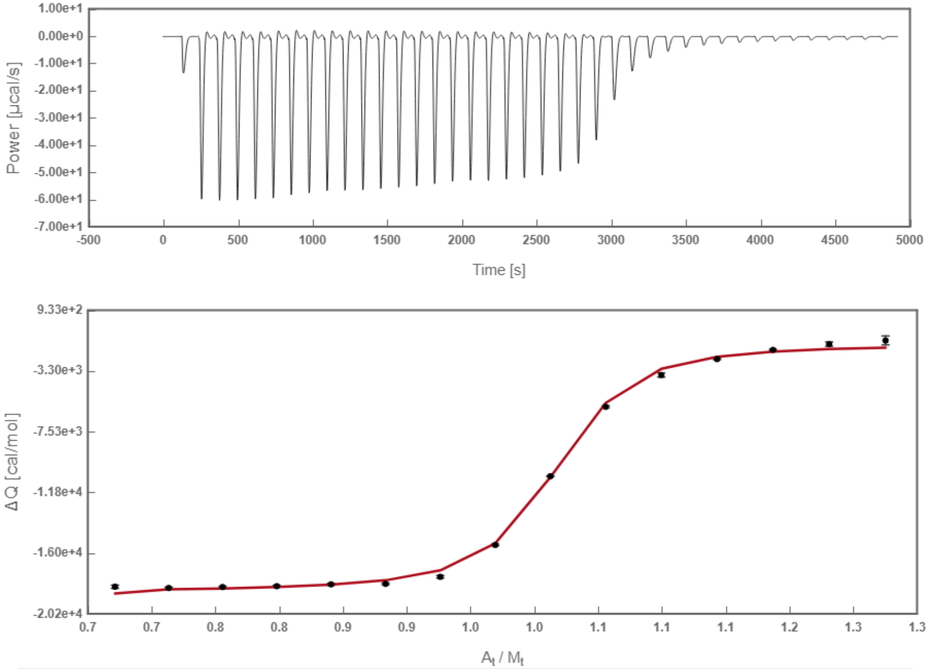

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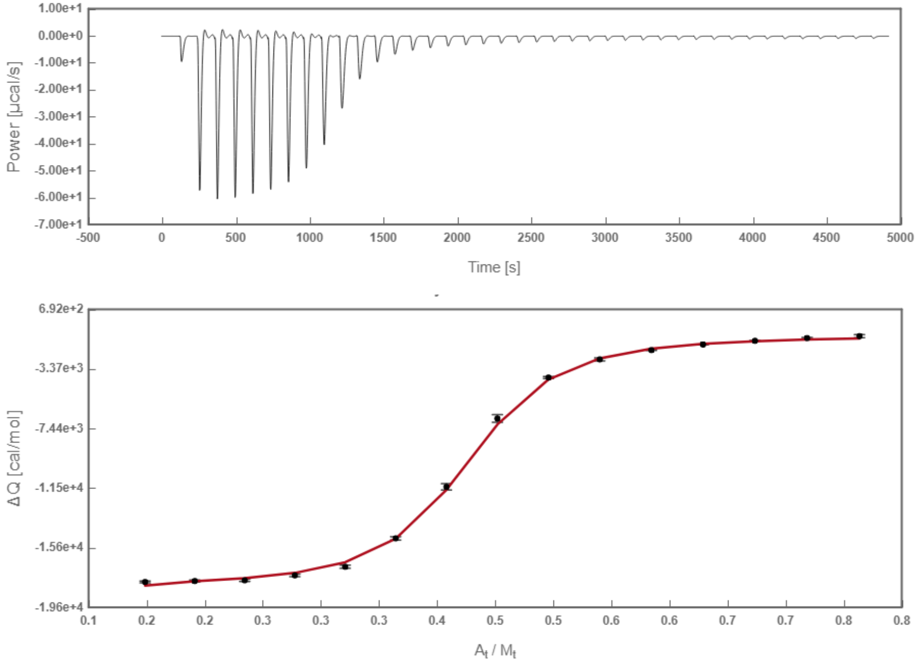

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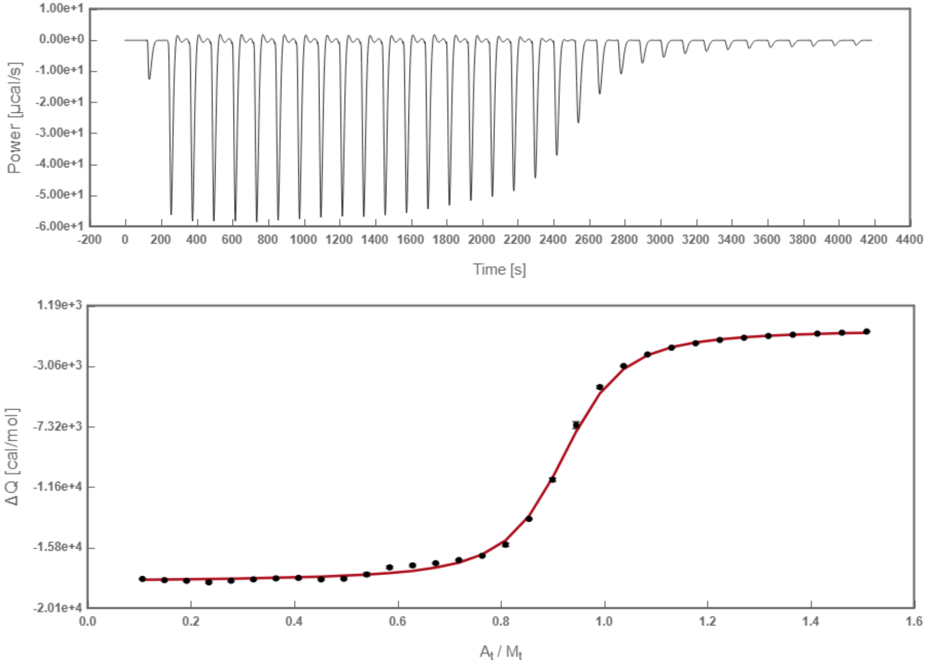

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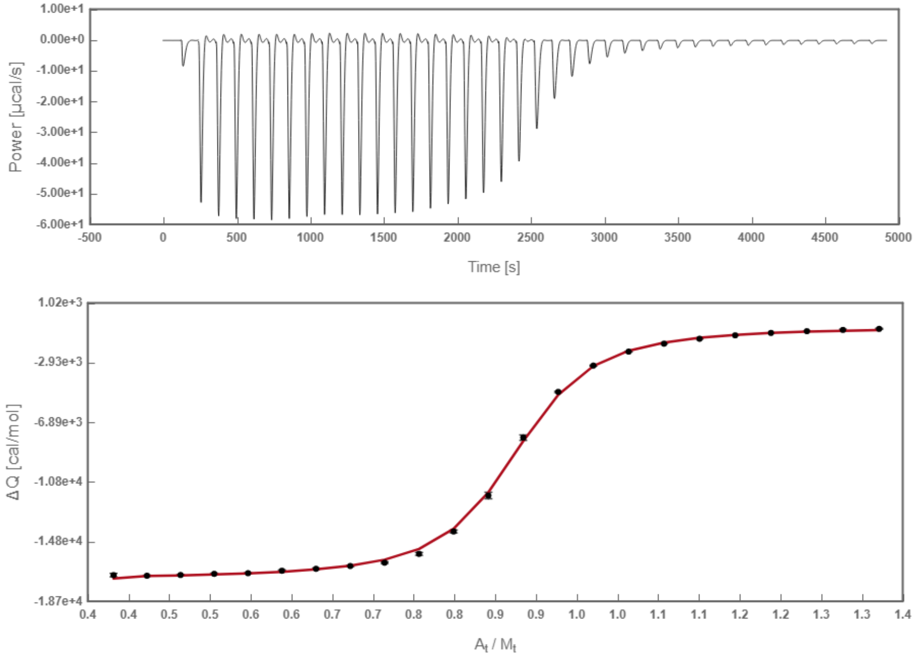

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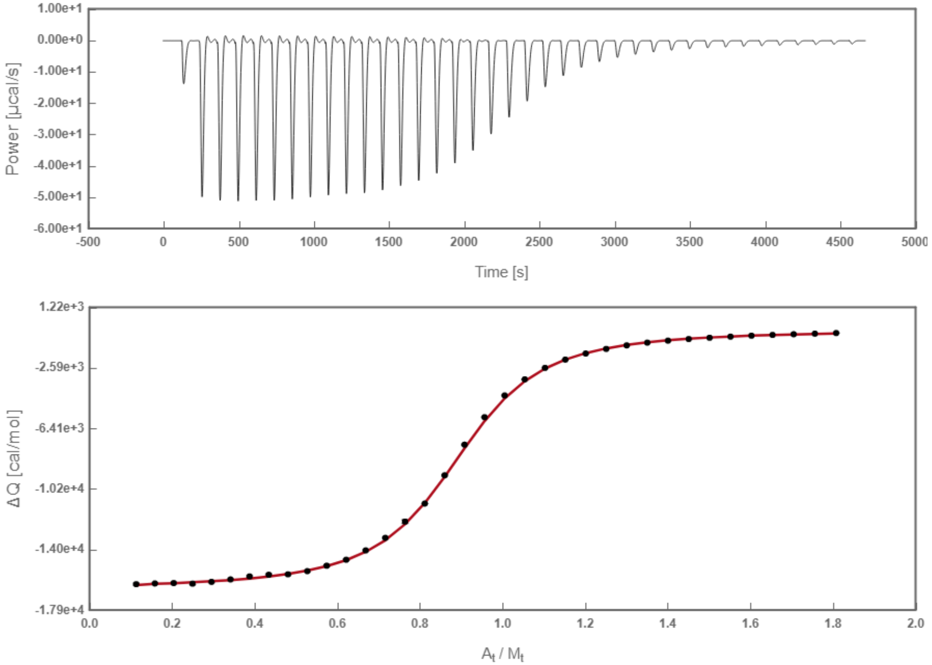

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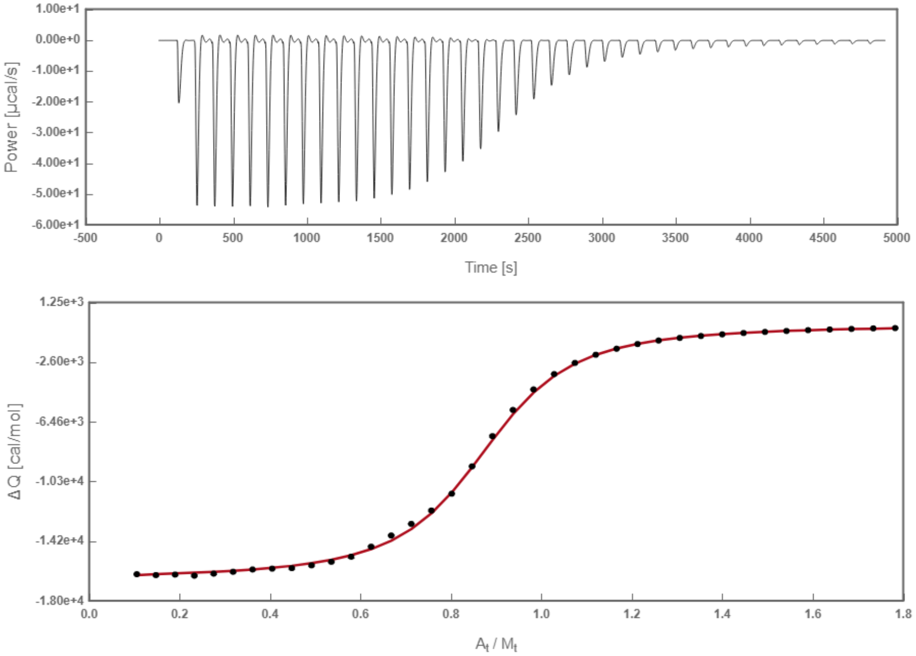

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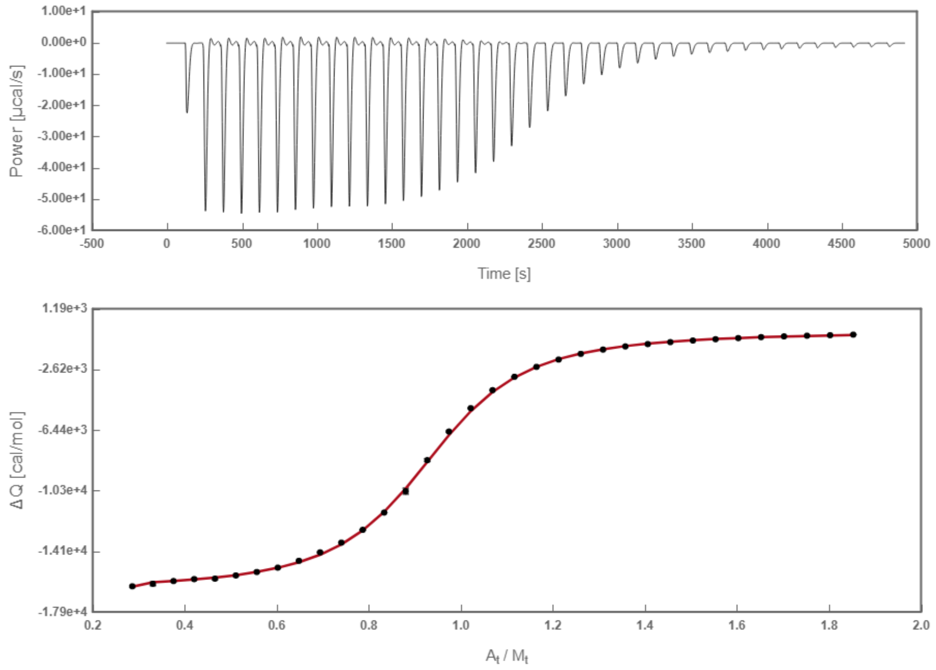

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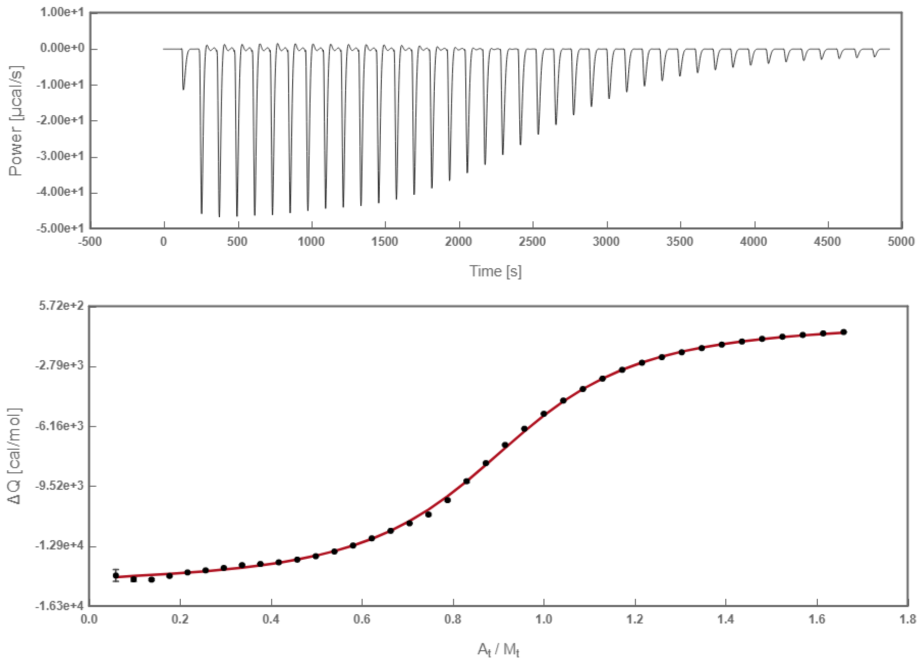

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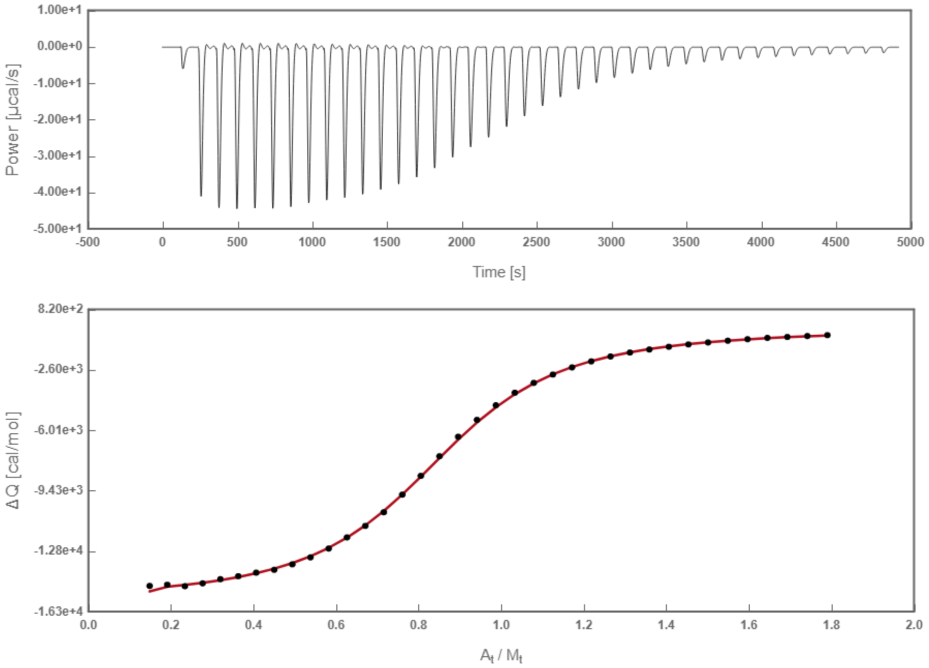

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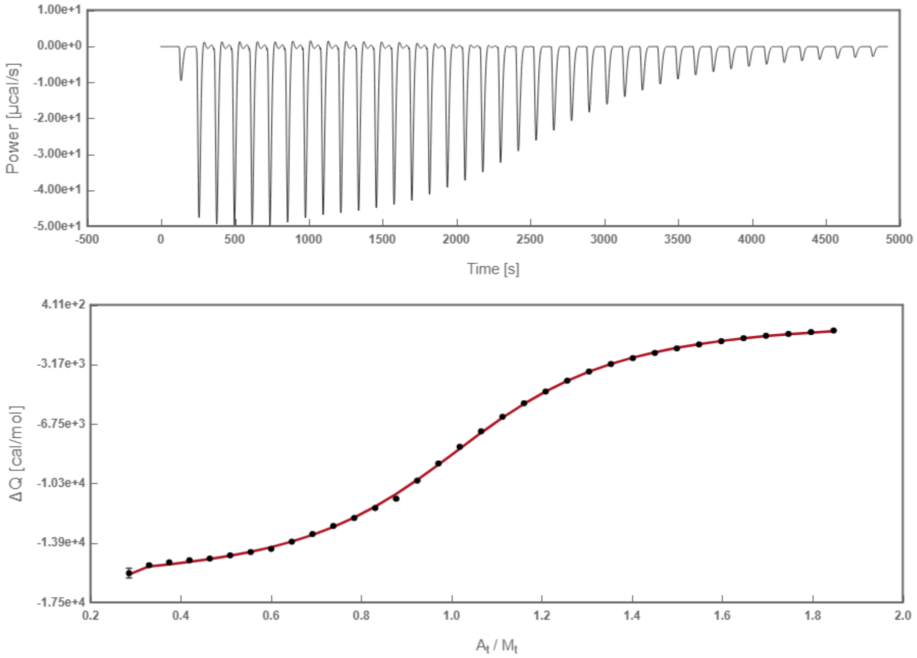

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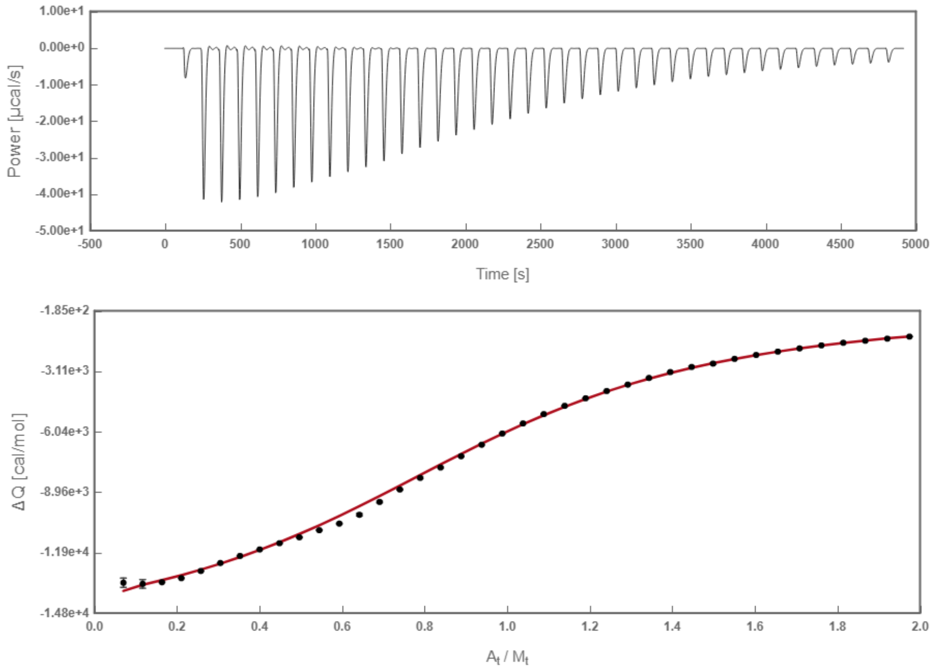

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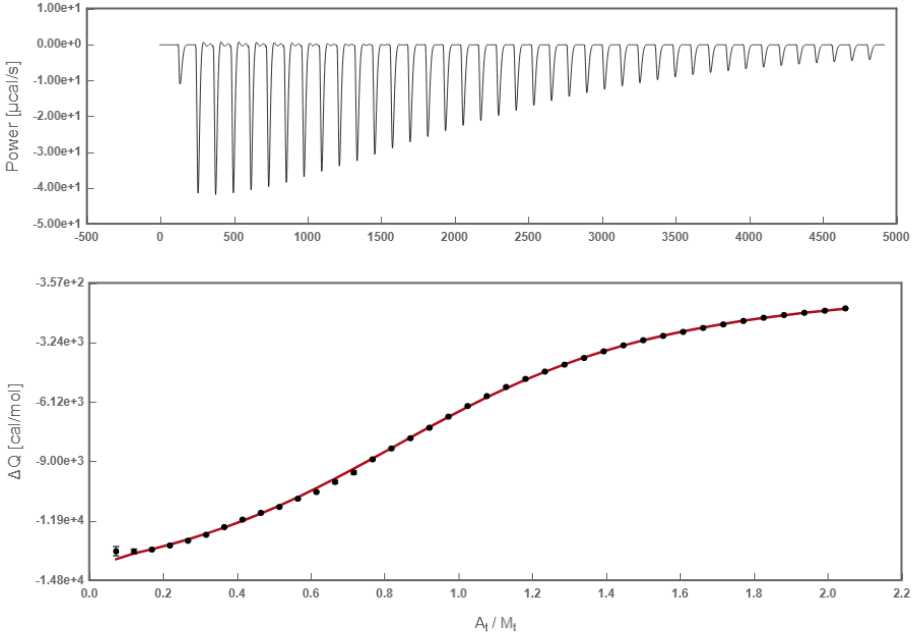

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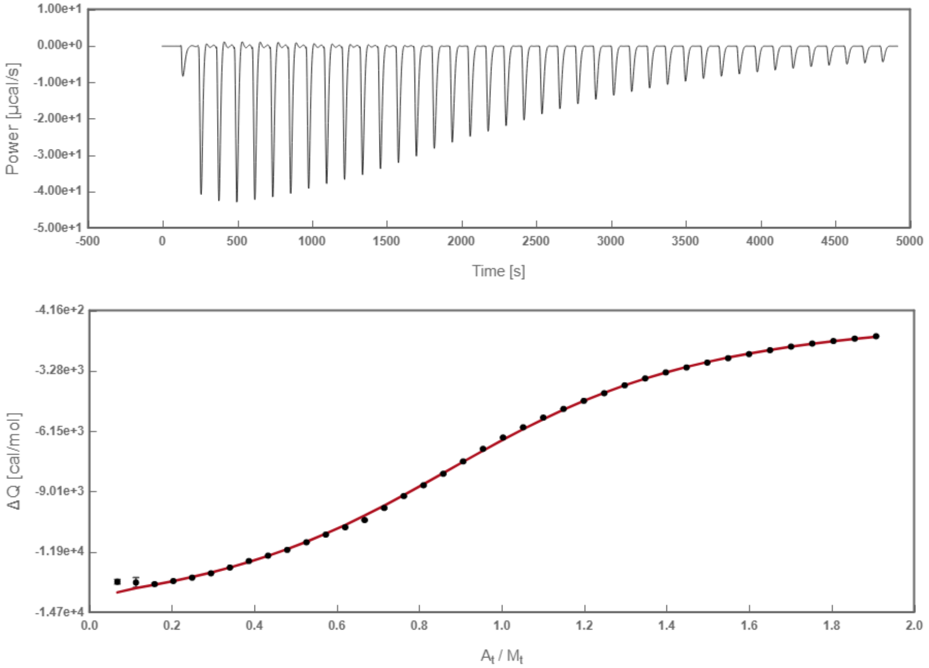
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1.6
1.8
2.0
A_t / M_t

VI. Determination of Equilibrium Constants by NMR Chemical Shift Changes

Summary

For the determination of equilibrium constants, typically 6 to 9 individual NMR samples with a constant Lewis acid concentration and a variable (excess) concentration of the Lewis base were prepared. Then ^{1}H NMR spectra were acquired for each individual sample in CD_2Cl_2 at 22°C, and the changes in the chemical shift of one resonance (unequivocally assigned to the Lewis acid) was evaluated.

To determine equilibrium constants for reactions of the perfluorinated Lewis acid **1i** with Lewis bases, 6 to 8 individual NMR samples with a constant Lewis base concentration and a variable (excess) concentration of **1i** were prepared. ^{1}H NMR spectra were acquired for each individual sample in CD_2Cl_2 at 22°C, and the change in the chemical shift of one resonance (unequivocally assigned to the Lewis base) was evaluated.

Errors correspond to the standard deviations of variables in the least-squares fitting of Eq (S1).

