Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

General Information and Syntheses

All chemicals were purchased from *ABCR*, *Acros Organics*, *Alfa Aesar*, *Carbolution*, *ChemPur*, *Sigma-Aldrich*, *TCI* or *VWR*. Commercially available chemicals were, unless mentioned otherwise, used without further purification. Dry dichloromethane, diethyl ether and tetrahydrofuran were received from a *MBRAUN MB SPS-800*. The solvents were distilled, dried over 4Å molecular sieve and finally dried on an Alox column. The moisture content of the solvents was determined with *Karl Fischer (Titroline®7500KF)* titration. Pentane, ethyl acetate, dichloromethane and acetone were used after single distillation. Dry CD_2Cl_2 for NMR-catalysis experiments were stored under argon and over molecular sieve 3Å. Oxygen- or moisture-sensitive reactions were carried out under standard *Schlenk* technique with argon as inert gas. Reagents were injected via a rubber septum or added under argon counterflow.

Thin-layer chromatography (TLC) was performed by using *Merck* TLC aluminium sheets (silica gel 60, F254). Detection of the substances was obtained by fluorescence detection under UV light (λ = 254 nm), iodine stain or potassium permanganate stain. Column chromatography was performed with silica gel (grain size 0.04-0.063 cm, Merck Si60).

Isothermal titration calorimetry (ITC) experiments were performed on a *MicroCal VP-ITC* instrument.

Nuclear magnetic resonance (NMR) spectra were obtained on instruments of the type *DPX 250*, *DRX 400, DRX 600*, *AVIII 300*, *AVIII 400 and AV-500c* from *Bruker* at 300 K. Chemical shifts (δ) are given as parts per million (ppm). Multiplicities are abbreviated as: s (singlet), d (doublet), t (triplet), q (quartet), sept (septet) and m (multiplet).

Infrared (IR) spectra were obtained with a *Shimadzu IR Affinity - 1S* spectrometer equipped with a *Specac Quest ATR* through attenuated total reflection (ATR).

Mass spectra were recorded with a *Bruker Daltonics Esquire 6000* instrument (ESI) or a *VG Instruments Autospec / EBEE-Geometrie* (EI).

CHNS Elemental Analysis was performed with a *vario Micro cube* from *Elementar Analysentechnik*.

A suitable crystal for X-Ray diffraction was grown by slow evaporation of (1 mg/1mL) hexane from a GC vile equipped with a cannula for slow vapour diffusion. Single crystal analysis was performed on a RIGAKU XtaLAB Synergy, Dualflex, HyPix using Cu-Kα radiation. The crystal structure was solved using WinGX[1] and shelXT,[2] and refined with shelXle[3] and SHELXL.

Synthesis of known compounds

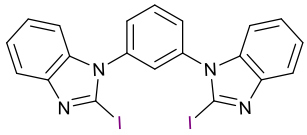
The halogen bond donors and reference compounds **3**[4], **4**[4], **5**[4], **6/BAr$^F_4$**[5], **7/OTf**[6], **7/BAr$^F_4$**[7], *syn*-**9/OTf**[8], *syn*-**9/BAr$^F_4$**[9], **12**[8] and **13**[8] were synthesized according to literature known procedures. The used octyl triflate [10] and tetramethylammonium BAr^F_4 (TMA-BAr^F_4)[11] were synthesized according to following procedures. The divinyl ketone **1** was synthesized according a slightly modified protocol published by *Trauner*[12] and stored in the dark at -30 °C.

[1] L. J. Farrugia, J. Appl. Crystallogr., **1999**, *32*, 837-838.
[2] G. M. Sheldrick, Acta Crystallogr., Sect. A: Found. Crystallogr. **2008**, *64*, 112-122.
[3] Huebschle, G. M. Sheldrick, B. Dittrich J. Appl. Cryst. **2011**, *44*, 1281-1284.
[4] F. Kniep, S.H. Jungbauer, Q. Zhang, S.M. Walter, S. Schindler, I. Schnapperelle, E. Herdtweck and S.M. Huber, *Angew. Chem. Int. Ed.*, 2013, **52**, 7028.
[5] N. Schulz, P. Sokkar, E. Engelage, S. Schindler, M. Erdelyi, E. Sanchez-Garcia and S. M. Huber, *Chem. Eur. J.*, 2018, ***24***, 3464.
[6] S.M. Walter, F. Kniep, E. Herdtweck and S.M. Huber, *Angew. Chem. Int. Ed.*, 2011, **50**, 7187.
[7] S.H. Jungbauer, S.M. Walter, S. Schindler, L. Rout, F.Kniep and S.M. Huber, *Chem. Commun.*, 2014, **50**, 6281.
[8] S. H. Jungbauer and S.M. Huber*, J. Am. Chem. Soc.*, 2015, **137**, 12110.
[9] J. Gliese, S.H. Jungbauer and S.M. Huber, *Chem. Commun.*, 2017, **53**, 12052.
[10] W.K. Fife, P. Ranganathan, M. Zeldin, *J. Org. Chem.,* 1990, **55**, 5610.
[11] P.N. Bartlett, D.C. Cook, M.W. George, J. Ke, W. Levason, G. Reid, W. Su, W. Zhang, *Phys. Chem. Chem. Phys.* ,2010, **12**, 492.
[12] G. Liang, S.N. Gradl and D. Trauner, *Org. Lett.*, 2003, **26**, 4931

General method A – Octylation

Under an argon atmosphere, the respective bis(benzimidazolyl)benzene derivative was dissolved in dry CH_2Cl_2 (50 mM). 2.5 equivalents of octyl trifluoromethanesulfonate were added and the solution was stirred at room temperature for 16 h. Removal of the solvent and repeated precipitation from acetonitrile via addition of diethyl ether yielded the desired products.

1,3-Bis(2-iodo-1H-benzimidazolyl)benzene



Under an argon atmosphere, 0.25 g of 1,3-bis(1*H*-benzimidazolyl)benzene (0.81 mmol, 1.0 equiv.) are dissolved in 40 mL of dry THF and cooled to –78 °C. Over the course of 45 min, 710 µL of 2.5 M *n*-BuLi (1.78 mmol, 2.2 equiv.) are added dropwise and the mixture is stirred for 1 h at –78 °C. Subsequently, 450 mg of iodine (1.78 mmol, 2.2 equiv.) in 5 mL of THF are added slowly, and the mixture is stirred at –50 °C for 2 h. After stirring at room temperature for 16 h, the solvent is removed, the residue re-dissolved in 30 mL of CH_2Cl_2 and washed with a saturated solution of $Na_2S_2O_3$ (2 × 30 mL), H_2O (30 mL), and brine (30 mL).The organic phase is dried over Na_2SO_4, filtered, and the solvent removed from the filtrate. Subsequent column chromatography (eluent: EtOAc/CH2Cl2 = 1/4, *R*f = 0.28) yields the product as 308 mg (0.55 mmol, 68%) of a yellow-white solid.

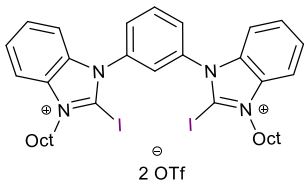
^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.86 (t, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 7.8 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.53 – 7.50 (m, 1H), 7.32 – 7.22 (m, 6H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ (ppm) = 145.58, 138.09, 137.41, 131.34, 129.49, 128.41, 124.19, 123.29, 119.65, 110.10, 102.94.

IR (ATR): ν (cm^{-1}) = 3062 (vw), 3046 (m), 3033 (vw), 1602 (m), 1496 (m), 1469 (w), 1454 (w), 1421 (vs), 1362 (w), 1299 (m), 1254 (s), 1210 (n), 1101 (w), 1003 (m).

ESI-MS: 563.1 [$(M+H^+)^+$]

1,3-Bis(2-iodo-3-octyl-1H-benzimidazolium) phenyl-bis(trifluoromethanesulfonate) (8/OTf)



The compound was synthesized by Method A.

Yield: 70% (white solid)

^{1}H-NMR (400 MHz, CD_3CN): δ (ppm) = 8.19 – 8.10 (m, 1H), 8.08 – 7.96 (m, 4H), 7.92 – 7.84 (m, 1H), 7.74 – 7.60 (m, 4H), 7.60 – 7.50 (m, 2H), 4.59 (t, J = 7.6 Hz, 4H), 2.00 (p, J = 7.7 Hz, 4H), 1.53 (p, J = 7.3 Hz, 4H), 1.48 – 1.27 (m, 16H), 0.94 – 0.85 (m, 6H).

^{13}C-NMR (100 MHz, CD_3CN): δ (ppm) = 137.3, 137.0, 136.2, 136.1, 134.4, 134.2, 132.6, 132.5, 129.7, 129.0, 128.8, 128.6, 128.3, 128.2, 126.6, 123.4, 120.2, 114.6, 114.4, 114.3, 114.2, 51.6, 32.5, 29.8, 27.2, 23.3, 14.4.

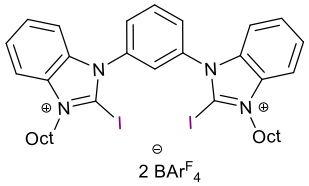
^{19}F-NMR (235 MHz, CD_3CN): δ (ppm) = –79.20.

Elemental Analysis: *calc.*: C: 42.00 H: 4.27 N: 5.16 S: 5.90
found: C: 41.34 H: 4.13 N: 5.29 S: 5.92

IR (ATR): ν (cm^{-1}) = 3063 (vw), 2928 (m), 2856 (w), 1604 (w), 1501 (m), 1478 (m), 1459 (m), 1435 (m), 1405 (w), 1355 (w), 1310 (vw), 1259 (vs), 1234 (s), 1221 (s), 1148 (s), 1097 (vw), 1082 (vw), 1023 (vs).

ESI-MS: 394.4 $[(M)^{2+}]$, 811.2 $[(M + Na)^{+}]$, 937.1 $(M + OTf^{-})^{+}$

1,3-Bis(2-iodo-3-octyl-1H-benzimidazolium)phenyl-bis(tetrakis(3,5-bis(trifluoromethyl)phenyl)borate) (8/BAr^F_4)



8/OTf was dissolved in CH_2Cl_2/MeOH = 3/1 (12 mM). 2.2 equivalents of tetramethylammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate were added and the solution was stirred at room temperature for 16 h. After removal of the solvent, the mixture was suspended in Et_2O (100 mL per mmol of employed triflate salt) and cooled to –20 °C. The resulting precipitate was filtered off via a syringe filter (25 μm), washed with cold Et_2O, and the solvent removed from the combined filtrates. The mixture was suspended in $CHCl_3$ (100 mL per mmol of employed triflate salt) and cooled to –20 °C. The resulting precipitate was filtered off via a syringe filter (25 μm), washed with cold $CHCl_3$, and the solvent removed from the combined filtrates. 200 mL of pentane per mmol of employed triflate salt were added and the mixture cooled to –20 °C. After decanting the solvent, the remaining oil was dried under high vacuum to yield the products as white solids.

Yield: 59% (white solid)

^{1}H-NMR (500 MHz, CD_3CN): δ (ppm) = 8.18–8.10 (m, 1H), 8.05–7.95 (m, 4H), 7.88–7.83 (m, 1H), 7.76–7.61 (m, 28H), 7.61–7.51 (m, 2H), 4.58 (t, J = 7.7 Hz, 4H), 1.61–1.17 (m, 20H), 0.89 (t, J = 6.6 Hz, 6H).

^{13}C-NMR (126 MHz, CD_3CN): δ (ppm) = 163.4–161.5 (m), 137.0, 136.8, 136.0, 135.9, 135.7–135.4 (m), 134.3–134.1 (m), 132.4, 130.3–129.8 (m), 129.0, 128.8–128.5 (m), 128.4–128.2 (m), 125.3 (q, J = 271.8 Hz), 118.7–118.4 (m), 114.4–113.6 (m), 51.6, 32.4, 29.7, 29.6, 29.5, 27.1, 23.2, 14.2.

^{19}F-NMR (471 MHz, CD_3CN): δ (ppm) = –63.50.

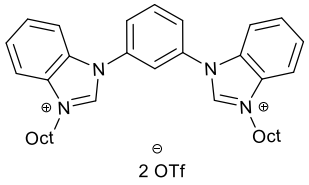
Elemental Analysis: calc.: C: 47.76 H: 2.81 N: 2.23 S: 0.00

found: C: 48.44 H: 3.10 N: 2.47 S: 0.15

IR (ATR): ν (cm^{-1}) = 2956 (w), 2931 (w), 2861 (w), 1609 (w), 1502 (w), 1478 (w), 1464 (vw), 1435 (w), 1354 (s), 1274 (vs), 1118 (vs), 1035 (vw), 1023 (vw), 1011 (vw).

ESI-MS: 1651.1 $[(M + BArF^{-})^{+}]$

1,3-Bis(3-octyl-1H-benzimidazolium)phenyl-bis(trifluoromethanesulfonate) (11)



The compound was synthesized by Method A.

Yield: 78% (white solid)

^{1}H-NMR (500 MHz, CD_3CN): δ (ppm) = 9.46 (s, 2H), 8.10–8.00 (m, 6H), 7.91–7.87 (m, 2H), 7.83–7.74 (m, 4H), 4.56 (t, J = 7.5 Hz, 4H), 2.12–1.91 (m, 4H), 1.53–1.23 (m, 20H), 0.88 (t, J = 6.9 Hz, 6H).

^{13}C NMR (101 MHz, CD_3CN) δ 142.3, 135.7, 133.7, 132.7, 132.6, 129.1, 128.7, 128.5, 123.6, 120.4, 114.9, 114.6, 48.9, 32.5, 29.8, 29.7, 27.1, 23.3, 14.4.

^{19}F-NMR (235 MHz, CD_3CN): δ (ppm) = –79.30.

Elemental Analysis: calc.: C: 54.66 H: 5.79 N: 6.71 S: 7.68

found: C: 54.08 H: 5.72 N: 6.66 S: 7.74

IR (ATR): ν (cm^{-1}) = 3133 (vw), 3072 (w), 2927 (m), 2858 (w), 1603 (w), 1593 (w), 1561 (s), 1503 (w), 1492 (w), 1469 (w), 1458 (w), 1374 (w), 1313 (w), 1271 (vs), 1259 (vs), 1246 (vs), 1221 (m), 1168 (s), 1026 (s).

