

Chemistry–A European Journal

Supporting Information

Entropy-Induced Selectivity Switch in Gold Catalysis: Fast Access to Indolo[1,2-*a*]quinolines

Robin Heckershoff, Garrett May, Janika Däumer, Lukas Eberle, Petra Krämer,
Frank Rominger, Matthias Rudolph, Florian F. Mulks,* and A. Stephen K. Hashmi*

Table of Contents

1	Experimental Procedures	2
1.1	General Information	2
1.2	Catalyst Screening	4
1.3	Synthesis Strategies	7
1.4	General Procedures	8
1.5	Synthesis of Compounds	10
2	NMR Spectra	44
3	UV-Vis and Fluorescence Spectra	93
4	Crystallographic Data	108
5	Computational Investigation	110
5.1	Computational Details	110
5.2	Overview of the Computed Molecules	111
5.3	Frontier Orbitals of 2a/f/h/o/r, 6, 8, 10 and 12	113
6	References	115

1 Experimental Procedures

1.1 General Information

Chemicals were bought from commercial suppliers (abcr, Acros, Alfa Aesar, Carbolution, Chempur, Fluka, Merck, Sigma Aldrich and TCI) and used as delivered. Anhydrous solvents were dispensed from a solvent purification system MB SPS-800. Solvents were degassed by freeze-pump-thaw technique. Deuterated solvents were bought from Euriso Top and Sigma Aldrich.

Melting points (mp) were measured in open glass capillaries on a Stuart SMP10 melting point apparatus and are uncorrected.

R_f -values were determined by analytical thin layer chromatography (TLC) on aluminum sheets coated with silica gel produced by Macherey-Nagel (ALUGRAM® Xtra SIL G/25 UV₂₅₄). Detection was accomplished using UV-light (254 and 365 nm) or a TLC staining solution (vanillin or ninhydrine).

Nuclear magnetic resonance (NMR) spectra were, if not mentioned otherwise, recorded at room temperature at the chemistry department of Heidelberg University under the supervision of Dr. J. Graf on the following spectrometers: Bruker Avance III 300 (300 MHz), Bruker Avance DRX 300 (300 MHz), Bruker Fourier 300 (300 MHz), Bruker Avance III 400 (400 MHz), Bruker Avance III 500 (500 MHz), Bruker Avance III 600 (600 MHz), Bruker Avance NEO 700 (700 MHz). For sensitive compounds CDCl₃ was filtered through a plug of aluminum oxide to remove acid impurities and the NMR sample was prepared under an atmosphere of argon. Chemical shifts (δ) are given in ppm and coupling constants J in Hz. Spectra were referenced to residual solvent protons according to Fulmer *et al.*^[1] The following abbreviations were used to describe the observed multiplicities: for ¹H NMR spectra: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, m = multiplet, dd = doublet of doublets, td = triplet of doublets, dt = doublet of triplets, br = broad signal; for ¹³C NMR spectra: s = quaternary carbon, d = CH carbon, t = CH₂ carbon and q = CH₃ carbon. ¹³C NMR spectra are proton decoupled (if necessary, ¹⁹F is proton decoupled as well) and interpreted with help of DEPT- and 2D spectra. All ¹⁹F spectra are proton decoupled. All spectra were integrated and processed using Bruker TopSpin 4.1.1 software.

High-resolution mass spectra (HR-MS) were recorded at the chemistry department of Heidelberg University under the supervision of Dr. J. Gross on the following spectrometers: JEOL AccuTOF GCx (EI), Bruker ApexQe hybrid 9.4 T FT-ICR (ESI, MALDI, DART), Finnigan LCQ (ESI) and Bruker AutoFlex Speed (MALDI).

Infrared spectra were recorded from a neat powder or oil on a FT-IR spectrometer (Bruker LUMOS) with a Germanium ATR-crystal. For the most significant bands the wave numbers are given.

UV-Vis spectra were recorded on a Jasco UV-Vis V-670. Fluorescence spectra were recorded on a Jasco FP6500. Quantum yields (QY) were recorded on a Jasco FP-8600 fluorescence spectrometer equipped with a ILF-835 100 mm dia. integrating sphere.

X-ray crystallography was carried out at the chemistry department of Heidelberg University under the supervision of Dr. F. Rominger on the following instruments: Bruker Smart APEX II Quazar (with Mo-

microsource) and Stoe Stadivari (with Co-microsource and Pilatus detector). The structures were processed with Mercury 4.3.0.

For flash column chromatography silica gel (Sigma-Aldrich, pore size 60 Å, 70–230 mesh, 63–200 µm) or aluminum oxide (Honeywell, pore size 60 Å, activated, neutral) was used as stationary phase. As eluents different mixtures of petroleum ether (PE), ethyl acetate (EA), DCM or MeOH were used.

All reactions were performed under air, if not otherwise specified. For handling of air and moisture sensitive reagents, standard Schlenk techniques with flame-dried glassware under an argon or nitrogen atmosphere were used.

1.2 Catalyst Screening

Detailed description of the catalyst and conditions screening

First, we tried to find an appropriate solvent for the reaction with the focus on a relatively high boiling point due to the demand for high temperature as seen in the previous results. With chlorobenzene, *N,N*-dimethylformamide, nitrobenzene and xylenes at 150 °C oil bath temperature little conversion was achieved and only trace amounts of **2a** could be detected. With 1,1,2,2-tetrachloroethane (TCE), anisole and *o*-dichlorobenzene (ODCB) all of the starting material was consumed and for anisole and ODCB a higher selectivity for **2a** (>50%) was observed, whereas TCE only led to trace amounts of product. Because of its higher temperature range ODCB was chosen as the appropriate solvent for the further screening of catalysts and conditions.

For the optimization of the selectivity, we tested a number of gold catalysts (Figure S1) at different temperatures and compared the product distribution after 90 min of reaction time (Table S1). The ratio of the desired product **2a**, the major side products **3a** and **3b** and the starting material **1a** was easily determined by the comparison of characteristic signals in the ¹H NMR spectra. First, AgNTf₂ and AgSbF₆, that were used as halide scavengers, as well as a blank test without any catalyst showed that silver catalysis and thermal activation can be excluded (Table S1, entries 1–3). PicAuCl₂ and XPhosAuCl/AgNTf₂ did not show significant reactivity at 140 °C (entries 4, 5). With the well-established NHC catalyst IPrAuNTf₂ full conversion was observed, but only trace amounts of **2a** were detected alongside a mixture of **3a/b** (entry 6). To our surprise higher temperatures changed the product distribution dramatically. At 160 °C more than half of the product mixture consist of **2a** and at 180 °C **2a** is produced almost exclusively (entries 7, 8). By changing the counter ion to SbF₆ an improved selectivity at lower temperatures was feasible and using the pre-activated counterpart IPrAu(MeCN)SbF₆ showed the best result for IPr catalysts (entries 9–11). In comparison to the temperature, the sterical demand of the catalyst seems not to be a significant factor and the even bulkier ligands IPr* (1,3-bis(2,6-bis(diphenylmethyl)-4-methylphenyl)imidazo-2-ylidene)^[2] and 9-Dipp (6,8-bis(2,6-diisopropylphenyl)-5,6,8,9-tetrahydro-7*H*-dibenzo[*e,g*][1,3]diazonin-7-ylidene)^[3] showed no improvement compared to the IPr catalysts (entries 12–16). The electron-poor phosphite ligand TDBPP (tris(2,4-ditert-butylphenyl) phosphite) did not perform well (entries 17, 18), but JohnPhosAu(MeCN)SbF₆ achieved full selectivity at 160 °C and even outperformed the other catalyst at 140 °C (entries 19, 20). Lowering the temperature even further results in higher proportion of dimers, whereby at 70 °C only partial conversion is observed and the product distribution is dominated by **3a/3b** (entries 21–23). It is noteworthy, that for different catalyst also the ratio between **3a** and **3b** is changing significantly.

To test for concentration dependency we compared the reaction of **1a** and 5 mol% JohnPhosAu(MeCN)SbF₆ with three different substrate concentrations in ODCB at 140 °C for 4 h. While concentrations of 1.02 and 10.2 μmol/mL did not show significant differences, using a substrate concentration of 102 μmol/mL produced a high amount of dimeric products (entries 24–26).

With lowering of the catalyst loading to 5 mol% full conversion was still achieved after 90 min at 170 °C and with 2.5 mol% after 180 min. With 1 mol% only 35% (90 min) and 40% (180 min) conversion was observed, which can be explained by the ongoing decomposition of the catalyst at these high temperatures. IPrAu(MeCN)SbF₆ showed similar results with lower yields, whereas

$\text{IPr}^*\text{Au}(\text{MeCN})\text{SbF}_6$ seems to be more temperature stable, but necessitates 2 days to achieve full conversion with a loading of 1 mol%.

At last, we tried to reduce the amount of the green decomposition product, which always occurred as a significant impurity. In assumption of an oxygen triggered decomposition, we compared two reactions of **1a** with $\text{JohnPhosAu}(\text{MeCN})\text{SbF}_6$ (2.5 mol%) on the one hand using commercial available ODCB under *open flask* conditions and on the other hand using degassed ODCB under an argon atmosphere. The crude products already differ strongly by color (deep green and bright yellow) and after purification the yield of **2a** for the reaction under oxygen-free condition was clearly higher (91%) than under *open flask* condition (84%).

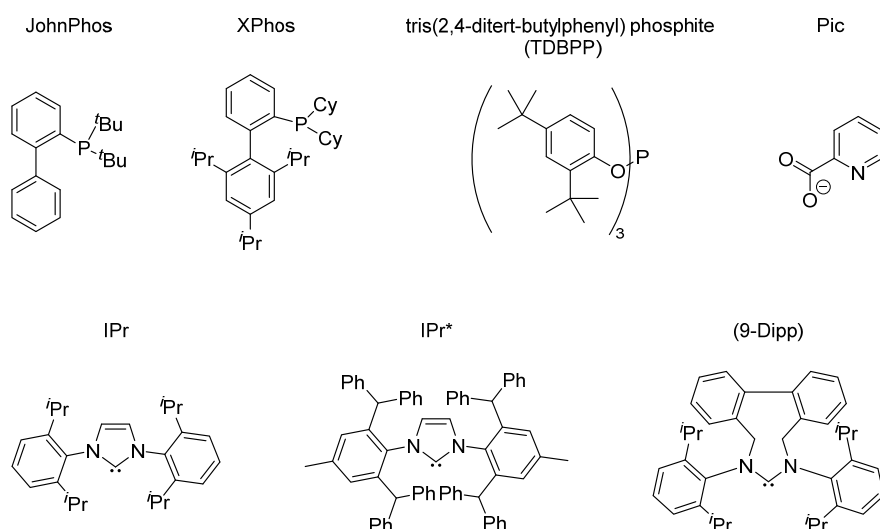
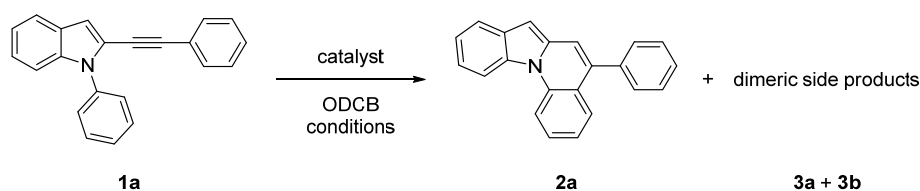


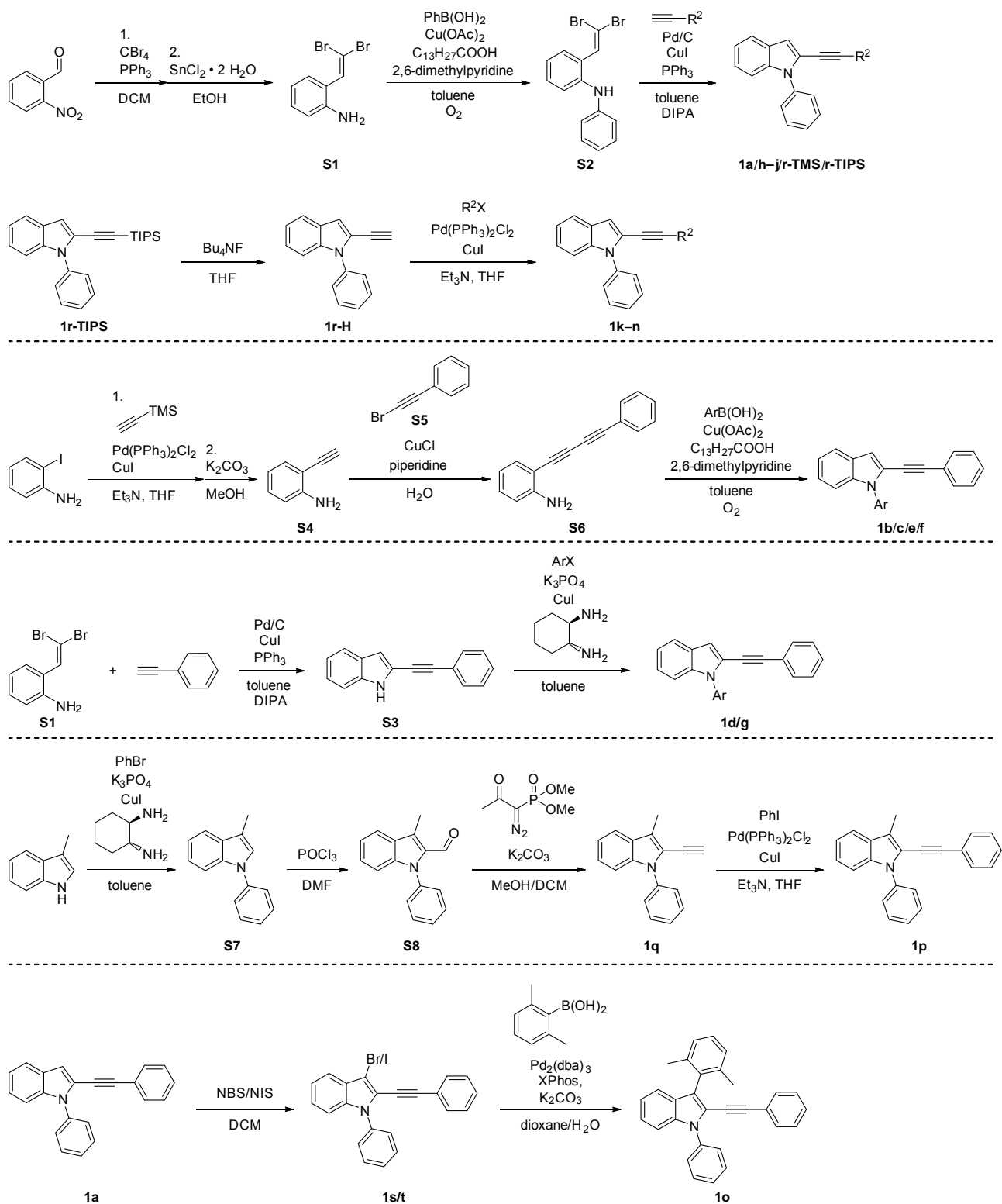
Figure S1. Structures of ligands used for gold-catalysts.

Table S1. Optimization of the reaction conditions for the synthesis of **2a**.^[a]

Entry	Catalyst	Temperature [°C]	Molar Ratio ^[b]			
			1a	2a	3a	3b
1	-	180	100	0	0	0
2	AgNTf ₂	180	100	0	0	0
3	AgSbF ₆	180	100	0	0	0
4	PicAuCl ₂	140	100	0	0	0
5	XPhosAuCl/AgNTf ₂	140	100	trace	trace	trace
6	IPrAuNTf ₂	140	0	trace	30	70
7	IPrAuNTf ₂	160	0	55	18	27
8	IPrAuNTf ₂	180	0	97	1	2
9	IPrAuCl/AgSbF ₆	160	4	81	6	9
10	IPrAu(MeCN)SbF ₆	140	0	49	21	30
11	IPrAu(MeCN)SbF ₆	160	0	100	trace	trace
12	IPr [*] Au(MeCN)SbF ₆	120	0	18	42	40
13	IPr [*] Au(MeCN)SbF ₆	140	0	34	35	31
14	IPr [*] Au(MeCN)SbF ₆	160	0	100	trace	trace
15	(9-Dipp)AuCl/AgSbF ₆	140	64	0	14	22
16	(9-Dipp)AuCl/AgSbF ₆	160	0	94	0	6
17	TDBPPAuCl/AgNTf ₂	140	90	10	trace	trace
18	TDBPPAuCl/AgSbF ₆	160	65	17	8	10
19	JohnPhosAu(MeCN)SbF ₆	140	0	85	12	3
20	JohnPhosAu(MeCN)SbF ₆	160	0	100	trace	trace
21	JohnPhosAu(MeCN)SbF ₆	135	0	84	13	3
22	JohnPhosAu(MeCN)SbF ₆	100	0	68	25	7
23	JohnPhosAu(MeCN)SbF ₆	70	85	trace	12	3
24 ^{[c],[d]}	JohnPhosAu(MeCN)SbF ₆	140	0	61	30	9
25 ^{[c],[e]}	JohnPhosAu(MeCN)SbF ₆	140	0	93	7	1
26 ^{[c],[f]}	JohnPhosAu(MeCN)SbF ₆	140	0	95	5	trace

^[a]The reactions were performed using **1a** (17.0 μmol) and 10 mol% catalyst in 10.0 mL ODCB for 90 min, if not stated otherwise; ^[b]determined by ¹H NMR spectroscopy; ^[c]5 mol% catalyst was used and the mixture was heated for 4 h; ^[d]**1a** (1.02 μmol/mL); ^[e]**1a** (10.2 μmol/mL) ^[f]**1a** (102 μmol/mL).

1.3 Synthesis Strategies



1.4 General Procedures

GP1: Chan-Lam cross coupling

According to a modified procedure by Lautens *et al.*,^[4] the amine, the corresponding arylboronic acid, copper(II) acetate, 2,6-dimethylpyridine and myristic acid were added to toluene in a round bottom flask and the resulting mixture was stirred under oxygen (balloon) at the given temperature for the given time until TLC showed full conversion. The mixture was poured into water and extracted with ethyl acetate. The combined organic layers were washed with water and brine, dried over Na₂SO₄ and the solvent was removed under reduced pressure. To remove the occurring by-product (myristic acid aryl ester), which can be difficult to remove by chromatographic methods, an excess of KOH in H₂O/THF/MeOH (1:1:1) was added to the residue and the resulting mixture was stirred at rt for 16 h. The mixture was extracted with ethyl acetate. The combined organic layers were washed with water and brine, dried over Na₂SO₄ and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography.

GP2: Alkynyl indole synthesis

According to a slightly modified procedure by Lautens *et al.*,^[5] a Schlenk flask containing the 2-(2,2-dibromovinyl)aniline derivative, CuI and PPh₃ was evacuated and refilled with inert gas three times. Then, degassed toluene, the alkyne compound, *i*Pr₂NH and 5% Pd/C were added and the resulting mixture was stirred at 110 °C for 16 h. The mixture was filtered through a plug of Celite® and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography.

GP3: Ullmann-type cross coupling

According to a procedure by Promarak *et al.*,^[6] a Schlenk flask containing the indole derivative, CuI and K₃PO₄ was evacuated and refilled with inert gas three times. Degassed toluene, the aryl halide and (±)-*trans*-1,2-diaminocyclohexane were added and the mixture was stirred at 110 °C for 16 h. The mixture was filtered through a plug of Celite® and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography.

GP4: Sonogashira cross coupling

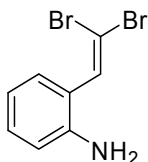
A Schlenk flask containing the palladium precatalyst was evacuated and refilled with inert gas three times. Degassed solvent, the aryl halide and the corresponding alkyne were added. After stirring at rt for 5 min, CuI was added and the mixture was stirred at rt for 16 h (if not stated otherwise). The solvents were removed under reduced pressure and the residue was purified by flash column chromatography.

GP5: Gold catalyzed hydroarylation

A Schlenk flask containing the substrate and JohnPhosAu(MeCN)SbF₆ was evacuated and refilled with inert gas three times. Degassed *o*-dichlorobenzene was added and the resulting solution was stirred at 170 °C for 4 h. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography.

1.5 Synthesis of Compounds

2-(2,2-Dibromovinyl)aniline (S1)

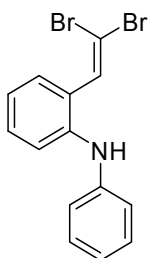


According to a slightly modified procedure by Lautens *et al.*,^[4] a solution of PPh₃ (23.6 g, 90.0 mmol) in DCM (100 mL) was added dropwise to a solution of 2-nitrobenzaldehyde (4.54 g, 30.0 mmol) and CBr₄ (14.9 g, 44.9 mmol) in DCM (150 mL) at 0–5 °C. The internal temperature was kept at 5 °C while the mixture was stirred for 30 min, then left to warm to rt and stirred for another hour. The mixture was filtered through a plug of silica gel (eluted with DCM) and the solvent was removed under reduced pressure. The residue was dissolved in ethanol (100 mL), SnCl₂·2H₂O (27.1 g, 120 mmol) was added and the resulting mixture was stirred at 80 °C for 45 min. The solvent was removed under reduced pressure and water (120 mL) was added. The mixture was brought to pH 9 with K₂CO₃ and extracted with ethyl acetate. The combined organic layers were washed with water and brine, dried over Na₂SO₄ and K₂CO₃ and the solvent was removed under reduced pressure. The residue was dissolved in diethyl ether and filtered through a plug of Celite®. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (silica gel, PE:EA = 20:1 to 10:1). The product was obtained as a pale yellow solid (6.34 g, 22.9 mmol, 76% over 2 steps).

R_f: 0.20 (silica gel, PE:EA = 10:1); **¹H NMR** (301 MHz, CDCl₃): δ = 7.34 (s, 1H), 7.32–7.29 (m, 1H), 7.19–7.14 (m, 1H), 6.79 (td, *J* = 7.5 Hz, *J* = 0.9 Hz, 1H), 6.71 (dd, *J* = 8.1 Hz, *J* = 0.9 Hz, 1H), 3.70 (bs, 2H).

The spectroscopic data correspond to those previously reported in the literature.^[4]

2-(2,2-Dibromovinyl)-*N*-phenylaniline (S2)

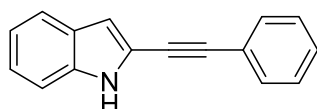


S1 (2.48 g, 8.95 mmol), phenylboronic acid (2.18 g, 17.9 mmol), copper(II) acetate (1.63 g, 8.95 mmol), 2,6-dimethylpyridine (1.06 g, 9.85 mmol) and myristic acid (818 mg, 3.58 mmol) in toluene (30 mL) were stirred under oxygen at rt for 1 d and treated according to GP1 (silica gel, PE:EA:Et₃N = 100:1:1). After further purification by recrystallization from DCM/pentane, the product was obtained as an off-white solid (2.41 g, 6.83 mmol, 76%).

R_f: 0.41 (silica gel, PE:EA = 10:1); **¹H NMR** (301 MHz, CDCl₃): δ = 7.51–7.48 (m, 1H), 7.40 (s, 1H), 7.31–7.22 (m, 4H), 7.00–6.94 (m, 4H), 5.48 (bs, 1H).

The spectroscopic data correspond to those previously reported in the literature.^[4]

2-(Phenylethynyl)-1H-indole (S3)

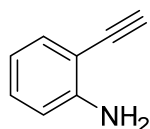


S1 (1.18 g, 4.26 mmol), CuI (40.6 mg, 213 μmol), PPh₃ (123 mg, 467 μmol), phenylacetylene (653 mg, 702 μmol), *i*Pr₂NH (1.08 g, 10.7 mmol) and 5% Pd/C (227 mg, 107 μmol) in toluene (15 mL) were used and treated according to GP2 (silica gel, PE:EA = 50:1 to 10:1). The product was obtained as a pale yellow solid (585 mg, 2.69 mmol, 63%).

R_f: 0.45 (silica gel, PE:EA = 10:1); **¹H NMR** (301 MHz, CDCl₃): δ = 8.24 (bs, 1H), 7.61 (d, *J* = 7.7 Hz, 1H), 7.56–7.53 (m, 2H), 7.39–7.33 (m, 4H), 7.26–7.24 (m, 1H), 7.16–7.11 (m, 1H), 6.84–6.83 (m, 1H).

The spectroscopic data correspond to those previously reported in the literature.^[5]

2-Ethynylaniline (S4)

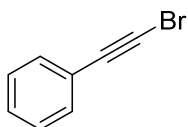


A Schlenk flask containing 2-iodoaniline (8.00 g, 35.5 mmol) and Pd(PPh₃)₂Cl₂ (256 mg, 365 μmol) was evacuated and refilled with nitrogen three times. Degassed Et₃N (150 mL) and ethynyltrimethylsilane (4.48 g, 45.7 mmol) were added and the mixture was stirred at rt for 5 min. CuI (139 mg, 731 μmol) was added and the mixture was stirred at rt for 2 h. The mixture was filtered through a plug of Celite® (eluted with EA), the solvents were removed under reduced pressure and the residue was dissolved in methanol (150 mL). K₂CO₃ (10.1 g, 73.1 mmol) was added and the resulting mixture was stirred at rt for 30 min. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (silica gel, PE:EA = 20:1 to 5:1). The product was obtained as a pale yellow oil (3.06 g, 26.1 mmol, 72%).

R_f: 0.24 (silica gel, PE:EA = 10:1); **¹H NMR** (301 MHz, CDCl₃): δ = 7.32 (dd, *J* = 7.7 Hz, *J* = 1.2 Hz, 1H), 7.17–7.12 (m, 1H), 6.71–6.65 (m, 2H), 4.24 (bs, 2H), 3.38 (s, 1H).

The spectroscopic data correspond to those previously reported in the literature.^[7]

(Bromoethynyl)benzene (**S5**)

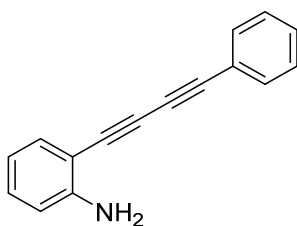


According to a slightly modified procedure by Wulff *et al.*,^[8] to a solution of phenylacetylene (3.50 g, 34.3 mmol) in acetone (150 mL) was added NBS (6.71 g, 37.7 mmol) and AgNO₃ (291 mg, 1.71 mmol) and the mixture was stirred at rt for 16 h. The solvent was removed under reduced pressure. PE was added and the mixture was filtered through a plug of silica and the solvent was removed under reduced pressure. The product was obtained as a brown oil (4.87 g, 26.9 mmol, 79%).

R_f: 0.80 (silica gel, PE); **¹H NMR** (301 MHz, CDCl₃): δ = 7.48–7.43 (m, 2H), 7.37–7.28 (m, 3H).

The spectroscopic data correspond to those previously reported in the literature.^[8]

2-(Phenylbuta-1,3-diyne-1-yl)aniline (**S6**)

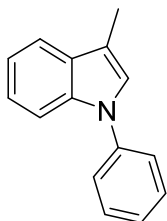


According to a procedure by Chinta and Baire,^[9] under a nitrogen atmosphere **S4** (1.10 g, 9.39 mmol) and **S5** (1.87 g, 10.3 mmol) were dissolved in degassed water (110 mL) and piperidine (4.00 g, 47.0 mmol). CuCl (139 mg, 1.41 mmol) was added and the resulting mixture was stirred at rt for 16 h. A saturated aqueous solution of NH₄Cl (25 mL) was added and the mixture was extracted with ethyl acetate. The combined organic layers were washed with water and brine, dried over Na₂SO₄ and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (silica gel, PE:EA:Et₃N = 100:5:1 to 100:20:1). The product was obtained as an orange-brown solid (1.90 g, 8.74 mmol, 93%).

R_f: 0.26 (silica gel, PE:EA = 10:1); **¹H NMR** (301 MHz, CDCl₃): δ = 7.55–7.51 (m, 2H), 7.40–7.30 (m, 4H), 7.19–7.13 (m, 1H), 6.71–6.66 (m, 2H), 4.32 (bs, 2H).

The spectroscopic data correspond to those previously reported in the literature.^[10]

3-Methyl-1-phenyl-1*H*-indole (**S7**)

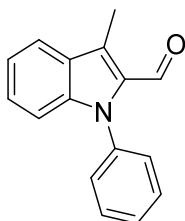


3-Methyl-1*H*-indole (1.50 g, 11.4 mmol), bromobenzene (2.69 g, 17.2 mmol), K₃PO₄ (5.10 g, 24.0 mmol), (±)-*trans*-1,2-diaminocyclohexane (326 mg, 2.86 mmol) and CuI (544 mg, 2.86 mmol) in toluene (30 mL) were used and treated according to GP3 (silica gel, PE:EA = 100:1). The product was obtained as a colorless oil (2.26 g, 10.9 mmol, 95%).

R_f: 0.73 (silica gel, PE:EA = 10:1); **¹H NMR** (301 MHz, CDCl₃): δ = 7.66–7.63 (m, 1H), 7.59–7.56 (m, 1H), 7.54–7.48 (m, 4H), 7.37–7.30 (m, 1H), 7.27–7.17 (m, 2H), 7.16 (d, *J* = 1.0 Hz, 1H), 2.41 (d, *J* = 1.1 Hz, 3H).

The spectroscopic data correspond to those previously reported in the literature.^[11]

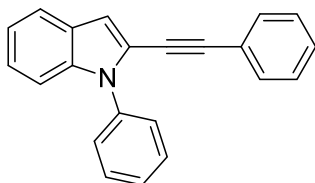
3-Methyl-1-phenyl-1*H*-indole-2-carbaldehyde (**S8**)



According to a procedure by Reddy *et al.*,^[12] to a stirred solution of **S7** (742 mg, 3.58 mmol) in DMF (20 mL) at 0 °C phosphoryl chloride (8.23 g, 53.7 mmol) was added and the mixture was stirred at 70 °C for 5 h. Water was added at 0 °C and the mixture was neutralized with 1 M aqueous KOH. The resulting precipitate was filtered off, washed with water and dried under reduced pressure. The crude product was purified by flash column chromatography (silica gel, PE:EA = 50:1). The product was obtained as a colorless solid (805 mg, 3.42 mmol, 96%).

Mp: 80 °C; **R_f**: 0.23 (silica gel, PE:EA = 20:1); **¹H NMR** (500 MHz, CDCl₃): δ = 10.01 (s, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.56–7.53 (m, 2H), 7.50–7.46 (m, 1H), 7.39–7.34 (m, 3H), 7.24–7.21 (m, 1H), 7.18 (d, *J* = 8.5 Hz, 1H), 2.75 (s, 3H); **¹³C{¹H} NMR** (126 MHz, CDCl₃): 182.3 (d, 1C), 139.9 (s, 1C), 137.4 (s, 1C), 132.1 (s, 1C), 129.5 (d, 2C), 128.3 (d, 1C), 128.1 (d, 2C), 127.5 (s, 1C), 127.5 (d, 1C), 125.3 (s, 1C), 121.4 (d, 1C), 121.1 (d, 1C), 111.5 (d, 1C), 9.5 (q, 1C); **HR-MS** (EI⁺): *m/z* calculated for [C₁₆H₁₃N]⁺, [M]⁺: 235.09917, found: 235.09932; **IR** (ATR): ν [cm⁻¹] = 3058, 2956, 2925, 2854, 1723, 1673, 1613, 1597, 1536, 1499, 1454, 1381, 1344, 1282, 1227, 1137, 1113, 1073, 948, 882, 747, 721, 699, 641.

1-Phenyl-2-(phenylethynyl)-1*H*-indole (1a)

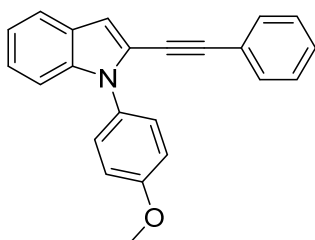


S2 (2.77 g, 7.85 mmol), CuI (74.7 mg, 392 μ mol), PPh₃ (113 mg, 432 μ mol), phenylacetylene (1.20 g, 11.8 mmol), *i*Pr₂NH (1.98 g, 19.6 mmol) and 5% Pd/C (417mg, 196 μ mol) in toluene (35 mL) were used and treated according to GP2 (silica gel, PE:DCM = 100:1). The product was obtained as a colorless solid (1.55 g, 5.28 mmol, 67%).

R_f: 0.58 (silica gel, PE:EA = 20:1); **¹H NMR** (301 MHz, CDCl₃): δ = 7.68–7.64 (m, 1H), 7.60–7.53 (m, 4H), 7.50–7.43 (m, 1H), 7.34–7.27 (m, 6H), 7.26–7.15 (m, 2H), 7.00 (d, *J* = 0.7 Hz, 1H).

The spectroscopic data correspond to those previously reported in the literature.^[13]

1-(4-Methoxyphenyl)-2-(phenylethynyl)-1*H*-indole (1b)

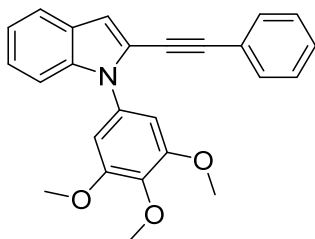


S6 (200 mg, 921 μ mol), (4-methoxyphenyl)boronic acid (280 mg, 1.84 mmol), copper(II) acetate (167 mg, 921 μ mol), 2,6-dimethylpyridine (108 mg, 1.01 mmol) and myristic acid (84.1 mg, 368 μ mol) in toluene (25 mL) were stirred under oxygen at 80 °C for 3 d and treated according to GP1. The crude product was a mixture of non-cyclized secondary amine and cyclized indole. To force cyclization IPrAuNTf₂ (7.97 mg, 9.21 μ mol) in DCE (10 mL) was added and the mixture was stirred at 80 °C for 5 h. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (silica gel, PE:EA = 50:1). The product was obtained as a pale yellow solid (101 mg, 313 μ mol, 34%).

R_f: 0.23 (silica gel, PE:EA = 50:1); **¹H NMR** (301 MHz, CDCl₃): δ = 7.66–7.64 (m, 1H), 7.50–7.45 (m, 2H), 7.35–7.27 (m, 5H), 7.25–7.13 (m, 3H), 7.10–7.04 (m, 2H), 6.98 (d, *J* = 0.4 Hz, 1H), 3.91 (s, 3H).

The spectroscopic data correspond to those previously reported in the literature.^[13]

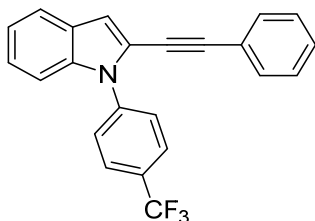
2-(Phenylethynyl)-1-(3,4,5-trimethoxyphenyl)-1H-indole (1c)



S6 (200 mg, 921 μmol), (3,4,5-trimethoxyphenyl)boronic acid (390 mg, 1.84 mmol), copper(II) acetate (167 mg, 921 μmol), 2,6-dimethylpyridine (108 mg, 1.01 mmol) and myristic acid (84.1 mg, 368 μmol) in toluene (25 mL) were stirred under oxygen at 60 °C for 2 d and treated according to GP1 (silica gel, PE:EA = 30:1 to 15:1). The product was obtained as a pale yellow solid (122 mg, 317 μmol , 34%).

Mp: 117 °C; **R_f:** 0.37 (silica gel, PE:EA = 5:1); **¹H NMR** (600 MHz, CD₂Cl₂): δ = 7.65 (d, J = 7.9 Hz, 1H), 7.38–7.32 (m, 6H), 7.26–7.23 (m, 1H), 7.18–7.15 (m, 1H), 7.00 (d, J = 0.7 Hz, 1H), 6.81 (s, 2H), 3.88 (s, 3H), 3.84 (s, 6H); **¹³C{¹H} NMR** (151 MHz, CD₂Cl₂): 153.9 (s, 2C), 138.0 (s, 1C), 137.8 (s, 1C), 133.5 (s, 1C), 131.4 (d, 2C), 129.0 (d, 1C), 128.9 (d, 2C), 127.9 (s, 1C), 124.1 (d, 1C), 122.9 (s, 1C), 122.3 (s, 1C), 121.3 (d, 1C), 121.3 (d, 1C), 111.0 (d, 1C), 109.6 (d, 1C), 105.1 (d, 2C), 95.7 (s, 1C), 82.0 (s, 1C), 61.0 (q, 1C), 56.6 (q, 2C); **HR-MS** (EI⁺): m/z calculated for [C₂₅H₂₁NO₃]⁺, [M]⁺: 383.15159, found: 383.15098; **IR** (ATR): ν [cm⁻¹] = 3060, 2938, 2832, 2212, 1596, 1505, 1475, 1455, 1419, 1354, 1331, 1305, 1231, 1182, 1129, 1067, 1008, 950, 853, 828, 794, 756, 692, 658, 632.

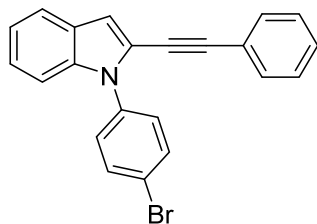
2-(Phenylethynyl)-1-(4-(trifluoromethyl)phenyl)-1H-indole (1d)



S3 (50.8 mg, 234 μmol), 1-bromo-4-(trifluoromethyl)benzene (131 mg, 584 μmol), K₃PO₄ (149 mg, 701 μmol), (±)-*trans*-1,2-diaminocyclohexane (13.3 mg, 117 μmol) and CuI (22.2 mg, 117 μmol) in toluene (6 mL) were used and treated according to GP3 (silica gel, PE). The product was obtained as a pale yellow solid (60.8 mg, 168 μmol , 72%).

Mp: 97 °C; **R_f:** 0.7 (silica gel, PE:EA = 20:1); **¹H NMR** (500 MHz, CD₂Cl₂): δ = 7.87 (d, J = 8.4 Hz, 2H), 7.77 (d, J = 8.4 Hz, 2H), 7.67 (d, J = 7.9 Hz, 1H), 7.37–7.32 (m, 6H), 7.28 (td, J = 7.6 Hz, J = 1.0 Hz, 1H), 7.21 (t, J = 7.4 Hz, 1H), 7.07 (s, 1H); **¹³C{¹H, ¹⁹F} NMR** (126 MHz, CD₂Cl₂): 141.2 (s, 1C), 137.6 (s, 1C), 131.5 (d, 2C), 129.5 (s, 1C), 129.2 (d, 1C), 128.9 (d, 2C), 128.3 (s, 1C), 127.8 (d, 2C), 126.7 (d, 2C), 124.6 (d, 1C), 124.5 (s, 1C), 122.7 (s, 1C), 121.9 (s, 1C), 121.9 (d, 1C), 121.5 (d, 1C), 110.8 (d, 1C), 110.7 (d, 1C), 96.1 (s, 1C), 81.4 (s, 1C); **¹⁹F{¹H} NMR** (471 MHz, CD₂Cl₂): -62.6 (3F); **HR-MS** (EI⁺): m/z calculated for [C₂₃H₁₄F₃N]⁺, [M]⁺: 361.10729, found: 361.10829; **IR** (ATR): ν [cm⁻¹] = 3068, 2927, 2215, 1618, 1523, 1489, 1477, 1454, 1418, 1383, 1327, 1218, 1166, 1119, 1069, 1020, 931, 842, 811, 796, 757, 739, 710, 690, 638, 623, 606.

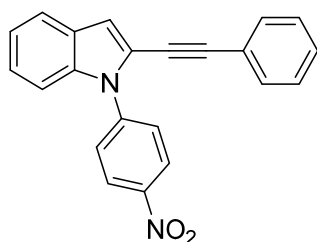
1-(4-Bromophenyl)-2-(phenylethynyl)-1H-indole (1e)



S6 (200 mg, 921 μmol), (4-bromophenyl)boronic acid (370 mg, 1.84 mmol), copper(II) acetate (167 mg, 921 μmol), 2,6-dimethylpyridine (108 mg, 1.01 mmol) and myristic acid (84.1 mg, 368 μmol) in toluene (25 mL) were stirred under oxygen at 80 °C for 3 d and treated according to GP1. The crude product was a mixture of non-cyclized secondary amine and cyclized indole. To force cyclization IPrAuNTf₂ (7.97 mg, 9.21 μmol) in DCE (10 mL) was added and the mixture was stirred at 80 °C for 5 h. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (silica gel, PE:EA = 100:1). The product was obtained as a pale yellow solid (168 mg, 450 μmol , 49%).

Mp: 138 °C; **R_f**: 0.33 (silica gel, PE:EA = 50:1); **¹H NMR** (600 MHz, CD₂Cl₂): δ = 7.73–7.71 (m, 2H), 7.66–7.65 (m, 1H), 7.51–7.49 (m, 2H), 7.38–7.33 (m, 5H), 7.31 (d, J = 8.3 Hz, 1H), 7.25 (td, J = 7.6 Hz, J = 1.1 Hz, 1H), 7.18 (td, J = 7.4 Hz, J = 0.9 Hz, 1H), 7.03 (s, 1H); **¹³C{¹H} NMR** (151 MHz, CD₂Cl₂): 137.7 (s, 1C), 137.1 (s, 1C), 132.7 (d, 2C), 131.5 (d, 2C), 129.2 (d, 2C), 129.1 (d, 1C), 128.9 (d, 2C), 128.1 (s, 1C), 124.3 (d, 1C), 122.8 (s, 1C), 122.0 (s, 1C), 121.6 (d, 1C), 121.5 (s, 1C), 121.4 (d, 1C), 110.7 (d, 1C), 110.2 (d, 1C), 95.8 (s, 1C), 81.5 (s, 1C); **HR-MS** (EI⁺): m/z calculated for [C₂₂H₁₄⁷⁹BrN]⁺, [M]⁺: 371.03041, found: 371.03231; **IR** (ATR): ν [cm⁻¹] = 3050, 1947, 1900, 1643, 1586, 1571, 1489, 1448, 1402, 1378, 1351, 1317, 1262, 1215, 1176, 1150, 1123, 1102, 1072, 1012, 935, 915, 847, 824, 806, 742, 709, 686, 651, 633, 620.

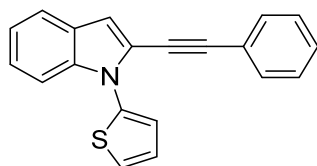
1-(4-Nitrophenyl)-2-(phenylethynyl)-1H-indole (1f)



S6 (250 mg, 1.15 mmol), (4-nitrophenyl)boronic acid (384 mg, 2.30 mmol), copper(II) acetate (209 mg, 1.15 mmol), 2,6-dimethylpyridine (137 mg, 1.28 mmol) and myristic acid (105 mg, 460 μmol) in toluene (50 mL) were stirred under oxygen at 80 °C for 3 d and treated according to GP1. The crude product was a mixture of non-cyclized secondary amine and cyclized indole. To force cyclization IPrAuNTf₂ (7.97 mg, 9.21 μmol) in DCE (10 mL) was added and the mixture was stirred at 80 °C for 5 h. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (silica gel, PE:EA = 100:1 to 20:1). The product was obtained as a pale yellow solid (93.0 mg, 275 μmol , 24%).

Mp: 125 °C; **R_f:** 0.6 (silica gel, PE:EA = 10:1); **¹H NMR** (301 MHz, CDCl₃): δ = 8.47–8.42 (m, 2H), 7.85–7.80 (m, 2H), 7.69–7.67 (m, 1H), 7.40–7.27 (m, 7H), 7.26–7.21 (m, 1H), 7.08 (d, *J* = 0.5 Hz, 1H); **¹³C{¹H} NMR** (101 MHz, CDCl₃): 146.3 (s, 1C), 143.5 (s, 1C), 137.0 (s, 1C), 131.3 (d, 2C), 129.0 (d, 1C), 128.7 (d, 2C), 128.3 (s, 1C), 127.4 (d, 2C), 124.8 (d, 2C), 124.7 (d, 1C), 122.3 (s, 1C), 122.1 (d, 1C), 121.6 (d, 1C), 121.6 (s, 1C), 111.7 (d, 1C), 110.4 (d, 1C), 96.4 (s, 1C), 80.9 (s, 1C); **HR-MS** (EI+): *m/z* calculated for [C₂₂H₁₄N₂O₂]⁺, [M]⁺: 338.10498, found: 338.10503; **IR** (ATR): ν [cm⁻¹] = 3079, 2922, 2850, 1605, 1591, 1522, 1497, 1450, 1376, 1341, 1312, 1213, 1153, 1105, 1069, 1018, 934, 913, 849, 807, 750, 695, 684, 637.

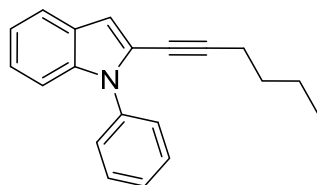
2-(Phenylethynyl)-1-(thiophen-2-yl)-1*H*-indole (1g)



S3 (173 mg, 795 μmol), 2-iodothiophene (251 mg, 1.19 mmol), K₃PO₄ (355 mg, 1.67 mmol), (±)-*trans*-1,2-diaminocyclohexane (22.7 mg, 199 μmol) and CuI (37.9 mg, 199 μmol) in toluene (6 mL) were used and treated according to GP3 (silica gel, PE:EA = 100:1 to 50:1). The product was obtained as a pale yellow oil (192 mg, 641 μmol, 81%).

R_f: 0.45 (silica gel, PE:EA = 20:1); **¹H NMR** (500 MHz, CDCl₃): δ = 7.64 (d, *J* = 7.9 Hz, 1H), 7.40–7.35 (m, 4H), 7.33–7.25 (m, 4H), 7.21–7.19 (m, 2H), 7.13 (dd, *J* = 5.6 Hz, *J* = 3.7 Hz, 1H), 6.99 (s, 1H); **¹³C{¹H} NMR** (126 MHz, CDCl₃): 139.0 (s, 1C), 138.8 (s, 1C), 131.4 (d, 2C), 128.7 (d, 1C), 128.5 (d, 2C), 127.7 (s, 1C), 125.7 (d, 1C), 125.1 (d, 1C), 124.2 (d, 1C), 124.2 (d, 1C), 123.5 (s, 1C), 122.7 (s, 1C), 121.5 (d, 1C), 121.1 (d, 1C), 110.9 (d, 1C), 109.9 (d, 1C), 96.0 (s, 1C), 81.2 (s, 1C); **HR-MS** (EI+): *m/z* calculated for [C₂₀H₁₃NS]⁺, [M]⁺: 299.07632, found: 299.07565; **IR** (ATR): ν [cm⁻¹] = 3058, 2209, 1597, 1548, 1487, 1474, 1452, 1377, 1338, 1312, 1226, 1210, 1185, 1147, 1123, 1069, 1014, 915, 845, 797, 754, 692, 636.

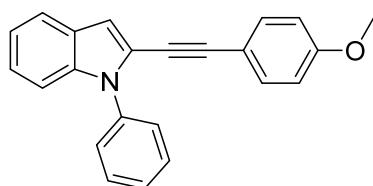
2-(Hex-1-yn-1-yl)-1-phenyl-1*H*-indole (1h)



S2 (250 mg, 708 μmol), CuI (6.74 mg, 35.4 μmol), PPh₃ (20.4 mg, 77.9 μmol), hex-1-yne (87.3 mg, 1.06 mmol), *i*Pr₂NH (179 mg, 1.77 mmol) and 5% Pd/C (75.4 mg, 35.4 μmol) in toluene (5 mL) were used and treated according to GP2 (silica gel, PE:DCM = 100:1). The product was obtained as an off-white solid (122 mg, 446 μmol, 63%).

Mp: 54 °C; **R_f:** 0.26 (silica gel, PE:EA = 50:1); **¹H NMR** (400 MHz, CD₂Cl₂): δ = 7.61–7.58 (m, 1H), 7.56–7.49 (m, 4H), 7.46–7.42 (m, 1H), 7.26–7.24 (m, 1H), 7.20–7.16 (m, 1H), 7.15–7.11 (m, 1H), 6.81 (s, 1H), 2.35 (t, *J* = 7.0 Hz, 2H), 1.46 (quint, *J* = 7.2 Hz, 2H), 1.31 (sext, *J* = 7.4 Hz, 2H), 0.87 (t, *J* = 7.3 Hz, 3H); **¹³C NMR** (101 MHz, CD₂Cl₂): δ = 138.2 (s, 1C), 137.6 (s, 1C), 129.4 (d, 2C), 128.0 (s, 1C), 127.8 (d, 1C), 127.7 (d, 2C), 123.5 (d, 1C), 123.2 (s, 1C), 121.1 (d, 1C), 121.0 (d, 1C), 110.7 (d, 1C), 108.4 (d, 1C), 97.2 (s, 1C), 72.9 (s, 1C), 30.8 (t, 1C), 22.2 (t, 1C), 19.5 (t, 1C), 13.7 (q, 1C); **HR-MS** (DART+): *m/z* calculated for [C₂₀H₂₀N]⁺, [M+H]⁺: 274.1590, found: 274.1590; **IR** (ATR): ν [cm⁻¹] = 3060, 2956, 2930, 2870, 2234, 1597, 1532, 1501, 1452, 1378, 1361, 1331, 1316, 1241, 1202, 1145, 1076, 1026, 1012, 929, 789, 759, 748, 738, 698, 645, 633, 609.

2-((4-Methoxyphenyl)ethynyl)-1-phenyl-1*H*-indole (1i)

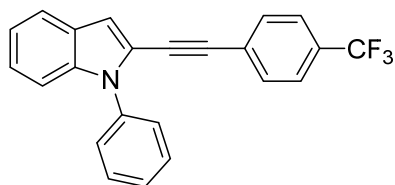


S2 (213 mg, 602 μmol), CuI (5.73 mg, 30.1 μmol), PPh₃ (17.4 mg, 66.2 μmol), 1-ethynyl-4-methoxybenzene (127 mg, 963 μmol), *i*Pr₂NH (152 mg, 1.50 mmol) and 5% Pd/C (25.6 mg, 12.0 μmol) in toluene (10 mL) were used and treated according to GP2 (silica gel, PE:EA = 40:1 to 10:1). After further purification by recrystallization from DCM/pentane, the product was obtained as a pale yellow solid (68.2 mg, 211 μmol, 35%).

R_f: 0.50 (silica gel, PE:EA = 10:1); **¹H NMR** (301 MHz, CDCl₃): δ = 7.66–7.63 (m, 1H), 7.61–7.52 (m, 4H), 7.47–7.42 (m, 1H), 7.31 (d, *J* = 8.4 Hz, 1H), 7.27–7.14 (m, 4H), 6.96 (d, *J* = 0.7 Hz, 1H), 6.82 (d, *J* = 8.9 Hz, 2H) 3.80 (s, 3H).

The spectroscopic data correspond to those previously reported in the literature.^[13]

1-Phenyl-2-((4-(trifluoromethyl)phenyl)ethynyl)-1*H*-indole (1j)

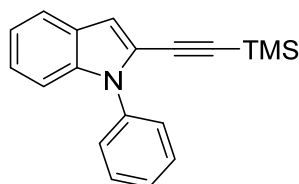


S2 (213 mg, 602 μmol), CuI (5.73 mg, 30.1 μmol), PPh₃ (17.4 mg, 66.2 μmol), 1-ethynyl-4-(trifluoromethyl)benzene (164 mg, 963 μmol), *i*Pr₂NH (152 mg, 1.50 mmol) and 5% Pd/C (25.6 mg, 12.0 μmol) in toluene (10 mL) were used and treated according to GP2 (silica gel, PE:EA = 80:1). The product was obtained as a pale yellow solid (150 mg, 415 μmol, 69%).

R_f: 0.78 (silica gel, PE:EA = 10:1); **¹H NMR** (301 MHz, CDCl₃): δ = 7.69–7.66 (m, 1H), 7.58–7.53 (m, 6H), 7.51–7.46 (m, 1H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.28–7.23 (m, 1H), 7.22–7.16 (m, 1H), 7.06 (s, 1H).

The spectroscopic data correspond to those previously reported in the literature.^[13]

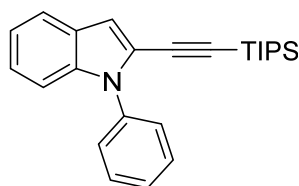
1-Phenyl-2-((trimethylsilyl)ethynyl)-1*H*-indole (1r-TMS)



S2 (3.00 g, 8.50 mmol), CuI (80.9 mg, 425 μmol), PPh₃ (245 mg, 935 μmol), TMS acetylene (1.67 g, 17.0 mmol), *i*Pr₂NH (2.15 g, 21.2 mmol) and 5% Pd/C (904 mg, 425 μmol) in toluene (30 mL) were used and treated according to GP2 (silica gel, PE:EA = 100:1). The product was obtained as a brown oil (1.81 g, 6.25 mmol, 74%).

R_f: 0.38 (silica gel, PE:EA = 100:1); **¹H NMR** (400 MHz, CDCl₃): δ = 7.63 (d, *J* = 7.7 Hz, 1H), 7.54–7.49 (m, 4H), 7.45–7.39 (m, 1H), 7.30–7.28 (m, 1H), 7.23–7.20 (m, 1H), 7.17–7.13 (m, 1H), 6.93 (s, 1H), 0.13 (s, 9H); **¹³C{¹H} NMR** (101 MHz, CDCl₃): δ = 137.7 (s, 1C), 137.5 (s, 1C), 129.0 (d, 2C), 127.6 (d, 1C), 127.5 (d, 2C), 127.5 (s, 1C), 123.9 (d, 1C), 122.0 (s, 1C), 121.3 (d, 1C), 121.0 (d, 1C), 110.7 (d, 1C), 109.9 (d, 1C), 101.6 (s, 1C), 96.9 (s, 1C), -0.3 (q, 3C); **HR-MS** (DART+): *m/z* calculated for [C₁₉H₂₀NSi]⁺, [M+H]⁺: 290.1360, found: 290.1362; **IR** (ATR): ν [cm⁻¹] = 3059, 2958, 2897, 2155, 1596, 1523, 1501, 1449, 1377, 1318, 1249, 1205, 1154, 1074, 995, 938, 868, 839, 791, 759, 697.

1-Phenyl-2-((triisopropylsilyl)ethynyl)-1*H*-indole (1r-TIPS)

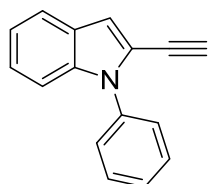


S2 (1.50 g, 4.25 mmol), CuI (40.5 mg, 212 μmol), PPh₃ (123 mg, 467 μmol), TIPS acetylene (1.55 g, 8.50 mmol), *i*Pr₂NH (1.07 g, 10.6 mmol) and 5% Pd/C (452 mg, 212 μmol) in toluene (18 mL) were used and treated according to GP2 (silica gel, PE:EA = 200:1). The product was obtained as a pale yellow solid (1.48 g, 3.96 mmol, 93%).

Mp: 35 °C; **R_f**: 0.50 (silica gel, PE:EA = 100:1); **¹H NMR** (400 MHz, CDCl₃): δ = 7.63 (d, *J* = 7.7 Hz, 1H), 7.52–7.47 (m, 4H), 7.44–7.38 (m, 1H), 7.26–7.19 (m, 2H), 7.17–7.13 (m, 1H), 6.96 (s, 1H), 1.03–

0.99 (m, 21H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ = 137.8 (s, 1C), 137.6 (s, 1C), 129.2 (d, 2C), 127.7 (d, 2C), 127.7 (d, 1C), 127.4 (s, 1C), 123.8 (d, 1C), 122.5 (s, 1C), 121.1 (d, 1C), 121.0 (d, 1C), 110.7 (d, 1C), 109.9 (d, 1C), 98.4 (s, 1C), 98.0 (s, 1C), 18.6 (q, 6C), 11.4 (d, 3C); **HR-MS** (DART+): m/z calculated for $[\text{C}_{25}\text{H}_{32}\text{NSi}]^+$, $[\text{M}+\text{H}]^+$: 374.2299, found: 374.2278; **IR** (ATR): ν [cm^{-1}] = 3059, 2942, 2890, 2864, 2724, 2152, 1922, 1887, 1798, 1771, 1665, 1596, 1523, 1501, 1449, 1414, 1378, 1362, 1318, 1286, 1236, 1205, 1155, 1115, 1073, 1033, 1016, 996, 919, 882, 863, 791, 760, 748, 731, 700, 676, 625, 608.

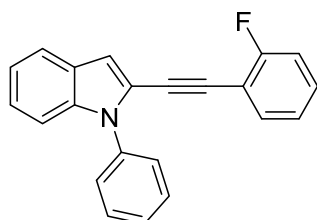
2-Ethynyl-1-phenyl-1H-indole (1r-H)



TBAF (1 M in THF, 7.01 mL, 7.01 mmol) was added to a solution of **1r-TIPS** (1.31 g, 3.51 mmol) in THF (50 mL) and the mixture was stirred at rt for 30 min. The solvent was removed under reduced pressure and 30 mL water was added. The mixture was extracted with ethyl acetate and the combined organic layers were washed with water and brine, dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (silica gel, PE:EA = 100:1). The product was obtained as a colorless oil, which quickly turns brown due to minor decomposition (690 mg, 3.18 mmol, 91%).

