A Rapid Pathway to Molecular Complexity: Palladium-Catalyzed Six-Fold Domino Process to Access Polycyclic Frameworks

Komal Goel,[a] and Gedu Satyanarayana*[a]

[a]Department of Chemistry, Indian Institute of Technology (IIT) Hyderabad

Kandi – 502 284, Sangareddy District, Telangana, INDIA

Phone: (040) 2301 6251; Fax: (040) 2301 6003/32

E-mail: gvsatya@chy.iith.ac.in

Supporting Information

Experimental Section

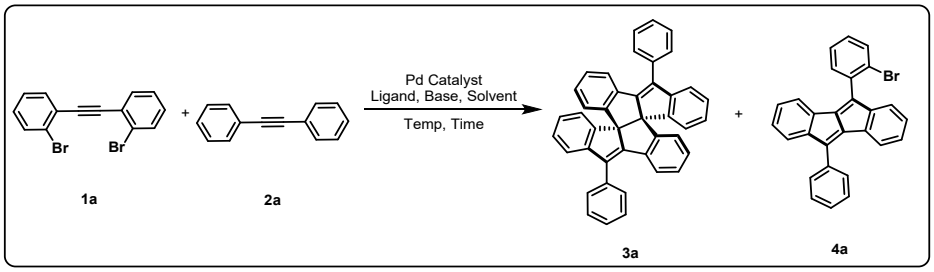
General Methods:

IR spectra were recorded on a Bruker Tensor 37 (FTIR) spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker Avance 400 (400 MHz) as well as 600 (600MHz) spectrometers at 295 K in $CDCl_3$; chemical shifts (δ ppm) and coupling constants (Hz) are reported in standard fashion concerning either internal standard tetramethylsilane (TMS) (δH = 0.00 ppm) or $CDCl_3$ (δH = 7.26 ppm). $^{13}C\{^{1}H\}$ NMR spectra were recorded on a Bruker Avance 400 (101 MHz) and 600 (151 MHz) spectrometers at RT in $CDCl_3$; chemical shifts (δ ppm) are reported relative to $CDCl_3$ [δC = 77.00 ppm (central line of the triplet)]. In the $^{13}C\{^{1}H\}$ NMR, the nature of carbons (C, CH, CH_2, and CH_3) was determined by recording the DEPT-135 spectra and is given in parentheses and noted as s = singlet (for C), d = doublet (for CH), t = triplet (for CH_2) and q = quartet (for CH_3). In the ^{1}H NMR, the following abbreviations were used throughout: s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet, sept = septet, dd = doublet of the doublet, m = multiplet, and br. s = broad singlet. The assignment of signals was confirmed by ^{1}H, $^{13}C\{^{1}H\}$ CPD, and DEPT spectra. High-resolution mass spectra (HR-MS) were recorded on an Agilent 6538 UHD Q-TOF electron spray ionization (ESI) mode and atmospheric pressure chemical ionization (APCI) modes. All small-scale reactions were carried out by using a Schlenk tube. Reactions were monitored by TLC on silica gel using a combination of hexane and ethyl acetate as eluents. Solvents were distilled before use; for petroleum ether, the boiling range of 60−80 °C was used. $Pd(OAc)_2$, Cs_2CO_3, and DPEPhos were purchased from Sigma-Aldrich and used as received. Toluene was dried over sodium metal, Acme's silica gel (230−400 mesh) was used for column chromatography (approximately 20 g per 1 g of crude material).

Initially, 1,2-bis(2-bromophenyl)ethyne **1a** and 1,2-diphenylethyne **2a** were initially selected as model substrates and exposed to palladium catalysis in order to determine the optimal conditions as depicted in Table S1. As expected, the intermediate product **4a** was obtained, but only in 30% of yield when screening was conducted using **1a** (1 equiv) and **2a** (1 equiv) in the presence of $Pd(OAc)_2$ (5 mol%), PPh_3 (10 mol%), and Cs_2CO_3 (3 equiv) at 120 °C for 24 hours in dry toluene (Table S1, entry 1). Remarkably, yield of **4a** was increased to 45% when DPE-Phos was employed as the ligand (Table S1, entry 2). Further to our delight, the yield (**4a**) was increased to 51% when the temperature was elevated to 140 °C and the amount of **2a** was increased to 2 equivalents (Table S1, entry 3). Nevertheless, there was still no sign of forming the polycyclic molecule even after using two equivalents of acetylene **2a**. It is noteworthy to mention that when the equivalents of **2a** were further increased to 3 and 5, respectively, then along with tetracyclic product **4a** (71% yield), the anticipated fused polycyclic product **3a** was also obtained albeit in trace amounts (Table S1, entries 4 & 5). The above-mentioned research revealed that the procedure to generate tetracyclic molecule **4a** was rather simple; however, obtaining an octacyclic framework 3a was difficult due to steric constraints, and it requires strong conditions which is 5 equivalents of other acetylene **2a** and high temperature to force the reaction. This intriguing outcome motivated us to investigate more conditions for obtaining high yields of fused polycyclic product **3a**. After an increased catalyst loading to 10 mol%, a slight increase in the yield of 10% of the anticipated product **3a** was noticed along with the significant yield (74%) of **4a** (Table S1, entry 6). While other ligands, including John-Phos, ^{t}Bu-Xphos, and BINAP, were found to be ineffective in producing product **3a**; instead, they slowed down the reaction and even decreased the yield of the intermediate product **4a** (Table S1, entries 7 to 9). It was clear from the aforementioned explorations that DPE-Phos ligand is best suited for this reaction. Consequently, the reaction with DPE-Phos ligand at 140 °C for 48 h, to our astonishment, generated the desired octacyclic product **3a** in 30% yield along with 50% of **4a** (Table S1, entry 10). Gratifyingly, increased catalyst loading of 10 mol% provided an exclusive polycyclic product **3a** with a 65% yield (Table S1, entry 11). On the other hand, increasing the ligand loading to 20 mol% resulted in a drop in yield (Table S1, entry 12). Moreover, screening the reactions using other palladium catalysts proved unsuccessful (Table S1, entries 13 to 15). In addition, explorations using other bases, including K_2CO_3, DBU, Na_2CO_3, CsF, and K_3PO_4, were proved inferior (Table S1, entries 16 to 20). Moreover, other solvents couldn't be more effective than toluene (Table S1, entries 21 to 24). Additionally, it was supposed that the reaction might work well with some additives, so the reaction was also optimized with different additives such as TEBAC, TBAI, CuI, and PivOH, but the results

were unsatisfactory (Table S1, entries 25 to 28). Moreover, reactions have also been performed under microwave assisting conditions, but the outcomes were not impressive (Table S1, entries 29 to 31).

Table S1: Screening conditions for the synthesis of fused polycyclic scaffold **3a**.[a,b,c,d]

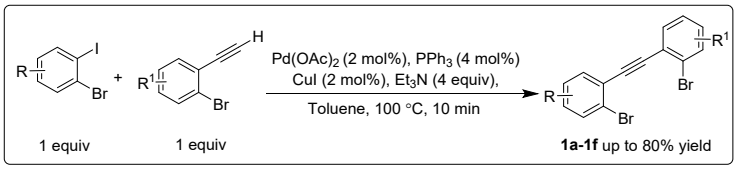


S. No.	**2a** (equiv)	Catalyst (10 mol%)	Ligand (10 mol%)	Base (3 equiv)	Solvent (1 mL)	Additive (1 equiv)	Temp (°C)	Time (h)	Yield **3a**[a] (%)	Yield **4a**[b] (%)
1[c]	1	$Pd(OAc)_2$	PPh_3	Cs_2CO_3	Toluene	-	120	24	-	30
2[c]	1	$Pd(OAc)_2$	DPE-Phos	Cs_2CO_3	Toluene	-	120	12	-	45
3[c]	2	$Pd(OAc)_2$	DPE-Phos	Cs_2CO_3	Toluene	-	140	9	-	51
4[c]	3	$Pd(OAc)_2$	DPE-Phos	Cs_2CO_3	Toluene	-	140	8	trace	60
5[c]	**5**	**$Pd(OAc)_2$**	**DPE-Phos**	**Cs_2CO_3**	**Toluene**	**-**	**140**	**8**	**trace**	**74**
6	5	$Pd(OAc)_2$	DPE-Phos	Cs_2CO_3	Toluene	-	140	2	10	76
7[c]	5	$Pd(OAc)_2$	John-Phos	Cs_2CO_3	Toluene	-	140	12	-	50
8[c]	5	$Pd(OAc)_2$	^{t}Bu-Xphos	Cs_2CO_3	Toluene	-	140	17	-	55
9[c]	5	$Pd(OAc)_2$	BINAP	Cs_2CO_3	Toluene	-	140	48	trace	58
10[c]	5	$Pd(OAc)_2$	DPE-Phos	Cs_2CO_3	Toluene	--	140	48	30	50
11	**5**	**$Pd(OAc)_2$**	**DPE-Phos**	**Cs_2CO_3**	**Toluene**	**-**	**140**	**48**	**65**	**-**
12[d]	5	$Pd(OAc)_2$	DPE-Phos	Cs_2CO_3	Toluene	-	140	48	63	-
13	5	$Pd(PPh_3)_4$	DPE-Phos	Cs_2CO_3	Toluene	-	140	24	-	30
14	5	$PdCl_2(PPh_3)_2$	DPE-Phos	Cs_2CO_3	Toluene	-	140	24	-	28
15	5	$Pd(COOCF_3)_2$	DPE-Phos	Cs_2CO_3	Toluene	-	140	24	-	50
16	5	$Pd(OAc)_2$	DPE-Phos	K_2CO_3	Toluene	-	140	24	22	60
17	5	$Pd(OAc)_2$	DPE-Phos	DBU	Toluene	-	140	24	trace	40
18	5	$Pd(OAc)_2$	DPE-Phos	Na_2CO_3	Toluene	-	140	24	-	55
19	5	$Pd(OAc)_2$	DPE-Phos	CsF	Toluene	-	140	24	trace	40
20	5	$Pd(OAc)_2$	DPE-Phos	K_3PO_4	Toluene	-	140	24	trace	30
21	5	$Pd(OAc)_2$	DPE-Phos	Cs_2CO_3	DCE	-	110	24	-	-
22	5	$Pd(OAc)_2$	DPE-Phos	Cs_2CO_3	DMF	-	140	48	10	65
23	5	$Pd(OAc)_2$	DPE-Phos	Cs_2CO_3	Xylene	-	140	48	10	60
24	5	$Pd(OAc)_2$	DPE-Phos	Cs_2CO_3	Dioxane	-	140	48	trace	54

25	5	$Pd(OAc)_2$	DPE-Phos	Cs_2CO_3	Toluene	TEBAC	140	48	55	10
26	5	$Pd(OAc)_2$	DPE-Phos	Cs_2CO_3	Toluene	TBAI	140	48	30	40
27	5	$Pd(OAc)_2$	DPE-Phos	Cs_2CO_3	Toluene	CuI	140	48	20	50
28	5	$Pd(OAc)_2$	DPE-Phos	Cs_2CO_3	Toluene	PivOH	140	48	32	30
29	5	$Pd(OAc)_2$	DPE-Phos	Cs_2CO_3	DMF	-	140 (MW)	45 min	-	68
30	5	$Pd(OAc)_2$	DPE-Phos	Cs_2CO_3	Toluene	-	130 (MW)	15 min	-	72
31	5	$Pd(OAc)_2$	DPE-Phos	Cs_2CO_3	Dioxane	-	140	30 min	-	70

Reaction conditions: 1a (0.1 mmol), **2a** (0.5 mmol), Pd catalyst (10 mol%), Ligand (10 mol%), Base (0.3 mmol), solvent (1 mL), 140 °C. [a]Isolated yields of **3a**. [b]Isolated yields of **4a**. [c]$Pd(OAc)_2$ (5 mol%). [d]DPE-Phos (20 mol%).

Scheme-S1: Synthesis of 1,2-bis(2-bromoaryl)ethynes **1a-1f**.



The following 1,2-bis(2-bromoaryl)ethynes **1a-1f**, expect **1e** (Table-S2) are known in the literature.[1–5]

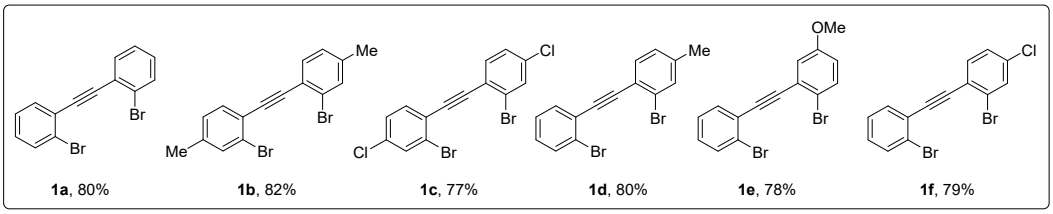


Table-S2: 1,2-bis(2-bromoaryl)ethynes **1a-1f**.

The following 1,2-diarylethynes **2a-2g** (Table-S3) are known in the literature and were prepared according to the previous literature reports.[6] The 1,2-diarylethynes **2i** and **2j** are commercially available and were used as purchased.

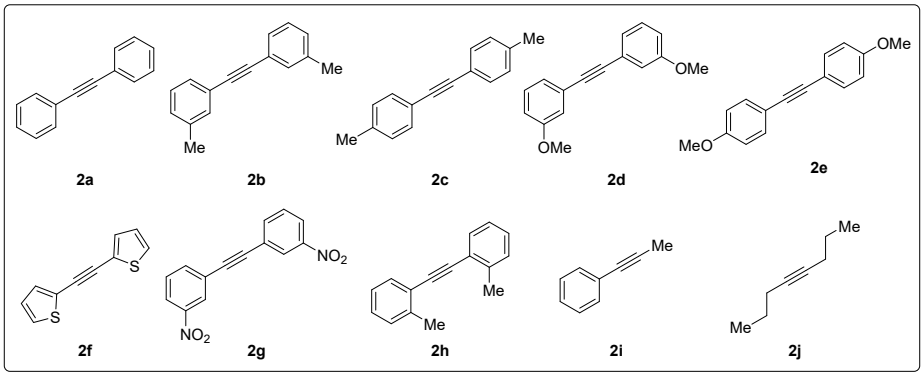
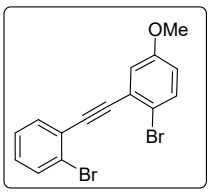


Table-S3: synthesis of 1,2-diarylethynes **2a-2j**.

Experimental:



Synthesis of 1-bromo-2-((2-bromophenyl)ethynyl)-4-methoxybenzene (1e):

To an oven-dried 10 mL Schlenk tube sealed with Teflon septum equipped with a magnetic stirring bar, were added 1-bromo-2-iodo-4-methoxybenzene (62.4 mg, 0.2 mmol), 1-bromo-2-ethynylbenzene (35.9 mg, 0.2 mmol), $Pd(OAc)_2$ (0.9 mg, 0.004 mmol), PPh_3 (2.1 mg, 0.008 mmol), CuI (0.4 mg, 0.004 mmol), Et_3N (80.8 mg, 0.8 mmol), and toluene (1 mL) at room temperature under inert atmosphere. The reaction mixture was subjected to an oil bath at 100 °C for 10 min. Progress of the reaction was monitored by TLC till the reaction was completed. The mixture was cooled to room temperature, quenched with aqueous $NaHCO_3$ solution, and extracted with ethyl acetate (3 × 10 mL). The organic layers were washed with saturated NaCl solution, dried (Na_2SO_4), and filtered. Evaporation of the solvent(s) under reduced pressure and purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:00 to 98:2) furnished the final product **1e** (57.1 mg, 78%) as off-white solid; mp = 38–40 °C.

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2938, 1577, 1467, 1398, 1221, 1016, 806, 749 cm^{-1}.

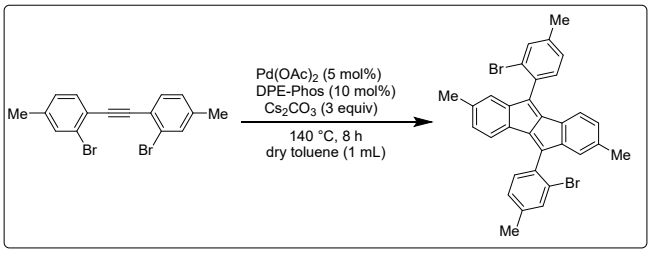
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 – 7.59 (m, 2H), 7.48 (d, J = 8.8 Hz, 1H), 7.31 (dd, J = 7.6, 7.6 Hz, 1H), 7.20 (dd, J = 11.5, 4.0 Hz, 1H), 7.13 (d, J = 3.0 Hz, 1H), 6.78 (dd, J = 8.9, 3.0 Hz, 1H), 3.81 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 133.7, 133.1, 132.5, 129.8, 127.0, 125.6, 125.5, 125.0, 118.1, 116.8, 116.2, 92.2, 91.9, 55.6 ppm.

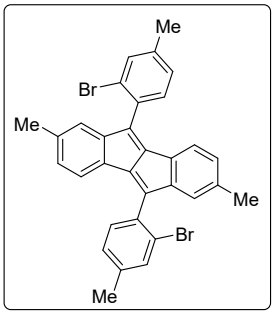
HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{15}H_{11}Br_2{}^{79}O]^+$ 364.9171; found 364.9168; calcd for $[C_{15}H_{11}Br_2{}^{81}O]^+$ 366.9151; found 366.9149.

To get the desired product **3**, it was observed that more equivalents (i.e., 5 equivalents) of external acetylene **2** are necessary to avoid forming a self-coupled product from bromo-substituted alkyne **1**. Therefore, to ascertain the formation of the self-coupled product, a separate reaction was performed with only bromo-substituted alkyne **1b** under standard conditions; as anticipated, the self-coupled product (presumably looks like atropisomers due to

the sterically bulky *ortho*-bromo substituent of the tetracyclic product) **6** was observed in 65% yield. This agrees with the earlier report by Tilley et al., as shown in Scheme S2.[7]



Scheme-S2: Synthesis of 5,10-bis(2-bromo-4-methylphenyl)-2,7-dimethylindeno[2,1-*a*]indene **6**.



Synthesis of 5,10-bis(2-bromo-4-methylphenyl)-2,7-dimethylindeno[2,1-a]indene (6):

To an oven-dried 10 mL Schlenk tube sealed with Teflon septum equipped with a magnetic stir bar, were added 1,2-bis(2-bromoaryl)ethyne **1b** (36.4 mg, 0.1 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), DPE-Phos (5.4 mg, 0.01 mmol), Cs_2CO_3 (97.5 mg, 0.3 mmol), and dry toluene (1 mL) at room temperature under inert atmosphere. The resultant reaction mixture was degassed two to three times under a high vacuum with nitrogen and was subjected to an oil bath at 140 °C for 8 h. Progress of the reaction was monitored by TLC till the reaction was completed. The mixture was cooled to room temperature, quenched with aqueous $NaHCO_3$ solution, and extracted with ethyl acetate (3 × 10 mL). The organic layers were washed with saturated NaCl solution, dried (Na_2SO_4), and filtered. Evaporation of the solvent(s) under reduced pressure and purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate) furnished the product (probably atropisomers) **6** (36.9 mg, 65%) as a yellow viscous oil.

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2292, 2251, 1439, 1379, 1039, 918, 885, 747 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (d, J = 3.5 Hz, 1H), 7.38 – 7.32 (m, 1H), 7.22 (ddd, J = 7.7, 3.8, 0.9 Hz, 1H), 6.69 – 6.54 (m, 2H), 6.49 (d, J = 5.0 Hz, 1H), 2.42 (s, 3H), 2.14 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.5 (2C), 147.2, 145.1, 145.0, 140.1, 138.3, 138.2, 137.9 (2C), 133.9, 133.8, 132.2, 132.2, 131.5, 131.4, 130.4, 130.1, 128.2, 128.2, 127.2 (2C), 123.7, 123.6, 122.7, 122.7, 122.5, 122.3, 21.5, 20.9 ppm.

HRMS (ESI) *m/z*: $[M+NH_4]^+$ calcd for $[C_{32}H_{28}Br_2{}^{79}N]^+$ 584.0583; found 584.0568; calcd for $[C_{32}H_{28}Br_2{}^{81}N]^+$ 586.0563; found 586.0561.

General Procedure - 1 (GP-1) for the Preparation of ±3a-±3s:

To an oven-dried 10 mL Schlenk tube sealed with Teflon septum equipped with a magnetic stir bar, were added 1,2-bis(2-bromoaryl)ethyne **1a-1f** (33.6–40.5 mg, 0.1 mmol), 1,2-diarylethyne **2a-2j** (55–134 mg, 0.5 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), DPE-Phos (5.4 mg, 0.01 mmol), Cs_2CO_3 (97.5 mg, 0.3 mmol), and dry toluene (1 mL) at room temperature under inert atmosphere. The resultant reaction mixture was degassed two to three times under high vacuum with nitrogen and was subjected to an oil bath at 140 °C for 24–48 h. Progress of the reaction was monitored by TLC till the reaction was completed. The mixture was cooled to room temperature, quenched with aqueous $NaHCO_3$ solution, and extracted with ethyl acetate (3 × 10 mL). The organic layers were washed with saturated NaCl solution, dried (Na_2SO_4), and filtered. Evaporation of the solvent(s) under reduced pressure and purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate), first starting material **2a-2g** (84-94%) was recovered followed by the isolation of final product **±3a-±3s** (47–65%) as off-white/light brown/dark brown semi-solid/solid.

General Procedure - 2a (GP-2a) for the Preparation of 4a-4d

To an oven-dried 10 mL Schlenk tube sealed with Teflon septum equipped with a magnetic stir bar, were added 1,2-bis(2-bromoaryl)ethyne **1a** and **1b** (67.2 & 72.8 mg, 0.2 mmol), 1,2-diarylethyne **2a**, **2c** and **2d** (178, 206 & 238 mg, 1 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), DPE-Phos (10.76 mg, 0.02 mmol), Cs_2CO_3 (195 mg, 0.6 mmol), and dry toluene (1 mL) at room temperature under inert atmosphere. The resultant reaction mixture was subjected to an oil bath at 140 °C for 6–8 h. Progress of the reaction was monitored by TLC till the reaction was completed. The mixture was cooled to room temperature, quenched with aqueous $NaHCO_3$ solution, and extracted with ethyl acetate (3 × 10 mL). The organic layers were washed with saturated NaCl solution, dried (Na_2SO_4), and filtered. Evaporation of the solvent(s) under reduced pressure and purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate), first starting material **2a**, **2c**, and **2d** (90-92%) was recovered followed by the isolation of final products **4a-4d** (70–74%) as yellow solid/semi-solid.

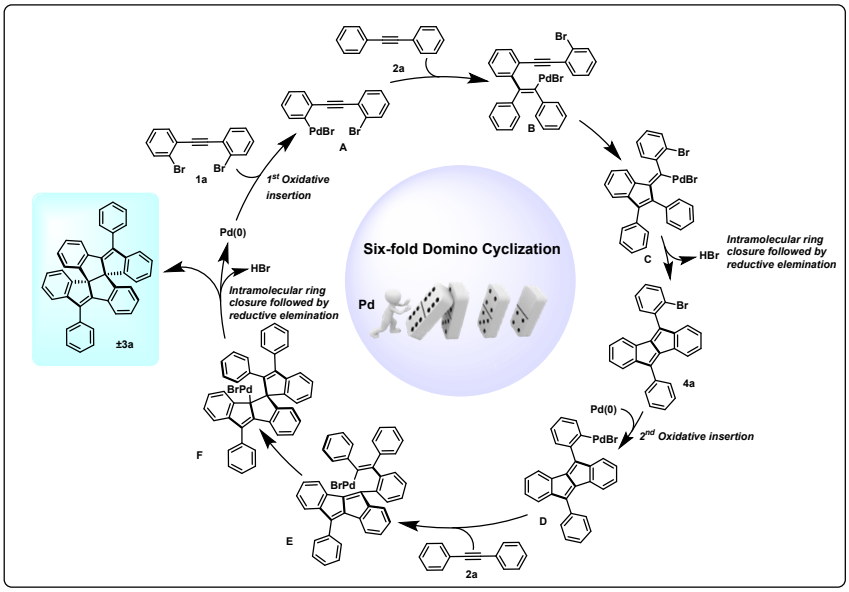
General Procedure - 2b (GP-2b) for the Preparation of ±5a-±5e

To an oven-dried 10 mL Schlenk tube sealed with Teflon septum equipped with a magnetic stir bar, were added *o*-bromophenyl indenoindene **4a**, **4c** and **4d** (43.3, 49.3 & 46.1 mg, 0.1 mmol), 1,2-diarylethyne **2a**, **2b** and **2c** (35.6, 41.2 & 47.6 mg, 0.2 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), DPE-Phos (5.4 mg, 0.01 mmol), Cs_2CO_3 (97.5 mg, 0.3 mmol), and dry toluene (1 mL) at room temperature under inert atmosphere. The resultant reaction mixture was subjected to an oil bath at 140 °C for 36–48 h. Progress of the reaction was monitored by TLC till the reaction was completed. The mixture was cooled to room temperature, quenched with aqueous $NaHCO_3$ solution, and extracted with ethyl acetate (3 × 10 mL). The organic layers were washed with saturated NaCl solution, dried (Na_2SO_4), and filtered. Evaporation of the solvent(s) under reduced pressure and purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate) furnished the final product ±**5a**-±**5e** (48–56%) as off-white/light brown/dark brown semi-solid/solid.

Note: The column chromatography must be performed very carefully to remove colour impurities that formed during the reaction.

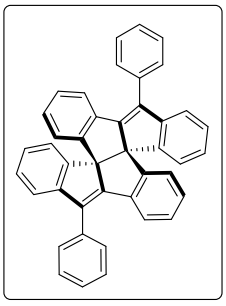
Plausible catalytic cycle for the formation of octacyclic product ±3a:

A viable reaction mechanism for synthesizing polycyclic product **±3a** based on our analysis and previous literature precedence of palladium-catalyzed domino reactions is depicted in Scheme S3. Primarily, the C−Br bond of 1,2-bis(2-bromophenyl)ethyne **1a** undergoes oxidative insertion by the active Pd(0)-catalyst and forms the intermediate **A**. The Pd(II) intermediate **A** subsequently inserts *via* first *syn*-addition onto the triple bond of 1,2-diphenylethyne **2a** and gives the intermediate **B**. Subsequently, this intermediate **B** migrates palladium entity intramolecularly to the proximal triple bond of 1,2-bis(2-bromophenyl)ethyne **1a** *via* second *syn*-addition, which produces the bicyclic intermediate **C**. Now **C** could further undergo a second intramolecular ring-closure step with the aromatic ring originated from external 1,2-diphenylethyne **2a** that generates the tetracyclic intermediate product **4a** containing bromine-atom, which completes the first catalytic cycle and reforms the active



Scheme S3. Proposed mechanistic cycle.

Pd(0)-catalyst. This intermediate product **4a** would now serve as a suitable intermediate to take up the second catalytic cycle *via* the attack by a second molecule of 1,2-diphenylethyne **2a** to yield the desired product **3a**. Thus, the tetracyclic product **4a** then undergoes a second oxidative insertion with the active Pd(0)-catalyst and affords the intermediate **D**, which then couples with a second molecule of 1,2-diphenylethyne **2a** *via* third *syn*-addition and leads to the formation of **E**. Subsequent palladium migration furnishes the hexacyclic intermediate **F** *via* fourth *syn*-addition. Ultimately, **F** undergoes reductive elimination and delivers the desired octacyclic product **3a** that concludes the second catalytic cycle and regenerates the active Pd(0)-catalyst.



Synthesis of (±3a):

GP-1 was carried out with 1,2-bis(2-bromoaryl)ethyne **1a** (33.6 mg, 0.1 mmol), 1,2-diarylethyne **2a** (89 mg, 0.5 mmol), $Pd(OAc)_2$ (2.24 mg, 0.01 mmol), DPE-Phos (5.38 mg, 0.01 mmol), Cs_2CO_3 (97.5 mg, 0.3 mmol), and dry toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1), first starting material **2a** (47.5 mg, 89%) was recovered followed by the isolation of final product **±3a** (34.4

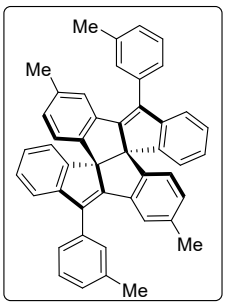
mg, 65%), as off white solid; mp = 168–170 °C. [TLC control (petroleum ether/ethyl acetate 99:1), R_f(**1a**) = 0.8, R_f(**±3a**) = 0.5, R_f(**2a**) = 0.9 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2960, 2921, 1489, 1342, 1084, 1022, 802, 740 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.82 (m, 4H), 7.60 (m, 6H), 7.54 – 7.44 (m, 4H), 7.19 (ddd, *J* = 7.6, 7.6, 1.1 Hz, 2H), 7.06 (ddd, *J* = 7.5, 7.5, 1.3 Hz, 2H), 6.98 (ddd, *J* = 7.5, 7.5, 1.2 Hz, 2H), 6.91 (ddd, *J* = 9.1, 9.1, 0.7 Hz, 2H), 6.89 – 6.85 (m, 2H), 6.56 (d, *J* = 7.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.7 (2C), 153.9 (2C), 148.3 (2C), 147.5 (2C), 135.9 (2C), 135.8 (2C), 134.6 (2C), 129.2 (4C), 128.6 (4C), 128.1 (2C), 127.8 (2C), 127.6 (2C), 127.2 (2C), 125.8 (2C), 123.9 (2C), 123.7 (2C), 122.7 (2C), 121.0 (2C), 73.4 (2C) ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{42}H_{27}]^+$ 531.2107; found 531.2102.



Synthesis of (±3b):

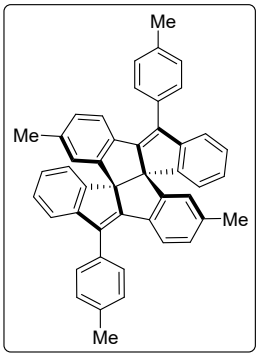
GP-1 was carried out with 1,2-bis(2-bromoaryl)ethyne **1a** (33.6 mg, 0.1 mmol), 1,2-diarylethyne **2b** (103 mg, 0.5 mmol), $Pd(OAc)_2$ (2.24 mg, 0.01 mmol), DPE-Phos (5.38 mg, 0.01 mmol), Cs_2CO_3 (97.5 mg, 0.3 mmol), and dry toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1), first starting material **2b** (51.9 mg, 84%) was recovered followed by the isolation of final product **±3b** (37.5 mg, 64%), as light brown solid; mp = 85–87 °C. [TLC control (petroleum ether/ethyl acetate 99:1), R_f(**1a**) = 0.8, R_f(**±3b**) = 0.5, R_f(**2b**) = 0.9 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2922, 2858, 1596, 1455, 1091, 1030, 743, 701 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.9 Hz, 4H), 7.50 (dd, *J* = 7.5, 7.5 Hz, 2H), 7.46 (d, *J* = 7.6 Hz, 2H), 7.39 (s, 2H), 7.31 (d, *J* = 7.6 Hz, 2H), 7.18 (ddd, *J* = 7.6, 7.6, 1.0 Hz, 2H), 6.87 (ddd, *J* = 7.4, 7.4, 0.8 Hz, 2H), 6.79 (s, 4H), 6.55 (d, *J* = 7.3 Hz, 2H), 2.53 (s, 6H), 2.19 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 154.7 (2C), 151.2 (2C), 148.5 (2C), 147.6 (2C), 138.1 (2C), 137.2 (2C), 135.8 (2C), 135.5 (2C), 134.6 (2C), 129.8 (2C), 128.8 (4C), 128.4 (2C), 127.0 (2C), 126.5 (2C), 125.6 (2C), 123.6 (2C), 123.5 (2C), 123.4 (2C), 120.9 (2C), 73.3 (2C), 21.6 (2C), 21.5 (2C) ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{46}H_{35}]^+$ 587.2733; found 587.2734.



