

Microwave-Assisted Palladium-Catalysed Threefold Domino Cyclisation of 2-(2-(Phenylethynyl)phenyl)-1*H*- benzo[*d*]imidazoles/indoles to Access Polycyclic Motifs

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Supporting Information

Supporting Information

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Experimental Procedure:

General methods:

IR spectra were recorded on a Bruker Tensor 37 (FTIR) spectrophotometer. ^1H NMR spectra were recorded on Bruker Advance 400 (400 MHz) and 600 (600 MHz) 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) ($\delta\text{H} = 0.00$ ppm) or CDCl_3 ($\delta\text{H} = 7.26$ ppm) or $\text{DMSO-}d_6$ ($\delta\text{H} = 2.50$ ppm) or $\text{Acetone-}d_6$ ($\delta\text{H} = 2.05$ ppm). $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on Bruker Advance 400 (101 MHz) and 600 (151 MHz) spectrometers at rt in CDCl_3 . Chemical shifts (δ ppm) are reported relative to CDCl_3 [$\delta = 77.16$ ppm (central line of the triplet)], $\text{DMSO-}d_6$ [$\delta = 39.52$ ppm (central line of the septet)], and $\text{Acetone-}d_6$ [$\delta = 29.84$ ppm (central line of the septet)]. In the $^{13}\text{C}\{^1\text{H}\}$ NMR, the nature of carbons (C, CH, CH_2 , and CH_3) was determined by recording the DEPT-135 spectra (some compounds). In the ^1H -NMR, the following abbreviations were used throughout: s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet, sept = septet, dd = doublet of doublet, m = multiplet, and bs = broad singlet. The assignment of signals was confirmed by ^1H , $^{13}\text{C}\{^1\text{H}\}$ CPD, and DEPT spectra. High-resolution mass spectra (HRMS) were recorded on an Agilent 6538 UHD Q-TOF electron spray ionization (ESI) mode and atmospheric pressure chemical ionization (APCI) modes. Melting points are recorded using Tempo and Mettler FP1 melting point apparatus in capillary tubes and are uncorrected. Single crystals of **3la**, **3ka**, and **3al** were selected and mounted on an Oxford SuperNova, Dual, Cu at zero, Eos diffractometer. The crystals were kept at 298 K during data collection. Using Olex2, the structures were solved with the olex2.solve structure solution program using direct methods and refined with the olex2.refinement package using Gauss–Newton minimization. All small-scale reactions were carried out in a 10 mL MW (150 W) reaction vial in a microwave reactor (CEM), and the temperature was monitored with an IR sensor. Reactions were monitored by TLC on silica gel using a hexane-ethyl acetate mixture as the eluent. Solvents were distilled before use; petroleum ether with a boiling range of 60–80 °C was used. *ortho*-bromobenzaldehydes, phenylacetylenes, iodobromobenzenes, *o*-phenylenediamines, DPEPhos, Cs_2CO_3 , other ligands, bases, and solvents were purchased from Sigma-Aldrich/Avra/BLD/TCI/local sources and used as received. Acme's silica gel (60–120 mesh and 100–200 mesh) was used for column chromatography (approximately 20 g per one gram of crude material).

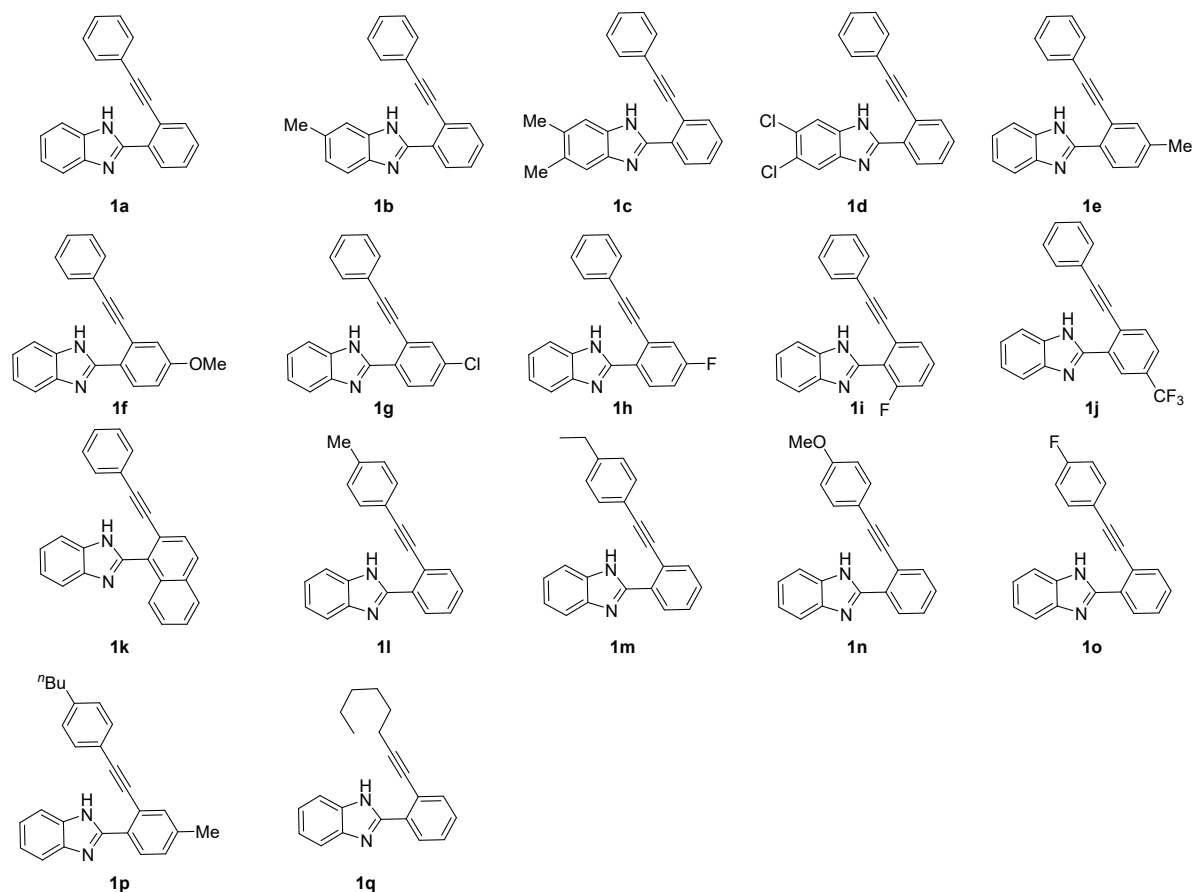
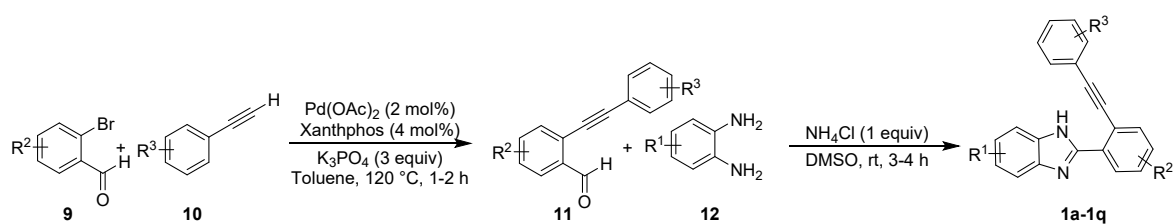
General Procedure - 1 (GP-1) for the Preparation of 2-(2-(Phenylethynyl)phenyl)-1*H*-benzo[*d*]imidazoles (**1a-1p**):¹⁻⁴

To an oven-dried 50 mL reaction vial equipped with a stir bar, were added *ortho*-bromobenzaldehyde derivatives **9** (1 equiv, 1.0 mmol), phenyl acetylenes **10** (1.1 equiv, 1.1 mmol), Pd(OAc)₂ (2 mol%, 0.02 mmol), Xanthphos (4 mol%, 0.04 mmol), K₃PO₄ (3 equiv, 3 mmol), and Toluene (3 mL). The resultant reaction mixture was purged with N₂, stirred at 120 °C for 1-2 hours. The reaction was monitored by thin-layer chromatography (TLC). The reaction was quenched with the saturated ammonium chloride solution (20 mL) and extracted with ethyl acetate (3 × 15 mL). The combined organic layers were washed with brine and dried over anhydrous sodium sulfate. The solvent was removed in vacuo, and the residue was purified by short silica gel column chromatography (petroleum ether: ethyl acetate = 98:02) to yield crude 2-(phenylethynyl)benzaldehyde products **11** as colourless/yellow liquids, which were directly subjected to subsequent condensation reaction as per the procedure below: To an oven-dried 50 mL reaction vial equipped with a stir bar, were added 2-(phenylethynyl)benzaldehyde derivatives **11** (1 equiv, 1.0 mmol), *o*-phenylenediamines **12** (1.1 equiv, 1.1 mmol), ammonium chloride (1 equiv, 1 mmol), and DMSO (3 mL). The resultant reaction mixture was stirred at room temperature for 3-4 hours. The reaction was monitored by thin-layer chromatography (TLC). The reaction was quenched with the saturated ammonium chloride solution (20 mL) and extracted with DCM (3 × 15 mL). The combined organic layers were washed with brine and dried over anhydrous sodium sulfate. The solvent was removed in vacuo, and the residue was purified by using silica gel column chromatography (petroleum ether: ethyl acetate = 95:05 to 90:10) to yield the desired products **1a-1q** (62-86%), as colourless/yellow solids.

Table S1: The following starting materials are prepared by literature reports **1a-1q**:¹⁻⁶

Among the prepared starting precursors, **1a**, **1c**, **1k**, and **1o** were reported in the literature.¹⁻⁶

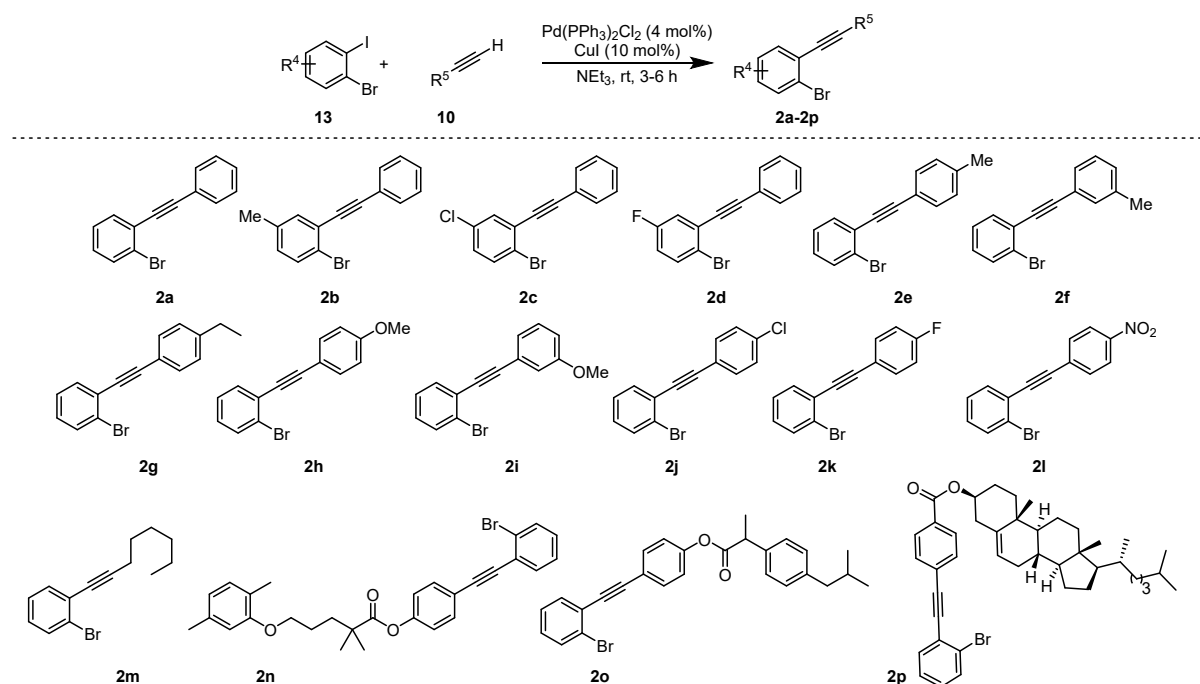
Note: It was worth mentioning that the following starting materials **1a-1q** had relaxation issues (in NMR) and solubility issues (in CDCl₃, DMSO-*d*₆, and Acetone-*d*₆) due to which it was observed that the peaks in ¹³C {¹H} NMR of these compounds with decreased intensity.



General Procedure - 2 (GP-2) for the Synthesis of 1-Bromo-2-(phenylethynyl)benzenes (2a-2p):^{7,8}

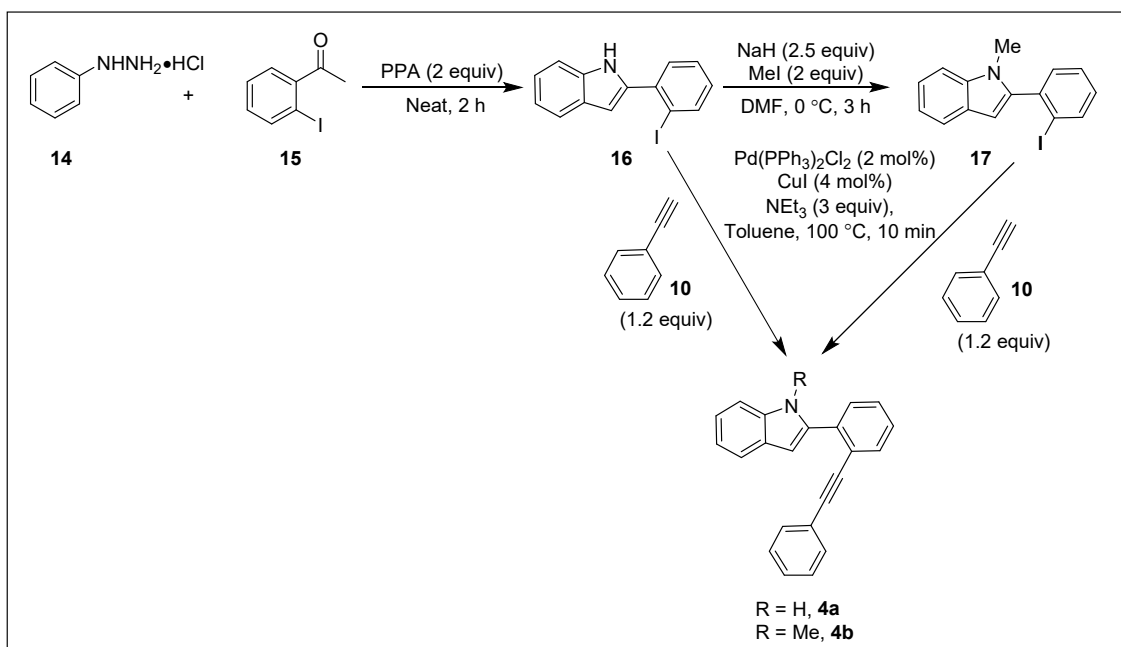
To an oven-dried 50 mL round-bottom flask equipped with a stir bar, were added 1-bromo-2-iodobenzene derivatives **13** (1 equiv, 1.0 mmol), phenyl acetylenes **10** (1.0 equiv, 1.0 mmol), Pd(PPh₃)₂Cl₂ (4 mol%, 0.04 mmol), CuI (10 mol%, 0.10 mmol), NEt₃ (3 mL). The resultant reaction mixture was stirred at room temperature for 3-6 hours. The reaction was monitored by thin-layer chromatography (TLC). The reaction was quenched with the saturated ammonium chloride solution (20 mL) and extracted with DCM (3 × 15 mL). The combined organic layers were washed with brine and dried over anhydrous sodium sulfate. The solvent was removed in vacuo, and the residue was purified by silica gel column chromatography (petroleum ether:ethyl acetate = 100:00 to 99:01) to yield the desired products **2a-2p** (80-91%) as colourless/yellow liquids.

Table S2: The following starting materials are prepared by literature reports **2a-2p**:^{7,8}



Among the prepared starting precursors, **2a-2m** were reported in the literature.^{7,8}

Scheme S1: Synthesis of 1-methyl-2-(2-(phenylethynyl)phenyl)-1*H*-indole/ 2-(2-(phenylethynyl)phenyl)-1*H*-indole (4a-4b**):⁹**



To an oven-dried 100 mL round-bottom flask equipped with a stir bar, were added phenylhydrazine hydrochloride **14** (1.41 g, 9.75 mmol), *o*-iodoacetophenone **15** (2 g, 8.13 mmol) and polyphosphoric acid (20 g), and the mixture was stirred at 100 °C under neat conditions for 2 h. The reaction was monitored by thin-layer chromatography (TLC). The

reaction was quenched with the saturated ammonium bicarbonate solution (20 mL) and extracted with ethyl acetate (3 × 15 mL). The combined organic layers were washed with brine and dried over anhydrous sodium sulfate. The solvent was removed in vacuo, and the resultant crude mixture of 2-(2-iodophenyl)-1*H*-indole **16** was carried out with the next step.

Sodium hydride (156 mg, 2.5 equiv) was added to a solution of 2-(2-iodophenyl)-1*H*-indole **16** (1.65 g, 5.17 mmol) in dry DMF (10 mL) at 0 °C. After stirring for 10 min at 0 °C, iodomethane (0.7 mL, 2 equiv) was added dropwise to the mixture at the same temperature. After stirring for 3 h at room temperature, the mixture was quenched with water and extracted with ethyl acetate. The organic phase was washed with brine, dried over Na₂SO₄. The solvent was removed in vacuo, and the crude mixture was filtered by short silica gel column chromatography (petroleum ether/ethyl acetate = 98:02), furnishing the 2-(2-iodophenyl)-1-methyl-1*H*-indole **17** (1.37 g, 80%) as a colorless, viscous oil.

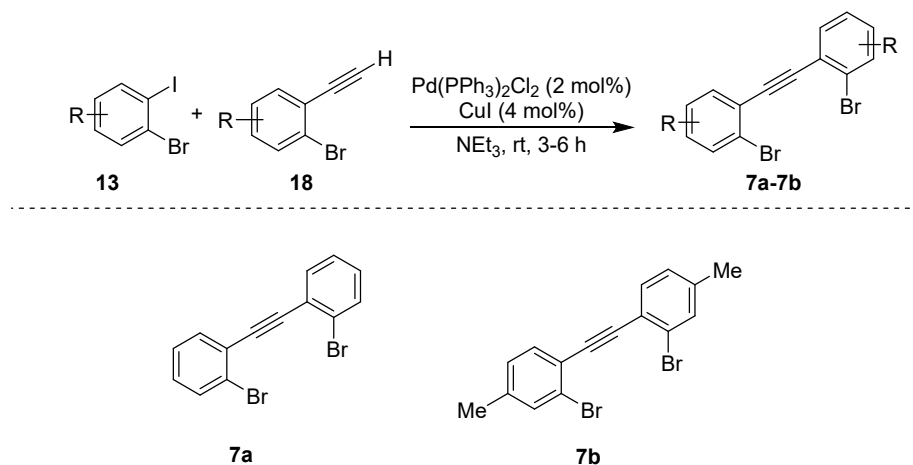
In an oven-dried Schlenk tube equipped with a magnetic stirring bar, were added 2-(2-iodophenyl)-1*H*-indole (crude) **16**/ 2-(2-iodophenyl)-1-methyl-1*H*-indole **17** (142–154 mg, 0.5 mmol), phenylacetylene **10** (65 mg, 0.6 mmol), PdCl₂(PPh₃)₂ (2 mol %), CuI (10 mol %), Et₃N (303 mg, 1.5 mmol), and toluene (2 mL) at room temperature. The resultant reaction mixture was carried out in an oil bath at 100 °C for 10 min. The progress of the reaction was monitored by TLC until completion. The mixture was cooled to room temperature, quenched with saturated ammonium solution, and extracted with ethyl acetate (3 × 10 mL). The organic layers were washed with saturated NaCl solution and dried over Na₂SO₄. The solvent was removed in vacuo, and the residue was purified by silica gel column chromatography (petroleum ether: ethyl acetate = 100:00 to 98:02) to yield the desired precursors **4a-4b** (85-87%) as yellow solids. These starting precursors **4a-4b** were reported in the literature reports.^{9,10}

General Procedure - 3 (GP-3) for the Synthesis of 1,2-bis(2-bromophenyl)ethynes (7a-7b):¹¹

To an oven-dried 50 mL round-bottom flask equipped with a stir bar, were added 1-bromo-2-iodobenzene derivatives **13** (1 equiv, 2.0 mmol), *ortho*-bromophenyl acetylenes **18** (1.0 equiv, 2.0 mmol), Pd(PPh₃)₂Cl₂ (4 mol%, 0.08 mmol), CuI (10 mol%, 0.20 mmol), NEt₃ (3 mL). The resultant reaction mixture was stirred at room temperature for 3 hours. The reaction was monitored by thin-layer chromatography (TLC). The reaction was quenched with the saturated ammonium chloride solution (20 mL) and extracted with DCM (3 × 15 mL). The combined organic layers were washed with brine and dried over anhydrous sodium sulfate. The solvent was removed in vacuo, and the residue was purified by silica gel column

chromatography (petroleum ether: ethyl acetate = 100:00 to 99:01) to yield the desired products **7a-7b** (85-87%) as yellow solids.

Table S3: The following starting materials **7a-7b** are reported in the literature:¹¹



General Procedure - 4 (GP-4) for the Preparation of 11,16-Diphenylbenzo[4,5]imidazo[1,2-*a*]indeno[2,1-*e*]naphtho[1,2-*c*]azepines (3aa-3ap)/ 11,16-diphenylbenzo[3,4]indeno[2',1':5,6]azepino[1,2-*a*]indole (5aa-5ab)/ 11-(2-bromophenyl)-16-phenylbenzo[*c*]benzo[4,5]imidazo[1,2-*a*]indeno[2,1-*e*]azepines (8ca-8ab):

To an oven-dried 10 mL MW reaction vial equipped with a stir bar, were added 2-(2-(phenylethynyl)phenyl)-1*H*-benzo[*d*]imidazoles **1a-1p**/ 2-(2-(phenylethynyl)phenyl)-1*H*-indole **4a**/ 1-methyl-2-(2-(phenylethynyl)phenyl)-1*H*-indole **4b** (1 equiv, 0.25 mmol), *ortho*-bromophenyl acetylenes **2a-2p**/1,2-bis(2-bromophenyl)ethynes **5a-5b** (1.2 equiv, 0.30 mmol), Pd(OAc)₂ (10 mol%, 0.025 mmol), DPEPhos (20 mol%, 0.05 mmol), Cs₂CO₃ (3 equiv, 0.75 mmol) and Toluene (2 mL). The resultant reaction mixture was charged with nitrogen gas and stirred at 120 °C for 30-45 minutes in a microwave reactor (150 W). The reaction was monitored by thin-layer chromatography (TLC). The reaction was quenched with the saturated ammonium chloride solution (20 mL) and extracted with ethyl acetate (3 × 15 mL). The combined organic layers were washed with brine and dried over anhydrous sodium sulfate. The solvent was removed in vacuo, and the residue was purified by silica gel column chromatography (petroleum ether: ethyl acetate = 100:00 to 95:05) to yield the desired products **3aa-3ap** (44-87%)/**5aa-5ab** (62-68%)/**8ca-8ab** (62-68%), as yellow solids/liquids/semisolids.

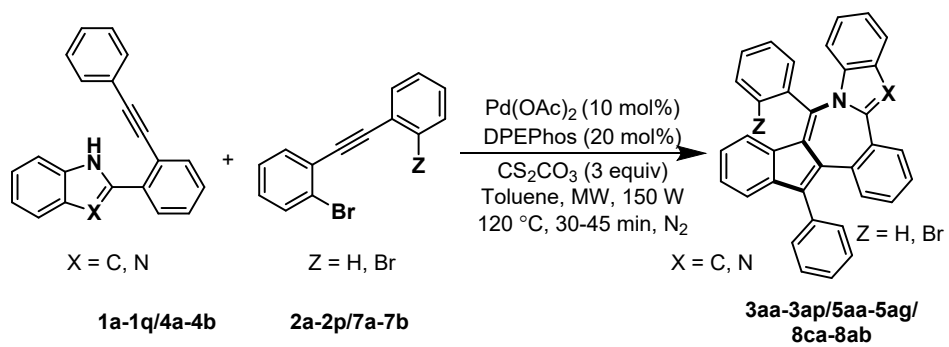
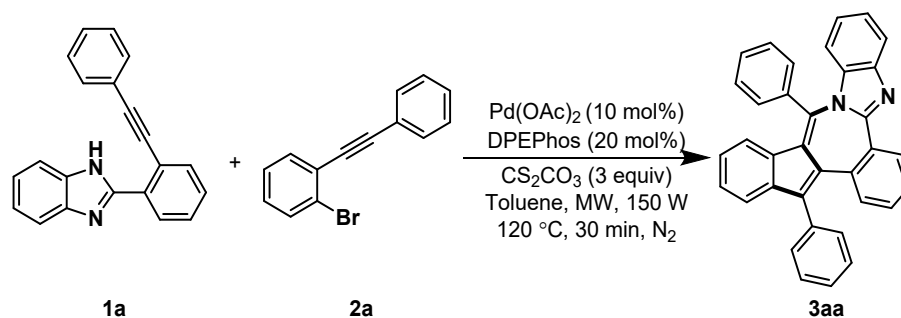


Table S4: Optimisation study.^{a-c}



S.No	Pd catalyst (10 mol%)	ligand (20 mol%)	base (3 equiv)	solvent	temp (°C)	time (min/h)	Yield of 3aa ^b
1	Pd(OAc)_2	DPEPhos	K_2CO_3	Toluene	80	60 min	15%
2	Pd(OAc)_2	DPEPhos	K_2CO_3	Toluene	100	60 min	53%
3	Pd(OAc)_2	DPEPhos	K_2CO_3	Toluene	120	30 min	85%
4	Pd(OAc)_2	DPEPhos	K_3PO_4	Toluene	120	30 min	81%
5	Pd(OAc)_2	DPEPhos	$t\text{BuOK}$	Toluene	120	30 min	35%
6	Pd(OAc)_2	DPEPhos	Cs_2CO_3	Toluene	120	30 min	87%
7	Pd(OAc)_2	DPEPhos	Cs_2CO_3	DMF	120	30 min	trace
8	Pd(OAc)_2	DPEPhos	Cs_2CO_3	DMSO	120	30 min	trace
9	Pd(OAc)_2	DPEPhos	Cs_2CO_3	1,4-dioxane	120	30 min	15%
10	$\text{Pd(PPh}_3)_4$	--	Cs_2CO_3	Toluene	120	30 min	trace
11	$\text{Pd(PPh}_3)_2\text{Cl}_2$	DPEPhos	Cs_2CO_3	Toluene	120	30 min	86%
12	PdCl_2	DPEPhos	Cs_2CO_3	Toluene	120	30 min	71%
13	Pd(OAc)_2	PPh_3	Cs_2CO_3	Toluene	120	30 min	trace
14	Pd(OAc)_2	PCy_3	Cs_2CO_3	Toluene	120	30 min	82%
15	Pd(OAc)_2	Xanthphos	Cs_2CO_3	Toluene	120	30 min	86%
16	Pd(OAc)_2	DPEPhos	Cs_2CO_3	Toluene	140	30 min	72%

17	Pd(OAc) ₂	DPEPhos	Cs ₂ CO ₃	Toluene	110	30 min	75%
18 ^c	Pd(OAc) ₂	DPEPhos	Cs ₂ CO ₃	Toluene	120	24 h	80%

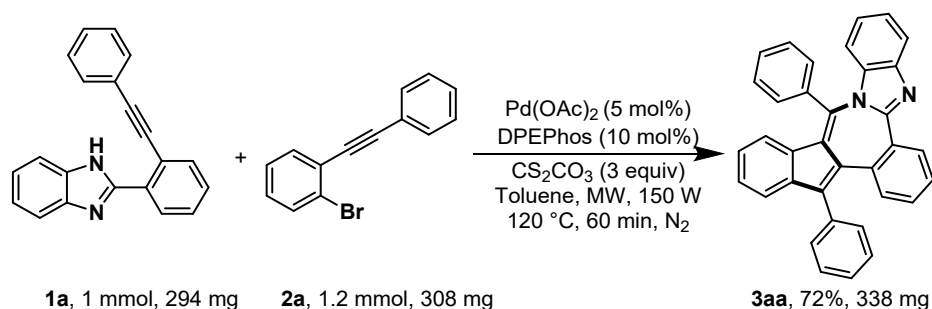
Reaction conditions: ^a**1** (0.25 mmol, 1 equiv), **2** (0.30 mmol, 1.2 equiv), Pd(OAc)₂ (0.025 mmol, 10 mol%), DPEPhos (0.05 mmol, 20 mol%), Cs₂CO₃ (0.75 mmol, 3 equiv), toluene (2 mL), MW, 150 W, 120 °C, 30 min, N₂. ^bIsolated yields of **3aa**. ^cReaction was conducted in an oil bath instead of MW reactor.

To obtain the anticipated product, 11,16-diphenylbenzo[*c*]benzo[4,5]imidazo[1,2-*a*]indeno[2,1-*e*]azepine (**3aa**) under palladium domino catalysis, 2-(2-(phenylethynyl)phenyl)-1*H*-benzo[*d*]imidazole (**1a**) and *o*-bromodiphenylacetylene (**2a**) were selected as model substrates. Thus, a reaction conducted between **1a** and **2a** using Pd(OAc)₂ (10 mol%), DPEphos (20 mol%), K₂CO₃ (3 equiv) in toluene (2 mL) at 80 °C under microwave irradiation for 30 min, the desired compound **3aa** was produced in 15% (Table S4, entry 1). Further increasing the temperatures from 80 °C to 100 °C and 120 °C resulted in improved yields of **3aa** in 53% and 85%, respectively (Table S4, entries 2-3). To evaluate the influence of reaction parameters, the reactions' screening using other bases, including K₃PO₄, ^tBuOK, and Cs₂CO₃, in place of K₂CO₃, furnished **3aa** in 81%, 35%, and 87% of yields, respectively (Table S4, entries 4–6). Among the bases, Cs₂CO₃ gave the product **3aa** in better yield (87%) (Table S4, entry 6). Later, a series of reaction parameters was checked. For example, replacing toluene with other solvents, such as DMF, DMSO, and 1,4-dioxane, resulted in almost no yield or very poor yield of the product **3aa** (Table S4, entries 7-9). Further, examining the reactions with various palladium catalysts, for instance, the reaction with Pd(PPh₃)₄ without additional ligand, a trace of the product **3aa** was observed (Table S4, entry 10); while with Pd(PPh₃)₂Cl₂ and PdCl₂, delivered **3aa** in 86% and 71% yields, respectively (Table S4, entries 11 & 12). Besides, the influence of ligands was investigated by substituting DPEphos with other phosphine ligands. For example, the reaction in the presence of PPh₃, only trace amount of **3aa** was observed (Table S4, entry 13); while PCy₃ provided 82% and Xantphos afforded 86% yields of **3aa**, respectively (Table S4, entries 14 & 15). Furthermore, altering the reaction temperatures at 140 °C and 110 °C, resulted in lower yields of **3aa** than at 120 °C (Table S4, entries 16 & 17). However, conducting the reaction under conventional oil-bath heating at 120 °C for 24 h, afforded **3aa** in slightly lower yield (83%) compared to the microwave irradiation (Table S4, entry 18). Overall, these findings demonstrate that microwave irradiation offers enhanced efficiency, affording the desired product **3aa** in a shorter reaction time and with an

improved yield than conventional heating methods, and as observed in entry 6 of Table S4, it was best with respect to the yield of **3aa**.

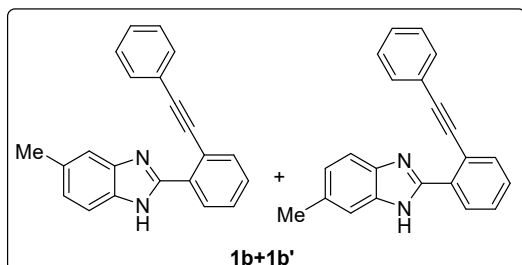
Scheme S2: Scale up reaction of 11,16-diphenylbenzo[4,5]imidazo[1,2-*a*]indeno[2,1-*e*]naphtho[1,2-*c*]azepine (3aa**):**

To an oven-dried 10 mL MW reaction vial equipped with a stir bar, were added 2-(2-(phenylethynyl)phenyl)-1*H*-benzo[*d*]imidazole **1a** (294 mg, 1 mmol), *ortho*-bromophenyl acetylene **2a** (308 mg, 1.2 equiv, 1.2 mmol), Pd(OAc)₂ (11.2 mg, 5 mol%, 0.05 mmol), DPEPhos (54 mg, 10 mol%, 0.10 mmol), Cs₂CO₃ (977 mg, 3 mmol), and Toluene (4 mL). The resultant reaction mixture was charged with nitrogen gas and stirred at 120 °C for 60 minutes in a microwave reactor (150 W). The reaction was monitored by thin-layer chromatography (TLC). The reaction was quenched with the saturated ammonium chloride solution (20 mL) and extracted with ethyl acetate (3 × 15 mL). The combined organic layers were washed with brine and dried over anhydrous sodium sulfate. The solvent was removed in vacuo, and the residue was purified by silica gel column chromatography (petroleum ether:ethyl acetate = 100:00 to 96:04) to yield the desired products **3aa** (338 mg, 72%) as yellow solids/liquids.



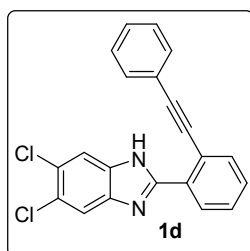
Characterisation of compounds:

5-Methyl-2-(2-(phenylethynyl)phenyl)-1*H*-benzo[*d*]imidazole/6-methyl-2-(2-(phenylethynyl)phenyl)-1*H*-benzo[*d*]imidazole (**1b+1b'**): (*rr* = 1:0.14)



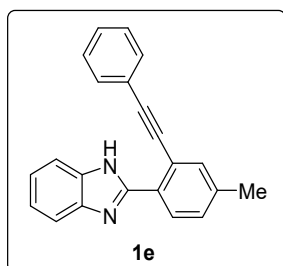
GP-1 was carried out with 2-bromobenzaldehyde **9** (184 mg, 1 mmol), phenylacetylene **10** (102 mg, 1 mmol), Pd(OAc)₂ (4.4 mg, 2 mol%, 0.02 mmol), Xanthphos (23 mg, 4 mol%, 0.04 mmol), Toluene (3 mL) at 120 °C temperature for 1 h. After filtration of the compound **11** by short silica gel column chromatography (petroleum ether: ethyl acetate = 98:02), 4-methylbenzene-1,2-diamine **12** (134 mg, 1.1 mmol), ammonium chloride (55 mg, 1 mmol), and DMSO (3 mL) were added, and the reaction was conducted at rt for 3 h. Purification of the crude material by silica gel column chromatography (petroleum ether: ethyl acetate = 95:05 to 90:10) furnished the product **1b+1b'** (*rr* = 1:0.14) (241 mg, 82%) as a yellow solid. mp = 102–104 °C. [TLC (petroleum ether: ethyl acetate = 90:10), *R_f*(**11**) = 0.90, *R_f*(**12**) = 0.60, *R_f*(**1b+1b'**) = 0.40, UV detection]. **IR:** (MIR-ATR, 4000–600 cm⁻¹) *v*_{max} = 3406, 3049, 2917, 2215, 1708, 1630, 1490, 1396, 1271, 750, 695 cm⁻¹. **¹H NMR (600 MHz, Acetone-*d*₆)** δ 8.24 – 8.17 (m, 1H), 7.72 – 7.68 (m, 1H), 7.67 – 7.64 (m, 1H), 7.59 – 7.55 (m, 2H), 7.51 – 7.45 (m, 3H), 7.42 – 7.36 (m, 3H), 7.08 (d, *J* = 8.2 Hz, 1H), 2.44 (s, 3H) ppm. **¹³C{¹H} NMR (151 MHz, Acetone-*d*₆)** δ 151.1 (2C), 134.2 (2C), 133.3, 132.3 (2C), 130.7 (2C), 130.2, 130.1 (2C), 129.8, 129.6, 129.4, 127.7, 124.8, 123.6, 121.5, 94.5, 89.2, 21.8 ppm. **HRMS (ESI):** *m/z* calcd for C₂₂H₁₆N₂⁺ [*M*]⁺: 308.1308, found: 308.1300.

5,6-Dichloro-2-(2-(phenylethynyl)phenyl)-1*H*-benzo[*d*]imidazole (**1d**):



GP-1 was carried out with 2-bromobenzaldehyde **9** (184 mg, 1 mmol), phenylacetylene **10** (102 mg, 1 mmol), Pd(OAc)₂ (4.4 mg, 2 mol%, 0.02 mmol), Xanthphos (23 mg, 4 mol%, 0.04 mmol), Toluene (3 mL) at 120 °C temperature for 1.5 h. After filtration of the compound **11** by short silica gel column chromatography (petroleum ether: ethyl acetate = 98:02), 4,5-dichlorobenzene-1,2-diamine **12** (177 mg, 1.1 mmol), ammonium chloride (55 mg, 1 mmol), and DMSO (3 mL) were added, and the reaction was conducted at rt for 3 h. Purification of the crude material by silica gel column chromatography (petroleum ether:ethyl acetate = 95:05 to 90:10) furnished the product **1d** (264 mg, 73%) as a yellow solid. mp = 156-158 °C. [TLC (petroleum ether: ethyl acetate = 90:10), *R_f*(**11**) = 0.90, *R_f*(**12**) = 0.60, *R_f*(**1d**) = 0.40, UV detection]. **IR:** (MIR-ATR, 4000–600 cm⁻¹) *v*_{max} = 3392, 3053, 2860, 2773, 2215, 1746, 1570, 1495, 1093, 962, 751, 686 cm⁻¹. **¹H NMR (600 MHz, CDCl₃)** δ 11.08 (bs, 1H), 8.44 – 8.36 (m, 1H), 7.81 (s, 1H), 7.65 – 7.59 (m, 1H), 7.55 – 7.50 (m, 2H), 7.49 – 7.36 (m, 6H) ppm. **¹³C{¹H} NMR (151 MHz, CDCl₃)** δ 152.6 (2C), 133.9, 131.7, 131.5 (2C), 130.1, 129.7, 129.7 (2C), 129.6, 129.4, 129.0 (2C), 121.8, 120.9, 119.6, 112.2 (2C), 95.2, 88.7 ppm. **HRMS (ESI):** *m/z* calcd for C₂₁H₁₆Cl₂N₃⁺ [M + NH₄]⁺: 380.0716, found: 380.0727.

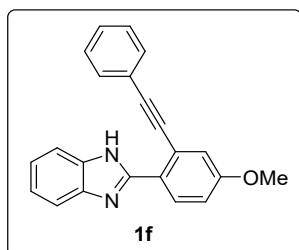
2-(4-Methyl-2-(phenylethynyl)phenyl)-1*H*-benzo[*d*]imidazole (1e):



GP-1 was carried out with 2-bromo-4-methylbenzaldehyde **9** (198 mg, 1 mmol), phenylacetylene **10** (102 mg, 1 mmol), Pd(OAc)₂ (4.4 mg, 2 mol%, 0.02 mmol), Xanthphos (23 mg, 4 mol%, 0.04 mmol), Toluene (3 mL) at 120 °C temperature for 1.5 h. After filtration of the compound **11** by short silica gel column chromatography (petroleum ether: ethyl acetate = 98:02), benzene-1,2-diamine **12** (118 mg, 1.1 mmol), ammonium chloride (55 mg, 1 mmol), and DMSO (3 mL) were added, and the reaction was conducted at rt for 3 h. Purification of the crude material by silica gel column chromatography (petroleum ether: ethyl acetate = 95:05 to 90:10) furnished the product **1e** (243 mg, 79%) as a yellow solid. mp = 102-104 °C. [TLC (petroleum ether: ethyl acetate = 90:10), *R_f*(**11**) = 0.90, *R_f*(**12**) = 0.60, *R_f*(**1e**) = 0.40, UV detection]. **IR:** (MIR-ATR, 4000–600 cm⁻¹) *v*_{max} = 3403, 3056, 2919, 1708, 1608, 1498, 1267, 826, 750, 693 cm⁻¹. **¹H NMR (600 MHz, DMSO-*d*₆)** δ 13.20 (bs, 1H), 8.38 (d, *J* = 8.0 Hz,

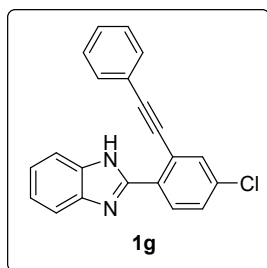
1H), 8.17 (s, 2H), 8.09 (s, 1H), 8.03 (d, $J = 6.1$ Hz, 2H), 7.96 – 7.86 (m, 4H), 7.75 (dd, $J = 5.8$, 3.1 Hz, 2H), 2.91 (s, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, DMSO- d_6) δ 150.6 (2C), 139.5 (2C), 133.4 (2C), 131.3 (2C), 129.9, 129.8 (2C), 129.3, 129.1, 128.9, 128.7, 126.7, 122.6, 122.1, 120.7, 92.7, 88.8, 39.5, 20.6 ppm. HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{18}\text{N}_2\text{O}^+$ [$\text{M} + \text{H}_2\text{O}$] $^+$: 326.1414, found: 326.1421.

2-(4-Methoxy-2-(phenylethynyl)phenyl)-1H-benzo[d]imidazole (1f):



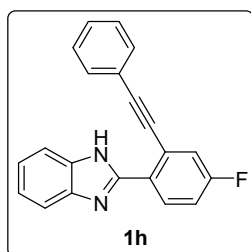
GP-1 was carried out with 2-bromo-4-methoxybenzaldehyde **9** (214 mg, 1 mmol), phenylacetylene **10** (102 mg, 1 mmol), $\text{Pd}(\text{OAc})_2$ (4.4 mg, 2 mol%, 0.02 mmol), Xanthphos (23 mg, 4 mol%, 0.04 mmol), Toluene (3 mL) at 120 °C temperature for 1.5 h. After filtration of the compound **11** by short silica gel column chromatography (petroleum ether: ethyl acetate = 97:03), benzene-1,2-diamine **12** (118 mg, 1.1 mmol), ammonium chloride (55 mg, 1 mmol), and DMSO (3 mL) were added, and the reaction was conducted at rt for 4 h. Purification of the crude material by silica gel column chromatography (petroleum ether: ethyl acetate = 95:05 to 90:10) furnished the product **1f** (259 mg, 80%) as a yellow solid. mp = 128-130 °C. [TLC (petroleum ether: ethyl acetate = 90:10), $R_f(\mathbf{11}) = 0.85$, $R_f(\mathbf{12}) = 0.60$, $R_f(\mathbf{1f}) = 0.30$, UV detection]. IR: (MIR-ATR, 4000–600 cm^{-1}) $\nu_{\text{max}} = 3411, 3059, 2928, 2214, 1733, 1603, 1482, 1273, 1086, 749, 694$ cm^{-1} . ^1H NMR (600 MHz, Acetone- d_6) δ 11.71 (bs, 1H), 8.19 (d, $J = 8.8$ Hz, 1H), 7.73 – 7.64 (m, 2H), 7.62 – 7.59 (m, 2H), 7.46 – 7.43 (m, 3H), 7.27 (d, $J = 2.7$ Hz, 1H), 7.25 – 7.21 (m, 2H), 7.16 (dd, $J = 8.8, 2.7$ Hz, 1H), 3.94 (s, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, Acetone- d_6) δ 161.3, 151.5 (2C), 132.5 (2C), 132.4 (2C), 130.3, 129.9 (2C), 129.5 (2C), 126.0, 123.7, 123.0, 122.7, 118.4, 118.2, 116.6, 94.4, 89.1, 56.0 ppm. HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{16}\text{KN}_2\text{O}^+$ [$\text{M} + \text{K}$] $^+$: 363.0894, found: 363.0890.

2-(4-Chloro-2-(phenylethynyl)phenyl)-1*H*-benzo[*d*]imidazole (**1g**):



GP-1 was carried out with 2-bromo-4-chlorobenzaldehyde **9** (217 mg, 1 mmol), phenylacetylene **10** (102 mg, 1 mmol), Pd(OAc)₂ (4.4 mg, 2 mol%, 0.02 mmol), Xanthphos (23 mg, 4 mol%, 0.04 mmol), Toluene (3 mL) at 120 °C temperature for 1.5 h. After filtration of the compound **11** by short silica gel column chromatography (petroleum ether: ethyl acetate = 98:02), benzene-1,2-diamine **12** (118 mg, 1.1 mmol), ammonium chloride (55 mg, 1 mmol), and DMSO (3 mL) were added, and the reaction was conducted at rt for 3 h. Purification of the crude material by silica gel column chromatography (petroleum ether:ethyl acetate = 95:05 to 90:10) furnished the product **1g** (249 mg, 76%) as a yellow solid. mp = 130-132 °C. [TLC (petroleum ether: ethyl acetate = 90:10), *R_f*(**11**) = 0.80, *R_f*(**12**) = 0.60, *R_f*(**1g**) = 0.40, UV detection]. **IR:** (MIR-ATR, 4000–600 cm⁻¹) ν_{\max} = 3408, 3054, 2216, 1767, 1593, 1494, 1271, 1110, 885, 746, 693 cm⁻¹. **¹H NMR (600 MHz, Acetone-*d*₆)** δ 12.01 (bs, 1H), 8.18 (d, *J*_{C-F} = 8.5 Hz, 1H), 7.72 – 7.69 (m, 3H), 7.59 – 7.55 (m, 2H), 7.53 (dd, *J*_{C-F} = 8.5, 2.2 Hz, 1H), 7.43 – 7.39 (m, 3H), 7.29 – 7.25 (m, 2H) ppm. **¹³C{¹H} NMR (151 MHz, Acetone-*d*₆)** δ 150.4 (2C), 135.6 (2C), 133.5 (2C), 132.5 (2C), 132.4, 131.9, 130.2, 130.1, 129.9, 129.8, 129.4 (2C), 123.5, 123.6, 123.2, 95.8, 87.7, 29.8 ppm. **HRMS (ESI):** *m/z* calcd for C₂₁H₁₇ClN₂O₂²⁺ [M + 2H₂O]²⁺: 182.0484, found: 182.0499.

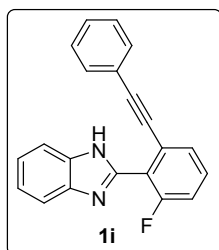
2-(4-Fluoro-2-(phenylethynyl)phenyl)-1*H*-benzo[*d*]imidazole (**1h**):



GP-1 was carried out with 2-bromo-4-fluorobenzaldehyde **9** (202 mg, 1 mmol), phenylacetylene **10** (102 mg, 1 mmol), Pd(OAc)₂ (4.4 mg, 2 mol%, 0.02 mmol), Xanthphos (23 mg, 4 mol%, 0.04 mmol), Toluene (3 mL) at 120 °C temperature for 1 h. After filtration of the

compound **11** by short silica gel column chromatography (petroleum ether: ethyl acetate = 98:02), benzene-1,2-diamine **12** (118 mg, 1.1 mmol), ammonium chloride (55 mg, 1 mmol), and DMSO (3 mL) were added, and the reaction was conducted at rt for 3 h. Purification of the crude material by silica gel column chromatography (petroleum ether: ethyl acetate = 95:05 to 90:10) furnished the product **1h** (265 mg, 85%) as a colorless solid. mp = 110-112 °C. [TLC (petroleum ether: ethyl acetate = 90:10), $R_f(\mathbf{11}) = 0.80$, $R_f(\mathbf{12}) = 0.60$, $R_f(\mathbf{1h}) = 0.40$, UV detection]. **IR:** (MIR-ATR, 4000–600 cm^{-1}) $\nu_{\text{max}} = 3409, 3056, 2211, 1765, 1606, 1483, 1314, 1198, 871, 745, 693 \text{ cm}^{-1}$. **^1H NMR (600 MHz, Acetone- d_6)** δ 11.99 (bs, 1H), 8.24 – 8.16 (m, 1H), 7.74 – 7.66 (m, 2H), 7.55 (s, 2H), 7.45 (d, $J = 7.7 \text{ Hz}$, 1H), 7.40 (s, 3H), 7.33 – 7.23 (m, 3H) ppm. **$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, Acetone- d_6)** δ 163.55 (d, $J_{\text{C-F}} = 248.8 \text{ Hz}$), 150.65 (2C), 133.26 (d, $J_{\text{C-F}} = 9.0 \text{ Hz}$), 132.49, 130.17 (2C), 130.01 (2C), 129.92 (d, $J_{\text{C-F}} = 3.3 \text{ Hz}$), 129.87 (2C), 129.41 (2C), 123.72 (d, $J = 9.9 \text{ Hz}$), 123.31, 123.19, 120.25 (d, $J_{\text{C-F}} = 23.7 \text{ Hz}$), 117.15 (d, $J_{\text{C-F}} = 21.8 \text{ Hz}$), 95.54, 87.87 (d, $J_{\text{C-F}} = 2.9 \text{ Hz}$) ppm. **HRMS (ESI):** m/z calcd for $\text{C}_{21}\text{H}_{15}\text{FN}_2^{2+}$ [$\text{M} + 2\text{H}$] $^{2+}$: 157.0604, found: 157.0607.

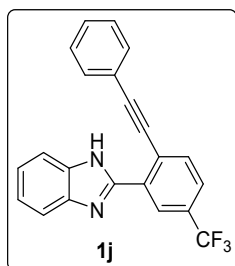
2-(2-Fluoro-6-(phenylethynyl)phenyl)-1H-benzo[d]imidazole (**1i**):



GP-1 was carried out with 2-bromo-6-fluorobenzaldehyde **9** (202 mg, 1 mmol), phenylacetylene **10** (102 mg, 1 mmol), $\text{Pd}(\text{OAc})_2$ (4.4 mg, 2 mol%, 0.02 mmol), Xanthphos (23 mg, 4 mol%, 0.04 mmol), Toluene (3 mL) at 120 °C temperature for 1 h. After filtration of the compound **11** by short silica gel column chromatography (petroleum ether: ethyl acetate = 98:02), benzene-1,2-diamine **12** (118 mg, 1.1 mmol), ammonium chloride (55 mg, 1 mmol), and DMSO (3 mL) were added, and the reaction was conducted at rt for 3 h. Purification of the crude material by silica gel column chromatography (petroleum ether: ethyl acetate = 95:05 to 90:10) furnished the product **1i** (193 mg, 62%) as a colorless solid. mp = 138-140 °C. [TLC (petroleum ether: ethyl acetate = 90:10), $R_f(\mathbf{11}) = 0.80$, $R_f(\mathbf{12}) = 0.60$, $R_f(\mathbf{1i}) = 0.40$, UV detection]. **IR:** (MIR-ATR, 4000–600 cm^{-1}) $\nu_{\text{max}} = 3058, 2924, 2855, 2213, 1773, 1616, 1563, 1433, 1267, 751, 699 \text{ cm}^{-1}$. **^1H NMR (600 MHz, Acetone- d_6)** δ 12.19 (bs, 1H), 7.70 (s, 2H), 7.58 – 7.50 (m, 2H), 7.35 – 7.29 (m, 6H), 7.29 – 7.25 (m, 2H) ppm. **$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz,**

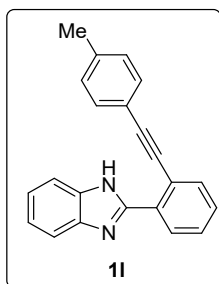
Acetone-*d*₆ δ 161.5 (d, J_{C-F} = 249.6 Hz), 146.0 (2C), 132.3 (2C), 132.1 (d, J_{C-F} = 9.4 Hz), 130.2 (2C), 130.0 (2C), 129.7, 129.40 (d, J_{C-F} = 3.1 Hz), 129.3 (2C), 126.3 (d, J_{C-F} = 3.7 Hz), 123.5, 123.2, 122.6 (d, J_{C-F} = 15.7 Hz), 117.0 (d, J_{C-F} = 22.6 Hz), 94.5, 87.9 (d, J_{C-F} = 3.9 Hz) ppm. **HRMS (ESI):** m/z calcd for C₂₁H₁₃FN₂Na⁺ [M + Na]⁺: 335.0955, found: 335.0957.

2-(2-(Phenylethynyl)-5-(trifluoromethyl)phenyl)-1*H*-benzo[*d*]imidazole (1j):



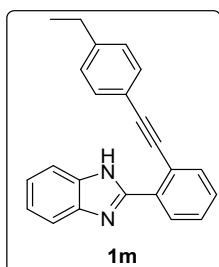
GP-1 was carried out with 2-bromo-5-(trifluoromethyl)benzaldehyde **9** (251 mg, 1 mmol), phenylacetylene **10** (102 mg, 1 mmol), Pd(OAc)₂ (4.4 mg, 2 mol%, 0.02 mmol), Xanthphos (23 mg, 4 mol%, 0.04 mmol), Toluene (3 mL) at 120 °C temperature for 1 h. After filtration of the compound **11** by short silica gel column chromatography (petroleum ether: ethyl acetate = 98:02), benzene-1,2-diamine **12** (118 mg, 1.1 mmol), ammonium chloride (55 mg, 1 mmol), and DMSO (3 mL) were added, and the reaction was conducted at rt for 3 h. Purification of the crude material by silica gel column chromatography (petroleum ether: ethyl acetate = 95:05 to 90:10) furnished the product **1j** (304 mg, 84%) as a yellow solid. mp = 160-162 °C. [TLC (petroleum ether: ethyl acetate = 90:10), R_f (**11**) = 0.80, R_f (**12**) = 0.60, R_f (**1j**) = 0.40, UV detection]. **IR:** (MIR-ATR, 4000–600 cm⁻¹) ν_{\max} = 3411, 3061, 2926, 2216, 1737, 1618, 1322, 1168, 1127, 1084, 751, 697 cm⁻¹. **¹H NMR (600 MHz, Acetone-*d*₆ & CDCl₃)** δ 11.76 (bs, 1H), 8.48 (s, 1H), 7.74 (d, J = 7.9 Hz, 2H), 7.61 (d, J = 8.2 Hz, 1H), 7.57 – 7.52 (m, 1H), 7.49 – 7.44 (m, 2H), 7.35 – 7.28 (m, 3H), 7.21 (dd, J = 7.2, 1.6 Hz, 2H) ppm. **¹³C{¹H} NMR (151 MHz, Acetone-*d*₆ & CDCl₃)** δ 149.4, 143.7, 134.8, 134.3, 132.7, 131.9 (2C), 130.5 (q, J_{C-F} = 33.2 Hz), 129.6, 128.8 (2C), 126.9 (q, J_{C-F} = 3.6 Hz), 125.8 (q, J_{C-F} = 3.4 Hz), 124.3, 123.9 (q, J_{C-F} = 271.9 Hz), 123.7, 122.7, 122.2, 119.8, 111.9, 96.7, 87.4 ppm. **HRMS (ESI):** m/z calcd for C₂₂H₁₃F₃N₂⁺ [M]⁺: 362.1025, found: 362.1023.

2-(2-(*p*-Tolylethynyl)phenyl)-1*H*-benzo[*d*]imidazole (**1l**):



GP-1 was carried out with 2-bromobenzaldehyde **9** (184 mg, 1 mmol), 1-ethynyl-4-methylbenzene **10** (116 mg, 1 mmol), Pd(OAc)₂ (4.4 mg, 2 mol%, 0.02 mmol), Xanthphos (23 mg, 4 mol%, 0.04 mmol), Toluene (3 mL) at 120 °C temperature for 1.5 h. After filtration of the compound **11** by short silica gel column chromatography (petroleum ether: ethyl acetate = 98:02), benzene-1,2-diamine **12** (118 mg, 1.1 mmol), ammonium chloride (55 mg, 1 mmol), and DMSO (3 mL) were added, and the reaction was conducted at rt for 3 h. Purification of the crude material by silica gel column chromatography (petroleum ether: ethyl acetate = 95:05 to 90:10) furnished the product **11** (253 mg, 82%) as a yellow solid. mp = 110-112 °C. [TLC (petroleum ether: ethyl acetate = 90:10), $R_f(\mathbf{11}) = 0.90$, $R_f(\mathbf{12}) = 0.60$, $R_f(\mathbf{11}) = 0.40$, UV detection]. **IR:** (MIR-ATR, 4000–600 cm⁻¹) $\nu_{\max} = 3403, 3055, 2923, 2213, 1770, 1616, 1514, 1314, 814, 745$ cm⁻¹. **¹H NMR (600 MHz, CDCl₃)** δ 11.05 (bs, 1H), 8.58 – 8.50 (m, 1H), 7.85 (s, 1H), 7.68 – 7.60 (m, 1H), 7.51 – 7.37 (m, 5H), 7.31 – 7.28 (m, 2H), 7.22 (d, $J = 6.6$ Hz, 2H), 2.40 (s, 3H) ppm. **¹³C{¹H} NMR (151 MHz, CDCl₃)** δ 150.67 (2C), 139.8, 133.7, 131.4 (2C), 130.6, 129.7 (2C), 129.6, 129.5, 129.2, 123.4 (2C), 122.8 (2C), 119.6, 119.0, 110.9, 95.1, 88.6, 21.7 ppm. **HRMS (ESI):** m/z calcd for C₂₂H₁₆N₂Na⁺ [M + Na]⁺: 331.1206, found: 331.1232.

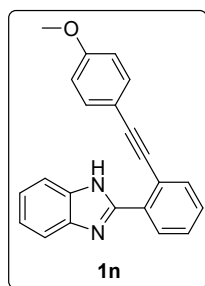
2-(2-((4-Ethylphenyl)ethynyl)phenyl)-1*H*-benzo[*d*]imidazole (**1m**):



GP-1 was carried out with 2-bromobenzaldehyde **9** (184 mg, 1 mmol), 1-ethyl-4-ethynylbenzene **10** (130 mg, 1 mmol), Pd(OAc)₂ (4.4 mg, 2 mol%, 0.02 mmol), Xanthphos (23 mg, 4 mol%, 0.04 mmol), Toluene (3 mL) at 120 °C temperature for 1.5 h. After filtration of

the compound **11** by short silica gel column chromatography (petroleum ether: ethyl acetate = 98:02), benzene-1,2-diamine **12** (118 mg, 1.1 mmol), ammonium chloride (55 mg, 1 mmol), and DMSO (3 mL) were added, and the reaction was conducted at rt for 3 h. Purification of the crude material by silica gel column chromatography (petroleum ether: ethyl acetate = 95:05 to 90:10) furnished the product **1m** (277 mg, 86%) as a yellow oil. [TLC (petroleum ether: ethyl acetate = 90:10), $R_f(\mathbf{11}) = 0.90$, $R_f(\mathbf{12}) = 0.60$, $R_f(\mathbf{1m}) = 0.40$, UV detection]. **IR:** (MIR-ATR, 4000–600 cm^{-1}) $\nu_{\text{max}} = 3401, 3054, 2963, 2925, 2213, 1702, 1611, 1441, 1270, 832, 746 \text{ cm}^{-1}$. **^1H NMR (600 MHz, Acetone-*d*6)** δ 7.99 (d, $J = 2.7$ Hz, 1H), 7.47 (s, 2H), 7.44 (s, 1H), 7.22 (s, 4H), 7.03 – 6.96 (m, 4H), 2.41 – 2.35 (m, 2H), 0.97 – 0.92 (m, 3H) ppm. **$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, Acetone)** δ 151.5 (2C), 146.2, 134.1, 133.0, 132.4 (2C), 130.8, 130.3, 129.7 (2C), 129.5, 129.2, 128.9 (2C), 123.2, 121.8 (2C), 120.8, 95.0, 88.5, 29.3, 15.8 ppm. **HRMS (ESI):** m/z calcd for $\text{C}_{23}\text{H}_{18}\text{K}_2\text{N}_2^{2+}$ $[\text{M} + 2\text{K}]^{2+}$: 200.0367, found: 200.0357.

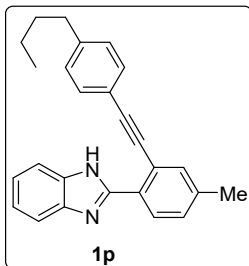
2-(2-((4-Methoxyphenyl)ethynyl)phenyl)-1H-benzo[d]imidazole (**1n**):



GP-1 was carried out with 2-bromobenzaldehyde **9** (184 mg, 1 mmol), 1-ethynyl-4-methoxybenzene **10** (132 mg, 1 mmol), $\text{Pd}(\text{OAc})_2$ (4.4 mg, 2 mol%, 0.02 mmol), Xanthphos (23 mg, 4 mol%, 0.04 mmol), Toluene (3 mL) at 120 °C temperature for 1.5 h. After filtration of the compound **11** by short silica gel column chromatography (petroleum ether: ethyl acetate = 97:03), benzene-1,2-diamine **12** (118 mg, 1.1 mmol), ammonium chloride (55 mg, 1 mmol), and DMSO (3 mL) were added, and the reaction was conducted at rt for 3 h. Purification of the crude material by silica gel column chromatography (petroleum ether: ethyl acetate = 95:05 to 90:10) furnished the product **1n** (256 mg, 81%) as a yellow oil. [TLC (petroleum ether: ethyl acetate = 90:10), $R_f(\mathbf{11}) = 0.90$, $R_f(\mathbf{12}) = 0.60$, $R_f(\mathbf{1n}) = 0.40$, UV detection]. **IR:** (MIR-ATR, 4000–600 cm^{-1}) $\nu_{\text{max}} = 3401, 3055, 3004, 2213, 1771, 1605, 1512, 1255, 833, 753 \text{ cm}^{-1}$. **^1H NMR (600 MHz, CDCl_3)** δ 11.05 (bs, 1H), 8.55 (d, $J = 7.7$ Hz, 1H), 7.85 (s, 1H), 7.64 (d, $J = 7.6$ Hz, 1H), 7.54 – 7.43 (m, 4H), 7.40 (dd, $J = 7.1, 7.0$ Hz, 1H), 7.29 (d, $J = 3.7$ Hz, 2H), 6.94 (d, $J = 8.3$ Hz, 2H), 3.85 (s, 3H) ppm. **$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3)** δ 160.5, 150.7 (2C), 133.6, 133.0 (2C), 130.4, 129.6 (2C), 129.1 (2C), 129.0, 128.3 (2C), 123.4, 122.8, 119.7, 114.6,

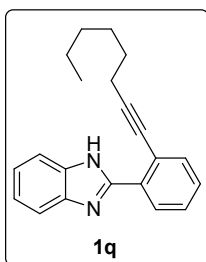
114.1, 95.0, 88.0, 55.5 ppm. **HRMS (ESI):** m/z calcd for $C_{22}H_{20}N_2O_3^{2+}$ $[M + 2H_2O]^{2+}$: 180.0731, found: 180.0732.

