Synthesis of Highly Fluorescent Helical Quinolizinium Salts by a Rh-catalyzed Cyclotrimerization/C–H Activation Sequence

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Contents

1 General Information

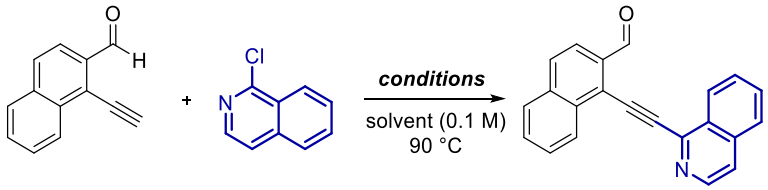
All commercially available reagents were purchased in the best quality and used without further purification unless otherwise noted. Solvents were purified and dried by distillation: tetrahydrofuran (THF) and toluene from sodium/benzophenone, dichloromethane and 1,2-dichloroethane from calcium hydride. Other solvents and all reagents were used without further purification. All reactions were per under argon atmosphere unless otherwise noted. Chromatography was performed on Silica gel 60A (40-60 μm) from Acros Organics. Thin layer chromatography was performed on Merck silica gel 60 F_{254} pre-coated aluminum sheets. NMR spectra were recorded on Bruker AVANCE III Spectrometer (^{1}H at 400 MHz and ^{13}C at 101 MHz, and ^{19}F at 376 MHz). All NMR spectra were measured in $CDCl_3$, CD_2Cl_2 solutions and referenced to residual solvent signal: $CDCl_3$ (^{1}H, δ_H = 7.26; ^{13}C, δ_C = 77.16), CD_2Cl_2 (^{1}H, δ_H = 5.32; ^{13}C, δ_C = 53.84). Coupling constants *J* are given in Hz. The IR samples were recorded in KBr powder or Attenuated Total Reflectance (ATR) with Ge crystal measured on spectrometer Thermo Nicolet AVATAR 370 FT-IR, and are reported in wave numbers (cm^{-1}). The MS spectra were recorded on an Agilent 5975 Inert MSD or GC×GC-TOFMS LECO Pegasus IVD device. All melting points are uncorrected and were determined on a Kofler apparatus KB T300. The UV/Vis absorption spectra were recorded using Unicam 340 spectrometer. Microwave reactions were performed in an Anton Paar Monowave 400 device. Crystallographic data were collected on Bruker D8 VENTURE Kappa Duo PHOTON100 by IμS micro-focus sealed tube at 150 K. Corrected steady-state emission spectra were recorded on an Aminco Bowman (AB2) spectrometer. SFC conditions: Waters Acquity Ultra Performance Convergence Chromatography system, column YMC CHIRAL ART Cellulose-SB (150 × 3 mm I.D., particle size 3μm). The values obtained from the enantiomeric ratio were rounded to the whole numbers.

2 Optimization of conditions

2.1 Tuning of Sonogashira´s conditions for the synthesis of S3

Sonogashira cross coupling of **S2** with the chloroisoquinoline required an optimization (Table S1) and it revealed that successful and selective preparation of **S3** was achieved by using the SPhosPdG$_3$ catalyst.[1]

Table S1. Sonogashira reaction of **S2** with1-chloroisoquinoline.



S2 **S3**

Entry[a]	Conditions	Solvent[b]	Yield (%)[c]
1	$PdCl_2(PPh_3)_2$ (5 mol%), CuI (5 mol%), Et_3N (7 eq.)	THF	46
2	$[Pd(allyl)Cl]_2$ (12.5 mol%), $P(Cy)_3$ (25 mol%) pyrrolidine (12 eq.)	MeCN	0
3	$Pd_2(dba)_3$ (12.5 mol%), $PH(tBu)_3BF_4$ (25 mol%), Et_3N (7 eq.)	THF	0
4	$PdCl_2(PPh_3)_2$ (12.5 mol%), Et_3N (7 eq.)	THF	n.d.
5	$Pd(OAc)_2$ (12.5 mol%), XPhos (25 mol%), Et_3N (7 eq.)	MeCN	48
6	$Pd(OAc)_2$ (5 mol%), PPh_3 (10 mol%), Et_3N (7 eq.)	MeCN	0
7	SPhosPdG3 (1 mol%), Et_3N (7 eq.)	MeCN	70

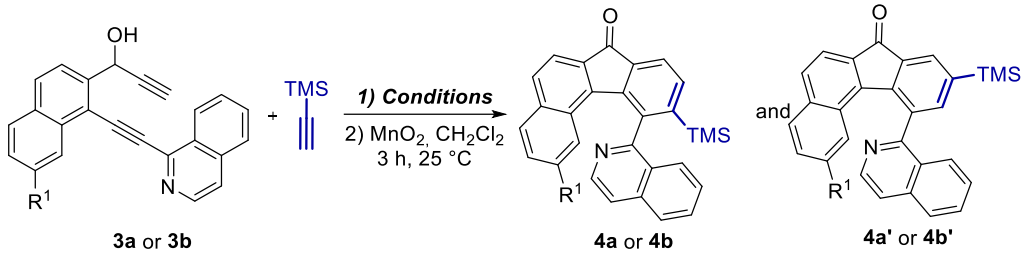
[a] Reaction scale: 0.1 mmol scale. [b] 0.1 M. [c] Isolated yield.

For synthesis and characterization of **S1**, **S2**, etc. see section 3.1.

[1] For a review on the use of SPhos, see: P. Y. Choy, K. B. Gan, F. Y. Kwong, *Chin. J. Chem.*, 2023, **41**, 1099−1118.

2.2 [2+2+2] Cyclotrimerization of 3 and TMS-acetylene under various conditions.

Table S2. Cyclotrimerization of **3** with trimethylsilylethyne under various conditions.



3a or **3b** **4a** or **4b** **4a'** or **4b'**

Entry[a]	R^1	Catalytic system (mol%)	Solvent	Temp (°C)	Yield (%)[b]	**4/4'**
1	H	CpCo[P(EtO)$_3$]dmfu (10)	toluene	110	0	
2	H	Ni(cod)QD (10), PPh_3 (20)	toluene	110	0	
3	H	[IrCl(cod)]$_2$ (10), PPh_3 (20)	toluene	110	0	
4	H	Rh(cod)$_2$BF$_4$ (5), dppb (6)	DCE	100	5	95/5
5[c]	H	$RhCl(PPh_3)_3$ (10)	THF	170	5	79/21
6	H	Rh(cod)$_2$BF$_4$ (5), dppb (6)	THF/MeOH	100	26	95/5
7[d]	H	Rh(cod)$_2$BF$_4$ (10), dppb (12)	THF/MeOH	100	59 (57)[e]	95/5
8[d]	OMe	Rh(cod)$_2$BF$_4$ (5), dppb (6)	THF/MeOH	100	61	98/2

[a] Reaction scale: 0.1 mmol [b] Combined isolated yield. [c] Performed in MW reactor. [d] 0.25 mmol scale. [e] 1.5 mmol scale.

CpCo[P(OEt)$_3$](dmfu)-catalyzed [2+2+2] cyclotrimerization followed by oxidation reaction (Table S2, Entry 1).

A dry microwave vial was charged with the diyne **3a** (0.1 mmol, 31 mg), trimethylsilylacetylene (1 mmol, 140 µL), CpCo[P(OEt)$_3$](dmfu) (10 µmol, 4.3 mg) in dry toluene (2 mL). Afterwards, the reaction mixture was sealed and heated up to 110 °C for 20 h. Then, the reaction mixture was cooled down to 20 °C and concentrated under reduced pressure. The crude mixture was directly oxidized to the corresponding ketone **4a/4a´** without any further purification. Pyridinium chlorochromate (0.3 mmol, 65 mg) and Celite® (65 mg) were added to a solution of the crude diol in dry CH_2Cl_2 (6 mL) under argon atmosphere and stirred at 25 °C for 3 hours. Afterwards, the reaction mixture was filtered through a pad of 1:4 silica gel/Celite®. Then, the pad was washed using CH_2Cl_2 and the filtrate was concentrated under reduced pressure. No product formation was observed according to ^{1}H NMR of the crude mixture.

Ni(cod)QD-catalyzed [2+2+2] cyclotrimerization followed by oxidation reaction (Table S2, Entry 2).

A dry microwave vial was charged with Ni(cod)(QD) (10 µmol, 3.3 mg) and PPh_3 (20 µmol, 5.2 mg) in dry toluene (2 mL). After 15 min of stirring, the diyne **3a** (0.1 mmol, 31 mg) and trimethylsilylacetylene (1 mmol, 140 µL) were added to the solution. Afterwards, the reaction mixture was sealed and heated up to 100 °C for 20 h. Then the reaction mixture was cooled down to 20 °C. Then, the reaction mixture was concentrated under reduced pressure. The crude product was directly oxidized to the corresponding diketone **4a/4a´** without any further purification. Pyridinium chlorochromate (0.3 mmol, 65 mg) and Celite® (65 mg) were added to a solution of the crude diols in dry CH_2Cl_2 (5 mL) under argon atmosphere and stirred at 25 °C for 3 hours. Afterwards, the reaction mixture was filtered through a pad of 1:4 silica gel/Celite®,

the pad was washed using CH_2Cl_2 and the filtrate was concentrated under reduced pressure. No product formation was observed according to ^1H NMR of the crude mixture.

General procedure for Rh- and Ir-catalyzed [2+2+2] cyclotrimerization followed by oxidation reaction (Table S2, Entries 3, 4, 6-8).

A dry microwave vial was charged with catalyst (5-10 µmol) and phosphine ligand (5-20 µmol) in a dry solvent (1 mL, 0.1 M) under argon atmosphere. H_2 gas was bubbled into the reaction mixture for 45 min.[2] Afterwards, the corresponding diyne **3a-b** (0.1 mmol) and trimethylsilylacetylene (1 mmol, 140 µL) were added under argon atmosphere. The reaction was stirred at 100 °C for 16 hours. Then, the reaction mixture was concentrated under reduced pressure. The crude mixture was directly oxidized to the corresponding ketone **4/4´** without any further purification. MnO_2 (1 mmol, 90 mg) was added to a solution of the crude alcohol in dry CH_2Cl_2 (6 mL) under argon atmosphere. The resulting mixture was stirred at 25 °C for 3 hours. Afterwards, the reaction mixture was filtered through a pad of Celite®. Then, the pad was washed using diethylether and the filtrate was concentrated under reduced pressure. Column chromatography of the residue on silica gel (4/1 hexanes/EtOAc) provided products **4/4´** in 5-61% yields.

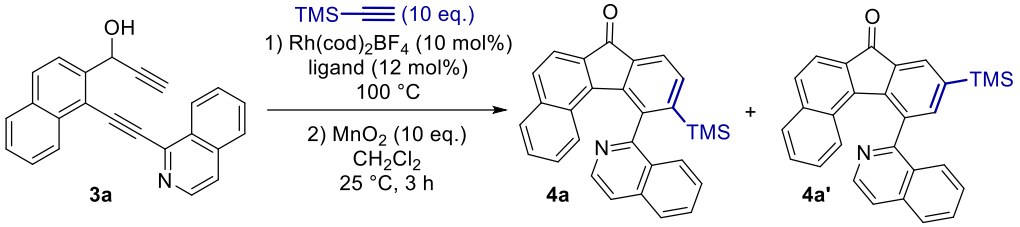
$RhCl(PPh_3)_3$ catalyzed [2+2+2] cyclotrimerization followed by oxidation reaction (Table S2, Entry 5).

A dry microwave vial was charged with diyne **3a** (0.1 mmol, 31 mg) and trimethylsilylacetylene (1 mmol, 140 µL), and dry THF (2 mL) under argon atmosphere After addition of Wilkinson's catalyst (10 µmol, 9.2 mg), the vial was sealed, and the reaction mixture was heated up to 170 °C for 1.5 h in a microwave reactor. Then the reaction mixture was cooled down to 20 °C and concentrated under reduced pressure. Pyridinium chlorochromate (0.3 mmol, 65 mg) and Celite® (65 mg) were added to a solution of the crude diol in dry CH_2Cl_2 (6 mL) under argon atmosphere and stirred at 25 °C for 3 hours. Afterwards, the reaction mixture was filtered through a pad of 1:4 silica gel/Celite®. Then, the pad was washed using CH_2Cl_2 and the filtrate was concentrated under reduced pressure. Column chromatography of the residue on silica gel (linear gradient: 8/1/1 to 6/1/1 hexanes/EtOAc/CH_2Cl_2) provided 2.2 mg (5%) of compounds **4a/4a´**.

[2] I. Thiel, M. Horstmann, P. Jungk, S. Keller, F. Fisher, H.-J. Drexler, D. Heller, M. Hapke, *Chem. Eur. J.*, **2017**, *23*, 17048-17057.

2.3 Effect of a ligand on cyclotrimerization yield and regioselectivity

Table S3. Ligand screening for [2+2+2] cyclotrimerization of **3a** and TMS-acetylene.



Entry[a]	Phosphine ligand	Bite angle	**4a**/**4a'** (%)[b]	Yield (%)[c]
1	dppp	91°	88/12	26
2	*rac*-BINAP	93°	97/3	54
3	dppb	94°	95/5	59
4	dppf	99°	97/3	54
5	dpePhos	104°	64/36	12
5	Xantphos	108°	58/42	3

[a] Reaction scale: 0.25 mmol. [b] The structure of the major product was determined by X-ray diffraction analysis. [c] Combined isolated yields.

General procedure for Rh-catalyzed [2+2+2] cyclotrimerization followed by oxidation reaction (Table S3).

A dry microwave vial was charged with $Rh(cod)_2BF_4$ (10 µmol, 4.1 mg) and the corresponding phosphine ligand (12 µmol) in a dry solvent (1 mL) under argon atmosphere. H_2 gas was bubbled into the reaction mixture for 45 min.[2] Afterwards, the corresponding diyne **3a** (0.1 mmol, 31 mg) and trimethylsilylacetylene (1 mmol, 140 µL) were added under argon atmosphere. The reaction was stirred at 100 °C for 16 hours. Then, the reaction mixture was concentrated under reduced pressure. The crude mixture was directly oxidized to the corresponding ketone **4a**/**4a'** without any further purification. MnO_2 (1mmol, 90 mg) was added to a solution of the crude alcohol in dry CH_2Cl_2 (6 mL) under argon atmosphere. The resulting mixture was stirred at 25 °C for 3 hours. Afterwards, the reaction mixture was filtered through a pad of Celite®. Then, the pad was washed using diethylether and the filtrate was concentrated under reduced pressure. Column chromatography of the residue on silica gel (4/1 hexanes/EtOAc) provided products **4a**/**4a'**.

2.4 Enantioselective C-H activation/annulation attempts of 5a.

Compounds **5a** constitute also suitable substrate to attempt an enantioselective C–H activation/annulation reaction sequence, which have been shown to proceed with high asymmetric induction as reported by You *et al* for the synthesis of helical azonia salts.[3] For preliminary experiments in this direction were chosen **5a** and 1,2-bis(4-(trifluoromethyl)phenyl)acetylene as model substrates (Table S4) and cyclopentadienylrhodium complexes **C1** and **C2** (Figure S1). An attempt to use You's conditions[3] in the presence an enantiopure acid **A** provided **1ac** in just 10% yield and 39% ee (Entry 1). A change of AgF for $AgBF_4$ led to the increase of the yield to 48%, but ee remained almost the same (42% ee) (Entry 2). Carrying out the reaction in the absence of **A** resulted in the improved asymmetric induction that rose to 60% ee, but at the expense of the yield (8%) (Entry 3). Extending the reaction time to 48 h did not lead to higher conversion either: 10% yield (62% ee) (Entry 4). In another attempt we utilized the using Cramer´s 2nd generation catalyst **C2** (12 mol%)[4] in presence $Cu(OAc)_2$ and $AgBF_4$ in DCE at 80 °C (Entry 5). Product **1ac** was obtained in 28% yield with low asymmetric induction of mere 14% ee. Changing DCE for MeOH had a positive effect on the yield of **1ac** (67%), but did not affect asymmetric induction that remained rather low (19% ee) (Entry 6). Albeit the level of asymmetric induction was not that high, it is close to the value obtained in synthesis of a [7]azoniahelicene, where it reached 73% ee.[3]

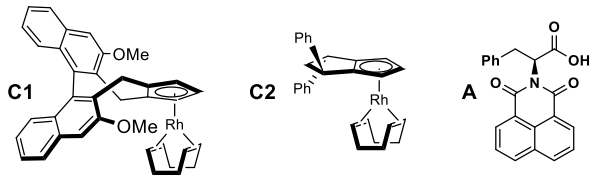
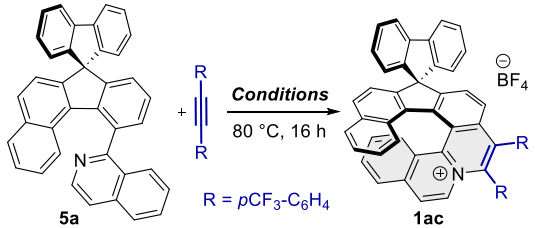


Figure S1. Structures **C1** and **C2** catalysts and **A**.

General procedure for enantioselective C-H activation/ annulation reaction (see Table S4 for details). A dry microwave vial was charged with silver salt (40 µmol), **C** (4 µmol), $Cu(OAc)_2$ (40 µmol, 7.3 mg), acid (8 µmol), when required, bis(4-trifluoromethylphenyl)ethyne (0.04 mmol, 12.6 mg) and **5a** (0.04 mmol, 19.4 mg) in corresponding solvent (5 mL) under argon atmosphere. The microwave vial was sealed and heated for 16 hours. Afterwards, the reaction mixture was filtered on a pad of Celite, then the pad was washed using CH_2Cl_2 (10 mL) and the filtrate was concentrated under reduced pressure. Column chromatography of the residue on silica gel provided products **1ac**.

[3] Q. Wang, W.-W. Zhang, C. Zheng, Q. Gu, S.-L. You, *J. Am. Chem. Soc.*, 2021, **143**, 114−120.
[4] S.-G. Wang, S. H. Park, N. Cramer, *Angew. Chem. Int. Ed.*, 2018, **57**, 5459–5462.

Table S4. Attempts of Rh-catalyzed enantioselective C–H activation/annulation.



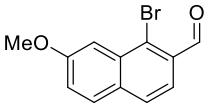
Entry[a]	Catalytic system	t (h)	Solvent	Yield (%)	ee (%)[b]
1[c,d]	**C1** (10 mol%), **A** (0.2 eq.), AgF (1 eq.), $Cu(OAc)_2$ (1 eq.)	16	MeOH	10	39
2	**C1** (10 mol%), **A** (0.2 eq.), $AgBF_4$ (1 eq.), $Cu(OAc)_2$ (1 eq.)	16	MeOH	48	42
3	**C1** (10 mol%), $AgBF_4$ (1 eq.), $Cu(OAc)_2$ (1 eq.)	16	MeOH	8	60
4[e]	**C1** (10 mol%), $AgBF_4$ (1 eq.), $Cu(OAc)_2$ (1 eq.)	16	MeOH	10	62
5	**C2** (12 mol%), $AgBF_4$ (1 eq.), PivOH (0.2 eq.)	48	DCE	28	14
6	**C2** (10 mol%), $AgBF_4$ (1 eq.), $Cu(OAc)_2$ (1 eq.)	16	MeOH	67	19

[a] Reaction scale: 0.04 mmol. [b] determined by HPLC using a chiral stationary phase. [c] With H_2O (10 eq.). [d] $NaBF_4$ (2 eq.) was added to the cooled reaction mixture and stirred for 3 hours. [e] Reaction time: 48 h.

3 Synthesis and characterization of substrates

3.1 Synthesis of starting materials

1-Bromo-7-methoxy-2-naphthaldehyde (S1b). To a solution of dry DMF (85 mmol, 6.6 mL) in dry CH_2Cl_2 (100 mL) was dropwise added PBr_3 (71 mmol, 6.7 mL) at 0 °C. After 1 hour of stirring, 7-methoxy-1-tetralone (14.2 mmol, 2.5 g) in CH_2Cl_2 (50 mL) was added and the rection mixture was stirred under reflux for 4 h. Then the reaction mixture was cooled to 0 °C and quenched with a saturated aqueous solution of $NaHCO_3$ (250 mL). After the end of the gas generation, the layers were separated. The aqueous phase was extracted with CH_2Cl_2 (3 × 200 mL). The combined organic phases were washed with H_2O, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. A solution of the crude product in dry toluene (50 mL) was heated with DDQ (31.2 mmol, 7.1 g) at 120 °C and stirred for 16 h. The mixture was diluted with hexanes (50 mL), filtered, and concentrated under reduced pressure. Column chromatography of the residue on silica gel (20/1 hexanes/EtOAc) furnished 2.8 g (74%) of the title compound as a yellow solid.



R_f (20/1 hexanes/EtOAc) = 0.23.

M.p. = 89−90 °C.

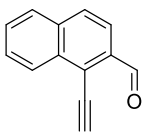
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.65 (s, 1H), 7.81-7.71 (m, 4H), 7.31 (ddd, J = 8.9, 2.5,1.0 Hz, 1H), 4.00 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 193.2, 159.6, 133.6, 132.8, 131.8, 130.1, 129.5, 128.0, 122.6, 122.2, 106.3, 55.7.

IR (KBr) ν 3336, 3007, 2965, 2935, 2905, 2869, 2857, 2830, 1673, 1595, 1455, 1308, 1269, 1237, 1216, 1201, 1186, 1135, 1045, 1033, 975, 848, 842 cm^{-1}.

HRMS (EI): *m/z* calcd for $C_{12}H_9BrO_2$ [$(M)^+$]: 263.9786, found: 263.9788.

1-Ethynyl-2-naphthaldehyde (S2a). In a Schlenk flask were dissolved $PdCl_2(PPh_3)_2$ (0.5 mmol, 351 mg), CuI (1.0 mmol, 190 mg) and 1-bromo-2-naphthaldehyde (10.0 mmol, 2.35 g) in THF (40 mL) followed by addition of trimethylsilylethyne (15.0 mmol, 2.1 mL) and Et_3N (10 mL). The reaction mixture was stirred at reflux for 3 hours and then it was cooled down to 25 °C, filtered through a pad of Celite®/silica, which was washed with Et_2O. The filtrate was concentrated under reduced pressure. The residue was treated with K_2CO_3 pellets in a mixture of MeOH/water at 0 °C for 1 h. The resulting mixture was quenched with 1M HCl, extracted with CH_2Cl_2 (3× 100 mL), the combined organic fractions were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Column chromatography of the residue on silica gel (19/1 hexanes/EtOAc) furnished 1.75 g (97%) of the title compound as a yellow solid.



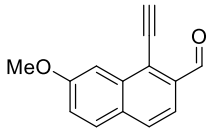
^{1}H NMR (400 MHz; $CDCl_3$) δ 10.79 (d, J = 0.9 Hz, 1H), 8.56-8.52 (m, 1H), 7.98 (d, J = 8.6 Hz, 1H), 7.92-7.88 (m, 2H), 7.70-7.65 (m, 2H), 3.92 (s, 1H).

^{13}C NMR (101 MHz; $CDCl_3$) δ 192.0, 135.8, 135.4, 133.5, 129.6, 129.6, 128.6, 128.0, 127.2, 126.2, 122.0, 90.2, 77.3.

The recorded spectral data agreed with the previously published values.[5]

[5] D. Schweinfurth, M. Zalibera, M. Kathan, C. Shen, M. Mazzolini, N. Trapp, J. Crassous, G. Gescheidt, F. Diederich, *J. Am. Chem. Soc.* **2014**, *136*, 13045-13052.

1-Ethynyl-7-methoxy-2-naphthaldehyde (S2b). In a Schlenk flask was dissolved



$PdCl_2(PPh_3)_2$ (0.2 mmol, 134 mg), CuI (0.38 mmol, 72 mg) and 1-bromo-7-methoxy-2-naphthaldehyde **S1b** (3.8 mmol, 1 g) in THF (15 mL). To the solution was added trimethylsilylethyne (5.7 mmol, 790 µL) and Et_3N (15 mL). The reaction mixture was stirred at reflux for 3 h. Then the mixture was cooled down to 25 °C, filtered through a pad of Celite®/silica gel, and washed with Et_2O. The filtrate was concentrated under reduced pressure. The residue was treated with K_2CO_3 pellets in a mixture of MeOH/water at 0 °C for 1 h. The resulting mixture was quenched with 1M HCl, extracted with CH_2Cl_2 (3× 100 mL), the combined organic fractions were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Column chromatography of the residue on silica gel (19/1 hexanes/EtOAc) furnished 574 mg (72%) of the title compound as a yellow solid.

R_f (19/1 hexanes/EtOAc) = 0.28.

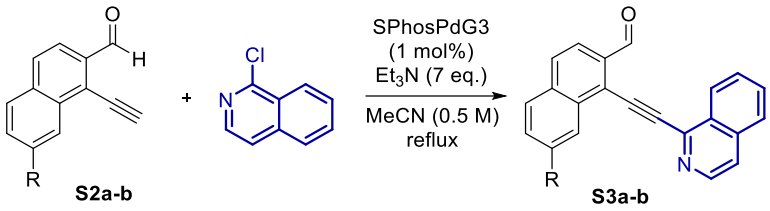
M.p. = 113−115 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.77 (s, 1H), 7.84-7.78 (m, 4H), 7.32 (dd, J = 8.9, 2.5 Hz, 1H), 4.00 (s, 3H), 3.93 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.3, 159.5, 135.8, 135.2, 131.3, 130.1, 129.3, 124.4, 122.3, 120.0, 105.2, 90.0, 77.6, 55.6.

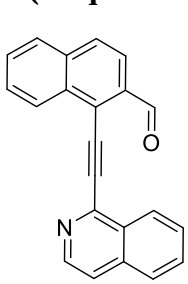
IR (KBr) ν 3279, 3261, 3240, 3064, 3010, 2962, 2941, 2863, 2830, 1739, 1685, 1625, 1595, 1509, 1461, 1320, 1216, 1051, 1027, 842 cm^{-1}.

HRMS (EI): *m/z* calcd for $C_{14}H_{10}O_2$ [$(M)^+$]: 210.0681, found: 210.0680.



General procedure for Sonogashira cross coupling (A). In a flask was dissolved SPhosPdG3 (1 mol%), the corresponding aldehyde **S2** (1 mmol) and 1-chloroisoquinoline (1 mmol) in MeCN (0.5 M) and Et_3N (7 mmol). The reaction mixture was stirred at reflux for 12 hours. Afterwards the reaction mixture was cooled down to 25 °C and filtered throught a pad of Celite®, washed with EtOAc, and concentrated under reduced pressure. Column chromatography of the residue on silica gel (hexanes/EtOAc) provided products **S3a-b**.

1-(Isoquinolin-1-ylethynyl)-2-naphthaldehyde (S3a).



According to general procedure **A** with SPhosPdG3 (0.8 mmol, 63 mg), 1-ethynyl-2-naphthaldehyde **S2** (7.78 mmol, 1.4 g) and 1-chloroisoquinoline (7.78 mmol, 1.27 g) in MeCN (16 mL) and Et_3N (8 mL). Column chromatography of the residue on silica gel (4/1 to 2/1 hexanes/EtOAc) furnished 1.96 g (82%) of the title compound as a yellow solid.

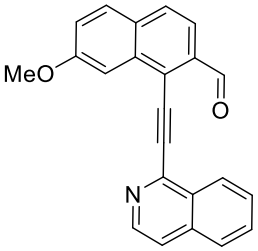
R_f (2/1 hexanes/EtOAc) = 0.62.

M.p. = 123−125 °C.

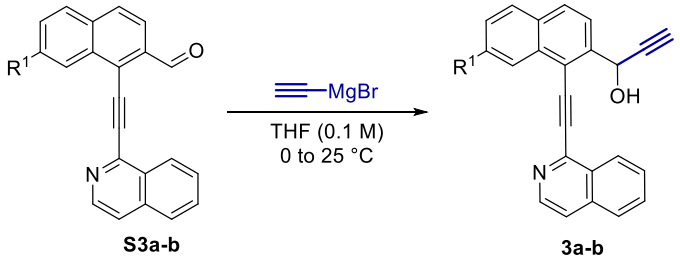
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.06 (d, J = 0.8 Hz, 1H), 8.81–8.79 (m, 1H), 8.67 (d, J = 5.7 Hz, 1H), 8.58–8.55 (m, 1H), 8.07 (d, J = 8.6 Hz, 1H), 8.02–7.90 (m, 3H), 7.83–7.68 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.7, 143.6, 143.3, 136.1, 135.9, 135.2, 133.5, 131.0, 130.1, 129.7, 129.7, 128.7, 128.7, 128.3, 127.5, 127.3, 126.6, 126.1, 122.4, 121.6, 99.3, 86.9.
IR (KBr) ν 3053, 2841, 2202, 1697, 1682, 1398, 818 cm^{-1}.
HRMS (ESI): *m/z* calcd for $C_{22}H_{13}NNaO$ [(M+Na)$^+$]: 330.0889, found: 330.0891.

1-(Isoquinolin-1-ylethynyl)-7-methoxy-2-naphthaldehyde (S3b). According to general procedure **A** with SPhosPdG3 (0.05 mmol, 39 mg), 1-ethynyl-7-methoxy-2-naphthaldehyde **S2b** (5.0 mmol, 1.0 g) and 1-chloroisoquinoline (5.0 mmol, 818 mg) in MeCN (10 mL) and Et_3N (5 mL). Column chromatography of the residue on silica gel (3/1 hexanes/EtOAc) furnished 1.35 g (84%) of the title compound as a yellow solid.



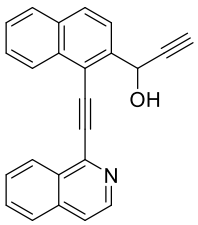
R_f (4/1 hexanes/EtOAc) = 0.54.
M.p. = 156−160 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.02 (s, 1H), 8.64 (dd, *J* = 15.0, 7.0 Hz, 2H), 8.09 (d, *J* = 2.5 Hz, 1H), 7.92-7.90 (m, 3H), 7.85 (d, *J* = 8.9 Hz, 1H), 7.80-7.70 (m, 3H), 7.37 (dd, *J* = 9.0, 2.5 Hz, 1H), 4.02 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 191.9, 159.6, 143.7, 143.4, 136.0, 135.5, 135.2, 131.3, 130.9, 130.1, 129.7, 129,6, 128.4, 127.3, 126.5, 124.3, 122.4, 121.3, 120.2, 105.4, 99.2, 87.3, 55.6.
IR (KBr) ν 3076, 3045, 2964, 2860, 2200, 1684, 1215, 1030, 834 cm^{-1}.
HRMS (ESI): *m/z* calcd for $C_{23}H_{15}NNaO_2$ [(M+Na)$^+$]: 360.0995, found: 360.0995.



S3a-b **3a-b**

General procedure for alkynylation reaction (B). Ethynylmagnesium bromide 0.5 M (2 mmol) was added dropwise to a solution of the corresponding aldehyde **S3a-b** (1 mmol) in anhydrous THF (10 mL) at 0 °C. Afterwards, the resulting mixture was allowed to warm up to 25 °C and stirred for 5 hours. After completion of the reaction on TLC, the reaction mixture was poured into a saturated NH_4Cl (aq.) solution and extracted with EtOAc. Organic phase was washed twice with a saturated NaCl (aq.) solution, dried over $MgSO_4$, and concentrated under reduced pressure The residue was recrystallized from hexanes/EtOAc. Then, the precipitate was dried under reduced pressure to provided the desired products **3a-b**.

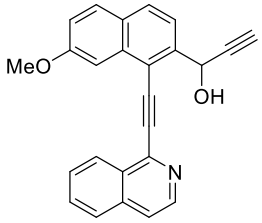
1-(1-(Isoquinolin-1-ylethynyl)naphthalen-2-yl)prop-2-yn-1-ol (3a). According to the general procedure **B** with **S3a** (4.8 mmol, 1.5 g), ethynylmagnesium bromide (9.7 mmol, 19.5 mL) in THF (50 mL). Recrystallizationfrom a mixture of hexanes/EtOAc (80/15 mL) furnished 1.3 g (80%) of the title compound as a light brown solid.



R_f (1/1 hexanes/EtOAc) = 0.48.
M.p. = 225-228 °C.

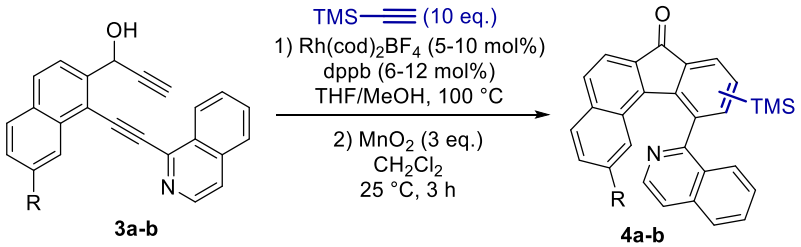
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, J = 7.7 Hz, 1H), 8.63 (d, J = 8.4 Hz, 1H), 7.99 (s, 2H), 7.92-7.86 (m, 2H), 7.85-7.72 (m, 3H), 7.70-7.55 (m, 3H), 6.48 (s, 1H), 2.71 (s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1, 141.9, 136.1, 133.1, 131.0, 130.5, 128.5, 128.5, 127.8, 127.2, 127.2, 127.1, 126.8, 124.2, 121.2, 118.0, 83.6, 75.2, 63.2; due to low solubility five signals of carbon atoms are not visible.
IR (KBr) ν 3269, 3060, 2827, 2667, 2189, 1550, 1406, 1068, 820 cm^{-1}.
HRMS (ESI$^+$): *m/z* calcd for $C_{24}H_{15}NNaO$ [(M+Na)$^+$]: 356.1046, found: 356.1047.
Note: Signals of 12 $C_{Ar}H$ atoms are clearly visible in ^{13}C NMR. Interestingly, signals of only 10 hydrogen atoms (attached to C_{Ar}) are visible in the aromatic region. Signals of 2 hydrogen atoms are apparently missing. However, the full set of aromatic hydrogen signals can be seen in compound **S3a** (the precursor of **3a**) as well in **4a** (the product of the subsequent cyclotrimerization of **3a**). Moreover, the X-ray structure **4a** confirms the presence of the naphthalene and isoquinoline moieties.

1-(1-(Isoquinolin-1-ylethynyl)-7-methoxynaphthalen-2-yl)prop-2-yn-1-ol (3b). According to the general procedure **B** with **S3b** (2.9 mmol, 1 g), ethynylmagnesium bromide (5.9 mmol, 11.9 mL) in THF (30 mL). Recrystallization from a mixture of hexanes/EtOAc (75/10 mL) furnished 0.9 g (83%) of the title compound as a light brown solid.



R_f (1/1 hexanes/EtOAc) = 0.37.
M.p. = 194−196 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, J = 8.3 Hz, 1H), 8.56 (d, J = 5.7 Hz, 1H), 7.86-7.64 (m, 8H), 7.17 (dd, J = 8.9, 2.6 Hz, 1H), 6.46 (d, J = 2.3 Hz, 1H), 3.99 (s, 3H), 2.69 (d, J = 2.3 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2, 144.3, 142.8, 142.7, 136.0, 135.1, 130.9, 130.2, 129.9, 129.4, 128.3, 128.3, 127.1, 127.0, 121.9, 121.0, 119.8, 116.3, 104.7, 97.0, 90.3, 84.1, 74.7, 62.9, 55.5.
IR (KBr) ν 3288, 3222, 3057, 2958, 2829, 2204, 1354, 1219, 1030, 845 cm^{-1}.
HRMS (ESI$^+$): *m/z* calcd for $C_{25}H_{18}NO_2$ [(M+H)$^+$]: 364.1332, found: 364.1331.

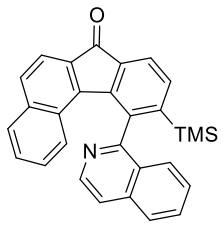
3.2 Catalytic cyclotrimerization reactions



General procedure for Rh-catalyzed [2+2+2] cyclotrimerization followed by oxidation reaction (C). A flame-dried microwave vial was charged with $Rh(cod)_2BF_4$ (0.05-0.10 mmol) and dppb (0.06-0.12 mmol) in a dry mixture of THF/MeOH (10 mL) under argon atmosphere. H_2 gas was bubbled into the reaction mixture for 45 min.[2] Afterwards, the corresponding diyne **3a** (1 mmol) and trimethylsilylacetylene (10 mmol) were added and the reaction mixture was stirred at 100 °C for 16 hours. Then, the reaction mixture was concentrated under reduced pressure. The crude mixture was directly oxidized to the corresponding ketone **4/4´** without any

further purification. MnO_2 (10 mmol) was added to a solution of the crude alcohol in dry CH_2Cl_2 (10 mL) under argon atmosphere. The resulting mixture was stirred at 25 °C for 3 hours. Afterwards, the reaction mixture was filtered through a pad of Celite®. Then, the pad was washed using diethyl ether and the filtrate was concentrated under reduced pressure. Column chromatography of the residue on silica gel (4/1 hexanes/EtOAc) provided products **4/4´**.

11-(Naphthalen-1-yl)-10-(trimethylsilyl)-7H-benzo[c]fluoren-7-one (4a). According to the general procedure **C** with **3a** (1.5 mmol, 0.5 g), trimethylsilylacetylene (15 mmol, 2.1 mL), $Rh(cod)_2BF_4$ (0.15 mmol, 61 mg) and dppb (0.18 mmol, 77 mg) in a 1:1 mixture of dry THF/MeOH (15 mL). Column chromatography of the residue on silica gel (4/1 hexanes/EtOAc) furnished 0.37 g (57%) of the title compound (as mixture of isomers 95:5) as an orange solid.



R_f major isomer (4/1 hexanes/EtOAc) = 0.53. *R_f minor isomer* (4/1 hexanes/EtOAc) = 0.41.

Major isomer (4a).

M.p. = 165–185 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (d, *J* = 5.7 Hz, 1H), 7.86-7.83 (m, 2H), 7.79 (d, *J* = 7.3 Hz, 1H), 7.75-7.72 (m, 2H), 7.61 (d, *J* = 8.1 Hz, 1H), 7.50–7.47 (m, 1H), 7.45–7.41 (m, 2H), 7.15-7.11 (m, 1H), 7.05 (ddd, *J* = 8.1, 6.8, 1.1 Hz, 1H), 6.49 (ddd, *J* = 8.8, 6.8, 1.4 Hz, 1H), 6.25 (dq, *J* = 8.8, 0.9 Hz, 1H), -0.15 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 194.4, 162.4, 150.5, 146.3, 144.5, 142.4, 139.8, 138.1, 136.9, 136.2, 135.8, 133.5, 130.6, 130.5, 129.4, 128.7, 128.2, 127.8, 127.6, 126.9, 126.6, 125.8, 125.7, 122.9, 121.8, 119.5, 0.5 (3 x CH_3).

IR (ATR) ν 3053, 2943, 1712, 1261, 837, 750 cm^{-1}.

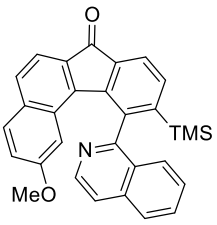
HRMS (ESI$^+$): *m/z* calcd for $C_{29}H_{24}NOSi$ [$(M+H)^+$]: 430.1622, found: 430.1624.

Minor isomer (4a´). - See figure page SI-31

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.68 (d, *J* = 5.7 Hz, 1H), 8.01 (s, 1H), 7.90 – 7.66 (m, 7H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.33 (d, *J* = 7.8 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.46 (t, *J* = 8.2 Hz, 1H), 6.29 (d, *J* = 9.1 Hz, 1H), 0.33 (s, 9H).

2-Methoxy-11-(naphthalen-1-yl)-10-(trimethylsilyl)-7H-benzo[c]fluoren-7-one (4b)

According to the general procedure **C** with **3b** (1.02 mmol, 0.37 mg), trimethylsilylacetylene (10 mmol, 1.42 mL), $Rh(cod)_2BF_4$ (0.05 mmol, 20.7 mg) and dppb (0.06 mmol, 26.1 mg) in a 1:1 dry mixture of THF/MeOH (10 mL). Column chromatography of the residue on silica gel (4/1 hexanes/EtOAc) furnished 0.25 g (53%) of the title compound (as the major isomer) as a red solid.



R_f major isomer (4/1 hexanes/EtOAc) = 0.56. *R_f minor isomer* (4/1 hexanes/EtOAc) = 0.44.

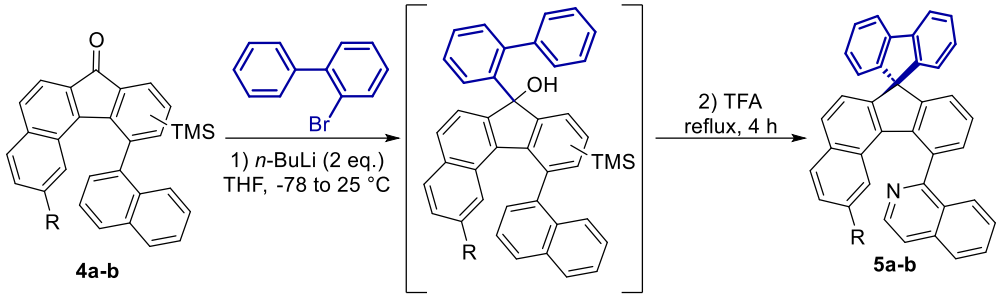
Major isomer (4b).

M.p. = 235−244 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (d, *J* = 5.7 Hz, 1H), 7.84-7.77 (m, 3H), 7.71 (q, *J* = 8.7, 8.0 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 8.1 Hz, 1H), 7.43-7.39 (m, 3H), 7.09 (t, *J* = 7.3 Hz, 1H), 6.79 (dd, *J* = 9.0, 2.4 Hz, 1H), 5.95 (d, *J* = 2.2 Hz, 1H), 3.45 (s, 3H), -0.15 (s, 9H).

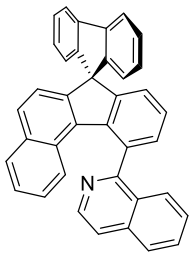
^{13}C NMR (101 MHz, $CDCl_3$) δ 194.3, 162.2, 157.7, 151.0, 145.1, 144.9, 142.4, 139.6, 137.0, 136.2, 135.9, 134.4, 133.8, 130.4, 130.3, 130.1, 129.9, 128.8, 127.7, 127.0, 126.6, 122.8, 121.8, 119.9, 117.4, 106.7, 56.1, 0.6 (3 x CH_3).
IR (ATR) ν 3059, 2939, 2891, 1707, 1227, 1040, 835, 748 cm^{-1}.
HRMS (ESI$^+$): *m/z* calcd for $C_{30}H_{26}NO_2Si$ [(M+H)$^+$]: 460.1727, found: 460.1724.
Minor isomer (4b´). - See figure page SI-33.

3.3 Spirocyclization



General procedure for the synthesis of the spirobifluorene scaffold (D).[6] *n*-BuLi 1.6 M (2.0 mmol, 1.88 mL) was added dropwise to a solution of 2-bromobiphenyl (2 mmol, 345 µL) in dry THF (2 mL) at -78 °C. The resulting mixture was stirred for 1 hour at the same temperature, followed by the dropwise addition of the corresponding ketone **4** (1 mmol) in dry THF (6 mL) and stirred for 30 min at -78 °C, it was allowed to reach 25 °C and stirred overnight. Then, the reaction mixture was poured into a saturated NH_4Cl (aq.) solution and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic fraction was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The alcohol (without further purification) was dissolved in trifluoroacetic acid (12 mL) and refluxed for 4 hours. The resulting mixture was neutralized with a saturated K_2CO_3 (aq.) solution, extracted with CH_2Cl_2 (3 × 50 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Column chromatography of the residue on silica gel of the residue afforded desired spiro-compounds **5**.

1-(Spiro[benzo[c]fluorene-7,9'-fluoren]-11-yl)isoquinoline (5a).

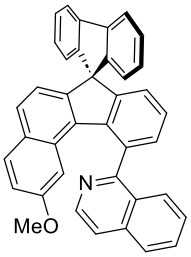


According to the general procedure **D** with **4a/4a´** (0.8 mmol, 0.36 g), *n*-BuLi (1.68 mmol, 1.05 mL) and 2-bromobiphenyl (1.68 mmol, 391 mg) in THF (8 mL). Column chromatography of the residue on silica gel (10/1 hexanes/EtOAc) furnished 400 mg (96%) of the title compound as off white solid.
R_f (10/1 hexanes/EtOAc) = 0.19.
M.p. = 247−250 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, *J* = 5.7 Hz, 1H), 7.94-7.85 (m, 4H), 7.82 (d, *J* = 5.7 Hz, 1H), 7.61-7.56 (m, 3H), 7.50 (d, *J* = 8.3 Hz, 1H), 7.46-7.36 (m, 2H), 7.35-7.27 (m, 2H), 7.20 (td, *J* = 7.5, 1.0 Hz, 1H), 7.12 (td, *J* = 7.5, 1.0 Hz, 1H), 7.08-7.04 (m, 1H), 6.93 (dd, *J* = 7.5, 1.3 Hz, 1H) 6.89 (d, *J* = 7.6 Hz, 1H), 6.82 (d, *J* = 7.6 Hz, 1H), 6.76 (d, *J* = 8.3 Hz, 1H), 6.53-6.52 (m, 2H).

[6] Z. Jiang, H. Yao, Z. Zhang, C. Yang, Z. Liu, Y. Tao, J. Qin, D. Ma; *Org. Lett.* **2009**, *11* 2607-2610.

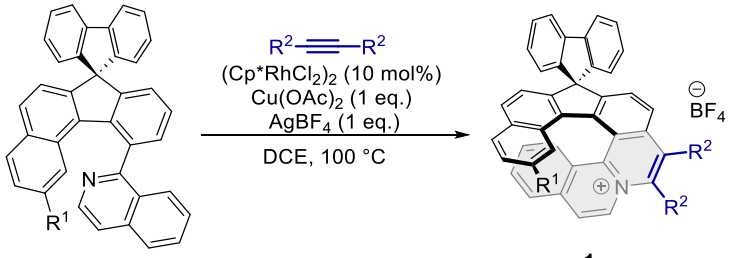
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8, 150.2, 148.4, 148.2, 148.1, 142.6, 142.2, 141.8, 137.5, 136.7, 134.0, 131.6, 130.6, 130.0, 128.5, 128.5, 128.4, 128.2, 128.1, 128.1, 128.1, 127.7, 127.4, 127.2, 127.1, 125.1, 125.1, 124.8, 124.6, 124.5, 124.0, 121.7, 120.7, 120.4, 120.2, 66.5, one signal of quaternary carbon atom is covered by other signals.
IR (ATR) ν 3062, 3045, 3022, 1583, 1556, 1473, 1360, 823, 739 cm^{-1}.
HRMS (ESI$^+$): *m/z* calcd for $C_{38}H_{24}N$ [(M+H)$^+$]: 494.1903, found: 494.1903.

