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Access to isoindole-derived BODIPYs by an aminopalladation cascade

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1. General Experimental

All solvents were distilled before use and stored over molecular sieves unless otherwise stated. Air- and moisture-sensitive reactions were carried out in oven-dried or flame-dried glassware, septum-capped under atmospheric pressure of argon. Commercially available compounds were used without further purification unless otherwise stated. For all purifications by column chromatography on silica gel silica gel Geduran Si 60 (40-63 µm pore size) from Merck, or Silica 60 (40-63 µm pore size) from Macherey-Nagel was used. Reactions were heated in an aluminium heating block with silicon oil in the vial slots.

Proton (^{1}H), carbon (^{13}C), fluorine (^{19}F), and boron (^{11}B) NMR spectra were recorded on a Bruker AVIII300, Bruker AVIII400, Bruker AVIIIHD500, Bruker DRX500, or Bruker AVII600 instrument using the residual signals from $CHCl_3$, δ = 7.26 ppm and δ = 77.16 ppm as internal reference for ^{1}H and ^{13}C chemical shifts, respectively. Additionally, tetramethylsilane (TMS; δ= 0.00 ppm; 0.03%) was added to NMR samples. The following abbreviations were used for ^{1}H, ^{13}C, ^{19}F, and ^{11}B NMR chemical shifts: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. The chemical shift δ is given in ppm. ESI-HRMS was carried out on an Exactive (Thermo Scientific) Orbitrap instrument. IR spectra were recorded on a thin film spectrometer Tensor 27 from Bruker, or on an FT-IR Paragon 1000 from Perkin Elmer as thin films. Melting points of solid products were recorded on a Schorpp MPM-HV2, or on a Büchi SMP-20 melting point meter. Exact reaction conditions are given in the following procedures. UV-vis and fluorescence spectra were measured on a Varian Cary 100 Bio photometer with temperature control or a Shimadzu UV-1900i and a Varian Cary Eclipse fluorescence spectrophotometer or a Jasco FP-8300, respectively. Fluorescence excitation spectra were measured but are not shown. The spectra were shown to be comparable to the UV-vis spectra of the corresponding compound. No significant discrepancy was observed. Absolute fluorescence quantum yields were determined using a spectrofluorometer (Edinburgh Instruments, FS5) with an integrating sphere.

2. Spectroscopic data

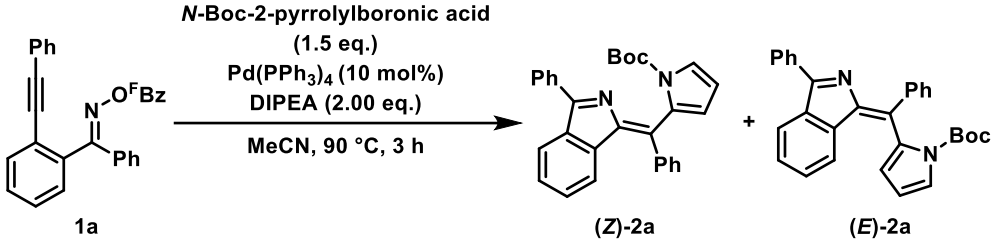
Table S1. Spectroscopic data at room temperature of a selection of prepared compounds in dichloromethane.[a]

	λ^A_{max} [nm]	λ^F_{max} [nm]	ε [10^3 M^{-1} cm^{-1}]	$\Delta\tilde{\nu}$ [cm^{-1}]	φ_F(RT)
5a	540	571	50.3	1005	0.03
5b	517	542	38.1	892	0.04
5e	547	599	42.7	1587	0.01
5f	519	545	35.4	919	0.04
6a	582	617	21.7	975	0.61
6e	564	602	13.9	1119	0.59
6f	544	574	24.1	961	0.84
5k	459	530	15.8	2919	< 0.01
5l	434	507	16.2	3318	< 0.01

[a] All measurements were performed in CH_2Cl_2. λ^A = absorption wavelength, λ^F = fluorescence wavelength.

3. Deviation tables

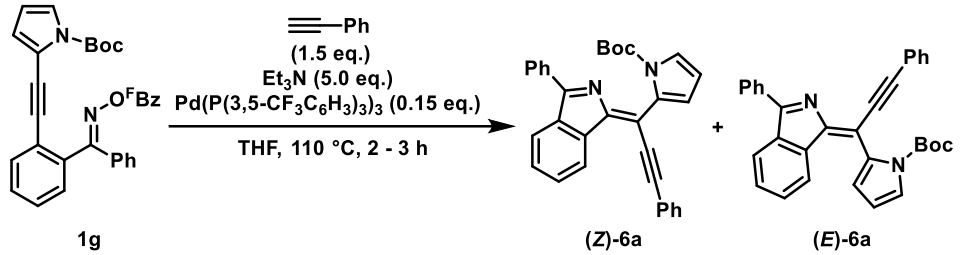
Table S2. Deviation table for the aminopalladation cascade terminated by Suzuki-Miyaura cross-coupling



Entry	Variation	Yield[a] [%]
1	None	56
2	DMF instead of MeCN	27
3	1,4-Dioxane instead of MeCN	7
4	PhMe instead of MeCN	5
5	CsF instead of DIPEA	17
6	Cs_2CO_3 instead of DIPEA	32
7	$Pd(P(3,5\text{-}(CF_3)_2C_6H_3)_3)_3$ instead of $Pd(PPh_3)_4$	32
8	NEt_3 instead of DIPEA	43
9	Additional JohnPhos (0.25 eq.)	24
10	Additional SPhos (0.25 eq.)	38
11	Additional dppe (0.25 eq.)	n.r.
12	boronic acid (3.00 eq.)	56[b]

[a] Yields refer to GC-FID yields and are the combined yields of the (*E*)- and (*Z*)-isomer. [b] Reaction time: 1 h

Table S3. Deviation table for the aminopalladation cascade terminated by Sonogashira cross-coupling



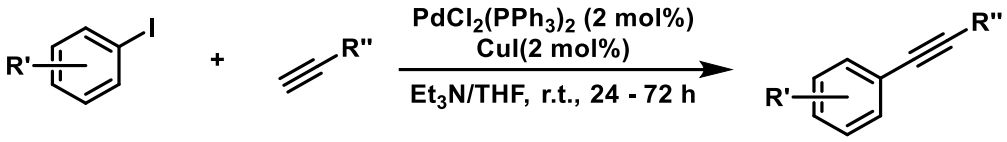
1g (*Z*)-6a (*E*)-6a

Entry	Variation	Yield[a] [%]
1	None	40%
2	with CuI	36%
3	$Pd(PPh_3)_4$ as catalyst	30%
4	$Pd(OAc)_2$ + PCy_3 as catalyst	11%
5	$Pd(OAC)_2$ + $P(C_6F_5)_3$ as catalyst	8%
6	Cs_2CO_3 instead of Et_3N	25%
7	Et_2NH instead of Et_3N	23%
8	DIPEA instead of Et_3N	22%
9	1,4-Dioxane instead of THF	33%
10	MeCN instead of THF	27%
11	DMF instead of THF	25%

[a] Yields refer to NMR yields and are the combined yields of the (*E*)- and (*Z*)-isomer.

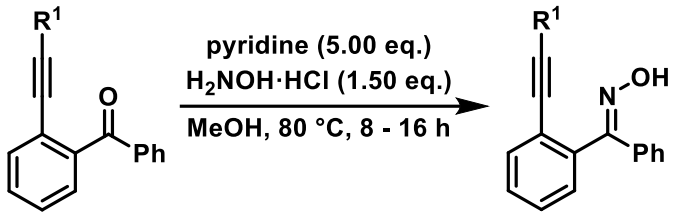
4. General Procedures

GP1: *Sonogashira* Reaction



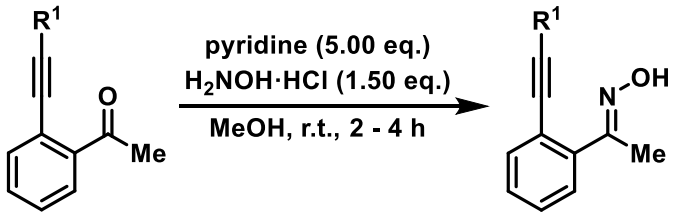
In a flame-dried round bottom flask, $PdCl_2(PPh_3)_2$ (2 mol%) and CuI (2 mol%) were dissolved in a dry and degassed mixture of Et_3N/THF (1:1, 4 mL/mmol). Then the aryl iodide (1.0 eq.) and the alkyne (1.1 – 2.0 eq.) were added at room temperature. The reaction was stirred at r.t. for 24 h – 72 h. After full conversion, the reaction was quenched by the addition of sat. aq. NH_4Cl-solution. The aqueous phase was extracted with EtOAc and the organic phase washed with brine and dried over Na_2SO_4. The solvent was then removed *in vacuo*.

GP2: Oxime formation of benzophenone derivatives[1]



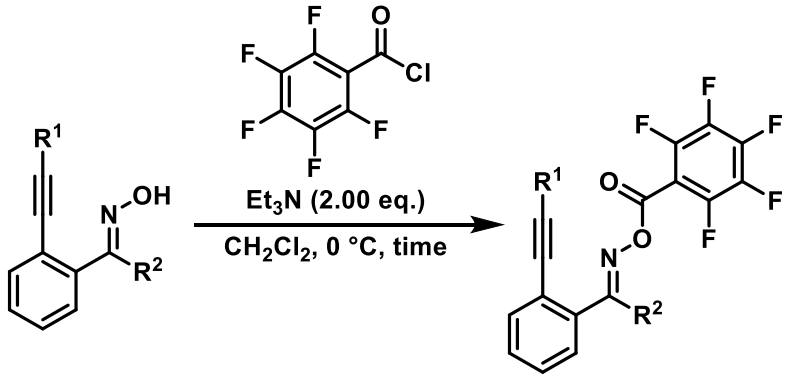
The ketone was dissolved in MeOH (10 mL/mmol). Then pyridine (5.00 eq.) and hydroxylamine hydrochloride (1.50 eq.) were added and the reaction was stirred at 80 °C for 8 – 16 h. The reaction was quenched by the addition of H_2O. The aqueous phase was extracted with EtOAc. The organic phase was washed with H_2O and brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*.

GP3: Oxime formation of acetophenone derivatives[2]



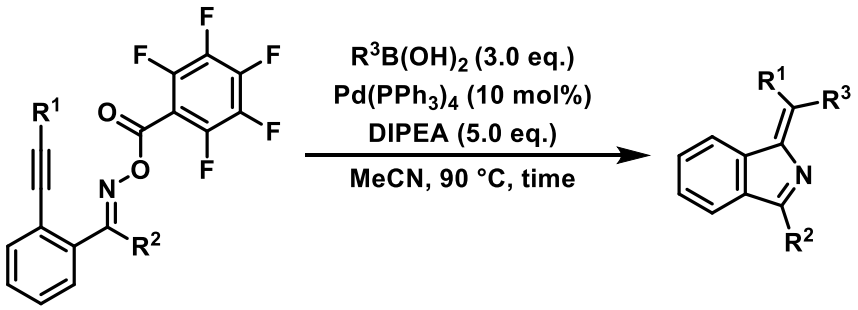
The ketone was dissolved in MeOH (10 mL/mmol). Then pyridine (5.00 eq.) and hydroxylamine hydrochloride (1.50 eq.) were added and the reaction was stirred at r.t. for 2 – 4 h. The reaction was quenched by the addition of H_2O. The aqueous phase was extracted with EtOAc. The organic phase was washed with H_2O and brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*.

GP4: Esterification of the oxime[3]



The oxime was dissolved in dry CH_2Cl_2 (3 mL/mmol) and cooled to 0 °C. After the addition of Et_3N (2.00 eq.), 2,3,4,5,6-pentafluorobenzoyl chloride (1.30 eq.) was added dropwise to the mixture. After full conversion of the starting material, the reaction was quenched by the addition of H_2O. The aqueous phase was extracted with CH_2Cl_2. The organic phase was washed with H_2O, dried over Na_2SO_4, filtered and concentrated *in vacuo.* If not stated otherwise, the residue was purified by flash column chromatography on silica gel.

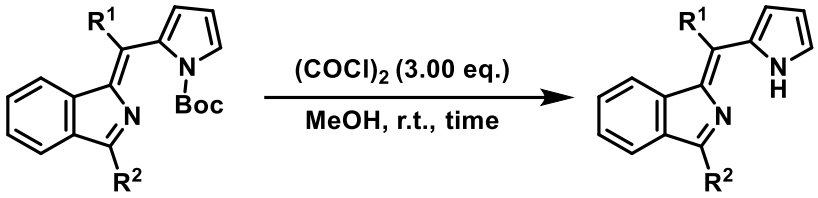
GP5: *syn*-Aza-*Suzuki-Miyaura* Cascade



Precursor **1** (1.0 eq.), a boronic acid (3.0 eq.) and $Pd(PPh_3)_4$ (10mol%) were dissolved in MeCN (0.025 M) in a sealed microwave vial under an argon atmosphere. DIPEA (5.0 eq.) was added and the reaction stirred at 90 °C for the indicated time. After cooling down to r.t. the reaction was quenched with sat. aq. NH_4Cl-solution. The aqueous phase was extracted with EtOAc. The organic phase was washed with H_2O and brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*.

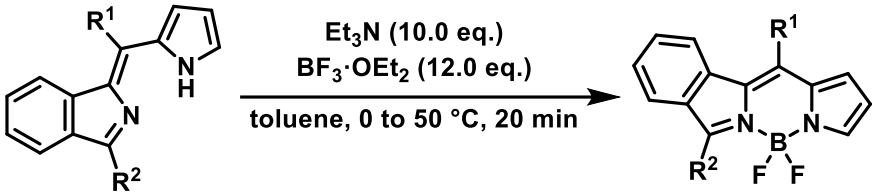
Note:
No microwave was employed. Microwave vials were used, since they can be used as pressurized vessels and therefore allow reaction temperatures over the boiling point of the solvent.

GP6: Boc deprotection



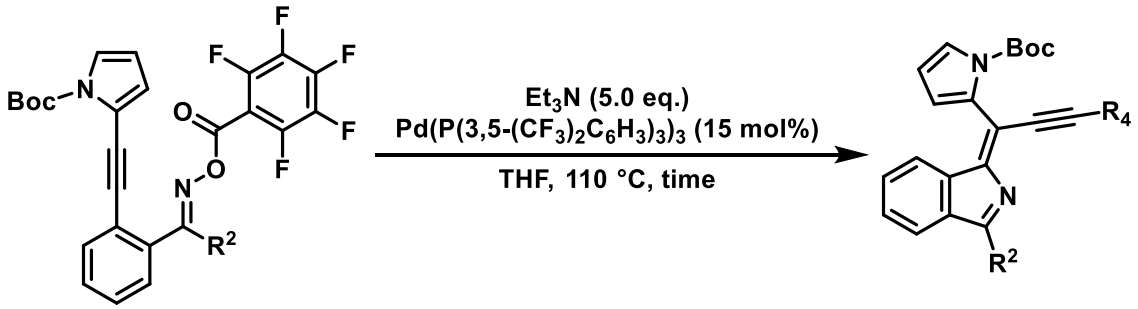
According to a literature procedure, the *N*-Boc protected dipyrromethene was dissolved in dry MeOH (6 mL/mmol).[4] After the addition of oxalyl chloride (3.00 eq.) at r.t. the reaction was stirred for the indicated time. The reaction was quenched by the addition of H_2O and the aqueous phase extracted with EtOAc. The organic phase was washed with H_2O and brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*.

GP7: Formation of the BODIPY



The crude product of the deprotection step, was dissolved in dry toluene (10 mL/mmol) and cooled to 0 °C. Et_3N (10.0 eq.) was added and the reaction mixture stirred for 5 minutes at the same temperature. Then $BF_3{\cdot}OEt_2$ (12.0 eq., 48%) was slowly added. The reaction was stirred at 50 °C for the indicated time. After completion, the reaction was quenched by the addition of H_2O. The aqueous phase was extracted with CH_2Cl_2 (3 x 50 mL). The organic phase was washed with H_2O, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel.

GP8: *syn*-Aza-*Sonogashira* Cascade

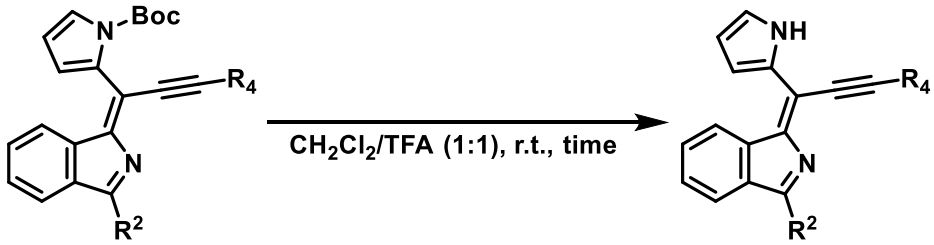


Precursor **1g** or **1h** (1.0 eq.), the alkyne (1.5 eq.) and $Pd(P(3,5\text{-}(CF_3)_2C_6H_3)_3)_3$ (15 mol%) were dissolved in dry THF (0.013 M) in a sealed microwave vial under an argon atmosphere. Et_3N

(5.0 eq.) was added and stirred at 110 °C for the indicated time. After cooling down to r.t. the reaction was quenched with sat. aq. NH_4Cl-solution. The aqueous phase was extracted with EtOAc. The organic phase was washed with H_2O and brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*.

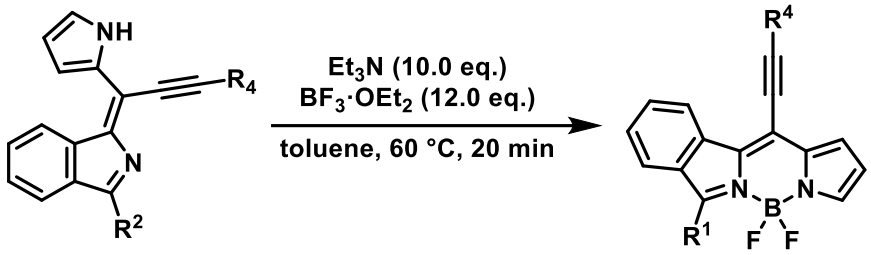
Note:
No microwave was employed. Microwave vials were used, since they can be used as pressurized vessels and therefore allow reaction temperatures over the boiling point of the solvent.

GP9: *N*-Boc deprotection with TFA



The starting material (1.0 eq.) was dissolved in a mixture of CH_2Cl_2/TFA (1:1, 0.05 M) and stirred at r.t. until full conversion of the starting material. Then the reaction was quenched at 0 °C with sat. aq. $NaHCO_3$ solution. The aqueous phase was extracted with CH_2Cl_2. The organic phase was washed with sat. aq. $NaHCO_3$ solution, water and brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*.

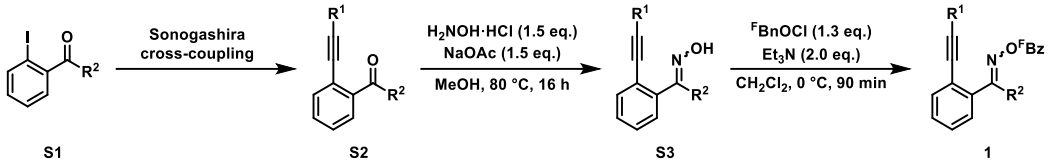
GP10: BODIPY formation (for *meso*-alkynyl BODIPYs)



The crude product of the deprotection step, was dissolved in dry toluene (10 mL/mmol) and cooled to 0 °C. Et_3N (10.0 eq.) was added and the reaction mixture stirred for 5 minutes at the same temperature. Then $BF_3{\cdot}OEt_2$ (12.00 eq., 48%) was slowly added. The reaction was stirred at 60 °C for the indicated time. After completion, the reaction was quenched by the addition of H_2O. The aqueous phase was extracted with CH_2Cl_2. The organic phase was washed with H_2O, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel.

5. Starting Material Synthesis

5.1. Overview



***Scheme 1**. Synthetic route to the starting material for the aminopalladation cascade*

To prepare precursor **1**, we started from ketone **S1** and performed a Sonogashira cross-coupling reaction. The product **S2** was reacted with hydroxylamine hydrochloride under basic conditions to form the oxime **S3** which was further reacted with pentafluorobenzoyl chloride to get the desired precursor **1 (**Scheme **1)**. The compounds and their synthesis were either literature known[1,5] or are given in the following chapters (Figure **1**).

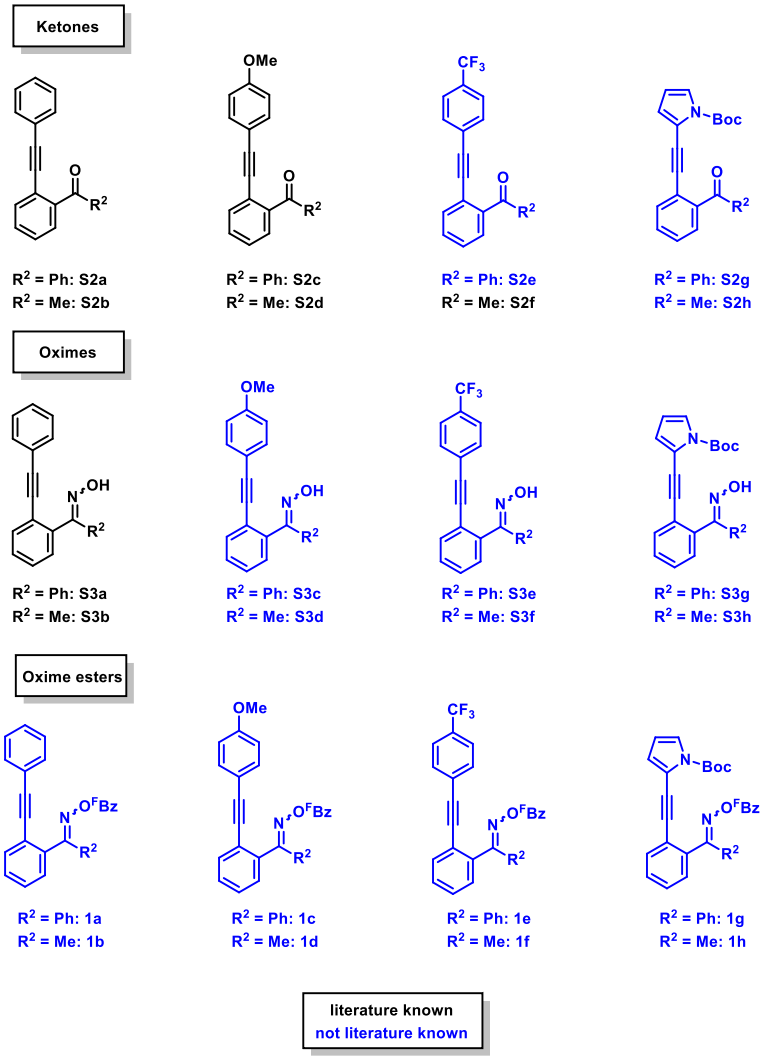
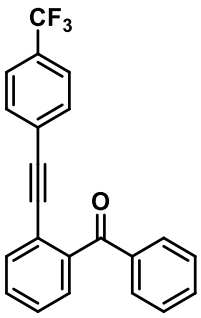


***Figure 1.** Overview over all synthesized compounds for the precursor synthesizes.*

5.2. Ketone Precursors

Phenyl(2-((4-(trifluoromethyl)phenyl)ethynyl)phenyl)methanone (S2e)



2-Iodobenzophenone (1.55 g, 5.03 mmol, 1.00 eq.) and 1-ethynyl-4-(trifluoromethyl)benzene (0.74 mL, 5.26 mmol, 1.10 eq.) were reacted according to **GP1**. The residue was purified by flash column chromatography on silica gel (*n*-Pentane: EtOAc 50:1→25:1) to give the title compound (1.71 g, 4.87 mmol, 97%) as a beige solid.

m.p.: 79 °C.

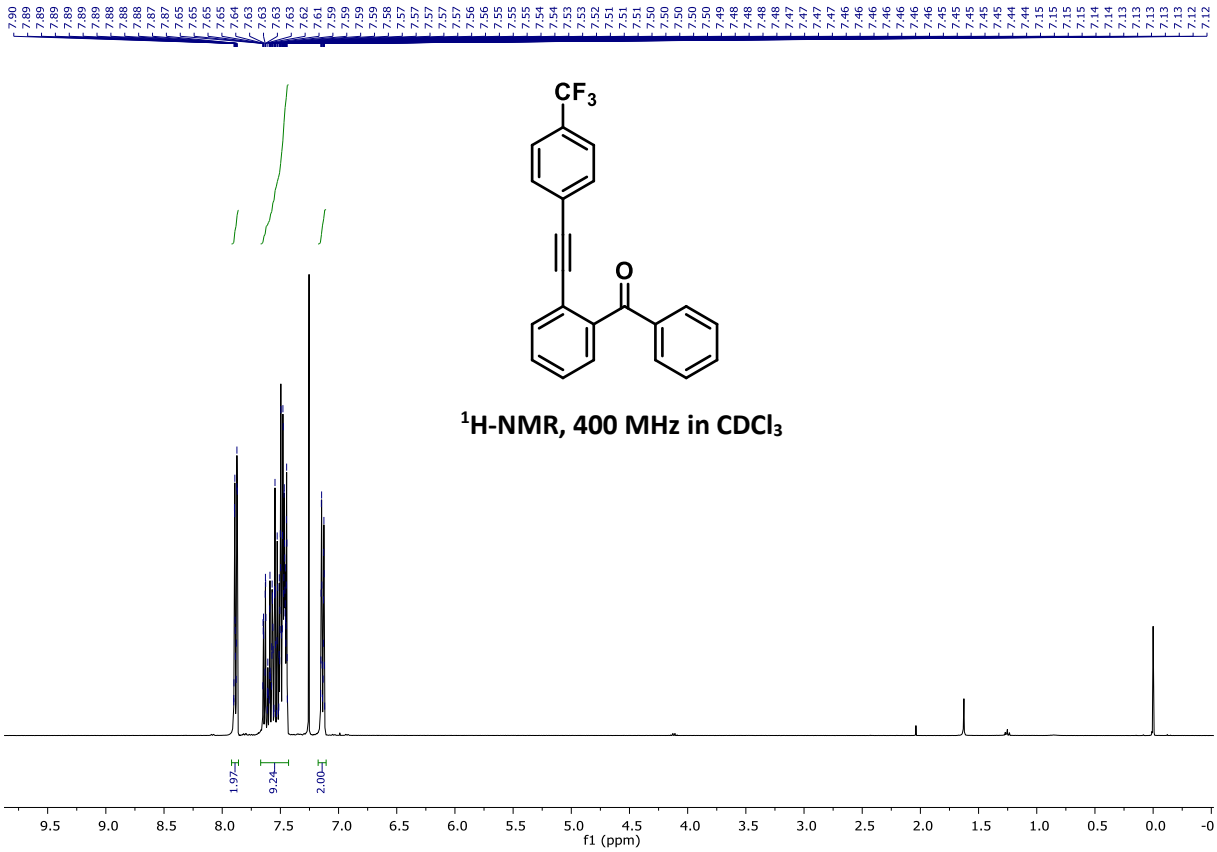
^{1}H-NMR (400 MHz, $CDCl_3$): δ = = 7.90 – 7.87 (m, 2 H), 7.66 – 7.44 (m, 9 H), 7.16 – 7.12 (m, 2 H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 196.7, 141.7, 137.3, 133.2, 132.7, 131.6, 130.4, 130.2, 130.0 (q, $^{2}J_{C\text{-}F}$ = 32.6 Hz), 128.8, 128.7, 128.4, 126.4 − 126.3 (m), 125.0 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 123.8 (q, $^{1}J_{C\text{-}F}$ = 272.2 Hz), 121.1, 93.4, 89.7.

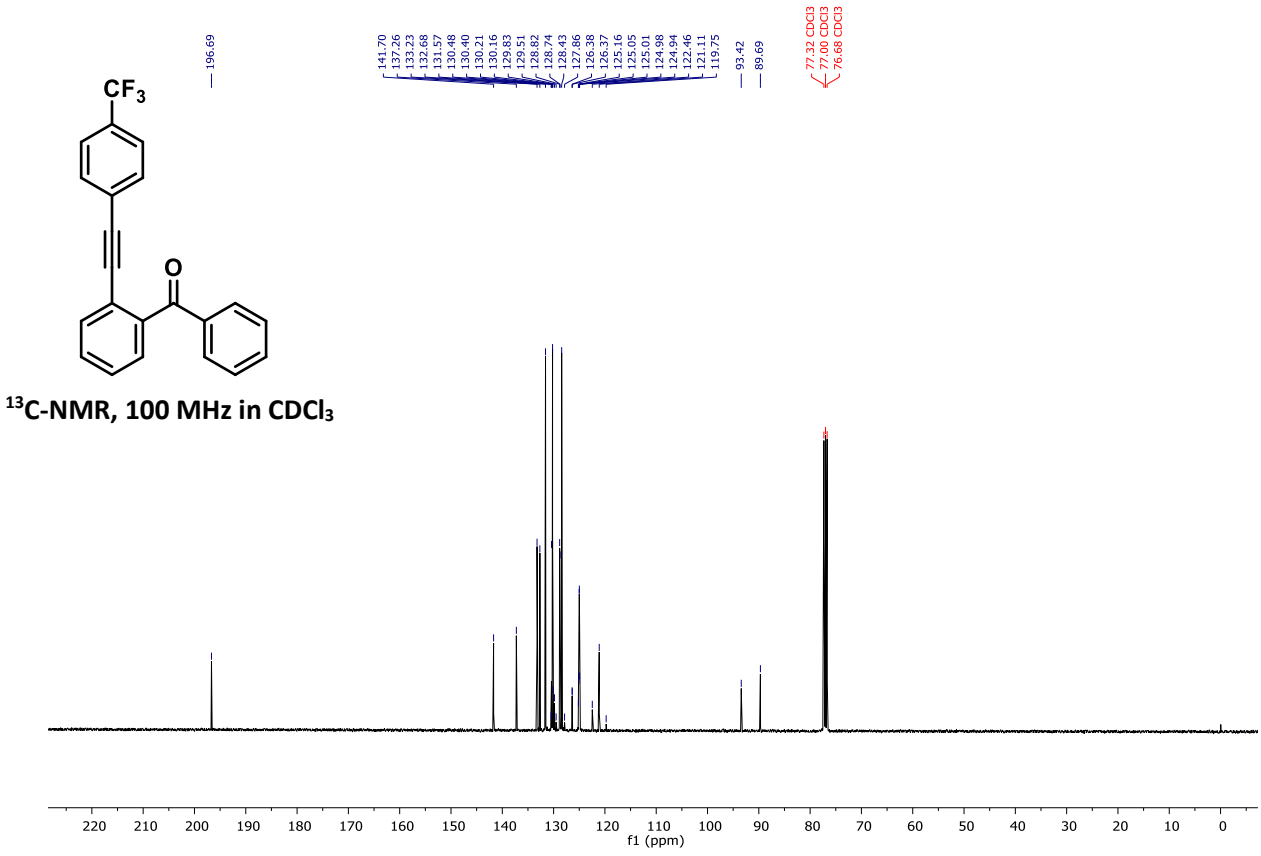
^{19}F-NMR (376 MHz, $CDCl_3$): δ = -63.29 (s).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3062, 2114, 1653, 1603, 1317, 1157, 1109, 1056.

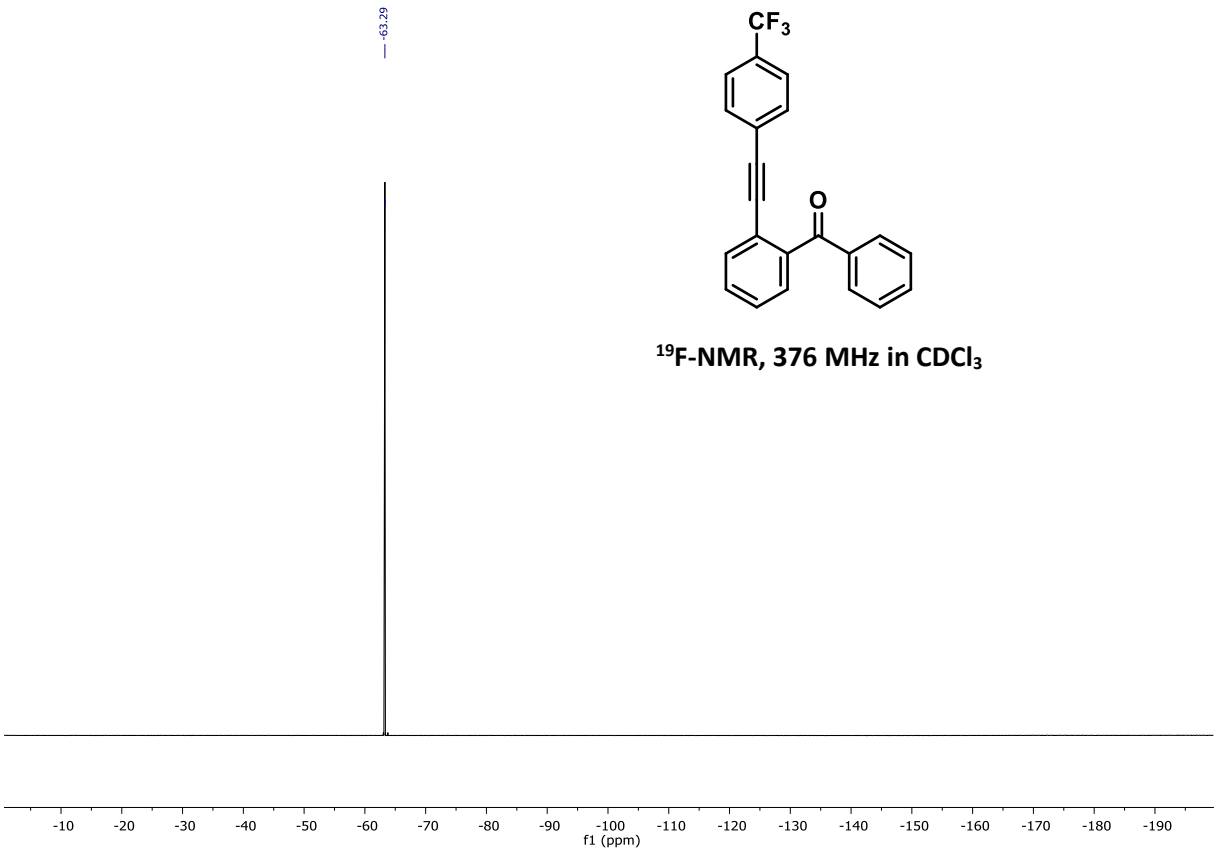
HRMS (ESI): $C_{22}H_{13}F_3O$ calcd.: 373.0816 found: 373.0811, $[M+Na]^+$.



^{1}H-NMR, 400 MHz in $CDCl_3$

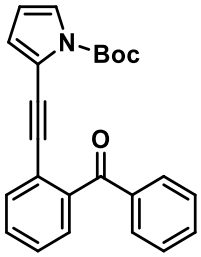


^{13}C-NMR, 100 MHz in $CDCl_3$



^{19}F-NMR, 376 MHz in $CDCl_3$

tert-Butyl 2-((2-benzoylphenyl)ethynyl)-1_H_-pyrrole-1-carboxylate (S2g)



2-Iodobenzophenone (2.15 g, 7.00 mmol, 1.00 eq.) and *tert*-butyl 2-ethynyl-1*H*-pyrrole-1-carboxylate (1.47 g, 7.70 mmol, 1.10 eq.) were reacted according to **GP1**. The residue was purified by flash column chromatography on silica gel (*n*-Pentane: EtOAc 50:1) to give the title compound (2.28 g, 6.15 mmol, 88%) as a brown solid.

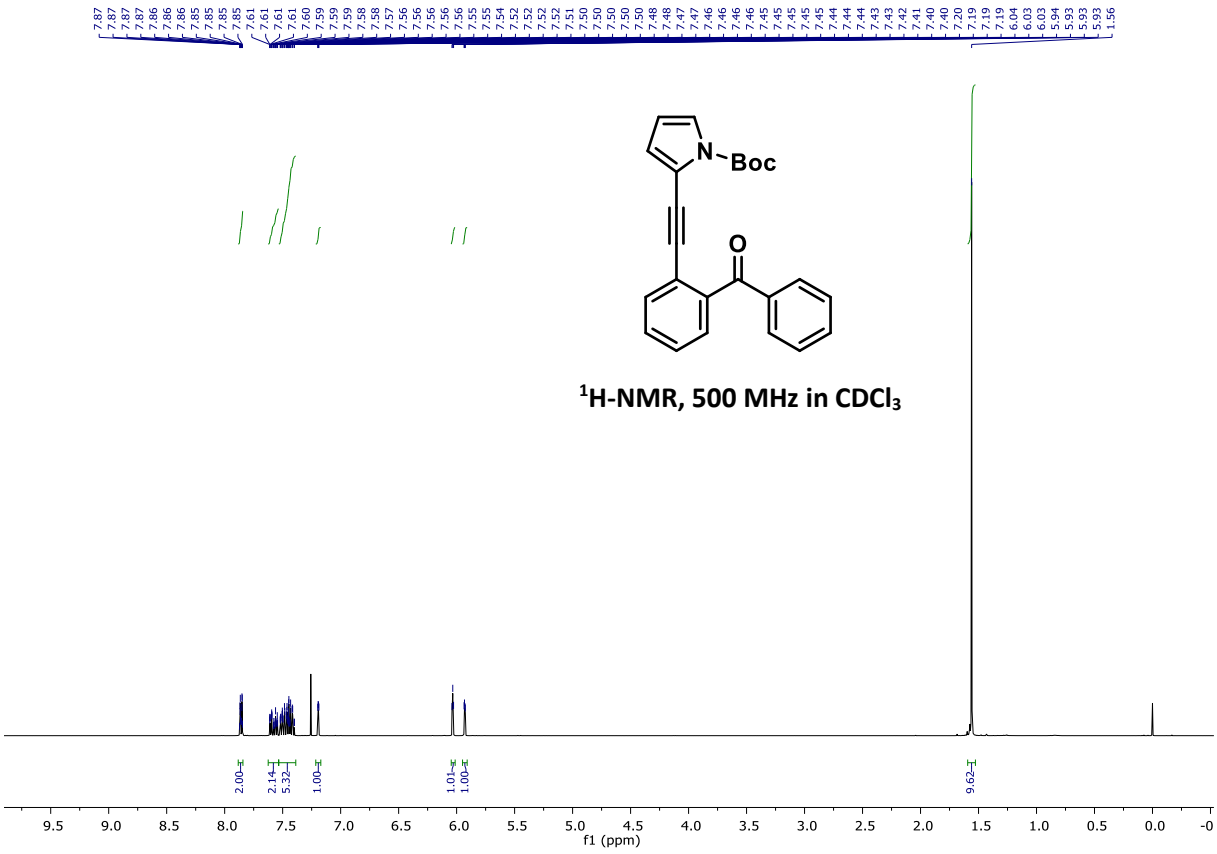
m.p.: 83 °C.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.88 – 7.84 (m, 2 H), 7.62 – 7.54 (m, 2 H), 7.53 – 7.39 (m, 5 H), 6.03 (t, *J* = 3.4 Hz, 1 H), 5.93 (dd, *J* = 3.5, 1.8 Hz, 1 H), 1.56 (s, 9 H).

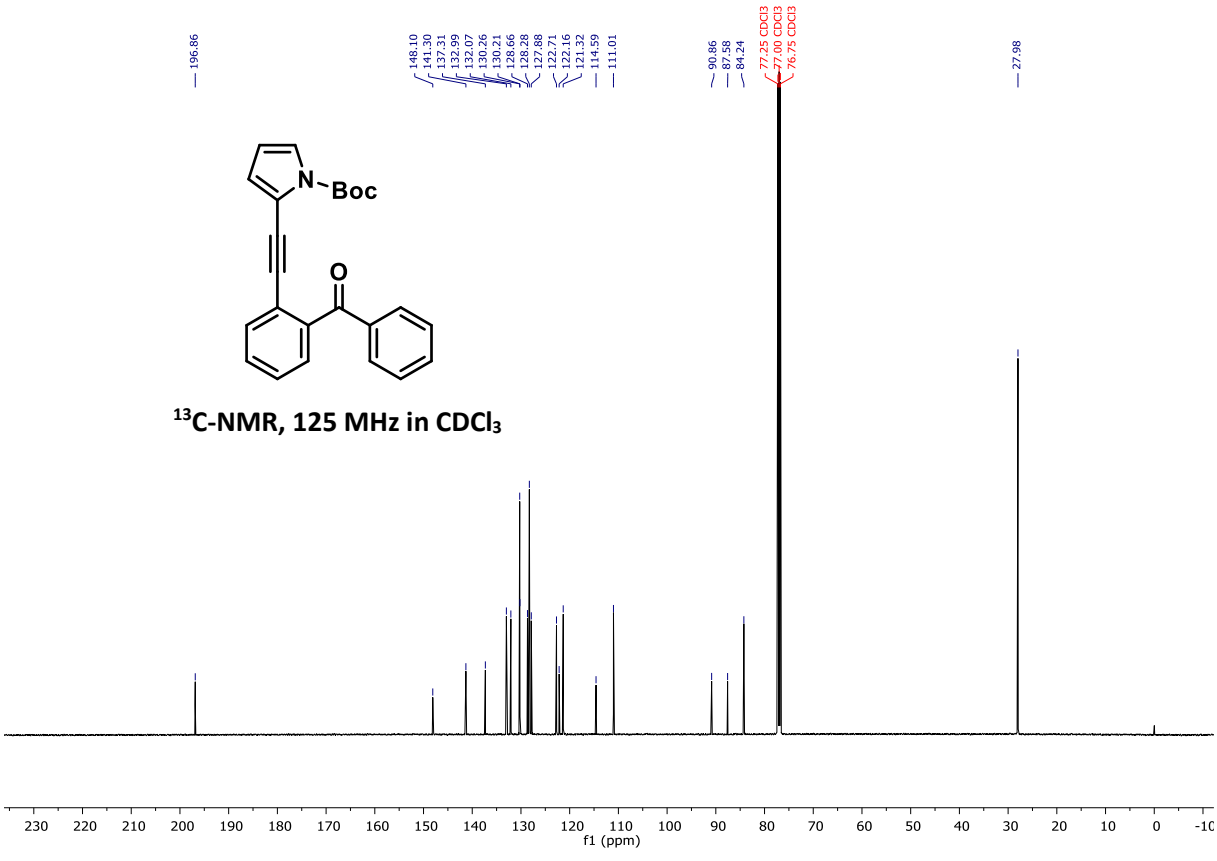
^{13}C-NMR (125 MHz, $CDCl_3$): δ = 196.9, 148.1, 141.3, 137.3, 133.0, 132.1, 130.3, 130.2, 128.7, 128.3, 127.9, 122.7, 122.2, 121.3, 114.6, 111.0, 90.9, 87.6, 84.2, 28.0.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2979, 2928, 2159, 1737, 1657, 1309, 1112.

HRMS (ESI): $C_{24}H_{21}NO_3$ calcd.: 394.1414 found: 394.1415, $[M+Na]^+$.

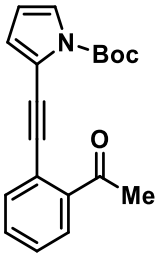


^{1}H-NMR, 500 MHz in $CDCl_3$



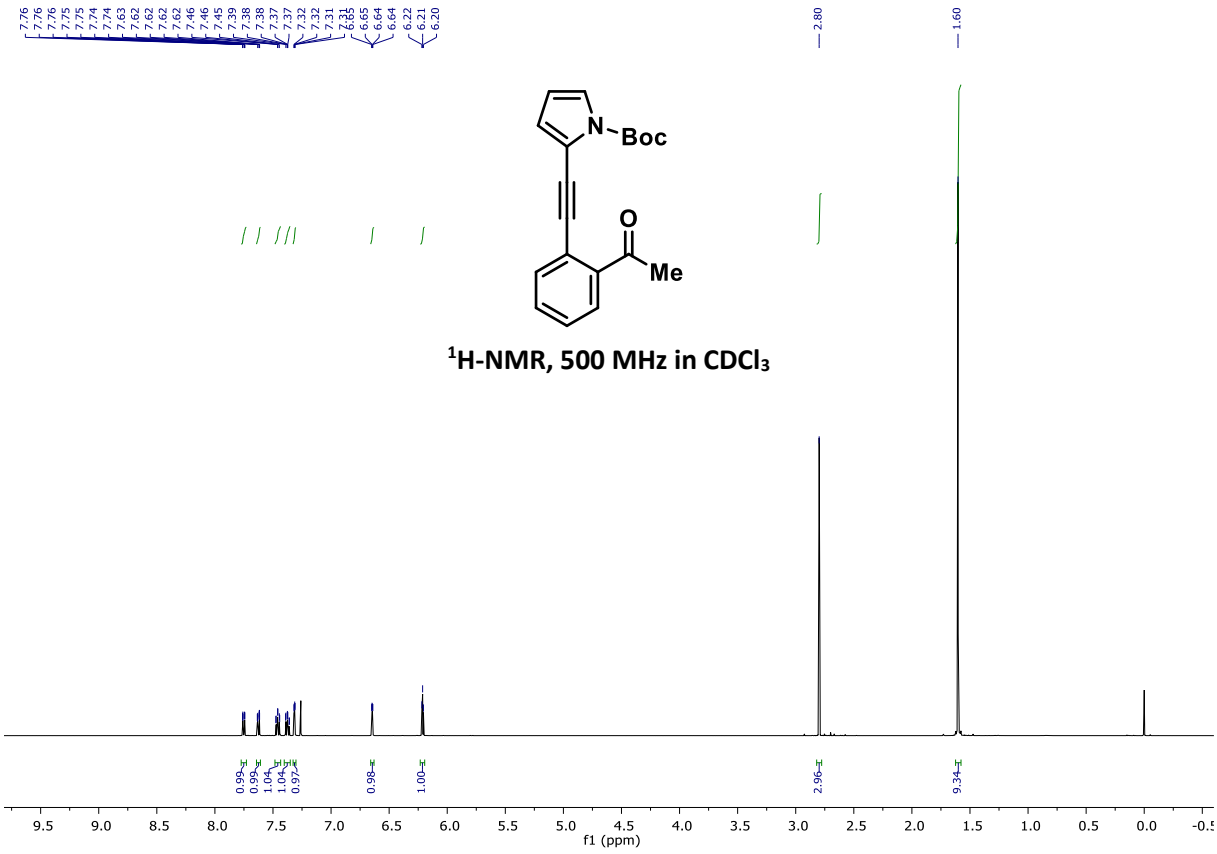
^{13}C-NMR, 125 MHz in $CDCl_3$

***tert*-Butyl 2-((2-acetylphenyl)ethynyl)-1*H*-pyrrole-1-carboxylate (S2h)**

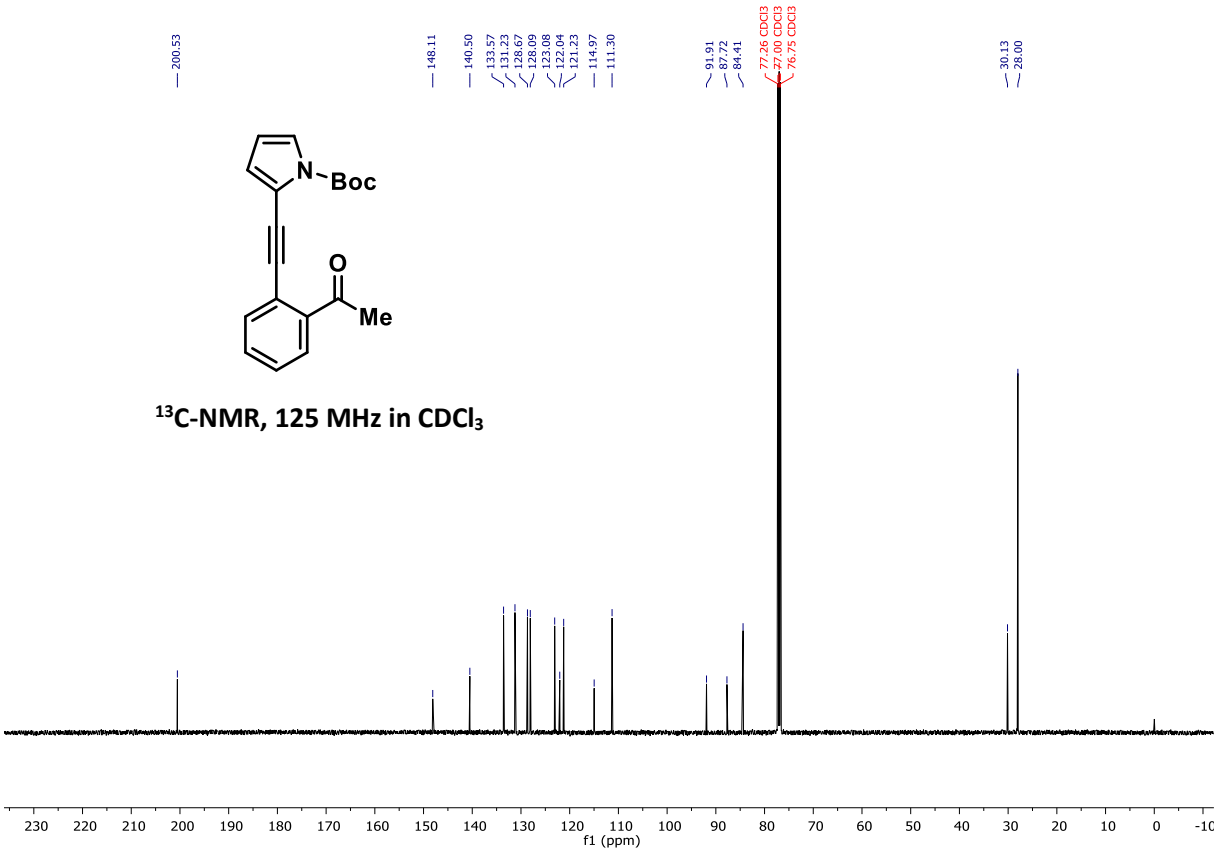


2'-Iodoacetophenone (1.23 g, 5.00 mmol, 1.00 eq.) and *tert*-butyl 2-ethynyl-1*H*-pyrrole-1-carboxylate (1.00 g, 5.25 mmol, 1.05 eq.) were reacted according to **GP1**. The residue was purified by flash column chromatography on silica gel (*n*-Petane: EtOAc 50:1) to give the title compound (1.25 g, 4.07 mmol, 81%) as a yellow oil.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.75 (ddd, *J* = 7.8, 1.4, 0.5 Hz, 1 H), 7.62 (ddd, *J* = 7.7, 1.3, 0.5 Hz, 1 H), 7.46 (td, *J* = 7.5, 1.4 Hz, 1 H), 7.37 (ddd, *J* = 7.8, 7.4, 1.3 Hz, 1 H), 7.31 (dd, *J* = 3.3, 1.7 Hz, 1 H), 6.65 (dd, *J* = 3.5, 1.7 Hz, 1 H), 6.21 (t, *J* = 3.4 Hz, 1 H), 2.80 (s, 3 H), 1.60 (s, 9 H).
^{13}C-NMR (125 MHz, $CDCl_3$): δ = 200.5, 148.1, 140.5, 133.6, 131.2, 128.7, 128.1, 123.1, 122.0, 121.2, 115.0, 111.3, 91.9, 87.7, 84.4, 30.1, 28.0.
IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2982, 2926, 2111, 1747, 1684, 1317, 1118.
HRMS (ESI): $C_{19}H_{19}NO_3$ calcd.: 332.1257 found: 332.1259, $[M+Na]^+$.



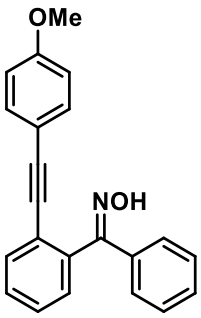
^{1}H-NMR, 500 MHz in $CDCl_3$



^{13}C-NMR, 125 MHz in $CDCl_3$

5.3. Oxime Intermediates

(*Z*)-(2-((4-Methoxyphenyl)ethynyl)phenyl)(phenyl)methanone oxime (S3c)



Ketone **S2c** (1.43 g, 4.58 mmol, 1.00 eq.) was reacted according to **GP2**. The residue was purified by flash column chromatography on silica gel (*n*-Pentane: EtOAc 10:1→ 5:1) to give the title compound as a light green solid (1.20 g, 3.66 mmol, 85%).

Sample contains 16% of the (*E*)-isomer. Analytical data is only given for the main isomer.

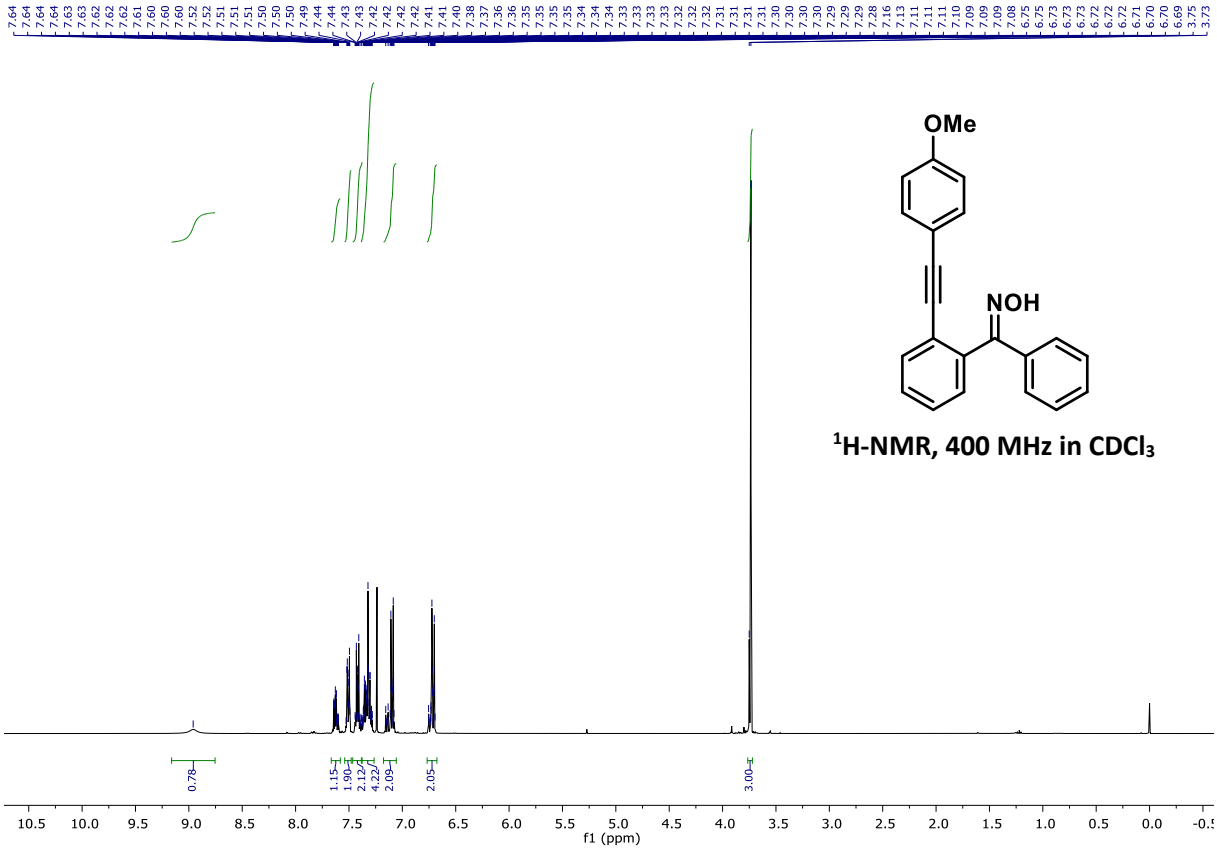
m.p.: 116 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.96 (s_{br}, 1 H), 7.69 – 7.59 (m, 1 H), 7.54 – 7.48 (m, 2 H), 7.44 – 7.39 (m, 2 H), 7.38 – 7.25 (m, 4 H), 7.16 – 7.05 (m, 2 H), 6.78 – 6.68 (m, 2 H), 3.73 (s, 3 H).

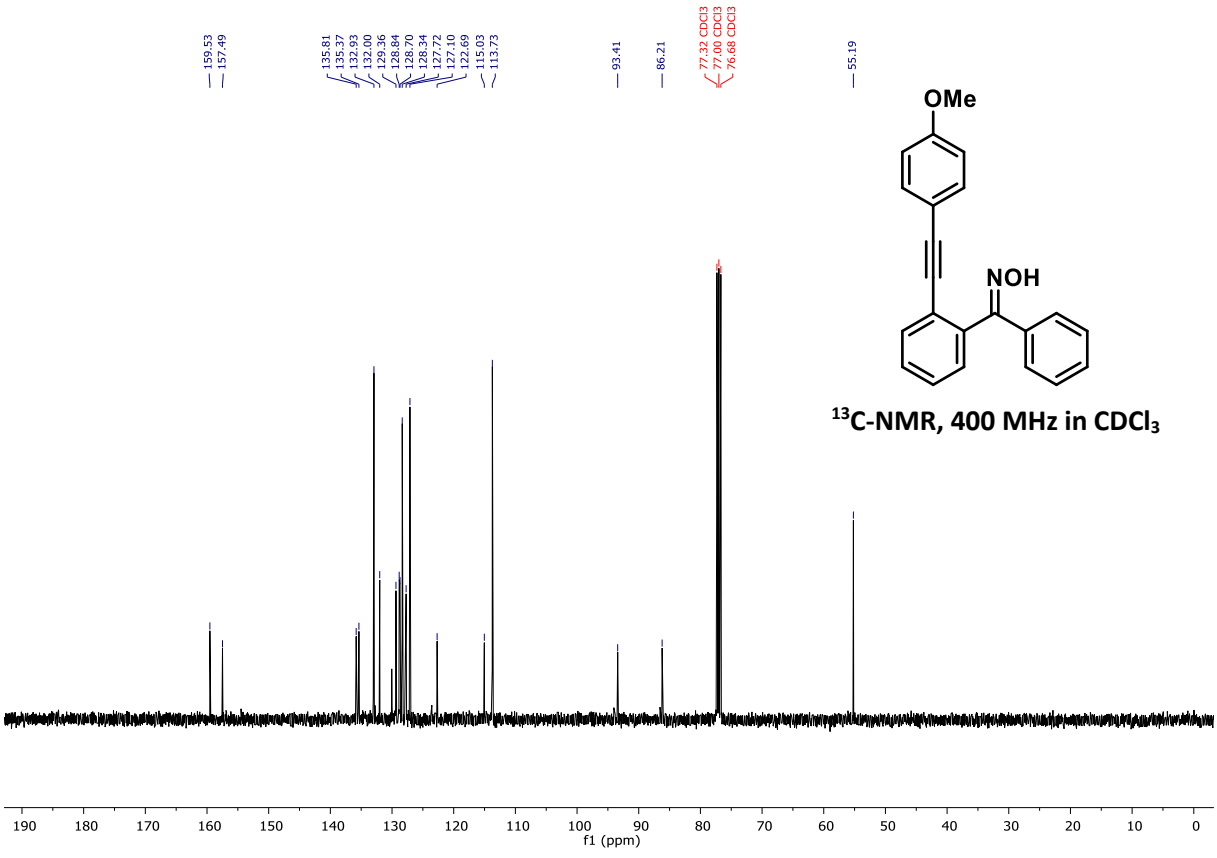
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 159.5, 157.5, 135.8, 135.4, 132.9, 132.0, 129.4, 128.8, 128.7, 128.3, 127.7, 127.1, 122.7, 115.0, 113.7, 93.4, 86.2, 55.2.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3229, 3058, 2899, 2837, 2215, 1597, 1506, 1446, 1244, 1023.

HRMS (ESI): $C_{22}H_{17}NO_2$ calcd.: 328.1332 found: 328.1333, $[M+Na]^+$.

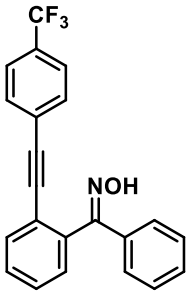


^{1}H-NMR, 400 MHz in $CDCl_3$



^{13}C-NMR, 400 MHz in $CDCl_3$

(*E*)-phenyl(2-((4-(trifluoromethyl)phenyl)ethynyl)phenyl)methanone oxime (S3e)



Ketone **S2e** (1.71 g, 4.87 mmol, 1.00 eq.) was reacted according to **GP2**. The residue was purified by flash column chromatography on silica gel (*n*-Pentane: EtOAc 20:1) to give the title compound (1.05 g, 2.89 mmol, 59%) as a blue solid.

m.p.: 131 °C, decomposition.