2-(2-((4-Butylphenyl)ethynyl)-4-methylphenyl)-1H-benzo[d]imidazole (1p):



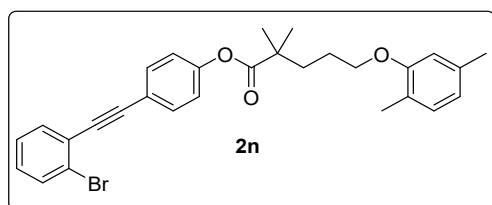
GP-1 was carried out with 2-bromo-4-methylbenzaldehyde **9** (198 mg, 1 mmol), 1-butyl-4-ethynylbenzene **10** (158 mg, 1 mmol), $Pd(OAc)_2$ (4.4 mg, 2 mol%, 0.02 mmol), Xanthphos (23 mg, 4 mol%, 0.04 mmol), Toluene (3 mL) at 120 °C temperature for 1.5 h. After filtration of the compound **11** by short silica gel column chromatography (petroleum ether: ethyl acetate = 98:02), benzene-1,2-diamine **12** (118 mg, 1.1 mmol), ammonium chloride (55 mg, 1 mmol), and DMSO (3 mL) were added, and the reaction was conducted at rt for 3 h. Purification of the crude material by silica gel column chromatography (petroleum ether: ethyl acetate = 95:05 to 90:10) furnished the product **1p** (273 mg, 75%) as a yellow oil. [TLC (petroleum ether: ethyl acetate = 90:10), $R_f(\mathbf{11}) = 0.90$, $R_f(\mathbf{12}) = 0.60$, $R_f(\mathbf{1p}) = 0.40$, UV detection]. **IR:** (MIR-ATR, $4000\text{--}600\text{ cm}^{-1}$) $\nu_{\max} = 3405, 3054, 2922, 2859, 2204, 1607, 1508, 1445, 1271, 826, 745\text{ cm}^{-1}$. **1H NMR (600 MHz, Acetone- d_6)** δ 11.79 (bs, 1H), 8.15 (d, $J = 8.0$ Hz, 1H), 7.69 (s, 2H), 7.53 (s, 1H), 7.49 (d, $J = 7.8$ Hz, 2H), 7.37 – 7.34 (m, 1H), 7.27 – 7.23 (m, 4H), 2.64 (t, $J = 7.7$ Hz, 2H), 2.41 (s, 3H), 1.59 (dd, $J = 15.3, 7.6$ Hz, 2H), 1.38 – 1.33 (m, 2H), 0.92 (t, $J = 7.4$ Hz, 3H) ppm. **$^{13}C\{^1H\}$ NMR (151 MHz, Acetone- d_6)** δ 151.5 (2C), 144.9, 140.5, 134.5, 132.4 (2C), 130.8, 130.6, 130.4 (2C), 130.2, 129.9, 129.5 (2C), 123.1, 121.5, 120.9, 94.7, 88.8, 36.1, 34.2, 22.9, 21.0, 14.2 ppm. **HRMS (ESI):** m/z calcd for $C_{26}H_{24}N_2Na_2^{2+}$ $[M + 2Na]^{2+}$: 205.0862, found: 205.0855.

2-(2-(Oct-1-yn-1-yl)phenyl)-1H-benzo[d]imidazole (1q):



GP-1 was carried out with 2-bromo-4-methylbenzaldehyde **9** (198 mg, 1 mmol), 1-Octyne **10** (110 mg, 1 mmol), Pd(OAc)₂ (4.4 mg, 2 mol%, 0.02 mmol), Xanthphos (23 mg, 4 mol%, 0.04 mmol), Toluene (3 mL) at 120 °C temperature for 1.5 h. After filtration of the compound **11** by short silica gel column chromatography (petroleum ether: ethyl acetate = 98:02), benzene-1,2-diamine **12** (118 mg, 1.1 mmol), ammonium chloride (55 mg, 1 mmol), and DMSO (3 mL) were added, and the reaction was conducted at rt for 3 h. Purification of the crude material by silica gel column chromatography (petroleum ether: ethyl acetate = 95:05 to 90:10) furnished the product **1q** (236 mg, 78%) as a yellow oil. [TLC (petroleum ether: ethyl acetate = 90:10), $R_f(\mathbf{11}) = 0.90$, $R_f(\mathbf{12}) = 0.60$, $R_f(\mathbf{1q}) = 0.40$, UV detection]. **IR:** (MIR-ATR, 4000–600 cm⁻¹) $\nu_{\max} = 3394, 3057, 2923, 2856, 1703, 1643, 1598, 1447, 1328, 1024, 740$ cm⁻¹. **¹H NMR (600 MHz, CDCl₃)** δ 11.11 (bs, 1H), 8.56 (dd, $J = 8.0, 1.1$ Hz, 1H), 7.84 (d, $J = 6.1$ Hz, 1H), 7.55 (dd, $J = 7.7, 1.1$ Hz, 1H), 7.45 (ddd, $J = 7.9, 7.8,$ and 1.3 Hz, 2H), 7.37 (ddd, $J = 7.5, 7.4, 1.3$ Hz, 1H), 7.31 – 7.28 (m, 2H), 2.61 (t, $J = 7.2$ Hz, 2H), 1.78 – 1.73 (m, 2H), 1.57 – 1.51 (m, 2H), 1.39 – 1.31 (m, 4H), 0.90 (t, $J = 7.1$ Hz, 3H) ppm. **¹³C{¹H} NMR (151 MHz, CDCl₃)** δ 150.9, 134.2, 130.3, 129.5, 129.4, 128.7, 123.4, 122.7, 119.9, 110.8, 96.7, 81.2, 31.5, 29.0, 28.6, 22.7, 19.9, 14.2 ppm. **HRMS (ESI):** m/z calcd for C₂₁H₂₂N₂⁺ [M]⁺: 302.1778, found: 302.1785.

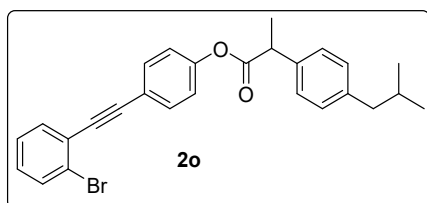
4-((2-Bromophenyl)ethynyl)phenyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (2n):



GP-2 was carried out with 4-iodophenyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (452 mg, 1 mmol) **13**, 1-bromo-2-ethynylbenzene **10** (182 mg, 1 mmol), Pd(PPh₃)₂Cl₂ (56 mg, 4 mol%, 0.04 mmol), CuI (18 mg, 10 mol%, 0.1 mmol), NEt₃ (3 mL) at room temperature for 3 h. Purification of the crude material by silica gel column chromatography (petroleum ether: ethyl acetate = 100:0 to 99:01) furnished the product **2n** (448 mg, 89%) as a yellow solid. mp = 64–66 °C. [TLC (petroleum ether: ethyl acetate = 98:02), $R_f(\mathbf{13}) = 0.70$, $R_f(\mathbf{10}) = 0.98$, $R_f(\mathbf{2n}) = 0.80$, UV detection]. **IR:** (MIR-ATR, 4000–600 cm⁻¹) $\nu_{\max} = 2924, 2869, 2221, 1749, 1611, 1505, 1261, 1199, 1043, 735, 705$ cm⁻¹. **¹H NMR (400 MHz, CDCl₃)** δ 7.65 – 7.54 (m, 4H), 7.30 (ddd, $J = 7.6, 7.5,$ and 1.1 Hz, 1H), 7.19 (ddd, $J = 7.8, 7.7, 1.7$ Hz, 1H), 7.08 – 7.00 (m,

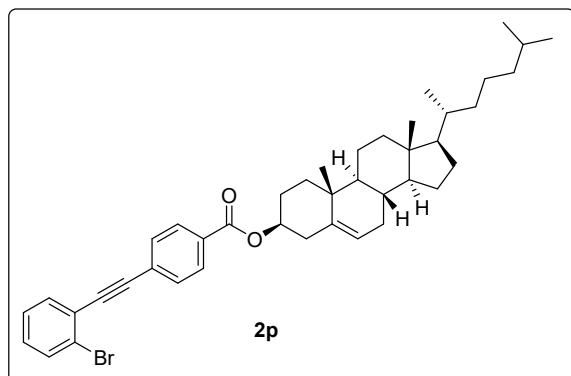
3H), 6.72 – 6.62 (m, 2H), 4.00 (t, $J = 5.1$ Hz, 2H), 2.32 (s, 3H), 2.19 (s, 3H), 1.90 (d, $J = 2.3$ Hz, 4H), 1.39 (s, 6H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 176.1, 156.9, 151.3, 136.6, 133.3, 132.9 (2C), 132.5, 130.5, 129.5, 127.1, 125.7, 125.3, 123.6, 121.9 (2C), 120.9, 120.5, 111.9, 93.3, 88.1, 67.7, 42.6, 37.2, 25.3, 25.2, 21.5, 15.9 ppm. HRMS (ESI): m/z calcd for $\text{C}_{29}\text{H}_{29}^{79}\text{BrNaO}_3^+$ $[\text{M}+\text{Na}]^+$: 527.1192, found: 527.1178. m/z calcd for $\text{C}_{29}\text{H}_{29}^{81}\text{BrNaO}_3^+$ $[\text{M}+\text{Na}]^+$: 529.1172, found: 529.1164.

4-((2-Bromophenyl)ethynyl)phenyl 2-(4-isobutylphenyl)propanoate (**2o**):



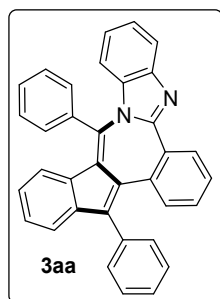
GP-2 was carried out with 4-iodophenyl 2-(4-isobutylphenyl)propanoate **13** (408 mg, 1 mmol), 1-bromo-2-ethynylbenzene **10** (182 mg, 1 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (56 mg, 4 mol%, 0.04 mmol), CuI (18 mg, 10 mol%, 0.10 mmol), NEt_3 (3 mL) at room temperature for 3 h. Purification of the crude material by silica gel column chromatography (petroleum ether: ethyl acetate = 100:0 to 99:01) furnished the product **2o** (392 mg, 85%) as a yellow solid. mp = 60–62 °C. [TLC (petroleum ether: ethyl acetate = 98:02), $R_f(\mathbf{13}) = 0.70$, $R_f(\mathbf{10}) = 0.98$, $R_f(\mathbf{2o}) = 0.80$, UV detection]. IR: (MIR-ATR, 4000–600 cm^{-1}) $\nu_{\text{max}} = 2958, 2216, 1756, 1632, 1509, 1266, 1198, 1131, 846, 750 \text{ cm}^{-1}$. ^1H NMR (400 MHz, CDCl_3) δ 7.62 (dd, $J = 8.0, 1.0$ Hz, 1H), 7.59 – 7.53 (m, 3H), 7.32 (d, $J = 8.1$ Hz, 2H), 7.30 – 7.25 (m, 1H), 7.21 – 7.13 (m, 3H), 7.06 – 7.01 (m, 2H), 3.96 (q, $J = 7.1$ Hz, 1H), 2.50 (d, $J = 7.2$ Hz, 2H), 1.89 (dp, $J = 13.6, 6.8$ Hz, 1H), 1.63 (d, $J = 7.2$ Hz, 3H), 0.93 (d, $J = 6.6$ Hz, 6H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 173.0, 151.1, 141.0, 137.2, 133.3, 132.9 (2C), 132.6, 129.7, 129.6, 127.3, 127.2, 125.7, 125.4, 121.8 (2C), 120.6, 93.3, 88.2, 45.4, 45.2, 30.3, 22.5, 18.6 ppm. HRMS (ESI): m/z calcd for $\text{C}_{27}\text{H}_{25}^{79}\text{BrNaO}_2^+$ $[\text{M} + \text{Na}]^+$: 483.0930, found: 483.0908. m/z calcd for $\text{C}_{27}\text{H}_{25}^{81}\text{BrNaO}_2^+$ $[\text{M} + \text{Na}]^+$: 485.0910, found: 485.0915.

(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 4-((2-bromophenyl)ethynyl)benzoate (2p**):**



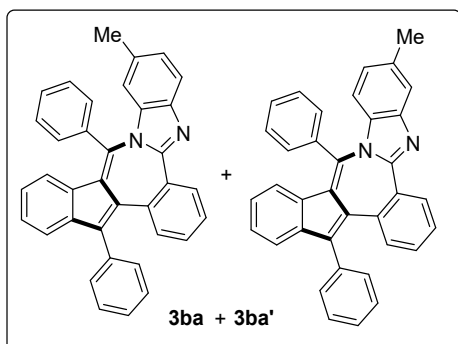
GP-2 was carried out with (3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 4-iodobenzoate (616 mg, 1 mmol) **13**, 1-bromo-2-ethynylbenzene **10** (182 mg, 1 mmol), Pd(PPh₃)₂Cl₂ (56 mg, 4 mol%, 0.04 mmol), CuI (18 mg, 10 mol%, 0.10 mmol), NEt₃ (3 mL) at room temperature for 3 h. Purification of the crude material by silica gel column chromatography (petroleum ether: ethyl acetate = 100:0 to 99:01) furnished the product **2i** (542 mg, 81%) as a yellow solid. mp = 90-92 °C. [TLC (petroleum ether: ethyl acetate = 98:02), *R_f*(**13**) = 0.80, *R_f*(**10**) = 0.98, *R_f*(**2p**) = 0.85, UV detection]. **IR:** (MIR-ATR, 4000–600 cm⁻¹) *v*_{max} = 3053, 2940, 2864, 2139, 1763, 1710, 1607, 1270, 1112, 853, 738 cm⁻¹. **¹H NMR (600 MHz, CDCl₃)** δ 8.06 – 8.01 (m, 2H), 7.65 – 7.60 (m, 3H), 7.56 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.30 (ddd, *J* = 7.6, 7.5, and 1.1 Hz, 1H), 7.20 (ddd, *J* = 7.9, 7.7, and 1.7 Hz, 1H), 5.42 (d, *J* = 3.6 Hz, 1H), 4.90 – 4.82 (m, 1H), 2.47 (d, *J* = 7.7 Hz, 2H), 2.06 – 1.95 (m, 3H), 1.91 (dt, *J* = 13.3, 3.3 Hz, 1H), 1.83 (tdd, *J* = 13.4, 8.6, 4.8 Hz, 1H), 1.79 – 1.69 (m, 1H), 1.61 – 1.42 (m, 6H), 1.41 – 1.31 (m, 3H), 1.30 – 1.08 (m, 8H), 1.08 – 1.06 (m, 3H), 1.03 – 0.96 (m, 3H), 0.92 (d, *J* = 6.6 Hz, 3H), 0.88 (dd, *J* = 6.6, 2.6 Hz, 6H), 0.69 (s, 3H). **¹³C{¹H} NMR (151 MHz, CDCl₃)** δ 165.5, 139.7, 133.5, 132.7, 131.6 (2C), 130.7, 129.9, 129.6 (2C), 127.5, 127.2, 125.9, 125.1, 123.0, 93.2, 90.8, 75.0, 56.8, 56.3, 50.2, 42.4, 39.9, 39.7, 38.3, 37.2, 36.8, 36.3, 35.9, 32.1, 32.0, 28.4, 28.2, 28.0, 24.4, 24.0, 23.0, 22.7, 21.2, 19.5, 18.9, 12.0 ppm. **HRMS (ESI):** *m/z* calcd for C₄₂H₅₄⁷⁹BrO₂⁺ [M + H]⁺: 669.3302, found: 669.3346. *m/z* calcd for C₄₂H₅₄⁸¹BrO₂⁺ [M + H]⁺: 671.3281, found: 671.3253.

11,16-Diphenylbenzo[*c*]benzo[4,5]imidazo[1,2-*a*]indeno[2,1-*e*]azepine (**3aa**):



GP-4 was carried out with 2-(2-(phenylethynyl)phenyl)-1*H*-benzo[*d*]imidazole **1a** (74 mg, 0.25 mmol), 1-bromo-2-(phenylethynyl)benzene **2a** (77 mg, 0.30 mmol), Pd(OAc)₂ (5.6 mg, 10 mol%, 0.025 mmol), DPEPhos (27 mg, 20 mol%, 0.05 mmol), Cs₂CO₃ (244 mg, 0.75 mmol), and Toluene (2 mL) purged with N₂ at 120 °C for 30 min in MW (150 W) reactor. Purification of the crude material by silica gel column chromatography (petroleum ether: ethyl acetate = 98:02 to 95:05) furnished the product **3aa** (103 mg, 87%) as a yellow solid. mp = 180-182 °C. [TLC (petroleum ether: ethyl acetate = 97:3), *R_f*(**1a**) = 0.40, *R_f*(**2a**) = 0.95, *R_f*(**3aa**) = 0.70, UV detection]. **IR:** (MIR-ATR, 4000–600 cm⁻¹) *v*_{max} = 3059, 2922, 2855, 1728, 1602, 1448, 1274, 1027, 751, 703 cm⁻¹. **¹H NMR (400 MHz, CDCl₃)** δ 8.57 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.83 (d, *J* = 7.7 Hz, 1H), 7.76 – 7.69 (m, 1H), 7.67 – 7.58 (m, 6H), 7.50 – 7.39 (m, 4H), 7.35 – 7.29 (m, 1H), 7.25 – 7.18 (m, 3H), 7.10 (ddd, *J* = 8.3, 7.2, and 1.4 Hz, 1H), 6.88 – 6.79 (m, 2H), 6.10 (d, *J* = 7.9 Hz, 1H), 5.71 (d, *J* = 8.7 Hz, 1H) ppm. **¹³C{¹H} NMR (101 MHz, CDCl₃)** δ 153.8, 142.2, 141.3, 138.1, 137.4, 136.1, 135.9, 135.9, 135.0, 134.1, 132.9, 131.5, 131.1 (2C), 130.9, 130.5, 130.1 (2C), 130.0, 129.7 (2C), 129.3 (2C), 129.2, 128.4, 127.6, 127.5, 127.0, 124.1, 124.0, 123.8, 123.2, 120.5, 120.0, 115.6 ppm. **HRMS (ESI):** *m/z* calcd for C₃₅H₂₃N₂⁺ [*M* + *H*]⁺: 471.1856, found: 471.1840.

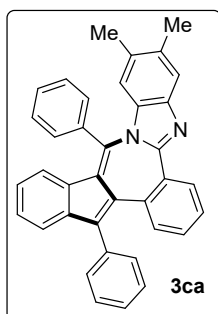
8-Methyl-11,16-diphenylbenzo[*c*]benzo[4,5]imidazo[1,2-*a*]indeno[2,1-*e*]azepine & 7-Methyl-11,16-diphenylbenzo[*c*]benzo[4,5]imidazo[1,2-*a*]indeno[2,1-*e*]azepine (3ba&3ba')



GP-4 was carried out with 6-methyl-2-(2-(phenylethynyl)phenyl)-1*H*-benzo[*d*]imidazole **1b** (77 mg, 0.25 mmol), 1-bromo-2-(phenylethynyl)benzene **2a** (77 mg, 0.30 mmol), Pd(OAc)₂ (5.6 mg, 10 mol%, 0.025 mmol), DPEPhos (27 mg, 20 mol%, 0.05 mmol), Cs₂CO₃ (244 mg, 0.75 mmol), and Toluene (2 mL) purged with N₂ at 120 °C for 30 min in MW (150 W) reactor. Purification of the crude material by silica gel column chromatography (petroleum ether: ethyl acetate = 98:02 to 95:05) furnished the product **3ba+3ba'** (*rr* = 1:0.8) (87 mg, 72%) as yellow solids. mp = 180-182 °C. [TLC (petroleum ether: ethyl acetate = 97:3), *R_f*(**1b**) = 0.40, *R_f*(**2a**) = 0.95, *R_f*(**3ba+3ba'**) = 0.70, UV detection]. **IR:** (MIR-ATR, 4000–600 cm⁻¹) *v*_{max} = 3055, 2921, 2859, 1732, 1585, 1438, 1331, 1276, 1034, 755, 706 cm⁻¹. **¹H NMR (400 MHz, CDCl₃)** δ 8.63 – 8.51 (m, 2H), 7.79 – 7.57 (m, 16H), 7.53 – 7.39 (m, 8H), 7.34 – 7.29 (m, 2H), 7.24 – 7.17 (m, 4H), 7.15 – 7.02 (m, 3H), 6.85 (t, *J* = 7.6 Hz, 2H), 6.66 (dd, *J* = 8.8, 1.5 Hz, 1H), 6.12 (d, *J* = 7.9 Hz, 1H), 6.08 (d, *J* = 7.9 Hz, 1H), 5.54 (d, *J* = 8.8 Hz, 1H), 5.40 (s, 1H), 2.39 (s, 3H), 2.11 (s, 3H) ppm. **¹³C{¹H} NMR (151 MHz, CDCl₃)** δ 153.8, 153.5, 142.2, 142.1, 141.0, 140.9, 140.8, 138.1, 138.0, 137.8, 137.7, 136.4, 136.3, 136.1, 136.0, 134.7, 134.6, 134.2, 134.1, 134.0, 133.6, 132.8 (2C), 132.7, 131.5, 131.3, 131.1, 130.4, 130.3, 130.2, 130.1, 130.0 (2C), 129.8, 129.7 (2C), 129.6, 129.3 (2C), 128.3, 128.0, 127.5, 126.8, 125.2, 124.7, 124.0, 123.9 (2C), 120.4, 119.8, 119.4, 115.9, 115.1, 22.1, 21.2 ppm. **HRMS (ESI):** *m/z* calcd for C₃₆H₂₅N₂⁺ [M + H]⁺: 485.2012, found: 485.1996.

7,8-Dimethyl-11,16-diphenylbenzo[*c*]benzo[4,5]imidazo[1,2-*a*]indeno[2,1-*e*]azepine

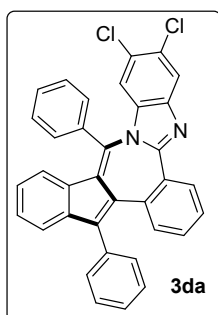
(**3ca**):



GP-4 was carried out with 5,6-dimethyl-2-(2-(phenylethynyl)phenyl)-1*H*-benzo[*d*]imidazole **1c** (81 mg, 0.25 mmol), 1-bromo-2-(phenylethynyl)benzene **2a** (77 mg, 0.30 mmol), Pd(OAc)₂ (5.6 mg, 10 mol%, 0.025 mmol), DPEPhos (27 mg, 20 mol%, 0.05 mmol), Cs₂CO₃ (244 mg, 0.75 mmol), and Toluene (2 mL) purged with N₂ at 120 °C for 30 min in MW (150 W) reactor. Purification of the crude material by silica gel column chromatography (petroleum ether: ethyl acetate = 98:02 to 95:05) furnished the product **3ca** (83 mg, 67%) as a yellow solid. mp = 298–300 °C. [TLC (petroleum ether: ethyl acetate = 97:3), *R_f*(**1c**) = 0.40, *R_f*(**2a**) = 0.95, *R_f*(**3ca**) = 0.70, UV detection]. **IR**: (MIR-ATR, 4000–600 cm⁻¹) *v*_{max} = 30001, 1602, 1449, 1336, 1267, 1029, 754, 707 cm⁻¹. **¹H NMR (400 MHz, CDCl₃)** δ 8.55 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.79 – 7.73 (m, 1H), 7.68 – 7.63 (m, 3H), 7.62 – 7.56 (m, 3H), 7.50 – 7.44 (m, 3H), 7.44 – 7.39 (m, 1H), 7.30 (ddd, *J* = 8.2, 7.2, 1.2 Hz, 1H), 7.23 – 7.18 (m, 2H), 7.07 (ddd, *J* = 8.4, 7.2, 1.5 Hz, 1H), 6.88 – 6.81 (m, 1H), 6.10 (d, *J* = 7.9 Hz, 1H), 5.33 (s, 1H), 5.30 (s, 1H), 2.29 (s, 3H), 1.99 (s, 3H) ppm. **¹³C{¹H} NMR (101 MHz, CDCl₃)** δ 153.1, 142.1, 141.3, 140.8, 138.0, 137.9, 136.5, 136.1, 134.5, 134.4, 134.2, 132.8, 132.0, 131.9, 131.6, 131.2 (2C), 130.3 (2C), 130.1, 129.7, 129.6 (4C), 129.3 (2C), 128.2, 128.0, 127.5, 126.7, 124.0, 123.9, 120.4, 119.9, 116.1, 20.9, 20.0 ppm. **HRMS (ESI)**: *m/z* calcd for C₃₇H₂₇N₂⁺ [M + H]⁺: 499.2169, found: 499.2188.

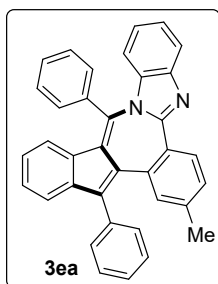
7,8-Dichloro-11,16-diphenylbenzo[*c*]benzo[4,5]imidazo[1,2-*a*]indeno[2,1-*e*]azepine

(**3da**):



GP-4 was carried out with 5,6-dichloro-2-(2-(phenylethynyl)phenyl)-1*H*-benzo[*d*]imidazole **1d** (91 mg, 0.25 mmol), 1-bromo-2-(phenylethynyl)benzene **2a** (77 mg, 0.30 mmol), Pd(OAc)₂ (5.6 mg, 10 mol%, 0.025 mmol), DPEPhos (27 mg, 20 mol%, 0.05 mmol), Cs₂CO₃ (244 mg, 0.75 mmol), and Toluene (2 mL) purged with N₂ at 120 °C for 30 min in MW (150 W) reactor. Purification of the crude material by silica gel column chromatography (petroleum ether: ethyl acetate = 98:02 to 95:05) furnished the product **3da** (88 mg, 65%) as a yellow solid. mp = 304–306 °C. [TLC (petroleum ether: ethyl acetate = 97:3), *R_f*(**1d**) = 0.40, *R_f*(**2a**) = 0.95, *R_f*(**3da**) = 0.70, UV detection]. **IR:** (MIR-ATR, 4000–600 cm⁻¹) *v*_{max} = 2923, 2854, 2349, 1727, 1606, 1440, 1338, 1267, 1025, 806, 755 cm⁻¹. **¹H NMR (400 MHz, CDCl₃)** δ 8.51 (d, *J* = 7.9 Hz, 1H), 7.84 (s, 1H), 7.79 (dd, *J* = 7.5 and 7.4 Hz, 1H), 7.68 (dd, *J* = 7.6 and 7.5 Hz, 2H), 7.63 – 7.56 (m, 4H), 7.50 – 7.41 (m, 4H), 7.31 (dd, *J* = 7.6 and 7.5 Hz, 1H), 7.24 – 7.19 (m, 2H), 7.11 (dd, *J* = 7.5 and 7.3 Hz, 1H), 6.86 (dd, *J* = 7.6 and 7.5 Hz, 1H), 6.13 (d, *J* = 7.9 Hz, 1H), 5.64 (s, 1H) ppm. **¹³C{¹H} NMR (101 MHz, CDCl₃)** δ 155.5, 142.3, 142.1, 137.8, 136.4, 135.7, 135.5, 135.0, 134.8, 133.7, 133.0, 131.6, 131.4, 131.1 (2C), 131.0, 130.5, 130.0 (2C), 129.9 (2C), 129.4 (3C), 128.5, 127.9, 127.7, 127.3, 127.0, 127.0, 126.8, 124.4, 124.1, 120.7, 120.5, 117.2 ppm. **HRMS (ESI):** *m/z* calcd for C₃₅H₂₁Cl₂N₂⁺ [M + H]⁺: 539.1076, found: 539.1067.

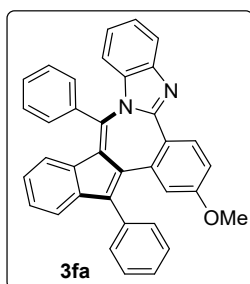
2-Methyl-11,16-diphenylbenzo[*c*]benzo[4,5]imidazo[1,2-*a*]indeno[2,1-*e*]azepine (3ea):



GP-4 was carried out with 2-(4-methyl-2-(phenylethynyl)phenyl)-1*H*-benzo[*d*]imidazole **1e** (77 mg, 0.25 mmol), 1-bromo-2-(phenylethynyl)benzene **2a** (77 mg, 0.30 mmol), Pd(OAc)₂ (5.6 mg, 10 mol%, 0.025 mmol), DPEPhos (27 mg, 20 mol%, 0.05 mmol), Cs₂CO₃ (244 mg, 0.75 mmol), and Toluene (2 mL) purged with N₂ at 120 °C for 30 min in MW (150 W) reactor. Purification of the crude material by silica gel column chromatography (petroleum ether: ethyl acetate = 98:02 to 95:05) furnished the product **3ea** (103 mg, 85%) as a yellow solid. mp = 240–242 °C. [TLC (petroleum ether: ethyl acetate = 97:3), *R_f*(**1e**) = 0.40, *R_f*(**2a**) = 0.95, *R_f*(**3ba**) = 0.70, UV detection]. **IR:** (MIR-ATR, 4000–600 cm⁻¹) *v*_{max} = 3056, 2924, 2856, 1729, 1603, 1449, 1357, 1270, 1027, 828, 754 cm⁻¹. **¹H NMR (400 MHz, CDCl₃)** δ 8.36 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 4.3 Hz, 1H), 7.53 – 7.43 (m, 6H), 7.37 – 7.26

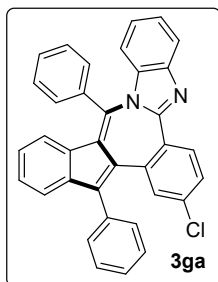
(m, 4H), 7.10 – 7.04 (m, 2H), 6.99 (d, $J = 8.2$ Hz, 1H), 6.86 (s, 1H), 6.73 – 6.63 (m, 2H), 5.92 (d, $J = 8.0$ Hz, 1H), 5.55 (d, $J = 8.7$ Hz, 1H), 1.88 (s, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 153.9, 142.7, 142.2, 141.0, 140.0, 138.0, 137.6, 136.2, 136.1, 135.9, 134.4, 134.1, 132.8, 132.0, 131.1 (2C), 130.4 (2C), 130.0 (2C), 129.7 (2C), 129.2 (2C), 128.6, 128.2, 126.8, 125.1, 124.0, 123.9, 123.7, 122.9, 120.3, 119.9, 115.6, 21.2 ppm. HRMS (ESI): m/z calcd for $\text{C}_{36}\text{H}_{25}\text{N}_2^+$ [$\text{M} + \text{H}$] $^+$: 485.2012, found: 485.1994.

2-Methoxy-11,16-diphenylbenzo[*c*]benzo[4,5]imidazo[1,2-*a*]indeno[2,1-*e*]azepine (3fa):



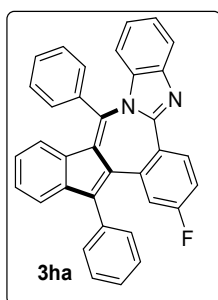
GP-4 was carried out with 2-(4-methoxy-2-(phenylethynyl)phenyl)-1*H*-benzo[*d*]imidazole **1f** (81 mg, 0.25 mmol), 1-bromo-2-(phenylethynyl)benzene **2a** (77 mg, 0.30 mmol), $\text{Pd}(\text{OAc})_2$ (5.6 mg, 10 mol%, 0.025 mmol), DPEPhos (27 mg, 20 mol%, 0.05 mmol), Cs_2CO_3 (244 mg, 0.75 mmol), and Toluene (2 mL) purged with N_2 at 120 °C for 30 min in MW (150 W) reactor. Purification of the crude material by silica gel column chromatography (petroleum ether: ethyl acetate = 98:02 to 95:05) furnished the product **3fa** (94 mg, 75%) as a yellow solid. mp = 192–194 °C. [TLC (petroleum ether: ethyl acetate = 97:3), $R_f(\mathbf{1f}) = 0.20$, $R_f(\mathbf{2a}) = 0.95$, $R_f(\mathbf{3fa}) = 0.50$, UV detection]. IR: (MIR-ATR, 4000–600 cm^{-1}) $\nu_{\text{max}} = 2996, 1602, 1453, 1323, 1266, 1115, 895, 734 \text{ cm}^{-1}$. ^1H NMR (400 MHz, CDCl_3) δ 8.56 (d, $J = 8.9$ Hz, 1H), 7.80 (d, $J = 7.9$ Hz, 1H), 7.78 – 7.71 (m, 1H), 7.68 – 7.61 (m, 6H), 7.51 (dd, $J = 7.3, 7.7$ Hz, 2H), 7.45 (dd, $J = 7.9, 8.8$ Hz, 2H), 7.22 (dd, $J = 7.5, 7.4$ Hz, 2H), 6.93 – 6.72 (m, 4H), 6.06 (d, $J = 7.9$ Hz, 1H), 5.68 (d, $J = 8.7$ Hz, 1H), 3.24 (s, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 160.4, 153.8, 142.8, 142.1, 141.1, 138.0, 137.9, 136.5, 136.3, 135.8, 135.8, 134.6, 134.2, 131.0 (2C), 130.4, 130.0 (2C), 129.7 (2C), 129.5 (2C), 129.4, 128.2, 126.8, 124.1, 124.0, 123.7, 122.7, 120.6, 120.3, 119.7, 116.6, 115.6, 113.7, 54.7 ppm. HRMS (ESI): m/z calcd for $\text{C}_{36}\text{H}_{24}\text{KN}_2\text{O}^+$ [$\text{M} + \text{K}$] $^+$: 539.1520, found: 539.1554.

2-Chloro-11,16-diphenylbenzo[*c*]benzo[4,5]imidazo[1,2-*a*]indeno[2,1-*e*]azepine (3fa):



GP-4 was carried out with 2-(4-chloro-2-(phenylethynyl)phenyl)-1*H*-benzo[*d*]imidazole **1g** (82 mg, 0.25 mmol), 1-bromo-2-(phenylethynyl)benzene **2a** (77 mg, 0.30 mmol), Pd(OAc)₂ (5.6 mg, 10 mol%, 0.025 mmol), DPEPhos (27 mg, 20 mol%, 0.05 mmol), Cs₂CO₃ (244 mg, 0.75 mmol), and Toluene (2 mL) purged with N₂ at 120 °C for 30 min in MW (150 W) reactor. Purification of the crude material by silica gel column chromatography (petroleum ether: ethyl acetate = 98:02 to 95:05) furnished the product **3ga** (85 mg, 67%) as a yellow solid. mp = 262–264 °C. [TLC (petroleum ether: ethyl acetate = 97:3), *R_f*(**1g**) = 0.40, *R_f*(**2a**) = 0.95, *R_f*(**3ga**) = 0.70, UV detection]. **IR:** (MIR-ATR, 4000–600 cm⁻¹) *v*_{max} = 3001, 1585, 1451, 1357, 1315, 1268, 1116, 755 cm⁻¹. **¹H NMR (400 MHz, CDCl₃)** δ 8.53 (d, *J* = 8.7 Hz, 1H), 7.80 (d, *J* = 7.5 Hz, 1H), 7.77 – 7.72 (m, 1H), 7.68 – 7.56 (m, 6H), 7.55 – 7.44 (m, 4H), 7.28 – 7.19 (m, 3H), 7.14 (d, *J* = 2.1 Hz, 1H), 6.90 – 6.79 (m, 2H), 6.07 (d, *J* = 7.9 Hz, 1H), 5.68 (d, *J* = 8.7 Hz, 1H) ppm. **¹³C{¹H} NMR (101 MHz, CDCl₃)** δ 152.8, 142.6, 142.5, 142.0, 138.1, 137.7, 136.1 (2C), 136.0, 135.9, 135.3, 134.3, 132.5, 131.1 (2C), 130.9, 130.6, 130.3, 129.9 (2C), 129.8 (2C), 129.5 (2C), 128.8, 127.6, 127.1, 126.1, 124.6, 124.1, 124.0, 123.4, 120.7, 120.1, 115.7 ppm. **HRMS (ESI):** *m/z* calcd for C₃₅H₂₂ClN₂⁺ [M + H]⁺: 505.1466, found: 505.1455.

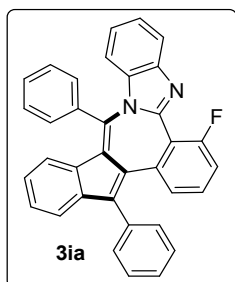
2-Fluoro-11,16-diphenylbenzo[*c*]benzo[4,5]imidazo[1,2-*a*]indeno[2,1-*e*]azepine (3ha):



GP-4 was carried out with 2-(4-fluoro-2-(phenylethynyl)phenyl)-1*H*-benzo[*d*]imidazole **1h** (78 mg, 0.25 mmol), 1-bromo-2-(phenylethynyl)benzene **2a** (77 mg, 0.30 mmol), Pd(OAc)₂ (5.6 mg, 10 mol%, 0.025 mmol), DPEPhos (27 mg, 20 mol%, 0.05 mmol), Cs₂CO₃ (244 mg, 0.75 mmol), and Toluene (2 mL) purged with N₂ at 120 °C for 30 min in MW (150 W) reactor. Purification of the crude material by silica gel column chromatography (petroleum ether: ethyl

acetate = 98:02 to 95:05) furnished the product **3ha** (92 mg, 75%) as a yellow solid. mp = 162–164 °C. [TLC (petroleum ether: ethyl acetate = 97:3), $R_f(\mathbf{1h}) = 0.40$, $R_f(\mathbf{2a}) = 0.95$, $R_f(\mathbf{3ha}) = 0.70$, UV detection]. **IR:** (MIR-ATR, 4000–600 cm^{-1}) $\nu_{\text{max}} = 3060, 1734, 1604, 1452, 1357, 1270, 1027, 833, 754, 709 \text{ cm}^{-1}$. **$^1\text{H NMR}$ (400 MHz, CDCl_3)** δ 8.58 (dd, $J = 8.9, 6.3 \text{ Hz}$, 1H), 7.83 – 7.70 (m, 2H), 7.68 – 7.61 (m, 4H), 7.59 (dd, $J = 8.1, 1.4 \text{ Hz}$, 2H), 7.54 – 7.43 (m, 4H), 7.25 – 7.18 (m, 2H), 7.01 (ddd, $J = 9.0, 7.4, 2.6 \text{ Hz}$, 1H), 6.90 – 6.78 (m, 3H), 6.08 (d, $J = 7.9 \text{ Hz}$, 1H), 5.69 (d, $J = 8.7 \text{ Hz}$, 1H) ppm. **$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3)** δ 163.4 (d, $J = 250.1 \text{ Hz}$), 153.0, 142.8, 142.4, 142.0, 138.1, 137.8, 137.1 (d, $J = 9.2 \text{ Hz}$), 136.1, 135.9, 135.4 (d, $J = 8.4 \text{ Hz}$), 135.4, 132.8 (d, $J = 2.1 \text{ Hz}$), 131.1 (2C), 130.6, 130.0, 129.9 (2C), 129.8 (2C), 129.5 (2C), 128.8, 127.0, 124.5, 124.2 (d, $J = 2.7 \text{ Hz}$), 124.1, 123.9, 123.2, 120.7, 120.0, 117.1 (d, $J = 24.0 \text{ Hz}$), 115.6, 115.3 (d, $J = 22.2 \text{ Hz}$) ppm. **HRMS (ESI):** m/z calcd for $\text{C}_{35}\text{H}_{22}\text{FN}_2^+$ [$\text{M} + \text{H}$] $^+$: 489.1762, found: 489.1728.

4-Fluoro-11,16-diphenylbenzo[*c*]benzo[4,5]imidazo[1,2-*a*]indeno[2,1-*e*]azepine (**3ia**):

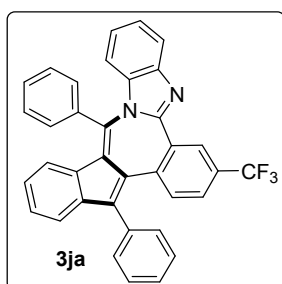


GP-4 was carried out with 2-(2-fluoro-6-(phenylethynyl)phenyl)-1*H*-benzo[*d*]imidazole **1i** (78 mg, 0.25 mmol), 1-bromo-2-(phenylethynyl)benzene **2a** (77 mg, 0.30 mmol), $\text{Pd}(\text{OAc})_2$ (5.6 mg, 10 mol%, 0.025 mmol), DPEPhos (27 mg, 20 mol%, 0.05 mmol), Cs_2CO_3 (244 mg, 0.75 mmol), and Toluene (2 mL) purged with N_2 at 120 °C for 30 min in MW (150 W) reactor. Purification of the crude material by silica gel column chromatography (petroleum ether: ethyl acetate = 98:02 to 95:05) furnished the product **3ia** (70 mg, 57%) as a yellow solid. mp = 300–302 °C. [TLC (petroleum ether: ethyl acetate = 97:3), $R_f(\mathbf{1i}) = 0.40$, $R_f(\mathbf{2a}) = 0.95$, $R_f(\mathbf{3ia}) = 0.70$, UV detection]. **IR:** (MIR-ATR, 4000–600 cm^{-1}) $\nu_{\text{max}} = 3055, 2922, 2854, 1728, 1604, 1579, 1447, 1319, 1263, 1087, 1022, 800, 735, 701 \text{ cm}^{-1}$. **$^1\text{H NMR}$ (400 MHz, CDCl_3)** δ 7.86 (d, $J = 7.9 \text{ Hz}$, 1H), 7.73 – 7.59 (m, 7H), 7.54 – 7.39 (m, 4H), 7.26 – 7.18 (m, 2H), 7.08 – 7.01 (m, 2H), 6.94 – 6.82 (m, 3H), 6.35 (d, $J = 7.8 \text{ Hz}$, 1H), 5.86 (d, $J = 8.6 \text{ Hz}$, 1H) ppm. **$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3)** δ 161.8 (d, $J = 256.0 \text{ Hz}$), 147.4 (d, $J = 6.6 \text{ Hz}$), 142.7, 142.6, 141.9, 138.9, 138.7, 136.9, 135.4, 135.3, 135.0, 133.8 ($J = 6.6 \text{ Hz}$), 132.9, 131.2 (2C), 130.6, 130.5

(d, $J = 10.1$ Hz), 130.1 (2C), 129.5 (2C), 129.3 (2C), 128.8, 127.1, 126.7 (d, $J = 3.5$ Hz), 124.4, 123.9, 123.8, 123.6, 121.0, 120.3, 116.7 (d, $J = 9.3$ Hz), 114.9, 114.8 (d, $J = 22.2$ Hz) ppm.

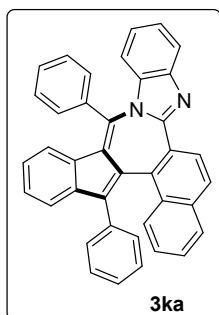
HRMS (ESI): m/z calcd for $C_{35}H_{21}FN_2Na^+$ $[M + Na]^+$: 511.1581, found: 511.1566.

11,16-Diphenyl-3-(trifluoromethyl)benzo[*c*]benzo[4,5]imidazo[1,2-*a*]indeno[2,1-*e*]azepine (3ja):



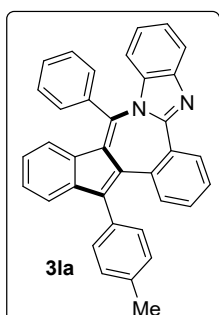
GP-4 was carried out with 2-(2-(phenylethynyl)-5-(trifluoromethyl)phenyl)-1*H*-benzo[*d*]imidazole **1j** (91 mg, 0.25 mmol), 1-bromo-2-(phenylethynyl)benzene **2a** (77 mg, 0.30 mmol), Pd(OAc)₂ (5.6 mg, 10 mol%, 0.025 mmol), DPEPhos (27 mg, 20 mol%, 0.05 mmol), Cs₂CO₃ (244 mg, 0.75 mmol), and Toluene (2 mL) purged with N₂ at 120 °C for 30 min in MW (150 W) reactor. Purification of the crude material by silica gel column chromatography (petroleum ether: ethyl acetate = 98:02 to 95:05) furnished the product **3ja** (97 mg, 72%) as a yellow solid. mp = 258-260 °C. [TLC (petroleum ether: ethyl acetate = 97:3), $R_f(\mathbf{1j}) = 0.40$, $R_f(\mathbf{2a}) = 0.95$, $R_f(\mathbf{3ja}) = 0.70$, UV detection]. **IR:** (MIR-ATR, 4000–600 cm⁻¹) $\nu_{\max} = 3001, 1726, 1606, 1451, 1317, 1269, 1127, 833, 755$ cm⁻¹. **¹H NMR (400 MHz, CDCl₃)** δ 8.91 (s, 1H), 7.85 (d, $J = 8.0$ Hz, 1H), 7.79 – 7.73 (m, 1H), 7.69 – 7.59 (m, 6H), 7.53 – 7.46 (m, 4H), 7.34 – 7.28 (m, 2H), 7.26 – 7.21 (m, 2H), 6.98 – 6.79 (m, 2H), 6.10 (d, $J = 7.9$ Hz, 1H), 5.70 (d, $J = 8.8$ Hz, 1H) ppm. **¹³C{¹H} NMR (101 MHz, CDCl₃)** δ 152.5, 143.3, 142.8, 141.9, 138.2, 138.0, 137.9, 136.0, 135.9, 135.4, 132.7, 132.0, 131.0 (2C), 130.7, 130.3 (q, $J_{C-H} = 4.2$ Hz), 130.2, 130.0 (2C), 129.8 (2C), 129.6 (2C), 129.11 (q, $J_{C-H} = 33.0$ Hz), 128.8, 128.3, 127.1, 125.9 (q, $J_{C-H} = 3.5$ Hz), 124.8, 124.1 (2C), 124.0 (q, $J_{C-H} = 272.2$ Hz), 123.7, 120.9, 120.4, 115.7 ppm. **HRMS (ESI):** m/z calcd for $C_{36}H_{22}F_3N_2^+$ $[M + H]^+$: 539.1730, found: 539.1712.

5,10-Diphenylbenzo[4,5]imidazo[1,2-*a*]indeno[2,1-*e*]naphtho[2,1-*c*]azepine (3ka):



GP-4 was carried out with 2-(1-(phenylethynyl)naphthalen-2-yl)-1*H*-benzo[*d*]imidazole **1k** (86 mg, 0.25 mmol), 1-bromo-2-(phenylethynyl)benzene **2a** (77 mg, 0.30 mmol), Pd(OAc)₂ (5.6 mg, 10 mol%, 0.025 mmol), DPEPhos (27 mg, 20 mol%, 0.05 mmol), Cs₂CO₃ (244 mg, 0.75 mmol), and Toluene (2 mL) purged with N₂ at 120 °C for 30 min in MW (150 W) reactor. Purification of the crude material by silica gel column chromatography (petroleum ether: ethyl acetate = 98:02 to 95:05) furnished the product **3ka** (90 mg, 69%) as a yellow solid. mp = 180–182 °C. [TLC (petroleum ether: ethyl acetate = 97:3), *R_f*(**1k**) = 0.40, *R_f*(**2a**) = 0.95, *R_f*(**3ka**) = 0.75, UV detection]. **IR:** (MIR-ATR, 4000–600 cm⁻¹) *v*_{max} = 3056, 1731, 1583, 1446, 1340, 1270, 1026, 821, 754 cm⁻¹. **¹H NMR (400 MHz, CDCl₃)** δ 8.64 (d, *J* = 8.8 Hz, 1H), 7.87 – 7.71 (m, 4H), 7.70 – 7.58 (m, 6H), 7.36 – 7.31 (m, 2H), 7.29 – 7.19 (m, 3H), 7.11 – 6.94 (m, 4H), 6.92 – 6.86 (m, 1H), 6.80 (ddd, *J* = 8.6, 7.2, 1.2 Hz, 1H), 6.00 (d, *J* = 7.9 Hz, 1H), 5.56 (d, *J* = 8.6 Hz, 1H) ppm. **¹³C{¹H} NMR (101 MHz, CDCl₃)** δ 154.0, 144.4, 140.5, 138.5, 137.8, 137.8, 136.1, 135.9, 135.9, 134.6, 132.5, 131.1 (2C), 130.9, 130.5, 129.8 (2C), 129.7, 129.6 (2C), 128.8, 128.7, 128.6, 128.4 (2C), 127.9, 127.4, 126.9, 126.9, 125.8, 125.5, 125.4, 124.4, 124.0, 123.4, 123.2, 120.3, 120.2, 116.0 ppm. **HRMS (ESI):** *m/z* calcd for C₃₉H₂₅N₂⁺ [M + H]⁺: 521.2012, found: 521.2008.

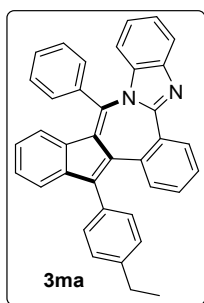
11-Phenyl-16-(*p*-tolyl)benzo[*c*]benzo[4,5]imidazo[1,2-*a*]indeno[2,1-*e*]azepine (3la):



GP-4 was carried out with 2-(2-(*p*-tolylethynyl)phenyl)-1*H*-benzo[*d*]imidazole **11** (77 mg, 0.25 mmol), 1-bromo-2-(phenylethynyl)benzene **2a** (77 mg, 0.30 mmol), Pd(OAc)₂ (5.6 mg, 10 mol%), DPEPhos (27 mg, 20 mol%, 0.05 mmol), Cs₂CO₃ (244 mg, 0.75 mmol), and Toluene (2 mL) purged with N₂ at 120 °C for 30 min in MW (150 W) reactor. Purification of the crude material by silica gel column chromatography (petroleum ether: ethyl acetate = 98:02 to 95:05) furnished the product **31a** (98 mg, 81%) as a yellow solid. mp = 240-242 °C. [TLC (petroleum ether: ethyl acetate = 97:3), *R_f*(**11**) = 0.40, *R_f*(**2a**) = 0.95, *R_f*(**31a**) = 0.70, UV detection]. **IR:** (MIR-ATR, 4000–600 cm⁻¹) *v*_{max} = 3055, 2922, 1734, 1598, 1445, 1329, 1275, 1028, 823, 748 cm⁻¹. **¹H NMR (400 MHz, CDCl₃)** δ 8.52 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.68 – 7.61 (m, 1H), 7.60 – 7.53 (m, 4H), 7.45 (d, *J* = 7.9 Hz, 2H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.27 – 7.10 (m, 6H), 7.09 – 7.01 (m, 1H), 6.77 (q, *J* = 7.9 Hz, 2H), 6.06 (d, *J* = 7.9 Hz, 1H), 5.67 (d, *J* = 8.7 Hz, 1H), 2.37 (s, 3H) ppm. **¹³C{¹H} NMR (101 MHz, CDCl₃)** δ 153.8, 142.8, 142.3, 141.2, 138.1, 138.0, 137.1, 136.0, 135.9, 135.1, 133.7, 132.8, 132.7, 131.3, 131.1 (2C), 130.8, 130.4, 130.0 (2C), 129.9 (3C), 129.6 (2C), 127.7, 127.3, 126.8, 124.0, 123.8, 123.6, 123.1, 120.4, 120.0, 115.5, 21.50 ppm. **HRMS (ESI):** *m/z* calcd for C₃₆H₂₅N₂⁺ [*M* + *H*]⁺: 485.2012, found: 485.1995.

16-(4-Ethylphenyl)-11-phenylbenzo[*c*]benzo[4,5]imidazo[1,2-*a*]indeno[2,1-*e*]azepine

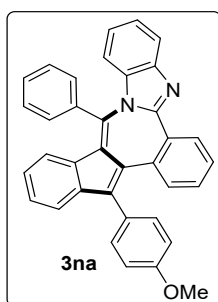
(3ma):



GP-4 was carried out with 2-(2-((4-ethylphenyl)ethynyl)phenyl)-1*H*-benzo[*d*]imidazole **1m** (81 mg, 0.25 mmol), 1-bromo-2-(phenylethynyl)benzene **2a** (77 mg, 0.30 mmol), Pd(OAc)₂ (5.6 mg, 10 mol%), DPEPhos (27 mg, 20 mol%, 0.05 mmol), Cs₂CO₃ (244 mg, 0.75 mmol), and Toluene (2 mL) purged with N₂ at 120 °C for 30 min in MW (150 W) reactor. Purification of the crude material by silica gel column chromatography (petroleum ether: ethyl acetate = 98:02 to 95:05) furnished the product **3ma** (100 mg, 80%) as a yellow solid. mp = 182-184 °C. [TLC (petroleum ether: ethyl acetate = 97:3), *R_f*(**1m**) = 0.40, *R_f*(**2a**) = 0.95, *R_f*(**3ma**) = 0.70, UV detection]. **IR:** (MIR-ATR, 4000–600 cm⁻¹) *v*_{max} = 2968, 2340, 1604, 1447, 1333, 1271, 1029, 838, 753 cm⁻¹. **¹H NMR (400 MHz, CDCl₃)** δ 8.51 (d, *J* = 8.0 Hz,

1H), 7.77 (d, $J = 7.9$ Hz, 1H), 7.71 – 7.63 (m, 1H), 7.61 – 7.53 (m, 4H), 7.47 (d, $J = 8.0$ Hz, 2H), 7.43 (d, $J = 7.6$ Hz, 1H), 7.29 – 7.22 (m, 3H), 7.21 – 7.12 (m, 3H), 7.09 – 7.01 (m, 1H), 6.81 – 6.74 (m, 2H), 6.06 (d, $J = 7.9$ Hz, 1H), 5.68 (d, $J = 8.7$ Hz, 1H), 2.69 (q, $J = 7.6$ Hz, 2H), 1.27 (t, $J = 7.6$ Hz, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 153.9, 144.5, 142.8, 142.4, 141.3, 138.1, 137.1, 136.1, 135.9, 135.2, 133.7, 133.1, 132.8, 131.4, 131.1 (2C), 131.0, 130.4, 130.0 (2C), 129.9, 129.6 (2C), 128.8 (2C), 127.7, 127.4, 126.8, 124.0, 123.9, 123.7, 123.1, 120.5, 120.0, 115.5, 28.8, 15.5 ppm. HRMS (ESI): m/z calcd for $\text{C}_{37}\text{H}_{26}\text{N}_2\text{Na}^+$ [$\text{M} + \text{Na}$] $^+$: 521.1988, found: 521.1995.

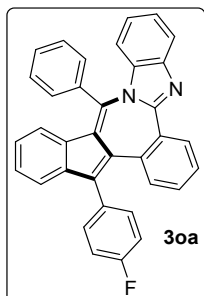
16-(4-Methoxyphenyl)-11-phenylbenzo[*c*]benzo[4,5]imidazo[1,2-*a*]indeno[2,1-*e*]azepine (3na):



GP-4 was carried out with 2-(2-((4-methoxyphenyl)ethynyl)phenyl)-1*H*-benzo[*d*]imidazole **1n** (81 mg, 0.25 mmol), 1-bromo-2-(phenylethynyl)benzene **2a** (77 mg, 0.30 mmol), $\text{Pd}(\text{OAc})_2$ (5.6 mg, 10 mol%, 0.025 mmol), DPEPhos (27 mg, 20 mol%, 0.05 mmol), Cs_2CO_3 (244 mg, 0.75 mmol), and Toluene (2 mL) purged with N_2 at 120 °C for 30 min in MW (150 W) reactor. Purification of the crude material by silica gel column chromatography (petroleum ether: ethyl acetate = 98:02 to 95:05) furnished the product **3na** (99 mg, 79%) as a yellow oil. [TLC (petroleum ether: ethyl acetate = 97:3), $R_f(\mathbf{1n}) = 0.20$, $R_f(\mathbf{2a}) = 0.95$, $R_f(\mathbf{3na}) = 0.50$, UV detection]. IR: (MIR-ATR, 4000–600 cm^{-1}) $\nu_{\text{max}} = 3059, 2928, 2842, 1730, 1604, 1501, 1448, 1336, 1246, 1073, 1030, 835, 745, 702$ cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 8.54 (dd, $J = 8.0, 1.0$ Hz, 1H), 7.80 (d, $J = 8.0$ Hz, 1H), 7.75 – 7.68 (m, 1H), 7.63 (s, 2H), 7.62 (s, 2H), 7.54 (d, $J = 8.7$ Hz, 2H), 7.46 (d, $J = 7.7$ Hz, 1H), 7.30 (dd, $J = 7.6, 7.5$ Hz, 1H), 7.24 – 7.19 (m, 3H), 7.15 – 7.08 (m, 1H), 7.00 (d, $J = 8.7$ Hz, 2H), 6.88 – 6.77 (m, 2H), 6.10 (d, $J = 7.9$ Hz, 1H), 5.72 (d, $J = 8.7$ Hz, 1H), 3.88 (s, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 161.2, 142.2, 141.4, 138.3, 137.2, 136.0, 135.1, 134.1, 132.8, 132.4 (2C), 131.8, 131.4, 130.1 (2C), 129.7, 129.5, 129.3 (2C), 128.5, 128.4, 128.3, 127.5, 127.1, 126.9, 124.2, 124.0, 123.9, 123.8, 123.3,

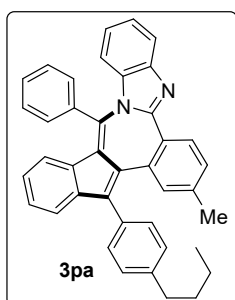
120.5, 119.9, 115.8, 115.0 (2C), 55.7 ppm. **HRMS (ESI):** m/z calcd for $C_{36}H_{25}N_2O^+$ $[M + H]^+$: 501.1961, found: 501.1919.

16-(4-Fluorophenyl)-11-phenylbenzo[*c*]benzo[4,5]imidazo[1,2-*a*]indeno[2,1-*e*]azepine (30a):



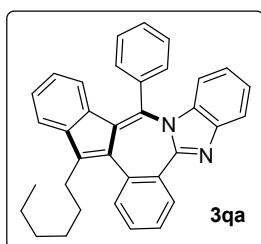
GP-4 was carried out with 2-(2-((4-fluorophenyl)ethynyl)phenyl)-1*H*-benzo[*d*]imidazole **1o** (78 mg, 0.25 mmol), 1-bromo-2-(phenylethynyl)benzene **2a** (77 mg, 0.30 mmol), Pd(OAc)₂ (5.6 mg, 10 mol%, 0.025 mmol), DPEPhos (27 mg, 20 mol%, 0.05 mmol), Cs₂CO₃ (244 mg, 0.75 mmol), and Toluene (2 mL) purged with N₂ at 120 °C for 30 min in MW (150 W) reactor. Purification of the crude material by silica gel column chromatography (petroleum ether: ethyl acetate = 98:02 to 95:05) furnished the product **30a** (94 mg, 77%) as a yellow solid. mp = 202–204 °C. [TLC (petroleum ether: ethyl acetate = 97:3), R_f (**1o**) = 0.40, R_f (**2a**) = 0.95, R_f (**30a**) = 0.70, UV detection]. **IR:** (MIR-ATR, 4000–600 cm⁻¹) ν_{\max} = 3057, 2925, 2855, 1602, 1543, 1446, 1325, 1275, 1028, 837, 746, 702 cm⁻¹. **¹H NMR (400 MHz, CDCl₃)** δ 8.64 – 8.56 (m, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.80 – 7.73 (m, 1H), 7.71 – 7.57 (m, 6H), 7.44 (d, J = 7.6 Hz, 1H), 7.39 – 7.32 (m, 1H), 7.30 – 7.12 (m, 6H), 6.91 – 6.81 (m, 2H), 6.12 (d, J = 7.9 Hz, 1H), 5.73 (d, J = 8.7 Hz, 1H) ppm. **¹³C{¹H} NMR (101 MHz, CDCl₃)** δ 162.8 (d, J = 248.2 Hz), 153.8 (2C), 142.9, 142.0, 140.0, 138.0, 137.7, 136.1, 135.9, 134.7, 134.3, 133.0, 131.9 (d, J = 3.4 Hz), 131.8 (d, J = 8.0 Hz, 2C), 131.3, 131.1 (2C), 130.5, 130.0, 129.7 (2C), 128.0, 127.6, 126.9, 124.2, 124.0, 123.8, 123.2, 120.2 (d, J = 6.1 Hz, 2C), 116.5, 116.3, 115.6 ppm. **HRMS (ESI):** m/z calcd for $C_{35}H_{22}FN_2^+$ $[M + H]^+$: 489.1762, found: 489.1739.

16-(4-Butylphenyl)-2-methyl-11-phenylbenzo[*c*]benzo[4,5]imidazo[1,2-*a*]indeno[2,1-*e*]azepine (3pa):



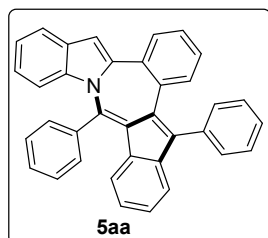
GP-4 was carried out with 2-(2-((4-butylphenyl)ethynyl)-4-methylphenyl)-1*H*-benzo[*d*]imidazole **1p** (91 mg, 0.25 mmol), 1-bromo-2-(phenylethynyl)benzene **2a** (77 mg, 0.30 mmol), Pd(OAc)₂ (5.6 mg, 10 mol%, 0.025 mmol), DPEPhos (27 mg, 20 mol%, 0.05 mmol), Cs₂CO₃ (244 mg, 0.75 mmol), and Toluene (2 mL) purged with N₂ at 120 °C for 30 min in MW (150 W) reactor. Purification of the crude material by silica gel column chromatography (petroleum ether: ethyl acetate = 98:02 to 95:05) furnished the product **3pa** (96 mg, 71%) as a yellow solid. mp = 174-176 °C. [TLC (petroleum ether: ethyl acetate = 97:3), *R_f*(**1p**) = 0.40, *R_f*(**2p**) = 0.95, *R_f*(**3pa**) = 0.70, UV detection]. **IR:** (MIR-ATR, 4000–600 cm⁻¹) *v*_{max} = 3058, 2922, 2857, 1735, 1604, 1450, 1357, 1280, 1027, 832, 744, 708 cm⁻¹. **¹H NMR (400 MHz, CDCl₃)** δ 8.47 (d, *J* = 8.2 Hz, 1H), 7.80 (d, *J* = 7.9 Hz, 1H), 7.75 – 7.68 (m, 1H), 7.64 (s, 2H), 7.62 (s, 2H) 7.52 – 7.45 (m, 3H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.21 (ddd, *J* = 7.4, 7.3, and 2.4 Hz, 2H), 7.12 (d, *J* = 8.2 Hz, 1H), 6.97 (s, 1H), 6.87 – 6.77 (m, 2H), 6.06 (d, *J* = 7.9 Hz, 1H), 5.69 (d, *J* = 8.6 Hz, 1H), 2.71 (t, *J* = 7.6 Hz, 2H), 2.01 (s, 3H), 1.73 – 1.63 (m, 2H), 1.43 – 1.35 (m, 2H), 0.97 (t, *J* = 7.2 Hz, 3H) ppm. **¹³C{¹H} NMR (151 MHz, CDCl₃)** δ 154.0, 143.2, 142.8, 142.4, 141.3, 139.9, 138.1, 137.3, 136.3, 135.9, 134.8, 133.8, 133.3, 132.8, 131.9, 131.2 (2C), 130.6, 130.4, 129.9 (2C), 129.7 (2C), 129.3 (2C), 128.5, 126.8, 125.1, 124.0, 123.9, 123.7, 122.9, 120.5, 119.9, 115.6, 35.6, 33.8, 22.3, 21.2, 14.1 ppm. **HRMS (ESI):** *m/z* calcd for C₄₀H₃₃N₂⁺ [*M* + *H*]⁺: 541.2638, found: 541.2624.