1-(2-Methoxyspiro[benzo[c]fluorene-7,9'-fluoren]-11-yl)isoquinoline (5b). According to the general procedure **D** with **4b/4b´** (0.44 mmol, 0.2 g), *n*-BuLi (0.87 mmol, 0.54 mL) and 2-bromobiphenyl (0.87 mmol, 0.15 mL) in THF (4.4 mL). Column chromatography of the residue on silica gel (10/1 hexanes/EtOAc) furnished 200 mg (87%) of the title compound as a off white solid.

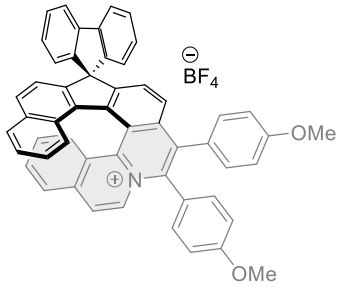


R_f (10/1 hexanes/EtOAc) = 0.14.
M.p. = 241–244 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 5.7 Hz, 1H), 8.16 (d, *J* = 8.6 Hz, 1H), 7.93-7.88 (m, 3H), 7.74 (d, *J* = 5.7 Hz, 1H), 7.63 (t, *J* = 7.1 Hz, 1H), 7.54-7.38 (m, 6H), 7.26-7.11 (m, 3H), 6.92-6.87 (m, 3H), 6.80 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.67 (d, *J* = 8.2 Hz, 1H), 6.37 (d, *J* = 2.5 Hz, 1H), 2.82 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8, 157.5, 150.3, 148.9, 148.6, 148.4, 142.8, 142.5, 142.1, 141.7, 137.1, 136.7, 134.4, 132.6, 130.5, 130.1, 130.1, 129.8, 129.6, 128.2, 128.1, 128.0, 127.8, 127.6, 127.5, 127.1, 126.8, 124.6, 124.3, 124.1, 120.4, 120.3, 120.2, 119.4, 117.7, 105.1, 66.5, 54.8.
IR (ATR) ν 3059, 3035, 3010, 1620, 1554, 1223, 835, 758, 731, 687 cm^{-1}.
HRMS (ESI$^+$): *m/z* calcd for $C_{39}H_{26}NO$ [(M+H)$^+$]: 524.2009, found: 524.2009.

3.4 C–H Activation/annulation



General procedure for C-H activation/annulation reaction (E). A microwave vial was charged with $AgBF_4$ (0.1 mmol, 19.4 mg), $(Cp^*RhCl_2)_2$ (0.01 mmol, 6.2 mg), $Cu(OAc)_2$ (0.1 mmol, 20 mg), the corresponding acetylene (0.1 mmol) and the spiro-compound **5** (0.1 mmol) in DCE (2 mL). The microwave was sealed and heated up to 100 °C for 16 hours. Afterwards, the reaction mixture was filtered on a pad of Celite®, then the pad was washed using CH_2Cl_2 (10 mL), and the filtrate was concentrated under reduced pressure. Column chromatography of the residue on silica gel provided products **1**.

4,5-Bis(4-methoxyphenyl)spiro[benzo[6,7]indeno[2,1-h]isoquinolino[1,2-a]isoquinoline-8,9'-fluoren]-3-ium tetrafluoroborate (1aa). 

According to the general procedure **E** with **5a** (0.15 mmol, 75 mg) and 4,4´-dimethoxydiphenylacetylene (0.15 mmol, 35.8 mg). Column chromatography of the residue on silica gel (98/2 CH_2Cl_2/MeOH) furnished 114 mg (92%) of the title compound as a bright orange solid.

R_f (98/2 CH_2Cl_2/MeOH) = 0.38.

M.p. = 262–268 °C.

^{1}H NMR (400 MHz, $CDCl_3$ + CD_2Cl_2) δ 8.75 (d, J = 7.4 Hz, 1H), 8.28-8.25 (m, 2H), 8.12-8.03 (m, 2H), 8.00 (dt, J = 7.7, 1.0 Hz, 1H), 7.75 (d, J = 8.3 Hz, 1H), 7.70-7.62 (m, 3H), 7.57 (td, J = 7.6, 1.0 Hz, 1H), 7.51-7.41 (m, 3H), 7.35-7.31 (m, 2H), 7.26 (dd, J = 8.4, 2.3 Hz, 1H), 7.19-7.05 (m, 7H), 6.98 (d, J = 8.3 Hz, 1H), 6.92-6.85 (m, 2H), 6.76 (ddd, J = 8.3, 6.9, 1.3 Hz, 1H), 6.49 (dt, J = 7.7, 1.0 Hz, 1H), 6.37 (dd, J = 8.5, 1.0 Hz, 1H), 3.89 (s, 3H), 3.79 (s, 3H).

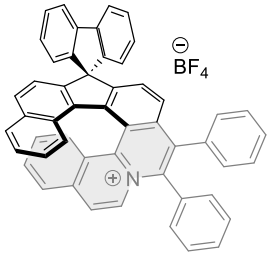
^{13}C NMR (101 MHz, CD_2Cl_2) δ 161.6, 160.1, 154.1, 149.1, 145.9, 145.4, 144.8, 143.5, 143.5, 142.9, 139.7, 137.4, 136.6, 135.0, 133.5, 133.5, 133.4, 132.7, 132.4, 132.4, 131.6, 131.5, 130.3, 130.2, 129.5, 129.3, 129.2, 128.8, 128.7, 128.4, 128.1, 127.8, 126.9, 126.6, 126.6, 126.5, 125.8, 124.5, 124.0, 123.0, 122.9, 121.8, 121.6, 121.1, 118.9, 115.8, 115.6, 114.4, 114.4, 67.3, 55.9 (OCH_3), 55.7 (OCH_3); two signals of quaternary carbon atoms are covered by other signals.

^{19}F NMR (376 MHz, CD_2Cl_2) δ -153.10 – -153.20 (m, 4F).

IR (ATR) ν 3064, 2956, 2929, 2833, 1608, 1504, 1248, 1178, 1055, 1026, 814, 748, 729 cm^{-1}.

HRMS (ESI$^+$): m/z calcd for $C_{54}H_{36}NO_2$ [M$^+$]: 730.2741, found: 730.2744.

4,5-Diphenylspiro[benzo[6,7]indeno[2,1-h]isoquinolino[1,2-a]isoquinoline-8,9'-fluoren]-3-ium tetrafluoroborate (1ab). According to the general procedure **E** with **5a** (0.15 mmol, 75 mg) and diphenylacetylene (0.15 mmol, 26.7 mg). Column chromatography of the residue on silica gel (98/2 CH_2Cl_2/MeOH) furnished 70 mg (60%) of the title compound as an orange-red solid.



R_f (98/2 CH_2Cl_2/MeOH) = 0.35.

M.p. = 308−309 °C.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.69 (d, J = 7.3 Hz, 1H), 8.28 (t, J = 8.2 Hz, 2H), 8.06 (dd, J = 10.6, 7.9 Hz, 2H), 7.99 (d, J = 7.7 Hz, 1H), 7.76 (d, J = 8.3 Hz, 1H), 7.70-7.50 (m, 8H), 7.48-7.39 (m, 3H), 7.36-7.30 (m, 5H), 7.29-7.21 (m, 1H), 7.22-7.15 (m, 3H), 7.09 (td, J = 7.5, 1.0 Hz, 1H), 6.98 (d, J = 8.3 Hz, 1H), 6.77 (ddd, J = 8.3, 7.0, 1.2 Hz, 1H), 6.49 (d, J = 7.6 Hz, 1H), 6.37 (dd, J = 8.5, 0.6 Hz, 1H).

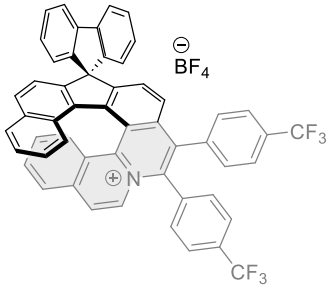
^{19}F NMR (376 MHz, CD_2Cl_2) δ -153.16 − -153.25 (m, 4F).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 154.4, 149.2, 145.8, 145.5, 144.7, 143.7, 143.5, 142.9, 139.3, 137.2, 136.6, 136.1, 135.2, 134.3, 133.5, 133.5, 132.5, 132.0, 131.6, 131.2, 131.1, 130.9, 130.4, 130.4, 130.3, 130.3, 130.2, 129.5, 129.3, 129.3, 129.1, 129.0, 128.8, 128.7, 128.4, 128.1, 127.9, 126.8, 126.7, 126.6, 125.8, 124.5, 124.0, 123.3, 121.8, 121.6, 121.2, 118.9; four signals of quaternary carbon atoms are covered by other signals.

IR ν 3053, 2922, 2850, 1633, 1444, 1049, 1028, 810, 800, 741 cm^{-1}.

HRMS (ESI$^+$): m/z calcd for $C_{52}H_{32}N$ [M$^+$]: 670.2529, found: 670.2529.

4,5-bis(4-(trifluoromethyl)phenyl)spiro[benzo[6,7]indeno[2,1-h]isoquinolino[1,2-a]isoquinoline-8,9'-fluoren]-3-ium tetrafluoroborate (1ac). According to the general procedure **E** with **5a** (0.1 mmol, 49.3 mg) and 1,2-bis(4-(trifluoromethyl)phenyl)ethyne (0.1 mmol, 31.4 mg). Column chromatography of the residue on silica gel (linear gradient: 99/1 to 95:5 CH_2Cl_2/MeOH) furnished 84 mg (93%) of the title compound as an orange solid.



R_f (98/2 CH_2Cl_2/MeOH) = 0.32.

M.p. = 287−290 °C.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.55 (d, J = 7.3 Hz, 1H), 8.30 (d, J = 8.6 Hz, 1H), 8.25 (d, J = 7.4 Hz, 1H), 8.06 (d, J = 7.2 Hz, 2H), 8.00 (d, J = 7.7 Hz, 1H), 7.96 (d, J = 8.1 Hz, 1H), 7.85 (d, J = 8.1 Hz, 1H), 7.77 (t, J = 7.1 Hz, 2H), 7.71-7.49 (m, 8H), 7.49-7.41 (m, 3H), 7.36-7.31 (m, 1H), 7.21-7.13 (m, 3H), 7.08 (t, J = 7.5 Hz, 1H), 6.98 (d, J = 8.3 Hz, 1H), 6.79 (t, J = 7.2 Hz, 1H), 6.49 (dd, J = 17.3, 8.1 Hz, 2H).

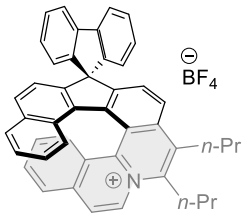
^{19}F NMR (376 MHz, CD_2Cl_2) δ -63.20 (s, 3F), -63.39 (s, 3F), -152.73 − -152.87 (m, 4F).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 154.7, 149.3, 146.1, 146.0, 144.9, 144.2, 143.6, 143.0, 138.3, 137.9, 136.7, 136.0, 135.6, 135.4, 134.8, 133.9, 133.6, 133.0, 132.7, 132.5, 132.0, 131.9, 131.2, 130.5, 130.5, 129.6, 129.4, 129.2, 129.0, 128.9, 128.6, 128.3, 127.9, 127.4, 127.4, 127.3, 127.3, 127.0, 126.8, 126.5, 126.2, 126.2, 126.2, 126.0, 125.1, 124.3, 124.3, 123.5, 121.8, 121.7, 121.3, 119.3, 67.5, one signal of quaternary carbon atom is covered by other signals.

IR (ATR) ν 3057, 3014, 2960, 2927, 1620, 1446, 1321, 1167, 1109, 1063, 1018, 798, 744 cm^{-1}.

HRMS (ESI$^+$): *m/z* calcd for $C_{54}H_{30}F_6N$ [M^+]: 806.2277, found: 806.2278.

4,5-Dipropylspiro[benzo[6,7]indeno[2,1-h]isoquinolino[1,2-a]isoquinoline-8,9'-fluoren]-3-ium tetrafluoroborate (1ad). According to the general procedure **E** with **5a** (0.1 mmol, 49.3 mg) and 4-octyne (0.1 mmol, 11 mg). Column chromatography of the residue on silica gel (98/2 CH_2Cl_2/MeOH) furnished 56 mg (80%) of the title compound as an orange solid.



R_f (98/2 CH_2Cl_2/MeOH) = 0.35.

M.p. = 205–209 °C.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 9.29 (d, J = 7.5 Hz, 1H), 8.55 (dd, J = 7.5, 0.8 Hz, 1H), 8.22-8.11 (m, 2H), 8.11-8.00 (m, 3H), 7.73-7.68 (m, 1H), 7.67-7.62 (m, 1H), 7.61-7.55 (m, 3H), 7.48 (td, J = 7.5, 1.1 Hz, 1H), 7.35-7.29 (m, 1H), 7.19-7.05 (m, 4H), 6.94 (d, J = 8.3 Hz, 1H), 6.78-6.73 (m, 1H), 6.44 (dt, J = 7.6, 0.9 Hz, 1H), 6.19 (dd, J = 8.4, 1.0 Hz, 1H), 3.62 (td, J = 7.8, 4.3 Hz, 2H), 3.30 (dt, J = 9.5, 5.5 Hz, 2H), 2.12-1.97 (m, 2H), 1.95-1.79 (m, 2H), 1.36 (t, J = 7.3 Hz, 3H), 1.22 (t, J = 7.3 Hz, 3H).

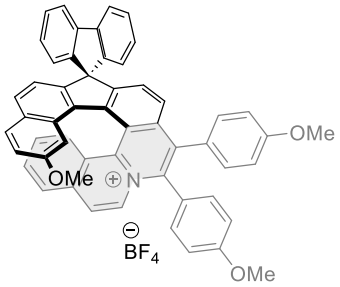
^{19}F NMR (376 MHz, CD_2Cl_2) δ -152.64 − -152.81 (m, 4F).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 153.0, 148.9, 146.0, 145.0, 144.8, 143.8, 143.5, 142.9, 139.5, 136.7, 135.2, 134.6, 134.3, 133.5, 133.1, 132.2, 131.4, 130.2, 129.9, 129.5, 129.3, 129.1, 128.8, 128.7, 127.9, 127.6, 127.0, 126.7, 126.6, 125.8, 124.2, 124.0, 124.0, 124.0, 123.5, 121.8, 121.6, 121.1, 118.5, 32.2, 31.6, 24.4, 21.7, 14.8, 14.3.

IR ν 3053, 2960, 2929, 2871, 1446, 1049, 1030, 808, 741 cm^{-1}.

HRMS (ESI$^+$): *m/z* calcd for $C_{46}H_{36}N$ [M^+]: 602.2842, found: 602.2838.

13-Methoxy-4,5-bis(4-methoxyphenyl)spiro[benzo[6,7]indeno[2,1-h]isoquinolino[1,2-a]isoquinoline-8,9'-fluoren]-3-ium tetrafluoroborate (1ba).



According to the general procedure **E** with **5b** (0.1 mmol, 52.3 mg) and 4,4´-dimethoxydiphenylacetylene (0.1 mmol, 23.8 mg). Column chromatography of the residue on silica gel (98/2 CH_2Cl_2/MeOH) furnished 76.2 mg (90%) of the title compound as a red solid.

R_f (98/2 CH_2Cl_2/MeOH) = 0.35.

Mp = 265−268 °C.

^{1}H NMR (400 MHz, CD_2Cl_2+$CDCl_3$) δ 8.75 (d, *J* = 7.3 Hz, 1H), 8.30 (d, *J* = 7.3 Hz, 1H), 8.16 (d, *J* = 8.5 Hz, 1H), 8.17-7.99 (m, 3H), 7.70 (d, *J* = 8.5 Hz, 1H), 7.67-7.62 (m, 3H), 7.56 (td, *J* = 7.6, 0.9 Hz, 1H), 7.49-7.44 (m, 3H), 7.34-7.28 (m, 4H), 7.16-7.06 (m, 5H), 6.92-6.83 (m, 4H), 6.52 (d, *J* = 7.6 Hz, 1H), 5.55 (d, *J* = 2.5 Hz, 1H), 3.88 (s, 3H), 3.79 (s, 3H), 3.47 (s, 3H).

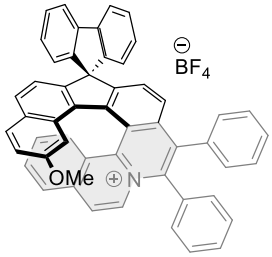
^{19}F NMR (376 MHz, CD_2Cl_2) δ -152.97 − -153.13 (m, 4F).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 161.5, 160.1, 157.5, 153.9, 149.9, 146.1, 145.1, 145.1, 143.7, 143.4, 142.8, 139.6, 137.5, 136.6, 135.4, 135.1, 133.4, 133.1, 132.6, 132.5, 132.1, 131.6, 131.0, 130.9, 130.2, 130.0, 129.6, 129.4, 129.2, 128.8, 128.7, 128.7, 128.0, 127.5, 126.7, 126.6, 126.3, 124.1, 123.1, 123.0, 121.5, 121.1, 119.3, 118.6, 115.7, 115.7, 115.6, 114.4, 114.3, 107.1, 67.2, 55.9, 55.7, 55.6; one signal of quaternary carbon atom is covered by other signals.

IR ν 3064, 2952, 2929, 2835, 1606, 1508, 1248, 1178, 1053, 1026, 804, 750, 731 cm^{-1}.

HRMS (ESI$^+$): *m/z* calcd for $C_{55}H_{38}NO_3$ [M$^+$]: 760.2846, found: 760.2841.

13-methoxy-4,5-diphenylspiro[benzo[6,7]indeno[2,1-h]isoquinolino[1,2-a]isoquinoline-8,9'-fluoren]-3-ium tetrafluoroborate (1bb).



According to the general procedure **E** with **5b** (0.1 mmol, 52.3 mg) and diphenylacetylene (0.1 mmol, 17.8 mg). Column chromatography of the residue on silica gel (98/2 CH_2Cl_2/MeOH) furnished 64 mg (81%) of the title compound as a red solid.

R_f (98/2 CH_2Cl_2/MeOH) = 0.32.

M.p. = 335−338 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 7.3 Hz, 1H), 8.37 (d, *J* = 7.4 Hz, 1H), 8.13 (t, *J* = 7.3 Hz, 2H), 7.99 (d, *J* = 7.6 Hz, 1H), 7.93 (d, *J* = 7.7 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.66-7.35 (m, 6H), 7.33-7.25 (m, 6H), 7.13-6.99 (m, 3H), 6.89-6.76 (m, 3H), 6.59 (d, *J* = 7.7 Hz, 2H), 5.65 (d, *J* = 2.4 Hz, 1H), 3.45 (s, 3H).

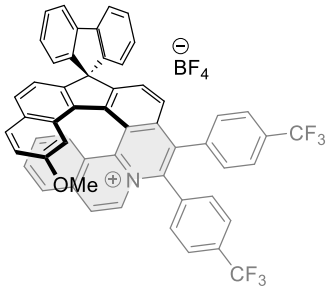
^{19}F NMR (376 MHz, $CDCl_3$) *δ* -153.58 − -153.73 (m, 4F).

^{13}C NMR (101 MHz, $CDCl_3$) *δ* 157.4, 153.5, 149.4, 145.8, 145.0, 144.8, 143.5, 143.1, 142.3, 139.3, 136.8, 135.8, 135.4, 134.6, 134.3, 133.0, 131.7, 131.6, 131.2, 131.1, 130.9, 130.8, 130.6, 130.4, 130.0, 130.0, 129.7, 129.7, 129.6, 129.1, 128.8, 128.6, 128.6, 128.6, 128.4, 128.4, 128.0, 127.5, 126.3, 126.0, 124.2, 123.8, 123.1, 121.1, 120.6, 119.0, 118.4, 116.3, 106.7, 66.9, 55.8; two signals of quaternary carbon atoms are covered by other signals.

IR ν 3309, 3062, 2922, 2848, 1624, 1442, 1271, 1045, 1028, 727, 700 cm^{-1}.

HRMS (ESI$^+$): *m/z* calcd for $C_{53}H_{34}NO$ [M$^+$]: 700.2635, found: 700.2631.

13-Methoxy-4,5-bis(4-(trifluoromethyl)phenyl)spiro[benzo[6,7]indeno[2,1-h]isoquinolino[1,2-a]isoquinoline-8,9'-fluoren]-3-ium tetrafluoroborate (1bc). According to the general procedure **E** with **5b** (0.1 mmol, 52.4 mg) and 1,2-bis(4-(trifluoromethyl)phenyl)ethyne (0.1 mmol, 31.4 mg). Column chromatography of the residue on silica gel (99/1 CH_2Cl_2/MeOH) furnished 76 mg (87%) of the title compound as a dark red solid.



R_f (98/2 CH_2Cl_2/MeOH) = 0.41.

Mp = 264−267 °C.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.52 (d, J = 7.3 Hz, 1H), 8.28 (d, J = 7.3 Hz, 1H), 8.17 (d, J = 8.6 Hz, 1H), 8.06 (dd, J = 11.9, 7.8 Hz, 2H), 7.99 (d, J = 7.6 Hz, 1H), 7.91 (d, J = 8.1 Hz, 1H), 7.85-7.74 (m, 2H), 7.72-7.52 (m, 8H), 7.51-7.41 (m, 4H), 7.32 (td, J = 7.5, 1.0 Hz, 1H), 7.21-7.04 (m, 3H), 6.89-6.79 (m, 2H), 6.54 (d, J = 7.6 Hz, 1H), 5.65 (d, J = 2.4 Hz, 1H), 3.42 (s, 3H).

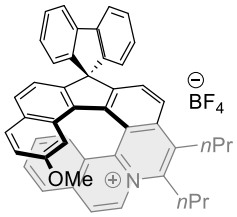
^{19}F NMR (376 MHz, CD_2Cl_2) δ -63.20 (s, 3F), -63.43 (s, 3F), -152.81 − -152.94 (m, 4F).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 157.7, 154.3, 150.1, 146.0, 145.7, 145.1, 144.3, 143.5, 142.8, 138.2, 137.6, 136.1, 135.5, 135.4, 135.3, 134.8, 133.2, 132.8, 132.3, 132.3, 131.9, 131.3, 131.3, 131.0, 131.0, 130.9, 130.3, 129.8, 129.4, 129.2, 128.8, 128.8, 127.9, 127.5, 127.4, 127.3, 127.2, 127.1, 126.4, 126.1, 126.1, 126.0, 126.0, 126.0, 124.2, 124.1, 123.3, 121.5, 121.1, 119.2, 118.9, 116.3, 106.9, 67.2, 55.9.

IR ν 3064, 3014, 2933, 2844, 1620, 1444, 1321, 1167, 1109, 1065, 1018, 827, 748 cm^{-1}.

HRMS (ESI$^+$): *m/z* calcd for $C_{55}H_{32}F_6NO$ [M$^+$]: 836.2383, found: 836.2374.

13-Methoxy-4,5-dipropylspiro[benzo[6,7]indeno[2,1-h]isoquinolino[1,2-a]isoquinoline-8,9'-fluoren]-3-ium tetrafluoroborate (1bd). According to the general procedure **E** with **5b** (0.1 mmol, 52.3 mg) and 4-octyne (0.1 mmol, 11 mg). Column chromatography of the residue on silica gel (98/2 CH_2Cl_2/MeOH) furnished 50.1 mg (70%) of the title compound as a red solid.



R_f (98/2 CH_2Cl_2/MeOH) = 0.32.

Mp = 204−209 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.58 (d, J = 7.5 Hz, 1H), 8.73 (d, J = 7.4 Hz, 1H), 8.14-7.89 (m, 5H), 7.63-7.49 (m, 5H), 7.45 (td, J = 7.5, 1.1 Hz, 1H), 7.37-7.23 (m, 1H), 7.10-7.00 (m, 3H), 6.88-6.75 (m, 2H), 6.50 (dt, J = 7.6, 0.9 Hz, 1H), 5.38 (d, J = 2.4 Hz, 1H), 3.71 (q, J = 8.6 Hz, 2H), 3.37 (s, 3H), 3.33-3.16 (m, 2H), 2.04-1.96 (m, 2H), 1.92-1.78 (m, 2H), 1.33 (t, J = 7.3 Hz, 3H), 1.22 (t, J = 7.4 Hz, 3H).

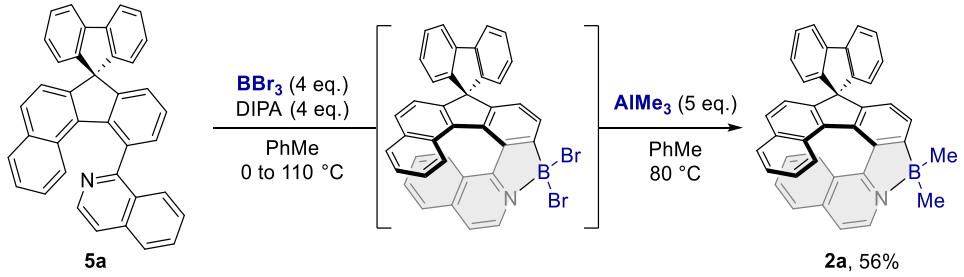
^{19}F NMR (376 MHz, $CDCl_3$) δ -152.83 − -152.98 (m, 4F).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.5, 152.5, 149.2, 145.9, 145.1, 143.7, 143.6, 143.1, 142.4, 139.9, 135.3, 134.7, 134.2, 133.6, 132.8, 131.7, 130.48, 130.46, 129.8, 129.20, 129.17, 128.9, 128.5, 128.4, 127.6, 127.3, 125.8, 124.5, 124.0, 123.6, 122.7, 121.3, 120.7, 119.1, 117.7, 116.9, 105.1, 66.9, 55.4, 32.2, 31.2, 24.1, 21.5, 14.9, 14.2.

IR ν 3060, 2960, 2927, 2871, 1622, 1444, 1051, 1030, 742, 733 cm^{-1}.

HRMS (ESI$^+$): *m/z* calcd for $C_{47}H_{38}NO$ [M$^+$]: 632.2948, found: 632.2949.

3.5 Synthesis of Azaborolo- and Azaplata complexes



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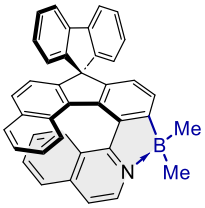
8,8-Dimethyl-8*H*-7λ⁴,8λ⁴-spiro[benzo[5',6']fluoreno[3',4':3,4][1,2]azaborolo[5,1]-isoquinoline-11,9'-fluorene] (2a). In a flame-dried pressure tube, boron tribromide (0.4 mmol, 0.4 mL) was added to 1-(spiro[benzo[c]fluorene-7,9'-fluoren]-11-yl)isoquinoline **5a** (0.1 mmol, 50 mg) in dry toluene (3 mL) at 0 °C, and the resulting reaction mixture was stirred for 20 min at the same temperature. After that the tube was sealed and the reaction mixture was stirred at 110 °C for 16 hours. Then, DIPEA (0.4 mmol, 70 µL) was added at 0 °C and the mixture was stirred at 20 °C for 3 hours. The reaction was quenched with a saturated K_2CO_3 (aq.) solution (2 mL) and diluted with water (2 mL) and CH_2Cl_2 (10 mL). The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was used in the following step without further purification. $AlMe_3$ (2M solution in hexanes, 0.25 mL, 0.5 mmol, 5 equiv.) was added to the crude product in dry toluene (5 mL) under an inert atmosphere, and the reaction was stirred for 16 h at 80 °C. The reaction was quenched with water, the organic layer was separated, and the aqueous phase was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concetrated under reduced pressure. Column chromatography of the residue on silica gel (90/10 CH_2Cl_2/hexanes) furnished 31 mg (57%) of **2a** as a bright yellow solid.



R_f (1/1 CH_2Cl_2/Hexanes) = 0.76.

M.p. = 135−140 °C.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.46 (d, J = 6.3 Hz, 1H), 8.03-7.91 (m, 4H), 7.88 (dd, J = 6.4, 0.8 Hz, 1H), 7.82-7.75 (m, 1H), 7.69 (d, J = 8.2 Hz, 1H), 7.56-7.39 (m, 4H), 7.21-7.08 (m, 4H), 7.03 (dt, J = 7.6, 1.0 Hz, 1H), 6.89 (dd, J = 7.7, 3.1 Hz, 2H), 6.79 (ddd, J = 8.4, 6.9, 1.2 Hz, 1H), 6.67 (dt, J = 7.6, 0.9 Hz, 1H), 6.58 (ddd, J = 8.4, 6.8, 1.3 Hz, 1H), 0.30 (s, 3H), 0.07 (s, 3H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 158.7, 148.55, 148.4, 148.2, 147.9, 142.9, 142.6, 139.7, 139.4, 137.3, 134.3, 133.9, 132.1, 131.3, 129.6, 129.5, 129.0, 128.7, 128.7, 128.5, 128.4, 128.3, 128.2, 127.3, 127.0, 127.0, 126.2, 125.3, 124.7, 124.6, 124.5, 124.0, 121.7, 120.9, 120.8, 120.5;

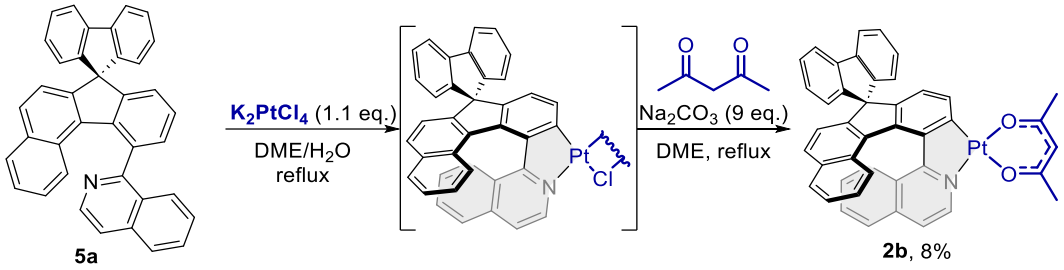
Two signals of quaternary carbon atoms are covered by other signals; signals corresponding to the carbon atom bound to the boron atom are not visible. The observation corresponds to the previously reported one.[7].

^{11}B NMR (128 MHz, $CDCl_3$) δ 0.9;

[7] Full, J.; Panchal, S. P.; Götz, J.; Krause, A.-M.; Nowak-Król, A. *Angew. Chem. Int. Ed.*, **2021**, *60*, 4350-4357.

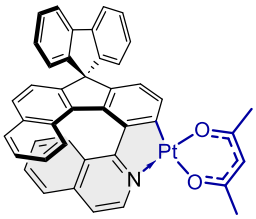
IR ν 3049, 3022, 2918, 2887, 1427, 812, 742 cm^{-1};
HRMS (ESI^+): *m/z* calcd for $C_{40}H_{29}BN$ [$(M+H)^+$]: 534.2388, found: 534.2386.

(1-(Spiro[benzo[*c*]fluorene-7,9'-fluoren]-11-yl)isoquinolinato-N,C^{10})platinum-acetylacetonate (2b)



Preparation of the platinum μ-chloro-bridged dimer, Pt(μ-Cl)$_2$Pt. In a dry pressure tube, 1-(spiro[benzo[*c*]fluorene-7,9'-fluoren]-11-yl)isoquinoline **5a** (50 mg, 0.1 mmol) was dissolved in ethoxyethanol (5 mL) and water (2 mL). The mixture was bubbled with argon for 20 minutes and then $K_2[PtCl_4]$ (50.5 mg, 0.12 mmol) was added. The tube was sealed and the suspension was gently warmed until all the platinum salt dissolved. The reaction mixture was then refluxed for 16 hours to yield a dark green suspension. Then water (10 mL) was added to the cooled reaction mixture and the green solid was filtered off. The solid was dissolved in dichloromethane, dried over Na_2SO_4, and the solution was concentrated under reduced pressure. The crude product (the dimer) was subsequently used in the next step without purification.

Reaction of the μ-chloro-bridged dimer with 2,4-pentadione. To a solution of the crude **5aPt(*μ*-Cl)$_2$** in ethoxyethanol (5 mL), were added 2,4-pentadione (0.5 mmol 52 μL) and Na_2CO_3 (1.01 mmol, 107 mg). The reaction mixture was refluxed for 2 hours and then concentrated under reduced pressure. Column chromatography of the residue on silica gel (CH_2Cl_2) yielded 6.5 mg (8%) of **2b** as a dark red solid.



R_f (1/1 CH_2Cl_2/hexanes) = 0.55.
Mp = 224−228 °C.
^{1}H NMR (400 MHz, CD_2Cl_2) δ 9.06 (d, J = 6.4 Hz, 1H), 7.95 (ddt, J = 8.8, 7.7, 1.0 Hz, 2H), 7.79 (ddd, J = 9.4, 8.4, 1.1 Hz, 2H), 7.71-7.63 (m, 2H), 7.60 (d, J = 8.2 Hz, 1H), 7.51-7.39 (m, 3H), 7.35 (ddd, J = 8.1, 6.9, 1.1 Hz, 1H), 7.21 (td, J = 7.5, 1.1 Hz, 1H), 7.15-7.01 (m, 3H), 6.91 (dd, J = 8.6, 1.1 Hz, 1H), 6.82 (d, J = 8.3 Hz, 1H), 6.72-6.60 (m, 3H), 6.54 (ddd, J = 8.4, 6.8, 1.3 Hz, 1H), 5.54 (s, 1H), 2.09 (s, 3H), 1.97 (s, 3H).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 186.6, 184.8, 170.6, 148.6, 148.1, 146.3, 142.7, 142.6, 141.1, 141.1, 140.9, 139.4, 139.3, 136.8, 133.4, 131.5, 129.7, 129.1, 128.6, 128.5, 128.3, 128.3, 128.2, 128.1, 127.1, 126.9, 126.8, 126.5, 125.0, 124.8, 124.5, 124.1, 123.9, 121.6, 120.9, 120.5, 120.5, 102.2, 66.9, 30.10, 28.4, 27.3; one signal of quaternary carbon atom is covered by other signals.
IR ν 3045, 2958, 2920, 2850, 1556, 1518, 1381, 1095, 812, 744, 733 cm^{-1}.
HRMS (ESI^+): *m/z* calcd for $C_{43}H_{29}NNaO_2Pt$ [$(M+Na)^+$]: 809.1738, found: 809.1746.

4 Photophysical properties

UV−vis absorption spectra were recorded on DS5 Dual Beam UV-Vis Spectrophotometer (Edinburgh Instruments). Steady-state fluorescence spectra were monitored on an FLS 980 spectrofluorometer (Edinburgh Instruments). Fluorescence quantum yields were determined using a Quantaurus-QY Plus spectrofluorometer (HamamatsuC13534-33). Fluorescence of air-saturated solutions of samples in DCM were measured in 1 cm path-length cuvettes using samples with an absorbance of 0.1 or less at the excitation wavelength. During measurement in DCM solution with N_2 gas saturation, the solution was bubbled with N_2 gas in a long neck cuvette sealed by a septum for 20 minutes.

UV/Vis absorption and fluorescence spectra of our [7]-helical quinolizinium salts **1** and complexes **2** in dichloromethane are showed in Figure S2 and S3, respectively, and the spectral data are summarized in Table S5 and S6. Fluorescence quantum yields of powder samples were determined using build-in correction for self-absorption using true spectra collected from a small amount of the same sample (Table S7).

Only small differences in emission maxima in series of **1aa-1ad** and **1ba-1bd** were recorded. The emission maxima for the methoxy substituted series **1ba-1bd** are bathochromically shifted by 40-50 nm with respect to unsubstituted series **1aa-1ad**. As far as substituent effect is concerned, the presence of methoxyphenyl substituents slightly shifts emissions towards blue light region (610 nm for **1aa** and 647 nm for **1ba**) with respect to the phenyl substituted derivatives **1ab** and **1bb** (611 and 653 nm, respectively), on the other hand the presence of trifluoromethylphenyl substituents shifts the emission maxima towards the red-light region (630 nm for **1ac** and 682 nm for **1bc**). It is worth of mentioning that the trend, albeit small, is opposite to the one observed for cationic 11-azapyrenes,[8] cationic 12-azapyrene,[9,10] and substituted quinolizinium compounds.[11] Concerning the quantum yields, higher Φ_f in the range of 86-99% were recorded for **1aa-1ad**, whereas for the series possessing the MeO group **1ba-1bd** they dropped to 28-55%. All of the compounds also possess the large Stokes shift with values up to 145 nm.

[8] J. Ulč, J. Jacko, I. Císařová, L. Pospíšil, D. Nečas, M. Kotora, *Eur. J. Org. Chem.*, 2023, **26**, e2023001.
[9] For a review, see: P. Karak, S. S. Rana, J. Choudhury, *Chem. Commun.*, 2022, **58**, 133–154.
[10] Q. Ge, Y. Hu, B. Li, B. Wang, *Org. Lett.*, 2016, **18**, 2483–2486.
[11] W.-M. Yip, Q. Yu, A. Tantipanjapotn, W.-C. Chan, J.-R. Deng, B. C. Ko, Wong, M.-K. *Org. Biomol. Chem.*, **2021**, *19*, 8507–8515.

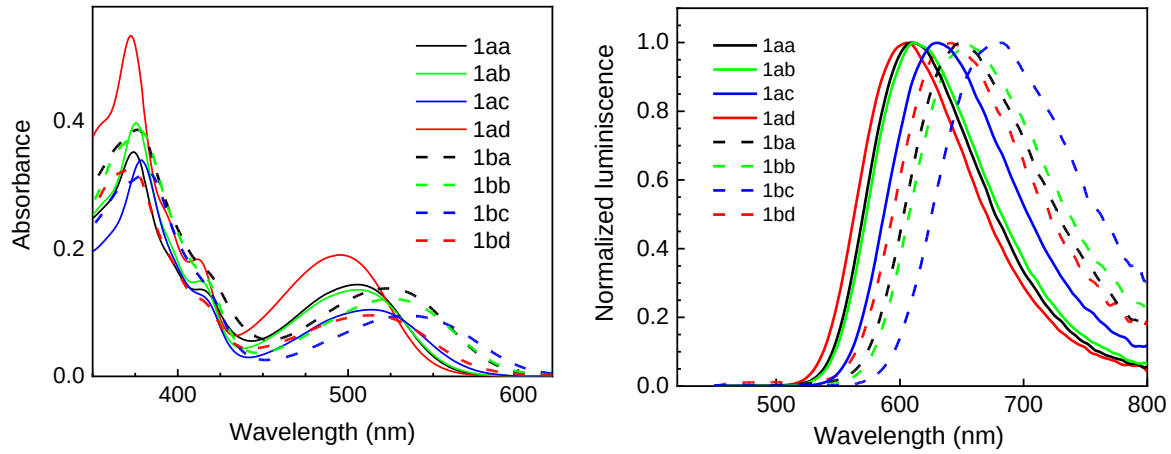


Figure S2. UV/Vis absorption (left) and normalized emission spectra (right) of **1** recorded in CH_2Cl_2 ((~ 2×10^{-5} M and for emission with an absorbance of 0.1 or less).

Concerning the metal complexes, azabora compound **2a** shows intense blue-green fluorescence with an emission maximum at 497 nm in solution and 505 nm in the solid state with quantum yields (Φ_f) up to 34%). (Emission maxima for structurally similar azabora-helical compounds were reported to be in the range of 459-477 nm.[12]) On the other hand, the emission maximum of **2b** is significantly shifted by almost 200 nm to the red-light region (690 nm in solution and 676 nm in the solid state) similarly to the [7]helical quinolizinium salts **1** (Table 1), but with rather low quantum yield typical for the previously reported Pt(II)-helicene complexes.[13]

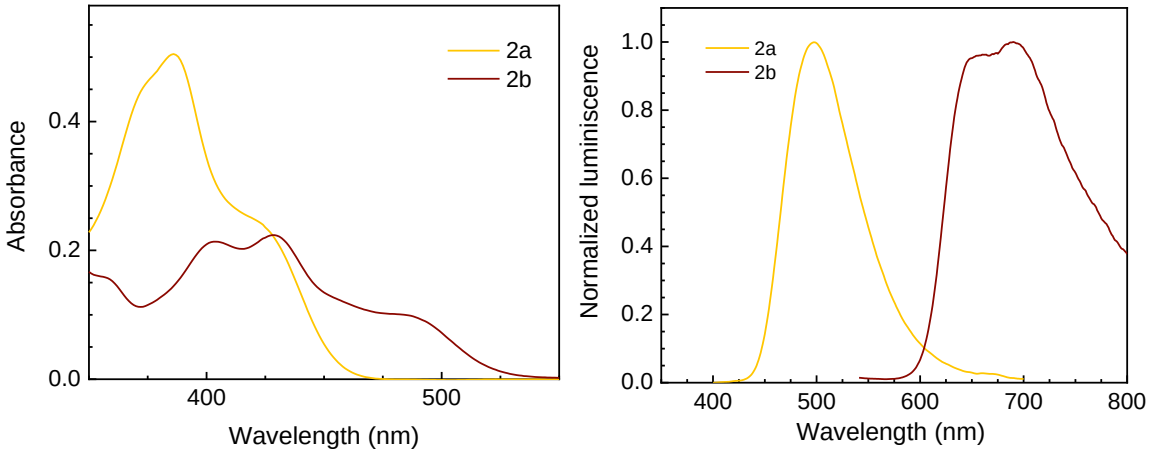


Figure S3. UV/Vis absorption (left) and normalized emission spectra (right) of **2a** and **2b** recorded in CH_2Cl_2 (0.016 mg/mL and for emission with an absorbance of 0.1 or less).

[12] J. Full, S. P. Panchal, J. Götz, A.-M. Krause, A. Nowak-Król, *Angew. Chem. Int. Ed.*, 2021, **60**, 4350–4357.

[13] For selected examples on helical platinum complexes, see: E. Anger, M. Rudolph, L. Norel, S. Zrig, C. Shen, N. Vanthuyne, L. Toupet, J. A. G. Williams, C. Roussel, J. Autschbach, J. Crassous, R. Réau, *Chem. Eur. J.*, 2011, **17**, 14178–14198.

Table S5. Photo-physical properties of 1 in solution (CH2Cl2) and solid state.

Compound	λ_{Amax} (nm)	ε (10^3 M^{-1} cm^{-1})	λ_{Aedge} (nm)	$E_{optical\ gap}$ (eV)	λ_{Fmax} (nm) solution[a]	Φ_f (%) solution[b]	Stokes shift (nm)	Stokes shift (eV)
1aa	374, 506	18, 7	560	2.21	610 (608)	>99 (62)	104	0.418
1ab	376, 506	19, 6	561	2.21	611 (622)	95 (34)	105	0.421
1ac	379, 514	19, 6	572	2.17	630 (610)	86 (66)	116	0.444
1ad	372, 496	23, 8	550	2.25	606 (614)	91 (21)	110	0.454
1ba	376, 523	21, 7	592	2.09	647 (657)	55 (34)	124	0.454
1bb	378, 525	19, 6	592	2.09	653 (636)	47 (21)	128	0.463
1bc	382, 537	18, 6	608	2.04	682 (676)	28 (24)	145	0.491
1bd	372, 514	15, 4	579	2.14	641 (670)	48 (4)	127	0.478

ε - molar absorption coefficient, λ_{Aedge} - absorption edge wavelength - inflection point between high absorption and high transmittance;[14]

[a] in parentheses are reported λ_{Fmax} (nm) in the solid state.

[b] in parentheses are reported ϕ_F (%) in the solid state corrected for self-absorption using true spectra from a small amount of the same sample.

Table S6. Photo-physical properties of **2** in solution (CH_2Cl_2) and solid state.

Compound	λ_{Amax} (nm)	ε (10^3 M^{-1} cm^{-1})	λ_{Aedge} (nm)	$E_{optical\ gap}$ (eV)	λ_{Fmax} (nm)[a]	Φ_f (%)[b]	Stokes shift (nm)	Stokes shift (eV)
2a	386, 423[d]	17, 8	456	2.72	497 (505)	34 (12)	74	0.436
2b	403, 429, 485[d]	11, 11, 5	525	2.36	690 (676)	2 or 8[c] (8)	169[e]	0.661

ε- molar absorption coefficient; λ_{Aedge} - absorption edge wavelength;

[a] in solution, in parentheses λ_{Fmax} (nm) in solid state;

[b] in solution, in parentheses are reported Φ_f (%) in solid state corrected for self-absorption using true spectra from a small amount of the same sample;

[c] quantum yield collected for N_2 saturated DCM solution;

[d] shoulder of a previous absorption band used for calculation of Stokes shift;

[e] shoulder of the main emission band at 654 nm was used for the calculation of Stokes shift.

[14] W.-M. Yip, Q. Yu, A. Tantipanjapotn, W.-C. Chan, J.-R. Deng, B. C. Ko, Wong, M.-K. *Org. Biomol. Chem.*, **2021**, *19*, 8507–8515.

Table S7. Reported quantum yields of fluorescence Φ_f collected for solid samples before and after correction for self-absorption using "true" spectra collected from a small amount of the same sample.

Compound	Φ_f	Φ_f (corrected for self-absorption)
1aa	0.53	0.62
1ab	0.27	0.34
1ac	0.58	0.66
1ad	0.18	0.21
1ba	0.15	0.34
1bb	0.18	0.21
1bc	0.16	0.24
1bd	0.04	0.04
2a	0.11	0.12
2b	0.05	0.08

The solvatochromic effect was assessed for **1bd** as a representative example in additional four solvents such as toluene, THF, MeCN, and DMSO. Shifts of emission maxima is rather small, and they are bathochromically shifted as the polarity of a solvent is increasing (Table S8 and Figure S4).).

Table S8. Photo-physical properties of **1bc** in different solvents.