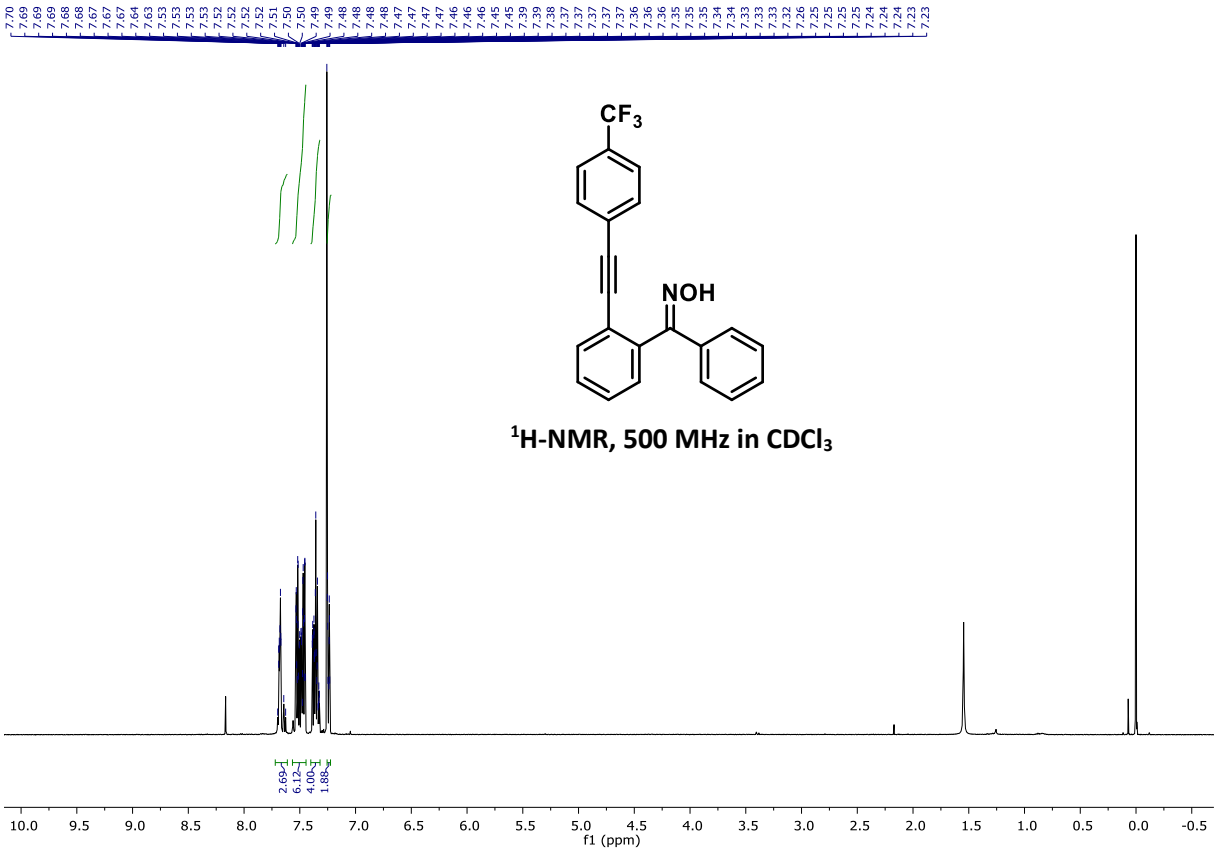
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.71 − 7.61 (m, 3 H), 7.57 − 7.44 (m, 6 H), 7.40 − 7.32 (m, 4 H), 7.26 − 7.23 (m, 2 H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 157.5, 136.3, 135.3, 132.4, 131.7, 129.9 (q, $^{2}J_{C\text{-}F}$ = 32.7 Hz), 129.6, 129.0, 128.9, 128.7, 128.4, 127.1, 126.7 (d, $^{4}J_{C\text{-}F}$ = 1.4 Hz), 125.1 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 123.9 (q, $^{1}J_{C\text{-}F}$ = 272.3 Hz), 121.6, 91.7, 89.8.

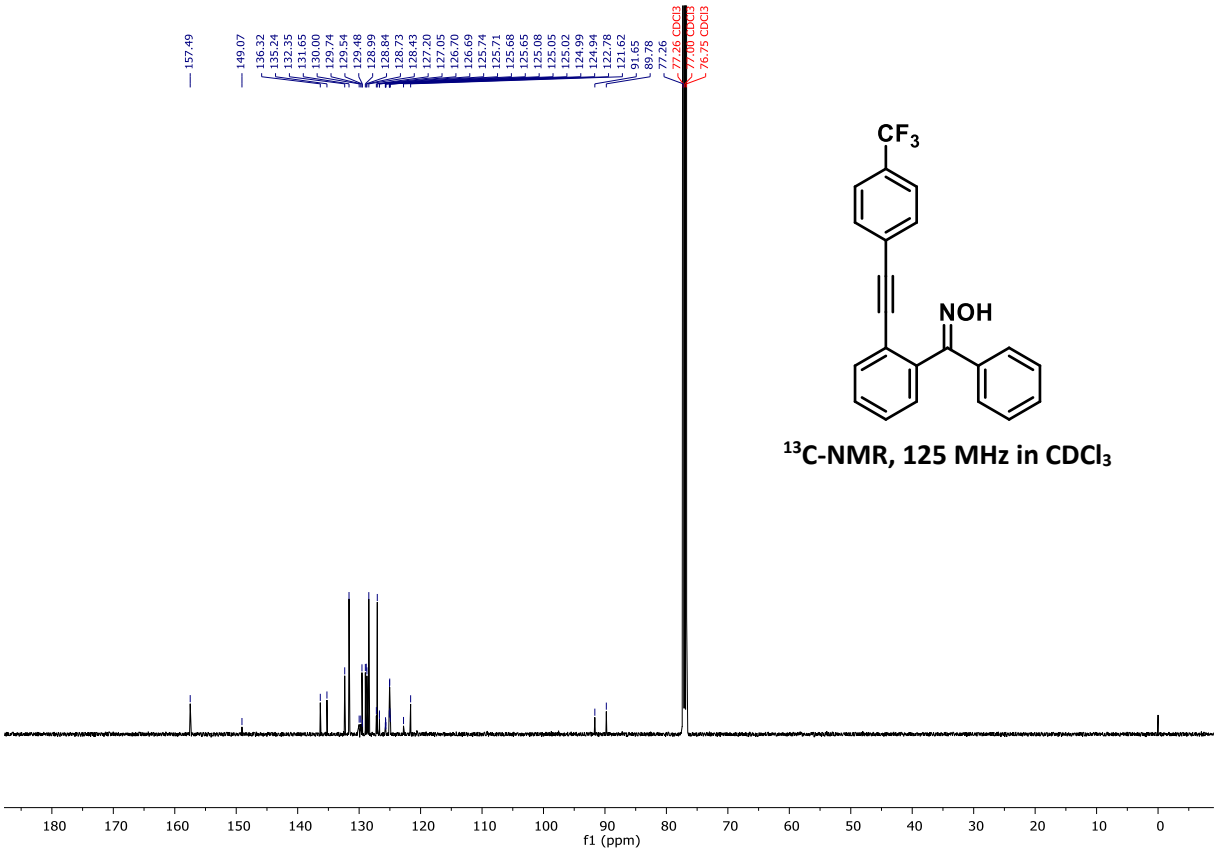
^{19}F-NMR (470 MHz, $CDCl_3$): δ = -63.32 (s).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3280, 3062, 2921, 2218, 1324, 1152, 1107, 1059, 995, 925, 837, 752, 686.

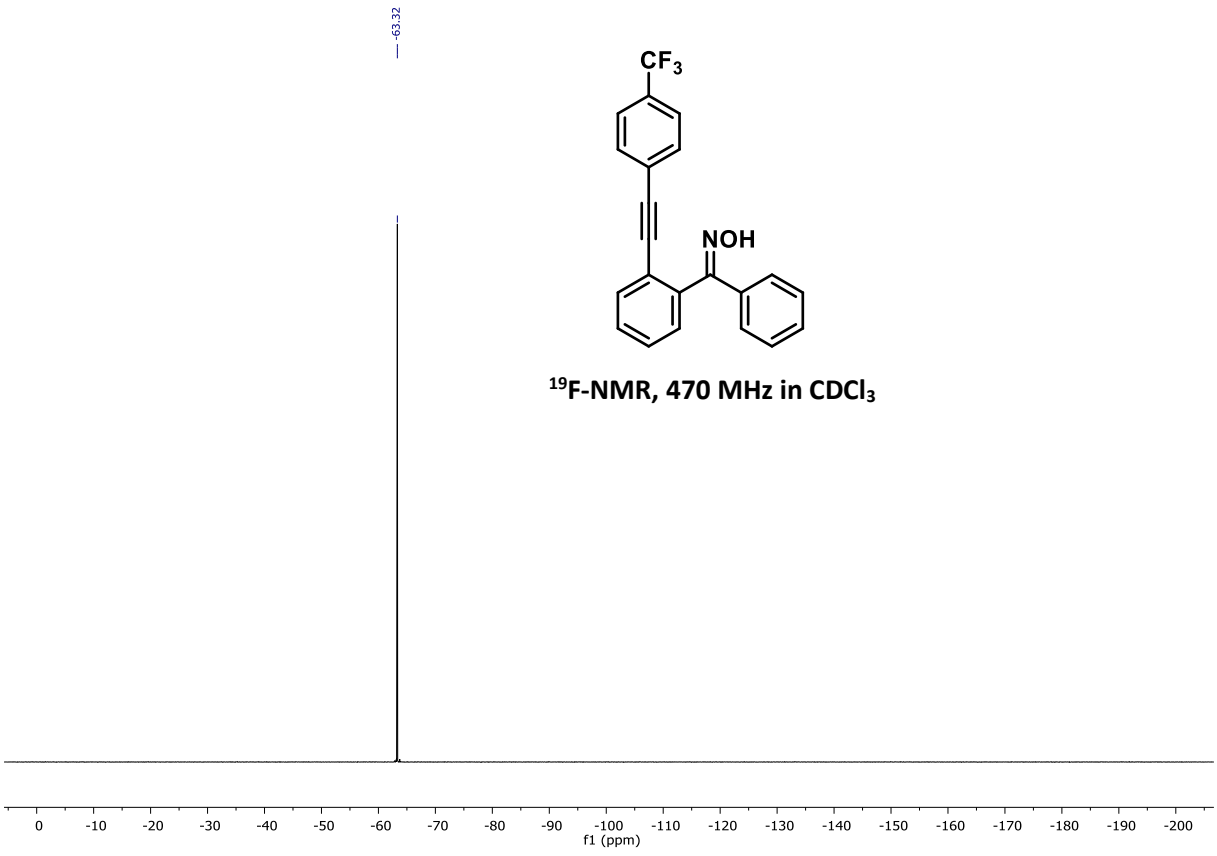
HRMS (ESI): $C_{22}H_{14}F_3NO$ calcd.: 388.0925 found: 388.0921, $[M+Na]^+$.



^{1}H-NMR, 500 MHz in $CDCl_3$

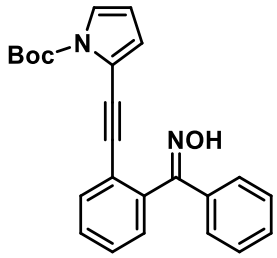


^{13}C-NMR, 125 MHz in $CDCl_3$



^{19}F-NMR, 470 MHz in $CDCl_3$

tert-Butyl (_Z_)-2-((2-((hydroxyimino)(phenyl)methyl)phenyl)ethynyl)-1_H_-pyrrole-1-carboxylate (S3g)



Ketone **S2g** (3.41 g, 9.19 mmol, 1.00 eq.) was reacted according to **GP2**. Flash column chromatography on silica gel (n-Pentane/EtOAc 10:1) afforded the desired product (2.78 g, 7.20 mmol, 72%) as a light green solid.

Note: The raction mixture slowly changes color from colorless to green within 6 h and turns blue, if heated for a longer period of time. The blue color indicates that the reaction has been heated for too long. If the reaction is blue, the product has undergone side reactions and the yield is diminished. The reaction should be terminated while being green. The leftover starting material can be recovered by column chromatography on silica gel.

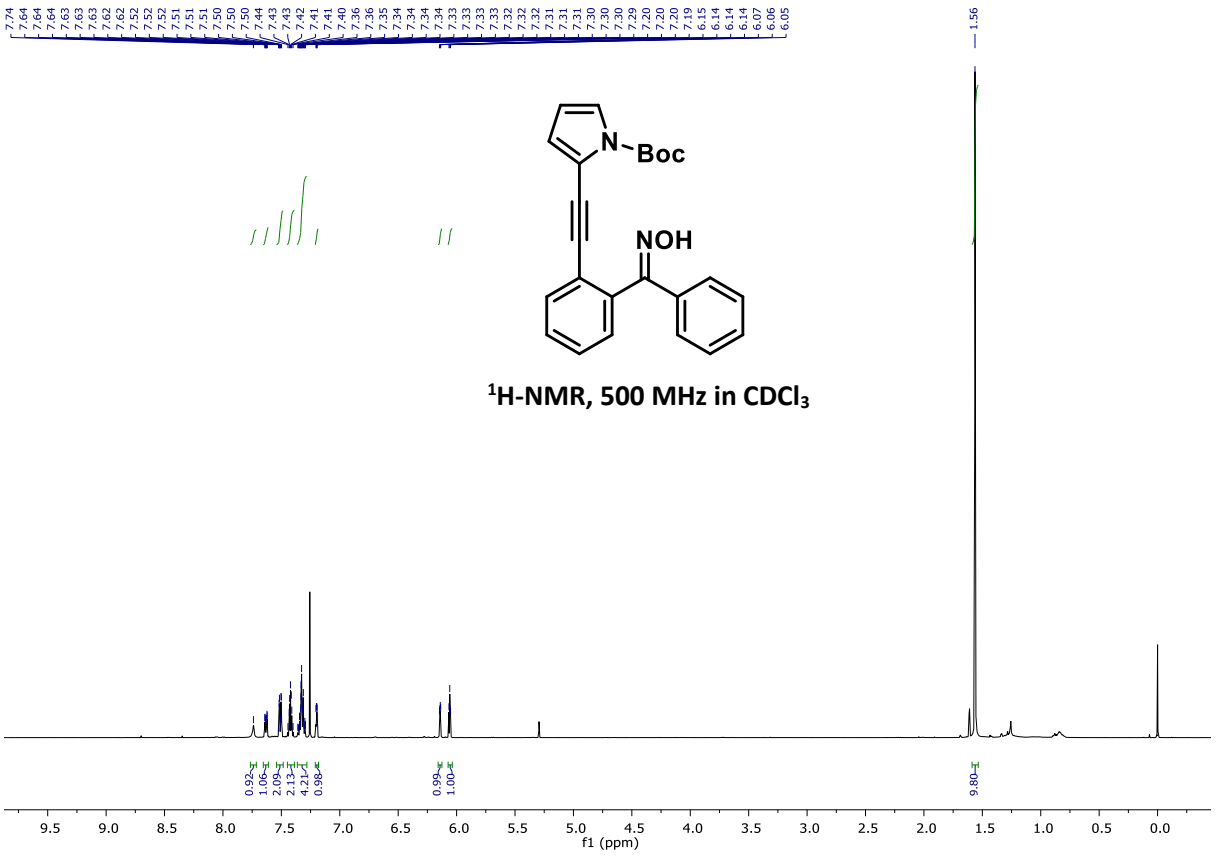
m.p.: 100 °C.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.74 (s, 1 H), 7.65 – 7.61 (m, 1 H), 7.54 – 7.48 (m, 2 H), 7.45 – 7.38 (m, 2 H), 7.36 – 7.28 (m, 4 H), 7.20 (dd, J = 3.3, 1.7 Hz, 1 H), 6.14 (dd, J = 3.4, 1.7 Hz, 1 H), 6.06 (t, J = 3.4 Hz, 1 H), 1.56 (s, 9 H).

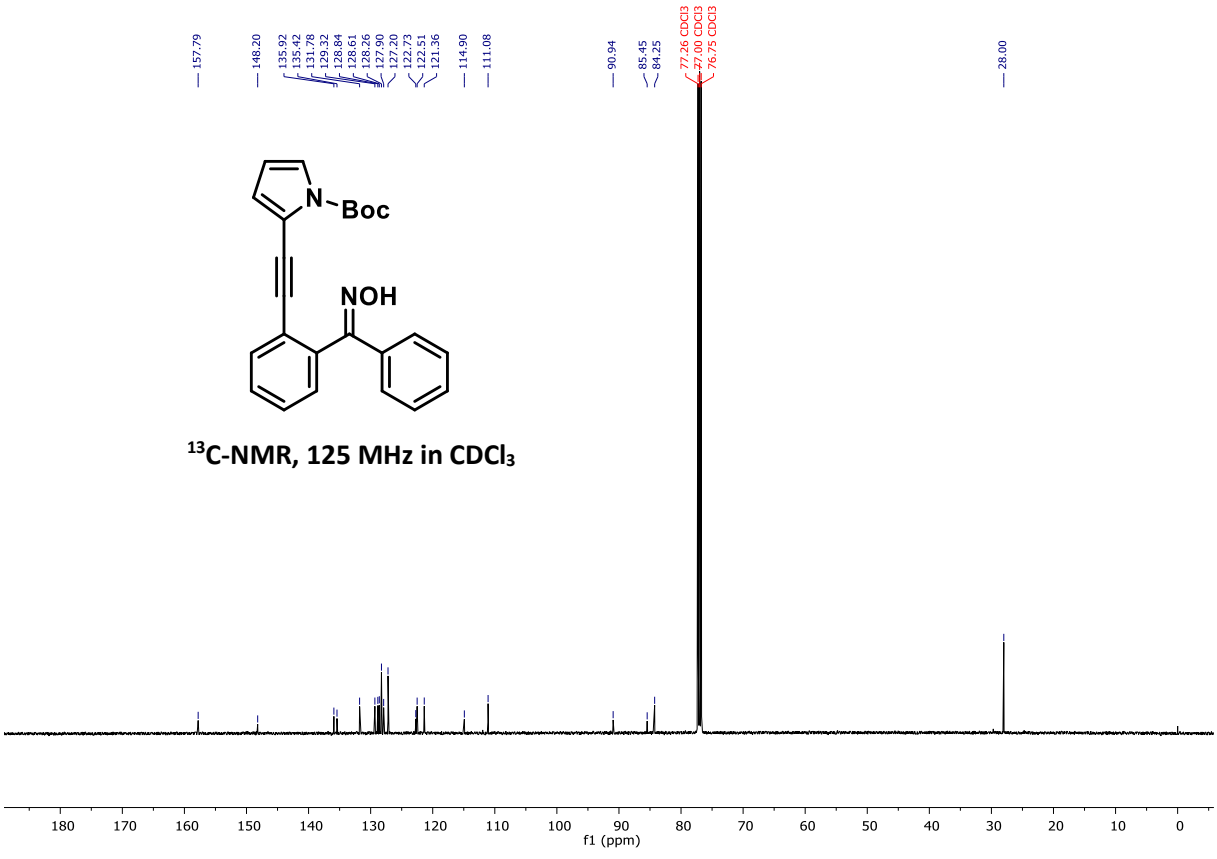
^{13}C-NMR (125 MHz, $CDCl_3$): δ = 157.8, 148.2, 135.9, 135.4, 131.8, 129.3, 128.8, 128.6, 128.3, 127.9, 127.2, 122.7, 122.5, 121.4, 114.9, 111.1, 90.9, 85.5, 84.3, 28.0.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3299, 3239, 1748, 1455, 1309, 1112.

HRMS (ESI): $C_{24}H_{22}N_2O_3$ calcd.: 409.1523 found: 409.1526, $[M+Na]^+$.



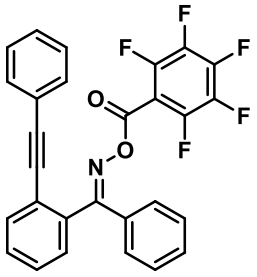
^{1}H-NMR, 500 MHz in $CDCl_3$



^{13}C-NMR, 125 MHz in $CDCl_3$

5.4. Oximester Precursors

(*E*)-phenyl(2-(phenylethynyl)phenyl)methanone *O*-perfluorobenzoyl oxime (1a)



Oxime **S3a** (1.08 g, 3.63 mmol, 1.00 eq.) was treated according to **GP4**. The residue was purified by flash column chromatography on silica gel (*n*-Pentane: EtOAc 50:1) to give the title compound (1.29 g, 2.63 mmol, 72%) as a colorless solid.

The compound contains 30% of the (*Z*)-isomer. Analytical data is given for the major isomer.

m.p.: 131 °C.

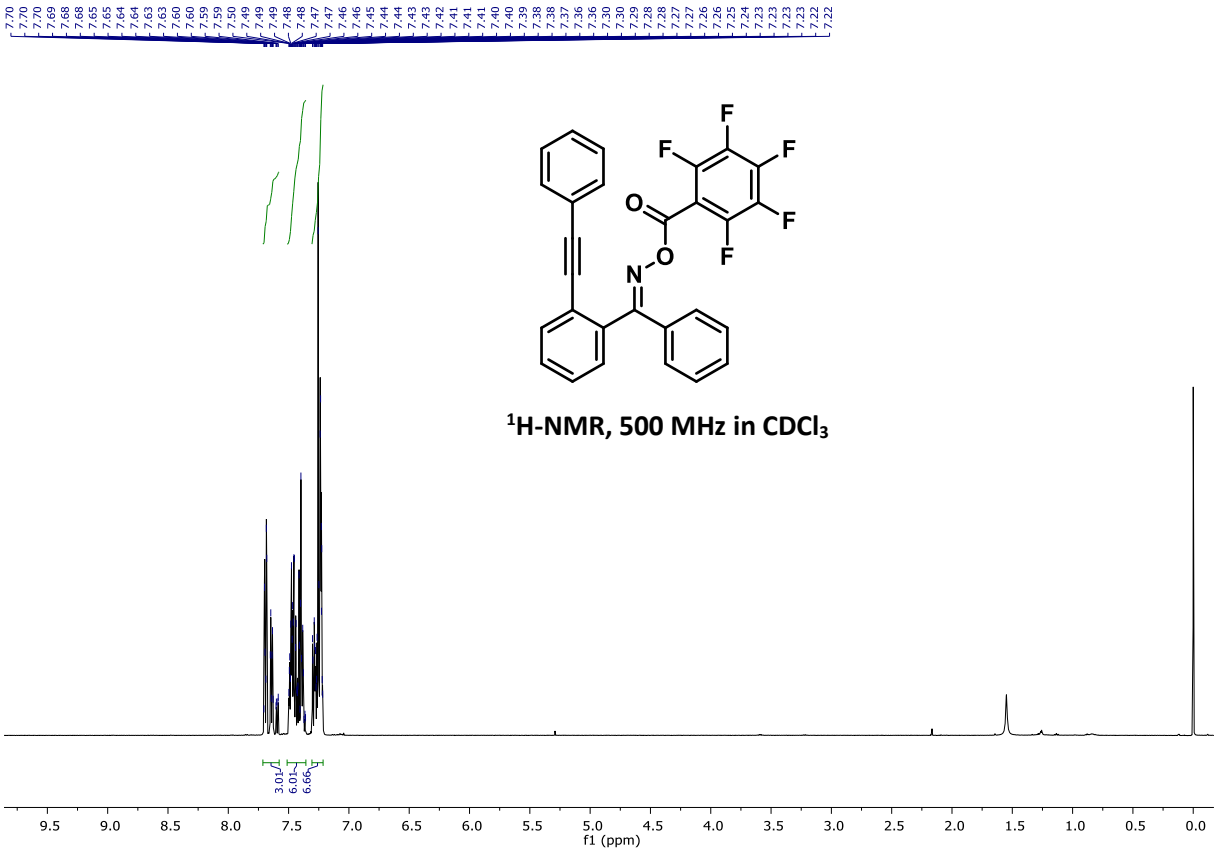
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.74 – 7.57 (m, 3 H), 7.53 – 7.35 (m, 6 H), 7.32 – 7.20 (m, 5 H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 166.2, 156.5, 146.65 – 146.19 (m), 144.60 – 144.18 (m), 142.56 – 142.19 (m), 138.92 – 138.26 (m), 136.59 (dt, J = 20.9, 7.2 Hz), 136.5, 135.2, 133.2, 132.2, 131.5, 130.5, 130.2, 129.8, 129.4, 128.6, 128.5, 128.2, 128.1, 128.0, 127.9, 122.4, 122.0, 106.82 (td, J = 16.4, 3.8 Hz), 94.0, 86.5.

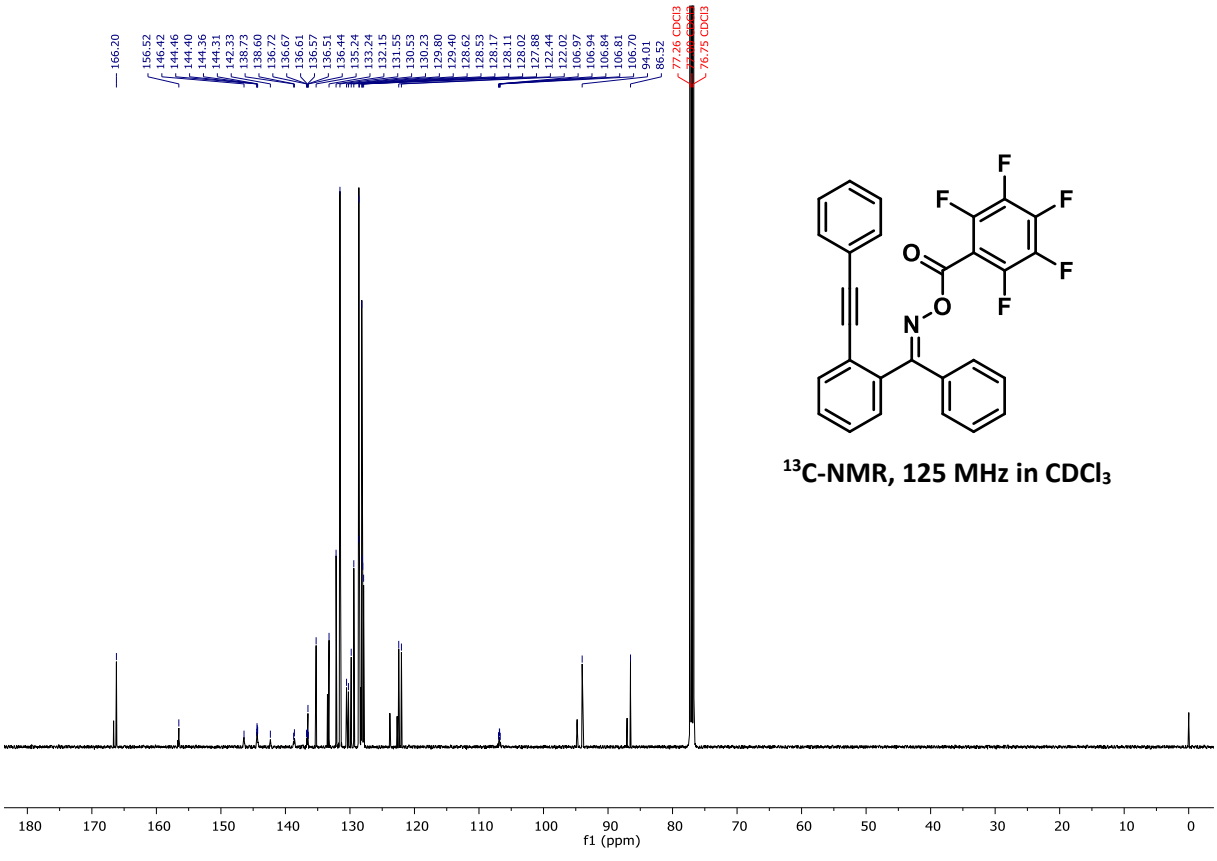
^{19}F-NMR (371 MHz, $CDCl_3$): δ =-137.07 – -137.34 (m), -148.47 (tt, J = 20.9, 4.8 Hz), -160.53 – -160.73 (m).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3056, 2162, 1771, 1502, 1322, 1178, 992.

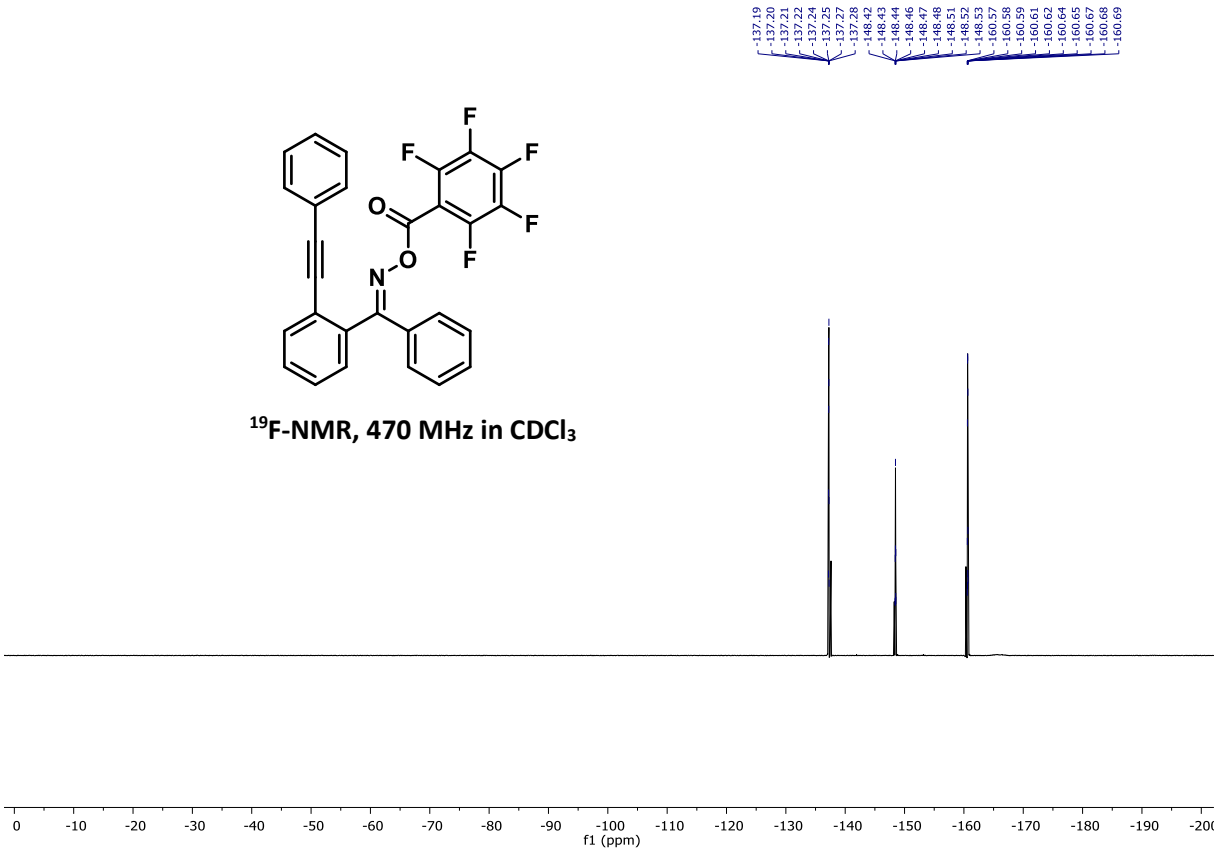
HRMS (ESI): $C_{28}H_{14}F_5NO_2$ calcd.: 514.0836 found: 514.0836, $[M+Na]^+$.



^{1}H-NMR, 500 MHz in $CDCl_3$

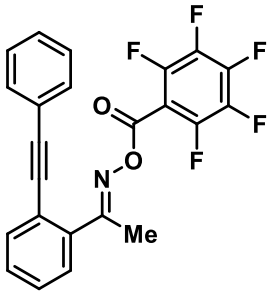


^{13}C-NMR, 125 MHz in $CDCl_3$



^{19}F-NMR, 470 MHz in $CDCl_3$

(*E*)-1-(2-(Phenylethynyl)phenyl)ethan-1-one *O*-perfluorobenzoyl oxime (1b)



The corresponding ketone (0.87 g, 3.97 mmol, 1.00 eq.) was reacted according to **GP3** and the crude product was further submitted to **GP4**. The crude product was dissolved in CH_2Cl_2 and added dropwise to *n*-pentane at -80 °C. The precipitate was filtered off to give the title compound (1.13 g, 2.63 mmol, 66%) as a colorless solid.

m.p.: 147 °C.

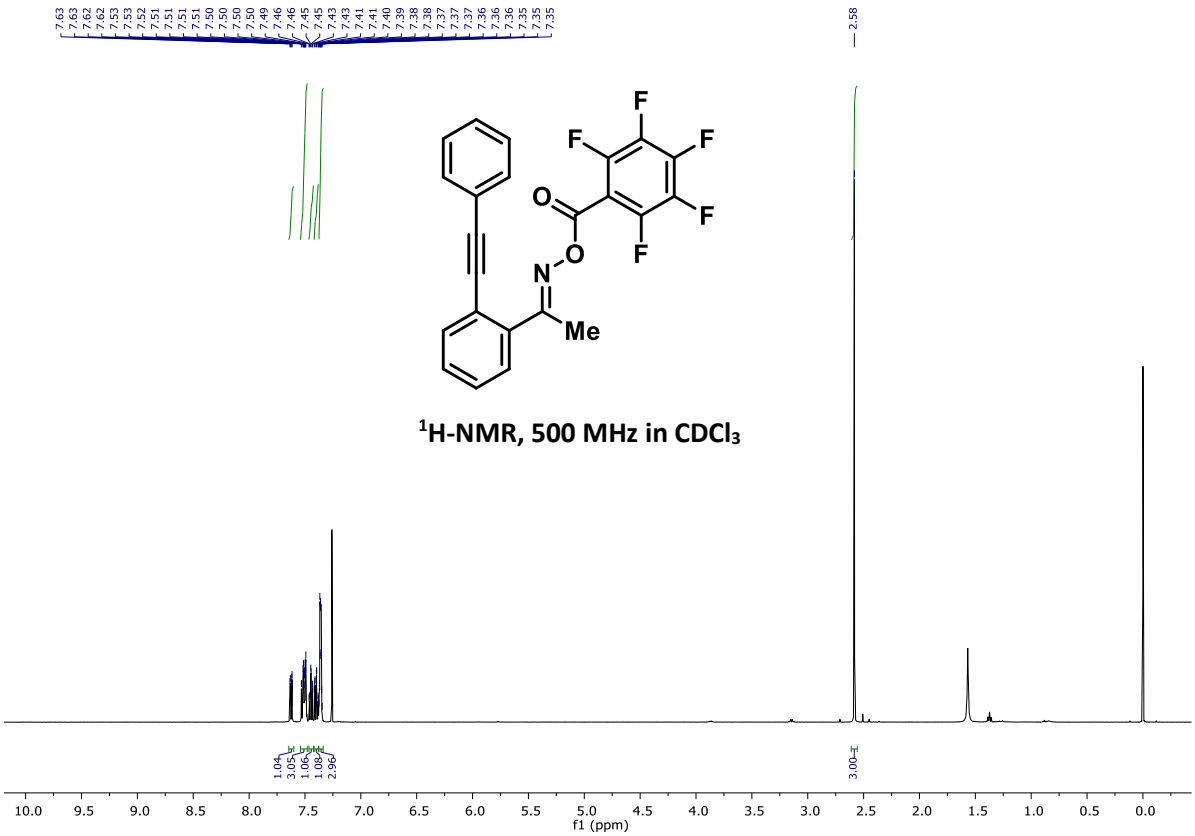
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.62 (dd, *J* = 7.6, 1.4 Hz, 1 H), 7.54 – 7.48 (m, 3 H), 7.45 (td, *J* = 7.6, 1.6 Hz, 1 H), 7.40 (td, *J* = 7.5, 1.4 Hz, 1 H), 7.36 (ddt, *J* = 5.0, 3.5, 1.9 Hz, 3 H), 2.58 (s, 3 H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 167.6, 156.4, 137.3, 133.1, 131.5, 129.9, 128.8, 128.7, 128.5, 128.5, 122.7, 122.1, 94.7, 87.1, 18.2.

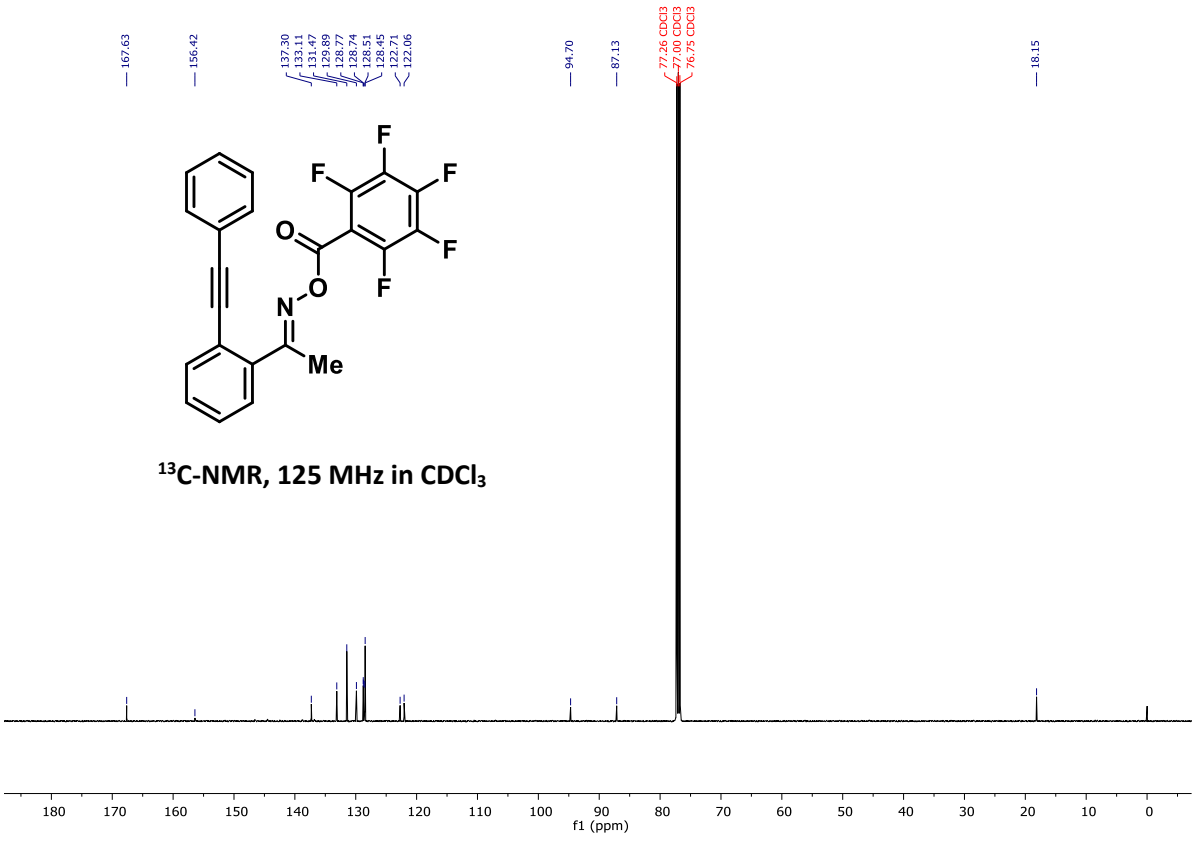
^{19}F-NMR (376 MHz, $CDCl_3$): δ = -137.37 (dqui, *J* = 17.0, 5.9 Hz), -148.04 (tt, *J* = 20.9, 4.9 Hz), -159.99 – -160.66 (m).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3077, 3029, 2216, 1762, 1495, 1321, 1192, 993, 877.

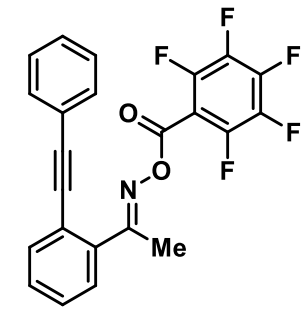
HRMS (ESI): $C_{23}H_{12}F_5NO_2$ calcd.: 452.0680 found: 452.0680, $[M+Na]^+$.



^{1}H-NMR, 500 MHz in $CDCl_3$

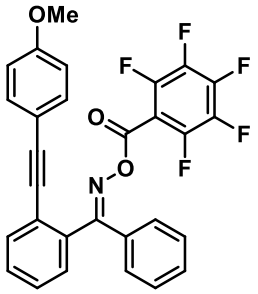


^{13}C-NMR, 125 MHz in $CDCl_3$



^{19}F-NMR, 376 MHz in $CDCl_3$

(*E*)-(2-((4-Methoxyphenyl)ethynyl)phenyl)(phenyl)methanone *O*-perfluorobenzoyl oxime (1c)



Oxime **S3c** (1.19 g, 3.66 mmol, 1.00 eq.) was reacted according to **GP4**. The crude product was purified by flash column chromatography on silica gel (*n*-pentane: EtOAc 10:1 → 5:1) to give the title compound (1.64 g, 3.14 mmol, 69%) as a colorless solid.

The compound contains 15% of the (*Z*)-isomer. Analytical data is given for the major isomer.

m.p.: 120°C.

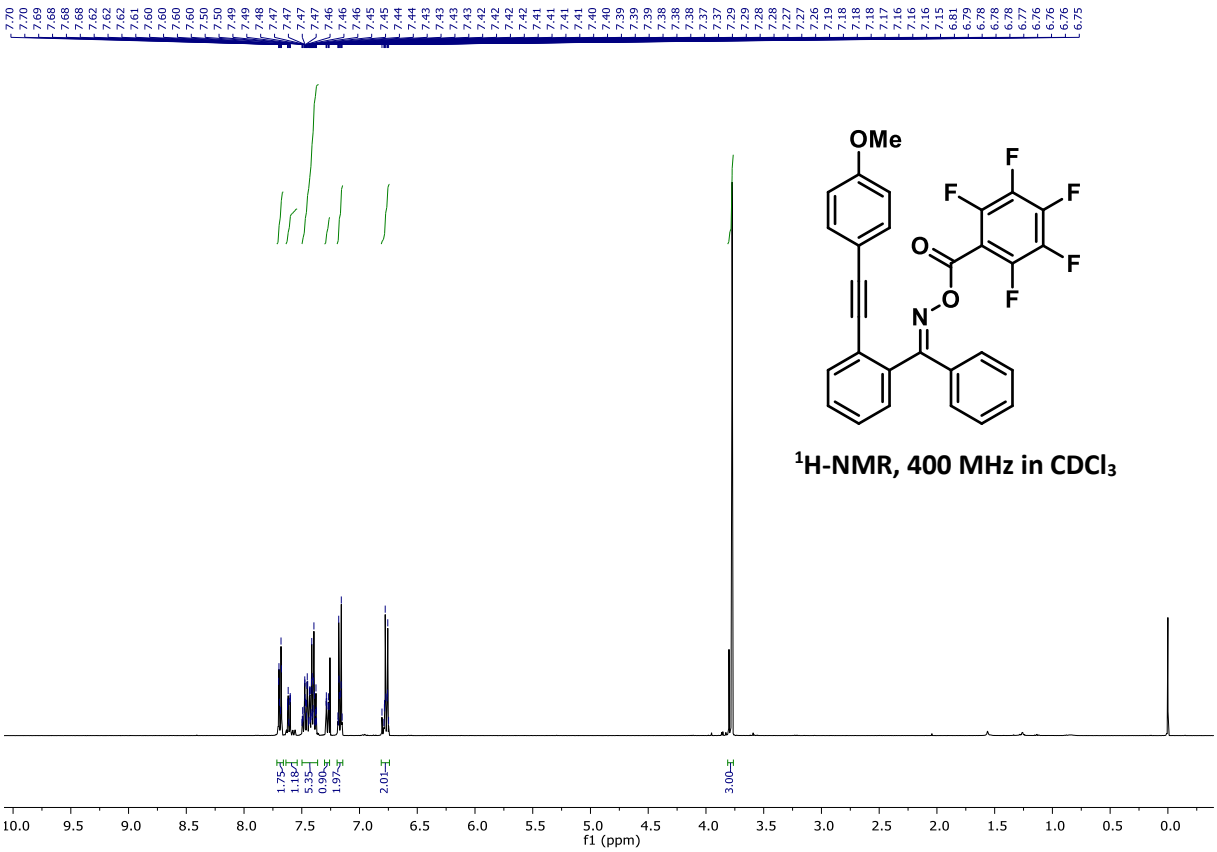
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.71 – 7.67 (m, 2H), 7.63 – 7.59 (m, 1 H), 7.51 – 7.36 (m, 5 H), 7.30 – 7.26 (m, 1 H), 7.21 – 7.14 (m, 2 H), 6.79 – 6.75 (m, 2 H), 3.77 (s, 3 H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 166.3, 159.8, 135.0, 133.3, 133.1, 131.9, 131.4, 129.8, 129.4, 128.6, 128.6, 128.1, 127.9, 127.6, 122.4, 114.5, 113.8, 113.8, 94.2, 85.4, 55.2.

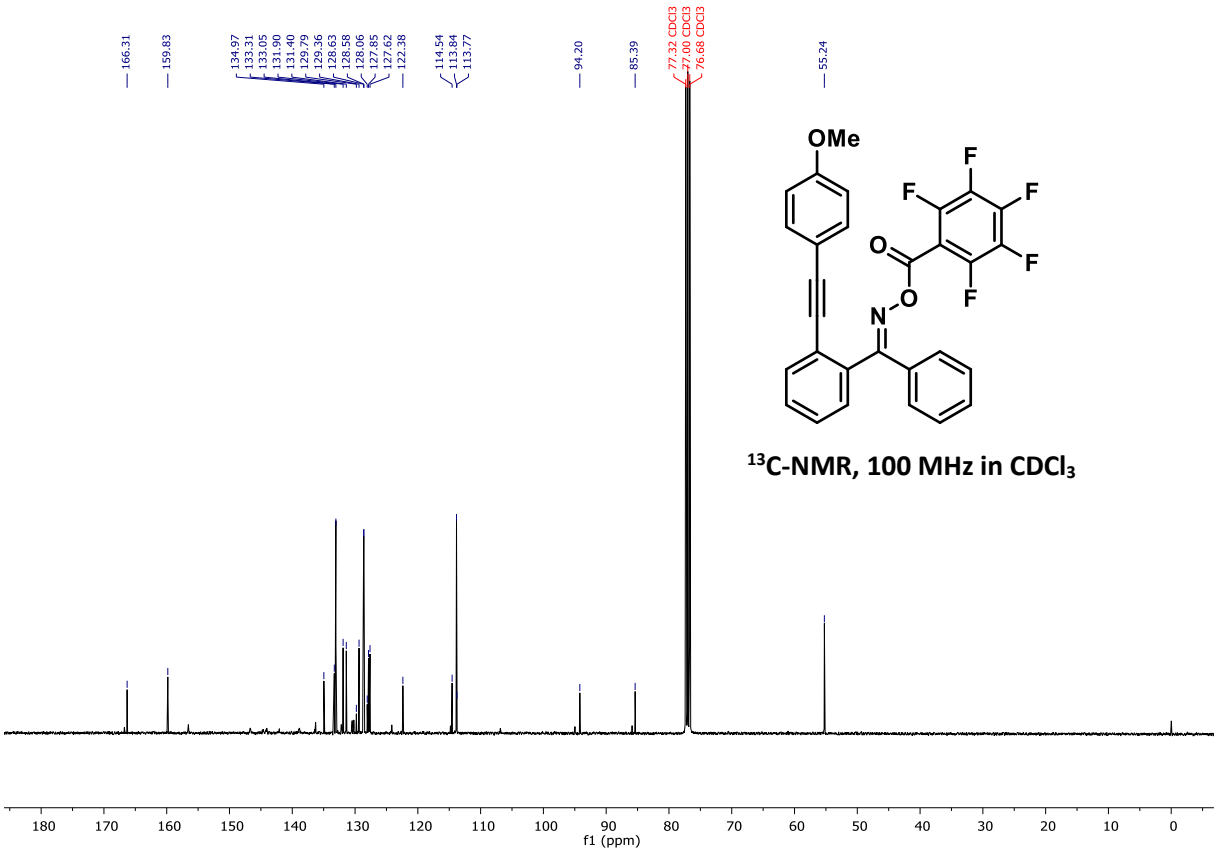
^{19}F-NMR (376 MHz, $CDCl_3$): δ = -136.87 – -137.37 (m), -148.44 (tt, *J* = 21.0, 4.8 Hz), -160.43 – -160.83 (m).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3067, 2908, 2832, 1753, 1499, 1323, 1187, 997.

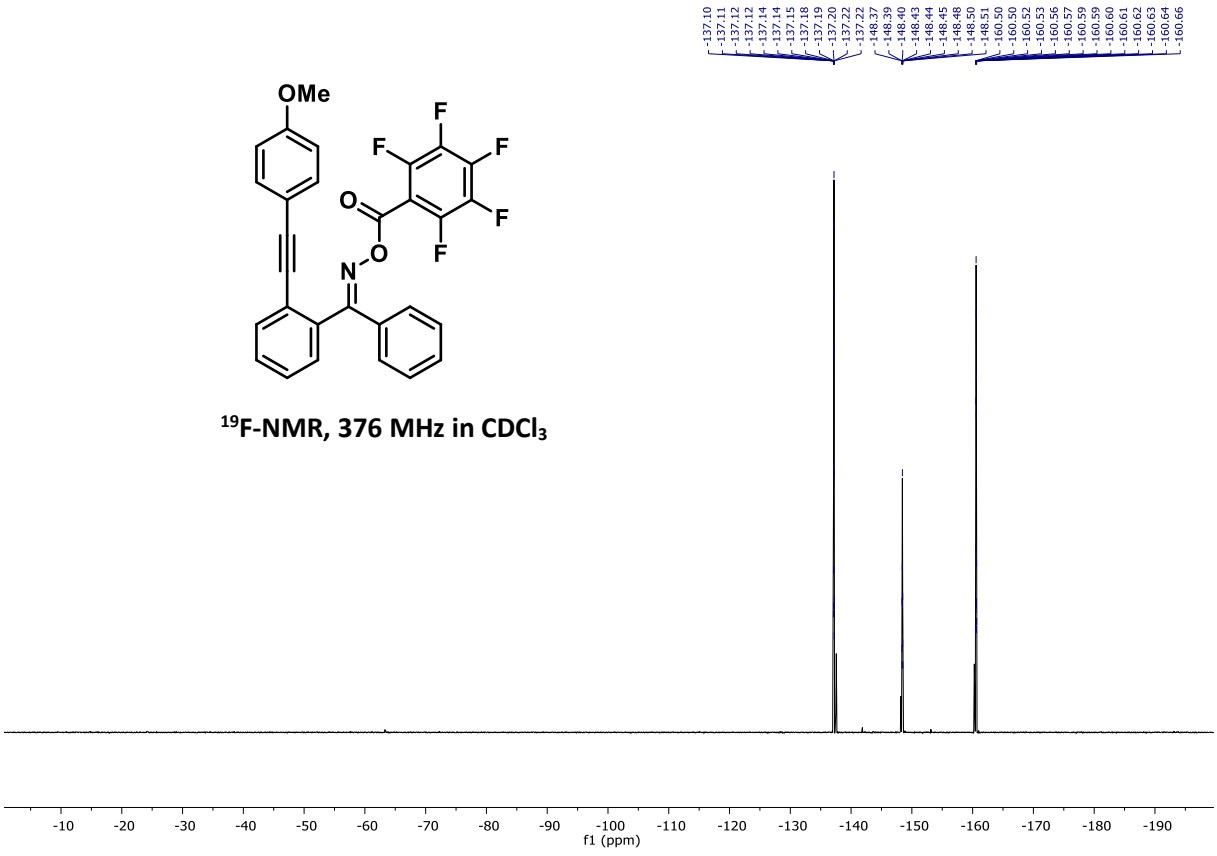
HRMS (ESI): $C_{29}H_{16}F_5NO_3$ calcd.: 544.0943 found: 544.0944, $[M+Na]^+$.



^{1}H-NMR, 400 MHz in $CDCl_3$

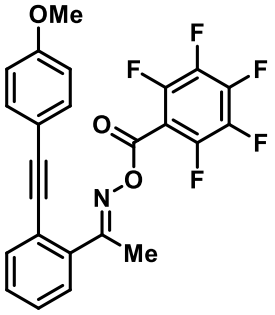


^{13}C-NMR, 100 MHz in $CDCl_3$



^{19}F-NMR, 376 MHz in $CDCl_3$

(*E*)-1-(2-((4-Methoxyphenyl)ethynyl)phenyl)ethan-1-one *O*-perfluorobenzoyl oxime (1d)



Ketone **S2d** (0.86 g, 3.45 mmol, 1.00 eq.) was treated according to **GP3**. The crude product was then reacted according to **GP4**. A saturated CH_2Cl_2 solution of the crude product was added dropwise to *n*-pentane at -80 °C. The solid was filtered off and dried in high vacuum to give the title compound (0.75 g, 1.63 mmol, 47% over two steps) as pale pink colored solid.

m.p.: 139°C.

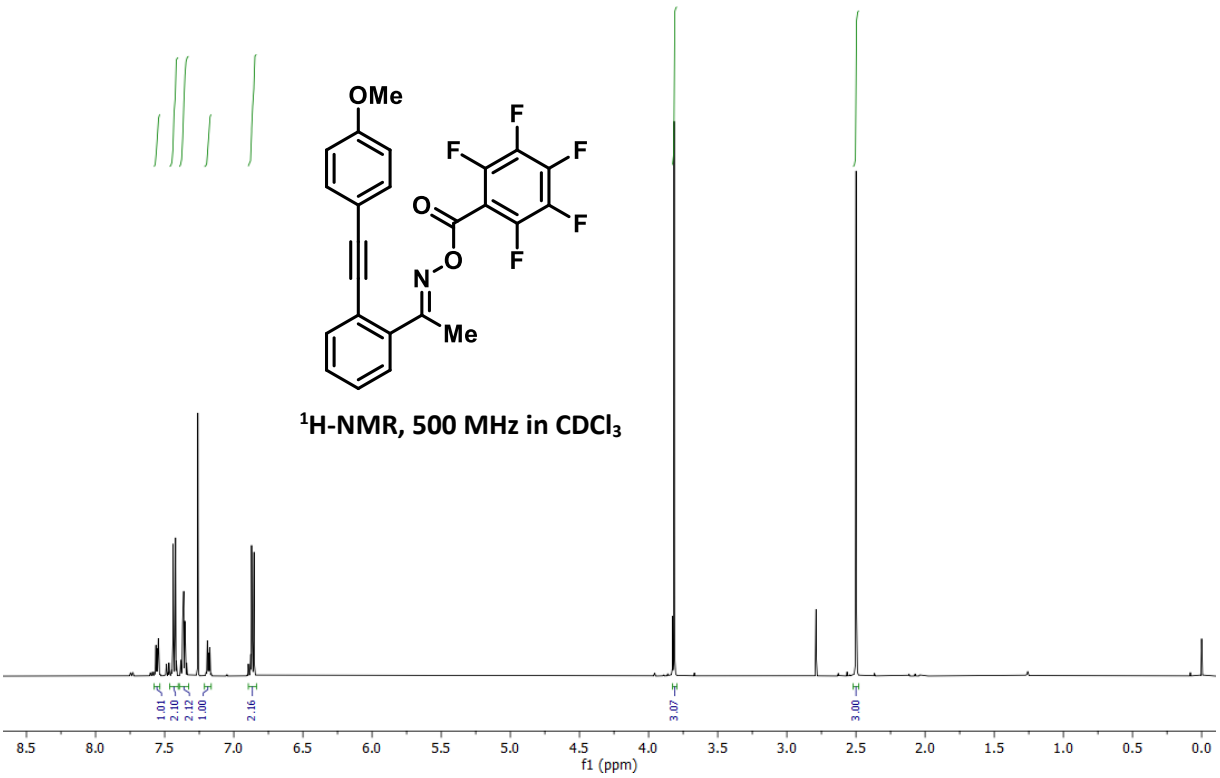
^{1}H-NMR (500 MHz, $CDCl_3$): *d* = 7.60 (dt, *J* = 7.6, 0.5 Hz, 1 H), 7.52 – 7.50 (m, 1 H), 7.46 – 7.41 (m, 3 H), 7.39 – 7.35 (m, 1 H), 6.90 − 6.87 (m, 2 H), 3.83 (s, 3 H), 2.57 (s, 3 H).

^{13}C-NMR (125 MHz, $CDCl_3$): *d* = 167.8, 160.0, 156.5, 146.7 − 146.5 (m, CF), 144.7 – 144.4 (m, CF), 142.5 − 142.4 (m, CF), 139.0 – 138.7 (m, CF), 137.1, 137.0 – 136.6 (m, CF), 133.0, 132.9, 129.9, 128.7, 128.2, 122.4, 114.8, 114.1, 107.3 − 106.9 (m, CF), 94.9, 86.0, 55.3, 18.1.

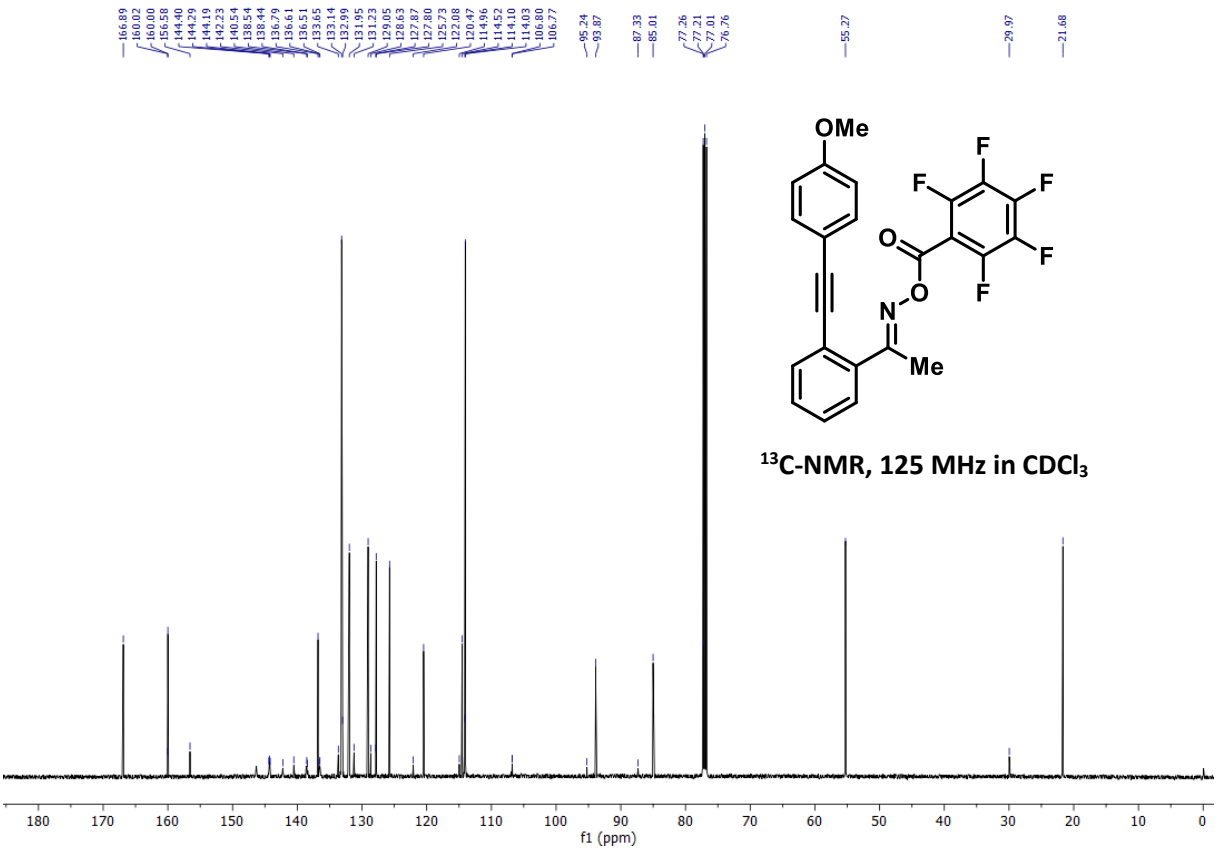
^{19}F-NMR (470 MHz, $CDCl_3$): d = -137.37 − -137.48 (m, 2 F), -148.15 (tt, *J* = 31.3, 4.6 Hz, 1 F), -160.24 − -160.39 (m, 2 F).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2963, 2839, 2212, 1762, 1501, 1195, 994, 871, 771.

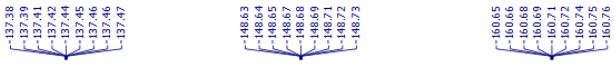
HRMS (ESI): $C_{24}H_{14}F_5NO_3$ calcd.: 482.0792 found: 482.0790, $[M+Na]^+$.