Table S5: Summary of equilibrium constants obtained from NMR titration experiments of boranes **1** with Lewis bases (CD_2Cl_2, 22 °C)

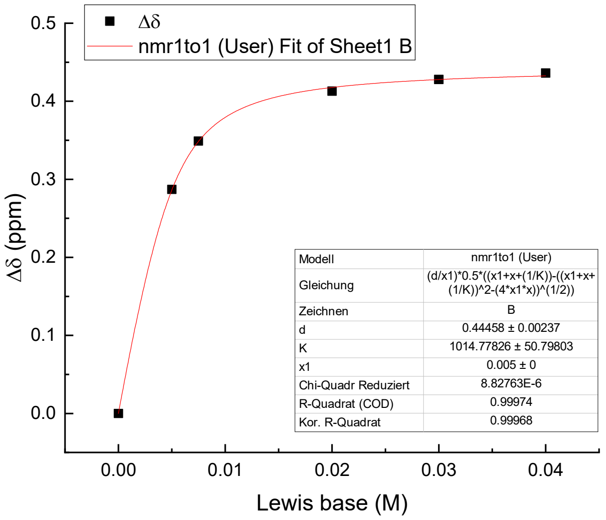
BAr_3	LB	Experiment	K_B (M^{-1})
1a	**2c**	RM1102	$(1.01 \pm 0.06) \times 10^3$
1a	**2d**	RM1110	$(7.81 \pm 0.04) \times 10^1$
1a	**2e**	RM1111	9.93 ± 0.42
1a	**2f**	RM1123	1.52 ± 0.29
1b	**2e**	RM1463	$(3.14 \pm 0.06) \times 10^3$
1b	**2f**	RM1120	$(7.99 \pm 1.81) \times 10^2$
1b	**2g**	RM1106	$(4.88 \pm 0.43) \times 10^2$
1b	**2h**	RM1122	$(1.68 \pm 0.04) \times 10^2$
1b	**2j**	RM1131	6.06 ± 0.30
1c	**2i**	RM1146	$(1.62 \pm 0.07) \times 10^1$
1c	**2j**	RM1129	$(1.22 \pm 0.11) \times 10^2$
1c	**2k**	RM1170	7.11 ± 0.61
1c	**10**	RM1262	$(1.90 \pm 0.12) \times 10^1$
1d	**2i**	RM1147	$(5.04 \pm 0.71) \times 10^1$
1d	**2j**	RM1130	$(4.33 \pm 0.85) \times 10^2$
1d	**2k**	RM1169	$(5.35 \pm 1.07) \times 10^1$
1d	**9**	RM1270	7.60 ± 0.18
1e	**2i**	RM1144	$(6.37 \pm 0.19) \times 10^1$
1e	**2j**	RM1128	$(7.56 \pm 0.56) \times 10^2$
1e	**2k**	RM1167	$(2.96 \pm 0.13) \times 10^1$
1e	**2l**	RM1157	$(2.38 \pm 0.51) \times 10^{-1}$
1e	**4a**	RM1260	$(3.60 \pm 0.36) \times 10^2$
1e	**10**	RM1261	$(1.98 \pm 0.33) \times 10^3$
1f	**2i**	RM1145	$(1.71 \pm 0.75) \times 10^3$
1f	**2j**	RM1133	$(9.29 \pm 0.22) \times 10^3$
1f	**2k**	RM1168	$(3.56 \pm 0.08) \times 10^2$
1f	**2l**	RM1155	7.91 ± 0.28

1f	**2m**	RM1166	4.87 ± 0.12
1f	**7a**	RM1188	6.75 ± 0.21
1f	**3a**	RM1258	4.93 ± 0.16
1f	**3b**	RM1195	1.87 ± 0.04
1f	**4b**	RM1259	$(1.58 \pm 0.04) \times 10^{2}$
1f	**4c**	RM1254	$(1.67 \pm 0.08) \times 10^{1}$
1e	**9**	RM1271	$(2.50 \pm 0.19) \times 10^{2}$
1g	**2l**	RM1239	$(4.50 \pm 1.11) \times 10^{3}$
1g	**2m**	RM1165	$(1.60 \pm 0.22) \times 10^{3}$
1g	**3b**	RM1238	$(2.39 \pm 0.28) \times 10^{3}$
1g	**4a**	RM1237	$(8.61 \pm 0.75) \times 10^{2}$
1g	**5a**	RM1148	$(9.79 \pm 0.32) \times 10^{1}$
1g	**5b**	RM1141	$(2.97 \pm 0.34) \times 10^{1}$
1g	**5c**	RM1177	6.22 ± 0.92
1g	**5d**	RM1153	5.42 ± 0.58
1g	**5e**	RM1158	5.02 ± 0.82
1g	**7a**	RM1187	$(4.90 \pm 2.02) \times 10^{3}$
1g	**7b**	RM1214	$(1.41 \pm 0.05) \times 10^{2}$
1g	**7c**	RM1186	$(5.34 \pm 0.12) \times 10^{1}$
1g	**7d**	RM1185	2.31 ± 0.28
1g	**8**	RM1184	$(1.38 \pm 0.21) \times 10^{3}$
1h	**2l**	RM1174	$(4.10 \pm 0.35) \times 10^{2}$
1h	**2m**	RM1173	$(1.94 \pm 0.07) \times 10^{2}$
1h	**3a**	RM1211	$(4.63 \pm 0.25) \times 10^{3}$
1h	**3b**	RM1201	$(2.10 \pm 0.38) \times 10^{3}$
1h	**5a**	RM1172	$(1.24 \pm 0.04) \times 10^{2}$
1h	**5b**	RM1163	$(2.78 \pm 0.25) \times 10^{1}$
1h	**7a**	RM1198	$(2.18 \pm 1.10) \times 10^{4}$
1h	**7b**	RM1257	$(2.24 \pm 0.06) \times 10^{2}$
1h	**7c**	RM1197	$(6.78 \pm 0.03) \times 10^{1}$
1h	**7d**	RM1196	1.02 ± 0.13
1h	**8**	RM1199	$(2.84 \pm 0.42) \times 10^{3}$
1i	**2n**	RM1240	$(5.47 \pm 1.02) \times 10^{1}$
1i	**5c**	RM1241	$(3.51 \pm 1.82) \times 10^{4}$
1i	**5d**	RM1251	$(1.01 \pm 0.60) \times 10^{4}$
1i	**5e**	RM1143	$(6.53 \pm 0.92) \times 10^{2}$
1i	**5f**	RM1150	$(1.31 \pm 0.37) \times 10^{1}$
1i	**6**	RM1200	$(7.31 \pm 2.19) \times 10^{1}$
1i	**7d**	RM1180	$(4.46 \pm 1.41) \times 10^{3}$
1j	**2a**	RM1256	$(4.54 \pm 0.26) \times 10^{-1}$

Individual NMR titrations

NMR titration of tris(4-dimethylaminophenyl)borane (1a) with 4-methoxypyridine (2c)

Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	5.0×10^{-3}	0.0	7.498	0.000
2	5.0×10^{-3}	5.0×10^{-3}	7.211	0.287
3	5.0×10^{-3}	7.5×10^{-3}	7.149	0.349
4	5.0×10^{-3}	2.0×10^{-2}	7.085	0.413
5	5.0×10^{-3}	3.0×10^{-2}	7.070	0.428
6	5.0×10^{-3}	4.0×10^{-2}	7.062	0.436

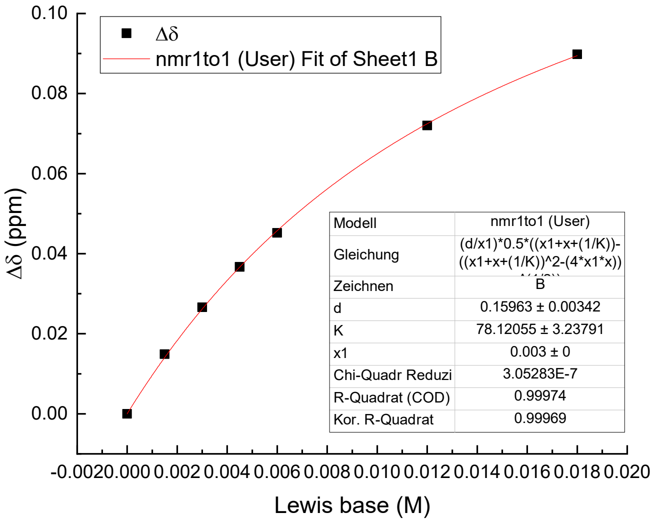


Modell	nmr1to1 (User)
Gleichung	(d/x1)*0.5*((x1+x+(1/K))-((x1+x+(1/K))^2-(4*x1*x))^(1/2))
Zeichnen	B
d	0.44458 ± 0.00237
K	1014.77826 ± 50.79803
x1	0.005 ± 0
Chi-Quadr Reduziert	8.82763E-6
R-Quadrat (COD)	0.99974
Kor. R-Quadrat	0.99968

(RM1102)

NMR titration of tris(4-dimethylaminophenyl)borane (1a) with pyridine (1d)

Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	3.0×10^{-3}	0.0	3.0350	0.0000
2	3.0×10^{-3}	1.5×10^{-3}	3.0201	0.0149
3	3.0×10^{-3}	3.0×10^{-3}	3.0084	0.0266
4	3.0×10^{-3}	4.5×10^{-3}	2.9983	0.0367
5	3.0×10^{-3}	6.0×10^{-3}	2.9898	0.0452
6	3.0×10^{-3}	1.2×10^{-2}	2.9630	0.0720
7	3.0×10^{-3}	1.8×10^{-2}	2.9452	0.0898

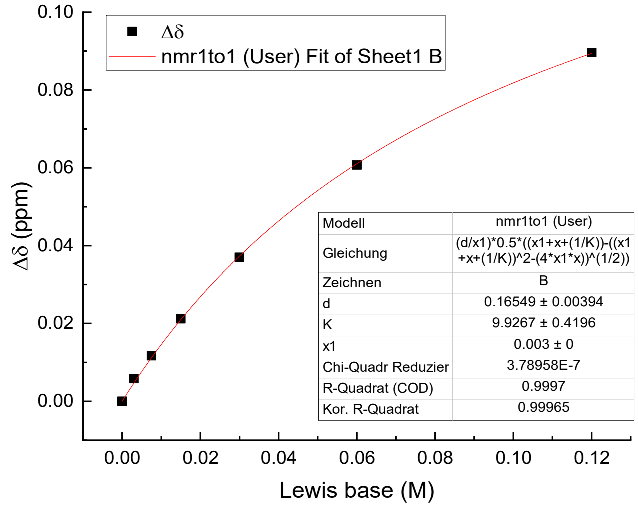


Modell	nmr1to1 (User)
Gleichung	(d/x1)*0.5*((x1+x+(1/K))-((x1+x+(1/K))^2-(4*x1*x))
Zeichnen	B
d	0.15963 ± 0.00342
K	78.12055 ± 3.23791
x1	0.003 ± 0
Chi-Quadr Reduzi	3.05283E-7
R-Quadrat (COD)	0.99974
Kor. R-Quadrat	0.99969

(RM1110)

NMR titration of tris(4-dimethylaminophenyl)borane (1a) with 4-benzoylpyridine (2e)

Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	3.0×10^{-3}	0.0	3.0351	0.0000
2	3.0×10^{-3}	3.0×10^{-3}	3.0293	0.0058
3	3.0×10^{-3}	7.5×10^{-3}	3.0234	0.0117
4	3.0×10^{-3}	1.5×10^{-2}	3.0139	0.0212
5	3.0×10^{-3}	3.0×10^{-2}	2.9981	0.0370
6	3.0×10^{-3}	6.0×10^{-2}	2.9744	0.0607
7	3.0×10^{-3}	1.2×10^{-1}	2.9455	0.0896

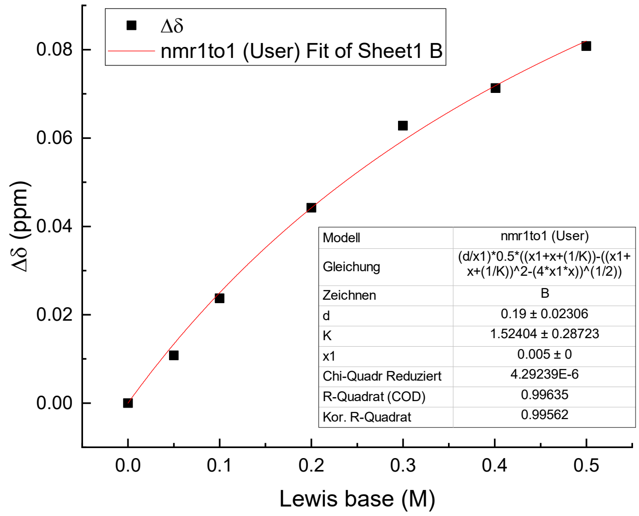


Modell	nmr1to1 (User)
Gleichung	(d/x1)*0.5*((x1+x+(1/K))-((x1+x+(1/K))^2-(4*x1*x))^(1/2))
Zeichnen	B
d	0.16549 ± 0.00394
K	9.9267 ± 0.4196
x1	0.003 ± 0
Chi-Quadr Reduzier	3.78958E-7
R-Quadrat (COD)	0.9997
Kor. R-Quadrat	0.99965

(RM1111)

NMR titration of tris(4-dimethylaminophenyl)borane (1a) with 3-chloropyridine (2f)

Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	5.0×10^{-3}	0.0	3.0347	0.0000
2	5.0×10^{-3}	5.0×10^{-2}	3.0239	0.0108
3	5.0×10^{-3}	1.0×10^{-1}	3.0110	0.0237
4	5.0×10^{-3}	2.0×10^{-1}	2.9905	0.0442
5	5.0×10^{-3}	3.0×10^{-1}	2.9719	0.0628
6	5.0×10^{-3}	4.0×10^{-1}	2.9634	0.0713
7	5.0×10^{-3}	5.0×10^{-1}	2.9539	0.0808

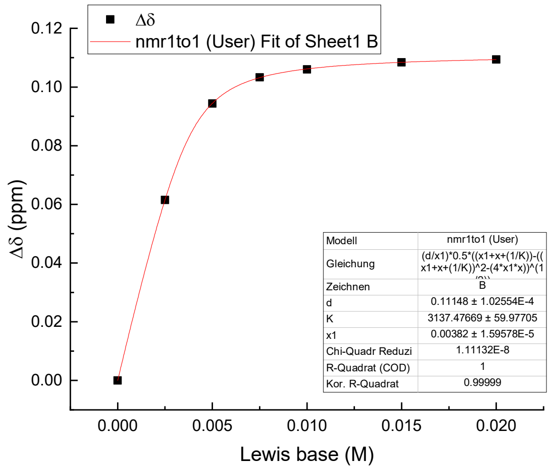


Modell	nmr1to1 (User)
Gleichung	(d/x1)*0.5*((x1+x+(1/K))-((x1+x+(1/K))^2-(4*x1*x))^(1/2))
Zeichnen	B
d	0.19 ± 0.02306
K	1.52404 ± 0.28723
x1	0.005 ± 0
Chi-Quadr Reduziert	4.29239E-6
R-Quadrat (COD)	0.99635
Kor. R-Quadrat	0.99562

(RM1123)

NMR titration of tris(p-anisyl)borane (1b) with 4-benzoylpyridine (2e)

Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	5.0×10^{-3}	0.0	3.878	0.000
2	5.0×10^{-3}	2.5×10^{-3}	3.816	0.062
3	5.0×10^{-3}	5.0×10^{-3}	3.783	0.094
4	5.0×10^{-3}	7.5×10^{-3}	3.774	0.103
5	5.0×10^{-3}	1.0×10^{-2}	3.772	0.106
6	5.0×10^{-3}	1.5×10^{-2}	3.769	0.108
7	5.0×10^{-3}	2.0×10^{-2}	3.768	0.109



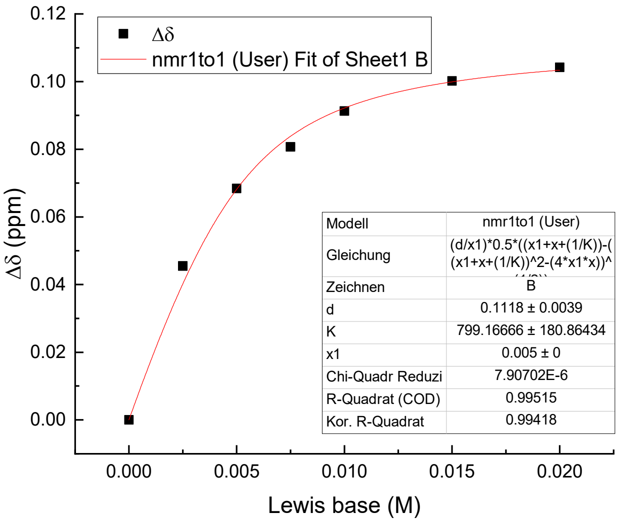
Modell	nmr1to1 (User)
Gleichung	(d/x1)*0.5*((x1+x+(1/K))-((x1+x+(1/K))^2-(4*x1*x))^(1
Zeichnen	B
d	0.11148 ± 1.02554E-4
K	3137.47669 ± 59.97705
x1	0.00382 ± 1.59578E-5
Chi-Quadr Reduzi	1.11132E-8
R-Quadrat (COD)	1
Kor. R-Quadrat	0.99999

(RM1463)

The value of x1 (that is, the borane concentration) was allowed to vary in the fitting process.

NMR titration of tris(p-anisyl)borane (1b) with 3-chloropyridine (2f)

Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	5.0×10^{-3}	0.0	3.8777	0.0000
2	5.0×10^{-3}	2.5×10^{-3}	3.8322	0.0455
3	5.0×10^{-3}	5.0×10^{-3}	3.8093	0.0684
4	5.0×10^{-3}	7.5×10^{-3}	3.7970	0.0807
5	5.0×10^{-3}	1.0×10^{-2}	3.7864	0.0913
6	5.0×10^{-3}	1.5×10^{-2}	3.7775	0.1002
7	5.0×10^{-3}	2.0×10^{-2}	3.7735	0.1042

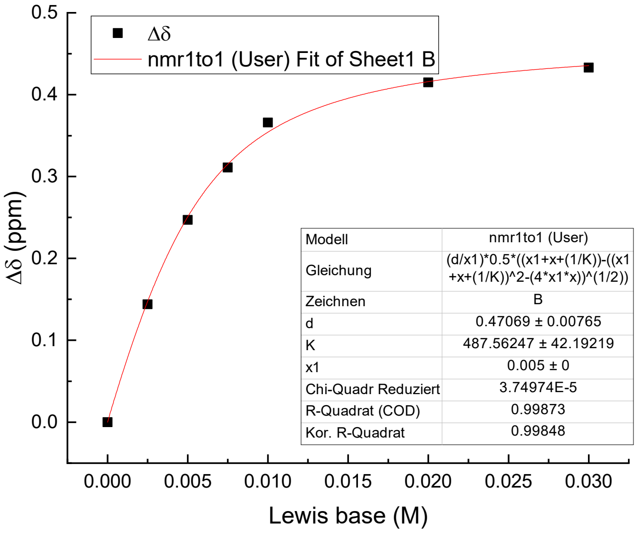


Modell	nmr1to1 (User)
Gleichung	(d/x1)*0.5*((x1+x+(1/K))-((x1+x+(1/K))^2-(4*x1*x))^
Zeichnen	B
d	0.1118 ± 0.0039
K	799.16666 ± 180.86434
x1	0.005 ± 0
Chi-Quadr Reduzi	7.90702E-6
R-Quadrat (COD)	0.99515
Kor. R-Quadrat	0.99418

(RM1120)

NMR titration of tris(p-anisyl)borane (1b) with 4-(trifluoromethyl)pyridine (2g)

Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	5.0×10^{-3}	0.0	7.560	0.000
2	5.0×10^{-3}	2.5×10^{-3}	7.416	0.144
3	5.0×10^{-3}	5.0×10^{-3}	7.313	0.247
4	5.0×10^{-3}	7.5×10^{-3}	7.249	0.311
5	5.0×10^{-3}	1.0×10^{-2}	7.194	0.366
6	5.0×10^{-3}	2.0×10^{-2}	7.145	0.415
7	5.0×10^{-3}	3.0×10^{-2}	7.127	0.433

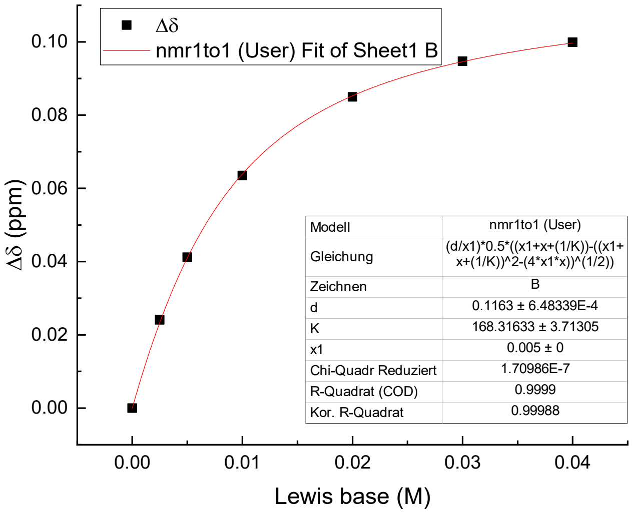


Modell	nmr1to1 (User)
Gleichung	(d/x1)*0.5*((x1+x+(1/K))-((x1+x+(1/K))^2-(4*x1*x))^(1/2))
Zeichnen	B
d	0.47069 ± 0.00765
K	487.56247 ± 42.19219
x1	0.005 ± 0
Chi-Quadr Reduziert	3.74974E-5
R-Quadrat (COD)	0.99873
Kor. R-Quadrat	0.99848

(RM1106)

NMR titration of tris(p-anisyl)borane (1b) with 4-cyanopyridine (2h)

Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	5.0×10^{-3}	0.0	3.8777	0.0000
2	5.0×10^{-3}	2.5×10^{-3}	3.8536	0.0241
3	5.0×10^{-3}	5.0×10^{-3}	3.8365	0.0412
4	5.0×10^{-3}	1.0×10^{-2}	3.8142	0.0635
5	5.0×10^{-3}	2.0×10^{-2}	3.7927	0.0850
6	5.0×10^{-3}	3.0×10^{-2}	3.7830	0.0947
7	5.0×10^{-3}	4.0×10^{-2}	3.7778	0.0999

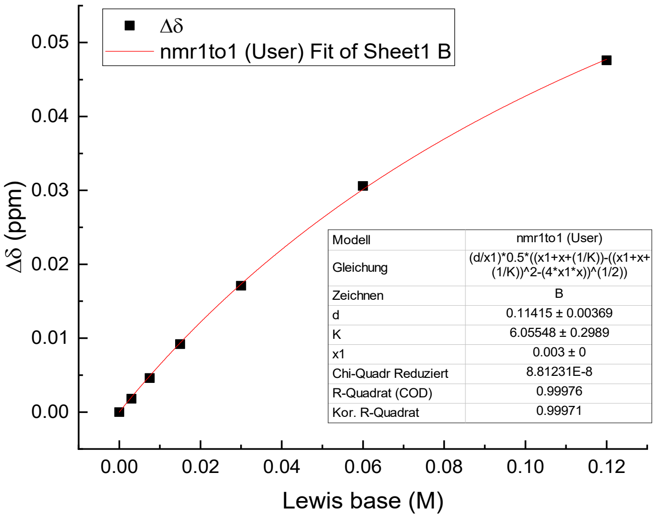


Modell	nmr1to1 (User)
Gleichung	(d/x1)*0.5*((x1+x+(1/K))-((x1+x+(1/K))^2-(4*x1*x))^(1/2))
Zeichnen	B
d	0.1163 ± 6.48339E-4
K	168.31633 ± 3.71305
x1	0.005 ± 0
Chi-Quadr Reduziert	1.70986E-7
R-Quadrat (COD)	0.9999
Kor. R-Quadrat	0.99988

(RM1122)

NMR titration of tris(p-anisyl)borane (1b) with 3,4,5-trichloropyridine (2j)

Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	3.0×10^{-3}	0.0	3.8777	0.0000
2	3.0×10^{-3}	3.0×10^{-3}	3.8759	0.0018
3	3.0×10^{-3}	7.5×10^{-3}	3.8731	0.0046
4	3.0×10^{-3}	1.5×10^{-2}	3.8685	0.0092
5	3.0×10^{-3}	3.0×10^{-2}	3.8606	0.0171
6	3.0×10^{-3}	6.0×10^{-2}	3.8471	0.0306
7	3.0×10^{-3}	1.2×10^{-1}	3.8301	0.0476

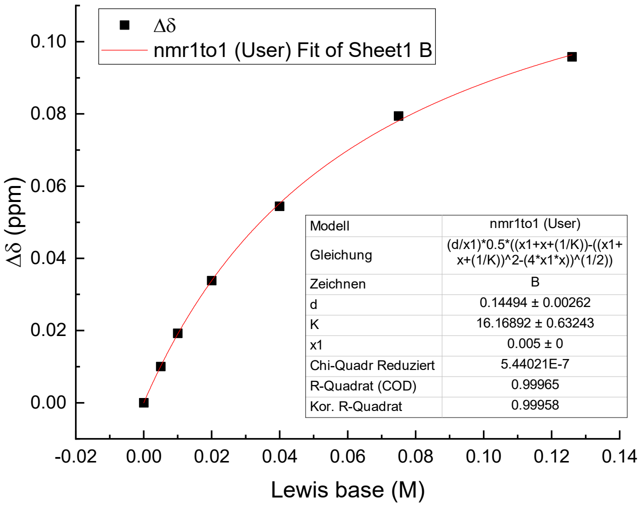


Modell	nmr1to1 (User)
Gleichung	(d/x1)*0.5*((x1+x+(1/K))-((x1+x+(1/K))^2-(4*x1*x))^(1/2))
Zeichnen	B
d	0.11415 ± 0.00369
K	6.05548 ± 0.2989
x1	0.003 ± 0
Chi-Quadr Reduziert	8.81231E-8
R-Quadrat (COD)	0.99976
Kor. R-Quadrat	0.99971

(RM1131)

NMR titration of tris(p-tolyl)borane (1c) with 3,5-bis(trifluoromethyl)pyridine (2i)

Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	5.0×10^{-3}	0.0	2.4378	0.0000
2	5.0×10^{-3}	5.0×10^{-3}	2.4278	0.0100
3	5.0×10^{-3}	1.0×10^{-2}	2.4186	0.0192
4	5.0×10^{-3}	2.0×10^{-2}	2.4040	0.0338
5	5.0×10^{-3}	4.0×10^{-2}	2.3834	0.0544
6	5.0×10^{-3}	7.5×10^{-2}	2.3584	0.0794
7	5.0×10^{-3}	1.26×10^{-1}	2.3420	0.0958

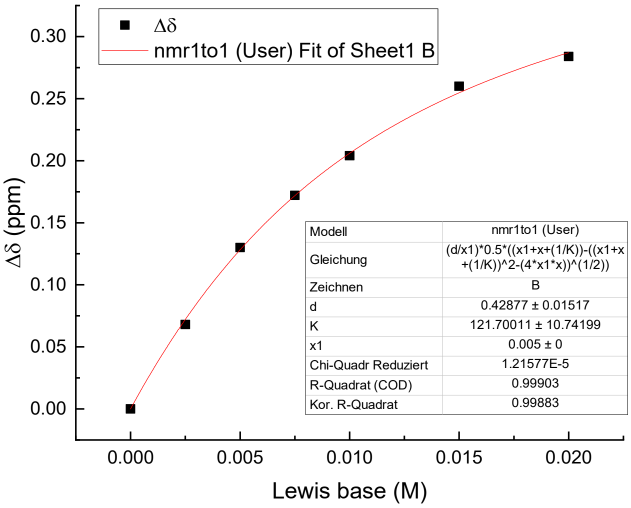


Modell	nmr1to1 (User)
Gleichung	(d/x1)*0.5*((x1+x+(1/K))-((x1+x+(1/K))^2-(4*x1*x))^(1/2))
Zeichnen	B
d	0.14494 ± 0.00262
K	16.16892 ± 0.63243
x1	0.005 ± 0
Chi-Quadr Reduziert	5.44021E-7
R-Quadrat (COD)	0.99965
Kor. R-Quadrat	0.99958

(RM1146)

NMR titration of tris(p-tolyl)borane (1c) with 3,4,5-trichloropyridine (2j)

Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	5.0×10^{-3}	0.0	7.489	0.000
2	5.0×10^{-3}	2.5×10^{-3}	7.421	0.068
3	5.0×10^{-3}	5.0×10^{-3}	7.359	0.130
4	5.0×10^{-3}	7.5×10^{-3}	7.317	0.172
5	5.0×10^{-3}	1.0×10^{-2}	7.285	0.204
6	5.0×10^{-3}	1.5×10^{-2}	7.229	0.260
7	5.0×10^{-3}	2.0×10^{-2}	7.205	0.284

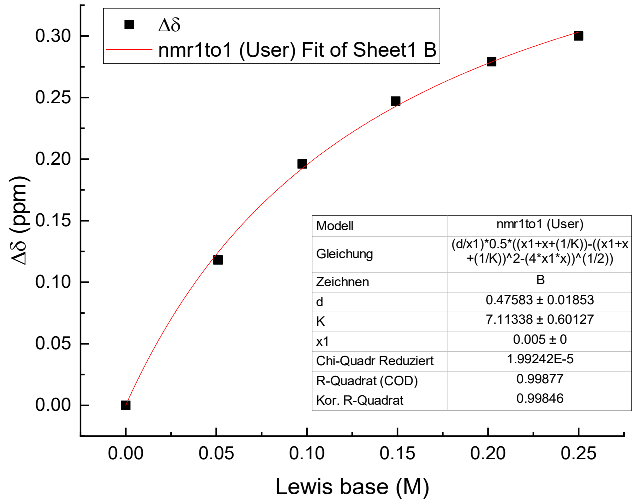


Modell	nmr1to1 (User)
Gleichung	(d/x1)*0.5*((x1+x+(1/K))-((x1+x+(1/K))^2-(4*x1*x))^(1/2))
Zeichnen	B
d	0.42877 ± 0.01517
K	121.70011 ± 10.74199
x1	0.005 ± 0
Chi-Quadr Reduziert	1.21577E-5
R-Quadrat (COD)	0.99903
Kor. R-Quadrat	0.99883

(RM1129)

NMR titration of tris(p-tolyl)borane (1c) with 3,5-difluoro-4-(trifluoromethyl)pyridine (2k)

Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	5.0×10^{-3}	0.0	7.490	0.000
2	5.0×10^{-3}	5.10×10^{-2}	7.372	0.118
3	5.0×10^{-3}	9.75×10^{-2}	7.294	0.196
4	5.0×10^{-3}	1.49×10^{-1}	7.243	0.247
5	5.0×10^{-3}	2.02×10^{-1}	7.211	0.279
6	5.0×10^{-3}	2.50×10^{-1}	7.190	0.300

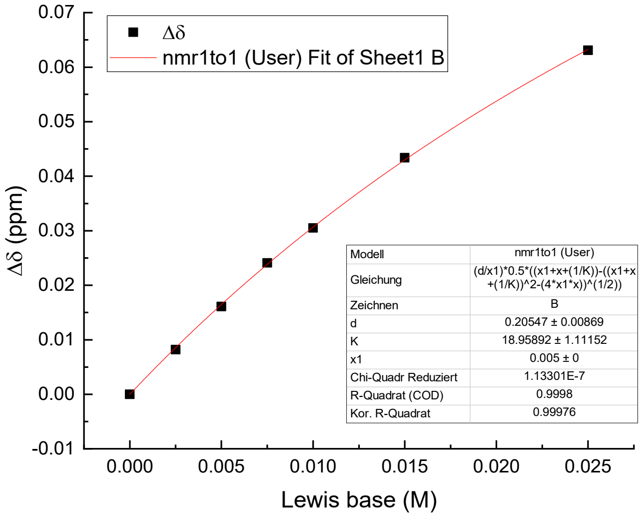


Modell	nmr1to1 (User)
Gleichung	(d/x1)*0.5*((x1+x+(1/K))-((x1+x+(1/K))^2-(4*x1*x))^(1/2))
Zeichnen	B
d	0.47583 ± 0.01853
K	7.11338 ± 0.60127
x1	0.005 ± 0
Chi-Quadr Reduziert	1.99242E-5
R-Quadrat (COD)	0.99877
Kor. R-Quadrat	0.99846

(RM1170)

NMR titration of tris(p-tolyl)borane (1c) with triethylphosphine oxide (10)

Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	5.0×10^{-3}	0.0	2.4381	0.0000
2	5.0×10^{-3}	2.5×10^{-3}	2.4299	0.0082
3	5.0×10^{-3}	5.0×10^{-3}	2.4220	0.0161
4	5.0×10^{-3}	7.5×10^{-3}	2.4140	0.0241
5	5.0×10^{-3}	1.0×10^{-2}	2.4076	0.0305
6	5.0×10^{-3}	1.5×10^{-2}	2.3947	0.0434
7	5.0×10^{-3}	2.5×10^{-2}	2.3750	0.0631

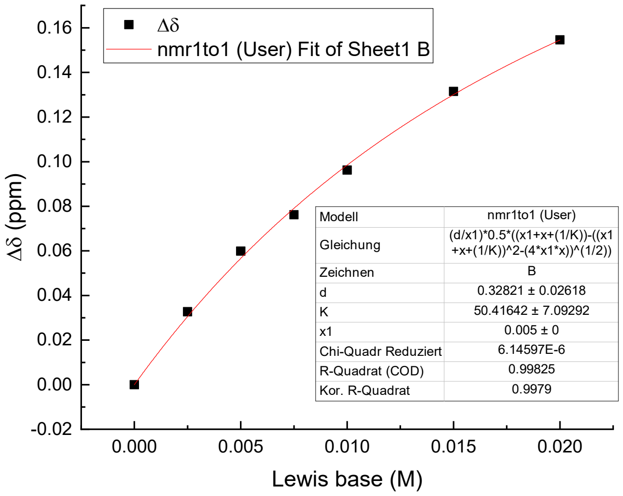


Modell	nmr1to1 (User)
Gleichung	(d/x1)*0.5*((x1+x+(1/K))-((x1+x+(1/K))^2-(4*x1*x))^(1/2))
Zeichnen	B
d	0.20547 ± 0.00869
K	18.95892 ± 1.11152
x1	0.005 ± 0
Chi-Quadr Reduziert	1.13301E-7
R-Quadrat (COD)	0.9998
Kor. R-Quadrat	0.99976

(RM1262)

NMR titration of triphenylborane (1d) with 3,5-bis(trifluoromethyl)pyridine (2i)

Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	5.0×10^{-3}	0.0	7.4669	0.0000
2	5.0×10^{-3}	2.5×10^{-3}	7.4342	0.0327
3	5.0×10^{-3}	5.0×10^{-3}	7.4070	0.0599
4	5.0×10^{-3}	7.5×10^{-3}	7.3907	0.0762
5	5.0×10^{-3}	1.0×10^{-2}	7.3707	0.0962
6	5.0×10^{-3}	1.5×10^{-2}	7.3354	0.1315
7	5.0×10^{-3}	2.0×10^{-2}	7.3123	0.1546

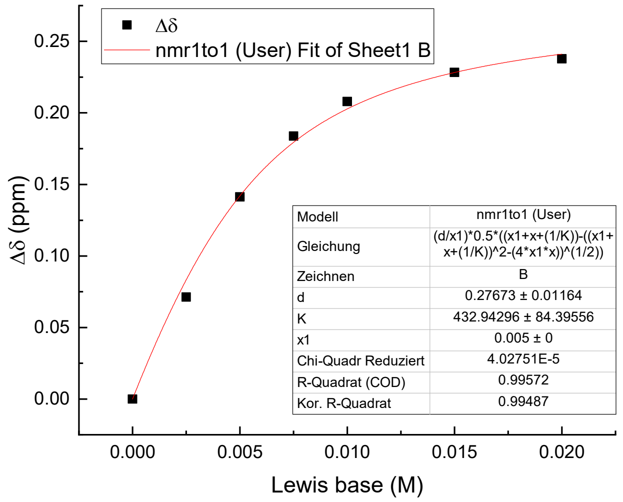


Modell	nmr1to1 (User)
Gleichung	(d/x1)*0.5*((x1+x+(1/K))-((x1+x+(1/K))^2-(4*x1*x))^(1/2))
Zeichnen	B
d	0.32821 ± 0.02618
K	50.41642 ± 7.09292
x1	0.005 ± 0
Chi-Quadr Reduziert	6.14597E-6
R-Quadrat (COD)	0.99825
Kor. R-Quadrat	0.9979

(RM1147)

NMR titration of triphenylborane (1d) with 3,4,5-trichloropyridine (2j)

Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	5.0×10^{-3}	0.0	7.4671	0.0000
2	5.0×10^{-3}	2.5×10^{-3}	7.3958	0.0713
3	5.0×10^{-3}	5.0×10^{-3}	7.3258	0.1413
4	5.0×10^{-3}	7.5×10^{-3}	7.2833	0.1838
5	5.0×10^{-3}	1.0×10^{-2}	7.2591	0.2080
6	5.0×10^{-3}	1.5×10^{-2}	7.2387	0.2284
7	5.0×10^{-3}	2.0×10^{-2}	7.2292	0.2379

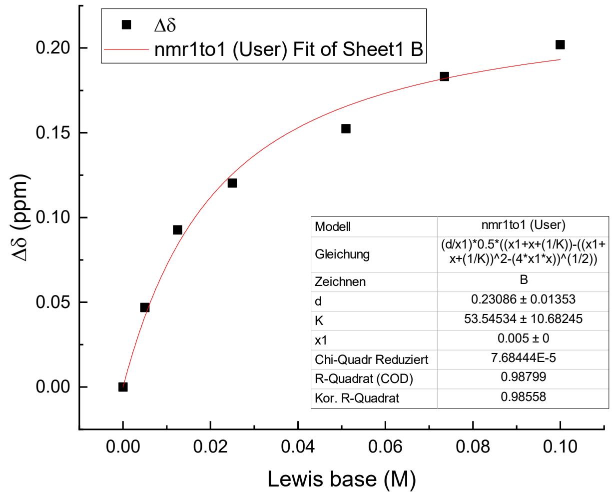


Modell	nmr1to1 (User)
Gleichung	(d/x1)*0.5*((x1+x+(1/K))-((x1+x+(1/K))^2-(4*x1*x))^(1/2))
Zeichnen	B
d	0.27673 ± 0.01164
K	432.94296 ± 84.39556
x1	0.005 ± 0
Chi-Quadr Reduziert	4.02751E-5
R-Quadrat (COD)	0.99572
Kor. R-Quadrat	0.99487

(RM1130)

NMR titration of triphenylborane (1d) with 3,5-difluoro-4-(trifluoromethyl)pyridine (2k)

Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	5.0 × 10^{-3}	0.0	7.4662	0.0000
2	5.0 × 10^{-3}	5.0 × 10^{-3}	7.4193	0.0469
3	5.0 × 10^{-3}	1.25 × 10^{-2}	7.3735	0.0927
4	5.0 × 10^{-3}	2.50 × 10^{-2}	7.3459	0.1203
5	5.0 × 10^{-3}	5.10 × 10^{-2}	7.3138	0.1524
6	5.0 × 10^{-3}	7.35 × 10^{-2}	7.2830	0.1832
7	5.0 × 10^{-3}	1.00 × 10^{-1}	7.2643	0.2019

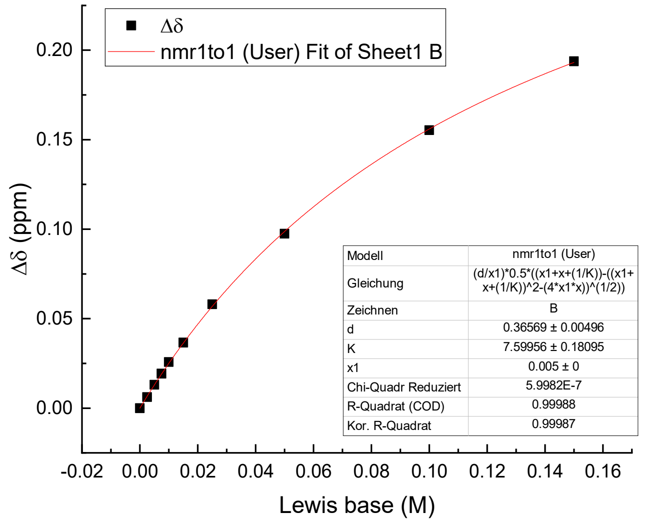


Modell	nmr1to1 (User)
Gleichung	(d/x1)*0.5*((x1+x+(1/K))-((x1+x+(1/K))^2-(4*x1*x))^(1/2))
Zeichnen	B
d	0.23086 ± 0.01353
K	53.54534 ± 10.68245
x1	0.005 ± 0
Chi-Quadr Reduziert	7.68444E-5
R-Quadrat (COD)	0.98799
Kor. R-Quadrat	0.98558

(RM1169)

NMR titration of triphenylborane (1d) with dimethylacetamide (9)

Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	5.0 × 10^{-3}	0.0	7.4670	0.0000
2	5.0 × 10^{-3}	2.5 × 10^{-3}	7.4608	0.0062
3	5.0 × 10^{-3}	5.0 × 10^{-3}	7.4539	0.0131
4	5.0 × 10^{-3}	7.5 × 10^{-3}	7.4477	0.0193
5	5.0 × 10^{-3}	1.0 × 10^{-2}	7.4412	0.0258
6	5.0 × 10^{-3}	1.5 × 10^{-2}	7.4304	0.0366
7	5.0 × 10^{-3}	2.5 × 10^{-2}	7.4089	0.0581
8	5.0 × 10^{-3}	5.0 × 10^{-2}	7.3695	0.0975
9	5.0 × 10^{-3}	1.0 × 10^{-1}	7.3117	0.1553
10	5.0 × 10^{-3}	1.5 × 10^{-1}	7.2732	0.1938

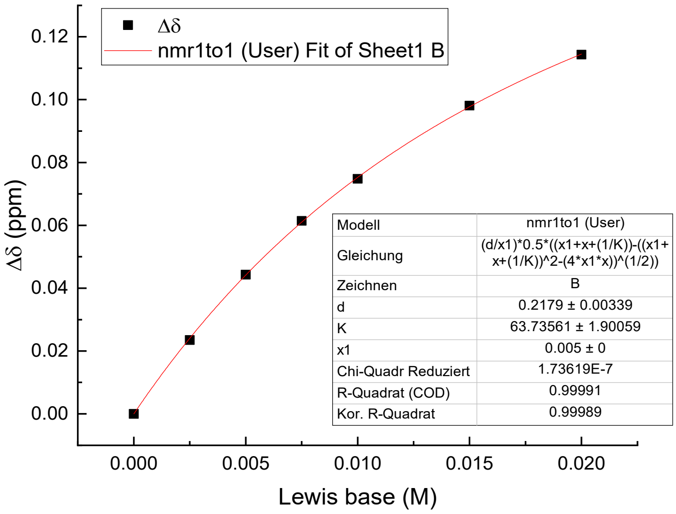


Modell	nmr1to1 (User)
Gleichung	(d/x1)*0.5*((x1+x+(1/K))-((x1+x+(1/K))^2-(4*x1*x))^(1/2))
Zeichnen	B
d	0.36569 ± 0.00496
K	7.59956 ± 0.18095
x1	0.005 ± 0
Chi-Quadr Reduziert	5.9982E-7
R-Quadrat (COD)	0.99988
Kor. R-Quadrat	0.99987

(RM1270)

NMR titration of tris(4-fluorophenyl)borane (1e) with 3,5-bis(trifluoromethyl)pyridine (2i)

Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	5.0×10^{-3}	0.0	7.1794	0.0000
2	5.0×10^{-3}	2.5×10^{-3}	7.1559	0.0235
3	5.0×10^{-3}	5.0×10^{-3}	7.1351	0.0443
4	5.0×10^{-3}	7.5×10^{-3}	7.1180	0.0614
5	5.0×10^{-3}	1.0×10^{-2}	7.1046	0.0748
6	5.0×10^{-3}	1.5×10^{-2}	7.0813	0.0981
7	5.0×10^{-3}	2.0×10^{-2}	7.0651	0.1143

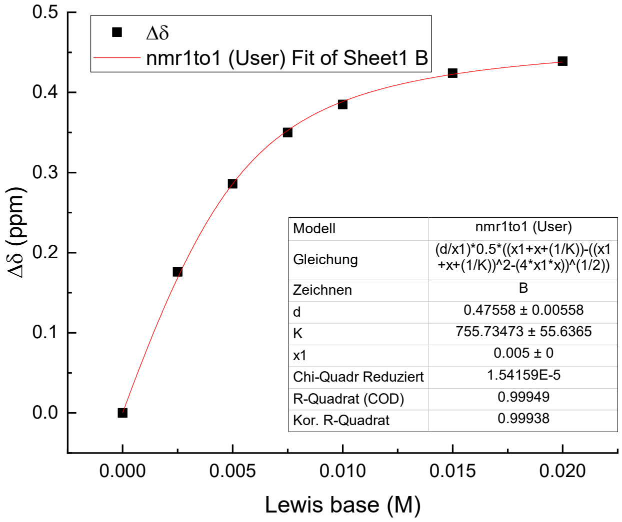


Modell	nmr1to1 (User)
Gleichung	(d/x1)*0.5*((x1+x+(1/K))-((x1+x+(1/K))^2-(4*x1*x))^(1/2))
Zeichnen	B
d	0.2179 ± 0.00339
K	63.73561 ± 1.90059
x1	0.005 ± 0
Chi-Quadr Reduziert	1.73619E-7
R-Quadrat (COD)	0.99991
Kor. R-Quadrat	0.99989

(RM1144)

NMR titration of tris(4-fluorophenyl)borane (1e) with 3,4,5-trichloropyridine (2j)

Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	5.0×10^{-3}	0.0	7.605	0.000
2	5.0×10^{-3}	2.5×10^{-3}	7.429	0.176
3	5.0×10^{-3}	5.0×10^{-3}	7.319	0.286
4	5.0×10^{-3}	7.5×10^{-3}	7.255	0.350
5	5.0×10^{-3}	1.0×10^{-2}	7.220	0.385
6	5.0×10^{-3}	1.5×10^{-2}	7.181	0.424
7	5.0×10^{-3}	2.0×10^{-2}	7.166	0.439

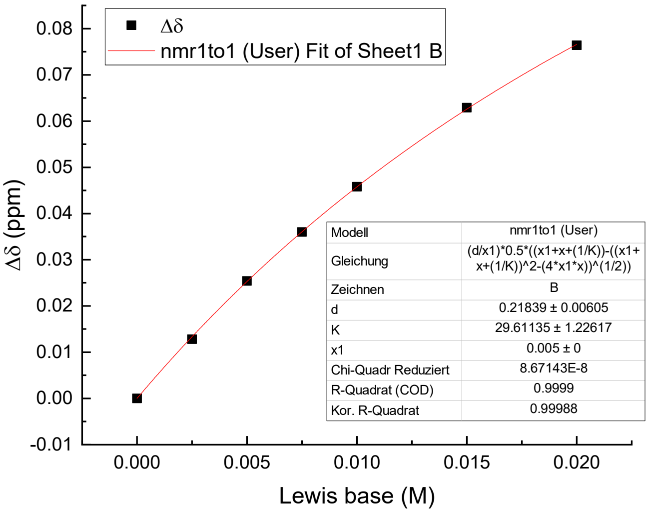


Modell	nmr1to1 (User)
Gleichung	(d/x1)*0.5*((x1+x+(1/K))-((x1+x+(1/K))^2-(4*x1*x))^(1/2))
Zeichnen	B
d	0.47558 ± 0.00558
K	755.73473 ± 55.6365
x1	0.005 ± 0
Chi-Quadr Reduziert	1.54159E-5
R-Quadrat (COD)	0.99949
Kor. R-Quadrat	0.99938

(RM1128)

NMR titration of tris(4-fluorophenyl)borane (1e) with 3,5-difluoro-4-(trifluoromethyl)pyridine (2k)

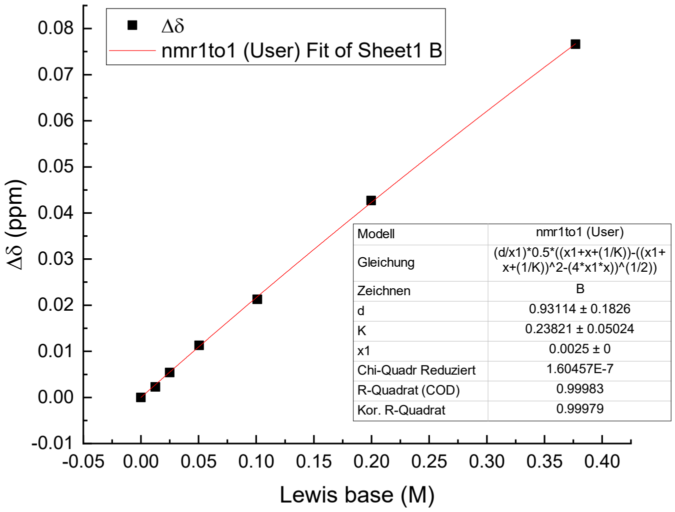
Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	5.0×10^{-3}	0.0	7.1794	0.0000
2	5.0×10^{-3}	2.5×10^{-3}	7.1666	0.0128
3	5.0×10^{-3}	5.0×10^{-3}	7.1540	0.0254
4	5.0×10^{-3}	7.5×10^{-3}	7.1434	0.0360
5	5.0×10^{-3}	1.0×10^{-2}	7.1336	0.0458
6	5.0×10^{-3}	1.5×10^{-2}	7.1165	0.0629
7	5.0×10^{-3}	2.0×10^{-2}	7.1030	0.0764



(RM1167)

NMR titration of tris(4-fluorophenyl)borane (1e) with 3,5-dinitropyridine (2l)

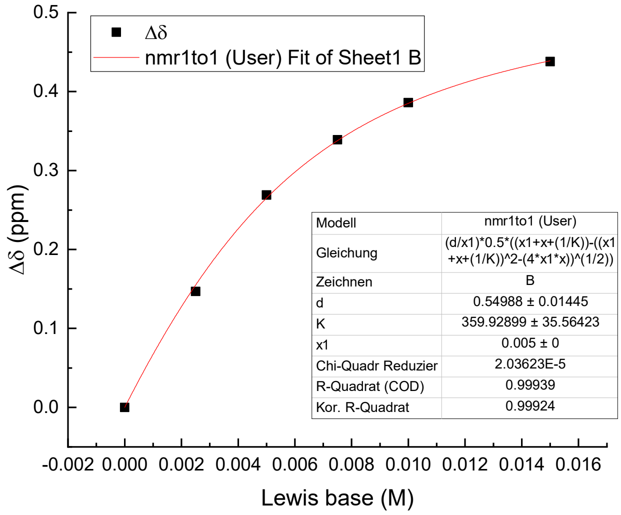
Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	2.5×10^{-3}	0.0	7.1787	0.0000
2	2.5×10^{-3}	1.25×10^{-2}	7.1764	0.0023
3	2.5×10^{-3}	2.50×10^{-2}	7.1733	0.0054
4	2.5×10^{-3}	5.05×10^{-2}	7.1674	0.0113
5	2.5×10^{-3}	1.01×10^{-1}	7.1574	0.0213
6	2.5×10^{-3}	2.00×10^{-1}	7.1360	0.0427
7	2.5×10^{-3}	3.77×10^{-1}	7.1021	0.0766



(RM1157)

NMR titration of tris(4-fluorophenyl)borane (1e) with tris(4-methoxyphenyl)phosphine (4a)

Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	5.0×10^{-3}	0.0	7.605	0.000
2	5.0×10^{-3}	2.5×10^{-3}	7.458	0.147
3	5.0×10^{-3}	5.0×10^{-3}	7.336	0.269
4	5.0×10^{-3}	7.5×10^{-3}	7.266	0.339
5	5.0×10^{-3}	1.0×10^{-2}	7.219	0.386
6	5.0×10^{-3}	1.5×10^{-2}	7.167	0.438

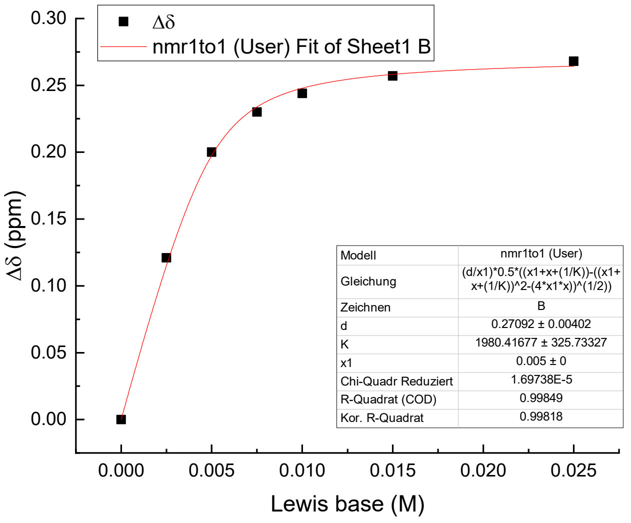


Modell	nmr1to1 (User)
Gleichung	(d/x1)*0.5*((x1+x+(1/K))-((x1+x+(1/K))^2-(4*x1*x))^(1/2))
Zeichnen	B
d	0.54988 ± 0.01445
K	359.92899 ± 35.56423
x1	0.005 ± 0
Chi-Quadr Reduzier	2.03623E-5
R-Quadrat (COD)	0.99939
Kor. R-Quadrat	0.99924

(RM1260)

NMR titration of tris(4-fluorophenyl)borane (1e) with triethylphosphine oxide (10)

Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	5.0×10^{-3}	0.0	7.604	0.000
2	5.0×10^{-3}	2.5×10^{-3}	7.483	0.121
3	5.0×10^{-3}	5.0×10^{-3}	7.404	0.200
4	5.0×10^{-3}	7.5×10^{-3}	7.374	0.230
5	5.0×10^{-3}	1.0×10^{-2}	7.360	0.244
6	5.0×10^{-3}	1.5×10^{-2}	7.347	0.257
7	5.0×10^{-3}	2.5×10^{-2}	7.336	0.268

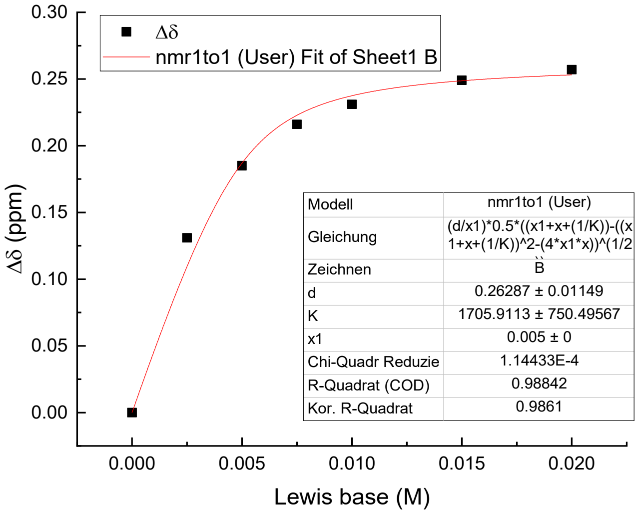


Modell	nmr1to1 (User)
Gleichung	(d/x1)*0.5*((x1+x+(1/K))-((x1+x+(1/K))^2-(4*x1*x))^(1/2))
Zeichnen	B
d	0.27092 ± 0.00402
K	1980.41677 ± 325.73327
x1	0.005 ± 0
Chi-Quadr Reduziert	1.69738E-5
R-Quadrat (COD)	0.99849
Kor. R-Quadrat	0.99818

(RM1261)

NMR titration of tris(4-chlorophenyl)borane (1f) with 3,5-bis(trifluoromethyl)pyridine (2i)

Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	5.0×10^{-3}	0.0	7.529	0.000
2	5.0×10^{-3}	2.5×10^{-3}	7.398	0.131
3	5.0×10^{-3}	5.0×10^{-3}	7.344	0.185
4	5.0×10^{-3}	7.5×10^{-3}	7.313	0.216
5	5.0×10^{-3}	1.0×10^{-2}	7.298	0.231
6	5.0×10^{-3}	1.5×10^{-2}	7.280	0.249
7	5.0×10^{-3}	2.0×10^{-2}	7.272	0.257

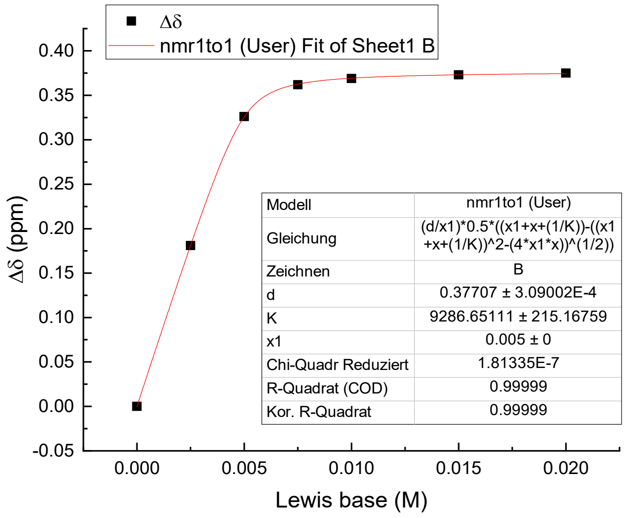


Modell	nmr1to1 (User)
Gleichung	(d/x1)*0.5*((x1+x+(1/K))-((x 1+x+(1/K))^2-(4*x1*x))^(1/2
Zeichnen	B
d	0.26287 ± 0.01149
K	1705.9113 ± 750.49567
x1	0.005 ± 0
Chi-Quadr Reduzie	1.14433E-4
R-Quadrat (COD)	0.98842
Kor. R-Quadrat	0.9861

(RM1145)

NMR titration of tris(4-chlorophenyl)borane (1f) with 3,4,5-trichloropyridine (2j)

Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	5.0×10^{-3}	0.0	7.465	0
2	5.0×10^{-3}	2.5×10^{-3}	7.284	0.181
3	5.0×10^{-3}	5.0×10^{-3}	7.139	0.326
4	5.0×10^{-3}	7.5×10^{-3}	7.103	0.362
5	5.0×10^{-3}	1.0×10^{-2}	7.096	0.369
6	5.0×10^{-3}	1.5×10^{-2}	7.092	0.373
7	5.0×10^{-3}	2.0×10^{-2}	7.090	0.375