Solvent	λ_{Amax} (nm)	λ_{Fmax} (nm)
toluene	364, 492	630
CH_2Cl_2 (DCM)	372, 514	641
THF	366, 487	650
MeCN (ACN)	363, 486	651
DMSO	364, 483	660

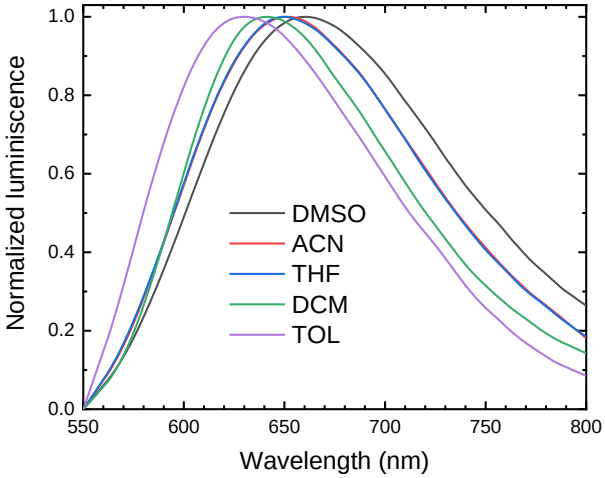


Figure S4. Solvatochromic effect on emission spectra of compound **1bd.**

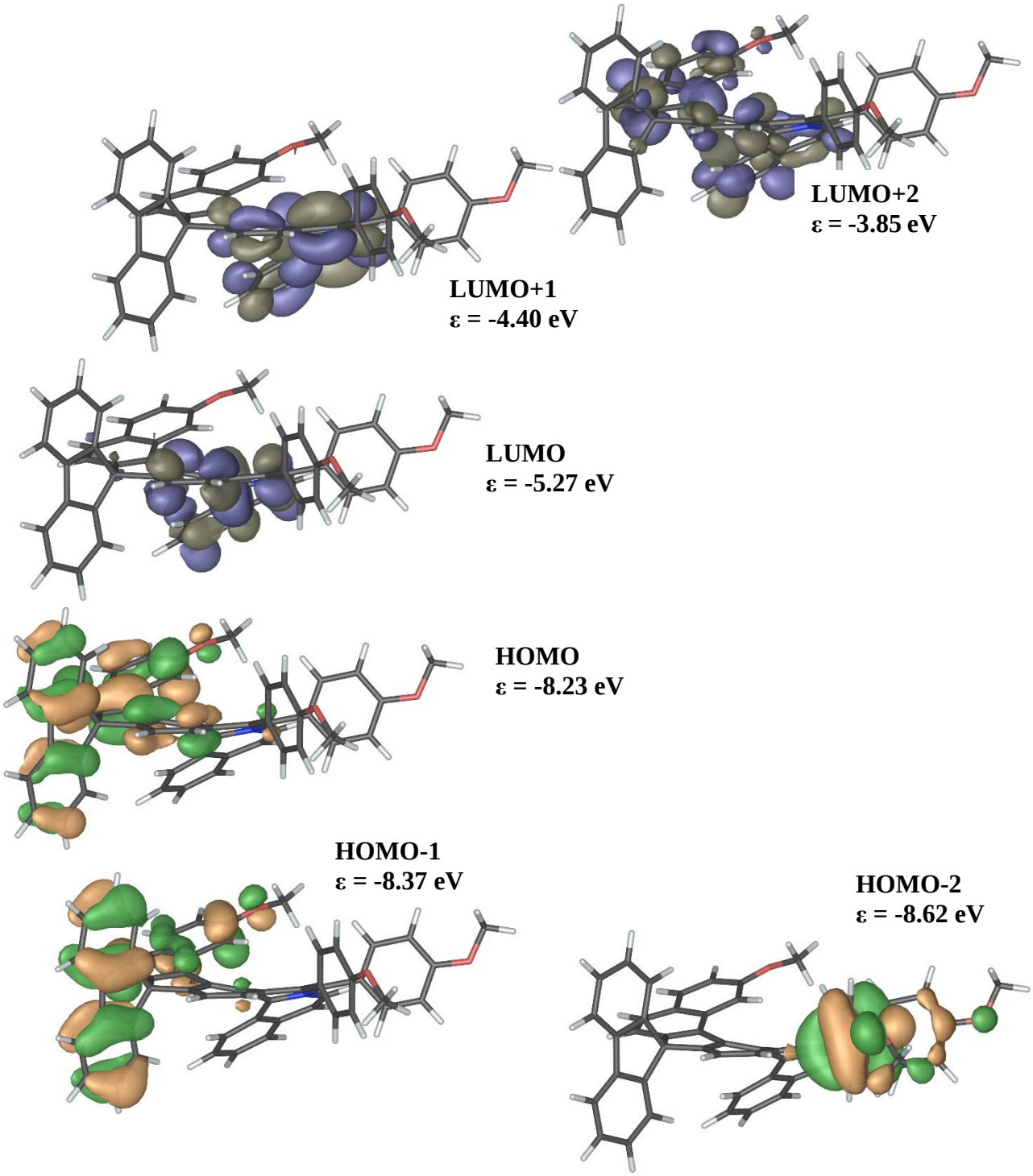
Compounds **1ba**, **1bb**, and **1bc** were select as representatives for DFT (Density Functional Theory computations) computation of HOMO and LUMO. The respective computations were carried out by using Gaussian16, Revision C.01.[15] Computations used the M06 functional,[16] an ultrafine DFT integration grid and the Def2TZVP basis set for all atoms.

Examination of their transition energies revealed the lowest energy band corresponds predomonatly to HOMO→LUMO transitions (66-95%, oscillator strength $f \approx 0.034$-0.042). Where HOMOs of **1ba**, **1bb**, and **1bc** are largely distributed on the spirobifluorene moiety, whereas the LUMOs are confined to the quinolizinium fragment.

[15] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ort, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman,bD. J. Fox, Gaussian, Inc., Wallingford CT, 2019.

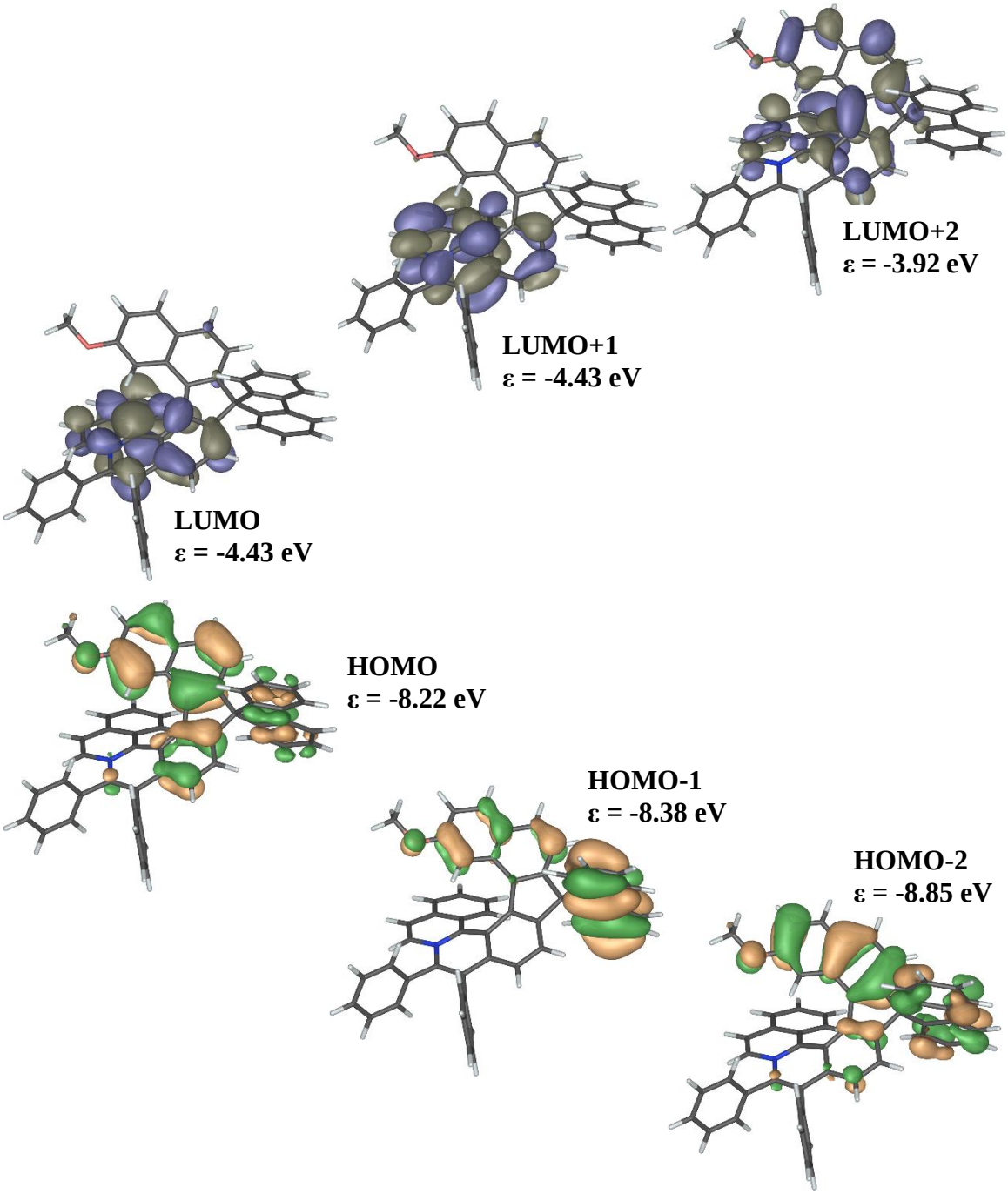
[16] Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.*, **2008**, *120*, 215.

Figure S5. Frontier orbital contour diagrams for **1ba** and table for the three electronic excitations of lowest computed energy.



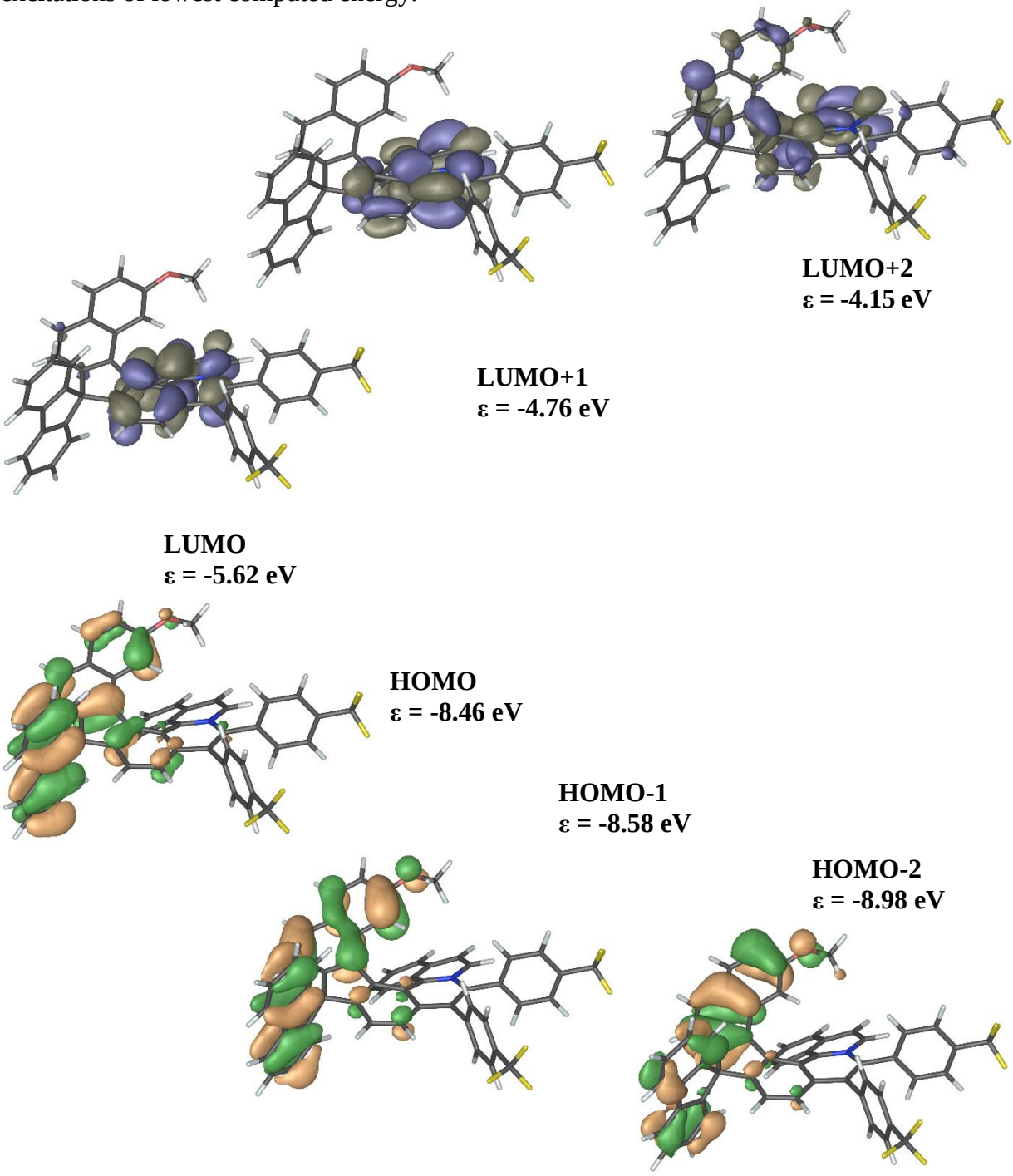
	Energy (nm)	Oscillator strength	Major contributions
1	581.27	0.0417	HOMO →LUMO (86%) HOMO-1→LUMO (13%)
2	507.49	0.0013	HOMO-1→LUMO (84%) HOMO →LUMO (12%)
3	465.69	0.0097	HOMO-2→LUMO (99%)

Figure S6. Frontier orbital contour diagrams for **1bb** and table for the three electronic excitations of lowest computed energy.



	Energy [nm]	Oscill. Strength	Major contributions
1	590.94	0.0396	HOMO →LUMO (95%)
2	503.44	0.0015	HOMO-1→LUMO (93%)
3	438.14	0.0145	HOMO-2→LUMO (94%)

Figure S7. Frontier orbital contour diagrams for **1bc** and table for the three electronic excitations of lowest computed energy.



	Energy (nm)	Oscillator strength	Major contributions
1	608.18	0.0340	HOMO →LUMO (66%) HOMO-1→LUMO (33%)
2	541.85	0.0016	HOMO-1→LUMO (65%) HOMO →LUMO (32%)
3	470.74	0.0136	HOMO-2→LUMO (96%)

5 Optimized geometries and energies

1ba (lf_t-792)

C	-4.660420	-0.783875	-1.047185
C	-4.122821	-0.602155	0.214111
C	-4.985359	-0.629587	1.313740
C	-6.334715	-0.836026	1.149188
C	-6.867637	-1.020294	-0.130883
C	-6.022575	-0.995441	-1.232152
C	-2.658635	-0.356097	0.387835
N	-1.832985	-1.470729	0.709786
C	-0.498067	-1.347582	0.861807
C	0.139639	-0.147936	0.370222
C	-0.663574	1.015354	0.336874
C	-2.107173	0.867570	0.310687
C	-0.064468	2.282654	0.276489
C	1.301804	2.395471	0.221939
C	2.077904	1.250316	0.068632
C	1.518975	-0.014325	0.027971
C	3.587239	1.191291	-0.086130
C	3.788994	-0.293861	-0.326851
C	2.589526	-0.964421	-0.389928
C	5.018588	-0.936537	-0.547772
C	5.006708	-2.255011	-0.886529
C	3.786849	-2.940579	-1.117737
C	2.548369	-2.290867	-0.924742
C	1.359891	-2.941570	-1.364518
C	1.413299	-4.193879	-1.904498
C	2.647467	-4.889984	-1.994732
C	3.792016	-4.271973	-1.622542
C	4.340610	1.781556	1.109194
C	5.172345	2.821851	0.7007240
C	5.037610	2.991010	-0.758001
C	4.127397	2.051418	-1.233105
C	5.648680	3.881798	-1.628141
C	5.335791	3.816000	-2.97816800
C	4.428157	2.874554	-3.451057
C	3.817040	1.983122	-2.578133
C	4.279591	1.411499	2.4392700
C	5.060740	2.092685	3.364736
C	5.890675	3.130602	2.957418
C	5.953231	3.503207	1.622340
C	-2.451165	-2.704733	0.925890
C	-1.792369	-3.753391	1.415532
C	-0.440352	-3.604977	1.850785

C	0.195422	-2.375353	1.612587
C	0.221218	-4.623716	2.556152
C	1.465010	-4.396734	3.077450
C	2.071716	-3.137899	2.928857
C	1.456037	-2.151471	2.212289
O	0.359524	-4.869689	-2.392675
C	-2.962159	2.082339	0.109452
C	-3.558714	2.718374	1.181907
C	-4.335414	3.860119	1.009881
C	-4.521226	4.377137	-0.264171
C	-3.917697	3.746201	-1.354842
C	-3.148926	2.620436	-1.165498
O	-5.249301	5.464381	-0.548440
C	-5.896888	6.175876	0.476841
O	-8.188345	-1.210242	-0.188408
C	-8.834580	-1.379899	-1.427467
C	-0.845034	-4.206365	-2.664636
H	0.429963	-2.413397	-1.328235
H	5.931533	-2.781800	-1.043223
H	5.9413280	-0.394205	-0.452616
H	1.767467	3.364394	0.237665
H	-0.679541	3.159475	0.290178
H	-3.483272	-2.747036	0.666596
H	-2.308967	-4.686046	1.539957
H	-0.272038	-5.567525	2.701115
H	1.968553	-5.170309	3.628132
H	3.024439	-2.946972	3.387091
H	1.924903	-1.194993	2.137302
H	3.642000	0.608516	2.764909
H	5.024448	1.814948	4.402831
H	6.490490	3.648386	3.684142
H	6.599269	4.305993	1.315098
H	6.353828	4.611071	-1.271401
H	5.801502	4.497844	-3.666836
H	4.200709	2.834485	-4.501129
H	3.120681	1.252250	-2.950915
H	-3.423991	2.333125	2.177642
H	-4.780715	4.321918	1.8692150
H	-4.066271	4.159115	-2.335249
H	-2.687313	2.153014	-2.018090
H	-4.595284	-0.484073	2.306245
H	-7.001595	-0.851634	1.990906
H	-6.400170	-1.125997	-2.227176
H	-4.021039	-0.755571	-1.912332

H	-1.475899	-4.923734	-3.167624
H	-0.679315	-3.352360	-3.313671
H	-1.334270	-3.882956	-1.752114
H	-6.408297	6.993620	-0.006658
H	-5.181619	6.570979	1.190330
H	-6.621051	5.551137	0.988776
H	-9.881955	-1.501652	-1.200268
H	-8.471800	-2.265338	-1.938116
H	-8.701295	-0.508007	-2.058375
H	2.644565	-5.884222	-2.400456
H	4.734476	-4.778345	-1.734271

1bb (lf_t_758)

O	1.306697	4.394371	2.048786
N	2.688558	0.689327	-0.603410
C	-0.177122	2.834679	1.215927
C	0.037860	4.091033	1.715220
C	-1.039561	4.995105	1.854763
C	-2.297363	4.581404	1.532090
C	-2.555319	3.280523	1.042191
C	-3.891611	2.835598	0.837306
C	-4.157168	1.546446	0.505663
C	-3.072628	0.673867	0.277975
C	-1.767777	1.094966	0.322990
C	-1.463921	2.403880	0.830512
C	-3.172870	-0.822795	0.048680
C	-1.705764	-1.186531	-0.091930
C	-1.174328	-2.466577	-0.208999
C	0.188319	-2.633136	-0.229595
C	1.030911	-1.514155	-0.288675
C	2.4731690	-1.651190	-0.190071
C	3.254993	-0.560151	-0.227694
C	3.5495290	1.770559	-0.802143
C	3.136474	2.914674	-1.344193
C	1.807279	3.022533	-1.853419
C	1.395150	4.133420	-2.608891
C	0.156979	4.143957	-3.188676
C	-0.697241	3.035906	-3.048913
C	-0.324171	1.965378	-2.288059
C	0.929187	1.949070	-1.632892
C	1.367384	0.825447	-0.833176
C	0.480390	-0.214612	-0.363609
C	-0.904381	-0.058213	-0.063388
C	-3.885086	-1.547366	1.195023

C	-3.575702	-1.536446	2.541979
C	-4.362296	-2.278520	3.4141840
C	-5.440751	-3.016424	2.938586
C	-5.751882	-3.024580	1.586552
C	-4.965547	-2.283128	0.717088
C	-5.053028	-2.098691	-0.743394
C	-5.950543	-2.611210	-1.668156
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C	-4.776329	-1.423409	-3.409622
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C	-4.023135	-1.253317	-1.150100
C	3.061167	-3.010720	0.052590
C	3.203056	-3.500425	1.345306
C	3.724017	-4.767458	1.560705
C	4.100379	-5.557474	0.484662
C	3.952932	-5.076728	-0.807769
C	3.434338	-3.808393	-1.022601
C	4.724758	-0.598422	0.05773000
C	5.636610	-0.892096	-0.949412
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C	7.448084	-0.684238	0.615607
C	6.542010	-0.390336	1.624083
C	5.184250	-0.3485880	1.346249
C	1.596586	5.583602	2.7431590
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H	-0.885663	5.986930	2.231754
H	-3.125106	5.254464	1.670476
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H	-5.166923	1.189131	0.420916
H	-1.8252910	-3.322174	-0.216884
H	0.612361	-3.616667	-0.206897
H	4.555208	1.617412	-0.486975
H	3.831963	3.724873	-1.451711
H	2.072909	4.956483	-2.744454
H	-0.155560	4.986971	-3.7777650
H	-1.647398	3.028056	-3.550208
H	-0.977955	1.123411	-2.218519
H	-2.745966	-0.962602	2.916610
H	-4.137860	-2.280303	4.465665
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H	-6.749235	-3.263083	-1.362567
H	-6.491801	-2.655723	-3.733519
H	-4.676891	-1.165222	-4.448636

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H	2.907913	-2.8953020	2.184439
H	3.833646	-5.135364	2.564929
H	4.503188	-6.540058	0.651876
H	4.239933	-5.685074	-1.646492
H	3.318444	-3.443169	-2.028268
H	5.289601	-1.091687	-1.947760
H	7.692349	-1.170234	-1.453723
H	8.500519	-0.720581	0.831551
H	6.888712	-0.200323	2.623668
H	4.484548	-0.125939	2.132974
H	2.651774	5.546734	2.967679
H	1.035265	5.643917	3.668982
H	1.393373	6.456676	2.132625

1bc **(l**f44)

C	-4.006146	-1.300064	-1.024846
C	-3.526483	-1.006741	0.245882
C	-4.403305	-1.005736	1.323586
C	-5.744780	-1.295212	1.134394
C	-6.213644	-1.590905	-0.136262
C	-5.346608	-1.592514	-1.217713
C	-2.077473	-0.673914	0.437113
N	-1.184641	-1.742287	0.721723
C	0.141694	-1.535398	0.865857
C	0.694779	-0.281954	0.400506
C	-0.180524	0.830105	0.416229
C	-1.610851	0.583425	0.398634
C	0.907910	-2.533182	1.581898
C	0.353475	-3.806192	1.800318
C	-0.995139	-4.028713	1.387462
C	-1.725290	-3.013982	0.928984
C	2.054110	-0.051833	0.038817
C	2.531715	1.247545	0.105094
C	1.688511	2.334673	0.299396
C	0.331454	2.132518	0.375551
C	3.176499	-0.918900	-0.417906
C	4.331145	-0.172920	-0.353782
C	4.038934	1.289418	-0.072084
C	3.213129	-2.233195	-0.982894
C	4.488335	-2.796255	-1.205909
C	5.664198	-2.037522	-0.975063
C	5.596219	-0.728858	-0.605958

C	2.063749	-2.950889	-1.421751
C	2.191333	-4.185974	-1.989236
C	3.466756	-4.797846	-2.109856
C	4.573536	-4.113585	-1.739645
C	4.503899	2.212014	-1.203553
C	5.355475	3.198694	-0.715422
C	5.523014	3.001946	0.736445
C	4.769832	1.897532	1.128493
C	2.162658	-2.245134	2.167217
C	2.849918	-3.207974	2.849423
C	2.325064	-4.505655	2.976124
C	1.088735	-4.797943	2.469462
C	6.270232	3.710606	1.665322
C	6.253536	3.300147	2.990632
C	5.502210	2.197982	3.381399
C	4.754597	1.489536	2.448737
C	4.179820	2.156043	-2.545896
C	4.716977	3.108410	-3.403006
C	5.565446	4.097158	-2.917046
C	5.892505	4.150308	-1.5697930
O	1.177399	-4.919215	-2.477604
C	-0.069599	-4.330679	-2.728525
C	-2.549672	1.744786	0.245106
C	-3.068687	2.372869	1.369708
C	-3.920291	3.458203	1.237635
C	-4.255009	3.921581	-0.024621
C	-3.736248	3.304875	-1.152777
C	-2.88310	2.222372	-1.016071
C	-5.14617	5.128860	-0.173074
F	-5.983617	5.246891	0.842845
C	-7.664403	-1.955399	-0.336267
F	-8.443380	-1.359251	0.547839
F	-4.437444	6.247681	-0.226428
F	-5.865102	5.0714910	-1.281111
F	-8.089577	-1.619713	-1.540963
F	-7.850006	-3.261201	-0.205121
H	1.101783	-2.485483	-1.364131
H	3.522883	-5.781380	-2.537117
H	5.545411	-4.554306	-1.874721
H	6.618801	-2.499397	-1.155903
H	6.483210	-0.130050	-0.510335
H	2.091015	3.331078	0.329947
H	-0.335409	2.969968	0.416730
H	-2.758529	-3.117350	0.692296

H	-1.452631	-4.992467	1.506075
H	0.657646	-5.773739	2.599525
H	2.885123	-5.258906	3.499647
H	3.796453	-2.969141	3.297794
H	2.570471	-1.260063	2.108586
H	4.178481	0.636479	2.761637
H	5.501274	1.891542	4.411987
H	6.828199	3.838479	3.722658
H	6.855883	4.562986	1.371071
H	6.551973	4.916495	-1.203335
H	5.974269	4.825984	-3.593530
H	4.478355	3.079092	-4.450910
H	3.529824	1.388778	-2.929285
H	-2.810702	2.020193	2.352461
H	-4.321783	3.932988	2.113158
H	-3.995905	3.661067	-2.132119
H	-2.480437	1.752202	-1.895308
H	-4.046134	-0.773603	2.310742
H	-6.418026	-1.282438	1.970824
H	-5.711320	-1.808785	-2.204280
H	-3.339592	-1.292101	-1.868942
H	-0.657515	-5.078408	-3.239077
H	0.035078	-3.456708	-3.363575
H	-0.570526	-4.055596	-1.806161

6 X-ray diffraction data

The diffraction experiments for **1bb** (**lf_t_758**), **2a** (**lf_38**), **2b** (**lf_35**), **4a** (**lf_21**), and **4b** (**lf_32**) were performed on Bruker D8 VENTURE Kappa Duo PHOTONIII with IμS micro-focus sealed tube either CuKα (λ = 1.54178 Å) or MoKα (λ= 0.71073) radiation at a low temperature. The structures were solved by direct methods (XT[17]) and refined by full matrix least squares based on F^2 (SHELXL2018[18]). The hydrogen atoms on carbon were fixed into idealized positions (riding model) and assigned temperature factors either $H_{iso}(H) = 1.2\ U_{eq}$(pivot atom) or $H_{iso}(H) = 1.5\ U_{eq}$ (pivot atom) for methyl moiety. The structure of **2a** (**lf_38**) requiare more detailed description. The unit cell contains two symmetrically independent molecules of **2a** (**lf_38**), however crystal is contaminated also by another derivative where the hydrogen atom on C6 is substituted by Br. The amount of this compound is indeed small 2% and 5% in each position. Therefore, only position of Br atoms could be discerned on final difference electron density Fourier map whereas positions of carbon atoms of the contaminant are overlapping with carbons of the major molecule. Another complication for this crystal was disordered solvent, its contribution was removed from diffraction patter using SQUEEZE procedure of PLATON[19] software before final refinement, to improve the precision of main molecules.

X-ray crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC), for the deposition numbers see **Table 1** and can be obtained free of charge from the Centre via its website (https://www.ccdc.cam.ac.uk/structures/).

The solid-state structure of the final products **1bb**, **2a**, and **2b** are molecular, incorporating no significant hydrogen bonds nor any significant π-π stacking.

The sums of its five inner rim dihedral angles (**1bb**, ∠C24–C25–C26–C27, ∠C25–C26–C27–C28, ∠C26–C27–C28–C9, ∠C27–C28–C9–C10, and ∠C28–C9–C10–C1; **2a**, ∠C1A–C10A–C9A–C17A, ∠C10A–C9A–C17A–C16A, ∠C9A–C17A–C16A–C18A, ∠C17A–C16A–C18A–C26A, ∠C16A–C18A–C26A–C25A; **2b**, ∠C1A–C10A–C9A–C17A, ∠C10A–C9A–C17A–C16A, ∠C9A–C17A–C16A–C18A, ∠C17A–C16A–C18A–C26A, ∠C16A–C18A–C26A–C25A) representing helical pitches are is 85.5°, 70.3°, and 87.9°. Regarding **1bb** ist helical pitch is 25° smaller then the one in the pristine [7]helicene (110.5°).[20]

[17] SHELXT: Sheldrick, G. M. *Acta Cryst.* **2015**, *A71*, 3-8.
[18] SHELXL: Sheldrick, G. M. *Acta Cryst.* **2015**, *C71*, 3-8.
[19] Speck, A. L. *Acta Cryst.* **2015**, *C71*, 9-18.
[20] Sýkora, J.; Cisarova, I.; Cirkva, V.; Storch, J.; CCDC 206539, *CSD Communication* **2021**, DOI: 10.5517/ccdc.csd.cc27668y

Table S9. Crystal data, data collection, and refinement parameters for **1bb**, **2a**, and **2b**.

Compound	**1bb (lf_t_758)**	**2a (lf_38)**	**2b (lf_35)**
CCDC	2373209	2373210	2373211
Formula	$C_{53}H_{34}NO{\cdot}BF_4{\cdot}CH_2Cl_2$	$C_{40}H_{27.98}BBr_{0.02}N{\cdot}$ $C_{40}H_{27.95}BBr_{0.05}N$	$3(C_{43}H_{29}NO_2Pt){\cdot}C_5H_{12}$
M.w.	872.55	1072.17	2432.43
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	*Pna*2$_1$ (No. 33)	*P*2$_1$/*c* (No. 14)	*P* -1 (No. 2)
a [Å]	15.7990 (5)	25.5585 (7)	12.7645 (6)
b [Å]	10.5487 (3)	9.9428 (3)	18.0822 (10)
c [Å]	24.3174 (7)	24.0807 (7)	22.7774 (13)
α [°]			89.964 (2)
β [°]		91.408 (2)	81.068 (2)
γ [°]			85.594 (2)
Z	4	4	2
V[Å^3]	4052.7 (2)	6117.6 (3)	5177.8 (5)
Temperature	120	120	150
D_x [g cm^{-3}]	1.430	1.164	1.560
Wavelength, Å	1.54178	1.54178	0.71073
Crystal size [mm]	0.42 × 0.30 × 0.23	0.43 × 0.07 × 0.04	0.48 × 0.07 × 0.01
Crystal color, shape	prism, red	bar, yellow	needle, orange
μ [mm^{-1}]	1.96	0.55	4.10
T_{min},T_{max}	0.52, 0.66	0.76, 0.98	0.77, 0.95
Measured reflections	45948	65917	100825
Independent diffractions (R_{int}[a])	8487, (0.040)	10814, (0.159)	23812, (0.090)
Observed diffract. [I>2σ(I)]	8437	6707	16851
No. of parameters	569	781	1323
R[b]	0.035	0.058	0.052
wR(F^2) for all data	0.096	0.141	0.127
GOF[c]	1.02	1.02	1.03
Residual electron density [e/Å^3]	0.54, −0.55	0.25, −0.25	2.36, −1.64
Absolute structure parameter	0.005(5)		

[a] $R_{int} = \Sigma|F_o^2 - F_{o,mean}^2|/\Sigma F_o^2$; [b] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR(F^2) = [\Sigma(w(F_o^2 - F_c^2)^2)/(\Sigma w(F_o^2)^2)]^{½}$;

[c] GOF = $[\Sigma(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{½}$

Table S10. Crystal data, data collection, and refinement parameters for **4a** and **4b**.

Compound	**4a (lf_21)**	**4b (lf_32)**
CCDC	2373212	2373208
Formula	$C_{29}H_{23}NOSi$	$C_{30}H_{25}NO_2Si$
M.w.	429.57	459.60
Crystal system	Monoclinic	Monoclinic
Space group	*P*2$_1$/*c* (No. 14)	*P*2$_1$/*n*(No. 14)
a [Å]	7.7962 (3)	8.0000 (2)
b [Å]	22.1366 (8)	21.9129 (7)
c [Å]	13.7791 (5)	14.2074 (5)
α [°]		
β [°]	105.129 (1)	105.405 (1)
γ [°]		
Z	4	4
V[Å^3]	2295.59 (15)	2401.12 (13)
Temperature [K]	150	150
D_x [g cm^{-3}]	1.243	1.271
Wavelength [Å]	0.71073	0.71073
Crystal size [mm]	0.36 × 0.26 × 0.17	0.31 × 0.28 × 0.16
Crystal color, shape	Prism, orange	Prism, orange-red
μ [mm^{-1}]	0.12	0.13
T_{min},T_{max}	0.92, 0.98	0.89, 0.98
Measured reflections	93008	37428
Independent diffractions (R_{int}[a])	5249, (0.029)	5515, (0.036)
Observed diffract. [I>2σ(I)]	4983	4838
No. of parameters	292	311
R[b]	0.036	0.037
wR(F^2) for all data	0.098	0.095
GOF[c]	1.04	1.05
Residual electron density [e/Å^3]	0.33, −0.29	0.35, -0.26
Absolute structure parameter		

[a] $R_{int} = \Sigma|F_o^2 - F_{o,mean}^2|/\Sigma F_o^2$; [b] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR(F^2) = [\Sigma(w(F_o^2 - F_c^2)^2)/(\Sigma w(F_o^2)^2)]^{½}$;

[c] $GOF = [\Sigma(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{½}$

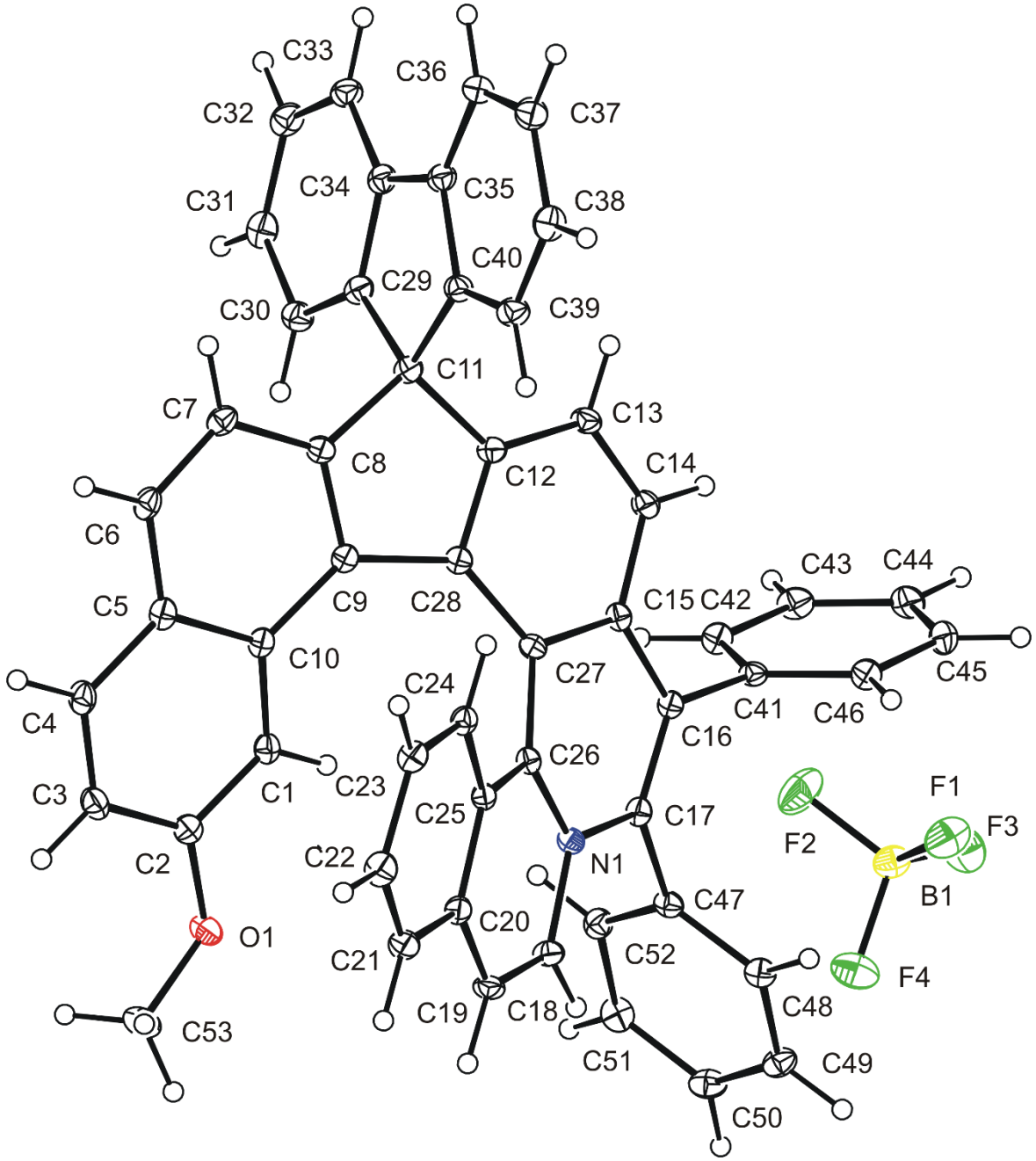


Figure S8. View on molecule of **1bb**. The displacement ellipsoids are drawn at 30% probability level.

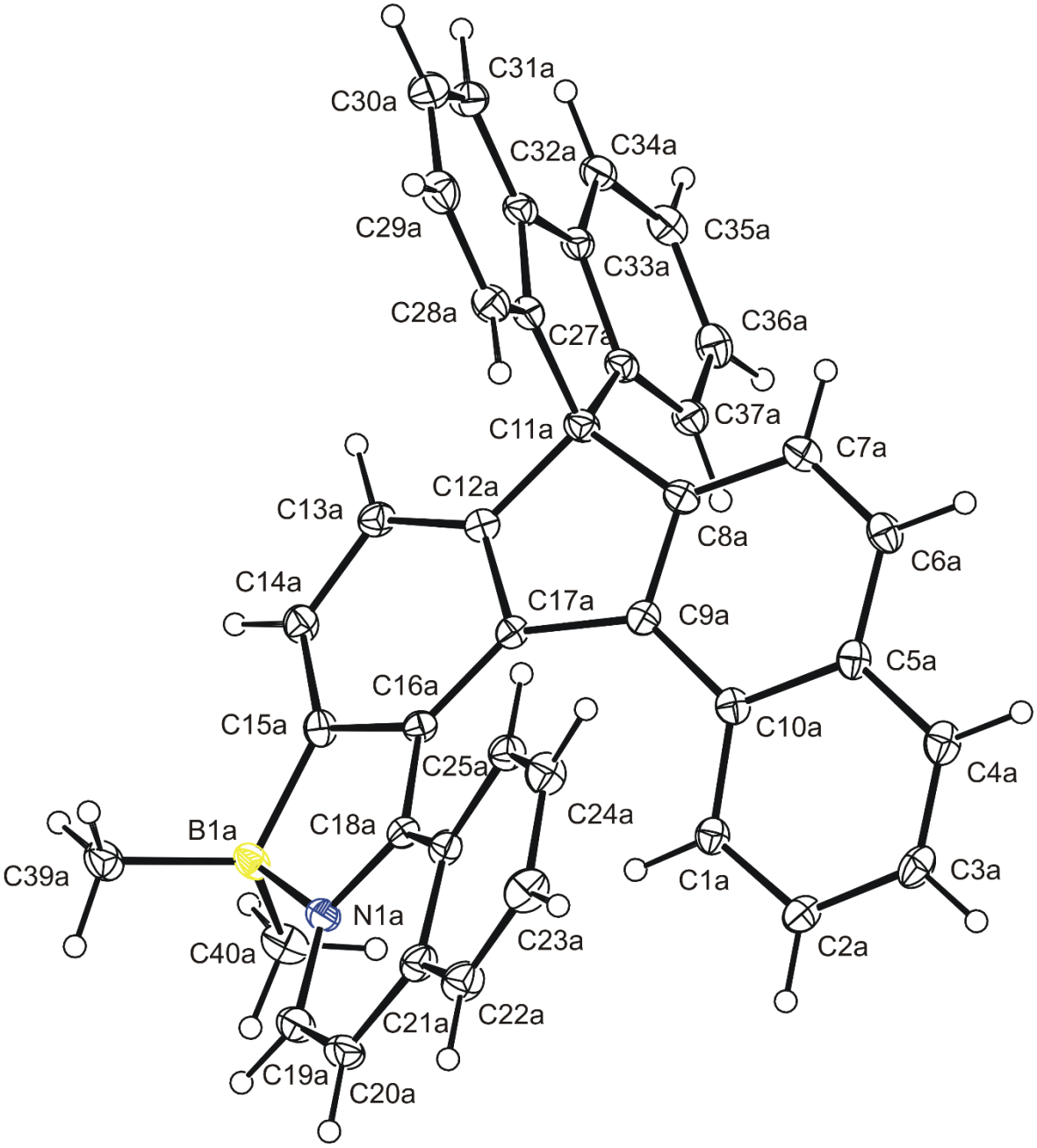


Figure S9. View on molecule of **2a**. The displacement ellipsoids are drawn at 30% probability level.

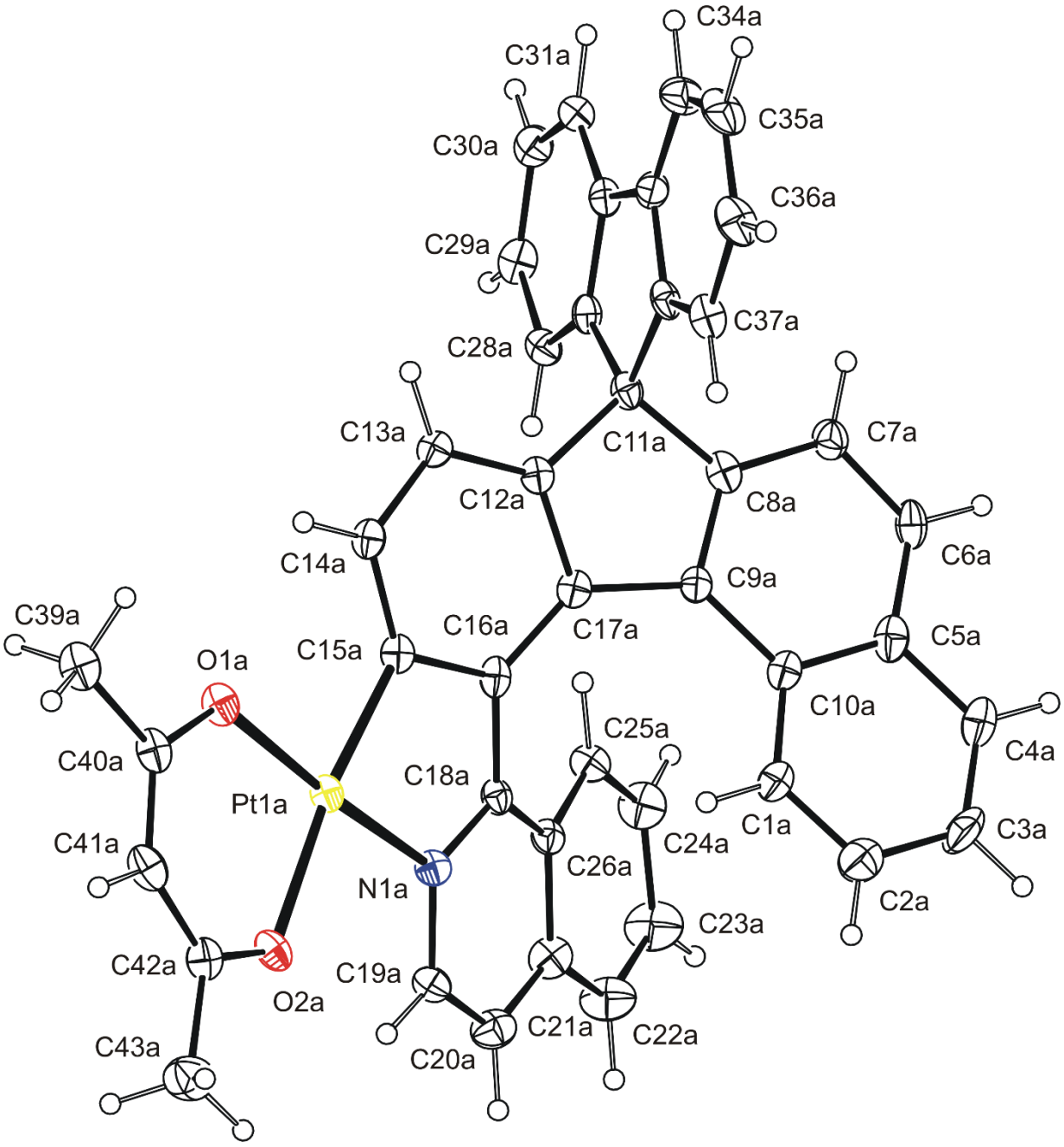


Figure S10. View on molecule of **2b**. The displacement ellipsoids are drawn at 30% probability level.

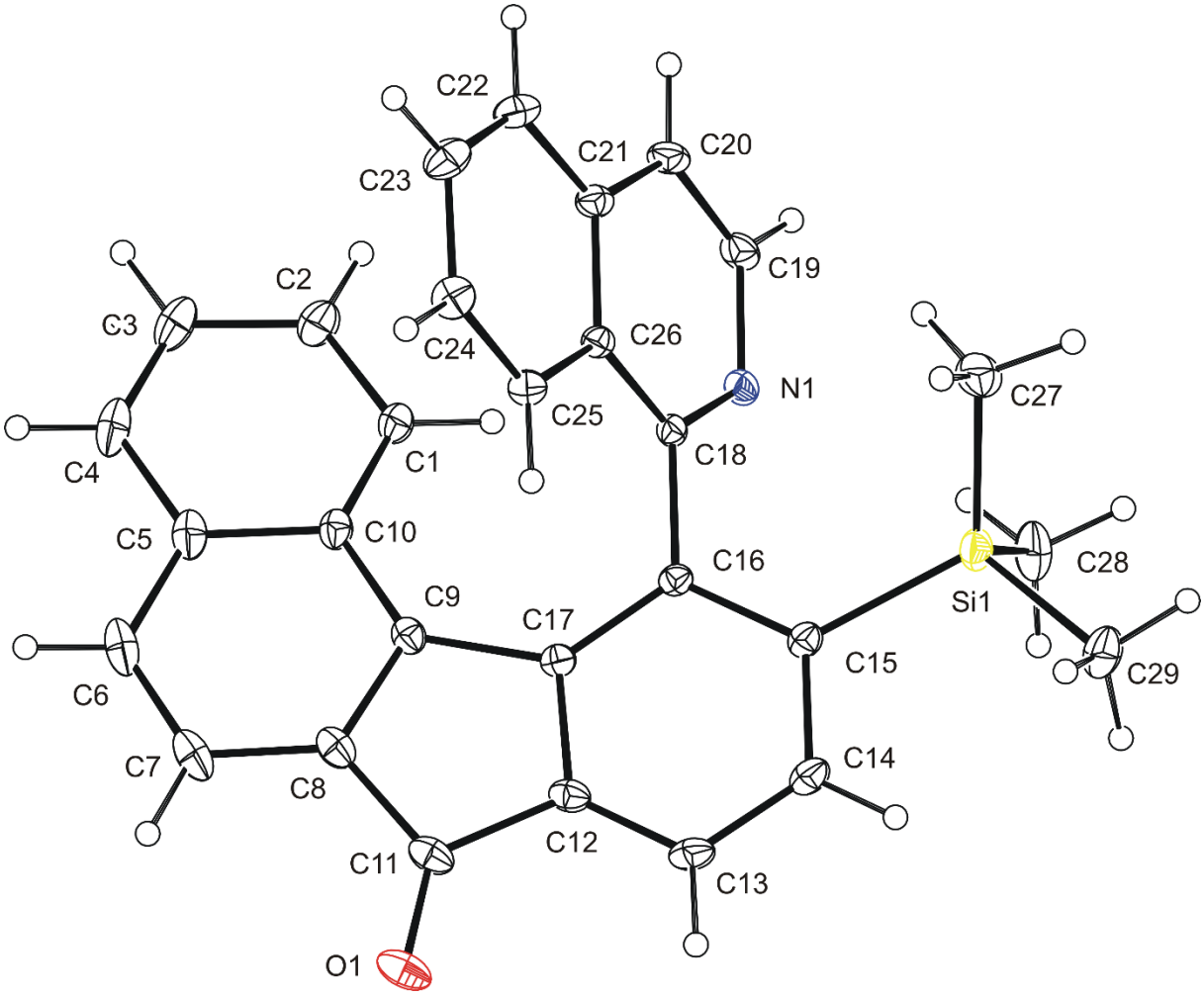


Figure S11. View on molecule of **4a**. The displacement ellipsoids are drawn at 30% probability level.