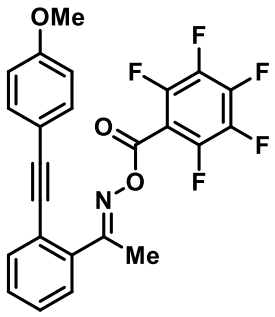


^{1}H-NMR, 500 MHz in $CDCl_3$

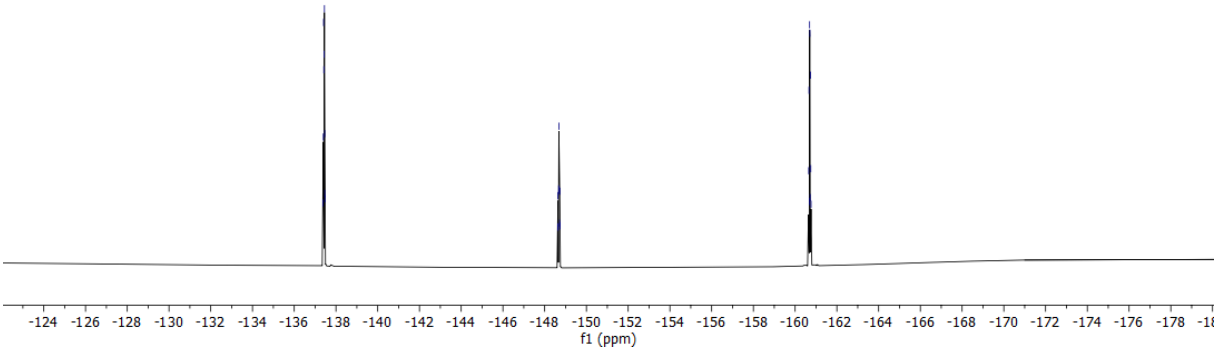


^{13}C-NMR, 125 MHz in $CDCl_3$

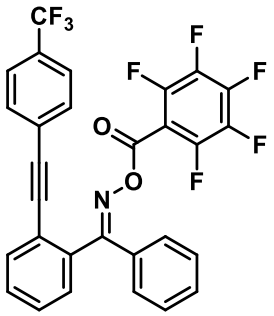




^{19}F-NMR, 470 MHz in $CDCl_3$



(*E*)-Phenyl(2-((4-(trifluoromethyl)phenyl)ethynyl)phenyl)methanone *O*-perfluorobenzoyl oxime (1e)



Oxime **S3e** (1.05 g, 2.89 mmol, 1.00 eq.) was reacted according to **GP4**. The crude product was purified by flash column chromatography on silica gel (*n*-Pentane: EtOAc 50:1 → 20:1) to give the title compound (1.18 g, 2.12 mmol, 79%) as a grey solid.

m.p.: 144 °C.

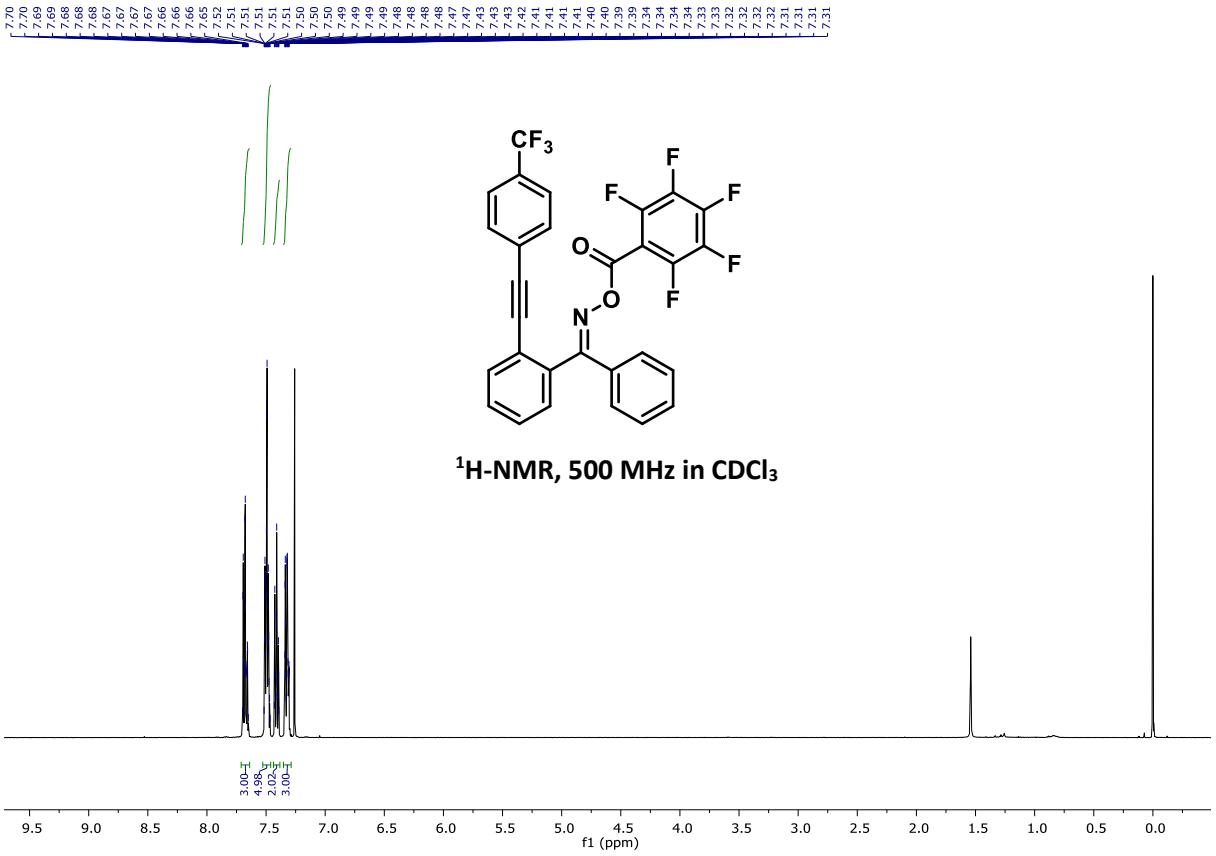
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.70 − 7.64 (m, 3 H), 7.52 − 7.46 (m, 5 H), 7.43 − 7.39 (m, 2 H), 7.35 − 7.28 (m, 3 H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 165.4, 156.5, 146.6 − 146.2 (m, CF), 144.5 − 144.3 (m, CF), 142.6 − 142.2 (m, CF), 138.8 − 138.5 (m, CF), 136.8 − 136.4 (m, CF), 135.5, 133.1, 132.3, 131.8, 131.6, 130.2 (q, $^{2}J_{C\text{-}F}$ = 32.7 Hz) 129.5, 128.7, 128.7, 128.6, 128.0, 126.3 − 126.1 (m), 125.1 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 123.8 (q, $^{1}J_{C\text{-}F}$ = 272.2 Hz), 121.3, 106.7 (td, *J* = 24.4, 3.9 Hz), 92.4, 88.7.

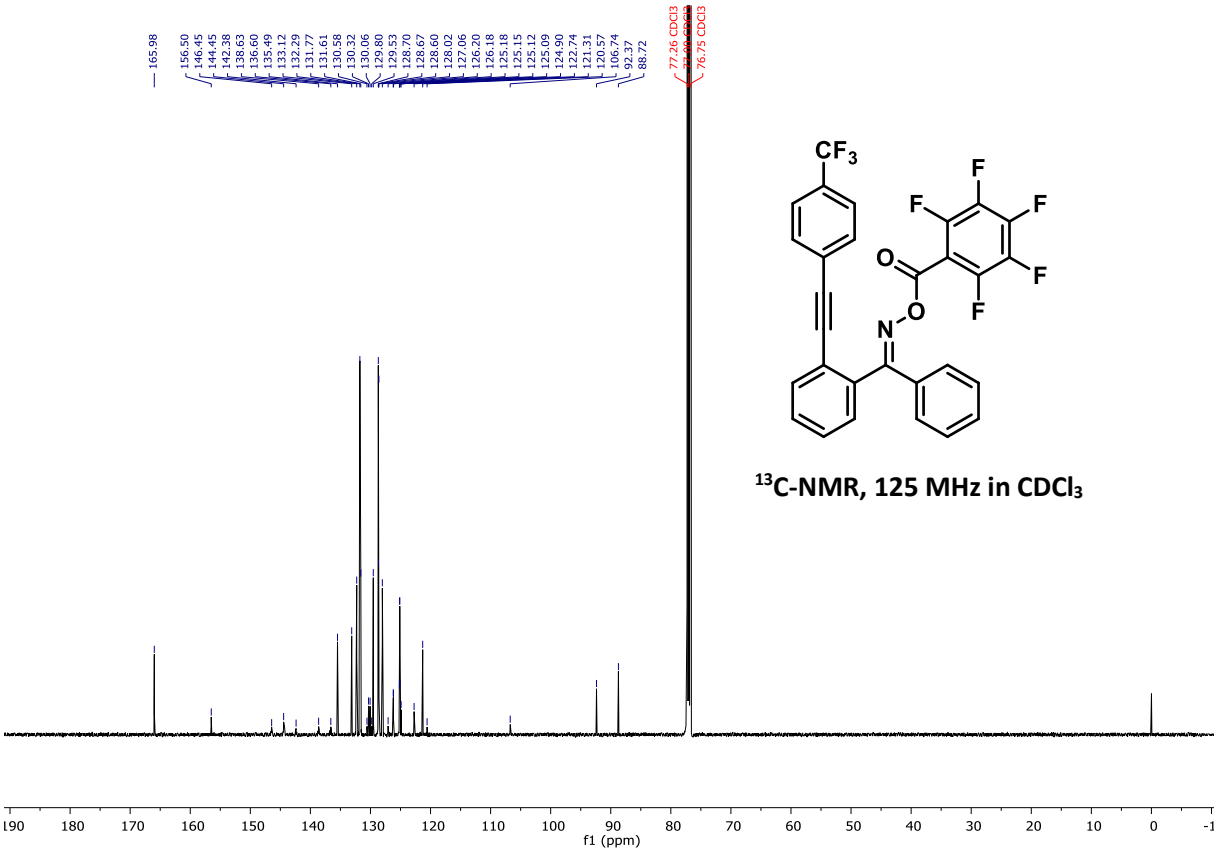
^{19}F-NMR (470 MHz, $CDCl_3$): δ = -63.37 (s), -137.26 − -137.37 (m), -148.22 (tt, *J* = 20.9, 4.8 Hz), -160.40 − -160.55 (m).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3068, 2322, 1751, 1493, 1320, 1191, 1109.

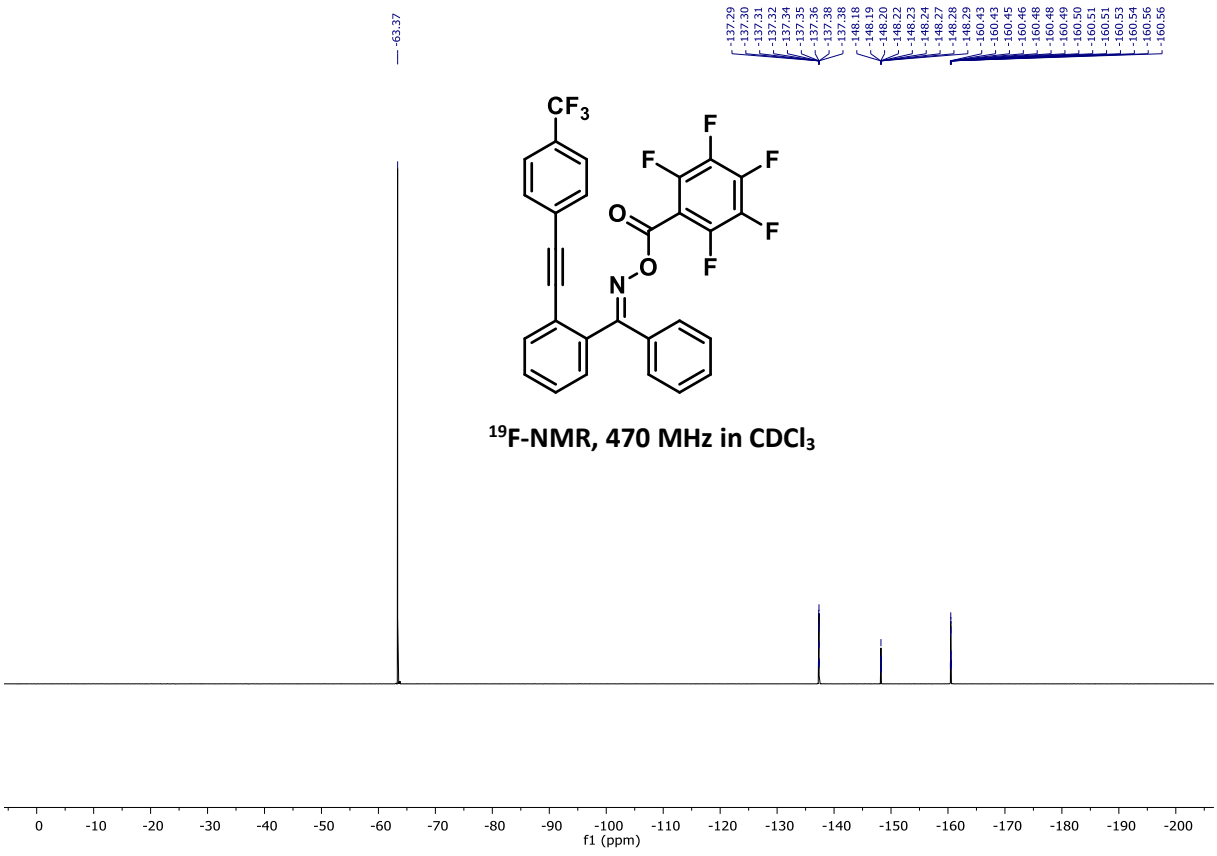
HRMS (ESI): $C_{29}H_{13}F_8NO_2$ calcd.: 582.0716 found: 582.0712, $[M+Na]^+$.



^{1}H-NMR, 500 MHz in $CDCl_3$

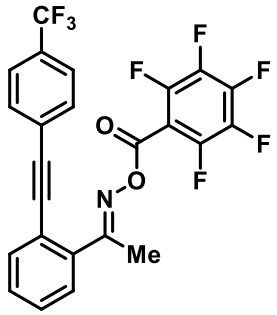


^{13}C-NMR, 125 MHz in $CDCl_3$



^{19}F-NMR, 470 MHz in $CDCl_3$

(*E*)-1-(2-((4-(Trifluoromethyl)phenyl)ethynyl)phenyl)ethan-1-one *O*-perfluorobenzoyl oxime (1f)



Ketone **S2f** (0.86 g, 3.45 mmol, 1.00 eq.) was treated according to **GP3**. The crude product was then reacted according to **GP4**. A saturated CH_2Cl_2 solution of the crude product was added dropwise to *n*-pentane at -80 °C. The solid was filtered off and dried in high vacuum to give the title compound (0.75 g, 1.63 mmol, 47% over two steps) as colorless solid.

m.p.: 103 °C.

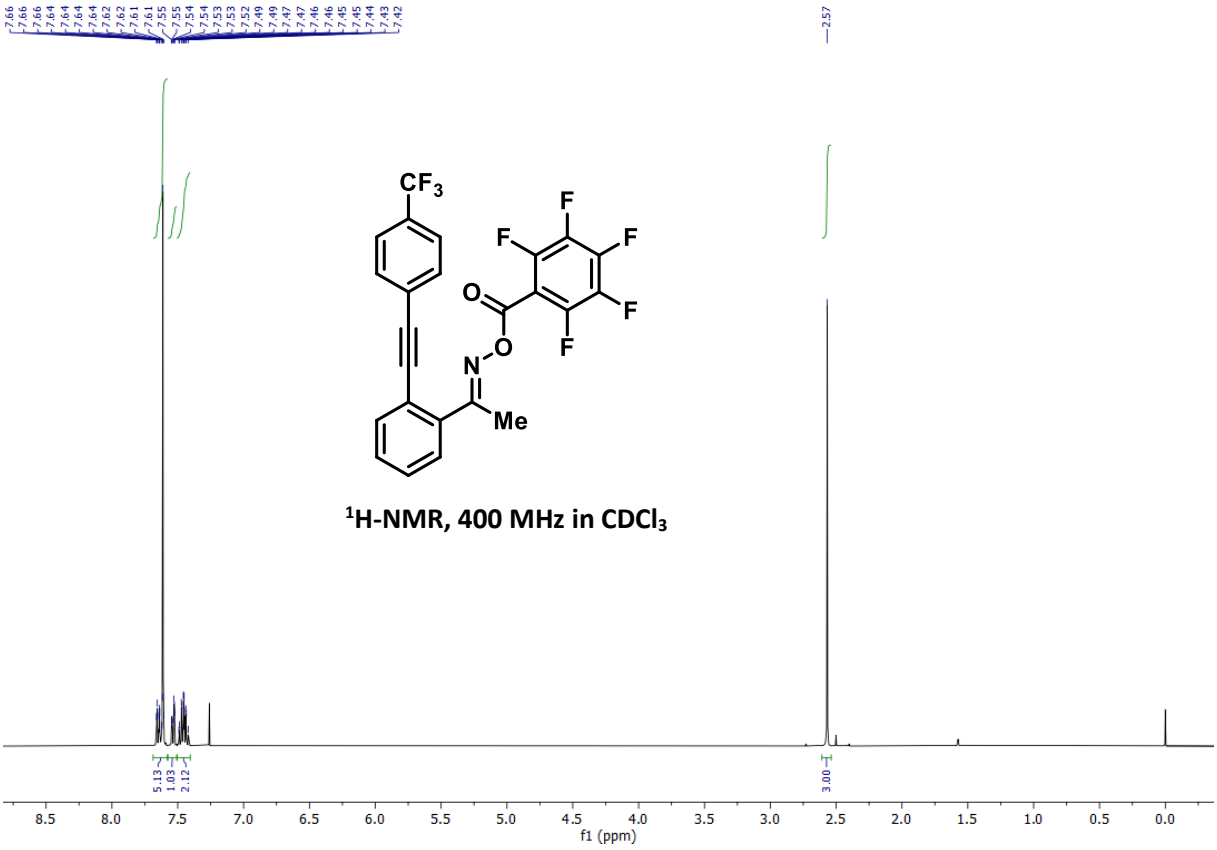
^{1}H-NMR (400 MHz, $CDCl_3$): *d* = 7.67 – 7.60 (m, 5H), 7.54 (dd, *J* = 7.2, 1.8 Hz, 1H), 7.50 – 7.41 (m, 2H), 2.57 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$): *d* =167.1, 156.3, 146.9 -146.7 (m, CF), 144.3 - 144.1 (m, CF), 137.4, 136.7-136.4(m, CF), 133.3, 131.7, 130.38 (q, $^{2}J_{C\text{-}F}$ = 32.7 Hz), 126.50 (d, $^{4}J_{C\text{-}F}$= 1.4 Hz), 129.9, 129.1, 128.8, 125.37 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz) 123.82 (d, $^{1}J_{C\text{-}F}$ 272.3 Hz), 121.3, 107.1-106.8 (m, CF), 18.1.

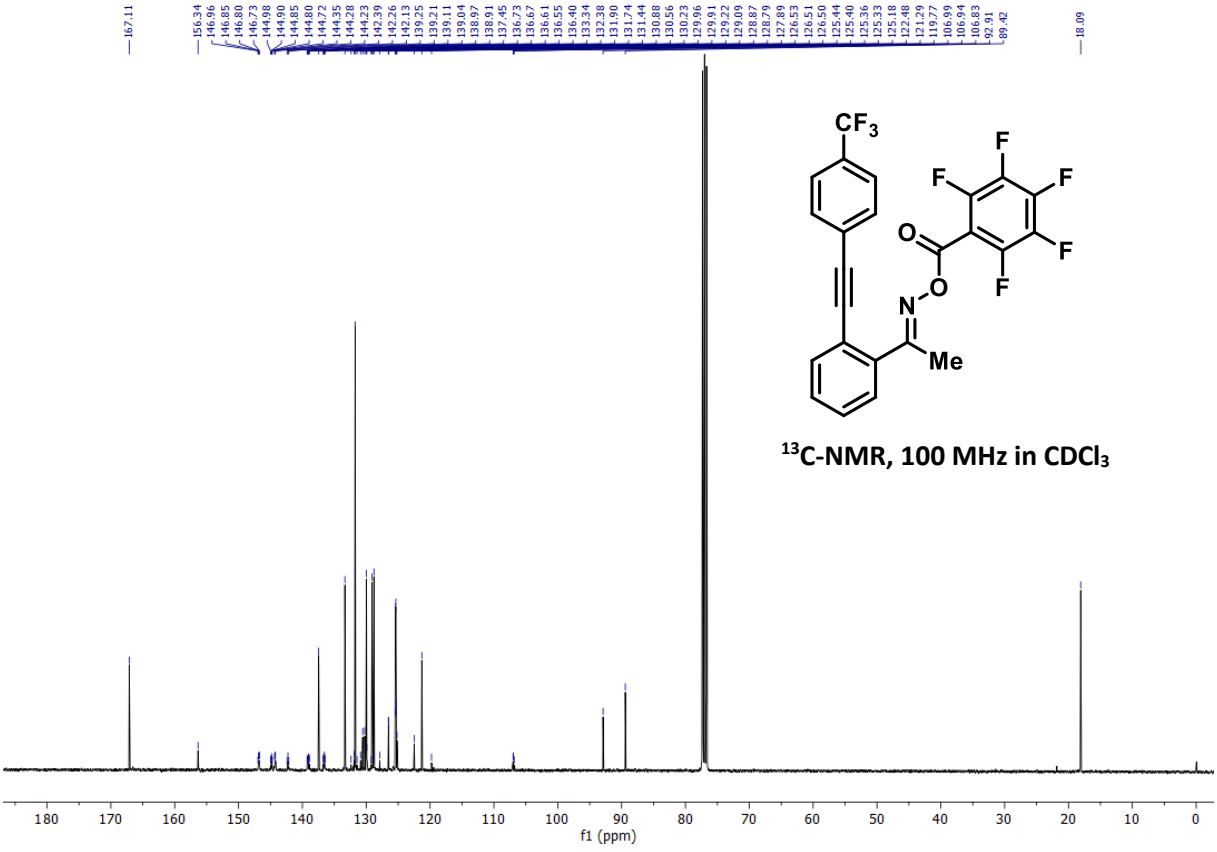
^{19}F-NMR (376 MHz, $CDCl_3$): d = -63.31, -137.45 (dp, *J* = 16.9, 5.9 Hz), -147.81 (tt, *J* = 20.9, 4.8 Hz), -160.02 – -160.33 (m).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3075, 2930, 2323, 1762, 1494, 1317, 1188, 1132.

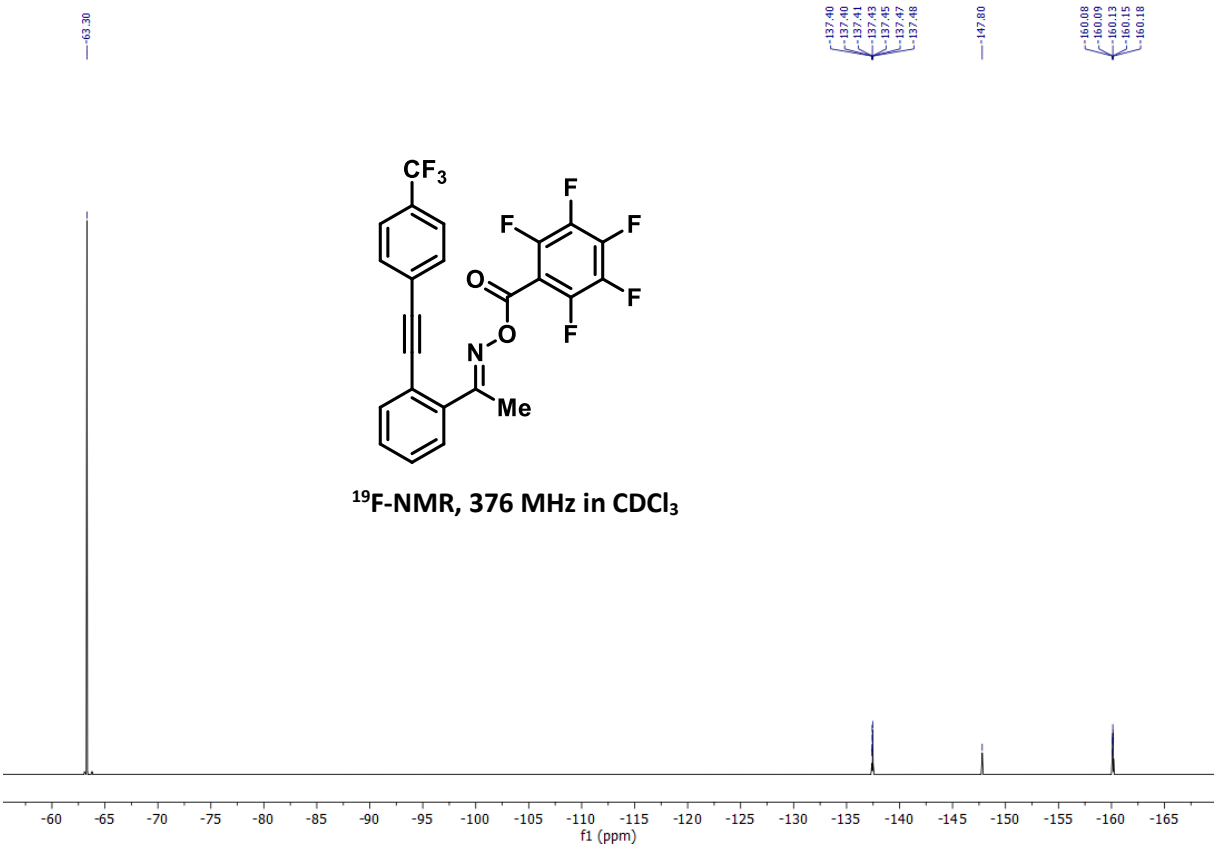
HRMS (ESI): $C_{24}H_{11}F_8NO_2$ calcd.: 520.0554 found: 520.0554, $[M+Na]^+$.



^{1}H-NMR, 400 MHz in $CDCl_3$

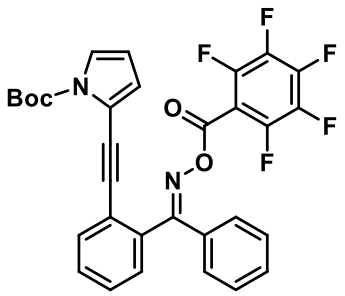


^{13}C-NMR, 100 MHz in $CDCl_3$



^{19}F-NMR, 376 MHz in $CDCl_3$

tert-Butyl (_E_)-2-((2-((((perfluorobenzoyl)oxy)imino)(phenyl)methyl)phenyl)ethynyl)-1_H_-pyrrole-1-carboxylate (1g)



Oxime **S3g** (2.78 g, 7.20 mmol, 1.00 eq.) was reacted according to **GP4**. A concentrated solution of the crude product in CH_2Cl_2 was added dropwise to *n*-pentane at -40 °C. The colorless solid was filtered off, washed with *n*-pentane and dried to give the product as a colorless solid (1.67 g, 2.88 mmol). The *n*-pentane was removed in vacuo and the residue was purified by flash column chromatography on silica gel (*n*-Pentane: EtOAc 25:1) to give the title compound (1.56 g, 2.69 mmol) as a light brown solid. Both fractions were combined (3.23 g, 5.57 mmol, 77%).

m.p.: 134 °C.

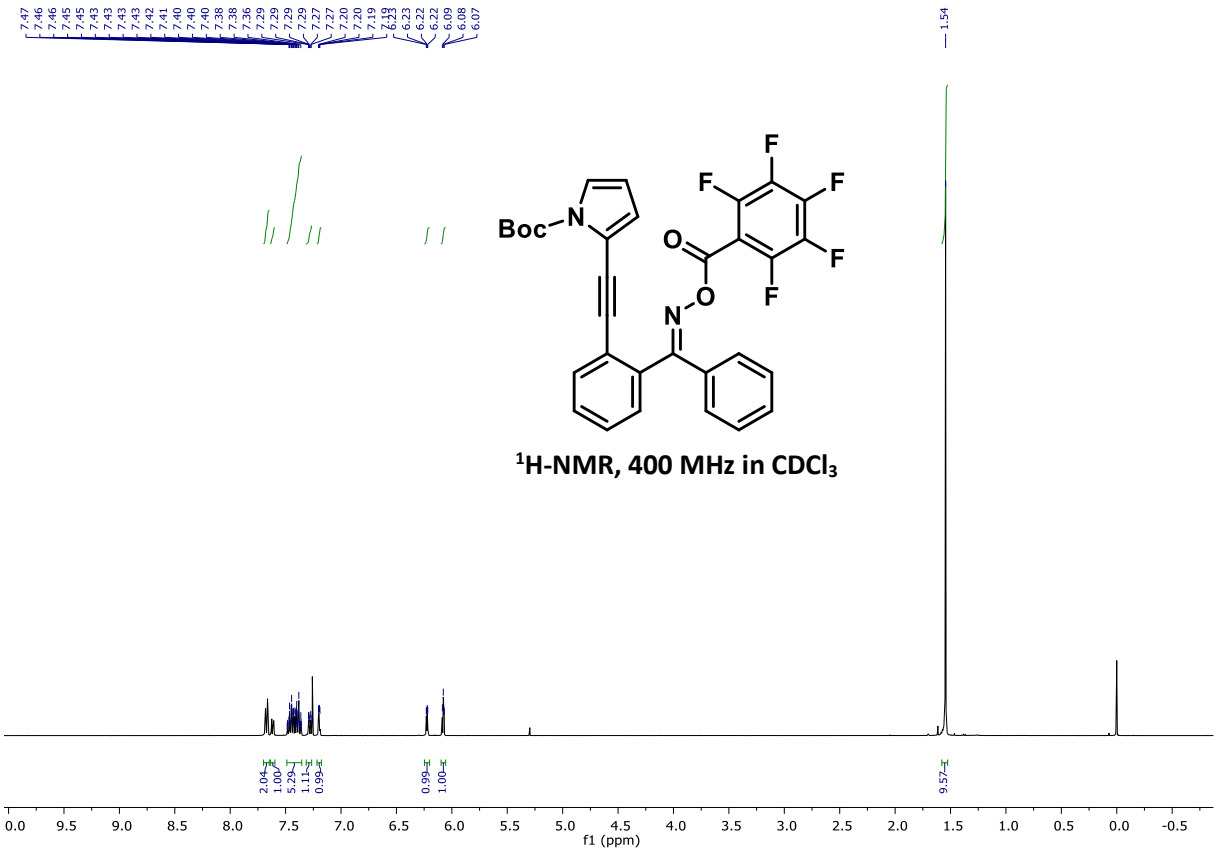
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.69 – 7.65 (m, 2 H), 7.64 – 7.60 (m, 1 H), 7.49 – 7.35 (m, 6 H), 7.30 – 7.26 (m, 1 H), 7.20 (dd, *J* = 3.3, 1.7 Hz, 1 H), 6.22 (dd, *J* = 3.5, 1.7 Hz, 1 H), 6.08 (t, *J* = 3.4 Hz, 1 H), 1.54 (s, 9 H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 166.1, 156.5, 148.0, 146.5 (m), 144.4 (m), 142.3 (m), 138.6 (m), 136.6 (m), 135.0, 133.3, 131.7, 131.3, 129.3, 128.7, 128.5, 127.9, 127.8, 122.7, 122.3, 121.7, 114.5, 111.2, 106.9 (m), 90.0, 86.5, 84.1, 27.9.

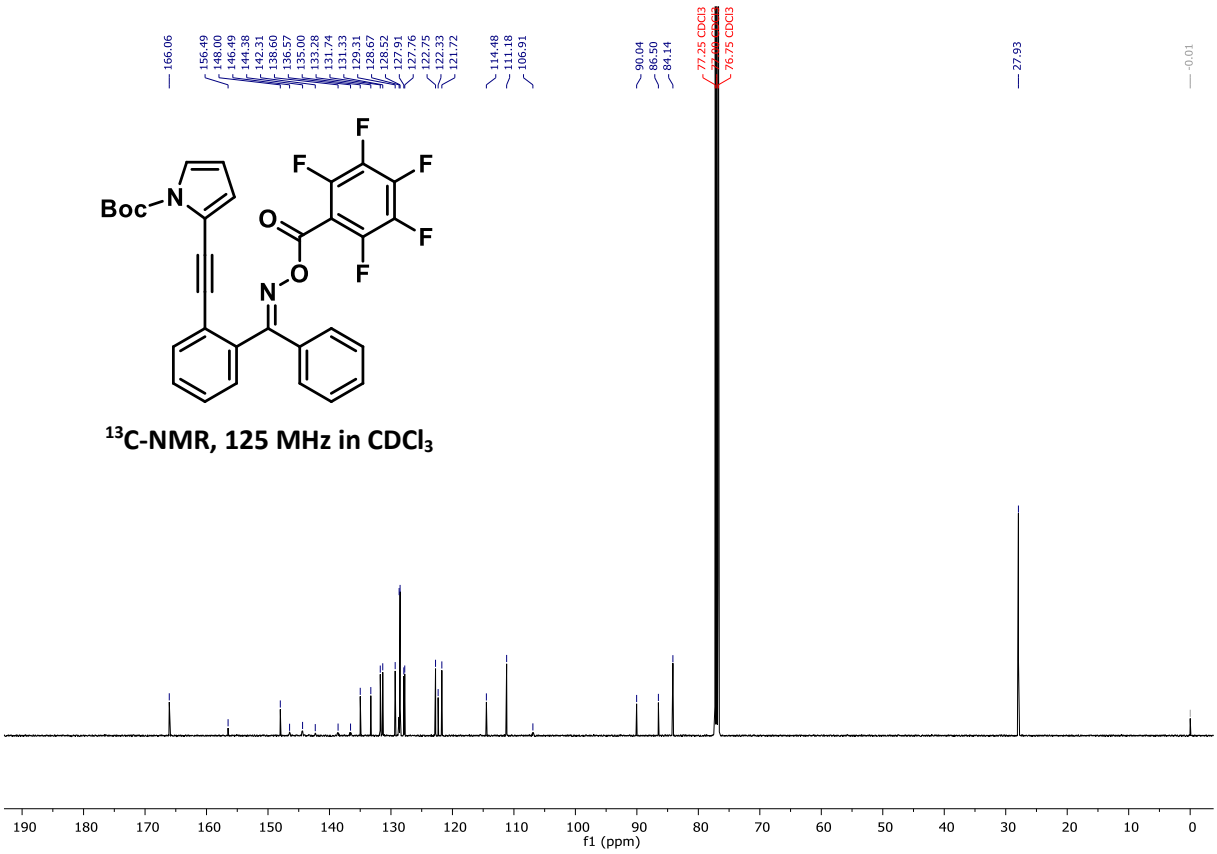
^{19}F-NMR (376 MHz, $CDCl_3$): δ = -136.86 – -137.38 (m), -148.51 (tt, *J* = 20.8, 4.7 Hz), -160.47 – -160.96 (m).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2986, 2934, 2211, 1742, 1496, 1318, 1186, 1115, 996.

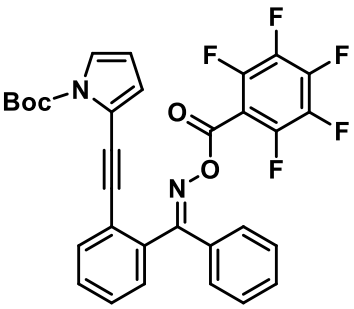
HRMS (ESI): $C_{31}H_{21}F_5N_2O_4$ calcd.: 603.1316 found: 603.1316, $[M+Na]^+$.



^{1}H-NMR, 400 MHz in $CDCl_3$

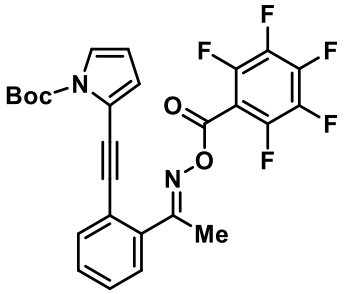


^{13}C-NMR, 125 MHz in $CDCl_3$



^{19}F-NMR, 376 MHz in $CDCl_3$

***tert*-Butyl (*E*)-2-((2-(1-(((perfluorobenzoyl)oxy)imino)ethyl)phenyl)ethynyl)-1*H*-pyrrole-1-carboxylate (1h)**



Ketone **S2h** (1.08 g, 3.50 mmol, 1.00 eq.) was reacted according to **GP3**. The crude product was then reacted according to **GP4**. A saturated CH_2Cl_2 solution of the residue was added dropwise to *n*-pentane at -80 °C. The solid was filtered and dried to give the title compound (1.40 g, 2.70 mmol, 68%) as a colorless solid.

m.p.: 146 °C.

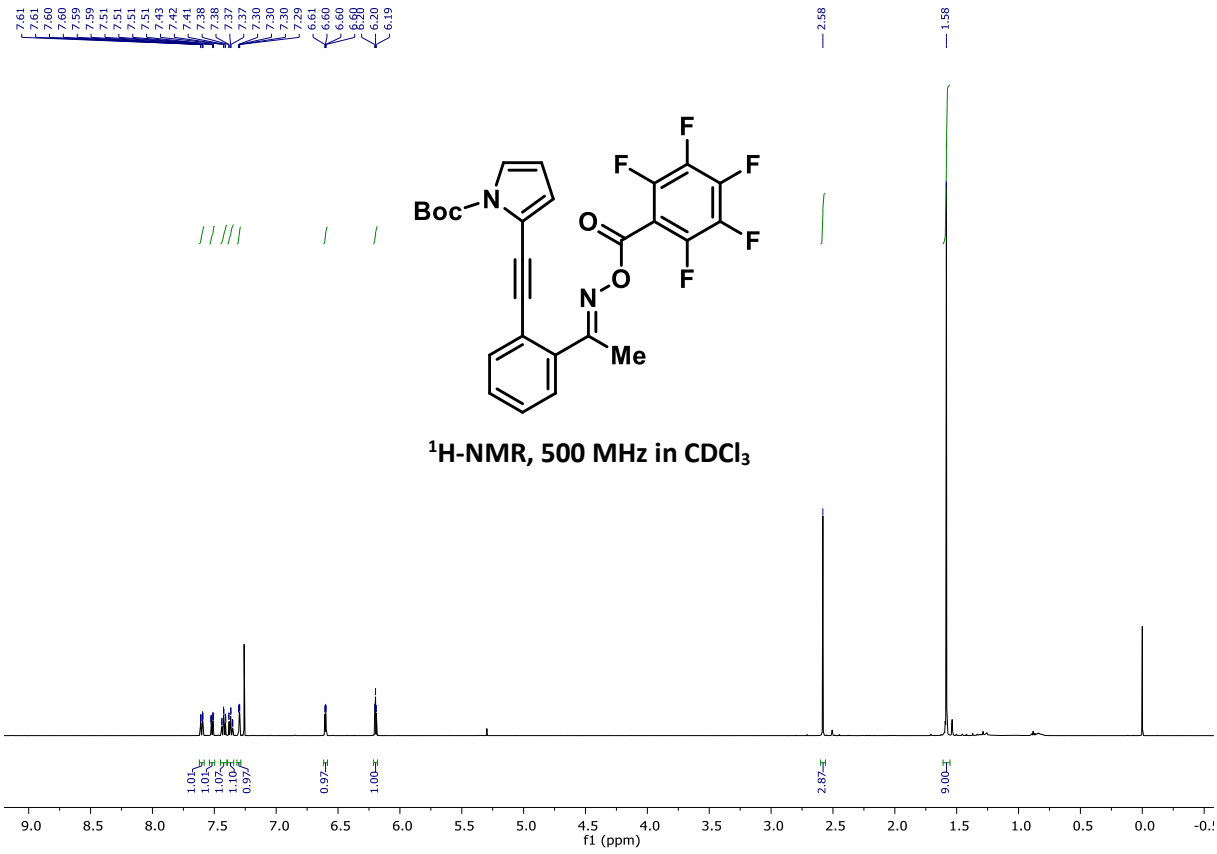
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.60 (ddd, *J* = 7.7, 1.4, 0.6 Hz, 1 H), 7.52 (ddd, *J* = 7.6, 1.5, 0.6 Hz, 1 H), 7.42 (td, *J* = 7.6, 1.5 Hz, 1 H), 7.37 (td, *J* = 7.6, 1.4 Hz, 1 H), 7.30 (dd, *J* = 3.3, 1.7 Hz, 1 H), 6.60 (dd, *J* = 3.5, 1.7 Hz, 1 H), 6.20 (t, *J* = 3.4 Hz, 1 H), 2.58 (s, 3 H), 1.58 (s, 9 H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 168.0, 156.5, 148.1, 137.1, 132.9, 129.8, 128.8, 128.3, 123.0, 122.3, 121.3, 114.8, 111.3, 90.5, 87.2, 84.4, 27.9, 18.2.

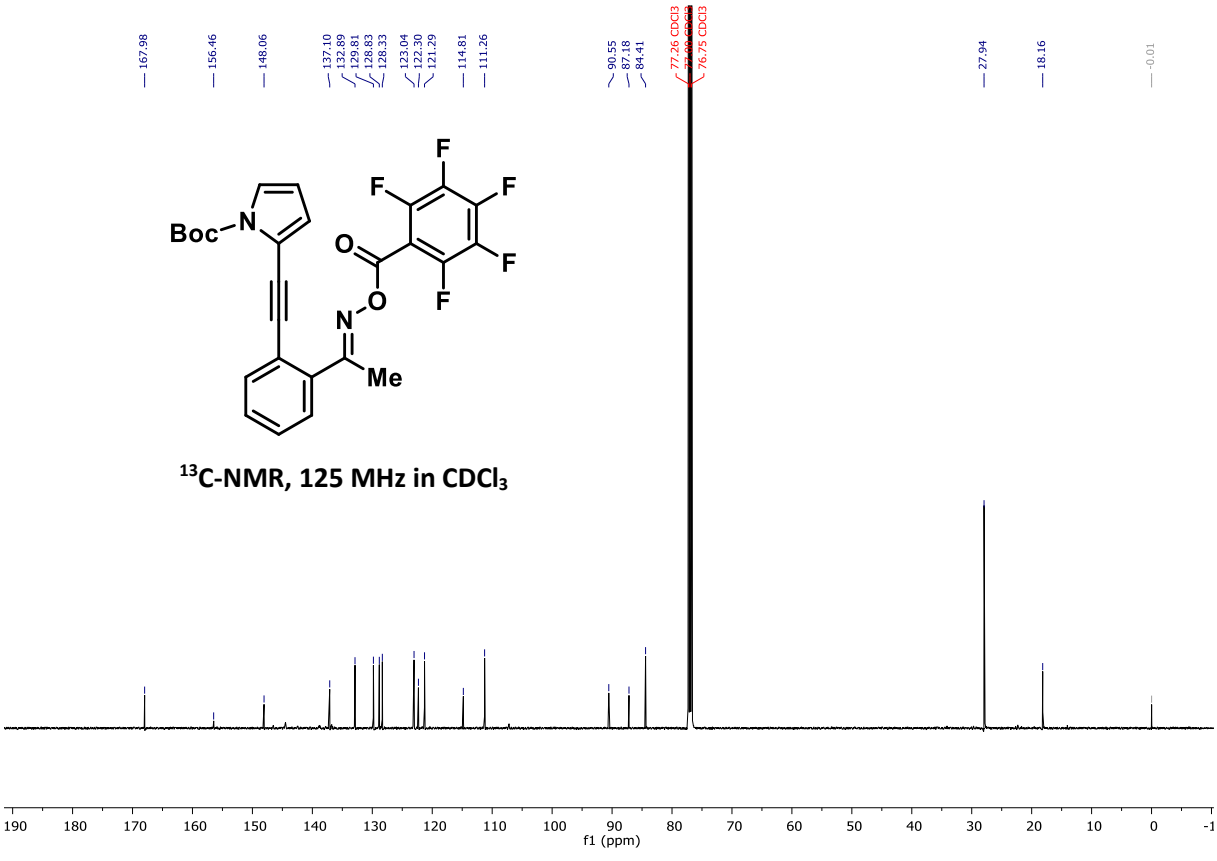
^{19}F-NMR (470 MHz, $CDCl_3$): δ = -137.14 – -137.47 (m), -148.25 (tt, *J* = 20.8, 4.7 Hz), -160.23 – -160.64 (m).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2984, 2931, 2158, 1750, 1491, 1321, 1122, 994.

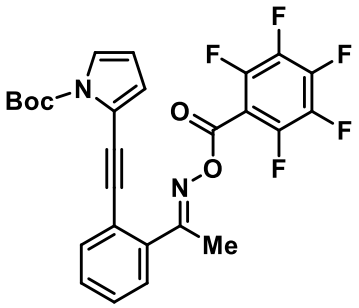
HRMS (ESI): $C_{26}H_{19}F_5N_2O_4$ calcd.: 541.1157 found: 541.1156, $[M+Na]^+$.



^{1}H-NMR, 500 MHz in $CDCl_3$



^{13}C-NMR, 125 MHz in $CDCl_3$

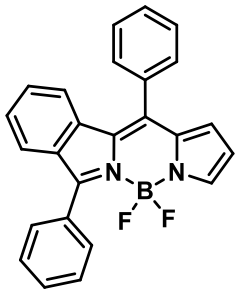


^{19}F-NMR, 470 MHz in $CDCl_3$

6. BODIPYs

6.1. *meso*-Aryl BODIPYs

5,5-Difluoro-7,12-diphenyl-5*H*-5λ^4,6λ^4-pyrrolo[1',2':3,4][1,3,2]diazaborinino[6,1-*a*]isoindole (5a)



The corresponding precursor **1a** (491 mg, 1.00 mmol, 1.00 eq.) was reacted with *N*-Boc-2-pyrroleboronic acid (633 mg, 3.00 mmol, 3.00 eq.) according to **GP5** for 2.5 h. The crude product was reacted according to **GP6** for 16 h. Without further purification, the product was subjected to **GP7** for 10 minutes. The product was purified by flash column chromatography on silica gel (*n*-pentane: EtOAc 20:1) The title compound was obtained as a dark red solid (179.40 mg, 455.00 µmol, 46%).

m.p.: 217 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.92 – 7.85 (m, 2 H), 7.68 – 7.50 (m, 10 H), 7.29 – 7.18 (m, 1 H), 6.51 (dt, *J* = 7.6, 0.9 Hz, 1 H), 6.41 (dd, *J* = 3.9, 1.2 Hz, 1 H), 6.35 (dd, *J* = 3.8, 2.2 Hz, 1 H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 161.2, 139.6, 136.3, 135.7, 134.3, 133.8, 132.8, 131.1, 130.7, 129.99 (t, *J* = 3.2 Hz), 129.8, 129.7, 129.5, 129.2, 128.8, 128.3, 126.5, 124.7, 123.9, 122.2, 114.9.

^{19}F-NMR (376 MHz, $CDCl_3$): δ = -137.63 (dd, *J* = 60.2, 29.0 Hz).

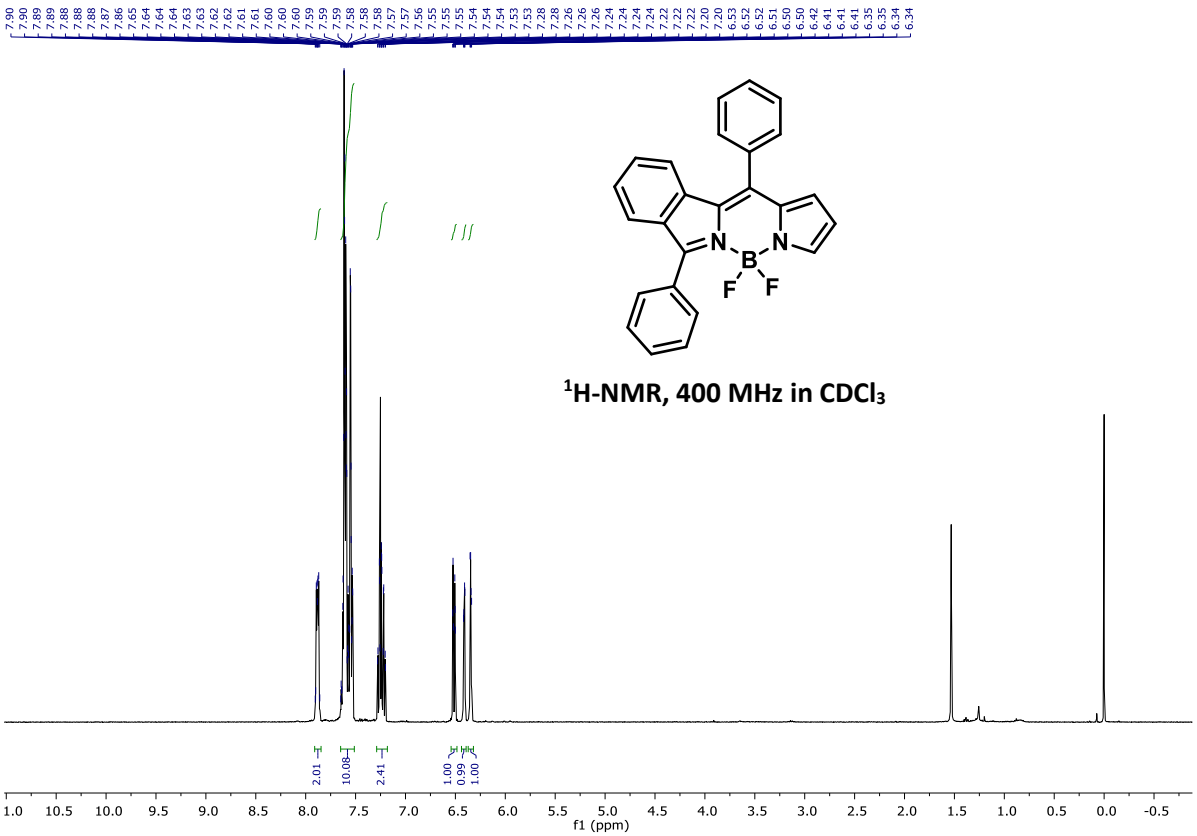
^{11}B-NMR (128 MHz, $CDCl_3$): δ = 1.43 (t, *J* = 30.4 Hz).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2921, 2853, 1607, 1554, 1520, 1392, 1033.

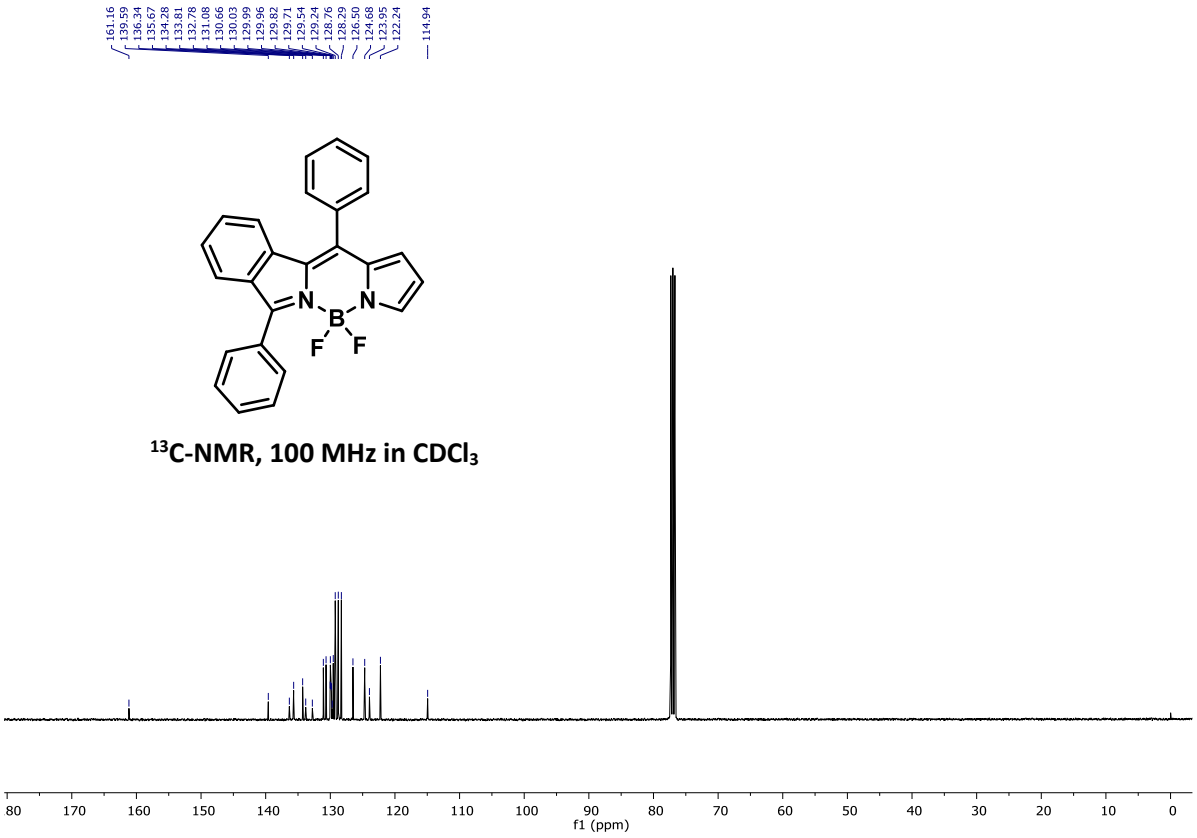
HRMS (ESI): $C_{25}H_{17}BF_2N_2$ calcd.: 417.1345 found: 417.1349, $[M+Na]^+$.

UV/Vis (0.0041 mg/mL in CH_2Cl_2): λ_{max} [nm] (log ε) = 540 (4.70).

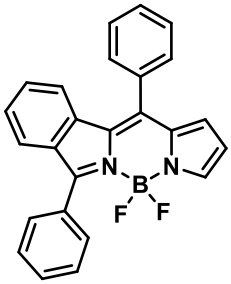
Emission (CH_2Cl_2): λ_{max} (nm) = 571.



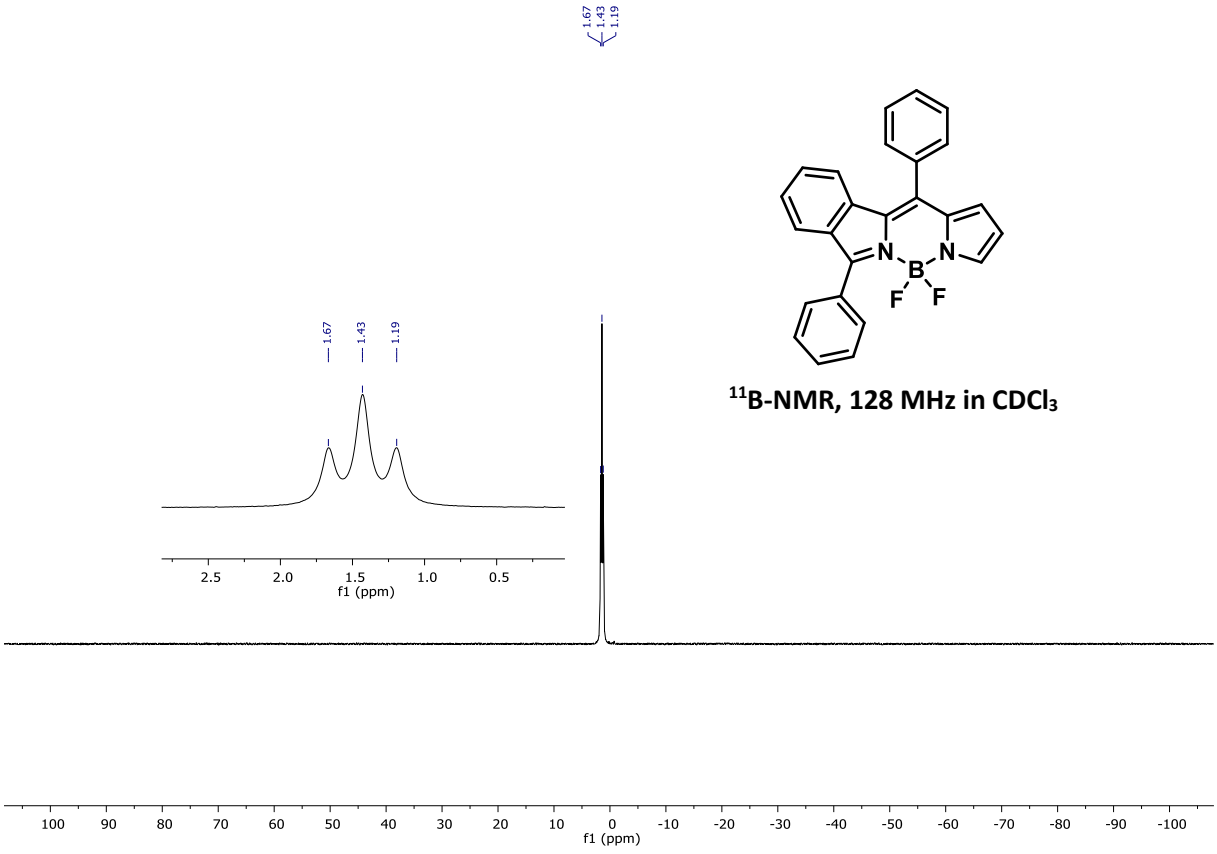
^{1}H-NMR, 400 MHz in $CDCl_3$



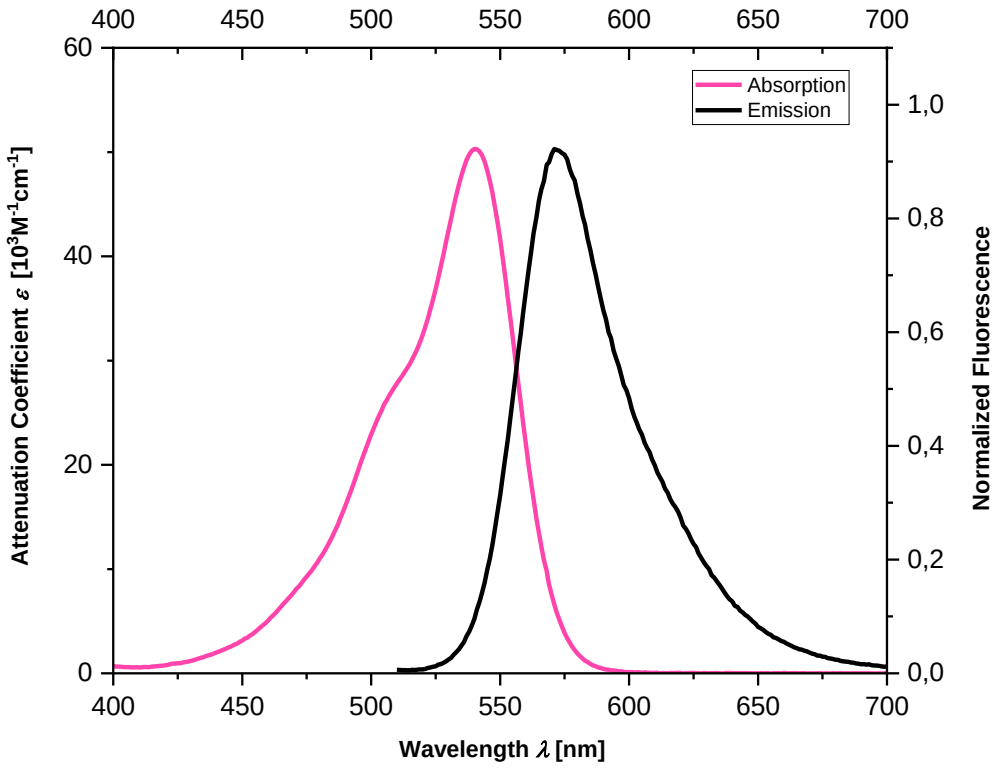
^{13}C-NMR, 100 MHz in $CDCl_3$



^{19}F-NMR, 376 MHz in $CDCl_3$

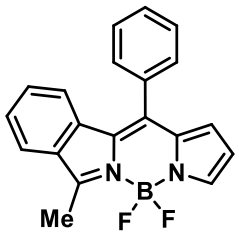


^{11}B-NMR, 128 MHz in $CDCl_3$



UV-Vis and normalized **fluorescence spectra** of **5a** at room temperature in CH_2Cl_2.

5,5-Difluoro-7-methyl-12-phenyl-5*H*-5λ^4,6λ^4-pyrrolo[1',2':3,4][1,3,2]diazaborinino[6,1-*a*]isoindole (5b)



Precursor **1b** (43 mg, 0.10 mmol, 1.0 eq.) was reacted with *N*-Boc-2-pyrroleboronic acid (64 mg, 0.30 mmol, 3.0 eq.) according to **GP5** for 1h. The crude product was then subjected to **GP6** (reaction time: 16 h). Without further purification the product was reacted according to **GP7** for 10 min. After purification by flash column chromatography on silica gel (*n*-pentane/EtOAc 10:1 → 5:1 and *n*-pentane/CH_2Cl_2 3:1 → 1:1) the title compound was obtained as an orange solid (11 mg, 0.033 mmol, 33%).

m.p.: 207 °C

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.74 (dt, *J* = 7.9, 1.1 Hz, 1 H), 7.62 – 7.52 (m, 4 H), 7.50 – 7.46 (m, 2 H), 7.30 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1 H), 7.22 (ddd, *J* = 8.2, 7.1, 1.2 Hz, 1 H), 6.50 (dt, *J* = 8.1, 1.0 Hz, 1 H), 6.35 – 6.30 (m, 2 H), 3.01 (t, *J* = 1.3 Hz, 3 H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 162.8, 137.7, 135.9, 134.1, 134.1, 133.5, 132.8, 131.4, 129.4, 129.2, 129.1, 128.7, 126.4, 123.0, 122.5, 122.4, 114.3, 13.33 (t, *J* = 2.9 Hz).

^{19}F-NMR (376 MHz, $CDCl_3$): δ = -144.63 (dd, *J* = 61.9, 30.3 Hz, 2 F).