11-Hexyl-16-phenylbenzo[*c*]benzo[4,5]imidazo[1,2-*a*]indeno[2,1-*e*]azepine (3qa):



GP-4 was carried out with 2-(2-(oct-1-yn-1-yl)phenyl)-1*H*-benzo[*d*]imidazole **1q** (76 mg, 0.25 mmol), 1-bromo-2-(phenylethynyl)benzene **2a** (77 mg, 0.30 mmol), Pd(OAc)₂ (5.6 mg, 10 mol%), 0.025 mmol), DPEPhos (27 mg, 20 mol%, 0.05 mmol), Cs₂CO₃ (244 mg, 0.75 mmol), and Toluene (2 mL) purged with N₂ at 120 °C for 30 min in MW (150 W) reactor. Purification of the crude material by silica gel column chromatography (petroleum ether: ethyl acetate = 98:02 to 95:05) furnished the product **3qa** (24 mg, 20%) as a yellow semisolid. [TLC (petroleum ether: ethyl acetate = 97:03), *R_f*(**1q**) = 0.40, *R_f*(**2a**) = 0.95, *R_f*(**3qa**) = 0.60, UV detection]. **IR:** (MIR-ATR, 4000–600 cm⁻¹) *v*_{max} = 3061, 2921, 2855, 1731, 1604, 1448, 1325, 1279, 1028, 746, 701 cm⁻¹. **¹H NMR (600 MHz, CDCl₃)** δ 8.60 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.78 (d, *J* = 7.9 Hz, 1H), 7.71 – 7.67 (m, 1H), 7.62 – 7.56 (m, 5H), 7.51 (ddd, *J* = 7.7, 7.6, 1.5 Hz, 1H), 7.48 – 7.45 (m, 1H), 7.40 (d, *J* = 7.5 Hz, 1H), 7.21 (d, *J* = 7.7 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 1H), 6.78 (dd, *J* = 7.8, 7.7 Hz, 2H), 5.99 (d, *J* = 7.8 Hz, 1H), 5.64 (d, *J* = 8.7 Hz, 1H), 3.12 – 3.03 (m, 2H), 1.83 – 1.74 (m, 2H), 1.46 – 1.42 (m, 2H), 1.33 – 1.29 (m, 4H), 0.86 (t, *J* = 7.1 Hz, 3H) ppm. **¹³C{¹H} NMR (151 MHz, CDCl₃)** δ 153.7, 143.2, 142.9, 142.3, 138.1, 136.3, 136.1, 135.5, 135.1, 134.4, 133.1, 131.4, 131.3 (2C), 130.4, 130.3, 130.1, 129.5 (2C), 128.9, 127.7, 126.8, 123.7, 123.6 (2C), 123.1, 120.1, 119.5, 115.6, 31.7, 29.9, 29.3, 28.1, 22.7, 14.2 ppm. **HRMS (ESI):** *m/z* calcd for C₃₅H₃₀K₂N₂²⁺ [*M* + 2*K*]²⁺: 278.0836, found: 278.0845.

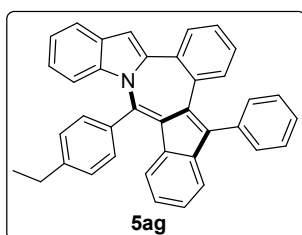
11,16-Diphenylbenzo[3,4]indeno[2',1':5,6]azepino[1,2-*a*]indole (**5aa**):



GP-4 was carried out with 2-(2-(phenylethynyl)phenyl)-1*H*-indole **4a** (73 mg, 0.25 mmol), 1-bromo-2-(phenylethynyl)benzene **2a** (77 mg, 0.30 mmol), Pd(OAc)₂ (5.6 mg, 10 mol%, 0.025 mmol), DPEPhos (27 mg, 20 mol%, 0.05 mmol), Cs₂CO₃ (244 mg, 0.75 mmol), and Toluene (2 mL) purged with N₂ at 120 °C for 30 min in MW (150 W) reactor. Purification of the crude material by silica gel column chromatography (petroleum ether: ethyl acetate = 98:02 to 95:05) furnished the product **5aa** (79 mg, 68%) as a yellow semisolid. [TLC (petroleum ether: ethyl acetate = 98:02), *R_f*(**4a**) = 0.40, *R_f*(**2a**) = 0.95, *R_f*(**5aa**) = 0.60, UV detection]. **IR:** (MIR-ATR, 4000–600 cm⁻¹) *v*_{max} = 3053, 2962, 2856, 1567, 1442, 1731, 1266, 1023, 804, 735 cm⁻¹. **¹H NMR (600 MHz, CDCl₃)** δ 7.72 – 7.68 (m, 2H), 7.64 – 7.59 (m, 6H), 7.56 (dd, *J* = 7.7, 0.7 Hz, 1H), 7.48 – 7.44 (m, 2H), 7.42 – 7.37 (m, 2H), 7.21 – 7.17 (m, 1H), 7.12 (tfd, *J* = 3.9, 1.0

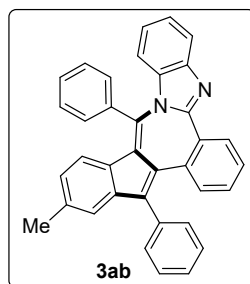
Hz, 2H), 7.11 – 7.09 (m, 1H), 7.09 – 7.06 (m, 1H), 6.97 (ddd, $J = 8.3, 7.2, 1.4$ Hz, 1H), 6.75 (ddd, $J = 8.4, 7.4, 1.2$ Hz, 1H), 6.72 (ddd, $J = 8.7, 7.1, 1.4$ Hz, 1H), 5.90 (d, $J = 7.9$ Hz, 1H), 5.72 (dd, $J = 8.9, 0.7$ Hz, 1H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 142.6, 141.9, 141.7, 139.7 (2C), 139.4, 137.7, 136.5, 135.0, 134.9, 131.7, 131.6, 131.3 (2C), 130.6, 130.3 (3C), 130.1, 129.5 (2C), 129.2 (2C), 128.0 (2C), 127.9, 127.4, 125.8, 123.7, 123.6, 122.6, 122.2, 120.4, 120.2, 116.4, 111.1 ppm. HRMS (ESI): m/z calcd for $\text{C}_{36}\text{H}_{27}\text{NO}_2^{2+}$ $[\text{M} + 2\text{H}_2\text{O}]^{2+}$: 252.6015, found: 252.6029.

11-(4-Ethylphenyl)-16-phenylbenzo[3,4]indeno[2',1':5,6]azepino[1,2-*a*]indole (5ag):



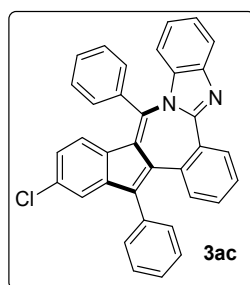
GP-4 was carried out with 2-(2-(phenylethynyl)phenyl)-1*H*-indole **4a** (73 mg, 0.25 mmol), 1-bromo-2-((4-ethylphenyl)ethynyl)benzene **2g** (86 mg, 0.30 mmol), $\text{Pd}(\text{OAc})_2$ (5.6 mg, 10 mol%), 0.025 mmol), DPEPhos (27 mg, 20 mol%, 0.05 mmol), Cs_2CO_3 (244 mg, 0.75 mmol), and Toluene (2 mL) purged with N_2 at 120 °C for 30 min in MW (150 W) reactor. Purification of the crude material by silica gel column chromatography (petroleum ether: ethyl acetate = 99:01 to 98:02) furnished the product **5ag** (77 mg, 62%) as a yellow semisolid. [TLC (petroleum ether: ethyl acetate = 98:02), $R_f(\mathbf{4a}) = 0.40$, $R_f(\mathbf{2a}) = 0.95$, $R_f(\mathbf{5ag}) = 0.60$, UV detection]. IR: (MIR-ATR, 4000–600 cm^{-1}) $\nu_{\text{max}} = 3056, 2922, 2854, 1733, 1566, 1442, 1330, 1272, 746, 703$ cm^{-1} . ^1H NMR (600 MHz, CDCl_3) δ 7.70 (dd, $J = 7.9, 1.1$ Hz, 1H), 7.62 – 7.58 (m, 2H), 7.55 (d, $J = 7.9$ Hz, 1H), 7.51 (d, $J = 8.0$ Hz, 2H), 7.47 – 7.43 (m, 3H), 7.42 – 7.37 (m, 3H), 7.20 – 7.16 (m, 1H), 7.13 – 7.06 (m, 4H), 6.98 – 6.94 (m, 1H), 6.78 – 6.70 (m, 2H), 5.98 (d, $J = 7.9$ Hz, 1H), 5.76 (d, $J = 8.5$ Hz, 1H), 2.88 (q, $J = 7.6$ Hz, 2H), 1.41 (t, $J = 7.6$ Hz, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 146.7, 142.6, 142.0, 141.9, 139.8, 139.6, 139.5, 136.6, 135.0, 134.9, 131.7, 131.6, 131.1 (2C), 130.6, 130.3 (2C), 129.5, 129.1 (2C), 129.0 (2C), 128.8, 128.0, 127.9, 127.9, 127.3, 125.7, 123.8, 123.5, 122.5, 122.1, 120.3, 120.2, 116.5, 111.0, 29.2, 16.1 ppm. HRMS (ESI): m/z calcd for $\text{C}_{38}\text{H}_{29}\text{NO}^+$ $[\text{M} + \text{H}_2\text{O}]^+$: 515.2244, found: 515.2253.

14-Methyl-11,16-diphenylbenzo[*c*]benzo[4,5]imidazo[1,2-*a*]indeno[2,1-*e*]azepine (**3ab**):



GP-4 was carried out with 2-(2-(phenylethynyl)phenyl)-1*H*-benzo[*d*]imidazole **1a** (74 mg, 0.25 mmol), 2-bromo-4-methyl-1-(phenylethynyl)benzene **2b** (81 mg, 0.30 mmol), Pd(OAc)₂ (5.6 mg, 10 mol%, 0.025 mmol), DPEPhos (27 mg, 20 mol%, 0.05 mmol), Cs₂CO₃ (244 mg, 0.75 mmol), and Toluene (2 mL) purged with N₂ at 120 °C for 30 min in MW (150 W) reactor. Purification of the crude material by silica gel column chromatography (petroleum ether: ethyl acetate = 98:02 to 95:05) furnished the product **3ab** (96 mg, 79%) as a yellow solid. mp = 260-262 °C. [TLC (petroleum ether: ethyl acetate = 97:3), *R_f*(**1a**) = 0.40, *R_f*(**2b**) = 0.95, *R_f*(**3ab**) = 0.70, UV detection]. **IR:** (MIR-ATR, 4000–600 cm⁻¹) *v*_{max} = 3056, 2922, 2856, 1733, 1604, 1445, 1336, 1274, 1030, 819, 751, 705 cm⁻¹. **¹H NMR (400 MHz, CDCl₃)** δ 8.46 (d, *J* = 7.9 Hz, 1H), 7.71 (d, *J* = 7.9 Hz, 1H), 7.62 – 7.56 (m, 1H), 7.54 – 7.45 (m, 6H), 7.39 – 7.27 (m, 3H), 7.22 – 7.14 (m, 2H), 7.13 – 7.06 (m, 2H), 7.00 – 6.93 (m, 1H), 6.73 – 6.65 (m, 1H), 6.55 (d, *J* = 8.0 Hz, 1H), 5.86 (d, *J* = 8.0 Hz, 1H), 5.60 (d, *J* = 8.7 Hz, 1H), 2.22 (s, 3H) ppm. **¹³C{¹H} NMR (101 MHz, CDCl₃)** δ 153.7, 142.5, 142.4, 141.2, 137.0, 136.7, 136.2, 136.1, 135.8, 135.5, 135.0, 134.3, 132.9, 131.4, 131.2 (2C), 130.9, 130.4, 130.1 (2C), 130.0, 129.7 (2C), 129.3 (2C), 128.3, 127.6, 127.4, 125.1, 123.7, 123.7, 123.1, 121.0, 119.9, 115.6, 21.65 ppm. **HRMS (ESI):** *m/z* calcd for C₃₆H₂₅N₂⁺ [M + H]⁺: 485.2012, found: 485.2002.

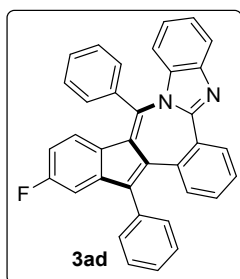
14-Chloro-11,16-diphenylbenzo[*c*]benzo[4,5]imidazo[1,2-*a*]indeno[2,1-*e*]azepine (**3ac**):



GP-4 was carried out with 2-(2-(phenylethynyl)phenyl)-1*H*-benzo[*d*]imidazole **1a** (74 mg, 0.25 mmol), 2-bromo-4-chloro-1-(phenylethynyl)benzene **2c** (87 mg, 0.30 mmol), Pd(OAc)₂

(5.6 mg, 10 mol%, 0.025 mmol), DPEPhos (27 mg, 20 mol%, 0.05 mmol), Cs₂CO₃ (244 mg, 0.75 mmol), and Toluene (2 mL) purged with N₂ at 120 °C for 30 min in MW (150 W) reactor. Purification of the crude material by silica gel column chromatography (petroleum ether: ethyl acetate = 98:02 to 95:05) furnished the product **3ac** (85 mg, 67%) as a yellow solid. mp = 168–170 °C. [TLC (petroleum ether: ethyl acetate = 97:3), *R_f*(**1a**) = 0.40, *R_f*(**2c**) = 0.95, *R_f*(**3ac**) = 0.70, UV detection]. **IR:** (MIR-ATR, 4000–600 cm⁻¹) ν_{\max} = 3062, 2924, 2855, 1728, 1595, 1447, 1337, 1268, 1028, 818, 754, 705 cm⁻¹. **¹H NMR (400 MHz, CDCl₃)** δ 8.58 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.82 (d, *J* = 7.7 Hz, 1H), 7.77 – 7.71 (m, 1H), 7.67 – 7.60 (m, 4H), 7.58 – 7.55 (m, 2H), 7.51 – 7.46 (m, 2H), 7.46 – 7.43 (m, 1H), 7.40 (d, *J* = 2.0 Hz, 1H), 7.36 – 7.31 (m, 1H), 7.26 – 7.19 (m, 2H), 7.14 – 7.09 (m, 1H), 6.85 – 6.78 (m, 2H), 5.92 (d, *J* = 8.4 Hz, 1H), 5.66 (d, *J* = 8.7 Hz, 1H) ppm. **¹³C{¹H} NMR (101 MHz, CDCl₃)** δ 143.7, 140.2, 140.0, 138.2, 136.2, 135.9, 135.8, 135.5, 135.3, 134.8, 134.7, 134.4, 133.0, 132.8, 131.5, 131.0 (2C), 130.7, 130.1, 129.9 (2C), 129.8 (2C), 129.5 (2C), 128.6, 127.9, 124.7, 124.0, 123.9, 123.4, 120.3, 120.1, 115.6, 113.9 ppm. **HRMS (ESI):** *m/z* calcd for C₃₅H₂₂ClN₂⁺ [M + H]⁺: 505.1466, found: 505.1443.

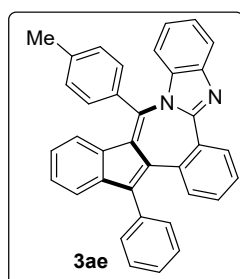
14-Fluoro-11,16-diphenylbenzo[*c*]benzo[4,5]imidazo[1,2-*a*]indeno[2,1-*e*]azepine (**3ad**):



GP-4 was carried out with 2-(2-(phenylethynyl)phenyl)-1*H*-benzo[*d*]imidazole **1a** (74 mg, 0.25 mmol), 2-bromo-4-fluoro-1-(phenylethynyl)benzene **2d** (83 mg, 0.30 mmol), Pd(OAc)₂ (5.6 mg, 10 mol%, 0.025 mmol), DPEPhos (27 mg, 20 mol%, 0.05 mmol), Cs₂CO₃ (244 mg, 0.75 mmol), and Toluene (2 mL) purged with N₂ at 120 °C for 30 min in MW (150 W) reactor. Purification of the crude material by silica gel column chromatography (petroleum ether: ethyl acetate = 98:02 to 95:05) furnished the product **3ad** (89 mg, 72%) as a yellow solid. mp = 208–210 °C. [TLC (petroleum ether: ethyl acetate = 97:3), *R_f*(**1a**) = 0.40, *R_f*(**2d**) = 0.95, *R_f*(**3ad**) = 0.70, UV detection]. **IR:** (MIR-ATR, 4000–600 cm⁻¹) ν_{\max} = 3061, 2924, 2855, 1730, 1597, 1447, 1337, 1269, 1029, 818, 753, 701 cm⁻¹. **¹H NMR (400 MHz, CDCl₃)** δ 8.51 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.76 (d, *J* = 7.8 Hz, 1H), 7.70 – 7.64 (m, 1H), 7.62 – 7.53 (m, 4H), 7.51 – 7.46 (m, 2H), 7.44 – 7.33 (m, 3H), 7.29 – 7.22 (m, 1H), 7.17 – 7.11 (m, 2H), 7.08 – 7.00 (m, 2H), 6.75 (ddd, *J* = 8.6, 7.2, 1.3 Hz, 1H), 6.45 (ddd, *J* = 8.8, 8.6, 2.5 Hz, 1H), 5.89 (dd, *J* = 8.7, 5.1

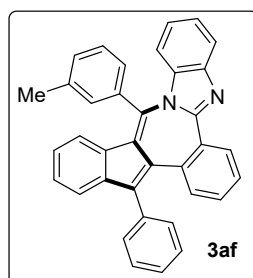
Hz, 1H), 5.61 (d, $J = 8.7$ Hz, 1H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 162.4 (d, $J = 245.8$ Hz), 153.5, 144.21 (d, $J = 8.6$ Hz), 140.3, 140.3, 137.4, 136.0, 135.7, 135.6, 135.5, 134.5, 133.6 (d, $J = 2.4$ Hz), 133.0, 131.5, 131.1 (2C), 130.7, 130.2, 129.9 (2C), 129.8 (2C), 129.5 (2C), 128.7, 128.6, 127.9, 127.5, 125.1, 125.0 (d, $J = 8.7$ Hz), 123.4, 120.0, 115.6, 110.9 (d, $J = 22.8$ Hz), 107.4 (d, $J = 23.9$ Hz) ppm. HRMS (ESI): m/z calcd for $\text{C}_{35}\text{H}_{22}\text{FN}_2^+$ [$\text{M} + \text{H}$] $^+$: 489.1762, found: 489.1734.

16-Phenyl-11-(*p*-tolyl)benzo[*c*]benzo[4,5]imidazo[1,2-*a*]indeno[2,1-*e*]azepine (3ae):



GP-4 was carried out with 2-(2-(phenylethynyl)phenyl)-1*H*-benzo[*d*]imidazole **1a** (74 mg, 0.25 mmol), 1-bromo-2-(*p*-tolylethynyl)benzene **2e** (81 mg, 0.30 mmol), $\text{Pd}(\text{OAc})_2$ (5.6 mg, 10 mol%, 0.025 mmol), DPEPhos (27 mg, 20 mol%, 0.05 mmol), Cs_2CO_3 (244 mg, 0.75 mmol), and Toluene (2 mL) purged with N_2 at 120 °C for 30 min in MW (150 W) reactor. Purification of the crude material by silica gel column chromatography (petroleum ether: ethyl acetate = 98:02 to 95:05) furnished the product **3ae** (87 mg, 71%) as a yellow solid. mp = 180–182 °C. [TLC (petroleum ether: ethyl acetate = 97:3), $R_f(\mathbf{1a}) = 0.40$, $R_f(\mathbf{2e}) = 0.95$, $R_f(\mathbf{3ae}) = 0.70$, UV detection]. IR: (MIR-ATR, 4000–600 cm^{-1}) $\nu_{\text{max}} = 3058, 2923, 2856, 1733, 1603, 1508, 1445, 1333, 1280, 1030, 819, 743, 702$ cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 8.55 (dd, $J = 8.0, 1.3$ Hz, 1H), 7.82 (d, $J = 8.1$ Hz, 1H), 7.62–7.57 (m, 2H), 7.53–7.41 (m, 8H), 7.33–7.29 (m, 1H), 7.25–7.17 (m, 3H), 7.12–7.06 (m, 1H), 6.90–6.81 (m, 2H), 6.19 (d, $J = 7.9$ Hz, 1H), 5.80 (d, $J = 8.7$ Hz, 1H), 2.61 (s, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 153.8, 142.2, 141.9, 141.2, 140.6, 138.2, 137.7, 136.1, 136.0, 135.0, 134.2, 133.2, 132.8, 131.5, 131.0 (2C), 130.4 (2C), 130.1 (2C), 130.0, 129.9, 129.3 (2C), 128.3, 127.5, 126.8, 124.1, 124.1, 123.7, 123.2, 123.1, 120.4, 120.0, 115.8, 21.9 ppm. HRMS (ESI): m/z calcd for $\text{C}_{36}\text{H}_{25}\text{N}_2^+$ [$\text{M} + \text{H}$] $^+$: 485.2012, found: 485.1987.

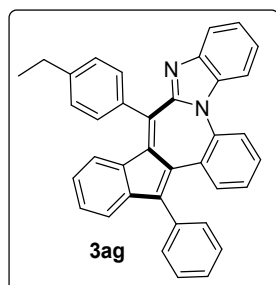
16-Phenyl-11-(*m*-tolyl)benzo[*c*]benzo[4,5]imidazo[1,2-*a*]indeno[2,1-*e*]azepine (**3af**):



GP-4 was carried out with 2-(2-(phenylethynyl)phenyl)-1*H*-benzo[*d*]imidazole **1a** (74 mg, 0.25 mmol), 1-bromo-2-(*m*-tolylethynyl)benzene **2f** (81 mg, 0.30 mmol), Pd(OAc)₂ (5.6 mg, 10 mol%, 0.025 mmol), DPEPhos (27 mg, 20 mol%, 0.05 mmol), Cs₂CO₃ (244 mg, 0.75 mmol), and Toluene (2 mL) purged with N₂ at 120 °C for 30 min in MW (150 W) reactor. Purification of the crude material by silica gel column chromatography (petroleum ether: ethyl acetate = 98:02 to 95:05) furnished the product **3af** (84 mg, 69%) as a yellow oil. [TLC (petroleum ether: ethyl acetate = 97:3), *R_f*(**1a**) = 0.40, *R_f*(**2f**) = 0.95, *R_f*(**3af**) = 0.70, UV detection]. **IR:** (MIR-ATR, 4000–600 cm⁻¹) *v*_{max} = 3056, 2923, 1732, 1600, 1446, 1332, 1273, 1031, 750, 702 cm⁻¹. **¹H NMR (400 MHz, CDCl₃)** δ 8.56 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.59 (dd, *J* = 8.1, 1.3 Hz, 2H), 7.56 – 7.50 (m, 2H), 7.50 – 7.38 (m, 6H), 7.35 – 7.28 (m, 1H), 7.26 – 7.17 (m, 3H), 7.10 (dd, *J* = 7.1, 1.3 Hz, 1H), 6.88 – 6.82 (m, 2H), 6.13 (d, *J* = 7.9 Hz, 1H), 5.78 (d, *J* = 8.7 Hz, 1H), 2.46 (s, 3H) ppm. **¹³C{¹H} NMR (101 MHz, CDCl₃)** δ 153.8, 142.2, 141.3, 140.4, 139.7, 138.1, 137.7, 137.6, 136.0, 135.9, 135.0, 134.3, 134.1, 132.9, 131.5 (2C), 131.1, 130.1 (2C), 130.0, 129.5, 129.3 (2C), 128.3, 128.3, 127.6, 127.5, 126.9, 124.1 (2C), 123.8, 123.3, 120.4, 119.9, 115.8, 21.6 ppm. **HRMS (ESI):** *m/z* calcd for C₃₆H₂₅N₂⁺ [*M* + *H*]⁺: 485.2012, found: 485.2007.

11-(4-Ethylphenyl)-16-phenylbenzo[*f*]benzo[4,5]imidazo[1,2-*a*]indeno[1,2-*d*]azepine

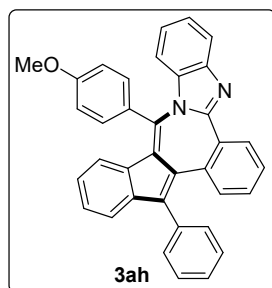
(**3ag**):



GP-4 was carried out with 2-(2-(phenylethynyl)phenyl)-1*H*-benzo[*d*]imidazole **1a** (74 mg, 0.25 mmol), 1-bromo-2-((4-ethylphenyl)ethynyl)benzene **2g** (85 mg, 0.30 mmol), Pd(OAc)₂ (5.6 mg, 10 mol%, 0.025 mmol), DPEPhos (27 mg, 20 mol%, 0.05 mmol), Cs₂CO₃ (244 mg,

0.75 mmol), and Toluene (2 mL) purged with N₂ at 120 °C for 30 min in MW (150 W) reactor. Purification of the crude material by silica gel column chromatography (petroleum ether: ethyl acetate = 98:02 to 95:05) furnished the product **3ag** (88 mg, 70%) as a yellow solid. mp = 162–164 °C. [TLC (petroleum ether: ethyl acetate = 97:3), *R_f*(**1a**) = 0.40, *R_f*(**2g**) = 0.95, *R_f*(**3ag**) = 0.70, UV detection]. **IR:** (MIR-ATR, 4000–600 cm⁻¹) ν_{\max} = 3056, 2967, 2870, 1734, 1602, 1508, 1446, 1331, 1276, 1030, 835, 749, 702 cm⁻¹. **¹H NMR (400 MHz, CDCl₃)** δ 8.58 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.84 (d, *J* = 7.9 Hz, 1H), 7.61 (dd, *J* = 8.1, 1.2 Hz, 2H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.51 – 7.38 (m, 6H), 7.35 – 7.29 (m, 1H), 7.26 – 7.19 (m, 3H), 7.10 (ddd, *J* = 8.3, 7.3, and 1.4 Hz, 1H), 6.93 – 6.79 (m, 2H), 6.18 (d, *J* = 7.9 Hz, 1H), 5.76 (d, *J* = 8.7 Hz, 1H), 2.91 (q, *J* = 7.6 Hz, 2H), 1.43 (t, *J* = 7.6 Hz, 3H) ppm. **¹³C{¹H} NMR (101 MHz, CDCl₃)** δ 153.7, 147.1, 142.5, 142.1, 141.1, 138.2, 137.6, 136.0, 135.9, 135.0, 134.1, 133.4, 132.8, 131.4, 130.9 (2C), 130.8, 130.0 (2C), 129.9, 129.3 (2C), 129.1 (2C), 128.3, 127.6, 127.4, 126.8, 124.0 (2C), 123.7, 123.1, 120.4, 119.9, 115.7, 29.1, 15.9 ppm. **HRMS (ESI):** *m/z* calcd for C₃₇H₂₇N₂⁺ [M + H]⁺: 499.2169, found: 499.2153.

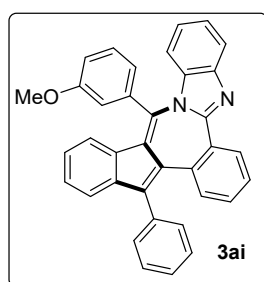
11-(4-Methoxyphenyl)-16-phenylbenzo[*c*]benzo[4,5]imidazo[1,2-*a*]indeno[2,1-*e*]azepine (3ah**):**



GP-4 was carried out with 2-(2-(phenylethynyl)phenyl)-1*H*-benzo[*d*]imidazole **1a** (74 mg, 0.25 mmol), 1-bromo-2-((4-methoxyphenyl)ethynyl)benzene **2h** (86 mg, 0.30 mmol), Pd(OAc)₂ (5.6 mg, 10 mol%, 0.025 mmol), DPEPhos (27 mg, 20 mol%, 0.05 mmol), Cs₂CO₃ (244 mg, 0.75 mmol), and Toluene (2 mL) purged with N₂ at 120 °C for 30 min in MW (150 W) reactor. Purification of the crude material by silica gel column chromatography (petroleum ether: ethyl acetate = 98:02 to 95:05) furnished the product **3ah** (96 mg, 76%) as a yellow solid. mp = 162–164 °C. [TLC (petroleum ether: ethyl acetate = 97:3), *R_f*(**1a**) = 0.40, *R_f*(**2h**) = 0.85, *R_f*(**3ah**) = 0.50, UV detection]. **IR:** (MIR-ATR, 4000–600 cm⁻¹) ν_{\max} = 2923, 2854, 1605, 1509, 1451, 1335, 1266, 1175, 1029, 830, 755 cm⁻¹. **¹H NMR (400 MHz, CDCl₃)** δ 8.59 – 8.50 (m, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.59 (dd, *J* = 8.1, 1.3 Hz, 2H), 7.54 – 7.50 (m, 2H), 7.49 – 7.39

(m, 4H), 7.33 – 7.29 (m, 1H), 7.24 – 7.19 (m, 2H), 7.17 – 7.13 (m, 3H), 7.12 – 7.06 (m, 1H), 6.88 (ddd, $J = 8.4, 7.5,$ and 1.1 Hz, 2H), 6.24 (d, $J = 7.9$ Hz, 1H), 5.85 (d, $J = 8.7$ Hz, 1H), 4.00 (s, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 161.2, 142.2 (2C), 141.4, 138.3, 137.2, 136.0, 135.1, 134.1, 132.8, 132.4 (2C), 131.8, 131.4, 130.1 (2C), 129.7, 129.5, 129.3 (2C), 128.5, 128.4 (2C), 127.5, 127.1, 126.9, 124.2, 124.0, 123.9, 123.3, 120.5, 119.9, 115.8, 115.0 (2C), 55.7 ppm. HRMS (ESI): m/z calcd for $\text{C}_{36}\text{H}_{25}\text{N}_2\text{O}^+$ $[\text{M} + \text{H}]^+$: 501.1961, found: 501.1945.

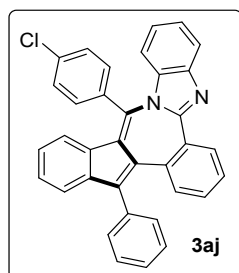
11-(3-Methoxyphenyl)-16-phenylbenzo[*c*]benzo[4,5]imidazo[1,2-*a*]indeno[2,1-*e*]azepine (3ai):



GP-4 was carried out with 2-(2-(phenylethynyl)phenyl)-1*H*-benzo[*d*]imidazole **1a** (74 mg, 0.25 mmol), 1-bromo-2-((3-methoxyphenyl)ethynyl)benzene **2i** (86 mg, 0.30 mmol), $\text{Pd}(\text{OAc})_2$ (5.6 mg, 10 mol%, 0.025 mmol), DPEPhos (27 mg, 20 mol%, 0.05 mmol), Cs_2CO_3 (244 mg, 0.75 mmol), and Toluene (2 mL) purged with N_2 at 120°C for 30 min in MW (150 W) reactor. Purification of the crude material by silica gel column chromatography (petroleum ether: ethyl acetate = 98:02 to 95:05) furnished the product **3ai** (99 mg, 79%) as a yellow solid. mp = $210\text{--}212^\circ\text{C}$. [TLC (petroleum ether: ethyl acetate = 97:3), $R_f(\mathbf{1a}) = 0.40$, $R_f(\mathbf{2i}) = 0.80$, $R_f(\mathbf{3ai}) = 0.50$, UV detection]. IR: (MIR-ATR, $4000\text{--}600\text{ cm}^{-1}$) $\nu_{\text{max}} = 3058, 2928, 2842, 1733, 1584, 1443, 1322, 1275, 1112, 1037, 859, 748, 701\text{ cm}^{-1}$. ^1H NMR (400 MHz, CDCl_3) δ 8.56 (dd, $J = 8.1, 1.3$ Hz, 1H), 7.87 – 7.76 (m, 1H), 7.63 – 7.58 (m, 2H), 7.54 (dd, $J = 8.2, 7.7$ Hz, 1H), 7.51 – 7.39 (m, 4H), 7.31 (ddd, $J = 8.2, 7.2,$ and 1.3 Hz, 1H), 7.28 – 7.16 (m, 6H), 7.09 (ddd, $J = 8.4, 7.2, 1.5$ Hz, 1H), 6.91 – 6.84 (m, 2H), 6.20 (d, $J = 7.9$ Hz, 1H), 5.85 (d, $J = 8.7$ Hz, 1H), 3.82 (s, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 160.7, 153.8, 142.8, 142.2, 141.3, 138.0, 137.3, 137.1, 136.0, 135.9, 134.9, 134.1, 132.9, 131.5, 130.8, 130.6, 130.1 (2C), 129.9, 129.3 (2C), 128.3, 127.8, 127.5, 127.0, 124.1 (2C), 123.8, 123.5, 123.3, 120.4, 120.0, 116.8, 115.8, 115.8, 55.7 ppm. HRMS (ESI): m/z calcd for $\text{C}_{36}\text{H}_{25}\text{N}_2\text{O}^+$ $[\text{M} + \text{H}]^+$: 501.1961, found: 501.1942.

11-(4-Chlorophenyl)-16-phenylbenzo[*c*]benzo[4,5]imidazo[1,2-*a*]indeno[2,1-*e*]azepine

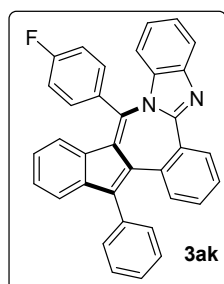
(**3aj**):



GP-4 was carried out with 2-(2-(phenylethynyl)phenyl)-1*H*-benzo[*d*]imidazole **1a** (74 mg, 0.25 mmol), 1-bromo-2-((4-chlorophenyl)ethynyl)benzene **2j** (87 mg, 0.30 mmol), Pd(OAc)₂ (5.6 mg, 10 mol%, 0.025 mmol), DPEPhos (27 mg, 20 mol%, 0.05 mmol), Cs₂CO₃ (244 mg, 0.75 mmol), and Toluene (2 mL) purged with N₂ at 120 °C for 30 min in MW (150 W) reactor. Purification of the crude material by silica gel column chromatography (petroleum ether: ethyl acetate = 98:02 to 95:05) furnished the product **3aj** (88 mg, 69%) as a yellow solid. mp = 260–262 °C. [TLC (petroleum ether: ethyl acetate = 97:3), *R_f*(**1a**) = 0.40, *R_f*(**2j**) = 0.95, *R_f*(**3aj**) = 0.70, UV detection]. **IR**: (MIR-ATR, 4000–600 cm⁻¹) *v*_{max} = 3060, 2923, 2855, 1732, 1604, 1447, 1334, 1271, 1023, 830, 752 cm⁻¹. **¹H NMR (400 MHz, CDCl₃)** δ 8.55 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.61 (ddd, *J* = 18.3, 6.3, and 1.7 Hz, 6H), 7.51 – 7.38 (m, 4H), 7.35 – 7.29 (m, 1H), 7.25 (d, *J* = 7.2 Hz, 1H) 7.24 – 7.21 (m, 1H), 7.17 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.12 – 7.06 (m, 1H), 6.95 – 6.85 (m, 2H), 6.21 (d, *J* = 7.9 Hz, 1H), 5.84 (d, *J* = 8.6 Hz, 1H) ppm. **¹³C{¹H} NMR (151 MHz, CDCl₃)** δ 153.7, 142.4 (2C), 141.7, 138.0 (2C), 136.7 (2C), 135.7 (3C), 135.0, 134.4, 134.3, 132.8 (2C), 132.7, 131.4, 130.1 (3C), 130.0, 129.4 (2C), 128.5, 127.6, 127.3, 124.3, 124.0, 123.8, 123.4, 120.7, 120.2, 115.2 ppm. **HRMS (ESI)**: *m/z* calcd for C₃₅H₂₂ClN₂⁺ [*M* + *H*]⁺: 505.1466, found: 505.1441.

11-(4-Fluorophenyl)-16-phenylbenzo[*c*]benzo[4,5]imidazo[1,2-*a*]indeno[2,1-*e*]azepine

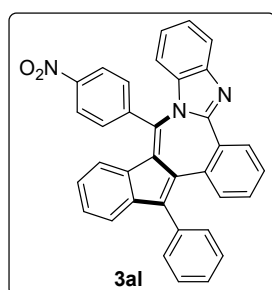
(**3ak**):



GP-4 was carried out with 2-(2-(phenylethynyl)phenyl)-1*H*-benzo[*d*]imidazole **1a** (74 mg, 0.25 mmol), 1-bromo-2-((4-fluorophenyl)ethynyl)benzene **2k** (83 mg, 0.30 mmol), Pd(OAc)₂

(5.6 mg, 10 mol%, 0.025 mmol), DPEPhos (27 mg, 20 mol%, 0.05 mmol), Cs₂CO₃ (244 mg, 0.75 mmol), and Toluene (2 mL) purged with N₂ at 120 °C for 30 min in MW (150 W) reactor. Purification of the crude material by silica gel column chromatography (petroleum ether: ethyl acetate = 98:02 to 95:05) furnished the product **3ak** (95 mg, 77%) as a yellow solid. mp = 218–220 °C. [TLC (petroleum ether: ethyl acetate = 97:3), *R_f*(**1a**) = 0.40, *R_f*(**2k**) = 0.95, *R_f*(**3ak**) = 0.70, UV detection]. **IR:** (MIR-ATR, 4000–600 cm⁻¹) *v*_{max} = 3060, 2924, 2855, 1663, 1603, 1447, 1356, 1277, 1230, 837, 745, 701 cm⁻¹. **¹H NMR (400 MHz, CDCl₃)** δ 8.45 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.57 – 7.46 (m, 4H), 7.41 – 7.29 (m, 4H), 7.27 – 7.18 (m, 3H), 7.18 – 7.12 (m, 2H), 7.12 – 7.07 (m, 1H), 7.03 – 6.96 (m, 1H), 6.82 – 6.76 (m, 2H), 6.04 (d, *J* = 7.9 Hz, 1H), 5.67 (d, *J* = 8.7 Hz, 1H) ppm. **¹³C{¹H} NMR (101 MHz, CDCl₃)** δ 163.9 (d, *J*_{C-F} = 251.6 Hz), 153.7, 142.3 (2C), 141.61, 138.0, 136.0, 135.7 (2C), 135.0, 134.1, 133.2 (d, *J*_{C-F} = 8.2 Hz), 132.8, 132.1 (d, *J*_{C-F} = 3.3 Hz), 131.7, 131.4, 130.2, 130.0 (2C), 129.4 (2C), 128.5, 127.6, 127.4, 127.2, 124.2, 124.0, 123.7, 123.4, 120.7, 120.1, 117.0 (d, *J*_{C-F} = 21.6 Hz), 115.3 ppm. **HRMS (ESI):** *m/z* calcd for C₃₅H₂₂FN₂⁺ [M + H]⁺: 489.1762, found: 489.1749.

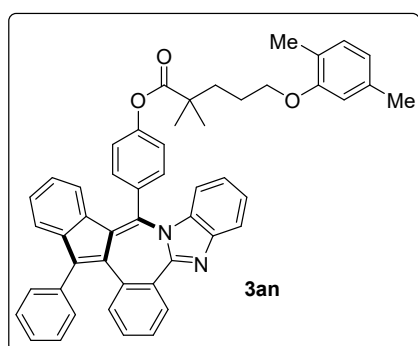
11-(4-Nitrophenyl)-16-phenylbenzo[*c*]benzo[4,5]imidazo[1,2-*a*]indeno[2,1-*e*]azepine (3al**):**



GP-4 was carried out with 2-(2-(phenylethynyl)phenyl)-1*H*-benzo[*d*]imidazole **1a** (74 mg, 0.25 mmol), 1-bromo-2-((4-nitrophenyl)ethynyl)benzene **2l** (91 mg, 0.30 mmol), Pd(OAc)₂ (5.6 mg, 10 mol%, 0.025 mmol), DPEPhos (27 mg, 20 mol%, 0.05 mmol), Cs₂CO₃ (244 mg, 0.75 mmol), and Toluene (2 mL) purged with N₂ at 120 °C for 30 min in MW (150 W) reactor. Purification of the crude material by silica gel column chromatography (petroleum ether: ethyl acetate = 98:02 to 95:05) furnished the product **3al** (87 mg, 67%) as a yellow solid. mp = 264–266 °C. [TLC (petroleum ether: ethyl acetate = 97:3), *R_f*(**1a**) = 0.40, *R_f*(**2l**) = 0.75, *R_f*(**3al**) = 0.45, UV detection]. **IR:** (MIR-ATR, 4000–600 cm⁻¹) *v*_{max} = 3059, 2926, 2857, 1728, 1598, 1524, 1448, 1339, 1270, 1024, 850, 752, 702 cm⁻¹. **¹H NMR (400 MHz, CDCl₃)** δ 8.56 (dd, *J*

= 8.0, 1.1 Hz, 1H), 8.53 – 8.47 (m, 2H), 7.93 – 7.87 (m, 2H), 7.84 (d, $J = 7.9$ Hz, 1H), 7.59 (dd, $J = 8.0, 1.5$ Hz, 2H), 7.54 – 7.40 (m, 4H), 7.33 (ddd, $J = 8.2, 7.1, 1.4$ Hz, 1H), 7.29 – 7.22 (m, 3H), 7.21 – 7.07 (m, 2H), 6.92 – 6.81 (m, 2H), 6.13 (d, $J = 7.8$ Hz, 1H), 5.76 (d, $J = 8.6$ Hz, 1H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 153.8, 148.9, 142.9, 142.6, 142.2, 142.1, 137.5, 135.4, 135.4, 134.9, 134.6, 134.1, 132.7 (2C), 132.7, 132.2, 131.3, 130.2, 129.9 (2C), 129.4 (2C), 128.7, 127.8 (2C), 127.7, 127.5, 124.8, 124.4, 124.1, 123.5, 123.4, 121.0, 120.6, 114.5 ppm. HRMS (ESI): m/z calcd for $\text{C}_{35}\text{H}_{25}\text{N}_4\text{O}_2^+ [\text{M} + \text{NH}_4]^+$: 533.1972, found: 533.1967.

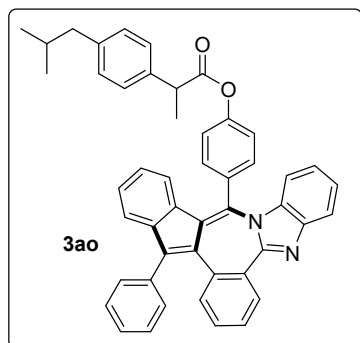
4-(16-Phenylbenzo[*c*]benzo[4,5]imidazo[1,2-*a*]indeno[2,1-*e*]azepin-11-yl)phenyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (3an):



GP-4 was carried out with 2-(2-(phenylethynyl)phenyl)-1*H*-benzo[*d*]imidazole **1a** (74 mg, 0.25 mmol), 4-((2-bromophenyl)ethynyl)phenyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate **2n** (152 mg, 0.30 mmol), $\text{Pd}(\text{OAc})_2$ (5.6 mg, 10 mol%, 0.025 mmol), DPEPhos (27 mg, 20 mol%, 0.05 mmol), Cs_2CO_3 (244 mg, 0.75 mmol), Na_2CO_3 (53 mg, 0.50 mmol), and Toluene (2 mL) purged with N_2 at 120 °C for 30 min in MW (150 W) reactor. Purification of the crude material by silica gel column chromatography (petroleum ether: ethyl acetate = 98:02 to 95:05) furnished the product **3an** (87 mg, 48%) as a yellow solid. mp = 142–144 °C. [TLC (petroleum ether: ethyl acetate = 97:3), $R_f(\mathbf{1a}) = 0.40$, $R_f(\mathbf{2n}) = 0.95$, $R_f(\mathbf{3an}) = 0.60$, UV detection]. **IR:** (MIR-ATR, 4000–600 cm^{-1}) $\nu_{\text{max}} = 2995, 1750, 1612, 1505, 1449, 1322, 1268, 1107, 1011, 819, 754, 706 \text{ cm}^{-1}$. ^1H NMR (400 MHz, CDCl_3) δ 8.56 (dd, $J = 8.1, 1.1$ Hz, 1H), 7.83 (d, $J = 7.8$ Hz, 1H), 7.67 – 7.62 (m, 2H), 7.59 (dd, $J = 8.1, 1.3$ Hz, 2H), 7.51 – 7.41 (m, 5H), 7.35 – 7.28 (m, 3H), 7.23 (d, $J = 7.8$ Hz, 1H), 7.21 – 7.17 (m, 1H), 7.13 – 7.06 (m, 1H), 7.01 (d, $J = 7.9$ Hz, 1H), 6.96 – 6.89 (m, 2H), 6.67 (d, $J = 5.5$ Hz, 2H), 6.23 (d, $J = 7.9$ Hz, 1H), 5.83 (d, $J = 8.7$ Hz, 1H), 4.05 (t, $J = 5.4$ Hz, 2H), 2.30 (s, 3H), 2.21 (s, 3H), 2.03 – 1.94 (m, 4H), 1.48 (s, 6H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 176.3, 156.9, 153.7, 152.6, 142.2, 141.4, 138.0, 136.7, 136.4, 135.8 (2C), 134.9, 134.1, 133.5, 132.8, 132.4 (2C),

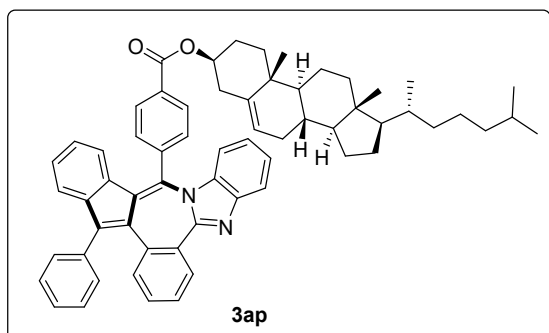
131.4, 130.5, 130.3, 130.0 (2C), 129.3 (2C), 128.8, 128.4, 127.5, 127.1, 124.4, 124.0, 123.9, 123.7, 123.5, 123.3 (2C), 120.9, 120.8, 120.5, 120.1, 115.5, 114.4, 112.0, 67.8, 42.8, 37.3, 25.5, 25.3, 21.6, 16.0 ppm. **HRMS (ESI):** m/z calcd for $C_{50}H_{43}N_2O_3^+$ $[M + H]^+$: 719.3268, found: 719.3231.

4-(16-Phenylbenzo[*c*]benzo[4,5]imidazo[1,2-*a*]indeno[2,1-*e*]azepin-11-yl)phenyl 2-(4-isobutylphenyl)propanoate (3ao):



GP-4 was carried out with 2-(2-(phenylethynyl)phenyl)-1*H*-benzo[*d*]imidazole **1a** (74 mg, 0.25 mmol), 4-((2-bromophenyl)ethynyl)phenyl 2-(4-isobutylphenyl)propanoate **2o** (138 mg, 0.30 mmol), Pd(OAc)₂ (5.6 mg, 10 mol%, 0.025 mmol), DPEPhos (27 mg, 20 mol%, 0.05 mmol), Cs₂CO₃ (244 mg, 0.75 mmol), Na₂CO₃ (53 mg, 0.50 mmol), and Toluene (2 mL) purged with N₂ at 120 °C for 30 min in MW (150 W) reactor. Purification of the crude material by silica gel column chromatography (petroleum ether: ethyl acetate = 98:02 to 95:05) furnished the product **3ao** (75 mg, 44%) as a yellow solid. mp = 140-142 °C. [TLC (petroleum ether: ethyl acetate = 97:3), R_f (**1a**) = 0.40, R_f (**2o**) = 0.75, R_f (**3ao**) = 0.60, UV detection]. **IR:** (MIR-ATR, 4000–600 cm⁻¹) ν_{max} = 2928, 1743, 1604, 1505, 1332, 1201, 1026, 753 cm⁻¹. **¹H NMR (400 MHz, CDCl₃)** δ 8.54 (d, J = 8.0 Hz, 1H), 7.81 (d, J = 8.3 Hz, 1H), 7.65 – 7.55 (m, 4H), 7.51 – 7.34 (m, 6H), 7.33 – 7.26 (m, 3H), 7.25 – 7.15 (m, 5H), 7.08 (dd, J = 7.4, 7.3 Hz, 1H), 6.89 (dd, J = 7.8, 7.6 Hz, 2H), 6.18 (d, J = 7.9 Hz, 1H), 5.78 (d, J = 8.6 Hz, 1H), 4.06 (q, J = 7.1 Hz, 1H), 2.50 (d, J = 7.2 Hz, 2H), 1.95 – 1.83 (m, 1H), 1.70 (d, J = 7.1 Hz, 3H), 0.93 (d, J = 6.6 Hz, 6H) ppm. **¹³C{¹H} NMR (151 MHz, DMSO)** δ 175.7, 159.3, 152.9, 142.4, 141.3, 140.5, 139.7, 138.6, 137.7, 135.7, 135.6, 134.1, 133.1, 132.9, 132.1 (2C), 131.1, 130.0, 129.8 (2C), 129.6 (2C), 129.3, 129.1, 128.6, 127.7, 127.6, 127.5, 127.3, 127.0, 126.3, 124.4 (2C), 123.9, 123.8, 123.3, 120.1, 119.9 (2C), 116.6 (2C), 115.8, 44.5, 44.4, 39.5, 29.8, 22.3, 18.7 ppm. **HRMS (ESI):** m/z calcd for $C_{48}H_{39}N_2O_2^+$ $[M + H]^+$: 675.3006, found: 675.2971.

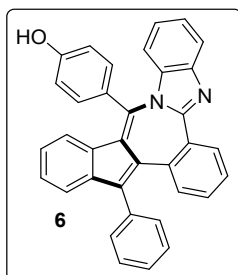
(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 4-((2-phenylethynyl)benzo[*c*]benzo[4,5]imidazo[1,2-*a*]indeno[2,1-*e*]azepin-11-yl)benzoate (3ap**):**



GP-4 was carried out with 2-(2-(phenylethynyl)phenyl)-1*H*-benzo[*d*]imidazole **1a** (74 mg, 0.25 mmol), (3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 4-((2-bromophenyl)ethynyl)benzoate **2p** (200 mg, 0.30 mmol), Pd(OAc)₂ (5.6 mg, 10 mol%, 0.025 mmol), DPEPhos (27 mg, 20 mol%, 0.05 mmol), Cs₂CO₃ (244 mg, 0.75 mmol), Na₂CO₃ (53 mg, 0.50 mmol), and Toluene (2 mL) purged with N₂ at 120 °C for 30 min in MW (150 W) reactor. Purification of the crude material by silica gel column chromatography (petroleum ether: ethyl acetate = 98:02 to 95:05) furnished the product **3ap** (125 mg, 56%) as a yellow oil. mp = 138-140 °C. [TLC (petroleum ether: ethyl acetate = 97:3), *R_f*(**1a**) = 0.40, *R_f*(**2p**) = 0.75, *R_f*(**3ap**) = 0.65, UV detection]. **IR:** (MIR-ATR, 4000–600 cm⁻¹) *v*_{max} = 3056, 2939, 2860, 1715, 1602, 1448, 1357, 1269, 1173, 1112, 854, 741 cm⁻¹. **¹H NMR (600 MHz, CDCl₃)** δ 8.54 (dd, *J* = 8.0, 1.2 Hz, 1H), 8.35 – 8.27 (m, 2H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.74 (d, *J* = 8.3 Hz, 2H), 7.62 – 7.56 (m, 2H), 7.49 – 7.44 (m, 3H), 7.44 – 7.40 (m, 1H), 7.33 – 7.29 (m, 1H), 7.24 – 7.20 (m, 2H), 7.17 (dd, *J* = 8.1, 0.8 Hz, 1H), 7.13 – 7.06 (m, 1H), 6.89 – 6.80 (m, 2H), 6.13 (d, *J* = 7.9 Hz, 1H), 5.77 (d, *J* = 8.7 Hz, 1H), 5.48 (d, *J* = 4.8 Hz, 1H), 5.04 – 4.93 (m, 1H), 2.63 – 2.52 (m, 2H), 2.15 – 2.10 (m, 1H), 2.08 – 2.01 (m, 2H), 2.00 – 1.96 (m, 1H), 1.89 – 1.82 (m, 2H), 1.64 – 1.58 (m, 3H), 1.57 – 1.47 (m, 5H), 1.40 (s, 1H), 1.37 – 1.34 (m, 2H), 1.31 – 1.26 (m, 3H), 1.24 – 1.21 (m, 1H), 1.17 – 1.14 (m, 2H), 1.11 (s, 3H), 1.07 – 1.01 (m, 3H), 0.94 (d, *J* = 6.5 Hz, 3H), 0.88 (dd, *J* = 6.6, 2.8 Hz, 6H), 0.71 (s, 3H) ppm. **¹³C{¹H} NMR (151 MHz, CDCl₃)** δ 178.0, 165.5, 153.8, 142.9, 142.4, 141.68, 140.1, 139.7, 137.8, 136.1, 135.8, 135.7, 134.9, 134.4, 132.8 (2C), 132.6, 131.4 (3C), 130.8 (2C), 130.1 (2C), 129.4 (2C), 128.5, 127.7, 127.6, 127.2, 124.3, 123.9, 123.8, 123.4, 123.2, 120.7, 120.3, 115.2, 75.6, 56.9, 56.3, 50.2, 42.5, 39.9, 39.67, 38.4, 37.2, 36.8, 36.3, 36.0, 32.1, 32.0, 28.4, 28.2, 28.1, 24.5, 24.0, 23.0,

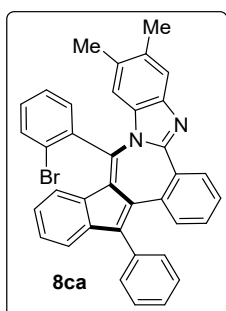
22.7, 21.2, 19.6, 18.9, 12.0 ppm. **HRMS (ESI):** m/z calcd for $C_{63}H_{66}N_2Na_2O_2^{2+}$ $[M + 2Na]^{2+}$: 464.2454, found: 464.2431.

4-(16-Phenylbenzo[*c*]benzo[4,5]imidazo[1,2-*a*]indeno[2,1-*e*]azepin-11-yl)phenol (6):



GP-4 was carried out with 2-(2-(phenylethynyl)phenyl)-1*H*-benzo[*d*]imidazole **1a** (74 mg, 0.25 mmol), 4-((2-bromophenyl)ethynyl)phenyl 2-(4-isobutylphenyl)propanoate **2o** (138 mg, 0.30 mmol), Pd(OAc)₂ (5.6 mg, 10 mol%, 0.025 mmol), DPEPhos (27 mg, 20 mol%, 0.05 mmol), Cs₂CO₃ (244 mg, 0.75 mmol), and Toluene (2 mL) purged with N₂ at 120 °C for 30 min in MW (150 W) reactor. Purification of the crude material by silica gel column chromatography (petroleum ether: ethyl acetate = 98:02 to 95:05) furnished the product **6** (70 mg, 57%) as a yellow solid. mp = 322-324 °C. [TLC (petroleum ether: ethyl acetate = 97:3), $R_f(\mathbf{1a}) = 0.40$, $R_f(\mathbf{2o}) = 0.75$, $R_f(\mathbf{6}) = 0.20$, UV detection]. **IR:** (MIR-ATR, 4000–600 cm⁻¹) $\nu_{\max} = 3379, 1647, 1462, 1268, 990, 822, 755, 620$ cm⁻¹. **¹H NMR (600 MHz, DMSO)** δ 10.24 (bs, 1H), 8.50 (d, $J = 8.0$ Hz, 1H), 7.75 (d, $J = 7.8$ Hz, 1H), 7.59 – 7.54 (m, 2H), 7.51 (dd, $J = 7.6, 7.5$ Hz, 2H), 7.46 (d, $J = 7.3$ Hz, 1H), 7.44 (d, $J = 8.5$ Hz, 2H), 7.38 – 7.31 (m, 2H), 7.27 – 7.21 (m, 2H), 7.15 – 7.13 (m, 2H), 7.06 (d, $J = 8.5$, 2H), 6.91 (ddd, $J = 8.6, 7.6,$ and 1.0 Hz, 2H), 6.16 (d, $J = 7.9$ Hz, 1H), 5.83 (d, $J = 8.7$ Hz, 1H) ppm. **¹³C{¹H} NMR (101 MHz, DMSO)** δ 159.2, 152.7, 142.2, 141.2, 140.4, 138.5, 137.5, 135.5, 135.4, 134.0, 133.0, 132.7, 131.9 (2C), 130.9, 129.9, 129.7 (2C), 129.4, 128.4 (2C), 127.4, 126.9, 126.8, 126.1, 124.2, 123.7, 123.6, 123.1, 119.9, 119.9, 119.7, 116.5 (2C), 115.6, 105.7 ppm. **HRMS (ESI):** m/z calcd for $C_{35}H_{23}N_2O^+$ $[M + H]^+$: 487.1805, found: 487.1778.

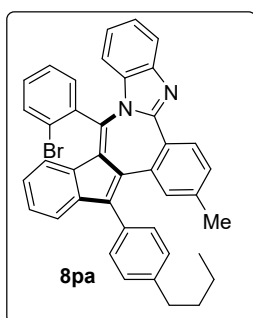
11-(2-Bromophenyl)-7,8-dimethyl-16-phenylbenzo[*c*]benzo[4,5]imidazo[1,2-*a*]indeno[2,1-*e*]azepine (8ca):



GP-4 was carried out with 5,6-dimethyl-2-(2-(phenylethynyl)phenyl)-1*H*-benzo[*d*]imidazole **1c** (81 mg, 0.25 mmol), 1,2-bis(2-bromophenyl)ethyne **7a** (101 mg, 0.30 mmol), Pd(OAc)₂ (5.6 mg, 10 mol%, 0.025 mmol), DPEPhos (27 mg, 20 mol%, 0.05 mmol), Cs₂CO₃ (244 mg, 0.75 mmol), and Toluene (2 mL) purged with N₂ at 120 °C for 30 min in MW (150 W) reactor. Purification of the crude material by silica gel column chromatography (petroleum ether: ethyl acetate = 98:02 to 95:05) furnished the product **8ca** (84 mg, 67%) as a yellow solid. mp = 248–250 °C. [TLC (petroleum ether: ethyl acetate = 97:3), *R_f*(**1c**) = 0.40, *R_f*(**7a**) = 0.95, *R_f*(**8ca**) = 0.70, UV detection]. **IR:** (MIR-ATR, 4000–600 cm⁻¹) *v*_{max} = 3063, 2922, 2855, 1725, 1599, 1457, 1350, 1266, 1103, 1028, 851, 756, 704 cm⁻¹. **¹H NMR (400 MHz, CDCl₃)** δ 8.58 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 7.1 Hz, 1H), 7.69 (dd, *J* = 7.1, 2.0 Hz, 1H), 7.66 – 7.57 (m, 5H), 7.51 – 7.39 (m, 4H), 7.31 (dd, *J* = 7.7, 7.5 Hz, 1H), 7.25 – 7.19 (m, 2H), 7.08 (dd, *J* = 7.7, 7.5 Hz, 1H), 6.85 (dd, *J* = 7.8, 7.5 Hz, 1H), 6.00 (d, *J* = 7.9 Hz, 1H), 5.47 (s, 1H), 2.30 (s, 3H), 2.01 (s, 3H) ppm. **¹³C{¹H} NMR (151 MHz, CDCl₃)** δ 142.3 (2C), 141.3, 137.7 (2C), 137.2, 136.2, 136.0, 134.4, 134.1, 134.0, 133.7, 133.2, 132.9, 132.5, 132.0, 131.7, 131.6, 130.1 (2C), 129.9, 129.7, 129.3 (2C), 128.7, 128.4, 128.3, 127.6, 127.1, 125.8, 124.4, 123.2, 120.5, 119.9, 115.1, 21.0, 20.1 ppm. **HRMS (ESI):** *m/z* calcd for C₃₇H₂₆⁷⁹BrN₂⁺ [M + H]⁺: 577.1274, found: 577.1270. *m/z* calcd for C₃₇H₂₆⁸¹BrN₂⁺ [M + H]⁺: 579.1253, found: 579.1256.

Conventional Method: A reaction was carried out with 5,6-dimethyl-2-(2-(phenylethynyl)phenyl)-1*H*-benzo[*d*]imidazole **1c** (81 mg, 0.25 mmol), 1,2-bis(2-bromophenyl)ethyne **7a** (101 mg, 0.30 mmol), Pd(OAc)₂ (5.6 mg, 10 mol%, 0.025 mmol), DPEPhos (27 mg, 20 mol%, 0.05 mmol), Cs₂CO₃ (244 mg, 0.75 mmol), and Toluene (2 mL) purged with N₂ at 140 °C for 24 h in oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether: ethyl acetate = 98:02 to 95:05) furnished the product **8ca** (52 mg, 42%) as a yellow solid.

11-(2-Bromophenyl)-16-(4-butylphenyl)-2-methylbenzo[*c*]benzo[4,5]imidazo[1,2-*a*]indeno[2,1-*e*]azepine (8pa):

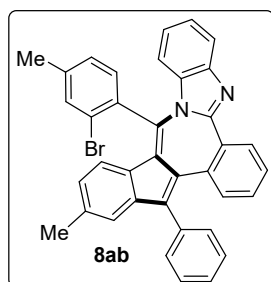


GP-4 was carried out with 2-(2-((4-butylphenyl)ethynyl)-4-methylphenyl)-1*H*-benzo[*d*]imidazole **1p** (91 mg, 0.25 mmol), 1,2-bis(2-bromophenyl)ethyne **7a** (101 mg, 0.30 mmol), Pd(OAc)₂ (5.6 mg, 10 mol%, 0.025 mmol), DPEPhos (27 mg, 20 mol%, 0.05 mmol), Cs₂CO₃ (244 mg, 0.75 mmol), and Toluene (2 mL) purged with N₂ at 120 °C for 30 min in MW (150 W) reactor. Purification of the crude material by silica gel column chromatography (petroleum ether: ethyl acetate = 98:02 to 95:05) furnished the product **8pa** (84 mg, 62%) as a yellow solid. mp = 170-172 °C. [TLC (petroleum ether: ethyl acetate = 97:3), *R_f*(**1p**) = 0.40, *R_f*(**7a**) = 0.95, *R_f*(**8pa**) = 0.70, UV detection]. **IR:** (MIR-ATR, 4000–600 cm⁻¹) *v*_{max} = 3058, 2922, 2855, 1733, 1664, 1608, 1452, 1363, 1267, 1177, 1027, 828, 740 cm⁻¹. **¹H NMR (400 MHz, CDCl₃)** δ 8.51 (d, *J* = 8.2 Hz, 1H), 7.92 – 7.79 (m, 2H), 7.75 – 7.66 (m, 1H), 7.62 – 7.58 (m, 2H), 7.53 – 7.42 (m, 3H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.26 – 7.20 (m, 2H), 7.14 (d, *J* = 8.0 Hz, 1H), 6.98 (s, 1H), 6.85 (dd, *J* = 7.9, 7.5 Hz, 2H), 5.96 (d, *J* = 7.9 Hz, 1H), 5.84 (d, *J* = 8.6 Hz, 1H), 2.70 (t, *J* = 7.6 Hz, 2H), 2.00 (s, 3H), 1.68 – 1.62 (m, 2H), 1.43 – 1.36 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H) ppm. **¹³C{¹H} NMR (151 MHz, CDCl₃)** δ 143.4, 142.5 (2C), 137.7 (2C), 137.0, 136.9, 135.2, 135.1, 134.8, 134.6, 134.2, 133.6 (2C), 133.5, 133.2, 132.9, 132.1, 132.0, 129.8 (2C), 129.6, 129.4 (2C), 128.7, 128.5, 127.2, 125.7, 124.4, 124.0, 123.5, 123.2, 120.7, 119.9, 114.7, 35.7, 33.8, 22.3, 21.2, 14.1 ppm. **HRMS (ESI):** *m/z* calcd for C₄₀H₃₂⁷⁹BrN₂⁺ [M + H]⁺: 619.1743, found: 619.1708. *m/z* calcd for C₄₀H₃₂⁸¹BrN₂⁺ [M + H]⁺: 621.1723, found: 621.1696.

Conventional Method: A reaction was carried out with 2-(2-((4-butylphenyl)ethynyl)-4-methylphenyl)-1*H*-benzo[*d*]imidazole **1p** (91 mg, 0.25 mmol), 1,2-bis(2-bromophenyl)ethyne **7a** (101 mg, 0.30 mmol), Pd(OAc)₂ (5.6 mg, 10 mol%, 0.025 mmol), DPEPhos (27 mg, 20 mol%, 0.05 mmol), Cs₂CO₃ (244 mg, 0.75 mmol), and Toluene (2 mL) purged with N₂ at 140 °C for 24 h in oil bath. Purification of the crude material by silica gel column chromatography

(petroleum ether: ethyl acetate = 98:02 to 95:05) furnished the product **8pa** (50 mg, 37%) as a yellow solid.