ESI-MS: 268.4 $[(M)^{2+}]$, 535.4 $(M - H^+)^+$, 685.3 $(M + OTf^-)^+$, 1519.2 $(2M + 3\ OTf^-)^+$

NMR Spectra:

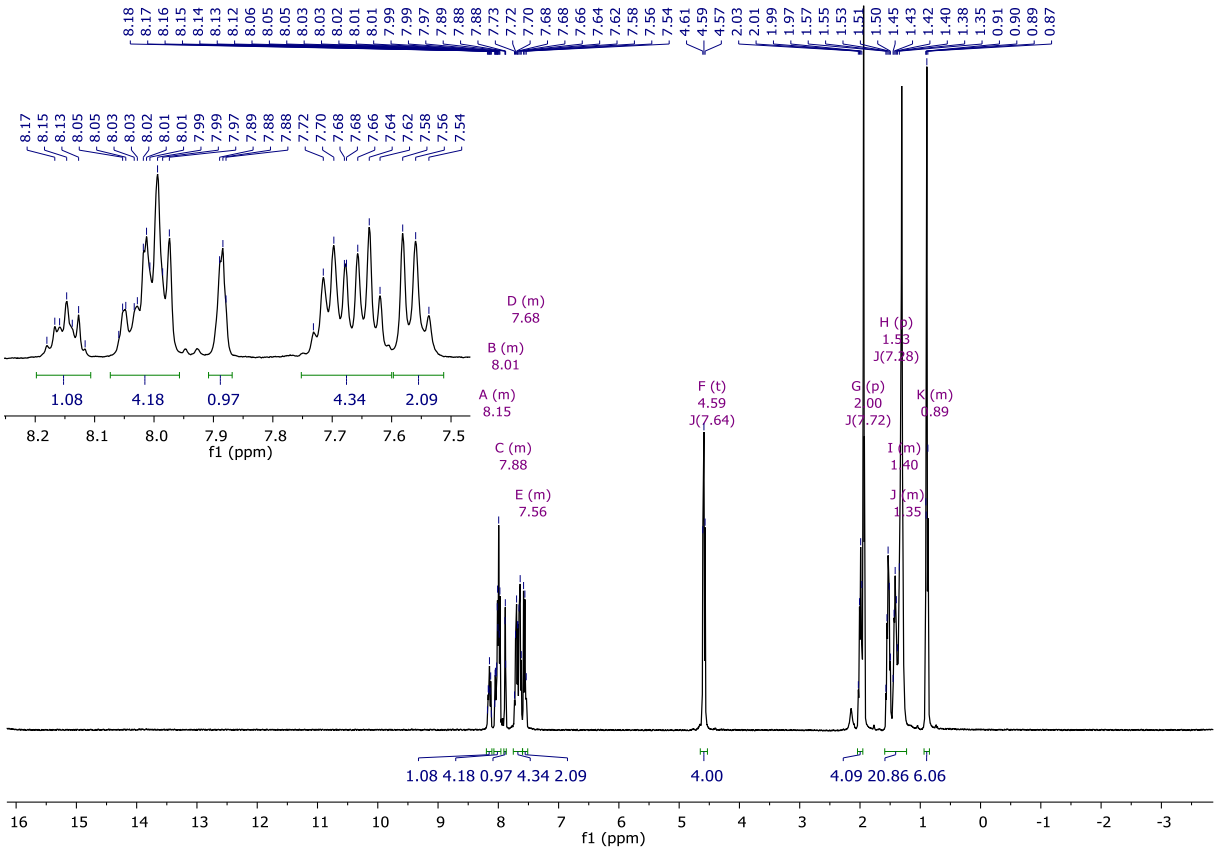


*Figure 1: ^{1}H-NMR Spectrum (400 MHz, CD_3CN) of **8/OTf**.*

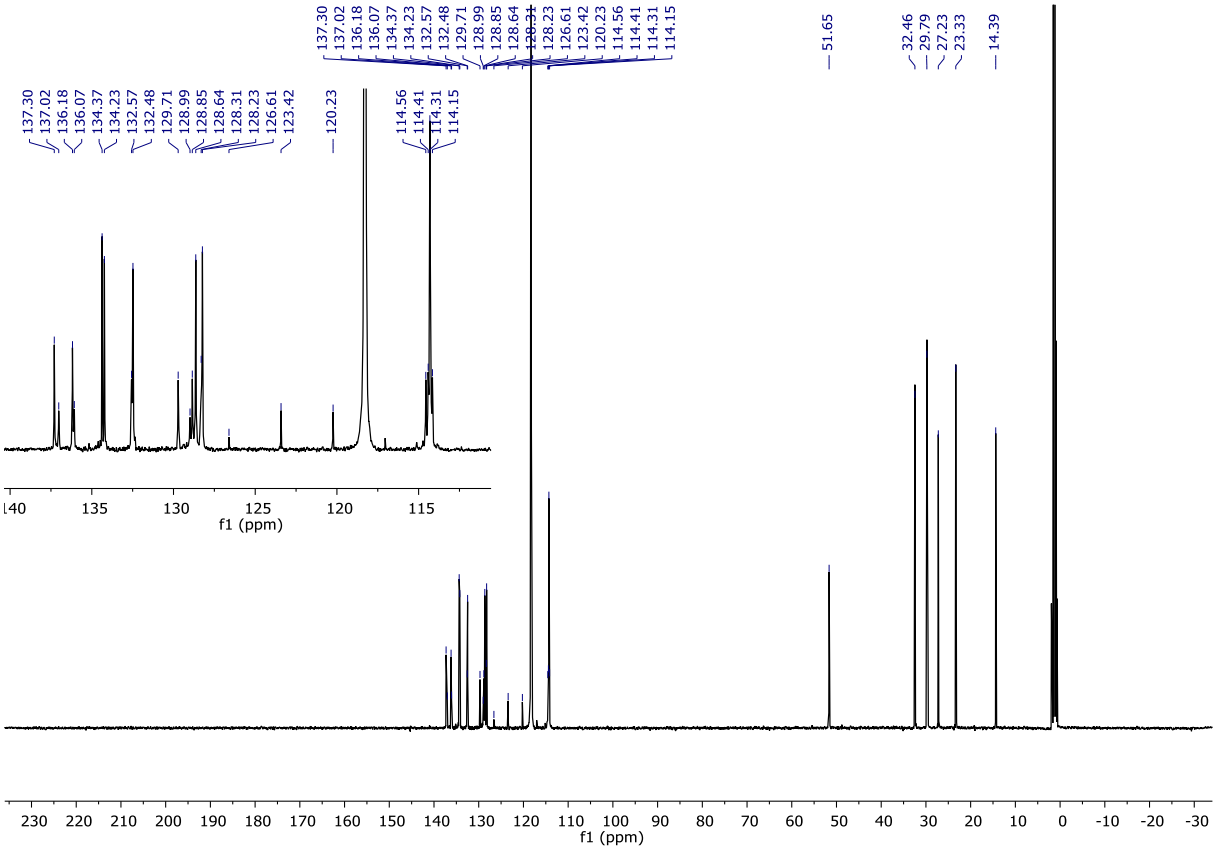


*Figure 2: ^{13}C-NMR (100 MHz, CD_3CN) of **8/OTf**.*

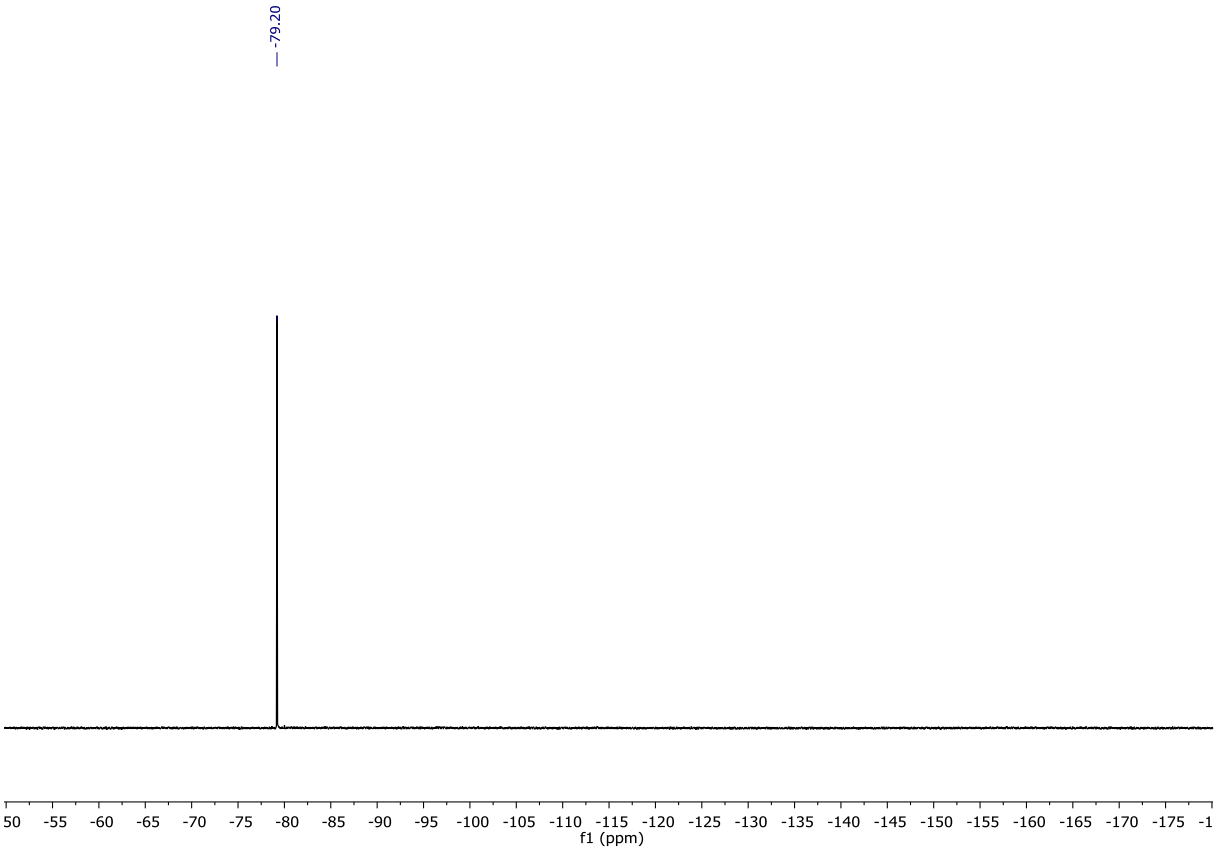


*Figure 3: ^{19}F-NMR (235 MHz, CD_3CN) of **8/OTf**.*

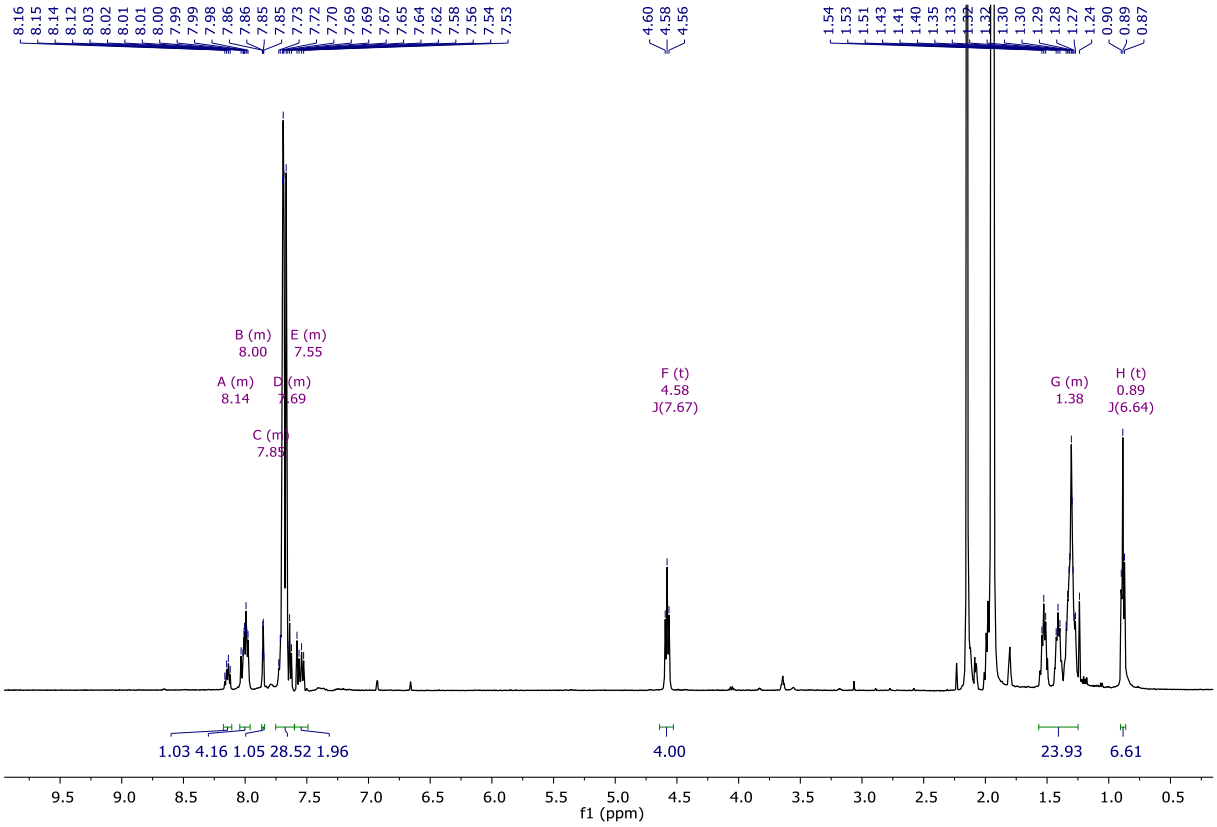


*Figure 4: ^{1}H-NMR Spectra (500 MHz, CD_3CN) of **8/BAr$^{F}_{4}$**.*

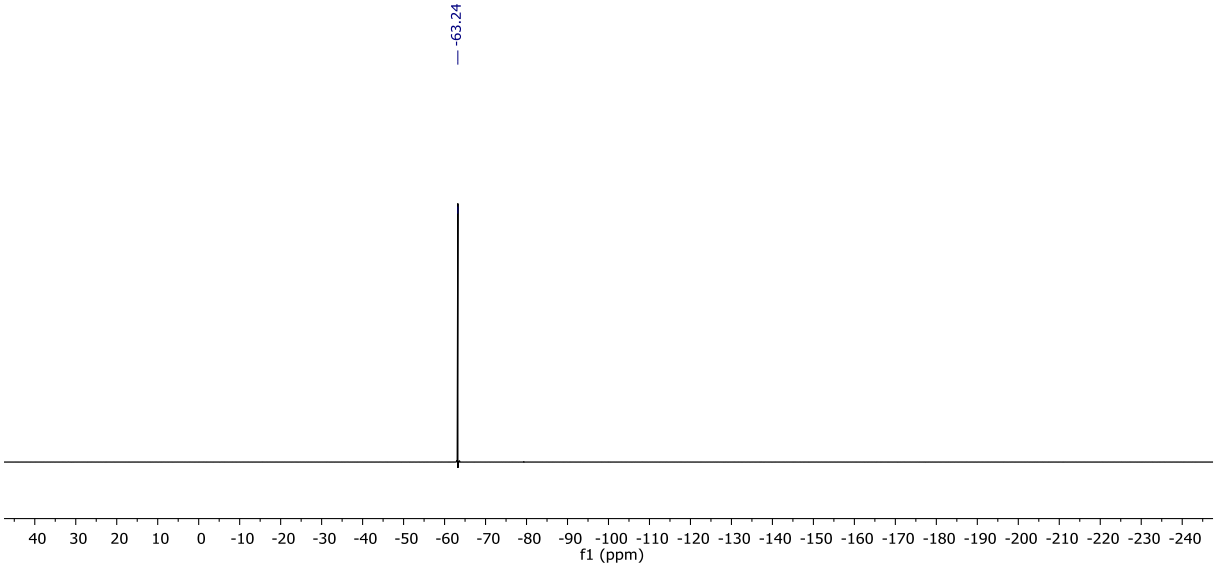