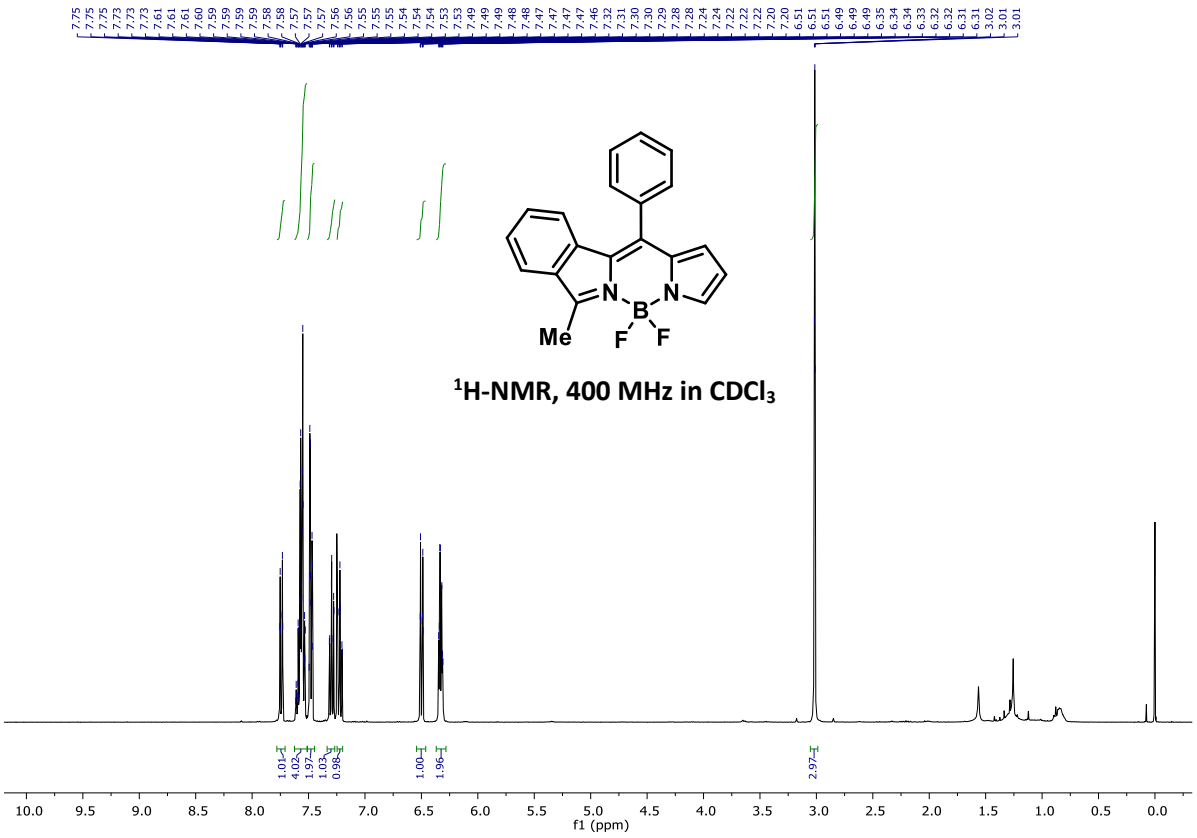
^{11}B-NMR (128 MHz, $CDCl_3$): δ = 1.38 (t, *J* = 31.1 Hz, 1 B).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3065, 2921, 2854, 1580, 1393, 1069, 1027, 722.

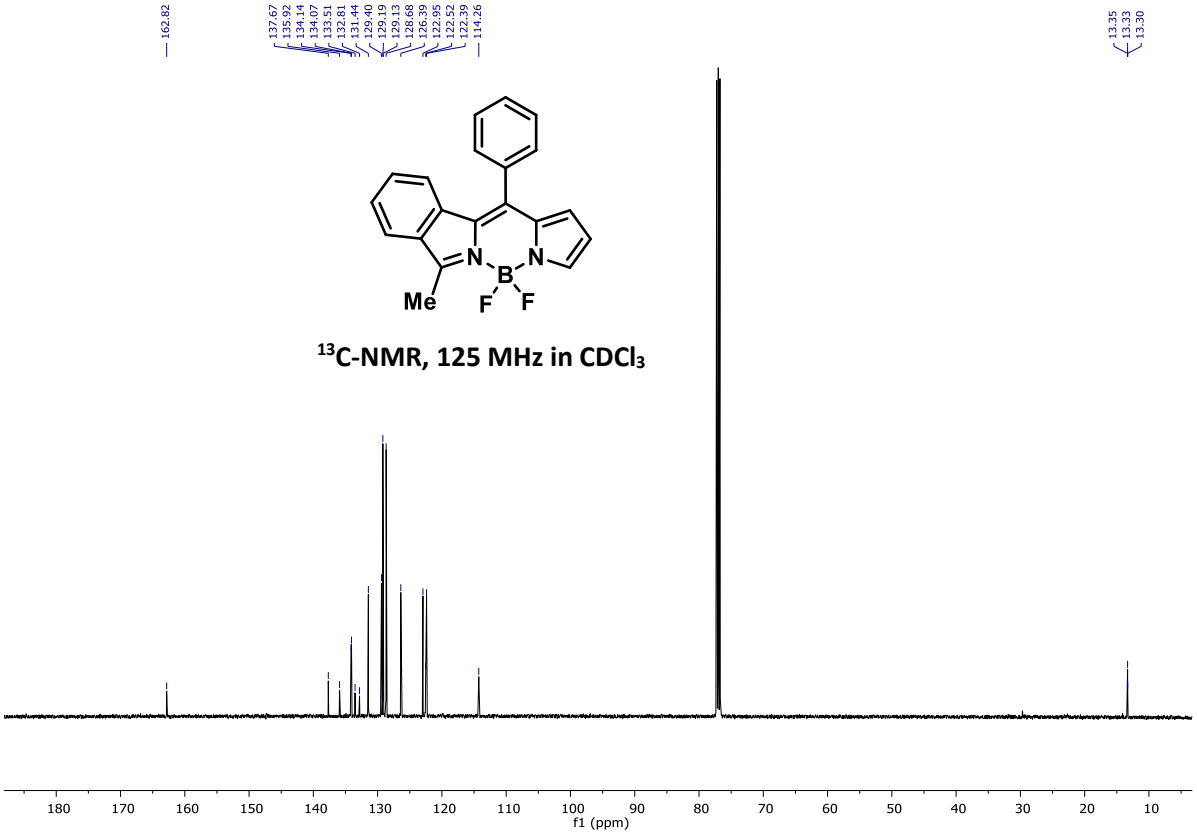
HRMS (ESI): $C_{20}H_{15}BF_2N_2$ calcd.: 333.1369 found: 333.1370, $[M+Na]^+$.

UV/Vis (0.0040 mg/mL in CH_2Cl_2): λ_{max} [nm] (log ε) = 517 (4.58).

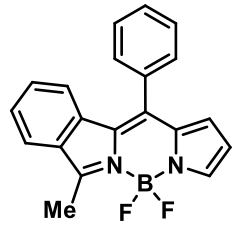
Emission (CH_2Cl_2): λ_{max} (nm) = 542.



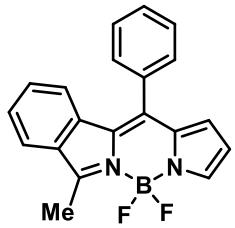
^{1}H-NMR, 400 MHz in $CDCl_3$



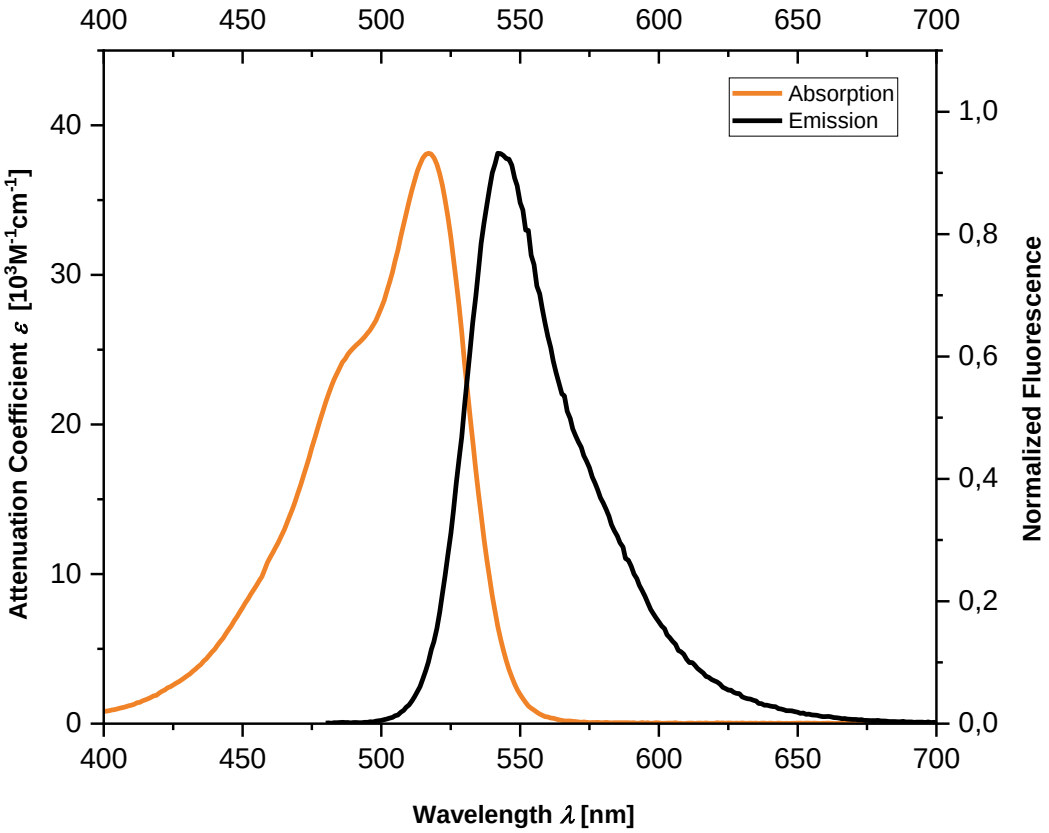
^{13}C-NMR, 125 MHz in $CDCl_3$



^{19}F-NMR, 376 MHz in $CDCl_3$

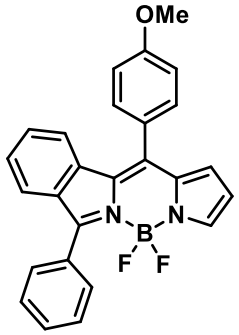


^{11}B-NMR, 128 MHz in $CDCl_3$



UV-Vis and normalized **fluorescence spectra** of **5b** at room temperature in CH_2Cl_2.

5,5-Difluoro-12-(4-methoxyphenyl)-7-phenyl-5*H*-5λ^4,6λ^{4}pyrrolo[1',2':3,4][1,3,2]diazaborinino[6,1-*a*]isoindole (5c)



First step (**Method A**):

Precursor **1c** (58 mg, 0.10 mmol, 1.0 eq.) was reacted with *N*-Boc-2-pyrroleboronic acid (64 mg, 0.30 mmol, 3.0 eq.) according to **GP5** for 1 h.

First step (**Method B**):

Precursor **1g** (58.01 mg, 0.10 mmol, 1.00 eq.) was reacted with *p*-methoxyphenyl boronic acid (45.59 mg, 0.30 mmol, 3.00 eq.) according to **GP5** for 1 h.

Continuing steps (**Methods A + B**):

The crude product was subjected to **GP6** (reaction time: 16 h). Without further purification the product was reacted according to **GP7** (reaction time: 10 min). After purification by flash column chromatography on silica gel (*n*-pentane: EtOAc 10:1 → 5:1) the title compound was obtained as a bright red solid (**method A**: 16.4 mg, 0.039 mmol, 39%; **method B**: 9.3 mg, 22 µmol, 22%).

m.p.: 217 °C.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.94 – 7.83 (m, 2 H), 7.65 – 7.57 (m, 4 H), 7.54 (dd, J = 2.2, 1.3 Hz, 1 H), 7.51 – 7.45 (m, 2 H), 7.31 – 7.22 (m, 2 H), 7.15 – 7.06 (m, 2 H), 6.73 – 6.65 (m, 1 H), 6.46 (dd, J = 3.8, 1.2 Hz, 1 H), 6.35 (dd, J = 3.8, 2.2 Hz, 1 H), 3.96 (s, 3 H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 160.7, 139.8, 136.4, 135.5, 134.1, 131.0, 130.8, 130.6, 130.0, 129.9, 128.3, 126.4, 126.4, 124.6, 123.9, 122.3, 114.9, 114.2, 55.5.

^{19}F-NMR (470 MHz, $CDCl_3$): δ = -137.74 (dd, *J* = 59.8, 28.3 Hz).

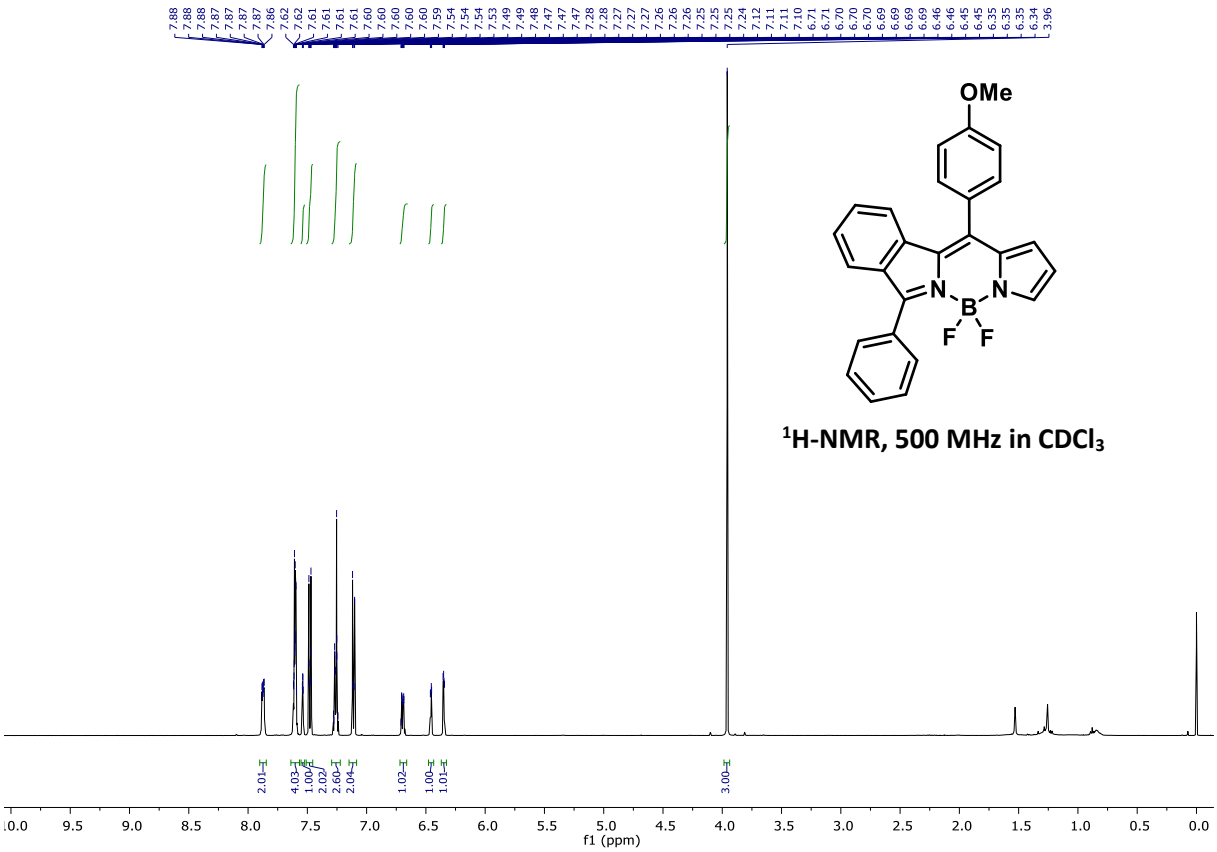
^{11}B-NMR (160 MHz, $CDCl_3$): δ = 1.41 (t, *J* = 30.4 Hz).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3109, 2919, 2845, 1603, 1553, 1389, 1248, 1181, 1021.

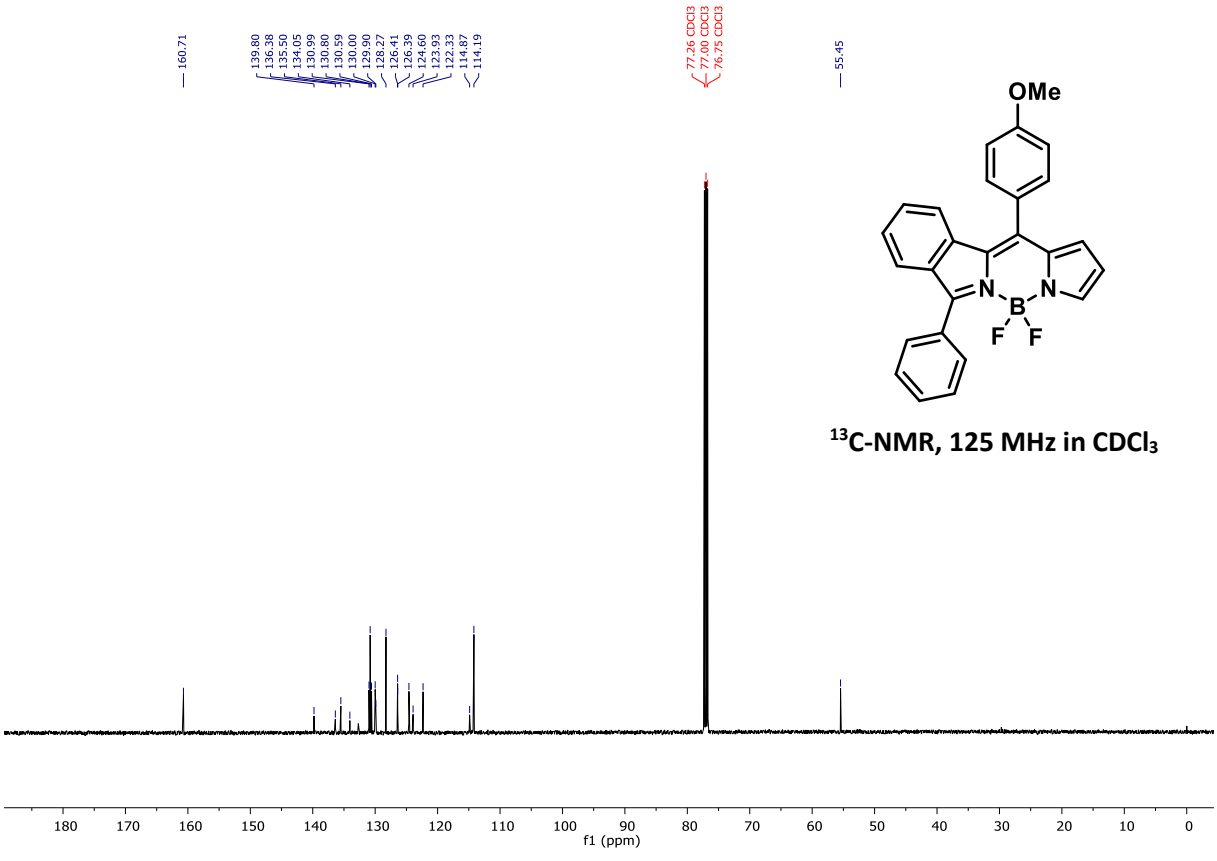
HRMS (ESI): $C_{26}H_{19}BF_2N_2O$ calcd.: 425.1631 found: 425.1633, $[M+Na]^+$.

UV/Vis (0.0069 mg/mL in CH_2Cl_2): λ_{max} [nm] (log ε) = 541 (4.67).

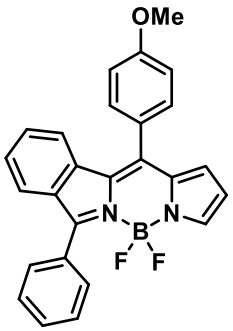
Emission (CH_2Cl_2): λ_{max} (nm) = 574.



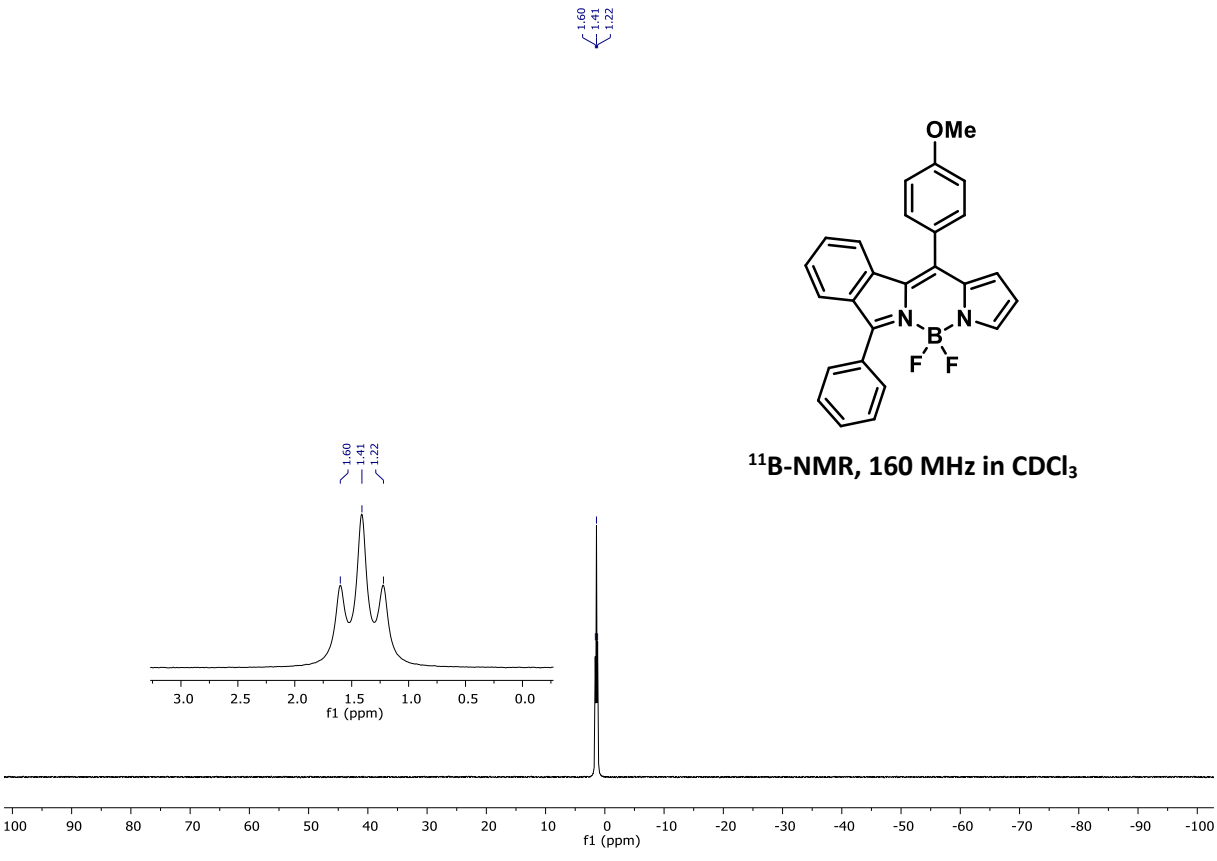
^{1}H-NMR, 500 MHz in $CDCl_3$



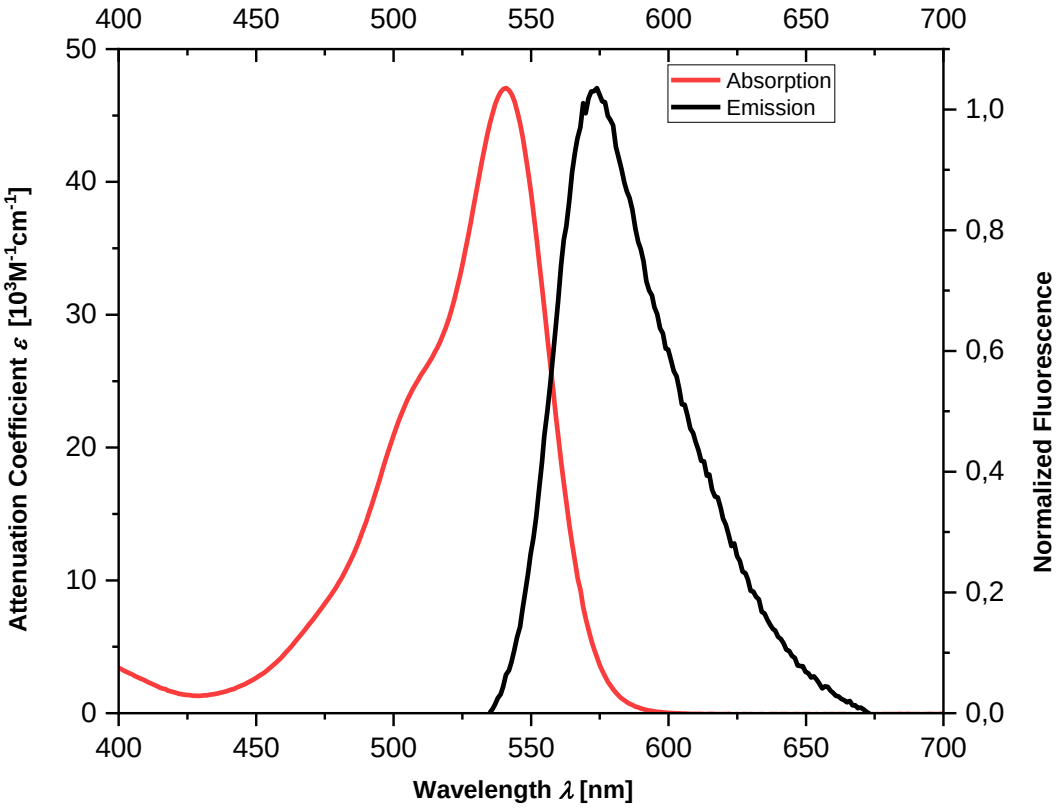
^{13}C-NMR, 125 MHz in $CDCl_3$



^{19}F-NMR, 470 MHz in $CDCl_3$

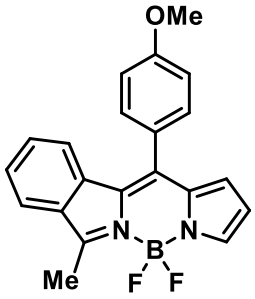


^{11}B-NMR, 160 MHz in $CDCl_3$



UV-Vis and normalized **fluorescence spectra** of **5c** at room temperature in CH_2Cl_2.

5,5-Difluoro-12-(4-methoxyphenyl)-7-methyl-5*H*-5λ^4,6λ^4-pyrrolo[1',2':3,4][1,3,2]diazaborinino[6,1-*a*]isoindole (5d)



First step (**Method A**):

Precursor **1d** (45 mg, 0.10 mmol, 1.0 eq.) was reacted with *N*-Boc-2-pyrroleboronic acid (64 mg, 0.30 mmol, 3.0 eq.) according to **GP5** for 2.5 h.

First step (**Method B**):

Precursor **1h** (52 mg, 0.10 mmol, 1.00 eq.) was reacted with *p*-methoxyphenyl boronic acid (45.59 mg, 0.30 mmol, 3.00 eq.) according to **GP5** for 1 h.

Continuing steps (**Methods A + B**):

The crude product was then subjected to **GP6** (reaction time: 16 h). Without further purification, the product was reacted according to **GP7** (reaction time: 15 min). After purification by flash column chromatography on silica gel (*n*-pentane/EtOAc 10:1 → 8:1), the title compound was obtained as light red solid (**method A**: 15 mg, 0.042 mmol, 42%; **method B**: 18 mg, 0.050 mmol, 50%).

m.p.: 143 °C**.**

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.75 (dt, *J* = 7.9, 1.1 Hz, 1 H), 7.55 (t, *J* = 1.8 Hz, 1 H), 7.45 – 7.39 (m, 2 H), 7.33 – 7.23 (m, 2 H), 7.15 – 7.03 (m, 2 H), 6.68 (dt, *J* = 8.0, 1.0 Hz, 1 H), 6.39 – 6.29 (m, 2 H), 3.94 (s, 3 H), 3.01 (t, *J* = 1.2 Hz, 3 H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 162.4, 160.6, 137.8, 136.0, 134.0, 133.8, 132.8, 131.4, 130.7, 129.3, 126.3, 126.2, 122.9, 122.5, 114.2, 114.1, 55.4, 13.3.

^{19}F-NMR (470 MHz, $CDCl_3$): δ = -144.77 (dd, J = 61.7, 29.8 Hz).

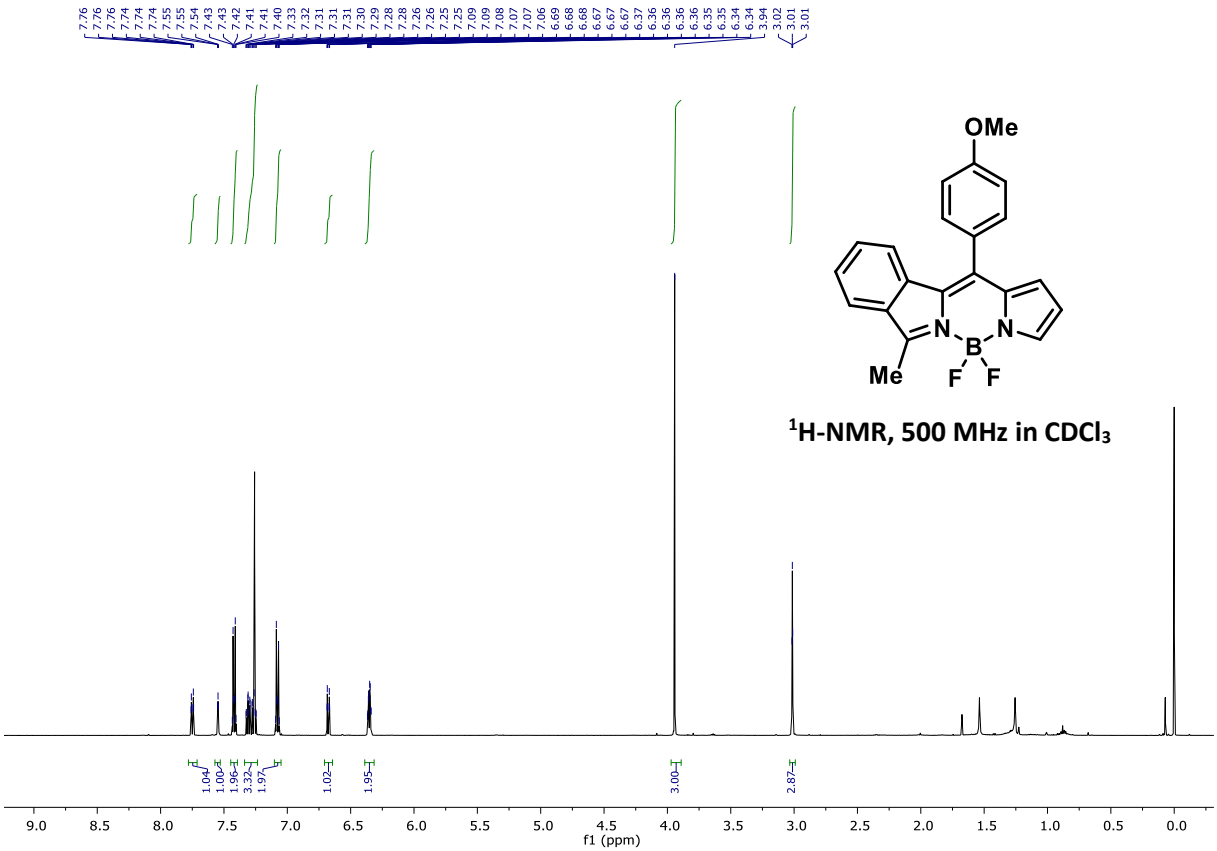
^{11}B-NMR (160 MHz, $CDCl_3$): δ = 1.36 (t, J = 31.1 Hz).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2924, 2845, 1572, 1515, 1391, 1249, 1077, 1025.

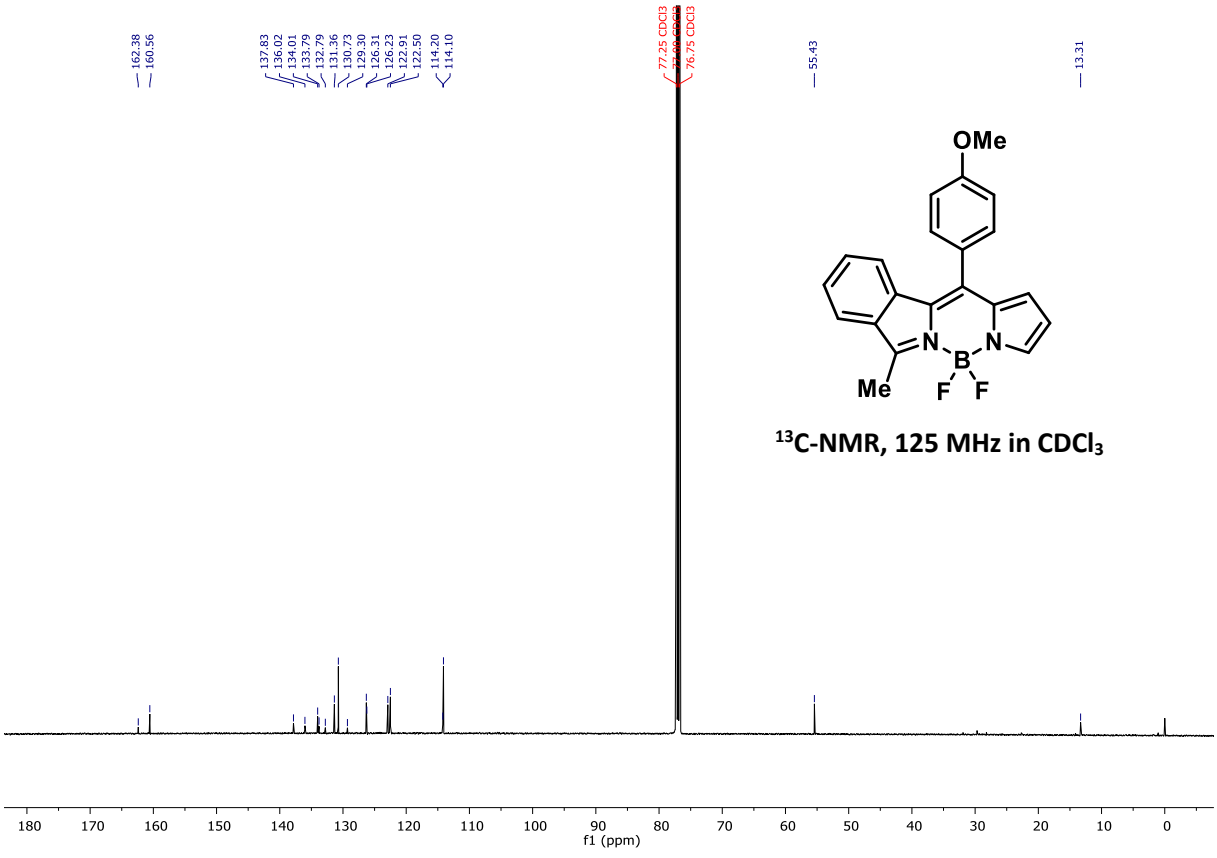
HRMS (ESI): $C_{21}H_{17}BF_2N_2O$ calcd.: 385.1299 found: 385.1297, $[M+Na]^+$.

UV/Vis (0.0072 mg/mL in CH_2Cl_2): λ_{max} [nm] (log ε) = 517 (4.58).

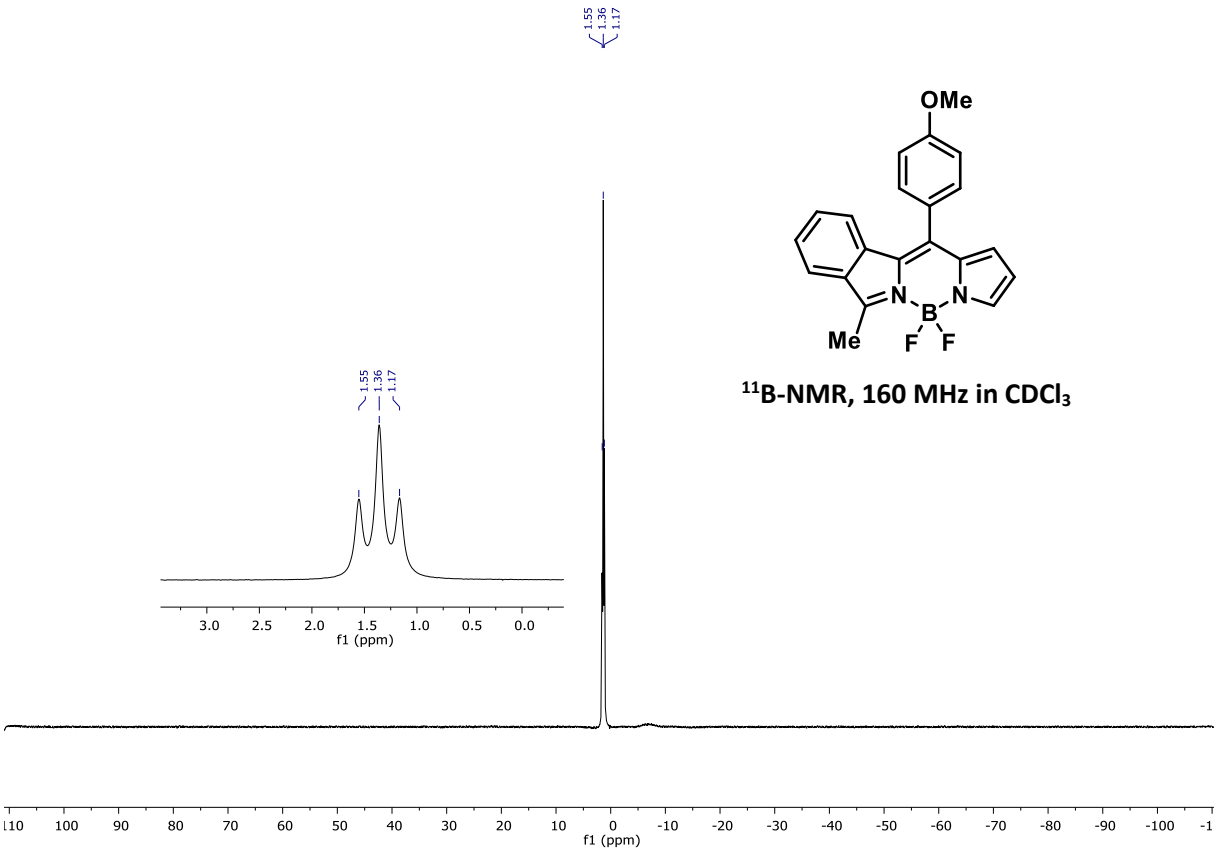
Emission (CH_2Cl_2): λ_{max} (nm) = 543.



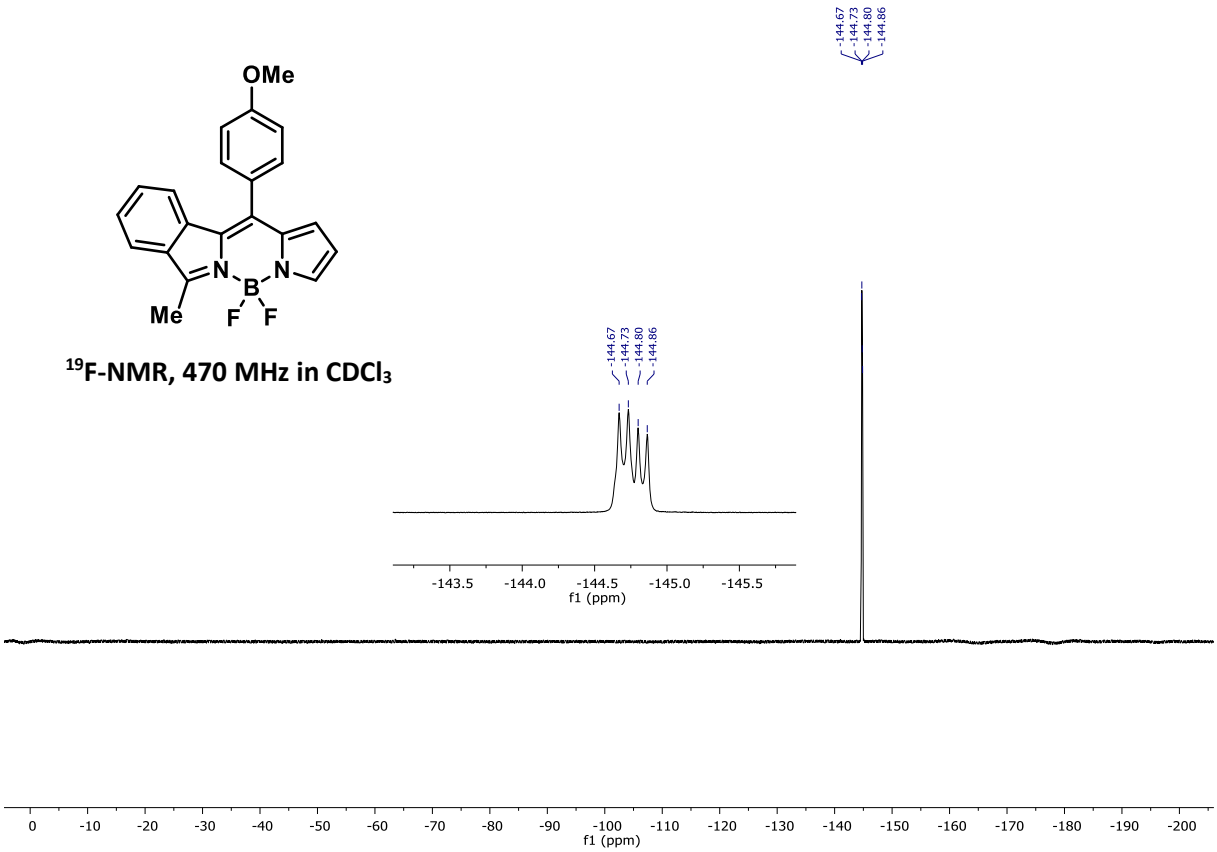
^{1}H-NMR, 500 MHz in $CDCl_3$



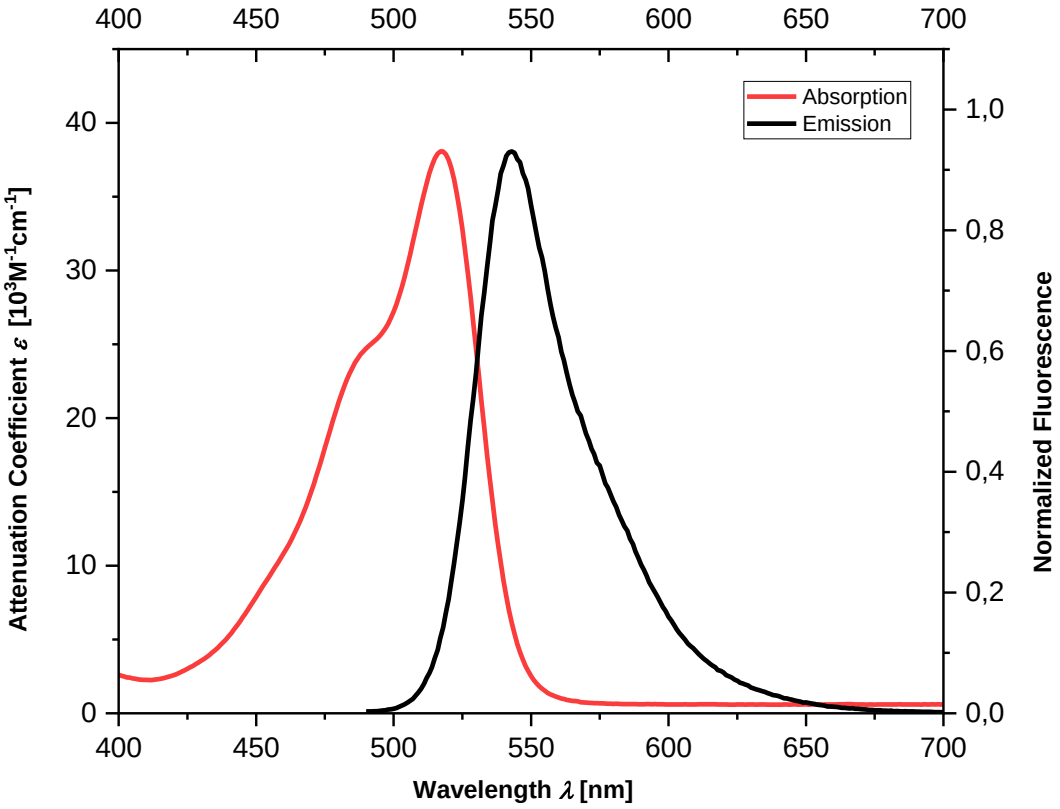
^{13}C-NMR, 125 MHz in $CDCl_3$



^{11}B-NMR, 160 MHz in $CDCl_3$

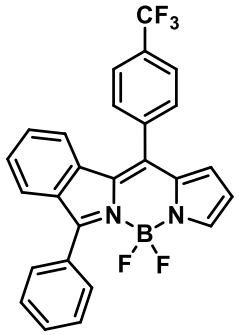


^{19}F-NMR, 470 MHz in $CDCl_3$



UV-Vis and normalized **fluorescence spectra** of **5d** at room temperature in CH_2Cl_2.

5,5-Difluoro-7-phenyl-12-(4-(trifluoromethyl)phenyl)-5*H*-5λ^4,6λ^4-pyrrolo[1',2':3,4][1,3,2]diazaborinino[6,1-*a*]isoindole (5e)



First step (**Method A**):

Precursor **1e** (49 mg, 0.10 mmol, 1.0 eq.) was reacted with *N*-Boc-2-pyrroleboronic acid (64 mg, 0.30 mmol, 3.0 eq.) according to **GP5** for 1 h.

First step (**Method B**):

Precursor **1g** (58 mg, 0.10 mmol, 1.0 eq.) was reacted with (4-(trifluoromethyl)phenyl)boronic acid (57 mg, 0.30 mmol, 3.0 eq.) according to **GP5** for 1 h.

Continuing steps (**Methods A + B**):

The crude product was reacted according to **GP6** for 16 h. Without further purification the product was subjected to **GP7** (reaction time: 15 min). After purification by column chromatography on silica gel (*n*-pentane/EtOAc 50:1 → 20:1, *n*-pentane/EtOAc/CH_2Cl_2 20:1:1 and *n*-pentane/EtOAc/toluene 12:1:1) the title compound was obtained as bright red solid (**method A**: 4.1 mg, 0.009 mmol, 9%; **method B**: 9.2 mg, 0.020 mmol, 20%).

m.p.: 233 °C.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.91 − 7.86 (m, 4 H), 7.70 (d, *J* = 7.9 Hz, 2 H), 7.65 − 7.61 (m, 4 H), 7.58 − 7.56 (m, 1 H), 7.32 − 7.27 (m, 2 H), 6.48 − 6.45 (m, 1 H), 6.37 − 6.35 (m, 1 H), 6.34 − 6.32 (m, 1 H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 162.2, 138.1 − 138.0 (m), 137.4, 136.1, 136.0, 133.3, 133.0, 131.8 (q, $^2J_{C\text{-}F}$ = 33.1 Hz, Cq), 131.5, 130.9, 130.0 (t, $^4J_{C\text{-}F}$ = 3.1 Hz), 129.9, 129.6, 129.5, 128.4, 126.9, 125.9 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 125.7, 123.7, 121.9, 115.2.

^{19}F-NMR (470 MHz, $CDCl_3$): δ = -63.02 (s, 3 F), -145.26 (q, *J* = 29.4 Hz, 2 F).

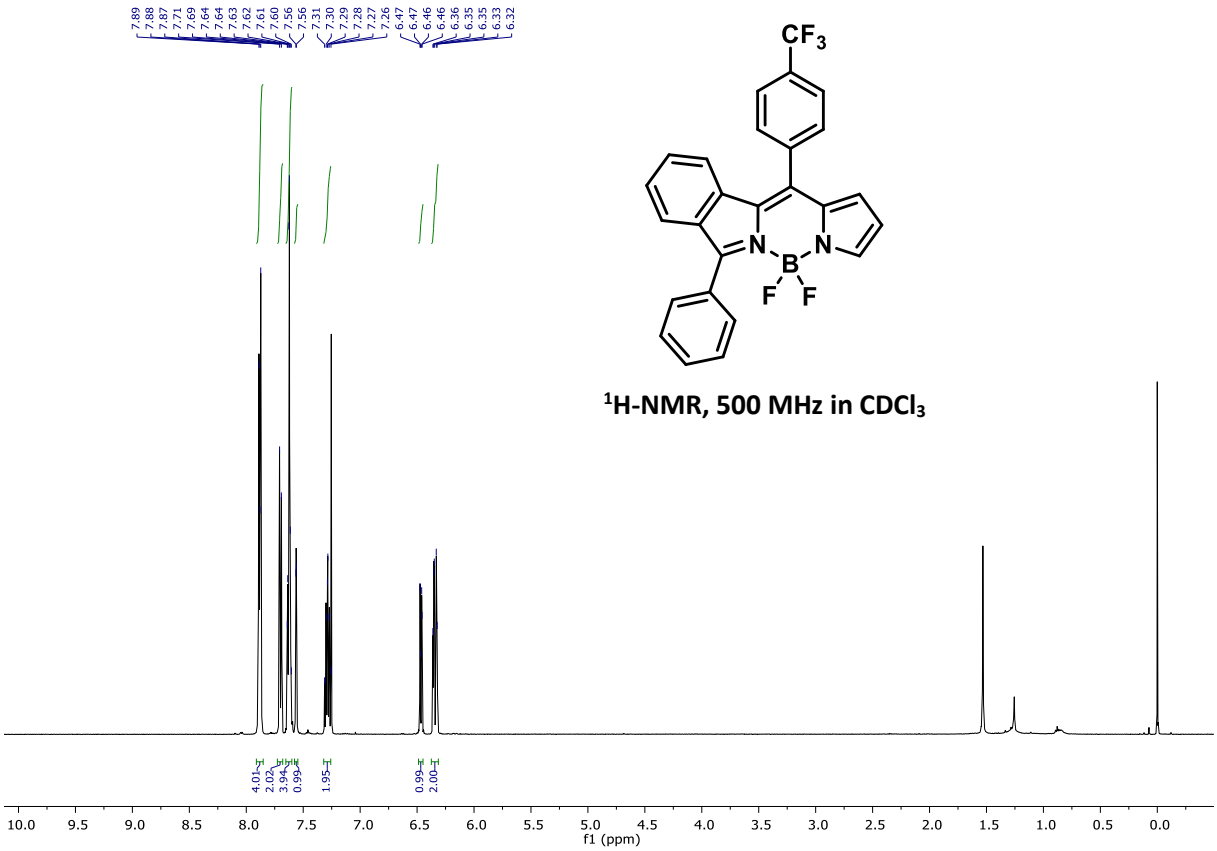
^{11}B-NMR (160 MHz, $CDCl_3$): δ = 1.39 (*t*, *J* = 30.2 Hz, 1 B).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1567, 1397, 1322, 1123, 908, 849, 745, 688.

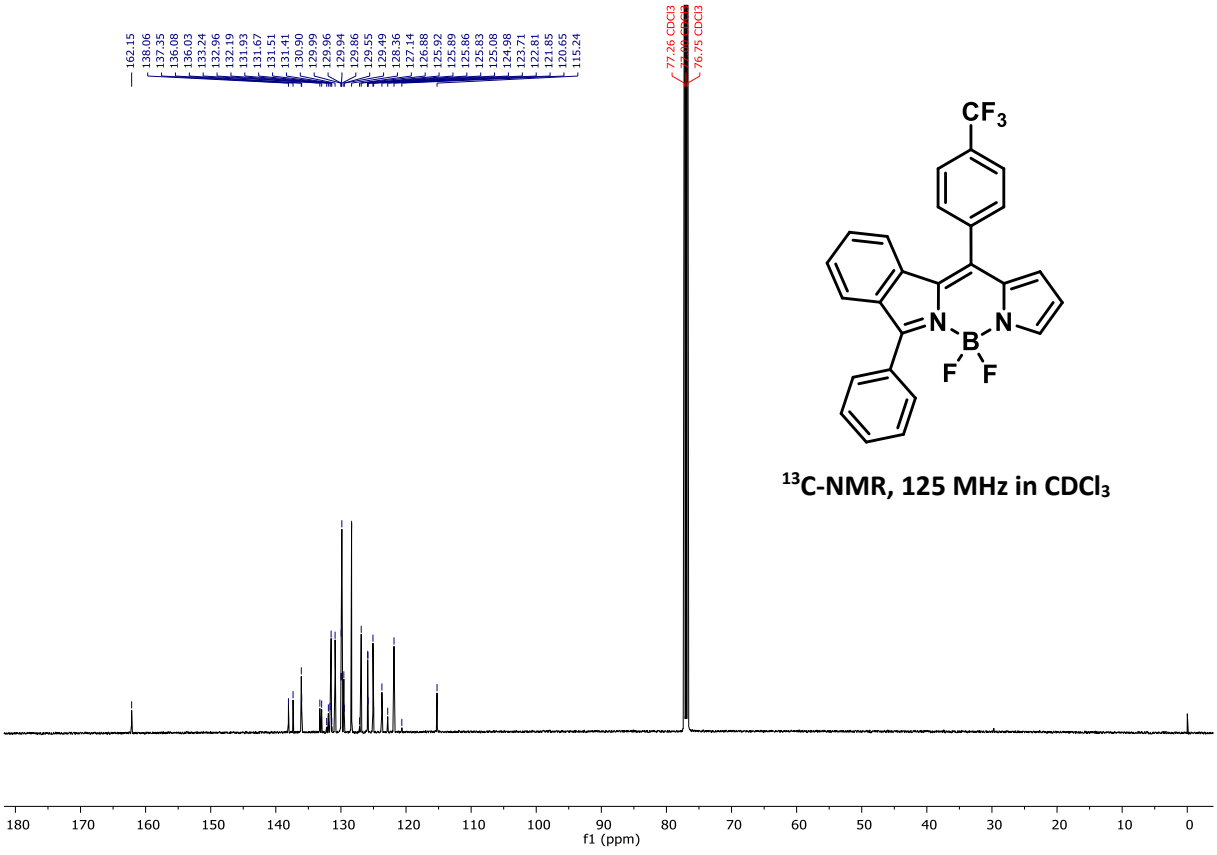
HRMS (ESI): $C_{26}H_{16}BF_5N_2$ calcd.: 485.1224 found: 485.1221, $[M+Na]^+$.

UV/Vis (0.0036 mg/mL in CH_2Cl_2): λ_{max} [nm] (log ε) = 542 (4.63).

Emission (CH_2Cl_2): λ_{max} (nm) = 575.



^{1}H-NMR, 500 MHz in $CDCl_3$



^{13}C-NMR, 125 MHz in $CDCl_3$

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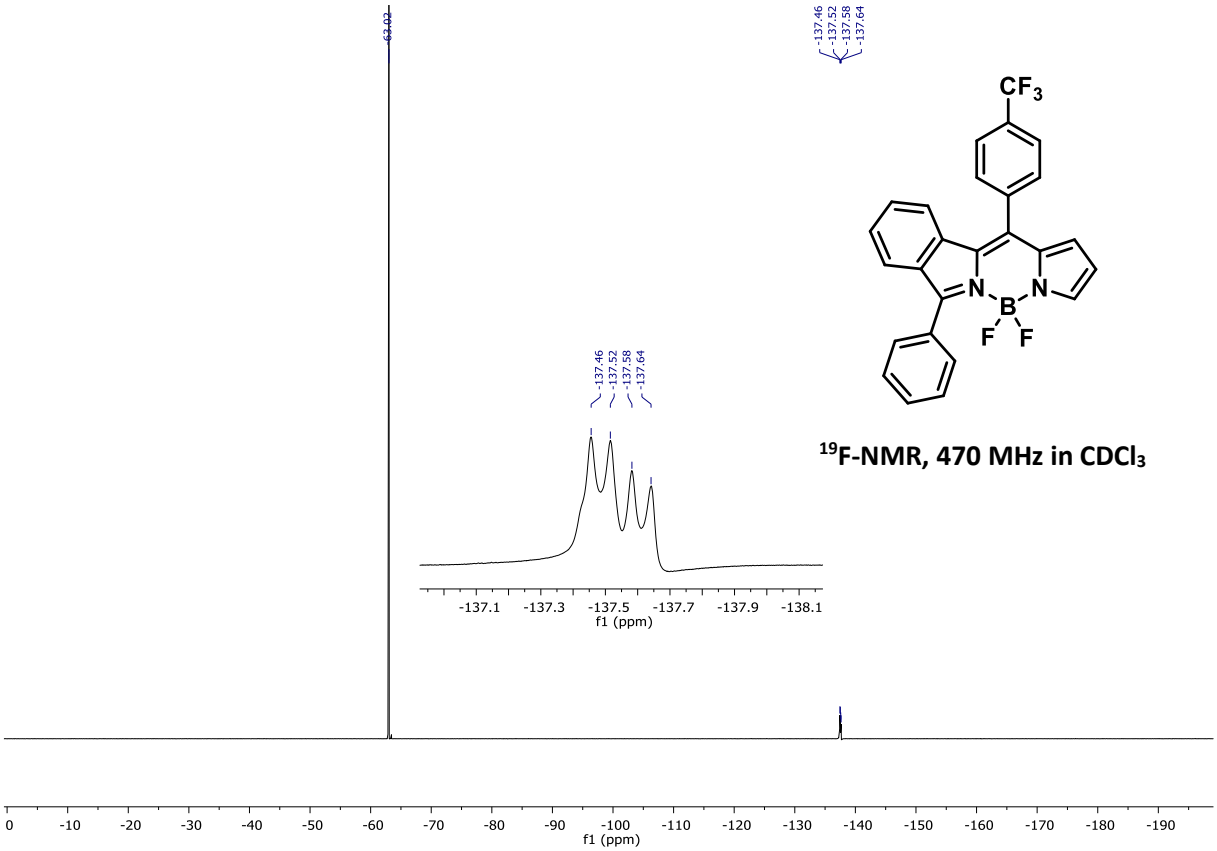
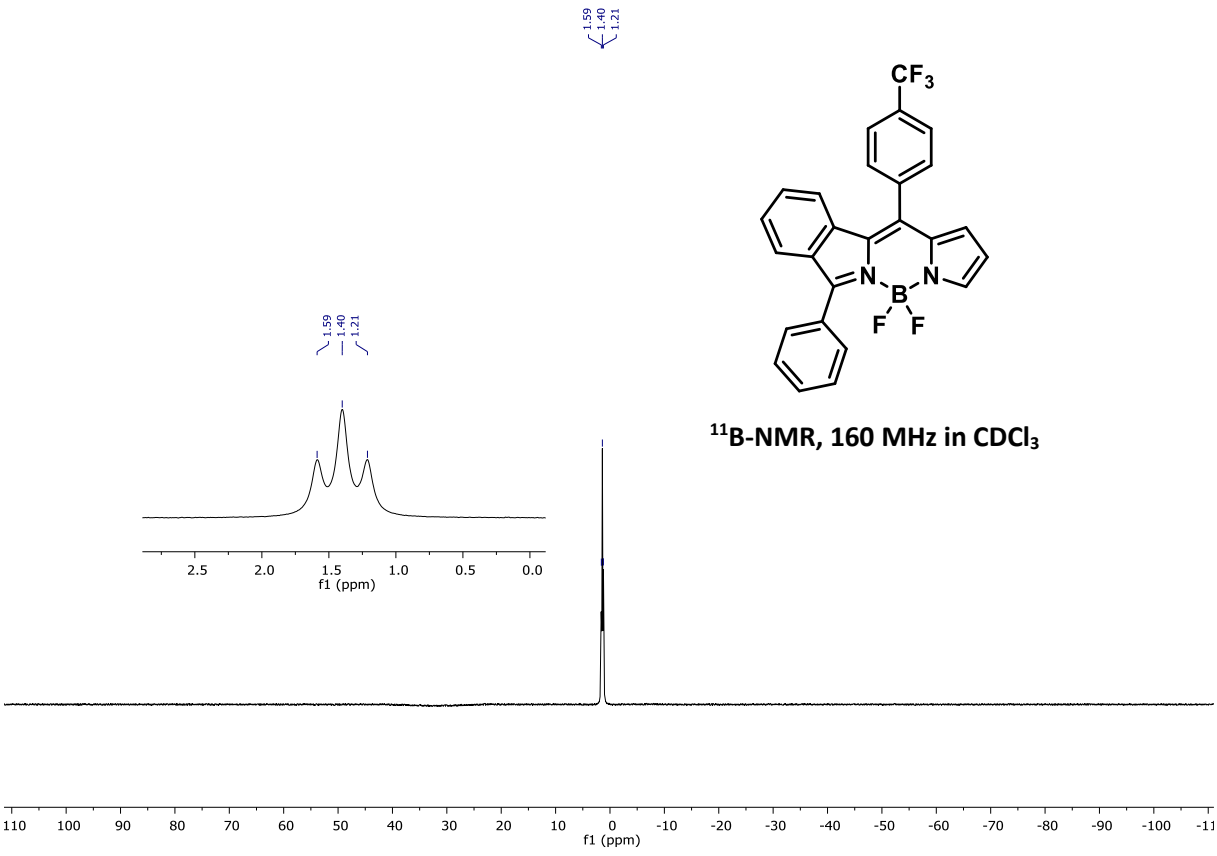
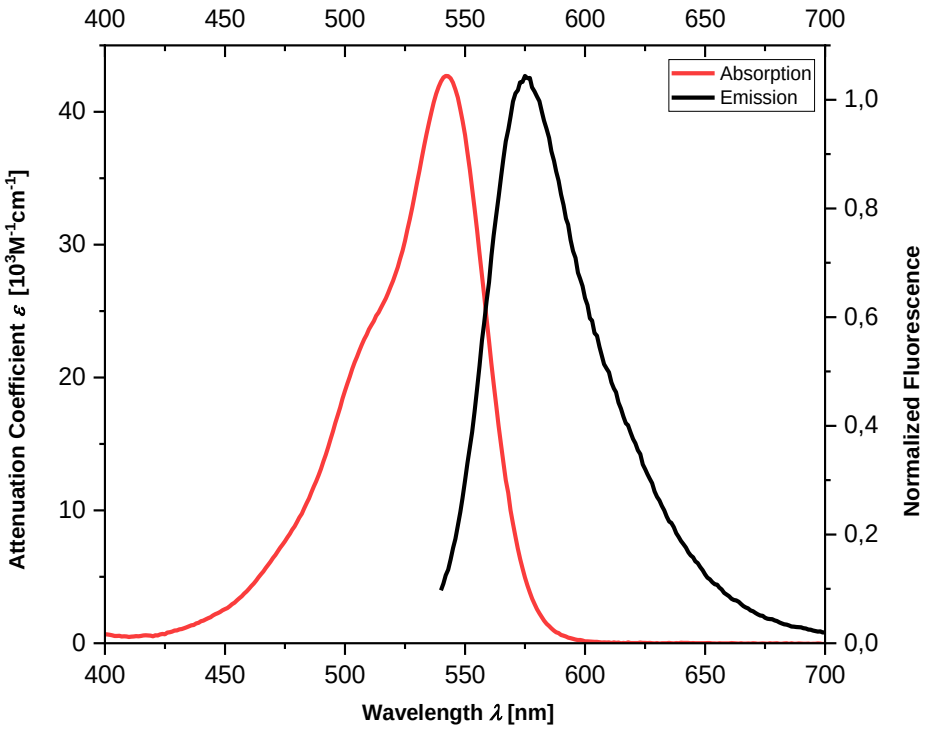


^{19}F-NMR, 470 MHz in $CDCl_3$

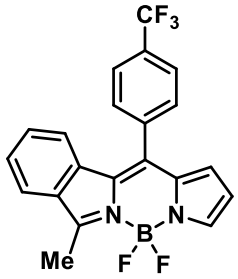


^{11}B-NMR, 160 MHz in $CDCl_3$



UV-Vis and normalized **fluorescence spectra** of **5e** at room temperature in CH_2Cl_2.