R_f: 0.26 (silica gel, PE:EA = 100:1); ^1H NMR (600 MHz, CD_2Cl_2): δ = 7.64 (d, J = 7.9 Hz, 1H), 7.58–7.55 (m, 2H), 7.53–7.51 (m, 2H), 7.49–7.46 (m, 1H), 7.28–7.26 (m, 1H), 7.25–7.23 (m, 1H), 7.19–7.16 (m, 1H), 7.02 (s, 1H), 3.35 (s, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CD_2Cl_2): δ = 137.9 (s, 1C), 137.7 (s, 1C), 129.6 (d, 2C), 128.2 (d, 1C), 127.7 (d, 2C), 127.5 (s, 1C), 124.4 (d, 1C), 121.4 (d, 1C), 121.4 (d, 1C), 121.1 (s, 1C), 111.0 (d, 1C), 110.9 (d, 1C), 83.7 (d, 1C), 76.0 (s, 1C); **HR-MS** (EI+): m/z calculated for $[\text{C}_{16}\text{H}_{11}\text{N}]^+$, $[\text{M}]^+$: 217.08860, found: 217.08991; **IR** (ATR): ν [cm^{-1}] = 3285, 3052, 2924, 2108, 1597, 1519, 1500, 1449, 1378, 1350, 1329, 1234, 1203, 1152, 1135, 1075, 1032, 1016, 932, 848, 797, 761, 750, 698, 676, 646, 619, 608.

2-((2-Fluorophenyl)ethynyl)-1-phenyl-1H-indole (1k)

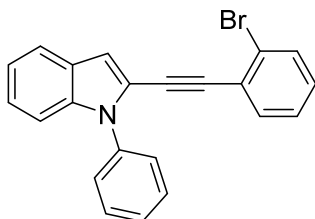


1r-H (200 mg, 921 μmol), 1-fluoro-2-iodobenzene (307 mg, 1.38 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (12.9 mg, 18.4 μmol) and CuI (7.01 mg, 36.8 μmol) in THF (5 mL) and Et_3N (5 mL) were used and treated

according to GP4 (silica gel, PE:EA = 200:1 to 50:1). The product was obtained as a pale yellow solid (247 mg, 793 μ mol, 86%).

Mp: 79 °C; **R_f:** 0.37 (silica gel, PE:EA = 50:1); **¹H{¹⁹F} NMR** (500 MHz, CD₂Cl₂): δ = 7.67 (d, *J* = 7.9 Hz, 1H), 7.61–7.56 (m, 4H), 7.50–7.46 (m, 1H), 7.35–7.30 (m, 3H), 7.26–7.23 (m, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.12–7.06 (m, 3H); **¹³C{¹H,¹⁹F} NMR** (126 MHz, CD₂Cl₂): 162.7 (s, 1C), 138.0 (s, 1C), 137.8 (s, 1C), 133.3 (d, 1C), 130.7 (d, 1C), 129.5 (d, 2C), 128.0 (d, 1C), 127.9 (s, 1C), 127.6 (d, 2C), 124.5 (d, 1C), 124.3 (d, 1C), 121.8 (s, 1C), 121.4 (d, 2C), 115.9 (d, 1C), 111.5 (s, 1C), 111.0 (d, 1C), 110.3 (d, 1C), 89.0 (s, 1C), 86.8 (s, 1C); **¹⁹F{¹H} NMR** (471 MHz, CD₂Cl₂): -110.1 (1F); **HR-MS** (EI+): *m/z* calculated for [C₂₂H₁₄FN]⁺, [M]⁺: 311.11048, found: 311.11054; **IR** (ATR): ν [cm⁻¹] = 3059, 2962, 2922, 2214, 1948, 1799, 1596, 1571, 1537, 1500, 1489, 1476, 1449, 1415, 1379, 1360, 1335, 1318, 1260, 1225, 1213, 1173, 1150, 1128, 1115, 1099, 1075, 1030, 1016, 937, 909, 868, 823, 795, 758, 708, 696, 636, 608.

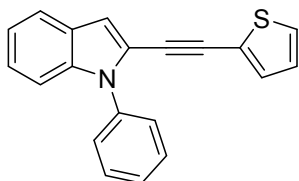
2-((2-Bromophenyl)ethynyl)-1-phenyl-1*H*-indole (1I)



1r-H (254 mg, 1.17 mmol), 1-bromo-2-iodobenzene (496 mg, 1.75 mmol), Pd(PPh₃)₂Cl₂ (16.4 mg, 23.4 μ mol) and CuI (8.91 mg, 46.8 μ mol) in THF (5 mL) and Et₃N (5 mL) were used and treated according to GP4 (silica gel, PE:EA = 200:1 to 100:1). The product was obtained as a pale yellow solid (344 mg, 924 μ mol, 79%).

Mp: 73 °C; **R_f:** 0.20 (silica gel, PE:EA = 100:1); **¹H NMR** (700 MHz, CD₂Cl₂): δ = 7.67 (d, *J* = 7.9 Hz, 1H), 7.60–7.55 (m, 5H), 7.47 (t, *J* = 7.0 Hz, 1H), 7.39 (d, *J* = 7.7 Hz, 1H), 7.30–7.23 (m, 3H), 7.18 (t, *J* = 7.3 Hz, 2H), 7.09 (s, 1H); **¹³C{¹H} NMR** (176 MHz, CD₂Cl₂): 138.2 (s, 1C), 137.9 (s, 1C), 133.5 (d, 1C), 132.8 (d, 1C), 130.0 (d, 1C), 129.7 (d, 2C), 128.1 (d, 1C), 127.9 (s, 1C), 127.9 (d, 2C), 127.5 (d, 1C), 125.2 (s, 1C), 125.1 (s, 1C), 124.3 (d, 1C), 121.9 (s, 1C), 121.4 (d, 2C), 110.9 (d, 1C), 110.5 (d, 1C), 93.9 (s, 1C), 86.2 (s, 1C); **HR-MS** (EI+): *m/z* calculated for [C₂₂H₁₄⁷⁹BrN]⁺, [M]⁺: 371.03041, found: 371.02990; **IR** (ATR): ν [cm⁻¹] = 3055, 2210, 1949, 1908, 1877, 1595, 1499, 1483, 1463, 1446, 1430, 1382, 1359, 1336, 1320, 1252, 1220, 1150, 1134, 1113, 1076, 1049, 1025, 943, 909, 804, 781, 750, 731, 697, 664, 633.

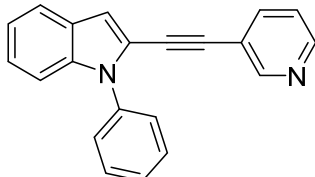
1-Phenyl-2-(thiophen-2-ylethynyl)-1H-indole (1m)



1r-H (181 mg, 831 μmol), 2-iodothiophene (262 mg, 1.25 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (11.7 mg, 16.6 μmol) and CuI (6.33 mg, 33.2 μmol) in THF (5 mL) and Et_3N (5 mL) were used and treated according to GP4 (silica gel, PE:DCM = 50:1). The product was obtained as an off-white solid (185 mg, 618 μmol , 74%).

Mp: 56 °C; **R_f**: 0.63 (silica gel, PE:EA = 20:1); **¹H NMR** (400 MHz, CD_2Cl_2): δ = 7.67–7.65 (m, 1H), 7.61–7.56 (m, 4H), 7.51–7.45 (m, 1H), 7.34–7.31 (m, 2H), 7.26–7.22 (m, 1H), 7.20–7.16 (m, 2H), 7.02 (d, J = 0.7 Hz, 1H), 6.99 (dd, J = 5.1 Hz, J = 3.7 Hz, 1H); **¹³C{¹H} NMR** (101 MHz, CD_2Cl_2): 138.1 (s, 1C), 138.0 (s, 1C), 132.5 (d, 1C), 129.6 (d, 2C), 128.3 (d, 1C), 128.1 (d, 1C), 128.1 (s, 1C), 127.6 (d, 1C), 127.5 (d, 2C), 124.3 (d, 1C), 122.9 (s, 1C), 122.0 (s, 1C), 121.4 (d, 1C), 121.4 (d, 1C), 110.9 (d, 1C); 110.0 (d, 1C), 88.8 (s, 1C), 85.6 (s, 1C); **HR-MS** (EI⁺): m/z calculated for $[\text{C}_{20}\text{H}_{13}\text{NS}]^+$, $[\text{M}]^+$: 299.07632, found: 299.07492; **IR** (ATR): ν [cm^{-1}] = 3104, 3057, 2202, 1596, 1500, 1451, 1419, 1377, 1317, 1256, 1223, 1209, 1182, 1148, 1113, 1075, 1043, 1015, 931, 844, 794, 761, 749, 701, 642.

1-Phenyl-2-(pyridin-3-ylethynyl)-1H-indole (1n)

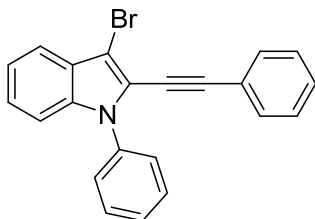


1r-H (197 mg, 907 μmol), 3-bromopyridine (215 mg, 1.36 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (12.7 mg, 18.1 μmol) and CuI (6.91 mg, 36.3 μmol) in THF (5 mL) and Et_3N (5 mL) were used and treated according to GP4 (silica gel, PE:DCM = 5:1). The product was obtained as a pale yellow oil (89.5 mg, 304 μmol , 34%).

R_f: 0.10 (silica gel, PE:EA = 10:1); **¹H NMR** (301 MHz, CDCl_3): δ = 8.53 (d, J = 1.4 Hz, 1H), 8.50 (dd, J = 4.9 Hz, J = 1.7 Hz, 1H), 7.67 (d, J = 7.5 Hz, 1H), 7.62–7.54 (m, 5H), 7.51–7.44 (m, 1H), 7.32 (d, J = 8.3 Hz, 1H), 7.28–7.16 (m, 3H), 7.05 (d, J = 0.5 Hz, 1H); **HR-MS** (EI⁺): m/z calculated for $[\text{C}_{21}\text{H}_{14}\text{N}_2]^+$, $[\text{M}]^+$: 294.11515, found: 294.11514.

The spectroscopic data correspond to those previously reported in the literature.^[13]

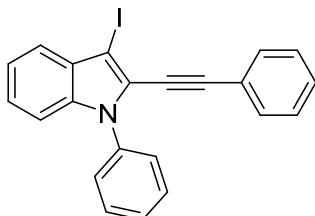
3-Bromo-1-phenyl-2-(phenylethynyl)-1H-indole (1s)



To a solution of **1a** (102 mg, 349 μmol) in DCM (5 mL) *N*-bromosuccinimide (156 mg, 365 μmol) was added and the reaction mixture was stirred at rt for 4 h. A saturated aqueous solution of Na_2SO_3 (3 mL) and water (5 mL) was added and the mixture was extracted with DCM. The combined organic layers were washed with water and brine, dried over Na_2SO_4 , filtered through a plug of silica gel and the solvent was removed under reduced pressure. The product was obtained as a pale yellow oil (91.5 mg, 246 μmol , 71%).

R_f: 0.50 (silica gel, PE:EA = 20:1); **¹H NMR** (300 MHz, CDCl_3): δ = 7.64–7.53 (m, 5H), 7.51–7.44 (m, 1H), 7.40–7.35 (m, 2H), 7.34–7.22 (m, 6H); **¹³C{¹H} NMR** (75 MHz, CDCl_3): 137.5 (s, 1C), 136.8 (s, 1C), 131.5 (d, 2C), 129.3 (d, 2C), 128.9 (d, 1C), 128.5 (d, 2C), 128.1 (d, 1C), 127.3 (d, 2C), 127.0 (s, 1C), 124.9 (d, 1C), 122.5 (s, 1C), 121.8 (s, 1C), 121.7 (d, 1C), 119.8 (d, 1C), 110.8 (d, 1C), 99.3 (s, 1C), 99.2 (s, 1C), 80.0 (s, 1C); **HR-MS** (EI+): *m/z* calculated for $[\text{C}_{22}\text{H}_{14}^{79}\text{BrN}]^+$, $[\text{M}]^+$: 371.03041, found: 371.03097; **IR** (ATR): ν [cm^{-1}] = 3060, 2212, 1949, 1891, 1804, 1596, 1499, 1486, 1448, 1378, 1340, 1325, 1217, 1149, 1117, 1070, 1043, 1023, 938, 839, 778, 742, 689, 648, 621.

3-Iodo-1-phenyl-2-(phenylethynyl)-1H-indole (1t)

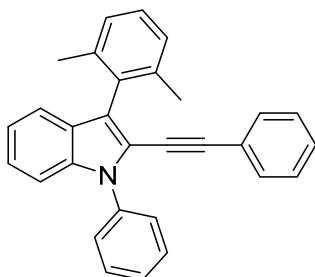


To a solution of **1a** (200 mg, 682 μmol) in DCM (10 mL) *N*-iodosuccinimide (156 mg, 695 μmol) was added and the reaction mixture was stirred at rt for 4 h. A saturated aqueous solution of Na_2SO_3 (5 mL) and water (10 mL) was added and the mixture was extracted with DCM. The combined organic layers were washed with water and brine, dried over Na_2SO_4 , filtered through a plug of silica gel and the solvent was removed under reduced pressure. The product was obtained as a pale yellow oil (280 mg, 668 μmol , 98%).

R_f: 0.63 (silica gel, PE:EA = 10:1); **¹H NMR** (400 MHz, CDCl_3): δ = 7.60–7.55 (m, 4H), 7.53–7.46 (m, 2H), 7.41–7.38 (m, 2H), 7.34–7.30 (m, 3H), 7.29–7.24 (m, 3H); **¹³C{¹H} NMR** (101 MHz, CDCl_3): 137.8 (s, 1C), 137.6 (s, 1C), 131.5 (d, 2C), 130.3 (s, 1C), 129.3 (d, 2C), 128.9 (d, 1C), 128.5 (d, 2C), 128.1 (d, 1C), 127.3 (d, 2C), 126.1 (s, 1C), 124.9 (d, 1C), 122.6 (s, 1C), 121.9 (d, 1C), 121.8 (d, 1C), 110.9 (d, 1C), 98.6 (s, 1C), 81.6 (s, 1C), 68.4 (s, 1C); **HR-MS** (EI+): *m/z* calculated for $[\text{C}_{22}\text{H}_{14}\text{IN}]^+$, $[\text{M}]^+$: 419.01654, found: 419.01610; **IR** (ATR): ν [cm^{-1}] = 3058, 2924, 2853, 2210, 1735, 1654, 1596, 1499,

1484, 1447, 1375, 1350, 1317, 1262, 1216, 1149, 1116, 1070, 1039, 1021, 937, 910, 842, 776, 754, 697, 648, 620.

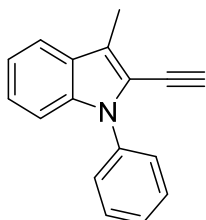
3-(2,6-Dimethylphenyl)-1-phenyl-2-(phenylethynyl)-1*H*-indole (1o)



A Schlenk flask containing **1t** (131 mg, 313 μmol), (2,6-dimethylphenyl)boronic acid (70.5 mg, 470 μmol), $\text{Pd}_2(\text{dba})_3$ (2.87 mg, 3.13 μmol), XPhos (5.98 mg, 12.5 μmol) and K_2CO_3 (130 mg, 940 μmol) was evacuated and refilled with nitrogen three times. Then, a degassed 4:1 mixture of 1,4-dioxane and water (6 mL) was added and the resulting mixture was stirred at 100 °C for 16 h. The solvents were removed under reduced pressure and then, water (20 mL) was added. The mixture was extracted with ethyl acetate and the combined organic layers were washed with water and brine and dried over Na_2SO_4 . The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (silica gel, PE:EA = 100:1). The product was obtained as a pale yellow solid (42.4 mg, 107 μmol , 34%).

Mp: 154 °C; **R_f**: 0.24 (silica gel, PE:EA = 50:1); **¹H NMR** (400 MHz, CDCl_3): δ = 7.69–7.67 (m, 2H), 7.62–7.58 (m, 2H), 7.49–7.45 (m, 1H), 7.43 (d, J = 8.2 Hz, 1H), 7.31–7.19 (m, 8H), 7.17–7.11 (m, 3H), 2.23 (s, 6H); **¹³C{¹H} NMR** (101 MHz, CDCl_3): 138.6 (s, 2C), 138.0 (s, 1C), 137.4 (s, 1C), 132.7 (s, 1C), 131.2 (d, 2C), 129.2 (d, 2C), 128.3 (d, 3C), 127.6 (d, 1C) 127.6 (d, 1C), 127.4 (d, 2C), 127.3 (d, 2C), 127.3 (s, 1C), 124.0 (d, 1C), 123.1 (s, 1C), 123.0 (s, 1C), 120.9 (d, 1C), 120.6 (d, 1C), 120.3 (s, 1C), 110.7 (d, 1C), 97.5 (s, 1C), 81.7 (s, 1C), 20.9 (q, 2C); **HR-MS** (EI⁺): m/z calculated for $[\text{C}_{30}\text{H}_{23}\text{N}]^+$, $[\text{M}]^+$: 397.18250, found: 397.18246; **IR** (ATR): ν [cm^{-1}] = 3060, 2924, 2855, 2208, 1597, 1500, 1451, 1369, 1323, 1264, 1234, 1189, 1166, 1096, 1071, 1018, 941, 802, 756, 691, 664, 625.

2-Ethynyl-3-methyl-1-phenyl-1*H*-indole (1q)



According to a procedure by Hashmi *et al.*,^[14] to a mixture of **S8** (519 mg, 2.21 mmol) and K_2CO_3 (610 mg, 4.41 mmol) in methanol (10 mL) and DCM (20 mL) was added dimethyl (1-diazo-2-oxopropyl)phosphonate (636 mg, 3.31 mmol) and the resulting mixture was stirred at rt for 2 d. Water

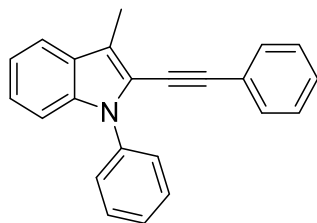
was added and the mixture was extracted with DCM. The combined organic layers were washed with water and brine and dried over Na₂SO₄. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (silica gel, PE). The product was obtained as a colorless oil, which quickly turns bluish black due to minor decomposition (313 mg, 1.35 mmol, 61%).

R_f: 0.65 (silica gel, PE:EA = 20:1); **¹H NMR** (400 MHz, CD₂Cl₂): δ = 7.64–7.62 (m, 1H), 7.58–7.50 (m, 4H), 7.47–7.43 (m, 1H), 7.30–7.23 (m, 2H), 7.21–7.17 (m, 1H), 3.53 (s, 1H), 2.51 (s, 3H);

¹³C{¹H} NMR (101 MHz, CD₂Cl₂): 137.8 (s, 1C), 137.1 (s, 1C), 129.1 (d, 2C), 127.6 (s, 1C), 127.3 (d, 1C), 127.1 (d, 2C), 124.1 (d, 1C), 120.3 (d, 1C), 120.3 (s, 1C), 119.4 (d, 1C), 118.8 (s, 1C), 110.3 (d, 1C), 85.9 (s, 1C), 75.2 (d, 1C), 9.4 (q, 1C); **HR-MS** (EI+): *m/z* calculated for [C₁₇H₁₃N]⁺, [M]⁺:

231.10425, found: 231.10421; **IR** (ATR): ν [cm⁻¹] = 3289, 3055, 2916, 2855, 2103, 1598, 1501, 1450, 1367, 1326, 1235, 1152, 1128, 1094, 1075, 1012, 938, 744, 699, 681, 643, 629.

3-Methyl-1-phenyl-2-(phenylethynyl)-1*H*-indole (1p)

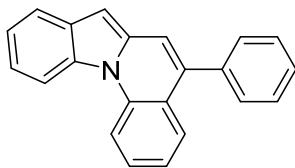


1q (93.6 mg, 405 μmol), iodobenzene (124 mg, 607 μmol), Pd(PPh₃)₂Cl₂ (5.68 mg, 8.09 μmol) and CuI (3.08 mg, 16.2 μmol) in THF (5 mL) and Et₃N (5 mL) were used and treated according to GP4 (silica gel, PE to PE:EA = 20:1). The product was obtained as a pale yellow oil (108 mg, 351 μmol, 87%).

R_f: 0.16 (silica gel, PE:EA = 100:1); **¹H NMR** (300 MHz, CDCl₃): δ = 7.62 (d, *J* = 7.5 Hz, 1H), 7.60–7.51 (m, 4H), 7.44–7.15 (m, 9H), 2.55 (s, 3H); **¹³C{¹H} NMR** (75 MHz, CDCl₃): 138.1 (s, 1C), 137.3 (s, 1C), 131.1 (d, 2C), 129.1 (d, 2C), 128.4 (d, 2C), 128.3 (d, 1C), 128.1 (s, 1C), 127.3 (d, 1C), 127.2 (d, 2C), 124.0 (d, 1C), 123.2 (s, 1C), 120.4 (d, 1C), 120.2 (s, 1C), 119.5 (d, 1C), 119.1 (s, 1C), 110.5 (d, 1C), 98.1 (s, 1C), 81.4 (s, 1C), 10.1 (q, 1C); **HR-MS** (EI+): *m/z* calculated for [C₂₃H₁₇N]⁺, [M]⁺:

307.13555, found: 307.13556; ; **IR** (ATR): ν [cm⁻¹] = 3055, 2913, 2856, 2207, 1948, 1885, 1801, 1671, 1597, 1572, 1499, 1451, 1402, 1379, 1367, 1330, 1268, 1226, 1188, 1174, 1150, 1127, 1092, 1071, 1026, 1012, 921, 840, 755, 696, 655, 641, 625.

5-Phenylindolo[1,2-a]quinoline (2a)



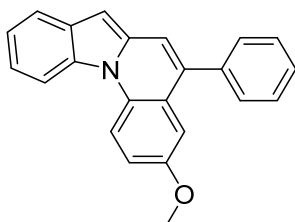
1a (44.0 mg, 150 μmol) and JohnPhosAu(MeCN)SbF₆ (2.90 mg, 3.75 μmol) in *o*-dichlorobenzene (15 mL) were used and treated according to GP5 (silica gel, PE:EA = 100:1). The product was obtained as a yellow solid (39.9 mg, 136 μmol , 91%).

Gram scale synthesis:

1a (1.02 g, 3.48 mmol) and JohnPhosAu(MeCN)SbF₆ (67.1 mg, 86.9 μmol) in *o*-dichlorobenzene (300 mL) were used and treated according to GP5 (silica gel, PE:EA = 100:1). The product was obtained as a yellow solid (883 mg, 3.01 mmol, 87%).

Mp: 82 °C; **R_f**: 0.23 (silica gel, PE:EA = 100:1); **¹H NMR** (301 MHz, CD₂Cl₂): δ = 8.67–8.65 (m, 1H), 8.52–8.49 (m, 1H), 7.89–7.86 (m, 1H), 7.70 (dd, J = 8.0 Hz, J = 1.5 Hz, 1H), 7.68–7.62 (m, 1H), 7.56–7.38 (m, 7H), 7.32 (s, 1H), , 7.31–7.25 (m, 1H), 6.84 (s, 1H); **¹³C{¹H} NMR** (101 MHz, CD₂Cl₂): 139.6 (s, 1C), 137.4 (s, 1C), 136.4 (s, 1C), 136.0 (s, 1C), 133.3 (s, 1C), 131.0 (s, 1C), 130.0 (d, 2C), 129.1 (d, 1C), 128.9 (d, 2C), 128.2 (d, 1C), 128.0 (d, 1C), 124.3 (s, 1C), 123.1 (d, 1C), 122.3 (d, 1C), 122.1 (d, 1C), 121.4 (d, 1C), 119.8 (d, 1C), 116.1 (d, 1C), 114.7 (d, 1C), 97.6 (d, 1C); **HR-MS** (EI⁺): m/z calculated for [C₂₂H₁₅N]⁺, [M]⁺: 293.11990, found: 293.12167; **IR** (ATR): ν [cm⁻¹] = 3054, 2922, 2850, 1735, 1599, 1561, 1492, 1472, 1445, 1383, 1334, 1283, 1253, 1202, 1153, 1133, 1064, 1025, 960, 878, 775, 751, 721, 703, 670, 632, 613; **UV-Vis** (DCM): λ_{max} [nm] = 257, 290, 341, 359, 384, 403, 424; (dioxane): λ_{max} [nm] = 255, 283, 292, 325, 341, 358, 384, 402, 424; (cyclohexane): λ_{max} [nm] = 256, 284, 290, 326, 341, 359, 384, 404, 428; **fluorescence** (DCM): λ_{ex} [nm] = 420, λ_{max} [nm] = 454, 474, 504; (dioxane): λ_{ex} [nm] = 385, λ_{max} [nm] = 451, 473, 503; (cyclohexane): λ_{ex} [nm] = 385, λ_{max} [nm] = 443, 469, 503; (powder): λ_{ex} [nm] = 385, λ_{max} [nm] = 483, 515, 537, 579; **quantum yield** (DCM): Φ = 79%; (dioxane): Φ = 76%; (cyclohexane): Φ = 57%.

3-Methoxy-5-phenylindolo[1,2-a]quinoline (2b)

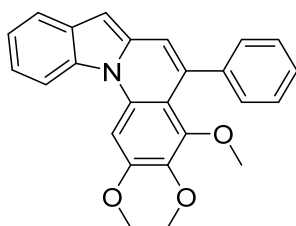


1b (53.0 mg, 164 μmol) and JohnPhosAu(MeCN)SbF₆ (3.16 mg, 4.10 μmol) in *o*-dichlorobenzene (15 mL) were used and treated according to GP5 (silica gel, PE:EA = 50:1). The product was obtained as a yellow solid (34.8 mg, 108 μmol , 66%).

Mp: 128 °C; **R_f**: 0.45 (silica gel, PE:EA = 20:1); **¹H NMR** (301 MHz, CDCl₃): δ = 8.60–8.57 (m, 1H), 8.46–8.42 (m, 1H), 7.88–7.85 (m, 1H), 7.54–7.43 (m, 5H), 7.42–7.34 (m, 2H), 7.31 (s, 1H), 7.23–7.20

(m, 2H), 6.81 (s, 1H), 3.79 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): 154.9 (s, 1C), 139.2 (s, 1C), 135.7 (s, 1C), 135.2 (s, 1C), 132.8 (s, 1C), 131.6 (s, 1C), 130.3 (s, 1C), 129.6 (d, 2C), 128.7 (d, 2C), 127.9 (d, 1C), 125.4 (s, 1C), 121.8 (d, 1C), 121.7 (d, 1C), 121.3 (d, 1C), 120.2 (d, 1C), 116.8 (d, 1C), 115.1 (d, 1C), 114.1 (d, 1C), 111.7 (d, 1C), 97.0 (d, 1C), 55.7 (q, 1C); **HR-MS** (EI+): m/z calculated for $[\text{C}_{23}\text{H}_{17}\text{NO}]^+$, $[\text{M}]^+$: 323.13047, found: 323.12943; **IR** (ATR): ν [cm^{-1}] = 3053, 2923, 2851, 1614, 1571, 1561, 1479, 1452, 1424, 1375, 1332, 1303, 1256, 1235, 1202, 1146, 1109, 1052, 1030, 970, 880, 801, 773, 740, 712, 702, 672; **UV-Vis** (DCM): λ_{max} [nm] = 258, 297, 332, 343, 359, 395, 412, 432; **fluorescence** (DCM): λ_{ex} [nm] = 420, λ_{max} [nm] = 464, 486, 520; **quantum yield** (DCM): $\Phi = 70\%$.

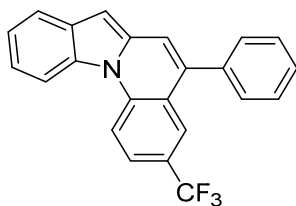
2,3,4-Trimethoxy-5-phenylindolo[1,2-a]quinoline (2c)



1c (73.0 mg, 190 μmol) and JohnPhosAu(MeCN)SbF₆ (3.68 mg, 4.76 μmol) in *o*-dichlorobenzene (18 mL) were used and treated according to GP5 (silica gel, PE:EA = 20:1). The product was obtained as a yellow solid (63.2 mg, 165 μmol , 87%).

Mp: 164–167 °C; **R_f**: 0.34 (silica gel, PE:EA = 10:1); ^1H NMR (400 MHz, CDCl_3): δ = 8.42–8.38 (m, 1H), 8.00 (s, 1H), 7.88–7.84 (m, 1H), 7.46–7.34 (m, 7H), 7.08 (s, 1H), 6.74 (s, 1H), 4.15 (s, 3H), 3.92 (s, 3H), 3.31 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): 154.1 (s, 1C), 151.9 (s, 1C), 143.2 (s, 1C), 138.9 (s, 1C), 135.9 (s, 1C), 134.3 (s, 1C), 133.9 (s, 1C), 132.5 (s, 1C), 131.1 (s, 1C), 128.4 (d, 2C), 127.3 (d, 2C), 126.4 (d, 1C), 122.1 (d, 1C), 121.2 (d, 1C), 121.2 (d, 1C), 119.8 (d, 1C), 113.8 (d, 1C), 112.3 (s, 1C), 96.3 (d, 1C), 95.9 (d, 1C), 61.2 (d, 1C), 61.0 (d, 1C), 56.4 (d, 1C); **HR-MS** (DART+): m/z calculated for $[\text{C}_{25}\text{H}_{22}\text{NO}_3]^+$, $[\text{M}+\text{H}]^+$: 384.1594, found: 384.1596; **IR** (ATR): ν [cm^{-1}] = 2919, 2850, 1600, 1553, 1490, 1478, 1448, 1411, 1363, 1323, 1278, 1263, 1233, 1200, 1134, 1122, 1100, 1055, 1032, 995, 951, 868, 799, 770, 744, 732, 711, 698, 664, 634; **UV-Vis** (DCM): λ_{max} [nm] = 252, 279, 290, 299, 343, 365, 385, 404, 425; **fluorescence** (DCM): λ_{ex} [nm] = 420, λ_{max} [nm] = 454, 472, 504; **quantum yield** (DCM): $\Phi = 90\%$.

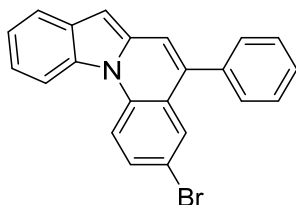
5-Phenyl-3-(trifluoromethyl)indolo[1,2-a]quinoline (2d)



1d (42.5 mg, 118 μmol) and JohnPhosAu(MeCN)SbF₆ (2.27 mg, 2.94 μmol) in *o*-dichlorobenzene (15 mL) were used and treated according to GP5 (silica gel, PE:EA = 100:1). The product was obtained as a yellow solid (35.7 mg, 98.8 μmol , 84%).

Mp: 112 °C; **R_f:** 0.25 (silica gel, PE:EA = 100:1); **¹H{¹⁹F} NMR** (301 MHz, CDCl₃): δ = 8.68 (d, *J* = 8.8 Hz, 1H), 8.44 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 2.1 Hz, 1H), 7.90–7.82 (m, 2H), 7.57–7.41 (m, 7H), 7.36 (s, 1H), 6.86 (s, 1H); **¹³C{¹H,¹⁹F} NMR** (126 MHz, CDCl₃): 139.1 (s, 1C), 138.3 (s, 1C), 135.8 (s, 1C), 134.8 (s, 1C), 133.1 (s, 1C), 130.9 (s, 1C), 129.5 (d, 2C), 128.9 (d, 2C), 128.3 (d, 1C), 125.3 (d, 1C), 124.6 (d, 1C), 124.6 (s, 1C), 124.3 (s, 1C), 124.1 (s, 1C), 122.7 (d, 1C), 122.6 (d, 1C), 121.6 (d, 1C), 121.0 (d, 1C), 115.9 (d, 1C), 114.4 (d, 1C), 98.7 (d, 1C); **¹⁹F{¹H} NMR** (283 MHz, CDCl₃): -61.8 (3F); **HR-MS** (EI⁺): *m/z* calculated for [C₂₃H₁₄F₃N]⁺, [M]⁺: 361.10729, found: 361.10618; **IR** (ATR): ν [cm⁻¹] = 3054, 2919, 2850, 1616, 1574, 1542, 1493, 1452, 1360, 1345, 1319, 1300, 1277, 1254, 1205, 1169, 1152, 1123, 1086, 1034, 966, 908, 881, 845, 807, 773, 743, 729, 704, 685, 659; **UV-Vis** (DCM): λ_{max} [nm] = 283, 296, 307, 334, 351, 369, 386, 405, 428; **fluorescence** (DCM): λ_{ex} [nm] = 420, λ_{max} [nm] = 460, 478, 514; **quantum yield** (DCM): Φ = 72%.

3-Bromo-5-phenylindolo[1,2-a]quinoline (2e)

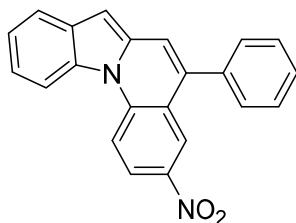


1e (82.5 mg, 222 μmol) and JohnPhosAu(MeCN)SbF₆ (4.28 mg, 5.54 μmol) in *o*-dichlorobenzene (25 mL) were used and treated according to GP5 (silica gel, PE:EA = 50:1). The product was obtained as a yellow solid (50.1 mg, 135 μmol , 61%).

Mp: 165 °C; **R_f:** 0.50 (silica gel, PE:EA = 20:1); **¹H NMR** (400 MHz, CDCl₃): δ = 8.48 (d, *J* = 9.0 Hz, 1H), 8.38 (d, *J* = 8.4 Hz, 1H), 7.88–7.86 (m, 1H), 7.77 (d, *J* = 2.3 Hz, 1H), 7.68 (dd, *J* = 8.9 Hz, *J* = 2.3 Hz, 1H), 7.55–7.39 (m, 7H), 7.31 (s, 1H), 6.83 (s, 1H); **¹³C{¹H} NMR** (101 MHz, CDCl₃): 138.6 (s, 1C), 136.0 (s, 1C), 135.7 (s, 1C), 134.5 (s, 1C), 133.0 (s, 1C), 131.3 (d, 1C), 130.7 (s, 1C), 130.0 (d, 1C), 129.6 (d, 2C), 128.9 (d, 2C), 128.2 (d, 1C), 126.1 (s, 1C), 122.4 (d, 1C), 122.3 (d, 1C), 121.5 (d, 1C), 120.8 (d, 1C), 117.3 (d, 1C), 115.8 (s, 1C), 114.3 (d, 1C), 98.1 (d, 1C); **HR-MS** (EI⁺): *m/z* calculated for [C₂₂H₁₄⁷⁹BrN]⁺, [M]⁺: 371.03041, found: 371.03039; **IR** (ATR): ν [cm⁻¹] = 2922, 2851, 1650, 1612, 1547, 1493, 1468, 1453, 1414, 1367, 1261, 1203, 1093, 1023, 960, 887, 802, 771, 740,

721, 704, 665, 631; **UV-Vis** (DCM): λ_{\max} [nm] = 261, 295, 347, 368, 392, 411, 432; **fluorescence** (DCM): λ_{ex} [nm] = 345, λ_{max} [nm] = 463, 485, 518.

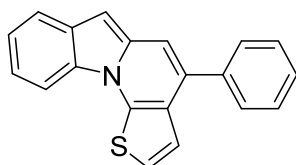
3-Nitro-5-phenylindolo[1,2-a]quinoline (2f)



1f (51.7 mg, 153 μmol) and JohnPhosAu(MeCN)SbF₆ (2.95 mg, 3.82 μmol) in *o*-dichlorobenzene (16 mL) were used and treated according to GP5. After stirring at 170 °C for 4 h, TLC did not show full conversion. JohnPhosAu(MeCN)SbF₆ (2.95 mg, 3.82 μmol) was added and the solution was stirred at 180 °C for 12 h. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (silica gel, PE:DCM = 10:1 to 1:1). The product was obtained as a red-orange solid (31.5 mg, 93.1 μmol , 61%).

Mp: 227 °C; **R_f**: 0.58 (silica gel, PE:EA = 5:1); **¹H NMR** (600 MHz, CDCl₃): δ = 8.66 (d, *J* = 9.2 Hz, 1H), 8.56 (d, *J* = 2.4 Hz, 1H), 8.46–8.42 (m, 2H), 7.89 (d, *J* = 7.7 Hz, 1H), 7.57–7.55 (m, 2H), 7.52–7.50 (m, 4H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.39 (s, 1H), 6.90 (s, 1H); **¹³C{¹H} NMR** (151 MHz, CDCl₃): 142.4 (s, 1C), 141.1 (s, 1C), 137.7 (s, 1C), 135.8 (s, 1C), 134.7 (s, 1C), 133.3 (s, 1C), 131.2 (s, 1C), 129.5 (d, 2C), 129.2 (d, 2C), 128.7 (d, 1C), 124.5 (s, 1C), 123.8 (d, 1C), 123.4 (d, 1C), 123.2 (d, 1C), 123.2 (d, 1C), 121.9 (d, 1C), 121.5 (d, 1C), 115.8 (d, 1C), 114.5 (d, 1C), 100.0 (d, 1C); **HR-MS** (EI⁺): *m/z* calculated for [C₂₂H₁₄N₂O₂]⁺, [M]⁺: 338.10498, found: 338.10488; **IR** (ATR): ν [cm⁻¹] = 3154, 3061, 2922, 2629, 2463, 1895, 1598, 1572, 1512, 1494, 1477, 1445, 1430, 1317, 1280, 1247, 1202, 1183, 1148, 1093, 1078, 1035, 971, 929, 904, 883, 869, 814, 787, 775, 765, 753, 736, 720, 705, 662, 635; **UV-Vis** (DCM): λ_{\max} [nm] = 258, 267, 332, 403; (dioxane): λ_{\max} [nm] = 257, 266, 330, 402; (cyclohexane): λ_{\max} [nm] = 254, 280, 319, 330, 391, 405; **fluorescence** (DCM): not observed; (dioxane): not observed; (cyclohexane): λ_{ex} [nm] = 400, λ_{max} [nm] = 482, 514, 544; **quantum yield** (cyclohexane): Φ = 8%.

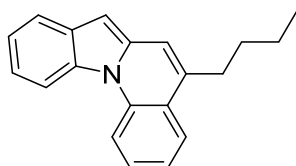
4-Phenylthieno[3',2':5,6]pyrido[1,2-a]indole (2g)



1g (79.0 mg, 264 μmol) and JohnPhosAu(MeCN)SbF₆ (5.09 mg, 6.60 μmol) in *o*-dichlorobenzene (20 mL) were used and treated according to GP5 (silica gel, PE:EA = 200:1). The product was obtained as a yellow solid (67.0 mg, 224 μmol , 85%).

Mp: 125 °C; **R_f:** 0.50 (silica gel, PE:EA = 20:1); **¹H NMR** (400 MHz, CDCl₃): δ = 8.31–8.27 (m, 1H), 7.93–7.89 (m, 1H), 7.66–7.63 (m, 2H), 7.55–7.50 (m, 2H), 7.49–7.43 (m, 3H), 7.39 (s, 1H), 7.37 (d, *J* = 5.6 Hz, 1H), 7.10 (d, *J* = 5.6 Hz, 1H), 6.89 (s, 1H); **¹³C{¹H} NMR** (101 MHz, CDCl₃): 139.7 (s, 1C), 138.6 (s, 1C), 136.8 (s, 1C), 133.7 (s, 1C), 130.0 (s, 1C), 129.8 (s, 1C), 128.8 (d, 2C), 128.8 (d, 2C), 128.0 (d, 1C), 123.7 (d, 1C), 123.3 (s, 1C), 122.6 (d, 1C), 120.7 (d, 1C), 120.7 (d, 1C), 115.3 (d, 1C), 115.2 (d, 1C), 112.7 (d, 1C), 94.7 (d, 1C); **HR-MS** (EI+): *m/z* calculated for [C₂₀H₁₃NS]⁺, [M]⁺: 299.07632, found: 299.07651; **IR** (ATR): ν [cm⁻¹] = 3057, 2919, 2850, 1614, 1594, 1567, 1510, 1494, 1469, 1443, 1422, 1366, 1320, 1259, 1221, 1103, 1016, 920, 864, 800, 769, 735, 703, 678, 657, 643; **UV-Vis** (DCM): λ_{max} [nm] = 281, 299, 302, 345, 361, 396, 412, 436; **fluorescence** (DCM): λ_{ex} [nm] = 410, λ_{max} [nm] = 471, 499, 530; **quantum yield** (DCM): Φ = 37%.

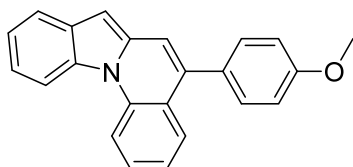
5-Butylindolo[1,2-*a*]quinoline (2h)



1h (49.1 mg, 180 μmol) and JohnPhosAu(MeCN)SbF₆ (3.47 mg, 4.49 μmol) in *o*-dichlorobenzene (17 mL) were used and treated according to GP5 (silica gel, PE). The product was obtained as a yellow oil (44.7 mg, 163 μmol, 91%).

R_f: 0.70 (silica gel, PE:EA = 20:1); **¹H NMR** (301 MHz, CDCl₃): δ = 8.60 (dd, *J* = 8.5 Hz, *J* = 0.8 Hz, 1H), 8.47–8.41 (m, 1H), 7.86–7.81 (m, 2H), 7.63–7.58 (m, 1H), 7.41–7.33 (m, 3H), 7.19 (s, 1H), 6.70 (s, 1H), 2.87 (t, *J* = 7.6 Hz, 2H), 1.76 (quint, *J* = 7.6 Hz, 2H), 1.51 (sext, *J* = 7.6 Hz, 2H), 1.01 (t, *J* = 7.3 Hz, 3H); **¹³C{¹H} NMR** (101 MHz, CDCl₃): 137.2 (s, 1C), 136.5 (s, 1C), 134.0 (s, 1C), 133.0 (s, 1C), 130.7 (s, 1C), 128.3 (d, 1C), 125.1 (d, 1C), 124.2 (s, 1C), 122.7 (d, 1C), 121.9 (d, 1C), 121.3 (d, 1C), 121.0 (d, 1C), 117.8 (d, 1C), 115.8 (d, 1C), 114.4 (d, 1C), 95.9 (d, 1C), 32.3 (t, 1C), 31.4 (t, 1C), 22.9 (t, 1C), 14.1 (q, 1C); **HR-MS** (DART+): *m/z* calculated for [C₂₀H₂₀N]⁺, [M+H]⁺: 274.1590, found: 274.1592; **IR** (ATR): ν [cm⁻¹] = 3060, 2956, 2930, 2870, 2234, 1597, 1532, 1501, 1452, 1378, 1367, 1331, 1316, 1241, 1202, 1145, 1076, 1026, 1012, 929, 789, 759, 748, 738, 698, 645, 633, 609; **UV-Vis** (DCM): λ_{max} [nm] = 281, 296, 339, 360, 379, 397, 418; **fluorescence** (DCM): λ_{ex} [nm] = 410, λ_{max} [nm] = 443, 468, 497; **quantum yield** (DCM): Φ = 52%.

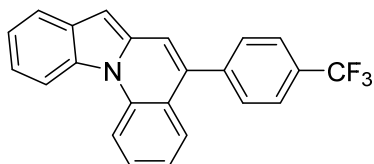
5-(4-Methoxyphenyl)indolo[1,2-a]quinoline (2i)



1i (48.3 mg, 149 μmol) and JohnPhosAu(MeCN)SbF₆ (2.88 mg, 3.73 μmol) in *o*-dichlorobenzene (15 mL) were used and treated according to GP5 (silica gel, PE:EA = 50:1). The product was obtained as a yellow solid (35.9 mg, 111 μmol , 74%).

Mp: 186 °C; **R_f:** 0.27 (silica gel, PE:EA = 20:1); **¹H NMR** (700 MHz, CD₂Cl₂): δ = 8.65 (d, *J* = 8.2 Hz, 1H), 8.49 (d, *J* = 8.1 Hz, 1H), 7.86 (d, *J* = 7.5 Hz, 1H), 7.72 (dd, *J* = 8.0 Hz, *J* = 1.5 Hz, 1H), 7.65–7.63 (m, 1H), 7.47–7.45 (m, 2H), 7.44–7.42 (m, 1H), 7.40–7.38 (m, 1H), 7.29–7.27 (m, 2H), 7.06–7.04 (m, 2H), 6.82 (s, 1H), 3.89 (s, 3H); **¹³C{¹H} NMR** (126 MHz, CD₂Cl₂): 159.8 (s, 1C), 137.4 (s, 1C), 136.5 (s, 1C), 135.6 (s, 1C), 133.2 (s, 1C), 131.6 (s, 1C), 131.0 (d, 2C), 131.0 (s, 1C), 129.0 (d, 1C), 128.0 (d, 1C), 124.5 (s, 1C), 123.0 (d, 1C), 122.3 (d, 1C), 121.9 (d, 1C), 121.3 (d, 1C), 119.5 (d, 1C), 116.0 (d, 1C), 114.6 (d, 1C), 114.3 (d, 2C), 97.2 (d, 1C), 55.7 (q, 1C); **HR-MS** (DART+): *m/z* calculated for [C₂₃H₁₈NO]⁺, [M+H]⁺: 324.1383, found: 324.1383; **IR** (ATR): ν [cm⁻¹] = 3068, 2921, 2850, 1654, 1646, 1636, 1602, 1560, 1541, 1508, 1447, 1382, 1346, 1284, 1252, 1206, 1178, 1130, 1105, 1064, 1036, 960, 876, 834, 802, 750, 701, 669, 615; **UV-Vis** (DCM): λ_{max} [nm] = 256, 292, 341, 362, 386, 403, 425; **fluorescence** (DCM): λ_{ex} [nm] = 405, λ_{max} [nm] = 453, 474, 505.

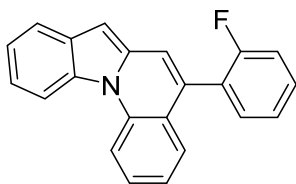
5-(4-(Trifluoromethyl)phenyl)indolo[1,2-a]quinoline (2j)



1j (58.9 mg, 163 μmol) and JohnPhosAu(MeCN)SbF₆ (3.15 mg, 4.07 μmol) in *o*-dichlorobenzene (15 mL) were used and treated according to GP5 (silica gel, PE:EA = 100:1). The product was obtained as a yellow solid (47.6 mg, 132 μmol , 81%).

Mp: 131 °C; **R_f:** 0.58 (silica gel, PE:EA = 20:1); **¹H{¹⁹F} NMR** (301 MHz, CD₂Cl₂): δ = 8.67 (d, *J* = 8.0 Hz, 1H), 8.51 (d, *J* = 8.5 Hz, 1H), 8.90–8.87 (m, 1H), 7.81–7.77 (m, 2H), 7.70–7.64 (m, 3H), 7.60 (dd, *J* = 8.0 Hz, *J* = 1.5 Hz, 1H), 7.49–7.38 (m, 2H), 7.34 (s, 1H), 7.32–7.27 (m, 1H), 6.88 (s, 1H); **¹³C{¹H,¹⁹F} NMR** (126 MHz, CD₂Cl₂): 143.4 (s, 1C), 137.3 (s, 1C), 136.0 (s, 1C), 134.4 (s, 1C), 133.3 (s, 1C), 130.9 (s, 1C), 130.4 (d, 2C), 130.0 (s, 1C), 129.4 (d, 1C), 127.5 (d, 1C), 125.8 (d, 2C), 124.8 (s, 1C), 123.7 (s, 1C), 123.2 (d, 1C), 122.4 (d, 1C), 122.4 (d, 1C), 121.6 (d, 1C), 120.4 (d, 1C), 116.2 (d, 1C), 114.7 (d, 1C), 98.2 (d, 1C); **¹⁹F{¹H} NMR** (283 MHz, CD₂Cl₂): -62.8 (3F); **HR-MS** (EI+): *m/z* calculated for [C₂₃H₁₄F₃N]⁺, [M]⁺: 361.10729, found: 361.10720; **IR** (ATR): ν [cm⁻¹] = 2920, 2851, 1616, 1602, 1562, 1446, 1409, 1383, 1324, 1284, 1260, 1167, 1128, 1108, 1067, 1020, 960, 880, 846, 803, 751, 725, 669, 620; **UV-Vis** (DCM): λ_{max} [nm] = 283, 294, 353, 359, 387, 404, 426; **fluorescence** (DCM): λ_{ex} [nm] = 420, λ_{max} [nm] = 454, 474, 520; **quantum yield** (DCM): Φ = 85%.

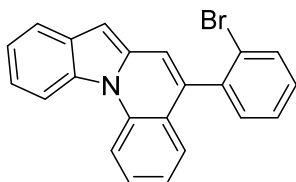
5-(2-Fluorophenyl)indolo[1,2-a]quinoline (2k)



1k (93.0 mg, 299 μmol) and JohnPhosAu(MeCN)SbF₆ (5.77 mg, 7.47 μmol) in *o*-dichlorobenzene (30 mL) were used and treated according to GP5 (silica gel, PE:DCM = 100:1). The product was obtained as a yellow solid (79.8 mg, 256 μmol , 86%).

Mp: 103–105 °C; **R_f:** 0.50 (silica gel, PE:EA = 20:1); **¹H{¹⁹F} NMR** (301 MHz, CD₂Cl₂): δ = 8.66 (dd, J = 8.5 Hz, J = 0.7 Hz, 1H), 8.53–8.50 (m, 1H), 7.90–7.87 (m, 1H), 7.68–7.63 (m, 1H), 7.52–7.24 (m, 9H), 6.88 (s, 1H); **¹³C{¹H,¹⁹F} NMR** (126 MHz, CD₂Cl₂): 160.6 (s, 1C), 137.1 (s, 1C), 136.0 (s, 1C), 133.4 (s, 1C), 132.3 (d, 1C), 130.8 (s, 1C), 130.5 (d, 1C), 130.0 (s, 1C), 129.2 (d, 1C), 127.6 (d, 1C), 126.8 (s, 1C), 124.9 (d, 1C), 123.9 (s, 1C), 123.2 (d, 1C), 122.4 (d, 1C), 122.3 (d, 1C), 121.6 (d, 1C), 121.1 (d, 1C), 116.1 (d, 1C), 116.0 (d, 1C), 114.7 (d, 1C), 98.0 (d, 1C); **¹⁹F{¹H} NMR** (283 MHz, CD₂Cl₂): -113.7 (1F); **HR-MS** (EI⁺): m/z calculated for [C₂₂H₁₄FN]⁺, [M]⁺: 311.11048, found: 311.11144; **IR** (ATR): ν [cm⁻¹] = 3068, 2918, 2850, 1602, 1561, 1542, 1489, 1449, 1384, 1335, 1283, 1253, 1215, 1155, 1097, 1063, 1023, 961, 881, 811, 752, 669, 633; **UV-Vis** (DCM): λ_{max} [nm] = 284, 290, 339, 357, 384, 402, 423; **fluorescence** (DCM): λ_{ex} [nm] = 337, λ_{max} [nm] = 451, 473, 503.

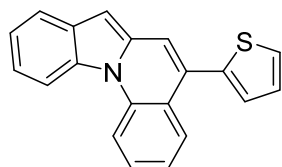
5-(2-Bromophenyl)indolo[1,2-a]quinoline (2l)



1l (136 mg, 365 μmol) and JohnPhosAu(MeCN)SbF₆ (7.05 mg, 9.13 μmol) in *o*-dichlorobenzene (45 mL) were used and treated according to GP5 (silica gel, PE:EA = 100:1). The product was obtained as a yellow solid (126 mg, 338 μmol , 92%).

Mp: 104–107 °C; **R_f:** 0.50 (silica gel, PE:EA = 20:1); **¹H NMR** (301 MHz, CDCl₃): δ = 8.65 (d, J = 8.4 Hz, 1H), 8.51 (d, J = 8.3 Hz, 1H), 7.90–7.87 (m, 1H), 7.74 (dd, J = 8.0 Hz, J = 0.6 Hz, 1H), 7.65–7.59 (m, 1H), 7.49–7.40 (m, 4H), 7.38–7.31 (m, 1H), 7.27–7.23 (m, 3H), 6.86 (s, 1H); **¹³C{¹H} NMR** (101 MHz, CDCl₃): 139.9 (s, 1C), 136.9 (s, 1C), 135.7 (s, 1C), 134.7 (s, 1C), 133.3 (s, 1C), 133.1 (d, 1C), 132.0 (d, 1C), 130.6 (s, 1C), 129.7 (d, 1C), 128.8 (d, 1C), 127.7 (d, 1C), 127.7 (d, 1C), 124.5 (s, 1C), 123.7 (s, 1C), 122.9 (d, 1C), 122.2 (d, 1C), 122.1 (d, 1C), 121.4 (d, 1C), 120.3 (d, 1C), 115.8 (d, 1C), 114.5 (d, 1C), 97.9 (d, 1C); **HR-MS** (EI⁺): m/z calculated for [C₂₂H₁₄⁷⁹BrN]⁺, [M]⁺: 371.03041, found: 371.03133; **IR** (ATR): ν [cm⁻¹] = 3054, 2961, 2920, 2850, 1656, 1604, 1561, 1467, 1445, 1382, 1333, 1283, 1261, 1201, 1099, 1027, 960, 878, 806, 750, 733, 694, 663, 633, 613; **UV-Vis** (DCM): λ_{max} [nm] = 282, 291, 339, 355, 383, 402, 424; **fluorescence** (DCM): λ_{ex} [nm] = 400, λ_{max} [nm] = 446, 470, 499.

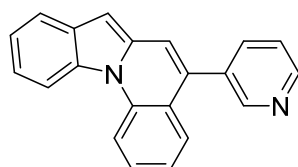
5-(Thiophen-2-yl)indolo[1,2-a]quinoline (2m)



1m (89.8 mg, 300 μmol) and JohnPhosAu(MeCN)SbF₆ (5.79 mg, 7.50 μmol) in *o*-dichlorobenzene (30 mL) were used and treated according to GP5 (silica gel, PE:EA = 200:1). The product was obtained as a yellow solid (71.9 mg, 240 μmol , 80%).

Mp: 83 °C; **R_f:** 0.25 (silica gel, PE:EA = 100:1); **¹H NMR** (600 MHz, CDCl₃): δ = 8.63 (d, J = 8.3 Hz, 1H), 8.48 (d, J = 8.3 Hz, 1H), 8.04 (dd, J = 8.0 Hz, J = 1.3 Hz, 1H), 7.88 (d, J = 7.5 Hz, 1H), 7.66–7.63 (m, 1H), 7.46 (s, 1H), 7.46–7.43 (m, 2H), 7.41 (t, J = 7.1 Hz, 1H), 7.32 (t, J = 7.6 Hz, 1H), 7.29 (dd, J = 3.4 Hz, J = 0.9 Hz, 1H), 7.20 (dd, J = 5.1 Hz, J = 3.5 Hz, 1H), 6.85 (s, 1H); **¹³C{¹H} NMR** (151 MHz, CDCl₃): 140.3 (s, 1C), 137.0 (s, 1C), 135.6 (s, 1C), 133.1 (s, 1C), 130.6 (s, 1C), 129.0 (d, 1C), 127.9 (s, 1C), 127.7 (d, 1C), 127.5 (d, 1C), 127.4 (d, 1C), 125.8 (d, 1C), 123.7 (s, 1C), 122.9 (d, 1C), 122.2 (d, 1C), 122.1 (d, 1C), 121.4 (d, 1C), 121.1 (d, 1C), 115.8 (d, 1C), 114.5 (d, 1C), 98.1 (d, 1C); **HR-MS** (EI+): m/z calculated for [C₂₀H₁₃NS]⁺, [M]⁺: 299.07632, found: 299.07636; **IR** (ATR): ν [cm⁻¹] = 3069, 2920, 2850, 1650, 1601, 1562, 1447, 1382, 1347, 1326, 1284, 1253, 1240, 1207, 1147, 1130, 1104, 1065, 1042, 1023, 950, 876, 856, 826, 750, 702, 668, 633; **UV-Vis** (DCM): λ_{max} [nm] = 258, 298, 332, 344, 363, 392, 406, 427; **fluorescence** (DCM): λ_{ex} [nm] = 420, λ_{max} [nm] = 478, 505.

5-(Pyridin-3-yl)indolo[1,2-a]quinoline (2n)

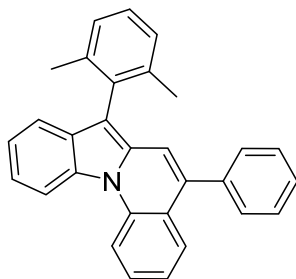


1n (28.4 mg, 96.5 μmol) and JohnPhosAu(MeCN)SbF₆ (1.86 mg, 2.41 μmol) in *o*-dichlorobenzene (10 mL) were used and treated according to GP5. After stirring at 170 °C for 4 h, TLC did not show full conversion. JohnPhosAu(MeCN)SbF₆ (5.59 mg, 7.24 μmol) was added and the solution was stirred at 180 °C for 16 h and again JohnPhosAu(MeCN)SbF₆ (7.45 mg, 9.65 μmol) was added and the solution was stirred at 180 °C for 24 h until full conversion was achieved. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (silica gel, PE:EA = 5:1 to 1:1). The product was obtained as a yellow solid (16.4 mg, 55.7 μmol , 58%).