Synthesis of (±3c):

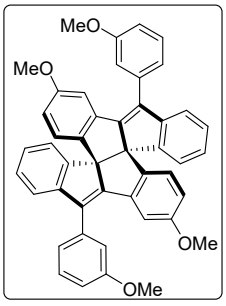
GP-1 was carried out with 1,2-bis(2-bromoaryl)ethyne **1a** (33.6 mg, 0.1 mmol), 1,2-diarylethyne **2c** (103 mg, 0.5 mmol), $Pd(OAc)_2$ (2.24 mg, 0.01 mmol), DPE-Phos (5.38 mg, 0.01 mmol), Cs_2CO_3 (97.5 mg, 0.3 mmol), and dry toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1), first starting material **2c** (55.6 mg, 90%) was recovered followed by the isolation of final product **±3c** (36.9 mg, 63%), as light brown semi solid. [TLC control (petroleum ether/ethyl acetate 99:1), R_f(**1a**) = 0.8, R_f(**±3c**) = 0.5, R_f(**2c**) = 0.9 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2924, 2859, 1728, 1452, 1263, 1084, 1028, 805 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.0 Hz, 4H), 7.49 (d, J = 7.9 Hz, 2H), 7.45 (d, J = 7.6 Hz, 2H), 7.40 (d, J = 7.8 Hz, 4H), 7.17 (ddd, J = 7.6, 7.6, 1.0 Hz, 2H), 6.85 (ddd, J = 7.4, 7.4, 0.9 Hz, 4H), 6.69 (s, 2H), 6.52 (d, J = 7.3 Hz, 2H), 2.50 (s, 6H), 2.12 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 154.4 (2C), 154.2 (2C), 148.4 (2C), 147.8(2C), 137.7 (4C), 134.8 (2C), 133.3 (2C), 131.8 (2C), 129.2 (4C), 129.1 (4C), 128.6 (2C), 127.0 (2C), 125.4 (2C), 124.3 (2C), 123.6 (2C), 122.4 (2C), 120.7 (2C), 73.6 (2C), 21.5 (2C), 21.4 (2C) ppm.

HRMS (ESI) *m/z*: $[M+K]^+$ calcd for $[C_{46}H_{34}K]^+$ 625.2292; found 625.2301.



Synthesis of (±3d):

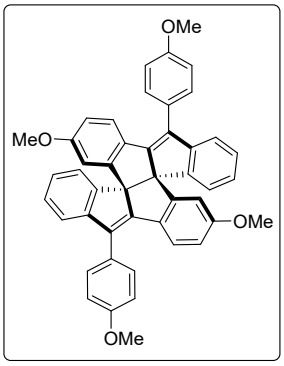
GP-1 was carried out with 1,2-bis(2-bromoaryl)ethyne **1a** (33.6 mg, 0.1 mmol), 1,2-diarylethyne **2d** (119 mg, 0.5 mmol), $Pd(OAc)_2$ (2.24 mg, 0.01 mmol), DPE-Phos (5.38 mg, 0.01 mmol), Cs_2CO_3 (97.5 mg, 0.3 mmol), and dry toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 99:1 to 98:2), first starting material **2d** (65.7 mg, 92%) was recovered followed by the isolation of final product **±3d** (42.3 mg, 65%), as light brown solid; mp = 176–178 °C. [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**1a**) = 0.9, R_f(**±3d**) = 0.3, R_f(**2d**) = 0.6 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2927, 2844, 1591, 1465, 1232, 1038, 785, 741 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.45 (m, 4H), 7.42 (d, J = 7.5 Hz, 2H), 7.35 (d, J = 2.3 Hz, 2H), 7.21 – 7.15 (m, 4H), 7.06 – 7.02 (m, 2H), 6.88 (ddd, J = 7.4, 7.4, 0.8 Hz, 2H), 6.81 (d, J = 8.5 Hz, 2H), 6.58 – 6.52 (m, 4H), 3.94 (s, 6H), 3.66 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8 (2C), 159.2 (2C), 154.5 (2C), 148.6 (2C), 147.2 (2C), 145.9 (2C), 136.7 (2C), 135.9 (2C), 135.6 (2C), 129.6 (2C), 127.1 (2C), 125.8 (2C), 124.4 (2C), 123.6 (2C), 121.8 (2C), 121.0 (2C), 114.5 (2C), 114.2 (2C), 113.8 (2C), 107.8 (2C), 73.2 (2C), 55.4 (2C), 55.2 (2C) ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{46}H_{35}O_4]^+$ 651.2530; found 651.2535.



Synthesis of (±3e):

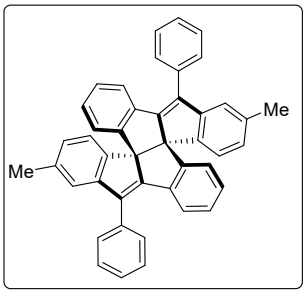
GP-1 was carried out with 1,2-bis(2-bromoaryl)ethyne **1a** (33.6 mg, 0.1 mmol), 1,2-diarylethyne **2e** (119 mg, 0.5 mmol), $Pd(OAc)_2$ (2.24 mg, 0.01 mmol), DPE-Phos (5.38 mg, 0.01 mmol), Cs_2CO_3 (97.5 mg, 0.3 mmol), and dry toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 99:1 to 98:2), first starting material **2e** (64.9 mg, 91%) was recovered followed by the isolation of final product **±3e** (35.8 mg, 55%), as light brown solid; mp = 238–240 °C. [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**1a**) = 0.9, R_f(**±3e**) = 0.3, R_f(**2e**) = 0.6 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2923, 2843, 1602, 1509, 1244, 1177, 1029, 699 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, J = 8.6, 2.3 Hz, 4H), 7.54 (dd, J = 8.5, 2.6 Hz, 2H), 7.45 (d, J = 7.6 Hz, 2H), 7.21 – 7.10 (m, 6H), 6.85 (dd, J = 7.4, 7.4 Hz, 2H), 6.63 (ddd, J = 8.5, 8.5, 2.0 Hz, 2H), 6.59 – 6.50 (m, 2H), 6.45 (dd, J = 2.5 Hz, 2H), 3.94 (s, 6H), 3.61 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5 (2C), 159.3 (2C), 156.3 (2C), 153.5 (2C), 147.9 (2C), 147.9 (2C), 133.4 (2C), 130.4 (4C), 128.9 (2C), 127.2 (2C), 127.1 (2C), 125.2 (2C), 123.5 (2C), 123.3 (2C), 120.6 (2C), 113.9 (4C), 113.5 (2C), 109.3 (2C), 73.8 (2C), 55.4 (2C), 55.3 (2C) ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{46}H_{35}O_4]^+$ 651.2530; found 651.2541.



Synthesis of (±3f):

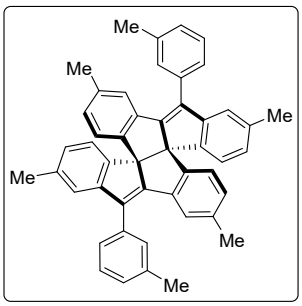
GP-1 was carried out with 1,2-bis(2-bromoaryl)ethyne **1b** (36.4 mg, 0.1 mmol), 1,2-diarylethyne **2a** (89 mg, 0.5 mmol), $Pd(OAc)_2$ (2.24 mg, 0.01 mmol), DPE-Phos (5.38 mg, 0.01 mmol), Cs_2CO_3 (97.5 mg, 0.3 mmol), and dry toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1), first starting material **2a** (49.7 mg, 93%) was recovered followed by the isolation of final product **±3f** (33.5 mg, 60%), as off white solid; mp = 290–292 °C. [TLC control (petroleum ether/ethyl acetate 99:1), R_f(**1b**) = 0.8, R_f(**±3f**) = 0.5, R_f(**2a**) = 0.9 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2920, 2860, 1602, 1486, 1262, 1028, 745, 702 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.72 (m, 4H), 7.65 – 7.53 (m, 6H), 7.53 – 7.46 (m, 2H) 7.26 (s, 2H), 7.04 (ddd, J = 7.4, 7.4, 1.3 Hz, 2H), 6.97 (ddd, J = 7.4, 7.4, 1.2 Hz, 2H), 6.91 (d, J = 7.1 Hz, 2H), 6.70 (d, J = 7.5 Hz, 2H), 6.46 (d, J = 7.5 Hz, 2H), 2.29 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 155.1 (2C), 154.2 (2C), 147.8 (2C), 145.6 (2C), 136.8 (2C), 135.8 (2C), 135.8 (2C), 134.7 (2C), 129.3 (4C), 128.6 (4C), 128.1 (2C), 127.7 (2C), 127.4 (2C), 126.6 (2C), 123.8 (2C), 123.4 (2C), 122.6 (2C), 121.7 (2C), 73.0 (2C), 21.6 (2C) ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{44}H_{31}]^+$ 559.2420; found 559.2430.



Synthesis of (±3g):

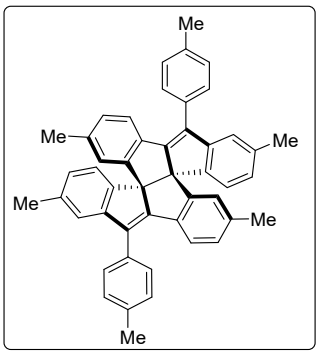
GP-1 was carried out with 1,2-bis(2-bromoaryl)ethyne **1b** (36.4 mg, 0.1 mmol), 1,2-diarylethyne **2b** (103 mg, 0.5 mmol), $Pd(OAc)_2$ (2.24 mg, 0.01 mmol), DPE-Phos (5.38 mg, 0.01 mmol), Cs_2CO_3 (97.5 mg, 0.3 mmol), and dry toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1), first starting material **2b** (55.0 mg, 89%) was recovered followed by the isolation of final product **±3g** (38.1 mg, 62%), as dark brown solid; mp = 140–142 °C. [TLC control (petroleum ether/ethyl acetate 99:1), R_f(**1b**) = 0.8, R_f(**±3g**) = 0.5, R_f(**2b**) = 0.9 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2921, 2859, 1601, 1462, 1032, 883, 804, 702 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 – 7.57 (m, 4H), 7.50 (dd, J = 7.5, 7.5 Hz, 2H), 7.35 (s, 2H), 7.31 (d, J = 7.6 Hz, 2H), 7.24 (s, 2H), 6.78 (d, J = 0.9 Hz, 4H), 6.68 (d, J = 7.5 Hz, 2H), 6.45 (d, J = 7.5 Hz, 2H), 2.53 (s, 6H), 2.29 (s, 6H), 2.17 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 155.0 (2C), 151.5 (2C), 147.9 (2C), 145.8 (2C), 138.1 (2C), 136.9 (2C), 136.6 (2C), 135.8 (2C), 135.5 (2C), 134.7 (2C), 129.8 (2C), 128.7 (4C), 128.4 (2C), 126.5 (2C), 126.4 (2C), 123.4 (2C), 123.3 (4C), 121.7 (2C), 72.9 (2C), 21.7 (2C), 21.6 (2C), 21.5 (2C) ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{48}H_{39}]^+$ 615.3046; found 615.3048.



Synthesis of (±3h):

GP-1 was carried out with 1,2-bis(2-bromoaryl)ethyne **1b** (36.4 mg, 0.1 mmol), 1,2-diarylethyne **2c** (103 mg, 0.5 mmol), $Pd(OAc)_2$ (2.24 mg, 0.01 mmol), DPE-Phos (5.38 mg,

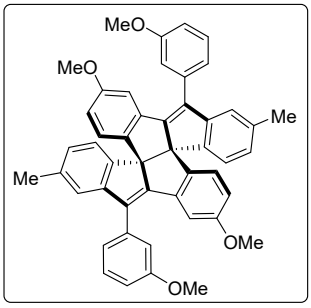
0.01 mmol), Cs_2CO_3 (97.5 mg, 0.3 mmol), and dry toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1), first starting material **2c** (54.4 mg, 88%) was recovered followed by the isolation of final product **±3h** (39.3 mg, 64%), as dark brown solid; mp = 218–220 °C. [TLC control (petroleum ether/ethyl acetate 99:1), R_f(**1b**) = 0.8, R_f(**±3h**) = 0.5, R_f(**2c**) = 0.9 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2918, 2859, 1506, 1454, 1182, 1027, 808, 733 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.0 Hz, 4H), 7.46 (d, J = 7.8 Hz, 2H), 7.41 (d, J = 7.8 Hz, 4H), 7.25 (s, 2H), 6.84 (dd, J = 7.8, 0.9 Hz, 2H), 6.68 (dd, J = 6.9, 4.6 Hz, 4H), 6.42 (d, J = 7.5 Hz, 2H), 2.50 (s, 6H), 2.28 (s, 6H), 2.12 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.7 (2C), 154.5 (2C), 147.9 (2C), 145.6 (2C), 137.6 (2C), 137.6 (2C), 136.6 (2C), 134.7 (2C), 133.3 (2C), 131.9 (2C), 129.2 (4C), 129.1 (4C), 128.4 (2C), 126.2 (2C), 124.3 (2C), 123.2 (2C), 122.3 (2C), 121.5 (2C), 73.2 (2C), 21.7 (2C), 21.5 (2C), 21.4 (2C) ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{48}H_{39}]^+$ 615.3046; found 615.3048.



Synthesis of (±3i):

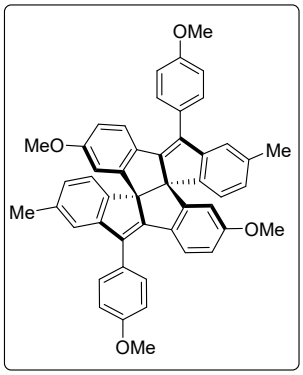
GP-1 was carried out with 1,2-bis(2-bromoaryl)ethyne **1b** (36.4 mg, 0.1 mmol), 1,2-diarylethyne **2d** (119 mg, 0.5 mmol), $Pd(OAc)_2$ (2.24 mg, 0.01 mmol), DPE-Phos (5.38 mg, 0.01 mmol), Cs_2CO_3 (97.5 mg, 0.3 mmol), and dry toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 99:1 to 98:2), first starting material **2d** (64.2 mg, 90%) was recovered followed by the isolation of final product **±3i** (41.4 mg, 61%), as dark brown solid; mp = 204–206 °C. [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**1b**) = 0.9, R_f(**±3i**) = 0.3, R_f(**2d**) = 0.6 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2925, 2804, 1587, 1466, 1231, 1035, 799, 733 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 – 7.47 (m, 2H), 7.40 (d, J = 7.6 Hz, 2H), 7.36 – 7.29 (m, 2H), 7.27 – 7.25 (m, 2H), 7.12 (d, J = 2.4 Hz, 2H), 7.03 (ddd, J = 8.3, 2.6, 0.7 Hz, 2H), 6.79 (d, J = 8.5 Hz, 2H), 6.72 – 6.67 (m, 2H), 6.54 (dd, J = 8.5, 2.5 Hz, 2H), 6.44 (d, J = 7.5 Hz, 2H), 3.94 (s, 6H), 3.65 (s, 6H), 2.28 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8 (2C), 159.1 (2C), 154.8 (2C), 147.4 (2C), 146.1 (2C), 145.9 (2C), 136.7 (2C), 136.7 (2C), 136.0 (2C), 135.6 (2C), 129.6 (2C), 126.6 (2C), 124.4 (2C), 123.3 (2C), 121.8 (2C), 121.8 (2C), 114.6 (2C), 114.1 (2C), 113.7 (2C), 107.7 (2C), 72.8 (2C), 55.4 (2C), 55.2 (2C), 21.7 (2C) ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{48}H_{39}O_4]^+$ 679.2843; found 679.2835.



Synthesis of (±3j):

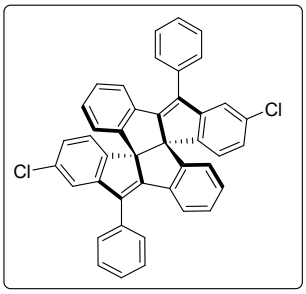
GP-1 was carried out with 1,2-bis(2-bromoaryl)ethyne **1b** (36.4 mg, 0.1 mmol), 1,2-diarylethyne **2e** (119 mg, 0.5 mmol), $Pd(OAc)_2$ (2.24 mg, 0.01 mmol), DPE-Phos (5.38 mg, 0.01 mmol), Cs_2CO_3 (97.5 mg, 0.3 mmol), and dry toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 99:1 to 98:2), first starting material **2e** (62.1 mg, 87%) was recovered followed by the isolation of final product **±3j** (39.3 mg, 58%), as off white solid; mp = 60–62 °C. [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**1b**) = 0.9, R_f(**±3j**) = 0.3, R_f(**2e**) = 0.6 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2922, 2845, 1603, 1506, 1456, 1244, 1028, 805 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.71 (m, 4H), 7.49 (d, J = 8.5 Hz, 2H), 7.22 (s, 2H), 7.15 – 7.10 (m, 4H), 6.65 (d, J = 6.9 Hz, 2H), 6.60 (dd, J = 8.5, 2.5 Hz, 2H), 6.45 – 6.39 (m, 4H), 3.94 (s, 6H), 3.60 (s, 6H), 2.28 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8 (2C), 159.5 (2C), 159.3 (2C), 156.6 (2C), 136.6 (2C), 133.3 (2C), 130.4 (4C), 128.9 (2C), 127.4 (2C), 127.3 (2C), 126.0 (2C), 123.2 (2C), 123.1 (2C), 122.9 (2C), 121.4 (2C), 113.9 (4C), 113.3 (2C), 109.3 (2C), 73.4 (2C), 55.4 (2C), 55.3 (2C), 26.7 (2C) ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{48}H_{39}O_4]^+$ 679.2843; found 679.2835.



Synthesis of (±3k):

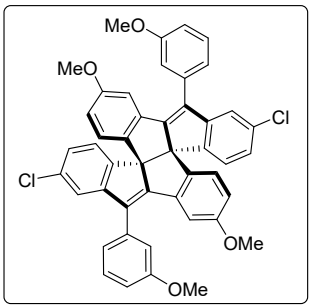
GP-1 was carried out with 1,2-bis(2-bromoaryl)ethyne **1c** (40.5 mg, 0.1 mmol), 1,2-diarylethyne **2a** (89 mg, 0.5 mmol), $Pd(OAc)_2$ (2.24 mg, 0.01 mmol), DPE-Phos (5.38 mg, 0.01 mmol), Cs_2CO_3 (97.5 mg, 0.3 mmol), and dry toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1), first starting material **2a** (50.2 mg, 94%) was recovered followed by the isolation of final product **±3k** (32.3 mg, 54%), as light brown solid; mp = 294–296 °C. [TLC control (petroleum ether/ethyl acetate 99:1), R_f(**1c**) = 0.7, R_f(**±3k**) = 0.5, R_f(**2a**) = 0.9 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2924, 2855, 1594, 1449, 1261, 1073, 753, 704 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, J = 7.1 Hz, 4H), 7.62 (dd, J = 7.6, 7.6 Hz, 4H), 7.58 (d, J = 7.6 Hz, 2H), 7.52 (dd, J = 7.5, 7.5 Hz, 2H), 7.42 (d, J = 1.7 Hz, 2H), 7.07 (dd, J = 10.9, 4.1 Hz, 2H), 7.05 – 6.99 (m, 2H), 6.91 (d, J = 7.6 Hz, 2H), 6.88 (dd, J = 7.9, 1.9 Hz, 2H), 6.45 (d, J = 7.9 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.9 (2C), 153.3 (2C), 149.3 (2C), 146.1 (2C), 135.4 (2C), 135.2 (2C), 133.8 (2C), 133.5 (2C), 129.1 (4C), 128.8 (4C), 128.5 (2C), 128.3 (2C), 128.0 (2C), 125.7 (2C), 124.5 (2C), 123.9 (2C), 123.0 (2C), 121.4 (2C), 72.9 (2C) ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{42}H_{25}Cl_2]^+$ 599.1328; found 599.1337.



Synthesis of (±3l):

GP-1 was carried out with 1,2-bis(2-bromoaryl)ethyne **1c** (40.5 mg, 0.1 mmol), 1,2-diarylethyne **2d** (119 mg, 0.5 mmol), $Pd(OAc)_2$ (2.24 mg, 0.01 mmol), DPE-Phos (5.38 mg, 0.01 mmol), Cs_2CO_3 (97.5 mg, 0.3 mmol), and dry toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 99:1 to 98:2), first

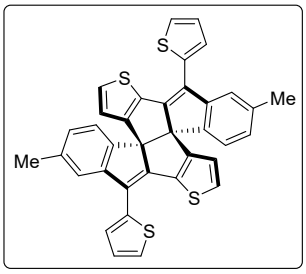
starting material **2d** (64.9 mg, 91%) was recovered followed by the isolation of final product **±3l** (39.6 mg, 55%), as dark brown solid; mp = 96–98 °C. [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**1c**) = 0.9, R_f(**±3l**) = 0.3, R_f(**2d**) = 0.6 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2927, 2843, 1590, 1465, 1238, 1040, 800, 740 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 – 7.48 (m, 2H), 7.42 (d, J = 1.8 Hz, 2H), 7.37 – 7.34 (m, 2H), 7.30 – 7.27 (m, 2H), 7.13 (d, J = 2.4 Hz, 2H), 7.05 (ddd, J = 8.3, 2.6, 0.8 Hz, 2H), 6.87 (dd, J = 7.9, 1.9 Hz, 2H), 6.80 (d, J = 8.5 Hz, 2H), 6.58 (dd, J = 8.5, 2.5 Hz, 2H), 6.43 (d, J = 7.9 Hz, 2H), 3.94 (s, 6H), 3.65 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9 (2C), 159.4 (2C), 155.7 (2C), 148.9 (2C), 146.4 (2C), 145.2 (2C), 136.4 (2C), 135.1 (2C), 134.8 (2C), 133.4 (2C), 129.9 (2C), 125.8 (2C), 124.5 (2C), 124.4 (2C), 121.6 (2C), 121.4 (2C), 114.7 (2C), 114.6 (2C), 113.9 (2C), 108.1 (2C), 72.7 (2C), 55.5 (2C), 55.2 (2C) ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{46}H_{33}Cl_2O_4]^+$ 719.1750; found 719.1764.



Synthesis of (±3m):

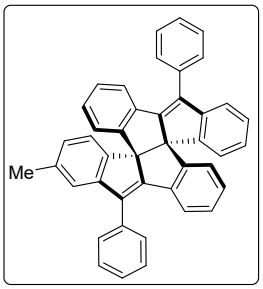
GP-1 was carried out with 1,2-bis(2-bromoaryl)ethyne **1b** (36.4 mg, 0.1 mmol), 1,2-diarylethyne **2f** (95.1 mg, 0.5 mmol), $Pd(OAc)_2$ (2.24 mg, 0.01 mmol), DPE-Phos (5.38 mg, 0.01 mmol), Cs_2CO_3 (97.5 mg, 0.3 mmol), and dry toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1), first starting material **2f** (51.3 mg, 90%) was recovered followed by the isolation of final product **±3m** (27.3 mg, 47%), as off white solid; mp = 146–148 °C. [TLC control (petroleum ether/ethyl acetate 99:1), R_f(**1b**) = 0.9, R_f(**±3m**) = 0.5, R_f(**2f**) = 0.8 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3096, 2920, 1602, 1499, 1196, 1036, 807, 698 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 7.9 Hz, 2H), 7.44 (d, J = 3.8 Hz, 2H), 7.36 (s, 2H), 7.31 – 7.26 (m, 4H), 7.22 (d, J = 3.9 Hz, 2H), 7.13 (d, J = 7.9 Hz, 2H), 7.01 (dd, J = 5.2, 3.7 Hz, 2H), 2.40 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.1 (2C), 138.9 (2C), 134.9 (2C), 133.6 (2C), 132.4 (2C), 132.0 (2C), 129.5 (2C), 128.6 (2C), 127.6 (2C), 127.1 (2C), 126.8 (2C), 123.1 (2C), 122.9 (2C), 118.0 (2C), 92.9 (2C), 87.0 (2C), 86.6 (2C), 21.5 (2C) ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{36}H_{23}S_4]^+$ 583.0677; found 583.0682.



Synthesis of (±3o):

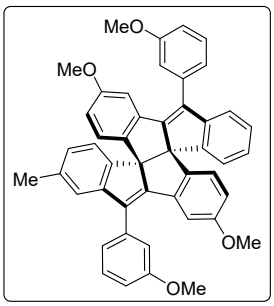
GP-1 was carried out with 1,2-bis(2-bromoaryl)ethyne **1d** (35.0 mg, 0.1 mmol), 1,2-diarylethyne **2a** (89 mg, 0.5 mmol), $Pd(OAc)_2$ (2.24 mg, 0.01 mmol), DPE-Phos (5.38 mg, 0.01 mmol), Cs_2CO_3 (97.5 mg, 0.3 mmol), and dry toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1), first starting material **2a** (50.2 mg, 94%) was recovered followed by the isolation of final product **±3o** (35.4 mg, 65%), as dark brown solid; mp = 253–255 °C. [TLC control (petroleum ether/ethyl acetate 99:1), R_f(**1d**) = 0.7, R_f(**±3o**) = 0.5, R_f(**2a**) = 0.9 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2922, 2857, 1600, 1261, 1082, 1025, 740, 700 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 – 7.75 (m, 4H), 7.68 – 7.54 (m, 6H), 7.52 – 7.45 (m, 3H), 7.27 (s, 1H), 7.19 (td, *J* = 7.5, 1.1 Hz, 1H), 7.05 (td, *J* = 7.6, 1.1 Hz, 2H), 6.98 (tdd, *J* = 7.4, 3.3, 1.1 Hz, 2H), 6.94 – 6.86 (m, 3H), 6.74 – 6.66 (m, 1H), 6.58 (d, *J* = 7.3 Hz, 1H), 6.45 (d, *J* = 7.5 Hz, 1H), 2.29 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 154.9, 154.8, 154.2, 153.8, 148.4, 147.8, 147.6, 145.5, 136.9, 135.9, 135.9, 135.8, 135.7, 134.7, 134.6, 129.3 (4C), 128.6 (4C), 128.1, 128.1, 127.8, 127.7, 127.5, 127.5, 127.2, 126.6, 125.8, 123.9 (2C), 123.7, 123.4, 122.7 (2C), 121.8, 120.9, 73.4, 73.1, 21.6 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{43}H_{29}]^+$ 545.2264; found 545.2279.



Synthesis of (±3p):

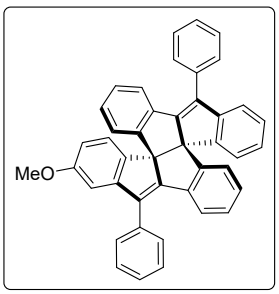
GP-1 was carried out with 1,2-bis(2-bromoaryl)ethyne **1d** (35.0 mg, 0.1 mmol), 1,2-diarylethyne **2d** (119 mg, 0.5 mmol), $Pd(OAc)_2$ (2.24 mg, 0.01 mmol), DPE-Phos (5.38 mg, 0.01 mmol), Cs_2CO_3 (97.5 mg, 0.3 mmol), and dry toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 99:1 to 98:2), first starting material **2d** (63.5 mg, 89%) was recovered followed by the isolation of final product **±3p** (42.5 mg, 64%), as dark brown solid; mp = 146–148 °C. [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**1d**) = 0.9, R_f(**±3p**) = 0.3, R_f(**2d**) = 0.6 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2923, 2843, 1587, 1465, 1231, 1035, 797, 736 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.47 (m, 3H), 7.44 – 7.39 (m, 2H), 7.35 (d, J = 0.9 Hz, 2H), 7.28 (s, 1H), 7.22 – 7.13 (m, 3H), 7.07 – 7.01 (m, 2H), 6.90 (t, J = 7.4 Hz, 1H), 6.81 (dd, J = 8.4, 3.5 Hz, 2H), 6.70 (d, J = 7.5 Hz, 1H), 6.61 – 6.50 (m, 3H), 6.44 (d, J = 7.5 Hz, 1H), 3.94 (2×s, 6H), 3.66 (2×s, 6H), 2.29 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8 (2C), 159.2, 159.1, 154.7, 154.6, 148.7, 147.4, 147.2, 146.2, 145.8 (2C), 136.8, 136.8, 136.7, 136.0, 135.9, 135.7, 135.5, 129.6 (2C), 127.1, 126.6, 125.8, 124.4 (2C), 123.6, 123.3, 121.8 (3C), 121.0, 114.6, 114.5, 114.2, 114.1, 113.2, 113.7, 107.8 (2C), 73.2, 72.9, 55.4, 55.4, 55.2 (2C), 21.6 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{47}H_{37}O_4]^+$ 665.2686; found 665.2698.



Synthesis of (±3q):

GP-1 was carried out with 1,2-bis(2-bromoaryl)ethyne **1e** (36.6 mg, 0.1 mmol), 1,2-diarylethyne **2a** (89 mg, 0.5 mmol), $Pd(OAc)_2$ (2.24 mg, 0.01 mmol), DPE-Phos (5.38 mg, 0.01

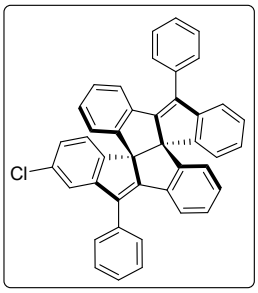
mmol), Cs_2CO_3 (97.5 mg, 0.3 mmol), and dry toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 99:1 to 98:2), first starting material **2a** (49.1 mg, 92%) was recovered followed by the isolation of final product **±3q** (32.5 mg, 58%), as light brown solid; mp = 230–232 °C. [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**1e**) = 0.6, R_f(**±3q**) = 0.4, R_f(**2a**) = 0.9 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2923, 2845, 1726, 1452, 1266, 1026, 805, 743 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (d, J = 7.9 Hz, 4H), 7.62 – 7.57 (m, 6H), 7.50 (ddd, J = 9.2, 6.3, 3.7 Hz, 2H), 7.48 – 7.44 (m, 1H), 7.37 (d, J = 8.4 Hz, 1H), 7.19 (ddd, J = 7.6, 7.6, 0.9 Hz, 1H), 7.09 – 7.02 (m, 2H), 7.02 – 6.86 (m, 5H), 6.73 (dd, J = 8.4, 2.4 Hz, 1H), 6.59 (d, J = 7.4 Hz, 1H), 6.15 (d, J = 2.4 Hz, 1H), 3.57 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 154.6, 154.1, 153.3, 152.7, 150.1, 148.2, 147.5, 140.6, 136.0, 135.9, 135.8, 135.7, 134.8, 134.6, 129.2 (2C), 129.2 (2C), 128.6 (2C), 128.6 (2C), 128.1, 128.1, 127.8, 127.6, 127.5, 127.5, 127.2, 125.8, 123.9, 123.8, 123.7, 122.7, 122.4, 121.4, 121.0, 111.4, 111.2, 73.5, 73.2, 55.2 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{43}H_{29}O]^+$ 561.2213; found 561.2247.