5,5-Difluoro-7-methyl-12-(4-(trifluoromethyl)phenyl)-5*H*-5λ^4,6λ^4-pyrrolo[1',2':3,4][1,3,2]diazaborinino[6,1-*a*]isoindole (5f)



First step (**Method A**):

Precursor **1f** (50 mg, 0.10 mmol, 1.0 eq.) was reacted with (*N*-Boc-2-pyrroleboronic acid (64 mg, 0.30 mmol, 3.0 eq.) according to **GP5** for 1 h.

First step (**Method B**):

Precursor **1h** (52 mg, 0.10 mmol, 1.0 eq.) was reacted with (4-(trifluoromethyl)phenyl)boronic acid (57 mg, 0.30 mmol, 3.0 eq.) according to **GP5** for 1 h.

Continuing steps (**Methods A + B**):

The crude product was subjected to **GP6** (reaction time: 16 h). Without further purification, the product was then reacted according to **GP7** (reaction time: 10 min). After purification by flash column chromatography on silica gel (*n*-pentane/EtOAc 10:1 → 5:1 and *n*-pentane/CH_2Cl_2 3:1 → 1:1) the title compound was obtained as a bright red solid (**method A**: 8.8 mg, 22 µmol, 22%, **method B**: 7.9 mg, 0.020 mmol, 20%).

m.p.: 209 °C.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.87 – 7.81 (m, 2 H), 7.78 (dt, *J* = 7.9, 1.0 Hz, 1 H), 7.67 – 7.61 (m, 2 H), 7.57 (t, *J* = 1.7 Hz, 1 H), 7.34 (ddd, *J* = 8.0, 7.2, 1.0 Hz, 1 H), 7.28 (ddd, *J* = 8.2, 7.1, 1.2 Hz, 1 H), 6.45 (dt, *J* = 8.1, 0.9 Hz, 1 H), 6.35 (dd, *J* = 3.8, 2.3 Hz, 1 H), 6.24 (dd, *J* = 3.8, 1.2 Hz, 1 H), 3.03 (t, *J* = 1.3 Hz, 3 H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 163.9, 137.8 (d, $^4J_{C\text{-}F}$ = 1.2 Hz), 135.6, 134.6, 133.0, 133.0, 131.9, 131.68 (d, $^2J_{C\text{-}F}$ = 32.8 Hz), 129.8, 128.9, 126.8, 125.79 (q, $^3J_{C\text{-}F}$ = 3.7 Hz), 123.89 (d, $^1J_{C\text{-}F}$ = 272.4 Hz), 123.3, 122.4, 122.0, 114.6, 13.4.

^{19}F-NMR (470 MHz, $CDCl_3$): δ = -63.04, -144.59 (dd, *J* = 62.3, 30.4 Hz).

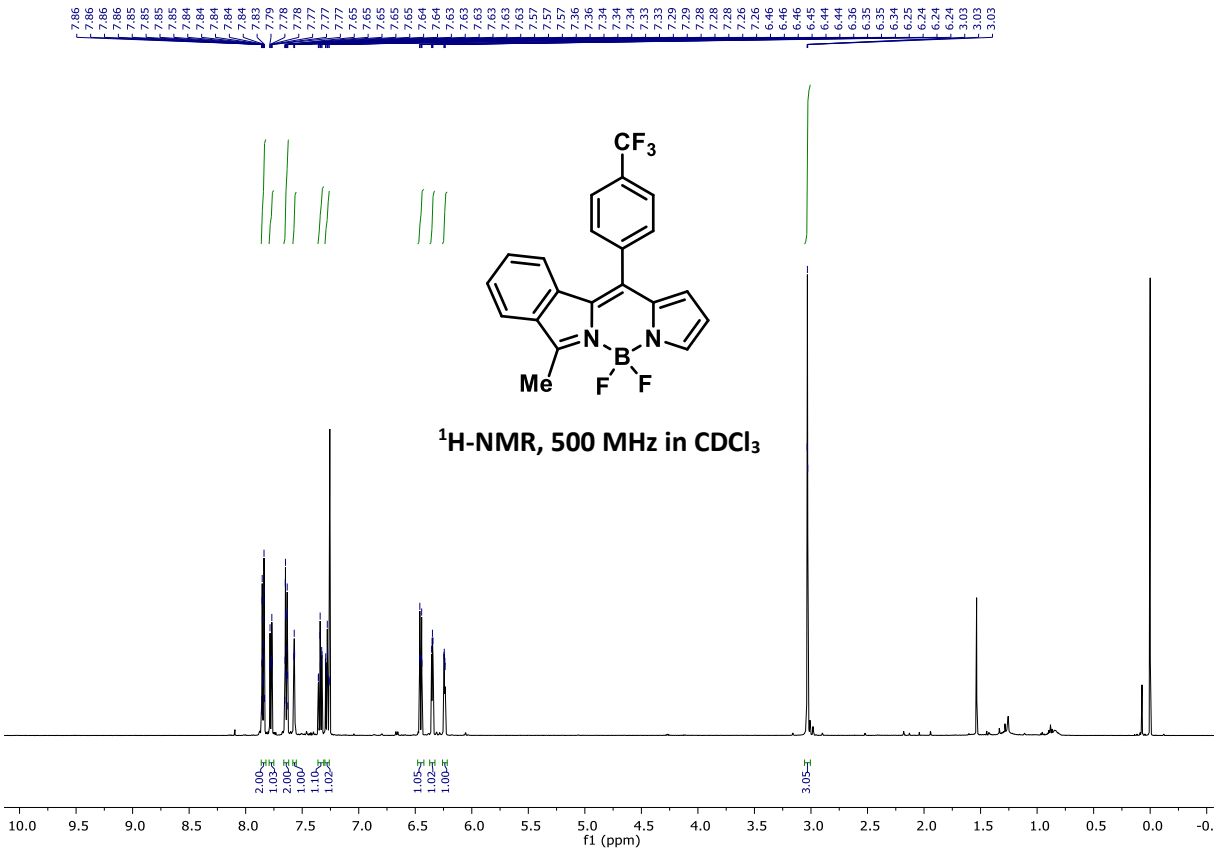
^{11}B-NMR (160 MHz, $CDCl_3$): δ = 1.35 (t, *J* = 30.9 Hz).

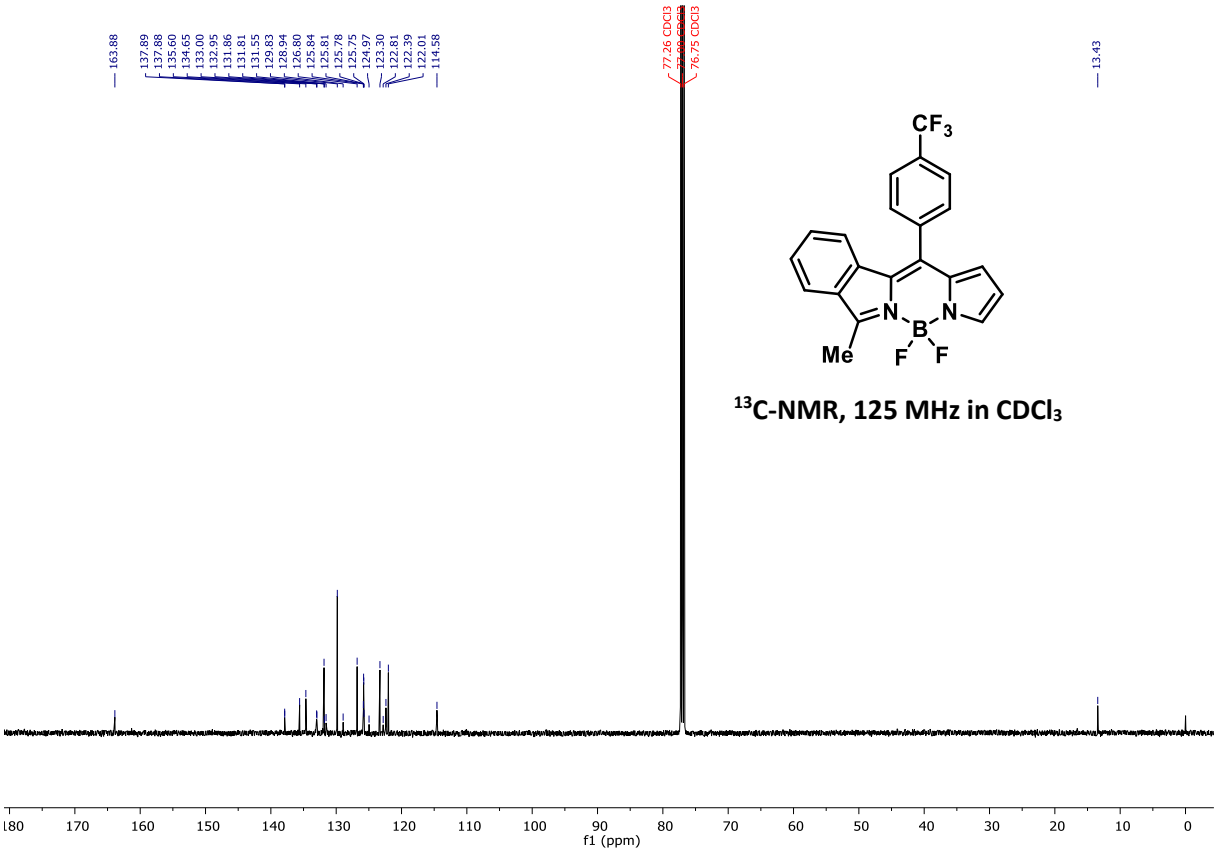
IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3105, 3078, 2926, 1590, 1528, 1393, 1325, 1159, 1035.

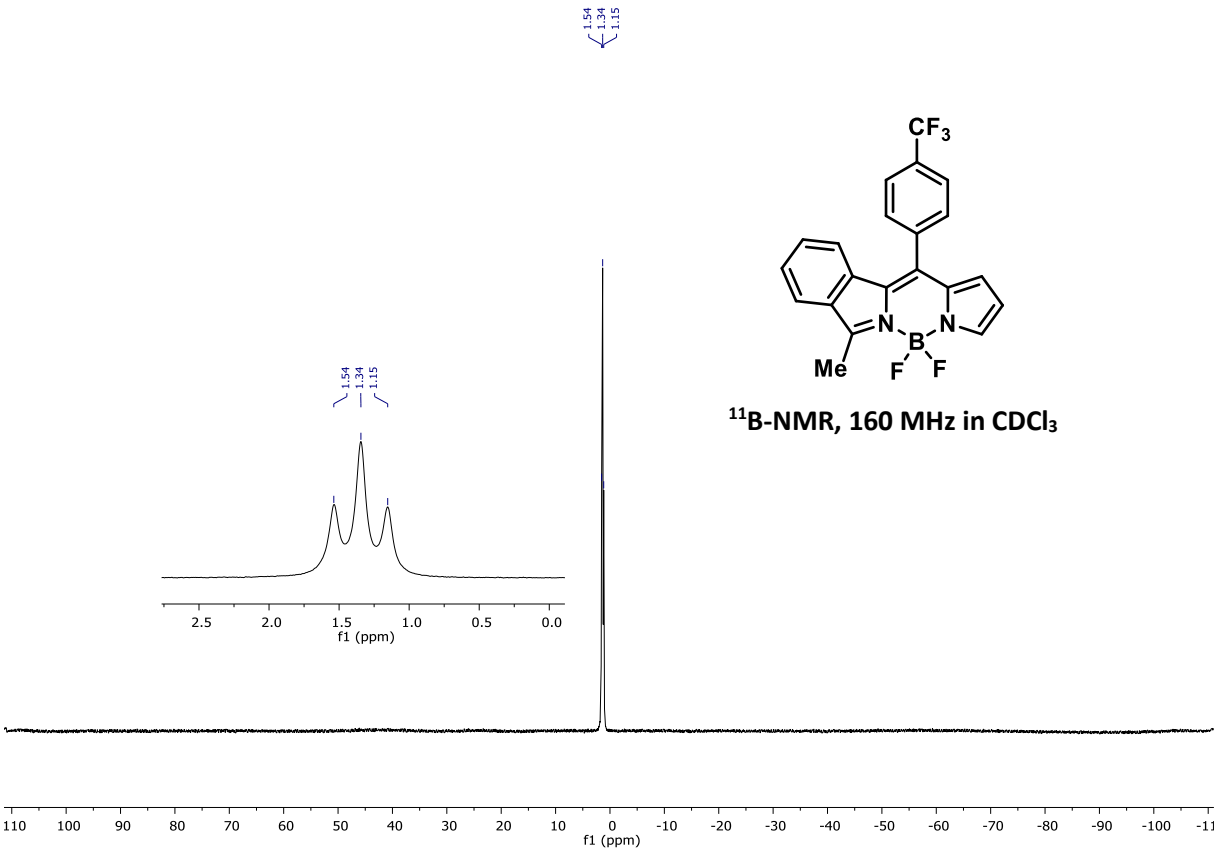
HRMS (ESI): $C_{21}H_{14}BF_5N_2$ calcd.: 381.1180 found 381.1183, $[M+Na]^+$.

UV/Vis (0.0022 mg/mL in CH_2Cl_2): λ_{max} [nm] (log ε) = 519 (4.55).

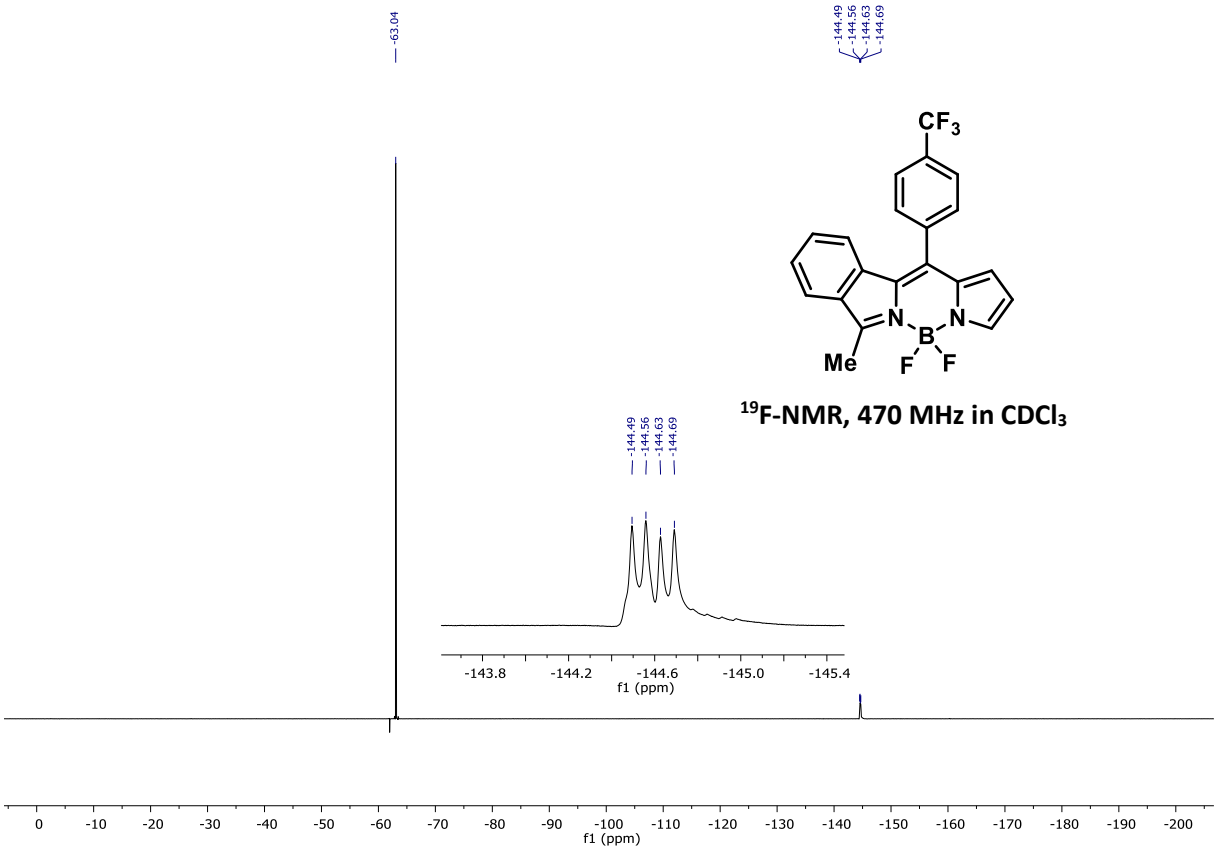
Emission (CH_2Cl_2): λ_{max} (nm) = 545.


CF3
N
B
N
F
F
Me
1H-NMR, 500 MHz in CDCl3
f1 (ppm)

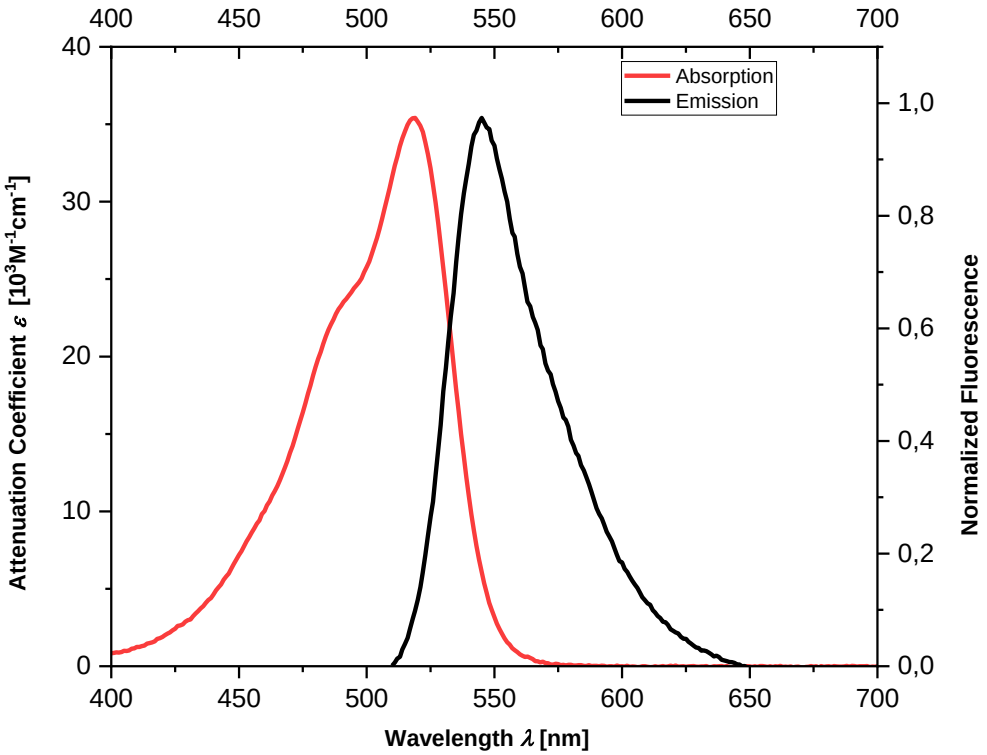

CF3
N
B
N
F
F
Me
13C-NMR, 125 MHz in CDCl3
f1 (ppm)



^{11}B-NMR, 160 MHz in $CDCl_3$

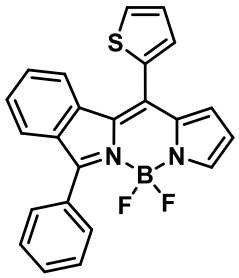


^{19}F-NMR, 470 MHz in $CDCl_3$



UV-Vis and normalized **fluorescence spectra** of **5f** at room temperature in CH_2Cl_2.

5,5-Difluoro-7-phenyl-12-(thien-2-yl)-5*H*-5λ^4,6λ^4-pyrrolo[1',2':3,4][1,3,2]diazaborinino[6,1-a]isoindole (5g)



Precursor **1g** (58 mg, 0.10 mmol, 1.0 eq.) was reacted with thien-2-ylboronic acid (38 mg, 0.30 mmol, 3.0 eq.) according to **GP5** for 1 h. The crude product was then subjected to **GP6** (reaction time: 16 h). The product was reacted without further purification according to **GP7** (reaction time: 10 min). After purification by flash column chromatography on silica gel (*n*-pentane/EtOAc 20:1 → 10:1 and *n*-pentane/CH_2Cl_2 3:1 → 1:1) the title compound was obtained as a dark red solid (10 mg, 0.025 mmol, 25%).

m.p.: 238 °C.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.88 (dd, *J* = 6.7, 3.0 Hz, 2 H), 7.66 (dd, *J* = 5.1, 1.2 Hz, 1 H), 7.63 – 7.57 (m, 4 H), 7.53 (dd, *J* = 2.2, 1.3 Hz, 1 H), 7.36 – 7.26 (m, 4 H), 6.76 – 6.71 (m, 1 H), 6.64 (d, *J* = 3.2 Hz, 1 H), 6.36 (dd, *J* = 3.9, 2.2 Hz, 1 H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 161.8, 136.1, 135.8, 134.1, 133.9, 132.8, 132.2, 131.4, 130.8, 130.0, 130.0, 130.0, 129.8, 129.7, 128.3, 128.2, 127.5, 126.8, 124.8, 123.9, 122.5, 115.0.

^{19}F-NMR (470 MHz, $CDCl_3$): δ = -137.83 (d, *J* = 30.5 Hz).

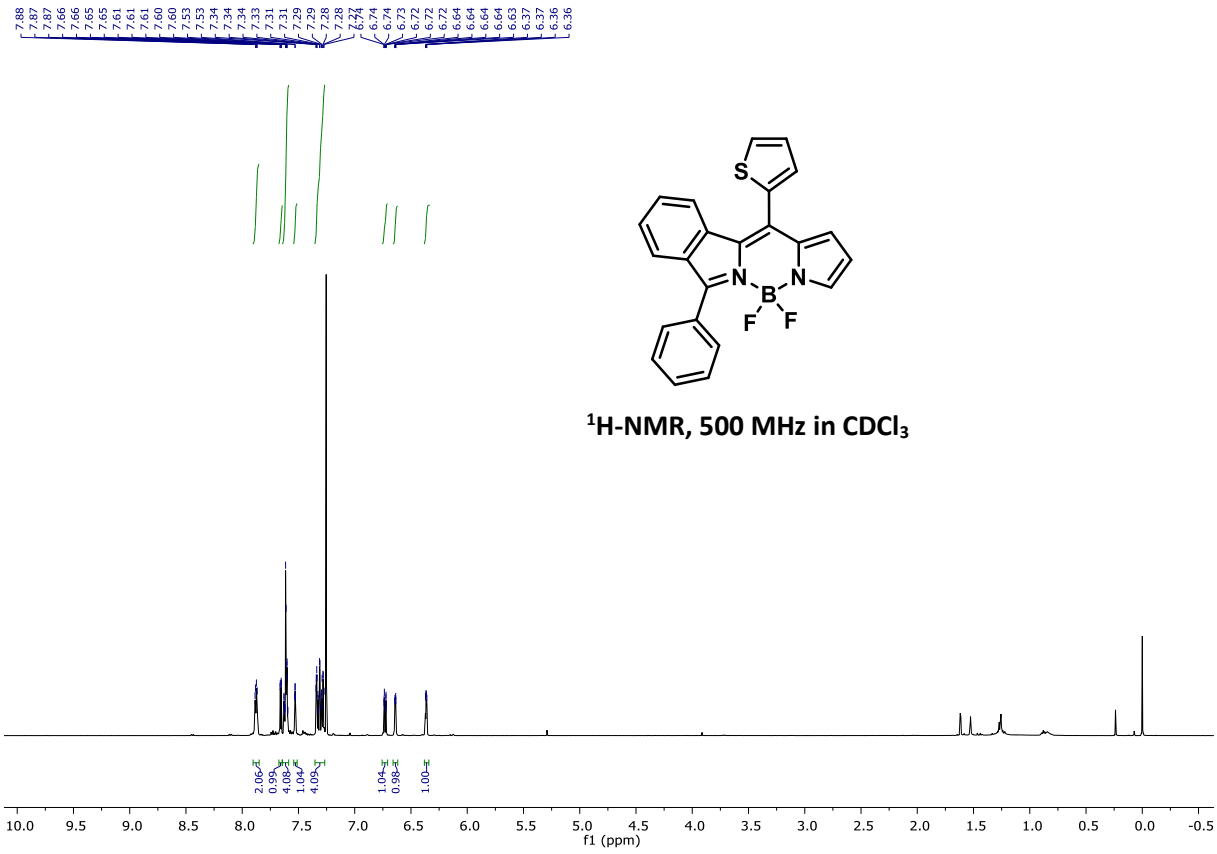
^{11}B-NMR (160 MHz, $CDCl_3$): δ = 1.38 (t, *J* = 30.2 Hz).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3109, 3065, 2919, 2319, 1608, 1560, 1386, 1131, 1029.

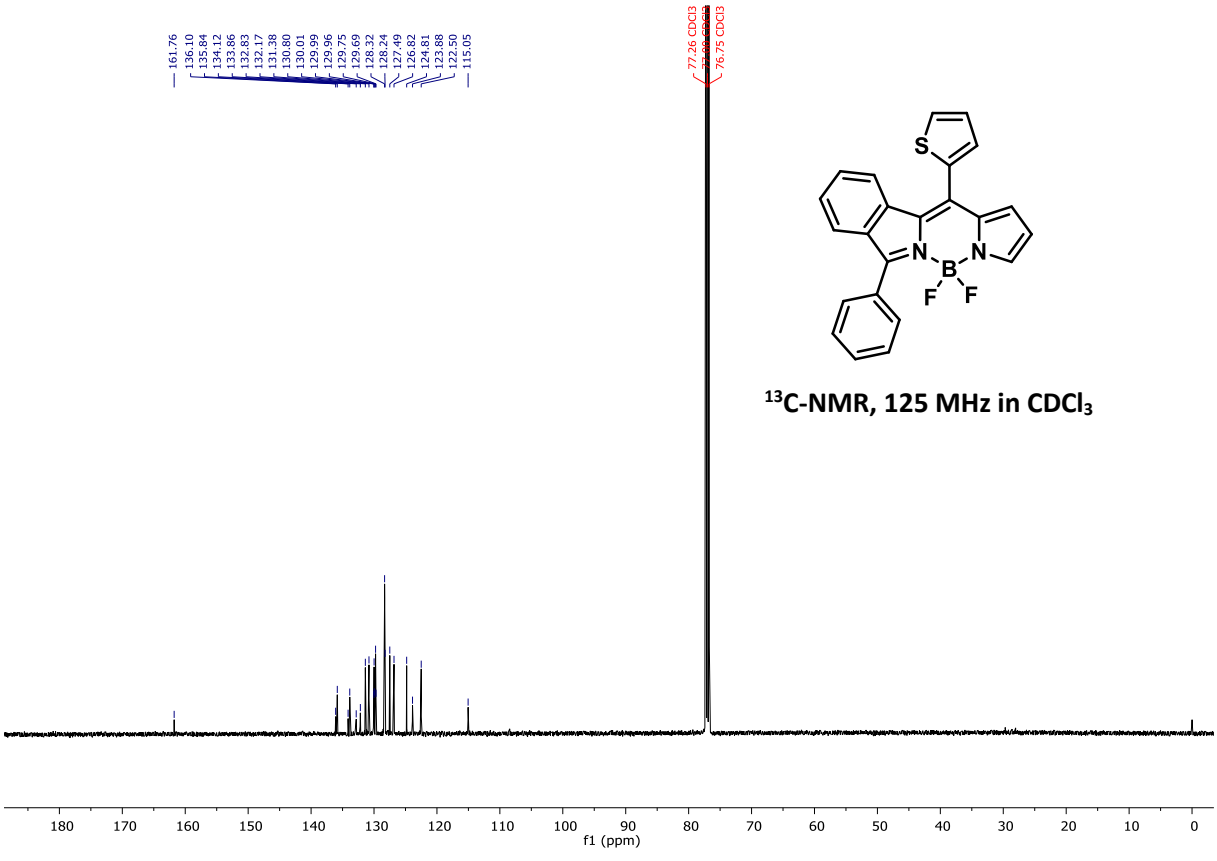
HRMS (ESI): $C_{23}H_{15}BF_2N_2S$ calcd.: 423.0915 found: 423.0913, $[M+Na]^+$.

UV/Vis (0.0020 mg/mL in CH_2Cl_2): λ_{max} [nm] (log ε) = 551 (4.67).

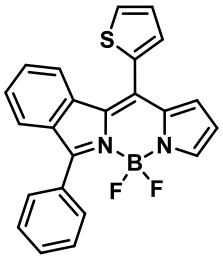
Emission (CH_2Cl_2): λ_{max} (nm) = 573.



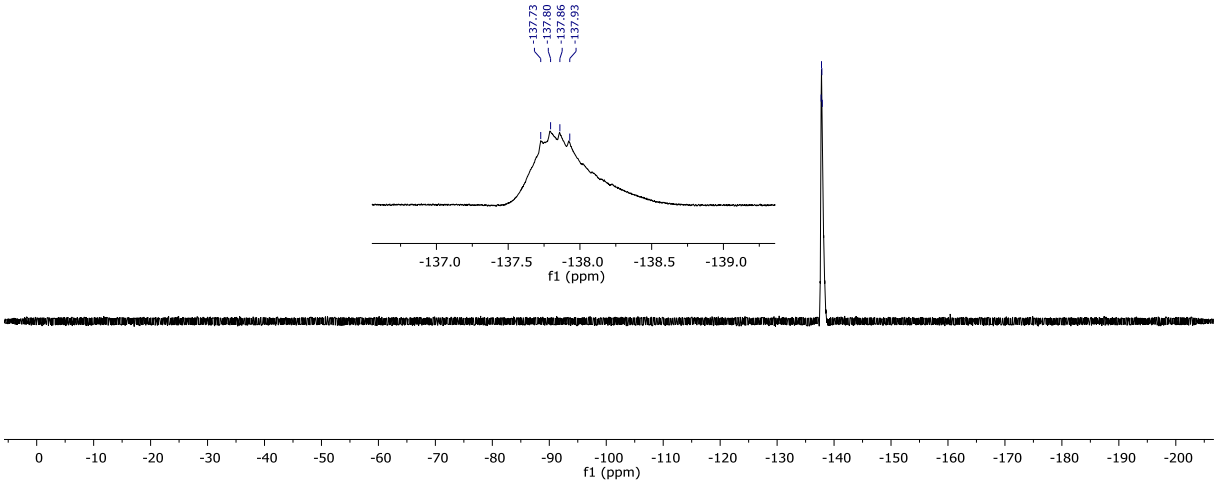
^{1}H-NMR, 500 MHz in $CDCl_3$

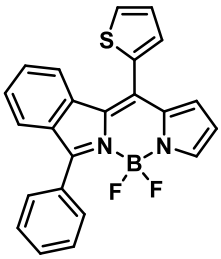


^{13}C-NMR, 125 MHz in $CDCl_3$

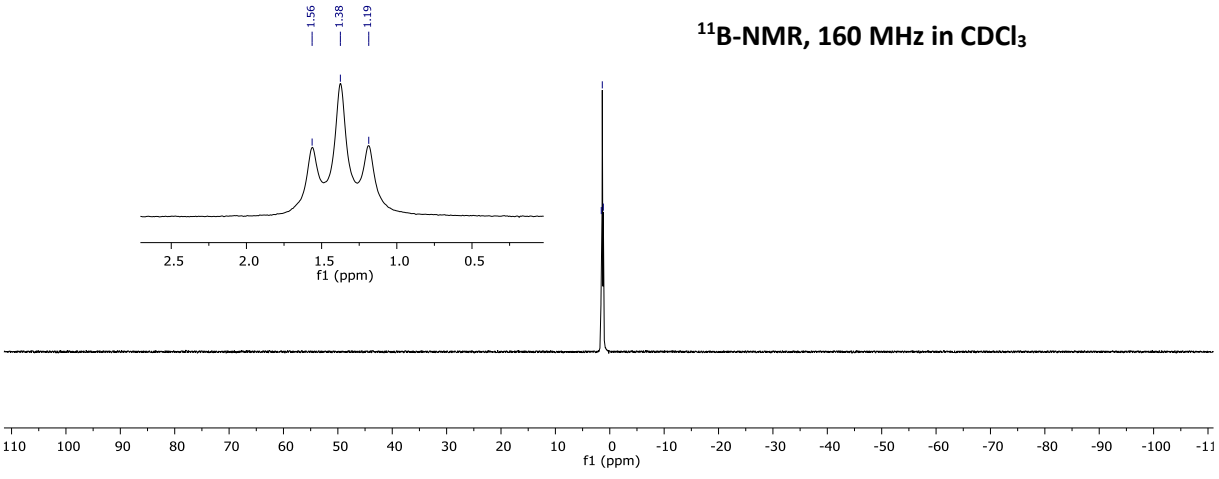


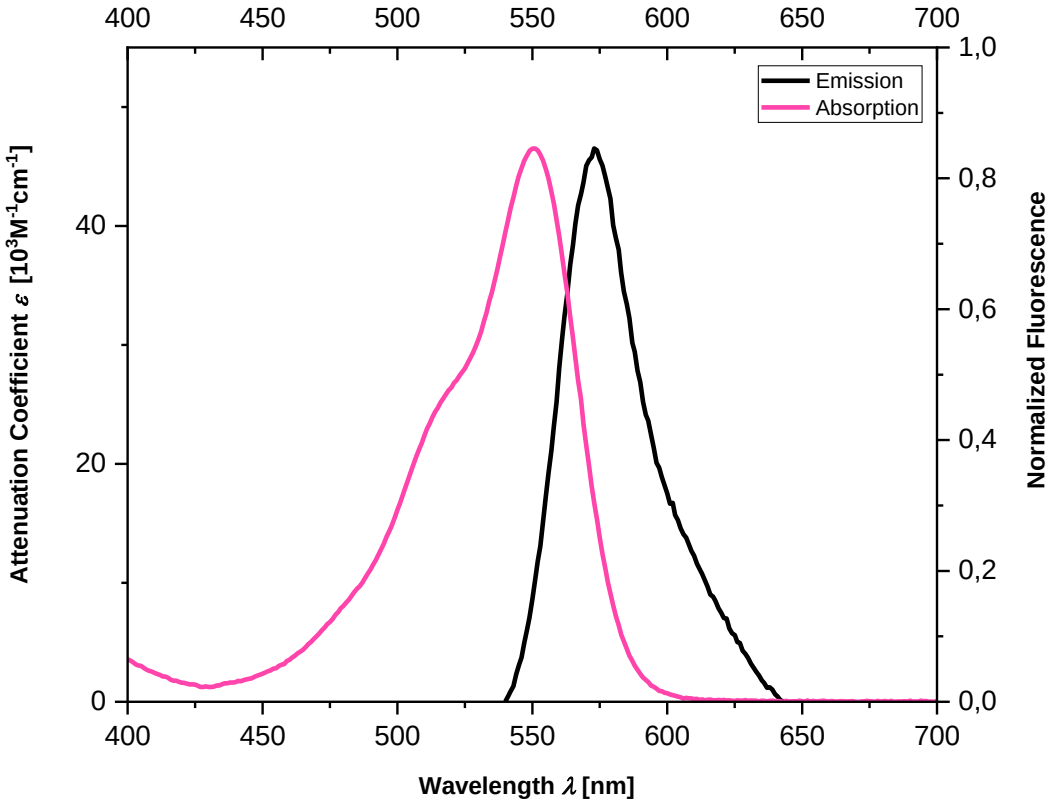
^{19}F-NMR, 470 MHz in $CDCl_3$





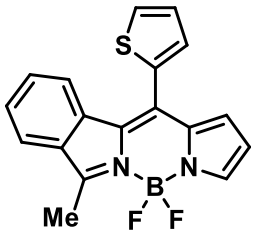
^{11}B-NMR, 160 MHz in $CDCl_3$





UV-Vis and normalized **fluorescence spectra** of **5g** at room temperature in CH_2Cl_2.

5,5-Difluoro-7-methyl-12-(thien-2-yl)-5*H*-5λ^4,6λ^4-pyrrolo[1',2':3,4][1,3,2]diazaborinino[6,1-*a*]isoindole (5h)



Precursor **1h** (52 mg, 0.10 mmol, 1.0 eq.) was reacted with thien-2-ylboronic acid (128 mg, 0.30 mmol, 3.0 eq.) according to **GP5** for 1 h. The crude product was subjected to **GP6** (reaction time: 16 h). Without further purification, the product was then reacted according to **GP7** (reaction time: 15 min). After purification by flash column chromatography on silica gel (*n*-pentane/EtOAc 20:1) the title compound was obtained as light red solid (12 mg, 0.036 mmol, 36%).

m.p.: 153 °C.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.78 – 7.73 (m, 1 H), 7.62 (dd, *J* = 5.0, 1.3 Hz, 1 H), 7.54 (t, *J* = 1.7 Hz, 1 H), 7.36 – 7.30 (m, 2 H), 7.28 – 7.23 (m, 2 H), 6.75 – 6.68 (m, 1 H), 6.55 – 6.52 (m, 1 H), 6.36 (dd, *J* = 3.8, 2.3 Hz, 1 H), 3.01 (s, 3 H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 163.6, 135.7, 134.3, 133.8, 133.7, 132.9, 131.8, 130.3, 130.3, 129.5, 128.0, 127.4, 126.7, 123.1, 122.7, 122.5, 114.4, 13.4.

^{19}F-NMR (376 MHz, $CDCl_3$): δ = -144.64 (dd, *J* = 61.6, 30.1 Hz).

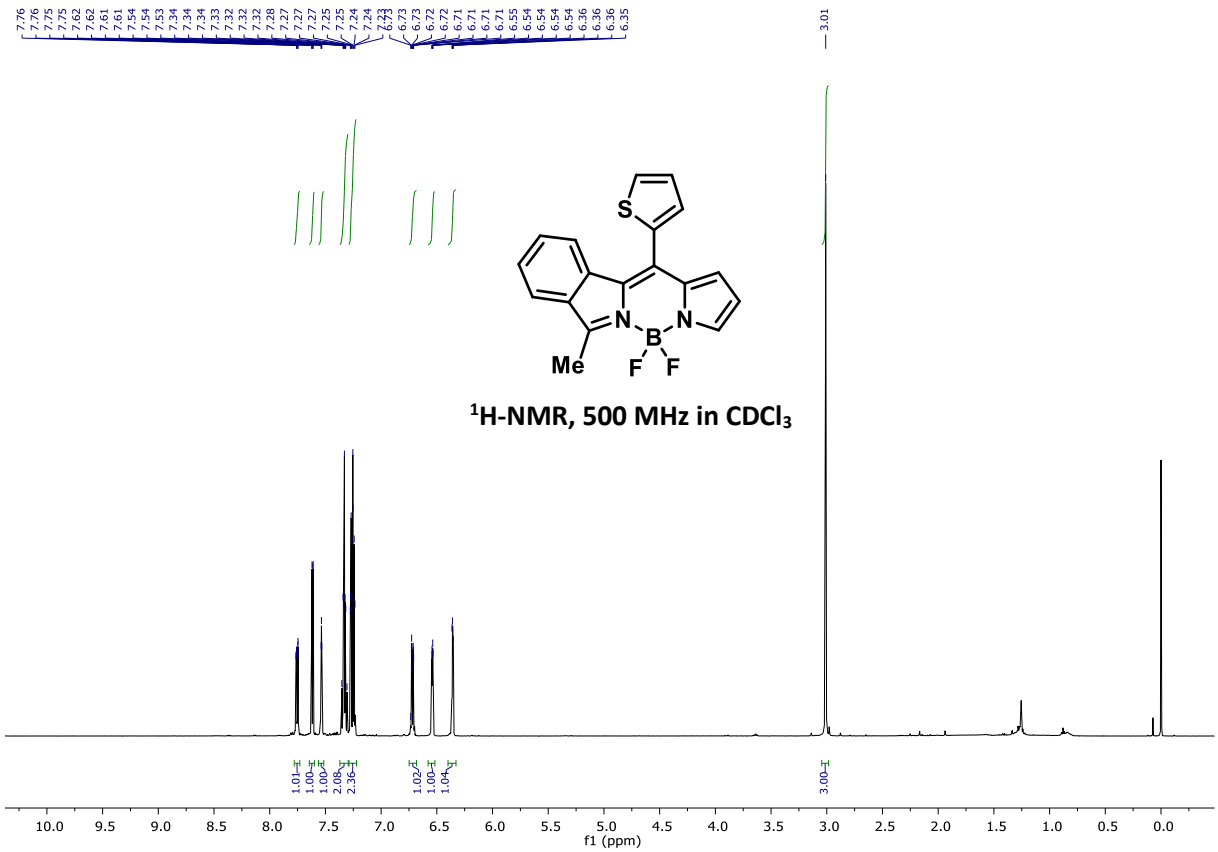
^{11}B-NMR (160 MHz, $CDCl_3$): δ = 1.32 (t, *J* = 30.9 Hz).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 103, 3068, 2922, 2854, 2110, 1572, 1523, 1387, 1337, 1209, 1072.

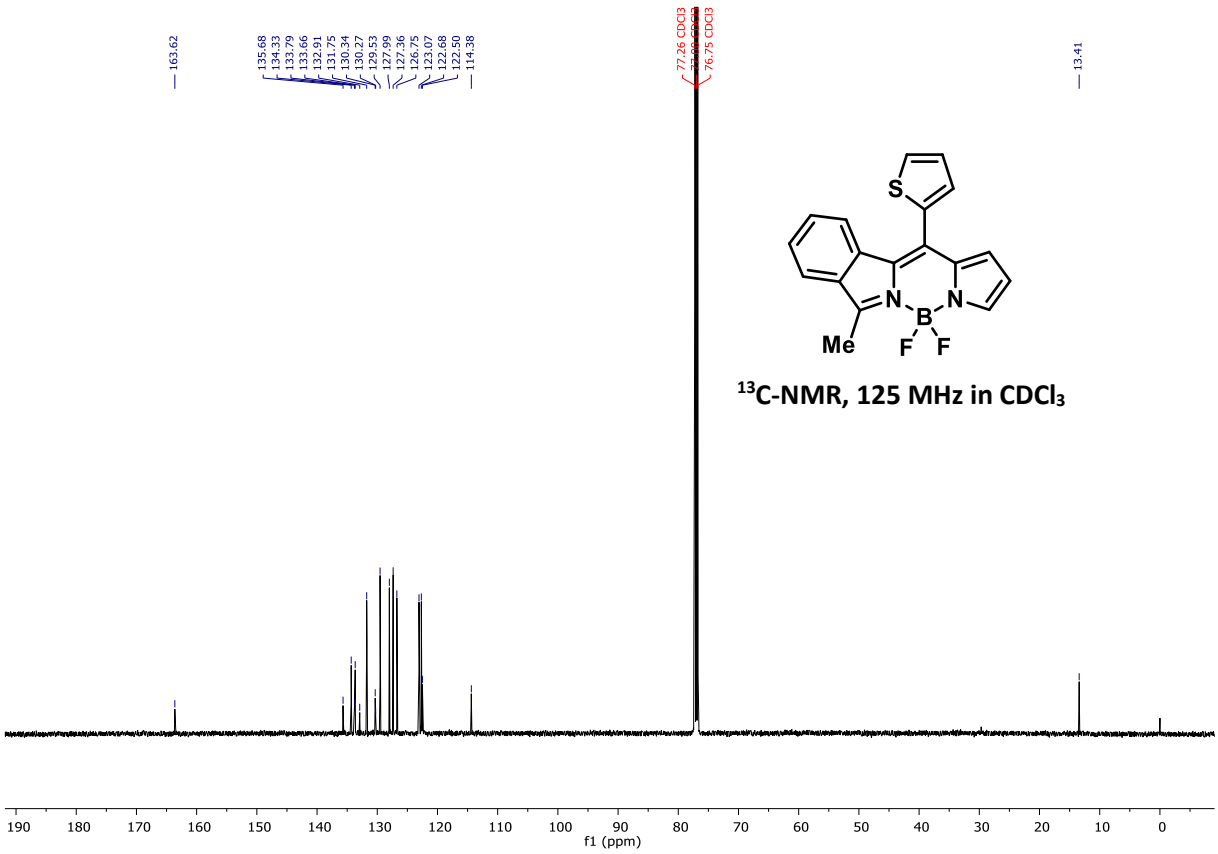
HRMS (ESI): $C_{18}H_{13}BF_2N_2S$ calcd.: 361.0753 found: 361.0755, $[M+Na]^+$.

UV/Vis (0.0019 mg/mL in CH_2Cl_2): λ_{max} [nm] (log ε) = 526 (4.50).

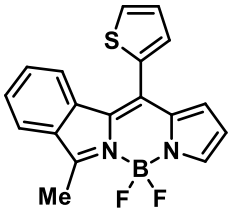
Emission (CH_2Cl_2): λ_{max} (nm) = 541.



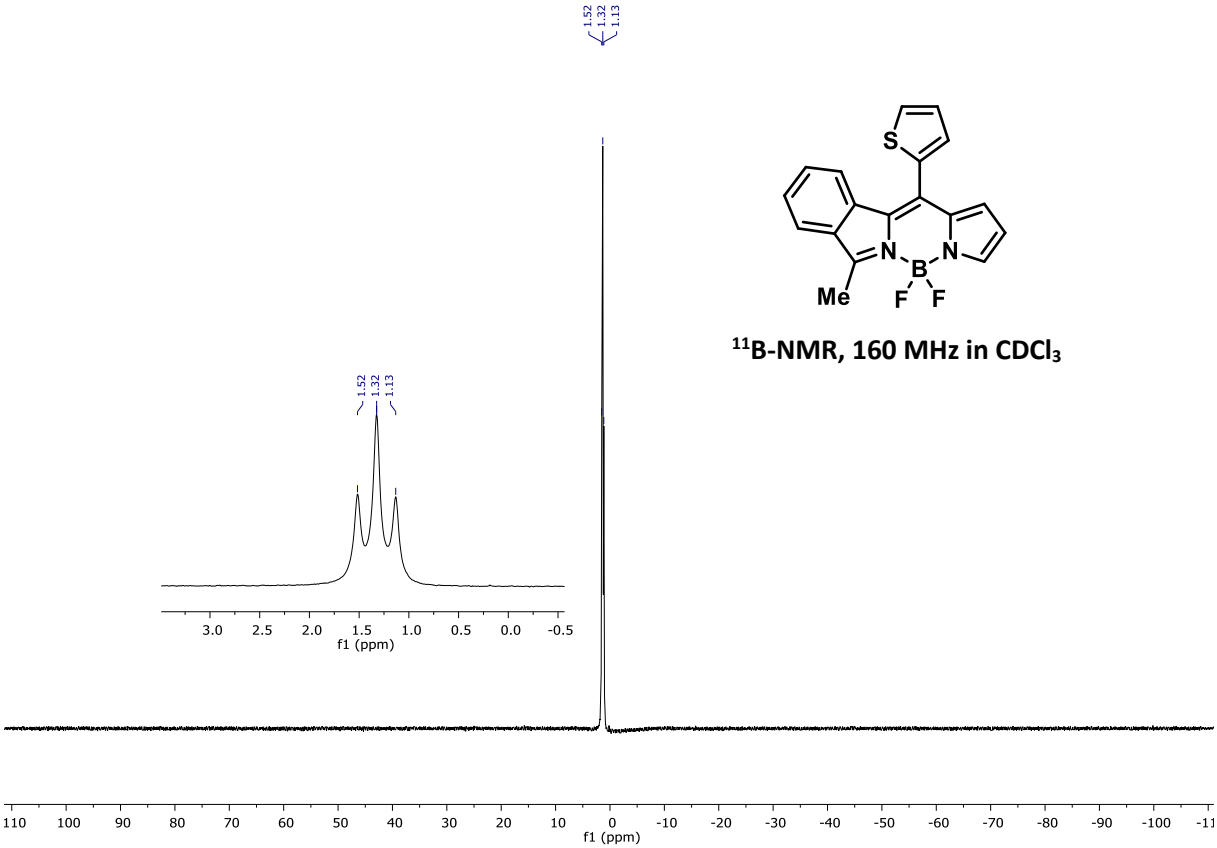
^{1}H-NMR, 500 MHz in $CDCl_3$



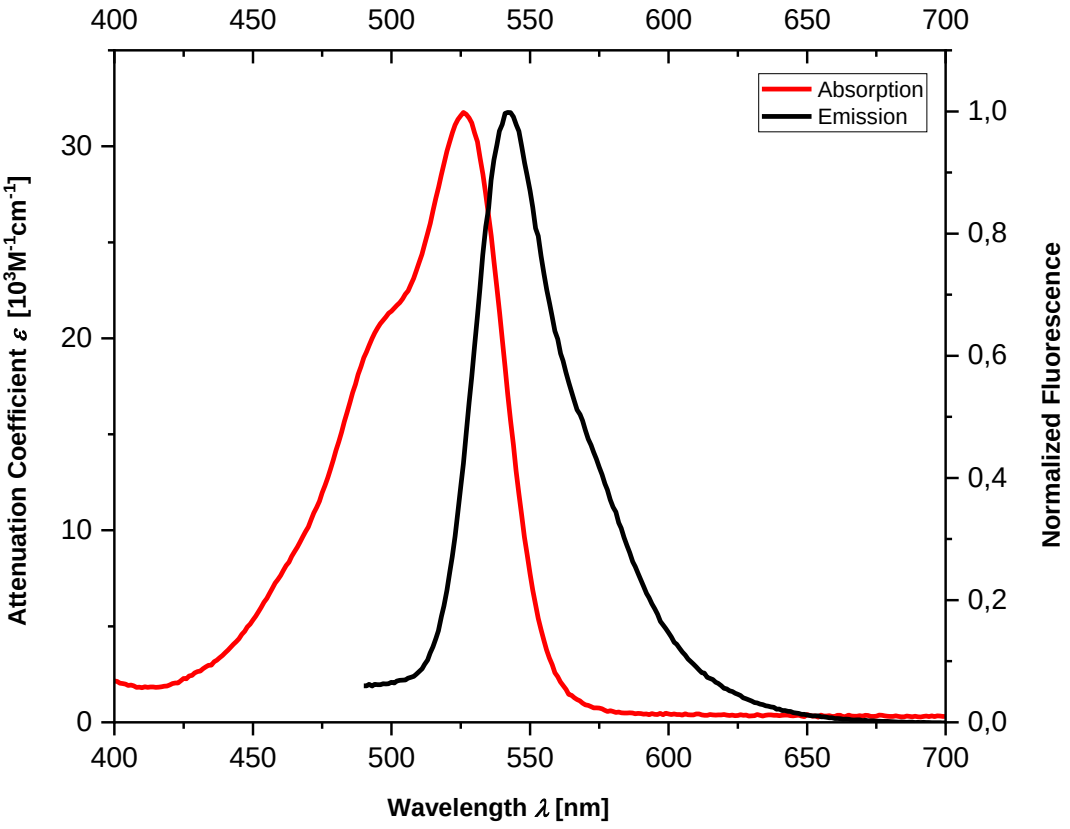
^{13}C-NMR, 125 MHz in $CDCl_3$



^{19}F-NMR, 376 MHz in $CDCl_3$

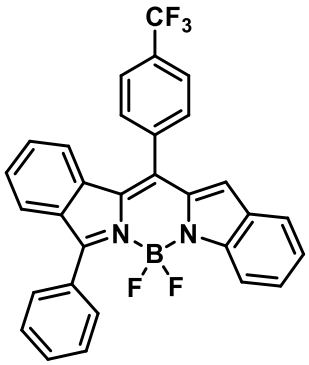


^{11}B-NMR, 160 MHz in $CDCl_3$



UV-Vis and normalized **fluorescence spectra** of **5h** at room temperature in CH_2Cl_2.

6,6-Difluoro-8-phenyl-13-(4-(trifluoromethyl)phenyl)-6*H*-6λ^4,7λ^4-isoindolo[2',1':1,6][1,3,2]diazaborinino[3,4-*a*]indole (5i)



Precursor **1e** (58 mg, 0.10 mmol, 1.0 eq.) was reacted with *N*-Boc (indol-2-yl)boronic acid (78 mg, 0.30 mmol, 3.0 eq.) according to **GP5** for 1 h. The crude product was then reacted according to **GP6** (reaction time: 16 h). Without further purification the product was subjected to **GP7** (reaction time: 20 min). After purification by flash column chromatography on silica gel (*n*-pentane/EtOAc 8:1 → 5:1 and *n*-pentane/EtOAc/PhMe 5:1:1) the title compound was obtained as a bright red solid (9 mg, 17 µmol, 17%).

m.p.: 273 °C.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.97 (dd, *J* = 7.6, 2.0 Hz, 2 H), 7.92 (d, *J* = 7.9 Hz, 2 H), 7.75 (d, *J* = 7.9 Hz, 2 H), 7.73 – 7.70 (m, 1 H), 7.69 – 7.64 (m, 4 H), 7.47 (dt, *J* = 8.1, 0.9 Hz, 2 H), 7.39 (td, *J* = 7.5, 1.3 Hz, 1 H), 7.37 – 7.34 (m, 1 H), 7.28 – 7.23 (m, 1 H), 7.01 (ddd, *J* = 8.0, 6.8, 0.9 Hz, 1 H), 6.54 (td, *J* = 4.0, 1.3 Hz, 2 H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 165.5, 145.0, 137.9 (d, $^4J_{C\text{-}F}$ = 1.1 Hz), 137.2, 136.9, 135.9, 134.1, 133.4, 132.3, 131.9 (d, $^2J_{C\text{-}F}$ = 32.7 Hz), 131.5, 130.2, 130.1, 130.0 (t, *J* = 3.3 Hz), 129.1, 128.5, 128.1, 127.4, 125.9 (q, $^3J_{C\text{-}F}$ = 3.7 Hz), 125.8, 123.8 (d, $^1J_{C\text{-}F}$ = 272.5 Hz), 122.8, 122.5, 121.1, 116.5, 114.8.

^{19}F-NMR (376 MHz, $CDCl_3$): δ = -62.96, -137.76 (dd, *J* = 59.8, 19.7 Hz).

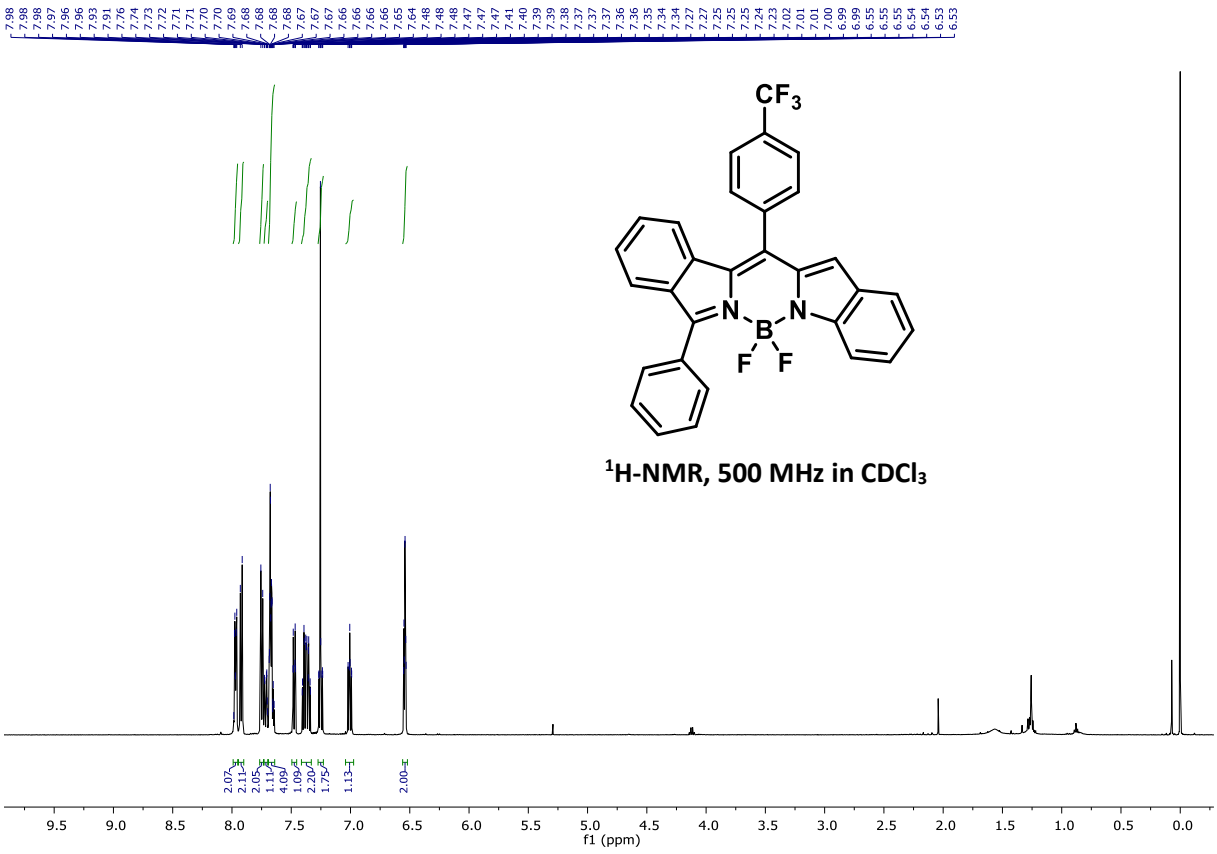
^{11}B-NMR (128 MHz, $CDCl_3$): δ = 2.10 (t, *J* = 31.0 Hz).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2922, 2854, 2323, 1721, 1577, 1458, 1329, 1103, 1018.