*Figure 5: ^{19}F-NMR (471 MHz, CD_3CN) of **8/BAr$^{F}_{4}$**.*

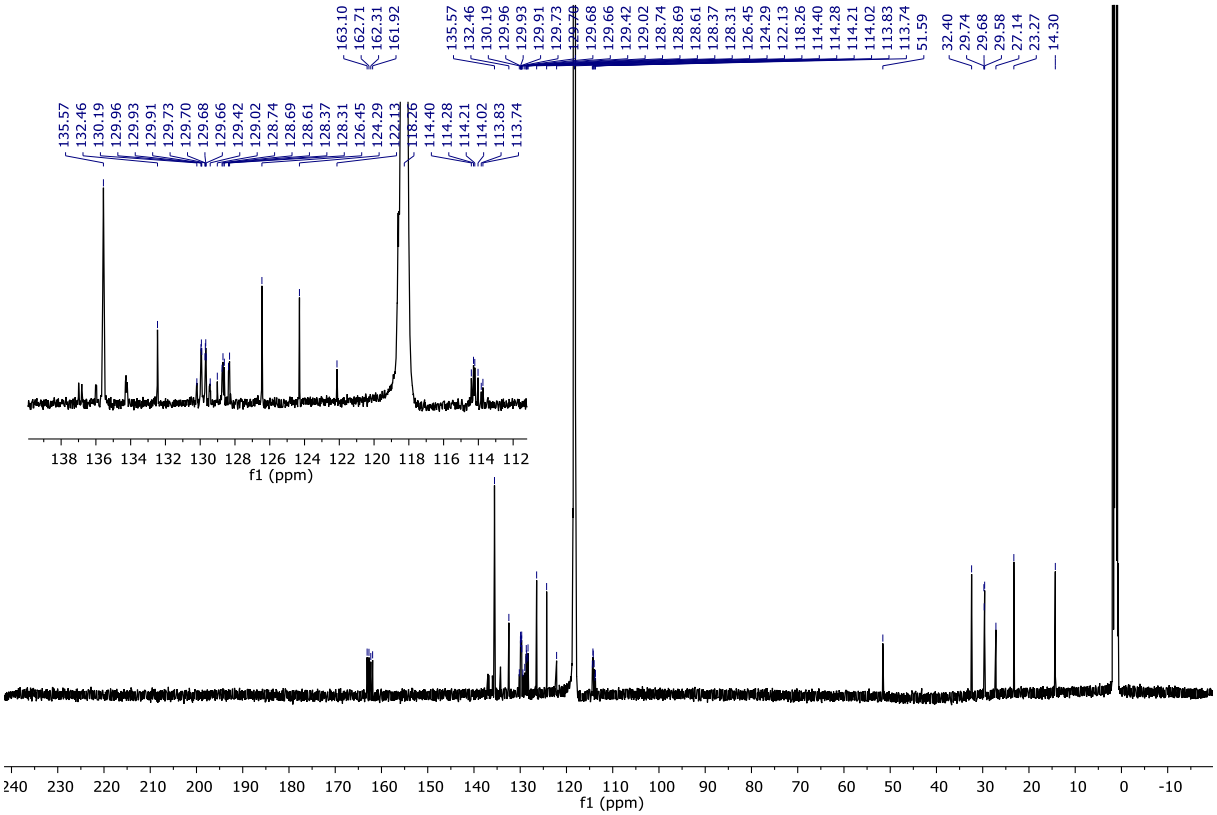


*Figure 6: ^{13}C NMR (126 MHz, CD_3CN) of **8/BAr$^F_4$**.*

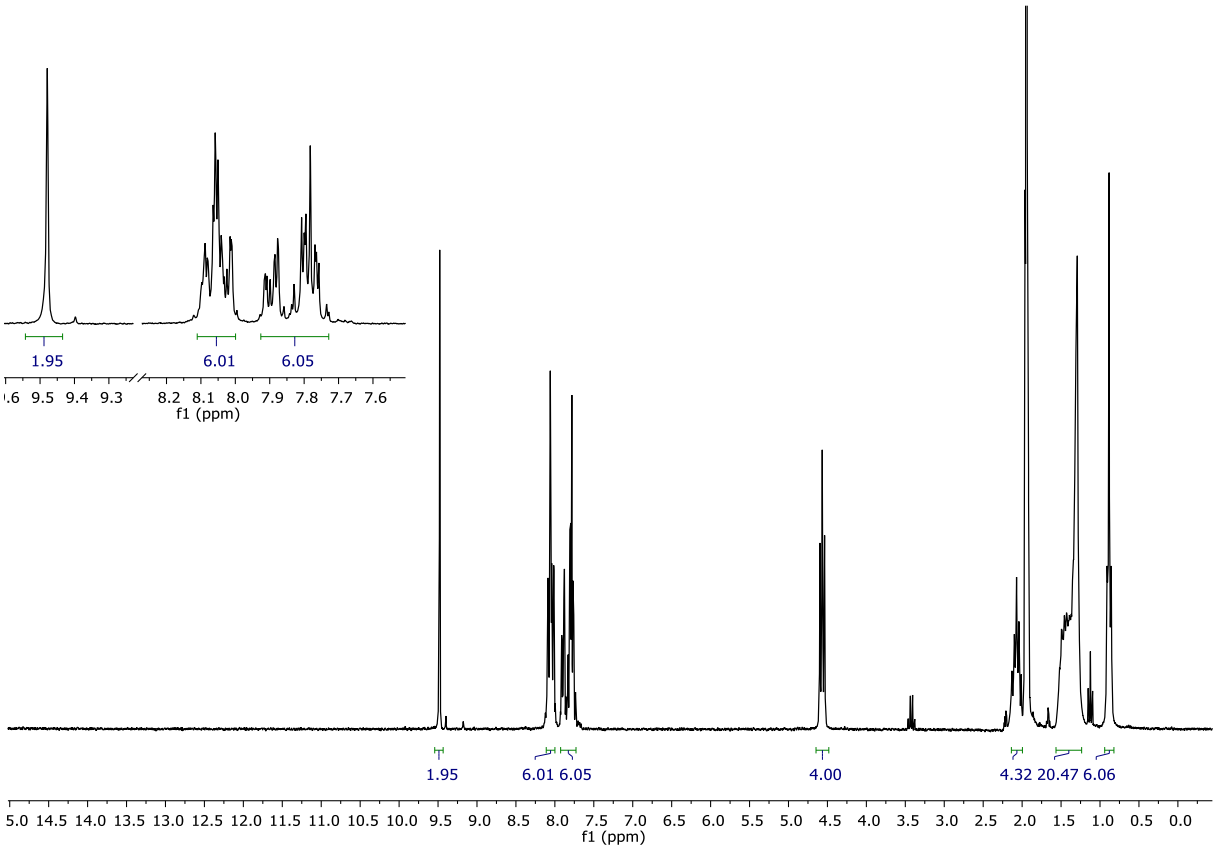


*Figure 7: ^1H-NMR (250 MHz, CD_3CN) of **11**.*

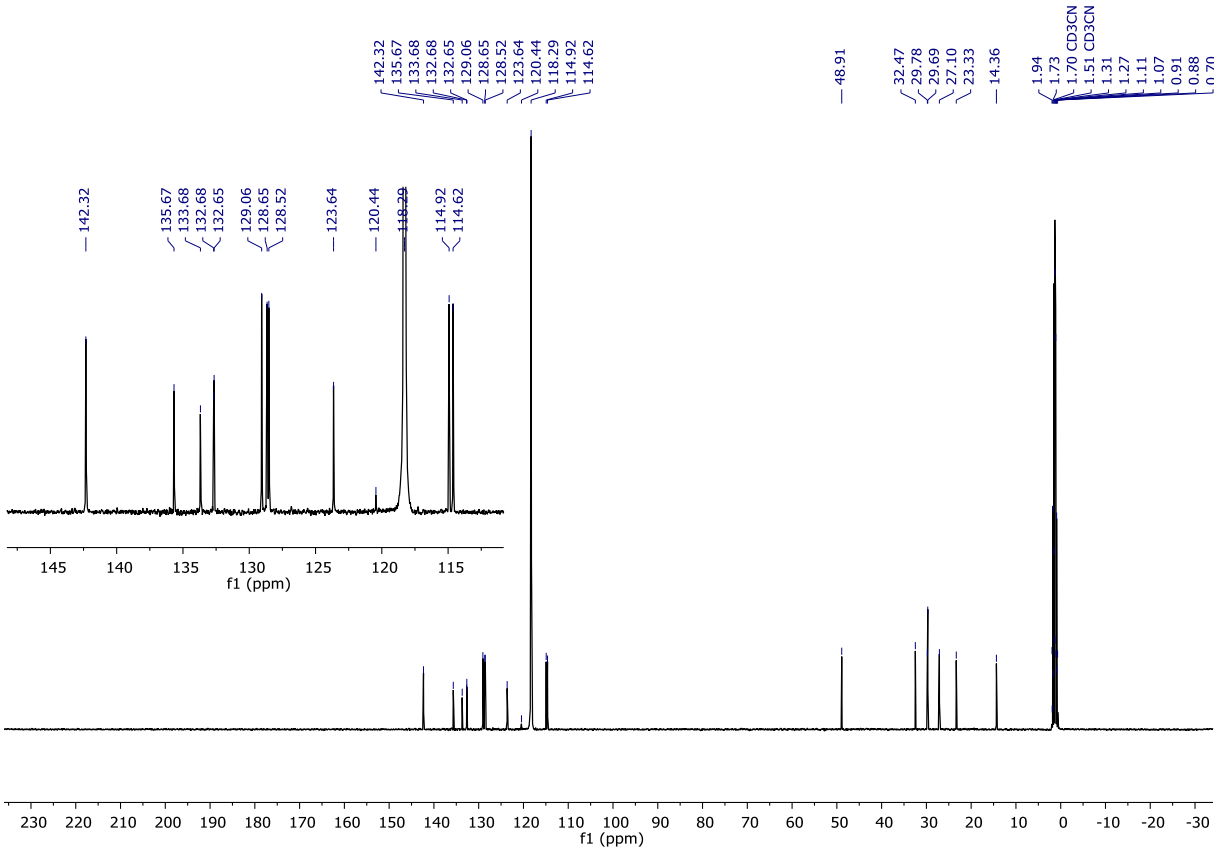


*Figure 8: ^{13}C-NMR (100 MHz, CD_3CN) of **11**.*

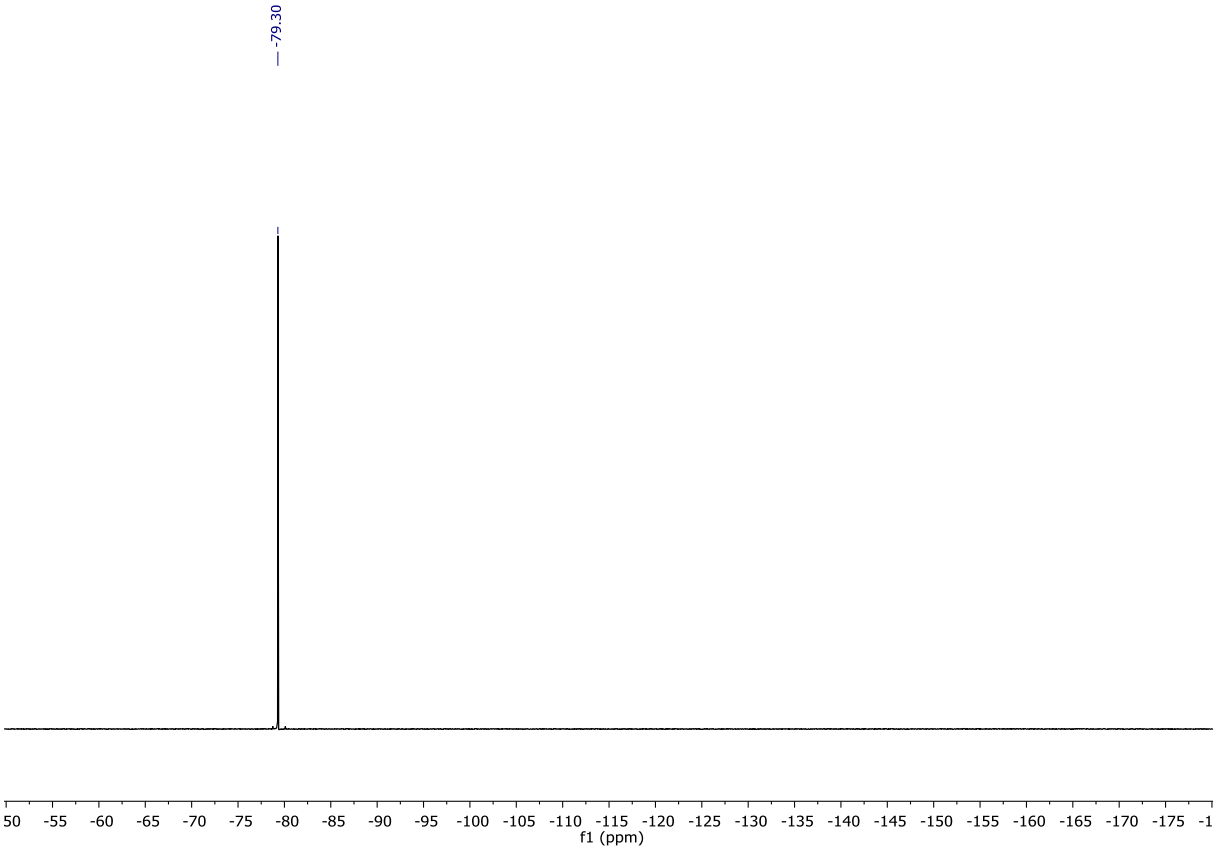


*Figure 9: ^{19}F-NMR (235 MHz, CD_3CN) of **11**.*

General information and procedure for the Nazarov cyclisation (NMR experiment)

Hamilton®-syringes were used for the preparation of all stock solutions and catalysis experiments.