Mp: 131–133 °C; **R_f:** 0.40 (silica gel, PE:EA = 1:1); **¹H NMR** (600 MHz, CDCl₃): δ = 8.80–8.79 (m, 1H), 8.71 (dd, J = 4.9 Hz, J = 1.6 Hz, 1H), 8.66 (d, J = 8.3 Hz, 1H), 8.50 (d, J = 8.3 Hz, 1H), 7.89 (d, J = 7.6 Hz, 1H), 7.85 (dt, J = 7.7 Hz, J = 2.0 Hz, 1H), 7.67–7.64 (m, 1H), 7.58 (dd, J = 8.0 Hz, J = 1.4 Hz, 1H), 7.47–7.44 (m, 2H), 7.43–7.40 (m, 1H), 7.32 (s, 1H), 7.30–7.27 (m, 1H), 6.87 (s, 1H); **¹³C{¹H} NMR** (151 MHz, CDCl₃): 150.3 (d, 1C), 149.2 (d, 1C), 137.2 (d, 1C), 137.1 (s, 1C), 135.6 (s, 1C), 135.1 (s, 1C), 133.1 (s, 1C), 131.7 (s, 1C), 130.6 (s, 1C), 129.2 (d, 1C), 127.1 (d, 1C), 123.6 (s, 1C), 123.4 (d, 1C), 123.0 (d, 1C), 122.3 (d, 1C), 122.3 (d, 1C), 121.5 (d, 1C), 120.6 (d, 1C), 116.0 (d,

1C), 114.5 (d, 1C), 98.2 (d, 1C); **HR-MS** (EI+): m/z calculated for $[C_{21}H_{14}N_2]^+$, $[M]^+$: 294.11515, found: 294.11437; **IR** (ATR): ν [cm^{-1}] = 3054, 2923, 2851, 1603, 1562, 1471, 1445, 1414, 1382, 1335, 1284, 1253, 1203, 1153, 1133, 1064, 1025, 961, 880, 812, 751, 717, 670, 633; **UV-Vis** (DCM): λ_{max} [nm] = 256, 284, 292, 340, 358, 386, 404, 425; **fluorescence** (DCM): λ_{ex} [nm] = 340, λ_{max} [nm] = 458, 476, 510; **quantum yield** (DCM): Φ = 60%.

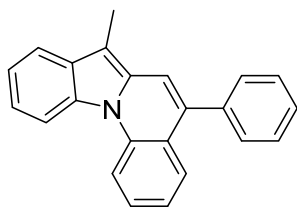
7-(2,6-Dimethylphenyl)-5-phenylindolo[1,2-a]quinoline (2o)



1o (25.0 mg, 63.9 μ mol) and JohnPhosAu(MeCN)SbF₆ (1.21 mg, 1.57 μ mol) in *o*-dichlorobenzene (6 mL) were used and treated according to GP5 (silica gel, PE:DCM = 10:1). The product was obtained as a yellow solid (23.5 mg, 59.0 μ mol, 94%).

Mp: 166–168 °C; **R_f**: 0.55 (silica gel, PE:EA = 20:1); **¹H NMR** (400 MHz, CDCl₃): δ = 8.77 (d, J = 8.4 Hz, 1H), 8.62 (d, J = 8.9 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.74–7.69 (m, 1H), 7.55–7.41 (m, 8H), 7.35–7.29 (m, 2H), 7.26–7.24 (m, 2H), 6.94 (s, 1H), 2.12 (s, 6H); **¹³C{¹H} NMR** (101 MHz, CDCl₃): 139.3 (s, 2C), 139.2 (s, 1C), 137.4 (s, 1C), 135.7 (s, 1C), 132.7 (s, 1C), 132.5 (s, 1C), 132.5 (s, 1C), 129.9 (s, 1C), 129.8 (d, 2C), 128.9 (d, 1C), 128.6 (d, 2C), 127.9 (d, 1C), 127.8 (d, 1C), 127.6 (d, 1C), 127.5 (d, 2C), 124.3 (s, 1C), 122.7 (d, 1C), 122.1 (d, 1C), 122.0 (d, 1C), 120.3 (d, 1C), 118.3 (d, 1C), 115.8 (d, 1C), 114.5 (d, 1C), 109.8 (s, 1C), 20.7 (q, 2C); **HR-MS** (EI+): m/z calculated for $[C_{30}H_{23}N]^+$, $[M]^+$: 397.18250, found: 397.17991; **IR** (ATR): ν [cm^{-1}] = 3057, 2960, 2920, 2853, 1598, 1563, 1492, 1446, 1391, 1372, 1342, 1284, 1262, 1213, 1180, 1062, 1026, 963, 937, 881, 815, 772, 749, 703, 661, 612; **UV-Vis** (DCM): λ_{max} [nm] ($\log \epsilon$) = 293 (4.53), 326 (3.77), 343 (3.76), 360 (3.79), 377 (3.85), 396 (3.99), 417 (4.04), 440 (3.82); **fluorescence** (DCM): λ_{ex} [nm] = 410, λ_{max} [nm] = 469, 500, 530; **quantum yield** (DCM): Φ = 72%.

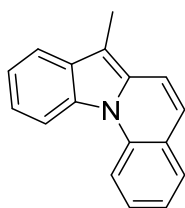
7-Methyl-5-phenylindolo[1,2-a]quinoline (2p)



1p (76.4 mg, 249 μmol) and JohnPhosAu(MeCN)SbF₆ (4.80 mg, 6.20 μmol) in *o*-dichlorobenzene (20 mL) were used and treated according to GP5 (silica gel, PE to PE:EA = 20:1). The product was obtained as a yellow solid (69.2 mg, 225 μmol , 91%).

Mp: 122 °C; **R_f:** 0.50 (silica gel, PE:EA = 20:1); **¹H NMR** (400 MHz, CDCl₃): δ = 8.59 (d, J = 8.1 Hz, 1H), 8.49–8.45 (m, 1H), 7.87–7.83 (m, 1H), 7.66 (dd, J = 8.0 Hz, J = 1.5 Hz, 1H), 7.61–7.57 (m, 1H), 7.57–7.50 (m, 4H), 7.48–7.41 (m, 3H), 7.30 (s, 1H), 7.24–7.20 (m, 1H), 2.55 (s, 3H); **¹³C{¹H} NMR** (101 MHz, CDCl₃): 139.7 (s, 1C), 137.4 (s, 1C), 134.4 (s, 1C), 132.8 (s, 1C), 132.4 (s, 1C), 130.9 (s, 1C), 129.8 (d, 2C), 128.7 (d, 1C), 128.6 (d, 2C), 127.8 (d, 1C), 127.6 (d, 1C), 124.1 (s, 1C), 122.4 (d, 1C), 121.9 (d, 1C), 121.5 (d, 1C), 119.2 (d, 1C), 117.9 (d, 1C), 115.5 (d, 1C), 114.2 (d, 1C), 104.6 (s, 1C), 8.3 (q, 1C); **HR-MS** (EI+): m/z calculated for [C₂₃H₁₇N]⁺, [M]⁺: 307.13555, found: 307.13614; **IR** (ATR): ν [cm⁻¹] = 3047, 2914, 2855, 1597, 1565, 1483, 1444, 1405, 1385, 1367, 1341, 1283, 1257, 1203, 1151, 1121, 1100, 1076, 1026, 935, 873, 833, 772, 747, 728, 704, 675, 632, 609; **UV-Vis** (DCM): λ_{max} [nm] (log ϵ) = 258 (4.25), 295 (4.51), 329 (3.57), 346 (3.61), 363 (3.59), 384 (3.73), 402 (3.87), 421 (3.91), 443 (3.68); **fluorescence** (DCM): λ_{ex} [nm] = 420, λ_{max} [nm] = 474, 506, 540; **quantum yield** (DCM): Φ = 77%.

7-Methylindolo[1,2-a]quinoline (2q)

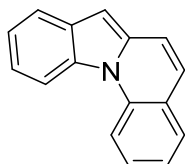


1q (81.4 mg, 352 μmol) and JohnPhosAu(MeCN)SbF₆ (6.79 mg, 8.80 μmol) in *o*-dichlorobenzene (30 mL) were used and treated according to GP5 (silica gel, PE). The product was obtained as a yellow solid (31.1 mg, 134 μmol , 38%).

Mp: 58 °C; **R_f:** 0.50 (silica gel, PE:EA = 50:1); **¹H NMR** (301 MHz, CDCl₃): δ = 8.51 (d, J = 8.4 Hz, 1H), 8.46–8.41 (m, 1H), 7.86–7.81 (m, 1H), 7.63–7.53 (m, 2H), 7.47–7.38 (m, 2H), 7.34 (d, J = 9.5 Hz, 1H), 7.28 (td, J = 7.5 Hz, J = 0.9 Hz, 1H), 7.06 (d, J = 9.5 Hz, 1H), 2.54 (s, 3H); **¹³C{¹H} NMR** (101 MHz, CDCl₃): 137.3 (s, 1C), 133.1 (s, 1C), 132.5 (s, 1C), 130.6 (s, 1C), 128.8 (d, 1C), 128.6 (d, 1C), 124.5 (s, 1C), 122.6 (d, 1C), 122.6 (d, 1C), 121.9 (d, 1C), 121.4 (d, 1C), 119.2 (d, 1C), 117.8 (d, 1C), 115.2 (d, 1C), 114.2 (d, 1C), 104.2 (s, 1C), 8.3 (q, 1C); **HR-MS** (EI+): m/z calculated for [C₁₇H₁₃N]⁺, [M]⁺: 231.10425, found: 231.10411; **IR** (ATR): ν [cm⁻¹] = 3046, 2916, 2854, 1606, 1567, 1486, 1445, 1420, 1387, 1366, 1354, 1324, 1277, 1257, 1205, 1134, 1096, 1019, 932, 789, 750, 732, 665, 628; **UV-Vis**

(DCM): λ_{max} [nm] = 254, 283, 297, 324, 342, 373, 392, 411, 434; **fluorescence** (DCM): λ_{ex} [nm] = 390, λ_{max} [nm] = 459, 483, 516; **quantum yield** (DCM): $\Phi = 75\%$.

Indolo[1,2-a]quinoline (2r)

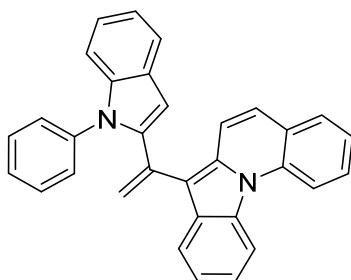


1r-H (68.2 mg, 314 μmol) and JohnPhosAu(MeCN)SbF₆ (6.06 mg, 7.85 μmol) in *o*-dichlorobenzene (125 mL) were used and treated according to GP5 (silica gel, PE:EA = 100:1). The product was obtained as a yellow solid (27.9 mg, 128 μmol , 45%).

R_f: 0.75 (silica gel, PE:EA = 10:1); **¹H NMR** (301 MHz, CDCl₃): $\delta = 8.58$ (d, $J = 8.4$ Hz, 1H), 8.48–8.45 (m, 1H), 7.88–7.85 (m, 1H), 7.67–7.58 (m, 2H), 7.43–7.30 (m, 4H), 7.13 (d, $J = 9.5$ Hz, 1H), 7.01 (s, 1H); **HR-MS** (EI⁺): m/z calculated for [C₁₆H₁₁N]⁺, [M]⁺: 217.08860, found: 217.08635; **UV-Vis** (DCM): λ_{max} [nm] = 280, 294, 341, 364, 377, 394, 417; **fluorescence** (DCM): λ_{ex} [nm] = 395, λ_{max} [nm] = 433, 460, 490, 525; **quantum yield** (DCM): $\Phi = 74\%$.

The spectroscopic data correspond to those previously reported in the literature.^[15]

7-(1-(1-Phenyl-1H-indol-2-yl)vinyl)indolo[1,2-a]quinoline (4)

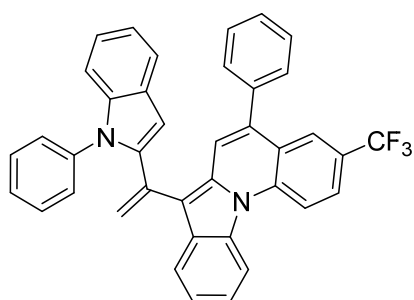


1r-H (50.0 mg, 230 μmol) and JohnPhosAu(MeCN)SbF₆ (4.44 mg, 5.75 μmol) in *o*-dichlorobenzene (15 mL) were used and treated according to GP5 (silica gel, PE:EA = 100:1). The product was obtained as a yellow solid (31.3 mg, 144 μmol , 63%).

Mp: 161 °C; **R_f**: 0.45 (silica gel, PE:EA = 10:1); **¹H NMR** (600 MHz, CD₂Cl₂): $\delta = 8.45$ (d, $J = 8.4$ Hz, 1H), 8.28 (d, $J = 8.5$ Hz, 1H), 7.70 (d, $J = 7.9$ Hz, 1H), 7.62–7.58 (m, 2H), 7.48 (d, $J = 8.0$ Hz, 1H), 7.34–7.31 (m, 3H), 7.22 (t, $J = 7.5$ Hz, 1H), 7.16 (td, $J = 7.0$ Hz, $J = 1.0$ Hz, 1H), 7.13–7.02 (m, 4H), 6.96 (s, 1H), 6.86–6.83 (m, 3H), 6.76–6.73 (m, 1H), 5.93 (d, $J = 2.0$ Hz, 1H), 5.60 (d, $J = 1.9$ Hz, 1H); **¹³C{¹H} NMR** (151 MHz, CD₂Cl₂): 142.7 (s, 1C), 139.2 (s, 1C), 138.3 (s, 1C), 136.7 (s, 1C), 134.4 (s, 1C), 133.9 (s, 1C), 132.8 (s, 1C), 129.5 (s, 1C), 129.1 (d, 2C), 128.3 (d, 2C), 126.7 (d, 2C), 126.6 (d, 1C), 124.7 (s, 1C), 124.5 (d, 1C), 123.3 (d, 1C), 122.7 (d, 1C), 122.3 (d, 1C), 122.2 (d, 1C), 121.0 (d, 1C), 120.8 (d, 1C), 120.5 (d, 1C), 118.5 (d, 1C), 118.0 (t, 1C), 115.8 (d, 1C), 114.1 (d, 1C), 110.7 (d,

1C), 109.8 (s, 1C), 104.3 (d, 1C), 77.9 (s, 1C); **HR-MS** (EI+): m/z calculated for $[C_{32}H_{22}N_2]^+$, $[M]^+$: 434.17775, found: 434.17835; **IR** (ATR): ν [cm^{-1}] = 3046, 2956, 2922, 2851, 1913, 1877, 1597, 1559, 1496, 1443, 1392, 1347, 1318, 1281, 1248, 1216, 1199, 1139, 1128, 1067, 1015, 961, 925, 887, 841, 796, 764, 749, 725, 696, 643, 618; **UV-Vis** (DCM): λ_{max} [nm] ($\log \epsilon$) = 289 (4.54), 404 (3.89), 422 (3.88), 447 (3.61); **fluorescence** (DCM): λ_{ex} [nm] = 400, λ_{max} [nm] = 473, 506, 539.

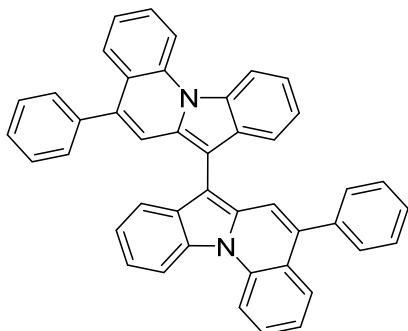
5-Phenyl-7-(1-(1-phenyl-1H-indol-2-yl)vinyl)-3-(trifluoromethyl)indolo[1,2-a]quinoline (5)



A Schlenk flask containing **1r-H** (5.40 mg, 24.9 μ mol), **2d** (13.5 mg, 37.3 μ mol) and JohnPhosAu(MeCN)SbF₆ (960 μ g, 1.24 μ mol) was evacuated and refilled with argon three times. Degassed *o*-dichlorobenzene (5 mL) was added and the resulting solution was stirred at 170°C for 4 h. The solvent was removed under reduced pressure and the residue was purified by preparative thin layer chromatography (silica gel, PE:DCM = 5:1). The product was obtained as a yellow solid (11.8 mg, 20.4 μ mol, 82%).

Mp: 200 °C; **R_f**: 0.40 (silica gel, PE:EA = 20:1); **¹H{¹⁹F} NMR** (500 MHz, CDCl₃): δ = 8.54 (d, J = 8.8 Hz, 1H), 8.24 (d, J = 8.5 Hz, 1H), 7.89 (s, 1H), 7.80 (d, J = 8.8 Hz, 1H), 7.71 (d, J = 7.9 Hz, 1H), 7.49–7.46 (m, 3H), 7.40 (d, J = 8.0 Hz, 1H), 7.38–7.32 (m, 3H), 7.23 (t, J = 7.5 Hz, 1H), 7.20–7.17 (m, 1H), 7.15–7.12 (m, 1H), 7.11 (s, 1H), 7.06 (d, J = 8.1 Hz, 1H), 6.96 (s, 1H), 6.83–6.80 (m, 2H), 6.77–6.74 (m, 3H), 5.92 (d, J = 1.9 Hz, 1H), 5.57 (d, J = 1.9 Hz, 1H); **¹³C{¹H,¹⁹F} NMR** (126 MHz, CDCl₃): 142.1 (s, 1C), 139.0 (s, 1C), 138.6 (s, 1C), 138.3 (s, 1C), 138.0 (s, 1C), 135.1 (s, 1C), 133.5 (s, 1C), 133.4 (s, 1C), 132.5 (s, 1C), 129.8 (s, 1C), 129.4 (d, 2C), 129.0 (d, 2C), 128.3 (d, 1C), 128.1 (d, 2C), 127.9 (s, 1C), 126.6 (d, 2C), 126.5 (d, 1C), 125.3 (d, 1C), 124.7 (s, 1C), 124.5 (d, 1C), 124.3 (s, 1C), 124.1 (s, 1C), 122.9 (d, 1C), 122.8 (d, 1C), 122.6 (d, 1C), 120.9 (d, 1C), 120.9 (d, 1C), 120.6 (d, 1C), 119.8 (d, 1C), 118.0 (t, 1C), 116.0 (d, 1C), 113.7 (d, 1C), 111.3 (s, 1C), 110.5 (d, 1C), 104.4 (d, 1C); **¹⁹F{¹H} NMR** (471 MHz, CDCl₃): -61.8 (3F); **HR-MS** (EI+): m/z calculated for $[C_{39}H_{25}F_3N_2]^+$, $[M]^+$: 578.19643, found: 578.19675; **IR** (ATR): ν [cm^{-1}] = 3055, 2955, 2921, 2851, 1728, 1599, 1493, 1452, 1390, 1354, 1317, 1265, 1241, 1213, 1170, 1154, 1109, 1090, 1063, 1029, 1016, 980, 958, 927, 901, 891, 833, 795, 773, 759, 738, 700, 676, 651, 610.

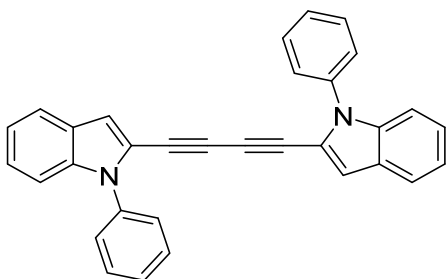
5,5'-Diphenyl-7,7'-biindolo[1,2-a]quinoline (6)



To a solution of **2a** (96.4 mg, 329 μmol) in DCM (5 mL) *N*-iodosuccinimide (81.3 mg, 361 μmol) was added and the reaction mixture was stirred at rt for 16 h. A saturated aqueous solution of Na_2SO_3 (5 mL) and water (10 mL) was added and the mixture was extracted with DCM. The combined organic layers were washed with water and brine and dried over Na_2SO_4 . The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (silica gel, PE:DCM = 10:1 to 1:1). The product was obtained as a yellow solid (67.3 mg, 115 μmol , 70%).

Mp: decomposition >129 $^\circ\text{C}$; **R_f**: 0.41 (silica gel, PE:EA = 20:1); **¹H NMR** (700 MHz, CD_2Cl_2): δ = 8.75 (d, J = 8.3 Hz, 2H), 8.62 (d, J = 8.7 Hz, 2H), 7.79 (d, J = 7.1 Hz, 2H), 7.71–7.68 (m, 4H), 7.53–7.51 (m, 2H), 7.43–7.40 (m, 10H), 7.39–7.36 (m, 2H), 7.30 (t, J = 7.5 Hz, 2H), 7.22 (s, 2H); **¹³C{¹H} NMR** (176 MHz, CD_2Cl_2): 139.4 (s, 2C), 137.5 (s, 2C), 135.9 (s, 2C), 134.0 (s, 2C), 133.4 (s, 2C), 130.8 (s, 2C), 129.9 (d, 4C), 129.2 (d, 2C), 128.7 (d, 4C), 128.1 (d, 2C), 128.0 (d, 2C), 124.6 (s, 2C), 123.1 (d, 2C), 122.5 (d, 2C), 122.3 (d, 2C), 121.1 (d, 2C), 119.4 (d, 2C), 116.1 (d, 2C), 114.8 (d, 2C), 102.8 (s, 2C); **HR-MS** (EI⁺): m/z calculated for $[\text{C}_{44}\text{H}_{28}\text{N}_2]^+$, $[\text{M}]^+$: 584.22470, found: 584.22556; **IR** (ATR): ν [cm^{-1}] = 3054, 2923, 2851, 1659, 1597, 1556, 1492, 1443, 1384, 1340, 1283, 1250, 1200, 1153, 1115, 1066, 1026, 926, 903, 877, 807, 770, 744, 699, 633, 613; **UV-Vis** (DCM): λ_{max} [nm] ($\log \epsilon$) = 303 (4.70), 346 (3.90), 436 (4.18); **fluorescence** (DCM): λ_{ex} [nm] = 435, λ_{max} [nm] = 543; **quantum yield** (DCM): Φ = 38%.

1,4-Bis(1-phenyl-1*H*-indol-2-yl)buta-1,3-diyne (7)

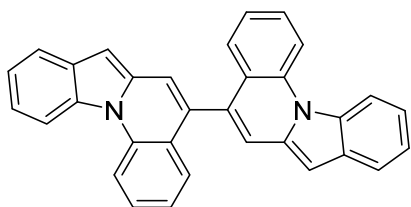


According to a modified procedure by Panda *et al.*,^[16] a mixture of **1r-H** (90.0 mg, 414 μmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (7.27 mg, 10.4 μmol) and CuI (3.94 mg, 20.7 μmol) in THF (5 mL) and Et_3N (5 mL) was stirred under air at rt for 5 h. The solvents were removed under reduced pressure and the residue was

purified by flash column chromatography (silica gel, PE:EA = 20:1 to 10:1). The product was obtained as a pale yellow solid (65.3 mg, 151 μmol , 73%).

Mp: 165 °C; **R_f:** 0.40 (silica gel, PE:EA = 20:1); **¹H NMR** (301 MHz, CDCl₃): δ = 7.63 (d, *J* = 7.8 Hz, 2H), 7.57–7.42 (m, 10H), 7.30–7.22 (m, 4H), 7.20–7.15 (m, 2H), 7.08 (s, 2H); **¹³C{¹H} NMR** (101 MHz, CDCl₃): 137.9 (s, 2C), 137.4 (s, 2C), 129.4 (d, 4C), 127.9 (d, 2C), 127.4 (s, 2C), 127.2 (d, 4C), 124.8 (d, 2C), 121.4 (d, 4C), 120.7 (s, 2C), 113.1 (d, 2C), 110.8 (d, 2C), 80.0 (s, 2C), 75.7 (s, 2C); **HR-MS** (EI+): *m/z* calculated for [C₃₂H₂₀N₂]⁺, [M]⁺: 432.16210, found: 432.16134; **IR** (ATR): ν [cm⁻¹] = 3061, 2955, 2924, 2851, 2146, 1595, 1500, 1444, 1371, 1349, 1318, 1234, 1201, 1148, 1137, 1115, 1076, 1015, 931, 842, 795, 754, 743, 694, 637, 624, 607.

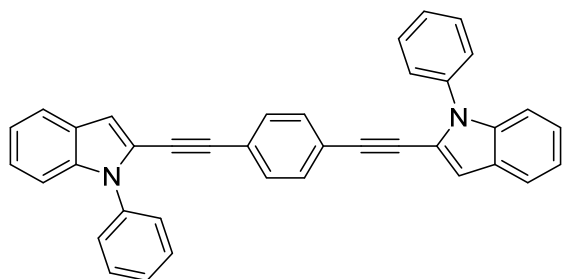
5,5'-Biindolo[1,2-*a*]quinoline (8)



7 (46.8 mg, 108 μmol) and JohnPhosAu(MeCN)SbF₆ (4.18 mg, 5.41 μmol) in *o*-dichlorobenzene (15 mL) were used and treated according to GP5 (silica gel, PE:DCM = 4:1). The product was obtained as a yellow solid (19.5 mg, 45.1 μmol , 42%).

Mp: decomposition >295 °C; **R_f:** 0.57 (silica gel, PE:EA = 10:1); **¹H NMR** (400 MHz, CDCl₃): δ = 8.68 (d, *J* = 8.1 Hz, 2H), 8.55–8.53 (m, 2H), 7.92–7.90 (m, 2H), 7.64–7.60 (m, 2H), 7.50 (s, 2H), 7.48–7.41 (m, 6H), 7.19–7.15 (m, 2H), 6.88 (s, 2H); **¹³C{¹H} NMR** (101 MHz, CDCl₃): 136.9 (s, 2C), 135.9 (s, 2C), 133.3 (s, 2C), 132.6 (s, 2C), 130.6 (s, 2C), 129.0 (d, 2C), 128.2 (d, 2C), 124.4 (s, 2C), 123.0 (d, 2C), 122.3 (d, 2C), 122.2 (d, 2C), 121.5 (d, 2C), 120.9 (d, 2C), 115.8 (d, 2C), 114.5 (d, 2C), 97.9 (d, 2C); **HR-MS** (EI+): *m/z* calculated for [C₃₂H₂₀N₂]⁺, [M]⁺: 432.16210, found: 432.16233; **IR** (ATR): ν [cm⁻¹] = 3062, 2955, 2922, 2851, 1599, 1560, 1443, 1376, 1341, 1282, 1252, 1203, 1135, 1062, 907, 876, 743, 667, 610; **UV-Vis** (DCM): λ_{max} [nm] = 283, 291, 299, 340, 363, 385, 403, 423; **fluorescence** (DCM): λ_{ex} [nm] = 405, λ_{max} [nm] = 471, 510; **quantum yield** (DCM): Φ = 66%.

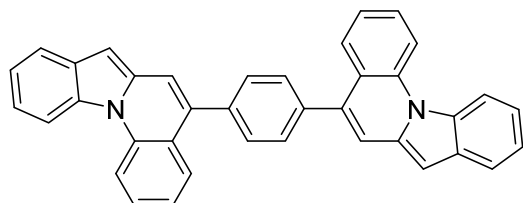
1,4-Bis((1-phenyl-1*H*-indol-2-yl)ethynyl)benzene (9)



1r-H (196 mg, 909 μmol), 1,4-diiodobenzene (120 mg, 364 μmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (12.8 mg, 18.2 μmol) and CuI (6.93 mg, 36.4 μmol) in THF (5 mL) and Et_3N (5 mL) were used and treated according to GP4 (silica gel, PE:DCM = 100:1 to 5:1). The product was obtained as a pale yellow solid (104 mg, 205 μmol , 56%).

Mp: 224 $^\circ\text{C}$; **R_f**: 0.40 (silica gel, PE:EA = 20:1); **¹H NMR** (400 MHz, CD_2Cl_2): δ = 7.67–7.65 (m, 2H), 7.62–7.57 (m, 8H), 7.52–7.47 (m, 2H), 7.33–7.31 (m, 2H), 7.26–7.22 (m, 6H), 7.19–7.15 (m, 2H), 7.03 (d, J = 0.7 Hz, 2H); **¹³C{¹H} NMR** (101 MHz, CD_2Cl_2): 138.1 (s, 2C), 138.0 (s, 2C), 131.4 (d, 4C), 129.6 (d, 4C), 128.2 (d, 2C), 128.0 (s, 2C), 127.7 (d, 4C), 124.3 (d, 2C), 123.0 (s, 2C), 122.0 (s, 2C), 121.4 (d, 2C), 121.4 (d, 2C), 110.9 (d, 2C), 110.1 (d, 2C), 95.3 (s, 2C), 84.2 (s, 2C); **HR-MS** (EI⁺): m/z calculated for $[\text{C}_{38}\text{H}_{24}\text{N}_2]^+$, $[\text{M}]^+$: 508.19340, found: 508.19367; **IR** (ATR): ν [cm^{-1}] = 3054, 2218, 1595, 1551, 1498, 1477, 1449, 1410, 1374, 1355, 1335, 1318, 1215, 1152, 1130, 1103, 1077, 1019, 934, 830, 808, 796, 762, 729, 698, 638, 623, 606.

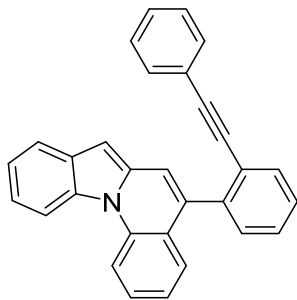
1,4-Bis(indolo[1,2-*a*]quinolin-5-yl)benzene (10)



9 (40.5 mg, 79.6 μmol) and $\text{JohnPhosAu}(\text{MeCN})\text{SbF}_6$ (3.07 mg, 3.98 μmol) in *o*-dichlorobenzene (15 mL) were used and treated according to GP5 (silica gel, PE:DCM = 8:1 to 2:1). The product was obtained as a yellow solid. This compound showed high instability in solution and it could not be purified completely. A full characterization was not possible.

Mp: decomposition >190 $^\circ\text{C}$; **R_f**: 0.33 (silica gel, PE:EA = 20:1); **¹H NMR** (301 MHz, CDCl_3): δ = 8.69 (d, J = 8.0 Hz, 2H), 8.54–8.51 (m, 2H), 7.91–7.88 (m, 2H), 7.84 (dd, J = 8.0 Hz, J = 1.5 Hz, 2H), 7.73–7.64 (m, 8H), 7.49–7.39 (m, 6H), 7.37–7.31 (m, 2H); **HR-MS** (EI⁺): m/z calculated for $[\text{C}_{38}\text{H}_{24}\text{N}_2]^+$, $[\text{M}]^+$: 508.19340, found: 508.19096.

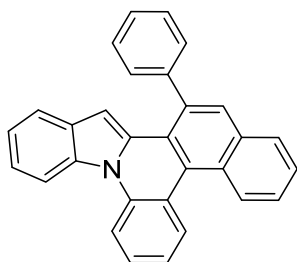
5-(2-(Phenylethynyl)phenyl)indolo[1,2-a]quinoline (11)



11 (87.0 mg, 234 μmol), phenylacetylene (71.6 mg, 701 μmol), $\text{Pd}(\text{PPh}_3)_4$ (13.5 mg, 11.7 μmol), CuI (4.45 mg, 23.4 μmol) and Et_3N (5 mL) were used and treated according to GP4 (90 $^\circ\text{C}$, 2 d; silica gel, PE to PE:DCM = 5:1). The product was obtained as a yellow solid (49.0 mg, 125 μmol , 53%).

Mp: 93–95 $^\circ\text{C}$; **R_f:** 0.40 (silica gel, PE:EA = 20:1); **$^1\text{H NMR}$** (400 MHz, CDCl_3): δ = 8.70–8.67 (m, 1H), 8.55–8.53 (m, 1H), 7.90–7.88 (m, 1H), 7.73–7.71 (m, 1H), 7.65–7.60 (m, 1H), 7.54 (dd, J = 8.0 Hz, J = 1.5 Hz, 1H), 7.51–7.39 (m, 6H), 7.28–7.24 (m, 1H), 7.17–7.07 (m, 3H), 6.95–6.92 (m, 2H), 6.86 (s, 1H); **$^{13}\text{C}\{^1\text{H}\}$ NMR** (101 MHz, CDCl_3): 141.5 (s, 1C), 136.9 (s, 1C), 136.1 (s, 1C), 134.4 (s, 1C), 133.2 (s, 1C), 132.5 (d, 1C), 131.4 (d, 2C), 130.7 (s, 1C), 130.5 (d, 1C), 128.6 (d, 1C), 128.5 (d, 1C), 128.2 (d, 4C), 128.0 (d, 1C), 124.0 (s, 1C), 123.8 (s, 1C); 123.1 (s, 1C), 122.7 (d, 1C), 122.0 (d, 1C), 121.9 (d, 1C), 121.3 (d, 1C), 120.5 (d, 1C), 115.6 (d, 1C), 114.5 (d, 1C), 97.6 (d, 1C), 93.9 (s, 1C), 88.7 (s, 1C); **HR-MS** (EI⁺): m/z calculated for $[\text{C}_{30}\text{H}_{19}\text{N}]^+$, $[\text{M}]^+$: 393.15120, found: 393.15211; **IR** (ATR): ν [cm^{-1}] = 3059, 2960, 2922, 2851, 1720, 1602, 1561, 1493, 1468, 1447, 1382, 1334, 1261, 1202, 1095, 1025, 961, 914, 873, 805, 756, 725, 691, 670, 632, 614.

1-Phenylbenzo[*k*]indolo[1,2-*f*]phenanthridine (12)

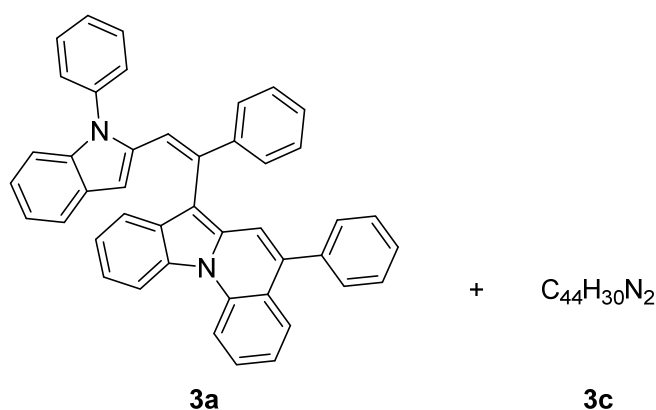


12 (22.7 mg, 62.8 μmol) and $\text{JohnPhosAu}(\text{MeCN})\text{SbF}_6$ (1.21 mg, 1.57 μmol) in *o*-dichlorobenzene (6 mL) were used and treated according to GP5 (silica gel, PE:DCM = 10:1). The product was obtained as a yellow solid (15.1 mg, 38.4 μmol , 61%).

Mp: 212–214 $^\circ\text{C}$; **R_f:** 0.60 (silica gel, PE:EA = 10:1); **$^1\text{H NMR}$** (600 MHz, CDCl_3): δ = 8.76 (d, J = 8.5 Hz, 1H), 8.57–8.55 (m, 1H), 8.50 (d, J = 8.1 Hz, 1H), 8.32 (d, J = 8.4 Hz, 1H), 7.91 (d, J = 7.8 Hz, 1H), 7.76 (s, 1H), 7.64–7.59 (m, 4H), 7.57–7.52 (m, 5H), 7.42 (t, J = 7.6 Hz, 1H), 7.35 (t, J = 7.3 Hz, 1H), 7.22 (t, J = 7.4 Hz, 1H), 5.88 (s, 1H); **$^{13}\text{C}\{^1\text{H}\}$ NMR** (151 MHz, CDCl_3): 142.9 (s, 1C), 137.2 (s, 1C), 135.6 (s, 1C), 135.0 (s, 1C), 133.3 (s, 1C), 132.6 (s, 1C), 130.5 (d, 1C), 130.3 (d, 1C), 130.0 (s, 1C), 130.0 (d, 2C), 129.0 (s, 1C), 128.9 (d, 2C), 128.7 (d, 1C), 128.5 (d, 1C), 128.0 (d, 1C), 127.4 (d,

1C), 126.6 (d, 1C), 126.5 (s, 1C), 126.4 (d, 1C), 124.5 (s, 1C), 123.6 (s, 1C), 123.1 (d, 1C), 122.4 (d, 1C), 121.7 (d, 1C), 121.4 (d, 1C), 117.2 (d, 1C), 113.5 (d, 1C), 101.1 (d, 1C); **HR-MS** (EI+): m/z calculated for $[C_{30}H_{19}N]^+$, $[M]^+$: 393.15120, found: 393.15085; **IR** (ATR): ν [cm^{-1}] = 2955, 2923, 2852, 1660, 1633, 1590, 1556, 1531, 1493, 1456, 1417, 1361, 1332, 1260, 1209, 1152, 1091, 1030, 893, 801, 781, 751, 736, 702, 656, 625; **UV-Vis** (DCM): λ_{max} [nm] = 255, 293, 306, 321, 346, 381, 407; **fluorescence** (DCM): λ_{ex} [nm] = 410, λ_{max} [nm] = 487, 511; **quantum yield** (DCM): $\Phi = 40\%$.

(Z)-5-Phenyl-7-(1-phenyl-2-(1-phenyl-1*H*-indol-2-yl)vinyl)indolo[1,2-*a*]quinoline (3a) + dimer 3c



1a (114 mg, 389 μ mol) and IPrAuNTf₂ (16.8 mg, 19.4 μ mol) in *o*-dichlorobenzene (25 mL) were stirred at 140 °C for 90 min. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (PE:EA = 200:1 to 10:1) to yield a mixture of the **3a–d** (99.1 mg, 338 μ mol, 87%). Repeated preparative thin layer chromatography (silica gel, PE:DCM = 5:1, 10:1 and 20:1) was applied to yield a 5:1 mixture of **3a** and **3c**. Through vapour diffusion of MeOH into a saturated solution of this mixture in CHCl₃ single crystals were grown and the structure of **3a** was confirmed by single crystal X-ray analysis. ¹H NMR of the sampled crystals confirmed the right assignment of **3a** to the observed structure.

3a:

R_f: 0.33 (silica gel, PE:EA = 20:1); **¹H NMR** (400 MHz, CDCl₃): δ = 8.77 (d, J = 8.3 Hz, 1H), 8.57 (d, J = 8.6 Hz, 1H), 7.70–7.67 (m, 1H), 7.46–7.21 (m, 20H), 7.16–7.14 (m, 2H), 7.10 (d, J = 0.4 Hz, 1H), 7.04–7.03 (m, 2H), 6.99 (s, 1H), 6.07 (s, 1H); **¹³C{¹H} NMR** (101 MHz, CDCl₃): 142.9 (s, 1C), 139.1 (s, 1C), 138.2 (s, 1C), 138.0 (s, 1C), 137.7 (s, 1C), 137.2 (s, 1C), 135.9 (s, 1C), 134.5 (s, 1C), 133.4 (s, 1C), 133.3 (s, 1C), 129.7 (s, 1C), 129.7 (d, 2C), 129.4 (d, 2C), 128.9 (d, 1C), 128.4 (d, 4C), 128.4 (s, 1C), 128.1 (d, 2C), 127.8 (d, 1C), 127.8 (d, 1C), 127.8 (d, 1C), 127.6 (d, 1C), 127.3 (d, 2C), 124.2 (s, 1C), 122.9 (d, 1C), 122.3 (d, 1C), 122.2 (d, 2C), 121.1 (d, 1C), 120.7 (d, 1C), 120.4 (d, 1C), 119.4 (d, 1C), 118.9 (d, 1C), 115.9 (d, 1C), 114.5 (d, 1C), 110.2 (d, 1C), 108.8 (s, 1C), 104.0 (d, 1C); **HR-MS** (EI+): m/z calculated for $[C_{44}H_{30}N_2]^+$, $[M]^+$: 586.24035, found: 586.23983.

3c:

R_f: 0.33 (silica gel, PE:EA = 20:1); **¹H NMR** (400 MHz, CDCl₃): δ = 8.62 (d, J = 8.2 Hz, 1H), 8.45 (d, J = 8.5 Hz, 1H), 7.71–7.69 (m, 1H), 7.63–7.59 (m, 1H), 7.68–7.00 (m, 21H), 6.98 (t, J = 2.6 Hz, 2H), 6.96 (d, J = 2.7 Hz, 1H), 6.74 (s, 1H), 6.26 (s, 1H); **¹³C{¹H} NMR** (101 MHz, CDCl₃): 141.5 (s, 1C),

139.2 (s, 1C), 138.0 (s, 1C), 137.9 (s, 1C), 137.8 (s, 1C), 137.1 (s, 1C), 137.0 (s, 1C), 136.0 (s, 1C), 134.5 (s, 1C), 132.9 (s, 1C), 130.2 (d, 2C), 129.7 (s, 1H) 129.6 (d, 2C), 129.5 (d, 2C), 128.9 (d, 1C), 128.8 (d, 2C), 128.6 (d, 2C), 128.6 (d, 2C), 128.4 (s, 1C), 128.0 (d, 1C), 127.9 (d, 1C), 127.8 (d, 1C), 127.6 (d, 1C), 124.3 (s, 1C), 123.1 (d, 1C), 122.2 (d, 1C), 122.2 (d, 2C), 121.1 (d, 1C), 120.6 (d, 1C), 120.5 (d, 1C), 119.0 (d, 1C), 118.1 (d, 1C), 116.1 (d, 1C), 114.2 (d, 1C), 113.3 (s, 1C), 110.3 (d, 1C), 103.4 (d, 1C); **HR-MS** (EI+): *m/z* calculated for [C₄₄H₃₀N₂]⁺, [M]⁺: 586.24035, found: 586.23983.

Dimer 3b + dimer 3d

1a (114 mg, 389 μmol) and IPrAuNTf₂ (16.8 mg, 19.4 μmol) in *o*-dichlorobenzene (25 mL) were stirred at 140 °C for 90 min. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (PE:EA = 200:1 to 10:1) to yield a mixture of **3a–d** (99.1 mg, 338 μmol, 87%). Repeated preparative thin layer chromatography (silica gel, PE:DCM = 5:1 and 10:1) was applied to yield a 7:3 and a 1:1 mixture of **3b** and **3d**, which allowed the assignment of NMR peaks by comparison.

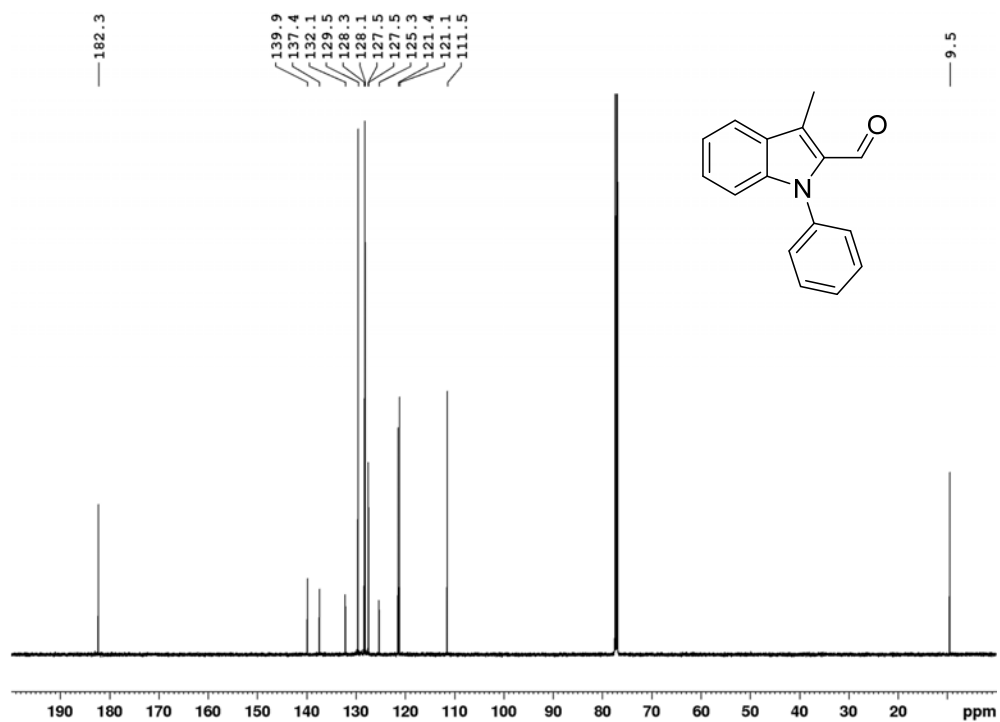
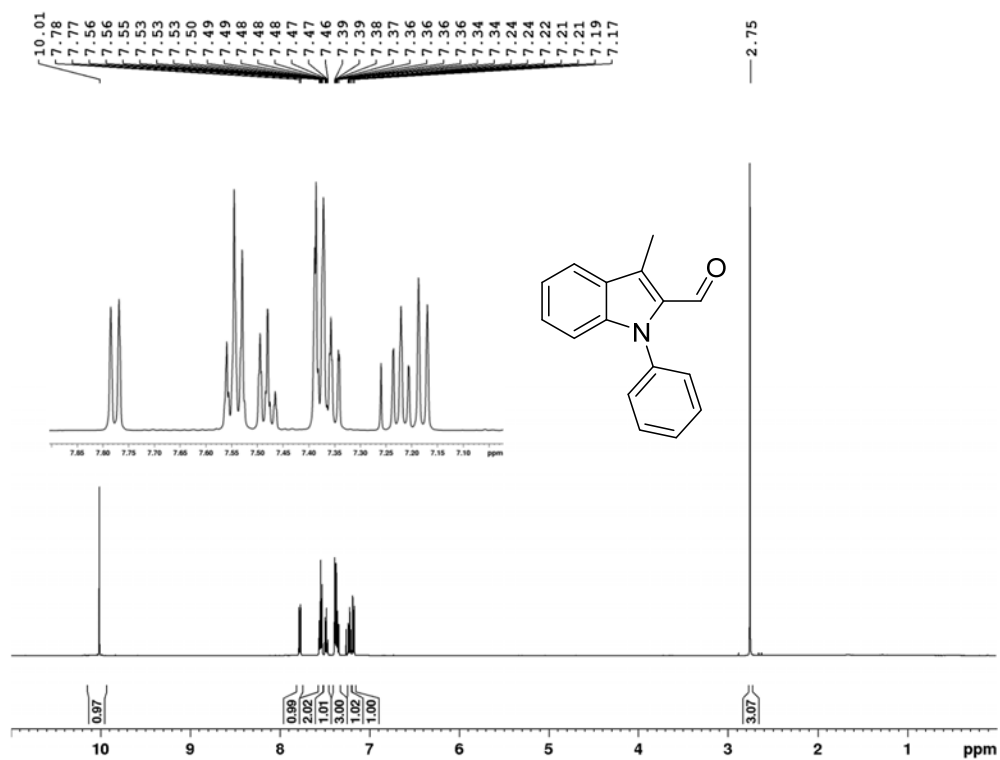
3b:

R_f: 0.35 (silica gel, PE:EA = 20:1); **¹H NMR** (400 MHz, CDCl₃): δ = 8.52 (d, *J* = 8.4 Hz, 1H), 8.29 (d, *J* = 8.6 Hz, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.64–7.58 (m, 2H), 7.39–7.03 (m, 18H), 6.98–6.95 (m, 1H), 6.69–6.59 (m, 6H); **¹³C{¹H} NMR** (101 MHz, CDCl₃): 144.6 (s, 1C), 139.4 (s, 1C), 139.2 (s, 1C), 138.0 (s, 1C), 138.0 (s, 1C), 136.6 (s, 1C), 135.7 (s, 1C), 133.1 (s, 1C), 132.9 (s, 1C), 130.4 (d, 1C), 129.8 (s, 1C), 129.6 (d, 2C), 129.1 (d, 2C), 128.6 (d, 1C), 128.5 (d, 2C), 128.3 (d, 2C), 127.9 (s, 1C), 127.8 (d, 2C), 127.8 (d, 1C), 127.5 (d, 1C), 126.9 (d, 1C), 126.5 (d, 2C), 126.0 (d, 1C), 125.9 (s, 1C), 123.7 (s, 1C), 122.7 (d, 1C), 122.3 (d, 1C), 122.2 (d, 1C), 121.9 (d, 1C), 121.2 (d, 1C), 120.7 (d, 1C), 120.4 (d, 1C), 119.3 (d, 1C), 115.8 (d, 1C), 113.9 (d, 1C), 110.4 (d, 1C), 107.4 (s, 1C), 104.4 (d, 1C); **HR-MS** (EI+): *m/z* calculated for [C₄₄H₃₀N₂]⁺, [M]⁺: 586.24035, found: 586.24243.

3d:

R_f: 0.35 (silica gel, PE:EA = 20:1); **¹H NMR** (400 MHz, CDCl₃): δ = 8.55 (d, *J* = 8.5 Hz, 1H), 8.35 (d, *J* = 8.6 Hz, 1H), 7.67–7.58 (m, 3H), 7.42–7.03 (m, 18H), 6.98–6.95 (m, 1H), 6.87–6.78 (m, 6H); **¹³C{¹H} NMR** (101 MHz, CDCl₃): 139.6 (s, 1C), 139.1 (s, 1C), 138.1 (s, 1C), 137.9 (s, 1C), 137.7 (s, 1C), 136.7 (s, 1C), 135.9 (s, 1C), 134.2 (s, 1C), 132.7 (s, 1C), 129.6 (s, 1C), 129.5 (d, 2C), 129.2 (d, 2C), 128.8 (d, 1C), 128.6 (d, 2C), 128.5 (s, 1C), 128.4 (d, 2C), 128.2 (d, 2C), 127.8 (d, 1C), 127.5 (d, 1C), 127.0 (d, 1C), 126.5 (d, 2C), 126.2 (d, 1C), 126.0 (s, 1C), 124.2 (s, 1C), 122.9 (d, 1C), 122.3 (d, 1C), 122.3 (d, 1C), 122.1 (d, 1C), 121.2 (d, 1C), 120.7 (d, 1C), 120.7 (d, 1C), 120.4 (d, 1C), 118.7 (d, 1C), 115.9 (d, 1C), 113.9 (d, 1C), 111.8 (s, 1C), 110.6 (d, 1C), 105.7 (d, 1C); **HR-MS** (EI+): *m/z* calculated for [C₄₄H₃₀N₂]⁺, [M]⁺: 586.24035, found: 586.24243.

2 NMR Spectra



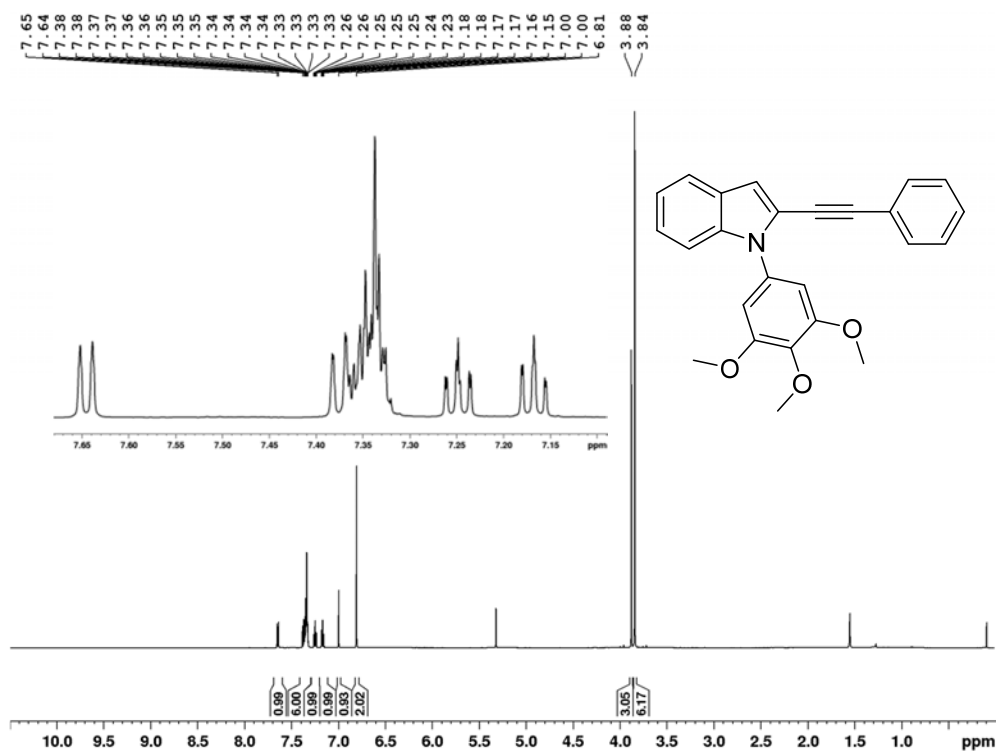


Figure S4. ¹H NMR spectrum (600 MHz, CD₂Cl₂) of **1c**.

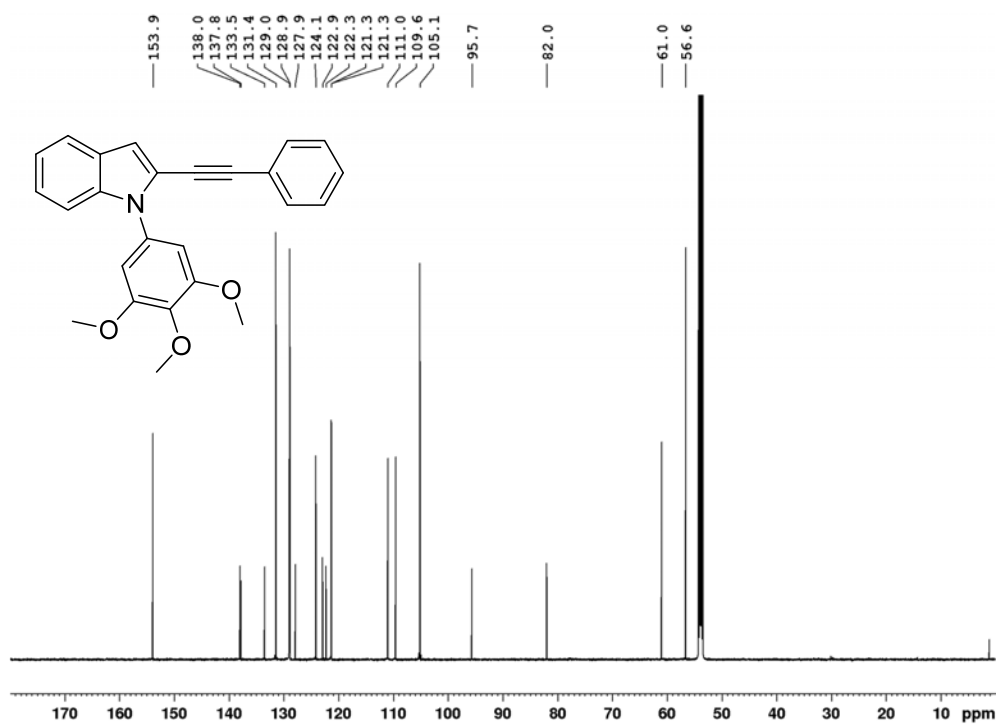


Figure S5. ¹³C{¹H} NMR spectrum (151 MHz, CD₂Cl₂) of **1c**.

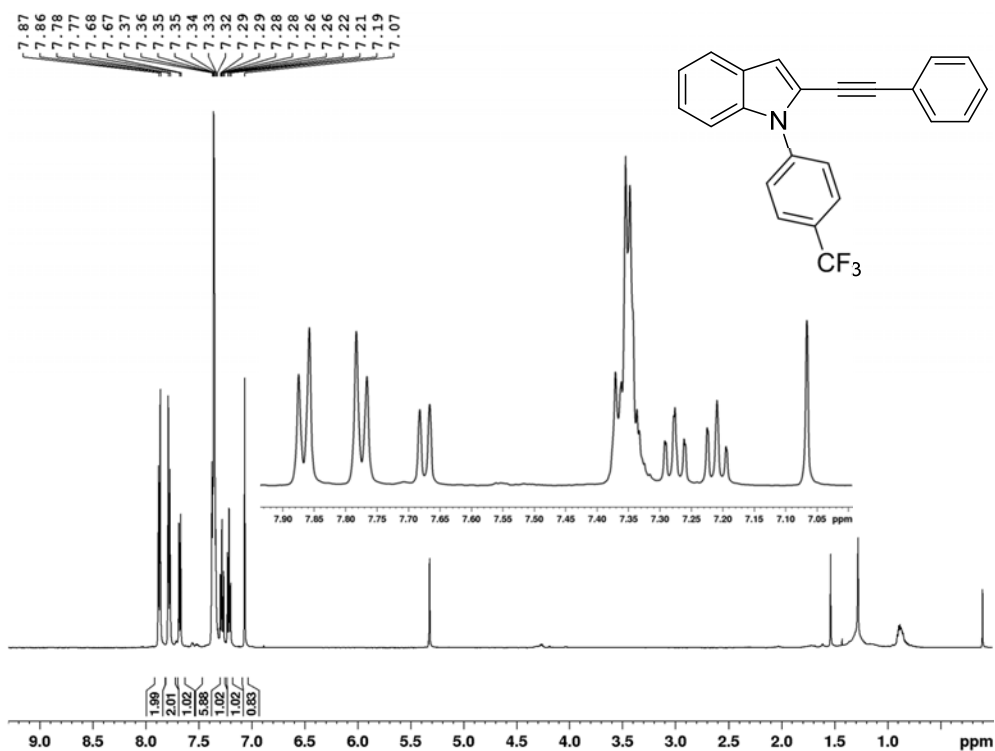


Figure S6. ^1H NMR spectrum (500 MHz, CD_2Cl_2) of **1d**.