Synthesis of (±3r):

GP-1 was carried out with 1,2-bis(2-bromoaryl)ethyne **1f** (37.0 mg, 0.1 mmol), 1,2-diarylethyne **2a** (89 mg, 0.5 mmol), $Pd(OAc)_2$ (2.24 mg, 0.01 mmol), DPE-Phos (5.38 mg, 0.01 mmol), Cs_2CO_3 (97.5 mg, 0.3 mmol), and dry toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1), first starting material **2a** (48.1 mg, 90%) was recovered followed by the isolation of final product **±3r** (32.7 mg, 58%), as dark brown solid; mp = 105–107 °C. [TLC control (petroleum ether/ethyl acetate 99:1), R_f(**1f**) = 0.7, R_f(**±3r**) = 0.5, R_f(**2a**) = 0.9 UV detection].

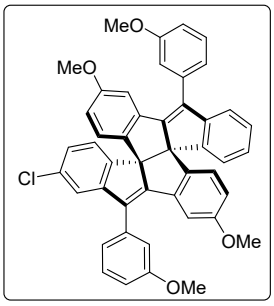
IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3059, 2925, 1815, 1729, 1449, 1074, 753, 703 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (ddd, J = 8.5, 8.5, 1.2 Hz, 4H), 7.64 – 7.57 (m, 5H), 7.54 – 7.46 (m, 3H), 7.42 (d, J = 1.8 Hz, 1H), 7.24 – 7.18 (m, 2H), 7.11 – 7.03 (m, 2H), 7.03 – 6.95

(m, 2H), 6.93 – 6.90 (m, 2H), 6.87 – 6.82 (m, 2H), 6.55 (d, *J* = 7.3 Hz, 1H), 6.46 (d, *J* = 7.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3, 154.3, 153.9, 153.1, 149.3, 148.0, 147.5, 146.4, 136.2, 135.7, 135.4, 134.9, 134.4, 133.9, 133.3, 131.3, 129.2 (2C), 129.1 (2C), 128.8 (2C), 128.6 (2C), 128.4, 128.2, 127.9, 127.8, 127.7, 127.4, 125.9, 125.6, 124.5, 123.9, 123.8, 123.6, 122.9, 122.8, 121.3, 121.1, 73.4, 72.9 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{42}H_{26}H]^+$ 565.1718; found 565.1706.



Synthesis of (±3s):

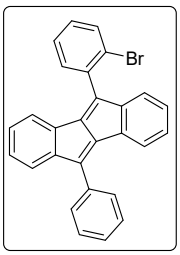
GP-1 was carried out with 1,2-bis(2-bromoaryl)ethyne **1f** (37.0 mg, 0.1 mmol), 1,2-diarylethyne **2d** (119 mg, 0.5 mmol), $Pd(OAc)_2$ (10.76 mg, 0.02 mmol), DPE-Phos (5.38 mg, 0.01 mmol), Cs_2CO_3 (97.5 mg, 0.3 mmol), and dry toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 99:1 to 98:2), first starting material **2d** (63.5 mg, 89%) was recovered followed by the isolation of final product **±3s** (37.6 mg, 55%), as light brown solid; mp = 82–84 °C. [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**1f**) = 0.8, R_f(**±3s**) = 0.3, R_f(**2d**) = 0.6 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2924, 2852, 1591, 1463, 1236, 1035, 800, 740 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.47 (m, 3H), 7.40 (ddd, *J* = 10.7, 6.7, 4.8 Hz, 3H), 7.35 – 7.26 (m, 2H), 7.20 (td, *J* = 7.6, 1.0 Hz, 1H), 7.14 (dd, *J* = 10.1, 2.4 Hz, 2H), 7.04 (ddd, *J* = 6.3, 5.4, 2.7 Hz, 2H), 6.91 (td, *J* = 7.4, 0.9 Hz, 1H), 6.84 (dd, *J* = 7.9, 1.9 Hz, 1H), 6.80 (dd, *J* = 8.5, 3.0 Hz, 2H), 6.59 – 6.52 (m, 3H), 6.44 (d, *J* = 7.9 Hz, 1H), 3.94 (2×s, 6H), 3.65 (2×s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9, 159.8, 159.4, 159.3, 156.1, 154.1, 149.0, 148.3, 147.1, 146.7, 145.9, 145.0, 136.7, 136.4, 135.9, 135.7, 135.2, 134.6, 133.2, 129.8, 129.6, 127.3, 125.9, 125.7, 124.5, 124.4, 124.4, 123.6, 121.8, 121.6, 121.3, 121.2, 114.6, 114.5 (2C), 114.2, 113.9, 113.9, 107.9, 107.9, 73.2, 72.7, 55.5, 55.4, 55.2 (2C) ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{46}H_{34}ClO_4]^+$ 685.2140; found 685.2154.



5-(2-bromophenyl)-10-phenylindeno[2,1-*a*]indene (4a):

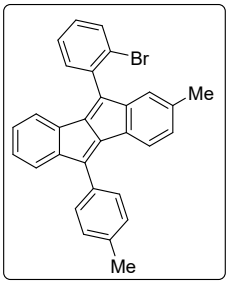
GP-2a was carried out with 1,2-bis(2-bromoaryl)ethyne **1a** (67.2 mg, 0.2 mmol), 1,2-diarylethyne **2a** (178 mg, 1 mmol), $Pd(OAc)_2$ (2.24 mg, 0.01 mmol), DPE-Phos (10.76 mg, 0.02 mmol), Cs_2CO_3 (195 mg, 0.6 mmol), and dry toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1), first starting material **2a** (128.2 mg, 90%) was recovered followed by the isolation of final product **4a** (64.1 mg, 74%), as yellow solid; mp = 150–152 °C. [TLC control (petroleum ether/ethyl acetate 99:1), R_f(**1a**) = 0.8, R_f(**4a**) = 0.5, R_f(**2a**) = 0.9 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3057, 2927, 1433, 1312, 1164, 1027, 947, 747 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, J = 8.1 Hz, 1H), 7.70 (d, J = 7.6 Hz, 2H), 7.53 (dd, J = 7.6 , 7.6 Hz, 2H), 7.49 – 7.42 (m, 3H), 7.31 (dd, J = 10.9, 4.5 Hz, 1H), 7.23 (d, J = 7.2 Hz, 1H), 7.02 (d, J = 7.4 Hz, 1H), 6.92 – 6.80 (m, 4H), 6.74 (d, J = 7.3 Hz, 1H), 6.70 (d, J = 7.3 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 149.8, 149.7, 144.8, 142.9, 141.5, 138.7, 135.1, 134.9, 134.4, 133.7, 133.4, 130.5, 129.8, 128.9, 128.6 (2C), 128.4 (2C), 127.9, 127.8, 127.4, 127.4, 127.3, 122.8, 122.8, 122.7, 122.5, 121.9 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{28}H_{18}Br^{79}]^+$ 433.0586; found 433.0547; calcd for $[C_{28}H_{18}Br^{81}]^+$ 435.0566; found 435.0516.



10-(2-bromophenyl)-2-methyl-5-(*p*-tolyl)indeno[2,1-*a*]indene (4b):

GP-2a was carried out with 1,2-bis(2-bromoaryl)ethyne **1a** (67.2 mg, 0.2 mmol), 1,2-diarylethyne **2c** (206 mg, 1 mmol), $Pd(OAc)_2$ (2.24 mg, 0.01 mmol), DPE-Phos (10.76 mg, 0.02 mmol), Cs_2CO_3 (195 mg, 0.6 mmol), and dry toluene (1 mL). Purification of the crude

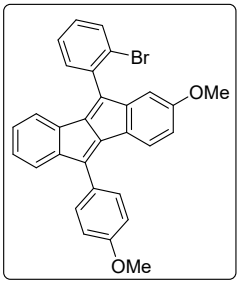
mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1), first starting material **2c** (151.6 mg, 92%) was recovered followed by the isolation of final product **4b** (66.4 mg, 72%), as yellow semi solid. [TLC control (petroleum ether/ethyl acetate 99:1), R_f(**1a**) = 0.8, R_f(**4b**) = 0.5, R_f(**2c**) = 0.9 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2924, 2858, 2314, 1998, 1441, 1103, 814, 749 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (dd, J = 8.1, 0.9 Hz, 1H), 7.58 (d, J = 8.0 Hz, 2H), 7.44 (dtd, J = 8.7, 7.5, 1.5 Hz, 2H), 7.35 – 7.28 (m, 3H), 7.12 (d, J = 7.6 Hz, 1H), 7.01 (d, J = 7.4 Hz, 1H), 6.87 (ddd, J = 7.5, 7.5, 1.1 Hz, 1H), 6.79 (ddd, J = 7.5, 7.5, 1.0 Hz, 1H), 6.69 (d, J = 7.0 Hz, 1H), 6.66 – 6.61 (m, 1H), 6.50 (s, 1H), 2.45 (s, 3H), 2.16 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 150.1, 149.9, 145.2, 142.5, 140.6, 138.8, 138.3, 137.7, 135.3, 134.9, 133.3, 131.7, 130.95, 130.5, 129.7, 129.3 (2C), 128.4 (2C), 127.8, 127.5, 127.4, 127.1, 123.7, 122.8, 122.7, 122.3, 121.8, 21.5, 21.4 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{30}H_{22}Br^{79}]^+$ 461.0899; found 461.0848; calcd for $[C_{30}H_{22}Br^{81}]^+$ 463.0879; found 463.0831.



10-(2-bromophenyl)-2-methoxy-5-(4-methoxyphenyl)indeno[2,1-*a*]indene (4c):

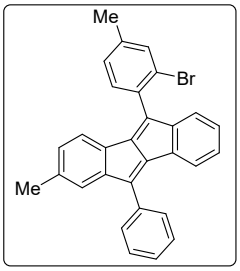
GP-2a was carried out with 1,2-bis(2-bromoaryl)ethyne **1a** (67.2 mg, 0.2 mmol), 1,2-diarylethyne **2d** (238 mg, 1 mmol), $Pd(OAc)_2$ (2.24 mg, 0.01 mmol), DPE-Phos (10.76 mg, 0.02 mmol), Cs_2CO_3 (195 mg, 0.6 mmol), and dry toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 99:1 to 98:2), first starting material **2d** (175.2 mg, 92%) was recovered followed by the isolation of final product **4c** (69.1 mg, 70%), as yellow semi-solid. [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**1a**) = 0.8, R_f(**4c**) = 0.3, R_f(**2d**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2928, 2845, 1719, 1671, 1277, 1040, 863, 750 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, J = 8.0, 0.8 Hz, 1H), 7.49 – 7.39 (m, 3H), 7.33 – 7.26 (m, 2H), 7.22 – 7.18 (m, 1H), 7.05 (d, J = 7.3 Hz, 1H), 7.01 – 6.96 (m, 1H), 6.92 – 6.79 (m, 3H), 6.72 (d, J = 6.8 Hz, 1H), 6.59 (d, J = 8.2 Hz, 1H), 6.35 (dd, J = 8.2, 2.4 Hz, 1H), 3.87 (s, 3H), 3.71 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9, 159.7, 149.1, 143.5, 142.6, 142.4, 141.1, 139.4, 136.3, 135.3, 135.0, 134.9, 133.4, 130.4, 129.8, 129.8, 127.5, 127.4 (2C), 123.3, 122.6, 122.5, 122.4, 120.8, 114.8, 113.4, 110.8, 110.3, 55.4, 55.4 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{30}H_{22}Br^{79}O_2]^+$ 493.0798; found 493.0793; calcd for $[C_{30}H_{22}Br^{81}O_2]^+$ 495.0777; found 495.0779.



5-(2-bromo-4-methylphenyl)-2-methyl-10-phenylindeno[2,1-*a*]indene (4d):

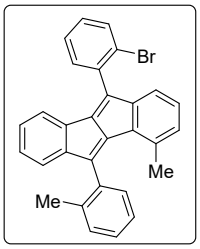
GP-2a was carried out with 1,2-bis(2-bromoaryl)ethyne **1b** (72.8 mg, 0.2 mmol), 1,2-diarylethyne **2a** (178 mg, 1 mmol), $Pd(OAc)_2$ (2.24 mg, 0.01 mmol), DPE-Phos (5.38 mg, 0.01 mmol), Cs_2CO_3 (195 mg, 0.6 mmol), and dry toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1), first starting material **2a** (128.2 mg, 90%) was recovered followed by the isolation of final product **4d** (64.5 mg, 70%), as yellow solid; mp = 62–64 °C. [TLC control (petroleum ether/ethyl acetate 99:1), R_f(**1a**) = 0.8, R_f(**4d**) = 0.5, R_f(**2a**) = 0.9 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3054, 2921, 1603, 1485, 1435, 1038, 819 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.64 (m, 2H), 7.59 – 7.52 (m, 3H), 7.49 – 7.43 (m, 1H), 7.36 (d, J = 7.8 Hz, 1H), 7.25 – 7.18 (m, 2H), 6.89 – 6.79 (m, 3H), 6.76 – 6.59 (m, 3H), 2.43 (s, 3H), 2.20 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.1, 149.9, 144.7, 143.3, 141.1, 140.1, 137.9, 137.9, 134.4, 133.9, 133.8, 132.2, 132.1, 130.2, 128.8, 128.6 (2C), 128.5 (2C), 128.2, 127.7, 127.6, 127.0, 123.6, 122.7, 122.6, 122.4, 121.8, 21.5, 20.9 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{30}H_{22}Br^{79}]^+$ 461.0899; found 461.0904; calcd for $[C_{30}H_{22}Br^{81}]^+$ 463.0879; found 463.0885.



10-(2-bromophenyl)-4-methyl-5-(*o*-tolyl)indeno[2,1-*a*]indene (4e):

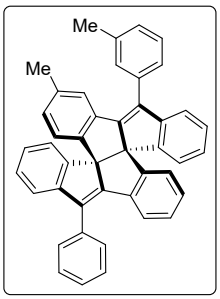
GP-1 was carried out with 1,2-bis(2-bromoaryl)ethyne **1a** (33.6 mg, 0.1 mmol), 1,2-diarylethyne **2h** (103 mg, 0.5 mmol), $Pd(OAc)_2$ (2.24 mg, 0.01 mmol), DPE-Phos (5.38 mg, 0.01 mmol), Cs_2CO_3 (97.5 mg, 0.3 mmol), and dry toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1), first starting material **2h** (66 mg, 80%) was recovered followed by the isolation of final product **4e** (13.8 mg, 30%), as yellow viscous oil [TLC control (petroleum ether/ethyl acetate 99:1), R_f(**1a**) = 0.7, R_f(**4e**) = 0.5, R_f(**2h**) = 0.9 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2921, 1728, 1439, 1266, 1093, 1025, 797, 742 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 7.4 Hz, 1H), 7.62 (d, J = 7.5 Hz, 1H), 7.43 – 7.34 (m, 3H), 7.34 – 7.27 (m, 5H), 7.09 (d, J = 7.5 Hz, 1H), 7.05 – 7.01 (m, 1H), 6.93 (ddd, J = 7.6, 7.6, 1.0 Hz, 1H), 6.71 (d, J = 7.5 Hz, 1H), 6.59 (d, J = 7.3 Hz, 1H), 2.36 (s, 3H), 1.62 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.0, 151.3, 147.9, 142.1, 136.8, 135.8, 134.2, 133.8, 133.3, 131.9, 131.1, 129.9, 129.8, 129.3, 129.0, 128.8, 128.6 (2C), 128.4, 127.8, 127.5, 127.2, 126.1, 125.4, 123.6, 122.8, 122.2, 119.8, 20.2, 19.4 ppm.

HRMS (ESI) *m/z*: $[M+2NH_4]^{+2}$ calcd for $[C_{30}H_{29}Br^{79}N_2]^{+2}$ 248.0752; found 248.0720; calcd for $[C_{30}H_{29}Br^{79}N_2]^{+2}$ 249.0741; found 249.0715.



Synthesis of (±5a):

GP-2b was carried out with *o*-bromophenyl indenoindene **4a** (43.3 mg, 0.1 mmol), 1,2-diarylethyne **2b** (41.2 mg, 0.2 mmol), $Pd(OAc)_2$ (2.24 mg, 0.01 mmol), DPE-Phos (5.38 mg, 0.01 mmol), Cs_2CO_3 (97.5 mg, 0.3 mmol), and dry toluene (1 mL). Purification of the crude

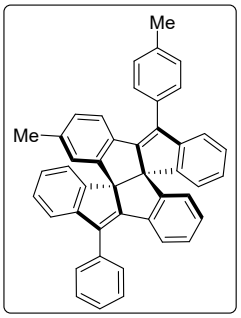
mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1) furnished the product **±5a** (30.7 mg, 55%), as off white solid; mp = 80–82 °C. [TLC control (petroleum ether/ethyl acetate 99:1), R_f(**4a**) = 0.6, R_f(**±5a**) = 0.5, R_f(**2b**) = 0.9 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2922, 2854, 1491, 1262, 1090, 1021, 734, 701 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.77 (m, 2H), 7.72 – 7.55 (m, 5H), 7.53 – 7.40 (m, 5H), 7.32 (d, J = 7.7 Hz, 1H), 7.19 (ddd, J = 7.6, 7.6, 0.8 Hz, 2H), 7.07 – 7.02 (m, 1H), 7.00 – 6.95 (m, 1H), 6.93 – 6.83 (m, 3H), 6.81 (d, J = 0.8 Hz, 2H), 6.56 (dd, J = 7.4, 3.7 Hz, 2H), 2.54 (s, 3H), 2.20 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 154.79, 154.65, 154.08, 151.01, 148.49, 148.35, 147.68, 147.52, 138.15, 137.23, 135.88, 135.75 (2C), 134.64, 134.51, 129.79, 129.25 (2C), 128.88, 128.85, 128.58 (3C), 128.48, 128.10, 127.79, 127.54, 127.14, 127.13, 126.46, 125.75, 125.66, 123.81, 123.68, 123.63, 123.54, 123.35, 122.76, 121.01, 120.93, 73.61, 73.11, 21.58, 21.47 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{44}H_{31}]^+$ 559.2420; found 559.2414.



Synthesis of (±5b):

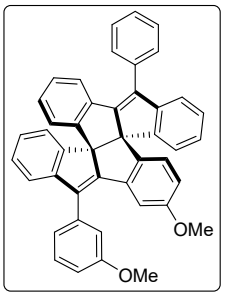
GP-2b was carried out with *o*-bromophenyl indenoindene **4a** (43.3 mg, 0.1 mmol), 1,2-diarylethyne **2c** (41.2 mg, 0.2 mmol), $Pd(OAc)_2$ (2.24 mg, 0.01 mmol), DPE-Phos (5.38 mg, 0.01 mmol), Cs_2CO_3 (97.5 mg, 0.3 mmol), and dry toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1) furnished the product **±5b** (28.5 mg, 51%), as off-white solid; mp = 300–302 °C. [TLC control (petroleum ether/ethyl acetate 99:1), R_f(**4a**) = 0.6, R_f(**±5b**) = 0.5, R_f(**2c**) = 0.9 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2923, 2852, 1589, 1458, 1255, 1034, 863, 794 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.81 (m, 2H), 7.72 (d, J = 8.0 Hz, 2H), 7.60 (dd, J = 7.4, 1.7 Hz, 3H), 7.51 – 7.44 (m, 4H), 7.40 (d, J = 7.8 Hz, 2H), 7.18 (dtd, J = 8.7, 7.6, 1.1 Hz, 2H), 7.07 – 7.02 (m, 1H), 6.97 (ddd, J = 7.4, 7.4, 1.0 Hz, 1H), 6.92 – 6.81 (m, 4H), 6.70 (s, 1H), 6.54 (dd, J = 8.3, 7.3 Hz, 2H), 2.50 (s, 3H), 2.13 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8, 154.3, 154.2, 153.9, 148.5, 148.2, 147.8, 147.5, 137.8 (2C), 135.8, 135.8, 134.9, 134.6, 133.3, 131.7, 129.2 (4C), 129.1 (2C), 128.6, 128.6 (2C), 128.1, 127.8, 127.5, 127.1 (2C), 125.7, 125.5, 124.4, 123.9, 123.7, 123.6, 122.7, 122.5, 120.9, 120.8, 73.6, 73.4, 21.5, 21.4 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{44}H_{31}]^+$ 559.2420; found 559.2433.



Synthesis of (±5c):

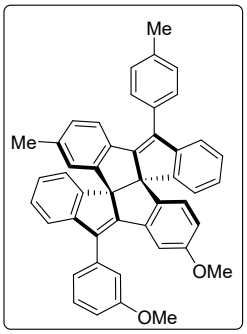
GP-2b was carried out with *o*-bromophenyl indenoindene **4c** (49.3 mg, 0.1 mmol), 1,2-diarylethyne **2a** (35.6 mg, 0.2 mmol), $Pd(OAc)_2$ (2.24 mg, 0.01 mmol), DPE-Phos (5.38 mg, 0.01 mmol), Cs_2CO_3 (97.5 mg, 0.3 mmol), and dry toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 99:1 to 98:2) furnished the product **±5c** (28.3 mg, 48%), as dark brown solid; mp = 62–64 °C. [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**4c**) = 0.5, R_f(**±5c**) = 0.4, R_f(**2a**) = 0.9 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2925, 2855, 1728, 1592, 1458, 1242, 1036, 748 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.78 (m, 2H), 7.60 (dd, J = 7.5, 7.5 Hz, 3H), 7.55 – 7.41 (m, 5H), 7.36 (dd, J = 2.4, 1.5 Hz, 1H), 7.21 – 7.13 (m, 3H), 7.08 – 7.02 (m, 2H), 6.98 (d, J = 1.1 Hz, 1H), 6.93 – 6.84 (m, 3H), 6.81 (d, J = 8.5 Hz, 1H), 6.62 – 6.46 (m, 3H), 3.94 (s, 3H), 3.65 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8, 159.2, 154.7, 154.6, 153.9, 148.6, 148.4, 147.4, 147.4, 145.9, 136.8, 135.8, 135.8, 135.8, 135.7, 134.6, 129.6, 129.2 (2C), 128.6 (2C), 128.1, 127.8, 127.6, 127.2, 127.1, 125.8, 125.8, 124.5, 123.8, 123.7 (2C), 122.8, 121.8, 121.1, 120.9, 114.49, 114.3, 113.9, 107.8, 73.8, 72.8, 55.4, 55.2 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{44}H_{31}O_2]^+$ 591.2319; found 591.2325.



Synthesis of (±5d):

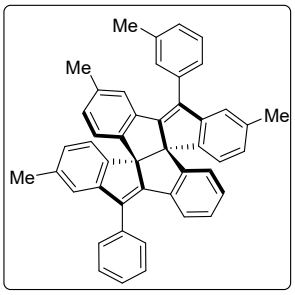
GP-2b was carried out with *o*-bromophenyl indenoindene **4c** (49.3 mg, 0.1 mmol), 1,2-diarylethyne **2c** (41.2 mg, 0.2 mmol), $Pd(OAc)_2$ (2.24 mg, 0.01 mmol), DPE-Phos (5.38 mg, 0.01 mmol), Cs_2CO_3 (97.5 mg, 0.3 mmol), and dry toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 99:1 to 98:2) furnished the product **±5d** (32.1 mg, 52%), as off-white solid; mp = 252–254 °C. [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**4c**) = 0.5, R_f(**±5d**) = 0.4, R_f(**2c**) = 0.9 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2923, 2858, 1728, 1459, 1259, 1021, 800, 746 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 7.9 Hz, 2H), 7.57 – 7.48 (m, 3H), 7.45 (d, J = 7.6 Hz, 2H), 7.40 (dd, J = 9.2, 4.7 Hz, 3H), 7.23 – 7.14 (m, 3H), 7.08 – 7.00 (m, 1H), 6.96 – 6.84 (m, 3H), 6.81 (d, J = 8.5 Hz, 1H), 6.71 (s, 1H), 6.62 – 6.44 (m, 3H), 3.95 (s, 3H), 3.66 (s, 3H), 2.50 (s, 3H), 2.15 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8, 159.1, 154.7, 154.2, 153.9, 148.5, 148.5, 147.7, 147.3, 146.2, 137.7, 137.7, 136.8, 135.9, 135.7, 134.8, 133.2, 131.8, 129.6, 129.2 (2C), 129.1 (2C), 128.6, 127.1, 127.0, 125.8, 125.5, 124.5, 124.3, 123.7, 123.5, 122.5, 121.8, 120.9, 120.8, 114.5, 114.2, 113.8, 107.7, 73.8, 72.9, 55.4, 55.2, 21.4, 21.4 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{46}H_{35}O_2]^+$ 619.2632; found 619.2616.



Synthesis of (±5e):

GP-2b was carried out with *o*-bromophenyl indenoindene **4d** (46.1 mg, 0.1 mmol), 1,2-diarylethyne **2b** (41.2 mg, 0.2 mmol), $Pd(OAc)_2$ (2.24 mg, 0.01 mmol), DPE-Phos (5.38 mg,

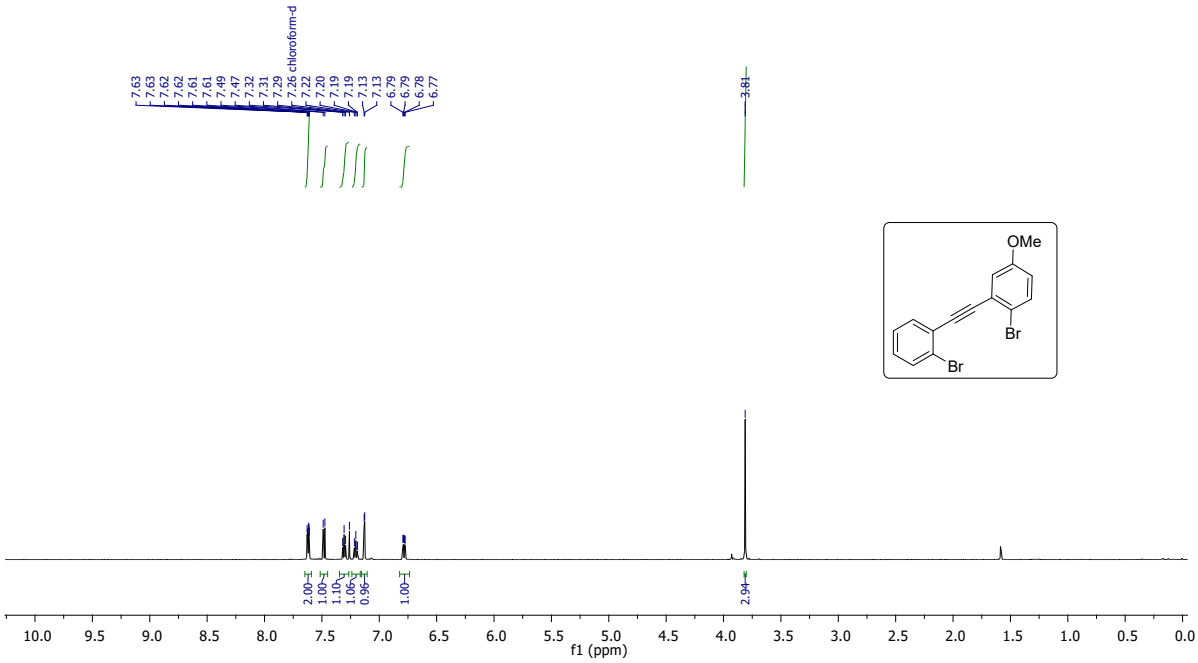
0.01 mmol), Cs_2CO_3 (97.5 mg, 0.3 mmol), and dry toluene (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1) furnished the product **±5e** (32.8 mg, 56%), as dark brown solid; mp = 88–90 °C. [TLC control (petroleum ether/ethyl acetate 99:1), R_f(**4d**) = 0.7, R_f(**±5e**) = 0.6, R_f(**2b**) = 0.9 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2922, 2856, 1599, 1455, 1260, 1031, 802, 745 cm^{-1}.

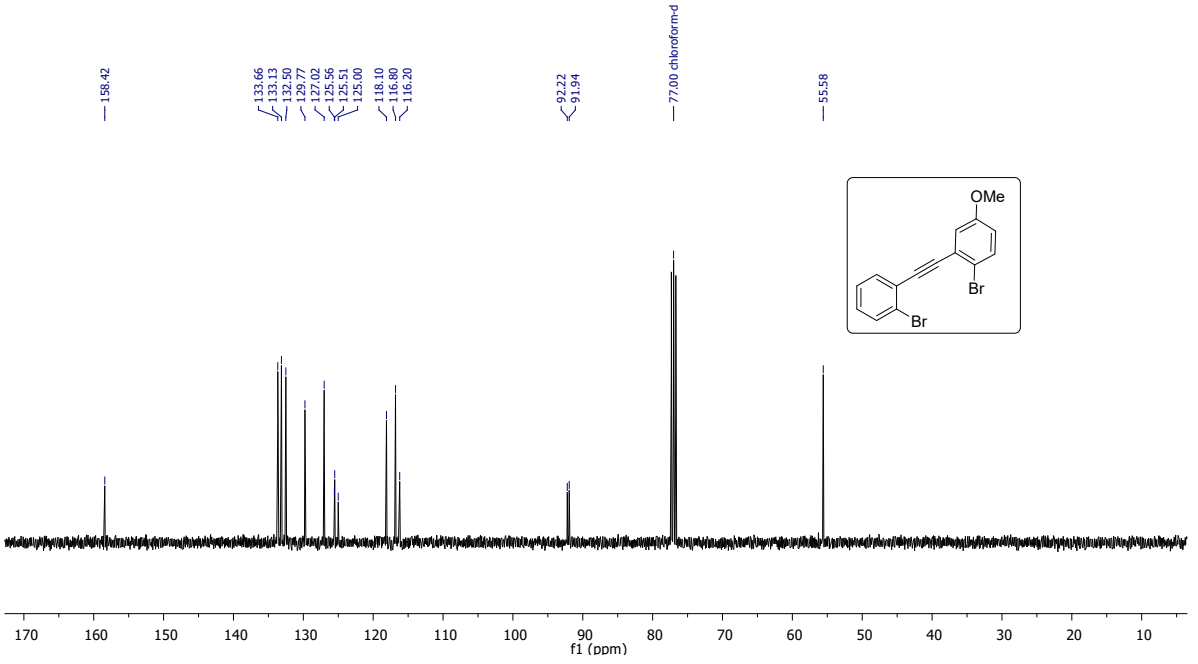
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 – 7.76 (m, 2H), 7.71 – 7.58 (m, 4H), 7.55 (d, J = 7.4 Hz, 1H), 7.50 (dd, J = 7.7, 7.7 Hz, 2H), 7.36 (s, 1H), 7.31 (d, J = 7.6 Hz, 1H), 7.25 (s, 2H), 7.04 – 7.00 (m, 1H), 6.96 (ddd, J = 7.5, 7.5, 1.1 Hz, 1H), 6.89 (d, J = 7.3 Hz, 1H), 6.79 (d, J = 0.8 Hz, 2H), 6.69 (dd, J = 8.0, 8.0 Hz, 2H), 6.45 (dd, J = 9.2, 7.5 Hz, 2H), 2.54 (s, 3H), 2.29 (2×s, 6H), 2.18 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.1, 154.9, 154.3, 151.3, 147.9, 147.7, 145.8, 145.6, 138.1, 137.1, 136.7, 136.7, 135.9, 135.8, 135.7, 135.7, 134.8, 134.7, 129.8, 129.3 (2C), 128.8 (2C), 128.6 (2C), 128.5, 128.0, 127.7, 127.40, 126.53 (2C), 126.4, 123.8, 123.5, 123.3, 123.3, 123.2, 122.7, 121.7, 121.7, 73.24, 72.7, 21.7, 21.6, 21.5 ppm.