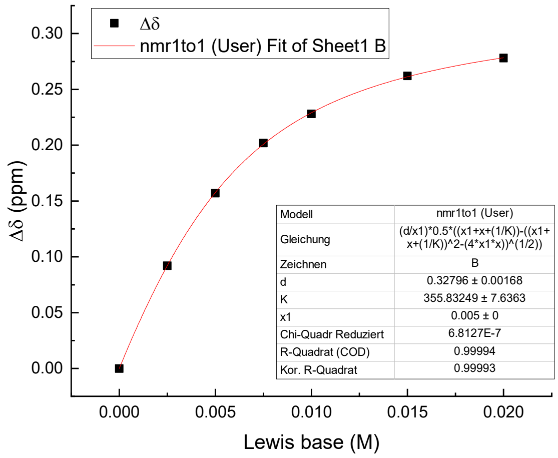


Modell	nmr1to1 (User)
Gleichung	(d/x1)*0.5*((x1+x+(1/K))-((x1 +x+(1/K))^2-(4*x1*x))^(1/2))
Zeichnen	B
d	0.37707 ± 3.09002E-4
K	9286.65111 ± 215.16759
x1	0.005 ± 0
Chi-Quadr Reduziert	1.81335E-7
R-Quadrat (COD)	0.99999
Kor. R-Quadrat	0.99999

(RM1133)

NMR titration of tris(4-chlorophenyl)borane (1f) with 3,5-difluoro-4-(trifluoromethyl)pyridine (2k)

Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	5.0×10^{-3}	0.0	7.500	0.000
2	5.0×10^{-3}	2.5×10^{-3}	7.408	0.092
3	5.0×10^{-3}	5.0×10^{-3}	7.343	0.157
4	5.0×10^{-3}	7.5×10^{-3}	7.298	0.202
5	5.0×10^{-3}	1.0×10^{-2}	7.272	0.228
6	5.0×10^{-3}	1.5×10^{-2}	7.238	0.262
7	5.0×10^{-3}	2.0×10^{-2}	7.222	0.278

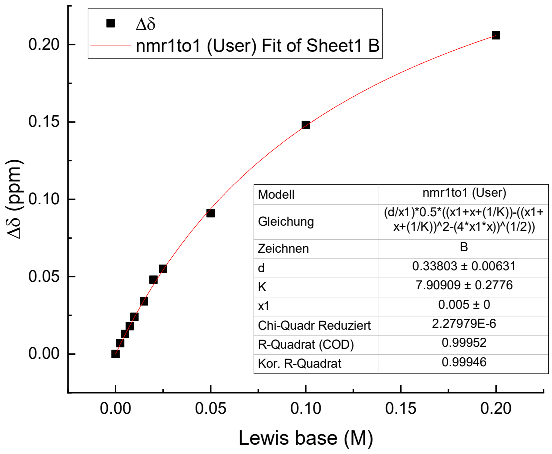


Modell	nmr1to1 (User)
Gleichung	(d/x1)*0.5*((x1+x+(1/K))-((x1+x+(1/K))^2-(4*x1*x))^(1/2))
Zeichnen	B
d	0.32796 ± 0.00168
K	355.83249 ± 7.6363
x1	0.005 ± 0
Chi-Quadr Reduziert	6.8127E-7
R-Quadrat (COD)	0.99994
Kor. R-Quadrat	0.99993

(RM1168)

NMR titration of tris(4-chlorophenyl)borane (1f) with 3,5-dinitropyridine (2l)

Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	5.0×10^{-3}	0.0	7.495	0.000
2	5.0×10^{-3}	2.5×10^{-3}	7.488	0.007
3	5.0×10^{-3}	5.0×10^{-3}	7.482	0.013
4	5.0×10^{-3}	7.5×10^{-3}	7.477	0.018
5	5.0×10^{-3}	1.0×10^{-2}	7.471	0.024
6	5.0×10^{-3}	1.5×10^{-2}	7.461	0.034
7	5.0×10^{-3}	2.0×10^{-2}	7.447	0.048
8	5.0×10^{-3}	2.5×10^{-2}	7.440	0.055
9	5.0×10^{-3}	5.0×10^{-2}	7.404	0.091
10	5.0×10^{-3}	1.0×10^{-1}	7.347	0.148
11	5.0×10^{-3}	2.0×10^{-1}	7.289	0.206

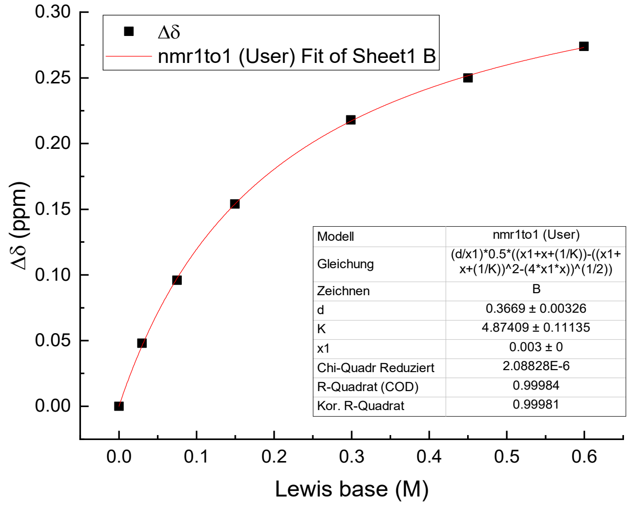


Modell	nmr1to1 (User)
Gleichung	(d/x1)*0.5*((x1+x+(1/K))-((x1+x+(1/K))^2-(4*x1*x))^(1/2))
Zeichnen	B
d	0.33803 ± 0.00631
K	7.90909 ± 0.2776
x1	0.005 ± 0
Chi-Quadr Reduziert	2.27979E-6
R-Quadrat (COD)	0.99952
Kor. R-Quadrat	0.99946

(RM1155)

NMR titration of tris(4-chlorophenyl)borane (1f) with 4-chloro-3,5-dinitropyridine (2m)

Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	3.0×10^{-3}	0.0	7.499	0.000
2	3.0×10^{-3}	3.0×10^{-2}	7.451	0.048
3	3.0×10^{-3}	7.5×10^{-2}	7.403	0.096
4	3.0×10^{-3}	1.5×10^{-1}	7.345	0.154
5	3.0×10^{-3}	3.0×10^{-1}	7.281	0.218
6	3.0×10^{-3}	4.5×10^{-1}	7.249	0.250
7	3.0×10^{-3}	6.0×10^{-1}	7.225	0.274

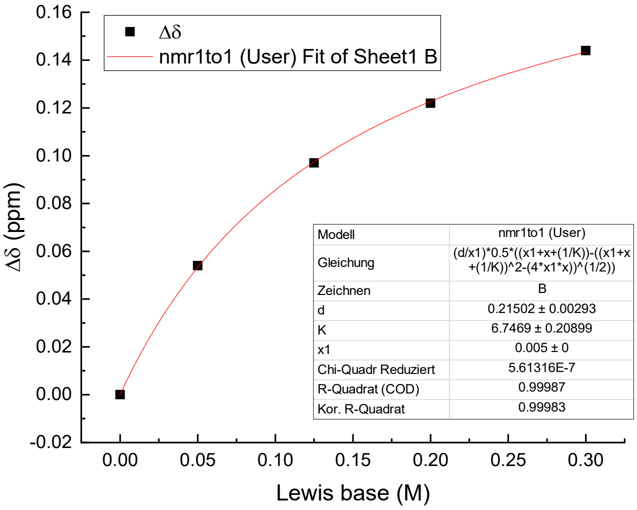


Modell	nmr1to1 (User)
Gleichung	(d/x1)*0.5*((x1+x+(1/K))-((x1+x+(1/K))^2-(4*x1*x))^(1/2))
Zeichnen	B
d	0.3669 ± 0.00326
K	4.87409 ± 0.11135
x1	0.003 ± 0
Chi-Quadr Reduziert	2.08828E-6
R-Quadrat (COD)	0.99984
Kor. R-Quadrat	0.99981

(RM1166)

NMR titration of tris(4-chlorophenyl)borane (1f) with 4-methoxybenzaldehyde (7a)

Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	5.0×10^{-3}	0.0	7.460	0.000
2	5.0×10^{-3}	5.00×10^{-2}	7.406	0.054
3	5.0×10^{-3}	1.25×10^{-1}	7.363	0.097
4	5.0×10^{-3}	2.00×10^{-1}	7.338	0.122
5	5.0×10^{-3}	3.00×10^{-1}	7.316	0.144

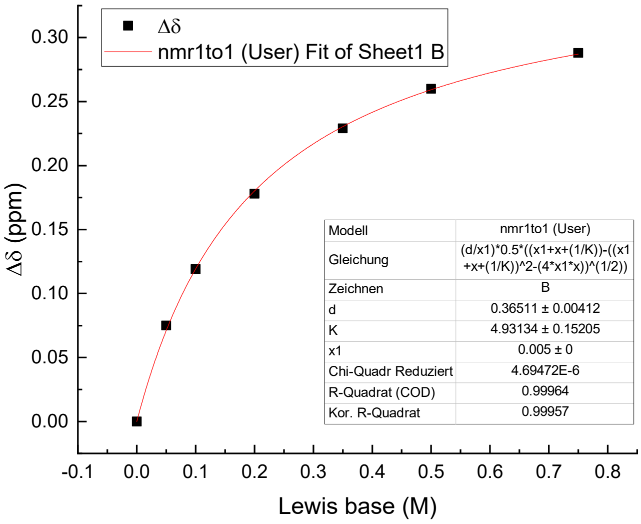


Modell	nmr1to1 (User)
Gleichung	(d/x1)*0.5*((x1+x+(1/K))-((x1+x+(1/K))^2-(4*x1*x))^(1/2))
Zeichnen	B
d	0.21502 ± 0.00293
K	6.7469 ± 0.20899
x1	0.005 ± 0
Chi-Quadr Reduziert	5.61316E-7
R-Quadrat (COD)	0.99987
Kor. R-Quadrat	0.99983

(RM1188)

NMR titration of tris(4-chlorophenyl)borane (1f) with acetonitrile (3a)

Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	5.0×10^{-3}	0.0	7.498	0.000
2	5.0×10^{-3}	5.0×10^{-2}	7.423	0.075
3	5.0×10^{-3}	1.0×10^{-1}	7.379	0.119
4	5.0×10^{-3}	2.0×10^{-1}	7.320	0.178
5	5.0×10^{-3}	3.5×10^{-1}	7.269	0.229
6	5.0×10^{-3}	5.0×10^{-1}	7.238	0.260
7	5.0×10^{-3}	7.5×10^{-1}	7.210	0.288

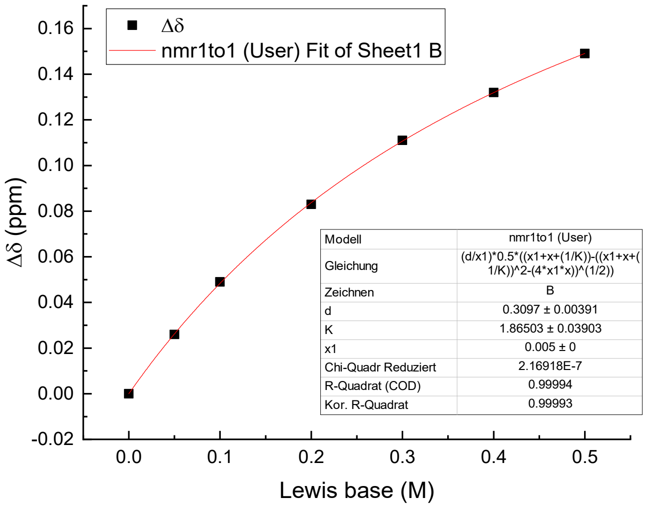


Modell	nmr1to1 (User)
Gleichung	(d/x1)*0.5*((x1+x+(1/K))-((x1+x+(1/K))^2-(4*x1*x))^(1/2))
Zeichnen	B
d	0.36511 ± 0.00412
K	4.93134 ± 0.15205
x1	0.005 ± 0
Chi-Quadr Reduziert	4.69472E-6
R-Quadrat (COD)	0.99964
Kor. R-Quadrat	0.99957

(RM1258)

NMR titration of tris(4-chlorophenyl)borane (1f) with 4-fluorobenzonitrile (3b)

Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	5.0×10^{-3}	0.0	7.499	0.000
2	5.0×10^{-3}	5.0×10^{-2}	7.473	0.026
3	5.0×10^{-3}	1.0×10^{-1}	7.450	0.049
4	5.0×10^{-3}	2.0×10^{-1}	7.416	0.083
5	5.0×10^{-3}	3.0×10^{-1}	7.388	0.111
6	5.0×10^{-3}	4.0×10^{-1}	7.367	0.132
7	5.0×10^{-3}	5.0×10^{-1}	7.350	0.149

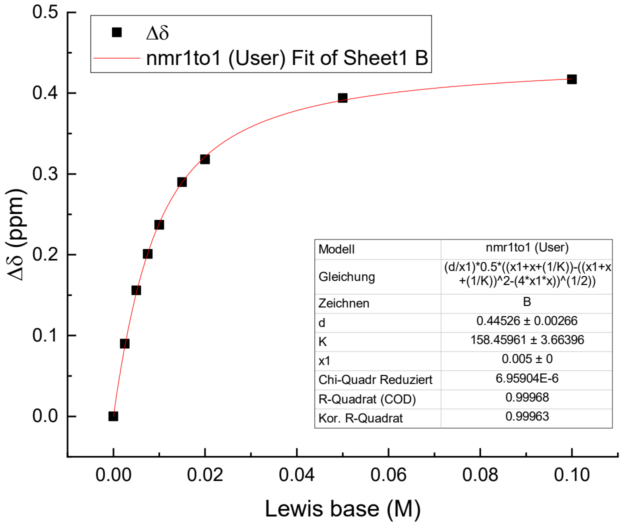


Modell	nmr1to1 (User)
Gleichung	(d/x1)*0.5*((x1+x+(1/K))-((x1+x+(1/K))^2-(4*x1*x))^(1/2))
Zeichnen	B
d	0.3097 ± 0.00391
K	1.86503 ± 0.03903
x1	0.005 ± 0
Chi-Quadr Reduziert	2.16918E-7
R-Quadrat (COD)	0.99994
Kor. R-Quadrat	0.99993

(RM1195)

NMR titration of tris(4-chlorophenyl)borane (1f) with triphenylphosphine (4b)

Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	5.0×10^{-3}	0.0	7.496	0.000
2	5.0×10^{-3}	2.5×10^{-3}	7.406	0.090
3	5.0×10^{-3}	5.0×10^{-3}	7.340	0.156
4	5.0×10^{-3}	7.5×10^{-3}	7.295	0.201
5	5.0×10^{-3}	1.0×10^{-2}	7.259	0.237
6	5.0×10^{-3}	1.5×10^{-2}	7.206	0.290
7	5.0×10^{-3}	2.0×10^{-2}	7.178	0.318
8	5.0×10^{-3}	5.0×10^{-2}	7.102	0.394
9	5.0×10^{-3}	1.0×10^{-1}	7.079	0.417

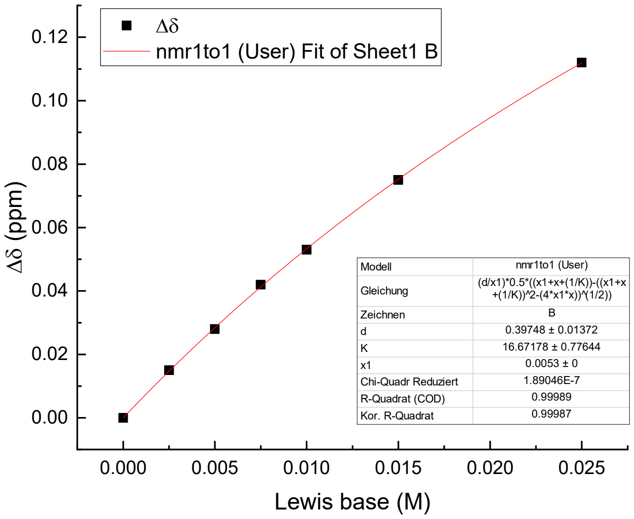


Modell	nmr1to1 (User)
Gleichung	(d/x1)*0.5*((x1+x+(1/K))-((x1+x+(1/K))^2-(4*x1*x))^(1/2))
Zeichnen	B
d	0.44526 ± 0.00266
K	158.45961 ± 3.66396
x1	0.005 ± 0
Chi-Quadr Reduziert	6.95904E-6
R-Quadrat (COD)	0.99968
Kor. R-Quadrat	0.99963

(RM1259)

NMR titration of tris(4-chlorophenyl)borane (1f) with tris(4-chlorophenyl)phosphine (4c)

Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	5.3×10^{-3}	0.0	7.499	0.000
2	5.3×10^{-3}	2.5×10^{-3}	7.484	0.015
3	5.3×10^{-3}	5.0×10^{-3}	7.471	0.028
4	5.3×10^{-3}	7.5×10^{-3}	7.457	0.042
5	5.3×10^{-3}	1.0×10^{-2}	7.446	0.053
6	5.3×10^{-3}	1.5×10^{-2}	7.424	0.075
7	5.3×10^{-3}	2.5×10^{-2}	7.387	0.112

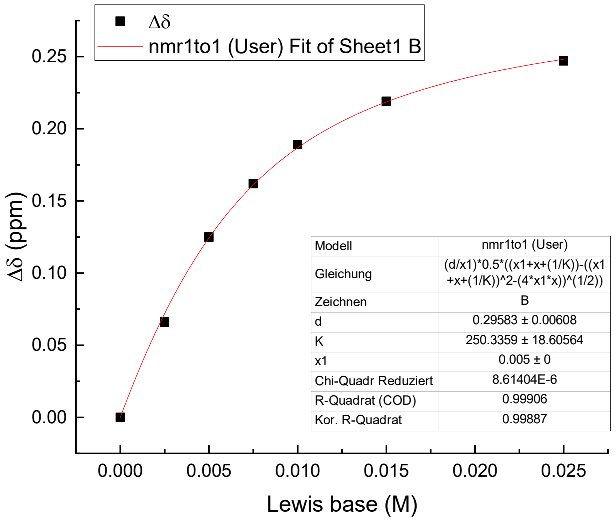


Modell	nmr1to1 (User)
Gleichung	(d/x1)*0.5*((x1+x+(1/K))-((x1+x+(1/K))^2-(4*x1*x))^(1/2))
Zeichnen	B
d	0.39748 ± 0.01372
K	16.67178 ± 0.77644
x1	0.0053 ± 0
Chi-Quadr Reduziert	1.89046E-7
R-Quadrat (COD)	0.99989
Kor. R-Quadrat	0.99987

(RM1254)

NMR titration of tris(4-chlorophenyl)borane (1f) with *N*,*N*-dimethylacetamide (9)

Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	5.0×10^{-3}	0.0	7.499	0.000
2	5.0×10^{-3}	2.5×10^{-3}	7.433	0.066
3	5.0×10^{-3}	5.0×10^{-3}	7.374	0.125
4	5.0×10^{-3}	7.5×10^{-3}	7.337	0.162
5	5.0×10^{-3}	1.0×10^{-2}	7.310	0.189
6	5.0×10^{-3}	1.5×10^{-2}	7.280	0.219
7	5.0×10^{-3}	2.5×10^{-2}	7.252	0.247

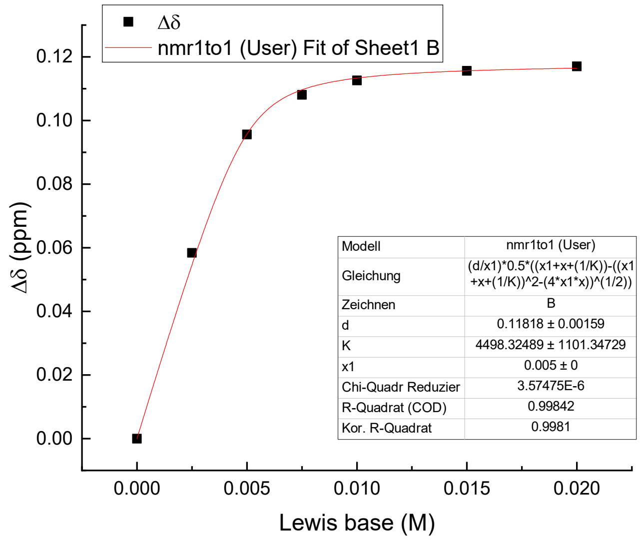


Modell	nmr1to1 (User)
Gleichung	(d/x1)*0.5*((x1+x+(1/K))-((x1+x+(1/K))^2-(4*x1*x))^(1/2))
Zeichnen	B
d	0.29583 ± 0.00608
K	250.3359 ± 18.60564
x1	0.005 ± 0
Chi-Quadr Reduziert	8.61404E-6
R-Quadrat (COD)	0.99906
Kor. R-Quadrat	0.99887

(RM1271)

NMR titration of tris(2,4,6-trifluorophenyl)borane (1g) with 3,5-dinitropyridine (2l)

Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	5.0×10^{-3}	0.0	6.6768	0.0000
2	5.0×10^{-3}	2.5×10^{-3}	6.6184	0.0584
3	5.0×10^{-3}	5.0×10^{-3}	6.5812	0.0956
4	5.0×10^{-3}	7.5×10^{-3}	6.5687	0.1081
5	5.0×10^{-3}	1.0×10^{-2}	6.5642	0.1126
6	5.0×10^{-3}	1.5×10^{-2}	6.5612	0.1156
7	5.0×10^{-3}	2.0×10^{-2}	6.5598	0.1170

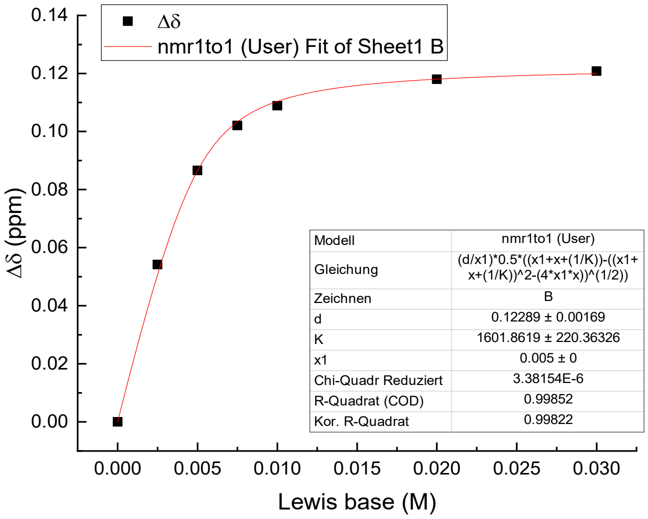


Modell	nmr1to1 (User)
Gleichung	(d/x1)*0.5*((x1+x+(1/K))-((x1+x+(1/K))^2-(4*x1*x))^(1/2))
Zeichnen	B
d	0.11818 ± 0.00159
K	4498.32489 ± 1101.34729
x1	0.005 ± 0
Chi-Quadr Reduzier	3.57475E-6
R-Quadrat (COD)	0.99842
Kor. R-Quadrat	0.9981

(RM1239)

NMR titration of tris(2,4,6-trifluorophenyl)borane (1g) with 4-chloro-3,5-dinitropyridine (2m)

Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	5.0×10^{-3}	0.0	6.6811	0.0000
2	5.0×10^{-3}	2.5×10^{-3}	6.6269	0.0542
3	5.0×10^{-3}	5.0×10^{-3}	6.5945	0.0866
4	5.0×10^{-3}	7.5×10^{-3}	6.5790	0.1021
5	5.0×10^{-3}	1.0×10^{-2}	6.5722	0.1089
6	5.0×10^{-3}	2.0×10^{-2}	6.5631	0.1180
7	5.0×10^{-3}	3.0×10^{-2}	6.5603	0.1208

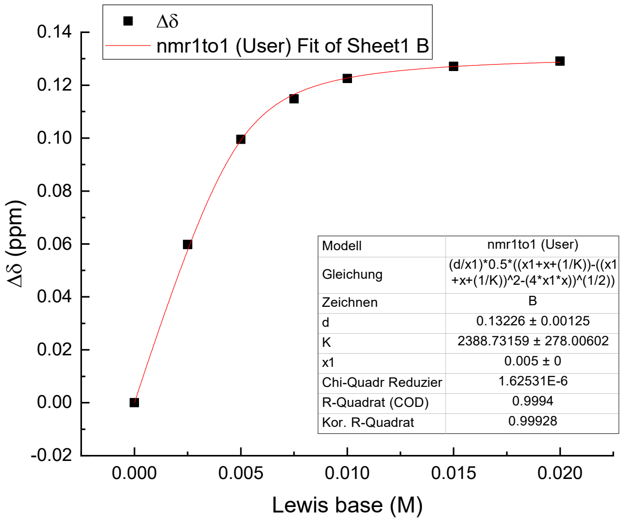


Modell	nmr1to1 (User)
Gleichung	(d/x1)*0.5*((x1+x+(1/K))-((x1+x+(1/K))^2-(4*x1*x))^(1/2))
Zeichnen	B
d	0.12289 ± 0.00169
K	1601.8619 ± 220.36326
x1	0.005 ± 0
Chi-Quadr Reduziert	3.38154E-6
R-Quadrat (COD)	0.99852
Kor. R-Quadrat	0.99822

(RM1165)

NMR titration of tris(2,4,6-trifluorophenyl)borane (1g) with 4-fluorobenzonitrile (3b)

Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	5.0×10^{-3}	0.0	6.6766	0.0000
2	5.0×10^{-3}	2.5×10^{-3}	6.6168	0.0598
3	5.0×10^{-3}	5.0×10^{-3}	6.5771	0.0995
4	5.0×10^{-3}	7.5×10^{-3}	6.5618	0.1148
5	5.0×10^{-3}	1.0×10^{-2}	6.5541	0.1225
6	5.0×10^{-3}	1.5×10^{-2}	6.5495	0.1271
7	5.0×10^{-3}	2.0×10^{-2}	6.5475	0.1291

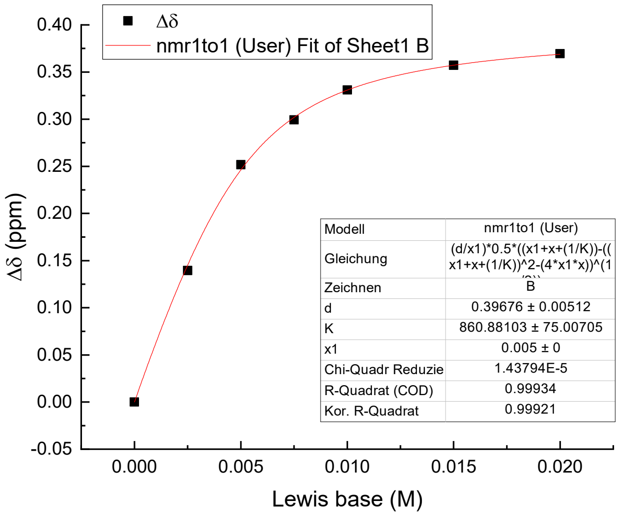


Modell	nmr1to1 (User)
Gleichung	(d/x1)*0.5*((x1+x+(1/K))-((x1+x+(1/K))^2-(4*x1*x))^(1/2))
Zeichnen	B
d	0.13226 ± 0.00125
K	2388.73159 ± 278.00602
x1	0.005 ± 0
Chi-Quadr Reduzier	1.62531E-6
R-Quadrat (COD)	0.9994
Kor. R-Quadrat	0.99928

(RM1238)

NMR titration of tris(2,4,6-trifluorophenyl)borane (1g) with tris(4-methoxyphenyl)phosphine (4a)

Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	5.0×10^{-3}	0.0	6.6759	0.0000
2	5.0×10^{-3}	2.5×10^{-3}	6.5364	0.1395
3	5.0×10^{-3}	5.0×10^{-3}	6.4241	0.2518
4	5.0×10^{-3}	7.5×10^{-3}	6.3767	0.2992
5	5.0×10^{-3}	1.0×10^{-2}	6.3449	0.3310
6	5.0×10^{-3}	1.5×10^{-2}	6.3187	0.3572
7	5.0×10^{-3}	2.0×10^{-2}	6.3065	0.3694