11-(2-Bromo-4-methylphenyl)-14-methyl-16-phenylbenzo[*c*]benzo[4,5]imidazo[1,2-*a*]indeno[2,1-*e*]azepine (8ab**):**

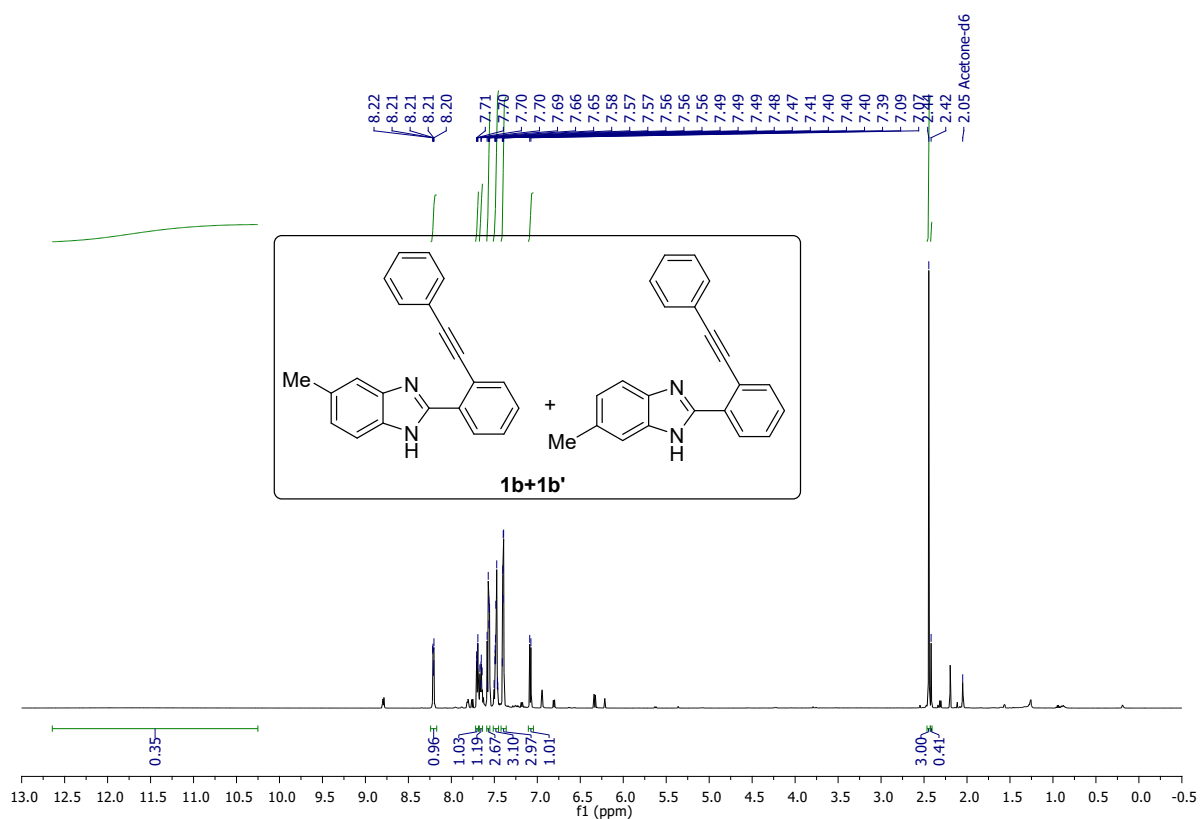


GP-4 was carried out with 2-(2-(phenylethynyl)phenyl)-1*H*-benzo[*d*]imidazole **1a** (74 mg, 0.25 mmol), 1,2-bis(2-bromo-4-methylphenyl)ethyne **7b** (109 mg, 0.30 mmol), Pd(OAc)₂ (5.6 mg, 10 mol%, 0.025 mmol), DPEPhos (27 mg, 20 mol%, 0.05 mmol), Cs₂CO₃ (244 mg, 0.75 mmol), and Toluene (2 mL) purged with N₂ at 120 °C for 30 min in MW (150 W) reactor. Purification of the crude material by silica gel column chromatography (petroleum ether: ethyl acetate = 98:02 to 95:05) furnished the product **8ab** (85 mg, 68%) as a yellow solid. mp = 260-262 °C. [TLC (petroleum ether: ethyl acetate = 97:3), *R_f*(**1a**) = 0.40, *R_f*(**7b**) = 0.95, *R_f*(**8ab**) = 0.70, UV detection]. **IR:** (MIR-ATR, 4000–600 cm⁻¹) ν_{\max} = 3046, 2920, 2853, 1732, 1604, 1445, 1341, 1277, 1116, 1031, 818, 738 cm⁻¹. **¹H NMR (400 MHz, CDCl₃)** δ 8.59 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.69 (s, 1H), 7.60 – 7.55 (m, 3H), 7.52 – 7.45 (m, 2H), 7.44 – 7.37 (m, 2H), 7.34 – 7.28 (m, 1H), 7.28 – 7.22 (m, 2H), 7.20 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.08 (ddd, *J* = 8.4, 7.2, and 1.4 Hz, 1H), 6.90 (ddd, *J* = 8.6, 7.2, and 1.3 Hz, 1H), 6.70 (dd, *J* = 8.0, 0.8 Hz, 1H), 5.93 (d, *J* = 8.1 Hz, 2H), 2.59 (s, 3H), 2.35 (s, 3H) ppm. **¹³C{¹H} NMR (151 MHz, CDCl₃)** δ 153.8, 142.7 (2C), 142.6 (2C), 141.4, 137.2, 136.1, 135.4, 135.2, 134.7, 134.5, 134.2, 134.1, 133.2, 133.0, 131.5, 130.1 (2C), 129.9, 129.3 (3C), 128.3, 127.5, 125.4, 125.3, 124.5, 123.8, 123.4, 123.1, 121.2, 120.1, 114.8, 112.3, 21.7, 21.6 ppm. **HRMS (ESI):** *m/z* calcd for C₃₇H₂₆⁷⁹BrN₂⁺ [M + H]⁺: 577.1274, found: 577.1249. *m/z* calcd for C₃₇H₂₆⁸¹BrN₂⁺ [M + H]⁺: 579.1253, found: 577.1237.

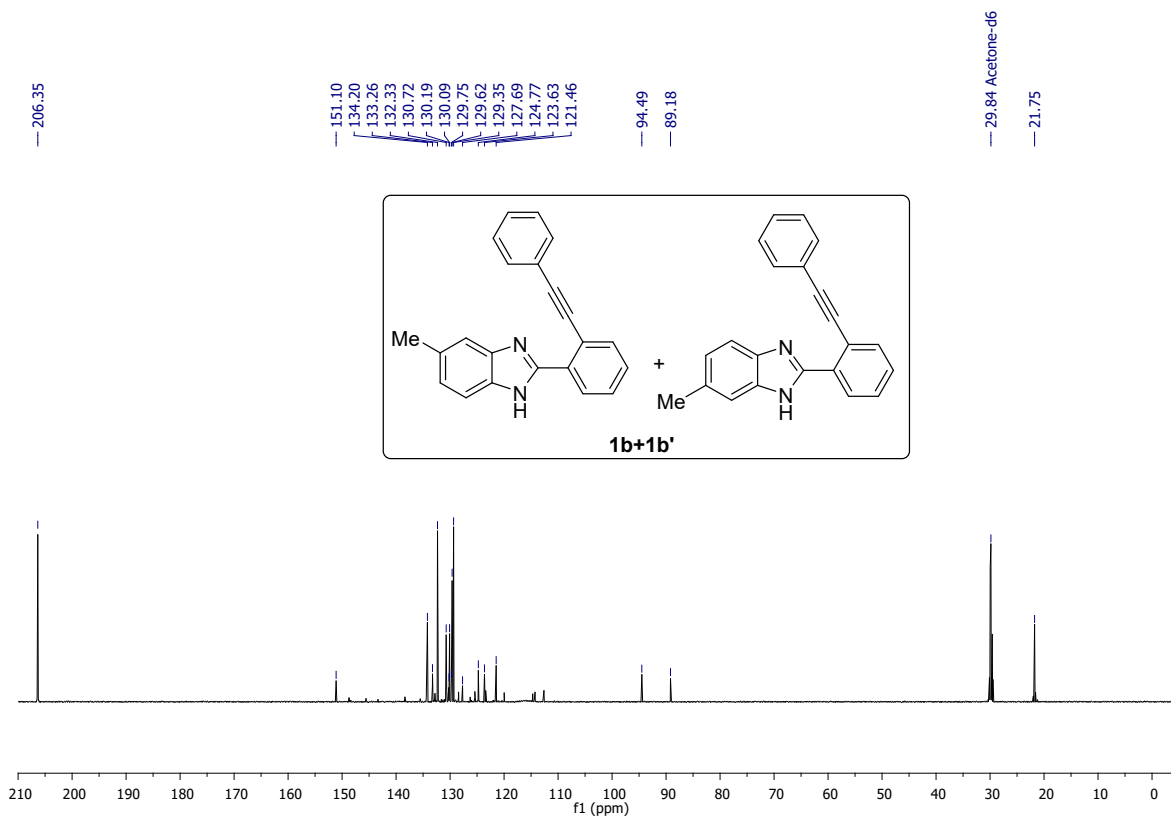
Conventional Method: A reaction was carried out with 2-(2-(phenylethynyl)phenyl)-1*H*-benzo[*d*]imidazole **1a** (74 mg, 0.25 mmol), 1,2-bis(2-bromo-4-methylphenyl)ethyne **7b** (109 mg, 0.30 mmol), Pd(OAc)₂ (5.6 mg, 10 mol%, 0.025 mmol), DPEPhos (27 mg, 20 mol%, 0.05

mmol), Cs₂CO₃ (244 mg, 0.75 mmol), and Toluene (2 mL) purged with N₂ at 140 °C for 24 h in oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether: ethyl acetate = 98:02 to 95:05) furnished the product **8ab** (49 mg, 40%) as a yellow solid.

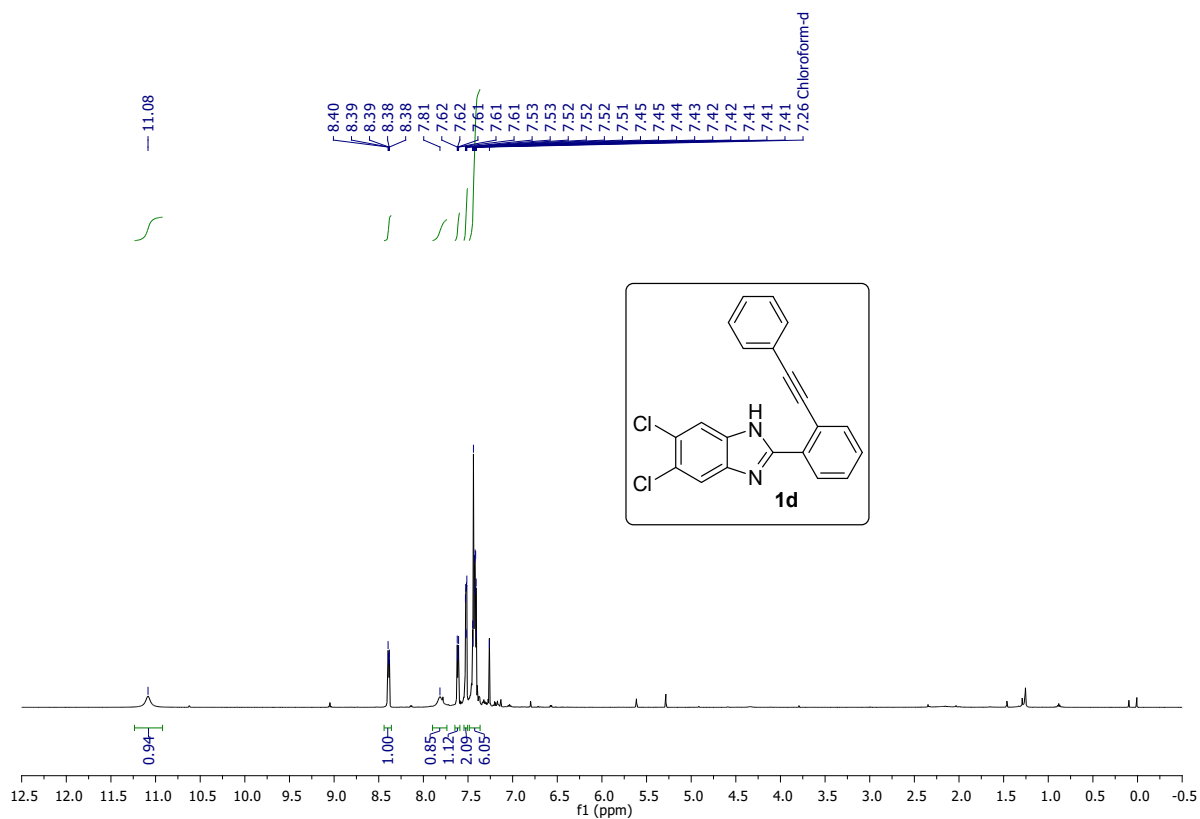
NMR spectral data:



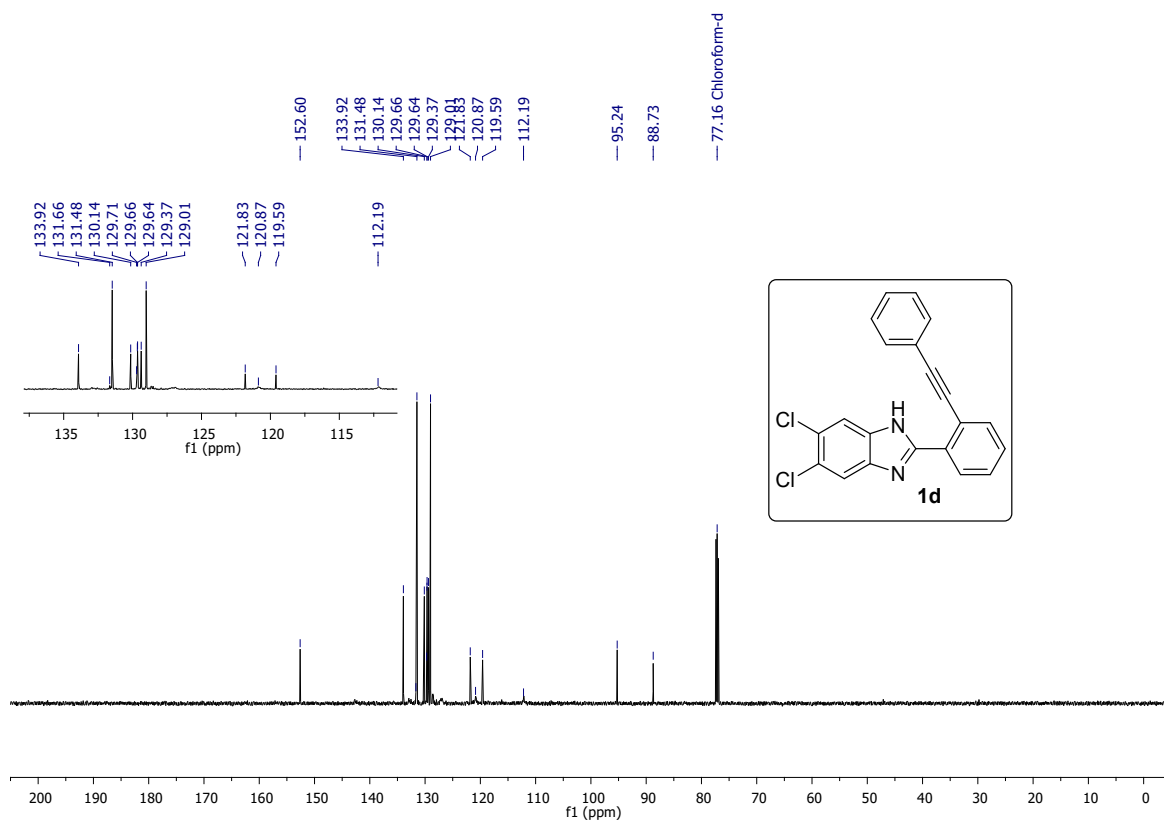
^1H NMR (600 MHz) spectrum of **1b+1b' in Acetone- d_6**



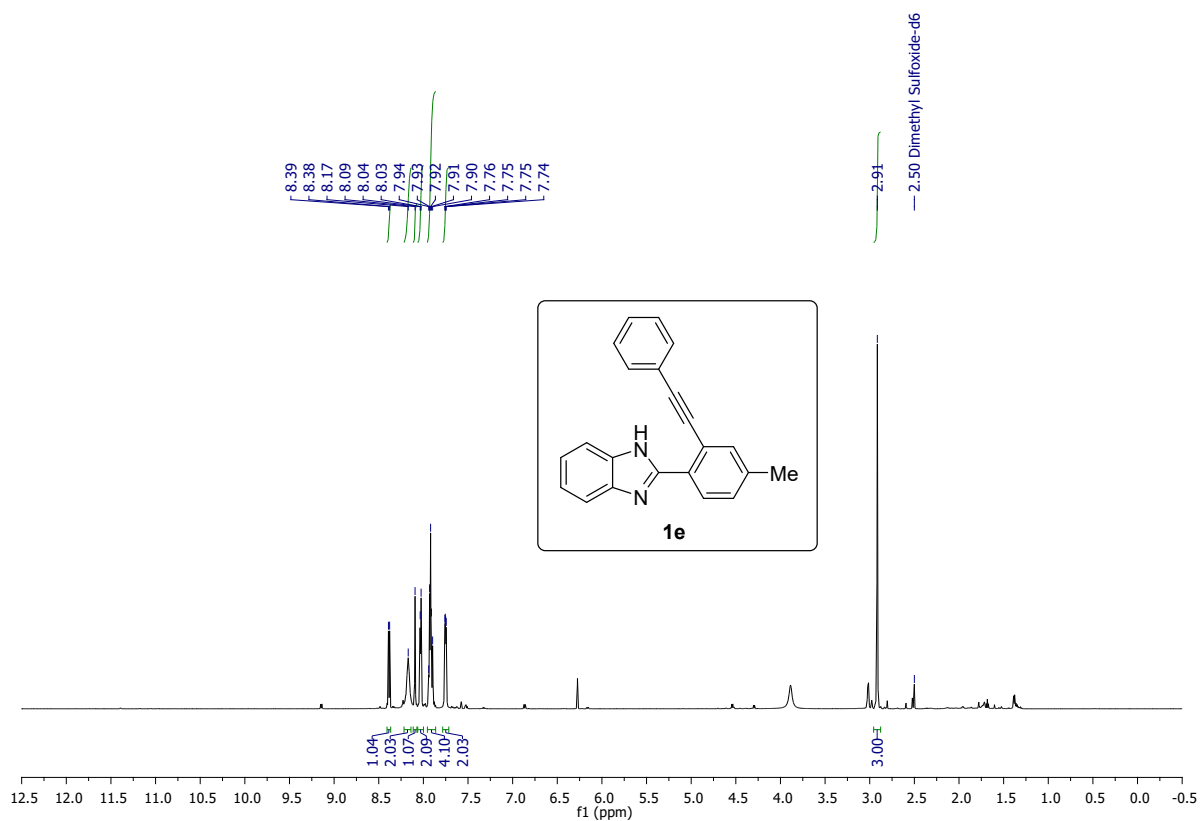
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz) spectrum of **1b+1b' in Acetone- d_6**



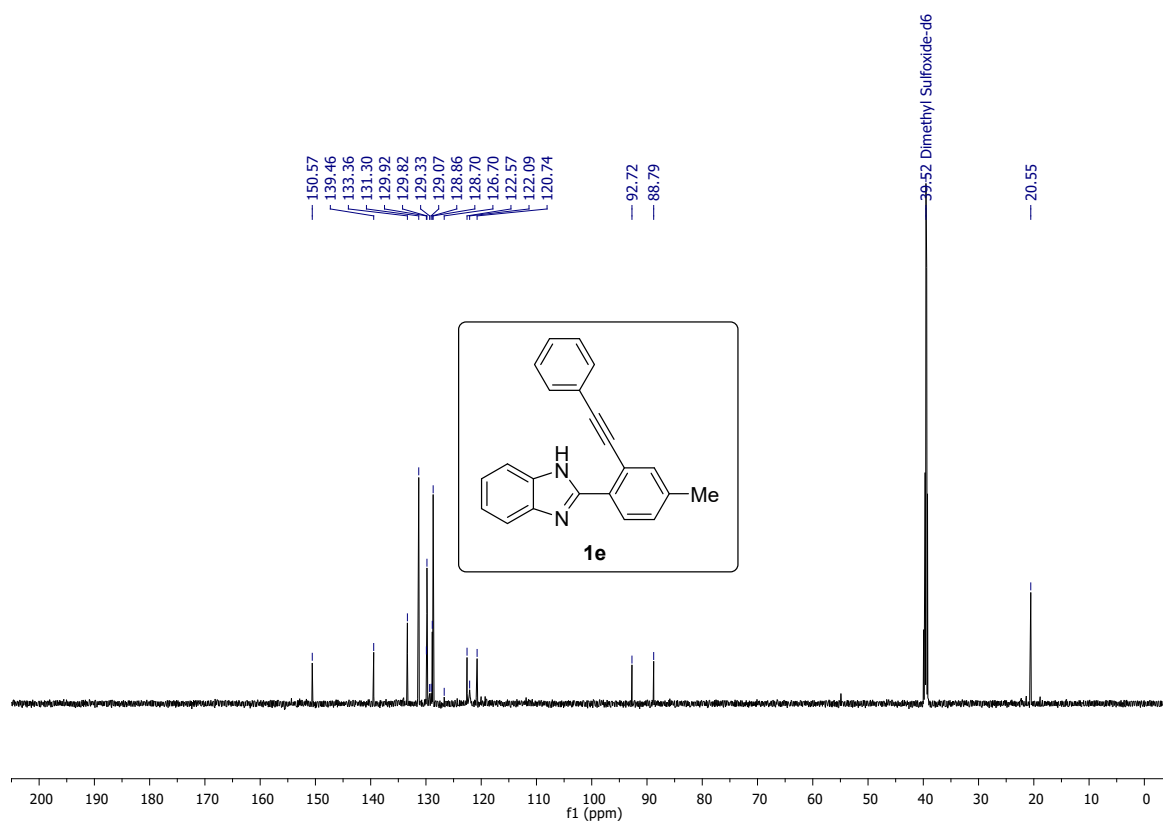
^1H NMR (600 MHz) spectrum of **1d** in CDCl_3



^{13}C { ^1H } NMR (151 MHz) spectrum of **1d** in CDCl_3

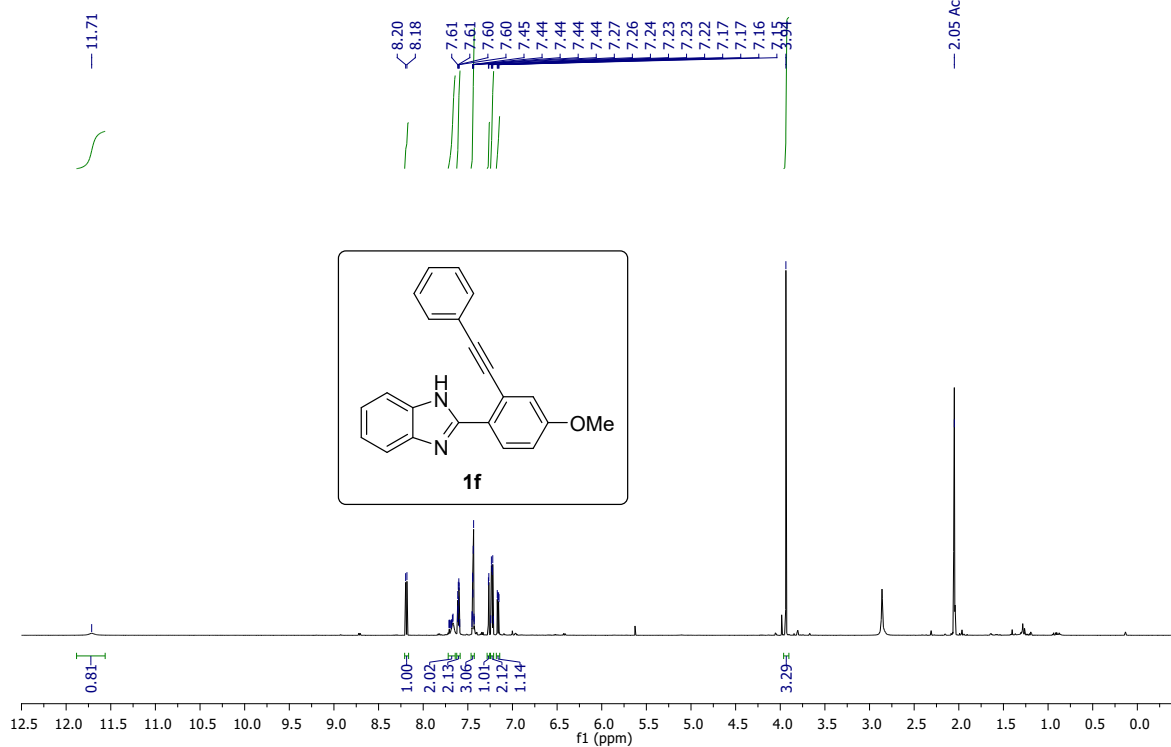


^1H NMR (600 MHz) spectrum of **1e** in $\text{DMSO-}d_6$

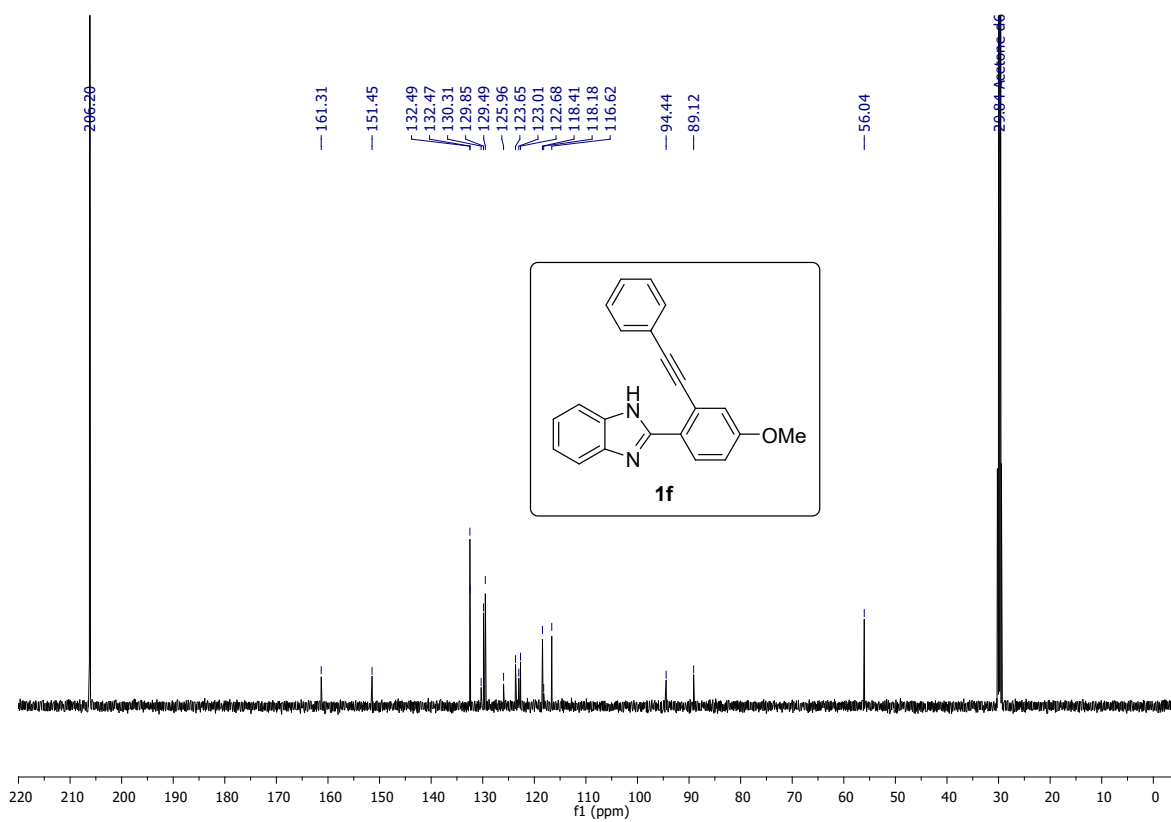


$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz) spectrum of **1e** in $\text{DMSO-}d_6$

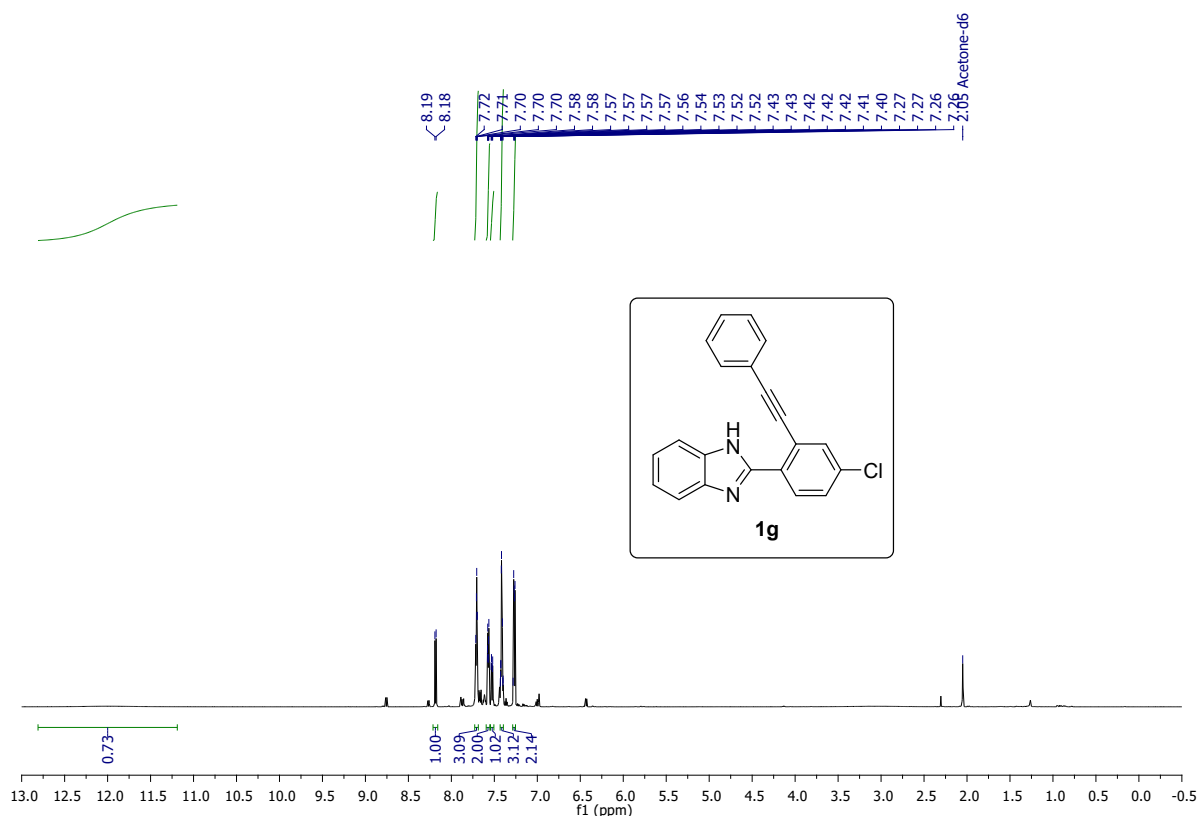
GS-JN-3-ISM3
GS-JN-3-ISM3-1H



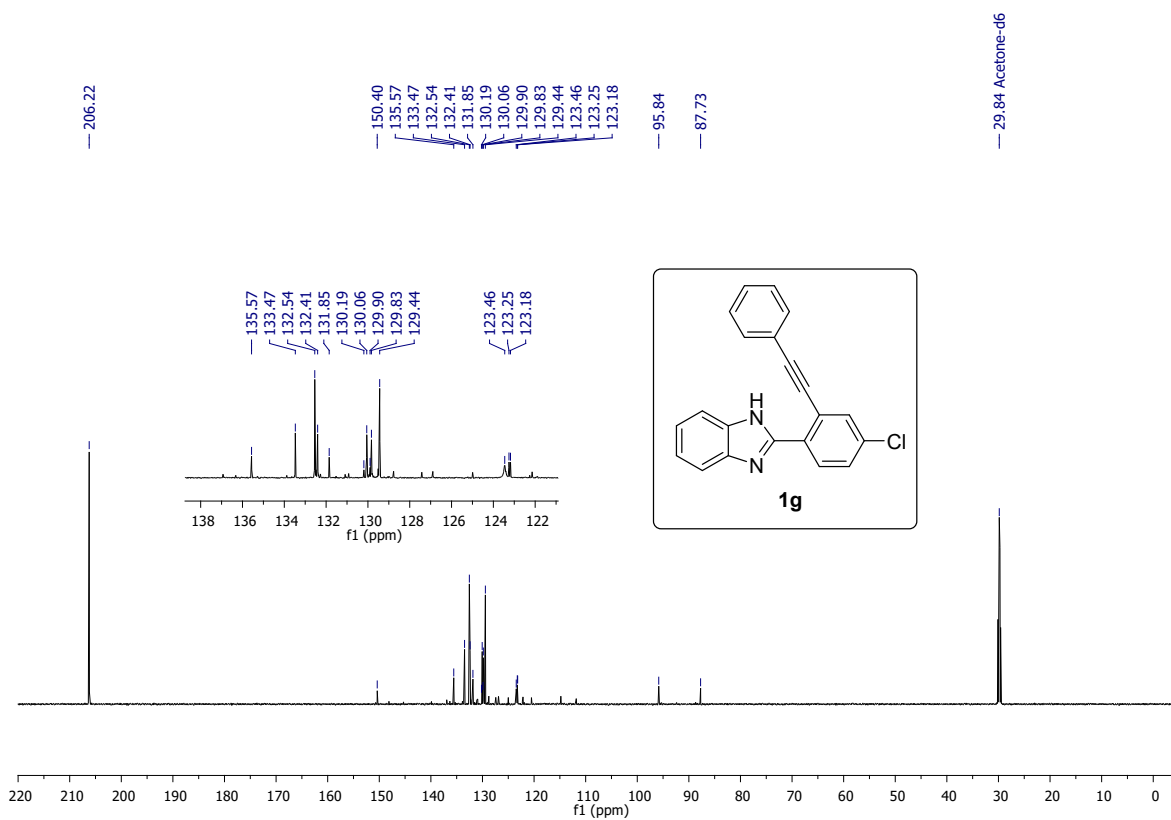
^1H NMR (600 MHz) spectrum of **1f** in Acetone- d_6



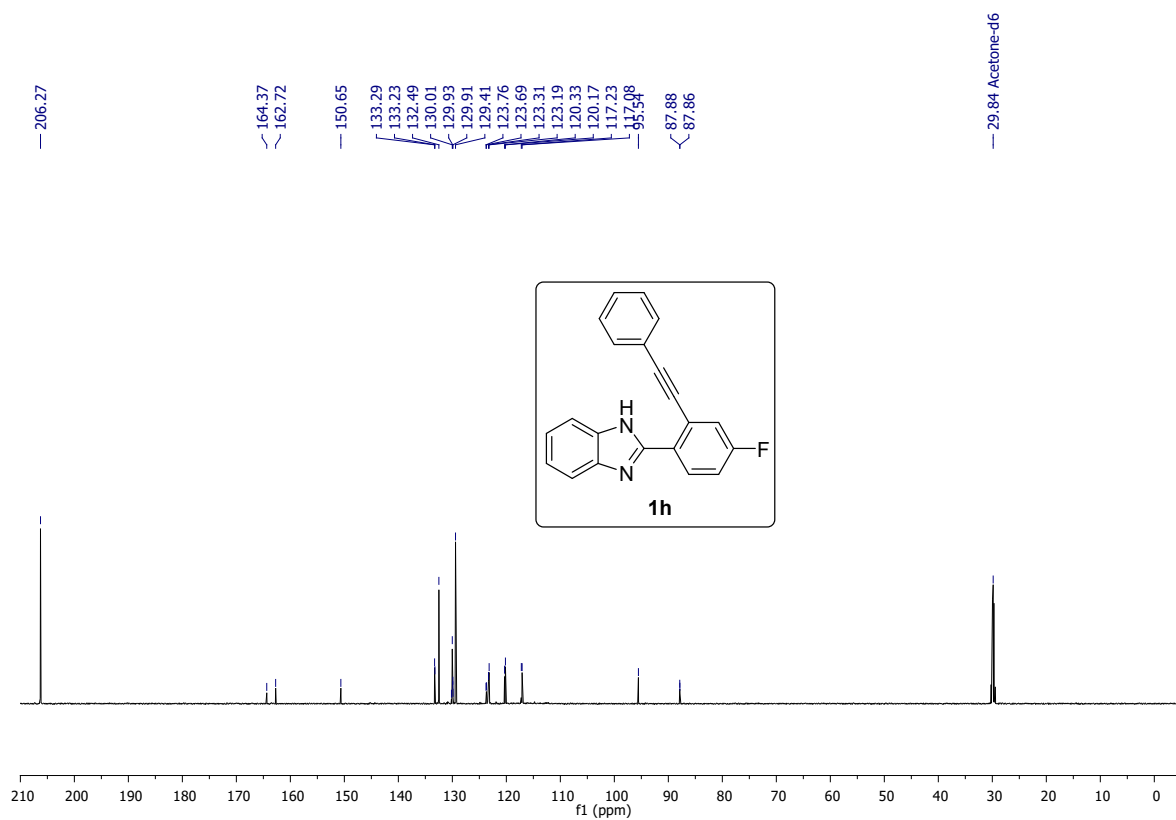
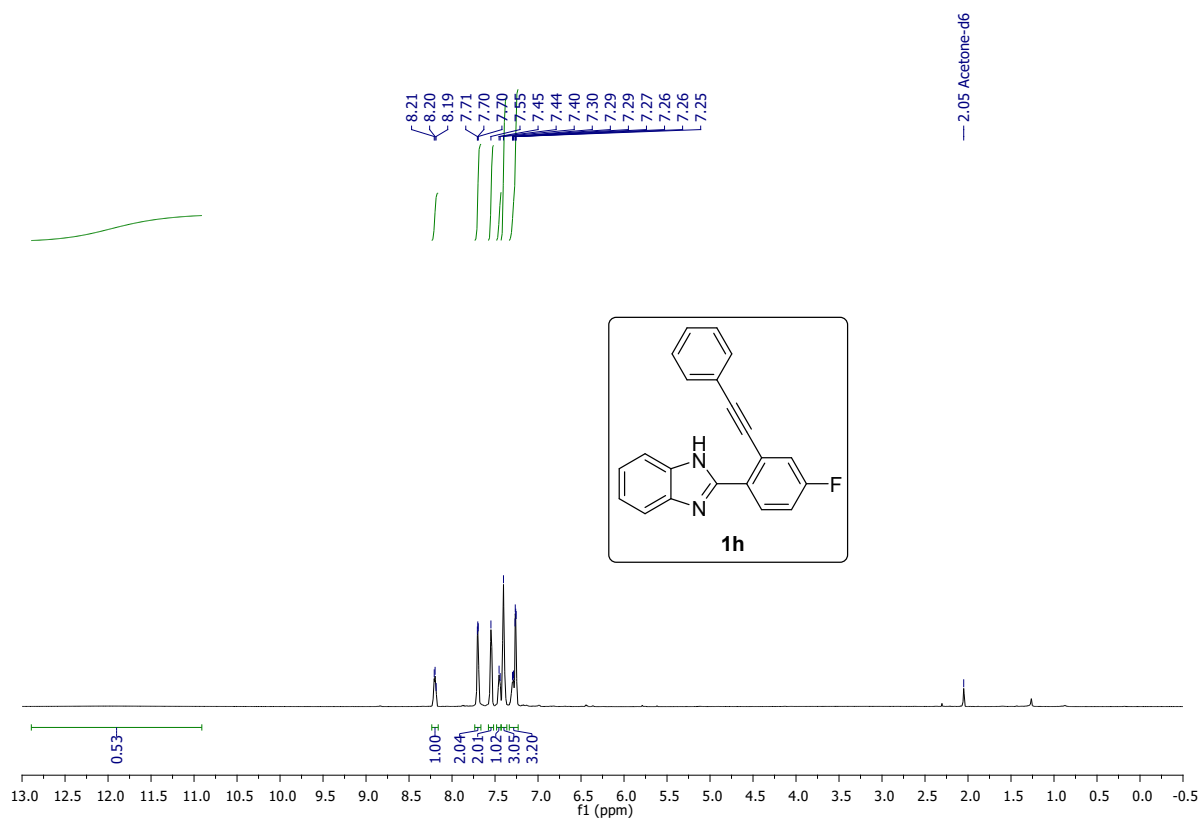
^{13}C NMR (151 MHz) spectrum of **1f** in Acetone- d_6

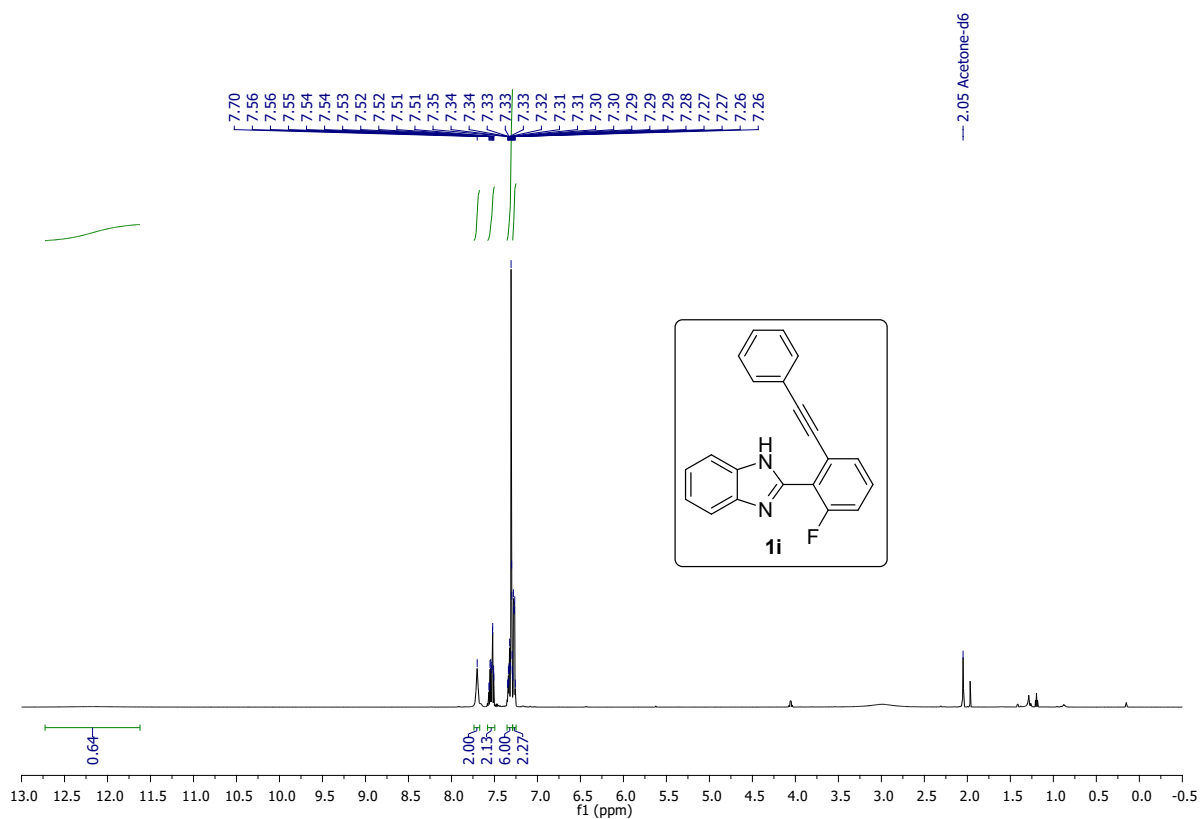


¹H NMR (600 MHz) spectrum of **1g in Acetone-*d*₆**

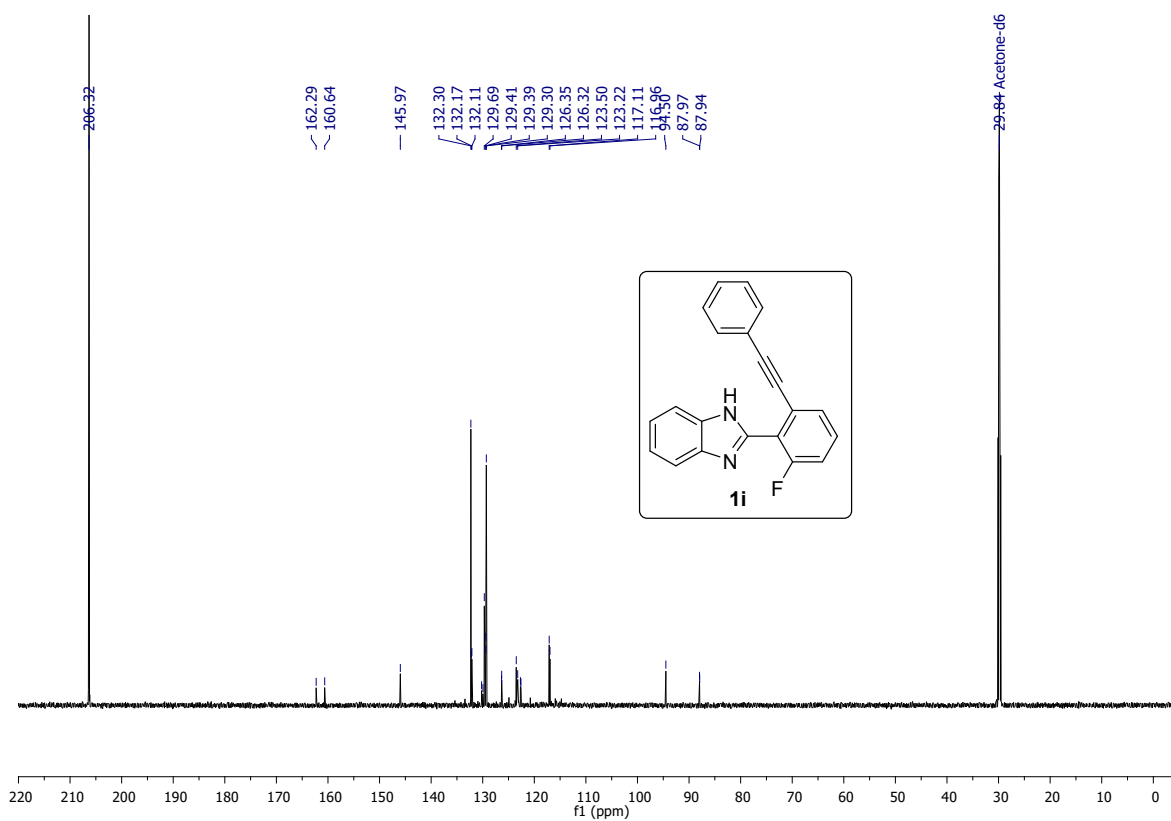


¹³C{¹H} NMR (151 MHz) spectrum of **1g in Acetone-*d*₆**

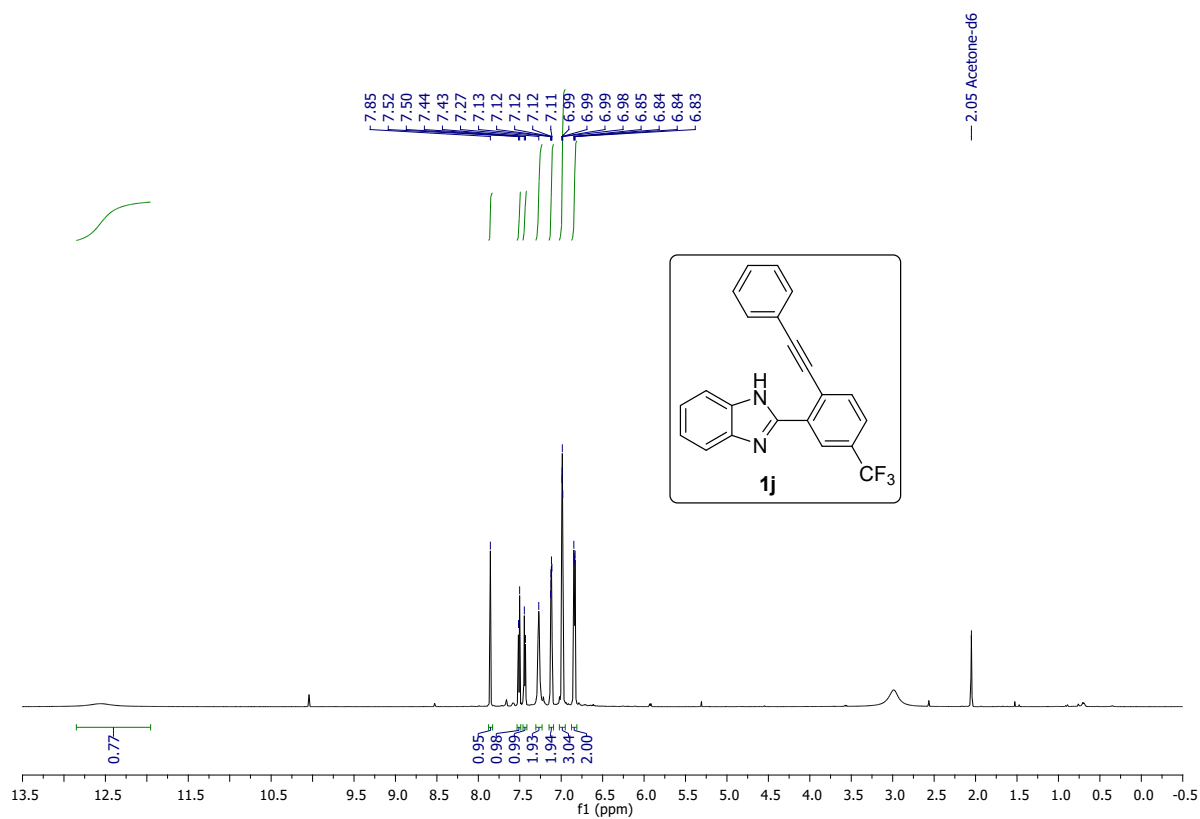




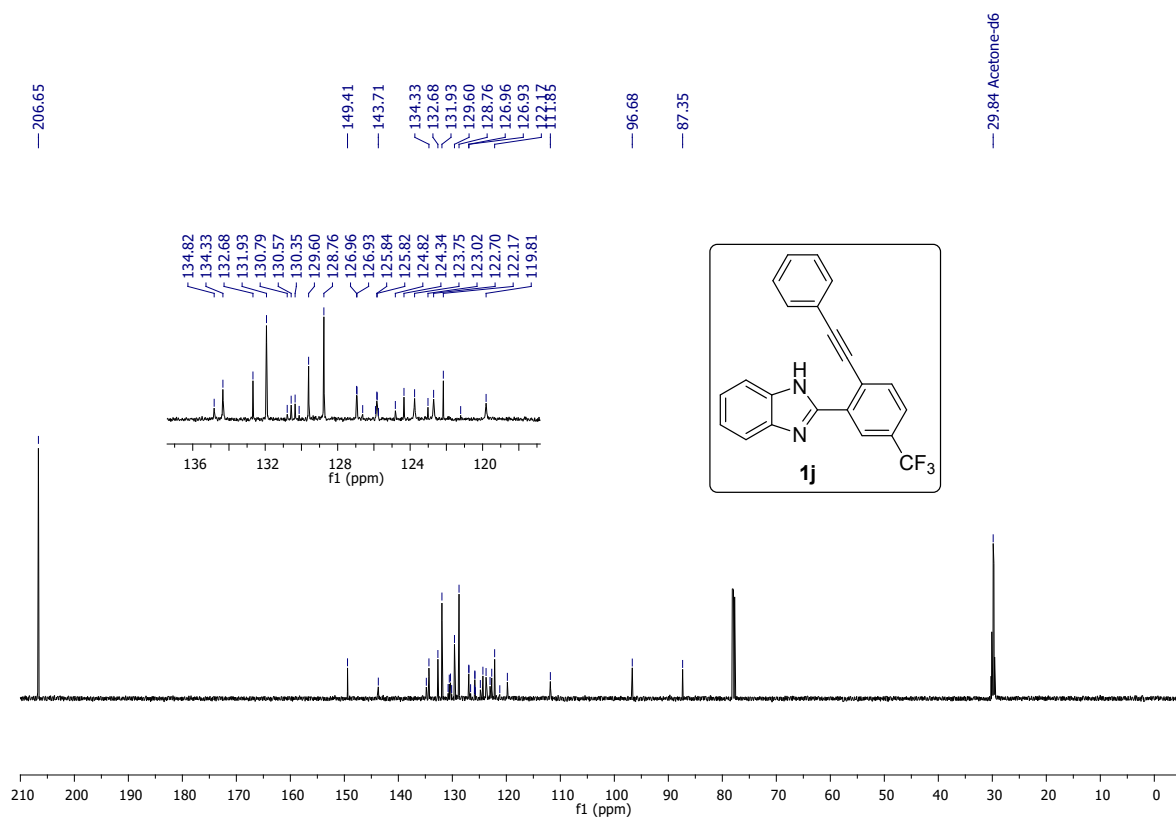
^1H NMR (600 MHz) spectrum of **1i** in Acetone- d_6



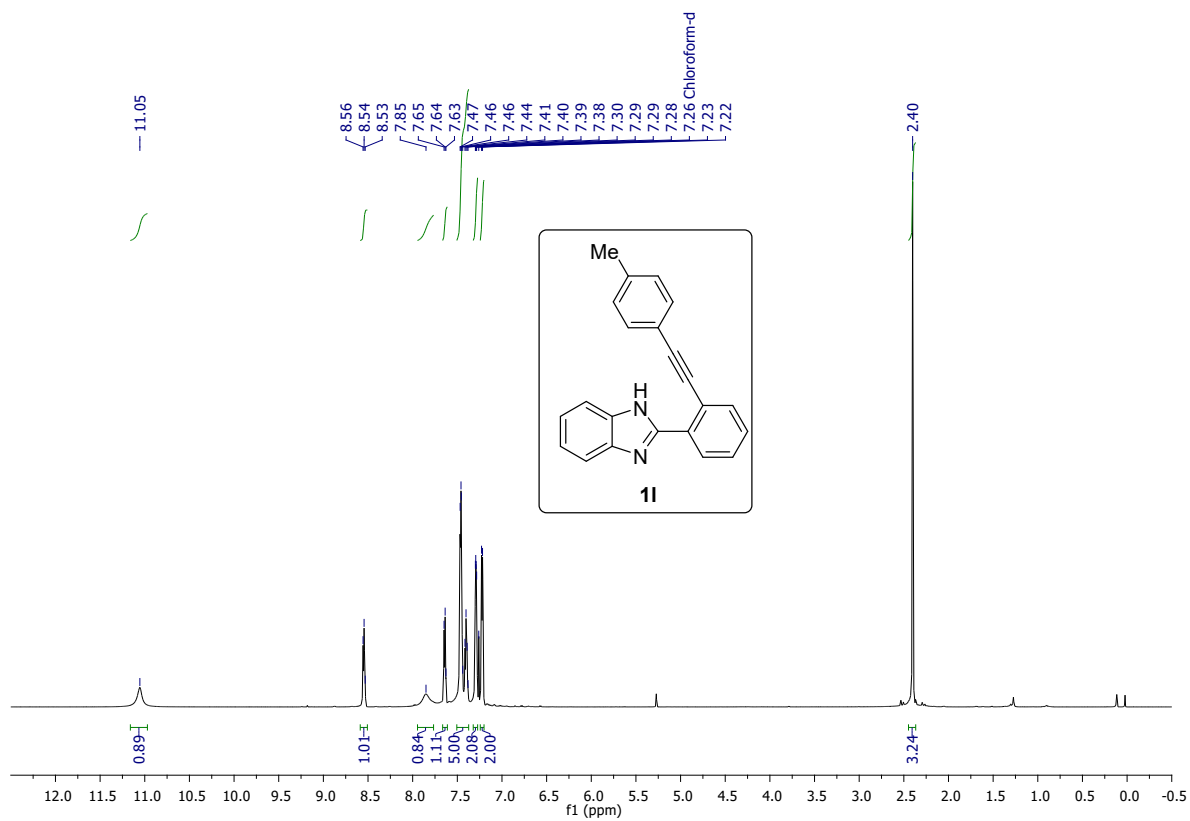
^{13}C { ^1H } NMR (151 MHz) spectrum of **1i** in Acetone- d_6



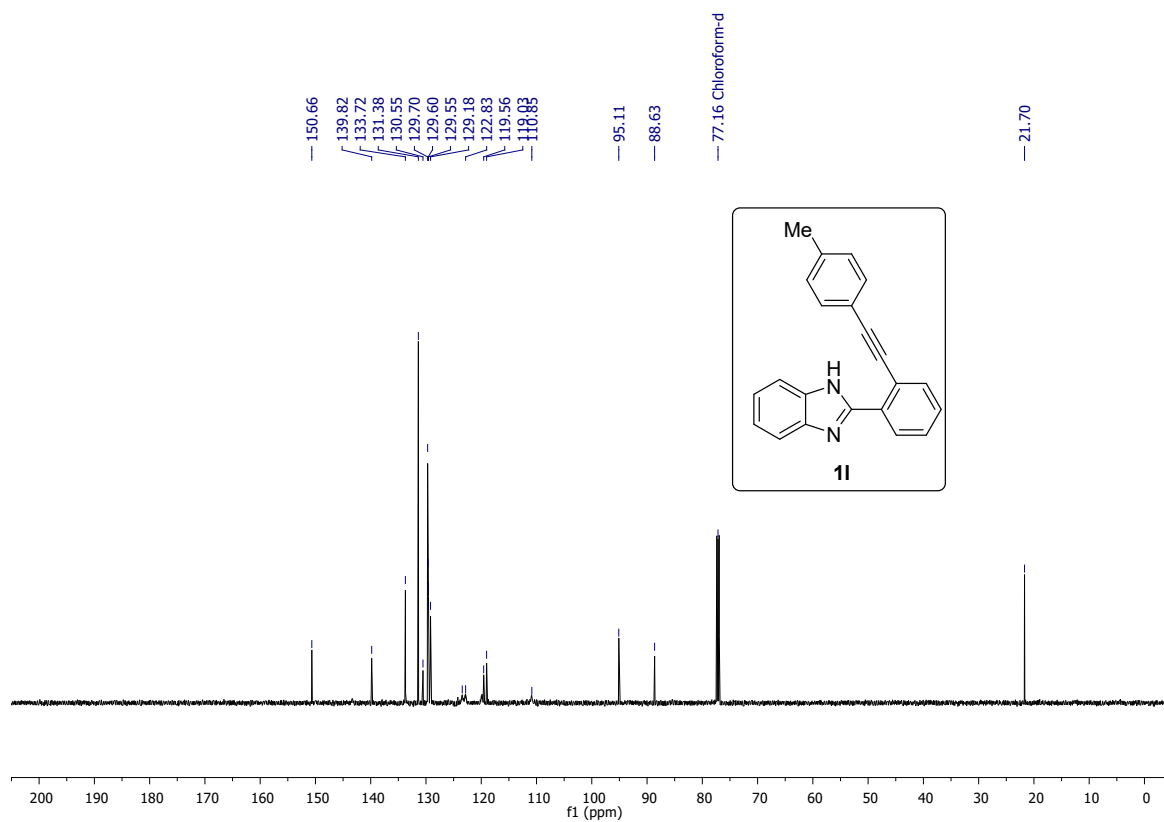
¹H NMR (600 MHz) spectrum of **1j** in CDCl₃ & Acetone-*d*₆



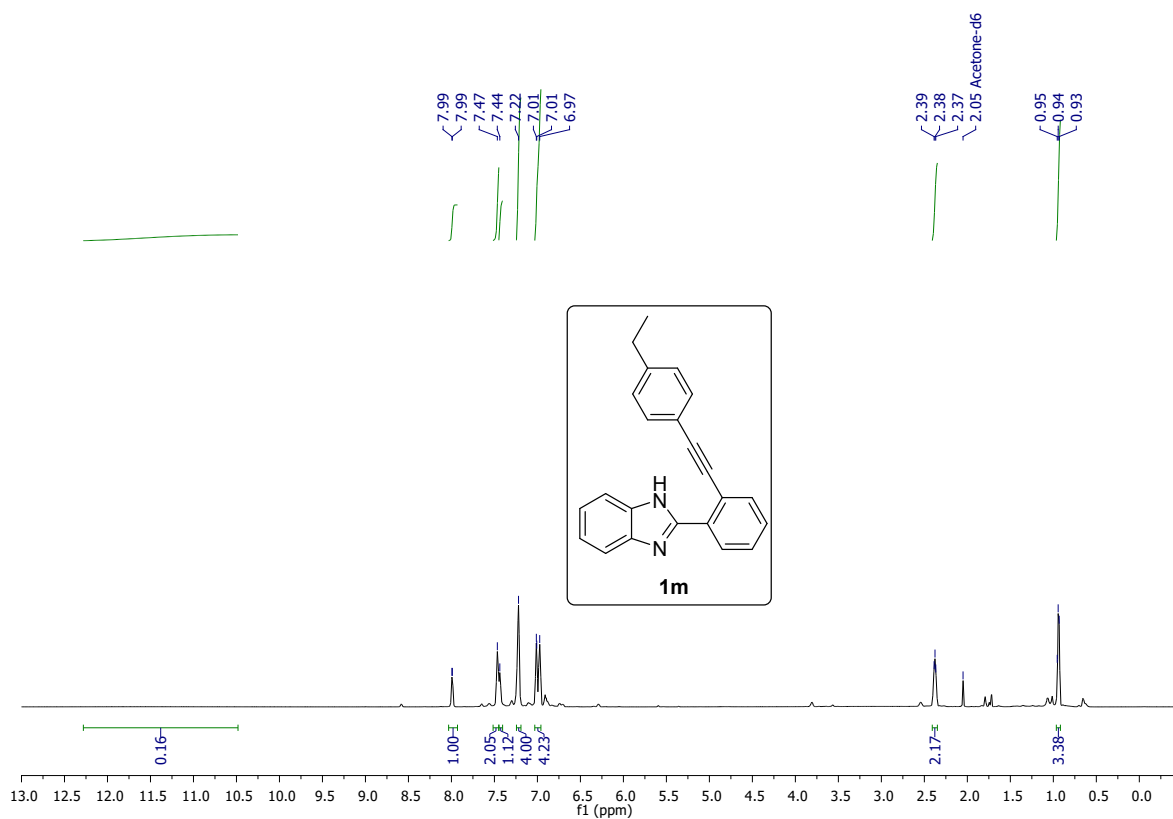
¹³C{¹H} NMR (151 MHz) spectrum of **1j** in CDCl₃ & Acetone-*d*₆