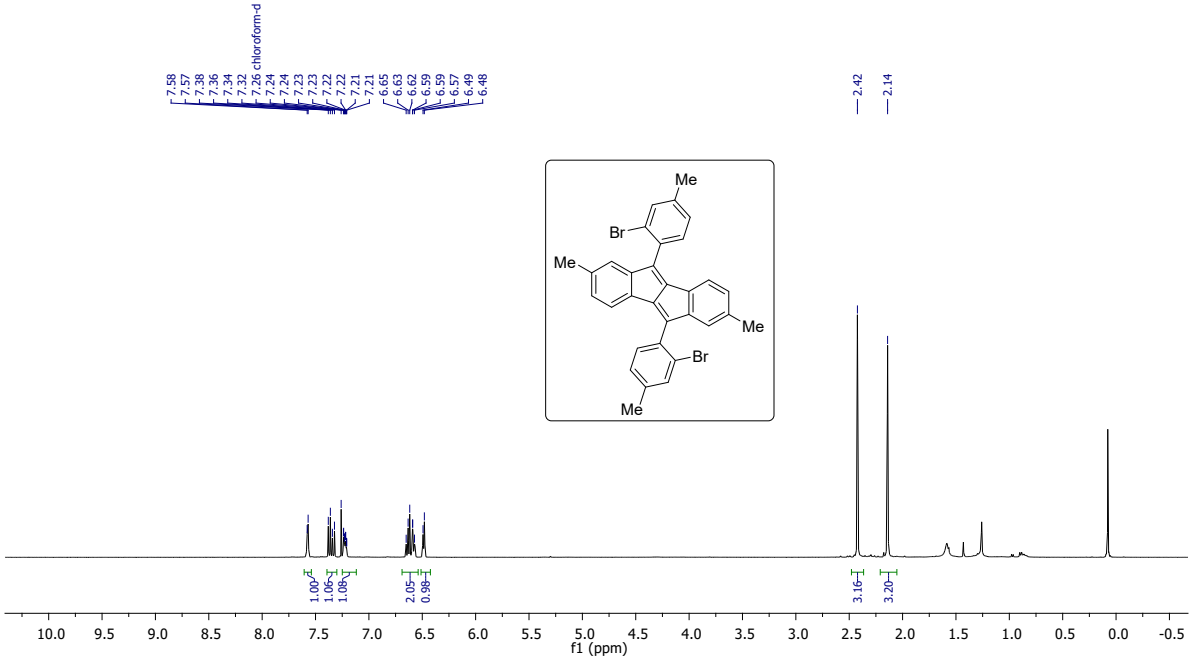
HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{46}H_{35}]^+$ 587.2733; found 587.2740.



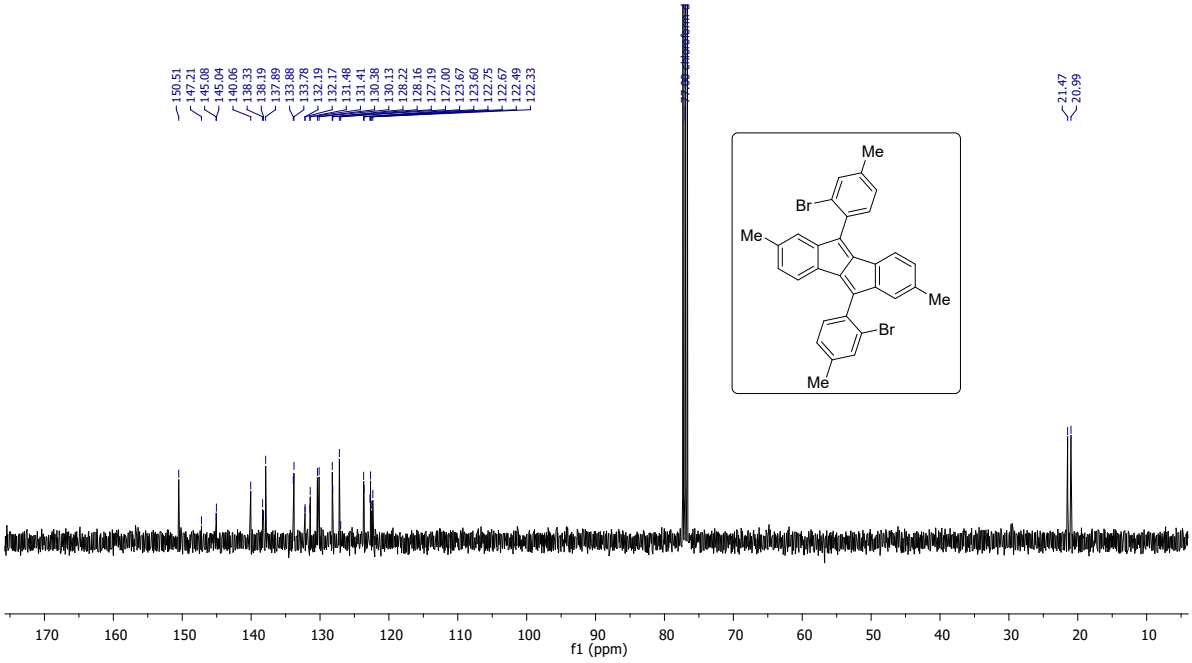
^{1}H NMR (600 MHz) spectrum of **1e** in $CDCl_3$



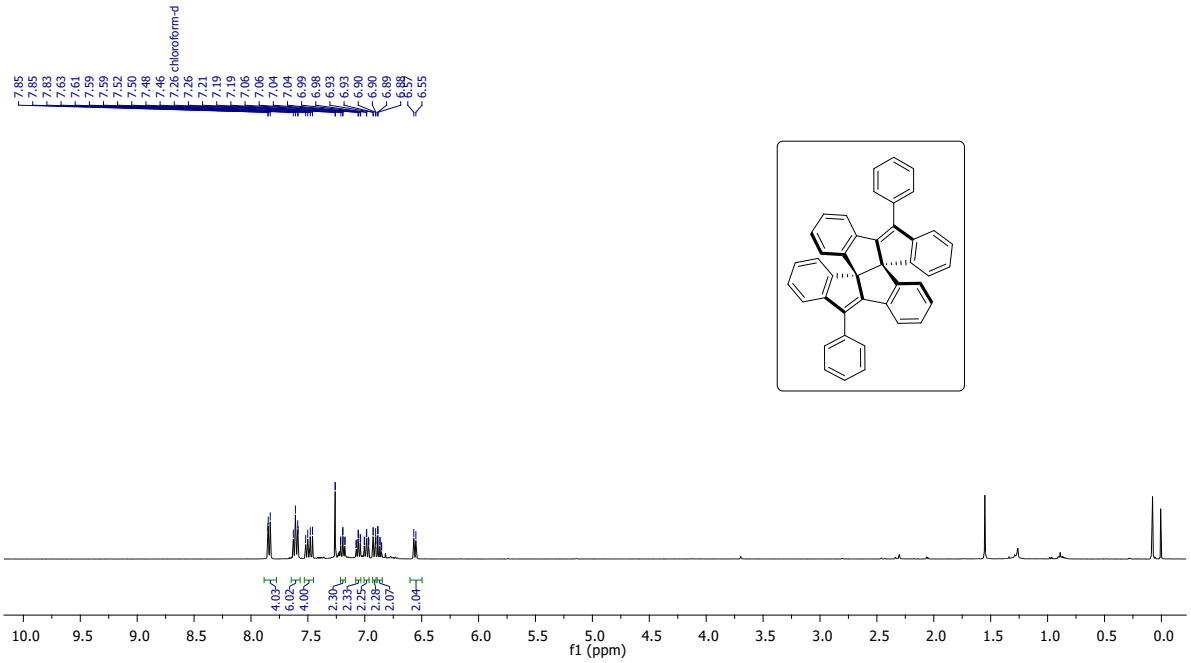
^{13}C{H} NMR (101 MHz) spectrum of **1e** in $CDCl_3$



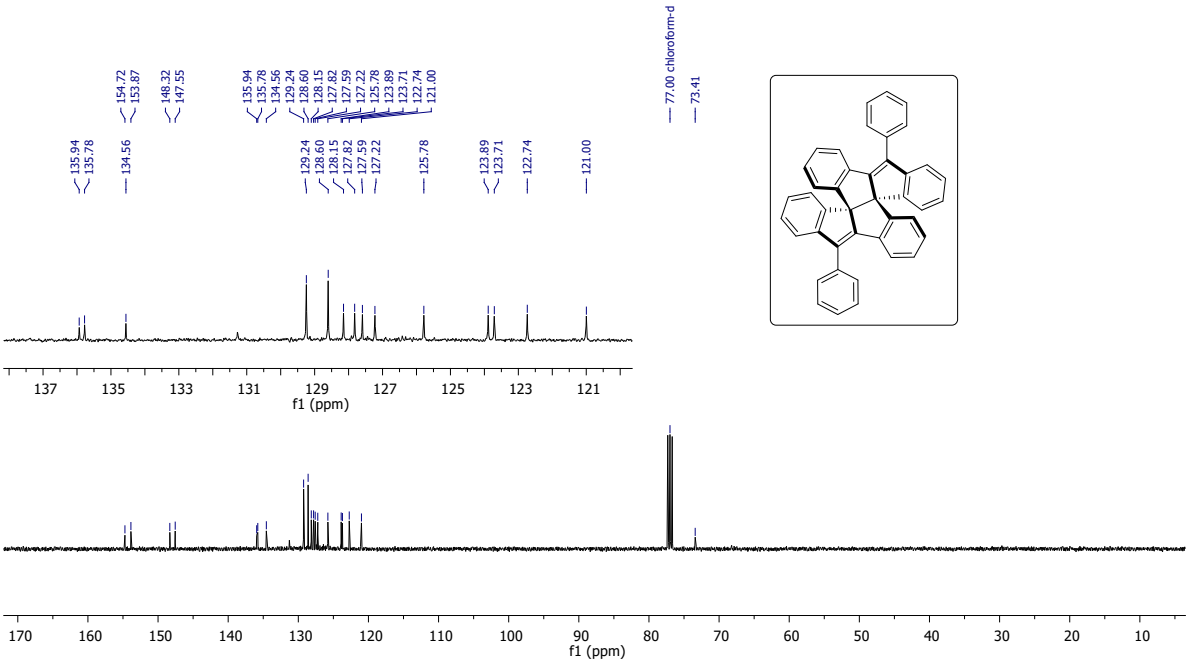
^{1}H NMR (400 MHz) spectrum of **6** in $CDCl_3$



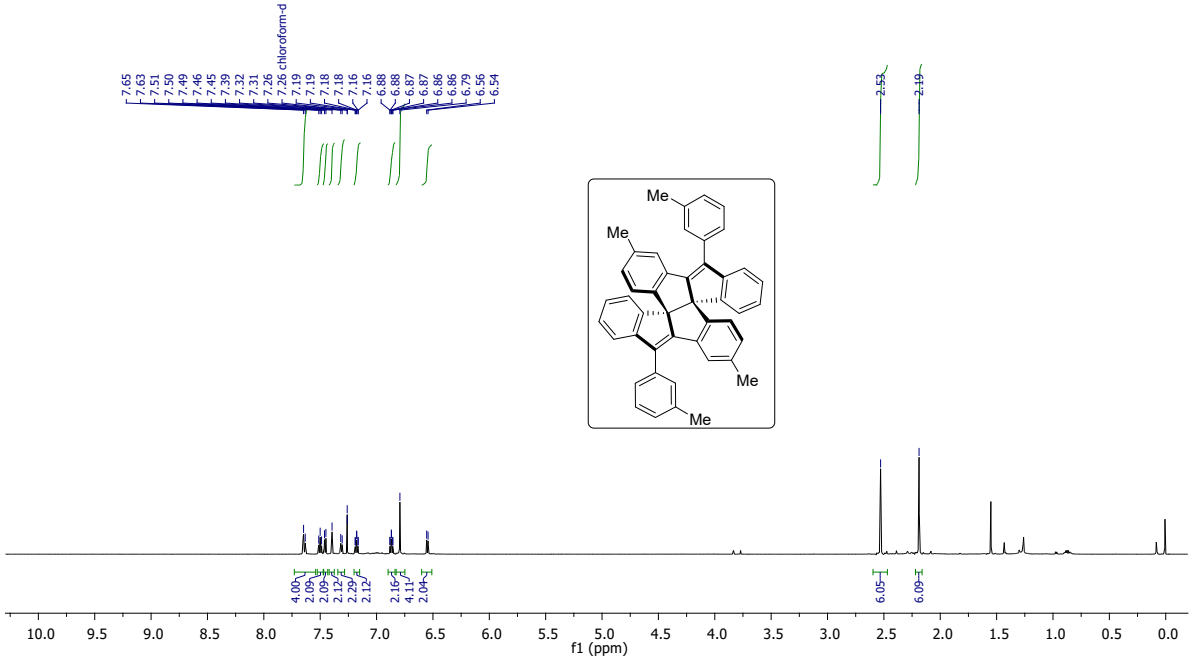
^{13}C{H} NMR (101 MHz) spectrum of **6** in $CDCl_3$



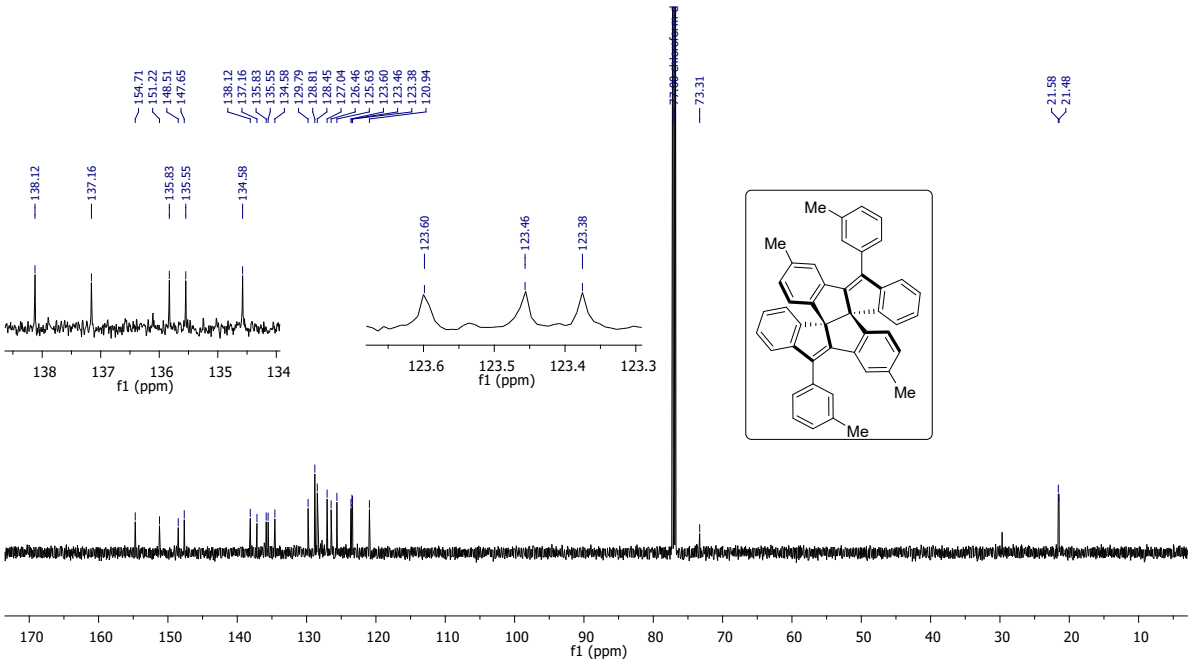
^{1}H NMR (400 MHz) spectrum of **3a** in $CDCl_3$



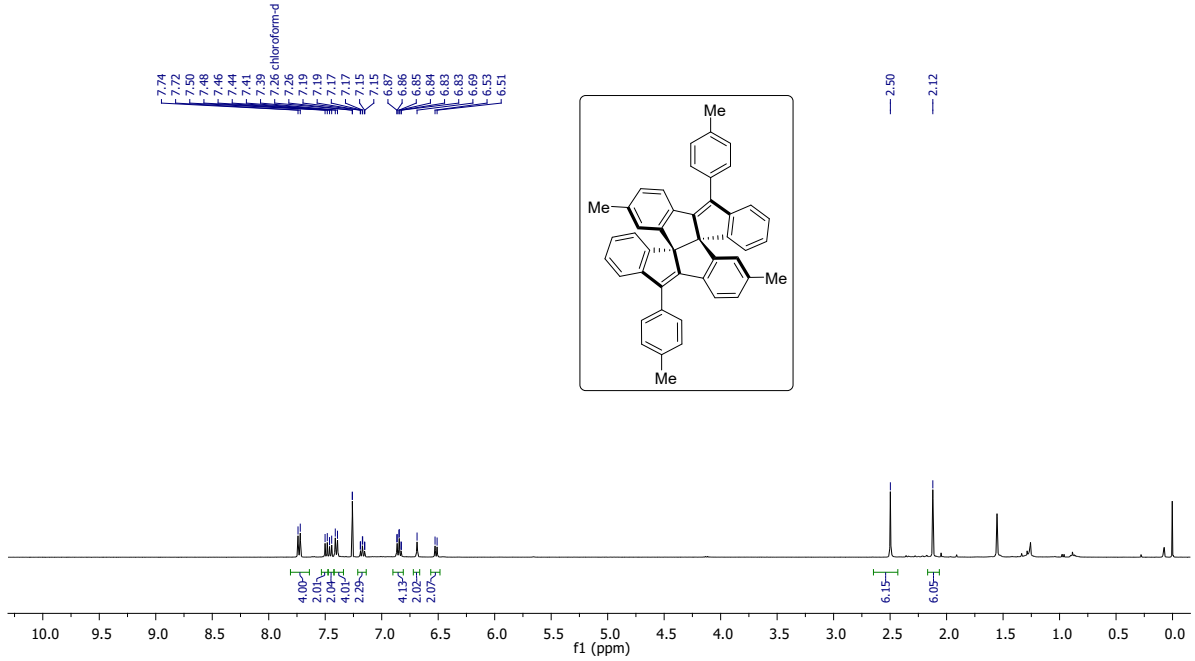
^{13}C{H} NMR (101 MHz) spectrum of **3a** in $CDCl_3$



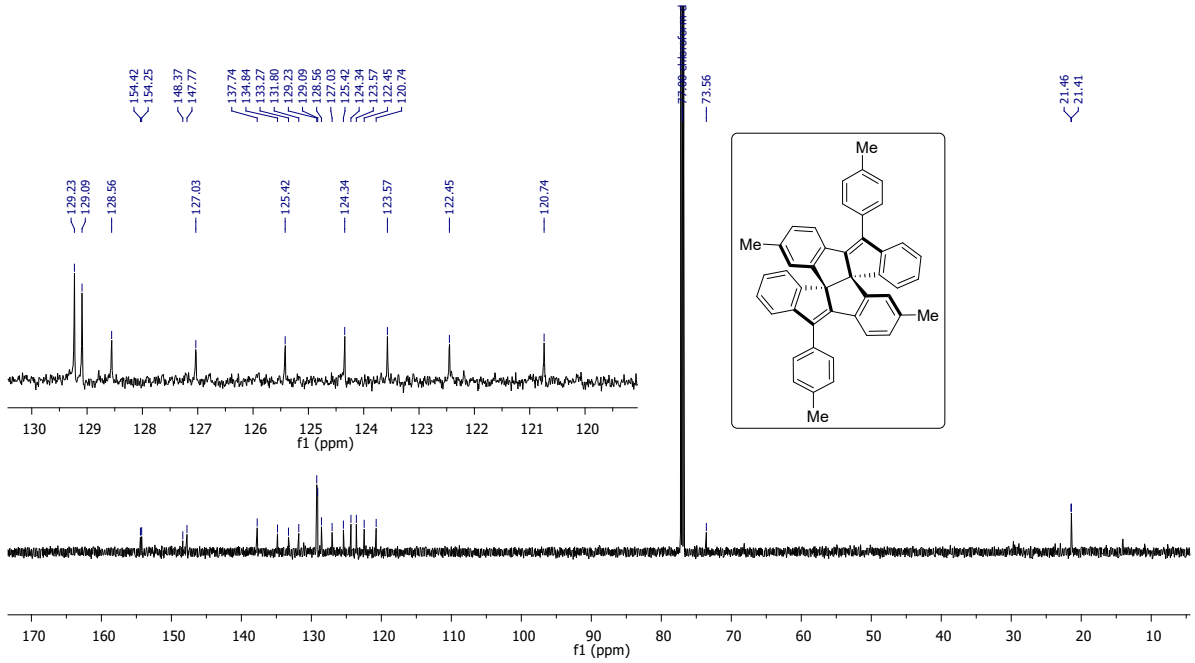
^{1}H NMR (600 MHz) spectrum of **3b** in $CDCl_3$



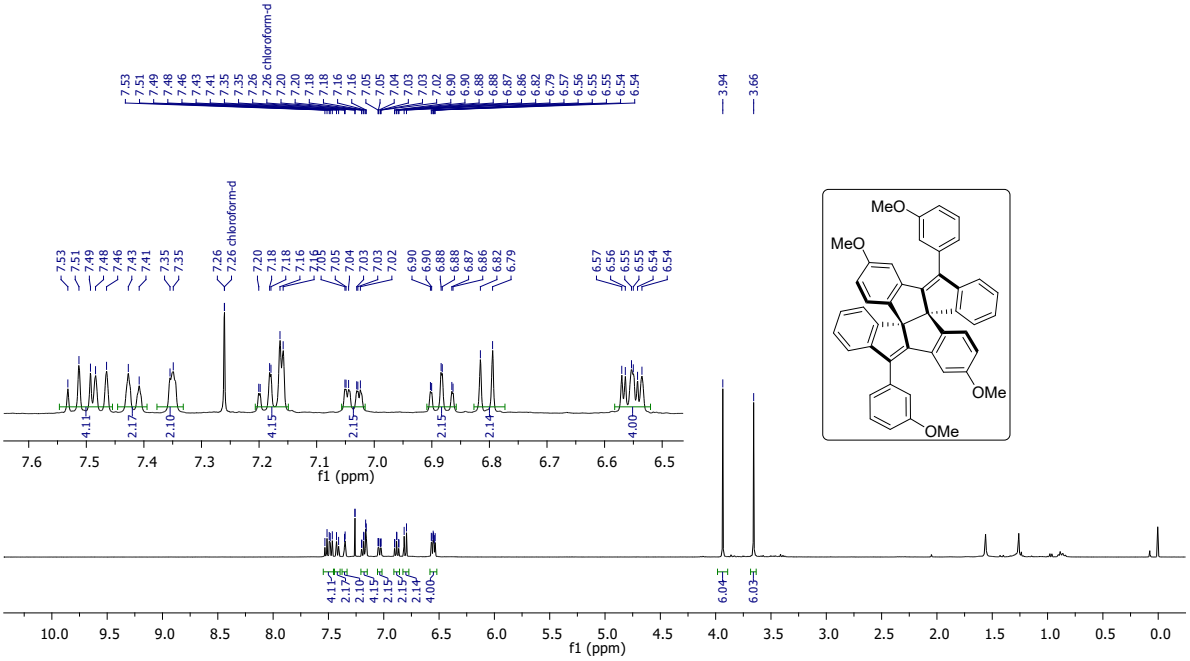
^{13}C{H} NMR (151 MHz) spectrum of **3b** in $CDCl_3$



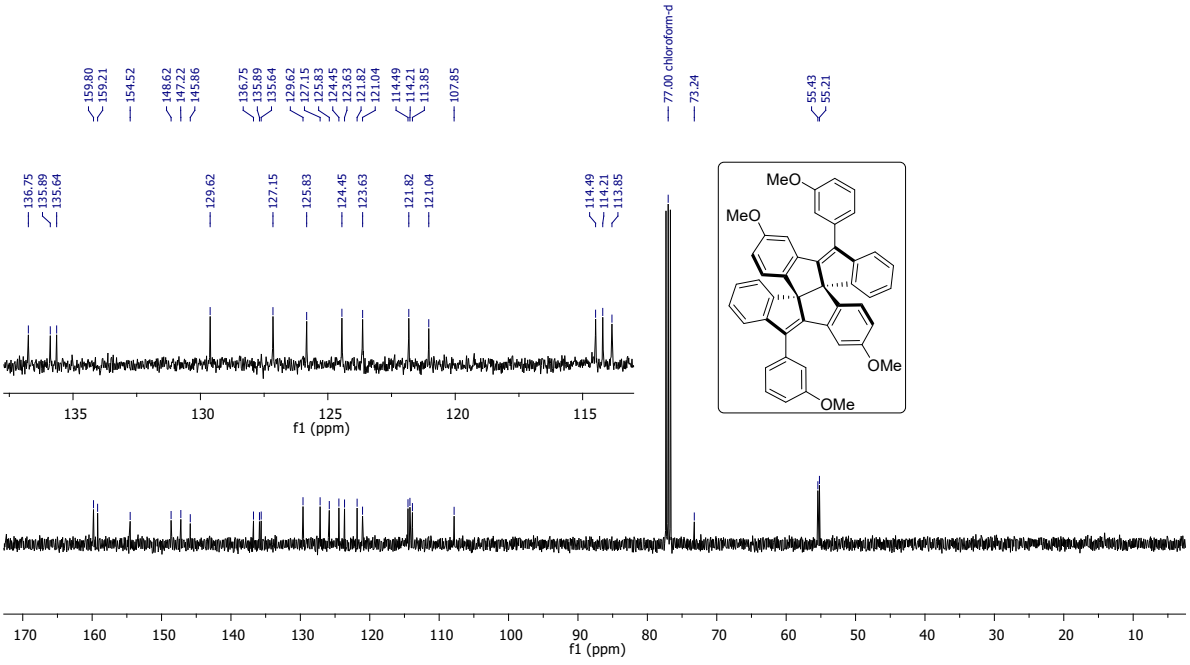
^{1}H NMR (400 MHz) spectrum of **3c** in $CDCl_3$



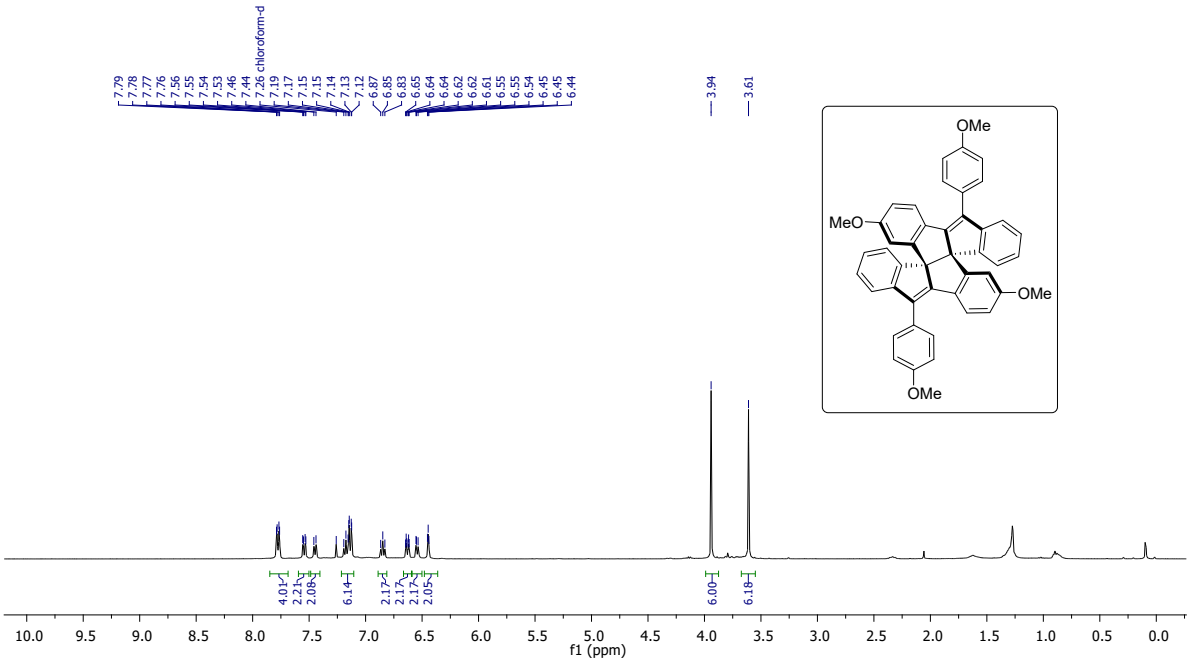
^{13}C{H} NMR (151 MHz) spectrum of **3c** in $CDCl_3$



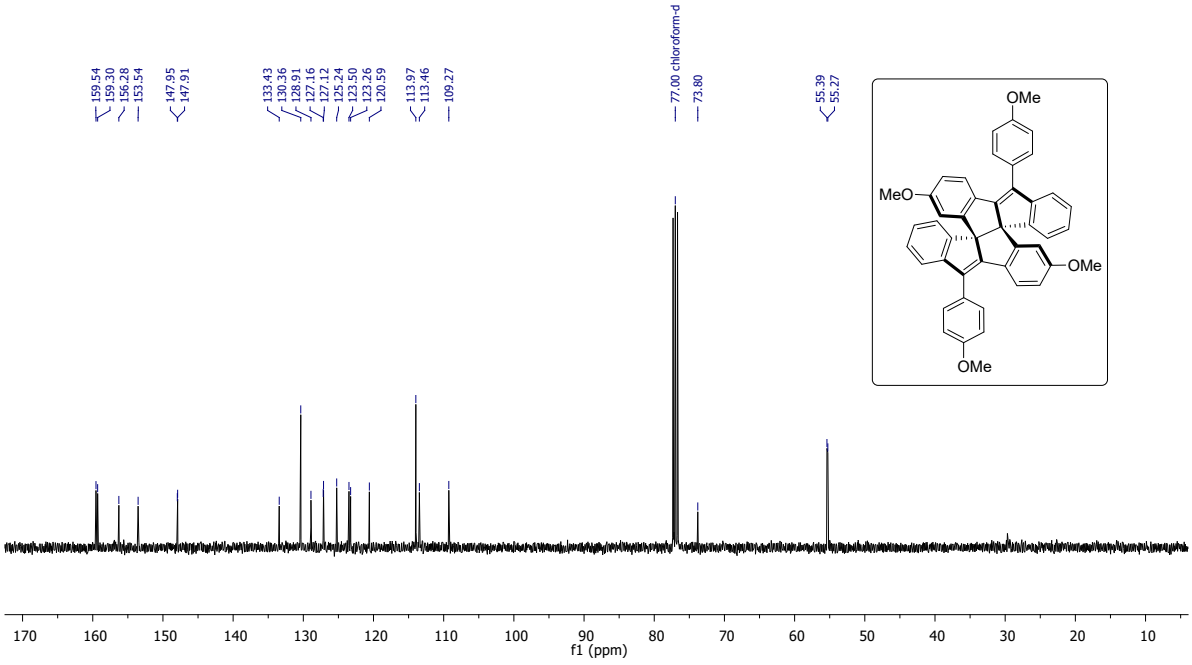
^{1}H NMR (400 MHz) spectrum of **3d** in $CDCl_3$