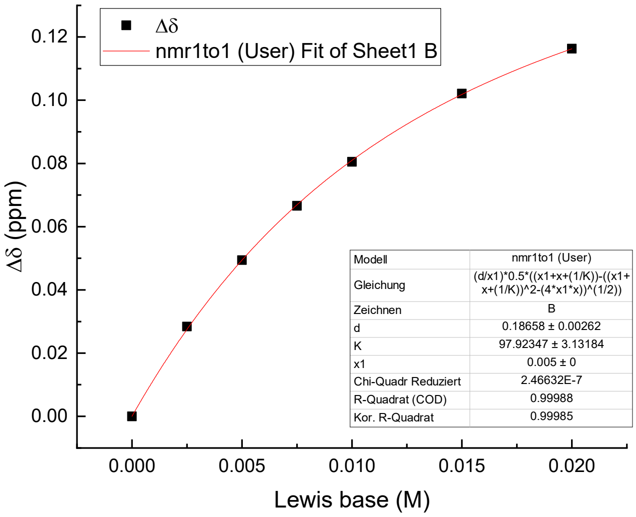


Modell	nmr1to1 (User)
Gleichung	(d/x1)*0.5*((x1+x+(1/K))-((x1+x+(1/K))^2-(4*x1*x))^(1
Zeichnen	B
d	0.39676 ± 0.00512
K	860.88103 ± 75.00705
x1	0.005 ± 0
Chi-Quadr Reduzie	1.43794E-5
R-Quadrat (COD)	0.99934
Kor. R-Quadrat	0.99921

(RM1237)

NMR titration of tris(2,4,6-trifluorophenyl)borane (1g) with 4-methoxyacetophenone (5a)

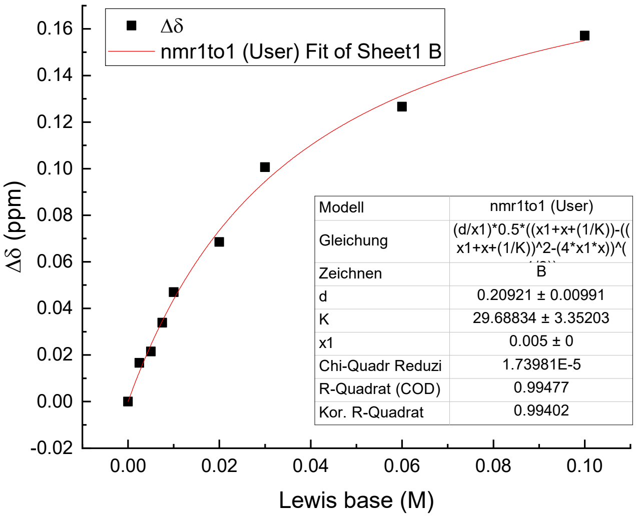
Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	5.0×10^{-3}	0.0	6.6790	0.0000
2	5.0×10^{-3}	2.5×10^{-3}	6.6506	0.0284
3	5.0×10^{-3}	5.0×10^{-3}	6.6296	0.0494
4	5.0×10^{-3}	7.5×10^{-3}	6.6124	0.0666
5	5.0×10^{-3}	1.0×10^{-2}	6.5985	0.0805
6	5.0×10^{-3}	1.5×10^{-2}	6.5769	0.1021
7	5.0×10^{-3}	2.0×10^{-2}	6.5627	0.1163



(RM1148)

NMR titration of tris(2,4,6-trifluorophenyl)borane (1g) with 4-methylacetophenone (5b)

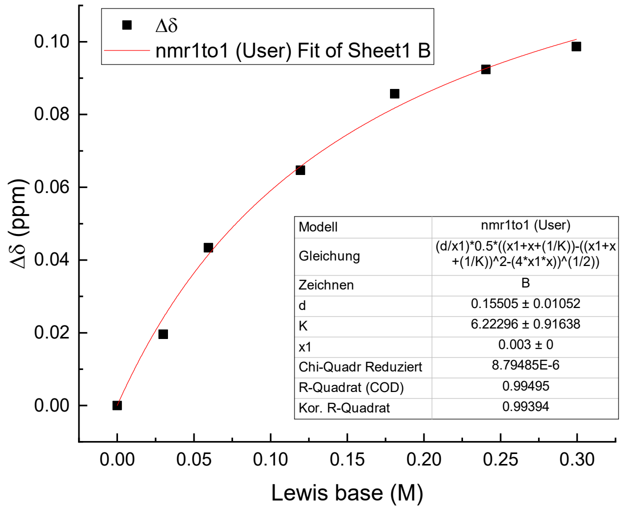
Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	5.0×10^{-3}	0.0	6.6823	0.0000
2	5.0×10^{-3}	2.5×10^{-3}	6.6657	0.0166
3	5.0×10^{-3}	5.0×10^{-3}	6.6608	0.0215
4	5.0×10^{-3}	7.5×10^{-3}	6.6484	0.0339
5	5.0×10^{-3}	1.0×10^{-2}	6.6353	0.0470
6	5.0×10^{-3}	2.0×10^{-2}	6.6138	0.0685
7	5.0×10^{-3}	3.0×10^{-2}	6.5817	0.1006
8	5.0×10^{-3}	6.0×10^{-2}	6.5557	0.1266
9	5.0×10^{-3}	1.0×10^{-1}	6.5252	0.1571



(RM1141)

NMR titration of tris(2,4,6-trifluorophenyl)borane (1g) with 4-bromoacetophenone (5c)

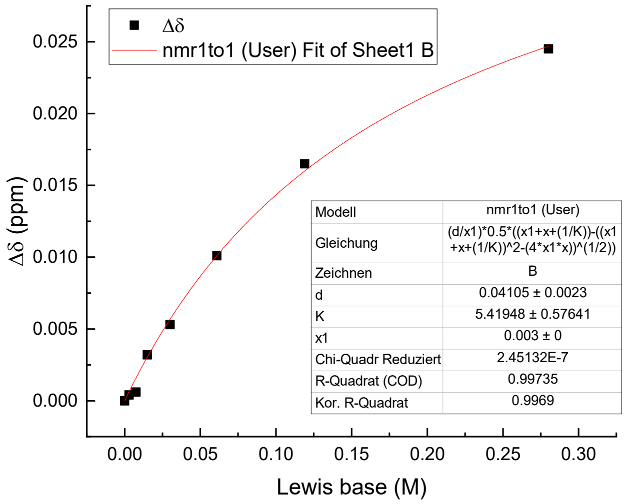
Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	3.0×10^{-3}	0.0	6.6815	0.0000
2	3.0×10^{-3}	3.00×10^{-2}	6.6619	0.0196
3	3.0×10^{-3}	5.95×10^{-2}	6.6381	0.0434
4	3.0×10^{-3}	1.12×10^{-1}	6.6168	0.0647
5	3.0×10^{-3}	1.81×10^{-1}	6.5958	0.0857
6	3.0×10^{-3}	2.41×10^{-1}	6.5891	0.0924
7	3.0×10^{-3}	3.00×10^{-1}	6.5828	0.0987



(RM1177)

NMR titration of tris(2,4,6-trifluorophenyl)borane (1g) with 4-(trifluoromethyl)acetophenone (5d)

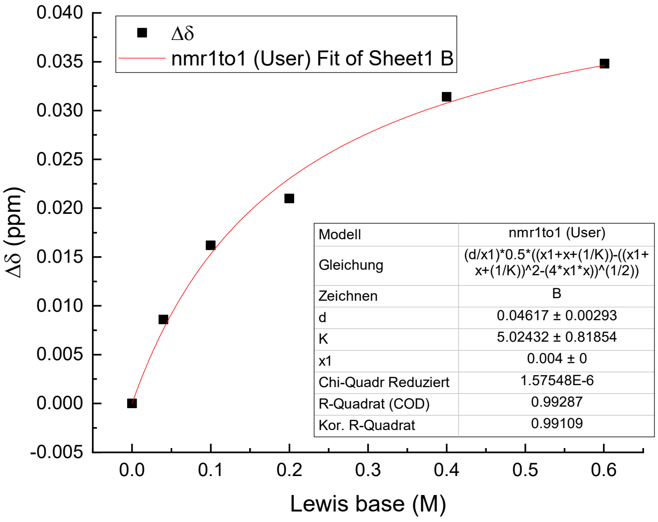
Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	3.0×10^{-3}	0.0	6.6783	0.0000
2	3.0×10^{-3}	3.0×10^{-3}	6.6779	0.0004
3	3.0×10^{-3}	7.5×10^{-3}	6.6777	0.0006
4	3.0×10^{-3}	1.5×10^{-2}	6.6751	0.0032
5	3.0×10^{-3}	3.0×10^{-2}	6.6730	0.0053
6	3.0×10^{-3}	6.1×10^{-2}	6.6682	0.0101
7	3.0×10^{-3}	1.2×10^{-1}	6.6618	0.0165
8	3.0×10^{-3}	2.8×10^{-1}	6.6538	0.0245



(RM1153)

NMR titration of tris(2,4,6-trifluorophenyl)borane (1g) with 4-nitroacetophenone (5e)

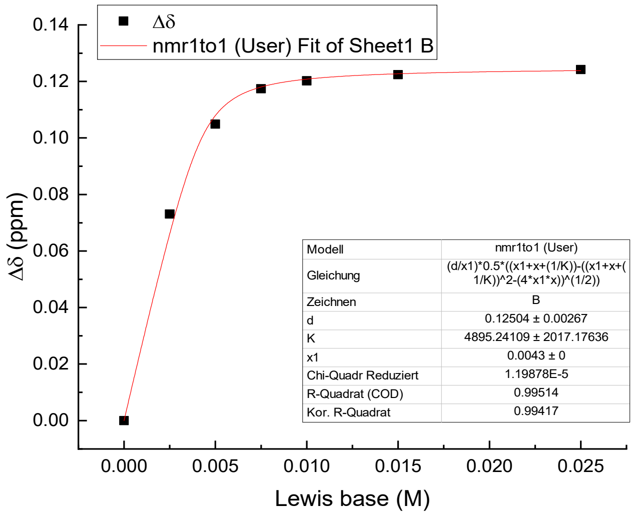
Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	4.0×10^{-3}	0.0	6.6807	0.0000
2	4.0×10^{-3}	4.00×10^{-2}	6.6721	0.0086
3	4.0×10^{-3}	1.00×10^{-1}	6.6645	0.0162
4	4.0×10^{-3}	2.00×10^{-1}	6.6597	0.0210
5	4.0×10^{-3}	4.00×10^{-1}	6.6493	0.0314
6	4.0×10^{-3}	6.01×10^{-1}	6.6459	0.0348



(RM1158)

NMR titration of tris(2,4,6-trifluorophenyl)borane (1g) with 4-methoxybenzaldehyde (7a)

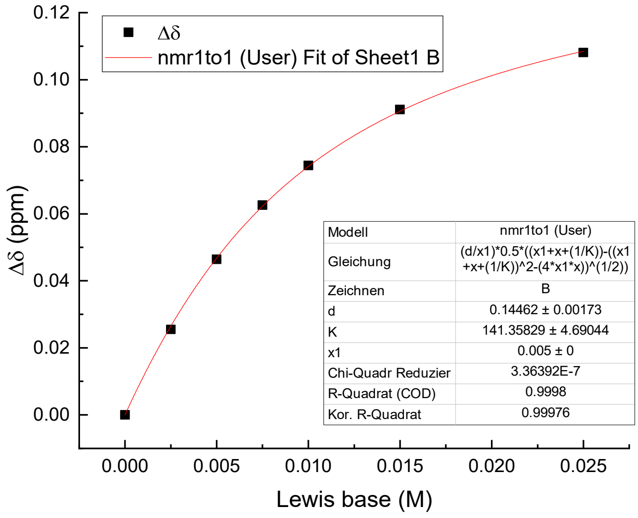
Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	4.3×10^{-3}	0.0	6.6481	0.0000
2	4.3×10^{-3}	2.5×10^{-3}	6.5750	0.0731
3	4.3×10^{-3}	5.0×10^{-3}	6.5432	0.1049
4	4.3×10^{-3}	7.5×10^{-3}	6.5307	0.1174
5	4.3×10^{-3}	1.0×10^{-2}	6.5279	0.1202
6	4.3×10^{-3}	1.5×10^{-2}	6.5257	0.1224
7	4.3×10^{-3}	2.5×10^{-2}	6.5239	0.1242



(RM1187)

NMR titration of tris(2,4,6-trifluorophenyl)borane (1g) with benzaldehyde (7b)

Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	5.0×10^{-3}	0.0	6.6803	0.0000
2	5.0×10^{-3}	2.5×10^{-3}	6.6548	0.0255
3	5.0×10^{-3}	5.0×10^{-3}	6.6339	0.0464
4	5.0×10^{-3}	7.5×10^{-3}	6.6177	0.0626
5	5.0×10^{-3}	1.0×10^{-2}	6.6059	0.0744
6	5.0×10^{-3}	1.5×10^{-2}	6.5892	0.0911
7	5.0×10^{-3}	2.5×10^{-2}	6.5722	0.1081

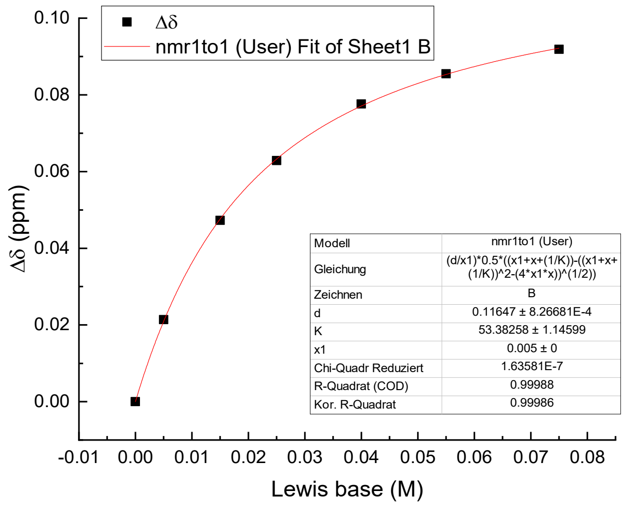


Modell	nmr1to1 (User)
Gleichung	(d/x1)*0.5*((x1+x+(1/K))-((x1 +x+(1/K))^2-(4*x1*x))^(1/2))
Zeichnen	B
d	0.14462 ± 0.00173
K	141.35829 ± 4.69044
x1	0.005 ± 0
Chi-Quadr Reduzier	3.36392E-7
R-Quadrat (COD)	0.9998
Kor. R-Quadrat	0.99976

(RM1214)

NMR titration of tris(2,4,6-trifluorophenyl)borane (1g) with 4-bromobenzaldehyde (7c)

Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	5.0×10^{-3}	0.0	6.6507	0.0000
2	5.0×10^{-3}	5.0×10^{-3}	6.6293	0.0214
3	5.0×10^{-3}	1.5×10^{-2}	6.6034	0.0473
4	5.0×10^{-3}	2.5×10^{-2}	6.5878	0.0629
5	5.0×10^{-3}	4.0×10^{-2}	6.5731	0.0776
6	5.0×10^{-3}	5.5×10^{-2}	6.5652	0.0855
7	5.0×10^{-3}	7.5×10^{-2}	6.5588	0.0919

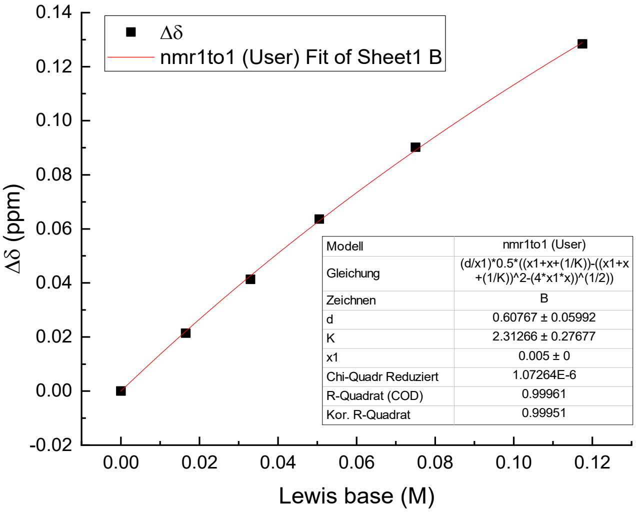


Modell	nmr1to1 (User)
Gleichung	(d/x1)*0.5*((x1+x+(1/K))-((x1+x+ (1/K))^2-(4*x1*x))^(1/2))
Zeichnen	B
d	0.11647 ± 8.26681E-4
K	53.38258 ± 1.14599
x1	0.005 ± 0
Chi-Quadr Reduziert	1.63581E-7
R-Quadrat (COD)	0.99988
Kor. R-Quadrat	0.99986

(RM1186)

NMR titration of tris(2,4,6-trifluorophenyl)borane (1g) with 4-nitrobenzaldehyde (7d)

Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	5.0×10^{-3}	0.0	10.1462	0.0000
2	5.0×10^{-3}	1.65×10^{-2}	10.1248	0.0214
3	5.0×10^{-3}	3.30×10^{-2}	10.1049	0.0413
4	5.0×10^{-3}	5.05×10^{-2}	10.0826	0.0636
5	5.0×10^{-3}	7.50×10^{-2}	10.0560	0.0902
6	5.0×10^{-3}	1.175×10^{-1}	10.0178	0.1284

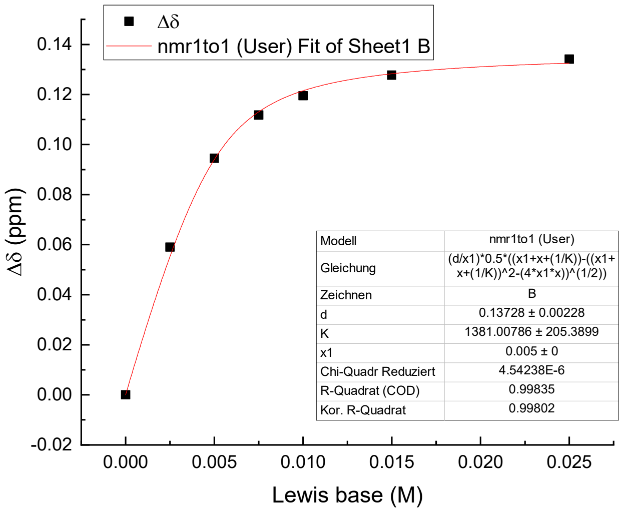


Modell	nmr1to1 (User)
Gleichung	(d/x1)*0.5*((x1+x+(1/K))-((x1+x+(1/K))^2-(4*x1*x))^(1/2))
Zeichnen	B
d	0.60767 ± 0.05992
K	2.31266 ± 0.27677
x1	0.005 ± 0
Chi-Quadr Reduziert	1.07264E-6
R-Quadrat (COD)	0.99961
Kor. R-Quadrat	0.99951

(RM1185)

NMR titration of tris(2,4,6-trifluorophenyl)borane (1g) with trans-crotonaldehyde (8)

Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	5.0×10^{-3}	0.0	6.6572	0.0000
2	5.0×10^{-3}	2.5×10^{-3}	6.5982	0.0590
3	5.0×10^{-3}	5.0×10^{-3}	6.5627	0.0945
4	5.0×10^{-3}	7.5×10^{-3}	6.5454	0.1118
5	5.0×10^{-3}	1.0×10^{-2}	6.5377	0.1195
6	5.0×10^{-3}	1.5×10^{-2}	6.5295	0.1277
7	5.0×10^{-3}	2.5×10^{-2}	6.5231	0.1341

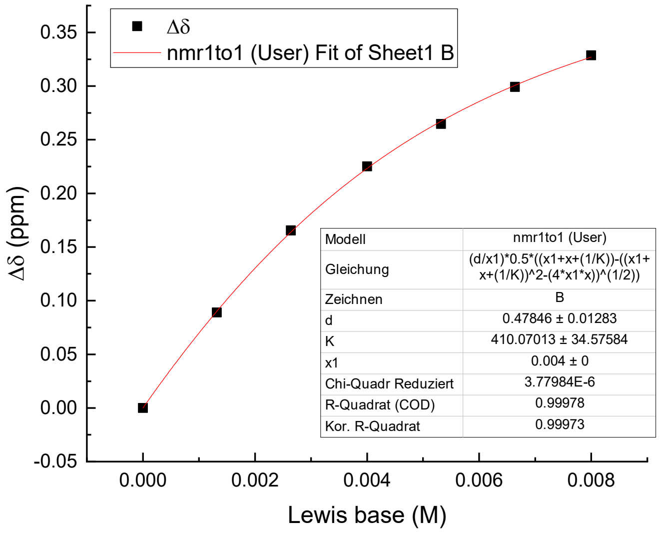


Modell	nmr1to1 (User)
Gleichung	(d/x1)*0.5*((x1+x+(1/K))-((x1+x+(1/K))^2-(4*x1*x))^(1/2))
Zeichnen	B
d	0.13728 ± 0.00228
K	1381.00786 ± 205.3899
x1	0.005 ± 0
Chi-Quadr Reduziert	4.54238E-6
R-Quadrat (COD)	0.99835
Kor. R-Quadrat	0.99802

(RM1184)

NMR titration of tris(3,4,5-trifluorophenyl)borane (1h) with 3,5-dinitropyridine (2l)

Entry	Borane (M)	LB (M)	δ (ppm)	$\Delta\delta$ (ppm)
1	4.0×10^{-3}	0.0	7.1927	0.0000
2	4.0×10^{-3}	1.32×10^{-3}	7.1036	0.0891
3	4.0×10^{-3}	2.64×10^{-3}	7.0273	0.1654
4	4.0×10^{-3}	4.00×10^{-3}	6.9675	0.2252
5	4.0×10^{-3}	5.32×10^{-2}	6.9280	0.2647
6	4.0×10^{-3}	6.64×10^{-2}	6.8935	0.2992
7	4.0×10^{-3}	8.00×10^{-2}	6.8640	0.3287

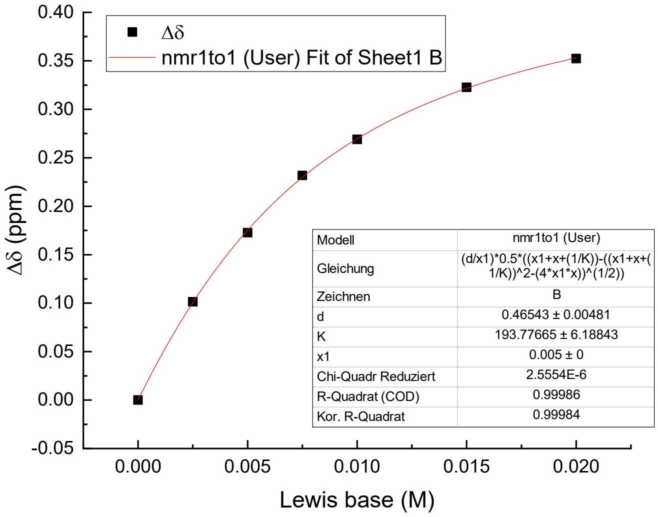


Modell	nmr1to1 (User)
Gleichung	(d/x1)*0.5*((x1+x+(1/K))-((x1+x+(1/K))^2-(4*x1*x))^(1/2))
Zeichnen	B
d	0.47846 ± 0.01283
K	410.07013 ± 34.57584
x1	0.004 ± 0
Chi-Quadr Reduziert	3.77984E-6
R-Quadrat (COD)	0.99978
Kor. R-Quadrat	0.99973

(RM1174)

NMR titration of tris(3,4,5-trifluorophenyl)borane (1h) with 4-chloro-3,5-dinitropyridine (2m)

Entry	Borane (M)	LB (M)	δ (ppm)	$\Delta\delta$ (ppm)
1	5.0×10^{-3}	0.0	7.1864	0.0000
2	5.0×10^{-3}	2.5×10^{-3}	7.0850	0.1014
3	5.0×10^{-3}	5.0×10^{-3}	7.0136	0.1728
4	5.0×10^{-3}	7.5×10^{-3}	6.9547	0.2317
5	5.0×10^{-3}	1.0×10^{-2}	6.9175	0.2689
6	5.0×10^{-3}	1.5×10^{-2}	6.8637	0.3227
7	5.0×10^{-3}	2.0×10^{-2}	6.8341	0.3523

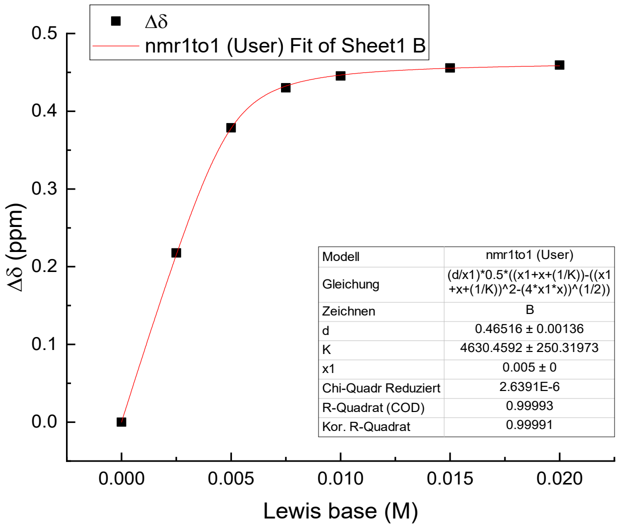


Modell	nmr1to1 (User)
Gleichung	(d/x1)*0.5*((x1+x+(1/K))-((x1+x+(1/K))^2-(4*x1*x))^(1/2))
Zeichnen	B
d	0.46543 ± 0.00481
K	193.77665 ± 6.18843
x1	0.005 ± 0
Chi-Quadr Reduziert	2.5554E-6
R-Quadrat (COD)	0.99986
Kor. R-Quadrat	0.99984

(RM1173)

NMR titration of tris(3,4,5-trifluorophenyl)borane (1h) with acetonitrile (3a)

Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	5.0×10^{-3}	0.0	7.1920	0.0000
2	5.0×10^{-3}	2.5×10^{-3}	6.9743	0.2177
3	5.0×10^{-3}	5.0×10^{-3}	6.8132	0.3788
4	5.0×10^{-3}	7.5×10^{-3}	6.7617	0.4303
5	5.0×10^{-3}	1.0×10^{-2}	6.7465	0.4455
6	5.0×10^{-3}	1.5×10^{-2}	6.7362	0.4558
7	5.0×10^{-3}	2.0×10^{-2}	6.7325	0.4595

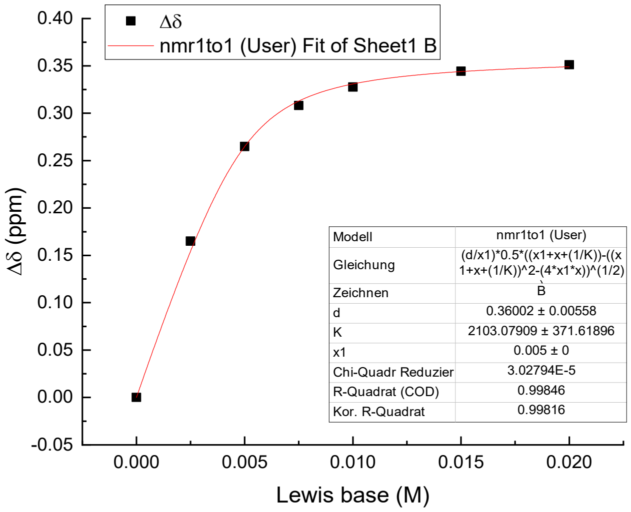


Modell	nmr1to1 (User)
Gleichung	(d/x1)*0.5*((x1+x+(1/K))-((x1+x+(1/K))^2-(4*x1*x))^(1/2))
Zeichnen	B
d	0.46516 ± 0.00136
K	4630.4592 ± 250.31973
x1	0.005 ± 0
Chi-Quadr Reduziert	2.6391E-6
R-Quadrat (COD)	0.99993
Kor. R-Quadrat	0.99991

(RM1211)

NMR titration of tris(3,4,5-trifluorophenyl)borane (1h) with 4-fluorobenzonitrile (3b)

Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	5.0×10^{-3}	0.0	7.1654	0.0000
2	5.0×10^{-3}	2.5×10^{-3}	7.0004	0.1650
3	5.0×10^{-3}	5.0×10^{-3}	6.9005	0.2649
4	5.0×10^{-3}	7.5×10^{-3}	6.8572	0.3082
5	5.0×10^{-3}	1.0×10^{-2}	6.8378	0.3276
6	5.0×10^{-3}	1.5×10^{-2}	6.8210	0.3444
7	5.0×10^{-3}	2.0×10^{-2}	6.8142	0.3512