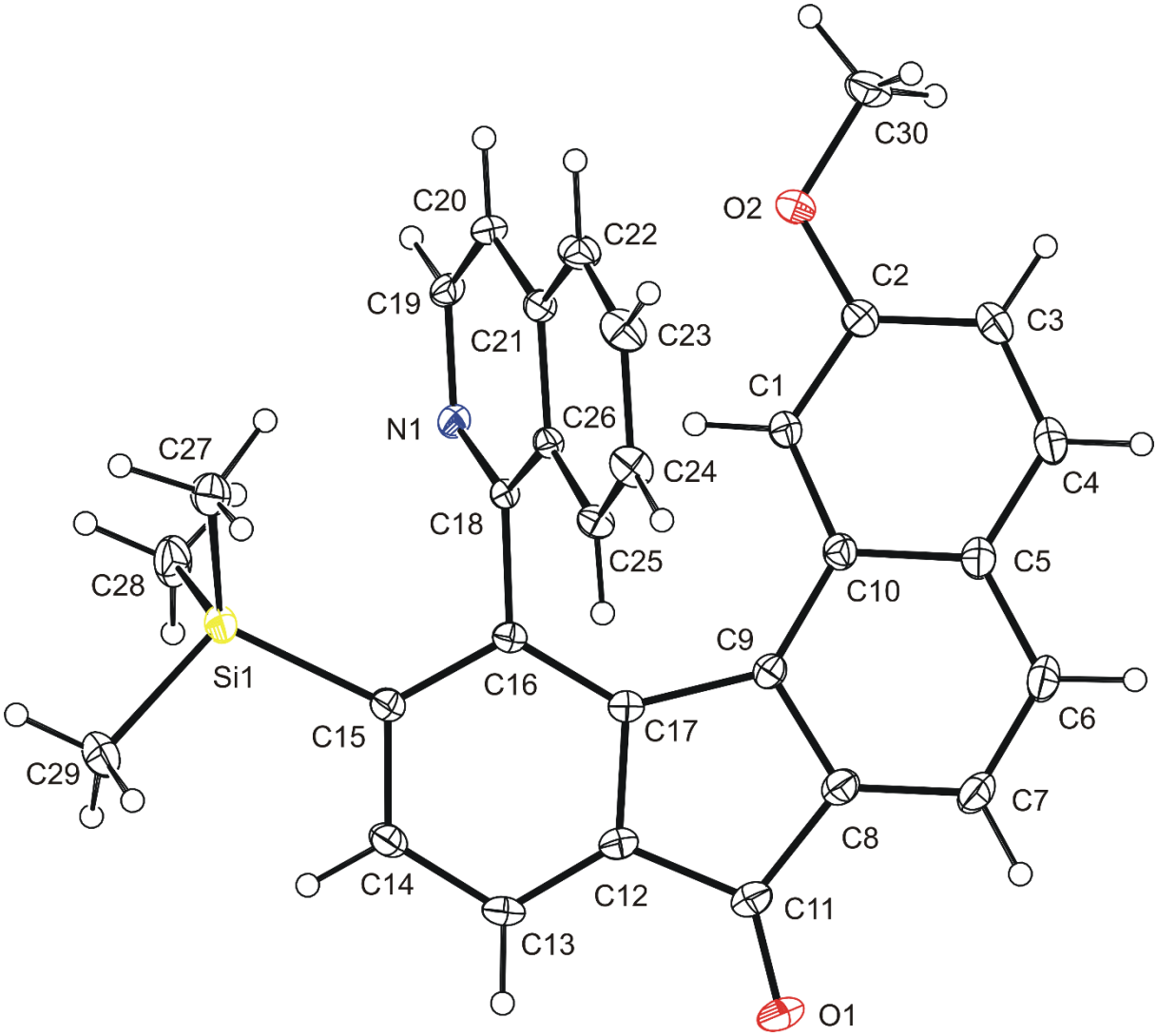
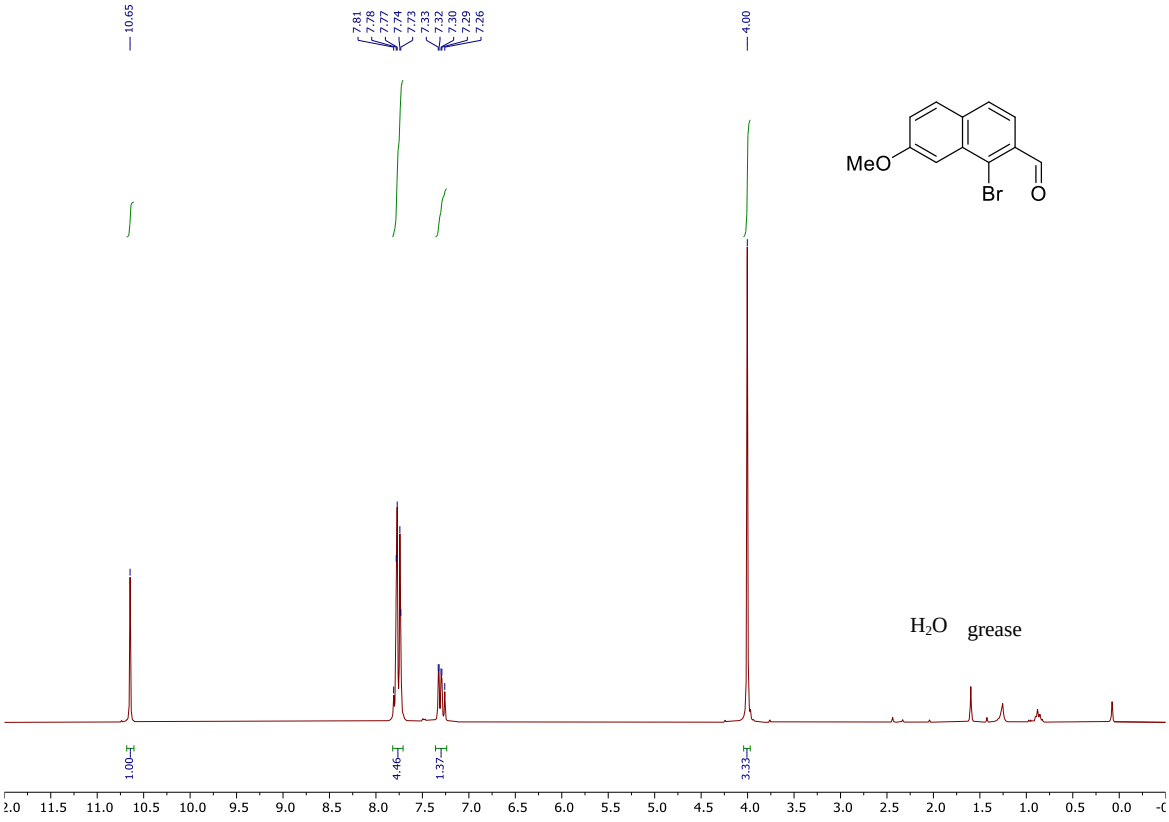


Figure S12. View on molecule of **4b**. The displacement ellipsoids are drawn at 30% probability level.

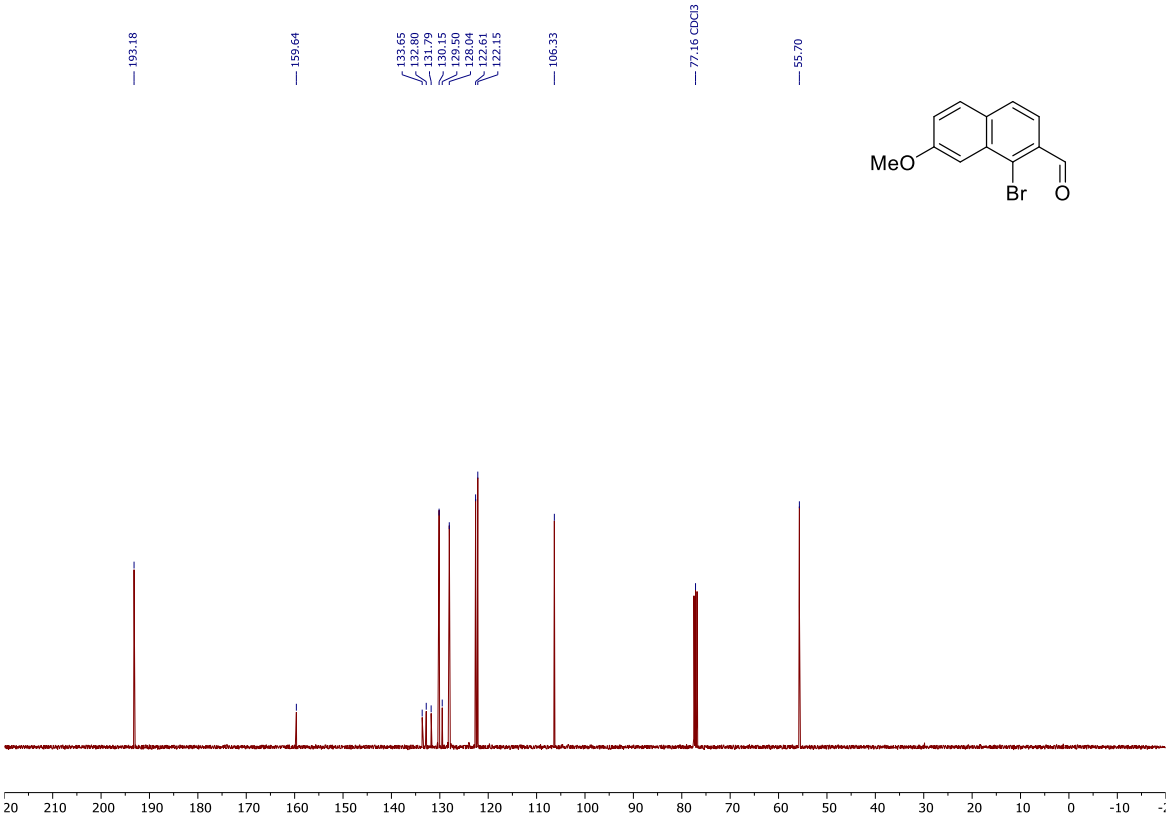
7 Copies of ^{1}H, ^{13}C NMR, ^{19}F NMR, and ^{11}B NMR spectra

1-Bromo-7-methoxy-2-naphthaldehyde (S1b).

^{1}H NMR ($CDCl_3$)

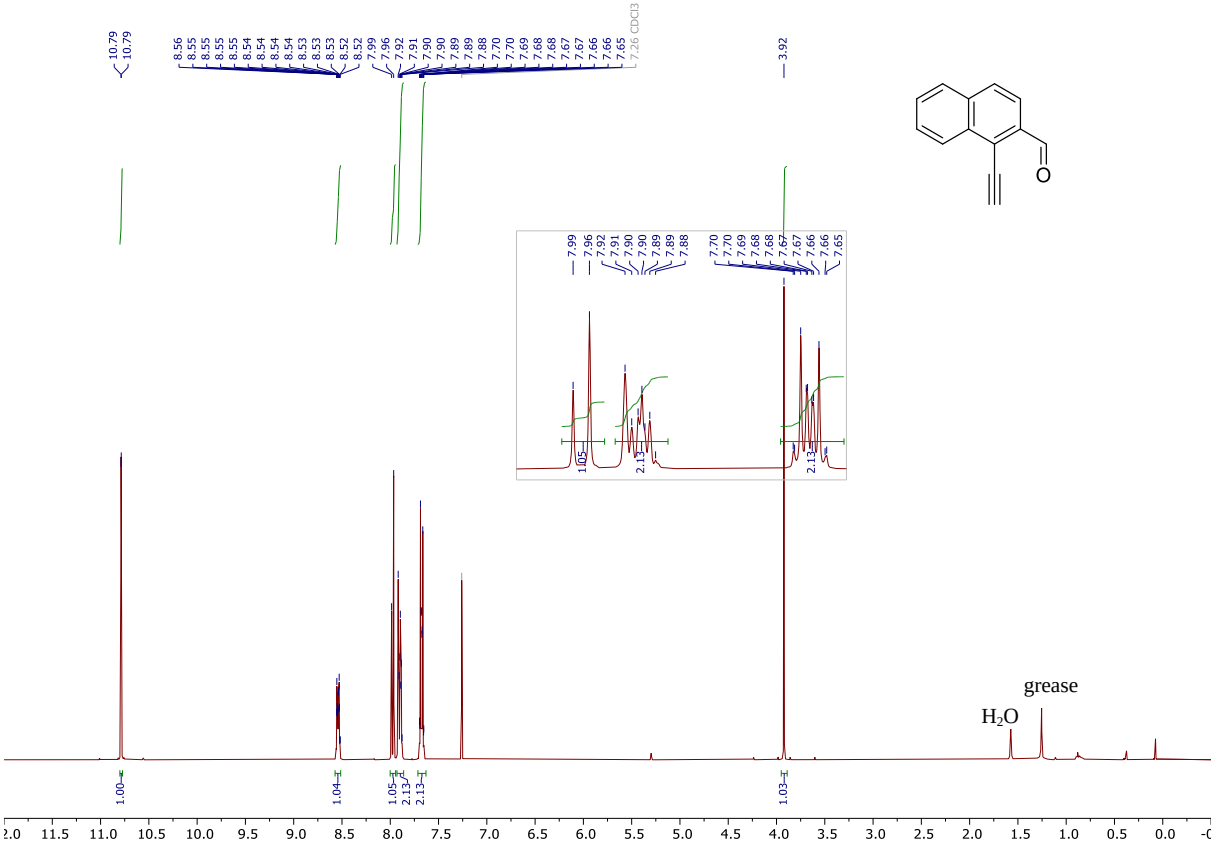


^{13}C NMR ($CDCl_3$)

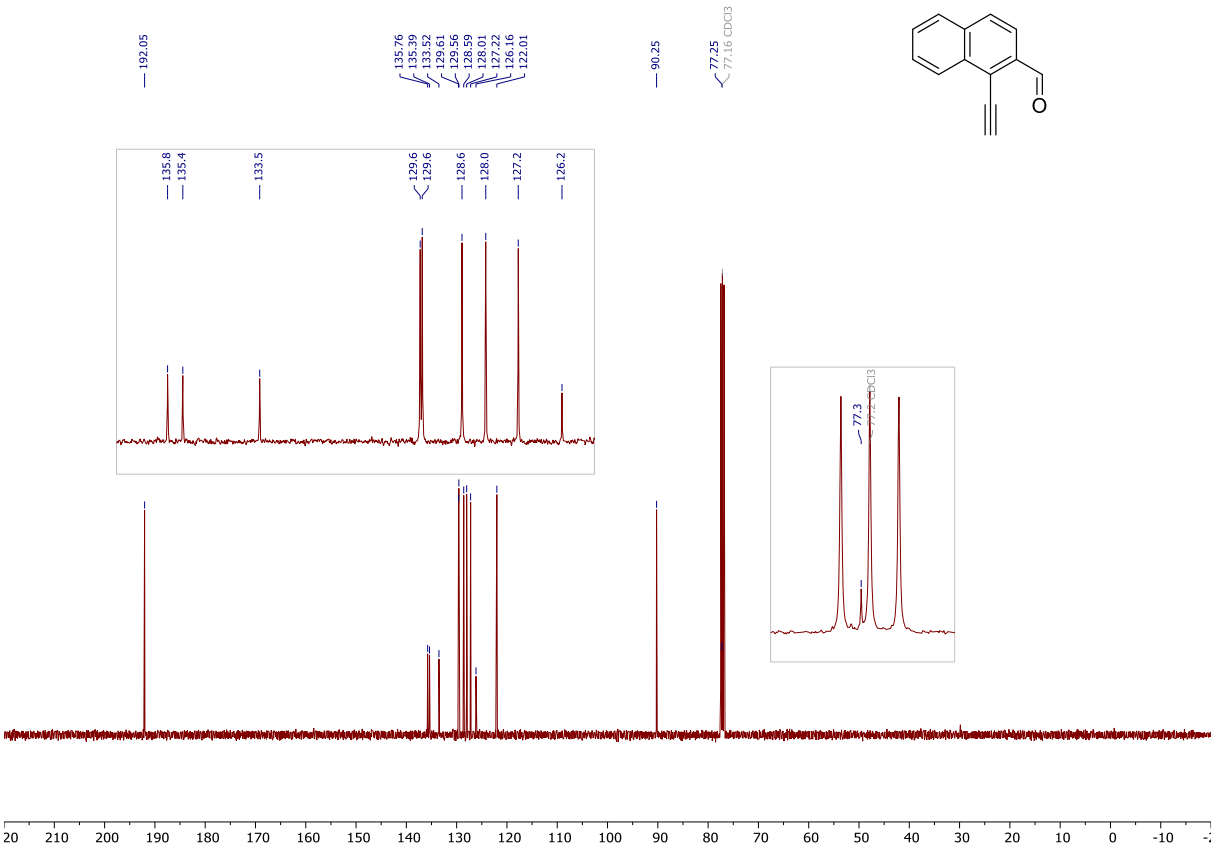


1-Ethynyl-2-naphthaldehyde (S2a).

^{1}H NMR ($CDCl_3$)

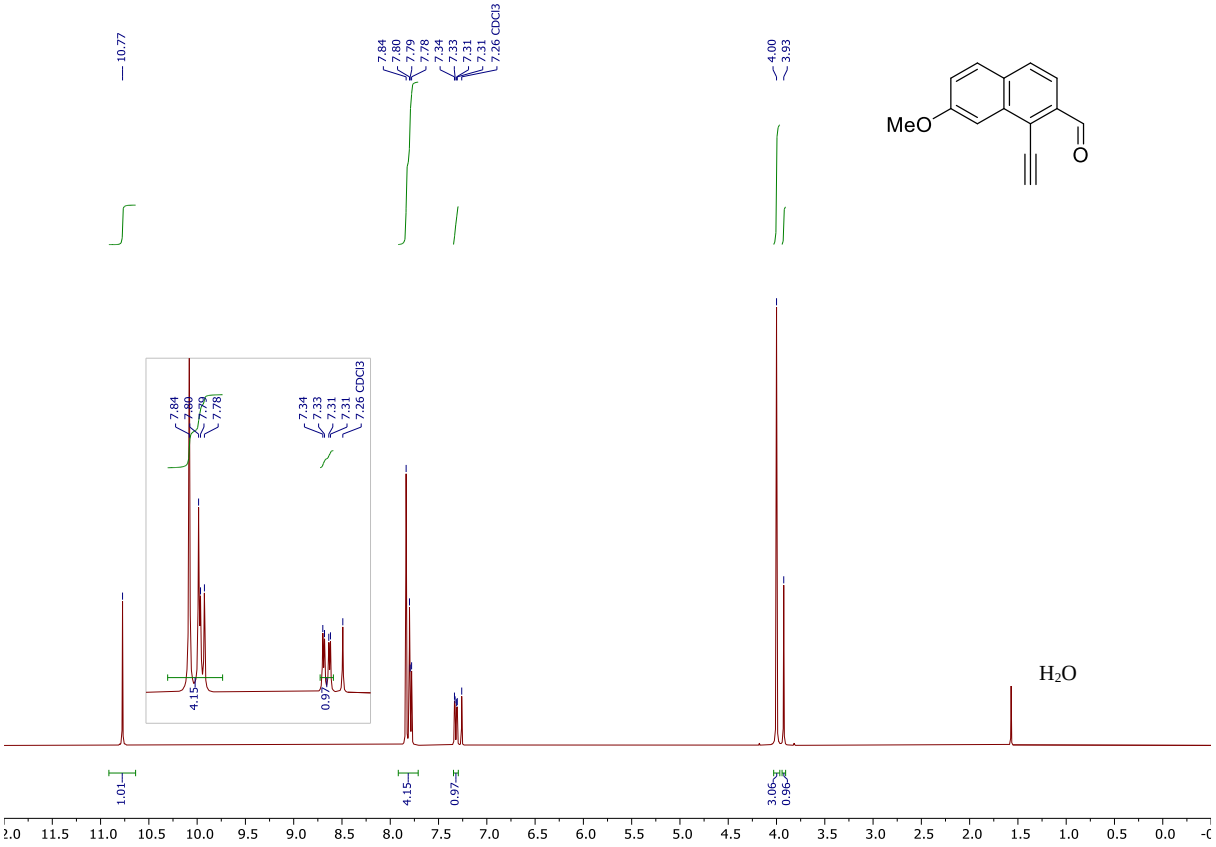


^{13}C NMR ($CDCl_3$)

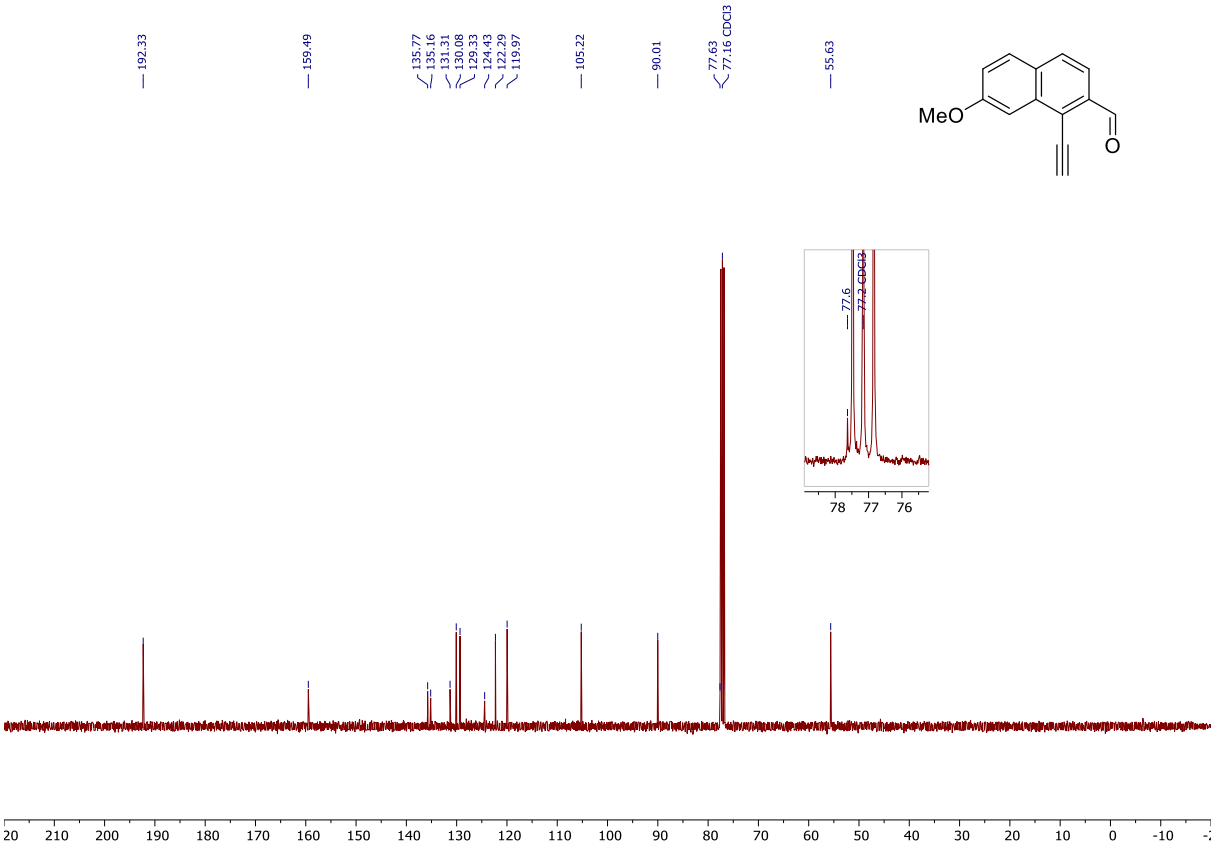


1-Ethynyl-7-methoxy-2-naphthaldehyde (S2b).

^{1}H NMR ($CDCl_3$)

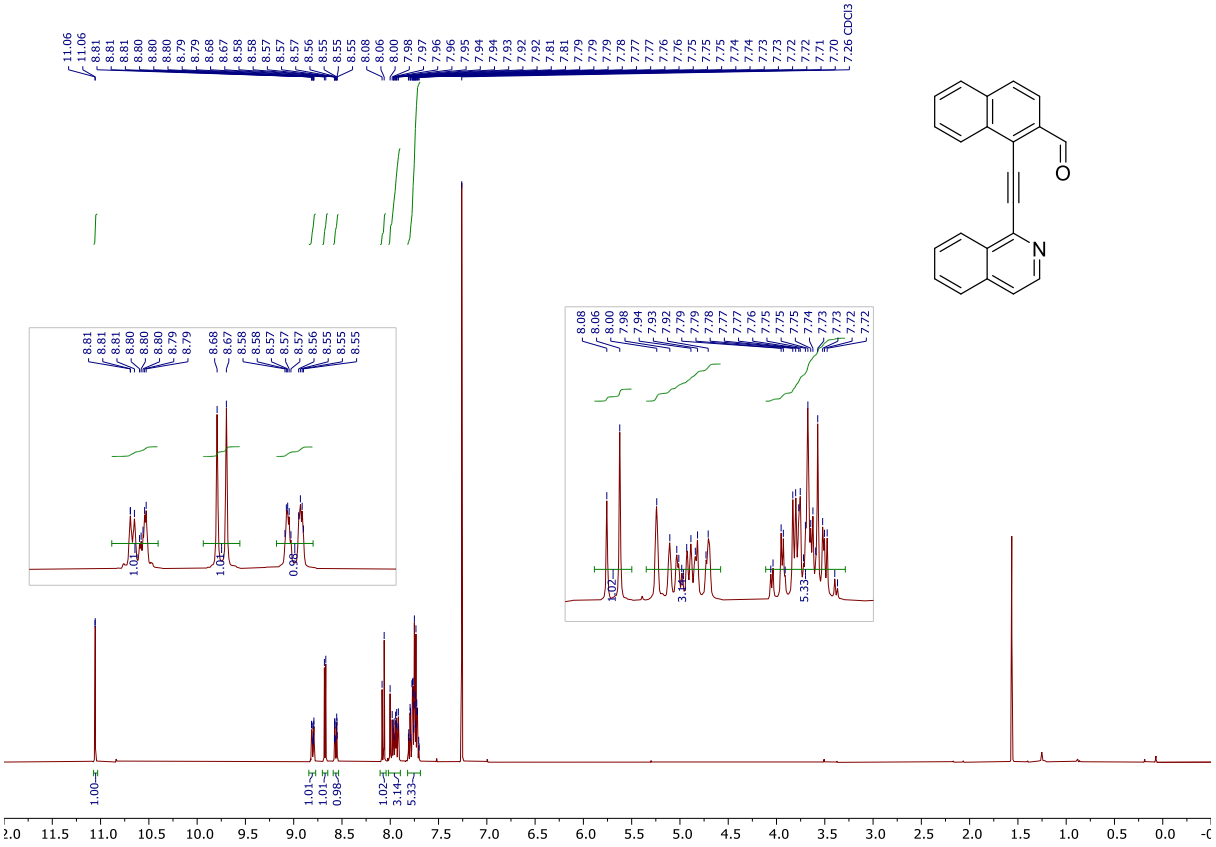


^{13}C NMR ($CDCl_3$)

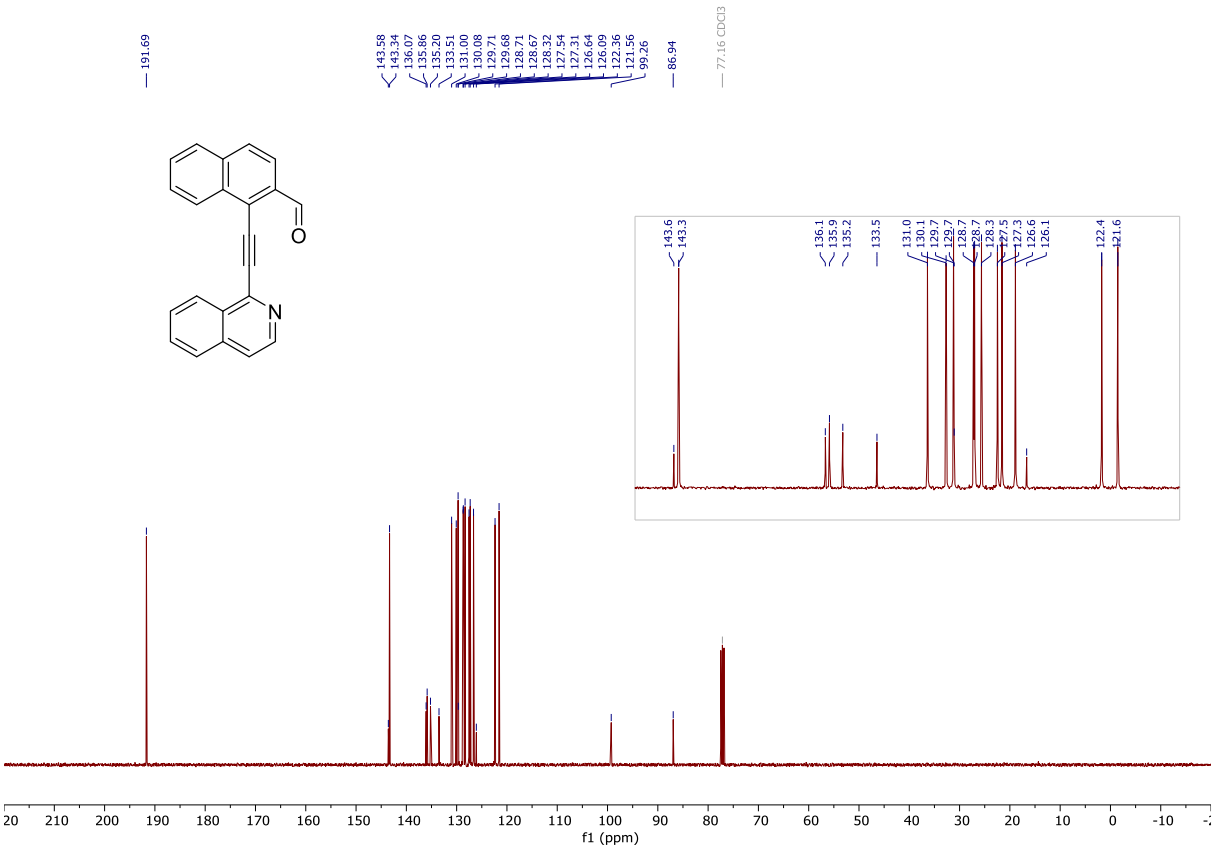


1-(Isoquinolin-1-ylethynyl)-2-naphthaldehyde (S3a).

^{1}H NMR ($CDCl_3$)

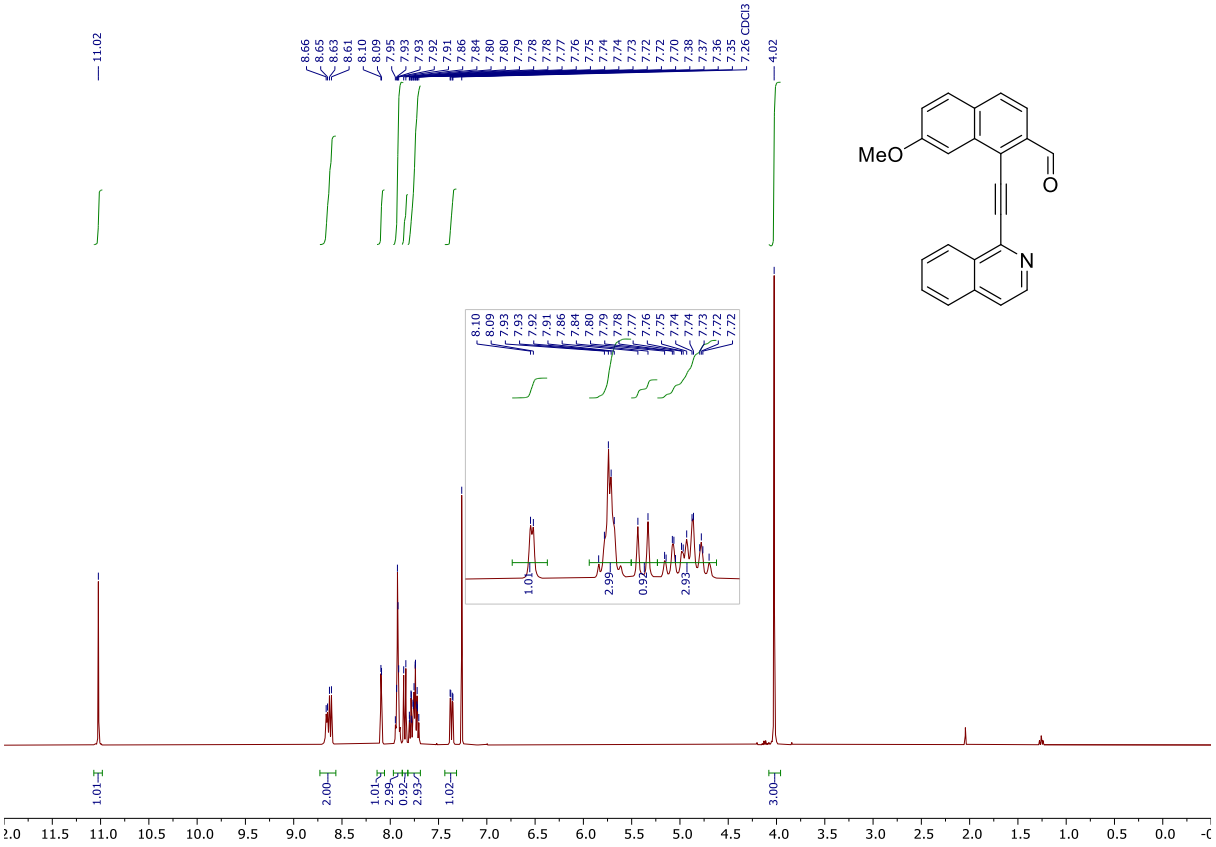


^{13}C NMR ($CDCl_3$)

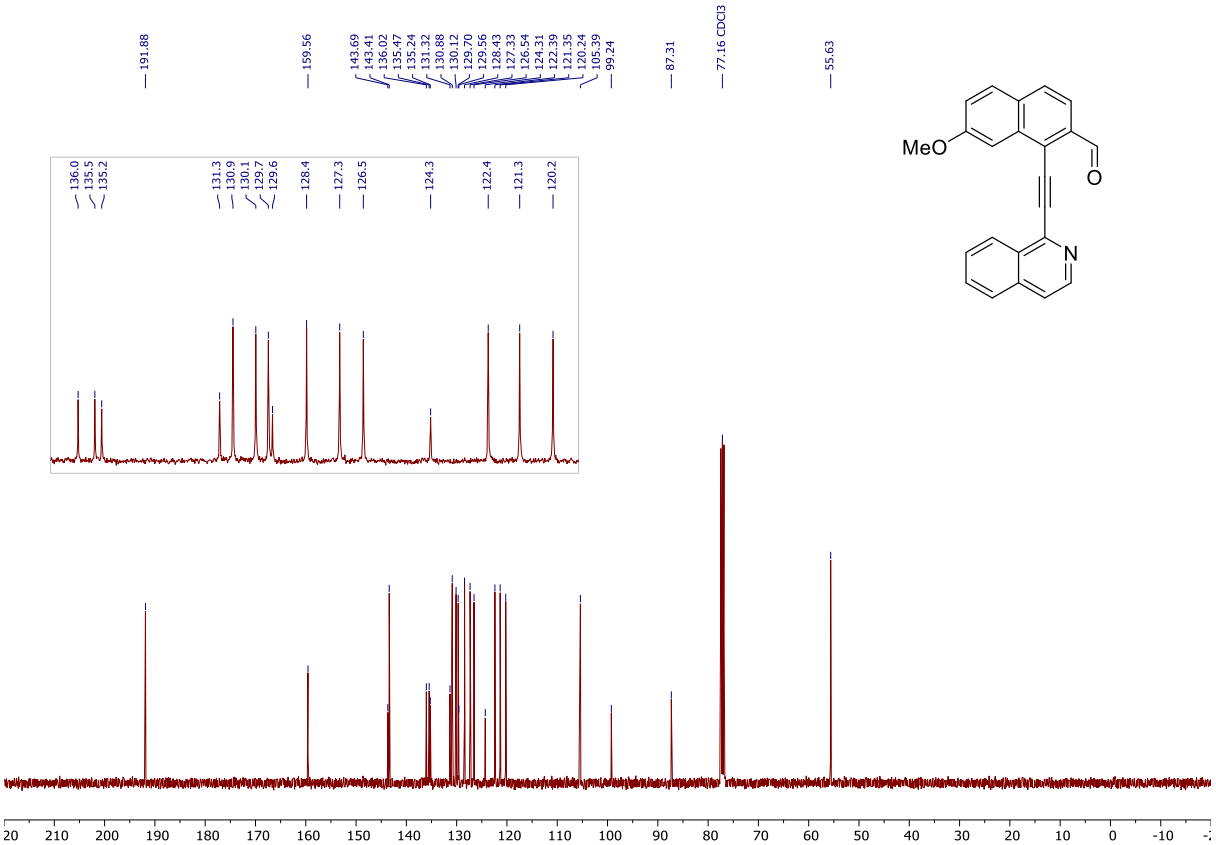


1-(Isoquinolin-1-ylethynyl)-7-methoxy-2-naphthaldehyde (S3b).

^{1}H NMR ($CDCl_3$)

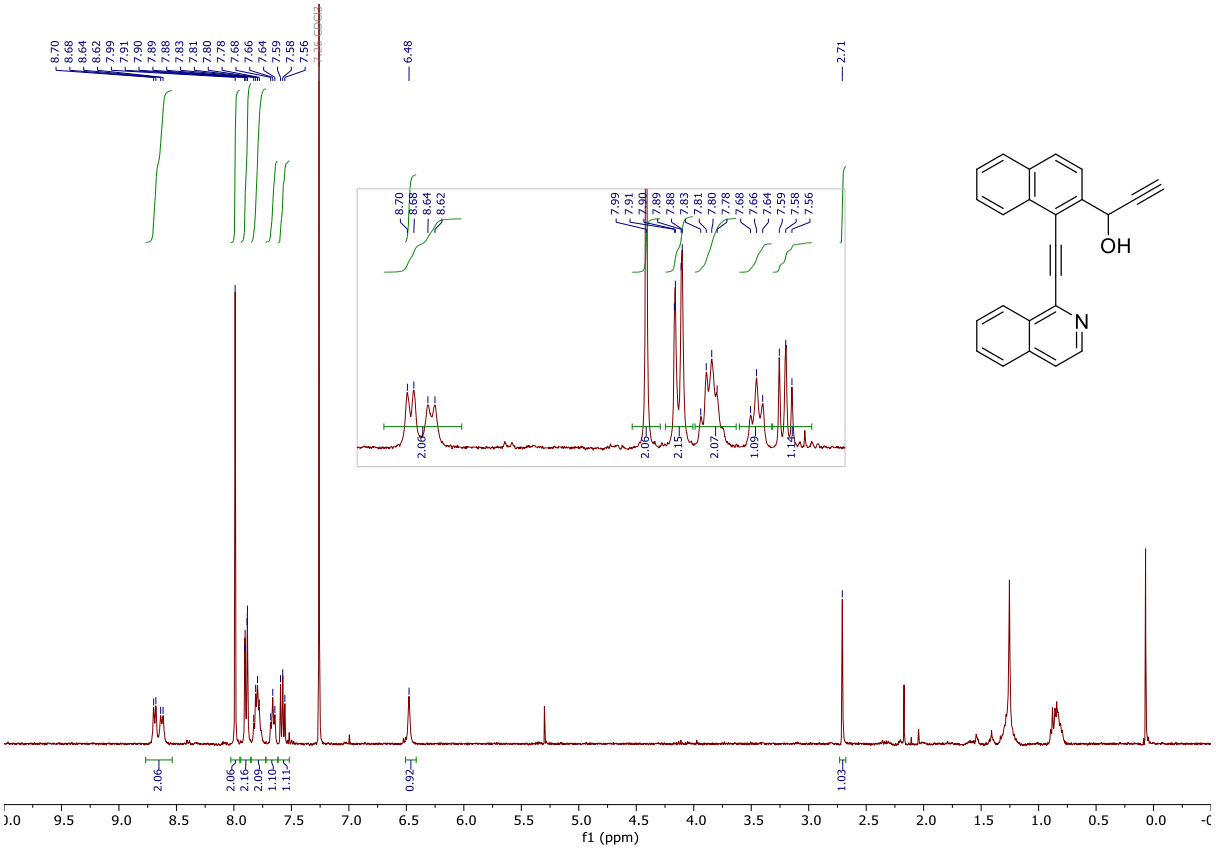


^{13}C NMR ($CDCl_3$)

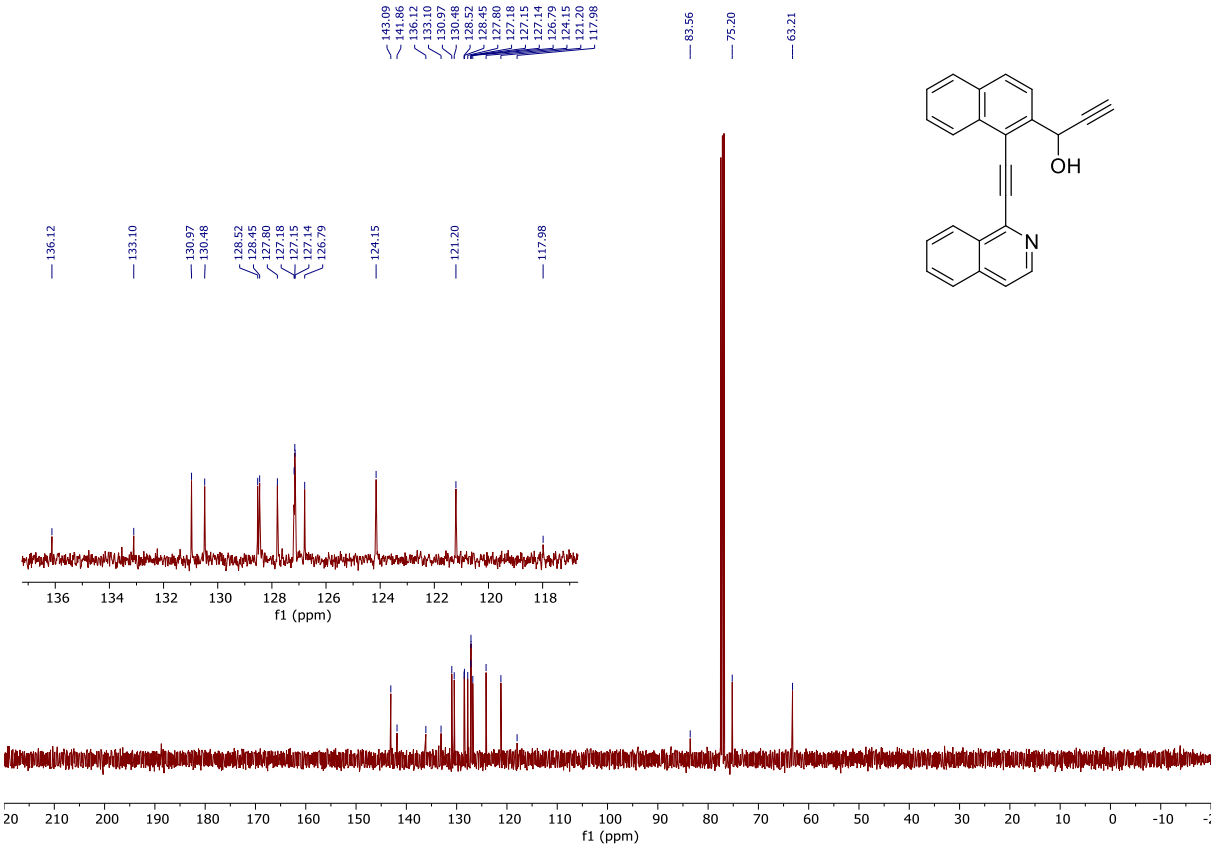


1-(1-(Isoquinolin-1-ylethynyl)naphthalen-2-yl)prop-2-yn-1-ol (3a).