In a dry NMR tube, 0.1 mL of 100 mM stock solution (CD_2Cl_2) of divinyl ketone **1** (with 1 eq. of 1,3,5-trifluorobenzene as internal standard) was added and filled up with 0.5 mL CD_2Cl_2. After the addition of 0,05 mL of 10 mM stock solution of catalyst or reference compound, the NMR tube was sealed, mixed and the ^1H measurement was directly started at an *AVIII 300* from *Bruker* at 300 K with 8 scans per measurement. In the first hour, the delay between the measurements was one to four minutes (depending on the used catalyst) and afterwards the delay between the measurements increases to 30 min to 3 hours.

MestReNova (Version 11.0.4-18998) was used for the analysis of the NMR data. The separated signal of 1,3,5-trifluorobenzene (^1H NMR: 6.75-6.61 ppm (m) and ^{19}F NMR: -118.18 ppm (s) in CD_2Cl_2) was used as internal standard. The ^1H signals 5.79-5.74 ppm (t) and 4.17-4.08 ppm (t) was used to determine the consumption of educt **1**. The increase and decrease of the concentration of the intermediate (likely **10**) was monitored via the ^1H signals at 3.58-3.52 ppm and/or 3.45-3.42 ppm. The kinetic profile of the product formation and the cis/trans ratio of cyclopentenone **2** is based on the ^1H Signals at 4.04-3.98 ppm (dt) and/or 0.65-0.60 (d) for *cis*-**2**. For *trans*-**2**, the signals at 3.35-3.31 ppm (q) and/or 1.23-1.19 ppm (d) were used.

Preparative experiment of the halogen bond-catalysed Nazarov cyclisation reaction

105 mg (0.426 mmol) of cyclodienone **1** and 24.6 mg (0.021 mmol) *syn*-**9/OTf** were dissolved in 0.65 ml CD_2Cl_2. The solution was transferred into an NMR tube. After standing for 12 h, the NMR yield (90%) and cis:trans ratio (2.3:1) were determined. Afterwards the product was purified by column chromatography (SiO_2, 1:1 pentane:Et_2O, Rf = 0.28 (**trans-2**) and Rf = 0.24 (**cis-2**)). The product was obtained in 80% isolated yield (84.7 mg, 0.343 mmol).

Kinetic Profiles

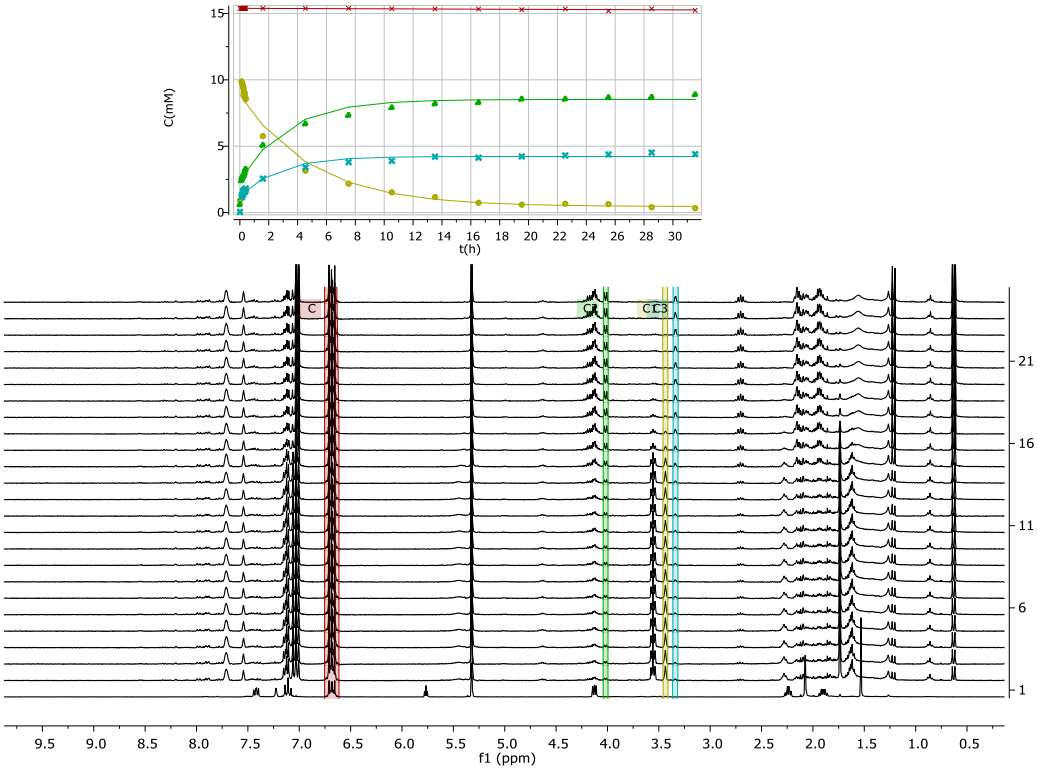


*Figure S10: Kinetic profile (top) and stacked ^{1}H NMR spectra (bottom) of the Nazarov cyclisation with **syn-9/BAr$^F_4$** (5 mol-%) as catalyst. The initial spectra 1 without a catalyst is shown in the bottom. Signal of the internal standard $C_6F_3H_3$ (red), the intermediate (yellow), the product cis-**2** (green) and the product trans-**2** (cyan) are marked.*

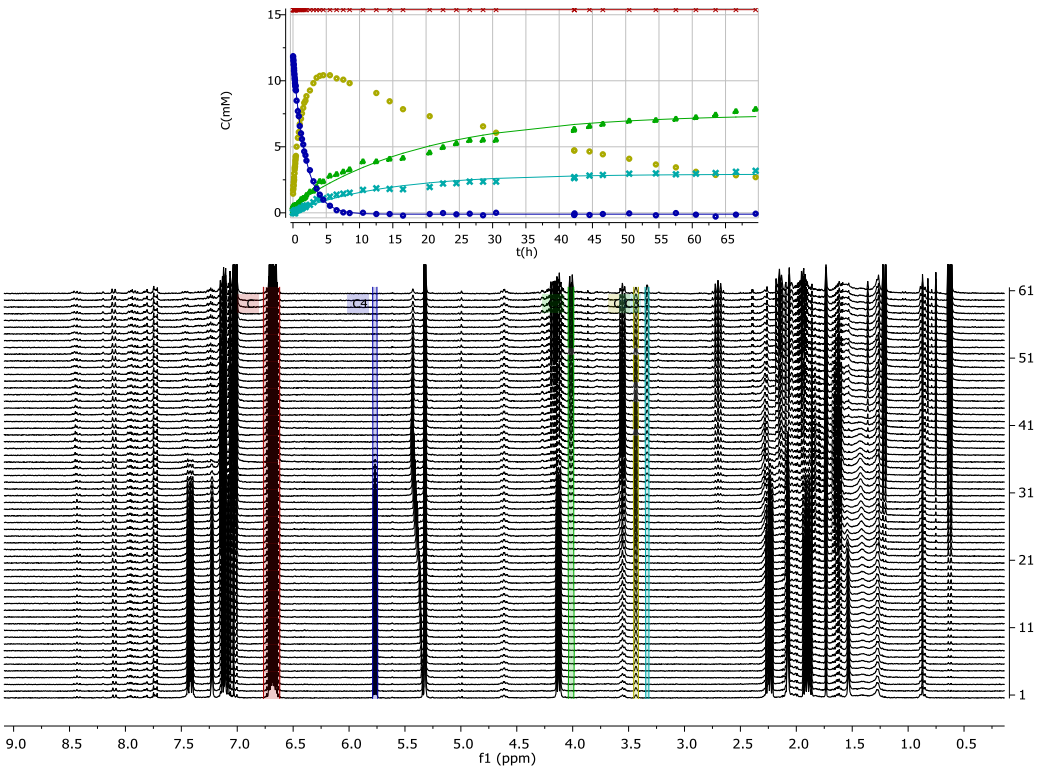


*Figure S11: Kinetic profile (top) and stacked ^{1}H NMR spectra (bottom) of the Nazarov cyclisation with **syn-9/OTf** (5 mol-%) as catalyst. Signal of the internal standard $C_6F_3H_3$ (red), the intermediate (yellow), the educt **1**(blue), the product cis-**2** (green) and the product trans-**2** (cyan) are marked.*

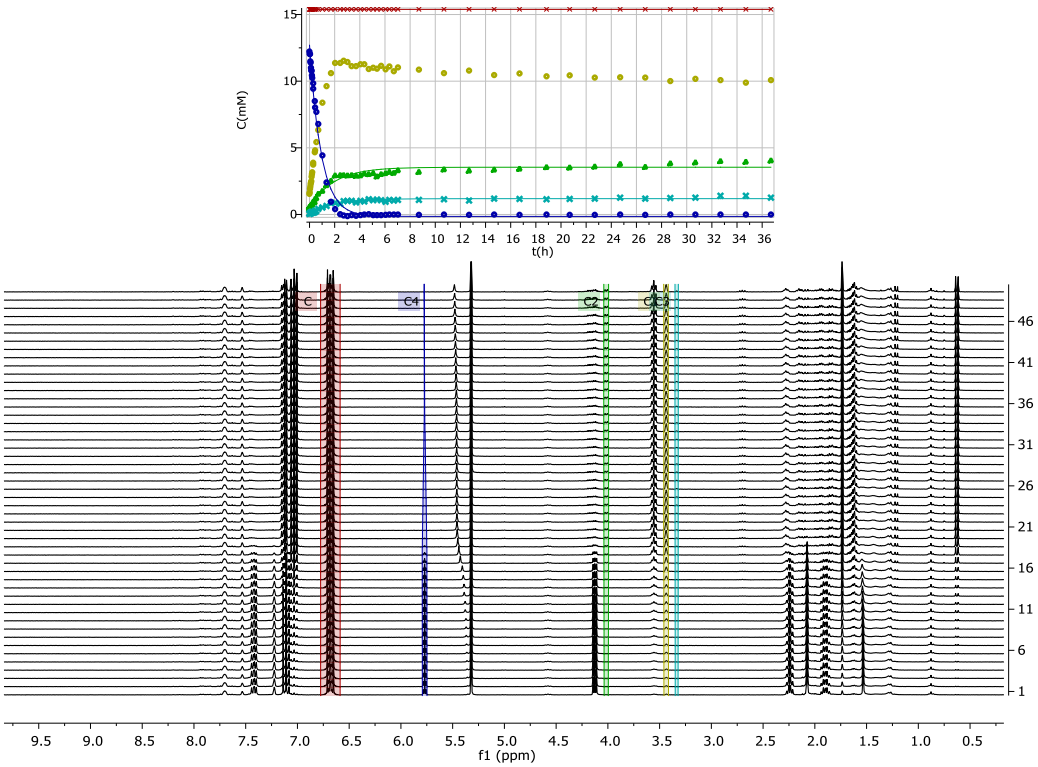


*Figure S12: Kinetic profile (top) and stacked ^{1}H NMR spectra (bottom) of the Nazarov cyclisation with **8/BAr$^F_4$** (5 mol-%) as catalyst. Signal of the internal standard $C_6F_3H_3$ (red), the intermediate (yellow), the educt **1**(blue), the product cis-**2** (green) and the product trans-**2** (cyan) are marked.*