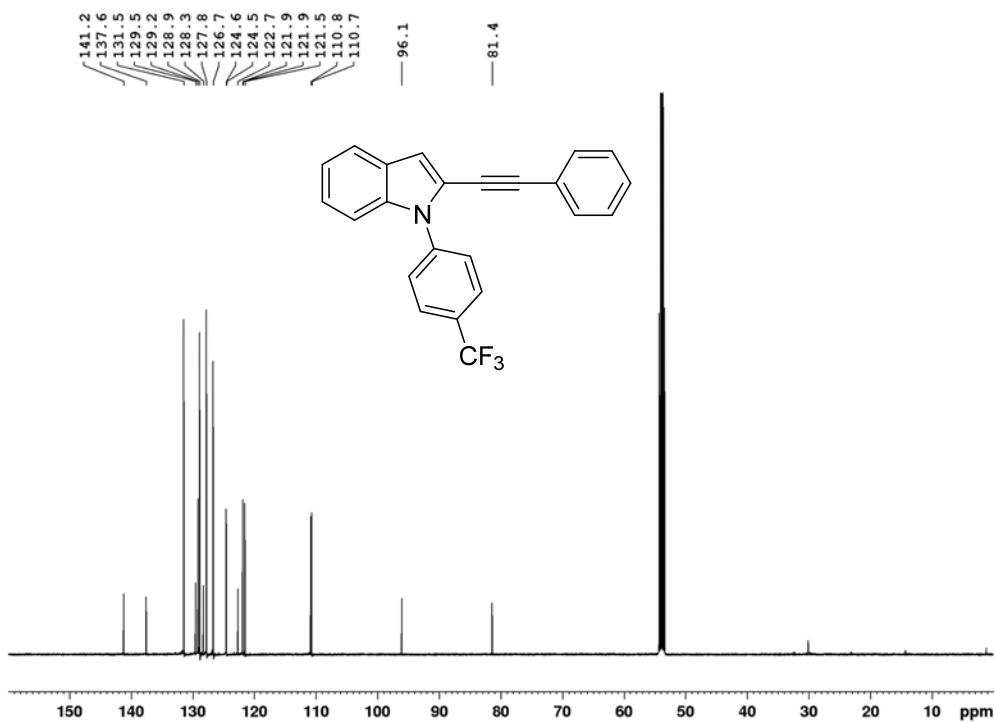


Figure S7. $^{13}\text{C}\{^1\text{H}, ^{19}\text{F}\}$ NMR spectrum (126 MHz, CD_2Cl_2) of **1d**.

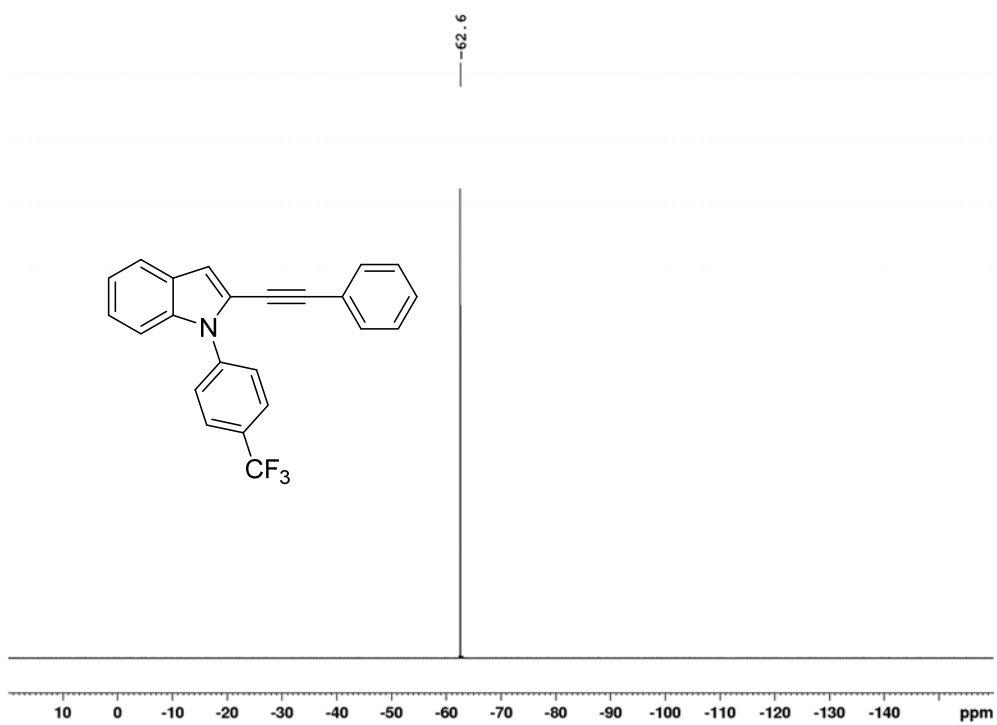


Figure S8. $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum (471 MHz, CD_2Cl_2) of **1d**.

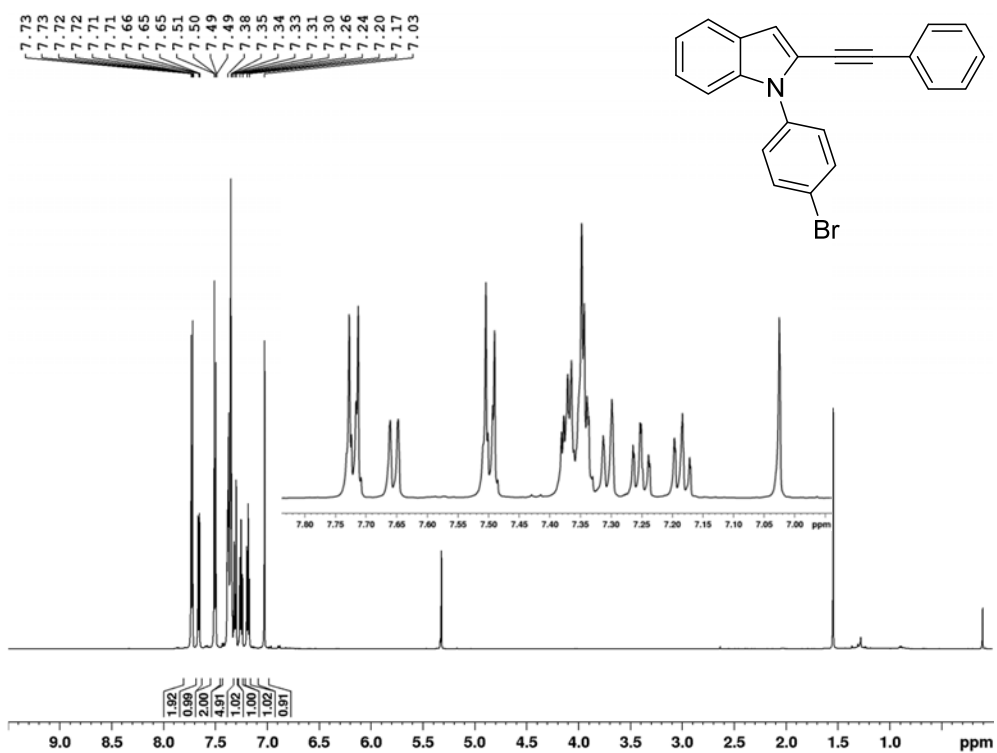


Figure S9. ^1H NMR spectrum (600 MHz, CD_2Cl_2) of **1e**.

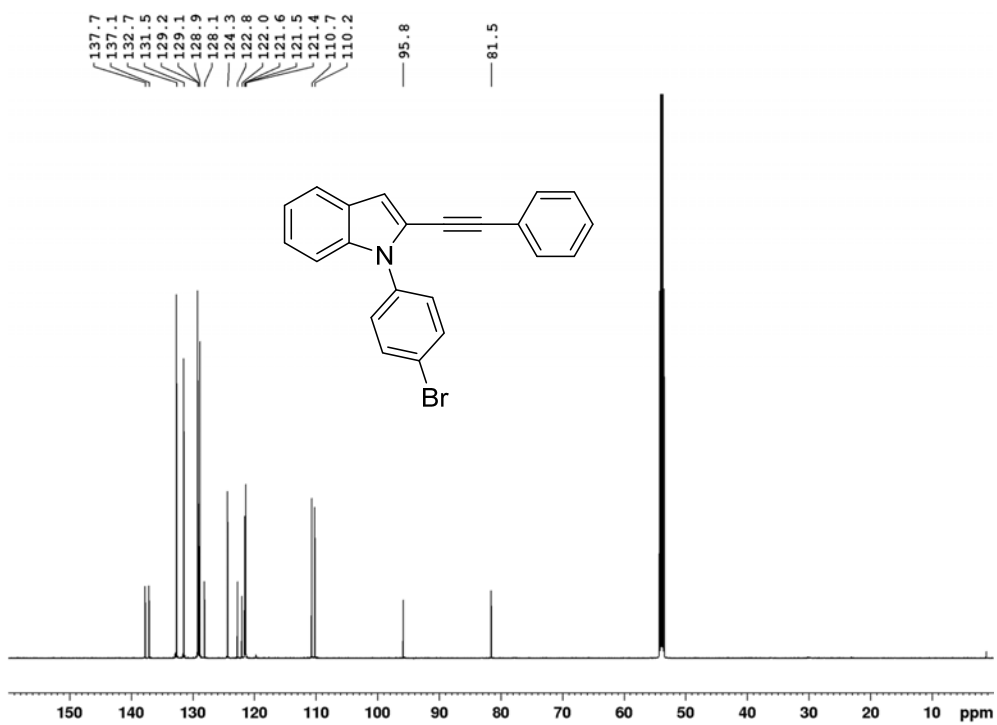


Figure S10. ¹³C{¹H} NMR spectrum (151 MHz, CD₂Cl₂) of 1e.

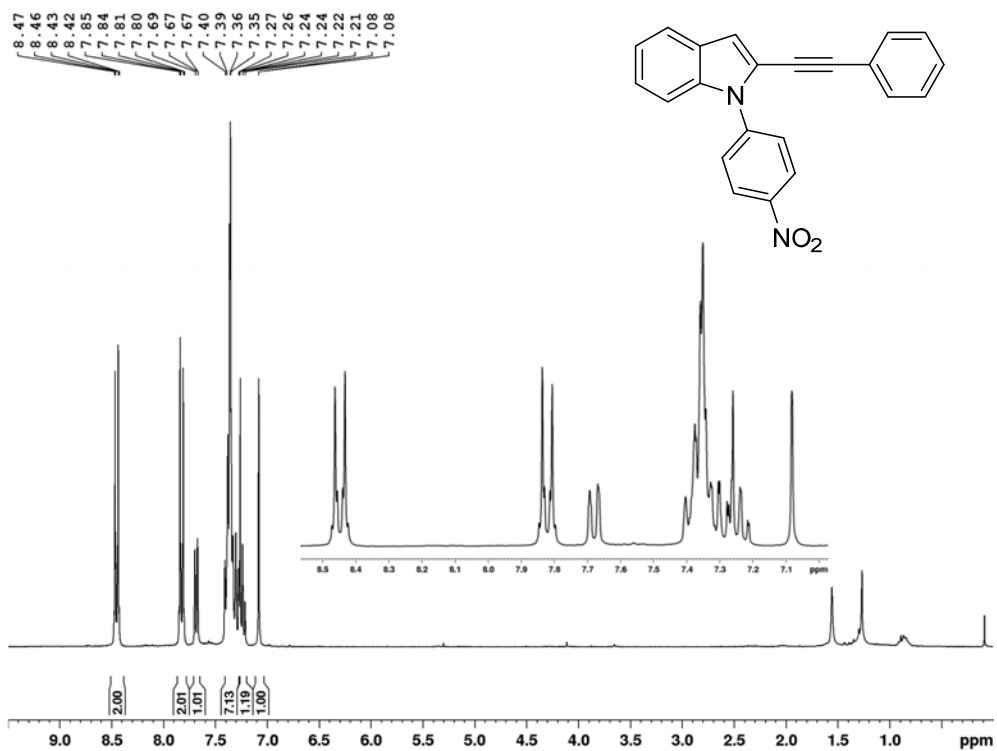


Figure S11. ¹H NMR spectrum (301 MHz, CDCl₃) of 1f.

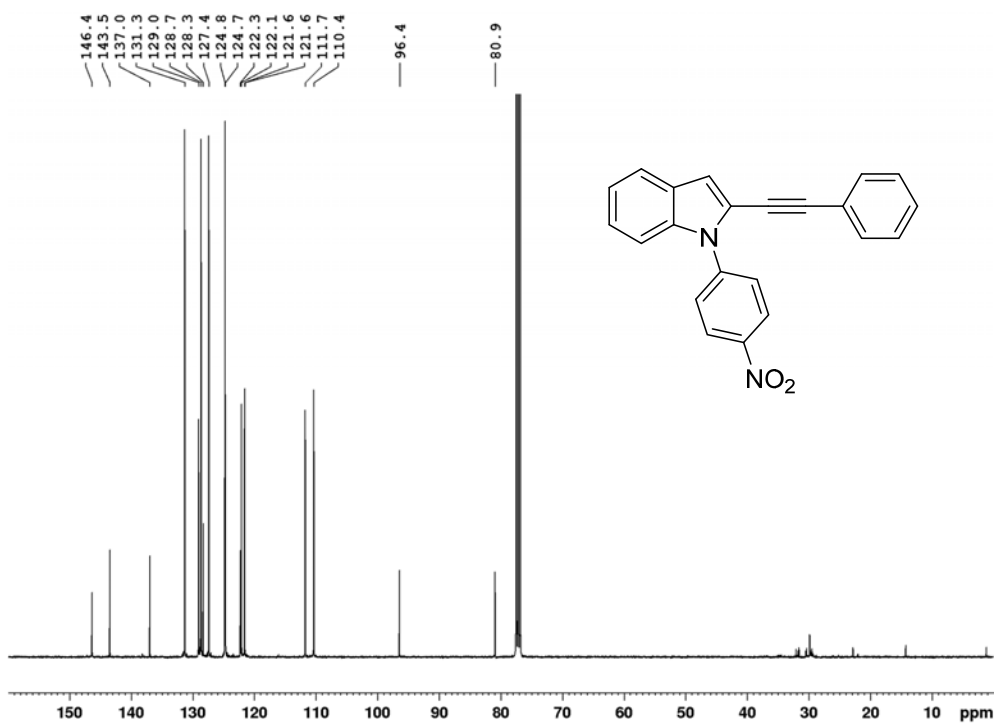


Figure S12. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, CDCl_3) of 1f.

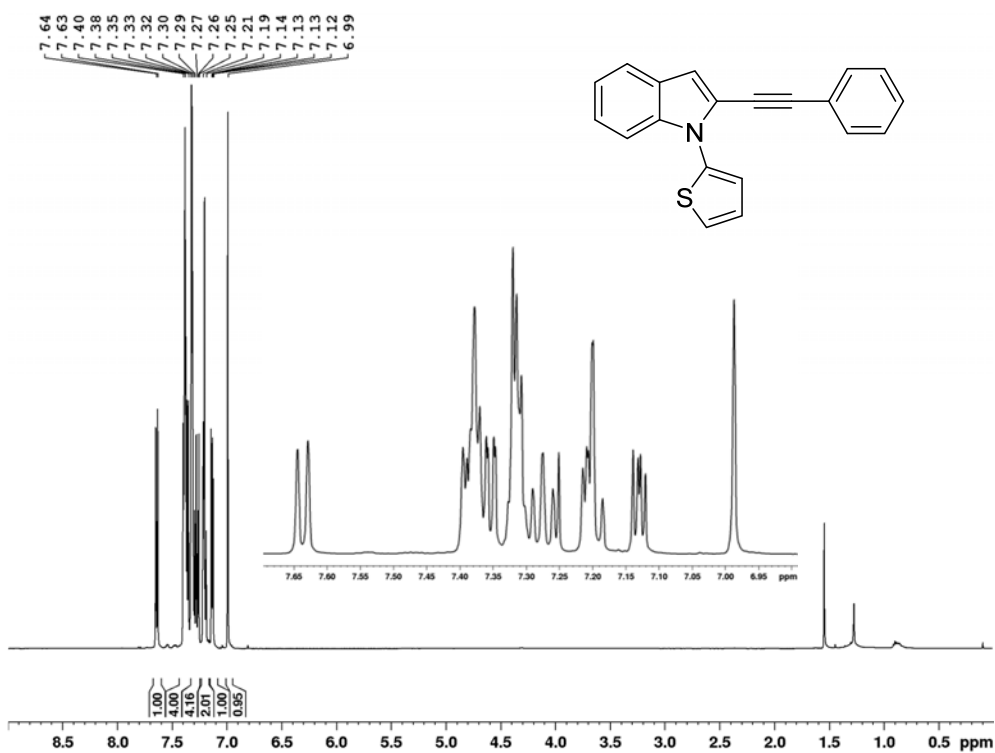


Figure S13. ^1H NMR spectrum (500 MHz, CDCl_3) of 1g.

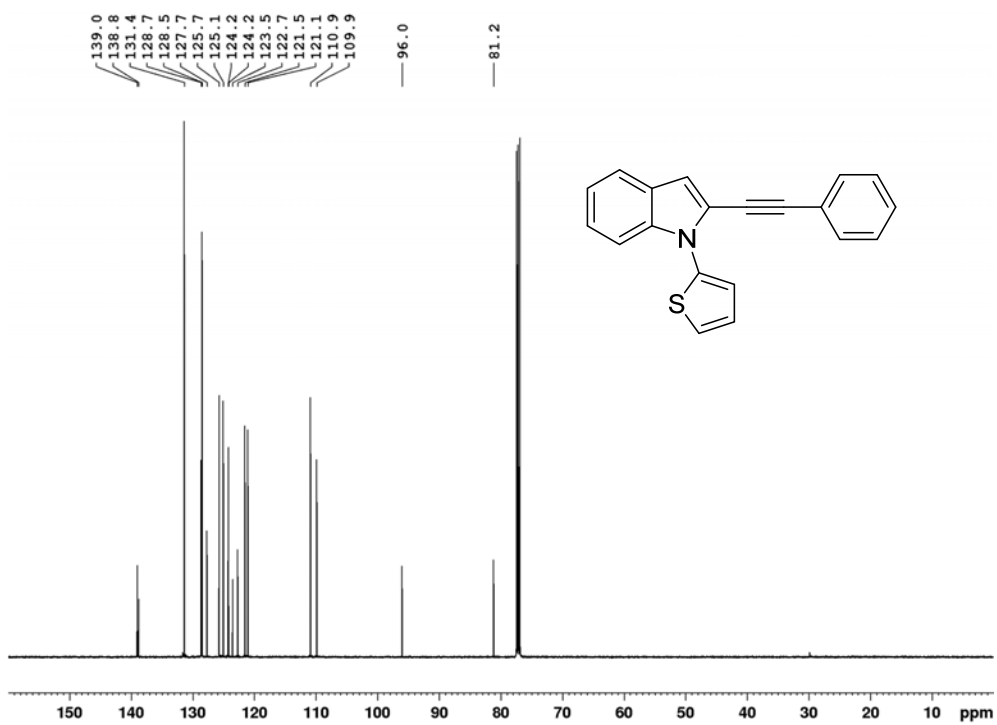


Figure S14. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, CDCl_3) of **1g**.

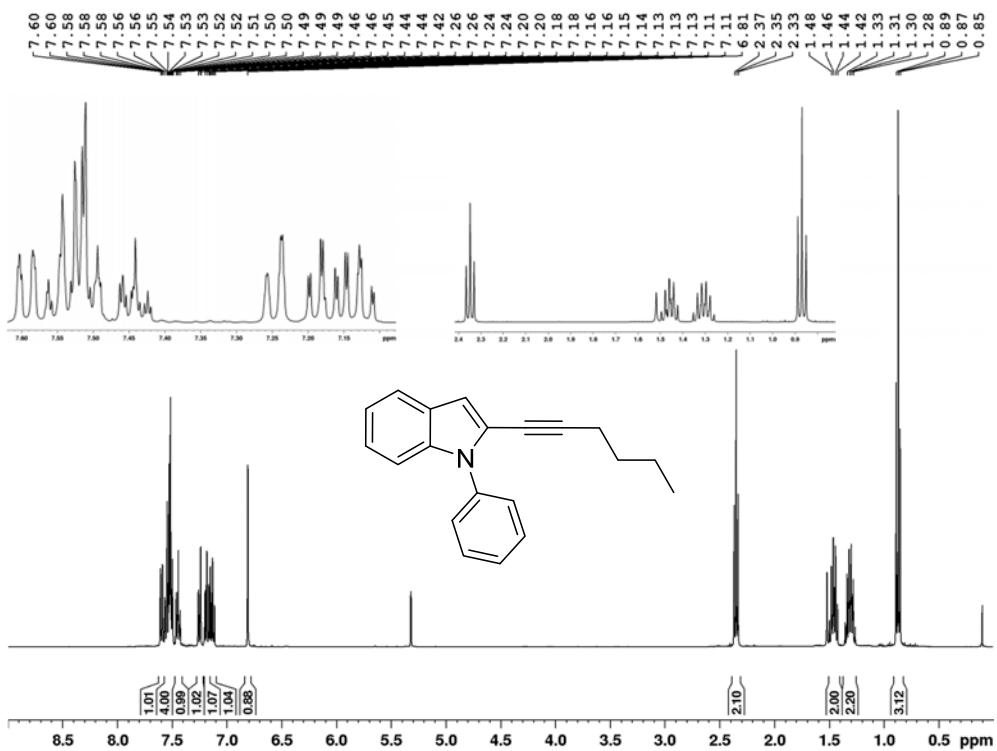


Figure S15. ^1H NMR spectrum (400 MHz, CD_2Cl_2) of **1h**.

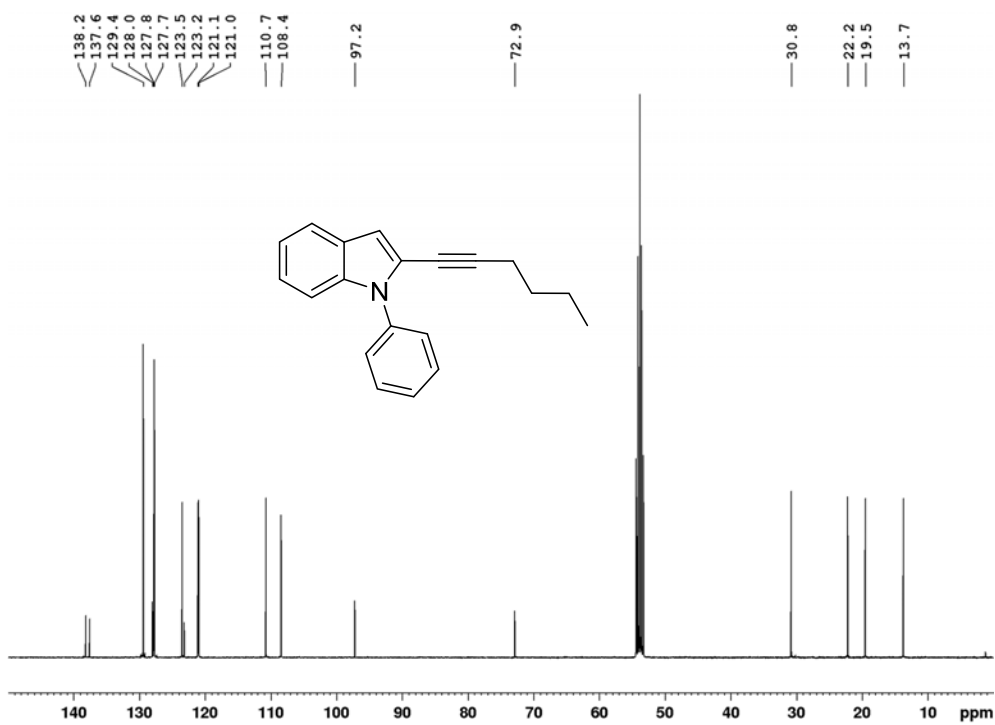


Figure S16. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, CD_2Cl_2) of 1h.

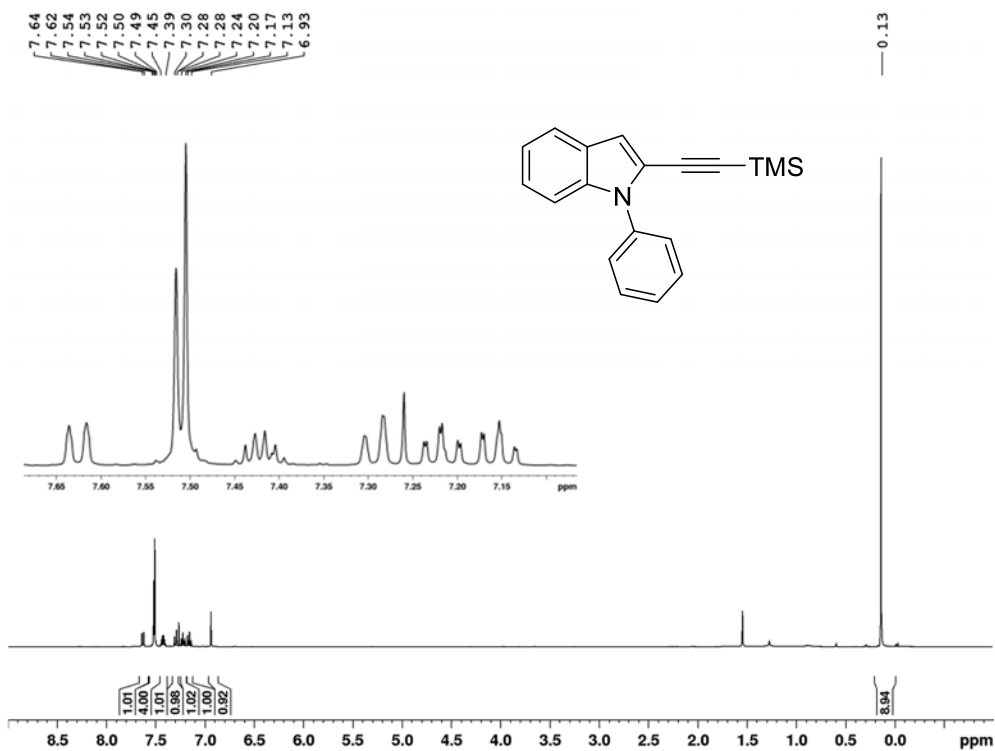


Figure S17. ^1H NMR spectrum (400 MHz, CDCl_3) of 1r-TMS.

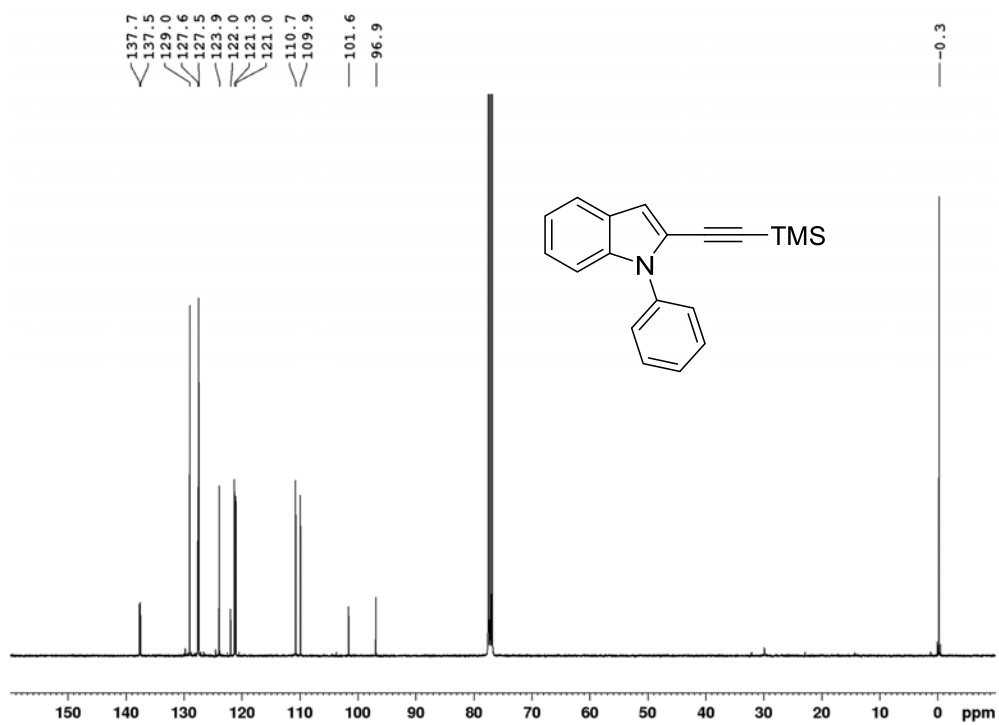


Figure S18. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, CDCl_3) of 1r-TMS.

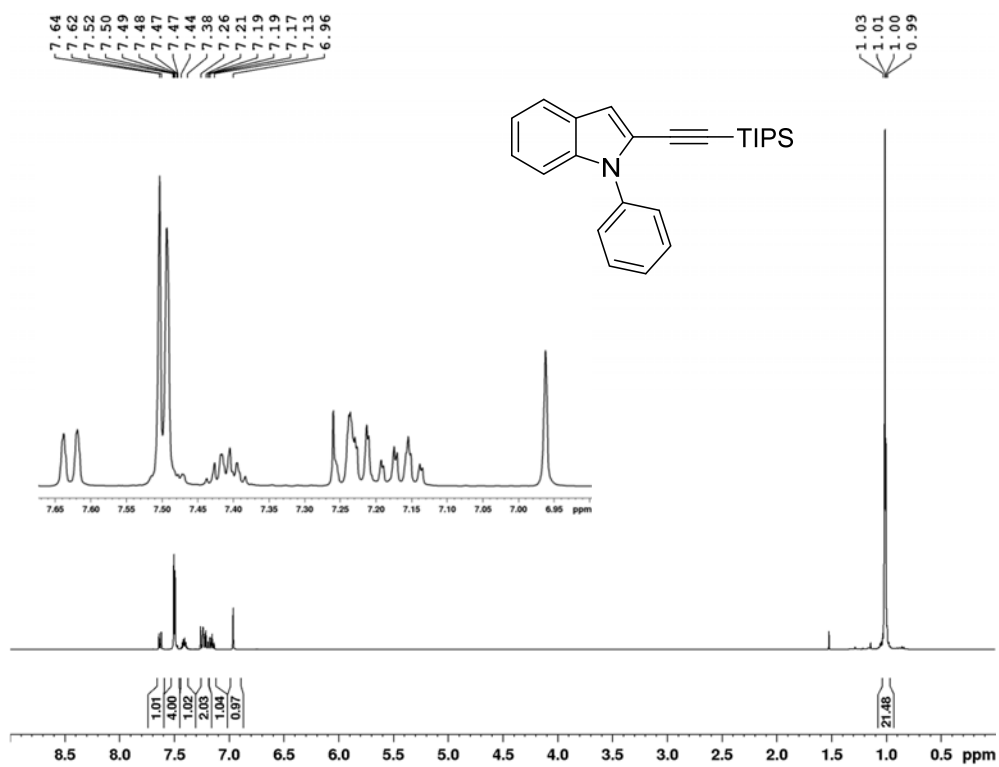


Figure S19. ^1H NMR spectrum (400 MHz, CDCl_3) of 1r-TIPS.

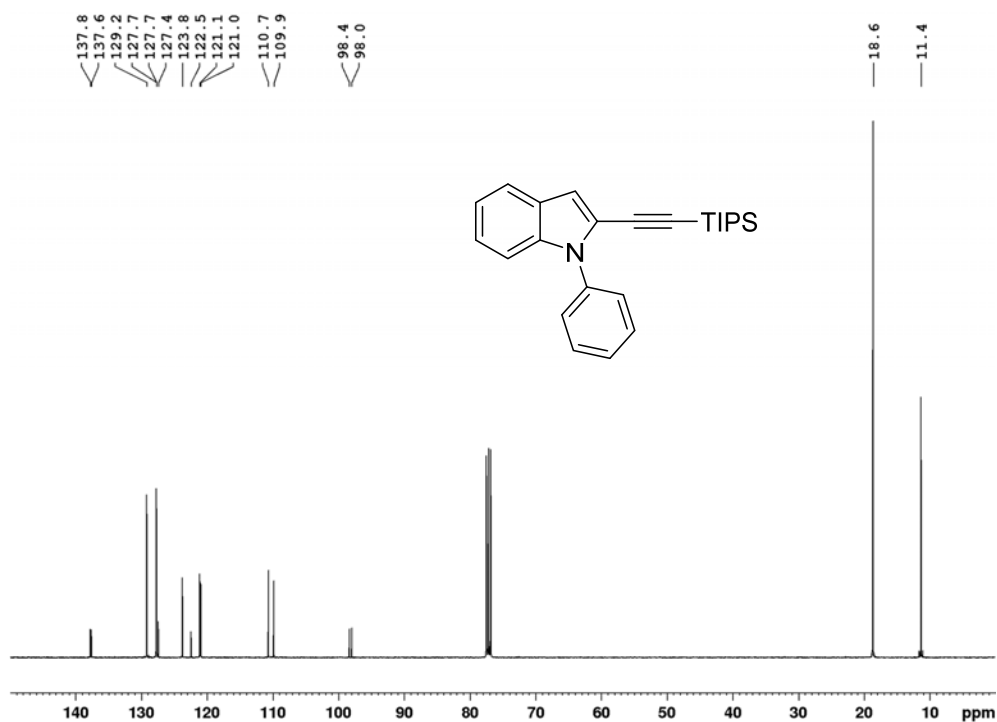


Figure S20. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, CDCl_3) of 1r-TIPS.

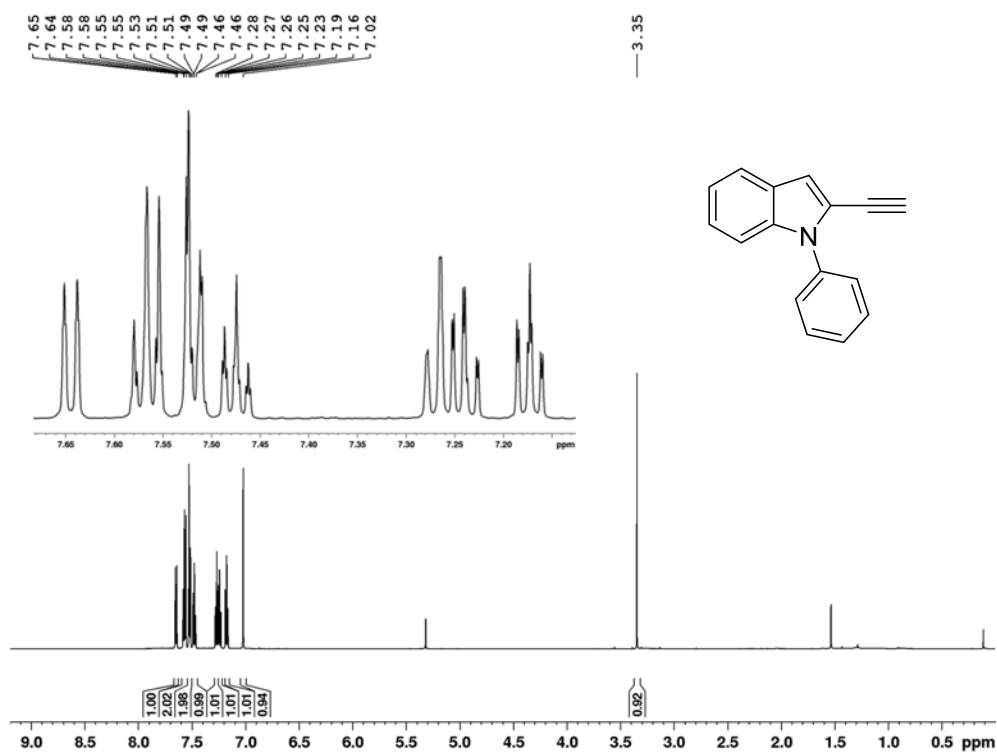


Figure S21. ^1H NMR spectrum (600 MHz, CD_2Cl_2) of 1r-H.

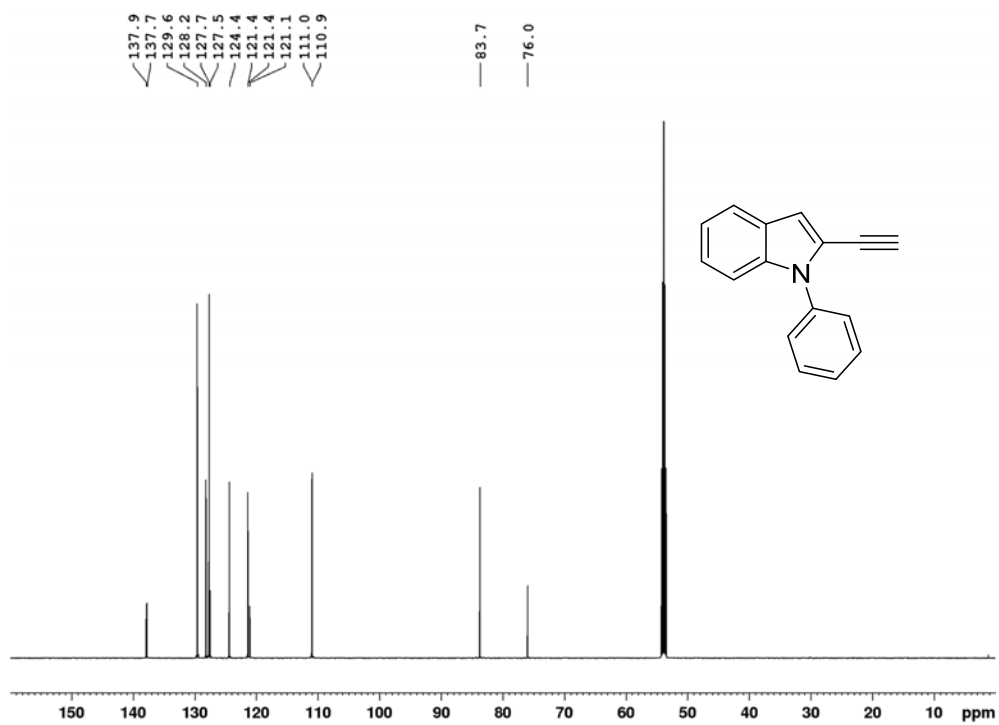


Figure S22. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (151 MHz, CD_2Cl_2) of 1r-H.

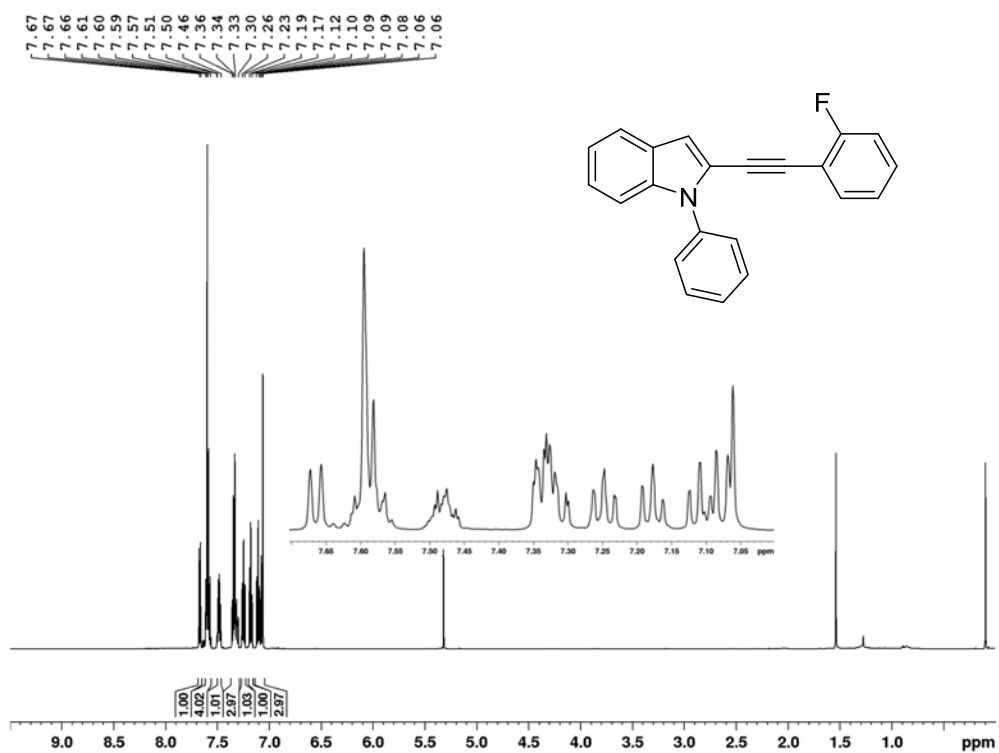


Figure S23. $^1\text{H}\{^{19}\text{F}\}$ NMR spectrum (500 MHz, CD_2Cl_2) of 1k.

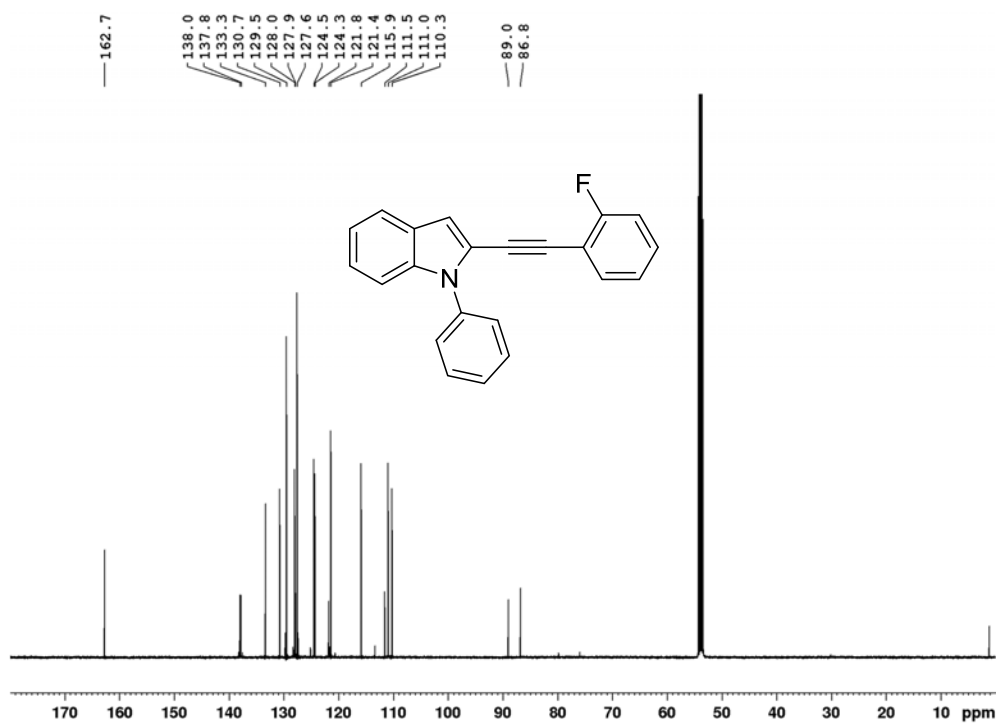


Figure S24. $^{13}\text{C}\{^1\text{H}, ^{19}\text{F}\}$ NMR spectrum (126 MHz, CD_2Cl_2) of 1k.



Figure S25. $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum (471 MHz, CD_2Cl_2) of 1k.

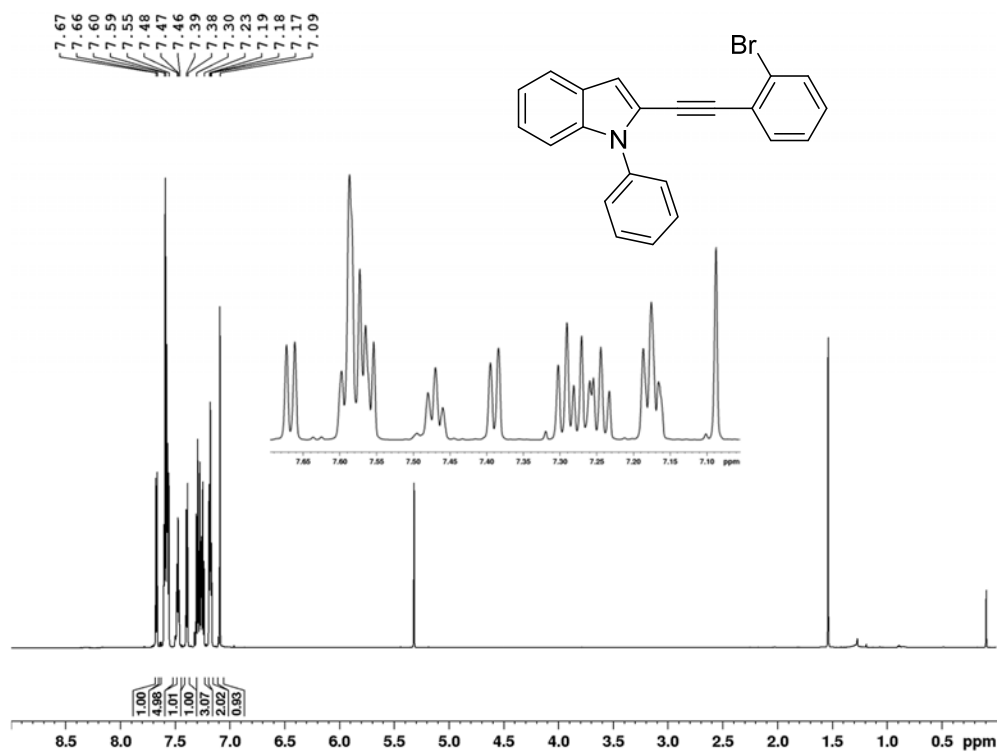


Figure S26. ¹H NMR spectrum (700 MHz, CD₂Cl₂) of 11.

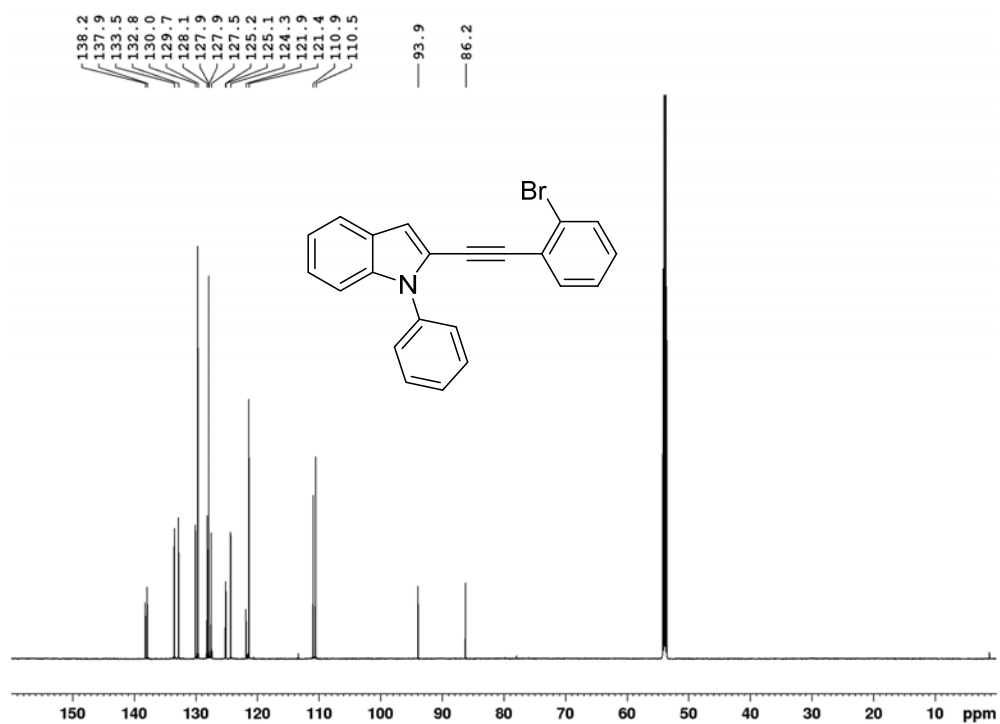


Figure S27. ¹³C{¹H} NMR spectrum (176 MHz, CD₂Cl₂) of 11.

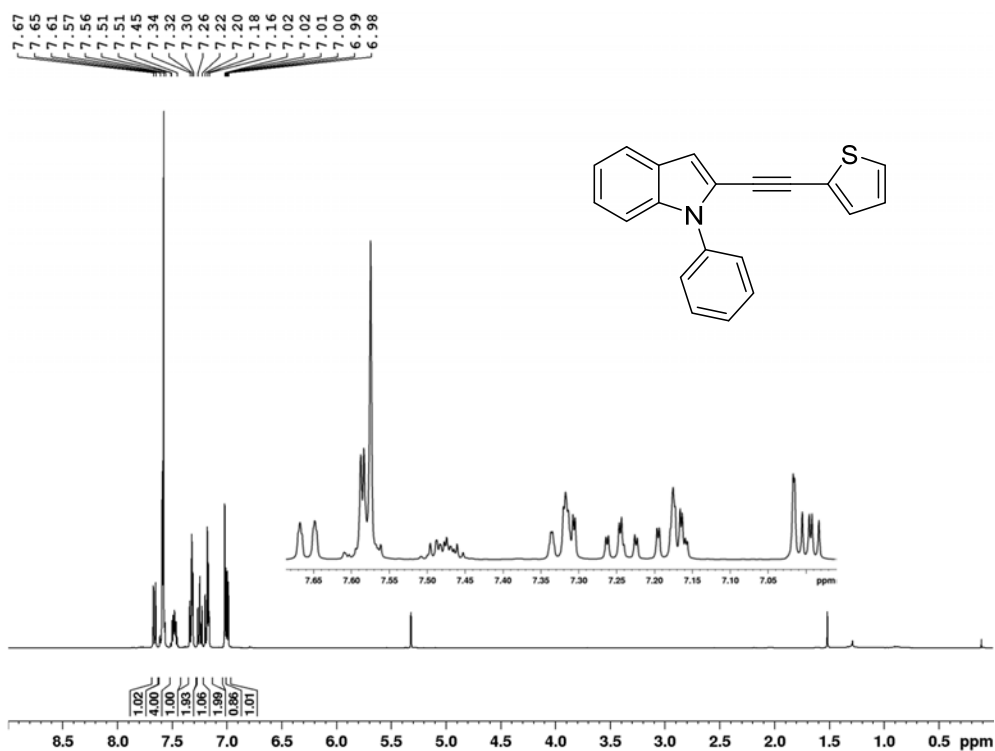


Figure S28. ¹H NMR spectrum (400 MHz, CD₂Cl₂) of 1m.

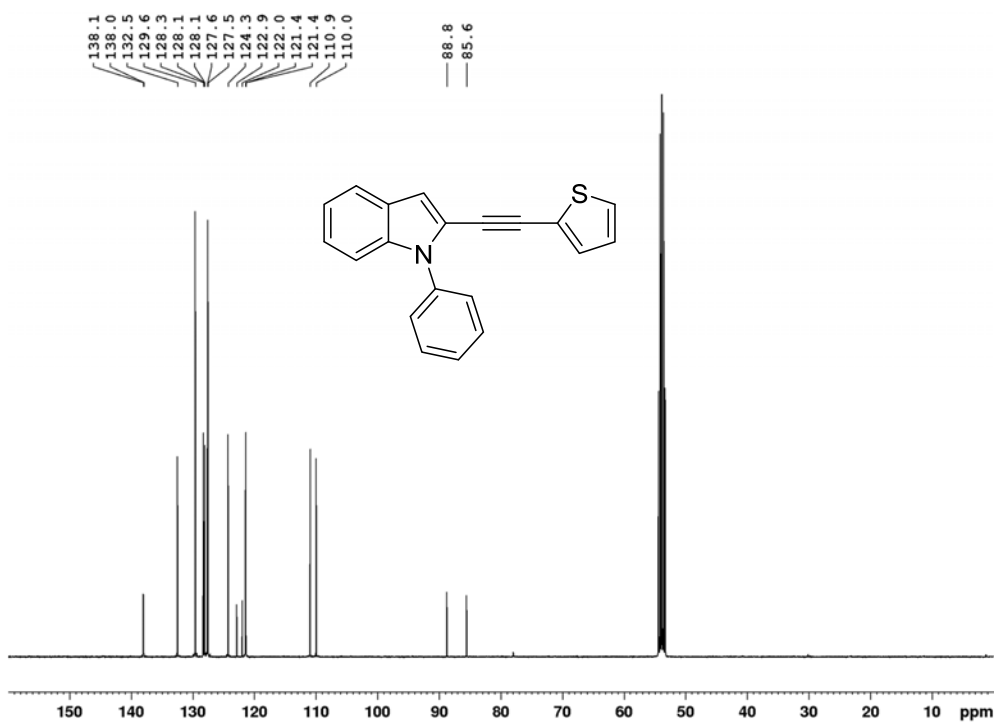


Figure S29. ¹³C{¹H} NMR spectrum (101 MHz, CD₂Cl₂) of 1m.

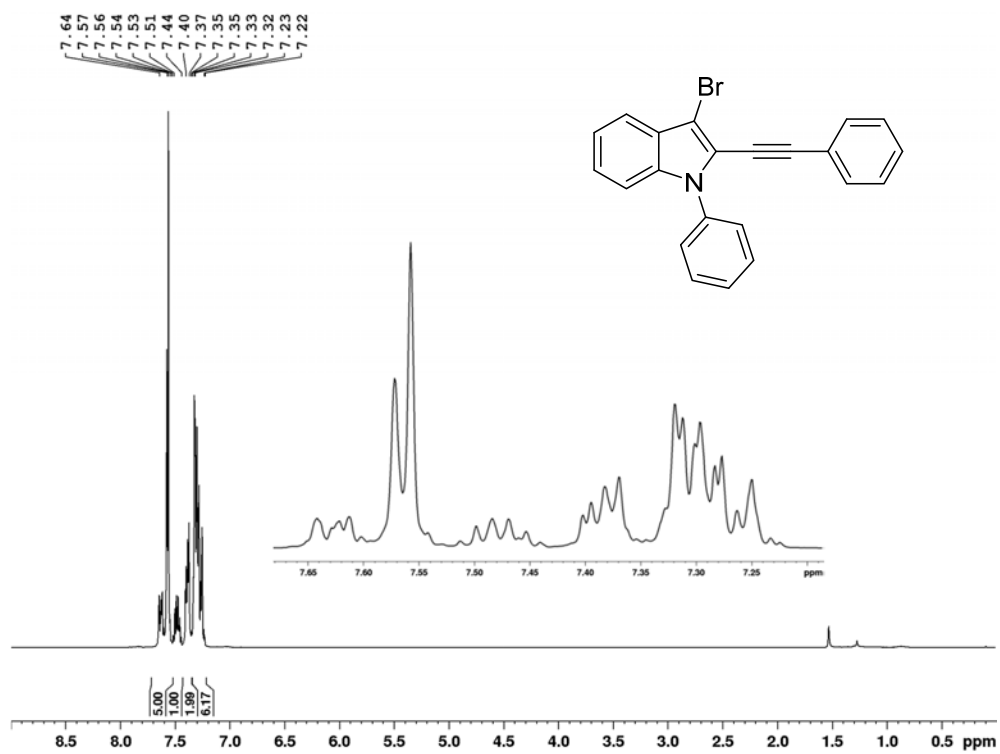


Figure S30. ¹H NMR spectrum (300 MHz, CDCl₃) of **1s**.

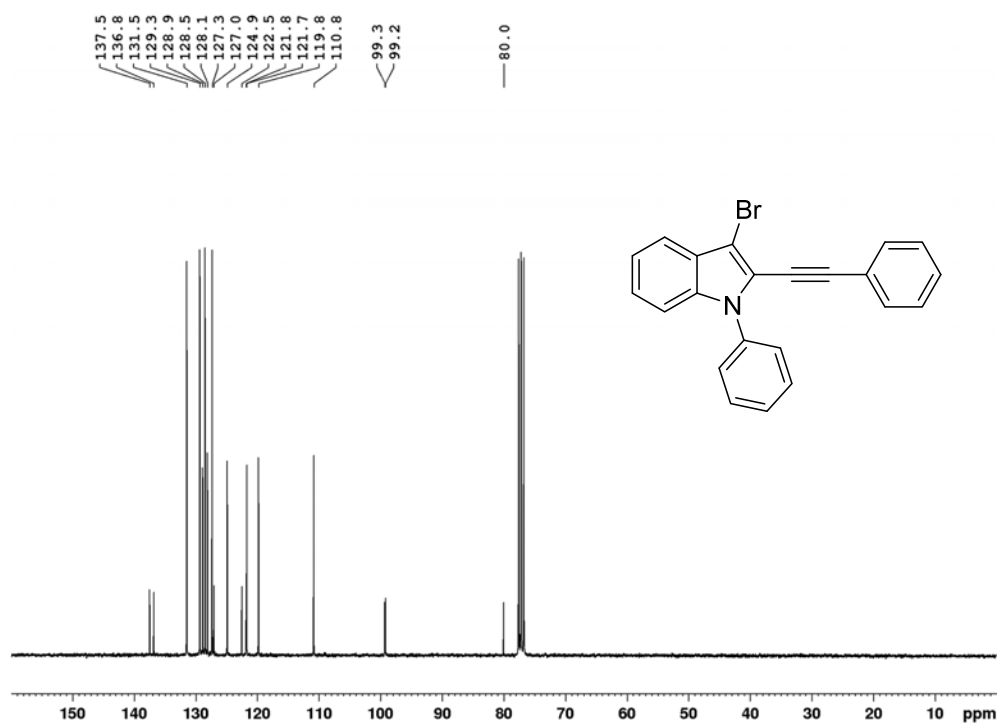


Figure S31. ¹³C{¹H} NMR spectrum (75 MHz, CDCl₃) of **1s**.