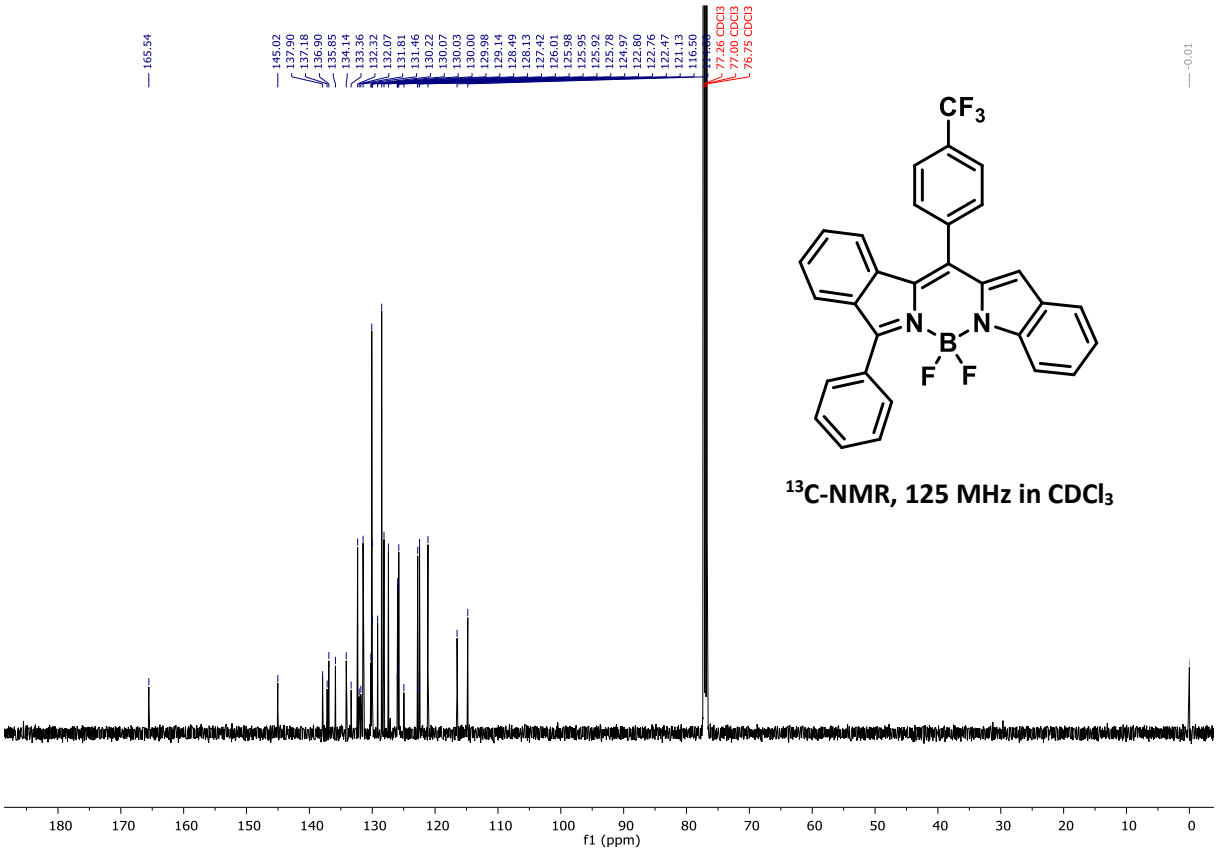
HRMS (ESI): $C_{30}H_{18}BF_5N_2$ calcd.: 535.1375 found: 535.1375, $[M+Na]^+$.

UV/Vis (0.0027 mg/mL in CH_2Cl_2): λ_{max} [nm] (log ε) = 547 (4.60).

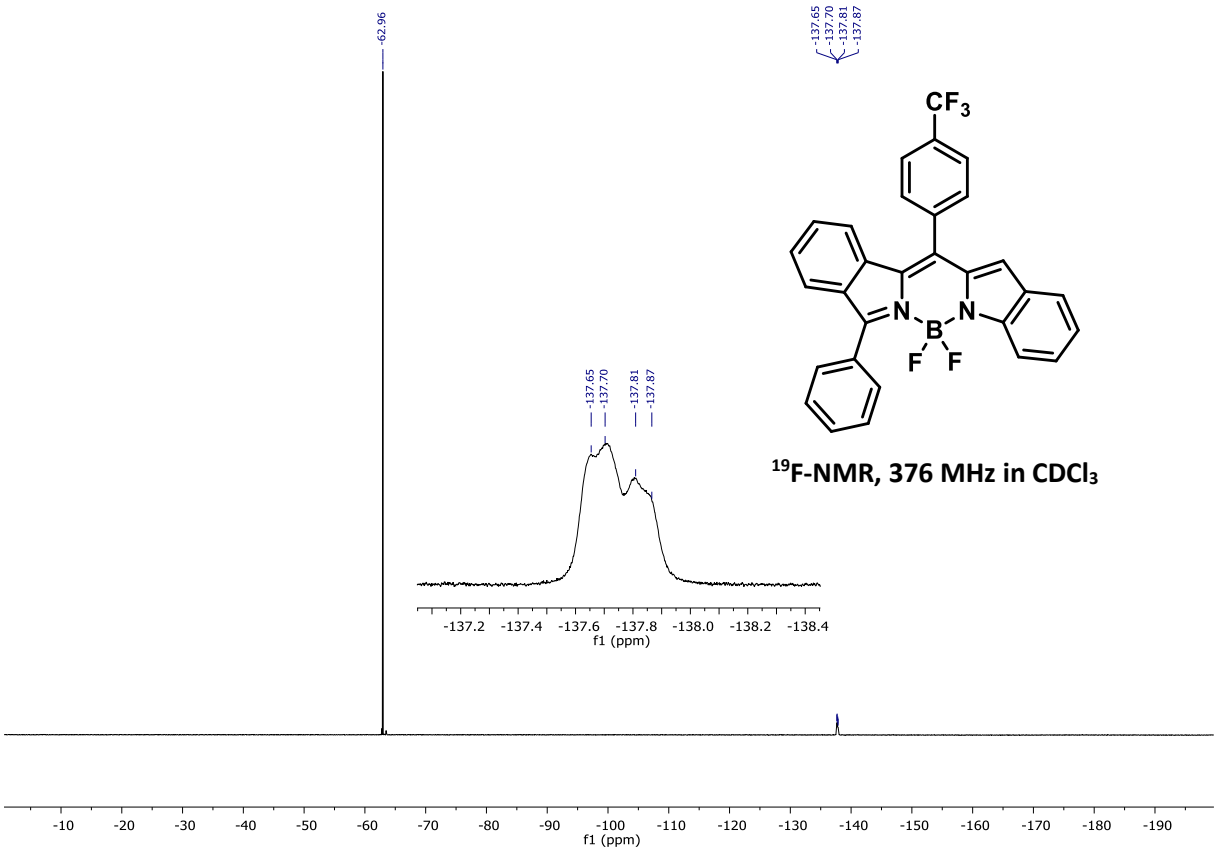
Emission (CH_2Cl_2): λ_{max} (nm) = 599.



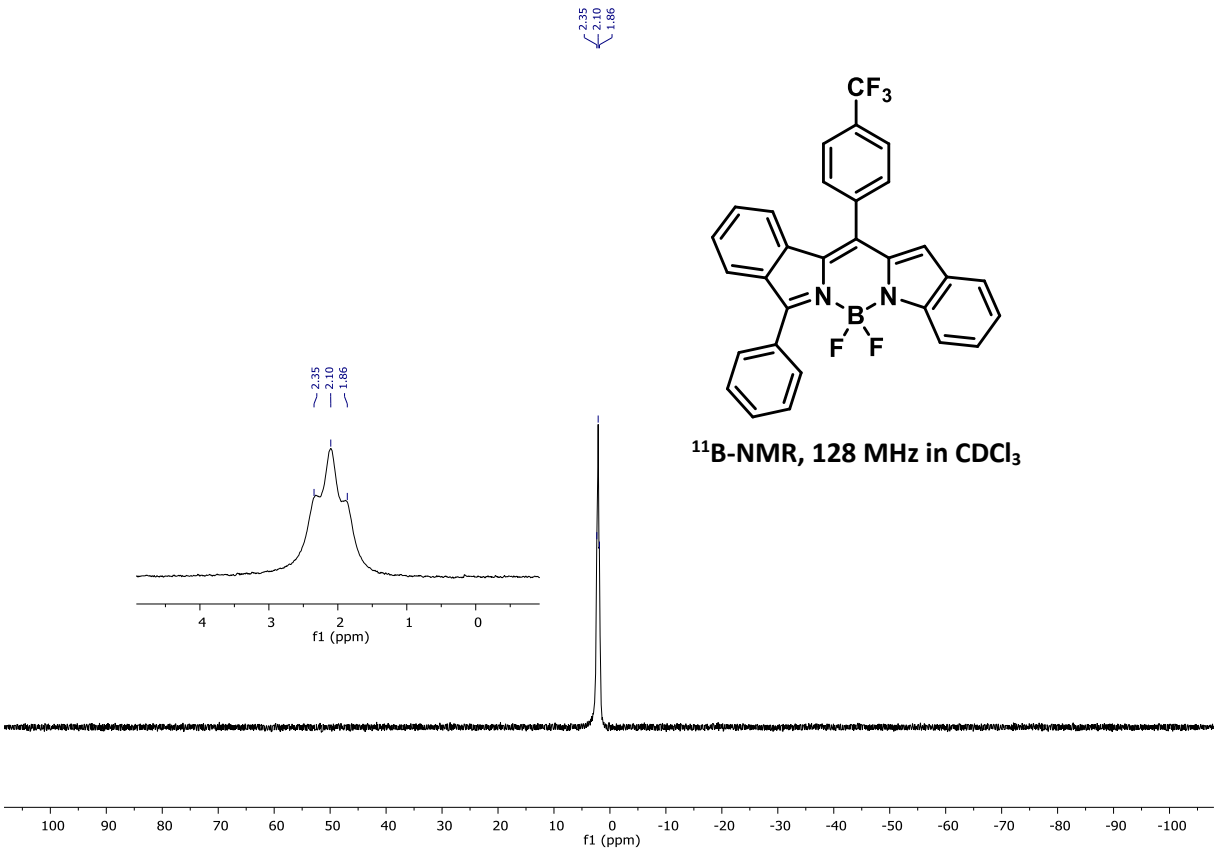
^{1}H-NMR, 500 MHz in $CDCl_3$



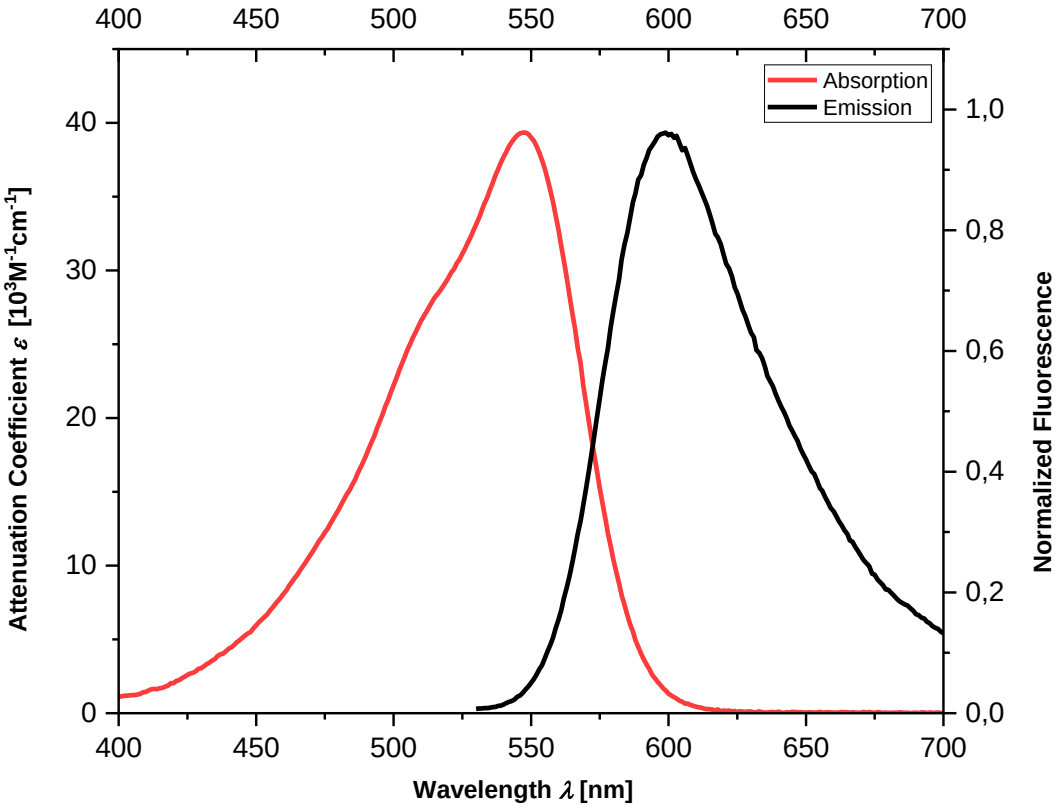
^{13}C-NMR, 125 MHz in $CDCl_3$



^{19}F-NMR, 376 MHz in $CDCl_3$

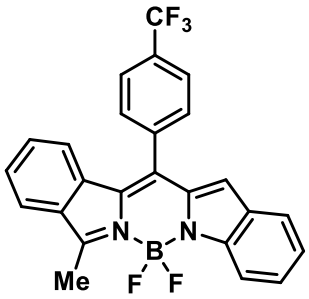


^{11}B-NMR, 128 MHz in $CDCl_3$



UV-Vis and normalized **fluorescence spectra** of **5i** at room temperature in CH_2Cl_2.

6,6-Difluoro-8-methyl-13-(4-(trifluoromethyl)phenyl)-6*H*-6λ^4,7λ^4-isoindolo[2',1':1,6][1,3,2]diazaborinino[3,4-*a*]indole (5j)



Precursor **1f** (58 mg, 0.10 mmol, 1.0 eq.) was reacted with *N*-Boc (indol-2-yl)boronic acid (78 mg, 0.30 mmol, 3.0 eq.) according to **GP5** for 1 h. The crude product was subjected to **GP6** (reaction time: 16 h). Without further purification the product was reacted according to **GP7** (reaction time: 20 min). After purification by flash column chromatography on silica gel (*n*-pentane/EtOAc 10:1 and *n*-pentane/CH_2Cl_2 3:2) the title compound was obtained as a bright orange solid (5.8 mg, 13 µmol, 13%).

m.p.: 266 °C.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.89 (d, *J* = 8.0 Hz, 2 H), 7.84 (dt, *J* = 7.9, 0.9 Hz, 2 H), 7.80 (d, *J* = 8.4 Hz, 1 H), 7.69 (d, *J* = 7.9 Hz, 2 H), 7.49 (dd, *J* = 8.1, 1.1 Hz, 1 H), 7.44 (td, *J* = 7.6, 0.9 Hz, 1 H), 7.36 (ddd, *J* = 8.2, 7.3, 1.1 Hz, 1 H), 7.32 (ddd, *J* = 8.2, 6.8, 1.2 Hz, 1 H), 7.04 (ddd, *J* = 8.0, 6.9, 0.9 Hz, 1 H), 6.53 (dt, *J* = 8.0, 0.8 Hz, 2 H), 6.47 (s, 1H), 3.13 (s, 3 H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 167.4, 144.4, 137.7, 137.0, 135.3, 135.2, 134.1, 132.7, 132.6, 130.1, 131.8 (d, $^2J_{C\text{-}F}$ = 32.8 Hz), 130.0, 128.1, 127.0, 125.9 (q, $^3J_{C\text{-}F}$ = 3.7 Hz), 123.8, 123.8 (d, $^1J_{C\text{-}F}$ = 272.4 Hz), 122.9, 122.3, 121.0, 115.3, 114.5, 13.8.

^{19}F-NMR (470 MHz, $CDCl_3$): δ = -63.04, -145.13 (dd, *J* = 61.9, 27.1 Hz).

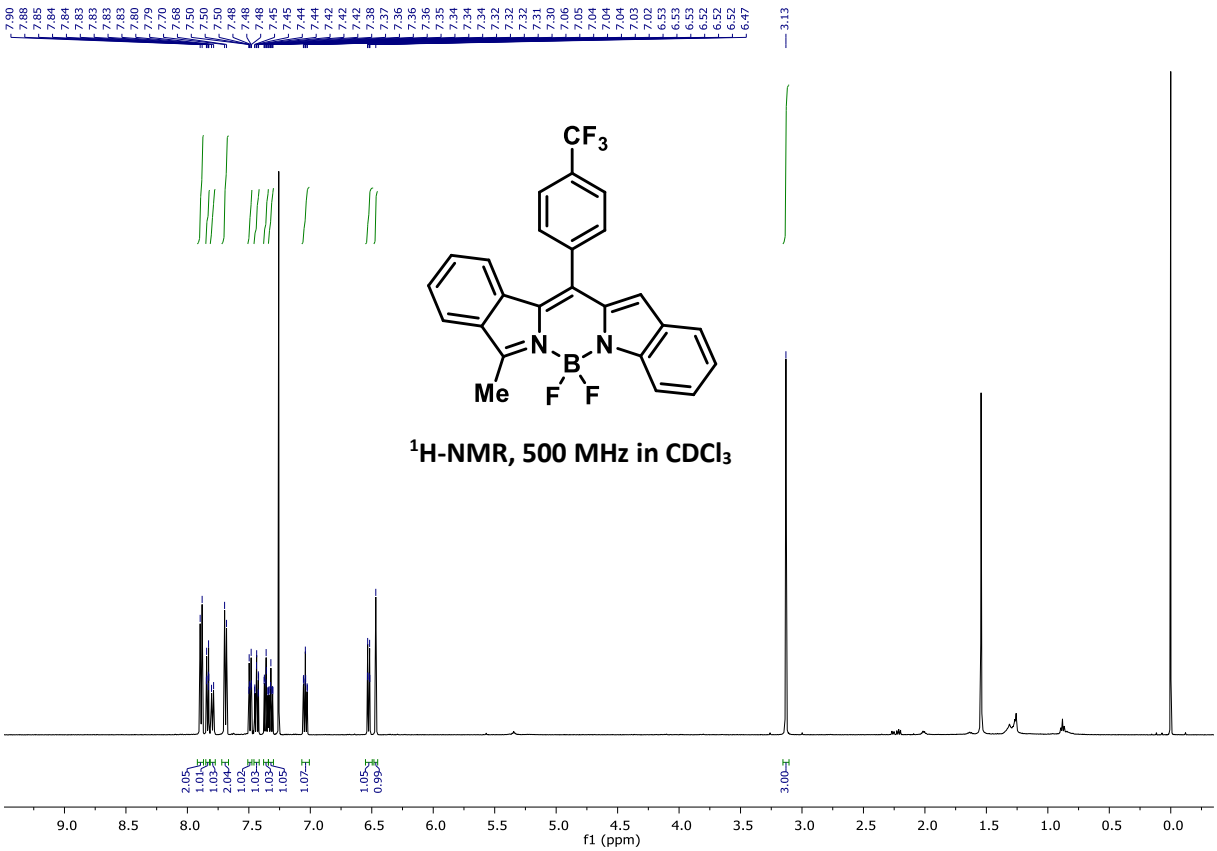
^{11}B-NMR (160 MHz, $CDCl_3$): δ = 2.00 (t, *J* = 31.8 Hz).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2922, 2854, 2323, 1591, 1518, 1329, 1125, 993.

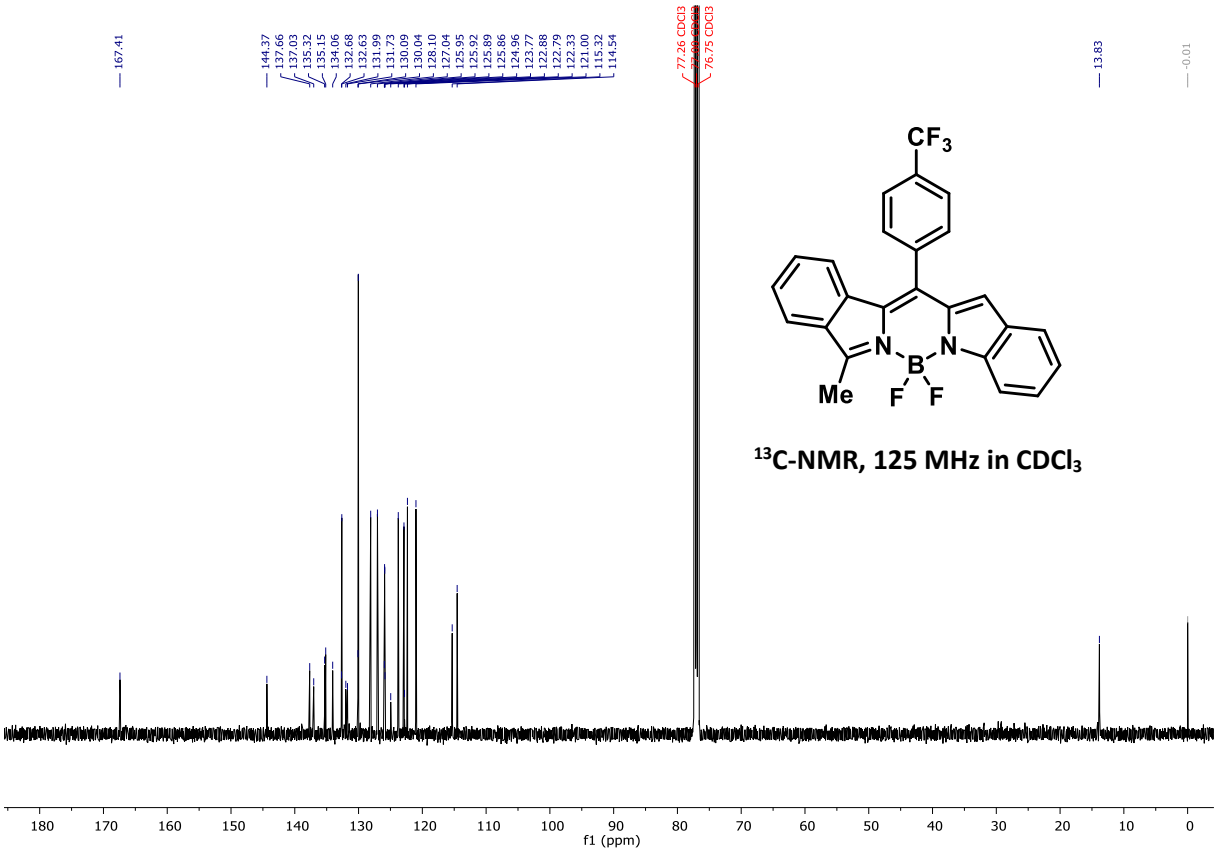
HRMS (ESI): $C_{25}H_{16}BF_5N_2$ calcd.: 451.1399 found: 451.1407, $[M+H]^+$.

UV/Vis (0.0054 mg/mL in CH_2Cl_2): λ_{max} [nm] (log ε) = 519 (4.59).

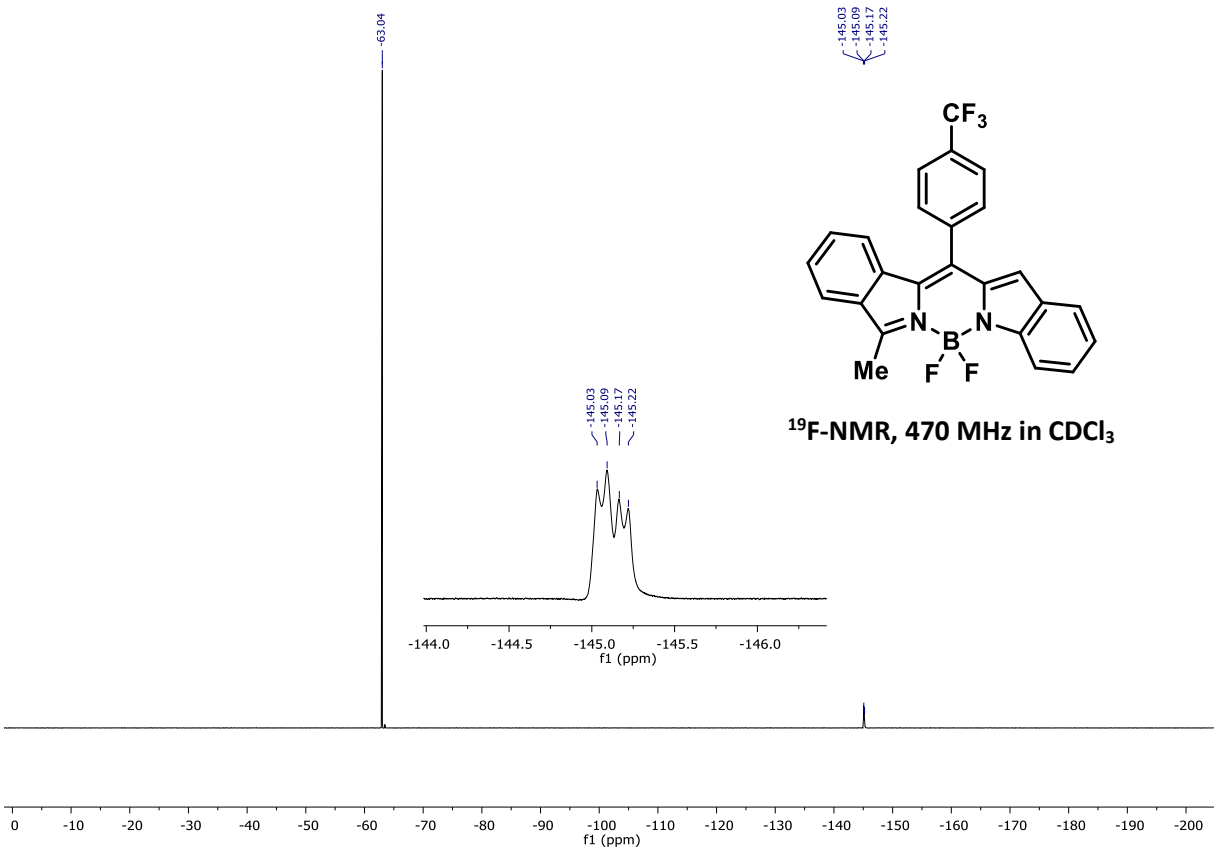
Emission (CH_2Cl_2): λ_{max} (nm) = 567.



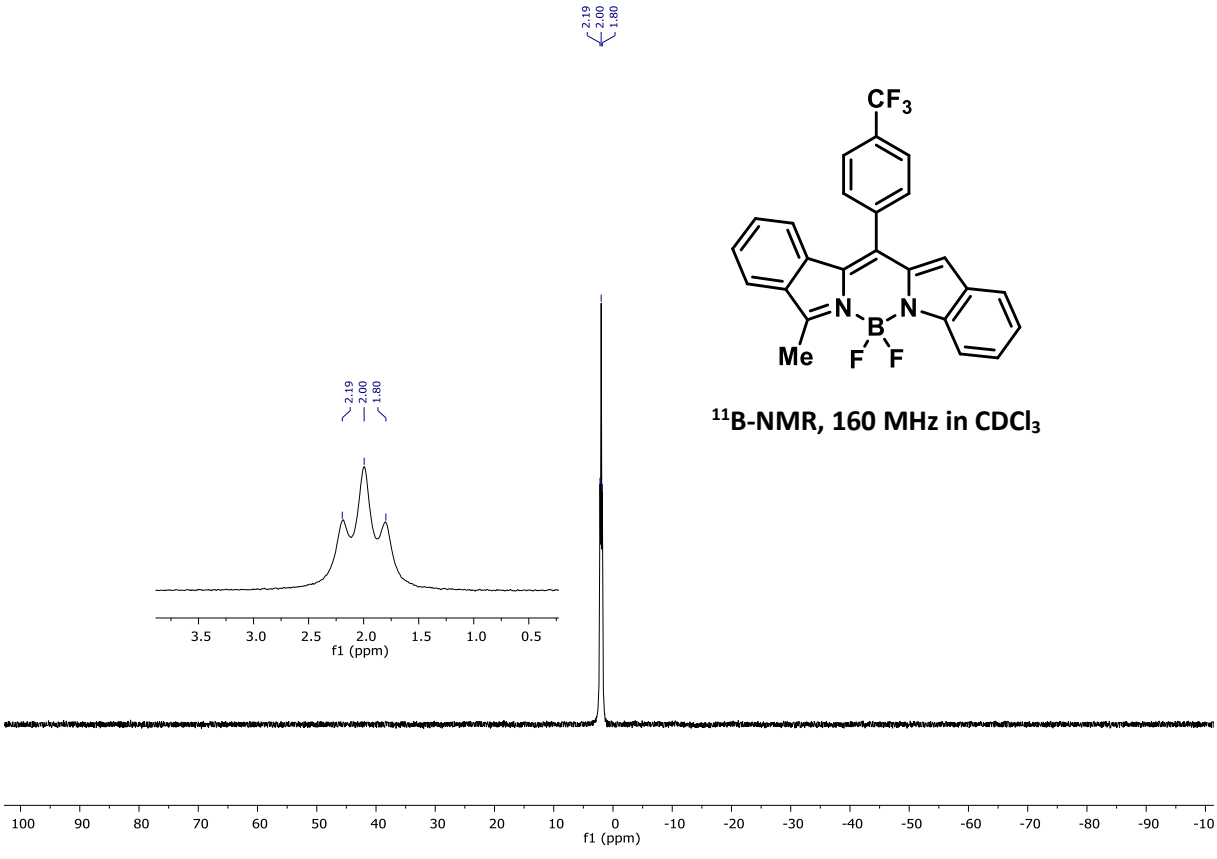
^{1}H-NMR, 500 MHz in $CDCl_3$



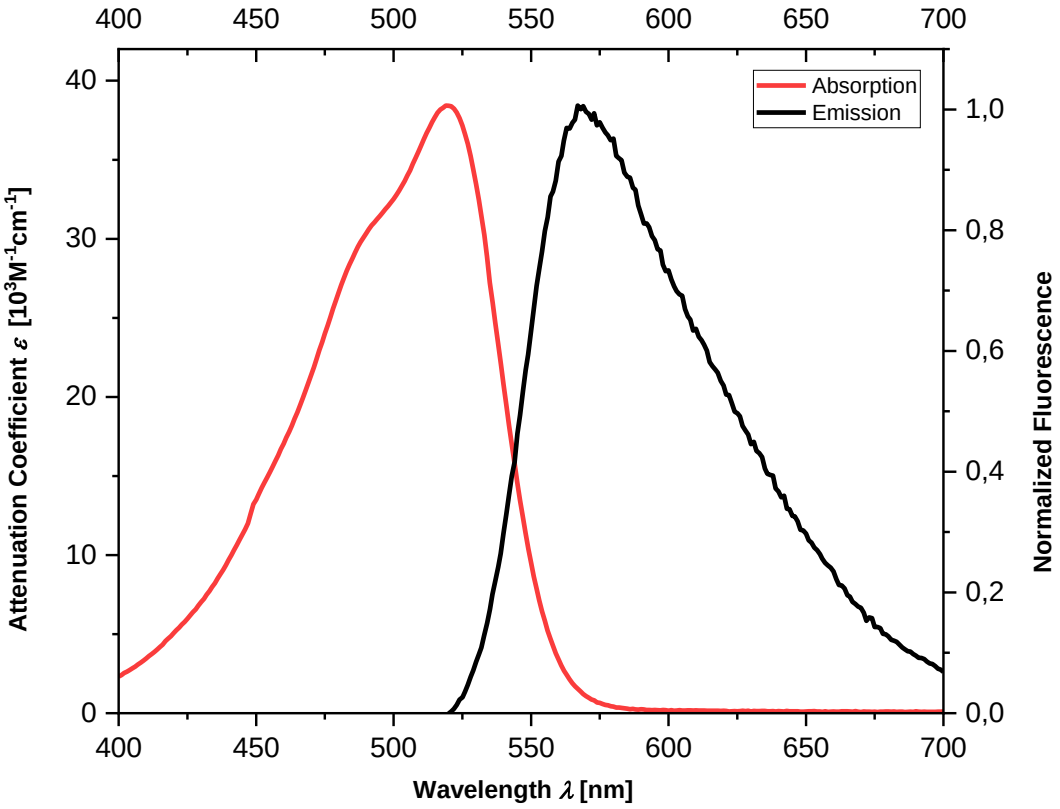
^{13}C-NMR, 125 MHz in $CDCl_3$



^{19}F-NMR, 470 MHz in $CDCl_3$

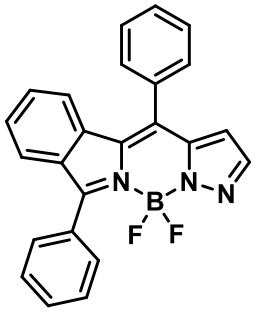


^{11}B-NMR, 160 MHz in $CDCl_3$



UV-Vis and normalized **fluorescence spectra** of **5j** at room temperature in CH_2Cl_2.

11,11-Difluoro-4,9-diphenyl-11*H*-10λ⁴,11λ⁴-pyrazolo[1',5':3,4][1,3,2]diazaborinino[6,1-*a*]isoindole (5k)



Precursor **1g** (49 mg, 0.10 mol, 1.0 eq.) was reacted with (*N*-Boc Pyrazol-5-yl)boronic acid (64 mg, 0.30 mmol, 3.0 eq.) according to **GP5** for 1 h. The crude product was subjected to to **GP6** (reaction time: 16 h). Without further purification the crude product was reacted according to **GP7** (reaction time: 15 min). After purification by flash column chromatography on silica gel (*n*-pentane : EtOAc 2:1 → 1:1) the title compounds was obtained as yellow solid (6.4 mg, 0.017 mmol, 17%).

m.p.: 200 °C.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.98 – 7.95 (m, 2 H), 7.73 – 7.60 (m, 8 H), 7.58 – 7.53 (m, 2 H), 7.40 (dtd, *J* = 19.2, 7.3, 1.1 Hz, 2 H), 6.70 (d, *J* = 7.7 Hz, 1 H), 6.20 (d, *J* = 1.7 Hz, 1 H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 170.0, 143.0, 141.3, 136.6, 135.9, 134.5, 133.5, 133.2, 132.0, 130.08 (dd, *J* = 6.7, 3.2 Hz), 129.2, 128.8, 128.7, 128.6, 128.5, 126.3, 123.4, 111.5.

^{19}F-NMR (470 MHz, $CDCl_3$): δ = -140.36 (dd, *J* = 53.0, 22.3 Hz).

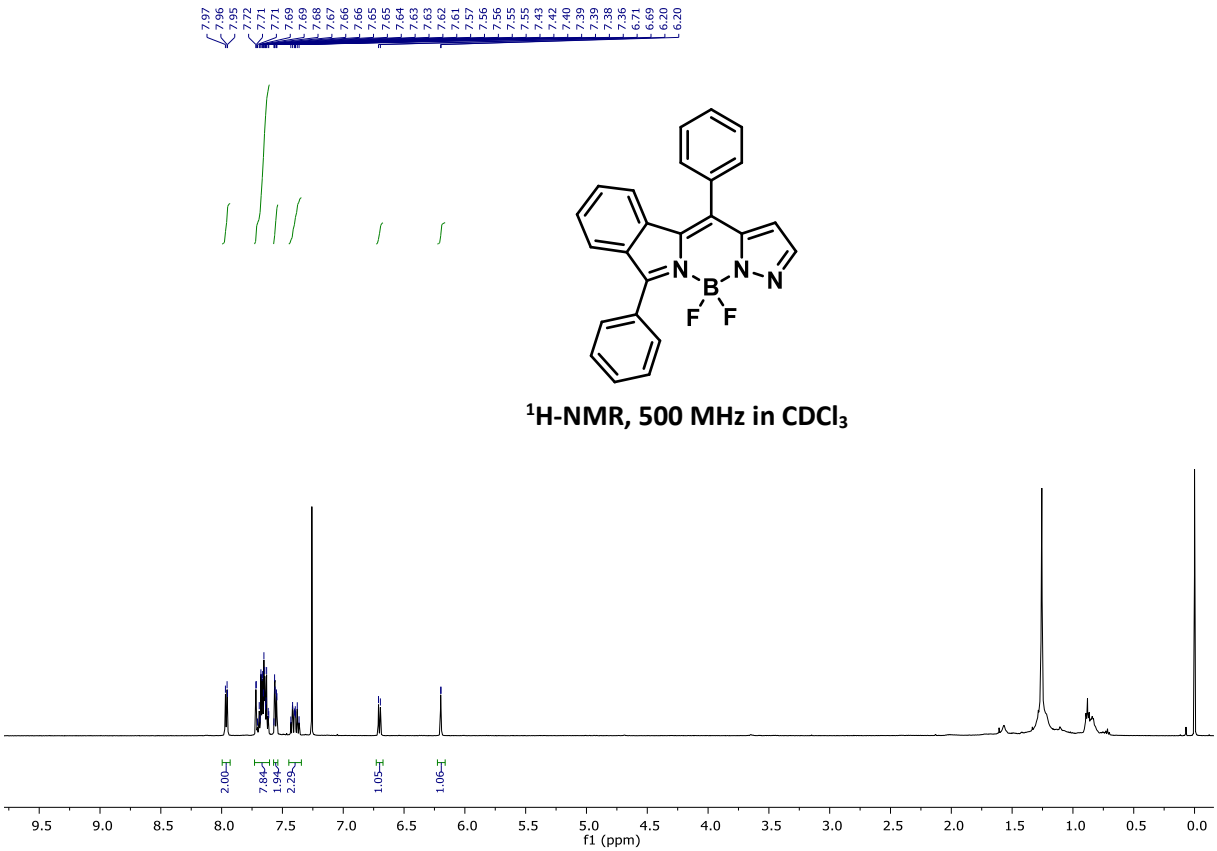
^{11}B-NMR (160 MHz, $CDCl_3$): δ = 1.26 (t, *J* = 27.0 Hz).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3063, 2921, 2853, 2114, 1712, 1597, 1479, 1437, 1110.

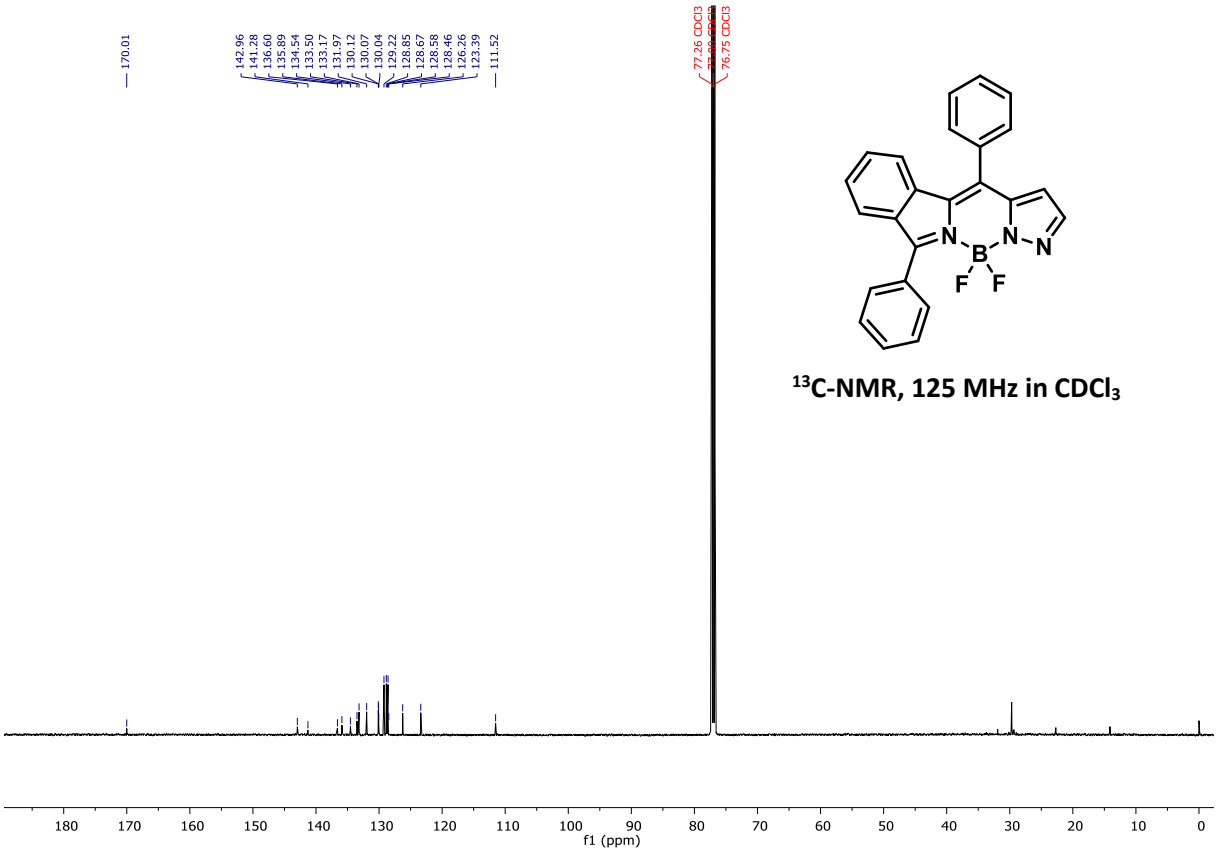
HRMS (ESI): $C_{24}H_{16}BF_2N_3$ calcd.: 396.1478 found: 396.1483, $[M+Na]^+$.

UV/Vis (0.0027 mg/mL in CH_2Cl_2): λ_{max} [nm] (log ε) = 459 (4.20).

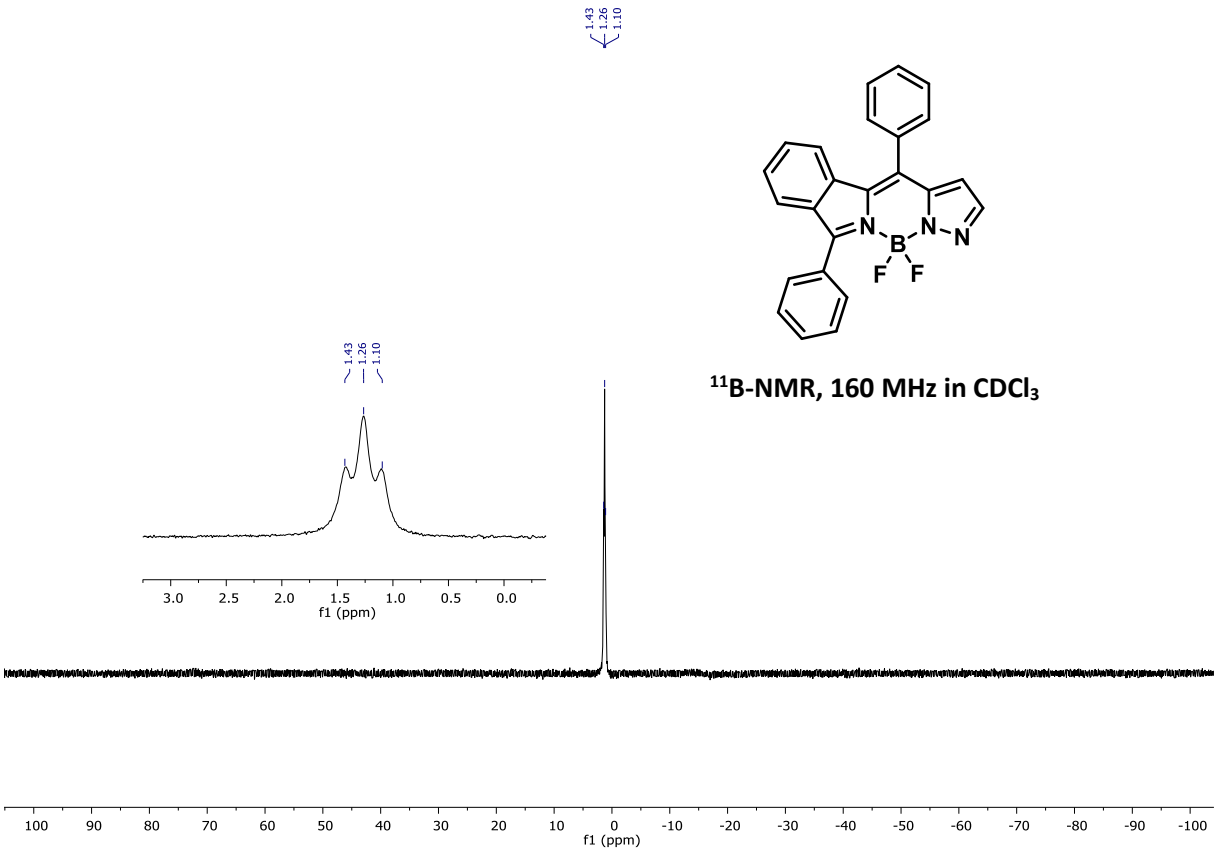
Emission (CH_2Cl_2): λ_{max} (nm) = 530.



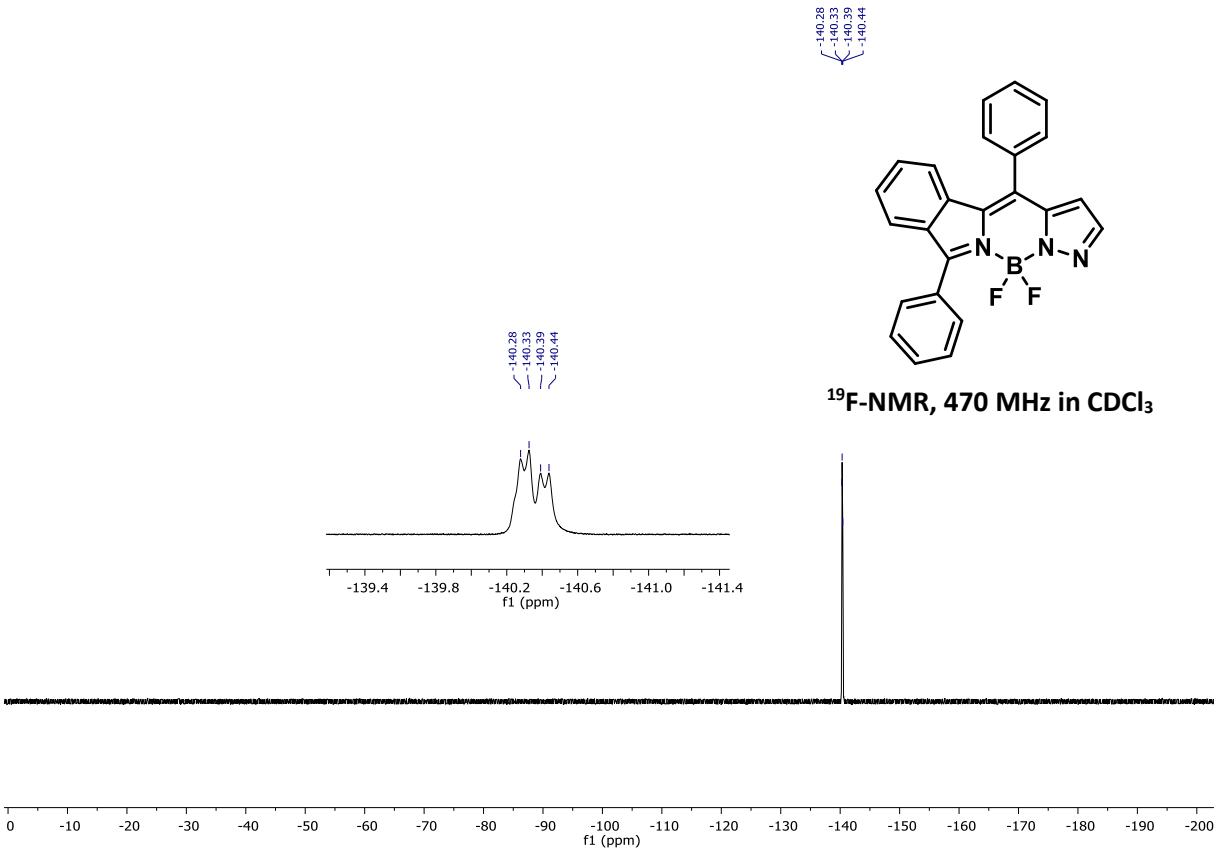
^{1}H-NMR, 500 MHz in $CDCl_3$



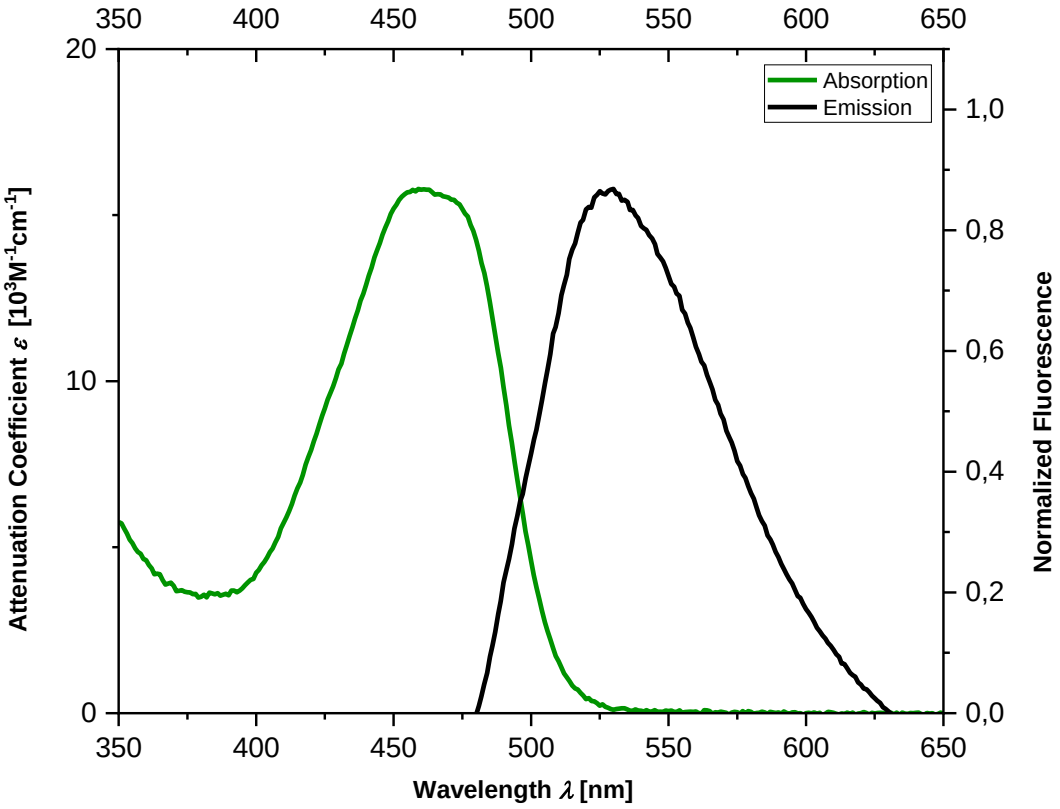
^{13}C-NMR, 125 MHz in $CDCl_3$



^{11}B-NMR, 160 MHz in $CDCl_3$

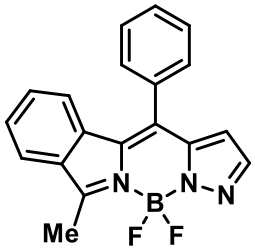


^{19}F-NMR, 470 MHz in $CDCl_3$



UV-Vis and normalized **fluorescence spectra** of **5k** at room temperature in CH_2Cl_2.

11,11-Difluoro-9-methyl-4-phenyl-11*H*-10λ⁴,11λ⁴-pyrazolo[1',5':3,4][1,3,2]diazaborinino[6,1-*a*]isoindole (5l)



Precursor **1h** (43 mg, 0.10 mmol, 1.0 eq.) was reacted with (*N*-Boc pyrazol-5-yl)boronic acid (64 mg, 0.30 µmol, 3.0 eq.) according to **GP5** for 1 h. The crude product was subjected to **GP6** (reaction time: 16 h). Without further purifications the product was reacted according to **GP7** (reaction time: 15 min). After purification by flash column chromatography on silica gel (*n*-pentane/EtOAc 1:1) the title compound was obtained as dark green solid (7.0 mg, 0.021 mmol, 21%).

m.p.: 192 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.84 (dt, *J* = 7.8, 1.0 Hz, 1 H), 7.72 (d, *J* = 1.8 Hz, 1 H), 7.68 – 7.56 (m, 3 H), 7.52 – 7.43 (m, 3 H), 7.38 (ddd, *J* = 8.0, 7.3, 1.1 Hz, 1 H), 6.69 (dt, *J* = 8.0, 0.9 Hz, 1 H), 6.16 (d, *J* = 1.8 Hz, 1 H), 3.13 (t, *J* = 1.3 Hz, 3 H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 171.9, 142.9, 136.0, 134.4, 134.1, 133.8, 133.5, 133.2, 130.0, 129.1, 128.8, 128.7, 124.0, 123.5, 111.1, 29.7, 14.1.

^{19}F-NMR (376 MHz, $CDCl_3$): δ = -147.66 (dd, *J* = 54.0, 25.3 Hz, 2 F).

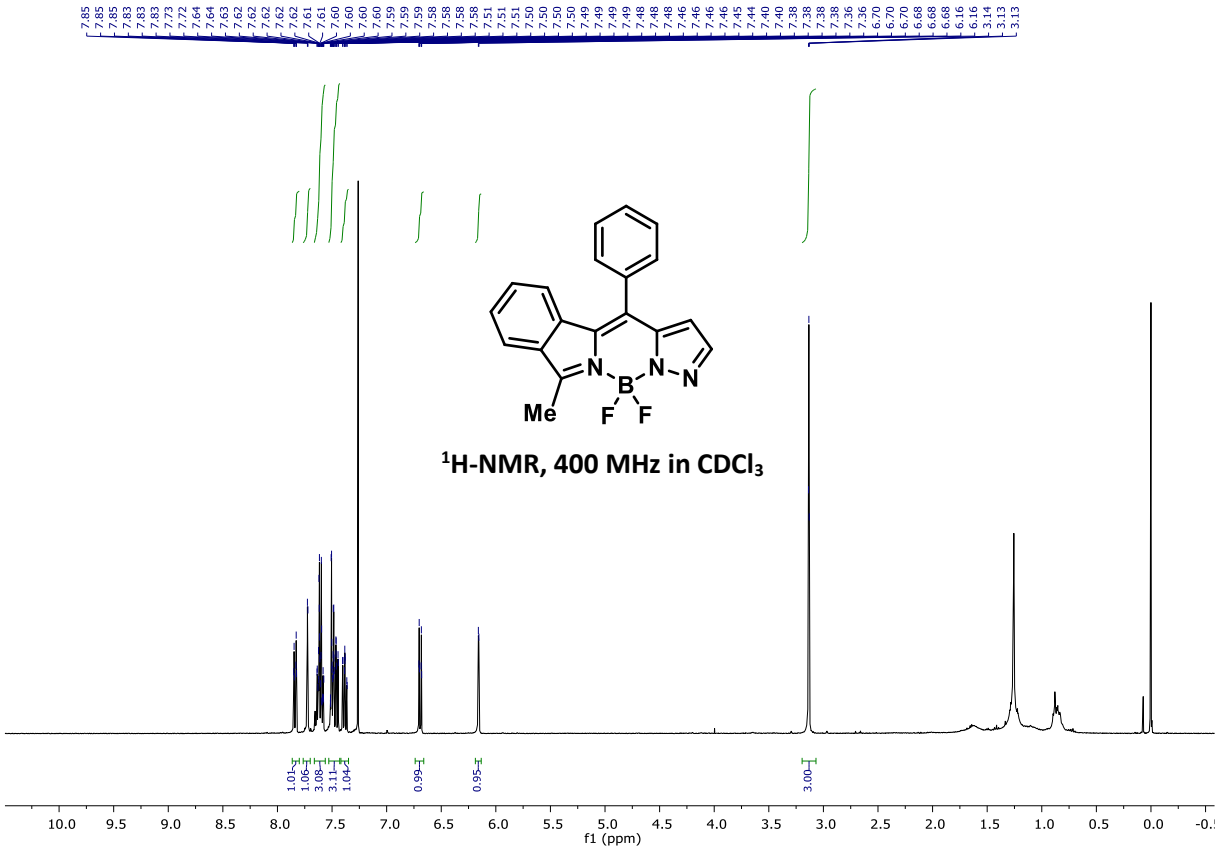
^{11}B-NMR (128 MHz, $CDCl_3$): δ = 1.17 (t, *J* = 27.5 Hz).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2923, 2853, 2115, 1738, 1616, 1445, 1221, 1093, 995.

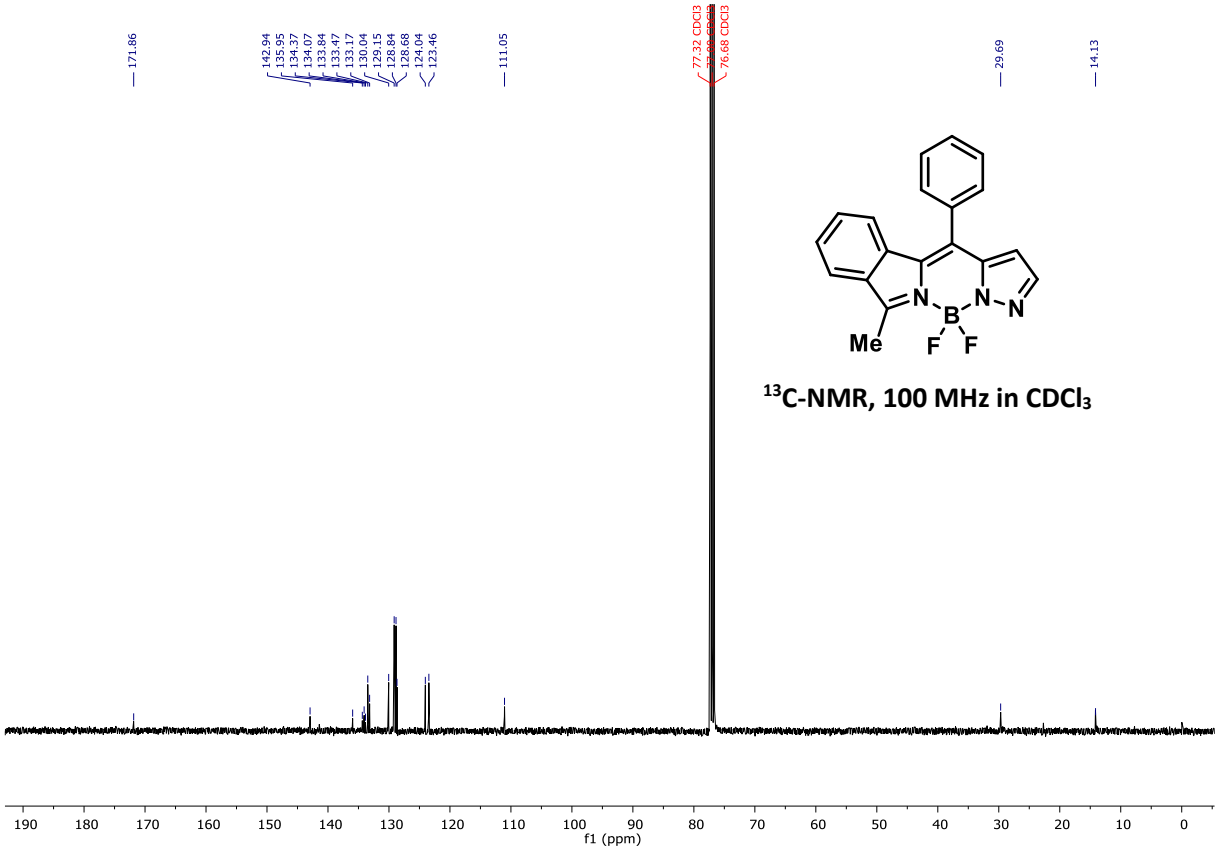
HRMS (ESI): $C_{19}H_{14}BF_2N_3$ calcd.: 334.1322 found: 334.1326, $[M+H]^+$.

UV/Vis (0.0088 mg/mL in CH_2Cl_2): λ_{max} [nm] (log ε) = 434 (4.21).

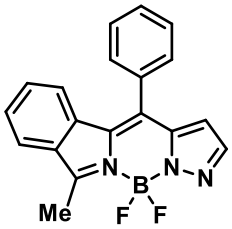
Emission (CH_2Cl_2): λ_{max} (nm) = 507.



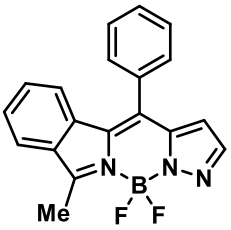
^{1}H-NMR, 400 MHz in $CDCl_3$



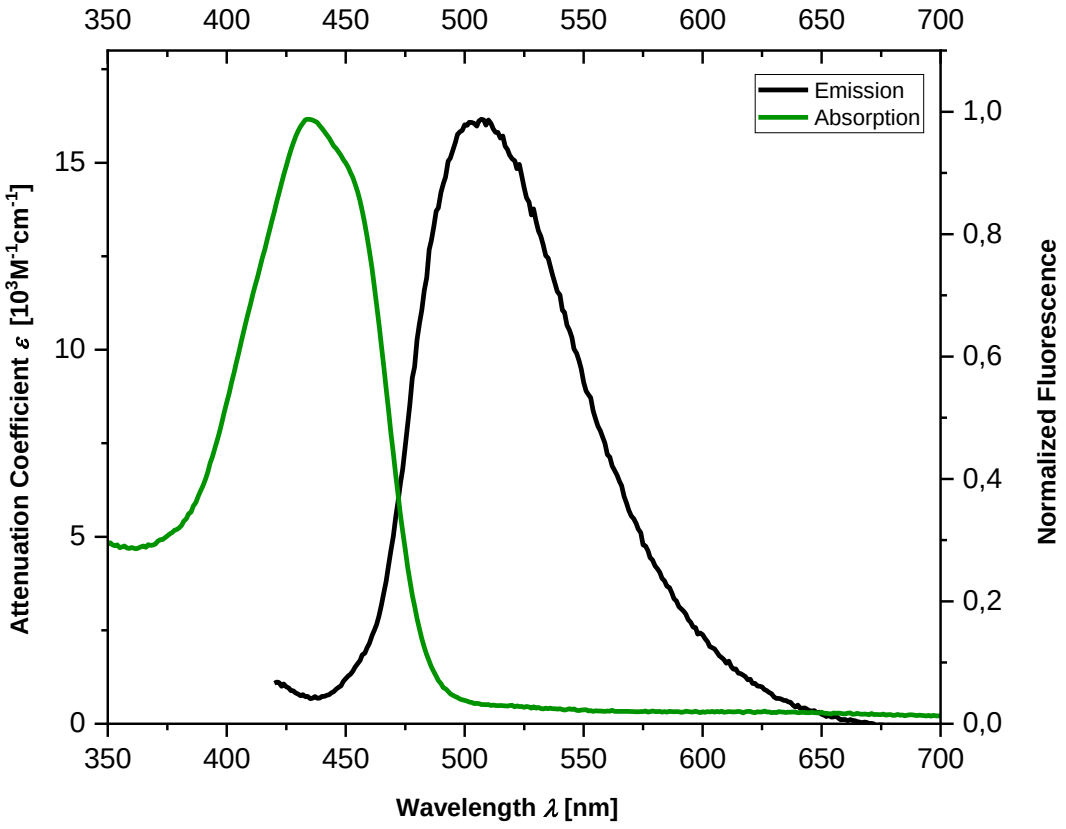
^{13}C-NMR, 100 MHz in $CDCl_3$



^{19}F-NMR, 376 MHz in $CDCl_3$



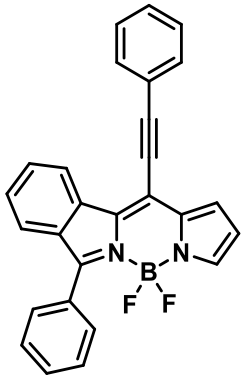
^{11}B-NMR, 128 MHz in $CDCl_3$



UV-Vis and normalized **fluorescence spectra** of **5l** at room temperature in CH_2Cl_2.