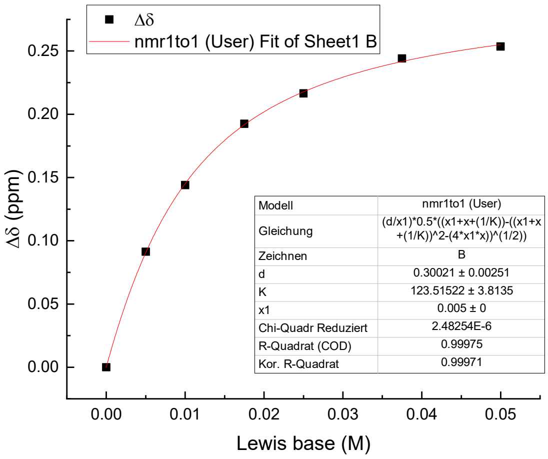


Modell	nmr1to1 (User)
Gleichung	(d/x1)*0.5*((x1+x+(1/K))-((x1+x+(1/K))^2-(4*x1*x))^(1/2)
Zeichnen	B
d	0.36002 ± 0.00558
K	2103.07909 ± 371.61896
x1	0.005 ± 0
Chi-Quadr Reduzier	3.02794E-5
R-Quadrat (COD)	0.99846
Kor. R-Quadrat	0.99816

(RM1201)

NMR titration of tris(3,4,5-trifluorophenyl)borane (1h) with 4-methoxyacetophenone (5a)

Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	5.0×10^{-3}	0.0	7.1869	0.0000
2	5.0×10^{-3}	5.0×10^{-3}	7.0956	0.0913
3	5.0×10^{-3}	1.0×10^{-2}	7.0429	0.1440
4	5.0×10^{-3}	1.75×10^{-2}	6.9944	0.1925
5	5.0×10^{-3}	2.50×10^{-2}	6.9704	0.2165
6	5.0×10^{-3}	3.75×10^{-2}	6.9427	0.2442
7	5.0×10^{-3}	5.0×10^{-2}	6.9333	0.2536

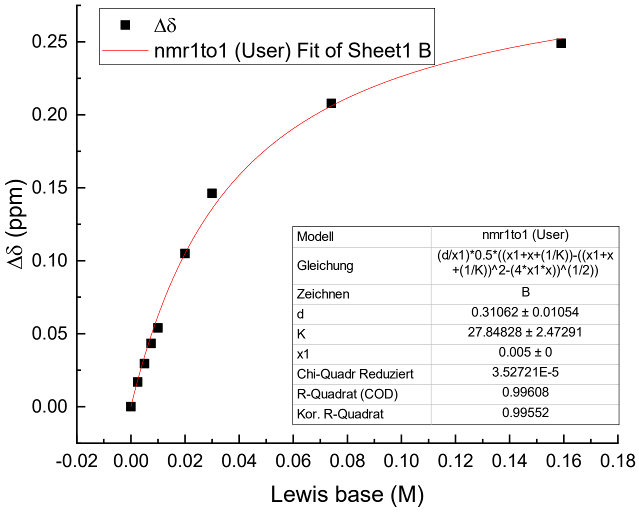


Modell	nmr1to1 (User)
Gleichung	(d/x1)*0.5*((x1+x+(1/K))-((x1+x+(1/K))^2-(4*x1*x))^(1/2))
Zeichnen	B
d	0.30021 ± 0.00251
K	123.51522 ± 3.8135
x1	0.005 ± 0
Chi-Quadr Reduziert	2.48254E-6
R-Quadrat (COD)	0.99975
Kor. R-Quadrat	0.99971

(RM1172)

NMR titration of tris(3,4,5-trifluorophenyl)borane (1h) with 4-methylacetophenone (5b)

Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	5.0×10^{-3}	0.0	7.193	0.000
2	5.0×10^{-3}	2.5×10^{-3}	7.176	0.017
3	5.0×10^{-3}	5.0×10^{-3}	7.164	0.029
4	5.0×10^{-3}	7.5×10^{-3}	7.150	0.043
5	5.0×10^{-3}	1.0×10^{-2}	7.139	0.054
6	5.0×10^{-3}	2.0×10^{-2}	7.088	0.105
7	5.0×10^{-3}	3.0×10^{-2}	7.047	0.146
8	5.0×10^{-3}	7.41×10^{-2}	6.985	0.208
9	5.0×10^{-3}	1.59×10^{-1}	6.944	0.249

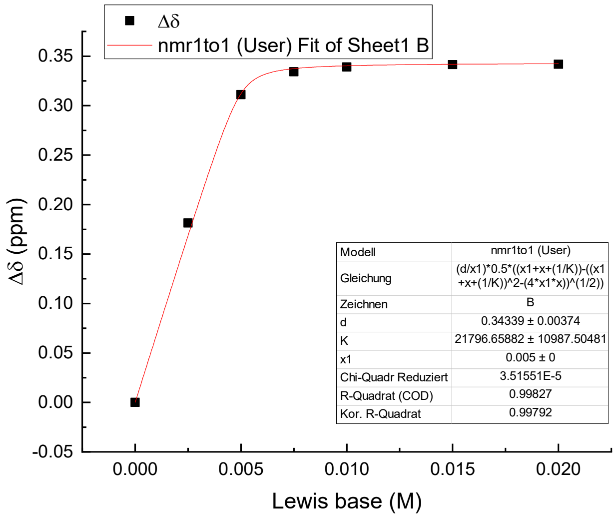


Modell	nmr1to1 (User)
Gleichung	(d/x1)*0.5*((x1+x+(1/K))-((x1+x+(1/K))^2-(4*x1*x))^(1/2))
Zeichnen	B
d	0.31062 ± 0.01054
K	27.84828 ± 2.47291
x1	0.005 ± 0
Chi-Quadr Reduziert	3.52721E-5
R-Quadrat (COD)	0.99608
Kor. R-Quadrat	0.99552

(RM1163)

NMR titration of tris(3,4,5-trifluorophenyl)borane (1h) with *p*-anisaldehyde (7a)

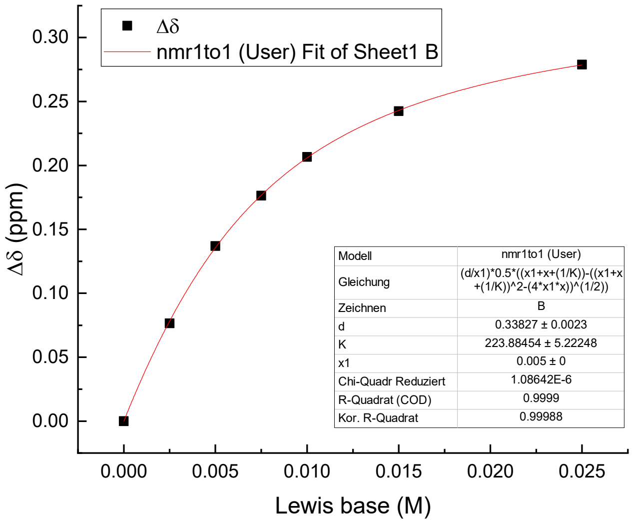
Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	5.0×10^{-3}	0.0	6.6584	0.0000
2	5.0×10^{-3}	2.5×10^{-3}	6.5893	0.0691
3	5.0×10^{-3}	5.0×10^{-3}	6.5609	0.0975
4	5.0×10^{-3}	7.5×10^{-3}	6.5529	0.1055
5	5.0×10^{-3}	1.0×10^{-2}	6.5493	0.1091
6	5.0×10^{-3}	1.5×10^{-2}	6.5465	0.1119
7	5.0×10^{-3}	2.0×10^{-2}	6.5466	0.1118



(RM1198)

NMR titration of tris(3,4,5-trifluorophenyl)borane (1h) with benzaldehyde (7b)

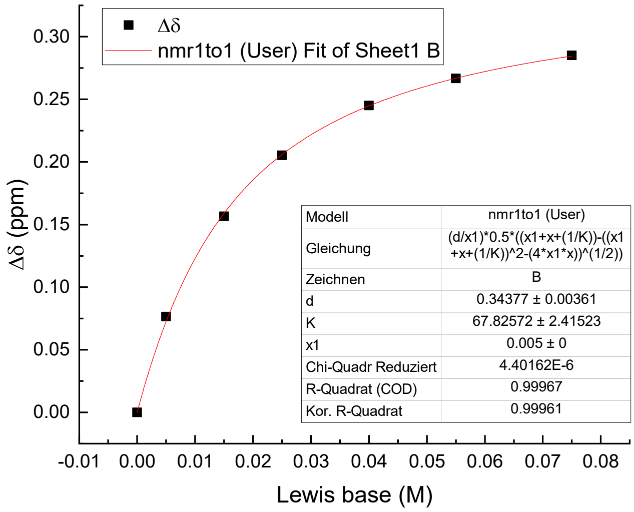
Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	5.0×10^{-3}	0.0	7.1840	0.0000
2	5.0×10^{-3}	2.5×10^{-3}	7.1075	0.0765
3	5.0×10^{-3}	5.0×10^{-3}	7.0470	0.1370
4	5.0×10^{-3}	7.5×10^{-3}	7.0076	0.1764
5	5.0×10^{-3}	1.0×10^{-2}	6.9774	0.2066
6	5.0×10^{-3}	1.5×10^{-2}	6.9415	0.2425
7	5.0×10^{-3}	2.5×10^{-2}	6.9052	0.2788



(RM1257)

NMR titration of tris(3,4,5-trifluorophenyl)borane (1h) with 4-bromobenzaldehyde (7c)

Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	5.0×10^{-3}	0.0	7.1720	0.0000
2	5.0×10^{-3}	5.0×10^{-2}	7.0955	0.0765
3	5.0×10^{-3}	1.5×10^{-1}	7.0154	0.1566
4	5.0×10^{-3}	2.5×10^{-1}	6.9667	0.2053
5	5.0×10^{-3}	4.0×10^{-1}	6.9269	0.2451
6	5.0×10^{-3}	5.5×10^{-1}	6.9053	0.2667
7	5.0×10^{-3}	7.5×10^{-1}	6.8869	0.2851

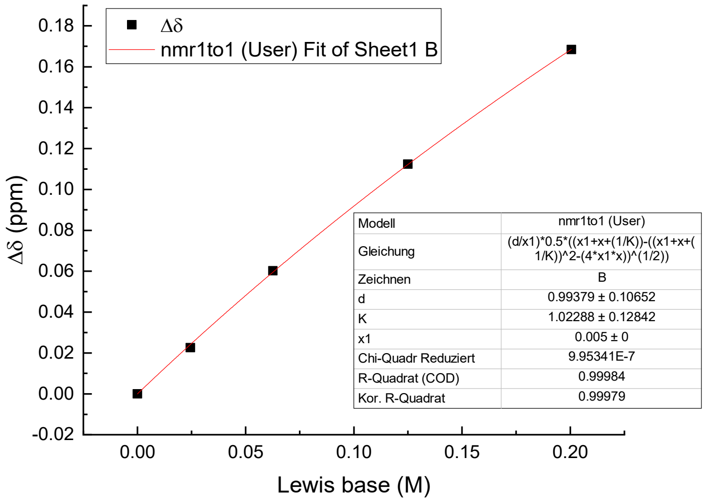


Modell	nmr1to1 (User)
Gleichung	(d/x1)*0.5*((x1+x+(1/K))-((x1+x+(1/K))^2-(4*x1*x))^(1/2))
Zeichnen	B
d	0.34377 ± 0.00361
K	67.82572 ± 2.41523
x1	0.005 ± 0
Chi-Quadr Reduziert	4.40162E-6
R-Quadrat (COD)	0.99967
Kor. R-Quadrat	0.99961

(RM1197)

NMR titration of tris(3,4,5-trifluorophenyl)borane (1h) with 4-nitrobenzaldehyde (7d)

Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	5.0×10^{-3}	0.0	10.1462	0.0000
2	5.0×10^{-3}	2.45×10^{-2}	10.1236	0.0226
3	5.0×10^{-3}	6.26×10^{-2}	10.0860	0.0602
4	5.0×10^{-3}	1.25×10^{-1}	10.0338	0.1124
5	5.0×10^{-3}	2.005×10^{-1}	9.9778	0.1684

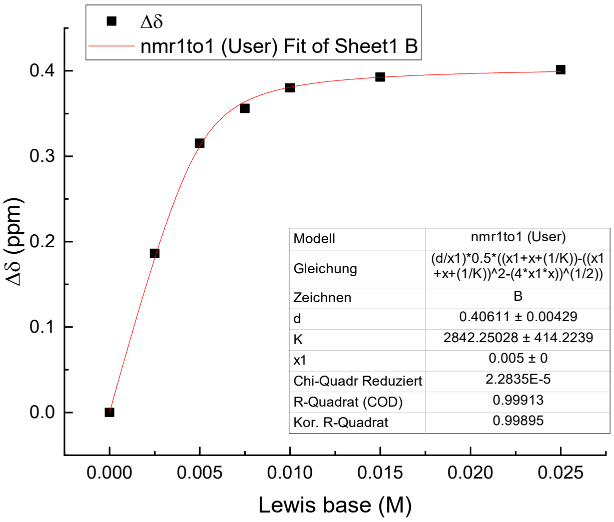


Modell	nmr1to1 (User)
Gleichung	(d/x1)*0.5*((x1+x+(1/K))-((x1+x+(1/K))^2-(4*x1*x))^(1/2))
Zeichnen	B
d	0.99379 ± 0.10652
K	1.02288 ± 0.12842
x1	0.005 ± 0
Chi-Quadr Reduziert	9.95341E-7
R-Quadrat (COD)	0.99984
Kor. R-Quadrat	0.99979

(RM1196)

NMR titration of tris(3,4,5-trifluorophenyl)borane (1h) with trans-crotonaldehyde (8)

Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	5.0×10^{-3}	0.0	7.1816	0.0000
2	5.0×10^{-3}	2.5×10^{-3}	6.9953	0.1863
3	5.0×10^{-3}	5.0×10^{-3}	6.8664	0.3152
4	5.0×10^{-3}	7.5×10^{-3}	6.8256	0.3560
5	5.0×10^{-3}	1.0×10^{-2}	6.8015	0.3801
6	5.0×10^{-3}	1.5×10^{-2}	6.7889	0.3927
7	5.0×10^{-3}	2.5×10^{-2}	6.7803	0.4013

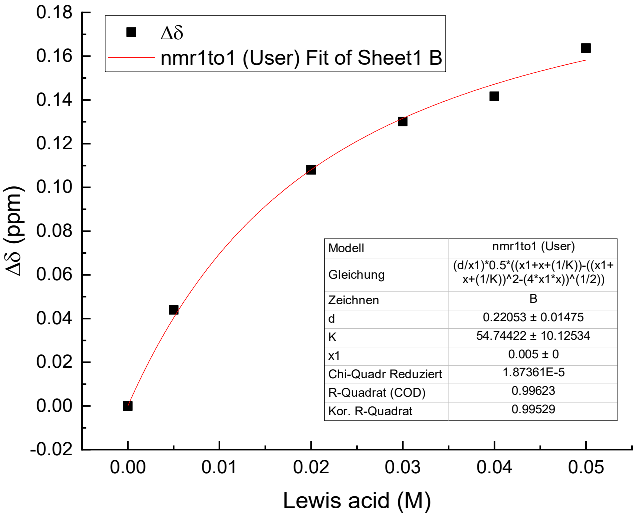


Modell	nmr1to1 (User)
Gleichung	(d/x1)*0.5*((x1+x+(1/K))-((x1+x+(1/K))^2-(4*x1*x))^(1/2))
Zeichnen	B
d	0.40611 ± 0.00429
K	2842.25028 ± 414.2239
x1	0.005 ± 0
Chi-Quadr Reduziert	2.2835E-5
R-Quadrat (COD)	0.99913
Kor. R-Quadrat	0.99895

(RM1199)

NMR titration of 2,6-lutidine (2n) with tris(pentafluorophenyl)borane (1i)

Entry	LB (M)	Borane (M)	δ (ppm)	Δδ (ppm)
1	5.0×10^{-3}	0.0	2.4587	0.0000
2	5.0×10^{-3}	5.0×10^{-3}	2.5026	0.0439
3	5.0×10^{-3}	2.0×10^{-2}	2.5667	0.1080
4	5.0×10^{-3}	3.0×10^{-2}	2.5888	0.1301
5	5.0×10^{-3}	4.0×10^{-2}	2.6004	0.1417
6	5.0×10^{-3}	5.0×10^{-2}	2.6224	0.1637

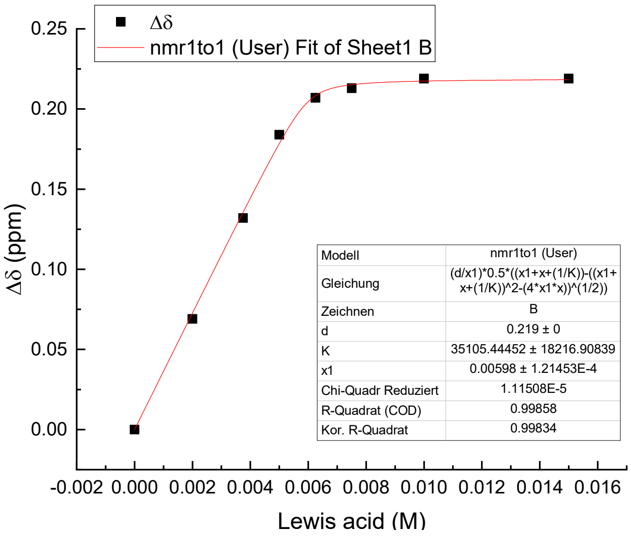


Modell	nmr1to1 (User)
Gleichung	(d/x1)*0.5*((x1+x+(1/K))-((x1+x+(1/K))^2-(4*x1*x))^(1/2))
Zeichnen	B
d	0.22053 ± 0.01475
K	54.74422 ± 10.12534
x1	0.005 ± 0
Chi-Quadr Reduziert	1.87361E-5
R-Quadrat (COD)	0.99623
Kor. R-Quadrat	0.99529

(RM1240)

NMR titration of 4-bromoacetophenone (5c) with tris(pentafluorophenyl)borane (1i)

Entry	LB (M)	Borane (M)	δ (ppm)	Δδ (ppm)
1	5.0×10^{-3}	0.0	7.722	0.000
2	5.0×10^{-3}	2.0×10^{-3}	7.791	0.069
3	5.0×10^{-3}	3.75×10^{-3}	7.854	0.132
4	5.0×10^{-3}	5.0×10^{-3}	7.906	0.184
5	5.0×10^{-3}	6.25×10^{-3}	7.929	0.207
6	5.0×10^{-3}	7.50×10^{-3}	7.935	0.213
7	5.0×10^{-3}	1.0×10^{-2}	7.941	0.219
8	5.0×10^{-3}	1.5×10^{-2}	7.941	0.219



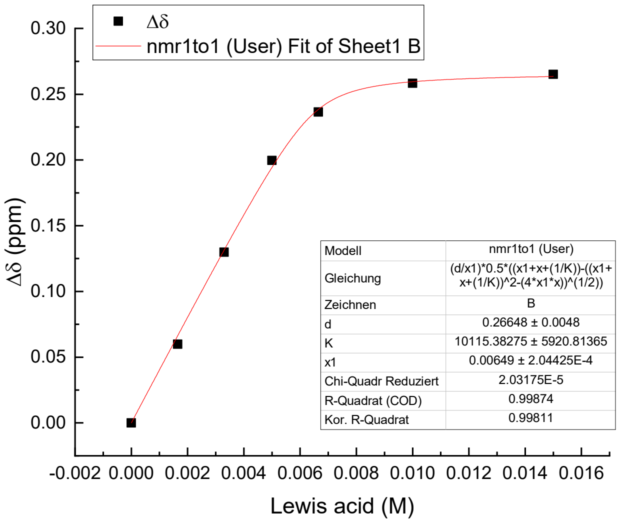
Modell	nmr1to1 (User)
Gleichung	(d/x1)*0.5*((x1+x+(1/K))-((x1+x+(1/K))^2-(4*x1*x))^(1/2))
Zeichnen	B
d	0.219 ± 0
K	35105.44452 ± 18216.90839
x1	0.00598 ± 1.21453E-4
Chi-Quadr Reduziert	1.11508E-5
R-Quadrat (COD)	0.99858
Kor. R-Quadrat	0.99834

(RM1176/RM1241)

The value of x1 (that is, the LB concentration) was allowed to vary in the fitting process.

NMR titration of 4-(trifluoromethyl)acetophenone (5d) with tris(pentafluorophenyl)borane (1i)

Entry	LB (M)	Borane (M)	δ (ppm)	Δδ (ppm)
1	5.0×10^{-3}	0.00	2.6261	0.0000
2	5.0×10^{-3}	1.65×10^{-3}	2.6860	0.0599
3	5.0×10^{-3}	3.30×10^{-3}	2.7559	0.1298
4	5.0×10^{-3}	5.00×10^{-3}	2.8257	0.1996
5	5.0×10^{-3}	6.65×10^{-3}	2.8625	0.2364
6	5.0×10^{-3}	1.00×10^{-2}	2.8844	0.2583
7	5.0×10^{-3}	1.50×10^{-2}	2.8912	0.2651

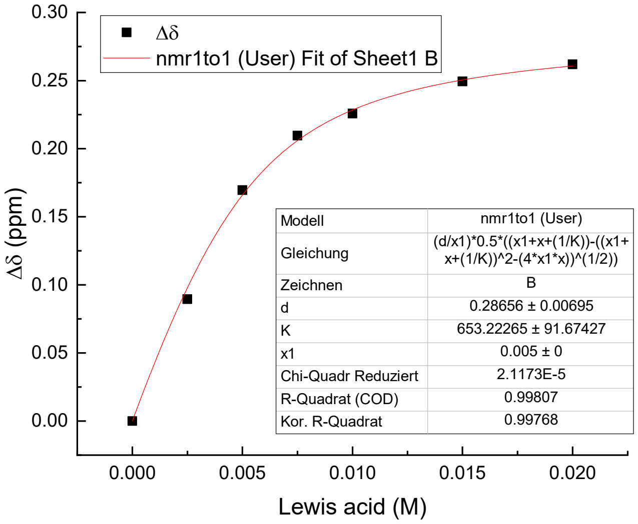


Modell	nmr1to1 (User)
Gleichung	(d/x1)*0.5*((x1+x+(1/K))-((x1+x+(1/K))^2-(4*x1*x))^(1/2))
Zeichnen	B
d	0.26648 ± 0.0048
K	10115.38275 ± 5920.81365
x1	0.00649 ± 2.04425E-4
Chi-Quadr Reduziert	2.03175E-5
R-Quadrat (COD)	0.99874
Kor. R-Quadrat	0.99811

(RM1251)

NMR titration of 4-nitroacetophenone (5e) with tris(pentafluorophenyl)borane (1i)

Entry	LB (M)	Borane (M)	δ (ppm)	Δδ (ppm)
1	5.0×10^{-3}	0.0	2.6542	0.0000
2	5.0×10^{-3}	2.5×10^{-3}	2.7437	0.0895
3	5.0×10^{-3}	5.0×10^{-3}	2.8238	0.1696
4	5.0×10^{-3}	7.5×10^{-3}	2.8638	0.2096
5	5.0×10^{-3}	1.0×10^{-2}	2.8800	0.2258
6	5.0×10^{-3}	1.5×10^{-2}	2.9036	0.2494
7	5.0×10^{-3}	2.0×10^{-2}	2.9161	0.2619

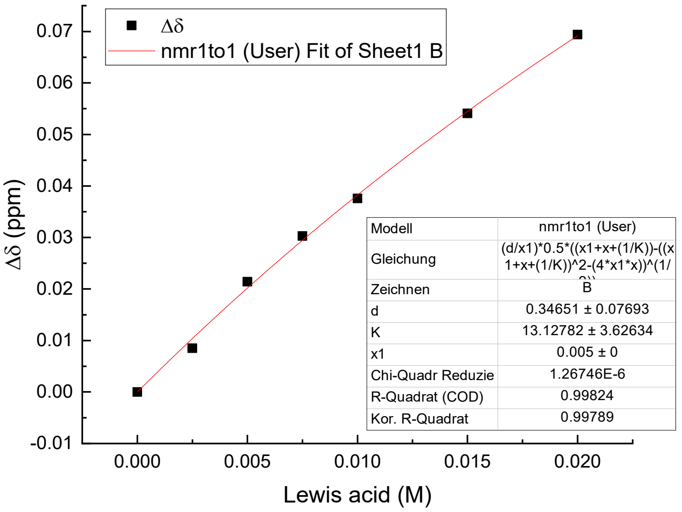


Modell	nmr1to1 (User)
Gleichung	(d/x1)*0.5*((x1+x+(1/K))-((x1+x+(1/K))^2-(4*x1*x))^(1/2))
Zeichnen	B
d	0.28656 ± 0.00695
K	653.22265 ± 91.67427
x1	0.005 ± 0
Chi-Quadr Reduziert	2.1173E-5
R-Quadrat (COD)	0.99807
Kor. R-Quadrat	0.99768

(RM1143)

NMR titration of 3,5-dinitroacetophenone (5f) with tris(pentafluorophenyl)borane (1i)

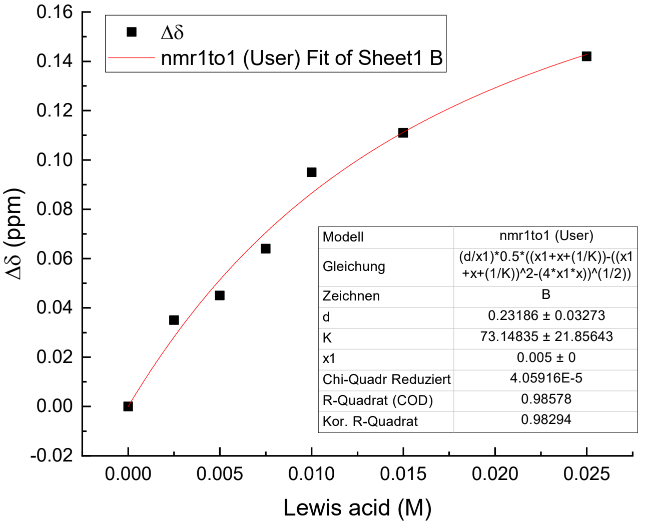
Entry	LB (M)	Borane (M)	δ (ppm)	Δδ (ppm)
1	5.0×10^{-3}	0.0	9.2197	0.0000
2	5.0×10^{-3}	2.5×10^{-3}	9.2282	0.0085
3	5.0×10^{-3}	5.0×10^{-3}	9.2411	0.0214
4	5.0×10^{-3}	7.5×10^{-3}	9.2500	0.0303
5	5.0×10^{-3}	1.0×10^{-2}	9.2573	0.0376
6	5.0×10^{-3}	1.5×10^{-2}	9.2738	0.0541
7	5.0×10^{-3}	2.0×10^{-2}	9.2891	0.0694



(RM1150)

NMR titration of methyl benzoate (6) with tris(pentafluorophenyl)borane (1i)

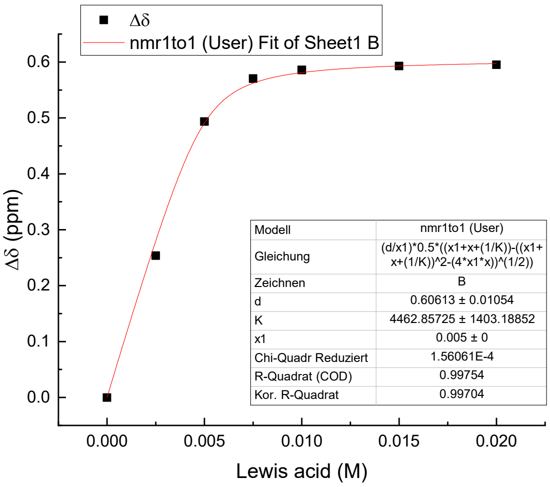
Entry	LB (M)	Borane (M)	δ (ppm)	Δδ (ppm)
1	5.0×10^{-3}	0.0	8.018	0.000
2	5.0×10^{-3}	2.5×10^{-3}	7.983	0.035
3	5.0×10^{-3}	5.0×10^{-3}	7.973	0.045
4	5.0×10^{-3}	7.5×10^{-3}	7.954	0.064
5	5.0×10^{-3}	1.0×10^{-2}	7.923	0.095
6	5.0×10^{-3}	1.5×10^{-2}	7.907	0.111
7	5.0×10^{-3}	2.5×10^{-2}	7.876	0.142



(RM1200)

NMR titration of 4-nitrobenzaldehyde (7d) with tris(pentafluorophenyl)borane (1i)

Entry	LB (M)	Borane (M)	δ (ppm)	Δδ (ppm)
1	5.0×10^{-3}	0.0	10.1462	0.0000
2	5.0×10^{-3}	2.5×10^{-3}	9.8925	0.2537
3	5.0×10^{-3}	5.0×10^{-3}	9.6528	0.4934
4	5.0×10^{-3}	7.5×10^{-3}	9.5759	0.5703
5	5.0×10^{-3}	1.0×10^{-2}	9.5604	0.5858
6	5.0×10^{-3}	1.5×10^{-2}	9.5534	0.5928
7	5.0×10^{-3}	2.0×10^{-2}	9.5510	0.5952