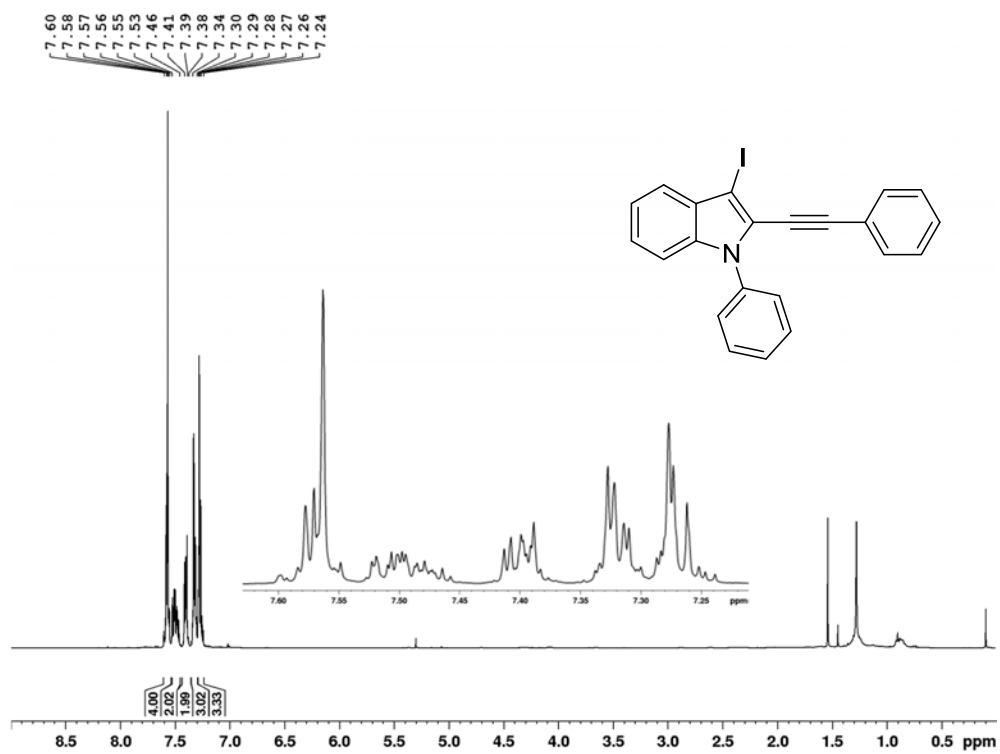


Figure S32. ¹H NMR spectrum (400 MHz, CDCl₃) of 1t.

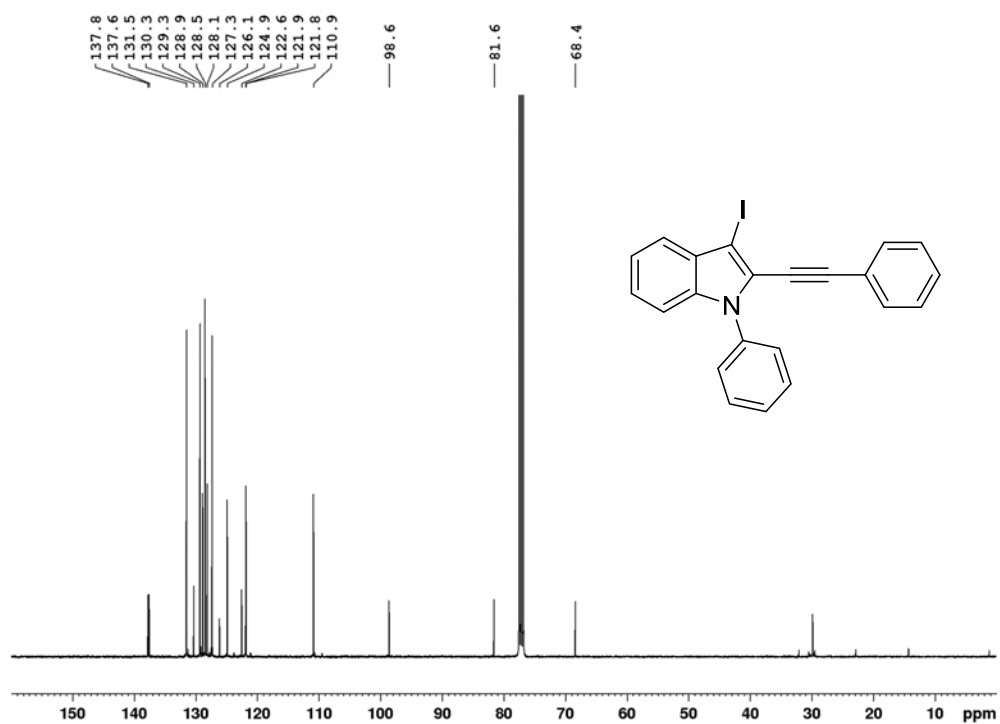


Figure S33. ¹³C{¹H} NMR spectrum (101 MHz, CDCl₃) of 1t.

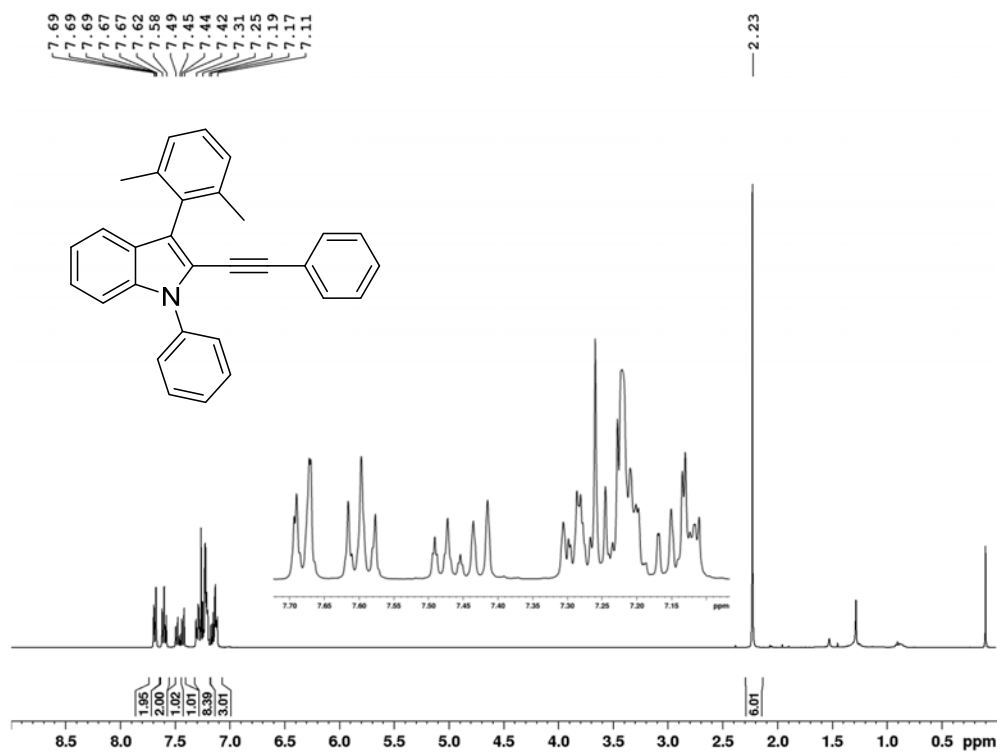


Figure S34. ¹H NMR spectrum (400 MHz, CDCl₃) of **1o**.

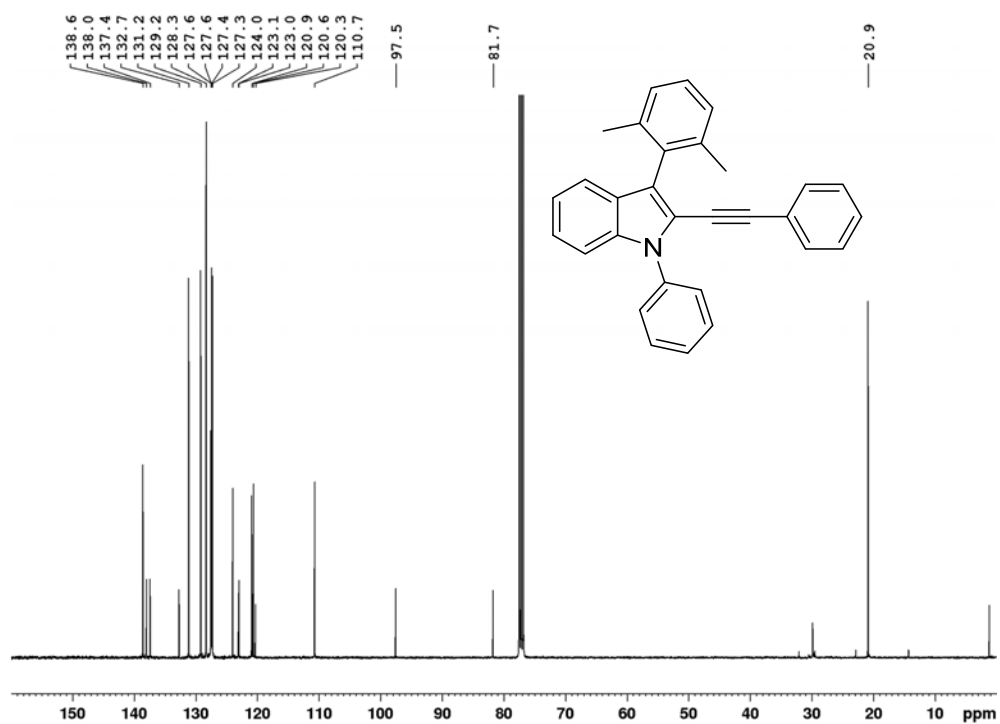


Figure S35. ¹³C{¹H} NMR spectrum (101 MHz, CDCl₃) of **1o**.

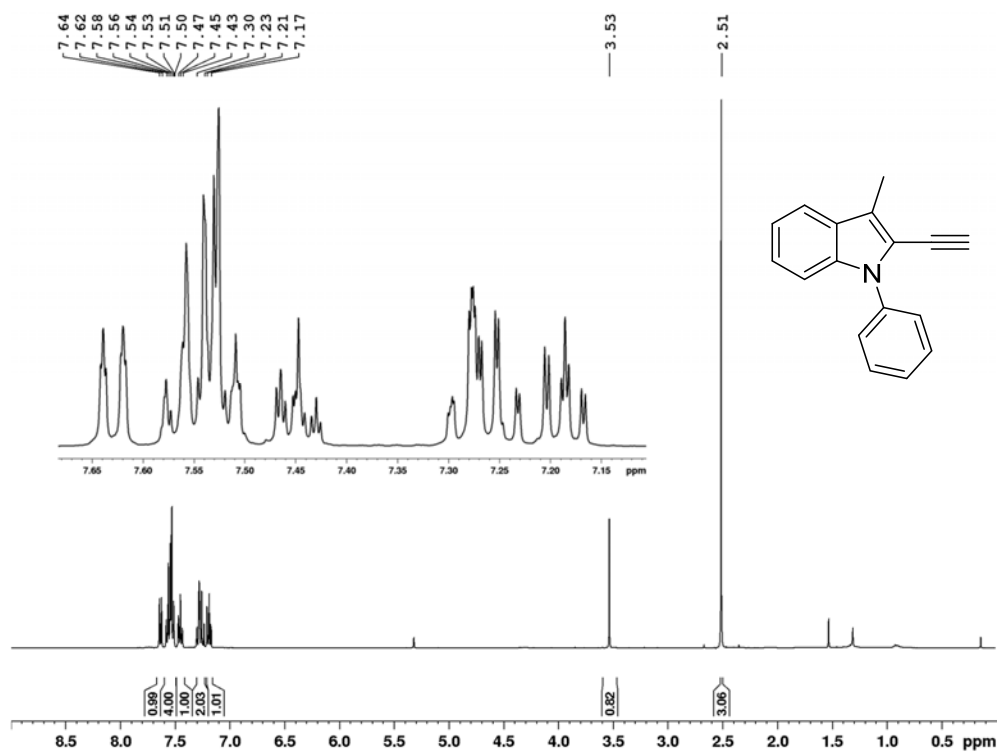


Figure S36. ¹H NMR spectrum (400 MHz, CD₂Cl₂) of 1q.

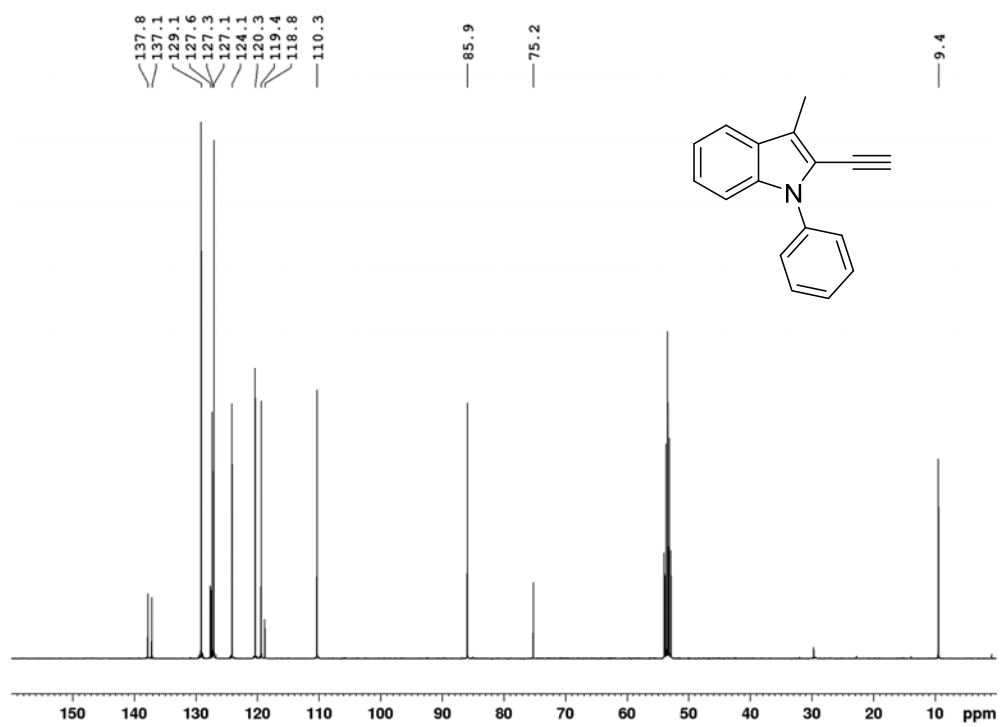


Figure S37. ¹³C{¹H} NMR spectrum (101 MHz, CD₂Cl₂) of 1q.

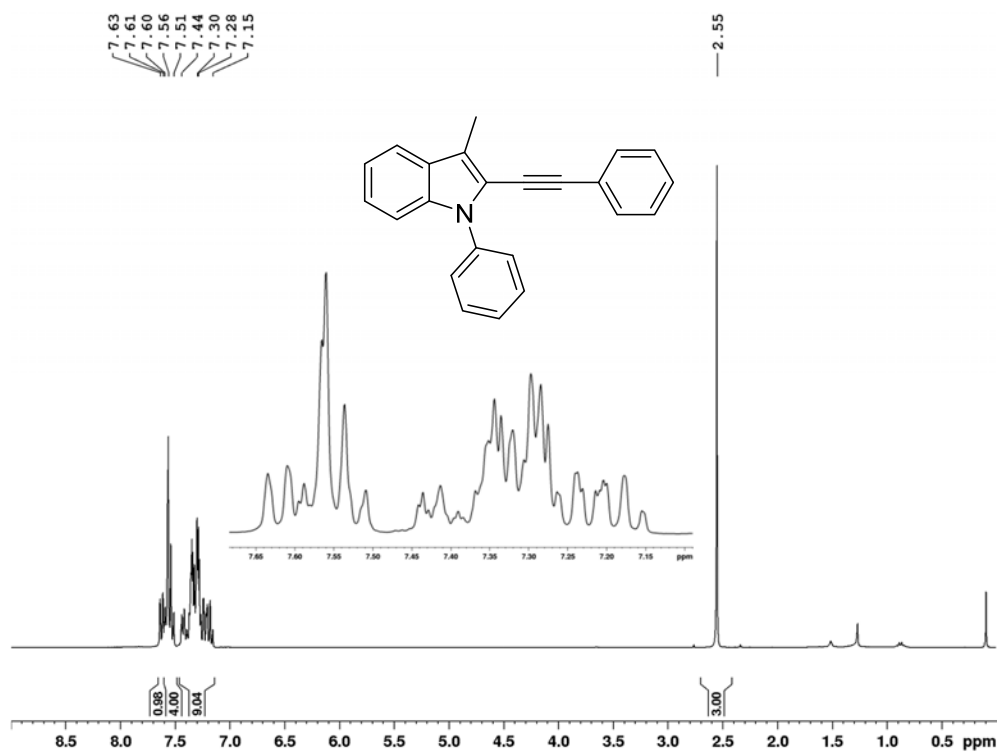


Figure S38. ¹H NMR spectrum (300 MHz, CDCl₃) of 1p.

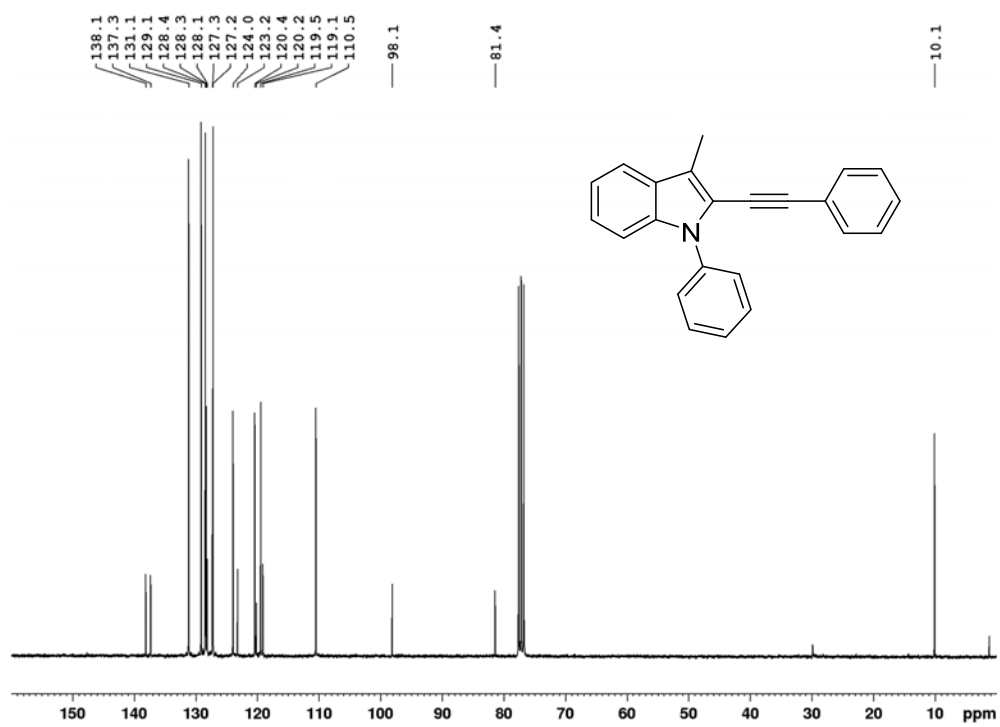


Figure S39. ¹³C{¹H} NMR spectrum (75 MHz, CDCl₃) of 1p.

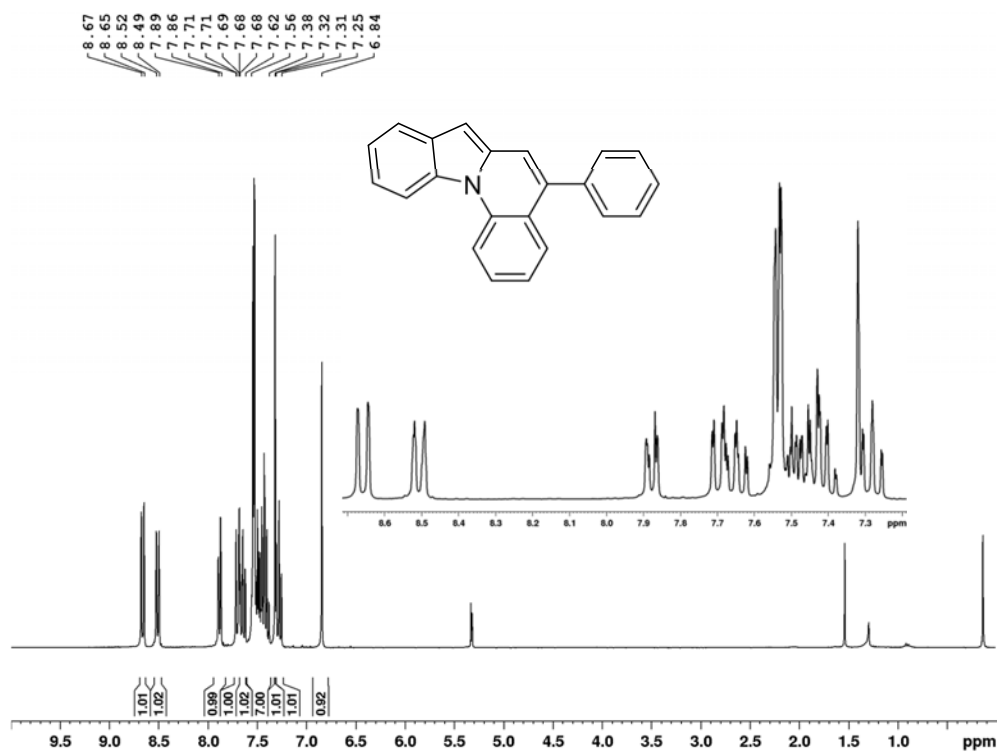


Figure S40. ¹H NMR spectrum (301 MHz, CD₂Cl₂) of 2a.

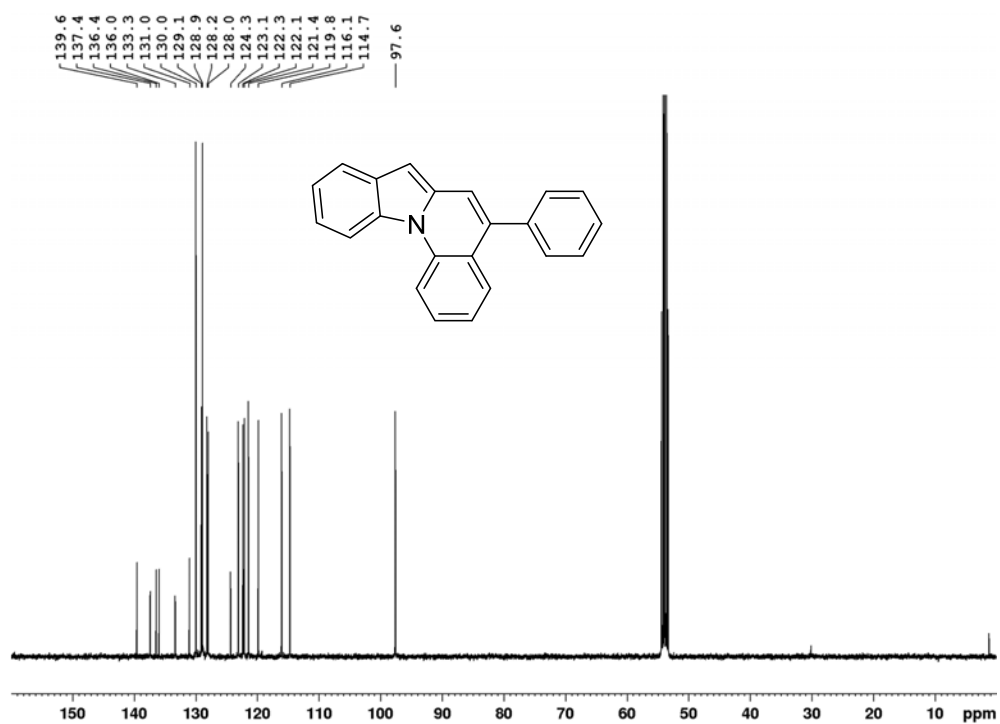


Figure S41. ¹³C{¹H} NMR spectrum (101 MHz, CD₂Cl₂) of 2a.

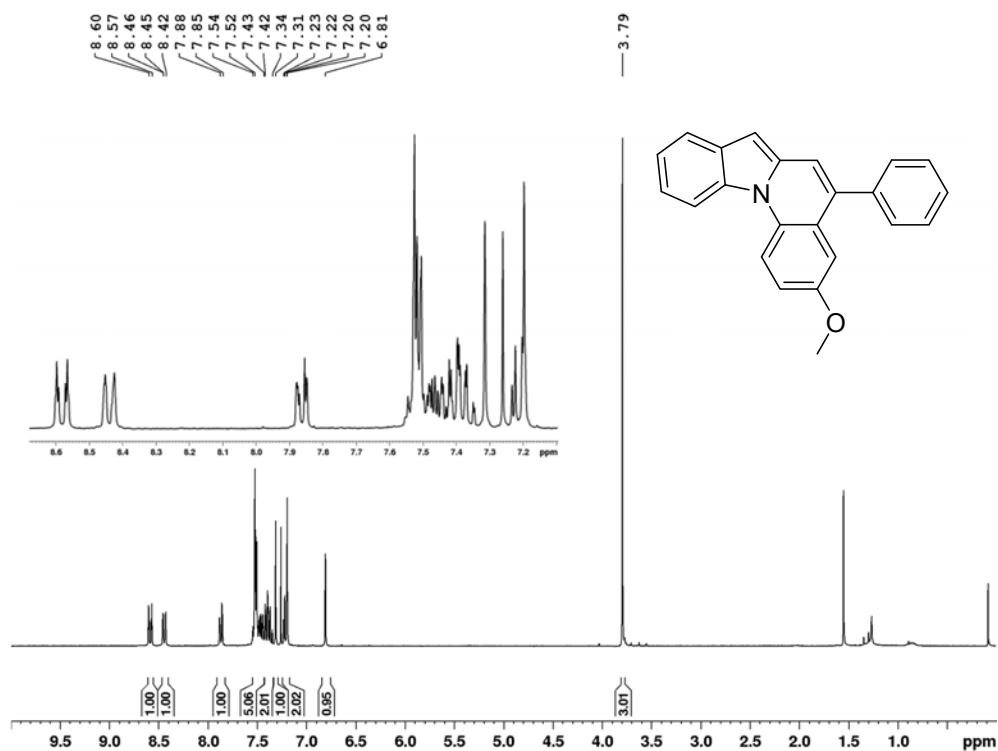


Figure S42. ¹H NMR spectrum (301 MHz, CDCl₃) of 2b.

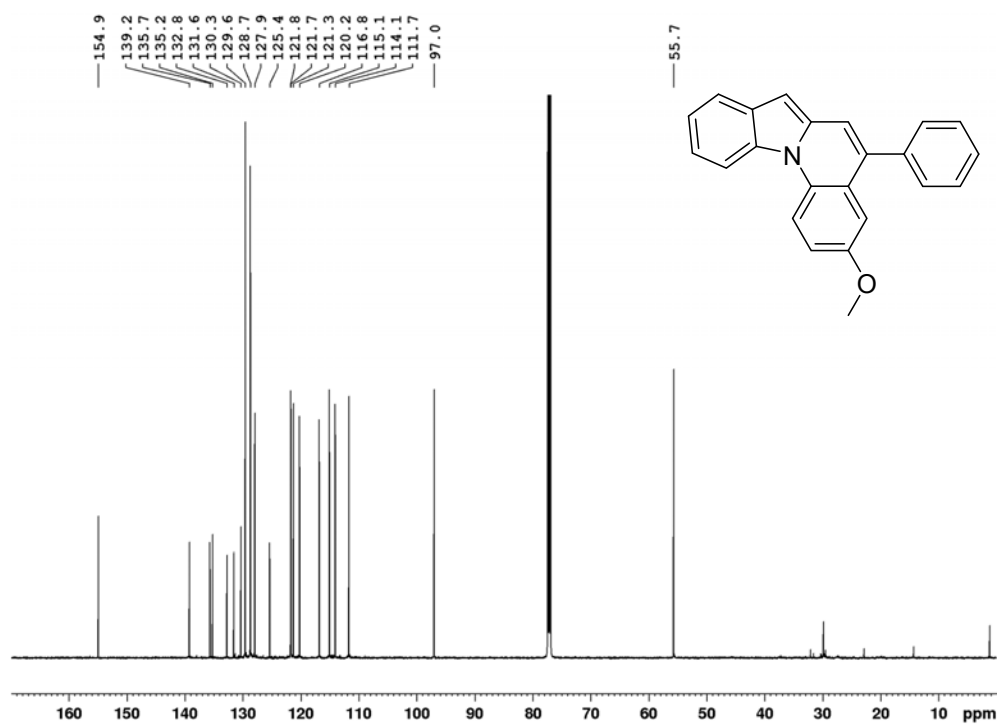


Figure S43. ¹³C{¹H} NMR spectrum (151 MHz, CDCl₃) of 2b.

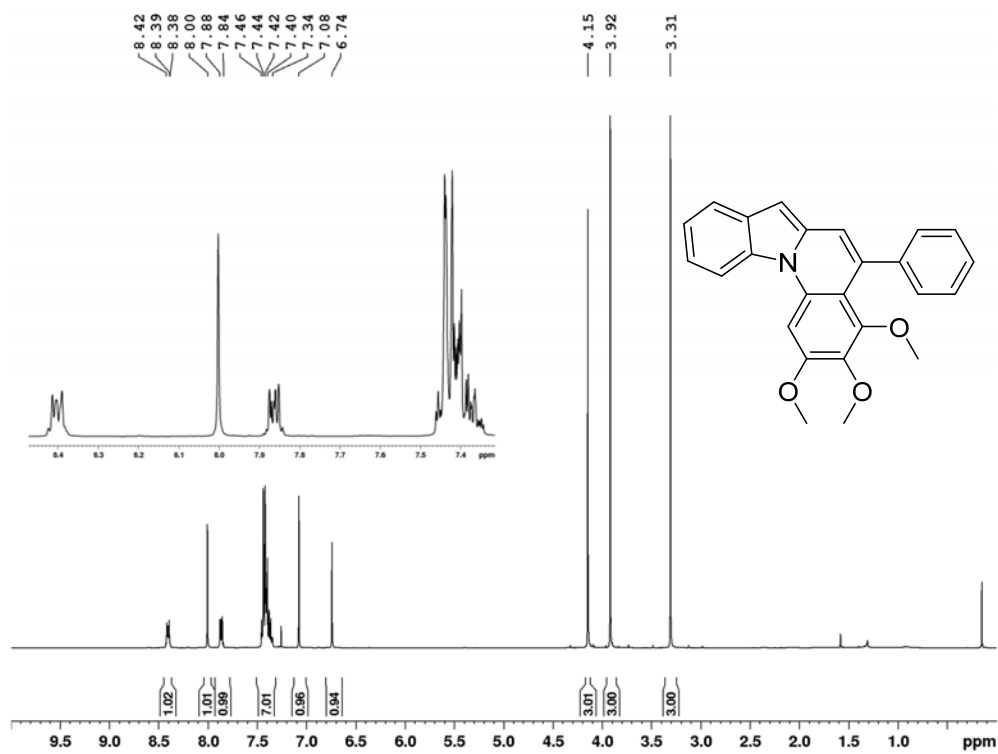


Figure S44. ¹H NMR spectrum (400 MHz, CDCl₃) of **2c**.

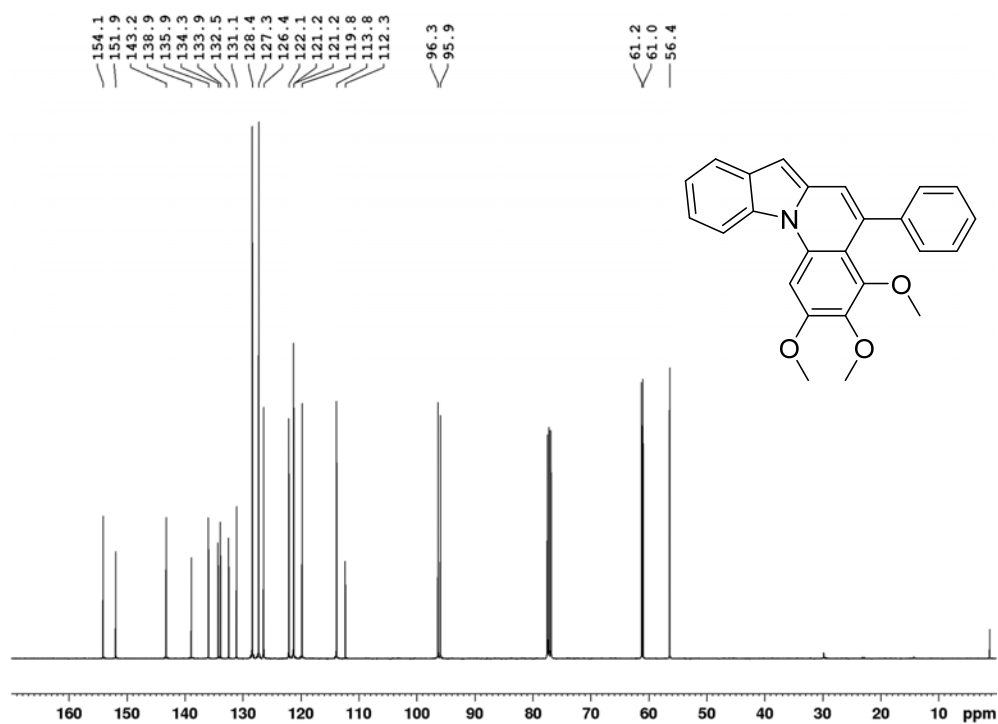


Figure S45. ¹³C{¹H} NMR spectrum (101 MHz, CDCl₃) of **2c**.

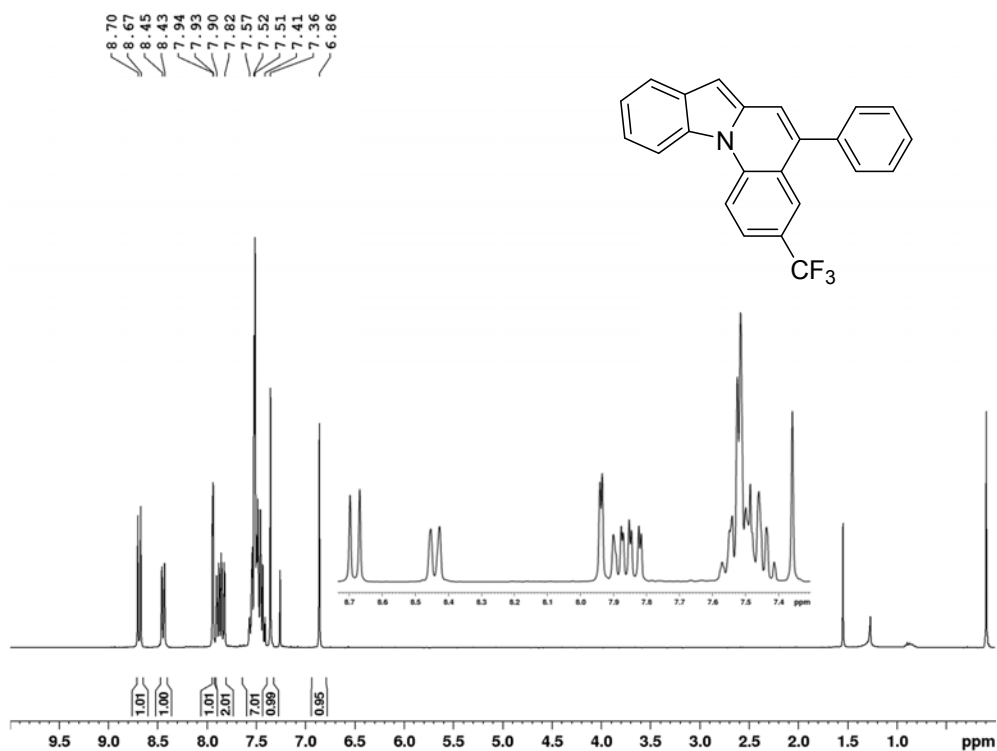


Figure S46. $^1\text{H}\{^{19}\text{F}\}$ NMR spectrum (301 MHz, CDCl_3) of **2d**.

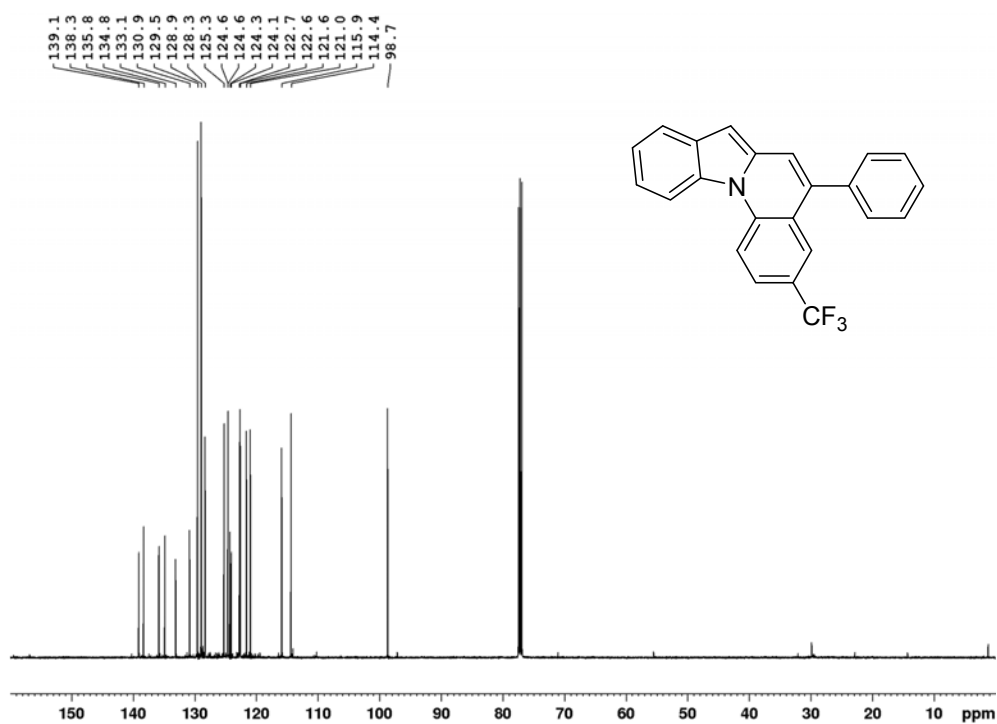


Figure S47. $^{13}\text{C}\{^1\text{H},^{19}\text{F}\}$ NMR spectrum (126 MHz, CDCl_3) of **2d**.

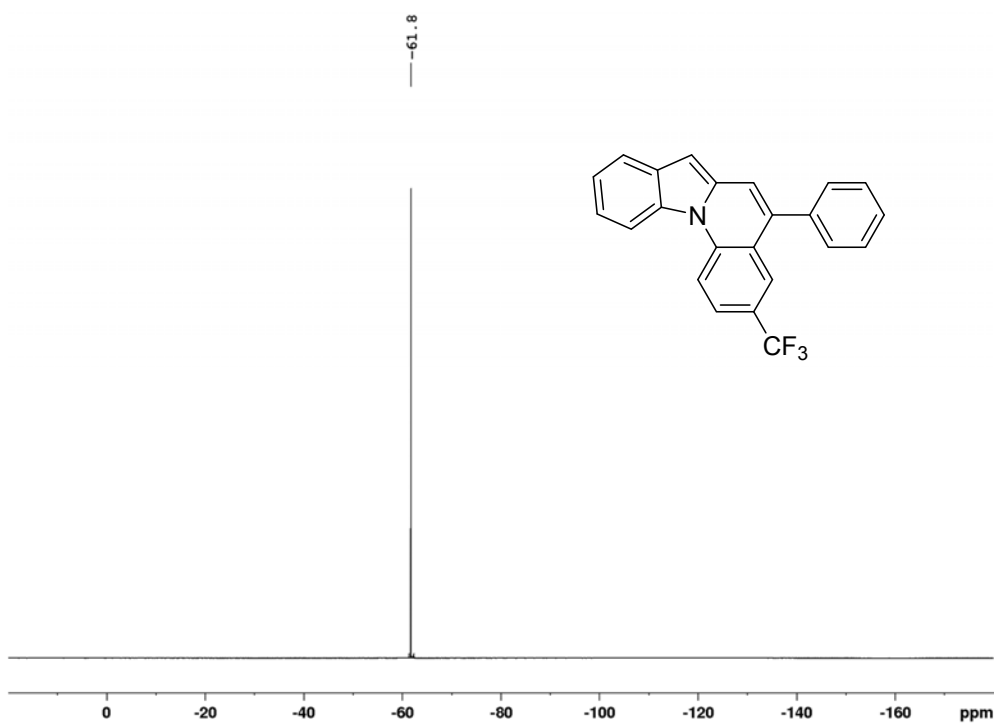


Figure S48. $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum (283 MHz, CDCl_3) of **2d**.

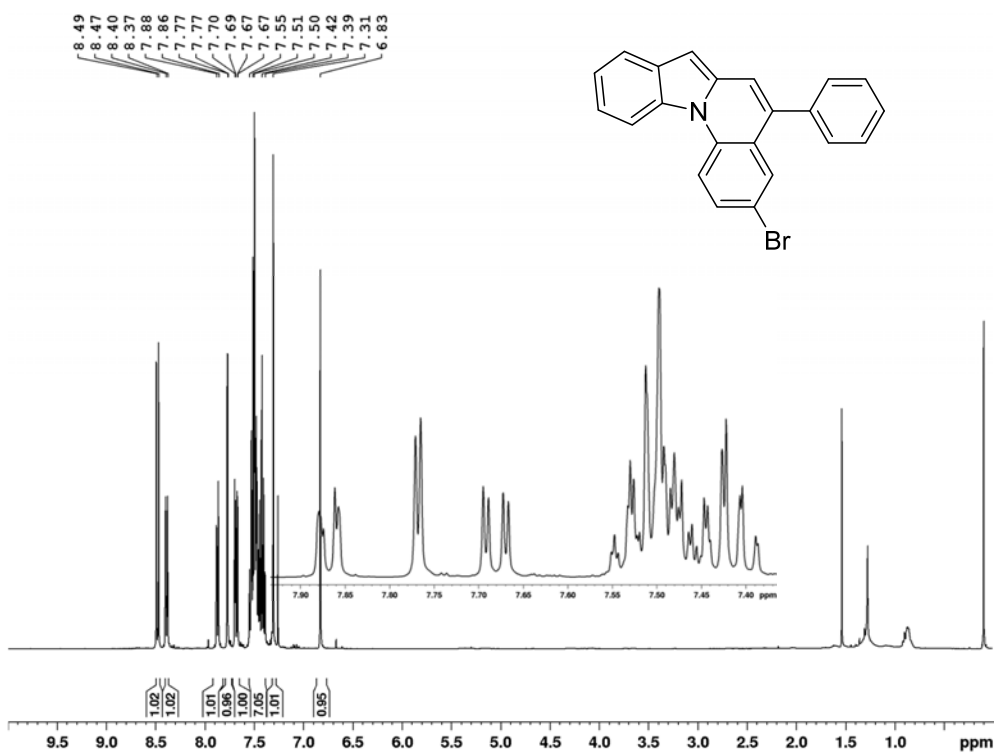


Figure S49. ^1H NMR spectrum (400 MHz, CDCl_3) of **2e**.

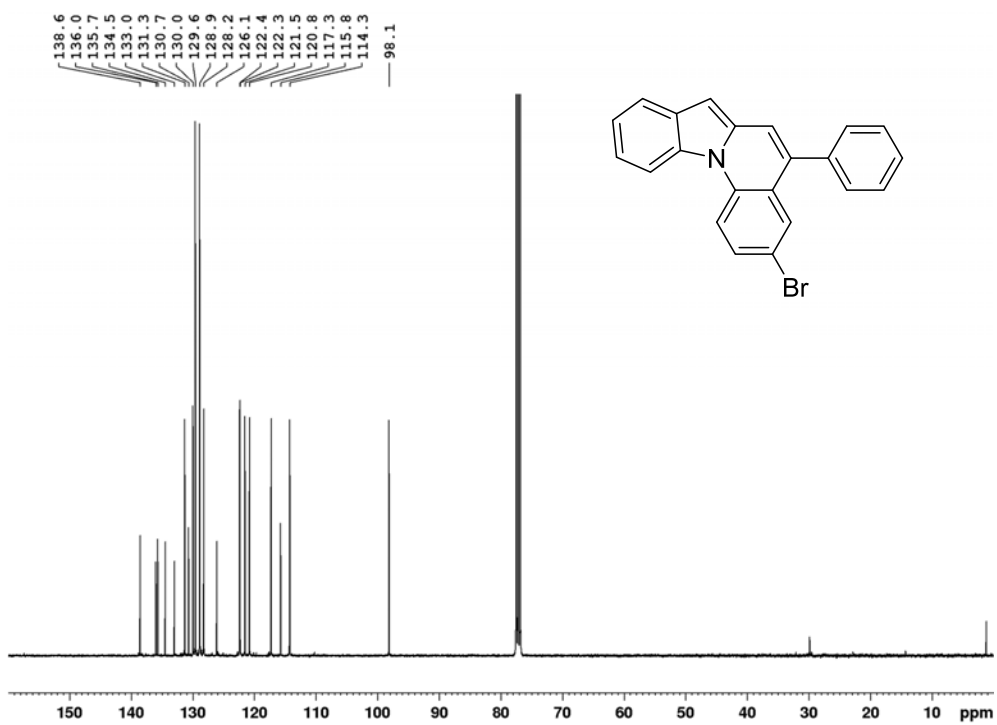


Figure S50. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, CDCl_3) of 2e.

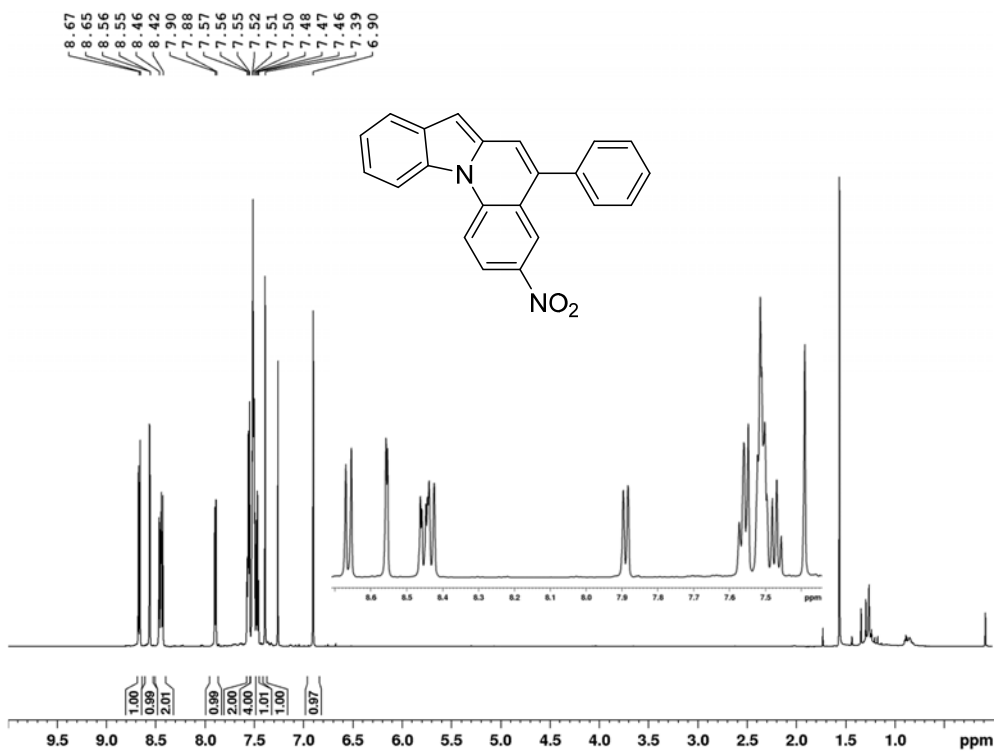
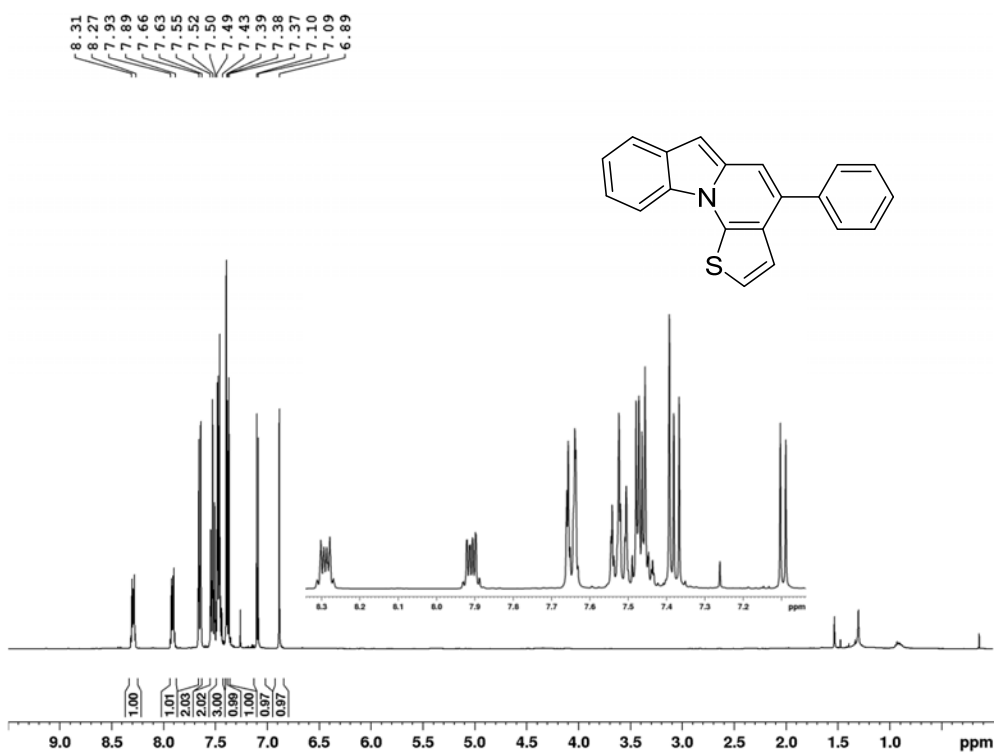
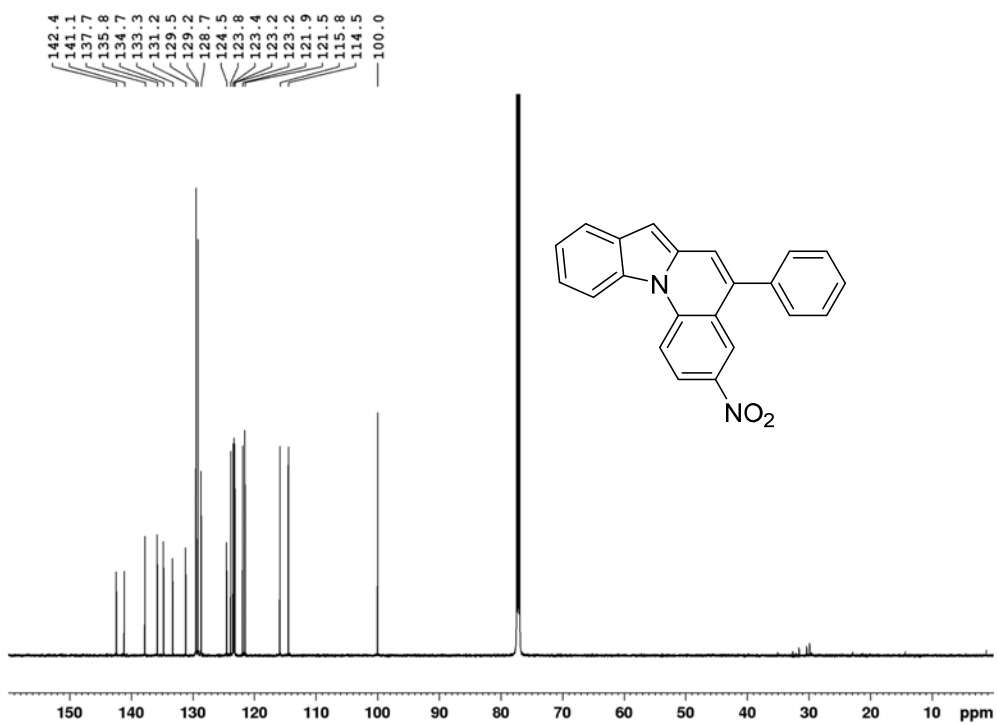


Figure S51. ^1H NMR spectrum (600 MHz, CDCl_3) of 2f.



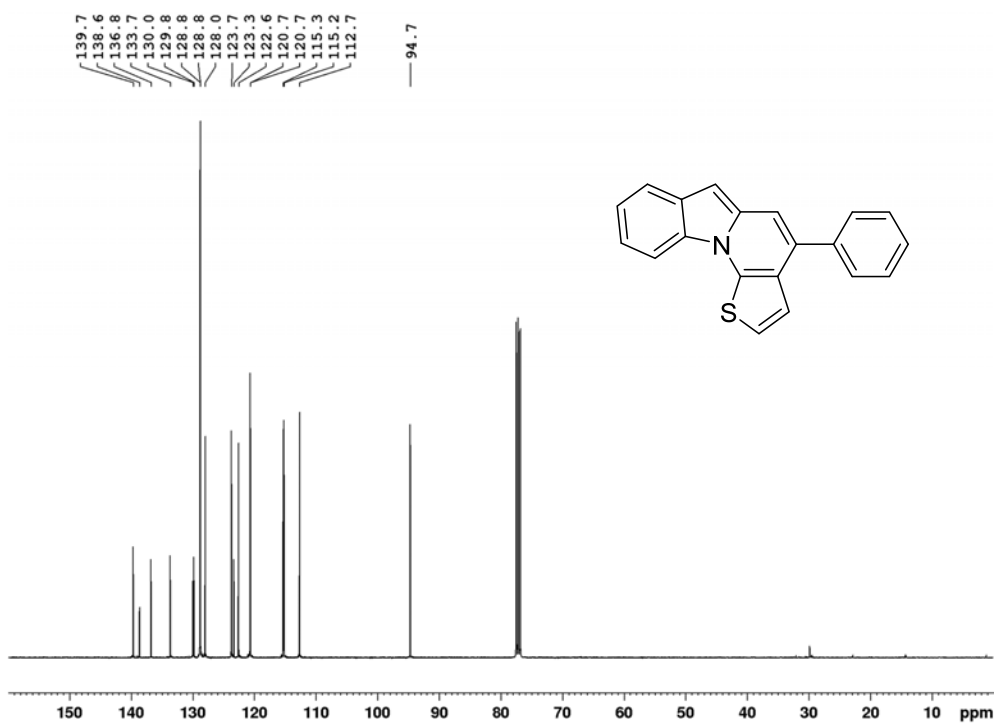


Figure S54. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, CDCl_3) of 2g.

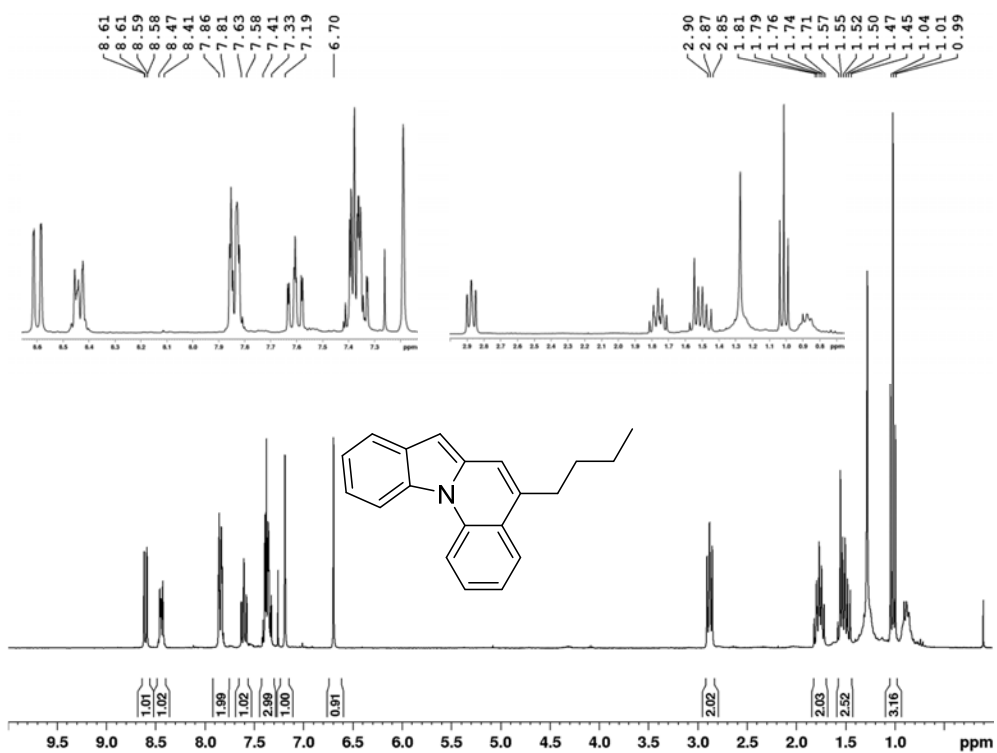


Figure S55. ^1H NMR spectrum (301 MHz, CDCl_3) of 2h.