6.2. *meso*-Alkynyl-BODIPYs

5,5-Difluoro-7-phenyl-12-(phenylethynyl)-5*H*-5λ^4,6λ^4-pyrrolo[1',2':3,4][1,3,2]diazaborinino[6,1-*a*]isoindole (6a)



Precursor **1h** (58 mg, 0.10 mmol, 1.0 eq.) was reacted with phenyl acetylene (15 mg, 0.15 mmol, 1.5 eq.) according to **GP8** for 3 h. The crude product was subjected to **GP9**. Without further purification the product was reacted according to **GP10**. After purification by flash column chromatography on silica gel (n-Pentane/EtOAc 99:1) the title compound was obtained as a red solid (16 mg, 0.038 mmol, 38%).

m.p.: 219 °C.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.65 (dt, *J* = 8.1, 0.8 Hz, 1 H), 7.90 (d, *J* = 2.2 Hz, 1 H), 7.89 (d, *J* = 4.0 Hz, 1 H), 7.75 (dd, *J* = 7.6, 2.3 Hz, 2 H), 7.71 – 7.64 (m, 2 H), 7.61 (dd, *J* = 4.7, 1.6 Hz, 3 H), 7.54 – 7.48 (m, 3 H), 7.46 – 7.45 (m, 1 H), 7.42 (ddd, *J* = 8.0, 7.1, 0.9 Hz, 1 H), 7.15 (dd J = 3.6, 0.8, 1 H), 6.42 (dd, *J* = 3.8, 2.2 Hz, 1 H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 160.6, 135.7, 134.7, 133.0, 132.8, 132.6, 132.2, 132.1, 130.9, 130.3, 130.14 (t, *J* = 3.4 Hz), 129.6, 128.9, 128.3, 127.3, 125.1, 122.6, 121.7, 121.7, 118.9, 114.8, 104.1, 84.9.

^{19}F-NMR (470 MHz, $CDCl_3$): δ = -137.81 (dd, *J* = 58.9, 27.5 Hz).

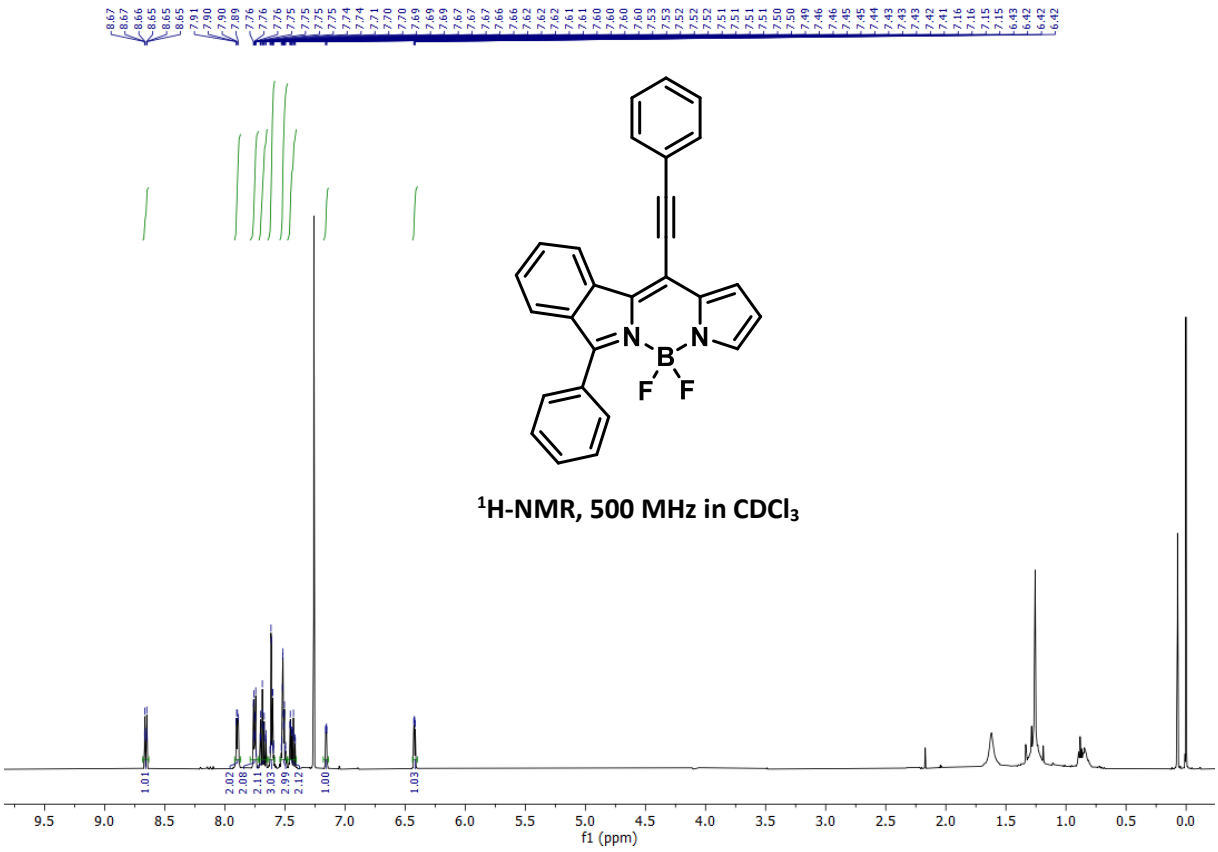
^{11}B-NMR (160 MHz, $CDCl_3$): δ = 1.32 (t, *J* = 30.0 Hz).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2923, 2856, 2318, 2203, 1560, 1396, 1186, 1126, 1075, 1031.

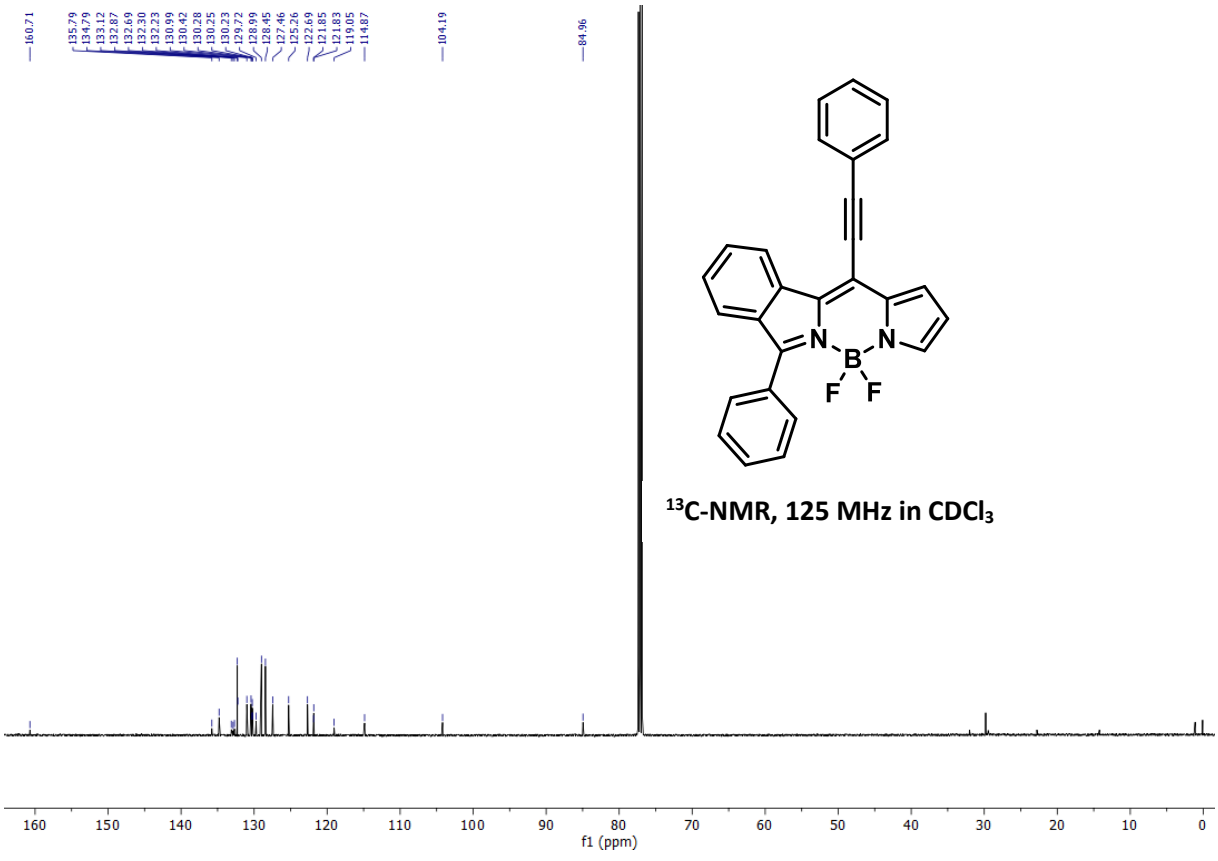
HRMS (ESI): $C_{27}H_{17}BF_2N_2$ calcd.: 419.1526, found: 419.1527, $[M+H]^+$.

UV/Vis (0.0058 mg/mL in CH_2Cl_2): λ_{max} [nm] (log ε) = 582 (4.34).

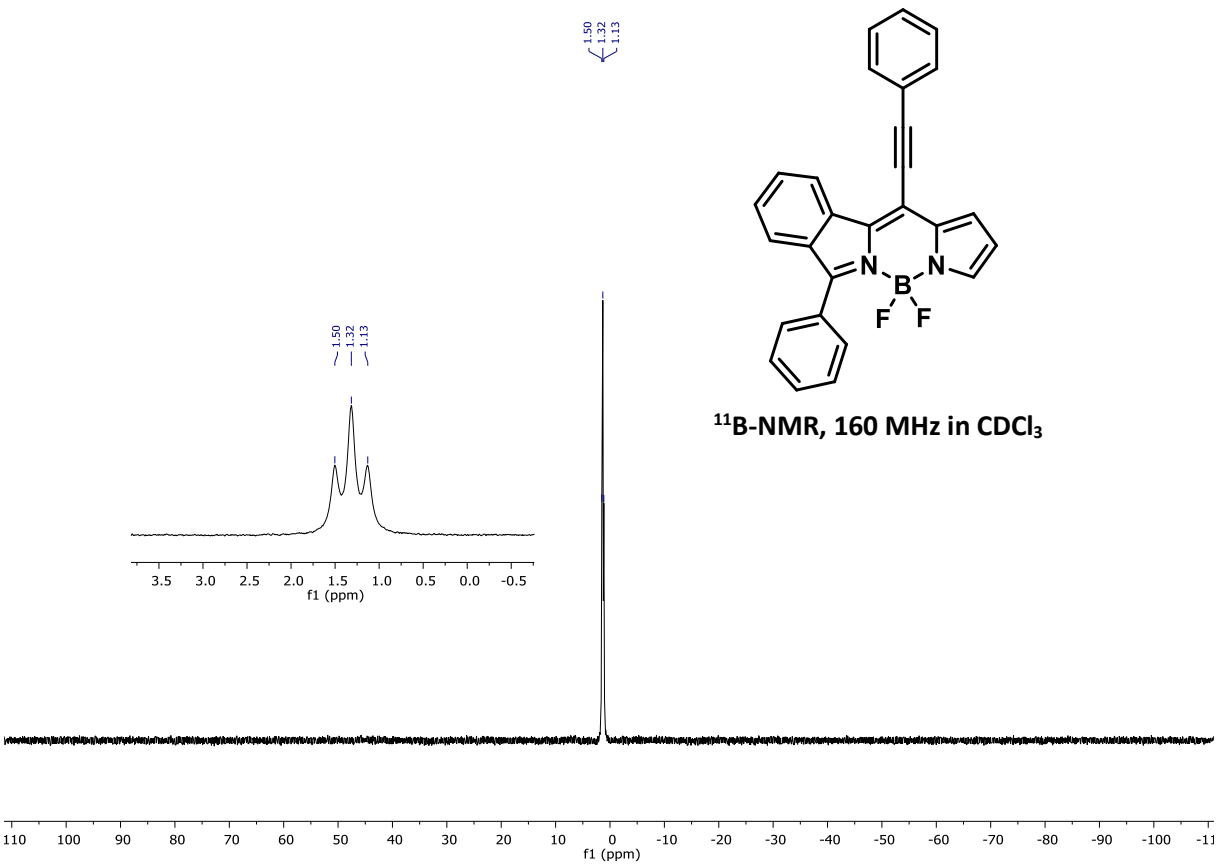
Emission (CH_2Cl_2): λ_{max} (nm) = 617.



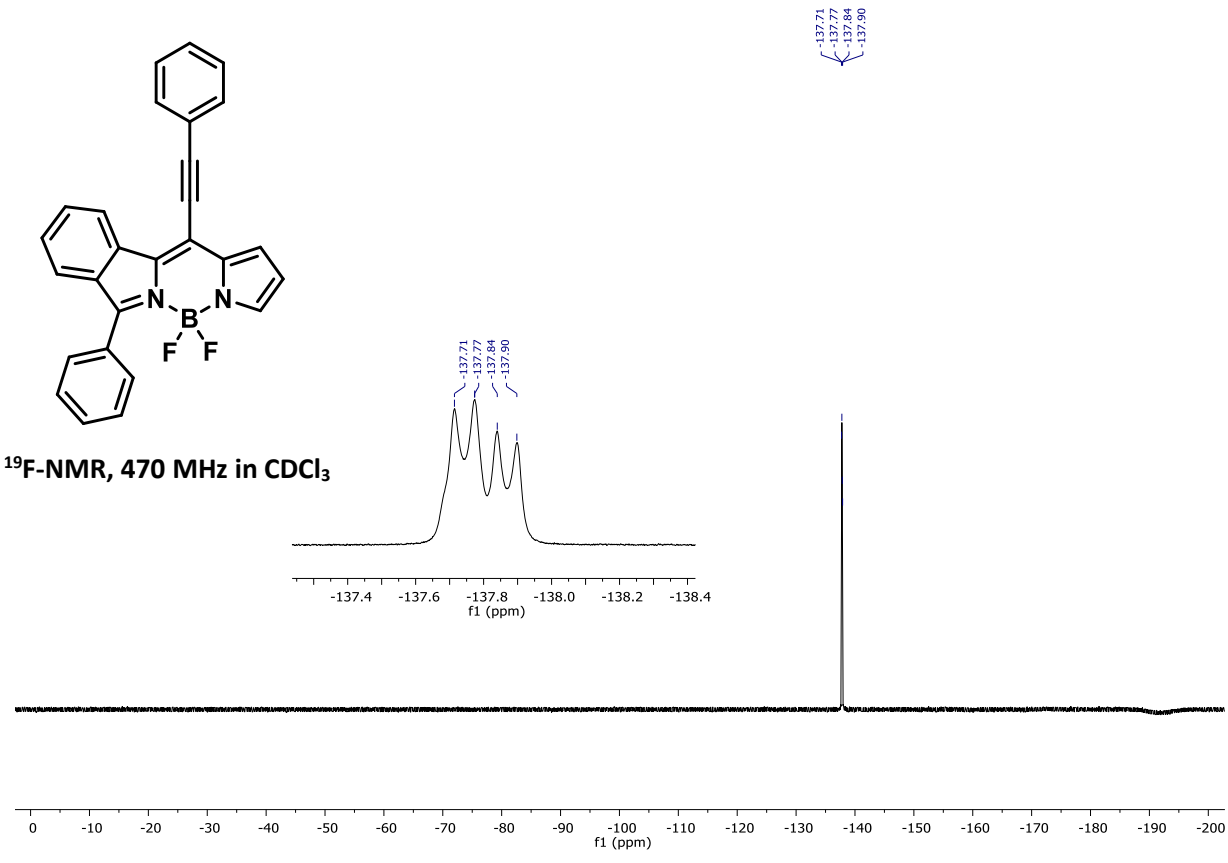
^{1}H-NMR, 500 MHz in $CDCl_3$



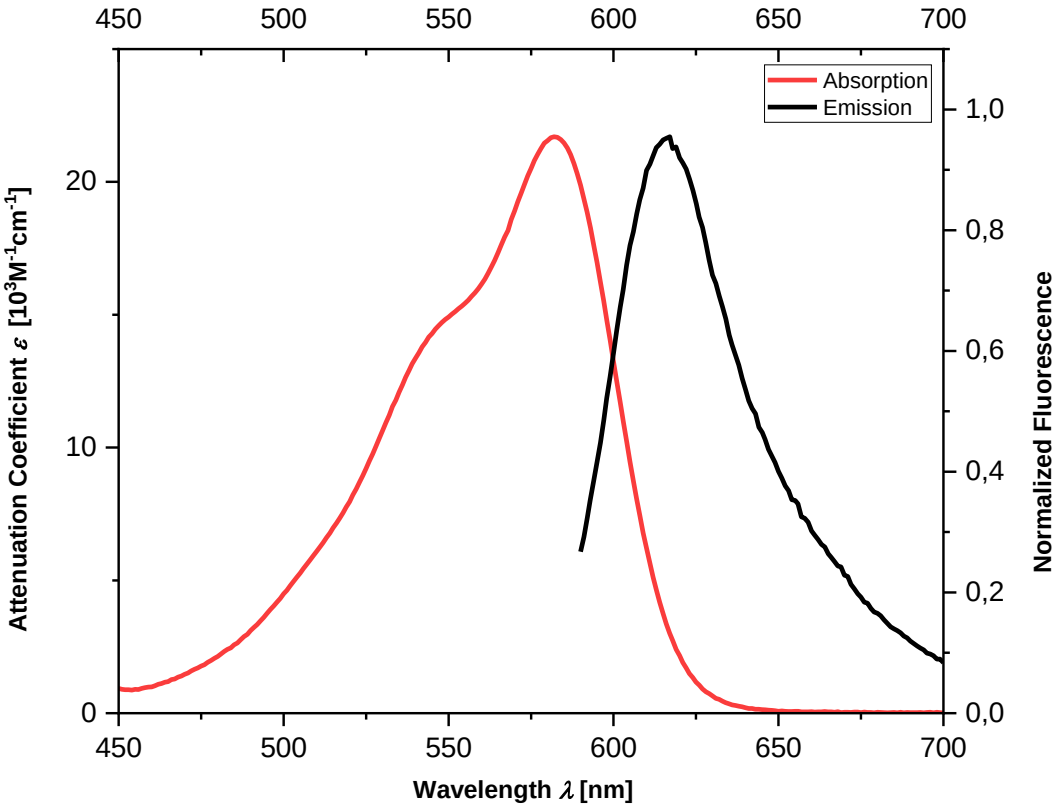
^{13}C-NMR, 125 MHz in $CDCl_3$



^{11}B-NMR, 160 MHz in $CDCl_3$

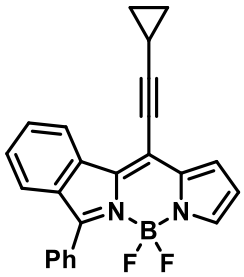


^{19}F-NMR, 470 MHz in $CDCl_3$



UV-Vis and normalized **fluorescence spectra** of **6a** at room temperature in CH_2Cl_2.

12-(Cyclopropylethynyl)-5,5-difluoro-7-phenyl-5*H*-5λ4,6λ4-pyrrolo[1',2':3,4][1,3,2]diazaborinino[6,1-*a*]isoindole



Precursor **1g** (58 mg, 0.10 mmol, 1.0 eq.) was reacted with ethynylcyclopropane (6.0 mg, 0.15 mmol, 1.5 eq.) according to **GP8** for 3 h. The crude product was subjected to **GP9**. Without further purification the product was reacted according to **GP10**. After purification by flash column chromatography on silica gel (n-Pentane/EtOAc 99:1) the title compound was obtained as a red solid (9.0 mg, 0.023 mmol, 23%).

m.p.: 186 °C

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.49 (dt, *J* = 8.1, 0.9 Hz, 1H), 7.89 – 7.83 (m, 2H), 7.68 – 7.56 (m, 5H), 7.42 – 7.37 (m, 2H), 6.99 (dd, *J* = 3.8, 1.3 Hz, 1H), 6.37 (dd, *J* = 3.8, 2.2 Hz, 1H), 1.82 – 1.75 (m, 1H), 1.20 – 1.09 (m, 4H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 159.7, 135.7, 134.3, 133.6, 132.9, 132.4, 132.0, 130.8 (t, *J* = 3.2 Hz), 130.2, 129.8, 128.4, 127.2, 125.0, 122.3, 121.7, 120.4, 114.6, 111.2, 72.2, 10.1, 1.5.

^{19}F-NMR (470 MHz, $CDCl_3$): δ = -137.53 (dd, *J* = 59.3, 28.3 Hz)

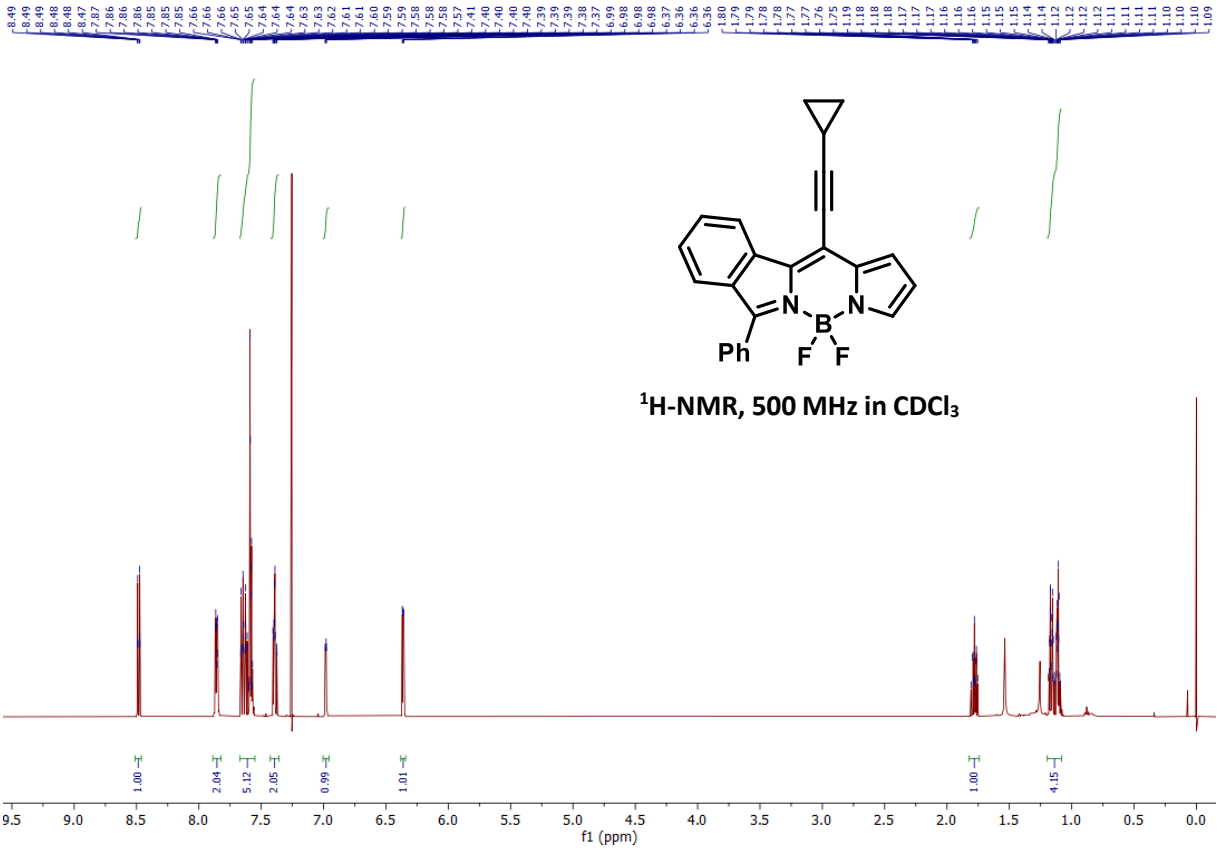
^{11}B-NMR (160 MHz, $CDCl_3$): δ = 1.05 (t, *J* = 30.1 Hz)

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2923, 2205, 1606, 1557, 1520, 1464, 1391, 1347, 1279, 1252, 1184, 1129, 1097, 1067, 1026, 977, 914, 740.

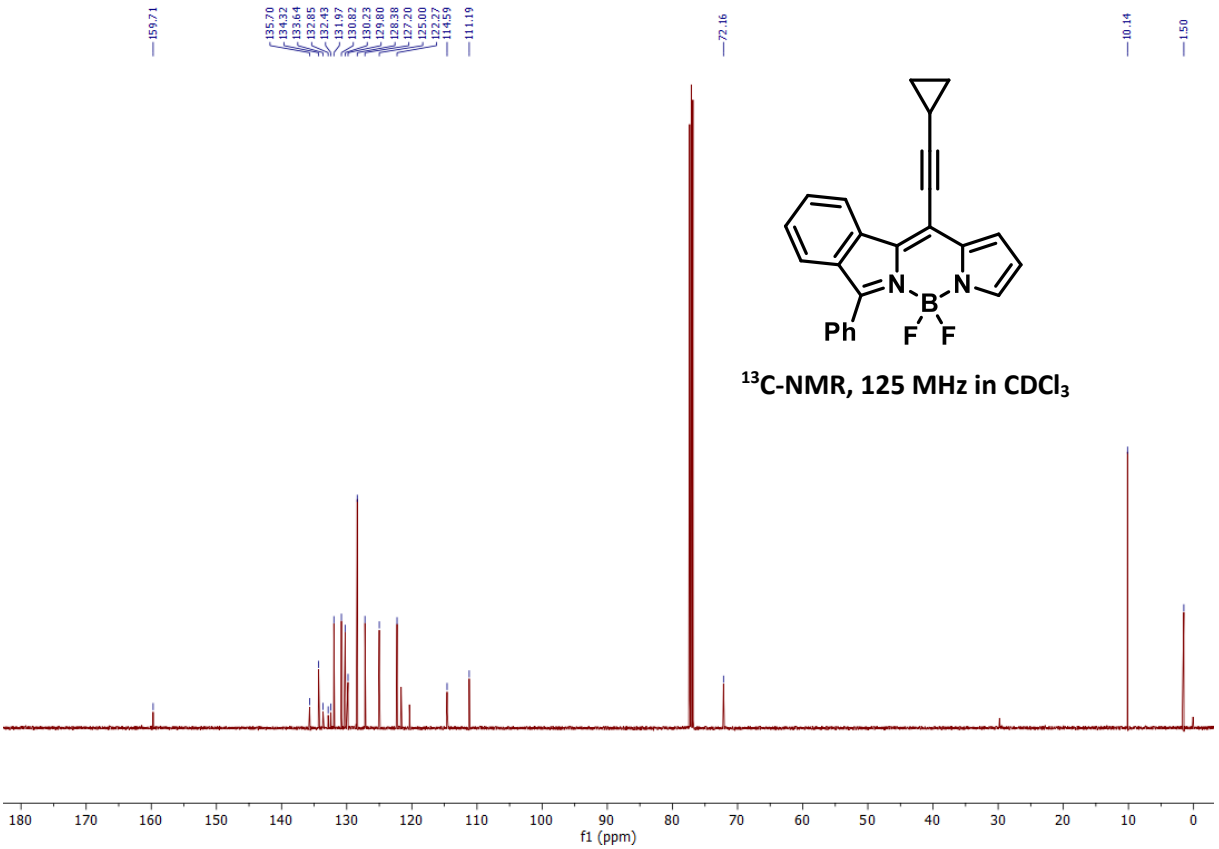
HRMS (ESI): $C_{24}H_{17}BF_2N_2$ calcd.: 383:1526 found: 383.1530, $[M+H]^+$.

UV/Vis (0.0030 mg/mL in CH_2Cl_2): λ_{max} [nm] (log ε) = 570 (4.60).

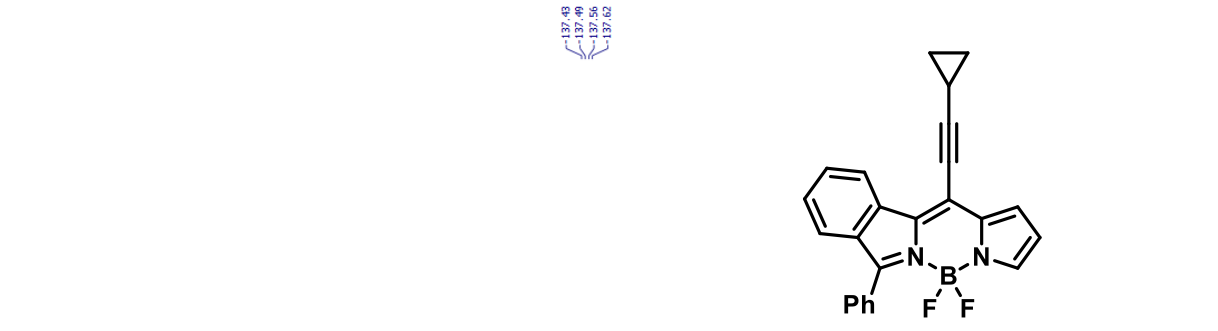
Emission (CH_2Cl_2): λ_{max} (nm) = 604.



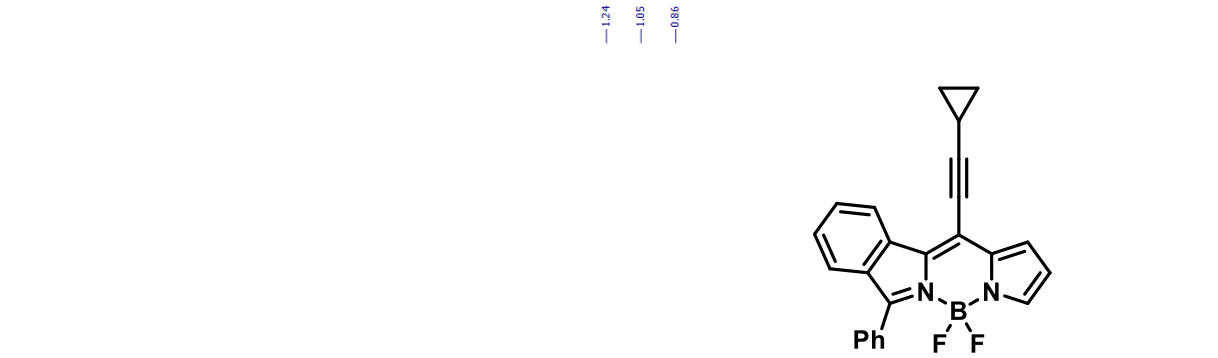
^{1}H-NMR, 500 MHz in $CDCl_3$



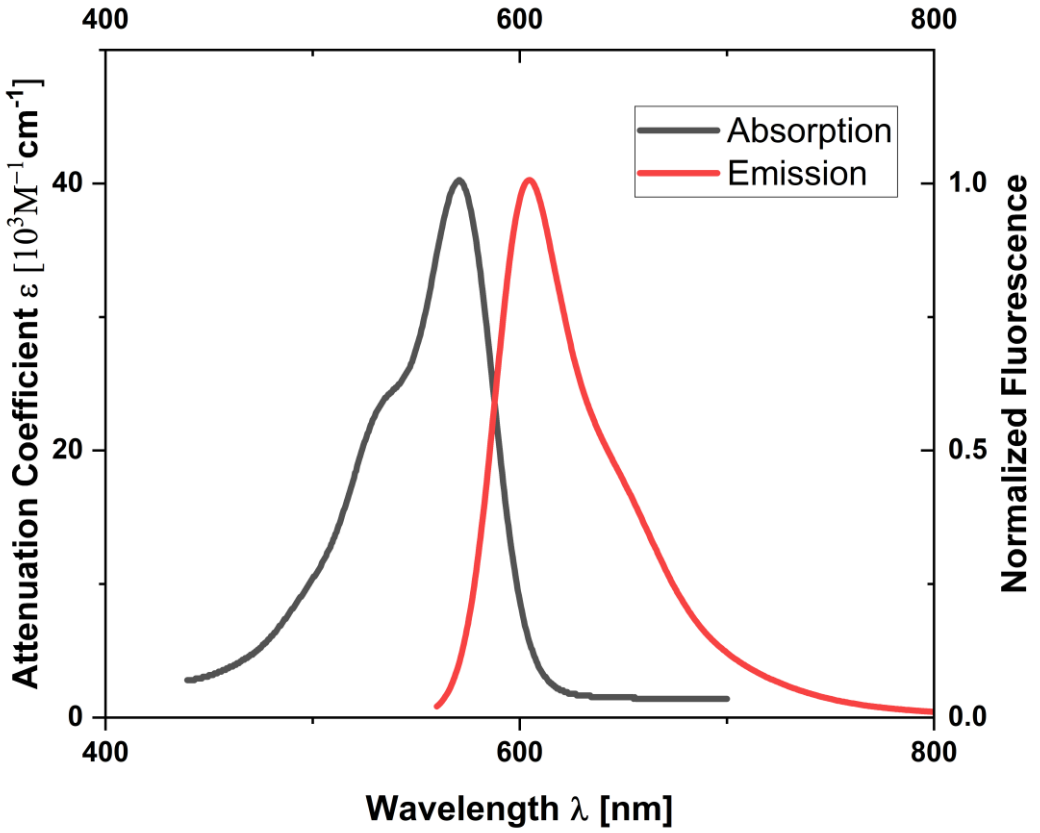
^{13}C-NMR, 125 MHz in $CDCl_3$



^{19}F-NMR, 470 MHz in $CDCl_3$

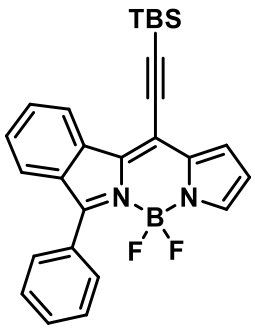


^{11}B-NMR, 160 MHz in $CDCl_3$



UV-Vis and normalized **fluorescence spectra** of **6a** at room temperature in CH_2Cl_2.

12-((*tert*-Butyldimethylsilyl)ethynyl)-5,5-difluoro-7-phenyl-5*H*-5λ^4,6λ^4-pyrrolo[1',2':3,4][1,3,2]diazaborinino[6,1-*a*]isoindole (6c)



Precursor **1g** (58 mg, 0.10 mmol, 1.0 eq.) was reacted with *tert*-butyl(ethynyl)dimethylsilane (21 mg, 0.15 mmol, 1.5 eq.) according to **GP8** for 3 h. The crude product was subjected to **GP9**. Without further purification the product was reacted according to **GP10**. After purification by flash column chromatography on silica gel (n-Pentane/EtOAc 99:1) the title compound was obtained as a red solid (35 mg, 0.077 mmol, 77%).

m.p.: 137 °C.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.65 (dt, *J* = 8.2, 0.9 Hz, 1 H), 7.89 – 7.85 (m, 2 H), 7.67 (dt, *J* = 8.1, 1.0 Hz, 1 H), 7.65 – 7.58 (m, 4 H), 7.43 – 7.39 (m, 2 H), 7.04 (dd, *J* = 3.6, 1.1 Hz, 1 H), 6.39 (dd, *J* = 3.8, 2.2 Hz, 1 H), 1.10 (s, 9 H), 0.37 (s, 6 H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 160.9, 135.7, 134.8, 133.3, 132.6, 132.0, 130.9, 130.1, 129.5, 128.3, 127.4, 125.1, 122.8, 121.9, 118.3, 114.7, 110.8, 99.9, 26.2, 16.9, 1.0, -4.8.

^{19}F-NMR (376 MHz, $CDCl_3$): δ = -137.85 (dd, *J* = 58.9, 27.6 Hz).

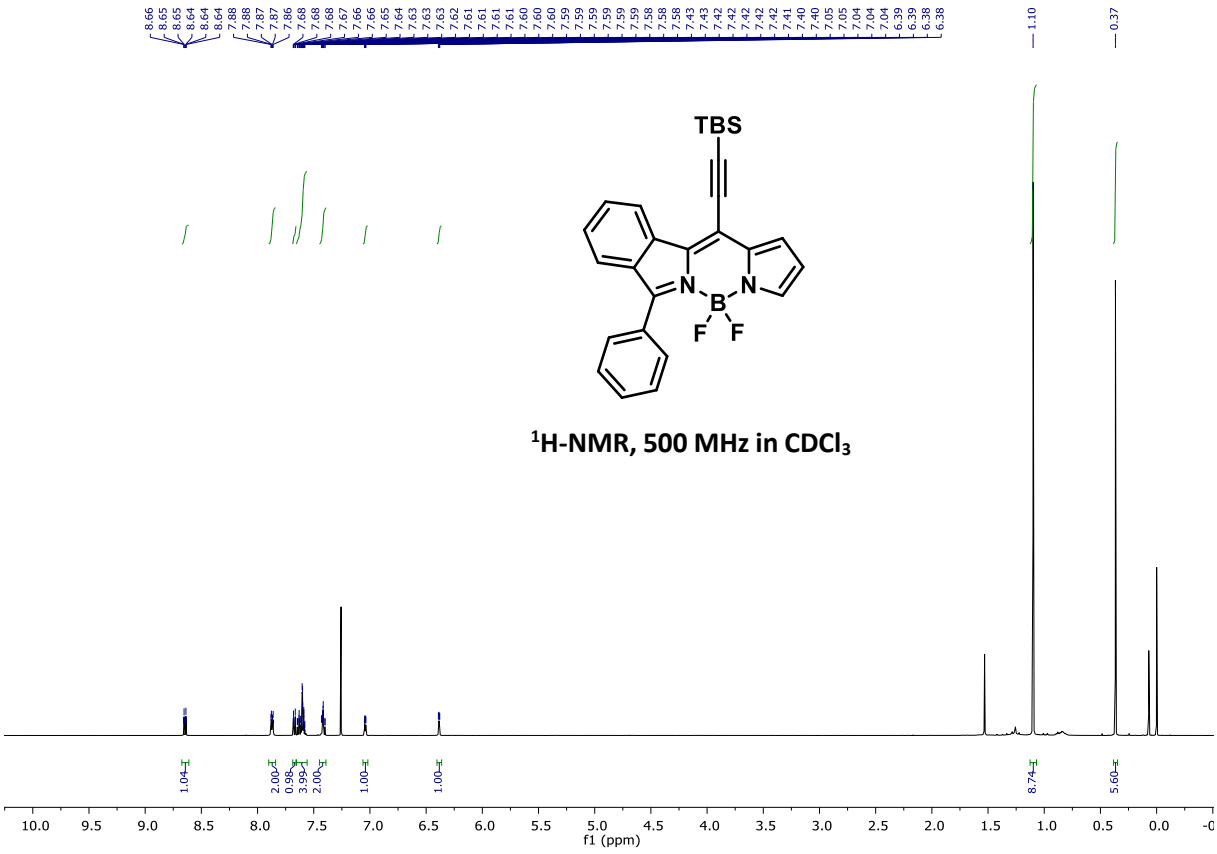
^{11}B-NMR (160 MHz, $CDCl_3$): δ = 1.26 (t, J = 30.0 Hz).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3108, 3058, 2939, 2851, 2114, 1755, 1559, 1390, 1119.

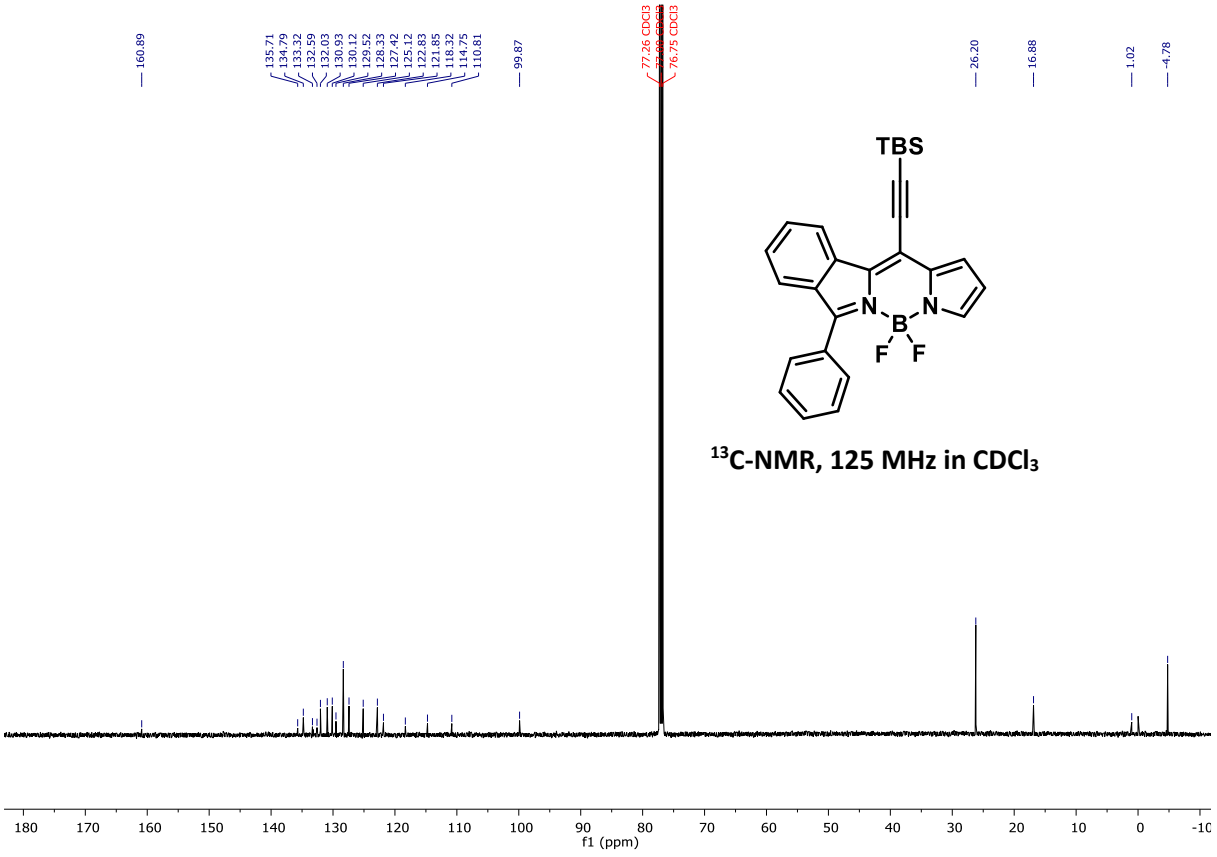
HRMS (ESI): $C_{27}H_{27}BF_2N_2Si$ calcd.: 479.1902 found: 479.1904, $[M+Na]^+$.

UV/Vis (0.0022 mg/mL in CH_2Cl_2): λ_{max} [nm] (log ε) = 580 (4.53).

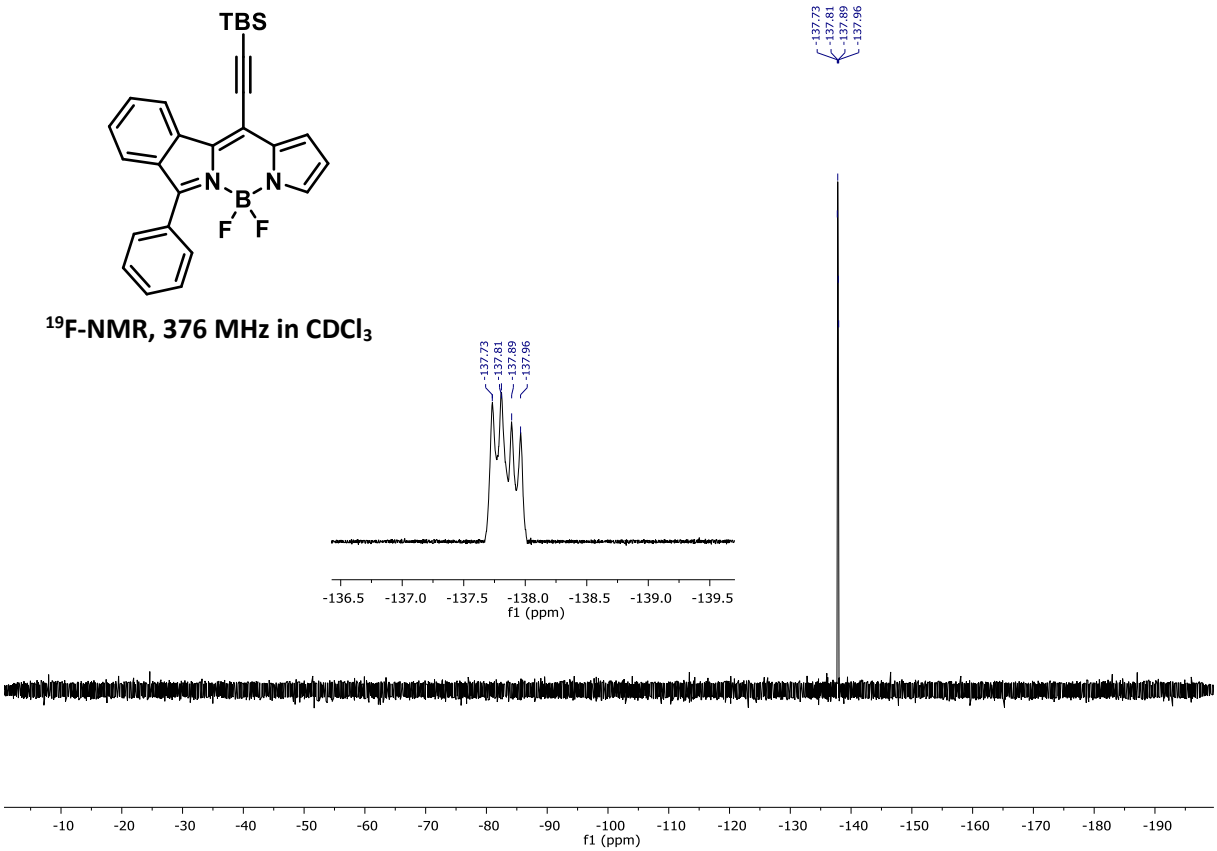
Emission (CH_2Cl_2): λ_{max} (nm) = 613.



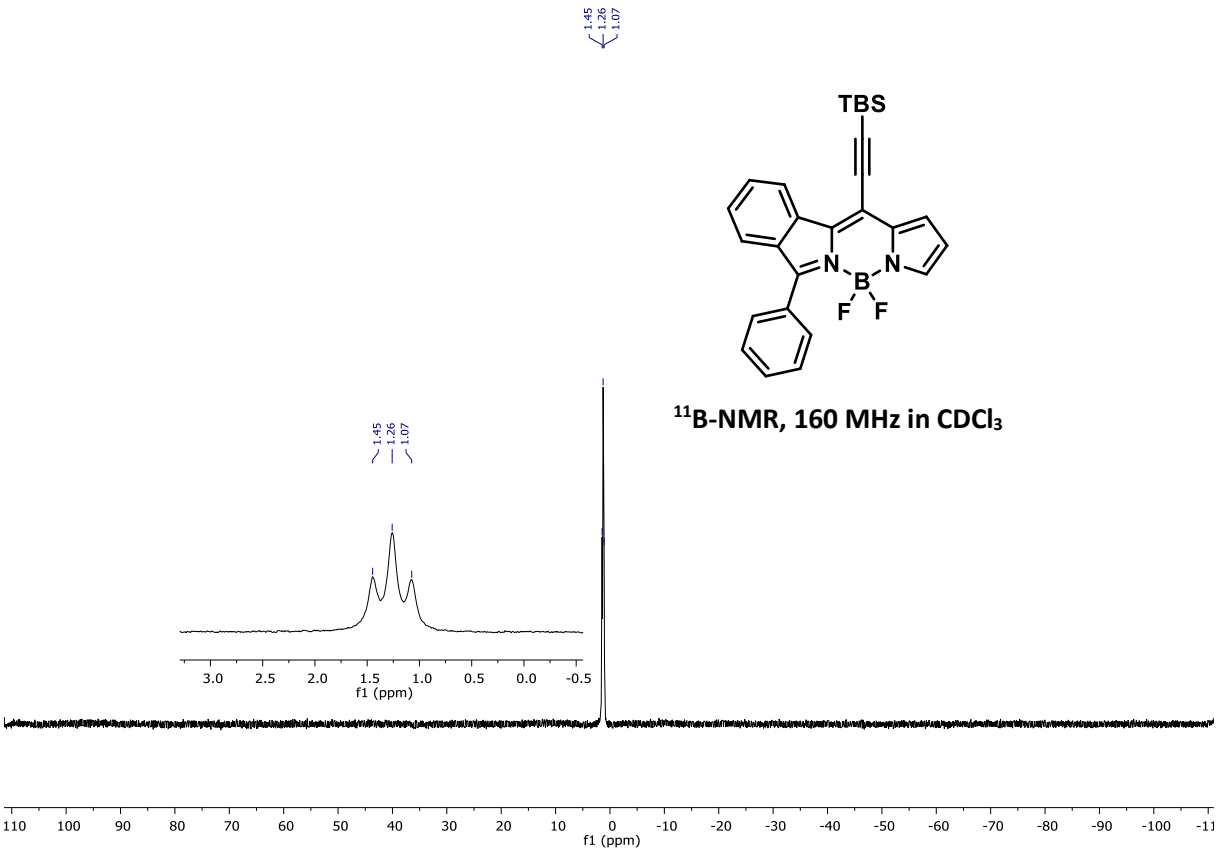
^{1}H-NMR, 500 MHz in $CDCl_3$



^{13}C-NMR, 125 MHz in $CDCl_3$

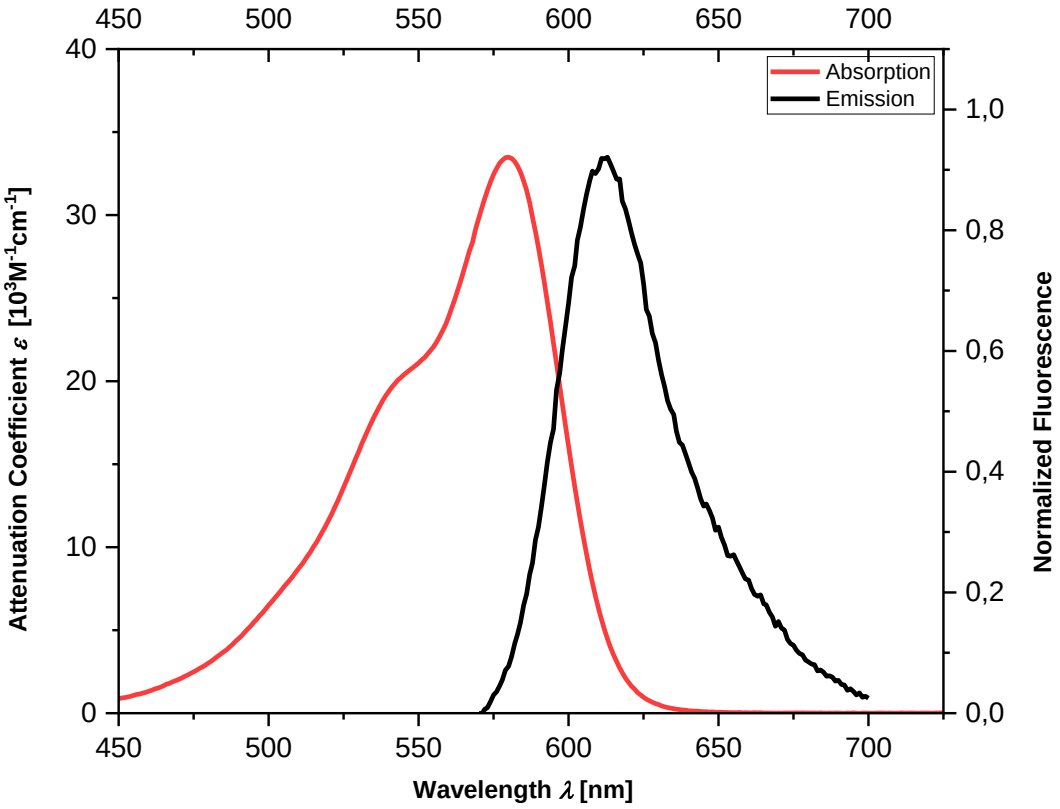


^{19}F-NMR, 376 MHz in $CDCl_3$



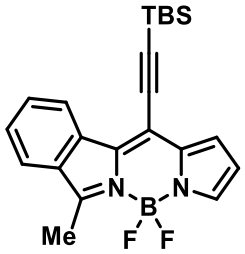
^{11}B-NMR, 160 MHz in $CDCl_3$

^{11}B-NMR (160 MHz, $CDCl_3$).



UV-Vis and normalized **fluorescence spectra** of **6c** at room temperature in CH_2Cl_2.

12-((*tert*-Butyldimethylsilyl)ethynyl)-5,5-difluoro-7-methyl-5*H*-5λ^4,6λ^4-pyrrolo[1',2':3,4][1,3,2]diazaborinino[6,1-*a*]isoindole (6d)



Precursor **1h** (52 mg, 0.10 mmol, 1.0 eq.) was reacted with *tert*-butyl(ethynyl)dimethylsilane (21 mg, 0.15 mmol, 1.5 eq.) according to **GP8** for 3 h. The crude product was subjected to **GP9**. Without further purification, the product was reacted according to **GP10**. After purification by flash column chromatography on silica gel (n-Pentane/EtOAc 99:1) the title compound was obtained as a red solid (19 mg, 0.048 mmol, 48%).

m.p.: 156 °C

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.51 (dt, *J* = 8.1, 0.9 Hz, 1H), 7.79 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.62 (ddd, *J* = 8.1, 7.1, 1.0 Hz, 1H), 7.46 – 7.42 (m, 2H), 6.96 (dd, *J* = 3.7, 1.3 Hz, 1H), 6.38 (dd, *J* = 3.7, 2.3 Hz, 1H), 2.98 (s, 3H), 1.08 (s, 9H), 0.34 (s, 6H).

^{13}C-NMR (125 MHz, $CDCl_3$): *δ* = 163.0, 135.4, 133.6, 133.0, 132.9, 132.7, 132.5, 127.4, 123.4, 123.1, 120.7, 116.8, 114.2, 109.9, 99.7, 26.3, 16.9, 13.5, -4.7.

^{19}F-NMR (470 MHz, $CDCl_3$): *δ* = -144.42 (dd, *J* = 60.8, 29.1 Hz).

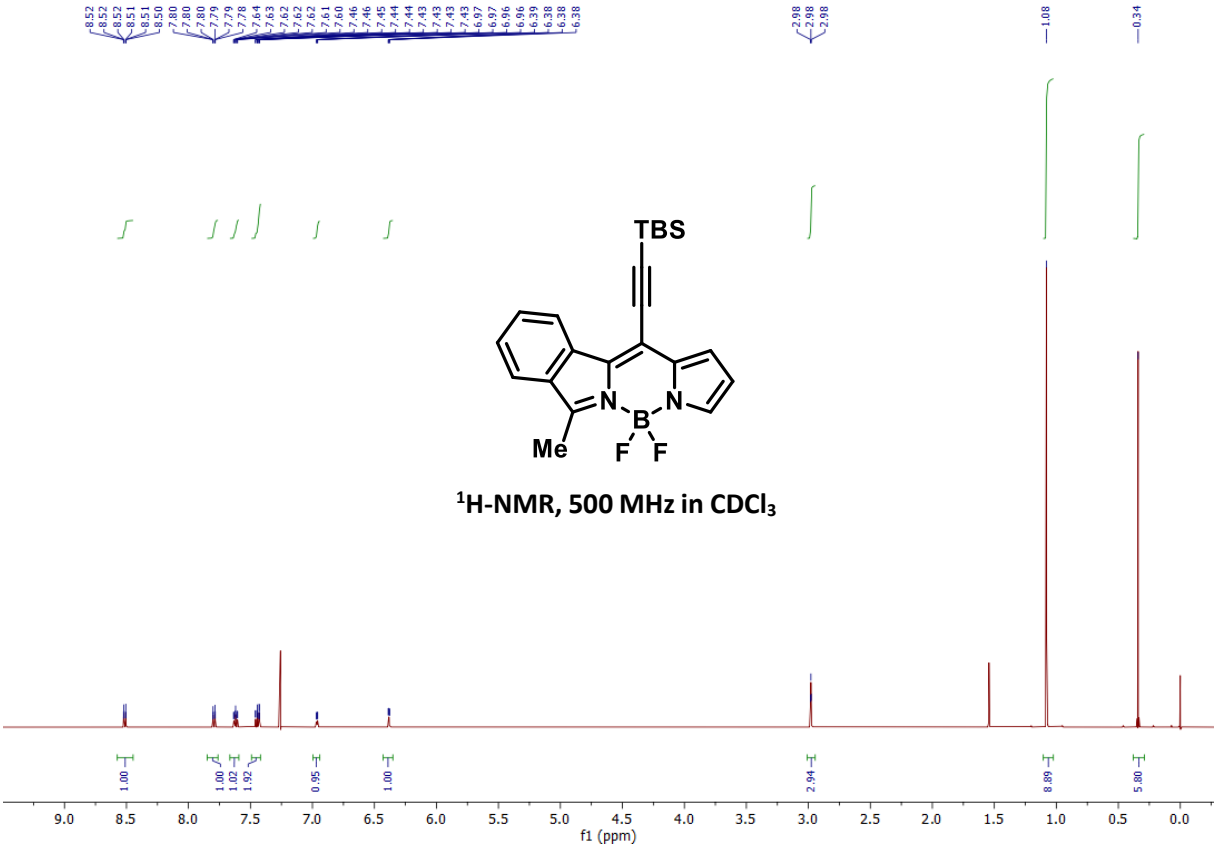
^{11}B-NMR (160 MHz, $CDCl_3$): *δ* = 0.97 (t, *J* = 30.6 Hz).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3660, 2981, 2888, 1740, 1574, 1471, 1394, 1236, 1144, 1086, 968, 831.

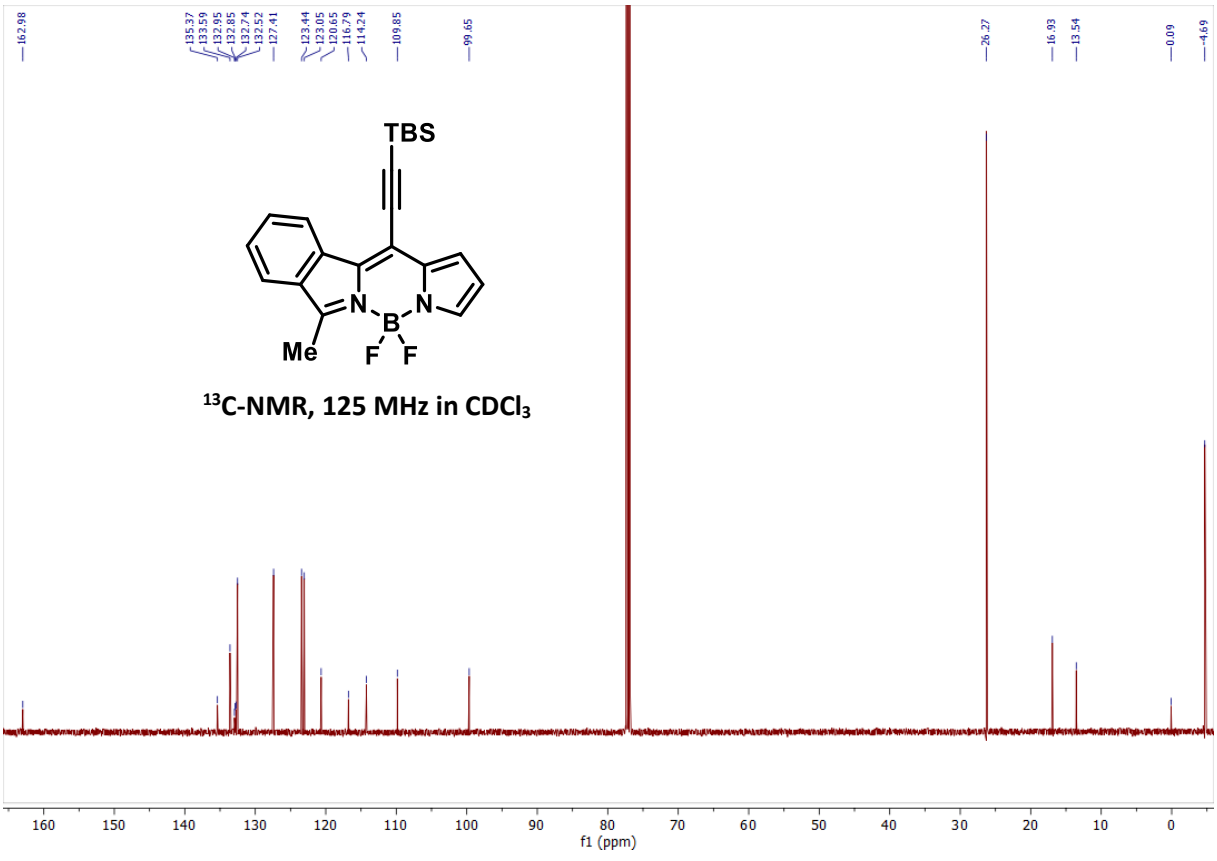
HRMS (ESI): $C_{22}H_{25}BF_2N_2Si$ calcd.: 395.1921 found: 395.1918, $[M+H]^+$.