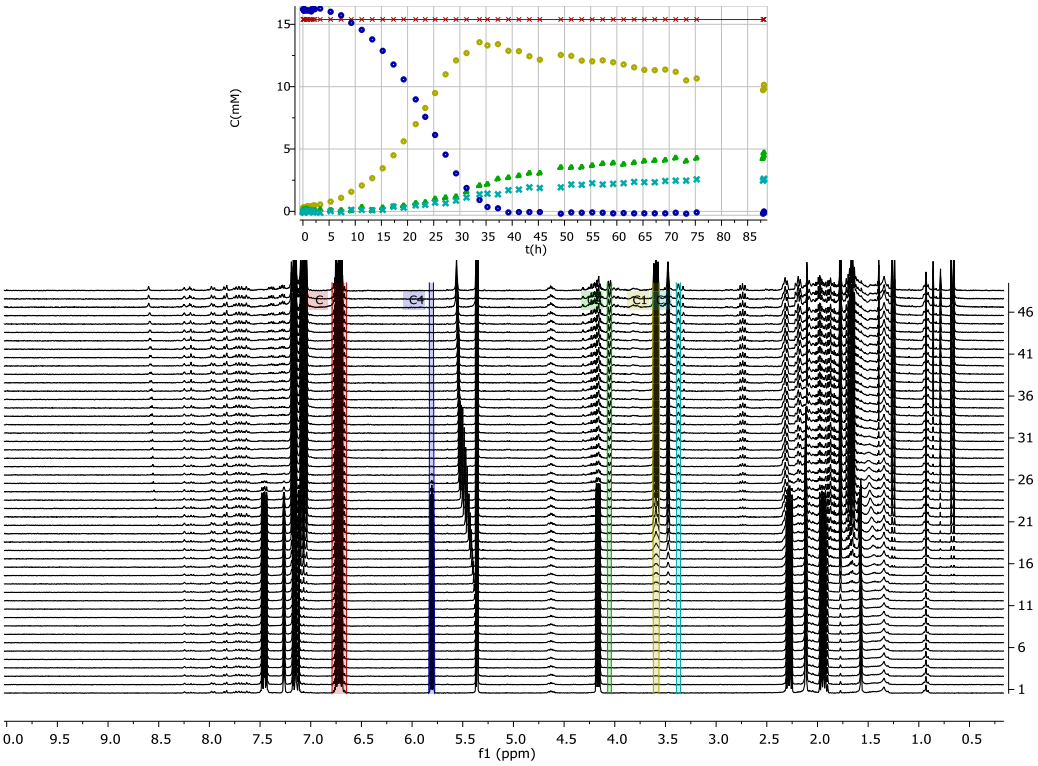


*Figure S13: Kinetic profile (top) and stacked ^{1}H NMR spectra (bottom) of the Nazarov cyclisation with **8/OTf** **(5 mol-%)** as catalyst. Signal of the internal standard $C_6F_3H_3$ (red), the intermediate (yellow), the educt **1**(blue), the product cis-**2** (green) and the product trans-**2** (cyan) are marked.*

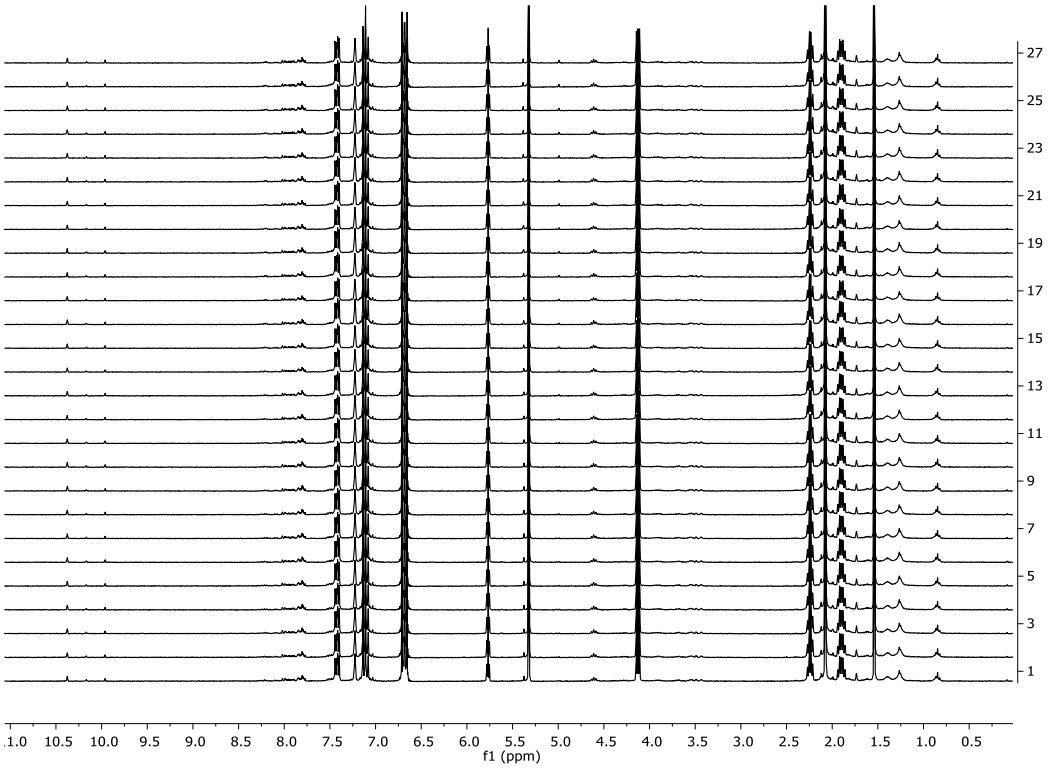


*Figure S14: Stacked ^{1}H-NMR spectra with reference compound **12** (as non-iodinated version of **syn-9/OTf**). Every spectrum is recorded after 2 h. No reaction in a time period of 48 h.*

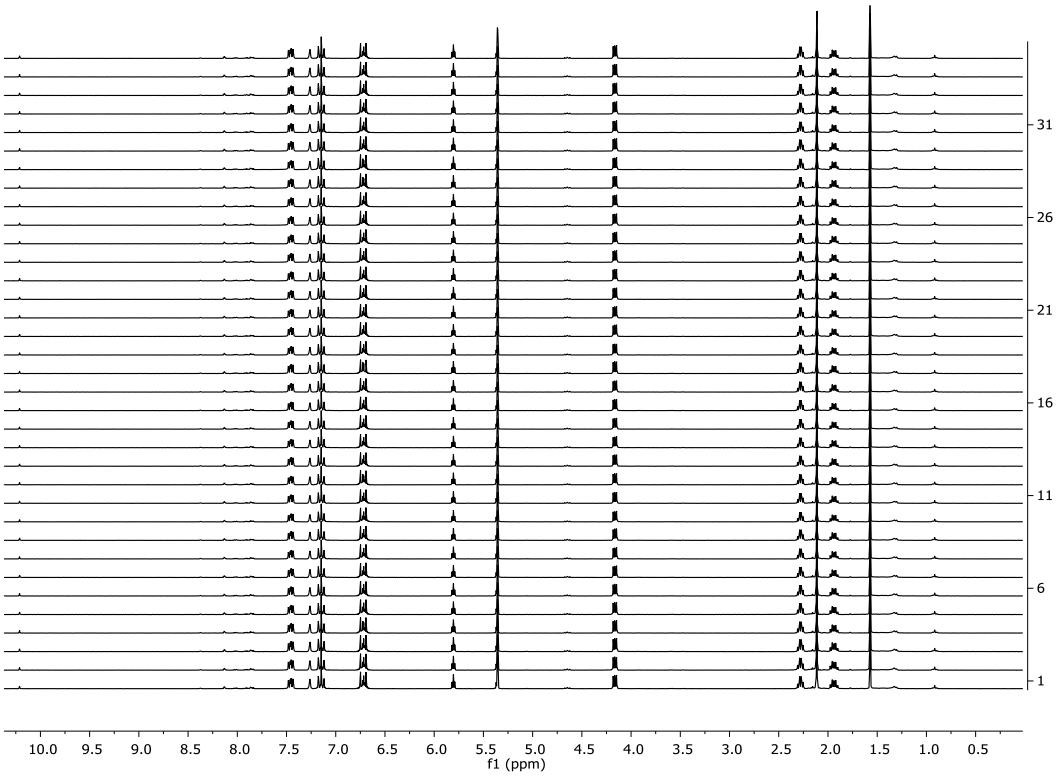


*Figure S15: Stacked ^{1}H-NMR spectra with reference compound **11** (as non-iodinated version of **8/OTf**). Every spectrum is recorded after 2 h. No reaction in a time period of 48 h.*

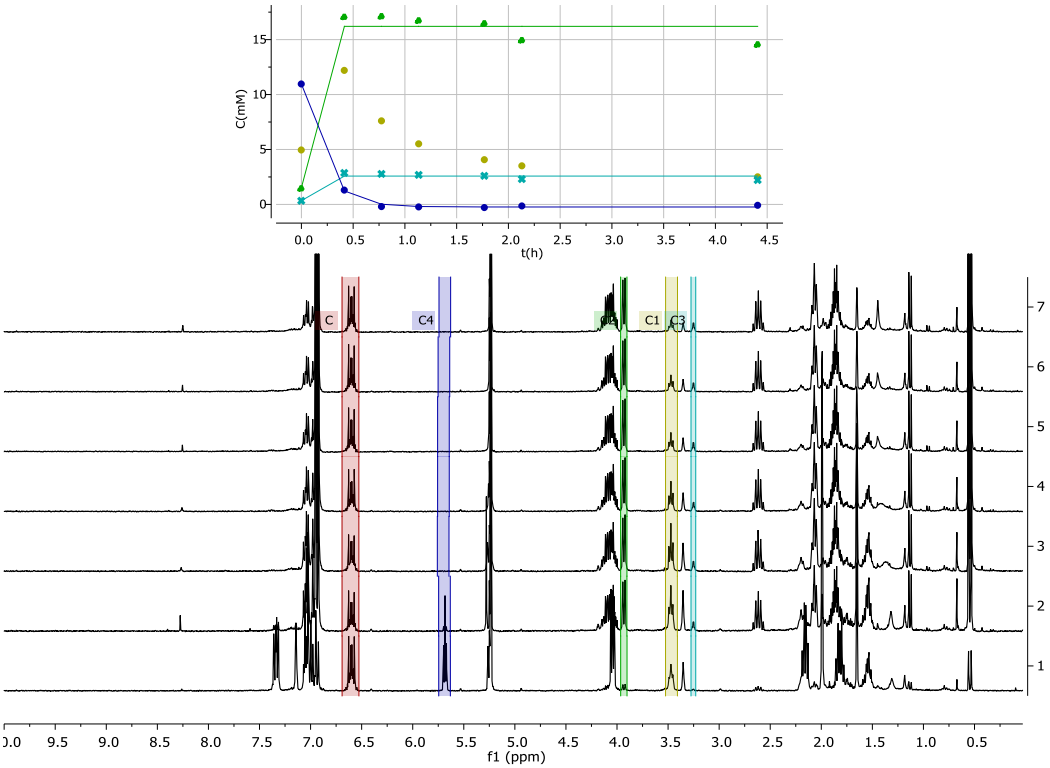


*Figure S16: Kinetic profile (top) and stacked ^{1}H NMR spectra (bottom) of the Nazarov cyclisation with **HOTf (1 mol%)** as catalyst. Signal of the internal standard $C_6F_3H_3$ (red), the intermediate (yellow), the educt **1**(blue), the product cis-**2** (green) and the product trans-**2** (cyan) are marked.*

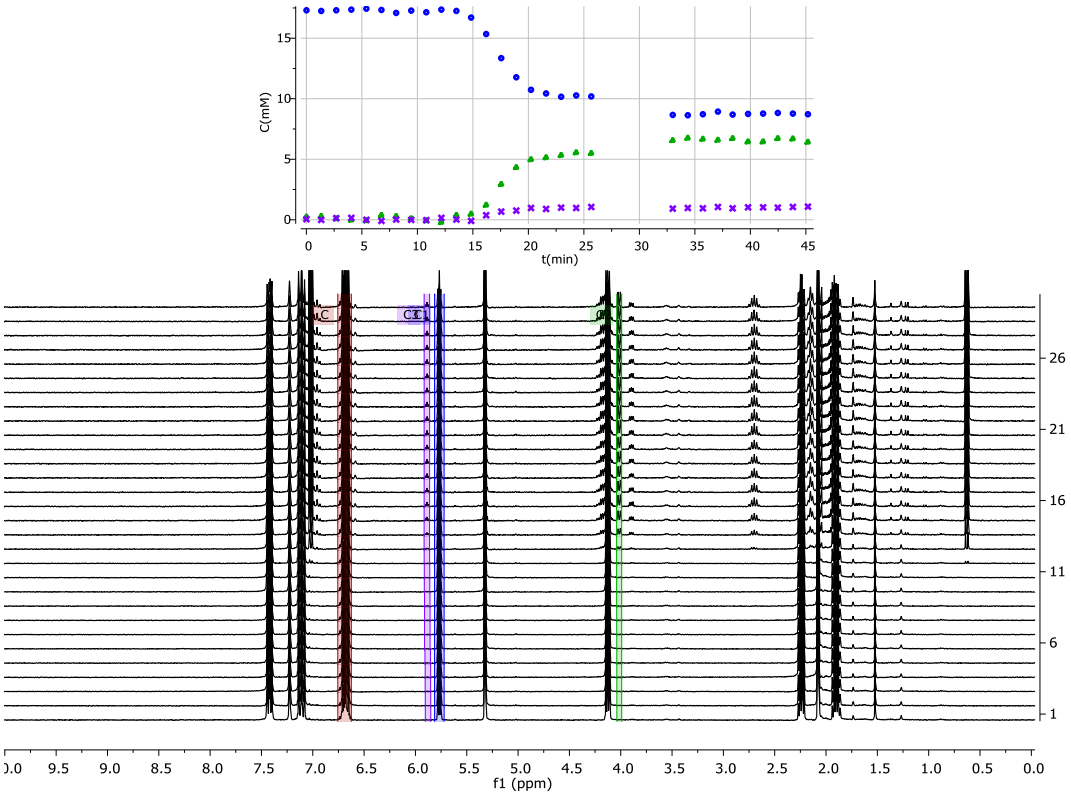


*Figure S17: Kinetic profile of an iodine (**0.1 mol%**) catalysed Nazarov cyclisation. Signal of the internal standard $C_6F_3H_3$ (red), the educt **1**(blue), the product cis-**2** (green) and a new set of signals of unknown compound (purple) are marked.*

Exemplary ^{19}F-NMR spectrum (to assess catalyst stability)