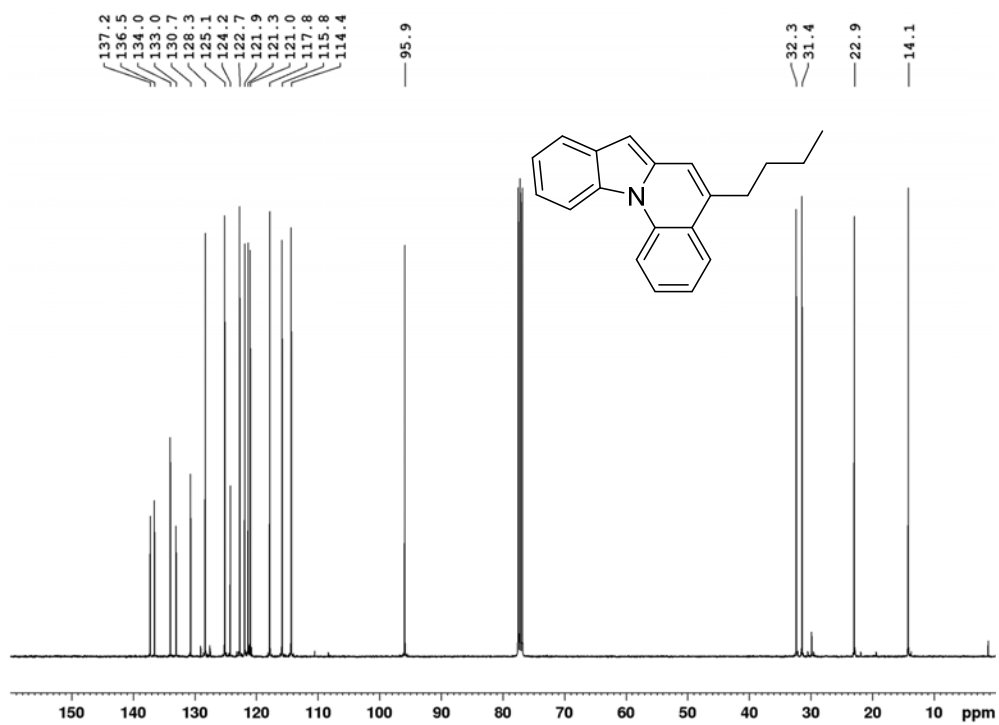


Figure S56. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, CDCl_3) of 2h.

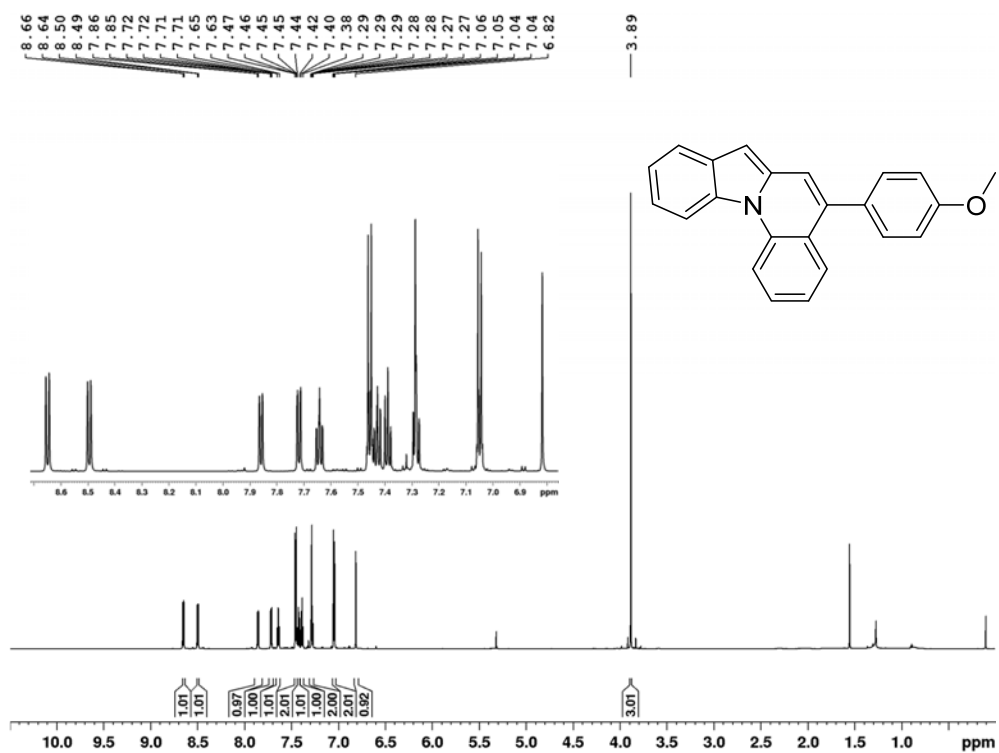


Figure S57. ^1H NMR spectrum (700 MHz, CD_2Cl_2) of 2i.

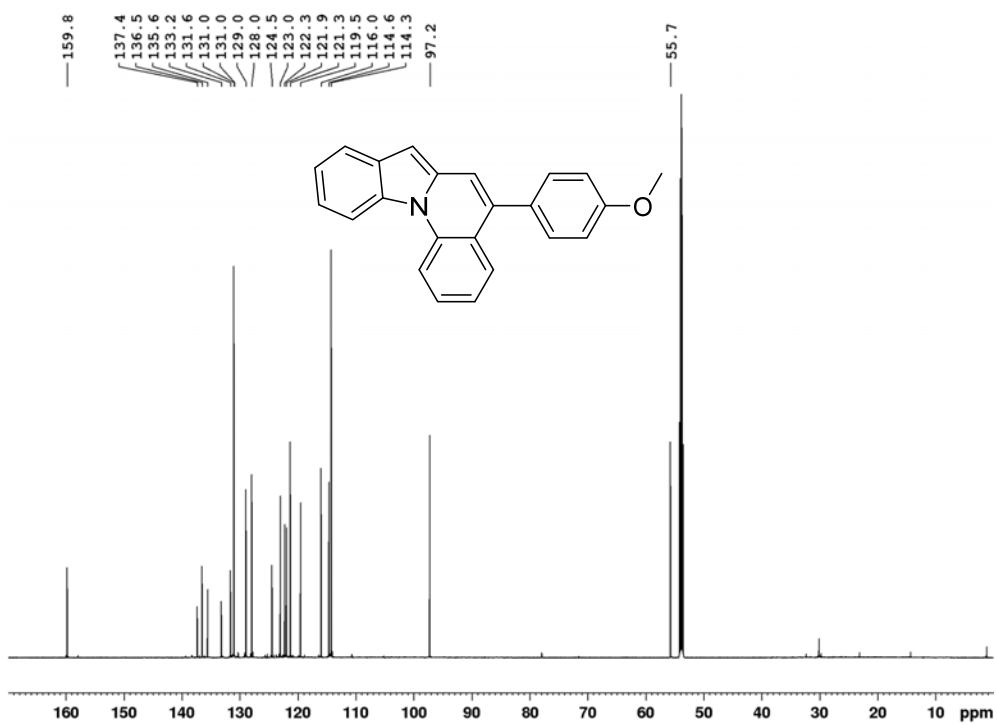


Figure S58. ¹³C{¹H} NMR spectrum (126 MHz, CD₂Cl₂) of 2i.

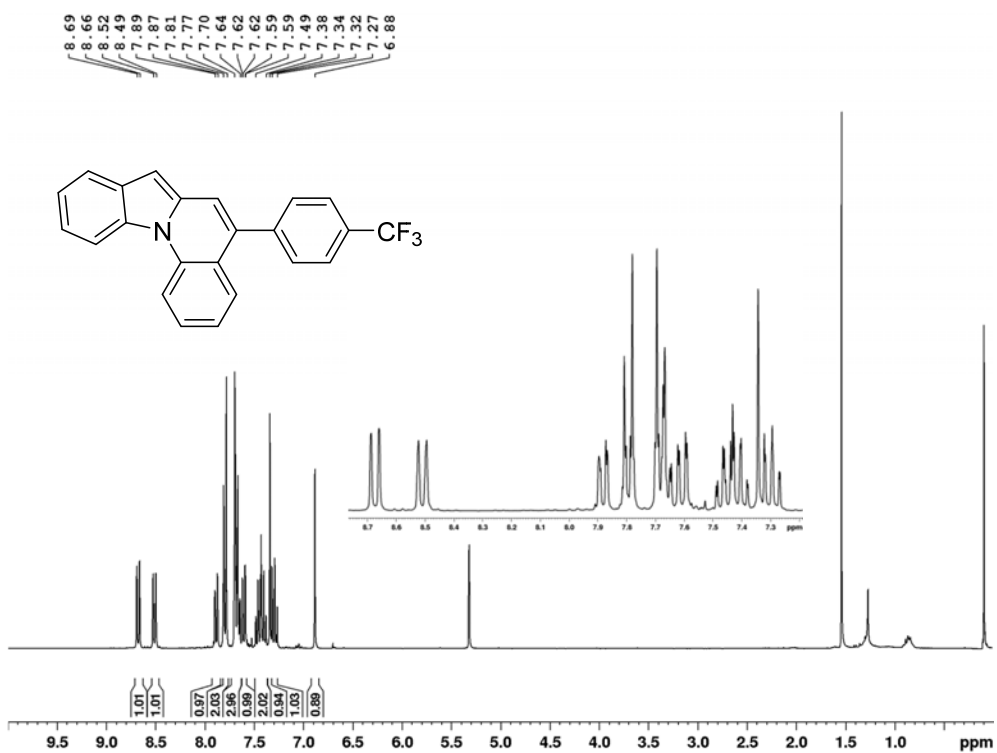


Figure S59. ¹H{¹⁹F} NMR spectrum (301 MHz, CD₂Cl₂) of 2j.

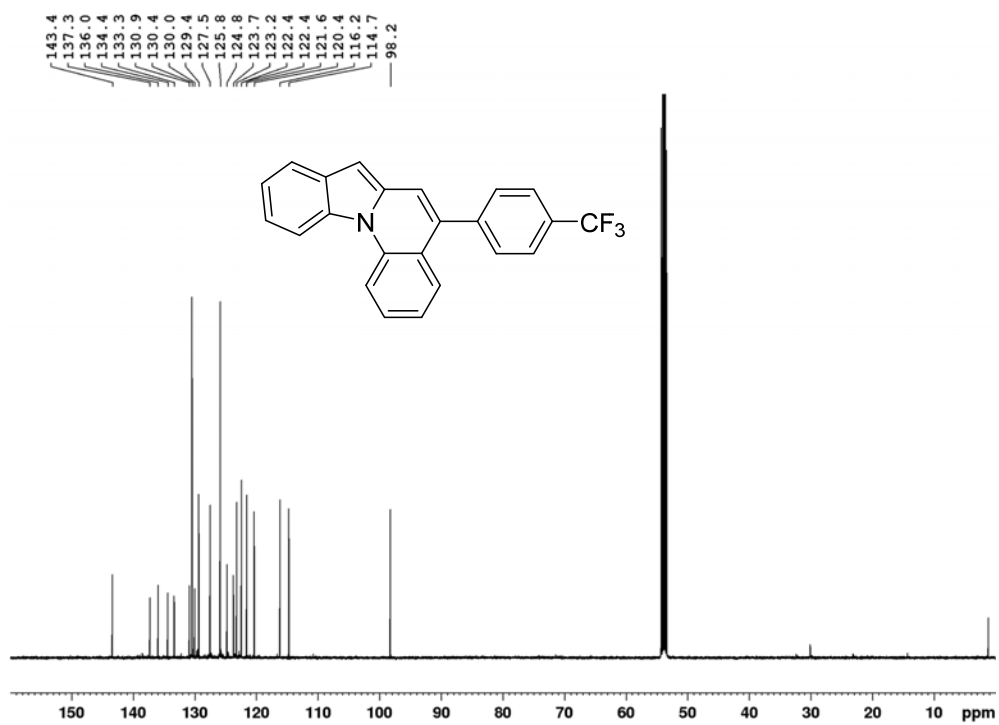


Figure S60. $^{13}\text{C}\{^1\text{H}, ^{19}\text{F}\}$ NMR spectrum (126 MHz, CD_2Cl_2) of **2j**.



Figure S61. $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum (283 MHz, CD_2Cl_2) of **2j**.

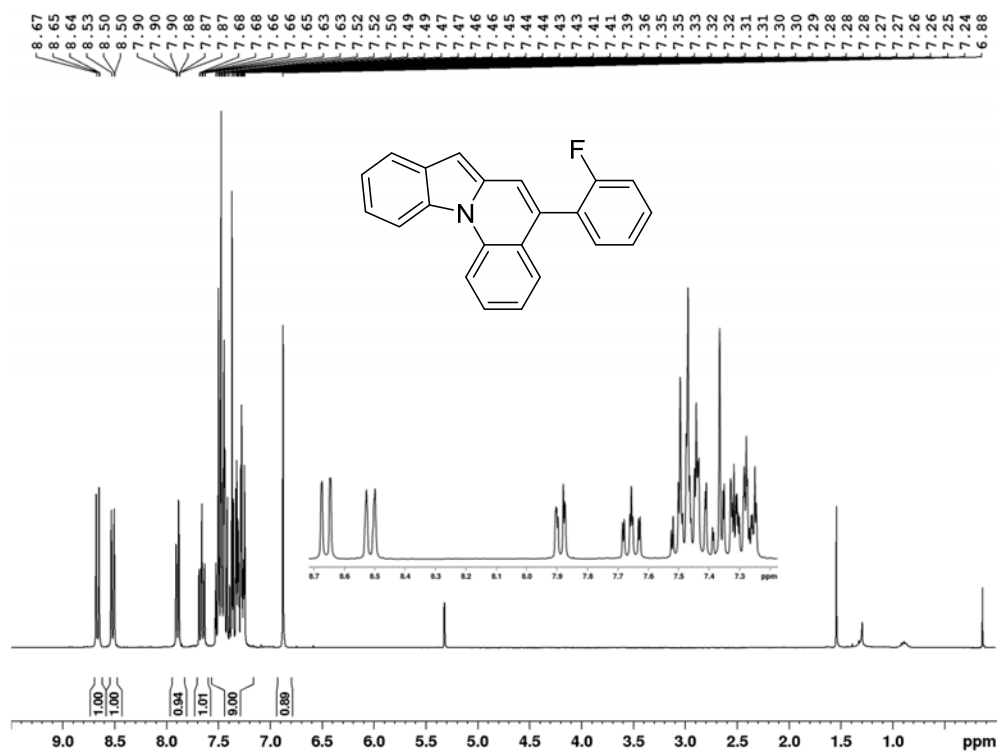


Figure S62. $^1\text{H}\{^{19}\text{F}\}$ NMR spectrum (301 MHz, CD_2Cl_2) of 2k.

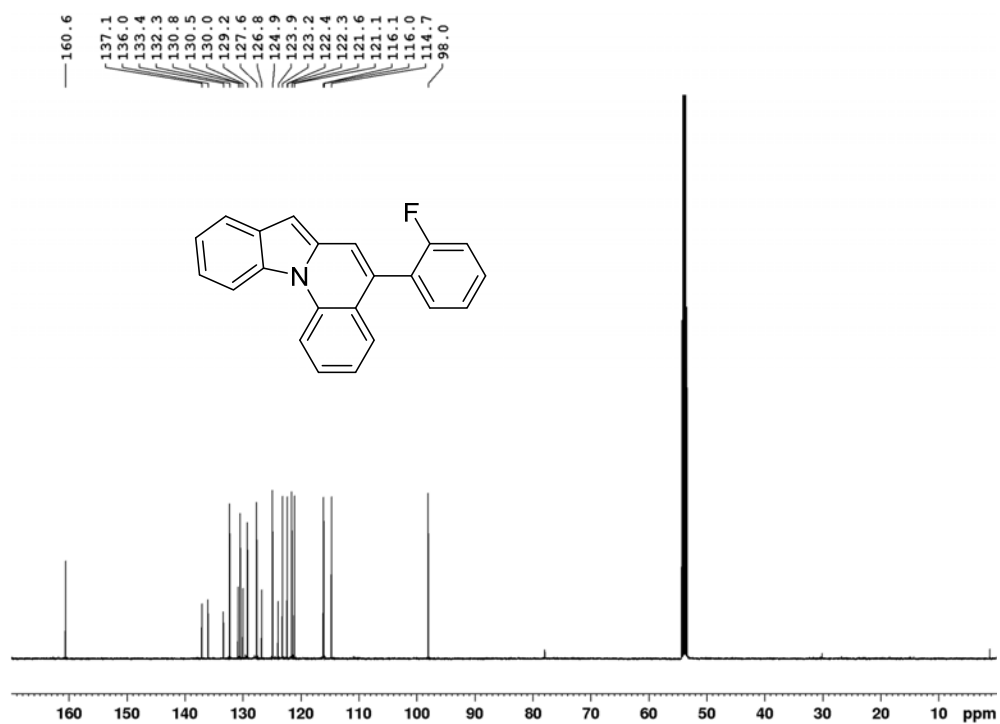


Figure S63. $^{13}\text{C}\{^1\text{H},^{19}\text{F}\}$ NMR spectrum (126 MHz, CD_2Cl_2) of 2k.

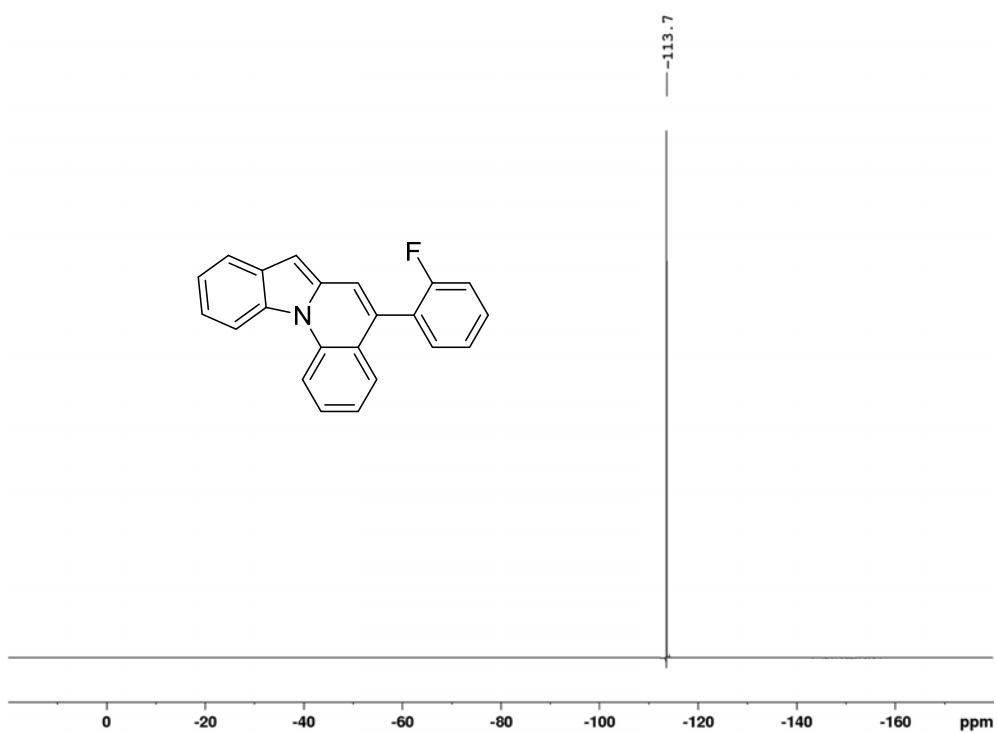


Figure S64. $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum (283 MHz, CD_2Cl_2) of 2k.

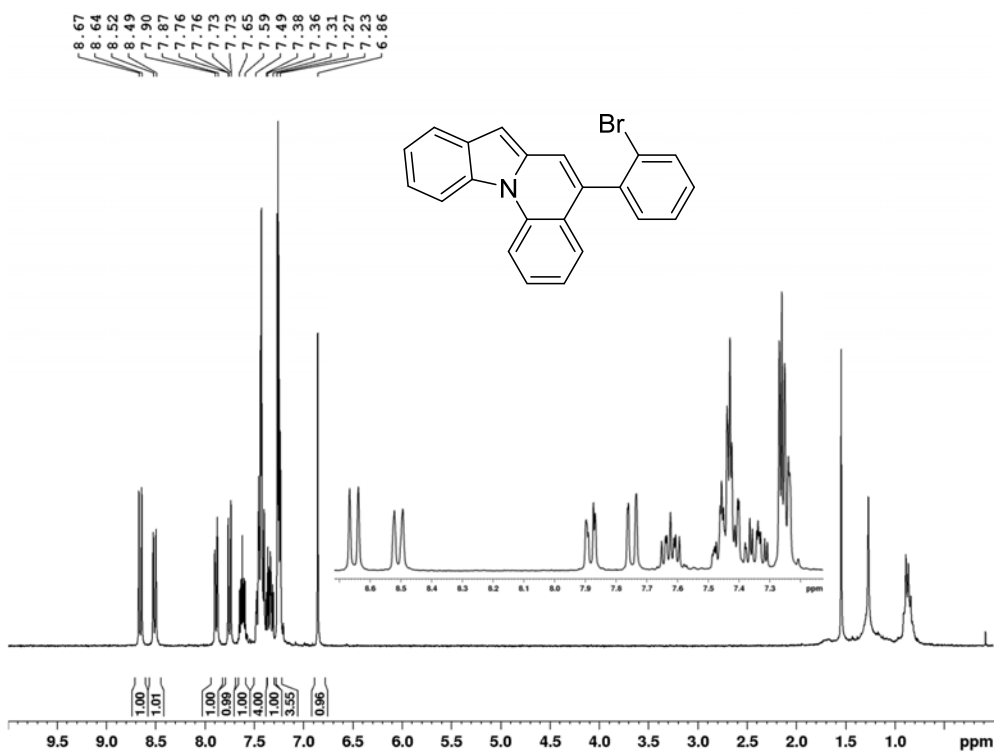


Figure S65. ^1H NMR spectrum (301 MHz, CDCl_3) of 2l.

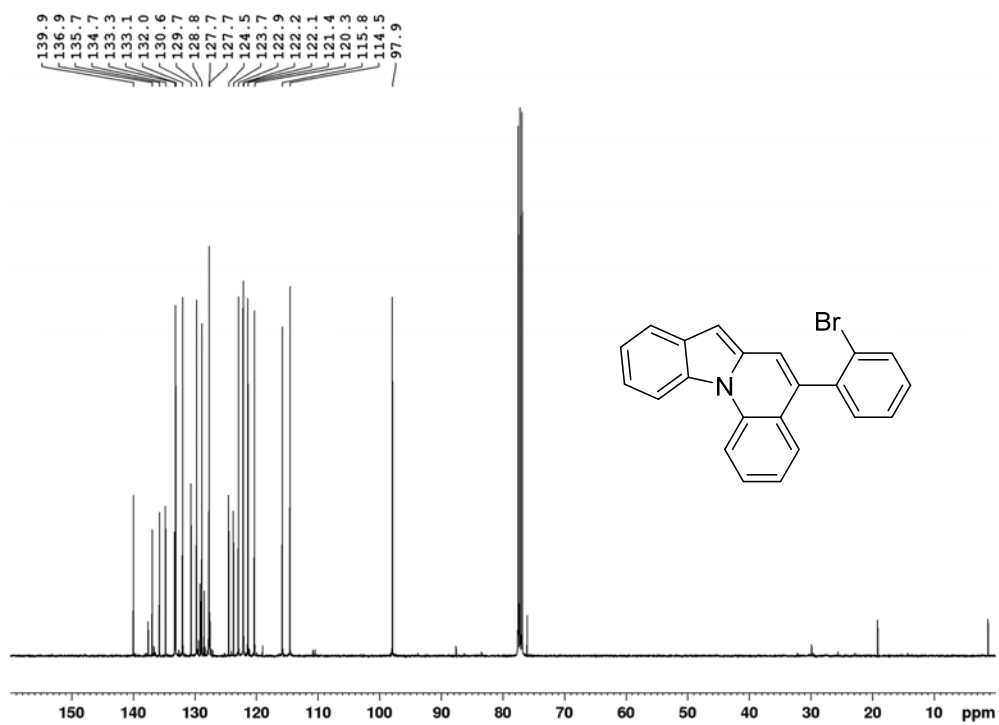


Figure S66. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, CDCl_3) of 2l.

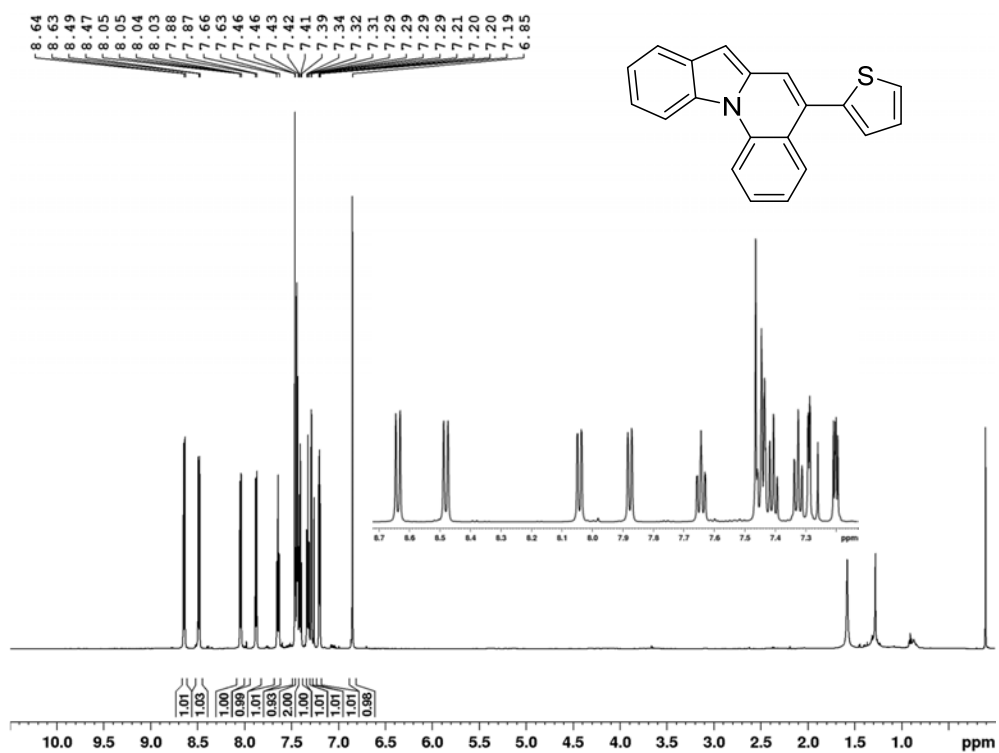


Figure S67. ^1H NMR spectrum (600 MHz, CDCl_3) of 2m.

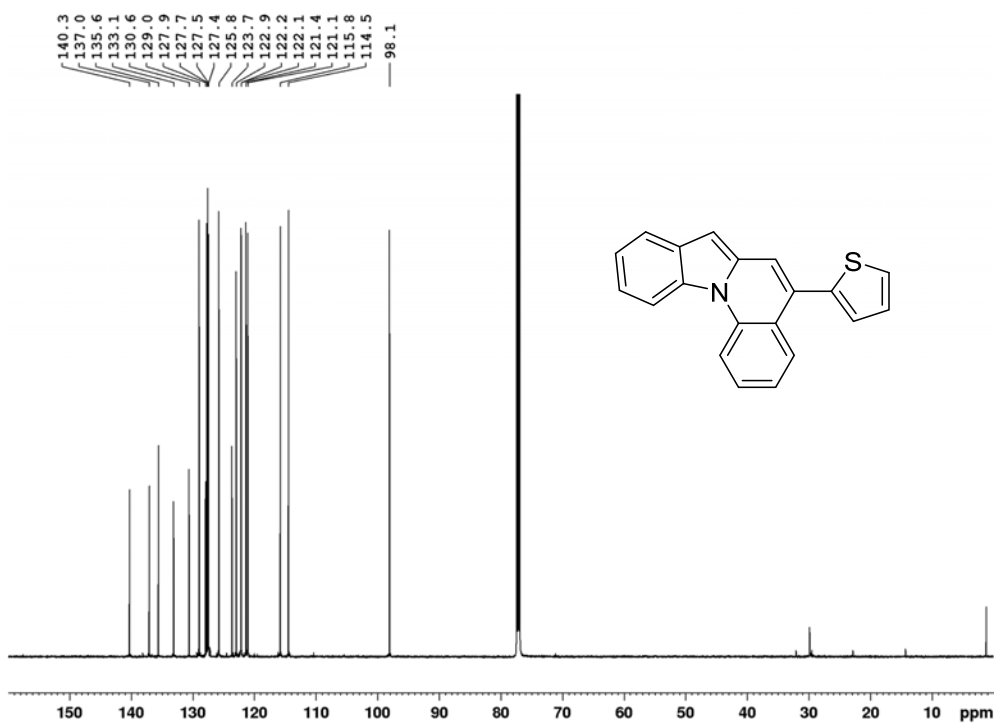


Figure S68. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (151 MHz, CDCl_3) of 2m.

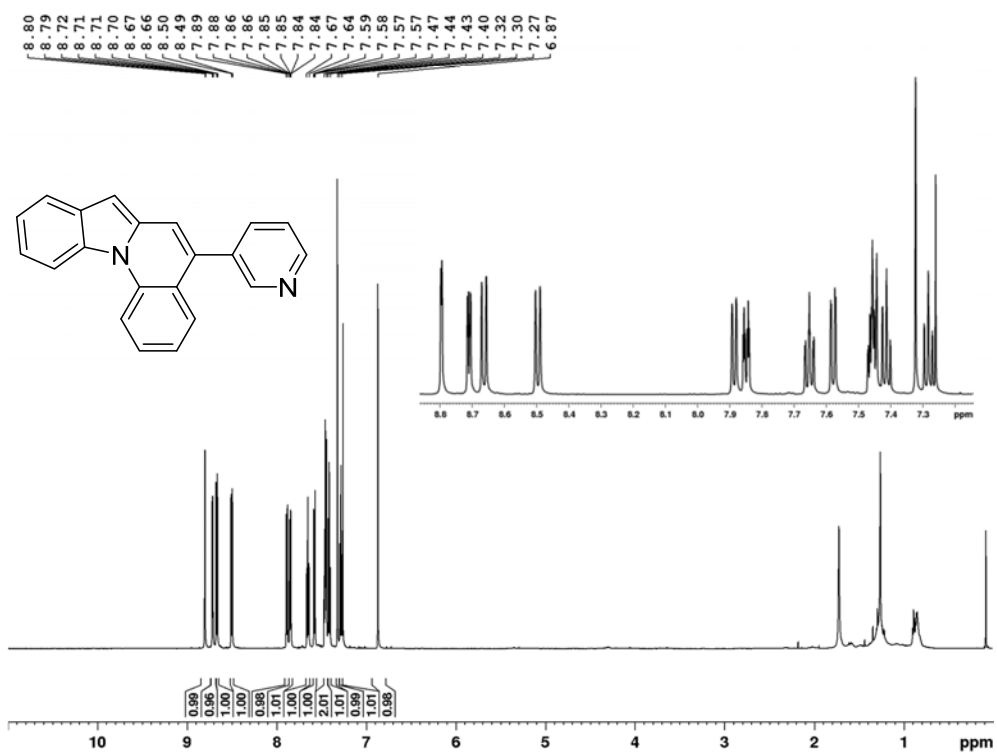


Figure S69. ^1H NMR spectrum (600 MHz, CDCl_3) of 2n.

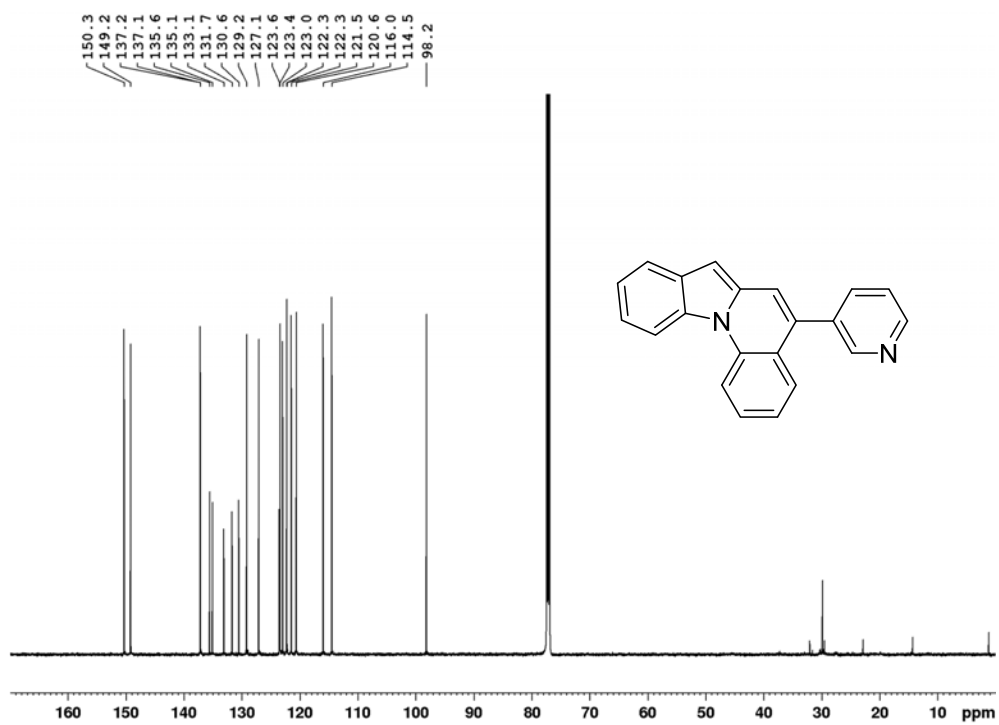


Figure S70. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (151 MHz, CDCl_3) of 2n.

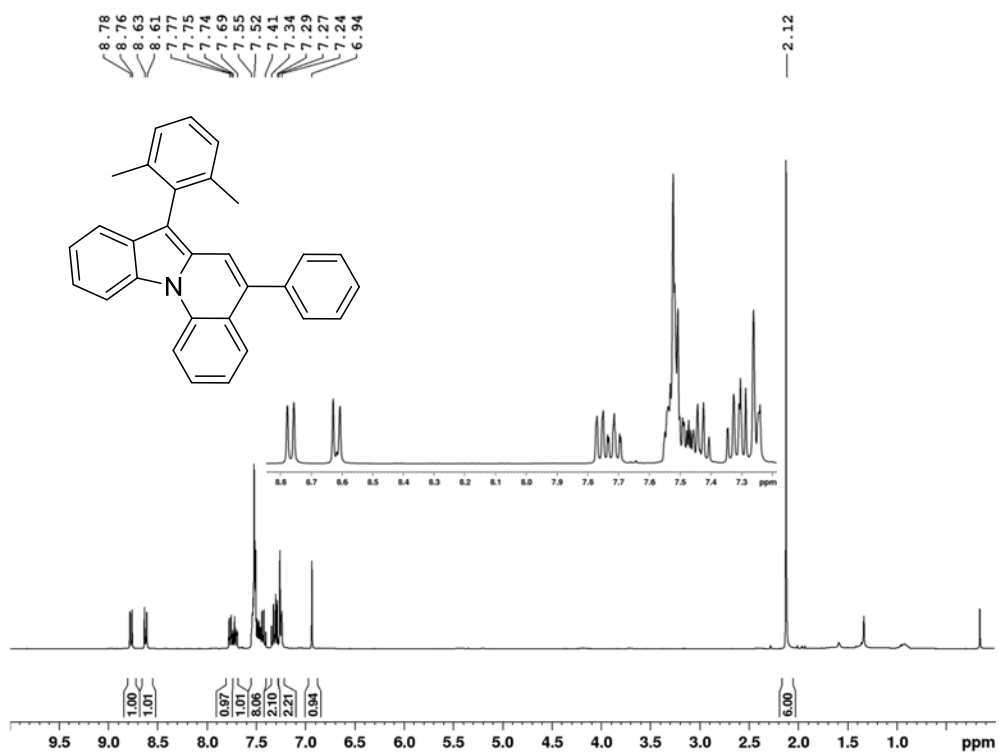


Figure S71. ^1H NMR spectrum (400 MHz, CDCl_3) of 2o.

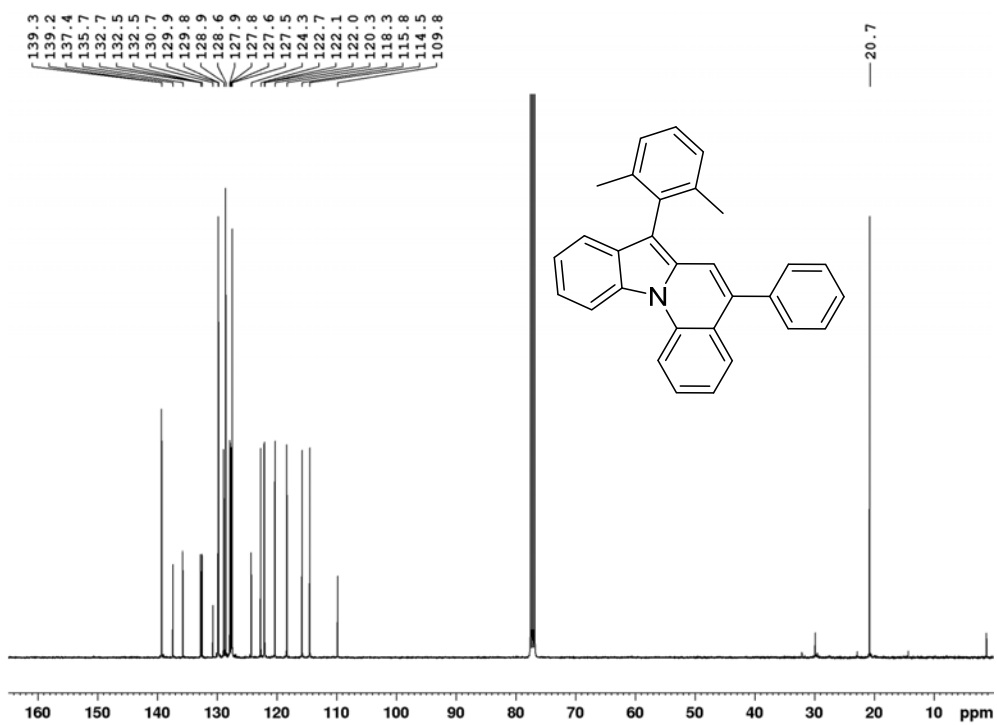


Figure S72. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, CDCl_3) of **2o**.

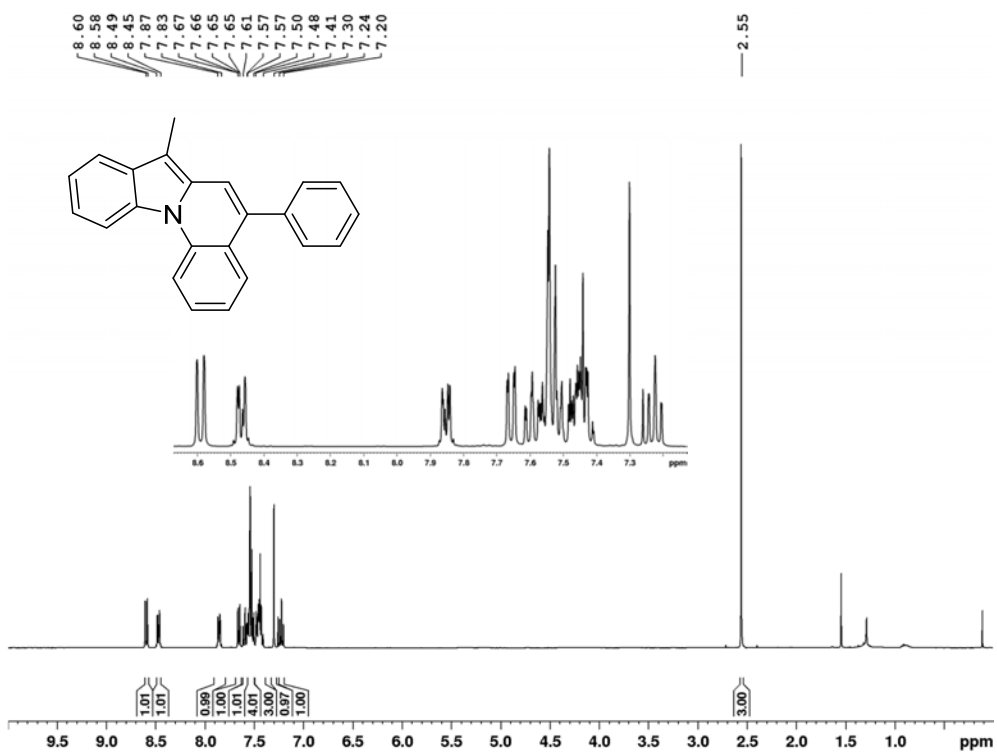


Figure S73. ^1H NMR spectrum (400 MHz, CDCl_3) of **2p**.

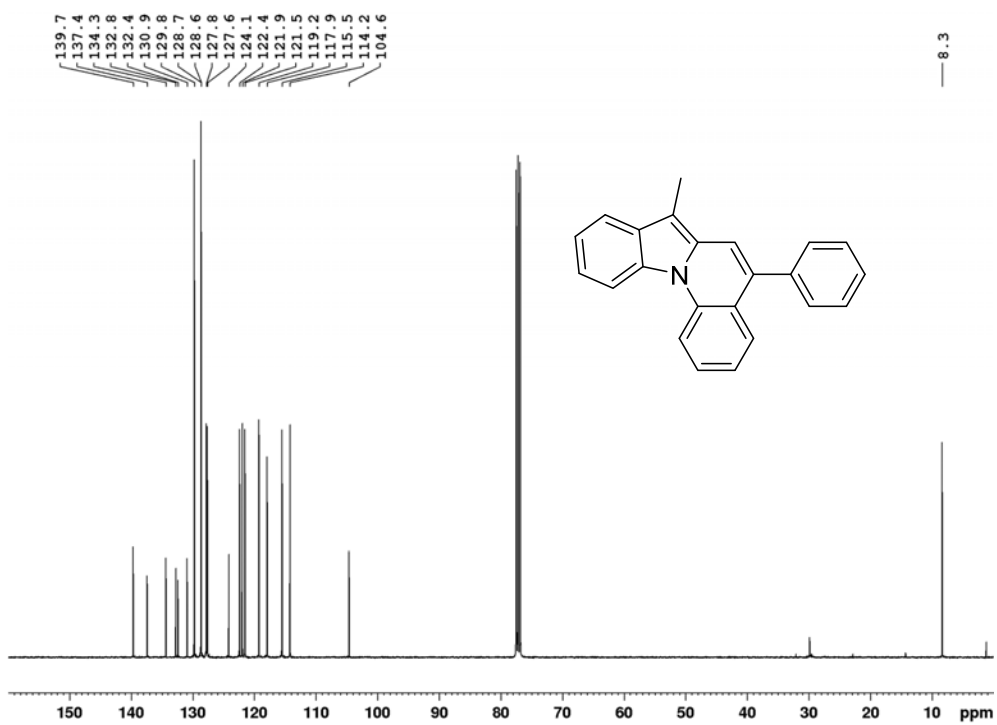


Figure S74. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, CDCl_3) of 2p.

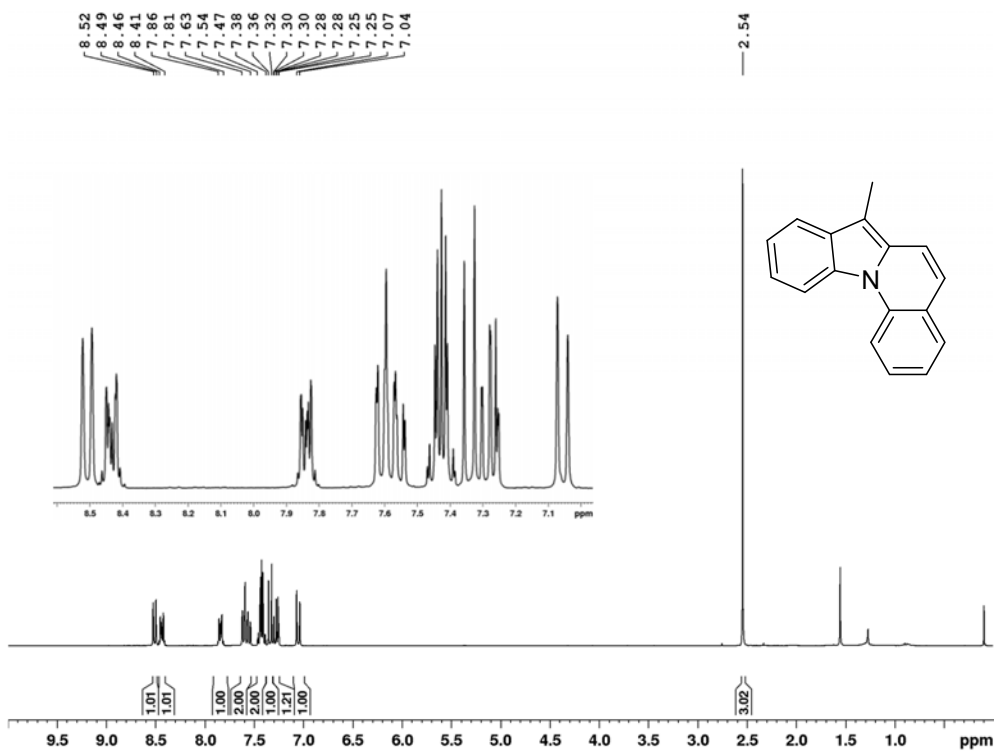


Figure S75. ^1H NMR spectrum (301 MHz, CDCl_3) of 2q.

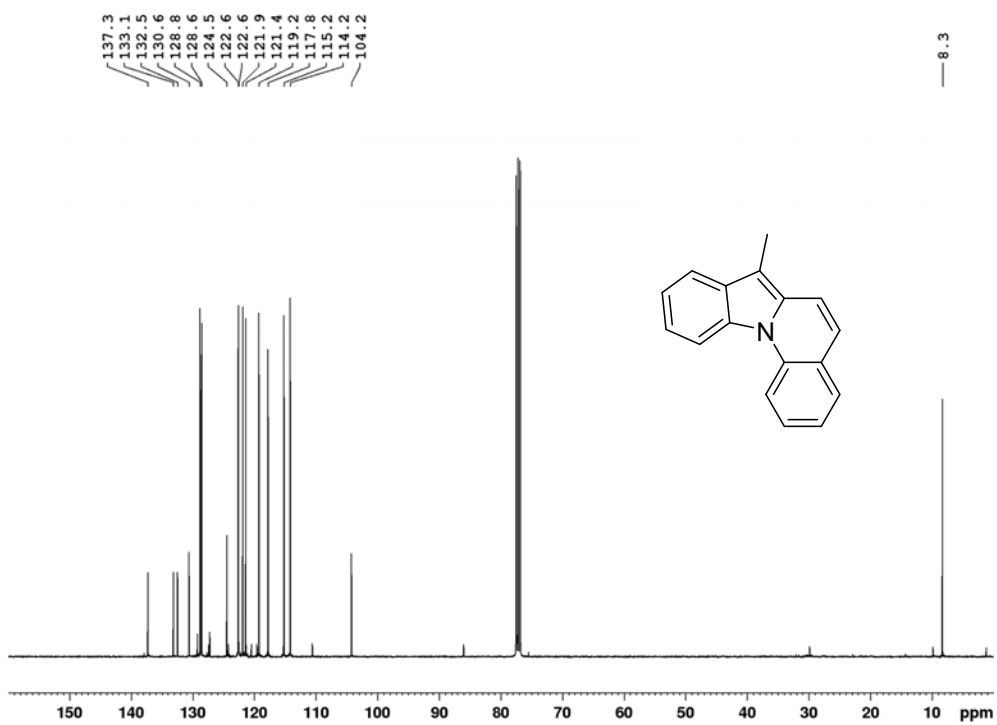


Figure S76. ¹³C{¹H} NMR spectrum (101 MHz, CDCl₃) of 2q.

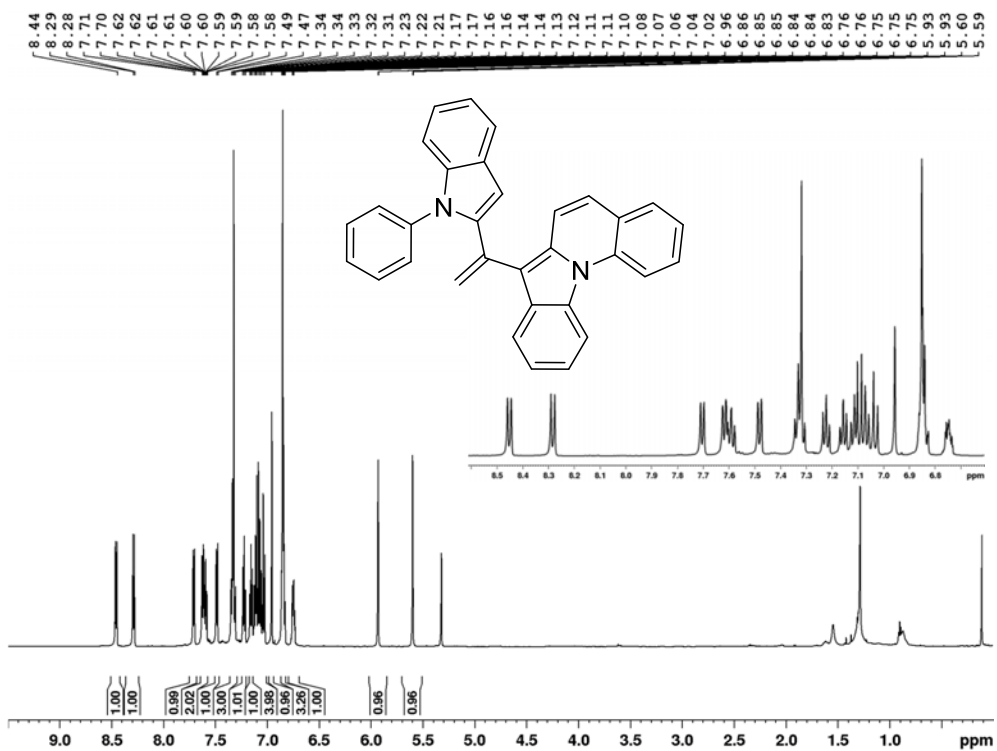


Figure S77. ¹H NMR spectrum (600 MHz, CD₂Cl₂) of 4.

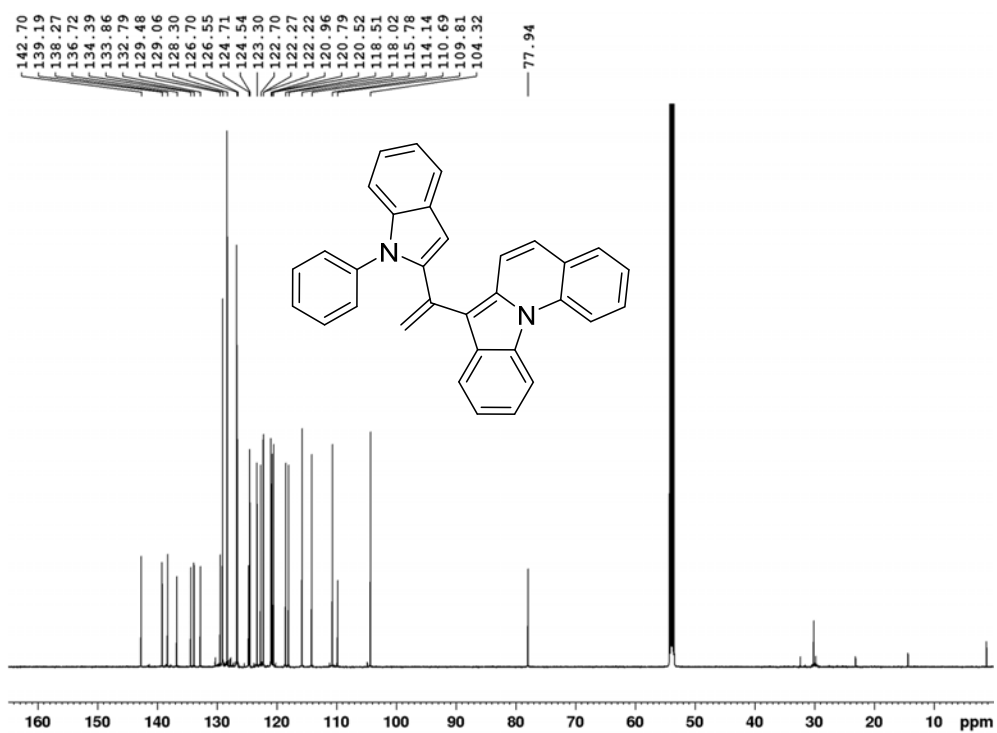


Figure S78. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (151 MHz, CD_2Cl_2) of 4.

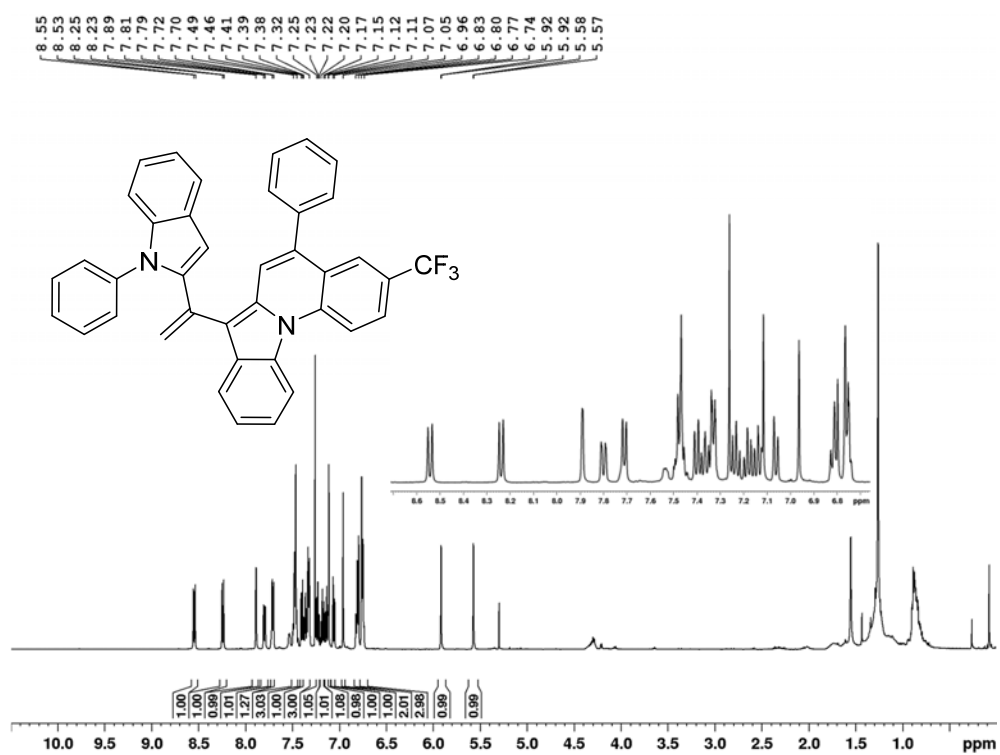


Figure S79. $^1\text{H}\{^{19}\text{F}\}$ NMR spectrum (500 MHz, CDCl_3) of 5.

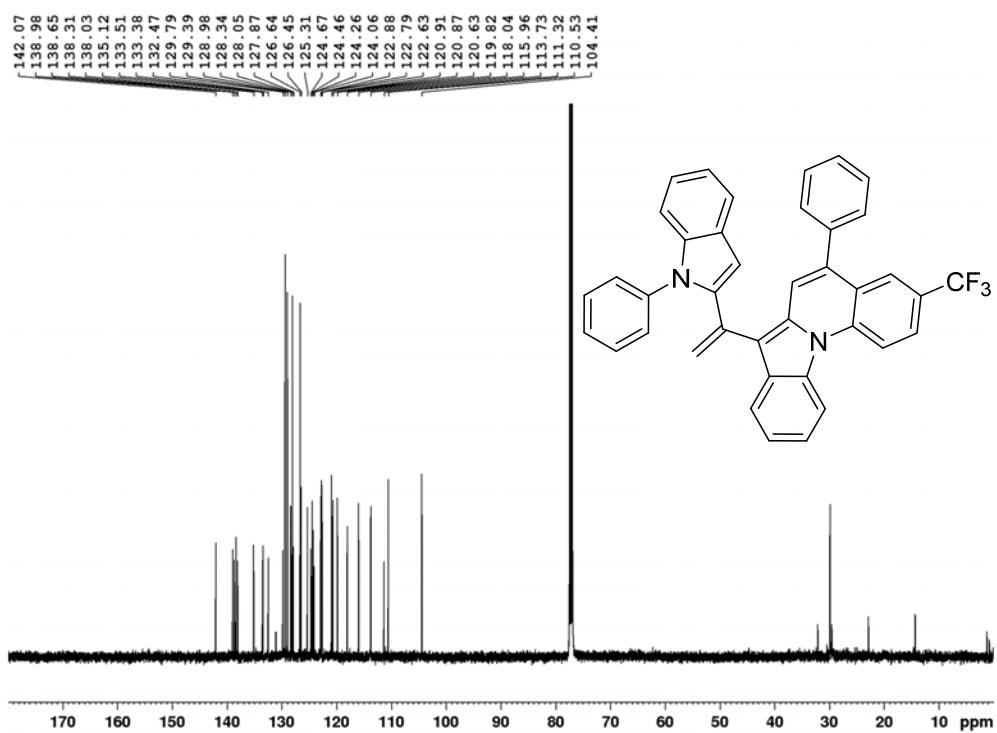


Figure S80. $^{13}\text{C}\{^1\text{H}, ^{19}\text{F}\}$ NMR spectrum (126 MHz, CDCl_3) of **5**.