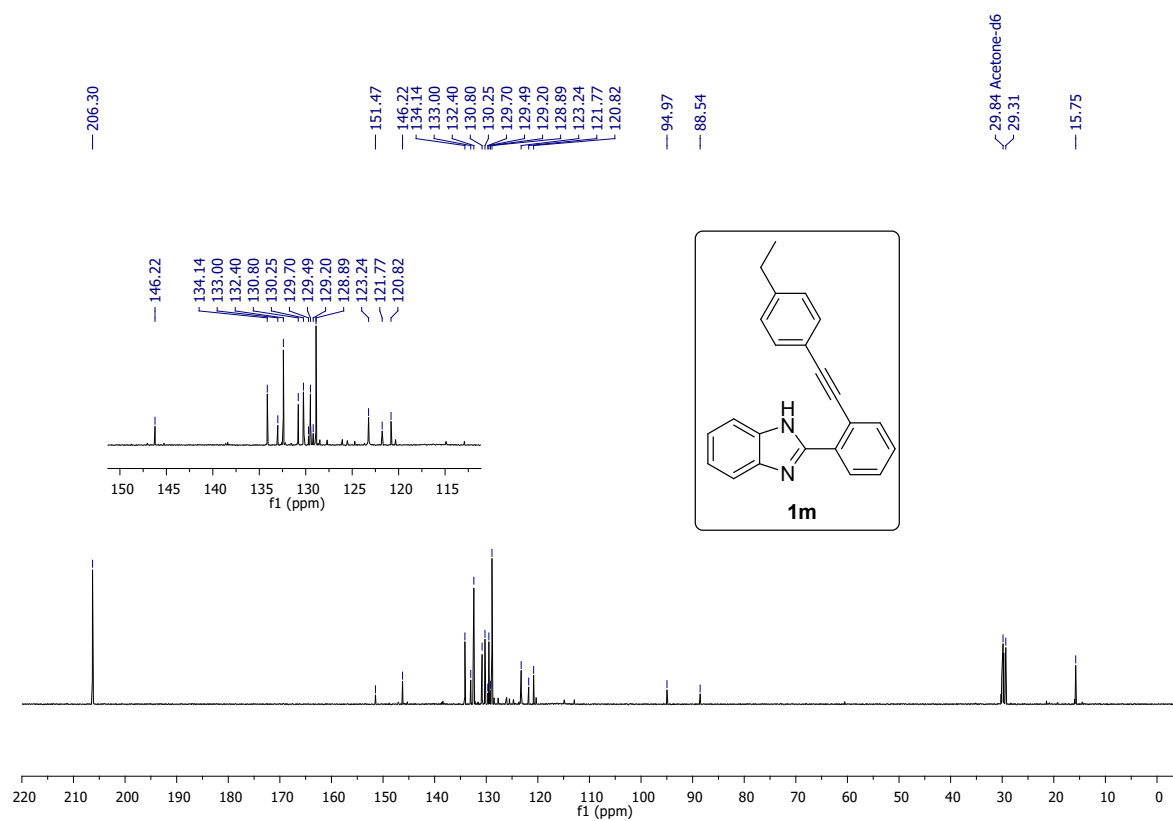
^1H NMR (600 MHz) spectrum of **1I** in CDCl_3



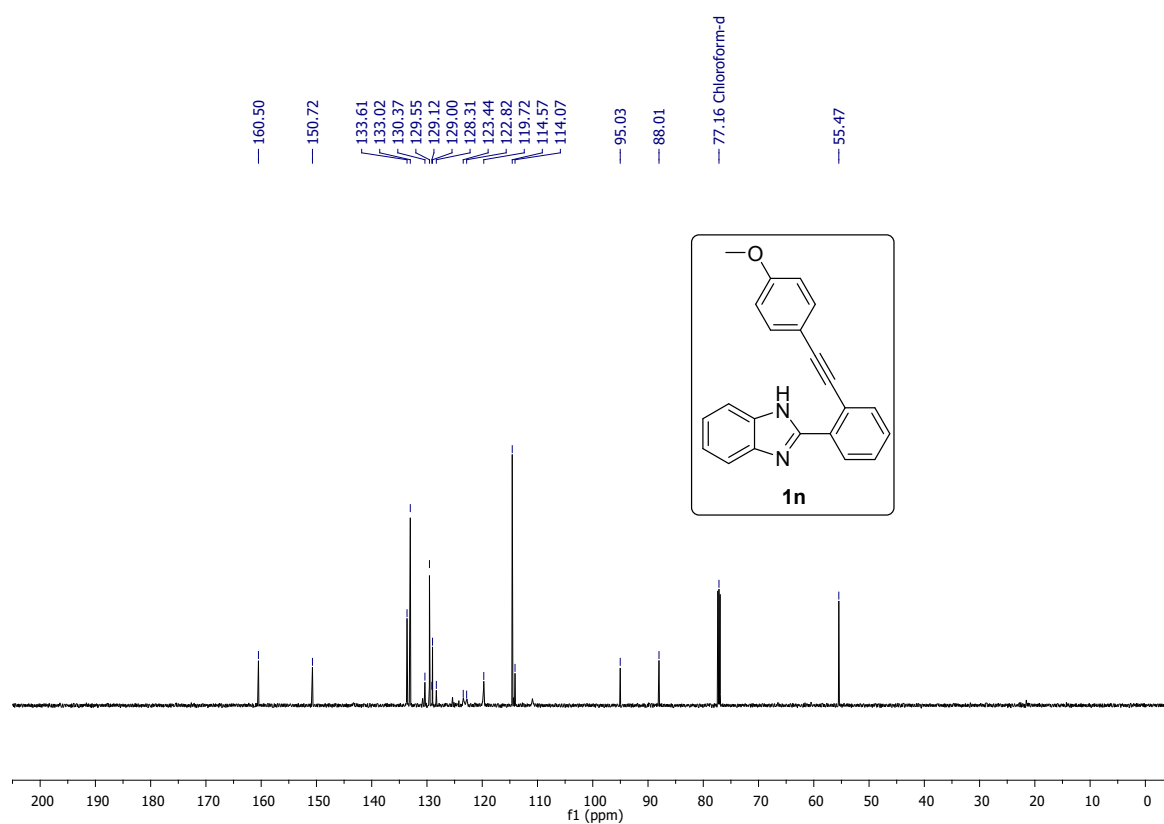
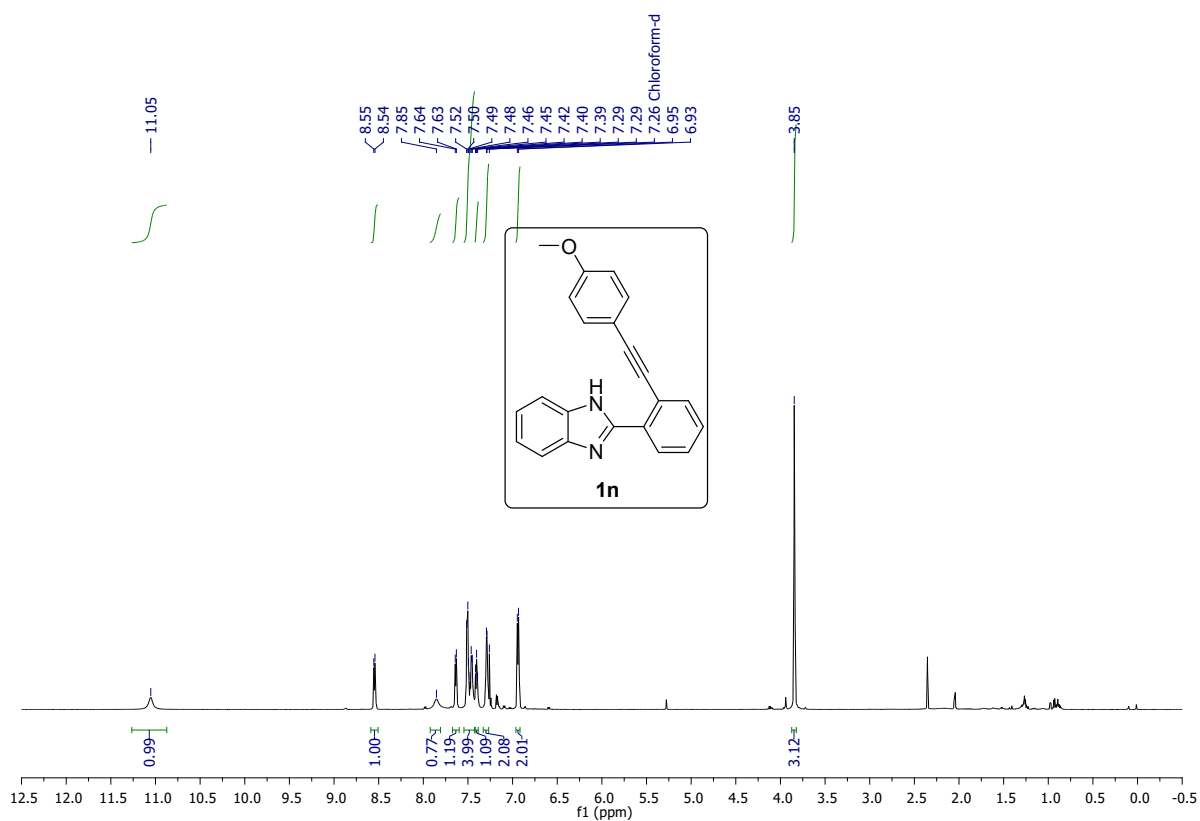
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz) spectrum of **1I** in CDCl_3

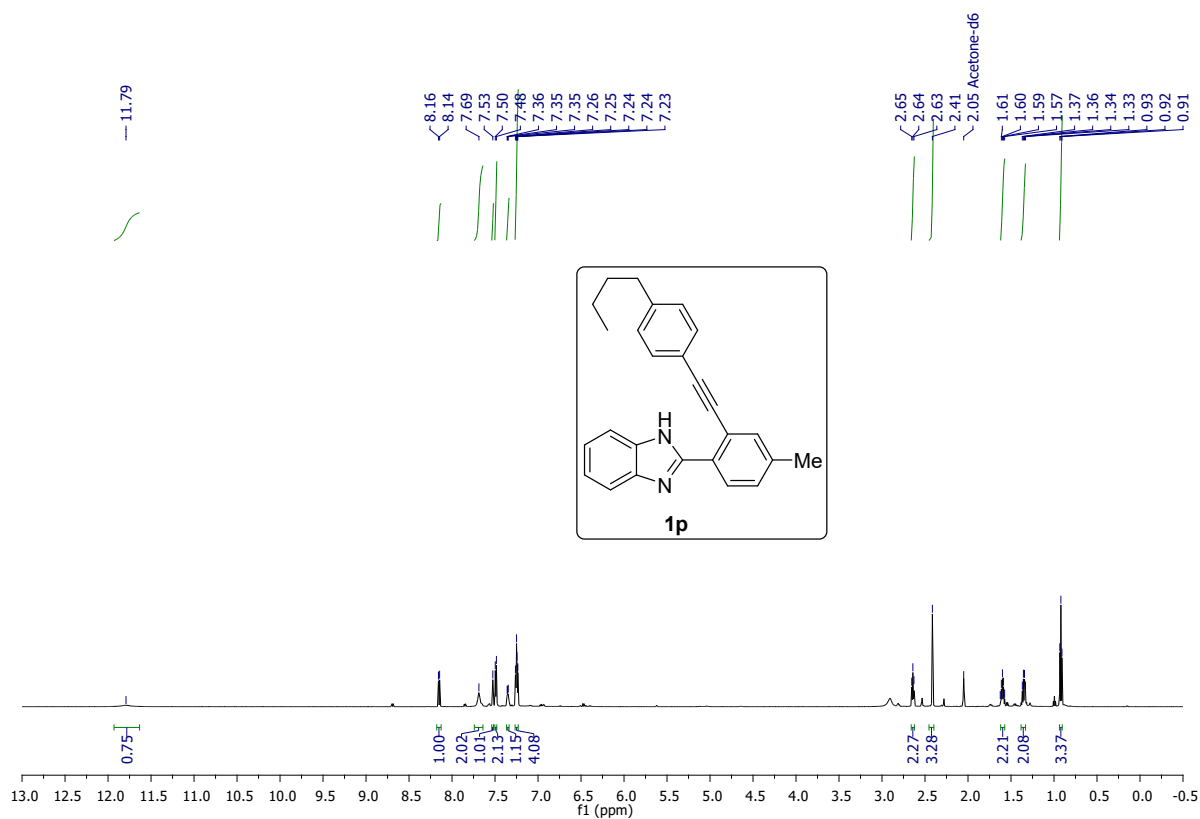


¹H NMR (600 MHz) spectrum of **1m in CDCl₃**

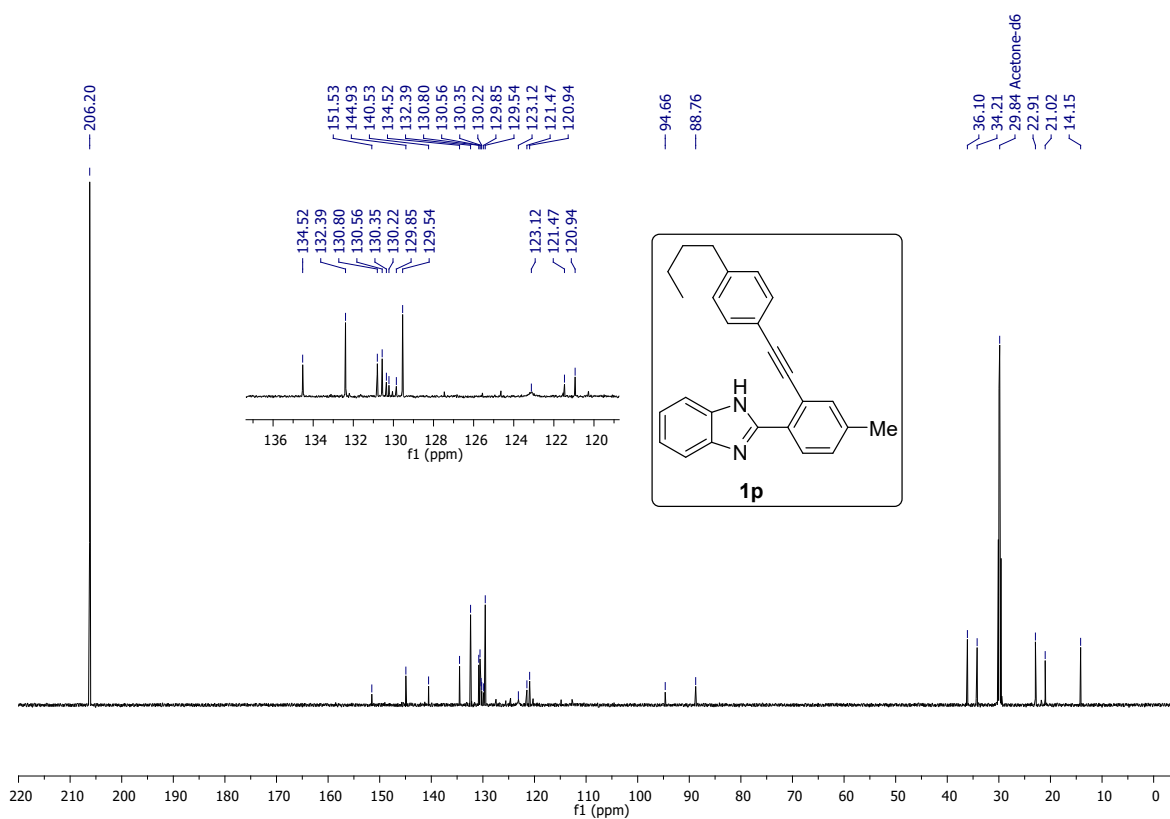


¹³C{¹H} NMR (151 MHz) spectrum of **1m in CDCl₃**

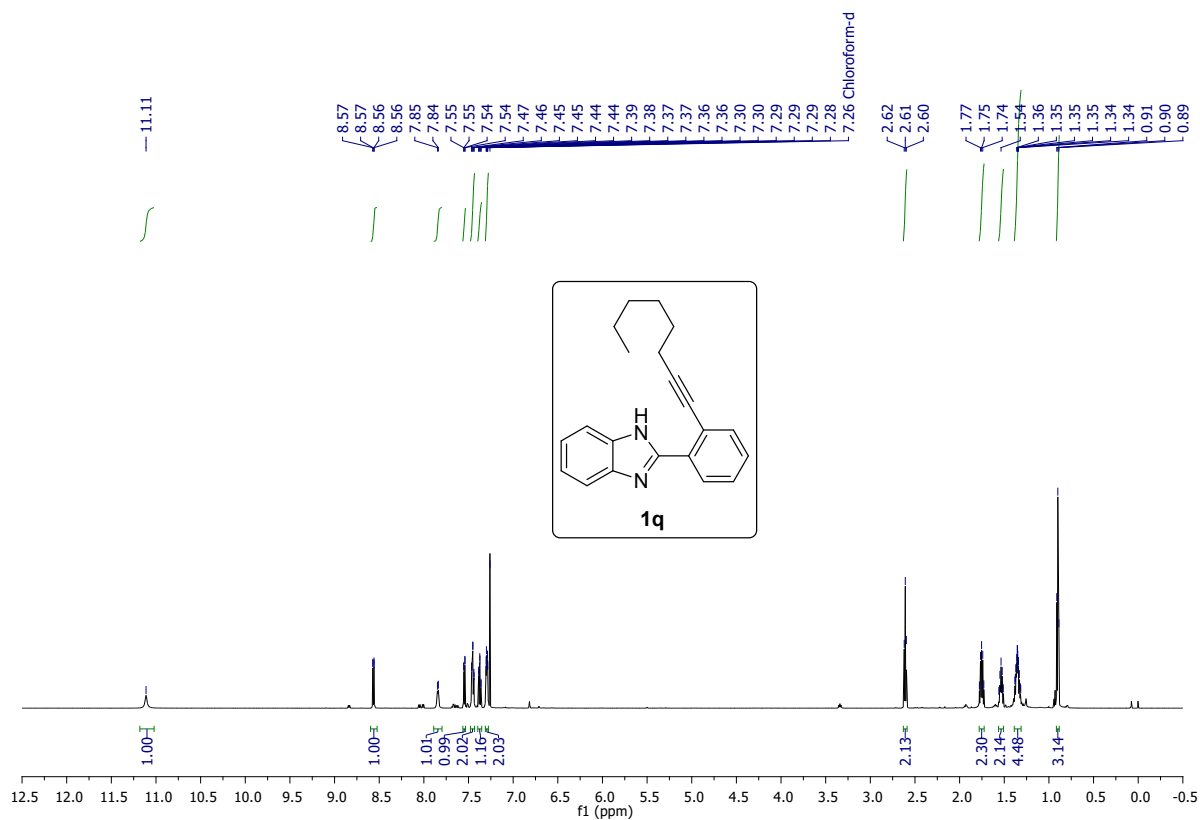




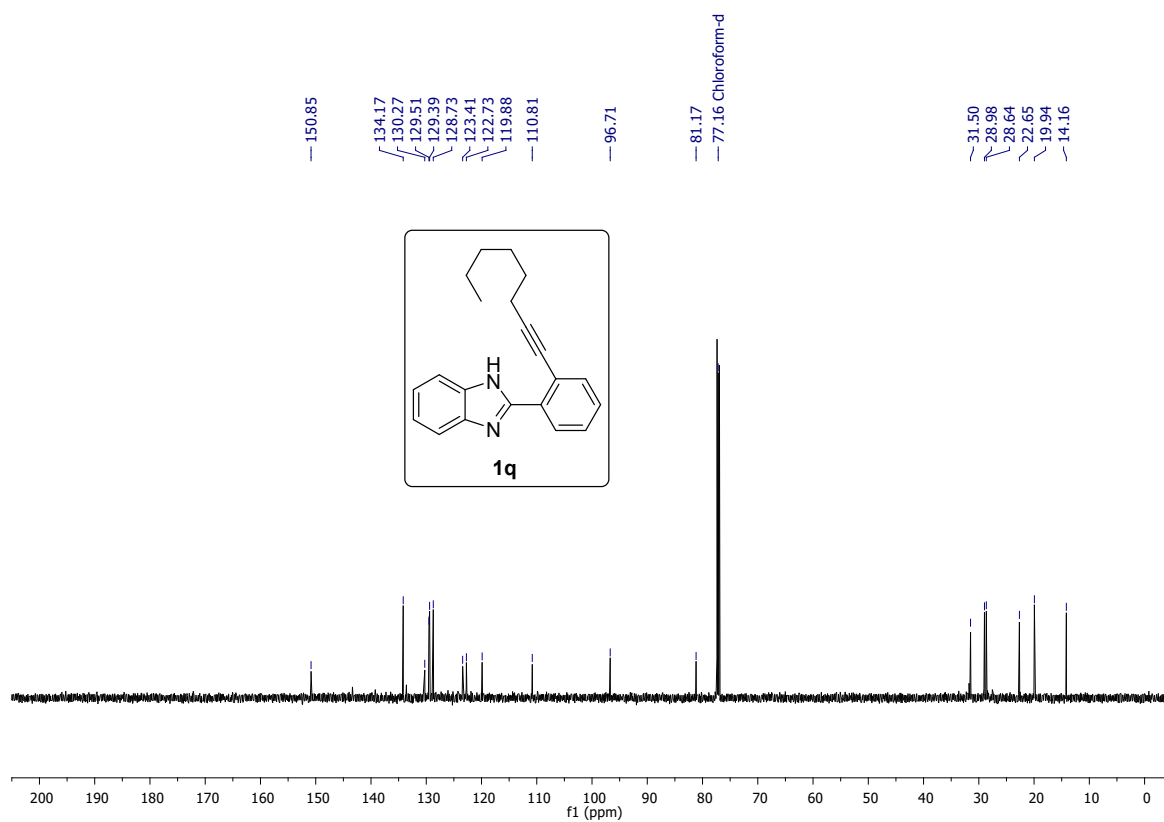
¹H NMR (600 MHz) spectrum of **1p in Acetone-*d*₆**



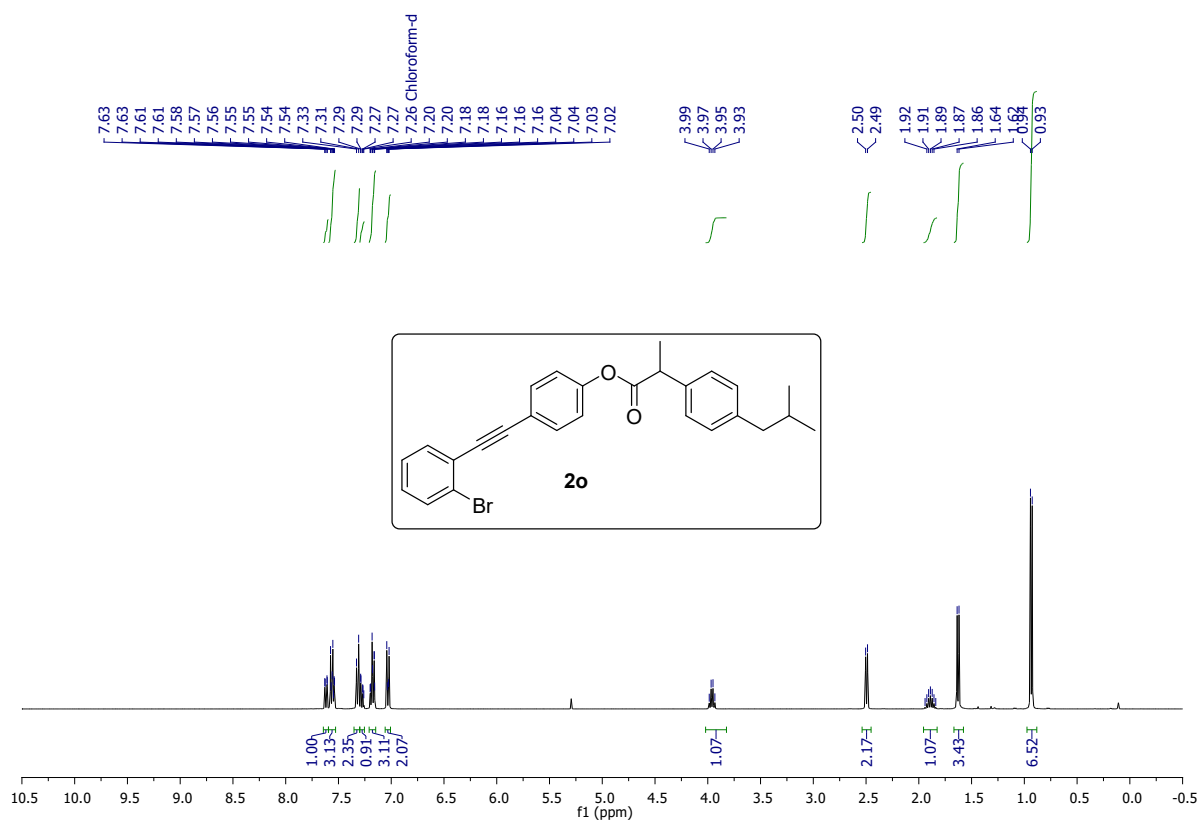
¹³C{¹H} NMR (151 MHz) spectrum of **1p in Acetone-*d*₆**



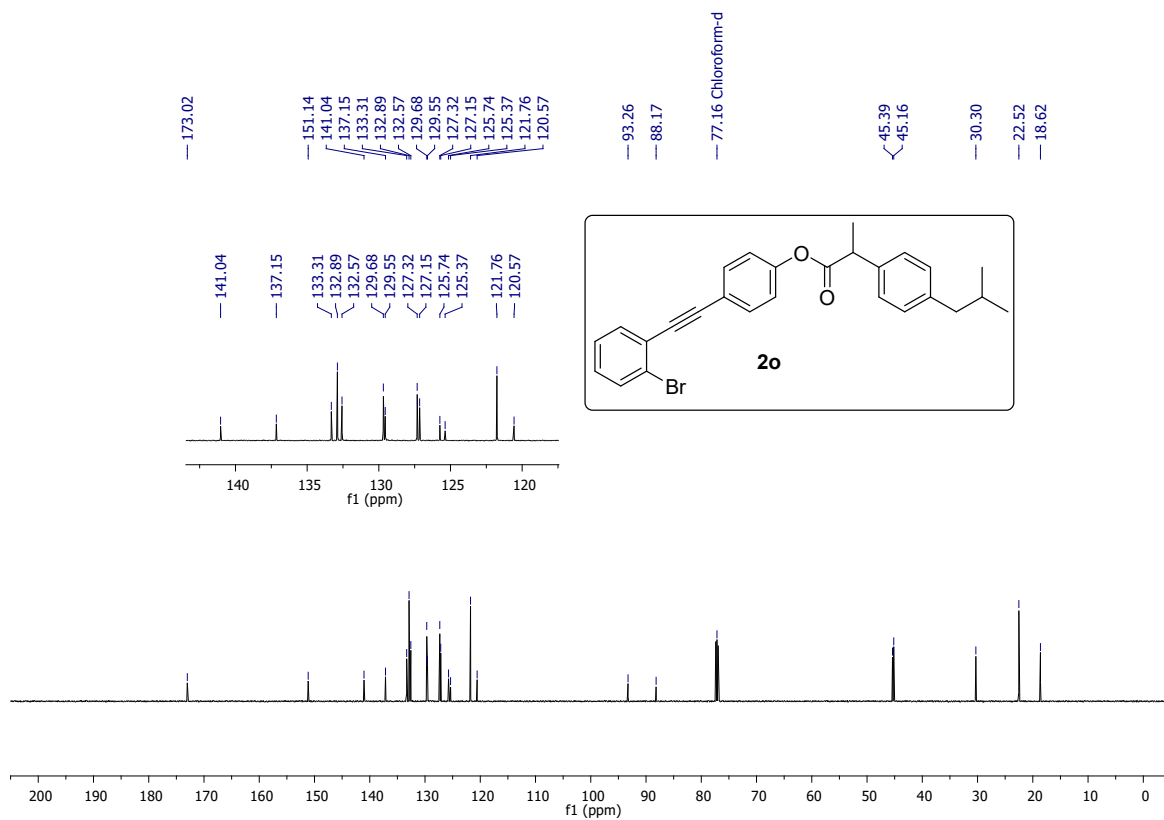
¹H NMR (600 MHz) spectrum of **1q in CDCl₃**



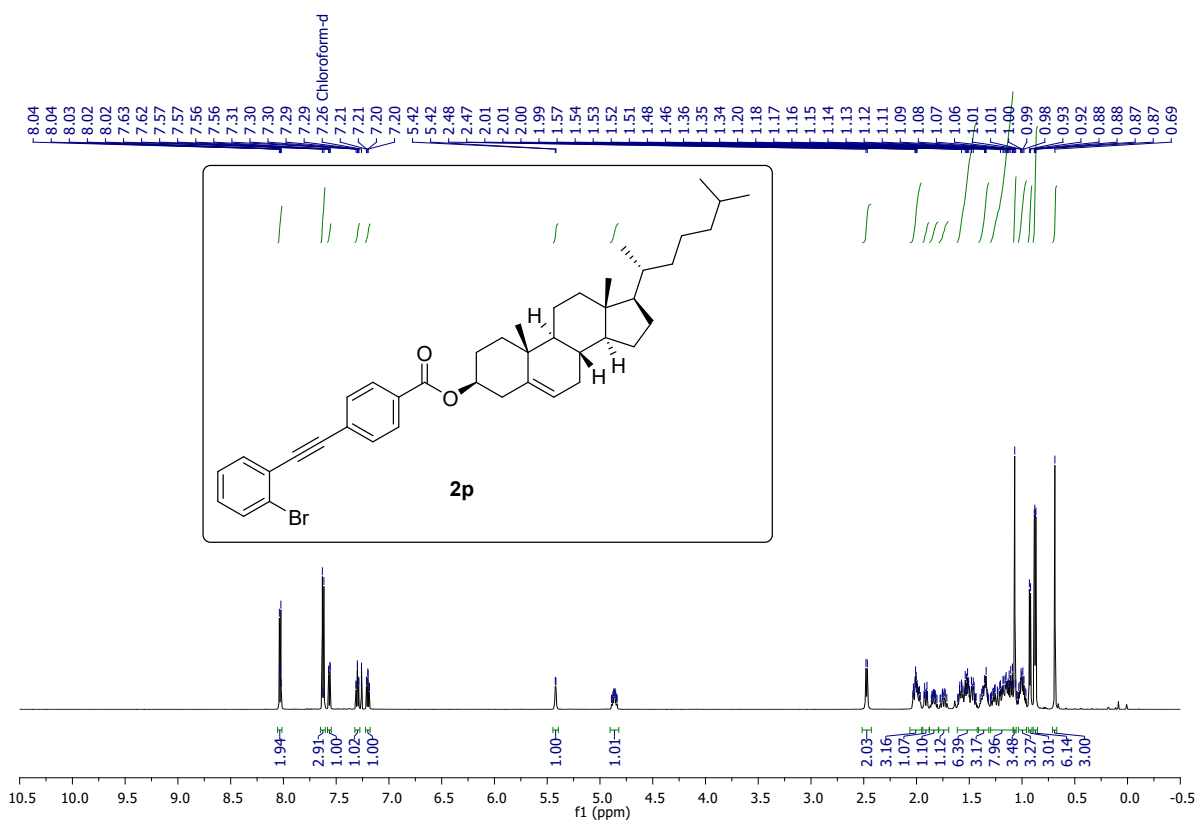
¹³C {¹H} NMR (151 MHz) spectrum of **1q in CDCl₃**



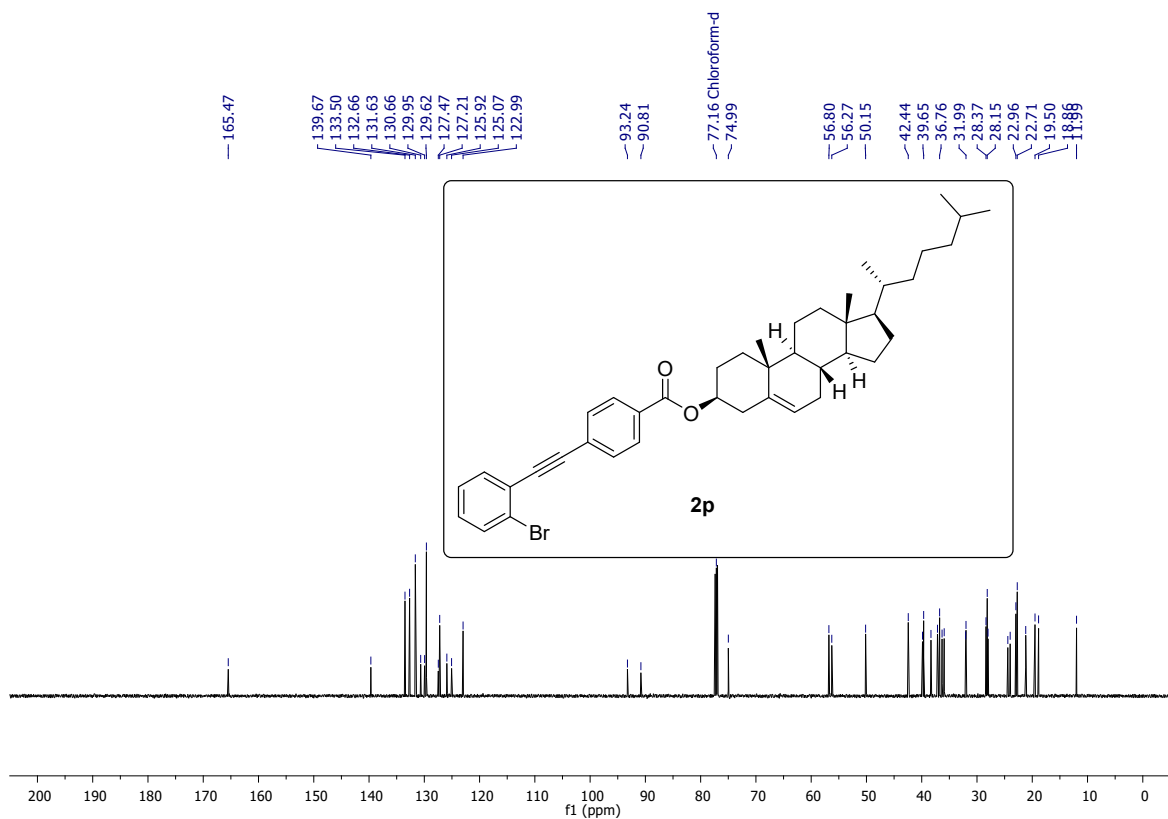
¹H NMR (400 MHz) spectrum of **2o in CDCl₃**



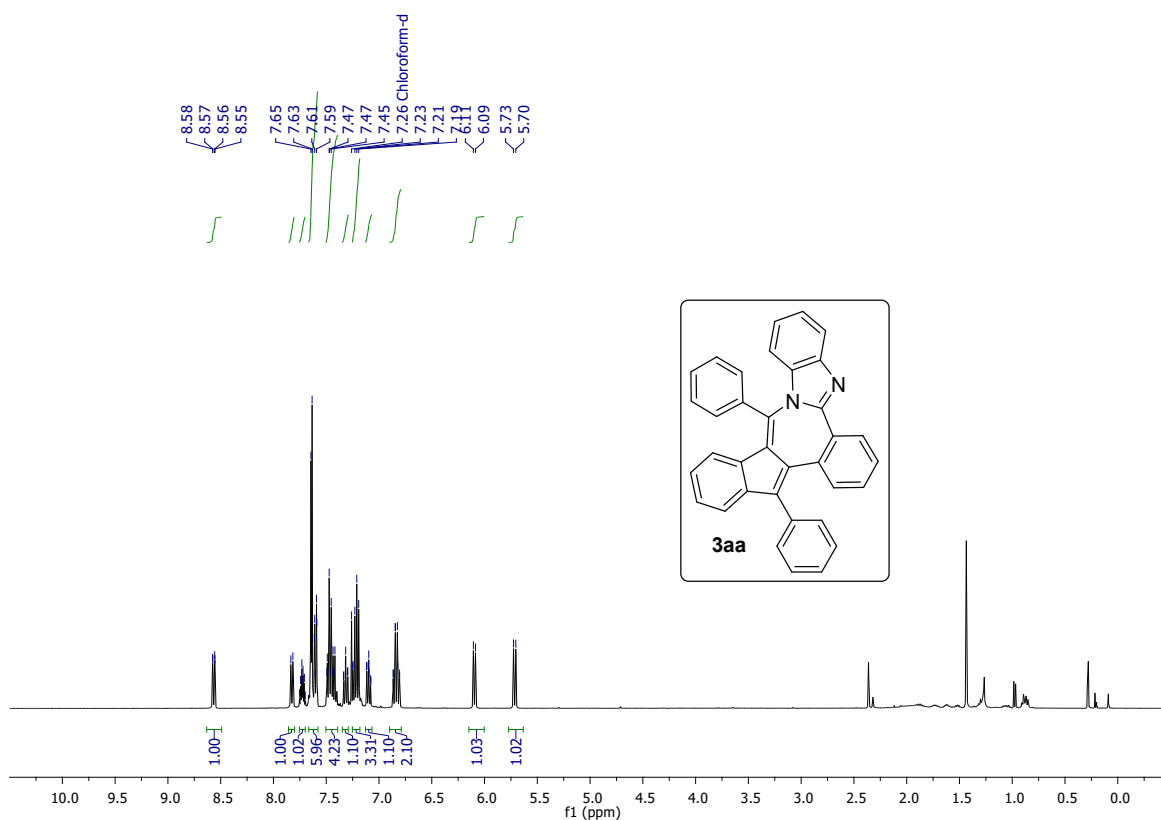
¹³C {¹H} NMR (151 MHz) spectrum of **2o in CDCl₃**



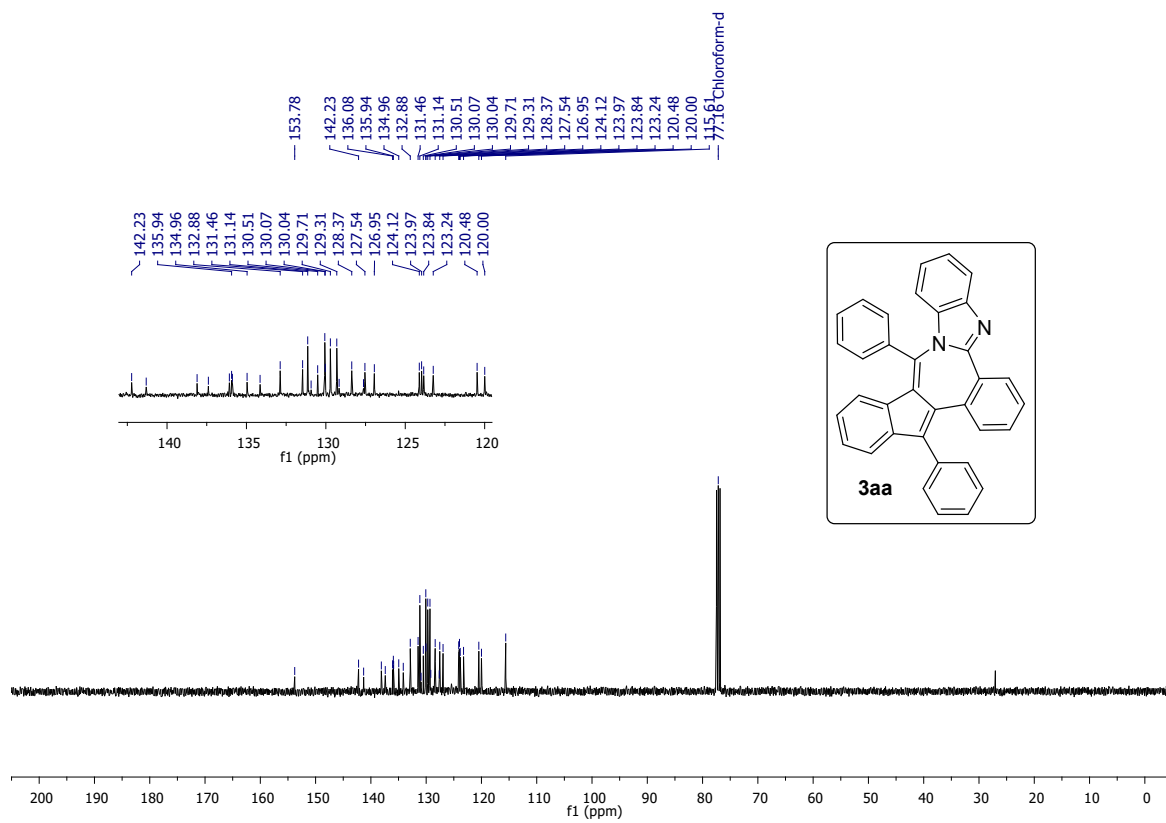
¹H NMR (600 MHz) spectrum of 2p in CDCl₃



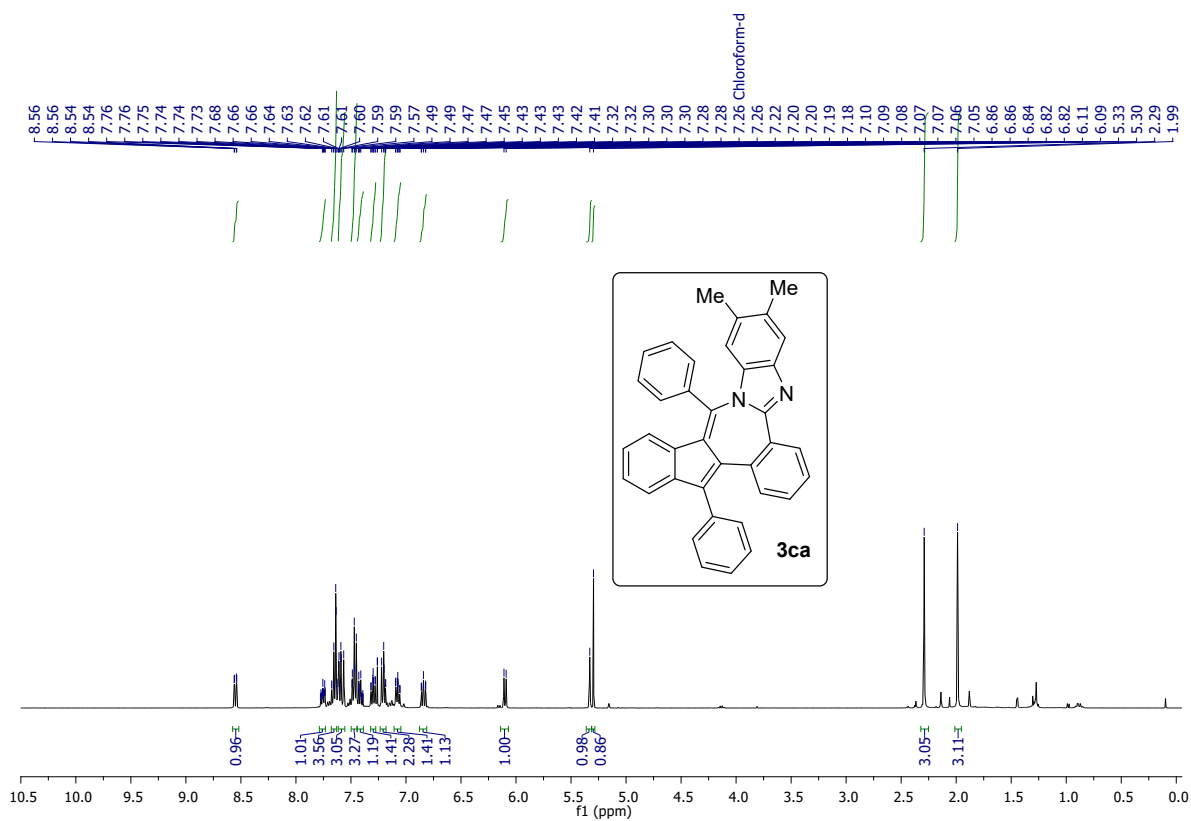
¹³C NMR (151 MHz) spectrum of 2p in CDCl₃



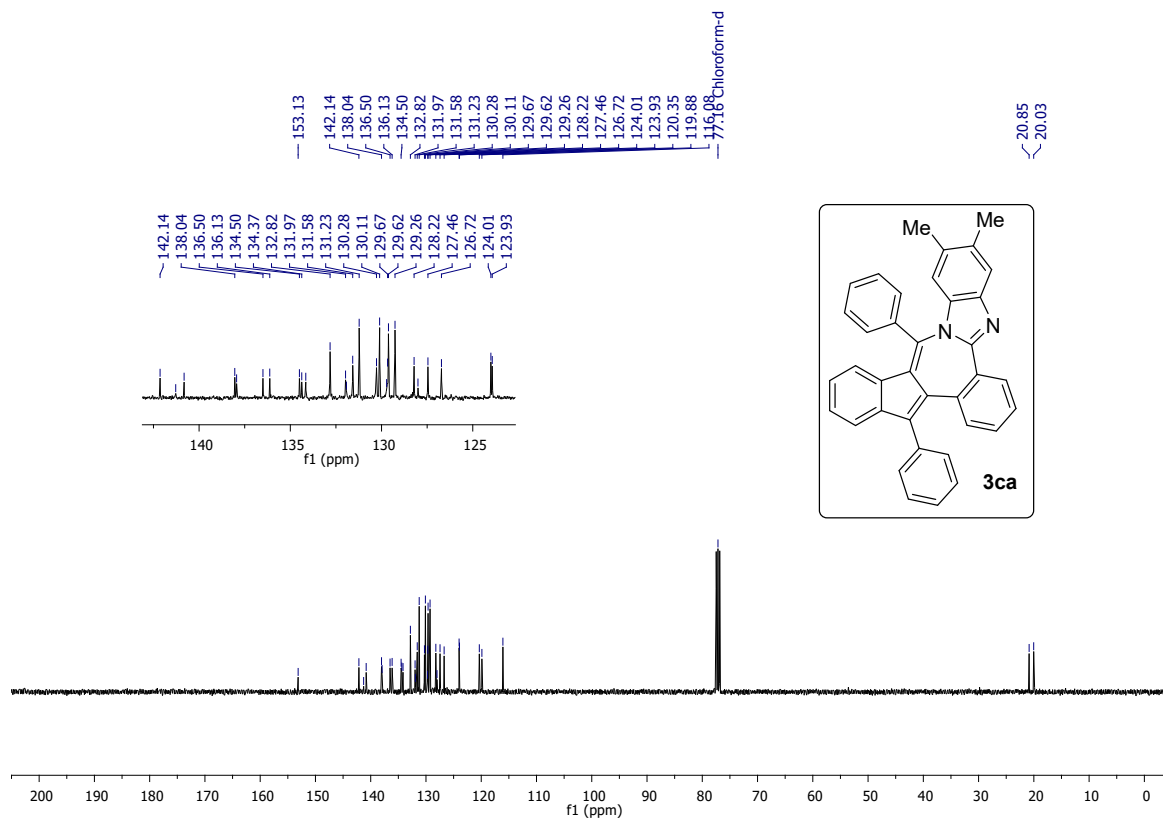
¹H NMR (400 MHz) spectrum of **3aa** in CDCl₃



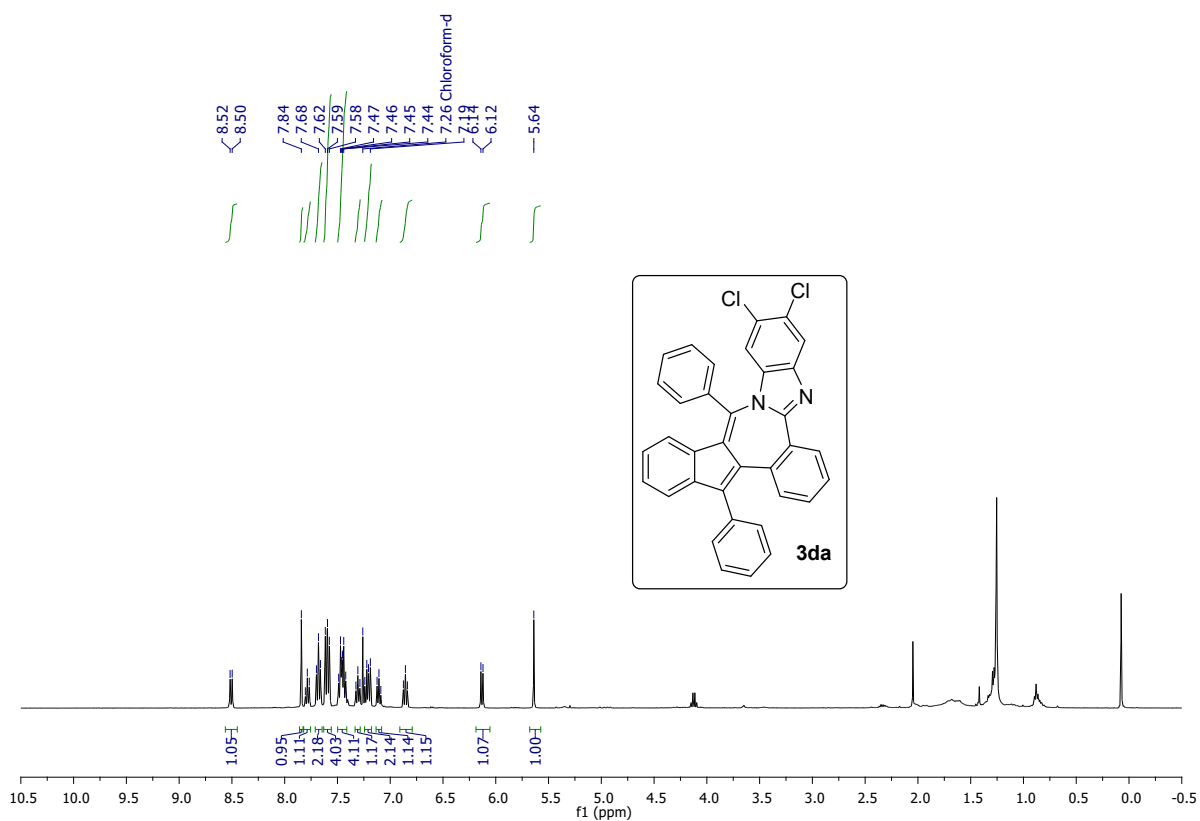
¹³C{¹H} NMR (101 MHz) spectrum of **3aa** in CDCl₃



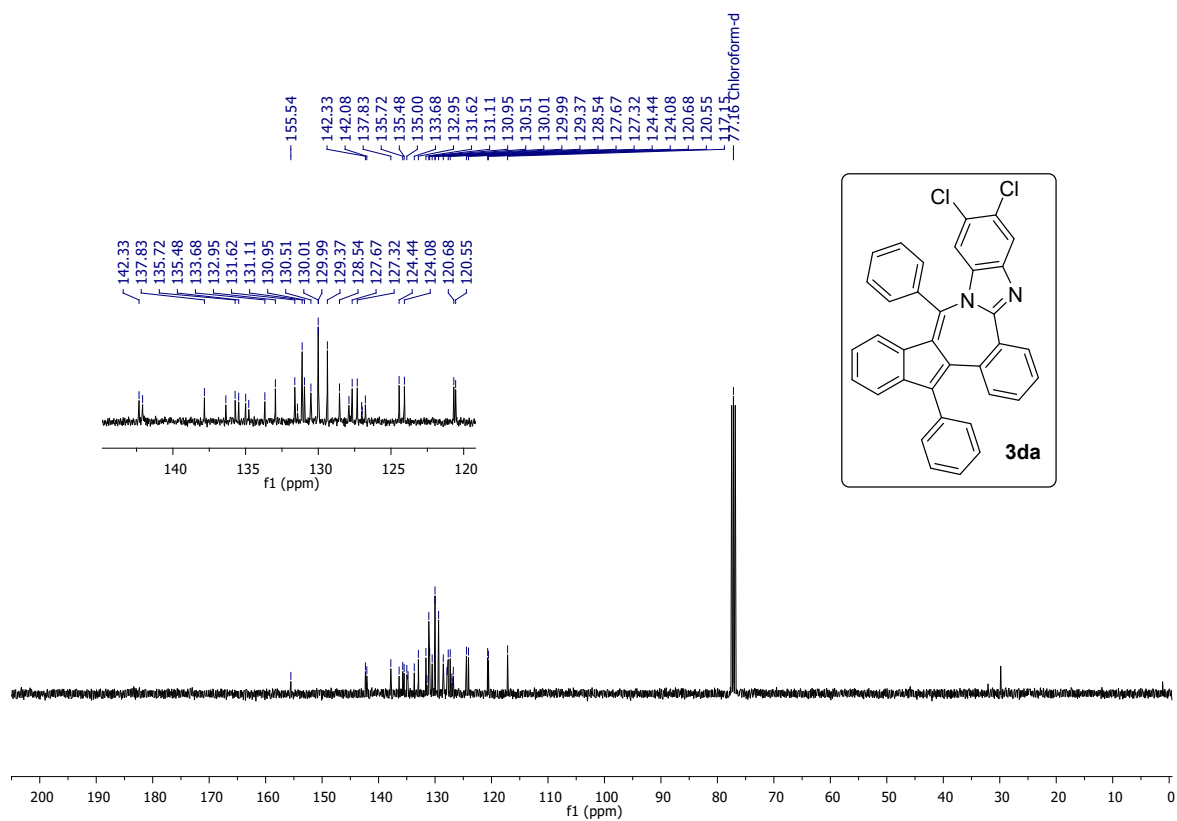
¹H NMR (400 MHz) spectrum of 3ca in CDCl₃



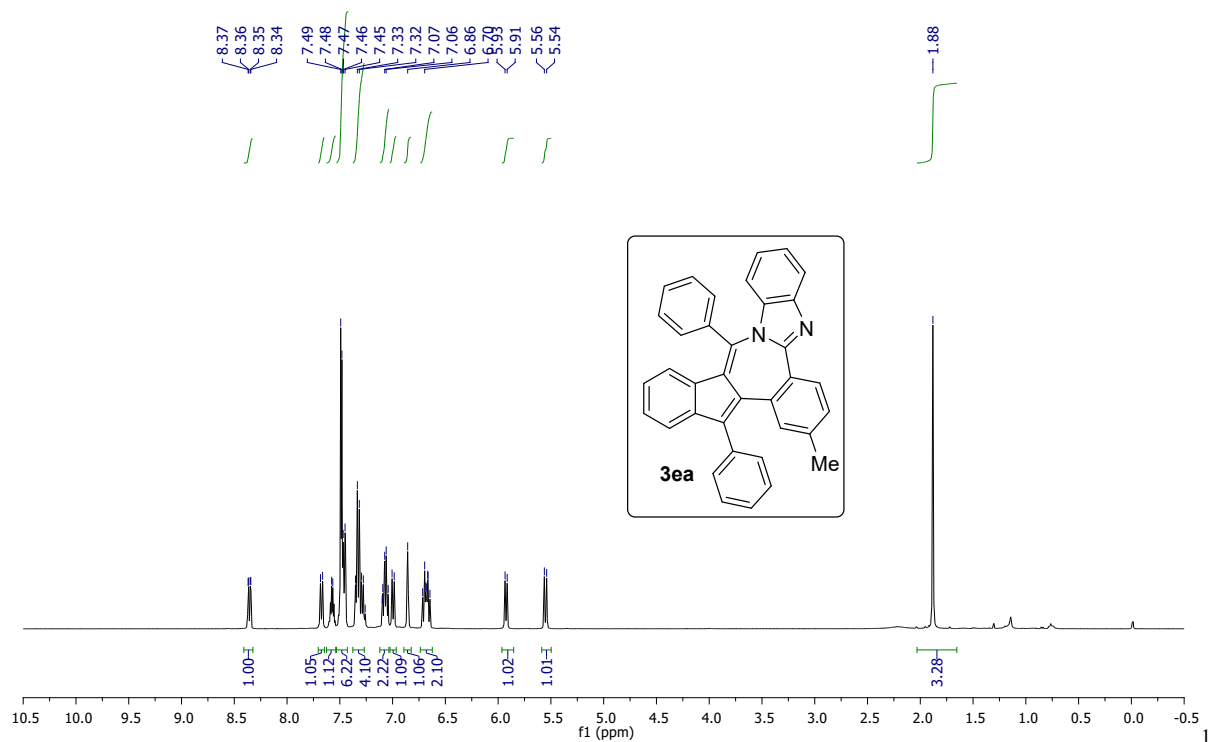
¹³C{¹H} NMR (101 MHz) spectrum of 3ca in CDCl₃



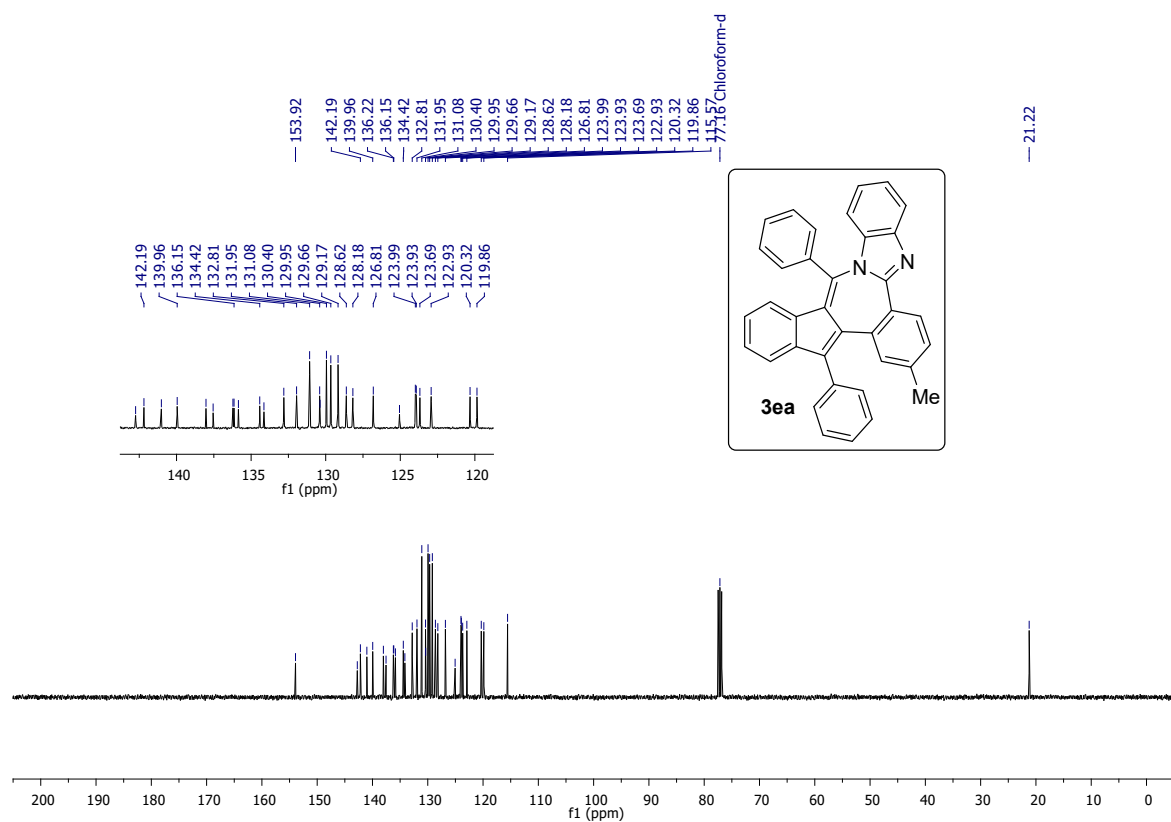
$^1\text{H NMR}$ (400 MHz) spectrum of **3da** in CDCl_3



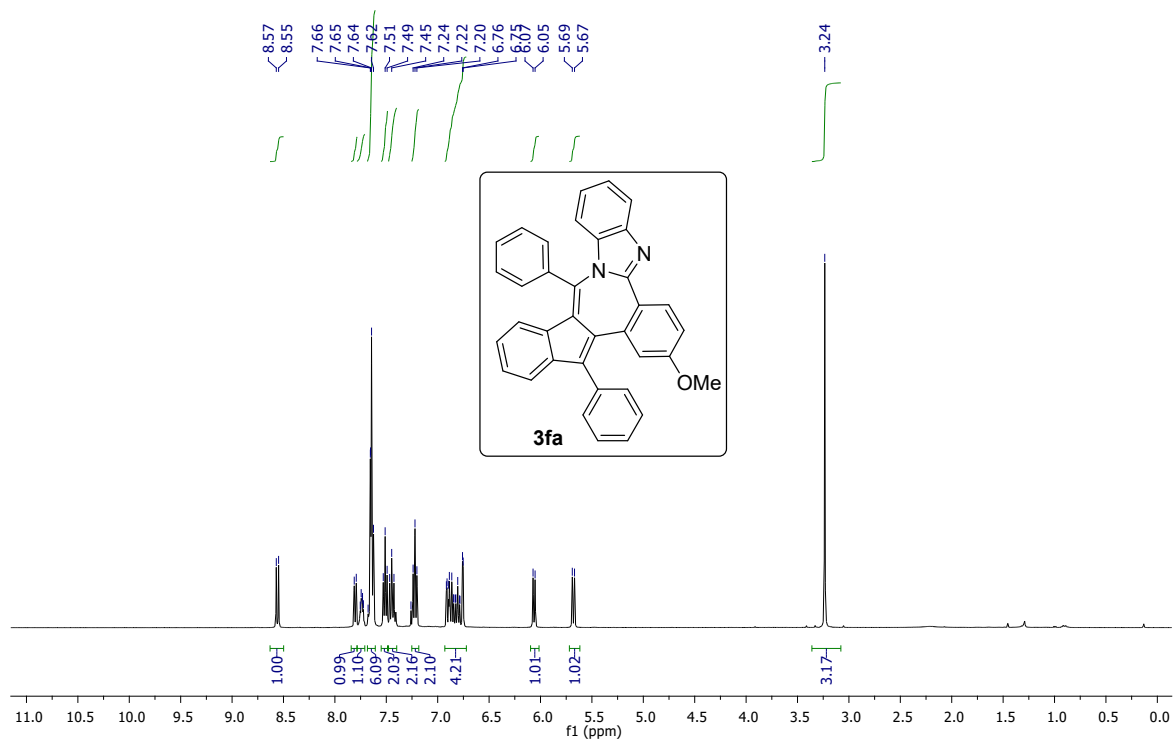
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz) spectrum of **3da** in CDCl_3



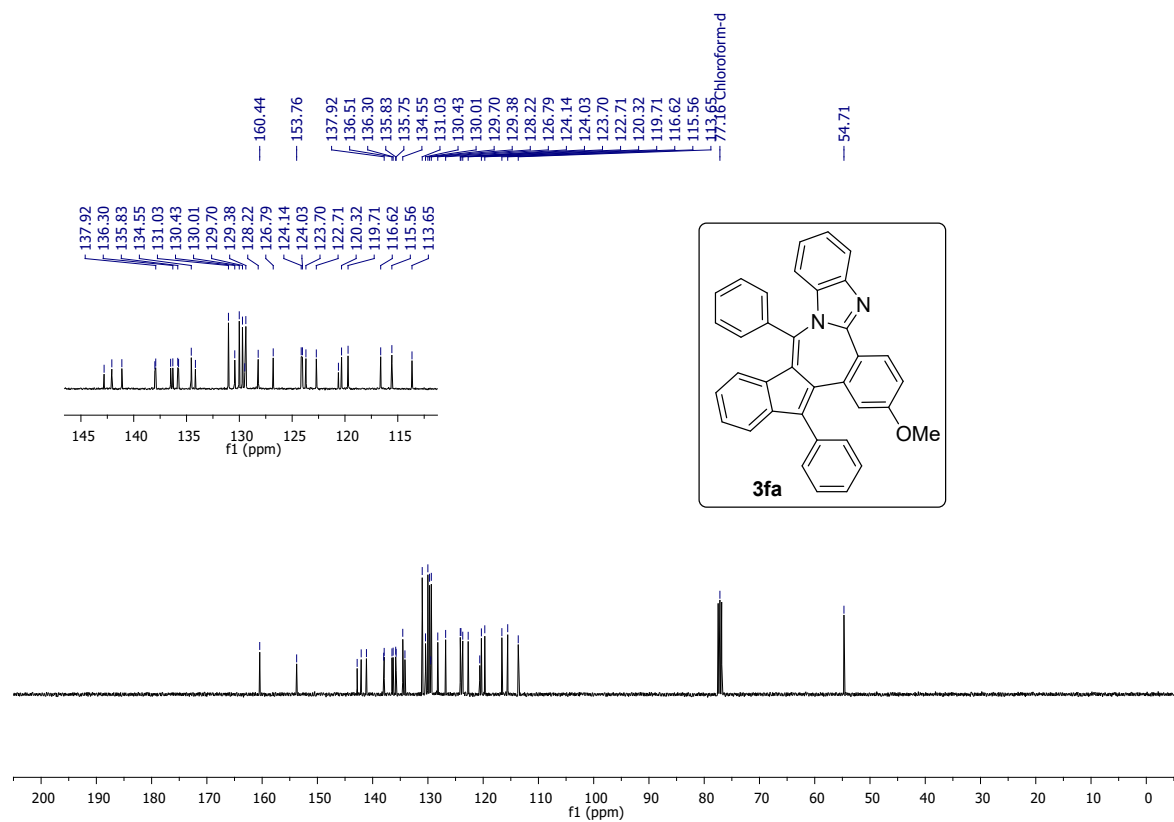
¹H NMR (400 MHz) spectrum of **3ea** in CDCl₃