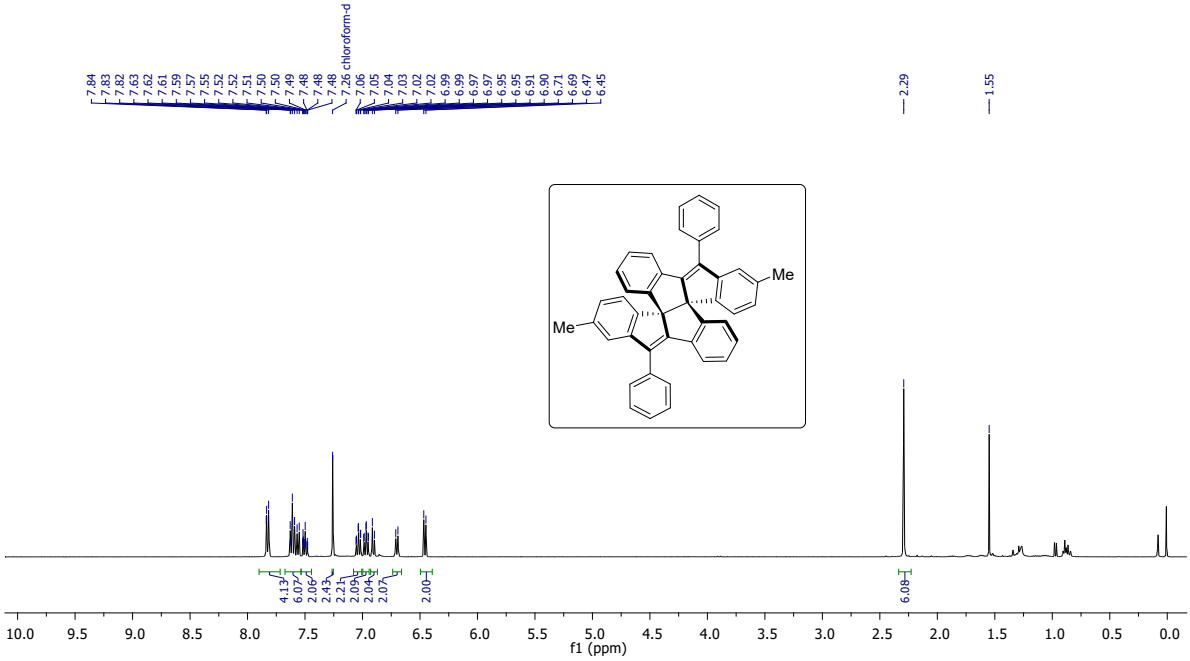
^{13}C{H} NMR (101 MHz) spectrum of **3d** in $CDCl_3$



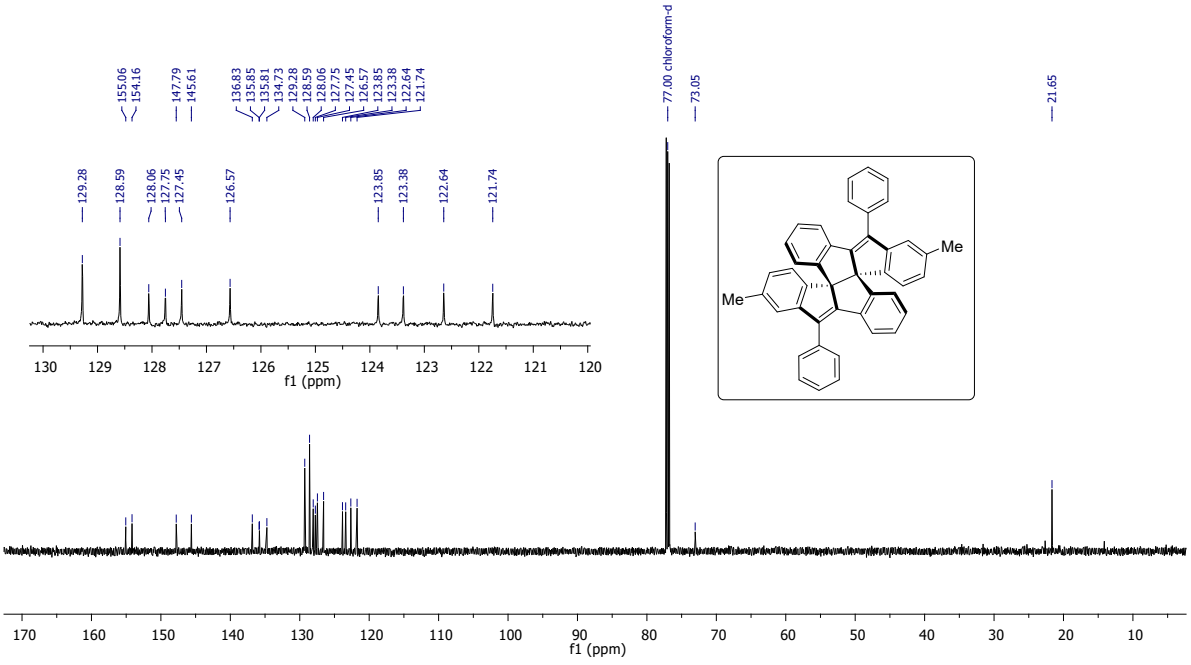
^{1}H NMR (400 MHz) spectrum of **3e** in $CDCl_3$



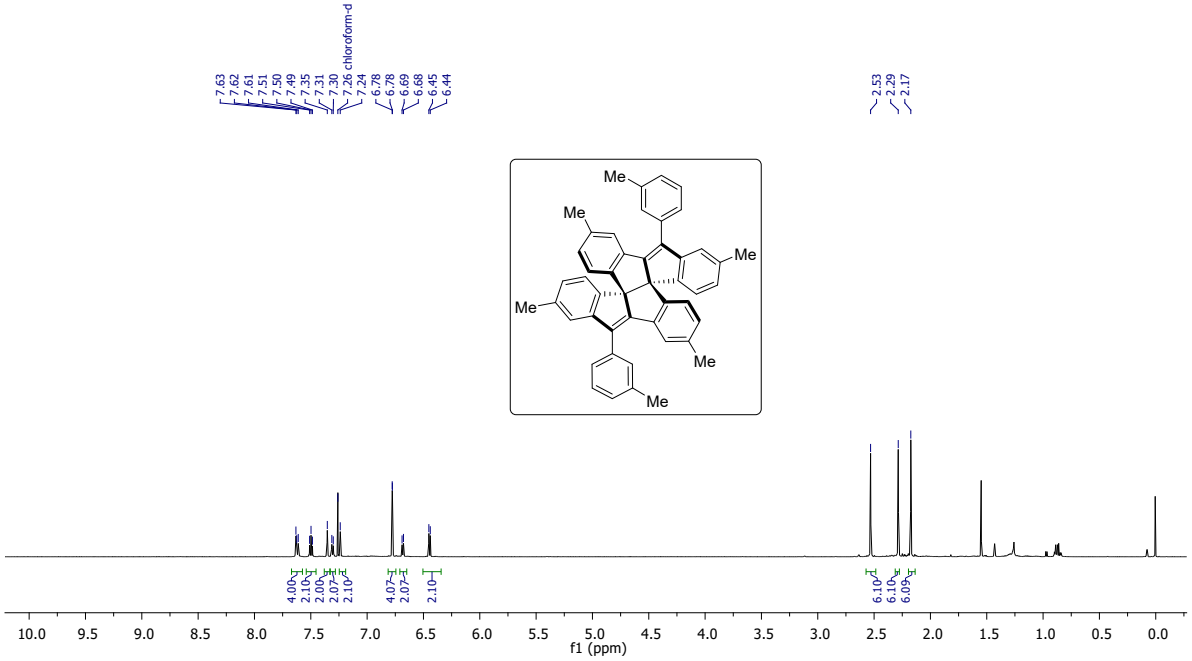
^{13}C{H} NMR (101 MHz) spectrum of **3e** in $CDCl_3$



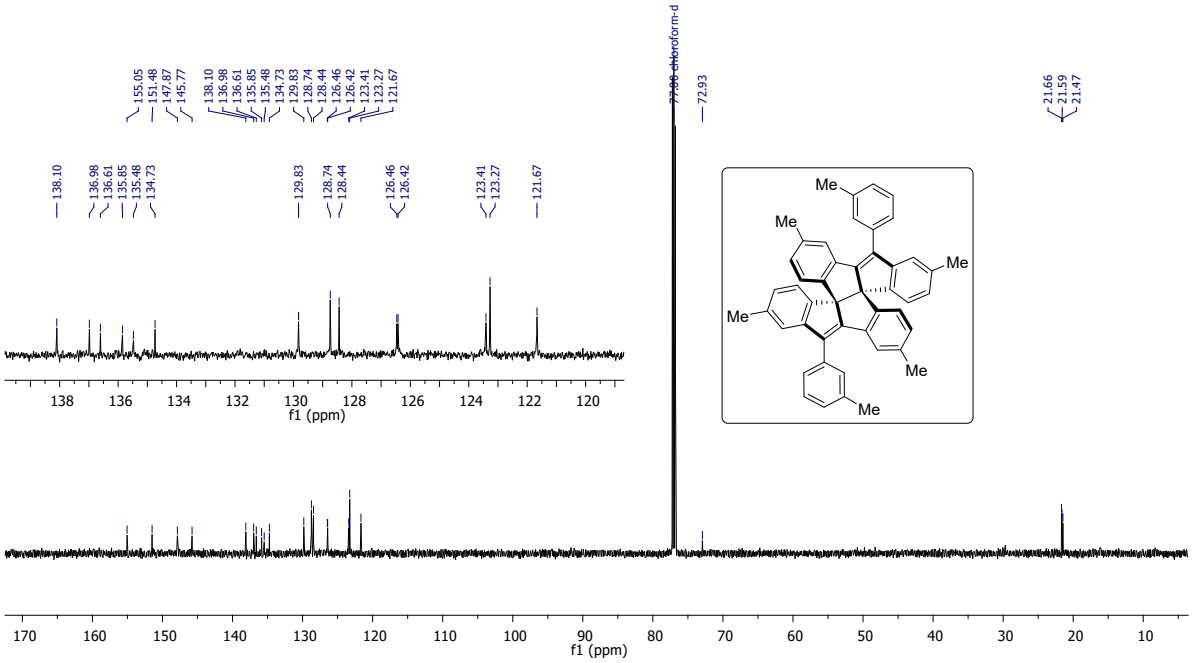
^{1}H NMR (400 MHz) spectrum of **3f** in $CDCl_3$



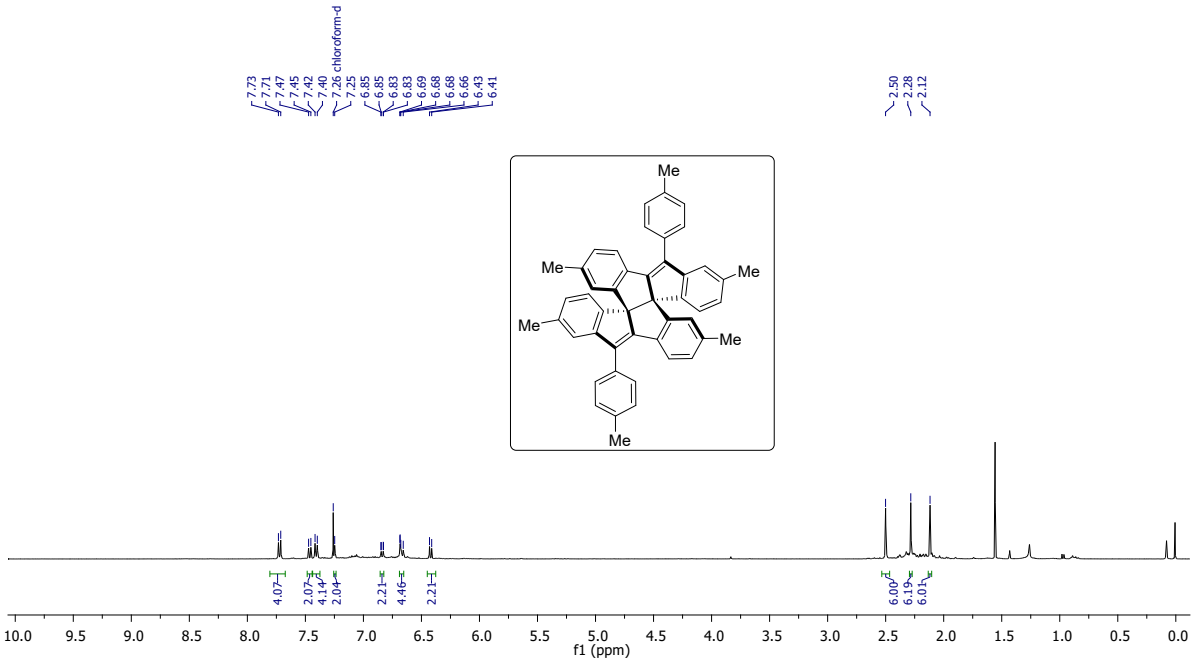
^{13}C{H} NMR (151 MHz) spectrum of **3f** in $CDCl_3$



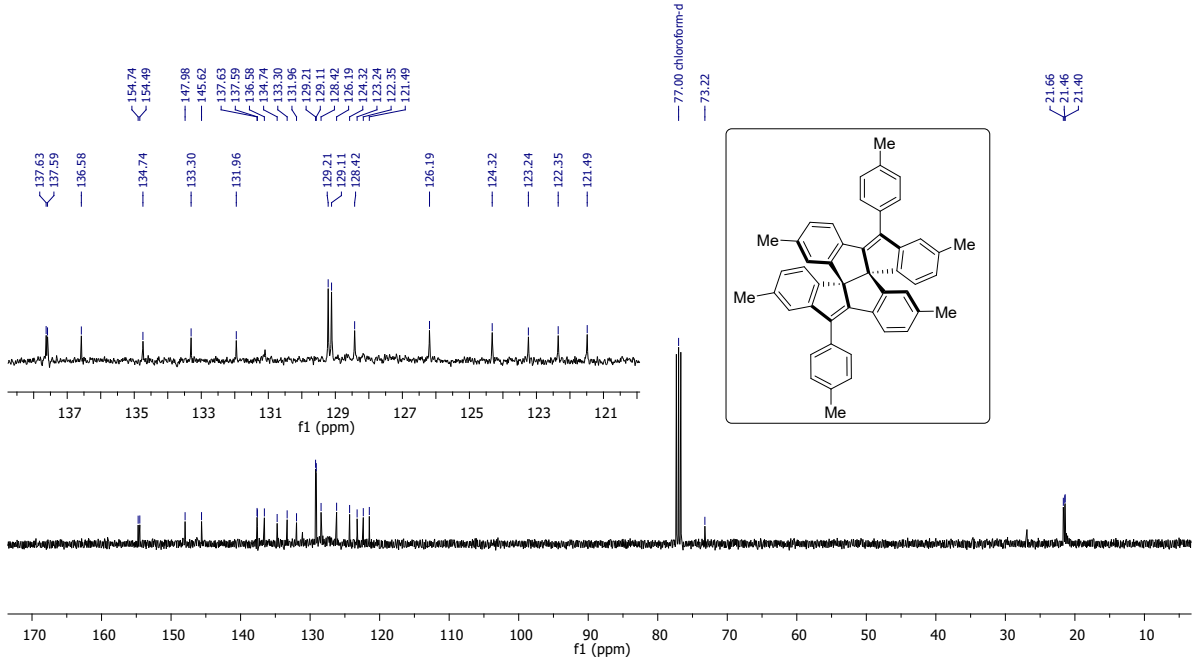
^{1}H NMR (600 MHz) spectrum of **3g** in $CDCl_3$



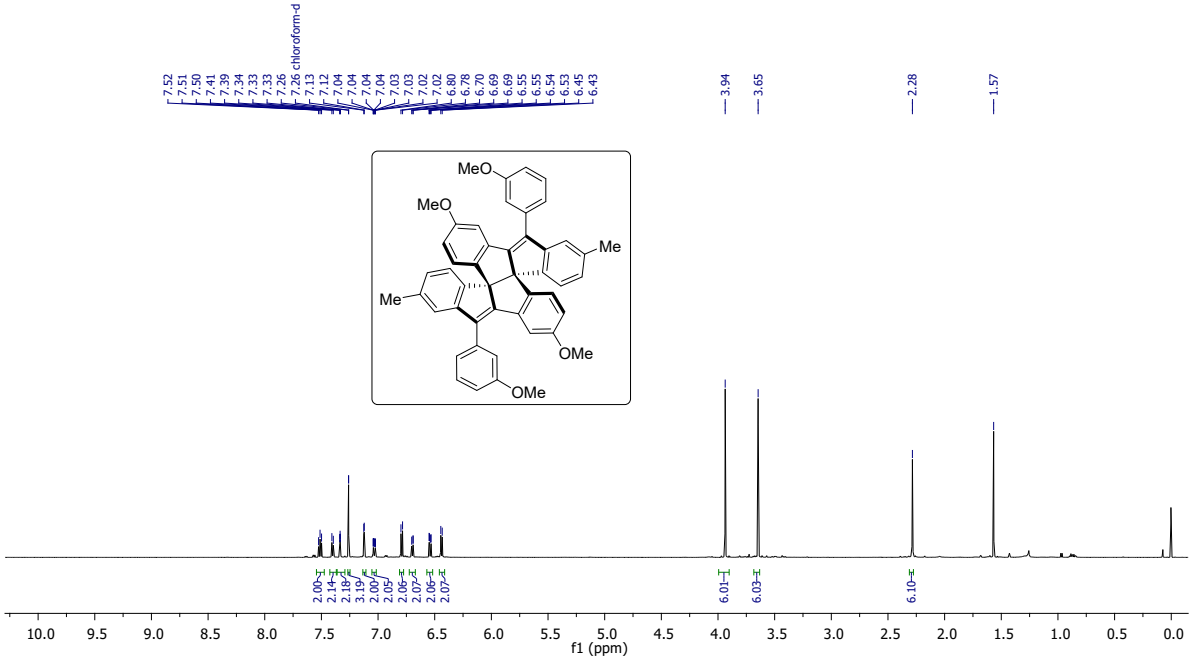
^{13}C{H} NMR (151 MHz) spectrum of **3g** in $CDCl_3$



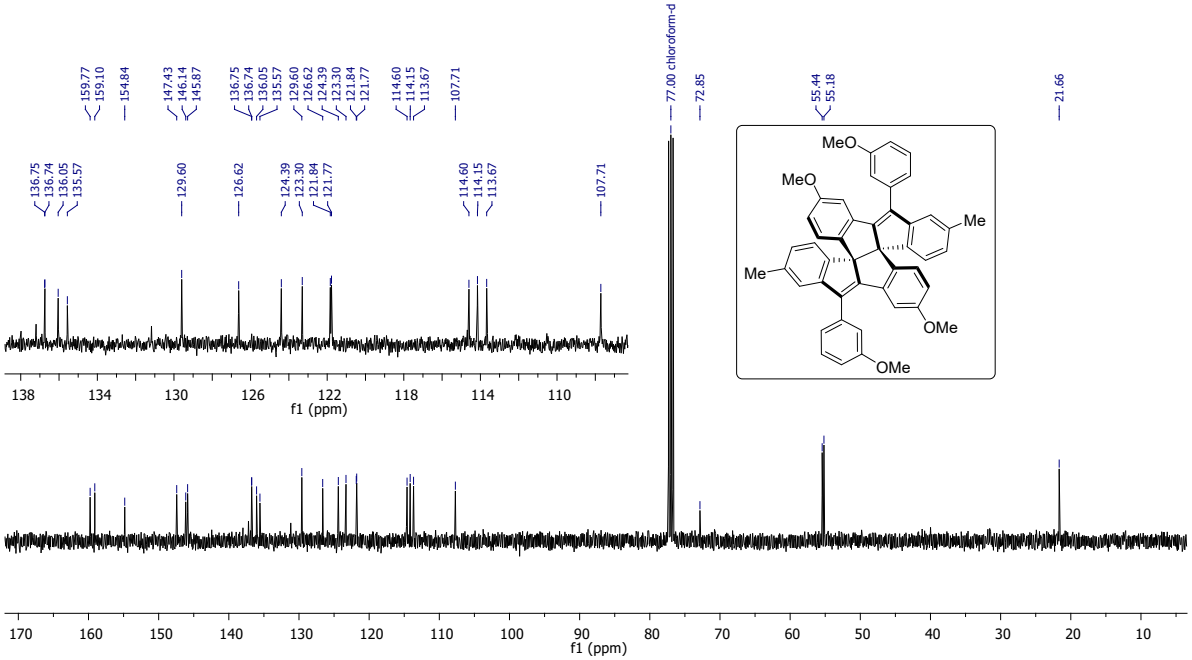
^{1}H NMR (400 MHz) spectrum of **3h** in $CDCl_3$



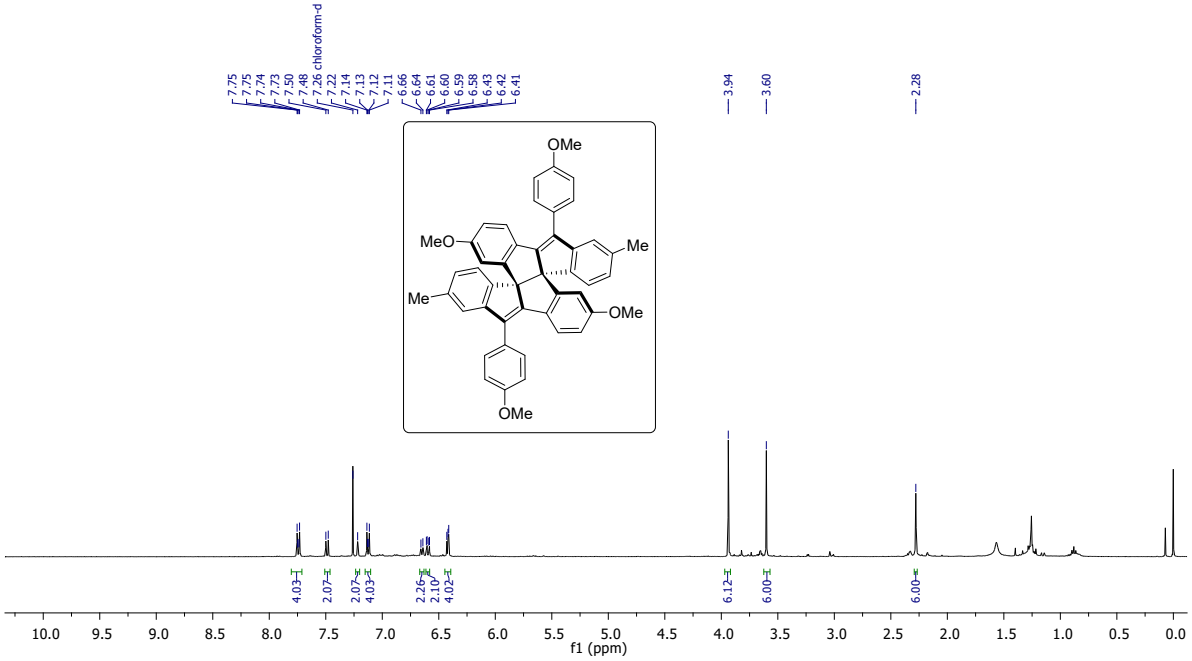
^{13}C{H} NMR (101 MHz) spectrum of **3h** in $CDCl_3$



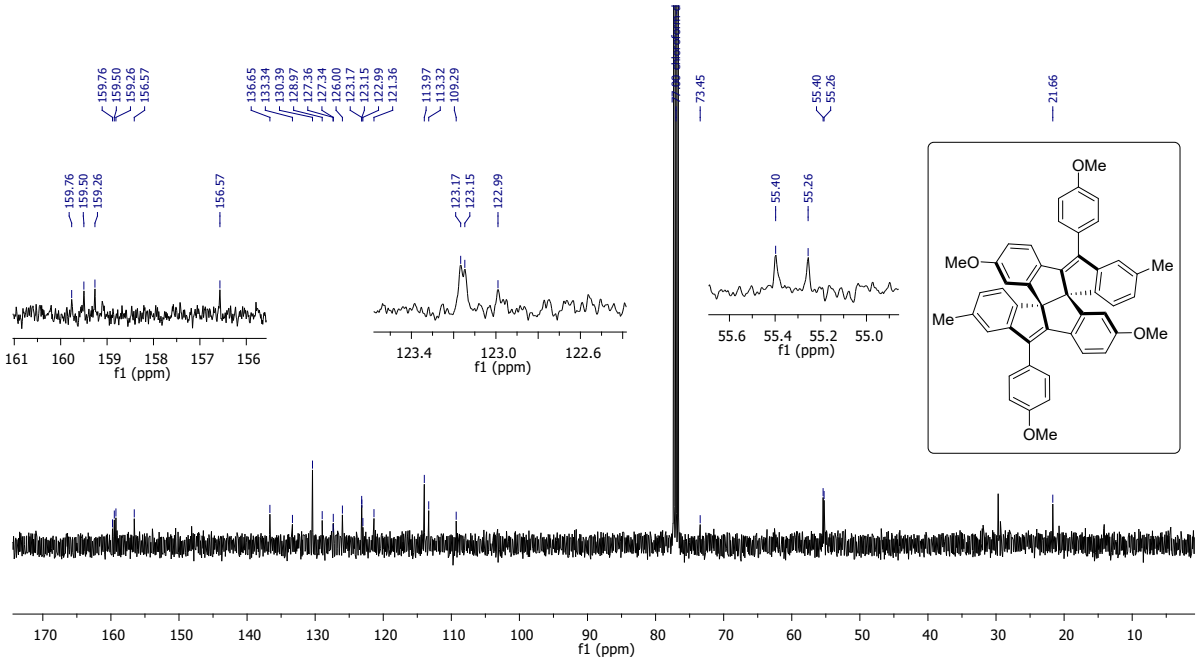
^{1}H NMR (600 MHz) spectrum of **3i** in $CDCl_3$



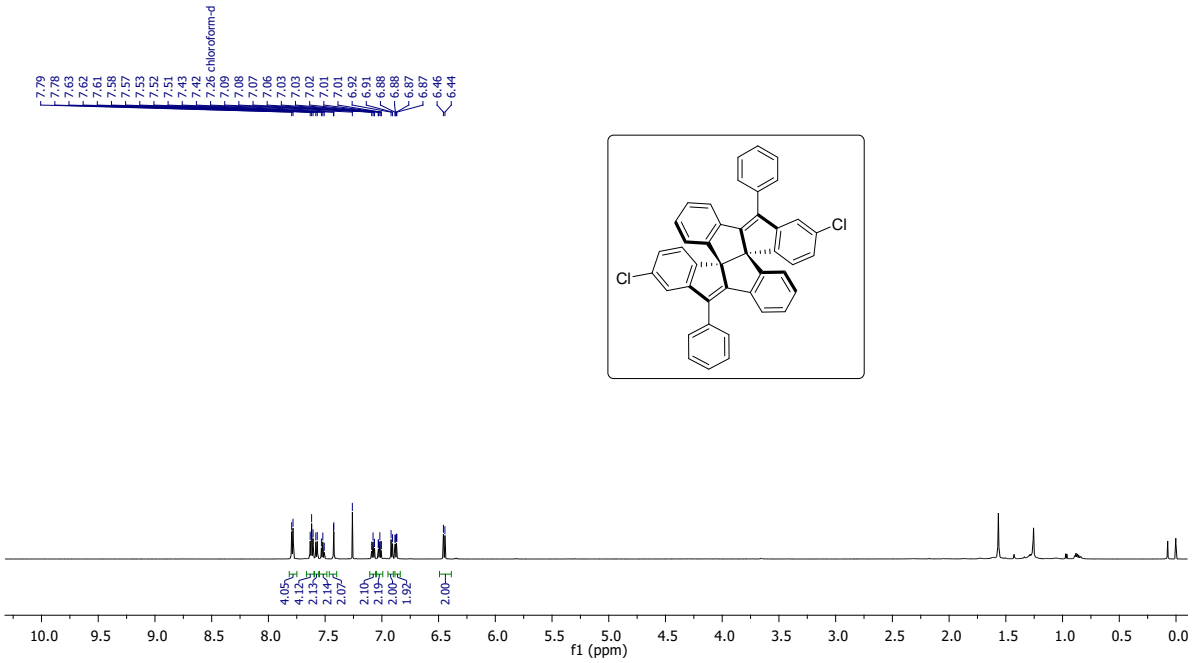
^{13}C{H} NMR (101 MHz) spectrum of **3i** in $CDCl_3$



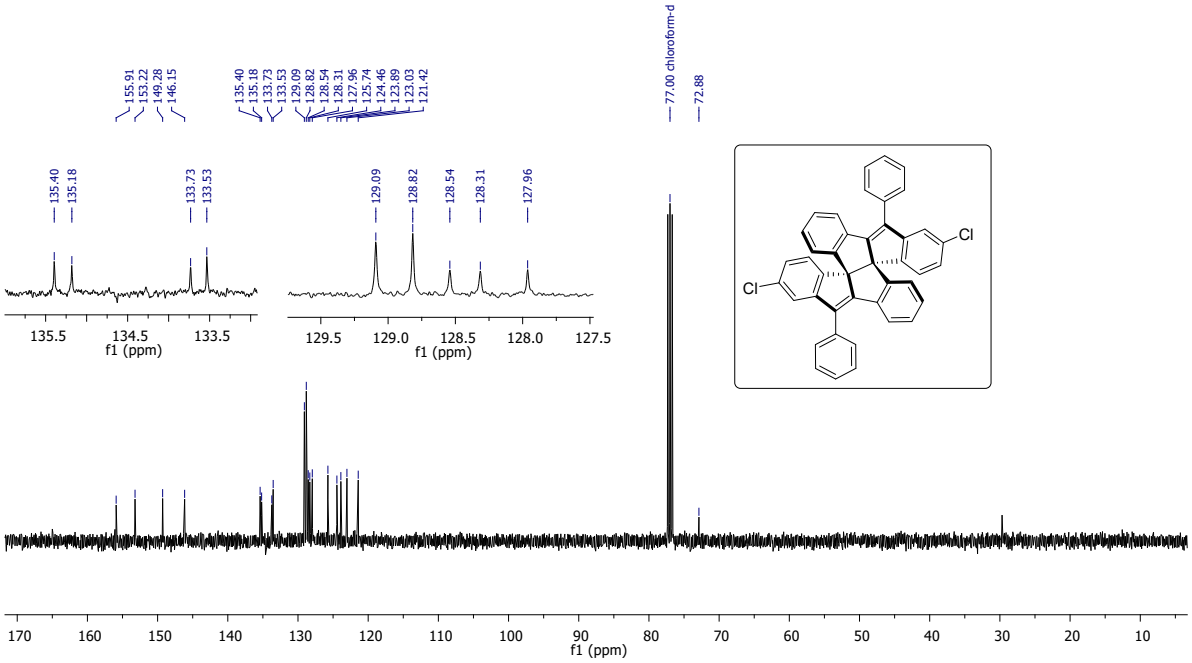
^{1}H NMR (400 MHz) spectrum of **3j** in $CDCl_3$