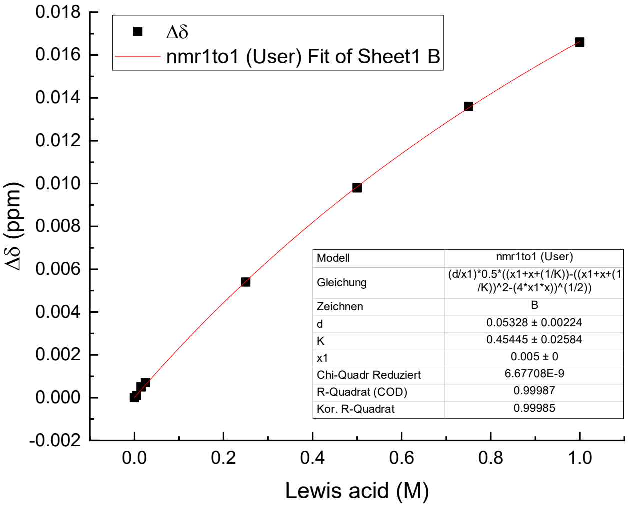


Modell	nmr1to1 (User)
Gleichung	(d/x1)*0.5*((x1+x+(1/K))-((x1+x+(1/K))^2-(4*x1*x))^(1/2))
Zeichnen	B
d	0.60613 ± 0.01054
K	4462.85725 ± 1403.18852
x1	0.005 ± 0
Chi-Quadr Reduziert	1.56061E-4
R-Quadrat (COD)	0.99754
Kor. R-Quadrat	0.99704

(RM1180)

NMR titration of 4-(dimethylamino)pyridine (2a) with tris(2,4,6-trimethylphenyl)borane (1j)

Entry	LB (M)	Borane (M)	δ (ppm)	Δδ (ppm)
1	5.0×10^{-3}	0.0	1.9521	0.0000
2	5.0×10^{-3}	5.0×10^{-3}	1.9522	0.0001
3	5.0×10^{-3}	1.5×10^{-2}	1.9526	0.0005
4	5.0×10^{-3}	2.5×10^{-2}	1.9528	0.0007
5	5.0×10^{-3}	2.5×10^{-1}	1.9575	0.0054
6	5.0×10^{-3}	5.0×10^{-1}	1.9619	0.0098
7	5.0×10^{-3}	7.5×10^{-1}	1.9657	0.0136
8	5.0×10^{-3}	1.0	1.9687	0.0166

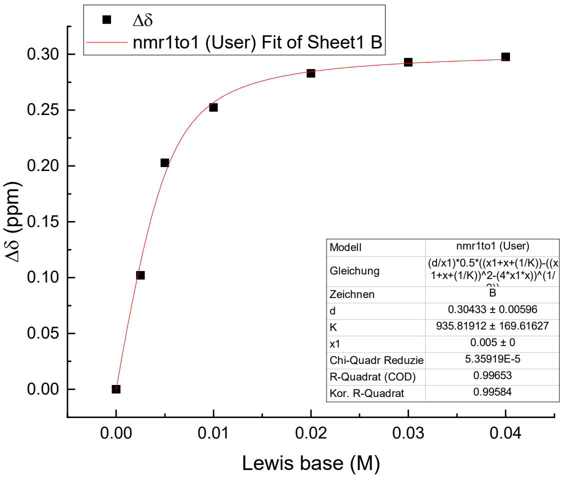


Modell	nmr1to1 (User)
Gleichung	(d/x1)*0.5*((x1+x+(1/K))-((x1+x+(1/K))^2-(4*x1*x))^(1/2))
Zeichnen	B
d	0.05328 ± 0.00224
K	0.45445 ± 0.02584
x1	0.005 ± 0
Chi-Quadr Reduziert	6.67708E-9
R-Quadrat (COD)	0.99987
Kor. R-Quadrat	0.99985

(RM1256)

NMR titration of tris(3,4,5-trifluorophenyl)borane (1h) with tetrahydrothiophene (11)

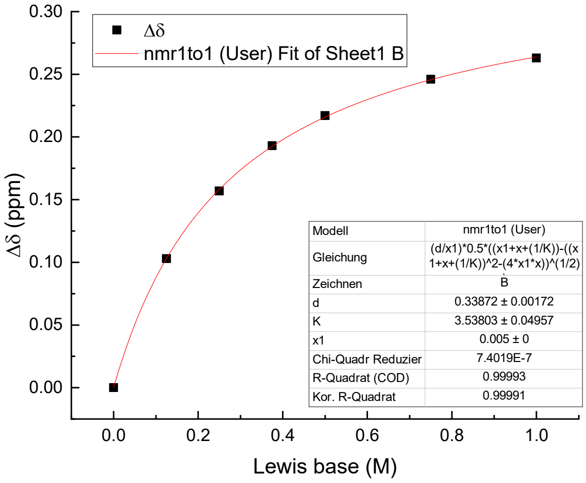
Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	5.0×10^{-3}	0.0	7.193	0.000
2	5.0×10^{-3}	2.5×10^{-3}	7.091	0.102
3	5.0×10^{-3}	5.0×10^{-3}	6.990	0.203
4	5.0×10^{-3}	1.0×10^{-2}	6.941	0.252
5	5.0×10^{-3}	2.0×10^{-2}	6.910	0.283
6	5.0×10^{-3}	3.0×10^{-2}	6.900	0.293
7	5.0×10^{-3}	4.0×10^{-2}	6.895	0.298



(RM1465)

NMR titration of tris(4-chlorophenyl)borane (1f) with tetrahydrothiophene (11)

Entry	Borane (M)	LB (M)	δ (ppm)	Δδ (ppm)
1	5.0×10^{-3}	0.00	7.498	0.000
2	5.0×10^{-3}	1.25×10^{-1}	7.395	0.103
3	5.0×10^{-3}	2.50×10^{-1}	7.341	0.157
4	5.0×10^{-3}	3.75×10^{-1}	7.305	0.193
5	5.0×10^{-3}	5.00×10^{-1}	7.281	0.217
6	5.0×10^{-3}	7.50×10^{-1}	7.252	0.246
7	5.0×10^{-3}	1.00	7.235	0.263



(RM1464)

VII.Computation Details

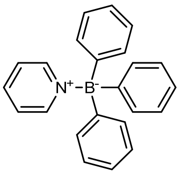
General

Initially, all structures were subjected to a conformational search using the OPLS3[S40] force field as implemented in Macromodel.[S41] All conformers were then optimized at the corresponding level of theory (see respective sections below) with the Gaussian 16 software package.[S42] Frequency analyses were performed to confirm that all structures correspond to minima.

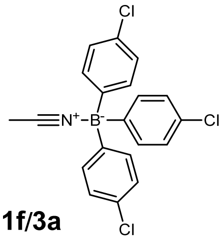
Test of DFT Functionals

We tested the overall quality of different commonly employed DFT functionals for the prediction of equilibrium constants for Lewis adduct formation in comparison to a set of experimental equilibrium constants determined in this work. To avoid a bias for a certain type of Lewis base, the set of Lewis adducts **1d/2d**, **1f/3a**, **1h/7b**, and **1f/4b** was selected under the aspect of diversity to reflect the formation of B-N, B-O, and B-P adducts. At the same time, the experimentally determined equilibrium constants for these four Lewis adducts cover the experimentally relevant range from 1.4 × 10^6 to 4.9 M^{-1}.

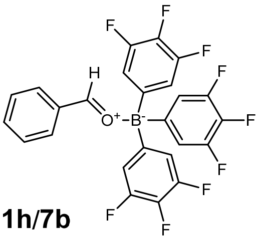
Within the test set, conformers of the Lewis adducts depicted below were first optimized at SMD(DCM)[S43]/B3LYP[S44]-D3BJ[S45]/def2-SVP[S46] level of theory. The minimum conformer of each species was subsequently optimized with further DFT methods. Thermochemical corrections were obtained at the same level using the rigid rotor harmonic oscillator (RRHO) model as implemented in Gaussian. Alternatively, we tested the Grimme's quasi-harmonic RRHO approximation.[S47] A free energy change of +7.91 kJ/mol (= R · 298 K · ln(22.46 L mol^{-1}/L mol^{-1})) was applied to all free energies for their conversion from gas phase (1 atm) to liquid phase (1 M).



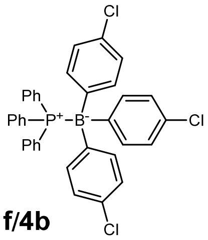
1d/2d



1f/3a



1h/7b



1f/4b

Table S6: Gibbs reaction energies Δ_rG calculated at different DFT levels with thermochemical analysis based on the RRHO model.

	1d/2d	**1f/3a**	**1h/7b**	**1f/4b**	**1d/2d**	**1f/3a**	**1h/7b**	**1f/4b**	**MUE**	**Error**
		Δ_rG (kJ/mol)				deviation from experiment (kJ/mol)				
Experimental	-34.5	-3.9	-13.2	-12.3	0.0	0.0	0.0	0.0		
B3LYP-D3BJ/def2-SVP	-42.5	-19.6	-23.1	-39.8	8.0	15.7	9.9	27.5	15.3	15.3 ± 7.6
B3LYP-D3BJ/def2-TZVP	-21.7	-1.3	-4.8	-23.4	-12.7	-2.5	-8.4	11.0	8.7	-3.2 ± 9.0
M06-2X/def2-TZVP	-31.3	-11.5	-17.9	10.6	-3.2	7.6	4.7	-22.9	9.6	-3.4 ± 11.9
wb97xd/def2-TZVP	-24.4	-2.7	-10.1	-18.1	-10.0	-1.2	-3.1	5.8	5.0	-2.1 ± 5.6
PBE-D3BJ/def2-TZVP	-35.3	-17.5	-14.5	-29.3	0.8	13.6	1.3	16.9	8.2	8.2 ± 7.2
PBE0-D3BJ/def2-TZVP	-38.0	-15.3	-14.7	-33.0	3.5	11.4	1.5	20.7	9.3	9.3 ± 7.5
M06/def2-TZVP	-13.4	-1.1	3.3	9.4	-21.1	-2.8	-16.5	-21.7	15.5	-15.5 ± 7.6
M06-L/def2-TZVP	-12.4	1.5	5.4	9.0	-22.0	-5.4	-18.6	-21.3	16.8	-16.8 ± 6.7
MN15/def2-TZVP	-33.2	-12.5	-20.8	-7.7	-1.3	8.6	7.6	-4.7	5.5	2.6 ± 5.7
BP86-D3BJ/def2-TZVP	-42.5	-11.9	-13.7	-57.1	8.1	8.0	0.5	44.7	15.3	15.3 ± 17.2
B97D3/def2-TZVP	-20.7	-1.7	1.7	-28.4	-13.8	-2.1	-14.9	16.1	11.7	-3.7 ± 12.5

MUE = mean unassigned error

Table S7 Gibbs reaction energies ΔG calculated at different DFT levels with thermochemical analysis based on Grimme's quasi-harmonic RRHO approximation.

	1d/2d	1f/3a	1h/7b	1f/4b	1d/2d	1f/3a	1h/7b	1f/4b	MUE	Error
	ΔG (kJ/mol)				deviation from experiment (kJ/mol)					
Experimental	-34.5	-3.9	-13.2	-12.3	0.0	0.0	0.0	0.0		
B3LYP-D3BJ/def2-SVP	-38.1	-10.6	-13.8	-34.3	3.7	6.7	0.6	21.9	8.2	8.2 ± 8.2
B3LYP-D3BJ/def2-TZVP	-17.3	9.4	5.0	-18.5	-17.1	-13.2	-18.2	6.2	13.7	-10.6 ± 9.9
M06-2X/def2-TZVP	-26.5	-0.5	-5.6	10.8	-7.9	-3.4	-7.6	-23.1	10.5	-10.5 ± 7.5
wb97xd/def2-TZVP	-21.1	6.4	2.0	-13.6	-13.3	-10.3	-15.2	1.2	10.0	-9.4 ± 6.4
PBE-D3BJ/def2-TZVP	-30.8	-6.8	-2.8	-24.4	-3.7	2.9	-10.4	12.1	7.3	0.2 ± 8.3
PBE0-D3BJ/def2-TZVP	-33.6	-5.9	-4.8	-29.2	-0.9	2.0	-8.4	16.9	7.0	2.4 ± 9.2
M06/def2-TZVP	-9.6	8.4	12.9	15.5	-24.9	-12.3	-26.1	-27.9	22.8	-22.8 ± 6.1
M06-L/def2-TZVP	-6.6	12.0	16.9	13.0	-27.8	-15.9	-30.1	-25.4	24.8	-24.8 ± 5.4
MN15/def2-TZVP	**-28.4**	**-1.9**	**-8.2**	**-3.9**	**-6.0**	**-2.0**	**-5.0**	**-8.4**	**5.4**	**-5.4 ± 2.4**
BP86-D3BJ/def2-TZVP	-38.1	-3.5	-4.0	-53.4	3.6	-0.4	-9.2	41.1	13.6	8.8 ± 19.2
B97D3/def2-TZVP	-16.0	11.0	12.3	-24.0	-18.5	-14.9	-25.5	11.7	17.6	-11.8 ± 14.1

MUE = mean unassigned error

The accuracy of the different DFTmethods in predicting the experimental Gibbs energies of reaction for the Lewis adduct formations **1d/2d**, **1f/3a**, **1h/7b**, and **1d/4b** is illustrated in Fig. S6. The best agreement of computed and experimental Δ_rG with the lowest scattering was obtained for the MN15 functional using the quasi-harmonic approximation by Grimme. By using the MN15 functional ΔG values are on average by −5.4 ± 2.4 kJ/mol lower than those determined by experiment. All other methods show a significantly stronger scattering and/or enhanced errors.

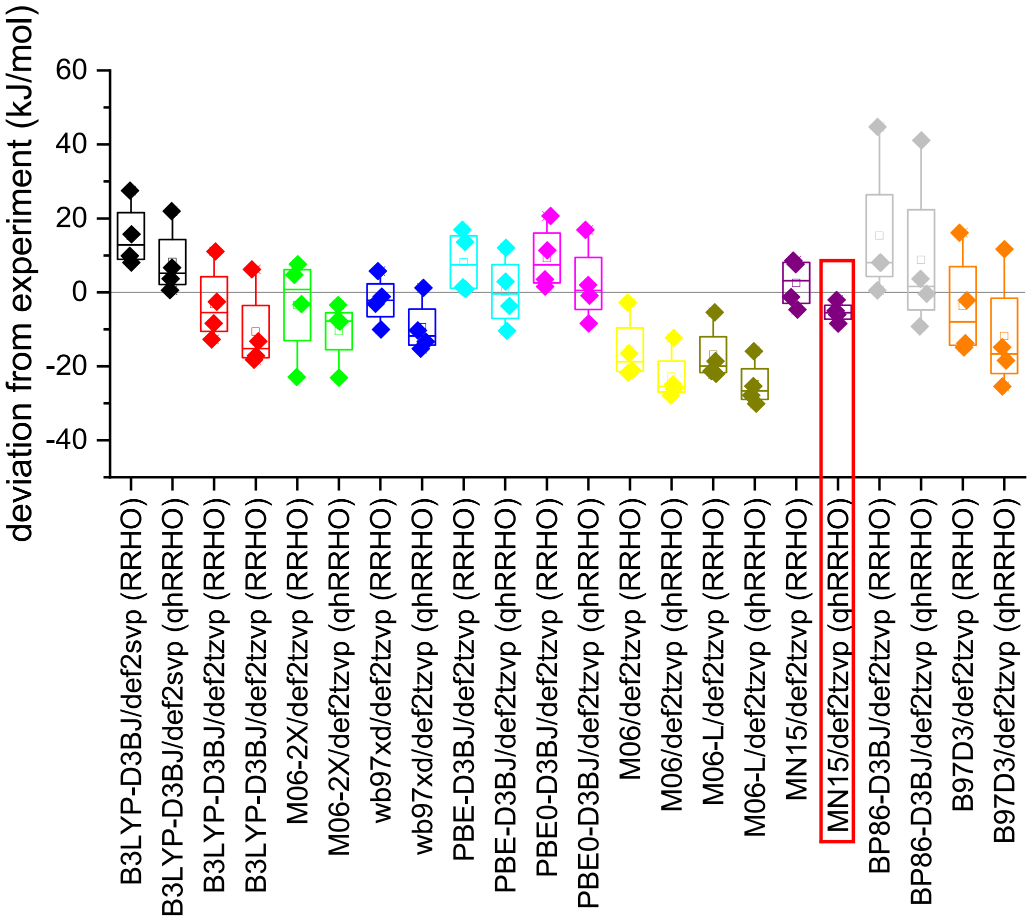


Fig. S6. Comparison of the predictive power of the tested DFT methods.

Table S8: Raw computational data at different levels of theory in dichloromethane.

Species	Filename	E_{tot} (hartree)	$G_{298,\ RRHO}$ (hartree)	$G_{298,\ qHRRHO}$ (hartree)
	SMD(DCM)/B3LYP-D3BJ/def2-SVP			
1d-2d	1d_2d_b3lyp_svp.log	-967.580904	-967.261964	-967.257686
1d	1d_b3lyp_svp.log	-719.411898	-719.178108	-719.175492
1f-3a	1f_3a_b3lyp_svp.log	-2230.516442	-2230.280204	-2230.272777
1f-4b	1f_4b_b3lyp_svp.log	-3133.687340	-3133.234860	-3133.224625
1f	1f_b3lyp_svp.log	-2097.826879	-2097.628483	-2097.624492
1h-7b	1h_7b_b3lyp_svp.log	-1957.187909	-1956.937739	-1956.929423
1h	1h_b3lyp_svp.log	-1611.800125	-1611.650875	-1611.646157
1d	2d_b3lyp_svp.log	-248.132100	-248.070679	-248.070681
3a	3a_b3lyp_svp.log	-132.668240	-132.647276	-132.647277
4b	4b_b3lyp_svp.log	-1035.821657	-1035.594213	-1035.590088
7b	7b_b3lyp_svp.log	-345.360643	-345.281089	-345.281040
	SMD(DCM)/B3LYP-D3BJ/def2-TZVP			
1d-2d	1d_2d_b3lyp.log	-968.619918	-968.302046	-968.297641
1d	1d_b3lyp.log	-720.184081	-719.951320	-719.948593
1f-3a	1f_3a_b3lyp.log	-2231.916474	-2231.682054	-2231.673940
1f-4b	1f_4b_b3lyp.log	-3135.801163	-3135.349237	-3135.339261
1f	1f_b3lyp.log	-2099.078392	-2098.880774	-2098.876735
1h-7b	1h_7b_b3lyp.log	-1959.441112	-1959.193556	-1959.184953
1h	1h_b3lyp.log	-1613.676211	-1613.528486	-1613.523710
1d	2d_b3lyp.log	-248.406839	-248.345462	-248.345465
3a	3a_b3lyp.log	-132.824924	-132.803781	-132.803783
4b	4b_b3lyp.log	-1036.689409	-1036.462575	-1036.458481
7b	7b_b3lyp.log	-345.745387	-345.666256	-345.666178
	SMD(DCM)/M06-2X/def2-TZVP			
1d-2d	1d_2d_m062x.log	-968.100562	-967.779940	-967.775479
1d	1d_m062x.log	-719.791317	-719.556428	-719.553786
1f-3a	1f_3a_m062x.log	-2231.382375	-2231.145307	-2231.137190
1f-4b	1f_4b_m062x.log	-3134.901979	-3134.443477	-3134.434943
1f	1f_m062x.log	-2098.608465	-2098.408712	-2098.404788
1h-7b	1h_7b_m062x.log	-1958.616550	-1958.366699	-1958.357276
1h	1h_m062x.log	-1613.026267	-1612.875443	-1612.870786
1d	2d_m062x.log	-248.276759	-248.214604	-248.214606
3a	3a_m062x.log	-132.756869	-132.735240	-132.735243
4b	4b_m062x.log	-1036.269873	-1036.041797	-1036.037265
7b	7b_m062x.log	-345.567578	-345.487449	-345.487360
	SMD(DCM)/wb97xd/def2-TZVP			
1d-2d	1d_2d_wb97xd.log	-968.168956	-967.847063	-967.842849
1d	1d_wb97xd.log	-719.843274	-719.608527	-719.605569
1f-3a	1f_3a_wb97xd.log	-2231.464208	-2231.225314	-2231.217923
1f-4b	1f_4b_wb97xd.log	-3135.048309	-3134.590520	-3134.580953
1f	1f_wb97xd.log	-2098.682607	-2098.482187	-2098.478264
1h-7b	1h_7b_wb97xd.log	-1958.709887	-1958.460350	-1958.450821
1h	1h_wb97xd.log	-1613.097827	-1612.947456	-1612.942642
1d	2d_wb97xd.log	-248.294468	-248.232249	-248.232251
3a	3a_wb97xd.log	-132.766630	-132.745101	-132.745102
4b	4b_wb97xd.log	-1036.334240	-1036.104451	-1036.100536
7b	7b_wb97xd.log	-345.592189	-345.512061	-345.511966
	SMD(DCM)/PBE-D3BJ/def2-TZVP			
1d-2d	1d_2d_pbe.log	-967.293236	-966.986715	-966.982117
1d	1d_pbe.log	-719.181463	-718.957143	-718.954274
1f-3a	1f_3a_pbe.log	-2230.165310	-2229.940207	-2229.931922
1f-4b	1f_4b_pbe.log	-3133.095328	-3132.660591	-3132.650168
1f	1f_pbe.log	-2097.498537	-2097.308682	-2097.304458
1h-7b	1h_7b_pbe.log	-1957.244910	-1957.009102	-1956.999658
1h	1h_pbe.log	-1611.923522	-1611.782716	-1611.777824
1d	2d_pbe.log	-248.077896	-248.019138	-248.019141
3a	3a_pbe.log	-132.647717	-132.627882	-132.627884
4b	4b_pbe.log	-1035.561851	-1035.343774	-1035.339435
7b	7b_pbe.log	-345.299640	-345.223866	-345.223777

	SMD(DCM)/PBE0-D3BJ/def2-TZVP			
1d-2d	1d_2d_pbe0.log	-967.387272	-967.067805	-967.063415
1d	1d_pbe0.log	-719.256980	-719.023109	-719.020394
1f-3a	1f_3a_pbe0.log	-2230.344786	-2230.108025	-2230.100235
1f-4b	1f_4b_pbe0.log	-3133.366539	-3132.912014	-3132.902272
1f	1f_pbe0.log	-2097.671216	-2097.472801	-2097.468589
1h-7b	1h_7b_pbe0.log	-1957.292343	-1957.042154	-1957.033463
1h	1h_pbe0.log	-1611.949681	-1611.800098	-1611.795266
1d	2d_pbe0.log	-248.095085	-248.033246	-248.033249
3a	3a_pbe0.log	-132.653753	-132.632424	-132.632426
4b	4b_pbe0.log	-1035.657668	-1035.429656	-1035.425561
7b	7b_pbe0.log	-345.319088	-345.239458	-345.239378

	SMD(DCM)/M06/def2-TZVP			
1d-2d	1d_2d_m06.log	-967.733609	-967.417800	-967.413369
1d	1d_m06.log	-719.516036	-719.284990	-719.282007
1f-3a	1f_3a_m06.log	-2231.046586	-2230.812920	-2230.805035
1f-4b	1f_4b_m06.log	-3134.336287	-3133.885260	-3133.876500
1f	1f_m06.log	-2098.313635	-2098.117557	-2098.113308
1h-7b	1h_7b_m06.log	-1958.250996	-1958.001934	-1957.993539
1h	1h_m06.log	-1612.770727	-1612.621481	-1612.616817
1d	2d_m06.log	-248.191668	-248.130716	-248.130719
3a	3a_m06.log	-132.719081	-132.697950	-132.697951
4b	4b_m06.log	-1036.003773	-1035.778522	-1035.774321
7b	7b_m06.log	-345.463559	-345.384724	-345.384645

	SMD(DCM)/M06L/def2-TZVP			
1d-2d	1d_2d_m06l.log	-968.357473	-968.039917	-968.035239
1d	1d_m06l.log	-719.988165	-719.754203	-719.751730
1f-3a	1f_3a_m06l.log	-2231.628541	-2231.393246	-2231.385488
1f-4b	1f_4b_m06l.log	-3135.308322	-3134.855736	-3134.846200
1f	1f_m06l.log	-2098.818832	-2098.620140	-2098.616394
1h-7b	1h_7b_m06l.log	-1959.037087	-1958.790129	-1958.781018
1h	1h_m06l.log	-1613.359921	-1613.211214	-1613.206559
1d	2d_m06l.log	-248.345402	-248.283996	-248.283998
3a	3a_m06l.log	-132.798126	-132.776694	-132.776695
4b	4b_m06l.log	-1036.468976	-1036.242020	-1036.237784
7b	7b_m06l.log	-345.663250	-345.583981	-345.583913

	SMD(DCM)/MN15/def2-TZVP			
1d-2d	1d_2d.log	-967.288983	-966.970440	-966.966127
1d	1d.log	-719.183183	-718.949547	-718.947039
1f-3a	1f_3a.log	-2230.425035	-2230.189357	-2230.181409
1f-4b	1f_4b.log	-3133.375826	-3132.922388	-3132.913002
1f	1f.log	-2097.759858	-2097.561415	-2097.557514
1h-7b	1h_7b.log	-1957.359664	-1957.112128	-1957.102630
1h	1h.log	-1612.040717	-1611.891398	-1611.886781
1d	2d.log	-248.073066	-248.011268	-248.011271
3a	3a.log	-132.647673	-132.626196	-132.626199
4b	4b.log	-1035.588730	-1035.361063	-1035.357020
7b	7b.log	-345.295354	-345.215818	-345.215736

	SMD(DCM)/BP86-D3BJ/def2-TZVP			
1d-2d	1d_2d_bp86.log	-968.575732	-968.269541	-968.264937
1d	1d_bp86.log	-720.140941	-719.917037	-719.914119
1f-3a	1f_3a_bp86.log	-2231.976088	-2231.749547	-2231.742032
1f-4b	1f_4b_bp86.log	-3135.864960	-3135.429199	-3135.419395
1f	1f_bp86.log	-2099.138799	-2098.949652	-2098.945347
1h-7b	1h_7b_bp86.log	-1959.411206	-1959.174476	-1959.165771
1h	1h_bp86.log	-1613.654461	-1613.514177	-1613.509268
1d	2d_bp86.log	-248.397924	-248.339318	-248.339321
3a	3a_bp86.log	-132.818123	-132.798366	-132.798368
4b	4b_bp86.log	-1036.679163	-1036.460823	-1036.456723
7b	7b_bp86.log	-345.733688	-345.658084	-345.657994

	SMD(DCM)/B97D3/def2-TZVP			
1d-2d	1d_2d.log	-967.863511	-967.554716	-967.549973
1d	1d.log	-719.614698	-719.388593	-719.385636

1f-3a	1f_3a.log	-2231.291166	-2231.065370	-2231.056388
1f-4b	1f_4b.log	-3134.713161	-3134.273861	-3134.263638
1f	1f.log	-2098.549749	-2098.358103	-2098.353959
1h-7b	1h_7b.log	-1958.191922	-1957.953159	-1957.944221
1h	1h.log	-1612.682208	-1612.539965	-1612.535138
1d	2d.log	-248.220603	-248.161254	-248.161257
3a	3a.log	-132.729784	-132.709617	-132.709618
4b	4b.log	-1036.128072	-1035.907940	-1035.903554
7b	7b.log	-345.493445	-345.416856	-345.416770

Isodesmic Reactions as Tool to Calculate Equilibrium Constants

Isodesmic reactions are appropriate tools to reduce the errors of computational methods. The MN15 DFT level was identified to reproduce experimental equilibrium constants of Lewis adduct formation in this work with acceptable accuracy, and we used the following Scheme for the computation of Gibbs energies of association of boranes and Lewis bases. By combining the experimental Δ_rG values from Eq (II) with the computationally accessible Δ_rG for the isodesmic reaction in Eq (I), we arrive at ΔG_{iso} which is founded on the experimental equilibrium constants for a certain Lewis base.

$$BX_3 + BAr_3\text{-}LB \xrightarrow{\Delta G \text{ by DFT}} BX_3\text{-}LB + BAr_3 \qquad \text{(I)}$$

$$BAr_3 + LB \xrightarrow{\Delta G \text{ from experiment}} BAr_3\text{-}LB \qquad \text{(II)}$$

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$$BX_3 + LB \xrightarrow{\Delta G_{iso}} BX_3\text{-}LB \qquad \Delta G_{iso} = \Delta G\text{ (I)} + \Delta G\text{ (II)}$$

Next, we set out to assess the Lewis acidity LA_B of BBr_3, BCl_3, and BF_3. Pyridine (**2d**), acetonitrile (**3a**), and benzaldehyde (**7b**) were chosen as reference Lewis bases which were optimized at the SMD(DCM)[S43]/MN15[S48]/def2-TZVP[S46] level of theory. Thermochemical corrections were calculated using Grimme's quasi-harmonic approximation.[S47]

Table S9: Energies of the reaction of boron halides with pyridine (**1d**) at the SMD(DCM)/MN15/def2-TZVP level of theory and calculation of LA_B via an isodesmic reaction.