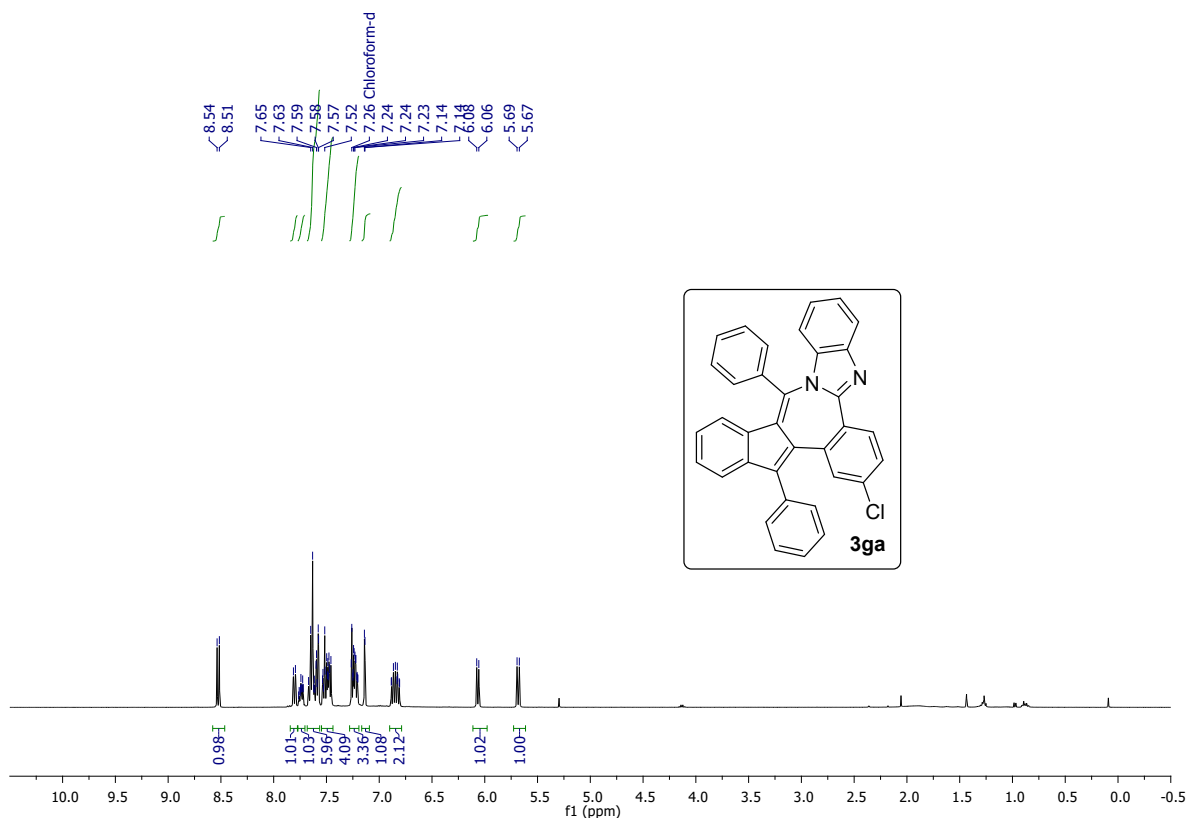
¹³C{¹H} NMR (101 MHz) spectrum of **3ea** in CDCl₃



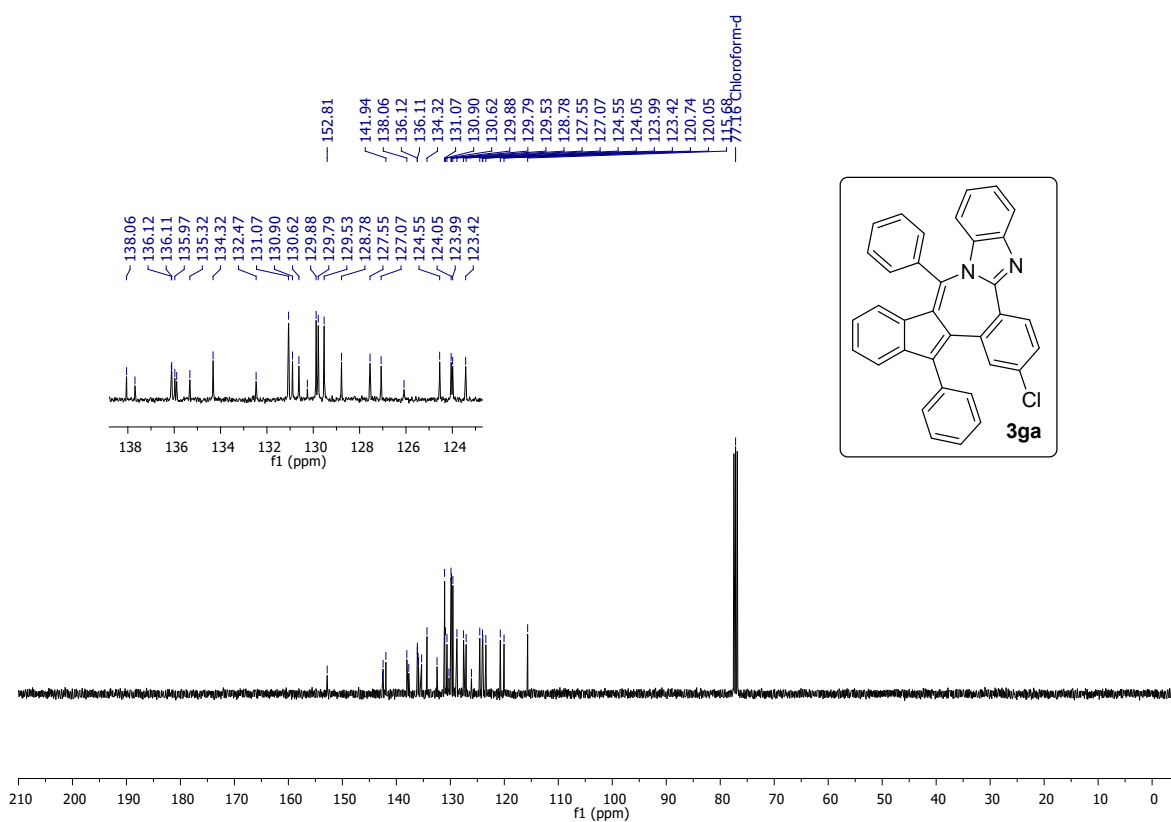
¹H NMR (400 MHz) spectrum of 3fa in CDCl₃



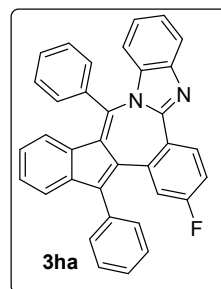
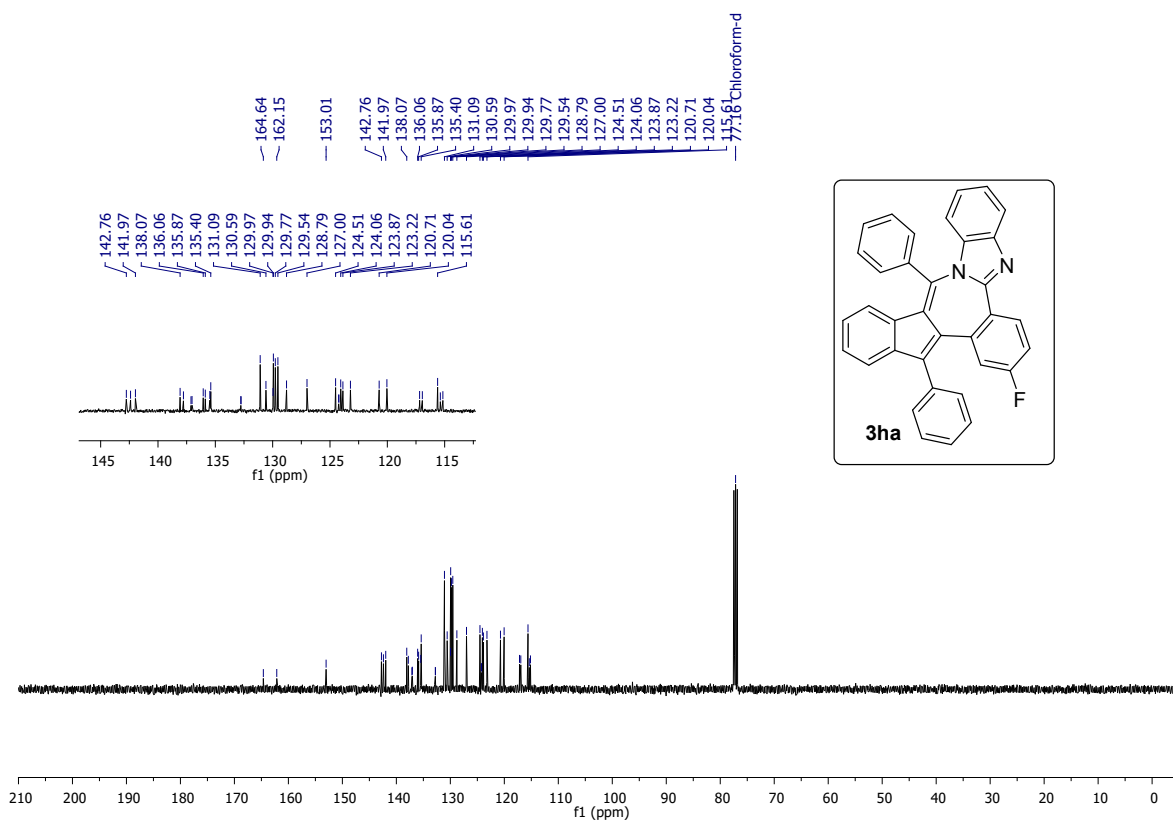
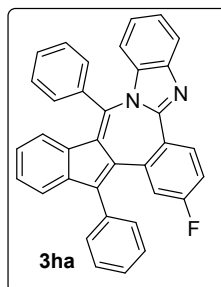
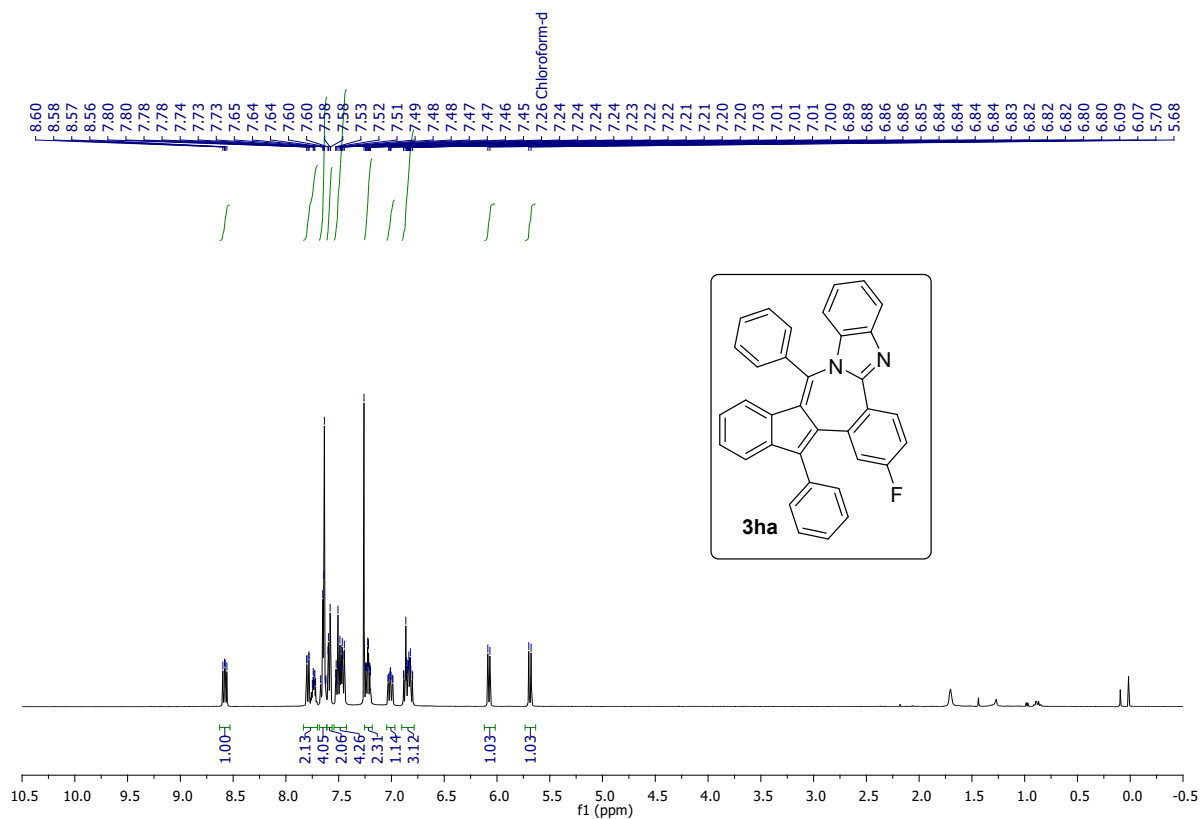
¹³C{¹H} NMR (101 MHz) spectrum of 3fa in CDCl₃

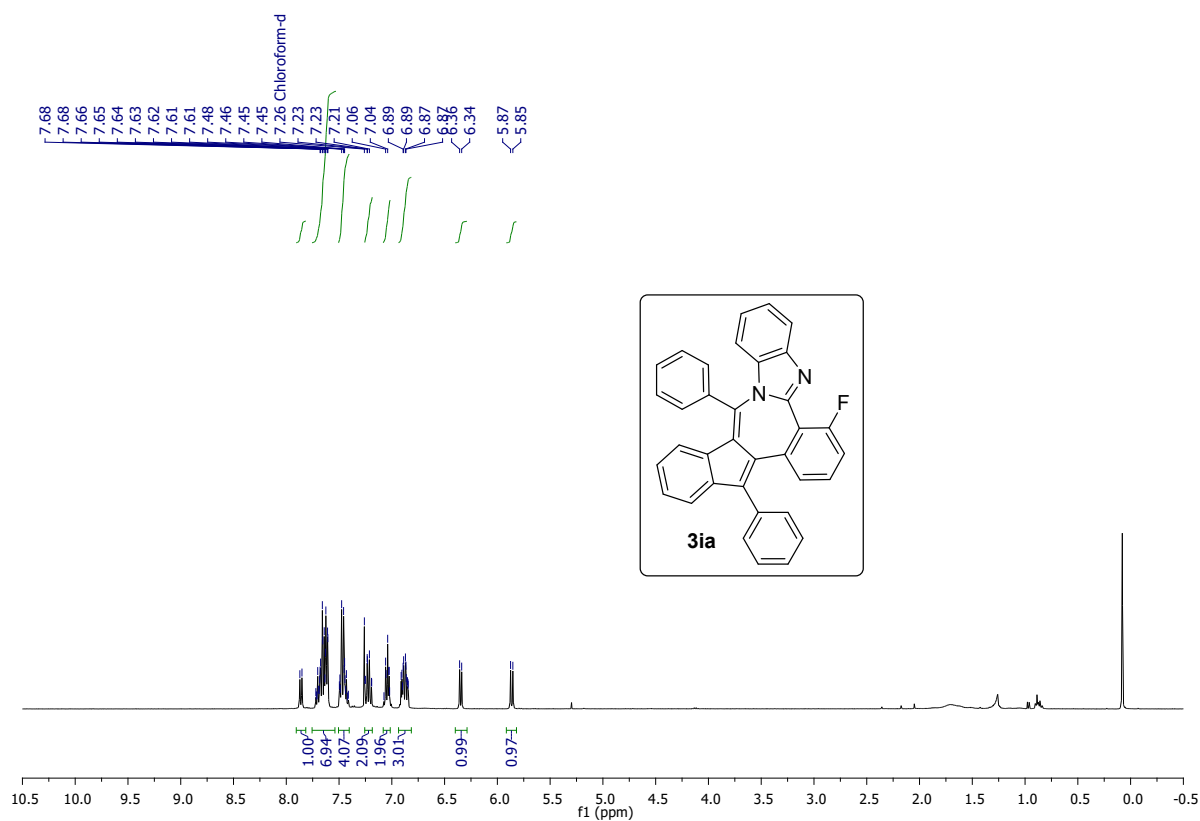


^1H NMR (400 MHz) spectrum of **3ga** in CDCl_3

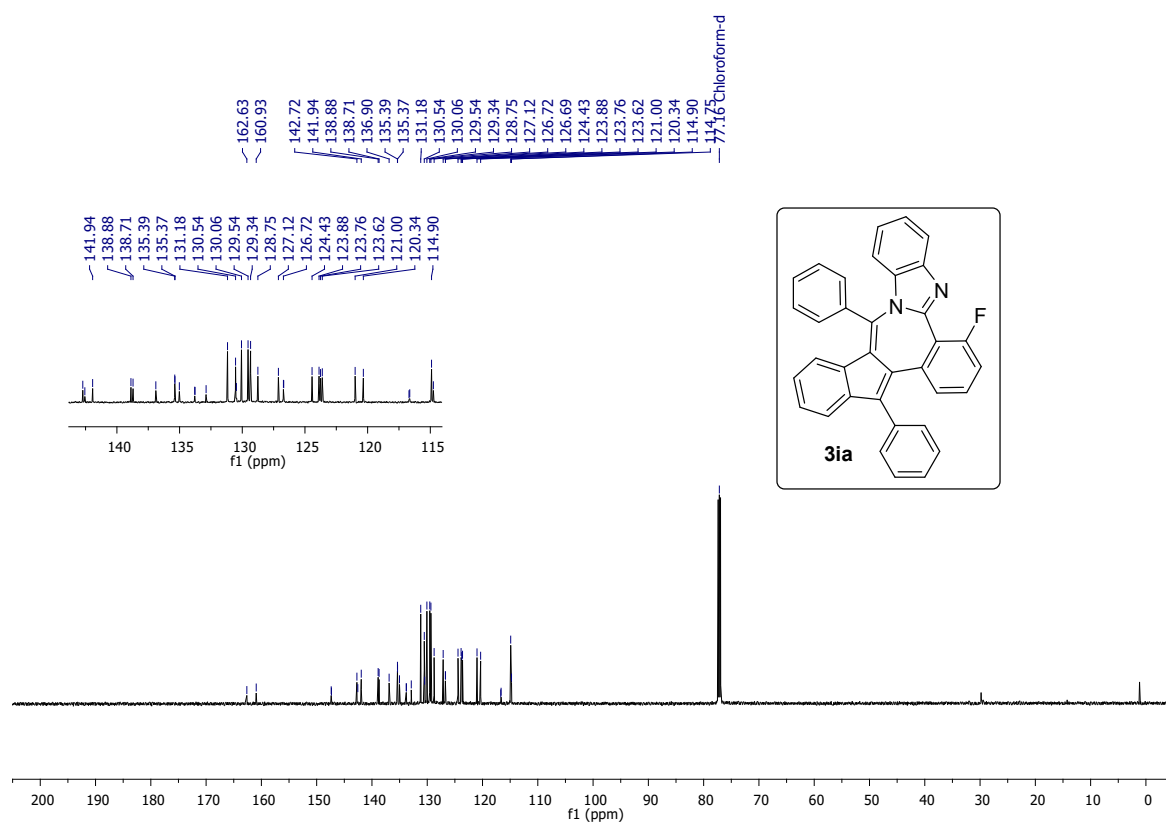


$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz) spectrum of **3ga** in CDCl_3

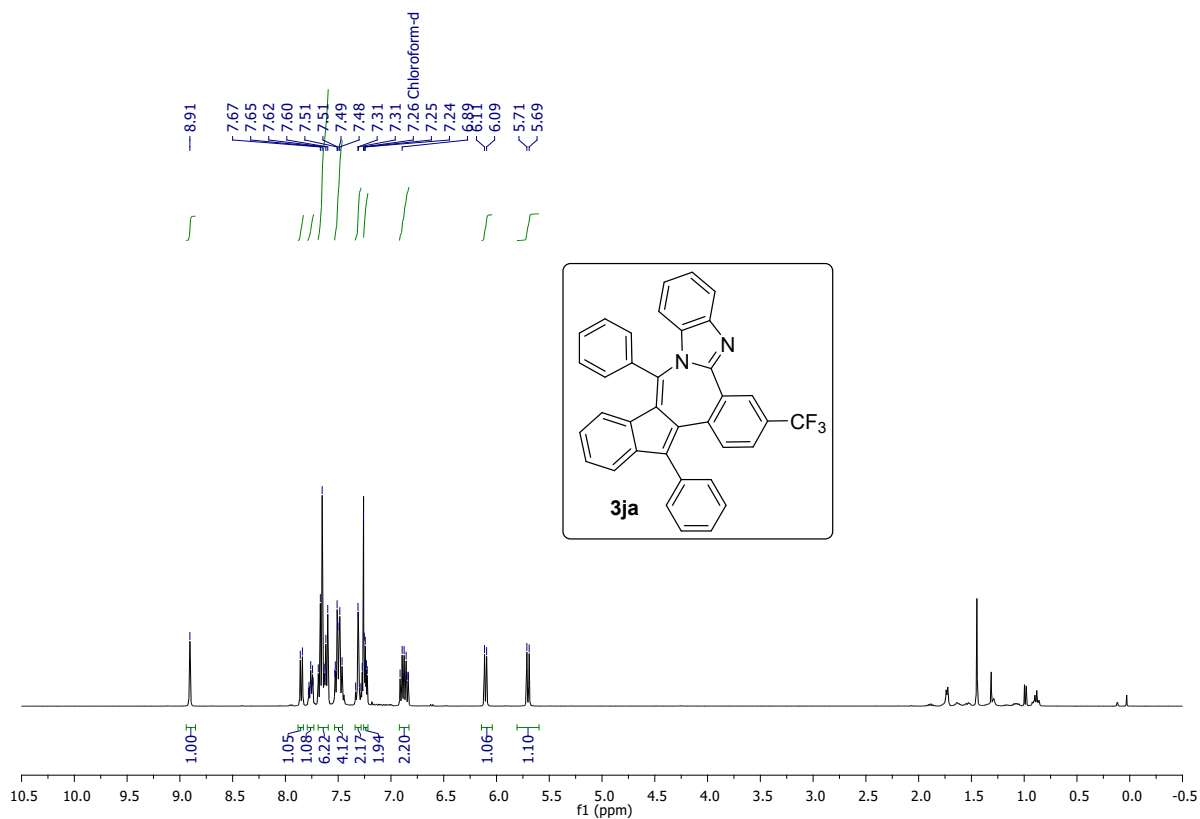




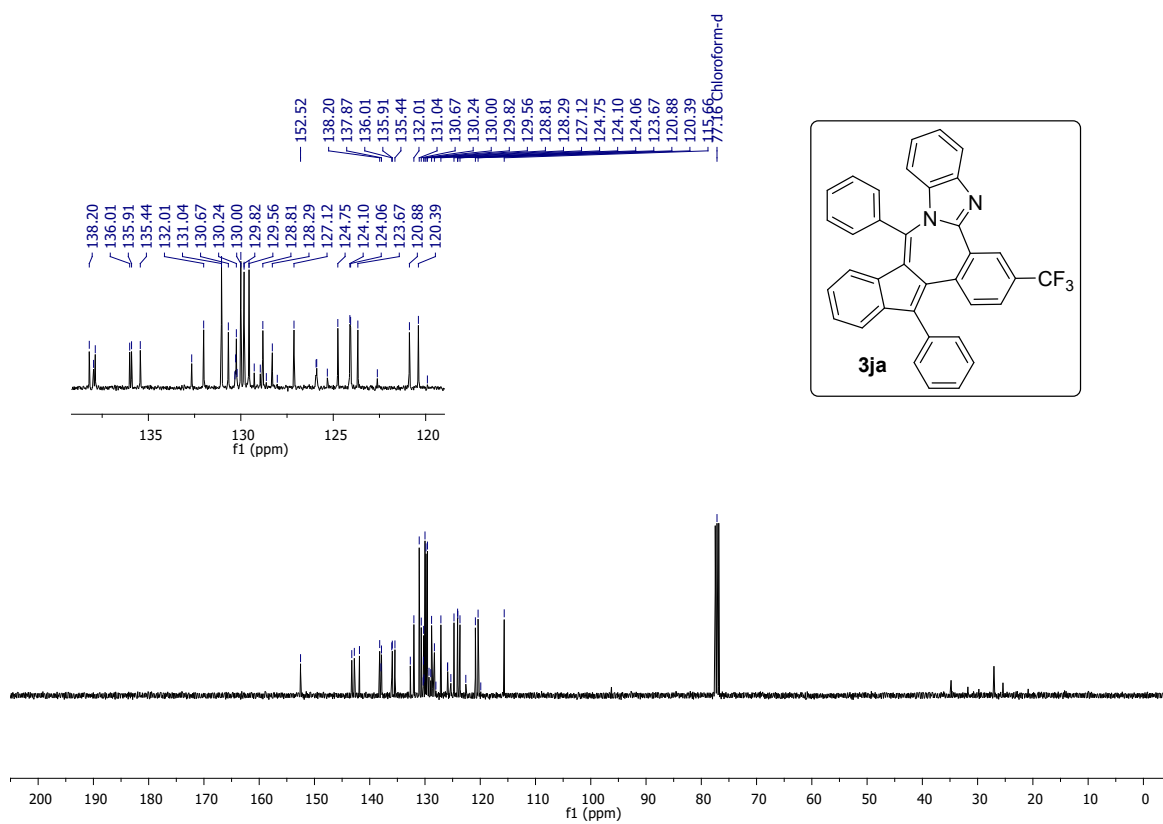
$^1\text{H NMR}$ (400 MHz) spectrum of **3ia** in CDCl_3



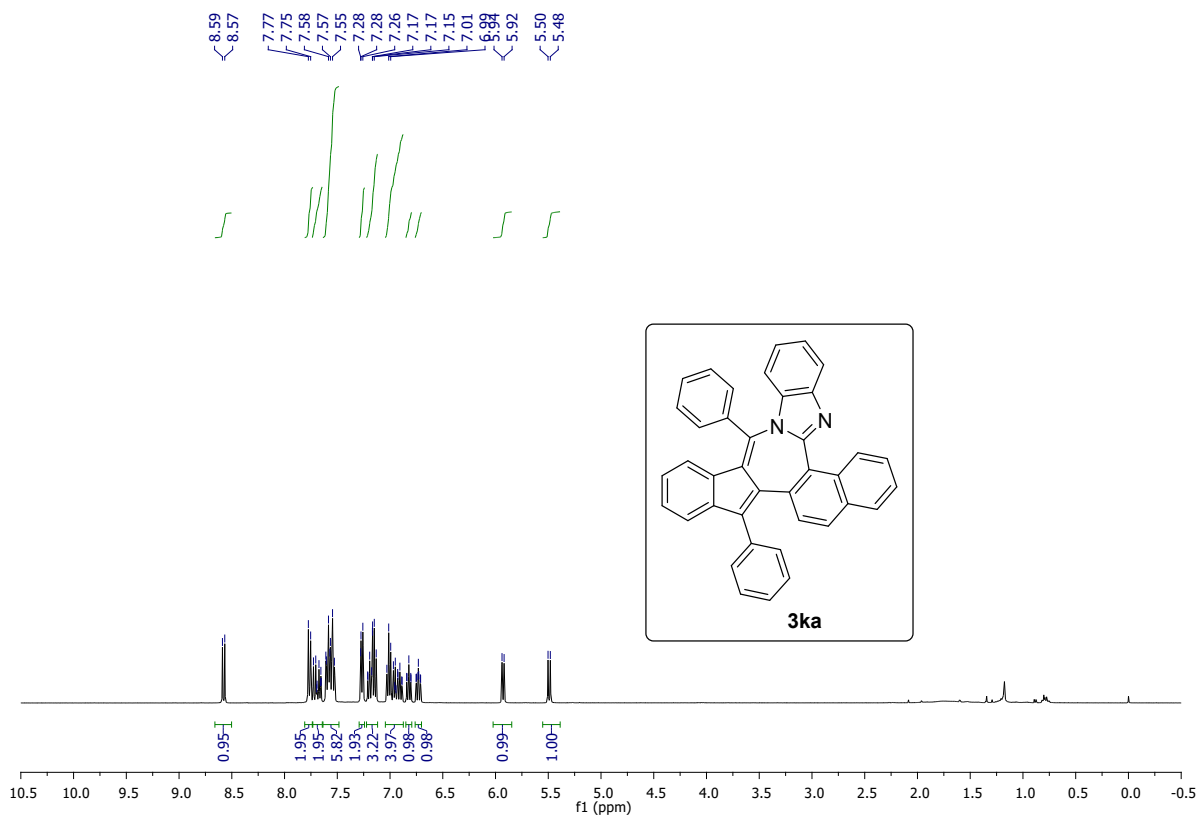
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz) spectrum of **3ia** in CDCl_3



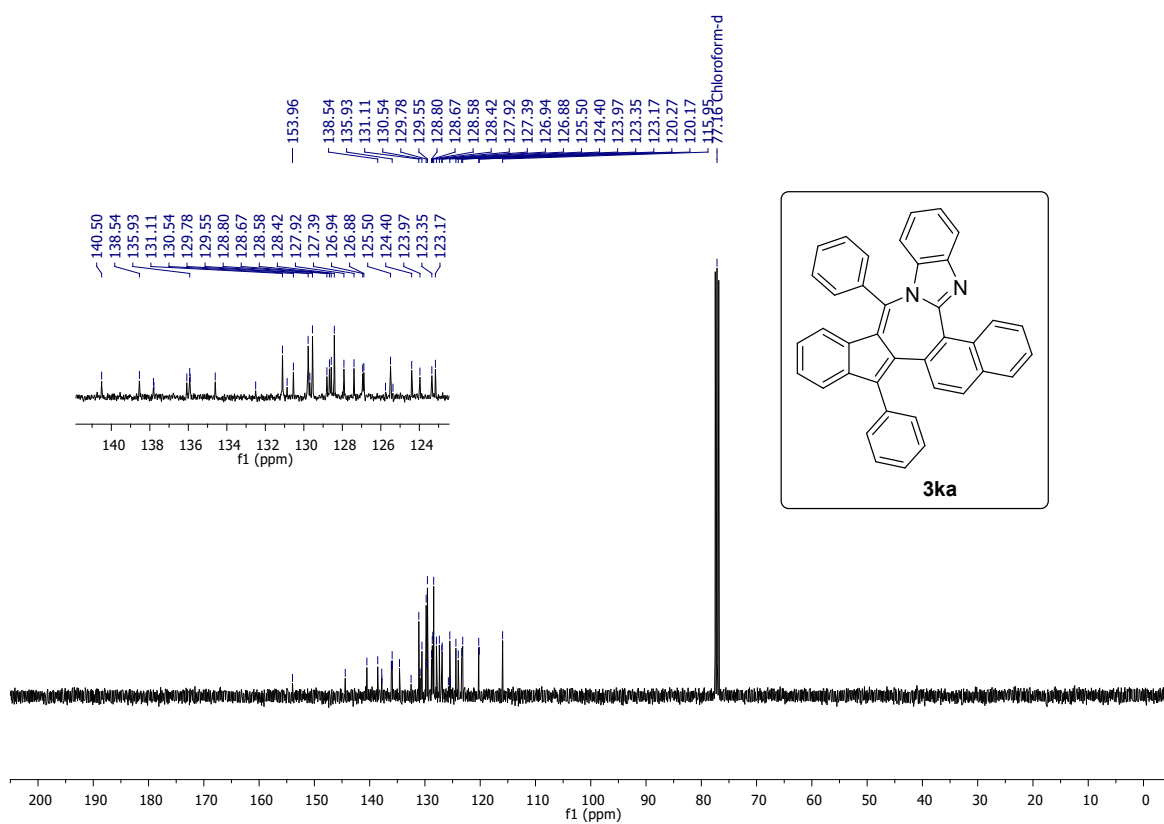
¹H NMR (400 MHz) spectrum of **3ja** in CDCl₃



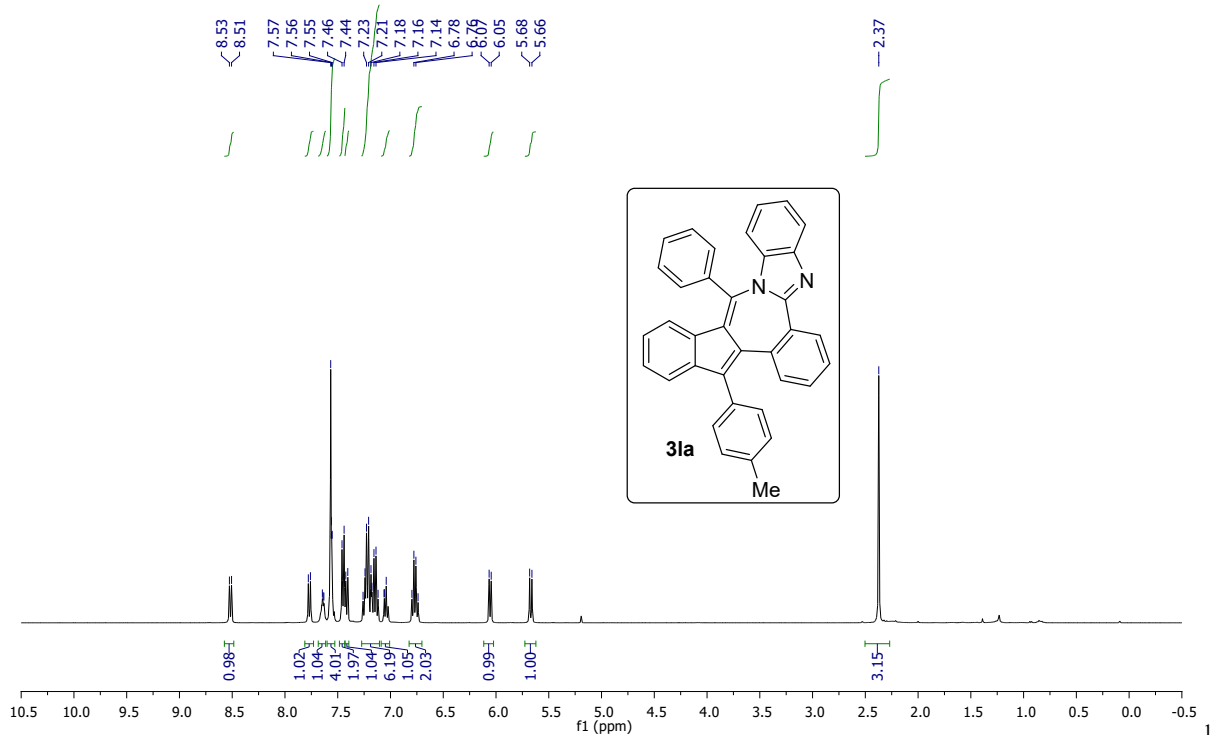
¹³C{¹H} NMR (101 MHz) spectrum of **3ja** in CDCl₃



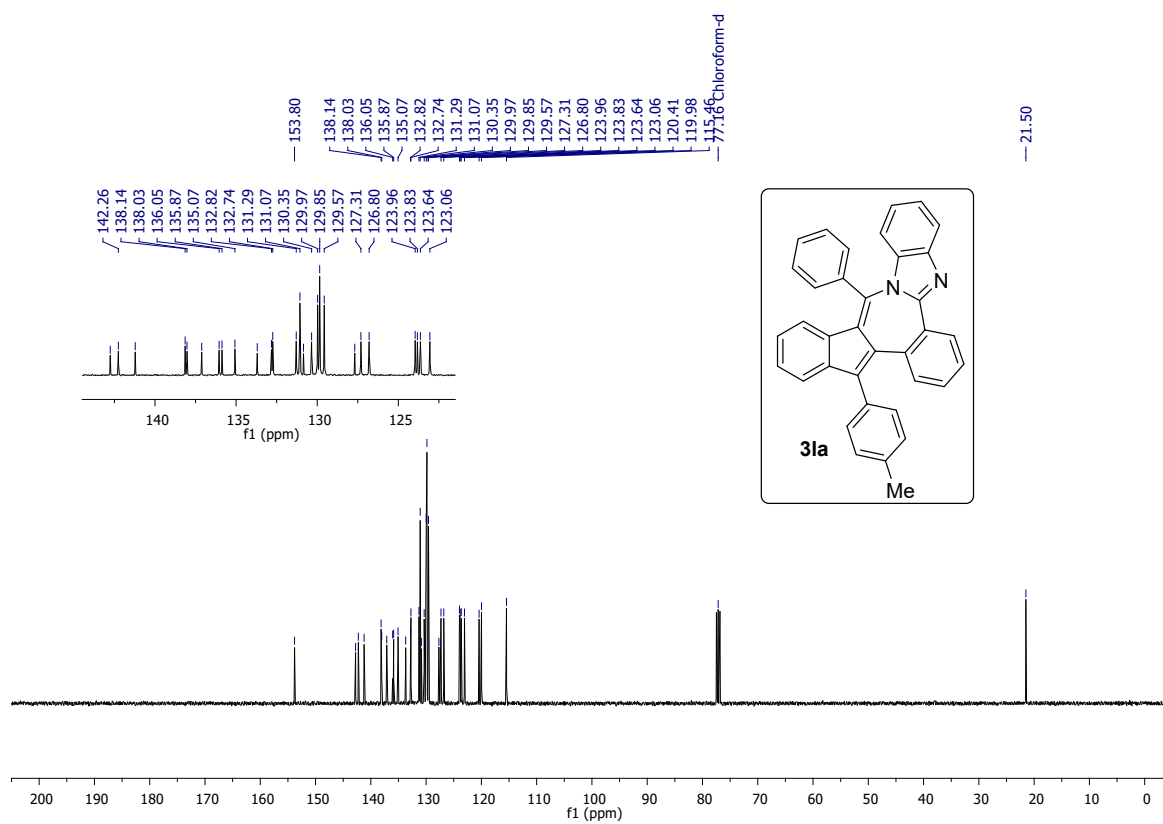
^1H NMR (400 MHz) spectrum of **3ka** in CDCl_3



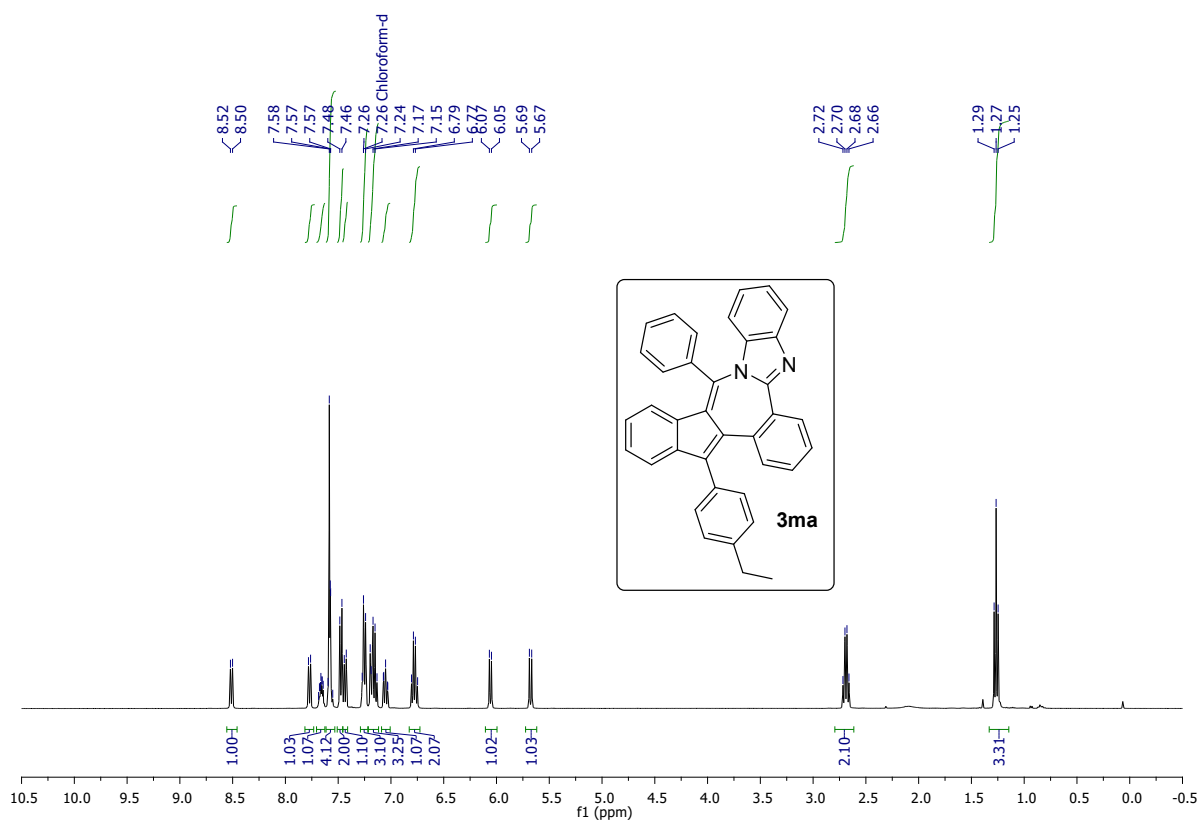
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz) spectrum of **3ka** in CDCl_3



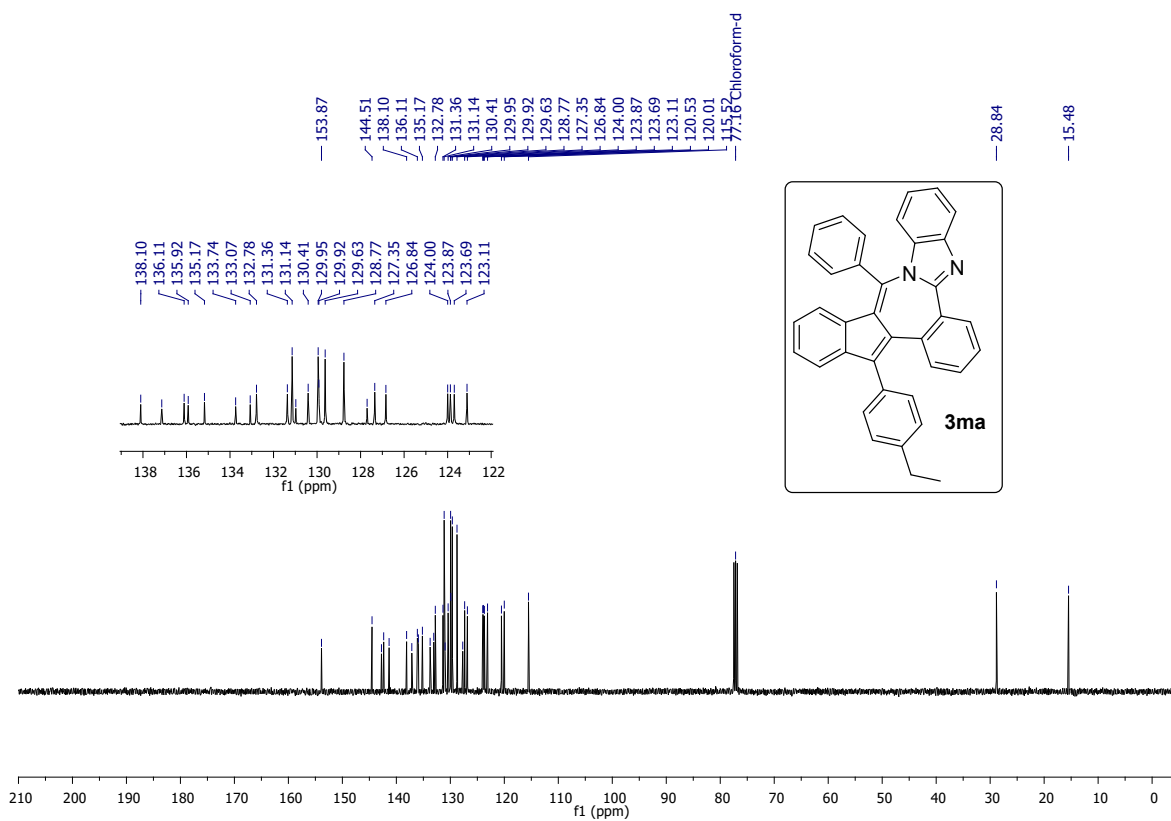
H NMR (400 MHz) spectrum of **3la** in CDCl₃



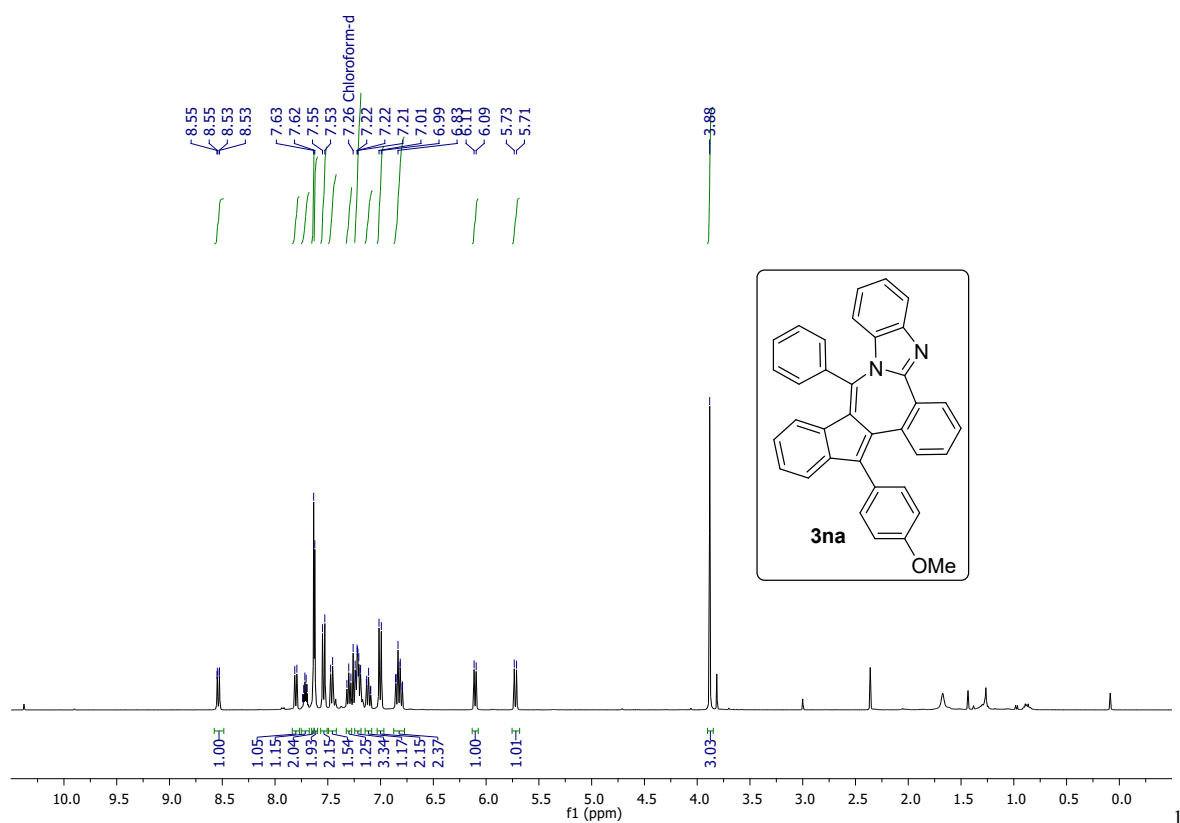
¹³C {¹H} NMR (101 MHz) spectrum of **3la** in CDCl₃



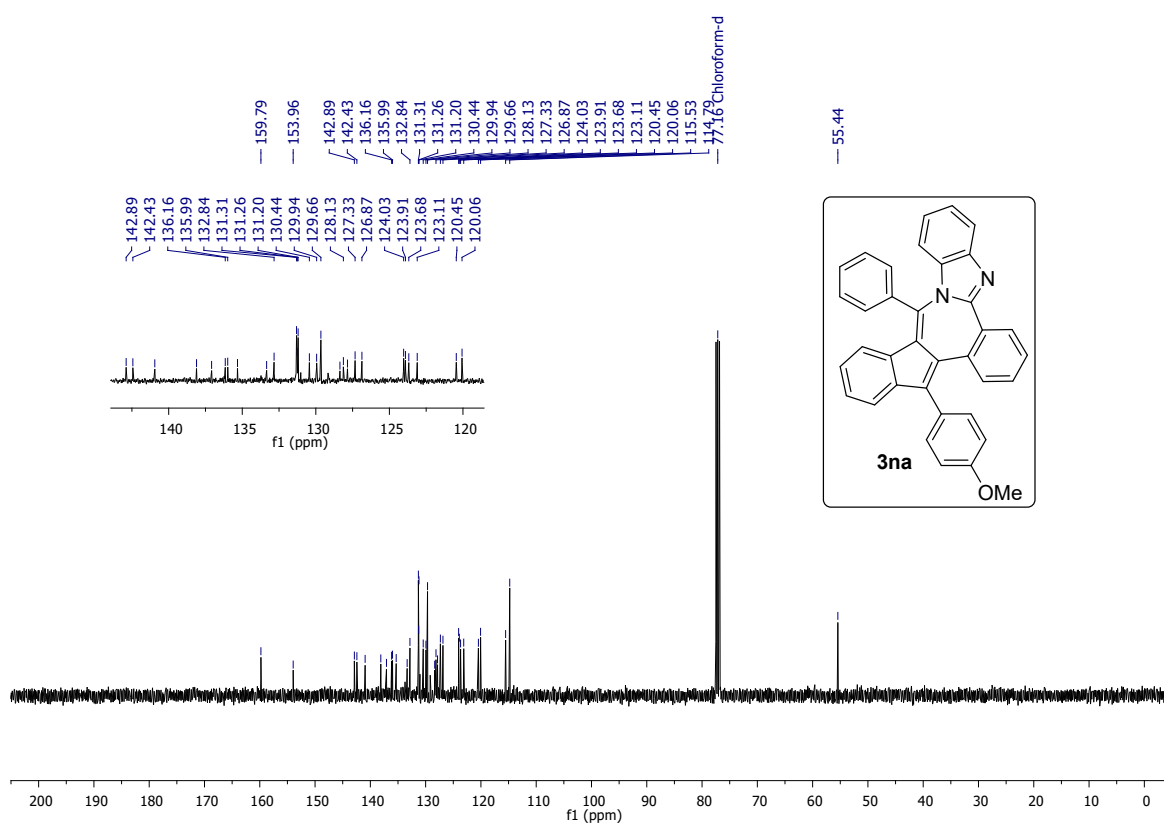
¹H NMR (400 MHz) spectrum of 3ma in CDCl₃



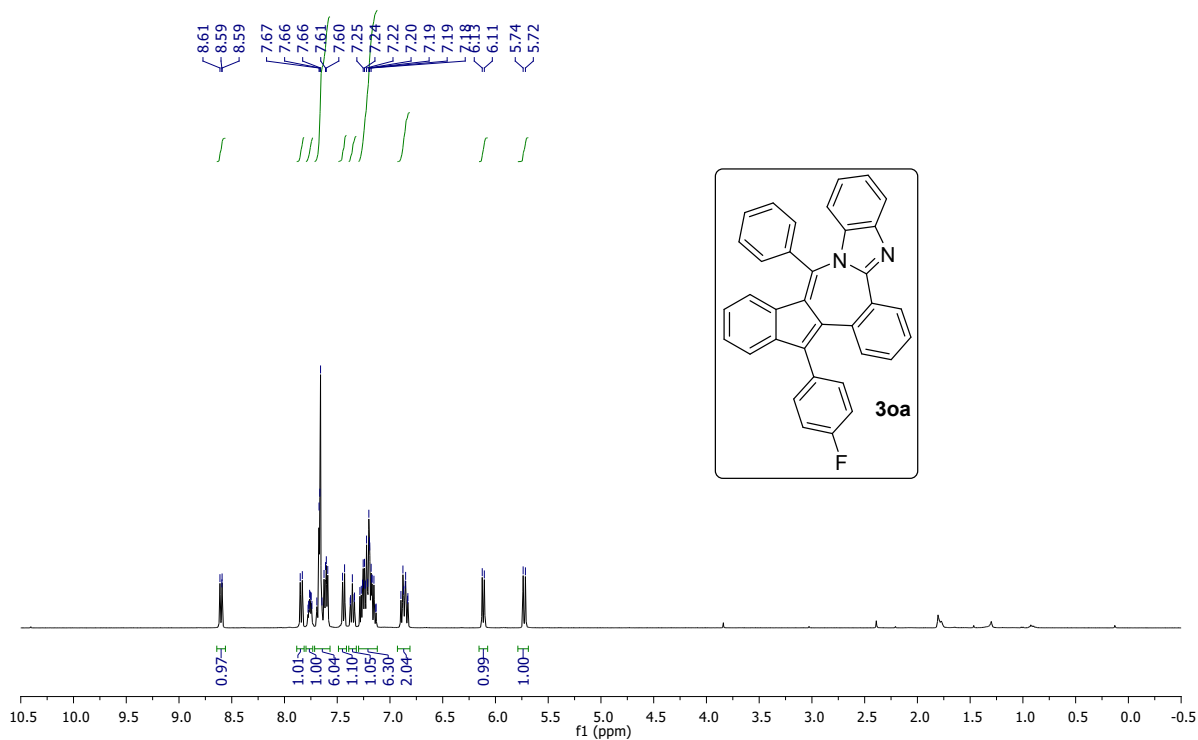
¹³C {¹H} NMR (101 MHz) spectrum of 3ma in CDCl₃



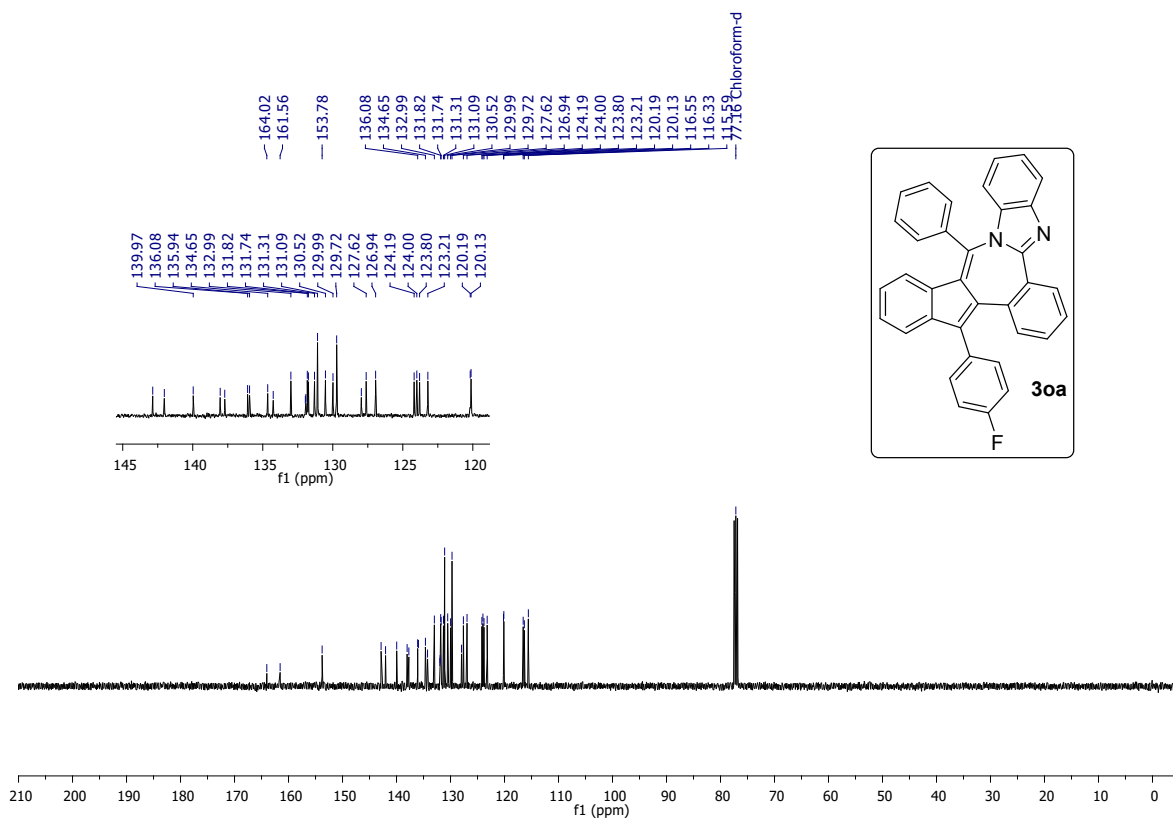
^1H NMR (400 MHz) spectrum of **3na** in CDCl_3



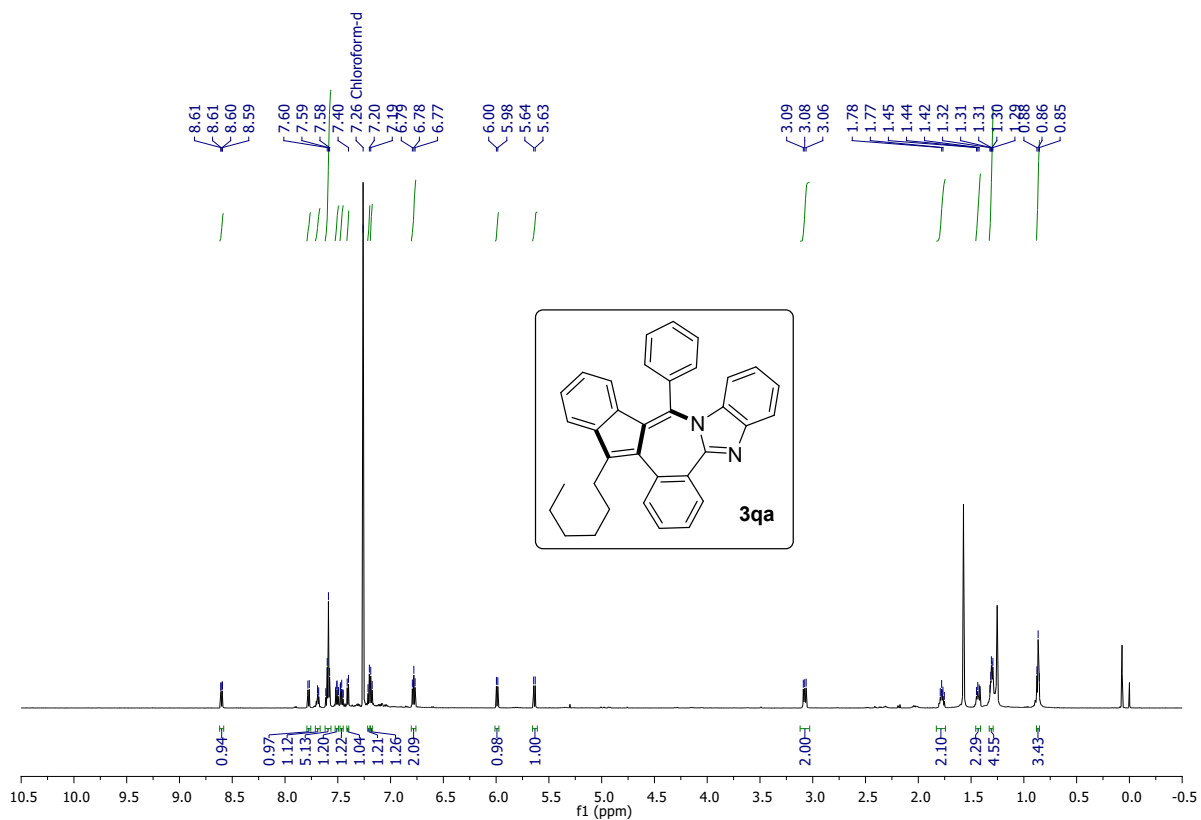
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz) spectrum of **3na** in CDCl_3



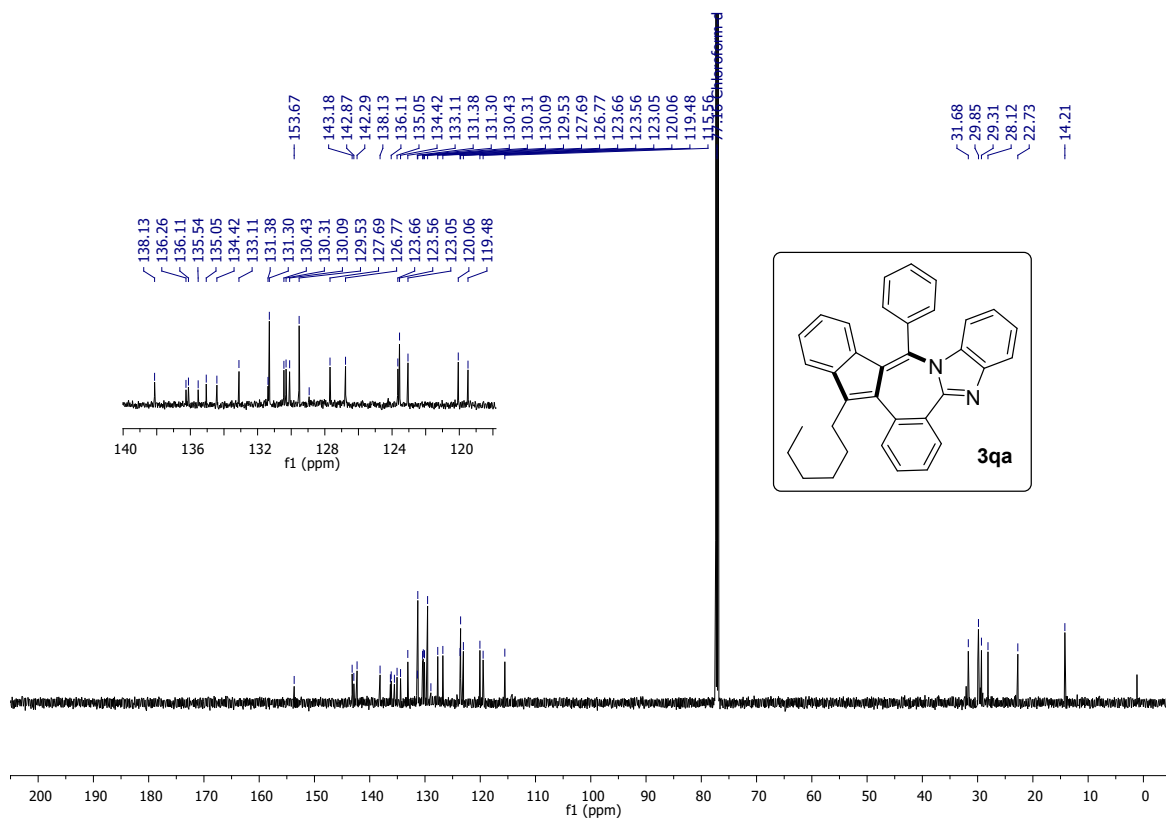
¹H NMR (400 MHz) spectrum of 30a in CDCl₃