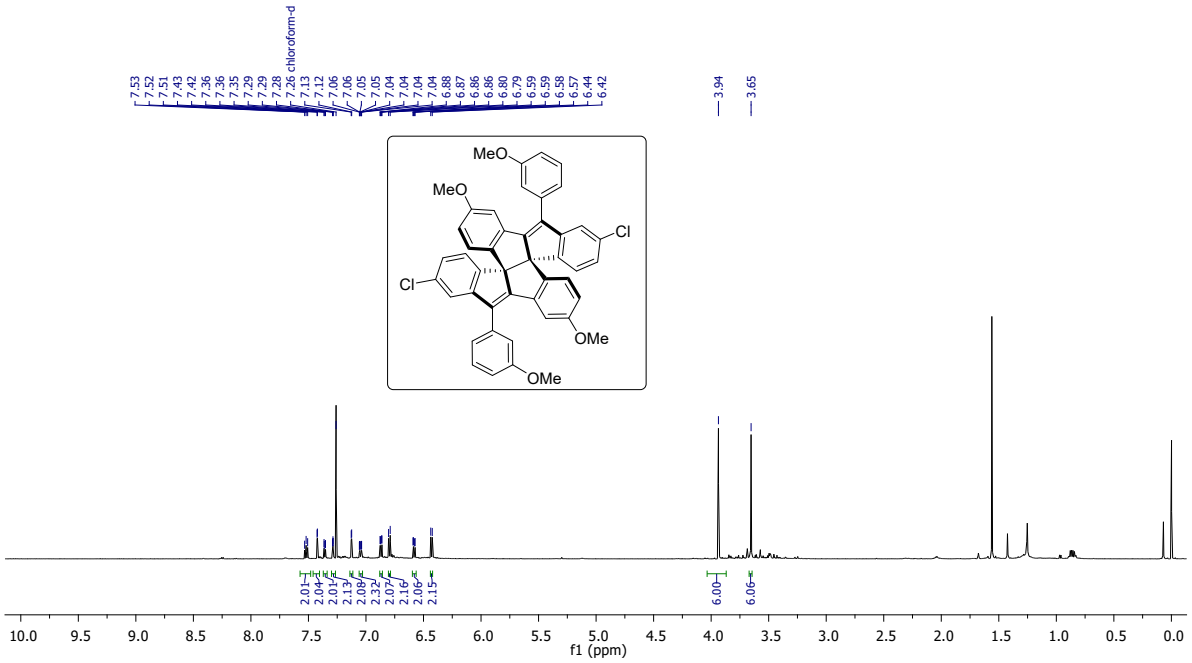
^{13}C{H} NMR (101 MHz) spectrum of **3j** in $CDCl_3$



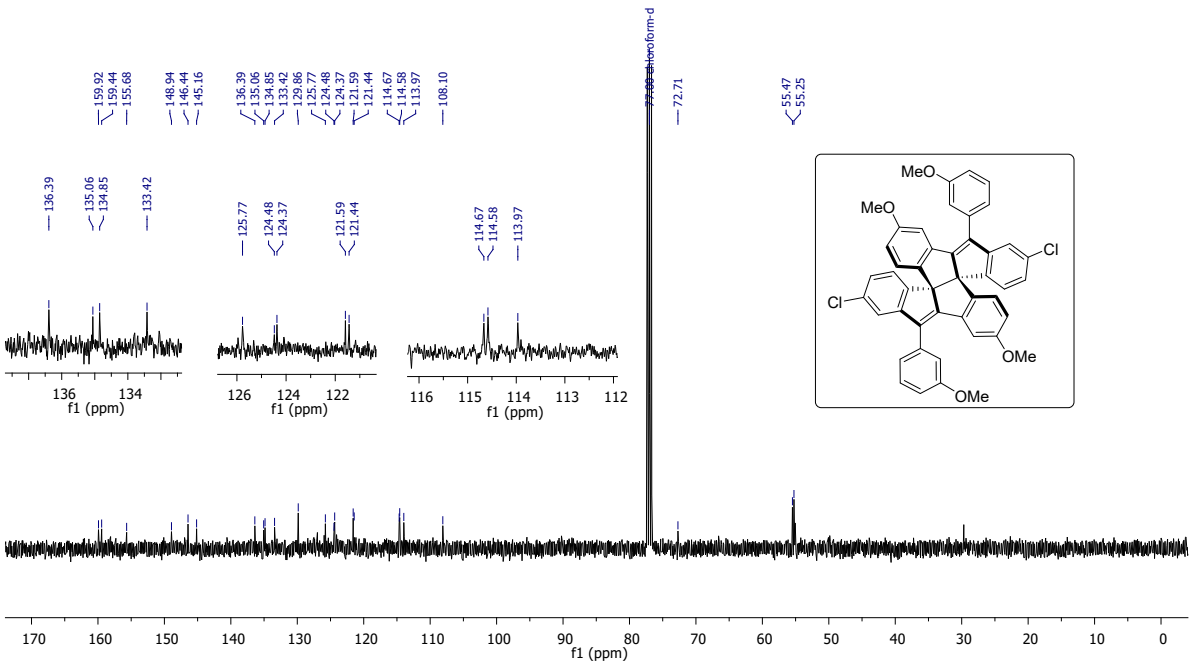
^{1}H NMR (600 MHz) spectrum of **3k** in $CDCl_3$



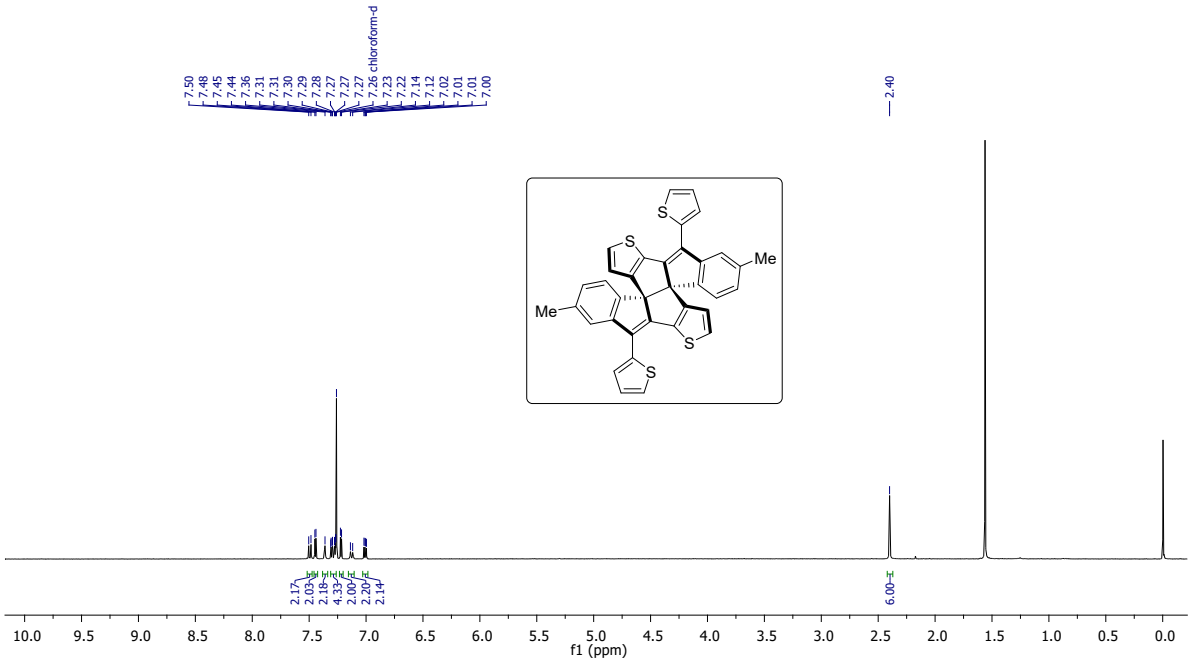
^{13}C{H} NMR (101 MHz) spectrum of **3k** in $CDCl_3$



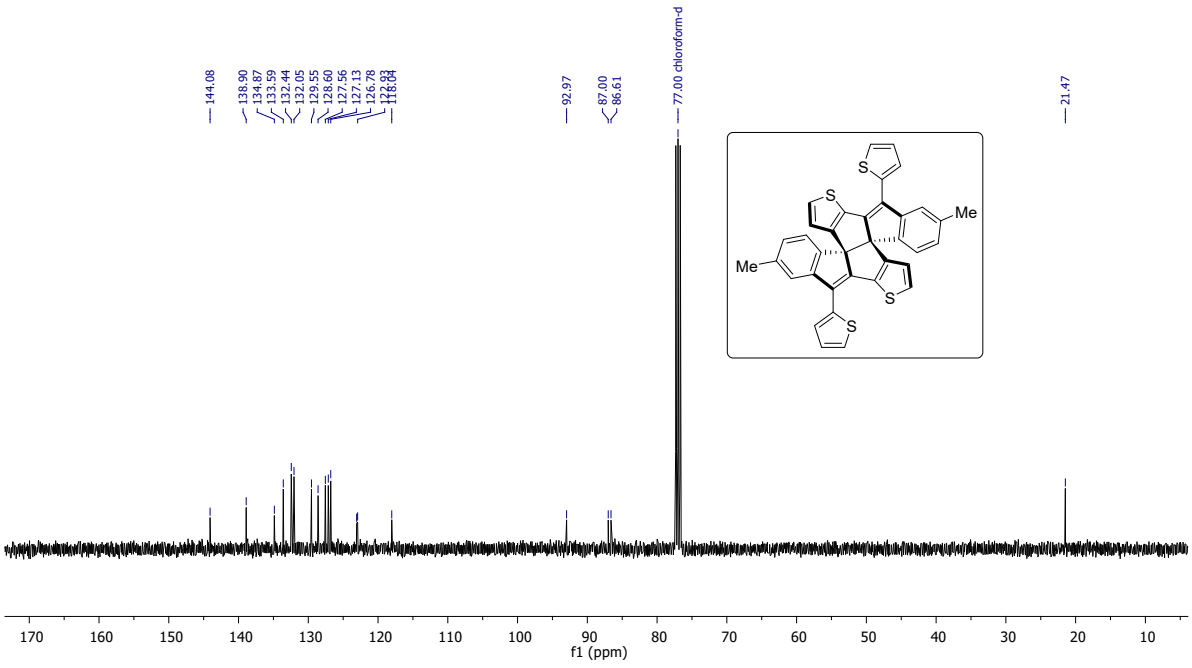
^{1}H NMR (600 MHz) spectrum of **3l** in $CDCl_3$



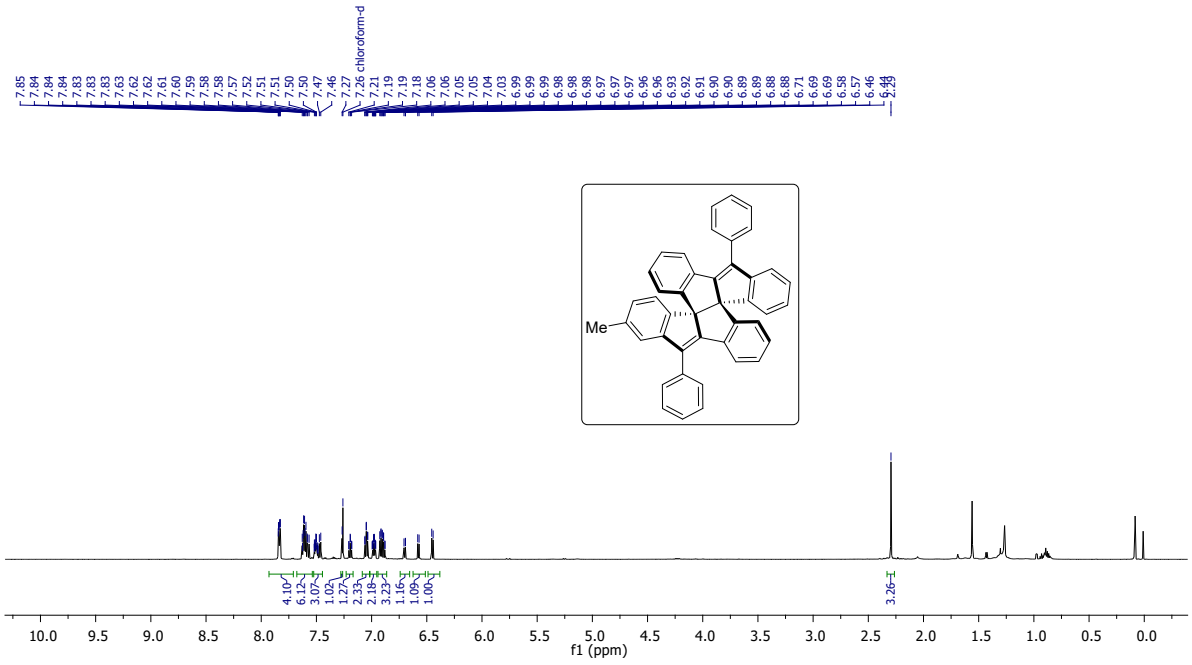
^{13}C{H} NMR (101 MHz) spectrum of **3l** in $CDCl_3$



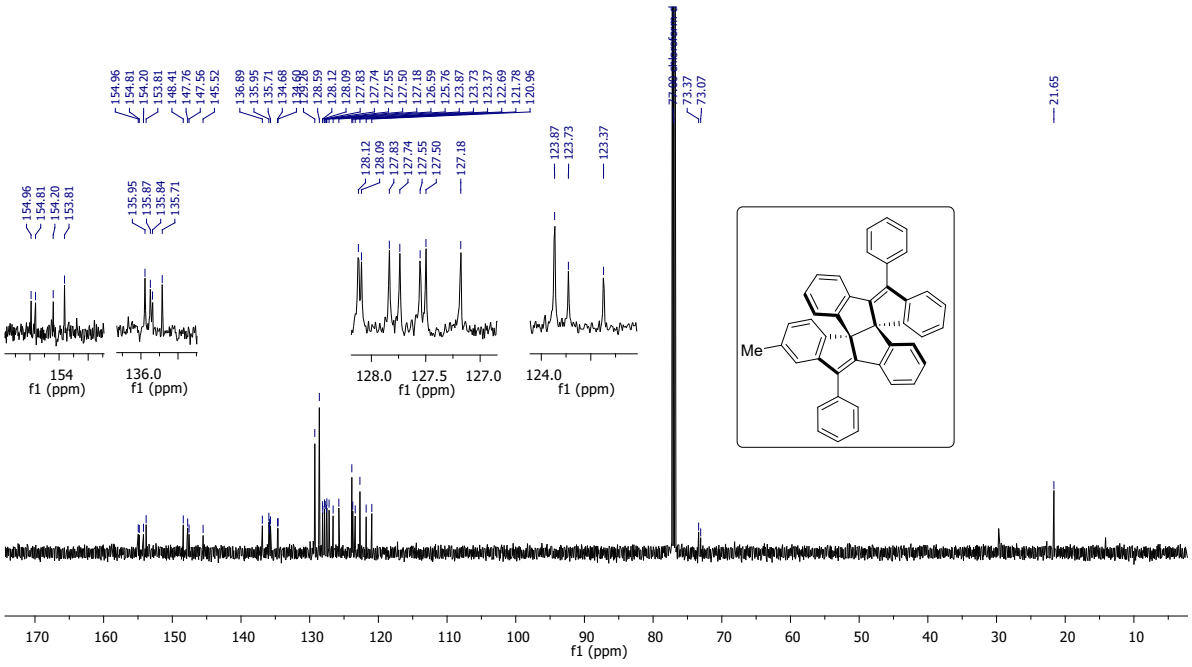
^{1}H NMR (400 MHz) spectrum of **3m** in $CDCl_3$



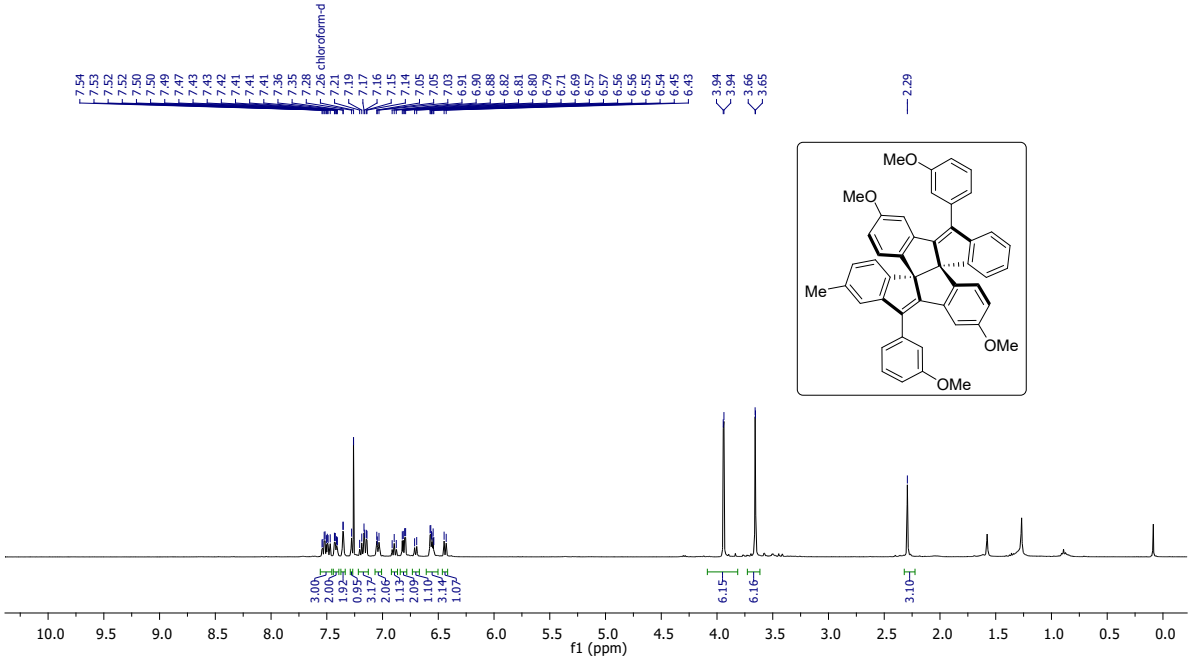
^{13}C{H} NMR (101 MHz) spectrum of **3m** in $CDCl_3$



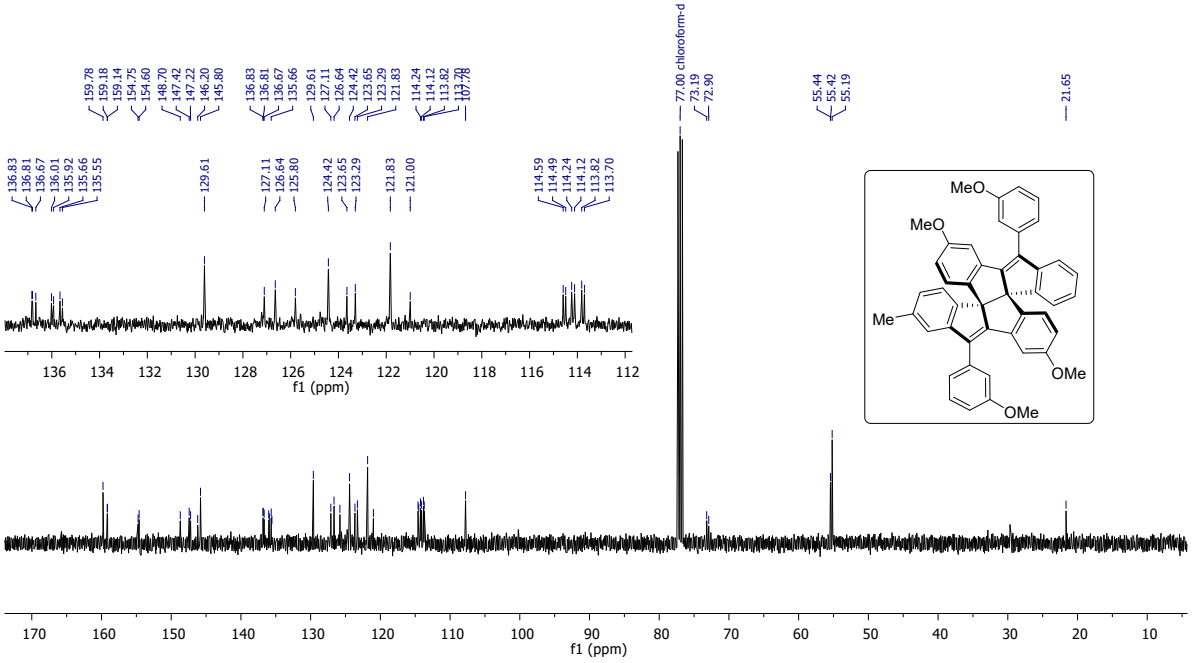
^{1}H NMR (600 MHz) spectrum of **3o** in $CDCl_3$



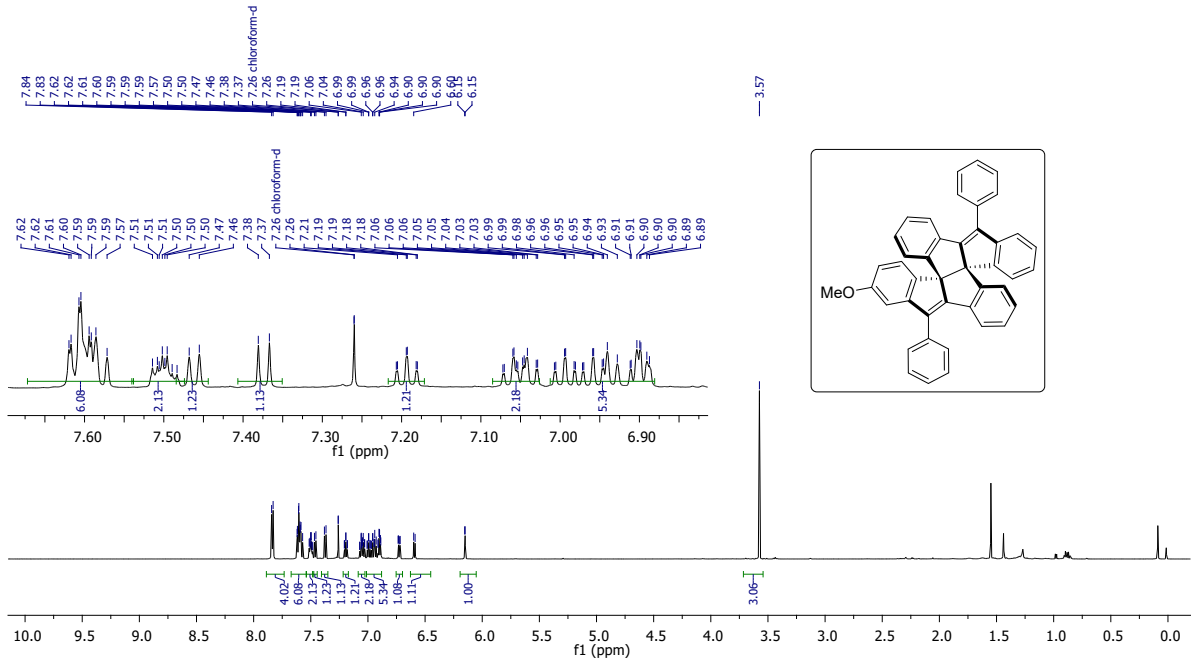
^{13}C{H} NMR (151 MHz) spectrum of **3o** in $CDCl_3$



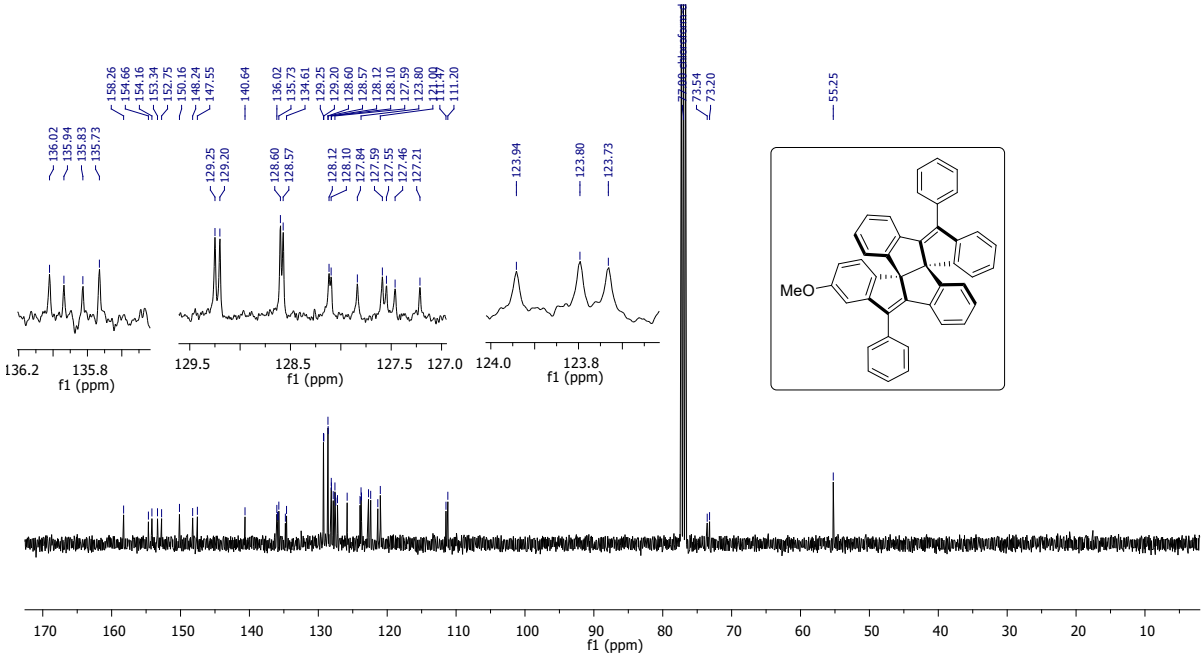
^{1}H NMR (400 MHz) spectrum of **3p** in $CDCl_3$



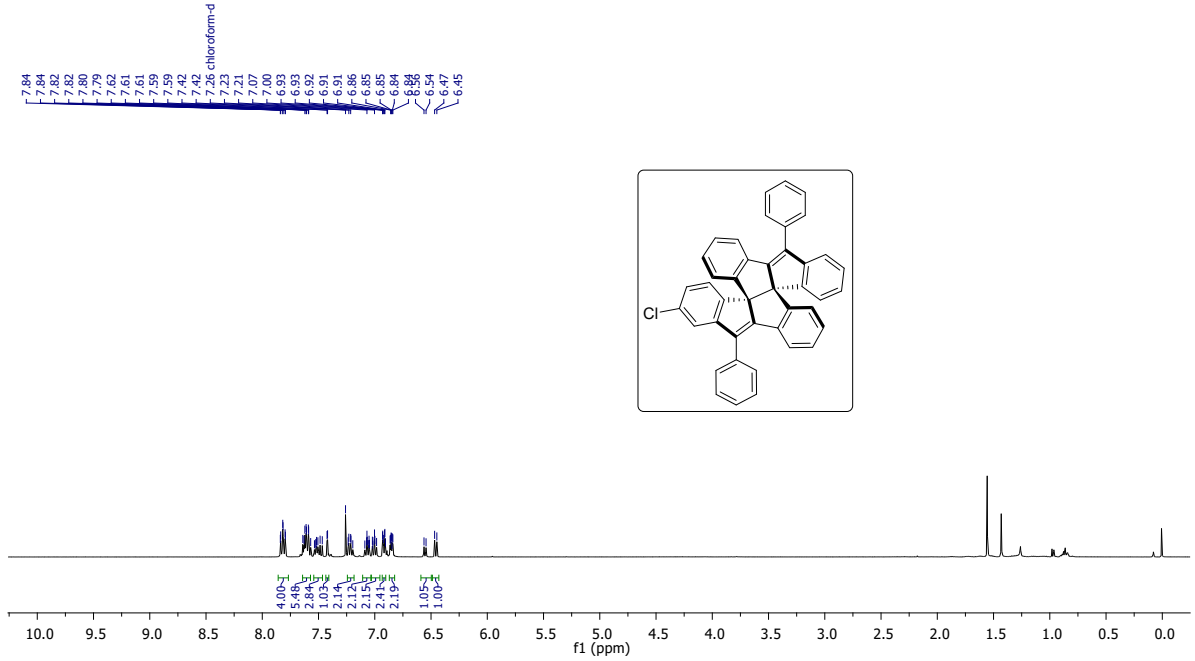
^{13}C{H} NMR (101 MHz) spectrum of **3p** in $CDCl_3$



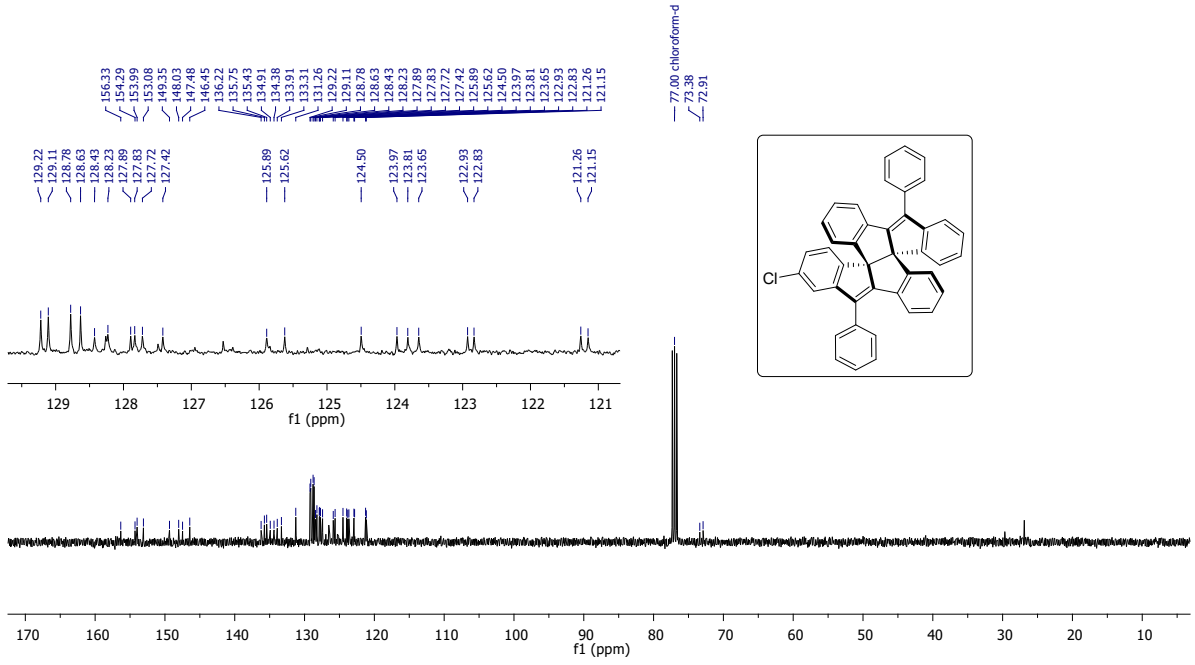
^{1}H NMR (600 MHz) spectrum of **3q** in $CDCl_3$