UV/Vis (0.0046 mg/mL in CH_2Cl_2): λ_{max} [nm] (log ε) = 553 (4.33).

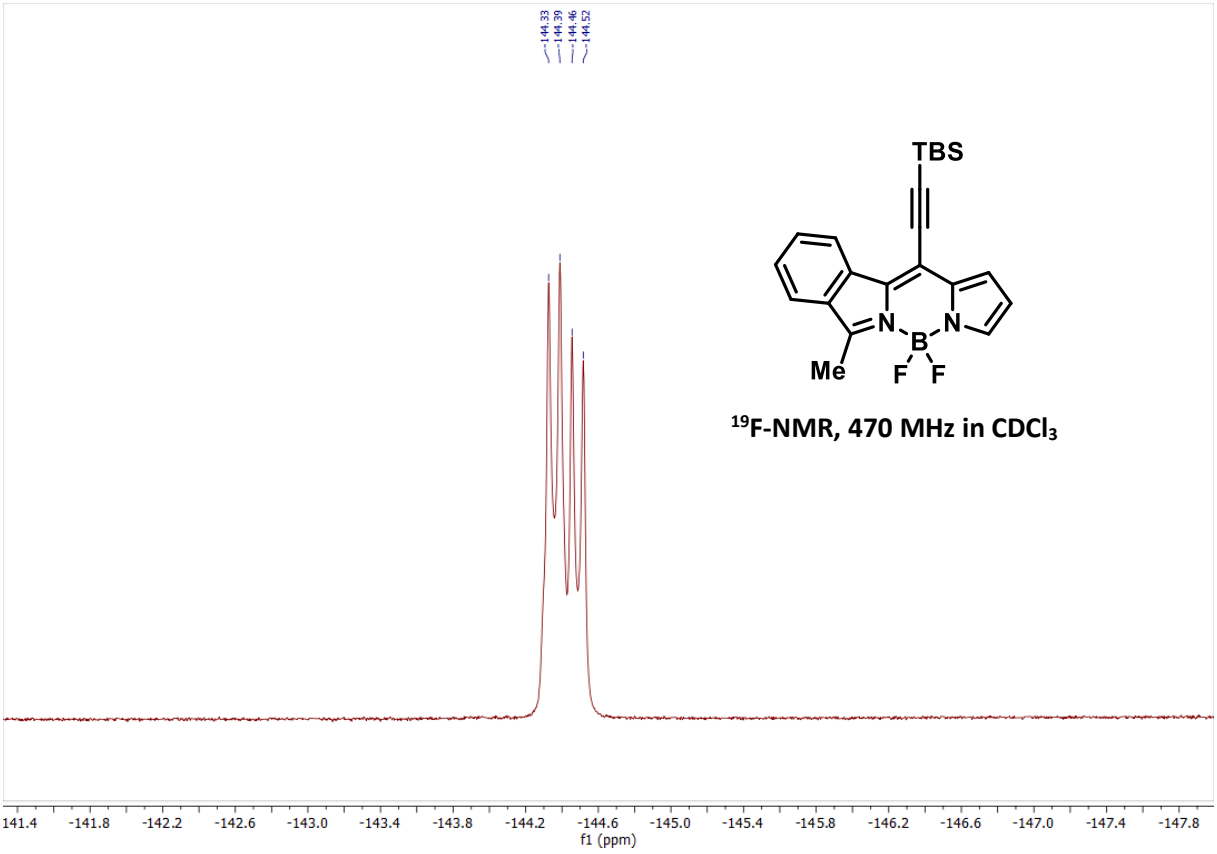
Emission (CH_2Cl_2): λ_{max} (nm) = 583.



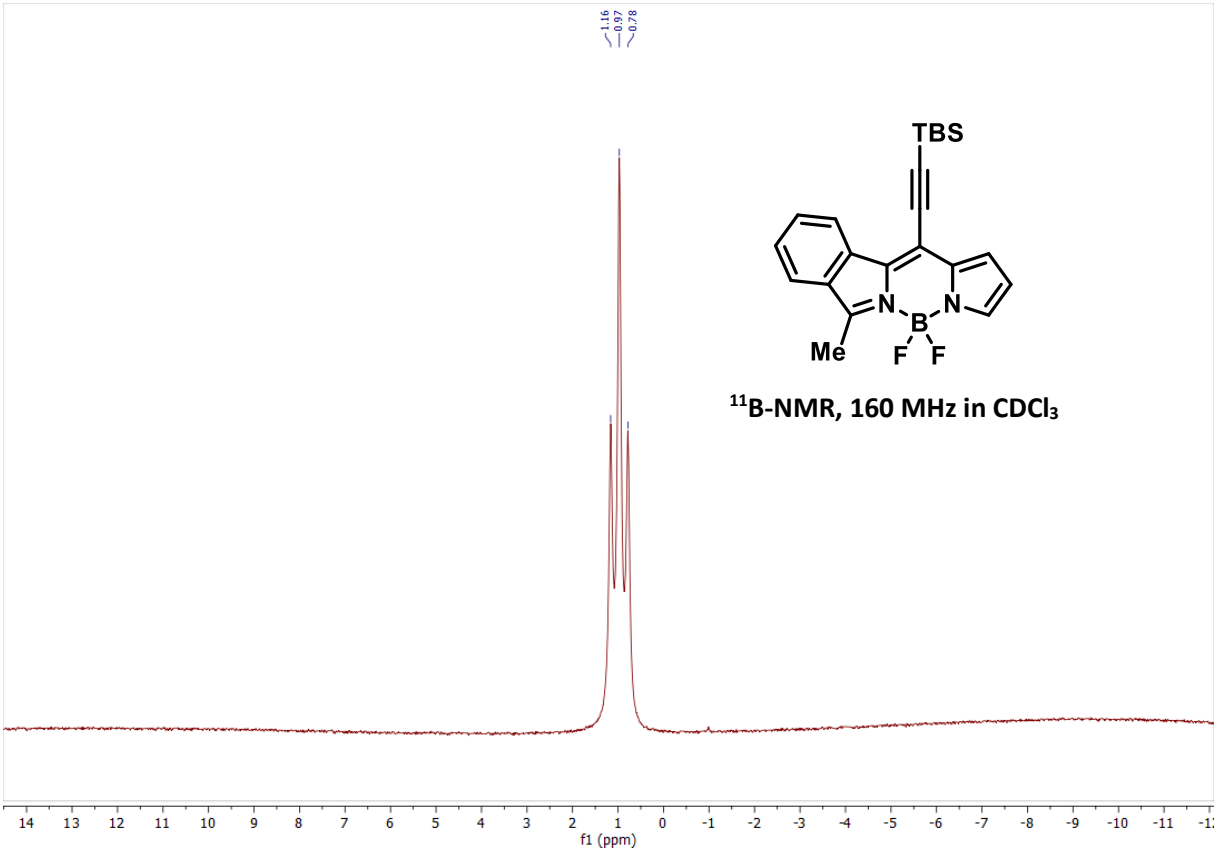
^{1}H-NMR, 500 MHz in $CDCl_3$



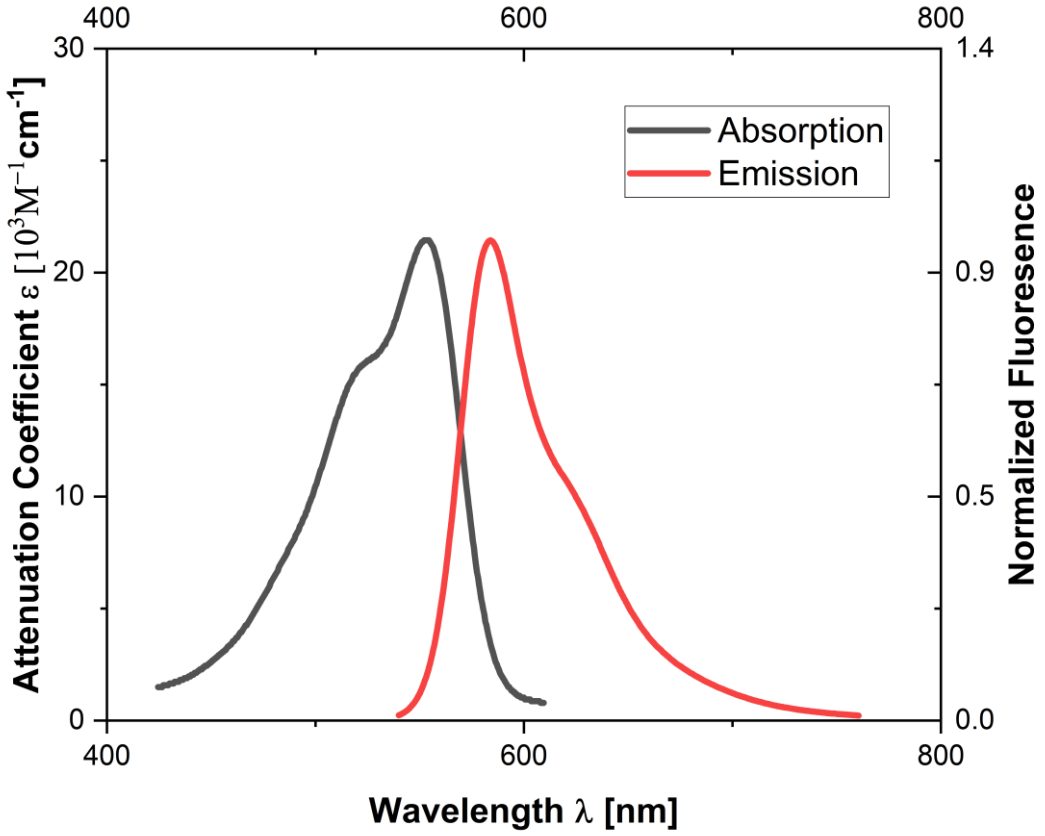
^{13}C-NMR, 125 MHz in $CDCl_3$



^{19}F-NMR, 470 MHz in $CDCl_3$

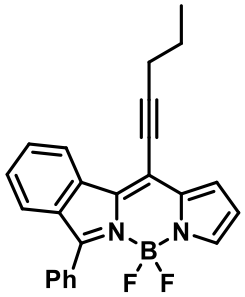


^{11}B-NMR, 160 MHz in $CDCl_3$



UV-Vis and normalized **fluorescence spectra** of **6d** at room temperature in CH_2Cl_2.

5,5-Difluoro-12-(pent-1-yn-1-yl)-7-phenyl-5*H*-5λ^4,6λ^4-pyrrolo[1',2':3,4][1,3,2]diazaborinino[6,1-*a*]isoindole (6e)



Precursor **1g** (58 mg, 0.10 mmol, 1.0 eq.) was reacted with pent-1-yne (10 mg, 0.15 mmol, 1.5 eq.) according to **GP8** for 3 h. The crude product was subjected to **GP9**. Without further purification, the product was reacted according to **GP10**. After purification by flash column chromatography on silica gel (n-Pentane/EtOAc 99:1) the title compound was obtained as a red solid (26 mg, 0.068 mmol, 68%).

m.p.: 132 °C

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.56 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.89 – 7.84 (m, 2H), 7.68 – 7.56 (m, 5H), 7.42 – 7.38 (m, 2H), 7.04 (dd, *J* = 3.8, 1.3 Hz, 1H), 6.38 (dd, *J* = 3.8, 2.2 Hz, 1H), 2.73 (t, *J* = 7.0 Hz, 2H), 1.85 (h, *J* = 7.2 Hz, 2H), 1.19 (t, *J* = 7.4 Hz, 3H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 160.1, 135.8, 134.5, 133.7, 132.9, 132.5, 132.0, 130.9, 130.2 (t, *J* = 3.2 Hz), 129.8, 128.4, 127.3, 125.0, 122.5, 121.9, 120.2, 114. 7, 107. 5, 76.7, 22.5, 22.0, 13.9.

^{19}F-NMR (470 MHz, $CDCl_3$): δ = -137.51 (dd, *J* = 59.4, 28.1 Hz).

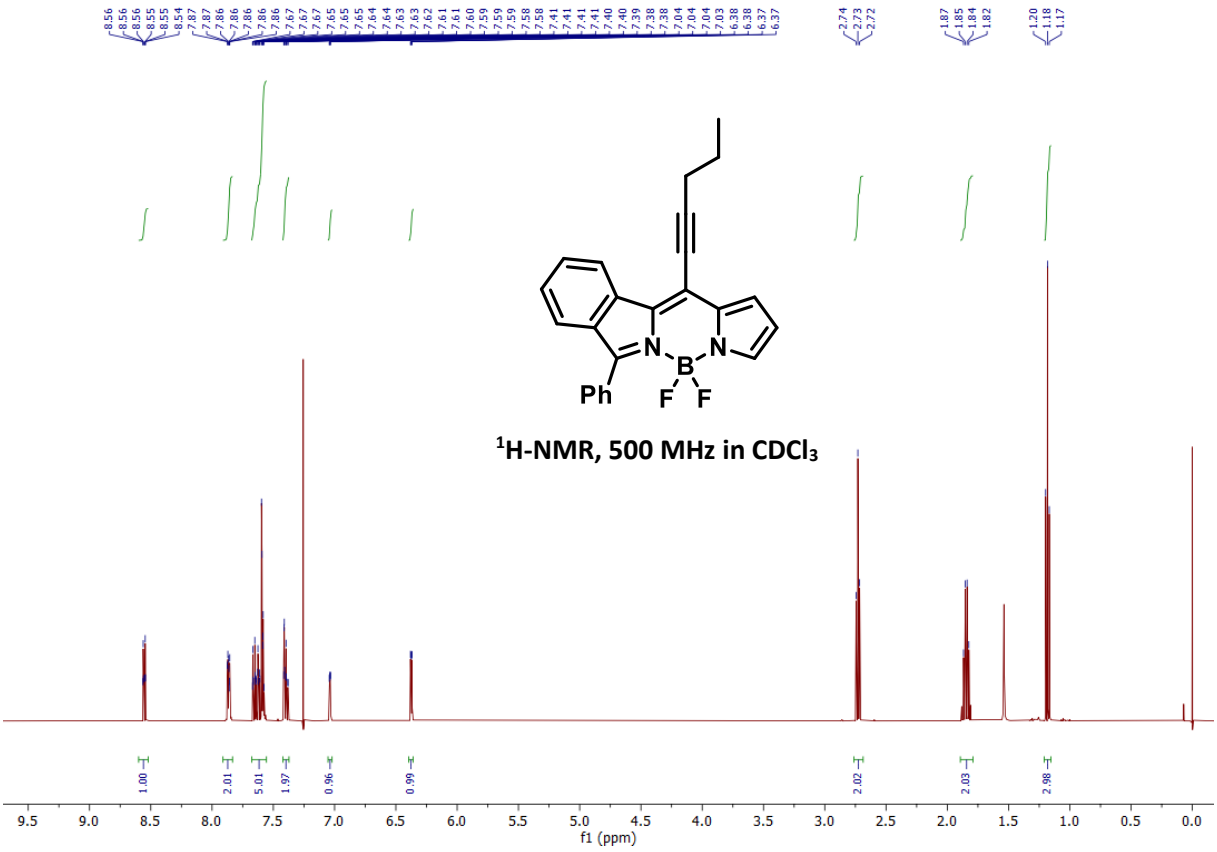
^{11}B-NMR (160 MHz, $CDCl_3$): δ = 1.06 (t, *J* = 30.1 Hz).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2922, 2853, 2220, 1608, 1558, 1461, 1391, 1347, 1280, 1219, 1184, 1127, 1097, 977, 784, 754, 697.

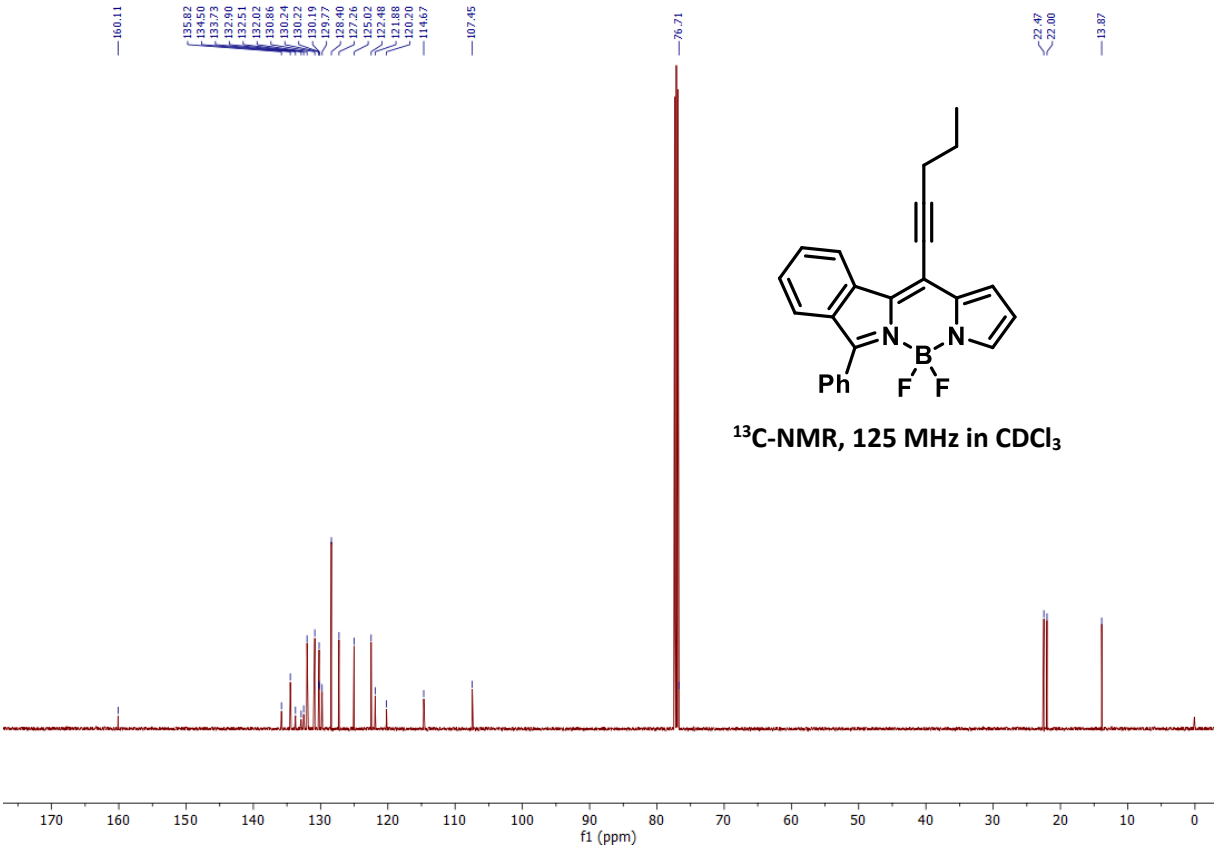
HRMS (ESI): $C_{24}H_{19}BF_2N_2$ calcd.: 385.1682 found: 385.1682, $[M+H]^+$.

UV/Vis (0.0056 mg/mL in CH_2Cl_2): λ_{max} [nm] (log ε) = 564 (4.14).

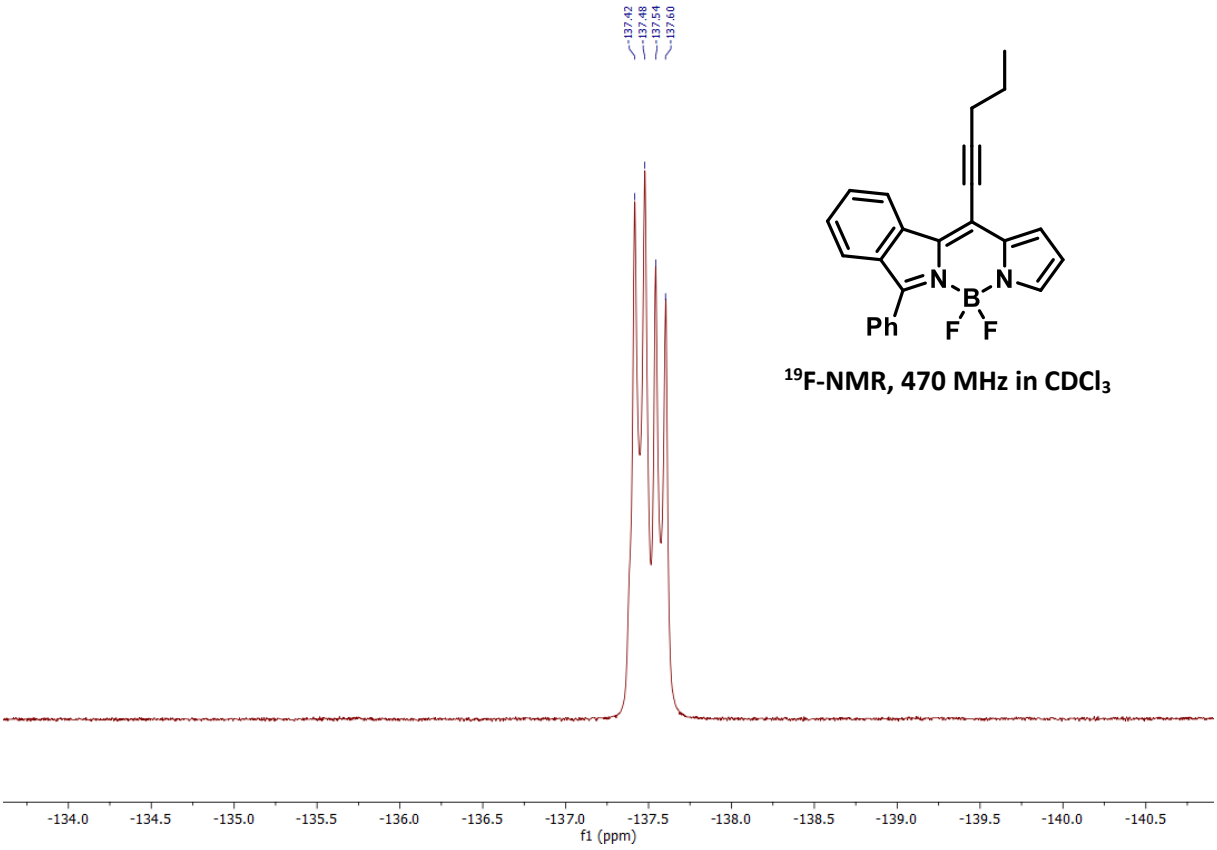
Emission (CH_2Cl_2): λ_{max} (nm) = 602.



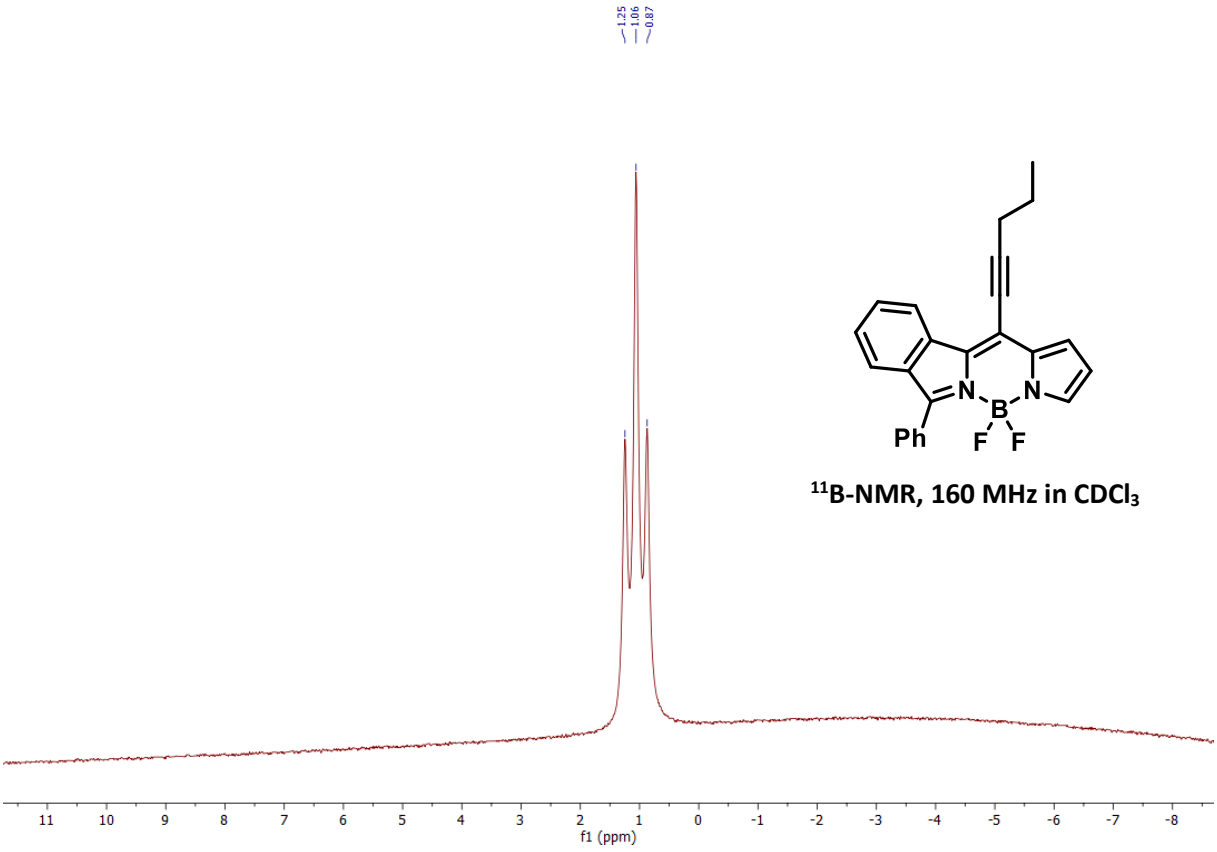
^{1}H-NMR, 500 MHz in $CDCl_3$



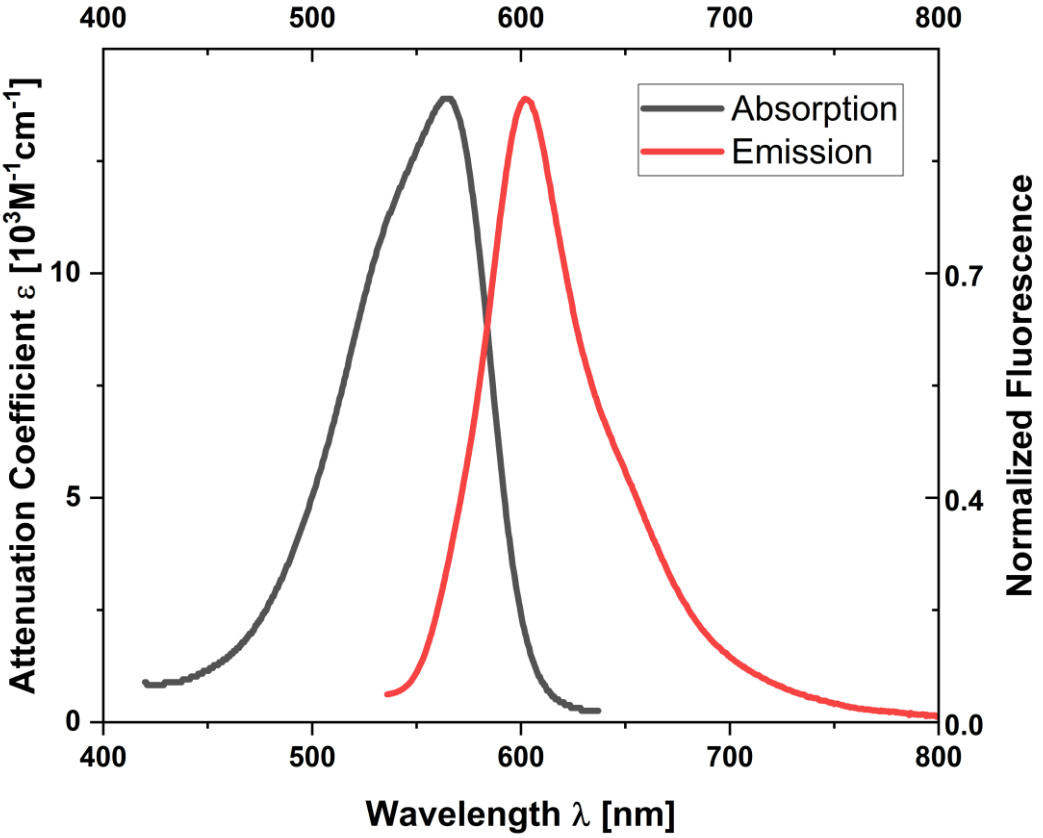
^{13}C-NMR, 125 MHz in $CDCl_3$



^{19}F-NMR, 470 MHz in $CDCl_3$

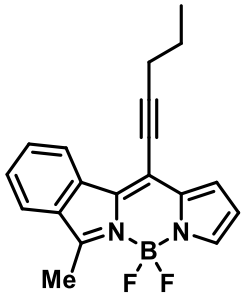


^{11}B-NMR, 160 MHz in $CDCl_3$



UV-Vis and normalized **fluorescence spectra** of **6e** at room temperature in CH_2Cl_2.

5,5-Difluoro-12-(pent-1-yn-1-yl)-7-methyl-5*H*-5λ^4,6λ^4-pyrrolo[1',2':3,4][1,3,2]diazaborinino[6,1-*a*]isoindole (6f)



Precursor **1h** (52 mg, 0.10 mmol, 1.0 eq.) was reacted with pent-1-yne (10 mg, 0.15 mmol, 1.5 eq.) according to **GP8** for 3 h. The crude product was subjected to **GP9**. Without further purification, the product was reacted according to **GP10**. After purification by flash column chromatography on silica gel (n-Pentane/EtOAc 99:1) the title compound was obtained as a red solid (6 mg, 0.019 mmol, 19%).

m.p.: 132 °C

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.43 (dt, *J* = 8.1, 0.9 Hz, 1H), 7.78 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.62 (ddd, *J* = 8.1, 7.1, 1.0 Hz, 1H), 7.45 – 7.41 (m, 2H), 6.96 (dd, *J* = 3.7, 1.3 Hz, 1H), 6.37 (dd, *J* = 3.7, 2.3 Hz, 1H), 2.97 (s, 3H), 2.69 (t, *J* = 7.0 Hz, 2H), 1.82 (q, *J* = 7.2 Hz, 2H), 1.16 (t, *J* = 7.4 Hz, 3H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 162.0, 135.4, 133.2, 132.6, 132.5, 132.5 132.4, 127.1, 123.3, 122.6, 120.5, 118.4, 114.1, 106.4, 76.3, 22.4, 22.0, 13.8, 13.4 (t, *J* = 2.9 Hz).

^{19}F-NMR (470 MHz, $CDCl_3$): δ = -144.53 (dd, J = 60.9, 29.8 Hz).

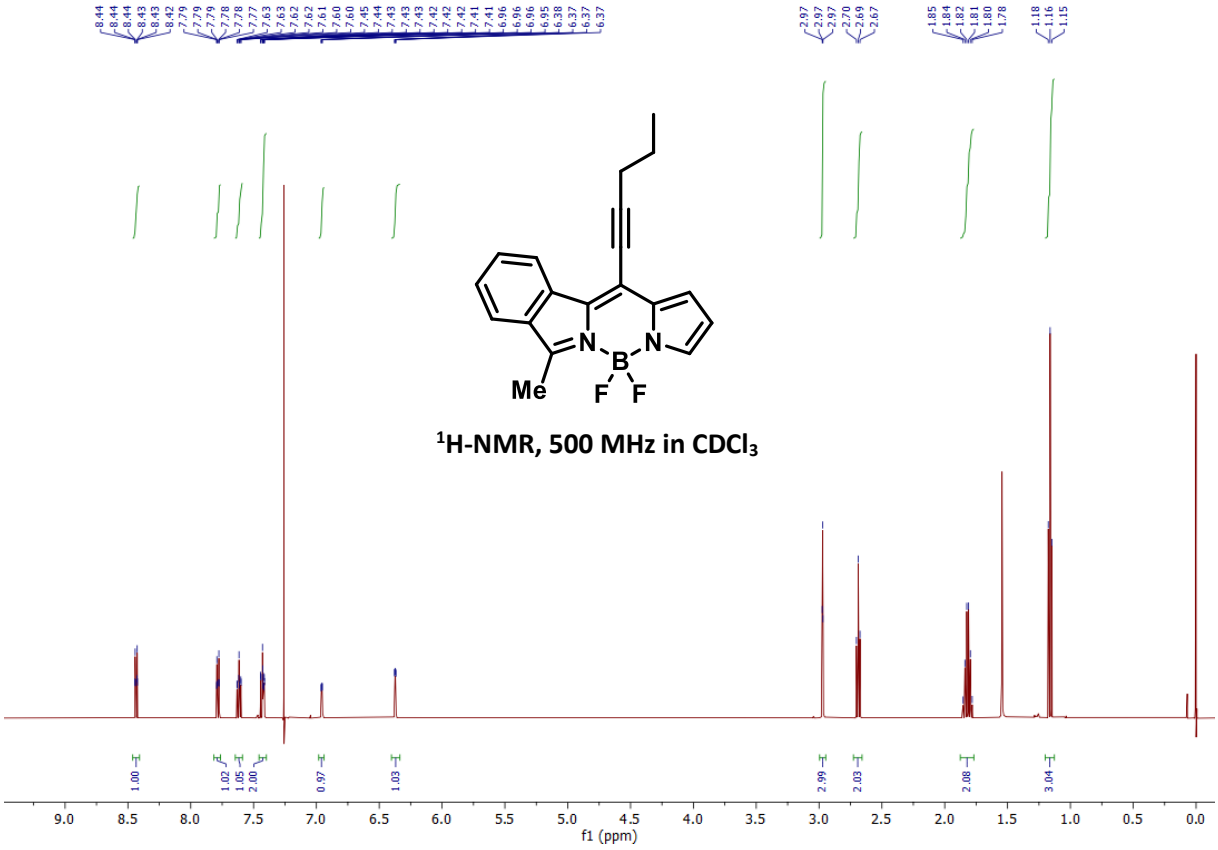
^{11}B-NMR (160 MHz, $CDCl_3$): δ = 0.99 (t, J = 30.7 Hz).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2960, 2927, 2853, 2218, 1731, 1568,1524, 1393, 1374, 1251, 1139, 1063, 981, 752.

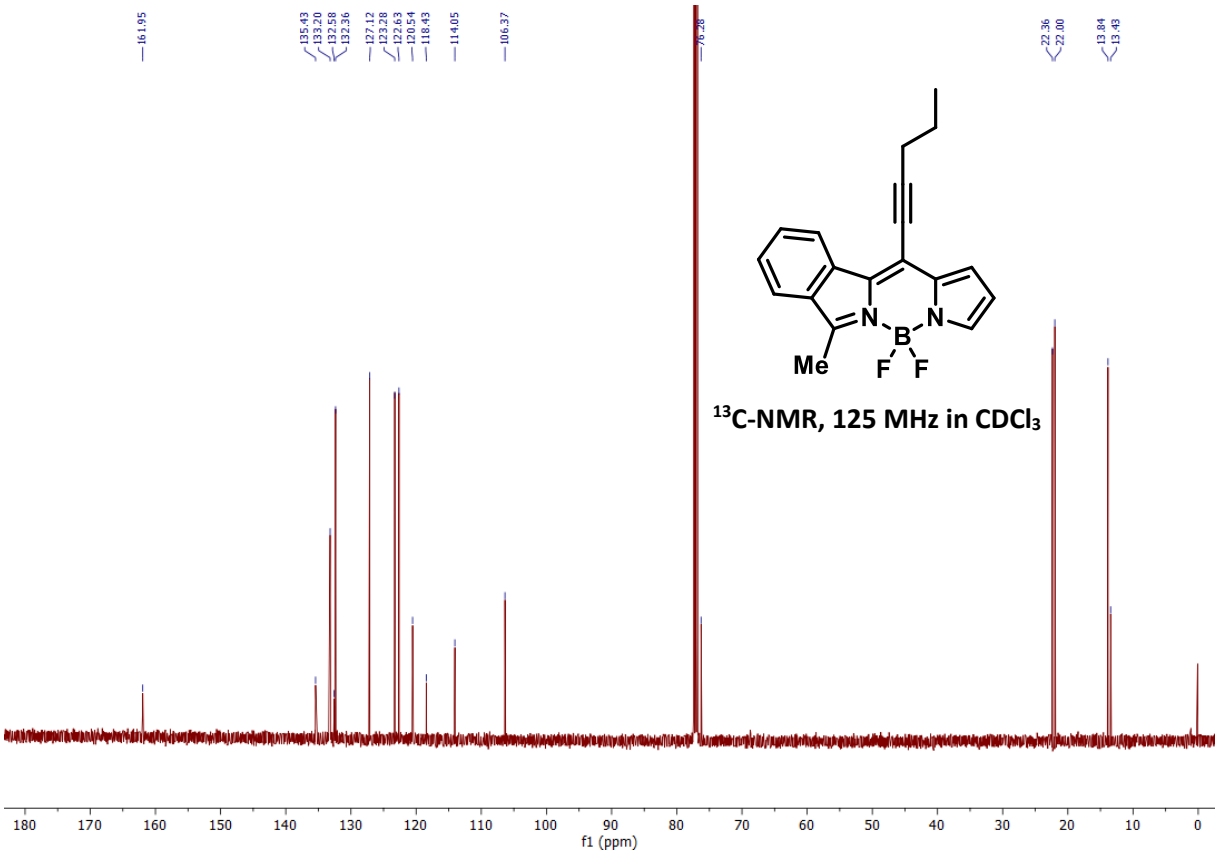
HRMS (ESI): $C_{19}H_{17}BF_2N_2$ calcd.: 323.1526 found: 323.1527, $[M+H]^+$.

UV/Vis (0.0042 mg/mL in CH_2Cl_2): λ_{max} [nm] (log ε) = 544 (4.38).

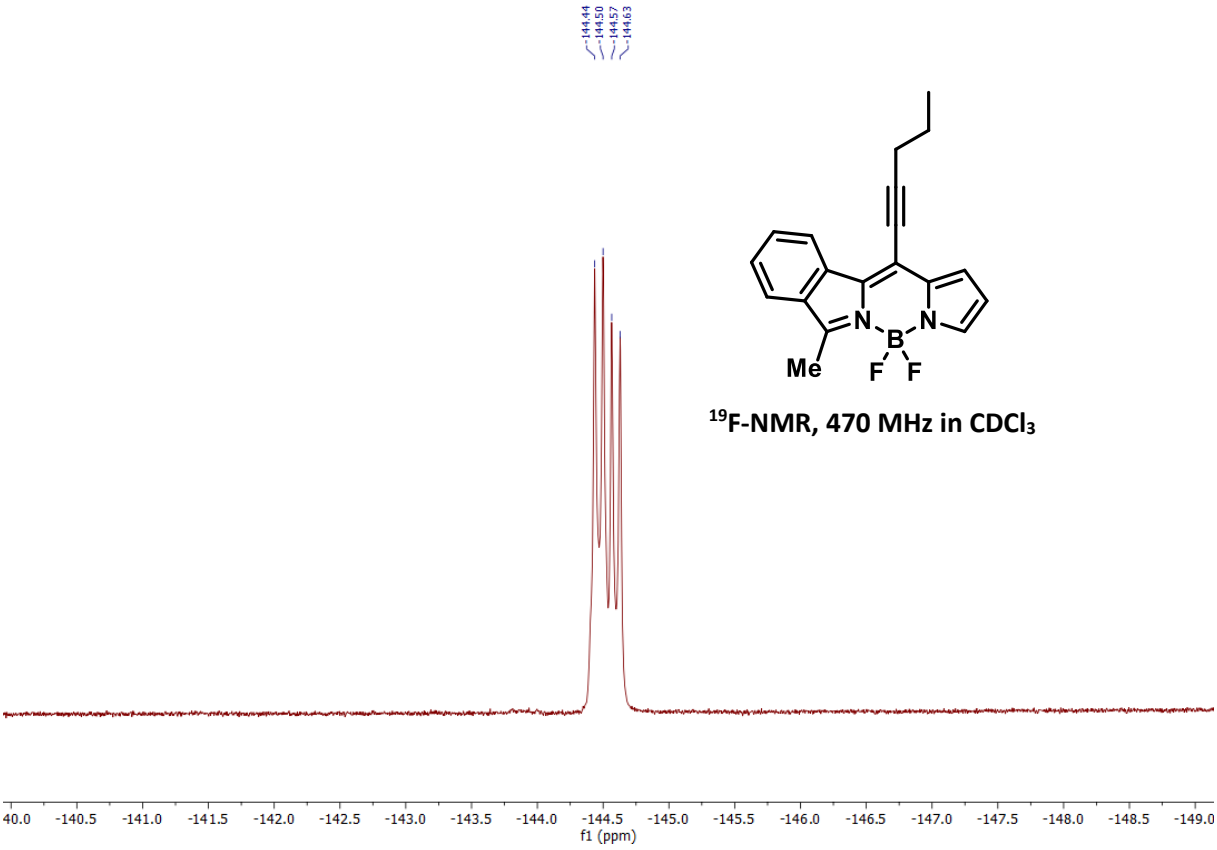
Emission (CH_2Cl_2): λ_{max} (nm) = 574.



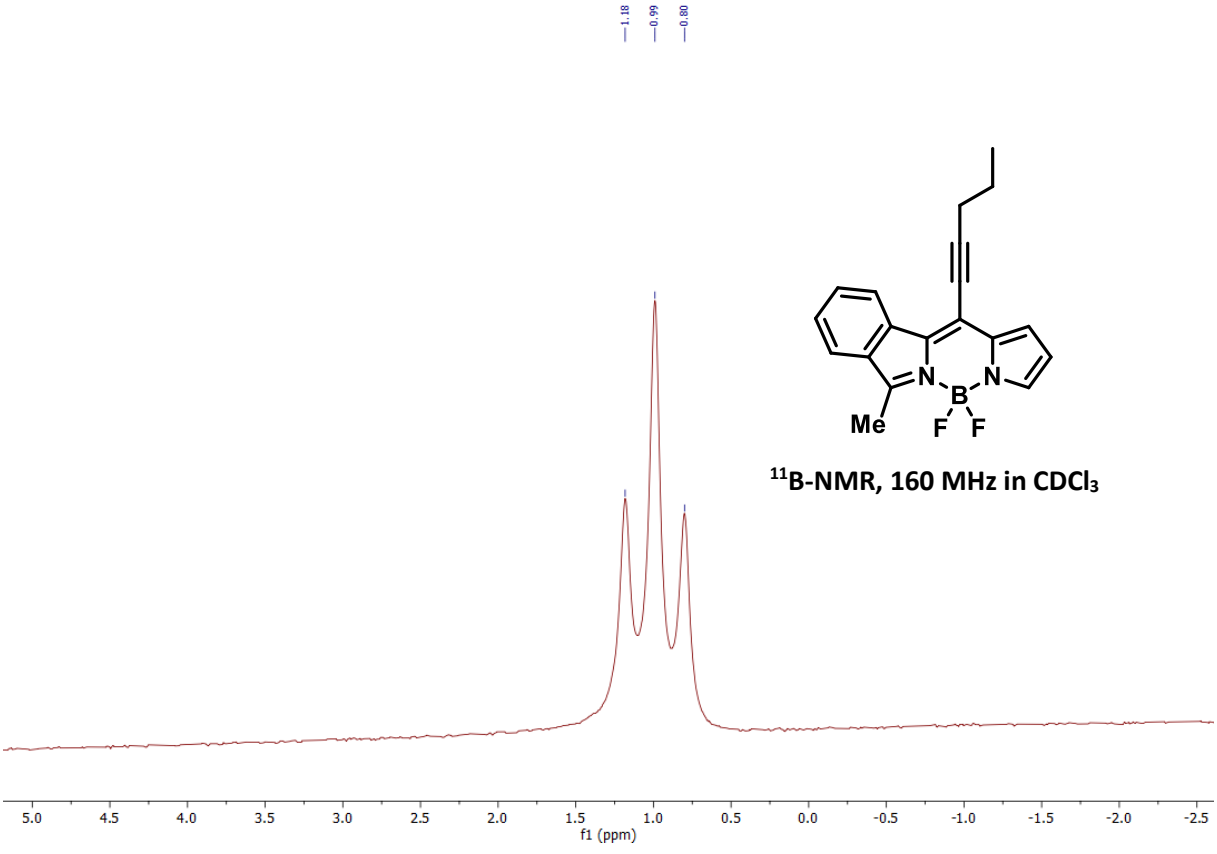
^{1}H-NMR, 500 MHz in $CDCl_3$



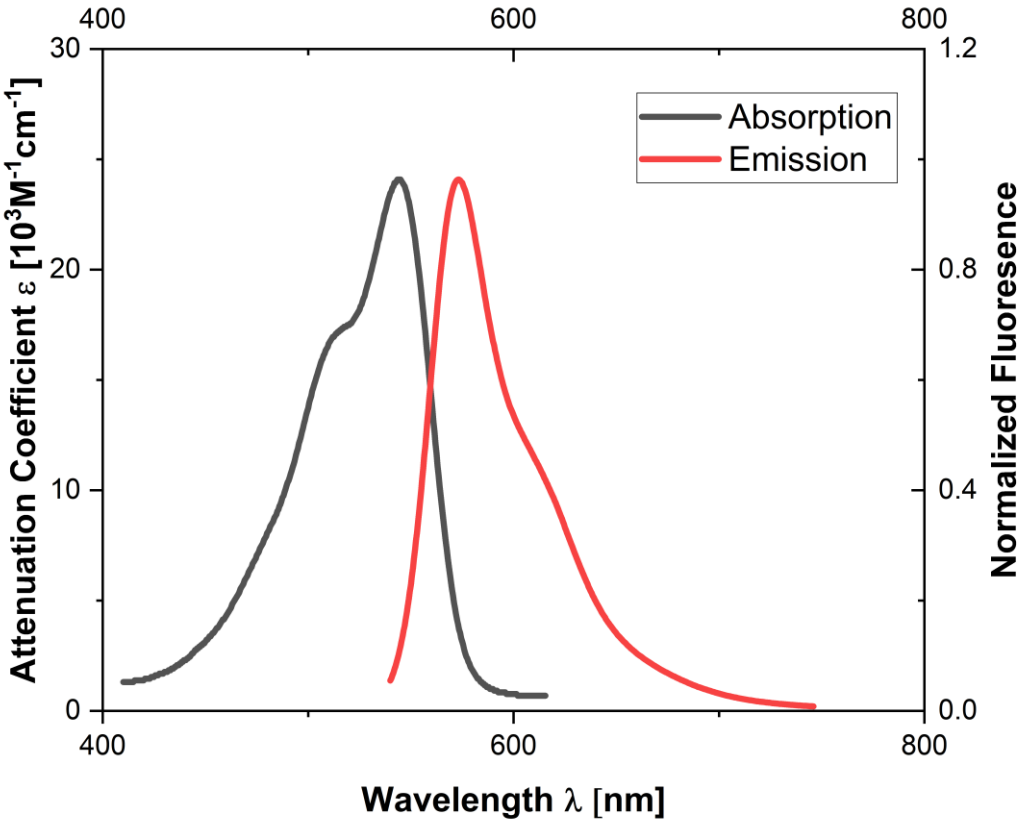
^{13}C-NMR, 125 MHz in $CDCl_3$



^{19}F-NMR, 470 MHz in $CDCl_3$



^{11}B-NMR, 160 MHz in $CDCl_3$



UV-Vis and normalized **fluorescence spectra** of **6f** at room temperature in CH_2Cl_2.

7. Crystal Structure Determinations

BODIPYs 5a, 5b, and 5l

Crystals of **5a**, **5b** and **5l** were obtained by vapour diffusion of *n*-hexane into solutions of the compounds in chloroform. Crystals were mounted in inert oil on Hampton loops and transferred to the cold gas stream of a Rigaku/OD XtaLAB Synergy diffractometer. Mirror-focussed Mo-*K*α radiation was employed for the intensity measurements of **5a** and **5l**, whereas for **5b** mirror-focussed Cu-Kα radiation was used. Absorption corrections were implemented on the basis of multi-scans. The structure was refined anisotropically on F^2 using the program SHELXL-2018.[6] Hydrogen atoms were included using rigid methyl groups or a riding model starting from calculated positions. *Exceptions/special details*: For **5b**, an extinction correction was performed; the SHELX extinction parameter refined to 0.00086(19). For **5l**, the methyl hydrogen atoms at C1 were indistinct. This group was therefore refined as a rigid group using a regular hexagon of half-occupied hydrogen positions (command "AFIX 127"). Compounds **5b** and **5l** are effectively isotypic.

Crystallographic data are summarized in Table S4, and ellipsoid plots are presented as Fig. S1-4. Additionally, complete data have been deposited with the Cambridge Crystallographic Data Centre under the numbers CCDC 2298671-3. Copies of the data can be obtained free of charge from www.ccdc.cam.ac.uk/data_request/cif.

BODIPY 6e

Crystals of **6e** were obtained at room temperature by slow solvent evaporation from a solution of the compound dissolved in a mixture of pentane and dichloromethane. A red, plate-shaped crystal of **6e** was mounted on a MiTeGen micromount with perfluoroether oil. Data were collected from a shock-cooled single crystal at 100(2) K on a Bruker D8 VENTURE dual wavelength Mo/Cu three-circle diffractometer with a microfocus sealed X-ray tube using mirror optics as the monochromator and a Bruker PHOTON III detector. The diffractometer was equipped with an Oxford Cryostream 800 low temperature device and used MoK_α radiation (λ = 0.71073 Å). All data were integrated with SAINT, and a multi-scan absorption correction using TWINABS was applied.[7,8] The structure was solved by direct methods using SHELXT and refined by full-matrix least-squares methods against F^2 by SHELXL-2019/2.[6,9] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were refined isotropically on calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms.

Crystallographic data for the structures reported here have been deposited with the Cambridge Crystallographic Data Centre.[10] CCDC 2284407 contains the supplementary crystallographic

data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures. This report and the CIF file were generated using FinalCif.[11]

Table S4: Crystallographic data and structure refinement details for compounds **5a**, **5b**, **5l**, and **6e**.

Compound	**5a**	**5b**	**5l**	**6e**
CCDC number	2298671	2298672	2298673	2284407
Formula	$C_{25}H_{17}BF_2N_2$	$C_{20}H_{15}BF_2N_2$	$C_{19}H_{14}BF_2N_3$	$C_{24}H_{19}BF_2N_2$
M_r	394.21	332.15	333.14	384.22
Cryst. size (mm)	0.15 x 0.15 x 0.06	0.09 x 0.07 x 0.02	0.17 x 0.10 x 0.04	0.15 × 0.12 × 0.06
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P\overline{1}$ (2)
Temperature (°C)	-173	-173	-173	-173
a (Å)	11.1893(2)	11.2668(3)	11.2238(3)	7.0095(10)
b (Å)	10.9459(2)	15.3965(4)	15.6385(4)	10.7904(16)
c (Å)	15.6815(3)	9.5029(3)	9.2476(3)	12.520(3)
α (°)	90	90	90	97.995(7)
β (°)	92.820(2)	106.696(3)	106.535	93.450(7)
γ (°)	90	90	90	95.353(7)
V (Å^3)	1918.29	1578.97	1556.04	931.1(3)
Z	4	4	4	2
D_x (Mg m^{-3})	1.365	1.397	1.422	1.371
λ (Å)	0.71073	1.54184	0.71073	0.71073
μ (mm^{-1})	0.09	0.81	0.10	0.09
Transmissions	0.809 – 1.000	0.800 – 1.000	0.938 – 1.000	0.986 – 0.995
F(000)	816	688	688	400
$2\theta_{max}$	71.9	155.5	72.6	61.2
Refl. measured	149697	64031	142487	121443
Refl. indep.	8633	3337	7548	5698
R_{int}	0.032	0.048	0.045	0.0657
Parameters	271	228	227	264
Restraints	0	0	0	0
$wR(F^2$, all refl.)	0.120	0.099	0.131	0.117
$R(F$, >4σ(F))	0.026	0.043	0.045	0.046
S	1.12	1.15	1.05	1.05
Max. Δp (e Å^{-3})	0.53, –0.23	0.26, –0.16	0.63, –0.24	0.40, –0.28

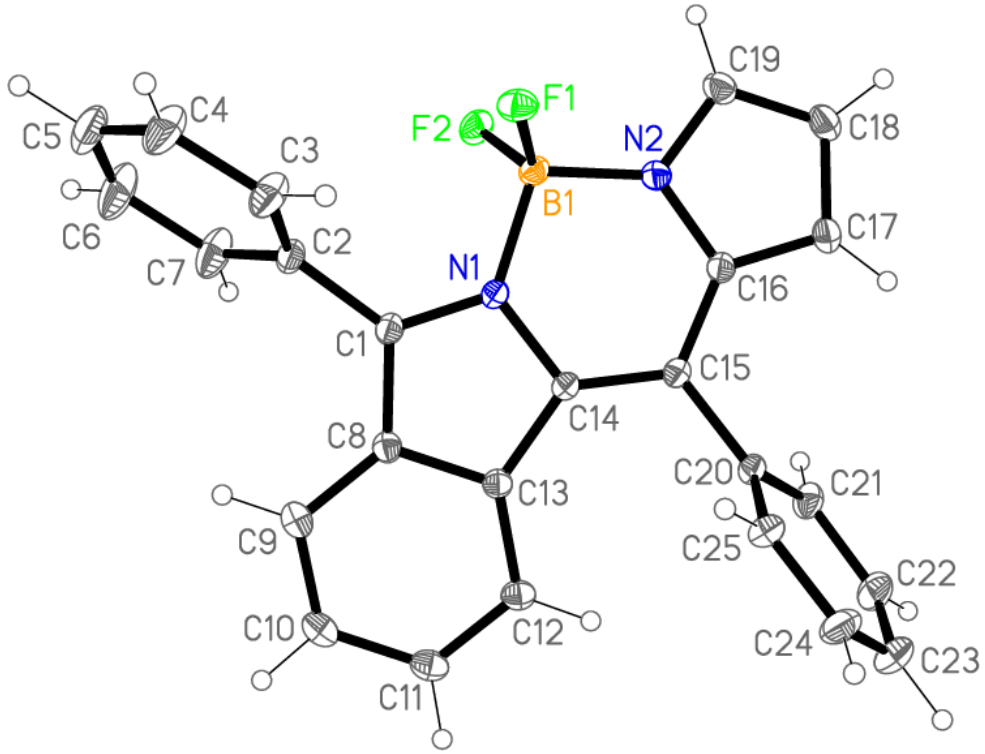


Fig. S1. The molecule of compound **5a** in the crystal. Ellipsoids correspond to 50% probability levels.

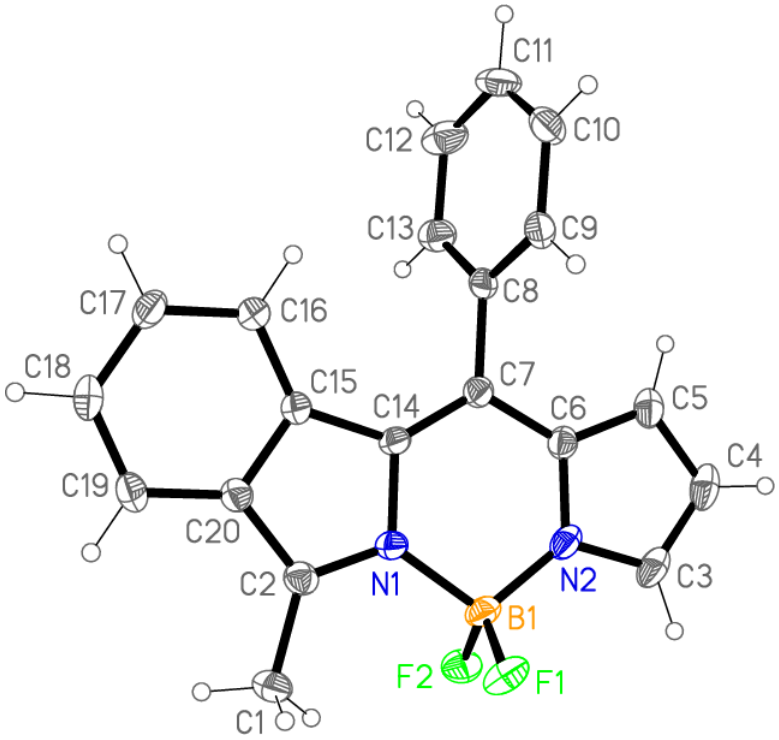


Fig. S2. The molecule of compound **5b** in the crystal. Ellipsoids correspond to 50% probability levels.

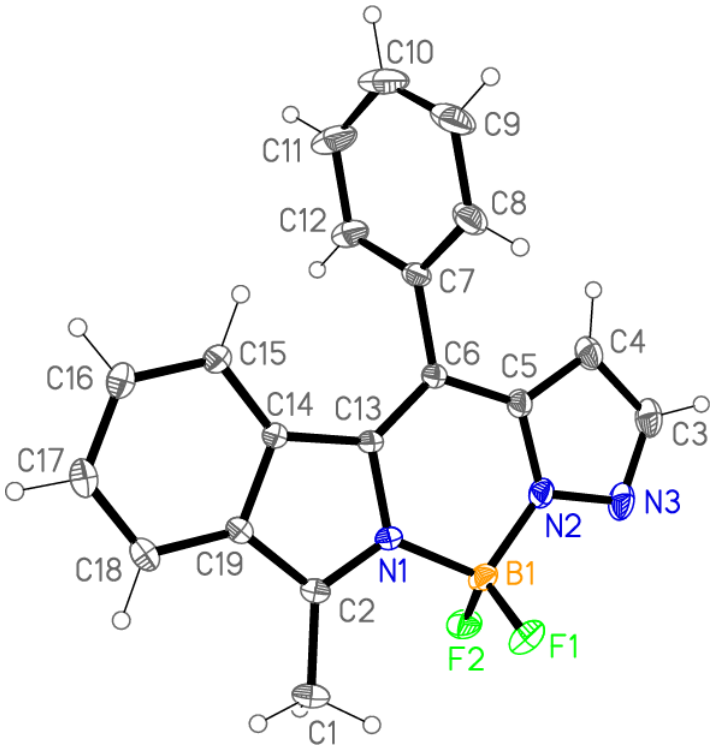


Fig. S3. The molecule of compound **5l** in the crystal. Ellipsoids correspond to 50% probability levels.

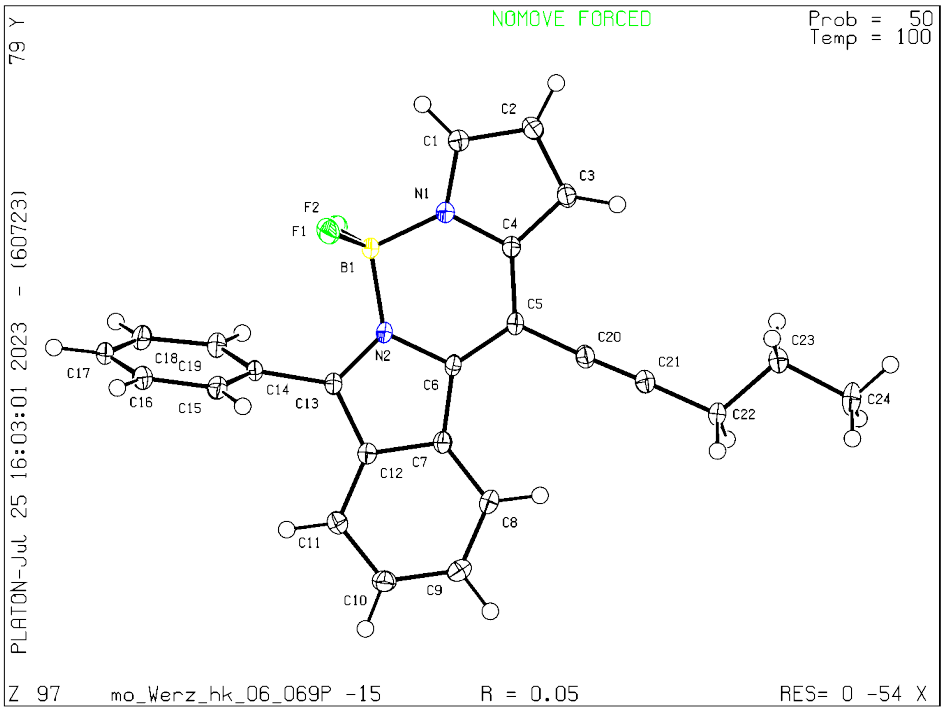


Fig. S4. The molecule of compound **6e** in the crystal. Ellipsoids correspond to 50% probability levels.

8. References

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