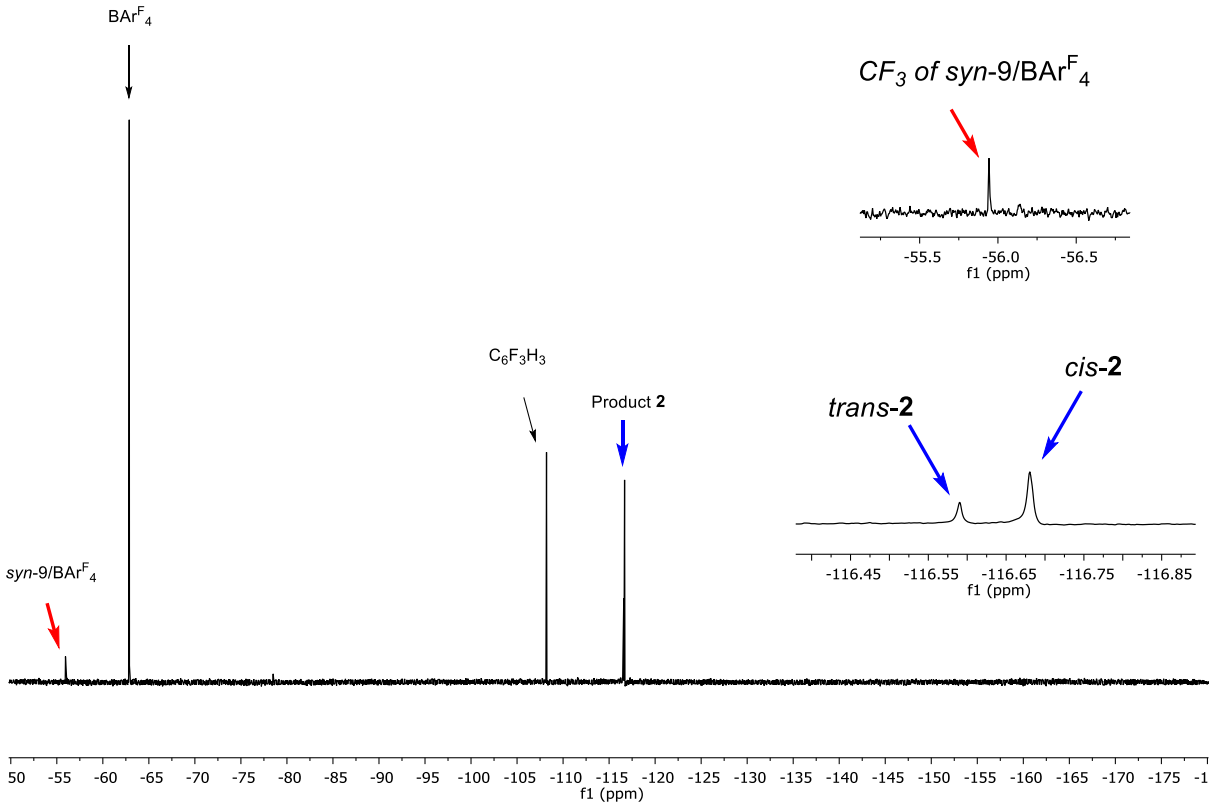


*Figure S18: ^{19}F-Spectrum of halogen bond catalysed Nazarov reaction (approx. 4 h after start). The signals (-116.x ppm) of the products cis-**2** and trans-**2** are marked with blue arrows and the signal (-55.9 ppm) of the catalyst **syn-9/BAr$^F_4$** is marked with a red arrow.*

X-Ray Structural Analysis of *cis*-2

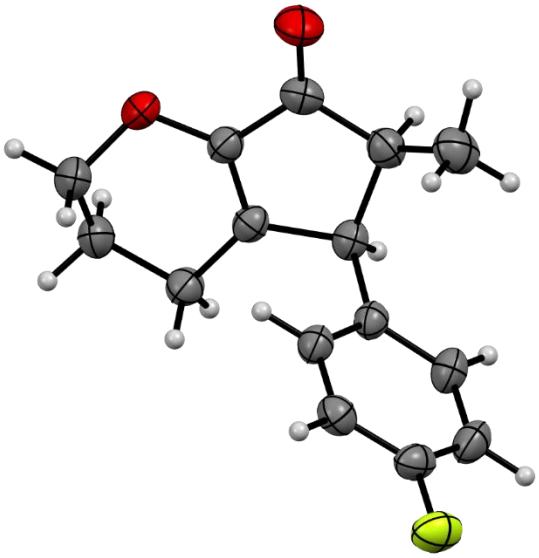


*Figure S19: Crystal structure of the product cis-**2**. Crystal was obtained by slow evaporation of n-hexane.*

Table S1. Crystallographic data of product cis-**2**.

	product cis-**2**
Emperical formula	$C_{15}H_{15}FO_2$
Formular weight [g/mol]	246.27
Crystal system	monoclinic
Space group (Nr.)	P2(1)/c (14)
Lattice parameters	
a [Å]	6.61050(10)
b [Å]	11.8833(2)
c [Å]	15.8503(4)
α [°]	90
β [°]	100.495(2)
γ [°]	90
Cell volume [$Å^3$]	1224.28(4)
Z	4
Density [g/cm^3]	1.336
Diffraction Device	XtaLAB Synergy, Dualflex, HyPix
Radiation type	1.54184 Å Cu-Kα
Temperature [K]	170
Absorption coefficient μ [mm^{-1}]	0.805
Absorption correction	semi-empirical

F(000)	520
Measured range	4.7 – 66.5
Index-range	-7 < h < 7
	-14 < k < 5
	-18 < l < 17
Measured reflections	6967
independent	2143
observed	1831
R_{int}	0.031
Structure solving/ refinement	SHELXT / SHELXL-2018/3
R_1 (observed/all)	0.036/0.043
wR_2 (observed/all)	0.088/0.092
GooF =	1.034
Residual electron density max/min [e Å^3]	0.183 / -0.165
CCDC number	1898636

Computational Details

DFT calculations were performed using the M06-2X functional with Grimme D3 dispersion corrections and the triple-zeta def2-TZVP(D) basis set (including the corresponding pseudopotential for iodine) using G09. The def2-TZVP(D) basis set consists of the def2-TZVP basis set for all main group elements up to Kr and the def2-TZVPD basis set for all d-block elements and all main-group elements from Rb on. All geometries were fully optimized and the nature of the respective species was confirmed by frequency calculations (N_{imag} = 0 for minima, N_{imag} = 1 for transition states). The reaction paths of the transition states were further elucidated by slight distortion along the negative frequency and subsequent reoptimization, leading to starting materials and products. Subsequently, single point calculations using the SMD18 intrinsic solvation model with parameters for dichloromethane were performed with the optimized gas-phase energies. All energies mentioned in the paper refer to Gibbs free energies. For all literature references see the paper.

Coordinates and Gibbs free energies of all relevant minima and transition states are provided below.

Starting Material (uncatalyzed)

ΔG (gas phase) = -731.395628 ht
ΔG (DCM single-point) = -731.395432 ht

C	-4.10880900	-0.80232000	-0.86063700
C	-4.36989000	-1.32018300	0.54164100
C	-3.04558200	-1.75449900	1.16278400
C	-1.98120200	-0.74449100	0.84672500
C	-2.15914300	0.21757800	-0.06480800
H	-3.14101600	-1.85685400	2.24566700
H	-4.81448600	-0.51591700	1.13150900
H	-5.08369300	-2.14361400	0.50680200
H	-3.63363900	-1.58261100	-1.46724600
H	-5.02086700	-0.47859900	-1.35764800
H	-1.06112900	-0.75007200	1.41235200
H	-2.75262600	-2.74048500	0.78812200
C	-1.23454500	1.38952800	-0.23249900
O	-1.69470400	2.45632800	-0.56161700
C	0.23397100	1.24017000	0.03670800
C	0.83968800	0.08349600	-0.26394600
H	0.22899400	-0.71212300	-0.67760600
C	0.92035900	2.50262000	0.46752900
H	1.96766500	2.51052400	0.17308700
H	0.40931600	3.35071600	0.01491500
H	0.86630800	2.63093000	1.55179700
C	2.26963400	-0.23649900	-0.15300800
C	2.84258500	-1.09390000	-1.09585600
C	3.07385700	0.24321300	0.88334100
C	4.18492700	-1.42902500	-1.03169000
H	2.22349100	-1.48998200	-1.89215100
C	4.41477400	-0.10211500	0.95554000
H	2.63870000	0.86778600	1.65174100
C	4.97714400	-0.93057300	-0.00567100
H	4.61306800	-2.08433800	-1.77904300
H	5.02151200	0.27277100	1.76966000
H	6.02475100	-1.19587300	0.05068800
O	-3.25941600	0.33614000	-0.84333000

Transition State (uncatalyzed)

ΔG (gas phase) = -731.343000 ht
ΔG (DCM single-point) = -731.342740 ht

C	-3.76581400	-1.30032300	-0.15426100
C	-2.88128200	-2.26334000	0.61044800
C	-1.43559900	-2.11734900	0.12451100
C	-1.03632100	-0.68651600	0.37985400
C	-1.99218700	0.29477300	0.08231300
H	-0.76950000	-2.80798300	0.63799900
H	-2.92754400	-2.05419800	1.68111300
H	-3.26132200	-3.27391800	0.45397700
H	-3.88483900	-1.63686400	-1.18684900
H	-4.75415700	-1.21226900	0.29406400
H	-0.39687400	-0.52865300	1.23507800
H	-1.38615300	-2.34765800	-0.94415400
C	-1.53299700	1.68452700	-0.05329500
O	-2.24264500	2.68520100	0.02220300
C	-0.11682400	1.61172100	-0.26091700
C	0.39377700	0.33780600	-0.62289300
H	0.02616600	-0.14719100	-1.52111900
C	0.68778000	2.85705800	-0.08377300
H	1.73440500	2.72558000	-0.35035400
H	0.24839300	3.63292200	-0.71696200
H	0.61844300	3.23636500	0.93940100
C	1.78184700	-0.06057600	-0.30365200
C	2.50346300	-0.86935800	-1.18001000
C	2.37633800	0.32476800	0.89894500
C	3.79835900	-1.26292600	-0.87729400
H	2.04451800	-1.18260300	-2.11081900
C	3.66773500	-0.07082000	1.20621200
H	1.81280200	0.93809300	1.59329400
C	4.38329800	-0.86313800	0.31633300
H	4.35101400	-1.88223600	-1.57171400
H	4.11774400	0.23500800	2.14174400
H	5.39229400	-1.17209700	0.55633800
O	-3.25170900	0.03728100	-0.22547300

Starting Material (catalyzed)

ΔG (gas phase) = -2731.087582 ht
ΔG (DCM single-point) = -2731.293732 ht

C	-3.00052900	-3.73983800	-1.76807800
C	-3.60644700	-3.54651000	-3.14330700
C	-4.93409900	-2.80845600	-3.00340600
C	-4.81042300	-1.70012300	-2.00360400
C	-3.76148700	-1.58781000	-1.18255800
H	-5.25497600	-2.39674600	-3.96138300
H	-2.91446800	-2.96392100	-3.75483500
H	-3.74185700	-4.51401000	-3.62561900
H	-3.67823500	-4.30581300	-1.12141100
H	-2.04114100	-4.25419500	-1.80825100
H	-5.56783800	-0.93067500	-1.97644000
H	-5.72706300	-3.49402800	-2.68921400
C	-3.47698100	-0.39296000	-0.34387600
O	-2.29149600	-0.09319200	-0.18181600
C	-4.55729900	0.42098400	0.23464300
C	-5.74145100	-0.16217100	0.51579900
H	-5.82838500	-1.22820600	0.33750000
C	-4.17026100	1.81524000	0.63597200
H	-4.89472600	2.24630200	1.32058000

H	-3.20409500	1.78696200	1.14046100
H	-4.07532000	2.47544100	-0.23014300
C	-6.93487500	0.45279400	1.09306800
C	-7.74182600	-0.32044100	1.93375200
C	-7.33418300	1.75798700	0.78816800
C	-8.88734100	0.21258000	2.49866500
H	-7.45759600	-1.34328000	2.15067800
C	-8.49312900	2.28187000	1.33567100
H	-6.75839000	2.34807900	0.08731500
C	-9.26359200	1.51623500	2.20163000
H	-9.49503700	-0.39084600	3.15939100
H	-8.80284300	3.28634800	1.08000200
H	-10.16644300	1.92983800	2.63093700
O	-2.73147400	-2.48179800	-1.14207900
C	2.76568500	0.34339800	0.56752700
C	2.28492400	0.70356200	3.31118700
C	2.70020600	-0.74344700	1.43744600
C	2.49740700	1.60669500	1.10117400
C	2.27452100	1.79309800	2.45404400
C	2.47263100	-0.56631500	2.79594400
H	2.07599800	2.79142900	2.82245300
H	2.43726700	-1.43819500	3.43649800
C	1.92692800	-2.80248100	0.30450800
N	2.44276600	-3.99367900	0.00462400
C	1.23772700	3.10371200	-0.39020100
N	1.44254500	4.24880300	-1.03364800
I	0.02240600	-2.13398400	-0.14019100
I	-0.48588400	1.96941600	-0.29307000
C	1.80224000	-5.09652400	-0.70093000
H	2.38399600	-5.33123600	-1.59054900
H	0.79705600	-4.80559100	-0.98664900
H	1.76224200	-5.96367500	-0.04400300
C	0.49208600	4.99144400	-1.85242400
H	0.88112700	5.06810500	-2.86616200
H	0.36035200	5.98559500	-1.42916200
H	-0.45838200	4.46786400	-1.86255100
H	2.11277100	0.84165700	4.36955000
C	4.01164300	-2.84663900	1.10756700
C	3.74729500	-4.06240100	0.48970200
C	3.34958800	3.71869300	0.01036100
C	2.75303800	4.67001900	-0.80865300
N	2.85119400	-2.08567200	0.97287100
N	2.37619500	2.74563900	0.24145600
C	4.69495100	-5.07671500	0.43218300
C	5.91568900	-4.80584100	1.01983300
H	6.68833700	-5.56195800	1.00262400
C	6.18255000	-3.57428400	1.63807500
H	7.15505600	-3.41089800	2.08154800
C	5.23776200	-2.56732400	1.69499300
C	4.66552100	3.83078000	0.43515000
C	5.35222800	4.94778700	-0.00072800
H	6.38113300	5.08568000	0.30168900
C	4.75260400	5.90952800	-0.82899900
H	5.33338300	6.76520800	-1.14439300
C	3.44267800	5.79169100	-1.25177900
H	4.49331800	-6.02564100	-0.04532500
H	5.44153600	-1.61739100	2.17005200
H	5.12700000	3.08421700	1.06686300
H	2.98335100	6.53301400	-1.89101900
C	3.15125600	0.23816900	-0.90065900
F	3.58286400	-0.97265200	-1.24012900
F	4.13511200	1.09779400	-1.16782900
F	2.12965500	0.53719000	-1.70552200