Figure S81. $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum (471 MHz, CDCl_3) of **5**.

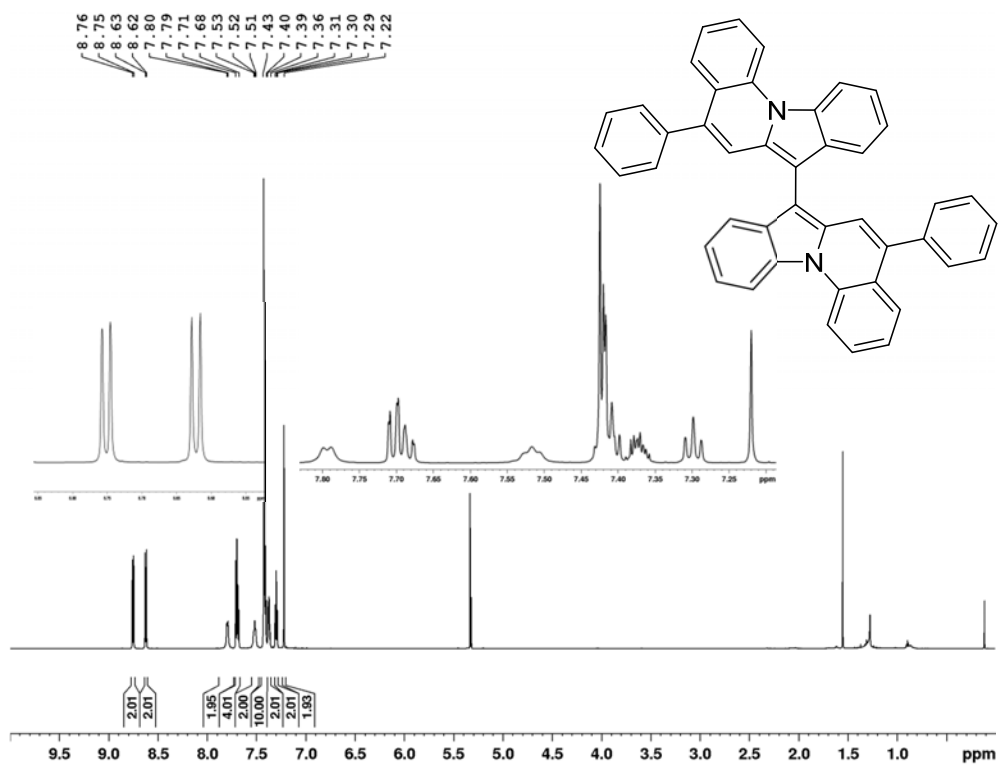


Figure S82. ¹H NMR spectrum (700 MHz, CD₂Cl₂) of 6.

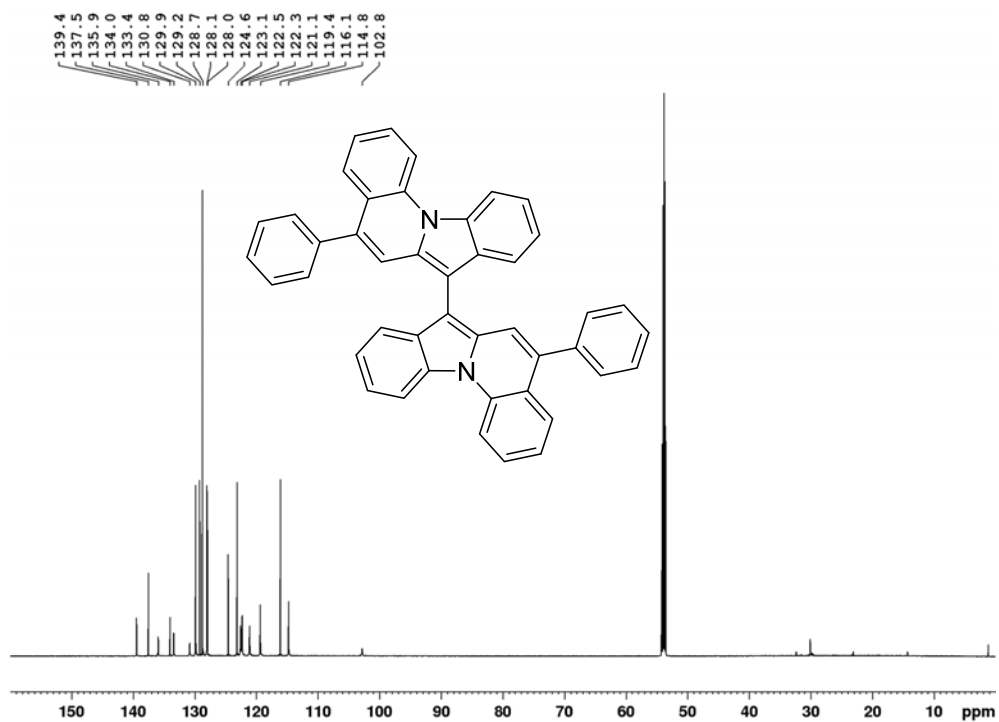


Figure S83. ¹³C{¹H} NMR spectrum (176 MHz, CD₂Cl₂) of 6.

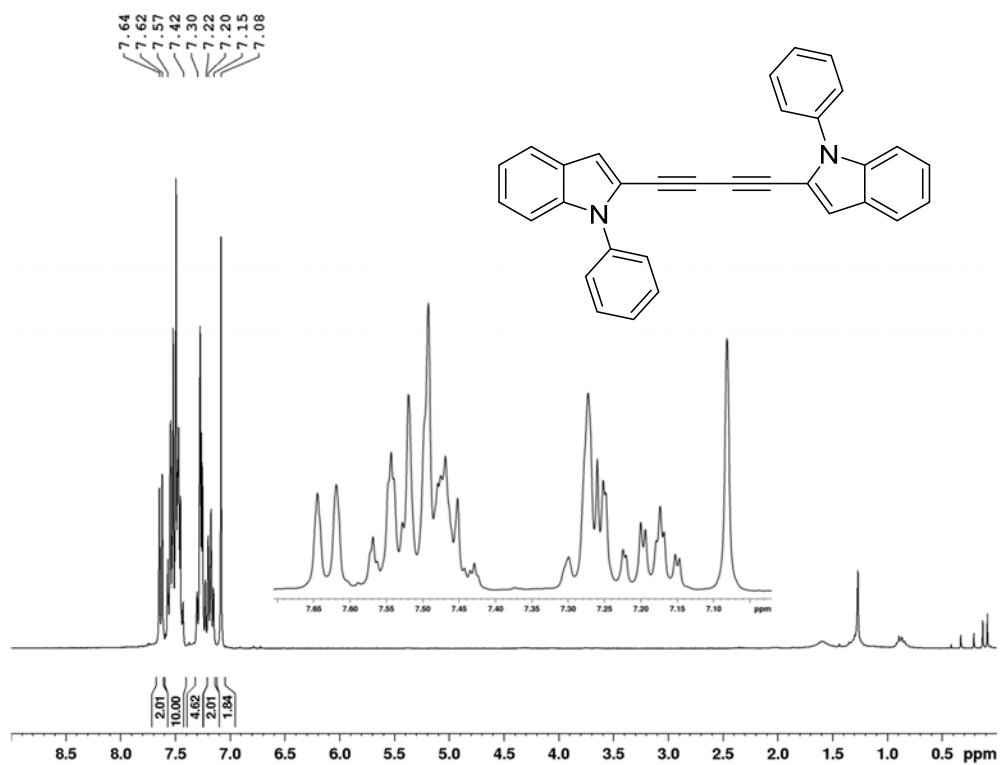


Figure S84. ¹H NMR spectrum (301 MHz, CDCl₃) of 7.

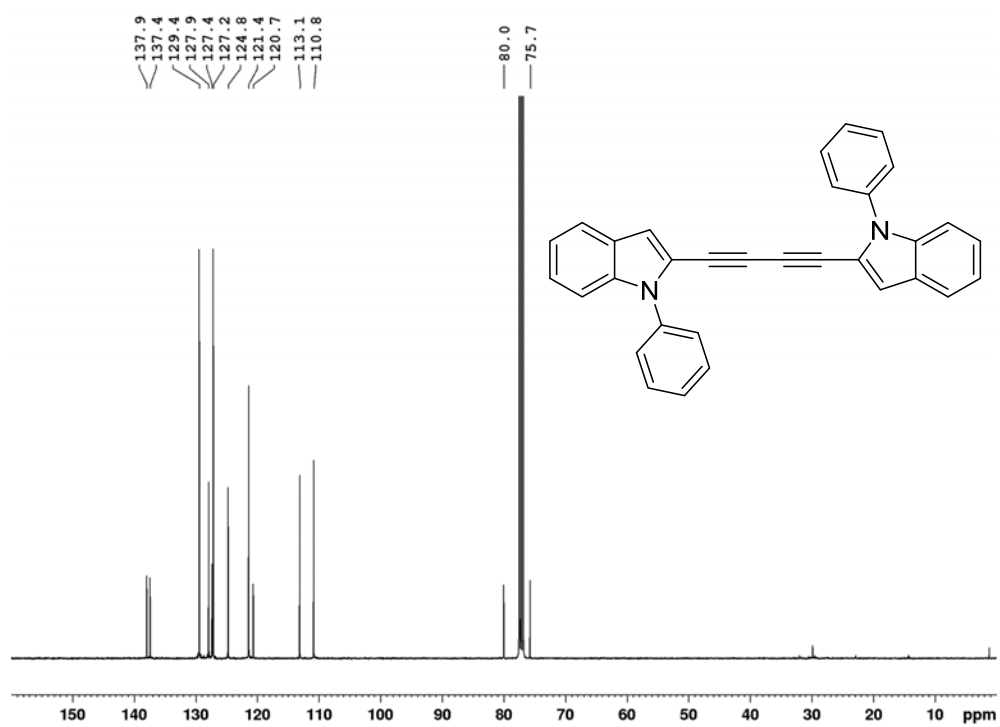


Figure S85. ¹³C{¹H} NMR spectrum (101 MHz, CDCl₃) of 7.

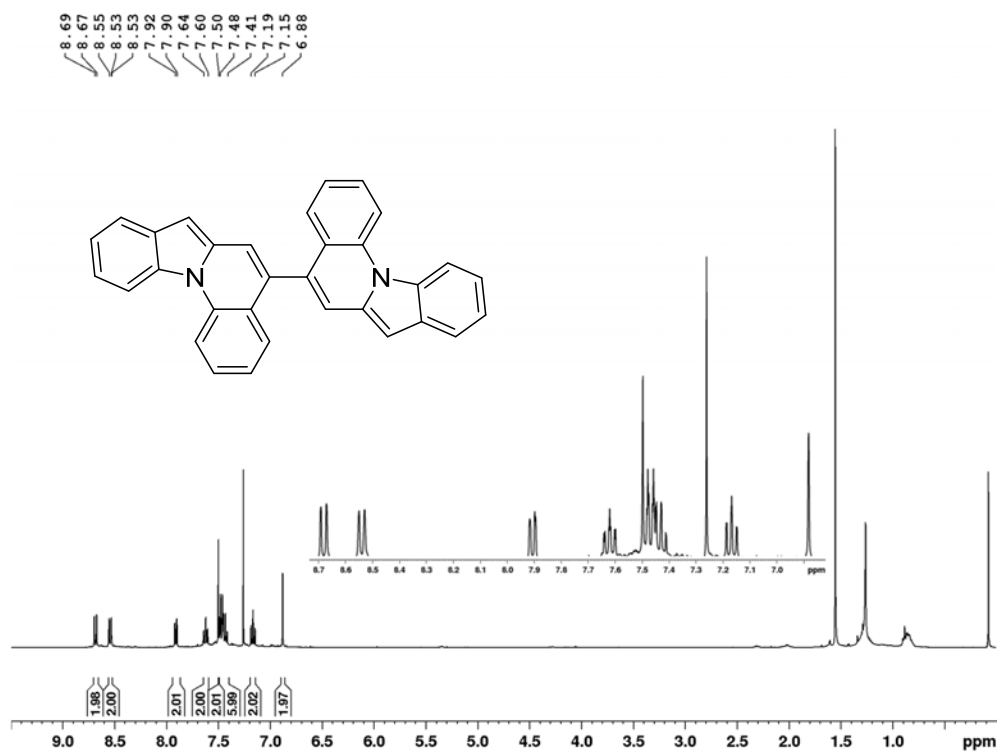


Figure S86. ¹H NMR spectrum (400 MHz, CDCl₃) of **8**.

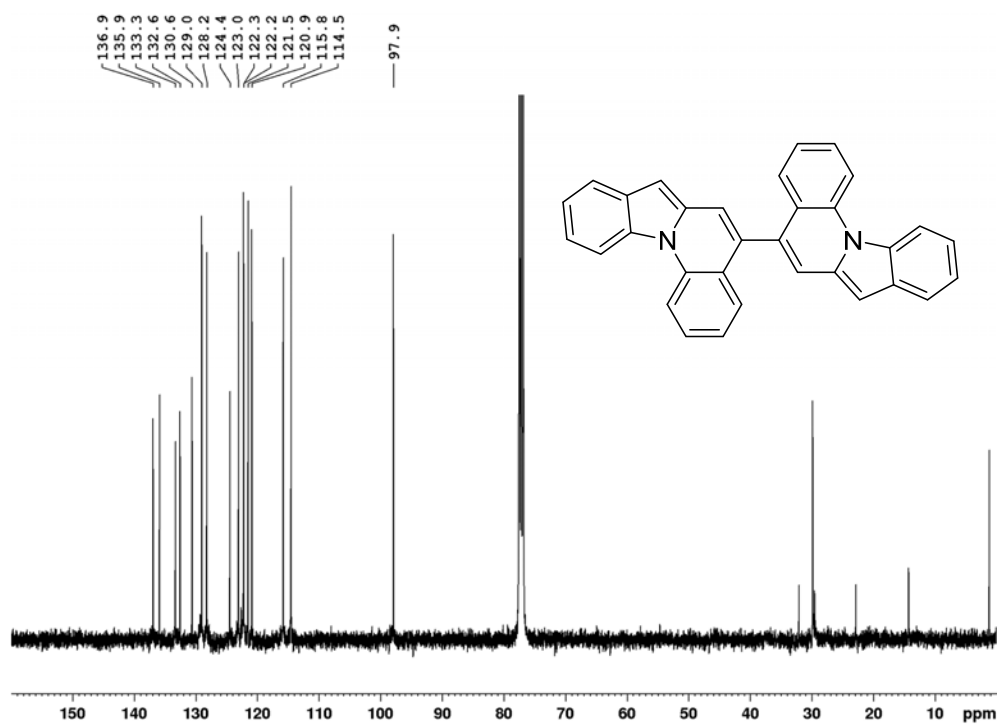


Figure S87. ¹³C{¹H} NMR spectrum (101 MHz, CDCl₃) of **8**.

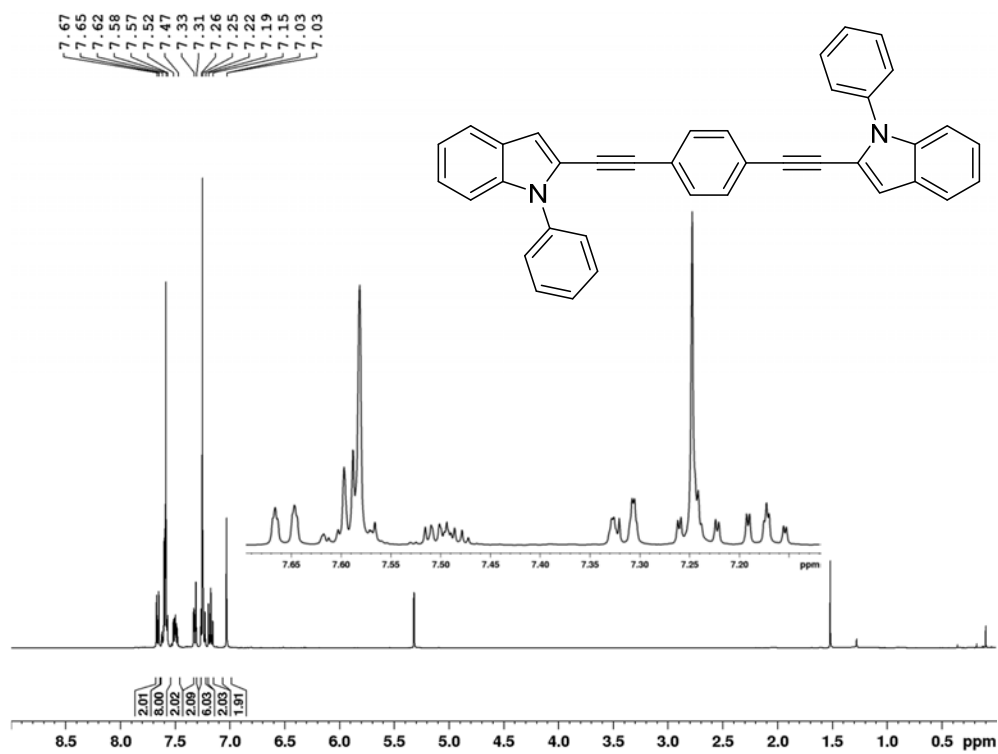


Figure S88. ¹H NMR spectrum (400 MHz, CD₂Cl₂) of 9.

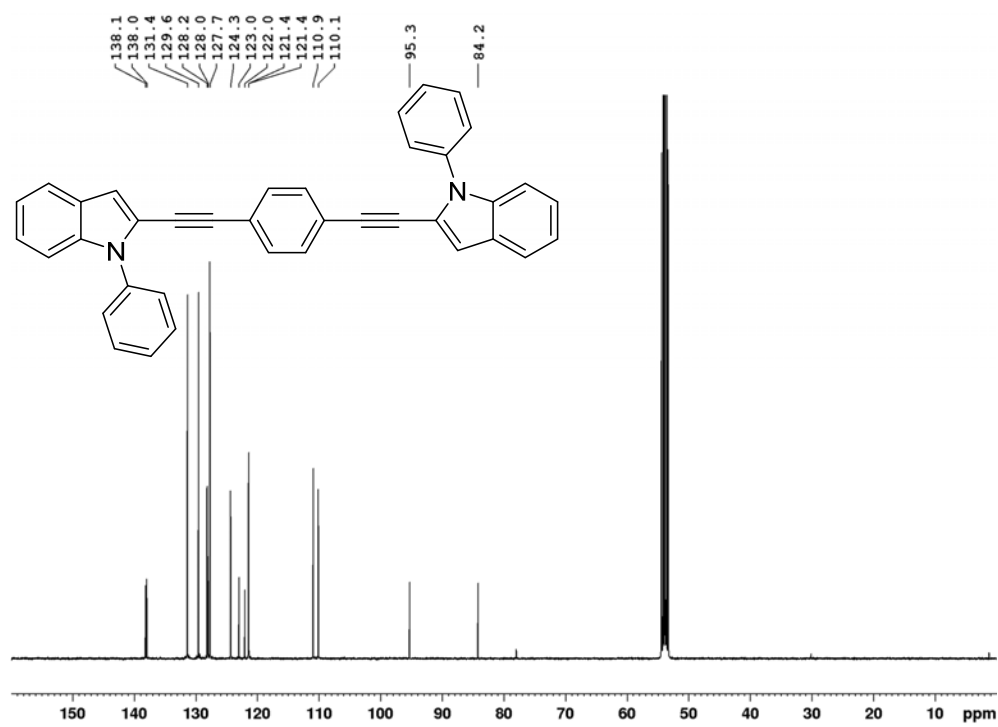


Figure S89. ¹³C{¹H} NMR spectrum (101 MHz, CD₂Cl₂) of 9.

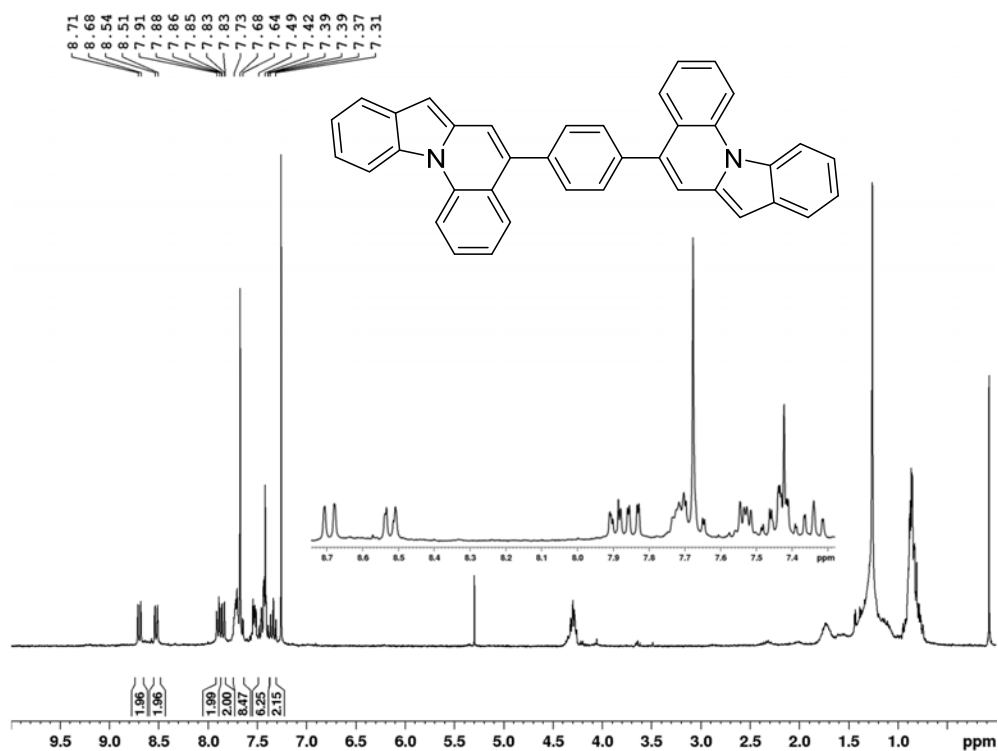


Figure S90. ¹H NMR spectrum (301 MHz, CDCl₃) of 10.

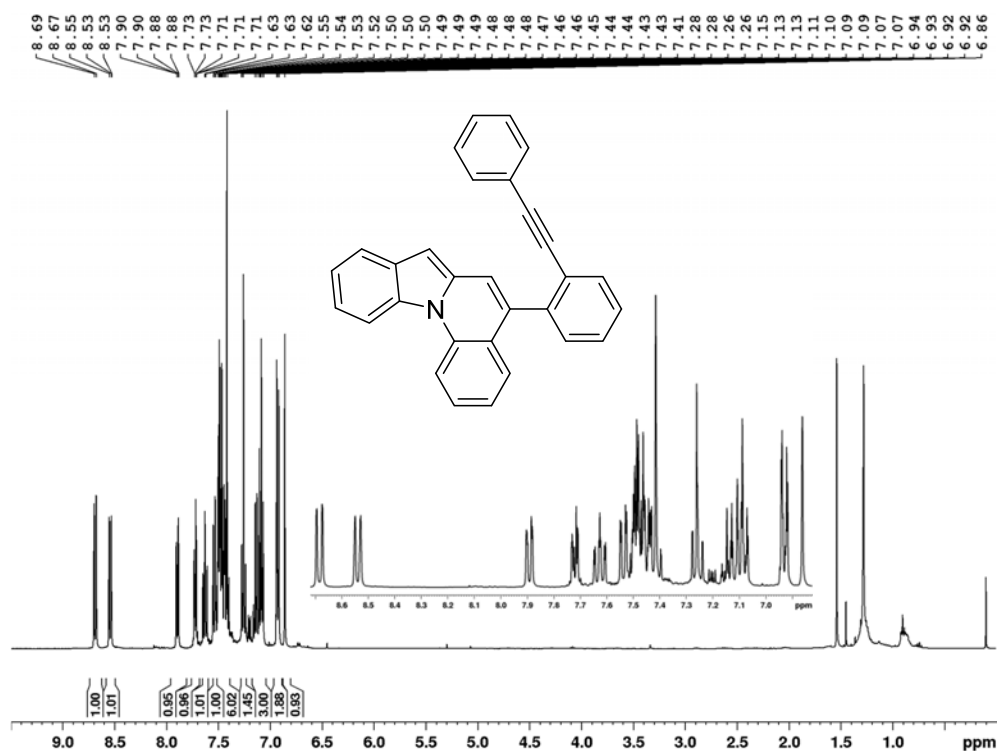


Figure S91. ¹H NMR spectrum (400 MHz, CDCl₃) of 11.

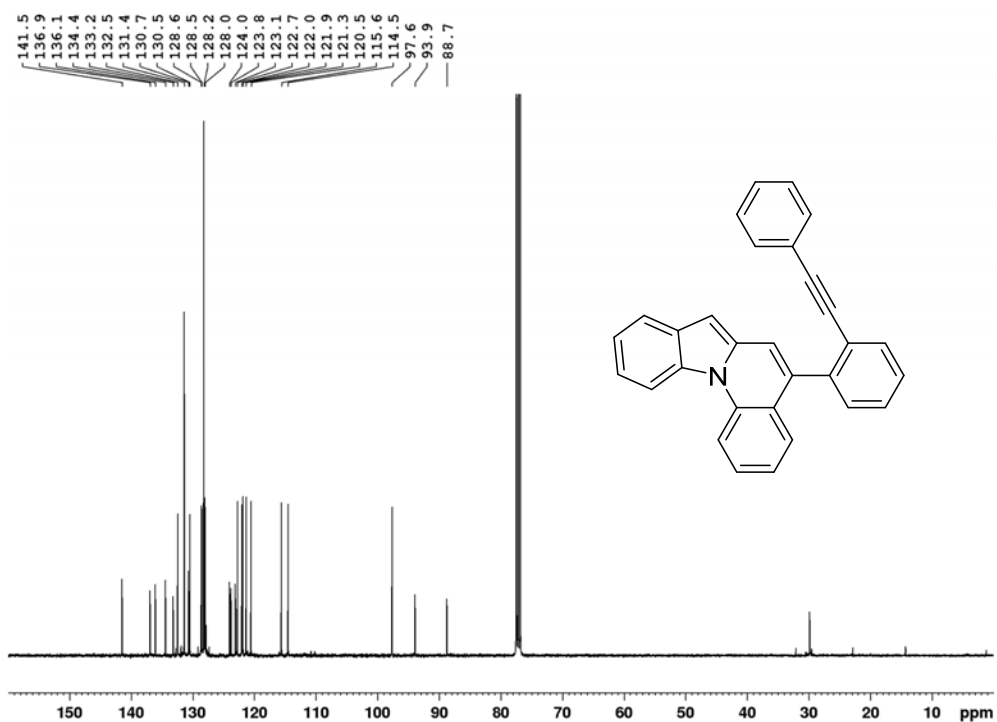


Figure S92. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, CDCl_3) of **11**.

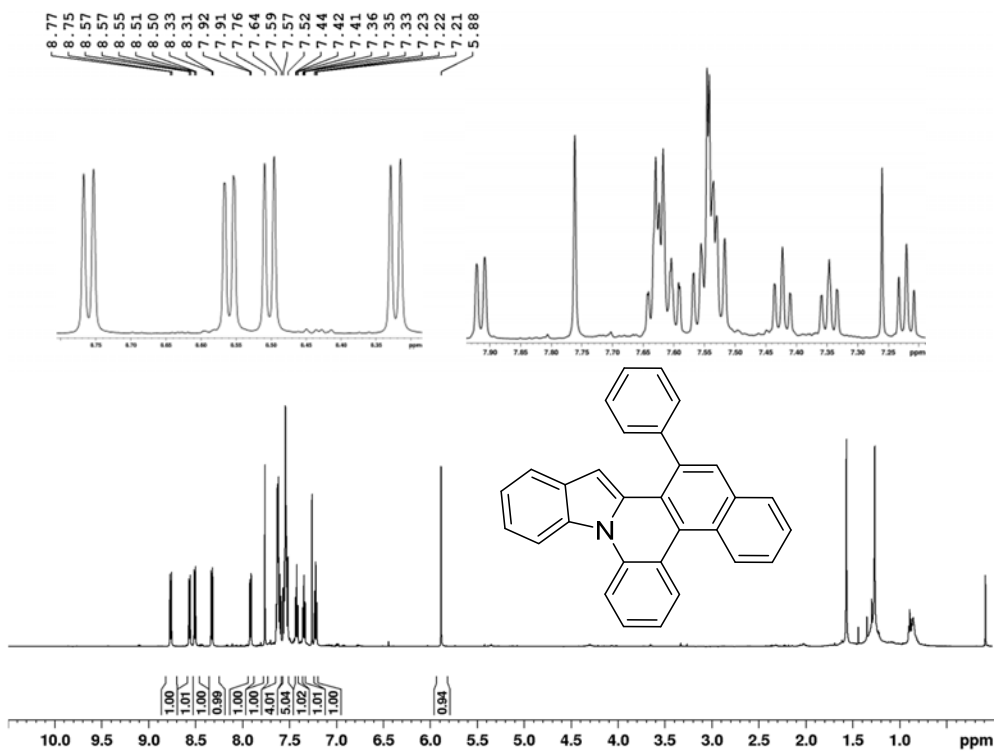


Figure S93. ^1H NMR spectrum (600 MHz, CDCl_3) of **12**.

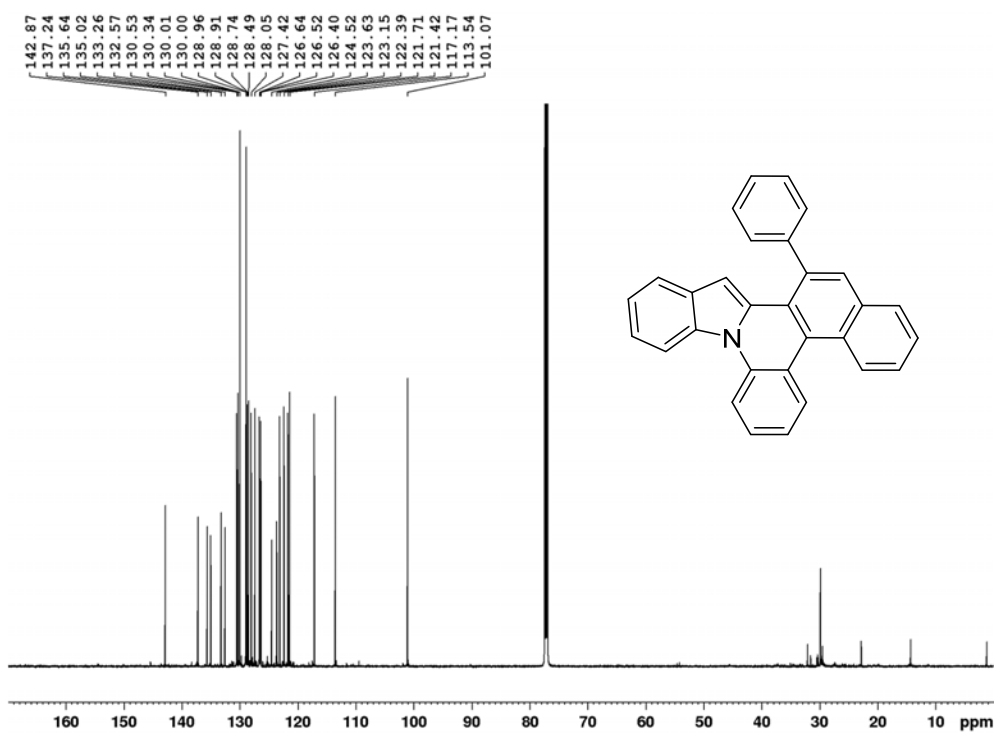


Figure S94. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (151 MHz, CDCl_3) of 12.

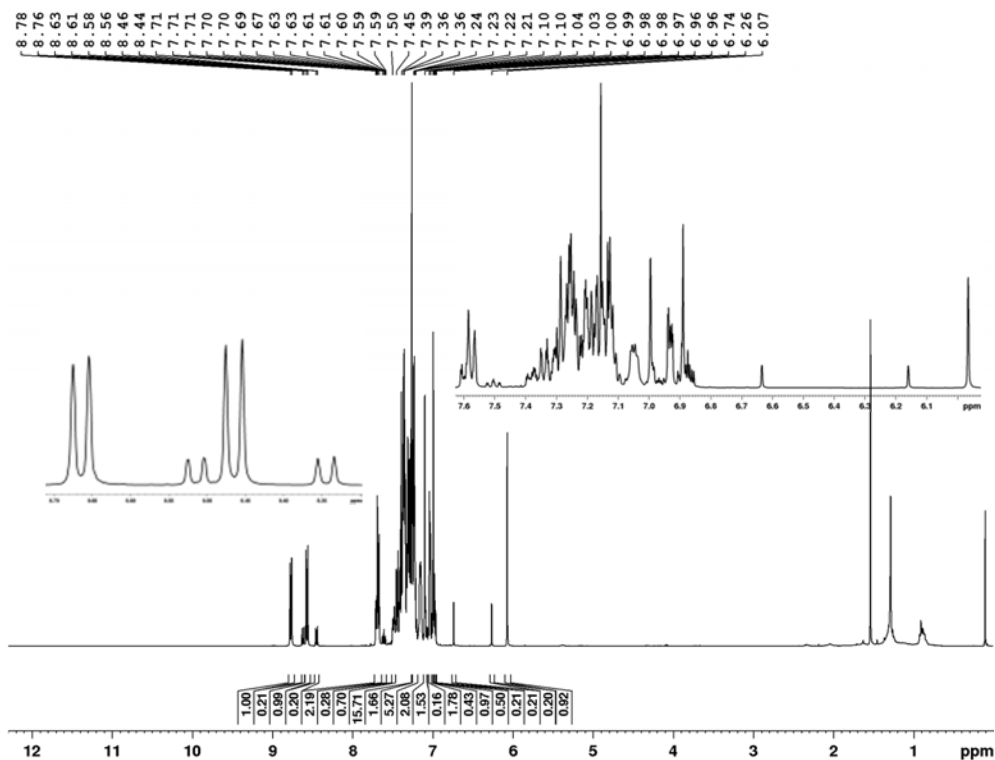


Figure S95. ^1H NMR spectrum (400 MHz, CDCl_3) of 3a/3c.

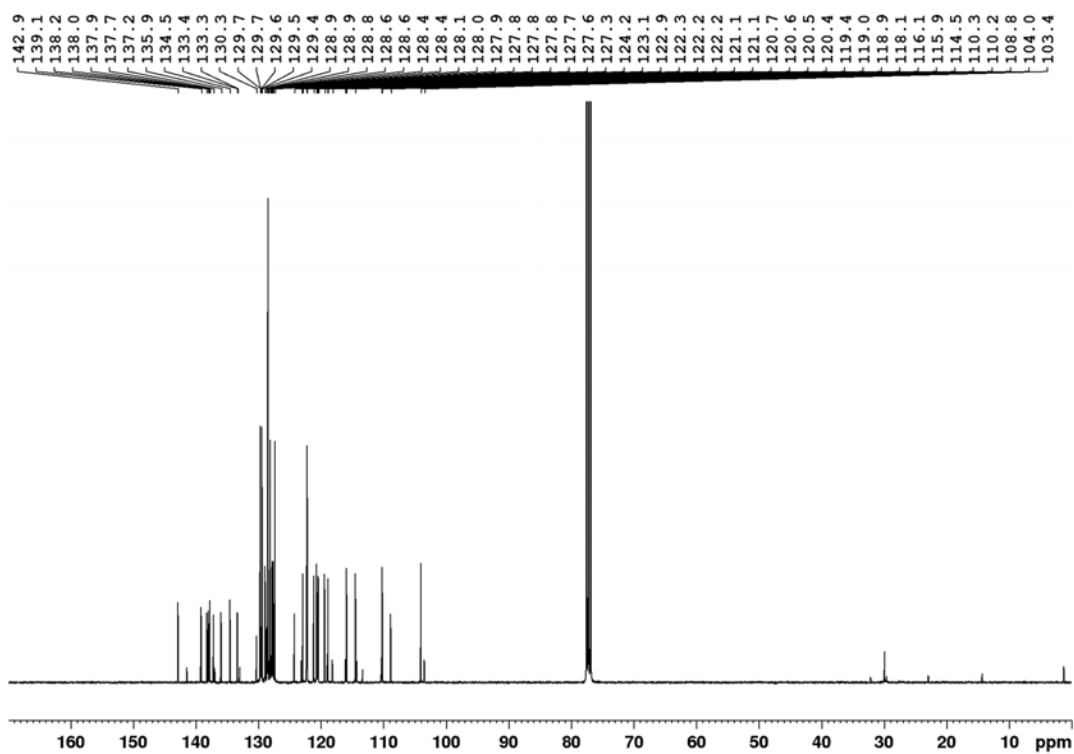


Figure S96. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, CDCl_3) of 3a/3c.

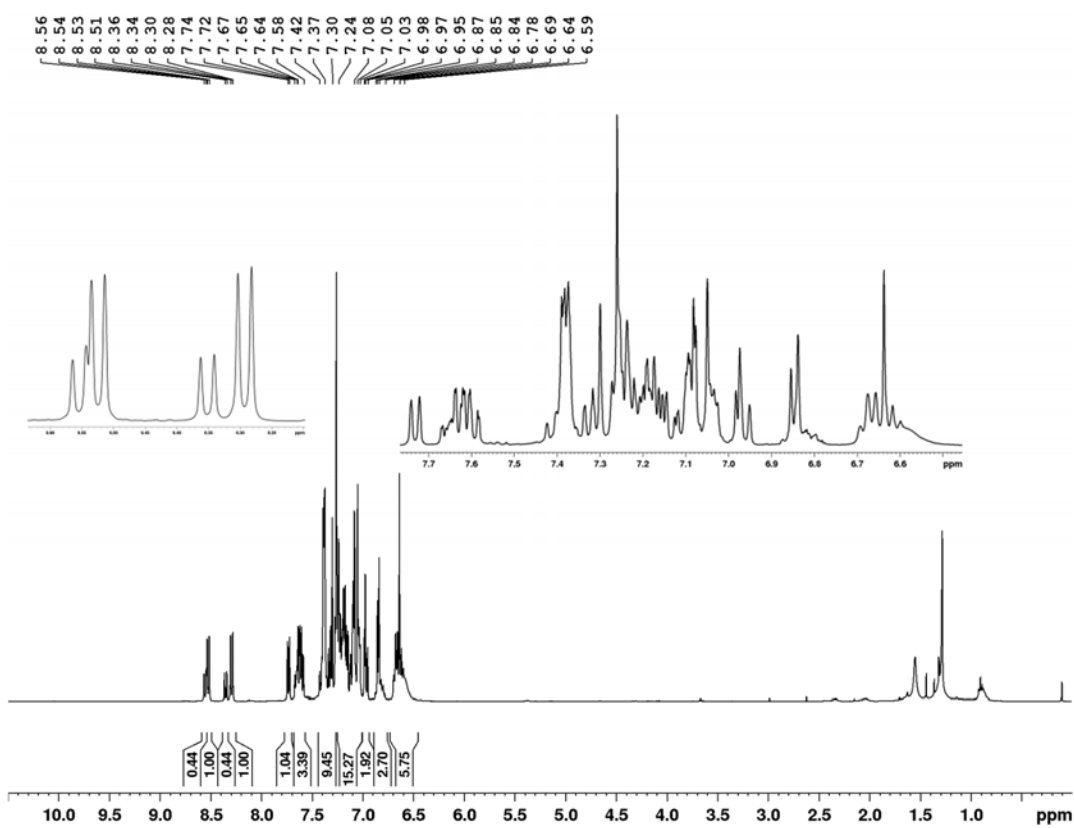


Figure S97. ^1H NMR spectrum (400 MHz, CDCl_3) of 3b/3d.

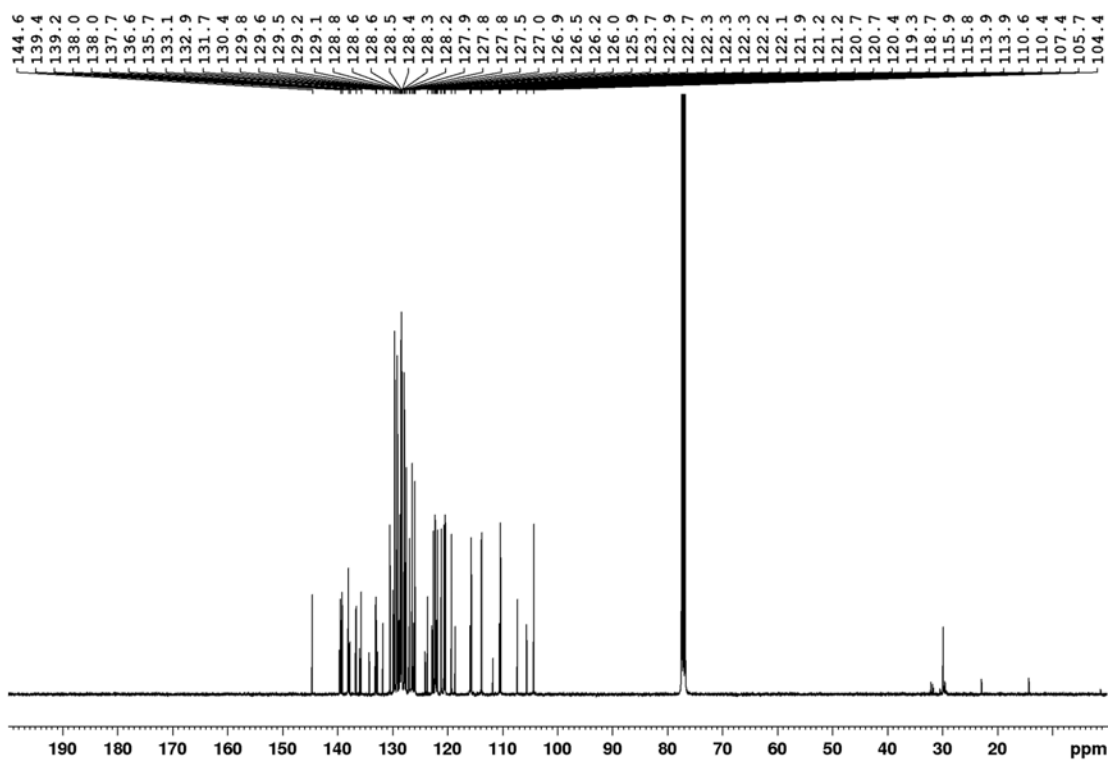


Figure S98. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, CDCl_3) of **3b/3d**.

3 UV-Vis and Fluorescence Spectra

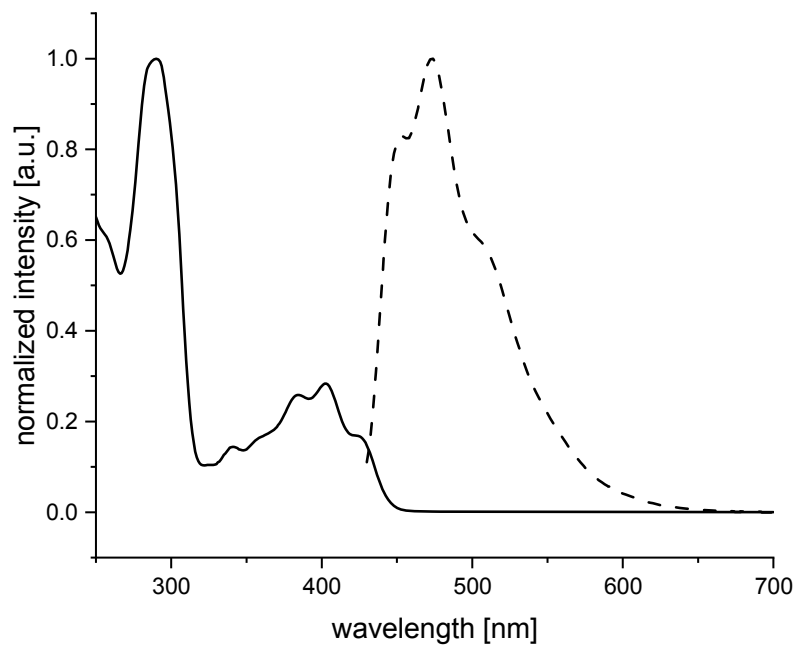


Figure S99. Absorption (solid line) and emission (dashed line) spectra of **2a** in DCM.

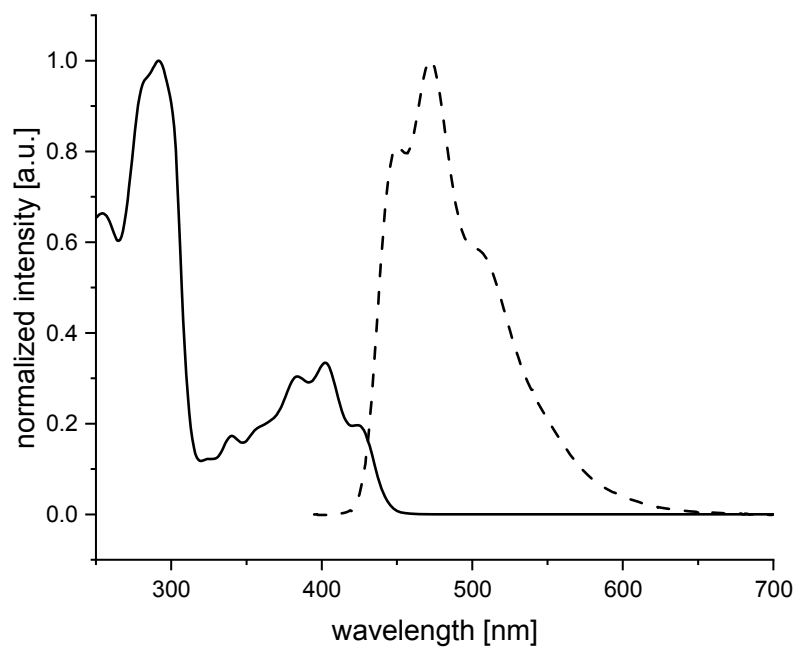


Figure S100. Absorption (solid line) and emission (dashed line) spectra of **2a** in dioxane.

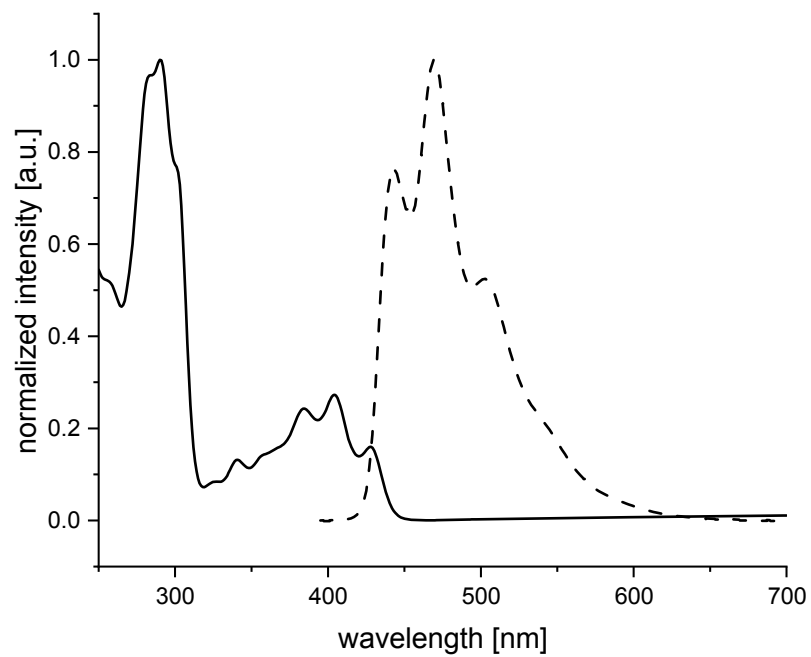


Figure S101. Absorption (solid line) and emission (dashed line) spectra of **2a** in cyclohexane.

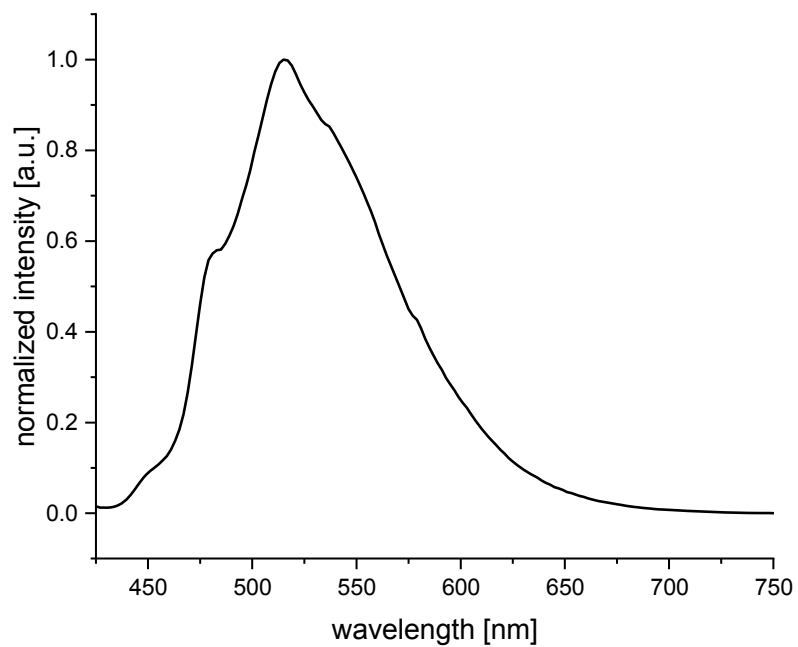


Figure S102. Emission spectra of **2a** as powder.

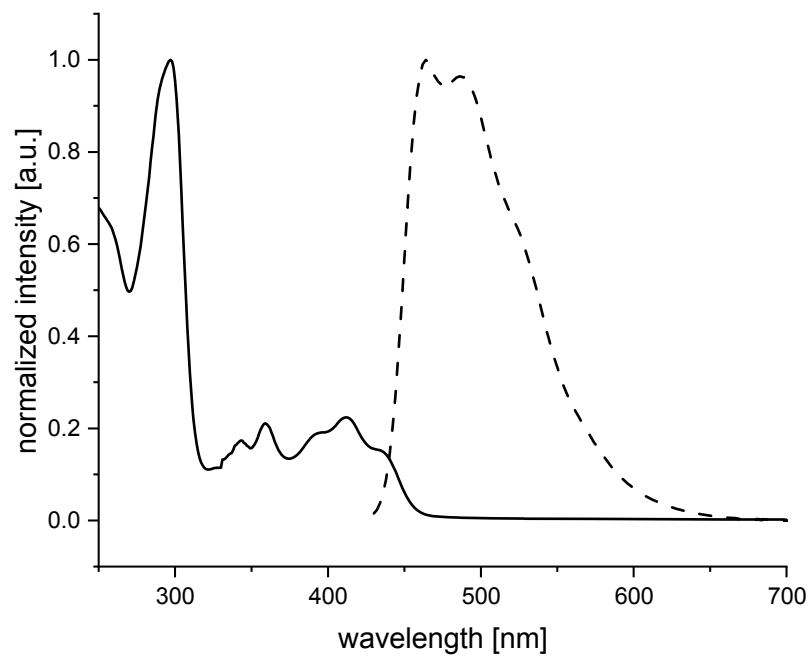


Figure S103. Absorption (solid line) and emission (dashed line) spectra of **2b** in DCM.

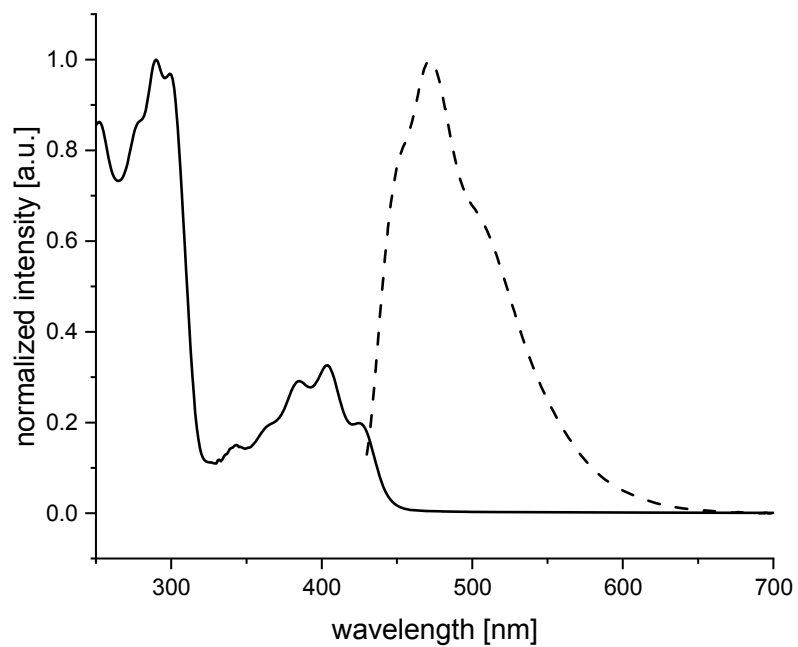


Figure S104. Absorption (solid line) and emission (dashed line) spectra of **2c** in DCM.

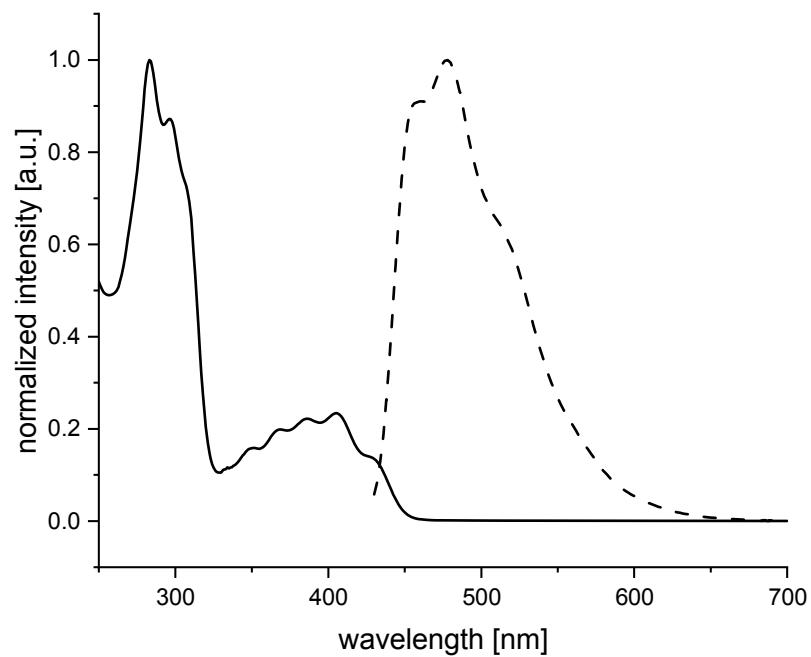


Figure S105. Absorption (solid line) and emission (dashed line) spectra of **2d** in DCM.

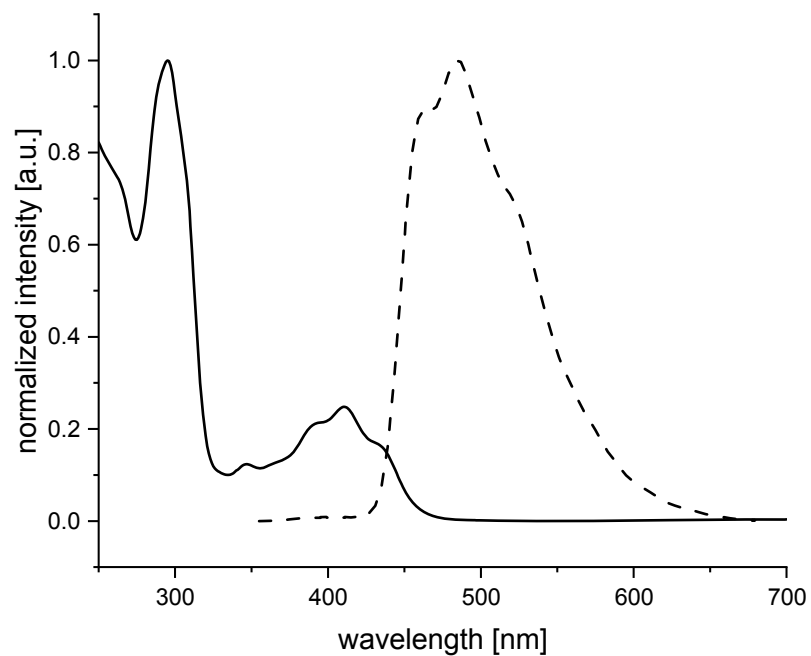


Figure S106. Absorption (solid line) and emission (dashed line) spectra of **2e** in DCM.