^{1}H NMR ($CDCl_3$)

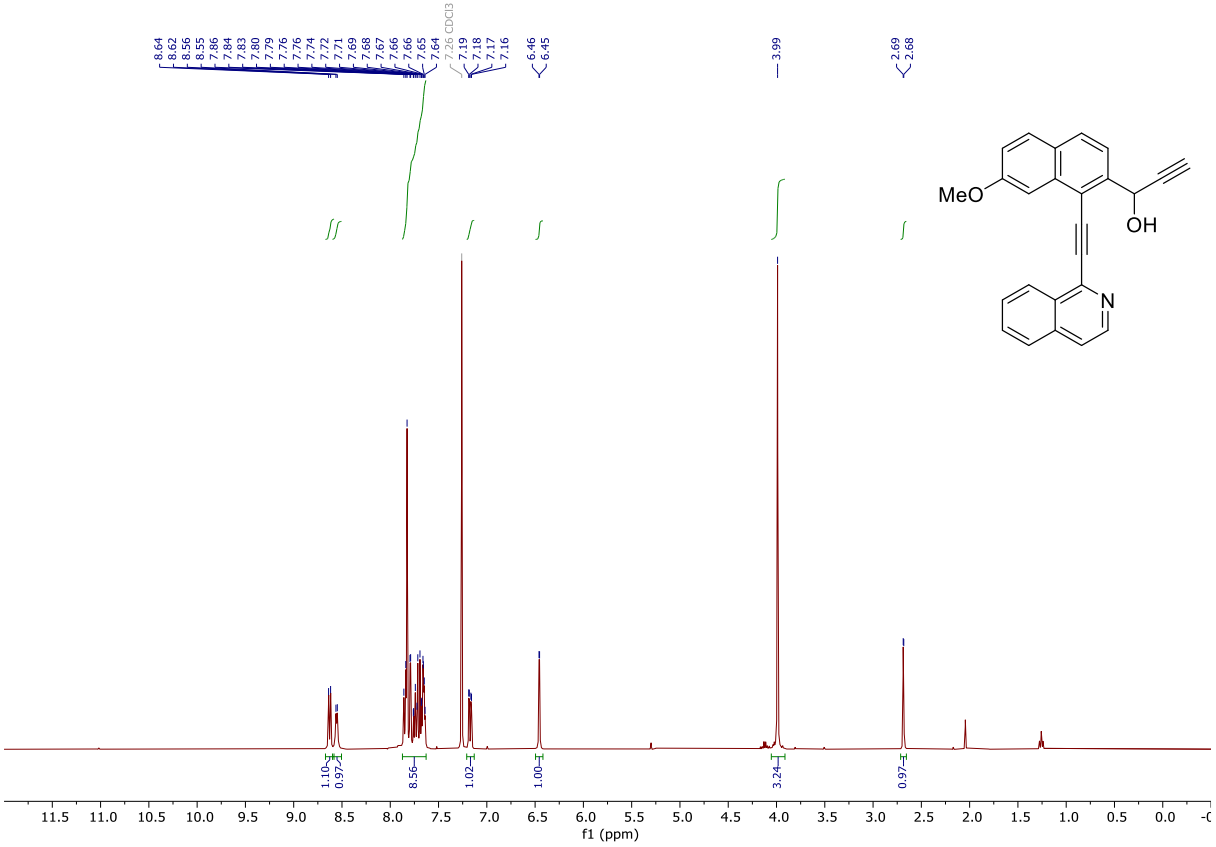


^{13}C NMR ($CDCl_3$)

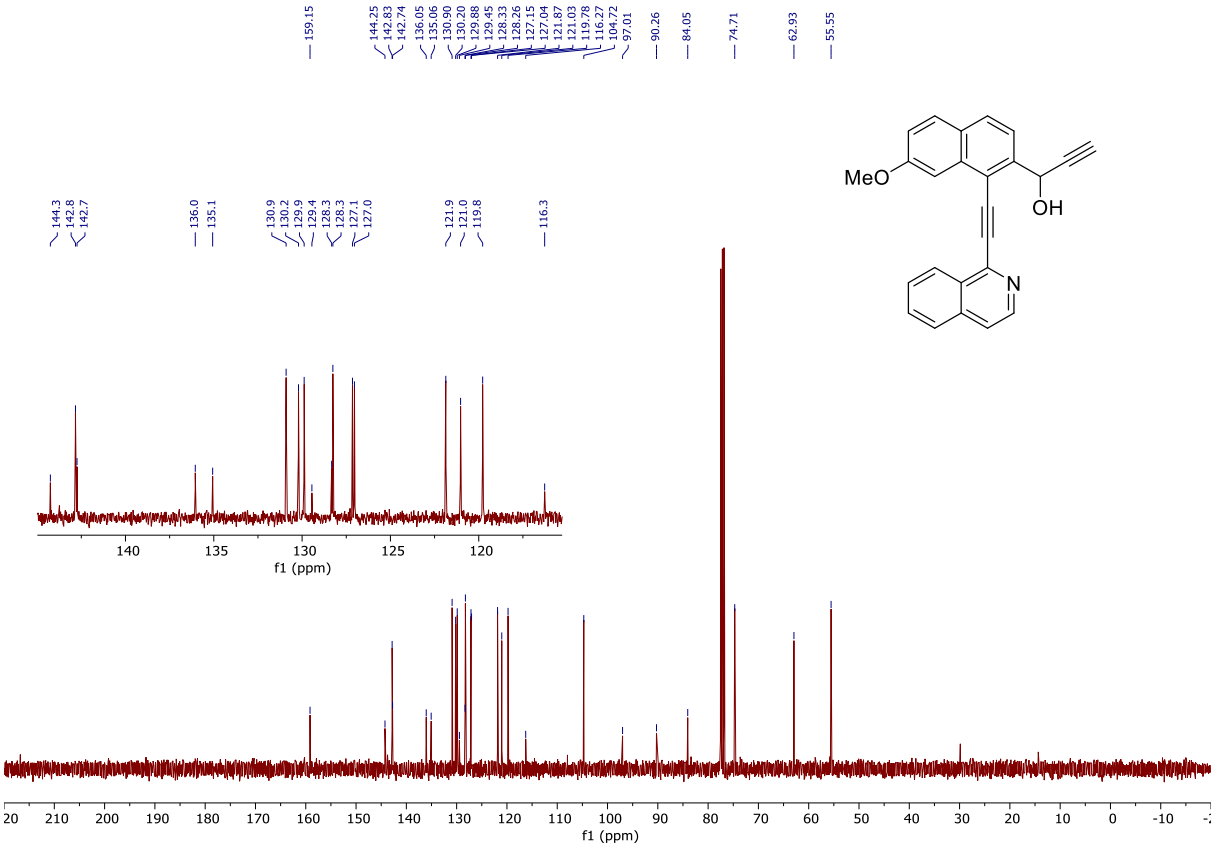


1-(1-(Isoquinolin-1-ylethynyl)-7-methoxynaphthalen-2-yl)prop-2-yn-1-ol (3b).

^{1}H NMR ($CDCl_3$)

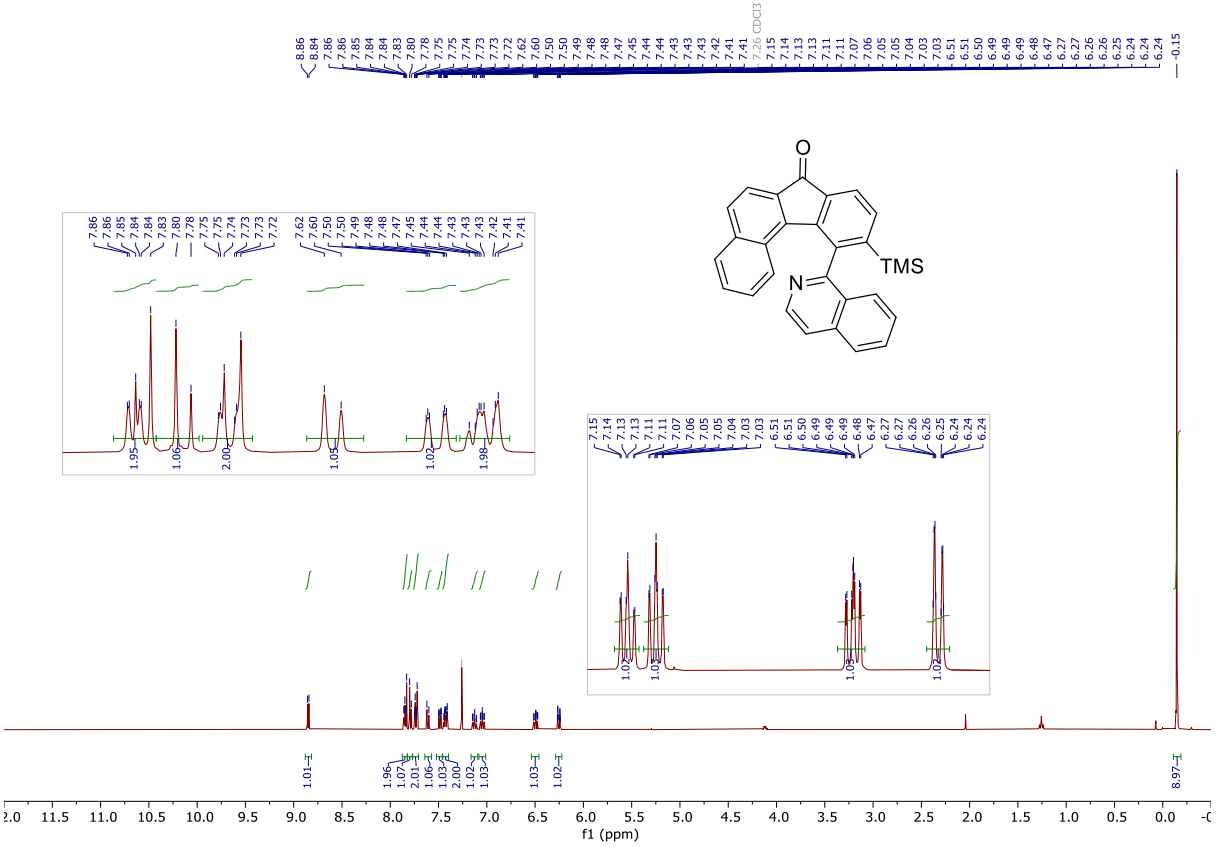


^{13}C NMR ($CDCl_3$)

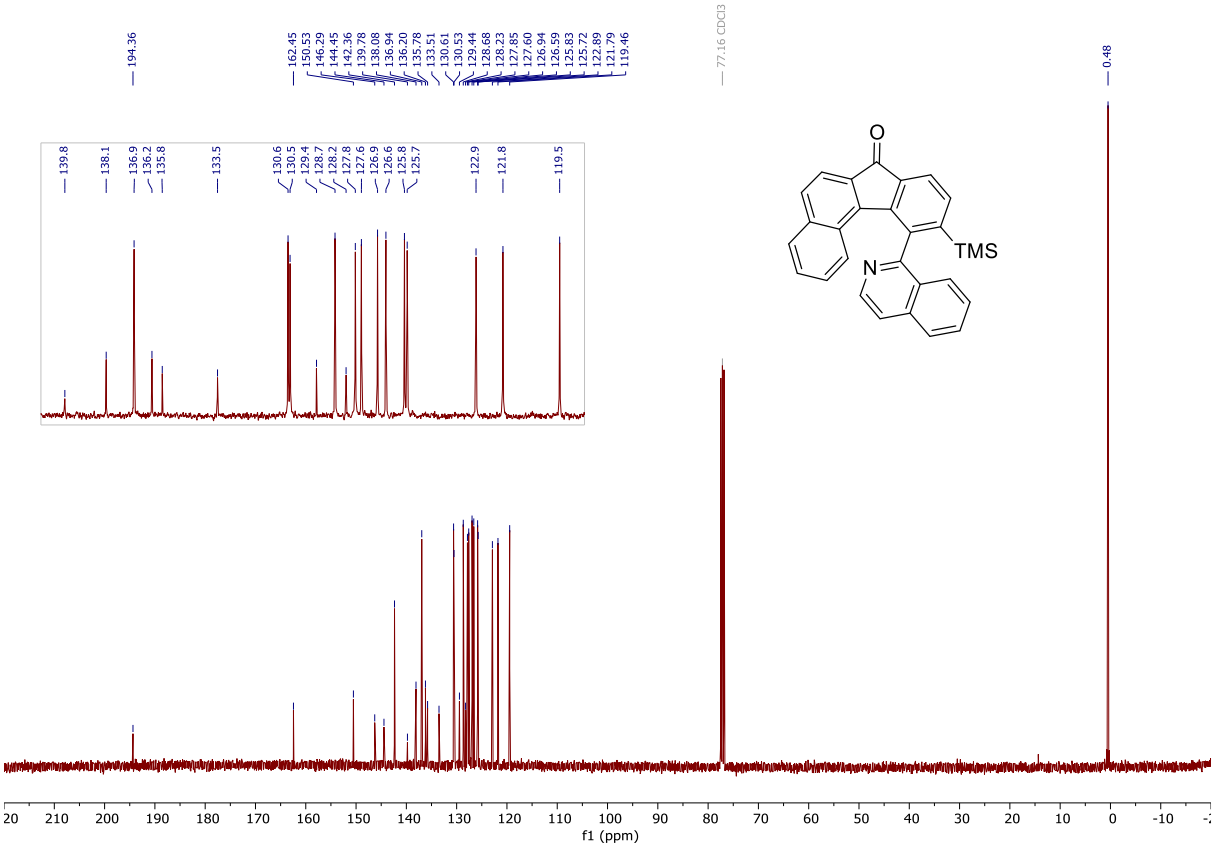


11-(Naphthalen-1-yl)-10-(trimethylsilyl)-7H-benzo[c]fluoren-7-one (4a).

^{1}H NMR ($CDCl_3$)

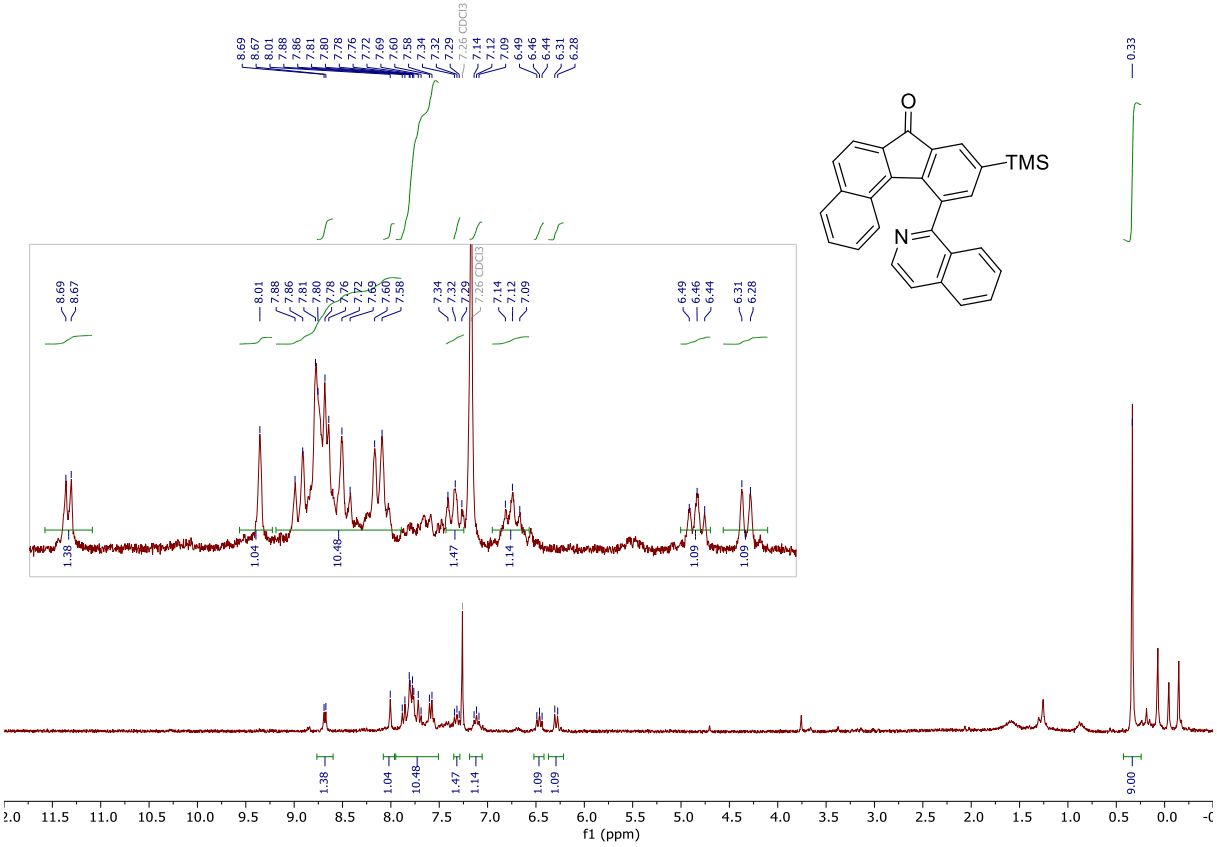


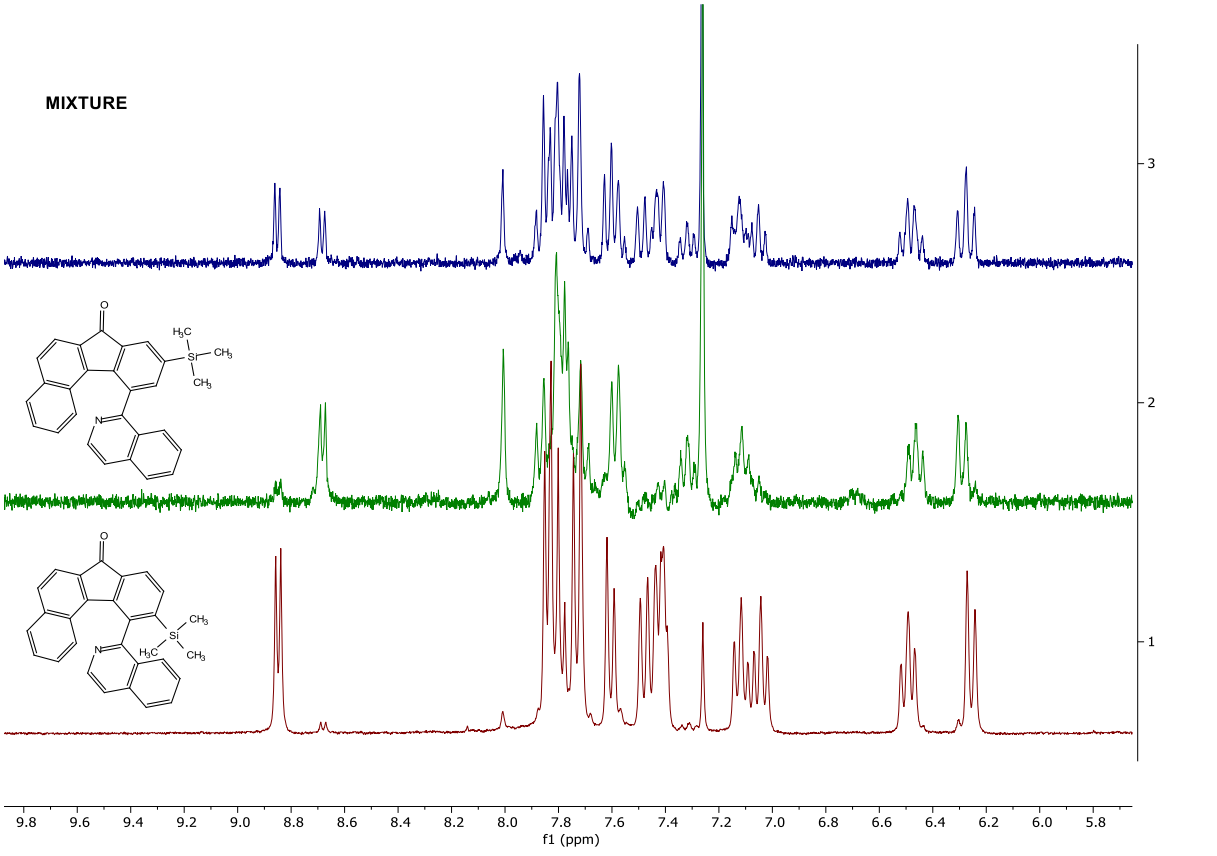
^{13}C NMR ($CDCl_3$)



11-(isoquinolin-1-yl)-9-(trimethylsilyl)-7H-benzo[c]fluoren-7-one (4a´)

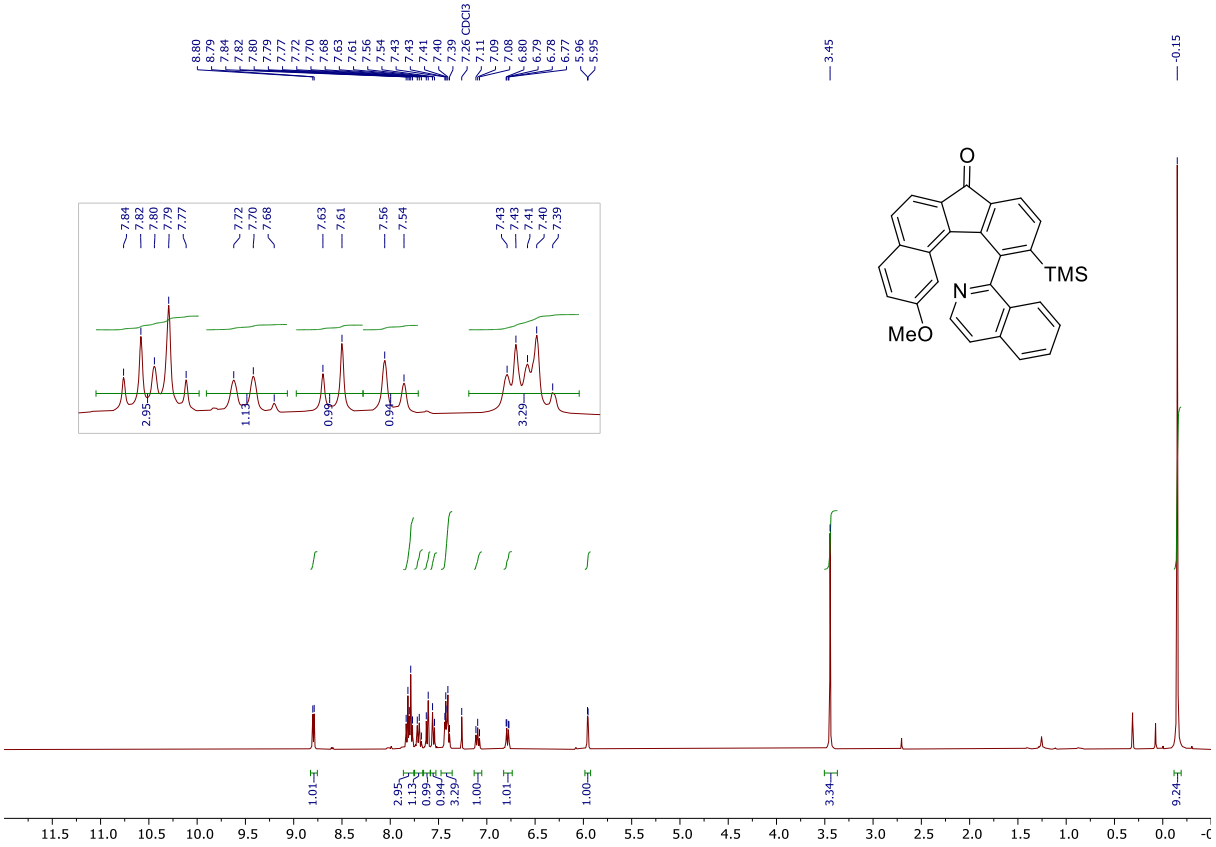
^{1}H NMR ($CDCl_3$)



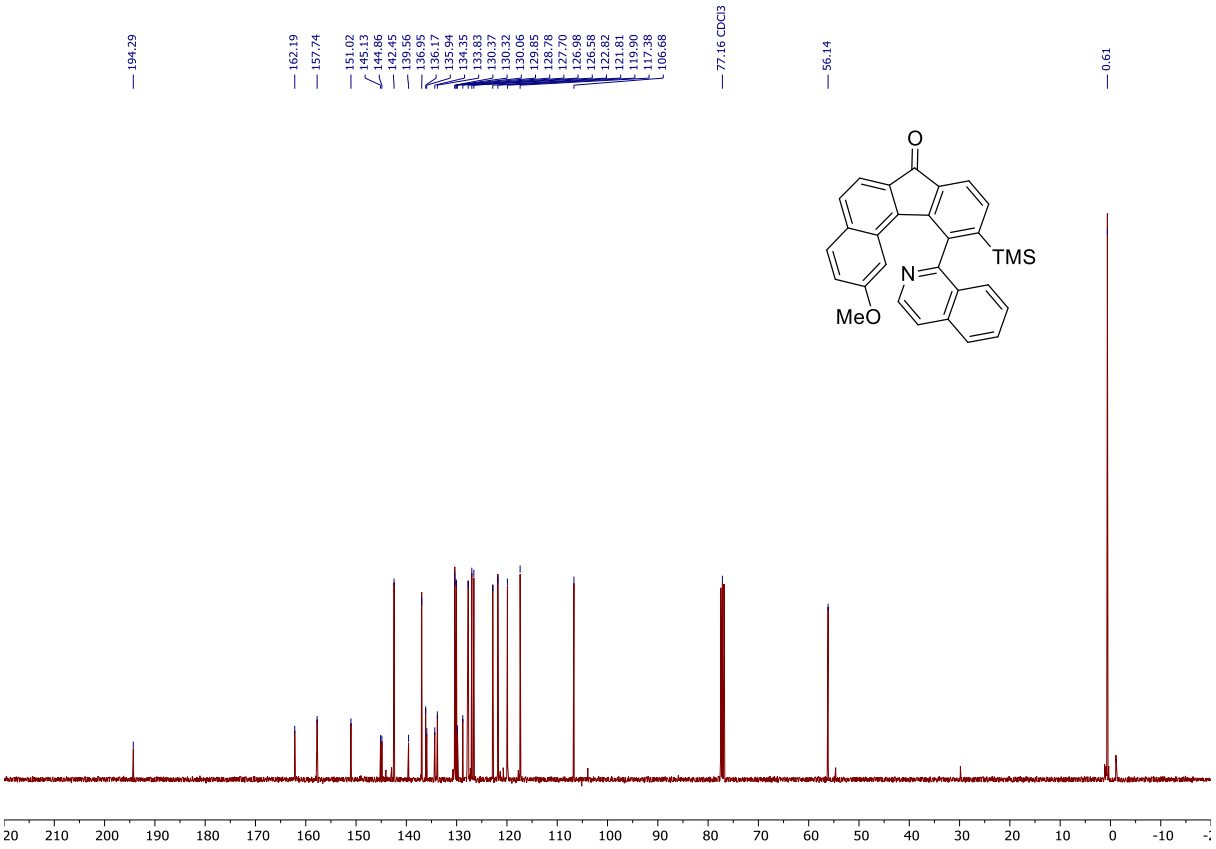


2-Methoxy-11-(naphthalen-1-yl)-10-(trimethylsilyl)-7H-benzo[c]fluoren-7-one (4b).

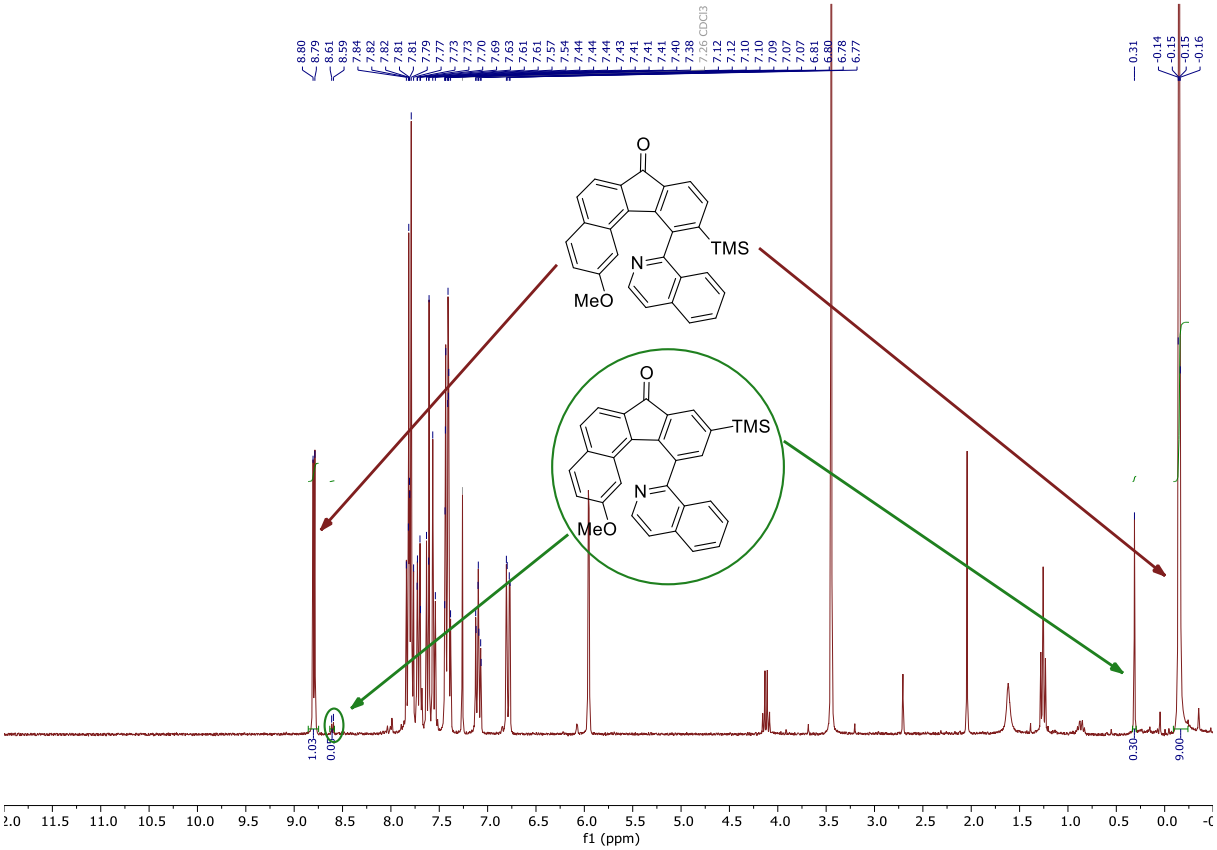
^{1}H NMR ($CDCl_3$)

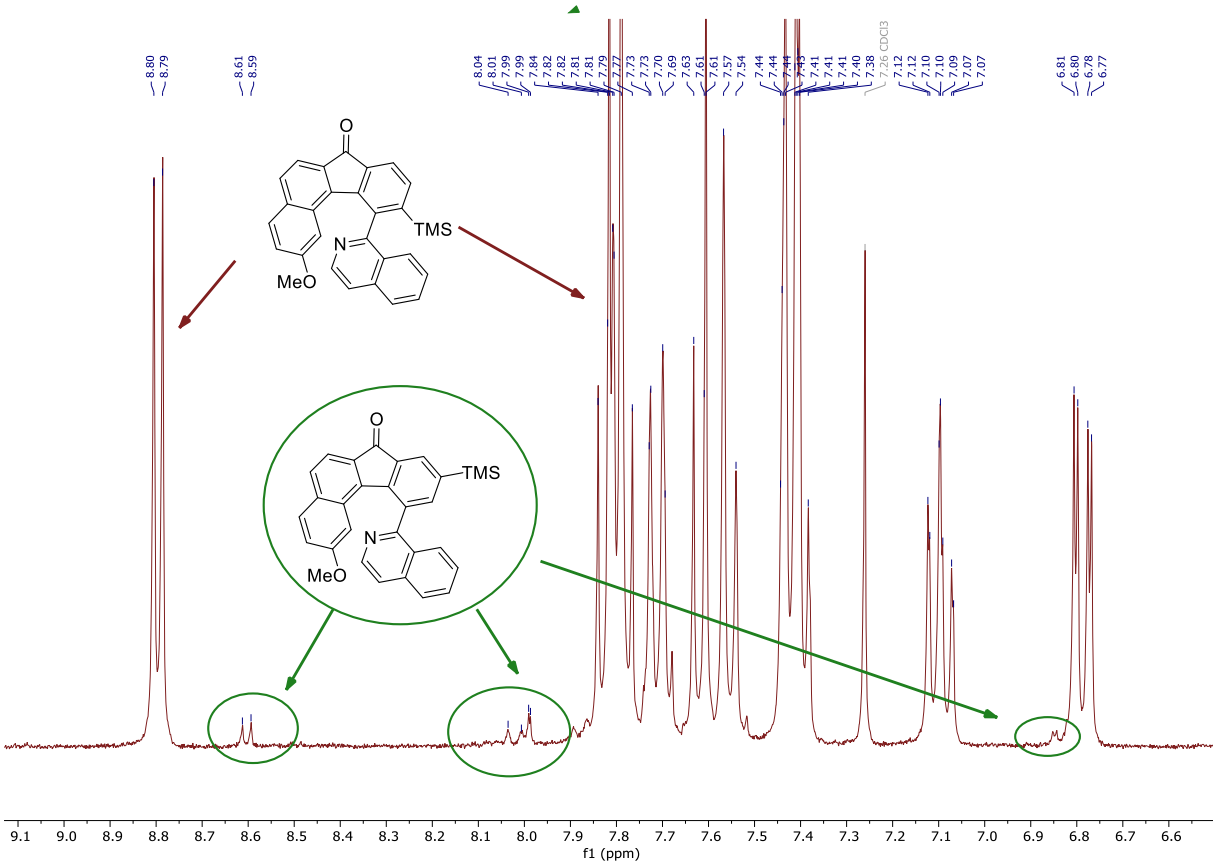


^{13}C NMR ($CDCl_3$)



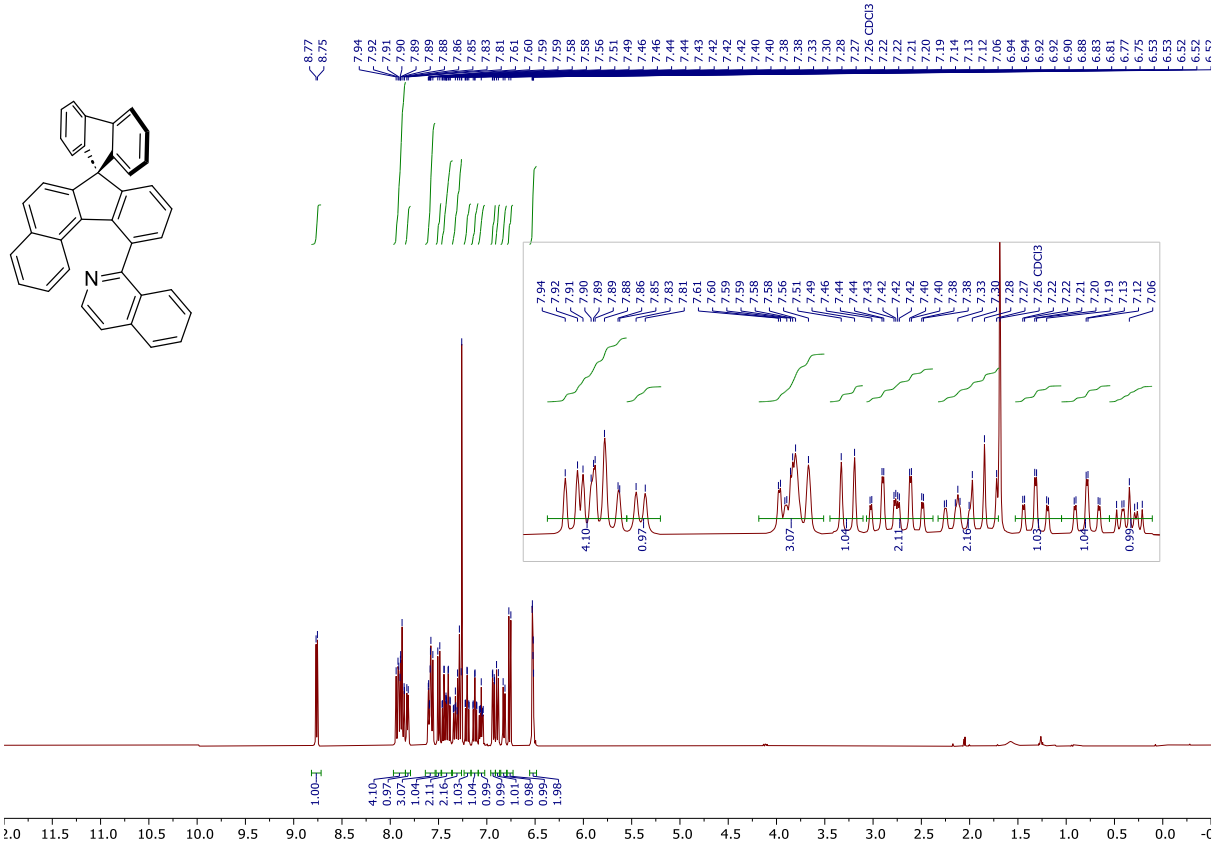
^{1}H NMR ($CDCl_3$) Mixture of minor and major isomers of **4b/4b´**



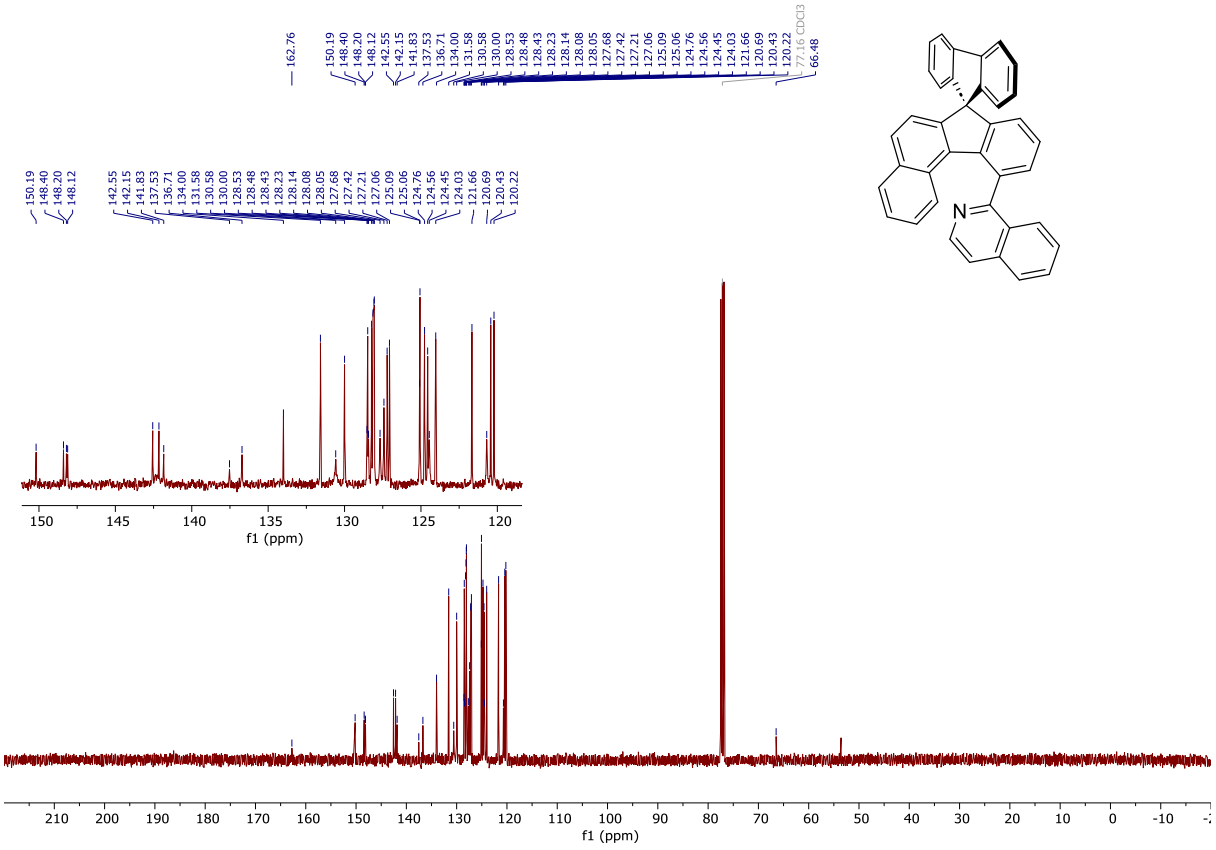


1-(Spiro[benzo[c]fluorene-7,9'-fluoren]-11-yl)isoquinoline (5a).

^{1}H NMR ($CDCl_3$)

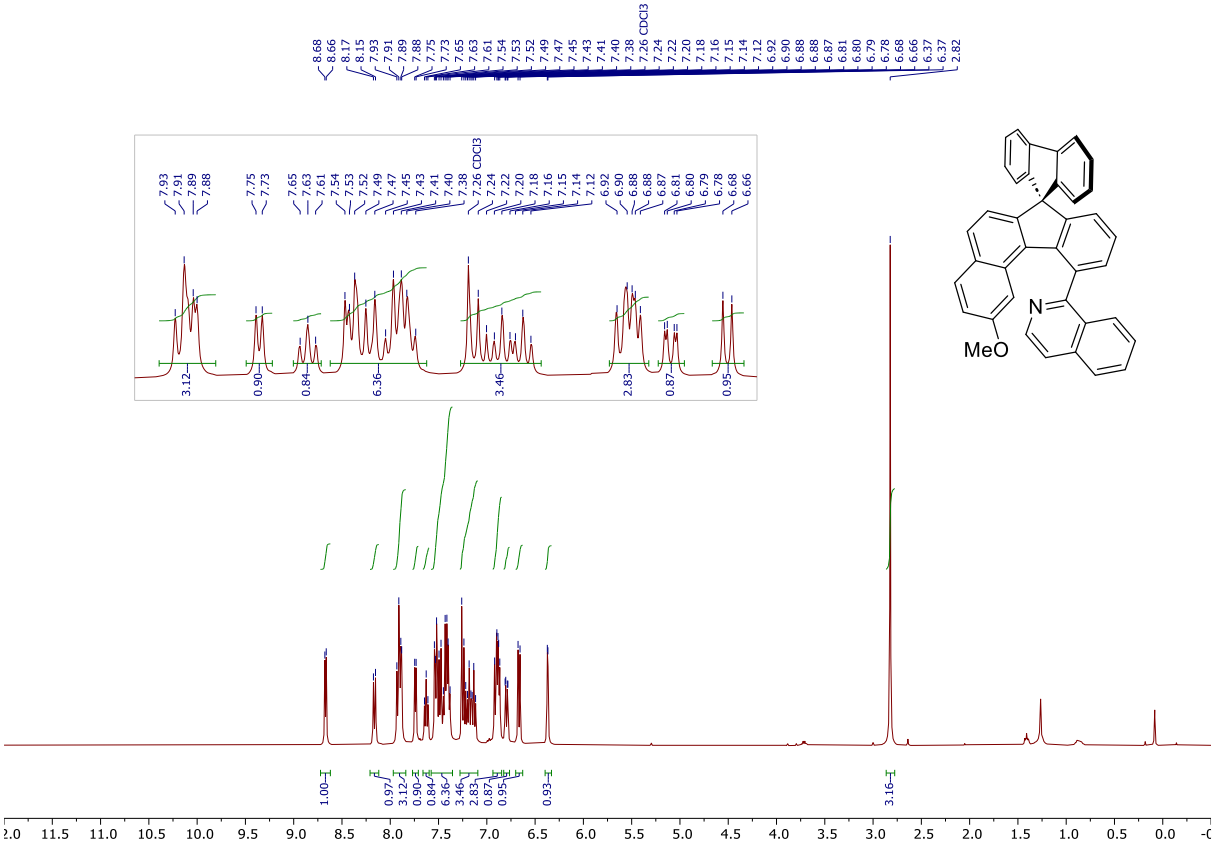


^{13}C NMR ($CDCl_3$)

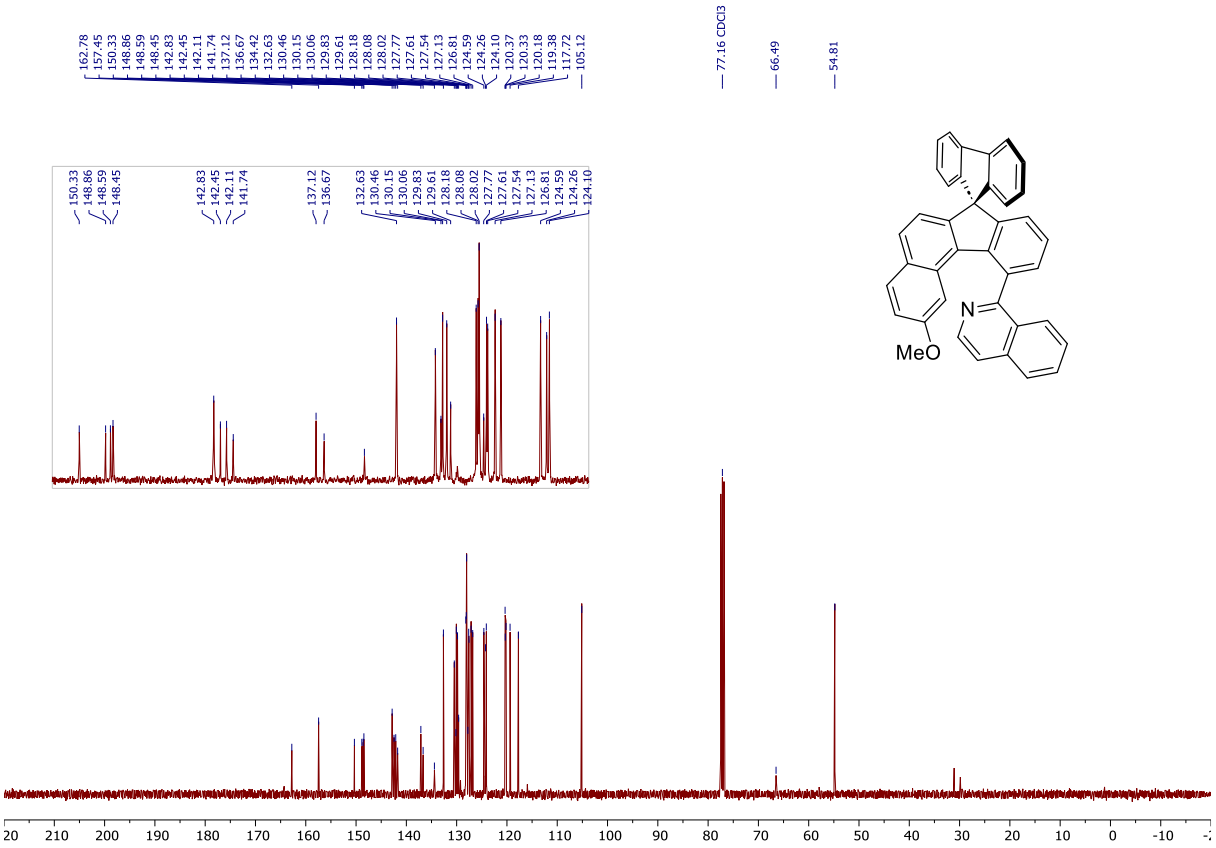


1-(2-Methoxyspiro[benzo[c]fluorene-7,9'-fluoren]-11-yl)isoquinoline (5b).