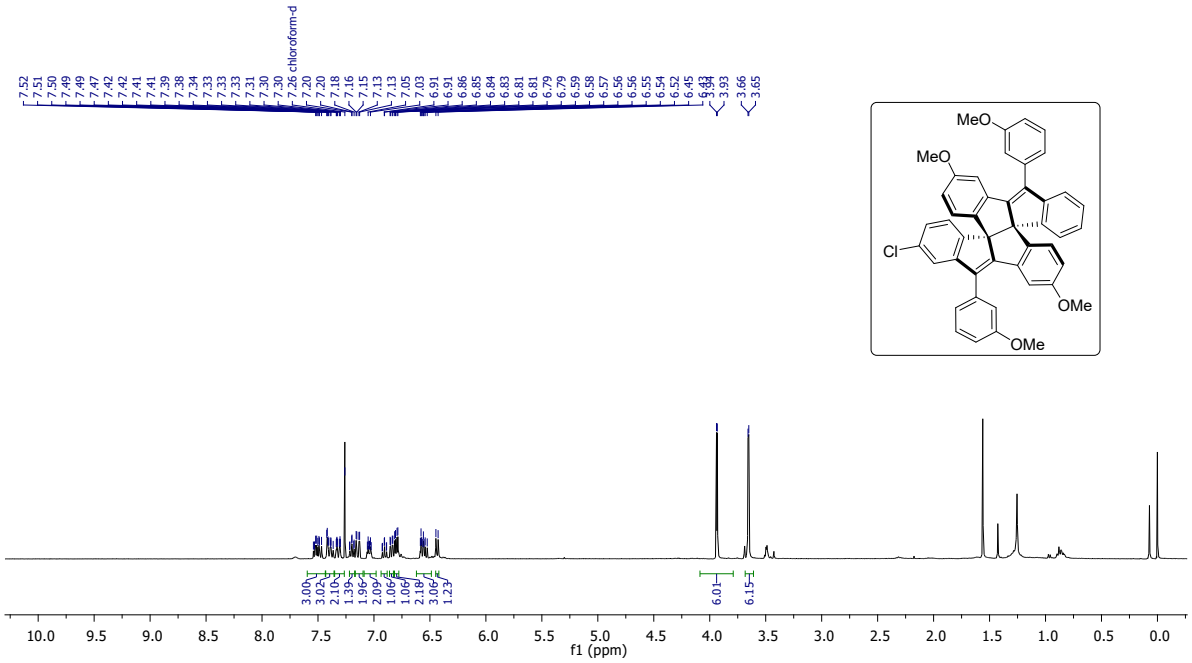
^{13}C{H} NMR (101 MHz) spectrum of **3q** in $CDCl_3$



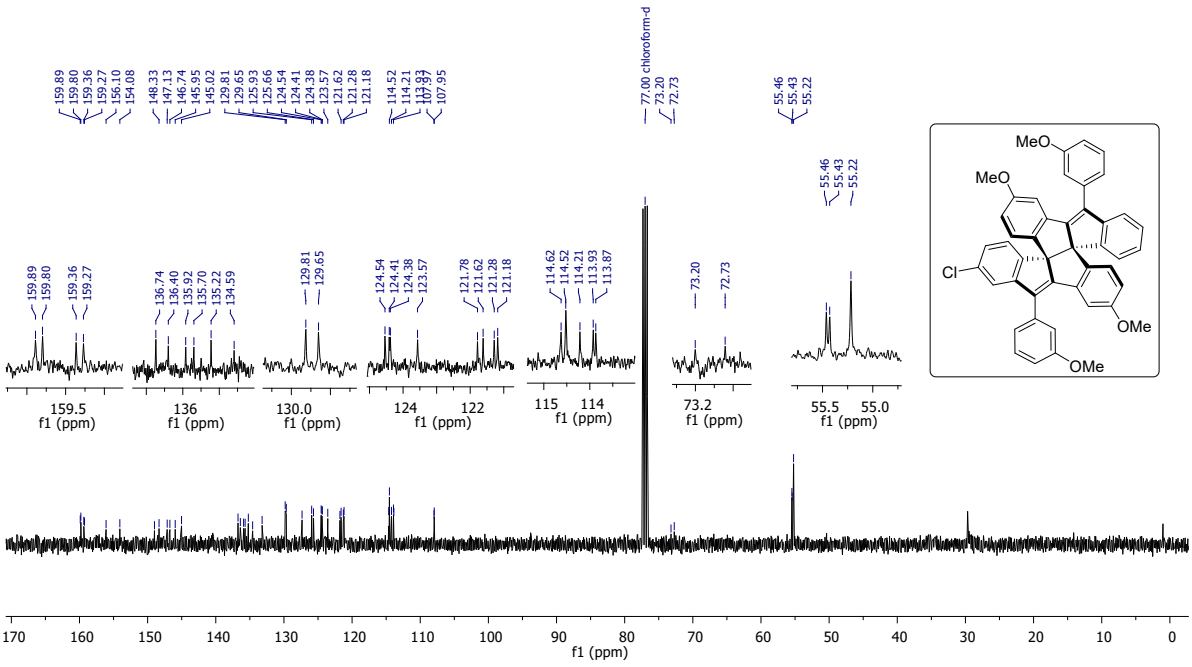
^{1}H NMR (400 MHz) spectrum of **3r** in $CDCl_3$



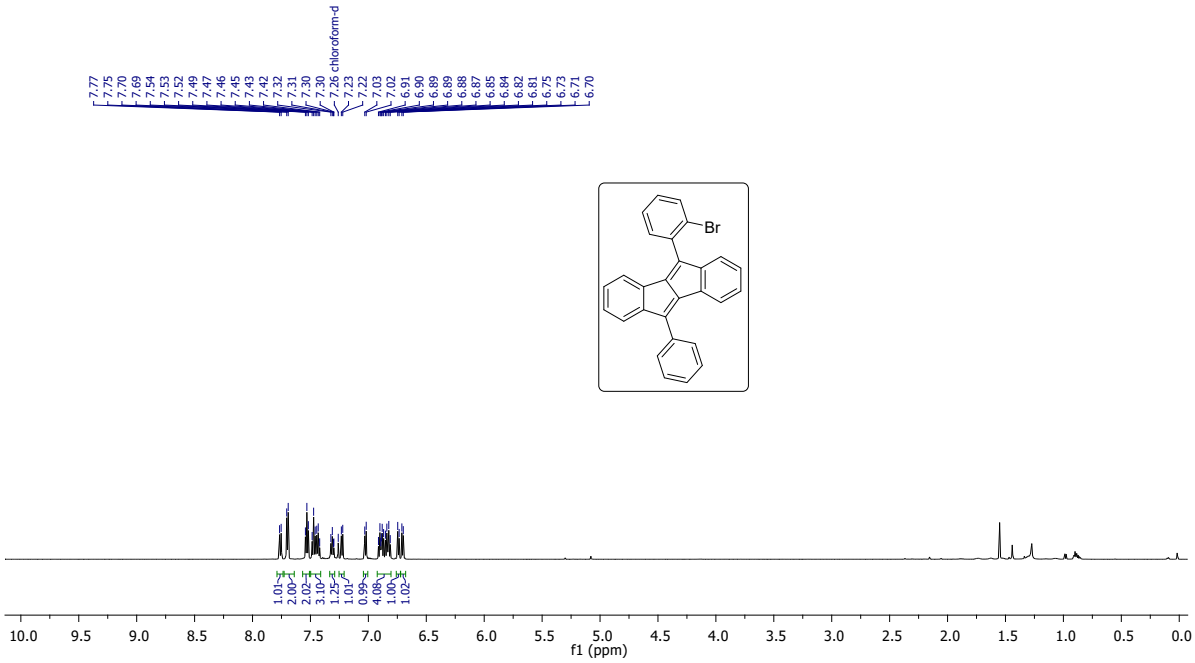
^{13}C{H} NMR (101 MHz) spectrum of **3r** in $CDCl_3$



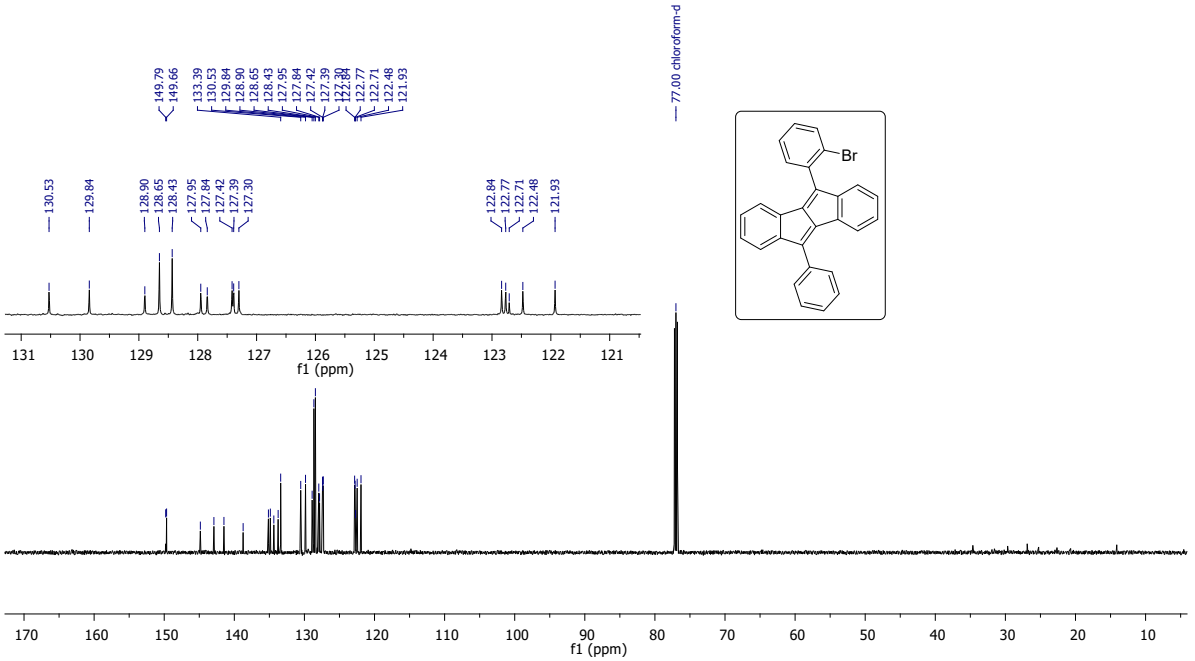
^{1}H NMR (400 MHz) spectrum of **3s** in $CDCl_3$



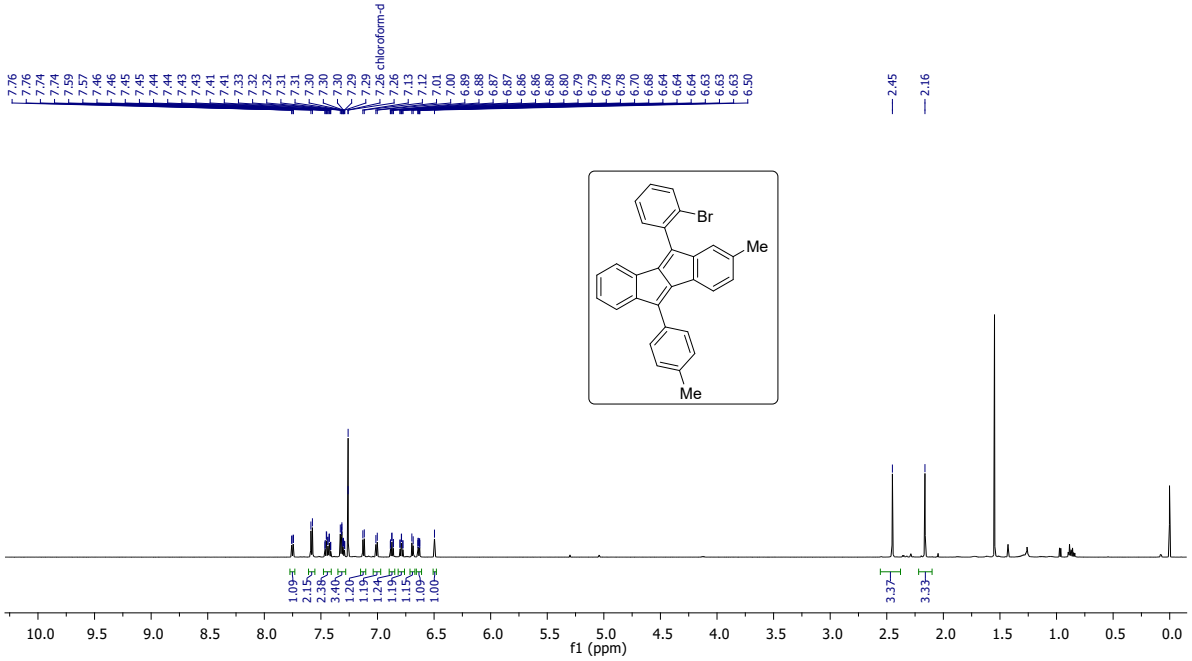
^{13}C{H} NMR (101 MHz) spectrum of **3s** in $CDCl_3$



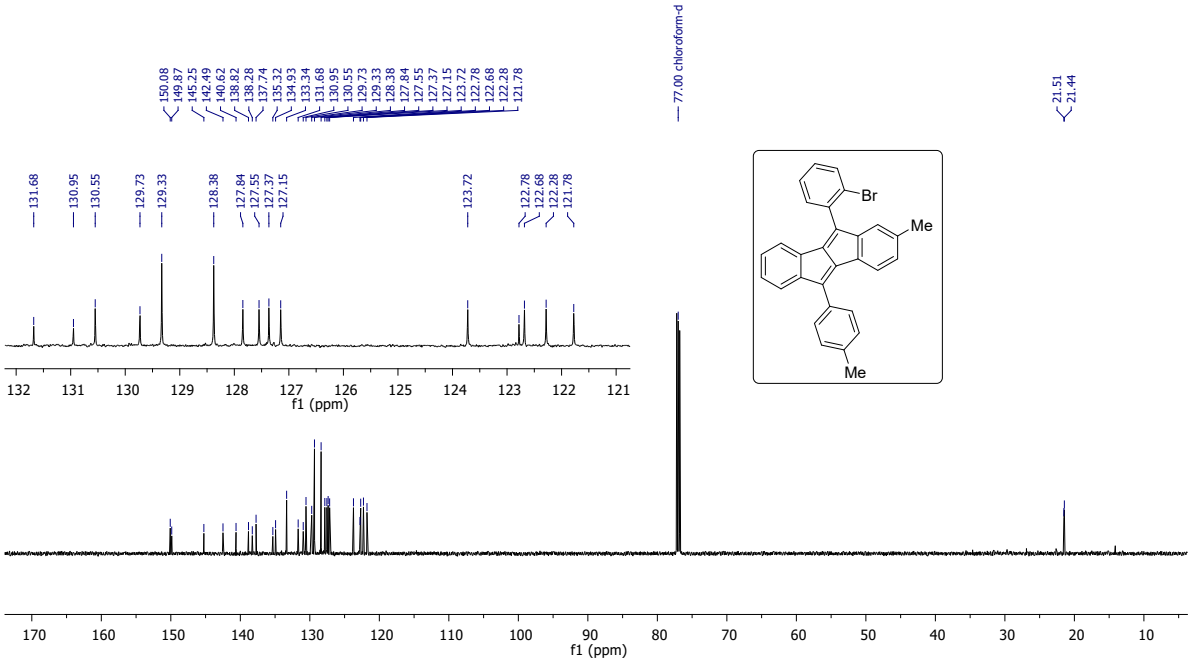
^{1}H NMR (600 MHz) spectrum of **4a** in $CDCl_3$



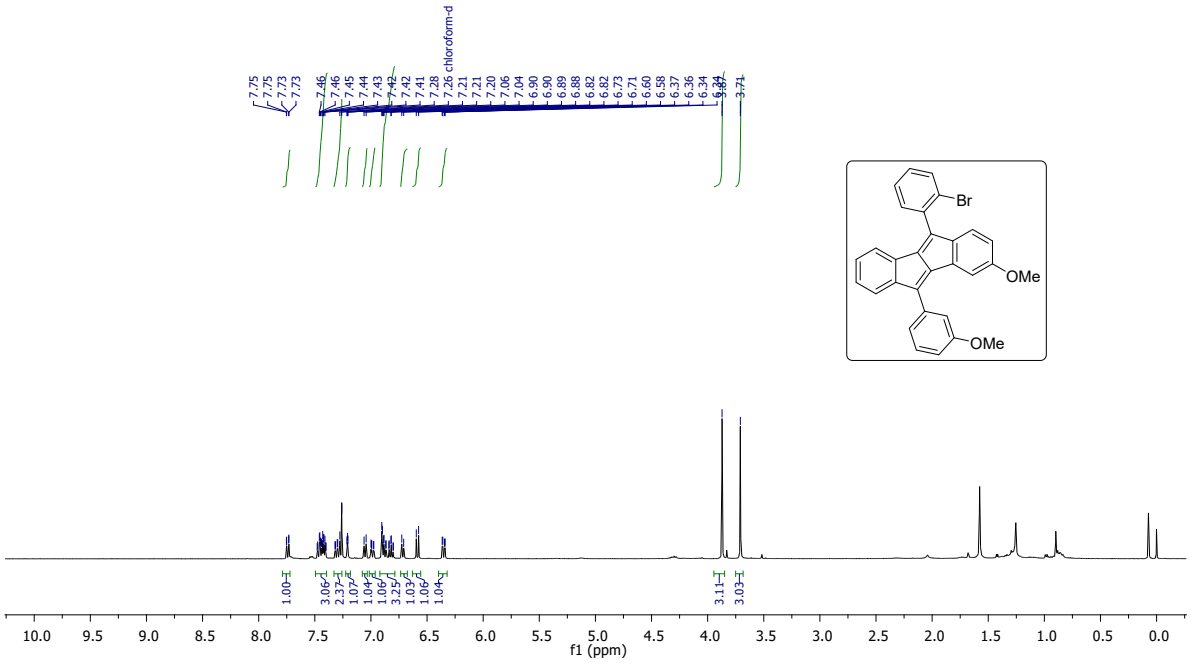
^{13}C{H} NMR (151 MHz) spectrum of **4a** in $CDCl_3$



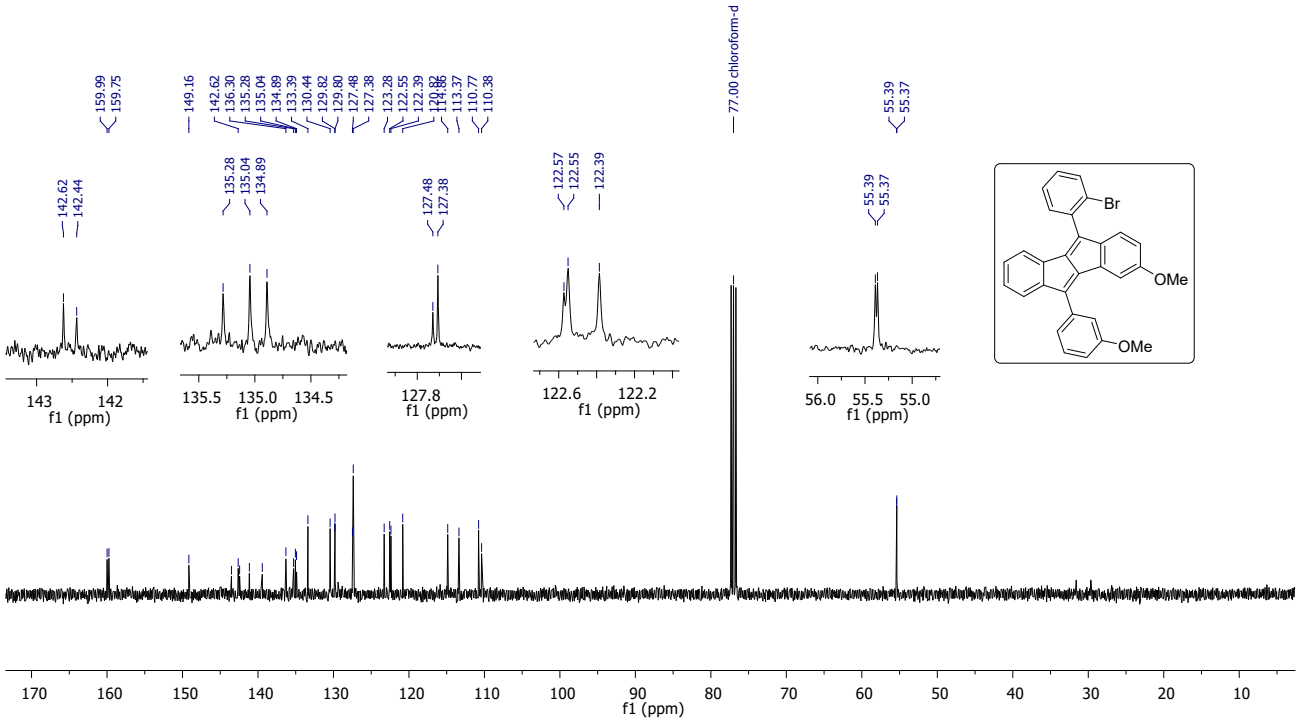
^{1}H NMR (600 MHz) spectrum of **4b** in $CDCl_3$



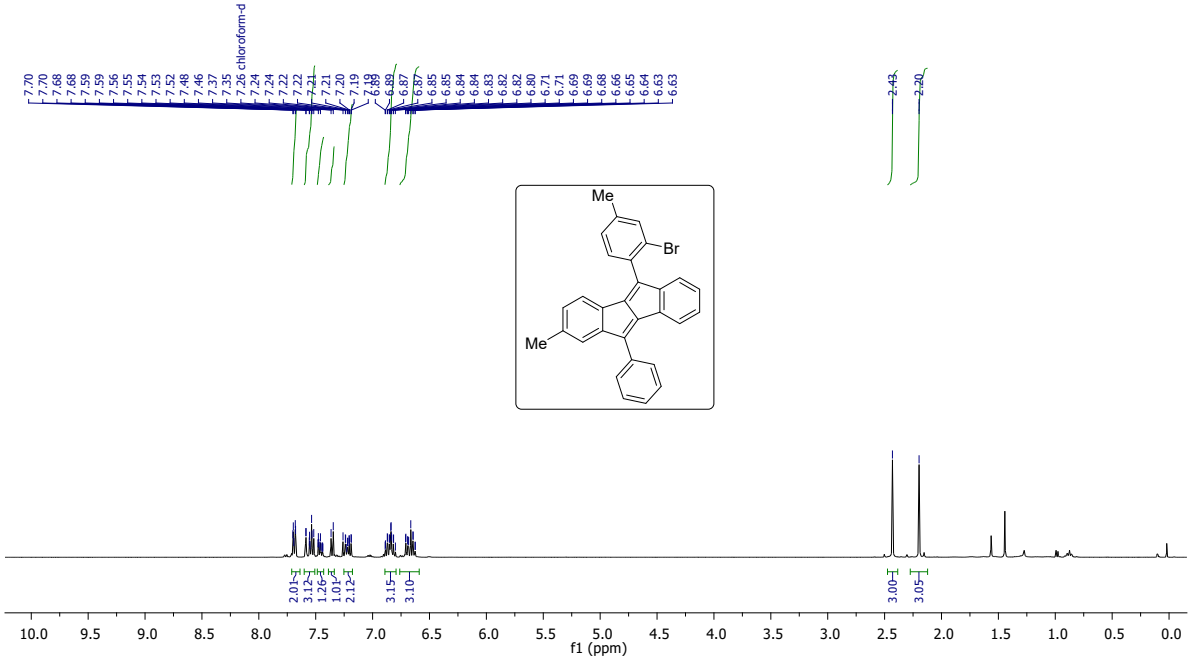
^{13}C{H} NMR (151 MHz) spectrum of **4b** in $CDCl_3$



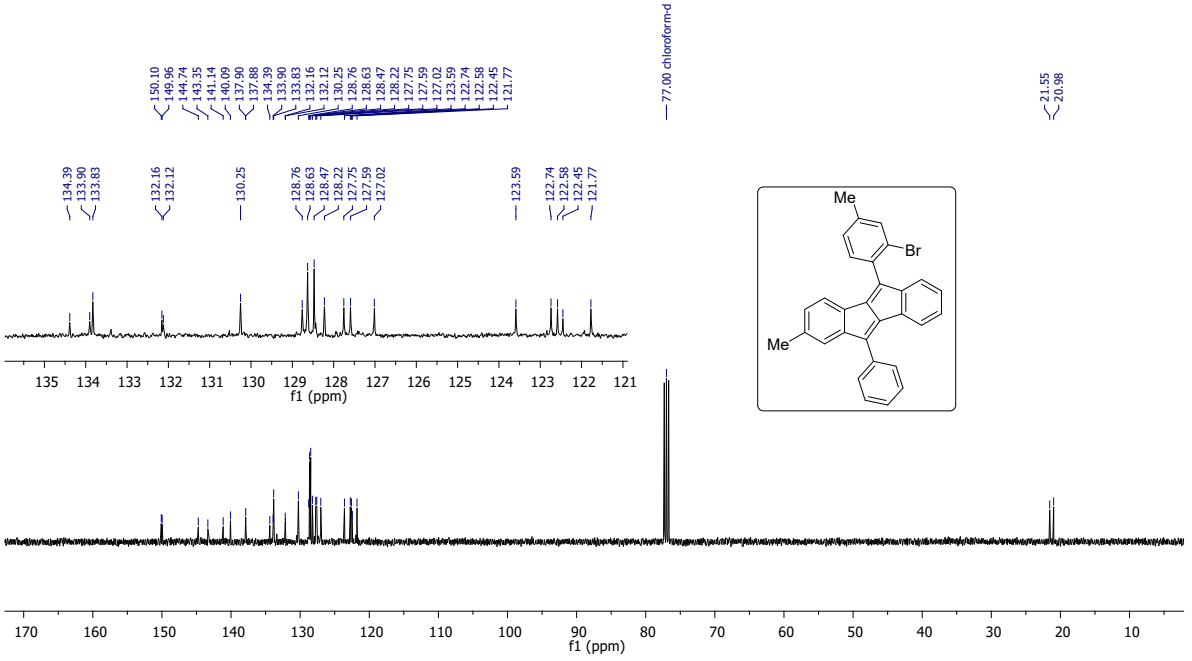
^{1}H NMR (400 MHz) spectrum of **4c** in $CDCl_3$



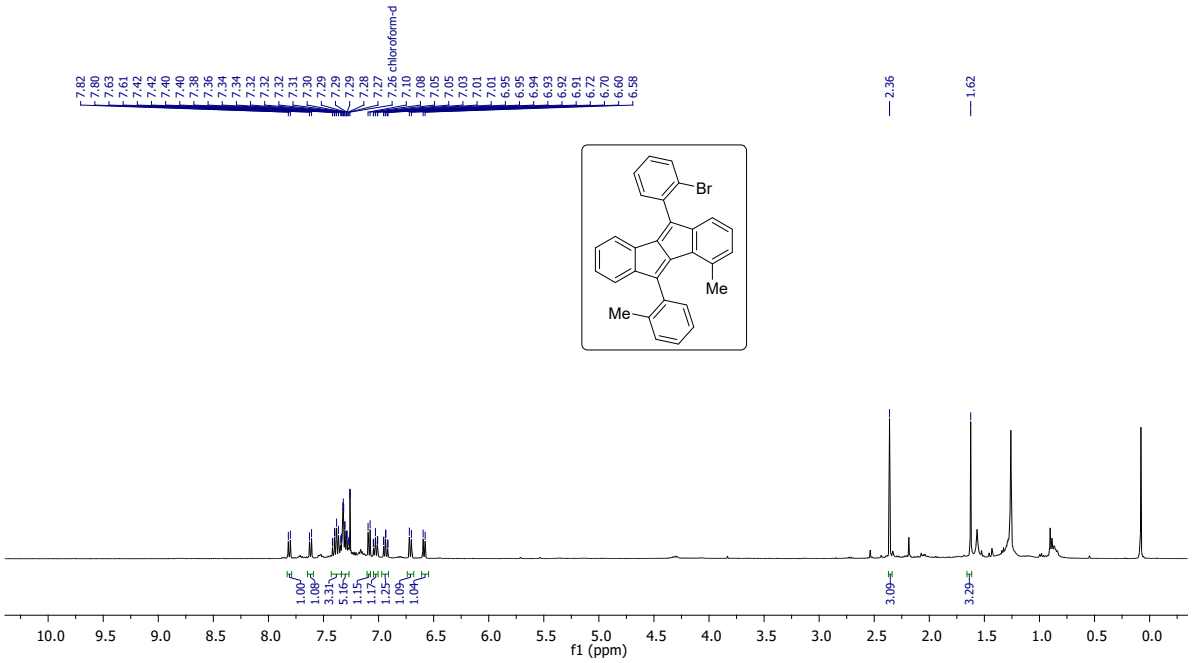
^{13}C{H} NMR (101 MHz) spectrum of **4c** in $CDCl_3$



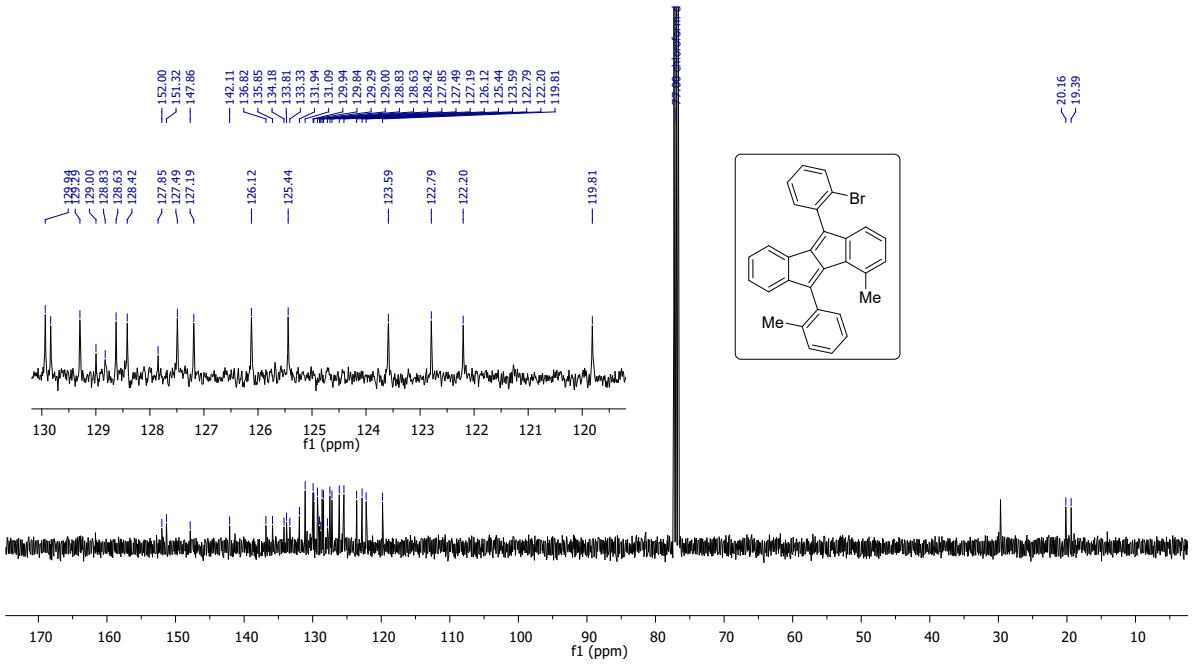
^{1}H NMR (400 MHz) spectrum of **4d** in $CDCl_3$