Species		E_{tot} (hartree)	G_{298} (hartree)	Δ_rG(I) (kJ/mol)	Δ_rG(II)^a (kJ/mol)	ΔG_{iso} (kJ/mol)	K_B (M^{-1})^b	LA_B^{b}
1d-Pyridine	1d_2d.log	-967.288983	-966.966127					
1d	1d.log	-719.183183	-718.947039					
BBr_3	bbr3.log	-7748.408212	-7748.434048					
BBr_3-Pyridine	bbr3_2d.log	-7996.538426	-7996.478099	-65.5	-34.5	-100.0	6.85×10^{17}	11.7
BCl_3	bcl3.log	-1405.317291	-1405.338254					
BCl_3-Pyridine	bcl3_2d.log	-1653.446263	-1653.381447	-63.3	-34.5	-97.8	2.72×10^{17}	11.3
BF_3	bf3.log	-324.456841	-324.470180					
BF_3-Pyridine	bf3_2d.log	-572.582190	-572.511173	-57.5	-34.5	-92.0	2.54×10^{16}	10.3

^{a} Experimental K_B for the reaction of **1d** with **2d** (see Table S1) converted to Δ_rG with $\Delta_rG = -RT \ln K_B$. ^{b} At 20 °C.

Table S10: Energies of the reaction of boron halides with benzaldehyde (**7b**) at the SMD(DCM)/MN15/def2-TZVP level of theory and calculation of LA_B via an isodesmic reaction.

Species		**E_{tot} (hartree)**	**G_{298} (hartree)**	**Δ_rG(I) (kJ/mol)**	**Δ_rG(II)^a (kJ/mol)**	**ΔG_{iso} (kJ/mol)**	**K_B (M^{-1})^b**	**LA_B^b**
1h-PhCHO	1h_7b.log	-1957.359664	-1957.102630					
1h	1h.log	-1612.040717	-1611.886781					
BBr$_3$	bbr3.log	-7748.408212	-7748.434048					
BBr$_3$-PhCHO	bbr3_7b.log	-8093.740174	-8093.662573	-33.3	-13.2	-46.5	1.94×10^8	10.1
BCl$_3$	bcl3.log	-1405.317291	-1405.338254					
BCl$_3$-PhCHO	bcl3_7b.log	-1750.647924	-1750.566009	-31.3	-13.2	-44.5	8.44×10^7	9.7
BF$_3$	bf3.log	-324.456841	-324.470180					
BF$_3$-PhCHO	bf3_7b.log	-669.786167	-669.697911	-31.2	-13.2	-44.4	8.23×10^7	9.7

[a]: Experimental K_B for the reaction of **1h** with **7b** (see Table 1) converted to Δ_rG with $\Delta_rG = -RT \ln K_B$. [b] At 20 °C.

Table S11: Energies of the reaction of boron halides with acetonitrile (**3a**) at the SMD(DCM)/MN15/def2-TZVP level of theory and calculation of LA_B via an isodesmic reaction.

Species		**E_{tot} (hartree)**	**G_{298} (hartree)**	**Δ_rG(I) (kJ/mol)**	**Δ_rG(II)^a (kJ/mol)**	**ΔG_{iso} (kJ/mol)**	**K_B (M^{-1})^b**	**LA_B^b**
1f-MeCN	1f_3a.log	-2230.425035	-2230.181409					
1f	1f.log	-2097.759858	-2097.557514					
BBr$_3$	bbr3.log	-7748.408212	-7748.434048					
BBr$_3$-MeCN	bbr3_3a.log	-7881.089538	-7881.073402	-40.6	-3.9	-44.5	8.53×10^7	8.4
BCl$_3$	bcl3.log	-1405.317291	-1405.338254					
BCl$_3$-MeCN	bcl3_3a.log	-1537.995002	-1537.974251	-31.8	-3.9	-35.7	2.29×10^6	6.8
BF$_3$	bf3.log	-324.456841	-324.470180					
BF$_3$-MeCN	bf3_3a.log	-457.130481	-457.103044	-23.5	-3.9	-27.4	7.82×10^4	5.4

[a]: Experimental K_B for the reaction of **1f** with **3a** (see Table 1) converted to Δ_rG with $\Delta_rG = -RT \ln K_B$. [b] At 20 °C.

Table S12: LA_B from the three reference reactions and averaged LA_B

Lewis Acid	**LA_B from Pyridine**	**LA_B from Benzaldehyde**	**LA_B from MeCN**	**LA_B Average**
BBr$_3$	11.7	10.1	8.4	10.1 ± 1.3
BCl$_3$	11.3	9.7	6.8	9.3 ± 1.8
BF$_3$	10.3	9.7	5.4	8.4 ± 2.0

Fluoride Ion Affinities (FIA)

First, we calculated gas-phase FIA (as ΔH) following the procedure outlined in ref.[S2] at the BP86-D3BJ/def2-SVP level of theory. As suggested, we used the isodesmic reaction of $Me_3Si^+ + F^- \rightarrow Me_3SiF$ (with ΔH at the G3 level as suggested in ref.[S3]) as anchor point. Therefore, all geometries were optimized in gas phase at the BP86[S49]-D3BJ[S45]/def2-SVP[S46] level of theory and confirmed to be energetic minima by frequency analyses.

$$BAr_3 + Me_3SiF \xrightarrow{\Delta H \text{ at BP86-D3BJ/def2svp}} Me_3Si^{\oplus} + F\text{-}BAr_3^{\ominus} \qquad \text{(I)}$$

$$Me_3SiF \xrightarrow{\Delta H \text{ at G3 (from Krossing)}} Me_3Si^{\oplus} + F^{\ominus} \qquad \text{(II)} \qquad \Delta H = 958.44 \text{ kJ/mol}$$

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$$BAr_3 + F^{\ominus} \xrightarrow{\Delta H \text{ at BP86-D3BJ/def2svp}} F\text{-}BAr_3^{\ominus} \qquad \Delta H = \Delta H\text{ (I)} - \Delta H\text{ (II)}$$

Table S13: Gas-phase FIA at the BP86-D3BJ/def2-SVP level of theory anchored to the $Me_3SiF/Me_3Si^{+}+F^{-}$ reaction (with ΔH at the G3 level from ref.[S3]).

Compound	**Name**	**E_{tot} (hartree)**	**ΔH (hartree)**	**ΔH(I) (kJ/mol)**	**FIA = ΔH – ΔH (II) (kJ/mol)**
Me_3SiF	tms_cation.log	-408.832819	-408.718535		
Me_3Si^+	tms_f.log	-508.947655	-508.828343		
1a	1a.log	-1121.022940	-1120.512056		
1a-F^-	1a_f.log	-1220.879285	-1220.368078	666.3	-292.1
1b	1b.log	-1062.706045	-1062.317768		
1b-F^-	1b_f.log	-1162.577430	-1162.188214	628.4	-330.0
1c	1c.log	-837.236925	-836.866150		
1c-F^-	1c_f.log	-937.115155	-936.743194	611.1	-347.3
1d	1d.log	-719.359926	-719.073788		
1d-F^-	1d_f.log	-819.242997	-818.955556	598.7	-359.7
1e	1e.log	-1016.851796	-1016.586953		
1e-F^-	1e_f.log	-1116.741597	-1116.475206	581.7	-376.7
1f	1f.log	-2097.875931	-2097.614239		
1f-F^-	1f_f.log	-2197.773400	-2197.509855	562.4	-396.1
1g	1g.log	-1611.827482	-1611.605375		
1g-F^-	1g_f.log	-1711.725270	-1711.501146	562.0	-396.5
1h	1h.log	-1611.783601	-1611.560989		
1h-F^-	1h_f.log	-1711.698201	-1711.473463	518.1	-440.3
1i	1i.log	-2206.709158	-2206.528720		
1i-F^-	1i_f.log	-2306.630948	-2306.448215	499.7	-458.8
1j	1j.log	-1072.981077	-1072.440991		
1j-F^-	1j_f.log	-1172.850930	-1172.309088	634.6	-323.8
BF_3	bf3.log	-324.301595	-324.284934		
BF_3-F^-	bf3_f.log	-424.180170	-424.160668	614.6	-343.9
BCl_3	bcl3.log	-1405.258983	-1405.246111		
BCl_3-F^-	bcl3_f.log	-1505.162885	-1505.146538	549.7	-408.7
BBr_3	bbr3.log	-7747.298444	-7747.286611		
BBr_3-F^-	bbr3_f.log	-7847.216865	-7847.201283	512.3	-446.1
1k	1k.log	-3262.302170	-3262.144122		
1k-F^-	1k_f.log	-3362.231906	-3362.073460	473.8	-484.6
1l	1l.log	-2007.206280	-2007.118481		
1l-F^-	1l_f.log	-2107.130738	-2107.044422	482.7	-475.7

Fluoride Ion Affinities in Dichloromethane (FIA^{DCM})

Fluoride ion affinities (as ΔG_{298}) in dichloromethane solution were calculated at the SMD(DCM)[S43]/MN15[S48]/def2-TZVP[S46] level of theory with thermochemical corrections calculated using Grimme's quasi-harmonic approximation.[S47] A free energy change of +7.91 kJ/mol (= R · 298 K · ln(22.46 L mol^{-1}/L mol^{-1})) was applied to all free energies for their conversion from gas phase (1 atm) to liquid phase (1 M).

$$BAr_3 + F^{\ominus} \xrightarrow{\Delta G \text{ at SMD(DCM)/MN15/def2tzvp}} F\text{-}BAr_3^{\ominus}$$

In contrast to gas-phase FIA, there is no reliable anchor reaction for fluoride association with a borane in dichloromethane solution, and due to ion pairing in organic solution it is also unlikely to exist. Therefore, the absolute FIA^{DCM} values reported herein should not be overinterpreted.

Table S14: FIA in dichloromethane solutions (FIA^{DCM}) at the SMD(DCM)/MN15/def2-TZVP level of theory.

Compound	Name	E_{tot} (hartree)	ΔG (hartree)	FIA^{DCM} (kJ/mol)
F^-	fluoride.log	-99.922600	-99.936759	
1a	1a.log	-1120.757210	-1120.317861	
1a-F^-	1a_f.log	-1220.727944	-1220.288428	-96.7
1b	1b.log	-1062.545388	-1062.218981	
1b-F^-	1b_f.log	-1162.525919	-1162.201148	-127.1
1c	1c.log	-837.018675	-836.707329	
1c-F^-	1c_f.log	-937.004045	-936.694851	-141.2
1d	1d.log	-719.183183	-718.947039	
1d-F^-	1d_f.log	-819.172812	-818.937033	-147.7
1e	1e.log	-1016.820334	-1016.611786	
1e-F^-	1e_f.log	-1116.811692	-1116.604241	-154.1
1f	1f.log	-2097.759858	-2097.557514	
1f-F^-	1f_f.log	-2197.755352	-2197.553620	-163.7
1g	1g.log	-1612.079522	-1611.925116	
1g-F^-	1g_f.log	-1712.084355	-1711.929353	-185.1
1h	1h.log	-1612.040717	-1611.886781	
1h-F^-	1h_f.log	-1712.048259	-1711.895637	-197.2
1i	1i.log	-2207.247423	-2207.146808	
1i-F^-	1i_f.log	-2307.270349	-2307.168786	-231.7
1j	1j.log[a]	-1072.672657	-1072.205711	
1j-F^-	1j_f.log	-1172.642414	-1172.172727	-87.4
BF_3	bf3.log	-324.456841	-324.470180	
BF_3-F^-	bf3_f.log	-424.481810	-424.495205	-239.7
BCl_3	bcl3.log	-1405.317291	-1405.338254	
BCl_3-F^-	bcl3_f.log	-1505.350042	-1505.370892	-259.6
BBr_3	bbr3.log	-7748.408212	-7748.434048	
BBr_3-F^-	bbr3_f.log	-7848.442427	-7848.468054	-263.2
1k	1k.log	-3262.995914	-3262.817370	
1k-F^-	1k_f.log	-3363.016997	-3362.8	-226.0
1l	1l.log	-2007.649645	-2007.551438	
1l-F^-	1l_f.log[a]	-2107.672320	-2107.572987	-230.5

[a] Structures have small imaginary frequencies (**1j**: −13.2 cm^{-1}, **1l**-F: −3.44 cm^{-1}) as convergence showed to be problematic.

Orbital Energies

Both LUMO energies as well as global electrophilicity indices (GEI) were proposed to be a suitable descriptor for Lewis acidity.[S2,S50] Parr global electrophilicity indices can be calculated from the electronic chemical potential (μ), chemical hardness (η) and the global electrophilicity index (ω) as follows:[S51]

$$\mu \approx \frac{\mathrm{E_{HOMO}} + \mathrm{E_{LUMO}}}{2}$$

$$\eta \approx \mathrm{E_{LUMO}} - \mathrm{E_{HOMO}}$$

$$\omega = \frac{\mu^2}{2\eta}$$

The following two tables list HOMO and LUMO energies, chemical potential (μ), chemical hardness (η) and the global electrophilicity index (ω) for both gas-phase optimized boranes (BP86-D3BJ/def2-SVP, Table S15) as well as the ones in dichloromethane solution (SMD(DCM)/MN15/def2-TZVP, Table S16. The corresponding correlation with experimental Lewis acidities is shown in Fig. S1.

Table S15: Orbital energies and GEI analysis for boranes optimized in the gas-phase at the BP86-D3BJ/def2-SVP level of theory.

Compound	Name	ε_{HOMO} (hartree)	ε_{LUMO} (hartree)	Chemical Potential (hartree)	Chemical Hardness (hartree)	Global Electrophilicity (eV)
1a	1a.log	-0.15683	-0.06001	-0.10842	0.09682	1.65
1b	1b.log	-0.19166	-0.08069	-0.13618	0.11097	2.27
1c	1c.log	-0.21392	-0.09261	-0.15327	0.12131	2.63
1d	1d.log	-0.22686	-0.10049	-0.16368	0.12637	2.88
1e	1e.log	-0.22650	-0.10466	-0.16558	0.12184	3.06
1f	1f.log	-0.22634	-0.11260	-0.16947	0.11374	3.44
1g	1g.log	-0.23176	-0.12108	-0.17642	0.11068	3.83
1h	1h.log	-0.24254	-0.12913	-0.18584	0.11341	4.14
1i	1i.log	-0.23790	-0.14437	-0.19114	0.09353	5.31
1j	1j.log	-0.19839	-0.09395	-0.14617	0.10444	2.78
BF_3	bf3.log	-0.35988	-0.01084	-0.18536	0.34904	1.34
BCl_3	bcl3.log	-0.27814	-0.08770	-0.18292	0.19044	2.39
BBr_3	bbr3.log	-0.25686	-0.10629	-0.18158	0.15057	2.98
1k	1k.log	-0.21513	-0.14906	-0.18210	0.06607	6.83
1l	1l.log	-0.22974	-0.15295	-0.19135	0.07679	6.49

Table S16: Orbital energies and GEI analysis for boranes optimized in dichloromethane solution at the SMD(DCM)/MN15/def2-TZVP level of theory.

Compound	Name	ε_{HOMO} (hartree)	ε_{LUMO} (hartree)	Chemical Potential (hartree)	Chemical Hardness (hartree)	Global Electrophilicity (eV)
1a	1a.log	-0.21710	-0.02941	-0.12326	0.18769	1.10
1b	1b.log	-0.25312	-0.04147	-0.14730	0.21165	1.39
1c	1c.log	-0.27054	-0.04908	-0.15981	0.22146	1.57
1d	1d.log	-0.28319	-0.05429	-0.16874	0.22890	1.69
1e	1e.log	-0.28154	-0.05390	-0.16772	0.22764	1.68
1f	1f.log	-0.28062	-0.06249	-0.17156	0.21813	1.84
1g	1g.log	-0.29157	-0.07655	-0.18406	0.21502	2.14
1h	1h.log	-0.29536	-0.07260	-0.18398	0.22276	2.07
1i	1i.log	-0.29833	-0.09589	-0.19711	0.20244	2.61
1j	1j.log	-0.25626	-0.04968	-0.15297	0.20658	1.54
BF_3	bf3.log	-0.48092	0.06314	-0.20889	0.54406	1.09
BCl_3	bcl3.log	-0.36253	-0.04009	-0.20131	0.32244	1.71
BBr_3	bbr3.log	-0.33101	-0.05910	-0.19506	0.27191	1.90
1k	1k.log	-0.26549	-0.10251	-0.18400	0.16298	2.83
1l	1l.log	-0.28042	-0.10311	-0.19177	0.17731	2.82

Borane (BH_3) Affinities (BA)

For the calculation of borane affinities BA (= ΔG_{BH3}, in kJ/mol), all structures were optimized at the SMD(DCM)[S43]/MN15[S48]/def2-TZVP[S46] level of theory. Frequency calculations including Grimme's quasi-harmonic RRHO approximation[S47] were obtained at the same level and converted from gas phase (1 atm) to liquid phase (1 M) by adding a free energy change of +7.91 kJ/mol (= $R \cdot 298\ K \cdot \ln(22.46\ L\ mol^{-1}/L\ mol^{-1})$) to all free energies.To reference borane affinities to experimental values, we used two isodesmic reactions as basis: the reaction of BH_3 with pyridine (**2d**), which can be connected with an isodesmic reaction to the experimental value for the reaction of pyridine (**2d**) with triphenylborane (**1d**) (see above), was taken as anchor point as described in equations (I)–(IV):

$$BH_3 + BPh_3\text{-Pyr} \xrightarrow{\Delta G \text{ by DFT}} BH_3\text{-Pyr} + BPh_3 \qquad \text{(I)}$$

$$BPh_3 + \text{Pyr} \xrightarrow{\Delta G \text{ from experiment}} BPh_3\text{-Pyr} \qquad \text{(II)} \quad \Delta G = -34.5 \text{ kJ/mol}$$

$$BH_3 + \text{Pyr} \xrightarrow{\Delta G_{BH3Pyr}} BH_3\text{-Pyr} \qquad \Delta G_{BH3Pyr} = \Delta G\ \text{(I)} + \Delta G\ \text{(II)}$$

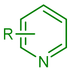
$$\text{LB} + BH_3\text{-Pyr} \xrightarrow{\Delta G \text{ by DFT}} BH_3\text{-LB} + \text{Pyr} \qquad \text{(III)}$$

$$BH_3 + \text{Pyr} \xrightarrow{\Delta G_{BH3Pyr}} BH_3\text{-Pyr} \qquad \text{(IV)}$$

$$\text{LB} + BH_3 \xrightarrow{\Delta G_{BH3}} BH_3\text{-LB} \qquad \Delta G_{BH3} = \Delta G\ \text{(III)} + \Delta G\ \text{(IV)} = \\ = \Delta G\ \text{(III)} + \Delta G_{BH3Pyr}$$

Table S17: Borane affinities in dichloromethane at the SMD(DCM)/MN15/def2-TZVP level of theory.

Compound	Name	E_{tot} (hartree)	ΔG (hartree)
BH_3	bh3.log	-26.571987	-26.564324
BH_3-2d	bh3_2d.log	-274.716247	-274.624257
1d	1d.log	-719.183183	-718.947039
2d	2d.log	-248.073066	-248.011271
1d-2d	1d_2d.log	-967.288983	-966.966127
		ΔG_{I} (kJ/mol):	-107.2
		$\Delta G_{II, exp}$ (kJ/mol):	-34.5
		ΔG_{BH3Py} (kJ/mol):	-141.7

Compound	R =		Name	E_{tot} (hartree)	ΔG (hartree)
	4-NMe_2	**2a**	2a.log bh3_2a.log	-381.934671 -408.583729	-381.805184 -408.423337
				ΔG_{BH3} (kJ/mol):	-155.3
	4-Morpholino	**2b**	2b.log bh3_2b.log	-534.464827 -561.112566	-534.295128 -560.912079
				ΔG_{BH3} (kJ/mol):	-152.2
	4-MeO	**2c**	2c.log bh3_2c.log	-362.528691 -389.173948	-362.437424 -389.052228
				ΔG_{BH3} (kJ/mol):	-146.5
	H	**2d**	2d.log bh3_2d.log	-248.073066 -274.716247	-248.011271 -274.624257
				ΔG_{BH3} (kJ/mol):	-141.7
	4-COPh	**2e**	2e.log bh3_2e.log	-592.183945 -618.825044	-592.040244 -618.650624
				ΔG_{BH3} (kJ/mol):	-134.9
	3-Cl	**2f**	2f.log bh3_2f.log	-707.596035 -734.235338	-707.546045 -734.154962
				ΔG_{BH3} (kJ/mol):	-131.1
	4-CF_3	**2g**	2g.log bh3_2g.log	-584.999106 -611.638527	-584.938099 -611.546893
				ΔG_{BH3} (kJ/mol):	-130.7
	4-CN	**2h**	2h.log bh3_2h.log	-340.246417 -366.884992	-340.188790 -366.797051
				ΔG_{BH3} (kJ/mol):	-129.3
	3,5-$(CF_3)_2$	**2i**	2i.log bh3_2i.log	-921.923968 -948.558534	-921.863313 -948.467577
				ΔG_{BH3} (kJ/mol):	-118.8
	3,4,5-$(Cl)_3$	**2j**	2j.log bh3_2j.log	-1626.635341 -1653.269439	-1626.608150 -1653.211890
				ΔG_{BH3} (kJ/mol):	-117.5
	3,5-$(F)_2$-4-CF_3	**2k**	2k.log bh3_2k.log	-783.403845 -810.036760	-783.361163 -809.963770
				ΔG_{BH3} (kJ/mol):	-114.5
	3,5-$(NO_2)_2$	**2l**	2l.log bh3_2l.log	-656.846806 -683.476479	-656.787791 -683.387257
				ΔG_{BH3} (kJ/mol):	-106.2
	4-Cl-3,5-$(NO_2)_2$	**2m**	2m.log bh3_2m.log	-1116.348325 -1142.976501	-1116.300644 -1142.898845
				ΔG_{BH3} (kJ/mol):	-102.9
	2,6-Me	**2n**	2n.log bh3_2n.log	-326.635224 -353.275512	-326.523532 -353.130321
				ΔG_{BH3} (kJ/mol):	-125.5
	Me	**3a**	3a.log bh3_3a.log	-132.647673 -159.272603	-132.626199 -159.222836
				ΔG_{BH3} (kJ/mol):	-98.8
	4-F-C_6H_4	**3b**	3b.log bh3_3b.log	-423.427299 -450.051296	-423.367386 -449.961957

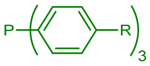
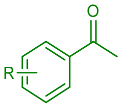
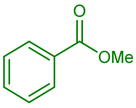
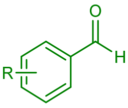
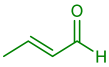
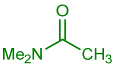
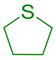
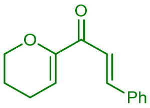
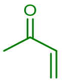
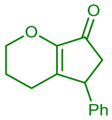
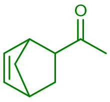
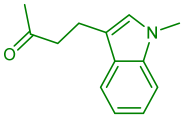
				ΔG_{BH3} (kJ/mol):	-93.4
	4-MeO	**4a**	4a.log bh3_4a.log	-1378.946594 -1405.591504 ΔG_{BH3} (kJ/mol):	-1378.625288 -1405.239627 -145.3
	H	**4b**	4b.log bh3_4b.log	-1035.588730 -1062.230358 ΔG_{BH3} (kJ/mol):	-1035.357020 -1061.968738 -138.4
	4-Cl	**4c**	4c.log bh3_4c.log	-2414.163212 -2440.803224 ΔG_{BH3} (kJ/mol):	-2413.965711 -2440.575235 -132.7
	4-MeO	**5a**	5a.log bh3_5a.log	-499.035065 -525.657975 ΔG_{BH3} (kJ/mol):	-498.899400 -525.492098 -88.5
	4-Me	**5b**	5b.log bh3_5b.log	-423.859519 -450.481111 ΔG_{BH3} (kJ/mol):	-423.728844 -450.320387 -85.4
	4-Br	**5c**	5c.log bh3_5c.log	-2958.474380 -2985.093870 ΔG_{BH3} (kJ/mol):	-2958.381682 -2984.971115 -79.9
	4-CF_3	**5d**	5d.log bh3_5d.log	-721.508489 -748.126799 ΔG_{BH3} (kJ/mol):	-721.403174 -747.991046 -75.8
	4-NO_2	**5e**	5e.log bh3_5e.log	-588.972745 -615.589804 ΔG_{BH3} (kJ/mol):	-588.867934 -615.455082 -73.9
	3,5-NO_2	**5f**	5f.log bh3_5f.log	-793.360191 -819.974823 ΔG_{BH3} (kJ/mol):	-793.255962 -819.840805 -67.9
		**6**	6.log bh3_6.log	-459.778391 -486.385602 ΔG_{BH3} (kJ/mol):	-459.668022 -486.245820 -49.4
	4-MeO	**7a**	7a.log bh3_7a.log	-459.750289 -486.373253 ΔG_{BH3} (kJ/mol):	-459.640878 -486.233653 -88.7
	H	**7b**	7b.log bh3_7b.log	-345.295354 -371.915384 ΔG_{BH3} (kJ/mol):	-345.215736 -371.805519 -80.8
	4-Br	**7c**	7c.log bh3_7c.log	-2919.188659 -2945.807705 ΔG_{BH3} (kJ/mol):	-2919.122201 -2945.710780 -77.7
	4-NO_2	**7d**	7d.log bh3_7d.log	-549.686430 -576.302788 ΔG_{BH3} (kJ/mol):	-549.607758 -576.193642 -70.6
		**8**	8.log bh3_8.log	-231.051410 -257.674619 ΔG_{BH3} (kJ/mol):	-230.990400 -257.583270 -88.9
		**9**	9.log bh3_9.log	-287.605958 -314.235888 ΔG_{BH3} (kJ/mol):	-287.506926 -314.106202 -105.7
$Et_3P=O$		**10**	10.log bh3_10.log	-653.944244 -680.580453 ΔG_{BH3} (kJ/mol):	-653.776810 -680.382227 -121.9
		**11**	11.log 11_bh3.log	-555.195297 -581.820771 ΔG_{BH3} (kJ/mol):	-555.109791 -581.705858 -97.3

Table S18: Borane affinities in dichloromethane at the SMD(DCM)/MN15/def2-TZVP level of theory for additional compounds.

Compound	**Name**	E_{tot} **(hartree)**	Δ**G (hartree)**
Et$_2$O	et2o.log	-233.465310	-233.358767
	bh3_et2o.log	-260.086473	-259.948304
		ΔG (kJ/mol):	-80.2
	nazarov_starting.log	-691.778042	-691.571430
	bh3_nazarov_starting.log	-718.397500	-718.160161
		ΔG_{BH3} (kJ/mol):	-78.1
	methylvinylketon.log	-231.053607	-230.992865
	bh3_methylvinylketon.log	-257.673518	-257.582480
		ΔG_{BH3} (kJ/mol):	-80.4
	nazarov_prod.log	-691.807860	-691.597841
	bh3_nazarov_prod.log	-718.432079	-718.192298
		ΔG_{BH3} (kJ/mol):	-93.1
	dielsalder_prod.log	-425.023820	-424.866890
	bh3_dielsalder_prod.log	-451.645604	-451.458589
		ΔG_{BH3} (kJ/mol):	-85.9
	michael_addition.log	-633.877139	-633.667021
	bh3_michael_addition.log	-660.498830	-660.257689
		ΔG_{BH3} (kJ/mol):	-83.1

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