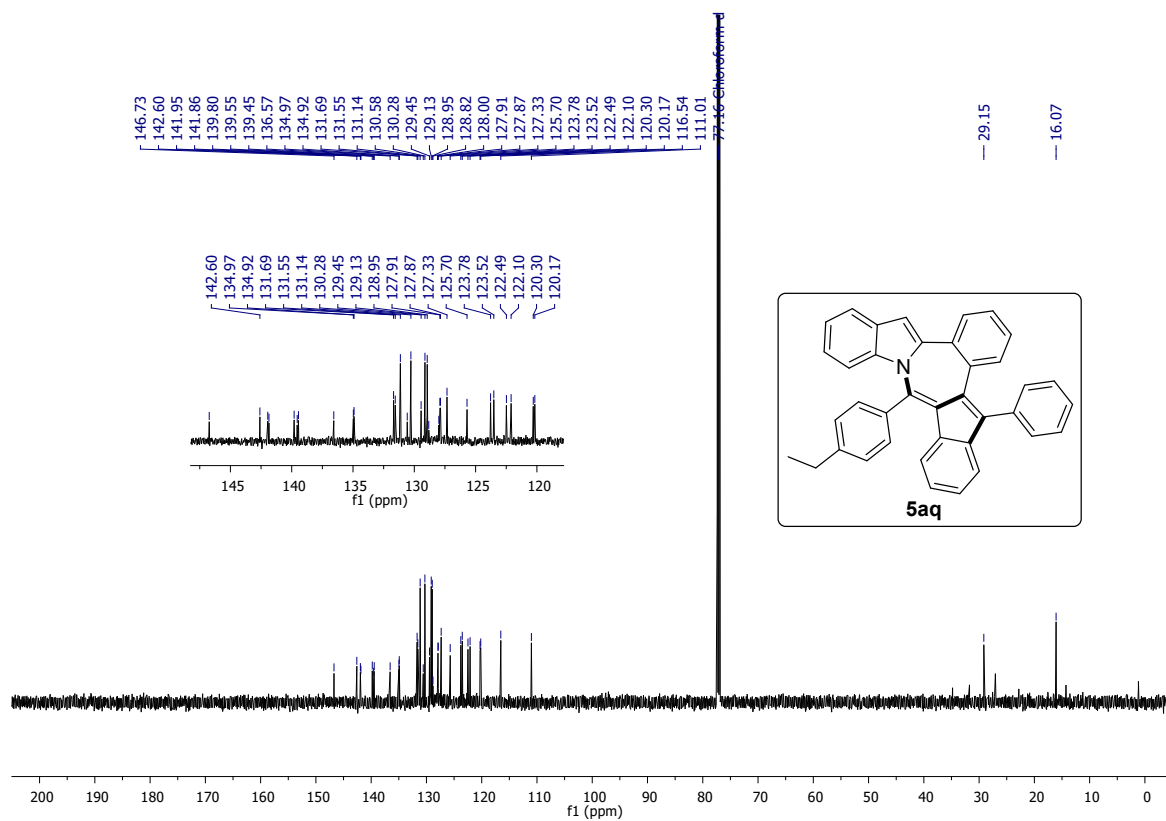
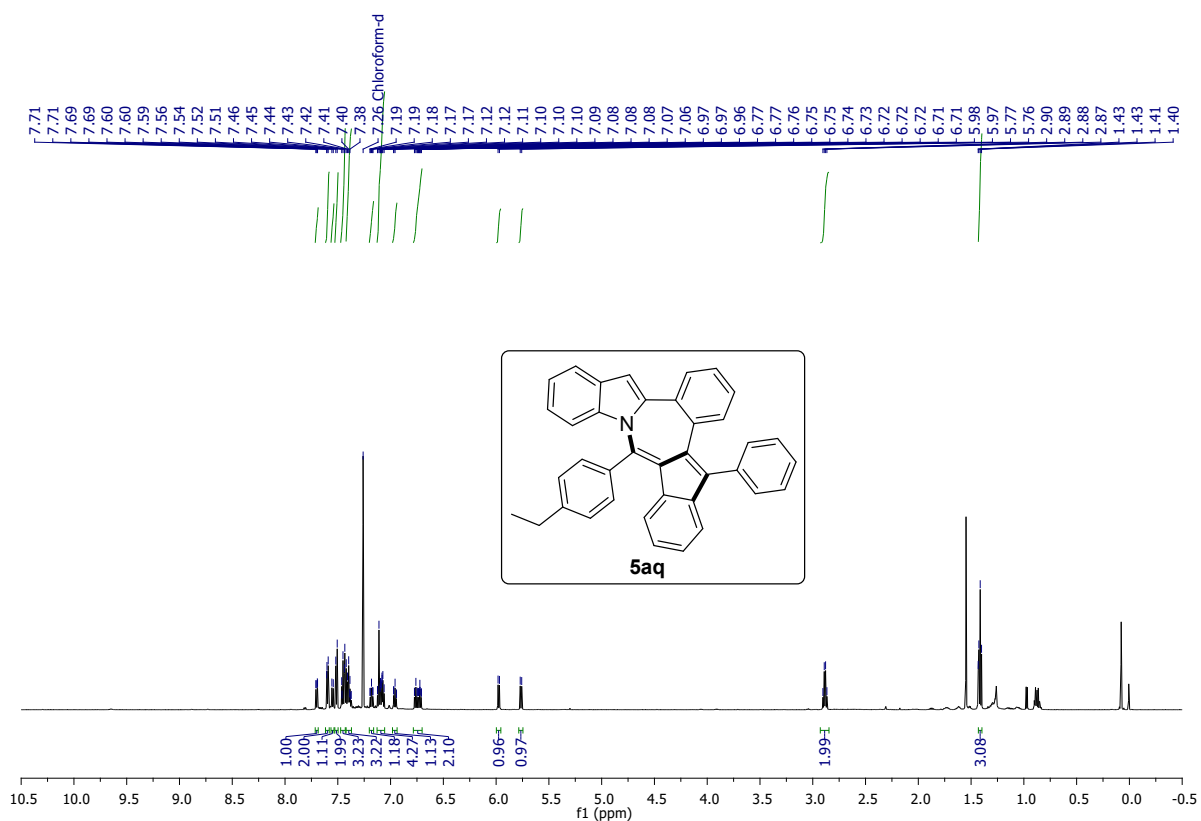
¹³C {¹H} NMR (101 MHz) spectrum of 30a in CDCl₃

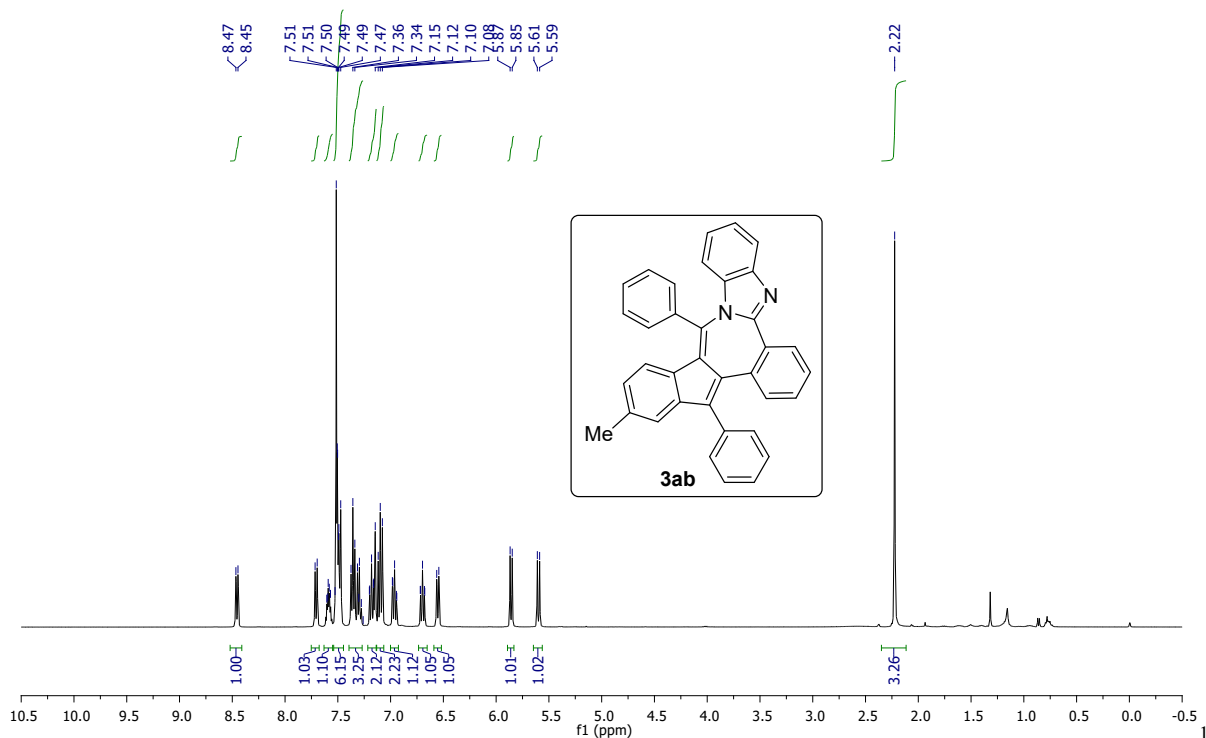


¹H NMR (600 MHz) spectrum of 3qa in CDCl₃

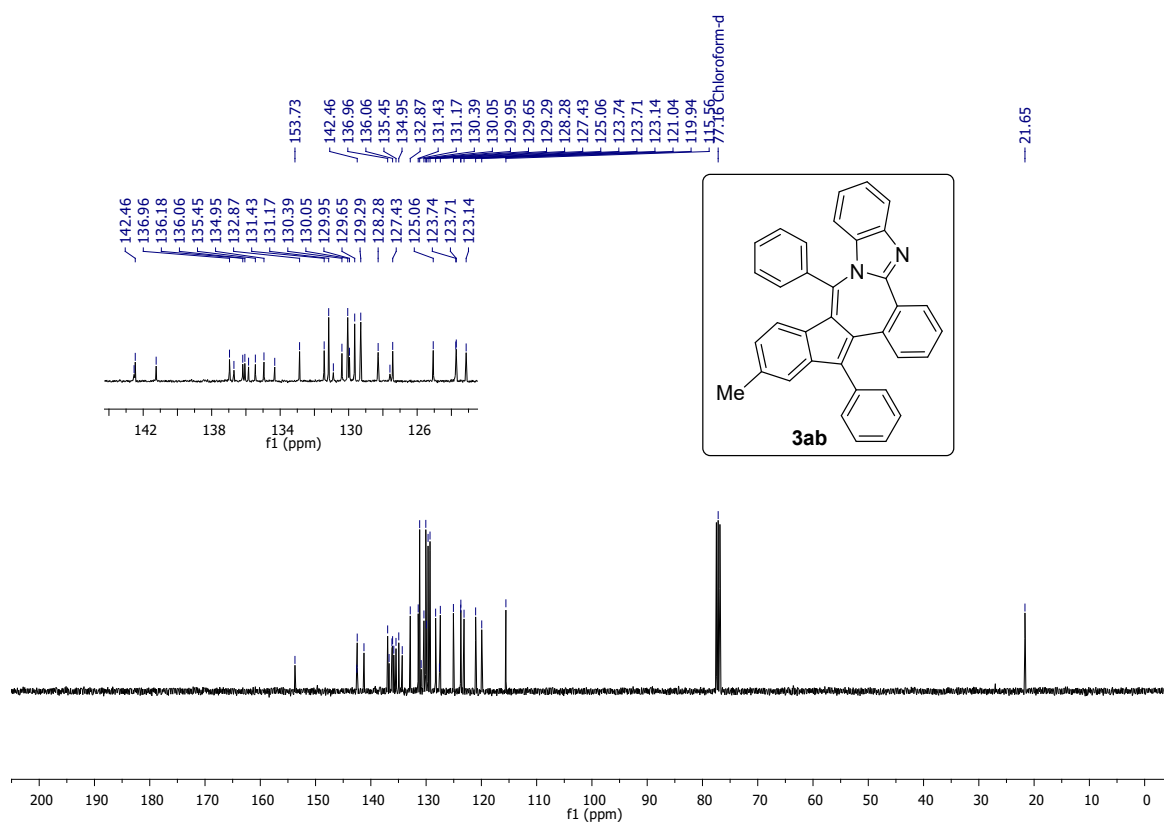


¹³C{¹H} NMR (151 MHz) spectrum of 3qa in CDCl₃

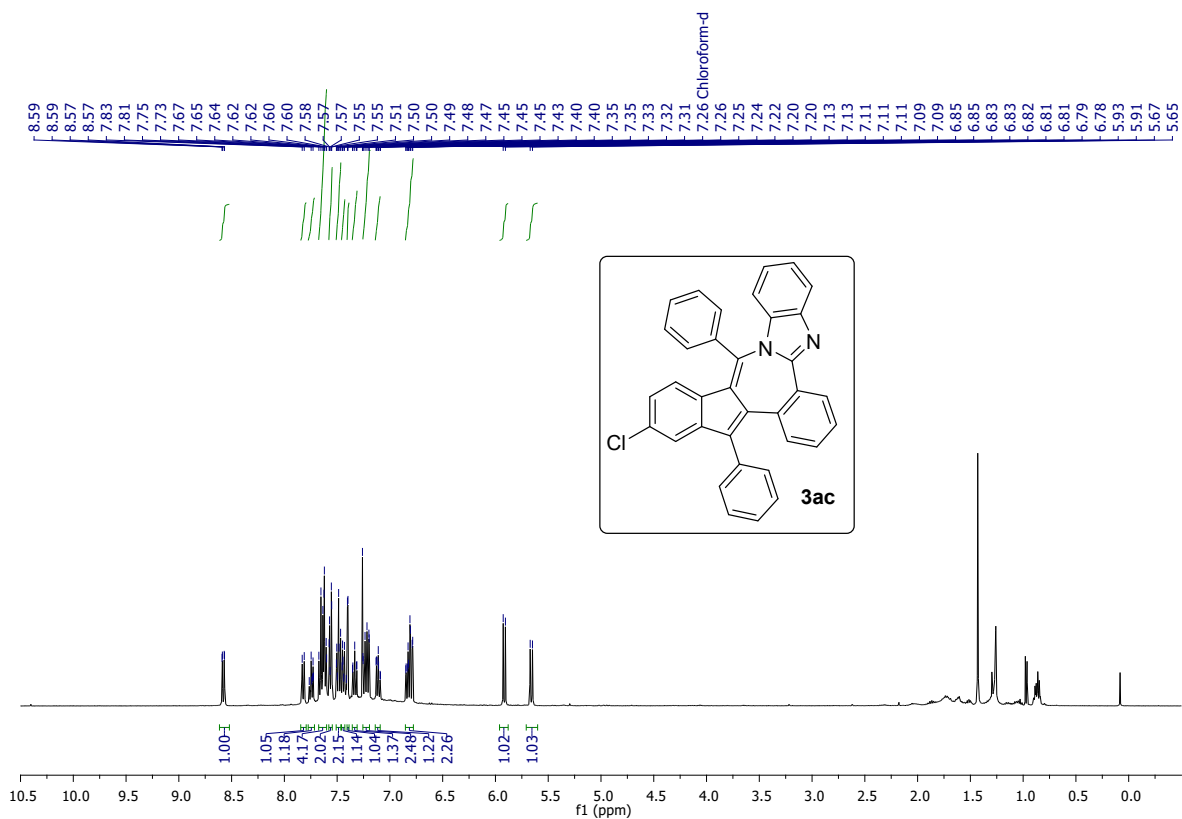




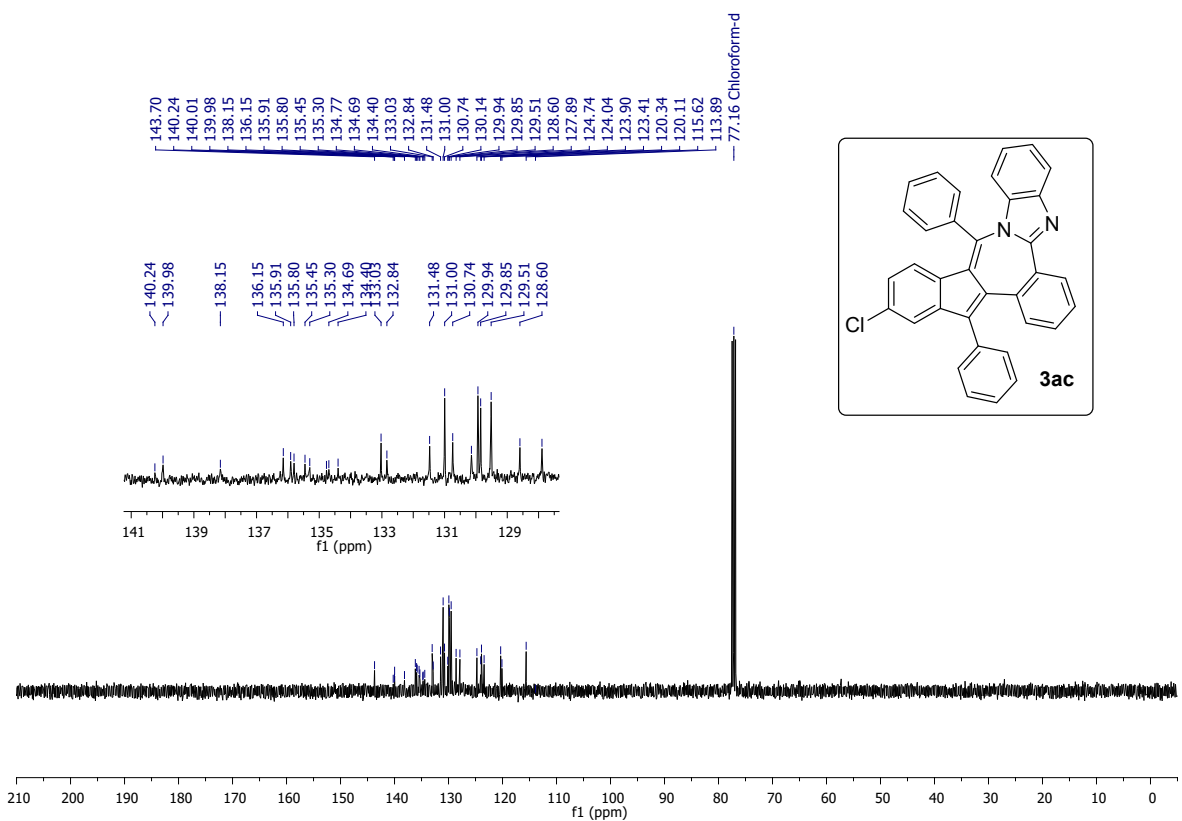
^1H NMR (400 MHz) spectrum of **3ab** in CDCl_3



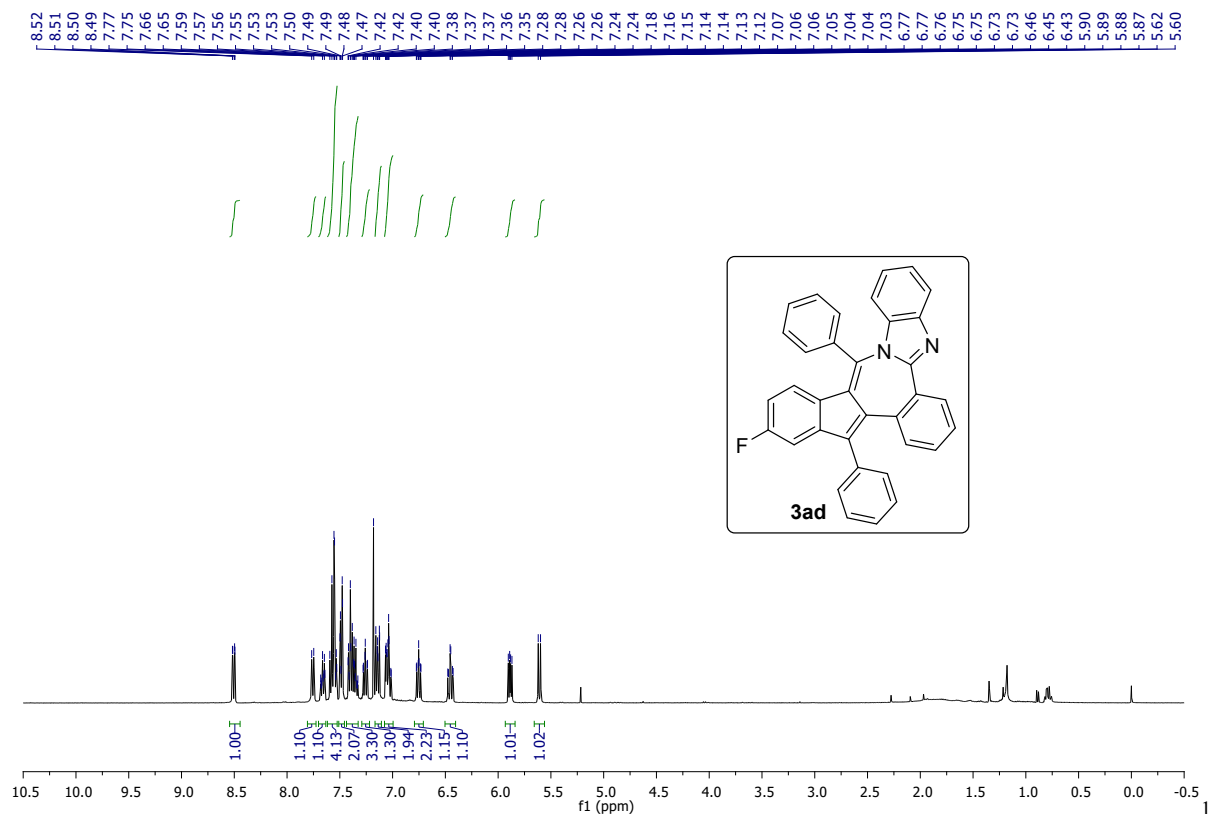
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz) spectrum of **3ab** in CDCl_3



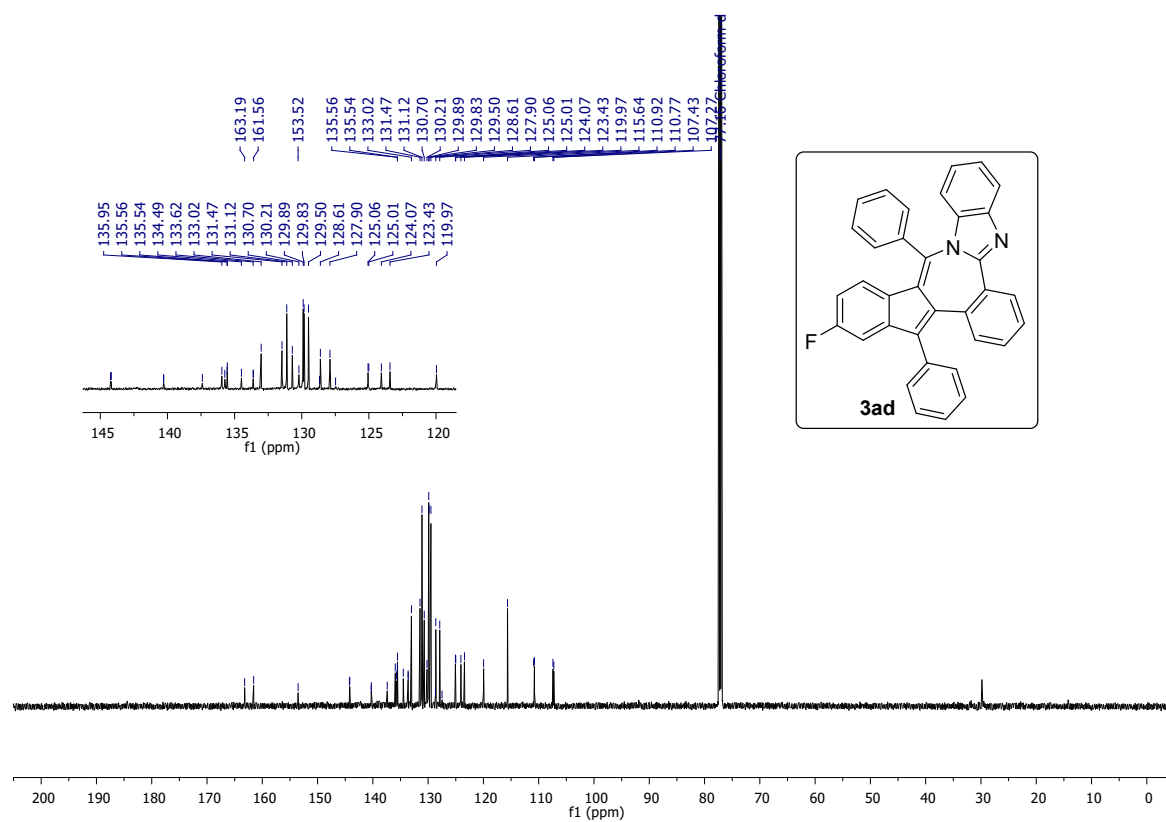
$^1\text{H NMR}$ (400 MHz) spectrum of **3ac** in CDCl_3



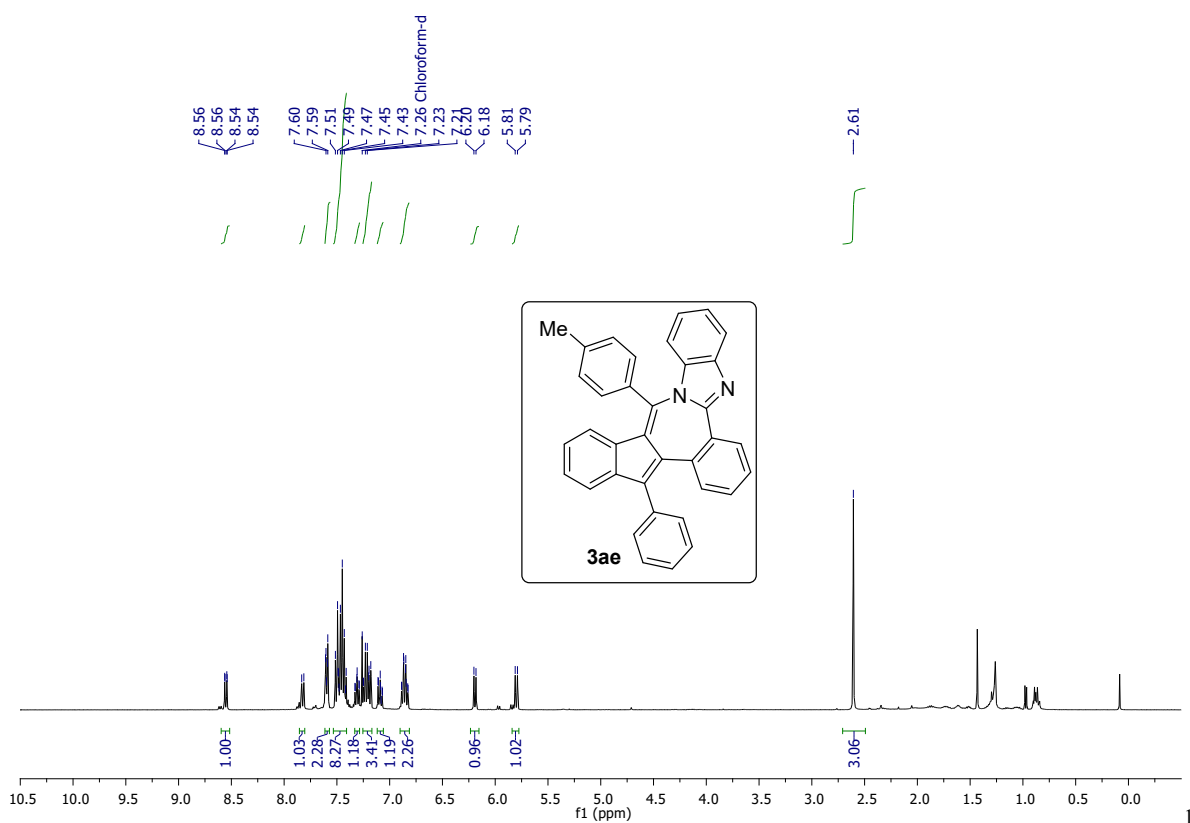
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz) spectrum of **3ac** in CDCl_3



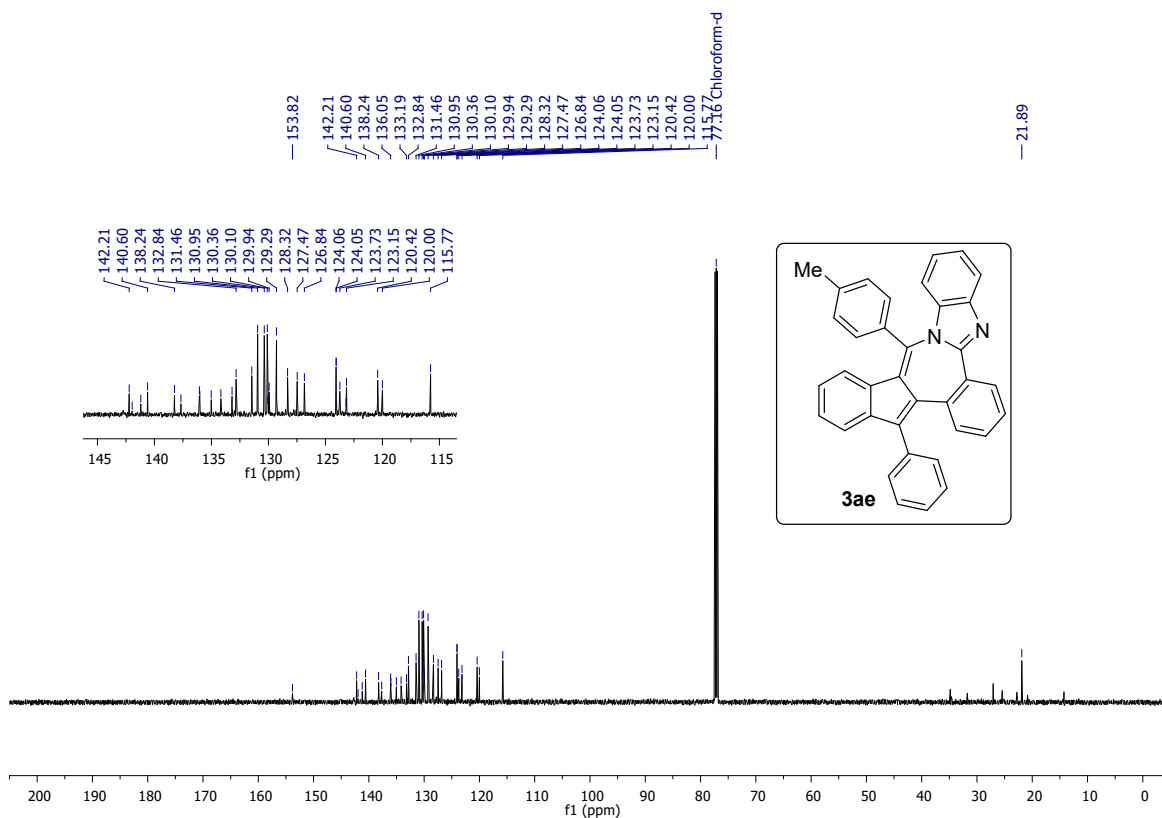
H NMR (400 MHz) spectrum of 3ad in CDCl₃



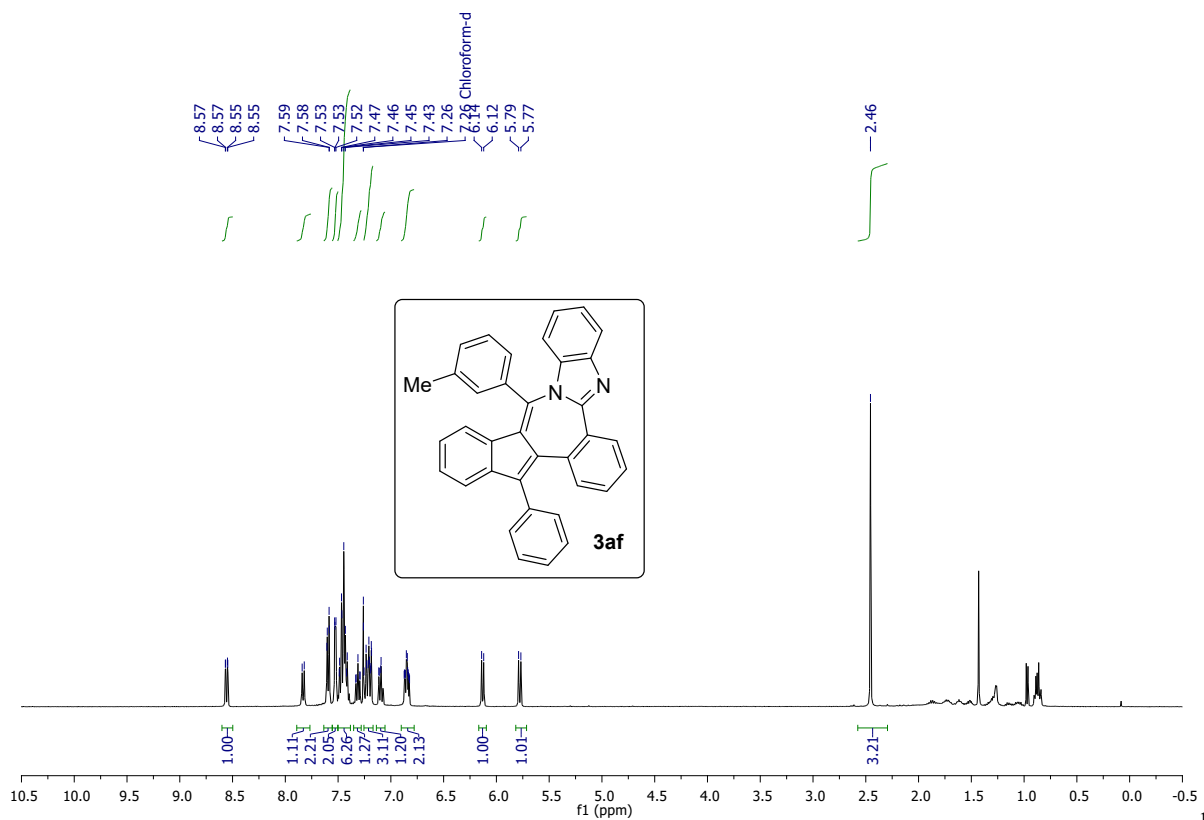
¹³C{¹H} NMR (151 MHz) spectrum of 3ad in CDCl₃



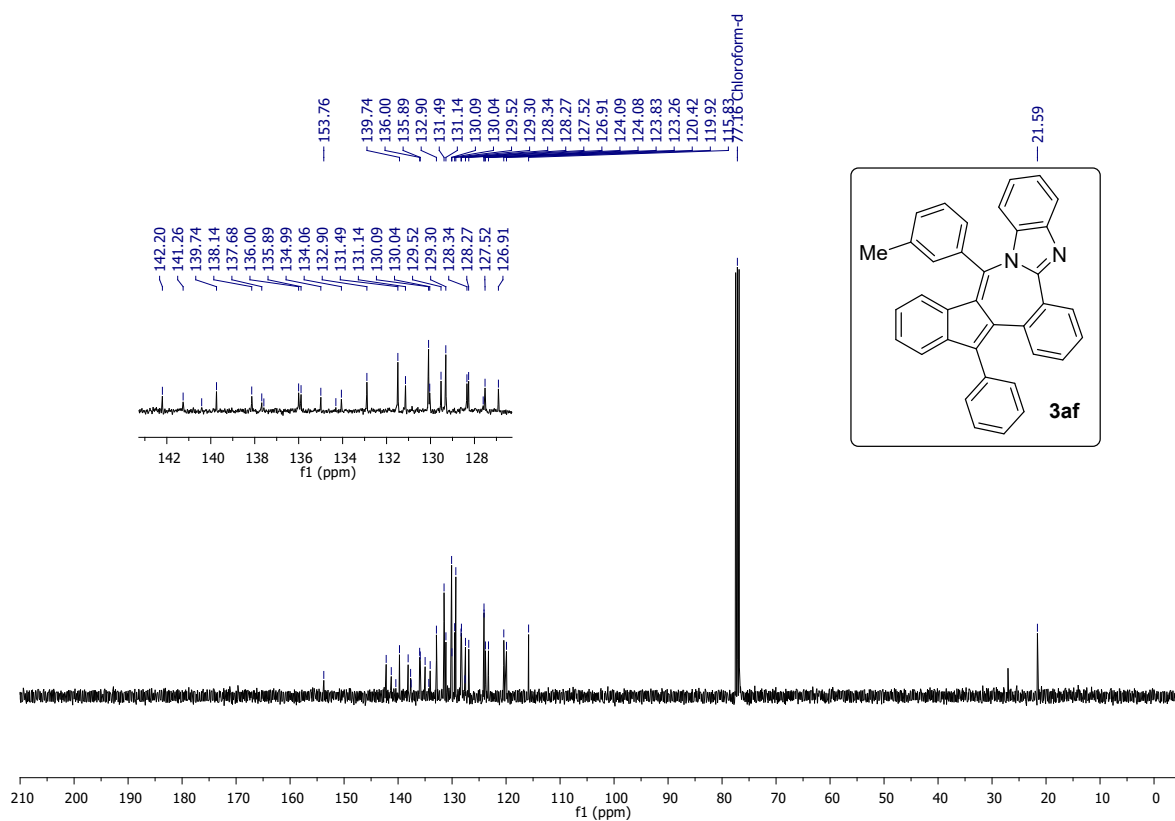
1H NMR (400 MHz) spectrum of 3ae in CDCl₃



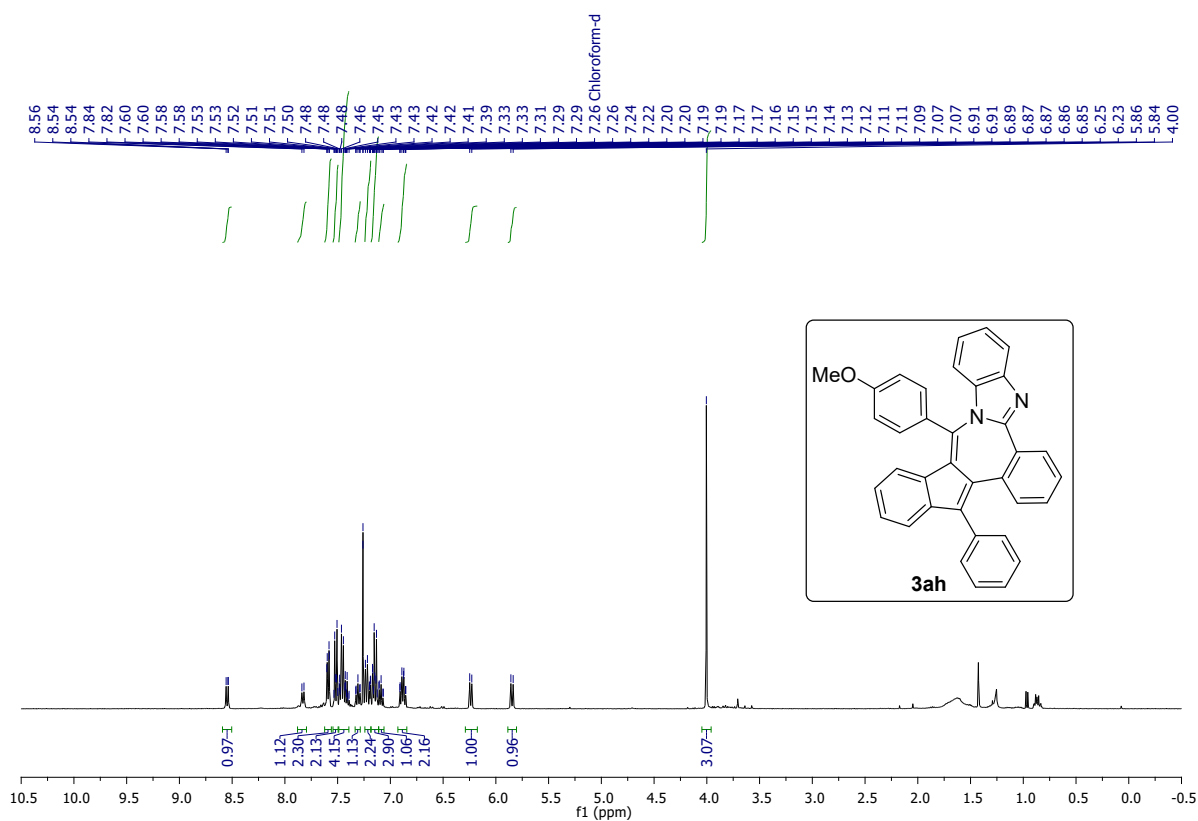
¹³C{¹H} NMR (151 MHz) spectrum of 3ae in CDCl₃



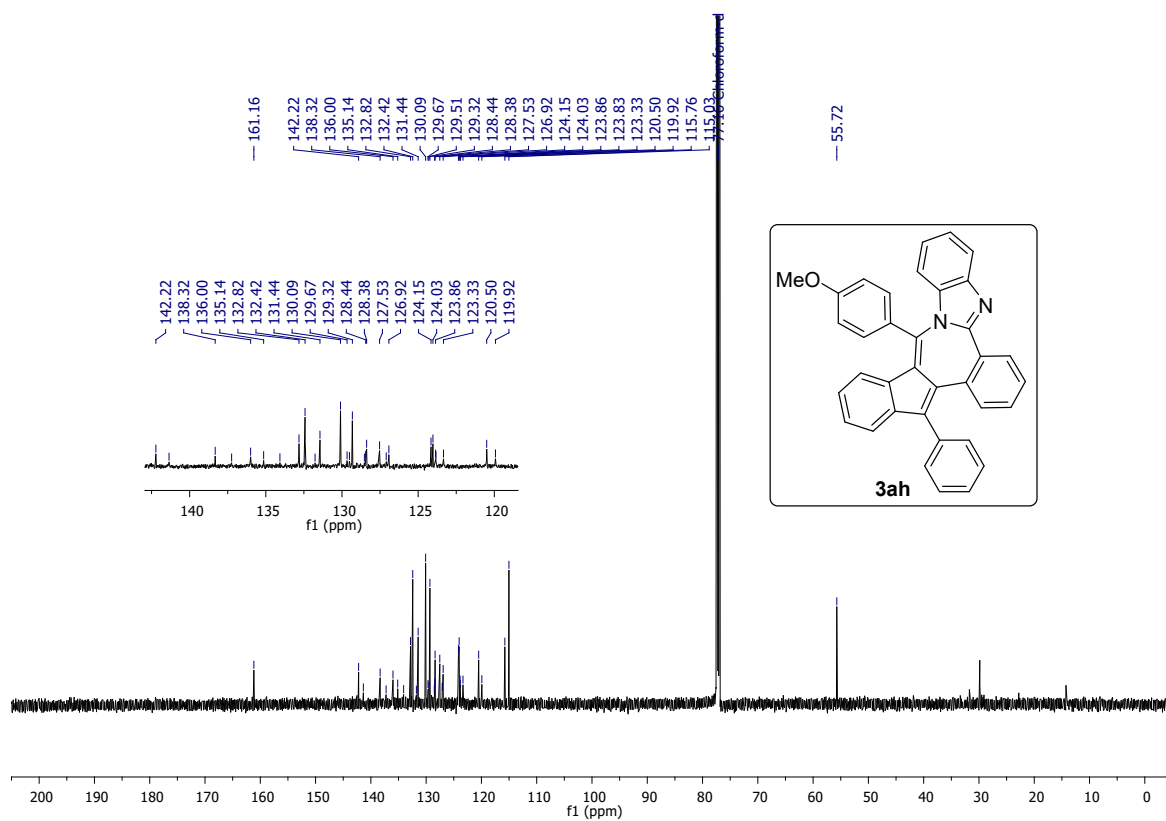
¹H NMR (400 MHz) spectrum of **3af** in CDCl₃



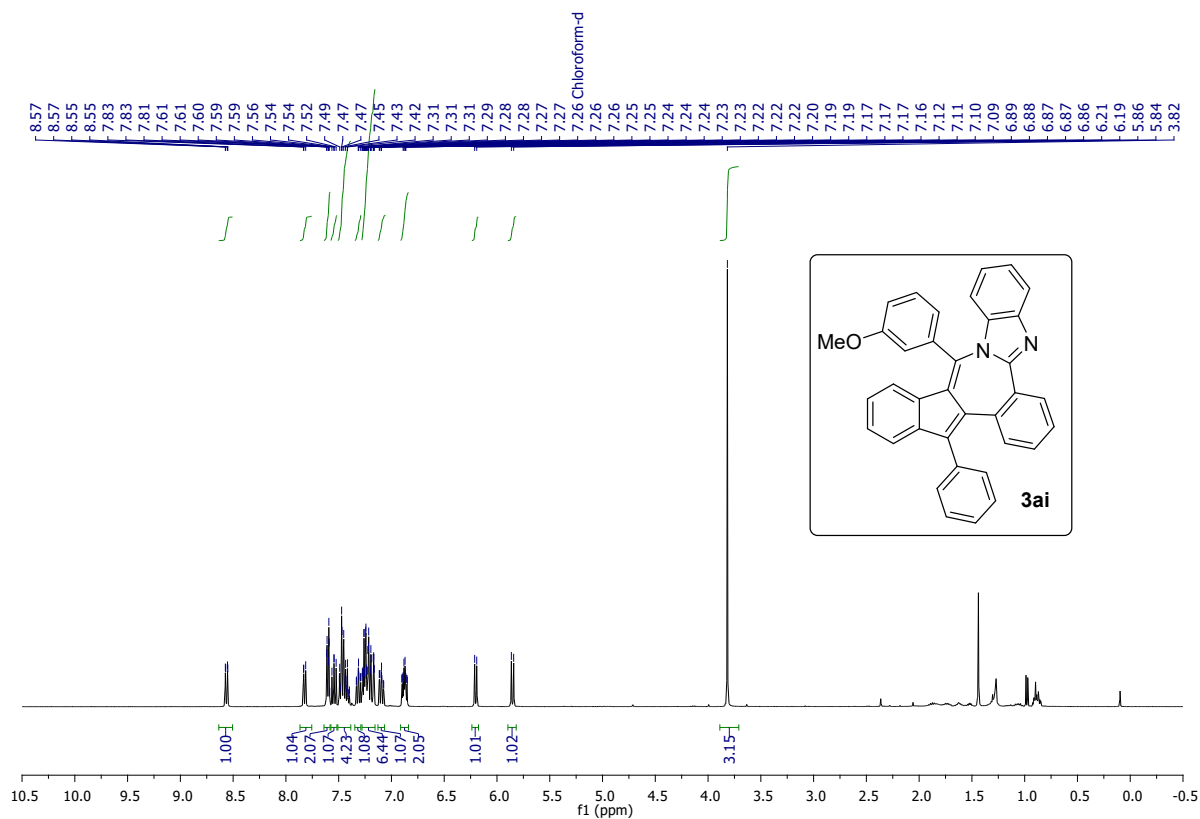
¹³C{¹H} NMR (101 MHz) spectrum of **3af** in CDCl₃



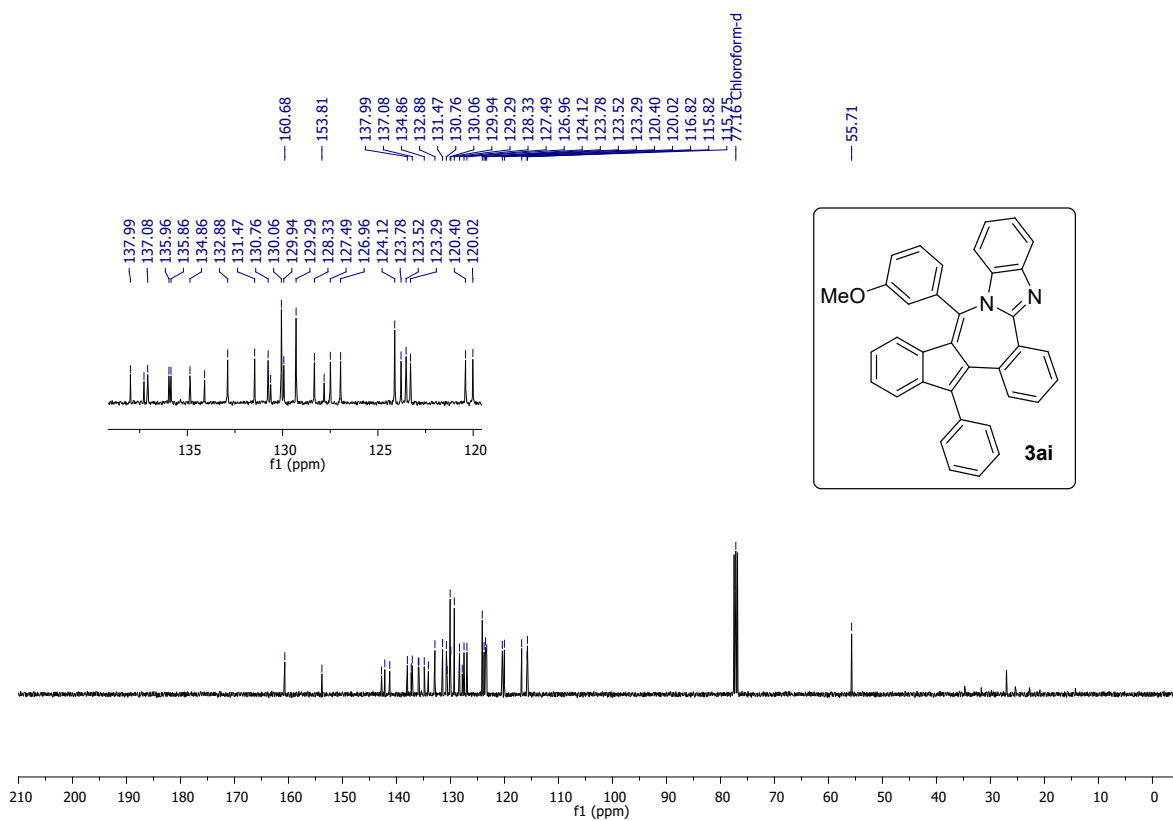
¹H NMR (400 MHz) spectrum of 3ah in CDCl₃



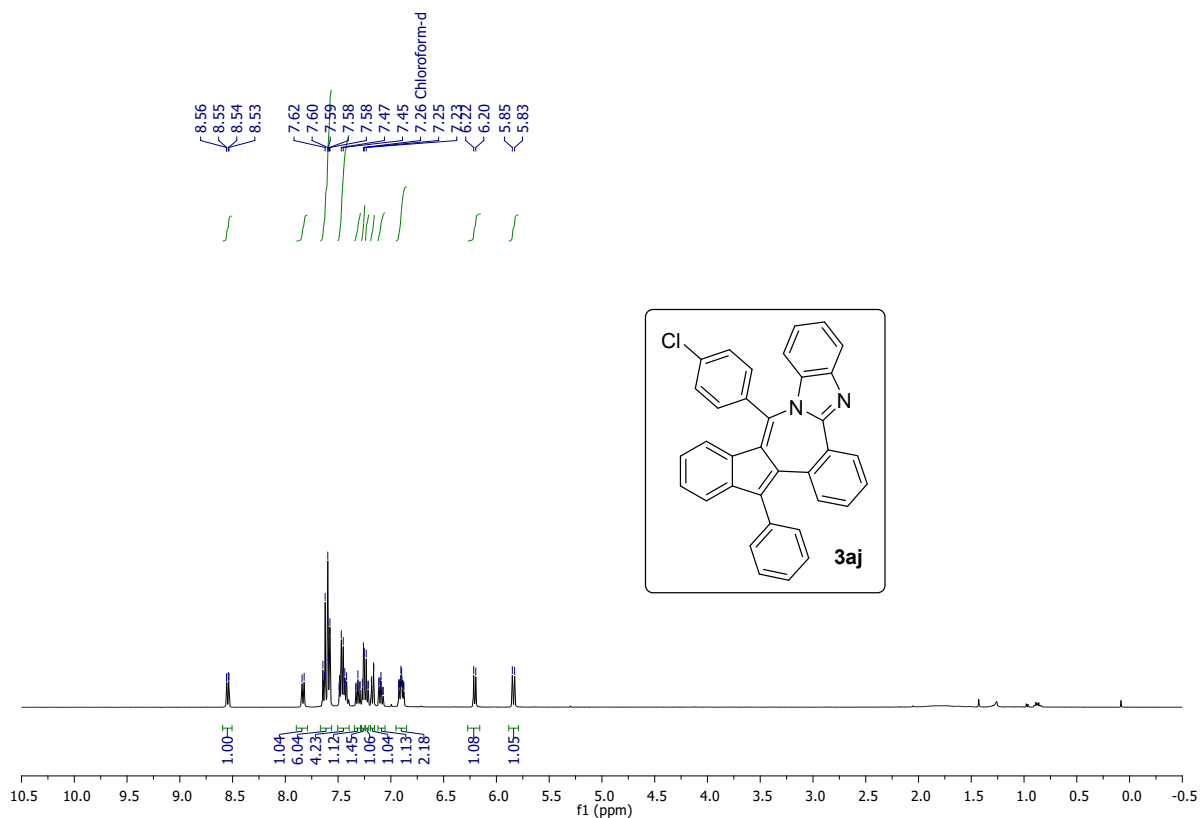
¹³C{¹H} NMR (151 MHz) spectrum of 3ah in CDCl₃



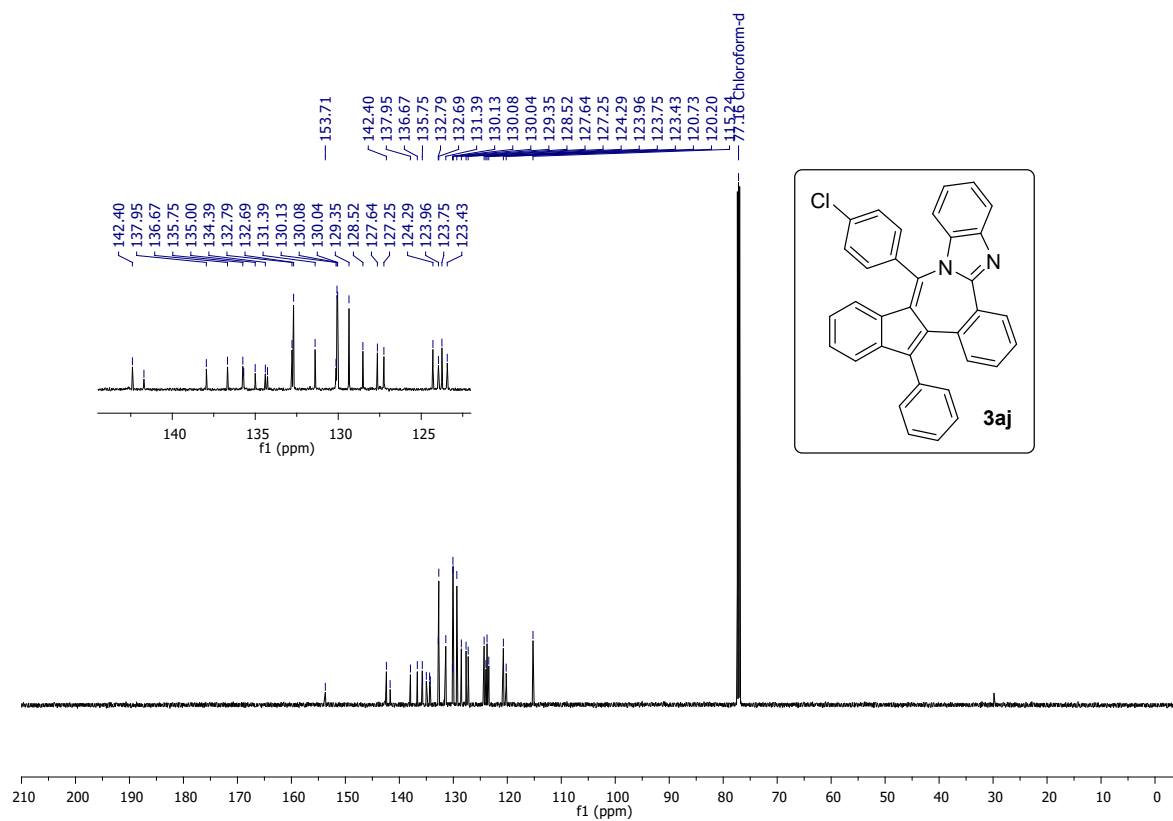
$^1\text{H NMR}$ (400 MHz) spectrum of **3ai** in CDCl_3



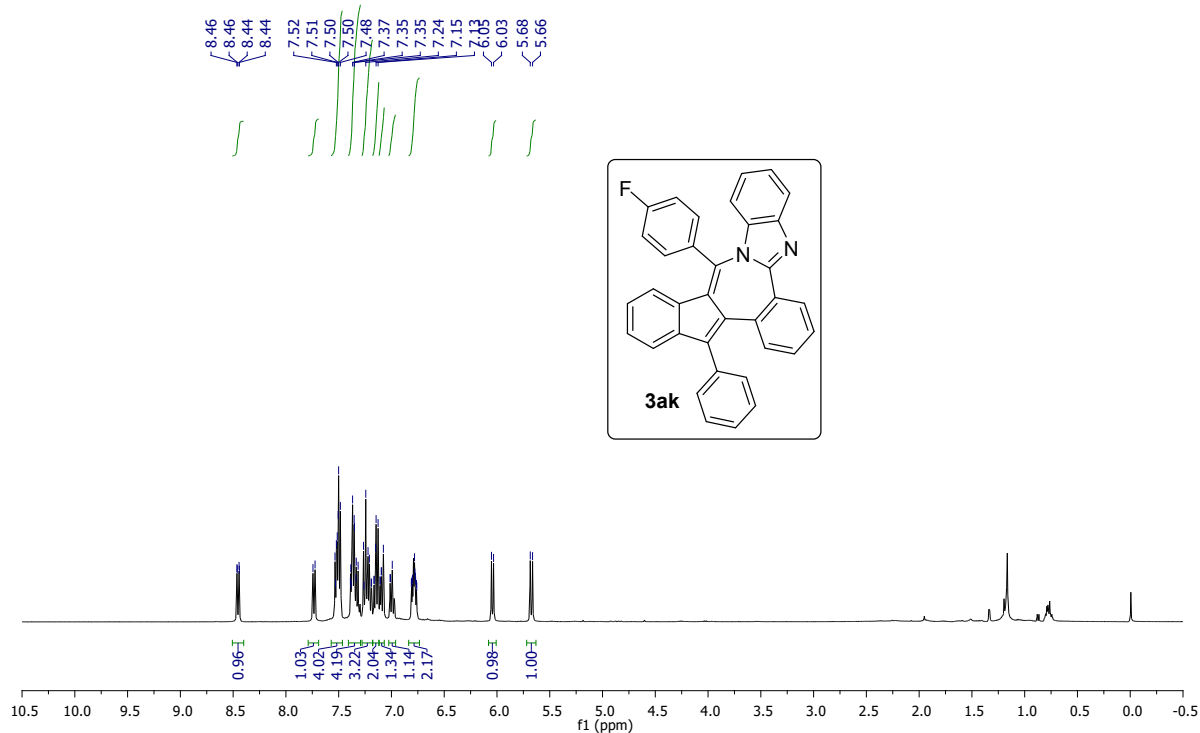
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz) spectrum of **3ai** in CDCl_3



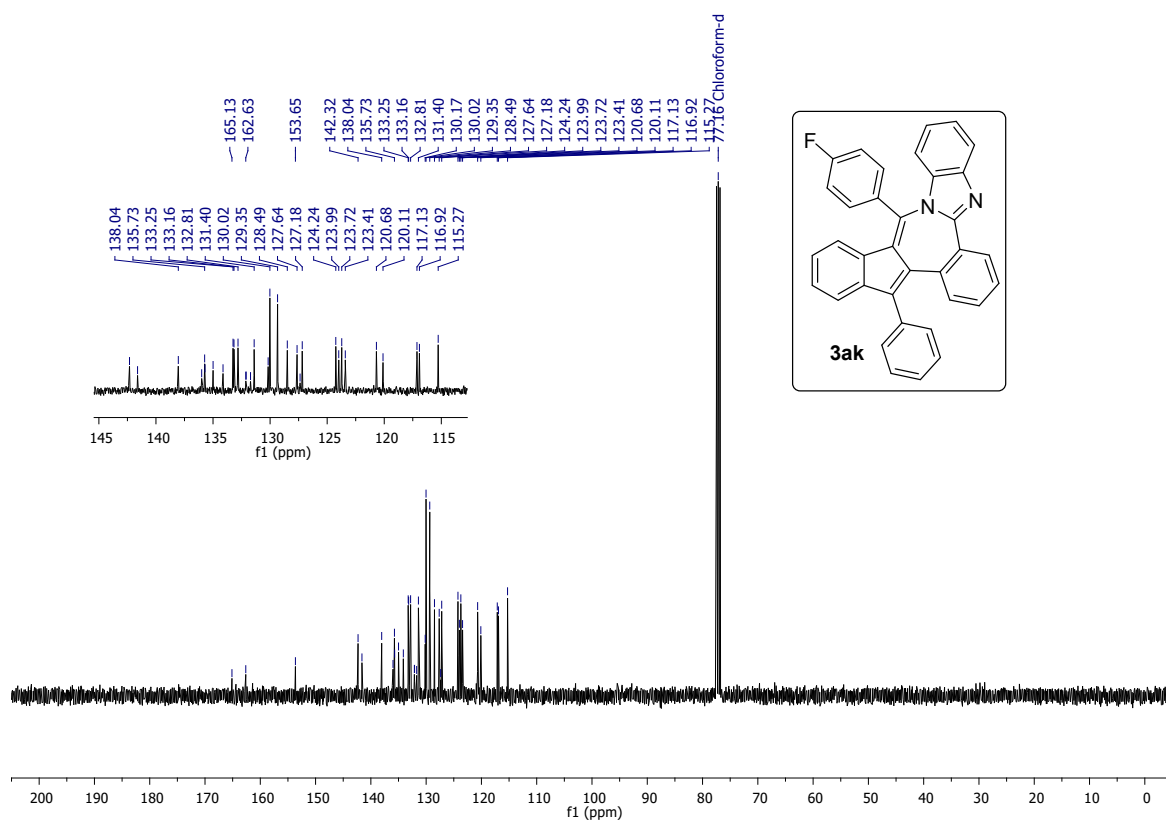
¹H NMR (400 MHz) spectrum of 3aj in CDCl₃