^{1}H NMR ($CDCl_3$)

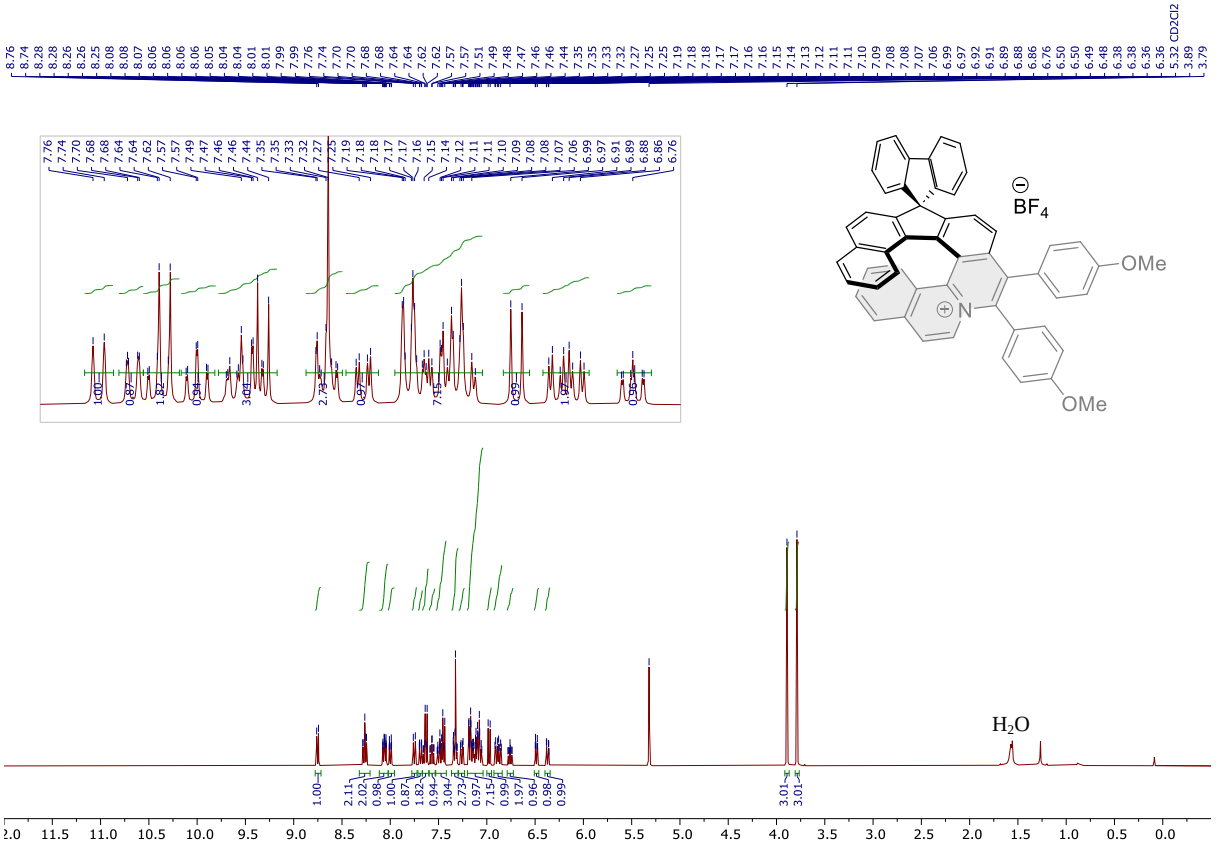


^{13}C NMR ($CDCl_3$)

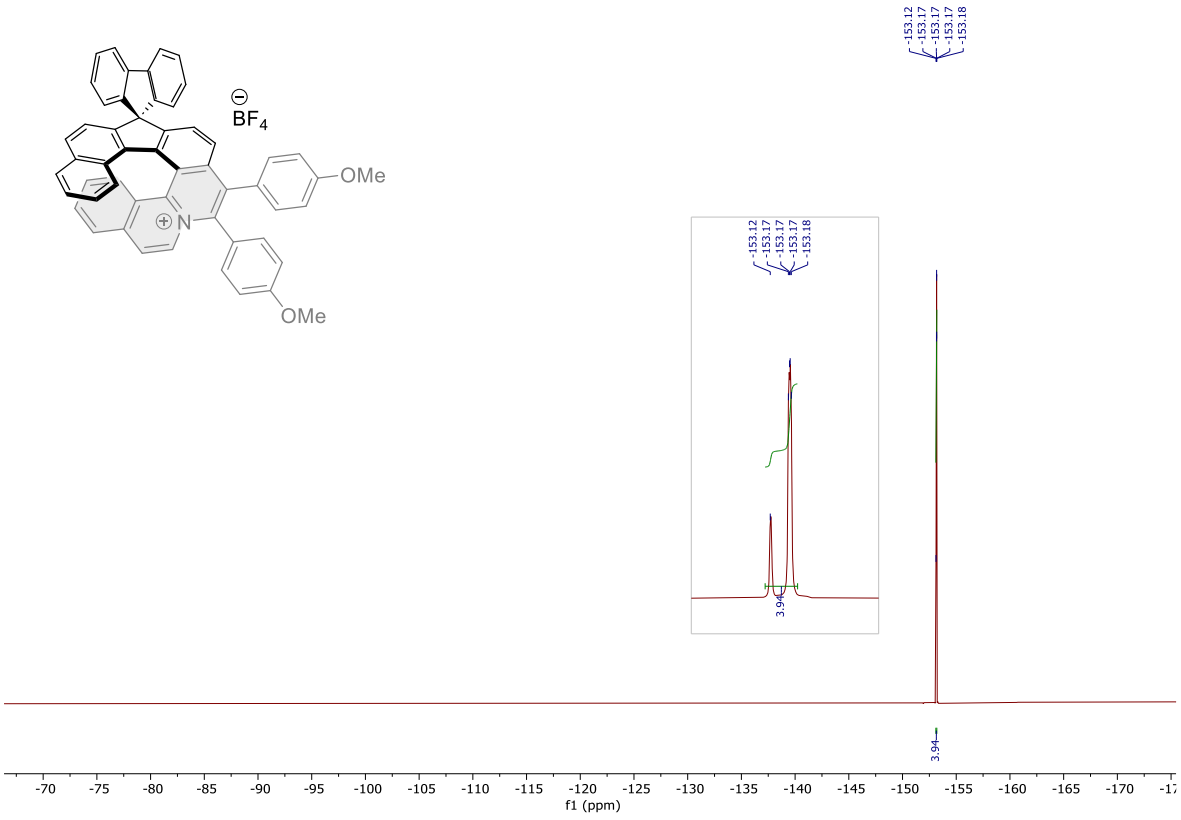


4,5-Bis(4-methoxyphenyl)spiro[benzo[6,7]indeno[2,1-h]isoquinolino[1,2-a]isoquinoline-8,9'-fluoren]-3-ium tetrafluoroborate (1aa)

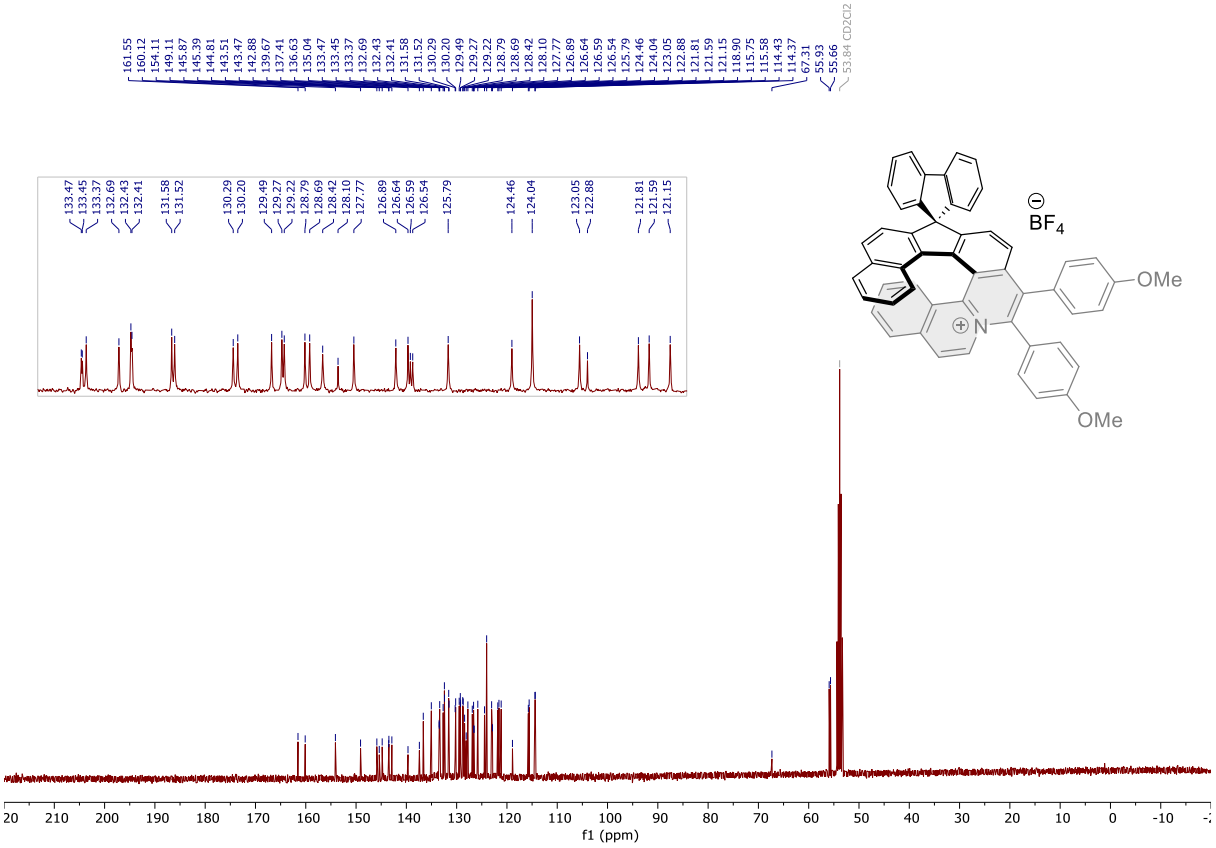
^{1}H NMR (CD_2Cl_2)



^{19}F NMR (CD_2Cl_2)

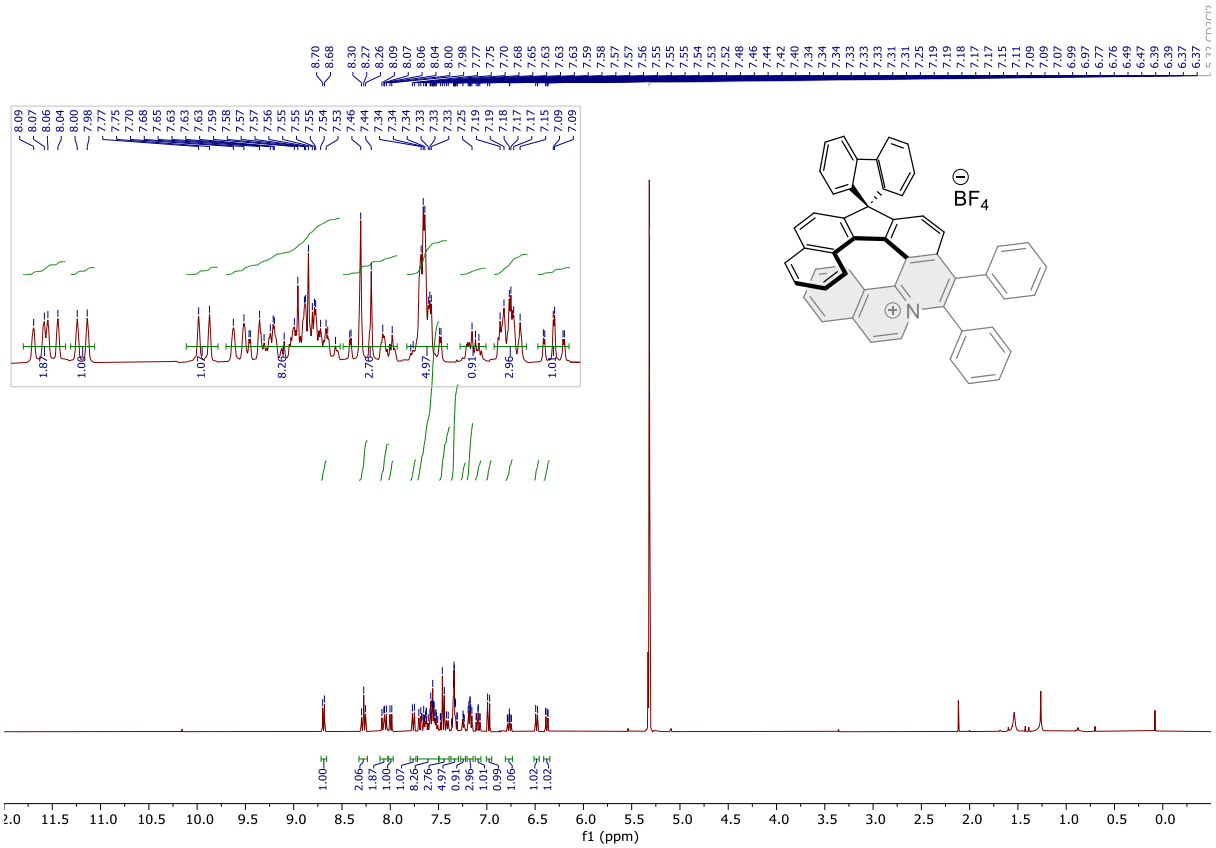


^{13}C NMR (CD_2Cl_2)

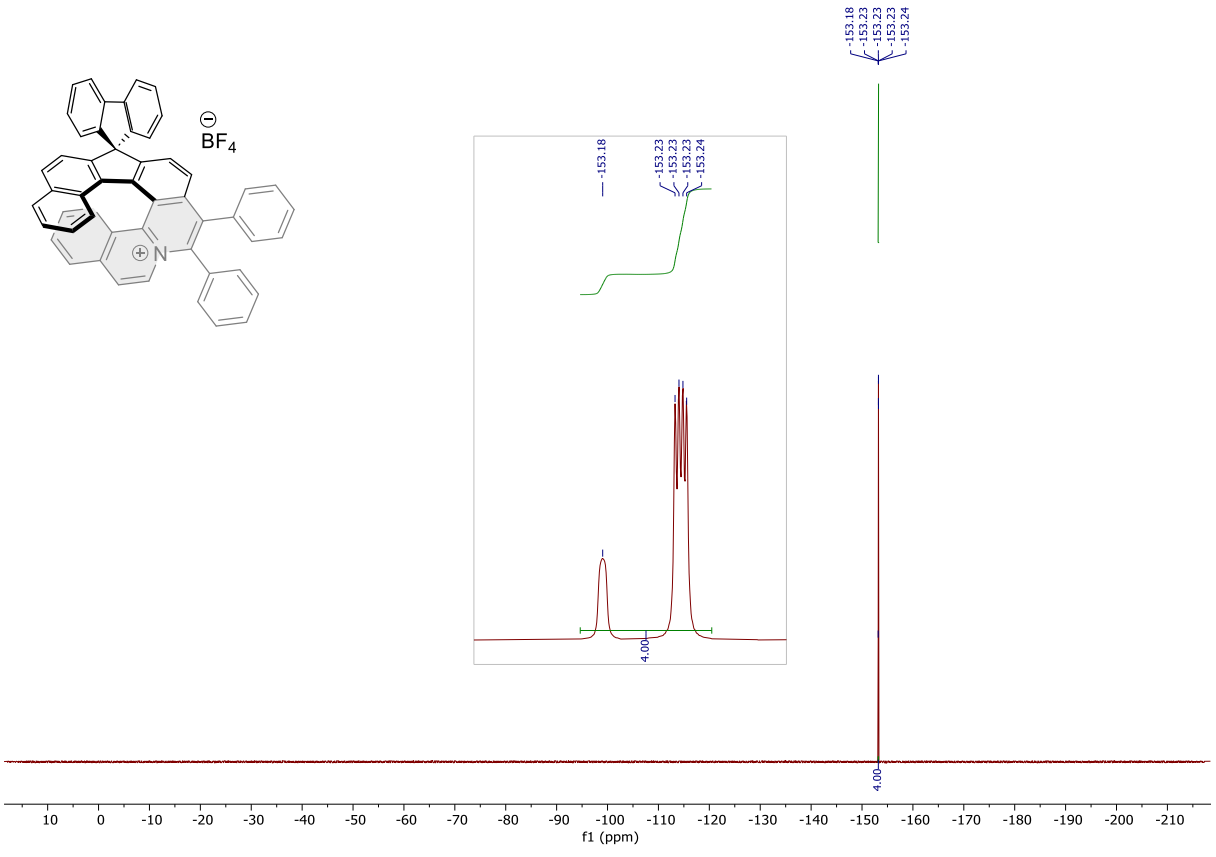


4,5-Diphenylspiro[benzo[6,7]indeno[2,1-h]isoquinolino[1,2-a]isoquinoline-8,9'-fluoren]-3-ium tetrafluoroborate (1ab).

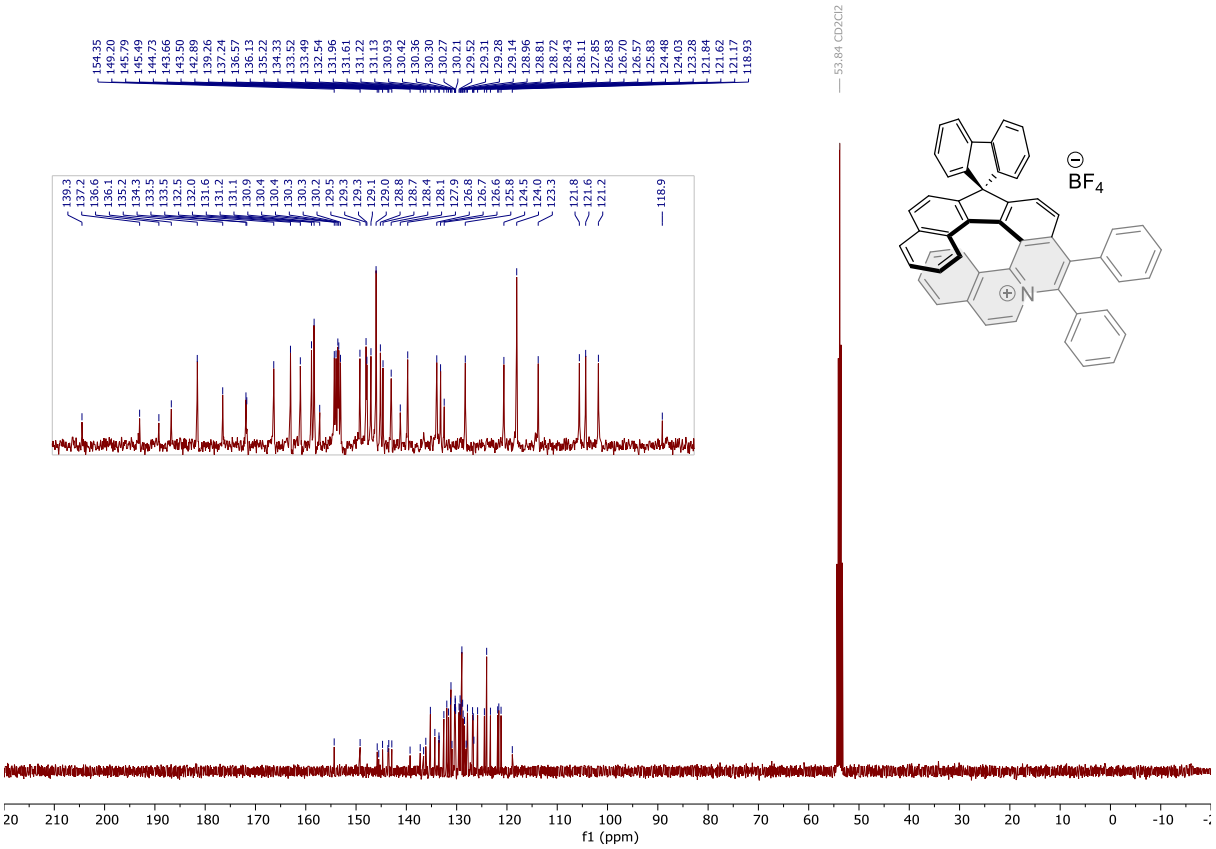
^{1}H NMR (CD_2Cl_2)



^{19}F NMR (CD_2Cl_2)

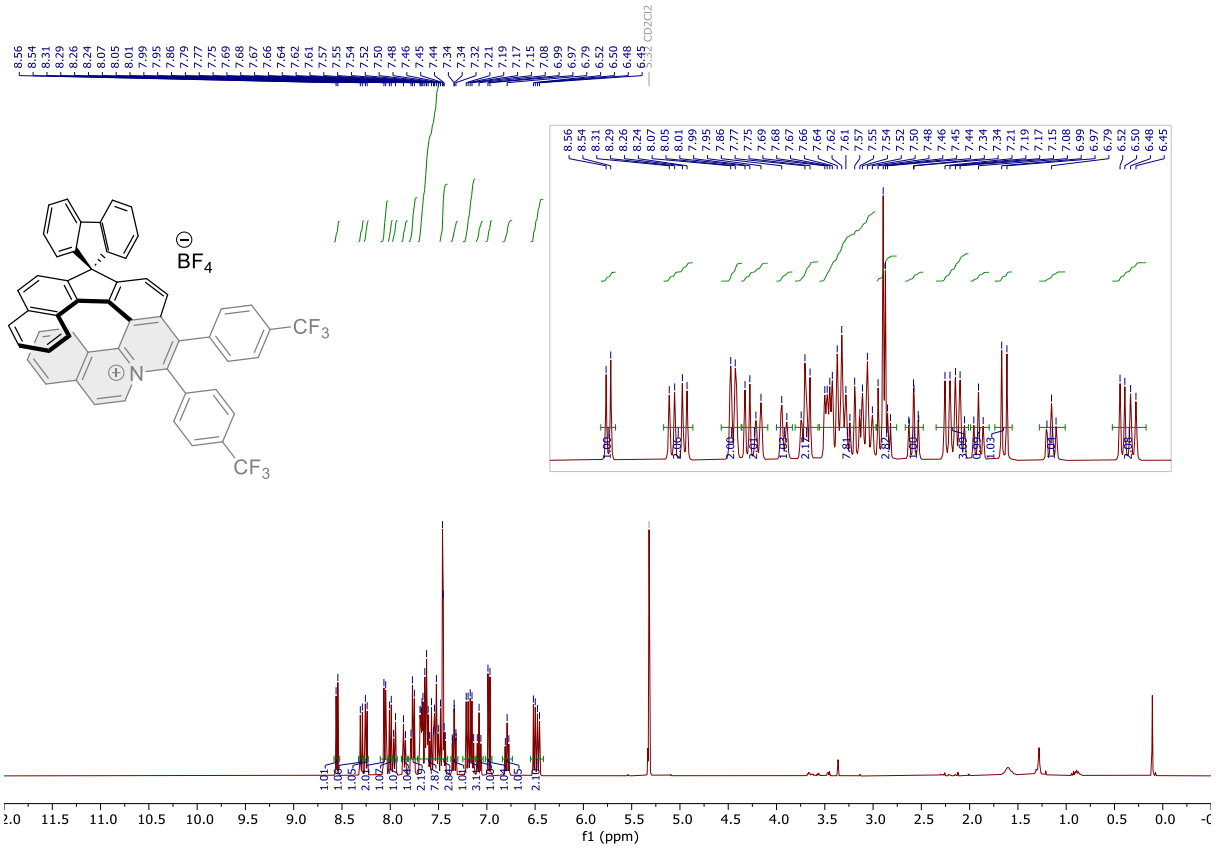


^{13}C NMR (CD_2Cl_2)

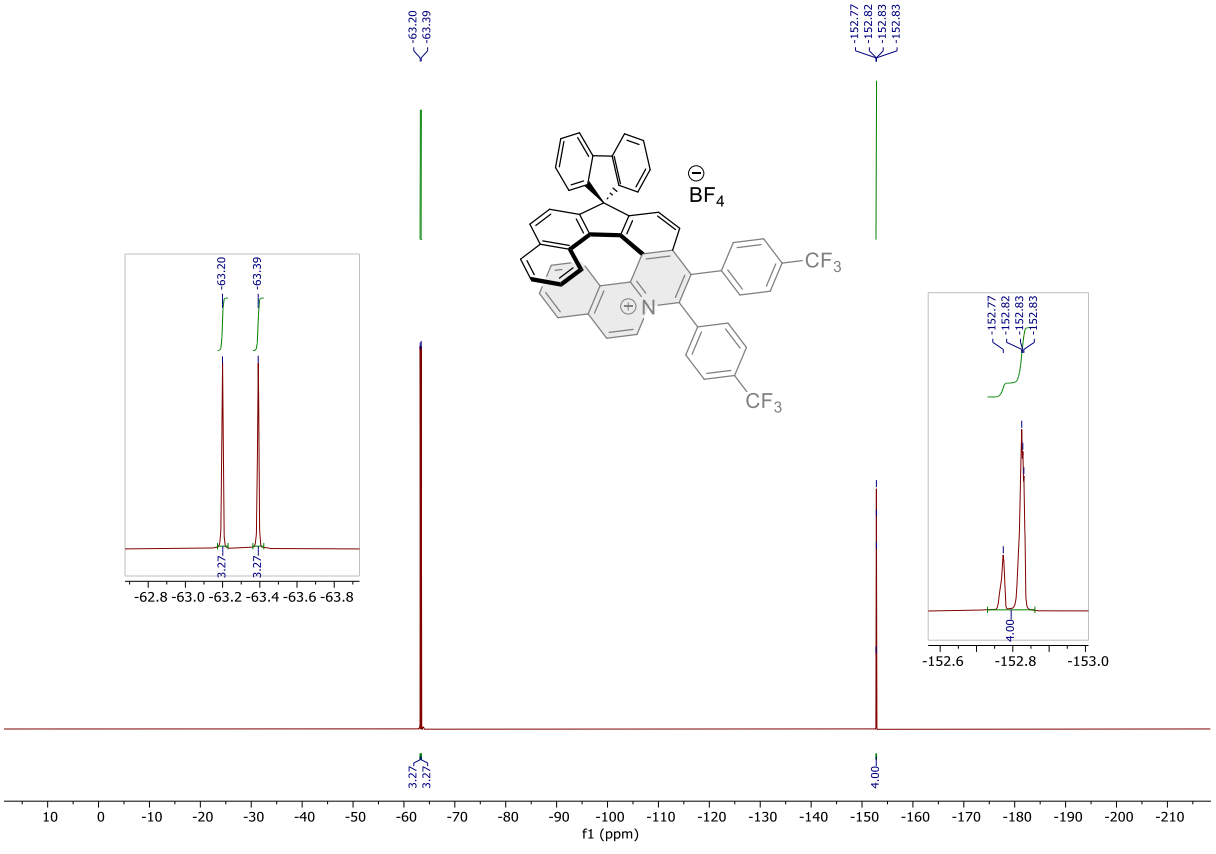


4,5-Bis(4-(trifluoromethyl)phenyl)spiro[benzo[6,7]indeno[2,1-h]isoquinolino[1,2-a]isoquinoline-8,9'-fluoren]-3-ium tetrafluoroborate (1ac)

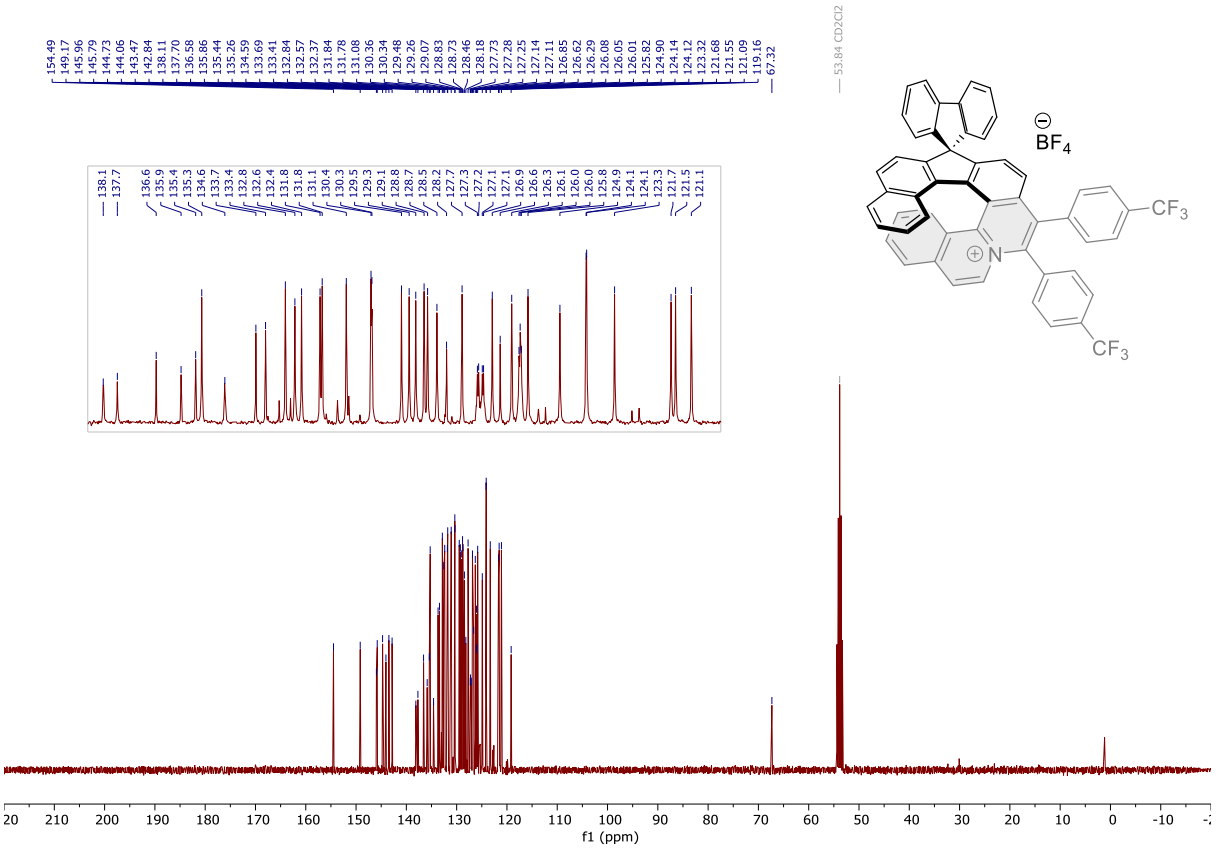
^{1}H NMR (CD_2Cl_2)



^{19}F NMR (CD_2Cl_2)

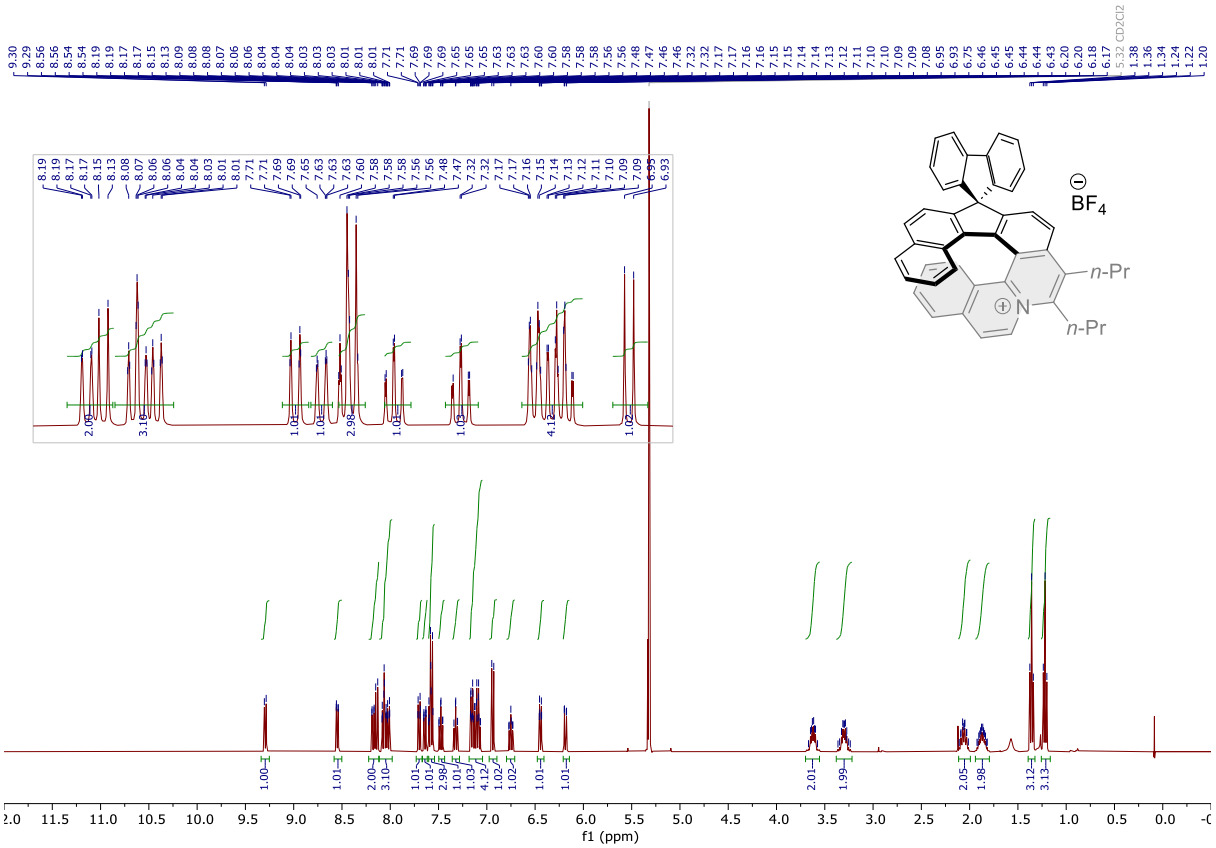


^{13}C NMR (CD_2Cl_2)

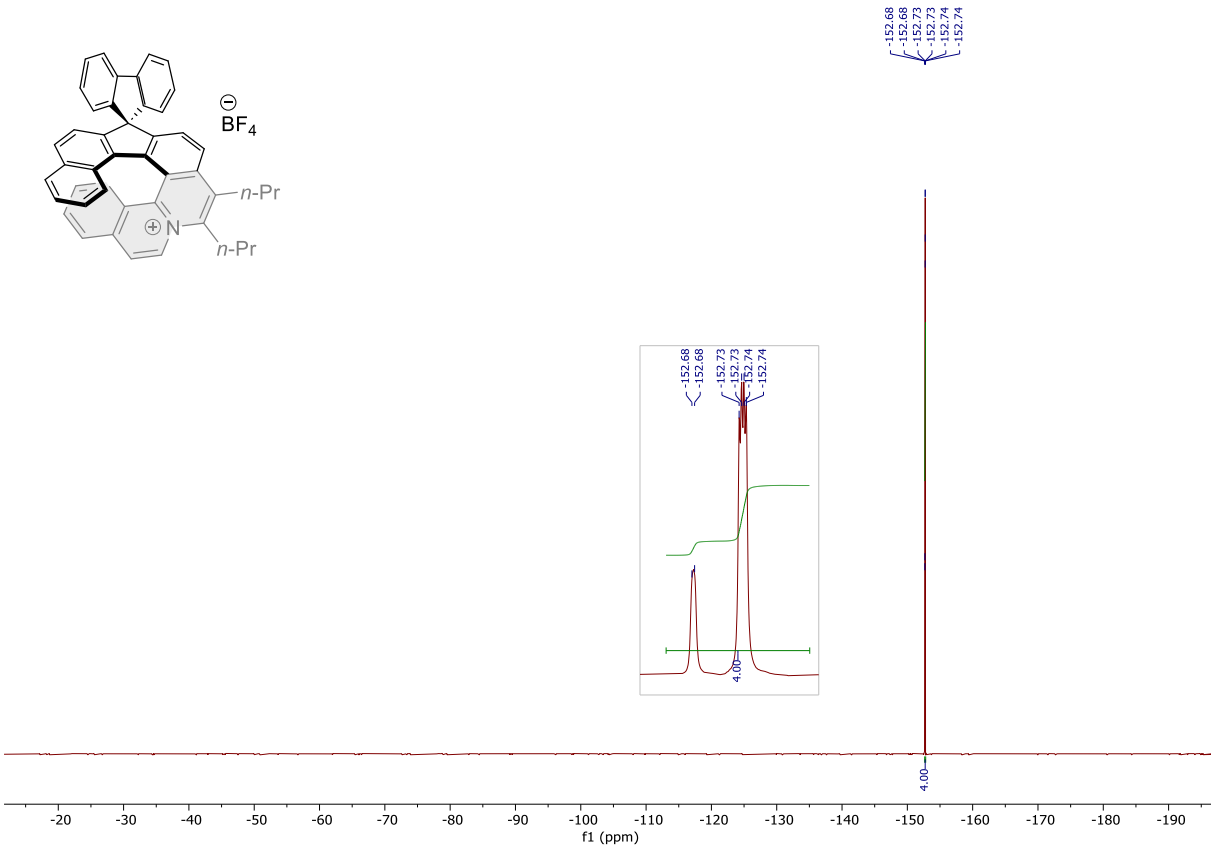


4,5-Dipropylspiro[benzo[6,7]indeno[2,1-h]isoquinolino[1,2-a]isoquinoline-8,9'-fluoren]-3-ium tetrafluoroborate (1ad)

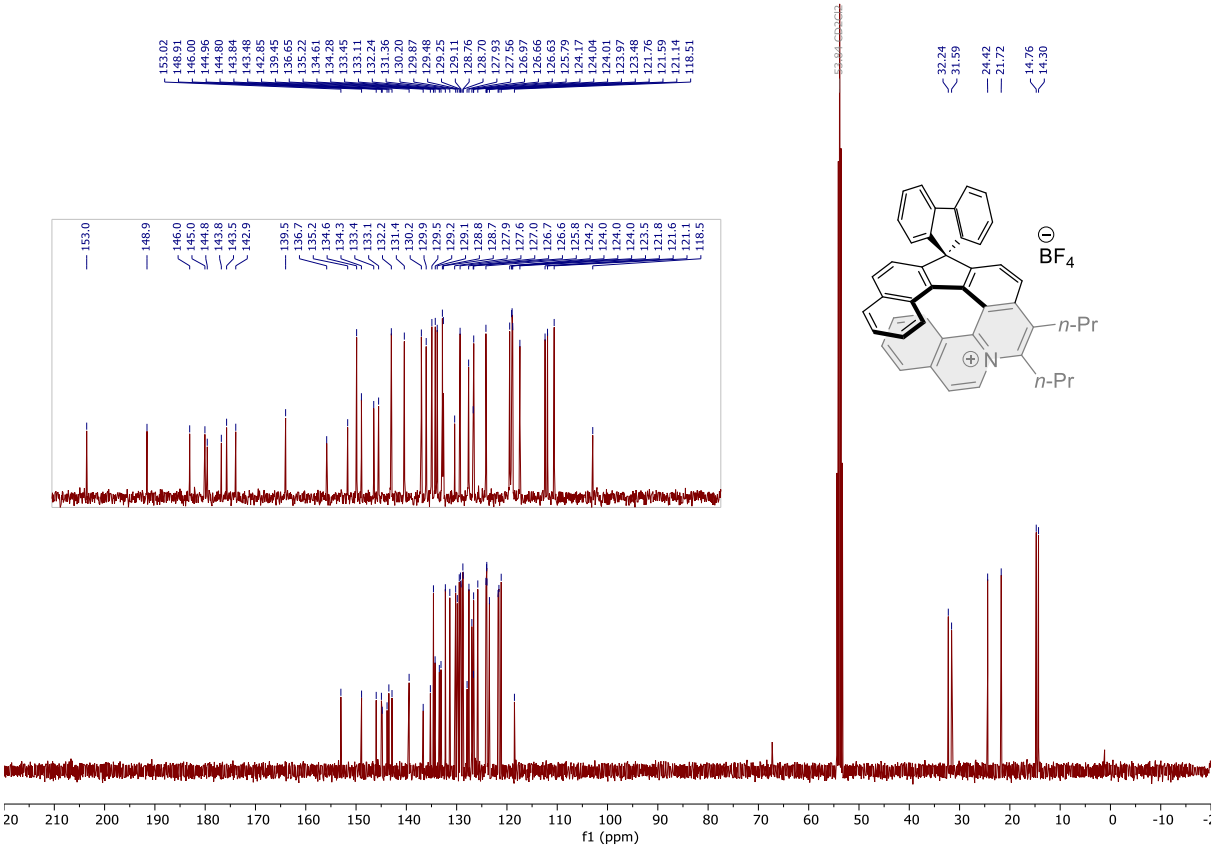
^{1}H NMR (CD_2Cl_2)



^{19}F NMR (CD_2Cl_2)

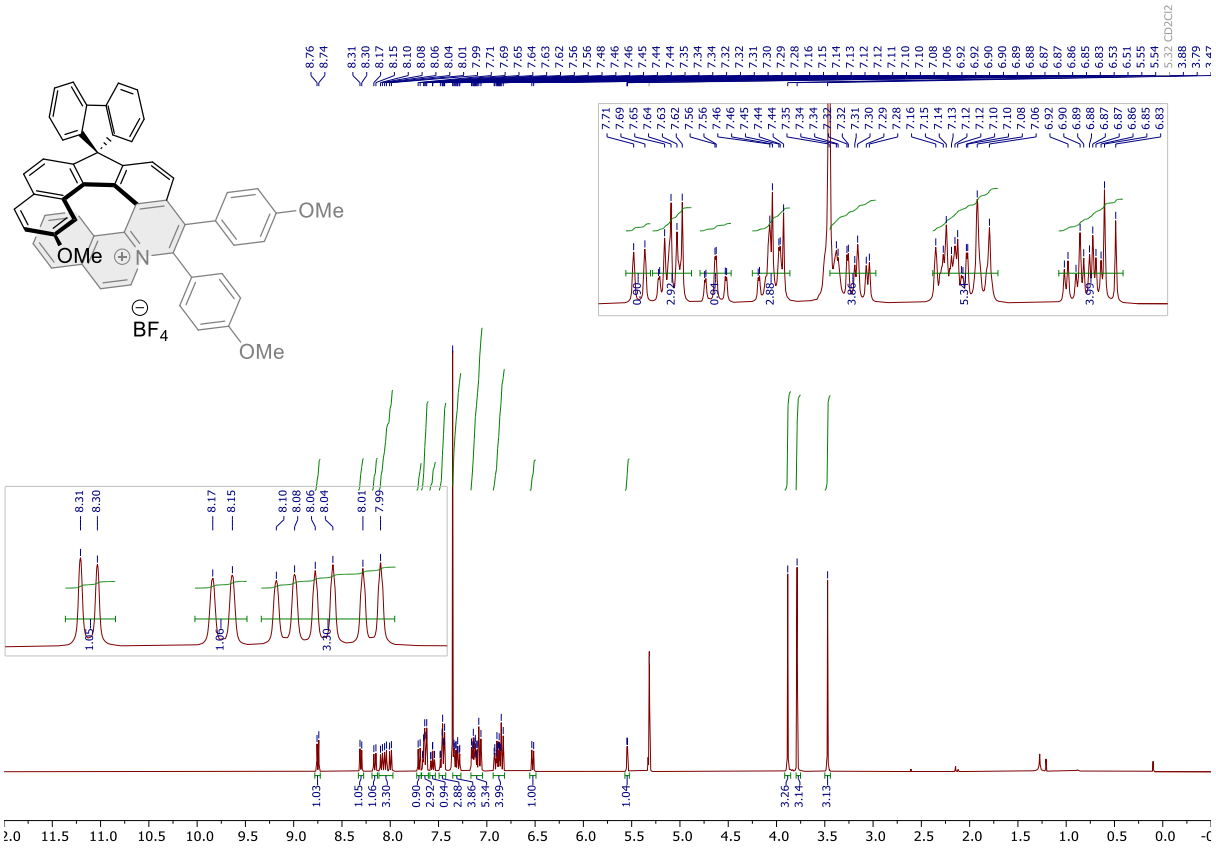


^{13}C NMR (CD_2Cl_2)

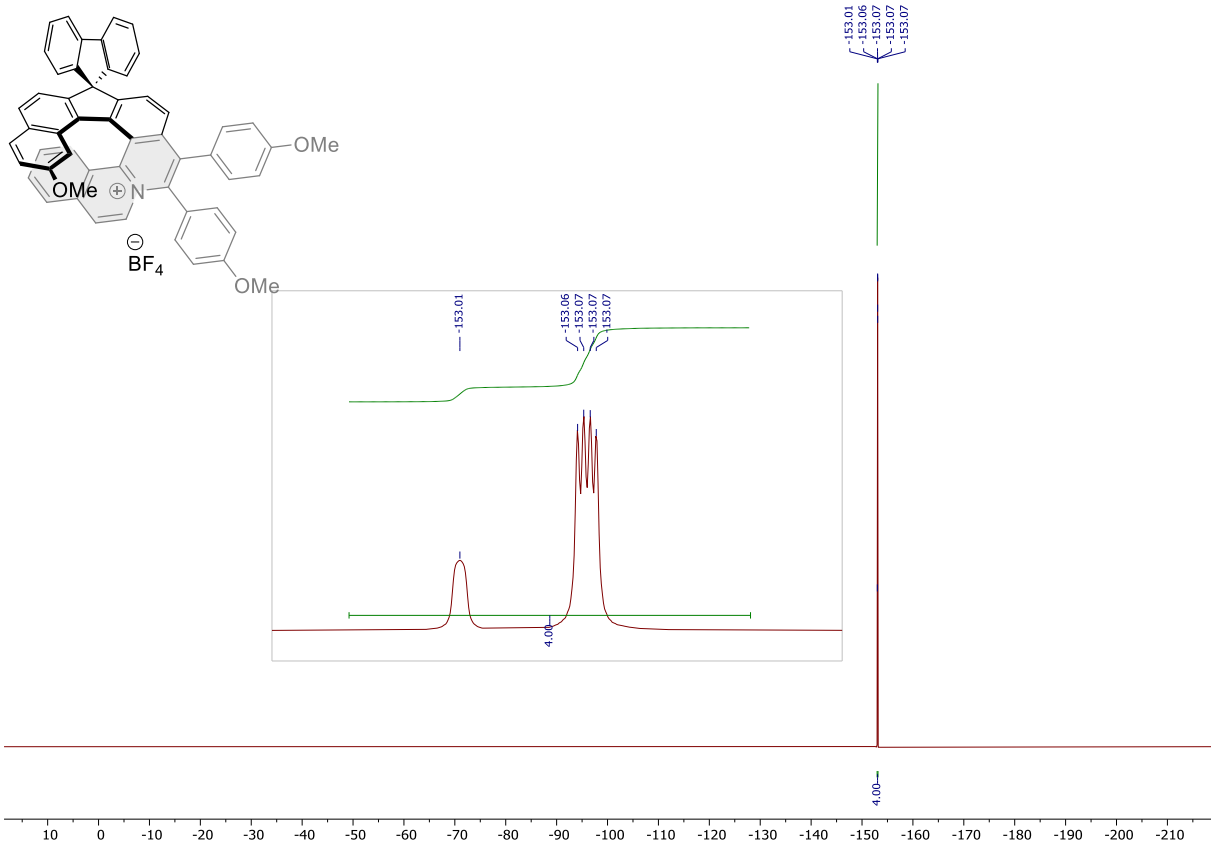


13-Methoxy-4,5-bis(4-methoxyphenyl)spiro[benzo[6,7]indeno[2,1-h]isoquinolino[1,2-a]isoquinoline-8,9'-fluoren]-3-ium tetrafluoroborate (1ba).