Transition State (catalyzed)

ΔG (gas phase) = -2731.048106 ht
ΔG (DCM single-point) = -2731.251707 ht

C	-3.78635300	-3.77828700	-1.40821700
C	-5.04120300	-3.49526400	-2.20412600
C	-6.00805900	-2.65341700	-1.36274200
C	-5.27386100	-1.39793200	-0.98853300
C	-3.92375800	-1.50049300	-0.66596200
H	-6.91656800	-2.42397900	-1.91415300
H	-4.79570000	-2.96288900	-3.12478800
H	-5.48961100	-4.44844400	-2.48436400
H	-4.00029500	-4.45717700	-0.58060400
H	-3.00405800	-4.21454100	-2.02636000
H	-5.61960000	-0.47439100	-1.42473400
H	-6.29963800	-3.21373000	-0.46982400
C	-3.29183500	-0.37949300	-0.00312700
O	-2.03232400	-0.18192200	-0.00129400
C	-4.27682100	0.41405000	0.60633900
C	-5.55668300	-0.19068700	0.75551200
H	-5.61208700	-1.15221400	1.25102800
C	-3.94016300	1.79415400	1.07833200
H	-4.75839800	2.25094300	1.62912800
H	-3.07014100	1.73092600	1.73772000
H	-3.66712200	2.45095500	0.24801300
C	-6.80621800	0.56767700	0.80466300
C	-7.87361500	0.08905400	1.56779100
C	-6.96868400	1.74485800	0.06744400
C	-9.06817100	0.78827600	1.61978300
H	-7.75829300	-0.83019400	2.13022900
C	-8.16485900	2.43758700	0.11149100
H	-6.15520000	2.10571300	-0.55213400
C	-9.21350000	1.96223200	0.89265000
H	-9.88673900	0.41766500	2.22175400
H	-8.28803300	3.34447600	-0.46507400
H	-10.14869500	2.50529000	0.92659700
O	-3.19521300	-2.59816800	-0.81858200
C	2.93642100	0.24309700	0.44899500
C	2.75881700	0.48338800	3.23976100
C	2.93375500	-0.88334200	1.27076600
C	2.74453100	1.48386500	1.06153600
C	2.67049600	1.61041000	2.43780700
C	2.86099700	-0.76482900	2.65197300
H	2.52718900	2.59286400	2.86901800
H	2.86792600	-1.66481400	3.25334400
C	1.89158200	-2.82000700	0.15662900
N	2.27371200	-4.02945800	-0.24936900
C	1.36661300	3.06414000	-0.23436100
N	1.53075300	4.24452700	-0.82538000
I	0.02028100	-1.92712200	-0.00970300
I	-0.35381800	1.91062800	-0.08664800
C	1.45979000	-5.03897300	-0.91191500
H	1.89600100	-5.26580900	-1.88322700
H	0.45308600	-4.65508900	-1.04202600
H	1.43555800	-5.93765200	-0.29793400
C	0.52170800	5.03730100	-1.51530500
H	0.82423400	5.17354400	-2.55211400
H	0.43313500	6.00508000	-1.02484300
H	-0.42968800	4.51681100	-1.47603700
H	2.70604500	0.57559900	4.31562300
C	4.05182300	-3.05406800	0.68974500
C	3.61879300	-4.21719800	0.06436900
C	3.51484600	3.64243800	0.01269100

C	2.86011000	4.64442800	-0.69329800
N	2.94724000	-2.20541100	0.72891300
N	2.55437100	2.66390900	0.27210600
C	4.47012500	-5.29359900	-0.15003700
C	5.77141200	-5.14150000	0.28987500
H	6.47429600	-5.95047800	0.14674800
C	6.20753400	-3.96403800	0.91628800
H	7.23670700	-3.89328800	1.24016800
C	5.35840200	-2.89424100	1.12892600
C	4.86439400	3.72018900	0.32436100
C	5.52406400	4.85598900	-0.10536700
H	6.57750200	4.96789300	0.11106300
C	4.86544000	5.86907700	-0.81924300
H	5.42643000	6.73770200	-1.13505300
C	3.52160200	5.78535100	-1.12959000
H	4.13794400	-6.20109300	-0.63512100
H	5.69256400	-1.98484300	1.60953000
H	5.37071600	2.93386700	0.86731600
H	3.01653100	6.56628800	-1.68116200
C	3.18787800	0.19903300	-1.05087000
F	3.56011300	-1.00368000	-1.47821000
F	4.16820900	1.05018400	-1.36027000
F	2.11335800	0.55789500	-1.75443300

NMR Data for the Assignment of the Observed Reaction Intermediate

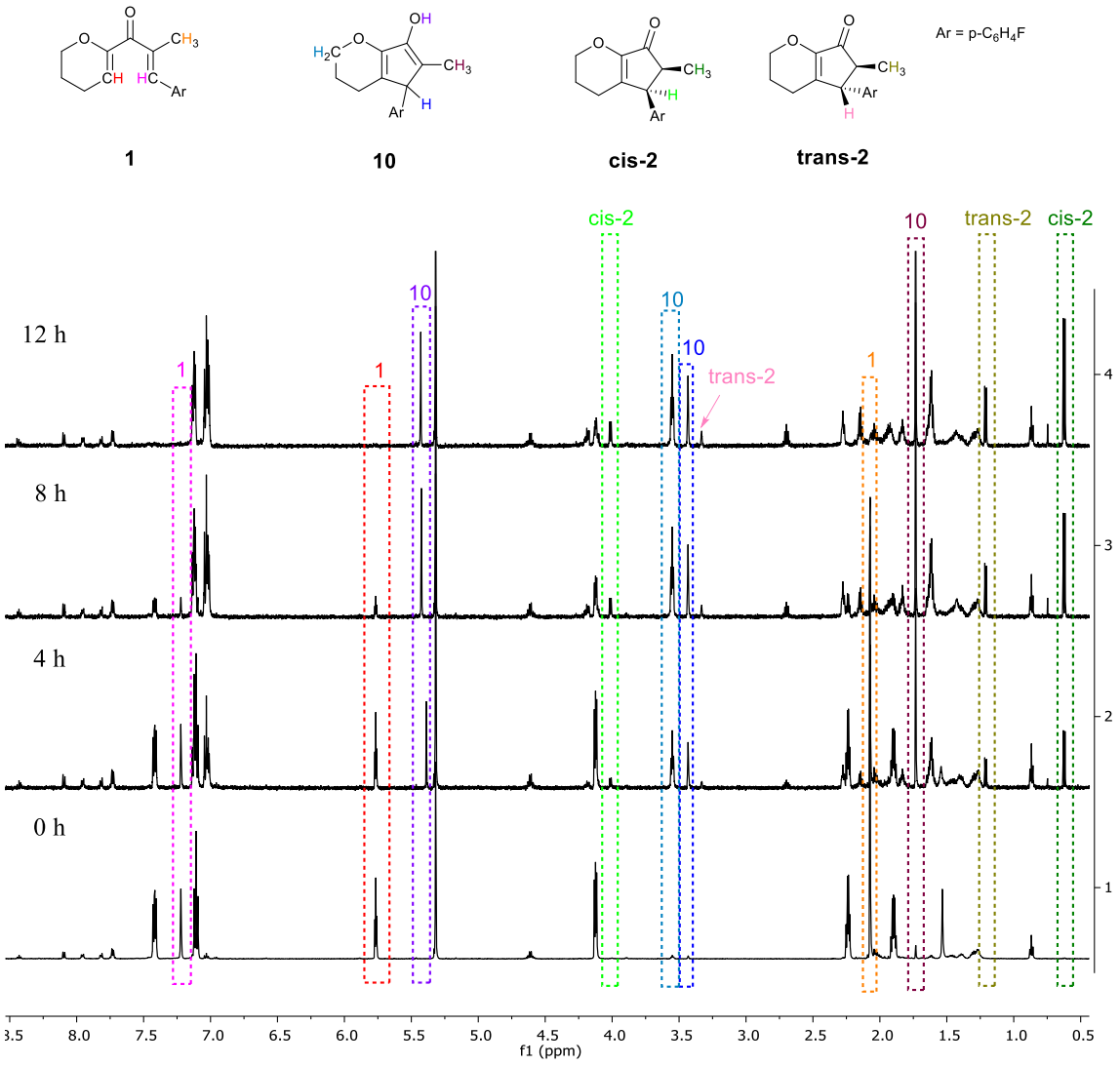


*Figure 20: ^{1}H-NMR Spectra (600 MHz) of the Nazarov reaction (c(**1**) = 15.4 mM) with **syn-9/OTf** (5 mol-%) after 0 h, 4 h, 8 h and 12 h. The corresponding Signals of **1**, **2** and **10** are marked.*

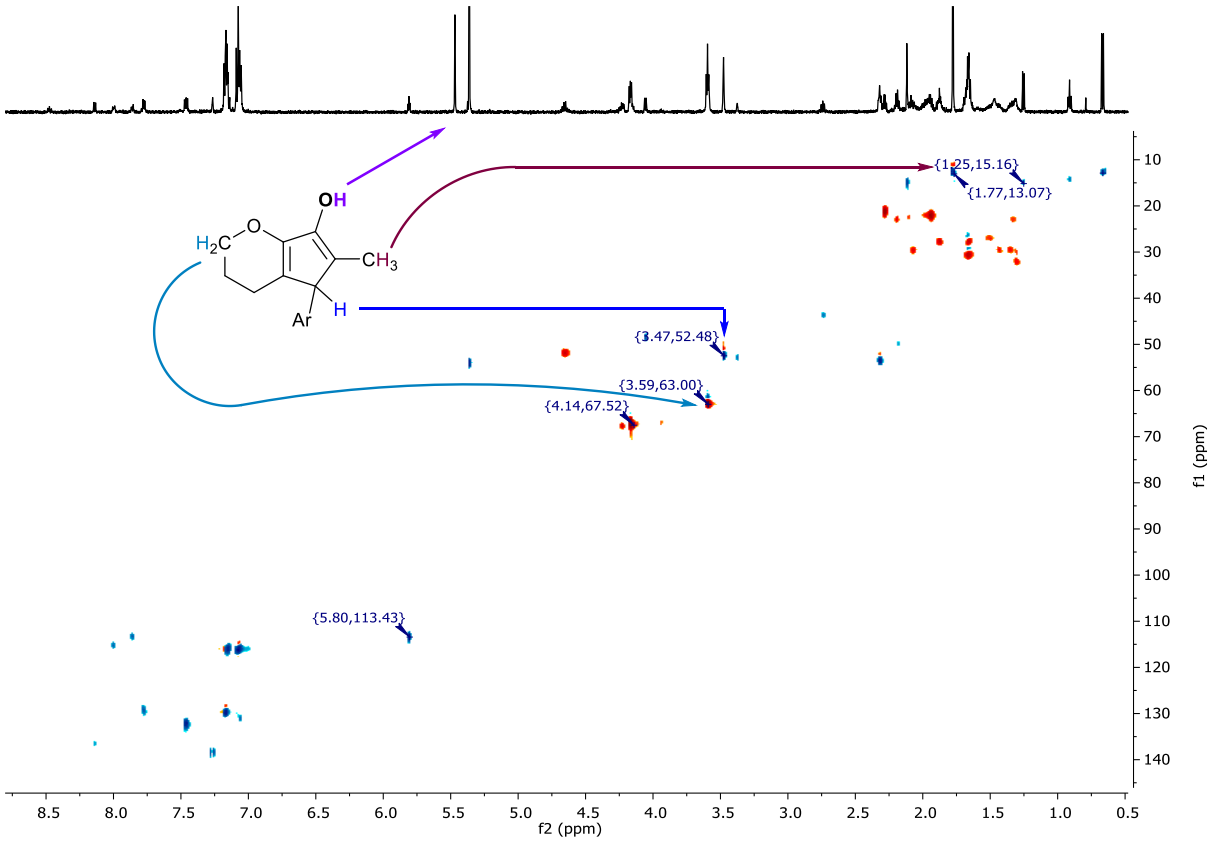


*Figure 21: HSQC Spectrum (600 MHz) of the Nazarov reaction (c(**1**) = 15.4 mM) with **syn-9/OTf** (5 mol-%) as average of the 4 h to 8 h after reaction start. The corresponding cross-peaks of the enol **10** are marked with arrows. The proton (5.4x ppm) has no carbon-cross peak.*

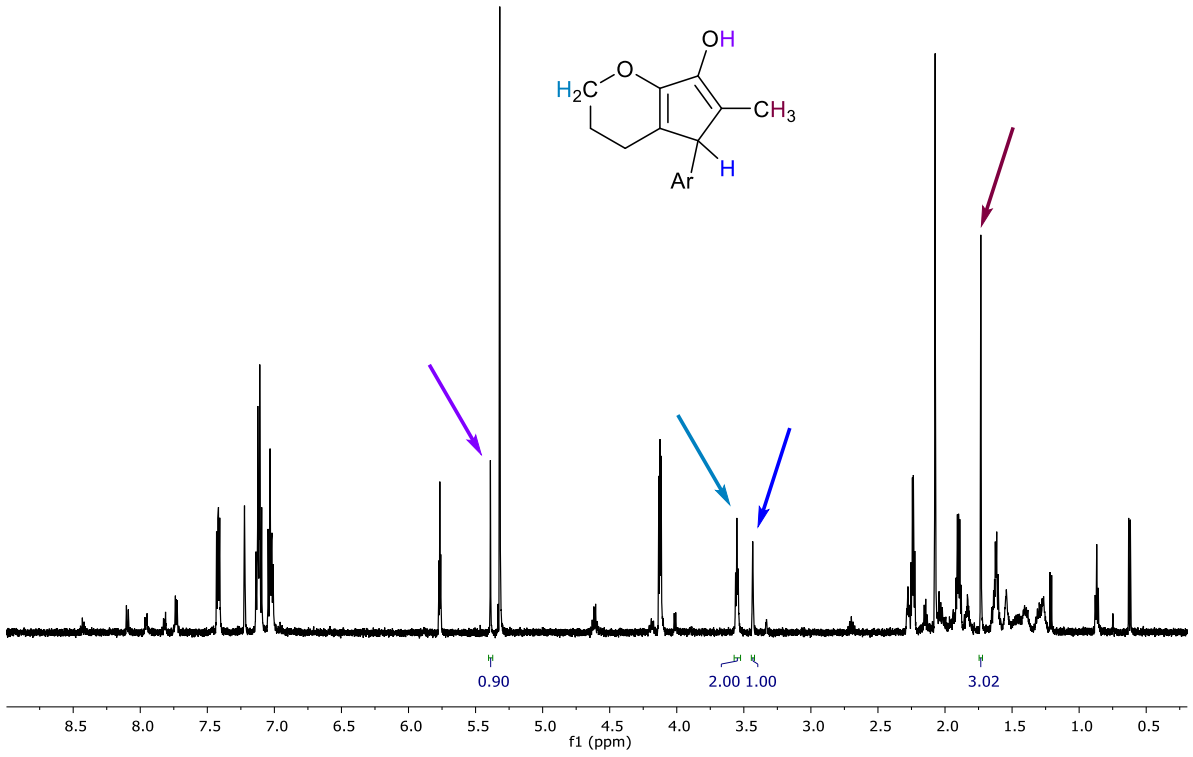


*Figure 22: ^{1}H-NMR Spectrum (600 MHz, CD_2Cl_2) of the Nazarov reaction (c_0(**1**) = 15.4 mM) with **syn-9/OTf** (5 mol-%) after 4 h.*