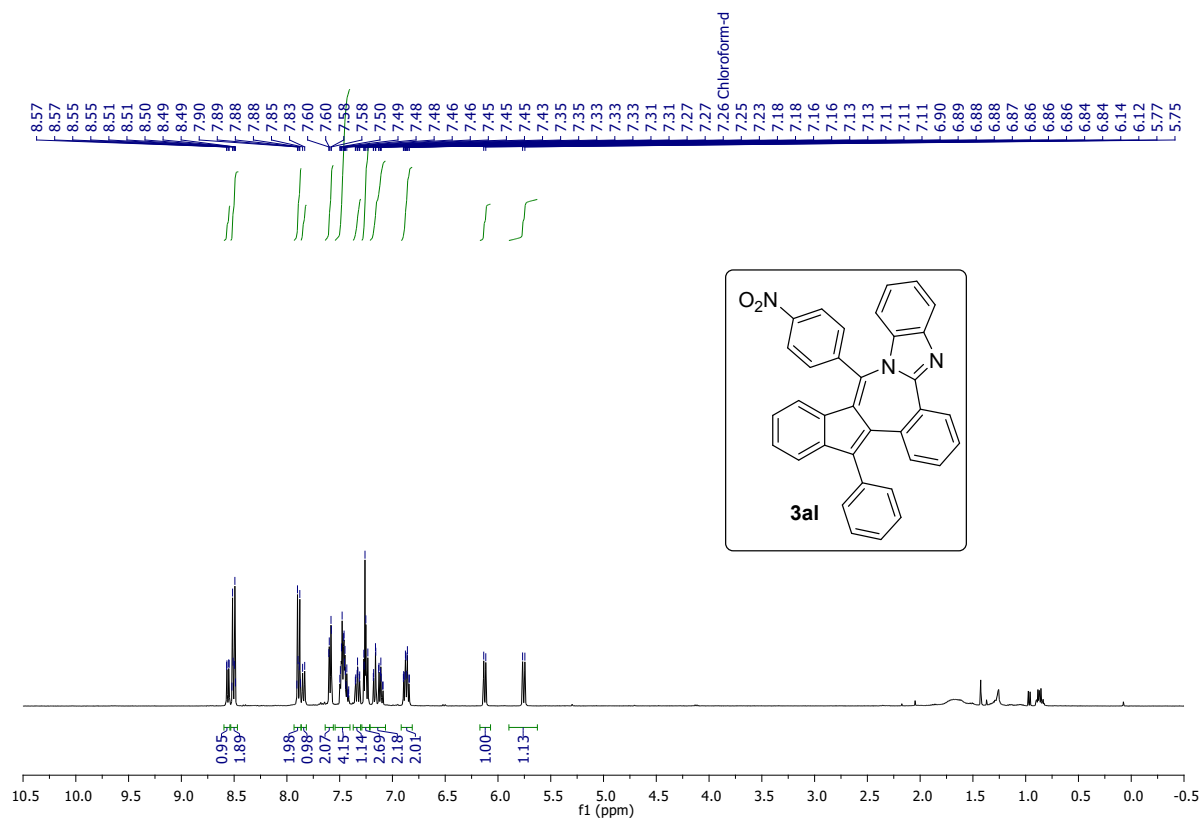
¹³C{¹H} NMR (151 MHz) spectrum of 3aj in CDCl₃



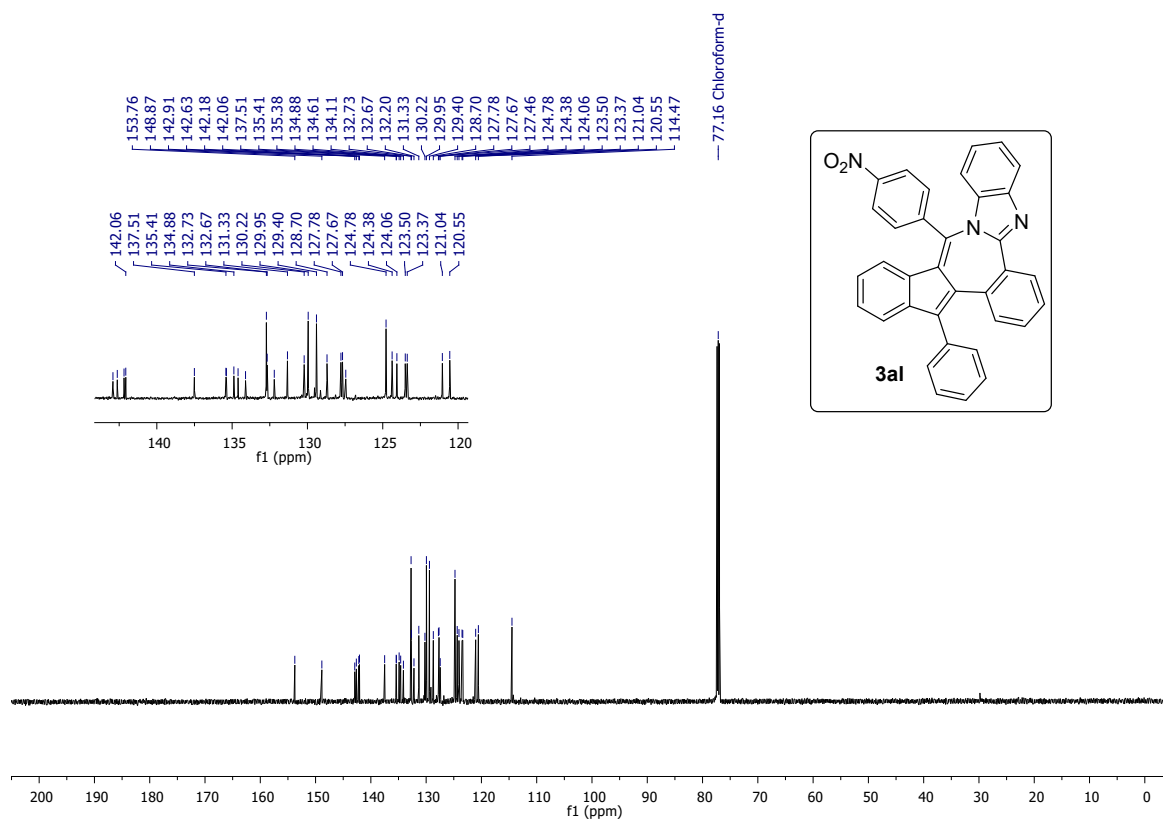
¹H NMR (400 MHz) spectrum of **3ak** in CDCl₃



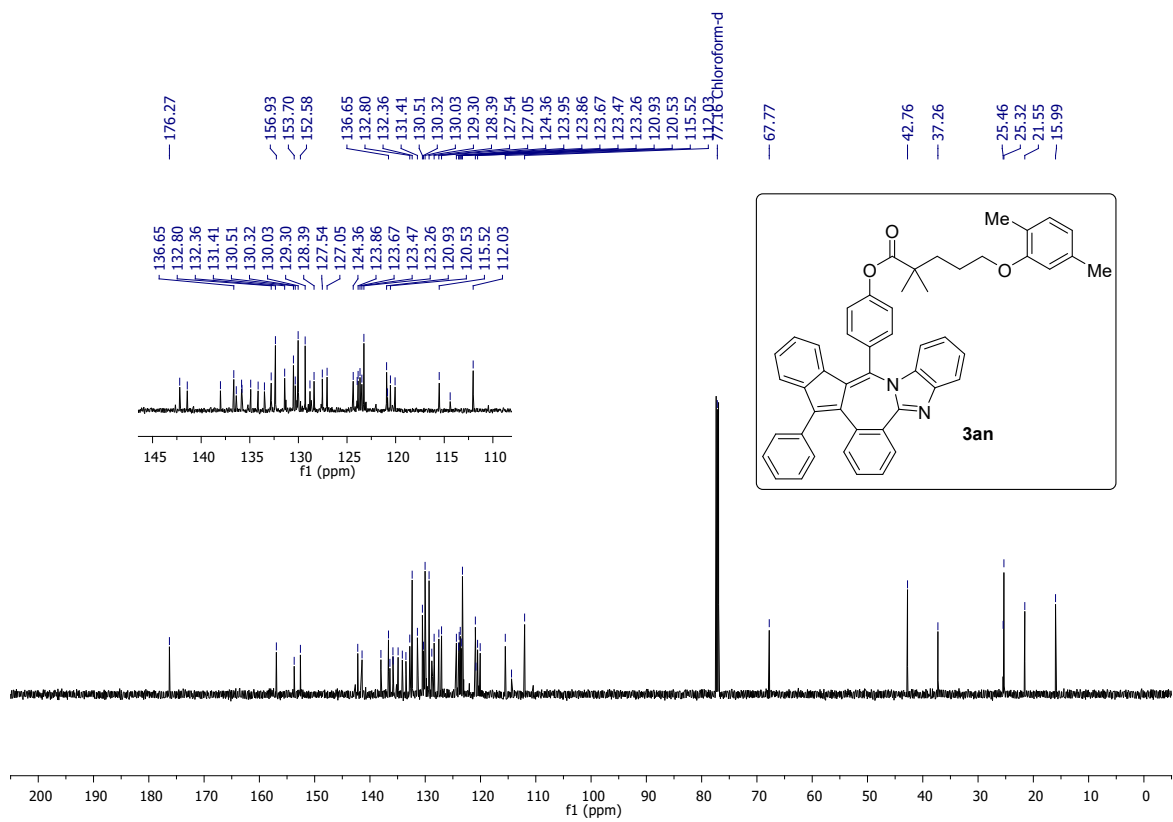
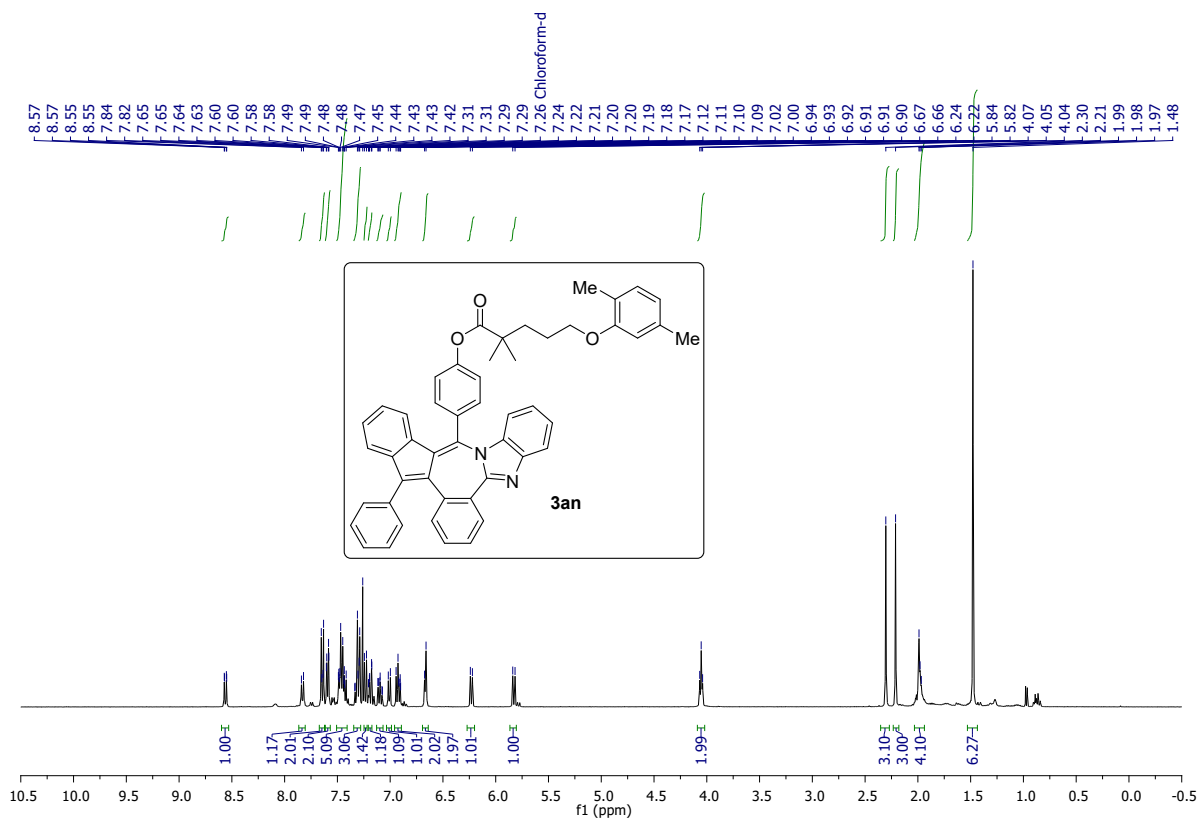
¹³C{¹H} NMR (101 MHz) spectrum of **3ak** in CDCl₃

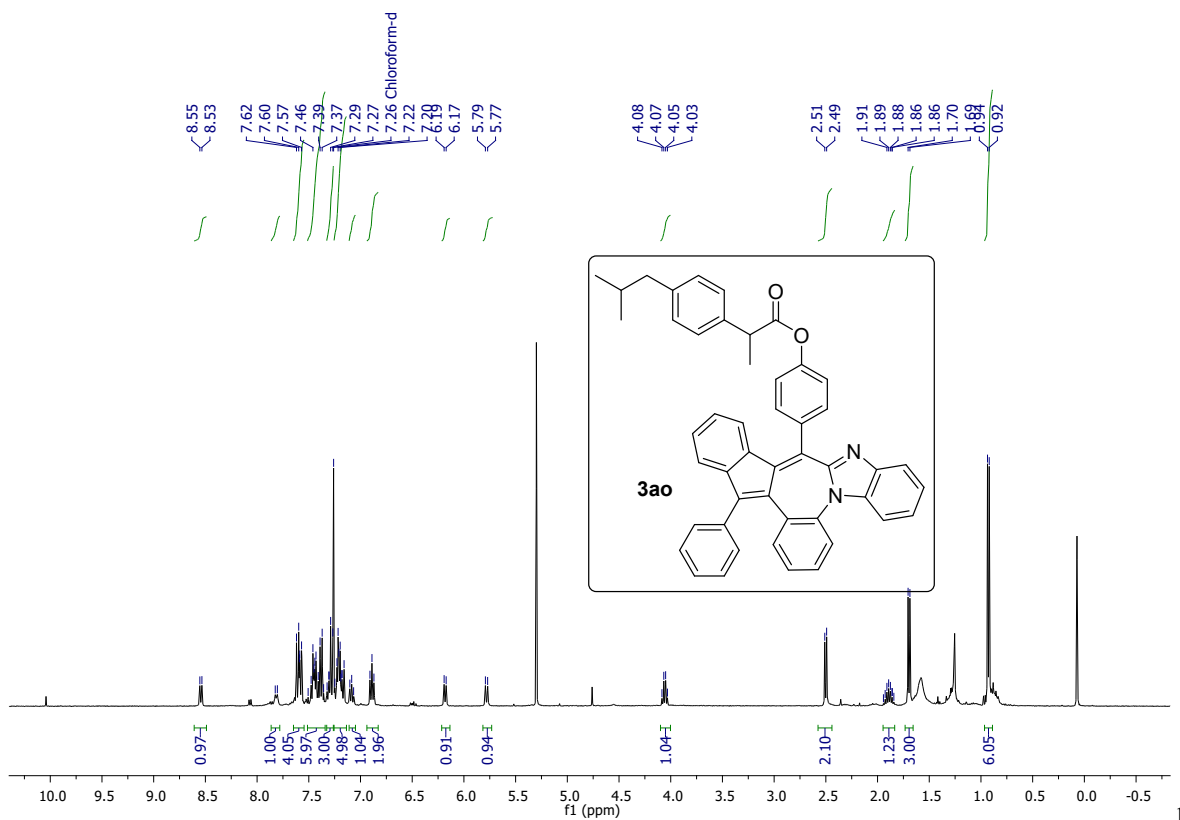


^1H NMR (400 MHz) spectrum of **3al** in CDCl_3

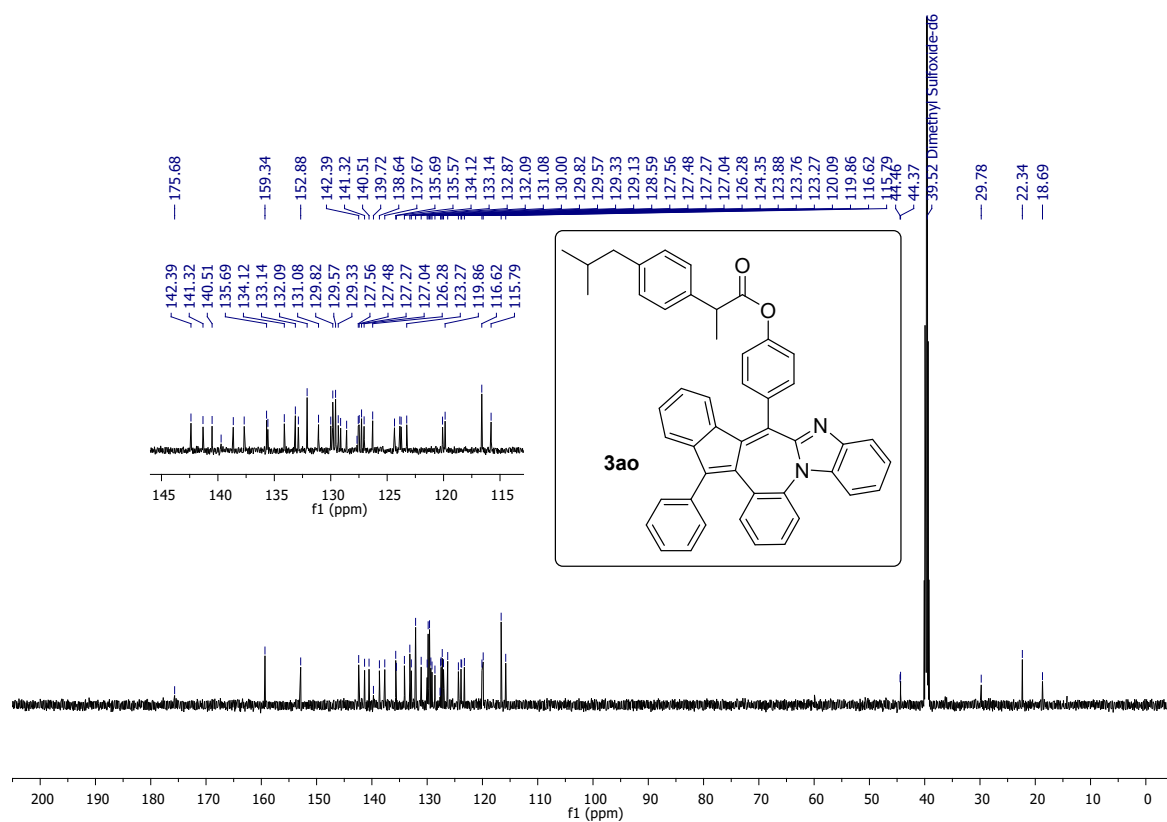


$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz) spectrum of **3al** in CDCl_3

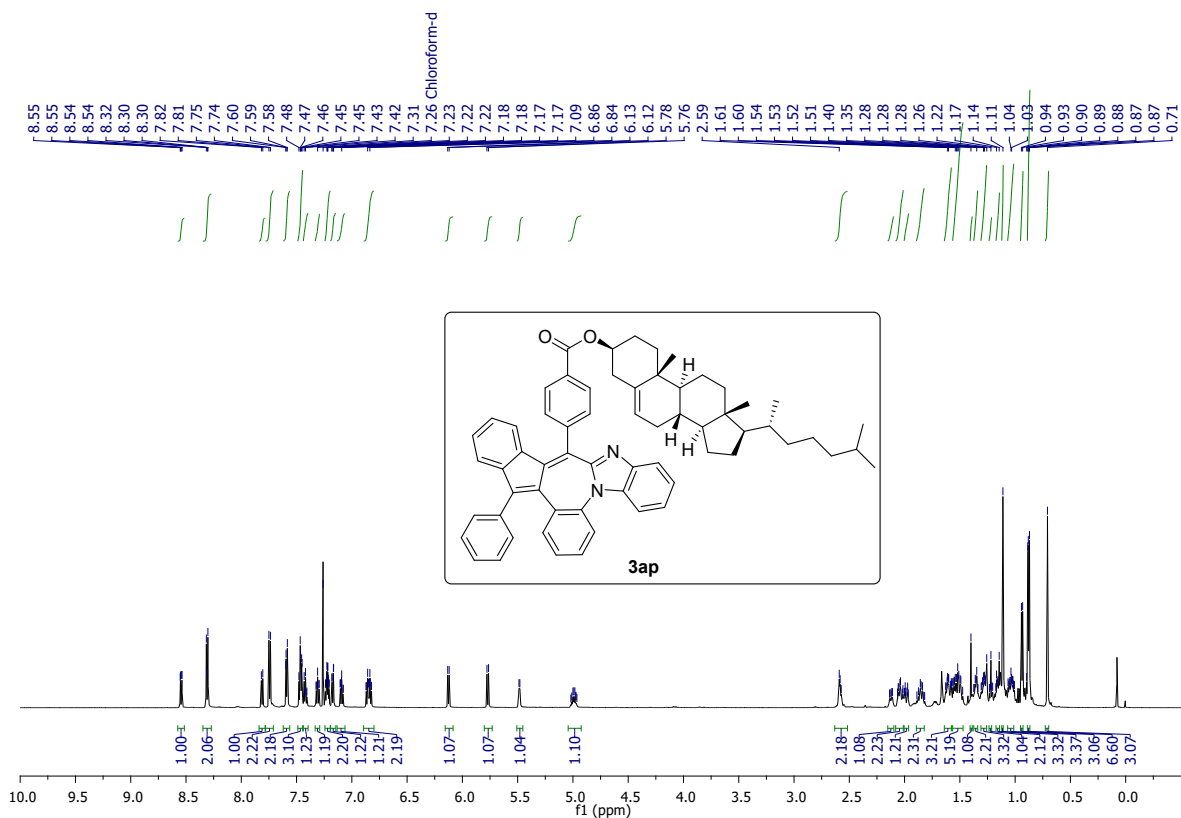




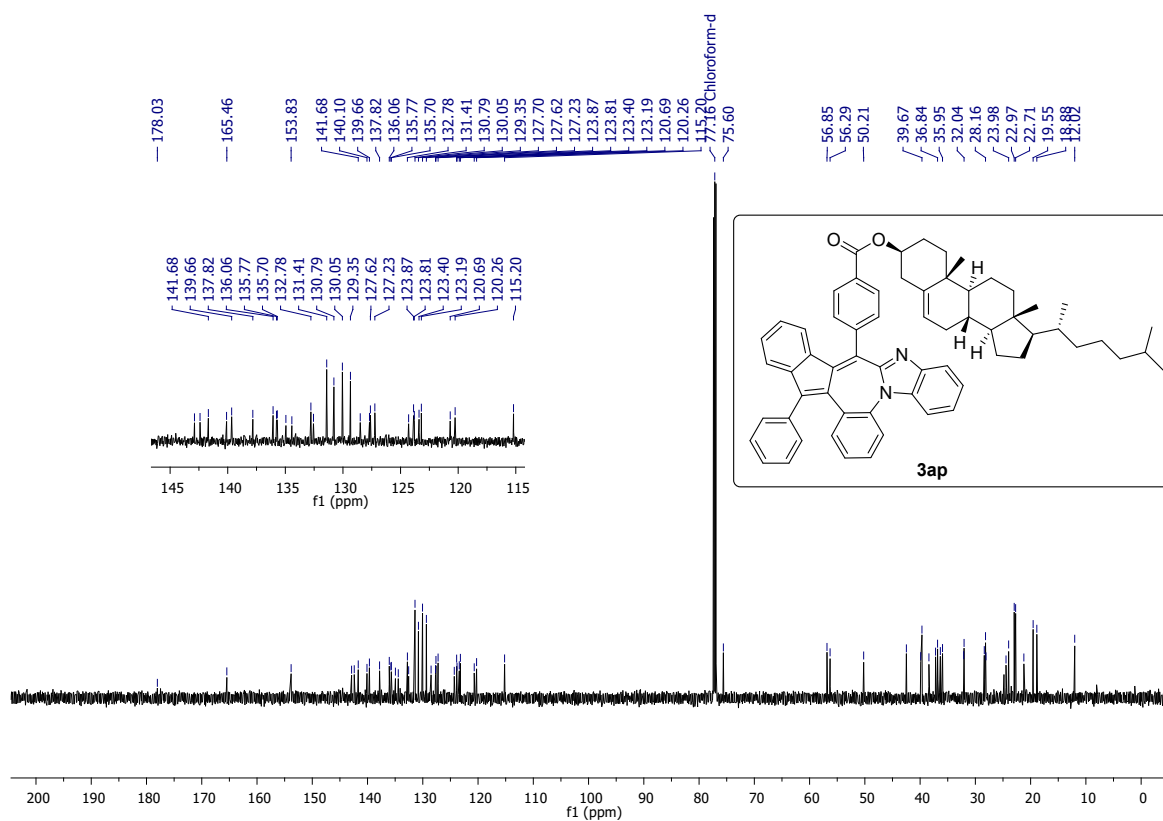
¹H NMR (400 MHz) spectrum of 3ao in CDCl₃



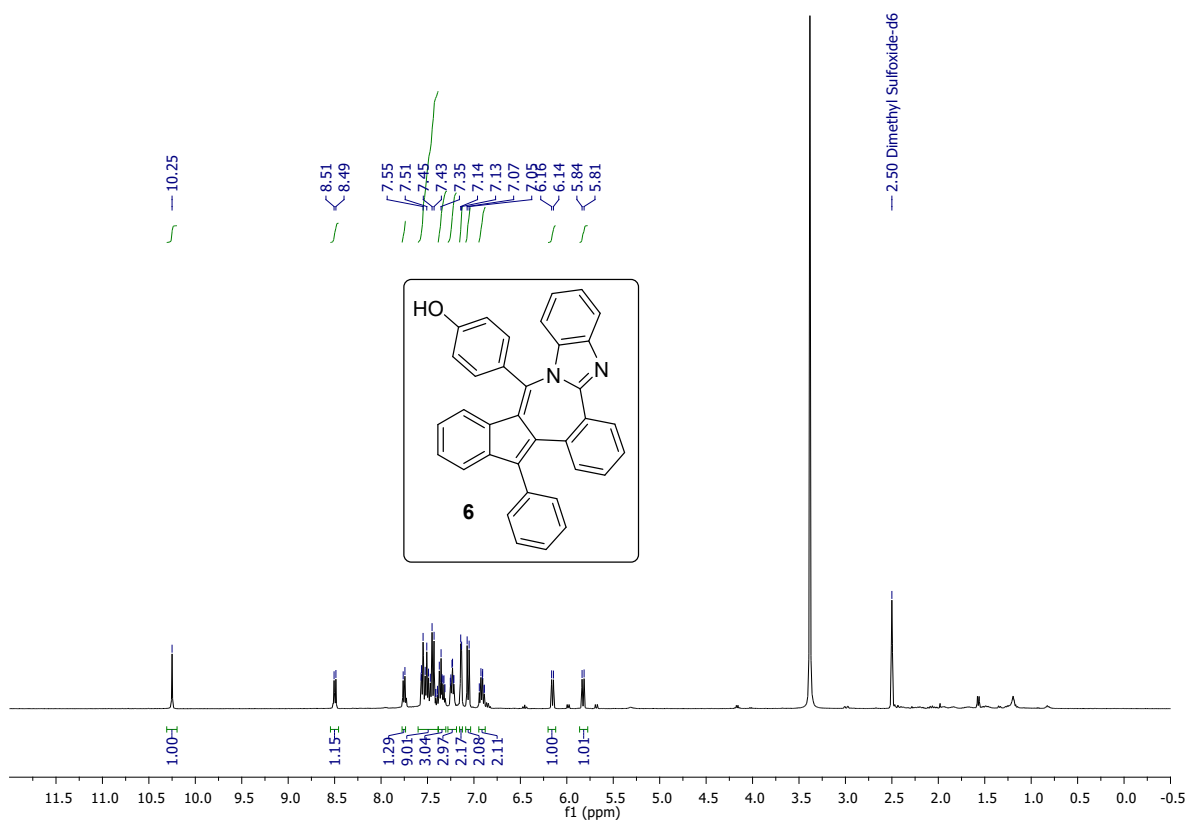
¹³C {¹H} NMR (151 MHz) spectrum of 3ao in DMSO-d₆



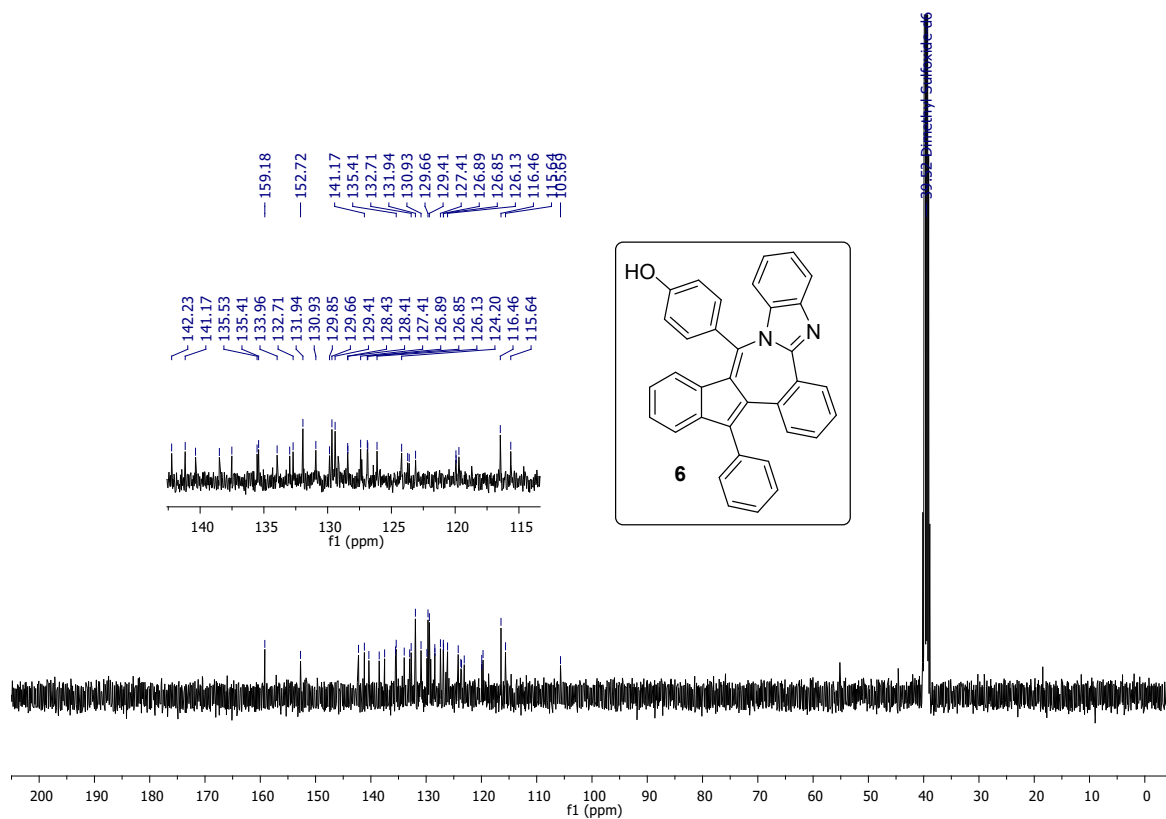
^1H NMR (600 MHz) spectrum of **3ap** in CDCl_3



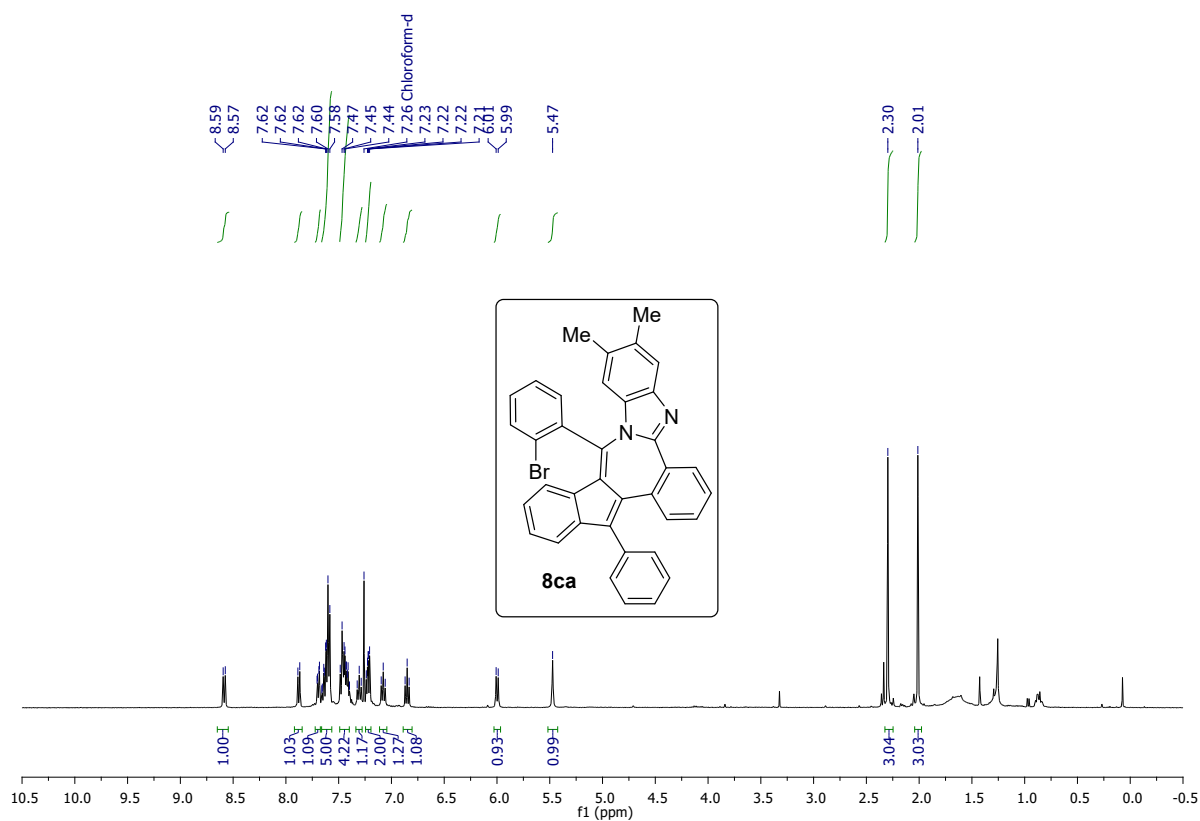
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz) spectrum of **3ap** in CDCl_3



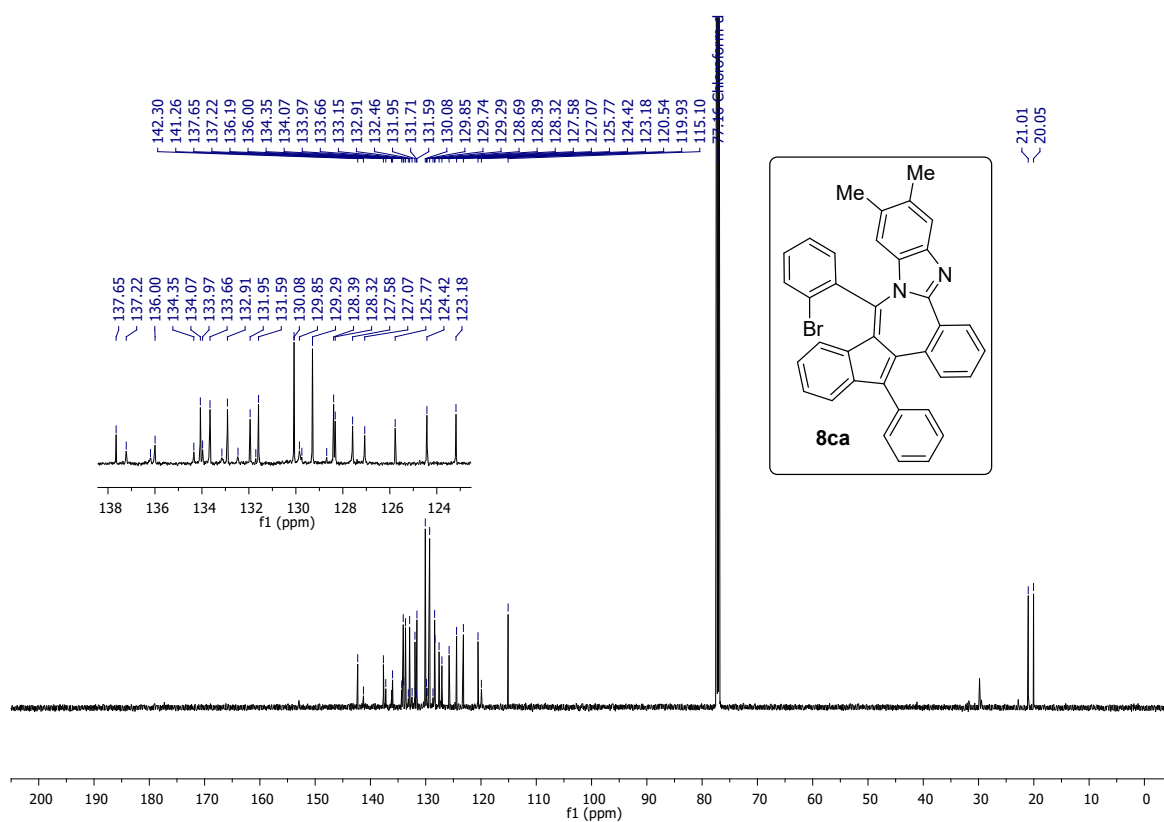
¹H NMR (600 MHz) spectrum of **6** in DMSO-*d*₆



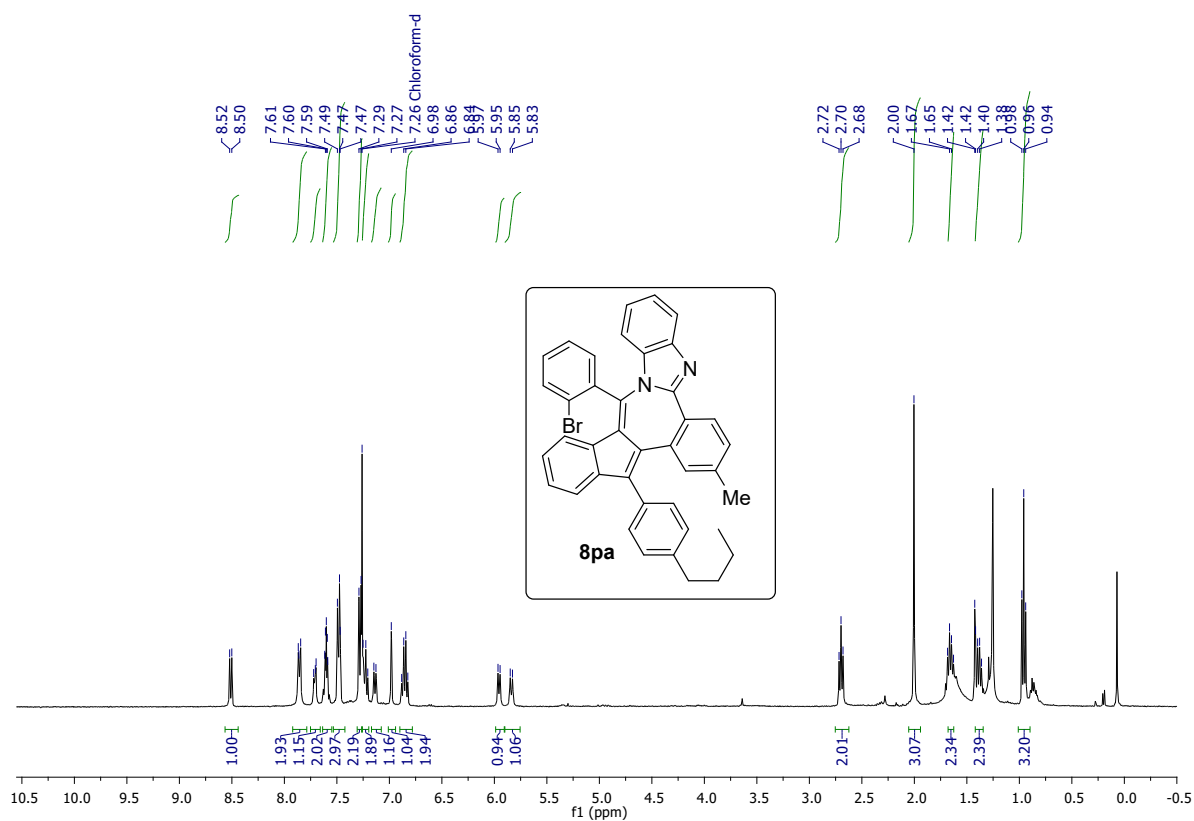
¹³C {¹H} NMR (101 MHz) spectrum of **6** in DMSO-*d*₆



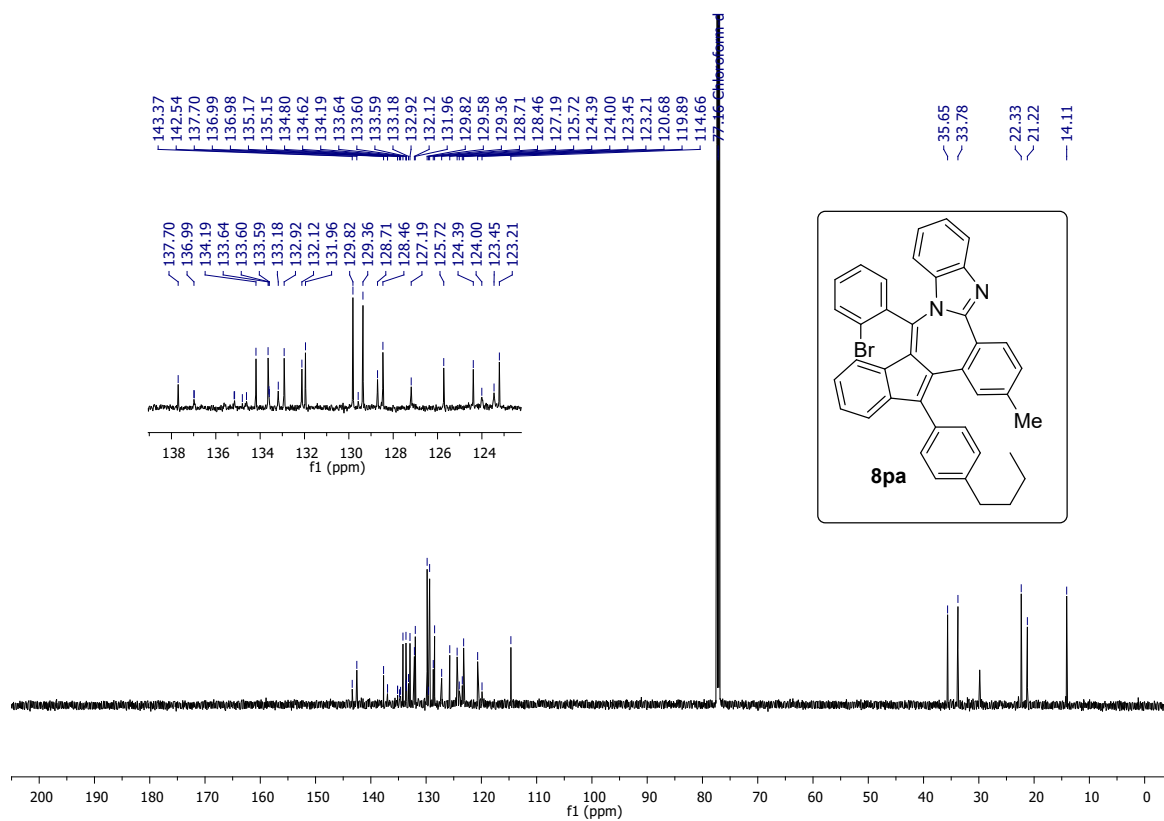
¹H NMR (400 MHz) spectrum of **8ca** in CDCl₃



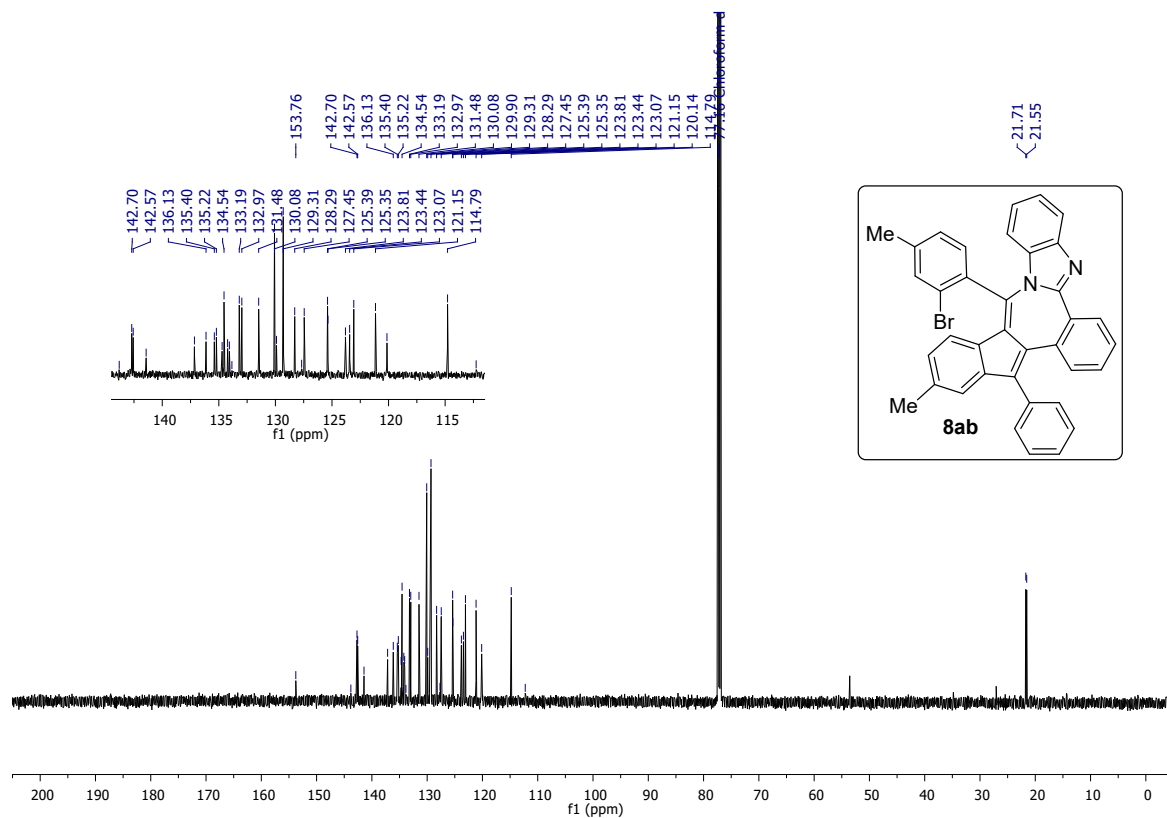
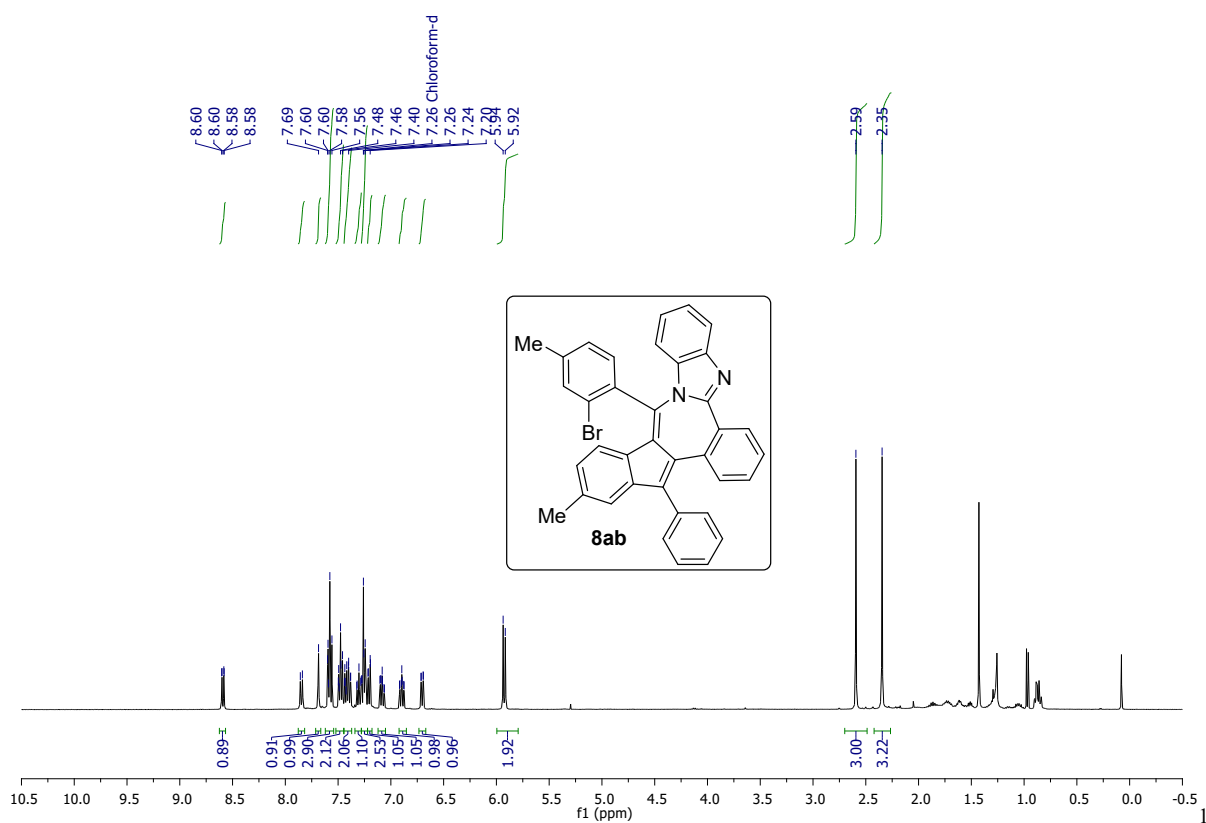
¹³C{¹H} NMR (151 MHz) spectrum of **8ca** in CDCl₃



$^1\text{H NMR}$ (400 MHz) spectrum of **8pa** in CDCl_3



$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz) spectrum of **8pa** in CDCl_3



Crystal data:

i) X-Ray crystal structure of compound 3ka:

Crystal of compound **3ka** was obtained by dissolving the product in Hexane/DCM/ CHCl_3 mixture and allowing the solvent to evaporate at room temperature slowly. A suitable crystal was selected and mounted onto the cryoloop on a Bruker APEX-II CCD diffractometer. Using Olex2, the structure was solved with the SHELXT structure solution program using Intrinsic Phasing and refined with the SHELXL refinement package using Least Squares minimisation.

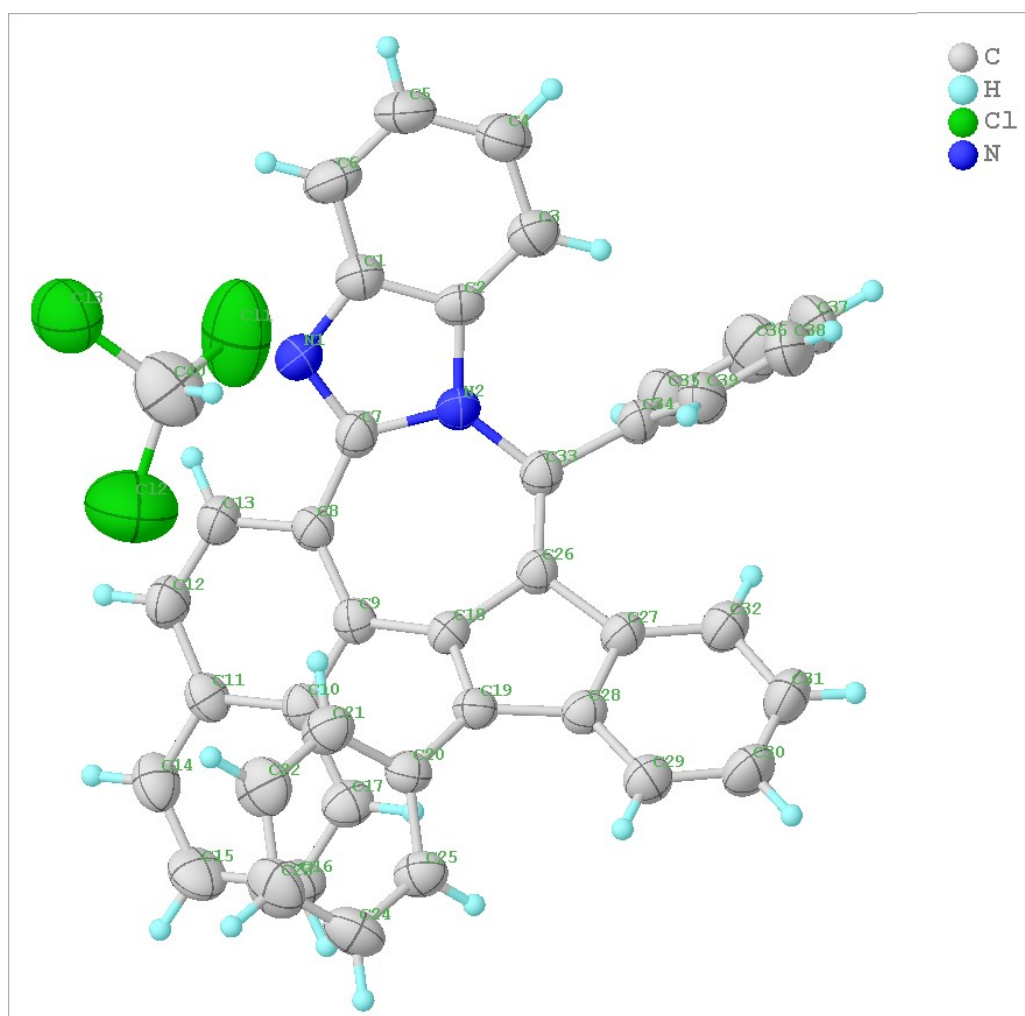


Figure S1: X-ray crystal diagram of compound **3ka** with ellipsoid shown at the 50% contour percent probability level (CCDC - 2532589).

Table S5: Crystal data and structure refinement for **3ka** (CCDC- 2532589)

Table: Crystal data and structure refinement for 3ka.	
Identification code	3ka
Empirical formula	C ₄₀ H ₂₅ Cl ₃ N ₂
Formula weight	639.97
Temperature/K	298
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	8.6005(10)
b/Å	21.208(2)
c/Å	18.482(2)
α/°	90
β/°	94.779(4)
γ/°	90
Volume/Å ³	3359.3(7)
Z	4
ρ _{calc} /g/cm ³	1.265
μ/mm ⁻¹	0.303
F(000)	1320.0
Crystal size/mm ³	0.32 × 0.19 × 0.12
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.432 to 54.242
Index ranges	-11 ≤ h ≤ 10, -27 ≤ k ≤ 26, -23 ≤ l ≤ 23
Reflections collected	47502
Independent reflections	7406 [R _{int} = 0.1511, R _{sigma} = 0.1205]
Data/restraints/parameters	7406/0/407
Goodness-of-fit on F ²	1.014
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0763, wR ₂ = 0.1898
Final R indexes [all data]	R ₁ = 0.1926, wR ₂ = 0.2454
Largest diff. peak/hole / e Å ⁻³	0.48/-0.63

ii) X-Ray crystal structure of compound 3la:

Crystal of compound **3la** was obtained by dissolving the product in Hexane/DCM mixture and allowing the solvent to evaporate at room temperature slowly. 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, the structure was solved with the SHELXT structure solution program using Intrinsic Phasing and refined with the SHELXL refinement package using Least Squares minimisation.

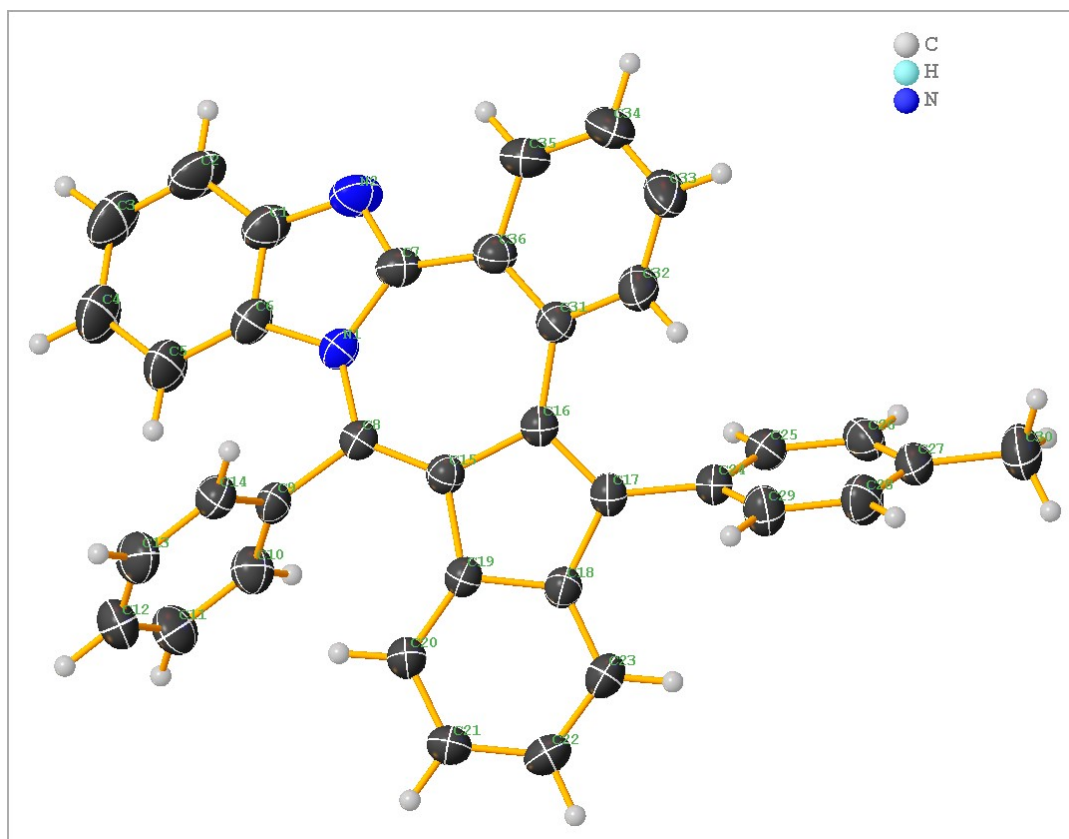


Figure S2: X-ray crystal diagram of compound **3la** with ellipsoid shown at the 50% contour percent probability level (CCDC - 2532590).

Table S6: Crystal data and structure refinement for **3la** (CCDC- 2532590)

Table: Crystal data and structure refinement for 3la.	
Identification code	3la
Empirical formula	C ₃₆ H ₂₄ N ₂

Formula weight	484.57
Temperature/K	189.00
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	5.9158(3)
b/Å	40.8072(16)
c/Å	10.3418(4)
α /°	90
β /°	101.068(2)
γ /°	90
Volume/Å ³	2450.15(18)
Z	4
ρ_{calc} /cm ³	1.314
μ /mm ⁻¹	0.076
F(000)	1016.0
Crystal size/mm ³	? × ? × ?
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/°	4.136 to 54.214
Index ranges	-7 ≤ h ≤ 7, -52 ≤ k ≤ 51, -12 ≤ l ≤ 13
Reflections collected	34527
Independent reflections	5397 [R _{int} = 0.0514, R _{sigma} = 0.0339]
Data/restraints/parameters	5397/0/344
Goodness-of-fit on F ²	1.045
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0487, wR ₂ = 0.1099
Final R indexes [all data]	R ₁ = 0.0658, wR ₂ = 0.1211
Largest diff. peak/hole / e Å ⁻³	0.22/-0.21

iii) X-Ray crystal structure of compound **3ak**:

Crystal of compound **3ak** was obtained by dissolving the product in a Hexane/DCM mixture and allowing the solvent to evaporate slowly 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, the structure was solved with the SHELXT structure solution program using Intrinsic Phasing and refined with the SHELXL refinement package using Least Squares minimisation.

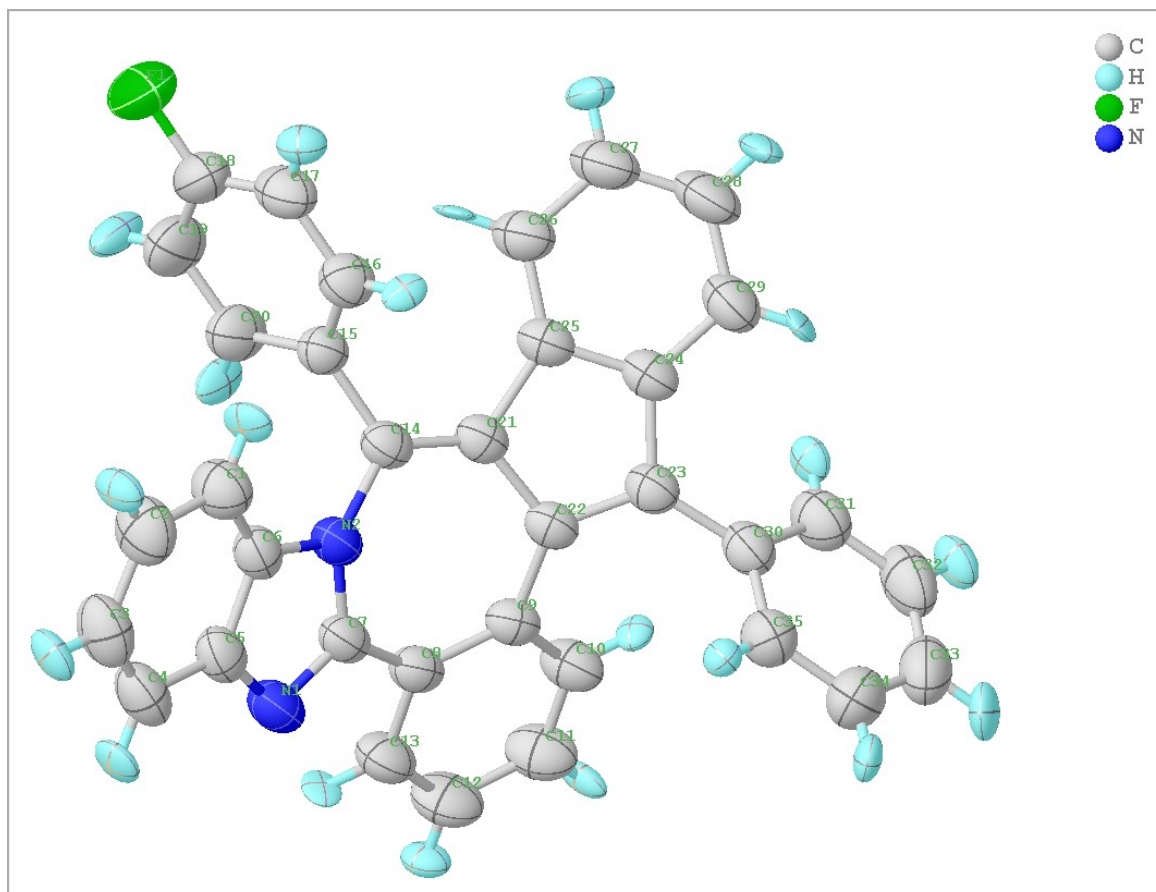


Figure S3: X-ray crystal diagram of compound **3ak** with ellipsoid shown at the 50% contour percent probability level (CCDC - 2532591).

Table S7: Crystal data and structure refinement for **3ak** (CCDC- 2532591)

Table: Crystal data and structure refinement for 3ak.	
Identification code	3ak
Empirical formula	$C_{35}H_{21}FN_2$
Formula weight	488.54
Temperature/K	298
Crystal system	monoclinic

Space group	P2 ₁ /n
a/Å	14.4826(14)
b/Å	9.1787(9)
c/Å	20.0058(19)
α /°	90
β /°	108.753(3)
γ /°	90
Volume/Å ³	2518.2(4)
Z	4
ρ_{calc} /g/cm ³	1.289
μ /mm ⁻¹	0.080
F(000)	1016.0
Crystal size/mm ³	0.23 × 0.19 × 0.12
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/°	4.19 to 54.29
Index ranges	-18 ≤ h ≤ 18, -11 ≤ k ≤ 11, -25 ≤ l ≤ 25
Reflections collected	50166
Independent reflections	5568 [R _{int} = 0.0839, R _{sigma} = 0.0463]
Data/restraints/parameters	5568/0/470
Goodness-of-fit on F ²	1.027
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0460, wR ₂ = 0.1053
Final R indexes [all data]	R ₁ = 0.0987, wR ₂ = 0.1302
Largest diff. peak/hole / e Å ⁻³	0.15/-0.24

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