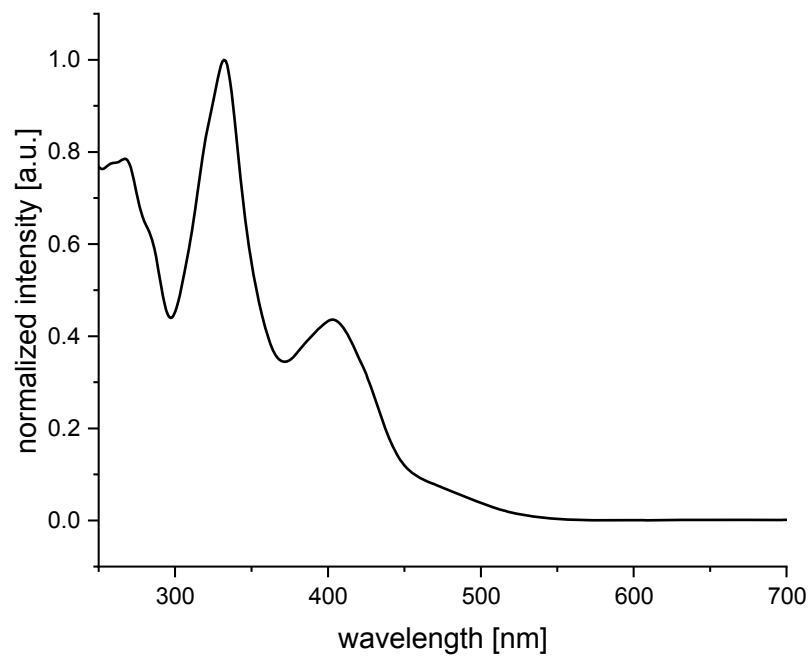


Figure S107. Absorption spectra of 2f in DCM.

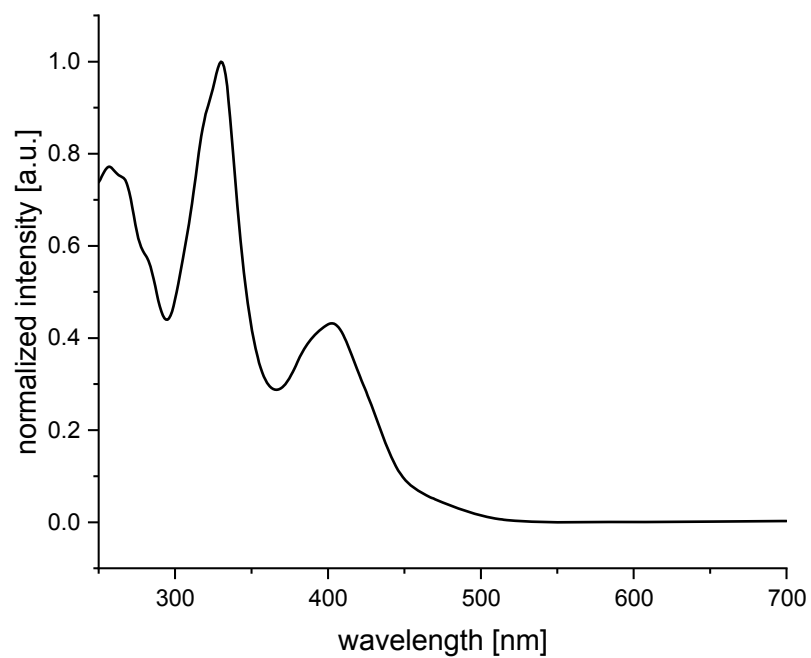


Figure S108. Absorption spectra of 2f in dioxane.

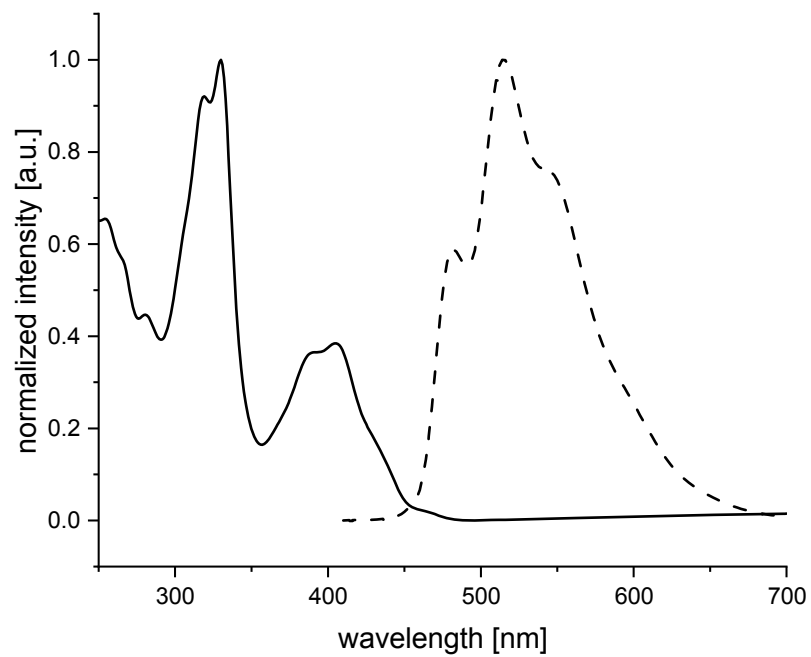


Figure S109. Absorption (solid line) and emission (dashed line) spectra of **2f** in cyclohexane.

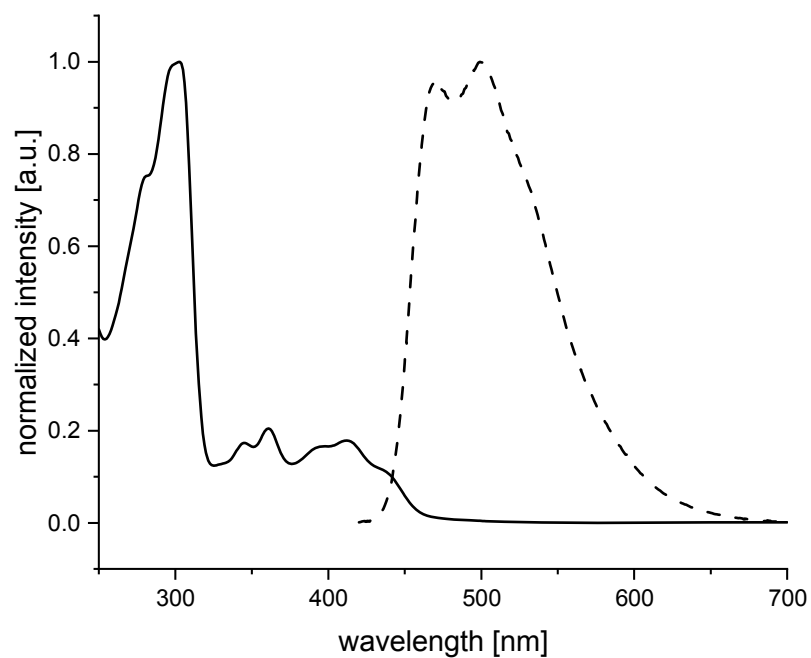


Figure S110. Absorption (solid line) and emission (dashed line) spectra of **2g** in DCM.

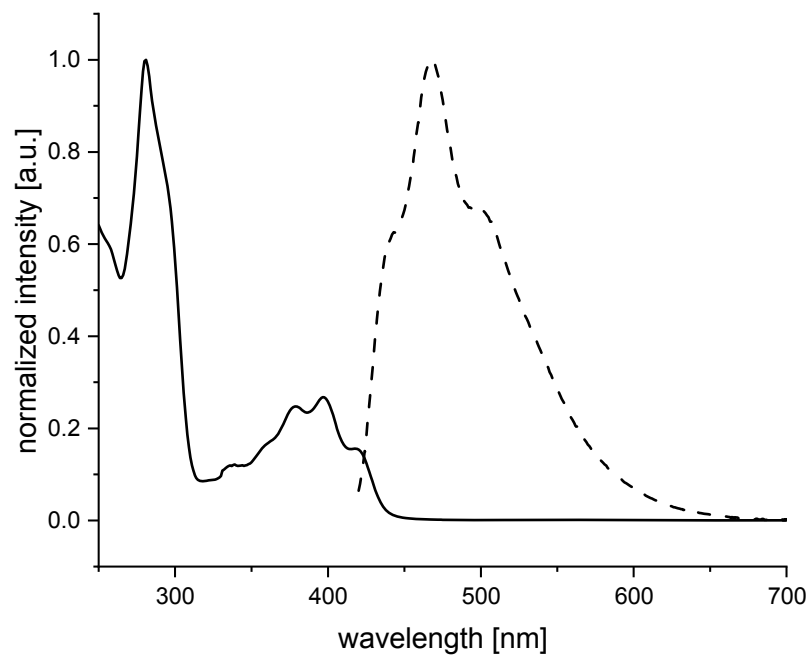


Figure S111. Absorption (solid line) and emission (dashed line) spectra of **2h** in DCM.

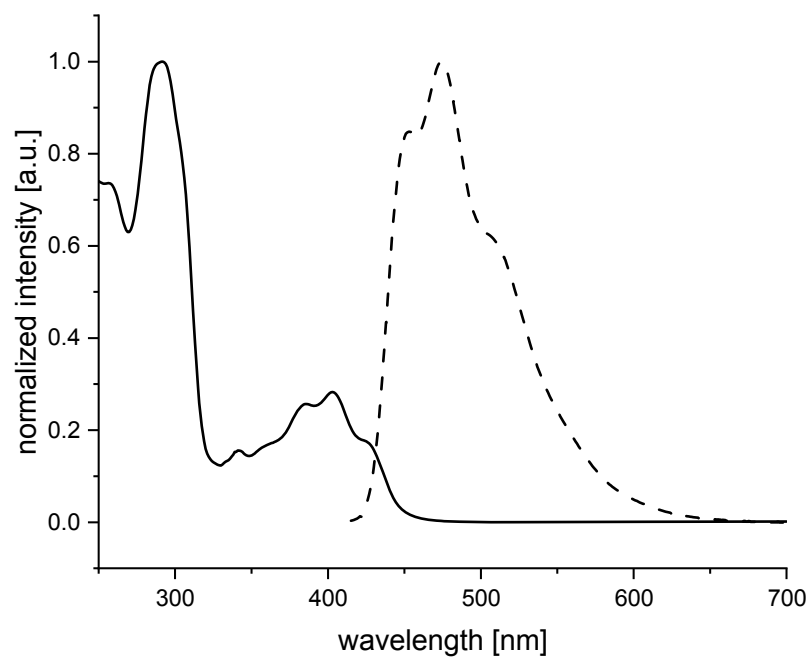


Figure S112. Absorption (solid line) and emission (dashed line) spectra of **2i** in DCM.

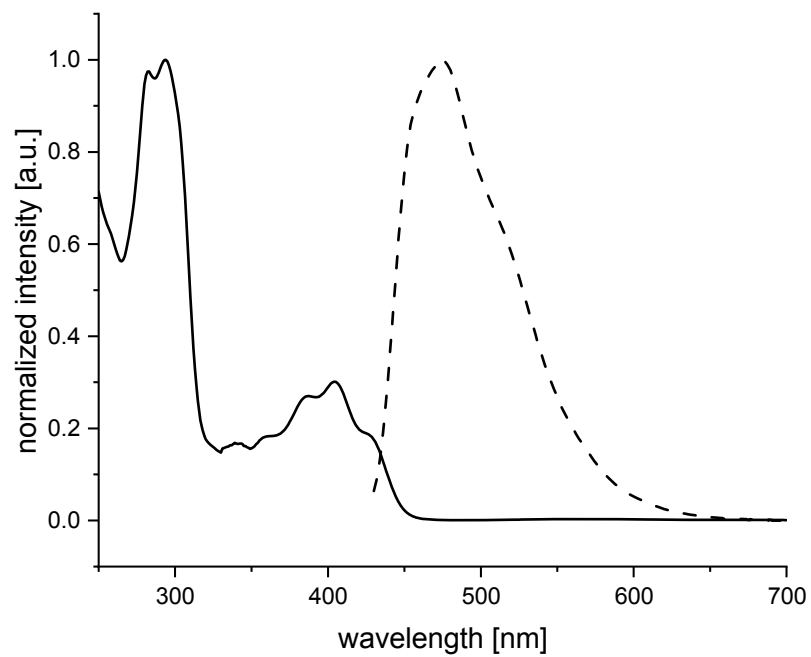


Figure S113. Absorption (solid line) and emission (dashed line) spectra of **2j** in DCM.

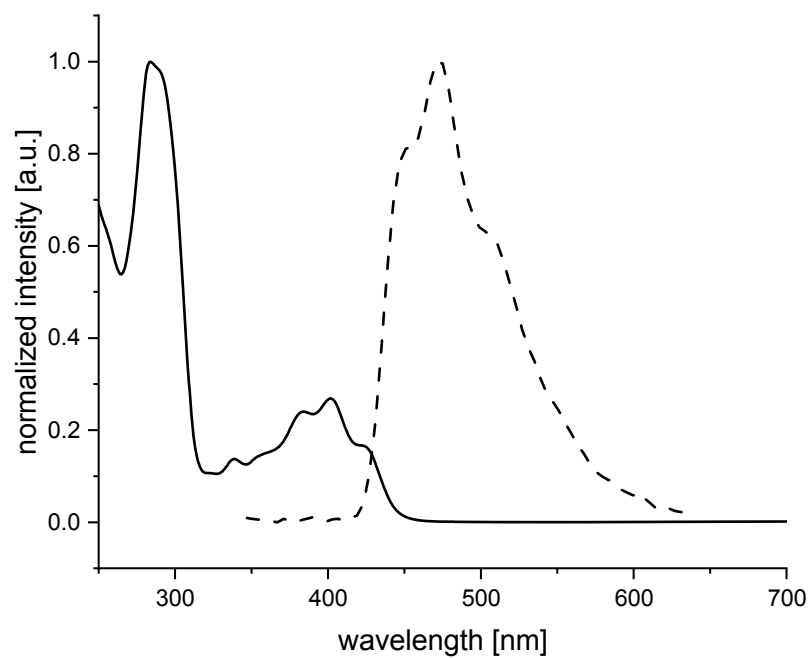


Figure S114. Absorption (solid line) and emission (dashed line) spectra of **2k** in DCM.

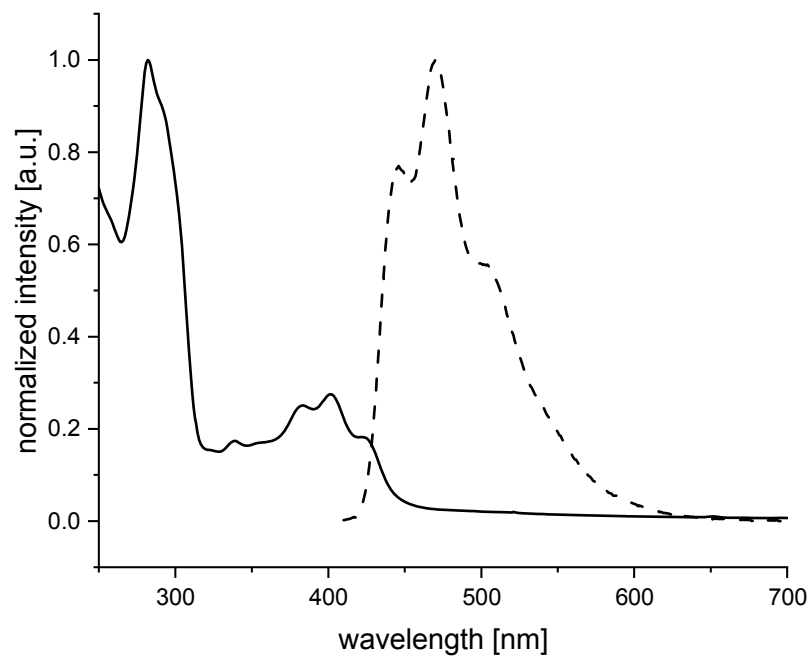


Figure S115. Absorption (solid line) and emission (dashed line) spectra of **2l** in DCM.

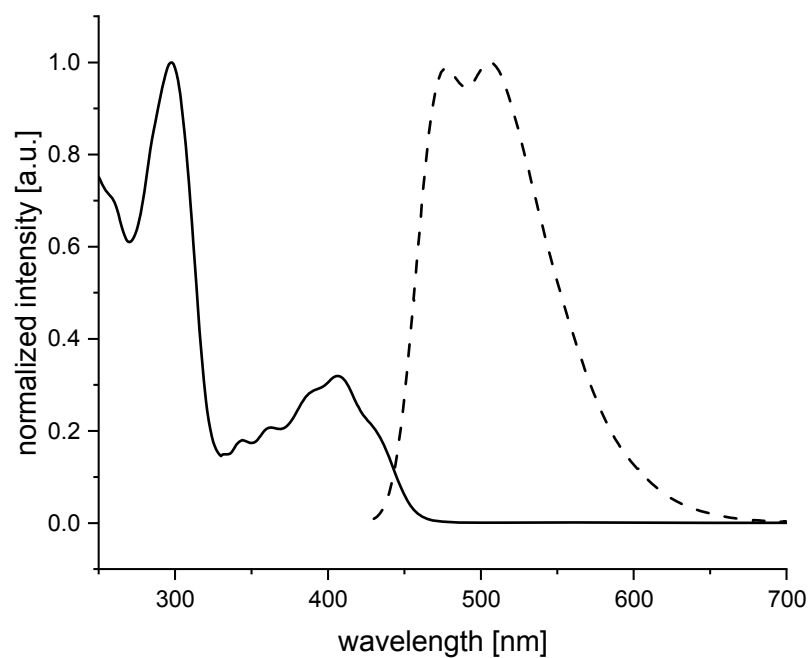


Figure S116. Absorption (solid line) and emission (dashed line) spectra of **2m** in DCM.

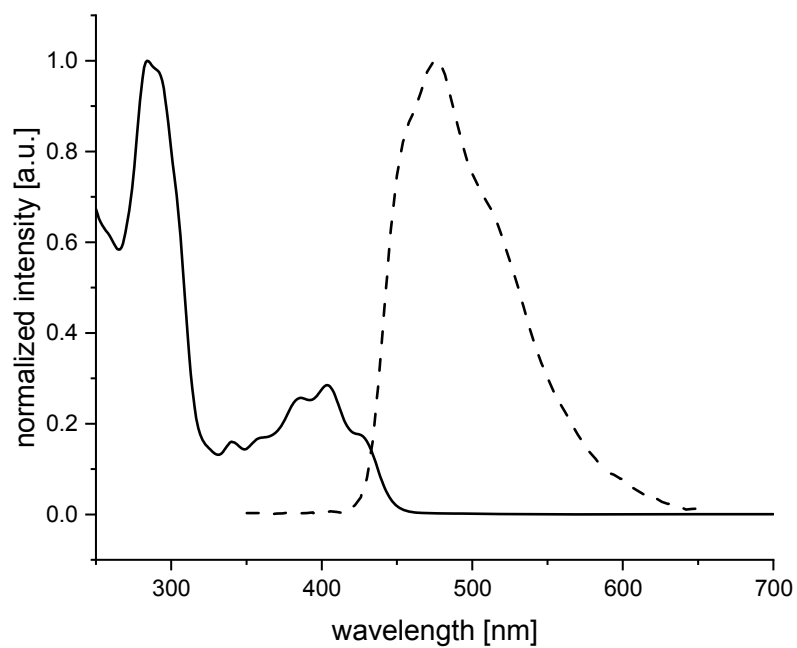


Figure S117. Absorption (solid line) and emission (dashed line) spectra of **2n** in DCM.

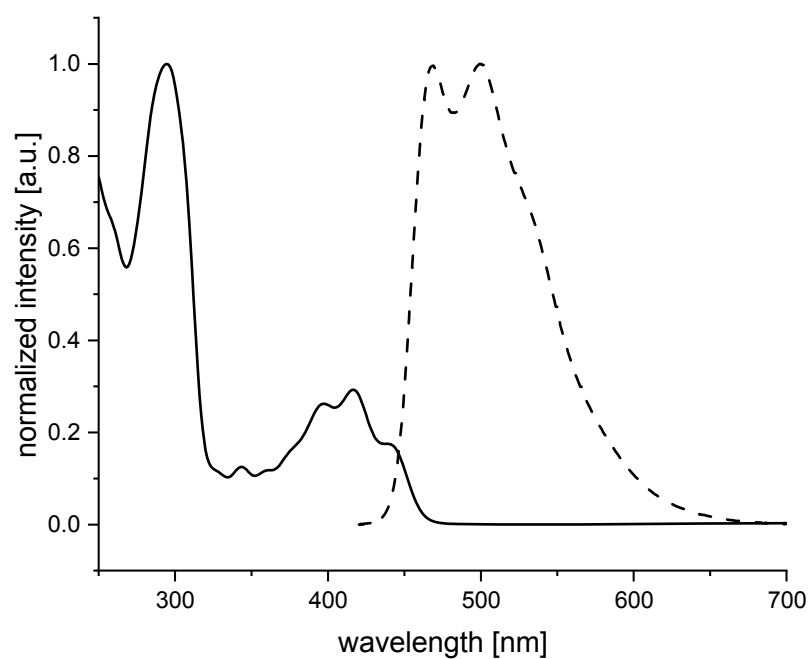


Figure S118. Absorption (solid line) and emission (dashed line) spectra of **2o** in DCM.

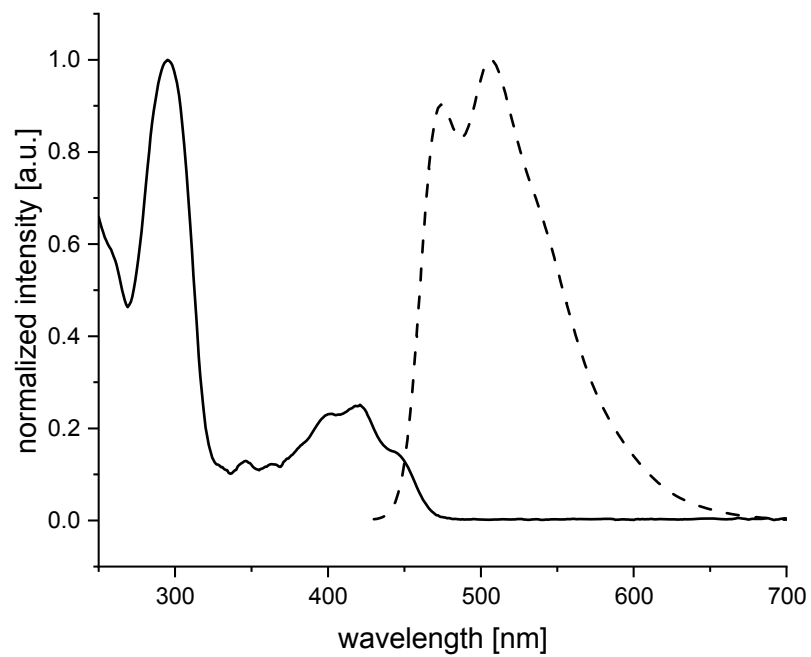


Figure S119. Absorption (solid line) and emission (dashed line) spectra of **2p** in DCM.

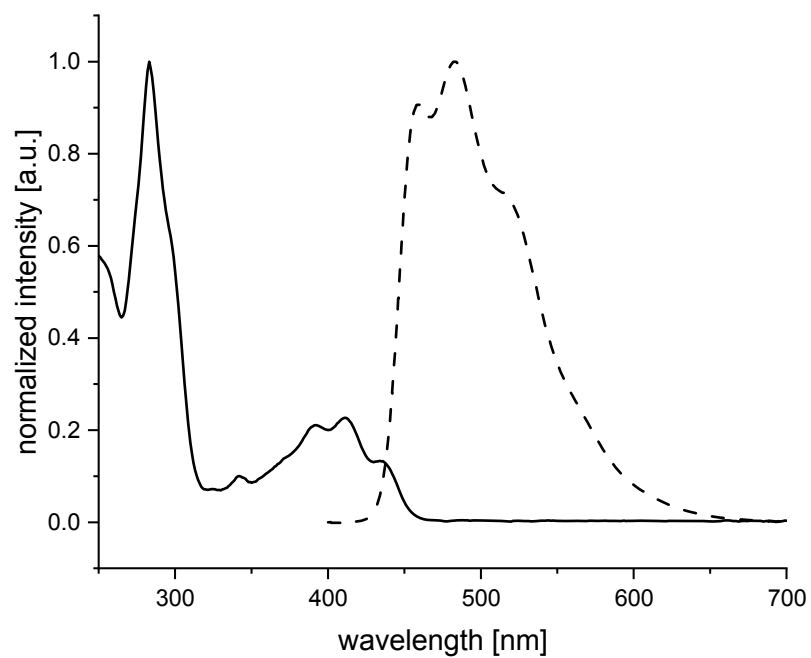


Figure S120. Absorption (solid line) and emission (dashed line) spectra of **2q** in DCM.

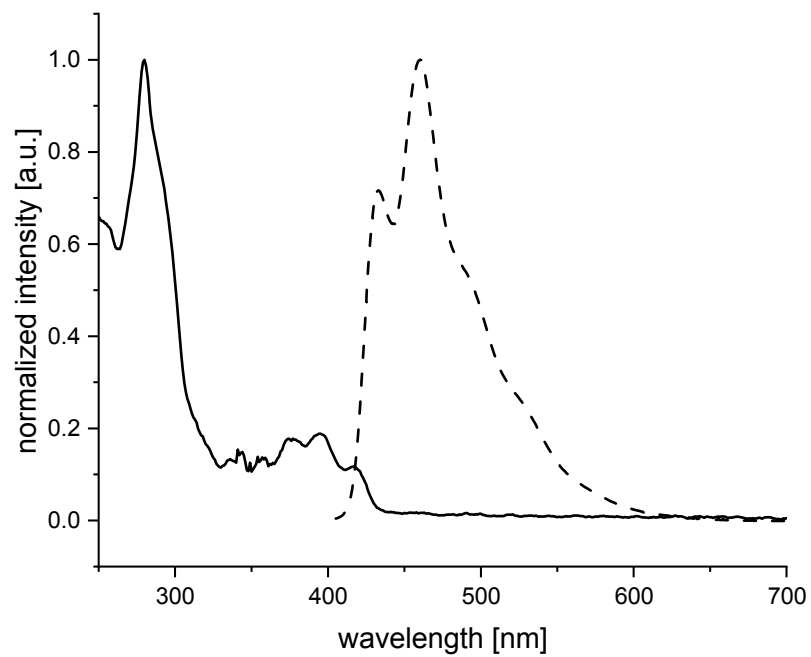


Figure S121. Absorption (solid line) and emission (dashed line) spectra of **2r** in DCM.

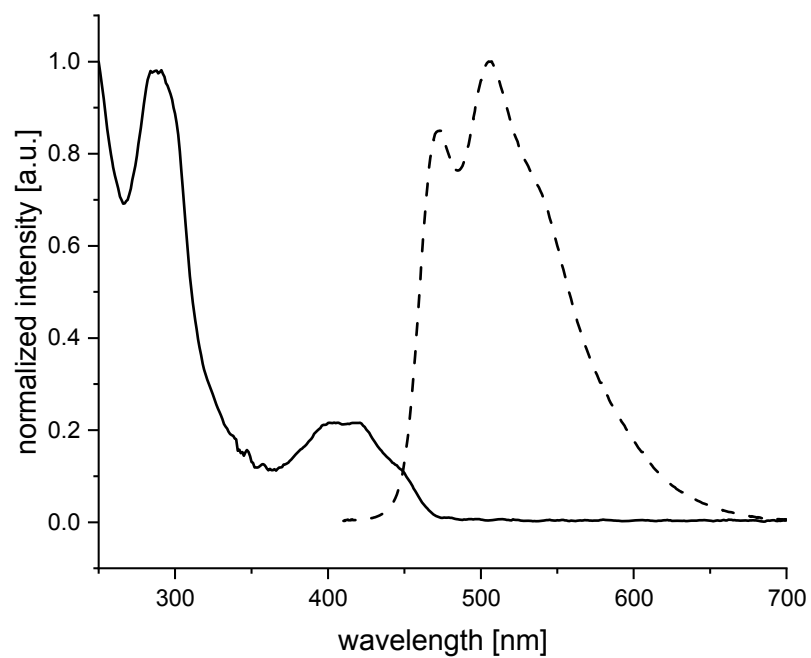


Figure S122. Absorption (solid line) and emission (dashed line) spectra of **4** in DCM.

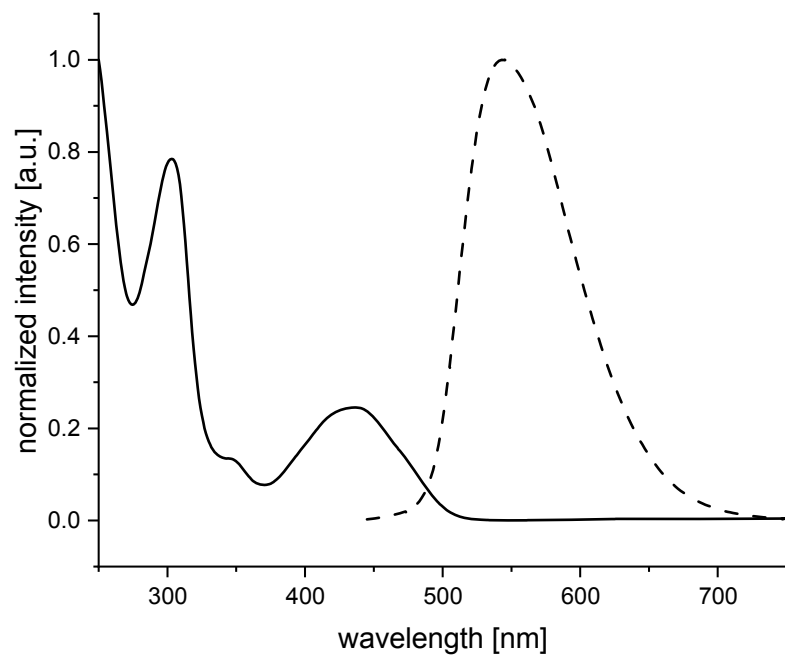


Figure S123. Absorption (solid line) and emission (dashed line) spectra of **6** in DCM.

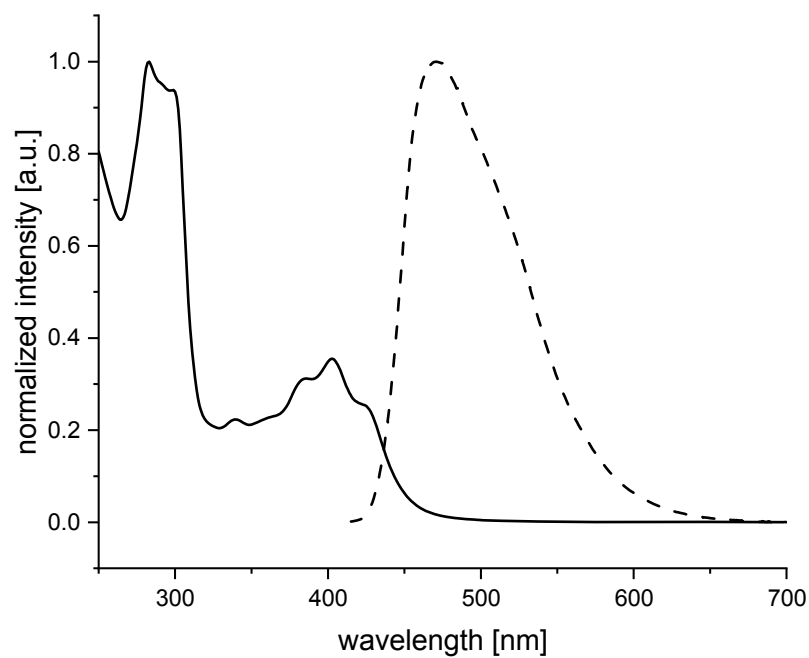


Figure S124. Absorption (solid line) and emission (dashed line) spectra of **8** in DCM.

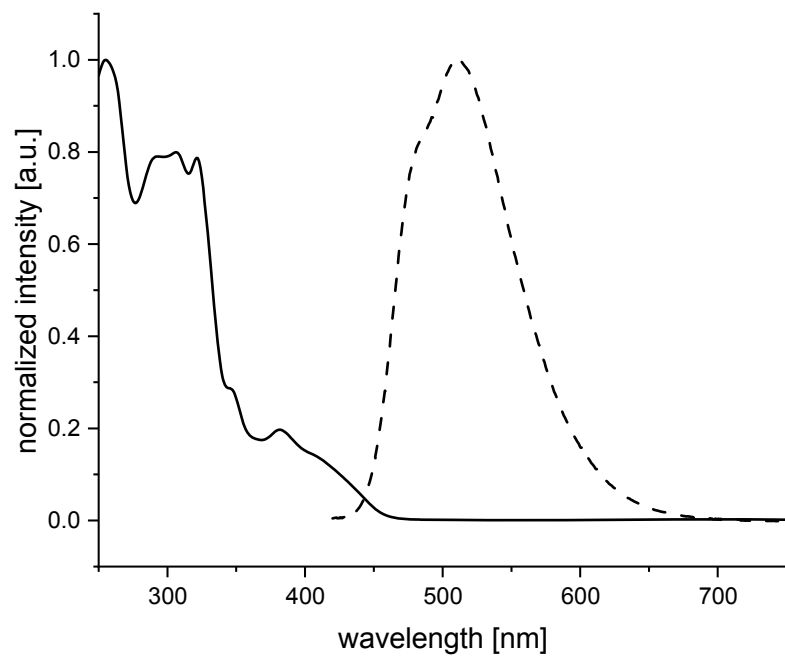


Figure S125. Absorption (solid line) and emission (dashed line) spectra of **12** in DCM.

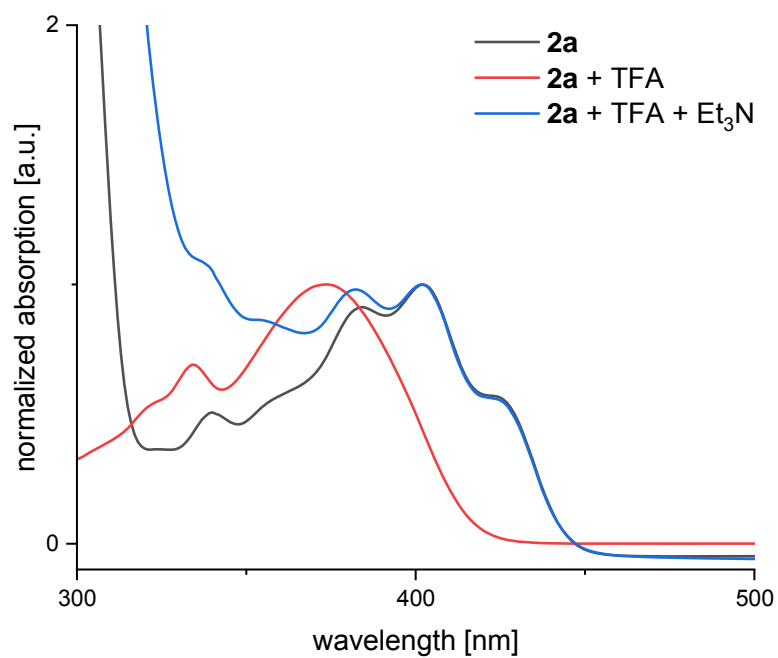


Figure S126. Absorption spectra of **2a**, **2a** with addition of trifluoroacetic acid (TFA), and **2a** with addition of TFA and a surplus of Et_3N in DCM.

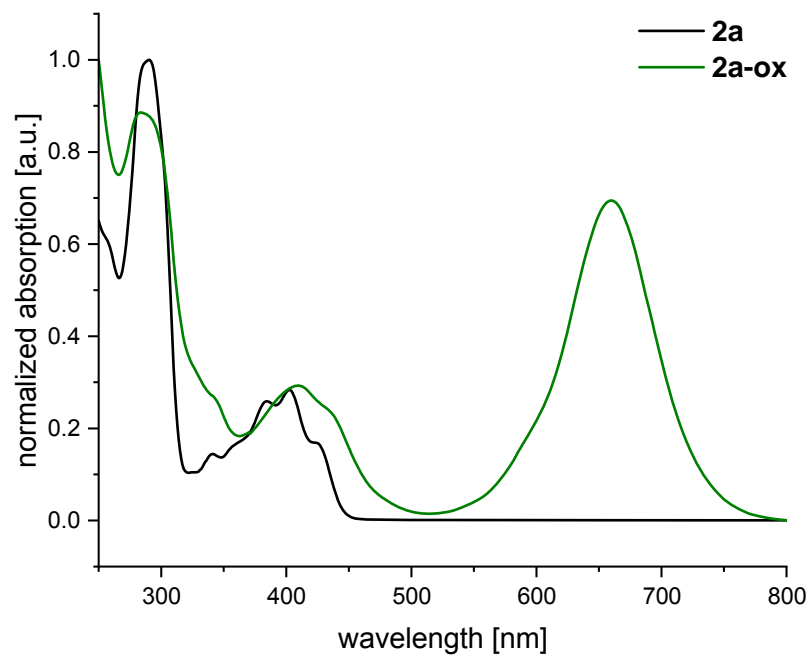
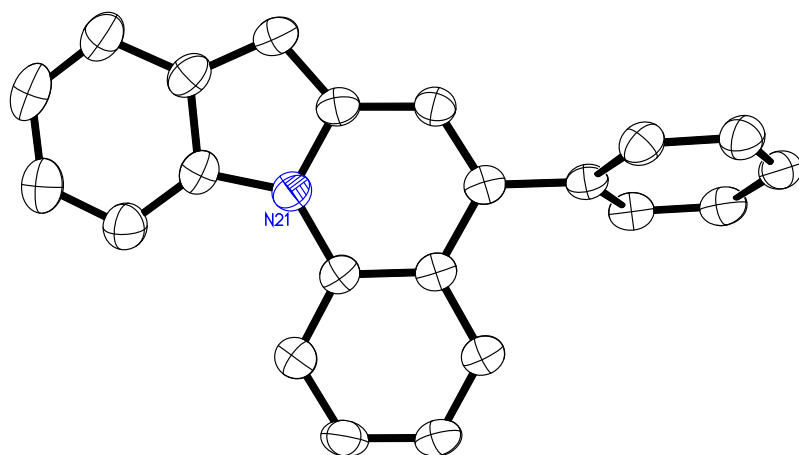


Figure S127. Absorption spectra of 2a and 2a-ox in DCM.

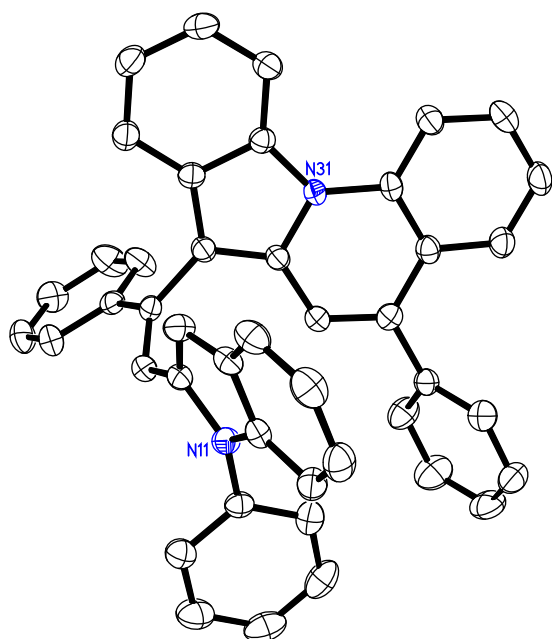
4 Crystallographic Data

Table S2. Crystal structure, crystal data and structure refinement of **2a** (CCDC 2169589).



Empirical formula	C ₂₂ H ₁₅ N
Formula weight	293.35
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	P2 ₁ /c
Z	4
Unit cell dimensions	a = 14.0207(13) Å α = 90 deg. b = 18.8671(17) Å β = 91.567(2) deg. c = 5.7298(5) Å γ = 90 deg.
Volume	1515.1(2) Å ³
Density (calculated)	1.29 g/cm ³
Absorption coefficient	0.07 mm ⁻¹
Crystal shape	brick
Crystal size	0.093 x 0.045 x 0.041 mm ³
Crystal colour	yellow
Theta range for data collection	1.5 to 27.5 deg.
Index ranges	-18 ≤ h ≤ 18, -24 ≤ k ≤ 24, -7 ≤ l ≤ 7
Reflections collected	16192
Independent reflections	3403 (R(int) = 0.0507)
Observed reflections	2015 (I > 2σ(I))
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.96 and 0.90
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	3403 / 0 / 208
Goodness-of-fit on F ²	1.05
Final R indices (I > 2σ(I))	R1 = 0.056, wR2 = 0.131
Largest diff. peak and hole	0.15 and -0.18 eÅ ⁻³

Table S3. Crystal structure, crystal data and structure refinement of **3a** (CCDC 2169590).



Empirical formula	C ₄₄ H ₃₀ N ₂	
Formula weight	586.70	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	P $\bar{1}$	
Z	2	
Unit cell dimensions	a = 9.1982(5) Å	α = 97.6574(12) deg.
	b = 10.6715(6) Å	β = 106.2367(12) deg.
	c = 16.2921(9) Å	γ = 91.1132(13) deg.
Volume	1519.03(15) Å ³	
Density (calculated)	1.28 g/cm ³	
Absorption coefficient	0.07 mm ⁻¹	
Crystal shape	cuboid	
Crystal size	0.150 x 0.130 x 0.086 mm ³	
Crystal colour	yellow	
Theta range for data collection	1.3 to 27.7 deg.	
Index ranges	-11 ≤ h ≤ 11, -13 ≤ k ≤ 13, -21 ≤ l ≤ 21	
Reflections collected	21096	
Independent reflections	6264 (R(int) = 0.0393)	
Observed reflections	4374 (I > 2σ(I))	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.96 and 0.92	
Refinement method	Full-matrix least-squares on F ²	
Data/restraints/parameters	6264 / 0 / 415	
Goodness-of-fit on F ²	1.02	
Final R indices (I > 2σ(I))	R1 = 0.048, wR2 = 0.103	
Largest diff. peak and hole	0.17 and -0.21 eÅ ⁻³	

5 Computational Investigation

5.1 Computational Details

Calculations were carried out at the B3LYP-D3/6-31G**/LACVP(Au)//cc-pVTZ(-f)/LACV3P(Au)^[17] level of theory. All calculations were carried out using DFT^[18] as implemented in the Jaguar 9.1 suite^[19] of ab initio quantum chemistry programs. Orbital visualizations were done with IboView.^[20] Geometry optimizations were performed with B3LYP-D3 functional and the 6-31G**/LACVP(Au) basis set. The energies of the optimized structures were reevaluated by additional single-point calculations on each optimized geometry using Dunning's correlation consistent triple- ζ basis set cc-pVTZ(-f), which includes a double set of polarization functions. For gold, we used a modified version of LACVP, designated as LACV3P, in which the exponents were decontracted to match the effective core potential with triple- ζ quality. Solvation energies were evaluated by a self-consistent reaction field (SCRF) approach based on accurate numerical solutions of the Poisson-Boltzmann equation with the dielectric constant $\epsilon = 9.93$ for *ortho*-dichlorobenzene. As is the case for all continuum models, the solvation energies are subject to empirical parameterization of the atomic radii that are used to generate the solute surface. We employed the standard set of optimized radii in Jaguar. Analytical vibrational frequencies within the harmonic approximation were computed with the 6-31G**/LACVP basis to confirm proper convergence to well-defined minima or saddle points on the potential energy surface. The energy components have been computed with the following protocol.

The free energy in the solution-phase $G(\text{sol})$ has been calculated as follows:

$$G(\text{sol}) = G(\text{gas}) + G_{\text{solv}} \quad (1)$$

Low frequencies were corrected using Truhlar's quasiharmonic protocol, i.e. all frequencies lower than 100 cm^{-1} were raised to 100 cm^{-1} before evaluating their contribution to the entropy.^[21] $G(\text{gas})$ was then derived from the Gibbs-Helmholtz equation with the entropy $S(\text{gas})$ retrieved from harmonic vibration calculations:

$$G(\text{gas}) = H(\text{gas}) - TS(\text{gas}) \quad (2)$$

$H(\text{gas})$ is the electronic energy from a self-consistent field optimization $E(\text{SCF})$ at the higher level single point calculation as detailed above corrected for the zero-point energy ZPE from harmonic vibration calculations:

$$H(\text{gas}) = E(\text{SCF}) + \text{ZPE} \quad (3)$$

Hess's law is applied for calculating reaction energies $\Delta E(\text{SCF})$ and $\Delta G(\text{sol})$ as shown below:

$$\Delta E(\text{SCF}) = \sum E(\text{SCF}) \text{ for products} - \sum E(\text{SCF}) \text{ for reactants} \quad (4)$$

$$\Delta G(\text{sol}) = \sum G(\text{sol}) \text{ for products} - \sum G(\text{sol}) \text{ for reactants} \quad (5)$$

The entropy we refer to is specifically vibrational/rotational/translational entropy of the solute(s), and the entropy of the solvent is implicitly included in the continuum solvation model.

5.2 Overview of the Computed Molecules

The optimized geometries of **1a**, **1a**^[Au], **IMeAu**⁺, **2a**^{[Au]-TS}, **2a**^[Au], **3a**^{[Au]-TS}, **3a**^[Au], **3b**^{[Au]-TS}, **3b**^[Au], **3c**^{[Au]-TS}, **3c**^[Au], **3d**^{[Au]-TS}, **3d**^[Au], **2a**, **2f**, **2h**, **2o**, **2r**, **6**, **8**, **10**, **12**, **3a**, **3b**, **3c**, **3d**, **IPrAu**⁺, **1a**^[IPrAu], **2a**^[IPrAu], and **3b**^[IPrAu] can be found in the xyz file that is supplied in the supporting documents of this publication.

Table S4. Energies of all computed structures.

Entry	Label	E(SCF)/TZ eV	ZPE kcal/mol	H eV	S cal/mol·K	G(gas) eV	G _{solv} kcal/mol	G(sol) eV	G(sol) kcal/mol
1	1a	-24555.135	189.153	-24546.933	130.847	-24549.277	-6.99	-24549.580	-566126.626
2	1a ^[Au]	-36535.919	271.140	-36524.161	175.859	-36527.312	-37.53	-36528.939	-842377.152
3	IMeAu ⁺	-11978.555	81.472	-11975.022	95.471	-11976.733	-54.60	-11979.100	-276244.546
4	2a ^{[Au]-TS}	-36535.067	271.125	-36523.310	171.987	-36526.391	-37.30	-36528.009	-842355.690
5	2a ^[Au]	-36535.526	272.143	-36523.725	170.997	-36526.788	-39.15	-36528.486	-842366.697
6	3a ^{[Au]-TS} ^[a]	-61092.984	463.505	-61072.885	241.970	-61077.220	-36.99	-61078.824	-1408510.797
7	3a ^[Au]	-61093.922	465.313	-61073.744	240.224	-61078.048	-37.97	-61079.694	-1408530.878
8	3b ^{[Au]-TS}	-61093.188	463.763	-61073.077	240.291	-61077.382	-36.20	-61078.952	-1408513.760
9	3b ^[Au]	-61094.146	465.285	-61073.969	240.523	-61078.279	-37.60	-61079.909	-1408535.825
10	3c ^{[Au]-TS} ^[a]	-61092.841	463.511	-61072.741	241.472	-61077.067	-37.71	-61078.703	-1408508.008
11	3c ^[Au]	-61093.935	465.854	-61073.734	238.718	-61078.010	-42.57	-61079.857	-1408534.615
12	3d ^{[Au]-TS}	-61092.783	463.909	-61072.666	239.526	-61076.957	-36.92	-61078.558	-1408504.678
13	3d ^[Au]	-61093.971	465.194	-61073.798	240.001	-61078.098	-39.13	-61079.795	-1408533.195
14	2a	-24556.795	191.312	-24548.499	124.115	-24550.723	-6.55	-24551.007	-566159.526
15	2f	-30123.549	192.989	-30115.180	135.060	-30117.600	-10.39	-30118.050	-694538.577
16	2h	-30978.440	296.703	-30965.574	162.598	-30968.487	-6.00	-30968.747	-714156.100
17	2o	-32986.939	276.864	-32974.933	157.508	-32977.755	-7.21	-32978.068	-760492.123
18	2r	-18267.389	140.448	-18261.299	103.389	-18263.151	-5.59	-18263.393	-421163.754
19	6	-49081.264	370.769	-49065.186	191.480	-49068.616	-10.62	-49069.077	-1131559.526
20	8	-49081.039	369.449	-49065.018	192.130	-49068.460	-10.45	-49068.914	-1131555.756
21	10	-49081.039	370.443	-49064.975	191.8773	-49068.413	-10.59	-49068.872	-1131554.797

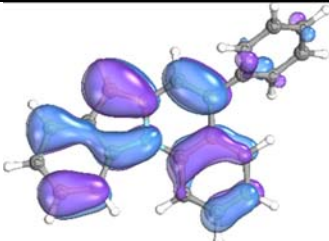
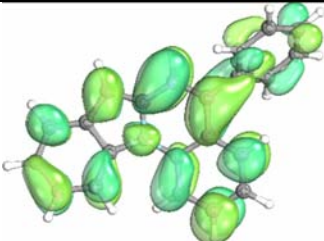
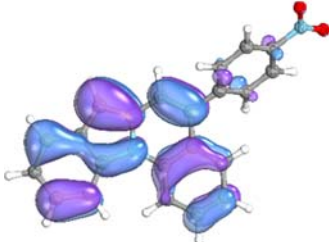
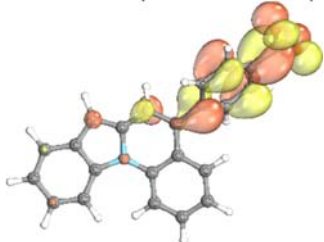
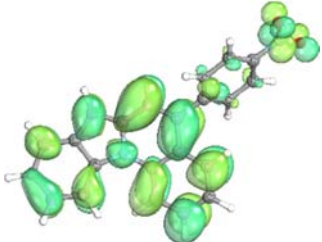
22	12	-26631.674	199.588	-26623.019	126.313	-26625.282	-6.86	-26625.580	-614000.303
23	3a	-49113.666	382.524	-49097.078	197.557	-49100.618	-10.36	-49101.067	-1132297.230
24	3b	-49113.794	382.702	-49097.198	197.281	-49100.733	-10.50	-49101.188	-1132300.029
25	3c	-49113.625	383.321	-49097.003	197.023	-49100.532	-10.57	-49100.991	-1132295.476
26	3d	-49113.778	383.177	-49097.162	196.555	-49100.683	-9.94	-49101.114	-1132298.325
27	IPrAu ⁺	-35260.441	360.3438	-35244.815	188.203	-35248.1868	-46.29	-35250.1942	-812888.5935
28	1a ^[IPrAu]	-59817.879	551.266	-59793.9738	262.3776	-59798.6746	-33.91	-59800.145	-1379023.774
29	2a ^[IPrAu]	-59817.286	551.6878	-59793.3626	257.7641	-59797.9806	-37.19	-59799.5933	-1379011.052
30	3b ^[IPrAu]	-84375.991	744.9128	-84343.6885	325.776	-84349.5251	-35.01	-84351.0433	-1945180.801

^[a] We were not able to remove two additional low imaginary frequencies of circa 10 cm⁻¹ in **3a**^[Au]-**TS** and **3c**^[Au]-**TS** corresponding to rotations of methyl groups. These vibrational modes were treated as low positive vibrations and set to 100 cm⁻¹ within the applied quasiharmonic correction.

5.3 Frontier Orbitals of 2a/f/h/o/r, 6, 8, 10 and 12

We found the HOMO-LUMO gap in **2f** (2.70 eV) to be 0.78 to 0.9 eV lower than in all other comparable compounds **2**. The optical gap was accordingly observed to be 0.29 eV lower (2.36 eV) than the next lowest example **2p**. This can easily be rationalized by the nitro-substituent on the non-annulated phenyl substituent which creates a localized LUMO that is energetically much lower than the typically observed excitation. The orbital that we usually expect to participate in the first excitation is found as LUMO+1 in **2f**.

Table S5. Relevant orbitals of **2a** and **2f**.^[a]

Entry	Compound	HOMO	LUMO	LUMO+1
1	2a	 $\epsilon = -5.19$	 $\epsilon = -1.72$ ($\Delta_{\text{HOMO}} = 3.48$)	
2	2f	 $\epsilon = -5.50$	 $\epsilon = -2.81$ ($\Delta_{\text{HOMO}} = 2.69$)	 $\epsilon = -1.93$ ($\Delta_{\text{HOMO}} = 3.57$)

^[a]Orbital energies (ϵ) and gaps to the HOMO (Δ_{HOMO}) given in eV.

Table S6. Frontier orbitals of selected products and the respective gap.

	ϵ_{HOMO} [eV]	ϵ_{LUMO} [eV]	Gap [eV]
2a	-5.192	-1.712	3.480
2f	-5.505	-2.805	2.699
2h	-5.108	-1.604	3.503
2o	-5.145	-1.764	3.382
2r	-5.244	-1.639	3.605
6	-4.752	-1.788	2.965
8	-5.055	-1.884	3.171
10	-4.745	-1.812	-2.934
12	-5.274	-1.865	3.409

6 References

- [1] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* **2010**, *29*, 2176–2179.
- [2] a) G. Berthon-Gelloz, M. A. Siegler, A. L. Spek, B. Tinant, J. N. H. Reek, I. E. Markó, *Dalton Trans.* **2010**, *39*, 1444–1446; b) A. Gómez-Suárez, R. S. Ramón, O. Songis, A. M. Z. Slawin, C. S. J. Cazin, S. P. Nolan, *Organometallics* **2011**, *30*, 5463–5470.
- [3] A. Cervantes-Reyes, F. Rominger, M. Rudolph, A. S. K. Hashmi, *Chem. Eur. J.* **2019**, *25*, 11745–11757.
- [4] Y.-Q. Fang, M. Lautens, *Org. Lett.* **2005**, *7*, 3549–3552.
- [5] M. Nagamochi, Y.-Q. Fang, M. Lautens, *Org. Lett.* **2007**, *9*, 2955–2958.
- [6] P. Kochapradist, T. Sunonnam, N. Prachumrak, S. Namuangruk, T. Keawin, S. Jungsuttiwong, T. Sudyoadsuk, V. Promarak, *Tetrahedron Lett.* **2014**, *55*, 6689–6693.
- [7] T. Kurisaki, T. Naniwa, H. Yamamoto, H. Imagawa, M. Nishizawa, *Tetrahedron Lett.* **2007**, *48*, 1871–1874.
- [8] M. X.-W. Jiang, M. Rawat, W. D. Wulff, *J. Am. Chem. Soc.* **2004**, *126*, 5970–5971.
- [9] B. S. Chinta, B. Baire, *RSC Adv.* **2016**, *6*, 54449–54455.
- [10] V. Fiandanese, D. Bottalico, G. Marchese, A. Punzi, *Tetrahedron* **2008**, *64*, 7301–7306.
- [11] H. Chen, M. Lei, L. Hu, *Tetrahedron* **2014**, *70*, 5626–5631.
- [12] B. V. Subba Reddy, R. Anji Babu, B. Jagan Mohan Reddy, B. Sridhar, T. Ramalinga Murthy, P. Pranathi, S. V. Kalivendi, T. Prabhakar Rao, *RSC Adv.* **2015**, *5*, 27476–27480.
- [13] Y. Liang, T. Meng, H.-J. Zhang, Z. Xi, *Synlett* **2011**, *2011*, 911–914.
- [14] C. M. Hendrich, V. D. Hannibal, L. Eberle, L. E. Hertwig, U. Zschieschang, F. Rominger, M. Rudolph, H. Klauk, A. S. K. Hashmi, *Adv. Synth. Catal.* **2021**, *363*, 1401–1407.
- [15] D. G. Hulcoop, M. Lautens, *Org. Lett.* **2007**, *9*, 1761–1764.
- [16] A. Rana, S. Lee, D. Kim, P. K. Panda, *Chem. Eur. J.* **2015**, *21*, 12129–12135.
- [17] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652; b) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104; c) P. C. Hariharan, J. A. Pople, *Theoret. Chim. Acta* **1973**, *28*, 213–222; d) P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 299–310; e) Lee, Yang, Parr, *Phys. Rev. B* **1988**, *37*, 785–789; f) B. Marten, K. Kim, C. Cortis, R. A. Friesner, R. B. Murphy, M. N. Ringnalda, D. Sitkoff, B. Honig, *J. Phys. Chem.* **1996**, *100*, 11775–11788.
- [18] R. G. Parr, W. Yang, *Density-Functional Theory of Atoms and Molecules*, Oxford University Press, New York, NY, **1994**.
- [19] A. D. Bochevarov, E. Harder, T. F. Hughes, J. R. Greenwood, D. A. Braden, D. M. Philipp, D. Rinaldo, M. D. Halls, J. Zhang, R. A. Friesner, *Int. J. Quantum Chem.* **2013**, *113*, 2110–2142.
- [20] G. Knizia, *J. Chem. Theory Comput.* **2013**, *9*, 4834–4843.
- [21] R. F. Ribeiro, A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B* **2011**, *115*, 14556–14562.