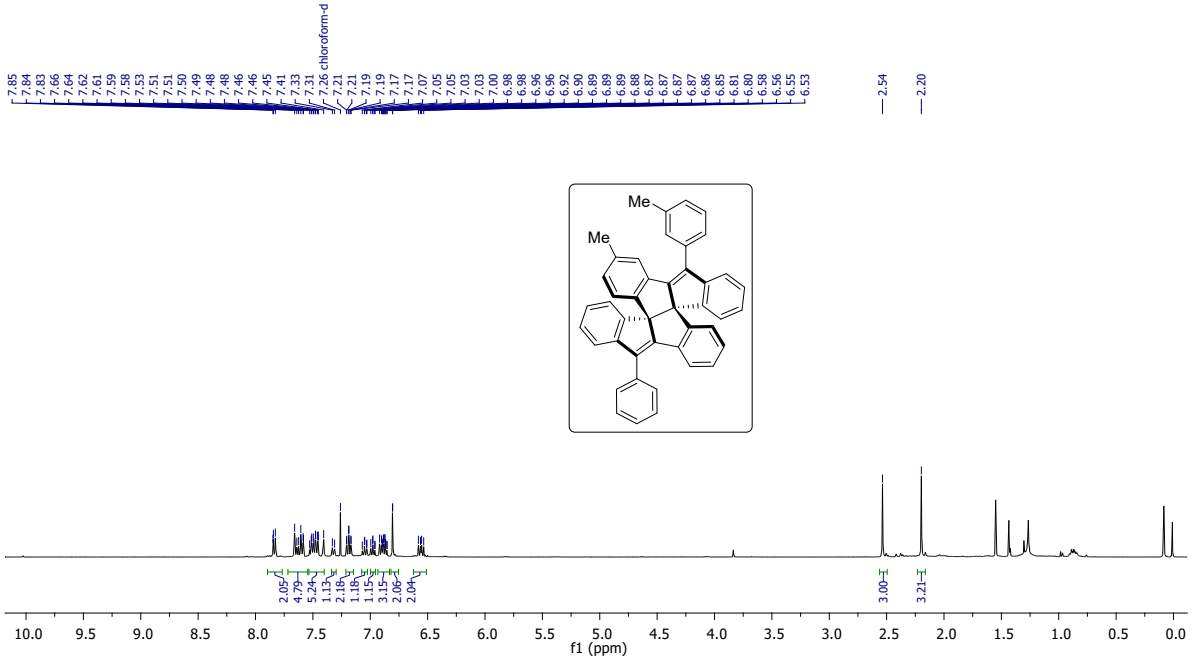
^{13}C{H} NMR (101 MHz) spectrum of **4d** in $CDCl_3$



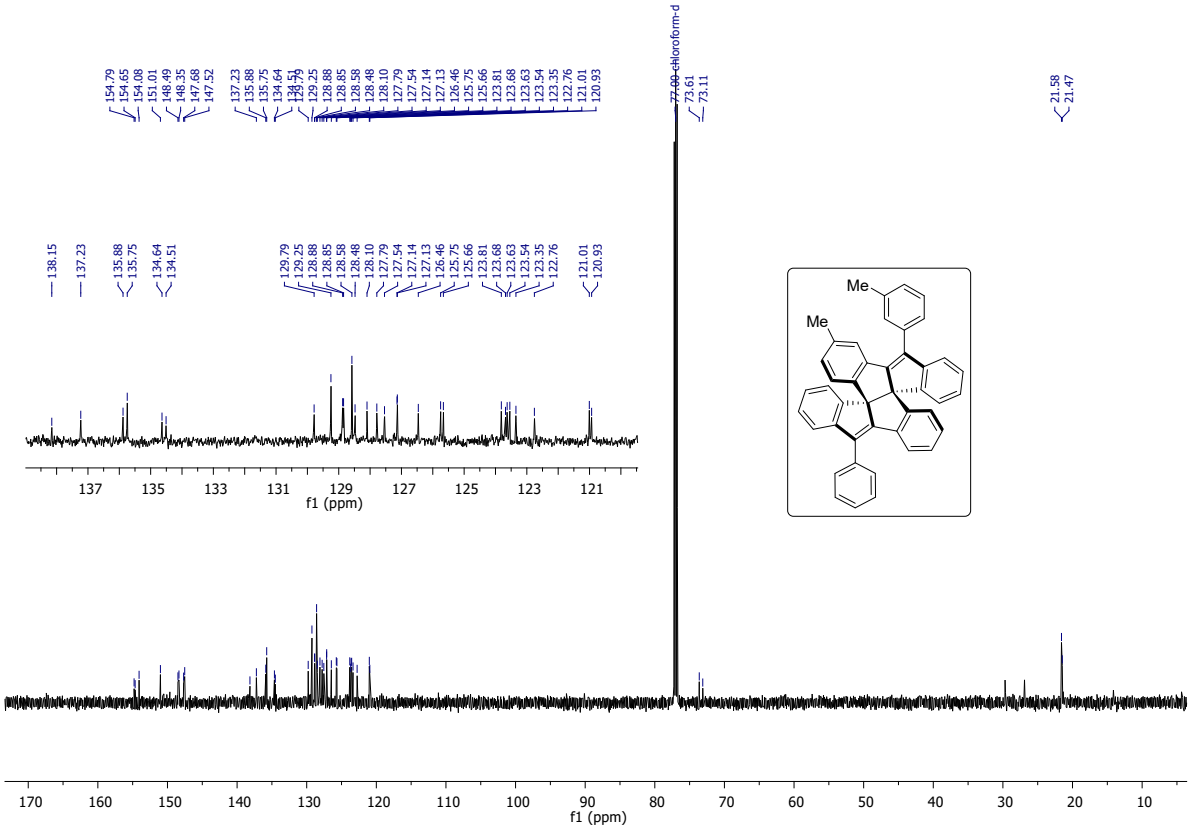
^{1}H NMR (400 MHz) spectrum of **4e** in $CDCl_3$



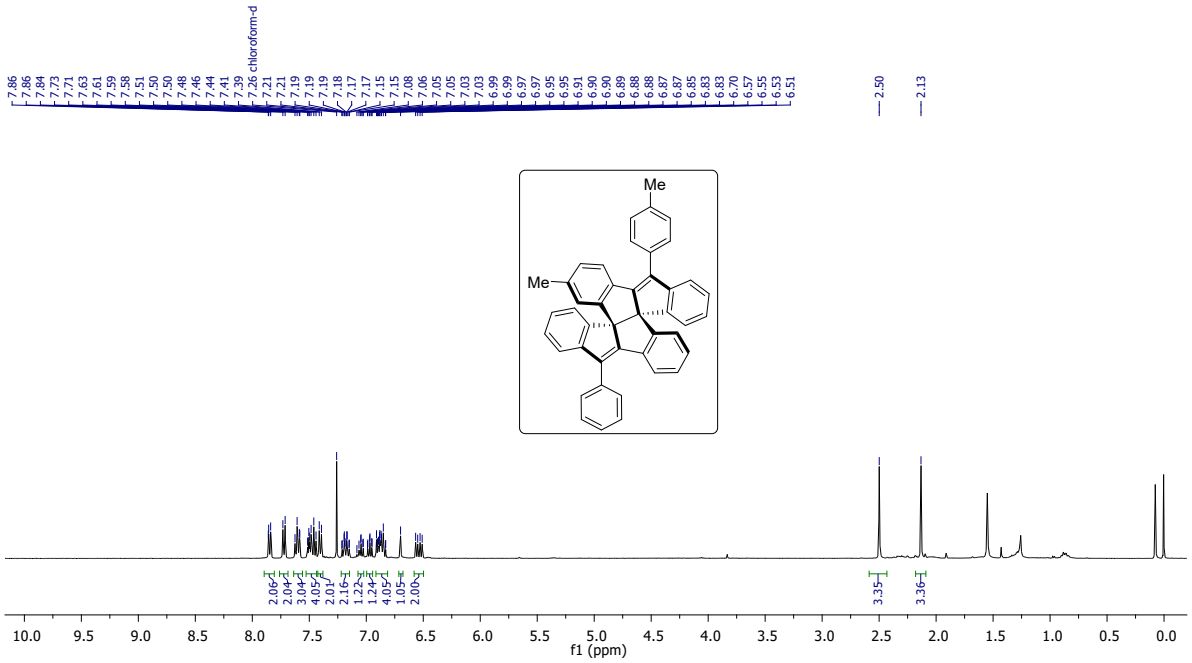
^{13}C{H} NMR (101 MHz) spectrum of **4e** in $CDCl_3$



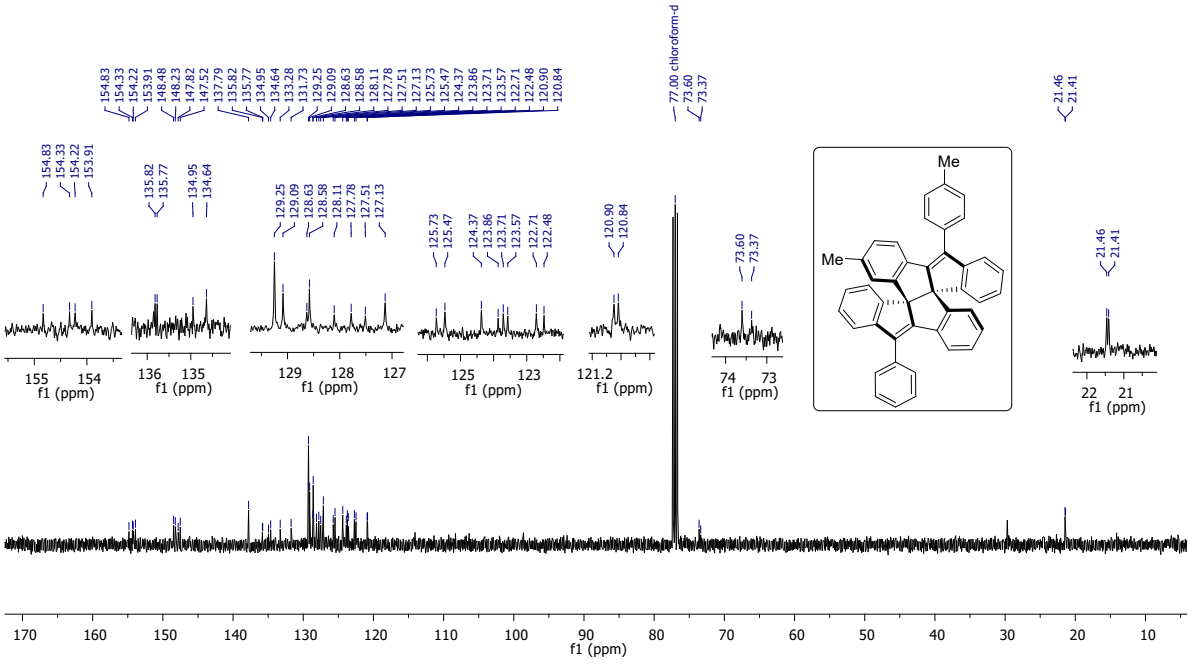
^{1}H NMR (400 MHz) spectrum of **5a** in $CDCl_3$



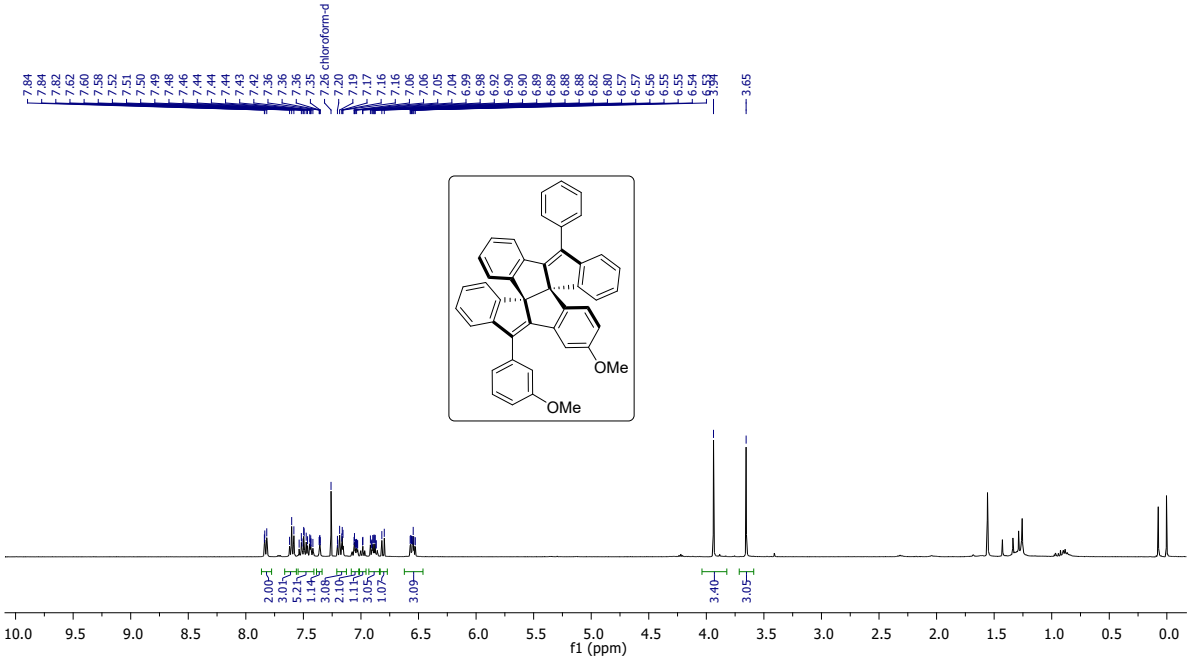
^{13}C{H} NMR (151 MHz) spectrum of **5a** in $CDCl_3$



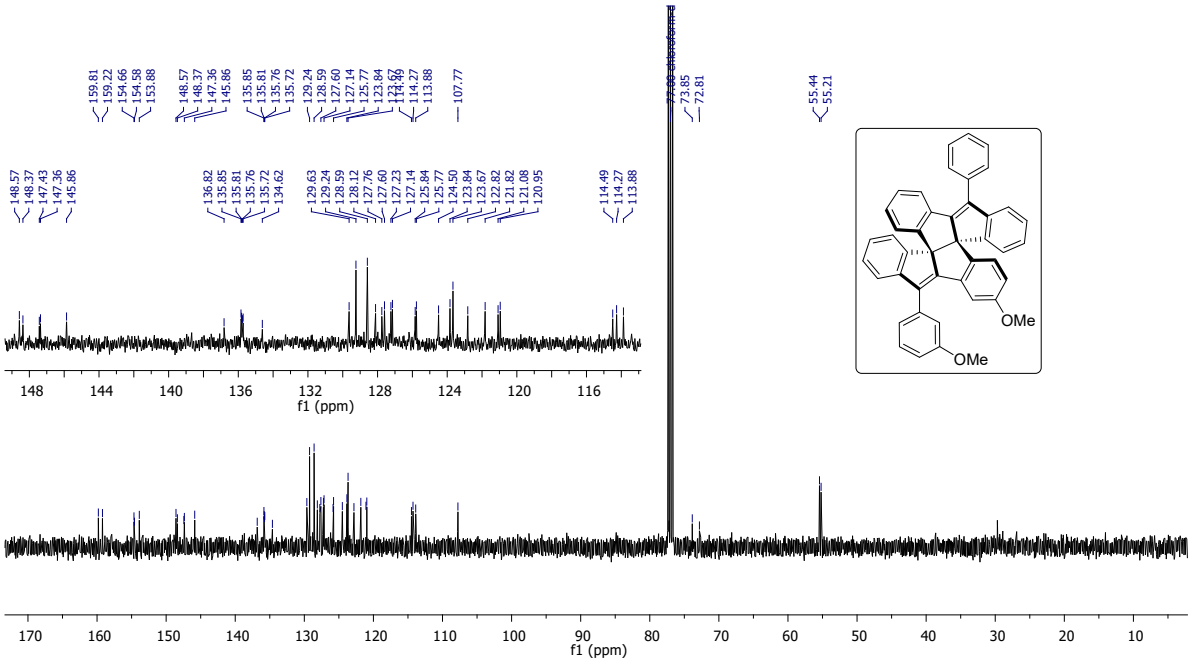
^{1}H NMR (400 MHz) spectrum of **5b** in $CDCl_3$



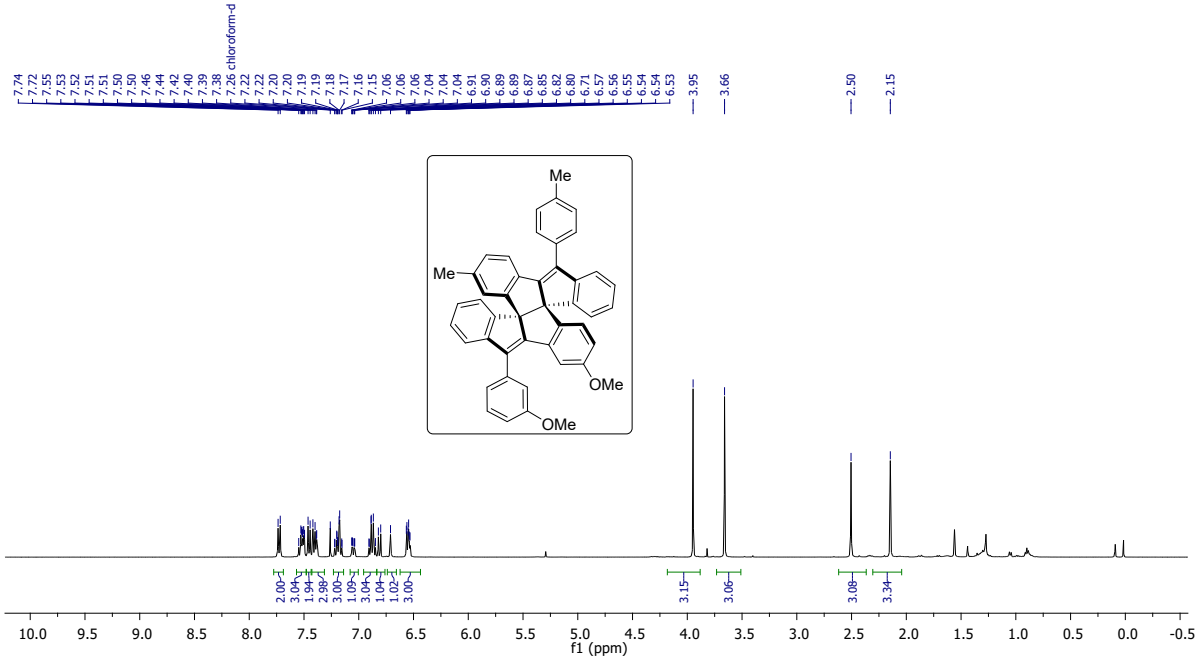
^{13}C{H} NMR (101 MHz) spectrum of **5b** in $CDCl_3$



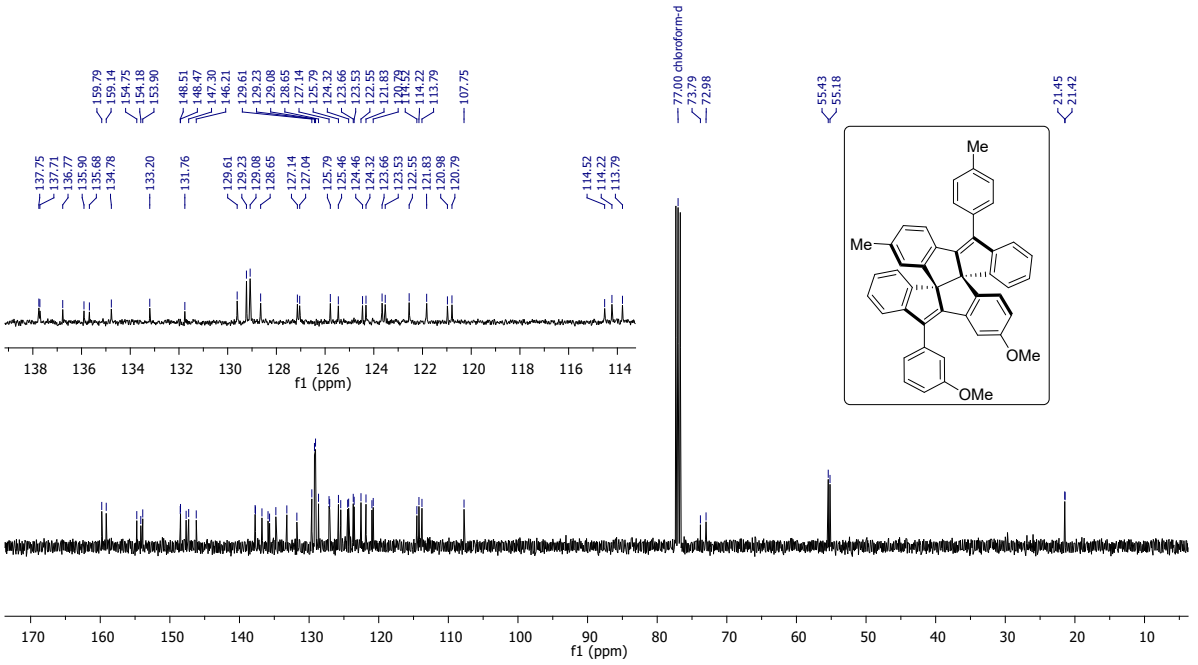
^{1}H NMR (400 MHz) spectrum of **5c** in $CDCl_3$



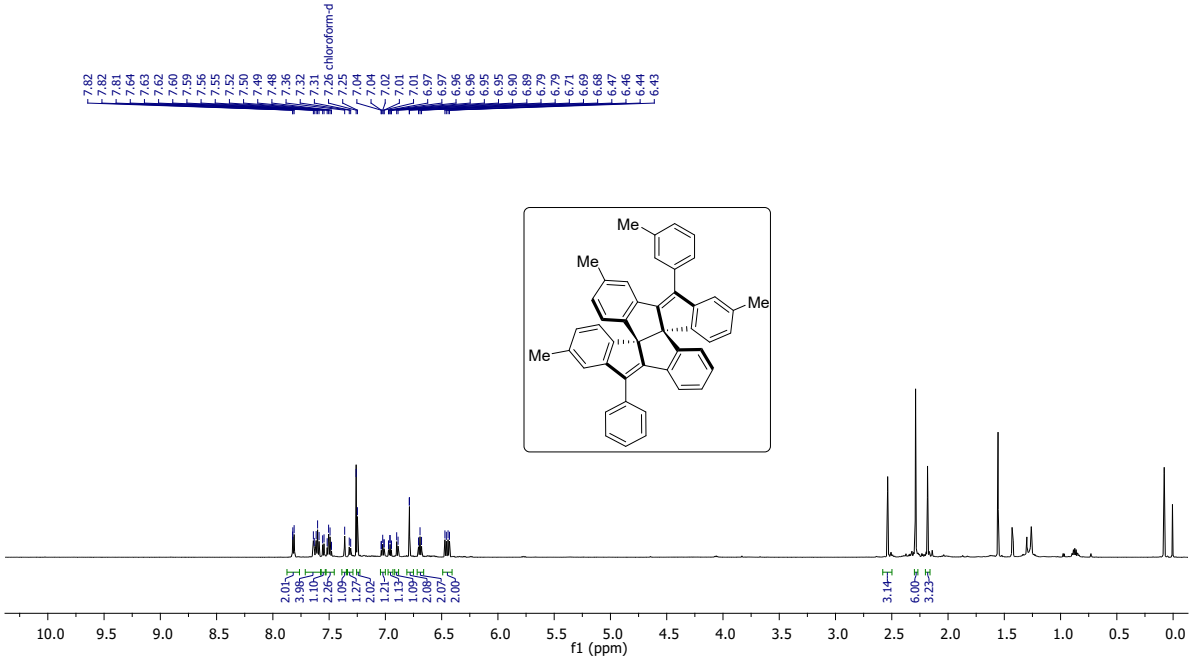
^{13}C{H} NMR (101 MHz) spectrum of **5c** in $CDCl_3$



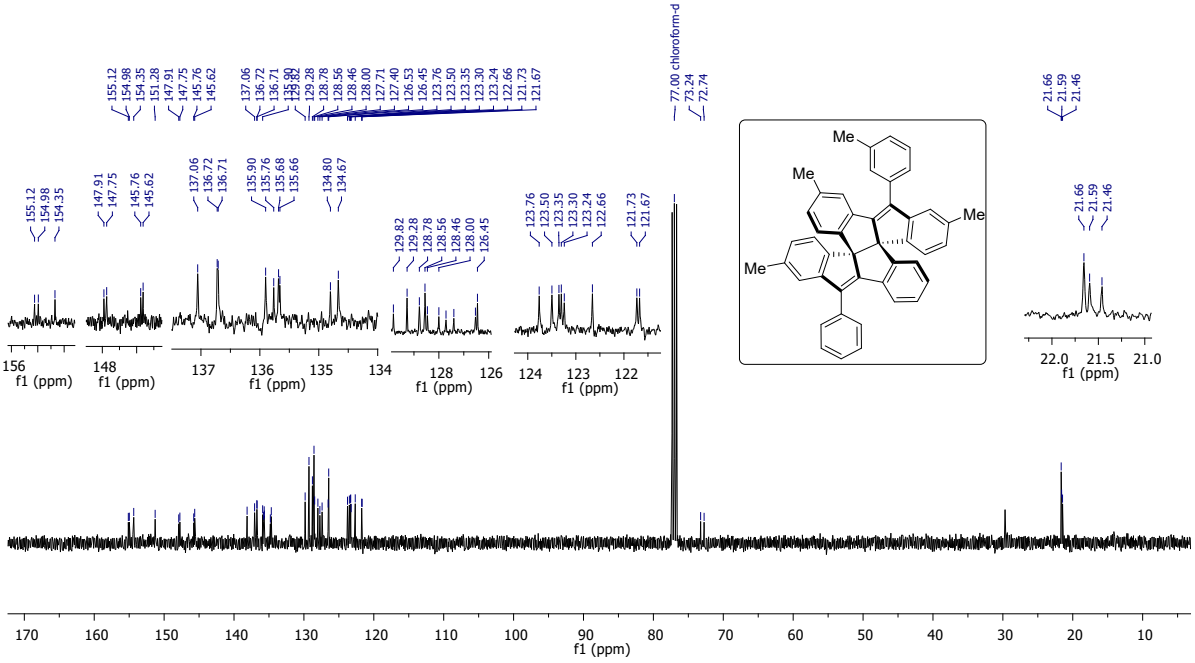
^{1}H NMR (400 MHz) spectrum of **5d** in $CDCl_3$



^{13}C{H} NMR (101 MHz) spectrum of **5d** in $CDCl_3$



^{1}H NMR (600 MHz) spectrum of **5e** in $CDCl_3$



^{13}C{H} NMR (101 MHz) spectrum of **5e** in $CDCl_3$

2. X-Ray crystal structure of compound ±3d:

Crystal of compounds **±3d** were obtained by dissolving the product in Hexane/CH_2Cl_2 mixture and allowing the solvent to slowly evaporate at room temperature. A suitable crystal was selected and mounted onto the cryoloop on a Bruker APEX-II CCD diffractometer. The crystal was kept at 273.15 K during data collection. Using Olex2,8 the structure was solved with the SHELXT9 structure solution program using Intrinsic Phasing and refined with the SHELXL10 refinement package using Least Squares minimization.

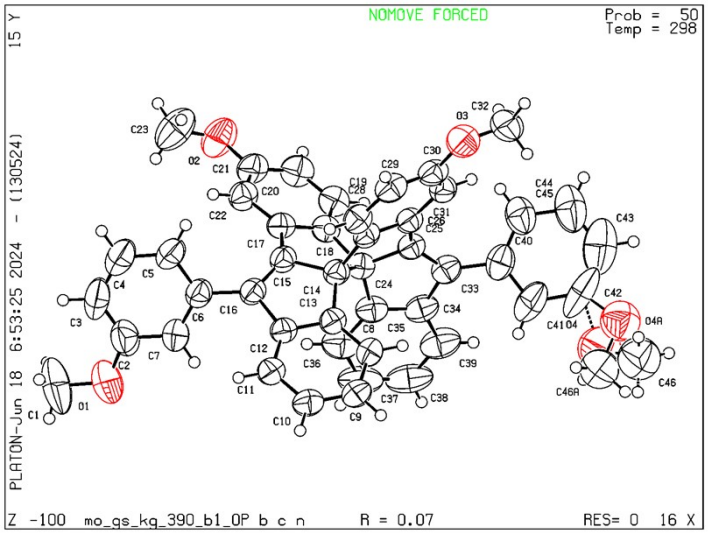


Figure S1: X-ray diagram of compound **±3d** with ellipsoid shown at the 50% contour percent probability level (CCDC: 2367924).

Table S4: Crystal data and structure refinement for **±3d** (CCDC: 2367924).

Table S4 Crystal data and structure refinement for ±3d.	
Identification code	**±3d**
Empirical formula	$C_{46}H_{34}O_4$
Formula weight	650.73
Temperature/K	298
Crystal system	orthorhombic
Space group	Pbcn
a/Å	33.896(3)
b/Å	12.2890(10)
c/Å	16.7731(15)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	6986.8(10)
Z	8

ρ_{calc}g/cm^3	1.237
μ/mm^{-1}	0.078
F(000)	2736.0
Crystal size/mm^3	0.31 × 0.25 × 0.15
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.28 to 50
Index ranges	-40 ≤ h ≤ 40, -14 ≤ k ≤ 14, -19 ≤ l ≤ 19
Reflections collected	48993
Independent reflections	6153 [R_{int} = 0.0924, R_{sigma} = 0.0498]
Data/restraints/parameters	6153/39/476
Goodness-of-fit on F^2	1.039
Final R indexes [I>=2σ (I)]	R_1 = 0.0692, wR_2 = 0.1566
Final R indexes [all data]	R_1 = 0.1293, wR_2 = 0.1865
Largest diff. peak/hole / e Å^{-3}	0.27/-0.27

References:

1 R. Gleiter and R. Merger, in *Modern Acetylene Chemistry*, eds. P. J. Stang and F. Diederich, Wiley, 1st edn., 1995, pp. 285–319.
2 C. Wang, A. Fukazawa, Y. Tanabe, N. Inai, D. Yokogawa and S. Yamaguchi, *Chem. Asian J.*, 2018, **13**, 1616–1624.
3 J. Nejedlý, M. Šámal, J. Rybáček, I. G. Sánchez, V. Houska, T. Warzecha, J. Vacek, L. Sieger, M. Buděšínský, L. Bednárová, P. Fiedler, I. Císařová, I. Starý and I. G. Stará, *J. Org. Chem.*, 2020, **85**, 248–276.
4 H. Chang, S. Datta, A. Das, A. Odedra and R. Liu, *Angew. Chem. Int. Ed.*, 2007, **46**, 4744–4747.
5 S. Resa, D. Miguel, S. Guisán-Ceinos, G. Mazzeo, D. Choquesillo-Lazarte, S. Abbate, L. Crovetto, D. J. Cárdenas, M. C. Carreño, M. Ribagorda, G. Longhi, A. J. Mota, L. Álvarez de Cienfuegos and J. M. Cuerva, *Chem. Eur. J.*, 2018, **24**, 2653–2662.
6 K. Goel and G. Satyanarayana, *Org. Biomol. Chem.*, 2023, **21**, 6919–6925.
7 Z. U. Levi and T. D. Tilley, *J. Am. Chem. Soc.*, 2009, **131**, 2796–2797.