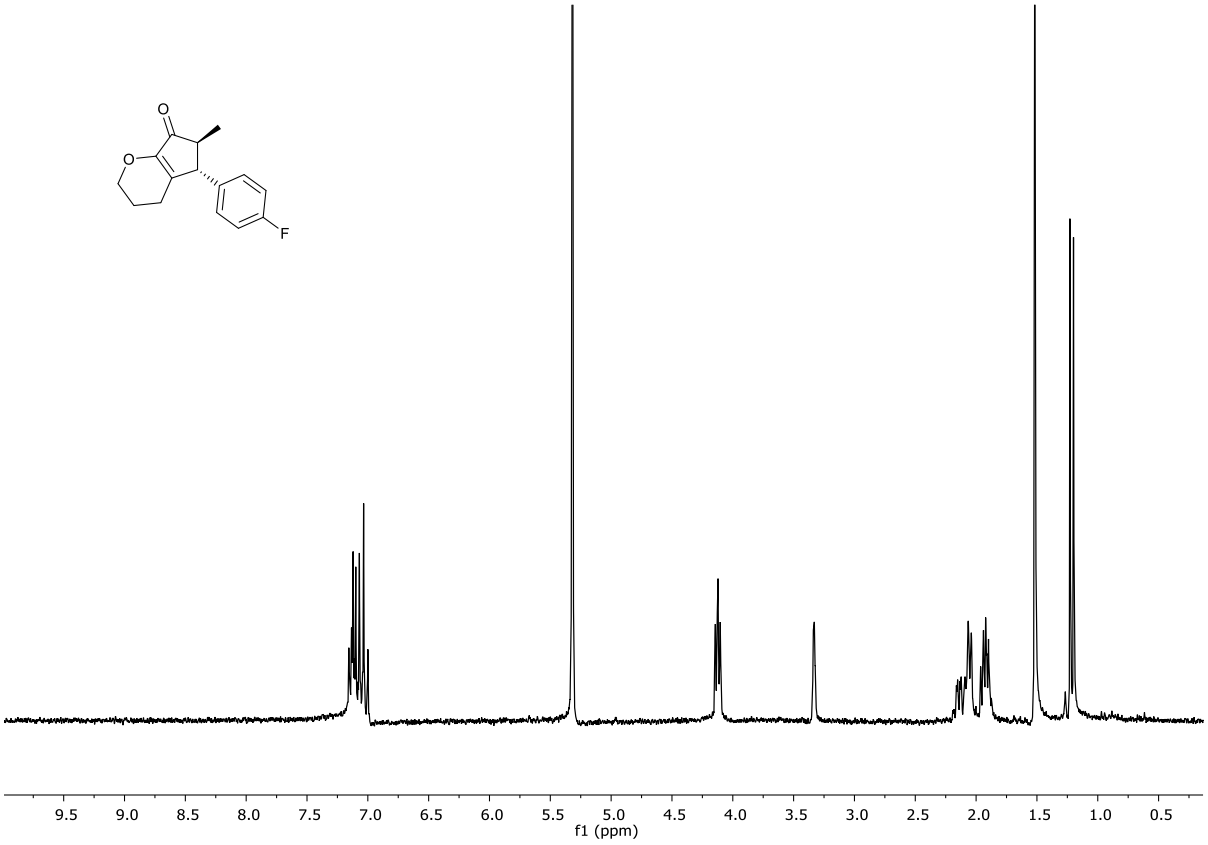


*Figure 23: ^{1}H NMR (250 MHz, CD_2Cl_2) of **trans-2**.*

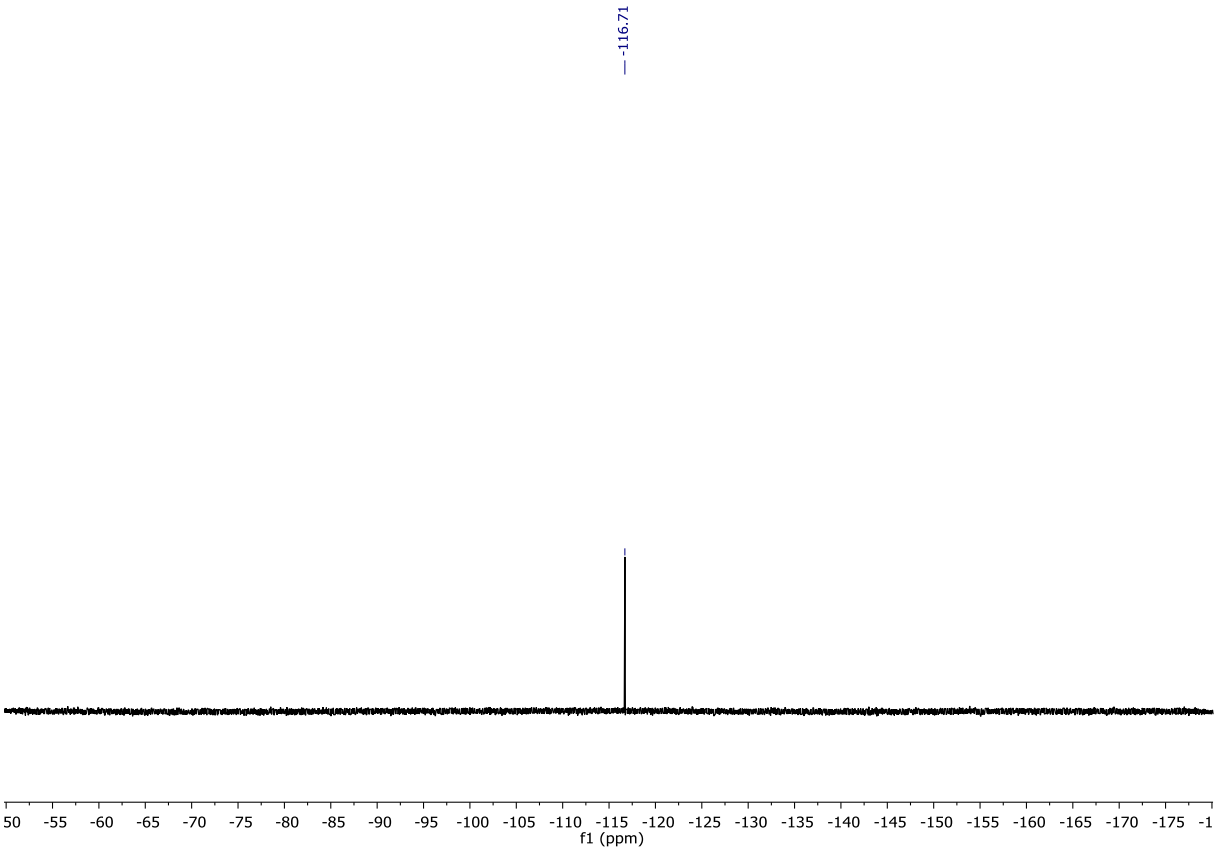


*Figure 24: ^{19}F NMR (235 MHz, CD_2Cl_2) of **trans-2**.*

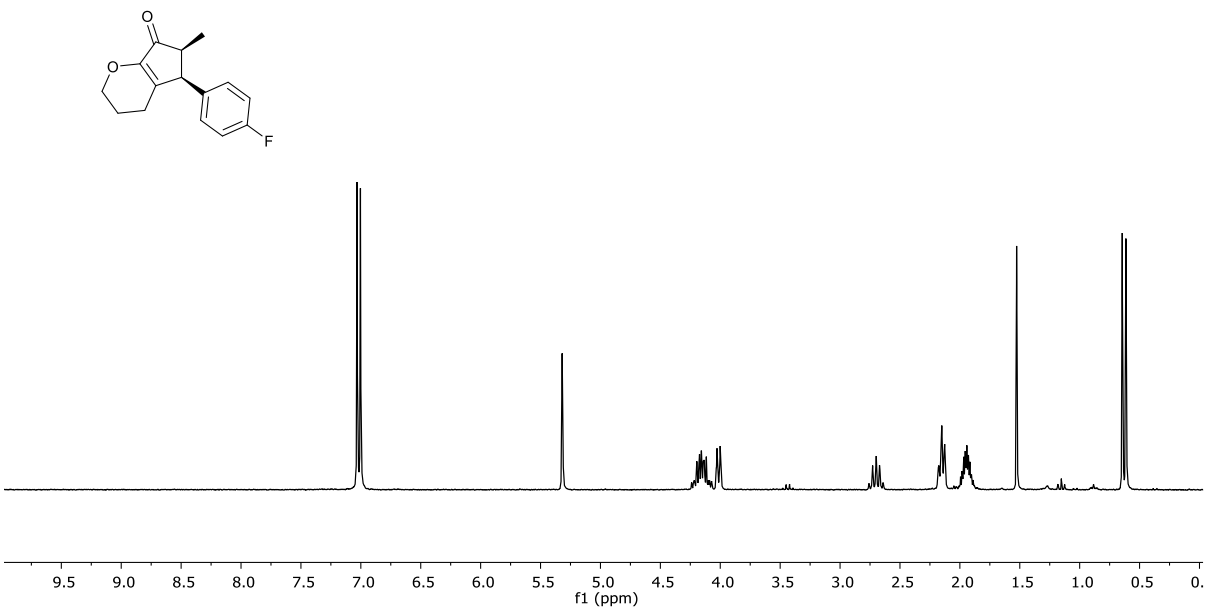


*Figure 25: ^{1}H NMR (250 MHz, CD_2Cl_2) of **cis-2**.*

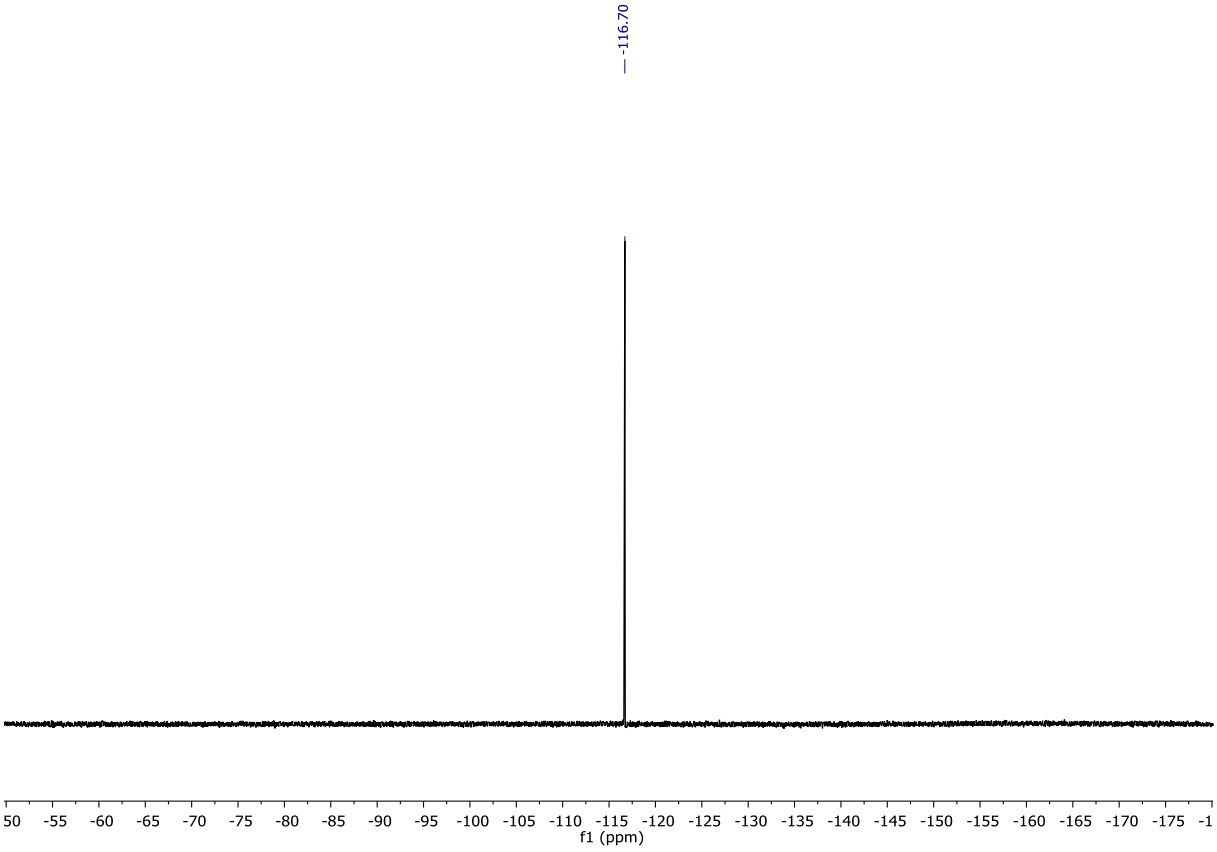


*Figure 26: ^{19}F NMR (235 MHz, CD_2Cl_2) of **cis-2**.*