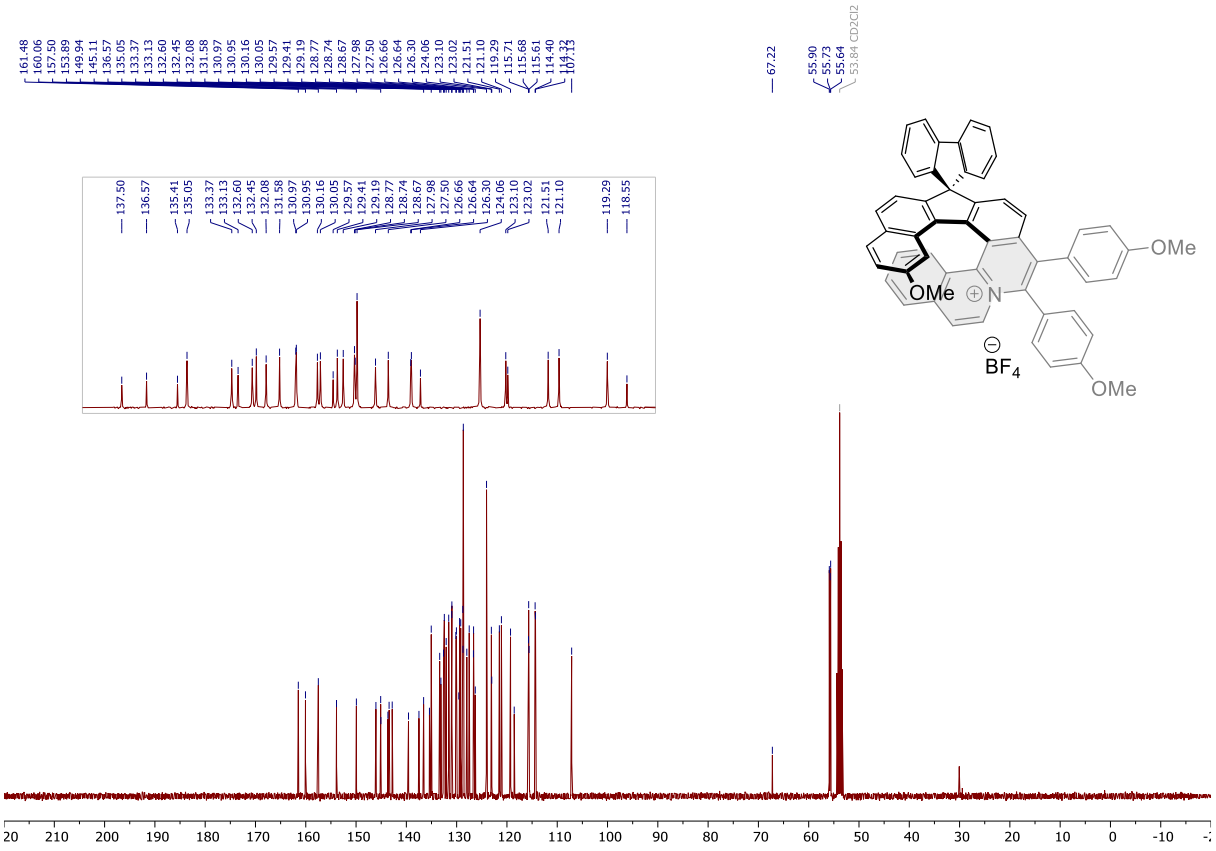
^{1}H NMR (CD_2Cl_2+$CDCl_3$)



^{19}F NMR (CD_2Cl_2)

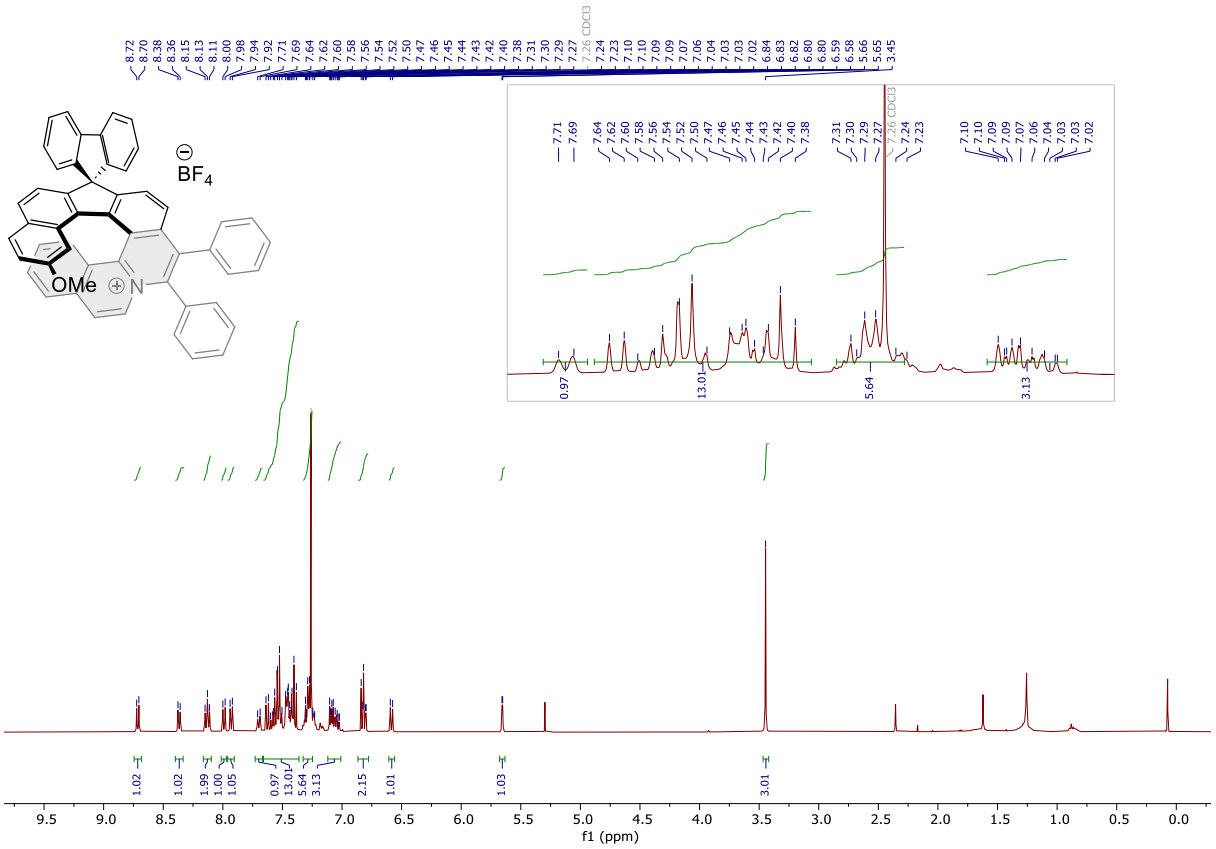


^{13}C NMR (CD_2Cl_2)

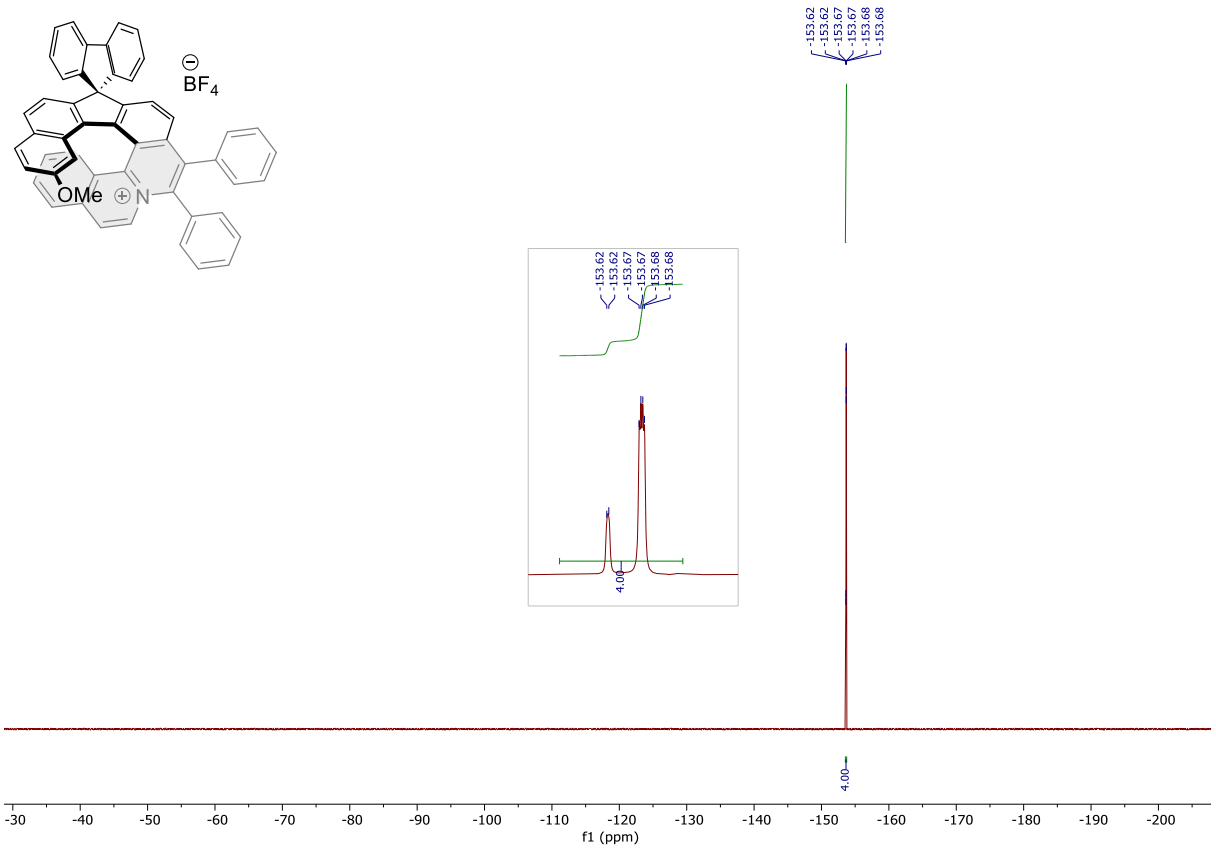


13-Methoxy-4,5-diphenylspiro[benzo[6,7]indeno[2,1-h]isoquinolino[1,2-a]isoquinoline-8,9'-fluoren]-3-ium tetrafluoroborate (1bb).

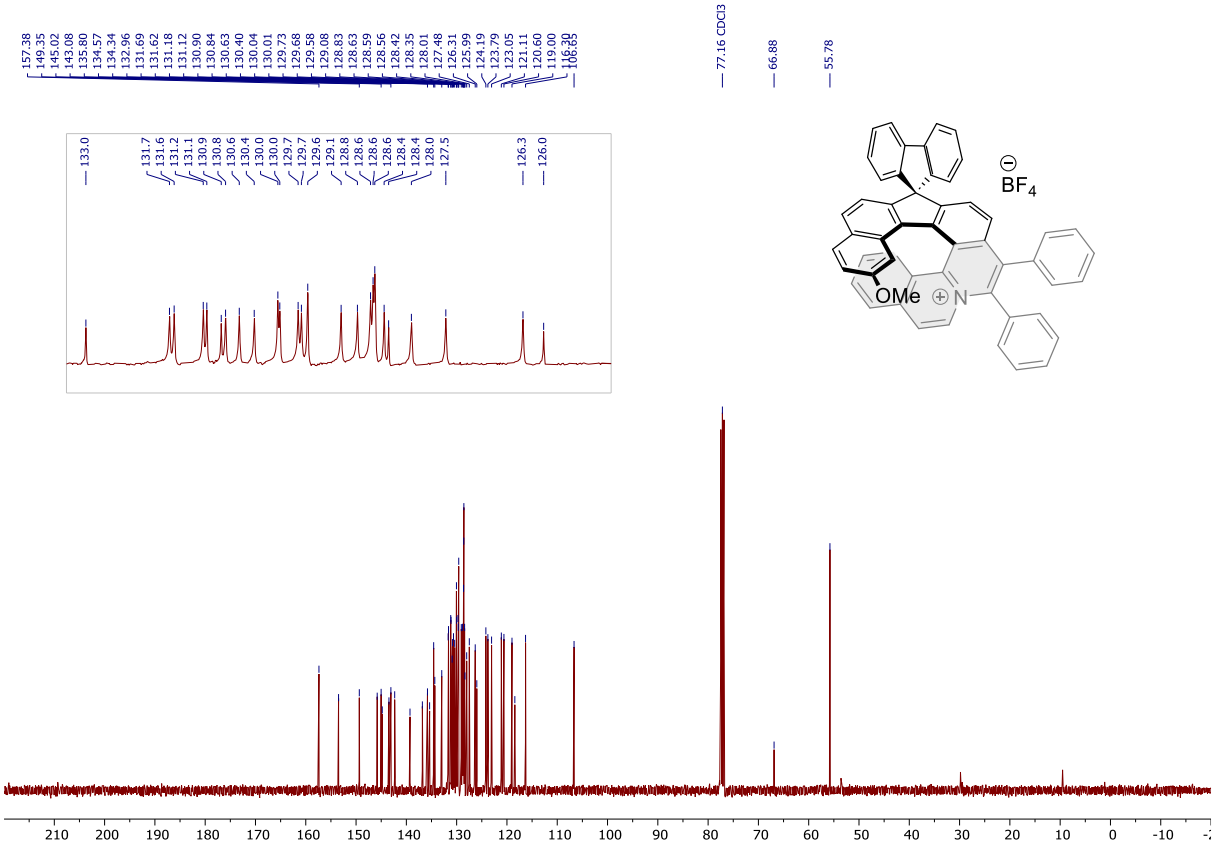
^{1}H NMR ($CDCl_3$)



^{19}F NMR ($CDCl_3$)

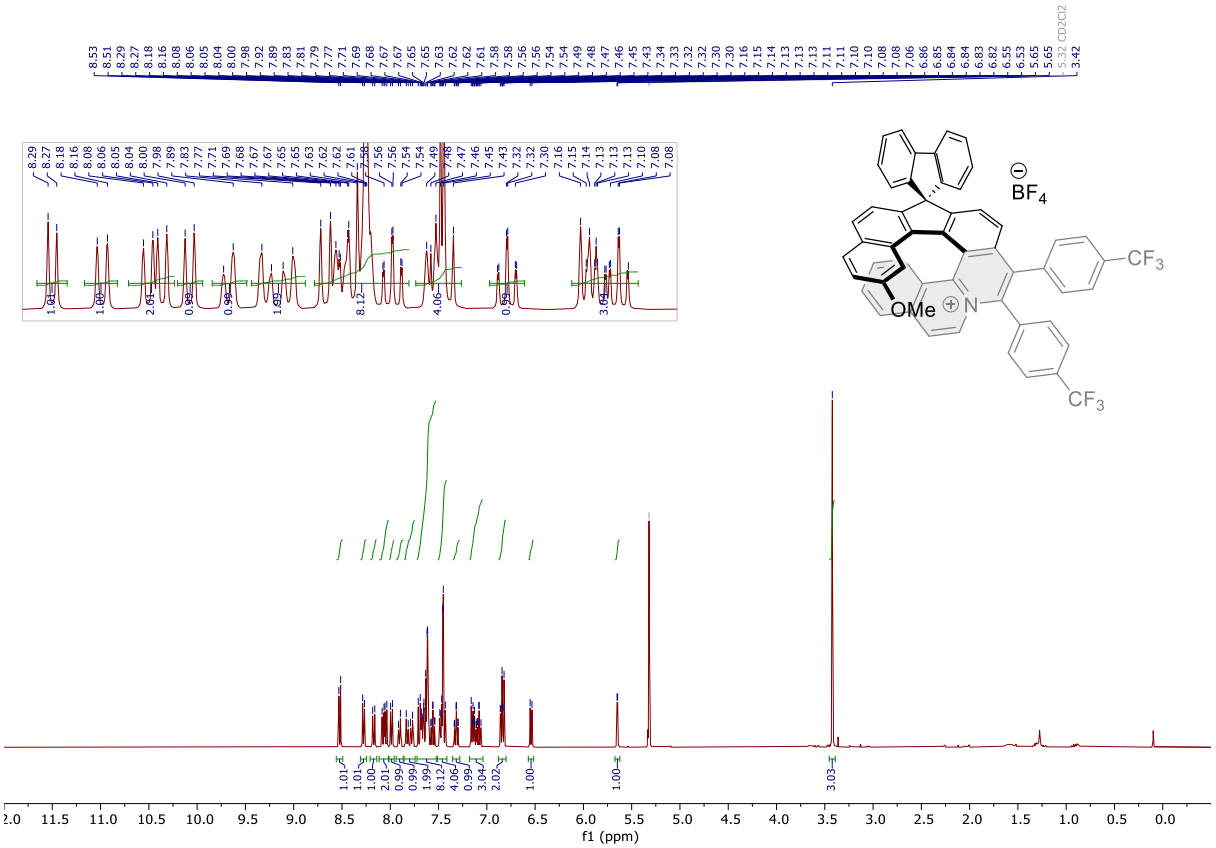


^{13}C NMR ($CDCl_3$)

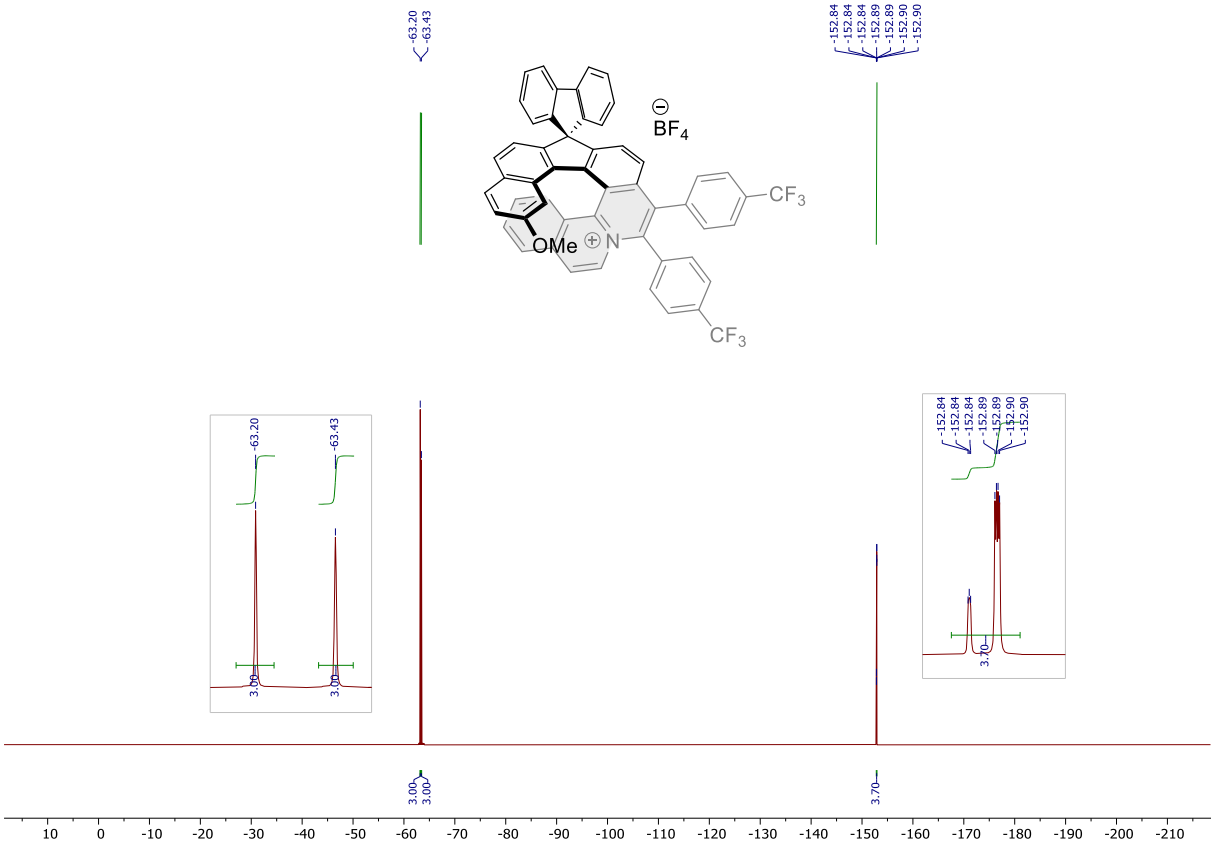


13-Methoxy-4,5-bis(4-(trifluoromethyl)phenyl)spiro[benzo[6,7]indeno[2,1-h]isoquinolino[1,2-a]isoquinoline-8,9'-fluoren]-3-ium tetrafluoroborate (1bc)

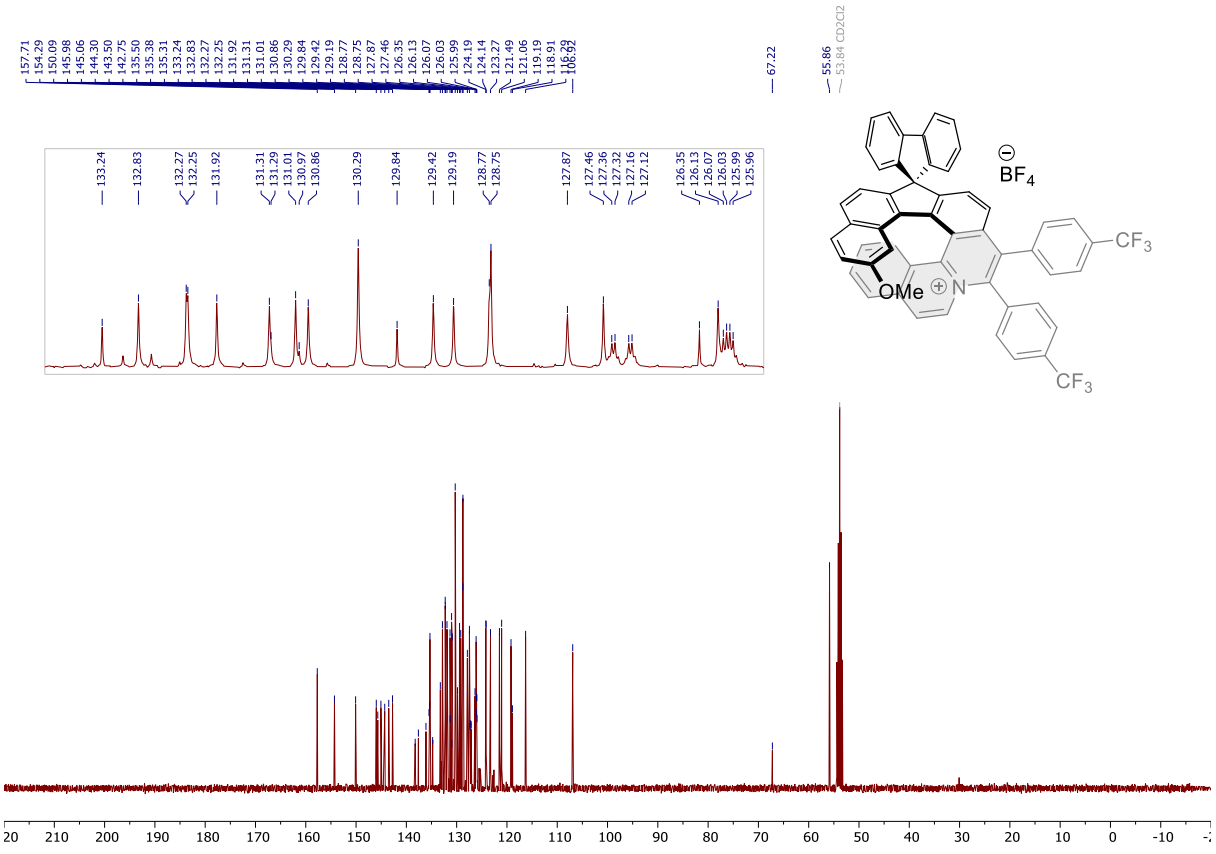
^{1}H NMR (CD_2Cl_2)



^{19}F NMR (CD_2Cl_2)

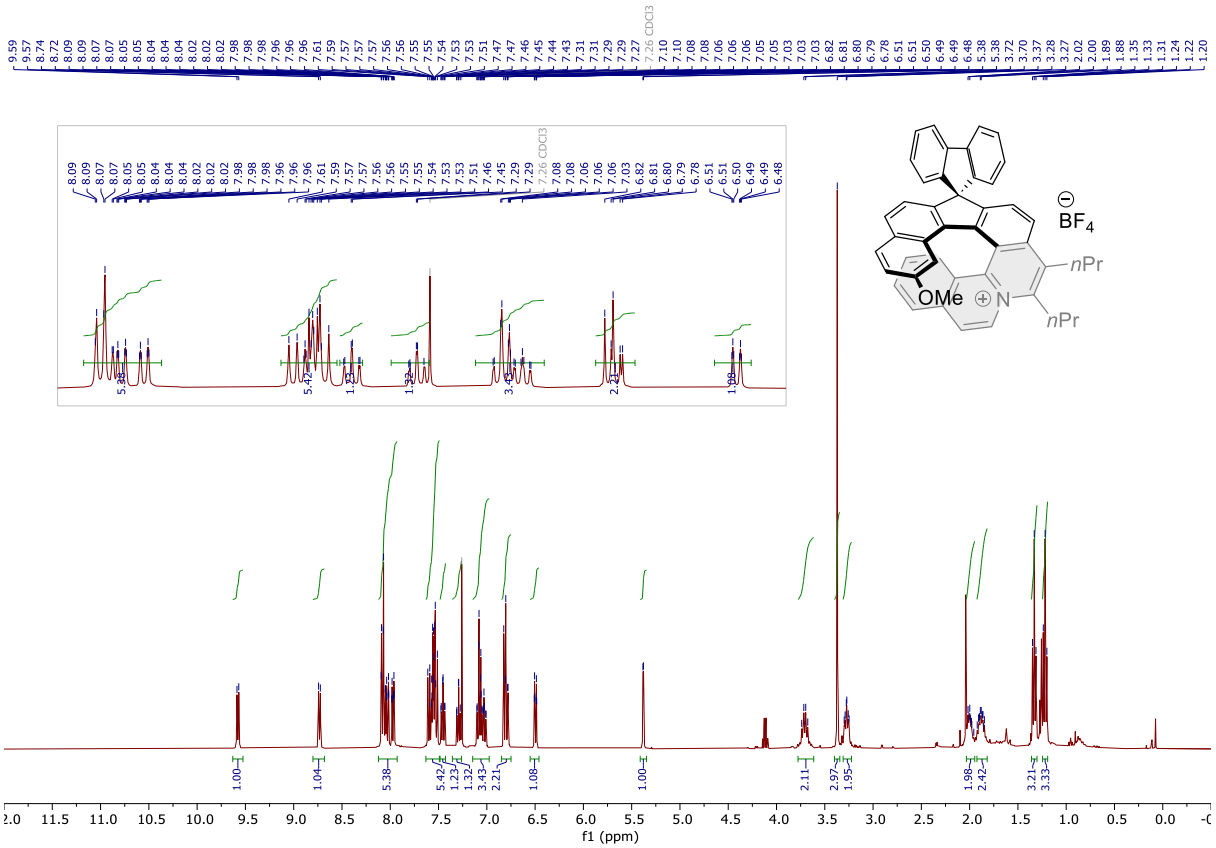


^{13}C NMR (CD_2Cl_2)

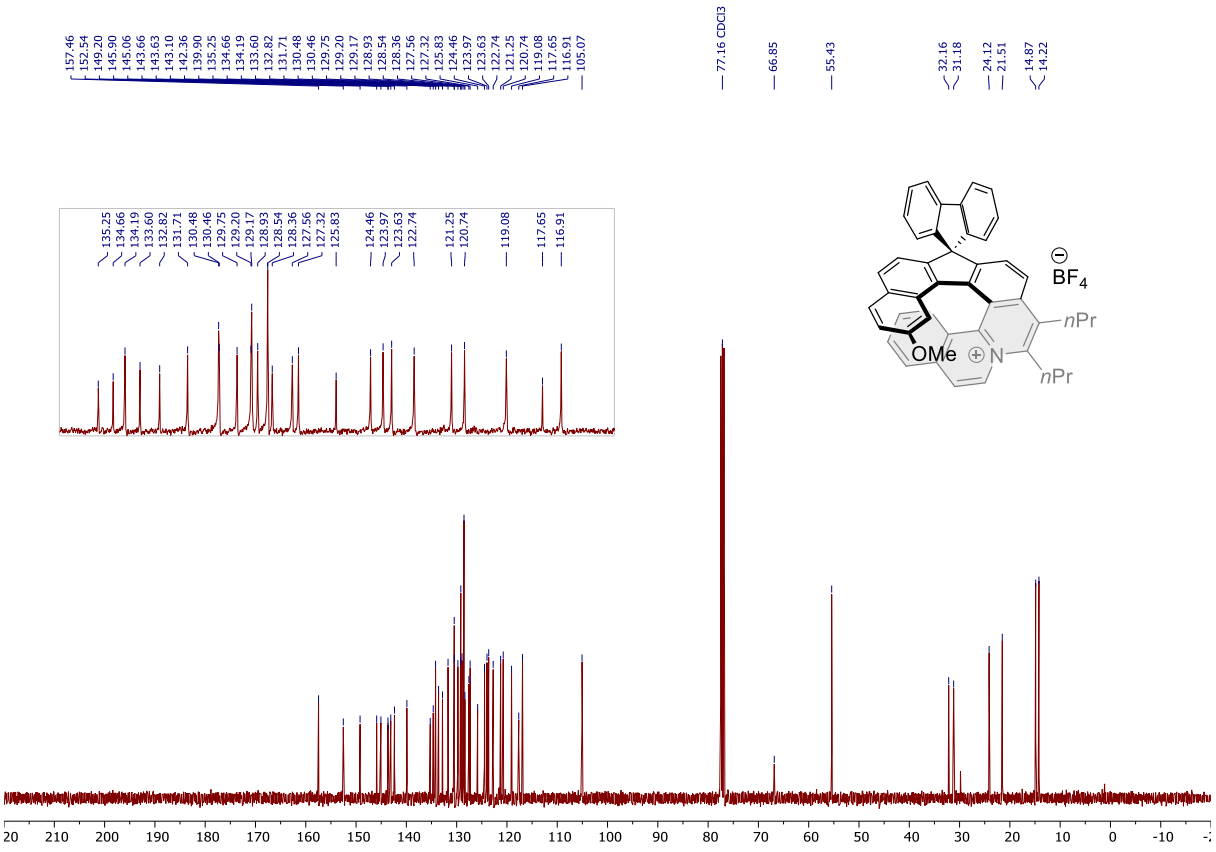


13-Methoxy-4,5-dipropylspiro[benzo[6,7]indeno[2,1-h]isoquinolino[1,2-a]isoquinoline-8,9'-fluoren]-3-ium tetrafluoroborate (1bd).

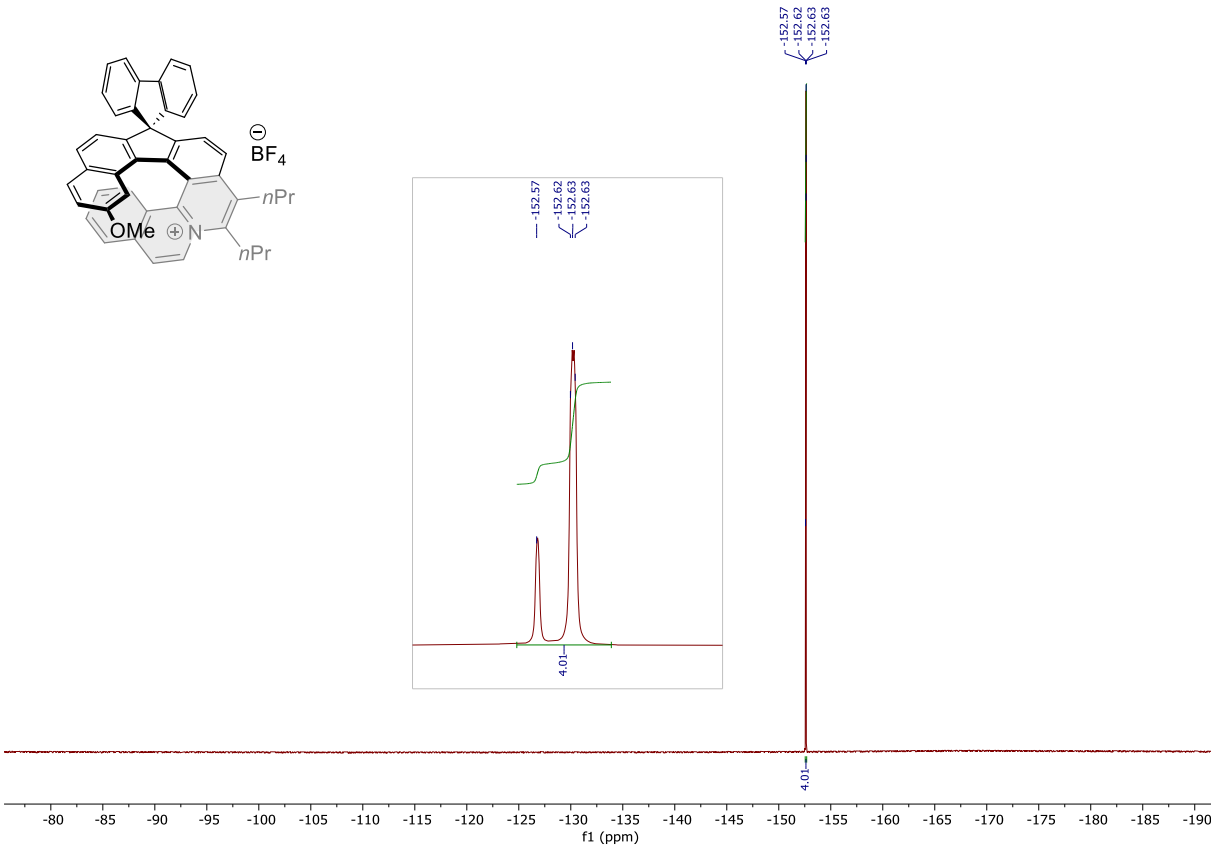
^{1}H NMR ($CDCl_3$)



^{13}C NMR ($CDCl_3$)

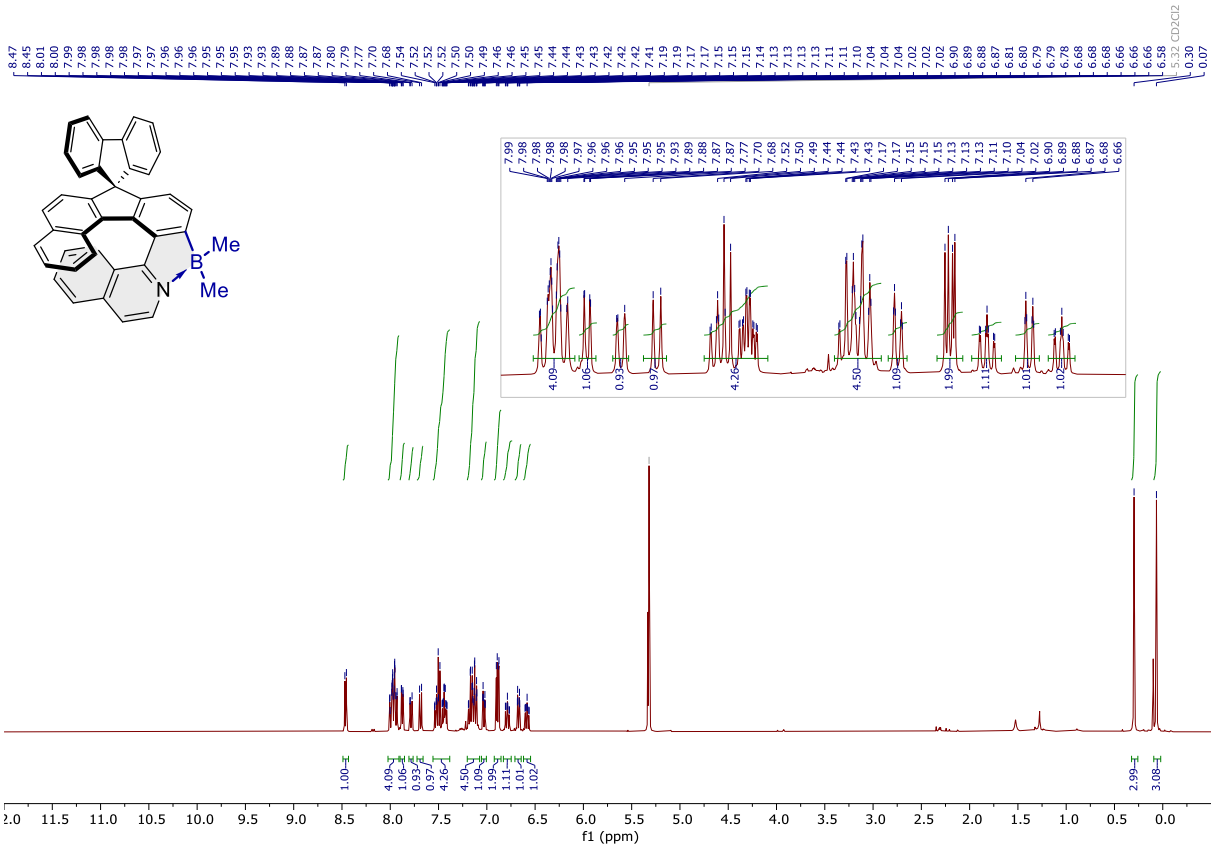


^{19}F NMR ($CDCl_3$)

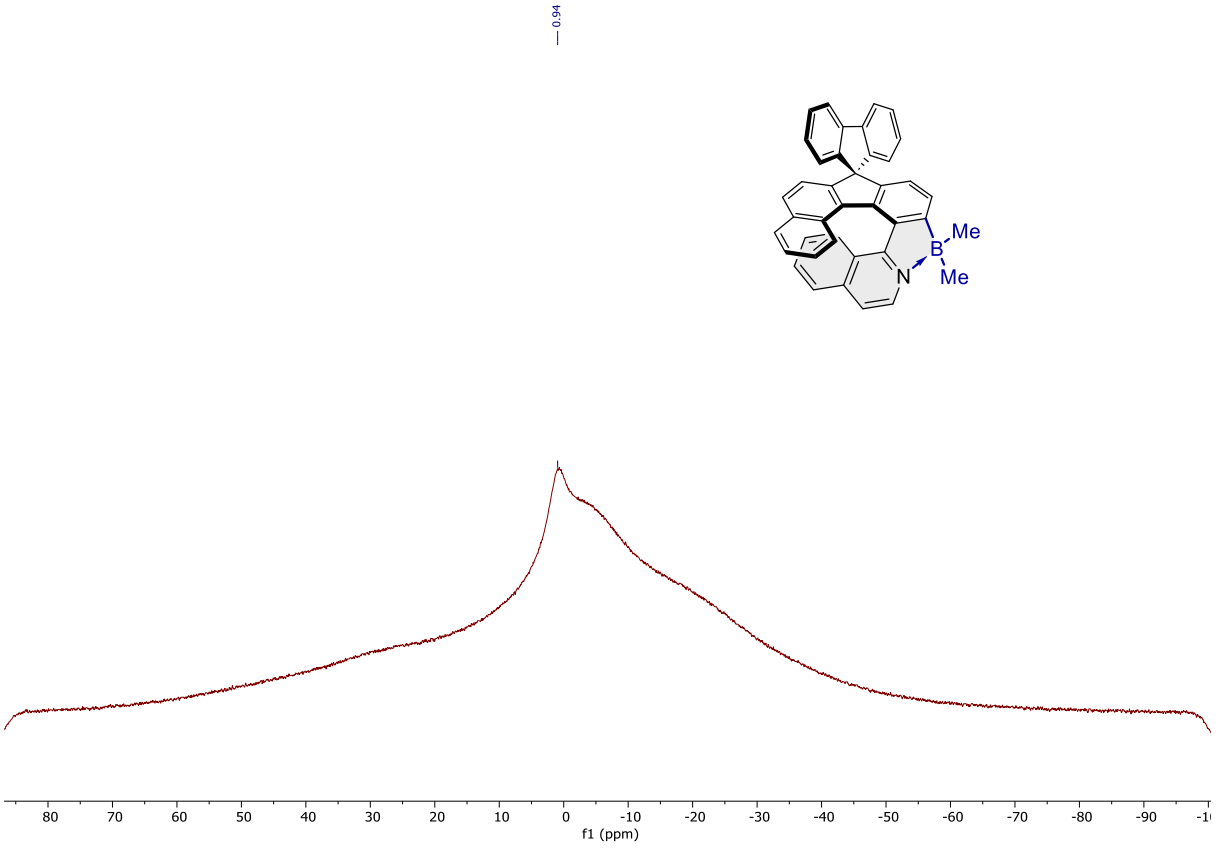


8,8-Dimethyl-8H-7l4,8l4-spiro[benzo[5',6']fluoreno[3',4':3,4][1,2]azaborolo[5,1-a]isoquinoline-11,9'-fluorene] (2a).

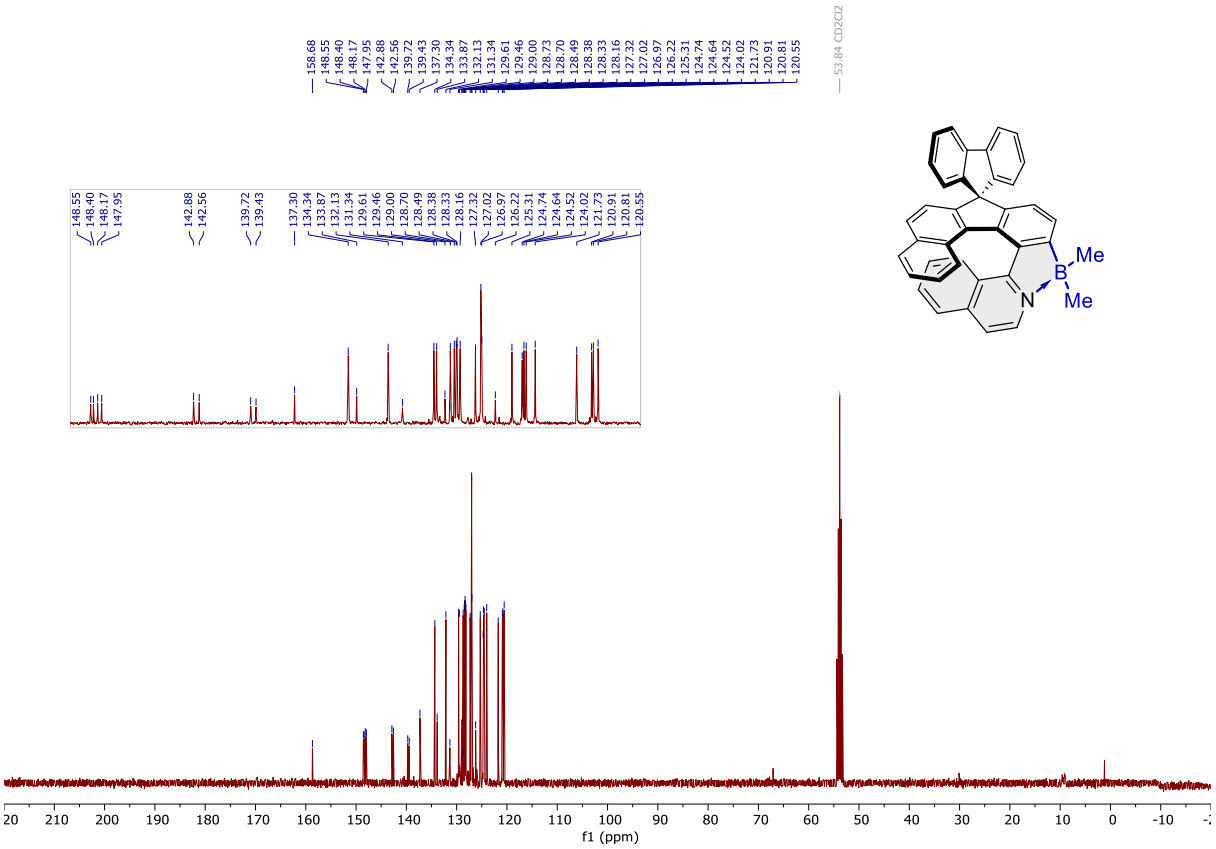
^{1}H NMR (CD_2Cl_2)



^{11}B NMR (CD_2Cl_2)

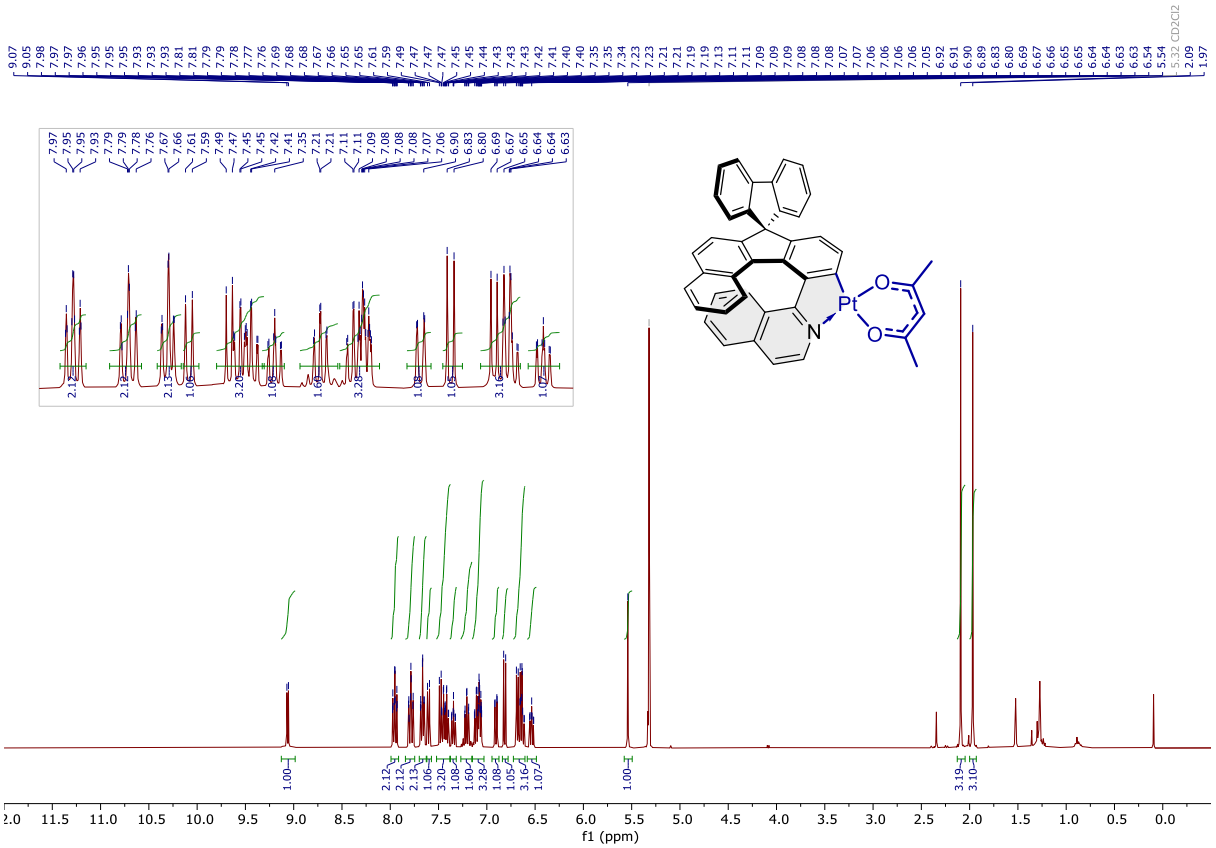


^{13}C NMR (CD_2Cl_2)

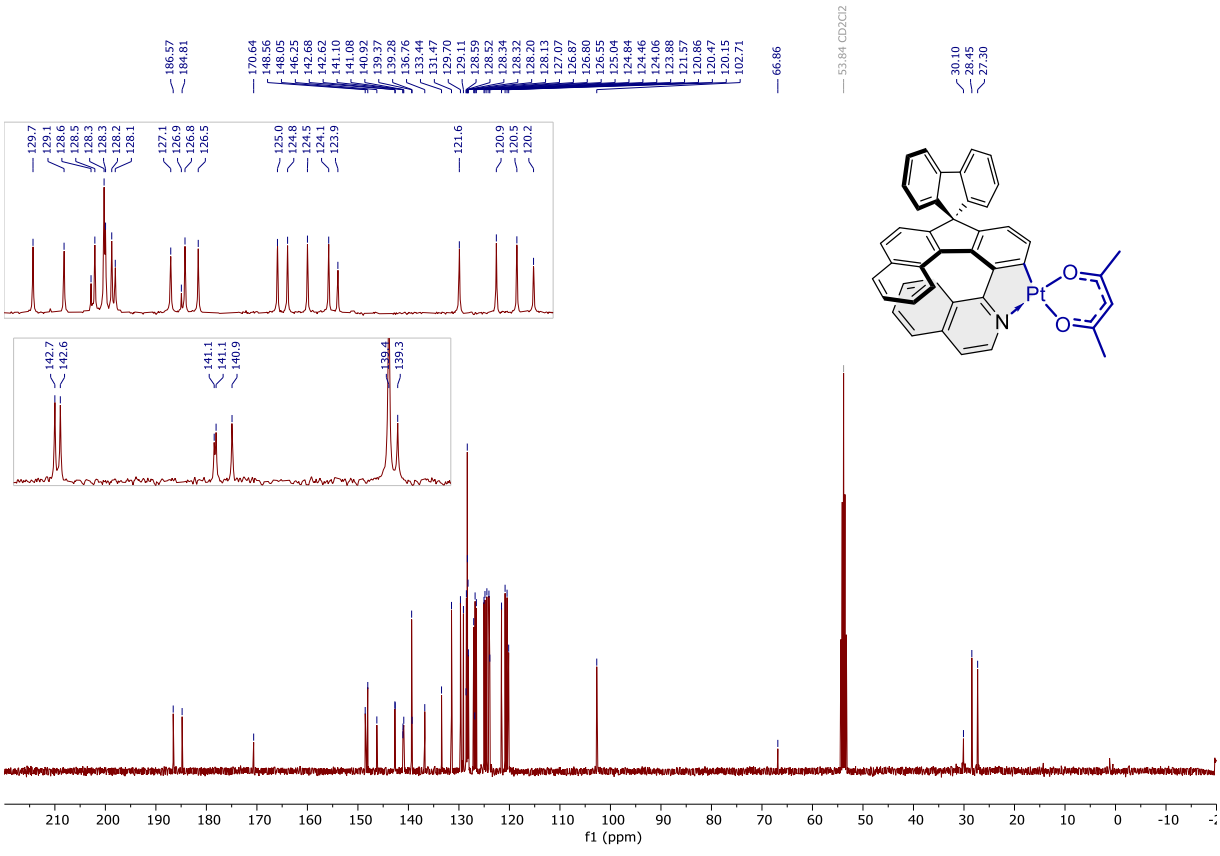


(1-(Spiro[benzo[*c*]fluorene-7,9'-fluoren]-11-yl)isoquinolinato-N,C^{10})platinum-acetylacetonate (2b).

^{1}H NMR (CD_2Cl_2)



^{13}C NMR (CD_2Cl_2)



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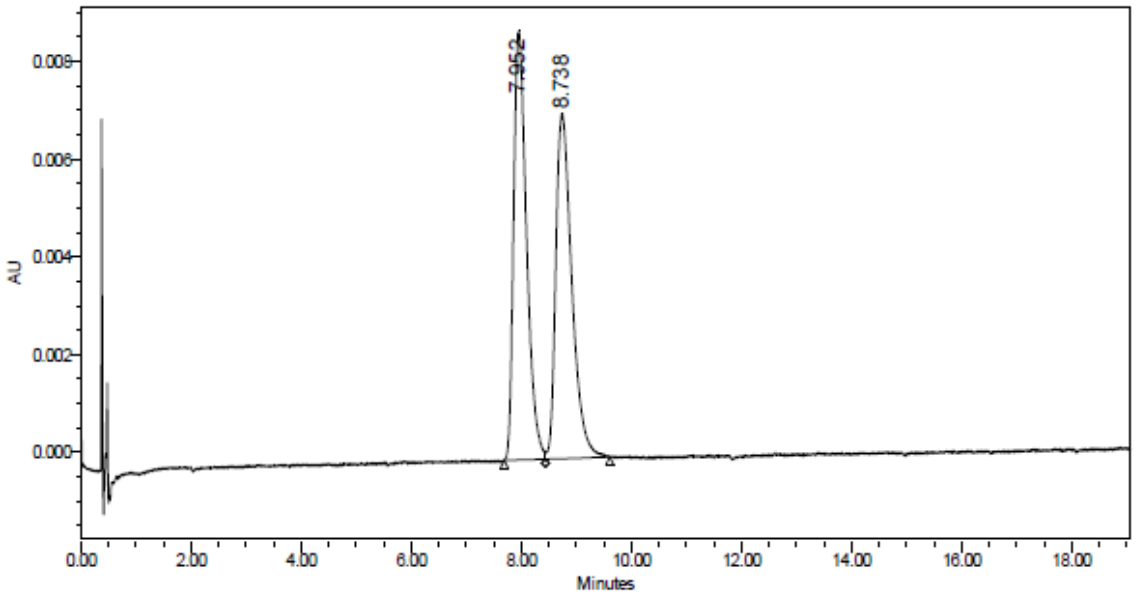
SFC conditions: Column Chiralart Cellulose-SB (150 x 3.0 mm I.D., 3µm), mobile phase: CO_2/ethanol/isopropylamine/trifluoroacetic acid 85/15/0.1/0.1 (v/v/v/v), column temperature 40°C, mobile phase flow: 2 mL/min, Back pressure regulator: 2000 psi.

SAMPLE INFORMATION

Sample Name:		Acquired By:	System
Sample Type:	Unknown	Sample Set Name:	
Vial:	1:E,1	Acq. Method Set:	85CO2_15B1_2ml40C2000ps
Injection #:	1	Processing Method	LF40
Injection Volume:	1.00 ul	Channel Name:	PDA Ch1 254nm@4.8nm
Run Time:	20.0 Minutes	Proc. Chnl. Descr.:	PDA Ch1 254nm@4.8nm
Date Acquired:	10/26/2022 10:15:19 AM CEST		
Date Processed:	5/11/2023 12:02:51 PM CEST		

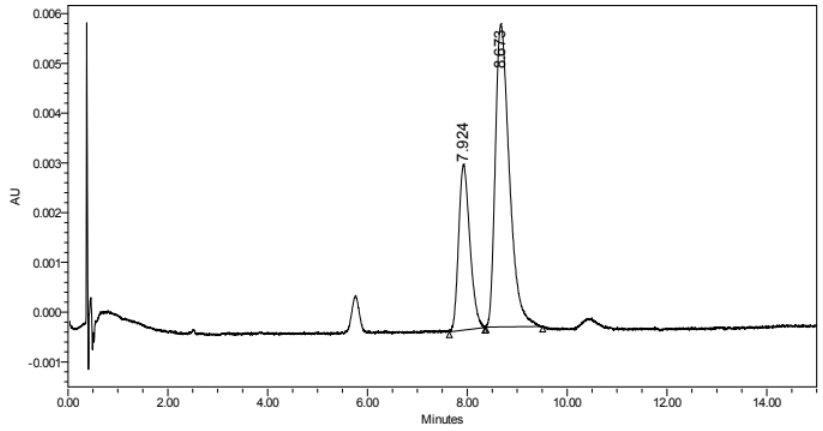


	RT	Area	% Area	Height
1	7.952	142838	49.97	8782
2	8.738	142986	50.03	7071

Figure S13. Chromatogram of racemic **1ac**.

SAMPLE INFORMATION

Sample Name:	LF135B	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	LF135B
Vial:	1:A,1	Acq. Method Set:	85CO2_15B1_2ml40C2000ps
Injection #:	1	Processing Method	0604
Injection Volume:	1.00 ul	Channel Name:	PDA Ch1 254nm@4.8nm
Run Time:	15.0 Minutes	Proc. Chnl. Descr.:	PDA Ch1 254nm@4.8nm
Date Acquired:	4/6/2023 11:40:49 AM CEST		
Date Processed:	4/6/2023 12:38:38 PM CEST		

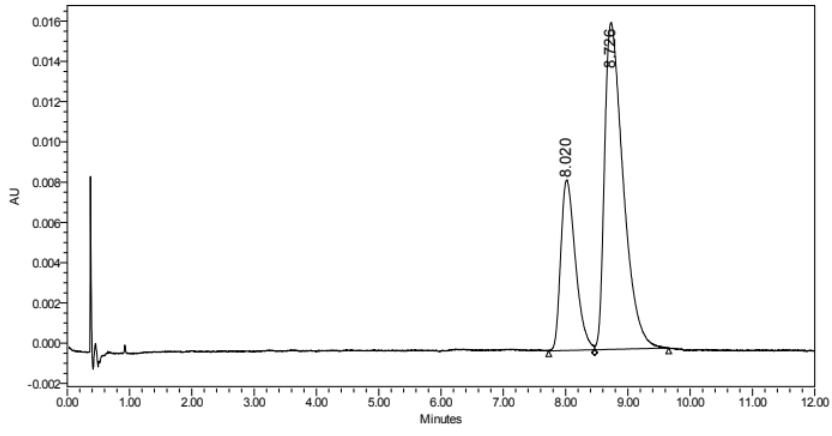


	RT	Area	% Area	Height
1	7.924	51987	30.45	3333
2	8.673	118751	69.55	6090

Figure S14. Table S4, chromatogram of Entry 1.

SAMPLE INFORMATION

Sample Name:		Acquired By:	Kveta
Sample Type:	Unknown	Sample Set Name	
Vial:	1:A,2	Acq. Method Set:	85CO2_15B1_2ml40C2000ps
Injection #:	2	Processing Method	LF111
Injection Volume:	1.00 ul	Channel Name:	PDA Ch1 254nm@4.8nm
Run Time:	12.0 Minutes	Proc. Chnl. Descr.:	PDA Ch1 254nm@4.8nm
Date Acquired:	1/31/2023 11:04:01 AM CET		
Date Processed:	1/31/2023 11:27:35 AM CET		

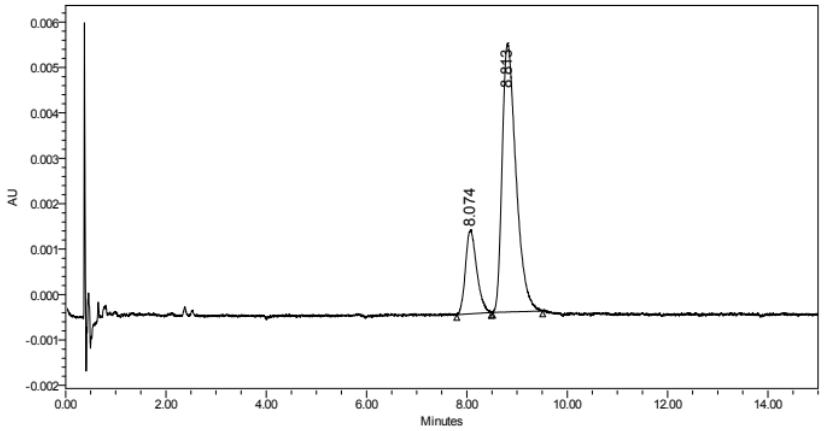


	RT	Area	% Area	Height
1	8.020	138490	29.04	8466
2	8.726	338366	70.96	16227

Figure S15. Table S4, chromatogram of Entry 2.

SAMPLE INFORMATION

Sample Name:		Acquired By:	Kveta
Sample Type:	Unknown	Sample Set Name	
Vial:	1:A,1	Acq. Method Set:	85CO2_15B1_2ml40C2000ps
Injection #:	1	Processing Method	LF108
Injection Volume:	1.00 ul	Channel Name:	PDA Ch1 254nm@4.8nm
Run Time:	15.0 Minutes	Proc. Chnl. Descr.:	PDA Ch1 254nm@4.8nm
Date Acquired:	1/24/2023 11:05:25 AM CET		
Date Processed:	1/24/2023 11:39:26 AM CET		

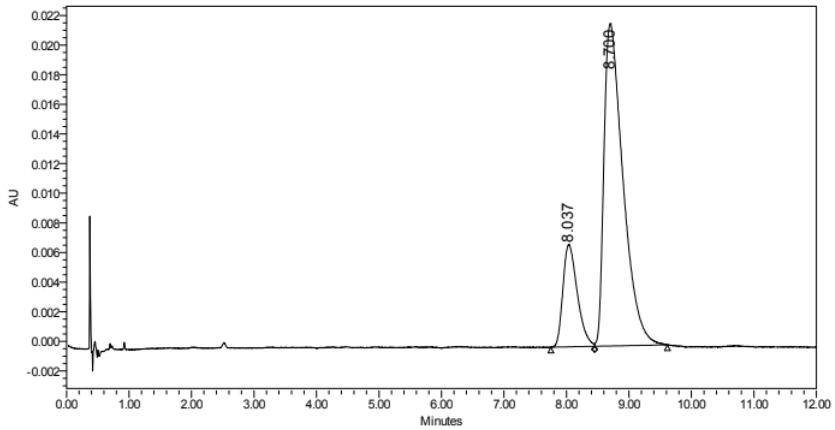


	RT	Area	% Area	Height
1	8.074	28703	20.24	1847
2	8.813	113099	79.76	5923

Figure S16. Table S4, chromatogram of Entry 3.

SAMPLE INFORMATION

Sample Name:		Acquired By:	Kveta
Sample Type:	Unknown	Sample Set Name	
Vial:	1:A,1	Acq. Method Set:	85CO2_15B1_2ml40C2000ps
Injection #:	2	Processing Method	LF110
Injection Volume:	1.00 ul	Channel Name:	PDA Ch1 254nm@4.8nm
Run Time:	12.0 Minutes	Proc. Chnl. Descr.:	PDA Ch1 254nm@4.8nm
Date Acquired:	1/31/2023 10:39:13 AM CET		
Date Processed:	1/31/2023 11:26:22 AM CET		

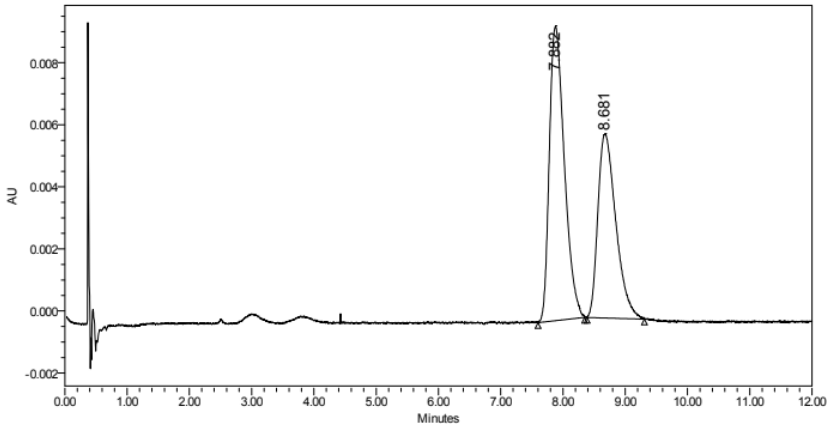


	RT	Area	% Area	Height
1	8.037	109904	19.24	6902
2	8.700	461437	80.76	21761

Figure S17. Table S4, chromatogram of Entry 4.

SAMPLE INFORMATION

Sample Name:		Acquired By:	System
Sample Type:	Unknown	Sample Set Name	
Vial:	1:E,4	Acq. Method Set:	85CO2_15B1_2ml40C2000ps
Injection #:	1	Processing Method	LF77
Injection Volume:	1.00 ul	Channel Name:	PDA Ch1 254nm@4.8nm
Run Time:	12.0 Minutes	Proc. Chnl. Descr.:	PDA Ch1 254nm@4.8nm
Date Acquired:	10/26/2022 11:14:16 AM CEST		
Date Processed:	10/26/2022 1:41:00 PM CEST		

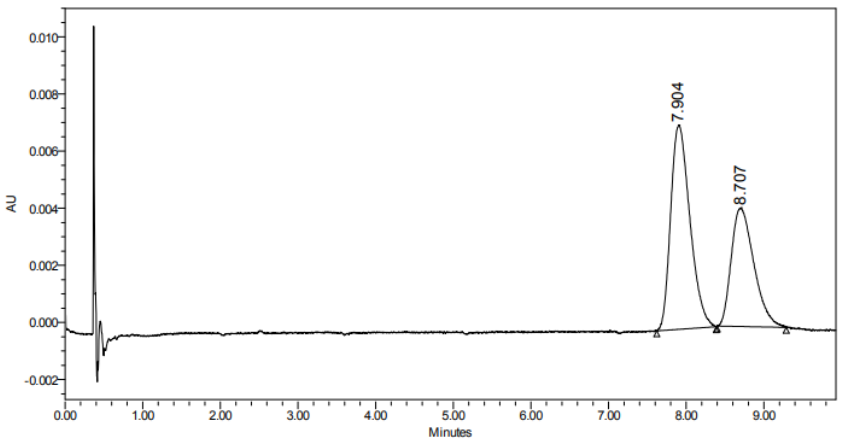


	RT	Area	% Area	Height
1	7.882	158608	57.15	9504
2	8.681	118925	42.85	5945

Figure S18. Table S4, chromatogram of Entry 5.

SAMPLE INFORMATION

Sample Name:		Acquired By:	System
Sample Type:	Unknown	Sample Set Name	
Vial:	1:E,3	Acq. Method Set:	85CO2_15B1_2ml40C2000ps
Injection #:	2	Processing Method	LF74
Injection Volume:	2.00 ul	Channel Name:	PDA Ch1 254nm@4.8nm
Run Time:	12.0 Minutes	Proc. Chnl. Descr.:	PDA Ch1 254nm@4.8nm
Date Acquired:	10/26/2022 10:57:20 AM CEST		
Date Processed:	10/26/2022 1:39:20 PM CEST		

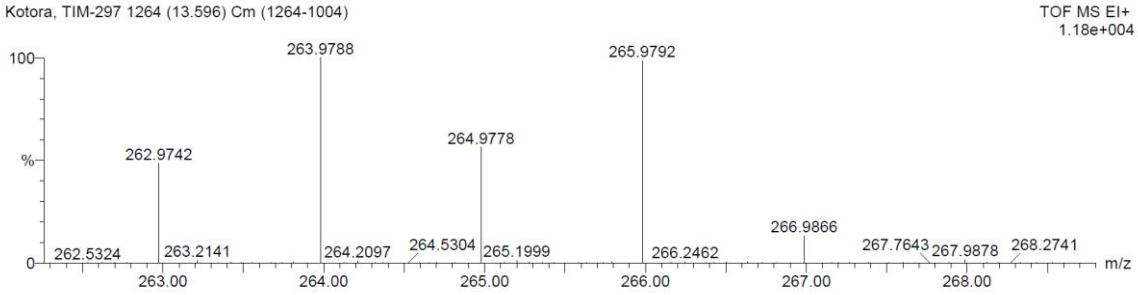


	RT	Area	% Area	Height
1	7.904	123403	59.47	7155
2	8.707	84091	40.53	4154

Figure S19. Table S4, chromatogram of Entry 6.

9 Copies of HRMS spectra

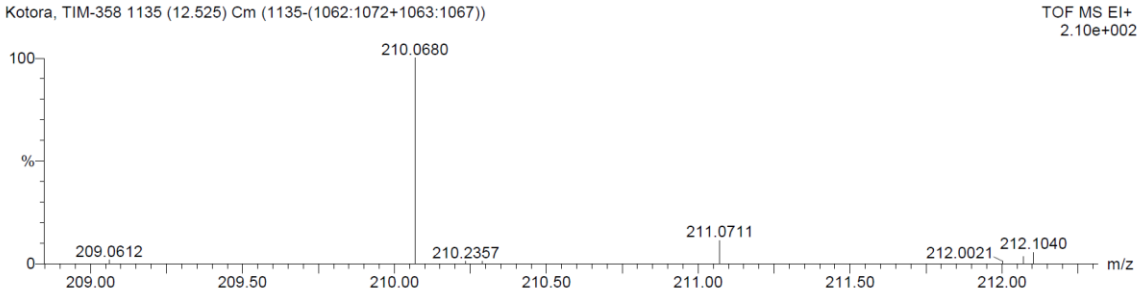
1-Bromo-7-methoxy-2-naphthaldehyde (S1b).



Minimum:				-1.5		
Maximum:		5.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
263.9788	263.9786	0.2	0.8	8.0	1887.2	C12 H9 O2 Br

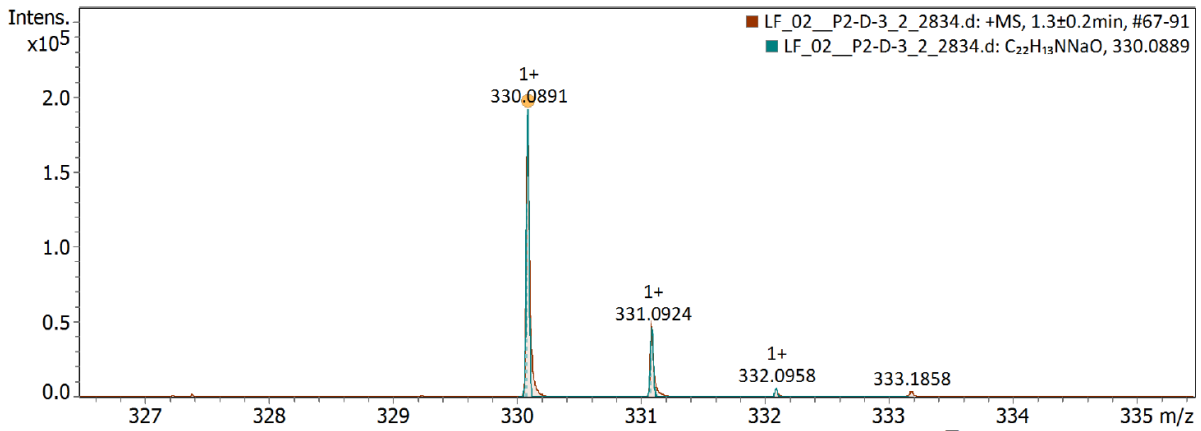
1-Ethynyl-7-methoxy-2-naphthaldehyde (S2b).

Monoisotopic Mass, Odd and Even Electron Ions
2 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-14 H: 0-10 O: 0-2



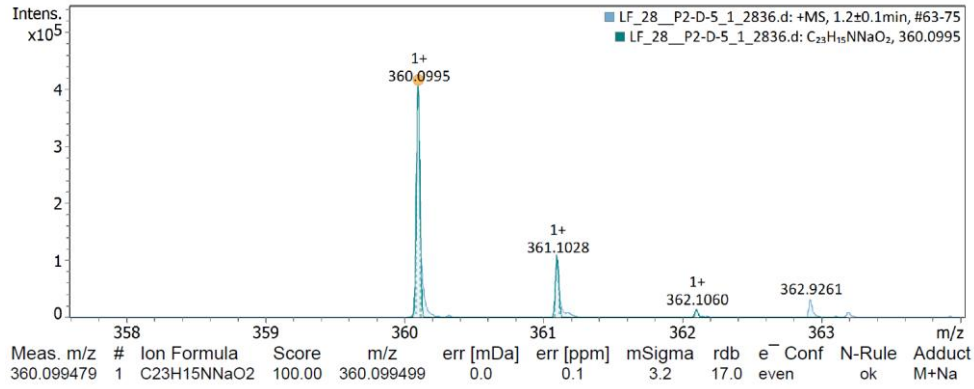
Minimum:				-1.5		
Maximum:		5.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
210.0680	210.0681	-0.1	-0.5	10.0	2.8	C14 H10 O2

1-(Isoquinolin-1-ylethynyl)-2-naphthaldehyde (S3a).

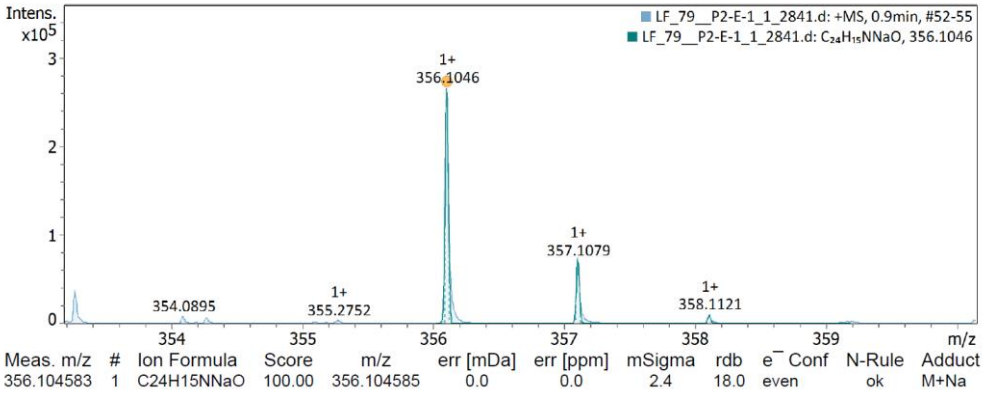


Meas. m/z	#	Ion Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule	Adduct
330.089128	1	C22H13NNaO	100.00	330.088935	-0.2	-0.6	2.1	17.0	even	ok	M+Na

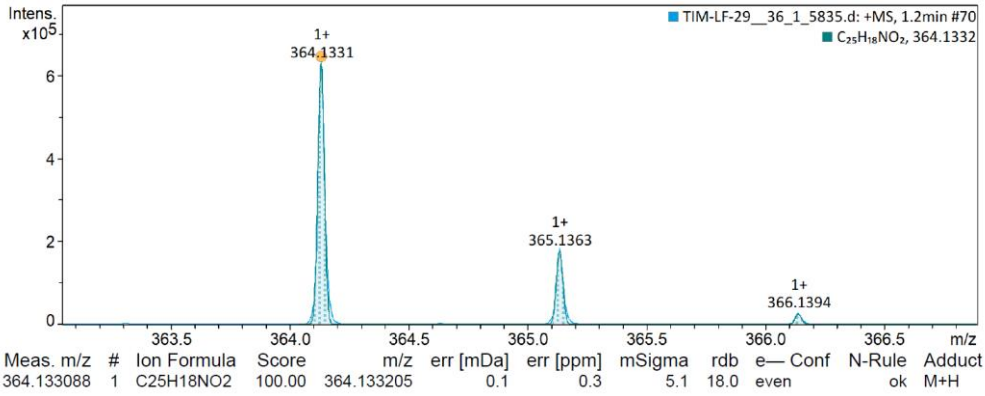
1-(Isoquinolin-1-ylethynyl)-7-methoxy-2-naphthaldehyde (S3b).



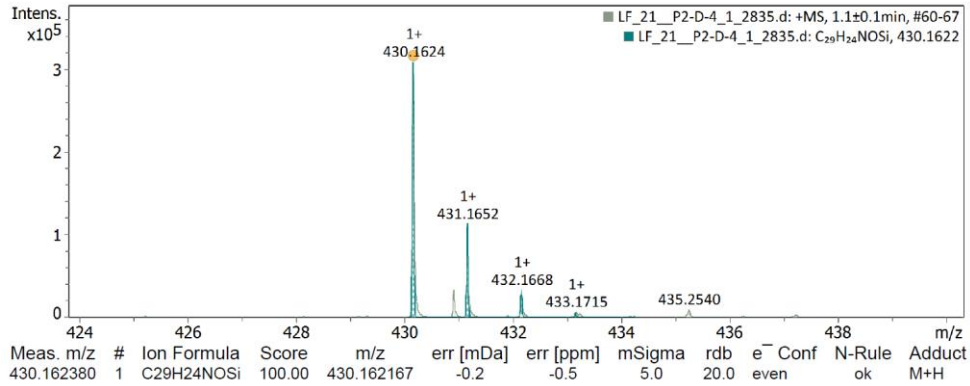
1-(1-(Isoquinolin-1-ylethynyl)naphthalen-2-yl)prop-2-yn-1-ol (3a).



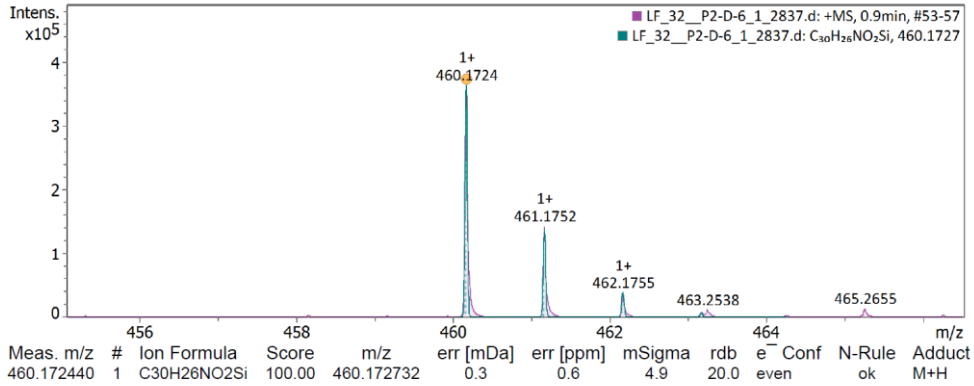
1-(1-(Isoquinolin-1-ylethynyl)-7-methoxynaphthalen-2-yl)prop-2-yn-1-ol (3b).



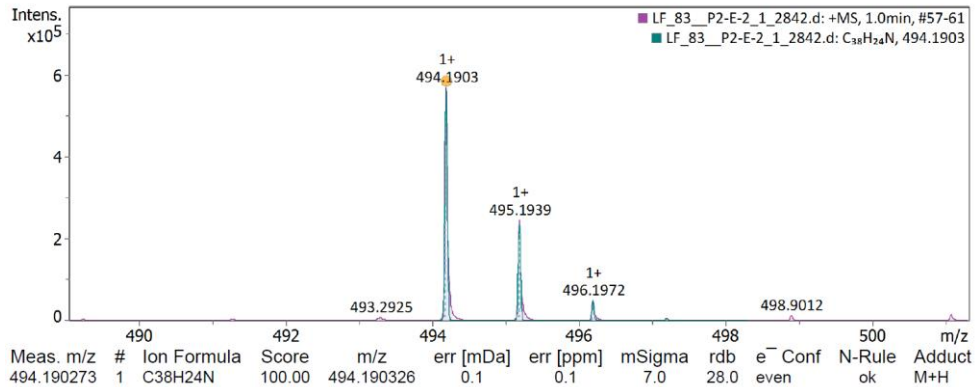
11-(Naphthalen-1-yl)-10-(trimethylsilyl)-7*H*-benzo[*c*]fluoren-7-one (4a).



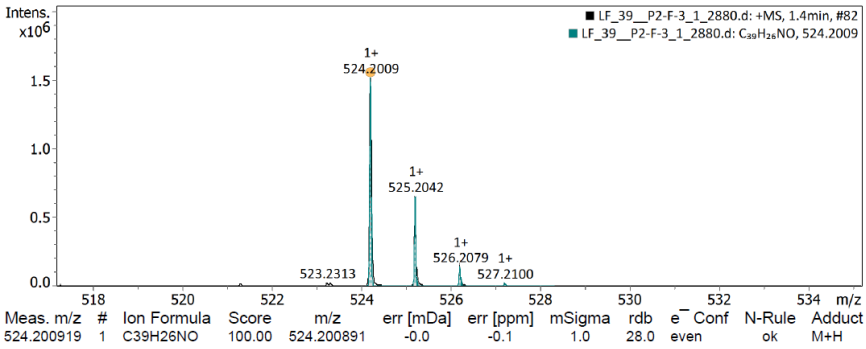
2-Methoxy-11-(naphthalen-1-yl)-10-(trimethylsilyl)-7*H*-benzo[*c*]fluoren-7-one (4b).



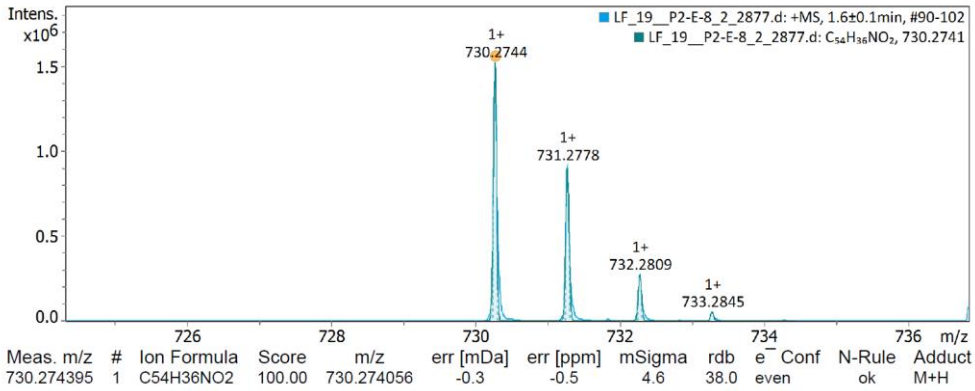
1-(Spiro[benzo[*c*]fluorene-7,9'-fluoren]-11-yl)isoquinoline (5a).



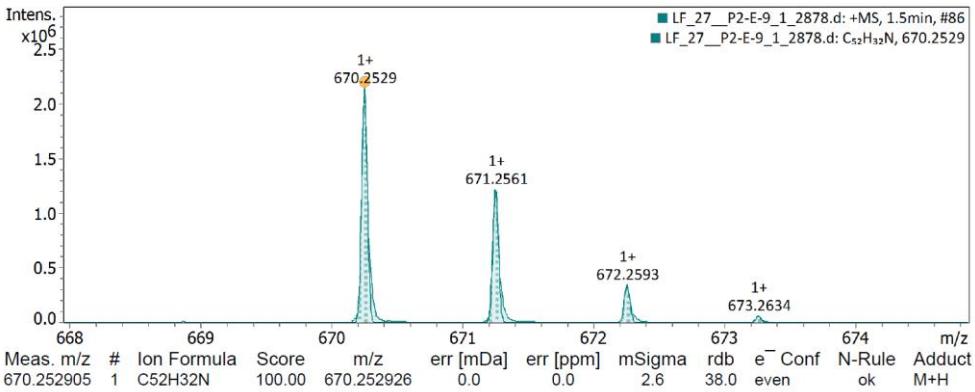
1-(2-Methoxyspiro[benzo[*c*]fluorene-7,9'-fluoren]-11-yl)isoquinoline (5b).



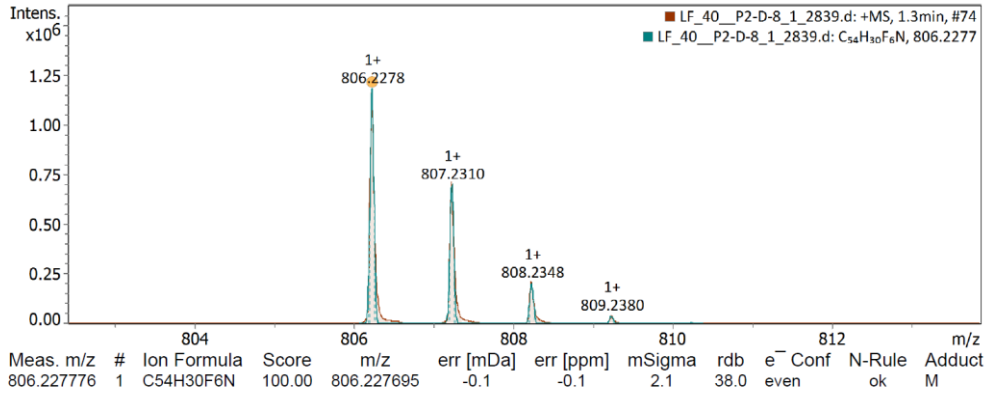
4,5-Bis(4-methoxyphenyl)spiro[benzo[6,7]indeno[2,1-*h*]isoquinolino[1,2-*a*]isoquinoline-8,9'-fluoren]-3-ium tetrafluoroborate (1aa).



4,5-Diphenylspiro[benzo[6,7]indeno[2,1-*h*]isoquinolino[1,2-*a*]isoquinoline-8,9'-fluoren]-3-ium tetrafluoroborate (1ab).

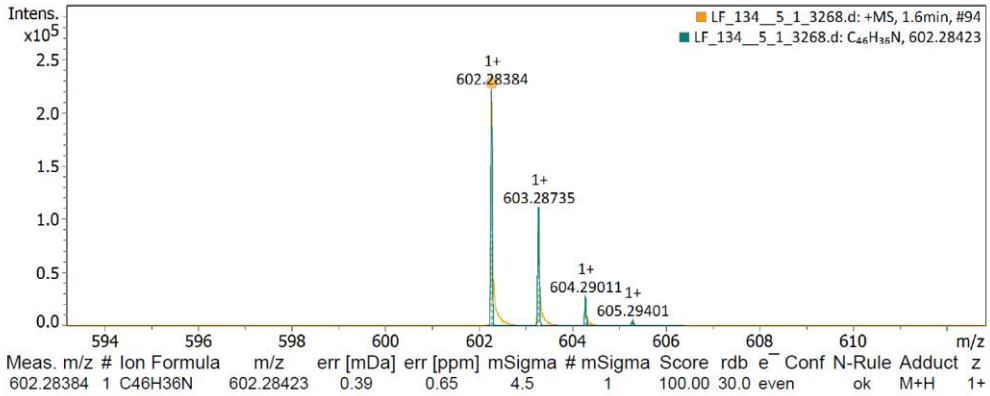


4,5-bis(4-(trifluoromethyl)phenyl)spiro[benzo[6,7]indeno[2,1-*h*]isoquinolino[1,2-*a*]isoquinoline-8,9'-fluoren]-3-ium tetrafluoroborate (1ac).



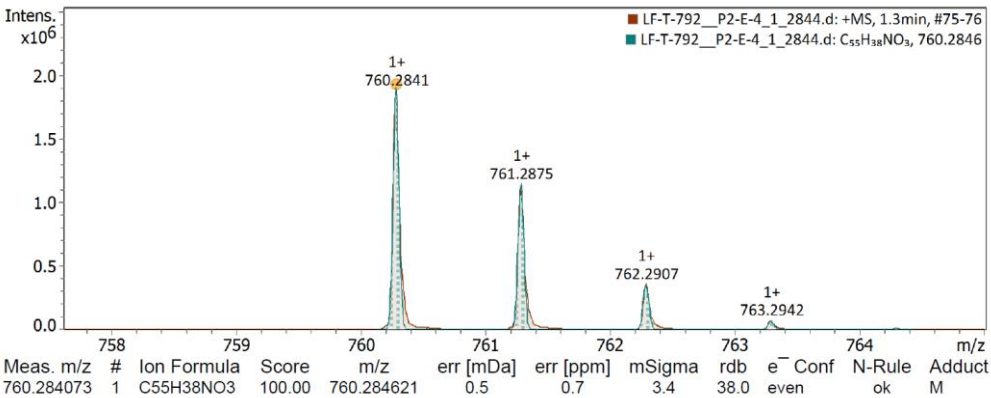
Meas. m/z	#	Ion Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule	Adduct
806.227776	1	C54H30F6N	100.00	806.227695	-0.1	-0.1	2.1	38.0	even	ok	M

4,5-Dipropylspiro[benzo[6,7]indeno[2,1-*h*]isoquinolino[1,2-*a*]isoquinoline-8,9'-fluoren]-3-ium tetrafluoroborate (1ad).



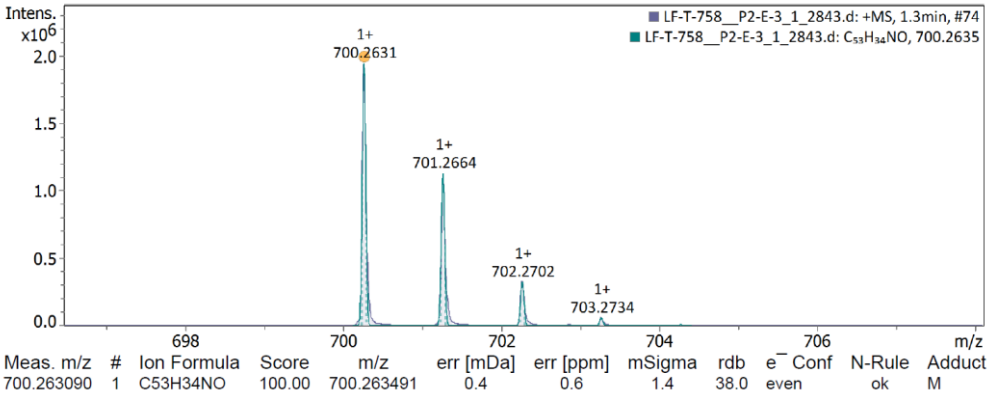
Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule	Adduct	z
602.28384	1	C46H36N	602.28423	0.39	0.65	4.5	1	100.00	30.0	even	ok	M+H	1+

13-Methoxy-4,5-bis(4-methoxyphenyl)spiro[benzo[6,7]indeno[2,1-*h*]isoquinolino[1,2-*a*]isoquinoline-8,9'-fluoren]-3-ium tetrafluoroborate (1ba).

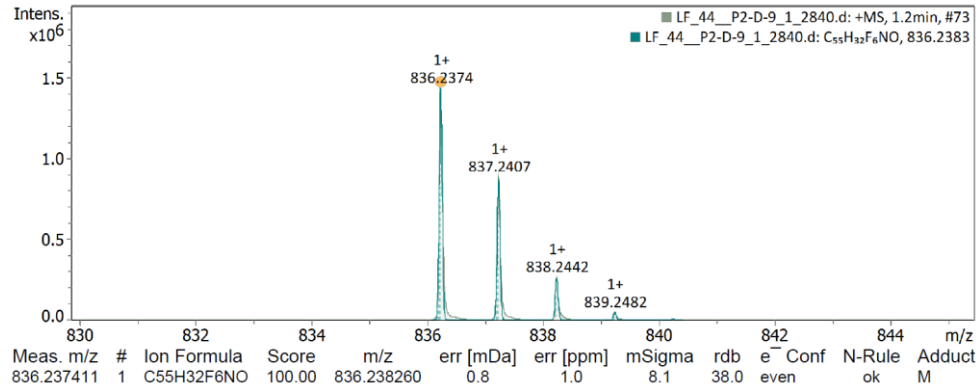


Meas. m/z	#	Ion Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule	Adduct
760.284073	1	C55H38NO3	100.00	760.284621	0.5	0.7	3.4	38.0	even	ok	M

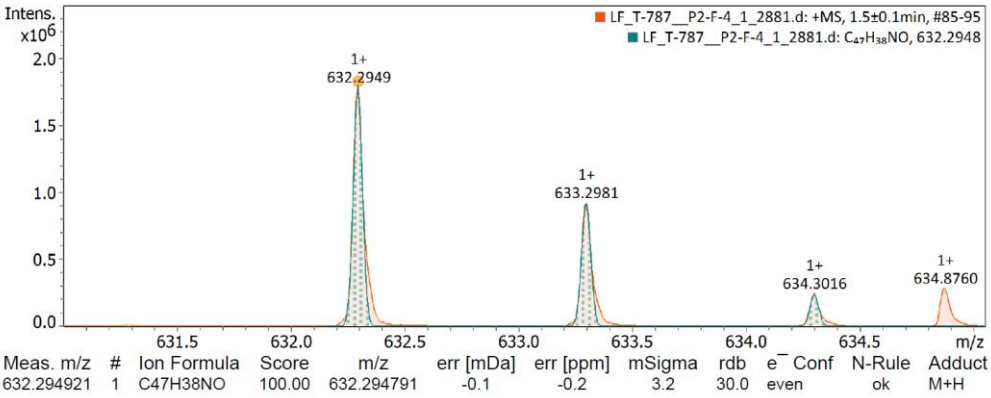
13-methoxy-4,5-diphenylspiro[benzo[6,7]indeno[2,1-*h*]isoquinolino[1,2-*a*]isoquinoline-8,9'-fluoren]-3-ium tetrafluoroborate (1bb).



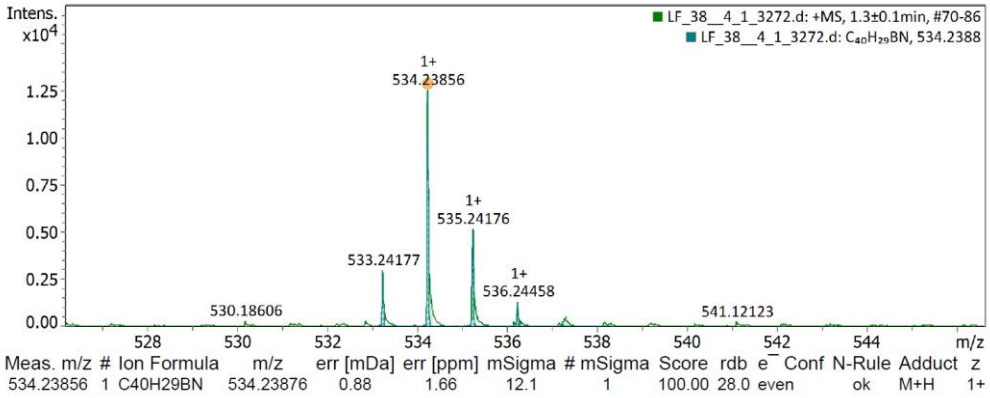
13-Methoxy-4,5-bis(4-(trifluoromethyl)phenyl)spiro[benzo[6,7]indeno[2,1-*h*]isoquinolino[1,2-*a*]isoquinoline-8,9'-fluoren]-3-ium tetrafluoroborate (1bc).



13-Methoxy-4,5-dipropylspiro[benzo[6,7]indeno[2,1-*h*]isoquinolino[1,2-*a*]isoquinoline-8,9'-fluoren]-3-ium tetrafluoroborate (1bd).



8,8-Dimethyl-8*H*-7λ^4,8λ^4-spiro[benzo[5',6']fluoreno[3',4':3,4][1,2]azaborolo[5,1]-isoquinoline-11,9'-fluorene] (2a).



(1-(Spiro[benzo[*c*]fluorene-7,9'-fluoren]-11-yl)isoquinolinato-N,C^{10})platinum-acetylacetonate (2b).